Supporting Information

Experimental and Computational Studies on the Mechanistic of Pd-Catalyzed C(sp^3)–H γ-Arylation of Amino Acid Derivatives Assisted by the 2-Pyridylsulfonyl Group

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1. General Information. Chromatography: silica gel Merck-60 (230-400 mesh). TLC: silica gel Merck 60 (0.25 mm). Visualization of the chromatograms was performed by UV lamp and phosphomolibdic acid staining. Mass spectra were recorded on Agilent LC/MSD TOF mass spectrometer (ESI+) using as a mobile phase 0.1% formic acid in methanol, unless otherwise indicated. ^{1}H and ^{13}C NMR were recorded on a Bruker (300 or 500 and 75.4 or 125 MHz, respectively) when indicated, using $CDCl_3$, CD_3CN or HFIP-d_2 as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 for ^{1}H, δ 77.0 for ^{13}C; CD_3CN: δ 1.94 for ^{1}H, δ 1.3 and 118.2 for ^{13}C; HFIP-d_2: δ 4.38 for ^{1}H). Data are reported as follows: chemical shifts, multiplicity (bs = broad single, s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz), and integration. All starting amino acids were purchased from Sigma-Aldrich or Bachem and used without further purification. The 2-pyridylsulfonyl chloride was synthesized form 2-mercaptopyridine following the procedure described in the literature.[1] The general procedures for the synthesis of all starting *N*-(2-

1 García-Rubia, A.; Urones, B.; Gómez Arrayás R.; Carretero, J. C. *Angew. Chem. Int. Ed*. **2011**, *50*, 10927.

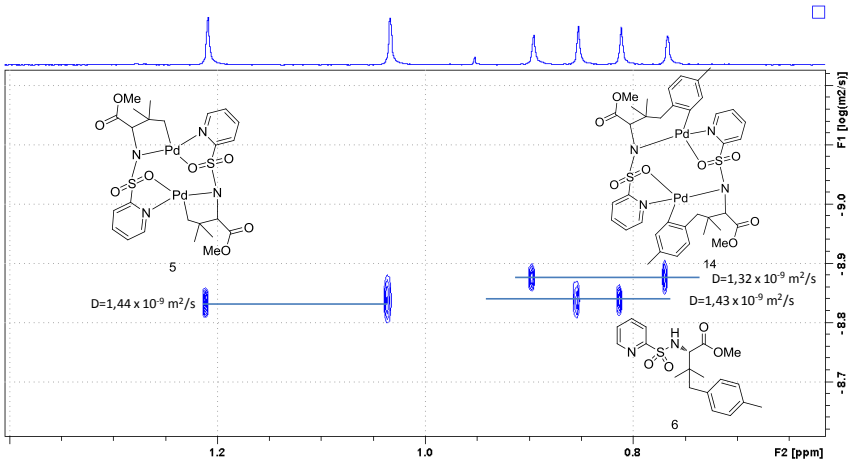
pyridylsulfonyl) amino acid esters, for the Pd(II)-catalyzed C(sp^3)–H arylation reaction of *N*-(2-pyridylsulfonyl) amino acid derivatives and for the preparation of the bimetallic complex **5** are described in the literature.[2]

2. DOSY NMR Experiments

The spectra were recorded on a Bruker DRX 500 spectrometer, using a BBOF Bruker 5-mm probe with Z-gradients. The temperature was regulated at 298 K and no spinning was applied to the NMR tube. The diffusion NMR experiments were performed with a pulsed-field gradient stimulated echo (PFGSTE) sequence, using bipolar gradients (ledbpgp2s).[3,4] The bipolar gradient duration and the diffusion time were optimized to 1.5 and 50 ms, respectively. DOSY spectra were generated by using the DOSY processing module in TopSpin v3.2 software. Diffusion coefficients *D* were derived fitting the intensity or the area of the desired peaks to a single exponential decay, using the Bruker software package T1/T2 Relaxation in the same program.

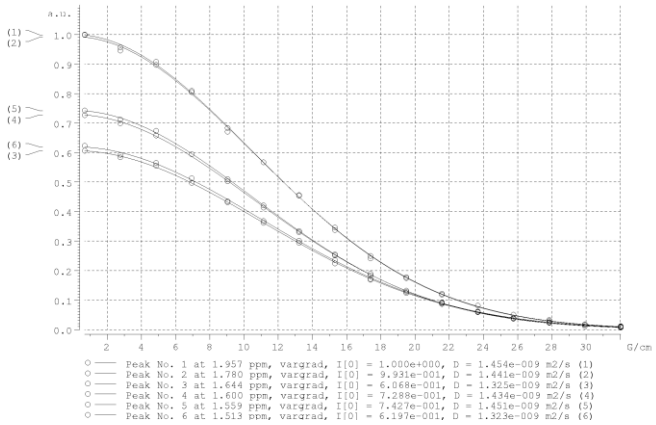
The value of the diffusion coefficient *D* in compounds **5**, **6** and **14** (mixture I) was determinated from the two methyl signals of each compound in five independent experiments. The final value is the average of ten measured values.

Molecular weights were calculated from measured diffusion coefficients applying the model proposed by *Evans et al* [5] and the Excel spreadsheet provided by the authors. The necessary parameters for CD_3CN (density d=0.844g/ml, viscosity at 298 K η= 0.341 x 10-3 Kg.m-1.s-1, MW=44.07) were found in literature and added in the provided "user defined solvent" place.[6]



Example of the output results generated with the T1/T2 Relaxation module in TopSpin Softwar

1. Graphic representation of the fitted curves to a single exponential decay



2 Rodríguez, N.; Romero-Revilla, J. A.; Fernández-Ibáñez, M. A.; Carretrero, J. C. *Chem. Sci*. **2013**, *4*, 175.
3 J. E. Tanner, *J. Chem. Phys*. **1970**, *52*, 2523.
4 R. M. Cotts, M. J. R. Hoch, T. Sun, J. T. Marker, *J. Magn. Reson.* **1989**, 252; R. Johnson, Jr., *Prog. Nucl. Magn. Reson. Spectrosc.* **1999**, 34, 203.
5 Evans, R., Deng, Z., Rogerson, A. K., McLachlan, A. S., Richards, J. J., Nilsson, M. and Morris, G. A., *Angew. Chem. Int. Ed.* **2013**, *52*: 3199–3202.
6 Values employed for CD3CN: density d=0.844g/ml, viscosity □= 0.341 x 10-3 Kg.m-1.s-1, MW=44.07

2. Numeric results of previous fitting

SIMFIT RESULTS

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INTENSITY fit : Diffusion : Variable Gradient :

I=I[0]*exp(-D*SQR(2*PI*gamma*Gi*LD)*(BD-LD/3)*1e4)

16 points for Peak 1, Peak Point = 1.957 ppm

Converged after 28 iterations!

Results Comp. 1

I[0] = 1.000e+000

Diff Con. = 1.454e-009 m2/s

Gamma = 4.258e+003 Hz/G

Little Delta = 3.000m

Big Delta = 49.950m

RSS = 2.853e-004

SD = 4.223e-003

Point	*Gradient*	*Expt*	*Calc*	*Difference*
1	*6.740e-001*	*1.000e+000*	*9.984e-001*	*-1.642e-003*
2	*2.765e+000*	*9.564e-001*	*9.660e-001*	*9.558e-003*
3	*4.855e+000*	*9.075e-001*	*8.980e-001*	*-9.528e-003*
4	*6.945e+000*	*8.045e-001*	*8.020e-001*	*-2.515e-003*
5	*9.036e+000*	*6.834e-001*	*6.881e-001*	*4.673e-003*
6	*1.113e+001*	*5.674e-001*	*5.673e-001*	*-1.102e-004*
7	*1.322e+001*	*4.537e-001*	*4.492e-001*	*-4.451e-003*
8	*1.531e+001*	*3.367e-001*	*3.418e-001*	*5.109e-003*
9	*1.740e+001*	*2.490e-001*	*2.499e-001*	*8.673e-004*
10	*1.949e+001*	*1.741e-001*	*1.755e-001*	*1.342e-003*
11	*2.158e+001*	*1.184e-001*	*1.184e-001*	*-2.358e-005*
12	*2.367e+001*	*8.061e-002*	*7.676e-002*	*-3.846e-003*
13	*2.576e+001*	*5.037e-002*	*4.780e-002*	*-2.577e-003*
14	*2.785e+001*	*2.885e-002*	*2.860e-002*	*-2.493e-004*
15	*2.994e+001*	*1.522e-002*	*1.644e-002*	*1.216e-003*
16	*3.203e+001*	*9.990e-003*	*9.079e-003*	*-9.110e-00*

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16 points for Peak 2, Peak Point = 1.780 ppm

Converged after 29 iterations!

Results Comp. 1

I[0] = 9.931e-001

Diff Con. = 1.441e-009 m2/s

Gamma = 4.258e+003 Hz/G

Little Delta = 3.000m

Big Delta = 49.950m

RSS = 7.771e-004

SD = 6.969e-003

Point	Gradient	Expt	Calc	Difference
1	6.740e-001	9.985e-001	9.910e-001	-7.418e-003
2	2.765e+000	9.454e-001	9.592e-001	1.378e-002
3	4.855e+000	8.967e-001	8.923e-001	-4.384e-003
4	6.945e+000	8.095e-001	7.977e-001	-1.180e-002
5	9.036e+000	6.709e-001	6.854e-001	1.447e-002
6	1.113e+001	5.671e-001	5.660e-001	-1.080e-003
7	1.322e+001	4.554e-001	4.492e-001	-6.173e-003
8	1.531e+001	3.455e-001	3.426e-001	-2.874e-003
9	1.740e+001	2.413e-001	2.512e-001	9.930e-003
10	1.949e+001	1.774e-001	1.770e-001	-4.726e-004
11	2.158e+001	1.210e-001	1.198e-001	-1.143e-003
12	2.367e+001	8.063e-002	7.800e-002	-2.635e-003
13	2.576e+001	5.016e-002	4.878e-002	-1.380e-003
14	2.785e+001	3.199e-002	2.932e-002	-2.662e-003
15	2.994e+001	1.782e-002	1.694e-002	-8.856e-004
16	3.203e+001	9.181e-003	9.406e-003	2.253e-004

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16 points for Peak 3, Peak Point = 1.644 ppm

Converged after 37 iterations!

Results Comp. 1

I[0] = 6.068e-001

Diff Con. = 1.325e-009 m2/s

Gamma = 4.258e+003 Hz/G

Little Delta = 3.000m

Big Delta = 49.950m

RSS = 1.029e-004

SD = 2.535e-003

Point	Gradient	Expt	Calc	Difference
1	6.740e-001	6.057e-001	6.056e-001	-9.599e-005
2	2.765e+000	5.833e-001	5.877e-001	4.417e-003
3	4.855e+000	5.551e-001	5.499e-001	-5.255e-003
4	6.945e+000	4.965e-001	4.961e-001	-4.750e-004
5	9.036e+000	4.317e-001	4.315e-001	-2.327e-004
6	1.113e+001	3.617e-001	3.618e-001	1.237e-004
7	1.322e+001	2.938e-001	2.925e-001	-1.224e-003
8	1.531e+001	2.236e-001	2.281e-001	4.495e-003
9	1.740e+001	1.693e-001	1.714e-001	2.148e-003

10	1.949e+001	1.238e-001	1.242e-001	4.191e-004
11	2.158e+001	8.986e-002	8.680e-002	-3.057e-003
12	2.367e+001	6.026e-002	5.848e-002	-1.776e-003
13	2.576e+001	3.727e-002	3.798e-002	7.067e-004
14	2.785e+001	2.503e-002	2.379e-002	-1.239e-003
15	2.994e+001	1.727e-002	1.436e-002	-2.910e-003
16	3.203e+001	1.079e-002	8.361e-003	-2.432e-003

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16 points for Peak 4, Peak Point = 1.600 ppm
Converged after 34 iterations!
Results Comp. 1
I[0] = 7.288e-001
Diff Con. = 1.434e-009 m2/s
Gamma = 4.258e+003 Hz/G
Little Delta = 3.000m
Big Delta = 49.950m
RSS = 1.426e-004
SD = 2.985e-003

Point	Gradient	Expt	Calc	Difference
1	6.740e-001	7.267e-001	7.273e-001	6.778e-004
2	2.765e+000	6.988e-001	7.041e-001	5.270e-003
3	4.855e+000	6.577e-001	6.552e-001	-2.524e-003
4	6.945e+000	5.947e-001	5.861e-001	-8.638e-003
5	9.036e+000	5.020e-001	5.039e-001	1.960e-003
6	1.113e+001	4.137e-001	4.165e-001	2.784e-003
7	1.322e+001	3.294e-001	3.309e-001	1.483e-003
8	1.531e+001	2.543e-001	2.528e-001	-1.499e-003
9	1.740e+001	1.842e-001	1.856e-001	1.414e-003
10	1.949e+001	1.316e-001	1.310e-001	-6.221e-004
11	2.158e+001	8.676e-002	8.886e-002	2.094e-003
12	2.367e+001	5.846e-002	5.795e-002	-5.013e-004
13	2.576e+001	3.804e-002	3.633e-002	-1.712e-003
14	2.785e+001	2.250e-002	2.189e-002	-6.052e-004
15	2.994e+001	1.526e-002	1.268e-002	-2.580e-003
16	3.203e+001	7.668e-003	7.061e-003	-6.067e-004

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16 points for Peak 5, Peak Point = 1.559 ppm
Converged after 36 iterations!
Results Comp. 1
I[0] = 7.427e-001
Diff Con. = 1.451e-009 m2/s
Gamma = 4.258e+003 Hz/G
Little Delta = 3.000m
Big Delta = 49.950m
RSS = 1.272e-004
SD = 2.819e-003

Point	Gradient	Expt	Calc	Difference
1	6.740e-001	7.425e-001	7.412e-001	-1.311e-003
16	3.203e+001	5.806e-003	6.800e-003	9.943e-004
2	2.765e+000	7.122e-001	7.172e-001	4.949e-003
3	4.855e+000	6.735e-001	6.668e-001	-6.685e-003
4	6.945e+000	5.944e-001	5.957e-001	1.273e-003
5	9.036e+000	5.096e-001	5.112e-001	1.579e-003
6	1.113e+001	4.212e-001	4.216e-001	3.747e-004
7	1.322e+001	3.343e-001	3.340e-001	-2.839e-004
8	1.531e+001	2.512e-001	2.543e-001	3.050e-003
9	1.740e+001	1.889e-001	1.860e-001	-2.910e-003
10	1.949e+001	1.271e-001	1.307e-001	3.617e-003
11	2.158e+001	9.120e-002	8.826e-002	-2.947e-003
12	2.367e+001	5.899e-002	5.726e-002	-1.725e-003
13	2.576e+001	3.683e-002	3.569e-002	-1.144e-003
14	2.785e+001	2.384e-002	2.138e-002	-2.465e-003
15	2.994e+001	1.128e-002	1.230e-002	1.023e-003

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16 points for Peak 6, Peak Point = 1.513 ppm
Converged after 36 iterations!
Results Comp. 1
I[0] = 6.197e-001
Diff Con. = 1.323e-009 m2/s
Gamma = 4.258e+003 Hz/G
Little Delta = 3.000m
Big Delta = 49.950m
RSS = 2.287e-004
SD = 3.781e-003

Point	Gradient	Expt	Calc	Difference
1	6.740e-001	6.235e-001	6.185e-001	-4.943e-003
2	2.765e+000	5.920e-001	6.002e-001	8.214e-003
3	4.855e+000	5.645e-001	5.617e-001	-2.831e-003
4	6.945e+000	5.128e-001	5.067e-001	-6.074e-003
5	9.036e+000	4.342e-001	4.408e-001	6.638e-003
6	1.113e+001	3.680e-001	3.697e-001	1.742e-003
7	1.322e+001	3.012e-001	2.990e-001	-2.234e-003
8	1.531e+001	2.356e-001	2.332e-001	-2.462e-003
9	1.740e+001	1.706e-001	1.753e-001	4.751e-003

10	1.949e+001	1.278e-001	1.271e-001	-7.456e-004	14	2.785e+001	2.373e-002	2.438e-002	6.461e-004
11	2.158e+001	9.065e-002	8.883e-002	-1.813e-003	15	2.994e+001	1.489e-002	1.473e-002	-1.633e-004
12	2.367e+001	6.046e-002	5.988e-002	-5.807e-004	16	3.203e+001	1.092e-002	8.578e-003	-2.338e-003
13	2.576e+001	3.994e-002	3.890e-002	-1.037e-003					

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Calculation of the molecular weight using the model proposed by *Evans et al*.[5]

Two mixtures coming from different reactions were analyzed:

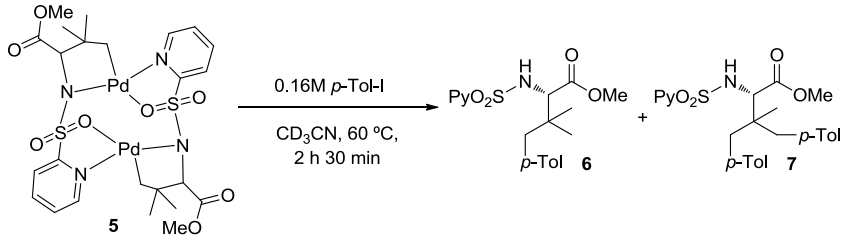
- Mixture I, compounds **5**, **6** and **14**
- Mixture II, complex solution with ten compounds. Due to signal overlapping, only compounds **4**, **6**, **7**, **15** and **16** were studied.

In both cases only isolated signals were used to measure the diffusion coefficients *D*.

Compound	MW[(a)]	D_M[(b)] (x 10^{-9} m^2/s)	MW_{Calc} [(c)]	MW/MW_{Calc} ratio
Mixture I				
5	781,5	1,44	381,4	2,05
6	376,47	1,43	382,5	0,98
14	961,65	1,32	463,5	2,07
Mixture II				
4	286,35	1,71	260	1,10
6	376,47	1,52	368	1,02
7	466,60	1,40	401,5	1,16
15	961,75	1,47	362,9	2,65
16	1142	1,29	484,8	2,36

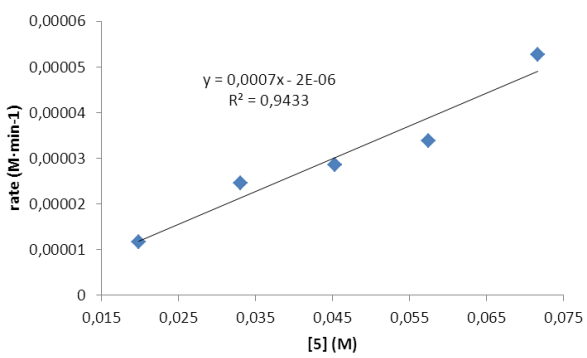
[(a)] Expected molecular weight, [(b)] Measured diffusion coefficient from DOSY experiments, [(c)] Estimated molecular weight from D_M.[5]

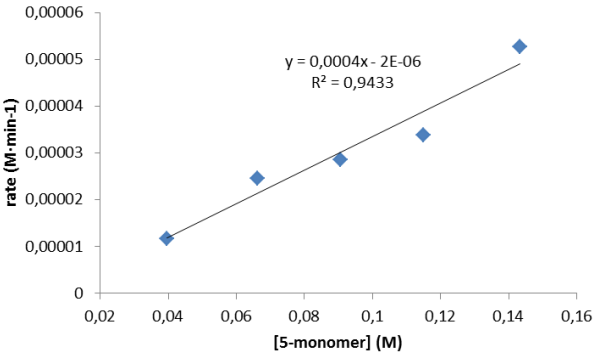
3. Reaction order of complex 5 in the arylation reaction with 4-iodotoluene



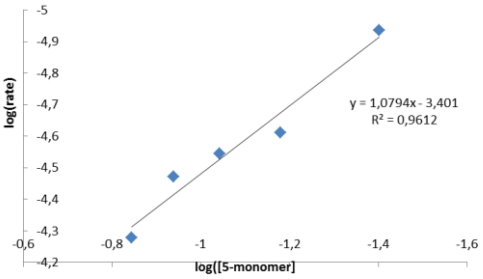
0.019-0.071M

The reaction order of complex **5** in the arylation reaction with 4-iodotoluene was determined using the method of initial rates. An oven dried Ace Pressure tube with Teflon stir bar was charged with the bimetallic complex **5** (3.1-11.2 mg, 0.008-0.028 mmol), 4-iodotoluene (14 mg, 0.064 mmol) and 1,1,1,3,3,3-hexaflouro-2-propranol (0.4 mL). The pressure tube was then sealed with a screw-cap and the reaction was placed in a preheated oil bath at 60 ºC and stirred for 2 h 30 min (ca. 10% conversion). At this point, the reaction mixture was removed from the oil bath and freezing at -78 ºC. The reaction was allowed to warm to room temperature, then a standard solution of 1,3,5-trimethoxybenzene (2.8 mg, 0.016 mmol) in CH_2Cl_2 was added. The reaction mixture was concentrated under reduced pressure. The residue was analyzed by ^{1}H NMR (500 MHz) spectroscopy and the amount of arylated products **6** and **7** was quantified versus the internal standard (1,3,5-trimethoxybenzene). The data obtained are presented below.



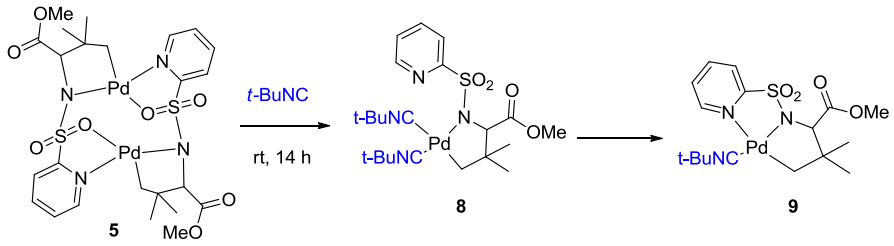


The plot of the logarithms of the reaction rate against the concentration of **5-monomer** provides a straight line with slope of 1.0, revealing that the reaction is first order in the complex **5-monomer**.



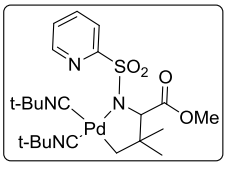
4. Synthesis of the monomeric complexes 8, 9 and 10

*4.1. Synthesis of the monomeric complexes **8** and **9***



The bimetallic complex **5** (15 mg, 0.019 mmol) was dissolved in *tert*-butylisocyanide (0.1 mL) and the resulting solution was stirred at room temperature for 14 h. At this point, the reaction mixture was concentrated under reduced pressure to afford cleanly the monomeric complex **5** as a white solid. ^{1}H NMR spectra showed the transformation over the time of **8** into **9** even in solid state. The crystallisation (hexane/CH_2Cl_2) of a mixture of **8** and **9** afforded two different types of crystals. The crystals which correspond to compound **8** were suitable for X-ray analysis while the crystals which correspond to compound **9** were not.

Monomeric complex $C_{22}H_{34}N_4O_4SPd$ **8**

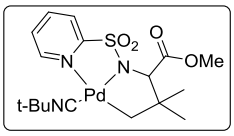


^{1}H NMR (300 MHz, $CDCl_3$): δ 8.58 (m, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.23 (m, 1H), 3.98 (s, 1H), 3.51 (s, 3H), 2.00 (d, *J* = 10.0 Hz, 1H), 1.62 (d, *J* = 10.0 Hz, 1H), 1.46 (s, 9H), 1.40 (s, 9H), 1.07 (s, 3H), 0.89 (s, 3H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ 174.4, 162.1, 148.9, 136.3, 128.9, 128.1, 132.9, 121.1, 74.6, 57.5, 56.2, 50.6, 47.0, 41.4, 30.5, 30.2, 29.8, 25.6.

MS (ESI, mobile phase: acetonitrile) *m/z*: 474 (M^+ - 83) (100), 557 (M^+ + H); HRMS calcd for $C_{22}H_{35}N_2O_4SPd$ (M^+ + H): 557.1408, found: 557.1417.

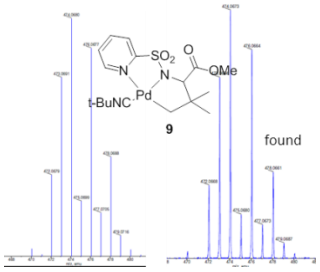
Monomeric complex $C_{17}H_{25}N_3O_4SPd$ **9**



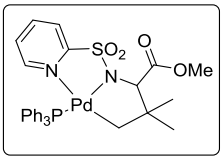
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15 (d, *J* = 4.4 Hz, 1H), 7.96 (m, 2H), 7.47 (m, 1H), 4.02 (s, 1H), 3.72 (s, 3H), 2.33 (d, *J* = 9.4 Hz, 1H), 2.04 (d, *J* = 9.6 Hz, 1H), 1.54 (s, 9H), 1.31 (s, 3H), 1.08 (s, 3H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ 173.2, 162.4, 148.9, 139.7, 135.0 (bs), 126.8, 122.5, 64.7, 57.7, 52.4, 51.4, 38.1, 30.4, 30.0, 25.5.

MS (ESI) *m/z*: 474 (M^+ + H) (100); HRMS calcd for $C_{17}H_{26}N_3O_4SPd$ (M^+ + H): 474.0680, found: 474.0673.



4.2. Synthesis of the monomeric complex $C_{30}H_{31}N_2O_4PSPd$ **10**



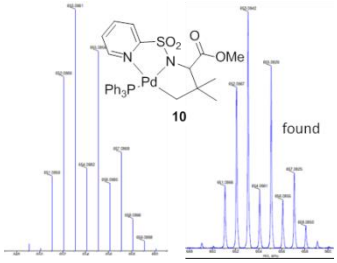
To a solution of the bimetallic complex **5** (10 mg, 0.013 mmol) in 1,1,1,3,3,3-hexaflouro-2-propranol (0.1 mL), PPh_3 (6.6 mg, 0.025 mmol, 1.0 equiv respect to Pd) was added and the mixture was stirred at room temperature for 15 h. At this point, the reaction mixture was concentrated under reduced pressure. The solid was purified by trituration (CH_2Cl_2/hexane) to afford the monomeric complex **10** as a white solid (yield 90%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.9 Hz, 1H), 7.83 (td, *J* = 7.7 and 1.9 Hz, 1H), 7.70-7.64 (m, 6H), 7.51-7.40 (m, 9H), 6.96-6.89 (m, 2H), 4.20 (s, 1H), 3.75 (s, 3H), 1.85 (dd, *J* = 9.4 and 3.6 Hz, 1H), 1.72 (dd, *J* = 9.4 and 6.4 Hz, 1H), 1.12 (s, 3H), 1.07 (s, 3H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ 173.3, 162.9, 148.4, 139.2, 134.4, 134.2, 131.1, 130.9, 130.8, 130.5, 128.8, 128.7, 126.0, 122.5, 64.4, 52.8, 51.5, 47.1, 29.5, 25.6.

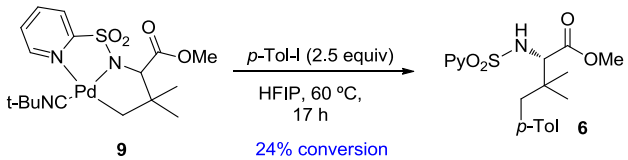
^{31}P NMR (121.5 MHz, $CDCl_3$): δ 35.0

MS (ESI) *m/z*: 653 (M^+ + H) (100); HRMS calcd for $C_{30}H_{32}N_2O_4PSPd$ (M^+ + H): 653.0861, found: 653.0842.



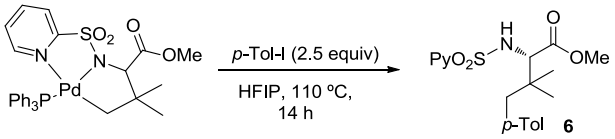
5. Reactivity of complexes 9 and 10

*5.1. Arylation reaction of complex **9** with 4-iodotoluene*



An oven dried Ace Pressure tube with Teflon stir bar was charged with complex **9** (5.0 mg, 0.01 mmol, 1.0 equiv), 4-iodotoluene (5.7 mg, 0. 026 mmol, 2.5 equiv), and 1,1,1,3,3,3-hexaflouro-2-propranol (0.1 mL). The pressure tube was then sealed with a screw-cap and the reaction was placed in a preheated oil bath at 60 ºC and stirring for 17 h. At this point, the reaction mixture was removed from the oil bath and allowed to cool to room temperature. The reaction mixture was then diluted with CH_2Cl_2, filtered through a pad of Celite® and concentrated under reduced pressure. ^{1}H NMR analysis (300 MHz) of the crude material showed 24% of conversion to the monoarylated product **6**. The arylation reaction of the bimetallic complex **5** with 4-iodotoluene under similar reaction conditions gave full conversion to mono- and diarylated products **6** and **7** in a ratio 54:46, respectively.

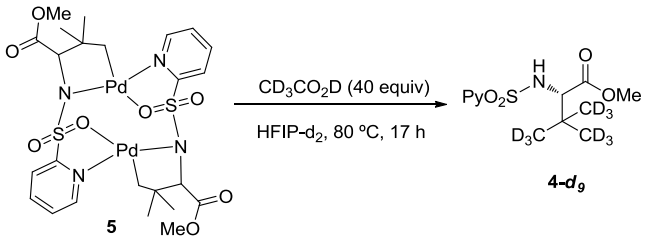
*5.2. Arylation reaction of complex **10** with 4-iodotoluene*



An oven dried Ace Pressure tube with Teflon stir bar was charged with complex **10** (5.0 mg, 0.007 mmol, 1.0 equiv), 4-iodotoluene (4.2 mg, 0.019 mmol, 2.5 equiv), and 1,1,1,3,3,3-hexaflouro-2-propranol (0.1 mL). The pressure tube was then sealed with a screw-cap and the reaction was placed in a preheated oil bath at 110 ºC and stirring for 14 h. At this point, the reaction mixture was removed from the oil bath and allowed to cool to room temperature. The reaction mixture was then diluted with CH_2Cl_2, filtered through a pad of Celite® and concentrated under reduced pressure. ^{1}H NMR analysis (300 MHz) of the crude material showed 13% of conversion to the monoarylated product **6**. The arylation reaction of the bimetallic complex **5** with 4-iodotoluene under similar reaction conditions gave full conversion to mono- and diarylated products **6** and **7** in a ratio 47:53, respectively.

