Supporting Information

$Pd(acac)(MeCN)_2]BF_4$: air-tolerant, activator-free catalyst for alkenes dimerization and polymerization

D.S. Suslov[a,1], M.V. Bykov[a], P.A. Abramov[b,c], M.V. Belova[a], I.A. Ushakov[d], V.K. Voronov[d], V.S. Tkach [a]

[a]Irkutsk State University, ul. K.Marksa, 1, Irkutsk, Russia, 664003

[b]Nikolaev Institute of Inorganic Chemistry SB RAS, pr-kt Akad. Lavrentieva, 3, Novosibirsk, Russia, 630090

[c]Novosibirsk State University,ul. Pirogova, 2, Novosibirsk, Russia, 630090

[d]Irkutsk State Tech Univ, Lermontov St, 83, Irkutsk, Russia, 664074

[1] Correspondence should be addressed: e-mail: suslov@chem.isu.ru; suslov.dmitry@gmail.com

Experimental details

All manipulations for air sensitive compounds were carried out under a stream of dry argon using standard inert techniques. Argon was purified before feeding to the reactor by passing through columns packed with oxygen scavenger (Fisher REDOX) and molecular sieve 5A (Aldrich), respectively. CH_2Cl_2 and CH_3CN were distilled from CaH_2. Solvents were stored over molecular sieves. Styrene, 4-methylstyrene, 4-^{t}Bu-styrene (99%, Aldrich) were purified by distillation under reduced pressure over CaH_2. Norbornene (Acros, 99%) were distilled from sodium-benzophenone and used as a solution (80 wt.%) in CH_2Cl_2. BF_3 OEt_2 (Acros, 99%) was distilled over CaH_2 prior to use. $Pd(acac)_2$ was synthesized according to a literature procedure[1] and recrystallized from acetone. All NMR spectra were recorded at room temperature on a Varian VXR-500S spectrometer or a Brucker DPX-250 spectrometer. IR spectra from KBr pellets were recorded on a Simex Infralum FT 801 spectrometer. Elemental analyses were measured using a CHN Thermo Finnigan Flash EA 1112 instrument. TG/DSC measurements were performed with a Netzsch STA 449-F3 instrument. The products of the catalytic runs were analyzed by GC–MS (Shimadzu QP2010 Ultra , GSBP-5MS capillary column) and GC (Chromatec, Crystall 5000.2, SGE BPX-5 capillary column).

Dimerization of styrenes

A mixture of the styrene (or styrene derivative) (22.7 mmol), 1.5 mL of CH_2Cl_2, and $[Pd(acac)(MeCN)_2]BF_4$ (22.7 μmol) were placed in a 10 mL glass flask equipped with a magnetic stirring bar. The reaction was carried out at 25 °C for 12 h with stirring. The conversion and selectivity were determined by GC. The products were isolated by vacuum distillation and analyzed by GS-MS and NMR spectroscopy.

Polymerization of norbornene

Polymerizations were carried out in a 10-mL glass reactor equipped with a magnetic stirrer. The reactor was filled with norbornene as a solution in CH_2Cl_2, the solution was kept at desired temperature for 15 min and then the palladium complex was added. After stirring for a time needed, the polymers formed were precipitated in ethanol. The precipitated polymers were washed three times with ethanol, and dried in vacuum at 80 °C for 6 h.

Preparation of $[Pd(acac)(MeCN)_2]BF_4$

$BF_3{\cdot}OEt_2$ (0.6 mL, 4.98 mmol) was added dropwise to solution of $Pd(acac)_2$ (0.75 g, 2.46 mmol) and MeCN (0.65 mL) in toluene (150 mL) and stirred at room temperature for 1 h. The reaction mixture was cooled to −18 °C and stored overnight. The crude product was then filtered, and the yellow solid was washed

twice with Et_2O and dried under vacuum. Yield: 0.88 g (96%). Anal. Calcd for $C_9H_{13}BF_4N_2O_2Pd$: C, 28.87; H, 3.50; N, 7.48. Found: C, 28.36; H, 3.38; N, 7.08. Melting point 117 °C. ^{1}H NMR (400.1 MHz, CD_3CN): δ 5.75 (s, 1H, acac-CH), 2.09 (s, 6H, acac-CH_3), 1.96 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (100.7 MHz, CD_3CN): δ 187.7 (acac-CO), 118.3 (C≡N), 102.4 (acac-CH), 24.3 (acac-CH_3), 1.5 (CH_3). ^{19}F NMR (376.3 MHz, CD_3CN): δ −152.09 (s, 1F), −152.15 (s, 4F) (BF_4, the integral ratio of the two signals is 1:4 equal to the $^{10}B/^{11}B$ isotopic ratio, natural isotopic abundance: $^{10}B/^{11}B$=19.4%/80.6%). ^{11}B NMR (128.3 MHz, CD_3CN): δ −1.82 (BF_4).

After evaporation in vacuo, the filtrate was observed to give 0.34 g of a white powder, BF_2(acac). The product was characterized by GS-MS analysis and FTIR.

Calculations

All density functional theory calculations were performed with the ORCA program.[2] All geometry optimizations were run with tight convergence criteria, using the BP86 functional,[3,4] making use of the resolution of the identity technique.[5] The applicability of gradient-corrected functionals as BP86 for the structural prediction of transition metal compounds and reliable determination of the kinetic balance are well documented[6–11]. The basis sets that were used were the Weigend–Ahlrichs basis sets.[12,13] Triple-ξ-quality basis sets with one set of polarization functions (def2-TZVP) were used for the palladium. The remaining atoms were described by slightly smaller def2-SVP basis sets. A scalar relativistic correction was applied using the zeroth-order regular approximation (ZORA) method.[14–16]

X-ray Diffraction Studies

Crystallographic data and refinement details are given in Table 1S. The diffraction data were collected on a New Xcalibur (Agilent Technologies) diffractometer with MoK_α radiation (λ = 0.71073) by doing φ and ω scans of narrow (0.5°) frames at 130 K. Absorption correction was done empirically using SCALE3 ABSPACK (CrysAlisPro, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET) (compiled Aug 13 2014,18:06:01)). Structure was solved by direct method and refined by full-matrix least-squares treatment against $|F|^2$ in anisotropic approximation with ShelXle program.[17] All non-hydrogen atoms of 1 were refined anisotropically. The hydrogen atoms were refined directly from experiment for γ-CH of $acac^-$ ligand and CH_3 groups of coordinated CH_3CN molecules. The hydrogen atoms of CH_3 groups of the $acac^-$ ligand were not localized.

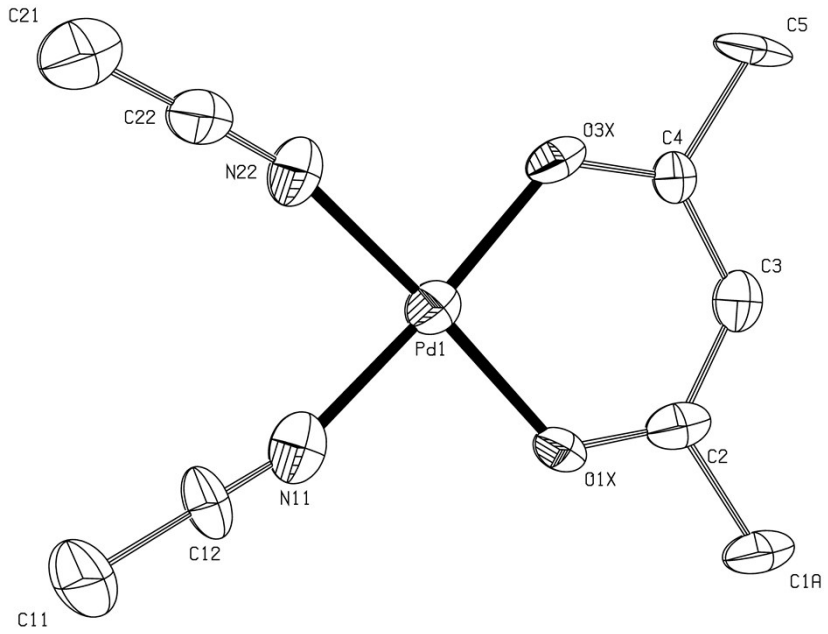


Fig. S1. Displacement ellipsoid plot (50% probability) of $[Pd(acac)(MeCN)_2]BF_4$(**1**). The counteranion BF_4 was omitted for clarity. Selected bond distances (Å): Pd1–O1X 1.953(9), Pd1–O3X 1.957(9), Pd1–N22 1.991(12), Pd1–N11 1.994(13).

