Supporting information

Catalytic transfer hydrogenation of azobenzene by low valent nickel complexes: a route to 1,2-disubstituted benzimidazoles and 2,4,5-trisubtituted Imidazolines

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NMR Spectra of Isolated Compounds

NMR spectra of Complex I

$^{31}P\{^{1}H\}$-NMR

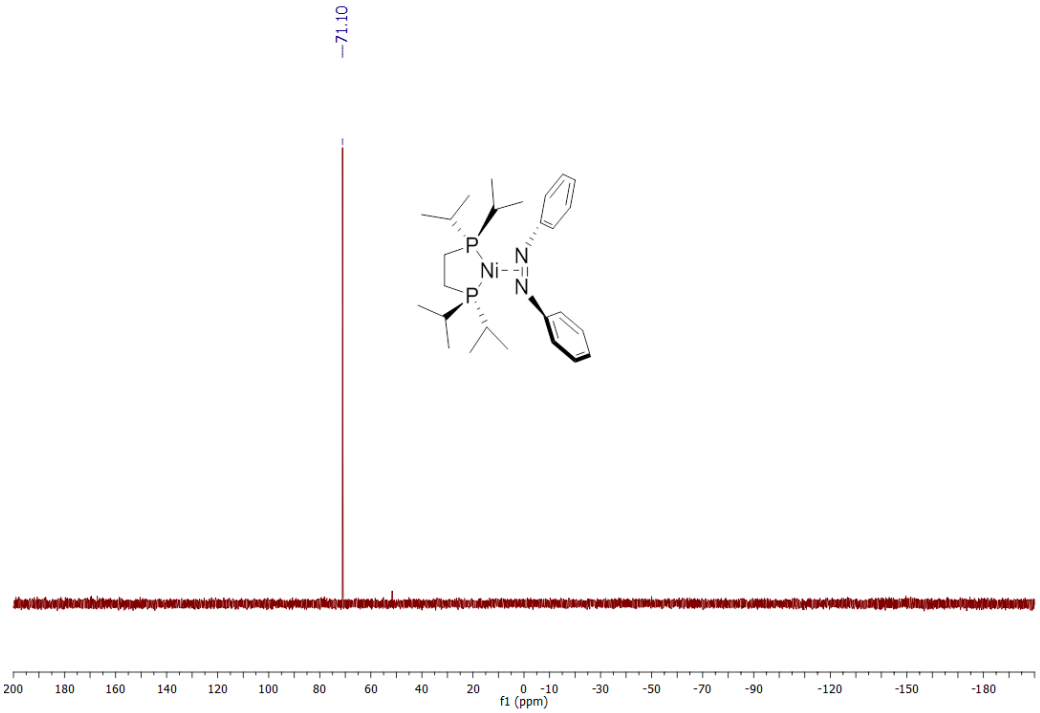


Figure S 1. $^{31}P\{^{1}H\}$-NMR of I

^{1}H-NMR

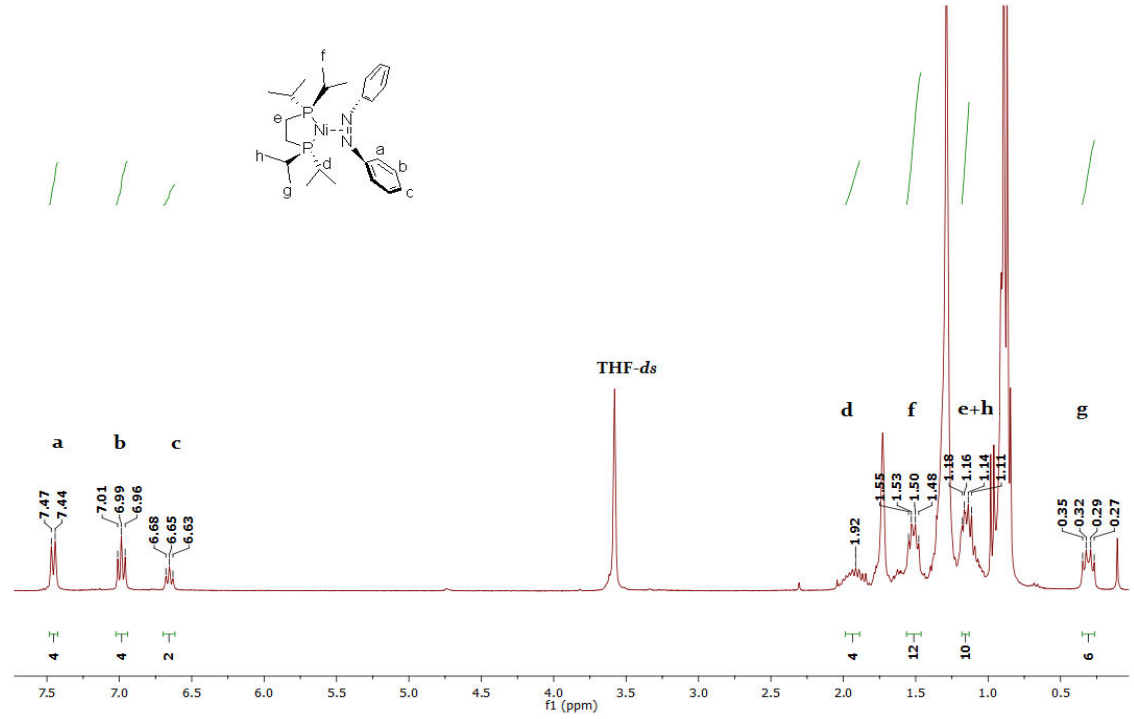


Figure S 2. ^{1}H-NMR of I

$^{13}C\{^{1}H\}$-NMR

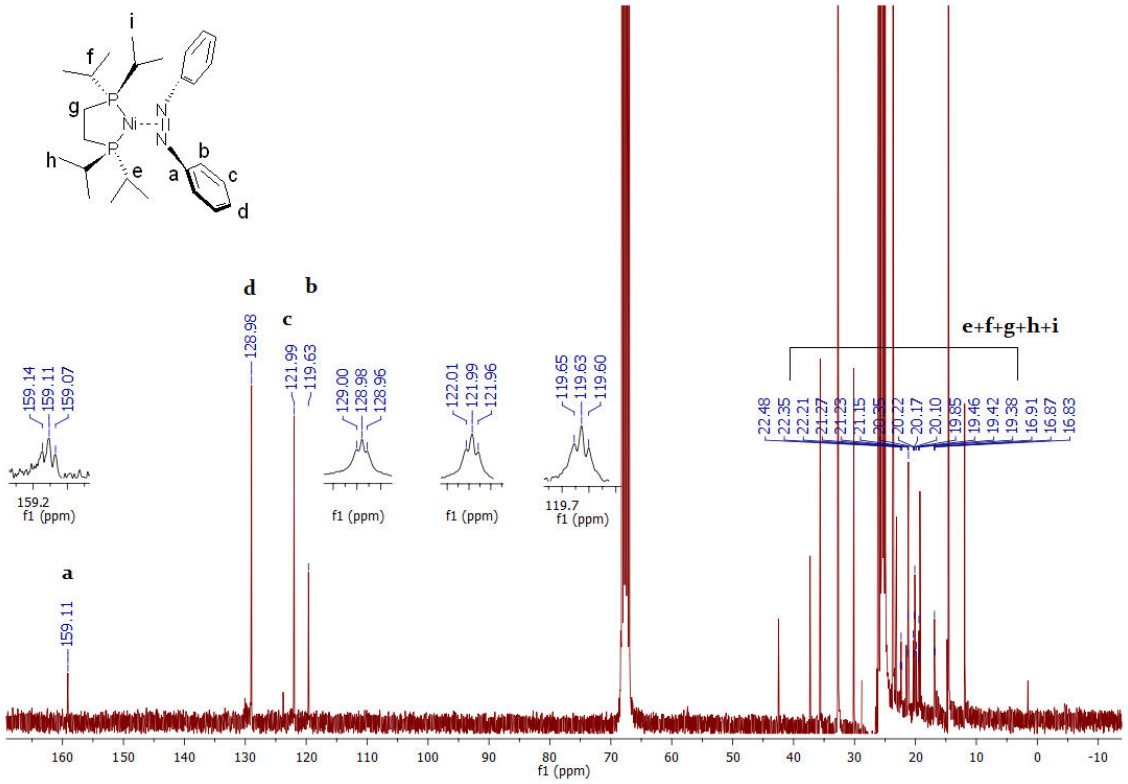


Figure S 3. $^{13}C\{^{1}H\}$-NMR of I

NMR Spectra of Complex II

$^{31}P\{^{1}H\}$-NMR

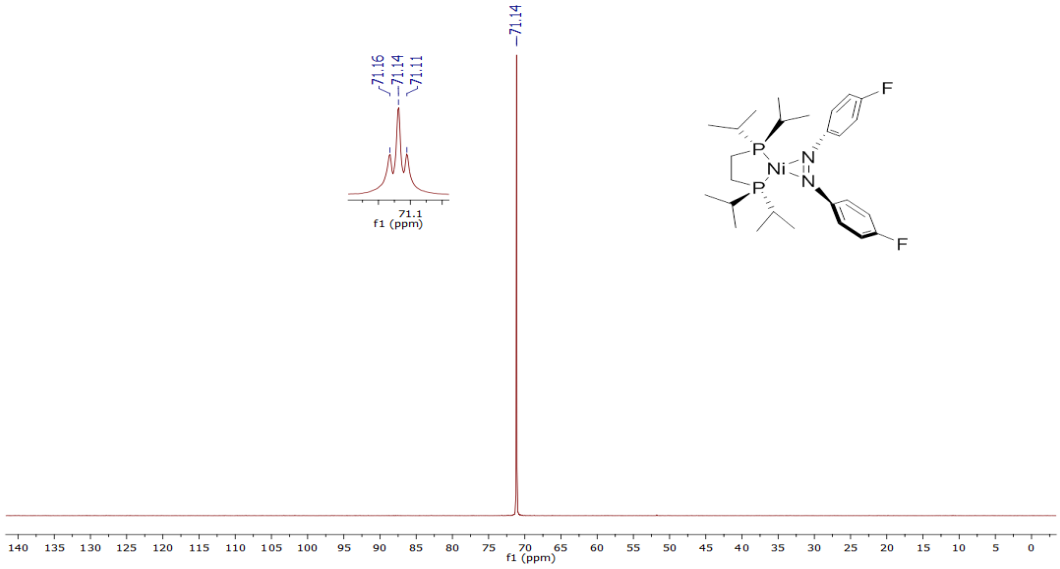


Figure S 4. $^{31}P\{^{1}H\}$-NMR of II

^{19}F-NMR

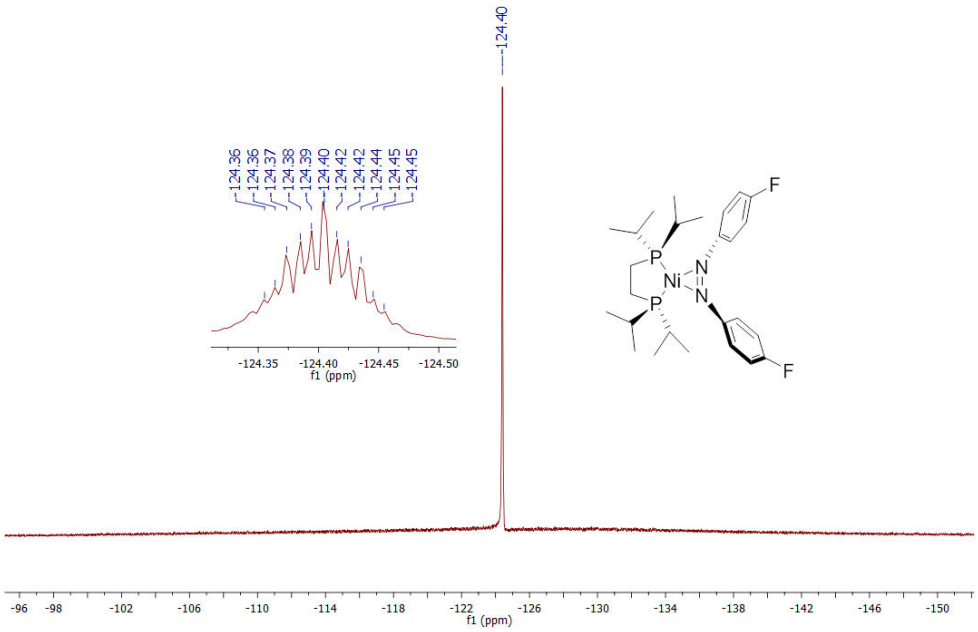


Figure S 5. ^{19}F-NMR of II

^{1}H-NMR

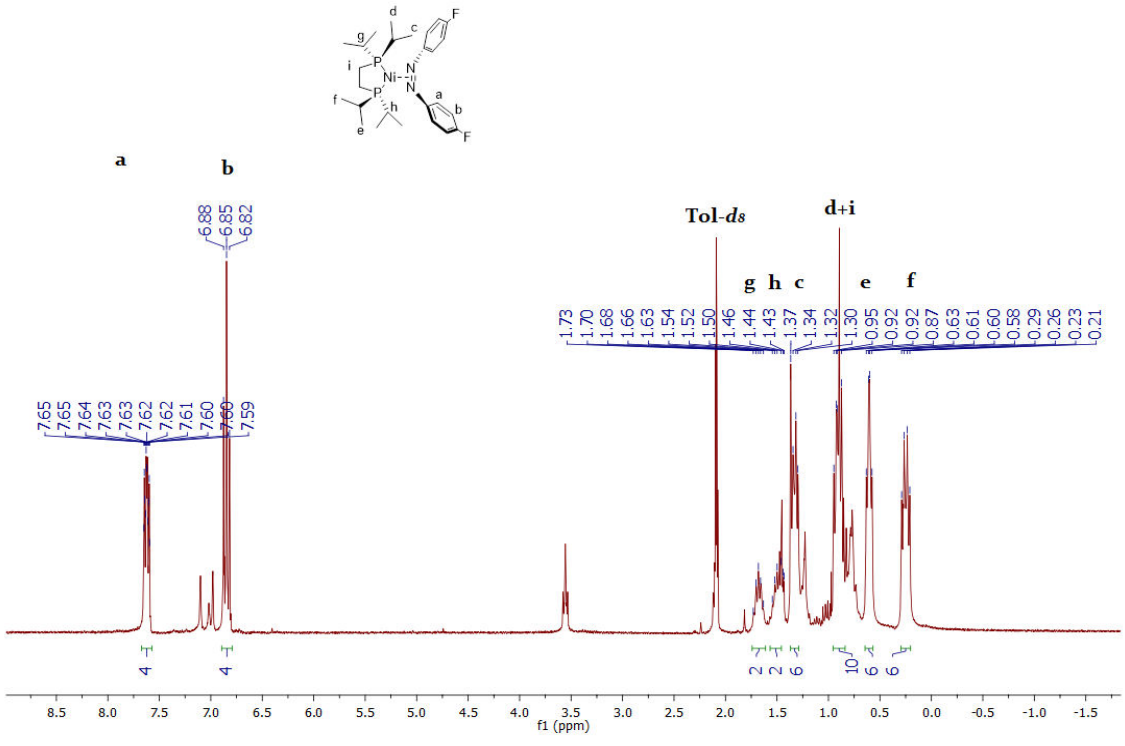


Figure S 6. ^{1}H-NMR of II

^{13}C{^{1}H}-NMR

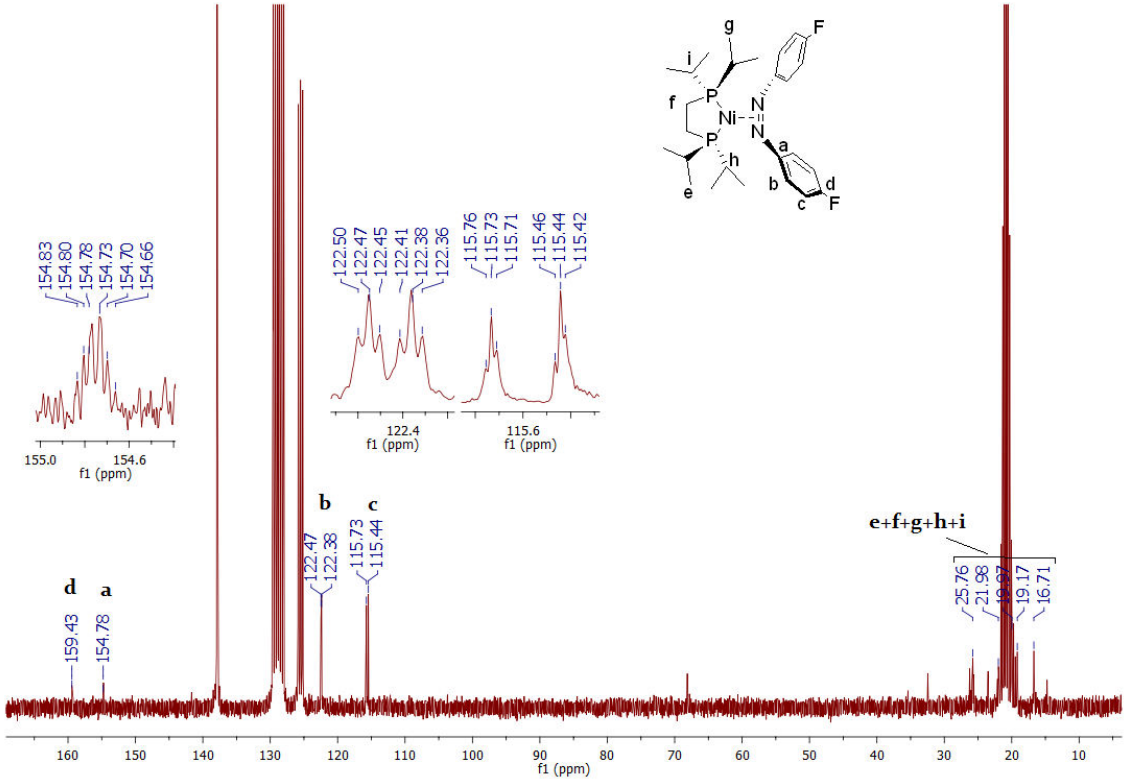


Figure S 7. $^{13}C\{^{1}H\}$-NMR of II

NMR Spectra of complex III

$^{31}P\{^{1}H\}$-NMR

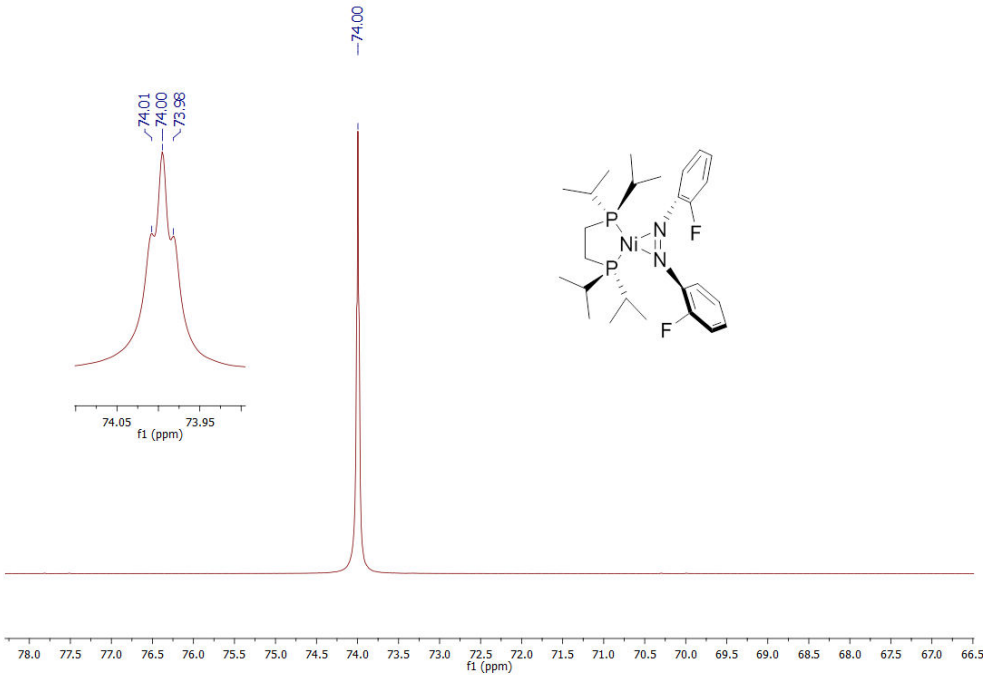


Figure S 8. $^{31}P\{^{1}H\}$-NMR of III

^{19}F-NMR

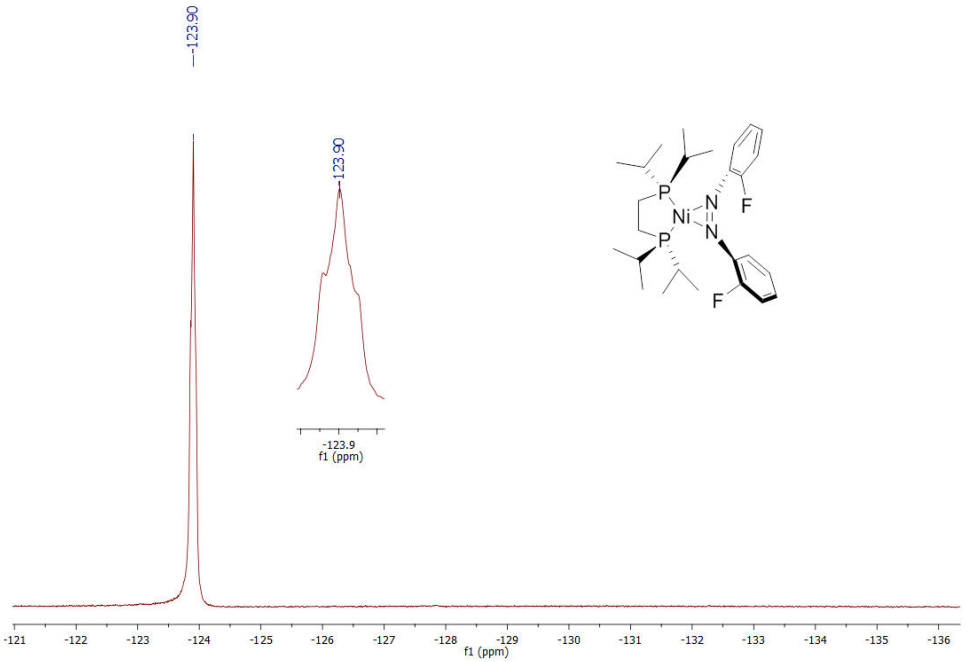


Figure S 9. ^{19}F-NMR of III

^{1}H-NMR

