Supplementary Information

New Mechanistic Insights into the Copper-free Heck–Cassar–Sonogashira cross-coupling reaction.

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1. General Information

Commercially available reagents (reagent grade, >99%) were purchased from Sigma Aldrich, Fluorochem and TCI Chemicals and used without any further purification.

Solvents (dichloromethane (DCM), tetrahydrofuran (THF), toluene, deuterated N,N-Dimethylformamide (DMF-d_7), deuterated chloroform ($CDCl_3$), ethyl acetate (EtOAc), cyclohexane (Cy), N-Methyl-2-pyrrolidone (NMP), N-Butyl-2-pyrrolidone (NBP), 1-(2-Hydroxyethyl)-2-pyrrolidone (HEP), Ethanol (EtOH), acetonitrile (ACN) are commercially available and solvent for reaction were used after degassing.

Tetrakis(triphenylphosphine)palladium $Pd(PPh_3)_4$, bis(triphenylphosphine)palladium chloride(II) $PdCl_2(PPh_3)_2$ 1,1'-Bis(diphenylphosphino)ferrocene] palladio(II)dichloride $PdCl_2$(dppf), Bis(acetonitrile)dichloropalladium(II) $PdCl_2(ACN)_2$, triphenylphospine (PPh_3), 3-Bis(diphenylphosphino)propane (dppp) and 1,1′-Bis(diphenylphosphino)ferrocene (dppf) from FaggiEnrico (Italy).

^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on Varian 400-MR (400 MHz) (equipped with autoswitchable PFG probe) and Bruker Avance Neo 600 MHz (equipped with CryoProbe Prodigy Broadband 5mm) spectrometers. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t =triplet, q = quartet, spt = septet, m = multiplet, bs = broad signal. Coupling constants *J* are given in Hz. All ^{1}H and ^{13}C chemical shifts are calibrated to residual protic-solvents and all ^{31}P chemical shifts are referenced to external 85% phosphoric acid (δ = 0 ppm).

HPLC-UV analysis were recorded with an Agilent 1260 InfinityLab instrument. Column: Zorbax® SB-C18; particle size 5 μm; pore size 100 Å; length 250 mm, internal diameter: 4.6 mm. Mobile phase A: H_2O, mobile phase B: ACN. Gradient (Time(min), %B): 0, 80; 25, 80; 28, 10; 30, 10; flow 0.5 mL min^{-1}column temperature 30°C; injection volume: 10 μL.

GC-MS analysis were recorded with a Hewlett-Packard 5971 spectrometer with GC injection and EI ionization at 70 eV coupled with an Agilent Technologies MSD1100 single-quadrupole mass spectrometer, reported as: m/z (rel. intensity).

High-Resolution transmission electron microscopy (HR-TEM) images were acquired on a ThermoFischer Talos F200X operated at 200 kV, which is equipped with an extreme field emission gun (FEG) electron source and Super-X Energy Dispersive X-ray Spectroscopy (EDS) system for chemical analysis.

HRMS spectra were obtained with a G2XS QTof mass spectrometer using either ESI.

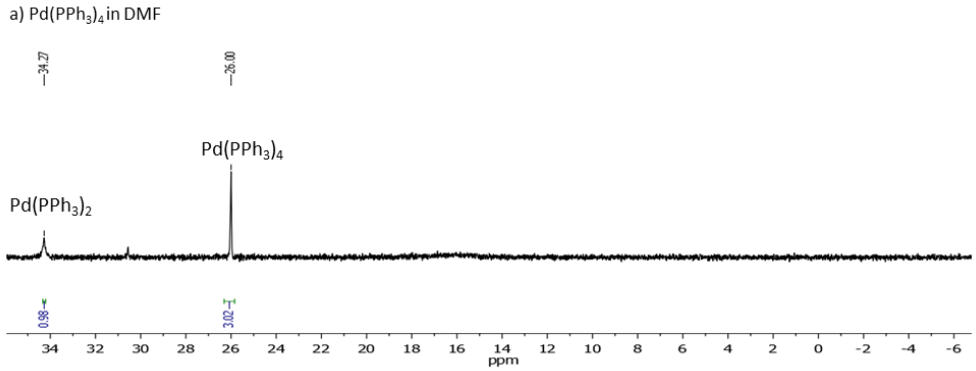
Room temperature (rt) refers to the ambient temperature of the laboratory, ranging from 22 °C to 26 °C.

2. Palladium species

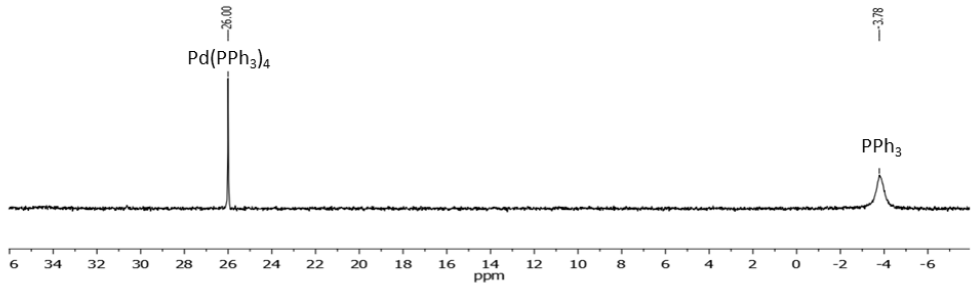
Table S1. ^{31}P NMR chemical shift in DMF-d_7 and $CDCl_3$ of palladium species

Entry	Compound	δ (ppm)	
		DMF-d_7	$CDCl_3$
1	$Pd(PPh_3)_4$	26.00	28.25
2	$Pd(PPh_3)_3$	24.84	23.85
3	$Pd(PPh_3)_2$	34.33	33.78
4	PPh_3	-4.83	-5.46
5	$OPPh_3$	26.00	29.70
6	$PdCl_2(PPh_3)_2$	24.85	23.86
7	complex **L**	24.06	23.43
8	complex **M**	27.19	26.56
9	complex $\mathbf{C_{NO_2}}$	28.05	27.53
10	complex $\mathbf{B^{I}_{NO_2}}$	23.43	23.17
11	complex $\mathbf{B^{I}_{Me}}$	22.81	22.53
12	complex $\mathbf{B^{Br}_{NO_2}}$	24.67	24.08
13	complex $\mathbf{B^{Cl}_{NO_2}}$	24.93	24.18
14	complex $\mathbf{B^{OTf}_{NO_2}}$	22.53	-
15	complex $\mathbf{B^{I}_{OMe}}$	23.79	24.15

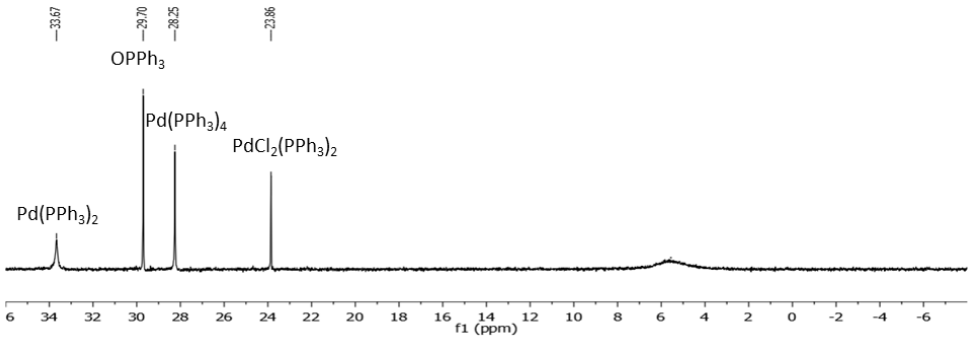
Entries 1-6, Table S1



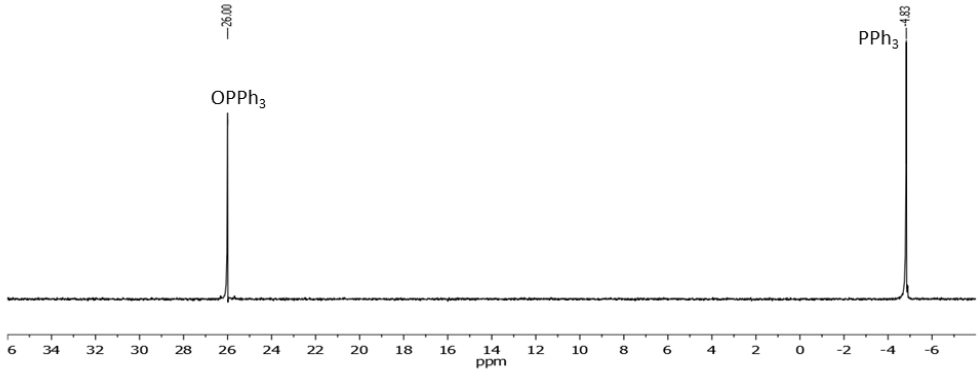
b) $Pd(PPh_3)_4$ in DMF after the addition of PPh_3



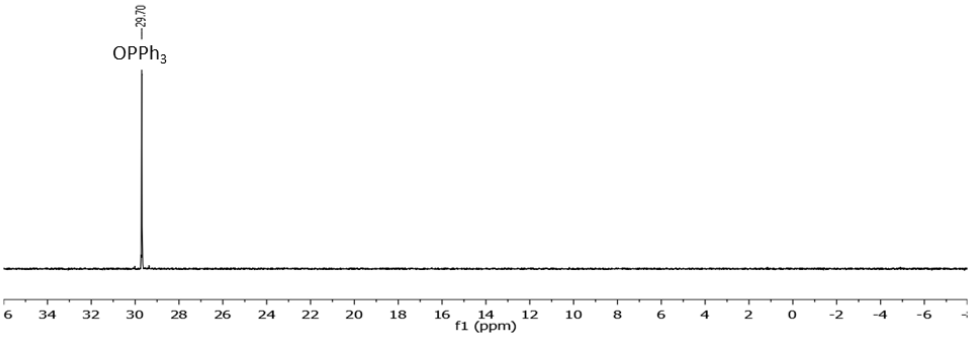
c) $Pd(PPh_3)_4$ in $CDCl_3$



d) $OPPh_3$ and PPh_3 in DMF



e) $OPPh_3$ in $CDCl_3$



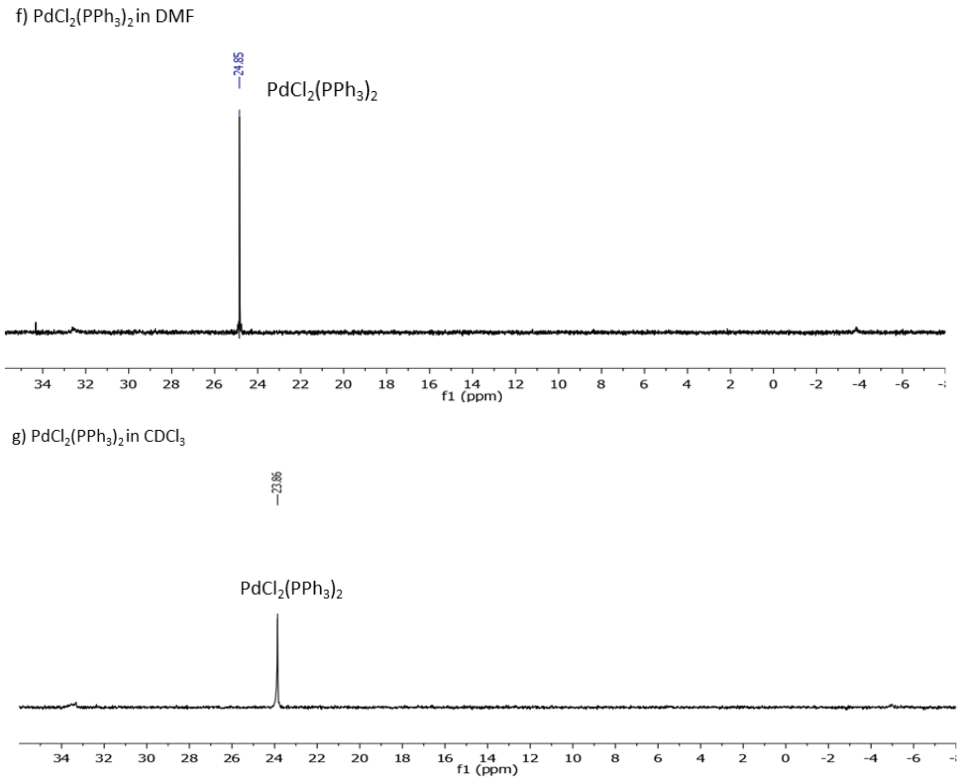


Figure S1. ^{31}P NMR spectra of: a) $Pd(PPh_3)_4$ in DMF-d_7, b) $Pd(PPh_3)_4$ with the addition of PPh_3, c) $Pd(PPh_3)_4$ in $CDCl_3$, d) Triphenylphosphine oxide ($OPPh_3$) and Triphenylphosphine (PPh_3) in DMF-d_7, e) $OPPh_3$ in $CDCl_3$, f) $PdCl_2(PPh_3)_2$ in DMF-d_7, g) $PdCl_2(PPh_3)_2$ in $CDCl_3$.

Entry 7, Table S1

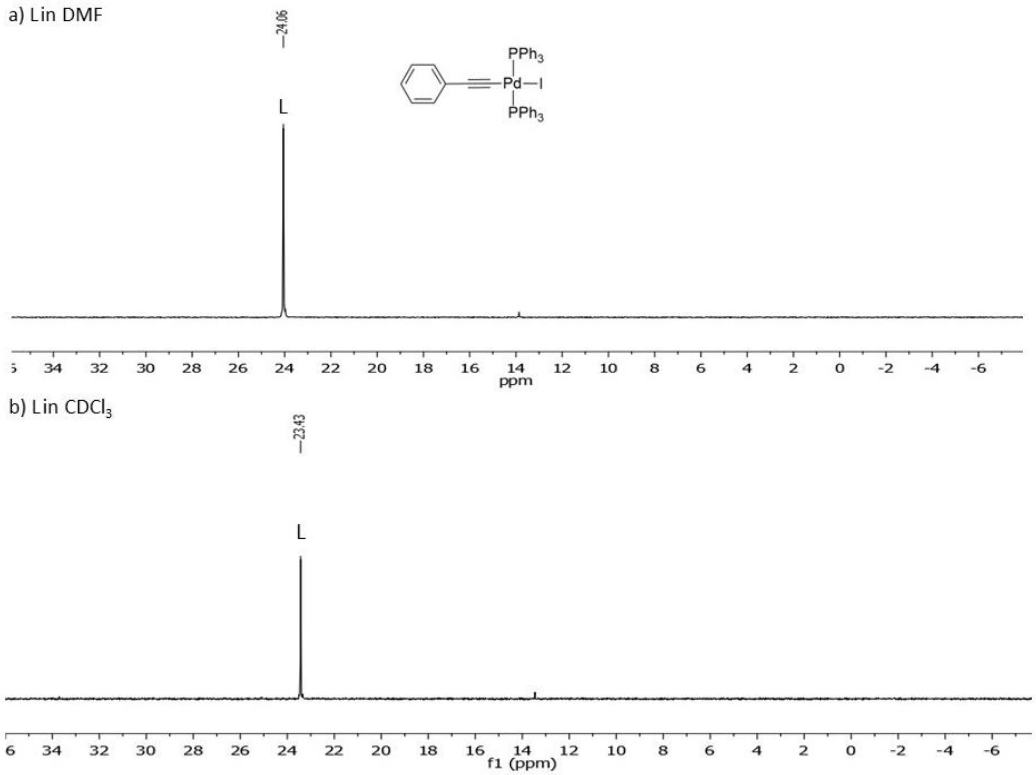


Figure S2. ^{31}P NMR spectra of the complex **L** in DMF-d_7 (a) and in $CDCl_3$ (b).

Entry 8, Table S1

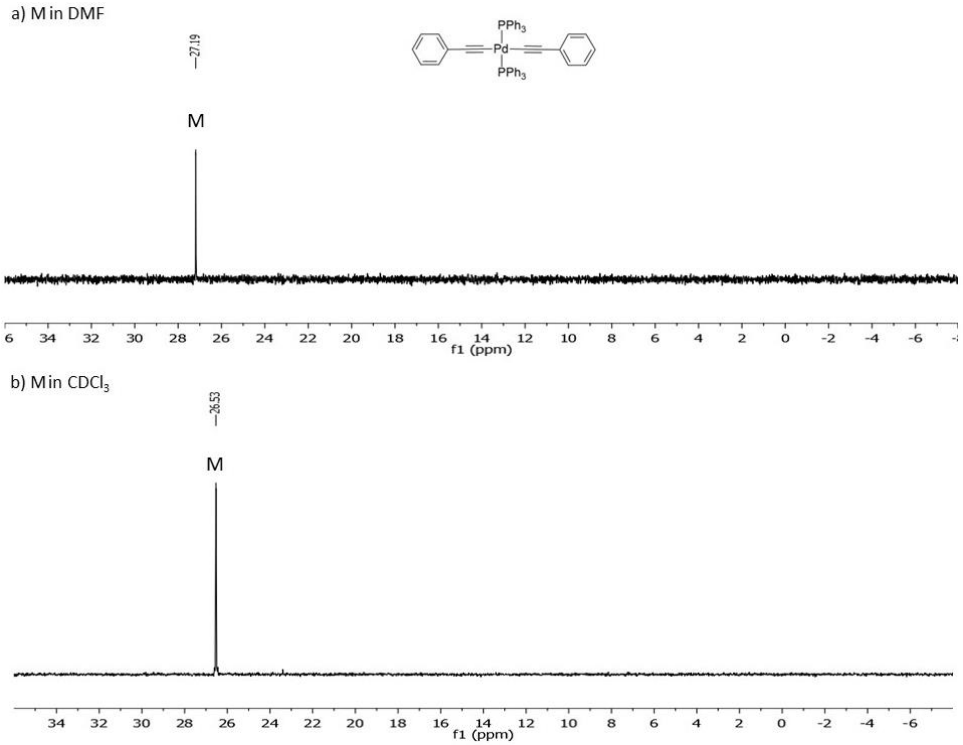


Figure S3. ^{31}P NMR spectra of the complex **M** in DMF-d_7 (a) and in $CDCl_3$ (b).

Entry 9, Table S1

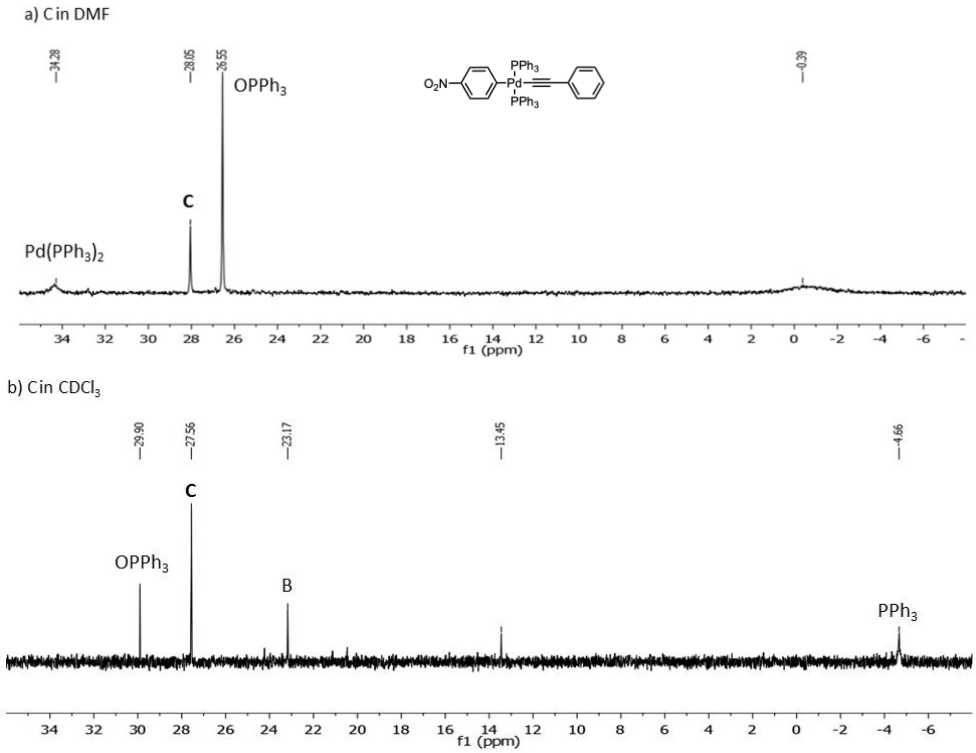


Figure S4. ^{31}P NMR spectra of the complex *trans*-**C** in DMF-d_7 (a) and in $CDCl_3$ (b).

Entry 10, Table S1

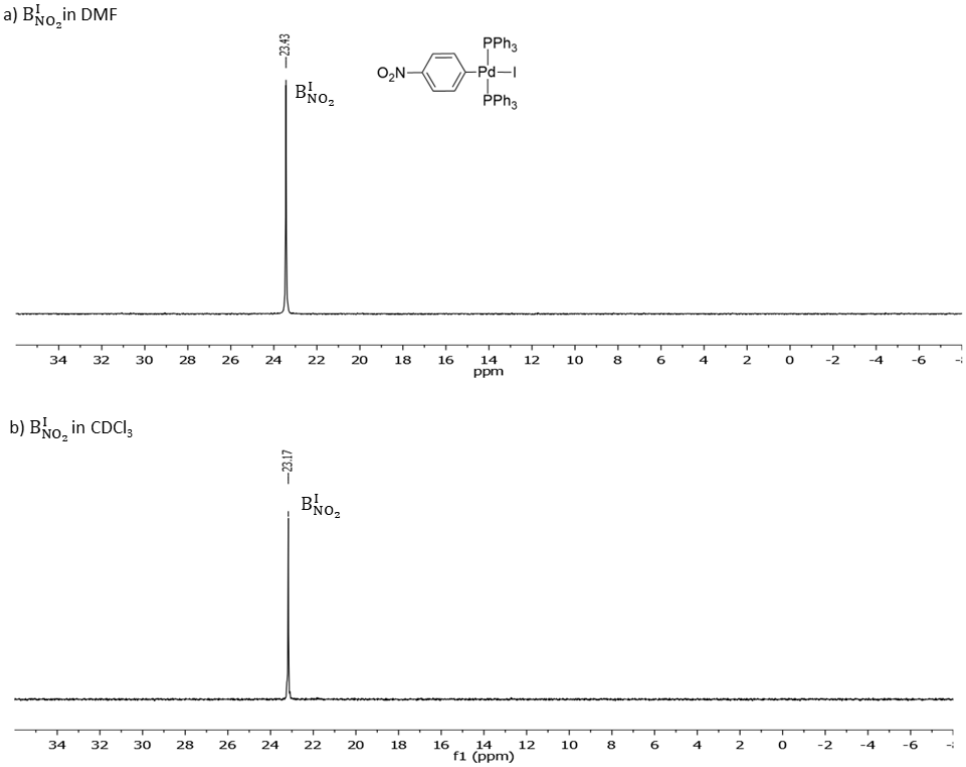


Figure S5. ^{31}P NMR spectra of the complex $\mathbf{B^{I}_{NO_2}}$ in DMF-d_7 (a) and in $CDCl_3$ (b).

Entry 11, Table S1

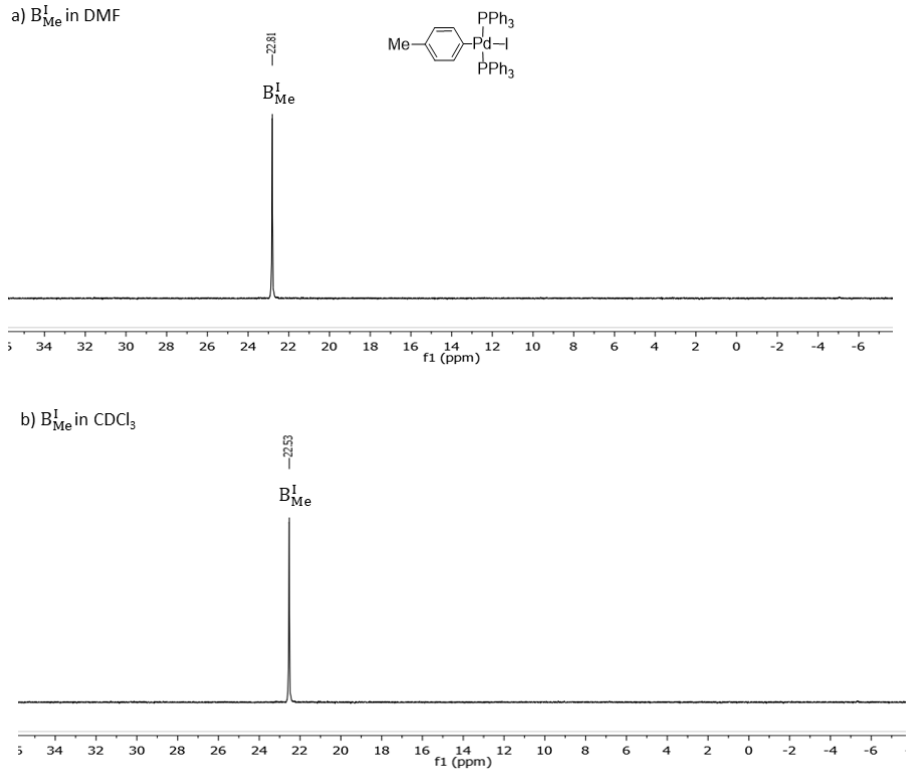


Figure S6. ^{31}P NMR spectra of the complex $\mathbf{B^{I}_{Me}}$ in DMF-d_7 (a) and in $CDCl_3$ (b).

Entry 12, Table S1

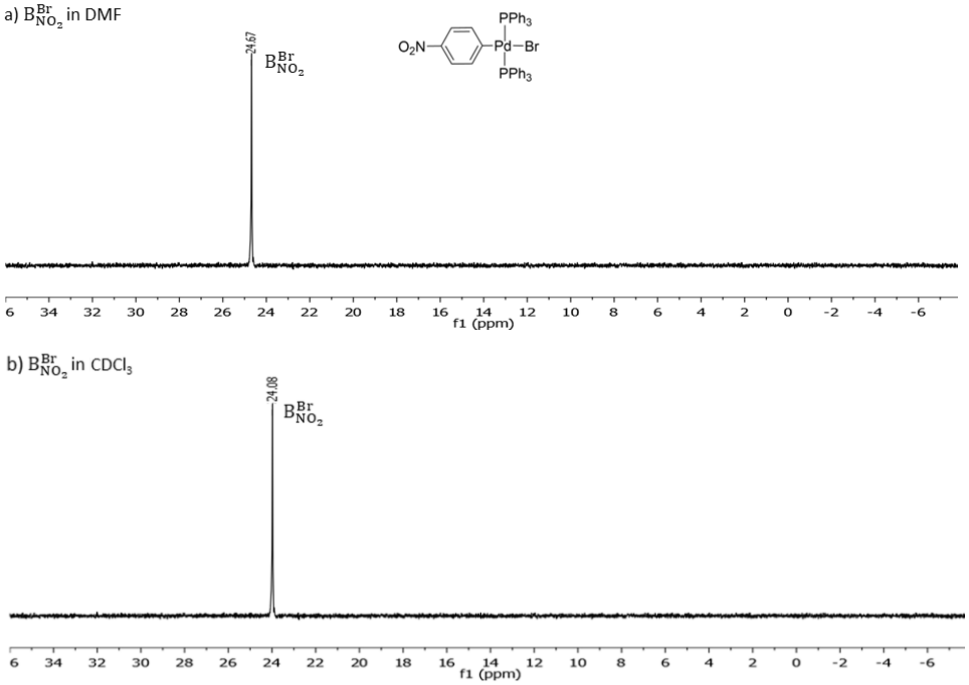


Figure S7. ^{31}P NMR spectra of the complex $\mathbf{B^{Br}_{NO_2}}$ in DMF-d_7 (a) and in $CDCl_3$ (b).

Entry 13, Table S1

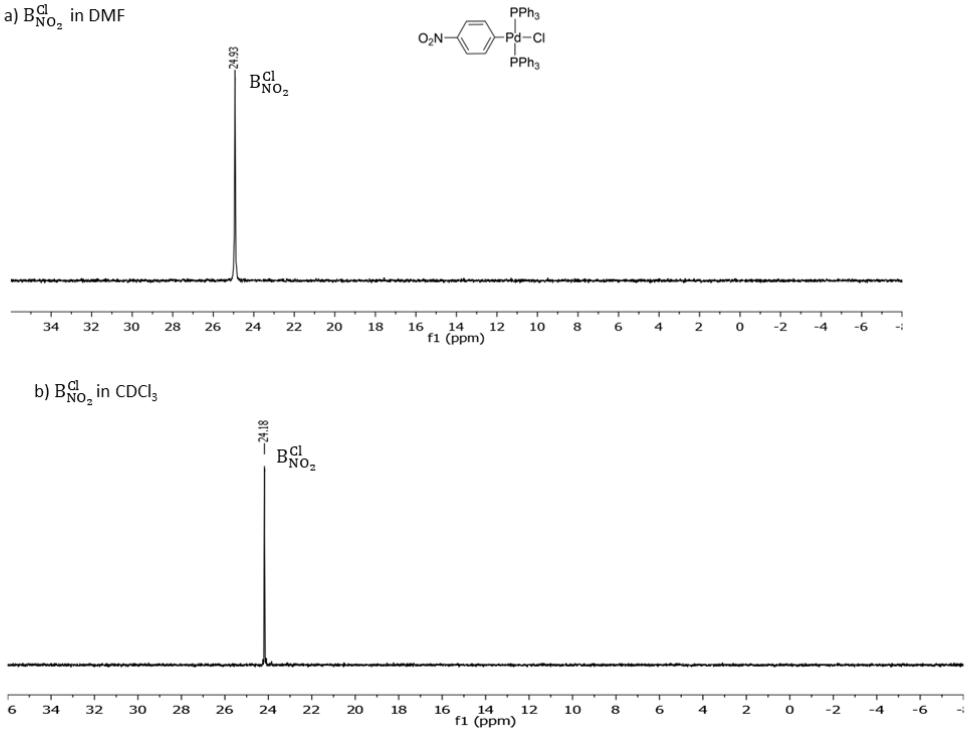


Figure S8. ^{31}P NMR spectra of the complex $\mathbf{B^{Cl}_{NO_2}}$ in DMF-d_7 (a) and in $CDCl_3$ (b).

Entry 14, Table S1

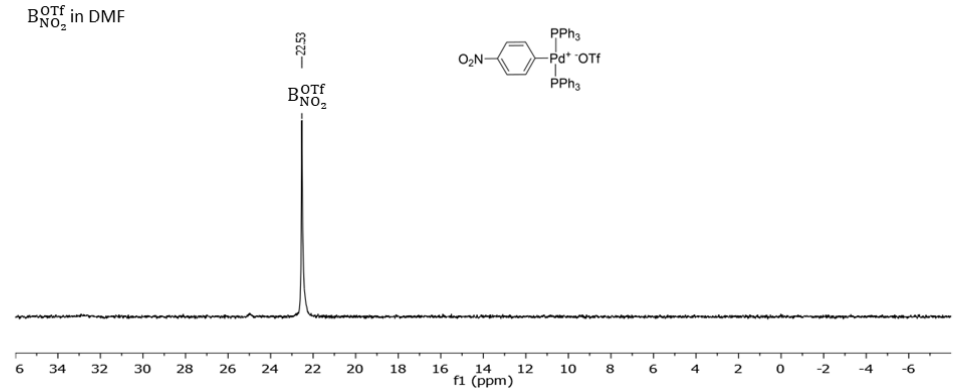


Figure S9. ^{31}P NMR spectra of the complex $\mathbf{B_{NO_2}^{OTf}}$ in DMF-d_7 (a) and in $CDCl_3$ (b).