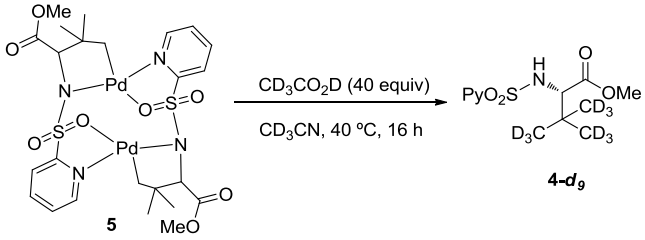
6. Deuterium labeling experiments

6.1. H/D Exchange experiment in HFIP-d_2 at 80 ºC



An oven dried Ace Pressure tube with Teflon stir bar was charged with the bimetallic complex **5** (3 mg, 0.004 mmol, 1.0 equiv), CD_3CO_2D (9.4 μL, 0.304 mmol, 40.0 equiv respect to Pd) and HFIP-d_2 (0.1 mL). The pressure tube was then sealed with a screw-cap and the reaction was placed in a preheated oil bath at 80 ºC and stirred for 17 h. At this point, the reaction mixture was removed from the oil bath and allowed to cool to room temperature. The reaction mixture was then diluted with CH_2Cl_2, filtered through a pad of Celite® and concentrated under reduced pressure. ^{1}H NMR analysis ($CDCl_3$, 300 MHz) of the crude material showed full conversion to the methyl *N*-(2-pyridylsulfonyl)-L-*tert*-leucinate **4-d$_9$** almost completely deuterated (*c.a.* 85%).

6.2. H/D Exchange experiment in CD_3CN-d_2 at 40 ºC

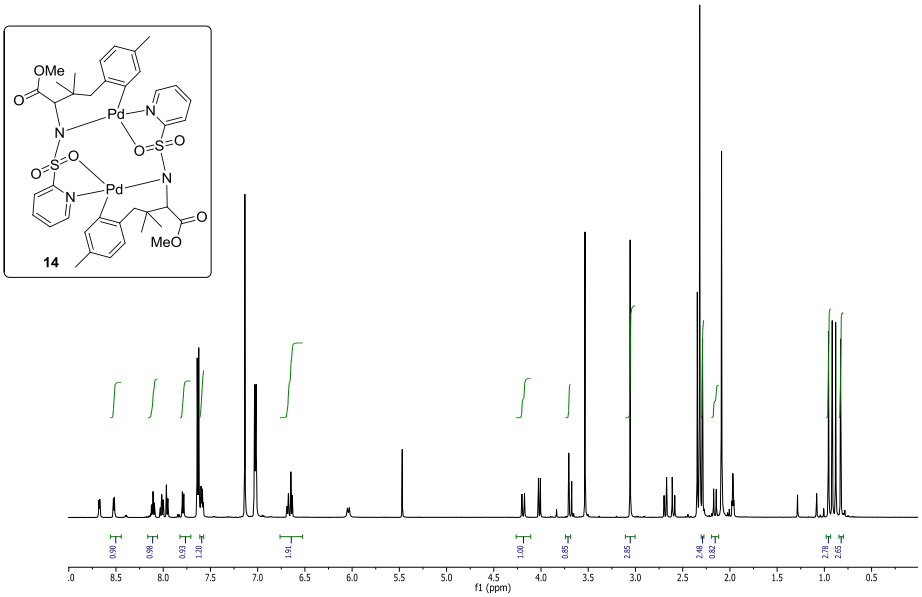


An oven dried Ace Pressure tube with Teflon stir bar was charged with the bimetallic complex **5** (3 mg, 0.004 mmol, 1.0 equiv), CD_3CO_2D (9.4 μL, 0.304 mmol, 40.0 equiv respect to Pd) and CD_3CN (0.1 mL). The pressure tube was then sealed with a screw-cap and the reaction was placed in a preheated oil bath at 40 ºC and stirred for 16 h. At this point, the reaction mixture was removed from the oil bath and allowed to cool to room temperature. The reaction mixture was then diluted with CD_3CN and directly analyzed by ^{1}H NMR spectroscopy (300 MHz). Three products were detected: *i)* the bimetallic complex **5**, with a value of two protons for the corresponding signal of the *ortho*-proton to the nitrogen of the pyridine moiety, *ii)* the *tert*-leucine derivative **4** partially deuterated (*c.a.* 18% deuterated) with a value of one proton for the corresponding signal of the *ortho*-proton and, *iii)* an unknown compound which value for the *ortho*-proton we assignment as one proton. Taking this into account, the ^{1}H NMR spectra showed 25% of conversion to the methyl *N*-(2-pyridylsulfonyl)-L-*tert*-leucinate **4** partially deuterated.

7. Characterization of complex 14

Palladacycle **14** could not be isolated, however, it was characterized by NMR studies, as well as high resolution mass spectra.

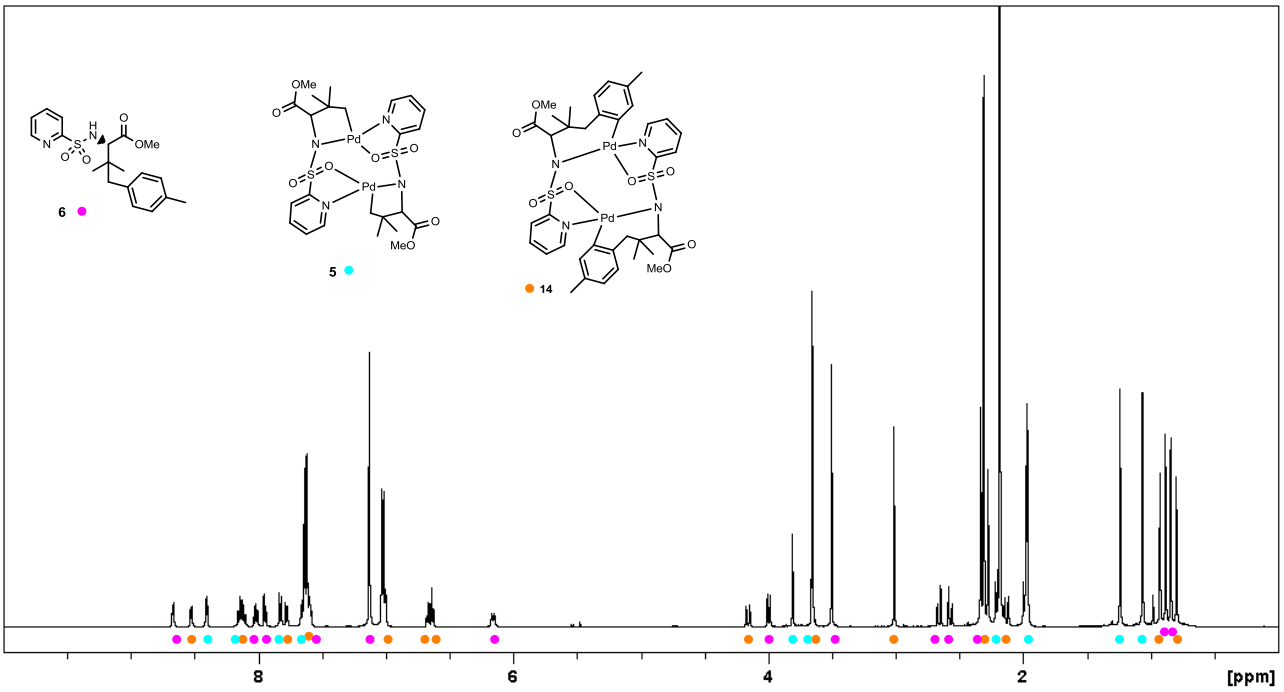
A Wilmad quick pressure valve NMR tube was charged with a freshly prepared solution of the bimetallic complex **5** (10 mg, 0.013 mmol, 1.0 equiv) and 4-iodotoluene (14 mg, 0.064 mmol, 2.5 equiv respect to Pd) in CD_3CN (0.3 mL). The reaction progress was monitored by ^1H NMR (500 MHz) at 60 ºC. The ^1H NMR (500 MHz) spectra shows, after 17 h, a mixture 2 to 1 of the monoarylated product **6** and the bimetallic complex **14**, with traces of the bimetallic complex **5**. See below the ^1H NMR spectra.

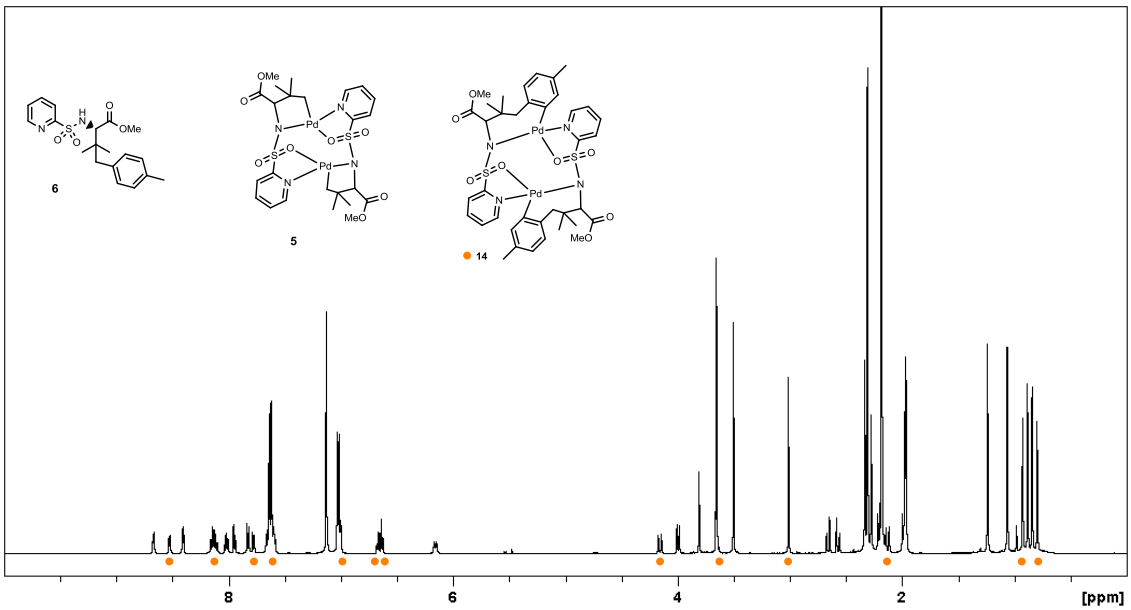


Bimetallic complex $C_{38}H_{44}N_4O_8S_2Pd_2$ **14**. In solution, bimetallic complex **14** seems to be a monomer on basis of the DOSY spectroscopy analysis (see, section 2).

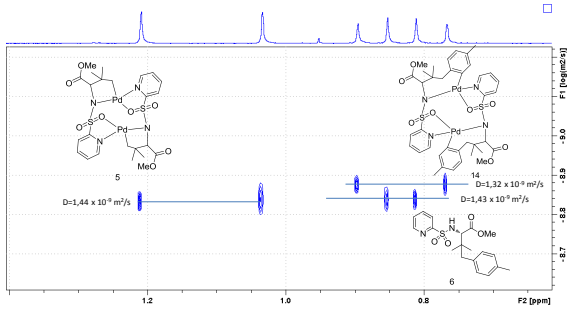
MS (ESI) *m/z*: 481 ($M^+/2$ + H), 961 (M^+ + H); HRMS calcd for $C_{19}H_{23}N_2O_4SPd$ ($M^+/2$ + H): 481.041, found: 481.040.; HRMS calcd for $C_{38}H_{45}N_4O_8S_2Pd_2$ (M^+ + H): 961.08, found: 961.07.

The full characterization by NMR (500 MHz) of palladacycle **14** was performed from a 2:1:1 mixture of monoarylated product **6**, the bimetallic complex **5** and the bimetallic complex **14**, respectively.

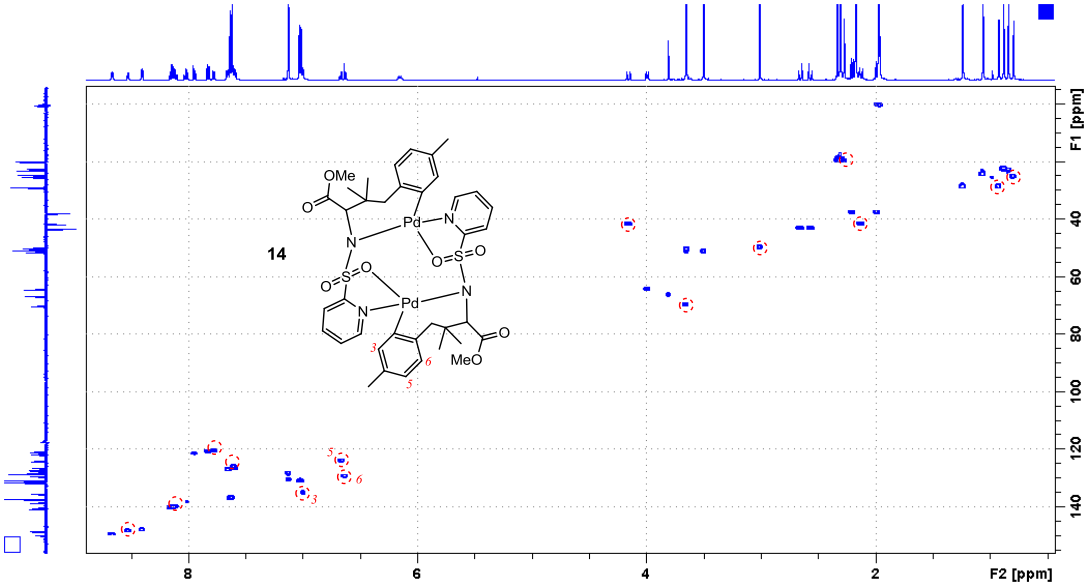




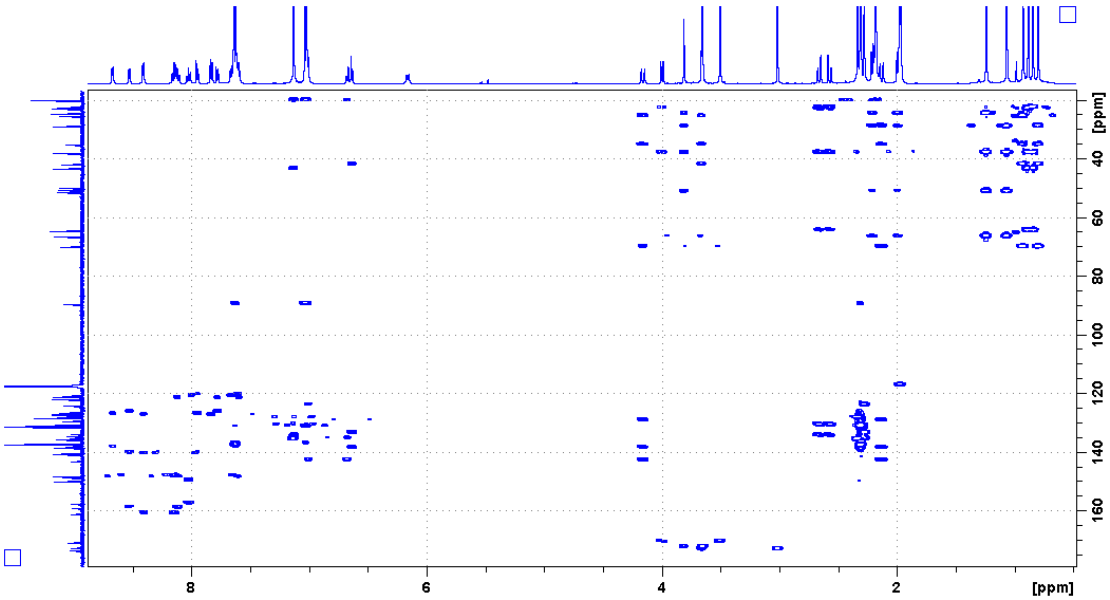
DOSY (see, section 2)



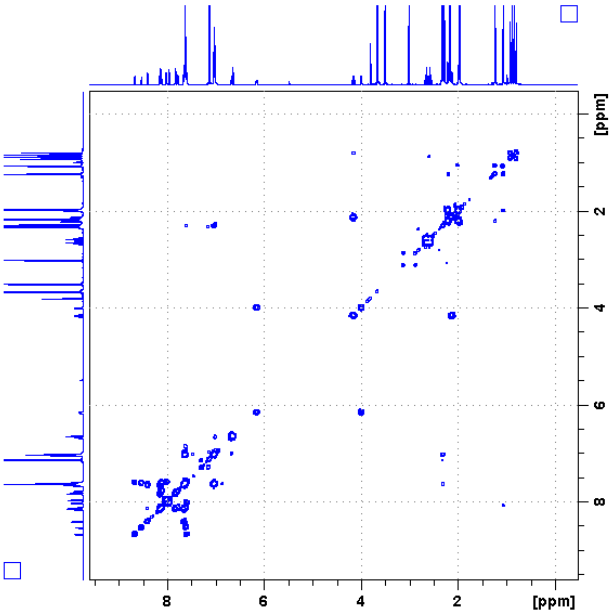
HSQC:



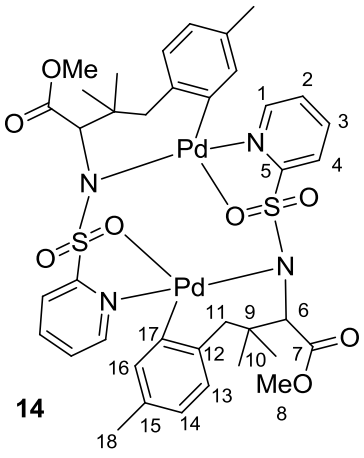
HMBC:



COSY:

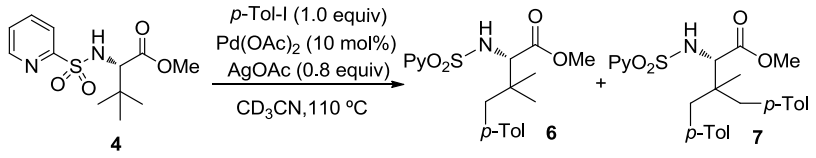


	^{1}H (multiplicity)	^{13}C
R-SO_2-Py (**5**)	-	160.16
R-SO_2-Py (**4**)	7.75 (d)	121.7
R-SO_2-Py (**3**)	8.1 (dd)	142.42
R-SO_2-Py (**2**)	7.58 (dd)	127.5
R-SO_2-Py (**1**)	8.49 (d)	149.75
(*tert*-Leu)-CH (**6**)	3.63 (s)	71.17
(*tert*-Leu)-CO (**7**)	-	174.4
(*tert*-Leu)-CH_3O (**8**)	2.98 (s)	51
(*tert*-Leu)-C- (**9**)	-	26.25
(*tert*-Leu)- CH_3 (**10**)	0.89 (s)	30
(*tert*-Leu)- CH_3 (**10'**)	0.77 (s)	26.5
(*tert*-Leu)- CH_2 (**11**)	4.1/2.1 (AB system)	43
Ar (**12**)	-	144
Ar-(Pd) (**17**)	-	139.9
Ar (**16**)	6.97 (broad s)	136.6
Ar-(CH_3) (**15**)	-	134.7
Ar (**14**)	6.64 (dd)	127.5
Ar (**13**)	6.60 (dd)	130.4
CH_3-(Ar) (**18**)	2.24 (s)	21

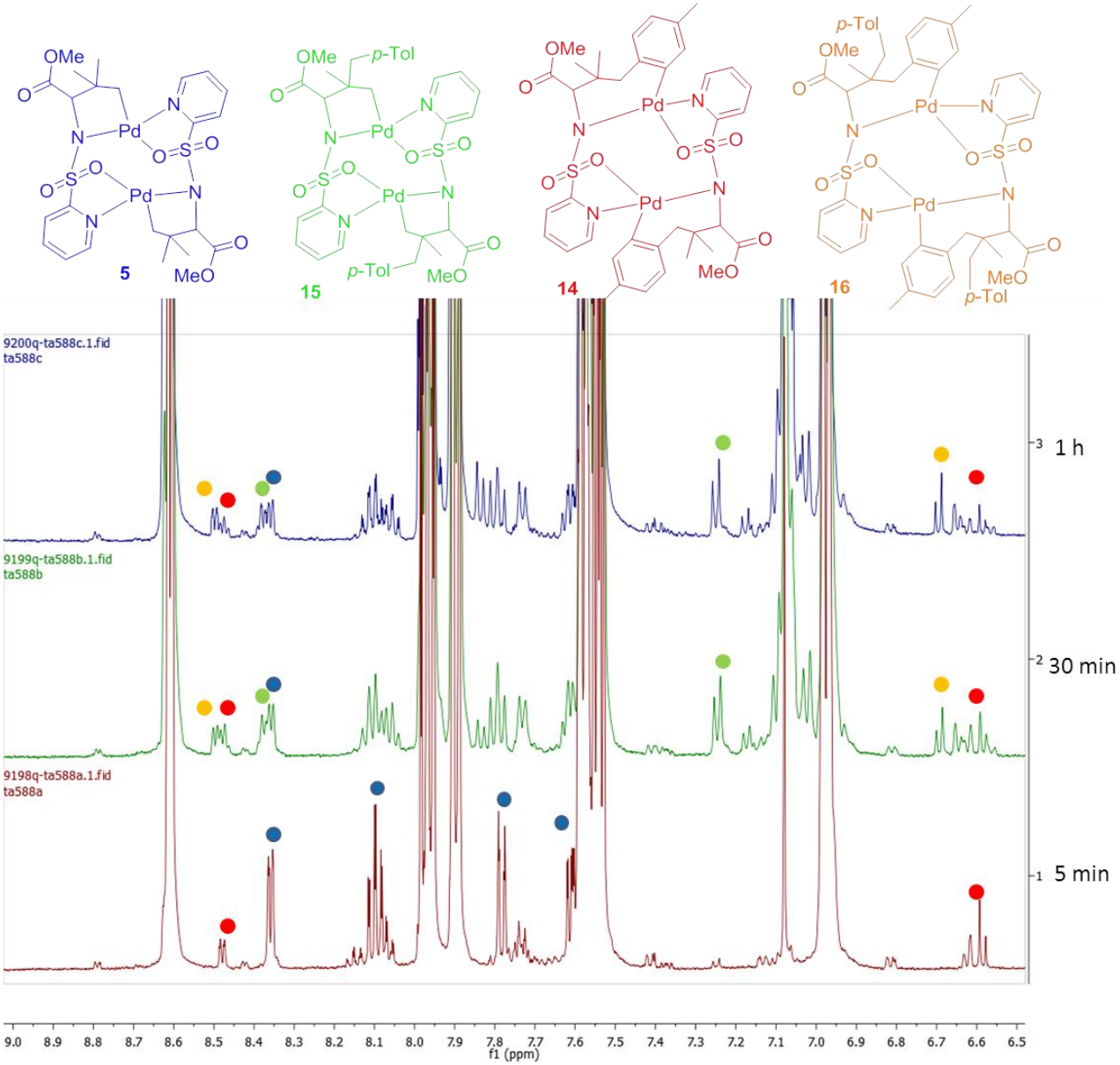


14

8. Observation of the Catalyst Resting State



An oven dried Ace Pressure tube with Teflon stir bar was charged with methyl *N*-(2-pyridylsulfonyl)-L-*tert*-leucinate **4** (14 mg, 0.05 mmol, 1.0 equiv), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 10 mol%), AgOAc (7 mg, 0.04 mmol, 0.8 equiv), 4-iodotoluene (11 mg, 0.005 mmol, 1.0 equiv) and CD_3CN (0.1 mL). The pressure tube was then sealed with a screw-cap and the reaction was placed in a preheated oil bath at 110 ºC. After the time period indicated for each experiment, the reaction mixture was removed from the oil bath and freezing at -78 ºC.[7] The reaction mixture was then diluted with CD_3CN, filtered through a 0.45μm nylon filter and directly analyzed by ^{1}H NMR (500 MHz). Examination of the ^{1}H NMR spectra after 5 min, 30 min and 1 h showed that, among other palladium species (complex **5**, **14**, **15**, **16**), the major palladium-containing compound is the bimetallic complex **5**. The amount of the bimetallic complex **15**, which is the monoarylated complex of **5**, is increasing over the time and after 1 h of reaction is present almost in the same ratio than the bimetallic complex **5**. The ^{1}H NMR (500 MHz) spectra and the assignment of some of the peaks of the palladium species are presented below.



7 The same results were obtained when the reaction was removed from the oil bath and cooling down to room temperature.

9. Characterization of complexes 15 and 16

Bimetallic complexes **15** and **16** were characterization from the follow reaction mixture:

A Wilmad quick pressure valve NMR tube was charged with a freshly prepared solution of the bimetallic complex **5** (10 mg, 0.013 mmol, 1.0 equiv), 4-iodotoluene (14 mg, 0.064 mmol, 2.5 equiv respect to Pd) and AcOH (2.9 μL, 0.051mmol, 2.0 equiv respect to Pd) in CD_3CN (0.3 mL). The reaction was placed in a 500 MHz NMR spectrometer at 60 ºC and after 16 h we observed the formation of the *tert*-leucine derivative **4**, the mono- and diarylated products **6** and **7**, and the bimetallic complexes **14**, **15**, **16** and **X**. Some of the spectra and the assignment of some of the peaks are presented below.

- Bimetallic complex $C_{38}H_{44}N_4O_8S_2Pd_2$ **15**. In solution, bimetallic complex **15** seems to be a monomer on basis of the DOSY spectroscopy analysis (see, section 2).

MS (ESI) *m/z*: 481 ($M^+/2 + H$), HRMS calcd for $C_{19}H_{23}N_2O_4SPd$ ($M^+/2 + H$): 481.041, found: 481.040.

- Bimetallic complex $C_{52}H_{56}N_4O_8S_2Pd_2$ **16**. In solution, bimetallic complex **16** seems to be a monomer on basis of the DOSY spectroscopy analysis (see, section 2).

