

Supporting Information

for

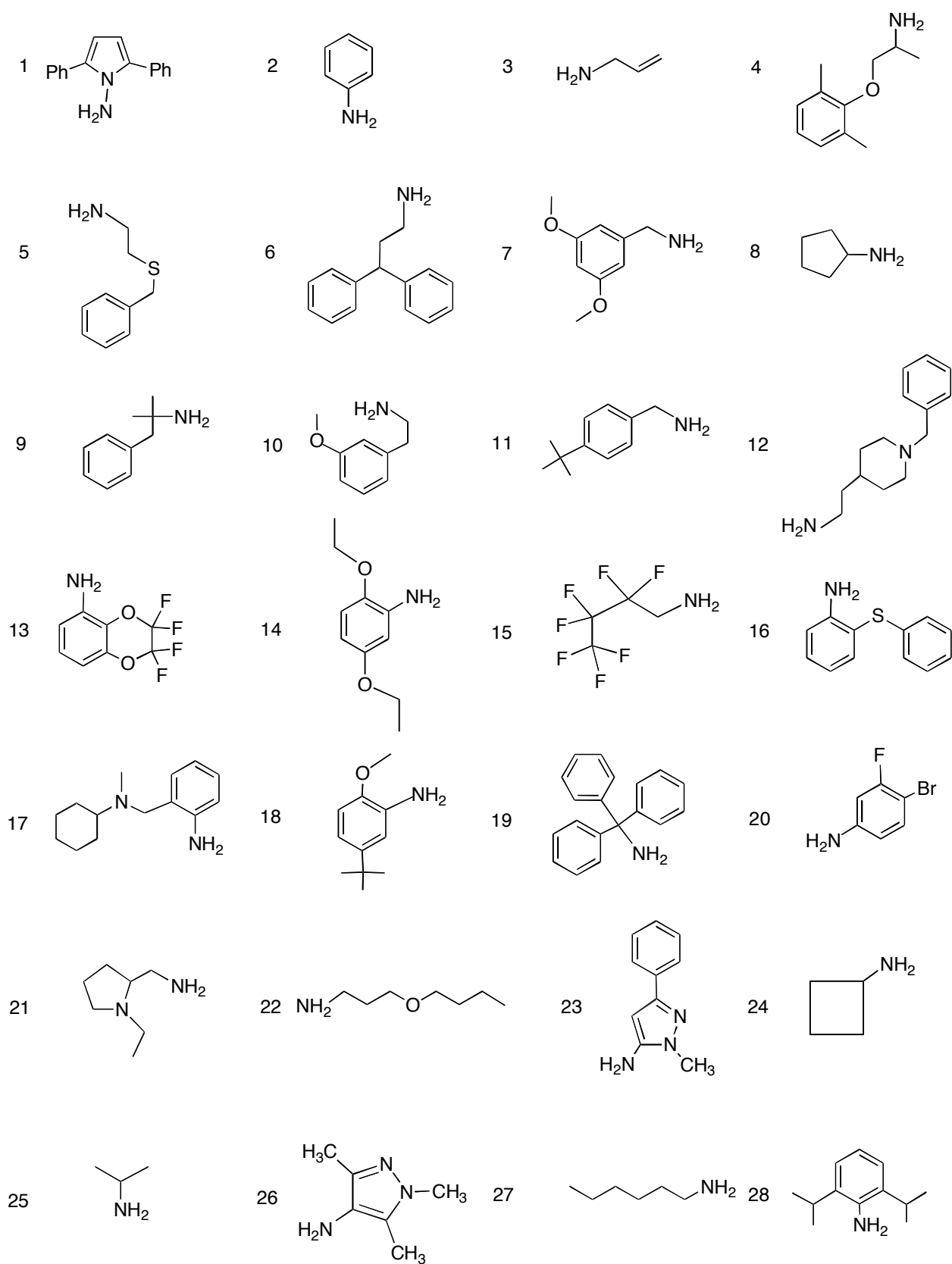
**Discovery and optimization of new chromium catalysts for ethylene oligomerization  
and polymerization aided by high throughput screening**

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David J. Williams.*

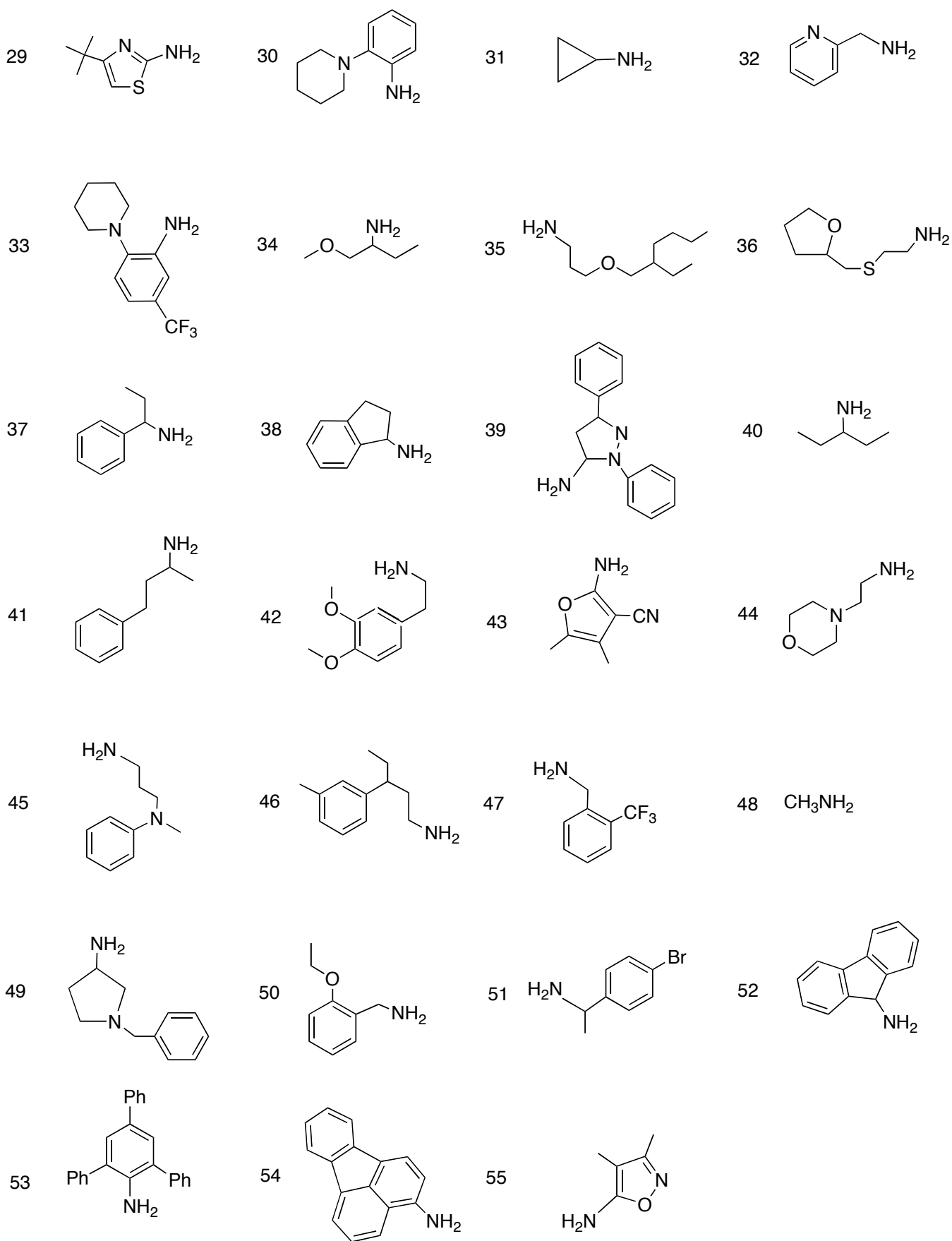
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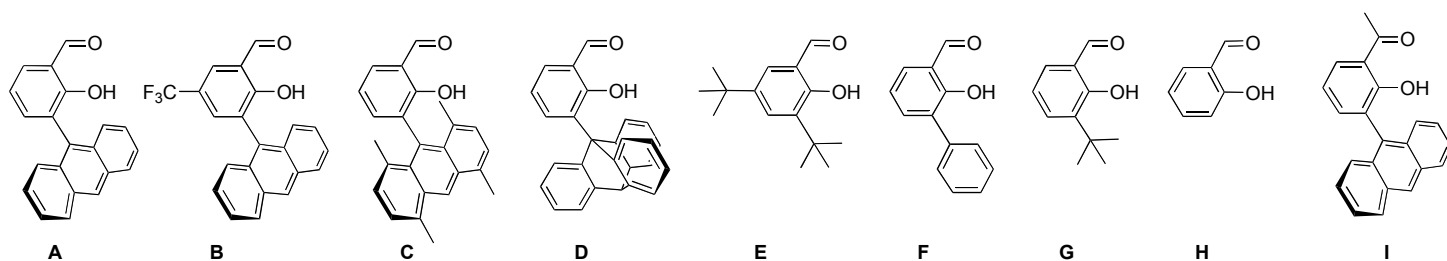
## Amines employed in the ligand library (with numbering)



## Amines (cont.)



## Salicylaldehydes and additional amines



<b>Additional amines</b>	<b>-<sup>i</sup>Butyl</b>	<b>60</b>		
	- <i>cyclo</i> -hexyl	<b>61</b>		
	-CH(CH <sub>2</sub> CH <sub>2</sub> Ph) <sub>2</sub>	<b>62</b>	AnthPhPPh <sub>2</sub>	<b>90</b>
	-NH <sub>2</sub>	<b>63</b>	AnthPhP <sup>i</sup> Pr <sub>2</sub>	<b>91</b>
	-CH <sub>2</sub> CH <sub>2</sub> CHMe <sub>2</sub>	<b>64</b>	AnthPh-Py	<b>92</b>
	-CH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub>	<b>65</b>	AnthPhCH <sub>2</sub> NMe <sub>2</sub>	<b>93</b>
	-(2,5-dimethylpyrrolyl)	<b>66</b>	TriptPhCH <sub>2</sub> N(CH <sub>2</sub> Py)	<b>94</b>
	-CH <sub>2</sub> CHMe <sub>2</sub>	<b>67</b>		
	adamantyl	<b>68</b>		
	-CH <sub>2</sub> Ph	<b>69</b>		
	CH <sub>2</sub> CH <sub>2</sub> Ph	<b>70</b>		
	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Ph	<b>71</b>		
	PhPPh <sub>2</sub>	<b>72</b>		
	quinolyl	<b>73</b>		
	CMe <sub>2</sub> Py	<b>74</b>		
	CPh <sub>2</sub> Py	<b>75</b>		
	CH <sub>2</sub> CH <sub>2</sub> -pyrrolidine	<b>76</b>		
	CHPy <sub>2</sub>	<b>77</b>		
	CH(Me)CH <sub>2</sub> CH <sub>2</sub> Ph	<b>78</b>		
	CH <sub>2</sub> CH <sub>2</sub> Py	<b>79</b>		
	Py	<b>80</b>		
	PhOH	<b>81</b>		

## Summary of polymerisation data

	Ligand	Cr	Cr:Al	T	Reactor	P	Yield	Prod.	Mn	Mw	Mw/Mn	Mpk	Methyls	Di-substituted Olefins	Vinyls
		(mmol)		(°C)		(Bar)	(g)	(g/mmol /bar/hour)							
1.	none	0.03	1:100	RT	Schlenk	1	0.07	2.3	11000	253000	22.4	53000	1.7	0.1	0.8
2.	1A	0.005	1:200	RT	Schlenk	1	NC								
3.	1A	0.005	1:200	RT	Schlenk	1	0.19	38							
4.	2A	0.03	1:100	RT	Schlenk	1	2.63	87.7	204000	457000	2.2	368000	0.8	0	0
5.	2A	0.03	1:100	RT	Schlenk	1	1.81	60.3	219000	448000	2	388000	0.9	0	0
6.	2A	0.03	1:100	RT	Schlenk	1	2.35	78.3	230000	475000	2.1	454000	1	0	0
7.	2A	0.03	1:300 <sup>a</sup>	50	Large <sup>a</sup>	4	9.7	80.8	3300	249000	75.3	8900	8.7	0	1.3
8.	2A	0.015	1:100	RT	Schlenk	1	1.42	94.7	213000	934000	4.4	982000	0.8	0	0.3
9.	2A	0.015	1:300 <sup>a</sup>	50	Large <sup>a</sup>	4	5.28	88	4700	404000	86.1	484000	8.6	0	0.8
10.	2A	0.015	1:30 <sup>c</sup>	RT	Schlenk	1	0.45	30	222000	860000	3.9	696000	1.2	0	0
11.	2B	0.03	1:100	RT	Schlenk	1	1.1	36.7	336000	714000	2.1	566000	1.5	0	0.3
12.	2E	0.03	1:100	RT	Schlenk	1	NC								
13.	(2E) <sub>2</sub> CrCl	0.03	1:200	RT	Schlenk	1	0.12	4							
14.	(2E) <sub>2</sub> CrCl	0.025	1:25	RT	Schlenk	1	1.23	49							
15.	(2E) <sub>2</sub> CrCl	0.03	1:25	RT	Schlenk	1	1.72	57							
16.	(2E) <sub>2</sub> CrCl	0.025	1:25	RT	FP	4	6.38	63.8	431000	2368000	5.5	1935000	0.47	0	0.28
17.	(2G) <sub>2</sub> CrCl	0.025	1:25	RT	Schlenk	1	0.19	6							
18.	(2G) <sub>2</sub> CrCl	0.025	1:25	RT	Schlenk	1	1.76	70.4	\$	\$	\$	\$	0.6	0	0.25
19.	(2G) <sub>2</sub> CrClMeCN <sub>2</sub>	0.005	1:200	RT	Schlenk	1	0.18	36	1800	463000	25.4	59000	2.8	0	1.9
20.	(2G) <sub>2</sub> CrClMeCN <sub>2</sub>	0.005	1:2200	25	FP	4	0.11	<1	11000	391000	35.6	48000	4.5	0	1.4
21.	(2G) <sub>2</sub> CrClMeCN <sub>2</sub>	0.005	1:200	RT	Schlenk	1	0.05	10							
22.	(2G) <sub>2</sub> CrClMeCN <sub>2</sub>	0.005	1:2200	25	FP	4	0.03	<10							
23.	6A	0.005	1:200	RT	Schlenk	1	0.93	168							
24.	6A	0.005	1:600	50	FP	4	4.79	239							
25.	6A	0.005	1:200	RT	Schlenk	1	0.56	112							
26.	8A	0.005	1:200	RT	Schlenk	1	1.12	920							
27.	8ACrCl <sub>2</sub> (thf)	0.005	1:200	RT	Schlenk	1	1.208	483	80000	167000	2.1	143000	1.2	0	0.3
28.	8ACrCl <sub>2</sub> (thf)	0.005	1:600	30	FP	4	2.78	278	138000	313000	2.3	247000	3.1	0	1.4
29.	8ACrCl <sub>2</sub> (thf)	0.001	1:2200	0	FP	4	1.94	488	744000	2642000	3.6	1586000	0.37	0	0.4
30.	19A	0.005	1:200	RT	Schlenk	1	0.24	48							
31.	24A	0.005	1:200	RT	Schlenk	1	1.61	1288							
32.	24A	0.0025	1:200	RT	Schlenk	1	1.57	628							
33.	24A	0.005	1:600	50	FP	4	13.26	661							
34.	24A	0.005	1:200	RT	Schlenk	1	0.57	912							
35.	25A	0.01	1:400	50	Large <sup>a</sup>	4	19	475							
36.	25A	0.005	1:200	RT	Schlenk	1	1.08	864	68000	143000	2.1	121000	0.6	0	0
37.	25A	0.002	1:200	RT	Schlenk	1	0.88	1760	\$	\$	\$	\$	0.8	0	0
38.	25A	0.005	1:200	50	FP	1	0.5	100							
39.	25A	0.002	1:200	RT	Schlenk	1	1.37	685	54000	130000	2.4	1100000	0.8	0	0
40.	25A	0.005	1:520	RT	FP	1	2.71	541	\$	\$	\$	\$	0.7	0	0.2
41.	25A	0.002	1:1000	O	FP		1.88	940							
42.	25A	0.005	1:600	50	Large <sup>a</sup>	4	3.69	184	12000	71000	59.9	704000	5		
43.	25A	0.002	1:10000	oC	FP	1	4.43	2215	379000	1260000	3.3	710000	0.4		
44.	25A	0.002	1:1000	RT	FP	1	nc								
45.	25A	0.005	1:600	20	Large <sup>a</sup>	4	12.91	646							
46.	25A	0.005	1:600	RT	Schlenk	1	1.06	212							
47.	25A	0.005	1:600	-20	Large <sup>a</sup>	4	9.91	496							
48.	(25A) <sub>2</sub> CrCl	0.005	1:200	RT	Schlenk	1	0.26	52	57000	211000	3.7	195000	2.4	0	1.3
49.	(25A) <sub>2</sub> CrCl	0.005	1:2200	25	FP	4	4.38	876	115000	259000	2.3	201000	1.5	0	1

	Ligand		Cr	Cr:Al	T	Reactor	P	Yield	Prod.	Mn	Mw	Mw/Mn	Mpk	Methyls	Di-substituted Olefins	Vinyls
			(mmol)		(°C)		(Bar)	(g)	(g/mmol /bar/hour)							
50.	(25A)2CrCl	DEAC	0.025	1:25	RT	Schlenk	1	0.06	2.4	\$	\$	\$	\$	5.65	0	1.29
51.	(25A)2CrCl	DEAC	0.025	1:25	RT	FP	4	0.42	4.2	58000	1878000	32.4	2422000			
52.	25E		0.03	1:100	RT	Schlenk	1	NC								
53.	25F		0.03	1:200	RT	Schlenk	1	NC								
54.	25H		0.03	1:200	RT	Schlenk	1	NC								
55.	25I		0.03	1:200	RT	Schlenk	1	NC								
56.	27A		0.002	1:200	RT	Schlenk	1	1.46	2920	728200	1550000	2.12		-		
57.	27A		0.005	1:200	RT	Schlenk	1	2.00	1600							
58.	28A		0.03	1:400	RT	Schlenk	1	0.2	6.7	8900	921000	103.3	543000	3.3	0	1.2
59.	31A		0.002	1:200	RT	Schlenk	1	1.25	2500	1369000	2365000	1.73		-		
60.	31A		0.005	1:200	RT	Schlenk	1	1.18	944							
61.	32A		0.005	1:200	RT	Schlenk	1	NC								
62.	32D		0.005	1:200	RT	Schlenk	1	7.87	1574	1100	1900	1.8		16.3		11.6
63.	32D		0.005	1:600	50	FP	4	68.14	3407	600	1200	2		26		21.7
64.	32D	1-hexene	0.005	1:200	RT	Schlenk	1	3.1	619	1100	1700	1.6		17.8		12.5
65.	32D	1-hexene	0.005	1:600	50	FP	4	8.5	425							
66.	32D		0.005	1:200	RT	Schlenk	1	5.22	1044							
67.	32D		0.005	1:600	50	Large <sup>a</sup>	4	NC								
68.	32DCrCl2		0.005	1:200	RT	Schlenk	1	10.99	2198							
69.	32DCrCl2	4 mls, 1-hexene	0.005	1:200	RT	Schlenk	1	7.36	1472	900	1300	1.6		26.5		11.6
70.	32DCrCl2	10 mls, 1-hexene	0.005	1:200	RT	Schlenk	1	10.32	2064	700	1100	1.6		39.9		11
71.	32DCrCl2		0.005	1:600	RT	FP	4	55.18	2759							
72.	32DCrCl2		0.002	1:1200	50	FP	4	24.44	3055							
73.	32DCrCl2	DEAC	0.005	1:15	RT	Schlenk	1	NC								
74.	32DCrCl2	TMA/Barf	0.005	1:15	RT	Schlenk	1	NC								
75.	32DCrCl2		0.005	1:200	RT	Schlenk	1	11.5	2300							
76.	32DCrCl2		0.005	1:600	50	Large <sup>a</sup>	4	84.85	4245							
77.	32DCrCl2		0.005	1:600	50	FP	4	27.35	1365							
78.	32DCrCl2		0.001	1:2200	50	Large <sup>a</sup>	4	27.87	6968							
79.	32DCrCl2		0.001	1:2200	50	FP	4	16.64	4160							
80.	32DCrCl2		0.001	1:2200	50	FP	3	11.2	3733							
81.	32DCrCl2		0.001	1:2200	70	Large <sup>a</sup>	4	18.02	4505							
82.	32DCrCl2		0.001	1:2200	50	FP	1	6.05	6050							
83.	32DCrCl2		0.001	1:2000	50	FP	5	18.41	3682							
84.	32DCrCl2		0.001	1:2000	40	FP	5	28.51	5702							
85.	32DCrCl2		0.001	1:2000	30	FP	5	16.72	2230							
86.	32DCrCl2		0.001	1:2200	40	FP	4	12.44	3110							
87.	32DCrCl2		0.001	1:200	RT	Schlenk	1	3	3000							
88.	32DCrCl2		0.001	1:2200	50	Large <sup>a</sup>	4	70.76	8845							
89.	32DCrCl2MeCN		0.005	1:600	50	Large <sup>a</sup>	4	1.49	75							
90.	32DAI Me2	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	0.005	1:200	RT	Schlenk	1									
91.	32J		0.005	1:200	RT	Schlenk	1	1.8	360	1500	5700	3.9	1600	8.5	0	9
92.	32J		0.005	1:600	50	FP	4	9.12	456							
93.	40A		0.005	1:200	RT	Schlenk	1	NR								
94.	48A		0.005	1:200	Rt	Schlenk	1	0.48	96							
95.	53A		0.005	1:200	RT	Schlenk	1	0.37	74							
96.	53A		0.005	1:600	50	FP	4	3.33	167							
97.	60A		0.002	1:200	RT	Schlenk	1	0.14	70							
98.	61A		0.005	1:200	RT	Schlenk	1	NC								
99.	62A		0.005	1:200	RT	Schlenk	1	0.07	14							
100.	62A		0.005	1:200	RT	Schlenk	1	NR								

Ligand		Cr	Cr:Al	T	Reactor	P	Yield	Prod.	Mn	Mw	Mw/Mn	Mpk	Methyls	Di-substituted Olefins	Vinyls				
		(mmol)		(°C)		(Bar)	(g)	(g/mmol /bar/hour)											
101.	62A	0.005	1:600	50	FP	4	0.99	50											
102.	63A	0.005	1:200	RT	Schlenk	1	0.38	76											
103.	64A	0.005	1:200	RT	Schlenk	1	0.25	80											
104.	65A	0.005	1:200	RT	Schlenk	1	0.2	40											
105.	65D	0.005	1:200	RT	Schlenk	1	2.84	568	17000	175000	10.1	3500, 6152000	1.3	0	0.8				
106.	65D	0.005	1:200	RT	Schlenk	1	4.71	942											
107.	65D	0.005	1:600	50	FP	4	11.87	594											
108.	65D	0.005	1:600	50	Large <sup>a</sup>	4	11.6	580											
109.	66A	0.005	1:200	RT	Schlenk	1	0.13	26											
110.	67A	0.005	1:200	RT	Schlenk	1	0.47	94											
111.	68A	0.002	1:200	RT	Schlenk	1	0.13	65											
112.	69A	0.005	1:200	RT	Schlenk	1	0.42	94	\$	\$	\$	\$							
113.	70A	0.005	1:200	RT	Schlenk	1	2.1	420	\$	\$	\$	\$							
114.	70A	0.005	1:600	RT	FP	4	8.06	402	\$	\$	\$	\$							
115.	71A	0.002	1:200	RT	Schlenk	1	1.3	650	\$	\$	\$	\$							
116.	71A	0.005	1:600	50	FP	4	9.05	453	\$	\$	\$	\$							
117.	72D	0.005	1:200	RT	Schlenk	1	1.64	328	1200	106000	88.2	1100, 706000	13	0	9.8				
118.	72D	0.005	1:200	RT	Schlenk	1	0.31	62											
119.	72E	0.03	1:100	RT	Schlenk	1	0.85	28.3	12000	754000	61.8	9300	2.5	0	0.3				
120.	73D	0.005	1:200	RT	Schlenk	1	9.29	1858	1000	1700	1.7								
121.	73D	0.005	1:600	50	FP	4	16.95	829.5											
122.	73D	0.005	1:600	50	FP	4	35.89	1793	600	1200	2								
123.	73D	2.0 mls, 1-hexene	0.005	1:200	RT	Schlenk	1	4.73	946										
124.	73DCrCl2	0.005	1:200	RT	Schlenk	1	10.9	2180											
125.	73DCrCl2	0.0005	1:2000	RT	Schlenk	1	5.06	10120											
126.	73DCrCl2	0.0005	1:4000	50	FP	4	18.7	9350											
127.	73DCrCl2.py	0.001	1:2200	50	FP	4	14.67	3668											
128.	73DCrCl2.py	0.001	1:2200	50	Large <sup>a</sup>	8	61.81	7726											
129.	73DCrCl2.py	0.001	1:2200	50	Large <sup>a</sup>	6	42	7000											
130.	73DCrCl2.py	0.001	1:2000	50	FP	4	27.85	6962											
131.	73DCrCl2.py	0.001	1:2200	50	Large <sup>a</sup>	4	36.58	9145											
132.	73DCrCl2.py	0.001	1:2000	50	Schlenk	1	6.58	6580											
133.	73DCrCl2.py	heptane	0.001	1:2000	50	Schlenk	1	4.45	4450										
134.	73DCrCl2.py	0.001	1:500	50	FP	4	0.314	78											
135.	73DCrCl2.py	0.001	1:2000	50	FP	4	16.77	4192											
136.	73DCrCl2.py	0.001	1:4000	50	FP	4	11	2750											
137.	73DCrCl2.py	0.001	1:2200	50	FP	4	29.79	7448											
138.	73DCrCl2.py	0.001	1:4200	50	Large <sup>a</sup>	10	101.96	10200											
139.	73DCrCl2.py	0.001	1:1200	50	FP	4	27.78	6945											
140.	73DCrCl2.py	0.001	1:700	50	FP	4	12.25	3063											
141.	73DCrCl2.py	0.001	1:3200	50	FP	4	23.43	5860											
142.	73DCrCl2.py	tiBal	0.001	1:2200	50	FP	4	1.17	292										
143.	73DCrCl2.py	0.001	1:4200	30	Large <sup>a</sup>	4	6.9	1725	500	1300	2.4	600	21.7	0.1	19.9				
144.	73DCrCl2.py	0.001	1:4200	40	Large <sup>a</sup>	4	19.17	4793	500	1100	2.2	600	26.5	0.2	24.1				
145.	73DCrCl2.py	0.001	1:4200	50	Large <sup>a</sup>	4	33.72	8430	500	1000	2.1	700	26.1	0.2	23.5				
146.	73DCrCl2.py	0.001	1:4200	60	Large <sup>a</sup>	4	23.63	5907	500	1200	2.3	700	25.4	0.2	22.6				
147.	73DCrCl2.py	0.001	1:4200	70	Large <sup>a</sup>	4	14.88	3720	500	1100	2.1	700	26.1	0.3	23.1				
148.	73DCrCl2.py	30 min	0.0005	1:4000	50	FP	1	2.13	8520	1100	1500	1.4	1100	16.26	0	11.95			
149.	73DCrCl2.py	30 min	0.0005	1:4000	50	FP	2	4.16	8320	1000	1500	1.5	1100	15.72	0	13.28			
150.	73DCrCl2.py	30 min	0.0005	1:4000	50	FP	3	5.42	7227	1000	1500	1.5	1100	16.07	0	13.71			