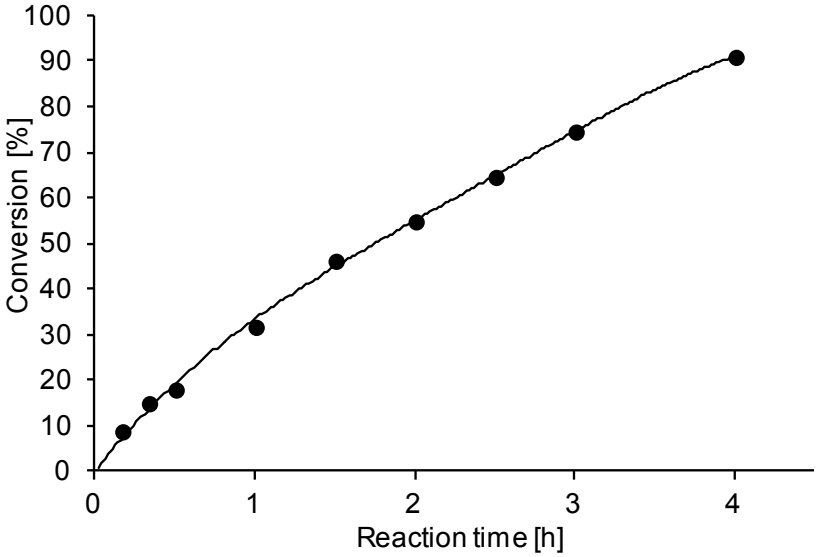


Fig. S2. Plot of Polymerization Yields vs. Reaction Time for **1** at 20°C in CH_2Cl_2; $[NB]_0/[Pd]_0$ = 10 000; 40.5 mmol NB; $C_{Pd} = 7.7 \cdot 10^{-4}$ mol/l

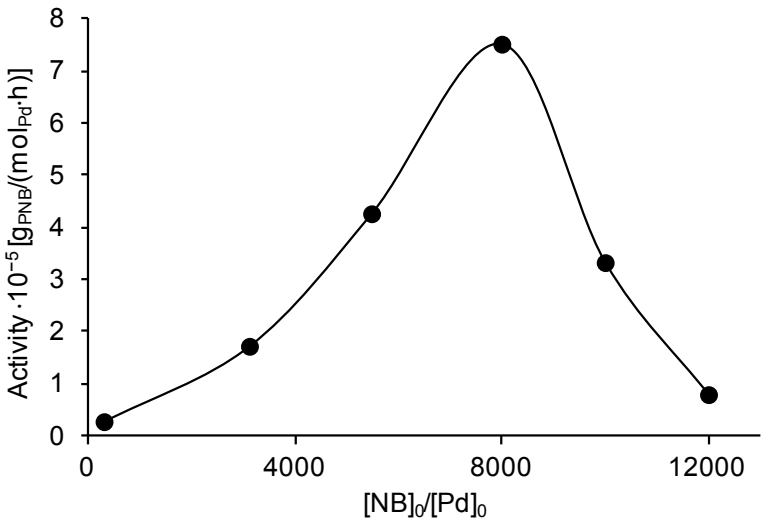


Fig. S3. Plot of activity vs. NB/Pd [mole ratio] for **1** at 20°C in CH_2Cl_2 ; 40.5 mmol NB; C_{Pd} = 7.7·10^{-4} mol/l

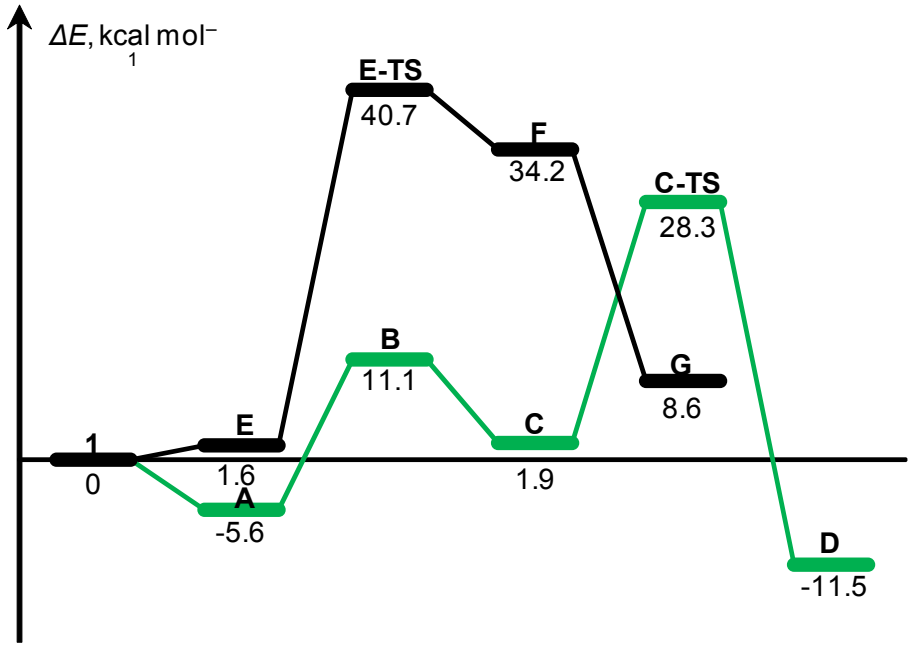


Fig. S4. Energy Diagram for the Reaction of **1** with Styrene.

1. Crystal Structure Determination of **1**

Table S1. X-Ray Crystal Structure Data for **1** (CCDC 1414861)

	(1)
Chemical formula	$C_9H_{13}BF_4N_2O_2Pd$
M_r	374.42
Crystal system, space group	Monoclinic, *C*2/*m*
Temperature (K)	130
a, *b*, *c* (Å)	14.4049 (4), 6.40080 (18), 14.9520 (5)
β (°)	106.995 (3)
V (Å^3)	1318.42 (7)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	1.886
Crystal size (mm)	0.12 × 0.04 × 0.02
Diffractometer	New Xcalibur, AtlasS2 diffractometer
Absorption correction	Multi-scan *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET) (compiled Aug 13 2014,18:06:01) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.777, 1.000
No. of measured, independent and observed reflections	3936, 1982, 1795
R_{int}	0.028
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.723
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.038, 0.099, 1.07
No. of reflections, parameters, restraints	1982, 124, 0
H-atom treatment	Only H-atom coordinates refined
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.97, -1.38

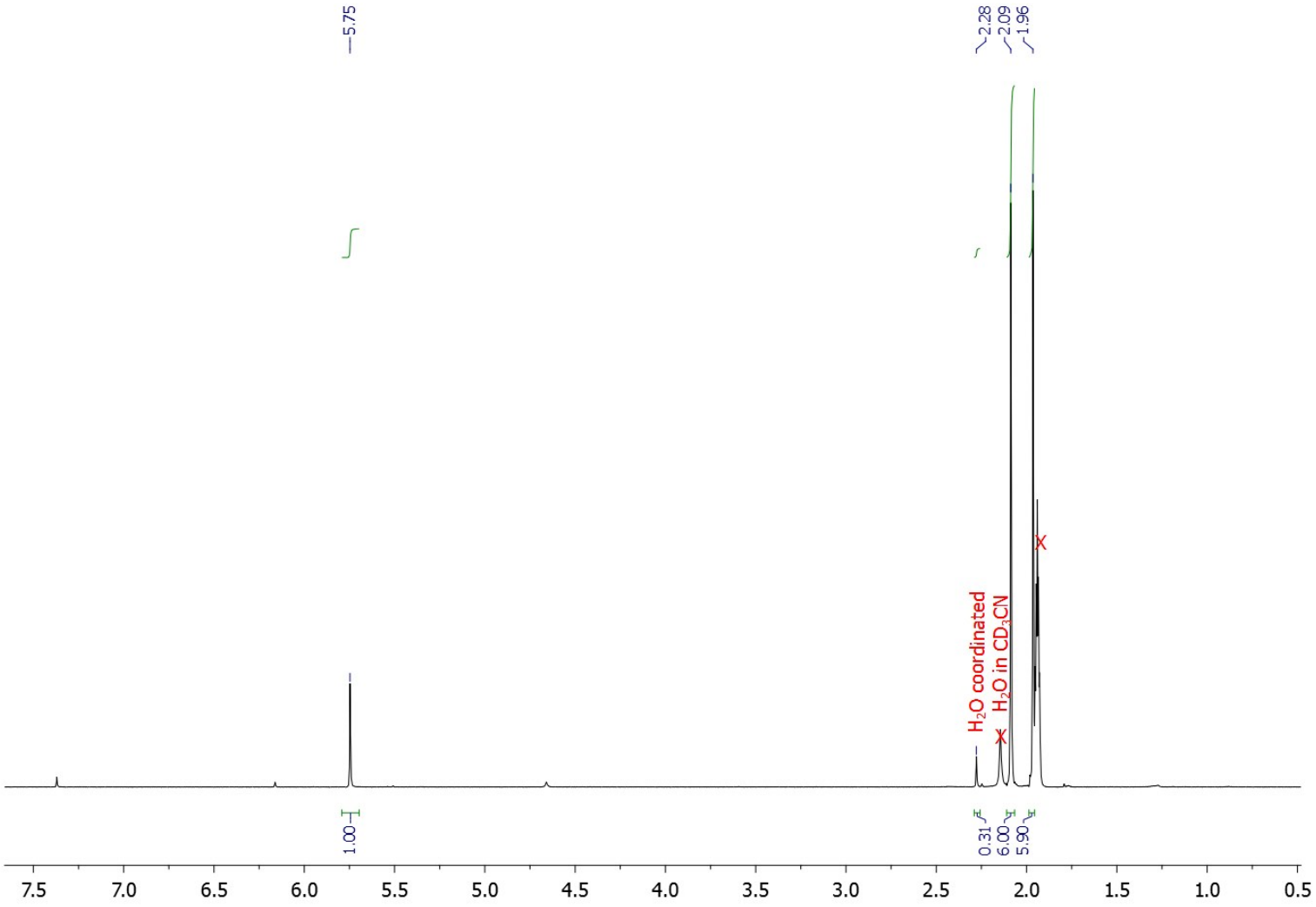
Computer programs: Computer programs: '*CrysAlis PRO*, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET) (compiled Aug 13 2014,18:06:01)', *SHELXL2013* (Sheldrick, 2013), SHELXLE.

