Supplementary Information

Amino acid-derived bisphenolate palladium complexes as C-C coupling catalysts

Eszter Fazekas, David T. Jenkins, Andrew A. Forbes, Brendan Gallagher, Georgina M. Rosair, Ruaraidh D. McIntosh[*]

Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS (UK)

Contents

1. ¹H and ¹³C NMR spectra of pro-ligands L1-L6

L1

Figure S1. ¹H NMR spectrum of **L1** (300 MHz, CDCl$_3$ at 298 K).

Figure S2. ¹³C NMR spectrum of **L1** (75 MHz, CDCl$_3$ at 298 K).

L2
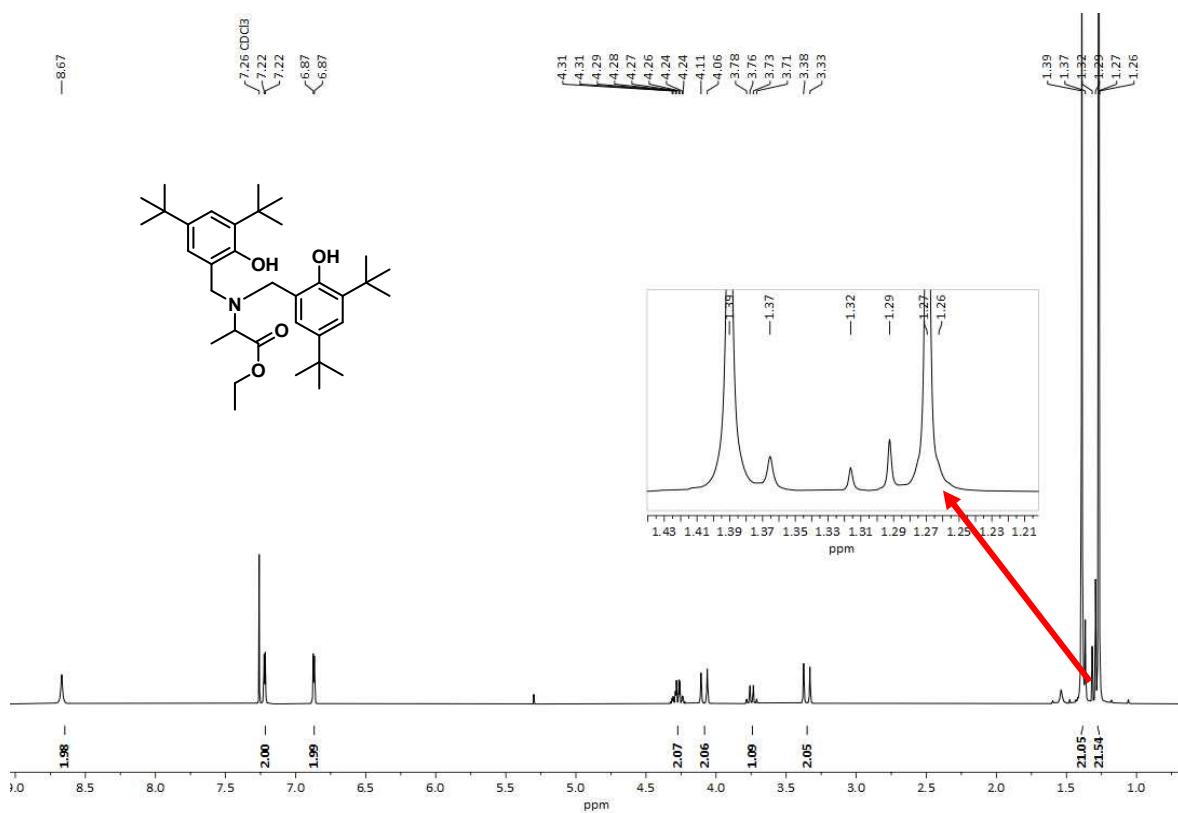
Figure S3. ^{1}H NMR spectrum of **L2** (300 MHz, CDCl$_3$ at 298 K).
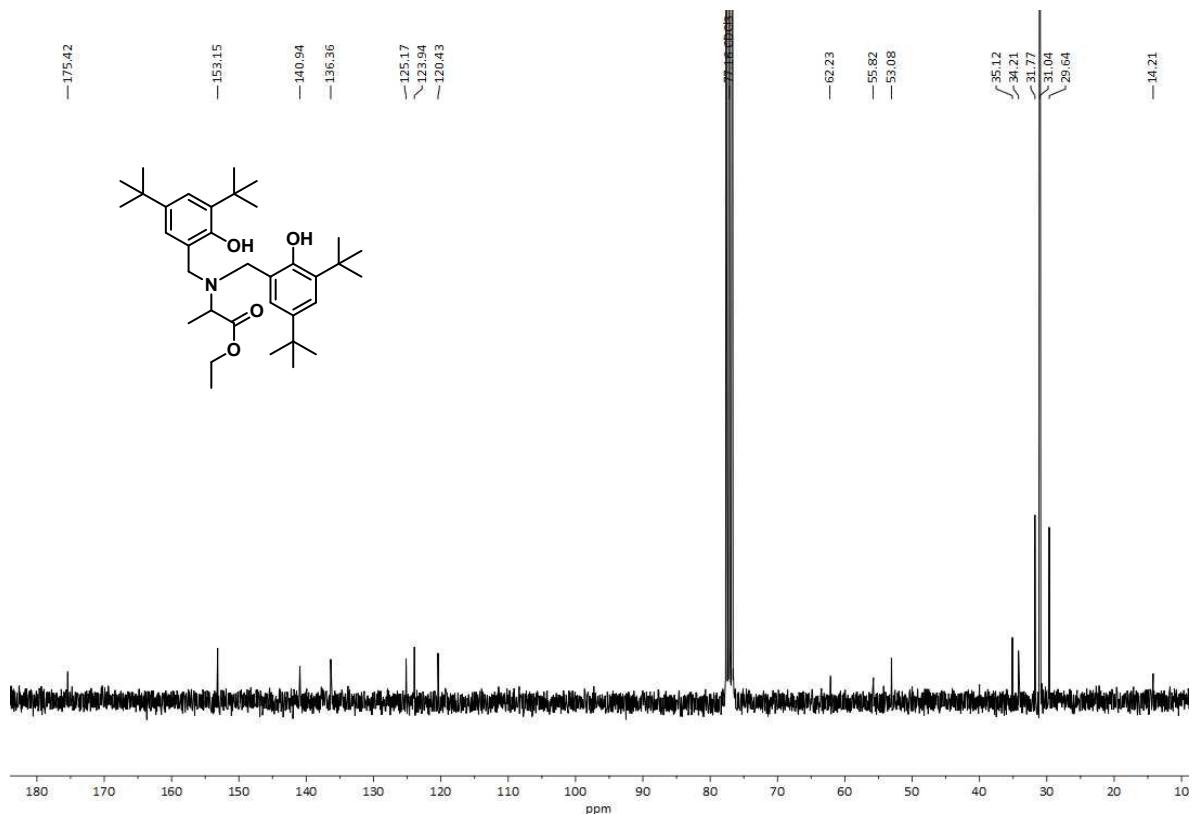
Figure S4. ^{13}C NMR spectrum of **L2** (75 MHz, CDCl$_3$ at 298 K).

L3
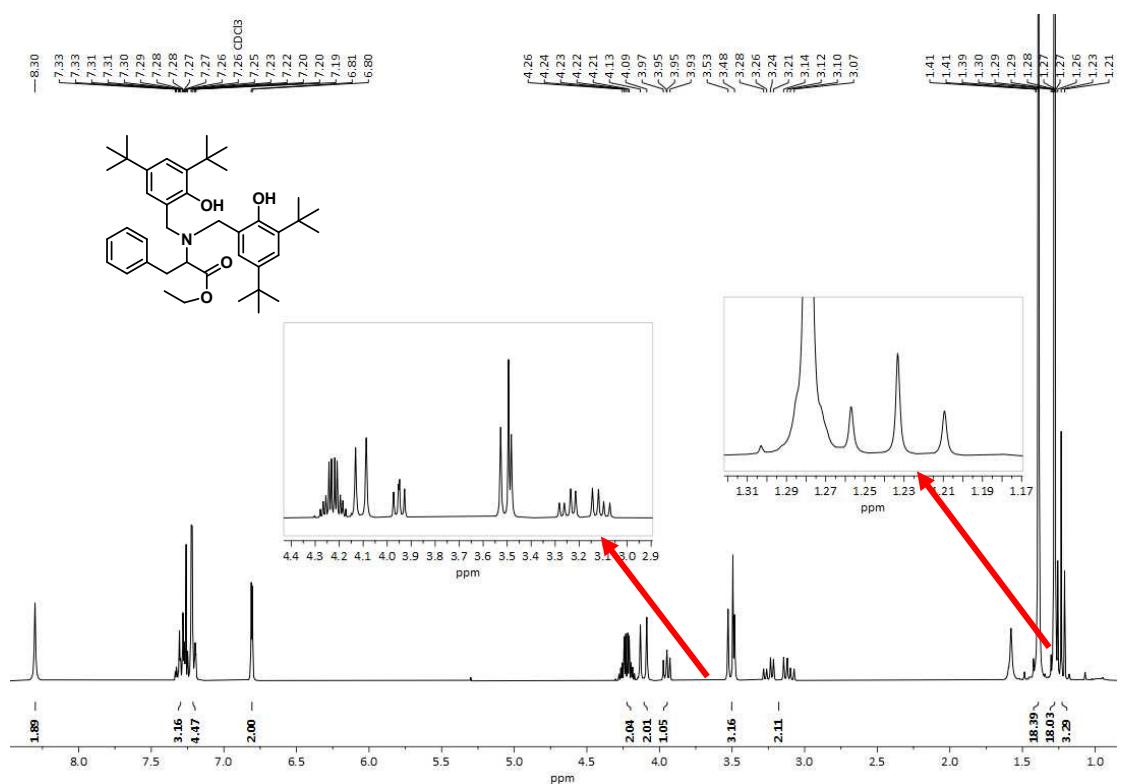
Figure S5. ^{1}H NMR spectrum of **L3** (300 MHz, CDCl$_3$ at 298 K).
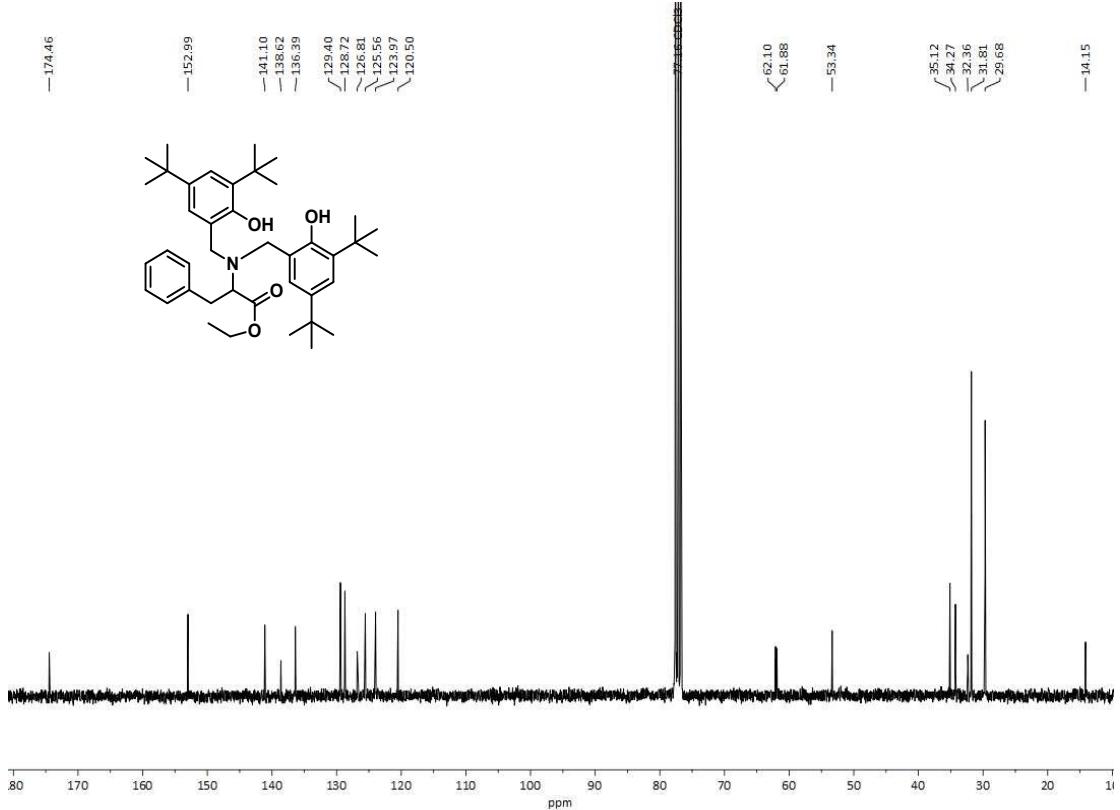
Figure S6. ^{13}C NMR spectrum of **L3** (75 MHz, CDCl$_3$ at 298 K).