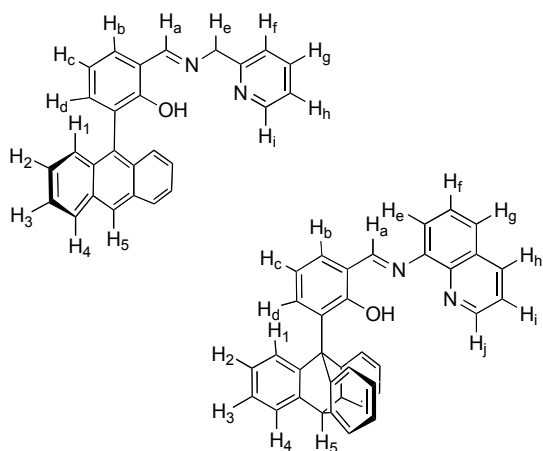
	Ligand		Cr	Cr:Al	T	Reactor	P	Yield	Prod.	Mn	Mw	Mw/Mn	Mpk	Methyls	Di-substituted Olefins	Vinyls
			(mmol)		(°C)		(Bar)	(g)	(g/mmol /bar/hour)							
151.	73DCrCl2.py	30 min	0.0005	1:4000	50	FP	4	8.8	8800	1000	1500	1.5	1100	15.88	0	13.96
152.	73DCrCl2.py	30 min	0.0005	1:4000	50	FP	5	9.7	9700	1000	1500	1.5	1100	15.31	0	14.36
153.	73DCrCl2.py	0 mls, 1-hexene	0.0005	1:4000	50	FP	4	19.97	9987	1000	1500	1.5	1200	16.2	0	14.29
154.	73DCrCl2.py	8 mls, 1-hexene	0.0005	1:4000	50	FP	4	15.35	7685	1000	1500	1.5	1100	17.05	0.49	14.03
155.	73DCrCl2.py	16 mls, 1-hexene	0.0005	1:4000	50	FP	4	13.15	6575	1000	1500	1.5	1100	19.17	0.83	13.55
156.	73DCrCl2.py	32 mls, 1-hexene	0.0005	1:4000	50	FP	4	12.1	6005	1000	1400	1.4	1100	22.08	1.26	13.2
157.	73DCrCl2.py		0.0005	1:4000	50	FP	4	20.32	10161							
158.	73DCrCl2.py	2 bar H2	0.0005	1:8000	50	FP	10	NR								
159.	73E		0.005	1:200	RT	Schlenk	1	0.24	48							
160.	73F		0.005	1:200	RT	Schlenk	1	NR								
161.	74D		0.005	1:200	RT	Schlenk	1	5.9	1180							
162.	74D		0.005	1:600	50	FP	4	8.03	401	900	40000	45.2	800			
163.	75D		0.005	1:200	RT	Schlenk	1	0.576	115	2200	58000	267.2	1600, 109000, 6042000	14	0	7.9
164.	75D		0.005	1:600	50	Large <sup>a</sup>	4	5.73	286							
165.	75D		0.005	1:200	RT	Schlenk	1	0.32	64							
166.	75D		0.005	1:600	50	FP	4	1.42	71							
167.	76D		0.005	1:200	RT	Schlenk	1	2.86	572.2							
168.	76D		0.005	1:600	50	Large <sup>a</sup>	4	6.72	336							
169.	76D		0.005	1:200	RT	Schlenk	1	0.5	100							
170.	76D		0.005	1:600	50	Large <sup>a</sup>	4	2.65	132.5	2600	6200	2.3	4700	8.1	0	2.2
171.	77D		0.005	1:200	RT	Schlenk	1	0.507	101	\$	\$	\$	\$	2.8	0	1.9
172.	77H		0.005	1:200	RT	Schlenk	1	NC								
173.	78A		0.005	1:200	RT	Schlenk	1	0.25	80							
174.	78H		0.005	1:200	RT	Schlenk	1	NC								
175.	79D		0.005	1:200	RT	Schlenk	1	2.23	446							
176.	80D		0.005	1:200	RT	Schlenk	1	0.59	118	7100	490000	69.4	51000	2.2	0	1.5
177.	81D		0.005	1:200	RT	Schlenk	1	NC								
178.	82		0.005	1:200	RT	Schlenk	1	NR								
179.	83		0.005	1:200	RT	Schlenk	1	NR								
180.	90		0.03	1:100	RT	Schlenk	1	NC								
181.	91		0.03	1:100	RT	Schlenk	1	NC								
182.	94		0.005	1:200	RT	Schlenk	1	0.18	36							
183.	I		0.03	1:100	RT	Schlenk	1	NC								
184.	I		0.005	1:100	RT	Schlenk	1	NC								

AC: 1L Autoclave Reactor; FP: Fisher-Porter Reactor; \$: insoluble polymer (MW > 2M Da)

## Experimental

### General

Salicylaldehydes **E**, **G** and **H** are commercially available. The following compounds were made by literature methods, amines **62**,<sup>1</sup> **1** & **66**,<sup>2</sup> **74**,<sup>3</sup> **75**,<sup>4</sup> **77**,<sup>5</sup> tetramethyl-anthraquinone,<sup>6</sup> salicylaldimines **2E**, **2G**,<sup>7</sup> **32E** & **73E**<sup>8</sup> and the complex *p*-tolylCrCl<sub>2</sub>(thf)<sub>3</sub>,<sup>9</sup> while the compounds **2A**, **25A**, **32A**, **32D** and **32D**CrCl<sub>2</sub> (**VIII**) have been reported previously.<sup>10</sup> The ligand *N*-*o*-(diphenylphosphino)phenyl 3,5-di-*tert*-butylsalicylaldimine(**72E**) was available within our laboratory and was used as received.



<sup>1</sup>H NMR data for the aldehydes and imines have been numbered following the system shown above so that all the assignments follow the same convention and are directly comparable.

### Synthesis of salicylaldehydes

*10-hydroxy-10-(2-(methoxymethoxy)-phenyl)-anthrone (1)*. Step 1 synthesis of *Methoxymethoxy-benzene*. Modified prep.<sup>11</sup> **NOTE : This reaction must be carried out in an efficient fume cupboard.** To a solution of phenol (188.21 g, 2.0 mols) dissolved in 1.5 litres of thf in a flask fitted with an efficient condenser was added chunks of sodium (52 g, excess) and the reaction mix allowed to react for 3 hours then heated under

reflux overnight to complete the reaction. A solution of MOMCl was formed in a 3 litre, 3 neck flask fitted with an efficient double surfaced condenser, pressure equalizing dropping funnel and a nitrogen inlet in a water bath at RT by the slow addition of AcCl (205 g, 2.6 mols) to dimethoxymethane (229 g, 3.0 mols) with a catalytic amount of  $\text{ZnCl}_2$  (2 g). **Caution: MOMCl is a known carcinogen and the reaction is exothermic.** After addition of the AcCl the reaction mixture was stirred for 30 minutes and the dropping funnel replaced with a septum. The thf solution of sodium phenolate was added by cannula and the reaction mixture stirred for 1 hour to complete the reaction. The reaction mixture was deactivated by the addition of 500 ml of 2 M NaOH solution and stirring for a further 60 minutes to decompose excess MOMCl. Ether (500ml) was added and the phases separated. The organic phase was washed with 3 x 500 ml of 2 M NaOH then 3 x 500 ml of distilled water and was dried over  $\text{MgSO}_4$ , filtered and the ether removed under reduced pressure. The material was purified by distillation under reduced pressure, 85-86°C 10 mm Hg. Yield 239.6 g, (86.7%).<sup>12</sup>  $^1\text{H-NMR}$  (250 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27-7.34(m, 2H, Ar-H), 6.99-7.08(m, 3H, Ar-H), 5.199(s, 2H,  $\text{OCH}_2$ ), 3.500(s, 3H, OMe).<sup>13</sup>  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.44, 157.57, 129.82, 122.22, 116.58, 94.73, 56.29. MS(EI<sup>+</sup>ve) (m/z) 138( $\text{M}^+$  35%), 108( $\text{M-CH}_2\text{O}^+$  15%).

Step 2:<sup>14</sup> To a solution of PhOMOM (16 g, 0.116 mols) in 200 ml of ether cooled in water bath was added BuLi (60 ml, 2.5 M, 0.15 mols) and the solution stirred overnight. A precipitate forms after 5-15 minutes. The slurry of MOMOPhLi was added slowly (dropwise over 3 hours) to a slurry of anthraquinone (45g, excess) in 500 ml of thf at RT, the solution turned a deep green. After addition the solution was stirred for 1 hour then dilute HCl added to acidify the mix. The slurry was filtered into a separating flask and the organic phase washed with 2 x 200 ml of distilled water. The solvent was removed under reduced pressure and the recovered solids slurried in 400 ml of THF ( $\approx$  10 ml / g of product). The excess anthraquinone was removed by filtration and the solids washed with 50 ml of THF. The THF was removed under reduced pressure and the solids slurried in a minimum of MeOH and filtered to remove most of the colored material. The dried solids were recrystallized from hot toluene. A second crop of crystals were recovered from the filtrates by removing the solvent, extracting with THF, filtering, drying and recrystallization from hot toluene, to yield clear colorless crystals. Yield 90.5%. The same procedure was followed reacting the lithium salt with

MgBr<sub>2</sub> to form the Grignard reagent. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.565 (s, 3H, -OMe), 2.802 (s, 1H, -OH), 4.470 (s, 2H, -OCH<sub>2</sub>), 6.785 (dd, 1H, *J* = 7.8 & 1.1, H<sub>a</sub>), 7.168 (dt, 1H, *J* = 7.6 & 1.1, H<sub>c</sub>), 7.246 (dt, 1H, *J* = 7.8 & 1.7, H<sub>b</sub>), 7.398 (dt, 2H, *J* = 7.4 & 1.4, H<sub>3</sub>), 7.440 (dd, 2H, *J* = 7.3 & 1.2, H<sub>1</sub>), 7.502 (dt, 2H, *J* = 7.5 & 1.4, H<sub>2</sub>), 8.252 (dd, 2H, *J* = 7.6 & 1.1, H<sub>4</sub>), 8.322 (dd, 1H, *J* = 7.7 & 1.7, H<sub>d</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 184.24, 151.93, 146.85, 133.84, 133.48, 130.49, 129.11, 127.94, 127.80, 126.24, 125.73, 121.73, 113.51, 92.50, 70.84, 55.00. IR (KBr, ν = CO) 1649 cm<sup>-1</sup>. EIMS (m/z): M<sup>+</sup>(%) 346(5), 316(15), 314(15), 301(5), 298(5), 285(35), 284(100), 255(95), 209(50), 152(40), 151(50). C<sub>22</sub>H<sub>18</sub>O<sub>4</sub> (346.39): Calc. C 76.29, H 5.24; Found C 76.42, H 5.12.

*9-(2-methoxymethoxy-phenyl)-anthracene (2)*. To a suspension of **1** (20 g, 57.7 mmol) in 900 ml of 40/60 H<sub>2</sub>O/HOAc was added ZnCl<sub>2</sub> (3.9 g, 28.9 mmol) then Zn (20 g, excess) and the suspension heated to 60°C overnight (with effective stirring the reaction is finished after ≈4 hours). The suspension was cooled and diluted with 2 liters of distilled water and stirred for 30 minutes then allowed to settle. The majority of the water was decanted, 200 ml of toluene added to dissolve the product and the solution filtered to remove unreacted Zn. The aqueous phase separated and the organic phase was washed with 2 x 200 ml of distilled water. The toluene was removed on a Roto-Vap. The solids were slurried in a minimum of methanol, filtered and dried. The impure material was recrystallized from a minimum of hot MeOH/toluene 80/20 to yield a pale yellow crystalline solid. Yield 90.2% <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.05 (s, 3H, -OMe), 4.919 (s, 2H, -OCH<sub>2</sub>), 7.252 (dt, 1H, *J* = 7.4 & 1.0, H<sub>c</sub>), 7.329 (dd, 1H, *J* = 7.5 & 1.8, H<sub>d</sub>), 7.370 (dt, 2H, *J* = 8.8 & 1.0, H<sub>3</sub>), 7.399 (d, 1H, *J* = 7.9, H<sub>a</sub>), 7.472 (dt, 2H, *J* = 8.7 & 1.0, H<sub>2</sub>), 7.543 (dt, 1H, *J* = 7.9 & 1.8, H<sub>b</sub>), 7.684 (d, 2H, *J* = 8.8, H<sub>4</sub>), 8.062 (d, 2H, *J* = 8.6, H<sub>1</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 155.42, 133.67, 132.88, 131.36, 130.33, 129.27, 128.34, 126.73, 126.50, 125.19, 125.00, 121.97, 115.20, 94.12, 55.76. EIMS (m/z): M<sup>+</sup>(%) 314(65), 282(30), 269(40), 268(50), 239(50), 57(50), 55(40), 45(100). C<sub>22</sub>H<sub>18</sub>O<sub>2</sub> (314.39): Calc. C 84.05, H 5.77; Found C 84.30, H 5.71. Lit.<sup>15</sup>

*3-(9-anthracenyl)-2-hydroxy-benzaldehyde* [*3-(9-anthracenyl)-salicylaldehyde*] (**4a or A**). To a slurry of **2** (5.57 g, 17.72 mmol) in ether (20 ml) was added BuLi (9.2 ml, 2.5 M, 23 mmol) and the slurry of **3** stirred overnight. The slurry was cooled to -78°C, dry ice/acetone bath, and DMF (5 ml, excess) added. The mixture was allowed to warm to RT and then stirred for 1 hour. The reaction mixture was deactivated by addition of dilute HCl then 100 ml of distilled water. The ether was removed under reduced pressure and the precipitated product was collected by filtration and washed with water. The crude product was dissolved in 50 ml of THF and 50 ml of 5 M HCl added. The slurry was heated under reflux for 3 hours, cooled and diluted with 100 ml of distilled water. The crude product was collected by filtration, washed with water, slurried with a minimum amount of methanol, filtered and washed with a small portion of cold methanol then dried under vacuum. The yellow solid was >99% pure and was used without further purification. Yield 89.9%. Recrystallization from hot toluene gave analytically pure material. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 11.18(s, 1H, OH), 10.083(s, 1H, H<sub>a</sub>), 8.558(s, 1H, H<sub>5</sub>), 8.078(d, 2H *J* = 8.5 Hz, H<sub>4</sub>), 8.799(dd, 1H *J* = 7.7 & 1.7 Hz, H<sub>b</sub>), 7.57-7.63(m, 3H, H<sub>3</sub> & H<sub>d</sub>), 7.35-7.51(m, 6H, H<sub>2</sub> & H<sub>3</sub>), 7.274(t, 1H *J* = 7.5 Hz, H<sub>c</sub>). IR (KBr, ν = CO) 1651 cm<sup>-1</sup>. MS-CI (m/z) 316(M+NH<sub>4</sub><sup>+</sup>, 100%). C<sub>21</sub>H<sub>14</sub>O<sub>2</sub> (298.34): Calc. C 84.54, H 4.73; Found C 85.49, H 4.59. Lit.<sup>16</sup>

*3'-(9-anthracenyl)-2'-hydroxyacetophenone* (**4b or I**). As above for **4a** except the slurry of **3** was added slowly to a solution of acetic anhydride (excess) in DME cooled to -78°C, dry ice/acetone bath. Pale yellow solid. Yield 67%. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 12.53(s, 1H, OH), 8.545(s, 1H, H<sub>5</sub>), 8.071(brd, 2H *J* = 7.7 Hz, H<sub>4</sub>), 7.985(dd, 1H *J* = 8.0 & 1.7 Hz, H<sub>d</sub>), 7.615(brd, 2H *J* = 9.0 Hz, H<sub>1</sub>), 7.35-7.57(m, 5H, H<sub>2</sub> & H<sub>3</sub> and H<sub>b</sub>), 7.151(dd, 1H *J* = 8.0 & 7.4 Hz, H<sub>c</sub>), 2.774(s, 3H, COMe). <sup>13</sup>C{<sup>1</sup>H} NMR (62.89 MHz, CDCl<sub>3</sub>) δ 204.8, 160.8, 139.7, 131.6, 131.5, 130.8, 130.3, 128.6, 128.1, 127.3, 126.2, 125.7, 125.1, 119.9, 118.8, 27.0. IR (KBr, ν = CO) 1635 cm<sup>-1</sup>. EIMS (m/z) 330(M+NH<sub>4</sub><sup>+</sup>, 100%), 313(M+H<sup>+</sup>, 15%). C<sub>22</sub>H<sub>16</sub>O<sub>2</sub> (312.37): Calc. C 84.59, H 5.16; Found C 84.83, H 5.04.

*6-(9-anthracenyl)-2-benzoylphenol (4c)*. As for **4a** except the solution was heated under reflux after addition of dimethylbenzamide for 4 hours. Recrystallized from toluene to yield a pale yellow solid. Yield 71.7%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 12.250(s, 1H, OH), 8.579(s, 1H, H<sub>5</sub>), 8.102(brd, *J* = 8.5 Hz, H<sub>4</sub>), 7.872(dd, 1H *J* = 8.0 & 1.7 Hz, H<sub>d</sub>), 7.840(dd, 2H *J* = 8.3 & 1.4 Hz, H<sub>e</sub>), 7.713(dq, 2H *J* = 8.7 & 1.0, H<sub>1</sub>), 7.666(tt, 1H *J* = 7.4 & 1.4 Hz, H<sub>g</sub>), 7.56-7.62(m, 3H, H<sub>f</sub> & H<sub>b</sub>), 7.503(ddd, 2H *J* = 8.3 & 6.7 & 1.4 Hz, H<sub>3</sub>), 7.428(ddd, 2H *J* = 8.7 & 6.5 & 1.4 Hz, H<sub>2</sub>), 7.142(dd, 1H *J* = 8.5 & 6.7 Hz, H<sub>c</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 161.46, 139.59, 137.95, 133.76, 132.05, 131.54, 131.43, 130.28, 129.27, 128.63, 128.40, 128.04, 127.30, 126.18, 125.67, 125.12, 119.28, 118.52. IR (KBr, ν = CO) 1604 cm<sup>-1</sup>. CI-MS (*m/z*) 392(M+NH<sub>4</sub><sup>+</sup> 100%), 375(M+H<sup>+</sup> 65%). C<sub>27</sub>H<sub>18</sub>O<sub>2</sub> (374.44): Calc. C 86.61, H 4.85; Found C 86.77, H 4.99.

*3-(9-anthracenyl)-2-hydroxy-benzoic acid [3-(9-anthracenyl)-salicylic acid] (4d)*. As for **4a** reacting **3**, generated *in-situ*, with CO<sub>2</sub>. Yield 83%. <sup>1</sup>H NMR (250 MHz, CD<sub>3</sub>OD) δ 8.473(s, 1H, H<sub>5</sub>), 8.110(dd, 1H *J* = 7.9 & 1.7 Hz, H<sub>d</sub>), 8.006(d, 2H *J* = 8.5 Hz, H<sub>4</sub>), 7.524(d, 2H *J* = 8.6 Hz, H<sub>1</sub>), 7.36-7.43(m, 3H, H<sub>3</sub> & H<sub>b</sub>), 7.26-7.33(m, 2H, H<sub>2</sub>), 7.089(t, 1H *J* = 7.7 Hz, H<sub>c</sub>), 4.939(s, 2H, OH). <sup>13</sup>C{<sup>1</sup>H} NMR (62.89 MHz, CDCl<sub>3</sub>) δ 173.9, 160.0, 139.8, 133.4, 132.9, 131.7, 131.6, 129.5, 128.3, 127.9, 127.3, 126.5, 126.1, 120.0, 114.3. IR (KBr, ν = CO) 1663 cm<sup>-1</sup>. CI-MS (*m/z*) 332(M+NH<sub>4</sub><sup>+</sup> 100%). C<sub>21</sub>H<sub>14</sub>O<sub>3</sub> (314.33): Calc. C 81.64, H 4.17; Found C 81.80, H 4.30.

*6-(9-anthracenyl)-2-diphenylphosphinophenol (4e)*.<sup>17</sup> As for **4a** above using ClPPh<sub>2</sub> as the electrophile. A HCl salt is formed on deprotection in 6 M HCl which was treated with ammonia solution to free up the required product. Crystals suitable for structure determination were grown by vapor diffusion of hexane into a toluene solution of **4e**. Yield 83%. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 8.557(s, 1H, H<sub>5</sub>), 8.069(d, 2H *J* = 8.2 Hz, H<sub>4</sub>), 7.701(dd, 2H *J* = 8.7 & 1.1 Hz, H<sub>1</sub>), 7.38-7.53(m, 14H, Ar-H), 7.328(dd, 1H *J*<sub>HH</sub> = 7.3 & 1.7 Hz, H<sub>d</sub>), 7.100(dt, 1H *J*<sub>HH</sub> = 7.5 Hz & *J*<sub>PH</sub> = 1.6 Hz, H<sub>c</sub>), 6.926(ddd, 1H *J*<sub>HH</sub> = 7.5 & 1.8 Hz & *J*<sub>PH</sub> = 3.8 Hz, H<sub>b</sub>), 5.211(s, 1H, OH). EIMS (*m/z*) 454(M<sup>+</sup>, 100%). C<sub>32</sub>H<sub>23</sub>OP (454.51): Calc. C 84.56, H 5.10, P 6.81; Found C 84.28, H 4.78.

6-(9-anthracenyl)-2-(*N,N*-dimethylaminomethyl)phenol (**4f**). As for **4a** above using [Me<sub>2</sub>NCH<sub>2</sub>]I as the electrophile. A HCl salt is formed on deprotection in 6 M HCl which was treated with ammonia solution to free up the required product. Yield 94%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 11.2(brs, 1H, OH), 8.517(s, 1H, H<sub>5</sub>), 8.067(d, 2H *J* = 8.4 Hz, H<sub>4</sub>), 7.726(brd, 2H *J* = 8.2 Hz, H<sub>1</sub>), 7.468(dd, 4H *J* = 7.4 & 1.0 Hz, H<sub>3</sub>), 7.388(dd, 4H *J* = 7.6 & 1.2 Hz, H<sub>2</sub>), 7.26-7.18(m, 2H, H<sub>b</sub> & H<sub>d</sub>), 7.022(t, 1H *J* = 7.5 Hz, H<sub>c</sub>), 3.823(s, 2H, CH<sub>2</sub>), 2.353(s, 6H, NMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>) δ 156.4, 133.77, 131.88, 131.51, 130.35, 128.47, 128.13, 126.66, 126.45, 125.51, 125.25, 124.93, 122.20, 118.68, 62.86, 44.26. CI-MS (*m/z*) 328(M+H<sup>+</sup>, 100%). C<sub>23</sub>H<sub>21</sub>NO (327.42): Calc. C 84.37, H 6.46, N 4.28; Found C 84.65, H 6.60, N 4.15.

2-(9-Anthracenyl)-6-(2-pyridyl)-phenol (**6**). To a slurry of **2** (5.57 g, 17.72 mmol) in ether (20 ml) was added BuLi (9.2 ml, 2.5 M, 23 mmol) and the slurry stirred overnight to generate **3** *in-situ*. The slurry was added to a solution of MgBr<sub>2</sub> (1.2 equiv. formed from Mg and dibromoethane) in 50 ml of thf at -20°C (ice / acetone) and the solution allowed to warm to RT. The Grignard was added dropwise to a solution of 2-bromopyridine (3.63 g, 2.2 ml, 23 mmol) premixed with 5 mol % of (dppe)NiCl<sub>2</sub> (0.243 g, 0.46 mmol) in 20 ml of thf at 0°C and the reaction stirred for 16 hours at reflux.<sup>18</sup> The Schlenk was cooled and distilled water added, the organic phase separated and washed with 2 x 20 ml of distilled water. The crude material was dissolved in 50 ml of thf and 50 ml of 6 M HCl added and the reaction mix was heated under reflux for 4 hours to deprotect the phenol. The thf and most of the water was removed under reduced pressure and the residue dissolved in 50 ml of ether and 20 ml of conc. ammonia added. The organic phase was separated and washed with 3 x 50 ml of distilled water, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and dried under vacuum. The crude material was purified by dissolving in a minimum of toluene, filtering through a plug of basic alumina and then precipitated with hexane to leave a pale yellow solid. Yield 0.85g (35.0%). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 14.821(s, 1H, OH), 8.555(s, 1H, H<sub>5</sub>), 8.378(ddd, 1H *J* = 5.1 & 1.8 & 0.9 Hz, H<sub>1</sub>), 8.025-8.11(m, 4H, H<sub>4</sub> & H<sub>f</sub> & H<sub>d</sub>), 7.857(ddd, 1H *J* = 8.4 & 7.0 & 1.8 Hz, H<sub>g</sub>) overlapping 7.813(brd, 2H *J* = 7.9 Hz, H<sub>1</sub>), 7.45-7.51(m, 2H, H<sub>3</sub>), 7.36-7.43(m, 3H, H<sub>2</sub> & H<sub>b</sub>), 7.217(ddd, 1H *J* = 7.4 & 4.9 & 1.0, H<sub>h</sub>) overlapping

7.614(dd, 1H  $J = 7.8$  &  $7.4$  Hz,  $H_c$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR (62.8 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 157.9, 145.6, 137.9, 134.7, 133.7, 131.6, 130.4, 128.5, 128.0, 126.8 (2 coincident peaks), 126.1, 125.4, 125.1, 121.6, 119.4, 119.0, 118.5. CI-MS ( $m/z$ ) 348( $M+H^+$ 100%).  $\text{C}_{25}\text{H}_{17}\text{NO}$  (347.41): Calc. C 86.43, H 4.93, N, 4.03; Found C 86.57, H 4.81, N 3.91.

