Supporting Information

Fluoride-free Hiyama Coupling by Palladium Abnormal N-heterocyclic Carbene Complexes

Sudipta Modak,[†] Manoj Kumar Gangwar,[†] Mitta Nageswar Rao,[†] Madasu Mahesh,[†] Alok Ch. Kalita,[†] Vincent Dorcet,[‡] Mayuri Arun Shejale,[†] Ray J. Butcher[¶] and Prasenjit Ghosh*[,†]

[†]Department of Chemistry,
Indian Institute of Technology Bombay,
Powai, Mumbai 400 076.

[‡]Université de Rennes 1,
Institut des Sciences chimiques de Rennes,
Campus de Beaulieu, 35042 – Rennes, France

[¶] Department of Chemistry
Howard University.
Washington DC 20059, USA

Email: pghosh@chem.iitb.ac.in

Fax: +91-22-2572-3480

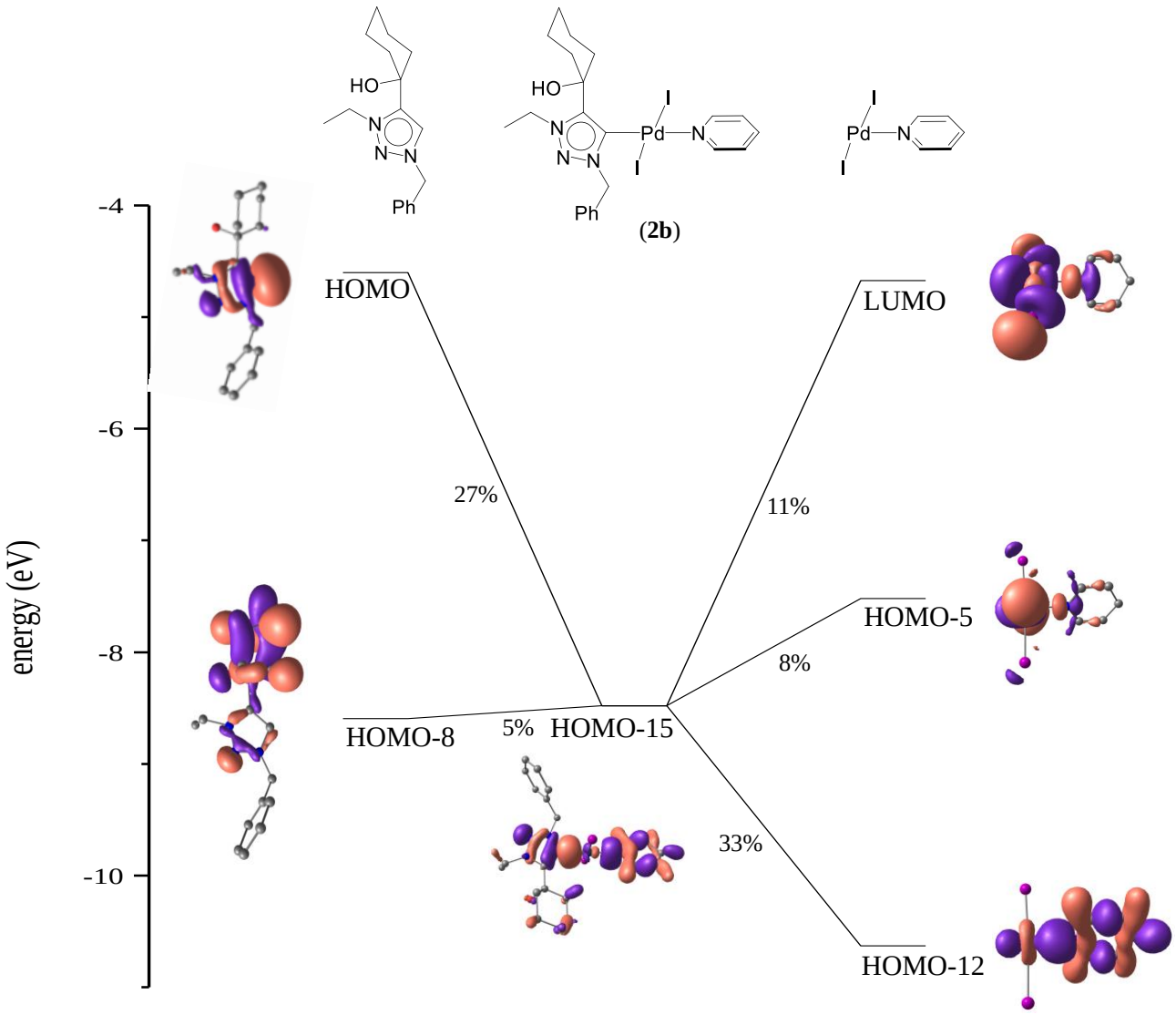


Figure S1. Simplified orbital interaction diagram showing major contribution to the (*a*-NHC)–Pd bonding orbital HOMO-15 in **2b**.

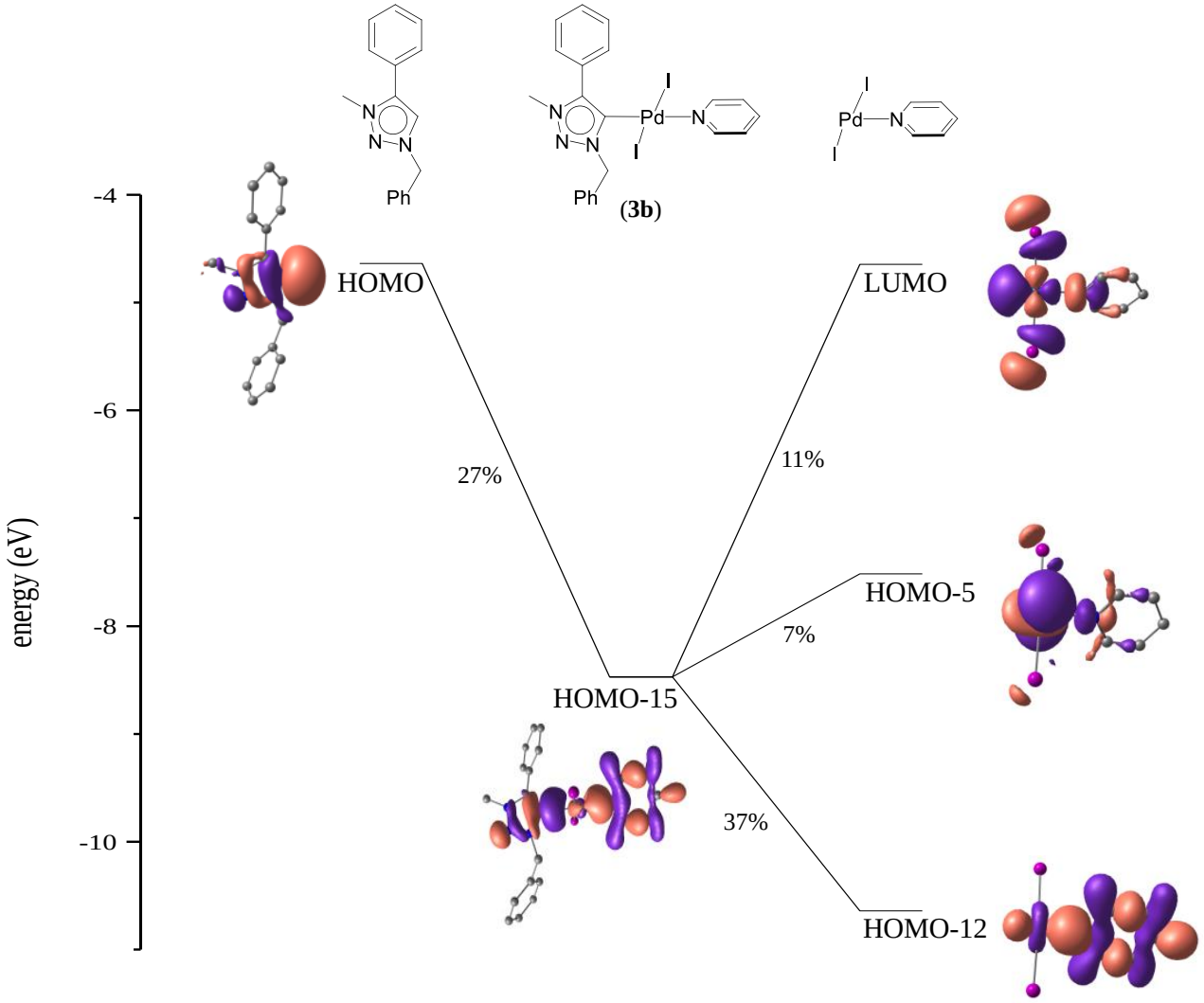


Figure S2. Simplified orbital interaction diagram showing major contribution to the (*a*-NHC)–Pd bonding orbital HOMO-15 in **3b**.

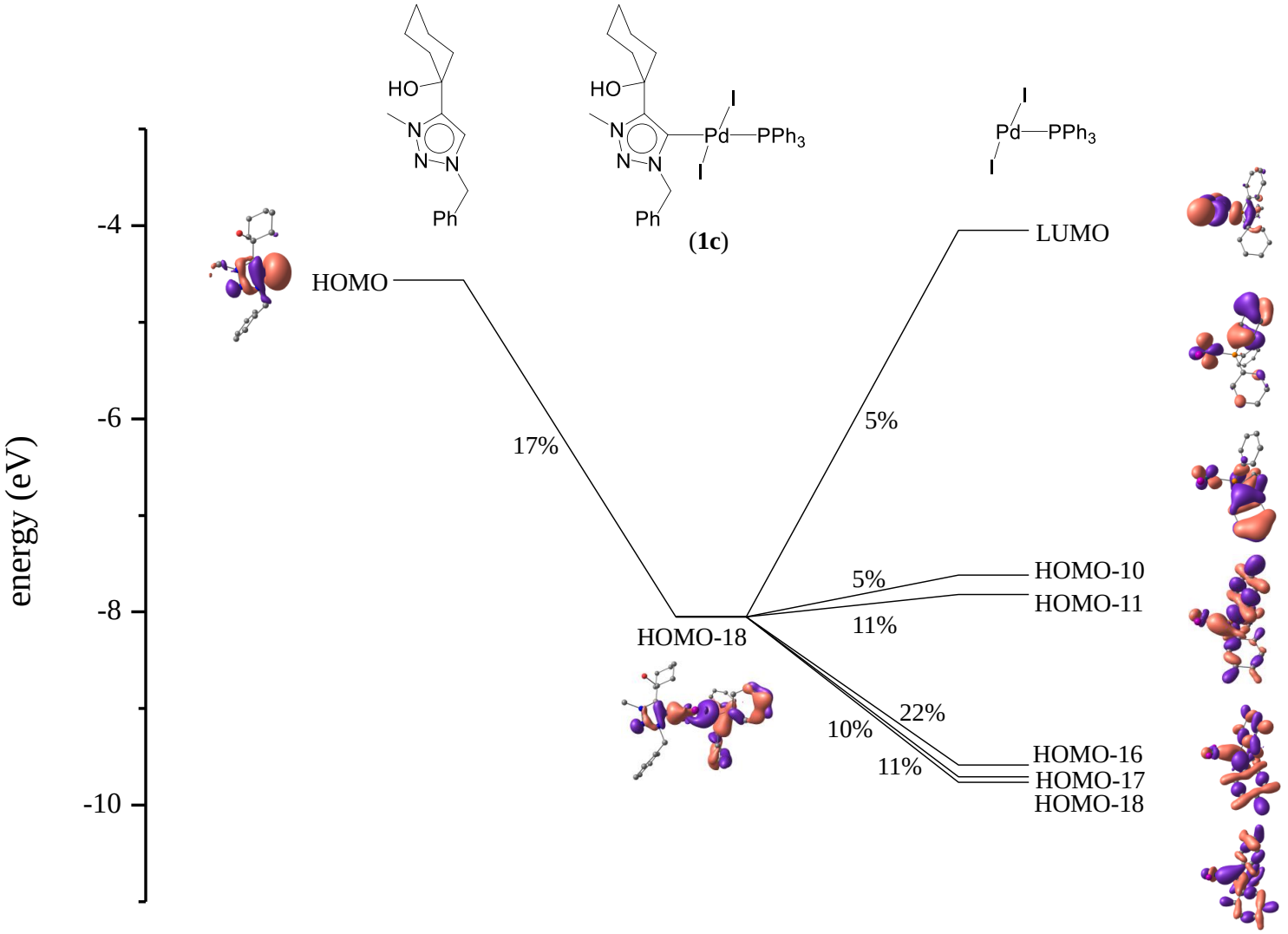


Figure S3. Simplified orbital interaction diagram showing major contribution to the (*a*-NHC)–Pd bonding orbitals in **1c**.

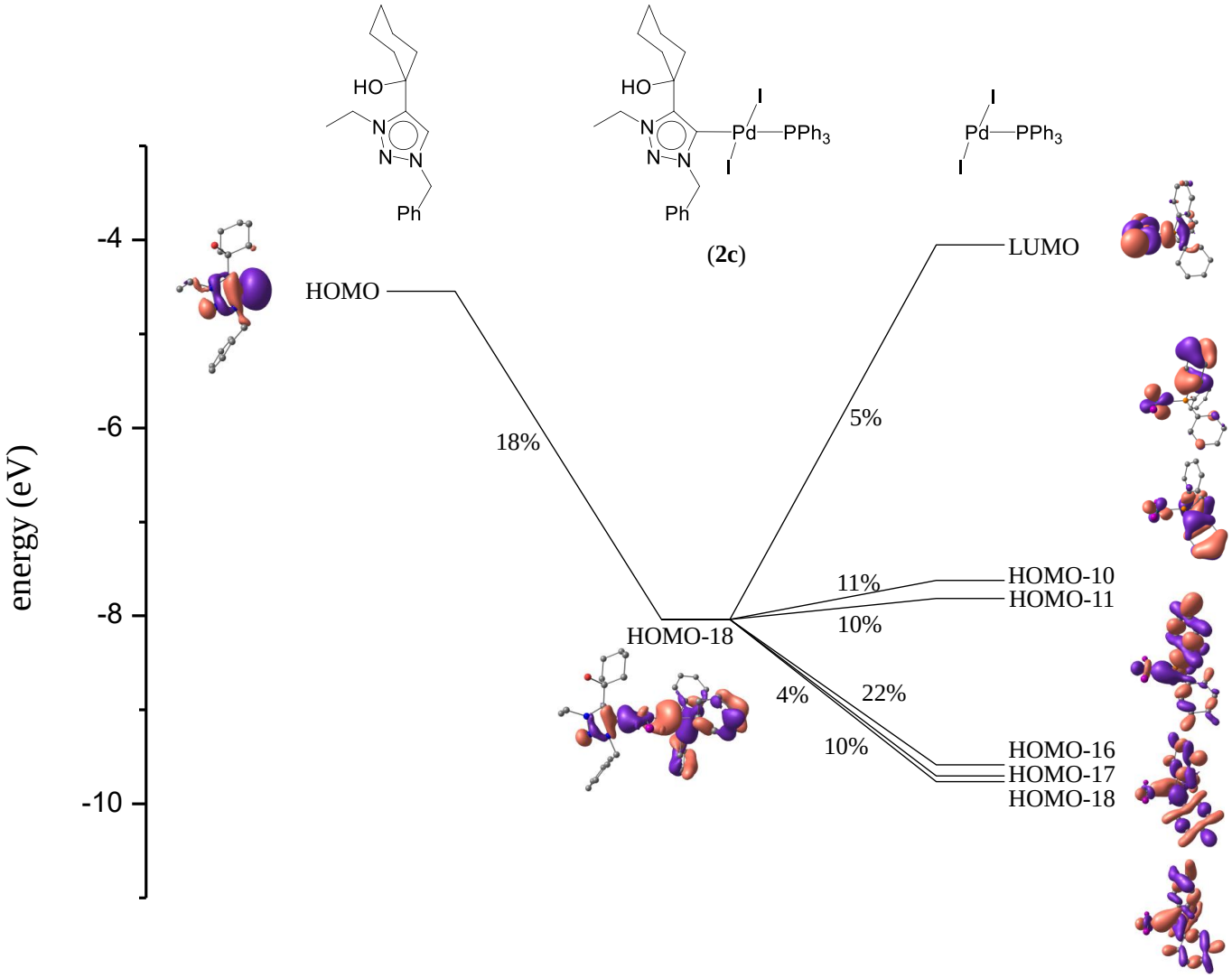


Figure S4. Simplified orbital interaction diagram showing major contribution to the (*a*-NHC)–Pd bonding orbitals in **2c**.

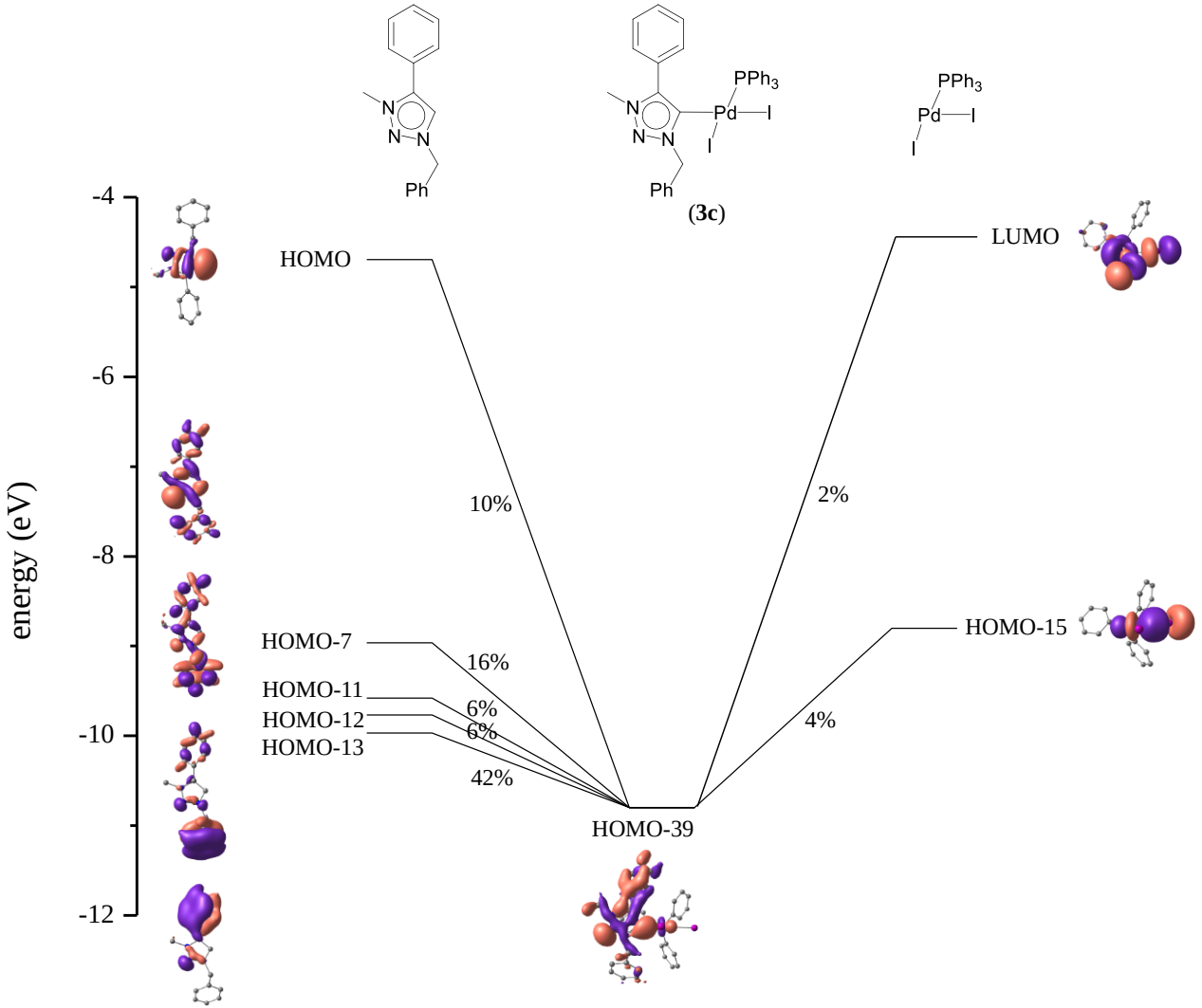


Figure S5. Simplified orbital interaction diagram showing major contribution to the (*a*-NHC)–Pd bonding orbitals in **3c**.

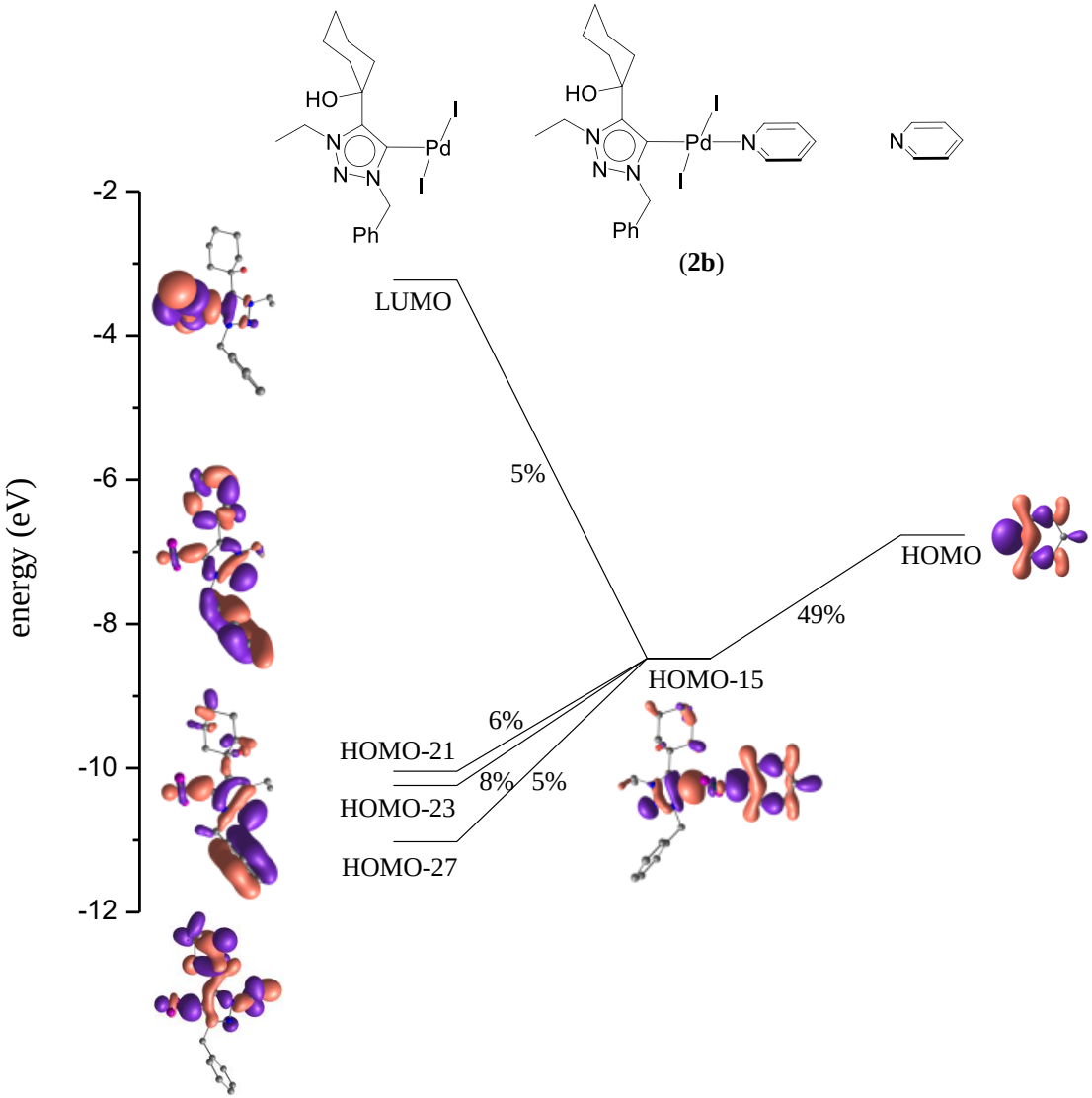


Figure S6. Simplified orbital interaction diagram showing major contribution to the Pd–NC_5H_5 bonding orbitals in **2b**.

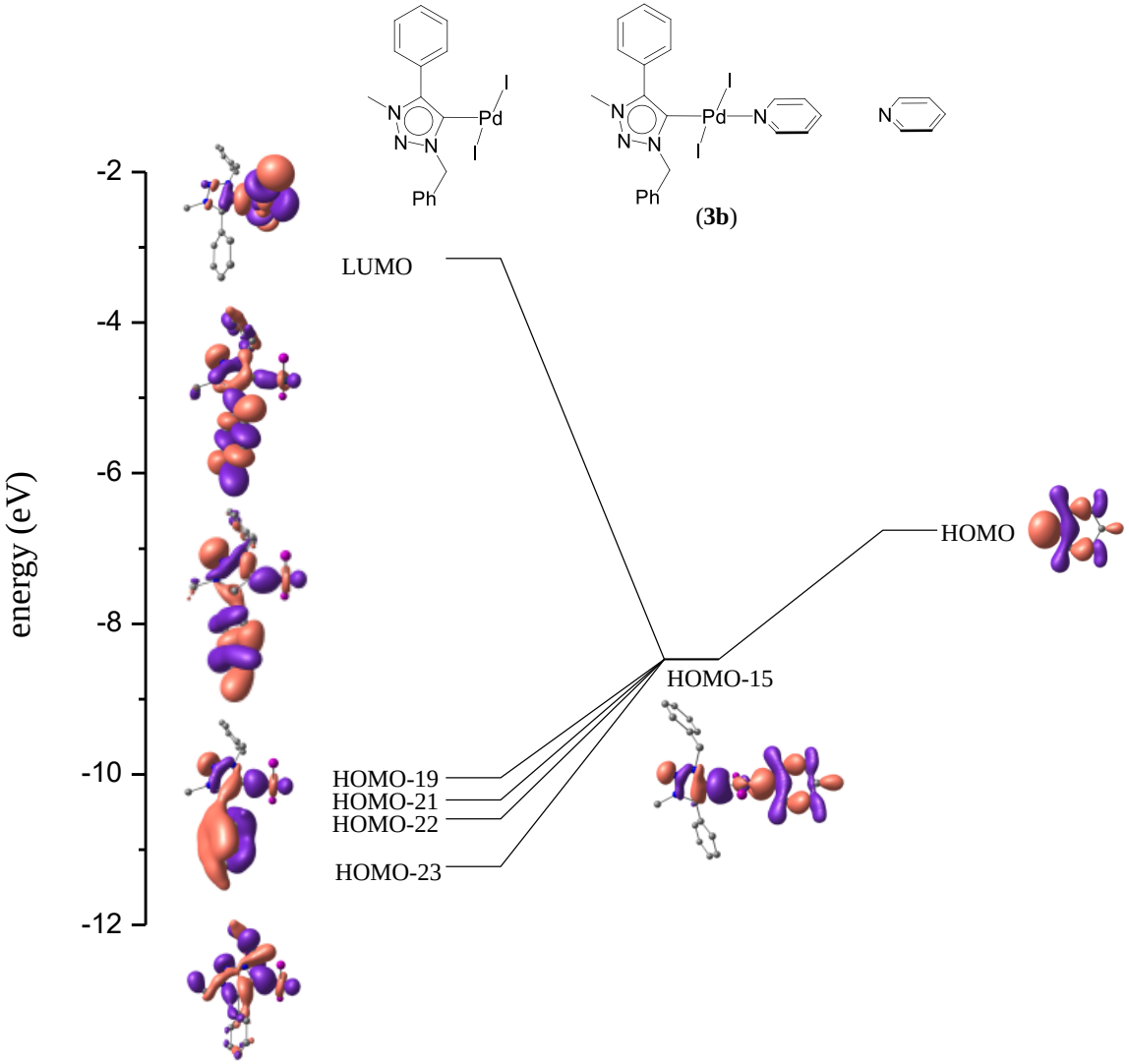


Figure S7. Simplified orbital interaction diagram showing major contribution to the Pd–NC_5H_5 bonding orbitals in **3b**.

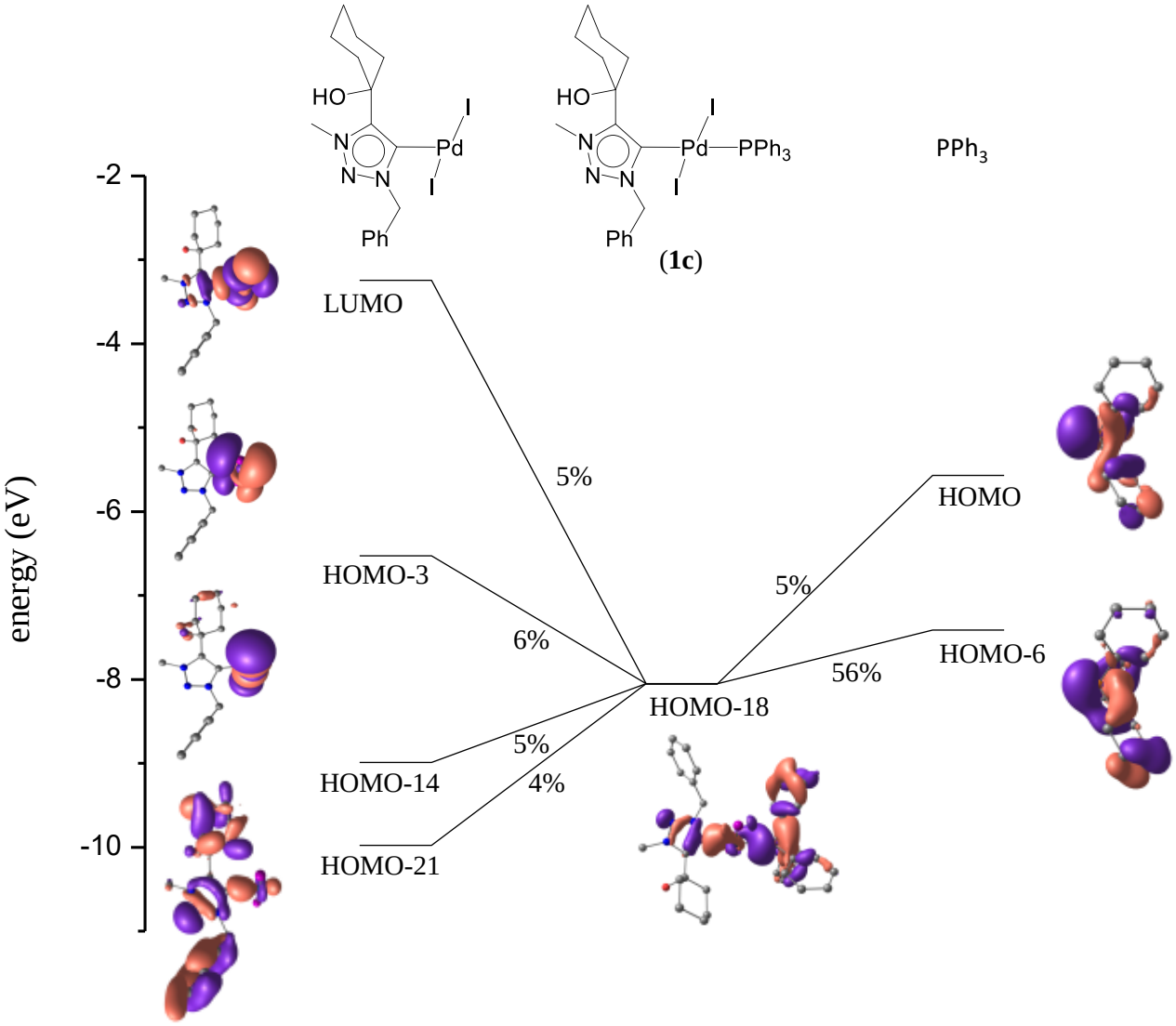


Figure S8. Simplified orbital interaction diagram showing major contribution to the Pd–PPh_3 bonding orbitals in **1c**.

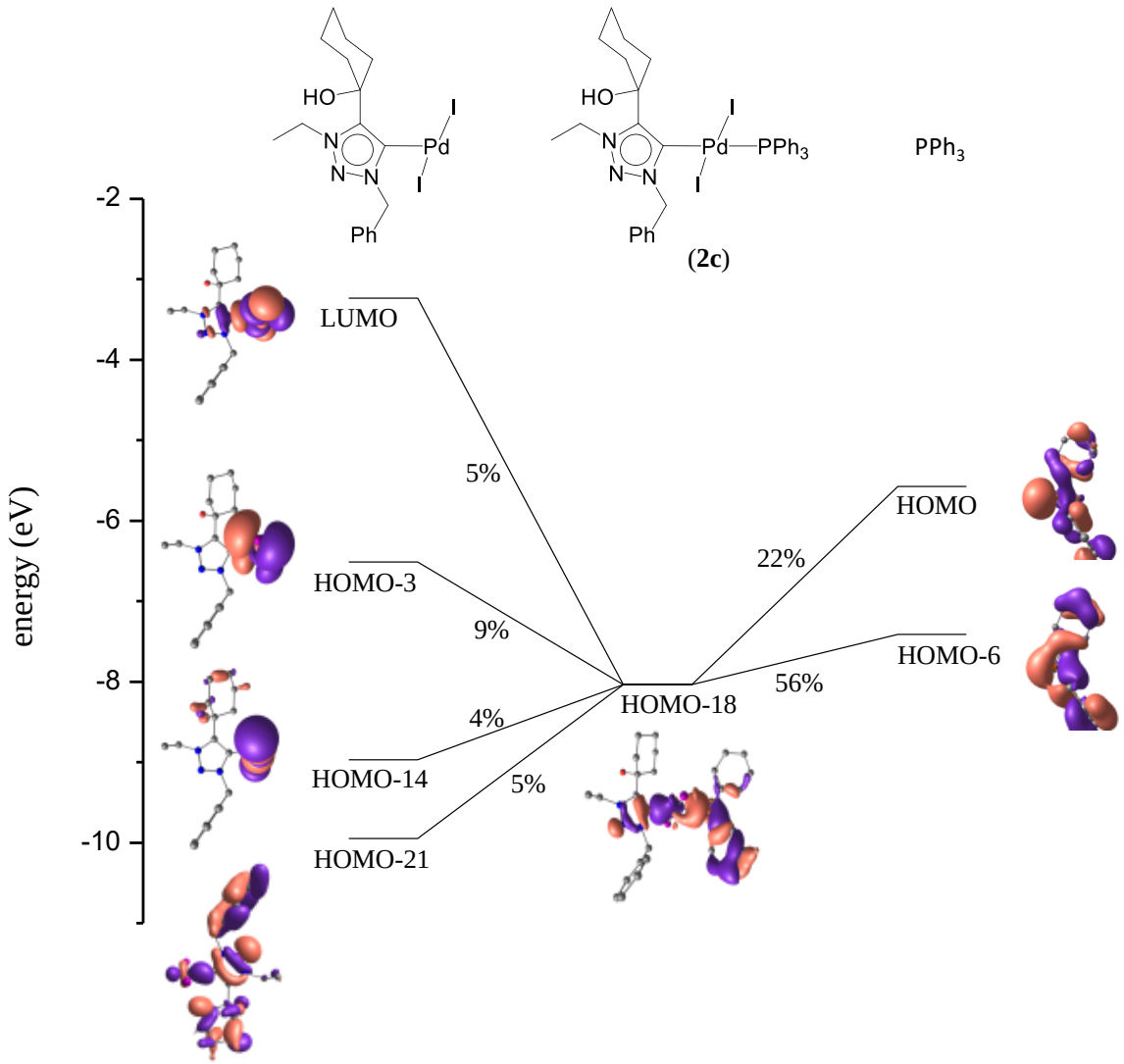


Figure S9. Simplified orbital interaction diagram showing major contribution to the Pd–PPh_3 bonding orbitals in **2c**.

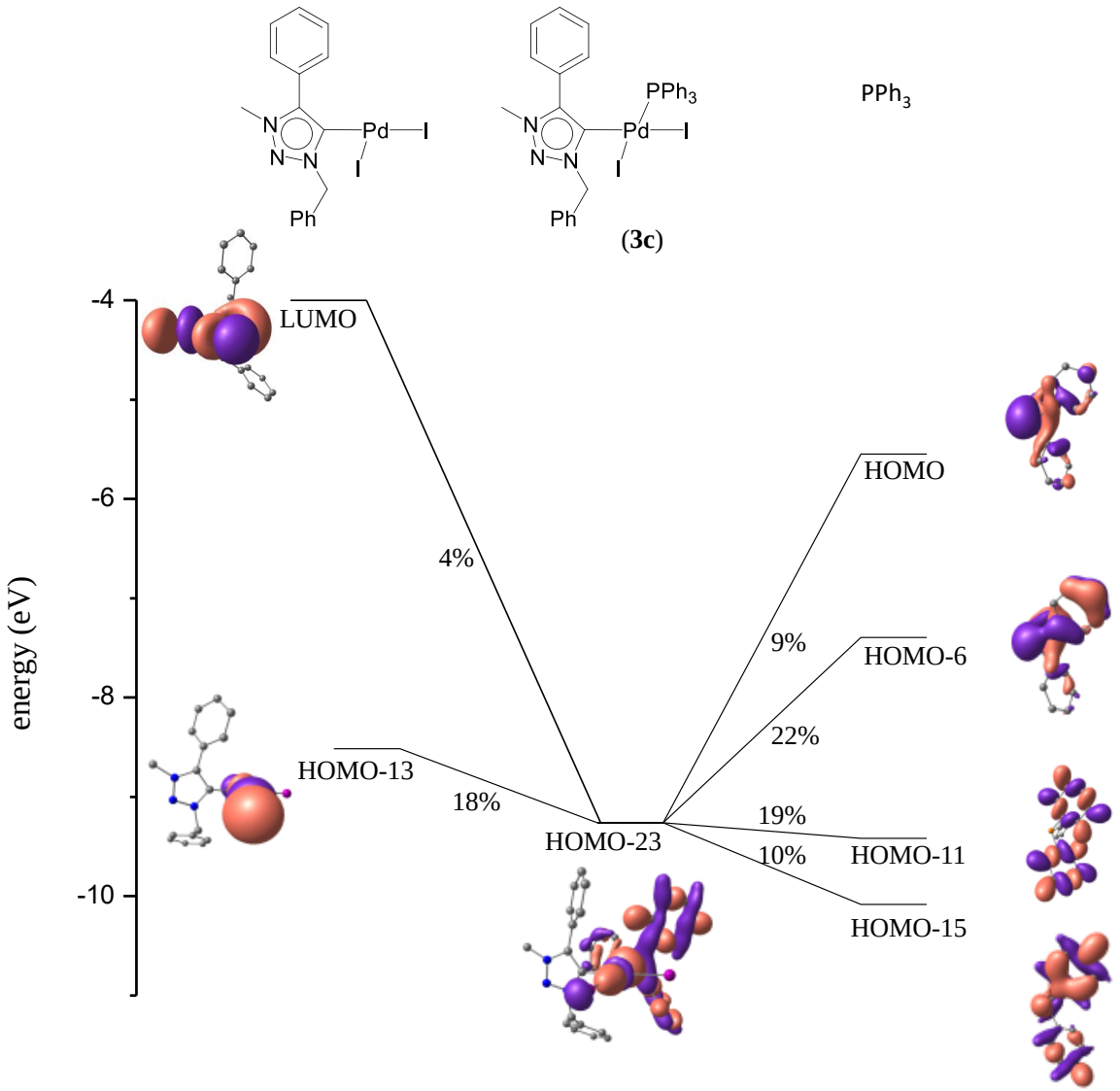


Figure S10. Simplified orbital interaction diagram showing major contribution to the Pd–PPh_3 bonding orbitals in **3c**.

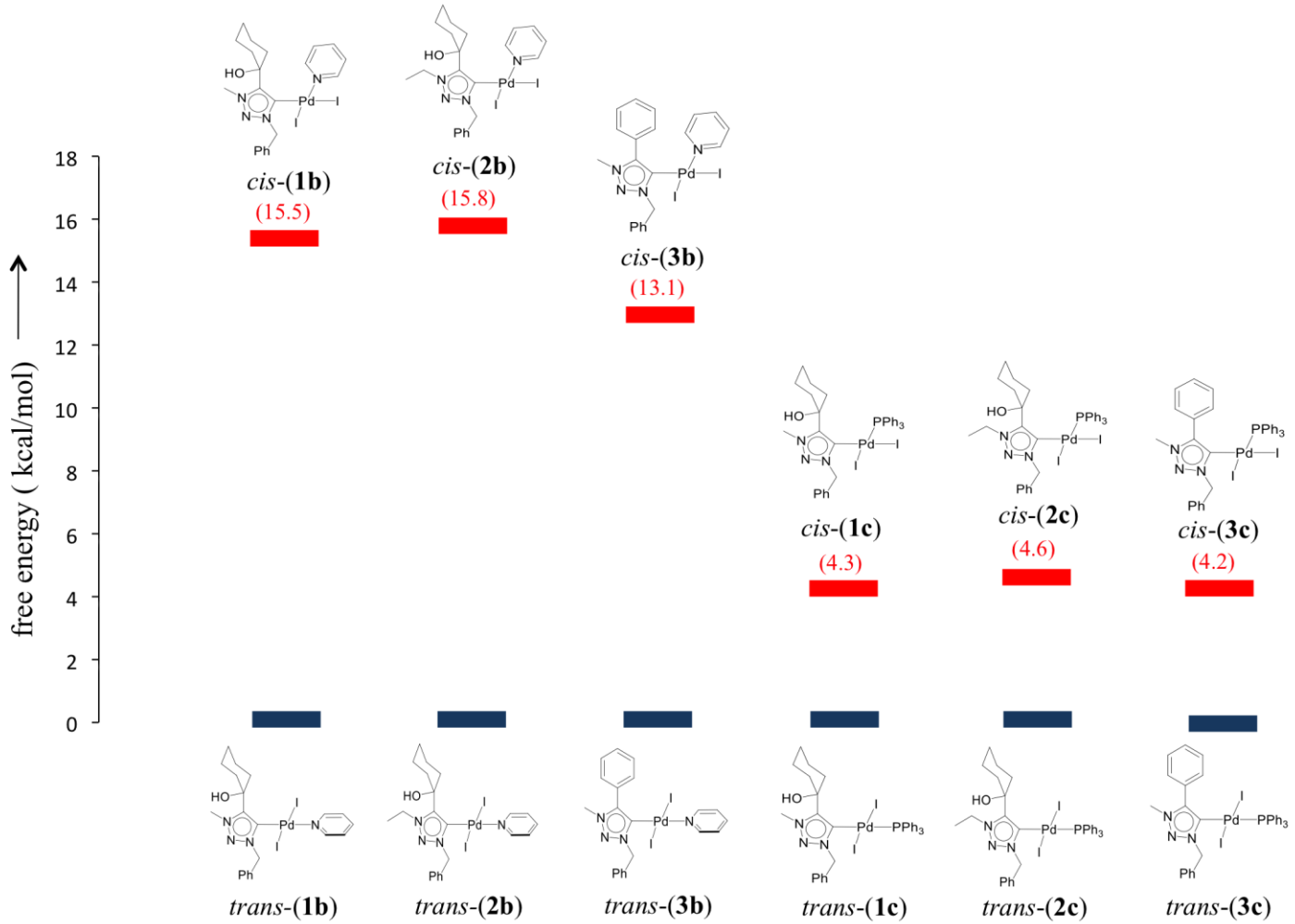


Figure S11. The relative free energies (ΔG, kcal/mol) in the isolated gas phase in B3LYP/SDD, 6-31G(d) level of theory for the *cis* and *trans* isomers of the (*a*-NHC)PdI_2(L) [L = pyridine, (**1-3**)**b** and PPh_3 (**1-3**)**c**] type complexes with the energy differences between each *cis-trans* pair shown (in red) within the parenthesis.