L4
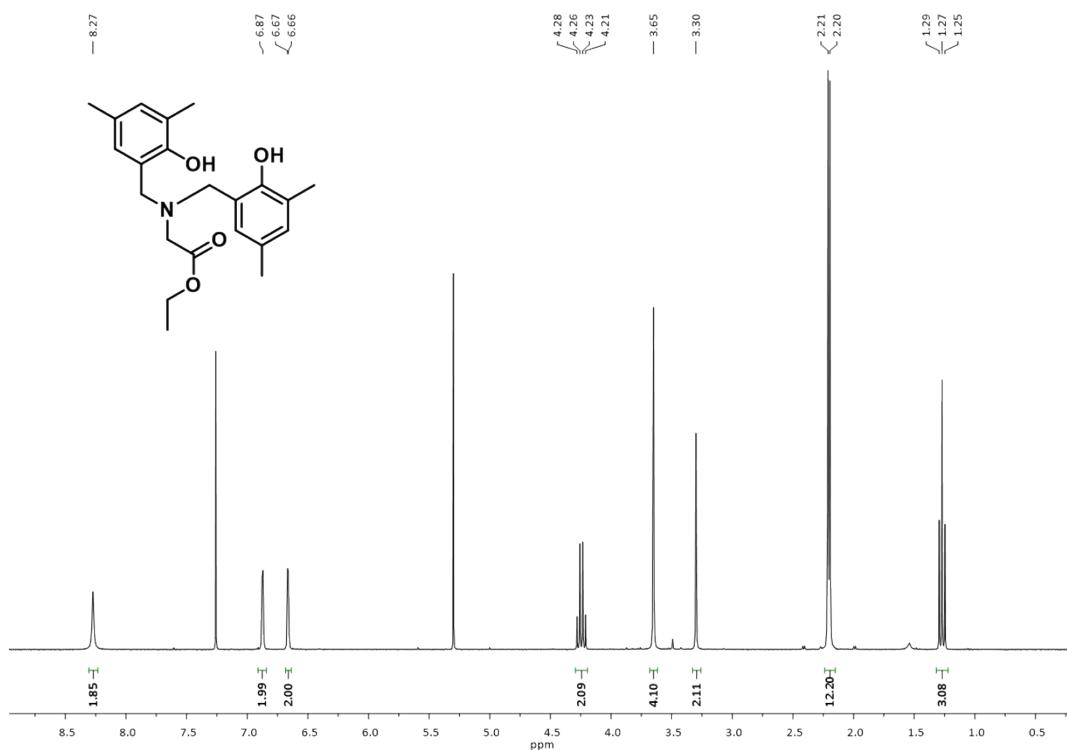
Figure S7. ^{1}H NMR spectrum of **L4** (300 MHz, CDCl$_3$ at 298 K).
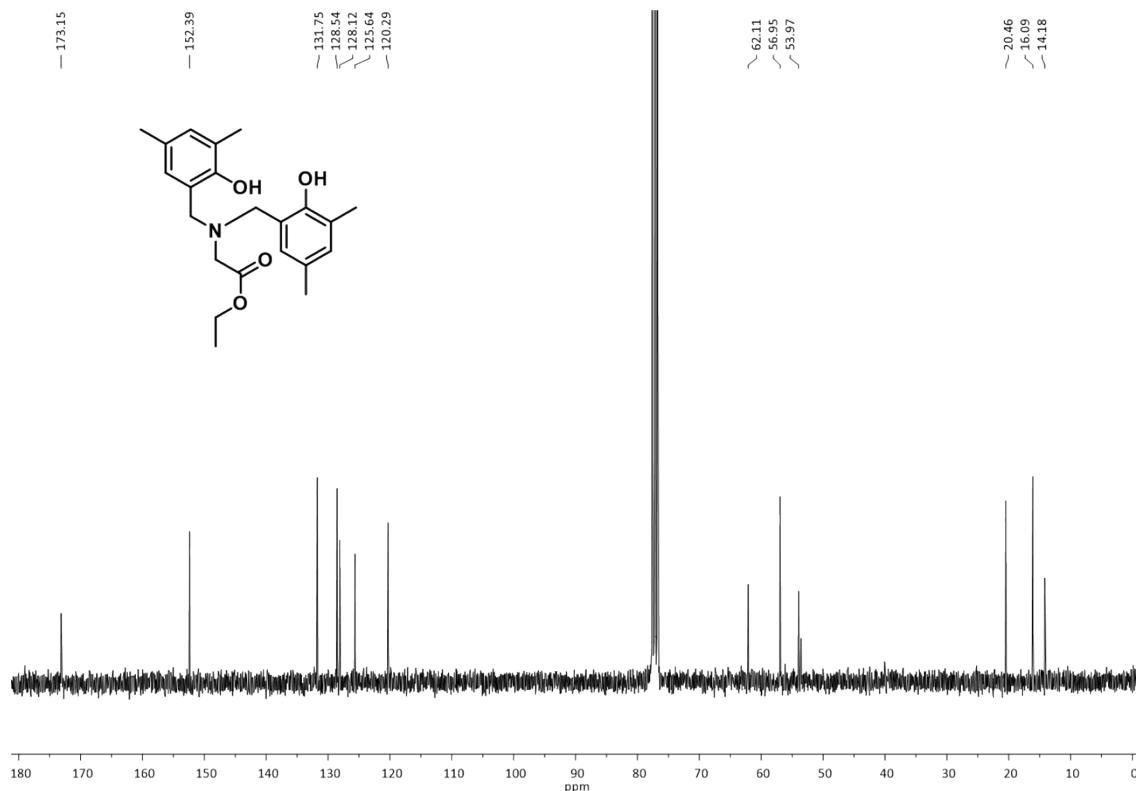
Figure S8. ^{13}C NMR spectrum of **L4** (75 MHz, CDCl$_3$ at 298 K).

L5
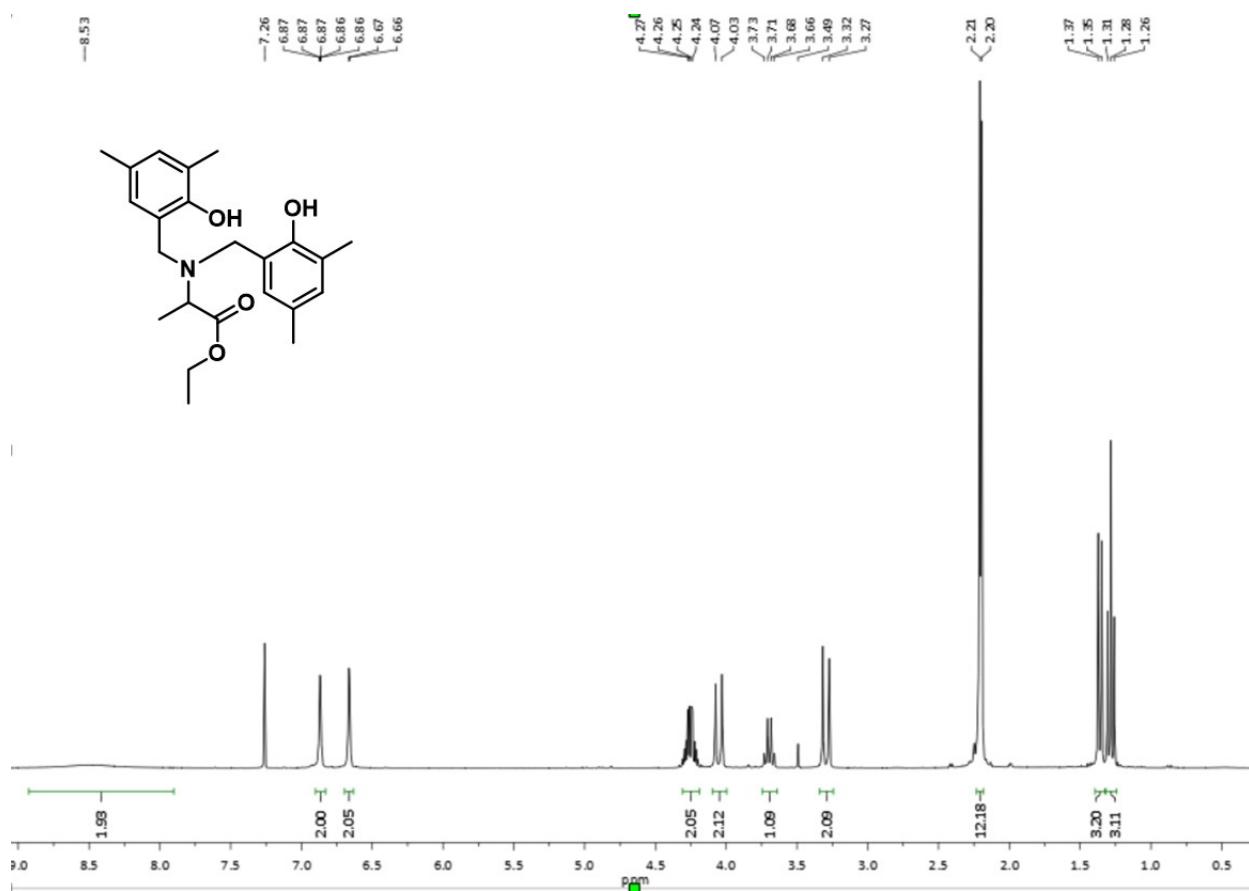
Figure S9. ^{1}H NMR spectrum of **L5** (300 MHz, CDCl$_3$ at 298 K).
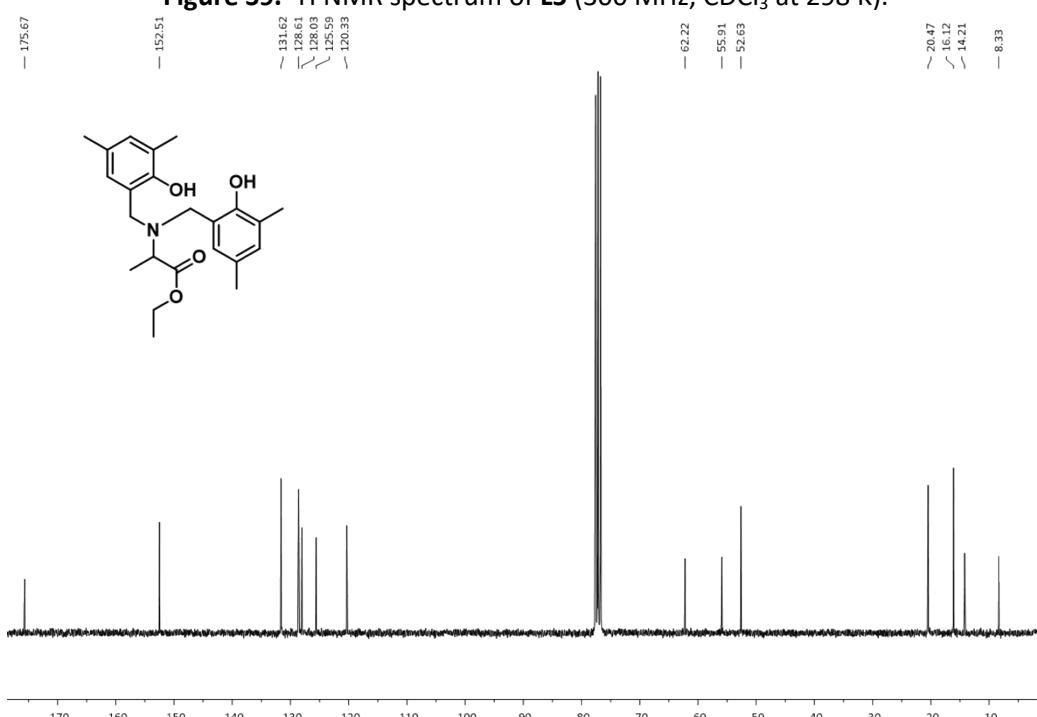
Figure S10. ^{13}C NMR spectrum of **L5** (75 MHz, CDCl$_3$ at 298 K).

L6
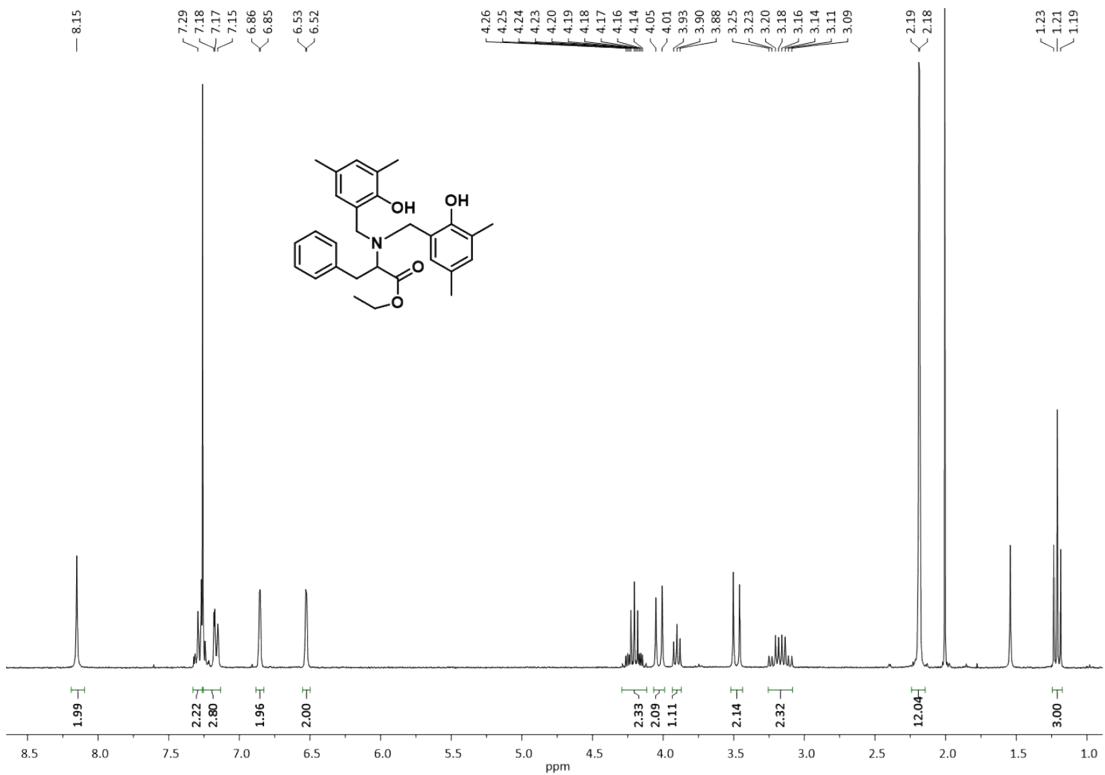
Figure S11. ^{1}H NMR spectrum of **L6** (300 MHz, CDCl$_3$ at 298 K).
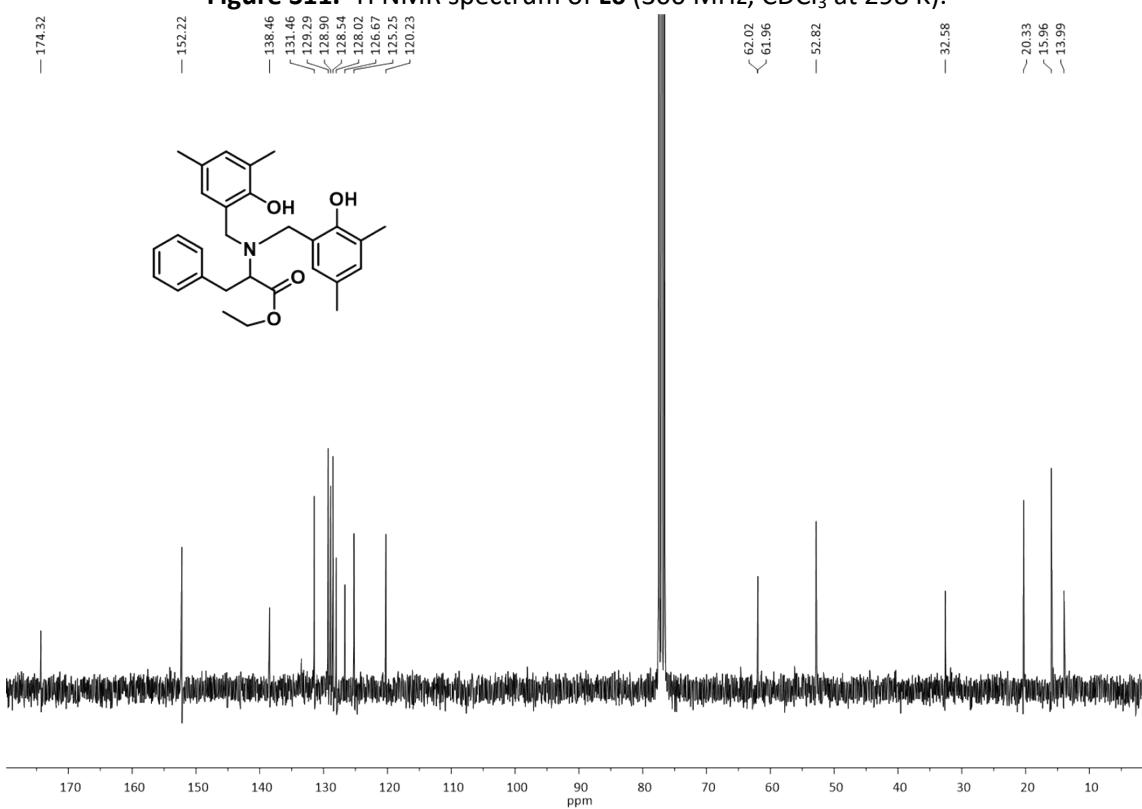
Figure S12. ^{13}C NMR spectrum of **L6** (75 MHz, CDCl$_3$ at 298 K).