Entry 15, Table S1

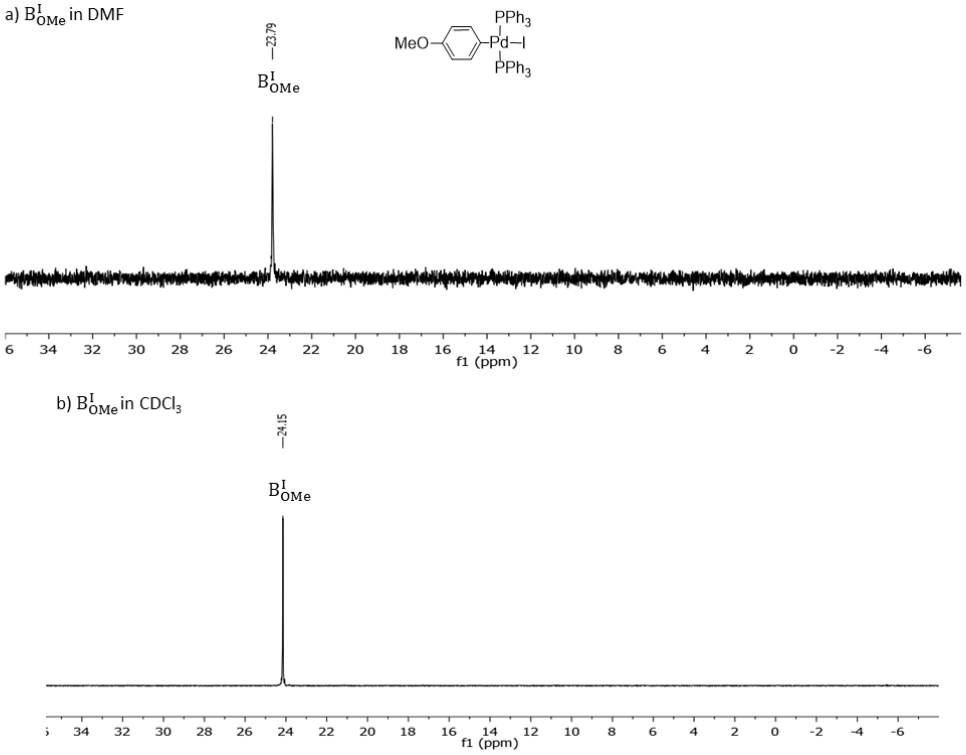
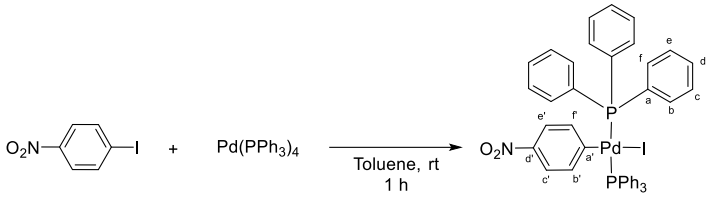


Figure S10. ^{31}P NMR spectra of the complex $\mathbf{B_{OMe}^{I}}$ in DMF-d_7 (a) and in $CDCl_3$ (b).

3. Synthesis of palladium complexes

3.1. Oxidation addition (OA) complexes:

3.1.1. Synthesis of OA complex $B^{I}_{NO_2}$ [1]



1_{NO2} B^{I}_{NO2}

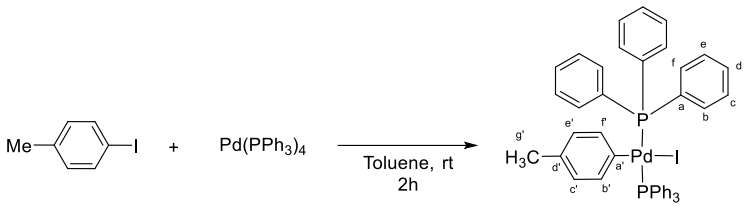
To an oven-dried 20 mL Schlenk purged under argon atmosphere, a mixture of 1-Iodo-4-nitrobenzene $\mathbf{1_{NO2}}$ (423 mg, 1.7 mmol, 2.46 eq) and tetrakis(triphenylphosphine)palladium(0) (798 mg, 0.69 mmol, 1 eq) was stirred in degassed toluene (13 mL), in the dark for 1 h at room temperature. The reaction mixture was filtered and the crude was washed with diethyl ether (Et_2O) to obtain the pure product (564 mg, 93 %) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56-7.53 (m, 12H, Hb-Hf); 7.36-7.33 (m, 6H, Hd); 7.27-7.25 (m, 12H, Hc-He); 7.02-7.01 (d, J=6 Hz 2H, Hc'-He'); 6.85-6.84 (m, 2H, Hb'-Hf')

^{13}C NMR (151.2 MHz, $CDCl_3$): δ 177.07 (s, Cd'); 143.84 (t, J=1.51 Hz, Ca'); 135.96 (t, J=4.53 Hz, Cb'-Cf'), 134.94 (t, 6.05 Hz, Cb-Cf), 131.49 (t, J=24.2 Hz, Ca), 130.37 (s, Cd), 128.10 (t, J=4.53, Cc-Ce), 120.95 (t, Cc'-Ce').

^{31}P NMR (242.4 MHz, $CDCl_3$): δ +23.17 (s)

3.1.2. Synthesis of OA complex B^{I}_{Me} [1]



1_{Me} B^{I}_{Me}

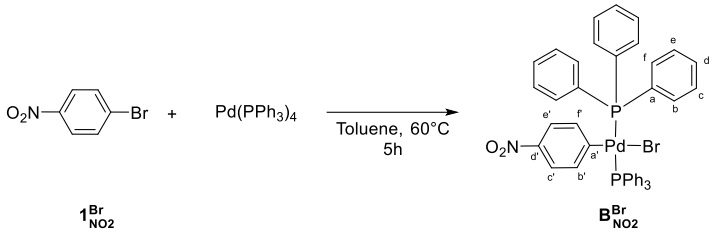
To an oven-dried 20 mL Schlenk purged under argon atmosphere, a mixture of 4-Iodotoluene $\mathbf{1_{Me}}$ (457 mg, 2.09 mmol, 2.46 eq) and tetrakis(triphenylphosphine)palladium(0) (982 mg, 0.85 mmol, 1 eq) was stirred in degassed toluene (11.5 mL), in the dark for 2 h at room temperature. The reaction mixture was filtered and the crude was washed with diethyl ether to obtain the pure product (671 mg, 93 %) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50-7.19 (m, 12H, Hb-Hf); 7.31-7.18 (m, 6H, Hd); 7.23-7.19 (m, 12H, Hc-He); 6.40-6.38 (d, J=4 Hz 2H, Hb'-Hf'); 6.06-6.05 (m, 2H, Hc'-He'); 1.92 (s, 3H, Hg').

^{13}C NMR (151.2 MHz, $CDCl_3$): *δ* 152.7 (t, J=1.51 Hz, Ca'), 135.5 (t, J=4.53 Hz, Cb'-Cf'), 134.9 (t, 6.05 Hz, Cb-Cf), 132.2 (t, J=1.51 Hz, Ca'), 129.6 (s, Cd), 130.9 (s, Cd'), 128.9 (t, Cc'-Ce'),127.7 (t, *J* = 5.0 Hz, (t, J=4.53, Cc-Ce), 20.1 (Cg');

^{31}P NMR (242.4 MHz, $CDCl_3$): δ +22.53 (s)

3.1.3. Synthesis of OA complex $\mathbf{B_{NO_2}^{Br}}$ [1]



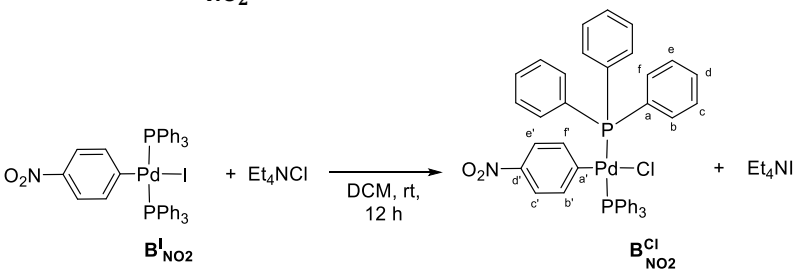
To an oven-dried 20 mL Schlenk purged under argon atmosphere, a mixture of 1-Bromo-4-nitrobenzene $\mathbf{1_{NO_2}^{Br}}$ (274 mg, 1.35 mmol, 2.46 eq) and tetrakis(triphenylphosphine)palladium(0) (634 mg, 0.55 mmol, 1 eq) was stirred in degassed toluene (13 mL). The reaction mixture was heated to 60°C with an oil bath and stirred for 5 h. The reaction mixture was filtered and the crude was washed with diethyl ether to obtain pure product (411 mg, 90 %) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56-7.53 (m, 12H, Hb-Hf); 7.36-7.34 (m, 6H, Hd); 7.28-7.25 (m, 12H, Hc-He); 7.02-7.00 (d, J=12 Hz, 2H, Hc'-He'); 6.87-6.86 (m, 2H, Hb'-Hf')

^{13}C NMR (151.2 MHz, $CDCl_3$): δ 174.27 (s, Cd'); 143.67 (t, J=1.51 Hz, Ca'); 136.06 (t, J=4.54 Hz, Cb'-Cf'), 134.66 (t, 6.05 Hz, Cb-Cf), 130.69 (t, J=24.2 Hz, Ca), 130.26 (s, Cd), 128.07 (t, J=4.54, Cc-Ce), 120.80 (t, Cc'-Ce').

^{31}P NMR (242.4 MHz, $CDCl_3$): δ +24.08 (s)

3.1.4. Synthesis of OA complex $\mathbf{B_{NO_2}^{Cl}}$ [2]



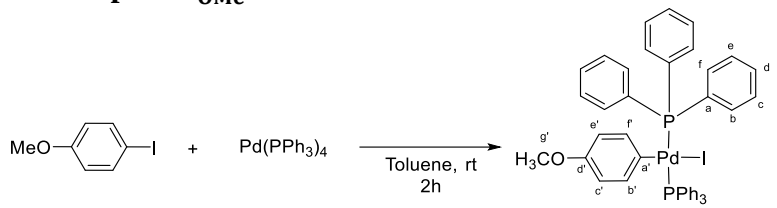
To an oven-dried 20 mL Schlenk purged under argon atmosphere, a mixture of $Pd(PPh_3)_2(PhNO_2)I$ $\mathbf{B_{NO_2}^{I}}$ (105 mg, 0.12 mmol, 1 eq) and Et_4NCl (40 mg, 0.24 mmol, 2 eq) was stirred in DCM (1.2 mL) for 12 h at room temperature. The reaction mixture was filtered, washed with toluene (1 mL) and concentrated to 1 mL under reduced pressure. Hexane (1 mL) was added dropwise and the precipitated was filtered. In order to obtain $\mathbf{B_{NO_2}^{Cl}}$ as white solid, the precipitate was washed with hexane and ethanol and dried under vacuum (94 mg, 80%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55-7.52 (m, 12H, Hb-Hf); 7.36-7.34 (m, 6H, Hd); 7.27-7.25 (m, 12H, Hc-He); 7.01-6.99 (d, J=12 Hz, 2H, Hc'-He'); 6.87-6.86 (m, 2H, Hb'-Hf')

^{13}C NMR (151.2 MHz, $CDCl_3$): δ 172.56 (s, Cd'); 143.77 (t, J=1.51 Hz, Ca'); 136.40 (t, J=4.53 Hz, Cb'-Cf'), 134.68 (t, 6.05 Hz, Cb-Cf), 130.52 (t, J=24.2 Hz, Ca), 130.41 (s, Cd), 128.27 (t, J=4.53, Cc-Ce), 120.85 (t, Cc'-Ce').

^{31}P NMR (242.4 MHz, $CDCl_3$): δ +24.18 (s)

3.1.5. Synthesis of OA complex B^{I}_{OMe} [1]



1^{I}_{OMe} B^{I}_{OMe}

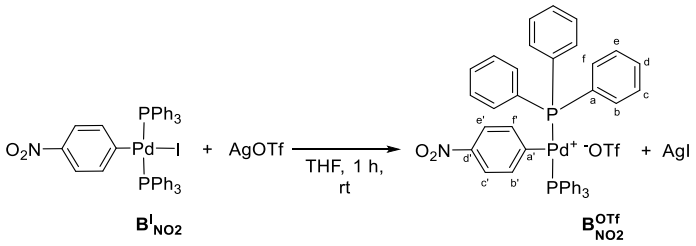
To an oven-dried 20 mL Schlenk purged under argon atmosphere, a mixture of 4-Iodoanisole $\mathbf{1^{I}_{OMe}}$(397 mg, 1.7 mmol, 2.46 eq) and tetrakis(triphenylphosphine)palladium(0) (798 mg, 0.69 mmol, 1 eq) was stirred in degassed toluene (13 mL), in the dark for 2 h at room temperature. The reaction mixture was filtered and the crude was washed with diethyl ether to obtain the pure product (543 mg, 91 %) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.48 (m, 12H, Hb-Hf); 7.33-7.30 (m, 6H, Hd); 7.26-7.21 (m, 12H, Hc-He); 6.42-6.40 (d, J=4 Hz 2H, Hb'-Hf'); 6.08-6.07 (m, 2H, Hc'-He'); 1.92 (s, 3H, Hg').

^{13}C NMR (100.8 MHz, $CDCl_3$): δ 152.90 (s, Ca'); 135.59 (t, J=5.04 MHz, Cb'-Cf'); 135.04 (t, J=7.06 MHz, Cb-Cf); 132.33 (t, J=23.18 MHz, Ca); 131.08 (s, Cd'); 129.74 (s, Cd); 129.07 (s, Cc'-Ce'); 127.82 (t, J=5.04 MHz, Cc-Ce); 22.24 (s, Cg').

^{31}P NMR (161.6 MHz, $CDCl_3$): δ +23.43 (s)

3.1.6. Synthesis of OA complex $B^{OTf}_{NO_2}$ [3]



B^{I}_{NO2} B^{OTf}_{NO2}

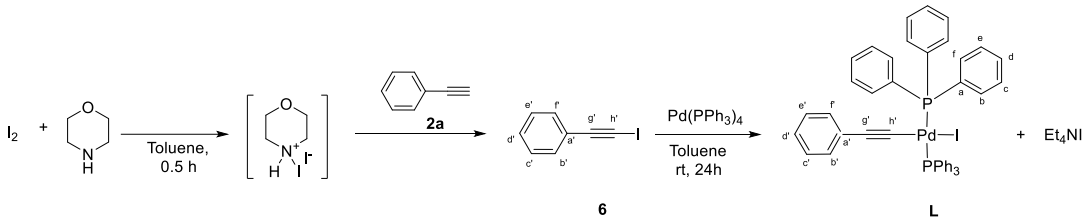
To an oven-dried 20 mL Schlenk purged under argon atmosphere, a mixture of $Pd(PPh_3)_2(PhNO_2)I$ $\mathbf{B^{I}_{NO_2}}$ (60 mg, 0.068 mmol, 1 eq) and Silver trifluoromethanesulfonate (AgOTf) (18 mg, 0.072 mmol, 1.06 eq) was stirred in THF (2 mL) for 1 h at room temperature in the dark. The reaction mixture was filtered through a pad of celite, washed with THF and concentrated to 0.5 mL of solvent under reduced pressure. The THF solution was layered with hexane and allowed to rest at -24° C overnight. The precipitated was filtered to obtain the pure product as white solid (13 mg, 20%).

^{1}H NMR (400 MHz, DMF-d_7): δ 7.60-7.53 (m, 30H, Hb-Hc-Hd-He-Hf); 7.32-7.30 (m, 6H, Hd); 7.32-7.15 (m, 4H, Hb'-Hc'-He'-Hf'). Spectroscopic data matches with the literature[4]

^{31}P NMR (161.6 MHz, DMF-d_7): δ +22.53 (s). Spectroscopic data matches with the literature[4]

^{19}F NMR (377 MHz, DMF-d_7): δ -74.37

3.2. Synthesis of Complex L [5]



The reaction was performed in presence of I_2 (2.80 g, 11 mmol, 1.1 eq) and morpholine (2.62 mL, 30 mmol, 3 eq) in toluene (12 mL) for 30 min at room temperature. After the formation of an orange solution, phenylacetylene **2a** (1.10 mL, 10 mmol, 1 eq) diluted in toluene (18 mL) was added dropwise and the mixture was stirred at 45°C for 24 h. After the filtration and washing with diethyl ether, the organic phase was washed with $NH_4Cl_{(aq)}$, $NaHCO_{3(aq)}$ and water. After drying with Na_2SO_4, the solvent was removed under reduce pressure to obtain **6** (1.35 g, 60%) as a brown oil [6].

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.47-7.46 (m, 2H, Hb'-Hf'); 7.35-7.32 (m, 3H, Hc'-Hd'-He')

^{13}C NMR (151.2 MHz, $CDCl_3$): δ 132.39 (s, Cb'-Cf'); 128.88 (s, Cd'); 128.32 (s, Cc'-Ce'); 127.48 (s, Ca'), 123.43 (s, Cg'); 94.23 (s, Ch')

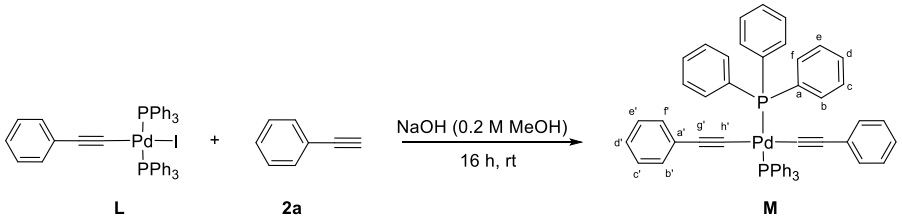
To an oven-dried 20 mL Schlenk purged under argon atmosphere, a mixture of **6** (675 mg, 2.96 mmol, 1.1 eq) and tetrakis(triphenylphosphine)palladium(0) (3.11 mg, 2.69 mmol, 1 eq) was stirred in degassed toluene (25 mL), in the darkness for 24h at room temperature. The reaction mixture was filtered and the crude was washed with diethyl ether to obtain pure product (2.15 mg, 80 %) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78-7.76 (m, 12H, Hb-Hf); 7.41-7.35 (m, 18H, Hc-Hd-He); 6.91-6.89 (m, 1H, Hd'); 6.86-6.83 (m, 2H, Hc'-He'); 6.09-6.08 (m, 2H, Hb'-Hf')

^{13}C NMR (151.2 MHz, $CDCl_3$): δ 135.16 (t, J= 6.05 Hz, Cb-Cf); 132.79 (t, J=24.2 Hz, Ca); 130.66 (t, J=1.51 Hz, Cb'-Cf'); 130.27 (s, Cd); 127.97 (t, J= 4.53, Cc-Ce); 127.34 (s, Ca'); 127.17 (s, Cc'-Ce'); 125.27 (s, Cd'); 109.67 (t, J=6.05 Hz, Cg'); 101.57 (t, J=13.61 Hz, Ch')

^{31}P NMR (242.4 MHz, $CDCl_3$): δ +23.43 (s)

3.3. Synthesis of Complex M [5]



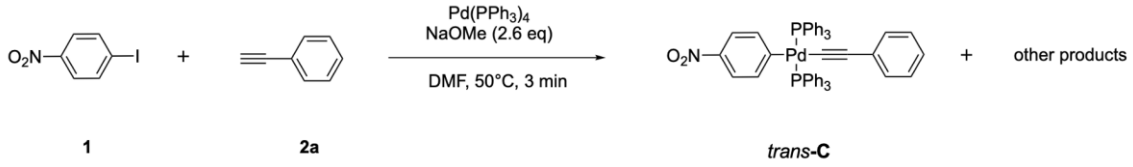
To an oven-dried 20 mL Schlenk purged under argon atmosphere, a mixture of complex **L** (240 mg, 0.28 mmol, 1 eq) and phenylacetylene **2a** (396 µL, 3.57 mmol, 12.78 eq) and 0.2 M NaOH in methanol (7 mL) was stirred for 16 h at room temperature. The reaction mixture was filtered, and the crude was washed with water and methanol to obtain pure product (207 mg, 89 %) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.84-7.81 (m, 12H, Hb-Hf); 7.41-7.38 (m, 6H, Hd); 7.36-7.33 (m, 12H, Hc-He); 6.92-6.91 (m, 6H, Hc'-Hd'-He'); 6.34-6.32 (m, 4H, Hb'-Hf')

^{13}C NMR (151.2 MHz, $CDCl_3$): δ 135.14 (t, J= 6.05 Hz, Cb-Cf); 132.66 (t, J=24.2 Hz, Ca); 130.91 (s, Cb'-Cf'); 130.09 (s, Cd); 128.23 (t, J= 1.51 Hz, Ca'); 128.02 (t, J=4.54 Hz, Cc-Ce); 127.20 (s, Cc'-Ce'); 124.86 (s, Cd'); 114.90 (t, J=4.53 Hz, Cg'); 113.74 (t, J=16.63 Hz, Ch')

^{31}P NMR (242.4 MHz, $CDCl_3$): δ +26.56 (s)

3.4. Synthesis of Complex *trans*-C [5]



To an oven-dried 20 mL Schlenk purged under argon atmosphere, tetrakis(triphenyilphosphine)palladium (0) (578 mg, 0.5 mmol, 1 eq) was dissolved in degassed DMF-d_7. The other reagents were added in the following order: 1-Iodo-4-nitrobenzene **1** (249 mg, 1 mmol, 2 eq), phenylacetylene **2a** (142.8 µL, 1.3 mmol, 2.6 eq) and sodium methoxide (70 mg, 1.3 mmol, 2.6 eq). After 3 minutes, an aliquot was collected and immediately analyzed by ^{31}P NMR. The isolation of complex *trans*-**C** was not possible, according to the data reported in literature[5]

^{31}P NMR (242.4 MHz, $CDCl_3$): δ +27.56 (s)

4. The Pd(II) reduction

4.1. Pd(II) reduction with triphenylphosphine:

To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $PdCl_2(PPh_3)_2$ (9.12 mg, 0.013 mmol, 1 eq) was dissolved in the degassed solvent (0.6 mL). The ligand triphenylphosphine (PPh_3) (6.81 mg, 0.026 mmol, 2 eq) and triethyl phosphonoacetate as internal standard (0.0065 mmol, 0.5 eq) were added and the reaction was stirred at room temperature. After 10 minutes, the ^{31}P NMR spectrum was acquired.

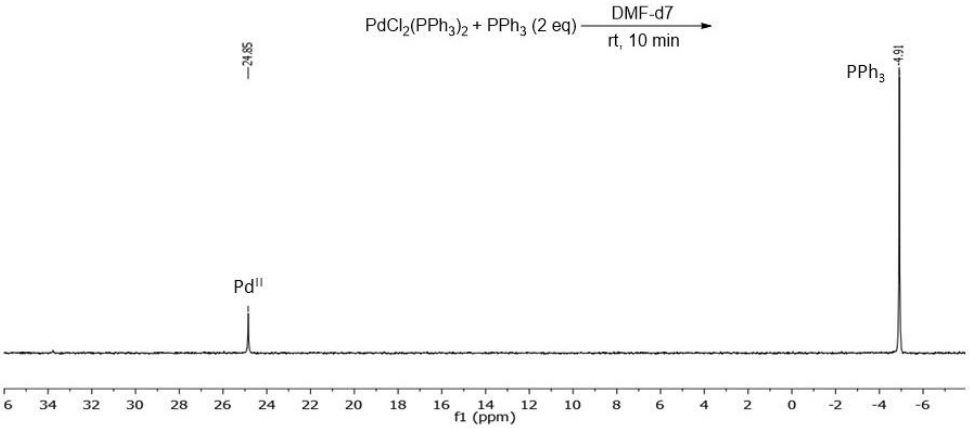


Figure S11. ^{31}P NMR spectrum of $PdCl_2(PPh_3)_2$ with PPh_3 2 eq in DMF-d_7.

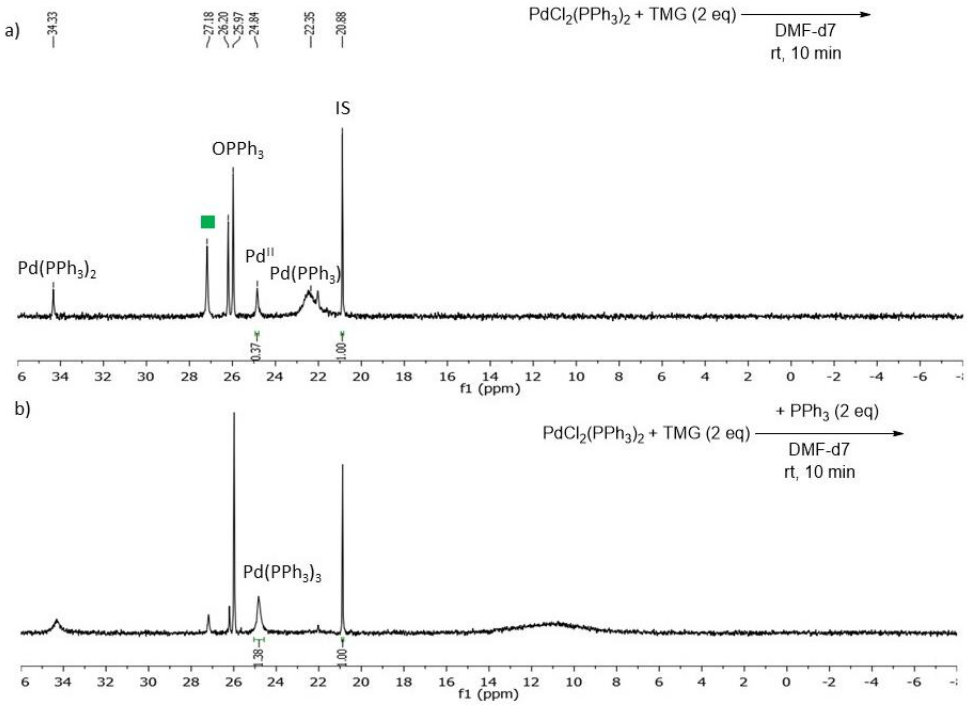
4.2. Pd(II) reduction with base and PPh_3.

To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $PdCl_2(PPh_3)_2$ (9.12 mg, 0.013 mmol, 1 eq) was dissolved in degassed solvent (0.6 mL). The base (0.026 mmol, 2 eq), triphenylphosphine (6.81 mg, 0.026 mmol, 2 eq) and triethyl phosphonoacetate as internal standard (0.0065 mmol, 0.5 eq) were added. The reaction was stirred at room temperature and after 10 minutes, the ^{31}P NMR spectra were collected.

Table S2. $PdCl_2(PPh_3)_2$ reduction and base effect

Entry	Base	Solvent	% Conversion	+ PPh_3 (% Conversion)
1	TMG	DMF-d_7	64	100
2	TMG	$CDCl_3$	85	100
3	Pyr	DMF-d_7	31	100
4	Pyr	$CDCl_3$	65	100
5	TEA	DMF-d_7	0	0
6	TEA	$CDCl_3$	0	0

Entry 1, Table S2



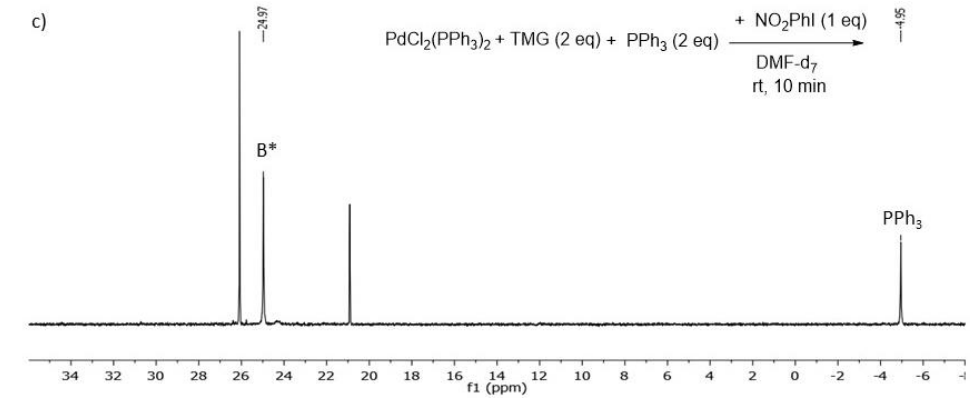


Figure S12. ^{31}P NMR spectra of the reduction of $PdCl_2(PPh_3)_2$ in DMF-d_7 with TMG 2 eq. The peak labelled in green represents (TMG)$Pd^0(PPh_3)$ but the complex is not isolable. (a); with TMG 2 eq and PPh_3 2 eq (b); with TMG 2 eq, PPh_3 2 eq and the reagent 4-NO_2PhI 1 eq (c) to show that the reduction of Pd(II) was complete.

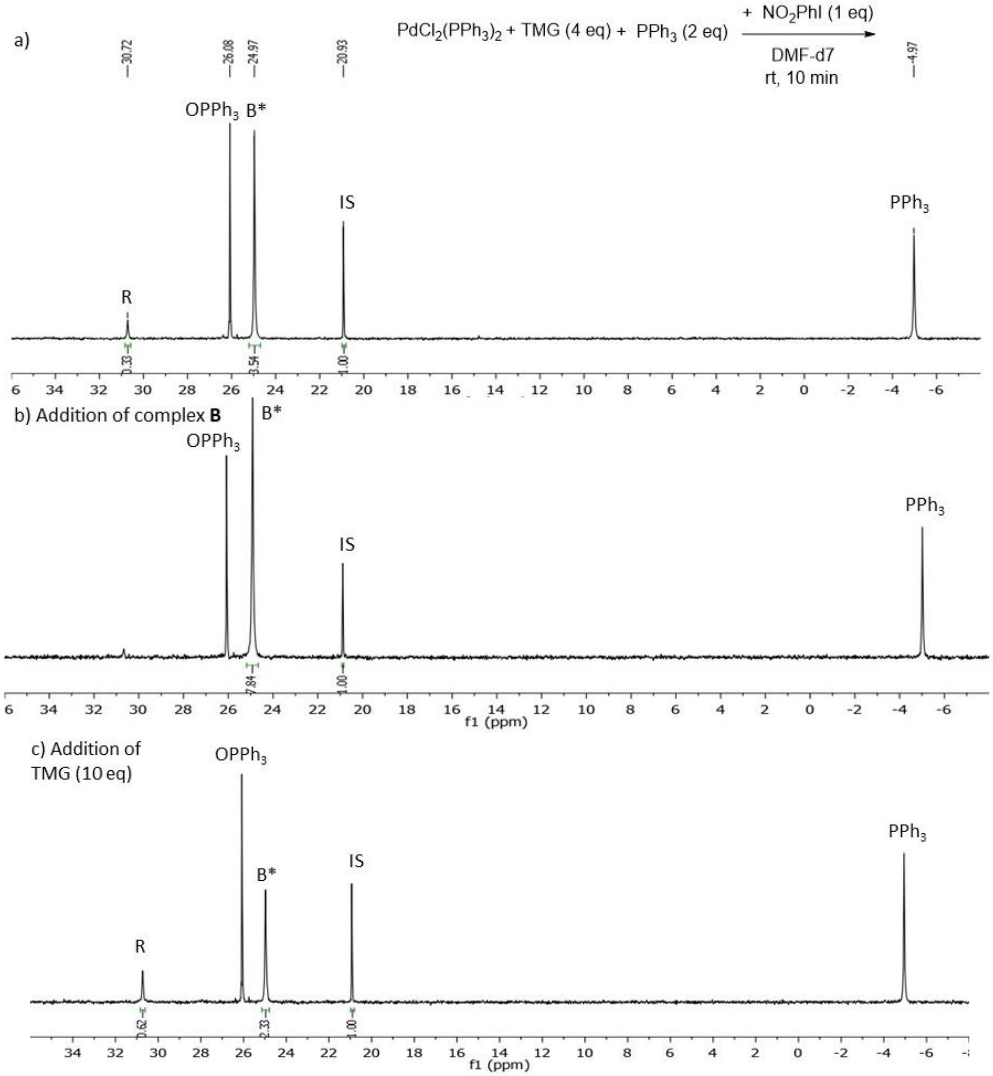


Figure S13. ^{31}P NMR spectra of the reduction of $PdCl_2(PPh_3)_2$ in DMF-d_7 in presence of: TMG 4 eq with PPh_3 2 eq and the reagent 4-NO_2PhI to show the formation of **R**, the complex bearing TMG coordinated to palladium (a); with the addition of the pre-synthesized oxidative addition (OA) complex **B,** to further demonstrate that the chemical shift referred to the OA complex (labelled as **B***) is 24.92 ppm in this condition (b); with the addition of TMG 10 eq to show that **R** increases while **B** decreases (c).