MS (ESI) *m/z*: 571 ($M^+/2 + H$), 1141 ($M^+ + H$),; HRMS calcd for $C_{26}H_{29}N_2O_4SPd$ ($M^+/2 + H$): 571.0887, found: 571.0882.; HRMS calcd for $C_{52}H_{57}N_4O_8S_2Pd_2$ ($M^+ + H$): 1141.172, found: 1141.170

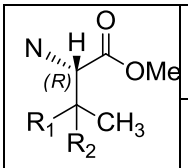
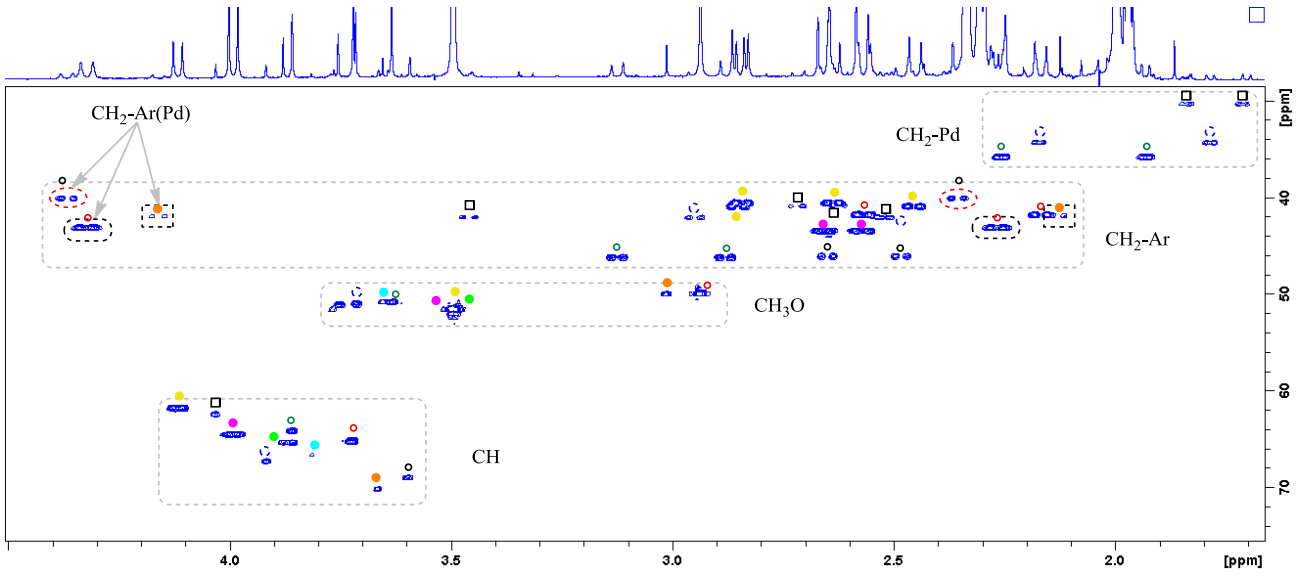
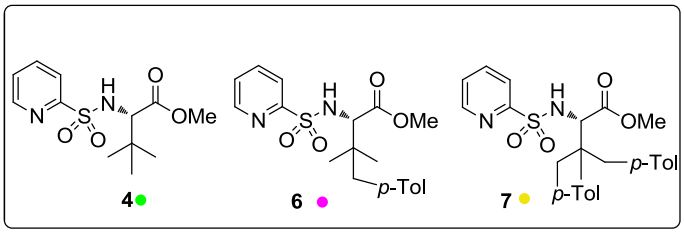
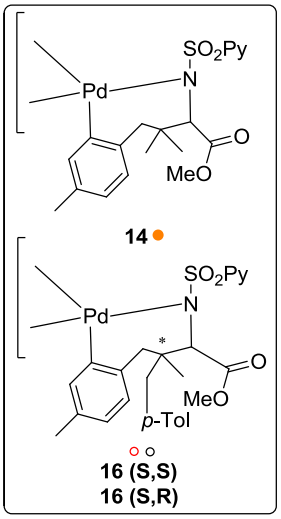
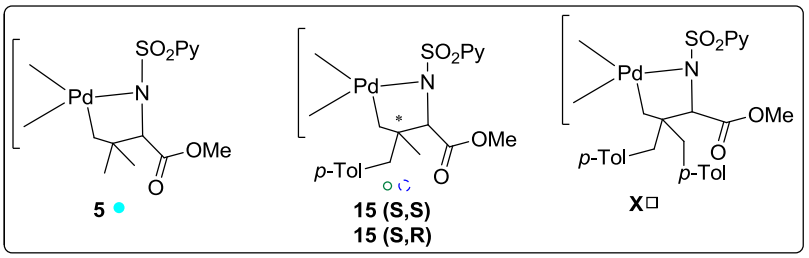
	CH		Me		CH_2-Pd		CH_2-Ar(1)		CH_2-Ar(2)		CH_2-Ar-Pd		-C-
	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^{13}C
15 ○ ◌ (S,S / R,S)	3.86	64.0	0.90	22.0	1.78/ 2.17	34.2	2.53/ 2.95	42.0	--	--	--	--	54.8
	3.92	67.1	1.12	25.5	1.93/ 2.25	35.8	2.88/ 3.12	46.0	--	--	--	--	*nd*
16 ○ ○ (S,S / R,S)	3.73	65.1	0.71	25.7	--	--	2.17/ 2.57	41.7	--	--	2.35/ 4.37	40.0	38.5
	3.6	68.9	0.71	22.0	--	--	2.48/ 2.65	45.9	--	--	2.49/ 2.65	43.0	*nd*
X □	4.03	62.2	--	--	1.71/ 1.83	30.3	2.53/ 3.46	41.9	2.62/ 2.72	40.8	--	--	58.7

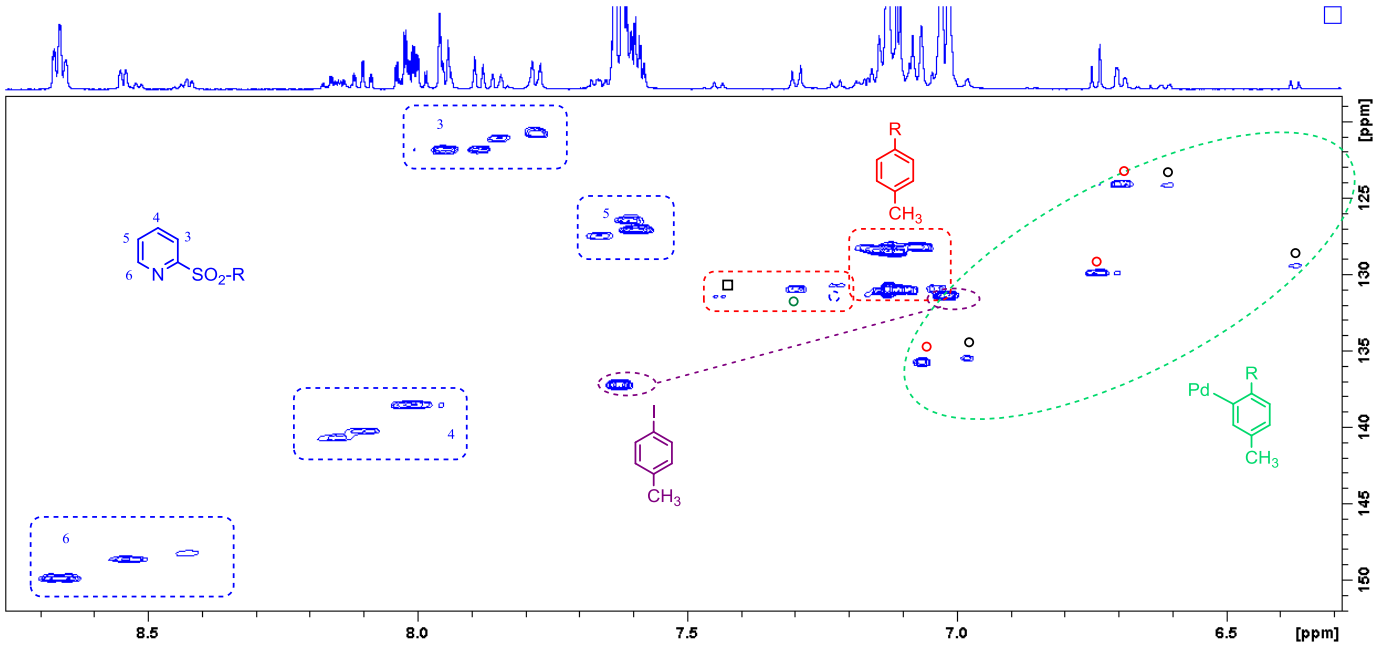
Table S1: ^1H and ^{13}C chemical shifts of the relevant signal derived from the *tert*-leucine skeleton for the products obtained from the reaction. The ^1H and ^{13}C chemical shift were deduced from an HSQC experiment, except for the quaternary carbon whose ^{13}C value was deduced from an HMBC experiment. The products were identified by the NOE and HMBC correlations from key protons as CH and CH_2 groups. For the products 15 and 16 the signals for the two diastereoisomers were found. *nd*: No determined.


CH2-Ar(Pd)
CH2-Pd
CH2-Ar
CH3O
CH
[ppm]
4.0
3.5
3.0
2.5
2.0


OMe
p-Tol
4
6
7


SO2Py
Pd
N
MeO
O
14
16 (S,S)
16 (S,R)


SO2Py
Pd
N
OMe
p-Tol
5
15 (S,S)
15 (S,R)
X


SO2-R
R
CH3
Pd
[ppm]
8.5
8.0
7.5
7.0
6.5

10. Theoretical calculations

Geometries were initially fully optimized at the DFT (B3LYP)[8] level using the SDD basis set for Pd and the standard 6-31G(d)[9] basis for all other atoms. Single point energies were calculated at the M06/SDD-6-311+G(2df,2p) level.[10] The reported free energies include zero-point energies and thermal corrections calculated at 298 K with B3LYP/SDD-6-31G(d). Solvation energy corrections were also calculated by M06/SDD–6-311+G(2df,2p) single point calculations with the CPCM solvation model[11] in CH_3CN for all structures. All calculations were performed with Gaussian 09.[12]

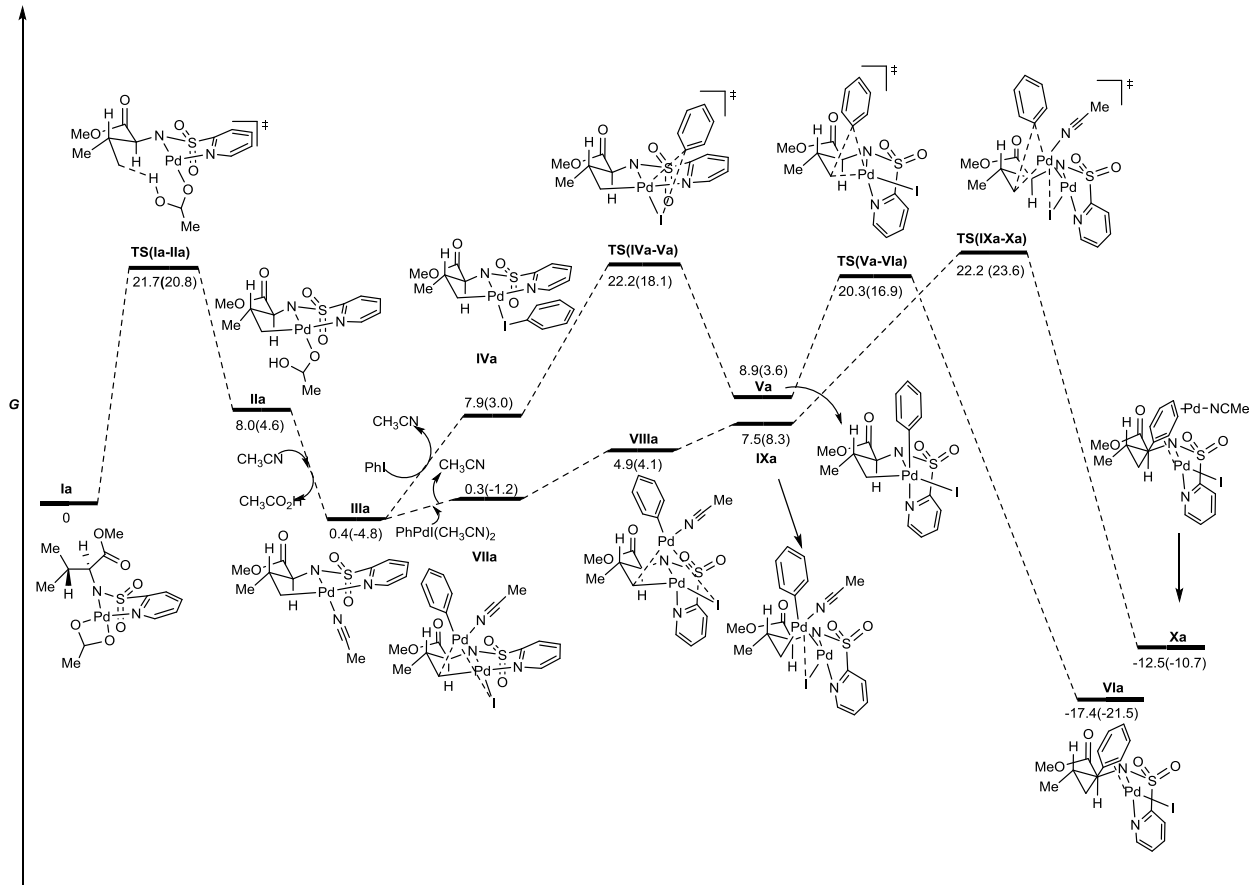


Figure S1. Complete energy profile for the reaction of the *N*-(2-pyridyl)sulfonyl valine derivative in the gas phase (M06 / 6-311+G(2df,2p) (C,H,N,O,S), SDD (Pd) // B3LYP / 6-31G(d) (C,H,N,O,S), SDD (Pd)). Relative G values at 298 K (kcal mol^{-1}). Single point solvation energy corrections (CH_3CN, CPCM model) are indicated in parentheses.

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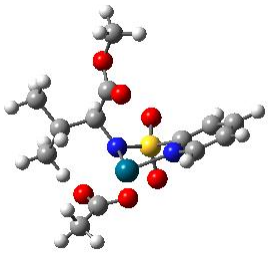
Cartesian coordinates (Å) and energies (hartrees) of all the optimized structures



Ia

E(RB3LYP) = -1593.16778215

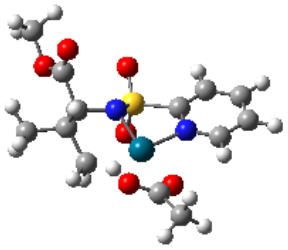
H(correction)= 0.340595

G(correction)= 0.256775
E(RM06) = -1592.89181476

E(CPCM$_{CH3CN}$RM06) = -1592.91606837

Number of imaginary frequencies: 0

46	0	1.08976	-0.65986	0.07095
7	0	-0.55717	-1.83446	-0.21962
7	0	-0.2029	0.64959	0.9613
8	0	2.69072	-1.74973	-0.74558
6	0	-1.66806	-1.52311	0.46631
6	0	-0.58414	-2.83639	-1.11501
6	0	-0.53015	1.93365	0.32481
16	0	-1.42216	-0.1862	1.67358
6	0	3.49298	-0.80933	-0.40927
6	0	-2.87137	-2.18984	0.28291
1	0	0.3465	-3.03564	-1.63538
6	0	-1.74815	-3.56257	-1.34745
6	0	0.7396	2.83401	0.27702
1	0	-1.28276	2.43998	0.93689
6	0	-1.13646	1.74999	-1.07174
8	0	-2.67221	0.58557	1.7312
8	0	-0.93533	-0.87546	2.87203
8	0	2.99847	0.20689	0.18632
6	0	4.95626	-0.88366	-0.72997
6	0	-2.9082	-3.23231	-0.64322
1	0	-3.74256	-1.8836	0.85175
1	0	-1.73916	-4.36683	-2.07505
6	0	1.24927	3.1039	1.69947
6	0	0.48448	4.15433	-0.46808
1	0	1.51229	2.27656	-0.26671
8	0	-0.79775	0.91109	-1.88519
8	0	-2.10875	2.65194	-1.30548
1	0	5.27128	-1.92537	-0.82384
1	0	5.13979	-0.3766	-1.68481
1	0	5.53685	-0.37441	0.04312
1	0	-3.83002	-3.78012	-0.81537
1	0	0.51556	3.68683	2.272
1	0	2.1812	3.67963	1.66348
1	0	1.44017	2.17251	2.23742
1	0	1.38545	4.77692	-0.43326
1	0	-0.33304	4.72188	-0.00712
1	0	0.23174	4.00108	-1.52277
6	0	-2.71886	2.59474	-2.60519
1	0	-1.97331	2.75854	-3.3882
1	0	-3.46451	3.38998	-2.61253
1	0	-3.1935	1.62259	-2.76227



TS(Ia-IIa)

E(RB3LYP) = -1593.1212511

H(correction)= 0.3346451

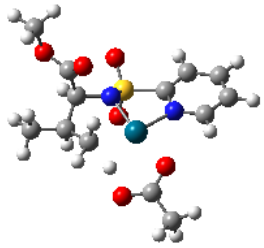
G(correction)= 0.2538001
E(RM06) = -1592.85432077

E(CPCM$_{CH3CN}$RM06) = -1592.87996179

Imaginary frequencies: 1 (-1378.1024 cm^{-1})

46	0	-1.04515	-0.45381	0.18676
7	0	0.89565	0.07143	-0.05792
8	0	-3.09733	-0.86093	0.18115
6	0	1.90354	-0.96581	0.24101
16	0	1.19643	1.55658	0.61474
6	0	-3.38359	-2.03839	-0.21227
6	0	1.25449	-2.32724	-0.06322
1	0	2.21238	-0.94102	1.29555
6	0	3.14039	-0.74943	-0.6418
8	0	2.33695	2.22762	-0.02708
8	0	1.13277	1.58041	2.08797
6	0	-0.31642	2.37159	0.02677
8	0	-2.50097	-2.91652	-0.45104
6	0	-4.83576	-2.39687	-0.41807
6	0	-0.10166	-2.4044	0.66028
6	0	2.17412	-3.4941	0.32982
1	0	1.09476	-2.36095	-1.14778
8	0	3.16023	-0.88184	-1.84515
8	0	4.21042	-0.41521	0.1028
7	0	-1.40356	1.59363	-0.0655
6	0	-0.33617	3.73525	-0.23052

1	0	-1.34013	-2.40525	-0.03994
1	0	-5.49103	-1.63939	0.01451
1	0	-5.03282	-2.4749	-1.49324
1	0	-5.04097	-3.37519	0.02464
1	0	-0.0265	-2.10796	1.71532
1	0	-0.42445	-3.45524	0.70287
1	0	1.70121	-4.45103	0.08169
1	0	2.38373	-3.4908	1.40674
1	0	3.12991	-3.45172	-0.20442
6	0	5.40149	-0.10138	-0.63691
6	0	-2.58154	2.1459	-0.40285
6	0	-1.55619	4.31376	-0.58154
1	0	0.58416	4.30472	-0.1614
1	0	5.70459	-0.94908	-1.25731
1	0	6.16121	0.12063	0.11284
1	0	5.22543	0.76839	-1.27492
1	0	-3.42184	1.46293	-0.45675
6	0	-2.6943	3.5094	-0.6621
1	0	-1.6173	5.37737	-0.79187
1	0	-3.65985	3.92479	-0.93022



TS(Ia-II'a)A

E(RB3LYP) = -1593.119972

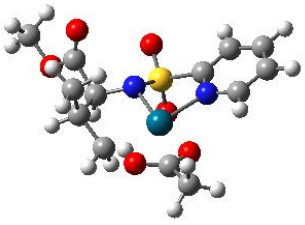
H(correction)= 0.33478701

G(correction)= 0.25385501
E(RM06) = -1592.85277621

E(CPCM$_{CH3CN}$RM06) = -1592.87731963

Imaginary frequencies: 1 (-1388.8455 cm^{-1})

46	0	0.72762	0.64507	-0.1589
7	0	1.74881	-1.17754	-0.3222
7	0	-0.86119	-0.55378	0.17145
6	0	2.92396	-1.36304	-0.94622
6	0	1.08313	-2.23849	0.15711
16	0	-0.43558	-1.85815	1.07798
6	0	-2.1501	0.08274	0.48146
1	0	3.41339	-0.46442	-1.30524
6	0	3.46379	-2.63651	-1.10967
6	0	1.54215	-3.54149	0.02658
8	0	-1.37957	-2.9715	0.8982
8	0	-0.00748	-1.55174	2.45591
1	0	-2.68243	-0.44991	1.275
6	0	-1.88367	1.54348	0.93275
6	0	-3.03138	0.03625	-0.77127
1	0	4.41451	-2.75356	-1.61872
6	0	2.76155	-3.74014	-0.62211
1	0	0.94686	-4.35931	0.41768
6	0	-0.85047	2.1995	-0.00892
6	0	-3.16665	2.3824	1.04851
1	0	-1.4435	1.4555	1.93396
8	0	-2.68075	0.33398	-1.89337
8	0	-4.28586	-0.35013	-0.45934
1	0	3.15728	-4.74362	-0.74764
1	0	-0.88282	3.28902	0.14111
1	0	-1.11111	2.06044	-1.06376
1	0	-3.62082	2.56163	0.06657
1	0	-3.91357	1.89249	1.68356
1	0	-2.93809	3.35884	1.49032
6	0	-5.20878	-0.40316	-1.5597
1	0	-5.31761	0.5836	-2.01832
1	0	-6.15516	-0.73499	-1.13202
1	0	-4.85861	-1.11031	-2.31602
1	0	0.47913	2.53529	0.39468
8	0	1.50432	3.35231	0.62761
6	0	2.49752	2.8693	0.00448
8	0	2.46973	1.7268	-0.55831
6	0	3.77769	3.66734	-0.052
1	0	4.41395	3.32438	-0.86965
1	0	3.55256	4.73084	-0.15994
1	0	4.31582	3.53364	0.89374



TS(Ia-II'a)B

E(RB3LYP) = -1593.11775601

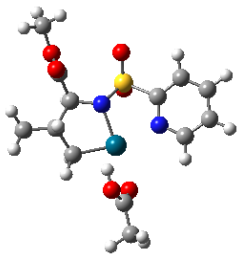
H(correction)= 0.33476001

G(correction)= 0.25410701
E(RM06) = -1592.85191713

Imaginary frequencies: 1 (-1383.4389 cm^{-1})

46	0	-1.00729	-0.44478	0.24066
7	0	0.9314	0.08858	-0.01702
7	0	-1.36921	1.58634	-0.13685
8	0	-3.05791	-0.85179	0.24426
6	0	1.93863	-0.92473	0.33671
16	0	1.18643	1.57946	0.66246
6	0	-0.28834	2.37331	-0.03589
6	0	-2.53121	2.11604	-0.55394
6	0	-3.34547	-2.0634	-0.02202

6	0	1.30274	-2.31385	0.07835
1	0	2.2	-0.88245	1.40266
6	0	3.23092	-0.73018	-0.46756
8	0	2.37195	2.24668	0.10686
8	0	1.01308	1.61052	2.12764
6	0	-0.29759	3.72151	-0.36243
1	0	-3.36874	1.42961	-0.60798
6	0	-2.63366	3.46431	-0.88843
8	0	-2.46429	-2.96521	-0.15706
6	0	-4.79705	-2.4371	-0.20302
6	0	-0.03601	-2.35998	0.8416
6	0	1.12755	-2.67044	-1.40568
1	0	1.97893	-3.057	0.52765
8	0	3.30601	-0.45912	-1.64305
8	0	4.30198	-0.96417	0.32306
6	0	-1.5017	4.27606	-0.79841
1	0	0.61777	4.29709	-0.27933
1	0	-3.58671	3.86187	-1.22067
1	0	-5.45285	-1.64347	0.15811
1	0	-4.98881	-2.60669	-1.26868
1	0	-5.00678	-3.37301	0.32141
1	0	0.05479	-1.99128	1.87101
1	0	-0.34274	-3.41019	0.9545
1	0	-1.30109	-2.41876	0.18175
1	0	0.60203	-3.62874	-1.49472
1	0	0.54079	-1.9083	-1.92774
1	0	2.08943	-2.75887	-1.91714
6	0	5.57798	-0.83425	-0.32365
1	0	-1.55519	5.32718	-1.06588
1	0	5.66192	-1.53874	-1.15593
1	0	6.31989	-1.05546	0.44428
1	0	5.70715	0.18247	-0.70353



IIa

E(RB3LYP) = -1593.14542447

H(correction)= 0.33476001

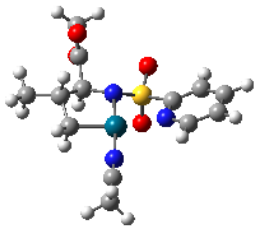
G(correction)= 0.25410701

E(RM06) = -1592.87925388

E(CPCM$_{CH3CN}$RM06) = -1592.90897084

Imaginary frequencies: 0

46	0	1.00265	-0.50314	-0.34178
7	0	-0.90675	0.02456	0.05769
6	0	0.16505	-2.33318	-0.6548
6	0	-1.90519	-1.03067	-0.25095
16	0	-1.24363	1.52509	-0.55394
6	0	-1.20192	-2.36404	0.04679
1	0	0.05477	-2.377	-1.7489
1	0	0.80066	-3.1739	-0.34494
1	0	-2.20919	-1.00086	-1.30654
6	0	-3.14797	-0.84699	0.62744
8	0	-2.3692	2.16329	0.15035
8	0	-1.24041	1.59941	-2.02853
6	0	0.27363	2.37004	-0.00118
6	0	-2.04437	-3.58459	-0.3544
1	0	-1.05088	-2.38995	1.13369
8	0	-3.18043	-1.02512	1.82554
8	0	-4.21275	-0.47846	-0.11025
7	0	1.41084	1.66275	-0.0367
6	0	0.21539	3.71259	0.35449
1	0	-1.49971	-4.51112	-0.13836
1	0	-2.27391	-3.57293	-1.42722
1	0	-2.99023	-3.62082	0.19885
6	0	-5.40231	-0.17582	0.63442
6	0	2.55992	2.28599	0.26826
6	0	1.41223	4.35598	0.66859
1	0	-0.74503	4.21489	0.38615
1	0	-5.71529	-1.03785	1.22989
1	0	-6.15833	0.07468	-0.1103
1	0	-5.22044	0.67408	1.29726
1	0	3.45702	1.6757	0.22522
6	0	2.6054	3.63328	0.61905
1	0	1.41377	5.40482	0.95061
1	0	3.55709	4.09856	0.85381
8	0	3.03815	-1.17577	-0.57198
6	0	3.53085	-1.85418	0.33799
8	0	2.87451	-2.13806	1.45244
6	0	4.91264	-2.43245	0.26607
1	0	1.96667	-1.7357	1.36432
1	0	5.43888	-2.03224	-0.60061
1	0	5.46284	-2.21412	1.18598
1	0	4.83977	-3.52234	0.17797



IIIa

E(RB3LYP) = -1496.82172436

H(correction)= 0.32287636

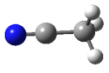
G(correction)= 0.24119436

E(RM06) = -1496.54482205

E(CPCM$_{CH3CN}$RM06) = -1496.57864948

Imaginary frequencies: 0

46	0	-1.08605	-0.7273	0.00247
7	0	0.809	-0.00008	-0.08709
6	0	-0.11521	-2.51248	0.16048
7	0	-2.9136	-1.59859	0.03245
6	0	1.86129	-1.01187	0.17029
16	0	0.95243	1.42977	0.71585
6	0	1.30346	-2.32491	-0.39924
1	0	-0.09556	-2.73468	1.23762
1	0	-0.65227	-3.31743	-0.35555
6	0	-3.93565	-2.13926	0.08755
1	0	2.05628	-1.12702	1.24608
6	0	3.16623	-0.60674	-0.52408
8	0	2.09922	2.22467	0.23921
8	0	0.7623	1.34365	2.17833
6	0	-0.54682	2.22542	0.05177
6	0	2.20998	-3.53296	-0.11557
1	0	1.24341	-2.18284	-1.48545
6	0	-5.21745	-2.83068	0.16449
8	0	3.34309	-0.60307	-1.7228
8	0	4.10867	-0.26587	0.37752
7	0	-1.6175	1.44429	-0.14444
6	0	-0.54745	3.59858	-0.16779
1	0	1.76333	-4.44849	-0.52087
1	0	2.35293	-3.67838	0.96273
1	0	3.19619	-3.41327	-0.57951
1	0	-5.66345	-2.91422	-0.83173
1	0	-5.07417	-3.83631	0.57249
1	0	-5.90415	-2.28101	0.81607
6	0	5.32864	0.24922	-0.1748
6	0	-2.7547	2.01908	-0.56658
6	0	-1.73368	4.19079	-0.59866
1	0	0.36563	4.16224	-0.01206
1	0	5.78768	-0.48028	-0.84785
1	0	5.97673	0.44789	0.67946
1	0	5.1266	1.17162	-0.72549
1	0	-3.59572	1.35049	-0.72376
6	0	-2.85831	3.38853	-0.79869
1	0	-1.77865	5.26043	-0.782
1	0	-3.7993	3.80983	-1.1372



CH_3CN

E(RB3LYP) = -132.754928457

H(correction)= 0.050178457

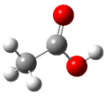
G(correction)= 0.022660457

E(RM06) = -132.70086471

E(CPCM$_{CH3CN}$RM06) = -132.70965107

Imaginary frequencies: 0

6	0	0.	0.	-1.18097
1	0	0.	1.02651	-1.56112
1	0	-0.88898	-0.51325	-1.56112
1	0	0.88898	-0.51325	-1.56112
6	0	0.	0.	0.28056
7	0	0.	0.	1.44083



CH_3CO_2H

E(RB3LYP) = -229.081787249

H(correction)= 0.067541249

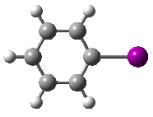
G(correction)= 0.034759249

E(RM06) = -229.04378443

E(CPCM$_{CH3CN}$RM06) = -229.05117636

Imaginary frequencies: 0

1	0	1.72374	-0.80245	0.
6	0	0.09225	0.12593	-0.00001
8	0	0.64501	1.20234	0.
8	0	0.77906	-1.04656	0.
6	0	-1.39725	-0.11036	0.
1	0	-1.68425	-0.69194	0.88225
1	0	-1.91786	0.84739	-0.00041
1	0	-1.68417	-0.69265	-0.88181



PhI

E(RB3LYP) = -243.053411112

H(correction)= 0.097117112

G(correction)= 0.058490112

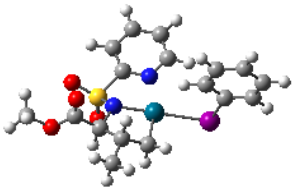
E(RM06) = -242.91706348

E(CPCM$_{CH3CN}$RM06) = -242.920334783

Imaginary frequencies: 0

6	0	-0.58713	-0.00013	-0.00014
6	0	-1.26742	1.21658	-0.00003
6	0	-2.66504	1.20748	-0.00004
6	0	-3.365	-0.0001	-0.00004
6	0	-2.66523	-1.20747	0.00008
6	0	-1.26731	-1.21629	-0.00007
1	0	-0.72559	2.1558	0.00015
1	0	-3.20289	2.15178	0.00023

1	0	-4.45127	-0.00004	0.00024
1	0	-3.20291	-2.15187	0.00027
1	0	-0.72563	-2.15557	-0.00018
53	0	1.57002	-0.00001	0.00001



