Supporting information

Development of (quinolinyl)amido-based pincer palladium complexes: A robust and phosphine-free catalyst system for C–H arylation of benzothiazoles

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Contents

1. Kinetics data

Table S1. Concentration of benzothiazole and product **7aa** at different time intervals.

Time (min)	Conc. of benzothiazole [M]	Conc. of **7aa** [M]
10	0.2691	0.0285
20	0.2403	0.0588
30	0.2196	0.0798
40	0.2068	0.0900
50	0.1803	0.1089
60	0.1559	0.1239
90	0.1232	0.1551
120	0.1076	0.1812
180	0.0634	0.2259

Conditions: Benzothiazole (0.3 M), 4-iodotoluene (0.45 M), K_2CO_3 (1.5 equiv), **3a** (0.0015 M), CuI (0.003 M), mesitylene (0.03 mL, 0.1078 M, internal standard), DMSO (required amount to make total volume 2.0 mL).

Table S2. Concentration of various arylation products at different time intervals.

Time (min)	Conc. of various arylated products of benzothiazole [M]				
	R = OMe	R = Me	R = H	R = Cl	R = C(O)OMe
10	0.0762	0.0285	0.0351	0.0165	0.0102
20	0.1092	0.0588	0.0504	0.0336	0.0238
30	0.1446	0.0798	0.0675	0.0513	0.0278
40	0.1665	0.0900	0.0840	0.0549	0.0328
50	0.1896	0.1089	0.0969	0.0648	0.0352
60	0.2100	0.1239	0.1110	0.0675	0.0426

Conditions: Benzothiazole (0.3 M), 4-iodoarene (0.45 M), K_2CO_3 (1.5 equiv), **3a** (0.0015 M), CuI (0.003 M), mesitylene (0.03 mL, 0.1078 M, internal standard), DMSO (required amount to make total volume 2.0 mL).

Table S3. Values of k_R, k_R/k_H, log (k_R/k_H) and Hammett substituent constant (σ_p).

	R = OMe	R = Me	R = H	R = Cl	R = C(O)OMe
k_R (x 10^{-3})	2.66	1.82	1.53	1.01	0.58
k_R/k_H	1.74	1.19	1.00	0.66	0.38
log (k_R/k_H)	0.24	0.08	0.00	-0.18	-0.42
σ_p	-0.27	-0.17	0.00	0.23	0.45

k_R = slope of corresponding plots of conc. of product *vs* time. σ_p values are *para* substituent constants determined by Hammett.

2. X-ray structure determination

The good quality single crystals of compounds **2a**, **3a** and **4a** were selected using Leica polorizing microscope. The selected crystals of compounds **2a** and **3a** were mounted on a Bruker APEX-II CCD diffractometer having graphite-monochromatized (MoK$_\alpha$= 0.71073Å) radiation for single crystal X-ray diffraction experiment. The crystals were kept at T = 150(2) K (**3a**) and T = 200(2) K (**2a**) during data collection. The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 12 frames (total 36 frames). Data were collected with ω scan width of 0.5° at eight different settings of φ and 2θ, keeping the sample-to-detector distance fixed at 5.00 cm for both the compounds. The X-ray data collection was monitored by APEX2 program (Bruker, 2006).[S1] All the data were corrected for Lorentzian, polarization and absorption effects using SAINT[S2] and SADABS programs (Bruker, 2006). Using ShelXTL[S3] (Bruker) program suite, the structure was solved with the ShelXS-97[S4] (Sheldrick, 2008) structure solution program, using direct methods. The model was refined with version of ShelXL-2013[S5] (Sheldrick, 2013) using Least Squares minimisation. All the hydrogen atoms were placed in geometrically idealized position and constrained to ride on their parent atoms, except water hydrogen atoms in **2a**, which were located in difference Fourier and refined isotropically.