Entry 2, Table S2

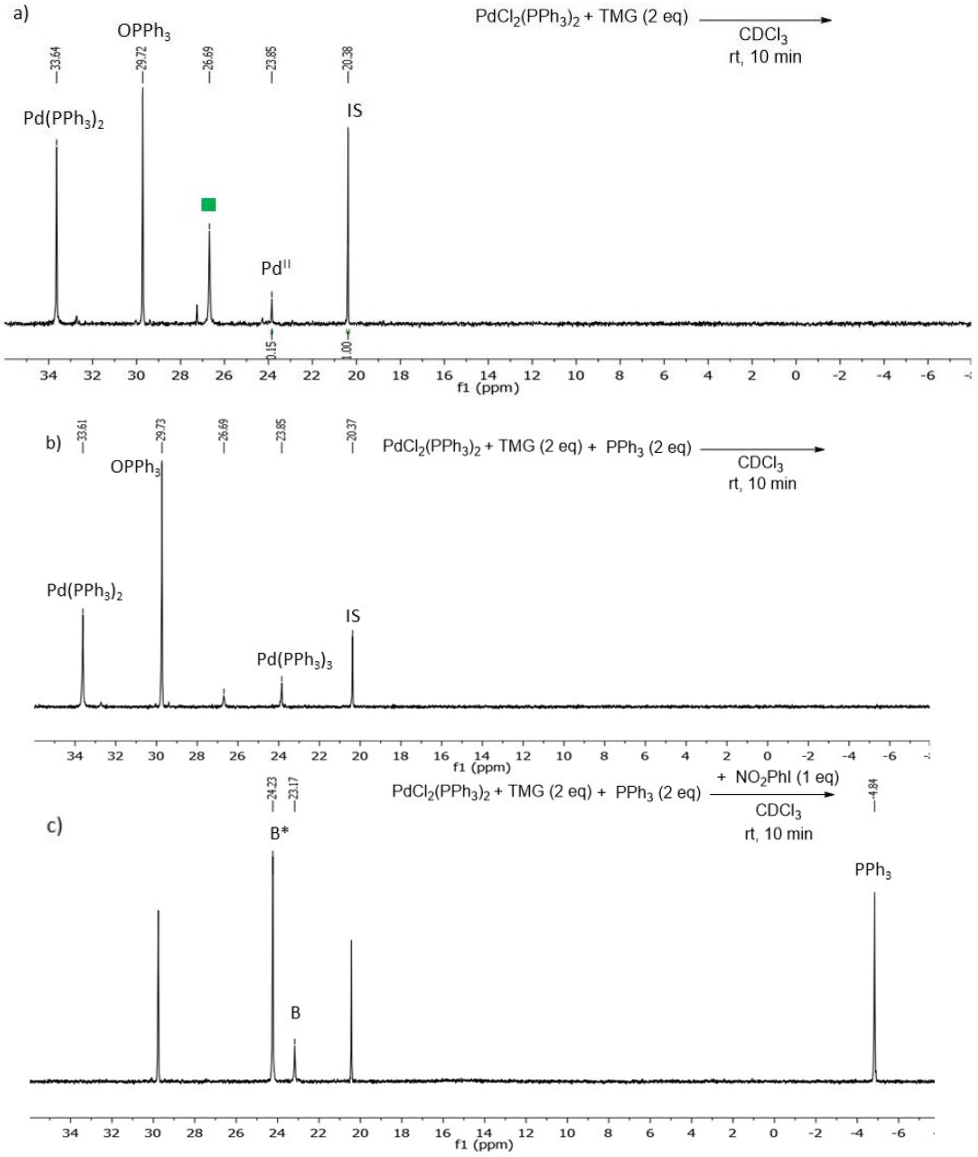


Figure S14. ^{31}P NMR spectra of the reduction of $PdCl_2(PPh_3)_2$ in $CDCl_3$ with TMG 2 eq. The peak labelled in green represents $(TMG)Pd^0(PPh_3)$ (a); with TMG 2 eq and PPh_3 2 eq (b); with TMG 2 eq, PPh_3 2 eq and the reagent 4-NO_2PhI 1 eq (c) to show that the reduction of Pd(II) was completed.

Entry 3, Table S2

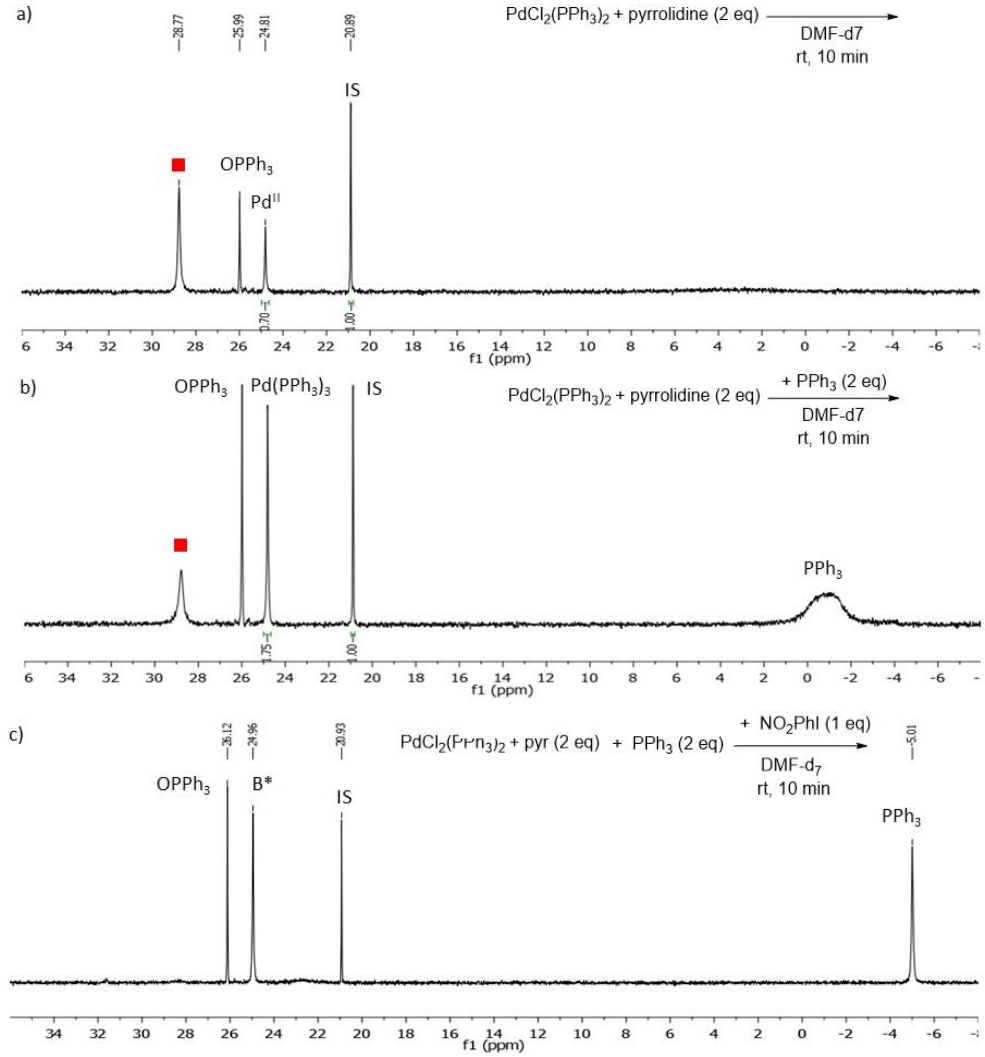


Figure S15. ^{31}P NMR spectra of the reduction of $PdCl_2(PPh_3)_2$ in DMF-d_7 with pyrrolidine 2 eq. The peak labelled in red represents (PYR)$Pd^0(PPh_3)$ but it is not isolable. (a); with pyrrolidine 2 eq and PPh_3 2 eq (b); with pyrrolidine 2 eq, PPh_3 2 eq and the reagent 4-NO_2PhI 1 eq (c) to show that the reduction of Pd(II) was completed.

Entry 4, Table S2.

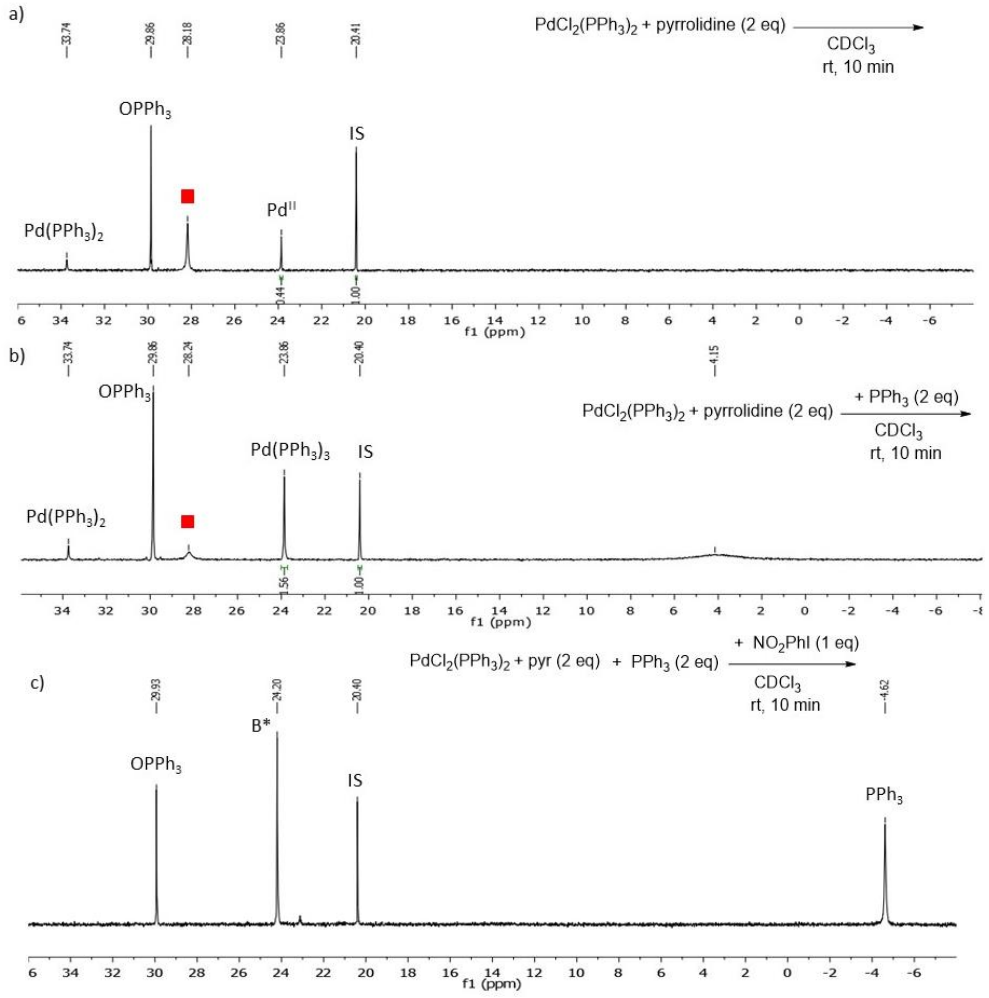


Figure S16. ^{31}P NMR spectra of the reduction of $PdCl_2(PPh_3)_2$ in $CDCl_3$ with pyrrolidine 2 eq. The peak labelled in red represents (PYR)$Pd^0(PPh_3)$ but it is not isolable (a); with pyrrolidine 2 eq and PPh_3 2 eq (b); with pyrrolidne 2 eq, PPh_3 2 eq and the reagent 4-NO_2PhI 1 eq (c) to show that the reduction of Pd(II) was completed.

Entry 5, Table S2

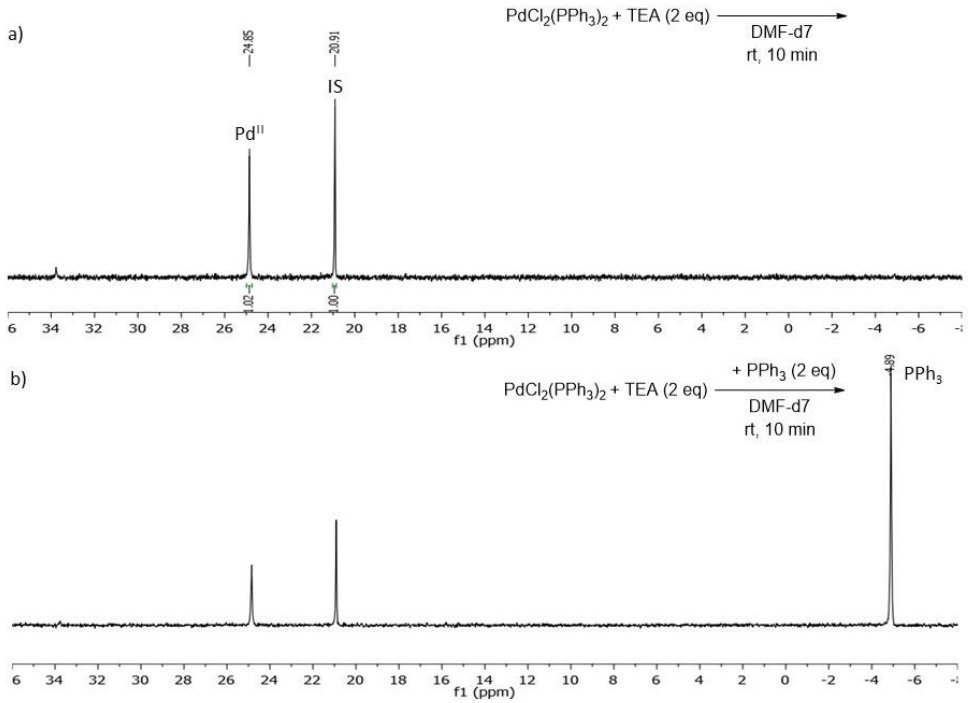


Figure S17. ^{31}P NMR spectra of $PdCl_2(PPh_3)_2$ in DMF-d_7 with TEA 2 eq (a) and with TEA 2 eq and PPh_3 2 eq (b).

Entry 6, Table S2

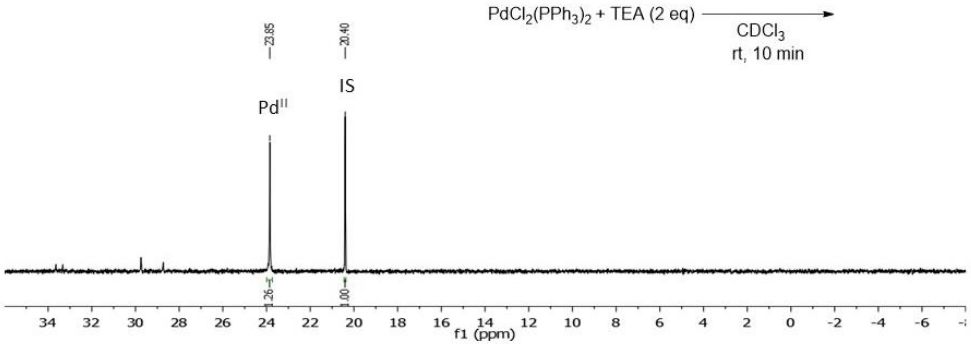


Figure S18. ^{31}P NMR spectrum of $PdCl_2(PPh_3)_2$ in $CDCl_3$ with TEA 2 eq.

4.3. Pd(II) reduction in presence of phenylacetylene, with and without PPh_3

To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $PdCl_2(PPh_3)_2$ (9.12 mg, 0.013 mmol, 1 eq) was dissolved in degassed $CDCl_3$ (0.6 mL). Base (0.65 mmol, 50 eq), phenylacetylene **2a** (71.38 µL, 0.65 mmol, 50 eq) and triphenylphosphine (6.81 mg, 0.026 mmol, 2 eq) were added. The reaction was stirred at room temperature and ^{31}P NMR spectra were collected after 10 minutes.

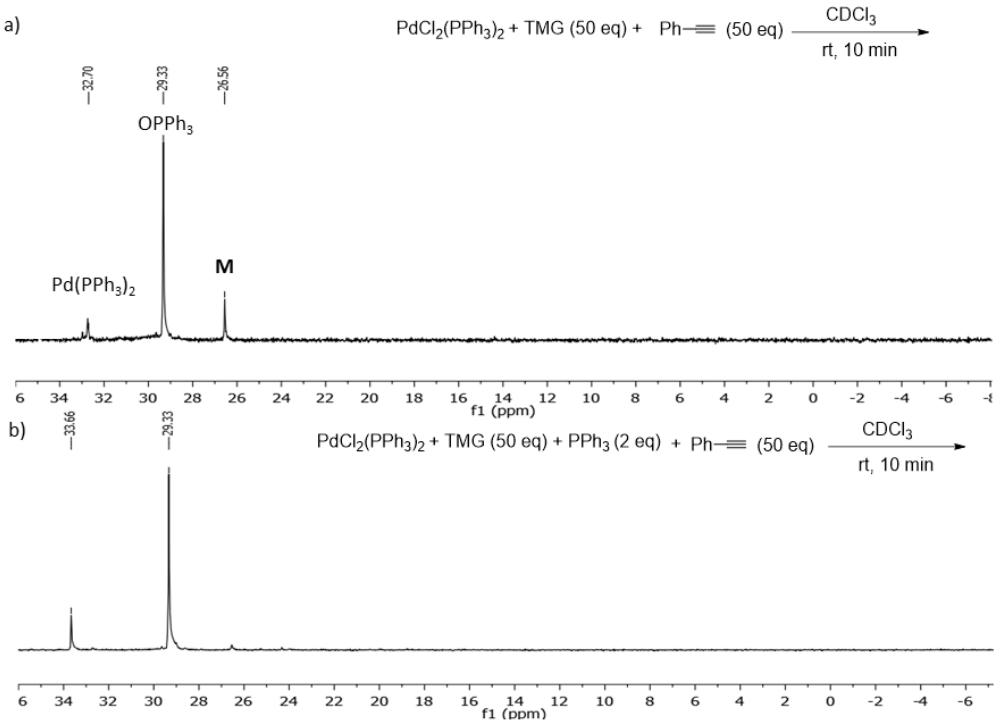


Figure S19. ^{31}P NMR spectra of $PdCl_2(PPh_3)_2$ in $CDCl_3$ with TMG 50 eq and **2a** 50 eq (a) and with PPh_3 2 eq (b).

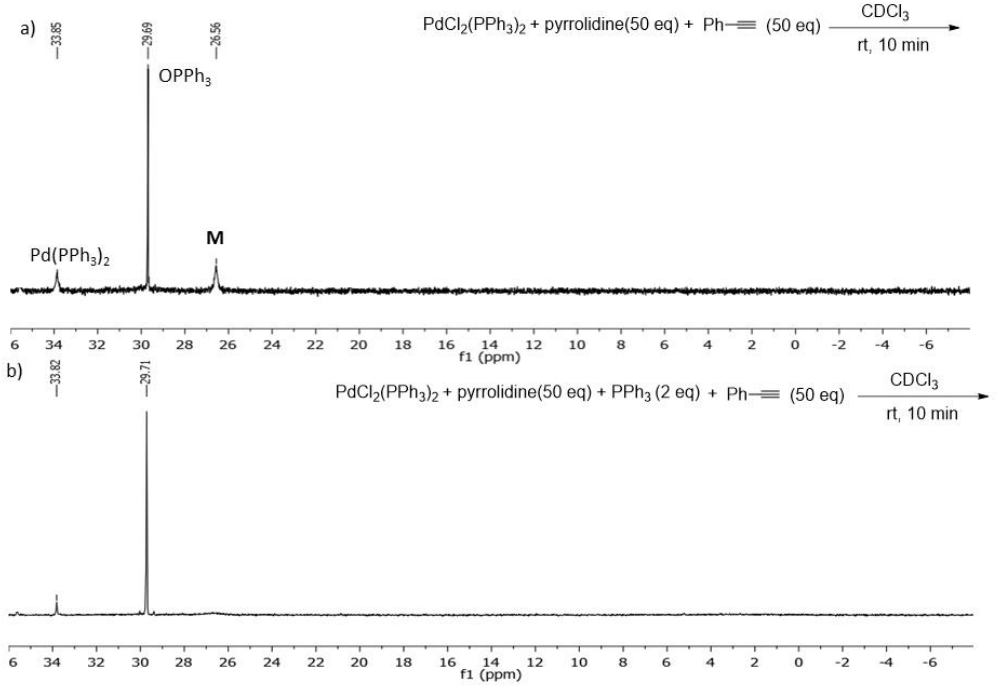


Figure S20. ^{31}P NMR spectra of $PdCl_2(PPh_3)_2$ in $CDCl_3$ with pyrrolidine 50 eq and **2a** 50 eq (a) and with PPh_3 2 eq (b).

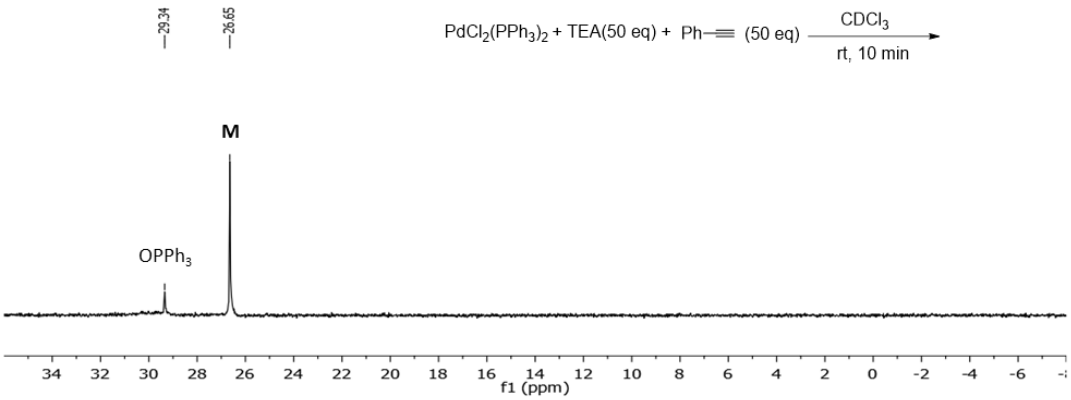
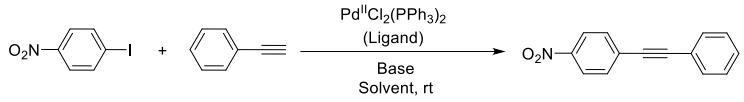


Figure S21. ^{1}P NMR spectra of $PdCl_2(PPh_3)_2$ in $CDCl_3$ with TEA 50 eq and **2a** 50 eq. The experiment with the addition of PPh_3 was not performed because TEA does not displace the ligand (see Table S2)

5. Heck-Cassar reaction with Palladium (II) and Palladium (0)

5.1. General procedure for the HC reaction with Palladium (II)



To an oven-dried 10 mL Schlenk purged under N_2 atmosphere, $PdCl_2(PPh_3)_2$ (20% mmol) and PPh_3 (40% mmol) were dissolved in the degassed solvent (1 ml). After the addition of 1-Iodo-4-nitrobenzene **1** (124.5 mg, 0.5 mmol, 1 eq), phenylacetylene **2a** (60 µL, 0.55, 1.1 eq) and the base (2 eq), the reaction mixture was stirred at room temperature. After a given time, the ^{31}P NMR spectra were collected to detect which species were formed.

5.1.1. TMG

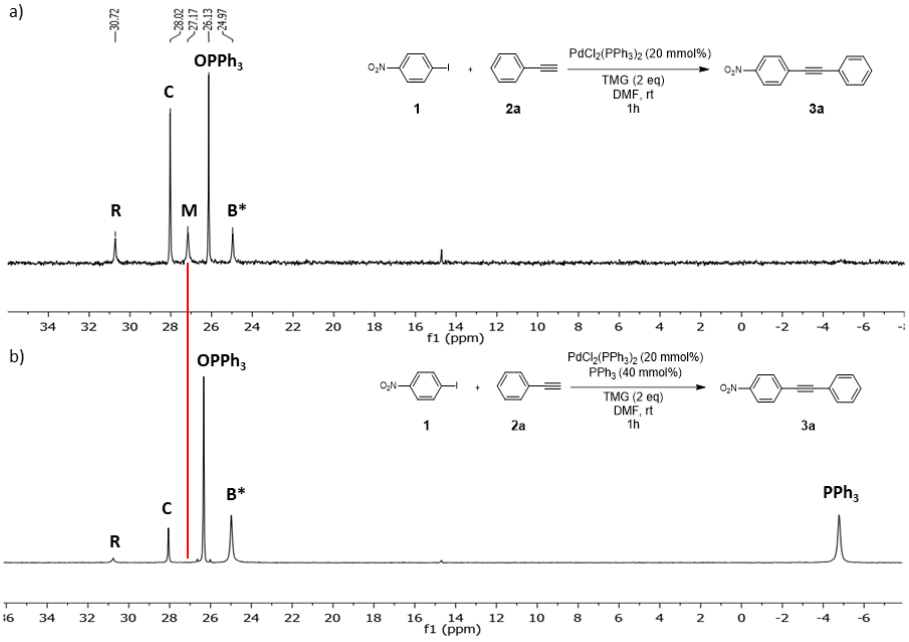


Figure S22. Stacking of ^{31}P NMR spectra after 1 h of the reaction between **1** and **2a** in DMF-d_7, with TMG 2 eq (a); with TMG 2 eq and 40 mmol% of PPh_3 (b).

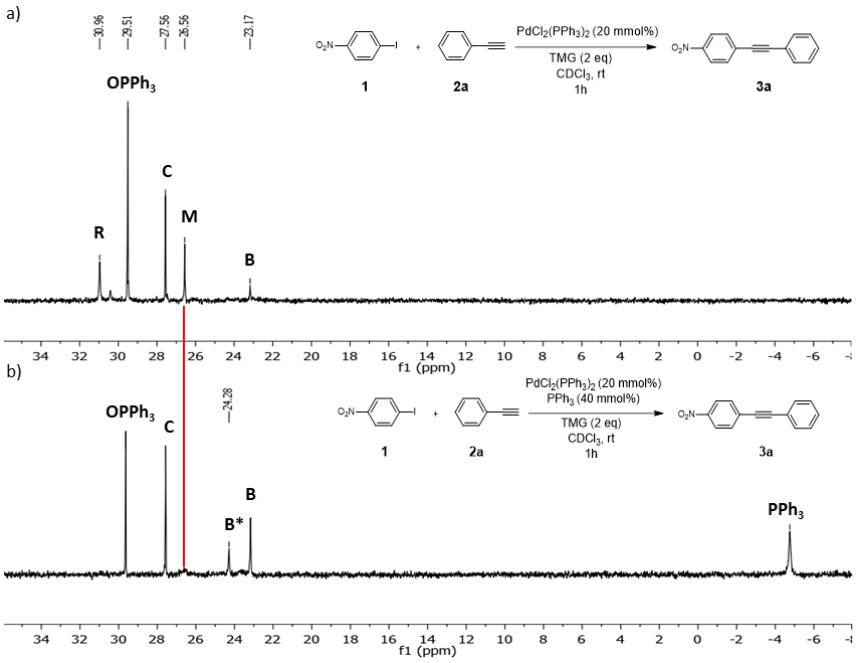


Figure S23. Stacking of ^{31}P NMR spectra after 1 h of the reaction between **1** and **2a** in $CDCl_3$, with TMG 2 eq (a); with TMG 2 eq and 40 mmol% of PPh_3 (b).

5.1.2. Pyrrolidine

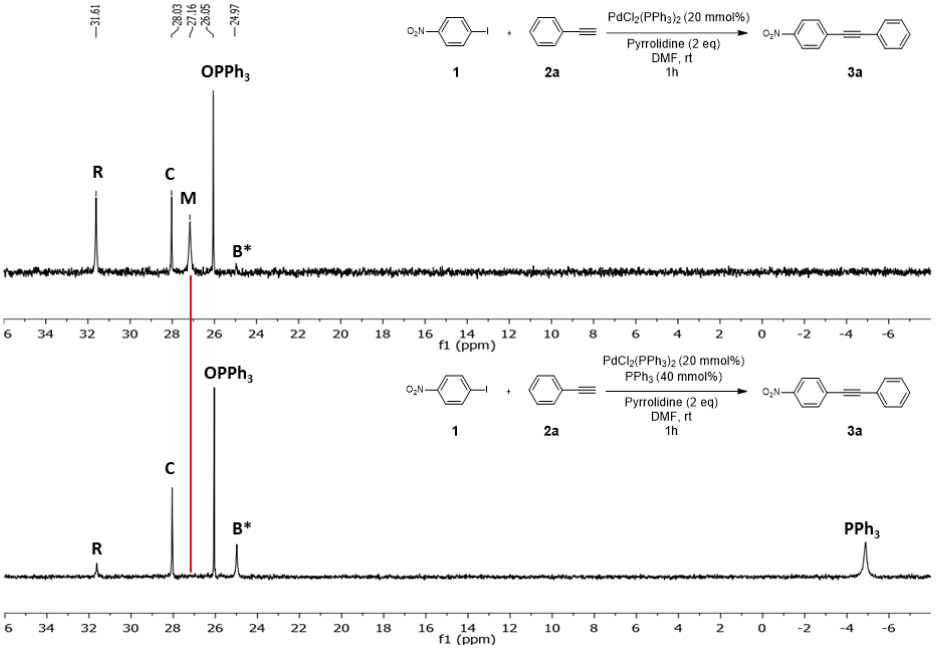


Figure S24. Stacking of ^{31}P NMR spectra after 1 h of the reaction between **1** and **2a** in DMF-d_7, with PYR 2 eq (a); with PYR 2 eq and 40 mmol% of PPh_3 (b).