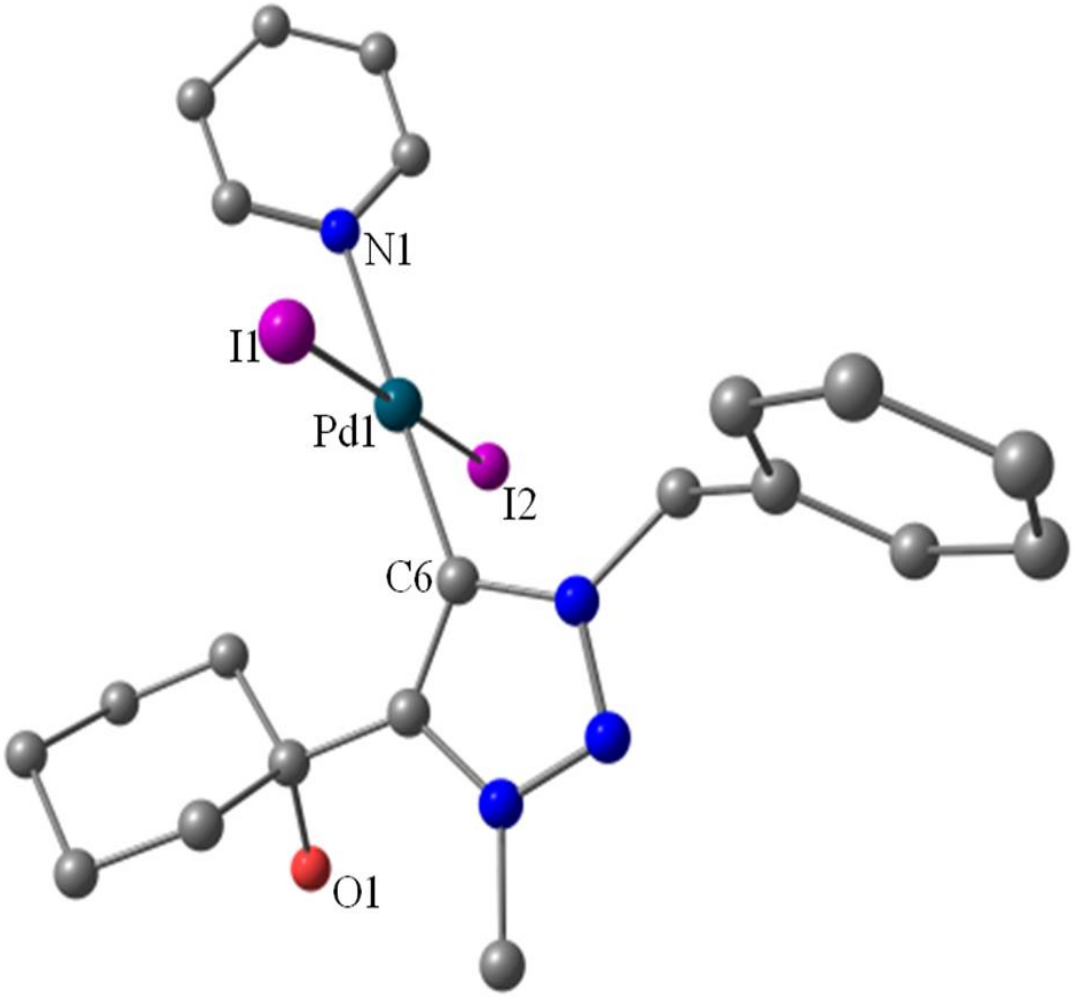


Figure S12. Computed structure of **1b** (*trans*). Selected bond lengths (Å) and bond angles (°): Pd(1)-C(6) 1.996, Pd(1)-N(1) 2.147, Pd(1)-I(1) 2.717, Pd(1)-I(2) 2.722, C(6)-Pd(1)-N(1) 179.59, C(6)-Pd(1)-I(1) 88.09, N(1)-Pd(1)-I(1) 91.52, C(6)-Pd(1)-I(2) 88.89, N(1)-Pd(1)-I(2) 91.47, I(1)-Pd(1)-I(2) 176.61.

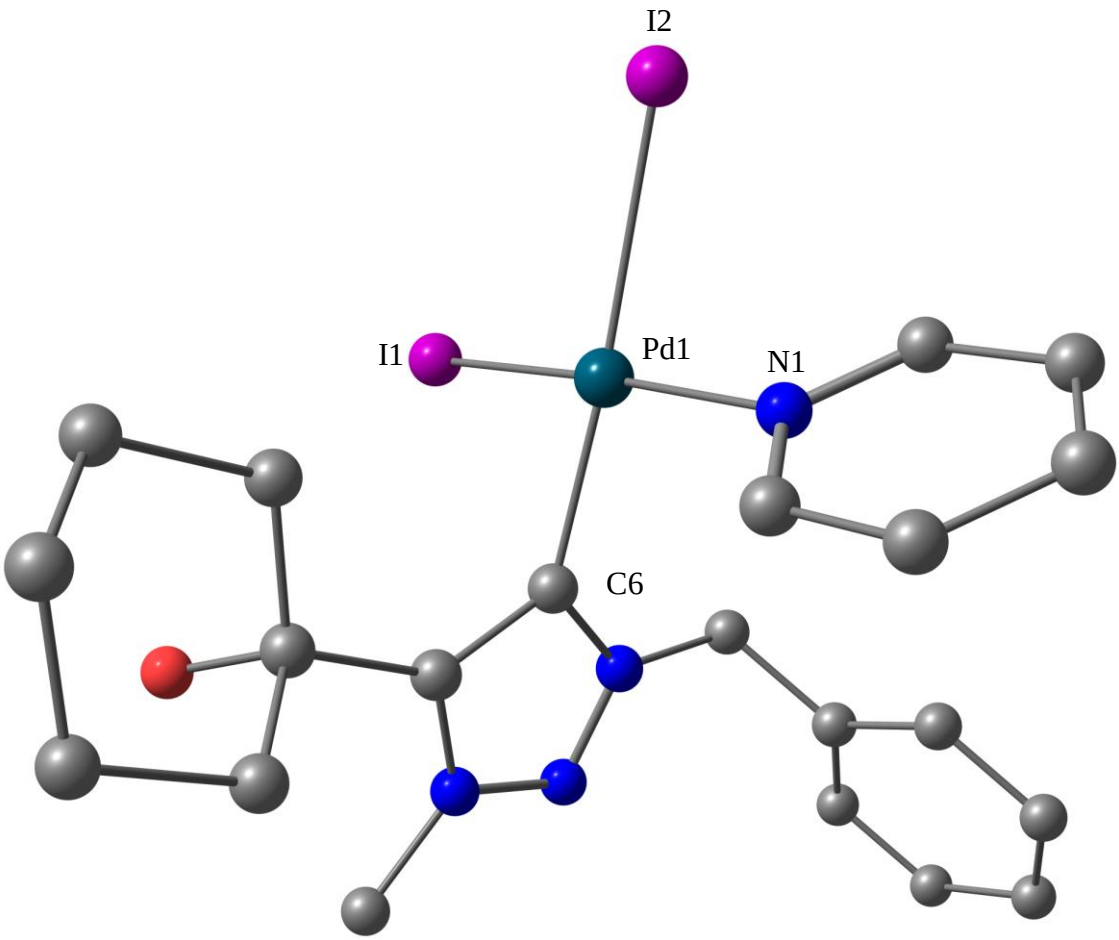


Figure S13. Computed structure of **1b** (*cis*). Selected bond lengths (Å) and bond angles (°): Pd(1)-C(6) 2.034, Pd(1)-N(1) 2.151, Pd(1)-I(1) 2.688, Pd(1)-I(2) 2.720, C(6)-Pd(1)-N(1) 93.11, C(6)-Pd(1)-I(1) 84.42, N(1)-Pd(1)-I(1) 174.66, C(6)-Pd(1)-I(2) 176.25, N(1)-Pd(1)-I(2) 89.92, I(2)-Pd(1)-I(1) 92.72.

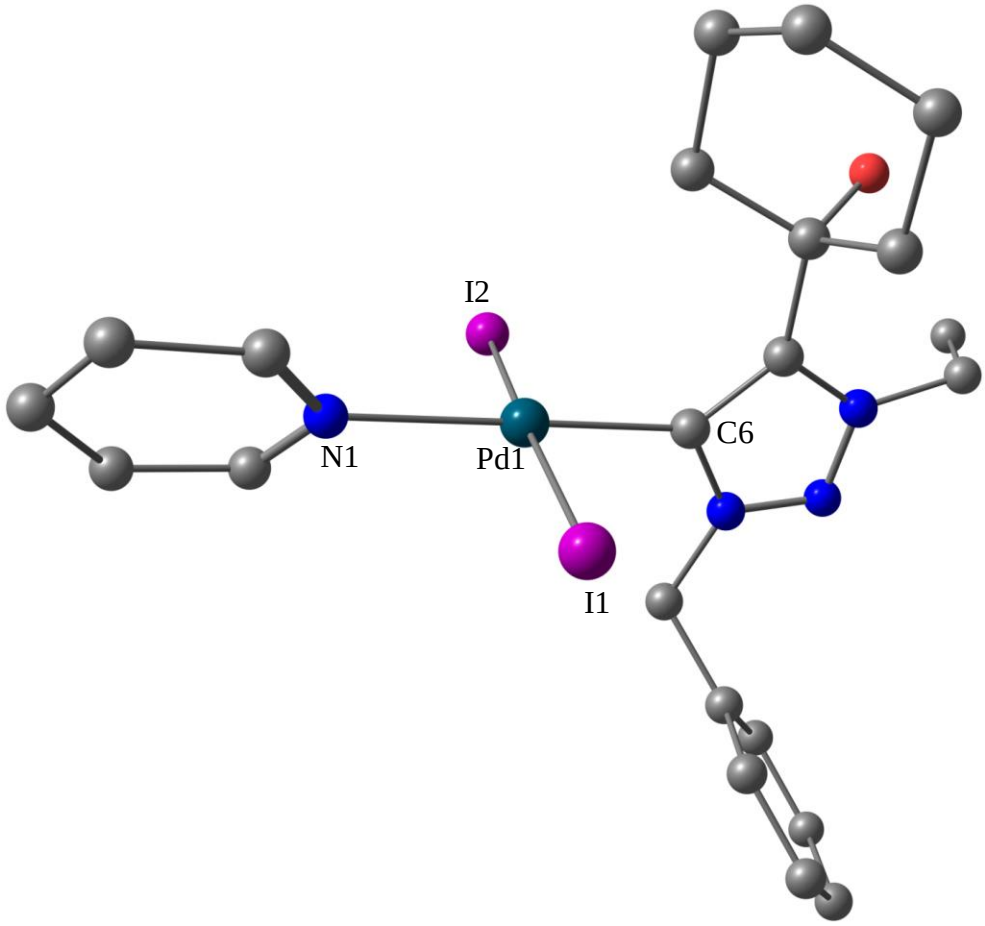


Figure S14. Computed structure of **2b** (*trans*). Selected bond lengths (Å) and bond angles (°): Pd(1)-C(6) 1.997, Pd(1)-N(4) 2.149, Pd(1)-I(1) 2.719, Pd-I(2) 2.718, C(6)-Pd(1)-N(4) 179.27, C(6)-Pd(1)-I(1) 87.67, N(4)-Pd(1)-I(1) 91.76, C(6)-Pd(1)-I(2) 89.28, N(4)-Pd(1)-I(2) 91.2, I(1)-Pd(1)-I(2) 176.24.

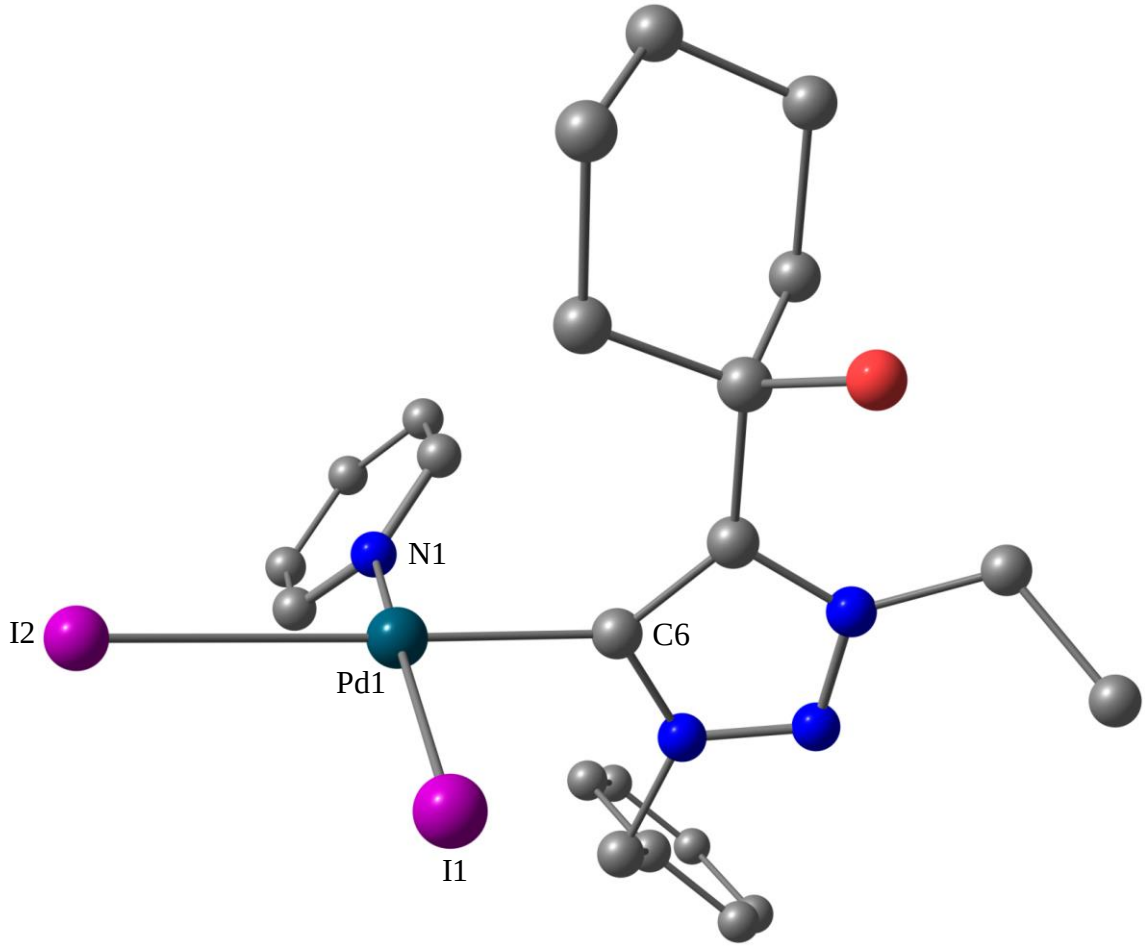


Figure S15. Computed structure of **2b** (*cis*). Selected bond lengths (Å) and bond angles (°): Pd(1)-C(6) 2.037, Pd(1)-N(4) 2.150, Pd(1)-I(1) 2.686, Pd(1)-I(2) 2.721, C(6)-Pd(1)-N(4) 93.36, C(6)-Pd(1)-I(1) 84.66, N(4)-Pd(1)-I(1) 174.61, C(6)-Pd(1)-I(2) 176.17, N(4)-Pd(1)-I(2) 89.58, I(1)-Pd(1)-I(2) 92.62.

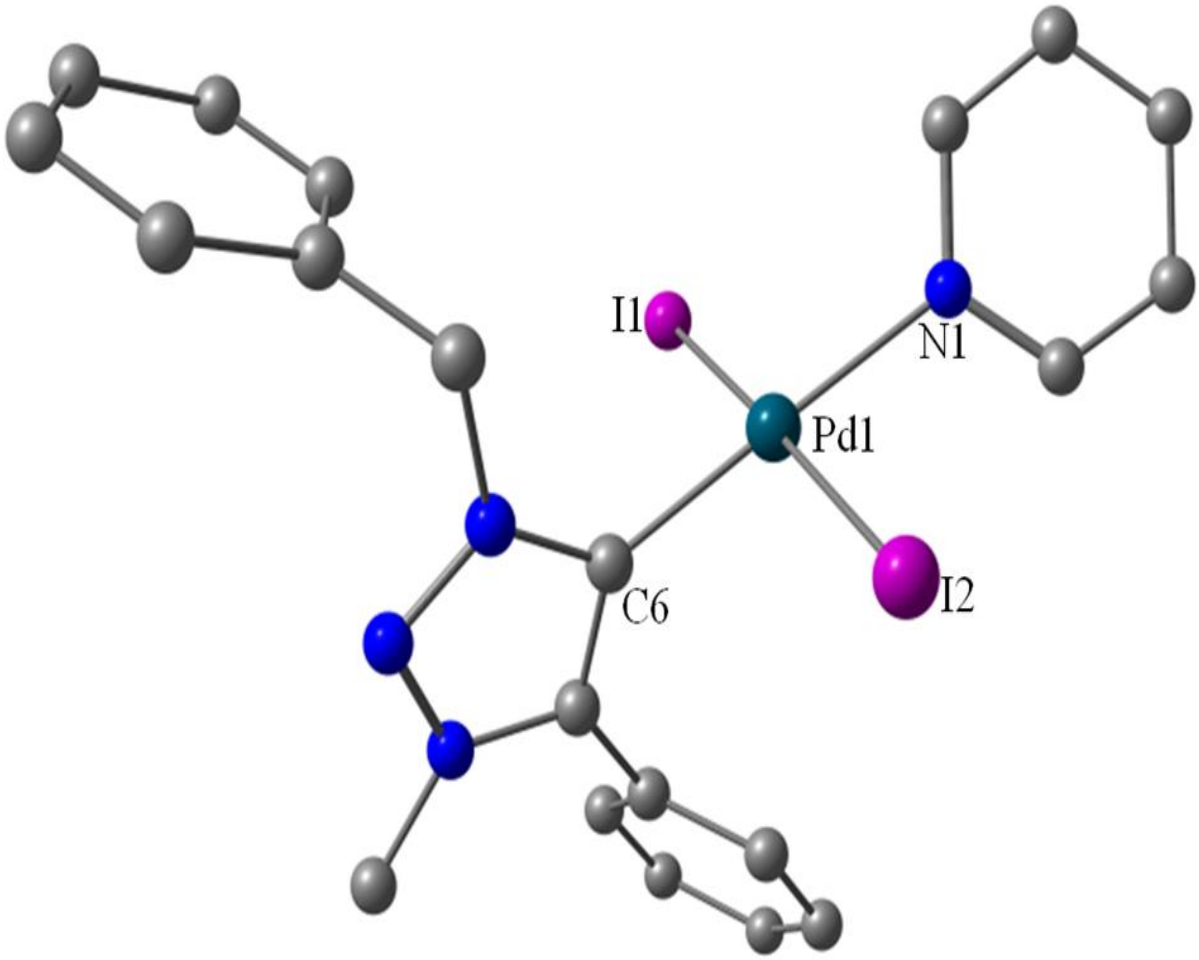


Figure S16. Computed structure of **3b** (*trans*). Selected bond lengths (Å) and bond angles (°): Pd(1)-C(6) 1.988, Pd(1)-N(1) 2.145, Pd(1)-I(1) 2.718, Pd(1)-I(2) 2.710, C(6)-Pd(1)-N(1) 178.71, C(6)-Pd(1)-I(1) 88.59, N(1)-Pd(1)-I(1) 91.45, C(6)-Pd(1)-I(2) 88.63, N(1)-Pd(1)-I(2) 91.38, I(2)-Pd(1)-I(1) 176.18.

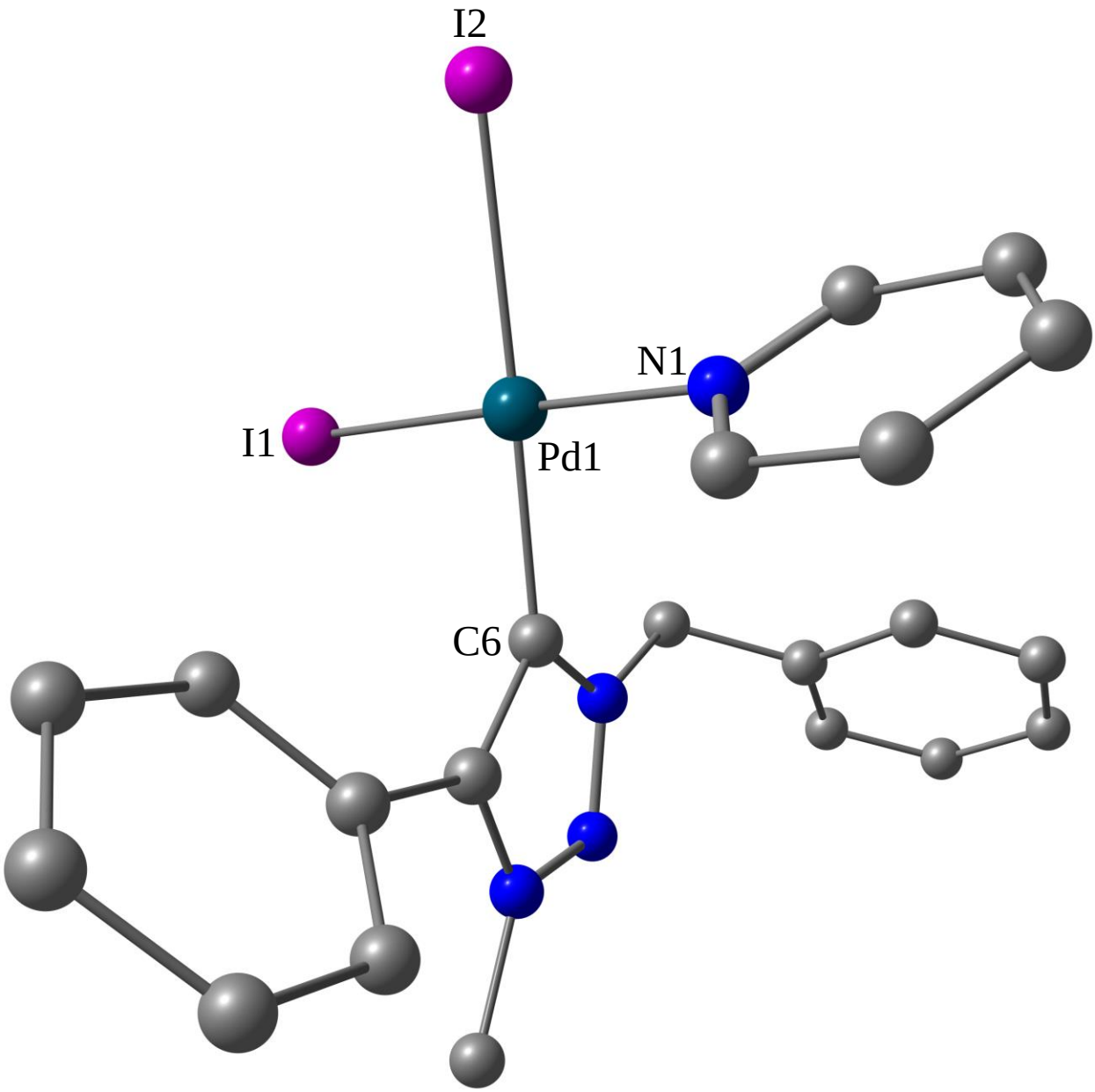


Figure S17. Computed structure of **3b** (*cis*). Selected bond lengths (Å) and bond angles (°): Pd(1)-C(6) 2.032, Pd(1)-N(1) 2.131, Pd(1)-I(1) 2.680, Pd(1)-I(2) 2.718, C(6)-Pd(1)-N(1) 93.00, C(6)-Pd(1)-I(1) 85.75, N(1)-Pd(1)-I(1) 178.68, C(6)-Pd(1)-I(2) 178.71, N(1)-Pd(1)-I(2) 88.07, I(2)-Pd(1)-I(1) 93.18.

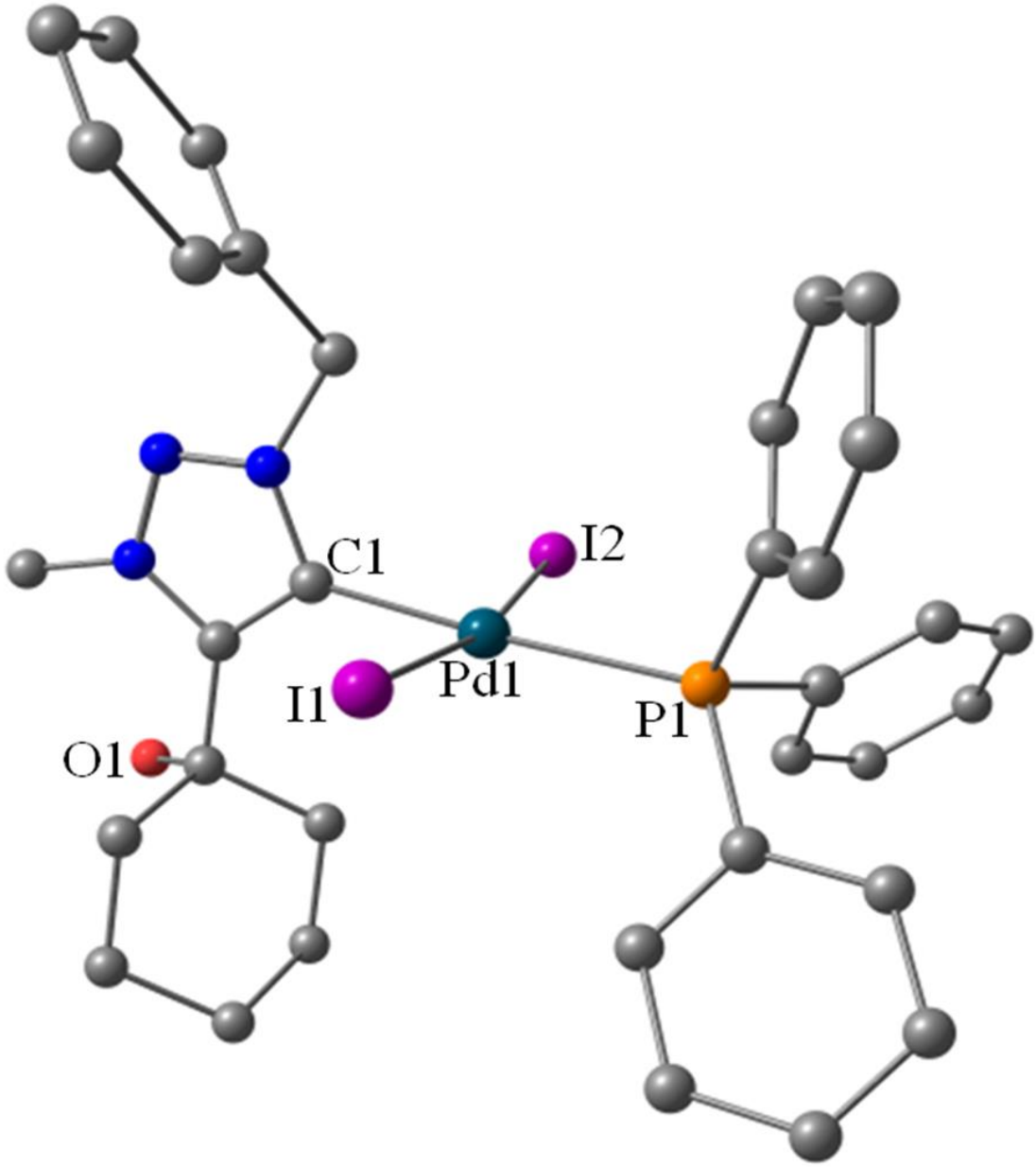


Figure S18. Computed structure of **1c** (*trans*). Selected bond lengths (Å) and bond angles (°): Pd(1)-P(1) 2.414, Pd(1)-I(2) 2.736, Pd(1)-I(1) 2.717, C(1)-Pd(1) 2.040, C(1)-Pd(1)-P(1) 176.06, C(1)-Pd(1)-I(2) 86.44, P(1)-Pd(1)-I(2) 92.49, C(1)-Pd(1)-I(1) 85.59, P(1)-Pd(1)-I(1) 94.94, I(2)-Pd(1)-I(1) 168.89.

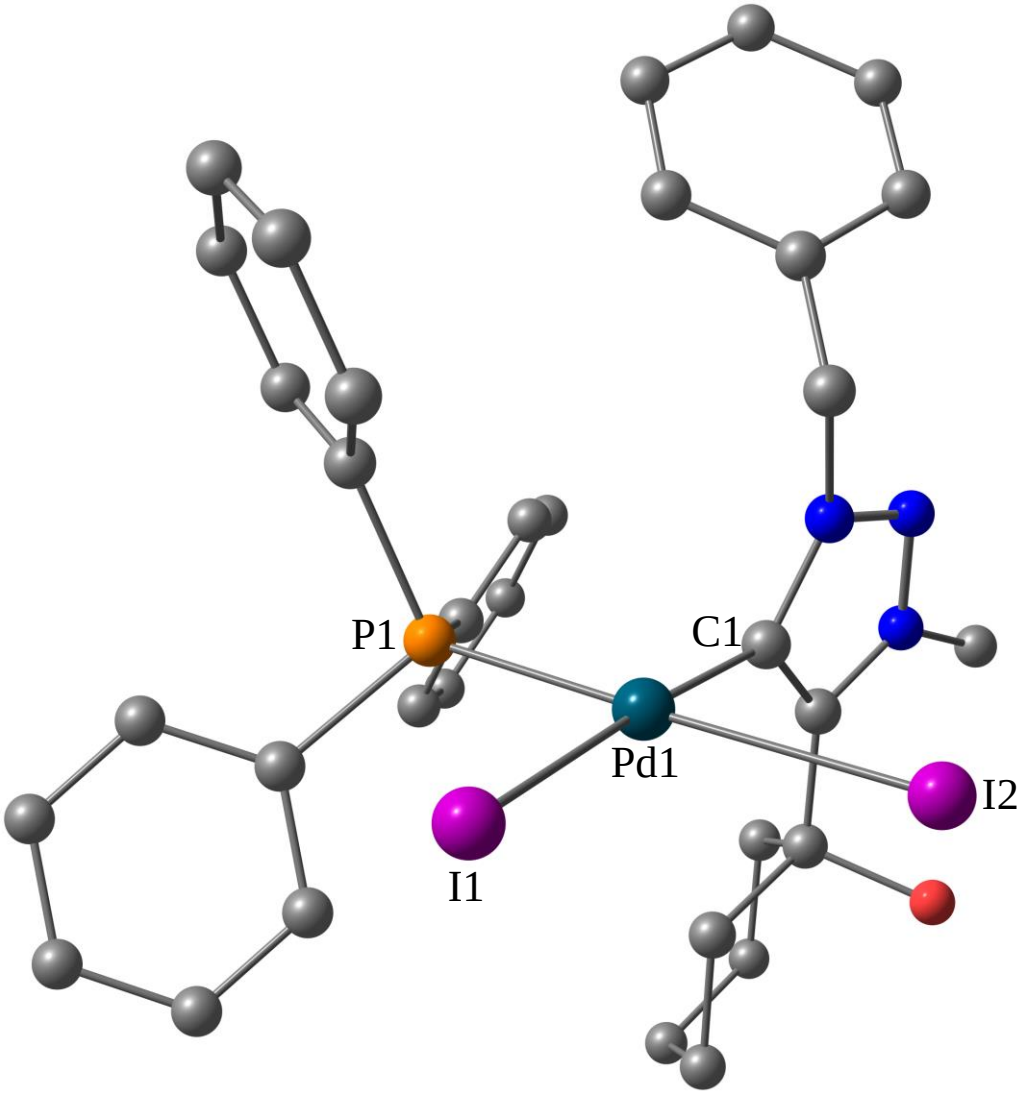


Figure S19. Computed structure of **1c** (*cis*). Selected bond lengths (Å) and bond angles (°): Pd(1)-P(1) 2.357, Pd(1)-I(2) 2.753, Pd(1)-I(1) 2.730, C(1)-Pd(1) 2.037, C(1)-Pd(1)-P(1) 95.52, C(1)-Pd(1)-I(2) 82.31, P(1)-Pd(1)-I(2) 177.78, C(1)-Pd(1)-I(1) 173.08, P(1)-Pd(1)-I(1) 91.20, I(2)-Pd(1)-I(1) 90.94.

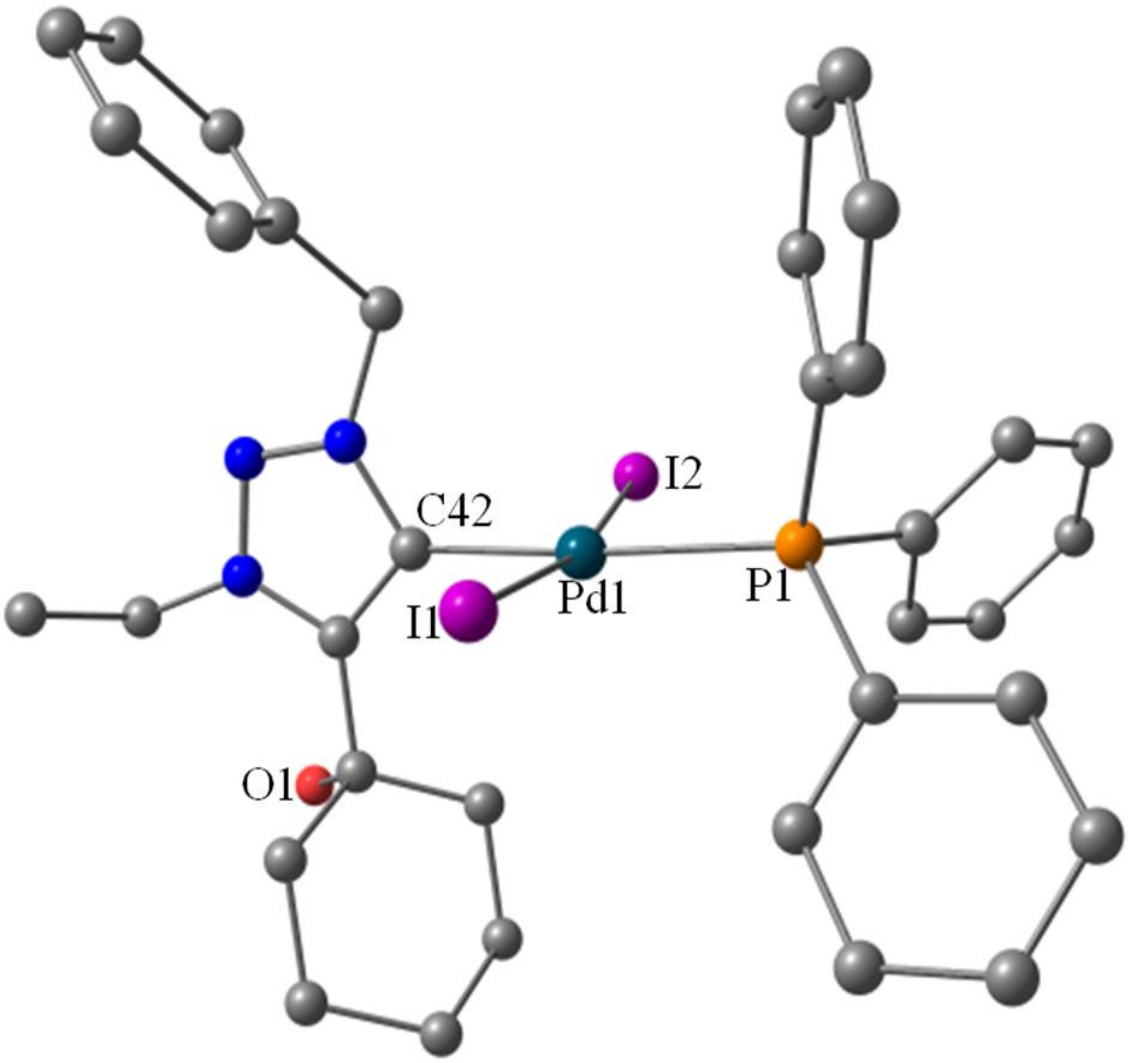


Figure S20. Computed structure of **2c** (*trans*). Selected bond lengths (Å) and bond angles (°): Pd(1)-P(1) 2.413, Pd(1)-I(1) 2.718, Pd(1)-I(2) 2.738 C(42)-Pd(1) 2.041, C(42)-Pd(1)-P(1) 176.31, C(42)-Pd(1)-I(2) 85.87, P(1)-Pd(1)-I(2) 95.02, C(42)-Pd(1)-I(1) 86.19, P(1)-Pd(1)-I(1) 92.41, I(2)-Pd(1)-I(1) 168.75.

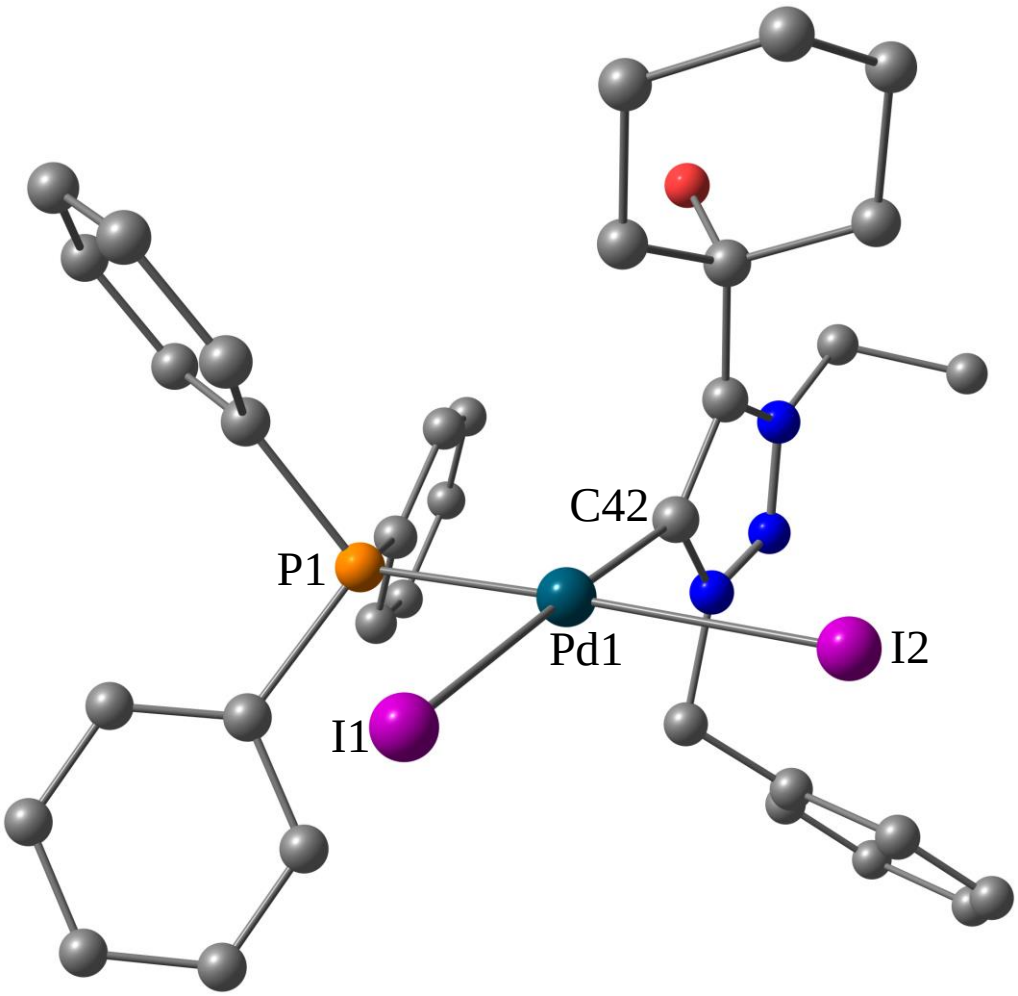


Figure S21. Computed structure of **2c** (*cis*). Selected bond lengths (Å) and bond angles (°): Pd(1)-P(1) 2.364, Pd(1)-I(1) 2.735, Pd(1)-I(2) 2.737, C(42)-Pd(1) 2.036, C(42)-Pd(1)-P(1) 94.04, C(42)-Pd(1)-I(2) 83.88, P(1)-Pd(1)-I(2) 176.14, C(42)-Pd(1)-I(1) 174.77, P(1)-Pd(1)-I(1) 91.02, I(2)-Pd(1)-I(1) 91.14.