The X-ray intensity measurements on crystals of **4a** carried out on a Bruker D8 VENTURE Kappa Duo PHOTON II CPAD diffractometer with (MoK$_\alpha$ = 0.71073Å) radiation. The crystal was kept at T = 100(2) K during data collection. The X-ray generator was operated at 50 kV and 1.4 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 12 frames (total 36 frames). Data were collected

with ω scan width of 0.5° at eight different settings of φ and 2θ, keeping the sample-to-detector distance fixed at 4.00 cm. The X-ray data collection was monitored by APEX3 program (Bruker, 2016).[S6] All the data were corrected for Lorentzian, polarization and absorption effects using SAINT[S2] and SADABS programs intregrated in APEX3 program suite (Bruker, 2016). Using APEX3 (Bruker) program suite, the structure was solved with the ShelXS-97[S4] (Sheldrick, 2008) structure solution program, using direct method. The model was refined with version of ShelXL-2014[S7] (Sheldrick, 2014) using Least Squares minimisation. All the hydrogen atoms were placed in geometrically idealized position and constrained to ride on their parent atoms, except water hydrogen atoms, which were located in difference Fourier and refined isotropically.

The *ORTEP* III[S8] view of all three compounds were drawn with 50% probability displacement ellipsoids and H atoms are not included for the clarity. Crystal data for the structures have been deposited in the Cambridge Crystallographic Data Center with numbers (compound numbers) CCDC-1487195 (**2a**), CCDC-1487196 (**3a**) and CCDC-1502139 (**4a**).
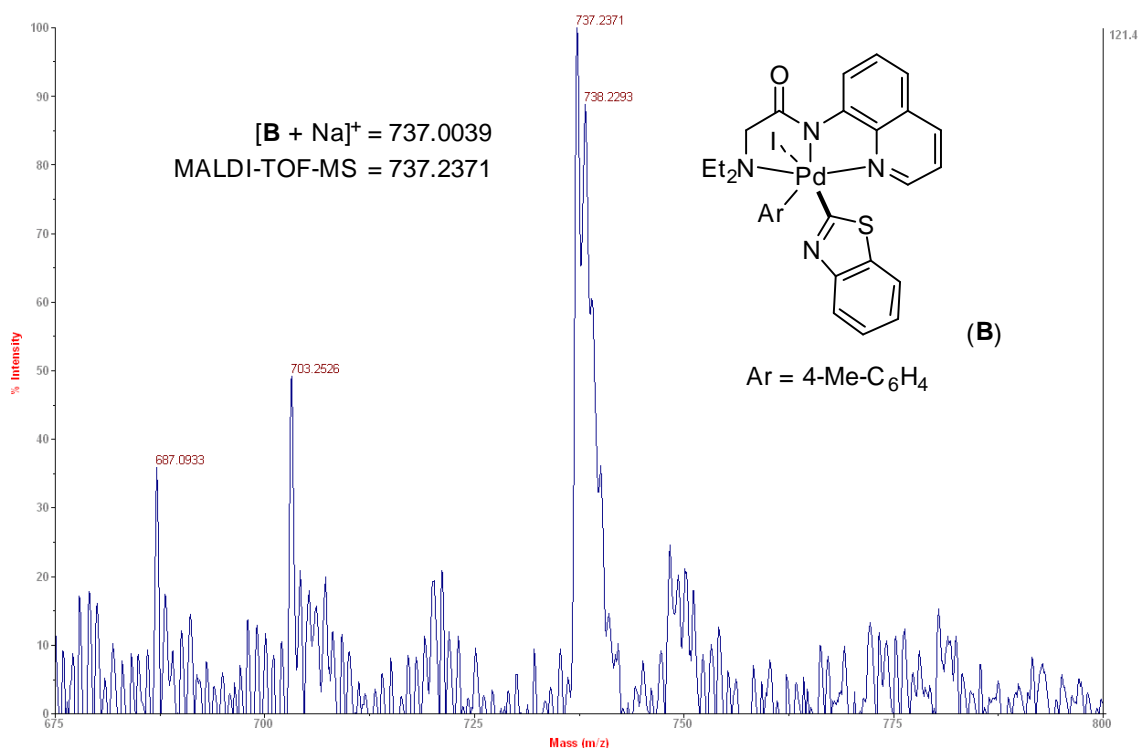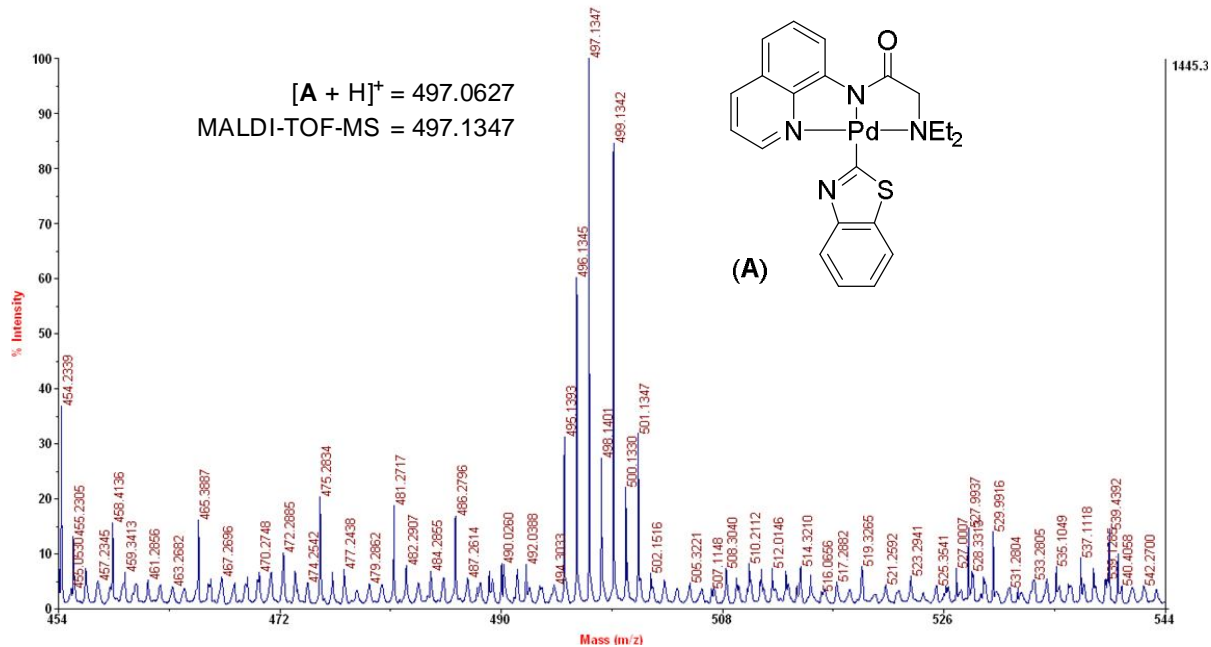
Table S4. Crystal data and structure refinement for complexes **2a**, **3a** and **4a**.