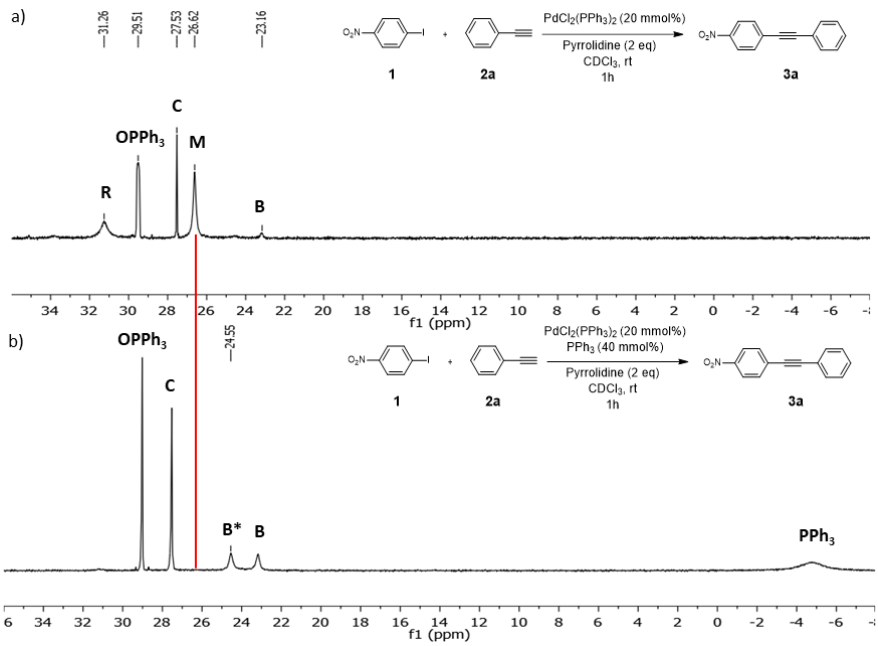
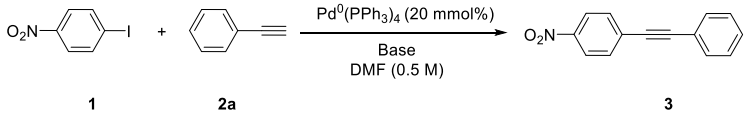


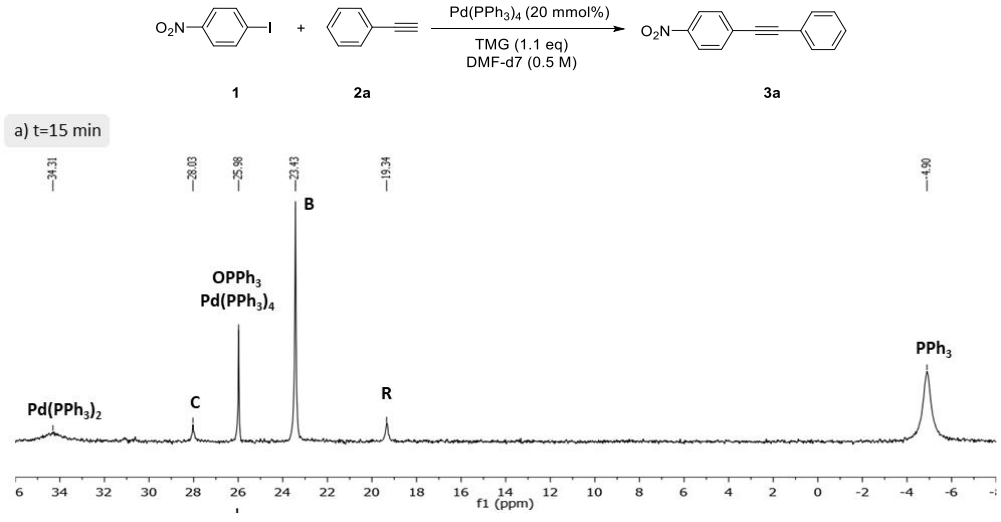
Figure S25. Stacking of ^{31}P NMR spectra after 1 h of the reaction between **1** and **2a** in $CDCl_3$, with PYR 2 eq (a); with PYR 2 eq and 40 mmol% of PPh_3 (b).

5.2. General procedure for the HCS reaction with Palladium (0)



To an oven-dried 10 mL Schlenk purged under N_2 atmosphere, Tetrakis(triphenylphosphine)palladium(0) (20% mmol) was dissolved in degassed DMF-d_7. After the addition of 1-Iodo-4-nitrobenzene **1** (124.5 mg, 0.5 mmol, 1 eq), phenylacetylene **2a** (60 µL, 0.55, 1.1 eq) and the base, the reaction mixture was stirred at room temperature. After a given time, the ^{31}P NMR spectra were collected to detect which species were formed.

5.2.1. TMG



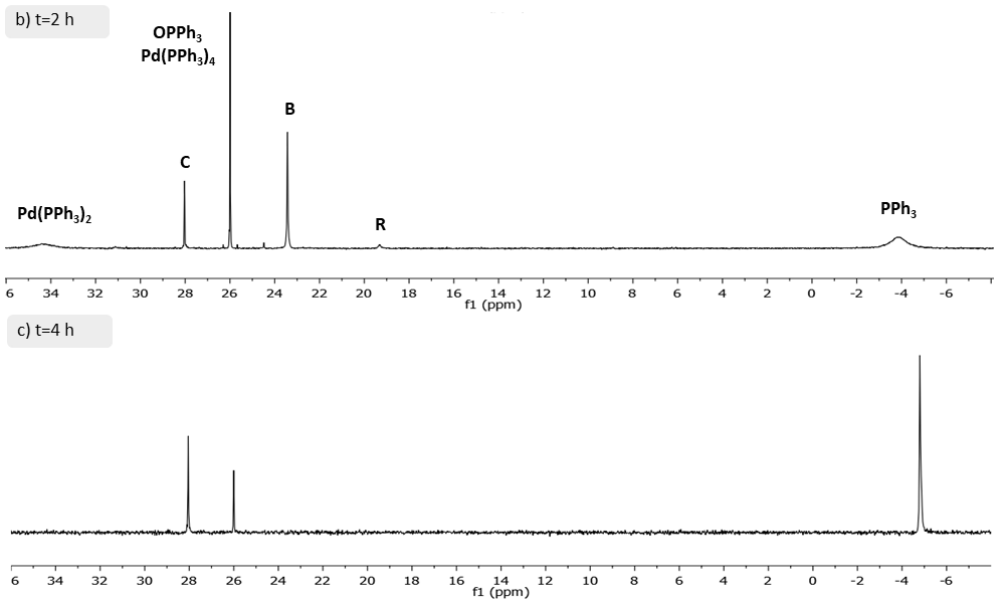


Figure S26. Stacking of ^{31}P NMR spectra of the reaction between **1** and **2a** in DMF-d_7 using TMG after 15 min (a); 1 h (b); 4 h (c).

5.2.2. Pyrrolidine

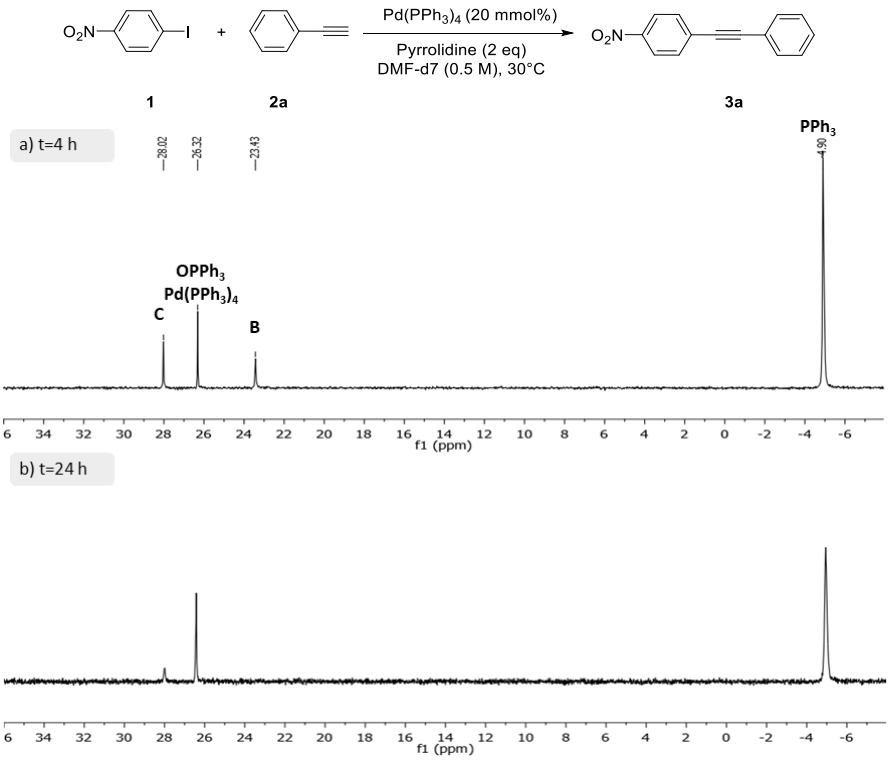


Figure S27. Stacking of ^{31}P NMR spectra of the reaction between **1** and **2a** in DMF-d_7 using PYR after 4 h (a) and 24 h (b).

5.2.3. Sodium Methoxide (NaOMe)

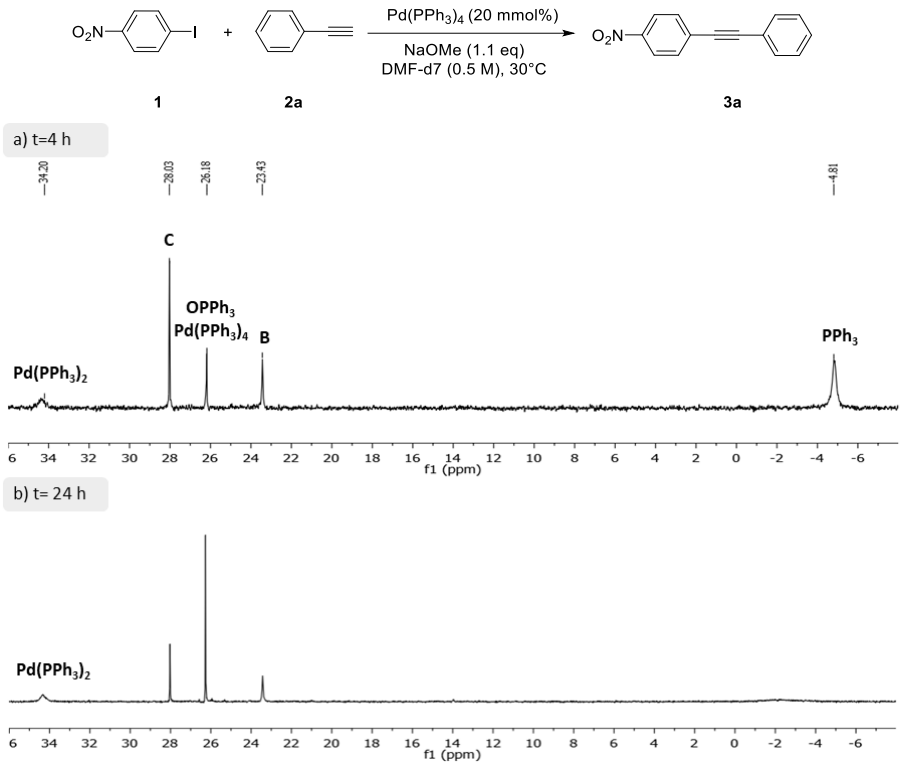
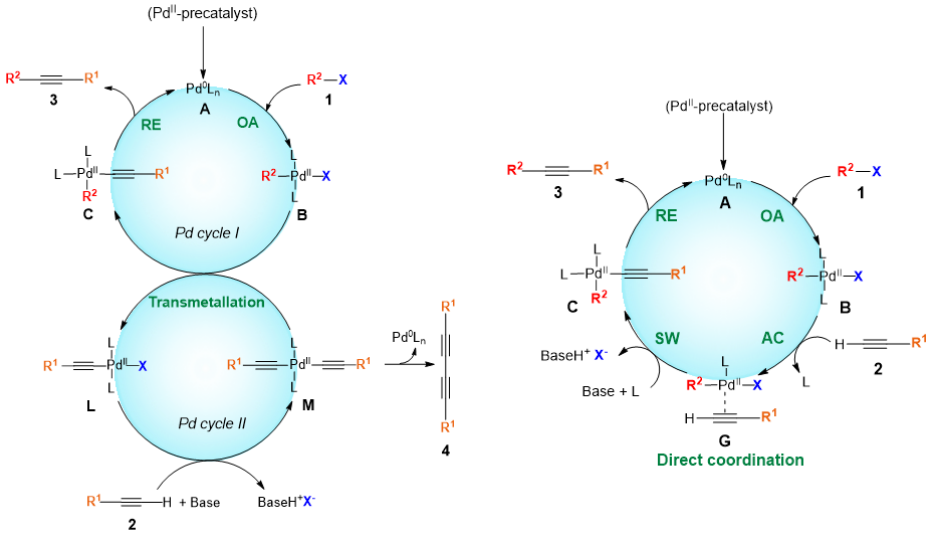


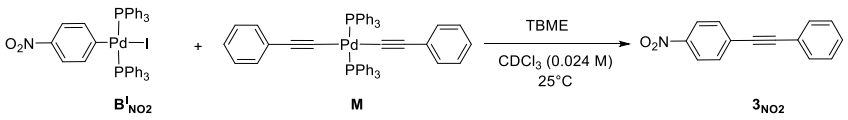
Figure S28. Stacking of ^{31}P NMR spectra of the reaction between **1** and **2a** in DMF-d_7 using NaOMe after 1 h (a) 4 h and 24 h (b).

6. Direct coordination versus transmetallation



6.1. Procedure for the Transmetallation step ($B^{I}_{NO_2}$):

The reaction was performed in an oven-dried NMR tube purged under nitrogen atmosphere. The complexes $\mathbf{B^{I}_{NO_2}}$ (15.8 mg, 0.018 mmol, 1 eq)) and **M** (15 mg, 0.0.18 mmol, 1 eq) were dissolved in $CDCl_3$ (0.750 mL). The mixture was let at room temperature and monitored by ^{1}H and ^{31}P NMR spectroscopy at intervals of 20 minutes for 7 hours using tert-butyl methyl ether (TBME) as internal standard. The reaction was repeated three times with consistent results. The following NMR spectra belong to one experiment and are given as examples.



^{1}H NMR spectra:

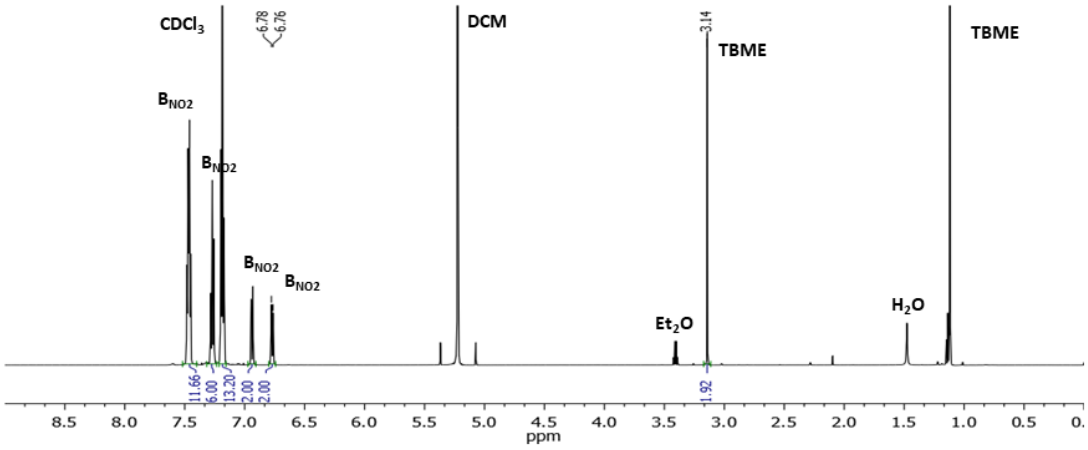


Figure S29. ^{1}H NMR spectrum before the addition of **M** (t=0).

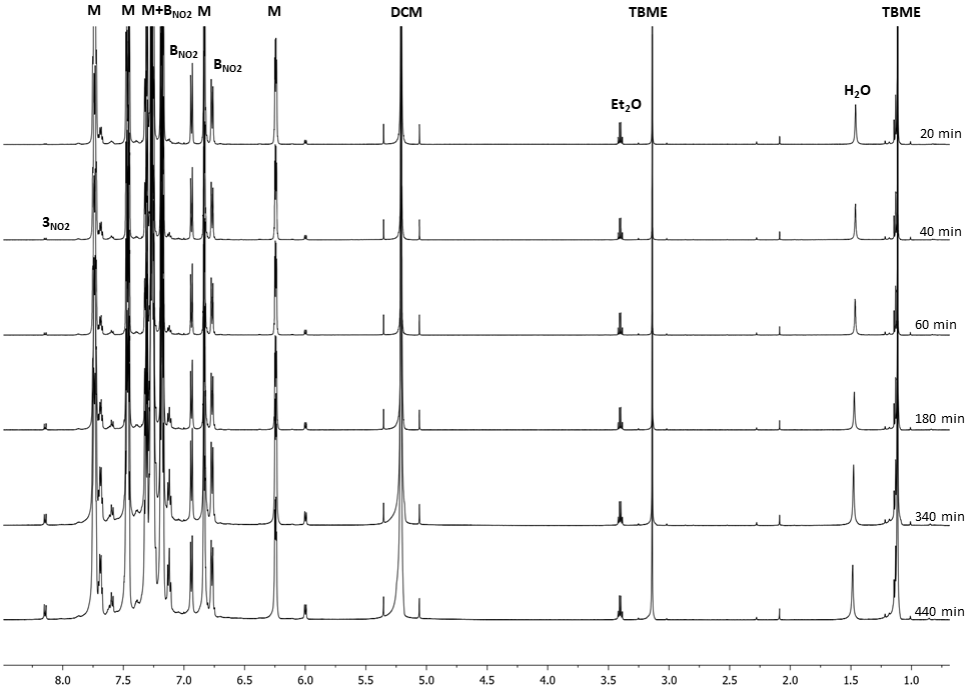
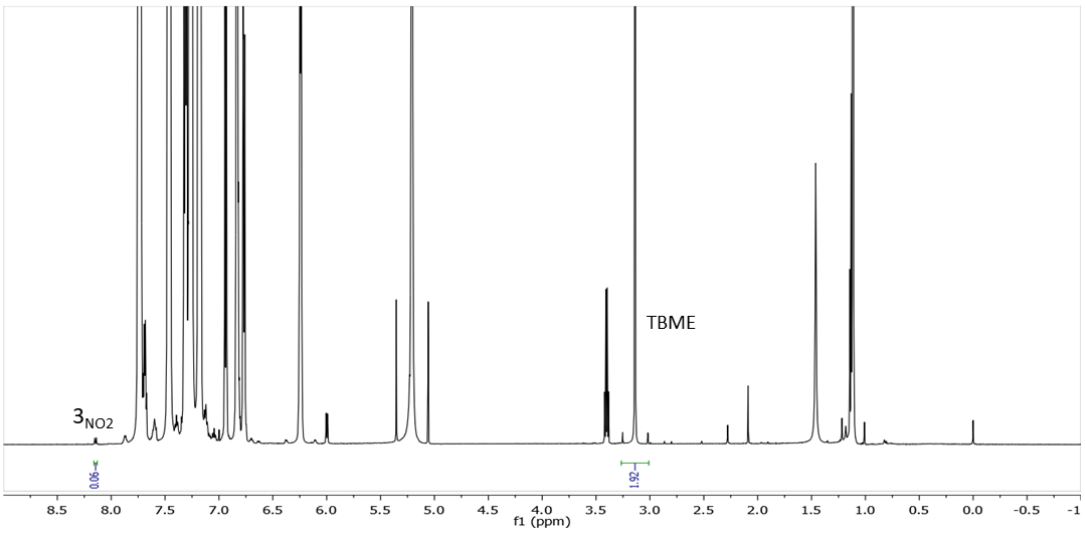
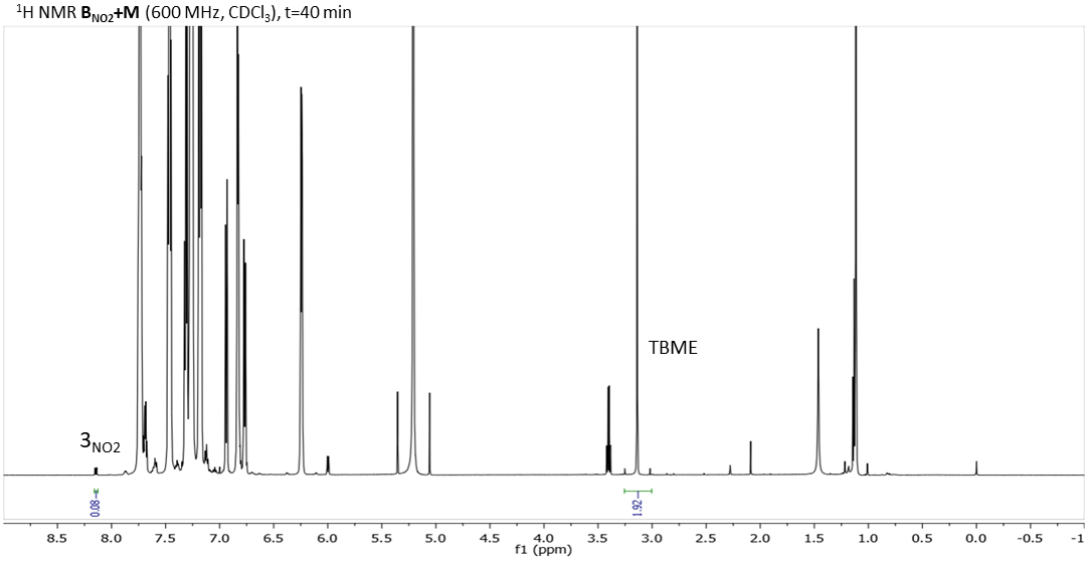


Figure S30. Stacking of ^{1}H NMR spectra of the stoichiometric reaction between $\mathbf{B^{I}_{NO_2}}$ and **M** in $CDCl_3$ at several times.

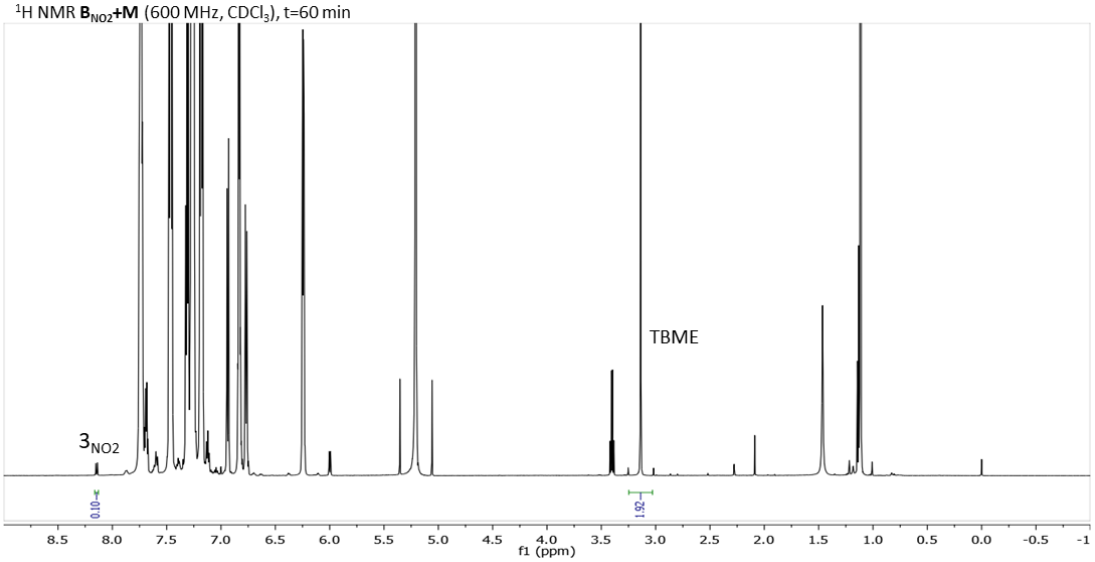
^{1}H NMR **B_{NO2}+M** (600 MHz, $CDCl_3$), t=20 min



^{1}H NMR **B_{NO2}+M** (600 MHz, $CDCl_3$), t=40 min



^{1}H NMR **B_{NO2}+M** (600 MHz, $CDCl_3$), t=60 min



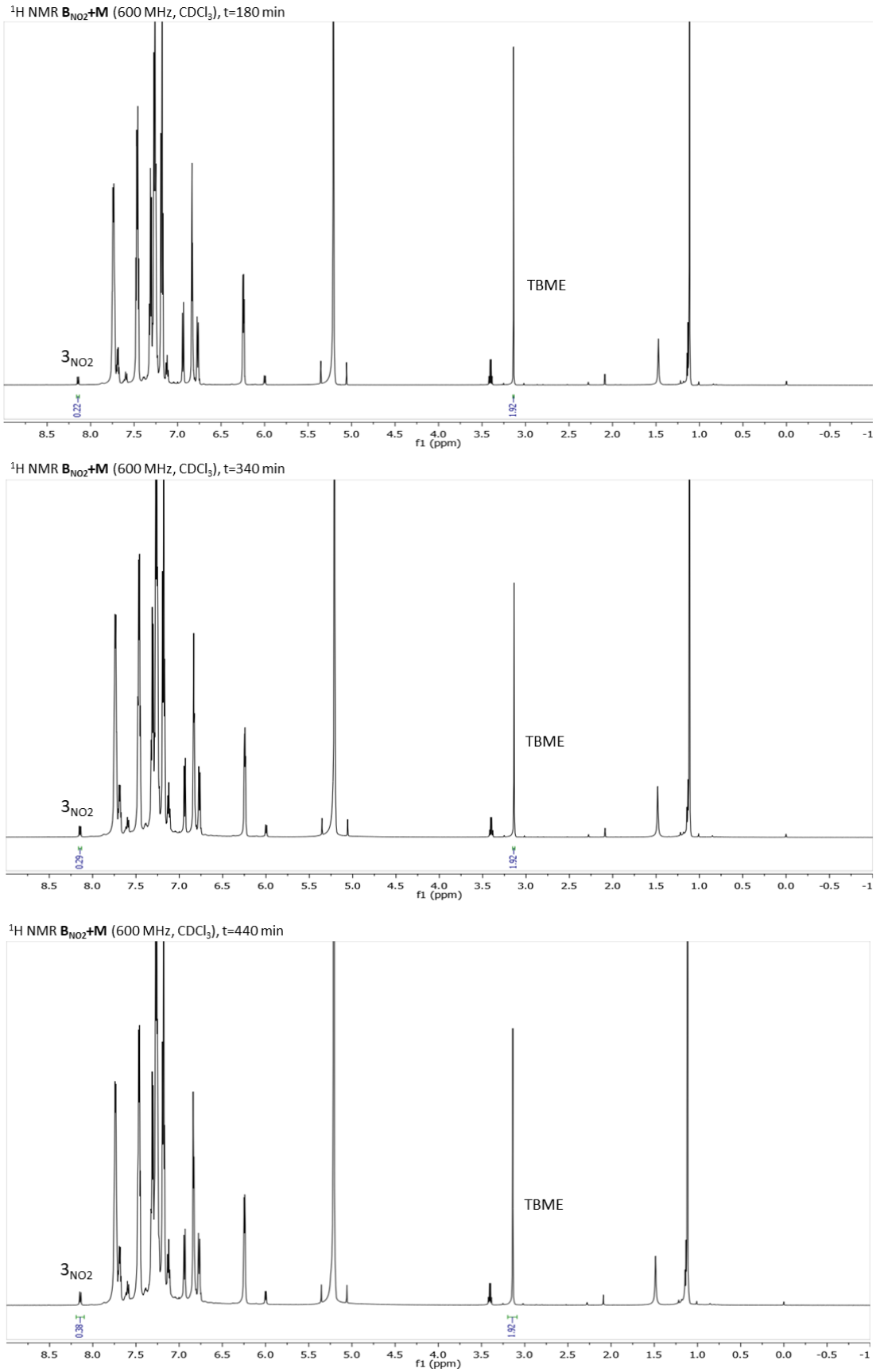


Figure S31. ^{1}H NMR spectra of the stoichiometric reaction between $\mathbf{B^I_{NO_2}}$ and **M** in $CDCl_3$ at t=20 min, 40 min, 60 min, 180 min, 340 min, 440 min.

^{31}P NMR spectra

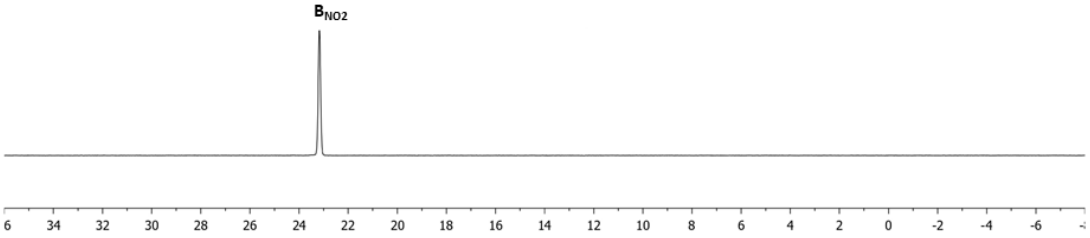


Figure S32. ^{31}P NMR spectrum before the addition of **M** (t=0).

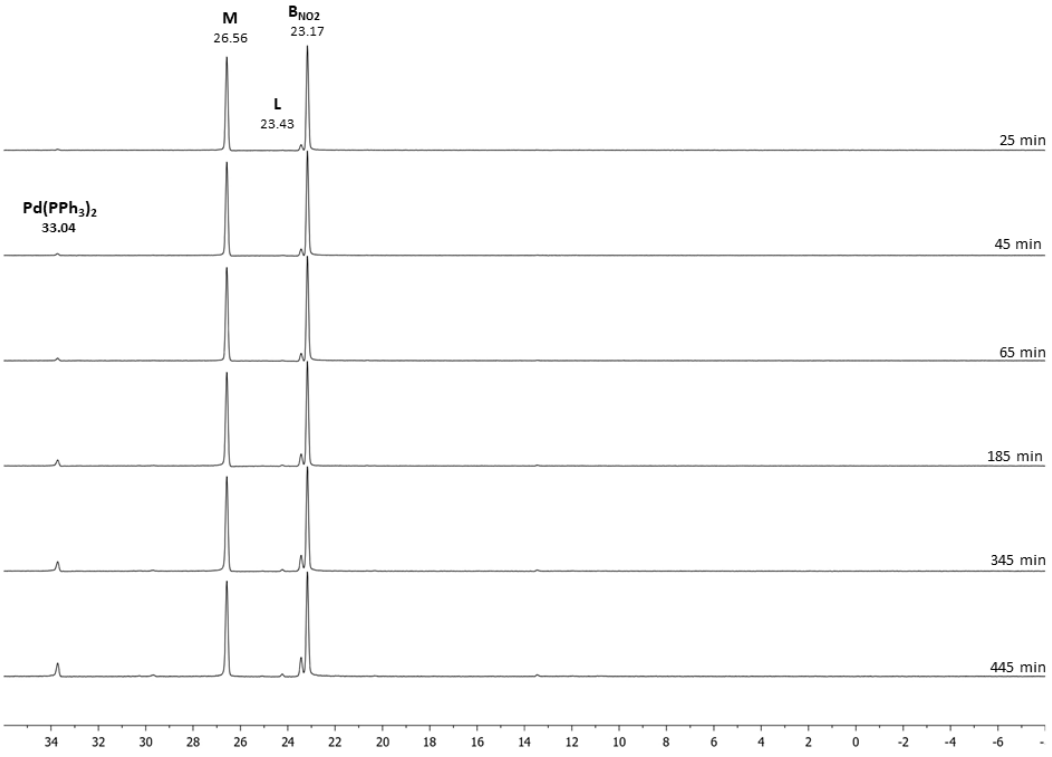
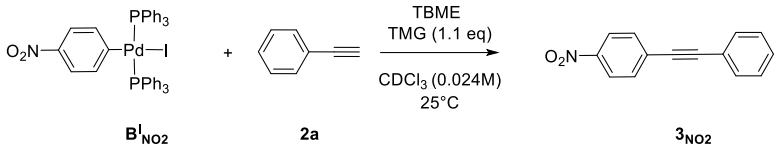


Figure S33. Stacking of ^{31}P NMR spectra of the stoichiometric reaction between $\mathbf{B^{I}_{NO_2}}$ and **M** in $CDCl_3$ at several times

6.2. Procedure for the Direct Coordination step ($\mathbf{B^{I}_{NO_2}}$):

The reaction was performed in an oven-dried NMR tube purged under nitrogen atmosphere. The complex $\mathbf{B^{I}_{NO_2}}$ (15.8 mg, 0.018 mmol, 1 eq) was dissolved in $CDCl_3$ (0.750 mL), followed by the addition of **2a** (29 µL from a stock solution of 0.66 M, 0.018 mmol, 1 eq) and TMG (32.5 µL from a stock solution of 0.66 M, 0.02 mmol, 1.1 eq). TBME (1 eq) was used as internal standard. The mixture was let at room temperature and monitored by ^{1}H and ^{31}P NMR spectroscopy at intervals of 20 minutes for 7 hours. The reaction was repeated three times with consistent results. The following NMR spectra belong to one experiment and are given as examples.