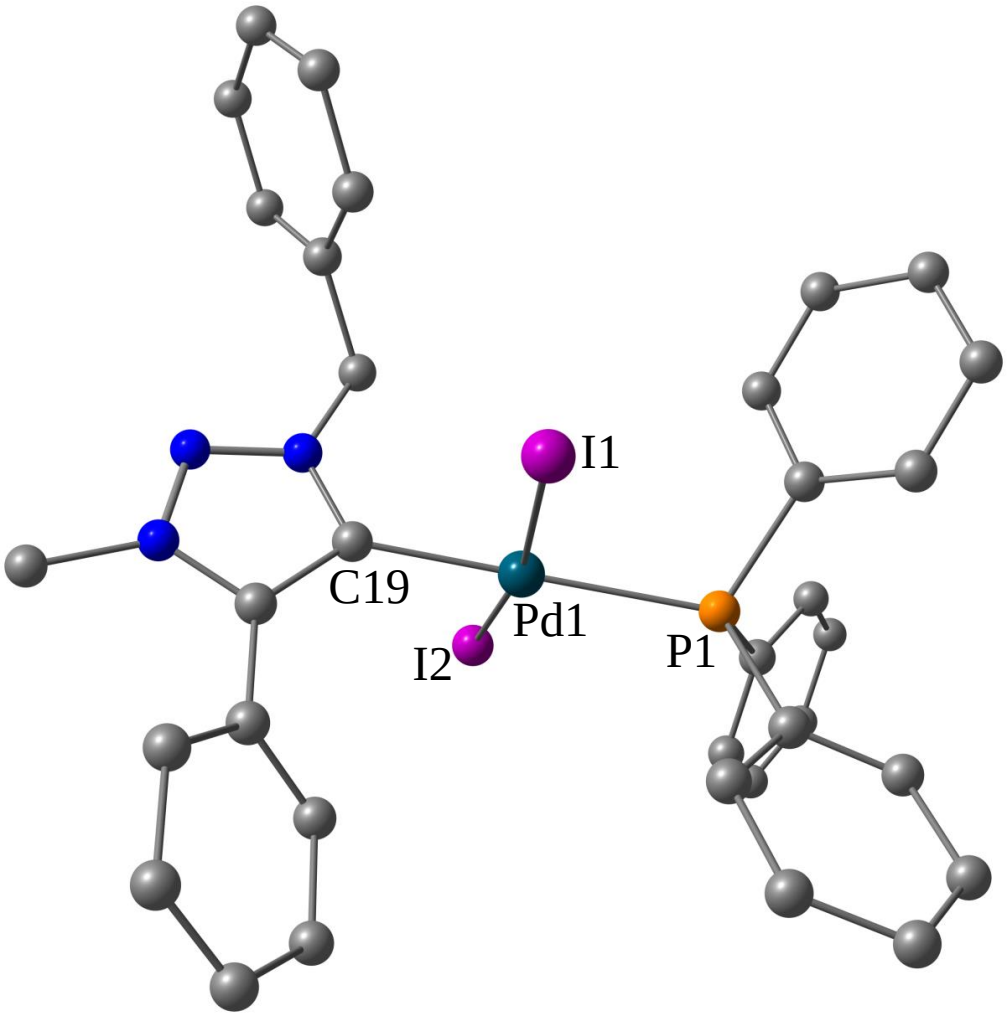


Figure S22. Computed structure of the **3c** (*trans*). Selected bond lengths (Å) and bond angles (°): Pd(1)-P(1) 2.418, Pd(1)-I(2) 2.718, Pd(1)-I(1) 2.728, C(19)-Pd(1) 2.032, C(19)-Pd(1)-P(1) 177.93, C(19)-Pd(1)-I(2) 85.49, P(1)-Pd(1)-I(2) 96.49, C(19)-Pd(1)-I(1) 85.78, P(1)-Pd(1)-I(1) 177.92, I(2)-Pd(1)-I(1) 170.46.

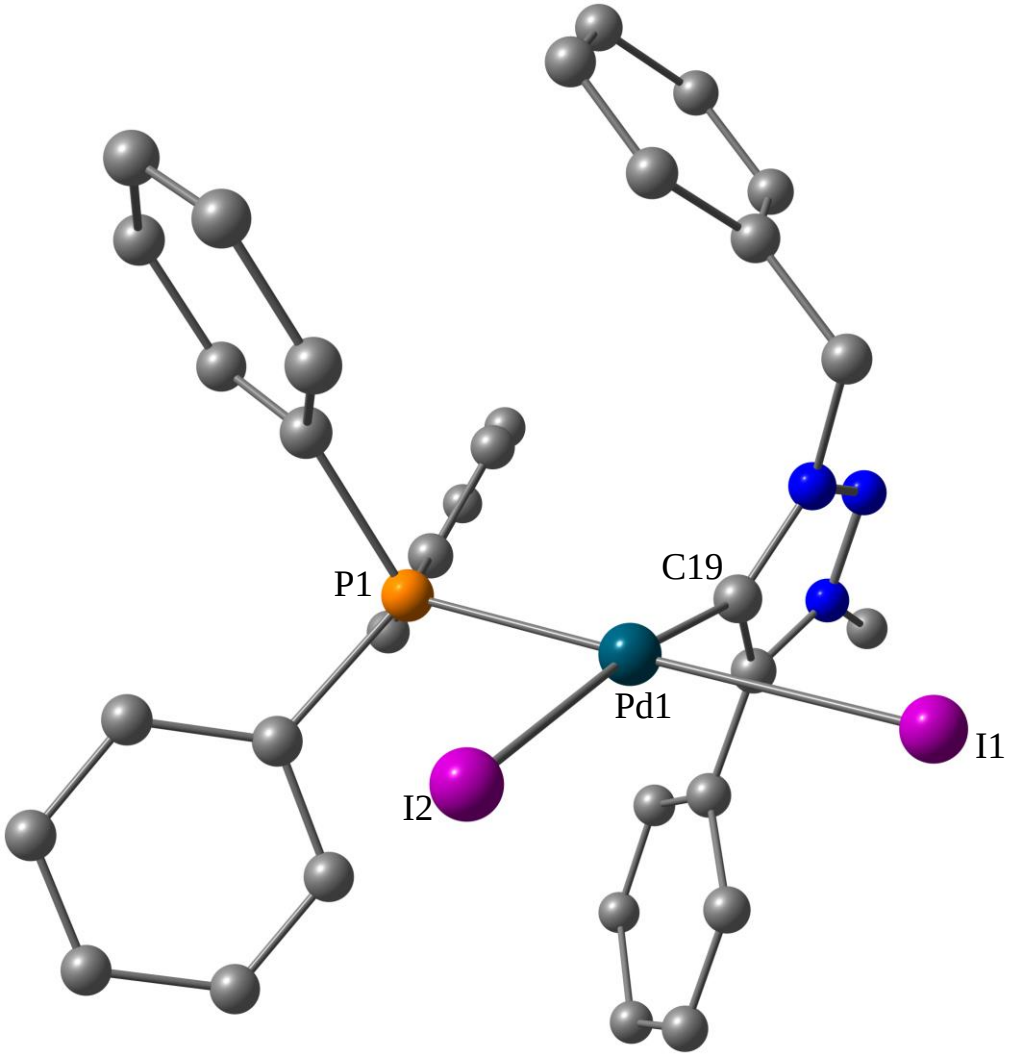


Figure S23. Computed structure of **3c** (*cis*). Selected bond lengths (Å) and bond angles (°): Pd(1)-P(1) 2.358, Pd(1)-I(2) 2.732, Pd(1)-I(1) 2.740, C(19)-Pd(1) 2.029, C(19)-Pd(1)-P(1) 95.27, C(19)-Pd(1)-I(2) 173.39, P(1)-Pd(1)-I(2) 89.91, C(19)-Pd(1)-I(1) 84.08, P(1)-Pd(1)-I(1) 179.05, I(2)-Pd(1)-I(1) 90.78.

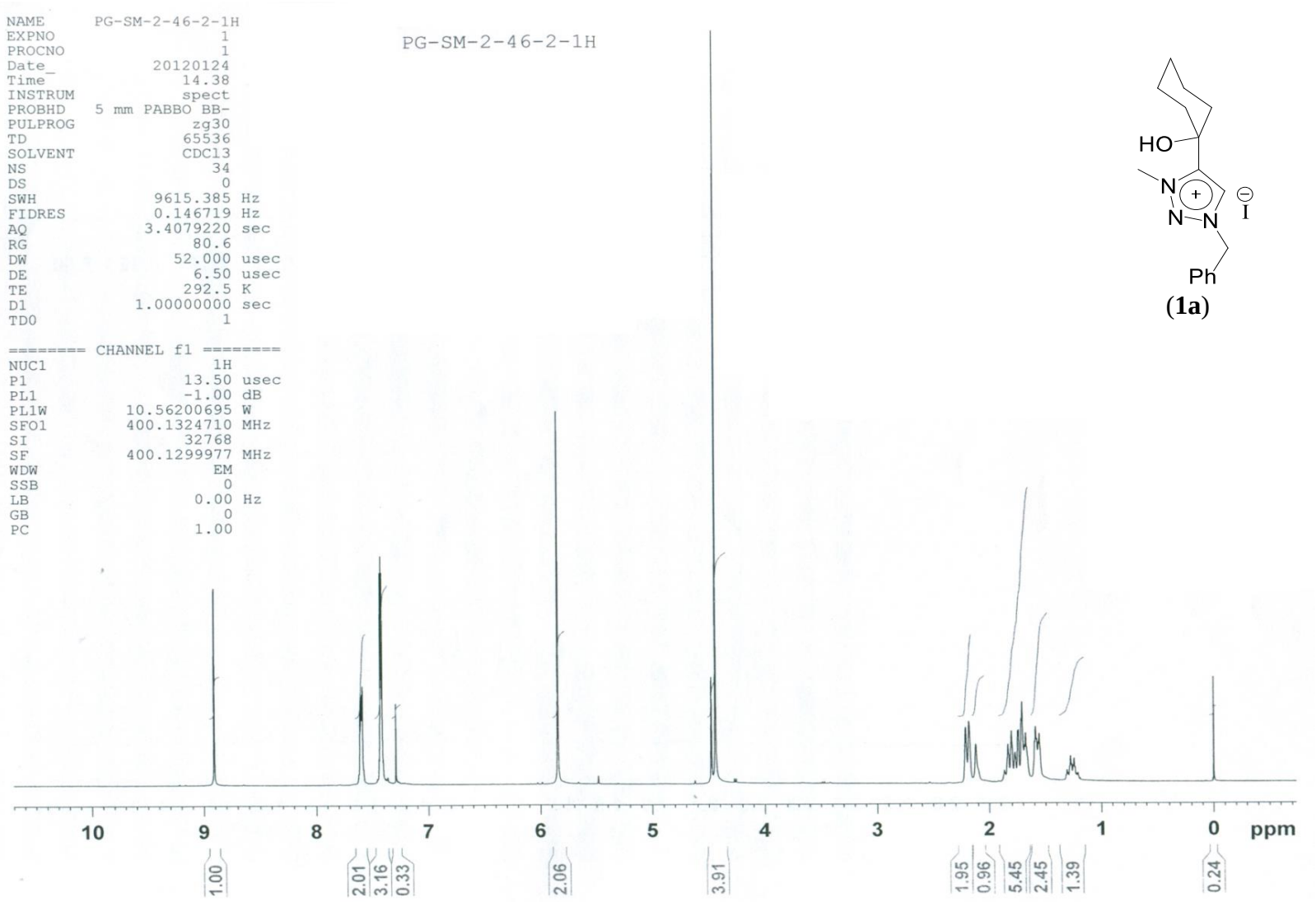


Figure S24. ^{1}H NMR spectrum of the compound **1a** in $CDCl_3$.

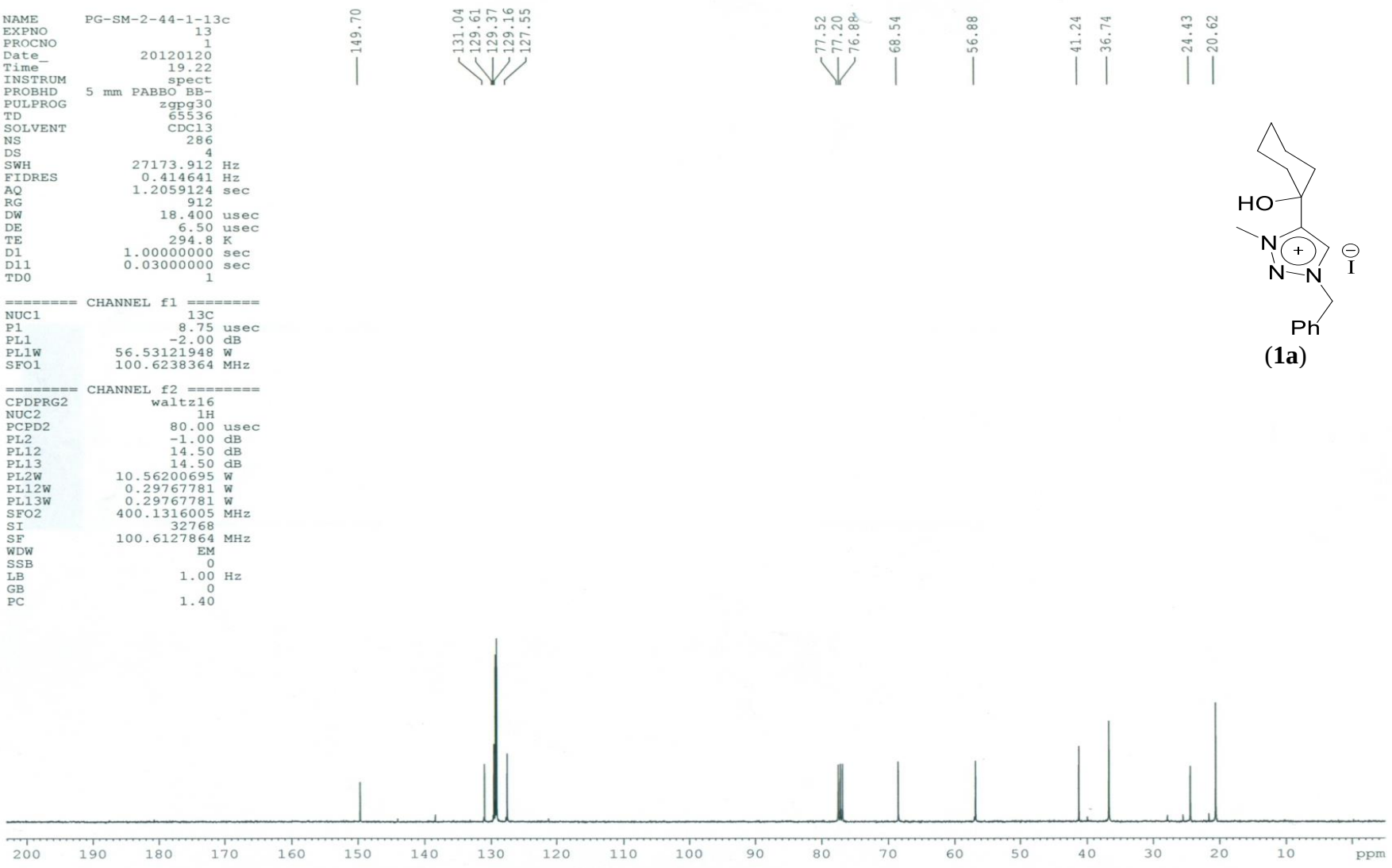


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **1a** in $CDCl_3$.

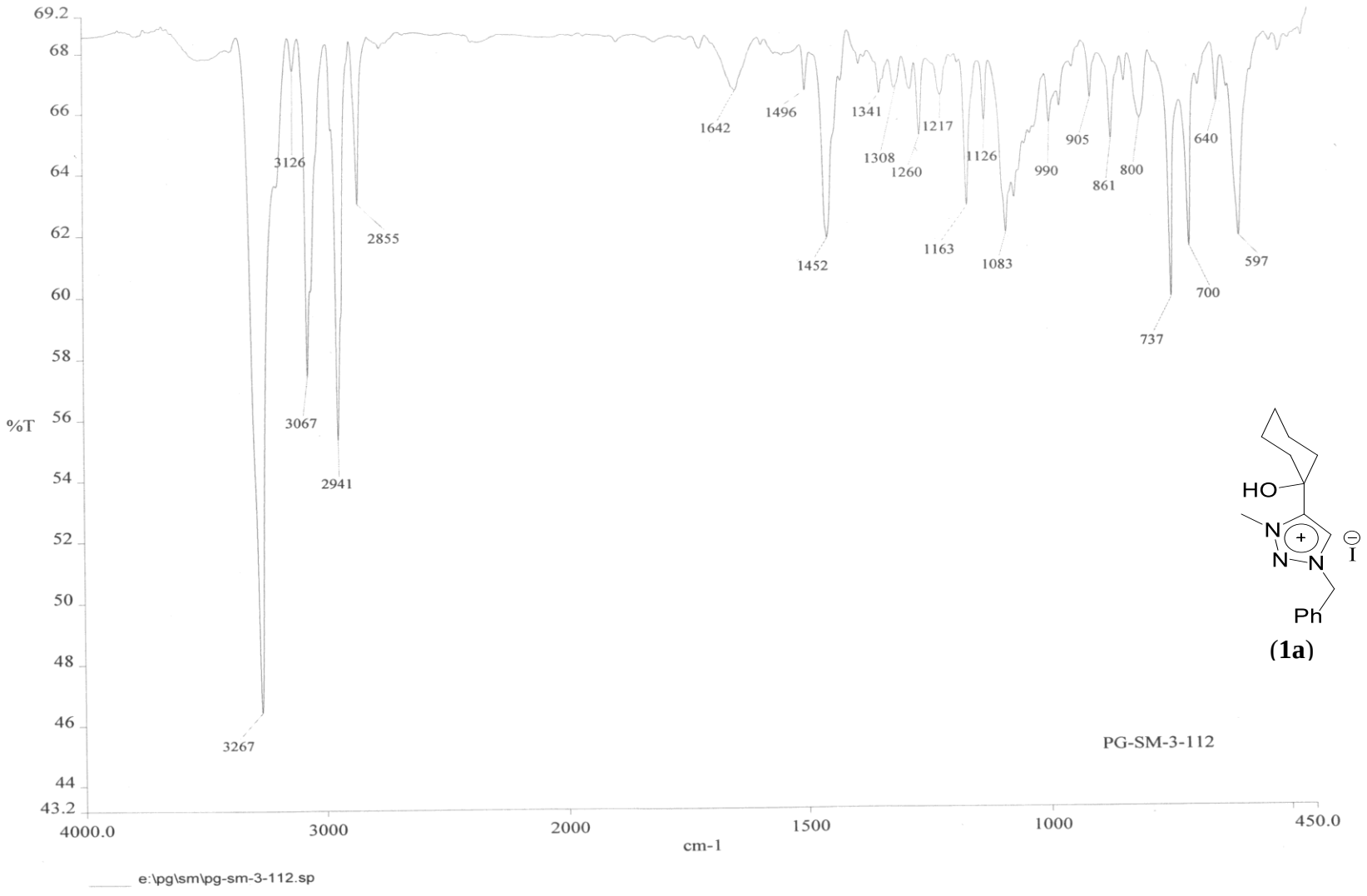
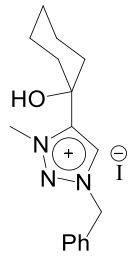


Figure S26. IR spectrum of the compound **1a.**

Elemental Composition Report

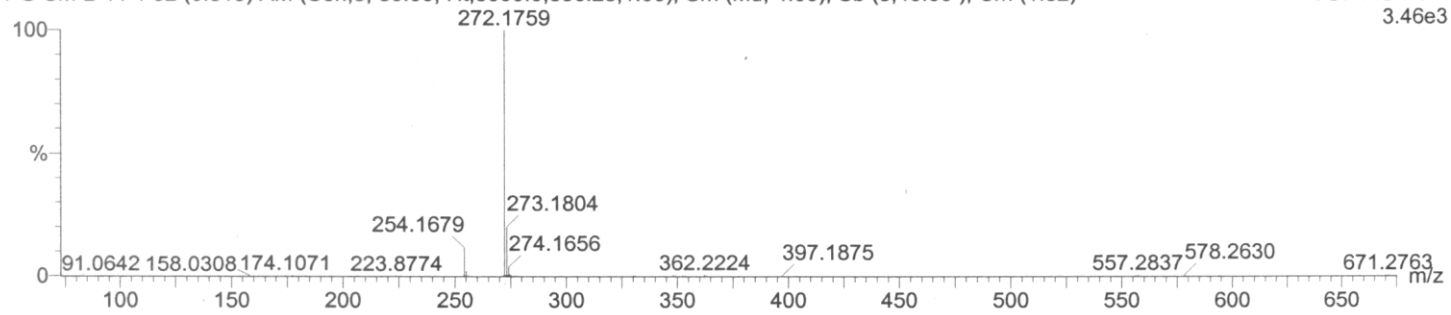
Single Mass Analysis (displaying only valid results)
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 100.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
6 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)



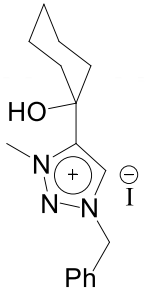
(1a)

Micromass : Q-Tof micro (YA-105) Dept. Of Chemistry I.I.T.(B) 07-Feb-201215:31:13
C16H22N3O
PG-SM-2-44-1 32 (0.319) AM (Cen,5, 80.00, Ht,5000.0,556.28,1.00); Sm (Md, 4.00); Sb (5,40.00); Cm (1:32) TOF MS ES+
3.46e3



Minimum:				-1.5		
Maximum:		200.0	10.0	100.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
272.1759	272.1763	-0.4	-1.5	7.5	1	C16 H22 N3 O

Figure S27. Mass spectrum of the compound **1a**.



(1a)

Eager 300 Report

Page: 1 Sample: PG-SM-2-44-1 (PG-SM-2-44-1)

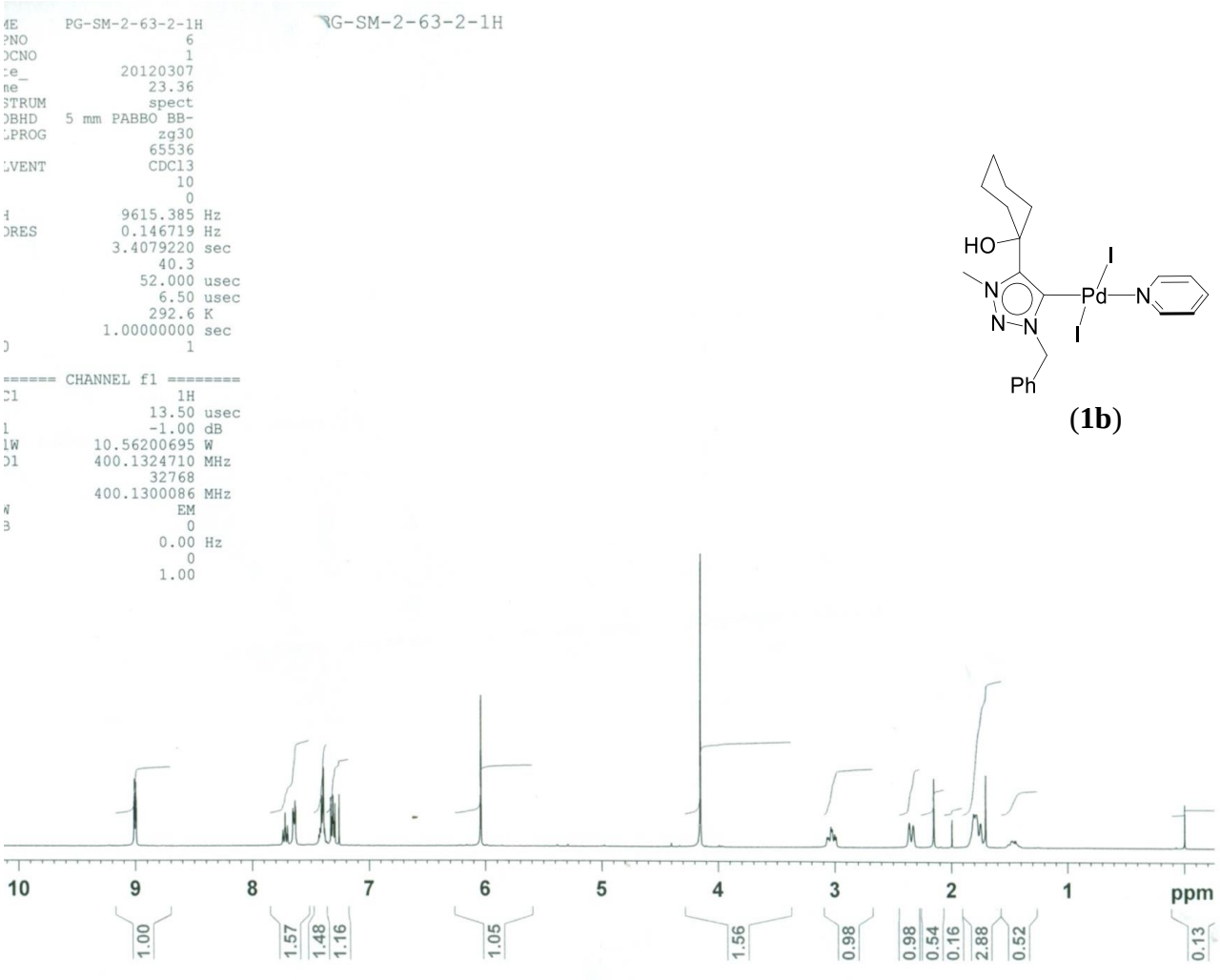
Method Name	: SP230112r		
Method File	: D:\CHNS2011\SP230112r.mth		
Chromatogram	: PG-SM-2-44-1		
Operator ID	: mnrao	Company Name	: C.E. Instruments
Analysed	: 01/23/2012 16:19	Printed	: 1/23/2012 19:45
Sample ID	: PG-SM-2-44-1 (# 15)	Instrument N.	: Instrument #1
Analysis Type	: UnkNown (Area)	Sample weight	: .883

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
1	0.0000	18	4756	RS		0.0000
Nitrogen	9.9863	44	148900	FU	7.641131	.168861E+07
Carbon	48.4099	67	1137762	FU	1.000000	.266168E+07
Hydrogen	5.9779	178	280394	RS	4.057727	.531204E+07
Totals	64.3741		1571812			

Figure S28. CHN analysis of the compound **1a**.



(**1b**)

Figure S29. ^{1}H NMR spectrum of the compound **1b** in $CDCl_3$.

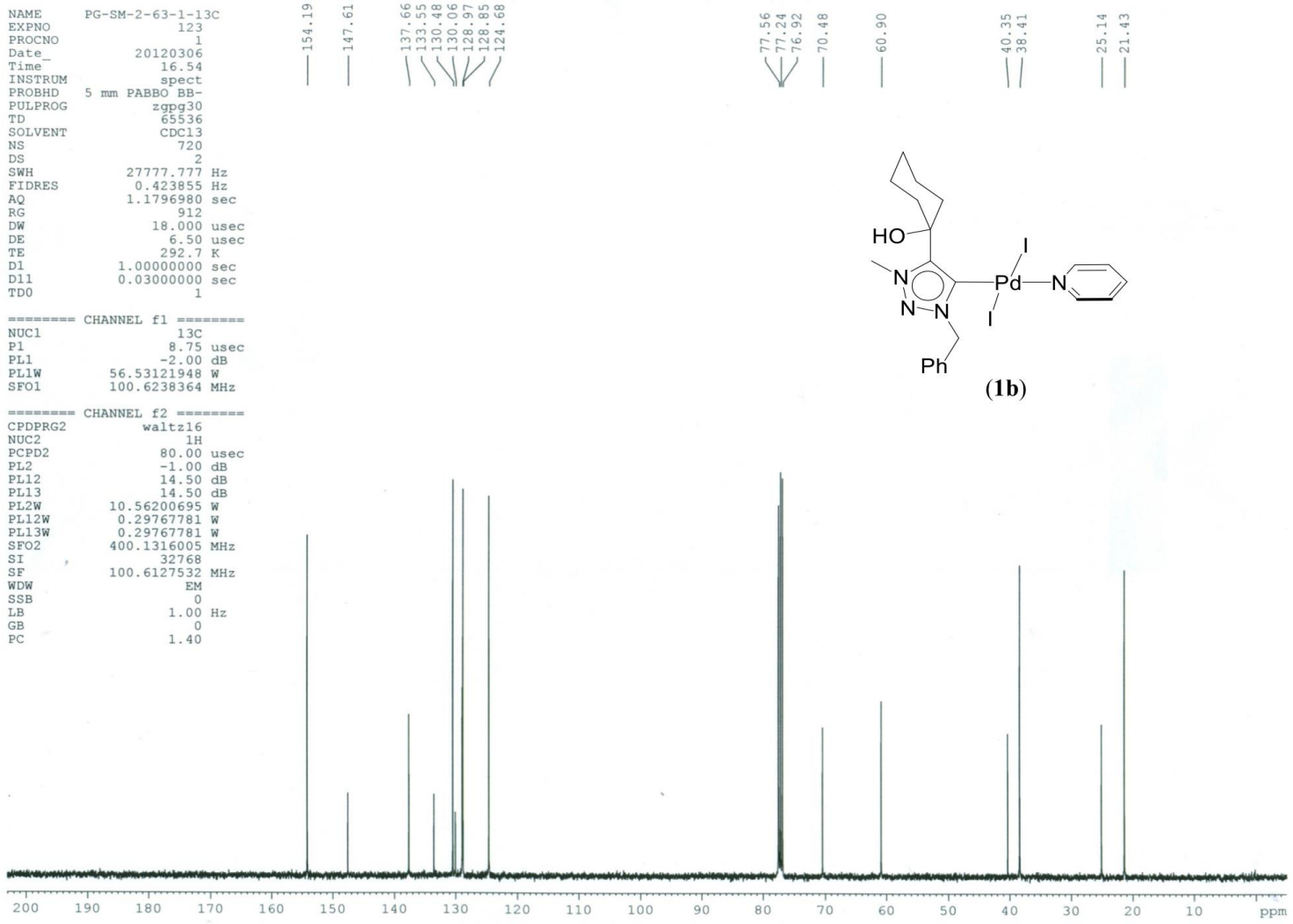


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **1b** in $CDCl_3$.

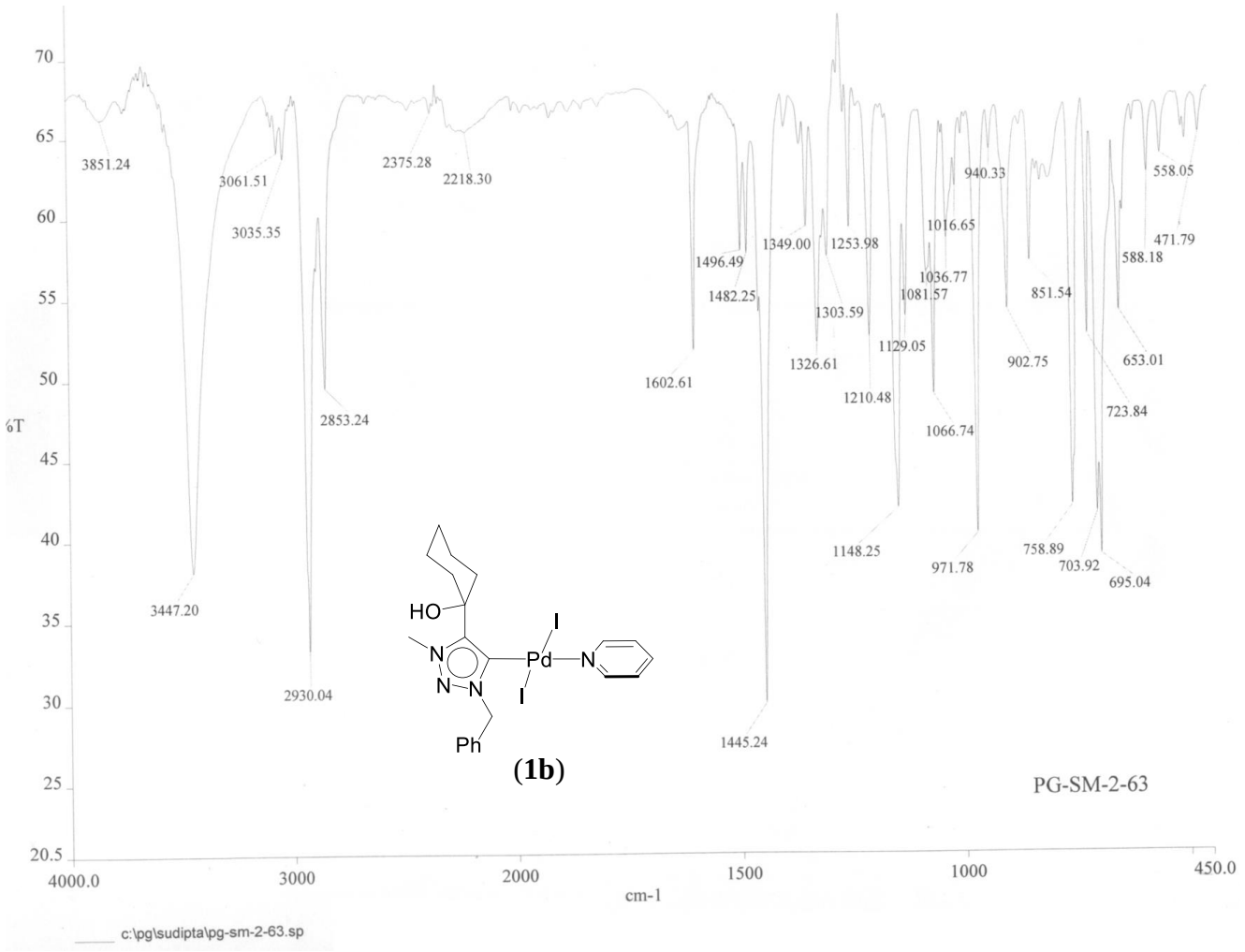


Figure S31. IR spectrum of the compound **1b**.

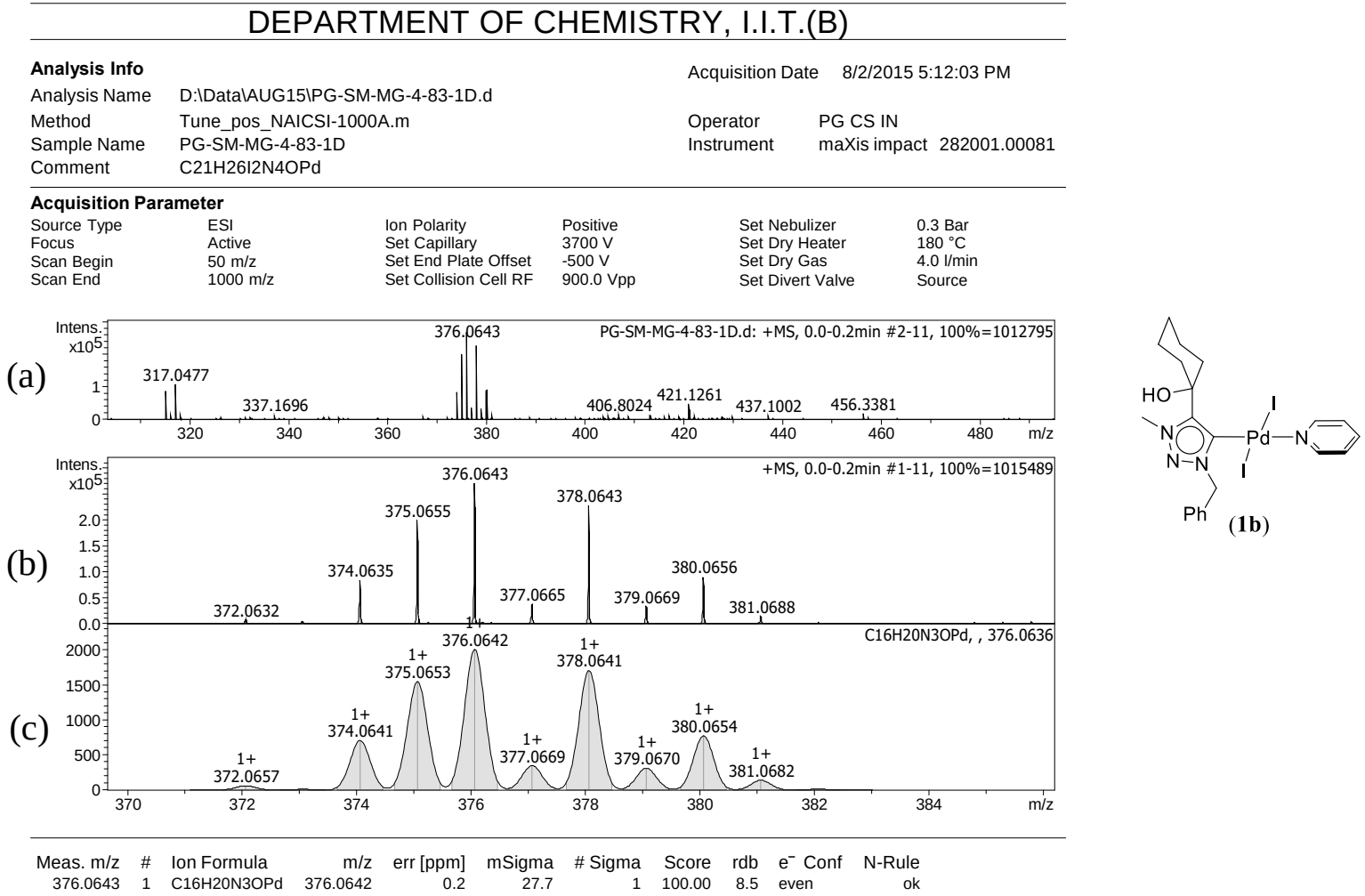
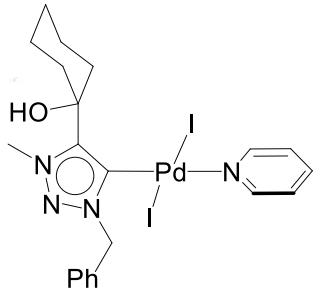


Figure S32. Mass spectrum of the compound **1b** [plot (a)] along with its experimental [plot (b)] and theoretical [plot (c)] isotopic mass distributions are shown.



(1b)

Eager 300 Report

Page: 1 Sample: PG-SM-2-63-2 (PG-SM-2-63-2)

Method Name	: SP-050312		
Method File	: D:\CHNS2012\SP-050312.mth		
Chromatogram	: PG-SM-2-63-2		
Operator ID	: MNRAO	Company Name	: C.E. Instruments
Analysed	: 03/05/2012 15:29	Printed	: 3/5/2012 19:58
Sample ID	: PG-SM-2-63-2 (# 13)	Instrument N.	: Instrument #1
Analysis Type	: UnkNown (Area)	Sample weight	: .845

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	7.4803	43	85282	FU	8.816761	.134923E+07
Carbon	35.3509	68	751915	FU	1.000000	.251716E+07
Hydrogen	3.3899	181	164092	RS	4.582274	.572859E+07
Totals	46.2210		1001289			

Figure S33. CHN analysis of the compound **1b**.

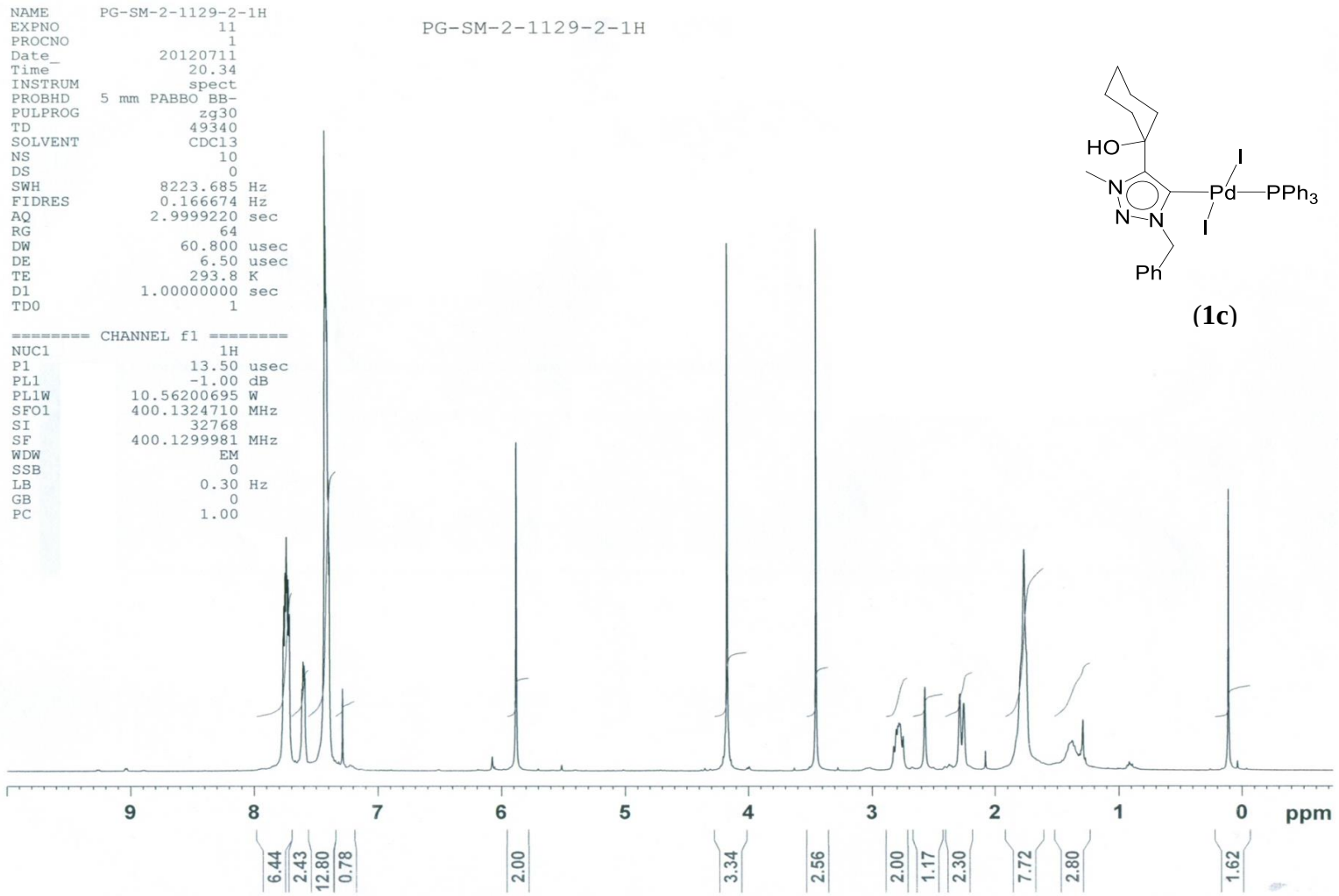


Figure S34. ^{1}H NMR spectrum of the compound **1c** in $CDCl_3$.