*10-hydroxy-10-(2-methoxymethoxy-5-trifluoromethylphenyl)-anthrone (10)*. Step 1: Synthesis of *4-Trifluoromethyl-1-(methoxymethoxy)benzene* : As above for methoxymethoxybenzene starting with 4-trifluoromethylphenol. Purified by filtration through basic alumina. Yield 91%.  $^1\text{H}$ -NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  7.551(brd, 2H  $J = 8.9$  Hz,  $m$ -Ph-H), 7.113(brd, 2H  $J = 8.9$  Hz,  $o$ -Ph-H), 5.221(s, 2H,  $\text{OCH}_2$ ), 3.484(s, 3H, OMe).  $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.64, 126.86(brq,  $p$ -Ph-C  $^3J_{\text{CF}} = 3.5$  Hz), 124.33(q,  $\text{CF}_3$   $^1J_{\text{CF}} = 269.5$  Hz), 123.88(q,  $p$ -PhC  $^2J_{\text{CF}} = 32.4$  Hz), 116.05, 94.13, 56.16.  $^{19}\text{F}$ -NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  -65.89. MS(EI $^{+ve}$ ) ( $m/z$ ) 206( $M^+$  20%), 145( $M$ - $\text{MeOCH}_2\text{O}^+$  15%). Lit.<sup>19</sup>

Step 2: Synthesis of **10**. Synthesized from  $\text{CF}_3\text{PhOMOM}$  and anthraquinone as for **1**. Yield 73%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.673(d, 1H,  $J = 2.0$  Hz,  $H_d$ ), 8.17(d, 2H,  $J = 7.1$  Hz,  $H_4$ ), 7.48-7.54(m, 4H,  $H_l$  &  $H_b$ ), 7.34-7.44(m, 4H,  $H_2$  &  $H_3$ ), 6.834(d, 1H,  $J = 8.6$  Hz,  $H_a$ ), 4.511(s, 2H,  $-\text{OCH}_2-$ ), 3.155(s, 1H,  $-\text{OH}$ ), 2.493(s, 3H,  $-\text{OMe}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  184.1, 154.20, 145.96, 134.65, 133.61, 130.54, 128.59, 128.08, 127.92, 126.50(bq), 126.29, 124.68(q  $J = 243$  Hz,  $-\text{CF}_3$ ), 123.2(brq), 122.82, 113.42, 92.51, 55.17.  $^{19}\text{F}$  NMR (235.3 MHz,  $\text{CDCl}_3$ )  $\delta$  -65.53(s). IR (KBr,  $\nu = \text{CO}$ )  $1669\text{ cm}^{-1}$ . EIMS ( $m/z$ ):  $M^+$ (%) 414(15), 397(15), 353(60), 352(100), 323(35), 152(45).  $\text{C}_{23}\text{H}_{17}\text{F}_3\text{O}_4$  (414.38): Calc. C 66.67, H 4.14; Found C 66.74, H 4.23.

*9-(2-methoxymethoxy-5-trifluoromethylphenyl)-anthracene (11)*. Synthesized from **10** as for **2**. Yield 87%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.565(s, 1H,  $H_5$ ), 8.095(d, 2H  $J = 7.5$  Hz,  $H_4$ ), 7.824(dd, 1H  $J = 8.7$  &  $1.9$  Hz,  $H_b$ ), 7.613(d, 1H  $J = 2.0$  Hz,  $H_c$ ), 7.595(d, 2H  $J = 9.0$  Hz,  $H_1$ ), 7.48-7.53(m, 3H,  $H_a$  &  $H_3$ ), 7.415(ddd, 2H  $J = 8.6$  &  $6.6$  &  $1.3$ ,  $H_2$ ), 5.006(s, 2H,  $\text{OCH}_2$ ), 3.135(s, 3H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.93, 157.93, 131.84, 131.34, 130.22, 130.00(q, C- $H_d$   $^3J_{\text{CF}} = 3.5$  Hz), 128.66, 128.56, 127.22, 126.74(q, C-



$H_b$   $^3J_{CF}$  = 3.6 Hz), 126.16, 125.72, 125.18, 124.07(q, C-CF<sub>3</sub>  $^2J_{CF}$  = 32.7 Hz), 114.56, 93.80, 56.10.  $^{19}F$  NMR (235 MHz, CDCl<sub>3</sub>)  $\delta$  -65.63(s). EI-MS (m/z) 382(M<sup>+</sup> 100%). C<sub>23</sub>H<sub>17</sub>F<sub>3</sub>O<sub>2</sub> (382.39): Calc. C 72.25, H 4.48; Found C 72.52, H 4.65.

*3-(9-anthracenyl)-2-hydroxy-5-trifluoromethylbenzaldehyde* [3-(9-anthracenyl)-5-trifluoromethyl-salicylaldehyde] (**13 or B**). Synthesized from **12** as for **4a**. Yield 91%.  $^1H$  NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  11.479(s, 1H, OH), 10.117(s, 1H, H<sub>a</sub>), 8.598(s, 1H, H<sub>5</sub>), 8.07-8.12(m, 3H, H<sub>d</sub> & H<sub>4</sub>), 7.872(d, 1H  $J$  = 2.2 Hz, H<sub>b</sub>), 7.39-7.54(m, 6H, H<sub>1</sub> & H<sub>2</sub> & H<sub>3</sub>).  $^{13}C\{^1H\}$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  195.98, 162.22, 136.48(brq, C-H<sub>d</sub>  $^3J_{CF}$  = 3.1 Hz), 131.33, 131.00(brq, C-H<sub>b</sub>  $^3J_{CF}$  = 3.7 Hz), 130.15, 129.02, 128.84, 128.22, 126.32, 125.44, 125.33, 123.62(q, CF<sub>3</sub>  $^1J_{CF}$  = 270 Hz), 122.69(q, CCF<sub>3</sub>  $^2J_{CF}$  = 33.8 Hz), 120.22.  $^{19}F$  NMR (235 MHz, CDCl<sub>3</sub>)  $\delta$  -65.95. IR (KBr,  $\nu$  = CO) 1653 cm<sup>-1</sup>. CI-MS (m/z) 384(M+NH<sub>3</sub><sup>+</sup> 100%). C<sub>22</sub>H<sub>13</sub>F<sub>3</sub>O<sub>2</sub> (366.34): Calc. C 72.13, H 3.58; Found C 72.26, H 3.61.

*9-(2-methoxymethoxyphenyl)-triptycene* (**7**). To a solution of **2** (5 g, 31.8 mmol) in 50 ml of refluxing DME was slowly added small portions of diazobenzenecarboxylate (formed from anthranilic acid,<sup>i20</sup> 4.35 g, 100% excess) slurried in DME. Gas evolution was allowed to cease before the next addition. The solution was cooled and the crude product precipitated by addition of 100 ml of distilled water. The solids were collected by filtration, slurried in  $\approx$  50 ml of MeOH and allowed to mix overnight, filtered and washed with 2 x 20 ml of MeOH to removed colored material. Yield 77%.  $^1H$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.454(dd, 1H,  $J$  = 7.9 & 1.5, H<sub>d</sub>), 7.550(dt, 1H,  $J$  = 7.5 & 1.4, H<sub>b</sub>), 7.495(dd, 1H,  $J$  = 8.3 & 1.4, H<sub>a</sub>), 7.409(dd, 3H,  $J$  = 7.3 & 1.1, H<sub>4</sub>), 7.320(dt, 1H,  $J$  = 7.5 & 1.5, H<sub>c</sub>), 7.219(d, 3H,  $J$  = 7.5, H<sub>1</sub>), 6.972(dt, 3H,  $J$  = 7.3 & 1.1, H<sub>3</sub>), 6.911(dt, 3H,  $J$  = 7.5 & 1.3, H<sub>2</sub>), 5.388(s, 1H, H<sub>5</sub>), 4.794(s, 2H, -OCH<sub>2</sub>), 3.081(s, 3H, -OMe).  $^{13}C\{^1H\}$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  157.58, 146.12(2 coincident peaks), 131.75, 129.27, 125.58, 124.82, 124.66, 124.18, 123.29, 121.45, 115.42, 94.34, 59.29, 56.01, 55.16. CI-MS (m/z) 408(M+NH<sub>4</sub><sup>+</sup> 100%). C<sub>28</sub>H<sub>22</sub>O<sub>2</sub> (390.49): Calc. C 86.13, H 5.68; Found C 86.24, H 5.84.

*2-hydroxy-3-(9-triptycyl)-benzaldehyde* [*3-(9-triptycyl)-salicylaldehyde*] (**9a or D**). Formed from **7** as for **4a** except that 2.2 equivalents of BuLi were used. Crystals suitable for structure determination were grown by vapor diffusion of hexane into a benzene solution of **D (9a)**. Yield 61%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 11.782 (s, 1H, -OH), 10.084 (s, 1H, -CHO), 8.750 (dd, 1H, *J* = 7.8 & 1.3, H<sub>b</sub>), 7.822 (dd, 1H, *J* = 7.6 & 1.5, H<sub>d</sub>), 7.460 (d, 3H, *J* = 7.2 & 1.0, H<sub>4</sub>), 7.367 (t, 1H, *J* = 7.7, H<sub>c</sub>), 7.217 (d, 3H, *J* = 7.5, H<sub>1</sub>), 7.029 (dt, 3H, *J* = 7.2 & 1.0, H<sub>3</sub>), 6.961 (dt, 3H, *J* = 7.5 & 1.3, H<sub>2</sub>), 5.447 (s, 1H, H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 196.94, 161.83, 146.15, 145.03, 139.55, 134.15, 125.55, 125.12, 124.56, 124.44, 123.63, 121.57, 119.51, 58.82, 55.19. IR (KBr, ν = CO) 1633 cm<sup>-1</sup>. EIMS (m/z): M<sup>+</sup>(%) 374(100), 252(75), 91(25). C<sub>27</sub>H<sub>18</sub>O<sub>2</sub> (374.44): Calc. C 86.61, H 4.85; Found C 86.49, H 4.79.

*2'-hydroxy-3'-(9-triptycyl)-acetophenone* (**9b**). Formed from **7** as for **4b** except that 2.2 equivalents of BuLi were used. Yield 80.4%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 11.26(1H, -OH), 8.711(dd, 1H, *J* = 7.8 & 1.5, H<sub>b</sub>), 8.047(dd, 1H, *J* = 7.9 & 1.6, H<sub>d</sub>), 7.458(d, 3H, *J* = 7.2 & 1.4, H<sub>4</sub>), 7.255(t, 1H, *J* = 7.8, H<sub>c</sub>) overlapping 7.234(dd, 3H, *J* = 7.6 & 1.0, H<sub>1</sub>), 7.024(dt, 3H, *J* = 7.3 & 1.2, H<sub>3</sub>), 6.958(dt, 3H, *J* = 7.5 & 1.4, H<sub>2</sub>), 5.447(s, 1H, H<sub>5</sub>), 2.803(s, 3H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 205.1, 162.7, 146.1, 145.2, 139.0, 130.9, 125.9, 125.0, 124.6, 124.3, 123.5, 120.4, 118.2, 58.9, 55.1, 27.1. IR (KBr, ν = CO) 1636 cm<sup>-1</sup>. CI-MS (m/z): 406(M+NH<sub>4</sub><sup>+</sup> 100%). C<sub>28</sub>H<sub>20</sub>O<sub>2</sub> (388.6): Calc. C 86.57, H 5.19; Found C 86.81, H 5.34.

*10-hydroxy-10-(2-methoxymethoxy-phenyl)-1,4,5,8-tetramethylantrone* (**14**). As for **1** using 1,4,5,8-tetramethylantraquinone. The slurry turned a deep red before acidic work up. Yield 85%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.326 (dd 1H, *J* = 7.9 & 1.7 Hz, H<sub>d</sub>) 7.169(dt 1H, *J* = 8.1 & 1.7 Hz, H<sub>b</sub>), 7.03-7.05(m, 5H, H<sub>c</sub> and H<sub>2</sub> & H<sub>3</sub>), 6.812 (d 1H, *J* = 8.1 Hz, H<sub>a</sub>), 2.645(s, 6H, -Me), 2.630 (s 3H, -Me), 2.377 (s 6H, -Me), 2.296 (s 1H, -OH). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 192.02, 152.11, 143.71, 135.81, 135.19, 134.99, 132.78, 130.86, 130.46, 128.45, 127.73, 118.75, 113.07, 91.45, 54.89, 22.08, 21.96. IR (KBr, ν = CO) 1660 cm<sup>-1</sup>. EIMS (m/z): M<sup>+</sup>(%) 402(55), 357(35), 325(100), 265(60), 121(36). C<sub>26</sub>H<sub>26</sub>O<sub>4</sub> (402.49): Calc. C 77.59, H 6.51; Found C 77.73, H 6.66.

2-(9-(1,4,5,8-tetramethylantracenyl))phenol (**15**). To a slurry of **14** (3 g, 7.45 mmol) in 20 ml of ether was added LiAlH<sub>4</sub> (0.60 g, 14.91 mmol) the BF<sub>3</sub>.OEt<sub>2</sub> (0.44 ml, 3.5 mmol) and the reaction mix heated under reflux for 4 hours. The slurry was deactivated by slow addition of dilute HCl. The organic phase was washed with 2 x 20 ml distilled water, dried over MgSO<sub>4</sub>, filtered and the solvent removed under vacuum. The crude material was recrystallized from MeOH/toluene 80/20. Yield 88.4%. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 8.855(s, 1H, H<sub>5</sub>), 7.419(dt, 1H *J* = 7.7 & 1.8 Hz, H<sub>b</sub>), 7.213(d, 2H *J* = 7.1 Hz, H<sub>2</sub>), 7.133(d, 2H *J* = 7.1 Hz, H<sub>3</sub>), 7.105(dd, 1H *J* = 7.7 & 1.7 Hz, H<sub>d</sub>), 6.94-7.01(m, 2H, H<sub>c</sub> & H<sub>a</sub>), 4.719(s, 1H, OH), 2.848(s, 6H, Me<sub>1</sub>), 1.952(s, 6H, Me<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (62.89 MHz, CDCl<sub>3</sub>) δ 155.24, 133.79, 133.27, 131.77, 131.39, 130.69, 130.63, 130.29, 129.77, 125.76, 122.92, 119.78, 114.74, 24.55, 20.30. MS (CI +ve), *m/z*(%) 346(M+NH<sub>4</sub><sup>+</sup>, 25%), 327(M+H<sup>+</sup>, 100%). C<sub>24</sub>H<sub>22</sub>O (326.44): Calc. C 88.31, H 6.79; Found C 88.54, H 6.75.

2-hydroxy-3-(9-(1,4,5,8-tetramethylantracenyl))-benzaldehyde [3-(9-(1,4,5,8-tetramethyl-anthracenyl))-salicylaldehyde] (**16 or C**) To a solution of **15** (11.6g, 35.5 mmol) in 100 ml of toluene was added EtMgBr (11.85 ml, 3M in ether, 35.5 mmol) and the reaction stirred for 30 minutes. To the reaction mix was added paraformaldehyde (2.66g, 88.8 mmol) and Et<sub>3</sub>N (7.43 g, 10.0 ml, 53.3 mmol) and the Schlenk heated to 80°C for 3 hours. The solution was cooled and 100 ml of 2M HCl added. The organic layer was separated, washed with distilled water (3 x 100 ml) dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent removed under vacuum. The crude material was recrystallized from hot heptane. Yield 10.9g (91.1%). Crystals suitable for structural analysis were grown by vapor diffusion of heptane into a benzene solution of **C (16)**. IR (KBr, ν = CO) 1655 cm<sup>-1</sup>. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 11.409(s, 1H, OH), 10.037(s, 1H, H<sub>a</sub>), 8.816(s, 1H, H<sub>5</sub>), 7.732(dd, 1H *J* = 7.7 & 1.8 Hz, H<sub>d</sub>), 7.366(dd, 1H *J* = 7.3 & 1.5 Hz, H<sub>b</sub>), 7.199(d, 2H *J* = 7.0 Hz, H<sub>2</sub>), 7.102(d, 2H *J* = 7.0 Hz, H<sub>3</sub>) overlapping 7.099(t, 1H *J* = 7.5 Hz, H<sub>c</sub>), 2.843(s, 6H, Me), 1.947(s, 6H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (62.89 MHz, CDCl<sub>3</sub>) δ 196.91, 160.98, 140.65, 134.53, 133.94, 133.32, 133.00, 131.16, 131.06, 130.17, 125.40, 122.12, 119.78, 119.08, 25.23, 20.30. CIMS (*m/z*) 372(M+NH<sub>4</sub><sup>+</sup>, 50%), 355(M+H<sup>+</sup>, 100%). C<sub>25</sub>H<sub>22</sub>O<sub>2</sub> (354.45): Calc. C 84.72, H 6.26; Found C 85.0, H 6.21.

*3-Phenyl-2-hydroxybenzaldehyde (F)*: Step 1: Synthesis of Ph-PhOMOM. From 2-phenyl phenol (170.21 g, 1.0 mols), as above for phenol. The material was purified by dissolving in 200 ml of hexane and filtering through a column of basic alumina to remove unreacted phenol, the solvent removed and the product distilled under vacuum, b.p. 93-95°C 0.15 mm Hg. Yield 176.3 g, (82.3%).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.567-7.59(m, 2Hm Ar-H), 7.43-7.48(m, 2H, Ar-H), 7.33-7.40(m, 3H, Ar-H), 7.274(dd, 1H, PhOH-H), 7.141(dt, 1H  $J = 7.4$  & 1.3 Hz,  $\text{H}_c$ ), 5.131(s, 2H,  $\text{OCH}_2$ ), 3.404(s, 3H, OMe).  $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.18, 138.61, 131.89, 131.02, 129.58, 128.67, 128.02, 126.96, 122.30, 115.67, 95.05, 56.12. IR (KBr,  $\nu = \text{CO}$ )  $1675\text{ cm}^{-1}$ . MS(EI+ve) (m/z) 214(M+ 35%), 182(M-MeOH 55%).  $\text{C}_{14}\text{H}_{14}\text{O}_2$  (214.26): Calc. C 78.48, H 6.59; Found C 78.56, H 6.51.

Step 2: To a solution of Ph-PhOMOM (20g, 93.4 mmol) dissolved in 100 ml of ether at RT in a water bath was added BuLi (45 ml of 2.5 M in hexanes, 112 mmol) and the reaction mix allowed to stir overnight during which time a precipitate formed. The slurry was cooled to  $-78^\circ\text{C}$  and an excess of DMF added (20 ml) and the reaction mix allowed to warm to RT. The mix was deactivated by addition of 50 ml of 2 M HCl and the organic phase separated and washed with 3 x 50 ml of distilled water. The solvent was removed under reduced pressure and an NMR of the crude material measured, showing diagnostic peaks at  $\delta$  10.49(s, 1H, CHO), 4.70(s, 2H,  $\text{OCH}_2$ ), 3.24(s, 3H, OMe). The crude material was dissolved in 50 ml of thf and 50 ml of 6 M HCl added. The mix was heated under reflux for 4 hours, cooled and 100 ml of ether added. The ether layer was separated and washed with 3 x 100 ml of distilled water, dried over sodium sulfate and the solvent removed under reduced pressure to leave a crude material. The crude material was re-crystallized from methanol at low temperature. Yield 15.6 g (91.7%).  $^1\text{H-NMR}$  (250 MHz,  $\text{CDCl}_3$ )  $\delta$  11.549(s, 1H, OH), 9.962(s, 1H,  $\text{H}_a$ ), 7.55-7.65(m, 4H, Ar-H), 7.34-7.49(m, 3H, Ar-H), 7.116(t, 1H  $J = 7.6$  Hz,  $\text{H}_c$ ). MS(CI+ve) (m/z) 216(M+ $\text{NH}_3^+$ , 100%), 199(M+ $\text{H}^+$ , 65%).  $\text{C}_{13}\text{H}_{10}\text{O}_2$  (198.22): Calc. C 78.77, H 5.09; Found C 78.50, H 4.80.

## Synthesis of salicylaldimines

*N*-cyclopentyl 3-(9-anthracenyl)-2-hydroxybenzalimine (**8A**) [*N*-cyclopentyl anthracenyl-salicylaldimine]: To a slurry of anthracenyl-salicylaldehyde **A** (0.50 g, 1.676 mmol) suspended in 10 ml of ethanol was added amine (0.50 ml, excess) and a drop of formic acid. The slurry was stirred overnight. The pale yellow product collected by filtration and washed with ethanol before being dried in a vacuum oven at 60°C. Yield 0.41 g (65%). <sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>) δ 13.892(s, 1H, OH), 8.531(s, 1H, CH), 8.496(s, 1H, CHN), 8.076(d, 2H *J* = 8.4 Hz, H<sub>4</sub>), 7.713(brd, 2H *J* = 8.7 Hz, H<sub>1</sub>), 7.33-7.49(brm, 6H, Anth-H<sub>2</sub> & H<sub>3</sub> and Ph-H<sub>b</sub> and H<sub>d</sub>), 7.110(t, 1H *J* = 7.5 Hz, H<sub>c</sub>), 3.80(sept, 1H, N-CH), 1.89-1.99(m, 2H, cyclopentyl-CH<sub>2</sub>), 1.56-1.78(brm, 6H, cyclopentyl-CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (62.9 MHz, CDCl<sub>3</sub>) δ. 168.35, 159.66, 135.18, 132.87, 131.56, 131.09, 130.42, 128.56, 126.88, 126.65, 126.55, 125.46, 125.06, 119.05, 118.30, 70.04, 34.70, 24.44. MS(CI+ve) (m/z) 366(M+H<sup>+</sup>, 100%). C<sub>26</sub>H<sub>23</sub>NO (365.47): Calc. C 85.45, H 6.34, N 3.83; Found C 85.45, H 6.30, N 3.78.

*N*-(2-pyridyl)-methyl 3-(9-triptycyl)-2-hydroxybenzylimine (**32D**) [*N*-(2-pyridyl)-methyl triptycyl-salicylaldimine]: To a slurry of triptycyl-salicylaldehyde **D** (0.50 g, 1.33 mmoles) suspended in 10 mls of ethanol was added 2-aminomethylpyridine (0.50 mls, excess) and a drop of formic acid. The slurry was stirred at reflux overnight then cooled to RT. The yellow product was collected by filtration and washed with ethanol before being dried in a vacuum oven at 60°C. Yield 0.48 g (77.7%).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 13.989(s, 1H, OH), 8.722(s, 1H, H<sub>a</sub>), 8.552(brd, 1H *J* = 4.5 Hz, H<sub>i</sub>), 8.511(dd, 1H *J* = 7.9 & 1.4 Hz, H<sub>d</sub>), 7.606(dt, 1H *J* = 7.7 & 1.8 Hz, H<sub>g</sub>), 7.564(dd, 1H *J* = 7.5 & 1.4 Hz, H<sub>b</sub>), 7.412(dd, 3H *J* = 7.2 & 1.1 Hz, H<sub>4</sub>), 7.255-7.294(m, 4H, H<sub>l</sub> & H<sub>f</sub>), 7.223(t, 1H *J* = 7.7 Hz, H<sub>c</sub>), 7.167(dd, 1H *J* = 7.4 & 1.3 Hz, H<sub>h</sub>), 6.976(dt, 3H, *J* = 7.3 & 1.0 Hz, H<sub>3</sub>), 6.917(dt, 3H *J* = 7.7 & 1.3 Hz, H<sub>2</sub>), 5.399(s, 1H, H<sub>5</sub>), 4.940(s, 2H<sub>e</sub>),

<sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>) δ 166.9, 161.3, 157.6, 149.3, 146.2, 145.5, 136.9, 135.2, 131.9, 125.0, 124.8, 124.5, 124.3, 123.4, 122.4, 122.3, 119.8, 118.1, 65.0, 59.1, 55.2.

MS(CI-ve) (m/z) 464 ( $M^+$  85%), 372 ( $M-CH_2Py^-$  100%).

$C_{33}H_{24}N_2O$  (464.57): Calc. C 85.32, H 5.21, N 6.03; Found C 85.36, H 5.15, N 5.95.

*N*-8-Quinoliny 3-(9-triptycenyl)-2-hydroxybenzyl imine (**73D**) [*N*-8-quinoliny triptycenyl-salicylaldimine]:

To a slurry of triptycenyl-salicylaldehyde **5** (0.50 g, 1.33 mmol) suspended in 10 ml of ethanol was added 8-aminoquinoline (0.30 g, excess) and a drop of formic acid. The slurry was stirred at reflux overnight then cooled to RT. The orange/red product was collected by filtration and washed with ethanol before being dried in a vacuum oven at 60°C. Yield 0.55 g 84.7(%).  $^1H$ -NMR (250 MHz,  $CDCl_3$ )  $\delta$  5.415(s, 1H,  $H_5$ ), 6.91-7.02(m, 6H,  $H_2$  &  $H_3$ ), 7.267(t, 1H  $J = 7.7$  Hz,  $H_c$ ), 7.34-7.50(m, 9H), 7.548(t, 1H  $J = 7.6$  Hz), 8.556(dd, 1H  $J = 7.9$  & 1.6 Hz), 8.178(dd, 1H  $J = 8.3$  & 1.7 Hz), 8.556(dd, 2H  $H = 7.9$  & 1.4 Hz,  $H_d$ ), 8.915(dd, 1H  $J = 4.2$  & 1.8 Hz), 9.305(s, 1H,  $H_a$ ), 14.335(s, 1H, OH).  $^{13}C$ -NMR (62.9 MHz,  $CDCl_3$ )  $\delta$  16.86, 162.01, 150.25, 146.27, 145.67, 144.85, 141.90, 136.07, 136.01, 132.94, 129.30, 126.54, 126.01, 125.21, 124.78, 124.38, 123.35, 121.54, 121.44, 120.61, 118.14, 59.33, 55.34. MS(CI+ve) (m/z) 500.60 ( $M^+$  20%), 129 (Quinoline+ 60%).  $C_{36}H_{24}N_2O$  (500.60): Calc. C 86.38, H 4.83, N 5.60; Found C 86.40, H 4.88, N 5.51.

## Synthesis of metal complexes

(*N*-isopropyl anthracenyl-salicylaldiminato)chromium(III) dichloride tetrahydrofuran (**II**): Ligand **25A** (0.25g, 0.74 mmol) and *p*-tolylCrCl<sub>2</sub>(thf)<sub>3</sub> (0.317g, 0.737 mmol) were reacted by dissolving in 20 ml of toluene for 1 hour. The solvent was removed under vacuum and the residue washed with 2 x 10 ml of hexane to leave a yellow/ green solid. Yield 0.16g (40.6%). FAB-MS (m/z) 728( $L_2Cr^+$ , 80%), 460( $M-thf^+$ , 5%), 340( $L-H^+$ , 55%).  $C_{28}H_{28}Cl_2CrNO_2$  (533.43): Calc. C 63.04, H 5.29, N 2.63; Found C 62.73 H 5.05, N 2.54.