^{1}H NMR spectra:

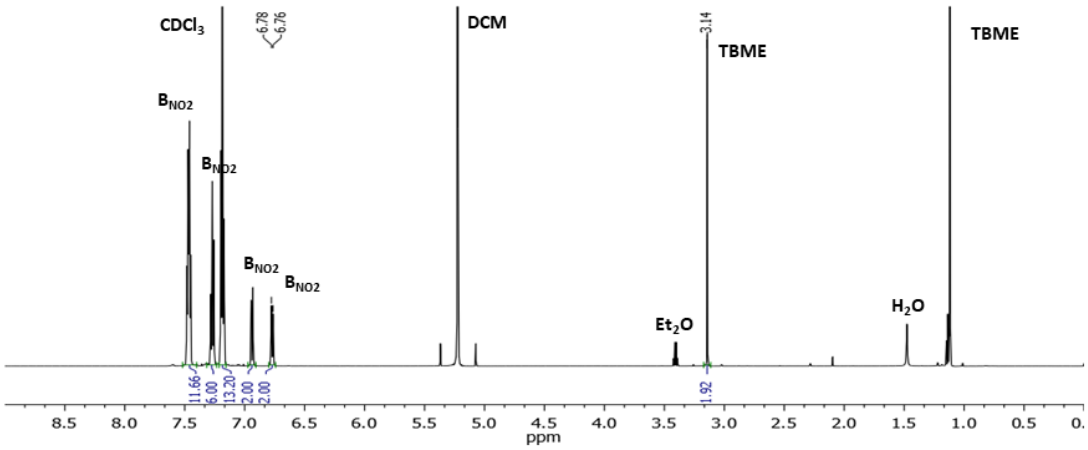


Figure S34. ^{1}H NMR spectrum before the addition of **2a** and TMG (t=0).

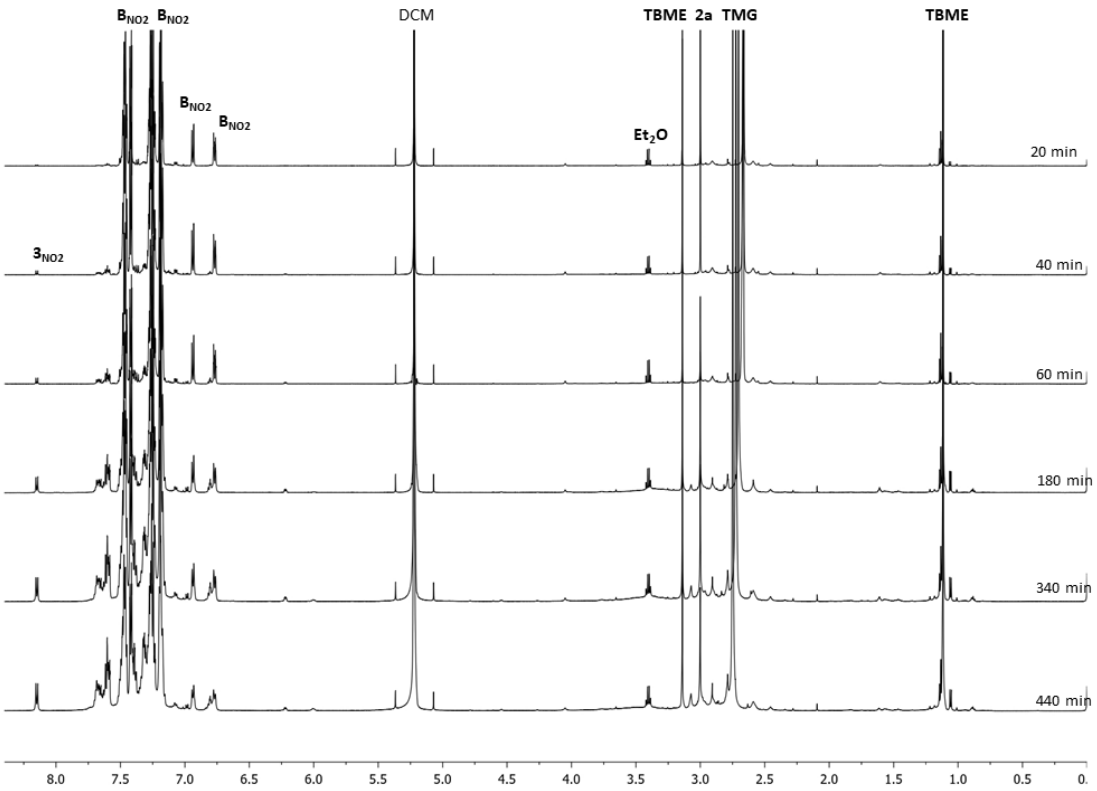
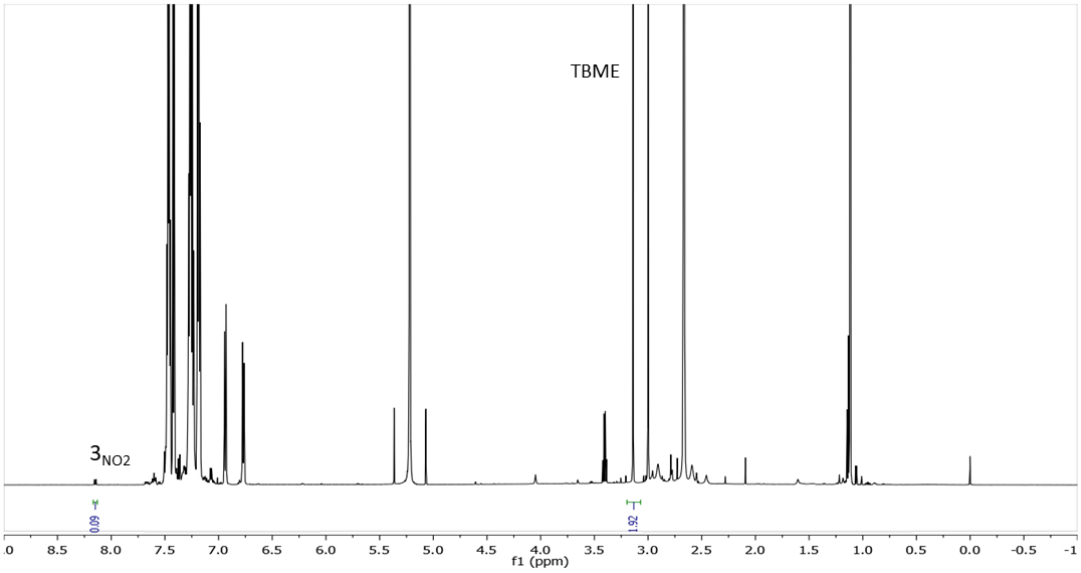
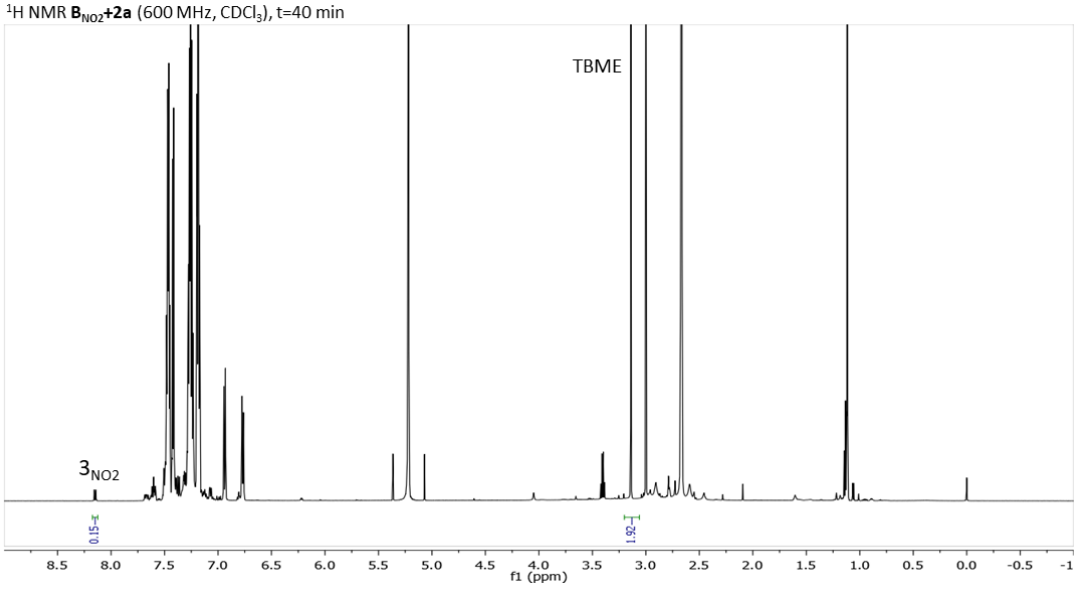


Figure S35. Stacking of ^{1}H NMR spectra of the stoichiometric reaction between$\mathbf{B^I_{NO_2}}$ and **2a** with TMG in $CDCl_3$ at several times.

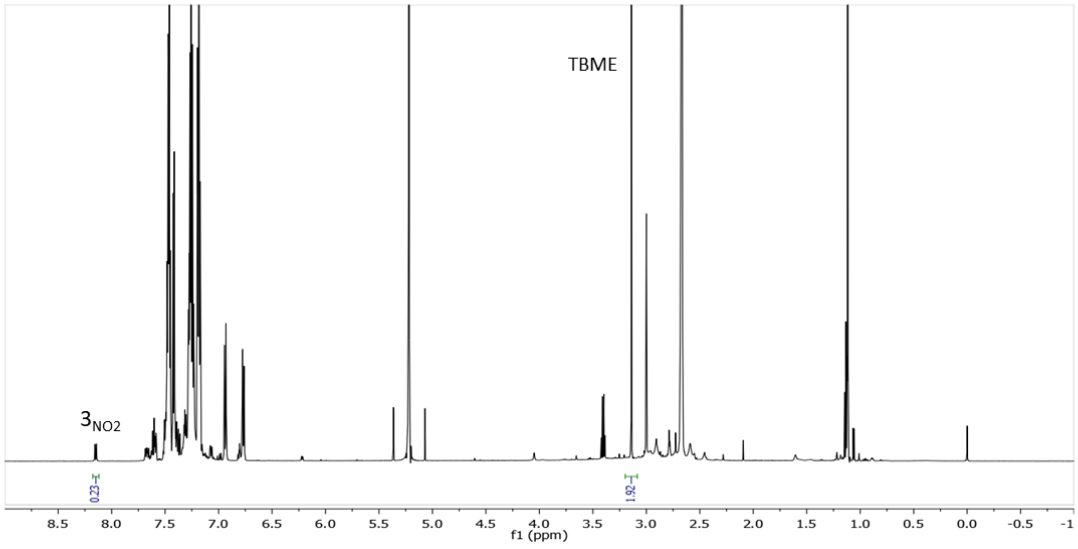
^{1}H NMR **B_{NO2}+2a** (600 MHz, $CDCl_3$), t=20 min



^{1}H NMR **B_{NO2}+2a** (600 MHz, $CDCl_3$), t=40 min



^{1}H NMR **B_{NO2}+2a** (600 MHz, $CDCl_3$), t=60 min



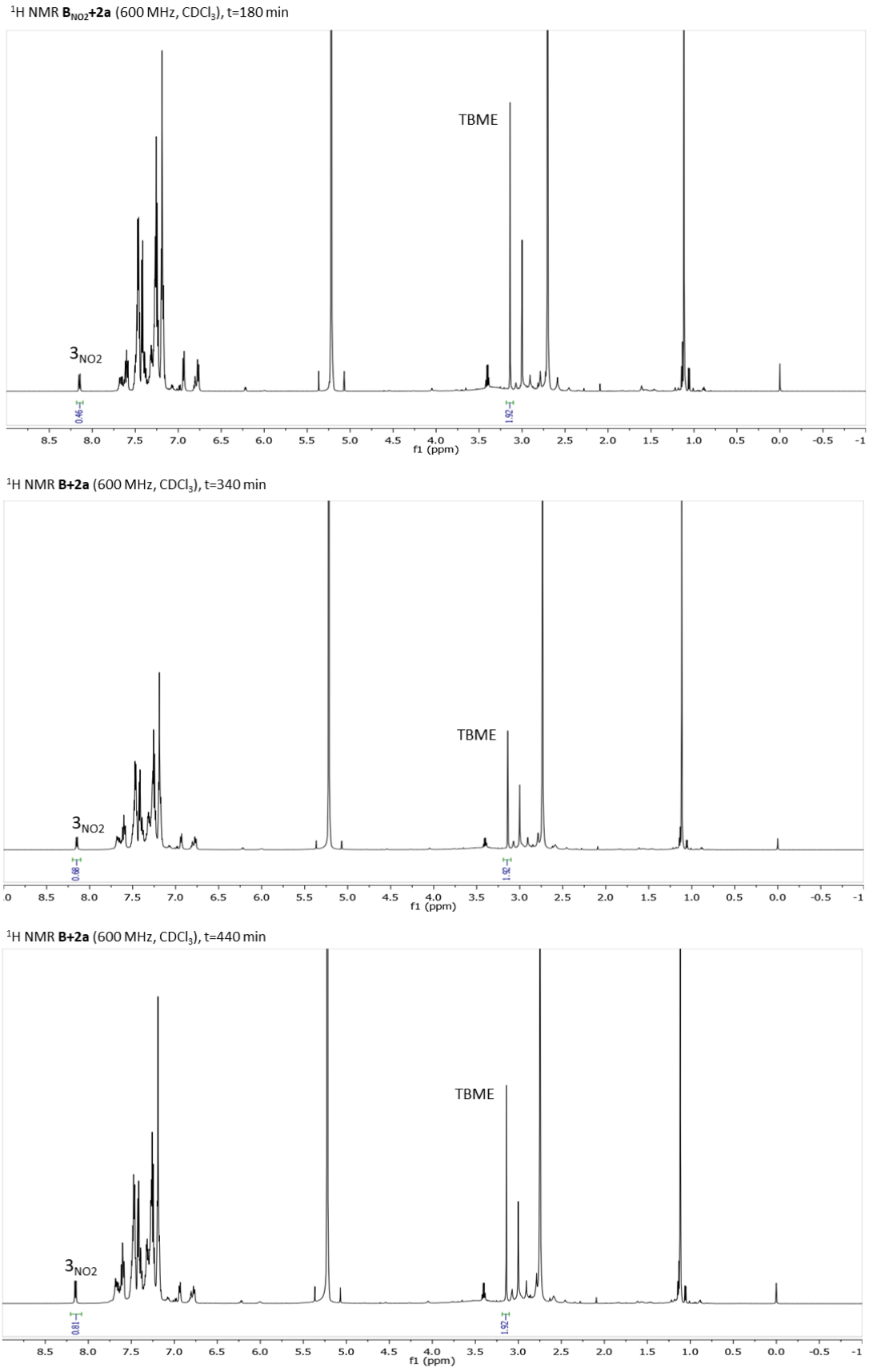


Figure S36. ^{1}H NMR spectra of the stoichiometric reaction between $\mathbf{B^I_{NO_2}}$ and **2a** with TMG in $CDCl_3$ at t=20 min, 40 min, 60 min, 180 min, 340 min, 440 min.

^{31}P NMR spectra:

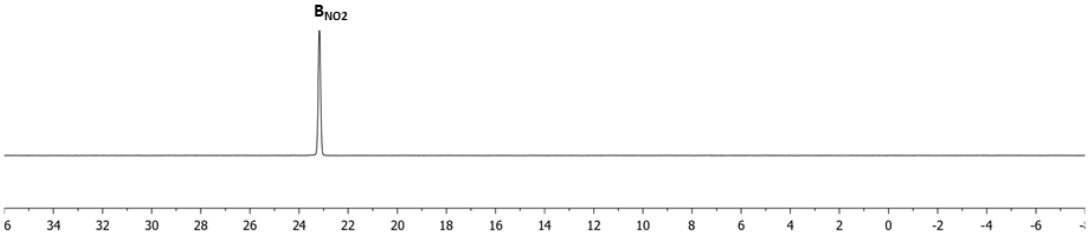


Figure S37. ^{31}P NMR spectrum before the addition of **2a** and TMG (t=0).

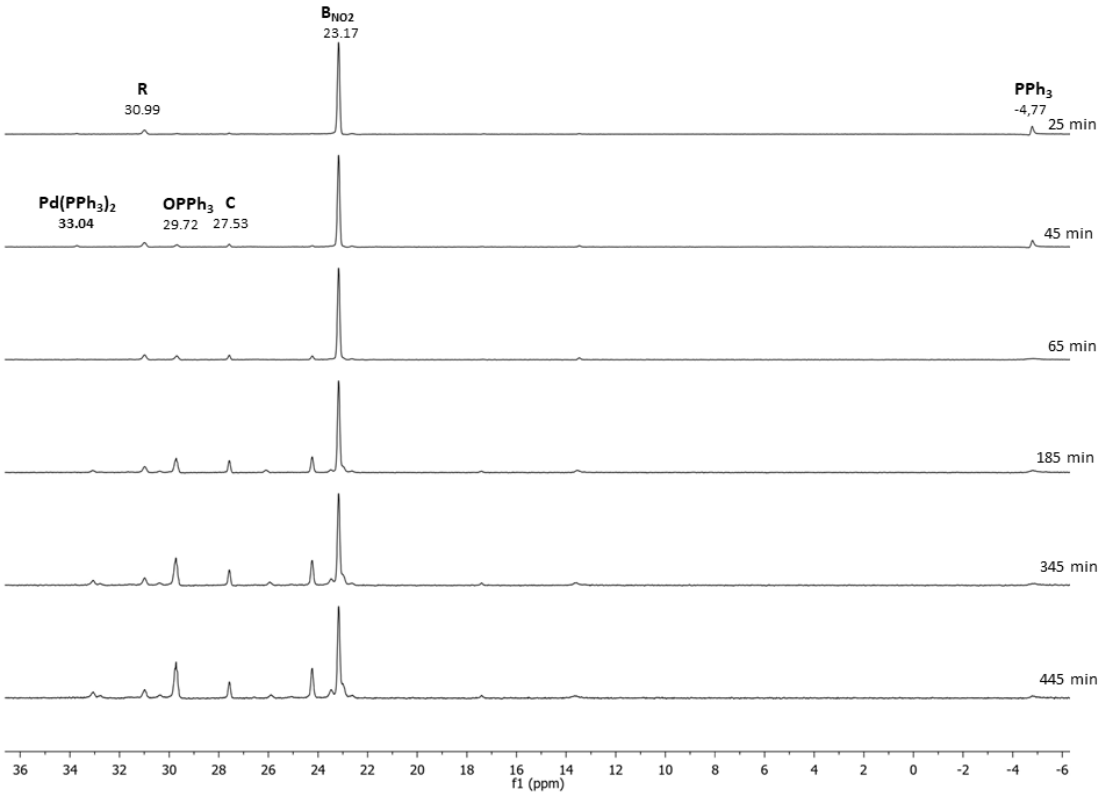


Figure S38. Stacking of ^{31}P NMR spectra of the stoichiometric reaction between $\mathbf{B^{I}_{NO_2}}$ and **2a** with TMG in $CDCl_3$ at several times

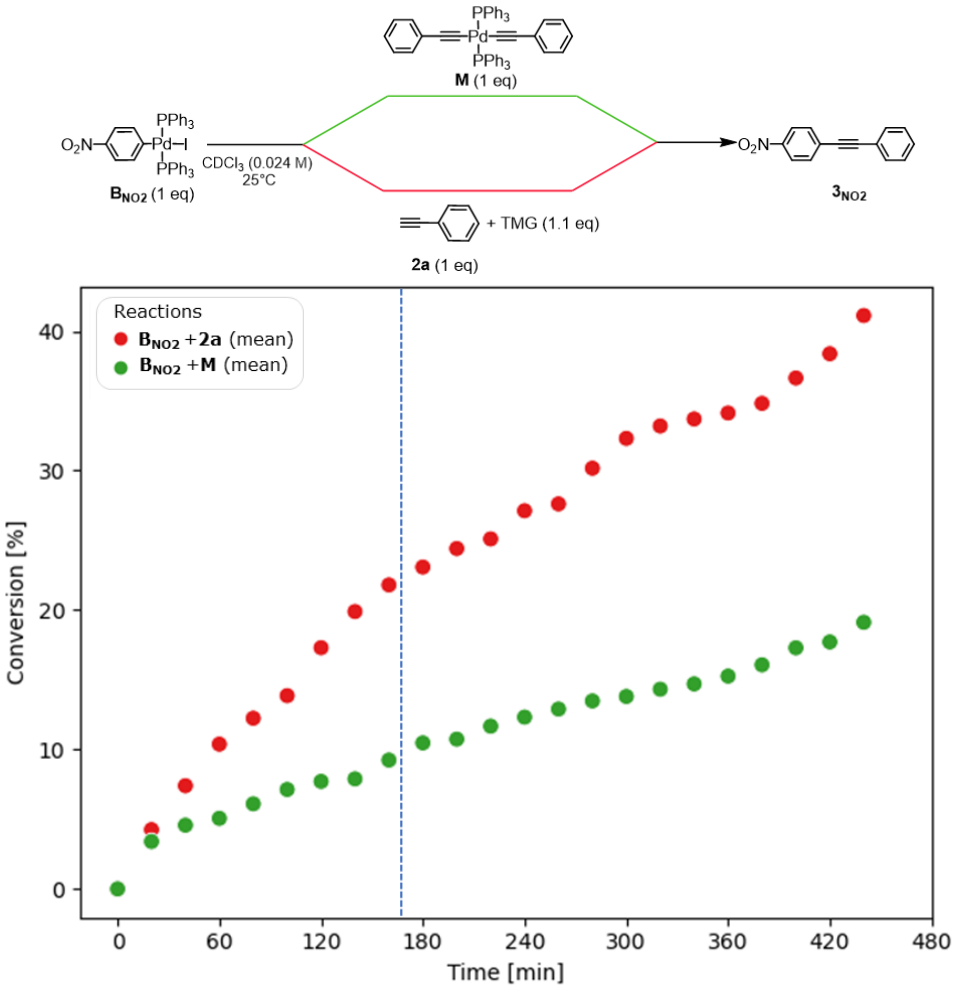


Figure S39. Conversions (%) of $\mathbf{B^{I}_{NO_2}}$ in product $\mathbf{3_{NO_2}}$ averaged over three experiments every 20 minutes. Reactions between $\mathbf{B^{I}_{NO_2}}$ and **M** (green) and $\mathbf{B^{I}_{NO_2}}$ and **2a** (red).

Time [min]	BNO2+M*	BNO2+M**	BNO2+M***	BNO2+M (mean)	error*	error**	error***	BNO2+2a*	BNO2+2a**	BNO2+2a***	BNO2+2a (mean)	error*	error**	error***
20	3,25	3,19	3,76	3,40	-0,15	-0,21	0,36	4,55	4,11	4,10	4,25	0,30	-0,14	-0,16
40	4,11	4,64	4,97	4,57	-0,46	0,07	0,40	7,68	7,09	7,44	7,40	0,28	-0,31	0,03
60	5,00	4,98	5,21	5,06	-0,06	-0,09	0,15	10,41	9,99	10,76	10,38	0,03	-0,40	0,37
80	6,06	6,09	6,16	6,10	-0,04	-0,02	0,06	12,45	11,86	12,42	12,24	0,20	-0,38	0,18
100	7,17	7,15	7,07	7,13	0,04	0,02	-0,06	13,19	12,82	13,77	13,26	-0,07	-0,44	0,51
120	7,57	7,90	7,66	7,71	-0,14	0,19	-0,05	17,54	17,43	16,94	17,30	0,24	0,13	-0,37
140	7,92	7,88	7,89	7,89	0,02	-0,02	0,00	20,36	19,82	19,49	19,89	0,47	-0,07	-0,40
160	9,37	9,21	9,13	9,24	0,13	-0,03	-0,11	21,94	21,79	21,69	21,80	0,13	-0,01	-0,12
180	10,95	10,49	9,97	10,47	0,48	0,02	-0,50	23,10	23,02	23,12	23,08	0,02	-0,06	0,04
200	10,87	10,63	10,73	10,74	0,13	-0,12	-0,01	24,72	24,21	24,30	24,41	0,31	-0,20	-0,11
220	11,71	11,75	11,57	11,67	0,03	0,08	-0,11	25,25	25,08	24,98	25,10	0,15	-0,03	-0,13
240	12,37	12,34	12,24	12,32	0,05	0,02	-0,07	27,20	27,47	26,71	27,12	0,07	0,34	-0,41
260	12,71	13,14	12,84	12,90	-0,19	0,24	-0,06	27,50	27,92	27,43	27,61	-0,12	0,31	-0,19
280	13,59	13,50	13,36	13,48	0,11	0,02	-0,12	30,20	30,29	30,02	30,17	0,03	0,12	-0,15
300	13,75	13,94	13,70	13,80	-0,05	0,14	-0,10	32,08	32,94	31,91	32,31	-0,23	0,63	-0,40
320	14,33	14,36	14,27	14,32	0,01	0,04	-0,05	33,35	33,12	33,15	33,20	0,15	-0,09	-0,06
340	14,76	14,62	14,73	14,70	0,06	-0,09	0,02	33,64	33,58	33,89	33,70	-0,06	-0,12	0,18
360	15,16	15,44	15,18	15,26	-0,10	0,18	-0,08	34,19	33,99	34,21	34,13	0,06	-0,14	0,08
380	16,16	16,21	15,85	16,07	0,09	0,13	-0,22	35,12	34,82	34,53	34,82	0,30	0,00	-0,30
400	17,31	17,28	17,28	17,29	0,02	-0,01	-0,01	36,96	36,64	36,33	36,64	0,32	0,00	-0,32
420	17,80	17,65	17,68	17,71	0,09	-0,06	-0,03	38,23	38,44	38,47	38,38	-0,15	0,06	0,09
440	19,30	19,10	18,95	19,12	0,18	-0,02	-0,17	40,45	41,67	41,23	41,12	-0,66	0,55	0,11

Figure S40. Errors of each measurement calculated by the difference between the average and calculated value of the conversion at the same time. Reactions between $\mathbf{B^{I}_{NO_2}}$ and **M** (green) and $\mathbf{B^{I}_{NO_2}}$ and **2a** (red).

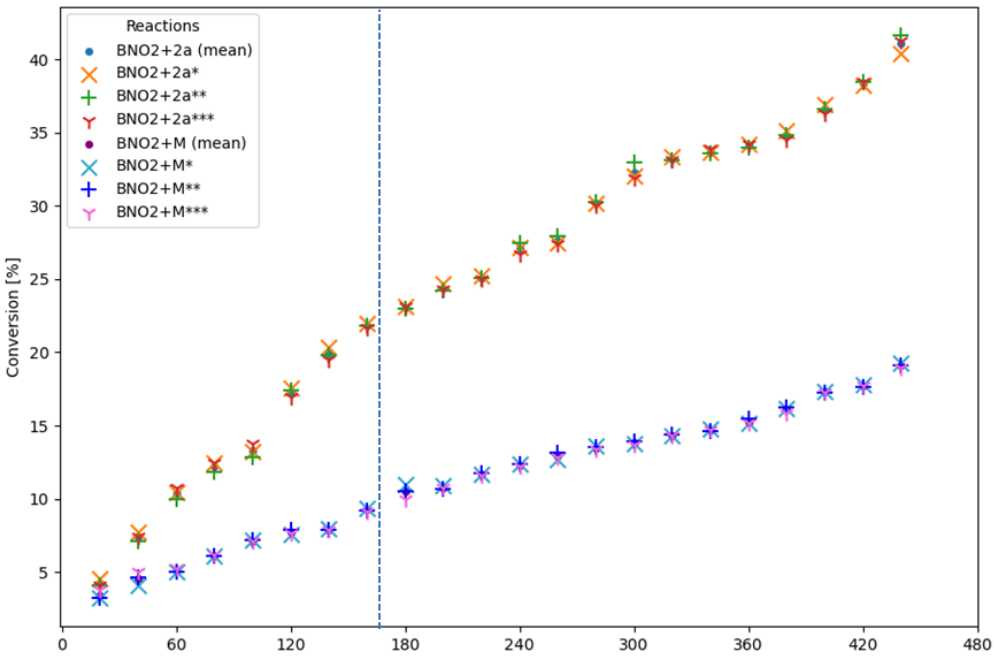
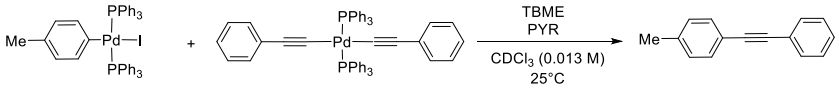


Figure S41. Values of conversions (%) every 20 minutes of reactions repeated three times between $\mathbf{B^{I}_{NO_2}}$ + **M** and $\mathbf{B^{I}_{NO_2}}$ + **2a.**

6.3. Procedure for the Transmetallation step ($\mathbf{B^{I}_{Me}}$):

The reaction was performed in an oven-dried NMR tube purged under nitrogen atmosphere. The complexes $\mathbf{B^{I}_{Me}}$ (8.1 mg, 0.0095 mmol, 1 eq), **M** (9.5 mg, 0.0114 mmol, 1.2 eq) followed by the addition of pyrrolidine (75.8 µL from a stock solution of 0.66 M, 0.0475 mmol, 5 eq). The mixture was let at room temperature and monitored by ^{1}H and ^{31}P NMR spectroscopy at intervals of 20 minutes for 7 hours using tert-butyl methyl ether (TBME) as internal standard. The reaction was repeated three times with consistent results. The following NMR spectra belong to one experiment and are given as examples.



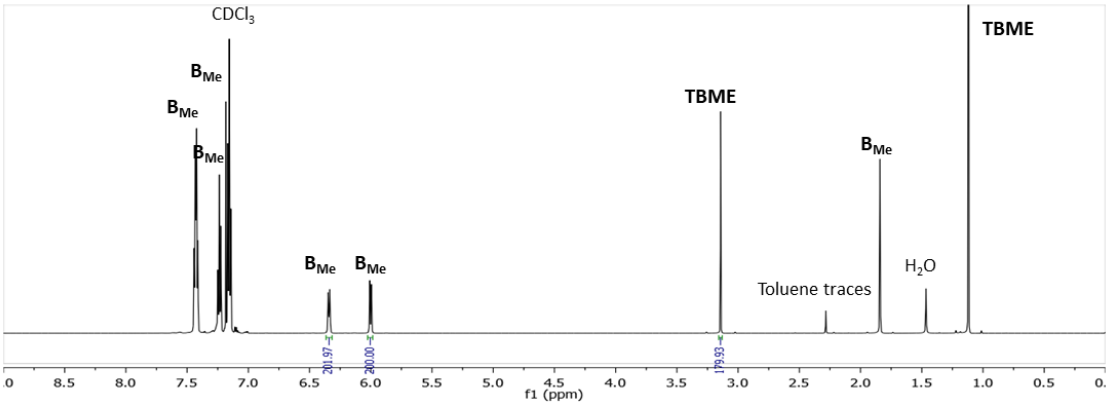


Figure S42. ^{1}H NMR spectrum before the addition of **M** and PYR (t=0).