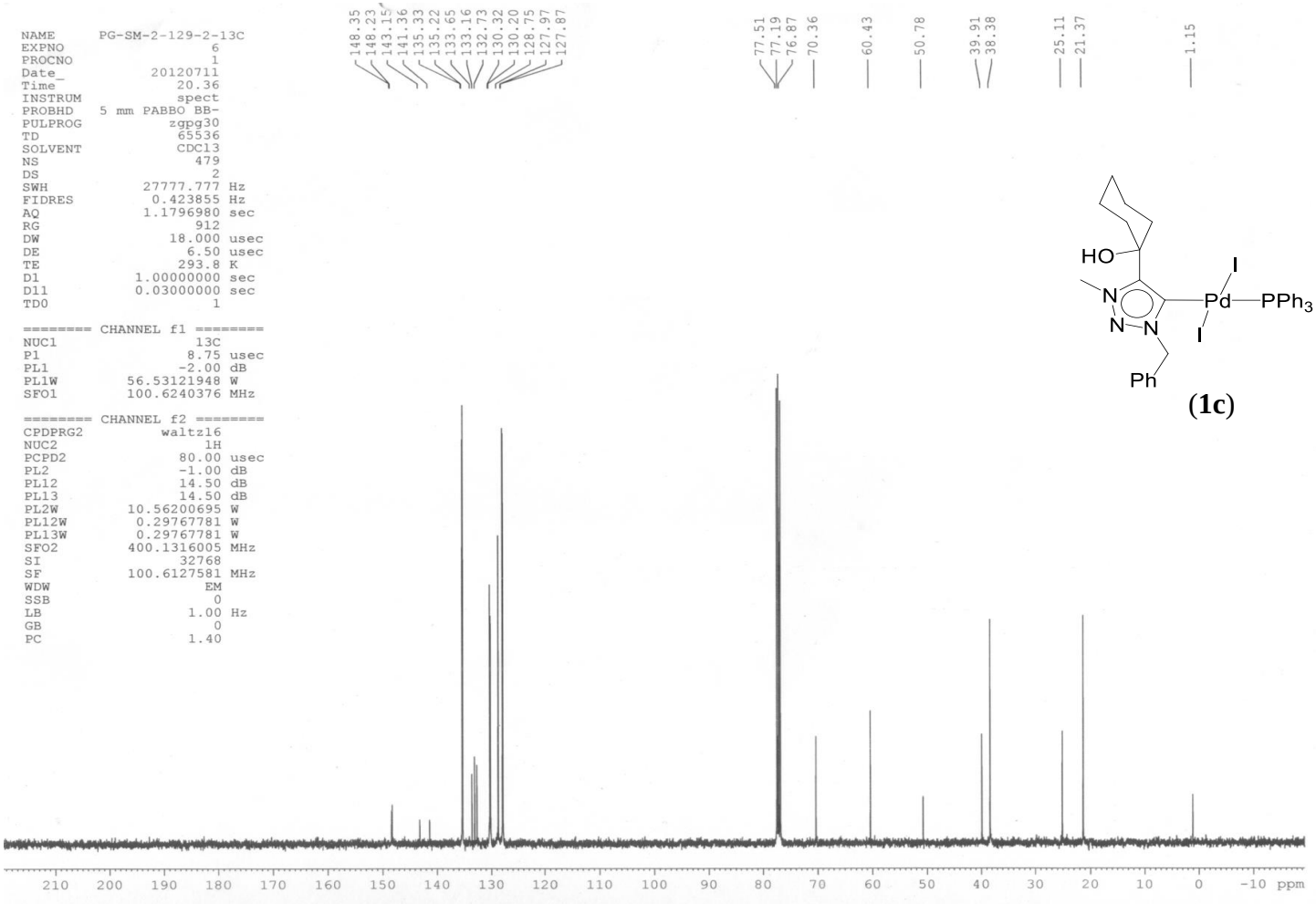


Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **1c** in $CDCl_3$.

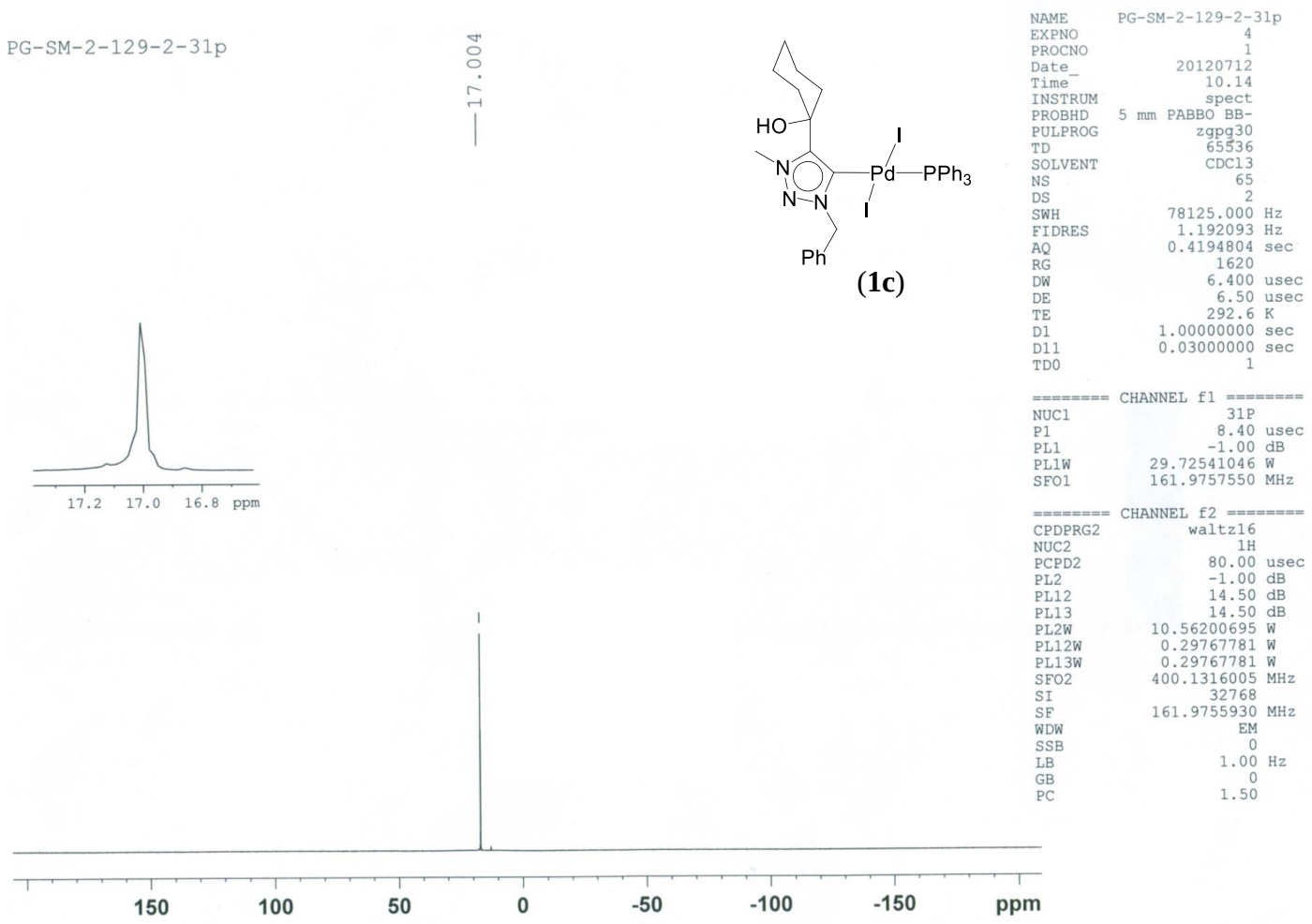


Figure S36. ^{31}P NMR spectrum of the compound **1c** in $CDCl_3$.

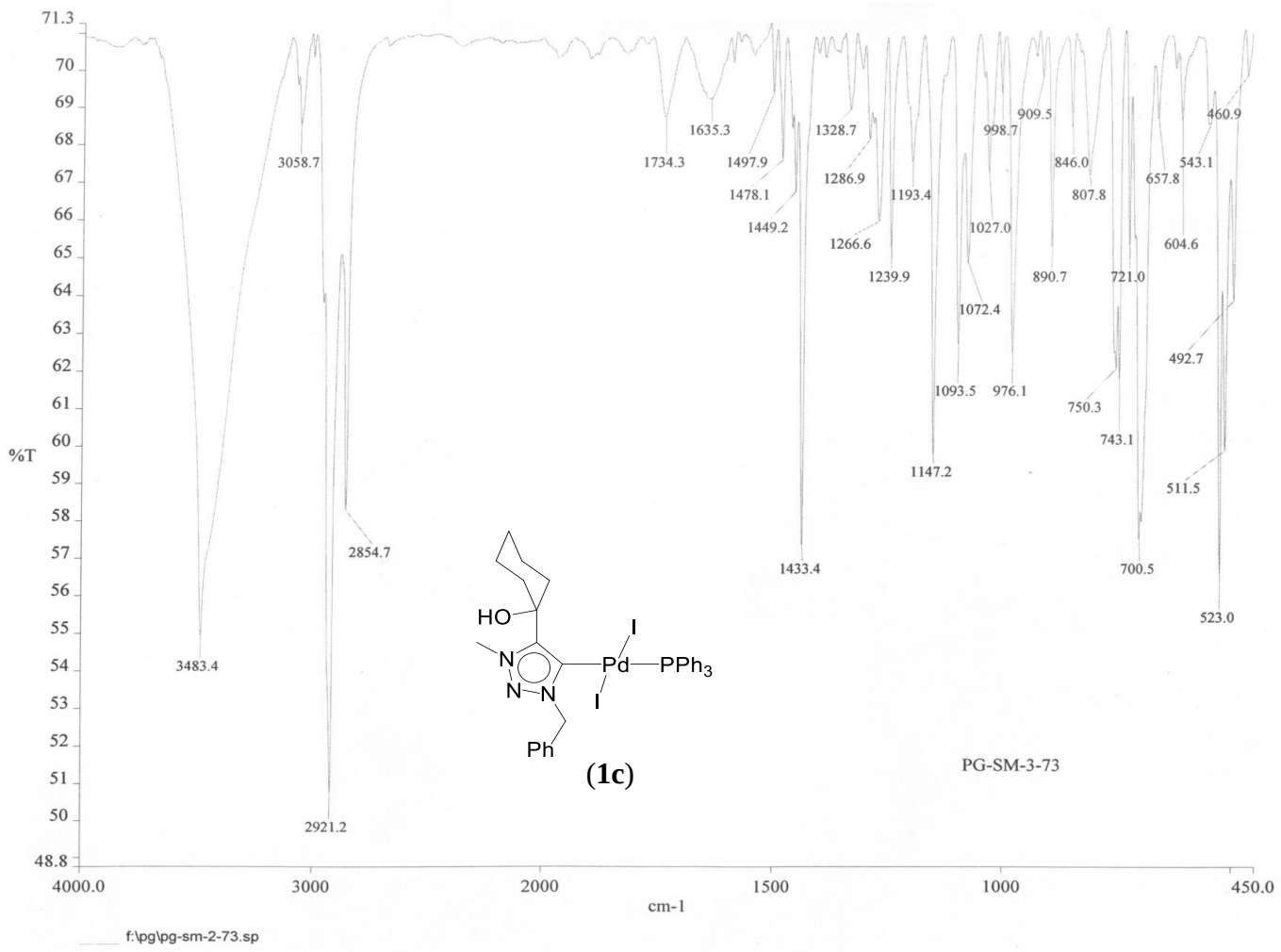


Figure S37. IR spectrum of the compound **1c**.

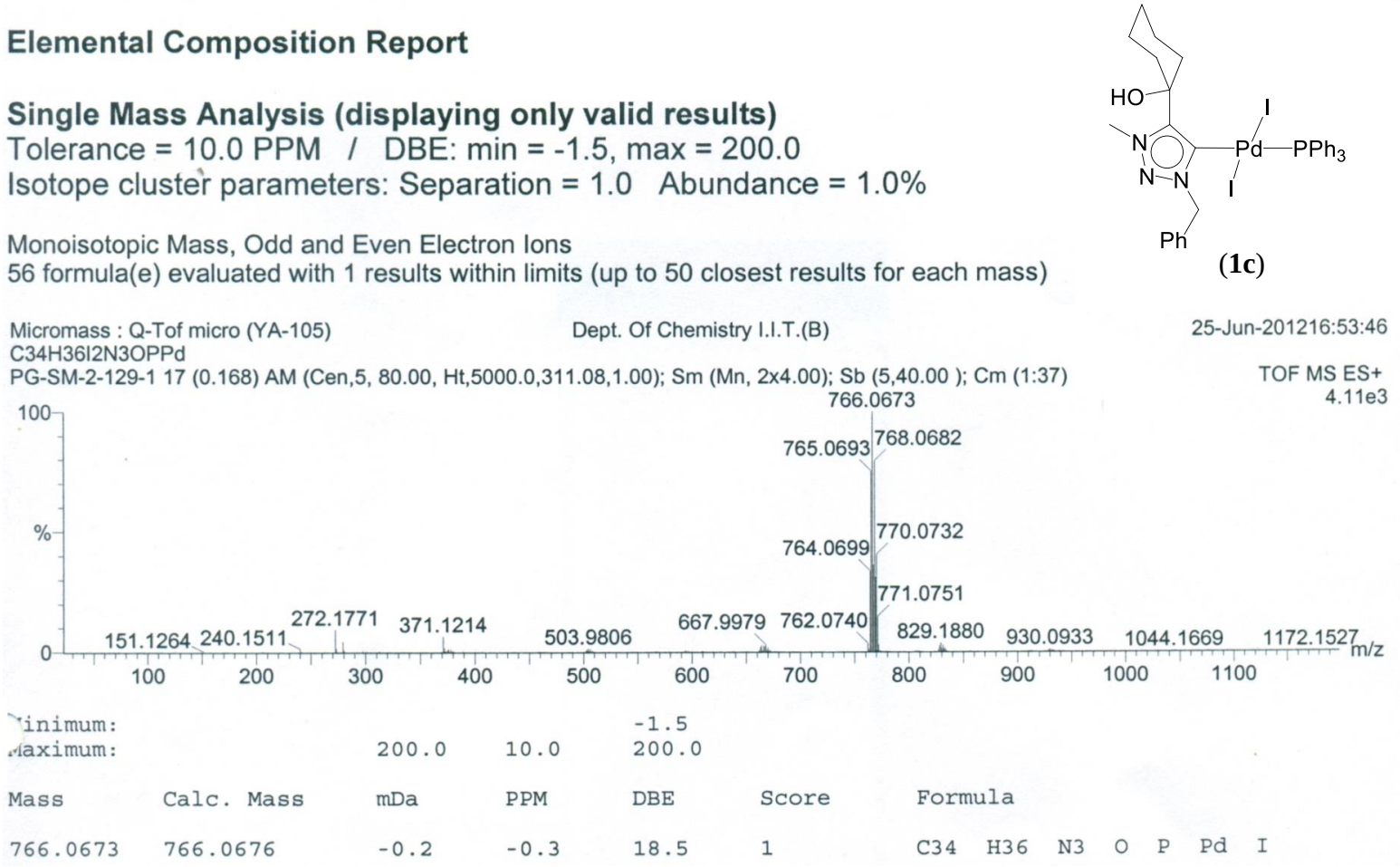
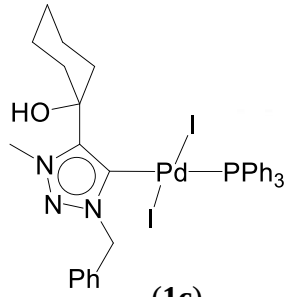


Figure S38. Mass spectrum of the compound **1c**.



(**1c**)

Eager 300 Report

Page: 1 Sample: PG-SM-2-129-1 (PG-SM-2-129-1)

Method Name	: SP240812		
Method File	: D:\CHNS2012\SP240812.mth		
Chromatogram	: PG-SM-2-129-1		
Operator ID	: SD	Company Name	: C.E. Instruments
Analysed	: 08/24/2012 16:31	Printed	: 8/24/2012 22:48
Sample ID	: PG-SM-2-129-1 (# 31)	Instrument N.	: Instrument #1
Analysis Type	: UnkNown (Area)	Sample weight	: 1.321

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
1	0.0000	17	52004	FU		0.0000
Nitrogen	5.6578	42	88671	FU	16.554720	.118640E+07
Carbon	45.0742	65	1467931	FU	1.000000	.246051E+07
Hydrogen	4.0484	184	285853	RS	5.135264	.534512E+07
Totals	54.7804		1894459			

Figure S39. CHN analysis of the compound **1c**.

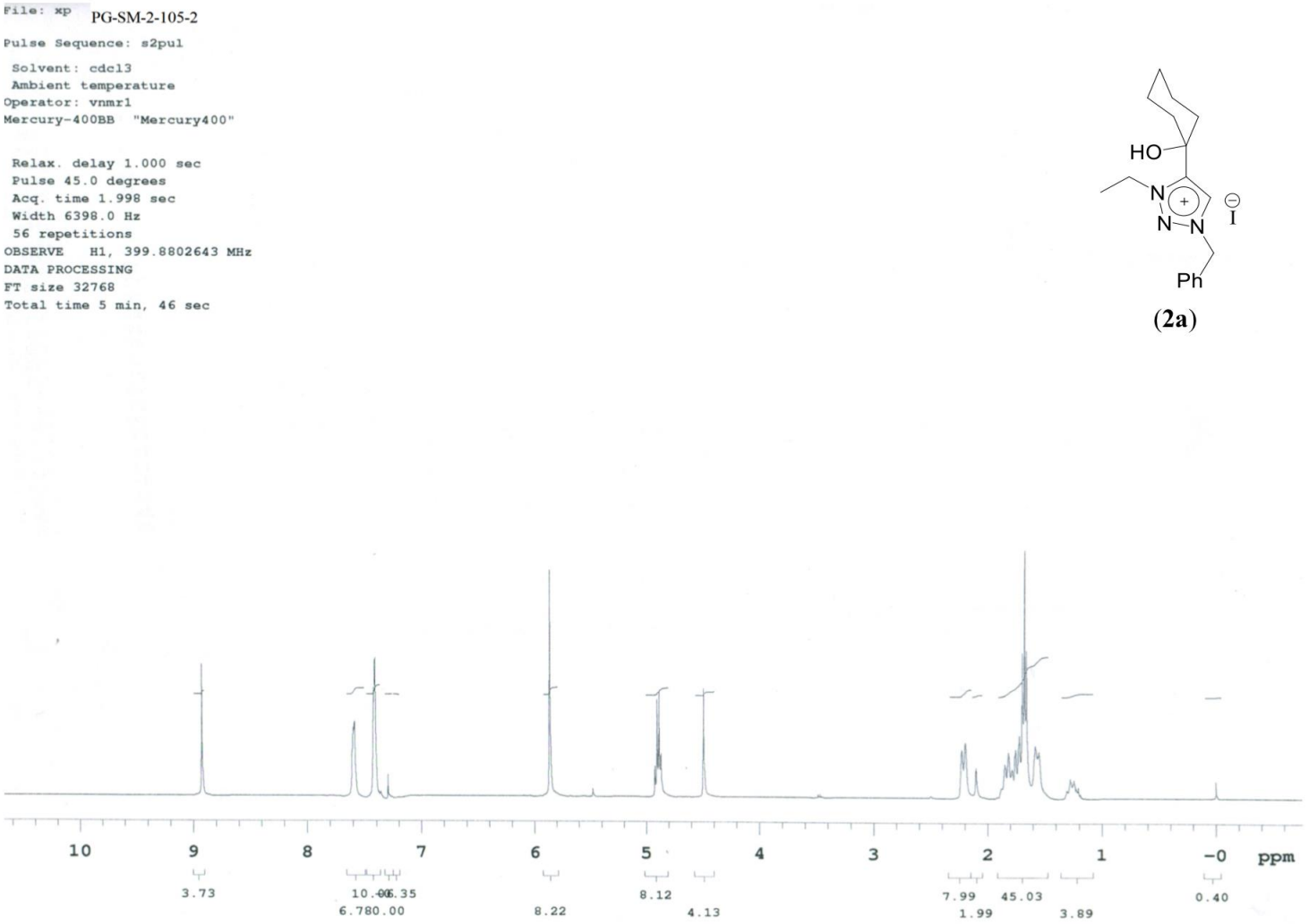


Figure S40. ^{1}H NMR spectrum of the compound **2a** in $CDCl_3$.

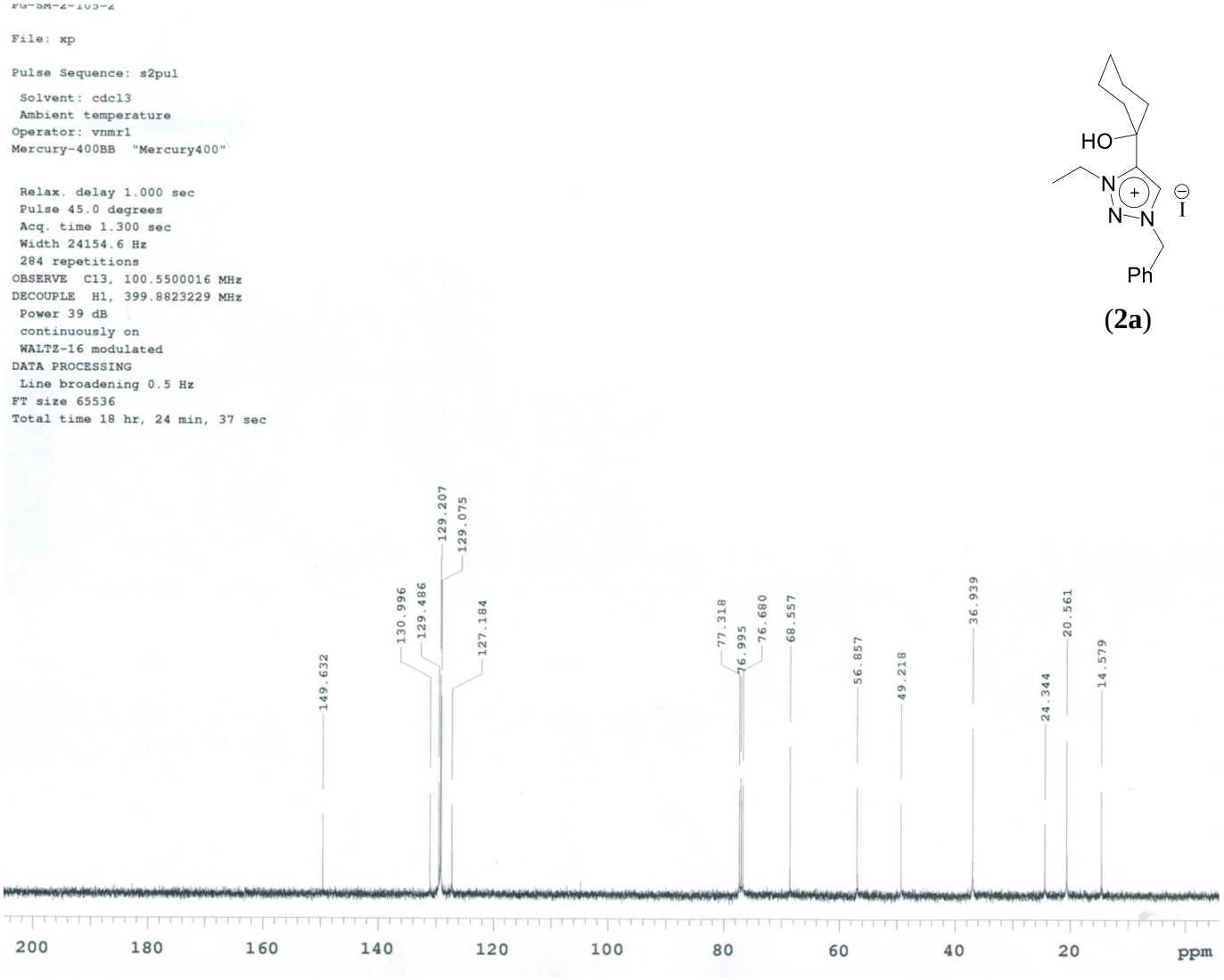
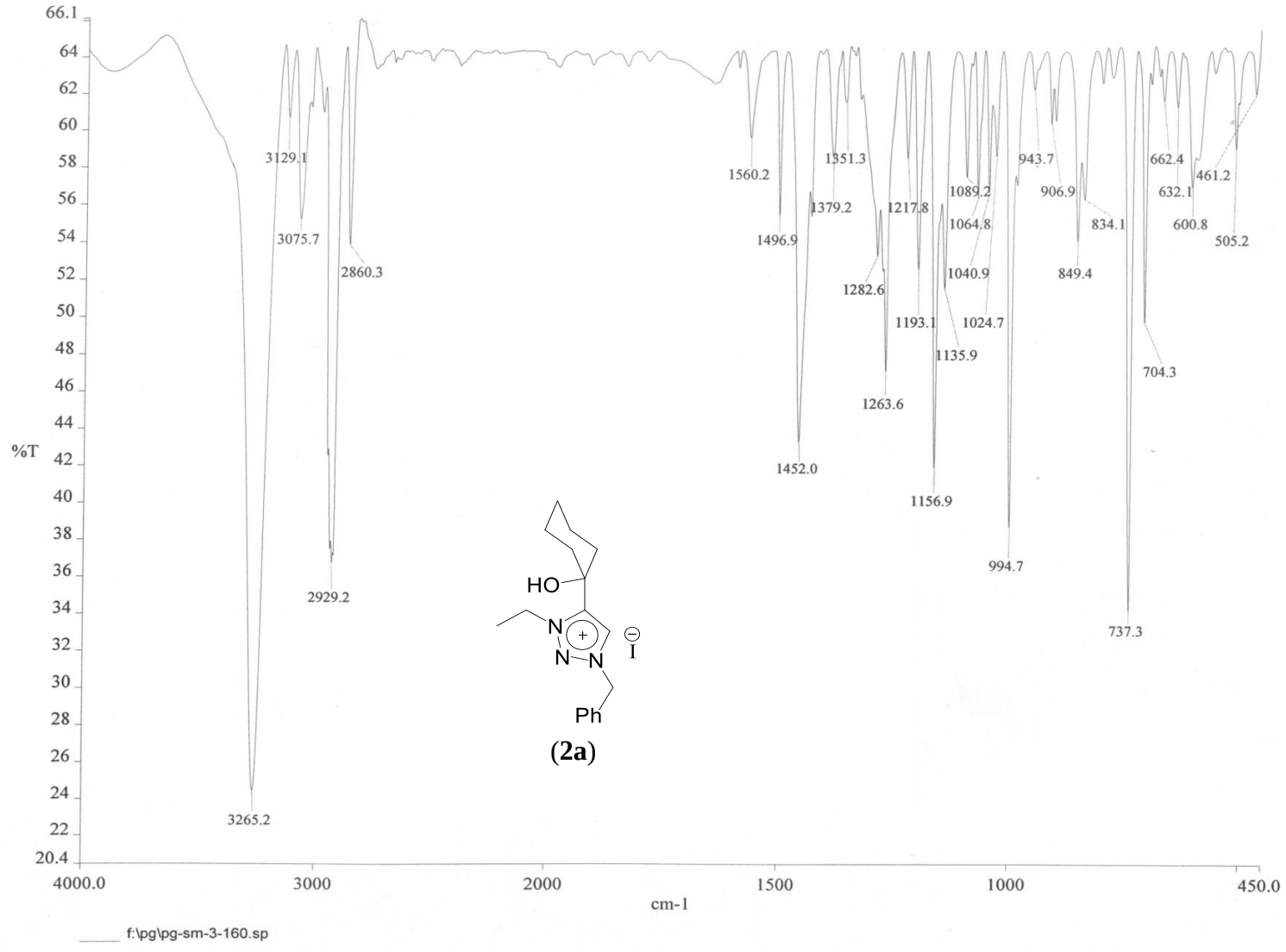


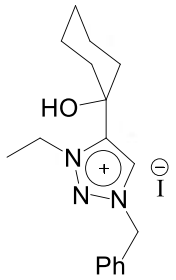
Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2a** in $CDCl_3$.



(**2a**)

Figure S42. IR spectrum of the compound **2a**.

Elemental Composition Report **Page 1**

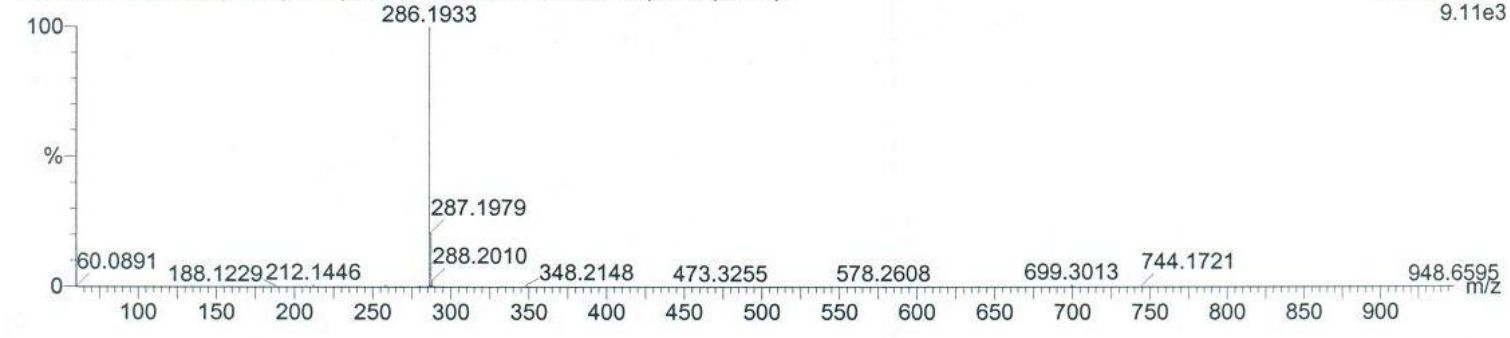


(2a)

Single Mass Analysis (displaying only valid results)
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 200.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
75 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Micromass : Q-Tof micro (YA-105) Dept. Of Chemistry I.I.T.(B) 16-May-201210:26:12
C17H24N3O
PG-SM-2-105-1 22 (0.221) AM (Med,5, Ht,5000.0,556.28,1.00); Cm (17:64) TOF MS ES+
9.11e3



Minimum:				-1.5		
Maximum:		200.0	20.0	200.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
286.1933	286.1919	1.3	4.6	7.5	1	C17 H24 N3 O

Figure S43. Mass spectrum of the compound **2a**.

Eager 300 Report

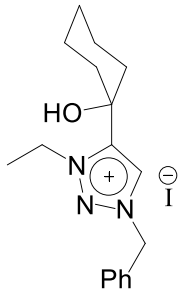
Page: 1 Sample: pg-sm-2-105-1

Method Name	: Nitrogen/Carbon/Hydrogen/Sulphur		
Method File	: D:\CHNS2012\SP-020712.mth		
Chromatogram	: pg-sm-2-53-1		
Operator ID	:	Company Name	: C.E. Instruments
Analysed	: 07/02/2012 13:39	Printed	: 7/2/2012 16:47
Sample ID	: pg-sm-2-53-1 (# 10)	Instrument N.	: Instrument #1
Analysis Type	: UnkNown (Area)	Sample weight	: .832

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	
Nitrogen	12.6818
Carbon	50.2822
Hydrogen	5.7598
Sulphur	0.
Totals	68.7238



(**2a**)

Figure S44. CHN analysis of the compound **2a**.

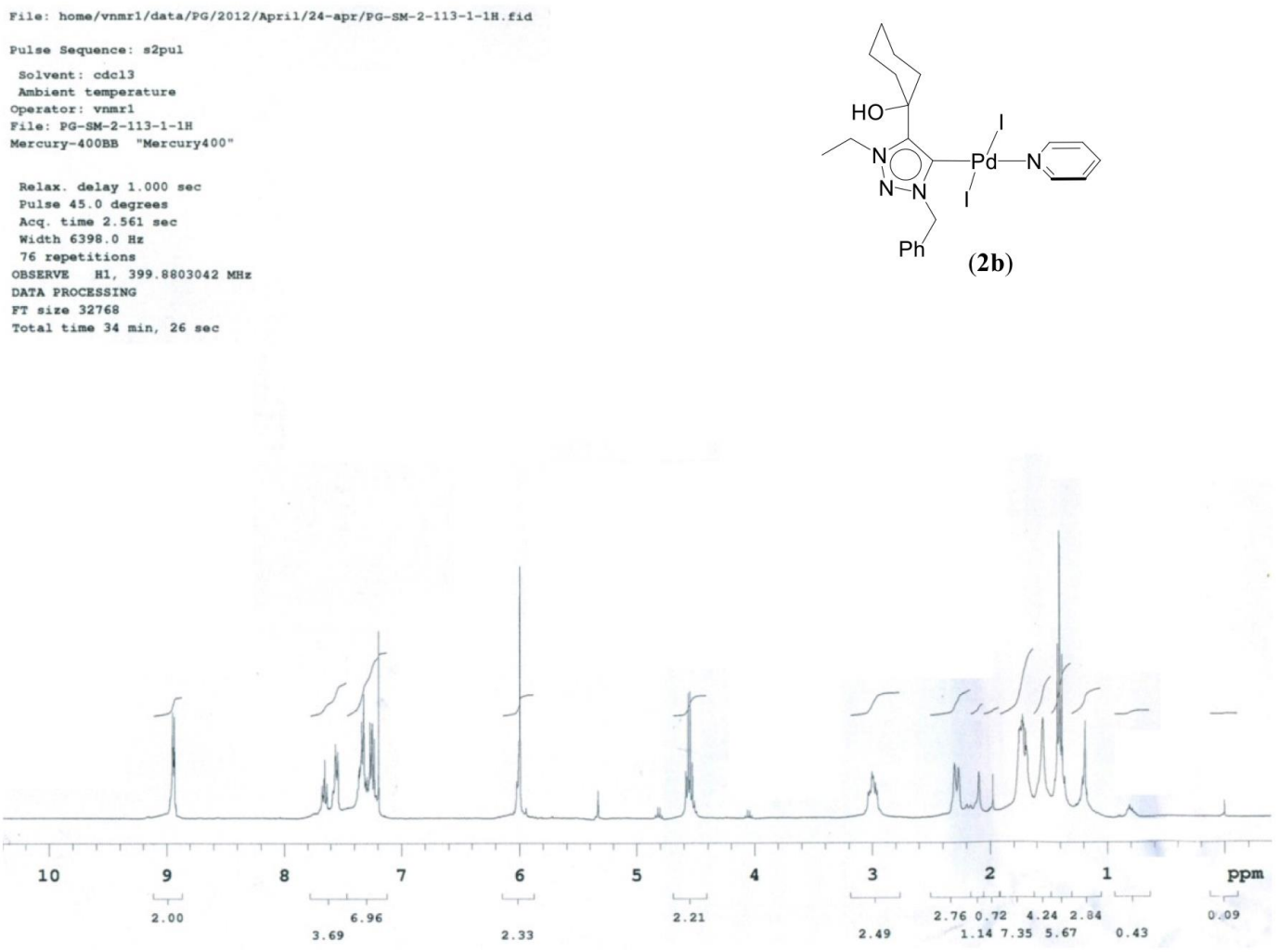
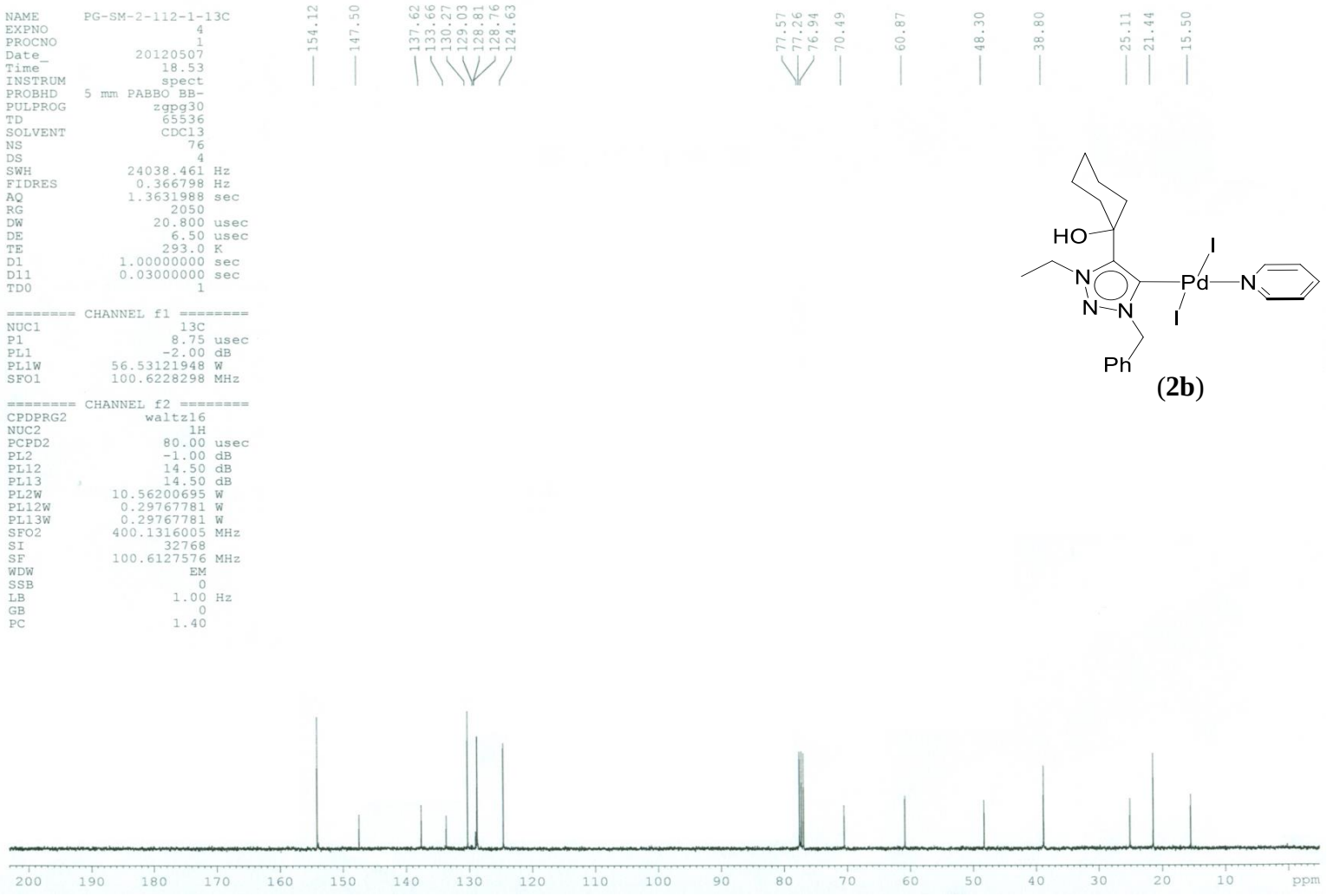
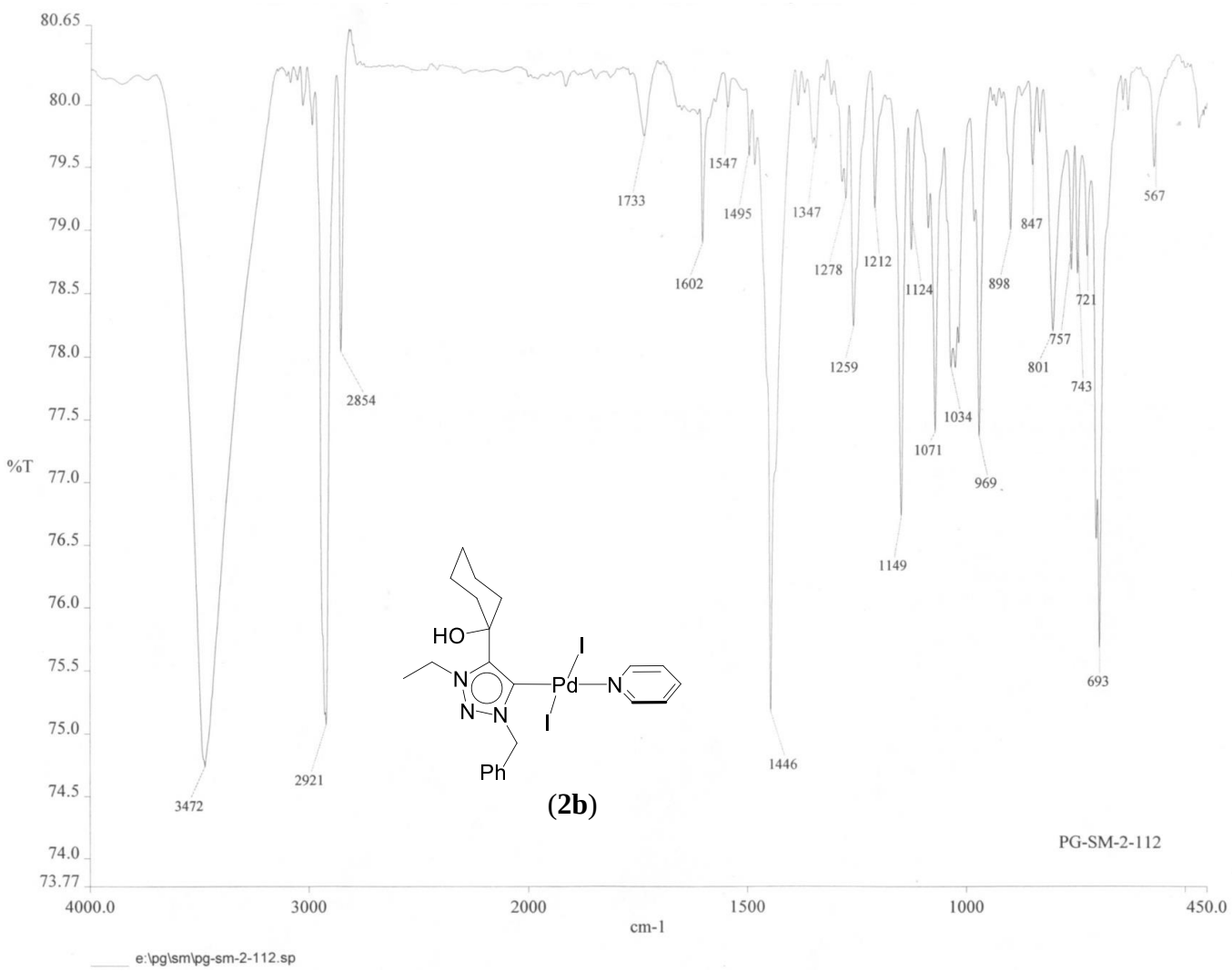


Figure S45. ^{1}H NMR spectrum of the compound **2b** in $CDCl_3$.