*(N-cyclopentyl anthracenyl-salicylaldiminato)chromium(III) dichloride tetrahydrofuran (III)*: Ligand **8A** (0.75g, 2.05 mmol) and *p*-tolylCrCl<sub>2</sub>(thf)<sub>3</sub> (0.86g, 2.05 mmol) were reacted by dissolving in 20 ml of toluene for 1 hour. The solvent was removed under vacuum and the residue washed with 2 x 10 ml of hexane to leave a yellow/ green solid. Yield 0.99g (86.3%). Crystals for structural analysis were grown from thf by slow vapor diffusion of benzene. FAB-MS (m/z) 780(L<sub>2</sub>Cr<sup>+</sup>, 100%), 513(LCrCl<sub>2</sub><sup>+</sup>, 15%), 451(LCrCl<sup>+</sup>, 40%). C<sub>30</sub>H<sub>30</sub>NO<sub>2</sub>CrCl<sub>2</sub> (559.47): Calc. C 64.40, H 5.40, N 2.50; Found C 64.40, H 5.36, N 2.41.

*Bis-(N-phenyl 3-tert-butyl-salicylaldiminato)chromium(III) chloride (IV)*: A solution of **2G** (1.00 g, 3.95 mmol) dissolved in 10 ml of thf was added to a slurry of NaH (0.2 g, excess) in 10 ml of thf and allowed to react until evolution of hydrogen ceased and stirred for an extra 30 minutes. The Schlenk was placed under a slight vacuum to remove any hydrogen and then cannula filtered into a Schlenk containing CrCl<sub>3</sub>(thf)<sub>3</sub> slurried in 20 ml of thf at 0°C. The reaction mixture was allowed to stir for 1 hour before the solvent was removed under vacuum. The residue was extracted with toluene, filtered and the toluene removed under vacuum. The residue was triturated with a 50/50 mix of thf/ether and the yellow/brown product recovered by filtration. Yield 0.64 g (100%). FAB-MS (m/z) 591(L<sub>2</sub>CrCl<sup>+</sup>, 20%), 556(L<sub>2</sub>Cr<sup>+</sup>, 100%), 340(L-H<sup>+</sup>). C<sub>34</sub>H<sub>36</sub>ClN<sub>2</sub>O<sub>2</sub>CrCl (592.11): Calc. C 68.97, H 6.13, N 4.73; Found C 69.09, H 6.02, N 4.54.

*Bis-(N-phenyl 3-tert-butyl-salicylaldiminato)chromium(III) chloride(CNMe).MeCN* : Crystals of an acetonitrile adduct (**V**) suitable for structural analysis were obtained on recrystallization of **IV** from MeCN. FAB-MS (m/z) 591(L<sub>2</sub>CrCl<sup>+</sup>, 15%), 556(L<sub>2</sub>Cr<sup>+</sup>, 100%). C<sub>38</sub>H<sub>42</sub>ClN<sub>4</sub>O<sub>2</sub>CrCl (674.21): Calc. C 67.69, H 6.28, N 8.31; Found C 67.72, H 6.16, N 8.22.

*(N-(2-pyridyl)-methyl triptycyl-salicylaldimino)chromium(III) dichloride (VI)*: Ligand **32D** (0.50 g, 1.105 mmol) and *p*-tolylCrCl<sub>2</sub>(thf)<sub>3</sub> (0.41 g, 1.105 mmol) were reacted by dissolving in 20 mls of thf. A brown solid precipitated almost immediately. The slurry was stirred for 1 hour and the solids recovered by filtration and washed with 2 x 10 mls of thf. Yield 0.586 g 90.5(%).

Ir(KBr disk) 3435br, 3067m, 3005m, 2958m, 2887w,  $\approx$ 2500br, 1950w, 1913w, 1630s, 1599s, 1571sh, 1473sh, 1453s, 1435s, 1377w, 1330w, 1288m, 1267m, 1147m, 1124w, 1100w, 1083w, 1050m, 1036m, 1019sh, 998w, 944w, 914w, 902w, 859w, 842w, 790w, 757s, 746s, 669w, 646s, 606m, 587w, 563w, 504m, 471w.§

FAB-MS (m/z) 1137( $\text{L}_2\text{Cr}_2\text{Cl}_3^+$ , 15%), 550( $\text{M}-\text{Cl}^+$ , 100%), 513( $\text{LCr}^+$ , 80%).  $\text{C}_{33}\text{H}_{23}\text{N}_2\text{OCrCl}_2$  (586.47): Calc. C 67.59, H 3.95, N 4.78; Found C 67.51, H 3.97, N 4.71.

(*N*-8-quinolyl triptycenyl-salicylaldiminato)chromium(III) dichloride (**VII**): Ligand **73D** (0.53g, 1.23 mmol) and *p*-tolyl $\text{CrCl}_2(\text{thf})_3$  (0.60 g, 1.31 mmol) were reacted by dissolving in 20 ml of thf. A brown solid precipitated almost immediately. The slurry was stirred for 1 hour then heated to 50°C for 4 hours, cooled and the solids recovered by filtration then washed with 2 x 10 ml of thf. Yield 0.61 g (84.6%). FAB-MS (m/z) 1137( $\text{L}_2\text{Cr}_2\text{Cl}_3^+$ , 15%), 550( $\text{M}-\text{Cl}^+$ , 100%), 513( $\text{LCr}^+$ , 80%)  $\text{C}_{33}\text{H}_{23}\text{N}_2\text{OCrCl}_2$  (586.47): Calc. C 67.59, H 3.95, N 4.78; Found C 67.51, H 3.97, N 4.71.

(*N*-8-quinolyl triptycenyl-salicylaldiminato)chromium(III) dichloride pyridine adduct (**IX**): Recrystallization of **IX** from pyridine generated the pyridine adduct as a red / brown solid. Recovered in near quantitative yield. Crystals suitable for structural analysis were grown by the slow vapor diffusion of benzene into a pyridine solution of **XII**.  $\text{C}_{41}\text{H}_{28}\text{N}_3\text{OCrCl}_2$  (701.58): Calc. C 70.19, H 4.02, N 5.99; Found C 70.25, H 3.93, N 6.06.

## Polymerization Procedures

Activated Catalyst Solution Formation: A mixture of the required ligand (0.030 mmol) and *p*-tolyl $\text{CrCl}_2(\text{thf})_3$  (12.9 mg, 0.030 mmol) were dissolved in 10 ml of dry degassed toluene and allowed to stir for 5 minutes, the initial yellow color turned a brown yellow. The solvent was removed under vacuum and



the brown residue dissolved in 26.2 ml of dry degassed toluene. The pro-catalyst was activated by the addition of MAO (3.8 ml, 1.6 M, 6.0 mmol) and the slightly darker solution allowed to stir for 5 minutes.

High Throughput Screening was carried out using 24 well plates in a Radleys Parallel Greenhouse Synthesizer adapted to use disposable 5ml vials. Twenty vials contained pre-weighed ligand (0.005 mmole) while three of the remaining vials contained ligand **25A** (0.005mmole), [N,N'-bis(2,6-diisopropylphenyl)-diiminopyridinoiron(II) chloride] as standards with the third as a solvent blank. A solution of *p*-tolylCrCl<sub>2</sub>(thf)<sub>3</sub> in toluene (1.0 ml) was added to the free ligands, they were stirred for 15 minutes, and then activated by addition of 1 ml of MAO solution. The volume of all vials was adjusted to 2 ml where necessary, the vials weighed, placed under one atmosphere of ethylene for 15 minutes, lightly degassed and re-weighed. Productivity was calculated from the weight gain compared to the solvent blank. A standard test of catalyst blanks (no ligand) across the rack gave a mean productivity value of 0.75 gmmol<sup>-1</sup>h<sup>-1</sup>bar<sup>-1</sup> with a standard deviation of 5.4 gmmol<sup>-1</sup>h<sup>-1</sup>bar<sup>-1</sup>. Therefore, for catalyst screens, values in excess of 20 gmmol<sup>-1</sup>h<sup>-1</sup>bar<sup>-1</sup> (> 3 esd) were classified as hits.

Schlenk Test: A 5 ml aliquot (5 μmols) of the activated catalyst solution was transferred to a Schlenk containing 95 ml of dry degassed toluene. The vessel was sealed and evacuated. The vessel was placed under 1 bar of ethylene pressure and allowed to react for 1 hour. The solution was deactivated by depressurising and addition of 100 ml of methanol containing 2 ml of dilute HCl. The polymer was recovered by filtration, washed with methanol and dried in a vacuum oven at 60°C overnight. The combined filtrates were collected and the solvent removed under reduced pressure. The residue was dissolved in 50 ml of toluene and filtered through 2 cm of alumina and washed with 2 x 10 ml of toluene. To the combined filtrates was added 1 ml of nonane and the sample submitted for GC analysis.

Co-Monomer Incorporation Test: A 5 ml aliquot (5 μmols) of the activated catalyst solution was transferred to a Schlenk containing 93 ml of dry degassed toluene and 2 ml of 1-hexene. The vessel was

sealed and evacuated. The vessel was placed under 1 bar of ethylene pressure and allowed to react for 1 hour. The solution was deactivated by depressurising and addition of 100 ml of methanol containing 2 ml of dilute HCl. The polymer was recovered by filtration, washed with methanol and dried in a vacuum oven at 60°C overnight. The combined filtrates were collected and the solvent removed under reduced pressure. The residue was dissolved in 50 ml of toluene and filtered through 2 cm of alumina and the alumina was washed with 2 x 10 ml of toluene. To the combined filtrates was added 1 ml of nonane and the sample submitted for GC analysis.

Large Reactor: A automated 1 litre Buchi reactor was prepared with 400 ml of isobutane at the required temperature and pressure of ethylene. The reactor was scavenged with 1.25 ml of 1.6 M MAO (2.0 mmol) solution in toluene. A 5 ml aliquot (5 mmols) of the activated catalyst solution was transferred to the large reactor and the ethylene uptake monitored for the catalyst run. After 60 minutes the isobutane was vented and the polymer collected and dried in a vacuum oven at 60°C overnight.

### Synthesis of imines screened by *in situ* testing.

*N*-phenyl 3-(9-anthracenyl)-2-hydroxy-3-trifluoromethyl-benzyl imine (**2B**) [*N*-Phenyl anthracenyl-CF<sub>3</sub>-salicylaldimine]: To a slurry of anthracenyl-salicylaldehyde **C** (0.50 g, 1.36 mmols) suspended in 10 mls of ethanol was added aniline (0.50 mls, excess) and a drop of formic acid. The slurry was stirred overnight. The pale yellow product collected by filtration and washed with ethanol before being dried in a vacuum oven at 60°C. Yield 0.36 g (60%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>) δ 14.272(s, 1H, OH), 8.858(s, 1H, CHN), 8.595(s, 1H, H<sub>5</sub>), 8.106(d, 2H J = 7.7 Hz, H<sub>4</sub>), 7.940(d, 1H J = 2.0 Hz, H<sub>d</sub>), 7.733(d, 1H J = 2.0 Hz, H<sub>b</sub>), 7.661(dd, 2H J = 8.6 & 0.9 Hz, H<sub>1</sub>), 7.37-7.55(brm, 6H, Ar-H), 7.24-7.35(brm, 3H, Ar-H).

<sup>19</sup>F-NMR (235.36 MHz, CDCl<sub>3</sub>) δ -65.55(s).

MS(CI-ve) (m/z) 442(M+H 10%)

C<sub>28</sub>H<sub>18</sub>NO (441.44): Calc. C 6.18, H 4.11, N 3.17; Found C 76.14, H 3.84, N 3.25.

*N*-phenyl 3,5-di-*t*-butyl-2-hydroxybenzalimine (**2E**) [*N*-Phenyl bis-*tert*butyl-salicylalimine]: As above.

Yield 0.96 g (77%).

<sup>1</sup>H-NMR δ 13.707(s, 1H, OH), 8.646(s, 1H, CHN), 7.461(d, 1H *J* = 2.5 Hz, H<sub>b</sub>), 7.38-7.45(m, 2H, Ph), 7.26-7.32(m, 3H, Ph), 7.230(d, 1H *J* = 2.5 Hz, H<sub>d</sub>), 1.486(s, 9H, *t*Bu), 1.339(s, 9H, *t*Bu).

<sup>13</sup>C-NMR δ 163.79, 158.24, 149.1(?), 140.55, 136.97, 129.32, 127.99, 126.79, 126.49, 121.17, 118.28, 35.08, 34.18, 31.47, 29.41.

*N*-3,3-diphenylpropyl 3-(9-anthracenyl)-2-hydroxybenzalimine (**8A**) [*N*-diphenylpropyl anthracenyl-salicylalimine]: As above. Yield 0.74 g (87%).

<sup>1</sup>H-NMR {400 MHz, CDCl<sub>3</sub>} δ 13.880(s, 1H, OH), 8.543(s, 1H, H<sub>5</sub>), 8.367(s, 1H, CHN), 8.076(d, 2H *J* = 8.4 Hz, H<sub>4</sub>), 7.707(dd, 2H *J* = 8.8 & 0.5 Hz, H<sub>1</sub>), 7.36-7.49(brm, 6H, Ar-H), 7.14-7.29(brm, 10H, Ar-H), 7.111(t, 1H *J* = 7.5 Hz, H<sub>c</sub>), 4.011(t, 1H *J* = 8.0 Hz, Ph<sub>2</sub>-CH), 3.541(t, 2H *J* = 6.7 Hz, CN-CH<sub>2</sub>), 2.409(q, 2H, CH<sub>2</sub>).

<sup>13</sup>C{<sup>1</sup>H}-NMR {100 MHz, CDCl<sub>3</sub>} δ 165.16, 159.69, 144.08, 135.47, 132.72, 131.53, 131.20, 130.40, 128.55, 127.83, 126.92, 126.60, 126.58, 126.34, 125.47, 125.06, 118.94, 118.37, 57.62, 48.49, 36.25.

*N*-trityl 3-(9-anthracenyl)-2-hydroxybenzalimine (**19A**) [*N*-trityl anthracenyl-salicylalimine]: As above.

Yield 0.832 g (92%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>) δ 13.938(s, 1H, OH), 8.534(s, 1H, Anth-H<sub>5</sub>), 8.166(s, 1H, CHN), 8.065(brd, 2H *J* = 7.8 Hz, Anth-H<sub>4</sub>), 7.722(brd, 2H *J* = 7.9 Hz, Anth-H<sub>1</sub>), 7.14-7.49(brm, 21H, Anth-H<sub>2</sub> & H<sub>3</sub> and trityl-Ph and Ph-H<sub>b</sub> & H<sub>d</sub>), 7.082(t, 1H *J* = 7.5 Hz, Ph-H<sub>c</sub>).

*N-cyclobutyl 3-(9-anthracenyl)-2-hydroxybenzaldimine (24A) [N-cyclobutyl anthracenyl-salicylaldimine]:*

As above. Yield 0.29 g (49%).

<sup>1</sup>H-NMR δ {400 MHz, CDCl<sub>3</sub>} 14.143(s, 1H, OH), 8.556(s, 1H, H<sub>5</sub>), 8.400(s, 1H, CHN), 8.091(d, 2H *J* = 8.4 Hz, H<sub>4</sub>), 7.731(d, 2H *J* = 8.7 Hz, H<sub>1</sub>), 7.37-7.51(brm, 6H, H<sub>2</sub> & H<sub>3</sub> and PH<sub>b</sub> and H<sub>d</sub>), 7.120(t, 1H *J* = 7.5 Hz, H<sub>c</sub>), 4.124(pent, 1H, cyclobutyl-CH), 2.28-2.38(m, 2H, cyclobutyl-CH<sub>2</sub>), 2.10-2.22(m, 2H, cyclobutyl-CH<sub>2</sub>), 1.78-1.87(m, 2H, cyclobutyl-CH<sub>2</sub>).

<sup>13</sup>C-NMR {100 MHz, CDCl<sub>3</sub>} δ 162.05, 159.85, 135.32, 132.84, 131.57, 131.27, 130.44, 128.57, 126.89, 126.66, 126.60, 125.48, 125.07, 118.92, 118.32, 61.51, 30.53, 15.78.

*N-isopropyl 3,5-di-<sup>t</sup>butyl-2-hydroxybenzaldimine (25E) [N-isopropyl di-<sup>t</sup>butyl-salicylaldimine]:* As above using 1g of 3,5-di-<sup>t</sup>butylsalicylaldehyde. Yield 0.75 g (64%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>) δ 13.992(s, 1H, OH), 8.369(s, 1H, CHN), 7.323(d, 1H *J* = 2.5 Hz, H<sub>c</sub>), 7.079(d, 1H *J* = 2.5 Hz, H<sub>d</sub>), 3.533(sept, 1H *J* = 6.3 Hz, <sup>i</sup>Pr-CH), 1.458(s, 9H, <sup>t</sup>Bu), 1.313(s, 9H, <sup>t</sup>Bu), 1.30(d, 6H *J* = 6.3 Hz, <sup>i</sup>Pr-Me).

<sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>) δ 163.06, 158.13, 139.84, 136.61, 126.57, 125.66, 117.85, 60.01, 34.99, 34.11, 31.51, 29.44, 24.27.

*N-isopropyl 3-(9-anthracenyl)-2-hydroxybenzylketimine (25I) [N-isopropyl anthracenyl-salicylketimine]:* As above. Yield 0.43 g (76%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>) δ 16.944(s, 1H, OH), 8.491(s, 1H, H<sub>5</sub>), 8.038(d, 2H *J* = 8.3 Hz, H<sub>4</sub>), 7.732(dd, 1H *J* = 8.03 & 1.7 Hz, H<sub>b</sub>), 7.711(d, 2H *J* = 8.7 Hz, H<sub>1</sub>), 7.28-7.47(brm, 5H, Anth-H<sub>2</sub> & H<sub>3</sub> and H<sub>d</sub>), 6.965(t, 1H *J* = 7.7 Hz, H<sub>c</sub>), 3.987(sept, 1H *J* = 6.3, <sup>i</sup>Pr-CH), 2.500(s, 3H, CNMe), 1.230(d, 6H *J* = 6.3 Hz, <sup>i</sup>Pr-Me).

<sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>) δ 169.13, 163.53, 161.50(?), 135.69, 134.02, 131.65, 130.53, 128.50, 128.27, 128.05, 126.92, 126.57, 126.11, 125.21, 124.95, 119.15, 116.14, 49.52, 23.56, 14.13.

*N-isopropyl 3-phenyl-2-hydroxybenzaldimine (25F) [N-isopropyl phenyl-salicylalimine]*: As above, isolated as a yellow oil. Yield 0.59 g (98%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>) δ 14.444(s, 1H, OH), 8.418(s, 1H, CHN), 7.657(d, 2H *J* = 8.3 Hz, *o*-Ph), 7.32-7.48(m, 4H, Ar-H), 7.254(d<sub>2</sub>, 1H *J* = 7.6 & 1.6 Hz, H<sub>d</sub>), 6.955(t, 1H *J* = 7.6 Hz, H<sub>c</sub>), 3.590(sept, 1H *J* = 6.3, <sup>i</sup>Pr-CH), 1.310(d, 6H *J* = 6.3 Hz, <sup>i</sup>Pr-Me).

*N-hexyl 3-(9-anthracenyl)-2-hydroxybenzaldimine (27A) [N-hexyl anthracenyl-salicylalimine]*: Yield 0.21 g FW 381.51(33%).

<sup>1</sup>H-NMR δ 13.967(s, 1H, OH), 8.514(s, 1H, H<sub>5</sub> or CHN), 8.493(s, 1H, CHN or H<sub>5</sub>), 8.055(brd, 2H *J* = 8.2 Hz, H<sub>4</sub>), 7.683(brd, 2H *J* = 8.8 Hz, H<sub>1</sub>), 7.50-7.30(brm, 6H, H<sub>2&3</sub> and H<sub>b&c</sub>), 7.094(t, 1H *J* = 7.5 Hz, H<sub>c</sub>), 3.576(t, 2H *J* = 6.9 Hz, hexyl-NCH<sub>2</sub>), 1.68-1.55(m, 2H, hexyl), 1.40-1.22(m, 6H, hexyl), 0.846(t, 3H *J* = 6.4 Hz, hexyl-Me).

*N-2,6-diisopropylphenyl 3-(9-anthracenyl)-2-hydroxybenzaldimine (29A) [N-diisopropylphenyl anthracenyl-salicylalimine]*: Yield 1.23 g (80.1%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>) δ (s, 1H, OH), 8.527(s, 1H, H<sub>5</sub>), 8.515(s, 1H, CHN), 8.065(brd, 2H *J* = 7.7 Hz, H<sub>4</sub>), 7.699(brd, 2H *J* = 7.7 Hz, H<sub>1</sub>), 7.52-7.34(brm, 6H, H<sub>2&3</sub> and H<sub>b&c</sub>), 7.105(t, 1H *J* = 7.5 Hz, H<sub>c</sub>), 3.583(sept, 1H *J* = 6.4 Hz, <sup>i</sup>Pr-CH), 1.245(d, 6H *J* = 6.4 Hz, <sup>i</sup>Pr-Me)

<sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>) δ 162.06, 159.83, 135.27, 132.81, 131.56, 131.11, 130.42, 128.53, 126.84, 126.61, 126.16(?), 125.43, 125.02, 118.98, 118.21, 59.84, 24.13.

*N-2,6-diisopropylphenyl 3-(9-anthracenyl)-2-hydroxy-5-trifluoromethylbenzaldimine (29C) [N-diisopropylphenyl anthracenyl-CF<sub>3</sub>-salicylalimine]*: As above, Yield 0.65 g (90.4%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>) δ 13.853(s, 1H, OH), 8.590(s, 1H, H<sub>5</sub>), 8.513(s, 1H, CHN), 8.100(dd, 2H *J* = 8.9 & 1.6 Hz, H<sub>4</sub>), 7.650(d, 1H *J* = 2.0 Hz, H<sub>d</sub>), 7.755(d, 1H *J* = 2.0 Hz, H<sub>b</sub>), 7.705(brd, 2H *J* = 8.5 Hz, H<sub>1</sub>),

7.41-7.55(brm, 4H, H<sub>2</sub> & H<sub>3</sub>), 7.197(s, 3H, *o* & *m*-<sup>*i*</sup>Pr<sub>2</sub>Ph-H), 2.981(sept, 1H *J* = 6.8 Hz, <sup>*i*</sup>Pr-CH), 1.181(d, 6H *J* = 6.8 Hz, <sup>*i*</sup>Pr-Me)

C<sub>34</sub>H<sub>30</sub>NO (525.6): Calc. C 77.69, H 5.75, N 2.66; Found C 77.93, H 5.82, N 2.71.

*N*-2,6-diisopropylphenyl 3-(9-triptycenyl)-2-hydroxybenzyl-imine (**29D**) [*N*-diisopropylphenyl triptycenyl-salicyl-aldimine]: To a slurry of triptycenyl-salicylaldehyde **D** (0.80 g, 1.33 mmols) suspended in 10 mls of ethanol was added 2,6-diisopropylaniline (0.75 mls, excess) and a drop of formic acid. The slurry was stirred at reflux overnight then cooled to RT. The yellow product was collected by filtration and washed with ethanol before being dried in a vacuum oven at 60°C. Yield 1.03 g (88%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>) δ 13.940(s, 1H, OH), 8.584(d, 1H *J* = 6.5 Hz, H<sub>d</sub>), 8.487(s, 1H, CHN), 7.604(dd, 1H *J* = 7.6 & 1.6 Hz, H<sub>b</sub>), 7.426(dd, 3H *J* = 7.0 & 1.6 Hz, Tript-H<sub>4</sub>), 7.25-7.34(brm, 5H, H<sub>1</sub> and H<sub>b&c</sub>), 7.163(s, 3H, *o* & *m*-<sup>*i*</sup>Pr<sub>2</sub>Ph-H), 6.89-7.03(brm, 6H, H<sub>2</sub> & H<sub>3</sub>), 5.414(s, 1H, H<sub>5</sub>), 3.005(sept, 1H *J* = 6.7 Hz, <sup>*i*</sup>Pr-CH), 1.171(d, 6H *J* = 6.7 Hz, <sup>*i*</sup>Pr-Me).

C<sub>39</sub>H<sub>35</sub>NO (533.27): Calc. C 87.77, H 6.61, N 2.62; Found C 87.98, H 6.85, N 2.72.

*N*-cyclopropyl 3-(9-anthracenyl)-2-hydroxybenzyl imine (**31A**) [*N*-cyclopropyl anthracenyl-salicylaldimine]: As above in methanol. FW 337.41 Yield 0.43 g (76%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>) δ 13.083(s, 1H, OH), 8.65(s, 1H, CHN), 8.512(s, 1H, H<sub>5</sub>), 8.050(d, 2H *J* = 8.6 Hz, H<sub>4</sub>), 7.664(dd, 2H *J* = 8.8 & 0.9 Hz, H<sub>1</sub>), 7.30-7.48(brm, 6H, H<sub>2</sub> & H<sub>3</sub> & H<sub>b</sub> & H<sub>d</sub>), 7.113(t, 1H *J* = 7.5 Hz, H<sub>c</sub>), 2.949-3.032(brm, 1H, N-CH), 0.798-0.975(brm, 4H, (CH<sub>2</sub>)<sub>2</sub>).

<sup>13</sup>C{<sup>1</sup>H}-NMR (62.9 MHz, CDCl<sub>3</sub>) δ. 162.47, 158.71, 134.76, 132.71, 131.52, 130.56, 130.37, 128.51, 126.83, 126.53, 125.42, 125.01, 119.28, 118.57, 40.19, 9.26.

*N*-methyl 3-(9-anthracenyl)-2-hydroxybenzylaldimine (**48A**) [*N*-methyl anthracenyl-salicylaldimine]: As above. Yield 0.25 g (42%).

$^1\text{H-NMR}$   $\delta$  13.889(s, 1H, OH), 8.527(s, 1H, CHN or Anth-H<sub>5</sub>), 8.498(s, 1H, Anth-H<sub>5</sub> or CHN), 8.063(brd, 2H  $J$  = 8.2 Hz, Anth-H<sub>4</sub>), 7.690(brd, 2H  $J$  = 8.4 Hz, Anth-H<sub>4</sub>), 7.33-7.49brm, 6H, Anth-H<sub>2</sub> & H<sub>3</sub> and Ph-H<sub>b</sub> & H<sub>d</sub>), 7.104(t, 1H  $J$  = 7.5 Hz, Ph-H<sub>c</sub>), 3.452(s, 3H, NMe).

*N*-<sup>1</sup>butyl 3-(9-anthracenyl)-2-hydroxybenzalimine (**60A**) [*N*-<sup>1</sup>butyl anthracenyl-salicylalimine]: As above. Yield 0.36 g (61%).