2. ESI High Resolution Mass Spectrometry data of pro-ligands L1-L6

L1
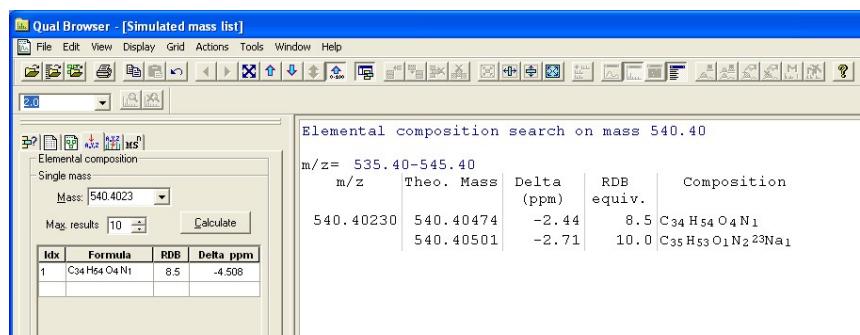
Figure S13. HRMS data of **L1**.

L2
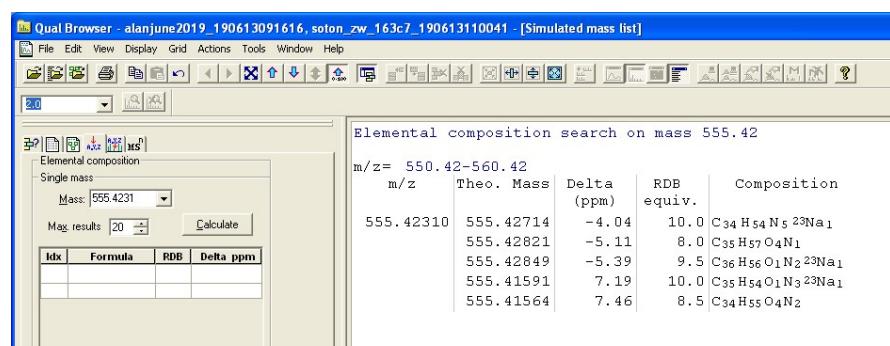
Figure S14. HRMS data of **L2**.

L3
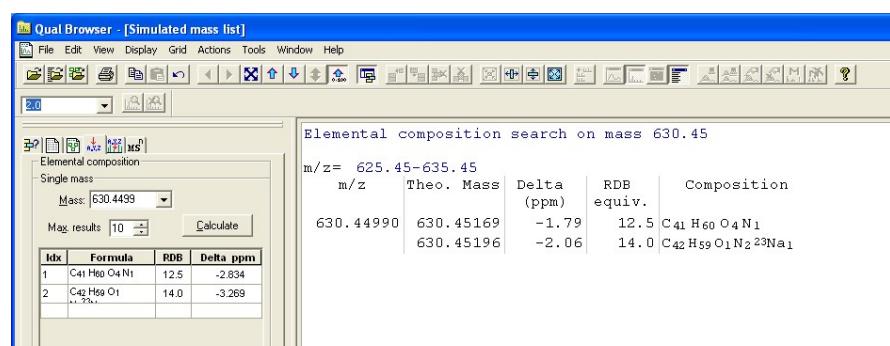
Figure S15. HRMS data of **L3**.

L4
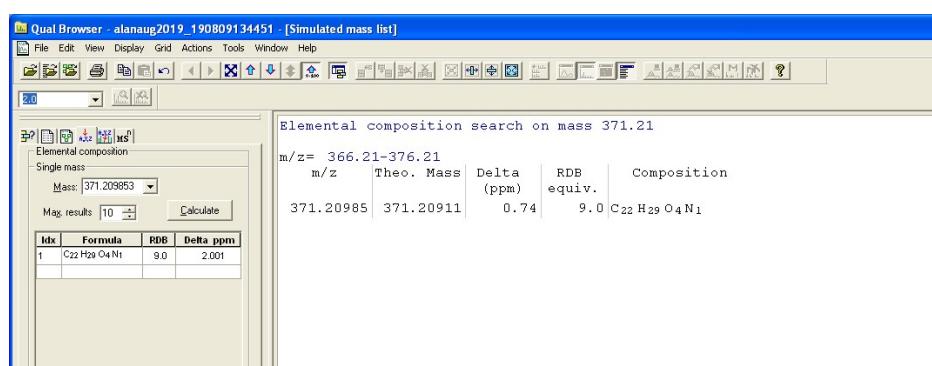
Figure S16. HRMS data of **L4**

L5
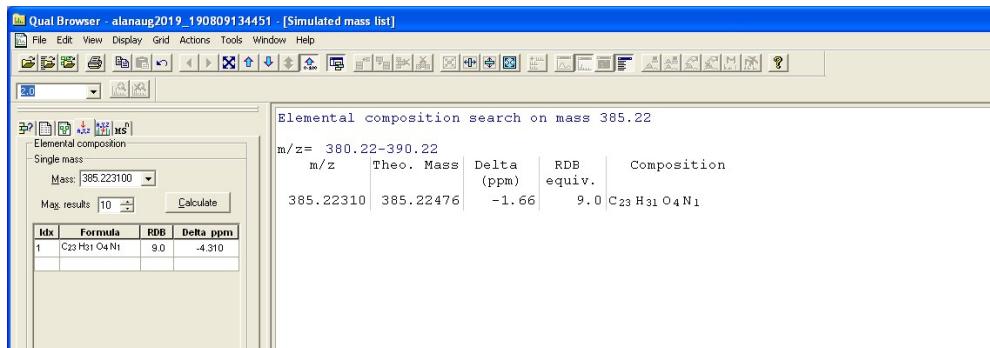
Figure S17. HRMS data of **L5**.

L6
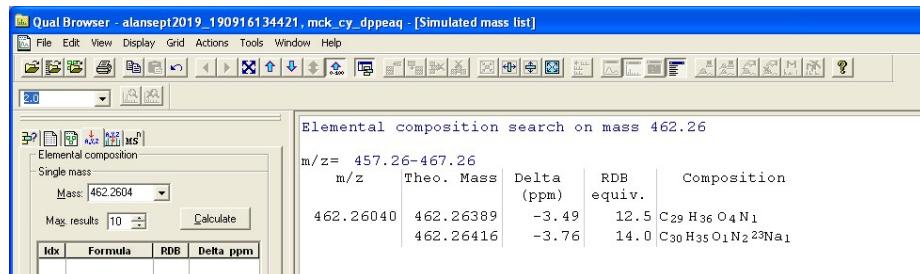
Figure S18. HRMS data of **L6**.

3. X-ray structures of pro-ligands L1-L6
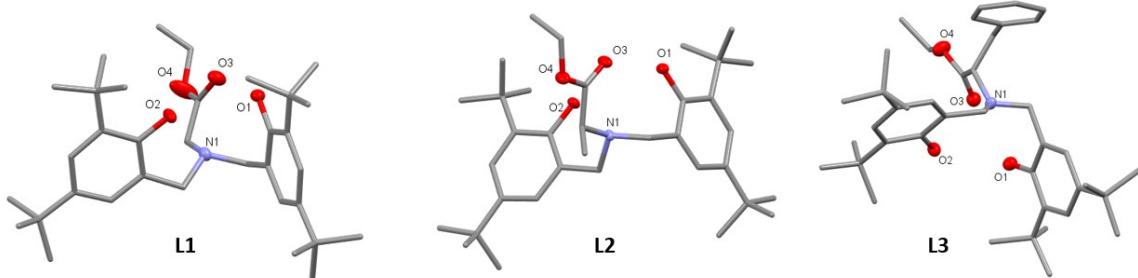
Figure S19. X-ray structures of **L1**, **L2** and **L3** (from left to right).
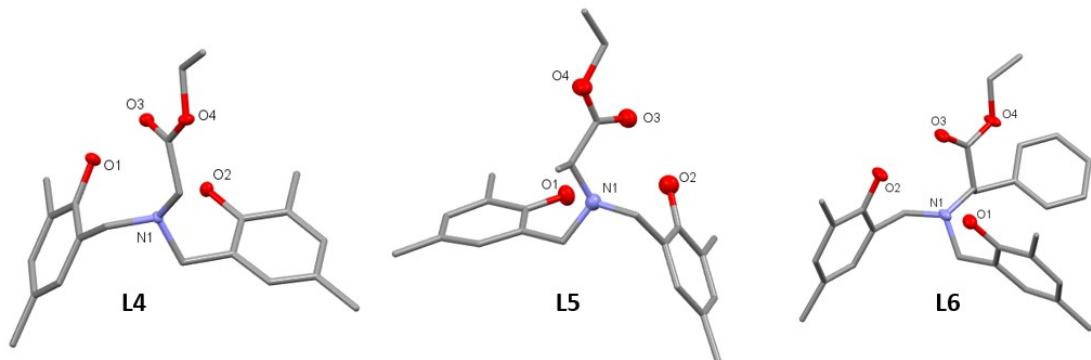
Figure S20. X-ray structures of **L4**, **L5** and **L6** (from left to right).

4. Data for the racemisation studies of chiral pro-ligands
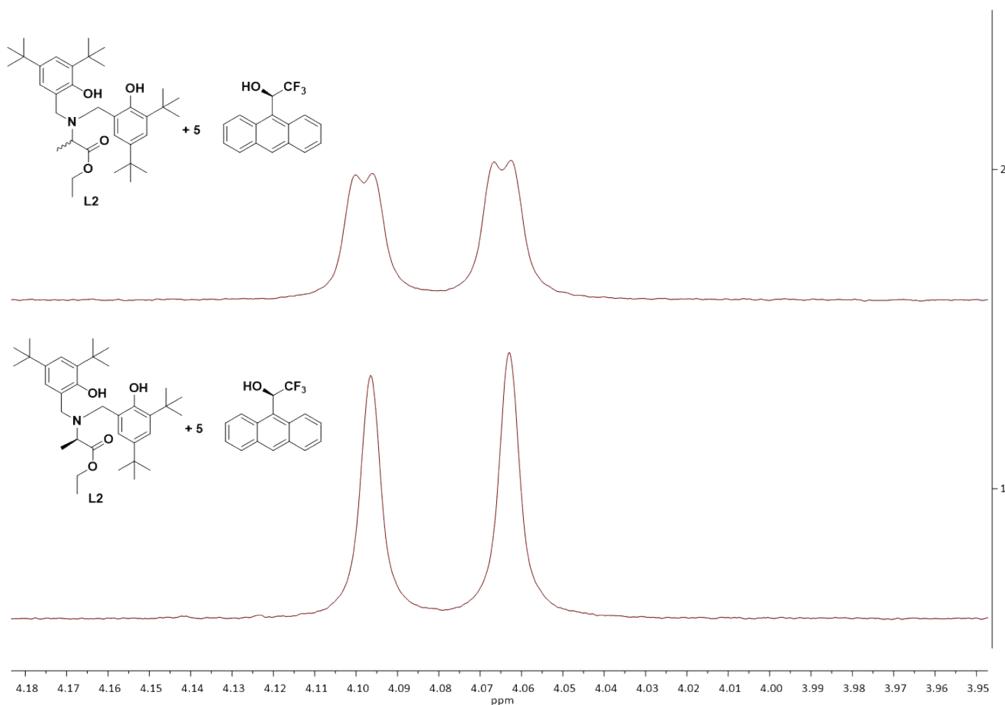
Figure S21. Comparison of the methylene resonances (4.08 ppm) in the ^{1}H NMR spectra of racemic (top) and enantiopure (bottom) pro-ligand **L2** in the presence of 5 equivalents of (*R*)-(−)-1-(9-anthryl)-2,2,2-trifluoroethanol shift reagent (300 MHz, CDCl$_3$ at 298 K).