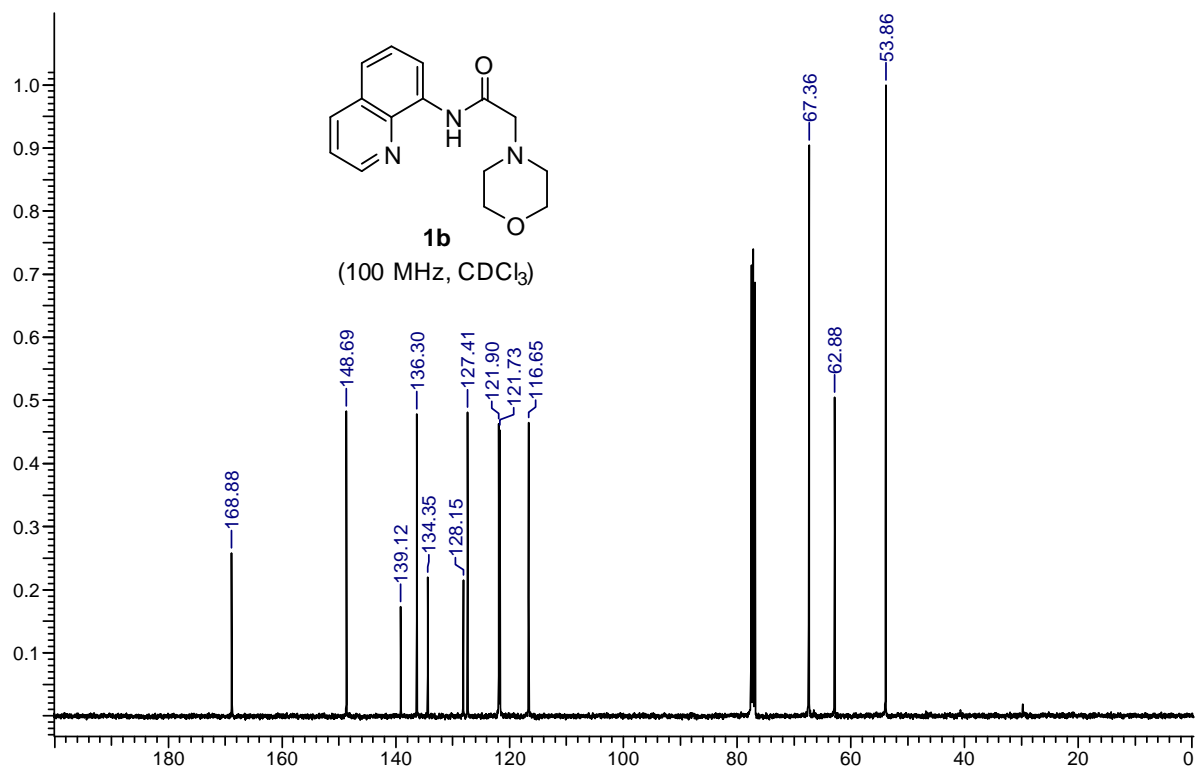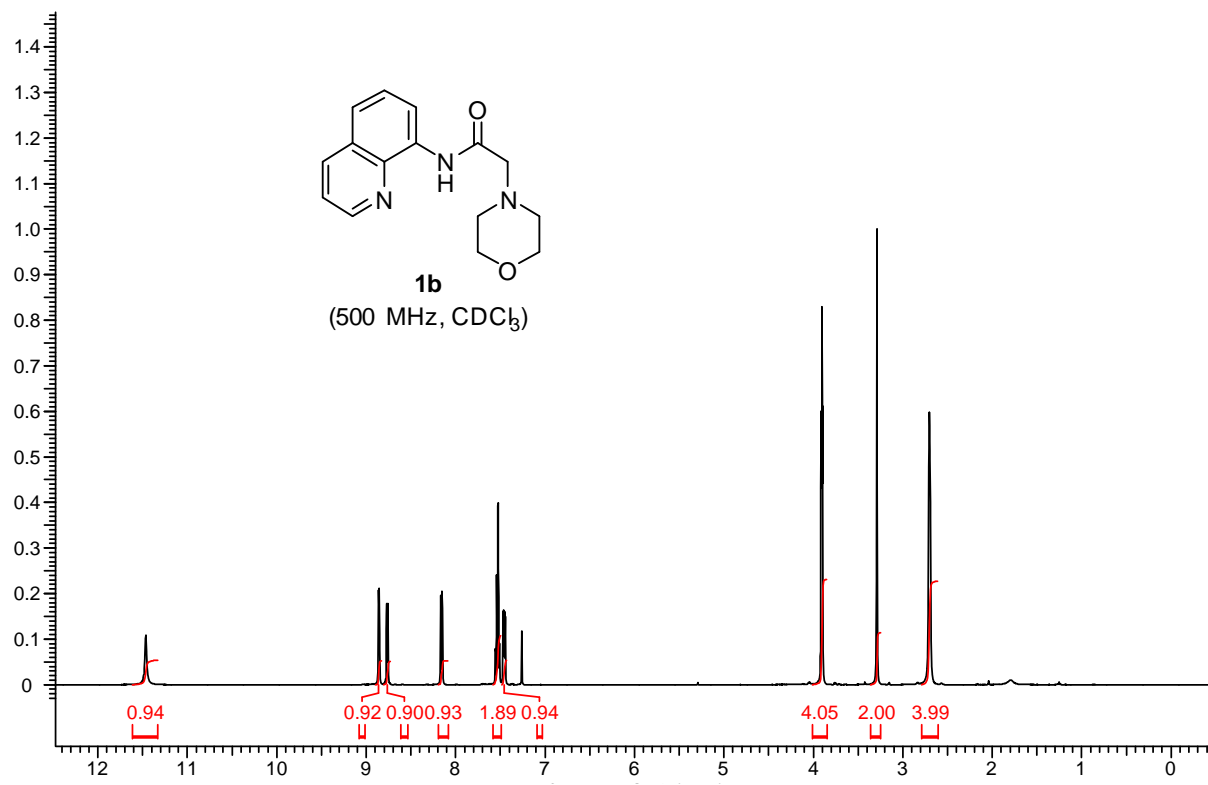|	2a	3a	4a
Empirical formula	$C_{17}H_{23}N_3O_4Pd$	$C_{15}H_{18}ClN_3OPd$	$C_{15}H_{18}IN_3OPd$
Formula weight	439.78	398.17	489.62
Temperature, K	200(2)	150(2)	100(2)
Cryst. Syst.	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	C2/c	P2(1)/c
a (Å)	10.8321(4)	14.7945(6)	10.5522(12)
b (Å)	23.7645(8)	13.1480(5)	11.3163(18)
c (Å)	6.9558(2)	16.0956(7)	13.8002(13)
α (°)	90	90	90
β (°)	103.107(2)	102.202(2)	104.277(4)
γ (°)	90	90	90
V (Å^3)	1743.91(10)	3060.2(2)	1597.0(3)
Z	4	8	4
ρ cald. Mg/m^3	1.675	1.728	2.036
ε (mm^{-1})	1.091	1.389	3.097
F (000)	896	1600	944
Crystal size (mm)	0.46 x 0.31 x 0.21	0.46 x 0.40 x 0.32	0.22 x 0.19 x 0.11
θ (min, max) (°)	1.714, 24.996	2.093, 24.995	2.685, 33.498
R(int)	0.0411	0.0179	0.0511
Independent reflections	3049	2696	6134
Completeness to θ (%)	96.5	97.5	99.8
Max. and min. transmission	0.8033, 0.6342	0.6649, 0.5675	0.727, 0.549
Data / restraints / parameters	3049 / 0 / 237	2696 / 0 / 192	6134 / 0 / 193
GOF on F^2	1.300	1.101	1.190
R1, wR2 ($I>2\sigma(I)$)	0.0621, 0.1062	0.0181, 0.0420	0.0195, 0.0379
R1, wR2 (all data)	0.0742, 0.1099	0.0187, 0.0423	0.0253, 0.0392