$^1\text{H-NMR}$   $\delta$  14.577(s, 1H, OH), 8.516(s, 1H, CHN or Anth-H<sub>5</sub>), 8.504(s, 1H, Anth-H<sub>5</sub> or CHN), 8.055(brd, 2H  $J$  = 8.5 Hz, Anth-H<sub>4</sub>), 7.699(brd, 2H  $J$  = 8.5 Hz, Anth-H<sub>4</sub>), 7.32-7.68(brm, 6H, Anth-H<sub>2</sub> & H<sub>3</sub> and Ph-H<sub>b</sub> & H<sub>d</sub>), 7.086(t, 1H  $J$  = 7.5 Hz, Ph-H<sub>c</sub>), 1.313(s, 9H, <sup>t</sup>Bu).

*N*-cyclohexyl 3-(9-anthracenyl)-2-hydroxybenzalimine (**61A**) [*N*-cyclohexyl anthracenyl-salicylalimine]: As above. Yield 0.41 g (65%).  $^1\text{H-NMR}$  (250 MHz, CDCl<sub>3</sub>)  $\delta$  14.038(s, 1H, OH), 8.522(s, 2H, CHN & CH), 8.058(d, 2H  $J$  = 8.3 Hz, Anth-H), 7.697(brd, 2H  $J$  = 9.7 Hz, Anth-H), 7.33-7.49(brm, 5H, Anth-H<sub>2</sub> & H<sub>3</sub> and Ph-H<sub>b</sub> and H<sub>d</sub>), 7.094(t, 1H  $J$  = 7.5 Hz, H<sub>c</sub>), 3.20-3.30(m, 1H, cyclohexyl-CH), 1.70-1.85(m, 4H,  $\beta$ -CH<sub>2</sub>), 1.10-1.65(brm, 6H,  $\gamma$  &  $\delta$ -CH<sub>2</sub>).  $^{13}\text{C-NMR}$   $\delta$  163.11, 162.29, 159.13, 135.24, 132.89, 131.56, 131.11, 130.41, 128.51, 126.83, 126.65, 125.40, 125.01, 119.11, 118.14, 67.49, 34.26, 25.44, 24.37. MS(CI+ve) (m/z) 380(M+H<sup>+</sup>, 20%), 319(M-C<sub>3</sub>H<sub>10</sub>N<sup>+</sup>, 80%), 98(C<sub>6</sub>H<sub>12</sub>N<sup>+</sup>, 100%). C<sub>27</sub>H<sub>25</sub>NO (379.49): Calc. C 85.45, H 6.64, N 3.69; Found C 85.53, H 6.78, N 3.65.

*N*-bis(2-phenylethyl)methyl 3-(9-anthracenyl)-2-hydroxybenzalimine (**62A**) [*N*-3-(1,5-diphenyl)pentyl anthracenyl-salicylalimine]: As above. Yield 0.62 g (71.2%).

$^1\text{H-NMR}$  (250 MHz, CDCl<sub>3</sub>)  $\delta$  13.827(s, 1H, OH), 8.534(s, 1H, H<sub>5</sub>), 8.410(s, 1H, H<sub>a</sub>), 8.070(d, 2H  $J$  = 7.7 Hz, H<sub>4</sub>), 7.728(d, 2H  $J$  = 8.1 Hz, H<sub>1</sub>), 7.10-7.50(m, 17H, Ph-H and H<sub>3</sub> & H<sub>2</sub> and H<sub>d</sub> & H<sub>b</sub> & H<sub>c</sub>), 3.217(pent, 1H  $J$  = 6.7 Hz, NCH(CH<sub>2</sub>)<sub>2</sub>), 2.45-2.71(m, 4H, CH<sub>2</sub>Ph), 1.84-1.97(m, 4H, CH<sub>2</sub>CH<sub>2</sub>Ph).

*N*-amino 3-(9-anthracenyl)-2-hydroxybenzalimine (**63A**) [*N*-amino anthracenyl-salicylalimine]: As above. Yield 0.513 g (98%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>) δ 11.272(s, 1H, OH), 8.516(s, 1H, H<sub>5</sub>), 8.056(d, 2H *J* = 8.4 Hz, H<sub>4</sub>), 7.948(s, 1H, CHN), 7.24-7.48(m, 6H, H<sub>3</sub> & H<sub>2</sub> and H<sub>d</sub> & H<sub>b</sub>), 7.085(t, 1H *J* = 7.5 Hz, H<sub>c</sub>), 5.310(s, 2H, NH<sub>2</sub>).

*N*-1-methy-3-phenylpropyl 3-(9-anthracenyl)-2-hydroxybenzalimine (**64A**) [*N*-4-phenylbut-2-yl anthracenyl-salicylalimine]: As above. Yield 0.62 g (71%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>) δ 14.877(s, 1H, OH), 8.521(s, 1H, H<sub>5</sub>), 8.489(s, 1H, H<sub>a</sub>), 8.057(dd, 2H *J* = 8.3 & 0.6 Hz, H<sub>4</sub>), 7.698(t, 2H *J* = 8.8 Hz, H<sub>1</sub>), 7.08-7.49(m, 12H, Ph-H and H<sub>2</sub> & H<sub>3</sub> and H<sub>d</sub> & H<sub>b</sub> & H<sub>c</sub>), 3.378(pseudo q, 1H *J* = 6.7 Hz, NCH), 2.47-2.71(m, 2H, CH<sub>2</sub>Ph), 1.82-1.92(m, 2H, C<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.259(d, 3H *J* = 7.2 Hz, Me).

*N*-dimethylaminoethyl 3-(9-anthracenyl)-2-hydroxybenzalimine (**65A**) [*N*- dimethylaminoethyl anthracenyl-salicylalimine]: As above. Yield 0.38 g (62%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>) δ 13.749(s, 1H, OH), 8.538(s, 1H, H<sub>a</sub>), 8.515(s, 1H, H<sub>5</sub>), 8.051(d, 2H *J* = 8.4 Hz, H<sub>4</sub>), 7.670(dd, 2H *J* = 8.2 & 1.1 Hz, H<sub>1</sub>), 7.32-7.49(m, 6H, H<sub>2</sub> & H<sub>3</sub> and H<sub>d</sub> & H<sub>b</sub>), 7.103(f, 1H *J* = 7.5 Hz, H<sub>c</sub>), 3.707(td, 2H *J* = 6.8 & 1.1 Hz, CHNCH<sub>2</sub>), 2.570(t, 2H *J* = 6.8 Hz, CH<sub>2</sub>NMe<sub>2</sub>), 2.249(s, 6H, Me<sub>2</sub>).

*N*-dimethylaminoethyl 3-(9-triptycenyl)-2-hydroxybenzyl-imine (**65D**) [*N*-dimethylaminoethyl triptycenyl-salicyl-alimine]: To a slurry of triptycenyl-salicylaldehyde **D** (0.50 g, 1.33 mmols) suspended in 10 mls of ethanol was added N,N-dimethylethylenediamine (1.0 ml, excess) and a drop of formic acid. The slurry was stirred at reflux overnight then cooled to RT. The yellow product was collected by filtration and washed with ethanol before being dried in a vacuum oven at 60°C. Yield 0.473 g (79.4%).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 14.238(s, 1H, OH), 8.555(s, 1H, CHN), 8.494(d, 1H *J* = 7.9 Hz, H<sub>d</sub>), 7.507 (d, 1H *J* = 7.4 Hz, H<sub>b</sub>), 7.418(d, 3H *J* = 6.9 Hz, Tript-H), 7.270(d, 3H *J* = 6.0 & Hz, Tript-H), 7.221(t, 1H *J* =



7.5 Hz, H<sub>c</sub>), 6.85-7.03(m, 6H, Tript-H), 5.408(s, 1H, Tript-CH), 3.708(t, 2H  $J = 6.9$  Hz, CHN-CH<sub>2</sub>), 2.579(m, 2H  $J = 6.9$  Hz, CH<sub>2</sub>N), 2.270(m, 6H, NMe<sub>2</sub>).

<sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.75, 161.62, 146.20, 145.60, 134.79, 131.46, 125.02, 124.76, 124.48, 124.26, 123.36, 119.66, 117.70, 59.69, 57.58, 55.27, 45.81.

MS(CI+ve) (m/z) 445(M<sup>+</sup> 50).

C<sub>31</sub>H<sub>28</sub>N<sub>2</sub>O (444.57): Calc. C 83.75, H 6.35, N 6.30; Found C 83.75, H 6.24, N 6.26.

*N*-(*N*-2,5-dimethylpyrrolyl) 3-(9-anthracenyl)-2-hydroxybenzalimine (**66A**) [*N*-(*N*-2,5-dimethylpyrrolyl) anthracenyl-salicylalimine]: As above. Yield 0.26 g (40%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  11.317(s, 1H, OH), 8.646(s, 1H, CHN), 8.545(s, 1H, Anth-H<sub>5</sub>), 8.072(brd, 2H  $J = 8.0$  Hz, Anth-H<sub>4</sub>), 7.692(brd, 2H  $J = 8.7$  Hz, Anth-H<sub>1</sub>), 7.35-7.56(brm, 6H, Anth-H<sub>2</sub> & H<sub>3</sub> and Ph-H<sub>b</sub> & H<sub>d</sub>), 7.207(t, 1H  $J = 7.6$  Hz, Ph-H<sub>c</sub>), 5.843(s, 2H, Pyrrole-CH), 2.292(s, 6H, Pyrrole-Me)..

*N*-isobutyl 3-(9-anthracenyl)-2-hydroxybenzalimine (**67A**) [*N*-isobutyl anthracenyl-salicylalimine]: As above. Yield 0.44 g (74.3%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  13.926(s, 1H, OH), 8.530(s, 1H, H<sub>5</sub>), 8.475(s, 1H, H<sub>a</sub>), 8.066(d, 2H  $J = 8.4$  Hz, H<sub>4</sub>), 7.094(d, 2H  $J = 8.4$  Hz, H<sub>1</sub>), 7.34-7.50(m, 6H, H<sub>3</sub> & H<sub>2</sub> and H<sub>d</sub> & H<sub>b</sub>), 7.109(t, 1H  $J = 7.6$  Hz, H<sub>c</sub>), 3.421(dd, 2H  $J = 6.5$  & 0.7 Hz, NCH<sub>2</sub>), 1.908(heptet, 1H  $J = 6.6$  Hz, CHMe<sub>2</sub>), 0.936(d, 6H  $J = 6.7$  Hz, Me<sub>2</sub>)

<sup>13</sup>C{<sup>1</sup>H}-NMR (62.9 MHz, CDCl<sub>3</sub>)  $\delta$  164.73, 159.88, 156.02, 135.38, 132.85, 131.57, 131.19, 130.42, 128.54, 126.88, 126.64, 125.40, 125.02, 119.00, 118.22, 67.54, 29.49, 20.52.

*N*-adamantyl 3-(9-anthracenyl)-2-hydroxybenzalimine (**68A**) [*N*-adamantyl anthracenyl-salicylalimine]: As above. Yield 0.66 g (91%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  14.72(s, 1H, OH), 8.517(s, 1H, Anth-H<sub>5</sub>), 8.497(s, 1H, CHN), 8.055(brd, 2H  $J = 8.4$  Hz, Anth-H<sub>4</sub>), 7.710(brd, 2H  $J = 8.6$  Hz, Anth-H<sub>1</sub>), 7.32-7.45(brm, 6H, Anth-H<sub>2</sub> & H<sub>3</sub> and Ph-H<sub>b</sub>

& H<sub>d</sub>), 7.073(t, 1H  $J$  = 7.5 Hz, Ph-H<sub>c</sub>), 2.152(brs, 3H,  $\beta$ -H), 1.822(d, 6H  $J$  = 2.7 Hz,  $\alpha$ -H), 1.697(pseudo quartet, 6H  $J$  = 11.7 Hz,  $\gamma$ -H).

*N*-benzyl 3-(9-anthracenyl)-2-hydroxybenzalimine (**69A**) [*N*-benzyl anthracenyl-salicylalimine]: As above. Yield 0.44 g (68%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  13.685(s, 1H, OH), 8.606(s, 1H, H<sub>a</sub>), 8.519(s, 1H, H<sub>5</sub>), 8.054(d, 2H  $J$  = 8.3 Hz, H<sub>4</sub>), 7.673(dd, 2H  $J$  = 8.7 & 1.0 Hz, H<sub>1</sub>), 7.20-7.52(m, 11H, Ph-H and H<sub>2</sub> & H<sub>3</sub> and H<sub>d</sub> and H<sub>b</sub>), 7.125(t, 1H  $J$  = 7.5 Hz, H<sub>c</sub>), 4.790(s, 2H, CH<sub>2</sub>).

*N*-2-phenylethyl 3-(9-anthracenyl)-2-hydroxybenzalimine (**70A**) [*N*-phenylethyl anthracenyl-salicylalimine]: As above. Yield 0.43 g (64%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  13.830(s, 1H, OH), 8.527(s, 1H, H<sub>5</sub>), 8.390(s, 1H, H<sub>a</sub>), 8.062(d, 2H  $J$  = 8.3 Hz, H<sub>4</sub>), 7.683(d, 2H  $J$  = 8.6 Hz, H<sub>1</sub>), 7.14-7.49(m, 11H, Ph-H and H<sub>2</sub> & H<sub>3</sub> and H<sub>d</sub> and H<sub>b</sub>), 7.086(t, 1H,  $J$  = 7.6 Hz, H<sub>c</sub>), 3.833(t, 2H  $J$  = 7.4 Hz, NCH<sub>2</sub>), 2.945(t, 2H  $J$  = 7.4 Hz, CH<sub>2</sub>Ph).

*N*-3-phenylpropyl 3-(9-anthracenyl)-2-hydroxybenzalimine (**71A**) [*N*-phenylpropyl anthracenyl-salicylalimine]: As above. Yield 0.38 g (55%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  13.870(s, 1H, OH), 8.525(s, 1H, H<sub>5</sub>), 8.493(s, 1H, H<sub>a</sub>), 8.060(d, 2H  $J$  = 8.2 Hz, H<sub>4</sub>), 7.693(d, 2H  $J$  = 8.3 Hz, H<sub>1</sub>), 7.11-7.71(m, 12H, Ph-H and H<sub>3</sub> & H<sub>2</sub> and H<sub>d</sub> & H<sub>b</sub> & H<sub>c</sub>), 3.603(t, 2H  $J$  = 6.7 Hz, NCH<sub>2</sub>), 2.674(t, 2H  $J$  = 7.6 Hz, CH<sub>2</sub>Ph), 1.970(pseudo pentet, 2H  $J$  = 7.2 Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).

*N*-2(diphenylphosphino)phenyl 3-(9anthracenyl)-2-hydroxybenzylimine (**72A**) [*N*-diphenylphosphinophenyl anthracenyl-salicylalimine]: To a slurry of anthracenyl-salicylaldehyde **A** (0.50 g, 1.68 mmols) suspended in 10 mls of ethanol was added 2-(diphenylphosphino)-aniline (0.47 g, 2.4 mmols) and a drop of formic acid. The slurry was stirred at reflux overnight then cooled to RT. The product

was collected by filtration and washed with ethanol before being dried in a vacuum oven at 60°C. Yield 0.86 g (93%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>) δ 12.921(s, 1H, OH), 8.525(s, 1H, H<sub>5</sub>), 8.416(s, 1H, CHN), 8.065(d, 2H *J* = 8.3 Hz, H<sub>4</sub>), 7.649(d, 2H *J* = 8.7 Hz, H<sub>1</sub>), 7.33-7.50(m, 7H, Ar-H), 7.13-7.26(m, 12H, Ar-H), 7.057(t, 1H *J* = 7.5 Hz, H<sub>c</sub>), 6.85-6.90(m, 1H, Ph<sub>2</sub>P-*o*-Ph-*H*-N). <sup>31</sup>P-NMR (101 MHz, CDCl<sub>3</sub>) δ -15.91.

*N*-2(diphenylphosphino)phenyl 3-(9-triptycenyl)-2-hydroxybenzylimine (**72D**) [*N*-diphenylphosphinophenyl triptycenyl-salicylaldimine]: To a slurry of triptycenyl-salicylaldehyde **D** (0.50 g, 1.12 mmols) suspended in 10 mls of ethanol was added 2-(diphenylphosphino)-aniline (0.31 g, 1.46 mmols) and a drop of formic acid. The slurry was stirred at reflux overnight then cooled to RT. The yellow product was collected by filtration and washed with ethanol before being dried in a vacuum oven at 60°C. Yield 0.52 g 73.3(%).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 13.052(s, 1H, OH), 8.477(dd, 1H *J* = 7.1 & 0.4 Hz, H<sub>d</sub>), 8.435(s, 1H, CHN), 7.38-7.46(m, 5H, Ar-H), 7.10-7.22(m, 15H, Ar-H), 6.92-7.20(m, 6H, Tript-H), 6.831(ddd, 1H *J* = 7.4 & 0.9 Hz <sup>3</sup>*J*<sub>HP</sub> = 3.9 Hz, Ar-H), 5.399(s, 1H, Tript-CH).

*N*-8-Quinoliny 3-phenyl-2-hydroxybenzyl imine (**73F**) [*N*-8-quinoliny phenyl-salicylaldimine]: To a slurry of phenyl-salicylaldehyde (0.50 g, 2.52 mmols) suspended in 10 mls of ethanol was added 8-aminoquinoline (1.0 g, excess) and a drop of formic acid. The slurry was stirred overnight. The orange/red product collected by filtration and washed with ethanol before being dried in a vacuum oven at 60°C. Yield 0.61 g (75.8%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>) δ 14.433(s, 1H, OH), 9.028(s, 1H, Ha), 8.965(dd, 1H *J* = 4.2 & 1.8 Hz, Quinyl-H), 8.188(dd, 1H *J* = 8.3 & 1.8 Hz, Quinyl-H), 7.68-7.76(m, 3H, Ar-H), 7.580(t, 1H *J* = 7.7 Hz, Ph-H), 7.42-7.53(m, 6H, Ar-H), 7.352(tt, 1H *J* = 7.3 & 1.5 Hz, Quinyl-H), 7.029(t, 1H *J* = 7.6 Hz, PhOH-Hc).

*N*-(dimethyl)-2-pyridylmethyl 3-(9-triptycenyl)-2-hydroxybenzylimine (**74D**) [*N*-(dimethyl)pyridylmethyl triptycenyl-salicylaldimine]: To a slurry of triptycenyl-salicylaldehyde **D** (0.50 g, 1.33 mmols) suspended in 10 mls of ethanol was added 2-amino(dimethyl)methylpyridine (0.50 g, excess) and a drop of formic acid. The slurry was stirred at reflux overnight then cooled to RT. The yellow product was collected by filtration and washed with ethanol before being dried in a vacuum oven at 60°C. Yield 0.33 g (50.0%).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 14.704(s, 1H, OH), 8.581(bris, 2H, CHN & Py-H), 8.479(d, 1H *J* = 7.8 Hz, H<sub>d</sub>), 7.591(dt, 1H *J* = 7.7 & 1.5 Hz, Py-H), 7.512(d, 1H *J* = 7.4 Hz, H<sub>b</sub>), 7.406(d, 3H *J* = 7.0 Hz, Tript-H), 7.353(d, 1H *J* = 8.0 Hz, Py-H), 7.287(d, 3H *J* = 6.0 & Hz, Tript-H), 7.184(t, 1H *J* = 7.7 Hz, H<sub>c</sub>), 6.973(t, 3H *J* = 7.3 Hz, Tript-H), 6.916(t, 3H *J* = 7.3 Hz, Tript-H), 5.392(s, 1H, Tript-CH), 1.728(m, 6H, CMe<sub>2</sub>).

<sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>) δ 164.64, 162.14, 161.89, 148.73, 146.17, 145.56, 136.56, 134.95, 132.20, 131.93, 125.10, 124.78, 124.45, 124.26, 123.42, 121.83, 120.41, 119.82, 117.61, 64.74, 55.26, 28.26.

*N*-diphenyl-(2-pyridyl)-methyl 3-(9-triptycenyl)-2-hydroxybenzylimine (**75D**) [*N*-(2-pyridyl)-methyl triptycenyl-salicylaldimine]: To a slurry of triptycenyl-salicylaldehyde **D** (0.50 g, 1.33 mmols) suspended in 10 mls of ethanol was added 2-amino(diphenylmethyl)pyridine (0.50 g, excess) and a drop of formic acid. The slurry was stirred at reflux overnight then cooled to RT. The yellow product was collected by filtration and washed with ethanol before being dried in a vacuum oven at 60°C. Yield 0.762 g (93%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>) δ 14.68 (s, 1H, OH), 8.641(d, 1H, py *J* = 4.8 Hz), 8.486(dd, 1H, *J* = 7.9 & 1.3 Hz, Hd), 8.124(s, 1H, CHN), 7.55(dt, 1H *J* = 7.58 & 1.8 Hz, Py), 7.435(dd, 4H *J* = 6.8 & 1.3 Hz, Tript-H), 7.12-7.4(m, 18H, Tript-H & Ph-H & Py-H & Ph<sub>2</sub>-H), 6.9-7.05(m, 6H, Tript-H) 5.456(s, 1H, Tript-CH).

*N*-pyrrolidinylethyl 3-(9-triptycenyl)-2-hydroxybenzylimine (**76D**) [*N*-pyrrolidinylethyl triptycenyl-salicylaldimine]: To a slurry of triptycenyl-salicylaldehyde **D** (0.50 g, 1.33 mmols) suspended in 10 mls of ethanol was added 2-aminoethylpyrrolidine (1.0 ml, excess) and a drop of formic acid. The slurry was stirred at reflux overnight then cooled to RT. The yellow product was collected by filtration and washed with ethanol before being dried in a vacuum oven at 60°C. Yield 0.52 g (83.1%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>) δ 14.24(s, 1H, OH), 8.558(s, 1H, CHN), 8.488(dd, 1H *J* = 7.8 & 1.7 Hz, H<sub>d</sub>), 7.503(dd, 1H *J* = 7.7 & 1.7 Hz, H<sub>b</sub>), 7.399(dd, 3H *J* = 6.9 & 1.3 Hz, Tript-H), 7.251(dd, 3H *J* = 6.0 & 1.5 Hz, Tript-H), 7.184(t, 1H *J* = 7.7 Hz, H<sub>c</sub>), 6.85-7.01(m, 6H, Tript-H), 5.393(s, 1H, Tript-CH), 3.762(t, 2H *J* = 7.0 Hz, CHN-CH<sub>2</sub>), 2.76(t, 2H *J* = 7.02 Hz, NCH<sub>2</sub>), 2.546(m, 4H, N(CH<sub>2</sub>)<sub>2</sub>), 1.775(m, 4H, (CH<sub>2</sub>)<sub>2</sub>).

*N*-2-pyridyl 3-(9-triptycenyl)-2-hydroxybenzylimine (**77D**) [*N*-pyridyl triptycenyl-salicylaldimine]: Yield 0.55 g 92(%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>) δ 14.274(s, 1H, OH), 9.669(s, 1H, CHN), 8.62(d, 1H *J* = 7.9 Hz, H<sub>d</sub>), 8.535(d, 1H *J* = 4.5 Hz, Py-H), 7.778(d, 1H *J* = 7.5 Hz, H<sub>b</sub>), 7.705(dt, 1H *J* = 7.6 & 1.3 Hz, Py-H), 7.437(dd, 3H *J* = 7.2 & 1.3 Hz, Tript-H), 7.17-7.32(m, 6H, Tript-H and H<sub>c</sub> and 2 x Py-H), 6.91-7.03(m, 6H, Tript-H<sub>2</sub> & H<sub>3</sub>), 5.420(s, 1H, Tript-H<sub>5</sub>).

*N*-(di-2-pyridyl)-methyl 3-(9-triptycenyl)-2-hydroxy-benzylimine (**78D**) [*N*-dipyridylmethyl triptycenyl-salicyl-aldimine]: To a slurry of triptycenyl-salicylaldehyde **D** (0.50 g, 1.33 mmols) suspended in 10 mls of ethanol was added dipyridylmethanamine (0.28 g, 1.47 mmols) and a drop of formic acid. The slurry was stirred at reflux overnight then cooled to RT. The yellow product was collected by filtration and washed with ethanol before being dried in a vacuum oven at 60°C. Yield 0.62 g 86.1(%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>) δ 13.932(s, 1H, OH), 8.826(s, 1H, CHN), 8.576(ddd, 2H *J* = 4.8, 1.7 & 0.9, Py-H), 8.507(dd, 1H *J* = 7.9 & 1.5 Hz, H<sub>d</sub>), 7.606(dt, 2H *J* = 8.0 & 1.8, Py-H) overlapping 7.557(dd, 1H *J* = 8.7 & 1.6 Hz, H<sub>b</sub>), 7.422(dd, 3H, *J* = 7.1 & 1.3 Hz, Tript-H), 7.105-7.35(m, 10H, Ar-H), 6.984(dt, 3H *J* = 7.2 & 1.3 Hz, Tript-H), 6.908(dt, 3H *J* = 7.5 & 1.5 Hz, Tript-H), 5.996(s, 1H, CN-CH), 5.408(s, 1H, Tript-CH).

MS(CI+ve) (*m/z*) 541(M<sup>+</sup> 40%).

C<sub>38</sub>H<sub>27</sub>N<sub>3</sub>O (541.64): Calc. C 84.26, H 5.02, N 7.76; Found C 84.36, H 4.90, N 7.60.

*N*-(2-pyridyl)-ethyl 3-(9-triptycenyl)-2-hydroxybenzyl-imine (**79D**) [*N*-(2-pyridyl)-ethyl triptycenyl-salicyl-aldimine]: To a slurry of triptycenyl-salicylaldehyde **D** (0.50 g, 1.33 mmols) suspended in 10 mls of ethanol

was added 2-aminoethylpyridine (0.50 mls, excess) and a drop of formic acid. The slurry was stirred at reflux overnight then cooled to RT. The yellow product was collected by filtration and washed with ethanol before being dried in a vacuum oven at 60°C. Yield 0.56 g (90.2%).