(**2b**)

Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2b** in $CDCl_3$.



(**2b**)

Figure S47. IR spectrum of the compound **2b**.

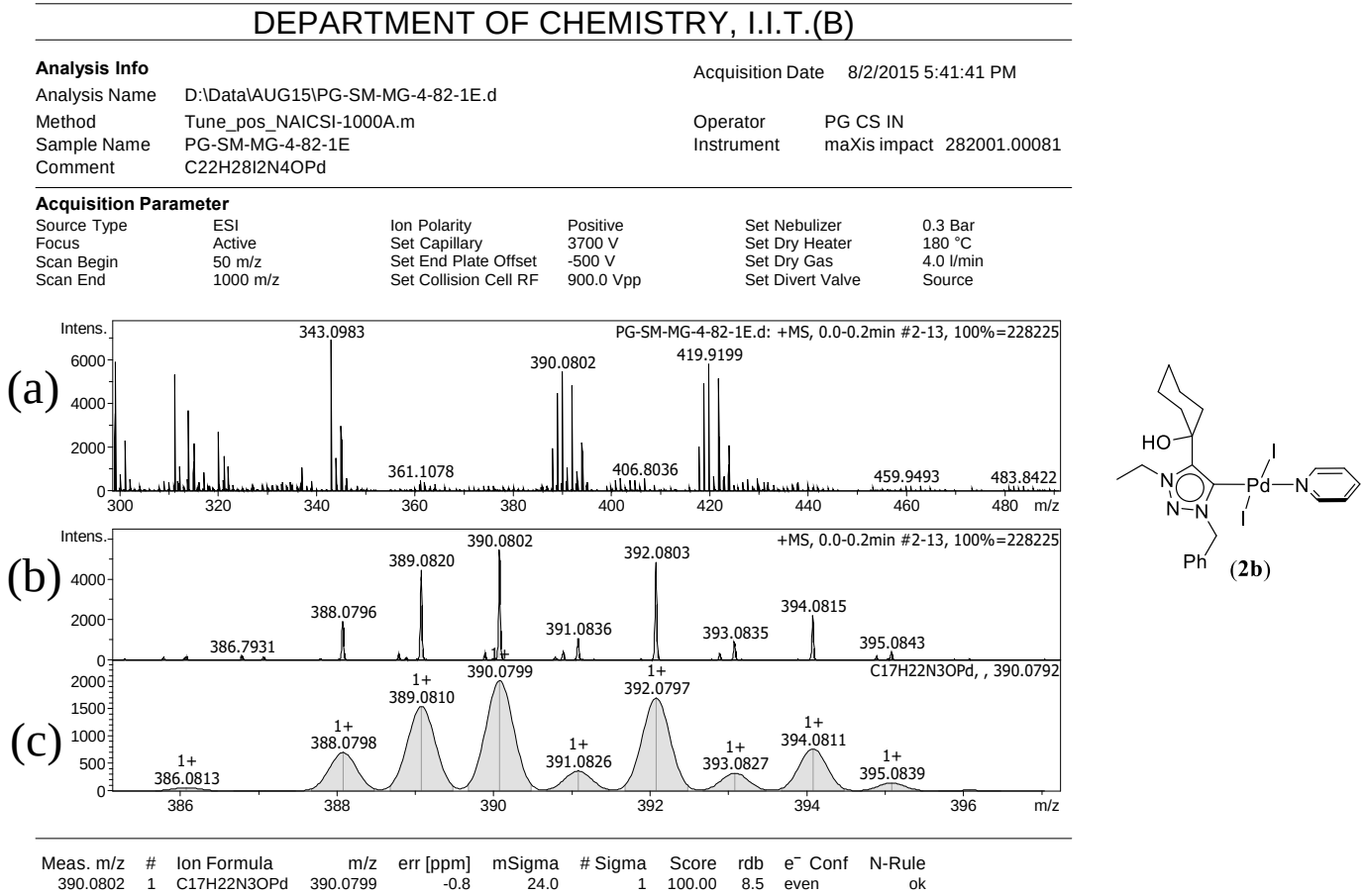
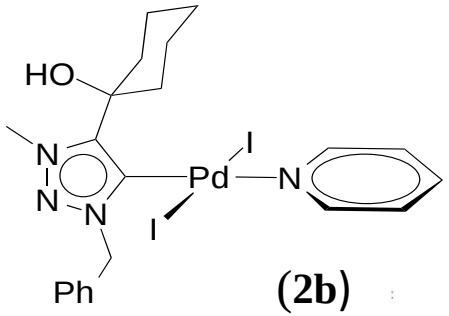


Figure S48. Mass spectrum of the compound **2b** [plot (a)] along with its experimental [plot (b)] and theoretical [plot (c)] isotopic mass distributions are shown.



(2b)

Eager 300 Report

Page: 1 Sample: PG-SM-2B-2 (PG-SM-2B-2)

Method Name : PGCP01062015
Method File : D:\CHNS-2015\PGCP01062015.mth
Chromatogram : PG-SM-2B-2
Operator ID : CHANDNI Company Name : C.E. Instruments
Analysed : 06/01/2015 18:10 Printed : 6/1/2015 23:39
Sample ID : PG-SM-2B-2 (# 14) Instrument N. : Instrument #1
Analysis Type : UnkNown (Area) Sample weight : .683

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	8.5996	41	74444	FU	8.834227	.126746E+07
Carbon	36.7489	65	657657	FU	1.000000	.262020E+07
Hydrogen	3.6232	178	178902	RS	3.676073	.661307E+07
Totals	48.9717		911003			

Figure S49. CHN analysis of the compound **2b**.

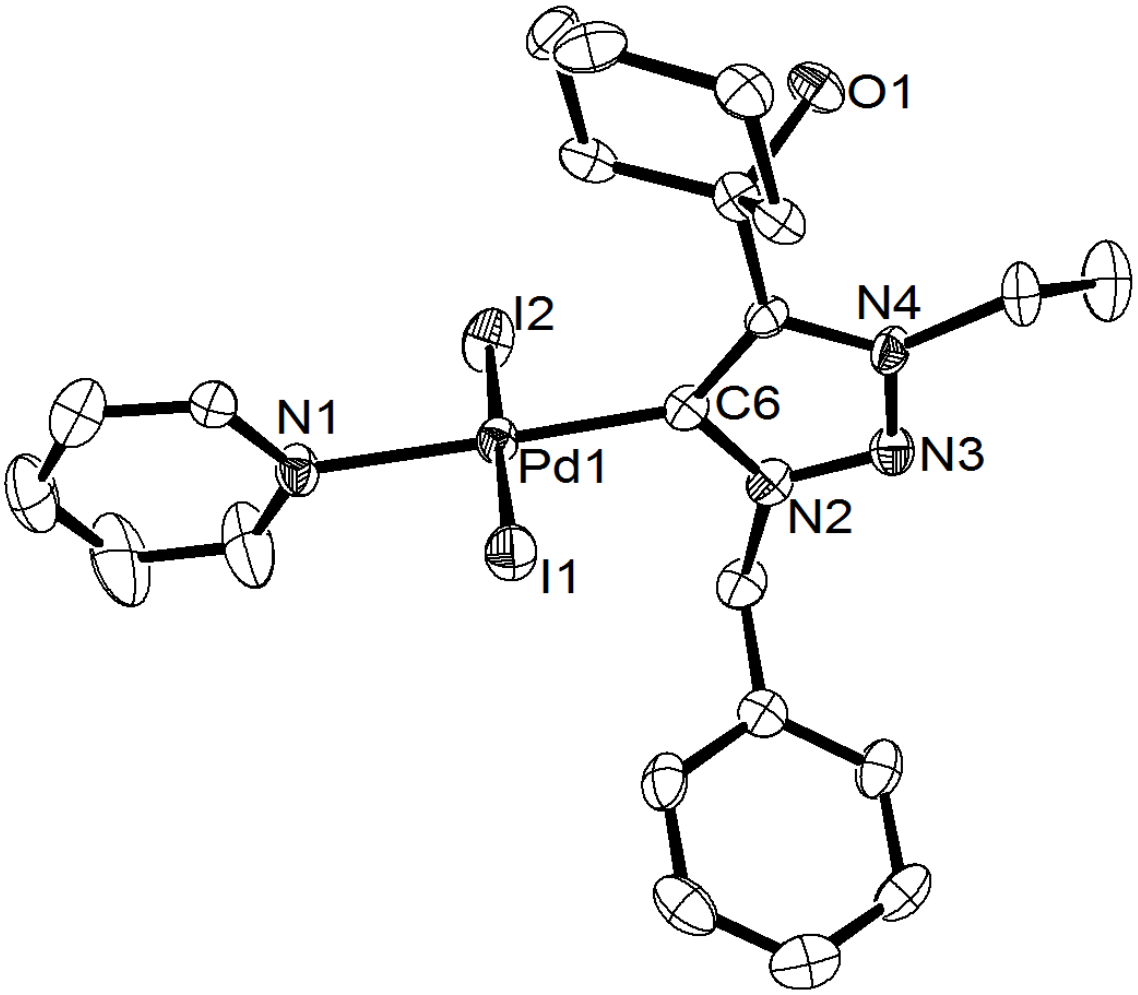


Figure S50. ORTEP diagram of **2b** with thermal ellipsoids shown at the 50 % probability level. Selected bond lengths (Å) and angles (°): Pd(1)-C(6) 1.986(5), Pd(1)-N(1) 2.094(4), Pd(1)-I(1) 2.6287(9), Pd(1)-I(2) 2.6017(9), C(6)-Pd(1)-N(1) 178.7(2), C(6)-Pd(1)-I(1) 90.55(15), N(1)-Pd(1)-I(1) 90.13(13), C(6)-Pd(1)-I(2) 88.80(15), N(1)-Pd(1)-I(2) 90.51(13), I(1)-Pd(1)-I(2) 179.33(2).

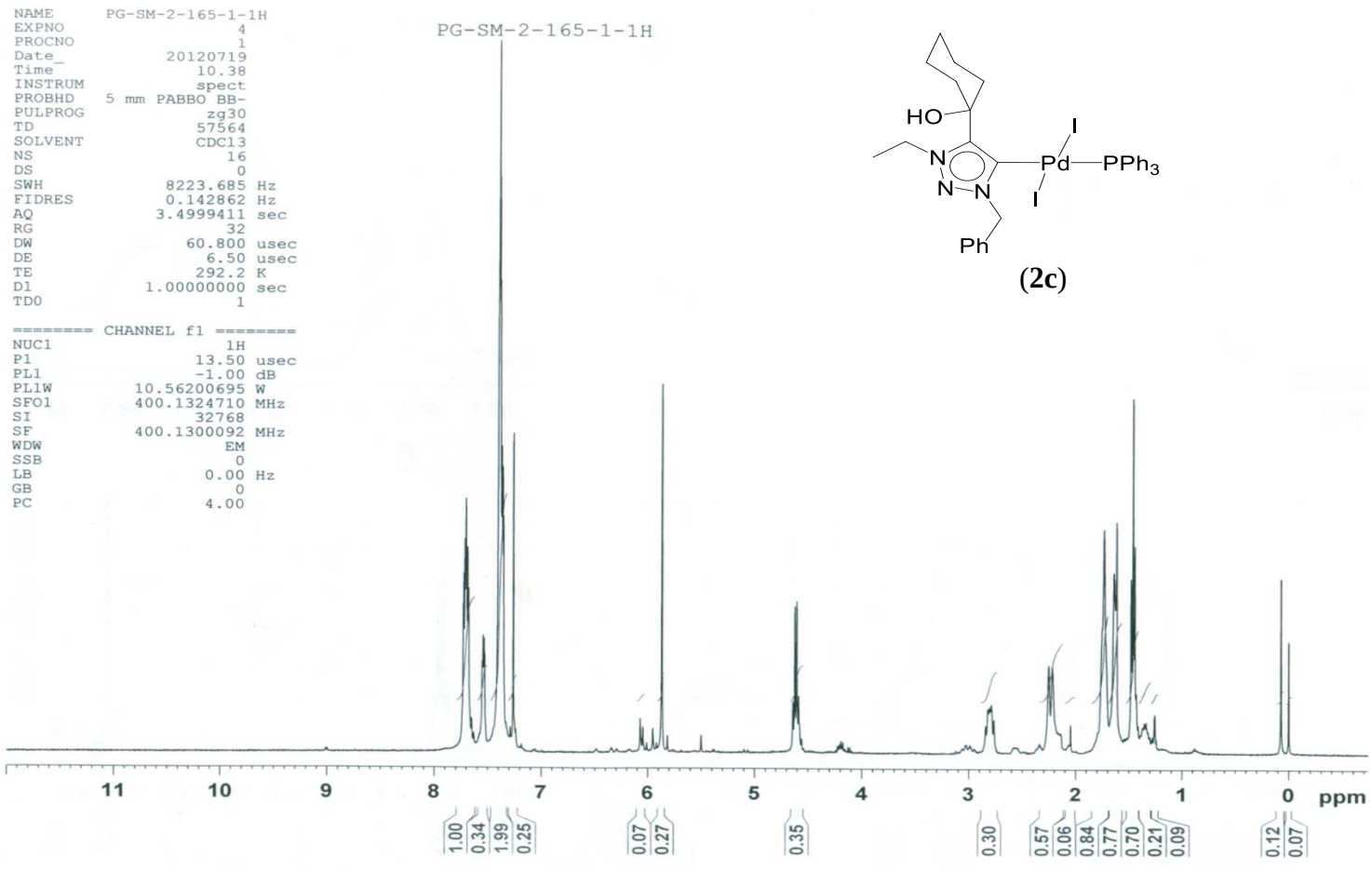


Figure S51. ^{1}H NMR spectrum of the compound **2c** in $CDCl_3$.

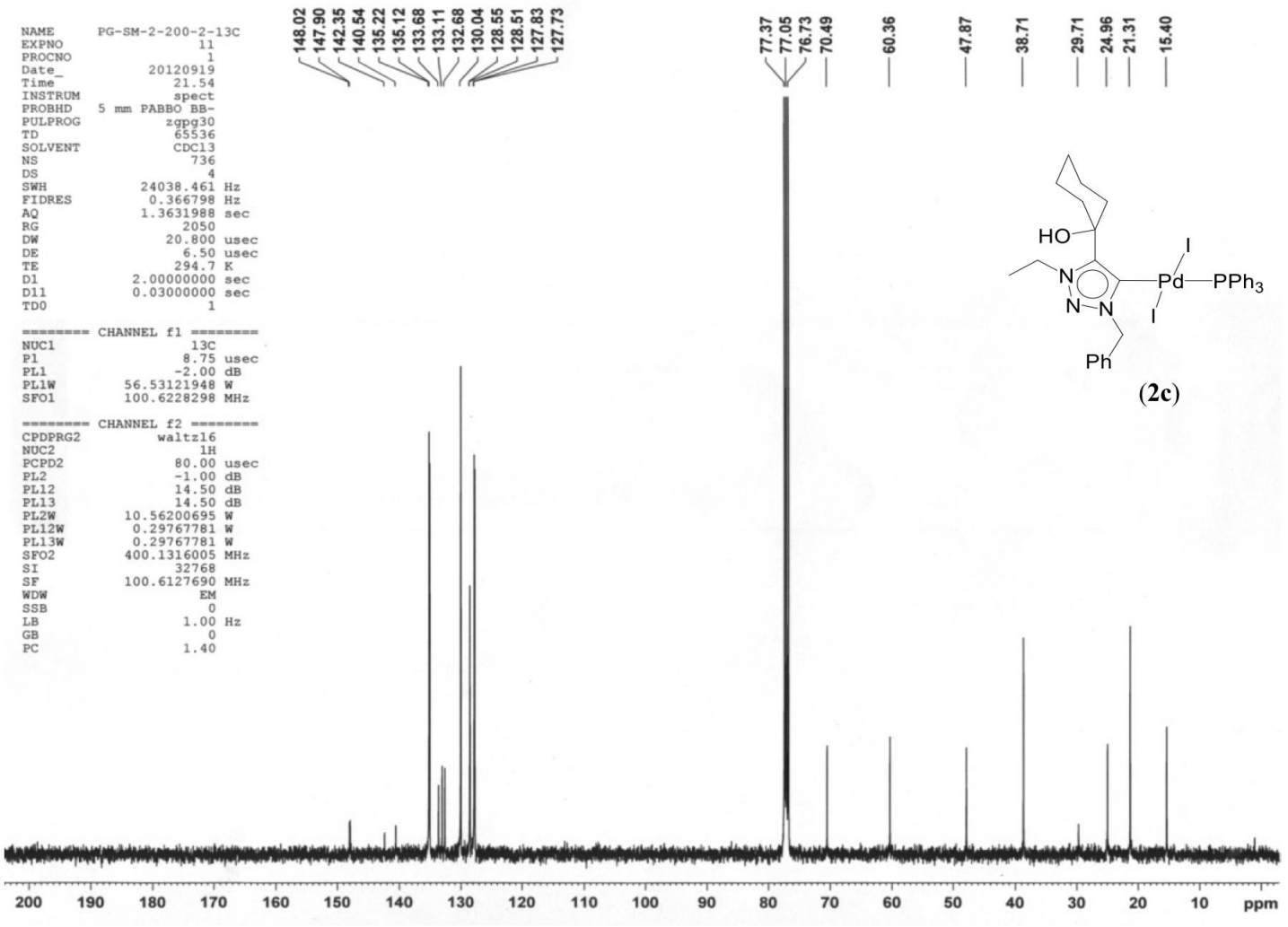


Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2c** in $CDCl_3$.

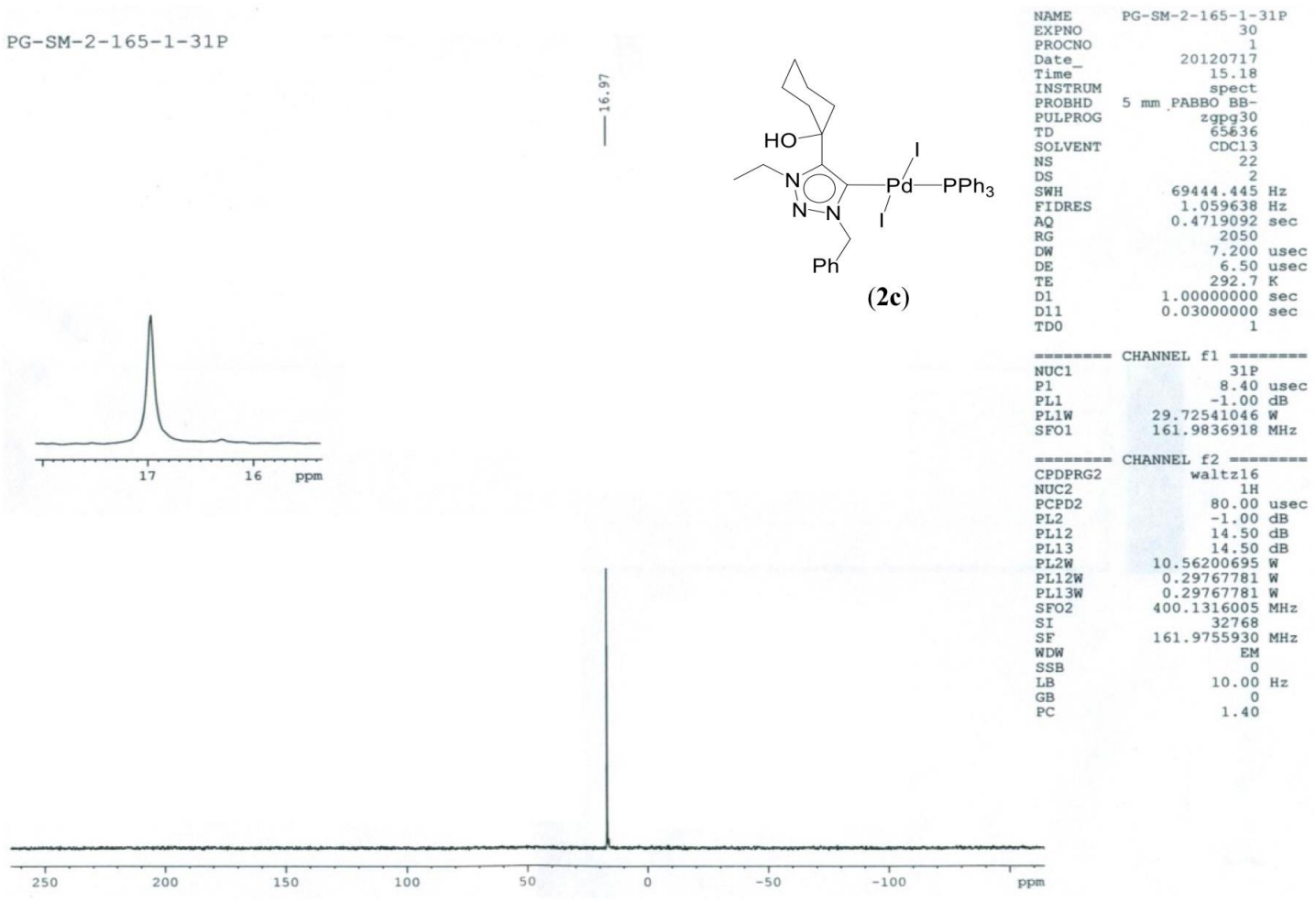


Figure S53. ^{31}P NMR spectrum of the compound **2c** in $CDCl_3$.

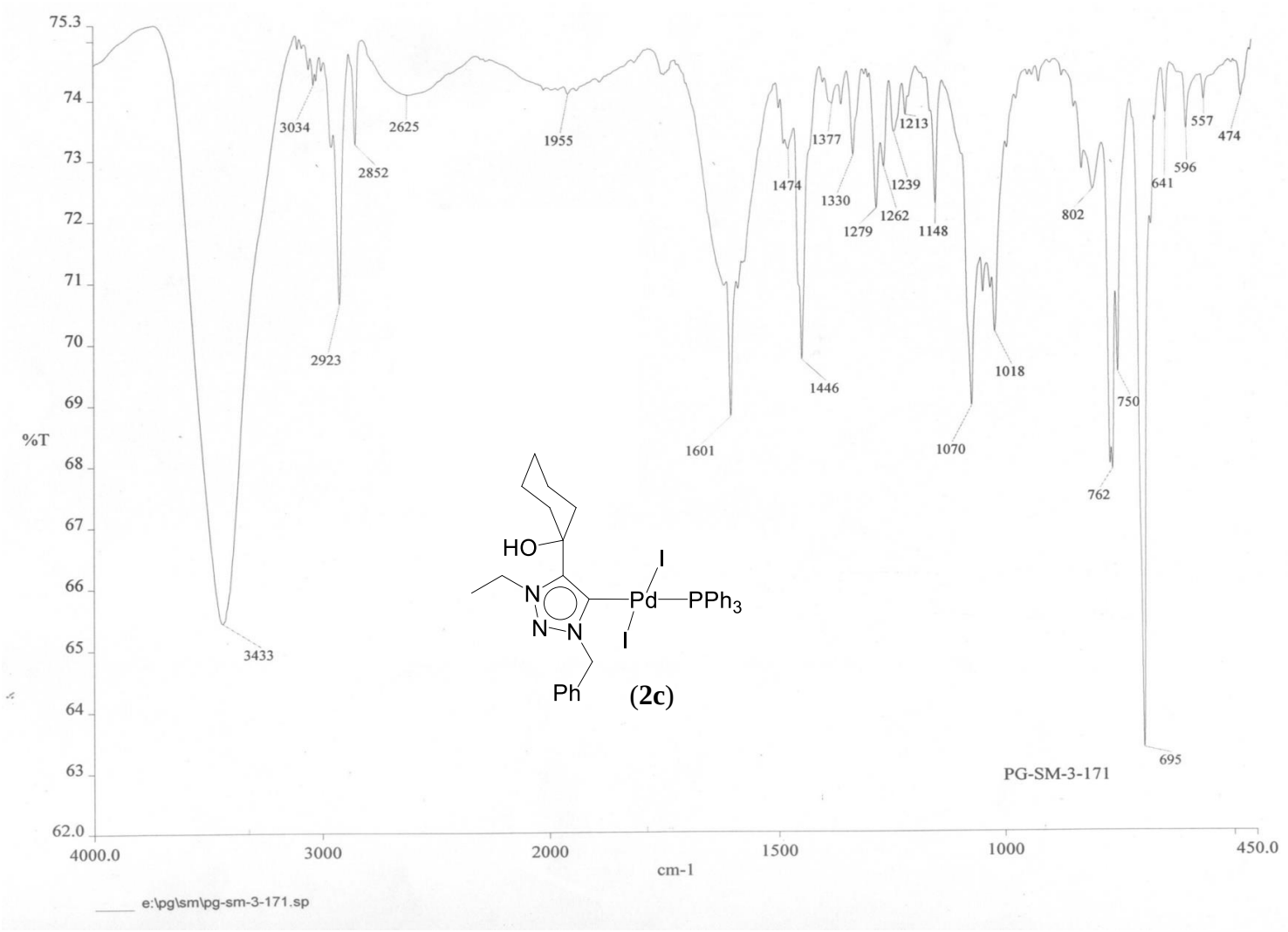
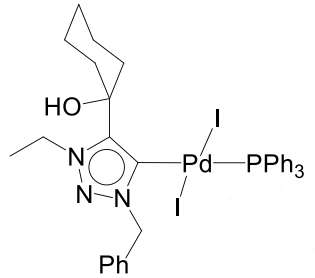


Figure S54. IR spectrum of the compound **2c**.

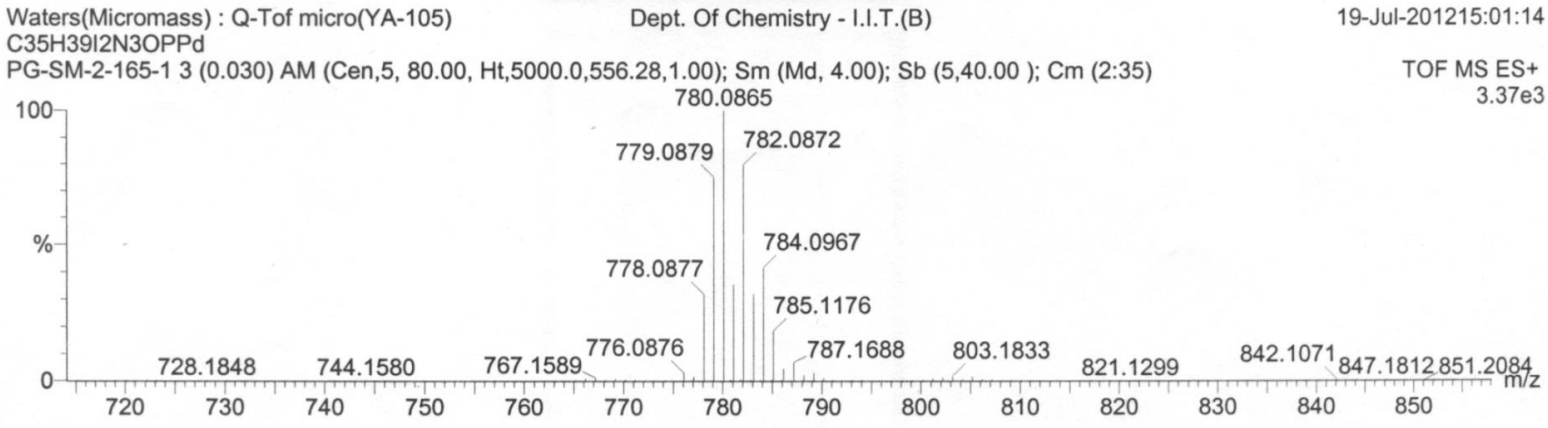
Elemental Composition Report

Single Mass Analysis (displaying only valid results)
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 200.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
297 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

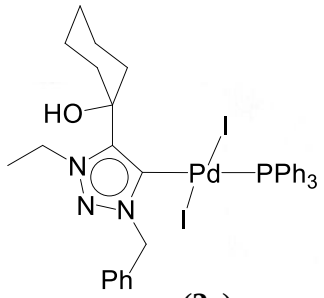


(2c)



Minimum:				-1.5		
Maximum:		50.0	5.0	200.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
780.0865	780.0832	3.3	4.2	18.5	1	C35 H38 N3 O I P Pd

Figure S55. Mass spectrum of the compound **2c**.



(**2c**)

Eager 300 Report

Page: 1 Sample: PG-SM-2-165-1 (PG-SM-2-165-1)

Method Name	: SP-081012		
Method File	: D:\CHNS2012\SP-081012.mth		
Chromatogram	: PG-SM-2-165-1		
Operator ID	: MNRAO	Company Name	: C.E. Instruments
Analysed	: 10/08/2012 12:49	Printed	: 10/8/2012 16:47
Sample ID	: PG-SM-2-165-1 (# 8)	Instrument N.	: Instrument #1
Analysis Type	: UnkNown (Area)	Sample weight	: .619

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
1	0.0000	18	18140	RS		0.0000
Nitrogen	5.2576	44	38795	RS	18.523130	.119206E+07
Carbon	46.5166	68	718605	RS	1.000000	.248813E+07
Hydrogen	3.7126	190	131712	RS	5.455881	.573142E+07
Totals	55.4867		907252			

Figure S56. CHN analysis of the compound **2c**.

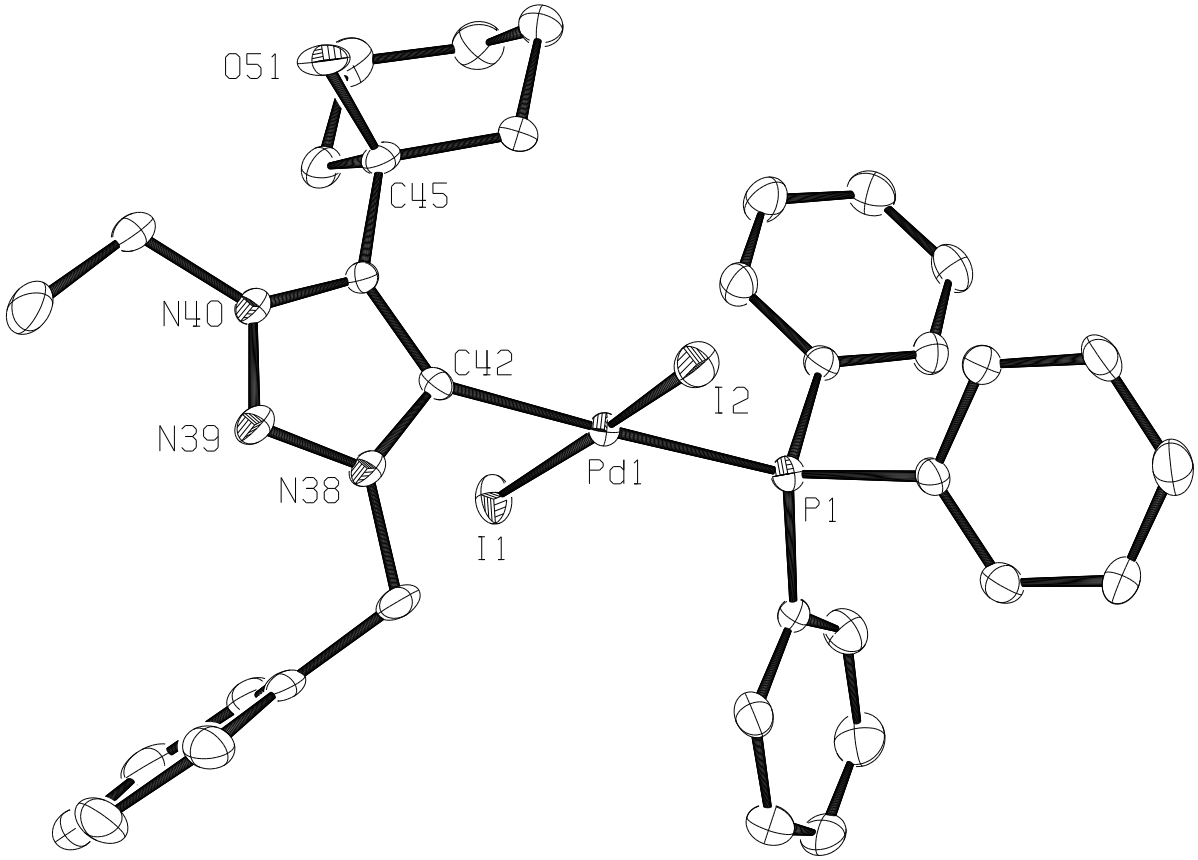


Figure S57. ORTEP diagram of **2c** with thermal ellipsoids shown at the 50 % probability level. Selected bond lengths (Å) and angles (°): Pd(1)-P(1) 2.3515(9), Pd(1)-I(2) 2.6017(3), Pd(1)-I(1) 2.6195(3) C(42)-Pd(1) 2.042(3), C(42)-Pd(1)-P(1) 177.97(9), C(42)-Pd(1)-I(2) 84.24(8), P(1)-Pd(1)-I(2) 96.58(2), C(42)-Pd(1)-I(1) 88.31(8), P(1)-Pd(1)-I(1) 91.04(2), I(2)-Pd(1)-I(1) 170.950(12).

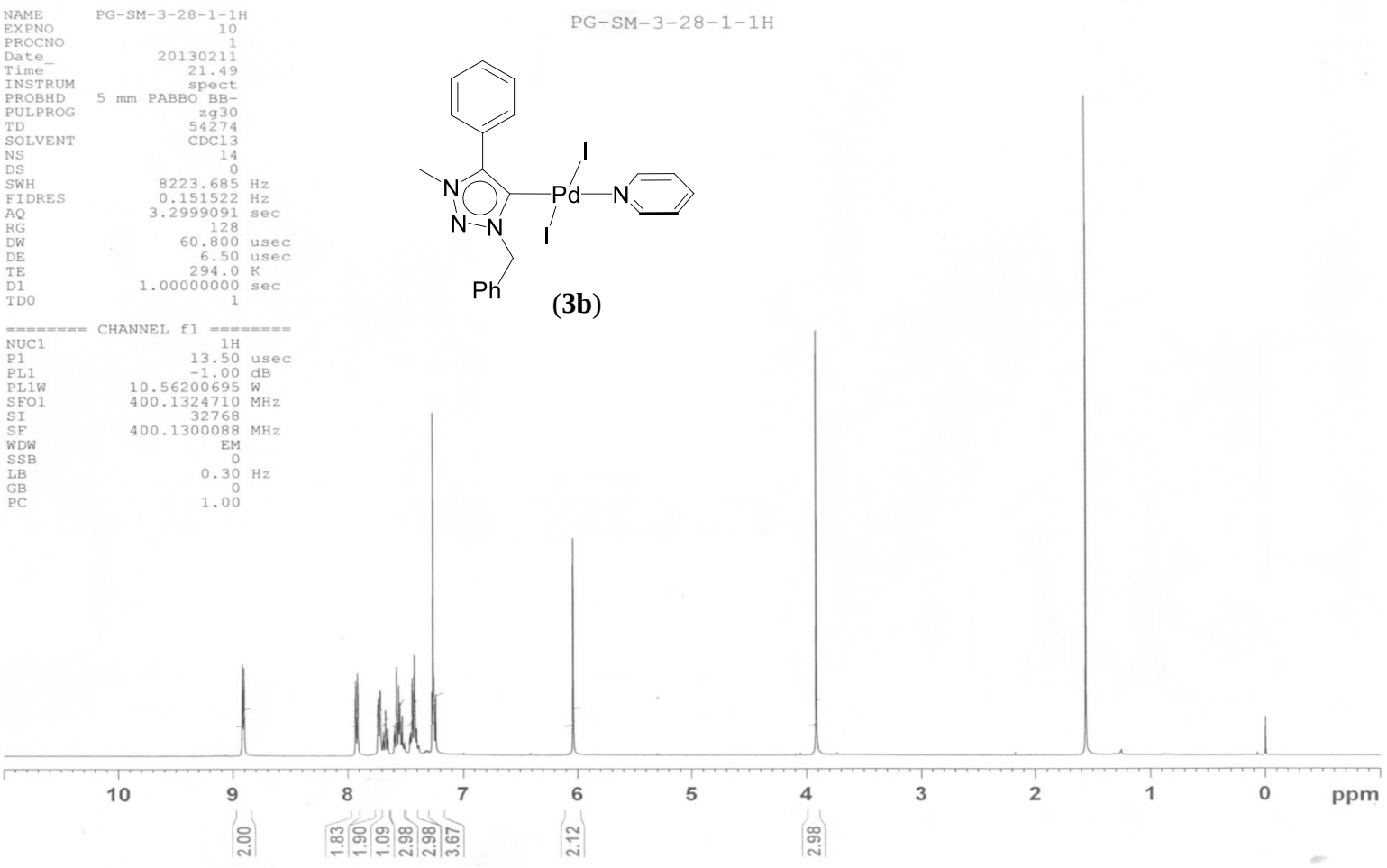


Figure S58. ^{1}H NMR spectrum of the compound **3b** in $CDCl_3$.

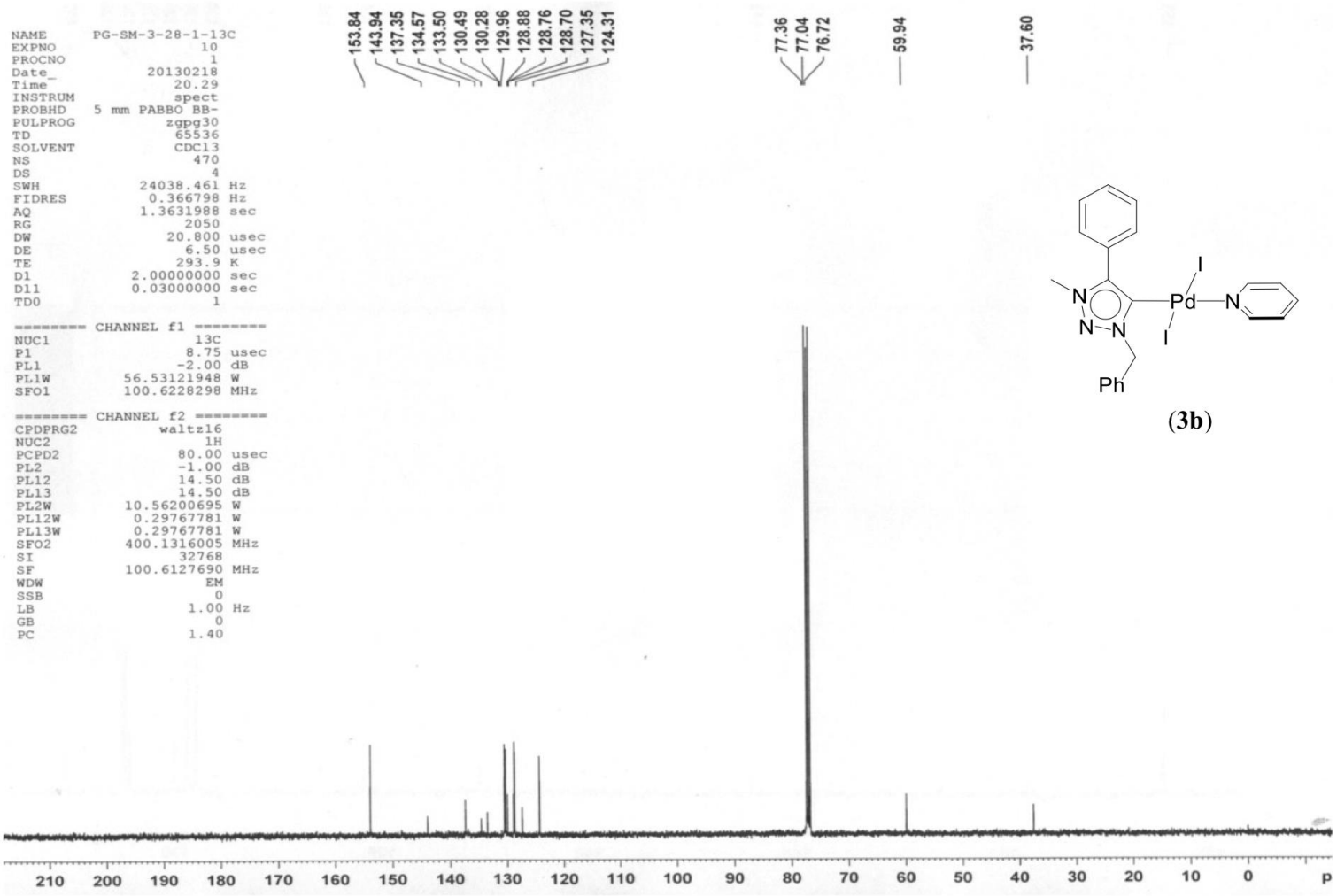


Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3b** in $CDCl_3$.