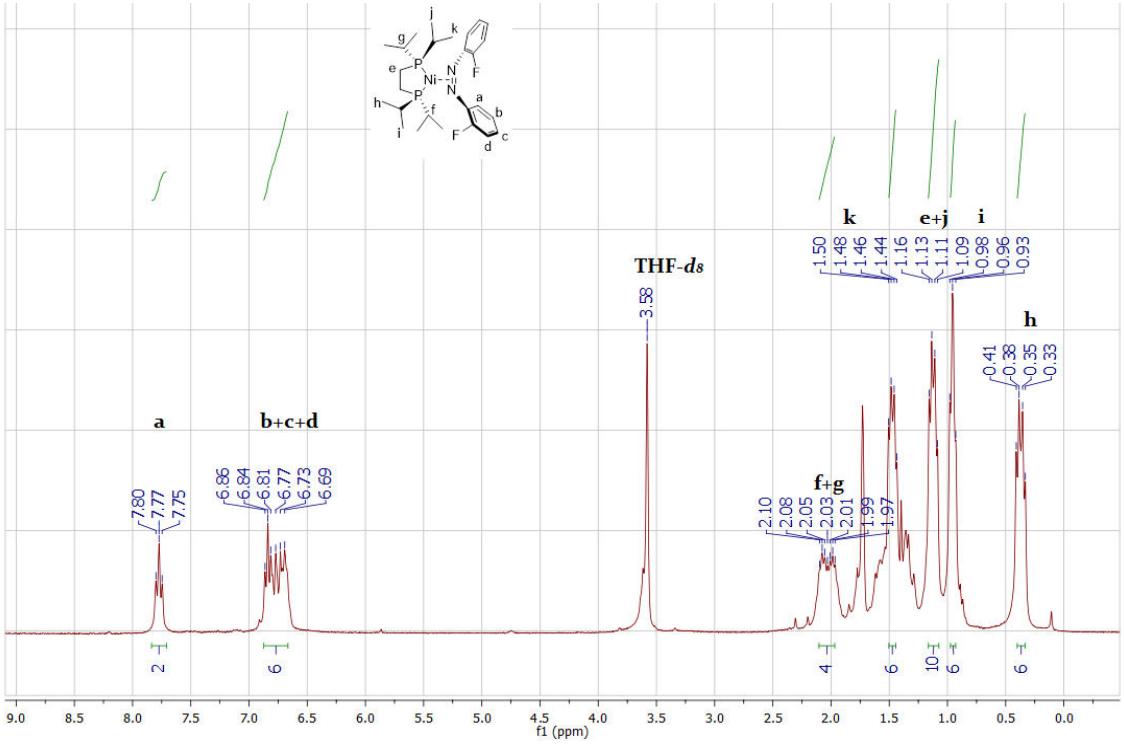


Figure S 10. ^{1}H-NMR of III

$^{13}C\{^{1}H\}$-NMR

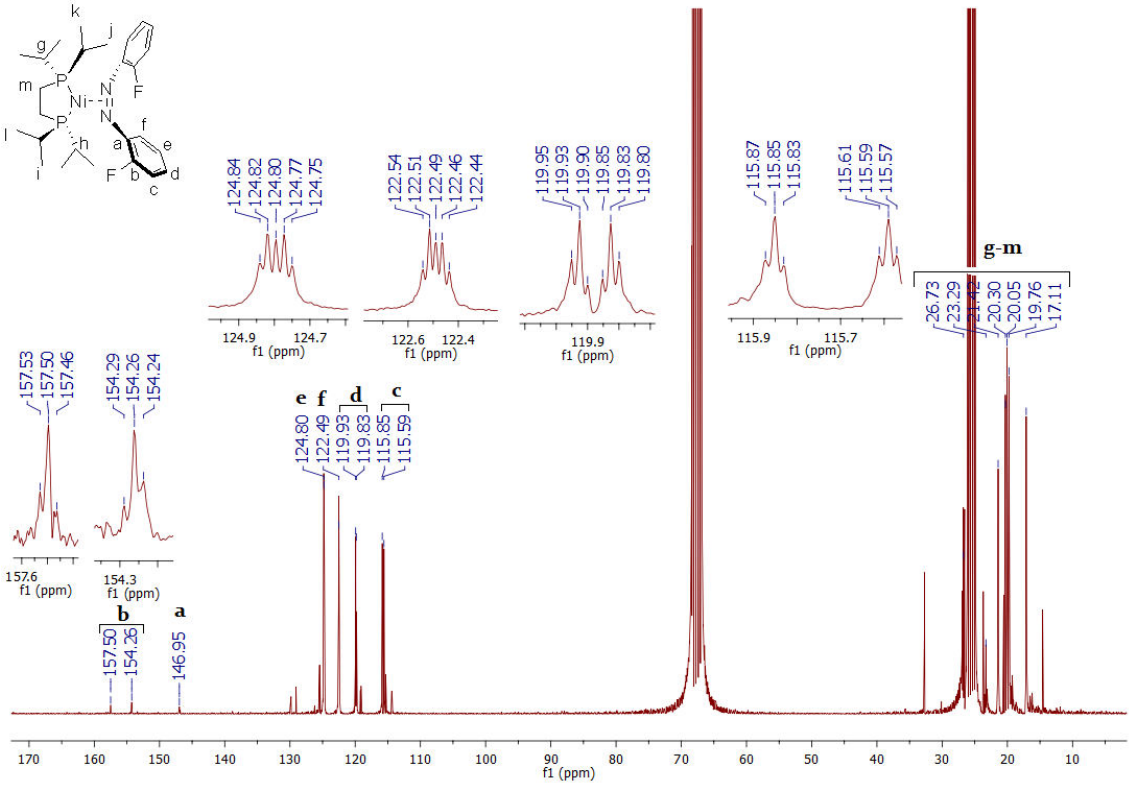


Figure S 11. $^{13}C\{^{1}H\}$-NMR of III

NMR spectra of azobenzenes

^{1}H-NMR

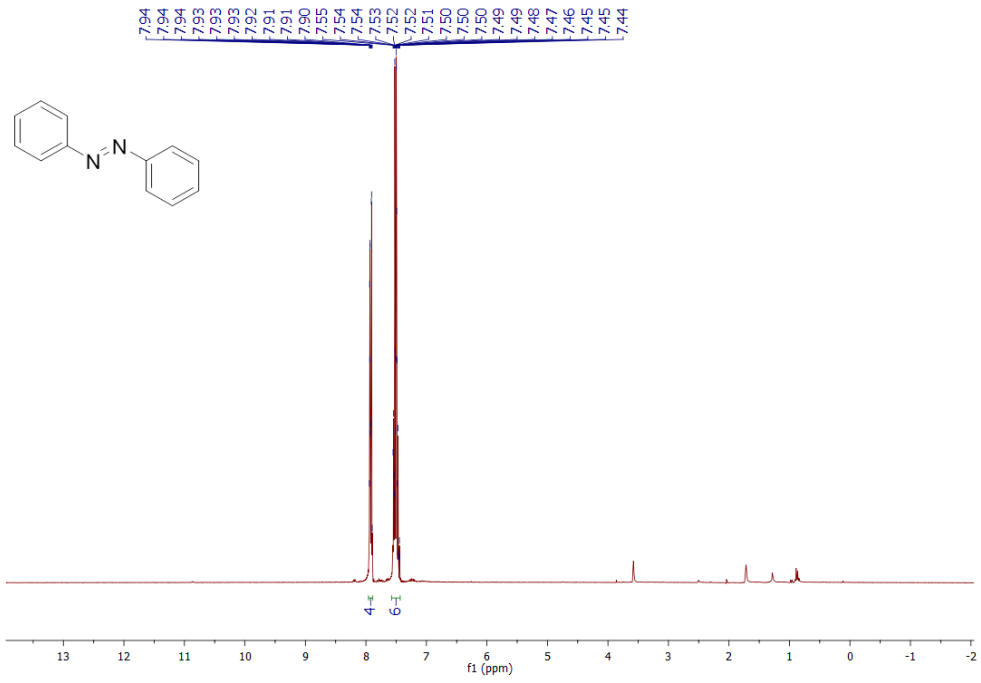


Figure S 12. ^{1}H-NMR of Azobenzene in THF-d_8

^{13}C{^{1}H}-NMR

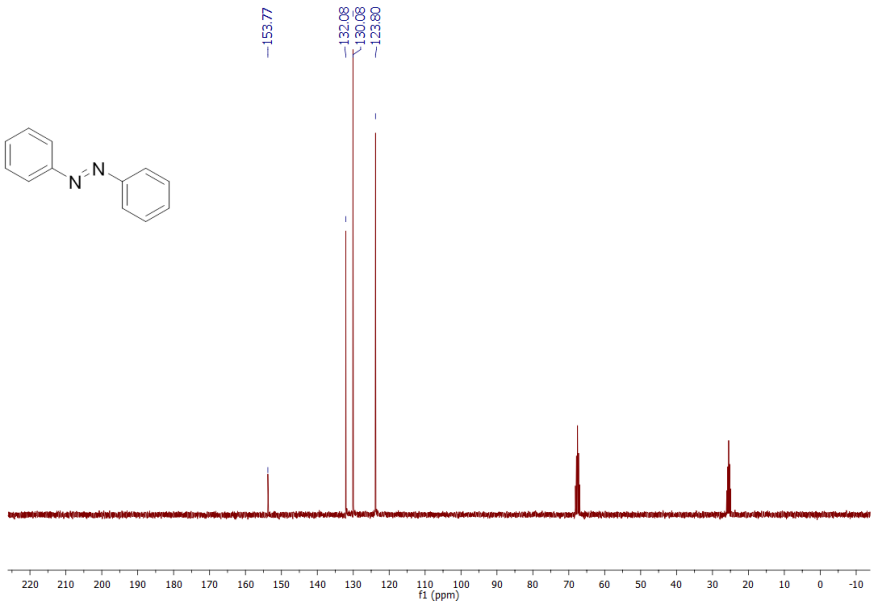


Figure S 13. ^{13}C{^{1}H} NMR of Azobenzene in THF-d_8.

^{1}H-NMR

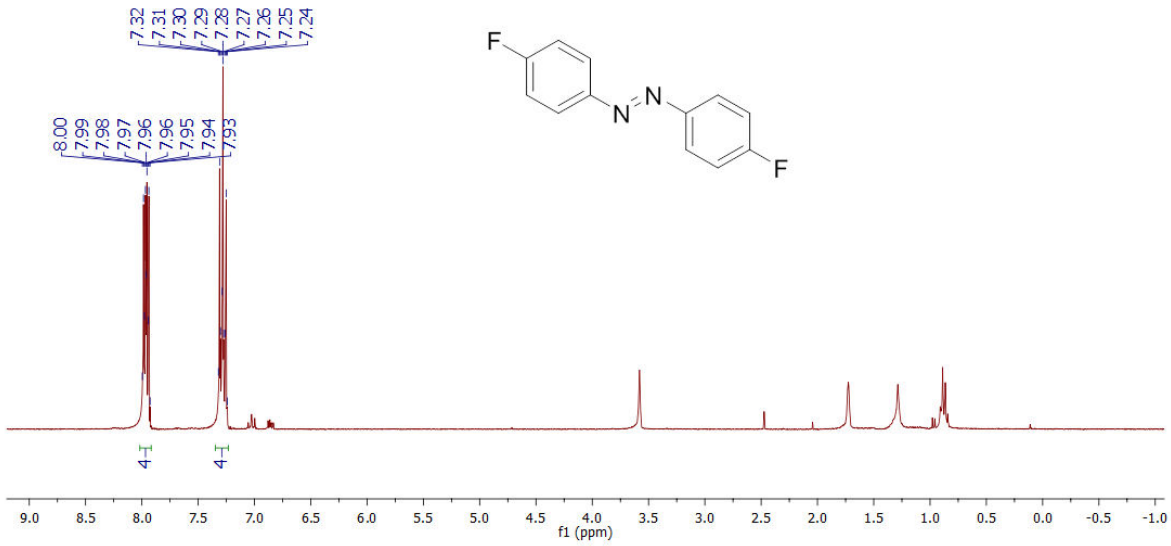


Figure S 14. ^{1}H-NMR of (E)-1,2-Bis(4-fluorophenyl)diazene in THF-d_8

^{13}C{^{1}H}-NMR

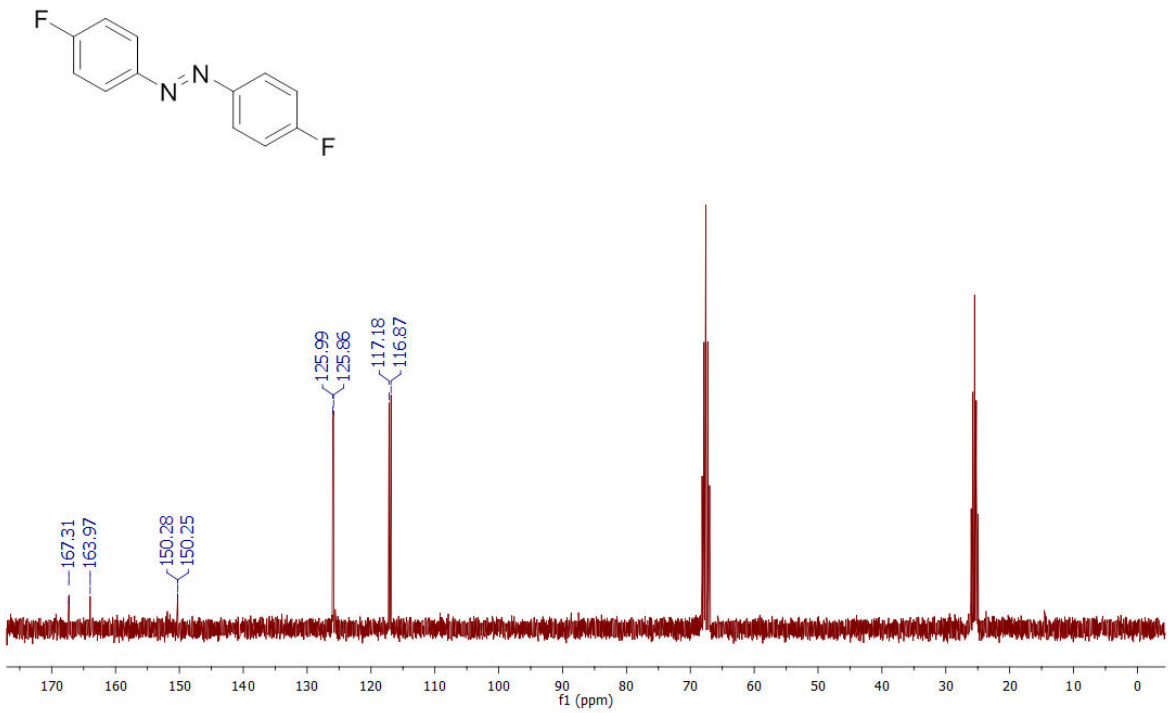


Figure S 15. $^{13}C\{^{1}H\}$ NMR of (E)-1,2-Bis(4-fluorophenyl)diazene in THF-d_8

^{19}F-NMR

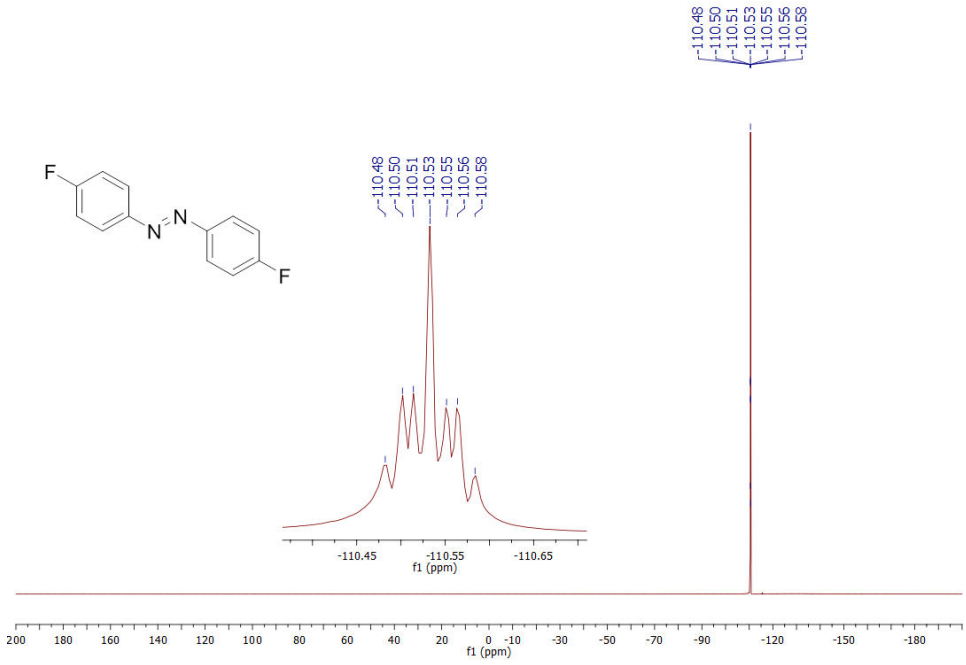


Figure S 16. ^{19}F NMR of (E)-1,2-Bis(4-fluorophenyl)diazene in THF-d_8

^{1}H-NMR

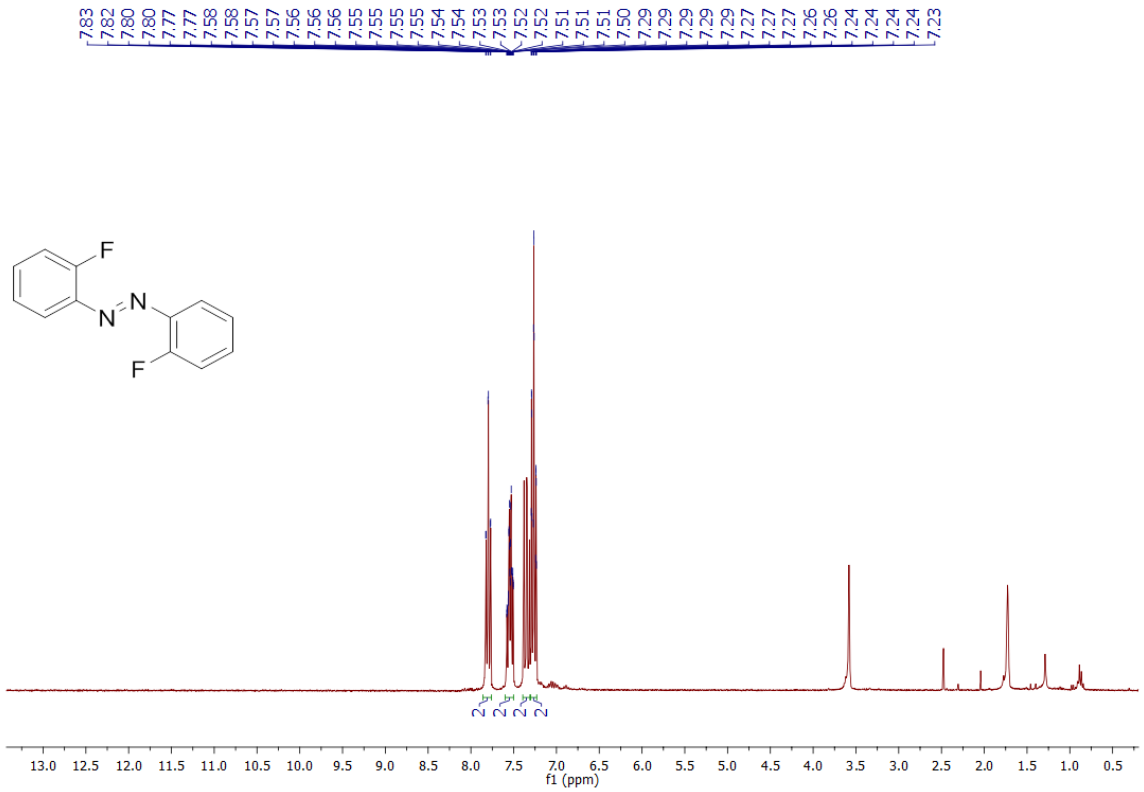


Figure S 17. ^{1}H NMR of (E)-1,2-Bis(2-fluorophenyl)diazene in THF-d_8

^{13}C{^{1}H}-NMR

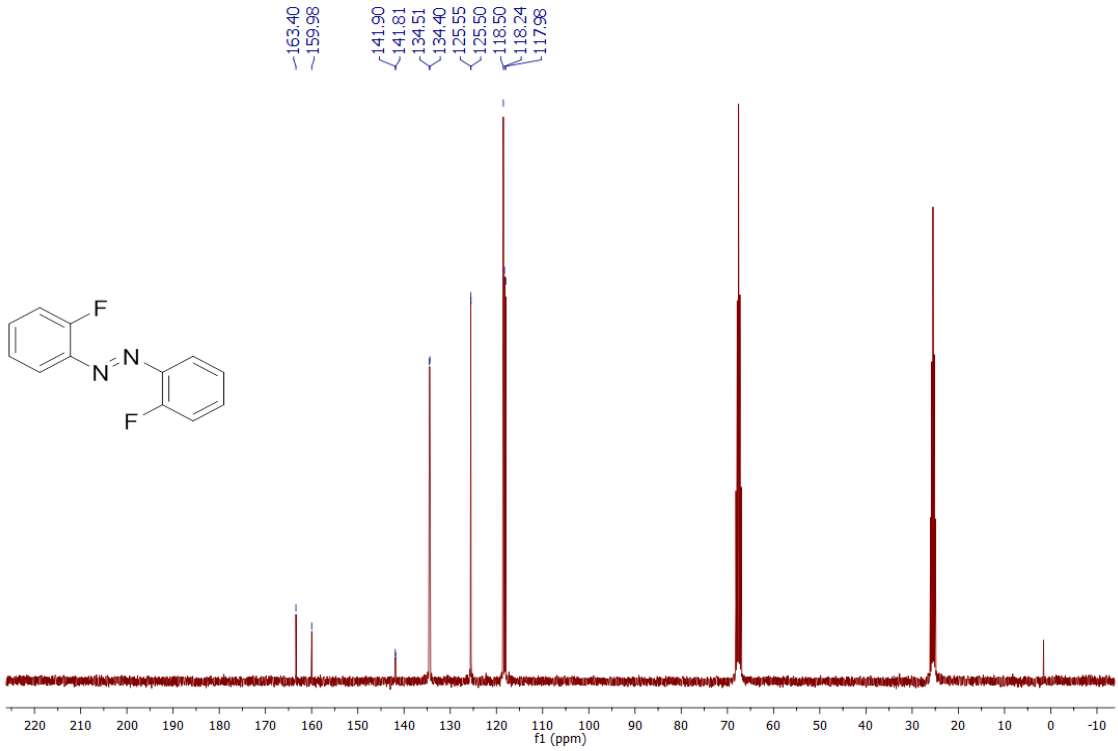


Figure S 18. $^{13}C\{^{1}H\}$ NMR of (E)-1,2-Bis(2-fluorophenyl)diazene in THF-d_8

^{19}F-NMR

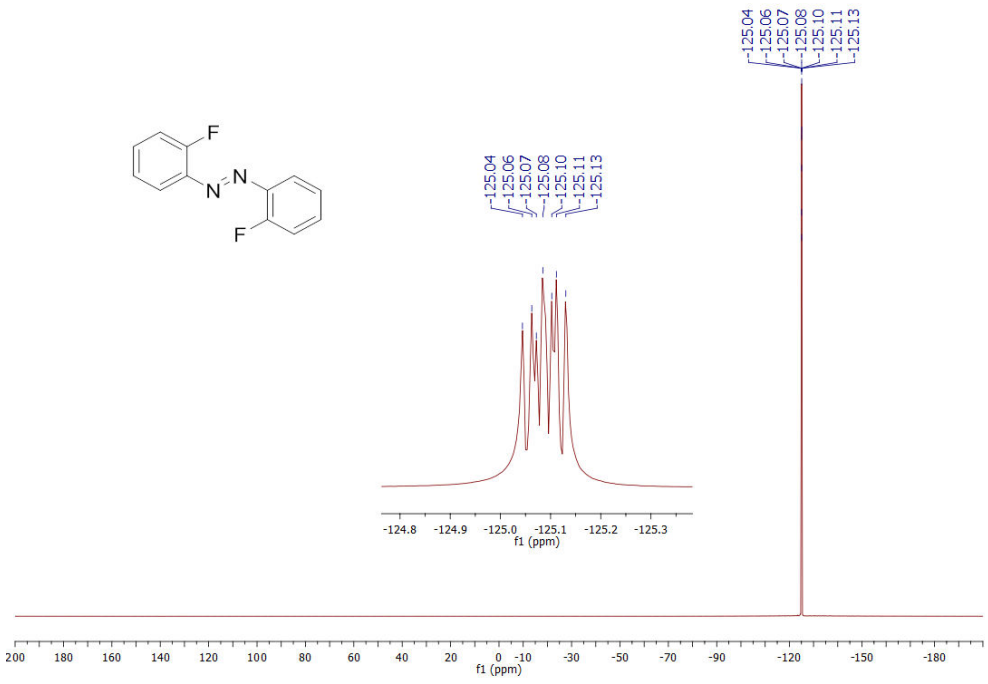


Figure S 19. ^{19}F NMR of (E)-1,2-Bis(2-fluorophenyl)diazene in THF-d_8

^{1}H NMR.