215 nm Results				
Retention Time	Area	Area %	Height	Height %
5.522	383352354	54.00	48033545	57.00
6.163	326553056	46.00	36238835	43.00
Totals	709905410	100.00	84272380	100.00
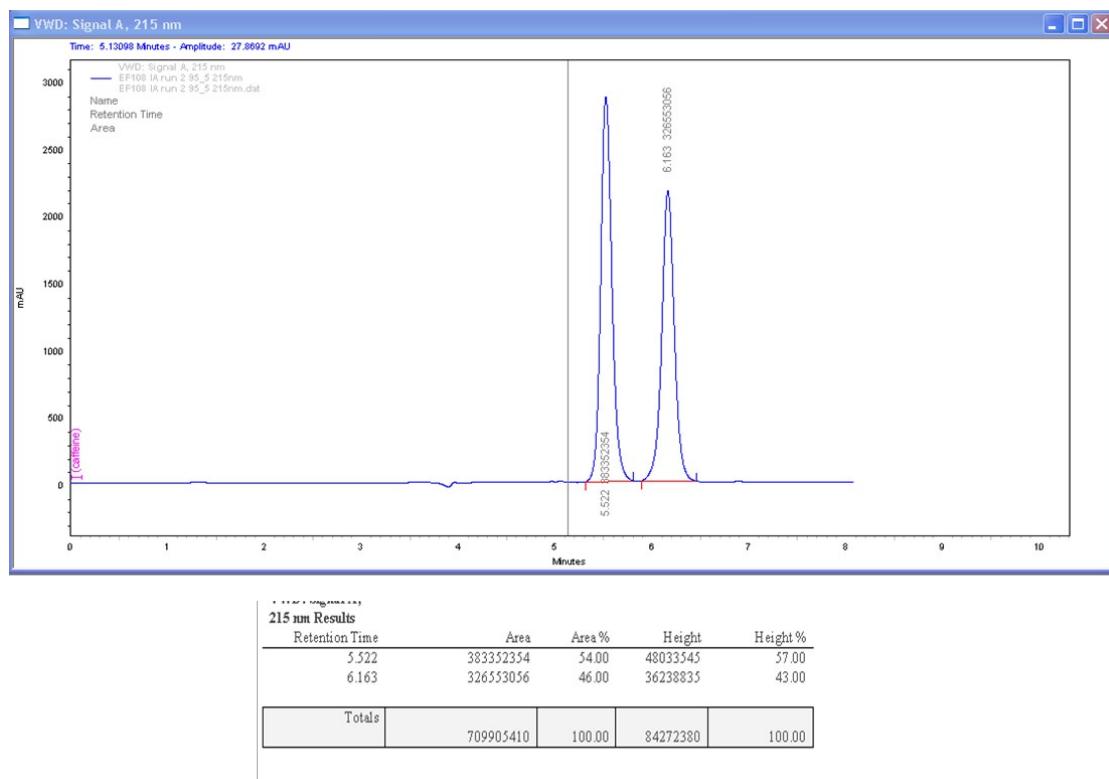
Figure S22. HPLC chromatogram of racemic pro-ligand **L5** on CHIRALPAK IA column, hexane:2-propanol 95:5, flow rate: 1.0 mL min^{-1}, detection UV 215 nm, 298 K) t$_R$ of isomers: 5.52 min and 6.16 min.

VWD: Signal A,
210 nm Results

Retention Time	Area	Area %	Height	Height %
5.875	219210099	96.29	24579618	96.78
6.725	8451988	3.71	818091	3.22
Totals	227662087	100.00	25397709	100.00
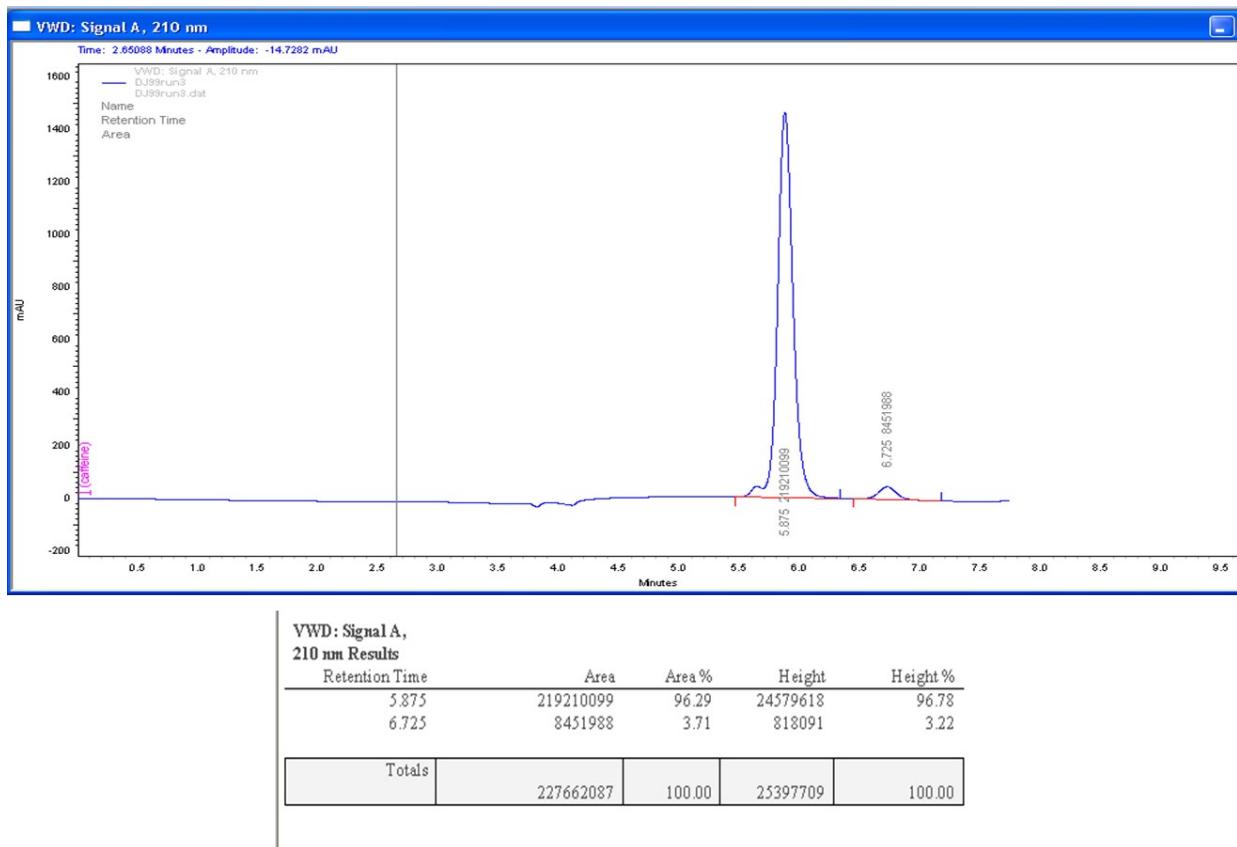
Figure S23. HPLC chromatogram of (L)-**L5** on CHIRALPAK IA column, hexane:2-propanol 95:5, flow rate: 1.0 mL min^{-1}, detection UV 215 nm, 298 K) t_R of major isomer: 5.87 min, t_R of minor isomer: 6.72 min.

5. ¹H and ¹³C NMR spectra of Pd complexes C1-C7

C1
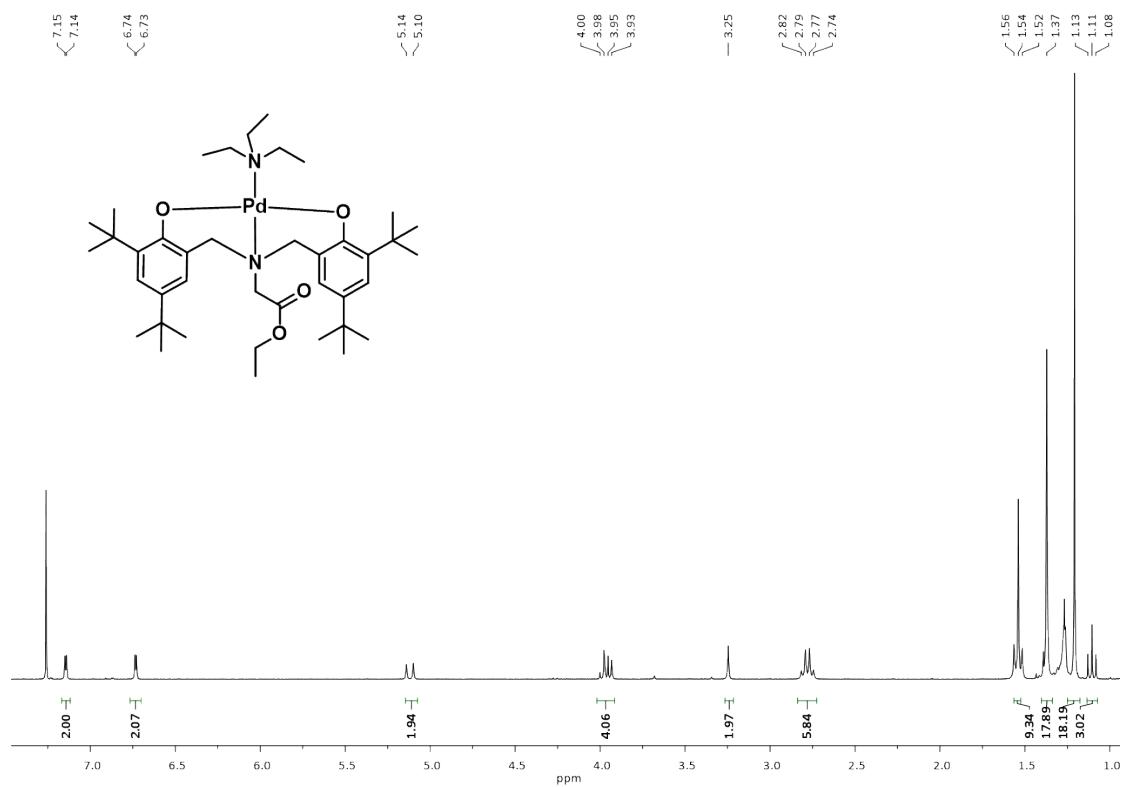
Figure S24. ¹H NMR spectrum of **C1** (300 MHz, CDCl₃ at 298 K).
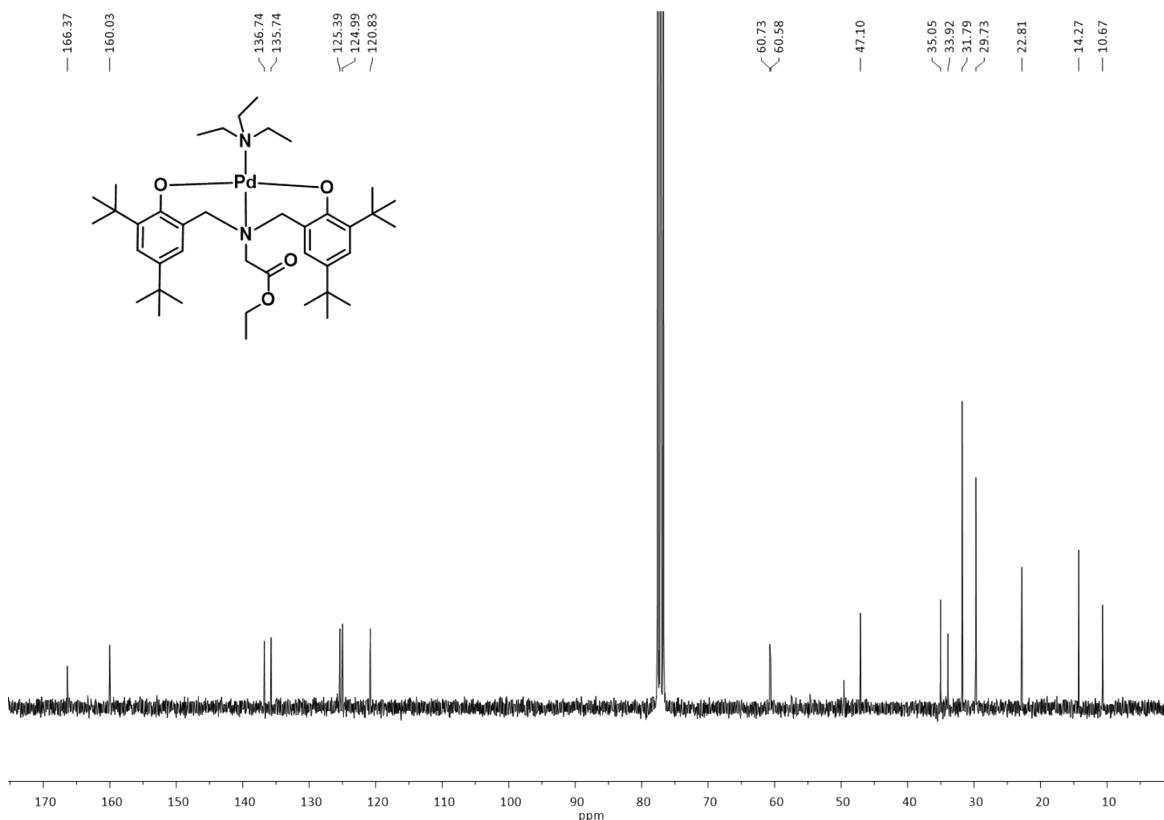
Figure S25. ¹³C NMR spectrum of **C1** (75 MHz, CDCl₃ at 298 K).

C2

Figure S26. ^{1}H NMR spectrum of **C2** (300 MHz, CDCl$_3$ at 298 K).
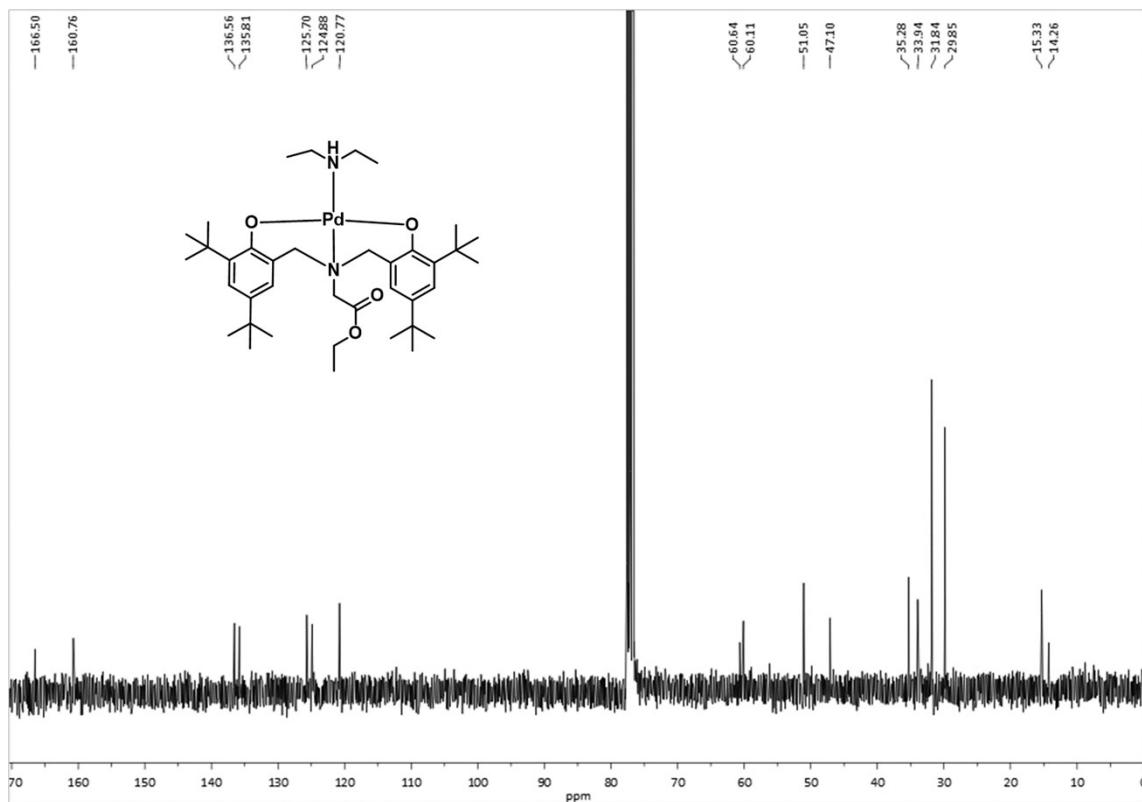
Figure S27. ^{13}C NMR spectrum of **C2** (75 MHz, CDCl$_3$ at 298 K).