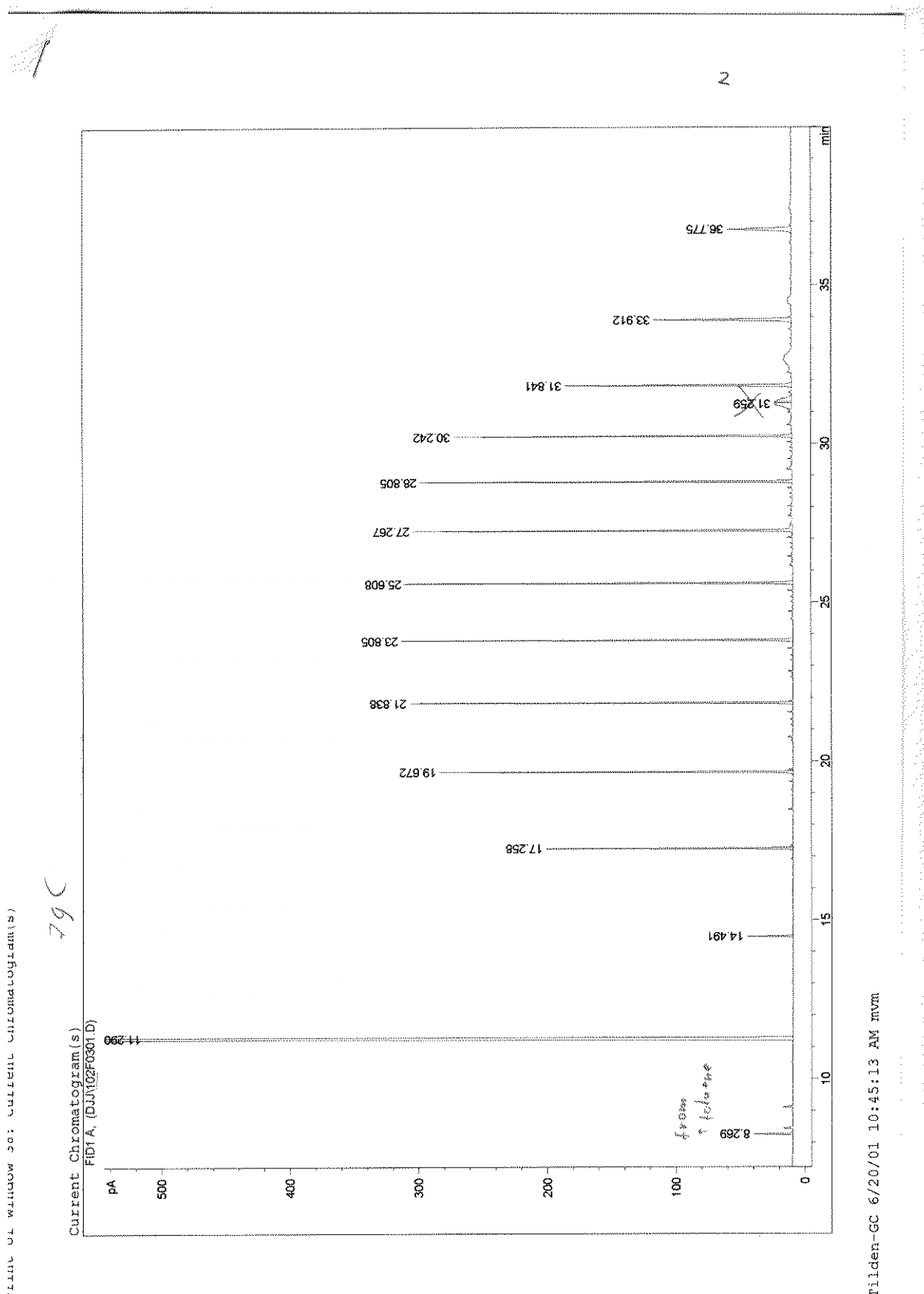
<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>) δ 14.233(s, 1H, OH), 8.547(dd, 1H *J* = 7.9 & 1.5, Hd), 8.459(dm, 1H *J* = 4.9, Py-H), 8.399(s, 1H, CHN), 7.531(dt, 1H *J* = 7.6 & 1.9, Py-H), 7.409(dd, 4H *J* = 7.1 & 1.3 Hz, Tript-H overlapping Hb), 7.227(dd, 3H, *J* = 7.4 & 1.4 Hz, Tript-H), 7.144(t, 1H *J* = 7.8 Hz, Hc) overlapping 7.041-7.145(m, 2H, Py-H), 6.88-7.02(m, 6H, Tript-H), 5.392(s, 1H, Tript-CH), 3.999(t, 2H *J* = 6.8 Hz, CN-CH<sub>2</sub>), 3.111(t, 2H *J* = 6.8 Hz, CH<sub>2</sub>Py).

*2-(N,N-dipyrid-2-ylaminomethyl)-6-triptycenyl-phenol* **94**: Triptycenyl-salicylaldehyde **D** (0.50 g, 1.33 mmols) was dissolved in 50 mls of ethanol with bis-(pyridylmethyl)amine (0.80 g, 4.0 mmols) and NaBH<sub>3</sub>CN (0.314 g, 5 mmols) slowly added. The slurry was refluxed overnight, cooled and water added. The crude product was collected by filtration. Yield 0.62 g (83%).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 11.202(s, 1H, OH), 8.455(d, 2H *J* = 2.9 Hz, Hi), 8.316(dd, 1H *J* = 7.9 & 1.0 Hz, H<sub>d</sub>), 7.508(dt, 2H *J* = 7.7 & 1.6 Hz, H<sub>g</sub>), 7.419(d, 3H *J* = 7.0 Hz, H<sub>4</sub>), 7.24-7.32(brm, 6H, H<sub>f</sub> & H<sub>i</sub> & H<sub>b</sub>), 7.121(dd, 2H *J* = 7.1 & 5.3 Hz, H<sub>h</sub>), 7.081(t, 1H *J* = 7.7 Hz, H<sub>c</sub>), 6.973(t, 3H *J* = 7.9 Hz, H<sub>3</sub>), 6.827(dt, 3H *J* = 7.6 & 0.8 Hz, H<sub>2</sub>), 5.406(s, 1H, H<sub>5</sub>), 4.001(s, 2H, CN-CH<sub>2</sub>), 3.912(s, 4H, CH<sub>2</sub>-Py).

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 157.77, 157.65, 148.91, 146.27, 146.16, 136.73, 131.70, 130.05, 125.36, 124.54, 124.12, 123.56, 123.51, 123.28, 123.23, 122.22, 118.21, 59.42, 58.96, 57.77, 55.32.

**Fig. S1.** Typical GC trace for the toluene soluble fraction from ethylene polymerization runs using tridentate ligands.



**Table S1.** Crystal Data, Data Collection and Refinement Parameters for compounds **4e**, **D (9a)**, **C (17)**, **32D**, **73C**, **III**, **V**, **VIII** and **IX**. [a]

data	<b>4e</b>	<b>D (9a)</b>	<b>C (17)</b>	<b>32D</b>
formula	C <sub>32</sub> H <sub>23</sub> OP	C <sub>27</sub> H <sub>18</sub> O <sub>2</sub>	C <sub>25</sub> H <sub>22</sub> O <sub>2</sub>	C <sub>33</sub> H <sub>24</sub> N <sub>2</sub> O
solvent	—	C <sub>6</sub> H <sub>6</sub>	—	C <sub>7</sub> H <sub>8</sub>
formula weight	454.47	452.52	354.43	556.68
colour, habit	pale yellow blocks	colourless prisms	orange prismatic needles	pale yellow/yellow dichroic blocks
crystal size / mm	0.57 × 0.50 × 0.18	0.48 × 0.33 × 0.25	0.47 × 0.43 × 0.43	0.63 × 0.43 × 0.33
temperature / K	293	293	293	293
crystal system	orthorhombic	monoclinic	monoclinic	triclinic
space group	<i>Pbca</i> (no. 61)	<i>P2<sub>1</sub>/c</i> (no. 14)	<i>P2<sub>1</sub>/c</i> (no. 14)	<i>P</i> $\bar{1}$ (no. 2)
<i>a</i> / Å	15.8683(10)	9.6680(6)	13.085(2)	8.7697(9)
<i>b</i> / Å	11.002(2)	18.5565(14)	11.329(2)	9.8373(7)
<i>c</i> / Å	26.673(3)	13.8635(17)	13.562(3)	18.649(2)
$\alpha$ / deg	—	—	—	97.780(6)
$\beta$ / deg	—	104.847(8)	109.002(14)	103.258(11)
$\gamma$ / deg	—	—	—	99.454(7)
<i>V</i> / Å <sup>3</sup>	4656.5(11)	2404.1(4)	1900.7(7)	1519.4(3)
<i>Z</i>	8	4	4	2
<i>D<sub>c</sub></i> / g cm <sup>-3</sup>	1.297	1.250	1.239	1.217
radiation used	Cu-K $\alpha$	Cu-K $\alpha$	Cu-K $\alpha$	Cu-K $\alpha$
$\mu$ / mm <sup>-1</sup>	1.216	0.597	0.604	0.562
$2\theta$ max / deg	120	120	120	120
no. of unique reflns				
measured	3452	3565	2821	4473
obs, $ F_o  > 4\sigma( F_o )$	2617	2673	1770	3438
no. of variables	288	322	250	470
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [c]	0.049, 0.123	0.053, 0.138	0.083, 0.237	0.050, 0.134

[a] Details in common: graphite monochromated radiation, refinement based on  $F^2$ . [b] Two independent molecules. [c]  $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ ;  $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$ ;  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ .



**Table S1.** Continued

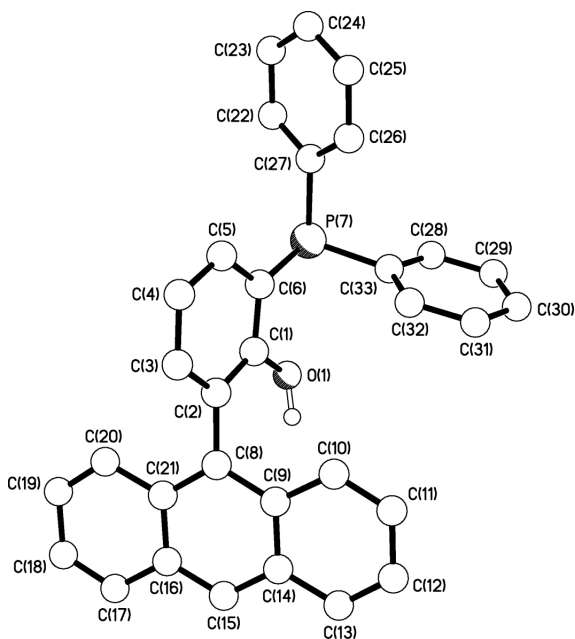
<b>data</b>	<b>73C</b>	<b>III</b>
<b>formula</b>	C <sub>34</sub> H <sub>28</sub> N <sub>2</sub> O	C <sub>34</sub> H <sub>38</sub> Cl <sub>2</sub> CrNO <sub>3</sub>
<b>solvent</b>	—	C <sub>6</sub> H <sub>6</sub>
<b>formula weight</b>	480.58	709.66
<b>colour, habit</b>	orange/red blocks	green platy needles
<b>crystal size / mm</b>	0.67 × 0.33 × 0.33	0.63 × 0.60 × 0.13
<b>temperature / K</b>	293	183
<b>crystal system</b>	monoclinic	monoclinic
<b>space group</b>	<i>P</i> 2 <sub>1</sub> / <i>n</i> (no. 14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (no. 14)
<b><i>a</i> / Å</b>	10.2408(5)	10.3635(12)
<b><i>b</i> / Å</b>	14.2305(8)	11.9949(17)
<b><i>c</i> / Å</b>	17.7423(13)	28.844(3)
<b><math>\alpha</math> / deg</b>	—	—
<b><math>\beta</math> / deg</b>	101.205(9)	99.327(8)
<b><math>\gamma</math> / deg</b>	—	—
<b><i>V</i> / Å<sup>3</sup></b>	2536.3(3)	3538.2(8)
<b><i>Z</i></b>	4	4
<b><i>D<sub>c</sub></i> / g cm<sup>-3</sup></b>	1.259	1.332
<b>radiation used</b>	Cu-K $\alpha$	Mo-K $\alpha$
<b><math>\mu</math> / mm<sup>-1</sup></b>	0.587	0.513
<b><math>\square\theta</math> max / deg</b>	120	47
<b>no. of unique reflns</b>		
<b>measured</b>	3756	5201
<b>obs, <math> F_o  &gt; 4\sigma( F_o )</math></b>	2986	3507
<b>no. of variables</b>	343	422
<b><i>R</i><sub>1</sub>, <i>wR</i><sub>2</sub> [c]</b>	0.051, 0.138	0.061, 0.156

**Table S1.** Continued

data	V	VIII	IX
formula	C <sub>36</sub> H <sub>39</sub> ClCrN <sub>3</sub> O <sub>2</sub>	C <sub>35</sub> H <sub>26</sub> Cl <sub>2</sub> CrNO <sub>3</sub>	C <sub>41</sub> H <sub>28</sub> Cl <sub>2</sub> CrN <sub>3</sub> O
solvent	CH <sub>3</sub> CN	CH <sub>3</sub> CN	3C <sub>5</sub> H <sub>5</sub> N
formula weight	674.21	668.54	938.86
colour, habit	dark green blocks	orange platy needles	deep red blocks
crystal size / mm	0.27 × 0.20 × 0.07	0.33 × 0.17 × 0.03	0.37 × 0.33 × 0.27
temperature / K	183	183	203
crystal system	monoclinic	orthorhombic	triclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)	<i>Pca</i> 2 <sub>1</sub> (no. 29)	<i>P</i> $\bar{1}$ (no. 2)
<i>a</i> / Å	13.1266(11)	20.824(3)	10.996(2)
<i>b</i> / Å	11.6335(4)	9.707(2)	11.8362(18)
<i>c</i> / Å	23.496(2)	31.106(4)	19.526(3)
$\alpha$ / deg	—	—	80.378(9)
$\beta$ / deg	96.357(8)	—	82.022(18)
$\gamma$ / deg	—	—	69.553(19)
<i>V</i> / Å <sup>3</sup>	3566.0(4)	6288(2)	2338.8(7)
<i>Z</i>	4	8 [b]	2
<i>D</i> <sub>c</sub> / g cm <sup>-3</sup>	1.256	1.412	1.333
radiation used	Cu-K $\alpha$	Cu-K $\alpha$	Mo-K $\alpha$
$\mu$ / mm <sup>-1</sup>	3.621	4.850	0.407
$\square\theta$ max / deg	120	120	50
no. of unique reflns			
measured	4887	4644	8216
obs, $ F_o  > 4\sigma( F_o )$	3765	3061	4630
no. of variables	404	812	581
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [c]	0.049, 0.114	0.067, 0.149	0.070, 0.146

Data were collected on Bruker P4 diffractometers, and the structures were refined based on  $F^2$  using the SHELXTL program system (SHELXTL PC version 5.1, Bruker AXS, Madison, WI, 1997). The structure of **IX** was shown to be a polar twin by a combination of *R*-factor tests [ $R_1^+ = 0.0691$ ,  $R_1^- = 0.0690$ ] and by use of the Flack parameter [ $x^+ = +0.48(4)$ ,  $x^- = +0.52(4)$ ]. CCDC 248415 – 248424.

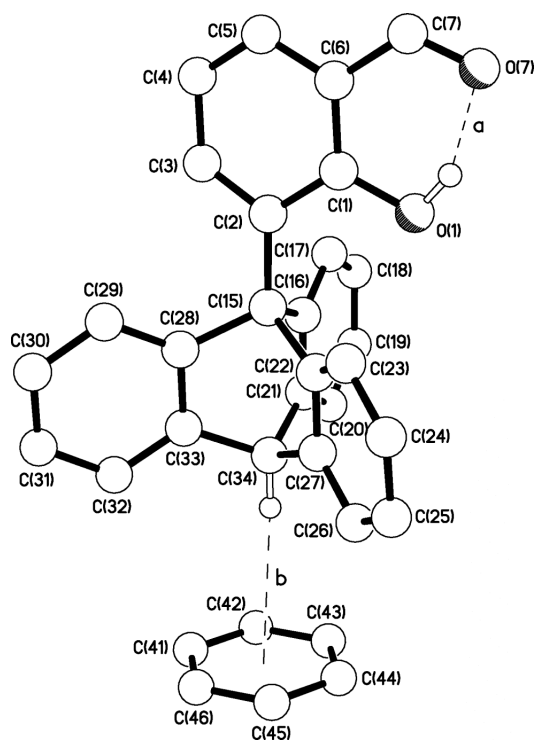
**Fig. S2.** Molecular structure of **4e**.

Bond lengths [Å] and angles [°] for **4e**.

O(1)-C(1)	1.379(3)	C(22)-C(27)	1.3900
C(1)-C(2)	1.388(4)	C(23)-C(24)	1.3900
C(1)-C(6)	1.401(4)	C(24)-C(25)	1.3900
C(2)-C(3)	1.390(4)	C(25)-C(26)	1.3900
C(2)-C(8)	1.498(4)	C(26)-C(27)	1.3900
C(3)-C(4)	1.385(4)	C(28)-C(29)	1.3900
C(4)-C(5)	1.381(4)	C(28)-C(33)	1.3900
C(5)-C(6)	1.402(4)	C(29)-C(30)	1.3900
C(6)-P(7)	1.830(3)	C(30)-C(31)	1.3900
P(7)-C(33)	1.8426(16)	C(31)-C(32)	1.3900
P(7)-C(27)	1.8443(15)	C(32)-C(33)	1.3900
C(8)-C(21)	1.413(4)		
C(8)-C(9)	1.419(4)	O(1)-C(1)-C(2)	120.6(2)
C(9)-C(10)	1.422(4)	O(1)-C(1)-C(6)	116.6(2)
C(9)-C(14)	1.435(4)	C(2)-C(1)-C(6)	122.9(2)
C(10)-C(11)	1.354(4)	C(1)-C(2)-C(3)	118.1(2)
C(11)-C(12)	1.407(5)	C(1)-C(2)-C(8)	119.4(2)
C(12)-C(13)	1.339(5)	C(3)-C(2)-C(8)	122.6(2)
C(13)-C(14)	1.429(4)	C(4)-C(3)-C(2)	121.0(3)
C(14)-C(15)	1.379(4)	C(5)-C(4)-C(3)	119.7(3)
C(15)-C(16)	1.390(4)	C(4)-C(5)-C(6)	121.6(3)
C(16)-C(17)	1.424(4)	C(1)-C(6)-C(5)	116.7(2)
C(16)-C(21)	1.430(4)	C(1)-C(6)-P(7)	118.22(19)
C(17)-C(18)	1.342(5)	C(5)-C(6)-P(7)	125.0(2)
C(18)-C(19)	1.402(5)	C(6)-P(7)-C(33)	102.01(11)
C(19)-C(20)	1.357(4)	C(6)-P(7)-C(27)	101.80(10)
C(20)-C(21)	1.425(4)	C(33)-P(7)-C(27)	101.51(9)
C(22)-C(23)	1.3900	C(21)-C(8)-C(9)	119.8(2)

C(21)-C(8)-C(2)	121.8(2)	C(8)-C(21)-C(20)	122.6(3)
C(9)-C(8)-C(2)	118.4(2)	C(8)-C(21)-C(16)	119.8(3)
C(8)-C(9)-C(10)	122.7(3)	C(20)-C(21)-C(16)	117.5(3)
C(8)-C(9)-C(14)	119.7(3)	C(23)-C(22)-C(27)	120.0
C(10)-C(9)-C(14)	117.6(3)	C(24)-C(23)-C(22)	120.0
C(11)-C(10)-C(9)	121.7(3)	C(23)-C(24)-C(25)	120.0
C(10)-C(11)-C(12)	120.3(3)	C(26)-C(25)-C(24)	120.0
C(13)-C(12)-C(11)	120.9(3)	C(25)-C(26)-C(27)	120.0
C(12)-C(13)-C(14)	121.0(3)	C(26)-C(27)-C(22)	120.0
C(15)-C(14)-C(13)	122.5(3)	C(26)-C(27)-P(7)	123.87(11)
C(15)-C(14)-C(9)	118.9(3)	C(22)-C(27)-P(7)	116.12(11)
C(13)-C(14)-C(9)	118.6(3)	C(29)-C(28)-C(33)	120.0
C(14)-C(15)-C(16)	122.8(3)	C(28)-C(29)-C(30)	120.0
C(15)-C(16)-C(17)	122.1(3)	C(29)-C(30)-C(31)	120.0
C(15)-C(16)-C(21)	118.9(3)	C(32)-C(31)-C(30)	120.0
C(17)-C(16)-C(21)	119.0(3)	C(33)-C(32)-C(31)	120.0
C(18)-C(17)-C(16)	121.7(3)	C(32)-C(33)-C(28)	120.0
C(17)-C(18)-C(19)	119.4(3)	C(32)-C(33)-P(7)	124.52(11)
C(20)-C(19)-C(18)	121.9(3)	C(28)-C(33)-P(7)	115.48(11)
C(19)-C(20)-C(21)	120.6(3)		

**Fig. S3.** Molecular structure of **D (9a)**.

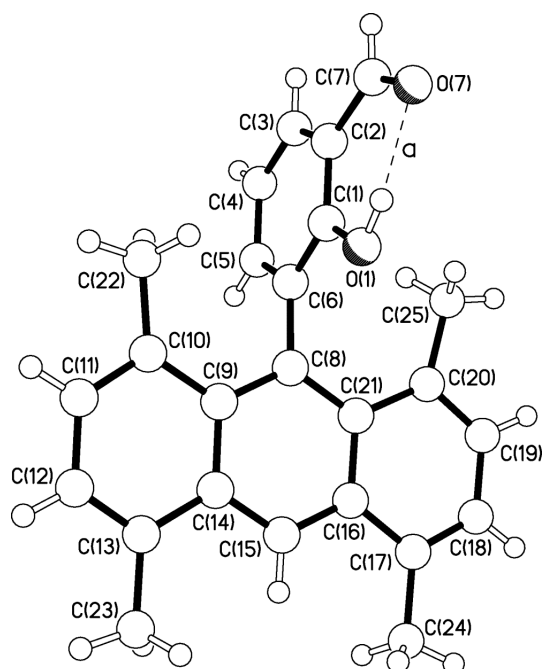


Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **D (9a)**.

O(1)-C(1)	1.354(3)	C(25)-C(26)	1.387(4)
C(1)-C(2)	1.397(3)	C(26)-C(27)	1.380(3)
C(1)-C(6)	1.413(3)	C(27)-C(34)	1.514(3)
C(2)-C(3)	1.397(3)	C(28)-C(29)	1.386(3)
C(2)-C(15)	1.530(3)	C(28)-C(33)	1.407(3)
C(3)-C(4)	1.385(3)	C(29)-C(30)	1.389(4)
C(4)-C(5)	1.366(4)	C(30)-C(31)	1.375(4)
C(5)-C(6)	1.392(4)	C(31)-C(32)	1.383(4)
C(6)-C(7)	1.442(4)	C(32)-C(33)	1.378(3)
C(7)-O(7)	1.229(4)	C(33)-C(34)	1.520(3)
C(15)-C(16)	1.545(3)		
C(15)-C(22)	1.550(3)	O(1)-C(1)-C(2)	119.7(2)
C(15)-C(28)	1.561(3)	O(1)-C(1)-C(6)	119.4(2)
C(16)-C(17)	1.385(3)	C(2)-C(1)-C(6)	120.8(2)
C(16)-C(21)	1.399(3)	C(1)-C(2)-C(3)	115.6(2)
C(17)-C(18)	1.391(4)	C(1)-C(2)-C(15)	123.92(19)
C(18)-C(19)	1.382(4)	C(3)-C(2)-C(15)	119.7(2)
C(19)-C(20)	1.383(4)	C(4)-C(3)-C(2)	123.8(2)
C(20)-C(21)	1.379(4)	C(5)-C(4)-C(3)	118.9(2)
C(21)-C(34)	1.504(3)	C(4)-C(5)-C(6)	120.1(2)
C(22)-C(23)	1.390(3)	C(5)-C(6)-C(1)	119.7(2)
C(22)-C(27)	1.402(3)	C(5)-C(6)-C(7)	119.6(2)
C(23)-C(24)	1.394(3)	C(1)-C(6)-C(7)	120.7(2)
C(24)-C(25)	1.379(4)	O(7)-C(7)-C(6)	125.1(3)

C(2)-C(15)-C(16)	109.13(17)	C(25)-C(24)-C(23)	120.9(2)
C(2)-C(15)-C(22)	118.69(18)	C(24)-C(25)-C(26)	120.0(2)
C(16)-C(15)-C(22)	107.23(17)	C(27)-C(26)-C(25)	119.4(2)
C(2)-C(15)-C(28)	115.40(18)	C(26)-C(27)-C(22)	121.2(2)
C(16)-C(15)-C(28)	106.09(17)	C(26)-C(27)-C(34)	124.7(2)
C(22)-C(15)-C(28)	99.23(16)	C(22)-C(27)-C(34)	113.76(19)
C(17)-C(16)-C(21)	119.5(2)	C(29)-C(28)-C(33)	118.8(2)
C(17)-C(16)-C(15)	126.2(2)	C(29)-C(28)-C(15)	127.7(2)
C(21)-C(16)-C(15)	114.31(19)	C(33)-C(28)-C(15)	112.95(19)
C(16)-C(17)-C(18)	119.5(2)	C(28)-C(29)-C(30)	119.8(2)
C(19)-C(18)-C(17)	120.5(2)	C(31)-C(30)-C(29)	120.8(3)
C(18)-C(19)-C(20)	120.2(3)	C(30)-C(31)-C(32)	120.0(2)
C(21)-C(20)-C(19)	119.6(2)	C(33)-C(32)-C(31)	119.8(2)
C(20)-C(21)-C(16)	120.7(2)	C(32)-C(33)-C(28)	120.6(2)
C(20)-C(21)-C(34)	126.3(2)	C(32)-C(33)-C(34)	125.4(2)
C(16)-C(21)-C(34)	113.0(2)	C(28)-C(33)-C(34)	113.52(19)
C(23)-C(22)-C(27)	118.7(2)	C(21)-C(34)-C(27)	107.57(18)
C(23)-C(22)-C(15)	127.40(19)	C(21)-C(34)-C(33)	107.08(18)
C(27)-C(22)-C(15)	113.18(19)	C(27)-C(34)-C(33)	103.50(18)
C(22)-C(23)-C(24)	119.5(2)		

**Fig. S4.** Molecular structure of **C (17)**.



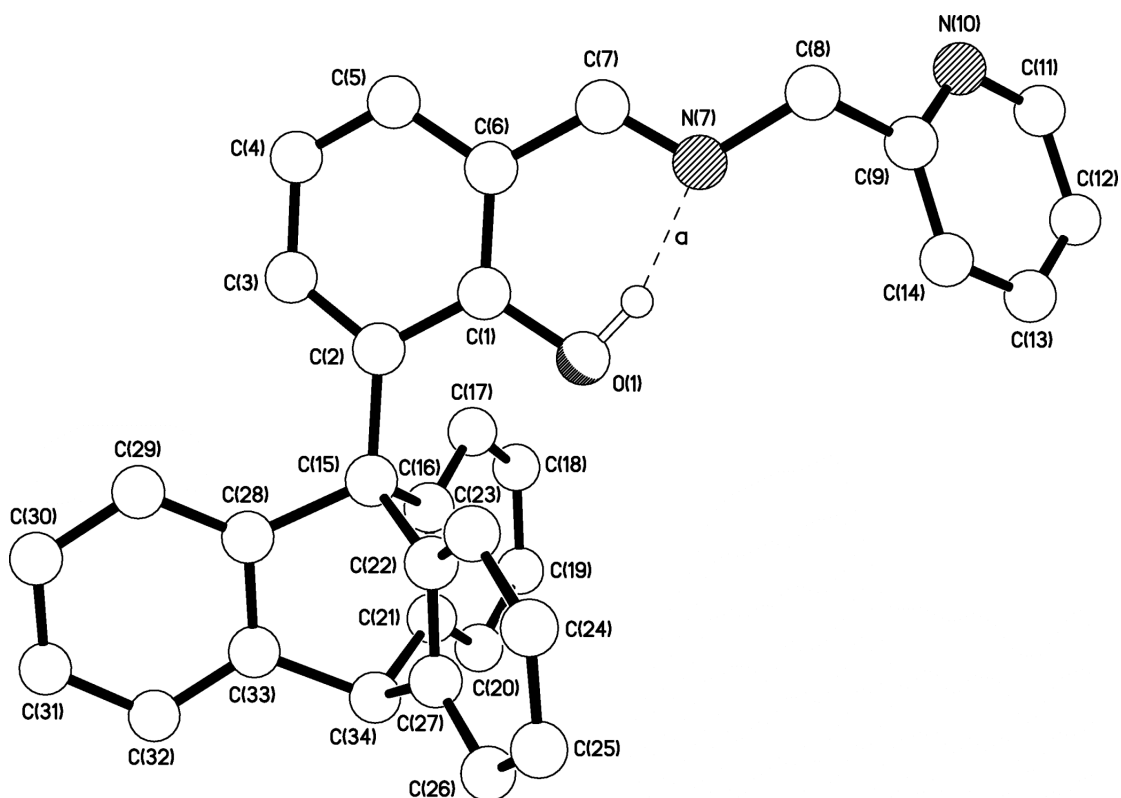
Bond lengths [Å] and angles [°] for **C (17)**.