IVa

E(RB3LYP) = -1607.10306341

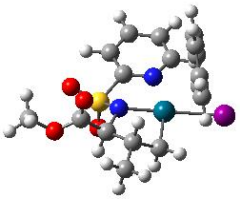
H(correction)= 0.36947541

G(correction)= 0.27775241
E(RM06) = -1606.74968851

E($CPCM_{CH3CN}$RM06) = -1606.77769258

Imaginary frequencies: 0

46	0	0.05658	0.03744	-0.57215
7	0	-1.86182	-0.17484	0.07725
6	0	-0.20169	-1.90531	-1.12505
53	0	2.69529	0.12354	-1.31587
6	0	-2.49627	-1.45937	-0.30224
16	0	-2.73704	1.18646	-0.25238
6	0	-1.35573	-2.48818	-0.29675
1	0	-0.46201	-1.84824	-2.19282
1	0	0.71368	-2.50034	-1.01987
6	0	3.66226	-0.6313	0.47407
1	0	-2.94638	-1.40971	-1.3035
6	0	-3.58435	-1.8284	0.71209
8	0	-3.93018	1.28995	0.607
8	0	-2.91821	1.47186	-1.68986
6	0	-1.53234	2.40458	0.36562
6	0	-1.79221	-3.87482	-0.79477
1	0	-1.03638	-2.58022	0.74936
6	0	5.05008	-0.73861	0.48134
6	0	2.8784	-0.99234	1.56548
8	0	-3.3814	-2.10854	1.87337
8	0	-4.80313	-1.82739	0.13799
7	0	-0.2355	2.15295	0.13764
6	0	-1.99618	3.5599	0.98414
1	0	-0.9427	-4.56761	-0.7859
1	0	-2.17439	-3.8259	-1.822
1	0	-2.57499	-4.30335	-0.15776
6	0	5.67139	-1.22694	1.6349
1	0	5.64308	-0.45389	-0.38174
6	0	3.52034	-1.47877	2.70923
1	0	1.79655	-0.90248	1.52973
6	0	-5.90231	-2.07262	1.02804
6	0	0.66352	3.07451	0.51905
6	0	-1.05715	4.51544	1.37094
1	0	-3.05977	3.68069	1.15672
6	0	4.91048	-1.59589	2.74575
1	0	6.75389	-1.31702	1.65693
1	0	2.92183	-1.76589	3.56921
1	0	-5.79054	-3.04139	1.52285
1	0	-6.79505	-2.05937	0.40205
1	0	-5.9523	-1.28534	1.78469
1	0	1.70435	2.83381	0.32491
6	0	0.29539	4.27053	1.13153
1	0	-1.37551	5.43353	1.85615
1	0	5.4006	-1.97511	3.63765
1	0	1.05859	4.98645	1.41853



TS(IVa-Va)

E(RB3LYP) = -1607.08163381

H(correction)= 0.36826181

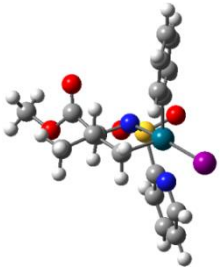
G(correction)= 0.28094781
E(RM06) = -1606.73023583

E($CPCM_{CH3CN}$RM06) = -1606.75687941

Imaginary frequencies: 1 (-163.5906 cm^{-1})

7	0	-1.53375	0.06562	-0.12699
6	0	-2.35017	-1.06955	-0.62168
16	0	-2.16242	1.55906	-0.43468
46	0	0.47403	-0.04712	-0.56852
6	0	-1.38842	-2.26376	-0.70935
1	0	-2.77079	-0.86217	-1.61533
6	0	-3.50013	-1.34951	0.35251
8	0	-3.35461	1.83137	0.38748
8	0	-2.24626	1.89517	-1.87045
6	0	-0.81677	2.58739	0.23612
53	0	3.12245	-0.34441	-1.0731
6	0	2.00503	-1.03262	0.94183
6	0	-0.14409	-1.78253	-1.45485
6	0	-2.02194	-3.50095	-1.36649
1	0	-1.11635	-2.51856	0.32273
8	0	-3.36399	-1.79405	1.47165
8	0	-4.68962	-1.05574	-0.20463
7	0	0.44033	2.14953	0.09598
6	0	-1.14391	3.8352	0.75916
6	0	1.86146	-2.41252	1.09789
6	0	2.12071	-0.18143	2.0423
1	0	-0.38066	-1.44205	-2.47265
1	0	0.64212	-2.54144	-1.50935

1	0	-1.29648	-4.32102	-1.4196
1	0	-2.35789	-3.2823	-2.38746
1	0	-2.88352	-3.8585	-0.7908
6	0	-5.82665	-1.18745	0.66232
6	0	1.44018	2.97998	0.43516
6	0	-0.10137	4.68557	1.12229
1	0	-2.18721	4.10871	0.87024
6	0	1.73692	-2.93108	2.3887
1	0	1.83682	-3.07462	0.24176
6	0	1.98972	-0.72233	3.32502
1	0	2.29103	0.88011	1.91918
1	0	-5.90431	-2.20887	1.04476
1	0	-6.69274	-0.93707	0.04919
1	0	-5.73763	-0.49348	1.50208
1	0	2.44624	2.59903	0.28454
6	0	1.21485	4.25617	0.94482
1	0	-0.31197	5.66904	1.53222
6	0	1.79299	-2.09173	3.50323
1	0	1.60145	-4.00195	2.51394
1	0	2.05058	-0.05907	4.18363
1	0	2.05643	4.89189	1.19973
1	0	1.69769	-2.50452	4.50289



Va

E(RB3LYP) = -1607.116188

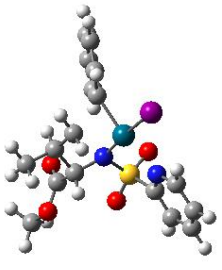
H(correction)= 0.370221

G(correction)= 0.28299
E(RM06) = -1606.75335971

E(CPCM$_{CH3CN}$RM06) = -1606.78200382

Imaginary frequencies: 0

46	0	0.7275	0.07011	0.06862
7	0	-1.26403	-0.42177	0.43198
6	0	0.1932	-0.43985	-1.85988
53	0	3.21056	0.89856	-0.44722
6	0	1.33728	-1.81743	0.46127
16	0	-1.8355	0.69246	1.49175
6	0	-2.04252	-0.61632	-0.80501
6	0	-1.07352	-1.28193	-1.79797
1	0	0.04276	0.5519	-2.29784
1	0	1.04383	-0.94096	-2.32016
6	0	2.1823	-2.57778	-0.34765
6	0	0.88365	-2.30403	1.69032
6	0	-1.36177	2.27233	0.71194
8	0	-0.99899	0.60624	2.69807
8	0	-3.30045	0.67859	1.57995
1	0	-2.40079	0.33163	-1.23457
6	0	-3.25792	-1.5149	-0.54587
6	0	-1.66414	-1.45104	-3.20984
1	0	-0.82671	-2.26813	-1.3915
6	0	2.5831	-3.846	0.08707
1	0	2.5613	-2.19357	-1.28833
6	0	1.30879	-3.56778	2.11785
1	0	0.20223	-1.7269	2.30529
7	0	-0.1814	2.2255	0.07976
6	0	-2.13438	3.42106	0.81903
8	0	-3.21617	-2.5893	0.00639
8	0	-4.37299	-0.97117	-1.07199
1	0	-0.93054	-1.9079	-3.88283
1	0	-1.96571	-0.48713	-3.63667
1	0	-2.54399	-2.10281	-3.18695
6	0	2.15088	-4.34081	1.31853
1	0	3.24926	-4.43504	-0.53832
1	0	0.9583	-3.94654	3.07435
6	0	0.29882	3.35166	-0.4684
6	0	-1.63546	4.59109	0.2426
1	0	-3.08875	3.38426	1.33252
6	0	-5.57674	-1.73286	-0.87338
1	0	2.46832	-5.32487	1.65242
1	0	1.26612	3.26738	-0.95448
6	0	-0.40047	4.55707	-0.40537
1	0	-2.20286	5.51546	0.30043
1	0	-5.48342	-2.72502	-1.32314
1	0	-6.36789	-1.16148	-1.35943
1	0	-5.77959	-1.84127	0.1949
1	0	0.02165	5.44682	-0.86056



TS(Va-VIa)

E(RB3LYP) = -1607.09125609

H(correction)= 0.36938409

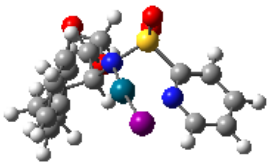
G(correction)= 0.28397409
E(RM06) = -1606.7362655

E(CPCM$_{CH3CN}$RM06) = -1606.76184266

Imaginary frequencies: 1 (-338.4843 cm^{-1})

46	0	-0.69767	0.08003	0.00369

7	0	1.32171	-0.24219	-0.34208
6	0	-0.23344	-1.49584	1.53944
53	0	-3.27327	0.70638	0.58705
6	0	-1.12317	-1.96063	-0.33714
16	0	1.94732	0.94052	-1.29078
6	0	2.05437	-0.66826	0.85753
6	0	1.24558	-1.84028	1.45876
1	0	-0.43722	-0.63553	2.18921
1	0	-0.84487	-2.32246	1.88404
6	0	-0.31346	-2.48527	-1.35957
6	0	-2.36504	-2.56248	-0.06064
6	0	1.11394	2.42134	-0.65669
8	0	1.44154	0.77608	-2.65557
8	0	3.3854	1.12927	-1.04588
1	0	2.16042	0.13439	1.60277
6	0	3.45543	-1.18754	0.49427
6	0	1.74711	-2.23334	2.86191
1	0	1.37691	-2.69331	0.78607
1	0	0.65851	-2.05649	-1.56416
6	0	-0.77743	-3.55657	-2.13023
6	0	-2.80931	-3.63351	-0.83126
1	0	-2.98203	-2.20154	0.75293
7	0	-0.11877	2.21272	-0.16298
6	0	1.71618	3.67073	-0.72414
8	0	3.67283	-2.02579	-0.35035
8	0	4.39191	-0.64939	1.29545
1	0	1.18614	-3.09113	3.2477
1	0	1.63885	-1.40607	3.57334
1	0	2.80525	-2.5135	2.83173
6	0	-2.02127	-4.13051	-1.87421
1	0	-0.15059	-3.93663	-2.93227
1	0	-3.77399	-4.08216	-0.60976
6	0	-0.8131	3.27865	0.27733
6	0	0.99273	4.77184	-0.26797
1	0	2.72339	3.7549	-1.11703
6	0	5.74274	-1.05538	1.01195
1	0	-2.37216	-4.96697	-2.47248
1	0	-1.80358	3.07079	0.6644
6	0	-0.29149	4.56946	0.23569
1	0	1.42463	5.76774	-0.30353
1	0	5.84409	-2.14085	1.09229
1	0	6.36093	-0.55292	1.75625
1	0	6.02025	-0.74085	0.00292
1	0	-0.89257	5.39529	0.60116



VIa

E(RB3LYP) = -1607.15051864

H(correction)= 0.37203264

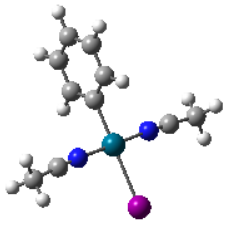
G(correction)= 0.28667764
E(RM06) = -1606.79907138

E($CPCM_{CH3CN}$RM06) = -1606.82562291

Imaginary frequencies: 0

46	0	0.69005	0.05051	0.12194
7	0	-1.33487	-0.34857	0.48441
53	0	3.26893	0.76661	-0.19363
16	0	-1.8649	0.99627	1.26178
6	0	-2.17054	-0.98903	-0.54218
6	0	-1.17893	2.30681	0.20881
8	0	-1.15318	1.109	2.53827
8	0	-3.32414	1.16596	1.2154
6	0	-1.63084	-2.40863	-0.8839
1	0	-2.22451	-0.39409	-1.467
6	0	-3.60765	-1.1903	-0.01587
7	0	0.0142	2.00766	-0.33459
6	0	-1.84171	3.50466	-0.01773
6	0	-0.18207	-2.45297	-1.40749
6	0	-2.54031	-3.06823	-1.94051
1	0	-1.70168	-2.99475	0.03991
8	0	-3.89135	-1.85897	0.95091
8	0	-4.50483	-0.59889	-0.8261
6	0	0.60018	2.91092	-1.14386
6	0	-1.23097	4.44529	-0.84673
1	0	-2.80993	3.66856	0.44206
1	0	-0.05067	-1.69353	-2.19247
1	0	-0.06374	-3.41455	-1.92533
6	0	0.98699	-2.37005	-0.43004
1	0	-2.20847	-4.09278	-2.1394
1	0	-2.51283	-2.51592	-2.88841
1	0	-3.58181	-3.12095	-1.6124
6	0	-5.86902	-0.67834	-0.37868
1	0	1.56218	2.63197	-1.5543
6	0	0.00426	4.13986	-1.41711
1	0	-1.71375	5.39697	-1.04855
6	0	2.25949	-2.76076	-0.91962
6	0	0.86946	-2.12483	0.96761
1	0	-6.18363	-1.72055	-0.27829
1	0	-6.45761	-0.17005	-1.14308
1	0	-5.96897	-0.17528	0.58615
1	0	0.51301	4.83852	-2.07265
1	0	2.37472	-2.95369	-1.98324

6	0	3.33214	-2.9465	-0.06815
6	0	1.99387	-2.28904	1.82269
1	0	-0.10899	-2.02648	1.42402
6	0	3.20564	-2.70822	1.31543
1	0	4.28604	-3.27447	-0.47143
1	0	1.86673	-2.10719	2.88563
1	0	4.0593	-2.84986	1.97099



PhPdI(CH$_3$CN)$_2$

E(RB3LYP) = -636.568919818

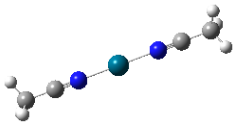
H(correction)= 0.204677818

G(correction)= 0.132530818
E(RM06) = -636.298758524

E(CPCM$_{CH3CN}$RM06) = -636.327034263

Imaginary frequencies: 0

6	0	0.00387	-3.15074	-0.00104
7	0	0.0593	-1.99851	0.00035
6	0	-0.10146	-4.60359	-0.00311
1	0	-1.05979	-4.90212	-0.43965
1	0	0.7128	-5.0406	-0.58919
1	0	-0.04538	-4.9817	1.02244
53	0	-2.74966	0.00006	0.
46	0	0.03766	0.	-0.00002
6	0	2.07137	-0.00005	-0.00002
6	0	2.77918	0.00599	-1.20801
6	0	2.77915	-0.00611	1.208
6	0	4.17929	0.00589	-1.20647
1	0	2.24636	0.01085	-2.15636
6	0	4.17926	-0.00608	1.2065
1	0	2.2463	-0.01095	2.15633
6	0	4.88212	-0.00012	0.00002
1	0	4.71795	0.01061	-2.15172
1	0	4.71789	-0.01084	2.15177
1	0	5.96918	-0.00015	0.00004
6	0	0.00409	3.15074	0.00105
7	0	0.05943	1.9985	-0.00037
6	0	-0.1011	4.6036	0.00318
1	0	-0.04391	4.98183	-1.02227
1	0	-1.05984	4.9022	0.43878
1	0	0.71262	5.04044	0.59014



Pd(CH$_3$CN)$_2$

E(RB3LYP) = -393.47569626

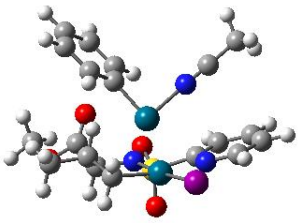
H(correction)= 0.10529126

G(correction)= 0.05502326
E(RM06) = -393.34937632

E(CPCM$_{CH3CN}$RM06) = -393.367868915

Imaginary frequencies: 0

46	0	-0.00001	0.00135	-0.00006
7	0	1.97976	0.00044	-0.00198
7	0	-1.97976	0.00156	0.00173
6	0	3.14009	-0.00041	0.00007
6	0	-3.14008	-0.00055	-0.00017
6	0	4.59827	-0.00346	0.00078
6	0	-4.59825	-0.00376	-0.00029
1	0	4.97935	0.5124	0.88848
1	0	4.97609	-1.03137	0.0047
1	0	4.97992	0.50591	-0.89039
1	0	-4.9765	-0.83907	0.59849
1	0	-4.9805	0.93113	0.42298
1	0	-4.97826	-0.10602	-1.02225



VIIa

E(RB3LYP) = -1867.85972989

H(correction)= 0.42447989

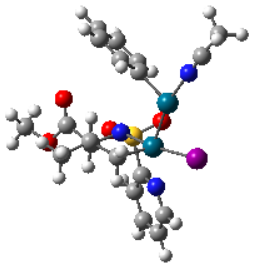
G(correction)= 0.31592989
E(RM06) = -1867.42949169

E(CPCM$_{CH3CN}$RM06) = -1867.46830216

Imaginary frequencies: 0

7	0	0.35252	-2.25828	1.0465
6	0	-0.55946	-2.91708	1.77848
6	0	1.60406	-2.17174	1.51285
1	0	-1.5605	-2.95699	1.36027
6	0	-0.24011	-3.50967	2.99934
6	0	2.01374	-2.71235	2.72607
16	0	2.83583	-1.40076	0.41699
1	0	-1.00544	-4.04009	3.55645
6	0	1.06435	-3.39981	3.48293
1	0	3.0405	-2.58352	3.04966
8	0	3.89893	-0.86377	1.28495
8	0	3.22096	-2.43635	-0.56405

7	0	1.88812	-0.19407	-0.21454
1	0	1.33909	-3.84198	4.43627
6	0	2.52985	0.59003	-1.30301
46	0	0.06364	-0.94539	-0.76254
1	0	3.03807	-0.06684	-2.02282
6	0	1.38743	1.33706	-2.00534
6	0	3.5634	1.55842	-0.71618
6	0	0.30264	0.31013	-2.35108
53	0	-2.50395	-1.68617	-1.39546
46	0	-1.88767	0.66137	0.09045
6	0	1.85773	2.11623	-3.24394
1	0	0.98985	2.05114	-1.27549
8	0	3.30403	2.54715	-0.06643
8	0	4.81492	1.17306	-1.03598
1	0	0.6383	-0.40285	-3.12086
1	0	-0.62617	0.77686	-2.69108
7	0	-3.63488	1.53009	0.65389
6	0	-0.90646	2.13728	0.99207
1	0	1.00758	2.61039	-3.72848
1	0	2.32406	1.45167	-3.98216
1	0	2.58234	2.89285	-2.97281
6	0	5.86853	1.94742	-0.44437
6	0	-4.64263	1.99822	0.97252
6	0	-1.00599	3.44205	0.50297
6	0	-0.08837	1.84307	2.08438
1	0	5.77959	3.00025	-0.72603
1	0	6.79604	1.52164	-0.82817
1	0	5.82855	1.85985	0.64454
6	0	-5.91539	2.58586	1.372
6	0	-0.24257	4.45692	1.09387
1	0	-1.65468	3.67346	-0.33817
6	0	0.6667	2.86661	2.66806
1	0	-0.00331	0.82841	2.46118
1	0	-6.54706	1.82543	1.84183
1	0	-5.74357	3.39771	2.08558
1	0	-6.43423	2.98563	0.49506
6	0	0.59123	4.17049	2.17504
1	0	-0.30406	5.46953	0.70217
1	0	1.3258	2.63362	3.50029
1	0	1.1873	4.95812	2.62733



VIIIa

E(RB3LYP) = -1867.84942489

H(correction)= 0.42427489

G(correction)= 0.31303089

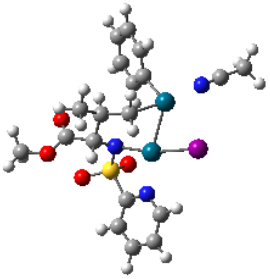
E(RM06) = -1867.41931252

E(CPCM$_{CH3CN}$RM06) = -1867.45689247

Imaginary frequencies: 0

46	0	0.18435	-0.89622	-0.16323
7	0	1.46443	0.65091	0.23529
6	0	0.33461	-0.1562	-2.05758
53	0	-1.73605	-2.77114	-0.54605
16	0	2.40723	0.2179	1.49878
6	0	2.09728	1.20612	-0.97398
6	0	0.96216	1.23601	-2.01351
1	0	1.00136	-0.91182	-2.49593
1	0	-0.63666	-0.18245	-2.55561
46	0	-2.2855	-0.02323	0.06365
6	0	3.24673	-1.31802	0.97667
8	0	1.48487	-0.20156	2.56975
8	0	3.47107	1.19901	1.76317
1	0	2.91693	0.57214	-1.34778
6	0	2.6543	2.61195	-0.72603
6	0	1.42509	1.6766	-3.41237
1	0	0.22057	1.9507	-1.64027
7	0	-4.28357	0.21246	0.41617
6	0	-2.02893	1.92235	0.39446
7	0	2.44861	-2.19046	0.35896
6	0	4.59286	-1.54277	1.24618
8	0	2.00949	3.55751	-0.33569
8	0	3.96099	2.67533	-1.06197
1	0	0.58698	1.65659	-4.11817
1	0	2.21015	1.01662	-3.80166
1	0	1.8169	2.69989	-3.39359
6	0	-5.40116	0.31866	0.69237
6	0	-2.61167	2.85139	-0.47237
6	0	-1.25591	2.34093	1.47997
6	0	2.96977	-3.36441	-0.01661
6	0	5.12996	-2.76958	0.85064
1	0	5.18142	-0.77883	1.74132
6	0	4.58595	3.94774	-0.83342
6	0	-6.80875	0.45075	1.0475
6	0	-2.39276	4.21946	-0.26339
1	0	-3.2249	2.52409	-1.30852
6	0	-1.04992	3.71103	1.67918
1	0	-0.7786	1.62277	2.13911
1	0	2.29091	-4.05214	-0.5146
6	0	4.30678	-3.69769	0.2123
1	0	6.17593	-2.99623	1.03758
1	0	4.08044	4.73445	-1.40034
1	0	5.6172	3.83328	-1.16932
1	0	4.55294	4.19541	0.2307

1	0	-7.0673	-0.27789	1.82232
1	0	-7.00342	1.45853	1.42745
1	0	-7.43676	0.27297	0.16893
6	0	-1.61589	4.64886	0.81303
1	0	-2.83577	4.94295	-0.94432
1	0	-0.42604	4.03727	2.50702
1	0	4.68848	-4.66172	-0.10867
1	0	-1.4433	5.70991	0.97196



IXa

E(RB3LYP) = -1867.84600384

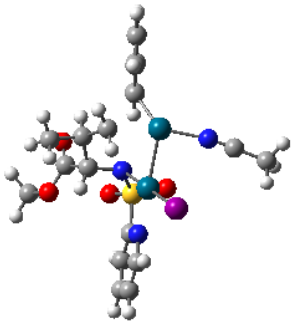
H(correction)= 0.42425484

G(correction)= 0.31738484
E(RM06) = -1867.41952798

E(CPCM$_{CH3CN}$RM06) = -1867.45449802

Imaginary frequencies: 0

7	0	1.93004	-2.16255	0.42141
6	0	2.09085	-3.45885	0.09686
6	0	2.94966	-1.5049	0.99868
1	0	1.2382	-3.94146	-0.36694
6	0	3.2855	-4.12955	0.34399
6	0	4.17958	-2.09367	1.26216
16	0	2.57076	0.21541	1.46269
1	0	3.37527	-5.17576	0.07144
6	0	4.34736	-3.43745	0.92926
1	0	4.96935	-1.49901	1.70811
8	0	1.91643	0.10476	2.77067
8	0	3.83284	0.95993	1.33525
7	0	1.44105	0.6538	0.3475
1	0	5.29243	-3.93708	1.12116
6	0	1.85094	1.32989	-0.90104
46	0	0.26205	-0.95898	-0.05051
1	0	2.40559	0.65476	-1.56971
6	0	0.58269	1.86106	-1.62906
6	0	2.74867	2.54376	-0.60067
53	0	-1.63666	-2.70642	-0.89553
6	0	-0.5112	0.80633	-1.8702
6	0	0.97903	2.48315	-2.98544
1	0	0.18515	2.65395	-0.99123
8	0	2.42974	3.48315	0.09049
8	0	3.9111	2.46122	-1.27965
1	0	-0.11504	-0.06395	-2.40817
1	0	-1.27915	1.24459	-2.52946
46	0	-2.00137	0.24218	-0.47977
1	0	0.09932	2.91899	-3.47125
1	0	1.39685	1.72776	-3.66334
1	0	1.72032	3.2817	-2.87233
6	0	4.83334	3.53404	-1.03168
6	0	-2.00047	2.1073	0.24642
7	0	-3.72284	-0.19193	0.75319
1	0	4.38534	4.49758	-1.28945
1	0	5.69779	3.32975	-1.66453
1	0	5.11947	3.54056	0.02316
6	0	-2.88163	3.01009	-0.35761
6	0	-1.26436	2.4774	1.37395
6	0	-4.56618	-0.42308	1.50867
6	0	-3.02949	4.29669	0.17735
1	0	-3.45585	2.72916	-1.23818
6	0	-1.42318	3.76551	1.89949
1	0	-0.55089	1.79519	1.82268
6	0	-5.6187	-0.72339	2.47149
6	0	-2.30192	4.67463	1.30668
1	0	-3.71319	4.99767	-0.29635
1	0	-0.84019	4.05618	2.76977
1	0	-5.59546	-1.78728	2.72708
1	0	-5.46791	-0.13403	3.38126
1	0	-6.59744	-0.47952	2.0471
1	0	-2.41218	5.67497	1.71713



TS(IXa-Xa)

E(RB3LYP) = -1867.81498794

H(correction)= 0.42332794

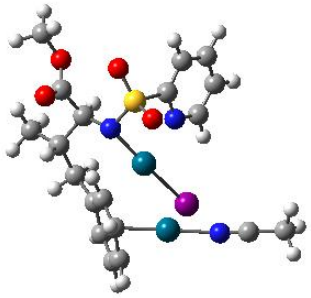
G(correction)= 0.31874294
E(RM06) = -1867.39746496

E(CPCM$_{CH3CN}$RM06) = -1867.43146086

Imaginary frequencies: 1 (-338.3831 cm^{-1})

7	0	2.54349	-0.9482	0.16587
6	0	3.39414	-1.84107	-0.37024
6	0	3.0387	0.04339	0.92691
1	0	2.94303	-2.62117	-0.97324
6	0	4.76776	-1.76225	-0.15024

6	0	4.39321	0.20241	1.18463
16	0	1.77112	1.1646	1.59786
1	0	5.4205	-2.50397	-0.5984
6	0	5.27634	-0.72799	0.63597
1	0	4.7244	1.03836	1.79073
8	0	1.1936	0.46747	2.75254
8	0	2.43502	2.46043	1.80317
7	0	0.63769	1.17073	0.39913
1	0	6.34431	-0.64412	0.81536
6	0	0.84938	1.96887	-0.83471
46	0	0.42727	-0.83349	-0.09962
1	0	1.54358	1.44613	-1.50815
6	0	-0.49496	2.22179	-1.57881
6	0	1.46046	3.3578	-0.54816
53	0	0.07486	-3.34226	-1.03905
46	0	-2.14334	-0.38707	-0.15266
6	0	-1.47434	1.03952	-1.66481
6	0	-0.1798	2.69103	-3.01547
1	0	-0.97584	3.05184	-1.05742
8	0	0.85572	4.29986	-0.09123
8	0	2.74808	3.4041	-0.9468
7	0	-2.43295	-1.98131	1.15335
1	0	-0.94369	0.1477	-2.05299
1	0	-2.25929	1.26223	-2.38845
1	0	-1.09531	3.00456	-3.52847
1	0	0.28084	1.88828	-3.60533
1	0	0.50569	3.54613	-3.01589
6	0	3.4338	4.6284	-0.63387
6	0	-2.43207	-2.88296	1.87584
1	0	2.92325	5.48202	-1.08698
1	0	4.43701	4.51623	-1.0466
1	0	3.47147	4.75984	0.4502
6	0	-2.38358	-4.03936	2.75807
1	0	-1.75686	-4.80914	2.29534
1	0	-1.95029	-3.75518	3.72204
1	0	-3.38919	-4.43984	2.91849
6	0	-2.83105	1.51208	-0.11993
6	0	-4.12894	1.61038	-0.6465
6	0	-2.41751	2.35165	0.92119
6	0	-5.03705	2.508	-0.07176
1	0	-4.43566	1.00265	-1.49341
6	0	-3.33367	3.24812	1.47488
1	0	-1.39874	2.29497	1.29008
6	0	-4.64203	3.32676	0.98601
1	0	-6.04493	2.57639	-0.47349
1	0	-3.01724	3.889	2.29368
1	0	-5.34325	4.03552	1.41787



Xa

E(RB3LYP) = -1867.86284198

H(correction)= 0.42607398

G(correction)= 0.31967098

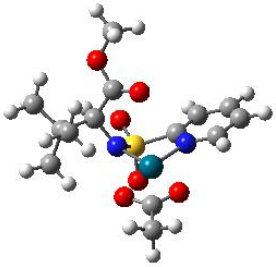
E(RM06) = -1867.45367684

E(CPCM$_{CH3CN}$RM06) = -1867.48711042

Imaginary frequencies: 0

7	0	-0.77231	2.00879	-0.70571
6	0	-0.4026	2.84397	-1.6936
6	0	-1.75341	2.3995	0.12519
1	0	0.39055	2.48956	-2.34145
6	0	-1.00087	4.09041	-1.86588
6	0	-2.41019	3.61847	0.01912
16	0	-2.17378	1.18838	1.41239
1	0	-0.66913	4.72884	-2.67809
6	0	-2.01881	4.48702	-0.99911
1	0	-3.20747	3.85206	0.71586
8	0	-1.14835	1.34074	2.44949
8	0	-3.58587	1.43439	1.74403
7	0	-1.92154	-0.23098	0.63255
1	0	-2.5045	5.45132	-1.11805
6	0	-2.99364	-0.80896	-0.19991
46	0	-0.05696	-0.00752	-0.30029
1	0	-3.18384	-0.20798	-1.10263
6	0	-2.66184	-2.27183	-0.63393
6	0	-4.30549	-0.89108	0.60911
53	0	2.16483	0.38037	-1.82513
46	0	2.66843	-0.78822	1.2486
6	0	-1.35767	-2.47245	-1.43716
6	0	-3.82602	-2.8239	-1.48298
1	0	-2.60779	-2.8614	0.28893
8	0	-4.44538	-1.54414	1.61718
8	0	-5.29494	-0.2108	-0.0016
7	0	4.00225	0.79496	1.50589
1	0	-1.31961	-1.75292	-2.26781
1	0	-1.43871	-3.45584	-1.92091
6	0	-0.01891	-2.47957	-0.70391
1	0	-3.64548	-3.87449	-1.73408
1	0	-3.92919	-2.26699	-2.42301
1	0	-4.78277	-2.77433	-0.95628
6	0	-6.53682	-0.17211	0.72061
6	0	4.65547	1.73741	1.67025