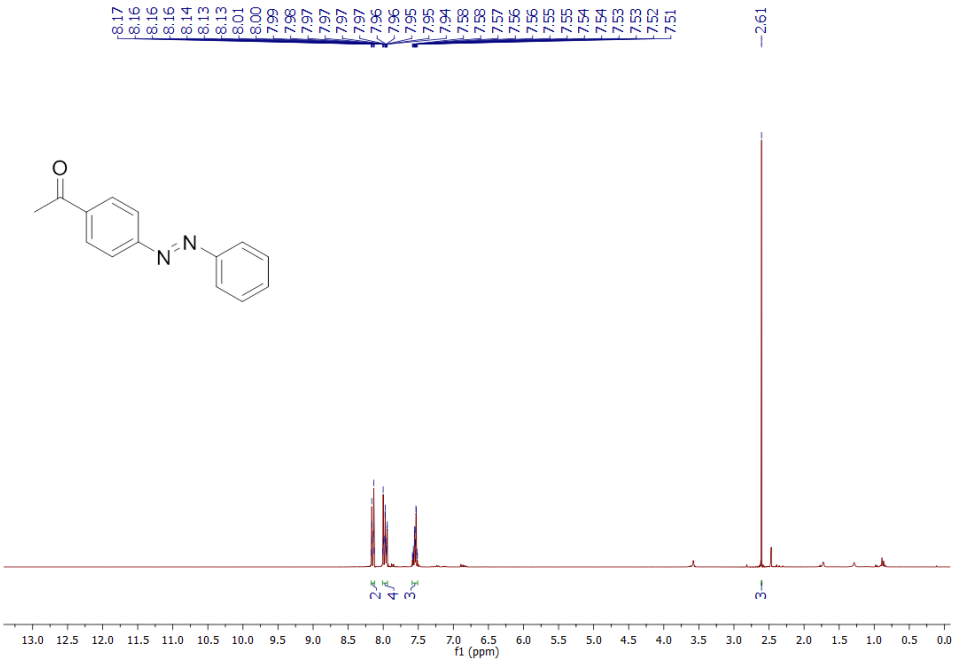


Figure S 20. ^{1}H NMR of 4-(phenylazo)acetophenone in THF-d_8

^{13}C{^{1}H}-NMR

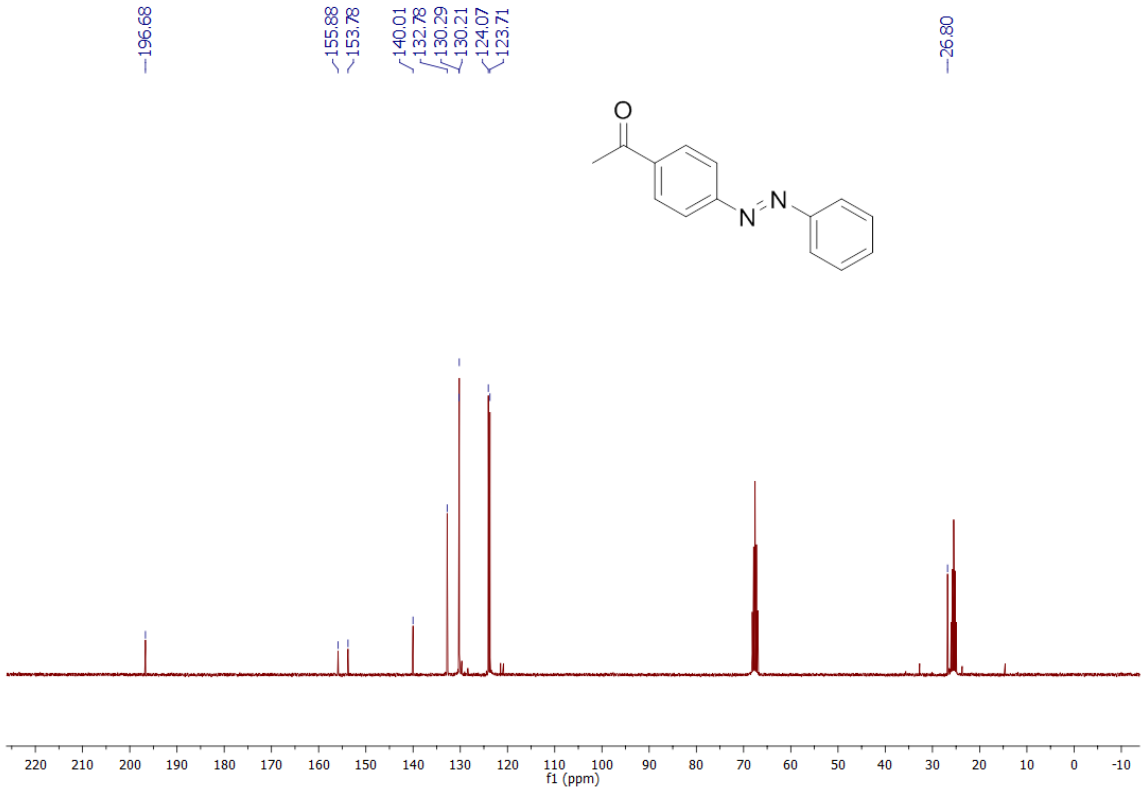


Figure S 21. ^{13}C NMR of 4-(phenylazo)acetophenone in THF-d_8

NMR of [(dippe)Ni(μ-H)]$_2$

^{1}H-NMR

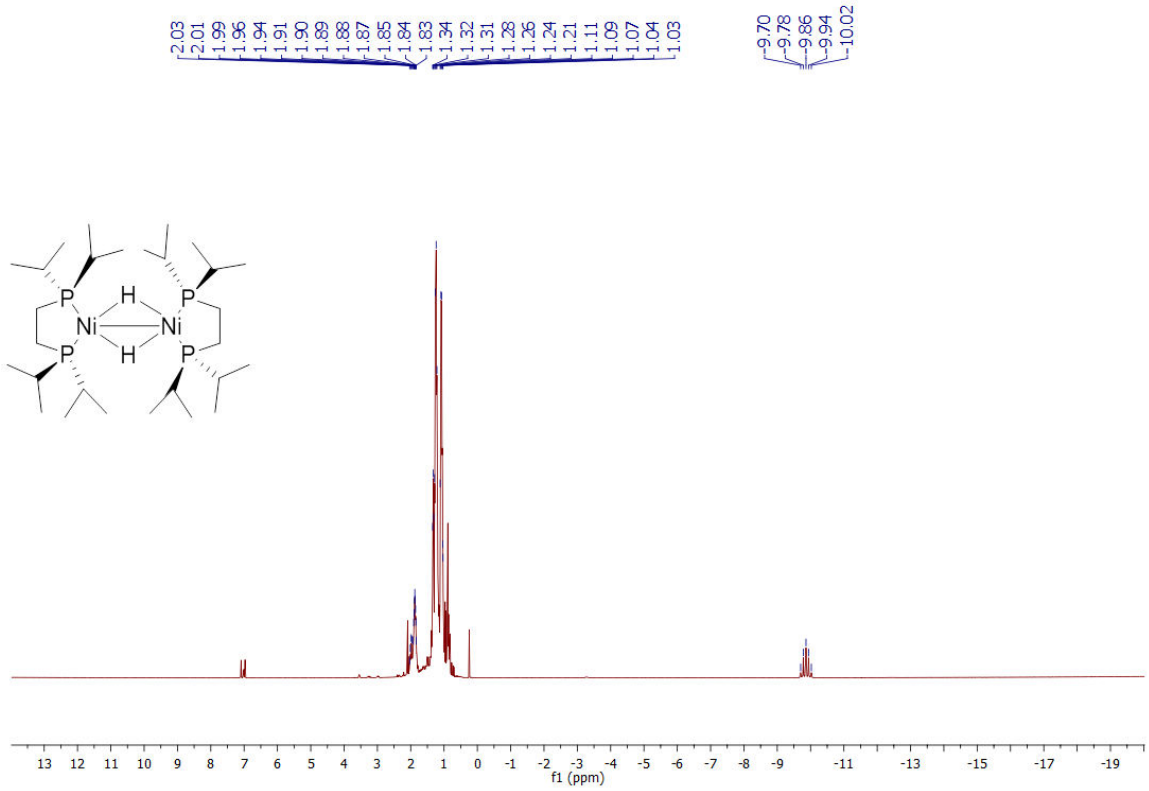


Figure S 22. ^{1}H NMR of [(dippe)Ni(μ-H)]$_2$ in Tol-d_8

^{31}P{^{1}H}-NMR

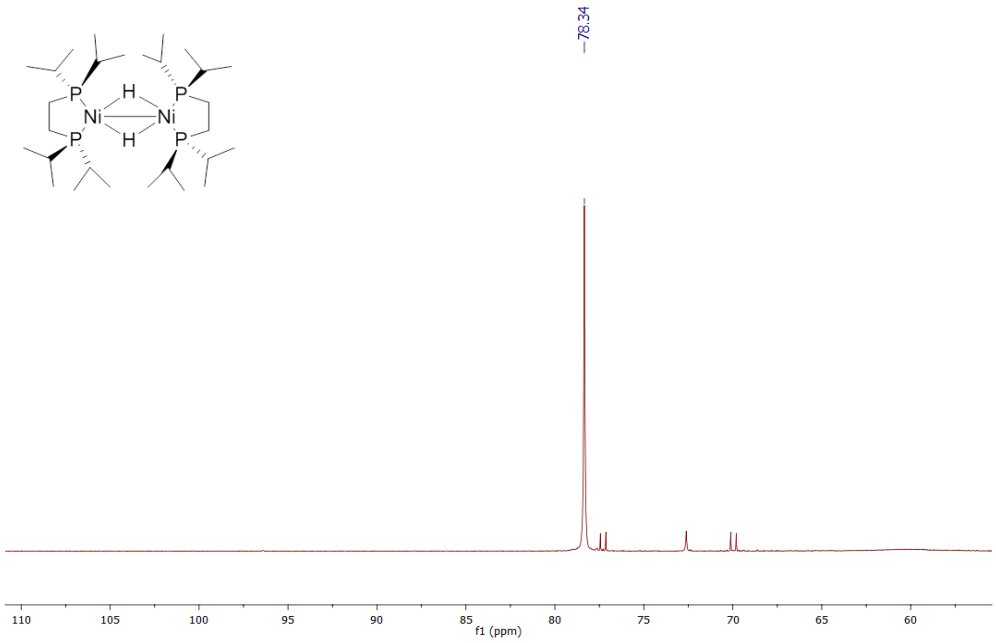


Figure S 23. ^{31}P{^{1}H} NMR of [(dippe)Ni(μ-H)]$_2$ in Tol-d_8

Crystallographic data of Complex I, II, III

Complex I

Table S 1. Crystal data and structure refinement for complex I.

Identification code	shelx	
Empirical formula	C26 H42 N2 Ni P2	
Formula weight	503.26	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.1202(3) Å	α= 90°.
	b = 15.6332(3) Å	β= 94.422(2)°.
	c = 16.5211(3) Å	γ = 90°.
Volume	2863.55(11) $Å^3$	
Z	4	
Density (calculated)	1.167 Mg/m^3	
Absorption coefficient	0.804 mm^{-1}	
F(000)	1080	
Theta range for data collection	3.369 to 29.554°.	
Index ranges	-14<=h<=15, -20<=k<=21, -22<=l<=19	
Reflections collected	24891	
Independent reflections	7095 [R(int) = 0.0231]	
Completeness to theta = 26.000°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7095 / 0 / 288	
Goodness-of-fit on F^2	1.073	
Final R indices [I>2sigma(I)]	R1 = 0.0316, wR2 = 0.0916	
R indices (all data)	R1 = 0.0369, wR2 = 0.0948	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.611 and -0.269 $e.Å^{-3}$	

Table S 2. **Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex I. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.**

	x	y	z	U(eq)
C(1)	7225(1)	2328(1)	3242(1)	22(1)
C(2)	8298(2)	2700(1)	3565(1)	26(1)
C(3)	9329(2)	2214(1)	3728(1)	32(1)
C(4)	9313(2)	1344(1)	3576(1)	37(1)
C(5)	8246(2)	961(1)	3268(1)	34(1)
C(6)	7202(2)	1443(1)	3106(1)	27(1)
C(7)	4141(1)	2964(1)	2920(1)	22(1)
C(8)	4140(2)	3792(1)	3239(1)	28(1)
C(9)	3060(2)	4221(1)	3303(1)	39(1)
C(10)	1965(2)	3835(2)	3064(1)	44(1)
C(11)	1955(2)	3012(1)	2761(1)	38(1)
C(12)	3030(2)	2580(1)	2691(1)	29(1)
C(13)	5682(2)	3374(1)	7(1)	29(1)
C(14)	7007(2)	3568(1)	256(1)	31(1)
C(15)	8913(2)	3288(1)	1520(1)	30(1)
C(16)	9022(2)	2328(1)	1372(1)	40(1)
C(17)	9776(2)	3793(2)	1026(1)	43(1)
C(18)	7373(2)	4799(1)	1606(1)	29(1)
C(19)	6093(2)	5155(1)	1539(1)	37(1)
C(20)	7976(2)	4955(1)	2453(1)	40(1)
C(21)	4926(2)	1624(1)	405(1)	35(1)
C(22)	6212(2)	1318(1)	306(2)	47(1)
C(23)	4291(2)	1056(1)	982(2)	50(1)
C(24)	3356(1)	3077(1)	645(1)	24(1)
C(27)	2751(2)	2933(1)	-209(1)	34(1)
C(28)	3239(2)	4007(1)	908(1)	30(1)
Ni(1)	5943(1)	2943(1)	1937(1)	17(1)
P(1)	7324(1)	3642(1)	1368(1)	22(1)
P(2)	4950(1)	2734(1)	776(1)	20(1)
N(1)	6229(1)	2893(1)	3094(1)	20(1)
N(2)	5180(1)	2455(1)	2829(1)	21(1)

Table S 3. Bond lengths [Å] and angles [°] for complex I.

C(1)-C(2)	1.396(2)	C(16)-H(16B)	0.9800
C(1)-C(6)	1.401(2)	C(16)-H(16C)	0.9800
C(1)-N(1)	1.424(2)	C(17)-H(17A)	0.9800
C(2)-C(3)	1.384(2)	C(17)-H(17B)	0.9800
C(2)-H(2)	0.9500	C(17)-H(17C)	0.9800
C(3)-C(4)	1.383(3)	C(18)-C(20)	1.524(3)
C(3)-H(3)	0.9500	C(18)-C(19)	1.525(3)
C(4)-C(5)	1.389(3)	C(18)-P(1)	1.8502(18)
C(4)-H(4)	0.9500	C(18)-H(18)	1.0000
C(5)-C(6)	1.393(2)	C(19)-H(19A)	0.9800
C(5)-H(5)	0.9500	C(19)-H(19B)	0.9800
C(6)-H(6)	0.9500	C(19)-H(19C)	0.9800
C(7)-C(8)	1.398(2)	C(20)-H(20A)	0.9800
C(7)-C(12)	1.400(2)	C(20)-H(20B)	0.9800
C(7)-N(2)	1.420(2)	C(20)-H(20C)	0.9800
C(8)-C(9)	1.387(3)	C(21)-C(23)	1.517(3)
C(8)-H(8)	0.9500	C(21)-C(22)	1.528(3)
C(9)-C(10)	1.389(3)	C(21)-P(2)	1.8401(18)
C(9)-H(9)	0.9500	C(21)-H(21)	1.0000
C(10)-C(11)	1.379(3)	C(22)-H(22A)	0.9800
C(10)-H(10)	0.9500	C(22)-H(22B)	0.9800
C(11)-C(12)	1.386(3)	C(22)-H(22C)	0.9800
C(11)-H(11)	0.9500	C(23)-H(23A)	0.9800
C(12)-H(12)	0.9500	C(23)-H(23B)	0.9800
C(13)-C(14)	1.529(2)	C(23)-H(23C)	0.9800
C(13)-P(2)	1.8539(17)	C(24)-C(28)	1.525(2)
C(13)-H(13A)	0.9900	C(24)-C(27)	1.532(2)
C(13)-H(13B)	0.9900	C(24)-P(2)	1.8482(17)
C(14)-P(1)	1.8474(17)	C(24)-H(24)	1.0000
C(14)-H(14A)	0.9900	C(27)-H(27A)	0.9800
C(14)-H(14B)	0.9900	C(27)-H(27B)	0.9800
C(15)-C(16)	1.527(3)	C(27)-H(27C)	0.9800
C(15)-C(17)	1.528(3)	C(28)-H(28A)	0.9800
C(15)-P(1)	1.8502(18)	C(28)-H(28B)	0.9800
C(15)-H(15)	1.0000	C(28)-H(28C)	0.9800
C(16)-H(16A)	0.9800	Ni(1)-N(2)	1.9148(12)

Ni(1)-N(1)	1.9149(13)	Ni(1)-P(2)	2.1629(4)
Ni(1)-P(1)	2.1598(4)	N(1)-N(2)	1.3933(18)

C(2)-C(1)-C(6)	118.54(15)	C(7)-C(12)-H(12)	119.4
C(2)-C(1)-N(1)	115.97(15)	C(14)-C(13)-P(2)	112.86(11)
C(6)-C(1)-N(1)	125.48(15)	C(14)-C(13)-H(13A)	109.0
C(3)-C(2)-C(1)	121.09(17)	P(2)-C(13)-H(13A)	109.0
C(3)-C(2)-H(2)	119.5	C(14)-C(13)-H(13B)	109.0
C(1)-C(2)-H(2)	119.5	P(2)-C(13)-H(13B)	109.0
C(4)-C(3)-C(2)	120.33(17)	H(13A)-C(13)-H(13B)	107.8
C(4)-C(3)-H(3)	119.8	C(13)-C(14)-P(1)	112.68(11)
C(2)-C(3)-H(3)	119.8	C(13)-C(14)-H(14A)	109.1
C(3)-C(4)-C(5)	119.27(17)	P(1)-C(14)-H(14A)	109.1
C(3)-C(4)-H(4)	120.4	C(13)-C(14)-H(14B)	109.1
C(5)-C(4)-H(4)	120.4	P(1)-C(14)-H(14B)	109.1
C(4)-C(5)-C(6)	120.88(18)	H(14A)-C(14)-H(14B)	107.8
C(4)-C(5)-H(5)	119.6	C(16)-C(15)-C(17)	111.18(16)
C(6)-C(5)-H(5)	119.6	C(16)-C(15)-P(1)	111.02(13)
C(5)-C(6)-C(1)	119.87(16)	C(17)-C(15)-P(1)	113.90(14)
C(5)-C(6)-H(6)	120.1	C(16)-C(15)-H(15)	106.8
C(1)-C(6)-H(6)	120.1	C(17)-C(15)-H(15)	106.8
C(8)-C(7)-C(12)	118.25(16)	P(1)-C(15)-H(15)	106.8
C(8)-C(7)-N(2)	125.66(15)	C(15)-C(16)-H(16A)	109.5
C(12)-C(7)-N(2)	116.06(15)	C(15)-C(16)-H(16B)	109.5
C(9)-C(8)-C(7)	120.14(17)	H(16A)-C(16)-H(16B)	109.5
C(9)-C(8)-H(8)	119.9	C(15)-C(16)-H(16C)	109.5
C(7)-C(8)-H(8)	119.9	H(16A)-C(16)-H(16C)	109.5
C(8)-C(9)-C(10)	120.9(2)	H(16B)-C(16)-H(16C)	109.5
C(8)-C(9)-H(9)	119.6	C(15)-C(17)-H(17A)	109.5
C(10)-C(9)-H(9)	119.6	C(15)-C(17)-H(17B)	109.5
C(11)-C(10)-C(9)	119.45(18)	H(17A)-C(17)-H(17B)	109.5
C(11)-C(10)-H(10)	120.3	C(15)-C(17)-H(17C)	109.5
C(9)-C(10)-H(10)	120.3	H(17A)-C(17)-H(17C)	109.5
C(10)-C(11)-C(12)	120.12(19)	H(17B)-C(17)-H(17C)	109.5
C(10)-C(11)-H(11)	119.9	C(20)-C(18)-C(19)	110.49(16)
C(12)-C(11)-H(11)	119.9	C(20)-C(18)-P(1)	110.80(12)
C(11)-C(12)-C(7)	121.13(18)	C(19)-C(18)-P(1)	109.29(12)
C(11)-C(12)-H(12)	119.4	C(20)-C(18)-H(18)	108.7

C(19)-C(18)-H(18)	108.7	C(24)-C(27)-H(27A)	109.5
P(1)-C(18)-H(18)	108.7	C(24)-C(27)-H(27B)	109.5
C(18)-C(19)-H(19A)	109.5	H(27A)-C(27)-H(27B)	109.5
C(18)-C(19)-H(19B)	109.5	C(24)-C(27)-H(27C)	109.5
H(19A)-C(19)-H(19B)	109.5	H(27A)-C(27)-H(27C)	109.5
C(18)-C(19)-H(19C)	109.5	H(27B)-C(27)-H(27C)	109.5
H(19A)-C(19)-H(19C)	109.5	C(24)-C(28)-H(28A)	109.5
H(19B)-C(19)-H(19C)	109.5	C(24)-C(28)-H(28B)	109.5
C(18)-C(20)-H(20A)	109.5	H(28A)-C(28)-H(28B)	109.5
C(18)-C(20)-H(20B)	109.5	C(24)-C(28)-H(28C)	109.5
H(20A)-C(20)-H(20B)	109.5	H(28A)-C(28)-H(28C)	109.5
C(18)-C(20)-H(20C)	109.5	H(28B)-C(28)-H(28C)	109.5
H(20A)-C(20)-H(20C)	109.5	N(2)-Ni(1)-N(1)	42.67(5)
H(20B)-C(20)-H(20C)	109.5	N(2)-Ni(1)-P(1)	155.40(4)
C(23)-C(21)-C(22)	111.67(18)	N(1)-Ni(1)-P(1)	112.74(4)
C(23)-C(21)-P(2)	109.73(14)	N(2)-Ni(1)-P(2)	113.35(4)
C(22)-C(21)-P(2)	109.95(14)	N(1)-Ni(1)-P(2)	155.94(4)
C(23)-C(21)-H(21)	108.5	P(1)-Ni(1)-P(2)	91.249(16)
C(22)-C(21)-H(21)	108.5	C(14)-P(1)-C(15)	102.95(8)
P(2)-C(21)-H(21)	108.5	C(14)-P(1)-C(18)	105.83(8)
C(21)-C(22)-H(22A)	109.5	C(15)-P(1)-C(18)	104.57(8)
C(21)-C(22)-H(22B)	109.5	C(14)-P(1)-Ni(1)	108.29(6)
H(22A)-C(22)-H(22B)	109.5	C(15)-P(1)-Ni(1)	119.55(6)
C(21)-C(22)-H(22C)	109.5	C(18)-P(1)-Ni(1)	114.33(6)
H(22A)-C(22)-H(22C)	109.5	C(21)-P(2)-C(24)	104.23(8)
H(22B)-C(22)-H(22C)	109.5	C(21)-P(2)-C(13)	106.02(9)
C(21)-C(23)-H(23A)	109.5	C(24)-P(2)-C(13)	103.37(8)
C(21)-C(23)-H(23B)	109.5	C(21)-P(2)-Ni(1)	115.54(6)
H(23A)-C(23)-H(23B)	109.5	C(24)-P(2)-Ni(1)	118.64(5)
C(21)-C(23)-H(23C)	109.5	C(13)-P(2)-Ni(1)	107.76(6)
H(23A)-C(23)-H(23C)	109.5	N(2)-N(1)-C(1)	111.73(12)
H(23B)-C(23)-H(23C)	109.5	N(2)-N(1)-Ni(1)	68.66(7)
C(28)-C(24)-C(27)	111.12(14)	C(1)-N(1)-Ni(1)	105.28(9)
C(28)-C(24)-P(2)	110.23(11)	N(1)-N(2)-C(7)	111.05(13)
C(27)-C(24)-P(2)	114.44(12)	N(1)-N(2)-Ni(1)	68.67(7)
C(28)-C(24)-H(24)	106.9	C(7)-N(2)-Ni(1)	105.68(9)
C(27)-C(24)-H(24)	106.9		
P(2)-C(24)-H(24)	106.9		

Table S 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for complex I. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	23(1)	30(1)	12(1)	4(1)	2(1)	1(1)
C(2)	24(1)	33(1)	19(1)	3(1)	-1(1)	-1(1)
C(3)	23(1)	46(1)	28(1)	7(1)	-1(1)	1(1)
C(4)	28(1)	46(1)	36(1)	11(1)	4(1)	13(1)
C(5)	38(1)	31(1)	32(1)	5(1)	6(1)	8(1)
C(6)	29(1)	30(1)	21(1)	4(1)	2(1)	1(1)
C(7)	24(1)	31(1)	12(1)	7(1)	2(1)	0(1)
C(8)	29(1)	36(1)	19(1)	0(1)	1(1)	4(1)
C(9)	42(1)	47(1)	30(1)	-4(1)	2(1)	15(1)
C(10)	31(1)	68(1)	33(1)	5(1)	4(1)	19(1)
C(11)	23(1)	64(1)	26(1)	11(1)	2(1)	-1(1)
C(12)	26(1)	39(1)	21(1)	9(1)	1(1)	-4(1)
C(13)	25(1)	47(1)	15(1)	4(1)	2(1)	0(1)
C(14)	32(1)	43(1)	16(1)	4(1)	3(1)	-5(1)
C(15)	24(1)	40(1)	25(1)	1(1)	3(1)	-1(1)
C(16)	33(1)	45(1)	41(1)	-3(1)	5(1)	9(1)
C(17)	28(1)	62(1)	41(1)	5(1)	9(1)	-9(1)
C(18)	32(1)	25(1)	30(1)	5(1)	-2(1)	-8(1)
C(19)	37(1)	26(1)	45(1)	5(1)	-6(1)	0(1)
C(20)	47(1)	32(1)	40(1)	-7(1)	-14(1)	-1(1)
C(21)	45(1)	31(1)	27(1)	-12(1)	-10(1)	4(1)
C(22)	54(1)	40(1)	47(1)	-13(1)	-1(1)	12(1)
C(23)	65(2)	28(1)	54(1)	-7(1)	-3(1)	-11(1)
C(24)	20(1)	33(1)	17(1)	2(1)	-1(1)	-3(1)
C(27)	29(1)	48(1)	24(1)	-2(1)	-8(1)	-1(1)
C(28)	24(1)	36(1)	31(1)	-1(1)	0(1)	4(1)
Ni(1)	19(1)	20(1)	11(1)	1(1)	0(1)	-1(1)
P(1)	24(1)	26(1)	16(1)	2(1)	1(1)	-4(1)
P(2)	21(1)	27(1)	13(1)	-1(1)	-1(1)	0(1)
N(1)	21(1)	26(1)	13(1)	2(1)	-1(1)	-1(1)
N(2)	21(1)	26(1)	16(1)	5(1)	0(1)	-2(1)

Complex II

Table S 5. Crystal data and structure refinement for complex II.

Identification code	shelx	
Empirical formula	C26 H40 F2 N2 Ni P2	
Formula weight	539.25	
Temperature	130(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.1670(2) Å	α = 90°.
	b = 15.7392(3) Å	β = 94.3740(10)°.
	c = 16.5550(3) Å	γ = 90°.
Volume	2901.23(9) $Å^3$	
Z	4	
Density (calculated)	1.235 Mg/m^3	
Absorption coefficient	2.237 mm^{-1}	
F(000)	1144	
Theta range for data collection	3.881 to 73.492°.	
Index ranges	-13<=h<=13, -18<=k<=19, -20<=l<=18	
Reflections collected	19891	
Independent reflections	5769 [R(int) = 0.0273]	
Completeness to theta = 67.684°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5769 / 0 / 306	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0808	
R indices (all data)	R1 = 0.0359, wR2 = 0.0841	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.344 and -0.279 $e.Å^{-3}$	

Table S 6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex II. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6885(2)	1497(1)	5270(1)	23(1)
C(2)	5556(1)	1674(1)	5025(1)	21(1)
C(3)	3230(1)	1943(1)	5658(1)	19(1)
C(4)	3112(2)	1017(1)	5921(1)	24(1)
C(5)	2645(2)	2083(1)	4802(1)	28(1)
C(6)	4778(2)	3401(1)	5439(1)	24(1)
C(7)	6054(2)	3723(1)	5350(1)	35(1)
C(8)	4130(2)	3954(1)	6024(1)	36(1)
C(9)	7274(2)	239(1)	6589(1)	21(1)
C(10)	6008(2)	-135(1)	6487(1)	28(1)
C(11)	7832(2)	72(1)	7446(1)	28(1)
C(12)	8782(1)	1762(1)	6548(1)	20(1)
C(13)	9648(2)	1291(1)	6034(1)	29(1)
C(14)	8860(2)	2723(1)	6427(1)	28(1)
C(15)	4015(1)	2013(1)	7943(1)	17(1)
C(16)	4029(1)	1179(1)	8236(1)	21(1)
C(17)	2960(2)	732(1)	8289(1)	29(1)
C(18)	1890(2)	1128(1)	8051(1)	30(1)
C(19)	1835(2)	1950(1)	7778(1)	26(1)
C(20)	2900(1)	2394(1)	7723(1)	21(1)
C(21)	7079(1)	2653(1)	8267(1)	16(1)
C(22)	8148(1)	2274(1)	8588(1)	18(1)
C(23)	9182(2)	2751(1)	8756(1)	22(1)
C(24)	9133(2)	3611(1)	8599(1)	24(1)
C(25)	8099(2)	4014(1)	8301(1)	24(1)
C(26)	7060(2)	3531(1)	8138(1)	19(1)
F(1)	844(1)	686(1)	8095(1)	48(1)
F(2)	10154(1)	4080(1)	8757(1)	39(1)
N(1)	5047(1)	2529(1)	7861(1)	16(1)
N(2)	6089(1)	2089(1)	8111(1)	16(1)
Ni(1)	5805(1)	2066(1)	6957(1)	13(1)
P(1)	7202(1)	1394(1)	6380(1)	15(1)
P(2)	4819(1)	2290(1)	5800(1)	15(1)

Table S 7. Bond lengths [Å] and angles [°] for complex II.