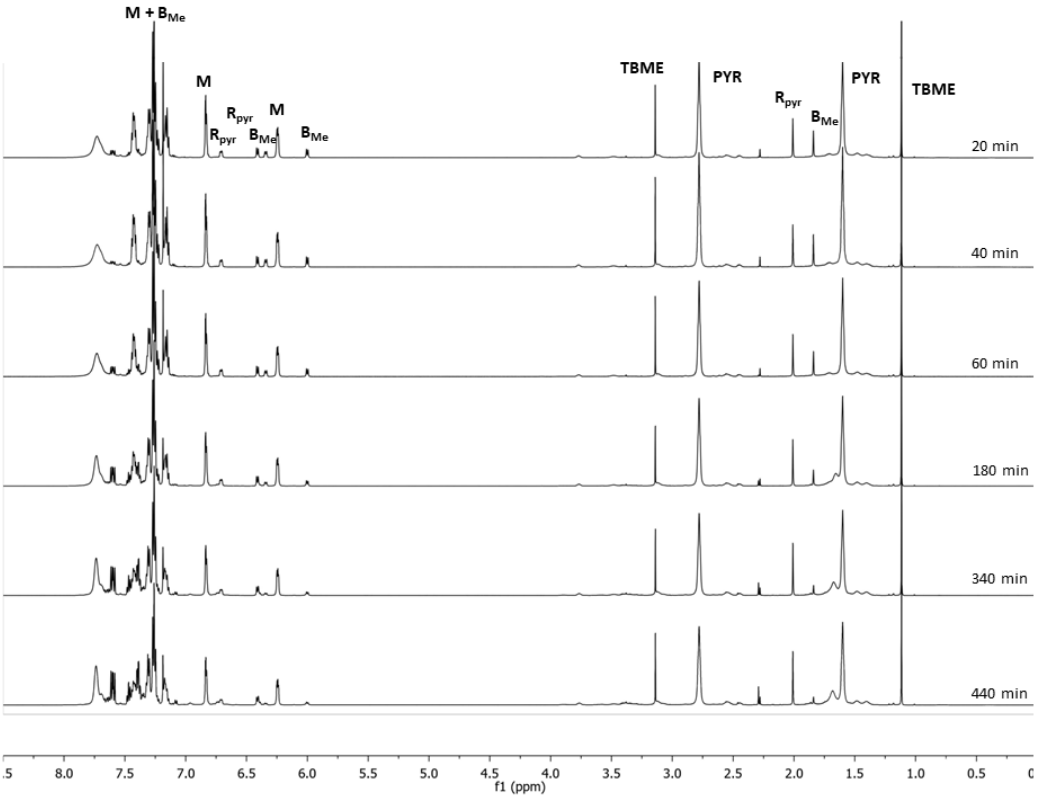
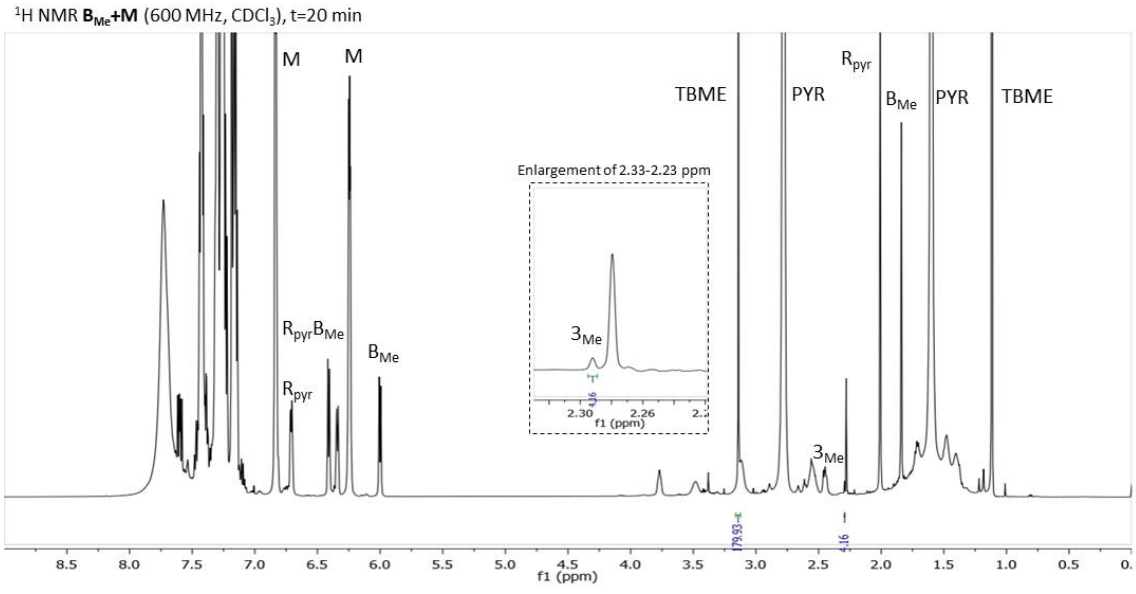
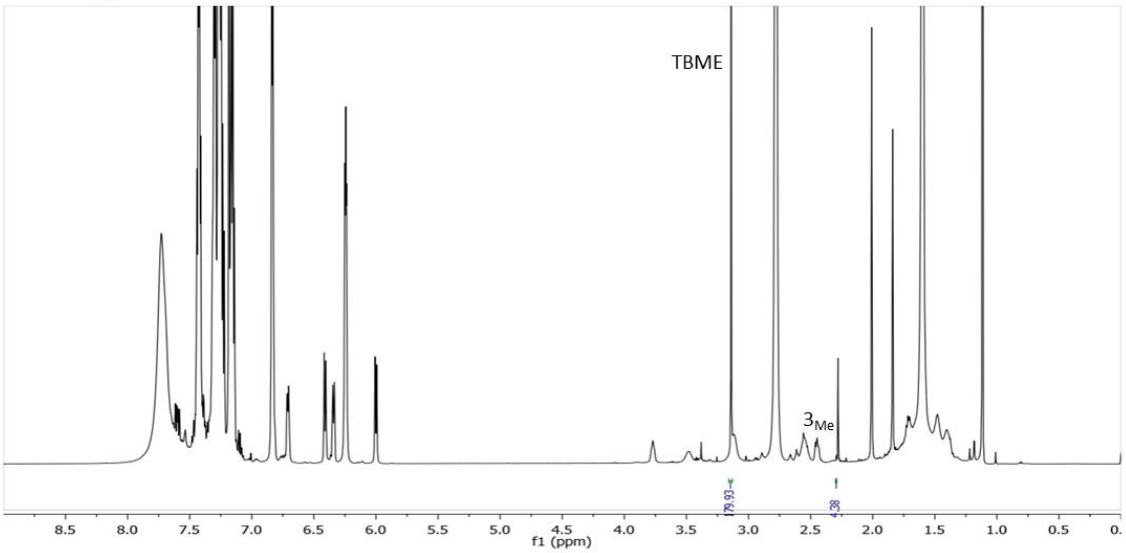


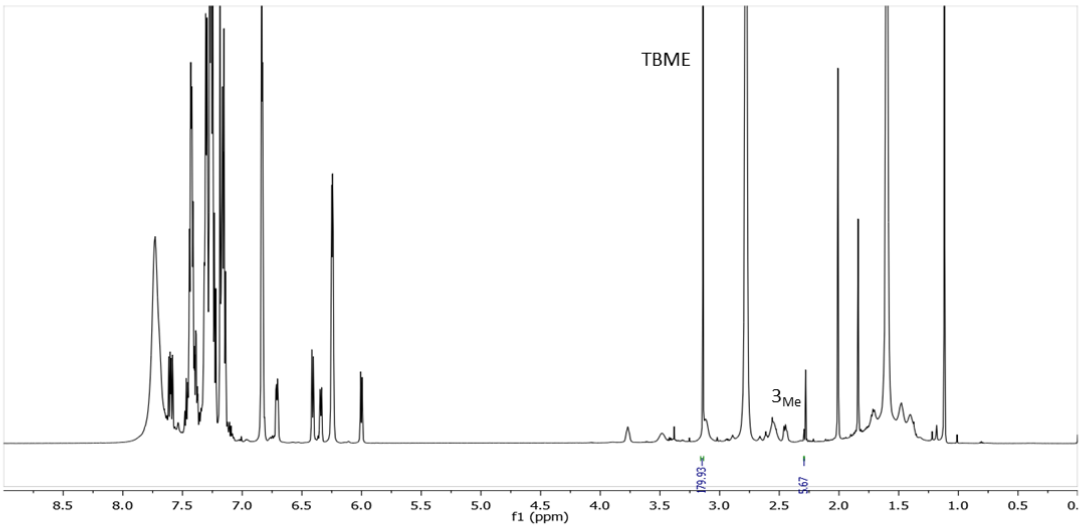
Figure S43. Stacking of ^{1}H NMR spectra of the stoichiometric reaction between $\mathbf{B^I_{Me}}$ and **M** with PYR in $CDCl_3$ at several times



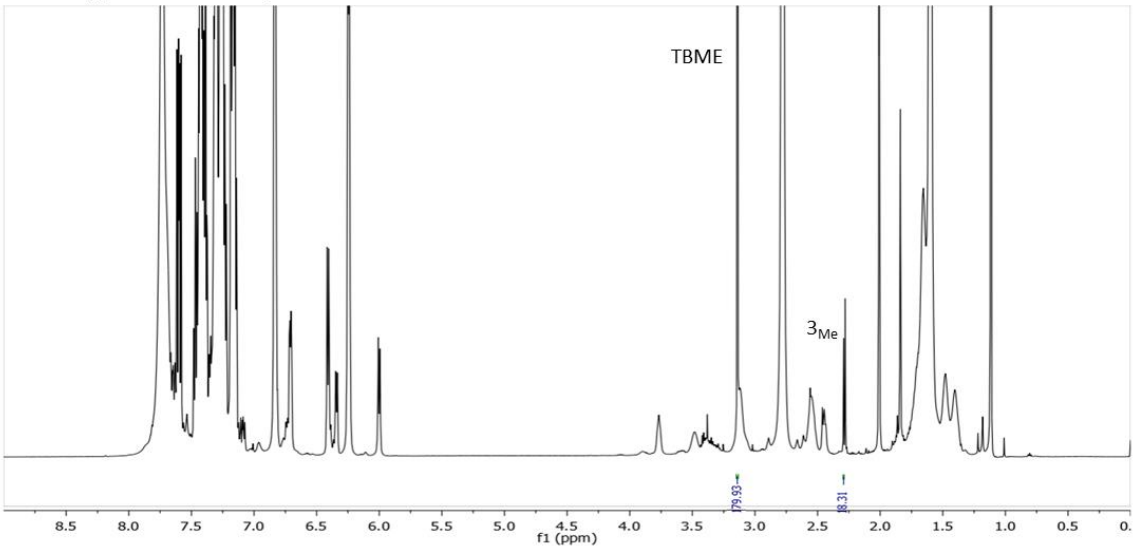
^{1}H NMR **B_{Me}+M** (600 MHz, $CDCl_3$), t=40 min



^{1}H NMR **B_{Me}+M** (600 MHz, $CDCl_3$), t=60 min



^{1}H NMR **B_{Me}+M** (600 MHz, $CDCl_3$), t=180 min



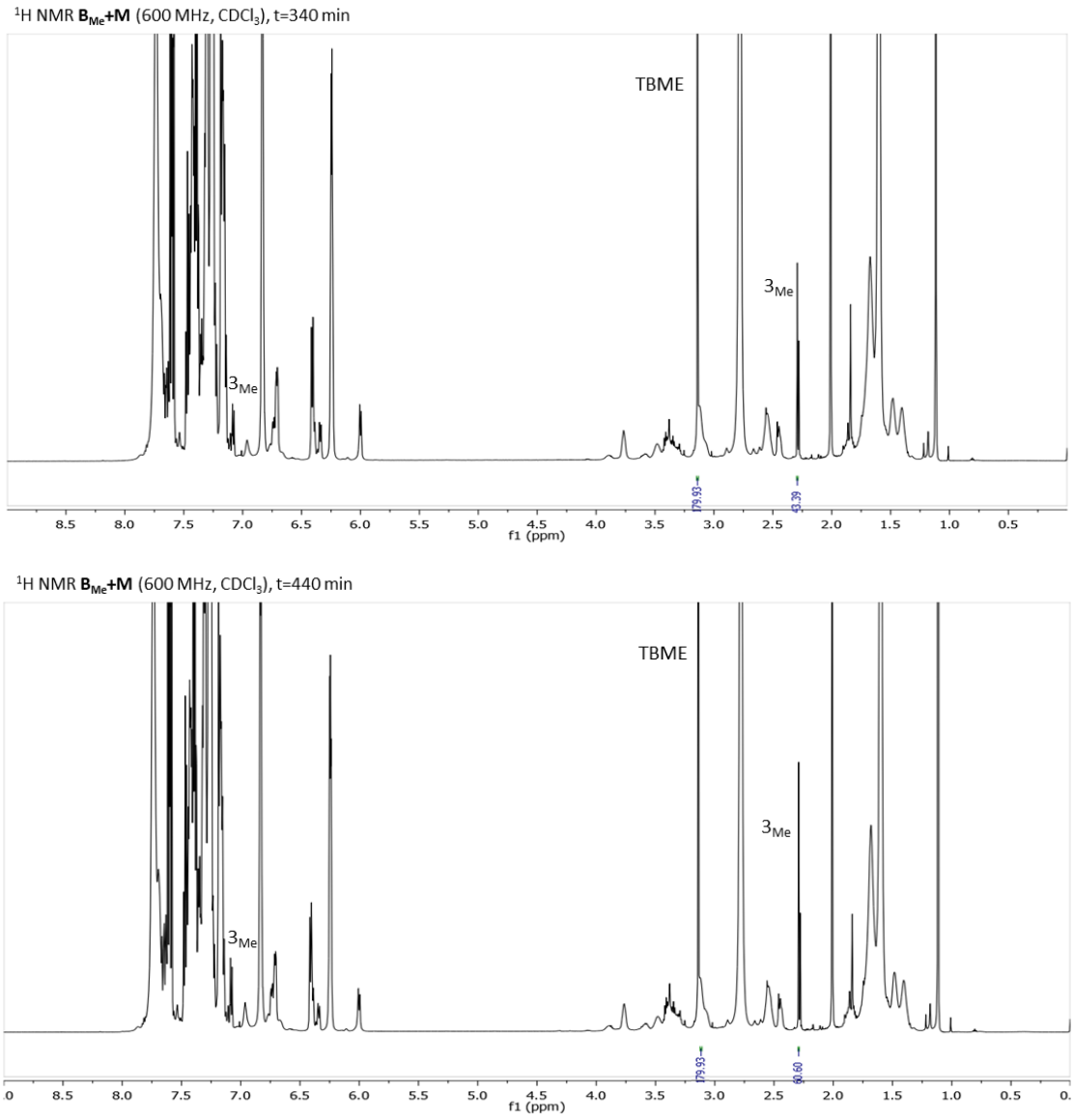


Figure S44. ^{1}H NMR spectra of the stoichiometric reaction between $\mathbf{B^I_{Me}}$ and **2a** with TMG in $CDCl_3$ at t=20 min, 40 min, 60 min, 180 min, 340 min, 440 min.

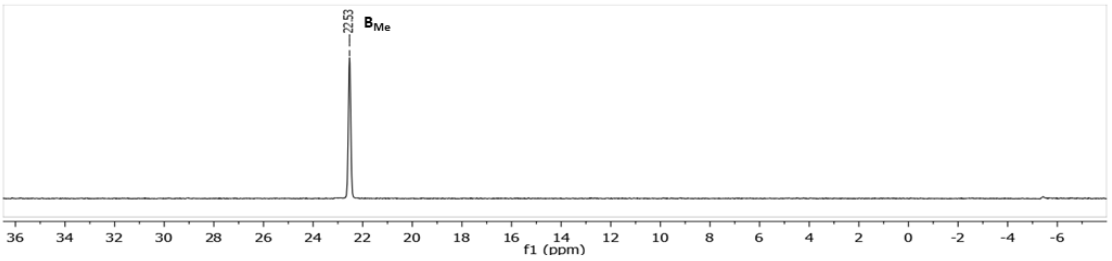


Figure S45. ^{31}P NMR spectrum before the addition of **M** and PYR (t=0).

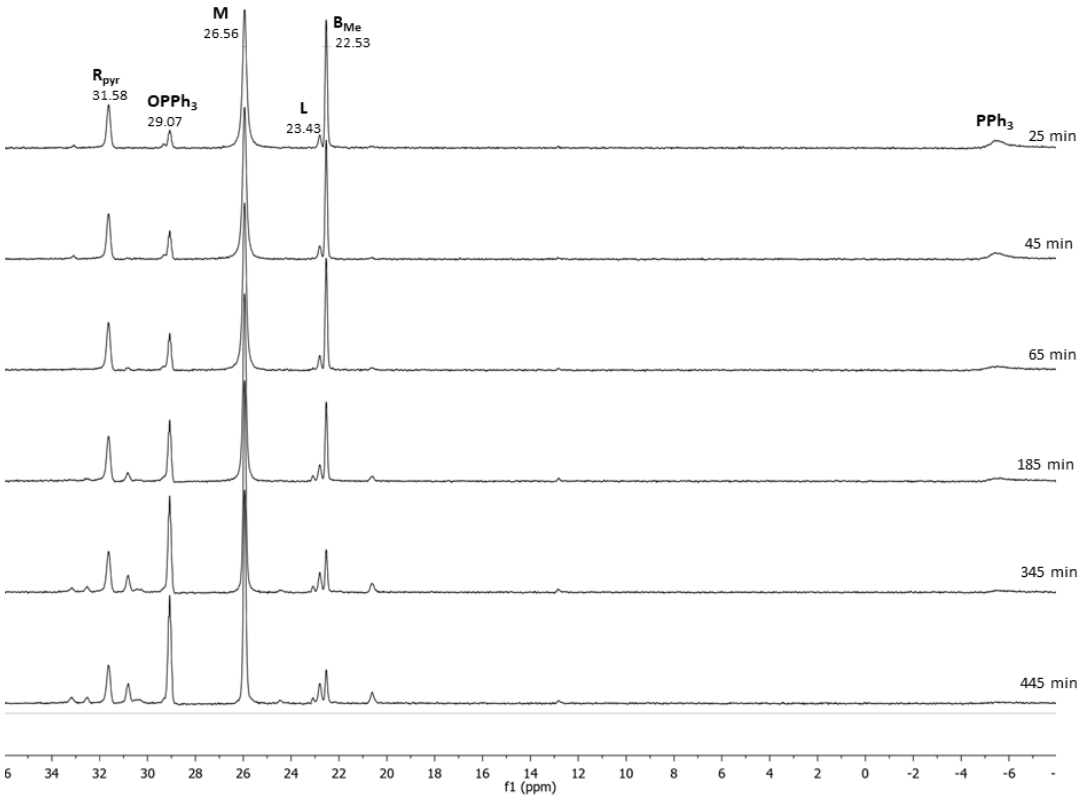
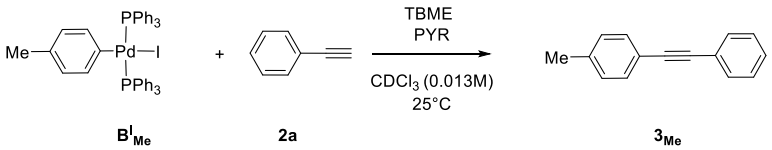


Figure S46. Stacking of ^{31}P NMR spectra of the stoichiometric reaction between $\mathbf{B^{I}_{Me}}$ and **M** with PYR in $CDCl_3$ at several times.

6.4. Procedure for the Direct Coordination step ($\mathbf{B^{I}_{Me}}$):

The reaction was performed in an oven-dried NMR tube purged under nitrogen atmosphere. The complex $\mathbf{B^{I}_{Me}}$ (8.1 mg, 0.0095 mmol, 1 eq) was dissolved in $CDCl_3$ (0.750 mL), followed by the addition of **2a** (32.2 µL from a stock solution of 0.66 M, 0.0114 mmol, 1.2 eq) and pyrrolidine (75.8 µL from a stock solution of 0.66 M, 0.0475 mmol, 5 eq). The mixture was let at room temperature and monitored by ^{1}H and ^{31}P NMR spectroscopy at intervals of 20 minutes for 7 hours using tert-butyl methyl ether (TBME) as internal standard. The reaction was repeated three times with consistent results. The following NMR spectra belong to one experiment and are given as examples.



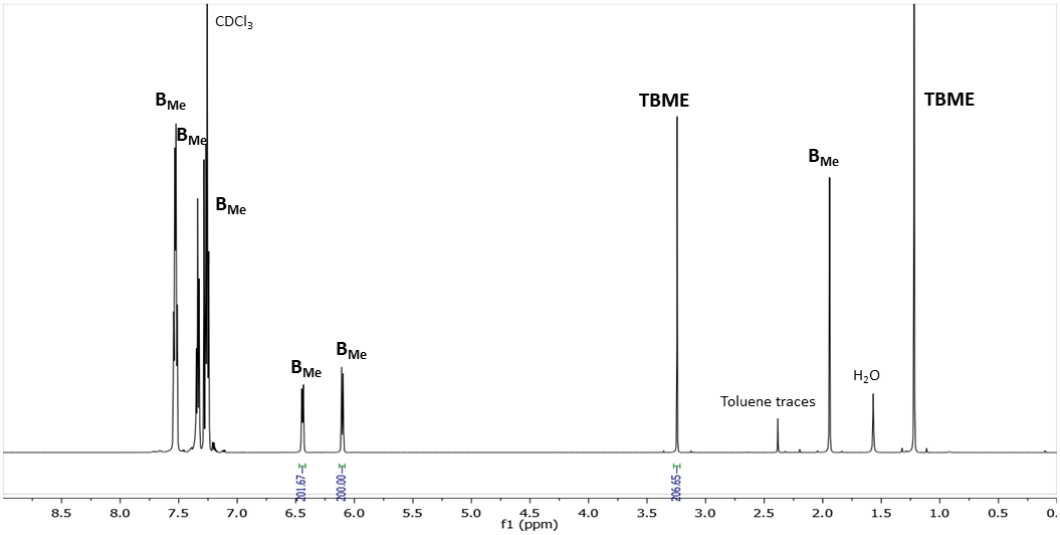


Figure S47. ^{1}H NMR spectrum before the addition of **2a** and PYR (t=0)

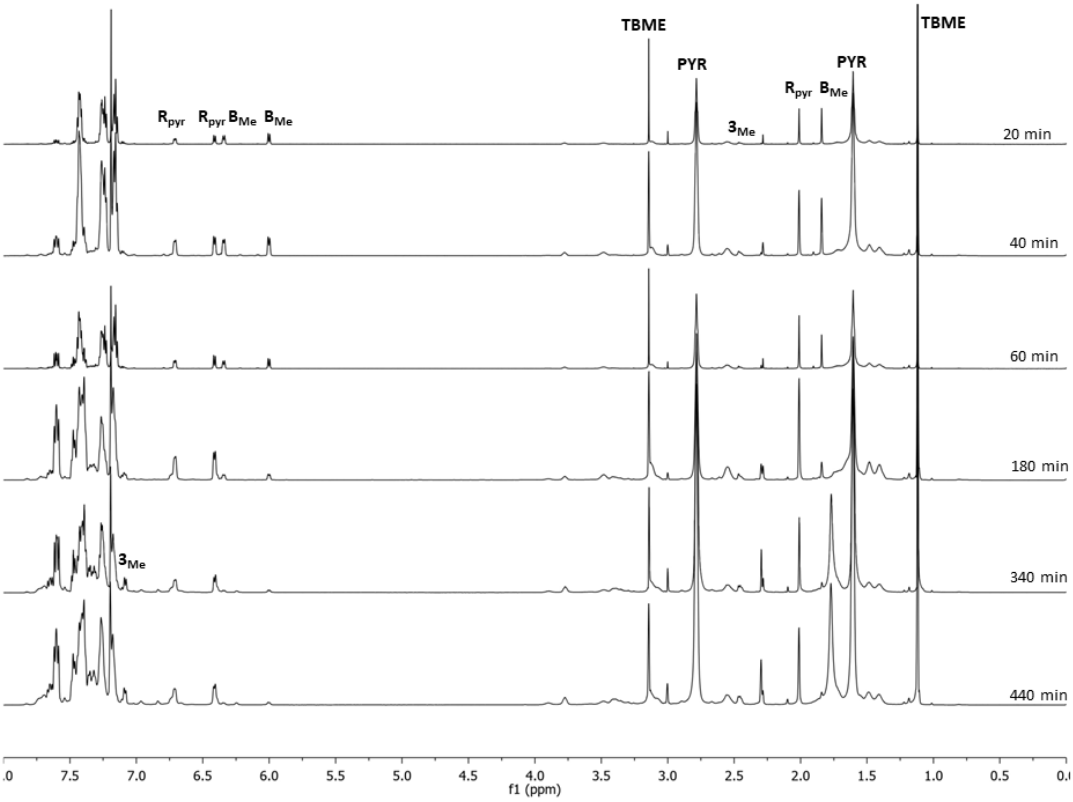
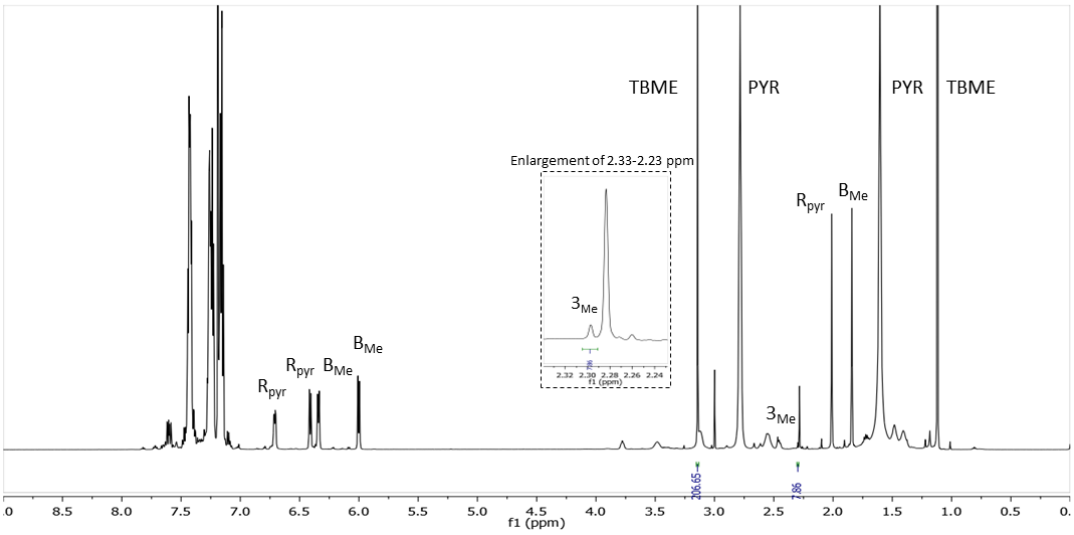
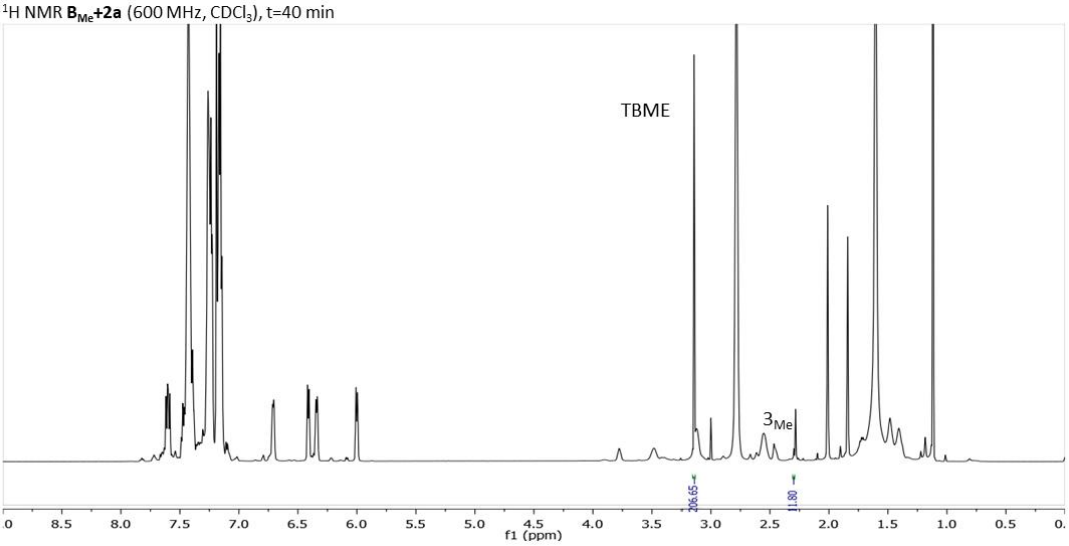


Figure S48. Stacking of ^{1}H NMR spectra of the stoichiometric reaction between $\mathbf{B^{I}_{Me}}$ and **2a** with PYR in $CDCl_3$ at several times.