6	0	1.11006	-3.0219	-1.37232
6	0	0.12462	-2.15251	0.66905
1	0	-6.91463	-1.18293	0.89641
1	0	-7.22494	0.39203	0.09005
1	0	-6.38879	0.33097	1.67932
6	0	5.47615	2.92763	1.86083
6	0	2.29415	-3.28185	-0.70427
1	0	1.02906	-3.25924	-2.42966
6	0	1.35116	-2.43449	1.38127
1	0	-0.75385	-1.97018	1.2749
1	0	5.62912	3.43321	0.90194
1	0	4.98053	3.61938	2.54948
1	0	6.45142	2.65449	2.27637
6	0	2.43515	-3.02629	0.68263
1	0	3.12722	-3.71818	-1.24888
1	0	1.27775	-2.51981	2.46569
1	0	3.27632	-3.45293	1.22115



Ib

E(RB3LYP) = -1632.4749979

H(correction)= 0.3698119

G(correction)= 0.2830189
E(RM06) = -1632.18285445

E(CPCM$_{CH3CN}$RM06) = -1632.20643337

Number of imaginary frequencies: 0

46	0	-0.83249	0.99464	-0.03974
7	0	-1.88903	-0.73488	0.22708
7	0	0.58723	-0.21327	-0.89918
8	0	-2.08302	2.49705	0.72389
6	0	-1.51887	-1.79383	-0.50999
6	0	-2.87291	-0.86159	1.13277
6	0	1.87104	-0.56109	-0.27518
16	0	-0.20509	-1.40387	-1.703
6	0	-1.23569	3.38648	0.36061
6	0	-2.10614	-3.04349	-0.37072
1	0	-3.1224	0.03195	1.69475
6	0	-3.5211	-2.07827	1.32434
6	0	2.97143	0.56684	-0.43693
1	0	2.25583	-1.43491	-0.80989
6	0	1.68478	-0.99919	1.18503
8	0	0.60779	-2.61916	-1.86481
8	0	-0.91903	-0.8497	-2.85724
8	0	-0.15878	2.98531	-0.1965
6	0	-1.51435	4.84775	0.54995
6	0	-3.13031	-3.18421	0.56625
1	0	-1.75545	-3.86874	-0.98076
1	0	-4.31269	-2.15105	2.06221
6	0	2.81995	1.21457	-1.82619
6	0	4.36847	-0.08722	-0.35819
6	0	2.86283	1.64779	0.65594
8	0	0.74653	-0.7098	1.90245
8	0	2.70222	-1.78088	1.60137
1	0	-2.21826	4.99687	1.37185
1	0	-0.58315	5.38813	0.73717
1	0	-1.96101	5.24675	-0.36856
1	0	-3.61749	-4.14489	0.70514
1	0	2.8564	0.46173	-2.62222
1	0	3.64451	1.91938	-1.98956
1	0	1.87647	1.75602	-1.92242
1	0	5.14196	0.6783	-0.49142
1	0	4.49992	-0.83553	-1.14947
1	0	4.54114	-0.57926	0.60245
1	0	1.8882	2.14222	0.64846
1	0	3.03256	1.2315	1.65681
1	0	3.62675	2.41717	0.49047
6	0	2.63044	-2.2298	2.96536
1	0	2.61333	-1.37806	3.65045
1	0	3.52674	-2.83059	3.12101
1	0	1.7322	-2.83261	3.12242

TS(Ib-IIb)

E(RB3LYP) = -1632.43100545

H(correction)= 0.36389345

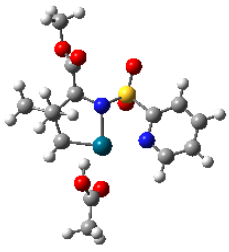
G(correction)= 0.28093245
E(RM06) = -1632.14929741

E(CPCM$_{CH3CN}$RM06) = -1632.17518111

Imaginary frequencies: 1 (-1380.8234 cm^{-1})

46	0	-1.04529	-0.45702	0.22611
7	0	0.82122	0.28035	-0.0453
7	0	-1.62774	1.53165	-0.0996
6	0	1.94113	-0.62389	0.26759
16	0	0.92884	1.77699	0.65997
6	0	-0.63356	2.42523	0.0016
6	0	-2.8458	1.94405	-0.48801
6	0	1.46758	-2.08525	-0.00526
1	0	2.2166	-0.57033	1.32955

6	0	3.18197	-0.23994	-0.55183
8	0	2.02727	2.57467	0.09611
8	0	0.78165	1.76519	2.12814
6	0	-0.78941	3.77115	-0.29638
1	0	-3.60717	1.17404	-0.54404
6	0	-3.09446	3.28017	-0.79316
6	0	0.13398	-2.25833	0.76198
6	0	2.5087	-3.07149	0.56512
6	0	1.2598	-2.37348	-1.50503
8	0	3.20953	-0.01938	-1.74043
8	0	4.27435	-0.215	0.24335
6	0	-2.05219	4.20427	-0.70294
1	0	0.06166	4.43832	-0.21493
1	0	-4.0892	3.58189	-1.10329
1	0	0.20094	-1.90104	1.79785
1	0	-0.06921	-3.33525	0.86379
1	0	2.17915	-4.10385	0.39861
1	0	2.64871	-2.92925	1.64314
1	0	3.48485	-2.95258	0.08175
1	0	2.20849	-2.37527	-2.04796
1	0	0.79175	-3.35794	-1.62712
1	0	0.61214	-1.62465	-1.96965
6	0	5.4984	0.15332	-0.41235
1	0	-2.21982	5.24885	-0.94789
1	0	5.73476	-0.55276	-1.21329
1	0	6.26501	0.1274	0.36266
1	0	5.41086	1.15721	-0.83549
1	0	-1.11672	-2.43272	0.09766
8	0	-2.21902	-3.09642	-0.25934
6	0	-3.19443	-2.30871	-0.07001
8	0	-3.04166	-1.08447	0.24701
6	0	-4.59727	-2.83955	-0.24348
1	0	-5.33393	-2.13066	0.13741
1	0	-4.78089	-3.01559	-1.3094
1	0	-4.69423	-3.80055	0.26876
46	0	0.99708	-0.48779	-0.3778
7	0	-0.83507	0.24982	0.05596
6	0	-0.07489	-2.17401	-0.7778
6	0	-1.94954	-0.66668	-0.27426
16	0	-0.97352	1.76613	-0.59538
6	0	-1.42321	-2.11247	-0.02307
1	0	-0.22649	-2.11001	-1.86509
1	0	0.45977	-3.11011	-0.56397
1	0	-2.22008	-0.60089	-1.3366
6	0	-3.20041	-0.3276	0.54479
8	0	-2.06301	2.53701	0.02606
8	0	-0.87788	1.80413	-2.06913
6	0	0.59861	2.4393	0.02945
6	0	-2.4048	-3.14976	-0.6061
6	0	-1.21179	-2.40275	1.47584
8	0	-3.24115	-0.13386	1.73844
8	0	-4.29237	-0.31509	-0.25338
7	0	1.65112	1.60966	0.01293
6	0	0.67443	3.771	0.41856
1	0	-2.00135	-4.16202	-0.48203
1	0	-2.5748	-2.98205	-1.67581
1	0	-3.37778	-3.11617	-0.10138
1	0	-2.16057	-2.45458	2.01654
1	0	-0.70093	-3.36764	1.59345
1	0	-0.61095	-1.62137	1.95157
6	0	-5.5265	0.005	0.40648
6	0	2.84898	2.09367	0.37536
6	0	1.92256	4.26909	0.79285
1	0	-0.22537	4.37595	0.42878
1	0	-5.74495	-0.72331	1.1927
1	0	-6.29138	-0.02643	-0.37025
1	0	-5.46888	1.00202	0.85078
1	0	3.67512	1.3895	0.34695
6	0	3.02919	3.41909	0.7657
1	0	2.02945	5.30429	1.10353
1	0	4.01666	3.76959	1.04744
8	0	2.93877	-1.37685	-0.65633
6	0	3.34702	-2.17808	0.19325
8	0	2.65084	-2.48882	1.27589
6	0	4.66448	-2.88571	0.07932
1	0	1.78838	-1.99391	1.22037
1	0	5.23653	-2.47573	-0.75304
1	0	5.22476	-2.79263	1.01434
1	0	4.48468	-3.95325	-0.09042



IIb

E(RB3LYP) = -1632.45491007

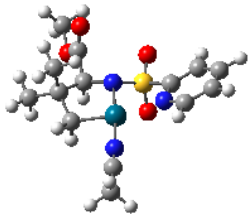
H(correction)= 0.36913707

G(correction)= 0.28409307

E(RM06) = -1632.17461528

E(CPCM$_{CH3CN}$RM06) = -1632.20444931

Imaginary frequencies: 0



IIIb

E(RB3LYP) = -1536.13110743

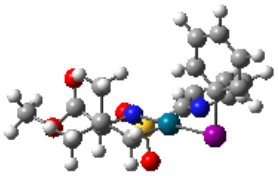
H(correction)= 0.35211643

G(correction)= 0.26797243
E(RM06) = -1535.83892296

E(CPCM$_{CH3CN}$RM06) = -1535.87319672

Imaginary frequencies: 0

46	0	1.05917	-0.74198	-0.0668
7	0	-0.72845	0.21514	0.06305
6	0	-0.1434	-2.36786	-0.32602
7	0	2.76265	-1.83612	-0.13588
6	0	-1.89608	-0.64076	-0.23031
16	0	-0.66071	1.6336	-0.77337
6	0	-1.53194	-2.06628	0.28532
1	0	-0.20805	-2.49104	-1.4165
1	0	0.2935	-3.27616	0.10718
6	0	3.70828	-2.49919	-0.21324
1	0	-2.07113	-0.72141	-1.31185
6	0	-3.17325	-0.07636	0.40239
8	0	-1.73499	2.56536	-0.38782
8	0	-0.39716	1.48443	-2.22028
6	0	0.88589	2.25313	-0.03858
6	0	-2.56205	-3.09793	-0.21936
6	0	-1.45837	-2.13127	1.82315
6	0	4.89299	-3.34337	-0.31745
8	0	-3.29849	0.30829	1.54263
8	0	-4.18927	-0.10193	-0.49257
7	0	1.85235	1.34884	0.173
6	0	1.03353	3.61137	0.21703
1	0	-2.26493	-4.10818	0.08706
1	0	-2.63987	-3.08461	-1.31282
1	0	-3.56108	-2.90729	0.19103
1	0	-2.43969	-1.98376	2.28216
1	0	-1.08138	-3.11644	2.12678
1	0	-0.78537	-1.36677	2.22032
1	0	5.32417	-3.51513	0.67399
1	0	4.62492	-4.30903	-0.75778
1	0	5.64381	-2.86296	-0.95283
6	0	-5.43541	0.42333	-0.0131
6	0	3.03014	1.77888	0.65055
6	0	2.26263	4.05277	0.70606
1	0	0.19731	4.27928	0.04287
1	0	-5.78983	-0.14644	0.85077
1	0	-6.13327	0.33169	-0.84635
1	0	-5.31669	1.47071	0.27662
1	0	3.78307	1.01464	0.81899
6	0	3.27969	3.12213	0.92403
1	0	2.42263	5.1056	0.91987
1	0	4.24873	3.42472	1.30739



IVb

E(RB3LYP) = -1646.41233558

H(correction)= 0.39870858

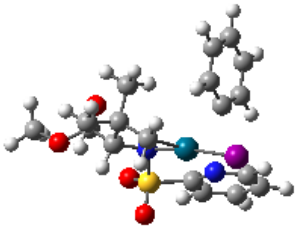
G(correction)= 0.30482058
E(RM06) = -1646.04455224

E(CPCM$_{CH3CN}$RM06) = -1646.07283692

Imaginary frequencies: 0

46	0	0.07255	0.09572	-0.53836
7	0	-1.85176	-0.00167	0.12322
6	0	-0.32293	-1.8209	-1.10196
53	0	2.68673	0.06206	-1.37558
6	0	-2.55983	-1.24022	-0.26331
16	0	-2.62407	1.40306	-0.28284
6	0	-1.49058	-2.37253	-0.25135
1	0	-0.61076	-1.72725	-2.15938
1	0	0.55965	-2.46936	-1.03445
6	0	3.72736	-0.67269	0.37958
1	0	-2.95387	-1.1738	-1.28632
6	0	-3.74386	-1.51232	0.67225
8	0	-3.85955	1.59705	0.49561
8	0	-2.7001	1.66327	-1.73529
6	0	-1.3781	2.55287	0.37873
6	0	-2.05375	-3.65368	-0.90051
6	0	-1.00258	-2.69923	1.17338
6	0	5.11744	-0.74035	0.34448
6	0	2.98859	-1.06224	1.49243
8	0	-3.72097	-1.48121	1.88168
8	0	-4.84064	-1.84323	-0.04712
7	0	-0.09298	2.22586	0.18016
6	0	-1.78931	3.72846	0.99506
1	0	-1.27345	-4.42209	-0.95773
1	0	-2.41568	-3.46186	-1.91719
1	0	-2.88596	-4.06869	-0.31918
1	0	-1.79264	-3.15534	1.77593
1	0	-0.16305	-3.40402	1.11666
1	0	-0.66873	-1.79767	1.69506
6	0	5.7877	-1.21686	1.4753
1	0	5.67546	-0.43336	-0.53412

6	0	3.67887	-1.53563	2.61322
1	0	1.9045	-1.00389	1.49093
6	0	-6.02163	-2.10352	0.72615
6	0	0.84903	3.08906	0.59159
6	0	-0.80474	4.62317	1.4141
1	0	-2.84807	3.91118	1.14082
6	0	5.07221	-1.6131	2.60672
1	0	6.8725	-1.2758	1.46372
1	0	3.11568	-1.84408	3.48953
1	0	-5.85809	-2.93821	1.41378
1	0	-6.79878	-2.34904	0.00146
1	0	-6.29805	-1.21654	1.30213
1	0	1.87853	2.78924	0.42027
6	0	0.53645	4.30017	1.20609
1	0	-1.07999	5.55499	1.89951
1	0	5.60007	-1.98255	3.48102
1	0	1.33302	4.96741	1.51861



TS(IVb-Vb)

E(RB3LYP) = -1646.38893062

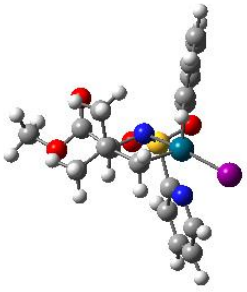
H(correction)= 0.39762362

G(correction)= 0.30852662
E(RM06) = -1646.02441835

E($CPCM_{CH3CN}$RM06) = -1646.05159423

Imaginary frequencies: 1 (-155.8575 cm^{-1})

7	0	-1.53491	0.22903	0.0229
6	0	-2.4596	-0.81065	-0.47897
16	0	-2.01087	1.76214	-0.37372
46	0	0.4496	-0.05313	-0.43586
6	0	-1.64638	-2.13536	-0.54242
1	0	-2.79455	-0.58578	-1.50037
6	0	-3.70687	-0.90971	0.40801
8	0	-3.23448	2.15989	0.3426
8	0	-1.96409	2.04408	-1.82355
6	0	-0.62937	2.6946	0.34936
53	0	3.00546	-0.26692	-1.3362
6	0	-0.33771	-1.75238	-1.2637
6	0	-2.39521	-3.19271	-1.38191
6	0	-1.36142	-2.71013	0.85737
8	0	-3.72496	-0.89766	1.61713
8	0	-4.81171	-1.0644	-0.35741
7	0	0.59607	2.17146	0.22193
6	0	-0.88224	3.9556	0.87985
1	0	-0.53125	-1.42299	-2.29309
1	0	0.37809	-2.57903	-1.27995
1	0	-1.79438	-4.10631	-1.46454
1	0	-2.60298	-2.82893	-2.39467
1	0	-3.35164	-3.46277	-0.9196
1	0	-2.27953	-3.06253	1.33603
1	0	-0.67455	-3.56035	0.77172
1	0	-0.90853	-1.96472	1.51505
6	0	-6.04698	-1.16317	0.36825
6	0	1.64302	2.93188	0.57992
6	0	0.20981	4.72999	1.26826
1	0	-1.90688	4.29727	0.97483
1	0	-6.03127	-2.02374	1.04303
1	0	-6.82334	-1.28136	-0.3884
1	0	-6.21366	-0.25522	0.95354
1	0	2.62477	2.4919	0.43076
6	0	1.49615	4.21549	1.10125
1	0	0.06	5.72096	1.68672
1	0	2.37506	4.79147	1.37173
1	0	2.11401	-3.0949	-0.06188
6	0	2.19424	-2.49339	0.83519
6	0	2.17652	-1.09756	0.77038
6	0	2.31827	-3.10975	2.08145
6	0	2.36272	-0.31784	1.91457
6	0	2.45154	-2.3468	3.24348
1	0	2.31793	-4.19515	2.13435
6	0	2.47363	-0.95478	3.15444
1	0	2.4009	0.76177	1.8621
1	0	2.55187	-2.83407	4.20865
1	0	2.58579	-0.348	4.04889



Vb

E(RB3LYP) = -1646.42362187

H(correction)= 0.39950687

G(correction)= 0.31096387
E(RM06) = -1646.04660749

E($CPCM_{CH3CN}$RM06) = -1646.0744761

Imaginary frequencies: 0

46	0	-0.7519	0.11767	-0.07185
7	0	1.20354	-0.4636	-0.52094
6	0	-0.1532	-0.46834	1.81928

53	0	-3.15856	1.08872	0.56632
6	0	-1.52917	-1.6886	-0.53132
16	0	1.74978	0.63535	-1.61615
6	0	2.03973	-0.60932	0.68576
6	0	1.15021	-1.27905	1.77438
1	0	-0.02611	0.52107	2.26758
1	0	-0.98818	-0.99619	2.2794
6	0	-2.42635	-2.40931	0.258
6	0	-1.15429	-2.14412	-1.79826
6	0	1.39094	2.22953	-0.80053
8	0	0.83964	0.58313	-2.77033
8	0	3.20536	0.58013	-1.79571
1	0	2.36514	0.36398	1.08336
6	0	3.30623	-1.41912	0.37276
6	0	1.80358	-1.13918	3.17203
6	0	0.90131	-2.77022	1.48519
6	0	-2.96058	-3.60407	-0.23527
1	0	-2.73691	-2.04918	1.23249
6	0	-1.71056	-3.33505	-2.28266
1	0	-0.43617	-1.5987	-2.40066
7	0	0.25907	2.22602	-0.08473
6	0	2.20011	3.34703	-0.95873
8	0	3.36922	-2.37687	-0.35947
8	0	4.35209	-0.93546	1.07959
1	0	1.15236	-1.56805	3.94197
1	0	1.99688	-0.09168	3.43009
1	0	2.75791	-1.67467	3.20264
1	0	0.14153	-3.16153	2.17125
1	0	0.56395	-2.93596	0.46228
1	0	1.81845	-3.34772	1.63215
6	0	-2.60693	-4.06697	-1.50414
1	0	-3.66668	-4.16136	0.37525
1	0	-1.42202	-3.68916	-3.26886
6	0	-0.13431	3.36671	0.50183
6	0	1.79306	4.53161	-0.3416
1	0	3.11241	3.27499	-1.54029
6	0	5.60028	-1.61609	0.86006
1	0	-3.0283	-4.99406	-1.8831
1	0	-1.06856	3.31912	1.05322
6	0	0.60814	4.54263	0.39496
1	0	2.3922	5.43264	-0.43619
1	0	5.51574	-2.67249	1.12862
1	0	6.32505	-1.11216	1.50004
1	0	5.89076	-1.53704	-0.19045
1	0	0.25741	5.44513	0.8844

$CH_3CO_2^-$

E(RB3LYP) = -228.497909613

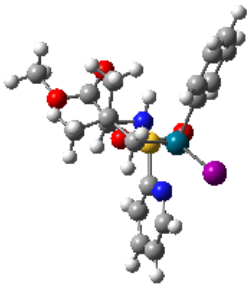
H(correction)= 0.053673613

G(correction)= 0.020793613
E(RM06) = -228.479832102

E($CPCM_{CH3CN}$RM06) = -228.581748127

Imaginary frequencies: 0

6	0	-0.22021	0.00185	-0.00358
8	0	-0.80851	-1.10869	0.00087
8	0	-0.69626	1.16604	0.0008
6	0	1.35409	-0.05472	-0.00108
1	0	1.74304	0.39441	0.9252
1	0	1.73421	-1.08147	-0.081
1	0	1.75769	0.54553	-0.82954



VbH

E(RB3LYP) = -1646.81326439

H(correction)= 0.41273739

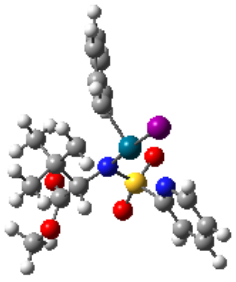
G(correction)= 0.32391439
E(RM06) = -1646.42795965

E($CPCM_{CH3CN}$RM06) = -1646.50067933

Imaginary frequencies: 0

46	0	-0.78933	0.11916	-0.07839
7	0	1.29484	-0.31738	-0.52736
6	0	-0.14589	-0.37343	1.84187
53	0	-3.21395	0.80039	0.59435
6	0	-1.45503	-1.71727	-0.59195
16	0	1.8879	0.957	-1.61565
6	0	2.10271	-0.49966	0.71926
1	0	1.38363	-1.18264	-1.08561
6	0	1.19302	-1.12642	1.82363
1	0	-0.07371	0.6375	2.25019
1	0	-0.94803	-0.92861	2.32554
6	0	-2.16824	-2.61325	0.20212
6	0	-1.16138	-1.99165	-1.93101
6	0	1.27016	2.41407	-0.73021
8	0	1.12017	0.7399	-2.8367
8	0	3.34351	1.01361	-1.59379
1	0	2.44773	0.48262	1.05349
6	0	3.30729	-1.37542	0.34332
6	0	1.82284	-0.87774	3.22101
6	0	1.01	-2.64257	1.6215
6	0	-2.5754	-3.82812	-0.35956

1	0	-2.42747	-2.38348	1.22936
6	0	-1.5887	-3.20971	-2.47867
1	0	-0.62819	-1.28547	-2.56427
7	0	0.10155	2.27848	-0.09255
6	0	1.98987	3.59745	-0.82271
8	0	3.28281	-2.10483	-0.62625
8	0	4.30729	-1.24677	1.20476
1	0	1.17463	-1.28052	4.00582
1	0	1.97635	0.1894	3.41545
1	0	2.79214	-1.37946	3.29199
1	0	0.30088	-3.03154	2.35899
1	0	0.63229	-2.89995	0.62994
1	0	1.95796	-3.16823	1.77102
6	0	-2.28718	-4.12641	-1.69349
1	0	-3.13435	-4.53201	0.25057
1	0	-1.36598	-3.4287	-3.51891
6	0	-0.42225	3.36852	0.49126
6	0	1.43267	4.72929	-0.21795
1	0	2.94123	3.62816	-1.34222
6	0	5.49249	-2.04428	0.93193
1	0	-2.61306	-5.06951	-2.12141
1	0	-1.37291	3.22681	0.99561
6	0	0.21156	4.6122	0.44269
1	0	1.94946	5.68266	-0.26551
1	0	5.23622	-3.1053	0.93543
1	0	6.18605	-1.80495	1.73589
1	0	5.90456	-1.76511	-0.03929
1	0	-0.25354	5.46772	0.92064



TS(Vb-VIb)

E(RB3LYP) = -1646.39564837

H(correction)= 0.39877137

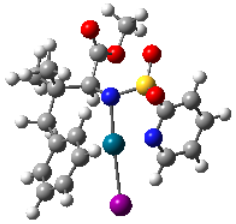
G(correction)= 0.31150637

E(RM06) = -1646.02623597

E($CPCM_{CH3CN}$RM06) = -1646.05143985

Imaginary frequencies: 1 (-322.6934 cm^{-1})

46	0	0.72091	0.14239	0.00192
7	0	-1.28507	-0.23444	0.4418
53	0	3.25997	0.76454	-0.72203
6	0	1.23361	-1.86133	0.40663
16	0	-1.87967	0.97483	1.38678
6	0	-2.03982	-0.63368	-0.75582
6	0	0.60968	-2.22736	1.61312
6	0	2.42904	-2.49979	0.02731
6	0	-1.07701	2.45292	0.70243
8	0	-1.32708	0.82636	2.73589
8	0	-3.3223	1.18343	1.19159
6	0	-1.28209	-1.84196	-1.40262
1	0	-2.08573	0.17394	-1.50095
6	0	-3.48891	-1.02168	-0.4115
1	0	-0.31406	-1.75465	1.91831
6	0	1.20487	-3.18754	2.43923
6	0	3.00115	-3.46429	0.85151
1	0	2.9143	-2.24599	-0.90801
7	0	0.13081	2.252	0.1494
6	0	-1.68519	3.69863	0.79061
6	0	0.21615	-1.52065	-1.44246
6	0	-1.71148	-1.97173	-2.88831
6	0	-1.55566	-3.18716	-0.70104
8	0	-3.83016	-1.71925	0.51379
8	0	-4.33454	-0.52678	-1.33998
6	0	2.39412	-3.80842	2.06393
1	0	0.72265	-3.44408	3.37853
1	0	3.92587	-3.94526	0.54434
6	0	0.79338	3.31964	-0.33487
6	0	-0.99457	4.802	0.29187
1	0	-2.67284	3.77701	1.23119
1	0	0.44689	-0.68384	-2.11197
1	0	0.80667	-2.37045	-1.76453
1	0	-1.20232	-2.81711	-3.36409
1	0	-1.48211	-1.06564	-3.46062
1	0	-2.79028	-2.14655	-2.95668
1	0	-2.56436	-3.54396	-0.92527
1	0	-0.84474	-3.93953	-1.0621
1	0	-1.46717	-3.11637	0.3816
6	0	-5.72511	-0.81119	-1.1055
1	0	2.84533	-4.56032	2.70561
1	0	1.76447	3.11628	-0.77031
6	0	0.26397	4.60608	-0.27575
1	0	-1.43213	5.79475	0.34277
1	0	-5.89976	-1.89014	-1.08268
1	0	-6.26163	-0.35078	-1.93555
1	0	-6.03784	-0.377	-0.15278
1	0	0.83867	5.43386	-0.67747



VIb

E(RB3LYP) = -1646.45536875

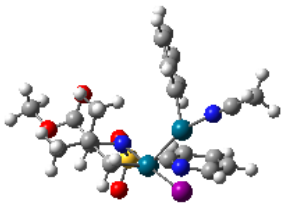
H(correction)= 0.40154475

G(correction)= 0.31397075
E(RM06) = -1646.0895221

E(CPCM$_{CH3CN}$RM06) = -1646.11392513

Imaginary frequencies: 0

46	0	0.72512	0.13609	0.15079
7	0	-1.21307	-0.52242	0.60138
53	0	3.15238	1.13	-0.46441
16	0	-1.82786	0.70682	1.49481
6	0	-1.91352	-1.14851	-0.5383
6	0	-1.39678	2.14058	0.46809
8	0	-1.00877	0.82158	2.70619
8	0	-3.29122	0.70044	1.61314
6	0	-1.41922	-2.62183	-0.73753
1	0	-1.67437	-0.60281	-1.46299
6	0	-3.45159	-1.07325	-0.41337
7	0	-0.23322	2.00659	-0.19429
6	0	-2.20987	3.25988	0.3654
6	0	0.07461	-2.64966	-1.17284
6	0	-2.19005	-3.21202	-1.94589
6	0	-1.67226	-3.52097	0.48947
8	0	-4.16785	-1.83828	0.18866
8	0	-3.91013	-0.03314	-1.1432
6	0	0.16702	3.00625	-1.00252
6	0	-1.78989	4.30068	-0.46261
1	0	-3.14251	3.28886	0.91767
1	0	0.1746	-2.04073	-2.08333
1	0	0.26327	-3.68027	-1.50493
6	0	1.26422	-2.30587	-0.27272
1	0	-1.83149	-4.22415	-2.16444
1	0	-2.04947	-2.60693	-2.85101
1	0	-3.26064	-3.28087	-1.73803
1	0	-2.74105	-3.69606	0.6213
1	0	-1.17342	-4.48823	0.34997
1	0	-1.30297	-3.07667	1.41509
6	0	-5.32276	0.21117	-1.02557
1	0	1.11131	2.8591	-1.51134
6	0	-0.58746	4.16712	-1.15593
1	0	-2.39354	5.19723	-0.56915
6	0	2.53723	-2.58217	-0.83867
6	0	1.23877	-1.92033	1.09843
1	0	-5.89154	-0.66229	-1.35447
1	0	-5.52589	1.06671	-1.67058
1	0	-5.5709	0.4374	0.01394
1	0	-0.22558	4.94826	-1.81591
1	0	2.59061	-2.86756	-1.88632
6	0	3.69283	-2.54563	-0.08265
6	0	2.44355	-1.85924	1.85398
1	0	0.30304	-1.88623	1.63994
6	0	3.65326	-2.18308	1.27873
1	0	4.64378	-2.79211	-0.54643
1	0	2.38063	-1.57533	2.90014
1	0	4.5694	-2.14906	1.86011