C(1)-C(2)	1.534(2)	C(11)-H(11B)	0.9800
C(1)-P(1)	1.8521(16)	C(11)-H(11C)	0.9800
C(1)-H(1A)	0.9900	C(12)-C(14)	1.529(2)
C(1)-H(1B)	0.9900	C(12)-C(13)	1.529(2)
C(2)-P(2)	1.8509(16)	C(12)-P(1)	1.8576(16)
C(2)-H(2A)	0.9900	C(12)-H(12)	1.0000
C(2)-H(2B)	0.9900	C(13)-H(13A)	0.9800
C(3)-C(4)	1.528(2)	C(13)-H(13B)	0.9800
C(3)-C(5)	1.531(2)	C(13)-H(13C)	0.9800
C(3)-P(2)	1.8548(16)	C(14)-H(14A)	0.9800
C(3)-H(3)	1.0000	C(14)-H(14B)	0.9800
C(4)-H(4A)	0.9800	C(14)-H(14C)	0.9800
C(4)-H(4B)	0.9800	C(15)-C(16)	1.400(2)
C(4)-H(4C)	0.9800	C(15)-C(20)	1.405(2)
C(5)-H(5A)	0.9800	C(15)-N(1)	1.425(2)
C(5)-H(5B)	0.9800	C(16)-C(17)	1.394(2)
C(5)-H(5C)	0.9800	C(16)-H(16)	0.9500
C(6)-C(8)	1.526(3)	C(17)-C(18)	1.378(3)
C(6)-C(7)	1.530(3)	C(17)-H(17)	0.9500
C(6)-P(2)	1.8474(18)	C(18)-F(1)	1.367(2)
C(6)-H(6)	1.0000	C(18)-C(19)	1.370(3)
C(7)-H(7A)	0.9800	C(19)-C(20)	1.389(2)
C(7)-H(7B)	0.9800	C(19)-H(19)	0.9500
C(7)-H(7C)	0.9800	C(20)-H(20)	0.9500
C(8)-H(8A)	0.9800	C(21)-C(26)	1.399(2)
C(8)-H(8B)	0.9800	C(21)-C(22)	1.402(2)
C(8)-H(8C)	0.9800	C(21)-N(2)	1.425(2)
C(9)-C(11)	1.527(2)	C(22)-C(23)	1.388(2)
C(9)-C(10)	1.529(2)	C(22)-H(22)	0.9500
C(9)-P(1)	1.8519(17)	C(23)-C(24)	1.379(3)
C(9)-H(9)	1.0000	C(23)-H(23)	0.9500
C(10)-H(10A)	0.9800	C(24)-F(2)	1.3658(19)
C(10)-H(10B)	0.9800	C(24)-C(25)	1.376(3)
C(10)-H(10C)	0.9800	C(25)-C(26)	1.396(2)
C(11)-H(11A)	0.9800	C(25)-H(25)	0.9500

C(26)-H(26)	0.9500	N(2)-Ni(1)	1.9131(12)
N(1)-N(2)	1.3897(18)	Ni(1)-P(2)	2.1637(4)
N(1)-Ni(1)	1.9190(13)	Ni(1)-P(1)	2.1653(4)

C(2)-C(1)-P(1)	112.66(11)	C(7)-C(6)-H(6)	108.6
C(2)-C(1)-H(1A)	109.1	P(2)-C(6)-H(6)	108.6
P(1)-C(1)-H(1A)	109.1	C(6)-C(7)-H(7A)	109.5
C(2)-C(1)-H(1B)	109.1	C(6)-C(7)-H(7B)	109.5
P(1)-C(1)-H(1B)	109.1	H(7A)-C(7)-H(7B)	109.5
H(1A)-C(1)-H(1B)	107.8	C(6)-C(7)-H(7C)	109.5
C(1)-C(2)-P(2)	112.61(11)	H(7A)-C(7)-H(7C)	109.5
C(1)-C(2)-H(2A)	109.1	H(7B)-C(7)-H(7C)	109.5
P(2)-C(2)-H(2A)	109.1	C(6)-C(8)-H(8A)	109.5
C(1)-C(2)-H(2B)	109.1	C(6)-C(8)-H(8B)	109.5
P(2)-C(2)-H(2B)	109.1	H(8A)-C(8)-H(8B)	109.5
H(2A)-C(2)-H(2B)	107.8	C(6)-C(8)-H(8C)	109.5
C(4)-C(3)-C(5)	111.16(14)	H(8A)-C(8)-H(8C)	109.5
C(4)-C(3)-P(2)	110.31(11)	H(8B)-C(8)-H(8C)	109.5
C(5)-C(3)-P(2)	114.27(12)	C(11)-C(9)-C(10)	110.16(15)
C(4)-C(3)-H(3)	106.9	C(11)-C(9)-P(1)	110.62(12)
C(5)-C(3)-H(3)	106.9	C(10)-C(9)-P(1)	109.27(12)
P(2)-C(3)-H(3)	106.9	C(11)-C(9)-H(9)	108.9
C(3)-C(4)-H(4A)	109.5	C(10)-C(9)-H(9)	108.9
C(3)-C(4)-H(4B)	109.5	P(1)-C(9)-H(9)	108.9
H(4A)-C(4)-H(4B)	109.5	C(9)-C(10)-H(10A)	109.5
C(3)-C(4)-H(4C)	109.5	C(9)-C(10)-H(10B)	109.5
H(4A)-C(4)-H(4C)	109.5	H(10A)-C(10)-H(10B)	109.5
H(4B)-C(4)-H(4C)	109.5	C(9)-C(10)-H(10C)	109.5
C(3)-C(5)-H(5A)	109.5	H(10A)-C(10)-H(10C)	109.5
C(3)-C(5)-H(5B)	109.5	H(10B)-C(10)-H(10C)	109.5
H(5A)-C(5)-H(5B)	109.5	C(9)-C(11)-H(11A)	109.5
C(3)-C(5)-H(5C)	109.5	C(9)-C(11)-H(11B)	109.5
H(5A)-C(5)-H(5C)	109.5	H(11A)-C(11)-H(11B)	109.5
H(5B)-C(5)-H(5C)	109.5	C(9)-C(11)-H(11C)	109.5
C(8)-C(6)-C(7)	111.25(16)	H(11A)-C(11)-H(11C)	109.5
C(8)-C(6)-P(2)	109.64(12)	H(11B)-C(11)-H(11C)	109.5
C(7)-C(6)-P(2)	110.16(13)	C(14)-C(12)-C(13)	111.23(14)
C(8)-C(6)-H(6)	108.6	C(14)-C(12)-P(1)	110.60(12)

C(13)-C(12)-P(1)	113.55(12)	C(23)-C(22)-H(22)	119.4
C(14)-C(12)-H(12)	107.0	C(21)-C(22)-H(22)	119.4
C(13)-C(12)-H(12)	107.0	C(24)-C(23)-C(22)	118.27(16)
P(1)-C(12)-H(12)	107.0	C(24)-C(23)-H(23)	120.9
C(12)-C(13)-H(13A)	109.5	C(22)-C(23)-H(23)	120.9
C(12)-C(13)-H(13B)	109.5	F(2)-C(24)-C(25)	119.02(16)
H(13A)-C(13)-H(13B)	109.5	F(2)-C(24)-C(23)	118.29(16)
C(12)-C(13)-H(13C)	109.5	C(25)-C(24)-C(23)	122.69(16)
H(13A)-C(13)-H(13C)	109.5	C(24)-C(25)-C(26)	118.73(16)
H(13B)-C(13)-H(13C)	109.5	C(24)-C(25)-H(25)	120.6
C(12)-C(14)-H(14A)	109.5	C(26)-C(25)-H(25)	120.6
C(12)-C(14)-H(14B)	109.5	C(25)-C(26)-C(21)	120.40(15)
H(14A)-C(14)-H(14B)	109.5	C(25)-C(26)-H(26)	119.8
C(12)-C(14)-H(14C)	109.5	C(21)-C(26)-H(26)	119.8
H(14A)-C(14)-H(14C)	109.5	N(2)-N(1)-C(15)	110.69(13)
H(14B)-C(14)-H(14C)	109.5	N(2)-N(1)-Ni(1)	68.51(7)
C(16)-C(15)-C(20)	118.47(15)	C(15)-N(1)-Ni(1)	105.40(9)
C(16)-C(15)-N(1)	125.42(14)	N(1)-N(2)-C(21)	111.34(12)
C(20)-C(15)-N(1)	116.09(15)	N(1)-N(2)-Ni(1)	68.96(7)
C(17)-C(16)-C(15)	120.53(16)	C(21)-N(2)-Ni(1)	105.11(9)
C(17)-C(16)-H(16)	119.7	N(2)-Ni(1)-N(1)	42.52(5)
C(15)-C(16)-H(16)	119.7	N(2)-Ni(1)-P(2)	156.25(4)
C(18)-C(17)-C(16)	118.76(18)	N(1)-Ni(1)-P(2)	113.82(4)
C(18)-C(17)-H(17)	120.6	N(2)-Ni(1)-P(1)	112.29(4)
C(16)-C(17)-H(17)	120.6	N(1)-Ni(1)-P(1)	154.79(4)
F(1)-C(18)-C(19)	118.74(17)	P(2)-Ni(1)-P(1)	91.391(17)
F(1)-C(18)-C(17)	118.67(18)	C(9)-P(1)-C(1)	105.87(8)
C(19)-C(18)-C(17)	122.59(17)	C(9)-P(1)-C(12)	104.50(8)
C(18)-C(19)-C(20)	118.66(16)	C(1)-P(1)-C(12)	103.22(8)
C(18)-C(19)-H(19)	120.7	C(9)-P(1)-Ni(1)	114.80(6)
C(20)-C(19)-H(19)	120.7	C(1)-P(1)-Ni(1)	107.82(6)
C(19)-C(20)-C(15)	120.97(17)	C(12)-P(1)-Ni(1)	119.33(6)
C(19)-C(20)-H(20)	119.5	C(6)-P(2)-C(2)	105.84(8)
C(15)-C(20)-H(20)	119.5	C(6)-P(2)-C(3)	103.78(8)
C(26)-C(21)-C(22)	118.75(15)	C(2)-P(2)-C(3)	103.28(7)
C(26)-C(21)-N(2)	125.79(14)	C(6)-P(2)-Ni(1)	116.05(6)
C(22)-C(21)-N(2)	115.45(14)	C(2)-P(2)-Ni(1)	107.76(5)
C(23)-C(22)-C(21)	121.12(16)	C(3)-P(2)-Ni(1)	118.76(5)

Table S 8. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for complex II. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	22(1)	33(1)	14(1)	-2(1)	2(1)	1(1)
C(2)	20(1)	31(1)	11(1)	-3(1)	1(1)	1(1)
C(3)	15(1)	24(1)	18(1)	0(1)	2(1)	0(1)
C(4)	17(1)	27(1)	26(1)	2(1)	0(1)	-4(1)
C(5)	19(1)	42(1)	22(1)	3(1)	-6(1)	-2(1)
C(6)	26(1)	26(1)	19(1)	8(1)	-5(1)	-3(1)
C(7)	36(1)	29(1)	39(1)	10(1)	1(1)	-9(1)
C(8)	44(1)	23(1)	42(1)	6(1)	4(1)	8(1)
C(9)	19(1)	18(1)	25(1)	-4(1)	1(1)	2(1)
C(10)	27(1)	20(1)	37(1)	-5(1)	-2(1)	-2(1)
C(11)	30(1)	21(1)	33(1)	6(1)	-5(1)	-2(1)
C(12)	16(1)	25(1)	21(1)	1(1)	4(1)	-1(1)
C(13)	17(1)	39(1)	32(1)	-3(1)	6(1)	3(1)
C(14)	24(1)	27(1)	33(1)	3(1)	6(1)	-6(1)
C(15)	16(1)	25(1)	10(1)	-4(1)	3(1)	0(1)
C(16)	18(1)	28(1)	15(1)	2(1)	-1(1)	-1(1)
C(17)	29(1)	36(1)	23(1)	5(1)	0(1)	-10(1)
C(18)	20(1)	48(1)	21(1)	1(1)	3(1)	-14(1)
C(19)	15(1)	47(1)	17(1)	-5(1)	0(1)	0(1)
C(20)	18(1)	28(1)	17(1)	-4(1)	2(1)	3(1)
C(21)	17(1)	21(1)	9(1)	-2(1)	2(1)	0(1)
C(22)	17(1)	21(1)	16(1)	-1(1)	0(1)	0(1)
C(23)	16(1)	29(1)	21(1)	-2(1)	0(1)	0(1)
C(24)	18(1)	29(1)	26(1)	-6(1)	1(1)	-9(1)
C(25)	28(1)	19(1)	23(1)	-2(1)	2(1)	-2(1)
C(26)	20(1)	22(1)	16(1)	-2(1)	0(1)	2(1)
F(1)	24(1)	71(1)	47(1)	12(1)	0(1)	-24(1)
F(2)	25(1)	36(1)	54(1)	-2(1)	-4(1)	-15(1)
N(1)	14(1)	22(1)	11(1)	-3(1)	0(1)	2(1)
N(2)	15(1)	21(1)	11(1)	-1(1)	-1(1)	1(1)
Ni(1)	13(1)	15(1)	9(1)	-1(1)	0(1)	1(1)
P(1)	14(1)	19(1)	13(1)	-1(1)	2(1)	2(1)

P(2)	14(1)	20(1)	11(1)	1(1)	0(1)	-1(1)

Table S 9. Hydrogen bonds for complex II [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(11)-H(11B)...F(1)#1	0.98	2.64	3.585(2)	161.9
C(13)-H(13B)...F(2)#2	0.98	2.54	3.502(2)	168.5

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z #2 -x+2,y-1/2,-z+3/2

Complex III

Table S 10. Crystal data and structure refinement for complex III.

Identification code	shelx	
Empirical formula	C26 H40 F2 N2 Ni P2	
Formula weight	539.25	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	F d d 2	
Unit cell dimensions	a = 38.069(2) Å	α= 90°.
	b = 17.3973(6) Å	β= 90°.
	c = 8.3793(3) Å	γ = 90°.
Volume	5549.6(4) $Å^3$	
Z	8	
Density (calculated)	1.291 Mg/m^3	
Absorption coefficient	0.844 mm^{-1}	
F(000)	2288	
Crystal size	0.360 x 0.230 x 0.060 mm^3	
Theta range for data collection	3.801 to 29.491°.	
Index ranges	-49<=h<=48, -23<=k<=23, -11<=l<=11	
Reflections collected	9727	
Independent reflections	3301 [R(int) = 0.0306]	
Completeness to theta = 25.242°	99.6 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3301 / 1 / 154	

Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0319, wR2 = 0.0661
R indices (all data)	R1 = 0.0391, wR2 = 0.0702
Absolute structure parameter	0.006(8)
Extinction coefficient	n/a
Largest diff. peak and hole	0.562 and -0.228 e.$Å^{-3}$

Table S 11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex III. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	150(1)	-294(2)	4859(3)	28(1)
C(2)	673(1)	-1057(2)	6887(4)	36(1)
C(3)	913(1)	-352(2)	6954(5)	47(1)
C(4)	781(1)	-1610(2)	5564(5)	52(1)
C(5)	-37(1)	-1673(2)	6646(4)	34(1)
C(6)	-431(1)	-1534(2)	6453(6)	51(1)
C(7)	34(1)	-2188(2)	8078(5)	50(1)
C(8)	459(1)	-103(2)	11070(4)	26(1)
C(9)	706(1)	-679(2)	11295(4)	33(1)
C(10)	1050(1)	-546(2)	11730(5)	41(1)
C(11)	1161(1)	207(2)	11912(5)	48(1)
C(12)	923(1)	803(2)	11686(5)	46(1)
C(13)	577(1)	655(2)	11282(4)	34(1)
F(1)	599(1)	-1423(1)	11126(3)	42(1)
N(1)	108(1)	-325(1)	10749(3)	23(1)
Ni(1)	0	0	8627(1)	21(1)
P(1)	205(1)	-758(1)	6823(1)	25(1)

Table S 12. Bond lengths [Å] and angles [°] for complex III.

C(1)-C(1)#1	1.535(6)	C(7)-H(7A)	0.9800
C(1)-P(1)	1.845(3)	C(7)-H(7B)	0.9800
C(1)-H(1A)	0.9900	C(7)-H(7C)	0.9800
C(1)-H(1B)	0.9900	C(8)-C(9)	1.386(4)
C(2)-C(4)	1.525(5)	C(8)-C(13)	1.403(4)
C(2)-C(3)	1.530(5)	C(8)-N(1)	1.417(3)
C(2)-P(1)	1.854(3)	C(9)-F(1)	1.364(4)
C(2)-H(2)	1.0000	C(9)-C(10)	1.378(4)
C(3)-H(3A)	0.9800	C(10)-C(11)	1.385(5)
C(3)-H(3B)	0.9800	C(10)-H(10)	0.9500
C(3)-H(3C)	0.9800	C(11)-C(12)	1.389(5)
C(4)-H(4A)	0.9800	C(11)-H(11)	0.9500
C(4)-H(4B)	0.9800	C(12)-C(13)	1.385(5)
C(4)-H(4C)	0.9800	C(12)-H(12)	0.9500
C(5)-C(7)	1.522(5)	C(13)-H(13)	0.9500
C(5)-C(6)	1.527(5)	N(1)-N(1)#1	1.398(5)
C(5)-P(1)	1.846(3)	N(1)-Ni(1)	1.911(2)
C(5)-H(5)	1.0000	Ni(1)-N(1)#1	1.911(2)
C(6)-H(6A)	0.9800	Ni(1)-P(1)#1	2.1531(8)
C(6)-H(6B)	0.9800	Ni(1)-P(1)	2.1532(8)
C(6)-H(6C)	0.9800		

C(1)#1-C(1)-P(1)	112.12(12)	C(2)-C(3)-H(3C)	109.5
C(1)#1-C(1)-H(1A)	109.2	H(3A)-C(3)-H(3C)	109.5
P(1)-C(1)-H(1A)	109.2	H(3B)-C(3)-H(3C)	109.5
C(1)#1-C(1)-H(1B)	109.2	C(2)-C(4)-H(4A)	109.5
P(1)-C(1)-H(1B)	109.2	C(2)-C(4)-H(4B)	109.5
H(1A)-C(1)-H(1B)	107.9	H(4A)-C(4)-H(4B)	109.5
C(4)-C(2)-C(3)	111.8(3)	C(2)-C(4)-H(4C)	109.5
C(4)-C(2)-P(1)	114.5(3)	H(4A)-C(4)-H(4C)	109.5
C(3)-C(2)-P(1)	110.5(2)	H(4B)-C(4)-H(4C)	109.5
C(4)-C(2)-H(2)	106.5	C(7)-C(5)-C(6)	110.6(3)
C(3)-C(2)-H(2)	106.5	C(7)-C(5)-P(1)	110.7(2)
P(1)-C(2)-H(2)	106.5	C(6)-C(5)-P(1)	111.3(2)
C(2)-C(3)-H(3A)	109.5	C(7)-C(5)-H(5)	108.0
C(2)-C(3)-H(3B)	109.5	C(6)-C(5)-H(5)	108.0
H(3A)-C(3)-H(3B)	109.5	P(1)-C(5)-H(5)	108.0

C(5)-C(6)-H(6A)	109.5	C(13)-C(12)-C(11)	121.0(3)
C(5)-C(6)-H(6B)	109.5	C(13)-C(12)-H(12)	119.5
H(6A)-C(6)-H(6B)	109.5	C(11)-C(12)-H(12)	119.5
C(5)-C(6)-H(6C)	109.5	C(12)-C(13)-C(8)	120.6(3)
H(6A)-C(6)-H(6C)	109.5	C(12)-C(13)-H(13)	119.7
H(6B)-C(6)-H(6C)	109.5	C(8)-C(13)-H(13)	119.7
C(5)-C(7)-H(7A)	109.5	N(1)#1-N(1)-C(8)	109.6(3)
C(5)-C(7)-H(7B)	109.5	N(1)#1-N(1)-Ni(1)	68.54(7)
H(7A)-C(7)-H(7B)	109.5	C(8)-N(1)-Ni(1)	107.42(17)
C(5)-C(7)-H(7C)	109.5	N(1)-Ni(1)-N(1)#1	42.92(14)
H(7A)-C(7)-H(7C)	109.5	N(1)-Ni(1)-P(1)#1	155.88(7)
H(7B)-C(7)-H(7C)	109.5	N(1)#1-Ni(1)-P(1)#1	113.20(8)
C(9)-C(8)-C(13)	116.5(3)	N(1)-Ni(1)-P(1)	113.20(8)
C(9)-C(8)-N(1)	117.8(3)	N(1)#1-Ni(1)-P(1)	155.88(7)
C(13)-C(8)-N(1)	125.6(3)	P(1)#1-Ni(1)-P(1)	90.83(4)
F(1)-C(9)-C(10)	118.0(3)	C(1)-P(1)-C(5)	104.41(15)
F(1)-C(9)-C(8)	118.1(3)	C(1)-P(1)-C(2)	104.91(15)
C(10)-C(9)-C(8)	123.9(3)	C(5)-P(1)-C(2)	103.96(15)
C(9)-C(10)-C(11)	118.6(3)	C(1)-P(1)-Ni(1)	108.46(10)
C(9)-C(10)-H(10)	120.7	C(5)-P(1)-Ni(1)	113.78(11)
C(11)-C(10)-H(10)	120.7	C(2)-P(1)-Ni(1)	119.95(12)
C(10)-C(11)-C(12)	119.4(3)		
C(10)-C(11)-H(11)	120.3		
C(12)-C(11)-H(11)	120.3		

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,z

Table S 13. Anisotropic displacement parameters ($Å^2$x 10^3)for complex III. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	45(2)	26(2)	13(1)	0(1)	1(1)	-4(1)
C(2)	45(2)	37(2)	25(2)	3(2)	2(2)	9(1)
C(3)	42(2)	57(2)	42(2)	2(2)	0(2)	0(2)
C(4)	69(3)	50(2)	37(2)	-8(2)	4(2)	22(2)
C(5)	63(2)	19(2)	21(2)	-2(1)	-2(2)	-6(1)
C(6)	64(2)	33(2)	57(3)	0(2)	-6(2)	-21(2)
C(7)	97(3)	24(2)	30(2)	6(2)	-1(2)	-14(2)

C(8)	33(1)	33(2)	12(1)	2(1)	1(1)	-6(1)
C(9)	38(2)	39(2)	21(2)	-1(1)	3(1)	-3(1)
C(10)	36(2)	58(2)	29(2)	0(2)	2(2)	2(2)
C(11)	34(2)	72(3)	37(2)	2(2)	-2(2)	-14(2)
C(12)	49(2)	50(2)	40(2)	3(2)	-6(2)	-23(2)
C(13)	42(2)	35(2)	24(2)	3(1)	-5(1)	-9(1)
F(1)	50(1)	32(1)	43(1)	-2(1)	-3(1)	5(1)
N(1)	34(1)	23(1)	13(1)	1(1)	0(1)	-5(1)
Ni(1)	33(1)	19(1)	11(1)	0	0	-4(1)
P(1)	41(1)	20(1)	13(1)	0(1)	2(1)	-3(1)

Table S 14. Torsion angles [°] for complex III.