Table S2. Selected geometric parameters for **1** (Å, º)

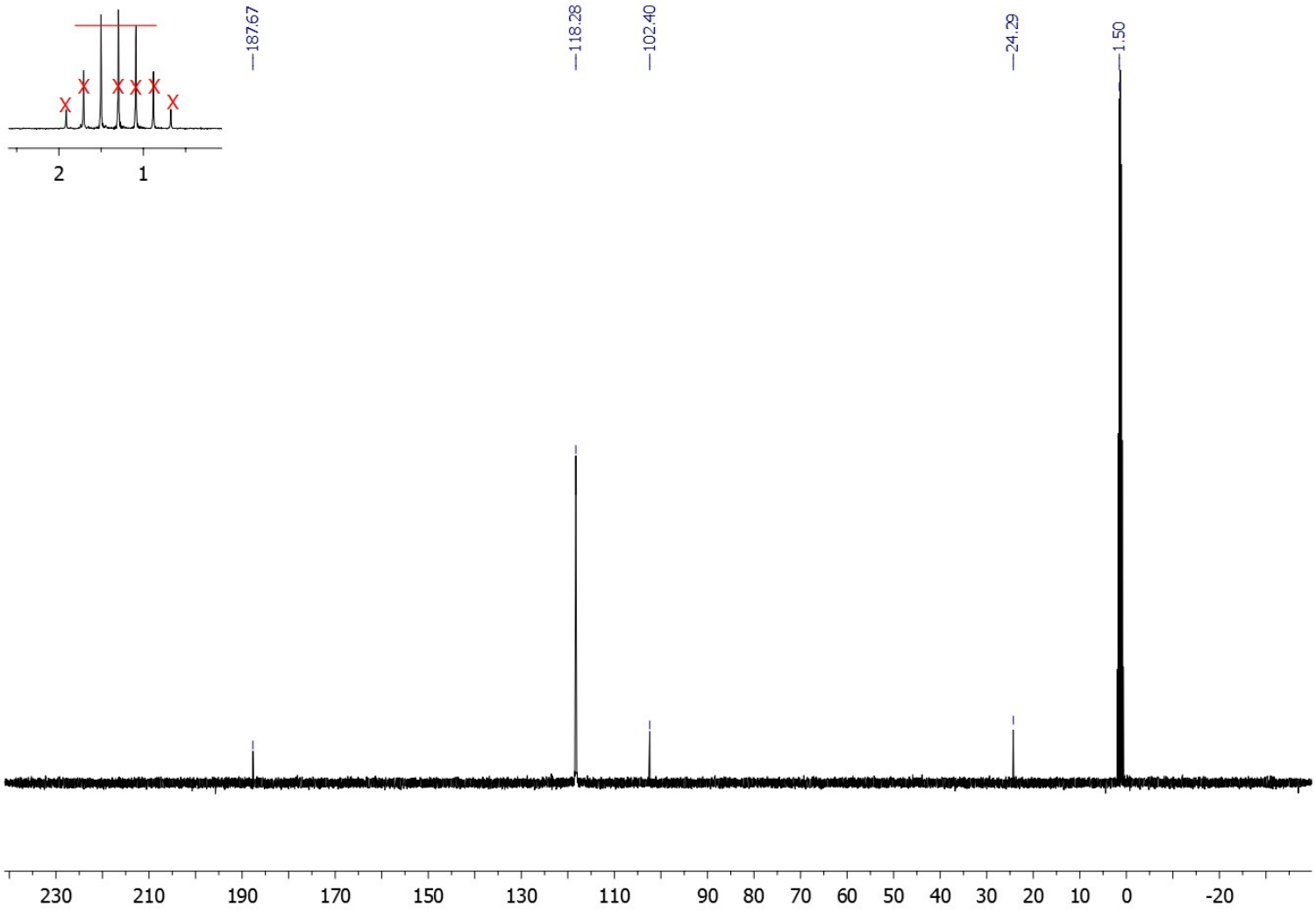
Pd1—O1X	1.953 (9)	C3—C2	1.391 (17)
Pd1—O3X	1.957 (9)	C2—O1X	1.268 (16)
Pd1—N22	1.991 (12)	C2—C1A	1.519 (17)
Pd1—N11	1.994 (13)	C22—C21	1.41 (2)
N11—C12	1.103 (18)	C12—C11	1.50 (2)
N22—C22	1.15 (2)	B1—F3^{i}	1.339 (16)
C4—O3X	1.262 (15)	B1—F3	1.339 (16)
C4—C3	1.403 (17)	B1—F2	1.34 (3)
C4—C5	1.516 (15)	B1—F1	1.38 (3)
O1X—Pd1—O3X	95.2 (3)	O1X—C2—C1A	113.3 (11)
O1X—Pd1—N22	176.3 (4)	C3—C2—C1A	119.3 (13)
O3X—Pd1—N22	88.4 (4)	N22—C22—C21	178.0 (17)
O1X—Pd1—N11	89.0 (4)	N11—C12—C11	179.9 (18)
O3X—Pd1—N11	175.8 (4)	F3^{i}—B1—F3	107.5 (18)
N22—Pd1—N11	87.4 (5)	F3^{i}—B1—F2	111.7 (16)
C12—N11—Pd1	165.4 (13)	F3—B1—F2	111.7 (16)
C22—N22—Pd1	165.6 (12)	F3^{i}—B1—F1	108.9 (16)
O3X—C4—C3	126.5 (11)	F3—B1—F1	108.9 (16)
O3X—C4—C5	115.0 (11)	F2—B1—F1	108.0 (16)
C3—C4—C5	118.5 (11)	C2—O1X—Pd1	122.7 (7)
C2—C3—C4	124.9 (12)	C4—O3X—Pd1	123.3 (8)
O1X—C2—C3	127.4 (12)		