VIIb

E(RB3LYP) = -1907.16514236

H(correction)= 0.45369136

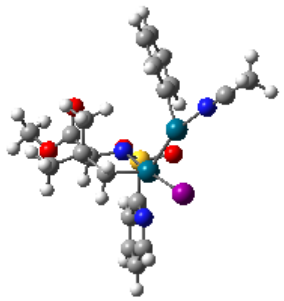
G(correction)= 0.34216436
E(RM06) = -1906.71980074

E(CPCM$_{CH3CN}$RM06) = -1906.76095408

Imaginary frequencies: 0

46	0	0.17313	-0.97432	-0.64924
7	0	1.94919	-0.20799	0.0261
6	0	0.74063	-0.08646	-2.38646
53	0	-2.28362	-1.78302	-1.57802
46	0	-1.93212	0.61441	-0.10284
16	0	2.69557	-1.3764	0.94501
6	0	2.81303	0.27515	-1.08214
6	0	1.88609	0.92422	-2.15395
1	0	1.09049	-0.97229	-2.93901
1	0	-0.09647	0.35892	-2.93168
7	0	-3.81547	1.31731	0.17671
6	0	-1.23632	2.14229	0.96893
6	0	1.2896	-1.85474	1.99439
8	0	3.72777	-0.81221	1.83061
8	0	3.0572	-2.5868	0.17573
1	0	3.33149	-0.5622	-1.56721
6	0	3.8834	1.23907	-0.5549
6	0	2.6596	1.11508	-3.4775
6	0	1.33012	2.28488	-1.69968
6	0	-4.9084	1.66216	0.32713
6	0	-1.53522	3.4598	0.60988
6	0	-0.40681	1.87492	2.06041
7	0	0.10174	-1.95619	1.3857
6	0	1.5069	-2.19026	3.32531

8	0	3.71096	2.13849	0.23458
8	0	5.07664	0.9722	-1.1369
1	0	1.99134	1.51682	-4.24854
1	0	3.07069	0.16736	-3.84418
1	0	3.49181	1.81834	-3.35687
1	0	0.57024	2.62579	-2.41421
1	0	0.87328	2.2249	-0.71115
1	0	2.11723	3.04344	-1.65512
6	0	-6.28815	2.09384	0.51345
6	0	-0.96998	4.51709	1.33258
1	0	-2.18218	3.6723	-0.2369
6	0	0.15094	2.94023	2.7776
1	0	-0.15812	0.85585	2.33671
6	0	-0.93854	-2.4302	2.08859
6	0	0.42277	-2.68222	4.05368
1	0	2.49393	-2.06078	3.75491
6	0	6.16079	1.81439	-0.71745
1	0	-6.91379	1.23745	0.78399
1	0	-6.34106	2.84108	1.31136
1	0	-6.67039	2.53355	-0.41315
6	0	-0.12944	4.25902	2.41662
1	0	-1.18973	5.54168	1.04154
1	0	0.81795	2.72928	3.6093
1	0	-1.87992	-2.49781	1.55205
6	0	-0.81593	-2.81242	3.4242
1	0	0.54427	-2.96094	5.09646
1	0	5.94712	2.86235	-0.94639
1	0	7.03295	1.4692	-1.27381
1	0	6.32439	1.71143	0.35845
1	0	0.31111	5.08131	2.97365
1	0	-1.67999	-3.19862	3.95494



VIIIb

E(RB3LYP) = -1907.15645456

H(correction)= 0.45350156

G(correction)= 0.34070256

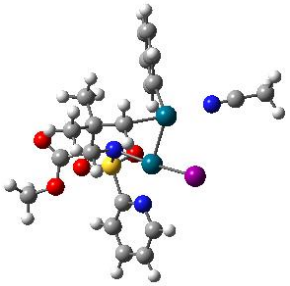
E(RM06) = -1906.71076363

E($CPCM_{CH3CN}$RM06) = -1906.74992581

Imaginary frequencies: 0

46	0	-0.14628	-0.84607	0.18501
7	0	-1.47504	0.66092	-0.20067
6	0	-0.58481	-0.35221	2.10792
53	0	1.77587	-2.70721	0.64576
46	0	2.35819	0.00771	-0.01956
16	0	-2.23494	0.26512	-1.59562
6	0	-2.30466	1.0047	0.9671
6	0	-1.34313	0.9855	2.1942
1	0	-1.21776	-1.21313	2.36143
1	0	0.32821	-0.36827	2.70722
7	0	4.36963	0.12648	-0.33051
6	0	2.19915	1.9175	-0.55954
6	0	-3.12854	-1.29772	-1.26853
8	0	-1.15807	-0.09811	-2.54044
8	0	-3.2677	1.23978	-1.97753
1	0	-3.08099	0.24616	1.1511
6	0	-3.01981	2.34888	0.78002
6	0	-2.15229	0.9961	3.5111
6	0	-0.35999	2.16854	2.19034
6	0	5.50086	0.14641	-0.56743
6	0	2.87139	2.91198	0.15659
6	0	1.393	2.24112	-1.65372
7	0	-2.42874	-2.20462	-0.58774
6	0	-4.4206	-1.49859	-1.74567
8	0	-2.51728	3.37756	0.39432
8	0	-4.31603	2.24278	1.15967
1	0	-1.47918	0.90677	4.37167
1	0	-2.87004	0.16848	3.55273
1	0	-2.71019	1.93307	3.62143
1	0	0.37105	2.03687	2.99806
1	0	0.17787	2.23921	1.24418
1	0	-0.87902	3.11692	2.35194
6	0	6.92658	0.16778	-0.87008
6	0	2.70495	4.25385	-0.20798
1	0	3.5062	2.6573	1.0014
6	0	1.23965	3.58725	-2.00914
1	0	0.85305	1.47686	-2.20402
6	0	-2.99916	-3.39297	-0.35711
6	0	-5.00832	-2.74119	-1.50088
1	0	-4.93038	-0.70602	-2.28124
6	0	-5.08913	3.44452	1.01522
1	0	7.17612	-0.6562	-1.54597
1	0	7.19104	1.11502	-1.35029
1	0	7.50763	0.06001	0.05118
6	0	1.89151	4.59157	-1.29075
1	0	3.2152	5.02977	0.35842
1	0	0.59331	3.84196	-2.84498
1	0	-2.40128	-4.11153	0.19827
6	0	-4.28684	-3.70671	-0.79813
1	0	-6.01434	-2.9512	-1.8533
1	0	-4.66537	4.25165	1.61925
1	0	-6.09234	3.19204	1.36076

1	0	-5.10803	3.75616	-0.0323
1	0	1.76192	5.63347	-1.57125
1	0	-4.70968	-4.68431	-0.58903



IXb

E(RB3LYP) = -1907.14530428

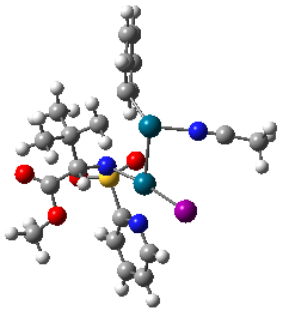
H(correction)= 0.45372328

G(correction)= 0.34639228
E(RM06) = -1906.70417927

E(CPCM$_{CH3CN}$RM06) = -1906.73780134

Imaginary frequencies: 0

7	0	2.0045	-1.83428	0.67801
6	0	2.35164	-3.10981	0.42737
6	0	2.87444	-1.03923	1.32573
1	0	1.61715	-3.70838	-0.09972
6	0	3.58503	-3.62117	0.82304
6	0	4.12937	-1.46436	1.73947
16	0	2.24124	0.63936	1.6329
1	0	3.82702	-4.65602	0.60513
6	0	4.48845	-2.78788	1.4848
1	0	4.79061	-0.7642	2.2381
8	0	1.38648	0.50709	2.81969
8	0	3.40385	1.53549	1.68713
7	0	1.25484	0.88635	0.34279
1	0	5.45914	-3.16345	1.79533
6	0	1.73665	1.28572	-1.00619
46	0	0.22578	-0.86087	0.05399
1	0	1.98225	0.37981	-1.57815
6	0	0.5791	2.00782	-1.77128
6	0	3.05578	2.08599	-0.97786
53	0	-1.2992	-2.83024	-0.99897
46	0	-2.00897	0.21669	-0.63063
6	0	-0.63834	1.05889	-1.95911
6	0	1.08717	2.30257	-3.20967
6	0	0.19002	3.33911	-1.10646
8	0	3.19089	3.28222	-0.87687
8	0	4.09469	1.23111	-1.14136
6	0	-2.27869	1.90866	0.39113
1	0	-0.33794	0.18909	-2.55867
1	0	-1.39823	1.60978	-2.53717
1	0	0.28702	2.75548	-3.80587
1	0	1.40811	1.38779	-3.72444
1	0	1.92534	3.00688	-3.19515
1	0	-0.71376	3.74234	-1.57717
1	0	-0.0142	3.20545	-0.04445
1	0	0.99483	4.06867	-1.2098
6	0	5.39492	1.82946	-1.01188
6	0	-3.20641	2.80704	-0.14283
6	0	-1.74032	2.10717	1.66415
1	0	5.52673	2.62561	-1.74894
1	0	6.10732	1.02237	-1.18742
1	0	5.51145	2.24079	-0.00636
6	0	-3.60515	3.91778	0.61228
1	0	-3.62004	2.6628	-1.13864
6	0	-2.14783	3.22245	2.40673
1	0	-0.99307	1.43493	2.0711
6	0	-3.07676	4.12662	1.88673
1	0	-4.32426	4.61821	0.19368
1	0	-1.72101	3.3832	3.39376
1	0	-3.38153	4.99257	2.46852
7	0	-3.7041	-0.64481	0.48443
6	0	-4.53343	-1.11783	1.13548
6	0	-5.56536	-1.73401	1.96024
1	0	-5.40551	-2.81587	2.00412
1	0	-5.52474	-1.32485	2.97439
1	0	-6.55427	-1.53589	1.53557



TS(IXb-Xb)

E(RB3LYP) = -1907.11566872

H(correction)= 0.45278672

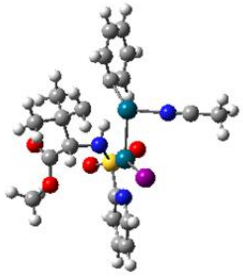
G(correction)= 0.34833872
E(RM06) = -1906.68418434

E(CPCM$_{CH3CN}$RM06) = -1906.71769267

Imaginary frequencies: 1 (-333.0471 cm^{-1})

7	0	-2.44375	0.94675	0.64225
6	0	-3.31149	1.9573	0.45376
6	0	-2.8543	-0.13593	1.32465
1	0	-2.93264	2.80698	-0.10271
6	0	-4.61131	1.909	0.95173
6	0	-4.13254	-0.2672	1.85028
16	0	-1.5857	-1.4223	1.52824

1	0	-5.27732	2.74757	0.77769
6	0	-5.02998	0.78312	1.6611
1	0	-4.4	-1.17521	2.37983
8	0	-0.82839	-1.01458	2.71973
8	0	-2.26672	-2.72594	1.52952
7	0	-0.64683	-1.18312	0.21535
1	0	-6.03939	0.72239	2.05776
6	0	-0.83136	-1.86226	-1.0882
46	0	-0.41195	0.83655	-0.0543
1	0	-1.03359	-1.06516	-1.81943
6	0	0.49532	-2.54234	-1.54093
6	0	-2.08753	-2.75197	-1.19687
53	0	-0.24438	3.39549	-0.93155
46	0	2.17882	0.29216	-0.42549
6	0	1.62602	-1.47656	-1.58505
6	0	0.33404	-2.98578	-3.02184
6	0	0.83801	-3.78131	-0.69543
8	0	-2.13003	-3.94393	-1.39097
8	0	-3.19512	-1.97339	-1.14224
7	0	2.7088	2.11119	0.41489
6	0	2.80008	-1.54287	0.2021
1	0	1.26635	-0.6404	-2.22148
1	0	2.49083	-1.89417	-2.09878
1	0	1.26938	-3.42466	-3.38709
1	0	0.08644	-2.13891	-3.67528
1	0	-0.45009	-3.74045	-3.11711
1	0	1.85421	-4.12504	-0.91888
1	0	0.78475	-3.569	0.37297
1	0	0.13763	-4.58871	-0.91607
6	0	-4.44099	-2.69057	-1.15373
6	0	2.94849	3.13126	0.90155
6	0	4.09687	-1.89253	-0.20846
6	0	2.34336	-1.90938	1.47514
1	0	-4.53964	-3.27161	-2.07395
1	0	-5.21735	-1.92707	-1.09698
1	0	-4.4902	-3.36139	-0.29261
6	0	3.18403	4.4412	1.48996
6	0	4.94669	-2.57053	0.67303
1	0	4.45345	-1.64457	-1.20439
6	0	3.20332	-2.59058	2.34086
1	0	1.33974	-1.6572	1.79399
1	0	2.36349	5.10541	1.19753
1	0	3.21565	4.3652	2.58122
1	0	4.13079	4.85588	1.13062
6	0	4.50225	-2.92388	1.94689
1	0	5.95017	-2.83355	0.34757
1	0	2.8464	-2.85861	3.33205
1	0	5.1586	-3.46232	2.62509



TS(IXb-Xb)H

E(RB3LYP) = -1907.50856178

H(correction)= 0.46653978

G(correction)= 0.36026378

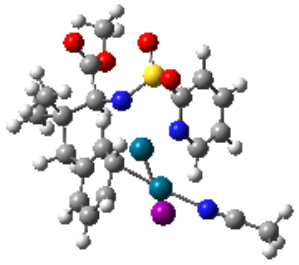
E(RM06) = -1907.06832533

$E(CPCM_{CH3CN}RM06)$ = -1907.14113681

Imaginary frequencies: 1 (-351.4871 cm^{-1})

7	0	2.23464	-1.49457	0.4978
6	0	2.8361	-2.64386	0.13838
6	0	2.95616	-0.60677	1.19875
1	0	2.23218	-3.33451	-0.43794
6	0	4.15551	-2.92848	0.49175
6	0	4.27486	-0.79449	1.58537
16	0	2.12203	0.90657	1.72874
1	0	4.59135	-3.87309	0.18455
6	0	4.88642	-1.99822	1.22585
1	0	4.79643	-0.02268	2.1404
8	0	1.24052	0.64404	2.86234
8	0	3.11177	1.97544	1.77278
7	0	0.96535	1.10309	0.39658
1	0	5.91473	-2.19627	1.51138
6	0	1.3099	1.70317	-0.95311
46	0	0.22309	-0.90108	0.00645
1	0	0.2365	1.67216	0.83627
1	0	1.48163	0.84739	-1.61013
6	0	0.08295	2.4979	-1.49689
6	0	2.64363	2.48885	-0.95448
53	0	-0.54448	-3.19939	-1.03086
46	0	-2.20253	0.02781	-0.33454
6	0	-1.1882	1.59211	-1.54552
6	0	0.39482	2.80784	-2.98763
6	0	-0.15216	3.84059	-0.77187
8	0	2.78159	3.68247	-0.85574
8	0	3.65377	1.61718	-1.1338
7	0	-3.12432	-1.58113	0.59458
6	0	-2.44911	2.00735	0.09287
1	0	-0.9064	0.65024	-2.0562
1	0	-1.92396	2.07187	-2.18676
1	0	-0.42829	3.37839	-3.42917
1	0	0.52744	1.89384	-3.57846
1	0	1.29912	3.41707	-3.07653
1	0	-1.1142	4.25744	-1.08374
1	0	-0.18276	3.74946	0.31751

1	0	0.63647	4.55073	-1.01638
6	0	4.97968	2.19902	-1.11886
6	0	-3.70045	-2.44058	1.10961
6	0	-3.59719	2.57815	-0.48332
6	0	-2.09898	2.33689	1.41415
1	0	5.0637	2.95678	-1.9
1	0	5.66023	1.37023	-1.30949
1	0	5.17021	2.65297	-0.14415
6	0	-4.39936	-3.55071	1.74039
6	0	-4.39867	3.44435	0.26904
1	0	-3.87729	2.36016	-1.50925
6	0	-2.90205	3.2146	2.14669
1	0	-1.25529	1.87946	1.92264
1	0	-3.89851	-4.4887	1.47851
1	0	-4.39181	-3.42975	2.82808
1	0	-5.4358	-3.58781	1.39066
6	0	-4.04853	3.77434	1.57742
1	0	-5.28607	3.87346	-0.18748
1	0	-2.63149	3.44488	3.17331
1	0	-4.66201	4.46194	2.15132



Xb

E(RB3LYP) = -1907.16701138

H(correction)= 0.45555138

G(correction)= 0.34690638

E(RM06) = -1906.7426741

E(CPCM$_{CH3CN}$RM06) = -1906.77443555

Imaginary frequencies: 0

7	0	0.84792	2.03713	0.47253
6	0	0.50833	2.94136	1.4086
6	0	1.80887	2.36173	-0.4089
1	0	-0.2674	2.63646	2.10177
6	0	1.1162	4.19308	1.47719
6	0	2.47418	3.5807	-0.4058
16	0	2.19347	1.05785	-1.61445
1	0	0.80937	4.88979	2.25035
6	0	2.11225	4.52118	0.55768
1	0	3.25383	3.7602	-1.1376
8	0	1.14462	1.13329	-2.63759
8	0	3.59394	1.26951	-2.00898
7	0	1.93813	-0.30436	-0.74139
1	0	2.60387	5.48911	0.59481
6	0	2.92118	-0.83122	0.23149
46	0	0.07341	0.01331	0.1878
1	0	2.81479	-0.30378	1.19071
6	0	2.67004	-2.3554	0.52239
6	0	4.37999	-0.58634	-0.21406
53	0	-2.03845	0.45665	1.84382
6	0	1.29961	-2.59264	1.22728
6	0	3.72818	-2.79496	1.56693
6	0	2.82278	-3.25061	-0.72543
8	0	5.00629	-1.22821	-1.02456
8	0	4.90123	0.44483	0.48786
1	0	1.25932	-1.96254	2.12801
1	0	1.34298	-3.6223	1.60927
6	0	-0.05552	-2.4856	0.52392
1	0	3.58279	-3.84886	1.82928
1	0	3.65418	-2.20753	2.49106
1	0	4.74338	-2.69423	1.17336
1	0	3.86816	-3.31003	-1.03125
1	0	2.46561	-4.26298	-0.4983
1	0	2.26173	-2.87462	-1.58217
6	0	6.22169	0.84248	0.08241
6	0	-1.16541	-3.0434	1.217
6	0	-0.28305	-2.02799	-0.80153
1	0	6.92495	0.01334	0.19589
1	0	6.4932	1.66909	0.74006
1	0	6.20324	1.16369	-0.96165
6	0	-2.3905	-3.23625	0.60473
1	0	-1.02949	-3.36295	2.24682
6	0	-1.56767	-2.21301	-1.4483
1	0	0.55428	-1.84616	-1.45983
6	0	-2.61244	-2.87186	-0.74924
1	0	-3.19511	-3.70767	1.16316
46	0	-2.94884	-0.64434	-1.06335
1	0	-1.56279	-2.18983	-2.53796
1	0	-3.47346	-3.27336	-1.27602
7	0	-4.4558	0.81048	-1.10792
6	0	-5.21348	1.68587	-1.15414
6	0	-6.16565	2.78969	-1.19801
1	0	-6.07842	3.39575	-0.29051
1	0	-5.96631	3.42459	-2.06722
1	0	-7.1883	2.40551	-1.26944

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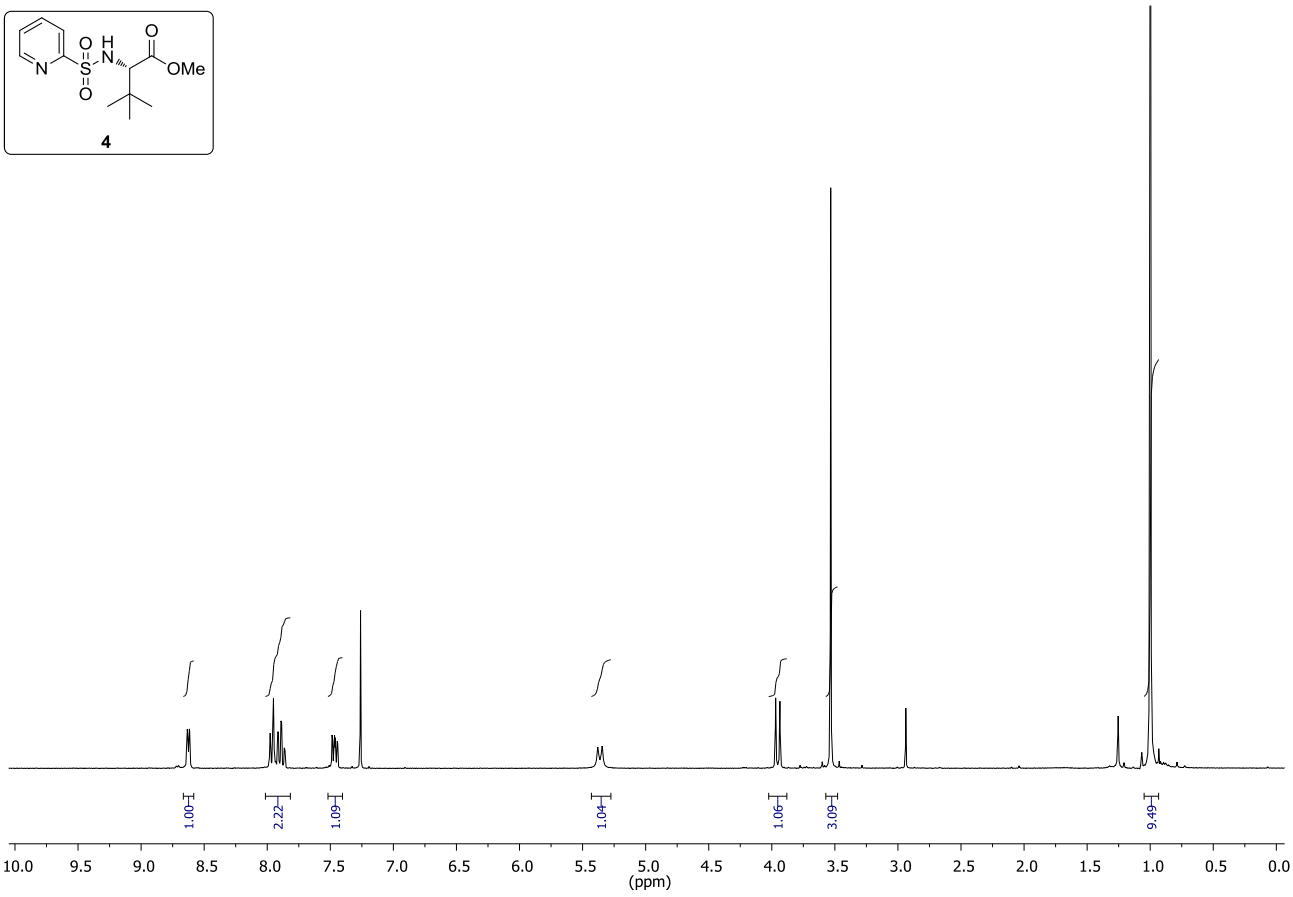
11. NMR spectra

4



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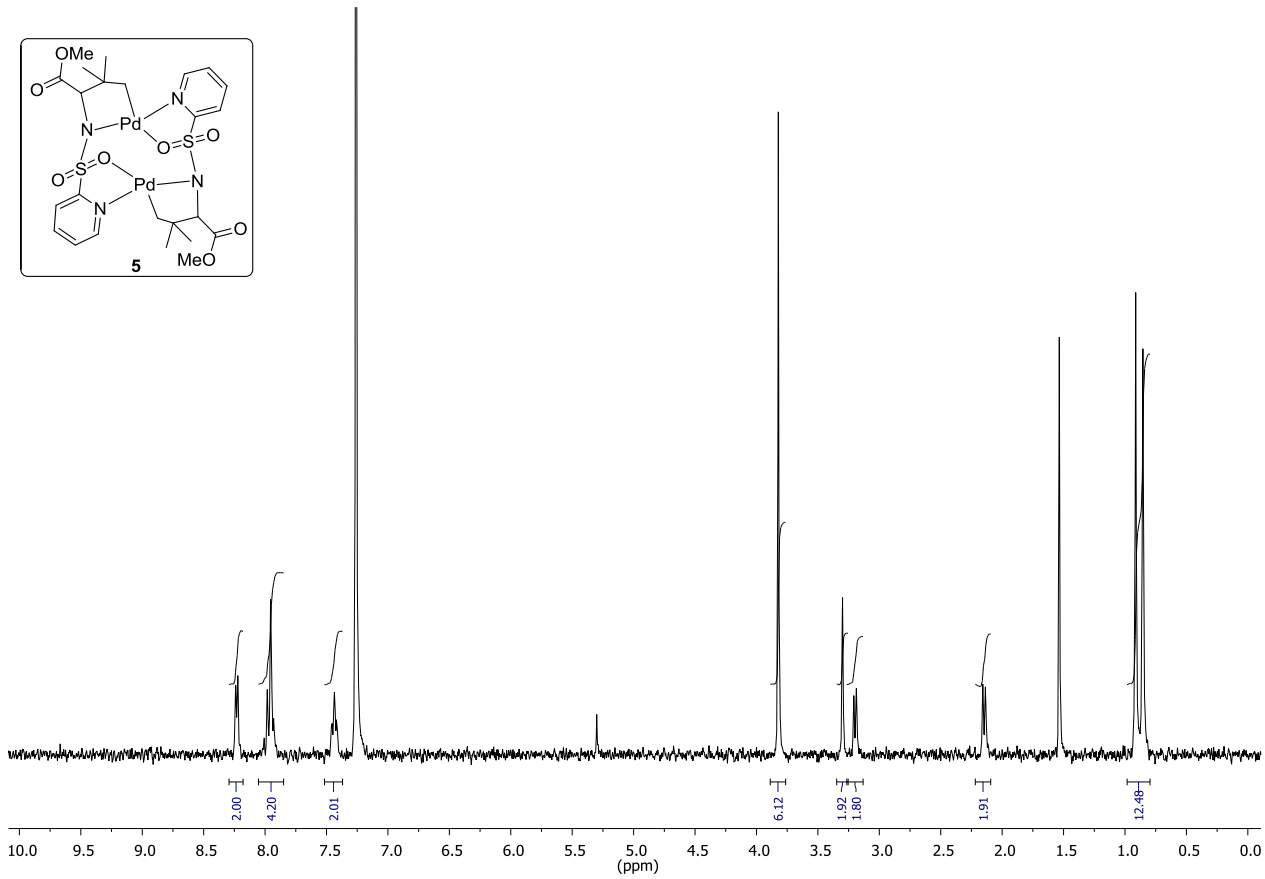
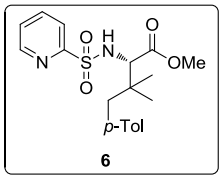
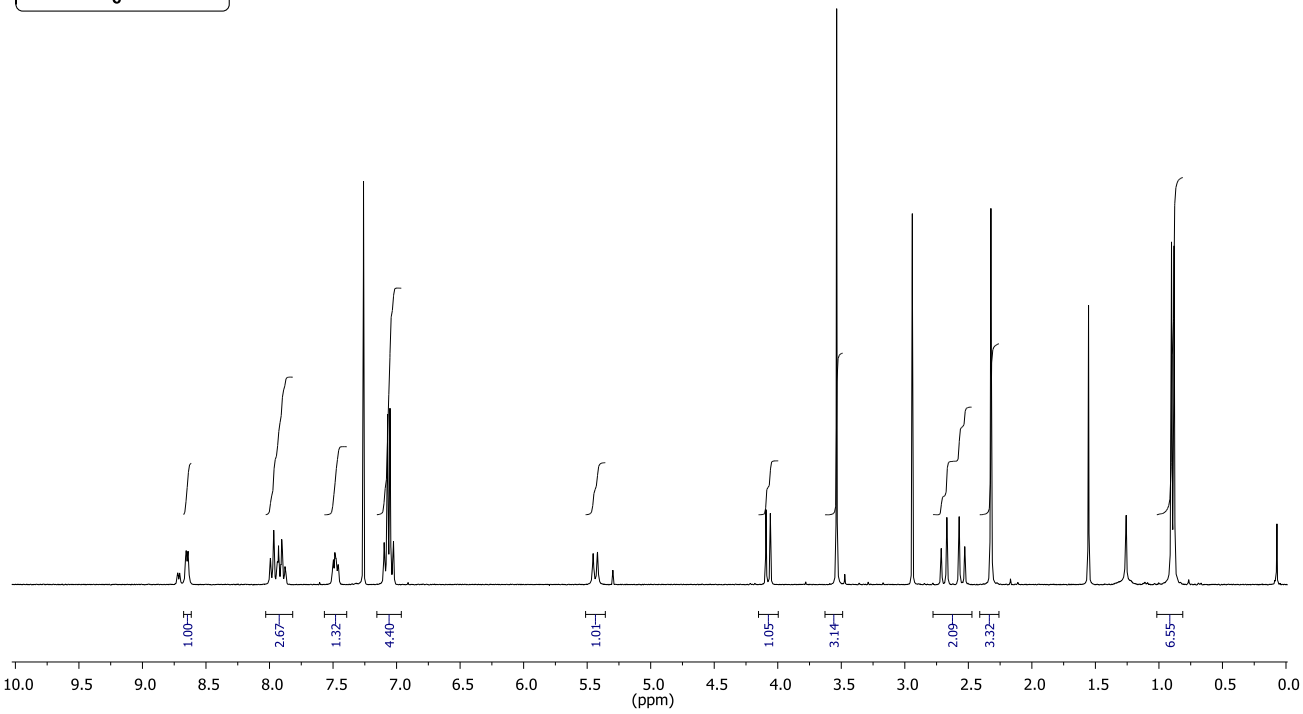
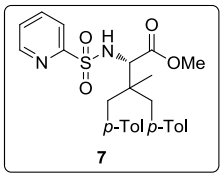