C(13)-C(8)-C(9)-F(1)	C(1)#1-C(1)-P(1)-Ni(1)	-24.
N(1)-C(8)-C(9)-F(1)	C(7)-C(5)-P(1)-C(1)	170.
C(13)-C(8)-C(9)-C(10)	C(6)-C(5)-P(1)-C(1)	-66.
N(1)-C(8)-C(9)-C(10)	C(7)-C(5)-P(1)-C(2)	60.6
F(1)-C(9)-C(10)-C(11)	C(6)-C(5)-P(1)-C(2)	-175
C(8)-C(9)-C(10)-C(11)	C(7)-C(5)-P(1)-Ni(1)	-71.
C(9)-C(10)-C(11)-C(12)	C(6)-C(5)-P(1)-Ni(1)	52.0
C(10)-C(11)-C(12)-C(13)	C(4)-C(2)-P(1)-C(1)	-59.
C(11)-C(12)-C(13)-C(8)	C(3)-C(2)-P(1)-C(1)	67.9
C(9)-C(8)-C(13)-C(12)	C(4)-C(2)-P(1)-C(5)	50.0
N(1)-C(8)-C(13)-C(12)	C(3)-C(2)-P(1)-C(5)	177.
C(9)-C(8)-N(1)-N(1)#1	C(4)-C(2)-P(1)-Ni(1)	178.
C(13)-C(8)-N(1)-N(1)#1	C(3)-C(2)-P(1)-Ni(1)	-54.
C(9)-C(8)-N(1)-Ni(1)	-114.2(3)	
C(13)-C(8)-N(1)-Ni(1)	70.0(3)	
C(1)#1-C(1)-P(1)-C(5)	96.9(3)	
C(1)#1-C(1)-P(1)-C(2)	-154.0(3)	

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,z

Reactivity of complex I with *N*-benzylidenebenzylamine

5mg (0.010 mmol) of **I** were dissolved in 0.8mL of Tol-d_8 with 2.1 mg (0.010 mmol) of *N*-benzylidenebenzylamine in NMR tube with young valve. The mixture was head for 12 hours at intervals of 20°C until 150 °C. The mixture was monitored by ^{1}H-NMR and ^{31}P{^{1}H} NMR spectroscopy. No color change was observed in complex solution; new signals were not observed during this experiment.

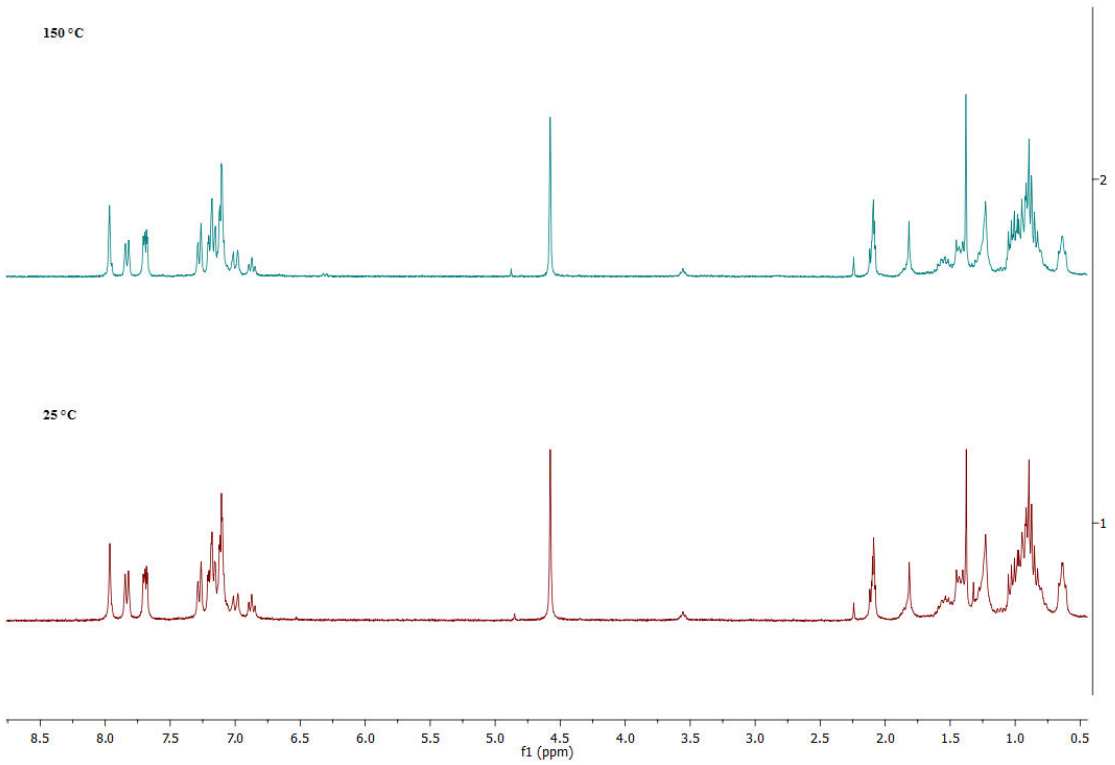


Figure S 24. ^{1}H-NMR spectra of mixture of *N*-benzylidenebenzylamine and complex I

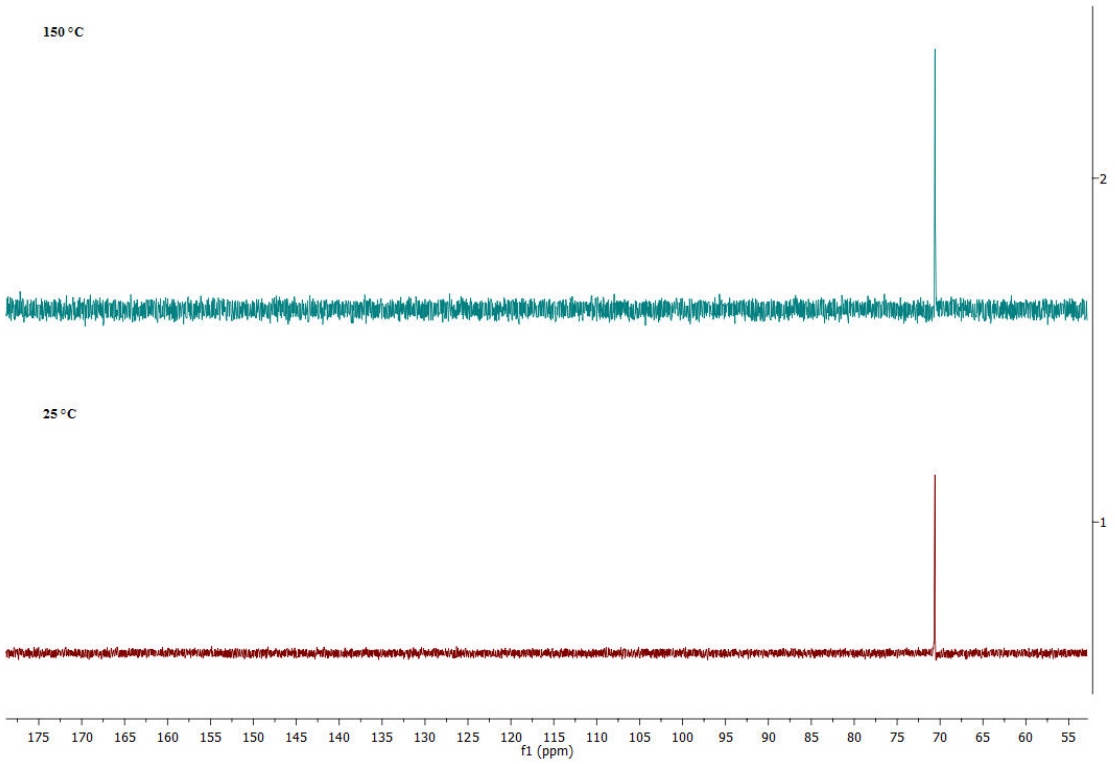


Figure S 25. $^{31}P\{^{1}H\}$-NMR spectra of mixture of *N*-benzylidenebenzylamine and complex I

Reactivity of complex I with benzonitrile

5mg (0.010 mmol) of **I** were dissolved in 0.8mL of THF-d_8 with 1.5 mg (0.010 mmol) of benzonitrile in NMR tube with young valve. The mixture was head for 12 hours at intervals of 20°C until 90 °C. The mixture was monitored by ^{1}H-NMR and $^{31}P\{^{1}H\}$ NMR spectroscopy. No color change was observed in the solution; new signals were not observed during this experiment even when solution was heated for 48 hours. Similar experiments with one and two equivalents of benzonitrile in Tol-d_8 show the same results, when mixtures were heated until 150 °C.

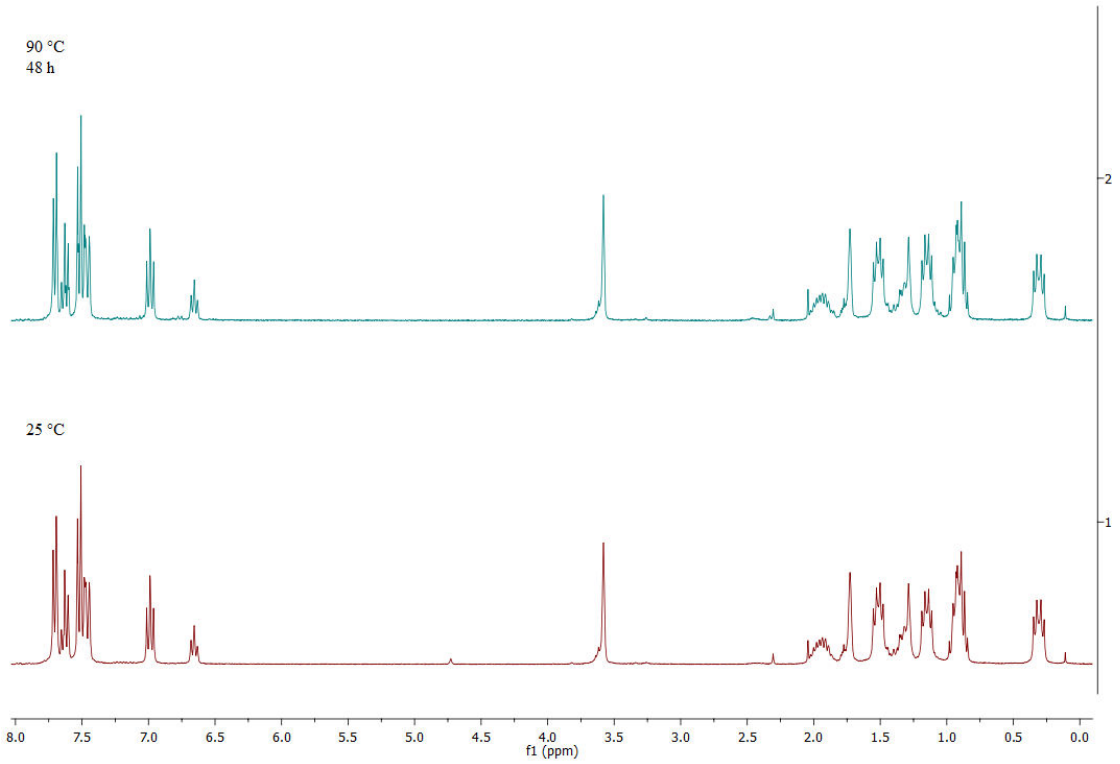


Figure S 26. ^{1}H-NMR spectra of mixture of benzonitrile and complex I

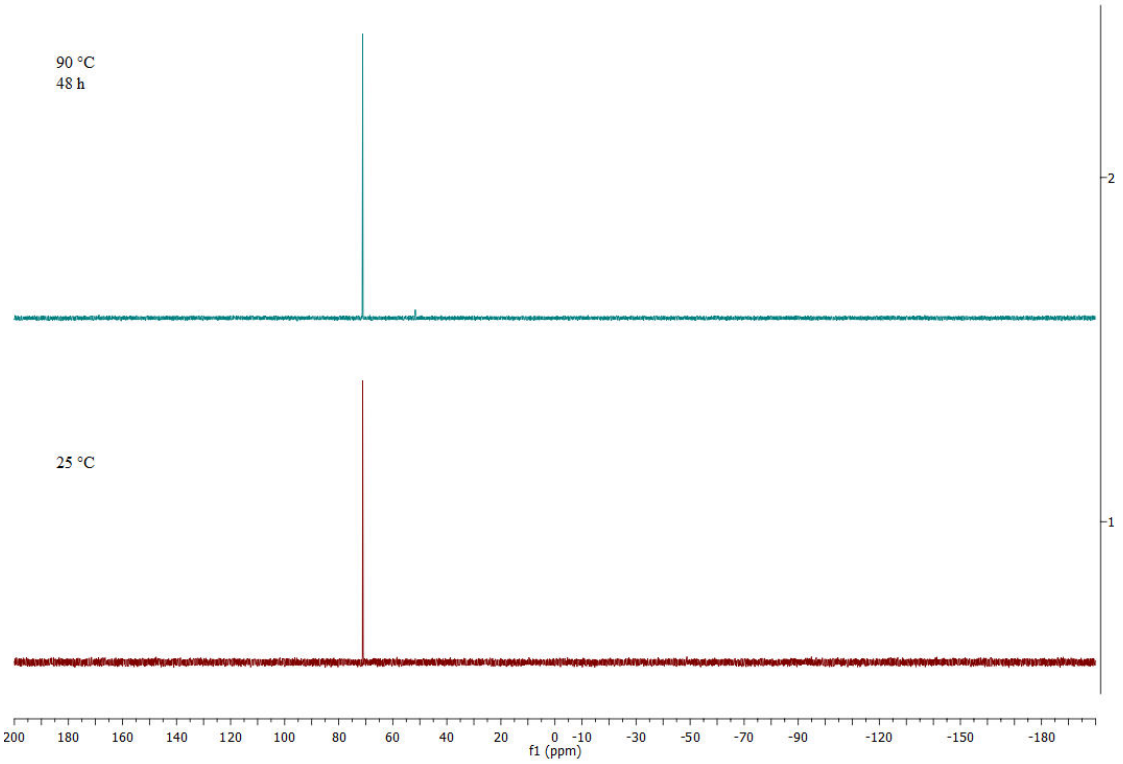


Figure S 27. ^{31}P{^{1}H}-NMR spectra of mixture of benzonitrile and complex I

Reactivity of complex I with benzylamine in presence of azobenzene.

12.5mg (0.025mmol) of **I** and 4.7 mg (0.025mmol) of azobenzene were dissolved in 0.8mL of Tol-d_8 with 2.8 mg (0.025mmol) of benzylamine in NMR tube with young valve. The mixture was head for 12 hours at 150 °C, and monitored by ^{1}H-NMR and ^{31}P{^{1}H} NMR spectroscopy. After heating, the solution changes from red to dark red color; new signals were observed during this experiment, however these signals are overlapping, 1uL of solution was injected to CG-MS and benzonitrile was the principal product detected.

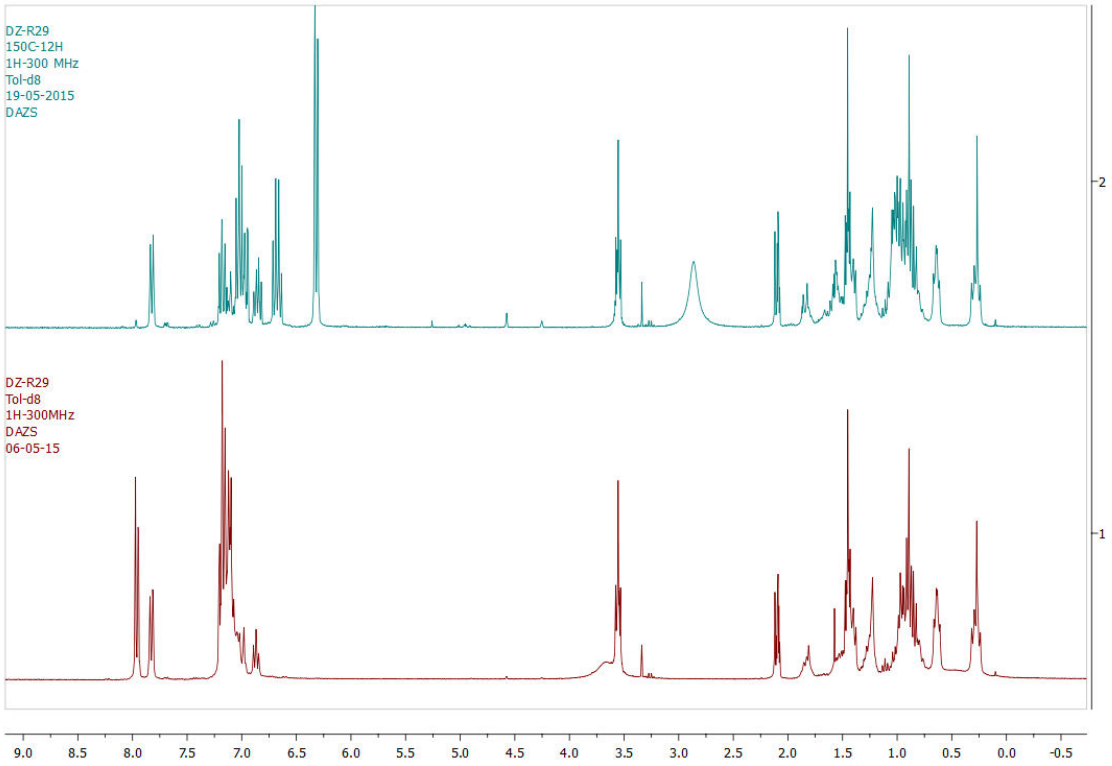


Figure S 28. ^{1}H-NMR spectra of reaction between azobenzene, complex I and benzylamine

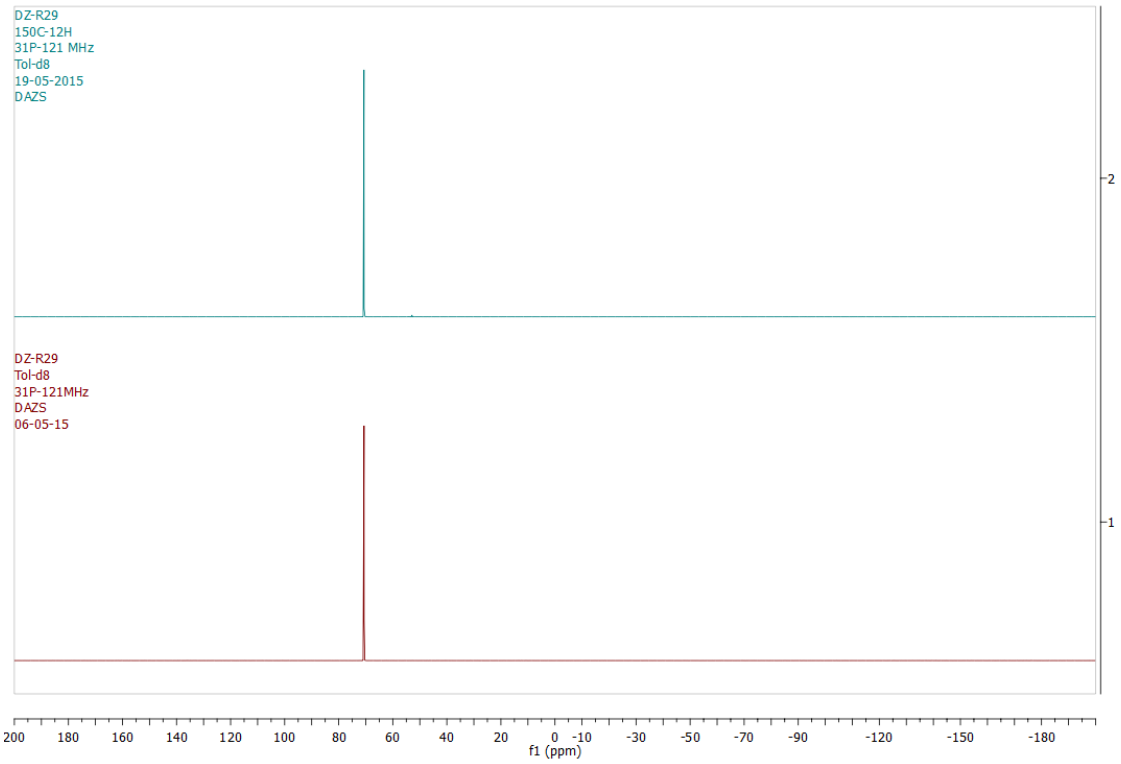


Figure S 29. $^{31}P\{^{1}H\}$-^{1}H-NMR spectra of reaction between azobenzene, complex I and benzylamine

Reaction Optimization

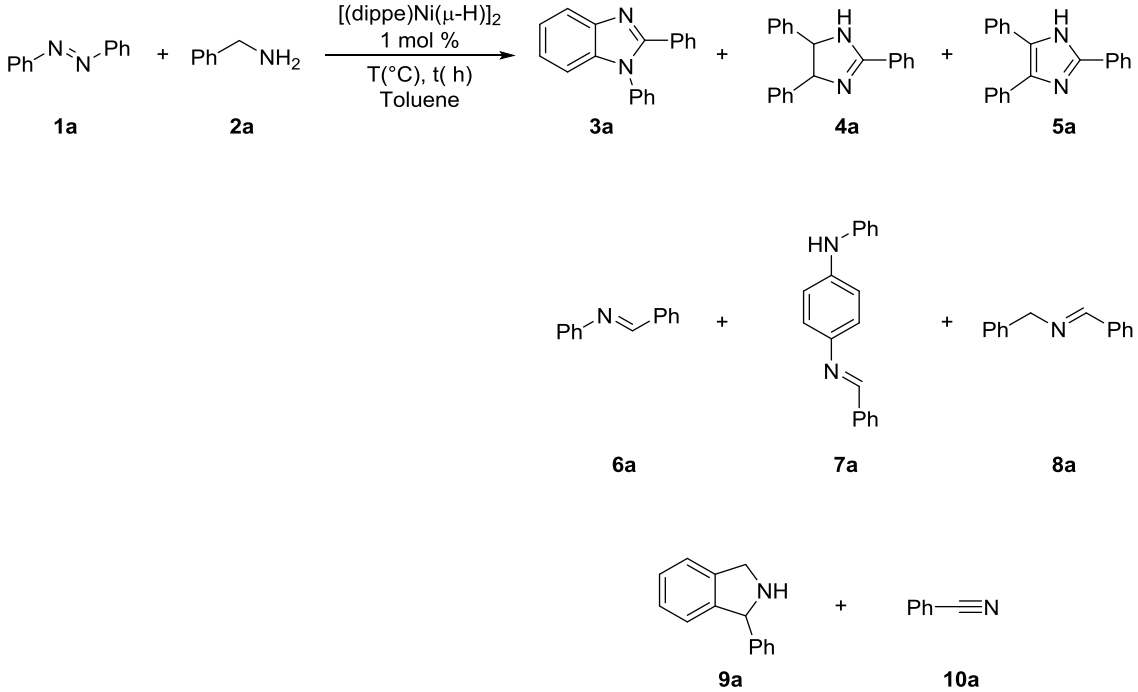


Table S 15. Reaction Optimization

Entry	t (h)	T (°C)	$PhCH_2NH_2$ conv. (%)	Selectivity (%)[b]							
				3a	**4a**	**5a**	**6a**	**7a**	**8a**	**9a**	**10a**
1	12	180	98	10	24	14	10	8	14	17	1
2	24	180	100	26	23	21	16	11	3	-	Traces
3	48	180	100	18	25	21	12	14	10	-	Traces
4[c]	72	180	100	13	9	23	26	-	3	-	20
5[d]	72	180	100	24	33	24	10	7	-	-	2
6	24	150	49	-	2	-	3	-	43	-	1
7	24	160	99	5	17	8	9	6	19	35	<1
8	24	170	100	7	19	5	36	7	14	11	1
9[e]	24	180	100	16	15	15	27	11	5	1	4
10[f]	72	180	48	-	-	-	-	-	48	-	-
11[g]	24	180	100	16	19	21	27	9	4	-	4
12[h]	24	180	100	22	44	23	2	7	2	-	-
13[i]	24	180	95	22	19	15	8	9	22	-	-

[a] Reaction conditions: **Ph_2N_2**, 0.250 mmol; **$PhCH_2NH_2$**, 0.250 mmol; **solvent**, 0.5 mL; **[(dippe)Ni(μ-H)]$_2$**, 1 mol %. [b] Selectivity was determined by GC-MS. [c] 6% 2,3-diphenylquinoxalina was detected. [d] **Ph_2N_2**, 1.000 mmol. [e] **solvent**, 1mL, 6% of tetra-substituted imidazolines and imidazoles was detected. [f] **solvent**, 1.5 mL. [g] **[(dippe)Ni(μ-H)]$_2$**, 2 mol %. [h] **Ph_2N_2**, 0.500 mmol. [i] **$PhCH_2NH_2$**, 0.500 mmol.