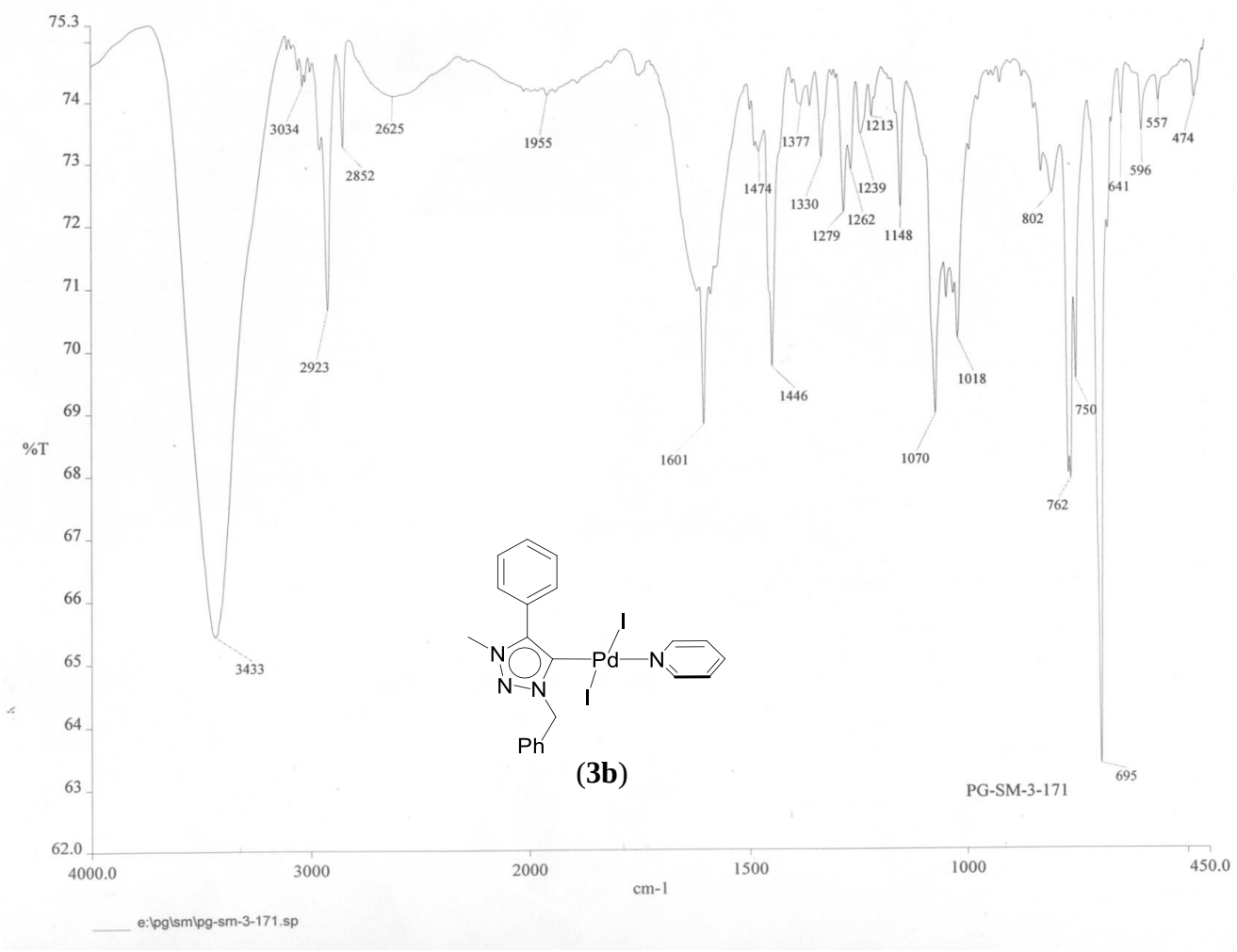


Figure S60. IR spectrum of the compound **3b**.

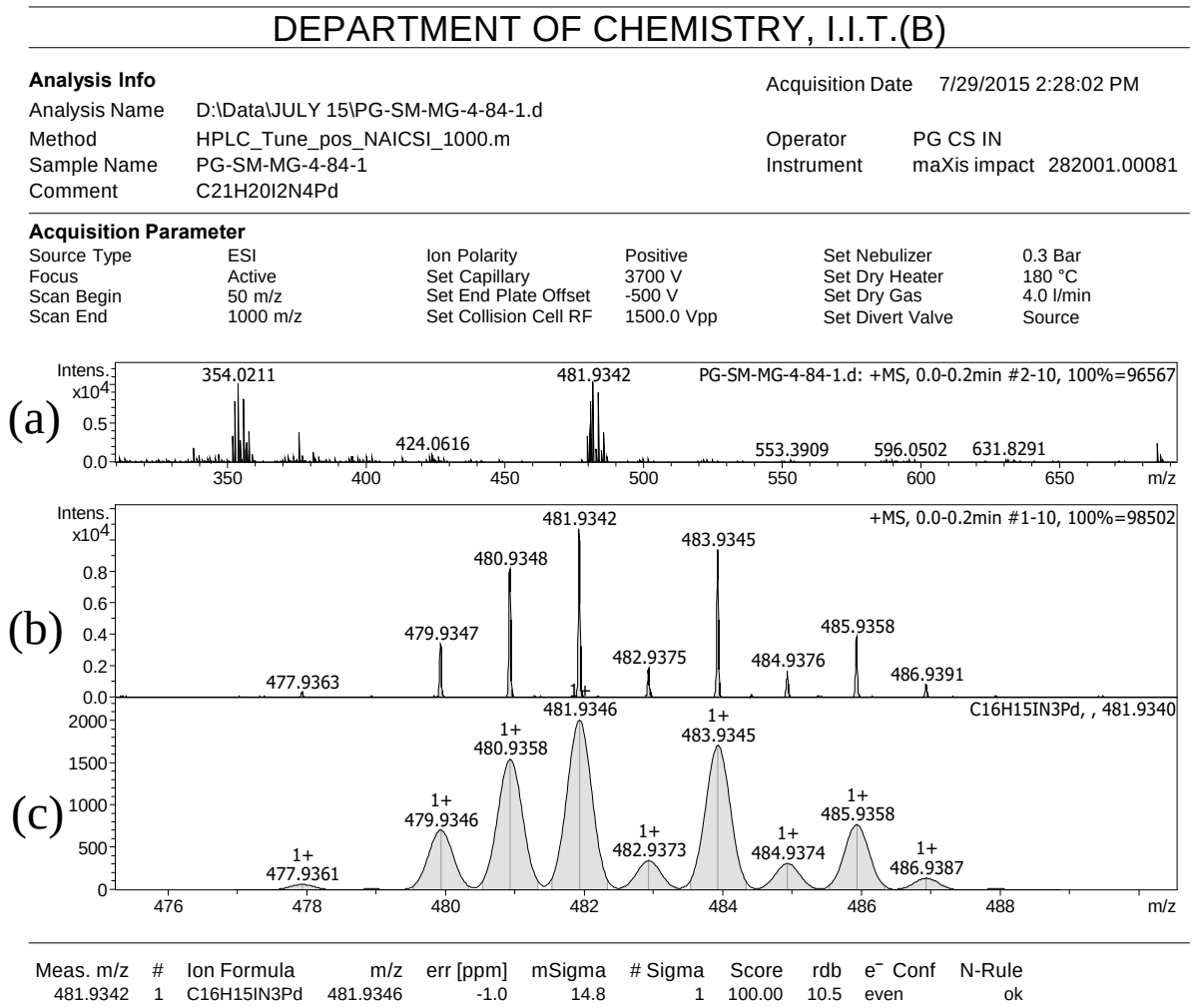
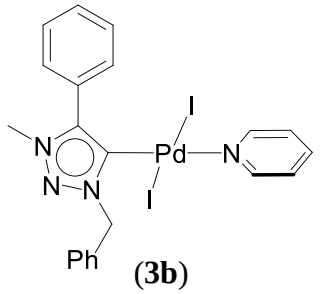


Figure S61. Mass spectrum of the compound **3b** [plot (a)] along with its experimental [plot (b)] and theoretical [plot (c)] isotopic mass distributions are shown.



(**3b**)

Eager 300 Report

Page: 1 Sample: PG-SM-3-28 (PG-SM-3-28)

Method Name	: SP-290413		
Method File	: D:\CHNS2012\SP-290413.mth		
Chromatogram	: PG-SM-3-28		
Operator ID	: MNRAO	Company Name	: C.E. Instruments
Analysed	: 04/29/2013 15:04	Printed	: 4/29/2013 17:10
Sample ID	: PG-SM-3-28 (# 18)	Instrument N.	: Instrument #1
Analysis Type	: UnkNown (Area)	Sample weight	: .862

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	7.4441	43	97728	RS	8.671081	.152300E+07
Carbon	36.8202	67	847403	RS	1.000000	.266991E+07
Hydrogen	2.6736	184	158256	RS	5.354634	.609525E+07
Totals	46.9379		1103387			

Figure S62. CHN analysis of compound **3b**.

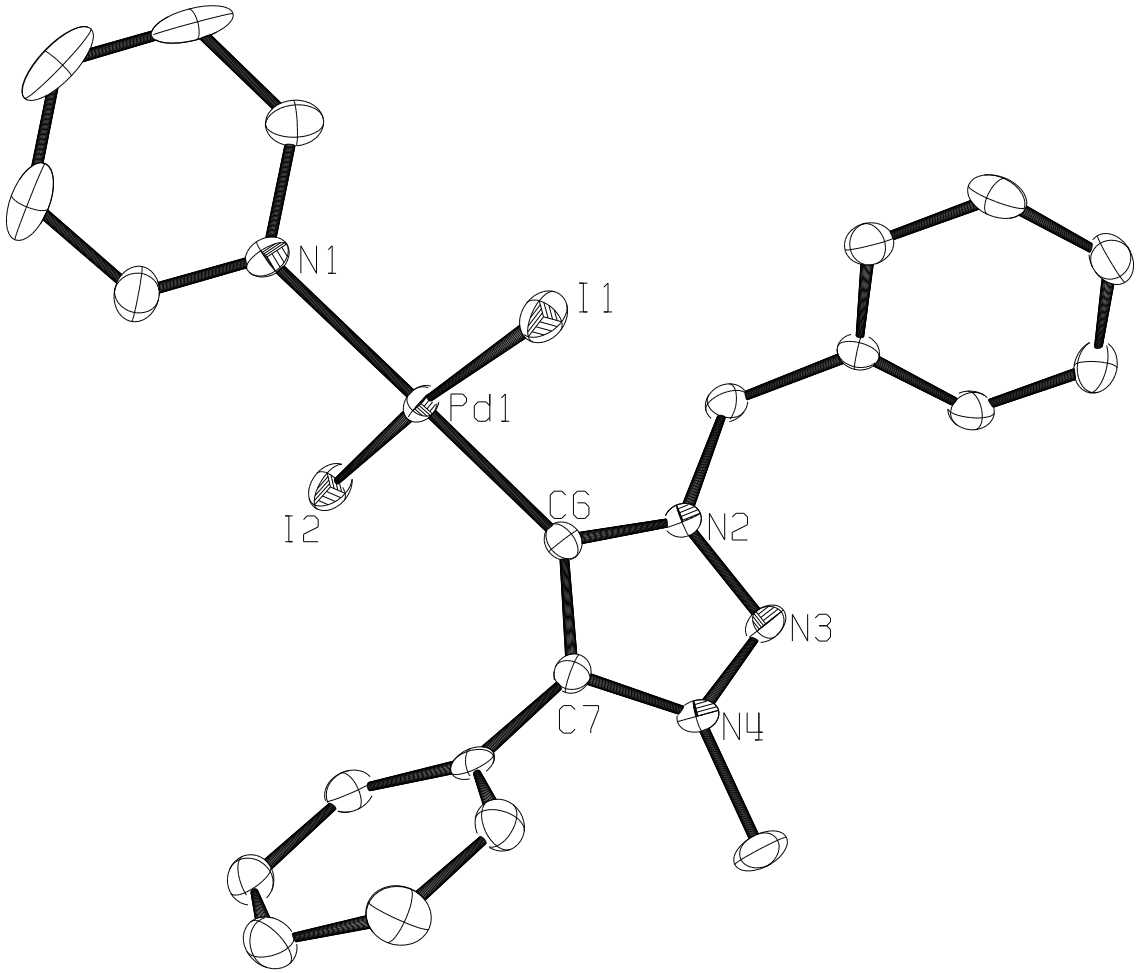


Figure S63. ORTEP diagram of **3b** with thermal ellipsoids shown at the 50 % probability level. Selected bond lengths (Å) and angles (°): Pd(1)-C6 1.967(3), Pd(1)-N(1) 2.104(2), Pd(1)-I(1) 2.5968(9), Pd(1)-I(2) 2.6104(9), C(6)-Pd(1)-N(1) 177.24(10), C(6)-Pd(1)-I(1) 86.56(7), N(1)-Pd(1)-I(1) 91.38(6), C(6)-Pd(1)-I(2) 89.39(7), N(1)-Pd(1)-I(2) 92.75(6), I(1)-Pd(1)-I(2) 175.183(10).

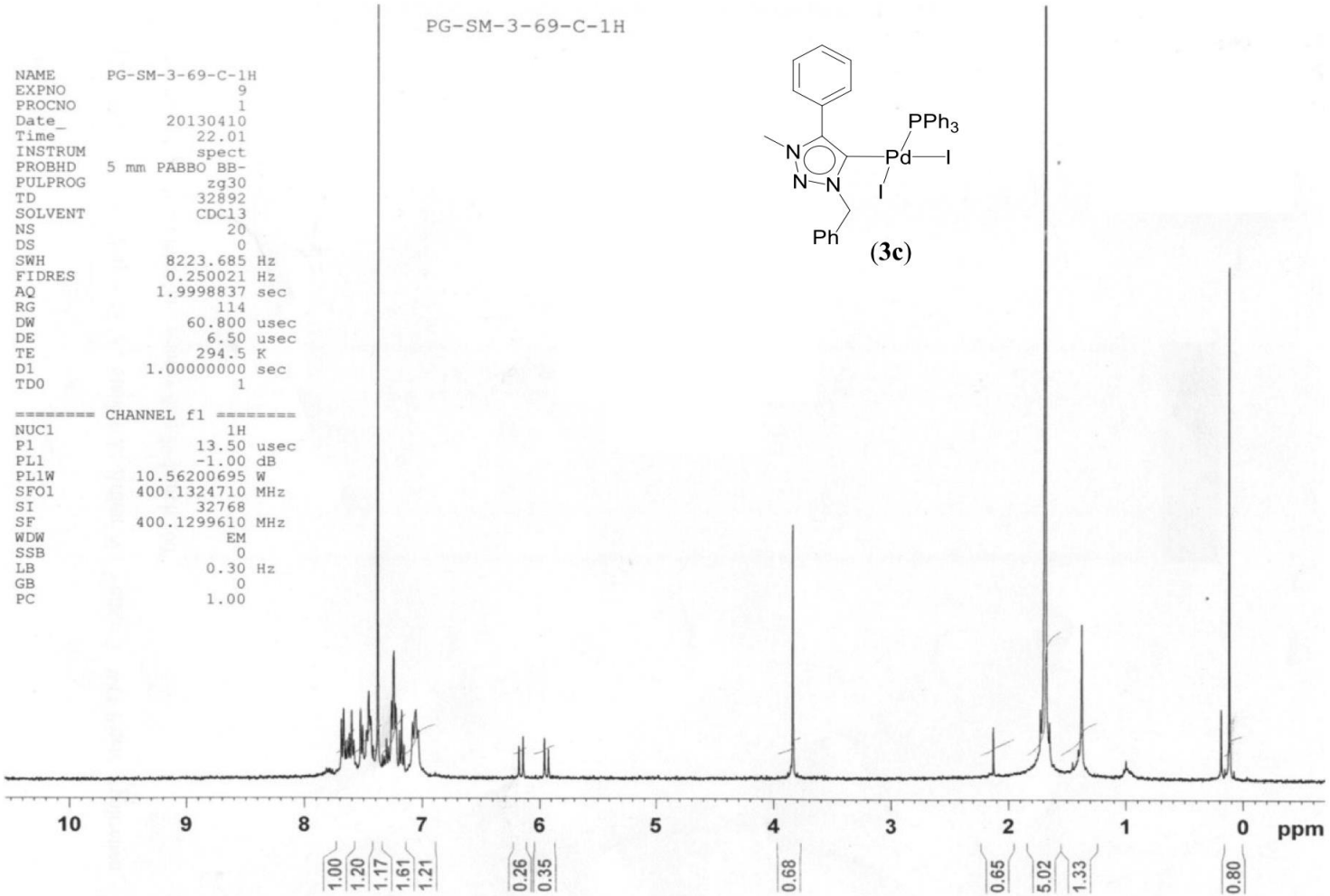


Figure S64. ^{1}H NMR spectrum of the compound **3c** in $CDCl_3$.

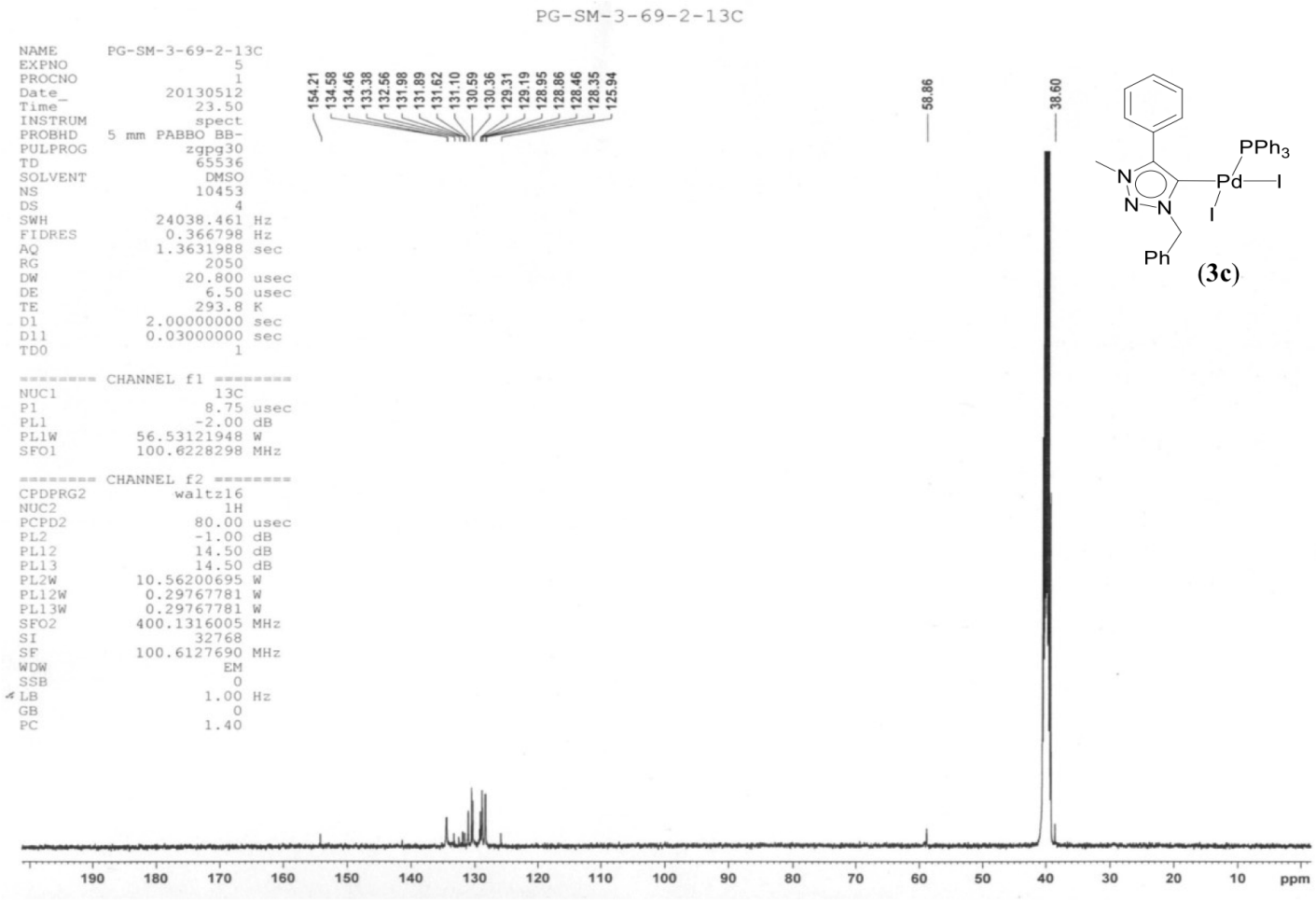


Figure S65. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3c** in $CDCl_3$.

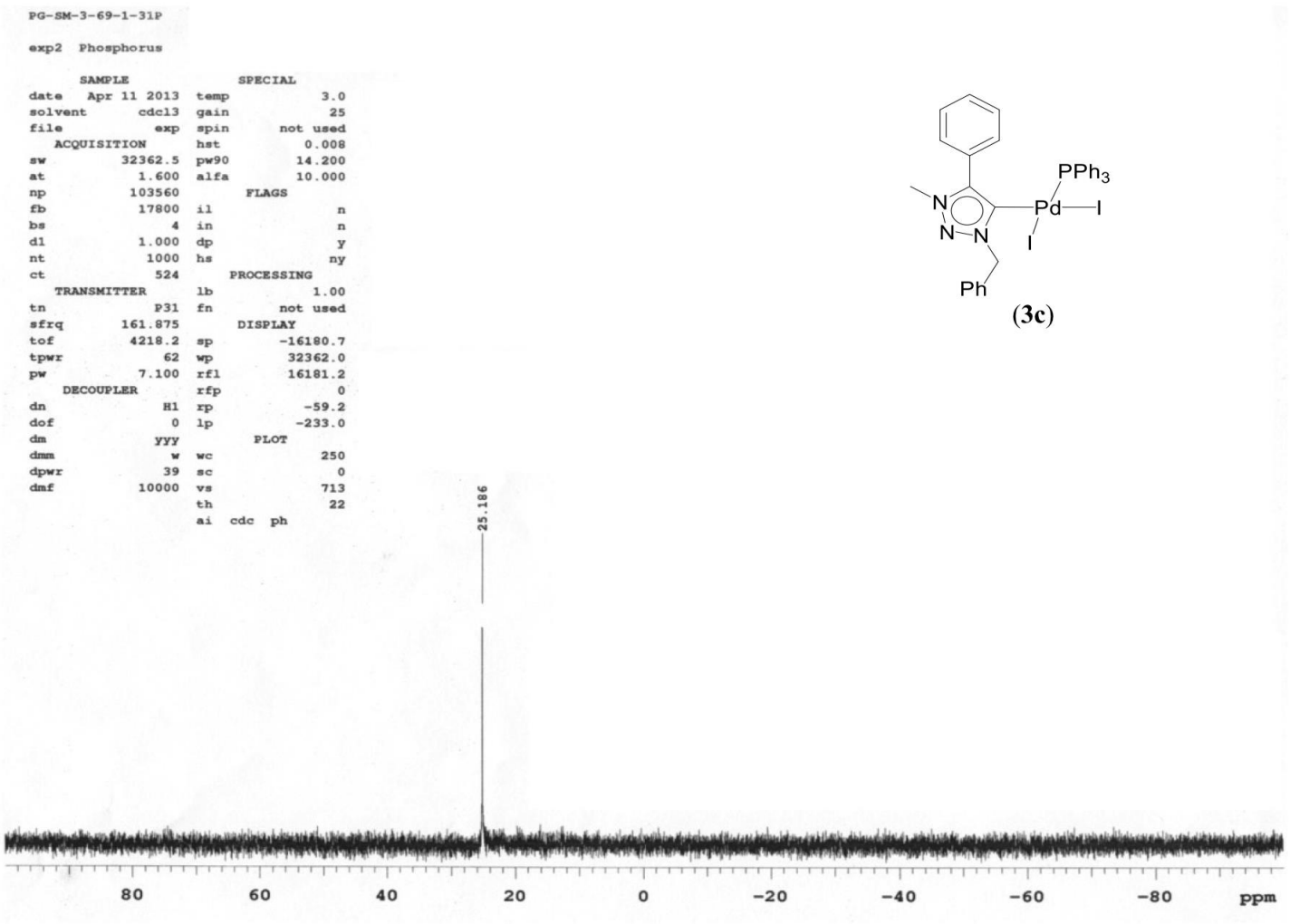


Figure S66. ^{31}P NMR spectrum of the compound **3c** in $CDCl_3$.

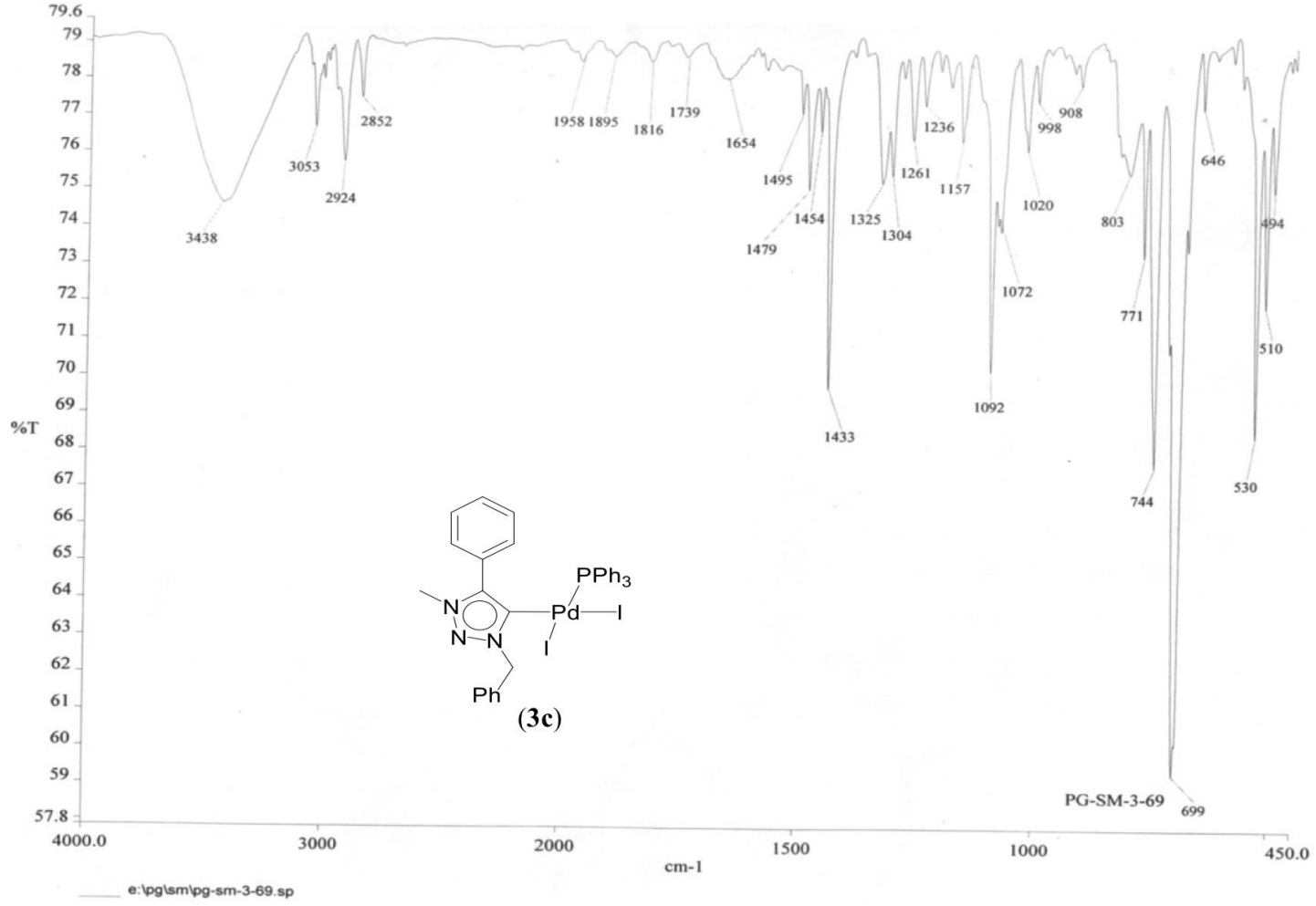


Figure S67. IR spectrum of the compound **3c**.

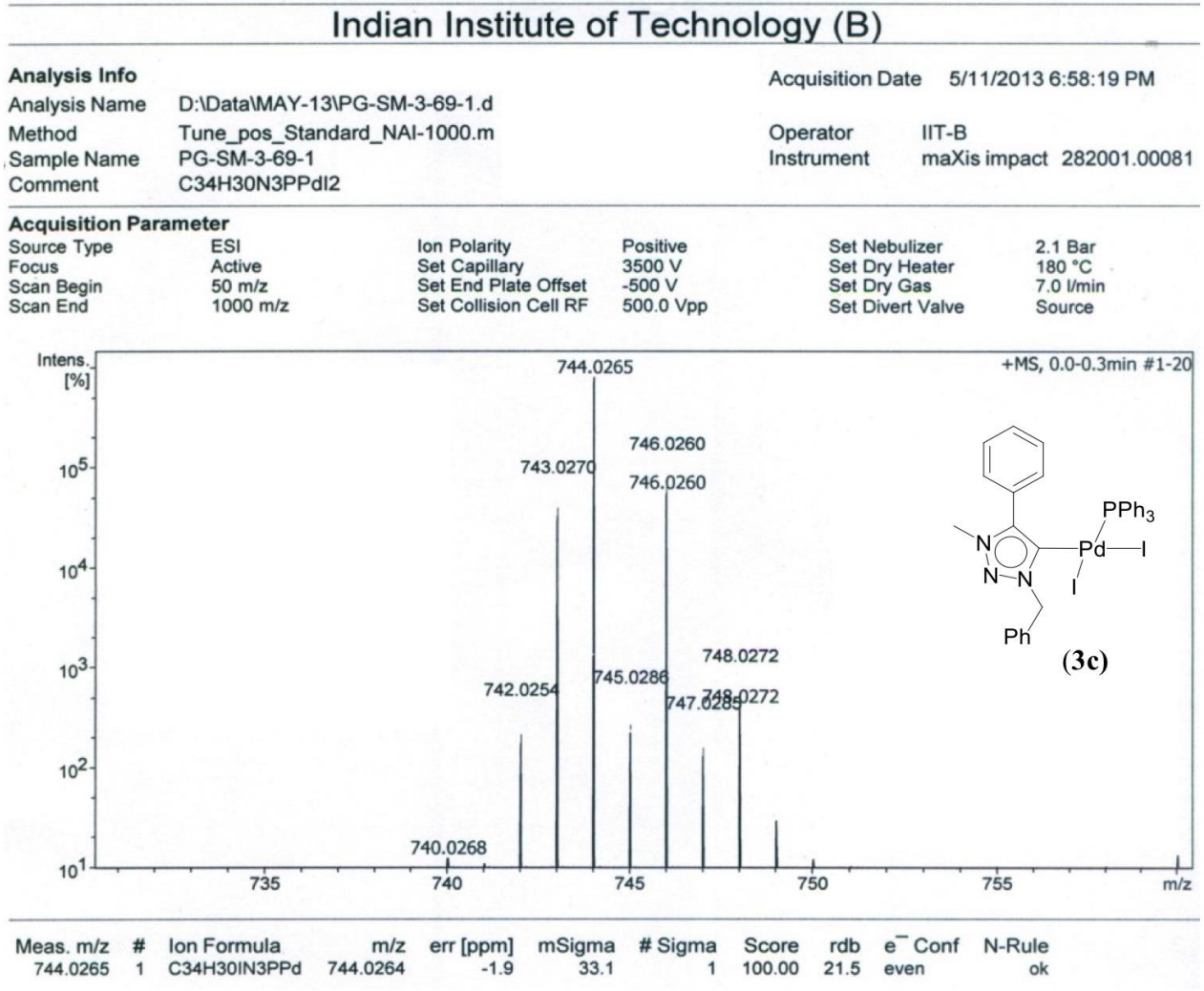
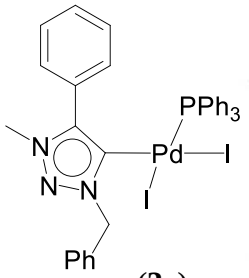


Figure S68. Mass spectrum of the compound **3c**.



(3c)

Eager 300 Report

Page: 1 Sample: PG-SM-3-69-1 (PG-SM-3-69-1)

Method Name : SP220413R
Method File : D:\CHNS2012\SP220413R.mth
Chromatogram : PG-SM-3-69-1
Operator ID : SONALI Company Name : C.E. Instruments
Analysed : 04/22/2013 15:52 Printed : 4/22/2013 21:26
Sample ID : PG-SM-3-69-1 (# 15) Instrument N. : Instrument #1
Analysis Type : UnkNown (Area) Sample weight : .731

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	5.7805	43	61639	FU	15.215250	.145872E+07
Carbon	47.9529	67	937846	FU	1.000000	.266884E+07
Hydrogen	3.4570	184	182901	RS	5.127613	.636350E+07
Totals	57.1903		1182385			

Figure S69. CHN analysis of compound **3c**.

Table S1. Selected ^{31}P NMR and the metrical data showing the $C_{carbene}$−Pd and Pd−$P_{phosphine}$ bond distances for the *trans*-(NHC)Pd(PR_3)X_2 (X = Cl, Br, and I; R = Ph, Cy, OMe, O^{i}Pr, OPh, and OC_6H_3-2,4-^{t}Bu$_2$) type complexes.

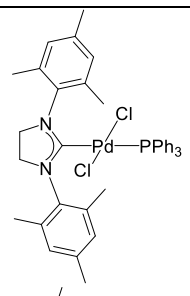
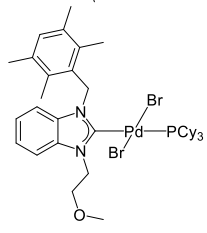
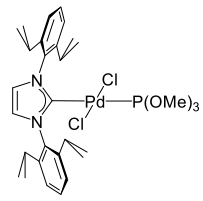
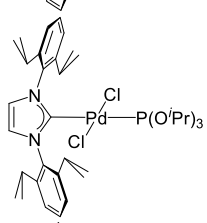
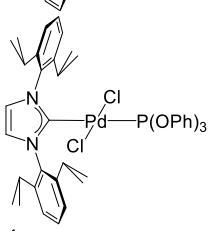
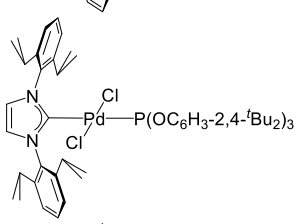
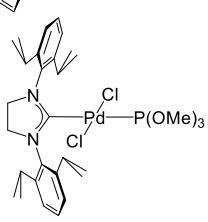
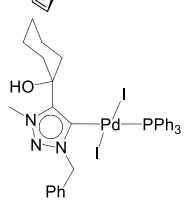
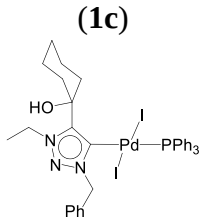
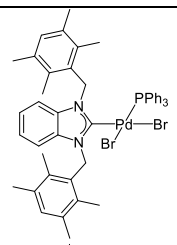
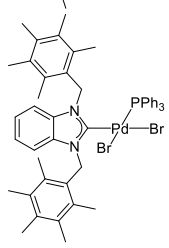
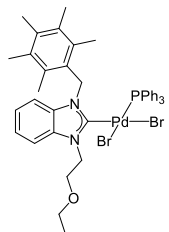
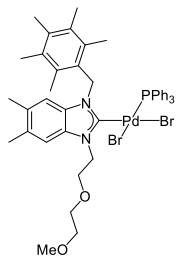
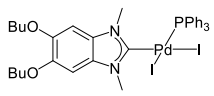
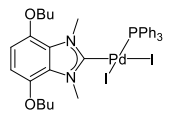
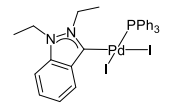
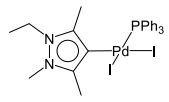
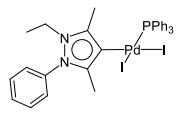
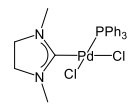
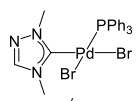
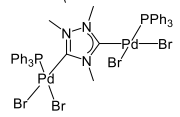
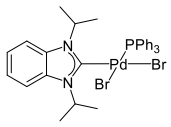
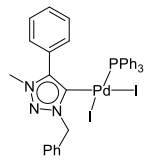
S. No.	compound	^{31}P NMR (δ, ppm)	$C_{carbene}$−Pd bond (Å)	Pd−$P_{phosphine}$ bond (Å)	Reference
1.		20.9	2.028(5)	2.3185(14)	[1]
2.		21.6	2.031(4)	2.3563(11)	[2]
3.		107.9	2.056(4)	2.2694(12)	[3]
4.		97.3	2.0482(11)	2.2845(3)	[3]
5.		92.2	2.0357(19)	2.2666(5)	[3]
6.		93.1	2.031(2)	2.2729(7)	[3]
7.		110.0	2.051(2)	2.2710(8)	[3]
8.	 (**1c**)	17.0	2.047(5)	2.3571(13)	this work
9.	 (**2c**)	16.9	2.042(3)	2.3515(9)	this work

Table S2. Selected ^{31}P NMR and the metrical data showing the $C_{carbene}$−Pd and Pd−$P_{phosphine}$ bond distances for the *cis*-(NHC)Pd(PR_3)X_2 (X = Cl, Br, and I) type complexes.

S. No.	compound	^{31}P NMR (δ, ppm)	$C_{carbene}$−Pd bond (Å)	Pd−$P_{phosphine}$ bond (Å)	Reference
1.		26.8	1.982(3)	2.2823(10)	2
2.		26.7	1.979(3)	2.2574(10)	2
3.		27.1	2.001(4)	2.2667(9)	4
4.		27.2	1.986(2)	2.2620(9)	4
5.		23.5	1.985(3)	2.2973(7)	5
6.		23.3	1.998(3) 1.995(3)	2.2762(8) 2.2686(8)	a, 5
7.		27.0	1.993(5)	2.2812(14)	6
8.		29.3	1.996(7)	2.2765(16)	7
9.		29.4	2.012(8)	2.266(3)	7
10.			1.968(8)	2.251(2)	8
11.		26.9	1.988(5)	2.2686(14)	9
12.		28.0	1.968(5)	2.2663(15)	9
13.		26.6	1.978(3)	2.2624(8)	10
14.	 (**3c**)	25.3	2.006(6)	2.2804(17)	this work

a. A small peak due to the *trans* isomer appeared at 16.3 ppm.

Table S3. Bond lengths (*d*), bond dissociation energies (D_e) and Charge Decomposition Analysis (CDA) studies of in (**1-3**)**b** depicting (*a*-NHC)→$PdI_2(NC_5H_5)$ σ-donation (*d*), the (*a*-NHC)←$PdI_2(NC_5H_5)$ π-back donation (*b*) and the *d*/*b* ratio. The experimental bond lengths are given in parenthesis.

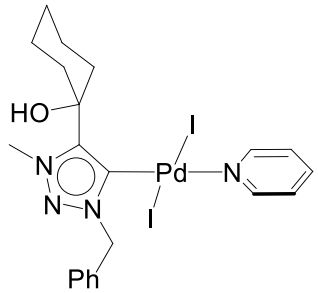
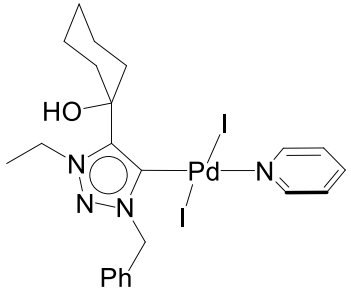
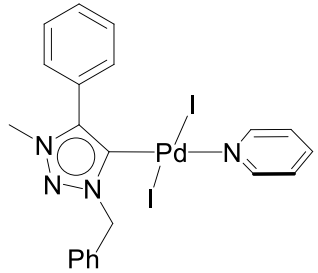
Complex	*d*/(*a*-NHC)–$PdI_2(NC_5H_5)$ (Å)	D_e/(*a*-NHC)–$PdI_2(NC_5H_5)$ (kcal/mol)	*a*-NHC→$PdI_2(NC_5H_5)$ (*d*)	*a*-NHC←$PdI_2(NC_5H_5)$ (*b*)	*d*/*b* ratio
 (**1b**)	1.996 [1.980(3)]	80.9	0.324	0.063	5.14
 (**2b**)	1.997 [1.986(5)]	81.2	0.325	0.065	5.00
 (**3b**)	1.988 [1.967(3)]	81.4	0.281	0.073	3.85

Table S4. Bond lengths (*d*), bond dissociation energies (D_e) and Charge Decomposition Analysis (CDA) studies of in (**1-3**)**c** depicting the (*a*-NHC)→$PdI_2(PPh_3)$ σ-donation (*d*), the (*a*-NHC)←$PdI_2(PPh_3)$ π-back donation (*b*) and the *d*/*b* ratio. The experimental bond lengths are given in parenthesis.