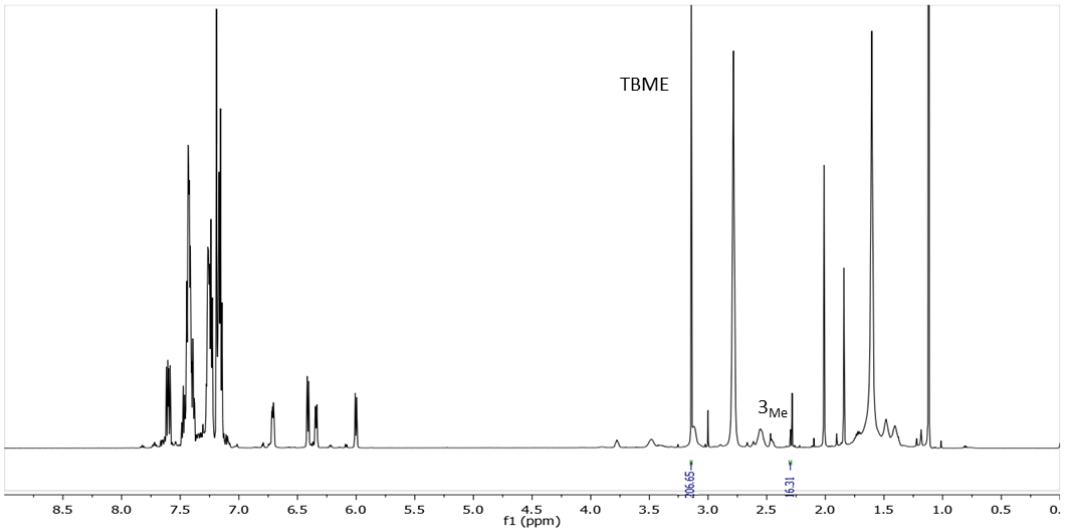
^{1}H NMR **B_{Me}+2a** (600 MHz, $CDCl_3$), t=20 min



^{1}H NMR **B_{Me}+2a** (600 MHz, $CDCl_3$), t=40 min



^{1}H NMR **B_{Me}+2a** (600 MHz, $CDCl_3$), t=60 min



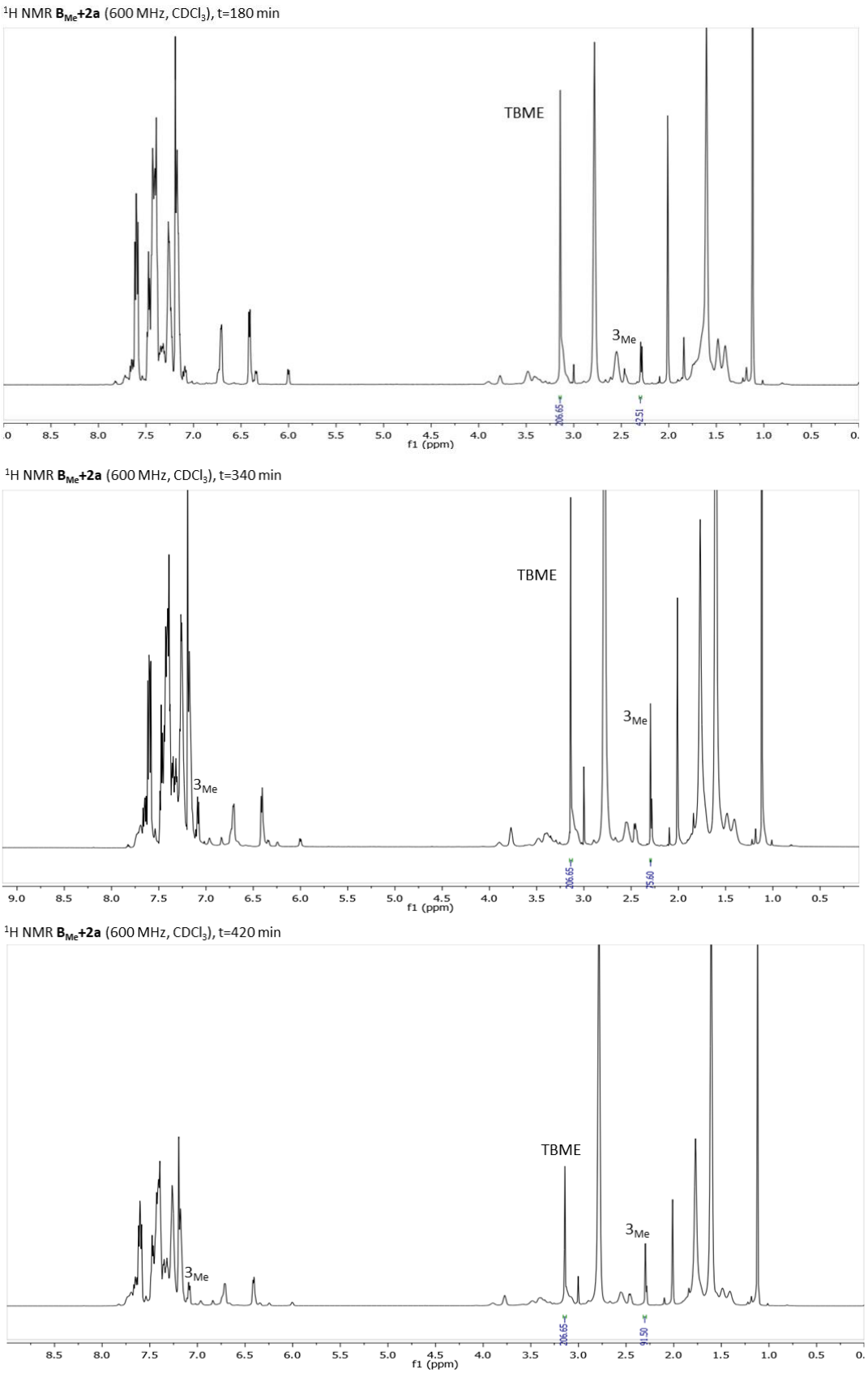


Figure S49. ^{1}H NMR spectra of the stoichiometric reaction between $\mathbf{B^I_{Me}}$ and **2a** with PYR in $CDCl_3$ at t=20 min, 40 min, 60 min, 180 min, 340 min, 440 min.

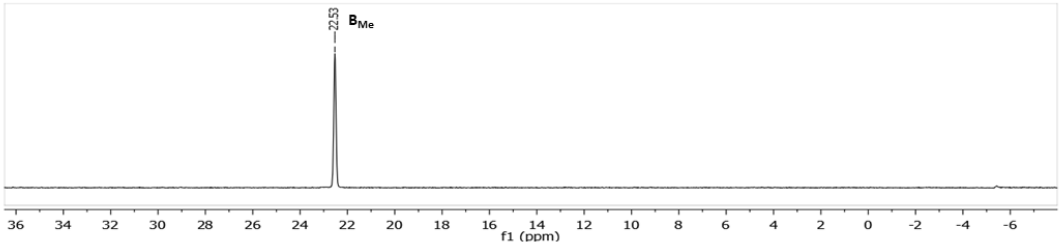


Figure S50. ^{31}P NMR spectrum before the addition of **2a** and PYR (t=0)

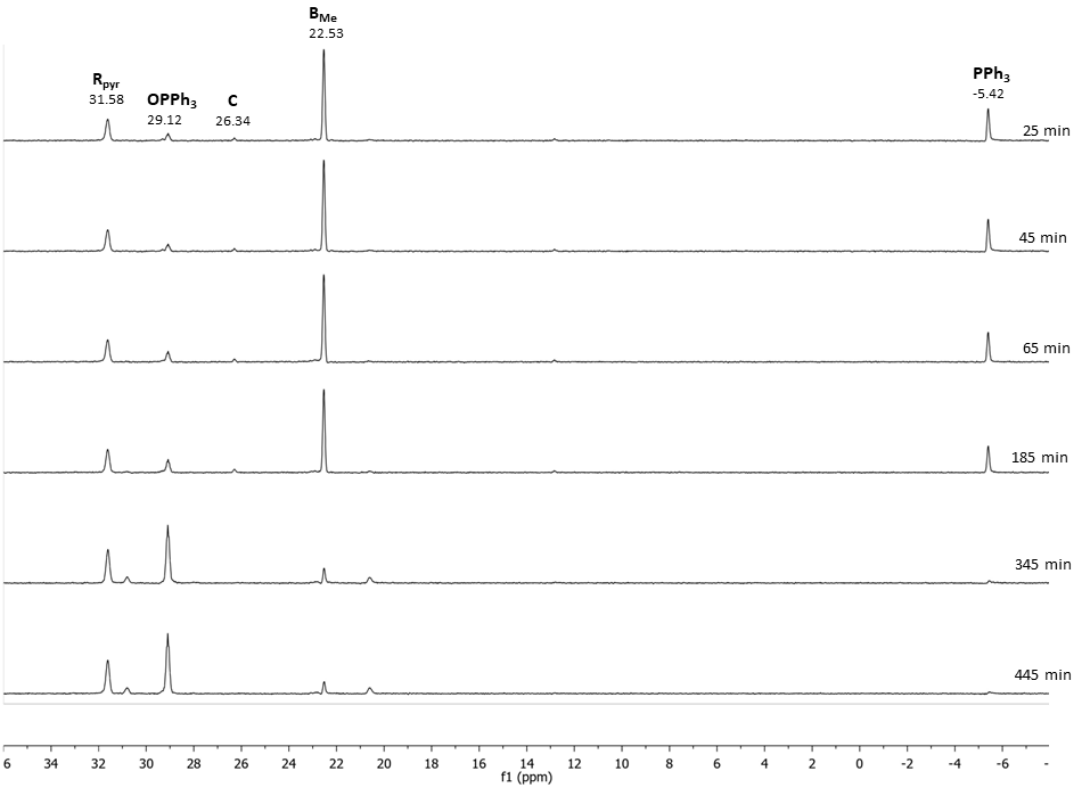


Figure S51. Stacking of ^{31}P NMR spectra of the stoichiometric reaction between $\mathbf{B^{I}_{Me}}$ and **2a** with PYR in $CDCl_3$ at several times.

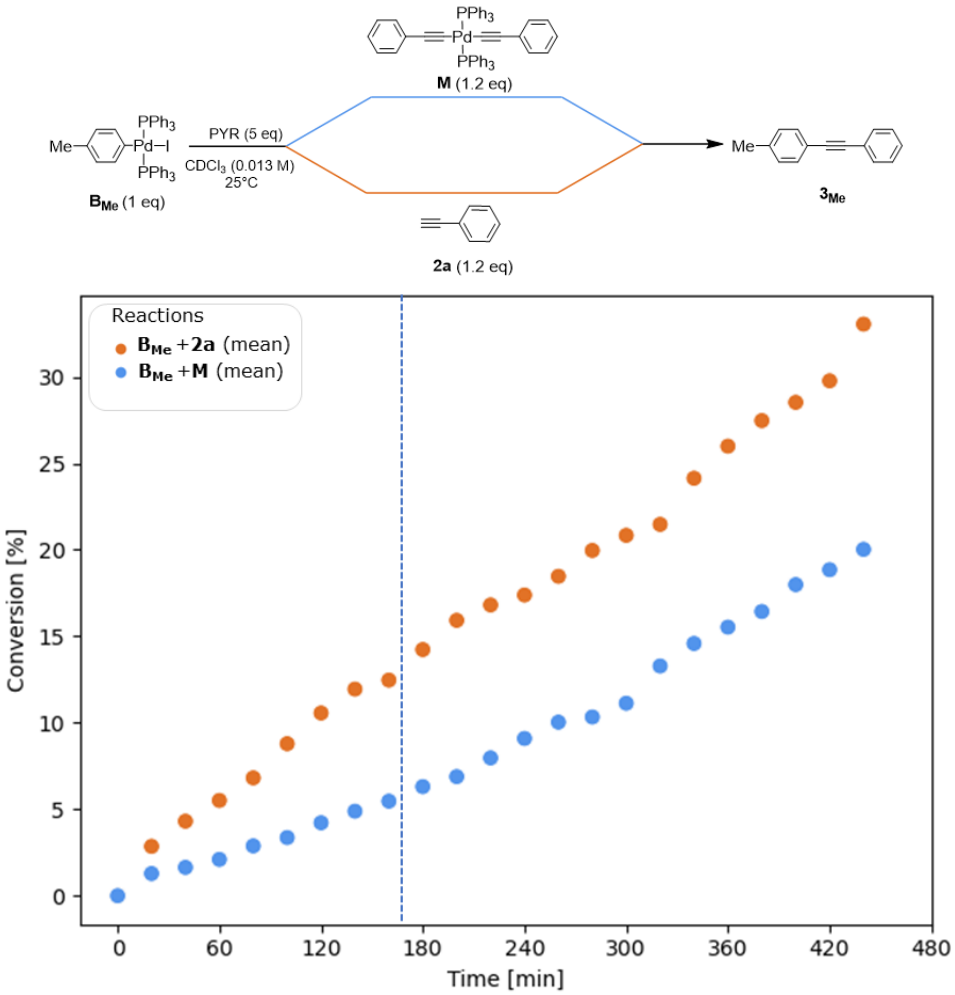


Figure S52. Conversions (%) of $\mathbf{B^{I}_{Me}}$ in product $\mathbf{3_{Me}}$ averaged over three experiments every 20 minutes. Reactions between $\mathbf{B^{I}_{Me}}$ and **M** (light blue) and $\mathbf{B^{I}_{Me}}$ and **2a** (orange).

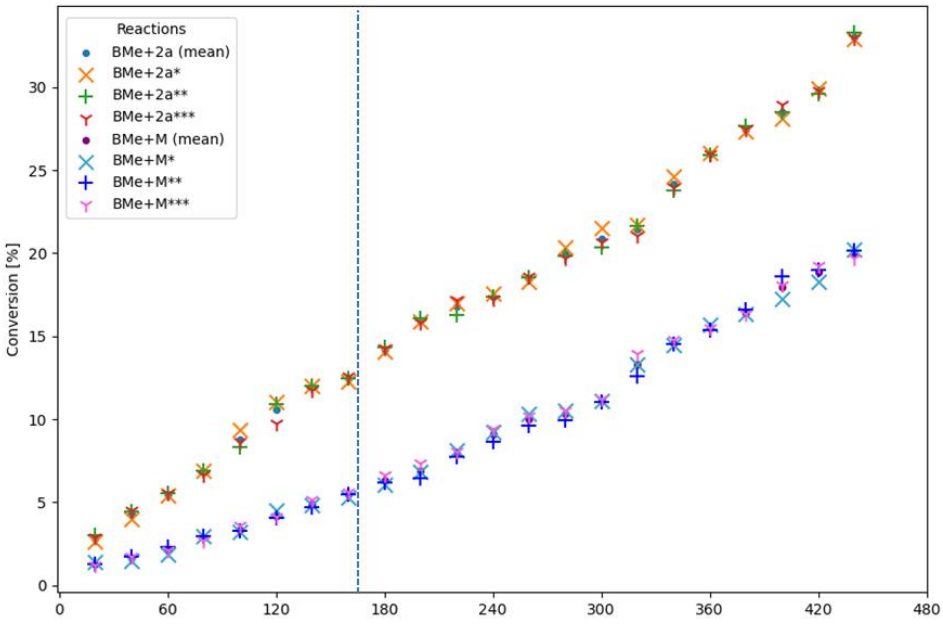


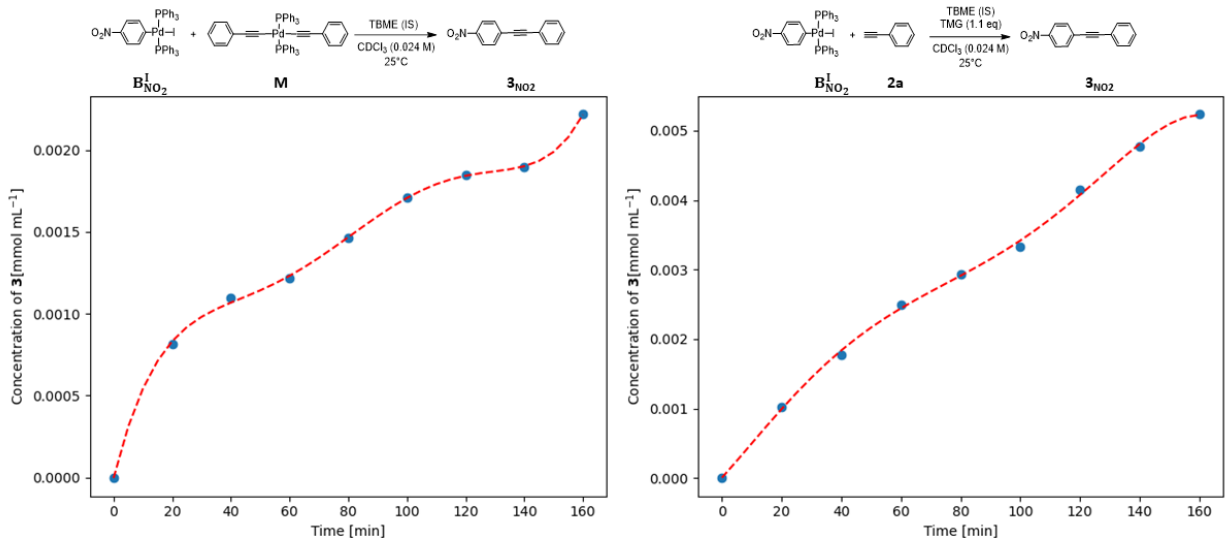
Figure S53. Values of conversions (%) every 20 minutes of reactions repeated three times between $\mathbf{B^{I}_{Me}}$ + **M** and $\mathbf{B^{I}_{Me}}$ + **2a.**

Time [min]	BMe+M*	BMe+M**	BMe+M***	BMe+M (mean)	error*	error*	error***	BMe+2a*	BMe+2a**	BMe+2a***	BMe+2a (mean)	error*	error**	error***
20	1,38	1,28	1,19	1,28	0,10	-0,01	-0,10	2,62	3,03	2,91	2,85	-0,23	0,18	0,06
40	1,46	1,74	1,71	1,64	-0,17	0,11	0,07	3,97	4,45	4,50	4,31	-0,34	0,14	0,19
60	1,89	2,29	2,12	2,10	-0,21	0,19	0,02	5,44	5,56	5,53	5,51	-0,07	0,05	0,02
80	2,93	2,99	2,72	2,88	0,05	0,11	-0,16	6,90	6,90	6,64	6,81	0,09	0,08	-0,17
100	3,22	3,28	3,59	3,36	-0,14	-0,09	0,23	9,39	8,34	8,63	8,79	0,60	-0,45	-0,15
120	4,49	4,03	4,12	4,22	0,28	-0,18	-0,09	11,02	10,93	9,74	10,56	0,45	0,37	-0,83
140	4,80	4,71	5,15	4,89	-0,08	-0,18	0,26	12,03	12,03	11,77	11,95	0,09	0,09	-0,18
160	5,27	5,51	5,62	5,47	-0,19	0,04	0,15	12,30	12,48	12,62	12,47	-0,17	0,02	0,15
180	6,07	6,19	6,67	6,31	-0,24	-0,12	0,36	14,08	14,33	14,28	14,23	-0,15	0,10	0,05
200	6,84	6,48	7,34	6,89	-0,05	-0,41	0,45	15,90	16,07	15,80	15,92	-0,02	0,15	-0,12
220	8,10	7,76	8,04	7,97	0,13	-0,20	0,07	17,00	16,28	17,15	16,81	0,19	-0,53	0,34
240	9,21	8,64	9,42	9,09	0,12	-0,45	0,33	17,54	17,36	17,26	17,38	0,16	-0,03	-0,13
260	10,30	9,62	10,18	10,03	0,27	-0,41	0,14	18,26	18,56	18,58	18,47	-0,20	0,09	0,11
280	10,53	9,93	10,54	10,33	0,20	-0,40	0,21	20,34	19,86	19,68	19,96	0,38	-0,10	-0,28
300	11,11	11,04	11,23	11,13	-0,02	-0,09	0,10	21,50	20,32	20,68	20,83	0,67	-0,51	-0,15
320	13,28	12,61	13,96	13,28	0,00	-0,67	0,68	21,68	21,65	21,08	21,47	0,21	0,18	-0,39
340	14,46	14,50	14,79	14,58	-0,13	-0,08	0,20	24,63	23,78	23,99	24,13	0,50	-0,35	-0,14
360	15,72	15,39	15,48	15,53	0,19	-0,14	-0,05	26,05	25,93	25,99	25,99	0,06	-0,06	0,00
380	16,36	16,60	16,33	16,43	-0,07	0,17	-0,10	27,33	27,64	27,44	27,47	-0,14	0,17	-0,03
400	17,23	18,63	18,09	17,99	-0,75	0,64	0,11	28,14	28,48	28,96	28,52	-0,39	-0,05	0,43
420	18,29	18,98	19,28	18,85	-0,56	0,13	0,43	29,92	29,60	29,79	29,77	0,15	-0,17	0,02
440	20,20	20,18	19,70	20,02	0,17	0,15	-0,33	32,92	33,29	32,94	33,05	-0,13	0,24	-0,11

Figure S54. Errors of each measurement calculated by the difference between the average and calculated value of the conversion at the same time. Reactions between $\mathbf{B^{I}_{Me}}$ and **M** (light blue) and $\mathbf{B^{I}_{Me}}$ and **2a** (orange).

6.5. Evaluation of the reaction rate

The concentration of the product **3** was calculated was calculated from the average conversion (%) given above (**Figure S39** e **Figure S52**). The value of maximum rate was determined by considering the range 0-160 min., because after this time side reactions start to occur. Experimental data were fitted using the curve_fit function of the free and open-source Python library SciPy. The reaction rates were calculated in each point obtaining the derivative with the polyder function of the open-source Python library NumPy.



$c(\mathbf{3}_{NO2}) = A_0 + A_1\,t^1 + A_2\,t^2 + A_3\,t^3 + A_4\,t^4 + A_5\,t^5$

A_0 = 0,000125

A_1 = 3,01 E-05

A_2 = -2,44 E-07

A_3 = 1,29 E-09

A_4 = -3,17 E-12

A_5 = 2,87 E-15

$v_{MAX\ (t=0)}$ = **3,01 E-05 mmol mL^{-1} min^{-1}**

Time [min]	B+M	B+2a
0	3,01E-05	5,20E-05
20	2,18E-05	4,32E-05
40	1,60E-05	3,66E-05
60	1,22E-05	3,19E-05
80	9,98E-06	2,85E-05
100	8,83E-06	2,61E-05
120	8,43E-06	2,44E-05
140	8,47E-06	2,31E-05
160	8,71E-06	2,20E-05

fast slow

$c(\mathbf{3}_{NO2}) = A_0 + A_1\,t^1 + A_2\,t^2 + A_3\,t^3 + A_4\,t^4 + A_5\,t^5$

A_0 = 1,99 E-05

A_1 = 5,20 E-05

A_2 = -2,53 E-07

A_3 = 1,16 E-09

A_4 = -2,88 E-12

A_5 = 2,72 E-15

$v_{MAX\ (t=0)}$ = **5,20 E-05 mmol mL^{-1} min^{-1}**

Figure S55. Concentration of $\mathbf{3}_{NO_2}$ calculated at several times within 160 minutes in the reaction between $\mathbf{B}^{\mathbf{I}}_{\mathbf{NO_2}}$ + **M** (left) and $\mathbf{B}^{\mathbf{I}}_{\mathbf{NO_2}}$ + **2a** (right). The maximum rate and the point at which the rate is highest were obtained by fitting the values and finding the derivatives.

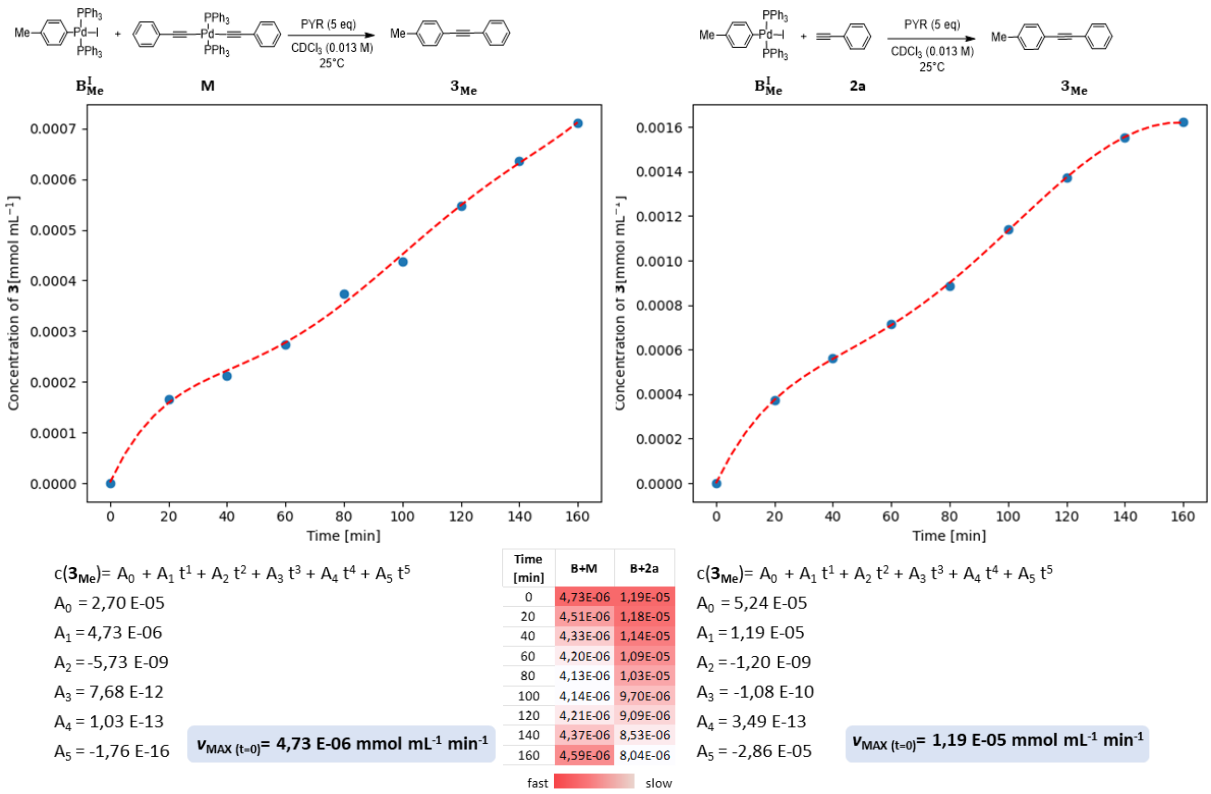


Figure S56. Concentration of $\mathbf{3_{Me}}$ calculated at several times within 160 minutes in the reaction between $\mathbf{B^{I}_{Me}}$ + **M** (left) and $\mathbf{B^{I}_{Me}}$+ **2a** (right). The maximum rate and the point at which the rate is highest were obtained by fitting the values and finding the derivatives.

7. Parallel side reactions

Table S3. Parallel side reactions

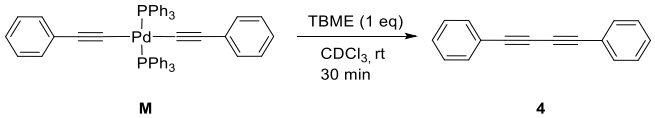
Entry	Solvent	T (°C)	B	2a	M	C (%)	3a/4a[b]
1	$CDCl_3$	25	-	-	1	**M** (0)[b]	0/0
2	DMF-d_7	25	-	-	1	**M** (0)[b]	0/0
3	$CDCl_3$	60	-	-	1	**M** (30)[b]	0/100
4	DMF-d_7	40	-	-	1	**M** (100)[c]	0/100
5	$CDCl_3$	25	1	-	1	**B** (5)[b]	100/0
6	DMF-d_7	60	1	-	1	**M** (100)[c]	21/79[d]
7	$CDCl_3$	25	1	1	-	**B** (36)[b]	100/0
8	DMF-d_7	60	1	1	-	**B** (42)[b]	100/0

[a.] All reactions were carried out for 30 min in deuterated solvents with [C]=0.024 M. For entries 7 and 8, 1.1 eq of TMG were added. [b.] The mixture was analyzed after 30 min by ^{1}H NMR. [c.] The mixture was analyzed after 30 min and the conversion was calculated using ^{31}P NMR. [d.] The ratio **3a**/**4a** was determined by HPLC.

7.1. Stability of complex M (entry 1-4), Table S3

To an oven-dried NMR tube purged under nitrogen atmosphere, complex **M** was dissolved in deuterated solvent (0.75 mL) at room temperature or at 60° C. TBME was used as internal standards. After 30 minutes of stirring, the samples were analyzed using ^{1}H NMR, ^{31}P NMR, HPLC-UV or GC-MS techniques.

Entry 1, Table S3



M **4**

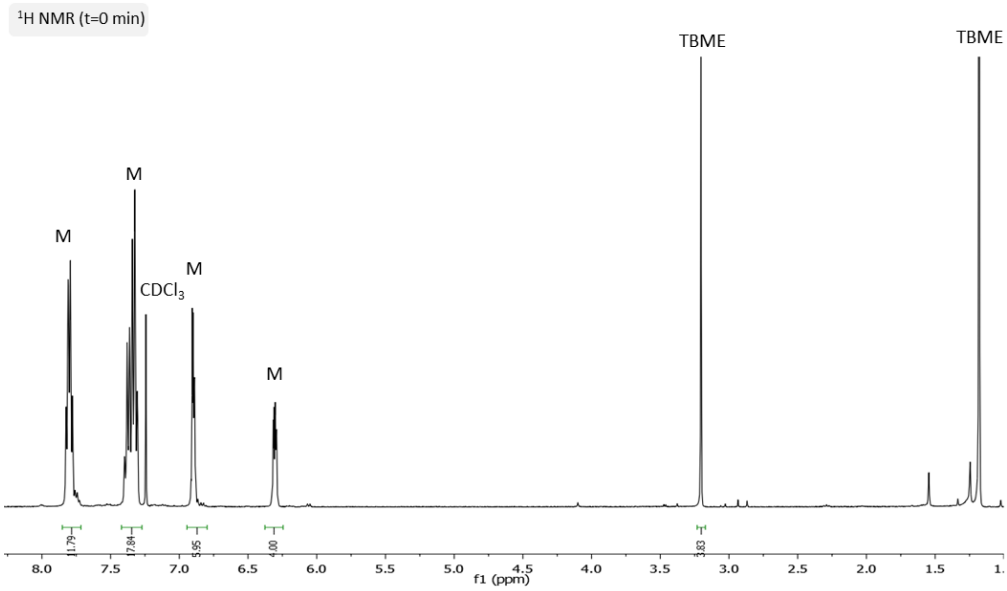


Figure S57. ^{1}H NMR spectrum of **M** in $CDCl_3$ at room temperature at t=0.

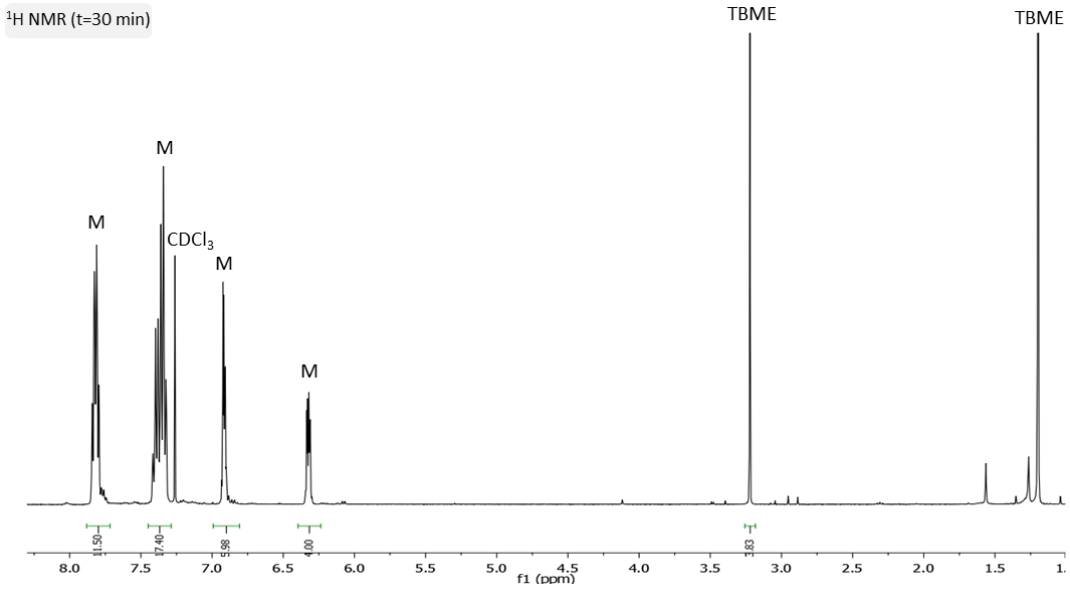
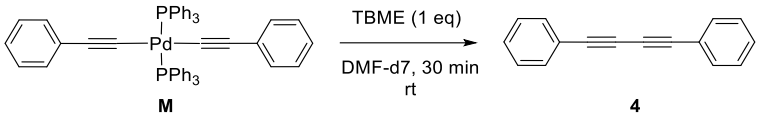


Figure S58. ^{1}H NMR spectrum of **M** in $CDCl_3$ at room temperature after 30 minutes.