3. References

S1.   APEX2 suite for crystallographic software, Bruker axs, Madison, WI (Bruker, 2006).

S2.   SAINT - Software for the Integration of CCD Detector System Bruker Analytical X-ray Systems, Bruker axs, Madison, WI (Bruker, 2006 and Bruker, 2016).

S3.   ShelXTL, Bruker axs, Madison, WI (Bruker, 2006).

S4.   G. M. Sheldrick, A short history of ShelX, *Acta Cryst.*, 2008, **A64**, 339-341.

S5.   T. Gruene, H. W. Hahn, A. V. Luebben, F. Meilleur and G. M. Sheldrick, *J. Appl. Cryst.* 2014, **47**, 462-466.

S6.   APEX3 suite for crystallographic software, Bruker axs, Madison, WI (Bruker, 2016).

S7.   G. M. Sheldrick, SHELXL 2014/7, University of Göttingen, Germany, 2014.

S8.   L. J. Farrugia, *J. Appl. Cryst.* 1997, **30**, 565-565.

4. MALDI-TOF-MS of intermediates A and B

[**A** + H]$^+$ = 497.0627
MALDI-TOF-MS = 497.1347

(A)

[**B** + Na]$^+$ = 737.0039
MALDI-TOF-MS = 737.2371

(B)

Ar = 4-Me-C$_6$H$_4$

5. NMR spectra of ligand precursors

1b
(500 MHz, CDCl₃)

1b
(100 MHz, CDCl₃)

1c

(400 MHz, CDCl$_3$)

0.93 0.93 0.92 0.95 1.92 0.98 2.00 7.79 2.99

1c

(100 MHz, CDCl$_3$)

169.30 148.64 139.18 136.30 134.51 128.19 127.47 121.84 121.70 116.68 62.49 55.49 53.45 46.24
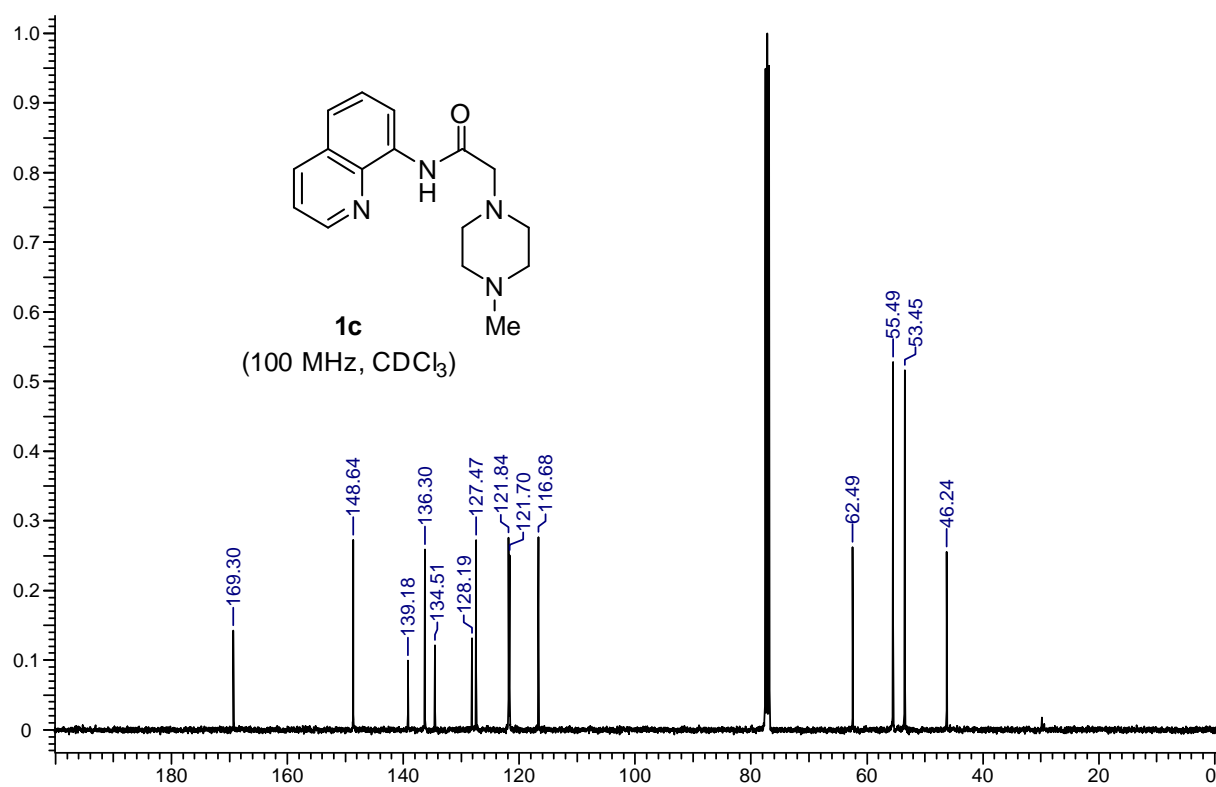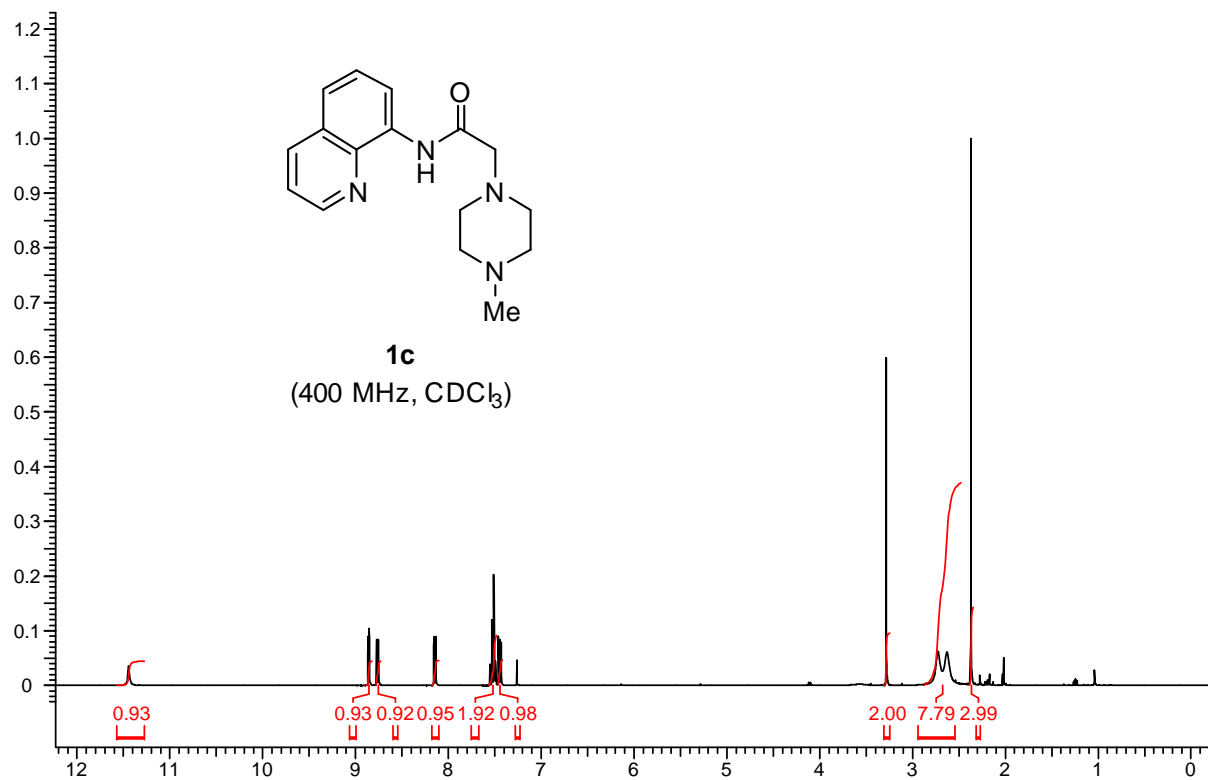
6. NMR spectra of palladium complexes