2. NMR spectra of **1**

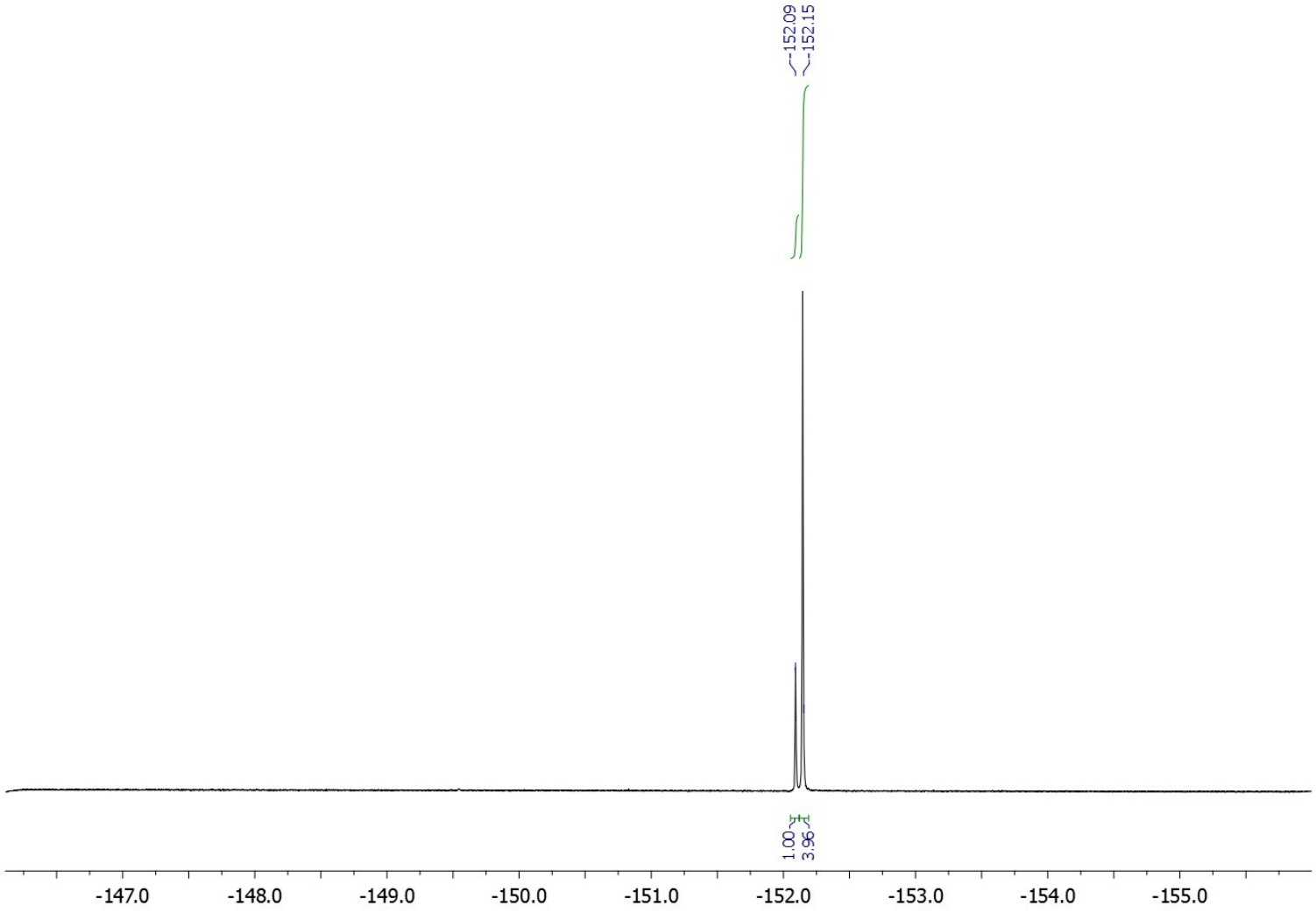
^{1}H NMR



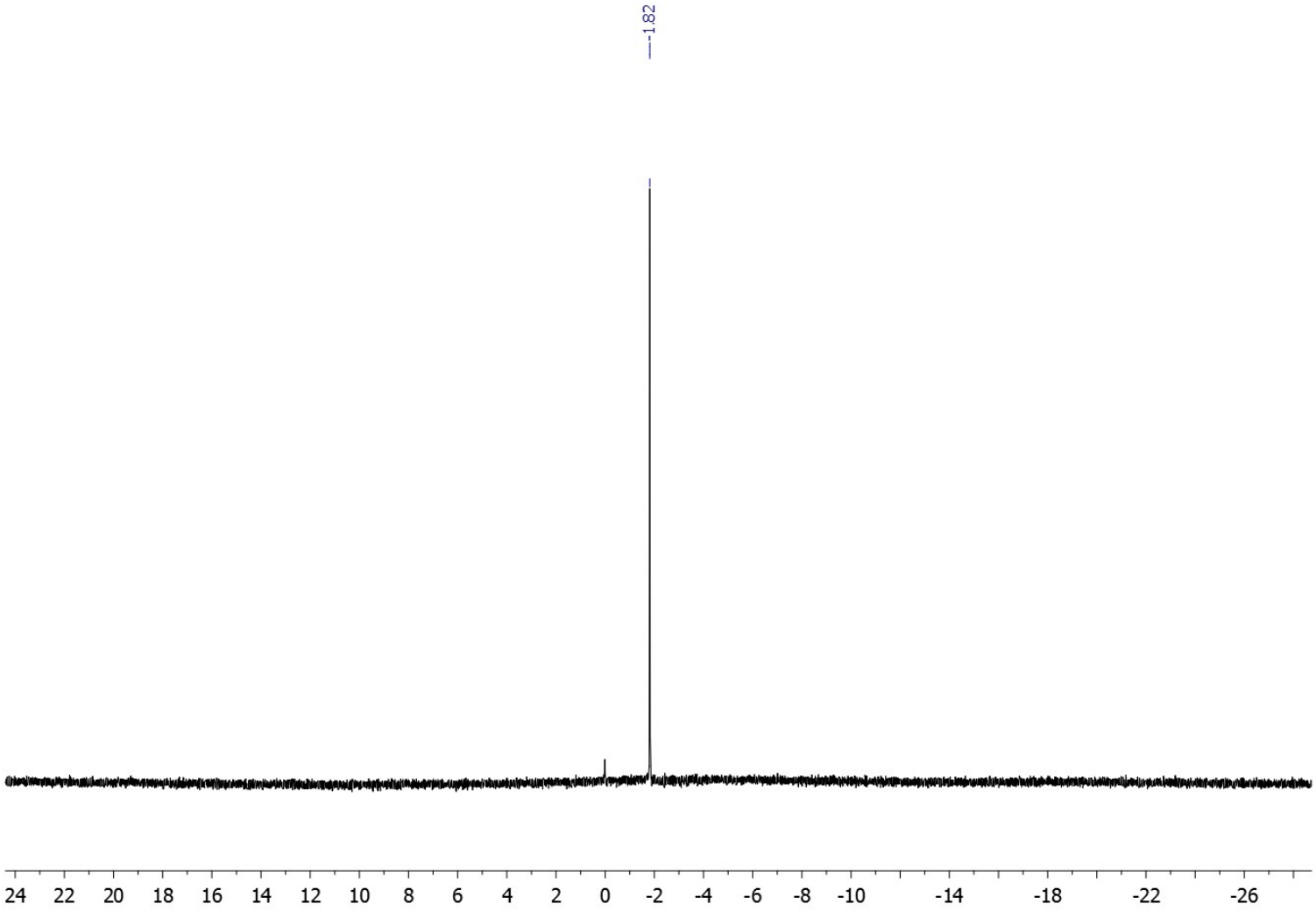
^{13}C NMR


187.67
118.28
102.40
24.29
1.50
2
1
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-20

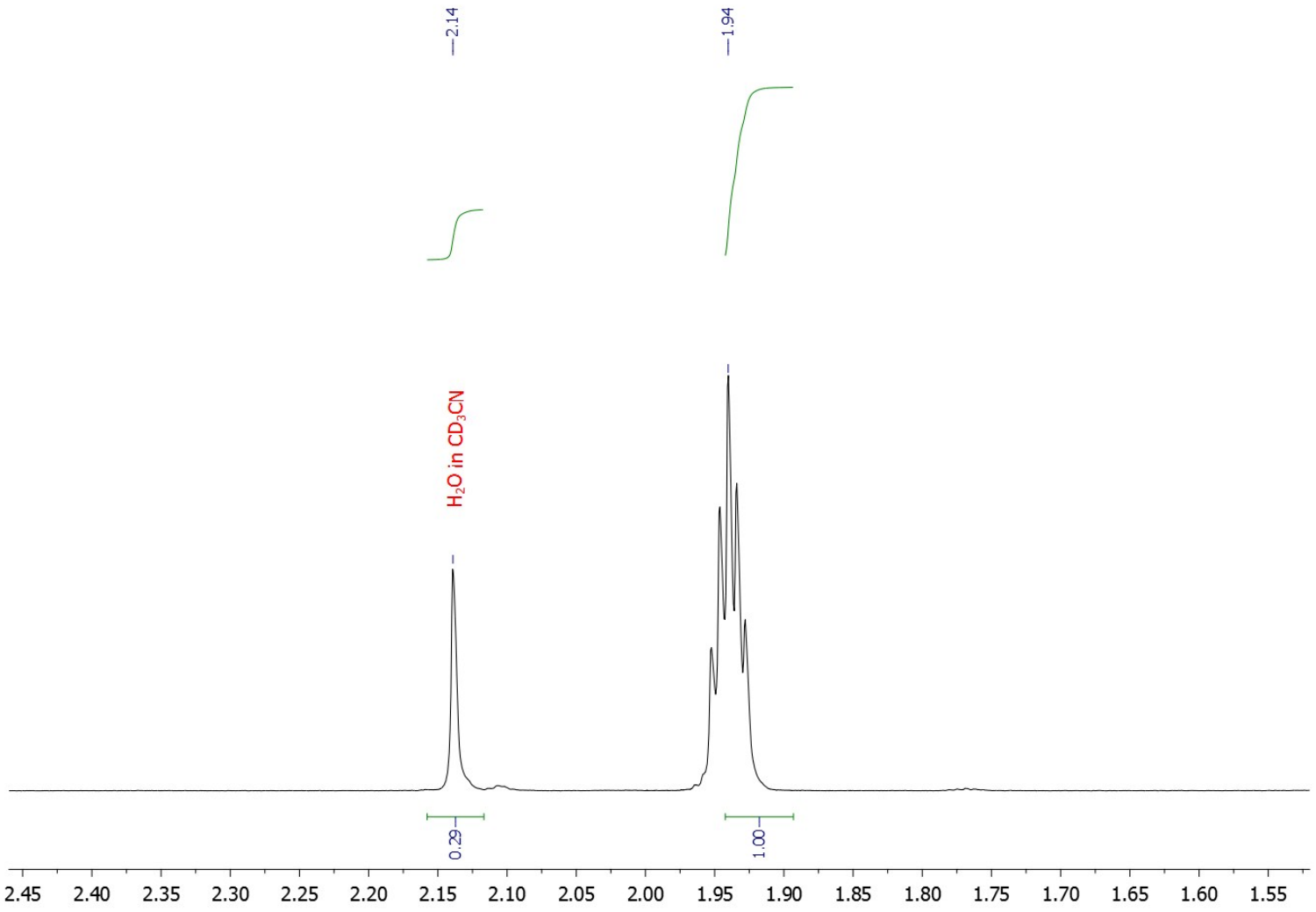
^{19}F NMR


-152.09
-152.15
1.00
3.96
-147.0
-148.0
-149.0
-150.0
-151.0
-152.0
-153.0
-154.0
-155.0

^{11}B NMR



Impurities in CD_3CN (^1H NMR):



3. Vinylarenes dimerization

1,3-Diphenylbut-1-ene: ^{1}H NMR δ (CDCl3): 7.45–7.24 (m, 10 H), 6.48–6.47 (m, 2H), 3.74-3.70 (m, 1H), 1.56-1.53 (m, 3H); ^{13}C NMR δ ($CDCl_3$): 145.8, 137.8, 135.4, 128.7, 127.5, 126.4, 42.8, 21.4.; GC/MS (EI): *m/z* = 208 (M^+), 207, 194, 193, 191, 189, 179, 178, 165, 131, 130, 129, 128, 116, 115, 103, 91, 89, 78, 77, 65, 51.

1,3-Di(4-methylphenyl)but-1-ene: ^{1}H NMR δ (CCl_4): 7.37-7.10 (m, 8H), 6.45-6.36 (m, 2H), 3.79-3.70 (m, 1H), 2.51-2.42 (m, 6H), 1.58-1.56 (m, 3H); ^{13}C NMR δ (CCl_4): 142.0, 135.6, 134.6, 134.4, 133.7, 128.6, 127.9, 126.7, 125.7, 41.7, 21.0, 20.7; GC/MS (EI): *m/z* = 236 (M^+), 235, 222, 221, 220, 207, 206, 205, 193, 192, 191, 178, 165, 144, 143, 130, 129, 128, 127, 117, 115, 109, 105, 103, 102, 101, 91, 89, 79, 77, 65.

1,3-Di(4-t-butylphenyl)but-1-ene: ^{1}H NMR δ (CCl_4): 7.47-7.32 (m, 8H), 6.58-6.48 (m, 2H), 3.78-3.69 (m, 1H), 1.59-1.56 (m, 3H), 1.44 (s, 18H); ^{13}C NMR δ (CCl_4): 148.9, 147.9, 142.0, 134.4, 133.9, 127.8, 126.5, 125.6, 124.7, 124.6, 41.6, 33.9, 31.1, 20.9; GC/MS (EI): *m/z* = 320 (M^+), 305, 264, 263, 262, 207, 145, 131, 129, 128, 117, 115, 109, 91, 57, 56, 41.