C3
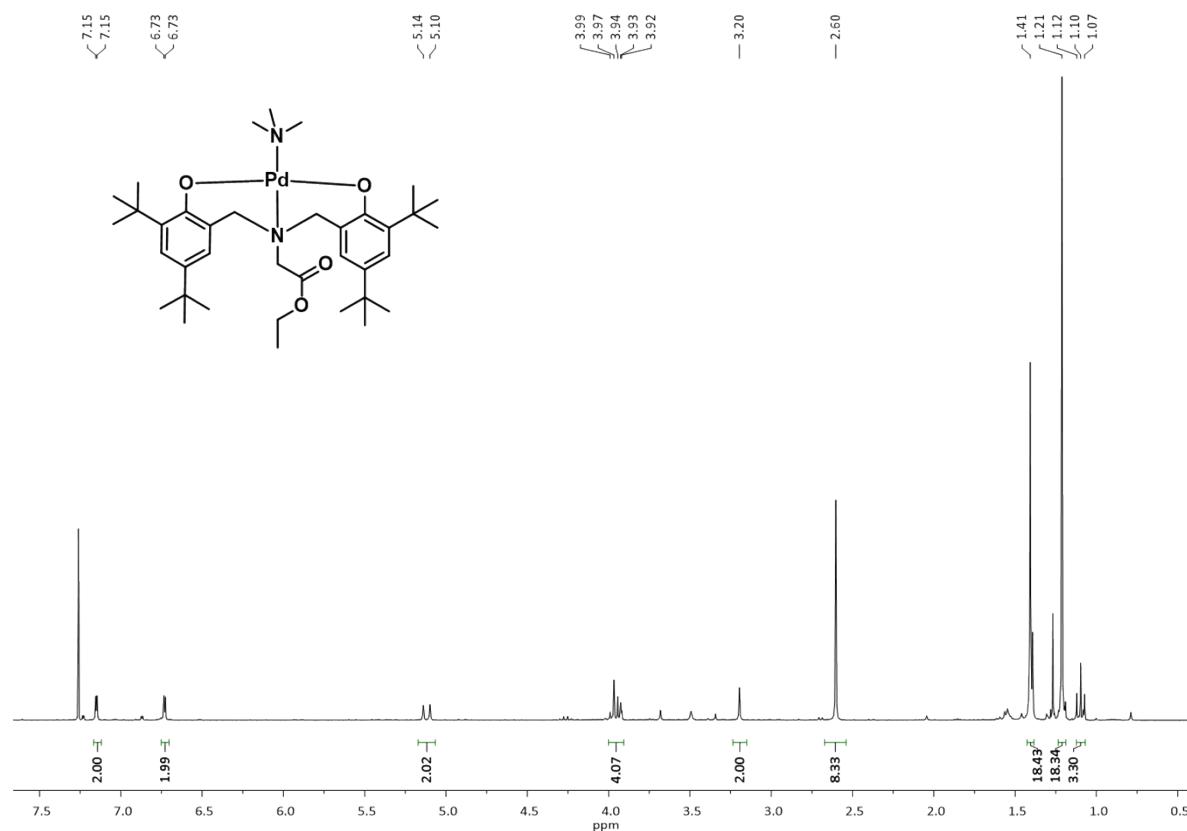
Figure S28. ^{1}H NMR spectrum of **C3** (300 MHz, CDCl$_3$ at 298 K).
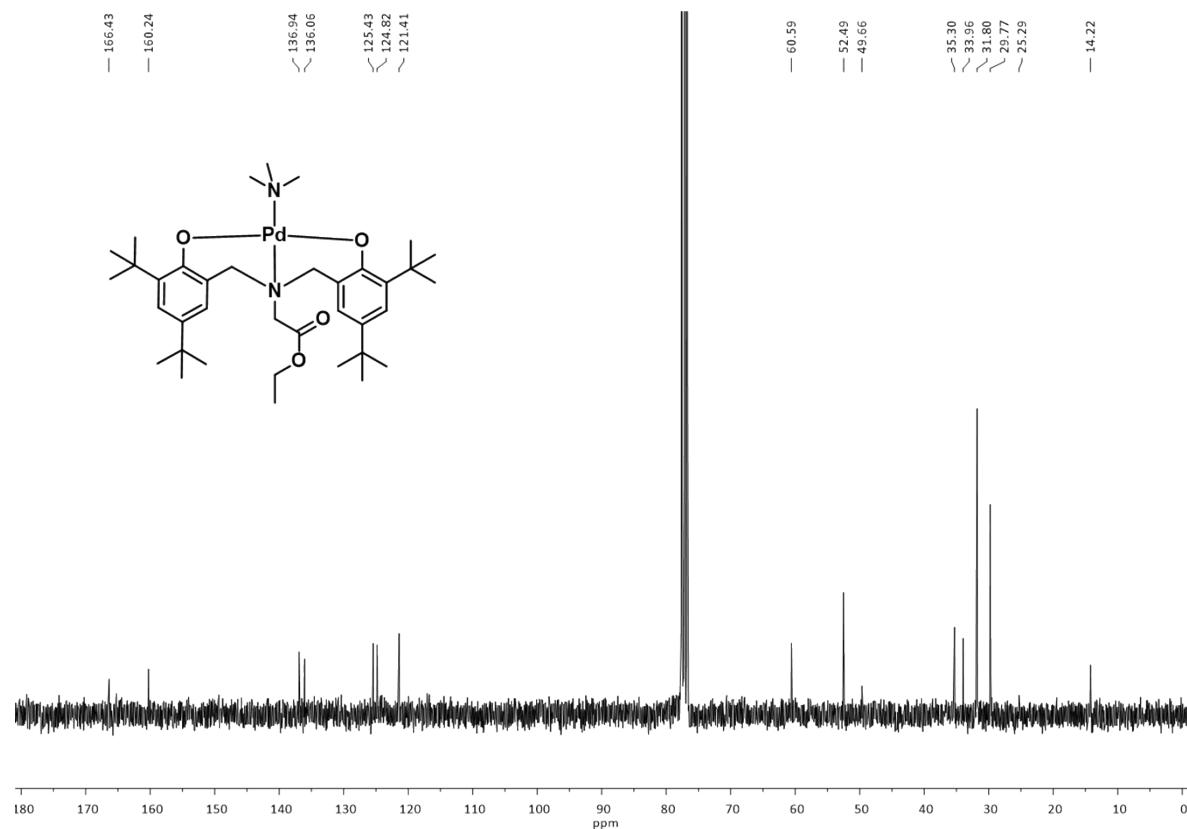
Figure S29. ^{13}C NMR spectrum of **C3** (75 MHz, CDCl$_3$ at 298 K).

C4

Figure S30. ^{1}H NMR spectrum of **C4** (300 MHz, CDCl$_3$ at 298 K).
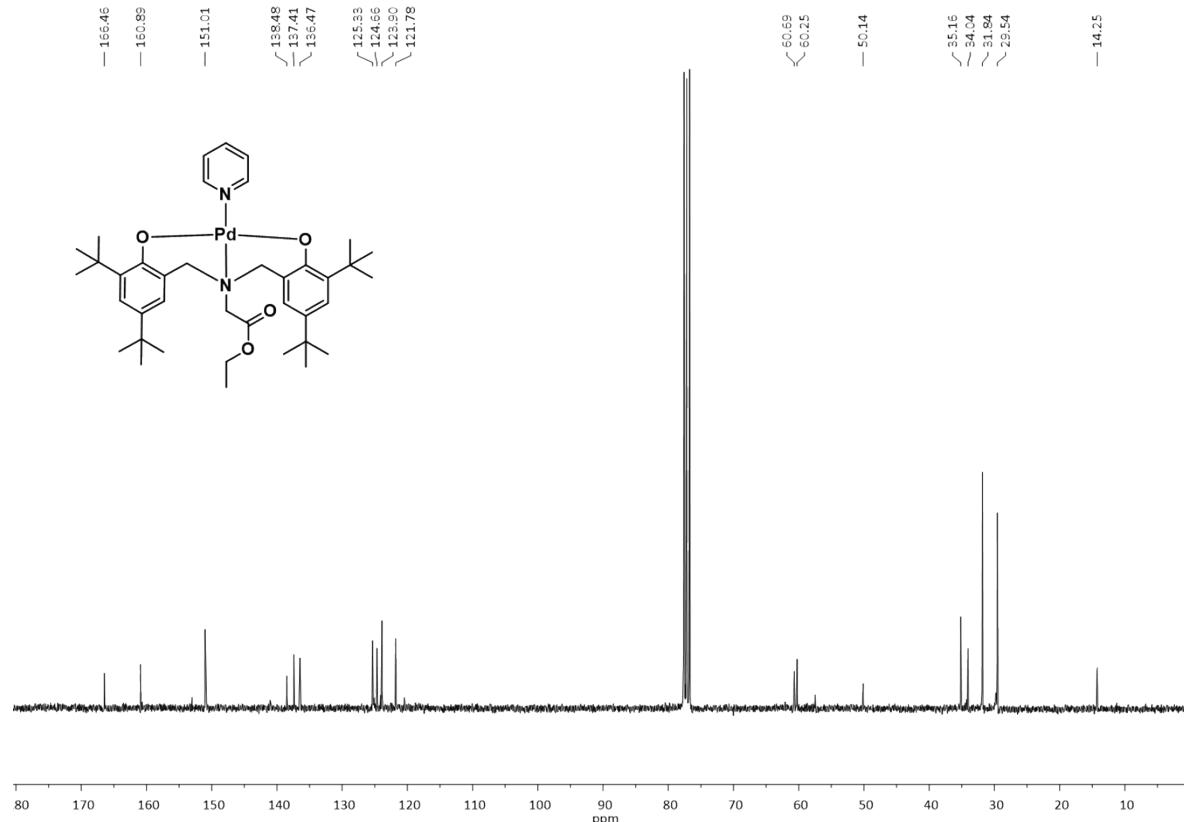
Figure S31. ^{13}C NMR spectrum of **C4** (75 MHz, CDCl$_3$ at 298 K).

C5
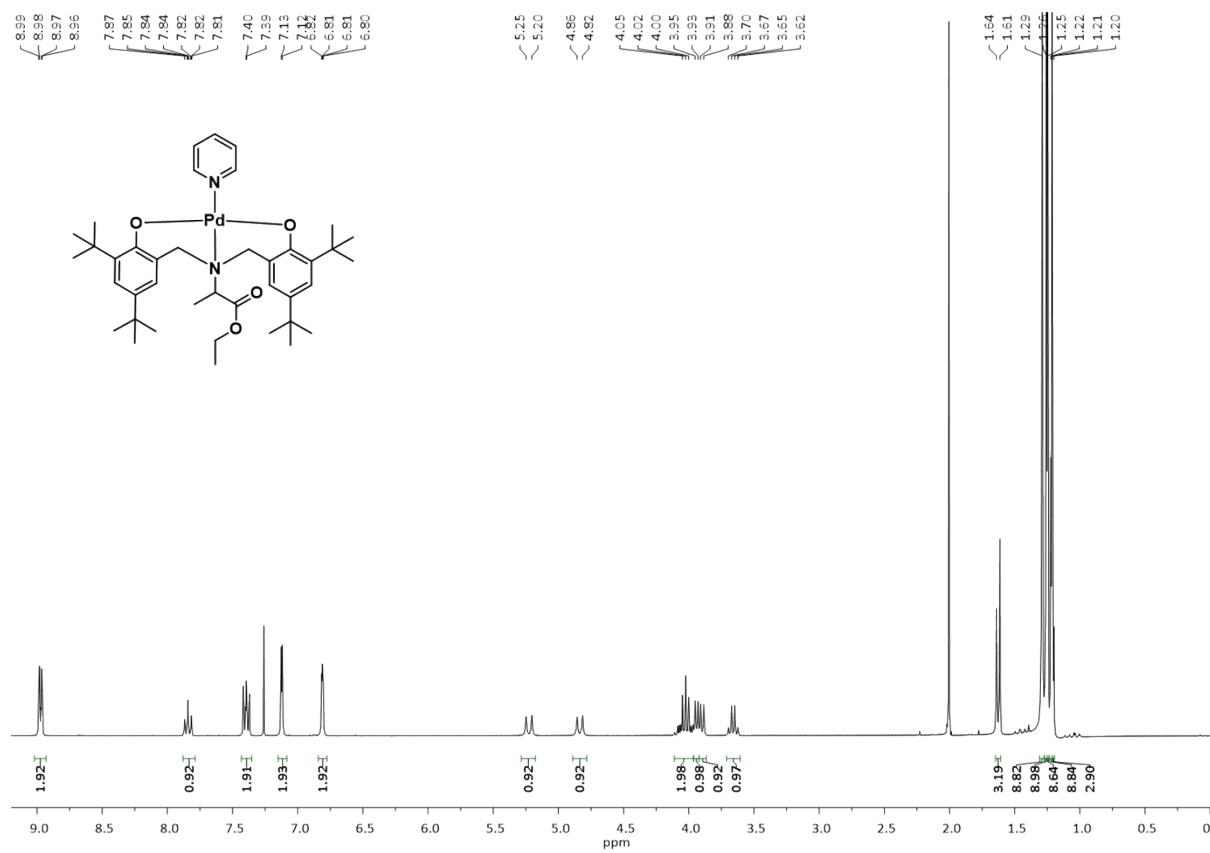
Figure S32. ^{1}H NMR spectrum of **C5** (300 MHz, CDCl$_3$ at 298 K).
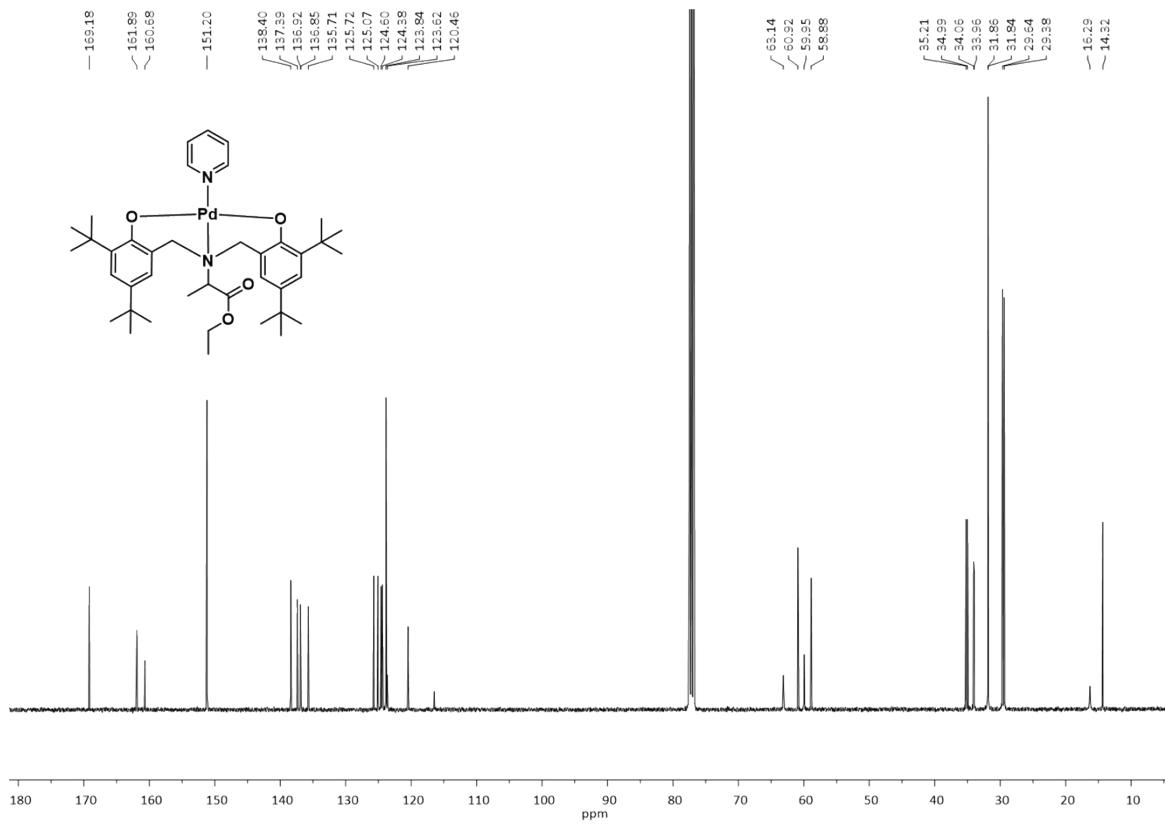
Figure S33. ^{13}C NMR spectrum of **C5** (75 MHz, CDCl$_3$ at 298 K).