2a
(500 MHz, CDCl$_3$)

2a
(125 MHz, CDCl$_3$)

2b

(500 MHz, CDCl₃)

0.91 0.92 0.90 0.99 0.97 0.95   2.00 4.09 1.92   1.96   3.02

2b

(100 MHz, CDCl₃)

178.60 172.85 148.66 146.55 145.02 139.38 129.90 129.64 121.25 121.02 120.49 69.35 62.36 59.25 29.84 24.37

S13

2c
(500 MHz, CDCl₃)

2c
(100 MHz, CDCl₃)

3a

(500 MHz, CDCl₃)

0.92 0.92 0.94 1.00 0.99 0.96   2.02 2.03 2.04 6.00

3a

(125 MHz, CDCl₃)

175.83 150.35 147.05 145.16 139.15 130.09 129.59 121.38 120.73 120.46 66.38 58.77 13.50

3c
(500 MHz, CDCl$_3$)

0.90 0.92 0.94 1.00 0.96 0.94   1.95 2.00 1.92 1.89 1.99 2.98

3c
(100 MHz, CDCl$_3$)

174.16 150.83 146.95 144.82 139.19 129.96 129.54 121.45 120.73 59.26 49.38 46.12

4a
(500 MHz, CDCl₃)

0.85 0.93 0.93 0.98 0.95 0.86 2.00 1.89 1.89 5.95

4a
(125 MHz, CDCl₃)

176.88 156.45 146.98 145.62 138.91 130.42 129.62 122.18 120.85 120.73 67.08 61.93 14.27