4. Characterization of the polynorbornene

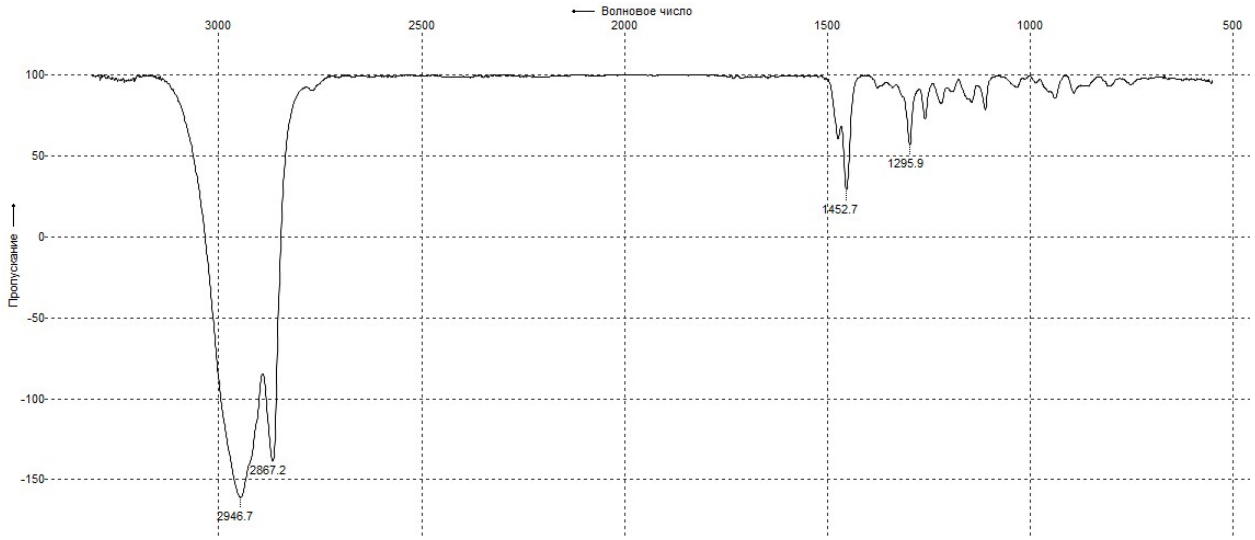


Fig. S5. The IR spectrum of the PNB in KBr

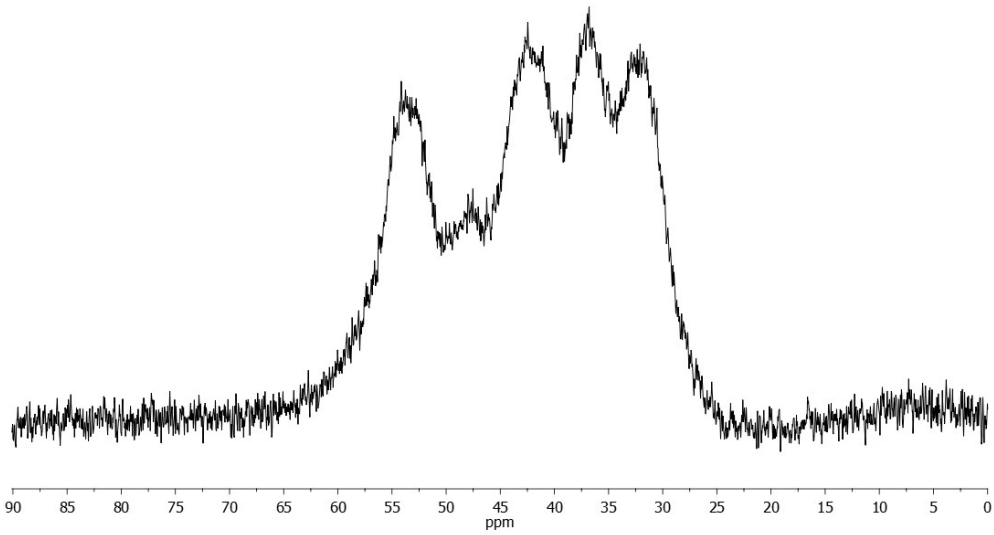


Fig. S6. ^{13}C NMR spectrum of the PNB in 1,2,4-trichlorobenzene

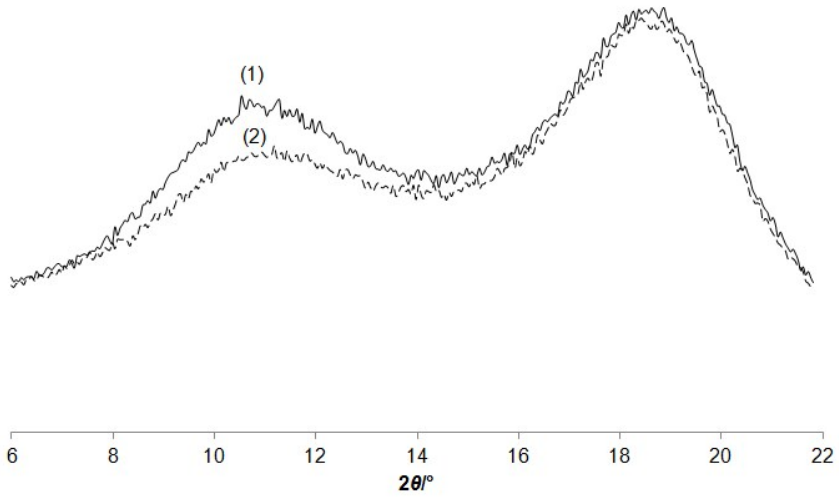


Fig. S7. The WXRD spectra of the polynorbornenes. (1) The polynorbornene produced by $[Pd(acac)(MeCN)_2]BF_4$ complex; (2) The polynorbornene produced by the $[Pd(acac)(MeCN)_2]BF_4/BF_3{\cdot}OEt_2$ catalyst system.

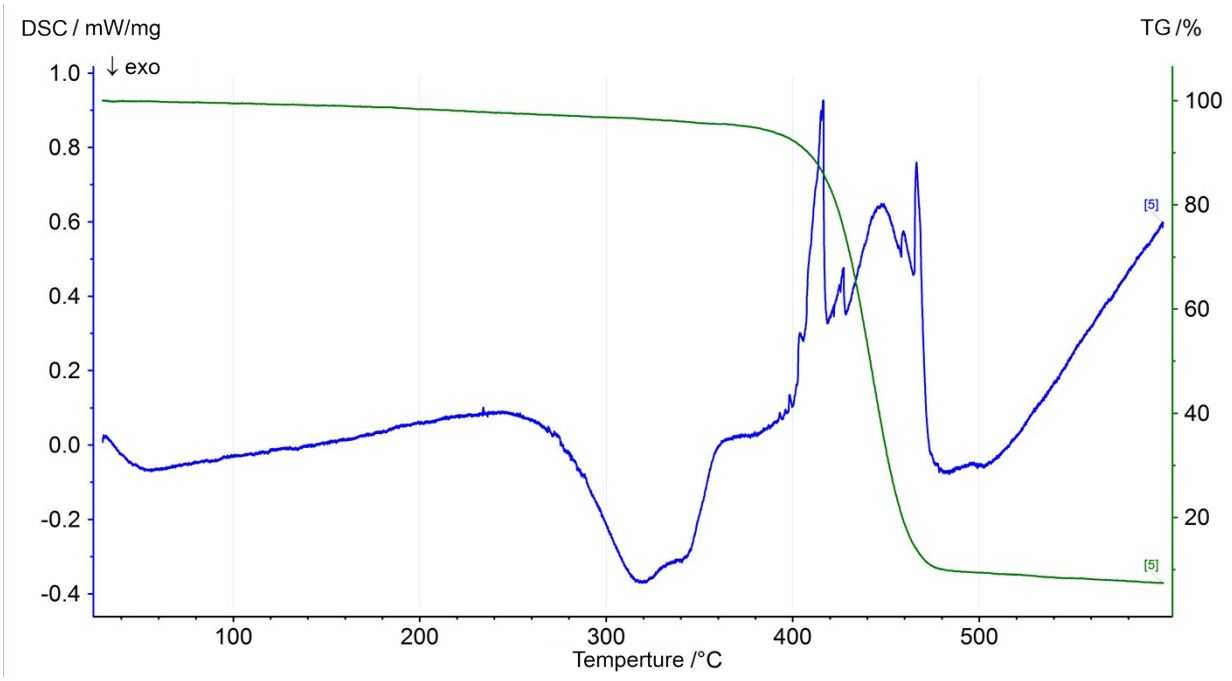


Fig. S8. The DSC/TGA spectrum of the polynorbornene.