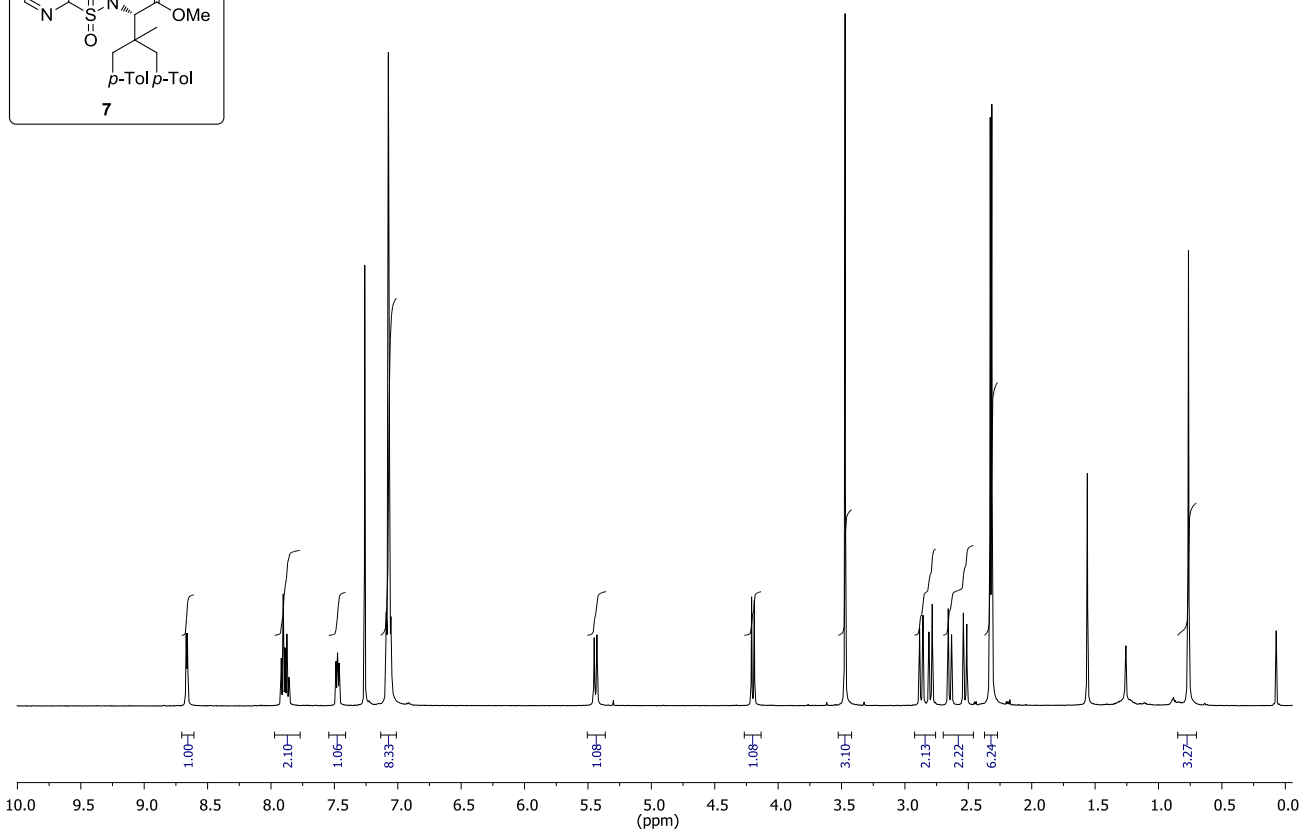

O
H
N
O
S
N
O
O
OMe
p-Tol

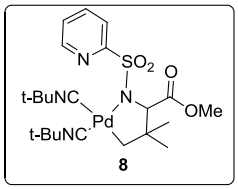
6


1.00
2.67
1.32
4.40
1.01
1.05
3.14
2.09
3.32
6.55
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

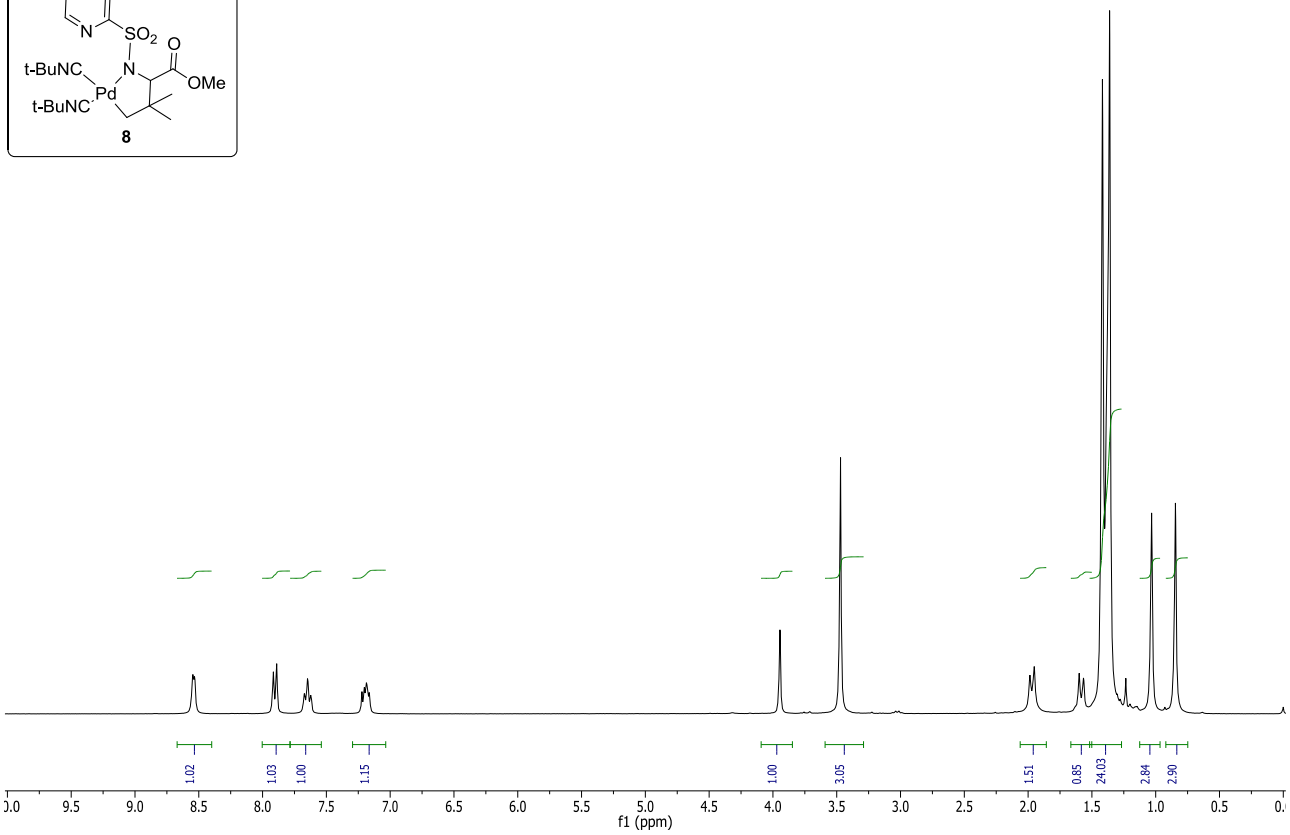

O
H
N
O
S
N
O
O
OMe
p-Tol
p-Tol

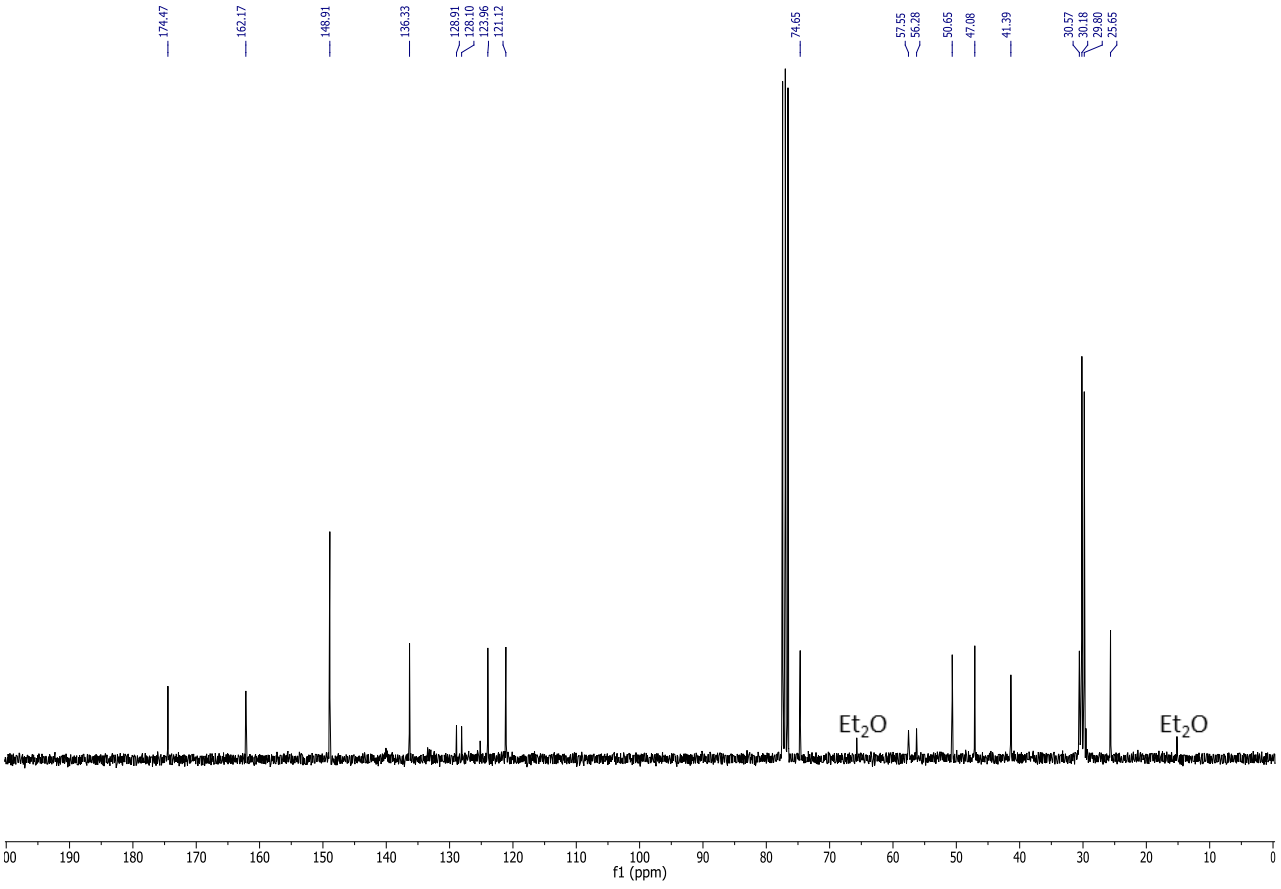
7

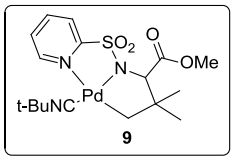

1.00
2.10
1.06
8.33
1.08
1.08
3.10
2.13
2.22
6.24
3.27
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)


N
SO2
O
t-BuNC
N
OMe
Pd
t-BuNC

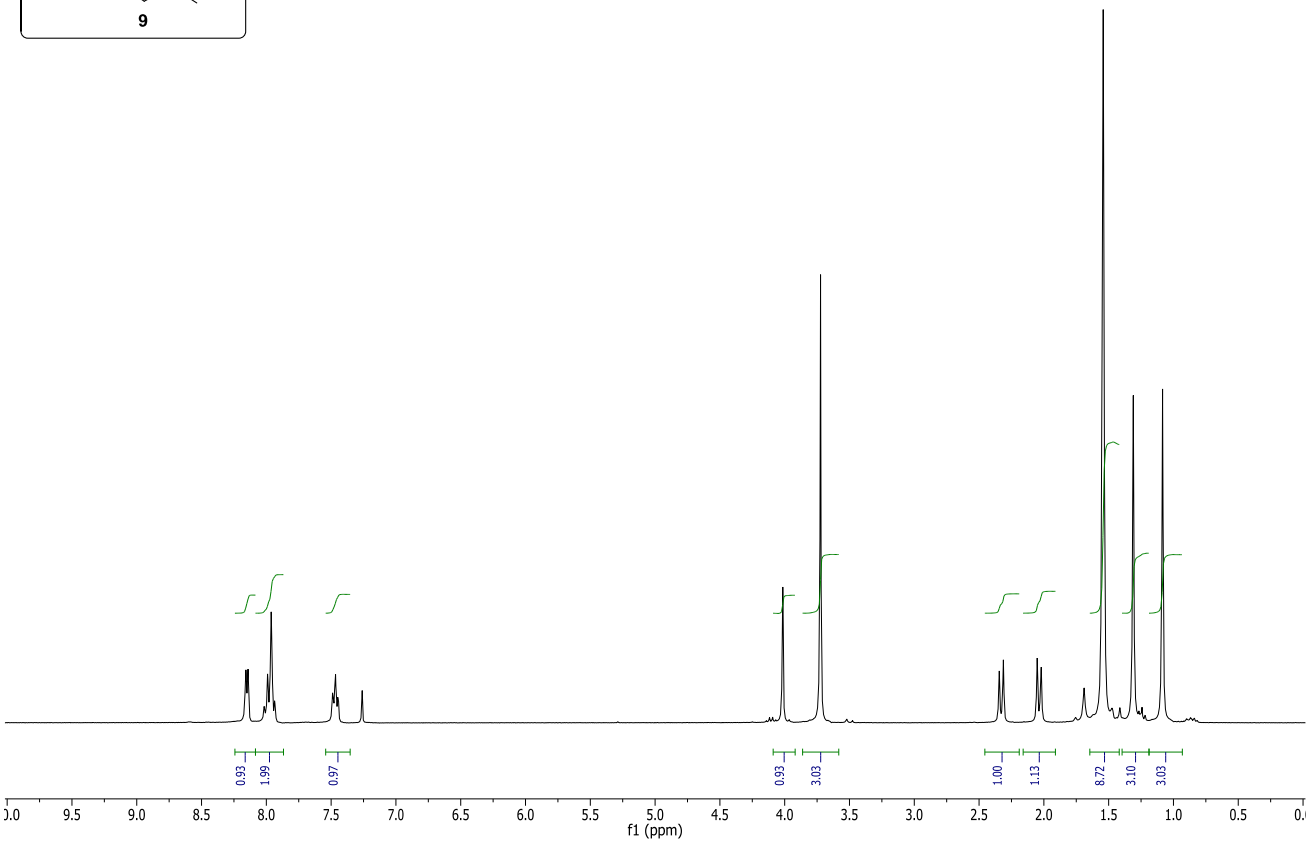
8

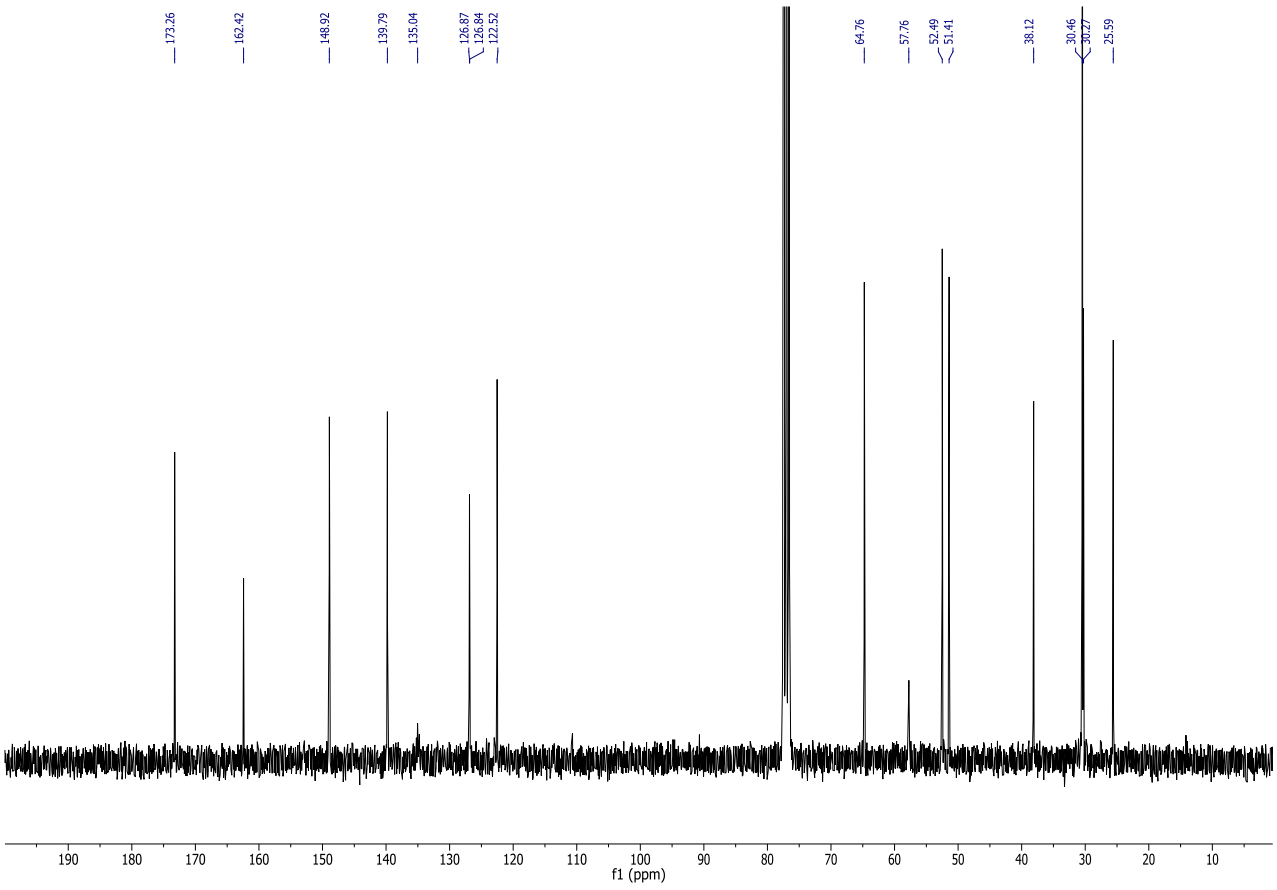

1.02
1.03
1.00
1.15
1.00
3.05
1.51
0.85
24.03
2.84
2.90
f1 (ppm)


174.47
162.17
148.91
136.33
128.91
128.10
123.96
121.12
74.65
57.55
56.28
50.65
47.08
41.39
30.57
30.18
29.80
25.65
Et2O
Et2O
f1 (ppm)

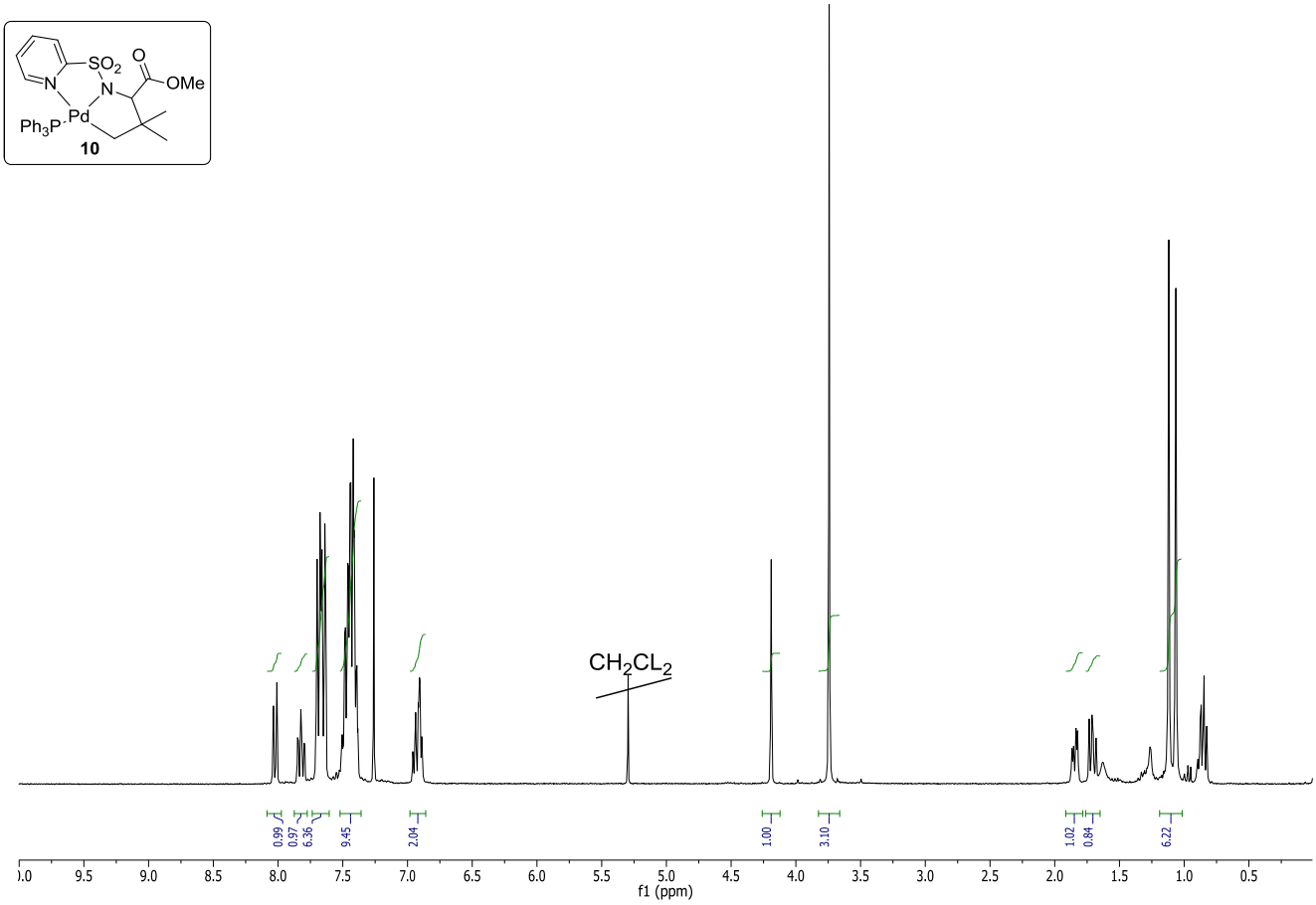

SO2
O
OMe
N
N
t-BuNC
Pd

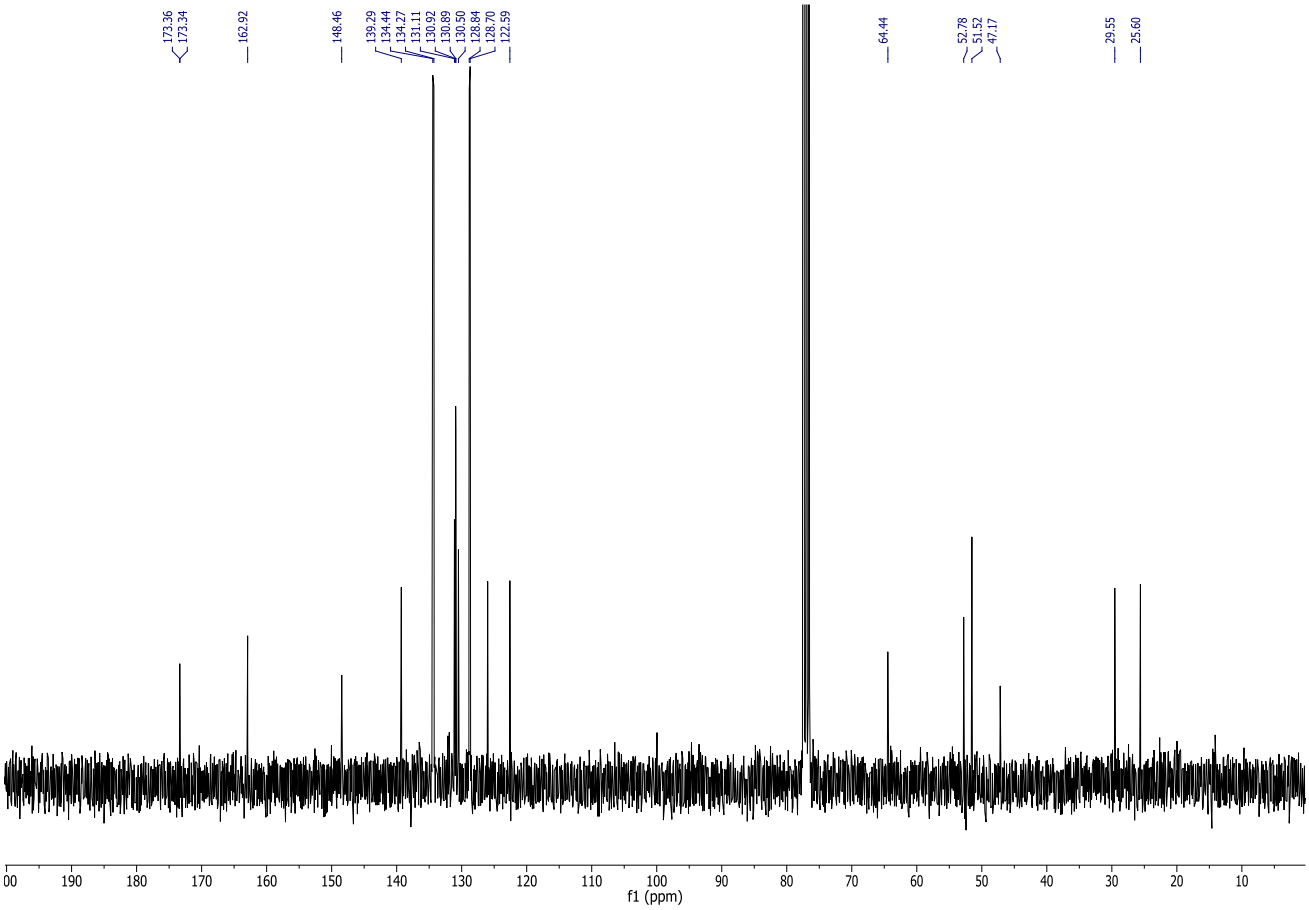
9

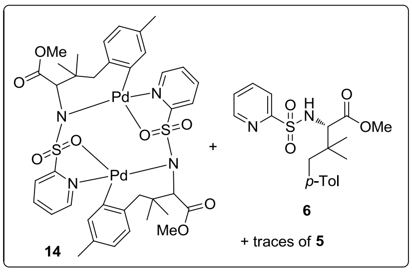

0.93
1.99
0.97
0.93
3.03
1.00
1.13
8.72
3.10
3.03
f1 (ppm)


173.26
162.42
148.92
139.79
135.04
126.87
126.84
122.52
64.76
57.76
52.49
51.41
38.12
30.46
30.27
25.59
f1 (ppm)

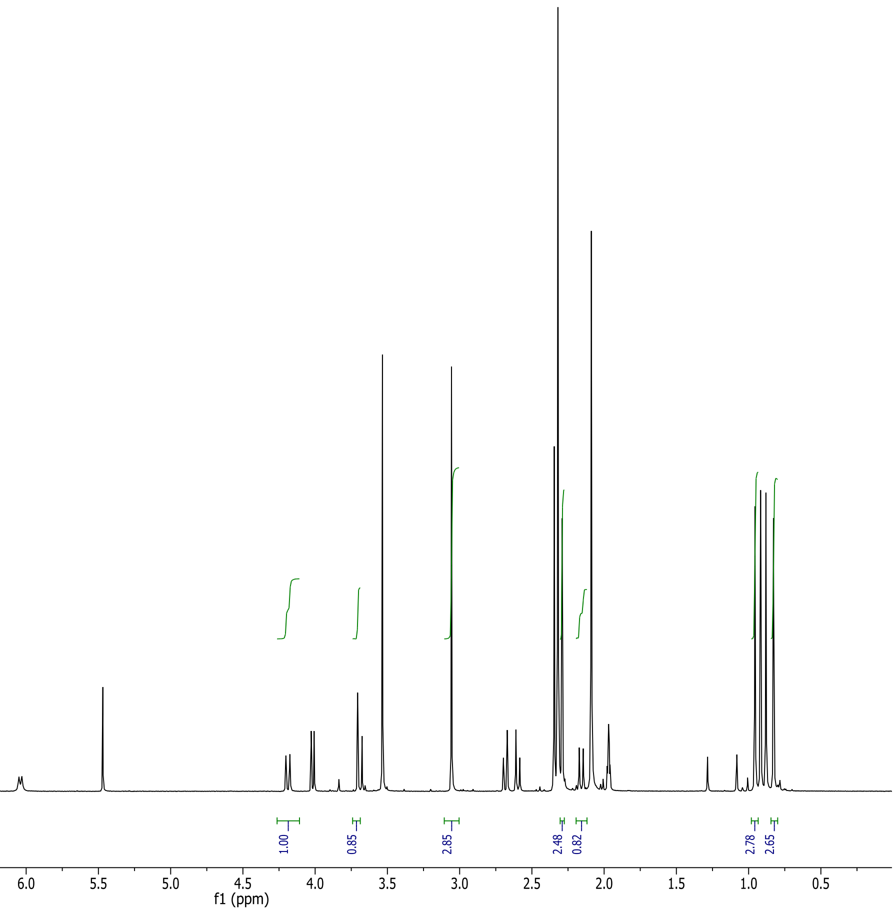
SO2
O
N
N
OMe
Ph3P
Pd
10


CH2CL2
0.99
0.97
6.36
9.45
2.04
1.00
3.10
1.02
0.84
6.22
f1 (ppm)