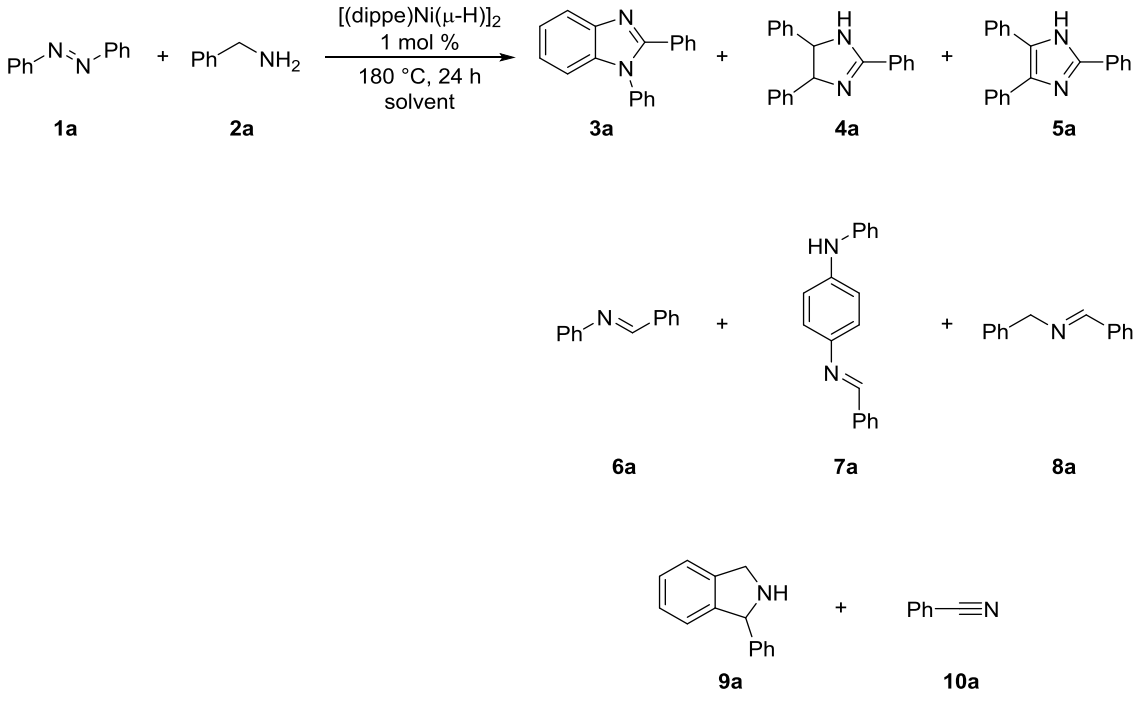


Table S 16. Solvent Screening

Entry	Solvent	$PhCH_2NH_2$ conv. (%)	Selectivity (%)							
			3a	**4a**	**5a**	**6a**	**7a**	**8a**	**9a**	**10a**
1	Dioxane	100	12	22	8	28	5	9	11	5
2	Toluene	100	26	23	21	16	11	3	-	<1
3	THF	92	14	14	14	6	5	33	-	6
4	CH_3CN	86	12	31	13	-	7	23	-	-

[a] Reaction conditions: **Ph_2N_2**, 0.250 mmol; **$PhCH_2NH_2$**, 0.250 mmol; **solvent**, 0.5 mL; **[(dippe)Ni(μ-H)]$_2$**, 1 mol %; 180°C. [b] Selectivity was determined by GC-MS. [c] Without catalyst.

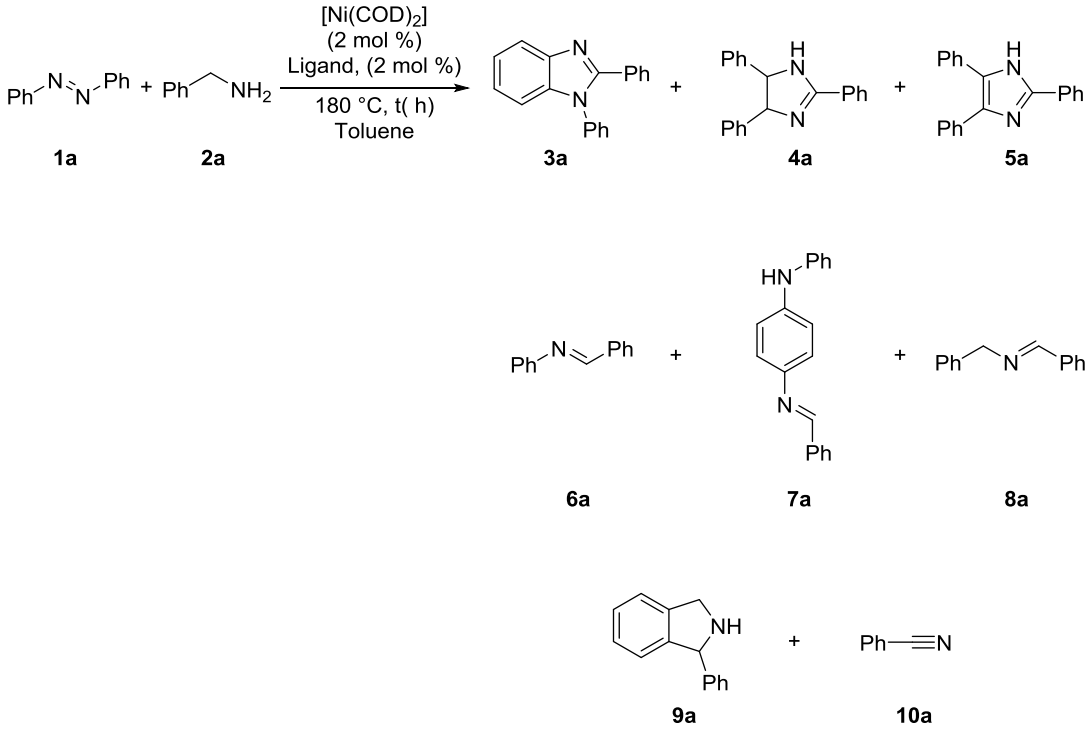
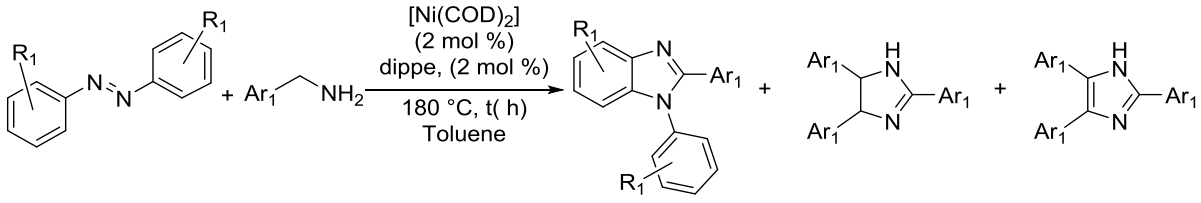


Table S 17. Ligand Scope

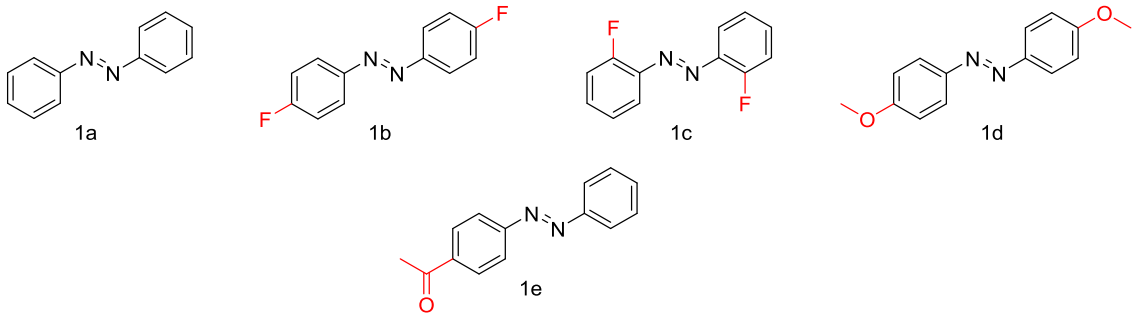
Entry	Ligand	Metal-ligand ratio	$PhCH_2NH_2$ conv. (%)	Selectivity (%)[f]							
				3a	**4a**	**5a**	**6a**	**7a**	**8a**	**9a**	**10a**
1[b]	Dippe	1:1	100	29	22	26	13	7	3	-	traces
2	Dcype	1:1	100	26	24	14	26	10	-	-	traces
3	Dppe	1:1	100	18	38	23	3	10	8	-	-
4	BINAP±	1:1	100	20	32	10	7	11	14	6	-
5	-	-	100	14	25	13	33	8	4	3	-
6[c]	PPh_3	1:2	96	20	39	18	4	7	8	-	-
7[d]	PEt_3	1:2	97	16	38	8	13	6	13	3	-
8[e]	-	-	100	5	3	-	84	3	4	1	-

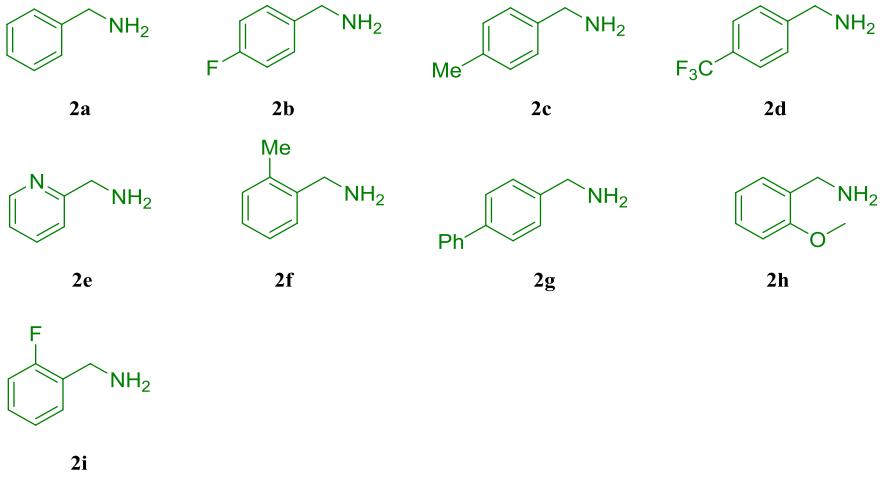
[a] Reaction conditions: **Ph_2N_2,** (0.250 mmol); **$PhCH_2NH_2$,** (0.250 mmol); **[$Ni(cod)_2$],** (2 mol %); **ligand**, (2 mol%); **Toluene**, (0.5 mL); 180 °C, 24 h. [b] Mercury-drop test of this reaction show no inhibition [c] **PPh_3,** (4 mol%), [d] **PEt_3,** (4 mol%), [e] Without catalyst. [f] Selectivity was determined by GC-MS.

Substrate Scope



1a-d **2a-i** **3a-l** **4a-i** **5a-i**





2a **2b** **2c** **2d** **2e** **2f** **2g** **2h** **2i**

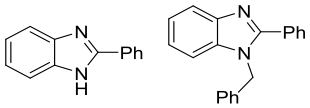
Main by-products for low yield reactions

Table S 18. Substrate scope I

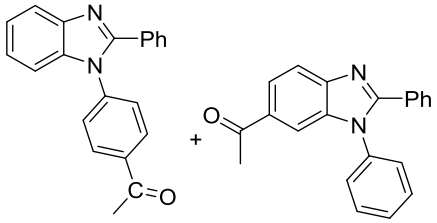
Entry	Azobenzene	Benzylamine	Selectivity (%)[d]			
			3	**4**	**5**	**6**
1	1a	2a	29	22	26	

2	1b	2a	21	37	15	
3	1c	2a	8	-	-	21[b]
4	1d	2a	28	4	-	
5	1a	2b	34	13	18	
6	1a	2c	23	5	17	
7	1a	2d	19	10	8	
8	1a	2e	34	-	-	
9	1a	2f	23	3	4	
10	1a	2g	10	-	-	52
11	1a	2h	32	2	6	
12	1a	2i	17	18	8	
13	1e	2a	10[c]	27	15	20

[a] Reaction conditions: **Azobenzene,** (0.250 mmol); **Benzylamine,** (0.250 mmol); **[Ni(cod)$_2$],** 1.4mg (2 mol %); **dippe**, 1.3mg (2 mol%); **Toluene**, (0.5 mL); 180 °C, 24 h. [b] 22% and 25% of 2-substituted benzimidazol and 1,2-disubstituted benzimidazol respectively were the other principal byproducts



[c] mixture of regioisomers:



[d] Selectivity was determined by GC-MS.

Table S 19. Substrate Scope II

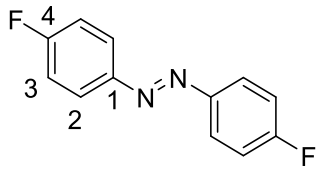
Entry	Azobenzene	Benzylamine	Selectivity (%)[b]		
			3a	**4**	**5**
1	1a	2b	10	45	9
2	1a	2c	3	34	19
3	1a	2d	11	26	13
4	1a	2f	15	8	8
5	1a	2i	6	29	11

[a] Reaction conditions: **Azobenzene,** (0.250 mmol); **Benzylamine,** (0.250 mmol); **[Ni(cod)$_2$],** 1.4mg (2 mol %); **PPh$_3$**, 2.6 mg (4 mol%); **Toluene**, (0.5 mL); 180 °C, 24 h. [b] Selectivity was determined by CG-EM.

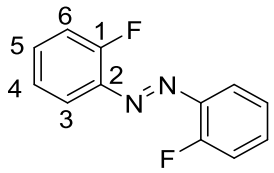
Synthesis of substituted azobenzenes[1]

General procedure: In a 50mL round-botton flask equipped with a stir bar were added CuBr (15mg, 0.1 mmol), pyridine (24mg, 0.3 mmol), aniline (2 mmol) and toluene

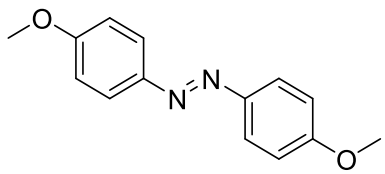
(4mL) under air. The reaction mixture was stirred at 70 °C for 24 h. The reaction crude was concentrated at vacuum and the residue was purified by chromatography on a short silica gel column (eluent: hexane/ethyl acetate).



(E)-1,2-Bis(4-fluorophenyl)diazene. CuBr (24 mg, 0.2 mmol), pyridine (50 mg, 0.6 mmol), 4-fluorobenzenamine (300 mg, 3 mmol) in toluene (4 mL). Afford 313.3 mg (91 %); yellow solid. GC-MS (EI, 70 eV): *m/z* (%): 218.1(17) [M^+], 123(16), 95(100). ^{1}H NMR (300 MHz, 295 K, THF-d_8): δ(ppm)= 8.10 – 7.84 (m, 4H, H_2), 7.45 – 7.18 (m, 4H, H_3). ^{19}F NMR (282 MHz, 295 K, THF-d_8): δ(ppm)= -105.08 – -114.18 (m). ^{13}C{^{1}H} NMR (75 MHz, 295 K, THF-d_8): δ(ppm)= 165.64 (d, J = 252.2 Hz, C_4), 150.27 (d, J = 2.1 Hz, C_1), 125.92 (d, J = 9.2 Hz, C_2), 117.02 (d, J = 23.2 Hz, C_3).



(E)-1,2-Bis(2-fluorophenyl)diazene. CuBr (24 mg, 0.2 mmol), pyridine (50 mg, 0.6 mmol), 2-fluorobenzenamine (300 mg, 3 mmol) in toluene (4 mL). Afford 79.3 mg (23 %); yellow solid. GC-MS (EI, 70 eV): *m/z* (%): 218.1(29) [M^+], 123 (35), 95 (100). ^{1}H NMR (300 MHz, 295 K, THF-d_8): δ(ppm)= 7.80 (td, J = 7.8, 1.7 Hz, 2H, H_3), 7.63 – 7.48 (m, 2H, H_5), 7.40 – 7.31 (m, 2H, H_6), 7.26 (tdt, J = 7.9, 1.2, 0.6 Hz, 2H, H_4). ^{19}F NMR (282 MHz, 295 K, THF-d_8): δ(ppm)= -125.02 – -125.18 (m). ^{13}C{^{1}H} NMR (75 MHz, 295 K, THF-d_8): δ(ppm)= 161.69 (d, J = 258.2 Hz, C_1), 141.86 (d, J = 6.8 Hz, C_2), 134.46 (d, J = 8.4 Hz, C_5), 125.52 (d, J = 3.9 Hz, C_3), 118.50 (s, C_4), 118.11 (d, J = 19.8 Hz, C_6).



(E)-1,2-Bis(4-methoxyphenyl)diazene. CuBr (15 mg, 0.1 mmol), pyridine (23 mg, 0.3 mmol), 4-methoxybenzenamine (240 mg, 2 mmol) in toluene (4 mL). Afford 77 mg (32 %); red-orange solid. GC-MS (EI, 70 eV): *m/z* (%): 242.0 (93) [M^+], 135.0 (40), 107.0 (100).