5. Pre-catalyst activation

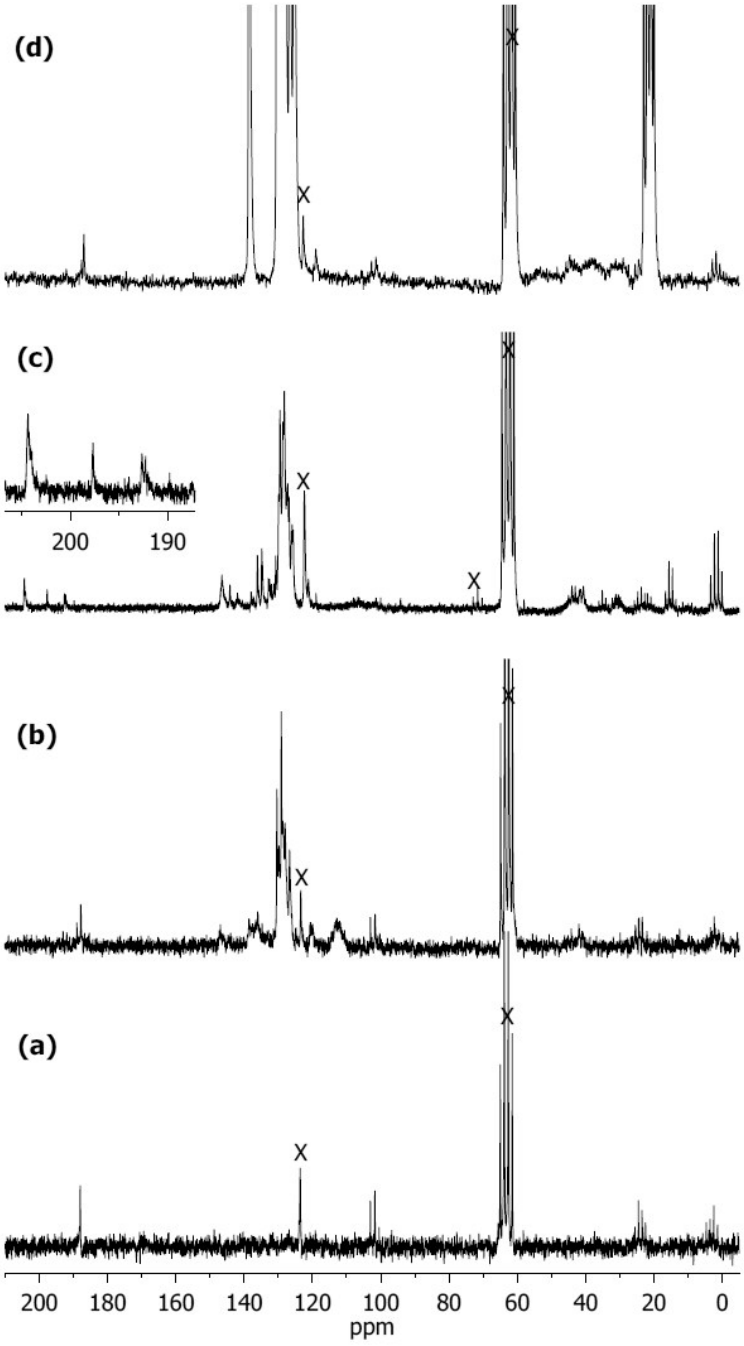


Fig. S9. ^{13}C NMR spectra of the (a) complex **1,** (b) reaction mixture of **1** and St (St:Pd = 4:1) after 2 h, (c) 20 h, (d) the reaction mixture of **1** and NB (NB:Pd = 4:1, NB 80 mol% in toluene) in CH_3NO_2 at 25 °C. Crosses mark signals assigned to solvents or impurities in solvent.

References:

1 I. Yoshida, H. Kobayashi and K. Ueno, *J. Inorg. Nucl. Chem.*, 1973, 35, 4061–4070.

2 F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2012, **2**, 73–78.

3 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100.

4 J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822–8824.

5 K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **242**, 652–660.

6 M. Bühl and H. Kabrede, *J. Chem. Theory Comput.*, 2006, **2**, 1282–1290.

7 M. Bühl, C. Reimann, D. A. Pantazis, T. Bredow and F. Neese, *J. Chem. Theory Comput.*, 2008, **4**, 1449–1459.

8 C. J. Cramer and D. G. Truhlar, *Phys. Chem. Chem. Phys.*, 2009, **11**, 10757–10816.

9 M. Waller, H. Braun, N. Hojdis and M. Bühl, *J. Chem. Theory Comput.*, 2007, **3**, 2234–2242.

10 M. J. Szabo, R. F. Jordan, A. Michalak, W. E. Piers, T. Weiss, S.-Y. Yang and T. Ziegler, *Organometallics*, 2004, **23**, 5565–5572.

11 S. Tobisch and T. Ziegler, *J. Am. Chem. Soc.*, 2004, **126**, 9059–9071.

12 F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057–65.

13 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–305.

14 E. van Lenthe, A. van der Avoird and P. E. S. Wormer, *J. Chem. Phys.*, 1998, **108**, 4783–4796.

15 E. van Lenthe, J. G. Snijders and E. J. Baerends, *J. Chem. Phys.*, 1996, **105**, 6505–6516.

16 E. van Lenthe, S. Faas and J. S. Snijders, *Chem. Phys. Lett.*, 2000, **328**, 107–112.

17 C. B. Hübschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Crystallogr.*, 2011, **44**, 1281–1284.

Computed Cartesian coordinates (Å) and energies (hartrees) for all species computed with the BP86 functional.

Cation of 1

BP86 Energy = -5715.171182466

Pd	-0.279111	-0.000472	0.007560
C	-2.402556	2.352748	0.029509
N	-1.668225	1.447058	0.021404
C	-3.312382	3.484538	0.038980
H	-3.921177	3.476082	0.960549
H	-2.737419	4.426522	0.000130
H	-3.984500	3.440363	-0.836478
C	-2.403771	-2.352778	0.000071
N	-1.668196	-1.448068	0.003486
C	-3.314127	-3.484603	-0.003050
H	-3.666352	-3.691334	1.022650
H	-4.185774	-3.271630	-0.646388
H	-2.796467	-4.380242	-0.389735
C	2.351445	-1.253962	-0.010949
O	1.074429	-1.455758	-0.005946
C	2.351229	1.253651	0.002753
O	1.074167	1.455133	0.010595
C	2.995402	-0.000075	-0.007623
H	4.089755	0.000051	-0.013386
C	3.163380	-2.528370	-0.021498
H	2.906695	-3.137222	0.864376
H	2.900709	-3.126196	-0.913153
H	4.245309	-2.327450	-0.024049
C	3.162933	2.528250	0.005998
H	2.895983	3.138425	-0.875912
H	2.910381	3.124593	0.901574
H	4.244868	2.327601	-0.004174

Path I

A

BP86 Energy = -6039.398695009

Pd	-0.033322	0.271637	-0.411909
C	2.098391	2.575299	-0.793475
N	1.243715	1.788426	-0.699317
C	3.176677	3.541105	-0.893662
H	2.801433	4.558493	-0.685425
H	3.953967	3.284608	-0.151856
H	3.618516	3.519502	-1.905428
C	-2.593342	2.031499	-1.024130
N	-1.623176	1.420280	-0.813427
C	-3.804765	2.789075	-1.284464
H	-4.281054	3.079502	-0.331404
H	-3.567150	3.701793	-1.858634
H	-4.514809	2.174693	-1.866739
C	-0.957131	-2.453220	0.031447
O	-1.315211	-1.228398	-0.162966
C	1.533344	-2.139563	0.114932
O	1.573736	-0.845583	-0.008709
C	0.369648	-2.928920	0.124886
H	0.502526	-4.006971	0.255676
C	-2.118322	-3.409780	0.164646
H	-2.731074	-3.121909	1.038502
H	-2.767115	-3.332313	-0.726278
H	-1.783869	-4.450724	0.286300
C	2.890575	-2.778476	0.272483
H	3.564523	-2.423222	-0.526854
H	3.324900	-2.459608	1.236212
H	2.832376	-3.877091	0.247510
F	2.667317	-0.782929	2.759319
F	3.369639	1.042786	1.569670
B	2.410578	0.381092	2.195022
F	1.217267	0.932573	2.337407

B

BP86 Energy = -6039.368469586

H	5.407091	-0.787819	1.088146
H	5.577522	-0.172500	-0.592570
C	5.050630	-0.900423	0.049026
H	5.286435	-1.921228	-0.300539
H	0.950774	4.360217	1.549192
C	3.617223	-0.676252	-0.014005
C	0.100493	4.072578	0.905656
H	0.036903	4.773216	0.054759
H	-0.835834	4.111969	1.491240
N	2.465149	-0.500321	-0.067877
C	0.267283	2.711818	0.432974
N	0.377161	1.606642	0.072870
Pd	0.416974	-0.349862	-0.262885
O	-0.093451	-2.359702	-0.391938
H	-2.587650	1.999955	-1.162296
F	-2.461817	2.556014	1.900973
C	-1.618350	-0.687006	-0.620246
H	-1.598547	-0.652076	-1.724736
F	-3.092351	1.088815	3.557995
C	-1.290057	-2.040516	-0.091327
C	-2.573158	0.233051	0.050674
B	-3.338084	1.621975	2.365920
O	-2.694268	0.168915	1.287732
C	-3.301855	1.235637	-0.801063
H	-4.100032	1.720991	-0.222680
H	-2.416486	-2.362643	1.670930
H	-1.650514	-3.853539	0.984338
C	-2.158354	-2.907776	0.743164
H	-3.720796	0.746469	-1.698949
F	-4.606594	1.739236	1.949648
H	-3.113640	-3.099934	0.220077