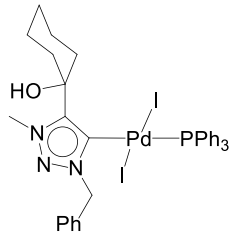
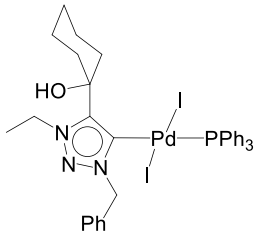
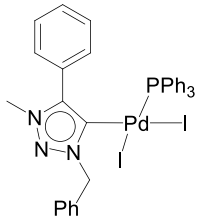
Complex	*d*/(*a*-NHC)–$PdI_2(PPh_3)$ (Å)	D_e /(*a*-NHC)–$PdI_2(PPh_3)$ (kcal/mol)	*a*-NHC→$PdI_2(PPh_3)$ (*d*)	*a*-NHC←$PdI_2(PPh_3)$ (*b*)	*d*/*b* ratio
 (**1c**)	2.040 [2.047(5)]	64.9	0.318	0.051	6.24
 (**2c**)	2.041 [2.042(3)]	64.8	0.322	0.049	6.57
 (**3c**)	2.029 [2.006(6)]	64.9	0.247	0.064	3.86

Table S5. Bond lengths (*d*), bond dissociation energies (D_e) and Charge Decomposition Analysis (CDA) studies of (**1-3**)**b** depicting the (*a*-NHC)PdI_2←(NC_5H_5) σ-donation (*d*), the (*a*-NHC)PdI_2→(NC_5H_5) π-back donation (*b*) and the *d*/*b* ratio. The experimental bond lengths are given in parenthesis.

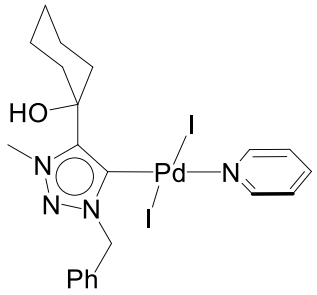
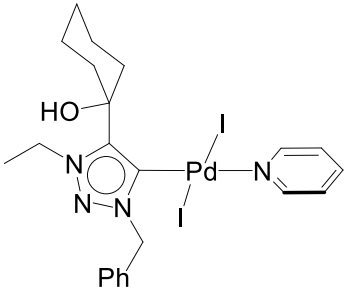
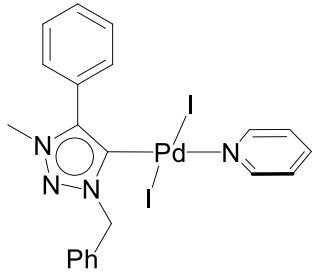
Complex	*d*/(*a*-NHC)PdI_2–(NC_5H_5) (Å)	D_e/(*a*-NHC)PdI_2–(NC_5H_5) (kcal/mol)	(NC_5H_5)→PdI_2(*a*-NHC) (*d*)	(NC_5H_5)←PdI_2(*a*-NHC) (*b*)	*d*/*b* ratio
 (**1b**)	2.147 [2.091(3)]	30.5	0.172	0.013	13.2
 (**2b**)	2.149 [2.094(4)]	30.3	0.173	0.014	12.4
 (**3b**)	2.145 [2.104(2)]	30.3	0.171	0.012	14.3

Table S6. Bond lengths (*d*), bond dissociation energies (D_e) and Charge Decomposition Analysis (CDA) studies of (**1-3**)**c** depicting the (*a*-NHC)PdI_2←(PPh_3) σ-donation (*d*), the (*a*-NHC)PdI_2→(PPh_3) π-back donation (*b*) and the *d*/*b* ratio. The experimental bond lengths are given in parenthesis.

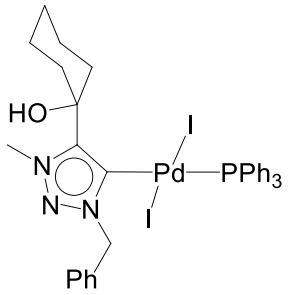
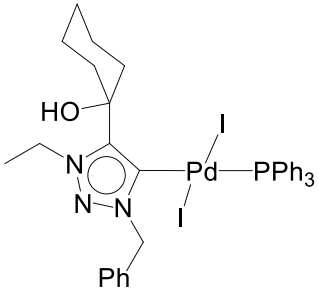
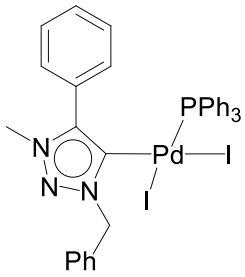
Complex	*d*/(PPh_3)–PdI_2(*a*-NHC) (Å)	D_e/(PPh_3)–PdI_2(*a*-NHC) (kcal/mol)	(PPh_3)→PdI_2(*a*-NHC) (*d*)	(PPh_3)←PdI_2(*a*-NHC) (*b*)	*d*/*b* ratio
 (**1c**)	2.414 [2.3571(13)]	32.7	0.274	0.054	5.07
 (**2c**)	2.413 [2.3515(9)]	32.7	0.274	0.055	4.98
 (**3c**)	2.358 [2.2804(17)]	37.9	0.262	0.127	2.06

Table S7. Natural charge distribution on selected atoms of in (**1-3**)**b** and in (**1-3**)**c**.

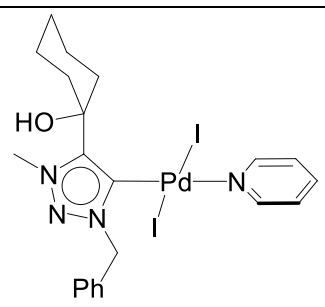
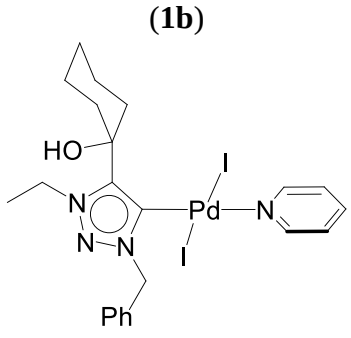
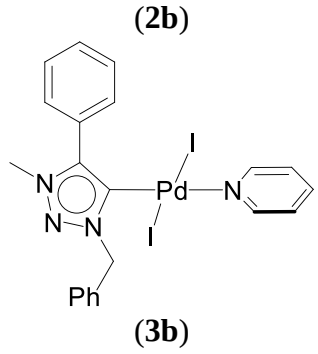
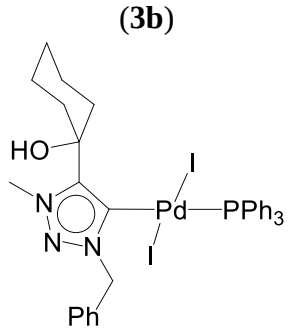
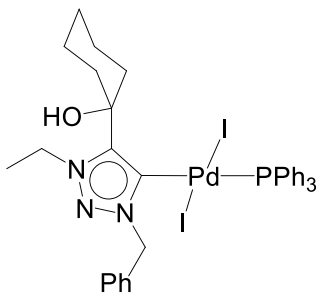
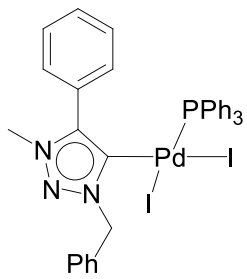
specie/compound	Natural Charge						
	Pd	$C_{carbene}$	$N_{Pyridine}$	P	I1	I2	O
 (**1b**)	-0.103	0.055	-0.447		-0.328	-0.333	-0.766
 (**2b**)	-0.105	0.055	-0.447		-0.329	-0.332	-0.769
 (**3b**)	-0.071	0.066	-0.448		-0.330	-0.342	
 (**1c**)	-0.313	0.027		1.14	-0.287	-0.309	-0.772
 (**2c**)	-0.317	0.027		1.14	-0.286	-0.311	-0.769
 (**3c**)	-0.299	0.027		1.17	-0.301	-0.311	

Table S8. Natural charge analyses of the **1b** and **2b** complexes.

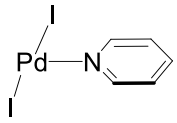
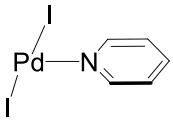
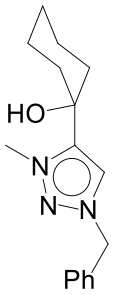
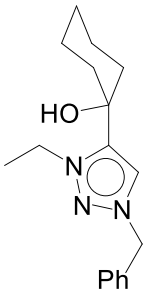
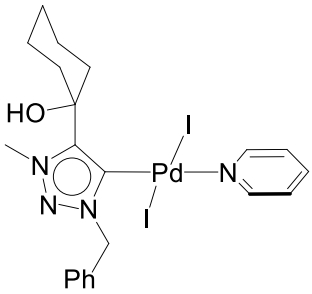
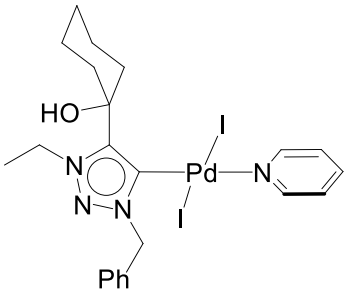
compound/specie	$C_{carbene}$	Pd	compound/specie	$C_{carbene}$	Pd
		0.250			0.250
	-0.163			-0.165	
	0.055	-0.103		0.055	-0.105
(**1b**)			(**2b**)		

Table S9. Natural charge analyses of the **3b** and **1c** complexes.

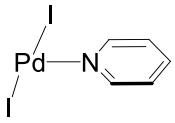
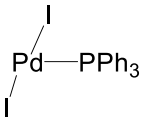
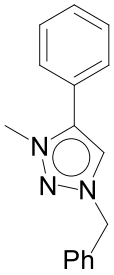
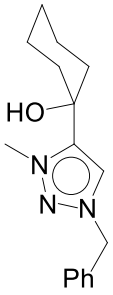
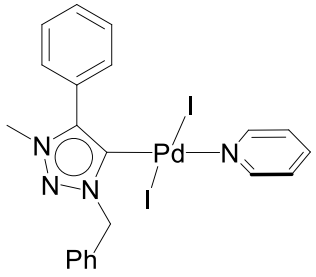
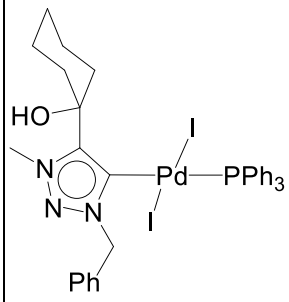
compound/specie	$C_{carbene}$	Pd	compound/specie	$C_{carbene}$	Pd
		0.245			-0.009
	-0.139			-0.164	
 (**3b**)	0.066	-0.071	 (**1c**)	0.027	-0.313

Table S10. Natural charge analyses of the **2c** and **3c** complexes.

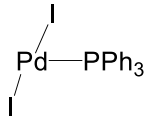
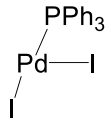
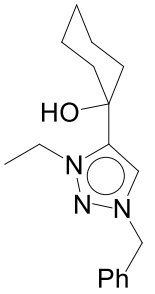
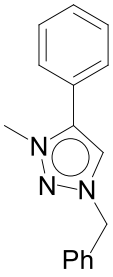
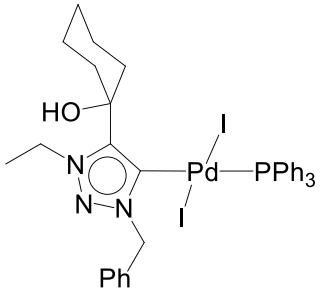
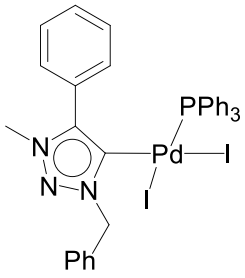
compound/specie	$C_{carbene}$	Pd	compound/specie	$C_{carbene}$	Pd
		-0.008			-0.023
	-0.166			-0.130	
 (**2c**)	0.027	-0.317	 (**3c**)	0.027	-0.299

Table S11. Natural charge analyses of the **1b** and **2b** complexes.

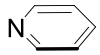
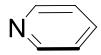
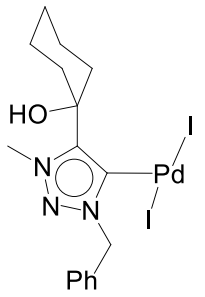
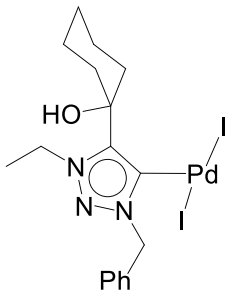
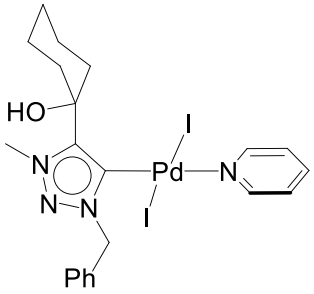
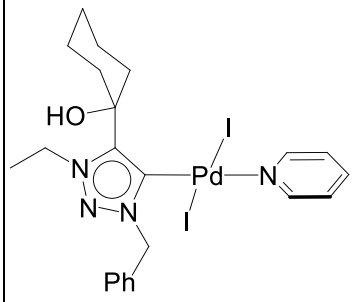
compound/specie	$N_{pyridine}$	Pd	compound/specie	$N_{pyridine}$	Pd
	-0.457			-0.457	
		0.044			0.042
	-0.447	-0.103		-0.447	-0.105
(**1b**)			(**2b**)		

Table S12. Natural charge analyses of the **3b** and **1c** complexes.

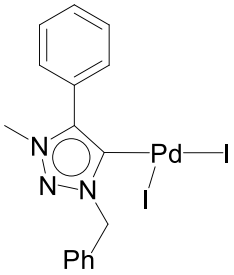
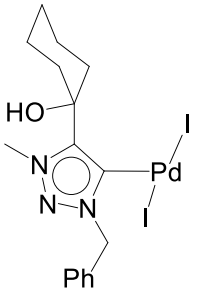
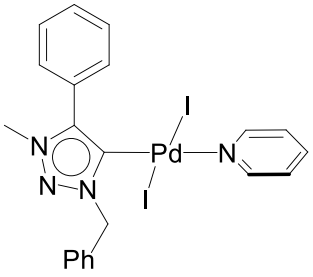
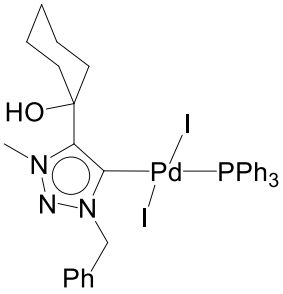
compound/specie	$N_{pyridine}$	Pd	compound/specie	$P_{triphenylphosphine}$	Pd
	-0.456			0.902	
		0.073			0.054
 (**3b**)	-0.447	-0.071	 (**1c**)	1.14	-0.314

Table S13. Natural charge analyses of the **2c** and **3c** complexes.

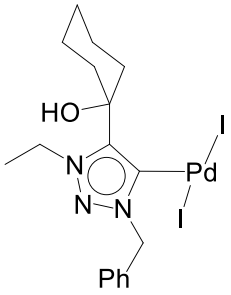
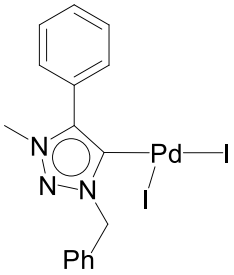
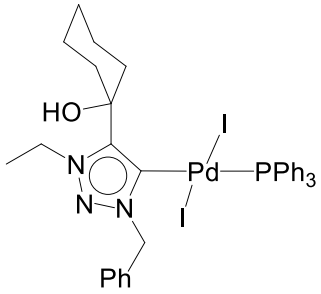
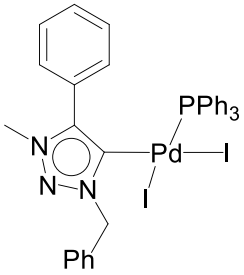
compound/specie	$P_{triphenylphosphine}$	Pd	compound/specie	$P_{triphenylphosphine}$	Pd
PPh_3	0.902		PPh_3	0.901	
		0.052			0.113
 (**2c**)	1.14	-0.317	 (**3c**)	1.17	-0.299

Table S14. Mulliken charge analyses of the **1b** and **2b** complexes.

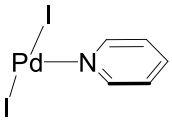
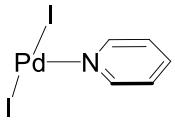
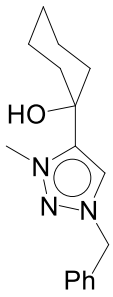
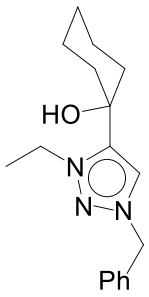
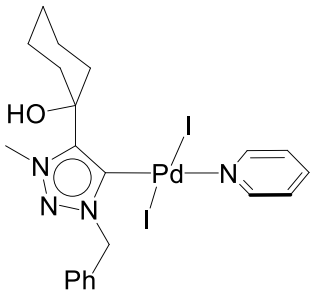
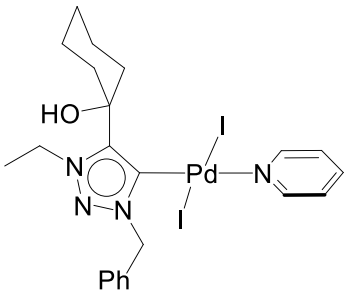
compound/specie	$C_{carbene}$	Pd	compound/specie	$C_{carbene}$	Pd
		0.147			0.147
	-0.130			-0.135	
	0.192	-0.242		0.187	-0.236
(**1b**)			(**2b**)		

Table S15. Mulliken charge analyses of the **3b** and **1c** complexes.

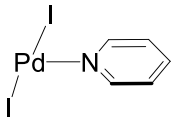
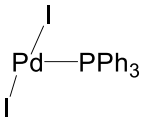
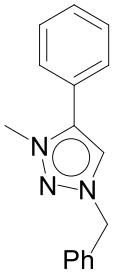
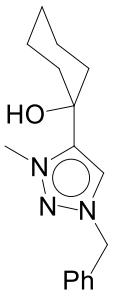
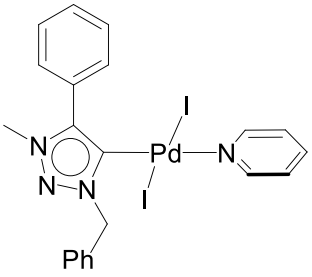
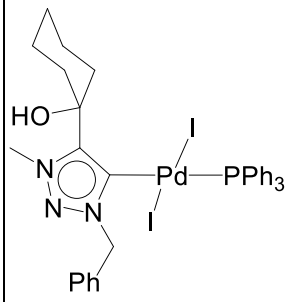
compound/specie	$C_{carbene}$	Pd	compound/specie	$C_{carbene}$	Pd
		0.140			-0.166
	-0.108			-0.134	
 **(3b)**	0.196	-0.146	 **(1c)**	0.169	-0.528

Table S16. Mulliken charge analyses of the **2c** and **3c** complexes.

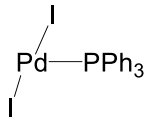
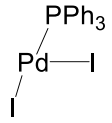
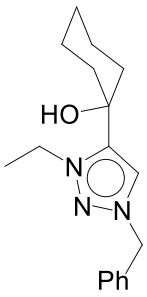
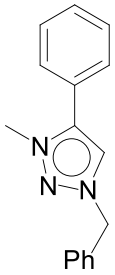
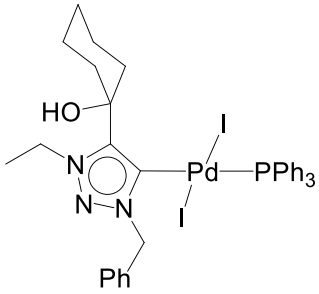
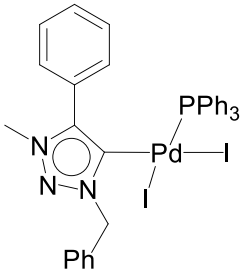
compound/specie	$C_{carbene}$	Pd	compound/specie	$C_{carbene}$	Pd
		-0.164			-0.168
	-0.135			-0.096	
 (**2c**)	0.169	-0.537	 (**3c**)	0.135	-0.342

Table S17. Mulliken charge analyses of the **1b** and **2b** complexes.

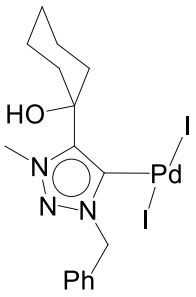
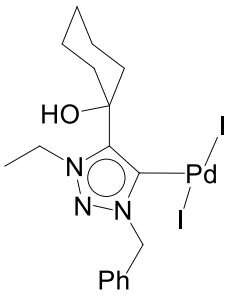
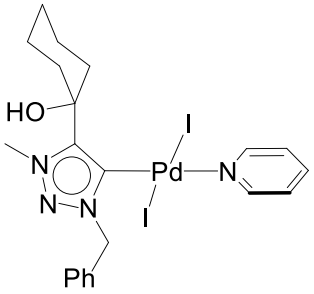
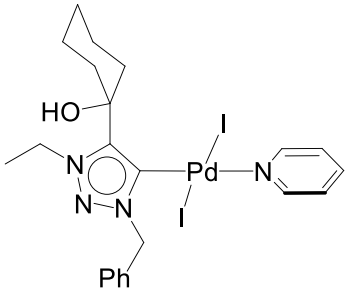
compound/specie	$N_{pyridine}$	Pd	compound/specie	$N_{pyridine}$	Pd
	-0.351			-0.351	
		-0.147			-0.144
	-0.392	-0.242		-0.392	-0.236
(**1b**)			(**2b**)		

Table S18. Mulliken charge analyses of the **3b** and **1c** complexes.

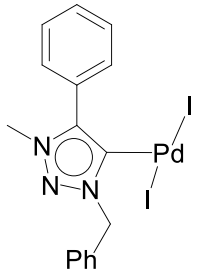
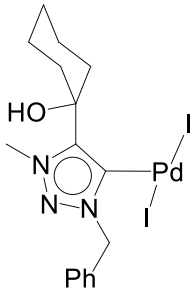
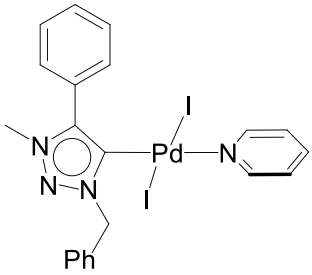
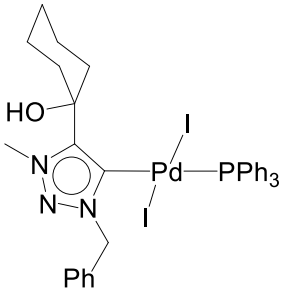
compound/specie	$N_{pyridine}$	Pd	compound/specie	$P_{triphenylphosphine}$	Pd
	-0.351		PPh_3	0.324	
		-0.051			-0.144
 (**3b**)	-0.393	-0.146	 (**1c**)	0.608	-0.528

Table S19. Mulliken charge analyses of the **2c** and **3c** complexes.

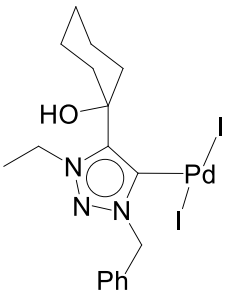
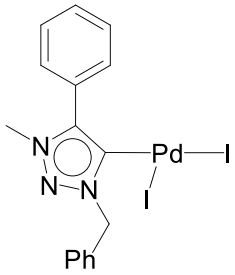
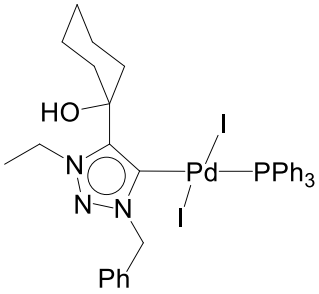
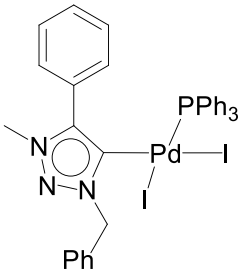
compound/specie	$P_{triphenylphosphine}$	Pd	compound/specie	$P_{triphenylphosphine}$	Pd
PPh_3	0.324		PPh_3	0.316	
		-0.151			-0.070
	0.610	-0.537		0.580	-0.342
(**2c**)			(**3c**)		

Table S20. Percentage (%) of electron contribution and repulsive polarization (*r*) in (**1-3**)**b** and (**1-3**)**c** are shown.

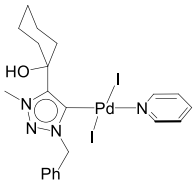
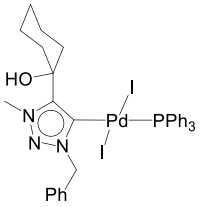
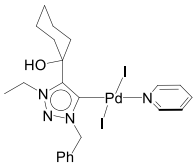
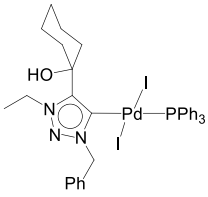
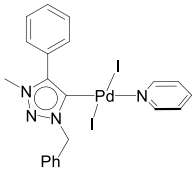
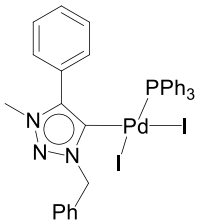
compound	% of electron contribution in (*a*-NHC)–Pd bond	repulsive polarization (*r*)	compound	% of electron contribution in (*a*-NHC)–Pd bond	repulsive polarization (*r*)
 (**1b**)	31.0% (Pd) 69.0% $C_{carbene}$)	-0.197	 (**1c**)	24.4% (Pd) 75.6% ($C_{carbene}$)	-0.218
 (**2b**)	31.1% (Pd) 68.9% $C_{carbene}$)	-0.195	 (**2c**)	24.5% (Pd) 75.5% ($C_{carbene}$)	-0.221
 (**3b**)	30.8% (Pd) 69.2% $C_{carbene}$)	-0.167	 (**3c**)	23.7% (Pd) 76.3% ($C_{carbene}$)	-0.242

Table S21. Repulsive polarization (*r*) in (**1-3**)**b** and (**1-3**)**c** are shown.

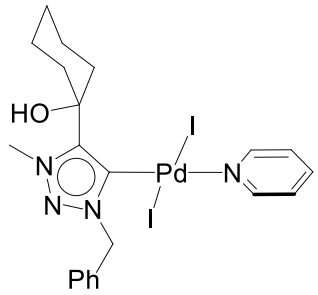
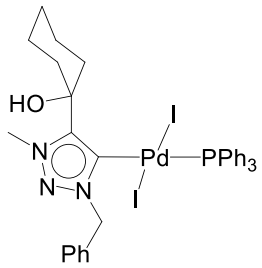
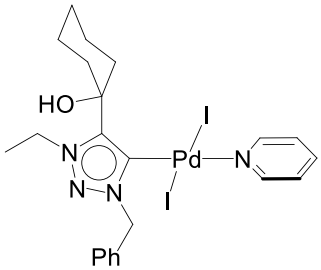
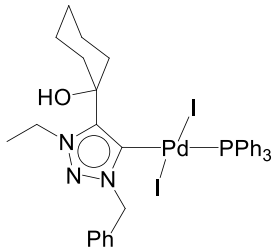
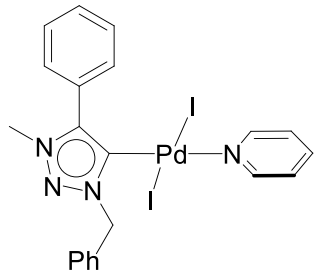
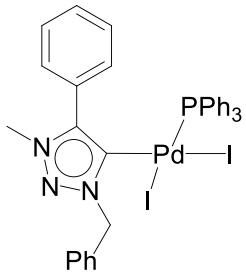
compound/specie	repulsive polarization (*r*) of (*a*-NHC)PdI_2–(NC_5H_5)	compound/specie	repulsive polarization (*r*) of (PPh_3)–PdI_2(*a*-NHC)
 (**1b**)	-0.132	 (**1c**)	-0.190
 (**2b**)	-0.132	 (**2c**)	-0.192
 (**3b**)	-0.130	 (**3c**)	-0.211

Table S22. X-ray crystallographic data for **1b**–**3b**.

compound	**1b**	**2b**	**3b**
lattice	Orthorhombic	Monoclinic	Triclinic
formula	$C_{21}H_{26}I_2N_4OPd$	$C_{22}H_{28}I_2N_4OPd$	$C_{21}H_{20}I_2N_4Pd$
formula weight	710.66	724.68	688.61
Space group	*Pbcn*	*Ia*	*P*-1
a/Å	18.784(5)	8.031(3)	9.668(3)
b/Å	16.650(5)	17.800(5)	10.097(4)
c/Å	15.453(4)	17.397(6)	13.798(5)
α/°	90.000	90.000	110.578(3).
β/°	90.000	95.552(14).	90.704(2)
γ/°	90.000	90.000	115.409(5)
V/Å^3	4833(2))	2475.2(14)	1117.6(7)
Z	8	4	2
temperature (K)	150(2)	150(2)	150(2)
radiation (λ,Å)	0.71075	0.71075	0.71075
ρ (calcd.), Mg m^3	1.953	1.945	2.046
μ(Mo Kα), mm^{-1}	3.342	3.265	3.606
θ max, deg.	25.000	24.990	25.000
No. of data	4243	4304	3875
No. of parameters	263	272	253
R_1	0.0271	0.0251	0.0185
wR_2	0.0504	0.0465	0.0376
GOF	1.247	0.941	0.975

Table S23. X-ray crystallographic data for **1c**–**3c**.

compound	**1c**	**2c**	**3c**
lattice	Orthorhombic	Orthorhombic	Orthorhombic
formula	$C_{34}H_{36}I_2N_3OPPd$	$C_{35}H_{38}I_2N_3OPPd$	$C_{34}H_{30}I_2N_3PPd$
formula weight	893.83	907.85	871.78
Space group	*Pbca*	*Pbca*	*Pbca*
a/Å	15.928(4)	16.1205(3)	17.887(6)
b/Å	16.099(4)	16.2538(5)	18.351(7)
c/Å	26.191(6)	26.3092(6)	19.356(6)
α/°	90.00	90	90.00
β/°	90.00	90	90.00
γ/°	90.00	90	90.00
V/Å^3	6716(3)	6893.5(3)	6353(4)
Z	8	8	8
temperature (K)	150(2)	150(2)	150(2)
radiation (λ,Å)	0.71075	0.71073	0.71075
ρ (calcd.), Mg m^{-3}	1.768	1.750	1.823
μ(Mo Kα), mm^{-1}	2.470	2.408	2.606
θ max, deg.	25.39°.	27.48	25.00
No. of data	6138	7871	5586
No. of parameters	379	390	370
R_1	0.0463	0.0323	0.0575
wR_2	0.0915	0.0644	0.0816
GOF	1.409	1.013	1.273

The Density Functional Theory (DFT) computation studies on complexes (**1**-**3**)**b** and (**1**-**3**)**c** were carried out using GAUSSIAN 09 suite of quantum chemical programs.

Table S24. B3LYP/SDD, 6-31G(d) level optimized coordinates of **1b** (*trans*).

Ground state electronic energy = −1260.9680148 Hartree/Particle.

Pd	-0.802618000	-0.526619000	0.085979000
I	-0.167279000	-0.446009000	-2.554894000
I	-1.282570000	-0.587513000	2.764325000
O	0.306589000	4.155789000	1.264555000
H	-0.125254000	3.803886000	2.061518000
N	-2.522036000	-1.750978000	-0.308198000
N	2.010747000	0.079315000	0.818643000
N	2.946036000	0.981174000	1.067992000
N	2.342642000	2.132815000	0.861930000
C	-2.654422000	-2.959152000	0.270315000
H	-1.861389000	-3.252038000	0.948080000
C	-3.751095000	-3.783687000	0.036747000
H	-3.806355000	-4.750777000	0.525486000
C	-4.760651000	-3.338751000	-0.815336000
H	-5.632358000	-3.956310000	-1.011876000
C	-4.628101000	-2.084809000	-1.410017000
H	-5.384184000	-1.693440000	-2.082575000
C	-3.492773000	-1.326989000	-1.138354000
H	-3.334849000	-0.359778000	-1.600742000
C	0.795911000	0.606455000	0.465473000
C	1.025187000	1.986460000	0.493574000
C	2.347804000	-1.347520000	1.025565000
H	1.476944000	-1.893413000	0.658777000
H	2.415204000	-1.506915000	2.105512000
C	3.617563000	-1.771106000	0.323299000
C	3.622504000	-1.987332000	-1.061890000
H	2.711064000	-1.835084000	-1.635465000
C	4.792370000	-2.393789000	-1.703328000
H	4.786336000	-2.560550000	-2.777047000
C	5.964363000	-2.593502000	-0.968681000
H	6.873457000	-2.914832000	-1.470122000
C	5.963600000	-2.384167000	0.411217000
H	6.870718000	-2.540919000	0.988665000
C	4.793853000	-1.973490000	1.053301000
H	4.793834000	-1.809912000	2.128340000
C	3.156976000	3.341745000	1.019314000
H	3.952746000	3.108463000	1.726784000
H	2.516180000	4.139053000	1.388828000
H	3.592724000	3.618613000	0.055867000
C	0.121164000	3.182605000	0.213504000

C	0.531513000	3.880131000	-1.104447000
H	0.487492000	3.127344000	-1.901412000
H	1.572586000	4.216177000	-1.037930000
C	-0.378962000	5.070481000	-1.445486000
H	-0.238625000	5.855822000	-0.692876000
H	-0.070515000	5.491250000	-2.410594000
C	-1.856249000	4.657202000	-1.487663000
H	-2.489356000	5.532458000	-1.680027000
H	-2.016370000	3.960913000	-2.323948000
C	-2.270183000	3.977486000	-0.175382000
H	-3.310230000	3.633030000	-0.231120000
H	-2.221449000	4.705501000	0.644453000
C	-1.364938000	2.778376000	0.147434000
H	-1.659186000	2.313291000	1.096572000
H	-1.483811000	2.006801000	-0.622007000

Table S25. B3LYP/SDD, 6-31G(d) level optimized coordinates of **1b** (*cis*).

Ground state electronic energy = −1260.9432886 Hartree/Particle.

Pd	0.619427000	-0.768322000	-0.128623000
I	1.615127000	0.013975000	-2.500318000
O	1.349419000	3.976683000	-0.365284000
H	1.756685000	3.478146000	-1.096300000
N	-1.741246000	0.917558000	-0.918947000
N	-2.253502000	2.122727000	-1.109769000
N	-1.373026000	2.933207000	-0.561318000
C	-0.525820000	0.905813000	-0.281260000
C	-0.296669000	2.263641000	-0.022046000
C	-2.455076000	-0.233536000	-1.514228000
H	-1.845663000	-1.101422000	-1.257225000
H	-2.414996000	-0.106423000	-2.599483000
C	-3.879136000	-0.363430000	-1.022260000
C	-4.151390000	-0.950389000	0.220969000
H	-3.332432000	-1.322963000	0.831512000
C	-5.465123000	-1.067421000	0.674813000
H	-5.664779000	-1.527902000	1.638679000
C	-6.522143000	-0.603920000	-0.112525000
H	-7.545914000	-0.699930000	0.238714000
C	-6.259502000	-0.024492000	-1.354903000
H	-7.077432000	0.332429000	-1.974646000
C	-4.943944000	0.095084000	-1.806097000
H	-4.741414000	0.547175000	-2.773672000
C	-1.647084000	4.370027000	-0.662580000
H	-2.295730000	4.514997000	-1.526372000
H	-0.697874000	4.886100000	-0.795316000
H	-2.154507000	4.721125000	0.239252000
C	0.884956000	3.009944000	0.597160000
C	0.447061000	3.816368000	1.844522000
H	0.009750000	3.108331000	2.562263000
H	-0.344010000	4.524920000	1.580847000

C	1.614837000	4.570039000	2.500404000
H	1.975112000	5.336575000	1.804119000
H	1.247934000	5.093314000	3.392391000
C	2.765689000	3.622710000	2.861538000
H	3.607962000	4.189973000	3.276246000
H	2.436070000	2.929518000	3.650739000
C	3.212633000	2.821280000	1.632780000
H	3.990805000	2.098577000	1.904098000
H	3.655464000	3.501712000	0.894920000
C	2.041646000	2.064208000	0.986467000
H	2.385245000	1.517675000	0.103039000
H	1.668300000	1.304495000	1.684695000
I	2.287019000	-2.912758000	0.010633000
N	-0.354775000	-1.412207000	1.677375000
C	-0.763387000	-2.691359000	1.805305000
H	-0.532723000	-3.348884000	0.976516000
C	-1.414377000	-3.155853000	2.945878000
H	-1.724399000	-4.194560000	2.993412000
C	-1.636582000	-2.279977000	4.006664000
H	-2.130380000	-2.618098000	4.913054000
C	-1.206421000	-0.959582000	3.879506000
H	-1.349190000	-0.237121000	4.676569000
C	-0.580371000	-0.566743000	2.700547000
H	-0.245567000	0.453598000	2.558865000

Table S26. B3LYP/SDD, 6-31G(d) level optimized coordinates of **2b** (*trans*).

Ground state electronic energy = −1300.2835972 Hartree/Particle.

Pd	0.995655000	-0.393937000	0.133417000
I	0.554530000	-0.727080000	-2.527642000
I	1.265066000	-0.098124000	2.823622000
O	-1.254160000	4.069864000	0.636053000
H	-0.827049000	4.012435000	1.507232000
N	2.956319000	-1.258139000	-0.034773000
N	-1.928487000	-0.356207000	0.631387000
N	-3.047967000	0.337593000	0.752661000
N	-2.688949000	1.577524000	0.490966000
C	3.874345000	-0.728567000	-0.864308000
H	3.555055000	0.131081000	-1.441528000
C	5.155057000	-1.256848000	-0.997762000
H	5.858968000	-0.787941000	-1.677341000
C	5.498791000	-2.387668000	-0.258458000
H	6.488260000	-2.827318000	-0.345455000
C	4.546005000	-2.942824000	0.594254000
H	4.763198000	-3.821939000	1.191897000
C	3.291910000	-2.345693000	0.683687000
H	2.530570000	-2.727416000	1.353580000
C	-0.829235000	0.396145000	0.311370000
C	-1.344812000	1.692974000	0.217365000

C	-1.969269000	-1.808509000	0.910108000
H	-2.016223000	-1.927835000	1.996552000
H	-0.999875000	-2.180762000	0.572819000
C	-3.114454000	-2.515950000	0.222783000
C	-3.097126000	-2.706152000	-1.166348000
H	-2.260939000	-2.329618000	-1.751353000
C	-4.146742000	-3.375165000	-1.794725000
H	-4.124317000	-3.519165000	-2.871555000
C	-5.218344000	-3.866279000	-1.043373000
H	-6.032959000	-4.391416000	-1.535102000
C	-5.237543000	-3.684456000	0.339999000
H	-6.066337000	-4.065924000	0.930317000
C	-4.189391000	-3.009467000	0.969195000
H	-4.206329000	-2.865871000	2.047041000
C	-3.760433000	2.591867000	0.588094000
H	-3.432356000	3.467610000	0.035915000
H	-4.629959000	2.152804000	0.093462000
C	-4.072089000	2.950477000	2.039249000
H	-4.894055000	3.673696000	2.063911000
H	-3.200561000	3.404969000	2.517730000
H	-4.371274000	2.064750000	2.606961000
C	-0.700322000	3.015927000	-0.179047000
C	-1.060384000	3.353245000	-1.645821000
H	-0.725904000	2.511431000	-2.265147000
H	-2.150158000	3.412565000	-1.754519000
C	-0.407851000	4.658626000	-2.125283000
H	-0.659745000	4.818315000	-3.181025000
H	-0.829927000	5.500416000	-1.562684000
C	1.114930000	4.625590000	-1.936117000
H	1.556194000	5.583987000	-2.237172000
H	1.546652000	3.857367000	-2.594454000
C	1.477567000	4.307167000	-0.479035000
H	1.146717000	5.130930000	0.166722000
H	2.565432000	4.230632000	-0.360217000
C	0.832066000	2.992910000	-0.010736000
H	1.080901000	2.785736000	1.038178000
H	1.238099000	2.154965000	-0.589562000

Table S27. B3LYP/SDD, 6-31G(d) level optimized coordinates of **2b** (*cis*).

Ground state electronic energy = −1300.2582901 Hartree/Particle.