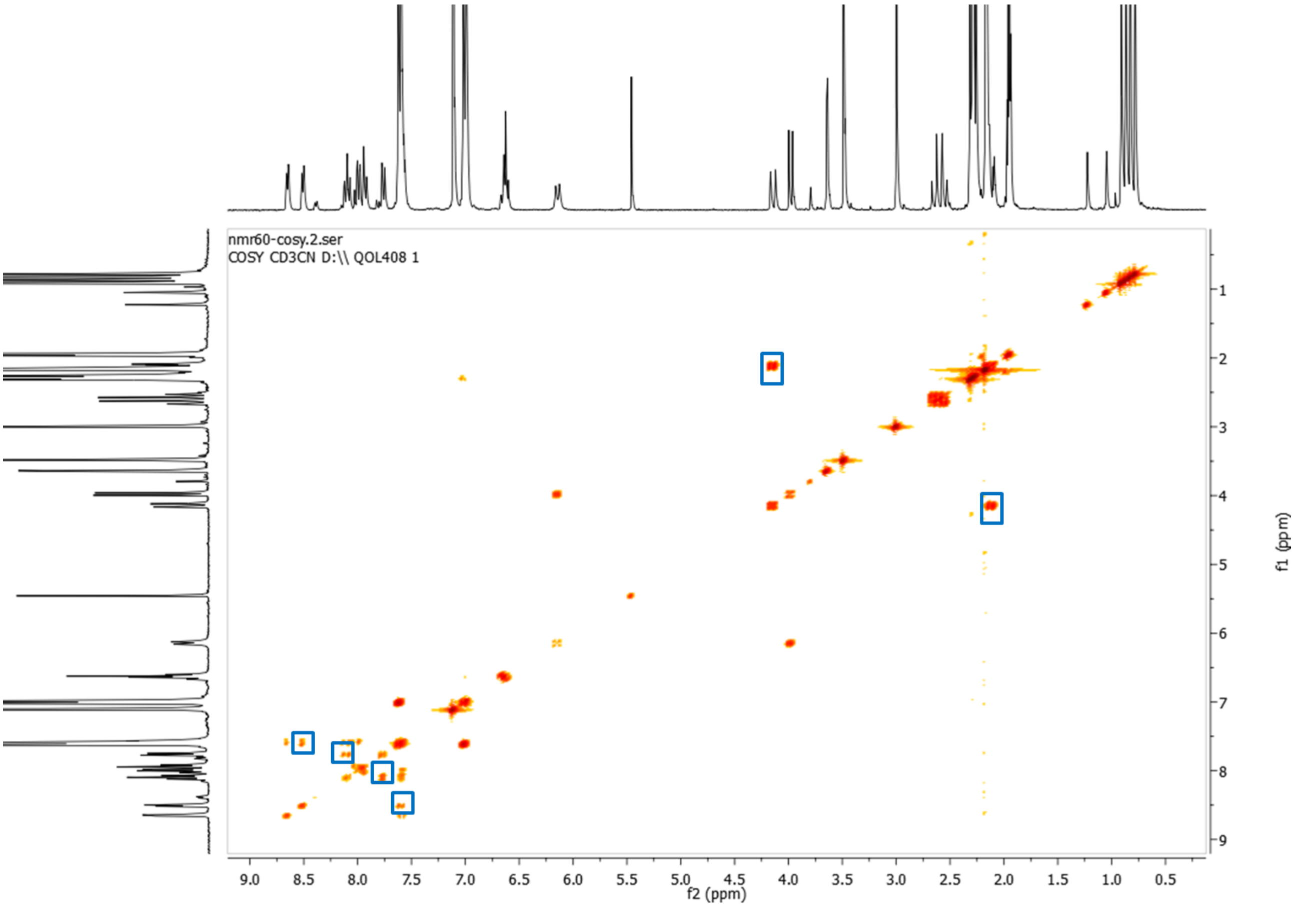

173.36
173.34
162.92
148.46
139.29
134.44
134.27
131.11
130.92
130.89
130.50
128.84
128.70
122.59
64.44
52.78
51.52
47.17
29.55
25.60
f1 (ppm)



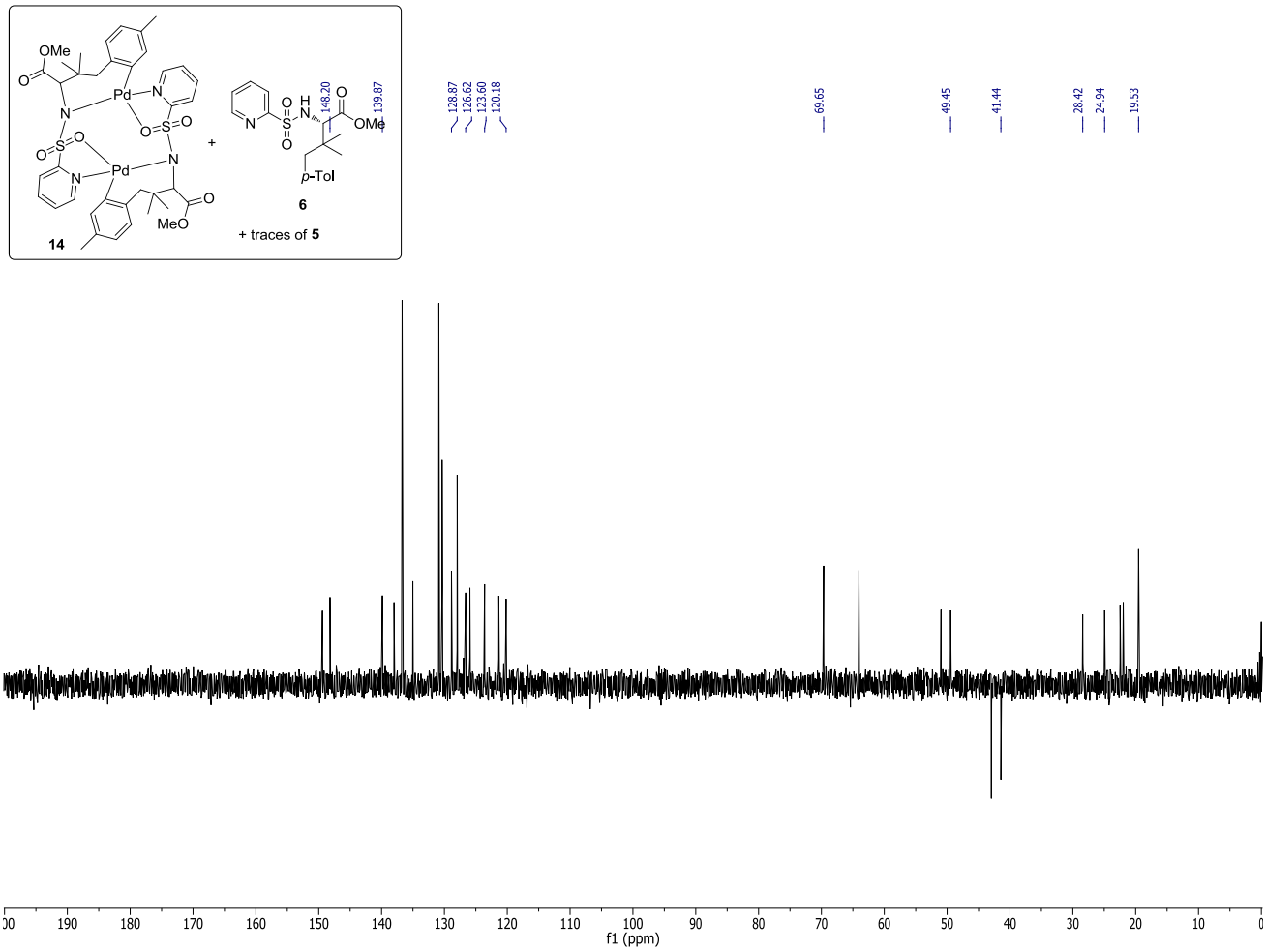
OMe
O
Pd
N
N
O=S=O
O
O=S
Pd
N
N
O
MeO
14
+
O
H
N
S
O
O
OMe
N
p-Tol
6
+ traces of 5



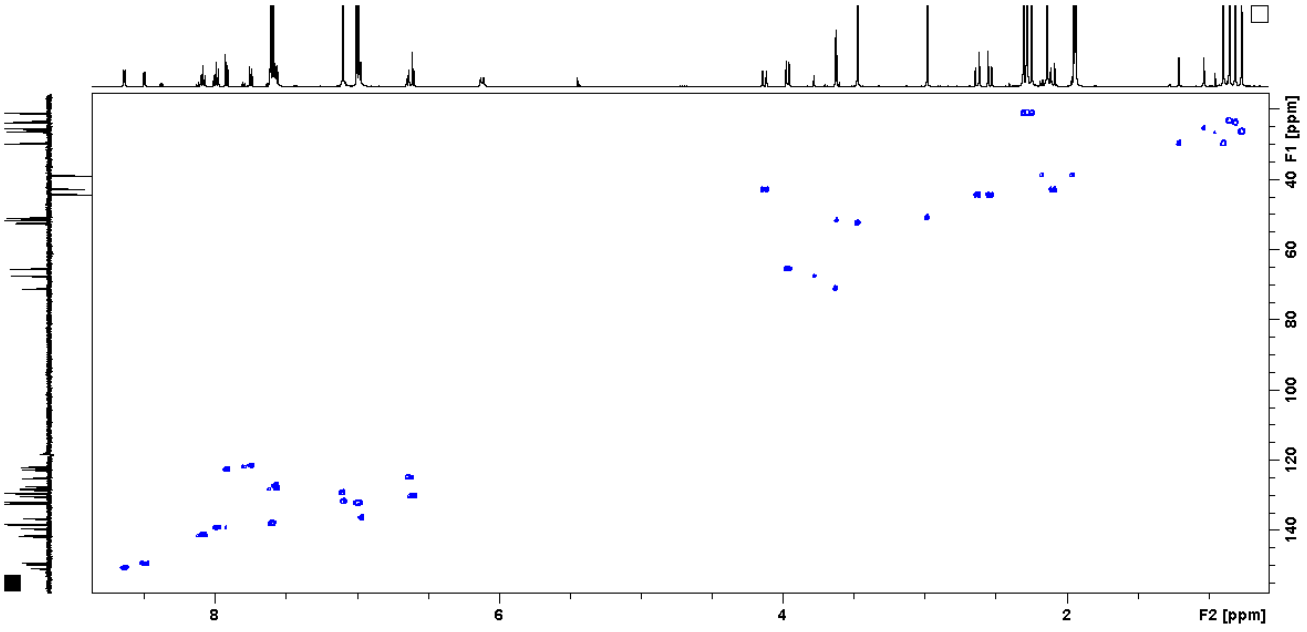
0.90
0.98
0.93
1.20
1.91
1.00
0.85
2.85
2.48
0.82
2.78
2.65
f1 (ppm)

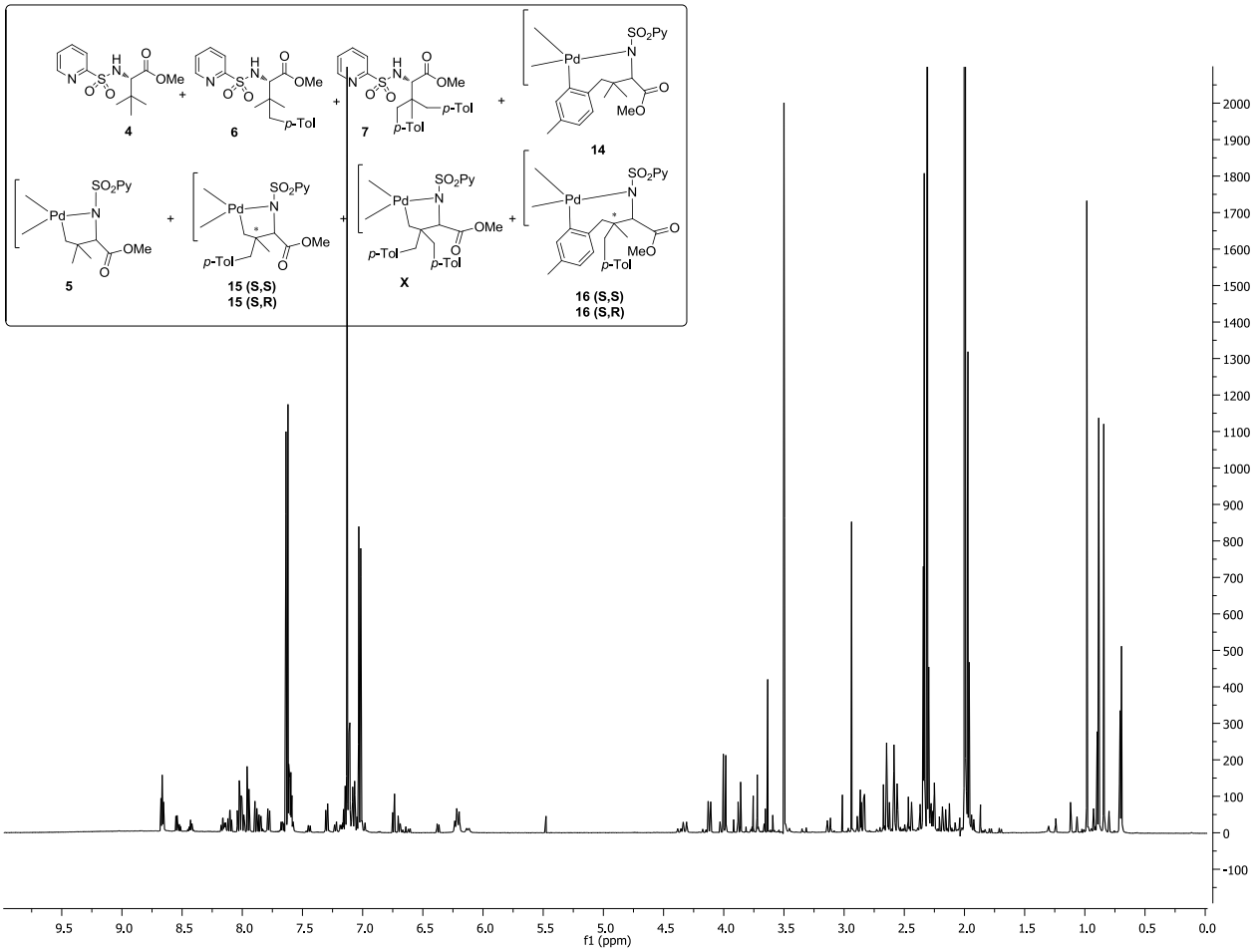


nmr60-cosy.2.ser
COSY CD3CN D:\\ QOL408 1
f2 (ppm)
f1 (ppm)

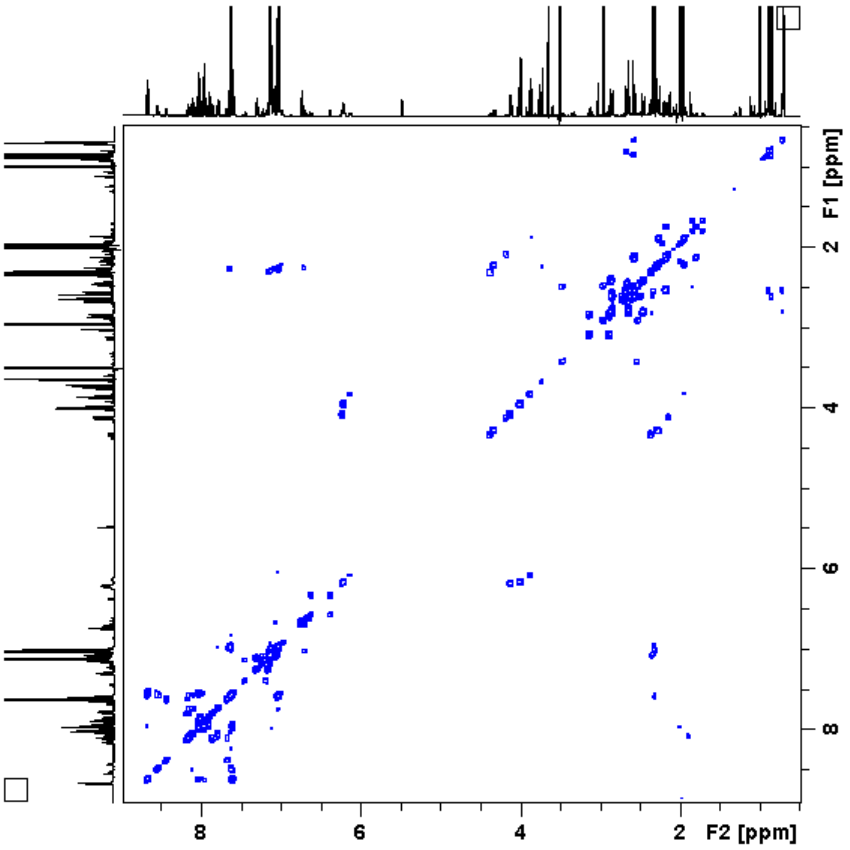

OMe
Pd
N
O
S
Pd
MeO
14
+
p-Tol
6
+ traces of 5
128.87
126.62
123.60
120.18
148.20
139.87
69.65
49.45
41.44
28.42
24.94
19.53
f1 (ppm)

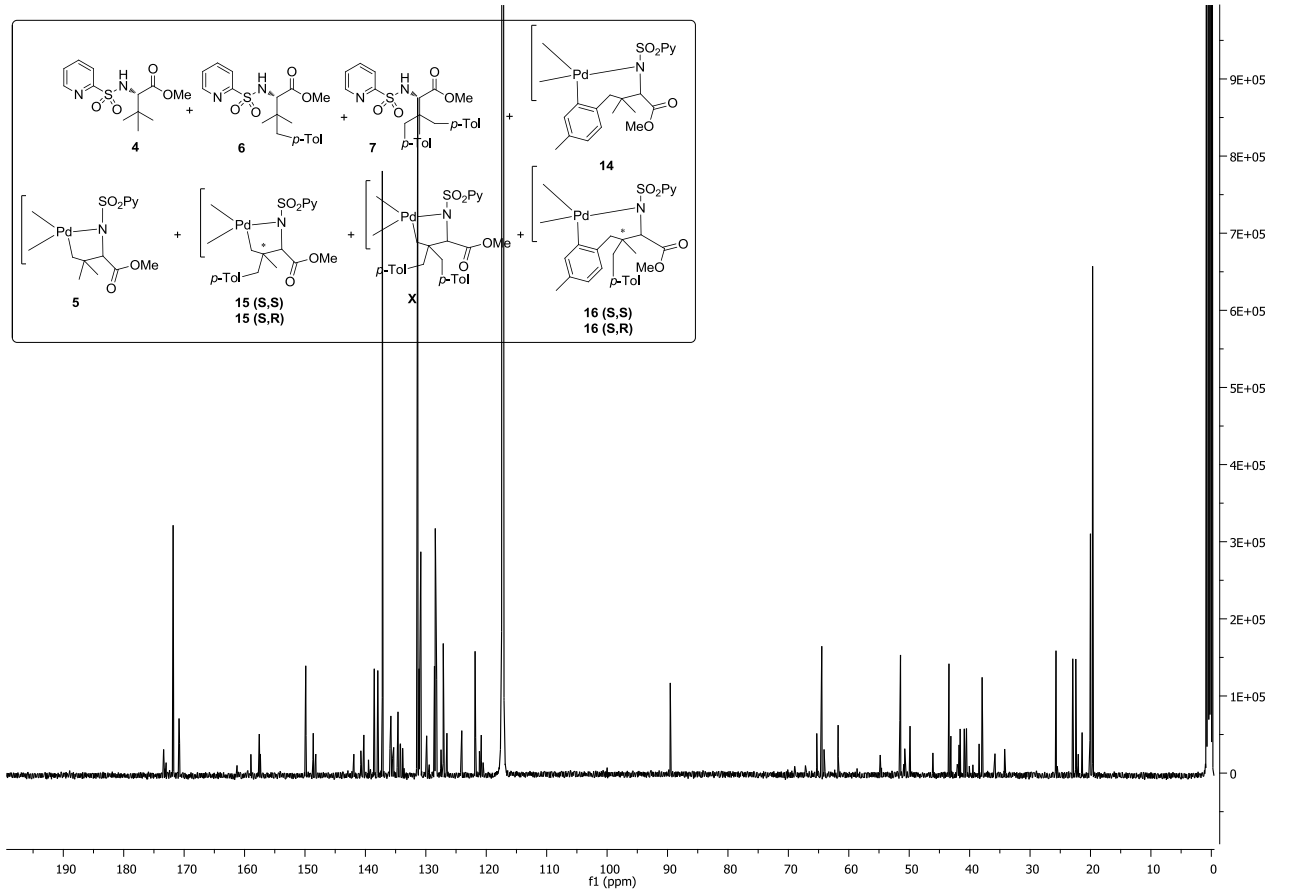
HSQC:


F1 [ppm]
F2 [ppm]

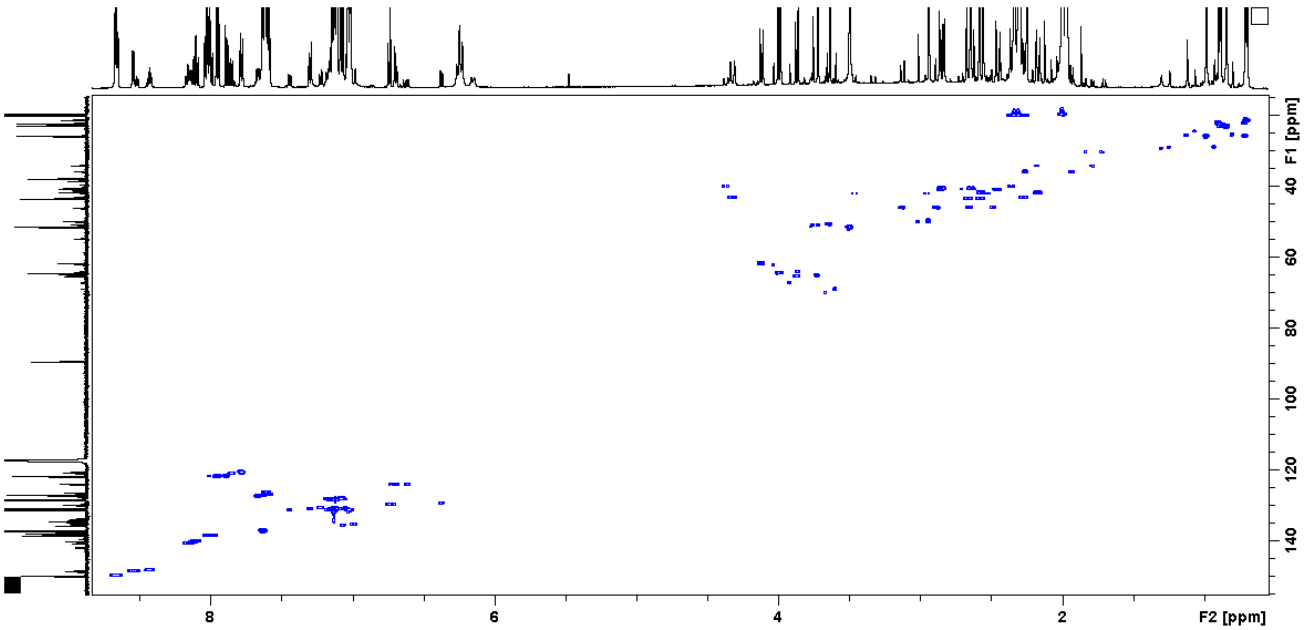


COSY:

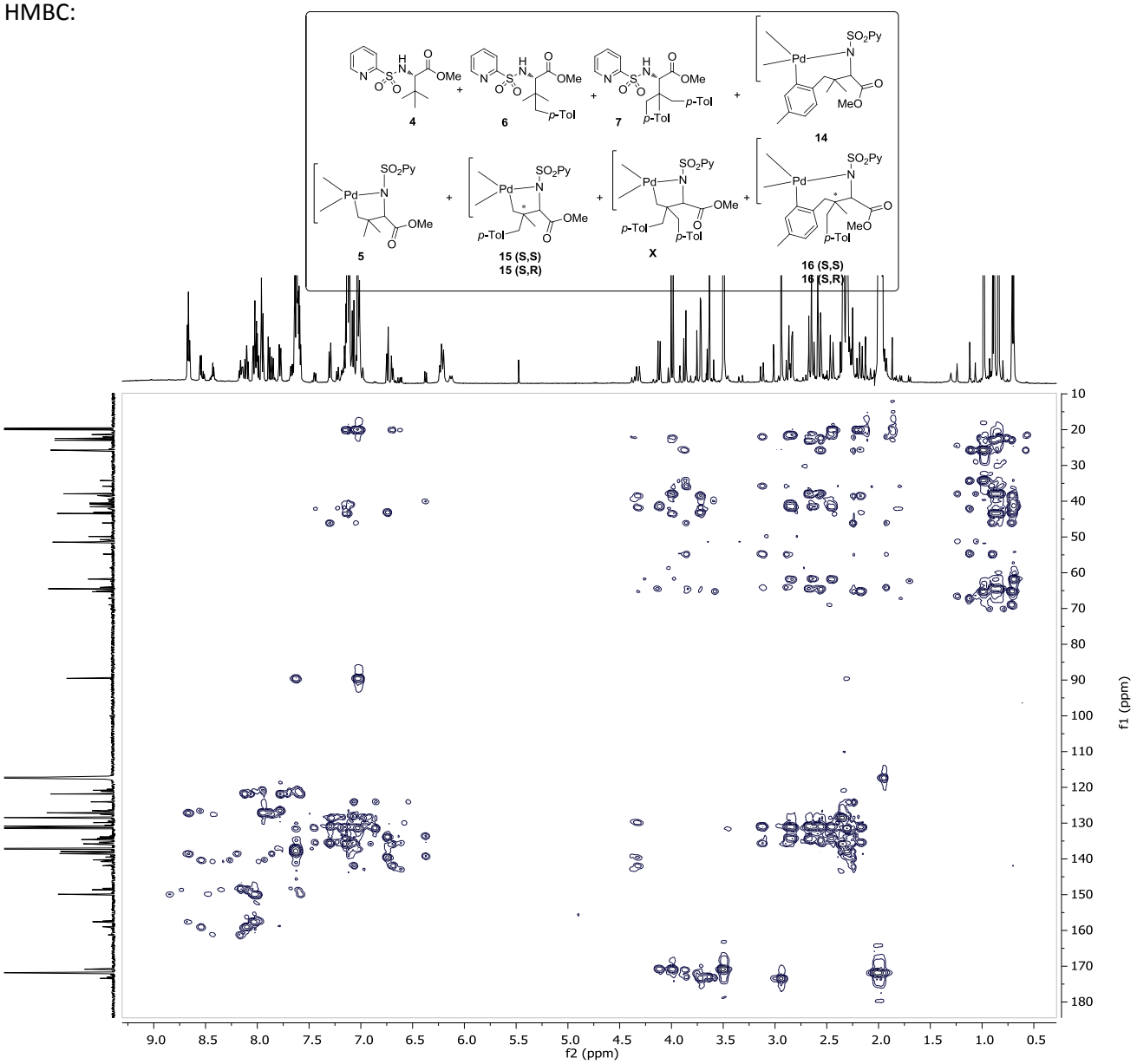




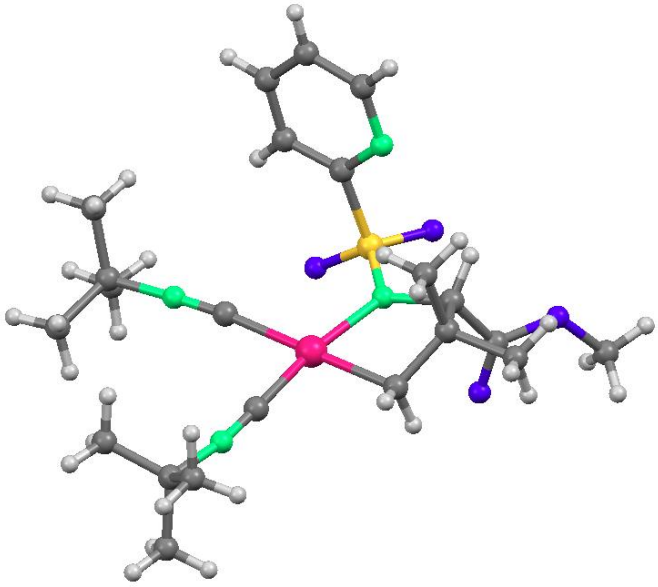
HSQC:



HMBC:



12. X-Ray Data of 8



Crystal data

Chemical formula sum: $C_{22}H_{34}N_4O_4PdS$

Chemical formula weight: 556.99

Symmetry cell: Orthorhombic

Symmetric space group name: *P* 2(1)2(1)2(1)

Cell volume: 2690.33 (13) $Å^3$

Cell formula units: *Z* = 4

Cell length a: 9.3740 (3) Å

Cell length b: 14.5468 (4) Å

Cell length c: 19.7294(5) Å

Cell measurement temperature: 296(2) K

Cell measurement reflections: 103234

Cell measurement theta (θ): 1.74 – 25.34 °

μ = 0.799 mm^{-1}

D_x= 1.375Mgm^{-3}

Crystal F(000): 1152

Crystal size: 0.16 x 0.22 x 0.34 mm