C

BP86 Energy = -6349.025974361

H	2.831329	3.893325	2.544514
H	2.952635	-1.119011	3.479412
H	3.273147	0.335483	2.452766
C	2.557182	4.096383	1.494217
H	4.148632	-1.177813	2.137753
H	3.471369	4.353401	0.930778
C	3.173385	-0.765137	2.460507
H	1.866322	4.957674	1.467262
C	1.923733	2.926501	0.909144
C	2.081953	-1.227290	1.511001
O	1.183474	-1.969872	1.880576
N	1.417623	1.983580	0.441622
H	3.002869	0.037958	-0.019983
C	2.225861	-0.739567	0.066823
H	-3.404283	-1.816254	3.454813
H	-1.244508	-2.051296	2.196514
H	4.193982	-2.057421	-2.157075
C	-3.356755	-1.559327	2.390221
C	-2.150468	-1.694344	1.691434
F	1.277643	-5.155697	-1.473297
C	2.450774	-1.780914	-0.971388
Pd	0.489742	0.367711	-0.476628
O	1.955385	-2.920232	-0.817533
H	-0.096914	-2.234982	0.147470
C	3.279832	-1.436006	-2.180450
B	1.968849	-4.192918	-2.092021
F	3.288125	-4.388261	-2.297135
H	3.547899	-0.370482	-2.226251
N	-1.091877	1.627852	-1.015783
H	-5.460921	-1.028780	2.261057
C	-4.511306	-1.116831	1.718599
C	-0.807963	-1.579516	-0.382072
C	-2.077349	-1.369138	0.307972
H	-2.809145	4.295489	-1.204765
H	2.740708	-1.749341	-3.091440
C	-1.942052	2.377281	-1.295596
F	1.313561	-3.523016	-3.095748
C	-0.455338	-1.173951	-1.686608
C	-3.009364	3.301267	-1.641109
H	0.306678	-1.756653	-2.219394
C	-4.459498	-0.809784	0.342481
C	-3.254852	-0.929270	-0.357718
H	-3.970911	2.928513	-1.246205
H	-1.181908	-0.660176	-2.329977
H	-3.086460	3.402628	-2.738113
H	-5.372281	-0.502212	-0.182245
H	-3.231539	-0.729654	-1.436001

C-TS

BP86 Energy = -6348.984058291

Nimag=1 (-252.20 cm**-1)

H	4.374848	2.632565	2.031726
H	2.118113	1.892348	-2.984057
H	0.619138	1.431237	-2.116780
C	3.496091	2.458590	2.677295
H	1.281898	0.337353	-3.358959
H	3.067754	3.433594	2.967304
C	1.557208	1.045884	-2.557386
H	3.819279	1.925394	3.588053
C	2.513629	1.667270	1.955604
C	2.404872	0.389092	-1.483666
O	3.399748	0.928323	-1.027589
N	1.743310	1.024024	1.360334
H	2.189522	-1.599985	-2.012127
C	2.012422	-1.061434	-1.061986
H	-5.553061	-0.905308	-0.693958
H	-3.465097	-1.770750	0.363387
H	4.885555	-2.487292	0.385260
C	-4.582823	-0.722057	-1.171579
C	-3.409212	-1.207743	-0.577183
F	0.439964	-1.984621	2.880131

C	2.912492	-1.754293	-0.031888
Pd	0.352781	-0.212888	0.346354
O	2.451918	-2.236153	0.998428
H	-1.177021	-2.219890	0.337403
C	4.380238	-1.857193	-0.362771
B	0.876770	-3.162582	2.443271
F	1.796050	-3.818861	3.112521
H	4.811554	-0.838772	-0.369353
N	-1.156026	0.580918	1.472658
H	-5.434905	0.356723	-2.857099
C	-4.517985	-0.018595	-2.387702
C	-0.947298	-1.577469	-0.527332
C	-2.145102	-1.007867	-1.188271
H	-3.229080	1.061746	3.829421
H	4.537336	-2.271066	-1.376392
C	-2.023850	1.042501	2.101888
F	0.206955	-3.761677	1.459431
C	0.254530	-1.971250	-1.250217
C	-3.109617	1.614409	2.881213
H	0.673528	-2.930006	-0.922546
C	-3.271338	0.190122	-3.006829
C	-2.099334	-0.300804	-2.415567
H	-4.053402	1.556256	2.310581
H	0.197643	-1.860782	-2.341169
H	-2.897592	2.673254	3.111047
H	-3.215675	0.729384	-3.959637
H	-1.139730	-0.131751	-2.918869

D

BP86 Energy = -6349.047358068

H	-1.606648	5.680586	1.689685
H	-0.071255	6.089362	0.854223
H	-1.610699	6.052197	-0.067876
C	-1.040765	5.572467	0.747429
C	-0.827617	4.164268	0.451312
N	-0.658280	3.033028	0.216934
H	3.797007	2.326664	0.985705
O	1.600727	1.267005	0.535058
H	-5.291116	1.065231	-1.268387
C	3.957069	1.286909	0.666028
Pd	-0.323670	0.927876	-0.131542
H	4.409952	0.695678	1.484655
N	-2.155877	0.702869	-0.885505
H	4.682878	1.237039	-0.166605
C	-3.242579	0.570288	-1.291116
C	2.657832	0.654776	0.281322
C	-4.595801	0.381649	-1.785711
H	-4.639964	0.581488	-2.871110
F	6.904152	-1.431652	-0.090169
H	-0.635319	-1.296977	2.290057
H	-4.915490	-0.658938	-1.598578
F	6.702977	-1.663053	2.180269
H	-2.445573	-2.650013	3.323392
C	-1.292508	-1.899054	1.647842
C	2.594202	-0.697243	-0.420261
H	1.431746	-1.548898	1.206438
C	0.000970	-1.101582	-0.399274
B	6.571191	-2.172506	0.967842
H	2.436864	-0.474896	-1.498713
C	-2.317653	-2.657238	2.233528
C	1.384721	-1.523291	0.101485
C	-1.106450	-1.887310	0.243001
O	4.438421	-1.580340	0.816276
H	-0.044617	-1.203504	-1.502671
C	3.855775	-1.563328	-0.265659
F	6.401891	-3.478927	0.803140
C	-3.176795	-3.427902	1.429169
C	-1.981213	-2.667317	-0.552177
H	1.529321	-2.576619	-0.218890
H	-3.972554	-4.026627	1.889068
C	-3.003164	-3.432959	0.033504
H	-1.841249	-2.689252	-1.642367
H	4.984910	-1.766506	-2.057834
C	4.298370	-2.385771	-1.447117
H	-3.656159	-4.047395	-0.599376
H	3.454946	-2.685616	-2.091859
H	4.863493	-3.264367	-1.100168

Path II

E

BP86 Energy = -5892.04873785

Pd	7.084035	1.227997	5.767812
C	9.026625	-1.274743	5.756408
N	8.321393	-0.347420	5.688149
C	9.904456	-2.428094	5.850980
H	10.269348	-2.713958	4.849161
H	10.770680	-2.190511	6.493552
H	9.358827	-3.282686	6.289326
C	5.434001	3.349226	6.925532
O	5.789614	2.740571	5.837780
C	6.821445	2.072019	8.590895
O	7.398652	1.248795	7.784827
C	5.889980	3.071947	8.228325
H	5.486548	3.690925	9.034331
C	4.429068	4.454139	6.692899
H	4.165773	4.974884	7.625009
H	4.841163	5.180477	5.969920
H	3.512398	4.030770	6.244450
C	7.215380	1.898639	10.040266
H	6.953391	0.877241	10.370668
H	8.311107	1.999417	10.139088
H	6.720766	2.628980	10.697385
C	8.905510	5.142193	2.785134
C	7.733548	5.886336	2.554362
C	8.813749	3.784860	3.114320
H	7.802707	6.946343	2.282241
H	9.728151	3.201014	3.283815
C	6.471431	5.267399	2.655270
C	7.548756	3.147109	3.228594
H	5.561605	5.845180	2.454240
C	6.375266	3.912830	2.991834
H	5.389915	3.439219	3.051540
H	9.888106	5.620562	2.697338
C	7.515798	1.716530	3.529428
H	8.484472	1.207747	3.410667
C	6.387914	0.901036	3.742995
H	5.374889	1.317528	3.692557
H	6.465294	-0.182051	3.587753

E-TS

BP86 Energy = -5891.986364276

Nimag=1 (-56.79 cm**-1)

Pd	6.937543	2.779552	5.555511
C	9.279734	0.271388	5.696959
N	8.412943	1.055600	5.652010
C	10.358153	-0.704220	5.753557
H	9.958809	-1.697709	6.022852
H	10.861187	-0.776898	4.773379
H	11.101160	-0.404204	6.513431
C	3.854811	1.891357	7.271672
O	4.181319	2.908072	6.443427
C	5.939678	2.321647	8.636423
O	6.667601	2.818868	7.742902
C	4.637201	1.707877	8.389089
H	4.247381	1.046902	9.171962
C	2.610479	1.097246	6.992776
H	1.750950	1.760452	6.783730
H	2.741121	0.429423	6.119469
H	2.360504	0.458308	7.853907
C	6.447941	2.310249	10.061999
H	7.469339	2.716886	10.106962
H	5.783170	2.917268	10.704947
H	6.436929	1.283976	10.473098
C	7.924686	3.630714	1.915918
C	8.189460	4.898136	2.504319
C	6.949147	2.799610	2.450617
H	8.973533	5.535934	2.077978
H	6.756652	1.807257	2.024572
C	7.446330	5.354674	3.596329
C	6.167889	3.239307	3.573889
H	7.634310	6.349747	4.015427
C	6.397706	4.560358	4.129199
H	5.675144	5.022090	4.814188
H	8.505060	3.305440	1.044655
C	5.300355	2.367704	4.355742
H	5.309476	1.301067	4.078626
C	4.011278	2.852339	5.013307
H	3.763328	3.881238	4.705636
H	3.165266	2.200245	4.728754

F

BP86 Energy = -5891.996822741

Pd	7.149407	2.362569	5.260056
C	8.422992	-0.531114	5.744041
N	7.881433	0.490290	5.566771
C	9.111534	-1.792354	5.967049
H	9.381333	-2.257659	5.002675
H	10.035454	-1.619286	6.547076
H	8.465061	-2.488532	6.530817
C	4.340957	1.883293	7.161781
O	4.584313	2.485630	5.970353
C	6.402186	2.935030	8.323026
O	7.207644	3.144673	7.386181
C	5.131967	2.195483	8.243346
H	4.747273	1.853864	9.211958
C	3.141873	0.981940	7.256431
H	2.240586	1.482985	6.857389
H	3.286147	0.052579	6.673173