Pd	0.947747000	-0.529683000	-0.191006000
I	1.454714000	0.709870000	-2.520030000
O	-0.273014000	4.176018000	0.088329000
H	0.246313000	3.999454000	-0.715835000
N	-1.916230000	0.170707000	-0.793789000
N	-2.866431000	1.089388000	-0.854792000
N	-2.340390000	2.137189000	-0.258478000
C	-0.757213000	0.584763000	-0.187731000

C	-1.057801000	1.900453000	0.190220000
C	-2.169721000	-1.119841000	-1.470964000
H	-1.249486000	-1.690832000	-1.338212000
H	-2.279464000	-0.903547000	-2.537038000
C	-3.381227000	-1.842552000	-0.925102000
C	-3.288467000	-2.598843000	0.251026000
H	-2.335340000	-2.674670000	0.768318000
C	-4.407572000	-3.260921000	0.756147000
H	-4.322476000	-3.848054000	1.666639000
C	-5.631500000	-3.178061000	0.087696000
H	-6.501962000	-3.698107000	0.478303000
C	-5.730504000	-2.431895000	-1.087798000
H	-6.677955000	-2.368577000	-1.615882000
C	-4.610350000	-1.767552000	-1.590249000
H	-4.689516000	-1.186855000	-2.505714000
C	-3.168206000	3.363928000	-0.189499000
H	-2.472749000	4.178170000	0.001303000
H	-3.845152000	3.257010000	0.664634000
C	-0.232260000	2.979292000	0.891116000
C	-0.858569000	3.356487000	2.257384000
H	-0.907280000	2.441835000	2.864623000
H	-1.890883000	3.695649000	2.121996000
C	-0.048959000	4.430755000	2.999858000
H	-0.091093000	5.364830000	2.427147000
H	-0.520740000	4.628589000	3.970691000
C	1.413496000	4.005919000	3.184776000
H	1.983486000	4.809053000	3.667786000
H	1.460040000	3.138570000	3.861224000
C	2.046407000	3.634930000	1.837680000
H	3.070593000	3.270748000	1.978545000
H	2.111612000	4.530434000	1.207182000
C	1.236233000	2.554924000	1.103843000
H	1.694596000	2.326751000	0.136674000
H	1.267583000	1.620148000	1.677046000
I	3.316168000	-1.868887000	-0.244613000
N	0.391108000	-1.617194000	1.577903000
C	0.497653000	-2.961637000	1.604084000
H	0.899594000	-3.423559000	0.711102000
C	0.146394000	-3.716025000	2.721179000
H	0.250075000	-4.795519000	2.686091000
C	-0.312791000	-3.064921000	3.864627000
H	-0.581242000	-3.626798000	4.754539000
C	-0.415404000	-1.674452000	3.841740000
H	-0.761835000	-1.116748000	4.705781000
C	-0.062381000	-0.993233000	2.680861000
H	-0.139514000	0.085444000	2.620265000
C	-3.946679000	3.608227000	-1.479626000
H	-3.267309000	3.706359000	-2.332029000
H	-4.653347000	2.802146000	-1.687317000
H	-4.505409000	4.544186000	-1.375620000

Table S28. B3LYP/SDD, 6-31G(d) level optimized coordinates of **3b** (*trans*).

Ground state electronic energy = −1182.1297983 Hartree/Particle.

Pd	-0.803557000	-0.408902000	0.073907000
I	-0.022800000	-0.665634000	-2.509121000
I	-1.413321000	-0.171349000	2.712829000
N	-2.515011000	-1.656592000	-0.265228000
N	1.981758000	0.403456000	0.857343000
N	2.859965000	1.391907000	0.973975000
N	2.197378000	2.450481000	0.550311000
C	-3.754563000	-1.184279000	-0.039475000
H	-3.815697000	-0.170172000	0.337543000
C	-4.896436000	-1.949396000	-0.257814000
H	-5.873769000	-1.519440000	-0.065101000
C	-4.753568000	-3.259457000	-0.712687000
H	-5.625268000	-3.883679000	-0.887142000
C	-3.469301000	-3.752073000	-0.939247000
H	-3.304522000	-4.763781000	-1.294865000
C	-2.378225000	-2.918495000	-0.711614000
H	-1.363695000	-3.249050000	-0.900276000
C	0.758032000	0.783400000	0.377622000
C	0.913365000	2.157552000	0.168999000
C	2.386213000	-0.948807000	1.299283000
H	1.550462000	-1.590453000	1.014032000
H	2.438200000	-0.929643000	2.391483000
C	3.690662000	-1.412259000	0.691574000
C	3.763794000	-1.730195000	-0.672109000
H	2.881105000	-1.624803000	-1.298957000
C	4.964070000	-2.176987000	-1.223440000
H	5.011216000	-2.421716000	-2.281129000
C	6.098781000	-2.317721000	-0.419269000
H	7.031764000	-2.670840000	-0.850573000
C	6.029683000	-2.007476000	0.939396000
H	6.907343000	-2.116737000	1.570785000
C	4.829491000	-1.554021000	1.491032000
H	4.777165000	-1.310534000	2.549614000
C	2.884953000	3.739064000	0.551279000
H	3.673151000	3.693242000	1.302426000
H	2.166268000	4.521099000	0.797971000
H	3.320900000	3.937307000	-0.431032000
C	-0.036465000	3.163926000	-0.337040000
C	0.277045000	3.956742000	-1.452611000
H	1.218643000	3.807366000	-1.973939000
C	-0.633454000	4.903263000	-1.921523000
H	-0.385073000	5.504431000	-2.791644000
C	-1.865947000	5.064130000	-1.284867000
H	-2.575717000	5.799985000	-1.652849000
C	-2.187021000	4.272640000	-0.179621000

H	-3.144879000	4.394082000	0.318642000
C	-1.280074000	3.325344000	0.295263000
H	-1.524407000	2.708788000	1.155187000

Table S29. B3LYP/SDD, 6-31G(d) level optimized coordinates of **3b** (*cis*).

Ground state electronic energy = −1182.1089253 Hartree/Particle.

Pd	0.747091000	-0.483848000	-0.107167000
I	1.286899000	-0.164086000	-2.712910000
N	-1.948183000	0.640225000	-0.963939000
N	-2.711020000	1.712278000	-1.135034000
N	-1.979414000	2.698757000	-0.654188000
C	-0.724782000	0.886327000	-0.398860000
C	-0.762916000	2.270619000	-0.179951000
C	-2.468697000	-0.656595000	-1.446233000
H	-1.652195000	-1.362581000	-1.283489000
H	-2.619548000	-0.560891000	-2.524170000
C	-3.742565000	-1.075196000	-0.745359000
C	-3.716013000	-1.491234000	0.593089000
H	-2.772293000	-1.507774000	1.133119000
C	-4.890344000	-1.885089000	1.233306000
H	-4.858119000	-2.208263000	2.270393000
C	-6.104092000	-1.874916000	0.540434000
H	-7.017941000	-2.187883000	1.038066000
C	-6.137445000	-1.467289000	-0.793542000
H	-7.076904000	-1.460348000	-1.339328000
C	-4.961420000	-1.066779000	-1.431397000
H	-4.989611000	-0.747384000	-2.470199000
C	-2.521661000	4.052920000	-0.745437000
H	-3.213327000	4.075477000	-1.587293000
H	-1.700024000	4.750494000	-0.909541000
H	-3.051746000	4.316349000	0.173444000
C	0.251849000	3.163186000	0.404896000
C	-0.089857000	4.134444000	1.363639000
H	-1.119699000	4.231139000	1.696773000
C	0.891025000	4.954538000	1.921029000
H	0.612801000	5.698346000	2.662577000
C	2.226080000	4.810115000	1.536396000
H	2.990146000	5.446955000	1.973342000
C	2.575561000	3.841600000	0.592450000
H	3.611657000	3.720974000	0.289986000
C	1.599175000	3.022297000	0.025911000
H	1.871156000	2.274861000	-0.712457000
I	2.750353000	-2.286797000	0.241917000
N	0.273746000	-0.718128000	1.957652000
C	0.374086000	0.317346000	2.810957000
H	0.667164000	1.266800000	2.378990000
C	0.128825000	0.187070000	4.175401000
H	0.238741000	1.051032000	4.822686000

C	-0.248365000	-1.057126000	4.678351000
H	-0.446901000	-1.190229000	5.737903000
C	-0.356032000	-2.129216000	3.793635000
H	-0.635288000	-3.120512000	4.135125000
C	-0.076171000	-1.924800000	2.445362000
H	-0.101956000	-2.738021000	1.730449000

Table S30. B3LYP/SDD, 6-31G(d) level optimized coordinates of **1c** (*trans*).

Ground state electronic energy = −2048.9638913 Hartree/Particle.

Pd	0.030366000	0.163397000	0.222587000
I	0.182488000	0.161618000	2.935818000
I	-0.560546000	-0.123039000	-2.433105000
P	2.337573000	-0.459538000	-0.115321000
O	-3.215572000	3.955368000	1.006984000
H	-2.991010000	4.884710000	0.849932000
N	-4.013245000	1.320100000	0.750933000
N	-2.873364000	-0.422124000	0.761286000
N	-4.109042000	0.018007000	0.931863000
C	-1.953775000	0.555630000	0.491095000
C	-2.726307000	1.719732000	0.483426000
C	-2.358991000	3.155581000	0.167862000
C	-0.881046000	3.452526000	0.497905000
H	-0.248833000	2.738473000	-0.045114000
H	-0.713503000	3.274946000	1.564781000
C	-0.477835000	4.883521000	0.103684000
H	-1.008974000	5.616207000	0.732412000
H	0.586361000	5.028030000	0.324817000
C	-0.765112000	5.171550000	-1.378094000
H	-0.122198000	4.531336000	-1.998965000
H	-0.509315000	6.209866000	-1.623456000
C	-2.234050000	4.885309000	-1.723078000
H	-2.883227000	5.612584000	-1.210231000
H	-2.413018000	5.030182000	-2.795103000
C	-2.634945000	3.454136000	-1.330467000
H	-2.066325000	2.734238000	-1.931533000
H	-3.696987000	3.283746000	-1.546028000
C	-5.256160000	2.087347000	0.882547000
H	-6.061066000	1.358505000	0.973051000
H	-5.401022000	2.708339000	-0.000957000
H	-5.200447000	2.726059000	1.762400000
C	-2.612168000	-1.867545000	0.947442000
H	-2.558022000	-2.047879000	2.025023000
H	-1.616003000	-2.026260000	0.530939000
C	-3.644852000	-2.751296000	0.286843000
C	-3.625855000	-2.944984000	-1.101549000
H	-2.870310000	-2.445155000	-1.703295000
C	-4.570479000	-3.773317000	-1.707056000

H	-4.546820000	-3.918830000	-2.783719000
C	-5.537708000	-4.420224000	-0.932950000
H	-6.269992000	-5.068960000	-1.406458000
C	-5.557675000	-4.235468000	0.450316000
H	-6.305028000	-4.738182000	1.058372000
C	-4.614571000	-3.403100000	1.056215000
H	-4.631419000	-3.257894000	2.133754000
C	2.330193000	-2.241998000	-0.576007000
C	1.847115000	-3.161749000	0.372923000
H	1.552549000	-2.816925000	1.361073000
C	1.745114000	-4.515640000	0.055363000
H	1.378837000	-5.216343000	0.800986000
C	2.106453000	-4.967332000	-1.216909000
H	2.021009000	-6.021683000	-1.465761000
C	2.571171000	-4.058219000	-2.167294000
H	2.845317000	-4.400084000	-3.161673000
C	2.682993000	-2.701697000	-1.851550000
H	3.035461000	-2.005172000	-2.604303000
C	3.533554000	-0.342975000	1.291493000
C	4.349679000	-1.407292000	1.696267000
H	4.260018000	-2.377382000	1.219075000
C	5.284231000	-1.231205000	2.720579000
H	5.907020000	-2.067582000	3.027005000
C	5.419009000	0.008892000	3.343738000
H	6.145803000	0.144038000	4.140295000
C	4.611336000	1.076423000	2.942552000
H	4.703040000	2.044013000	3.428321000
C	3.671790000	0.900366000	1.928952000
H	3.033710000	1.730804000	1.641157000
C	3.307976000	0.421632000	-1.418180000
C	4.622332000	0.022820000	-1.718407000
H	5.058251000	-0.835425000	-1.215310000
C	5.381082000	0.728018000	-2.650827000
H	6.393510000	0.404239000	-2.877021000
C	4.845136000	1.853366000	-3.283326000
H	5.439201000	2.405828000	-4.006493000
C	3.548751000	2.267184000	-2.978971000
H	3.125613000	3.141913000	-3.465313000
C	2.782145000	1.554065000	-2.053308000
H	1.767418000	1.868646000	-1.837454000

Table S31. B3LYP/SDD, 6-31G(d) level optimized coordinates of **1c** (*cis*).

Ground state electronic energy = −2048.9570302 Hartree/Particle.

Pd	0.533702000	-0.139535000	-0.970943000
I	0.224700000	-1.924203000	-3.044307000
O	-0.167021000	-4.622764000	0.372784000
H	0.046780000	-4.462247000	-0.564933000
N	-2.418741000	-2.772767000	0.501877000

N	-2.320281000	-0.955669000	-0.508652000
N	-3.173118000	-1.891318000	-0.119301000
C	-1.011193000	-1.208947000	-0.182095000
C	-1.089365000	-2.420640000	0.516659000
C	-0.018758000	-3.363755000	1.060183000
C	1.405384000	-2.810235000	0.845159000
H	1.479106000	-1.842437000	1.355543000
H	1.570810000	-2.618266000	-0.220050000
C	2.480687000	-3.764590000	1.387212000
H	2.451596000	-4.701178000	0.817193000
H	3.469433000	-3.321269000	1.216580000
C	2.272088000	-4.065359000	2.876692000
H	2.418462000	-3.143082000	3.459299000
H	3.021386000	-4.783831000	3.231806000
C	0.858062000	-4.604878000	3.125225000
H	0.750646000	-5.586548000	2.648425000
H	0.683590000	-4.749563000	4.199055000
C	-0.216626000	-3.657983000	2.566519000
H	-0.186142000	-2.698966000	3.098561000
H	-1.205410000	-4.090014000	2.745552000
C	-3.088148000	-3.977482000	0.999650000
H	-4.008797000	-4.093546000	0.428001000
H	-3.325082000	-3.866896000	2.060356000
H	-2.421583000	-4.823511000	0.839792000
C	-2.833581000	0.103422000	-1.410862000
H	-3.061455000	-0.388828000	-2.361438000
H	-1.984873000	0.766182000	-1.580974000
C	-4.030293000	0.852343000	-0.865586000
C	-3.869578000	2.136374000	-0.328804000
H	-2.884332000	2.593929000	-0.310424000
C	-4.969532000	2.843170000	0.163049000
H	-4.826981000	3.839511000	0.572180000
C	-6.242629000	2.274135000	0.118802000
H	-7.100273000	2.823919000	0.497129000
C	-6.413284000	0.998675000	-0.426367000
H	-7.404254000	0.555447000	-0.475272000
C	-5.315377000	0.294104000	-0.919350000
H	-5.453175000	-0.695127000	-1.345704000
I	2.537024000	1.141766000	-2.312798000
P	0.717977000	1.360968000	0.837752000
C	2.430379000	1.757017000	1.395505000
C	3.429797000	0.779151000	1.278798000
H	3.210773000	-0.160520000	0.782346000
C	4.715089000	1.023570000	1.762619000
H	5.481908000	0.261147000	1.658301000
C	5.021053000	2.253161000	2.349724000
H	6.026249000	2.448065000	2.713503000
C	4.035729000	3.236091000	2.454929000
H	4.270069000	4.199657000	2.899226000
C	2.744665000	2.989741000	1.984695000

H	1.989850000	3.764702000	2.068303000
C	-0.090055000	2.994274000	0.523738000
C	-0.638309000	3.761703000	1.566724000
H	-0.616835000	3.392584000	2.586935000
C	-1.223670000	5.001125000	1.301531000
H	-1.642603000	5.582399000	2.118688000
C	-1.269027000	5.491236000	-0.005605000
H	-1.725694000	6.455842000	-0.210423000
C	-0.723896000	4.737527000	-1.046593000
H	-0.751295000	5.111205000	-2.066317000
C	-0.139010000	3.496204000	-0.787274000
H	0.296776000	2.923846000	-1.600023000
C	-0.089789000	0.789237000	2.406674000
C	0.668022000	0.357218000	3.505578000
H	1.751312000	0.395483000	3.467524000
C	0.040252000	-0.111268000	4.663826000
H	0.645803000	-0.434823000	5.506232000
C	-1.351760000	-0.151519000	4.743594000
H	-1.838311000	-0.508360000	5.647340000
C	-2.116495000	0.278670000	3.655661000
H	-3.201892000	0.261644000	3.707801000
C	-1.492326000	0.739535000	2.497069000
H	-2.106798000	1.080958000	1.670158000

Table S32. B3LYP/SDD, 6-31G(d) level optimized coordinates of **2c** (*trans*).

Ground state electronic energy = −2088.2791849 Hartree/Particle.

C	-3.679925000	0.177428000	1.236099000
C	-3.737511000	-1.063768000	1.889759000
H	-3.023688000	-1.842337000	1.637546000
C	-4.693623000	-1.302188000	2.874929000
H	-4.721973000	-2.266980000	3.373916000
C	-5.598935000	-0.299307000	3.231386000
H	-6.339156000	-0.482633000	4.005638000
C	-5.544388000	0.939168000	2.592664000
H	-6.243216000	1.725854000	2.864794000
C	-4.593137000	1.176986000	1.596754000
H	-4.566427000	2.144677000	1.107069000
C	-2.542716000	2.148652000	-0.599466000
C	-2.855820000	2.587631000	-1.892802000
H	-3.123167000	1.871510000	-2.662000000
C	-2.813861000	3.949054000	-2.204024000
H	-3.056889000	4.274793000	-3.211825000
C	-2.457256000	4.883823000	-1.231954000
H	-2.425620000	5.941947000	-1.477443000
C	-2.134809000	4.453264000	0.057935000
H	-1.852503000	5.174076000	0.820691000
C	-2.168824000	3.095116000	0.371997000

H	-1.906107000	2.767827000	1.374811000
C	-3.351227000	-0.560401000	-1.469262000
C	-2.760120000	-1.677116000	-2.074163000
H	-1.741738000	-1.949053000	-1.820996000
C	-3.465531000	-2.428150000	-3.018239000
H	-2.991607000	-3.289478000	-3.481139000
C	-4.765684000	-2.068346000	-3.371281000
H	-5.311993000	-2.649871000	-4.109172000
C	-5.366807000	-0.959603000	-2.768802000
H	-6.382567000	-0.677794000	-3.033046000
C	-4.668895000	-0.216712000	-1.818216000
H	-5.154836000	0.628898000	-1.340321000
C	3.357324000	3.125690000	-1.053914000
H	2.648636000	2.560432000	-1.654681000
C	4.245248000	4.010940000	-1.664215000
H	4.223978000	4.135118000	-2.743624000
C	5.152254000	4.742088000	-0.891856000
H	5.839954000	5.435207000	-1.369332000
C	5.169025000	4.583613000	0.494575000
H	5.869599000	5.150951000	1.101492000
C	4.283075000	3.693811000	1.105460000
H	4.297816000	3.569272000	2.185657000
C	3.373350000	2.958615000	0.338077000
C	2.398534000	2.015516000	1.004943000
H	2.350266000	2.185761000	2.084474000
H	1.388764000	2.123989000	0.604872000
N	2.734159000	0.588169000	0.803032000
N	3.993613000	0.213819000	0.956033000
N	3.967871000	-1.089601000	0.770889000
C	2.698463000	-1.559445000	0.523572000
C	1.865816000	-0.435827000	0.539681000
C	5.278786000	-1.773477000	0.813403000
H	5.067842000	-2.838432000	0.858784000
H	5.749674000	-1.471399000	1.752530000
C	6.151291000	-1.394467000	-0.382676000
H	5.680923000	-1.687482000	-1.326975000
H	7.113344000	-1.912246000	-0.303920000
H	6.336894000	-0.317249000	-0.407715000
C	2.379075000	-3.018257000	0.248123000
C	2.732069000	-3.378833000	-1.219316000
H	2.189491000	-2.689660000	-1.878085000
H	3.802520000	-3.209239000	-1.385911000
C	2.364576000	-4.829356000	-1.572597000
H	2.595415000	-5.014221000	-2.628434000
H	2.997021000	-5.524581000	-0.999031000
C	0.884372000	-5.121467000	-1.285020000
H	0.651922000	-6.171470000	-1.502042000
H	0.262846000	-4.512949000	-1.957372000
C	0.528381000	-4.781797000	0.169634000
H	1.039652000	-5.484330000	0.848100000

H	-0.542292000	-4.933580000	0.351028000
C	0.892315000	-3.329423000	0.522699000
H	0.672692000	-3.111637000	1.572360000
H	0.272321000	-2.651576000	-0.077557000
O	3.198650000	-3.775227000	1.165627000
H	2.928364000	-4.703539000	1.098499000
P	-2.460150000	0.367490000	-0.141953000
Pd	-0.131629000	-0.135325000	0.244020000
I	0.490422000	0.157344000	-2.406551000
I	-0.328667000	-0.108883000	2.954376000

Table S33. B3LYP/SDD, 6-31G(d) level optimized coordinates of **2c** (*cis*).

Ground state electronic energy = −2088.2718763 Hartree/Particle.

C	-3.891900000	-2.565120000	-1.172832000
H	-3.431844000	-1.895904000	-1.896003000
C	-5.106557000	-3.185644000	-1.464157000
H	-5.589076000	-2.999502000	-2.419745000
C	-5.695592000	-4.049707000	-0.537068000
H	-6.639303000	-4.536215000	-0.769273000
C	-5.066269000	-4.291707000	0.685124000
H	-5.517318000	-4.965872000	1.408340000
C	-3.852348000	-3.668137000	0.978893000
H	-3.362479000	-3.855530000	1.931596000
C	-3.258378000	-2.800787000	0.055455000
C	-1.930938000	-2.148959000	0.366157000
H	-1.418113000	-2.667235000	1.181765000
H	-1.275399000	-2.138705000	-0.506859000
N	-2.046025000	-0.725647000	0.758967000
N	-3.021717000	-0.379768000	1.582169000
N	-2.861848000	0.915844000	1.744751000
C	-1.781233000	1.404833000	1.045690000
C	-1.223239000	0.304716000	0.384846000
C	-3.849604000	1.585511000	2.618136000
H	-3.466360000	2.585859000	2.802963000
H	-3.841379000	1.036586000	3.563809000
C	-5.247550000	1.584763000	2.001603000
H	-5.263536000	2.121854000	1.048043000
H	-5.942727000	2.080563000	2.687625000
H	-5.598116000	0.563772000	1.828802000
C	-1.415459000	2.878708000	1.025493000
C	-2.460583000	3.682810000	0.205509000
H	-2.496733000	3.249781000	-0.802043000
H	-3.454951000	3.553897000	0.647232000
C	-2.117529000	5.179067000	0.112010000
H	-2.867527000	5.680576000	-0.510978000
H	-2.194978000	5.644880000	1.107509000
C	-0.708475000	5.400389000	-0.454849000

H	-0.464653000	6.469855000	-0.467670000
H	-0.681309000	5.054371000	-1.497139000
C	0.334328000	4.621108000	0.357925000
H	0.415705000	5.052981000	1.369266000
H	1.330209000	4.728344000	-0.086862000
C	-0.010685000	3.124024000	0.438315000
H	0.731936000	2.599008000	1.046308000
H	0.034736000	2.695825000	-0.569076000
O	-1.430214000	3.281333000	2.418551000
H	-1.164913000	4.213754000	2.451437000
Pd	0.338102000	0.063465000	-0.898917000
I	-1.520878000	0.675616000	-2.812212000
I	2.301753000	-0.135940000	-2.792740000
P	1.850195000	-0.586497000	0.798094000
C	1.046825000	-1.040837000	2.408683000
C	0.467571000	-0.038765000	3.208278000
H	0.522427000	1.003120000	2.909450000
C	-0.179117000	-0.364694000	4.399965000
H	-0.612747000	0.426625000	5.005570000
C	-0.265676000	-1.696812000	4.813902000
H	-0.769477000	-1.949270000	5.743006000
C	0.304688000	-2.698788000	4.029320000
H	0.252827000	-3.737289000	4.345567000
C	0.958339000	-2.374496000	2.836479000
H	1.409953000	-3.164814000	2.246299000
C	2.831656000	-2.097851000	0.404601000
C	4.087850000	-2.335501000	0.980108000
H	4.540552000	-1.594302000	1.630516000
C	4.773368000	-3.520600000	0.707871000
H	5.751405000	-3.688638000	1.150675000
C	4.209549000	-4.481422000	-0.133318000
H	4.747008000	-5.401436000	-0.346695000
C	2.959638000	-4.250560000	-0.711604000
H	2.523445000	-4.983355000	-1.384597000
C	2.277952000	-3.061502000	-0.451769000
H	1.328928000	-2.865791000	-0.941048000
C	3.082164000	0.691341000	1.315716000
C	3.619047000	0.705112000	2.615622000
H	3.290411000	-0.022540000	3.350534000
C	4.573612000	1.656389000	2.978156000
H	4.979394000	1.652083000	3.986340000
C	5.003533000	2.607942000	2.051081000
H	5.746337000	3.348684000	2.335027000
C	4.474358000	2.603119000	0.759639000
H	4.804610000	3.337117000	0.029725000
C	3.518788000	1.653887000	0.391446000
H	3.127083000	1.647457000	-0.620363000

Table S34. B3LYP/SDD, 6-31G(d) level optimized coordinates of **3c** (*trans*).

Ground state electronic energy = −1970.1291288 Hartree/Particle.

Pd	-0.044167000	0.154436000	0.223794000
I	0.138574000	0.507919000	2.912399000
N	-3.016169000	-0.056133000	0.841385000
N	-4.189772000	0.560119000	0.918239000
N	-3.918171000	1.795356000	0.544203000
C	-1.978535000	0.737220000	0.440068000
C	-2.593725000	1.976662000	0.233236000
C	-2.945808000	-1.476751000	1.244055000
H	-3.028402000	-1.508775000	2.334095000
H	-1.934134000	-1.786801000	0.975795000
C	-3.997908000	-2.338907000	0.583974000
C	-3.932374000	-2.612247000	-0.789845000
H	-3.129371000	-2.185569000	-1.386849000
C	-4.894783000	-3.424536000	-1.388518000
H	-4.835657000	-3.631607000	-2.453655000
C	-5.925813000	-3.976316000	-0.622574000
H	-6.672027000	-4.612606000	-1.091122000
C	-5.992592000	-3.710974000	0.745678000
H	-6.790396000	-4.137967000	1.347450000
C	-5.032364000	-2.892875000	1.344927000
H	-5.086607000	-2.684077000	2.410795000
C	-5.014068000	2.760933000	0.533434000
H	-5.746132000	2.440149000	1.274378000
H	-5.480703000	2.796115000	-0.454257000
H	-4.618498000	3.744410000	0.788091000
C	-2.026940000	3.258475000	-0.217043000
C	-2.613576000	3.984447000	-1.267063000
H	-3.483817000	3.585952000	-1.781080000
C	-2.059406000	5.193736000	-1.685694000
H	-2.518298000	5.740870000	-2.504504000
C	-0.910122000	5.689009000	-1.066111000
H	-0.477901000	6.630558000	-1.393863000
C	-0.314729000	4.967247000	-0.028786000
H	0.579968000	5.346918000	0.456860000
C	-0.865752000	3.758614000	0.396232000
H	-0.407233000	3.198196000	1.205028000
I	-0.671421000	-0.254149000	-2.399687000
P	2.251388000	-0.524631000	-0.119573000
C	3.358493000	-0.761846000	1.344244000
C	3.717941000	0.369040000	2.096843000
H	3.339375000	1.348097000	1.819693000
C	4.556569000	0.247268000	3.202475000
H	4.825328000	1.132445000	3.772490000
C	5.038798000	-1.007731000	3.583666000
H	5.688499000	-1.102714000	4.449648000
C	4.680622000	-2.136698000	2.848150000
H	5.052192000	-3.116953000	3.134938000
C	3.847445000	-2.016252000	1.732357000

H	3.589114000	-2.903740000	1.165049000
C	3.249214000	0.653413000	-1.132701000
C	4.648093000	0.528875000	-1.210557000
H	5.153254000	-0.264637000	-0.668050000
C	5.397914000	1.426356000	-1.969757000
H	6.477723000	1.315446000	-2.023066000
C	4.763724000	2.468564000	-2.651384000
H	5.349689000	3.170441000	-3.239016000
C	3.378331000	2.608218000	-2.569242000
H	2.877304000	3.418361000	-3.091959000
C	2.622980000	1.706418000	-1.815152000
H	1.545460000	1.816831000	-1.765656000
C	2.322158000	-2.151022000	-0.983662000
C	3.126599000	-2.397018000	-2.103367000
H	3.747518000	-1.608120000	-2.514119000
C	3.123729000	-3.655002000	-2.710853000
H	3.746025000	-3.829035000	-3.584606000
C	2.325163000	-4.680545000	-2.204297000
H	2.324578000	-5.657700000	-2.679746000
C	1.519079000	-4.443689000	-1.087992000
H	0.887502000	-5.234092000	-0.691445000
C	1.510152000	-3.185163000	-0.488125000
H	0.865125000	-3.001733000	0.367509000

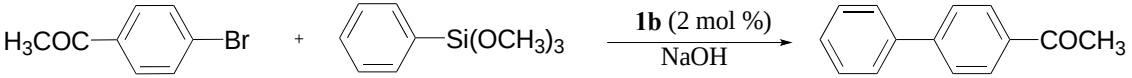
Table S35. B3LYP/SDD, 6-31G(d) level optimized coordinates of **3c** (*cis*).

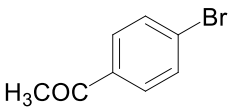
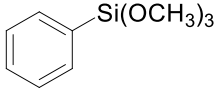
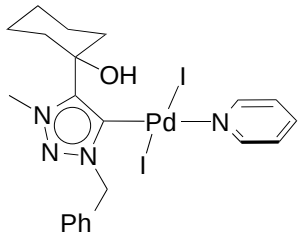
Ground state electronic energy = −1970.1224475 Hartree/Particle.

Pd	0.620330000	-0.126673000	-0.927633000
I	1.402944000	-1.833261000	-2.924059000
I	2.120547000	1.885001000	-2.007910000
P	-0.089815000	1.328267000	0.786828000
N	-1.471886000	-2.350860000	-0.632656000
N	-1.798135000	-3.480718000	-0.012613000
N	-0.837296000	-3.641808000	0.876001000
C	1.287901000	2.224334000	1.618256000
C	2.479841000	1.526176000	1.869046000
H	2.590826000	0.501615000	1.526822000
C	3.533734000	2.149285000	2.535937000
H	4.452327000	1.598887000	2.719322000
C	3.417457000	3.480408000	2.943197000
H	4.244683000	3.969759000	3.450266000
C	2.240500000	4.183601000	2.684226000
H	2.147435000	5.223273000	2.986335000
C	1.177547000	3.559508000	2.028016000
H	0.272386000	4.121557000	1.824535000
C	-1.306805000	2.621522000	0.268892000
C	-2.170462000	3.212842000	1.208280000
H	-2.142397000	2.901121000	2.247497000

C	-3.075237000	4.200043000	0.816512000
H	-3.733544000	4.648912000	1.555583000
C	-3.134829000	4.607484000	-0.518257000
H	-3.839136000	5.377574000	-0.822059000
C	-2.283542000	4.023957000	-1.457931000
H	-2.317755000	4.337413000	-2.497785000
C	-1.374834000	3.036615000	-1.069670000
H	-0.702133000	2.605333000	-1.803001000
C	-0.982213000	0.524992000	2.202956000
C	-0.433406000	0.446979000	3.490378000
H	0.541509000	0.875954000	3.693713000
C	-1.137443000	-0.175488000	4.526229000
H	-0.699039000	-0.217029000	5.519994000
C	-2.395741000	-0.729324000	4.290643000
H	-2.944641000	-1.205447000	5.099072000
C	-2.951877000	-0.655753000	3.009758000
H	-3.935506000	-1.072713000	2.811057000
C	-2.251570000	-0.035677000	1.976178000
H	-2.706311000	0.025809000	0.992994000
C	-0.318510000	-1.764238000	-0.183127000
C	0.096386000	-2.638342000	0.830852000
C	-2.326047000	-1.935959000	-1.764884000
H	-2.569274000	-2.855273000	-2.304027000
H	-1.688468000	-1.326524000	-2.405320000
C	-3.579001000	-1.195311000	-1.345530000
C	-3.732544000	0.158966000	-1.663484000
H	-2.942118000	0.679605000	-2.196710000
C	-4.890764000	0.847840000	-1.293072000
H	-4.988545000	1.901443000	-1.537636000
C	-5.906784000	0.185576000	-0.603845000
H	-6.808594000	0.719123000	-0.315959000
C	-5.764160000	-1.169472000	-0.288898000
H	-6.557988000	-1.692708000	0.237766000
C	-4.608662000	-1.856795000	-0.659848000
H	-4.500963000	-2.910505000	-0.416686000
C	-0.873835000	-4.837011000	1.714795000
H	-1.445703000	-5.597246000	1.183114000
H	-1.351433000	-4.614869000	2.672352000
H	0.147499000	-5.178873000	1.884722000
C	1.309910000	-2.624856000	1.666637000
C	1.242026000	-2.781951000	3.061344000
H	0.275791000	-2.868300000	3.549809000
C	2.406527000	-2.781040000	3.829008000
H	2.340273000	-2.897961000	4.907258000
C	3.650608000	-2.617406000	3.215603000
H	4.556926000	-2.616932000	3.815038000
C	3.725600000	-2.451587000	1.830459000
H	4.689301000	-2.324786000	1.345396000
C	2.565055000	-2.455674000	1.055763000
H	2.623878000	-2.339187000	-0.022031000

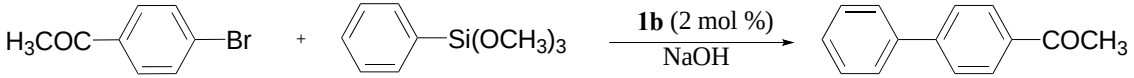
Table S36. Selected results for the Hiyama cross-coupling reaction of aryl halides (ArX; X = I, Br) with $PhSi(OMe)_3$ as catalyzed by **1b.**

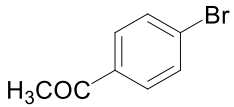
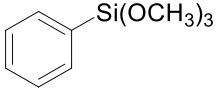
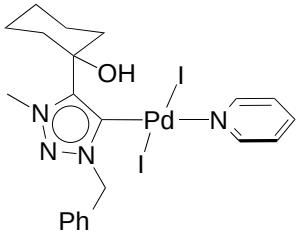
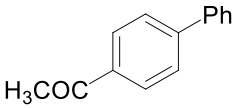


entry	reactant	reactant	catalyst	solvent	temp (^oC)	yield[a]
1			 (**1b**)	MeOH	80	0
				DMSO	80	0
				DMF	80	0
				1,4-dioxane	80	2
				toluene	80	1
				DMSO:H_2O	80	0
				1,4dioxane:H_2O	80	96
				DMF:H_2O	80	0

[a] The yields (%) were determined by GC using diethylene glycol dibutyl ether as an internal standard. Reaction conditions: 1.00 mmol of aryl halides, 1.20 mmol of $PhSi(OMe)_3$, 3.00 mmol of NaOH, 1.00 mmol of diethylene glycol dibutyl ether, 2 mol% of catalyst **1b** and 6 mL of MeOH, DMSO, DMF, 1,4-dioxane, and in mixed media of DMSO:H_2O, 1,4-dioxane:H_2O and DMF:H_2O (each in a 4:2 *v/v* ratio) at 80 °C for 4 hours.

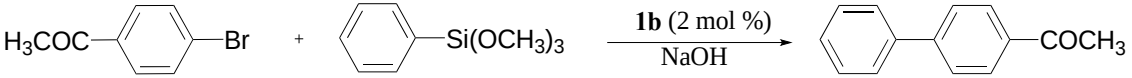
Table S37. Selected results for the Hiyama cross-coupling reaction of aryl halides (ArX; X = I, Br) with $PhSi(OMe)_3$ as catalyzed by **1b** in the presence of NEt_3, K_2CO_3, Cs_2CO_3, NaO^tBu, KO^tBu and NaOH.

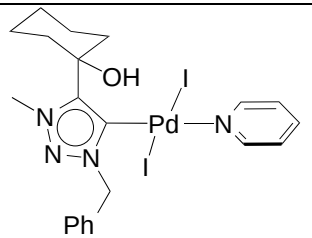
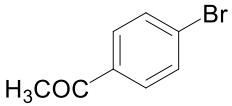
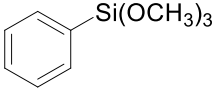


entry	reactant	reactant	catalyst	cross-coupled product	base	Yields [a]
1			 (**1b**)		NEt_3	0
					K_2CO_3	0
					Cs_2CO_3	0
					NaO^tBu	86
					KO^tBu	75
					NaOH	96

[a] The yields (%) were determined by GC using diethylene glycol dibutyl ether as an internal standard. Reaction conditions: 1.00 mmol of aryl halides, 1.20 mmol of $PhSi(OMe)_3$, 3.00 mmol of base, 1.00 mmol of diethylene glycol dibutyl ether, 2 mol% of catalyst **1b** and 6 mL of 1,4-dioxane/H_2O (2:1) at 80 °C for 4 hours.

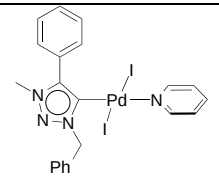
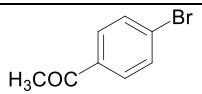
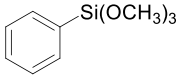
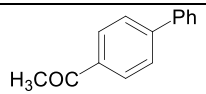
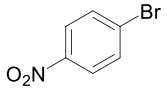
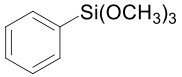
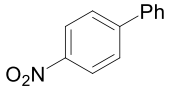
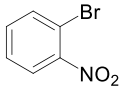
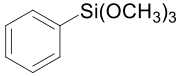
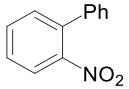
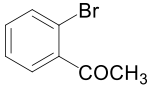
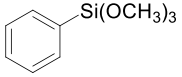
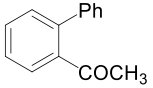
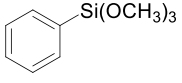
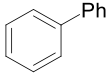
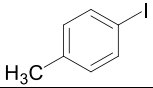
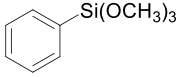
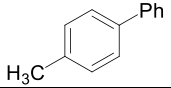
Table S38. Selected results for the Hiyama cross-coupling reaction of aryl halides (ArX; X = I, Br) with $PhSi(OMe)_3$ as catalyzed by **1b.**



entry	reactant	reactant	 (**1b**) (mol %)	yield[a]
1			0.5	94
			1	96
			1.5	90
			2	96

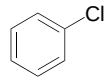
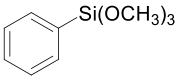
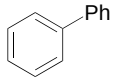
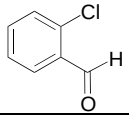
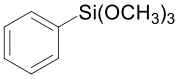
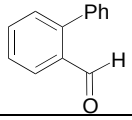
[a] The yields (%) were determined by GC using diethylene glycol dibutyl ether as an internal standard. Reaction conditions: 1.00 mmol of aryl halides, 1.20 mmol of $PhSi(OMe)_3$, 3.00 mmol of NaOH, 1.00 mmol of diethylene glycol dibutyl ether, 2 mol % of catalyst **1b** and 6 mL of 1,4-dioxane/H_2O (2:1) at 80 °C for 4 hours.

Table S39. Selected results for Hiyama cross-coupling reaction of aryl halides (ArX; X = I, Br) catalyzed by $PdCl_2$ and **3b**/Hg alongside the blank runs.

entry	reactant	reactant	cross-coupled product	yields[a]		
				$PdCl_2$	 (**3b**)/Hg	blank
1				73	83	0
2				58	94	0
3				61	60	0
4				59	57	0
5				66	67	0
6				34	58	0

[a] The yields (%) were determined by GC using diethylene glycol dibutyl ether as an internal standard. Reaction conditions: 1.00 mmol of aryl halides, 1.20 mmol of phenyltrimethoxysilane, 3.00 mmol of NaOH, 2 mol % of catalyst $PdCl_2$ and **3b**/Hg in 6 mL of 1,4-dioxane/H_2O (2:1) at 80 °C for 4 hours.

Table S40. Selected results for Hiyama cross-coupling reaction of aryl chlorides with with $PhSi(OMe)_3$ as catalyzed by **3c**.

entry	reactant	reactant	cross-coupled product	yields[a] (**3c**)
1				> 1 (trace amount)
2				> 1 (trace amount)

[a] The yields (%) were determined by GC using diethylene glycol dibutyl ether as an internal standard. Reaction conditions: 1.00 mmol of aryl halides, 1.20 mmol of phenyltrimethoxysilane, 3.00 mmol of NaOH, 2 mol % of catalyst **3c** in 6 mL of 1,4-dioxane/H_2O (2:1) at 80 °C for 4 hours.

References

1. R. Sevincek, H. Turkmen, M. Aygun, B. Cetinkaya and S. Garcia-Granda, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, 2007, **63**, M277-M279.
2. H. Tuerkmen, T. Pape, F. E. Hahn and B. Cetinkaya, *Eur. J. Inorg. Chem.*, 2009, 285-294.
3. O. Diebolt, V. Jurcik, R. C. da Costa, P. Braunstein, L. Cavallo, S. P. Nolan, A. M. Z. Slawin and C. S. J. Cazin, *Organometallics*, 2010, **29**, 1443-1450.
4. S. Gulcemal, S. Kahraman, J.-C. Daran, E. Cetinkaya and B. Cetinkaya, *J. Organomet. Chem.*, 2009, **694**, 3580-3589.
5. M. V. Baker, D. H. Brown, P. V. Simpson, B. W. Skelton and A. H. White, *Eur. J. Inorg. Chem.*, 2009, 1977-1988.
6. R. Jothibasu and H. V. Huynh, *Chem. Commun.*, 2010, **46**, 2986-2988.
7. Y. Han and H. V. Huynh, *Chem. Commun.*, 2007, 1089-1091.
8. A. Furstner, G. Seidel, D. Kremzow and C. W. Lehmann, *Organometallics*, 2003, **22**, 907-909.
9. S. Guo and H. Han Vinh, *Organometallics*, 2014, **33**, 2004-2011.
10. H. V. Huynh, Y. Han, J. H. H. Ho and G. K. Tan, *Organometallics*, 2006, **25**, 3267-3274.