O(1)-C(1)	1.323(5)	C(20)-C(21)	1.471(5)
C(1)-C(6)	1.390(6)	C(20)-C(25)	1.503(7)
C(1)-C(2)	1.428(6)		
C(2)-C(3)	1.372(8)	O(1)-C(1)-C(6)	117.2(4)
C(2)-C(7)	1.438(8)	O(1)-C(1)-C(2)	122.6(4)
C(3)-C(4)	1.348(8)	C(6)-C(1)-C(2)	120.2(4)
C(4)-C(5)	1.403(6)	C(3)-C(2)-C(1)	117.8(5)
C(5)-C(6)	1.427(6)	C(3)-C(2)-C(7)	122.7(5)
C(6)-C(8)	1.475(5)	C(1)-C(2)-C(7)	119.5(5)
C(7)-O(7)	1.228(8)	C(4)-C(3)-C(2)	123.9(5)
C(8)-C(21)	1.423(5)	C(3)-C(4)-C(5)	119.6(5)
C(8)-C(9)	1.431(5)	C(4)-C(5)-C(6)	119.2(4)
C(9)-C(14)	1.433(5)	C(1)-C(6)-C(5)	119.3(4)
C(9)-C(10)	1.465(5)	C(1)-C(6)-C(8)	121.0(4)
C(10)-C(11)	1.369(7)	C(5)-C(6)-C(8)	119.7(4)
C(10)-C(22)	1.513(7)	O(7)-C(7)-C(2)	125.7(6)
C(11)-C(12)	1.416(8)	C(21)-C(8)-C(9)	122.2(3)
C(12)-C(13)	1.344(8)	C(21)-C(8)-C(6)	119.1(3)
C(13)-C(14)	1.450(6)	C(9)-C(8)-C(6)	118.5(3)
C(13)-C(23)	1.500(7)	C(8)-C(9)-C(14)	117.3(3)
C(14)-C(15)	1.387(6)	C(8)-C(9)-C(10)	124.8(3)
C(15)-C(16)	1.382(6)	C(14)-C(9)-C(10)	117.9(3)
C(16)-C(21)	1.424(5)	C(11)-C(10)-C(9)	116.7(4)
C(16)-C(17)	1.447(6)	C(11)-C(10)-C(22)	116.6(4)
C(17)-C(18)	1.355(8)	C(9)-C(10)-C(22)	126.6(4)
C(17)-C(24)	1.494(7)	C(10)-C(11)-C(12)	124.5(5)
C(18)-C(19)	1.402(8)	C(13)-C(12)-C(11)	121.2(4)
C(19)-C(20)	1.357(6)	C(12)-C(13)-C(14)	117.7(5)

C(12)-C(13)-C(23)	120.3(5)	C(18)-C(17)-C(24)	121.2(5)
C(14)-C(13)-C(23)	121.9(5)	C(16)-C(17)-C(24)	121.5(5)
C(15)-C(14)-C(9)	119.3(3)	C(17)-C(18)-C(19)	121.8(5)
C(15)-C(14)-C(13)	118.8(4)	C(20)-C(19)-C(18)	123.8(5)
C(9)-C(14)-C(13)	121.9(4)	C(19)-C(20)-C(21)	117.5(4)
C(16)-C(15)-C(14)	123.8(3)	C(19)-C(20)-C(25)	114.9(4)
C(15)-C(16)-C(21)	119.1(3)	C(21)-C(20)-C(25)	127.5(4)
C(15)-C(16)-C(17)	118.9(4)	C(8)-C(21)-C(16)	118.2(3)
C(21)-C(16)-C(17)	121.9(4)	C(8)-C(21)-C(20)	124.2(3)
C(18)-C(17)-C(16)	117.3(5)	C(16)-C(21)-C(20)	117.6(3)



**Fig. S5.** Molecular structure of **32D**.

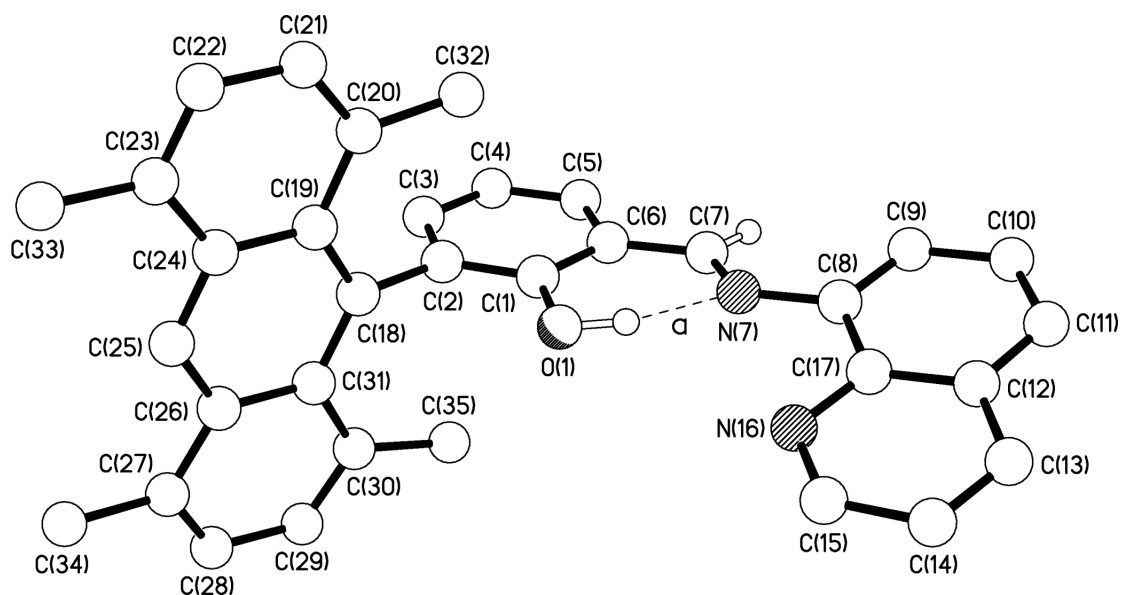


Bond lengths [Å] and angles [°] for **32D**.

O(1)-C(1)	1.349(2)	C(18)-C(19)	1.372(4)
C(1)-C(2)	1.406(3)	C(19)-C(20)	1.386(4)
C(1)-C(6)	1.413(2)	C(20)-C(21)	1.387(3)
C(2)-C(3)	1.392(3)	C(21)-C(34)	1.508(3)
C(2)-C(15)	1.524(2)	C(22)-C(23)	1.377(3)
C(3)-C(4)	1.385(3)	C(22)-C(27)	1.397(3)
C(4)-C(5)	1.370(3)	C(23)-C(24)	1.393(3)
C(5)-C(6)	1.392(3)	C(24)-C(25)	1.374(4)
C(6)-C(7)	1.457(3)	C(25)-C(26)	1.385(3)
C(7)-N(7)	1.268(3)	C(26)-C(27)	1.381(3)
N(7)-C(8)	1.461(3)	C(27)-C(34)	1.524(3)
C(8)-C(9)	1.497(3)	C(28)-C(29)	1.378(3)
C(9)-N(10)	1.317(3)	C(28)-C(33)	1.403(3)
C(9)-C(14)	1.371(3)	C(29)-C(30)	1.391(3)
N(10)-C(11)	1.331(4)	C(30)-C(31)	1.368(4)
C(11)-C(12)	1.349(4)	C(31)-C(32)	1.382(3)
C(12)-C(13)	1.350(5)	C(32)-C(33)	1.389(3)
C(13)-C(14)	1.372(5)	C(33)-C(34)	1.516(3)
C(15)-C(16)	1.552(2)		
C(15)-C(22)	1.559(2)	O(1)-C(1)-C(2)	119.67(15)
C(15)-C(28)	1.563(2)	O(1)-C(1)-C(6)	119.27(16)
C(16)-C(17)	1.385(3)	C(2)-C(1)-C(6)	120.95(17)
C(16)-C(21)	1.388(3)	C(3)-C(2)-C(1)	116.13(16)
C(17)-C(18)	1.383(3)	C(3)-C(2)-C(15)	121.30(16)

C(1)-C(2)-C(15)	121.64(16)	C(18)-C(19)-C(20)	120.2(2)
C(4)-C(3)-C(2)	123.28(18)	C(19)-C(20)-C(21)	119.0(2)
C(5)-C(4)-C(3)	119.27(19)	C(20)-C(21)-C(16)	120.8(2)
C(4)-C(5)-C(6)	120.41(18)	C(20)-C(21)-C(34)	126.18(19)
C(5)-C(6)-C(1)	119.31(18)	C(16)-C(21)-C(34)	113.02(16)
C(5)-C(6)-C(7)	119.57(17)	C(23)-C(22)-C(27)	119.22(18)
C(1)-C(6)-C(7)	121.06(18)	C(23)-C(22)-C(15)	127.35(16)
N(7)-C(7)-C(6)	123.08(17)	C(27)-C(22)-C(15)	113.17(15)
C(7)-N(7)-C(8)	119.67(18)	C(22)-C(23)-C(24)	119.74(19)
N(7)-C(8)-C(9)	111.33(17)	C(25)-C(24)-C(23)	120.5(2)
N(10)-C(9)-C(14)	121.5(2)	C(24)-C(25)-C(26)	120.1(2)
N(10)-C(9)-C(8)	116.32(19)	C(27)-C(26)-C(25)	119.4(2)
C(14)-C(9)-C(8)	122.2(2)	C(26)-C(27)-C(22)	120.73(18)
C(9)-N(10)-C(11)	117.1(2)	C(26)-C(27)-C(34)	125.26(18)
N(10)-C(11)-C(12)	125.3(3)	C(22)-C(27)-C(34)	113.89(17)
C(11)-C(12)-C(13)	117.1(3)	C(29)-C(28)-C(33)	118.70(17)
C(12)-C(13)-C(14)	119.5(3)	C(29)-C(28)-C(15)	128.87(17)
C(9)-C(14)-C(13)	119.5(3)	C(33)-C(28)-C(15)	112.09(16)
C(2)-C(15)-C(16)	108.20(14)	C(28)-C(29)-C(30)	120.1(2)
C(2)-C(15)-C(22)	117.19(14)	C(31)-C(30)-C(29)	120.8(2)
C(16)-C(15)-C(22)	106.38(14)	C(30)-C(31)-C(32)	119.9(2)
C(2)-C(15)-C(28)	118.01(15)	C(31)-C(32)-C(33)	119.7(2)
C(16)-C(15)-C(28)	105.61(13)	C(32)-C(33)-C(28)	120.37(19)
C(22)-C(15)-C(28)	100.34(13)	C(32)-C(33)-C(34)	124.69(18)
C(17)-C(16)-C(21)	119.58(17)	C(28)-C(33)-C(34)	114.79(16)
C(17)-C(16)-C(15)	125.62(16)	C(21)-C(34)-C(33)	106.59(16)
C(21)-C(16)-C(15)	114.80(16)	C(21)-C(34)-C(27)	106.31(15)
C(18)-C(17)-C(16)	119.4(2)	C(33)-C(34)-C(27)	104.34(15)
C(19)-C(18)-C(17)	121.0(2)		

**Fig. S6.** Molecular structure of **73C**.

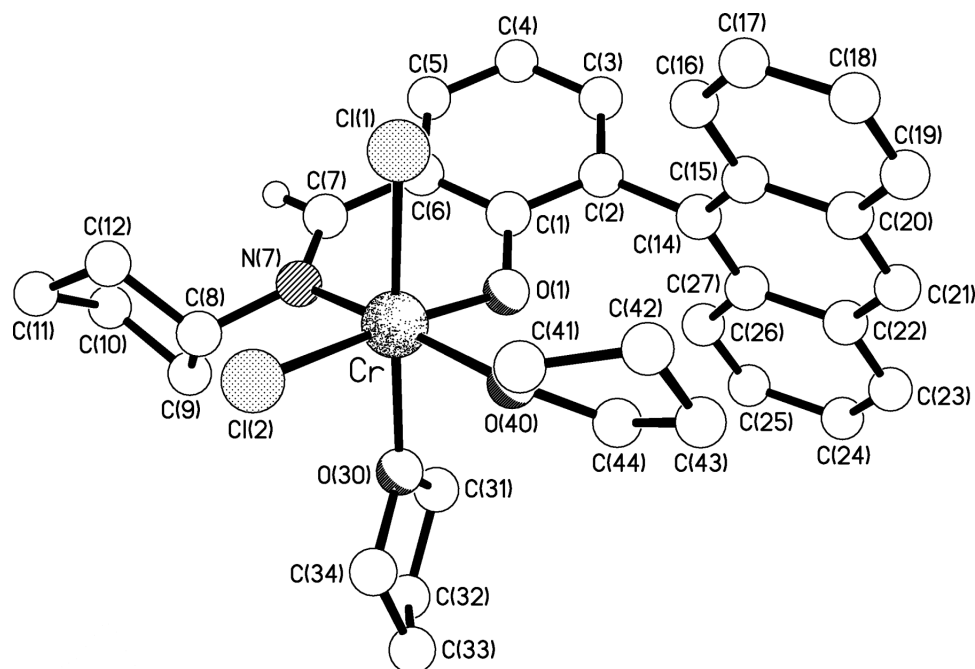


Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **73C**.

O(1)-C(1)	1.344(2)	C(23)-C(24)	1.437(3)
C(1)-C(2)	1.399(3)	C(23)-C(33)	1.505(4)
C(1)-C(6)	1.408(3)	C(24)-C(25)	1.392(3)
C(2)-C(3)	1.383(3)	C(25)-C(26)	1.389(3)
C(2)-C(18)	1.499(3)	C(26)-C(31)	1.438(3)
C(3)-C(4)	1.386(3)	C(26)-C(27)	1.442(3)
C(4)-C(5)	1.370(3)	C(27)-C(28)	1.349(4)
C(5)-C(6)	1.404(3)	C(27)-C(34)	1.503(3)
C(6)-C(7)	1.443(3)	C(28)-C(29)	1.408(4)
C(7)-N(7)	1.283(3)	C(29)-C(30)	1.367(3)
N(7)-C(8)	1.409(3)	C(30)-C(31)	1.457(3)
C(8)-C(9)	1.370(3)	C(30)-C(35)	1.510(3)
C(8)-C(17)	1.431(3)		
C(9)-C(10)	1.410(4)	O(1)-C(1)-C(2)	118.21(18)
C(10)-C(11)	1.360(4)	O(1)-C(1)-C(6)	121.47(18)
C(11)-C(12)	1.402(4)	C(2)-C(1)-C(6)	120.31(18)
C(12)-C(13)	1.418(4)	C(3)-C(2)-C(1)	118.78(19)
C(12)-C(17)	1.420(3)	C(3)-C(2)-C(18)	118.02(18)
C(13)-C(14)	1.348(4)	C(1)-C(2)-C(18)	123.20(17)
C(14)-C(15)	1.397(4)	C(2)-C(3)-C(4)	121.6(2)
C(15)-N(16)	1.317(3)	C(5)-C(4)-C(3)	119.7(2)
N(16)-C(17)	1.366(3)	C(4)-C(5)-C(6)	120.8(2)
C(18)-C(19)	1.421(3)	C(5)-C(6)-C(1)	118.76(19)
C(18)-C(31)	1.427(3)	C(5)-C(6)-C(7)	119.99(19)
C(19)-C(24)	1.442(3)	C(1)-C(6)-C(7)	121.25(18)
C(19)-C(20)	1.461(3)	N(7)-C(7)-C(6)	120.84(19)
C(20)-C(21)	1.356(3)	C(7)-N(7)-C(8)	123.09(18)
C(20)-C(32)	1.503(3)	C(9)-C(8)-N(7)	124.4(2)
C(21)-C(22)	1.403(4)	C(9)-C(8)-C(17)	119.7(2)
C(22)-C(23)	1.351(4)	N(7)-C(8)-C(17)	115.82(18)

C(8)-C(9)-C(10)	120.7(3)	C(23)-C(22)-C(21)	121.3(2)
C(11)-C(10)-C(9)	120.4(2)	C(22)-C(23)-C(24)	118.0(2)
C(10)-C(11)-C(12)	121.0(2)	C(22)-C(23)-C(33)	120.4(2)
C(11)-C(12)-C(13)	123.4(2)	C(24)-C(23)-C(33)	121.7(2)
C(11)-C(12)-C(17)	119.4(3)	C(25)-C(24)-C(23)	119.2(2)
C(13)-C(12)-C(17)	117.1(2)	C(25)-C(24)-C(19)	118.75(19)
C(14)-C(13)-C(12)	119.6(2)	C(23)-C(24)-C(19)	122.0(2)
C(13)-C(14)-C(15)	119.1(3)	C(26)-C(25)-C(24)	123.9(2)
N(16)-C(15)-C(14)	124.5(3)	C(25)-C(26)-C(31)	118.87(19)
C(15)-N(16)-C(17)	117.3(2)	C(25)-C(26)-C(27)	119.1(2)
N(16)-C(17)-C(12)	122.3(2)	C(31)-C(26)-C(27)	122.0(2)
N(16)-C(17)-C(8)	118.87(19)	C(28)-C(27)-C(26)	118.0(2)
C(12)-C(17)-C(8)	118.8(2)	C(28)-C(27)-C(34)	120.4(2)
C(19)-C(18)-C(31)	122.27(18)	C(26)-C(27)-C(34)	121.6(2)
C(19)-C(18)-C(2)	118.74(17)	C(27)-C(28)-C(29)	121.1(2)
C(31)-C(18)-C(2)	118.47(18)	C(30)-C(29)-C(28)	123.8(2)
C(18)-C(19)-C(24)	118.05(18)	C(29)-C(30)-C(31)	118.1(2)
C(18)-C(19)-C(20)	125.41(19)	C(29)-C(30)-C(35)	116.0(2)
C(24)-C(19)-C(20)	116.52(19)	C(31)-C(30)-C(35)	125.8(2)
C(21)-C(20)-C(19)	118.4(2)	C(18)-C(31)-C(26)	118.05(18)
C(21)-C(20)-C(32)	115.5(2)	C(18)-C(31)-C(30)	124.99(19)
C(19)-C(20)-C(32)	126.0(2)	C(26)-C(31)-C(30)	116.96(18)
C(20)-C(21)-C(22)	123.8(2)		

**Fig. S7.** Molecular structure of **III**.

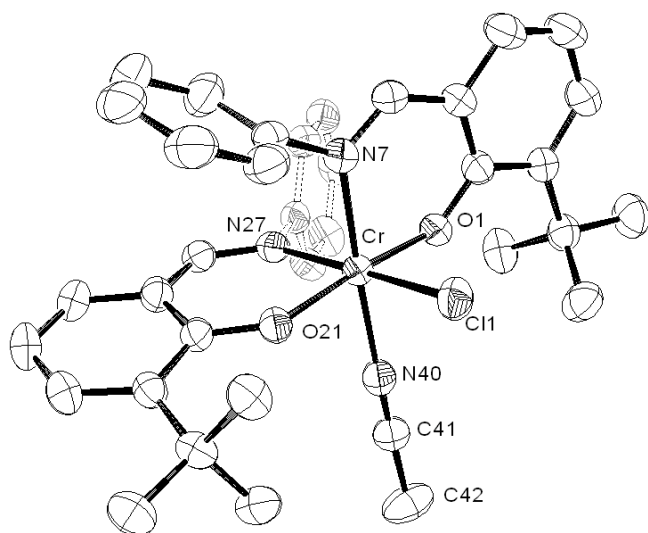


Bond lengths [Å] and angles [°] for **III**.

Cr-O(1)	1.907(3)	C(15)-C(20)	1.435(7)
Cr-N(7)	2.038(4)	C(16)-C(17)	1.351(8)
Cr-O(30)	2.062(5)	C(17)-C(18)	1.410(8)
Cr-O(40)	2.071(4)	C(18)-C(19)	1.361(9)
Cr-Cl(1)	2.3266(16)	C(19)-C(20)	1.417(8)
Cr-Cl(2)	2.3402(16)	C(20)-C(21)	1.405(8)
O(1)-C(1)	1.320(6)	C(21)-C(22)	1.391(8)
C(1)-C(6)	1.410(7)	C(22)-C(23)	1.429(8)
C(1)-C(2)	1.414(7)	C(22)-C(27)	1.435(7)
C(2)-C(3)	1.388(7)	C(23)-C(24)	1.354(9)
C(2)-C(14)	1.503(7)	C(24)-C(25)	1.432(9)
C(3)-C(4)	1.395(8)	C(25)-C(26)	1.346(9)
C(4)-C(5)	1.379(8)	C(26)-C(27)	1.429(8)
C(5)-C(6)	1.404(7)	O(30)-C(31)	1.433(9)
C(6)-C(7)	1.441(7)	O(30)-C(34)	1.462(8)
C(7)-N(7)	1.295(7)	C(31)-C(32)	1.516(12)
N(7)-C(8)	1.493(7)	C(32)-C(33)	1.536(17)
C(8)-C(12)	1.509(7)	C(33)-C(34)	1.405(16)
C(8)-C(9)	1.517(7)	O(40)-C(41)	1.431(8)
C(9)-C(10')	1.481(9)	O(40)-C(44)	1.450(8)
C(9)-C(10)	1.562(8)	C(41)-C(42)	1.488(10)
C(10)-C(11)	1.501(9)	C(42)-C(43)	1.494(12)
C(11)-C(12)	1.481(8)	C(43)-C(44)	1.470(9)
C(10')-C(11')	1.528(9)	C(51)-C(52)	1.3900
C(11')-C(12)	1.530(9)	C(51)-C(56)	1.3900
C(14)-C(27)	1.409(8)	C(52)-C(53)	1.3900
C(14)-C(15)	1.410(7)	C(53)-C(54)	1.3900
C(15)-C(16)	1.430(8)	C(54)-C(55)	1.3900

C(55)-C(56)	1.3900	C(8)-C(12)-C(11')	103.0(6)
O(1)-Cr-N(7)	88.00(16)	C(27)-C(14)-C(15)	120.2(4)
O(1)-Cr-O(30)	87.07(17)	C(27)-C(14)-C(2)	120.2(4)
N(7)-Cr-O(30)	88.56(18)	C(15)-C(14)-C(2)	119.5(5)
O(1)-Cr-O(40)	87.13(15)	C(14)-C(15)-C(16)	122.7(4)
N(7)-Cr-O(40)	172.1(2)	C(14)-C(15)-C(20)	119.9(5)
O(30)-Cr-O(40)	85.00(18)	C(16)-C(15)-C(20)	117.4(5)
O(1)-Cr-Cl(1)	92.02(12)	C(17)-C(16)-C(15)	121.4(5)
N(7)-Cr-Cl(1)	94.69(15)	C(16)-C(17)-C(18)	121.2(6)
O(30)-Cr-Cl(1)	176.59(13)	C(19)-C(18)-C(17)	119.7(5)
O(40)-Cr-Cl(1)	91.68(14)	C(18)-C(19)-C(20)	121.2(5)
O(1)-Cr-Cl(2)	175.59(12)	C(21)-C(20)-C(19)	121.7(5)
N(7)-Cr-Cl(2)	95.01(13)	C(21)-C(20)-C(15)	119.1(5)
O(30)-Cr-Cl(2)	89.78(14)	C(19)-C(20)-C(15)	119.2(5)
O(40)-Cr-Cl(2)	89.52(12)	C(22)-C(21)-C(20)	121.3(5)
Cl(1)-Cr-Cl(2)	90.95(7)	C(21)-C(22)-C(23)	121.6(5)
C(1)-O(1)-Cr	125.5(3)	C(21)-C(22)-C(27)	119.9(5)
O(1)-C(1)-C(6)	121.9(4)	C(23)-C(22)-C(27)	118.6(5)
O(1)-C(1)-C(2)	118.9(4)	C(24)-C(23)-C(22)	121.5(5)
C(6)-C(1)-C(2)	119.1(4)	C(23)-C(24)-C(25)	119.5(6)
C(3)-C(2)-C(1)	118.9(4)	C(26)-C(25)-C(24)	121.1(6)
C(3)-C(2)-C(14)	120.3(4)	C(25)-C(26)-C(27)	121.1(5)
C(1)-C(2)-C(14)	120.7(4)	C(14)-C(27)-C(26)	122.2(5)
C(2)-C(3)-C(4)	122.1(5)	C(14)-C(27)-C(22)	119.5(5)
C(5)-C(4)-C(3)	119.2(5)	C(26)-C(27)-C(22)	118.3(5)
C(4)-C(5)-C(6)	120.5(5)	C(31)-O(30)-C(34)	110.4(6)
C(5)-C(6)-C(1)	120.2(4)	C(31)-O(30)-Cr	124.7(4)
C(5)-C(6)-C(7)	117.9(4)	C(34)-O(30)-Cr	124.7(6)
C(1)-C(6)-C(7)	121.7(4)	O(30)-C(31)-C(32)	102.4(7)
N(7)-C(7)-C(6)	126.7(5)	C(31)-C(32)-C(33)	103.3(8)
C(7)-N(7)-C(8)	117.3(4)	C(34)-C(33)-C(32)	102.7(9)
C(7)-N(7)-Cr	121.0(3)	C(33)-C(34)-O(30)	107.4(9)
C(8)-N(7)-Cr	121.7(3)	C(41)-O(40)-C(44)	107.9(5)
N(7)-C(8)-C(12)	113.4(5)	C(41)-O(40)-Cr	126.6(4)
N(7)-C(8)-C(9)	114.4(5)	C(44)-O(40)-Cr	123.6(4)
C(12)-C(8)-C(9)	105.1(4)	O(40)-C(41)-C(42)	105.3(6)
C(10')-C(9)-C(8)	104.9(6)	C(41)-C(42)-C(43)	103.7(6)
C(10')-C(9)-C(10)	39.1(8)	C(44)-C(43)-C(42)	104.6(6)
C(8)-C(9)-C(10)	101.7(5)	O(40)-C(44)-C(43)	107.9(6)
C(11)-C(10)-C(9)	102.5(6)	C(52)-C(51)-C(56)	120.0
C(12)-C(11)-C(10)	97.9(6)	C(51)-C(52)-C(53)	120.0
C(9)-C(10')-C(11')	96.8(9)	C(54)-C(53)-C(52)	120.0
C(10')-C(11')-C(12)	103.4(8)	C(55)-C(54)-C(53)	120.0
C(11)-C(12)-C(8)	107.0(5)	C(54)-C(55)-C(56)	120.0
C(11)-C(12)-C(11')	22.7(13)	C(55)-C(56)-C(51)	120.0

**Fig. S8.** Molecular structure of **V**.



Bond lengths [Å] and angles [°] for **V**.