H	2.952216	0.686615	8.298923
C	6.773602	3.439173	9.703563
H	7.761192	3.923726	9.676162
H	6.016319	4.160188	10.065162
H	6.790831	2.605130	10.429772
C	7.769844	4.592431	2.047941
C	7.857908	5.590863	3.064381
C	7.000987	3.456215	2.237212
H	8.480287	6.477942	2.895508
H	6.953722	2.675029	1.467963
C	7.136146	5.463897	4.244764
C	6.239569	3.290888	3.447271
H	7.168411	6.255168	5.003434
C	6.296698	4.328804	4.462524
H	5.537285	4.375427	5.251319
H	8.325763	4.724674	1.111981
C	5.661675	2.017081	3.830639
H	5.803487	1.198216	3.107587
C	4.407435	1.830522	4.689430
H	3.525176	2.274501	4.185548
H	4.218858	0.752021	4.826012

G

BP86 Energy = -6024.796806168

Pd	3.767052	2.791900	6.114944
C	3.148833	4.801737	3.696526
N	3.389202	4.071644	4.576666
C	2.838196	5.707622	2.601813
H	2.499406	5.137146	1.718999
H	2.036478	6.405604	2.901566
H	3.732494	6.293419	2.324622
C	8.157943	2.497970	5.639864
O	6.836594	2.194969	5.716533
C	8.130967	3.479017	7.990965
O	6.959352	3.218035	8.295953
C	8.761674	3.103189	6.713659
H	9.824578	3.342424	6.594314
C	8.907051	2.161949	4.378490
H	9.953086	2.492637	4.458976
H	8.909604	1.072780	4.185164
H	8.462903	2.652701	3.492506
C	9.028755	4.235591	8.964034
H	8.463070	4.476968	9.876799
H	9.911124	3.624945	9.232079
H	9.410980	5.167374	8.507641
C	2.674578	-0.783527	7.451984
C	3.122242	-0.238916	8.688733
C	3.208568	-0.343151	6.249686
H	2.692089	-0.607910	9.627517
H	2.853366	-0.754728	5.296982
C	4.107064	0.742159	8.707507
C	4.266532	0.630031	6.237695
H	4.474631	1.149535	9.656586
C	4.706011	1.197253	7.496011
H	5.615198	1.822304	7.559824
H	1.897282	-1.557846	7.451112
C	4.701072	1.285951	5.009332
H	4.134186	0.981742	4.113118
C	6.136400	1.595646	4.628754
H	6.625986	0.644882	4.323928
H	6.136041	2.265167	3.745472
H	1.106330	5.023820	10.004864
C	2.050849	5.439828	9.613122
H	2.802286	5.442768	10.422882
C	2.526649	4.637196	8.497728
H	1.873558	6.479766	9.288352
N	2.914638	3.989809	7.606897

BF3

BP86 Energy = -324.218579688

F	4.018860	6.360486	1.011983
F	5.896529	6.987151	2.147684
B	5.031041	6.056836	1.798967
F	5.177170	4.823028	2.237865

Styrene

BP86 Energy = -309.639317220

C	-0.884513	-0.027009	-1.074814
C	-2.027857	-0.354397	-0.305107
C	0.329175	0.328431	-0.465185
H	1.199252	0.577812	-1.085636
C	-1.908068	-0.312184	1.107154
C	0.427907	0.365069	0.935701
H	-2.773287	-0.560450	1.734114
H	1.373770	0.643419	1.417092
C	-0.698015	0.042300	1.717921
H	-0.629671	0.068254	2.813317
H	-0.955759	-0.054650	-2.171029
C	-3.277017	-0.719461	-0.998656
H	-3.210829	-0.699960	-2.098079
C	-4.460733	-1.065177	-0.444637
H	-4.617768	-1.111702	0.640759
H	-5.323238	-1.317960	-1.071469

MeCN

BP86 Energy = -132.759232161

C	-1.699669	-0.000012	0.844914
H	-2.733702	-0.009016	1.230914
H	-1.174546	-0.891294	1.231151
H	-1.190190	0.900317	1.231134
C	-1.699586	-0.000002	-0.615904
N	-1.699585	0.000007	-1.786629

MeCN*BF3

BP86 Energy = -456.988510799

F	5.756501	7.374376	4.006476
N	4.834358	6.453829	1.688191
C	4.825425	6.436736	0.521838
B	4.811720	6.450714	3.841912
C	4.811266	6.416537	-0.934858
F	5.136344	5.167621	3.992089
F	3.535610	6.808725	3.975163
H	4.329063	7.330374	-1.323668
H	4.249925	5.537879	-1.297696
H	5.841761	6.365381	-1.326257

1

BP86 Energy = -6139.366778033

Pd	-0.151849	-0.004167	0.399651
C	-2.492939	2.071537	0.703775
N	-1.542270	1.401240	0.605680
C	-3.650032	2.924449	0.840772
H	-4.513947	2.299218	1.184123
H	-3.444237	3.738684	1.557066
H	-3.907864	3.355275	-0.142440
C	-2.571828	-1.975694	0.763975
N	-1.591272	-1.354219	0.640563
C	-3.768870	-2.765518	0.931912
H	-4.606872	-2.082388	1.227119
H	-4.033606	-3.243921	-0.027469
H	-3.610363	-3.543261	1.699256
C	2.421289	-1.305975	-0.042250
O	1.167858	-1.488607	0.190333
C	2.459186	1.205385	-0.080323
O	1.212735	1.432120	0.150419
C	3.074227	-0.061578	-0.179570
H	4.149114	-0.080913	-0.383693
C	3.209651	-2.591927	-0.173903
H	3.065531	-3.206363	0.732887
H	2.816434	-3.176774	-1.025531
H	4.284308	-2.408054	-0.326020
C	3.283754	2.462898	-0.255898
H	2.906337	3.028594	-1.127410
H	3.158062	3.112613	0.628790
H	4.352491	2.243688	-0.402125
F	-4.358395	0.095504	0.419714
B	-5.733050	0.131435	0.803400
F	-5.930597	1.290916	1.598430
F	-6.533774	0.149756	-0.315698
F	-5.991674	-1.013881	1.600492

Pd(acac)(F*BF3)(MeCN)

BP86 Energy = -6006.585379831

H	3.960950	1.207036	3.397390
H	2.714587	2.344075	4.031843
H	3.369324	4.589893	4.153949
C	3.334368	2.084474	3.159904
H	5.577944	7.236164	4.279305
H	3.846501	6.833353	4.553062
C	4.103487	4.496071	3.347868
C	4.218257	3.232732	2.722112
C	4.634081	6.933963	3.790585
H	2.678123	1.792680	2.319976
C	4.854005	5.645933	3.023999
O	5.025583	2.932803	1.769199
O	5.756507	5.742285	2.109222
H	4.362315	7.740073	3.086253
Pd	6.273734	4.225479	0.930755
F	6.109665	1.568487	-2.141494
F	6.888183	2.691800	-0.272664
F	5.344258	3.696908	-1.691971
B	6.417287	2.832481	-1.754041
N	7.568198	5.348611	-0.081621
H	10.154161	6.050688	-1.821303
C	8.259325	5.672956	-0.963248

F	7.500346	3.382522	-2.424531
C	9.088235	6.009267	-2.104742
H	8.785536	6.978339	-2.537166
H	8.927039	5.203520	-2.844829

Pd(acac)(F)(MeCN)
BP86 Energy = -5682.318618961

H	2.796934	2.510170	3.776165
H	3.959205	1.373482	3.002232
C	3.359211	2.288990	2.855468
H	3.604083	4.672847	4.060479
H	2.647793	2.078148	2.036553
H	4.218531	6.833957	4.649825
C	4.271499	4.628373	3.193828
C	4.272229	3.428422	2.444559
H	5.921293	7.242637	4.241939
C	4.929949	6.991462	3.824140
C	5.053254	5.775966	2.923758
O	4.982297	3.175310	1.405868
H	4.603273	7.861320	3.225872
O	5.891629	5.917260	1.962336
Pd	6.282870	4.465012	0.597836
F	6.670734	3.106082	-0.694111
N	7.584442	5.639428	-0.295157
C	8.369954	6.281500	-0.872376
H	10.373546	6.810449	-1.265664
C	9.353248	7.066206	-1.602831
H	9.185292	8.145802	-1.438445
H	9.276935	6.855978	-2.685073

[Pd(acac)(MeCN)]+
BP86 Energy = -5582.343669773

Pd	6.271851	3.969774	1.223553
C	8.394695	2.454860	-0.569623
N	7.616088	3.008407	0.101091
C	9.362141	1.764351	-1.401463
H	8.969319	0.775798	-1.698212
H	9.564954	2.357436	-2.310938
H	10.307209	1.624245	-0.847134
C	4.275027	5.791853	2.253598
O	5.012618	4.756684	2.478367
C	5.036087	6.224877	-0.096148
O	5.895111	5.266256	-0.236171
C	4.259818	6.517742	1.041033
H	3.587223	7.377570	0.981421
C	3.391216	6.191559	3.409038
H	2.685550	5.370515	3.631449
H	4.008969	6.343863	4.311709
H	2.826032	7.108801	3.189081
C	4.913931	7.072533	-1.346801
H	5.910256	7.442991	-1.643286
H	4.533460	6.448340	-2.175183
H	4.234680	7.922833	-1.188079