Selected Mass Spectrum of Representative Products

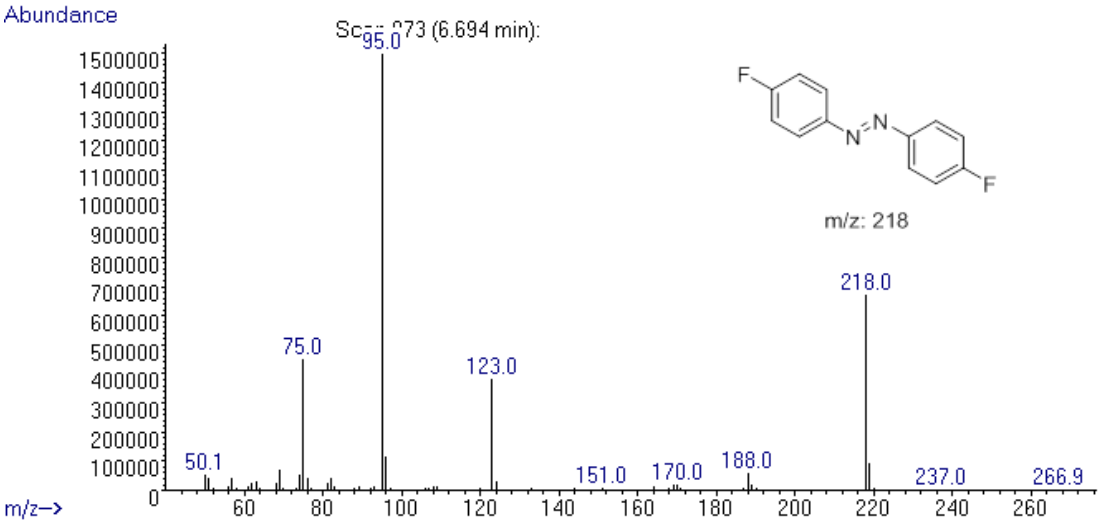


Figure S 30. Mass spectrum of (E)-1,2-Bis(4-fluorophenyl)diazene

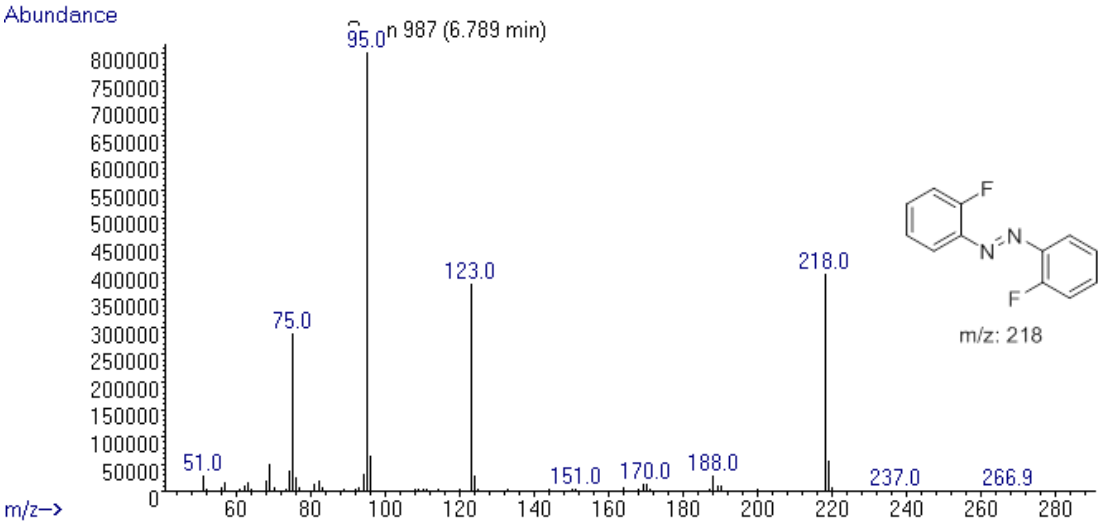


Figure S 31. Mass spectrum of (E)-1,2-Bis(2-fluorophenyl)diazene

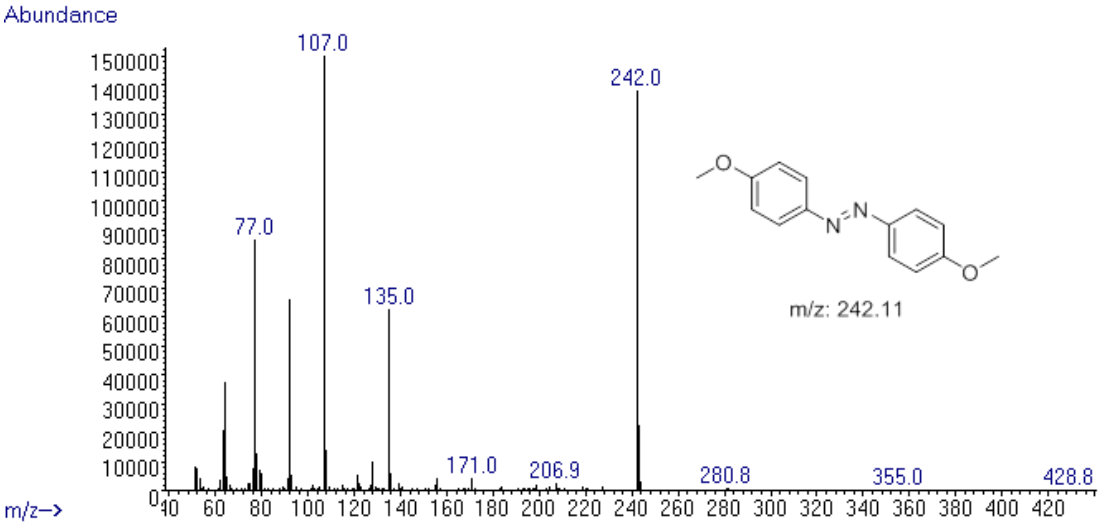


Figure S 32. Mass spectrum of (E)-1,2-Bis(4-methoxyphenyl)diazene

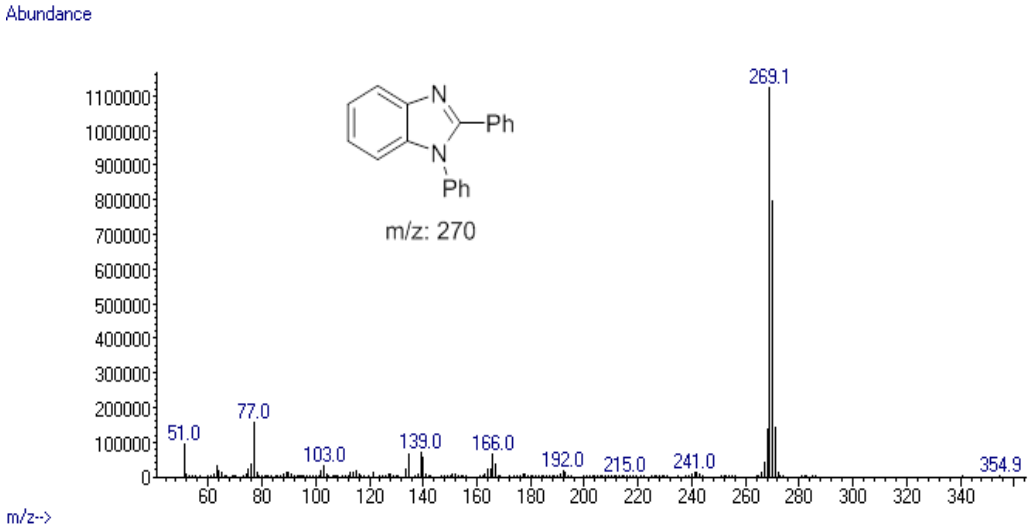


Figure S 33. Mass spectrum of 1,2-diphenylbenzimidazol, 3a

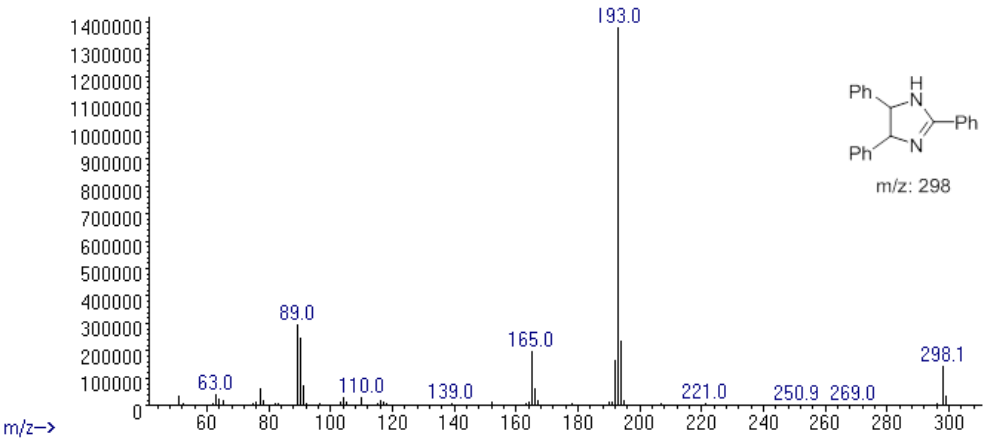


Figure S 34. Mass spectrum of 2,4,5-triphenylimidazoline, 4a

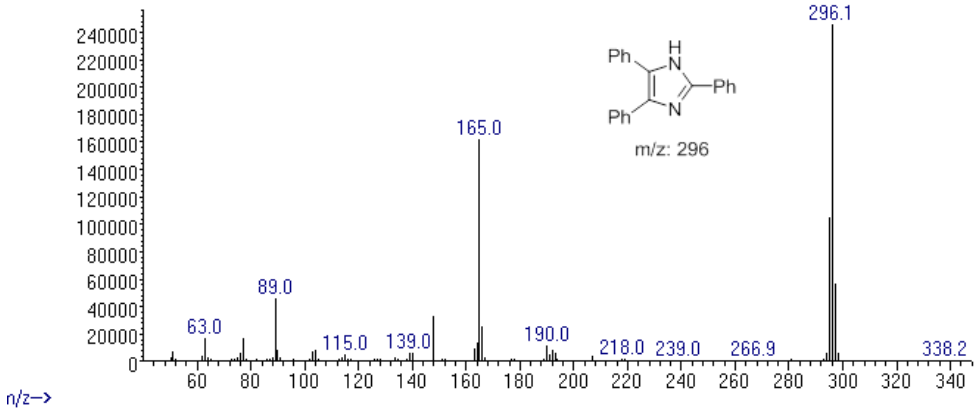


Figure S 35. Mass spectrum of 2,4,5-triphenylimidazol, 5a

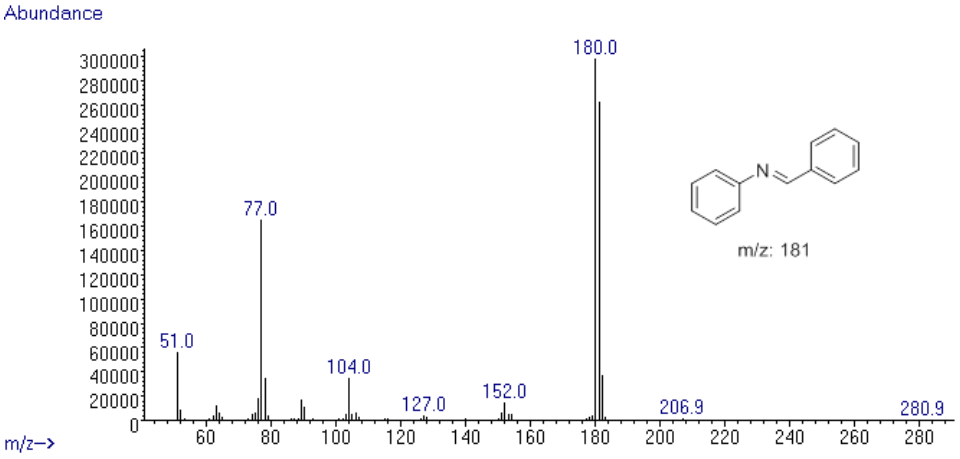


Figure S 36. Mass spectrum of 6a

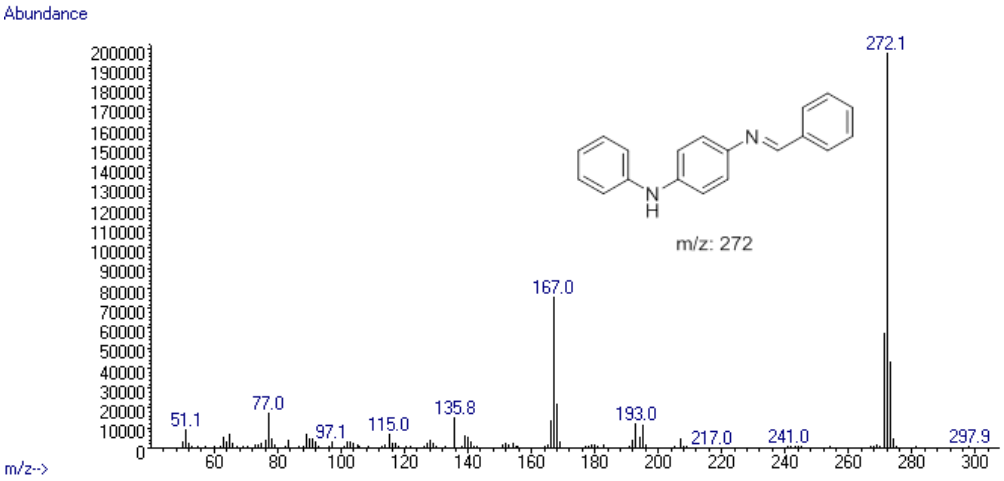


Figure S 37. Mass spectrum of 7a

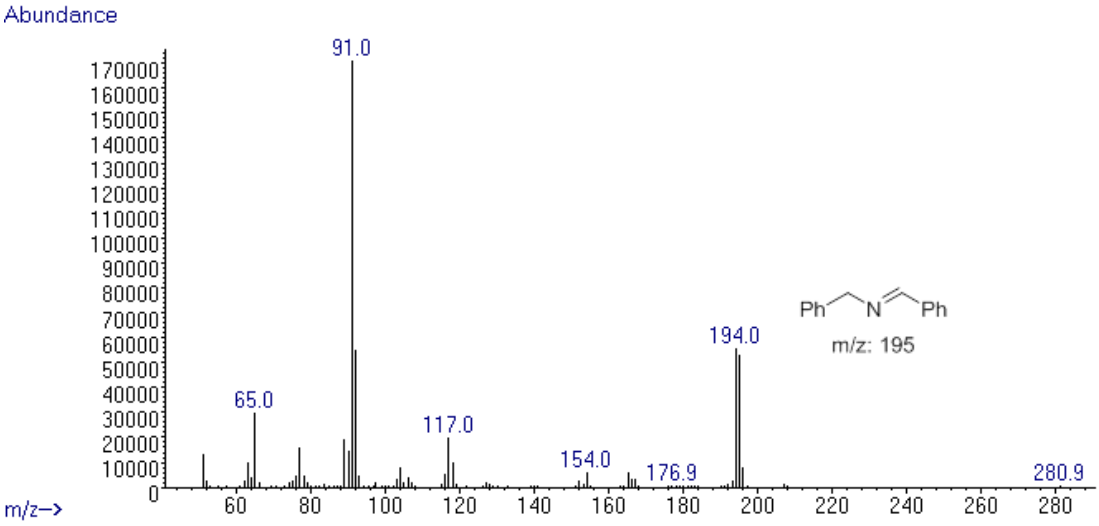


Figure S 38. Mass spectrum of 8a

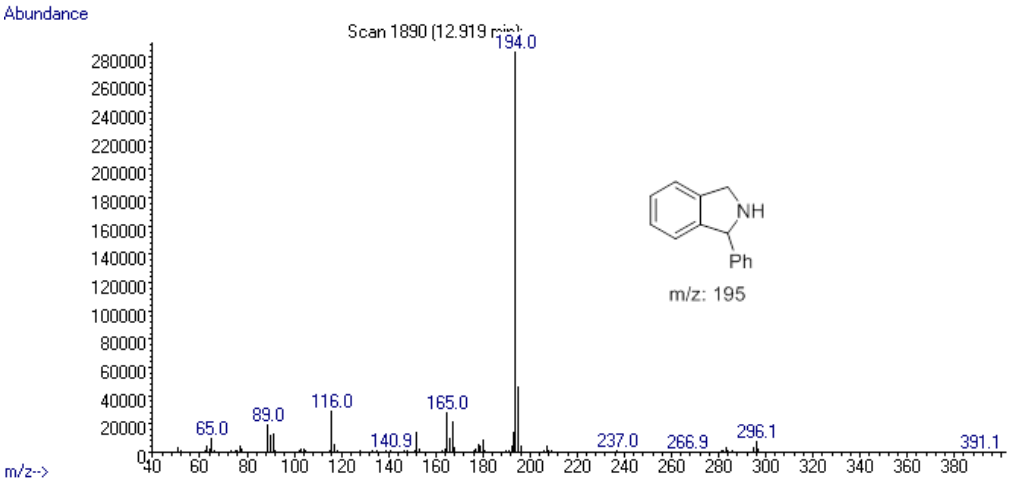


Figure S 39. Mass spectrum of 9a

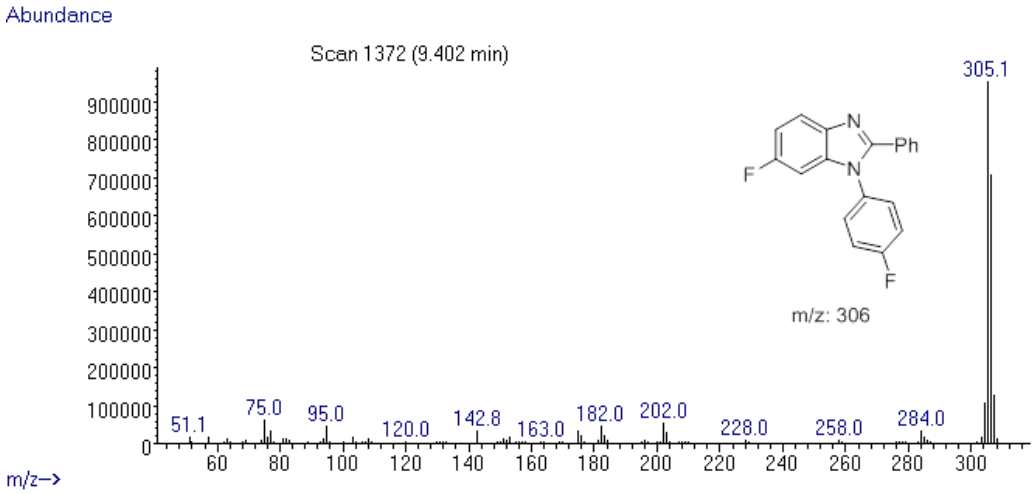


Figure S 40. Mass spectrum of 3b

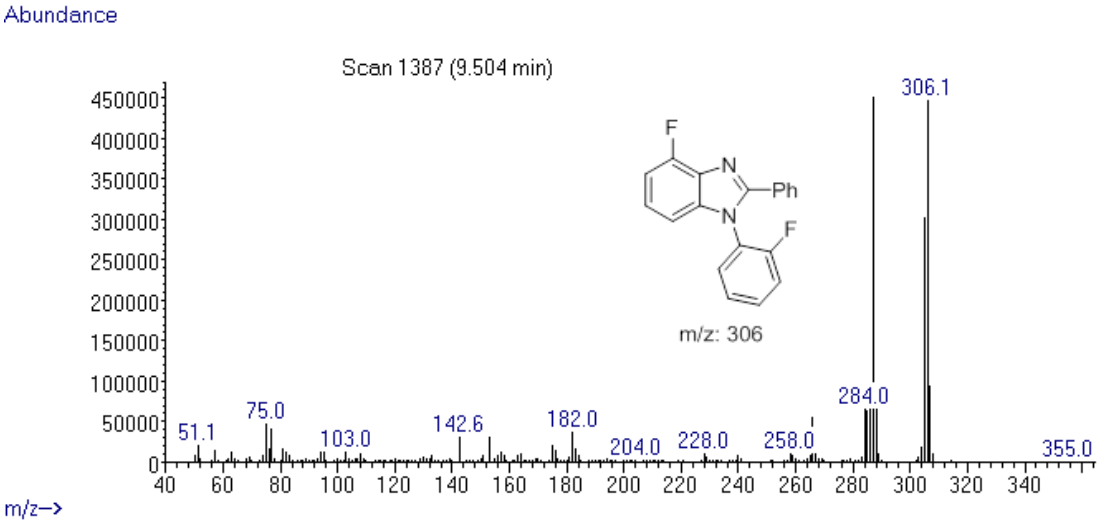


Figure S 41. Mass spectrum of 3c

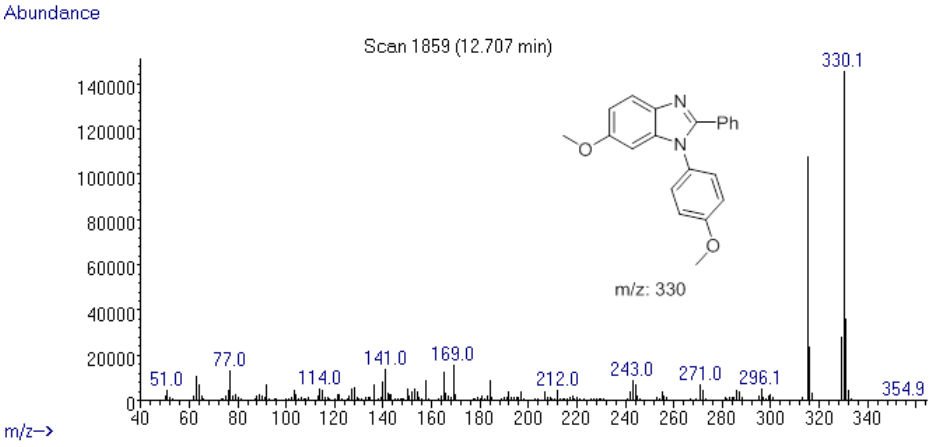


Figure S 42. Mass spectrum of 3d

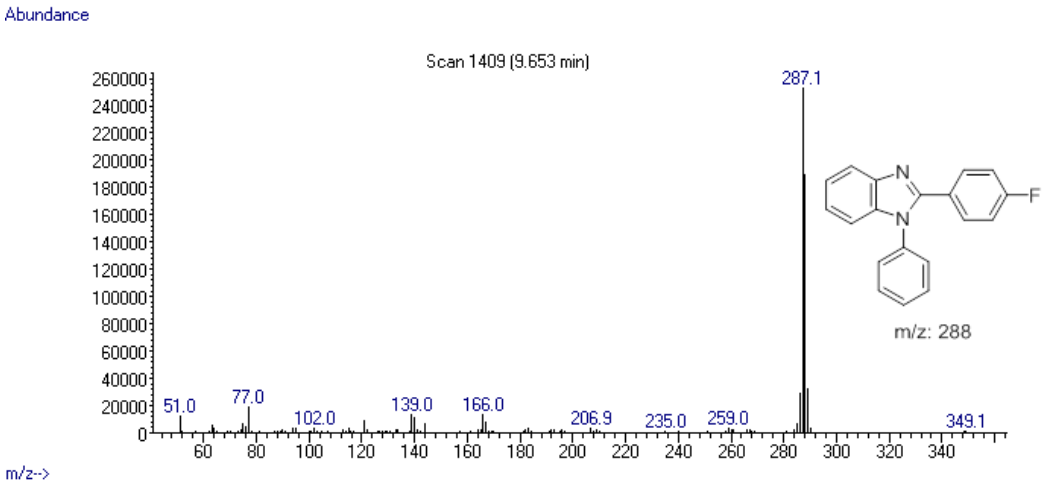


Figure S 43. Mass spectrum of 3e

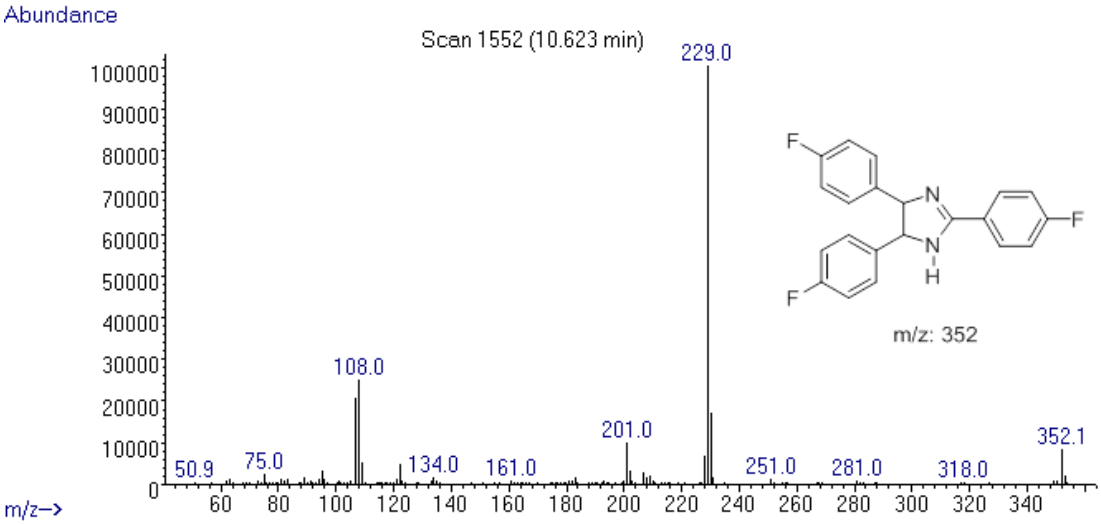


Figure S 44. Mass spectrum of 4b

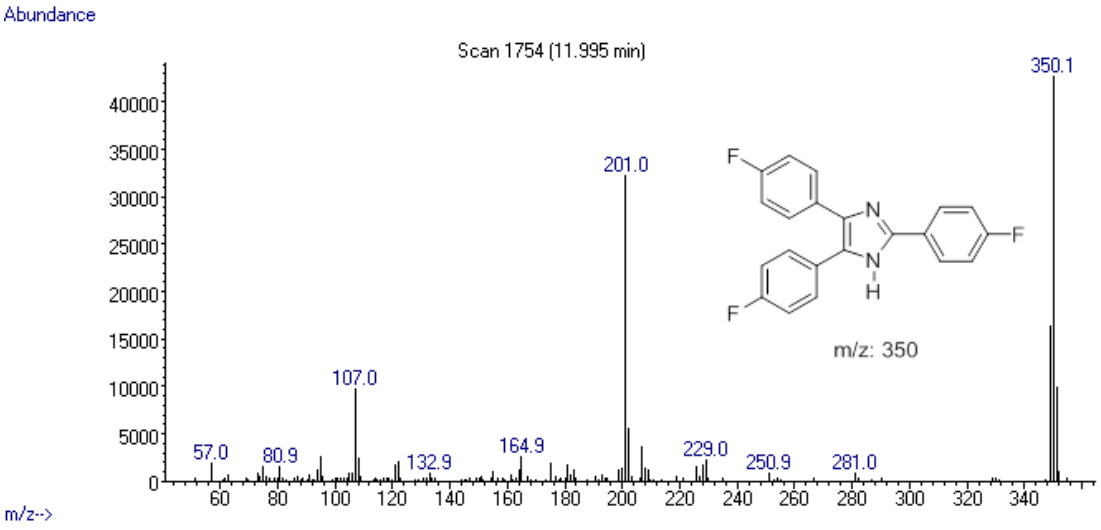


Figure S 45. Mass spectrum of 5b