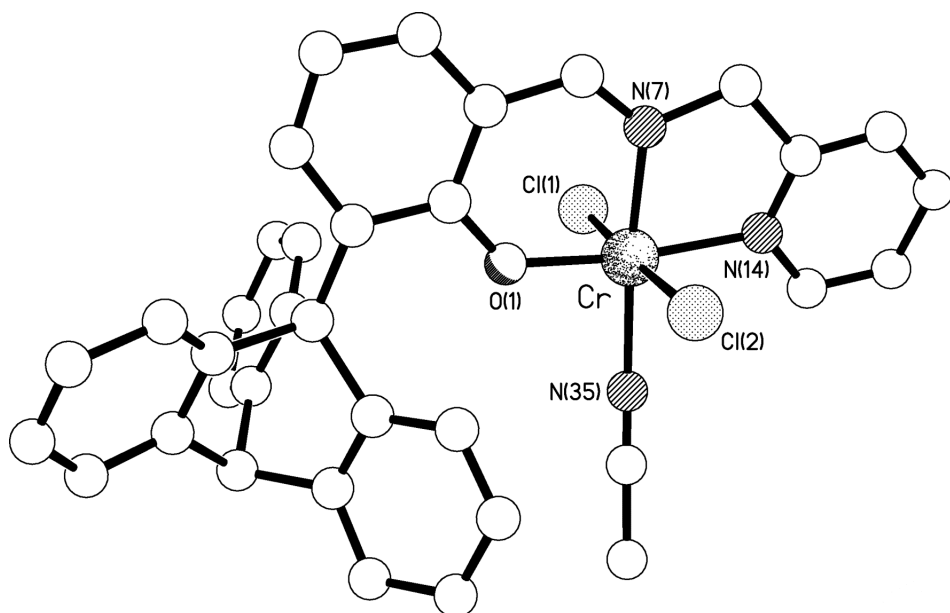
Cr-O1	1.913(2)	O21-C21	1.301(4)
Cr-O21	1.923(2)	C21-C26	1.415(5)
Cr-N7	2.035(3)	C21-C22	1.429(5)
Cr-N27	2.057(3)	C22-C23	1.375(5)
Cr-N40	2.094(3)	C22-C34	1.535(5)
Cr-Cl1	2.3395(11)	C23-C24	1.404(6)
O1-C1	1.300(4)	C24-C25	1.371(6)
C1-C6	1.415(6)	C25-C26	1.405(5)
C1-C2	1.434(5)	C26-C27	1.431(5)
C2-C3	1.383(6)	C27-N27	1.304(5)
C2-C14	1.527(5)	N27-C33	1.432(3)
C3-C4	1.383(7)	C28-C29	1.39
C4-C5	1.359(7)	C28-C33	1.39
C5-C6	1.409(6)	C29-C30	1.39
C6-C7	1.427(6)	C30-C31	1.39
C7-N7	1.295(5)	C31-C32	1.39
N7-C13	1.434(3)	C32-C33	1.39
C8-C9	1.39	C34-C35	1.536(5)
C8-C13	1.39	C34-C37	1.538(5)
C9-C10	1.39	C34-C36	1.543(5)
C10-C11	1.39	N40-C41	1.135(5)
C11-C12	1.39	C41-C42	1.441(6)
C12-C13	1.39	N50-C51	1.25(2)
C14-C15	1.530(6)	C51-C52	1.399(14)
C14-C16	1.540(6)	N50'-C51'	1.09(3)
C14-C17	1.542(6)	C51'-C52'	1.47(4)

O1-Cr-O21	173.47(11)
O1-Cr-N7	88.82(11)
O21-Cr-N7	97.67(11)
O1-Cr-N27	91.76(11)
O21-Cr-N27	87.76(11)
N7-Cr-N27	87.96(12)
O1-Cr-N40	85.98(11)
O21-Cr-N40	87.52(11)
N7-Cr-N40	174.43(12)
N27-Cr-N40	90.22(11)
O1-Cr-Cl1	92.21(8)
O21-Cr-Cl1	88.49(8)
N7-Cr-Cl1	90.42(9)
N27-Cr-Cl1	175.68(9)
N40-Cr-Cl1	91.76(9)
C1-O1-Cr	132.2(2)
O1-C1-C6	121.2(3)
O1-C1-C2	119.5(3)
C6-C1-C2	119.3(3)
C3-C2-C1	117.2(4)
C3-C2-C14	122.4(4)
C1-C2-C14	120.4(3)
C2-C3-C4	123.5(4)
C5-C4-C3	119.8(4)
C4-C5-C6	120.3(4)
C5-C6-C1	120.0(4)
C5-C6-C7	117.4(4)
C1-C6-C7	122.6(3)
N7-C7-C6	128.0(4)
C7-N7-C13	116.9(3)
C7-N7-Cr	123.7(3)
C13-N7-Cr	119.3(2)
C9-C8-C13	120.0
C10-C9-C8	120.0
C9-C10-C11	120.0
C12-C11-C10	120.0
C11-C12-C13	120.0
C12-C13-C8	120.0
C12-C13-N7	120.8(2)
C8-C13-N7	119.1(2)

C2-C14-C15	110.9(3)
C2-C14-C16	110.0(3)
C15-C14-C16	109.5(4)
C2-C14-C17	111.2(3)
C15-C14-C17	107.8(4)
C16-C14-C17	107.3(4)
C21-O21-Cr	134.7(2)
O21-C21-C26	121.5(3)
O21-C21-C22	119.3(3)
C26-C21-C22	119.2(3)
C23-C22-C21	117.5(3)
C23-C22-C34	122.7(3)
C21-C22-C34	119.8(3)
C22-C23-C24	123.7(3)
C25-C24-C23	118.5(3)
C24-C25-C26	120.6(4)
C25-C26-C21	120.3(3)
C25-C26-C27	117.2(3)
C21-C26-C27	122.1(3)
N27-C27-C26	127.4(3)
C27-N27-C33	115.7(3)
C27-N27-Cr	124.7(2)
C33-N27-Cr	119.5(2)
C29-C28-C33	120.0
C30-C29-C28	120.0
C29-C30-C31	120.0
C32-C31-C30	120.0
C31-C32-C33	120.0
C32-C33-C28	120.0
C32-C33-N27	120.0(2)
C28-C33-N27	120.0(2)
C22-C34-C35	109.0(3)
C22-C34-C37	111.9(3)
C35-C34-C37	108.1(3)
C22-C34-C36	111.2(3)
C35-C34-C36	109.6(3)
C37-C34-C36	107.1(3)
C41-N40-Cr	178.7(3)
N40-C41-C42	179.0(4)
N50-C51-C52	165.6(14)
N50'-C51'-C52'	155.4(25)



**Fig. S9.** Molecular structure of **VIII**.

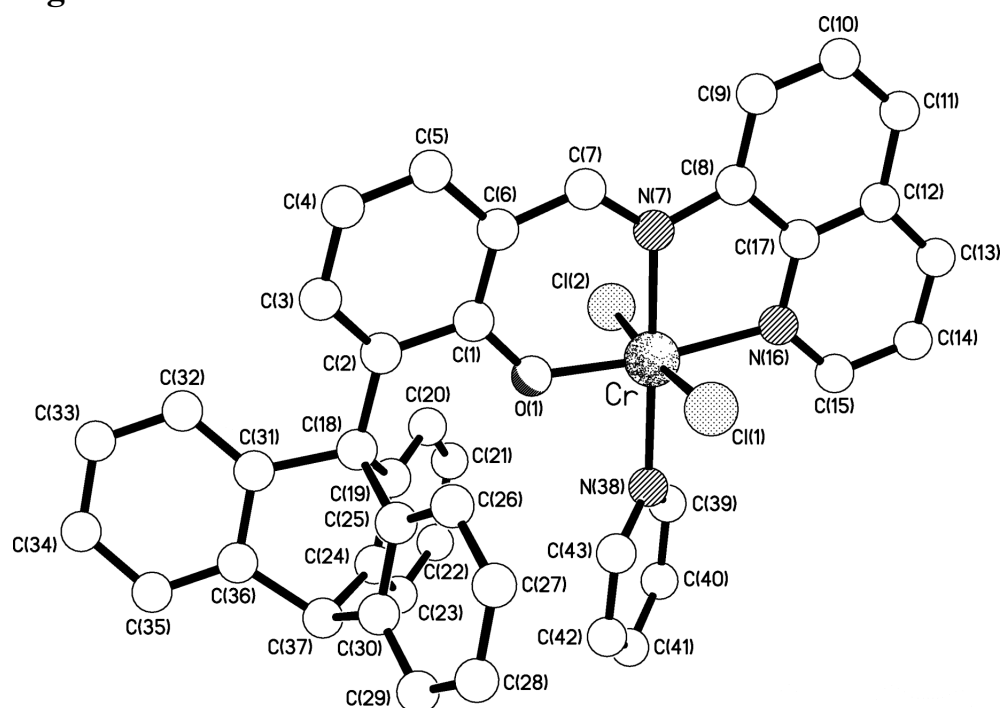


Bond lengths [Å] and angles [°] for **VIII**.

Cr-O1	1.890(9)	C17-C18	1.41(2)
Cr-N7	1.984(13)	C18-C19	1.36(2)
Cr-N14	2.086(12)	C19-C20	1.36(2)
Cr-N35	2.087(15)	C20-C21	1.36(2)
Cr-Cl1	2.350(5)	C21-C34	1.52(2)
Cr-Cl2	2.376(4)	C22-C27	1.37(2)
O1-C1	1.32(2)	C22-C23	1.40(2)
C1-C2	1.43(2)	C23-C24	1.34(2)
C1-C6	1.45(2)	C24-C25	1.43(2)
C2-C3	1.39(2)	C25-C26	1.45(3)
C2-C15	1.52(2)	C26-C27	1.39(2)
C3-C4	1.36(2)	C27-C34	1.54(2)
C4-C5	1.36(2)	C28-C29	1.33(2)
C5-C6	1.40(2)	C28-C33	1.39(2)
C6-C7	1.43(2)	C29-C30	1.40(3)
C7-N7	1.28(2)	C30-C31	1.40(3)
N7-C8	1.51(2)	C31-C32	1.36(3)
C8-C9	1.49(3)	C32-C33	1.44(3)
C9-N14	1.31(2)	C33-C34	1.58(2)
C9-C10	1.33(2)	N35-C36	1.11(2)
C10-C11	1.38(2)	C36-C37	1.45(2)
C11-C12	1.41(2)	N40-C41	0.98(3)
C12-C13	1.37(2)	C41-C42	1.60(3)
C13-N14	1.36(2)	N50-C51	1.27(3)
C15-C28	1.57(2)	C51-C52	1.32(3)
C15-C16	1.59(2)		
C15-C22	1.59(2)		
C16-C17	1.32(2)		
C16-C21	1.45(3)		

O1-Cr-N7	91.7(5)	C2-C15-C28	109.7(11)
O1-Cr-N14	172.5(5)	C2-C15-C16	114.4(13)
N7-Cr-N14	80.9(5)	C28-C15-C16	105.4(12)
O1-Cr-N35	92.6(5)	C2-C15-C22	119.6(13)
N7-Cr-N35	174.5(6)	C28-C15-C22	107.6(13)
N14-Cr-N35	94.9(5)	C16-C15-C22	99.0(11)
O1-Cr-Cl1	92.0(4)	C17-C16-C21	118.7(15)
N7-Cr-Cl1	92.1(4)	C17-C16-C15	129.9(16)
N14-Cr-Cl1	87.4(4)	C21-C16-C15	111.3(14)
N35-Cr-Cl1	91.3(4)	C16-C17-C18	121.6(16)
O1-Cr-Cl2	92.0(3)	C19-C18-C17	118.6(15)
N7-Cr-Cl2	88.0(4)	C18-C19-C20	122.0(15)
N14-Cr-Cl2	88.6(4)	C21-C20-C19	119.4(15)
N35-Cr-Cl2	88.3(4)	C20-C21-C16	119.7(15)
Cl1-Cr-Cl2	175.9(2)	C20-C21-C34	124.6(15)
C1-O1-Cr	132.2(9)	C16-C21-C34	114.9(14)
O1-C1-C2	121.2(13)	C27-C22-C23	121.5(17)
O1-C1-C6	119.7(14)	C27-C22-C15	111.9(15)
C2-C1-C6	119.1(14)	C23-C22-C15	126.5(15)
C3-C2-C1	115.4(14)	C24-C23-C22	120.1(16)
C3-C2-C15	121.7(15)	C23-C24-C25	120.1(16)
C1-C2-C15	120.3(13)	C24-C25-C26	120.1(15)
C4-C3-C2	125.8(16)	C27-C26-C25	116.3(16)
C5-C4-C3	117.9(16)	C22-C27-C26	121.9(17)
C4-C5-C6	122.6(16)	C22-C27-C34	117.1(14)
C5-C6-C7	117.6(14)	C26-C27-C34	120.1(14)
C5-C6-C1	117.8(14)	C29-C28-C33	114.7(16)
C7-C6-C1	124.5(14)	C29-C28-C15	128.1(15)
N7-C7-C6	125.8(14)	C33-C28-C15	117.1(13)
C7-N7-C8	119.3(14)	C28-C29-C30	125.4(18)
C7-N7-Cr	126.0(10)	C29-C30-C31	116.7(17)
C8-N7-Cr	114.6(12)	C32-C31-C30	123.6(19)
C9-C8-N7	111.3(16)	C31-C32-C33	114.2(18)
N14-C9-C10	124.0(17)	C28-C33-C32	125.4(17)
N14-C9-C8	116.6(15)	C28-C33-C34	110.7(14)
C10-C9-C8	119.2(16)	C32-C33-C34	123.9(15)
C9-C10-C11	119.4(16)	C21-C34-C27	105.0(13)
C10-C11-C12	118.3(16)	C21-C34-C33	103.6(12)
C13-C12-C11	118.0(17)	C27-C34-C33	106.9(12)
N14-C13-C12	121.1(16)	C36-N35-Cr	168.3(13)
C9-N14-C13	119.0(14)	N35-C36-C37	178.9(19)
C9-N14-Cr	115.9(11)	N40-C41-C42	172.9(30)
C13-N14-Cr	125.1(11)	N50-C51-C52	176.8(25)

**Fig. S10.** Molecular structure of **IX**.



Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **IX**.

Cr-O(1)	1.900(3)	C(18)-C(25)	1.551(7)
Cr-N(7)	2.020(4)	C(18)-C(31)	1.558(7)
Cr-N(16)	2.077(4)	C(18)-C(19)	1.565(6)
Cr-N(38)	2.105(4)	C(19)-C(20)	1.380(7)
Cr-Cl(2)	2.3693(17)	C(19)-C(24)	1.394(7)
Cr-Cl(1)	2.3709(17)	C(20)-C(21)	1.398(7)
O(1)-C(1)	1.303(6)	C(21)-C(22)	1.388(8)
C(1)-C(6)	1.429(6)	C(22)-C(23)	1.381(8)
C(1)-C(2)	1.441(7)	C(23)-C(24)	1.388(8)
C(2)-C(3)	1.386(7)	C(24)-C(37)	1.513(7)
C(2)-C(18)	1.529(6)	C(25)-C(26)	1.384(7)
C(3)-C(4)	1.390(7)	C(25)-C(30)	1.392(7)
C(4)-C(5)	1.367(7)	C(26)-C(27)	1.393(8)
C(5)-C(6)	1.416(7)	C(27)-C(28)	1.381(10)
C(6)-C(7)	1.424(7)	C(28)-C(29)	1.384(10)
C(7)-N(7)	1.306(6)	C(29)-C(30)	1.391(8)
N(7)-C(8)	1.419(6)	C(30)-C(37)	1.509(8)
C(8)-C(9)	1.385(6)	C(31)-C(32)	1.391(8)
C(8)-C(17)	1.428(7)	C(31)-C(36)	1.412(7)
C(9)-C(10)	1.400(7)	C(32)-C(33)	1.406(8)
C(10)-C(11)	1.364(8)	C(33)-C(34)	1.375(10)
C(11)-C(12)	1.427(7)	C(34)-C(35)	1.393(10)
C(12)-C(13)	1.410(7)	C(35)-C(36)	1.382(8)
C(12)-C(17)	1.418(6)	C(36)-C(37)	1.525(8)
C(13)-C(14)	1.356(7)	N(38)-C(43)	1.342(6)
C(14)-C(15)	1.409(7)	N(38)-C(39)	1.345(6)
C(15)-N(16)	1.321(6)	C(39)-C(40)	1.374(7)
N(16)-C(17)	1.365(6)	C(40)-C(41)	1.368(8)

C(41)-C(42)	1.385(8)	N(38)-Cr-Cl(1)	91.98(13)
C(42)-C(43)	1.380(7)	Cl(2)-Cr-Cl(1)	174.52(6)
N(51)-C(56)	1.315(10)	C(1)-O(1)-Cr	130.9(3)
N(51)-C(52)	1.335(9)	O(1)-C(1)-C(6)	122.3(4)
C(52)-C(53)	1.344(10)	O(1)-C(1)-C(2)	118.3(4)
C(53)-C(54)	1.387(12)	C(6)-C(1)-C(2)	119.3(4)
C(54)-C(55)	1.385(11)	C(3)-C(2)-C(1)	117.1(4)
C(55)-C(56)	1.343(11)	C(3)-C(2)-C(18)	122.2(4)
N(61)-C(62)	1.3900	C(1)-C(2)-C(18)	119.5(4)
N(61)-C(66)	1.3900	C(2)-C(3)-C(4)	122.8(5)
C(62)-C(63)	1.3900	C(5)-C(4)-C(3)	120.2(5)
C(63)-C(64)	1.3900	C(4)-C(5)-C(6)	120.3(5)
C(64)-C(65)	1.3900	C(5)-C(6)-C(7)	116.2(4)
C(65)-C(66)	1.3900	C(5)-C(6)-C(1)	119.3(4)
N(61')-C(62')	1.3900	C(7)-C(6)-C(1)	124.4(4)
N(61')-C(66')	1.3900	N(7)-C(7)-C(6)	126.2(4)
C(62')-C(63')	1.3900	C(7)-N(7)-C(8)	121.7(4)
C(63')-C(64')	1.3900	C(7)-N(7)-Cr	124.0(3)
C(64')-C(65')	1.3900	C(8)-N(7)-Cr	114.2(3)
C(65')-C(66')	1.3900	C(9)-C(8)-N(7)	126.7(5)
N(71)-C(72)	1.3900	C(9)-C(8)-C(17)	118.9(4)
N(71)-C(76)	1.3900	N(7)-C(8)-C(17)	114.4(4)
C(72)-C(73)	1.3900	C(8)-C(9)-C(10)	120.5(5)
C(73)-C(74)	1.3900	C(11)-C(10)-C(9)	121.8(5)
C(74)-C(75)	1.3900	C(10)-C(11)-C(12)	119.9(5)
C(75)-C(76)	1.3900	C(13)-C(12)-C(17)	117.6(5)
N(71')-C(72')	1.3900	C(13)-C(12)-C(11)	123.7(5)
N(71')-C(76')	1.3900	C(17)-C(12)-C(11)	118.7(5)
C(72')-C(73')	1.3900	C(14)-C(13)-C(12)	119.4(5)
C(73')-C(74')	1.3900	C(13)-C(14)-C(15)	120.1(5)
C(74')-C(75')	1.3900	N(16)-C(15)-C(14)	122.0(5)
C(75')-C(76')	1.3900	C(15)-N(16)-C(17)	119.2(4)
N(71'')-C(72'')	1.3900	C(15)-N(16)-Cr	128.3(3)
N(71'')-C(76'')	1.3900	C(17)-N(16)-Cr	112.5(3)
C(72'')-C(73'')	1.3900	N(16)-C(17)-C(12)	121.7(5)
C(73'')-C(74'')	1.3900	N(16)-C(17)-C(8)	118.0(4)
C(74'')-C(75'')	1.3900	C(12)-C(17)-C(8)	120.2(4)
C(75'')-C(76'')	1.3900	C(2)-C(18)-C(25)	108.9(4)
		C(2)-C(18)-C(31)	116.4(4)
O(1)-Cr-N(7)	91.97(15)	C(25)-C(18)-C(31)	107.1(4)
O(1)-Cr-N(16)	172.81(15)	C(2)-C(18)-C(19)	118.5(4)
N(7)-Cr-N(16)	80.84(16)	C(25)-C(18)-C(19)	105.6(4)
O(1)-Cr-N(38)	87.50(15)	C(31)-C(18)-C(19)	99.3(4)
N(7)-Cr-N(38)	178.88(19)	C(20)-C(19)-C(24)	119.6(5)
N(16)-Cr-N(38)	99.68(16)	C(20)-C(19)-C(18)	127.5(4)
O(1)-Cr-Cl(2)	93.74(12)	C(24)-C(19)-C(18)	112.8(4)
N(7)-Cr-Cl(2)	88.04(12)	C(19)-C(20)-C(21)	120.2(5)
N(16)-Cr-Cl(2)	85.77(12)	C(22)-C(21)-C(20)	119.7(5)
N(38)-Cr-Cl(2)	91.02(13)	C(23)-C(22)-C(21)	120.2(5)
O(1)-Cr-Cl(1)	90.97(11)	C(22)-C(23)-C(24)	119.9(5)
N(7)-Cr-Cl(1)	89.01(12)	C(23)-C(24)-C(19)	120.3(5)
N(16)-Cr-Cl(1)	89.21(13)	C(23)-C(24)-C(37)	124.7(5)

C(19)-C(24)-C(37)	114.9(5)	C(52)-C(53)-C(54)	119.0(7)
C(26)-C(25)-C(30)	119.4(5)	C(55)-C(54)-C(53)	118.3(8)
C(26)-C(25)-C(18)	126.2(4)	C(56)-C(55)-C(54)	117.3(8)
C(30)-C(25)-C(18)	114.3(5)	N(51)-C(56)-C(55)	125.9(8)
C(25)-C(26)-C(27)	119.9(5)	C(62)-N(61)-C(66)	120.0
C(28)-C(27)-C(26)	120.6(6)	N(61)-C(62)-C(63)	120.0
C(27)-C(28)-C(29)	119.6(6)	C(62)-C(63)-C(64)	120.0
C(28)-C(29)-C(30)	120.1(6)	C(65)-C(64)-C(63)	120.0
C(29)-C(30)-C(25)	120.4(6)	C(64)-C(65)-C(66)	120.0
C(29)-C(30)-C(37)	125.8(5)	C(65)-C(66)-N(61)	120.0
C(25)-C(30)-C(37)	113.8(5)	C(62')-N(61')-C(66')	120.0
C(32)-C(31)-C(36)	117.7(5)	N(61')-C(62')-C(63')	120.0
C(32)-C(31)-C(18)	128.6(5)	C(62')-C(63')-C(64')	120.0
C(36)-C(31)-C(18)	113.0(5)	C(65')-C(64')-C(63')	120.0
C(31)-C(32)-C(33)	121.5(6)	C(64')-C(65')-C(66')	120.0
C(34)-C(33)-C(32)	118.9(7)	C(65')-C(66')-N(61')	120.0
C(33)-C(34)-C(35)	120.9(6)	C(72)-N(71)-C(76)	120.0
C(36)-C(35)-C(34)	119.7(6)	N(71)-C(72)-C(73)	120.0
C(35)-C(36)-C(31)	120.9(6)	C(72)-C(73)-C(74)	120.0
C(35)-C(36)-C(37)	124.6(5)	C(75)-C(74)-C(73)	120.0
C(31)-C(36)-C(37)	113.8(5)	C(74)-C(75)-C(76)	120.0
C(30)-C(37)-C(24)	105.2(4)	C(75)-C(76)-N(71)	120.0
C(30)-C(37)-C(36)	107.9(4)	C(72')-N(71')-C(76')	120.0
C(24)-C(37)-C(36)	103.4(5)	N(71')-C(72')-C(73')	120.0
C(43)-N(38)-C(39)	117.8(4)	C(72')-C(73')-C(74')	120.0
C(43)-N(38)-Cr	118.4(3)	C(75')-C(74')-C(73')	120.0
C(39)-N(38)-Cr	123.5(3)	C(76')-C(75')-C(74')	120.0
N(38)-C(39)-C(40)	122.3(5)	C(75')-C(76')-N(71')	120.0
C(41)-C(40)-C(39)	119.5(5)	C(72'')-N(71'')-C(76'')	120.0
C(40)-C(41)-C(42)	119.1(5)	N(71'')-C(72'')-C(73'')	120.0
C(43)-C(42)-C(41)	118.4(5)	C(72'')-C(73'')-C(74'')	120.0
N(38)-C(43)-C(42)	122.8(5)	C(75'')-C(74'')-C(73'')	120.0
C(56)-N(51)-C(52)	116.2(7)	C(76'')-C(75'')-C(74'')	120.0
N(51)-C(52)-C(53)	123.4(7)	C(75'')-C(76'')-N(71'')	120.0

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