C6
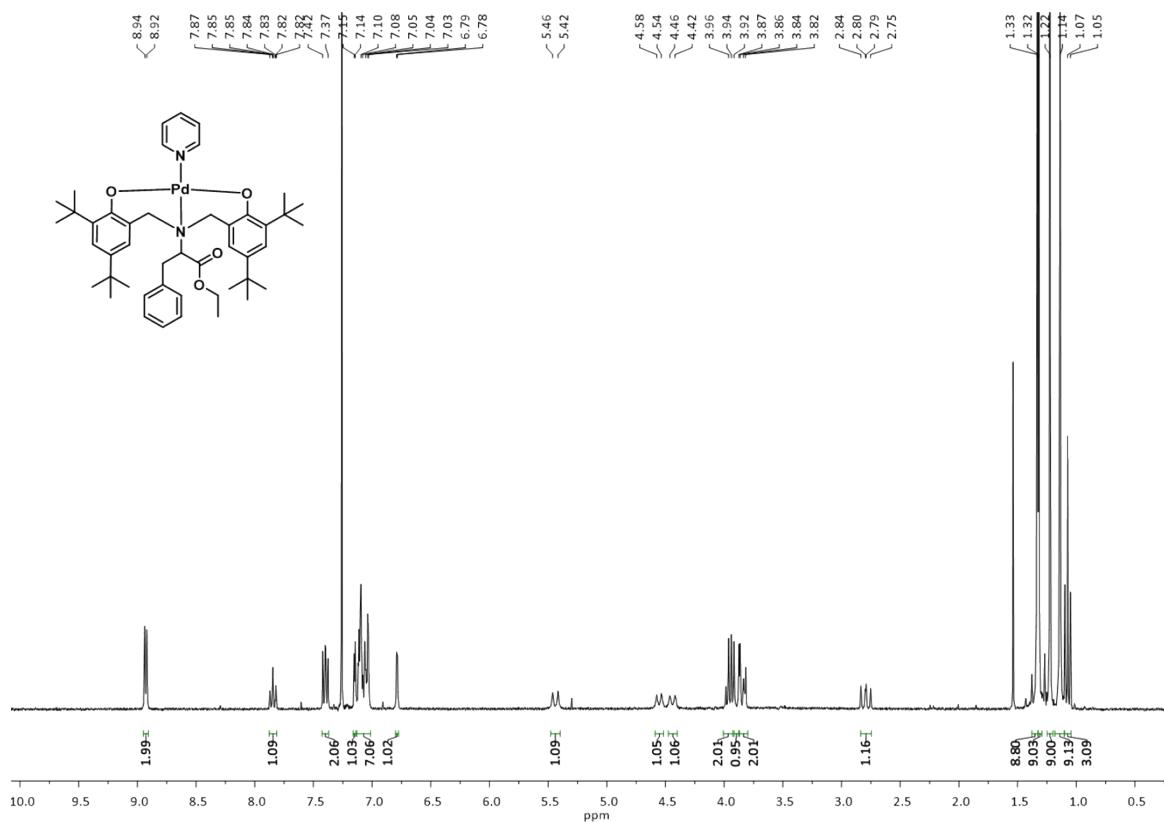
Figure S34. ^{1}H NMR spectrum of **C6** in CDCl$_3$ (300 MHz, CDCl$_3$ at 298 K).
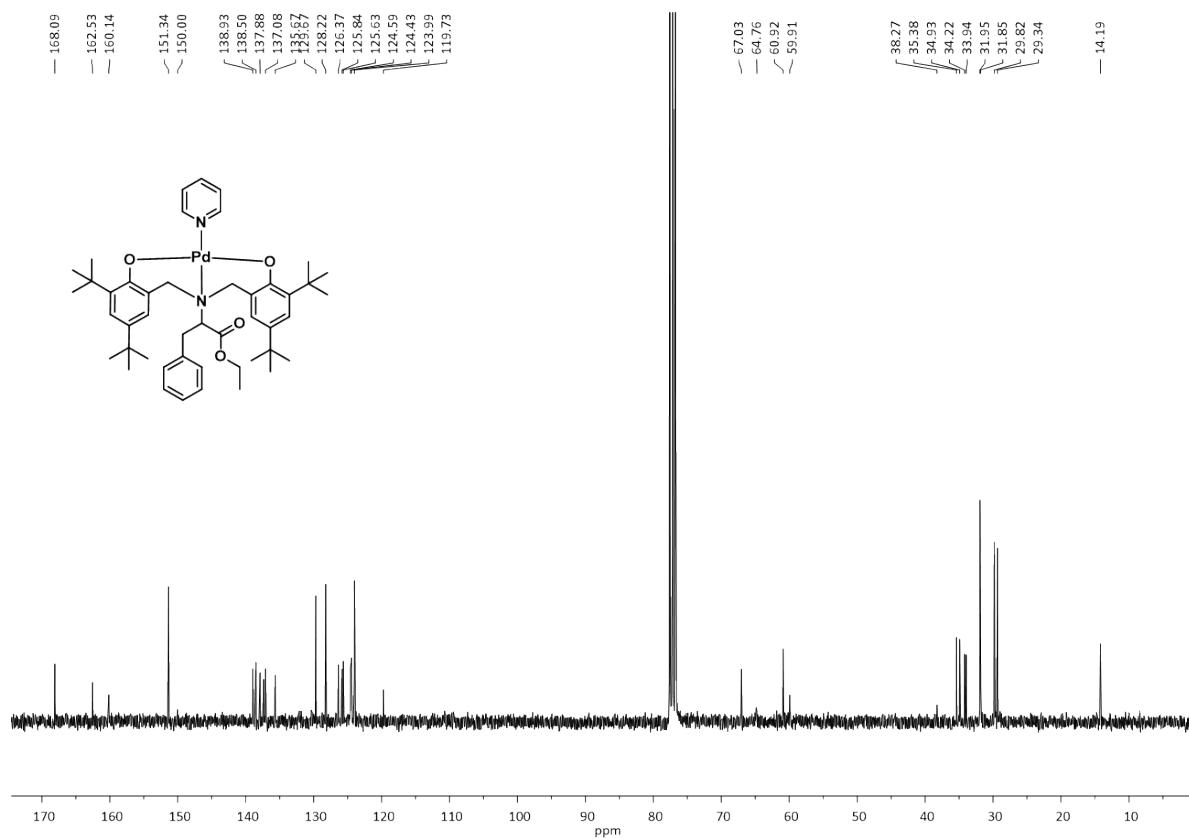
Figure S35. ^{13}C NMR spectrum of **C6** (75 MHz, CDCl$_3$ at 298 K).

C7
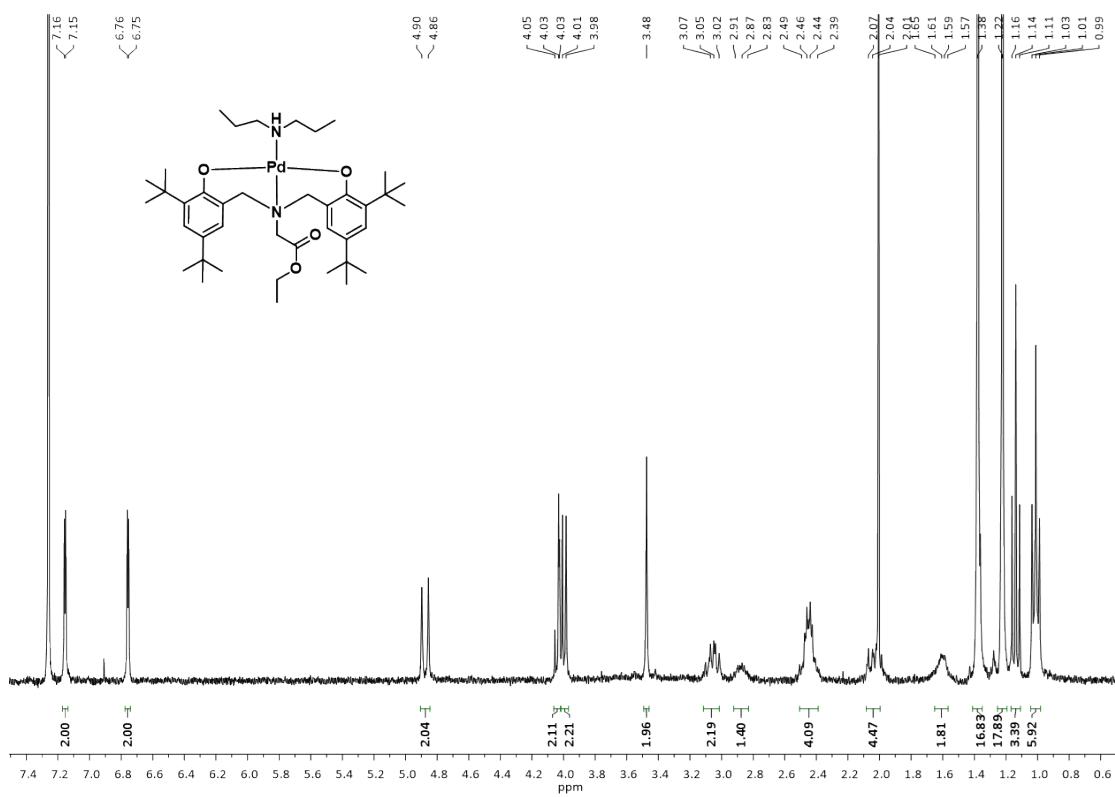
Figure S36. ^{1}H NMR spectrum of **C7** (300 MHz, CDCl$_3$ at 298 K).
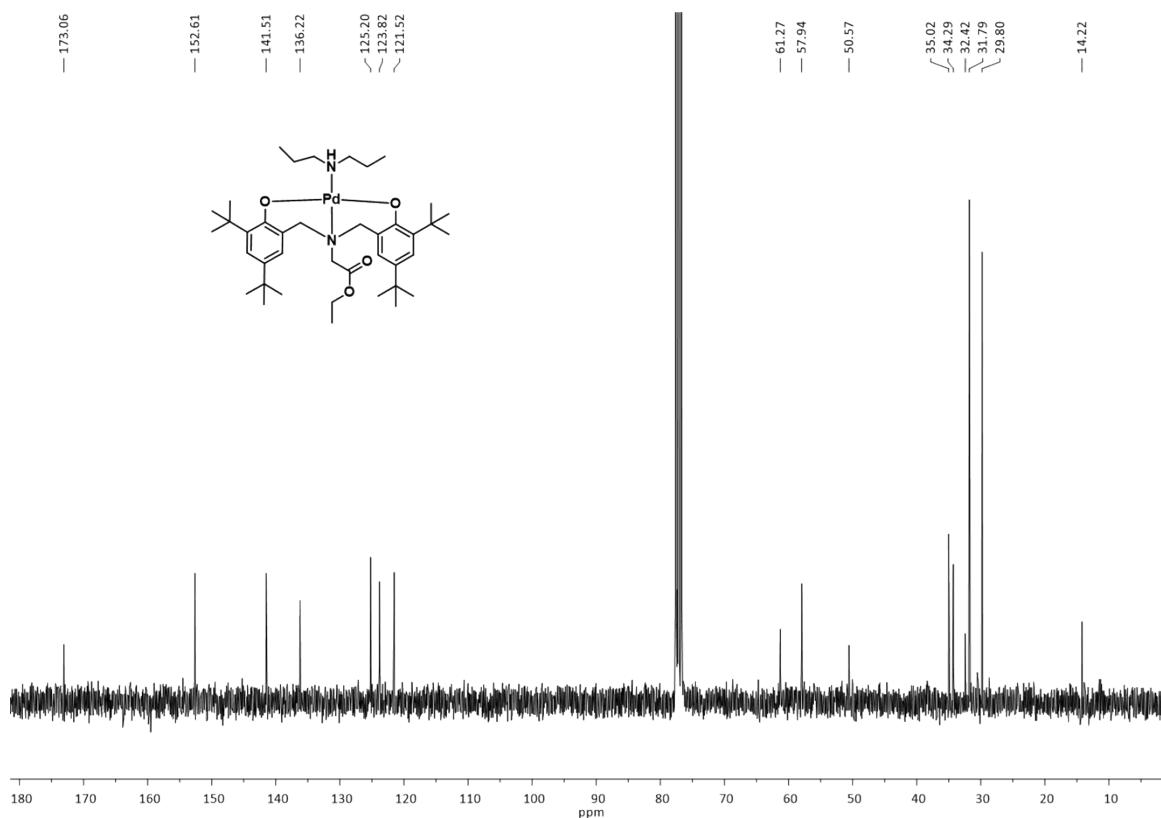
Figure S37. ^{13}C NMR spectrum of **C7** (75 MHz, CDCl$_3$ at 298 K).