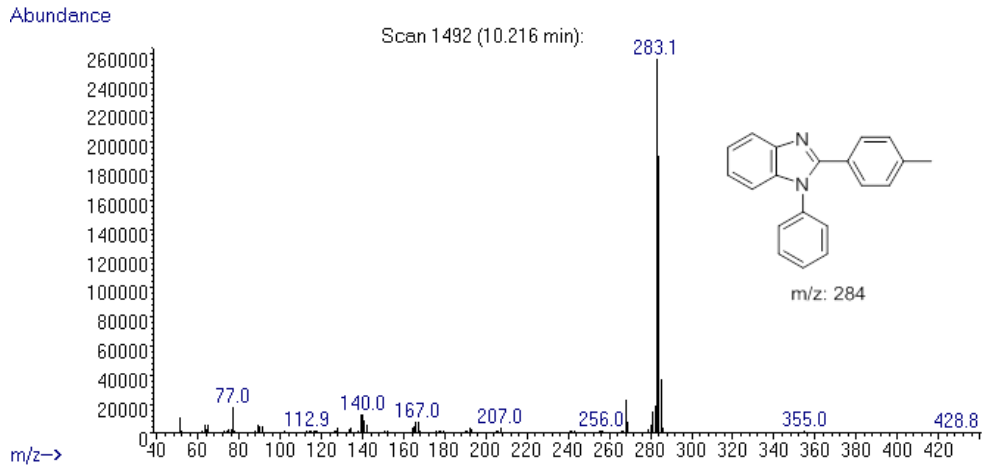


Figure S 46. Mass spectrum of 3f

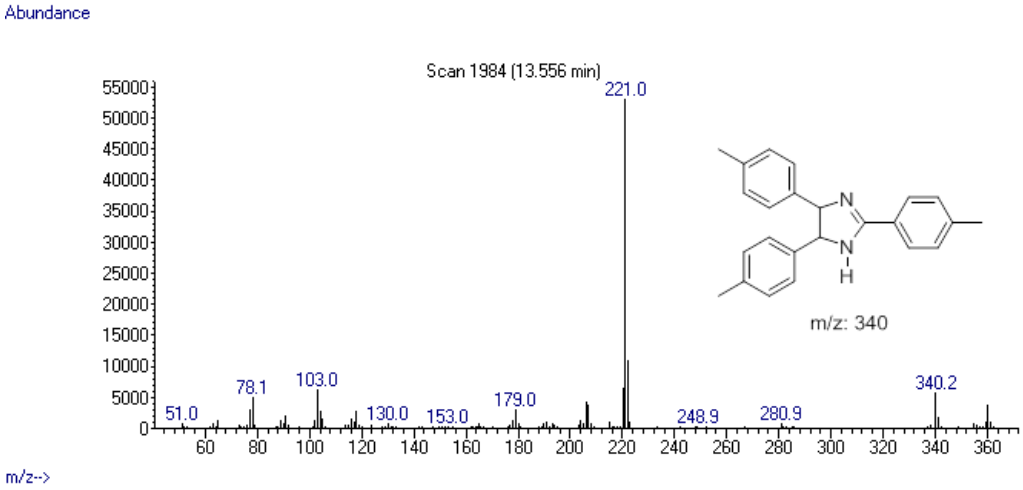


Figure S 47. Mass spectrum of 4c

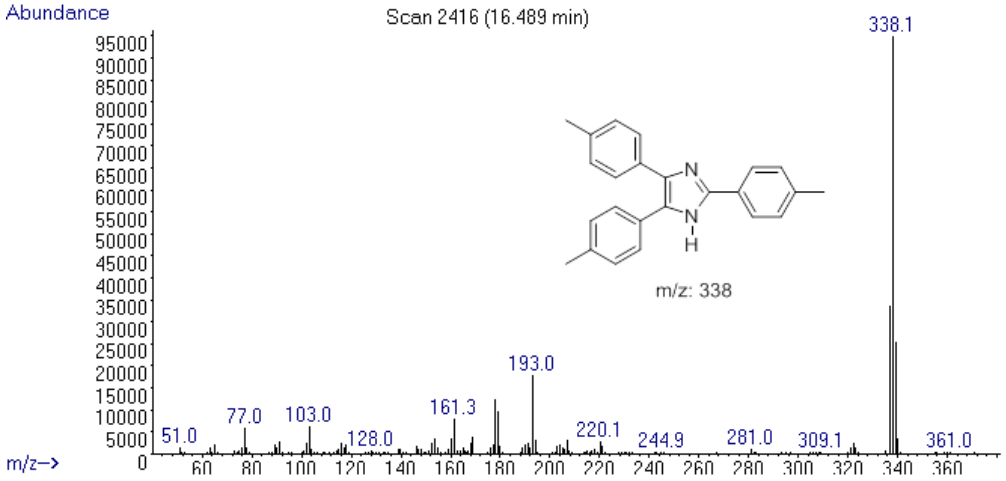


Figure S 48. Mass spectrum of 5c

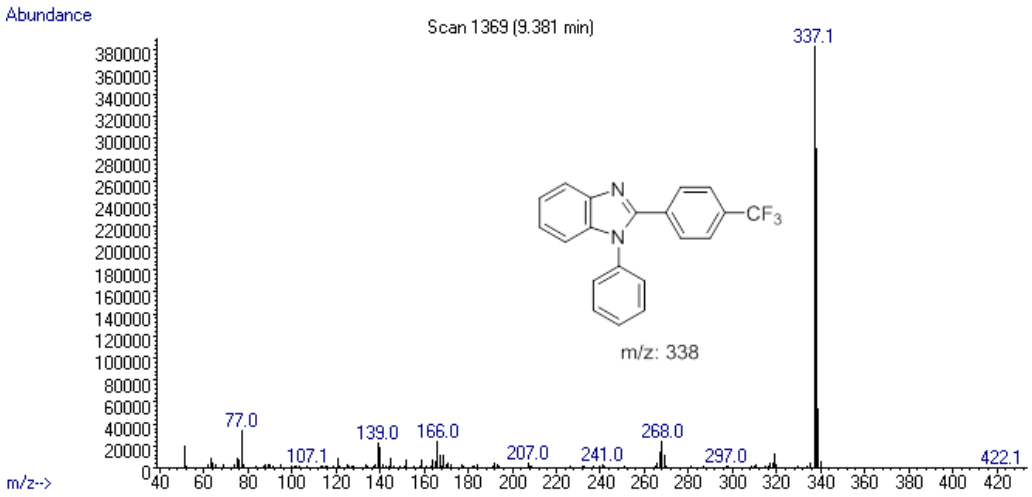


Figure S 49. Mass spectrum of 3g

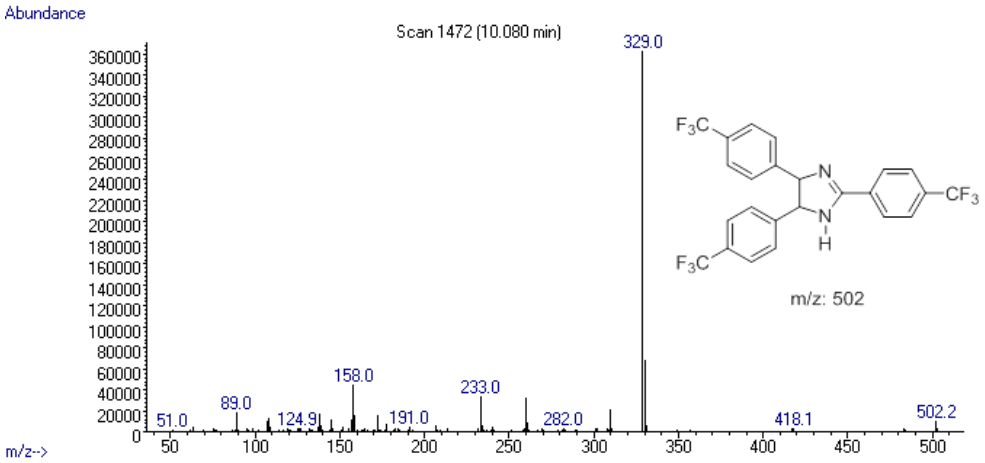


Figure S 50. Mass spectrum of 4d

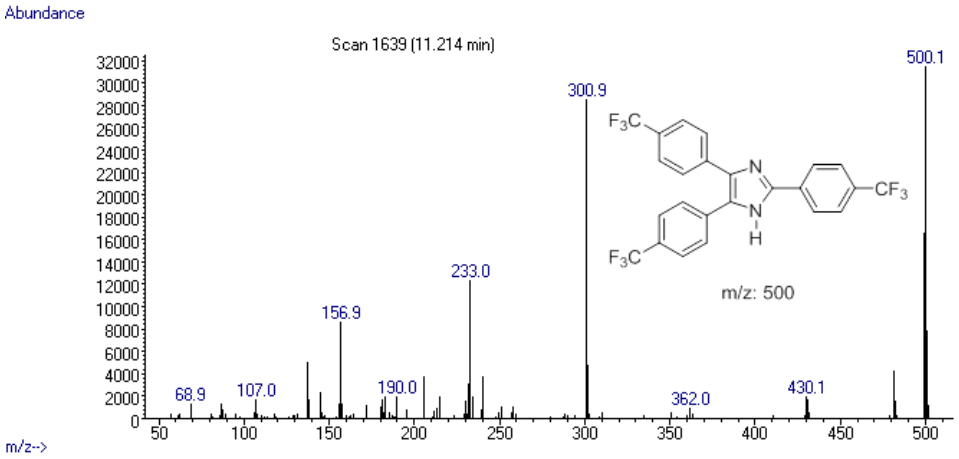


Figure S 51. Mass spectrum of 5d

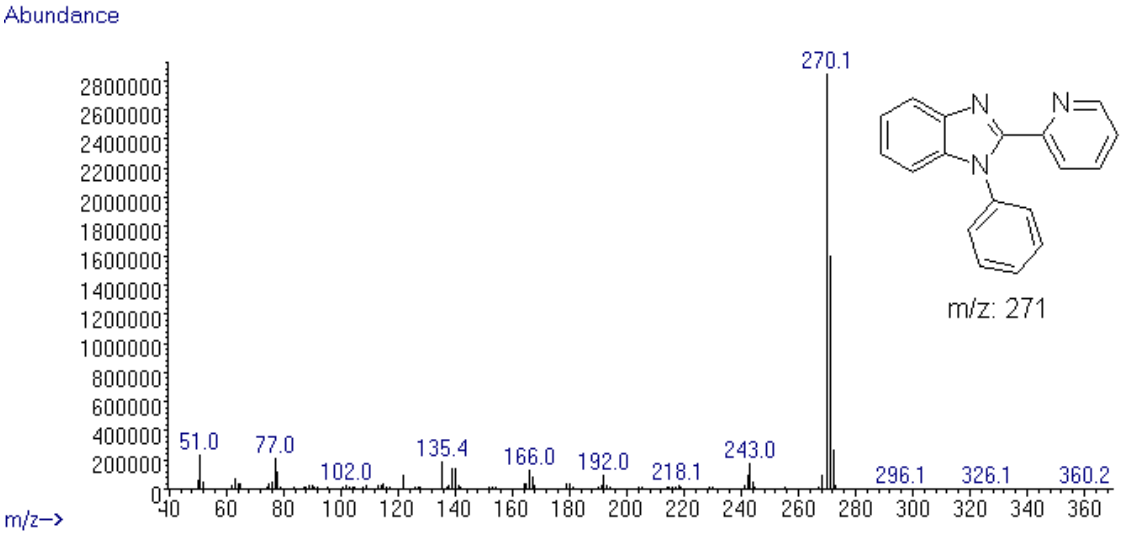


Figure S 52. Mass spectrum of 3h

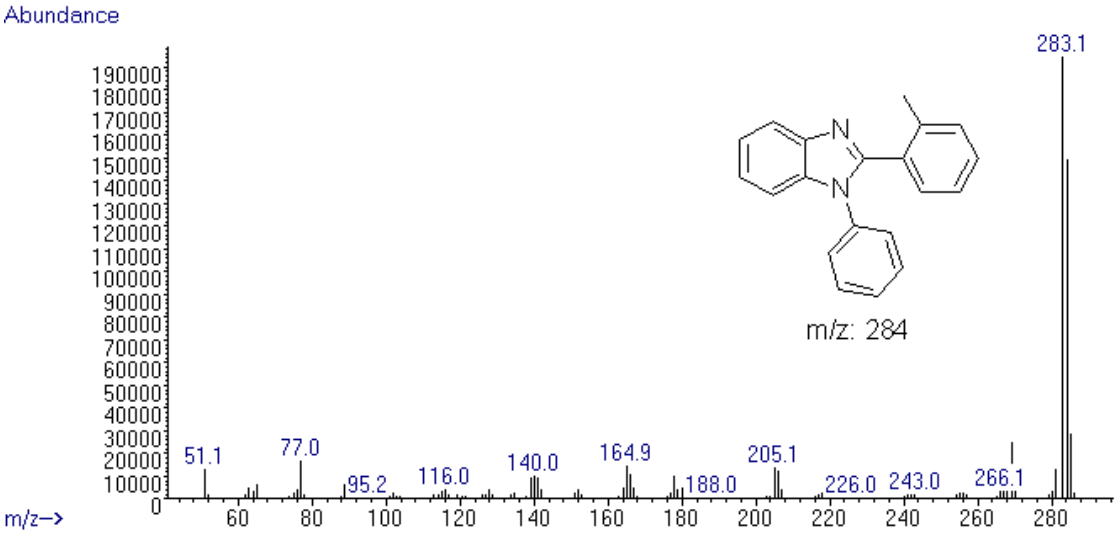


Figure S 53. Mass spectrum of 3i

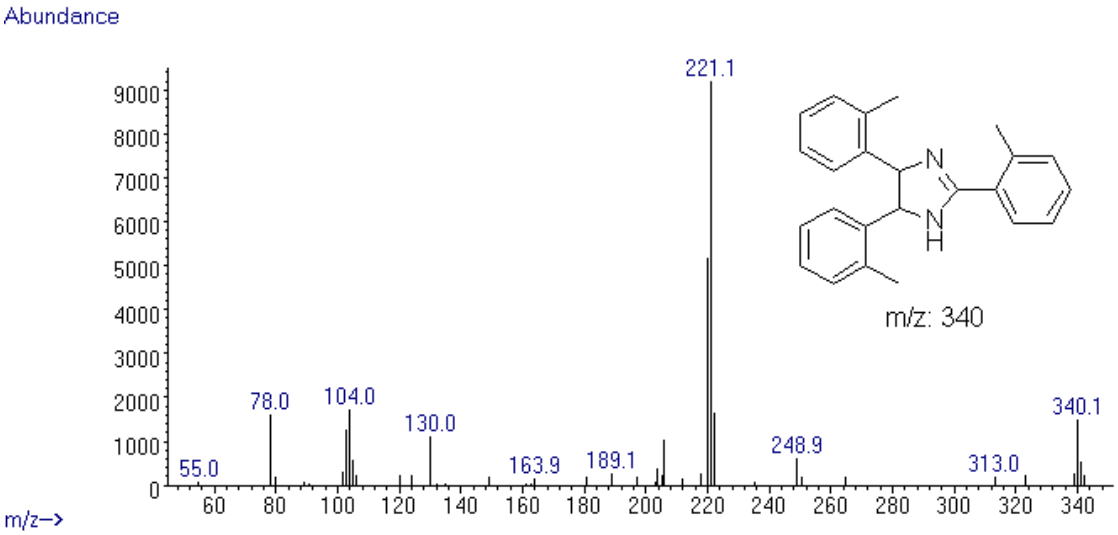


Figure S 54. Mass spectrum of 4e

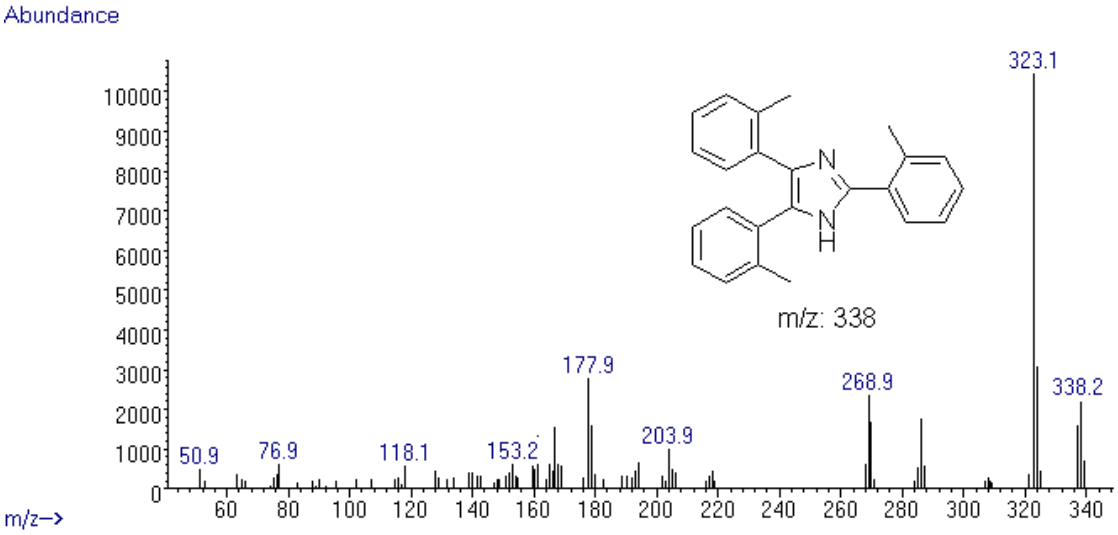


Figure S 55. Mass spectrum of 5e

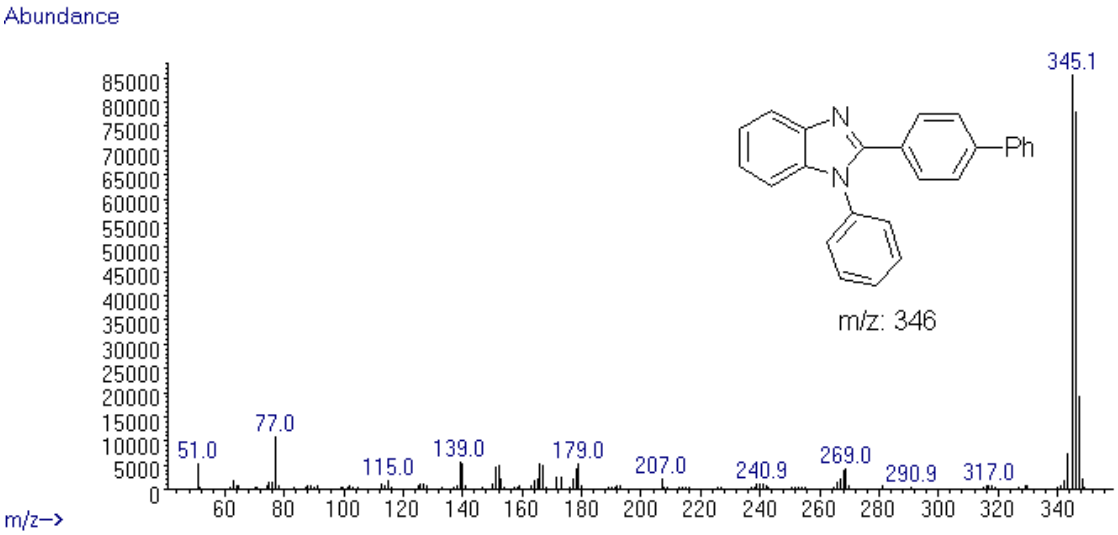


Figure S 56. Mass spectrum of 3j

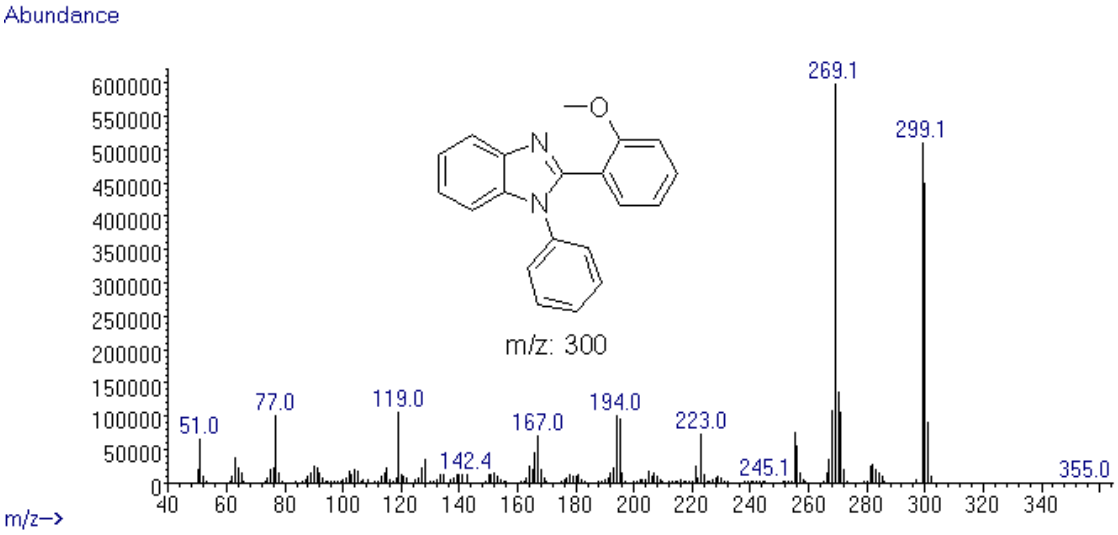


Figure S 57. Mass spectrum of 3k

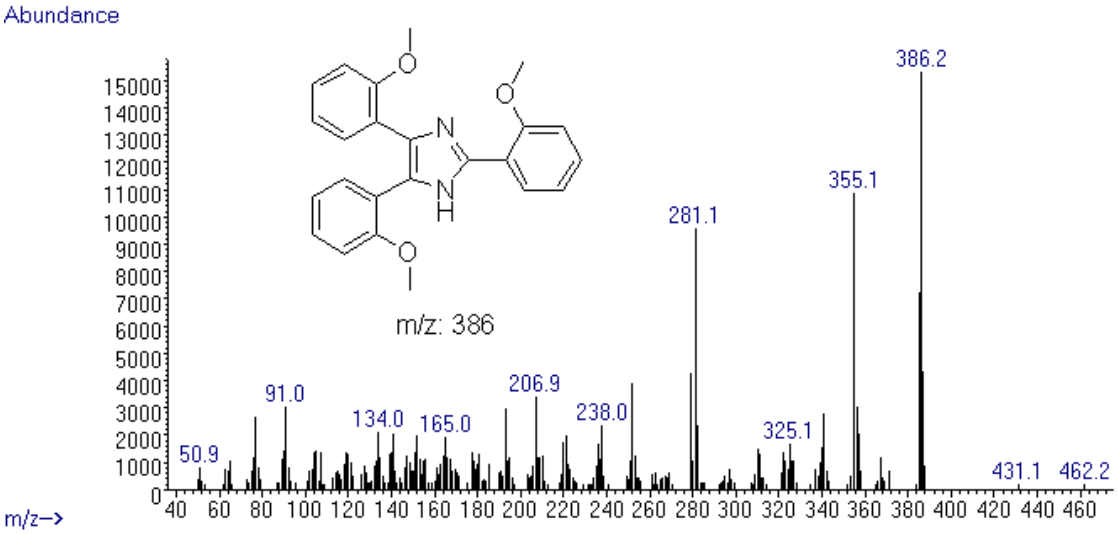


Figure S 58. Mass spectrum of 5g

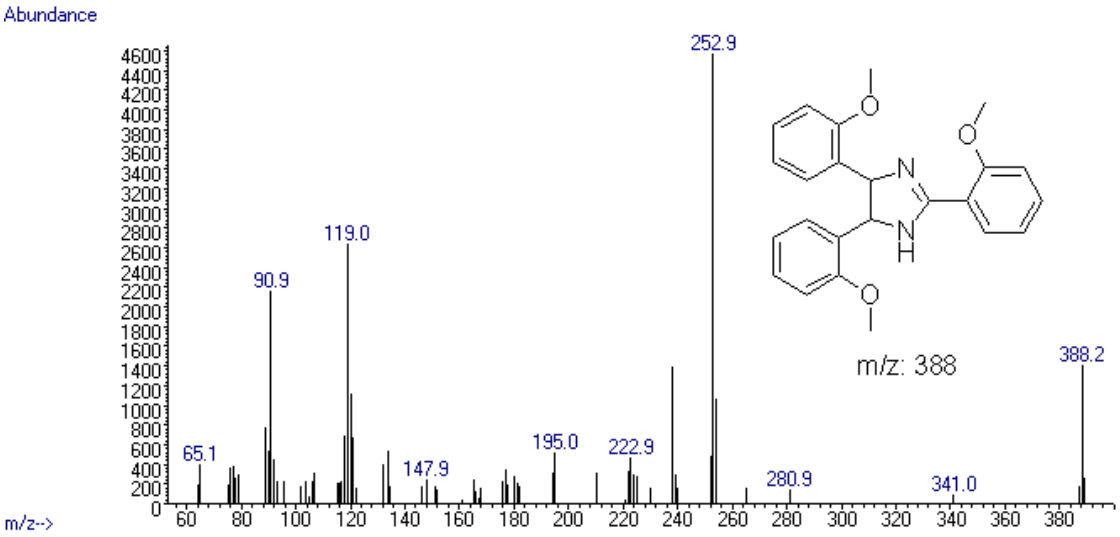


Figure S 59. Mass spectrum of 4g

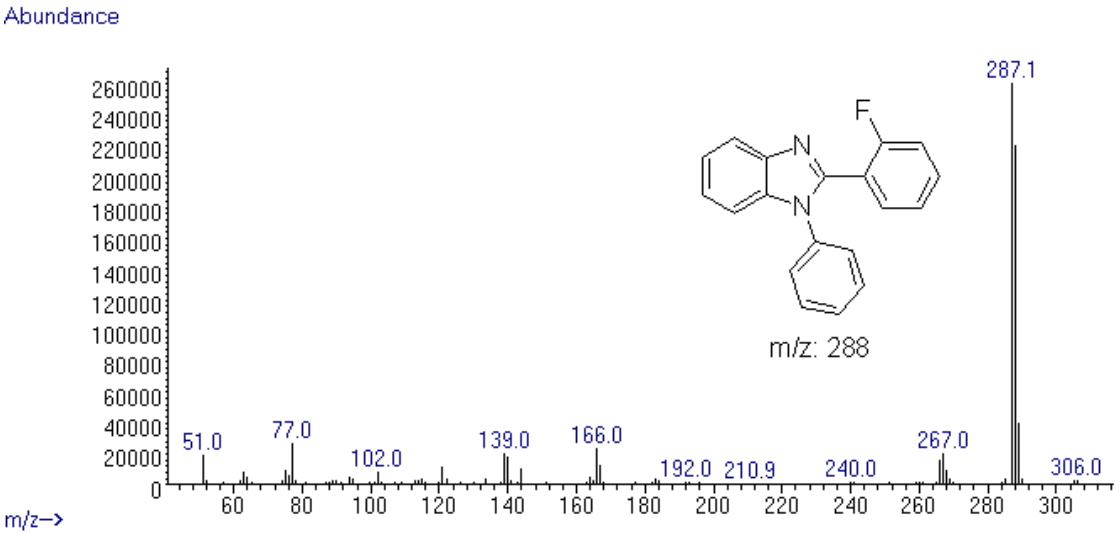


Figure S 60. Mass spectrum of 3l

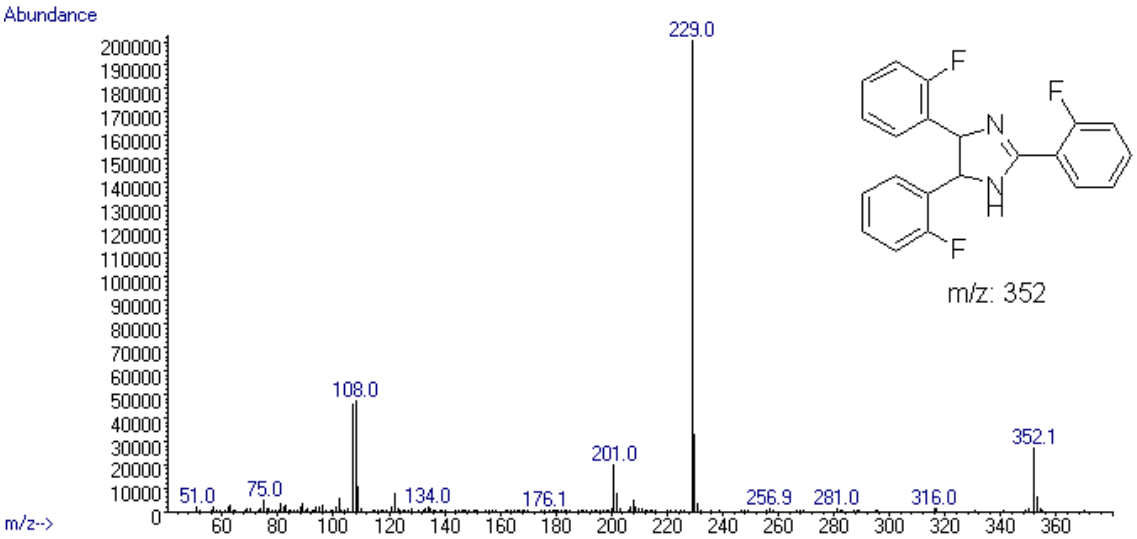


Figure S 61. Mass spectrum of 4f

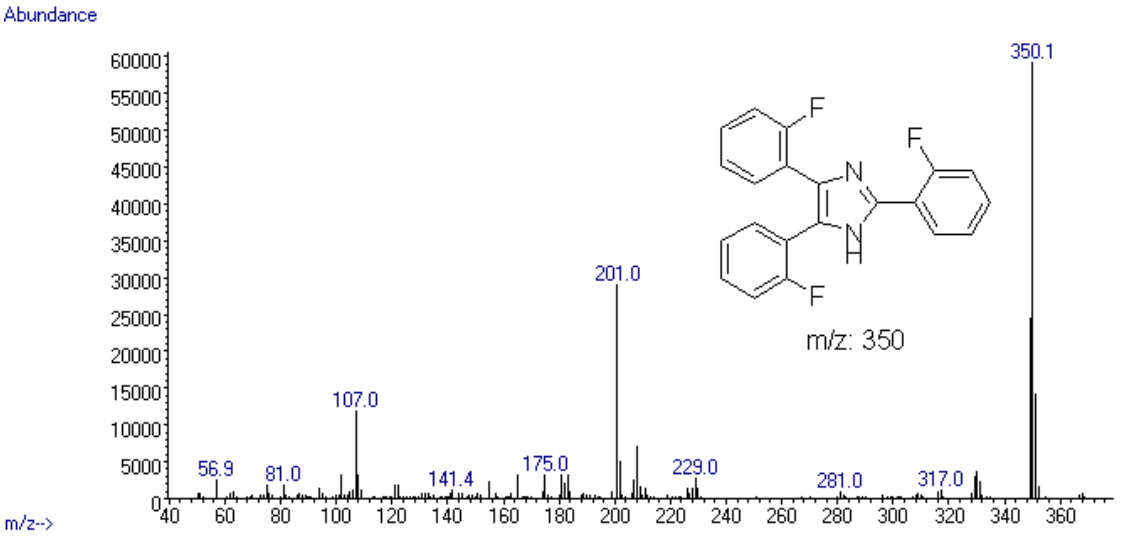


Figure S 62. Mass spectrum of 5f

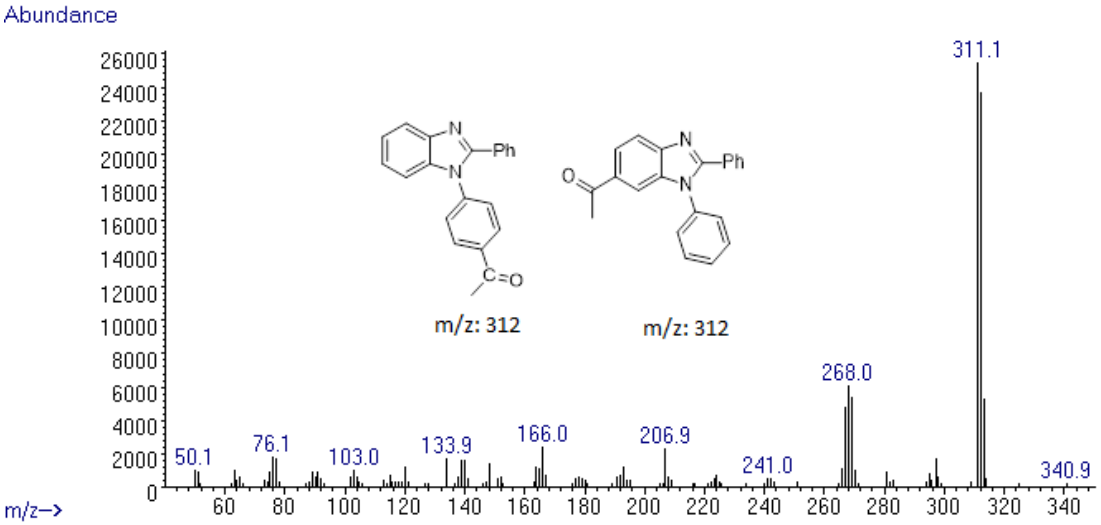


Figure S 63. Mass spectrum of 3m and 3n

References

[1] Zhang, C.; Jiao, N. *Angew. Chem. Int. Ed.* **2010**, *49*, 6174-6177.