6. ESI High Resolution Mass Spectrometry data of Pd complexes C1-C7

C1
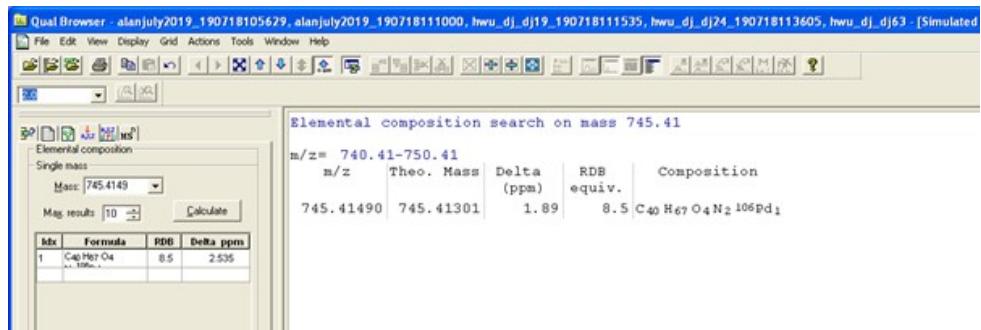
Figure S38. HRMS data of **C1**.

C2
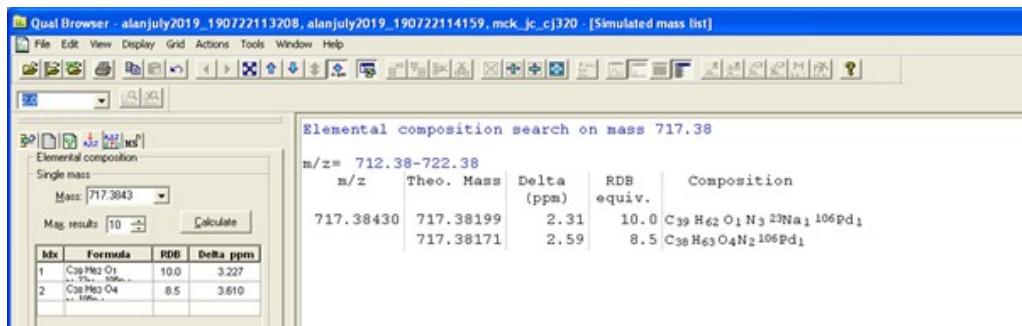
Figure S39. HRMS data of **C2**.

C3
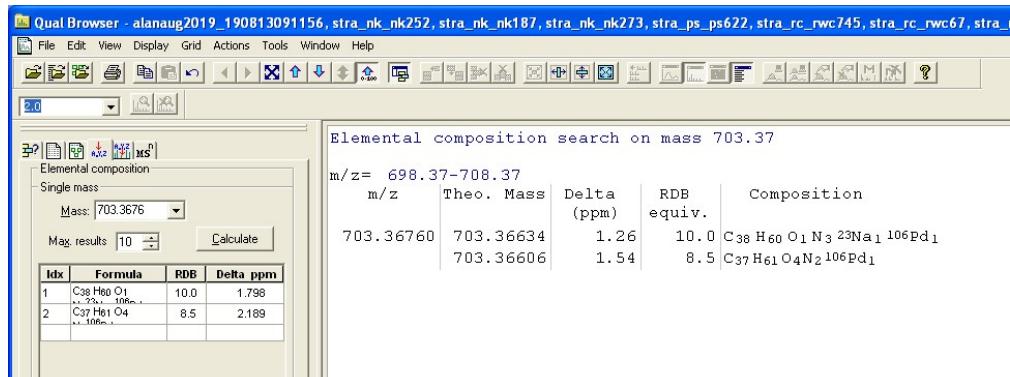
Figure S40. HRMS data of **C3**.

C4
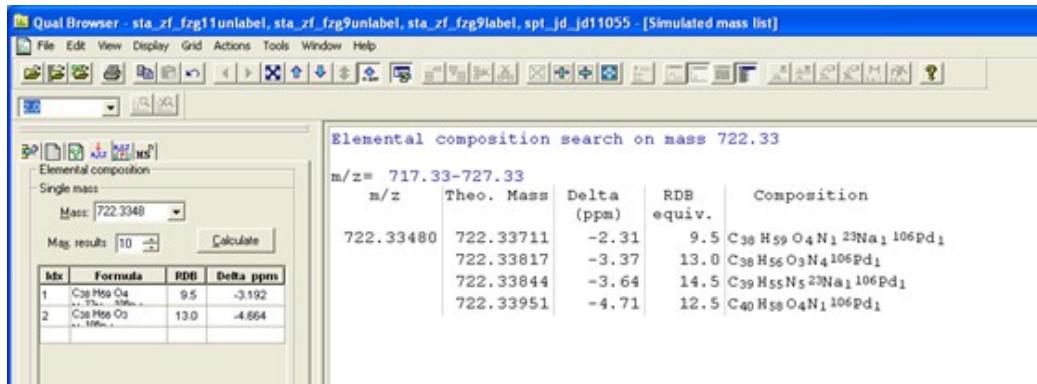
Figure S41. HRMS data of **C4**.

C5
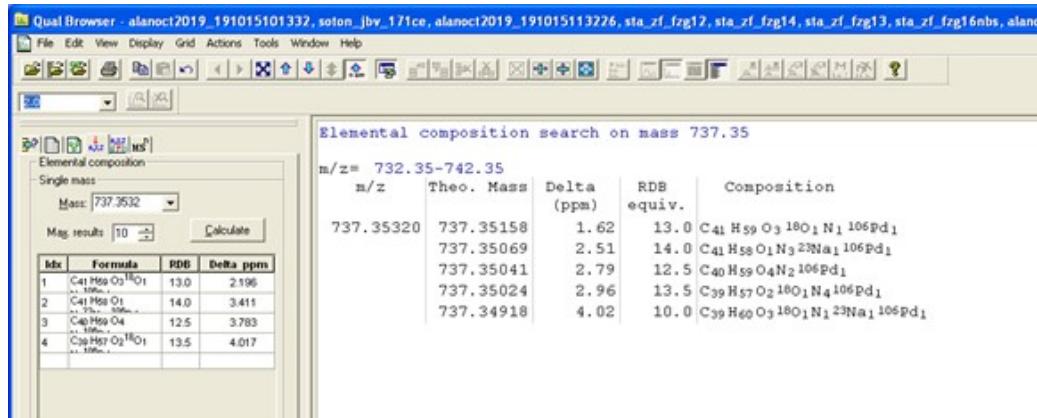
Figure S42. HRMS data of **C5**.

C6
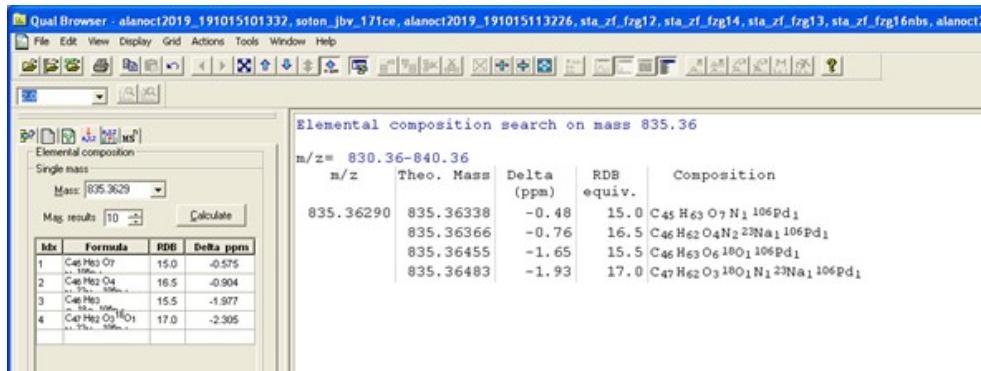
Figure S43. HRMS data of **C6**.

C7
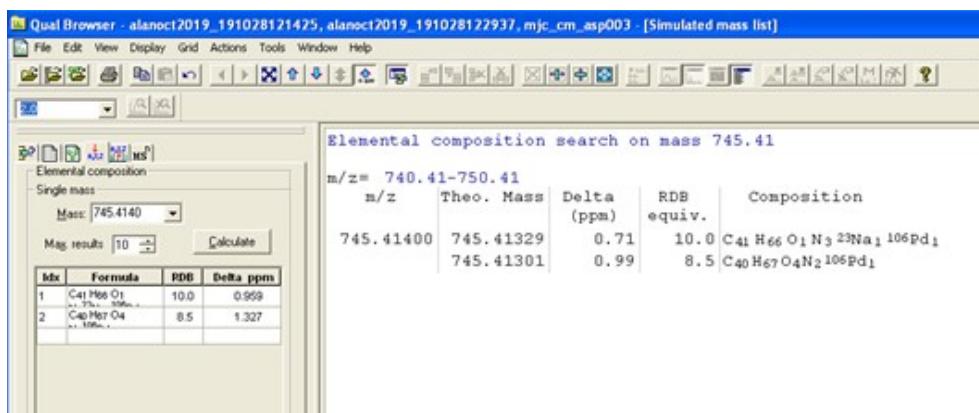
Figure S44. HRMS data of **C7**.

7. Typical ¹H NMR spectra of Suzuki-Miyaura and Mizoroki-Heck crude reaction mixtures

Suzuki-Miyaura reactions:
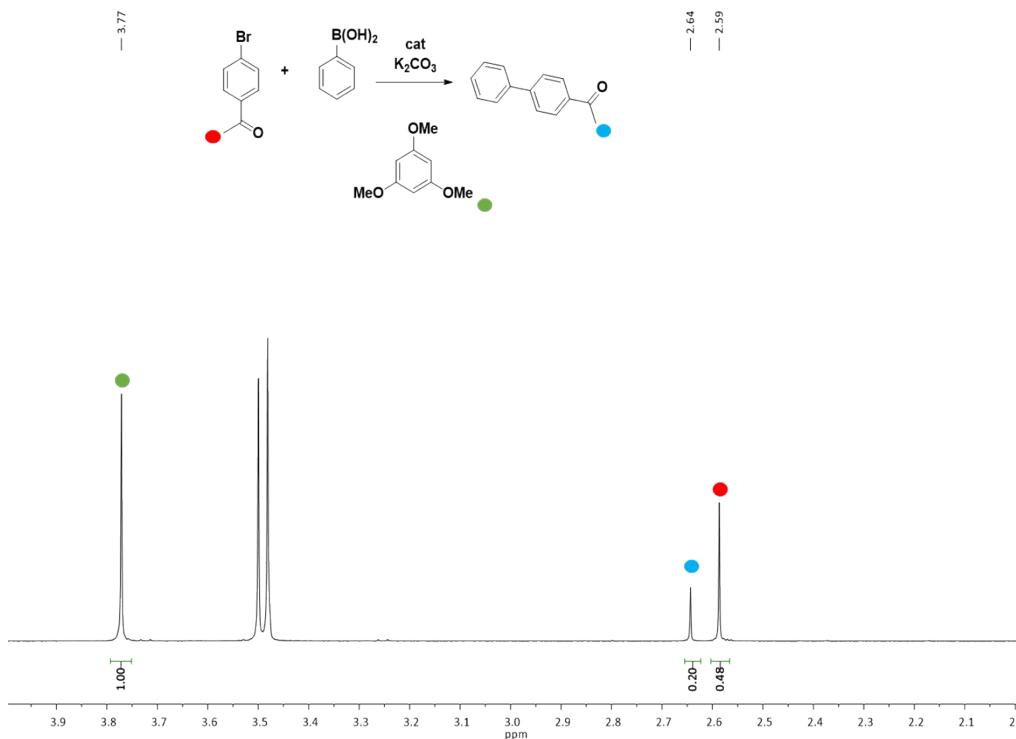
Figure S45. Typical ¹H NMR spectrum (298 K, CDCl$_3$, 300 MHz) of a Suzuki-Miyaura reaction mixture indicating the CH$_3$ shifts of starting material (4'-bromoacetophenone, 2.59 ppm, red), product (4-acetylbiphenyl, 2.64 ppm, blue) and internal standard (1,3,5-trimetoxybenzene, 3.77 ppm, green).[1]

Substrate scope:

All aryl-halides tested in the Suzuki-Miyaura coupling reactions with phenylboronic acid using catalyst **C4** afforded known biaryl species with reported full characterisations. Conversions were calculated *via* ¹H NMR, integrating the internal standard peak (1,3,5-trimetoxybenzene, 3.77 ppm) against product peaks matched with literature values for bromo-4-nitrobenzene,[2] 4-bromoaniline,[3] 4-bromo-2-fluoronitrobenzene,[4] 1-bromo-2-methoxynaphthalene,[5] 1-bromo-4-^{t}Bu-benzene,[6] 1-bromotoluene, 2-bromotoluene and 3-bromotoluene.[7]

Asymmetric reaction:
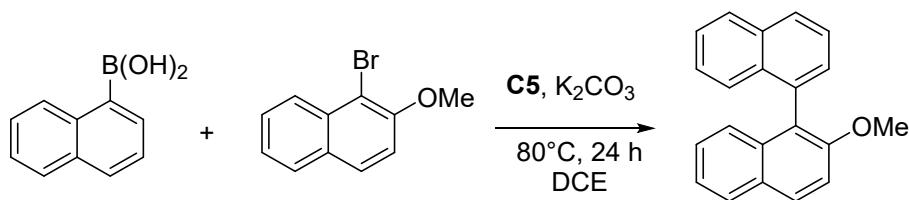
Scheme S1. Suzuki-Miyaura coupling of 1-napthaleneboronic acid and 1-bromo-2-methoxynaphthalene.

Mizoroki-Heck reactions:
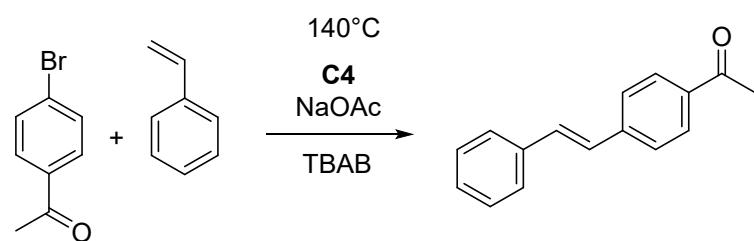
Scheme S2. Mizoroki-Heck reaction of 4'-bromoacetophenone and styrene.
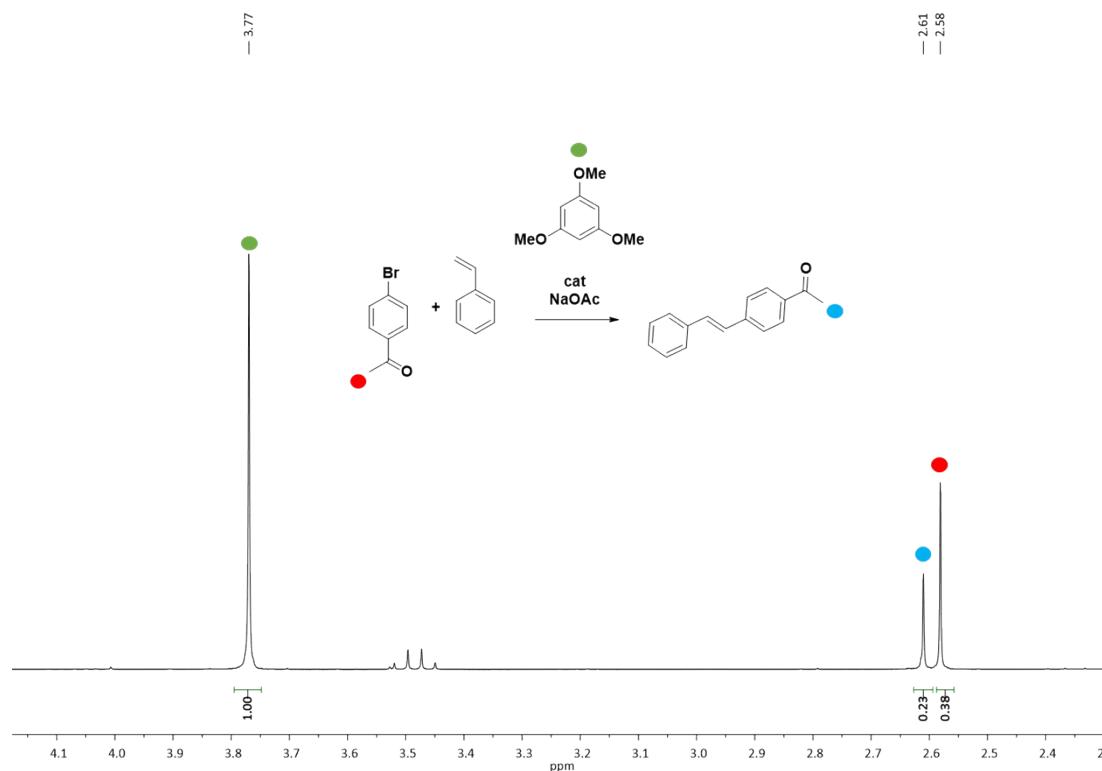
Figure S46. Typical ^{1}H NMR spectrum (298 K, CDCl$_3$, 300 MHz) of a Heck-Mizoroki reaction mixture indicating the CH$_3$ shifts of starting material (4'-bromoacetophenone, 2.59 ppm, red), product (4-acetylstilbene, 2.61 ppm, blue) and internal standard (1,3,5-trimetoxybenzene, 3.77 ppm, green).[8]

8. Crystallographic data and refinement details for ligands L1-L6 (Table S1) and Complexes C1-C6 (Table S2)

Table S1. Crystallographic data and refinement details for ligands **L1-L6**.

| Identification code	**L1**	**L2**	**L3**	**L4**	**L5**	**L6**
CCDC number	2070846	2070847	2070849	2070850	2070851	2070853
Empirical formula	$C_{34.5}H_{54}NO_4Cl$	$C_{35}H_{55}NO_4$	$C_{41}H_{59}NO_4$	$C_{23}H_{31}Cl_2NO_4$	$C_{23}H_{31}NO_4$	$C_{30}H_{37}Cl_2NO_4$
Formula weight	582.23	553.8	629.89	456.39	385.49	546.5
Temperature/K	100	100	100	100	100	100
Crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$	$C2/c$	$P-1$	$P2_1/c$
a/Å	14.4965(2)	9.08240(10)	10.4115(2)	22.1011(3)	10.5479(2)	14.3845(4)
b/Å	19.9546(3)	11.7694(2)	11.7529(2)	12.1705(2)	14.5535(3)	16.8171(4)
c/Å	12.0794(2)	31.5208(5)	31.8349(5)	17.0857(3)	15.4442(3)	11.7263(3)
α/°	90	90	90	90	70.3610(10)	90
β/°	103.8657(8)	90	90	92.1340(10)	70.5070(10)	99.9650(10)
γ/°	90	90	90	90	76.5600(10)	90
Volume/Å^3	3392.41(9)	3369.40(9)	3895.49(12)	4592.55(13)	2085.52(7)	2793.86(13)
Z	4	4	4	8	4	4
ρ_{calc}g/cm^3	1.14	1.092	1.074	1.32	1.228	1.299
μ/mm^{-1}	1.269	0.543	0.525	0.312	0.667	2.375
F(000)	1268	1216	1376	1936	832	1160
Crystal size/mm^3	$0.28 \times 0.22 \times 0.06$	$0.4 \times 0.36 \times 0.12$	$0.25 \times 0.18 \times 0.14$	$0.3 \times 0.2 \times 0.2$	$0.32 \times 0.2 \times 0.16$	$0.32 \times 0.04 \times 0.04$
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	CuKα (λ = 1.54178)
2Θ range for data coll./°	6.28 to 140.358	5.608 to 144.242	8.018 to 136.742	5.922 to 54.202	6.328 to 145.126	6.238 to 153.202
Index ranges	$-17 \le h \le 16, -24 \le k \le 24, -14 \le l \le 14$	$-11 \le h \le 11, -14 \le k \le 14, -38 \le l \le 38$	$-12 \le h \le 12, -14 \le k \le 14, -36 \le l \le 38$	$-27 \le h \le 28, -15 \le k \le 15, -21 \le l \le 21$	$-13 \le h \le 13, -17 \le k \le 16, -19 \le l \le 18$	$-17 \le h \le 17, -20 \le k \le 20, -14 \le l \le 14$
Reflections collected	46320	47117	48693	42089	24899	33650
Independent reflections	6446 [R_{int} = 0.0405, R_{sigma} = 0.0216]	6637 [R_{int} = 0.0279, R_{sigma} = 0.0151]	7128 [R_{int} = 0.0419, R_{sigma} = 0.0219]	5056 [R_{int} = 0.0306, R_{sigma} = 0.0158]	8049 [R_{int} = 0.0550, R_{sigma} = 0.0542]	5696 [R_{int} = 0.0739, R_{sigma} = 0.0472]
Data/restraints/parameters	6446/0/448	6637/0/377	7128/1/441	5056/12/311	8049/0/521	5696/0/341
Goodness-of-fit on F^2	1.052	1.036	1.087	1.045	1.078	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0415, wR_2 = 0.1016	R_1 = 0.0262, wR_2 = 0.0693	R_1 = 0.0567, wR_2 = 0.1615	R_1 = 0.0417, wR_2 = 0.1168	R_1 = 0.0494, wR_2 = 0.1295	R_1 = 0.0631, wR_2 = 0.1566
Final R indexes [all data]	R_1 = 0.0477, wR_2 = 0.1065	R_1 = 0.0265, wR_2 = 0.0696	R_1 = 0.0583, wR_2 = 0.1632	R_1 = 0.0493, wR_2 = 0.1237	R_1 = 0.0716, wR_2 = 0.1405	R_1 = 0.0814, wR_2 = 0.1719
Largest diff. peak/hole/e Å^{-3}	0.30/-0.25	0.27/-0.16	1.34/-0.21	0.38/-0.59	0.22/-0.25	0.37/-0.82

Table S2. Crystallographic data and refinement details for complexes **C1-C6**.

Identification code	C1	C2	C3	C4	C5	C6
CCDC number	2063653	2063654	2060147	2060195	2060200	2060206
Empirical formula	$C_{40}H_{66}N_2O_4Pd$	$C_{41}H_{69.5}N_2O_4Pd$	$C_{36.66}H_{59.32}N_2O_4Pd$	$C_{39}H_{56}N_2O_4Pd$	$C_{42}H_{61}N_3O_4Pd$	$C_{46}H_{62}N_2O_4Pd$
Formula weight	745.34	760.88	698.5	723.25	778.33	813.37
Temperature/K	100	100	100	100	100	100
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic	monoclinic
Space group	Pn	C2/c	P-1	P2$_1$/c	Pna2$_1$	P2$_1$
a/Å	9.9356(4)	27.3384(7)	10.8890(2)	23.5009(5)	18.1718(8)	13.3749(3)
b/Å	26.4605(11)	9.7533(2)	11.7145(3)	5.88070(10)	11.3807(4)	10.4918(2)
c/Å	15.5658(6)	31.2674(8)	15.3877(3)	28.0066(6)	20.0056(7)	16.3394(3)
α/°	90	90	103.1830(10)	90	90	90
β/°	105.0420(10)	96.1430(10)	104.3440(10)	106.1280(10)	90	112.5780(10)
γ/°	90	90	99.5060(10)	90	90	90
Volume/Å^3	3952.0(3)	8289.3(3)	1799.70(7)	3718.23(13)	4137.3(3)	2117.13(7)
Z	4	8	2	4	4	2
ρ_{calc}g/cm^3	1.253	1.219	1.289	1.292	1.25	1.276
μ/mm^{-1}	0.509	3.908	4.456	4.336	3.94	3.867
F(000)	1592	3260	743	1528	1648	860
Crystal size/mm^3	0.3 × 0.2 × 0.2	0.22 × 0.08 × 0.04	0.18 × 0.06 × 0.04	0.38 × 0.04 × 0.04	0.38 × 0.10 × 0.06	0.1 × 0.03 × 0.03
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
2Θ range for data coll./°	5.354 to 52.802	5.686 to 119.832	6.178 to 149.518	6.57 to 149.684	10.18 to 150.324	10.86 to 149.778
Index ranges	-12 ≤ h ≤ 12, -33 ≤ k ≤ 33, -19 ≤ l ≤ 19	-29 ≤ h ≤ 30, -10 ≤ k ≤ 10, -33 ≤ l ≤ 34	-13 ≤ h ≤ 13, -13 ≤ k ≤ 14, -19 ≤ l ≤ 19	-29 ≤ h ≤ 29, -7 ≤ k ≤ 7, -34 ≤ l ≤ 35	-22 ≤ h ≤ 22, -14 ≤ k ≤ 14, -25 ≤ l ≤ 25	-16 ≤ h ≤ 15, -13 ≤ k ≤ 13, -20 ≤ l ≤ 20
Reflections collected	146440	44289	141515	81773	55090	56149
Independent reflections	15877 [R$_{int}$ = 0.0551, R$_{sigma}$ = 0.0239]	6054 [R$_{int}$ = 0.0382, R$_{sigma}$ = 0.0249]	7359 [R$_{int}$ = 0.0707, R$_{sigma}$ = 0.0224]	7626 [R$_{int}$ = 0.0323, R$_{sigma}$ = 0.0167]	8373 [R$_{int}$ = 0.0409, R$_{sigma}$ = 0.0277]	8347 [R$_{int}$ = 0.0358, R$_{sigma}$ = 0.0312]
Data/restraints/parameters	15877/7/905	6054/1/462	7359/0/414	7626/0/428	8373/7/498	8347/1/492
Goodness-of-fit on F^2	1.057	1.039	1.058	1.05	1.054	1.035
Final R indexes [I>=2σ (I)]	R$_1$ = 0.0293, wR$_2$ = 0.0646	R$_1$ = 0.0271, wR$_2$ = 0.0639	R$_1$ = 0.0429, wR$_2$ = 0.0870	R$_1$ = 0.0217, wR$_2$ = 0.0567	R$_1$ = 0.0199, wR$_2$ = 0.0515	R$_1$ = 0.0179, wR$_2$ = 0.0444
Final R indexes [all data]	R$_1$ = 0.0314, wR$_2$ = 0.0656	R$_1$ = 0.0316, wR$_2$ = 0.0664	R$_1$ = 0.0483, wR$_2$ = 0.0900	R$_1$ = 0.0229, wR$_2$ = 0.0576	R$_1$ = 0.0201, wR$_2$ = 0.0516	R$_1$ = 0.0180, wR$_2$ = 0.0444
Largest diff. peak/hole/e Å^{-3}	0.56/-0.47	0.43/-0.56	1.25/-1.37	0.39/-0.72	0.37/-0.99	0.35/-0.49

10. References

1. A. K. Bowser, A. M. Anderson-Wile, D. H. Johnston and B. M. Wile, *Appl. Organomet. Chem.*, 2016, **30**, 32-39.
2. S.-D. Cho, H.-K. Kim, H.-s. Yim, M.-R. Kim, J.-K. Lee, J.-J. Kim and Y.-J. Yoon, *Tetrahedron*, 2007, **63**, 1345-1352.
3. E. Alacid and C. Nájera, *Org. Lett.*, 2008, **10**, 5011-5014.
4. D.-D. Li, W.-L. Chen, X.-L. Xu, F. Jiang, L. Wang, Y.-Y. Xie, X.-J. Zhang, X.-K. Guo, Q.-D. You and H.-P. Sun, *Eur. J. Med. Chem.*, 2016, **118**, 1-8.
5. H. Li, Y. Wu and W. Yan, *J. Organomet. Chem.*, 2006, **691**, 5688-5696.
6. H. Li, C.-L. Sun, M. Yu, D.-G. Yu, B.-J. Li and Z.-J. Shi, *Chem. Eur. J.*, 2011, **17**, 3593-3597.
7. D. Zhang, L. Le, R. Qiu, W.-Y. Wong and N. Kambe, *Angew. Chem. Int. Ed.*, 2021, **60**, 3104-3114.
8. L.-C. Liu, Y.-H. Tzeng, C.-H. Hung and H. M. Lee, *Eur. J. Inorg. Chem.*, 2020, 3601-3611.