Entry 2, Table S3



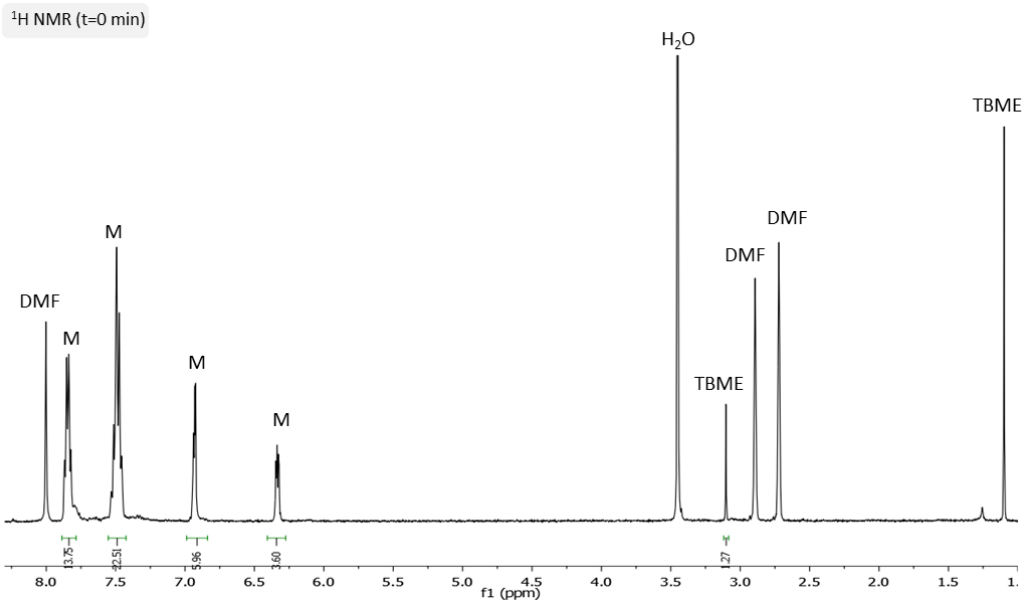


Figure S59. ^{1}H NMR spectrum of **M** in DMF-d_7 at room temperature at t=0.

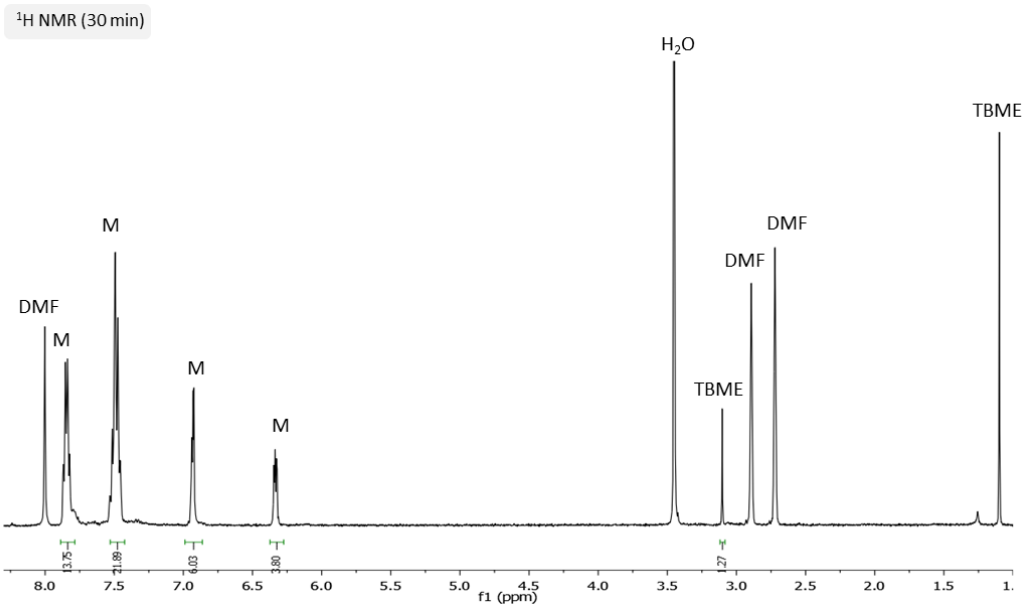
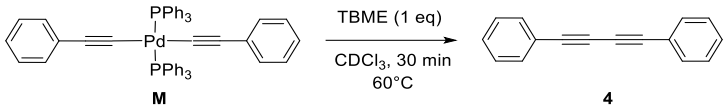


Figure S60. ^{1}H NMR spectrum of **M** in DMF-d_7 at room temperature after 30 minutes.

Entry 3, Table S3



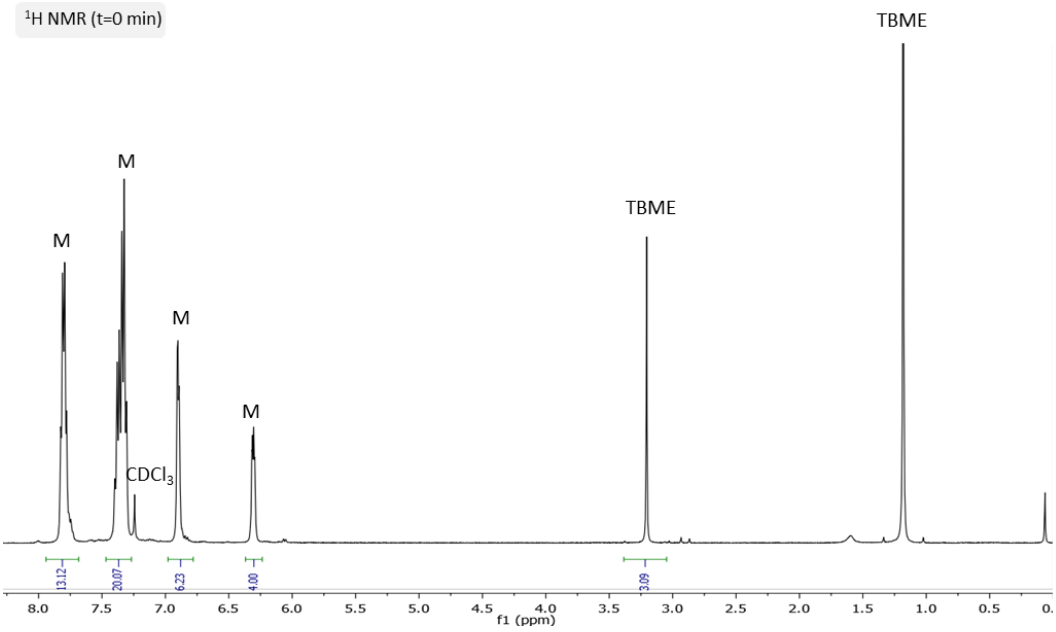


Figure S61. ^{1}H NMR spectrum of **M** in $CDCl_3$ at t=0

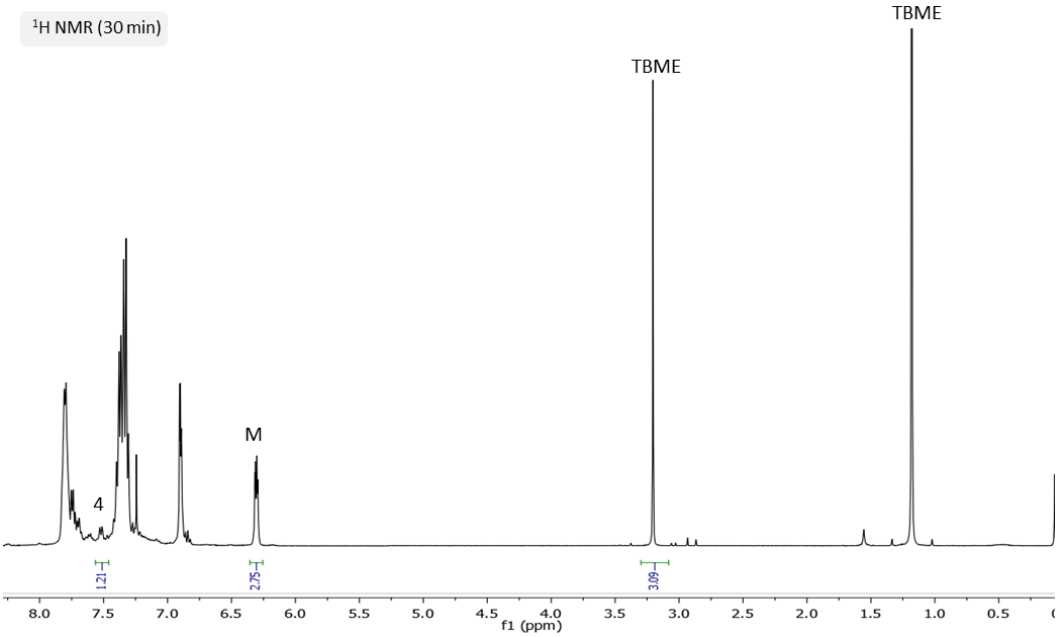


Figure S62. ^{1}H NMR spectrum of **M** in $CDCl_3$ at 60°C after 30 minutes.

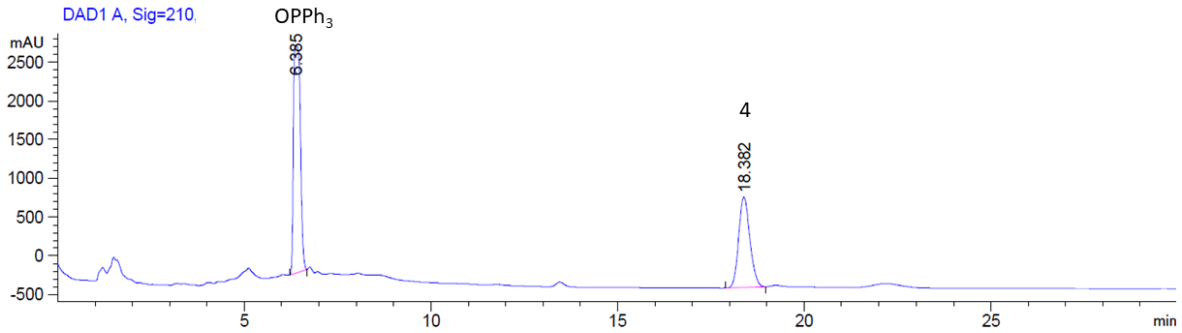
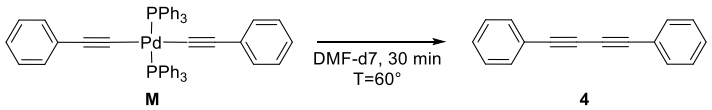


Figure S63. HPLC chromatogram of complex **M** at 60°C in $CDCl_3$ after 30 minutes; peak at 6.385 min = $OPPh_3$; peak at 18.382 min = **4**

Entry 4, Table S3



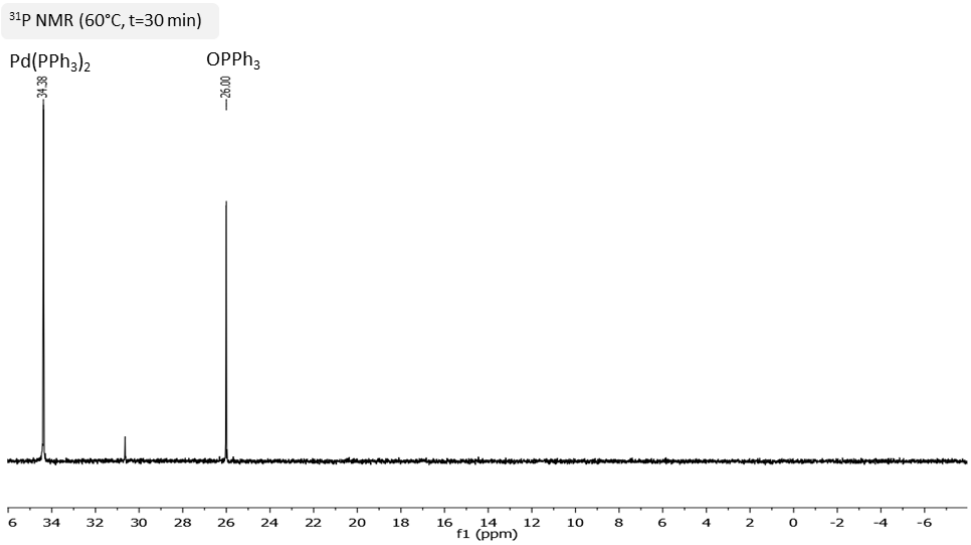


Figure S64. ^{31}P NMR spectrum of **M** in DMF-d_7 at t=60°C after 30 minutes.

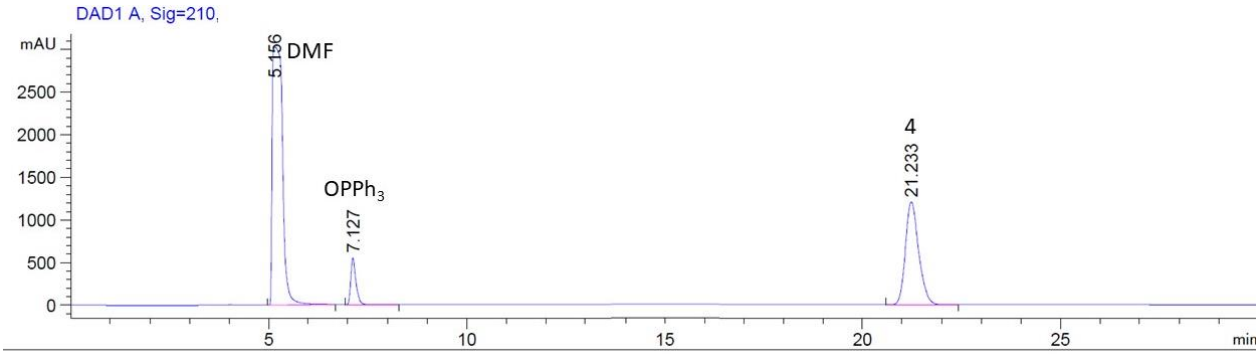
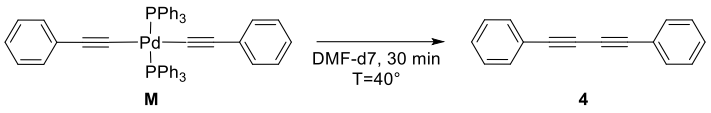


Figure S65. HPLC chromatogram of complex **M** at 60°C in DMF-d_7 after 30 minutes; peak at 5.156 min = DMF; peak at 7.127 min = $OPPh_3$; peak at 21.233 min = **4**



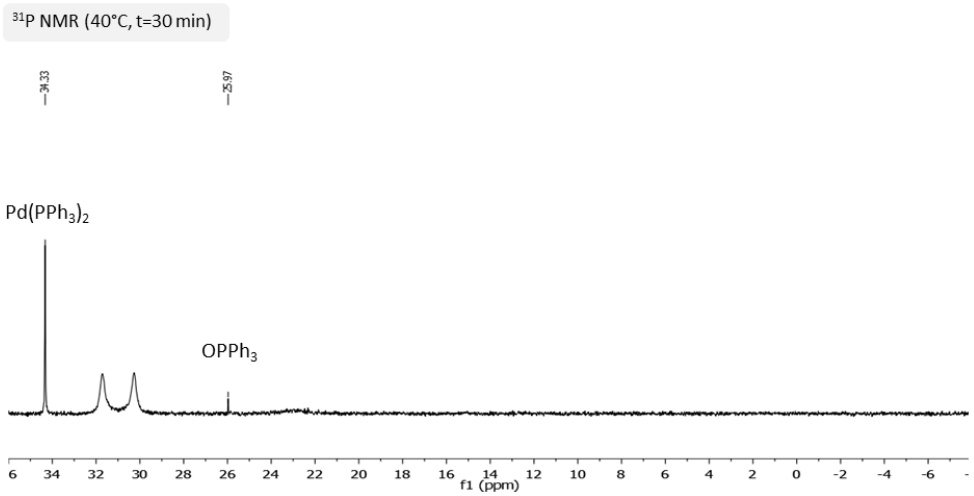


Figure S66. ^{31}P NMR spectrum of **M** in DMF-d_7 at t=40°C after 30 minutes.

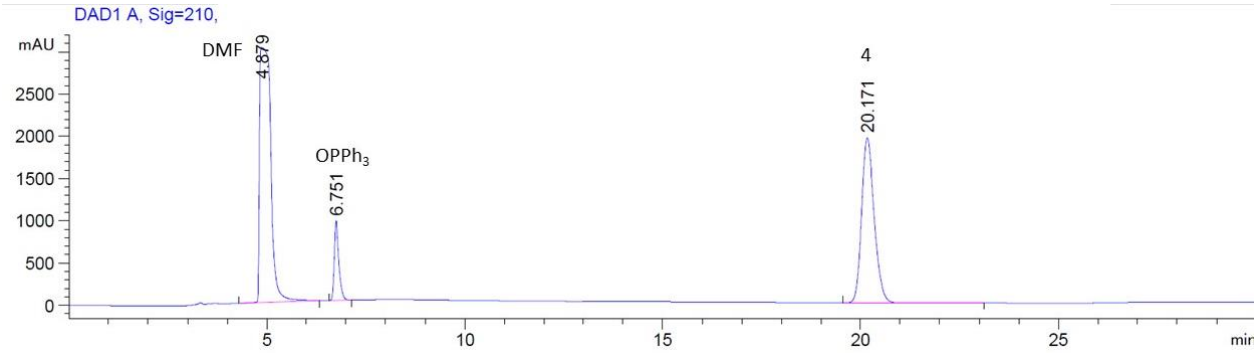
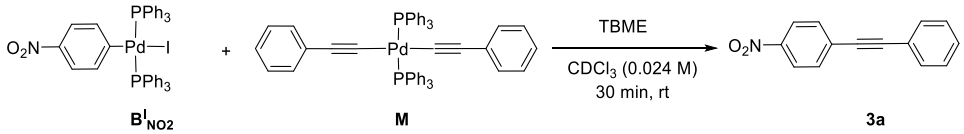


Figure S67. HPLC chromatogram of complex **M** at 40°C in DMF-d_7 after 30 minutes; peak at 4.879 min = DMF; peak at 6.751 min = $OPPh_3$; peak at 20.171 min = **4.**

7.2. General procedure for entries 5-6, Table S3

The reaction was performed in an oven-dried NMR tube purged under nitrogen atmosphere. complexes $\mathbf{B^{I}_{NO_2}}$(15.8 mg, 0.018 mmol, 1 eq) and **M** (15 mg, 0.0.18 mmol, 1 eq) were dissolved in solvent (0.750 mL). It was let at room temperature or at 60°C for 30 minutes using TBME as internal standard. The mixture was analyzed with ^{1}H NMR or ^{31}P NMR spectroscopy.

Entry 5, Table S3



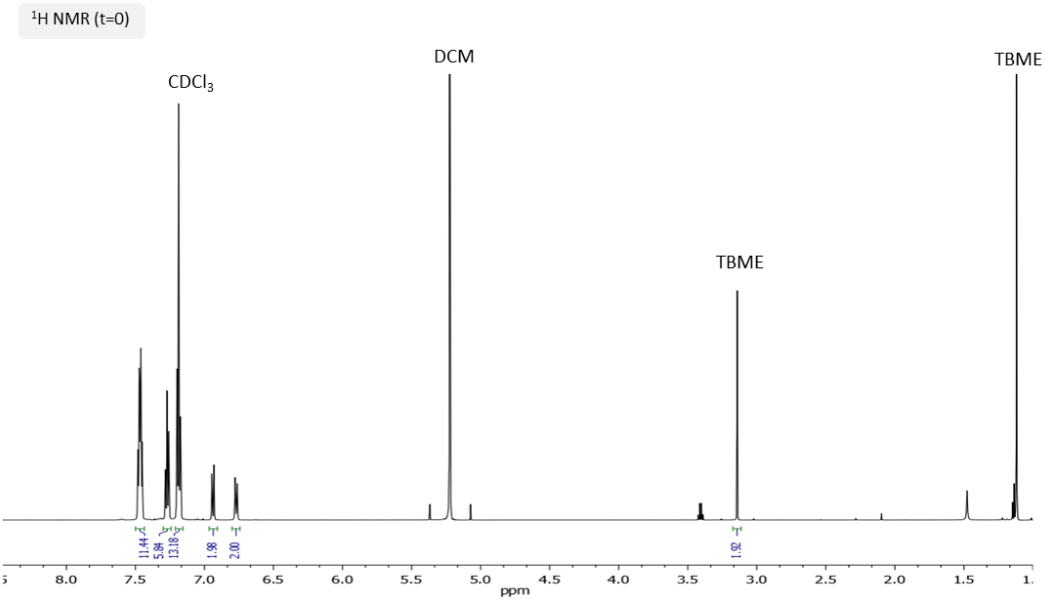


Figure S68. ^{1}H NMR spectrum in $CDCl_3$ before the addition of **M**

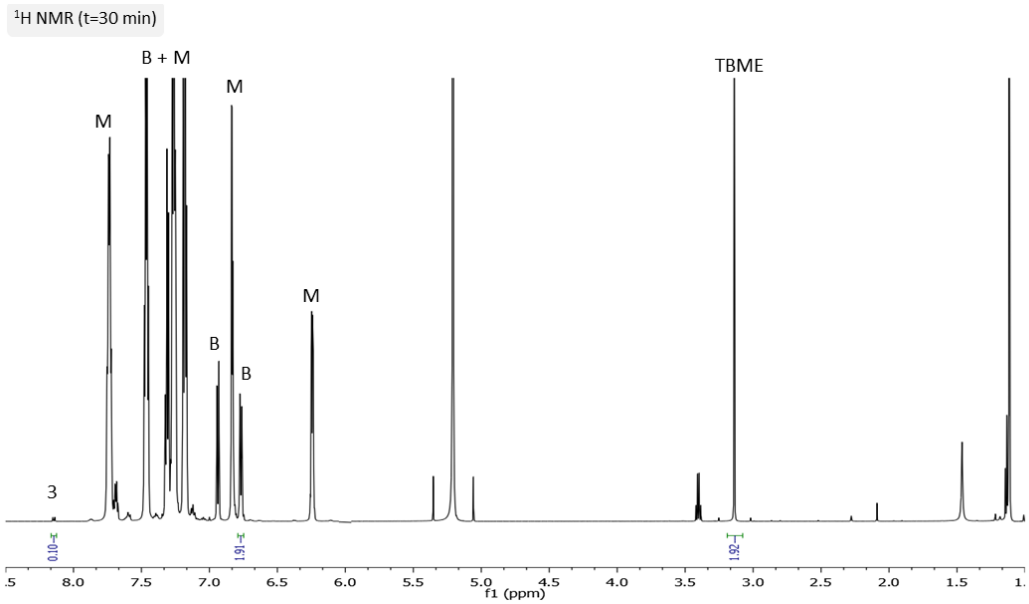
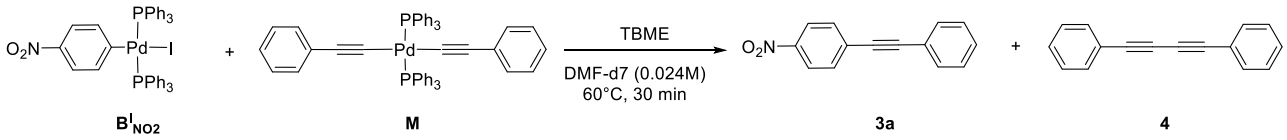


Figure S69. ^{1}H NMR spectrum of the stoichiometric reaction between $\mathbf{B^{I}_{NO_2}}$ and **M** in $CDCl_3$ after 30 minutes at rt.

Entry 6, Table S3



The ratio **3a**/**4a** was calculated using HPLC-UV analyses, because it was impossible to quantify the ratio with NMR

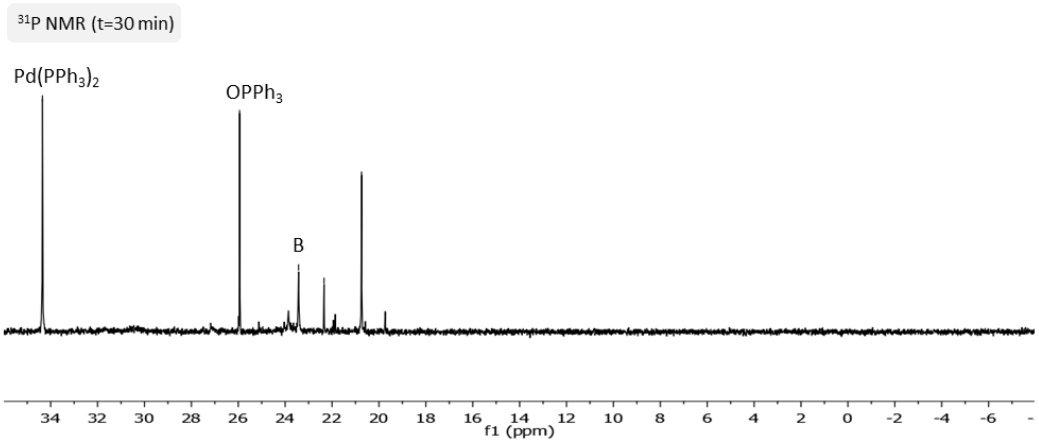
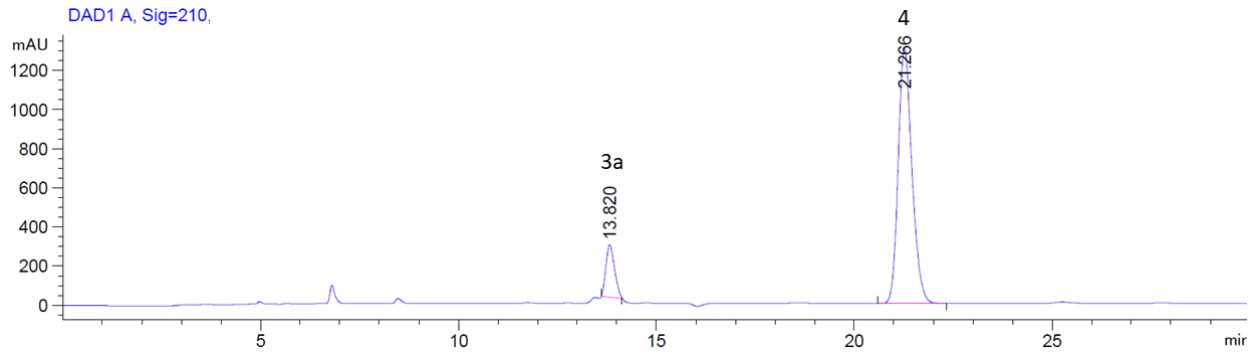


Figure S70. ^{31}P NMR spectrum of the stoichiometric reaction between $\mathbf{B^{I}_{NO_2}}$ and **M** in DMF-d$_7$ after 30 minutes at 60° C. **M** completely disappeared.



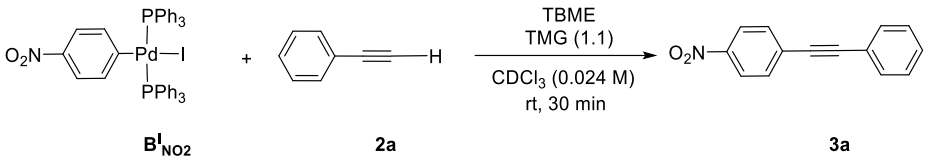
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.831	MM	0.1830	1747.83301	159.19141	5.2716
2	21.266	BB	0.3668	3.14076e4	1305.00317	94.7284

Figure S71. HPLC chromatogram of the crude of the reaction between complexes $\mathbf{B^{I}_{NO_2}}$ and **M** in DMF after 30 minutes. The crude was extracted with cyclohexane. Peak at 13.820 min = **3a**; peak at 21.266 min = **4**. The Relative Response Factor (RRF) between **3a** and **4** is 0.21.

7.3. General procedure for entries 7-8, Table S3

The reaction was performed in an oven-dried NMR tube purged under nitrogen atmosphere. The complexe $\mathbf{B^{I}_{NO_2}}$ (15.8 mg, 0.018 mmol, 1 eq) was dissolved in solvent (0.750 mL) followed by the addition of **2a** (29 µL from a stock solution of 0.66 M, 0.018 mmol, 1eq) and TMG (32.5 µL from a stock solution of 0.66 M, 0.02 mmol, 1.1 eq). Tert-Butyl methyl ether (TBME) was used as internal standard. The mixture was let at room temperature and it was monitored by ^{1}H and ^{31}P NMR spectroscopy at several times.

Entry 7, Table S3



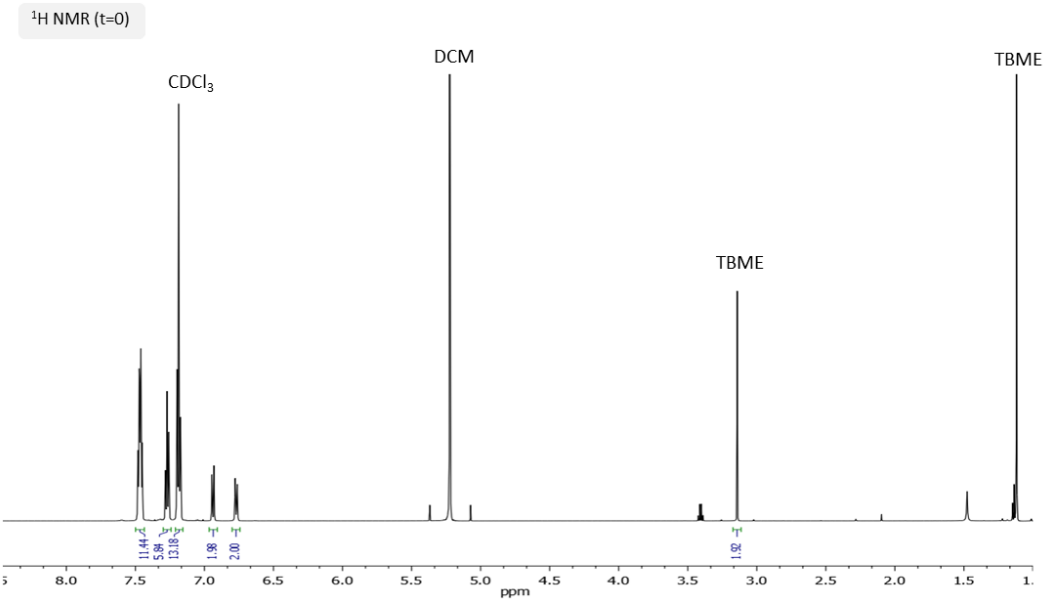


Figure S72. ^{1}H NMR spectrum in $CDCl_3$ before the addition of **2a** and TMG.

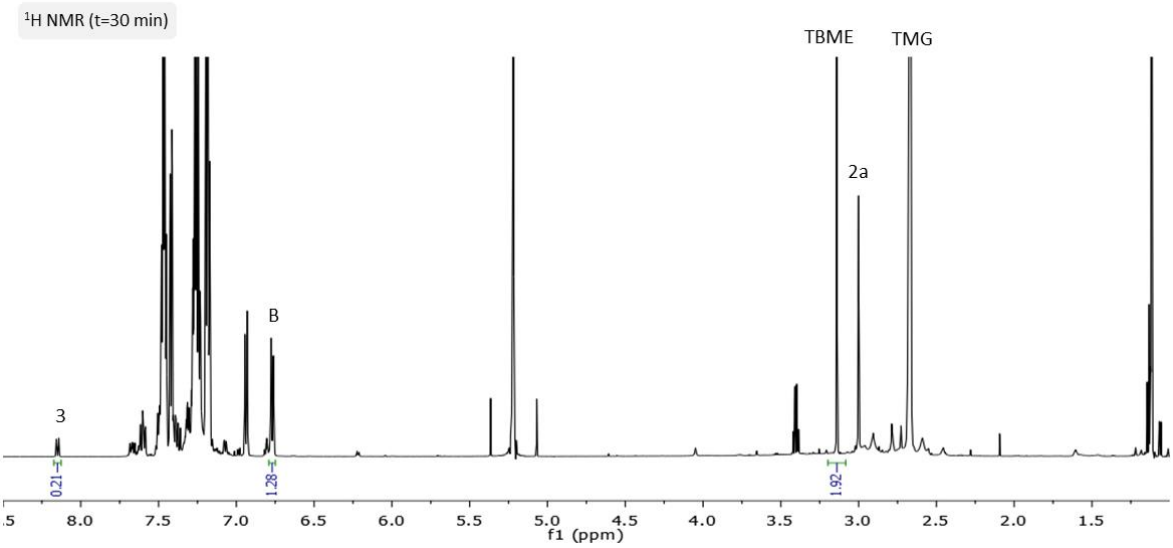
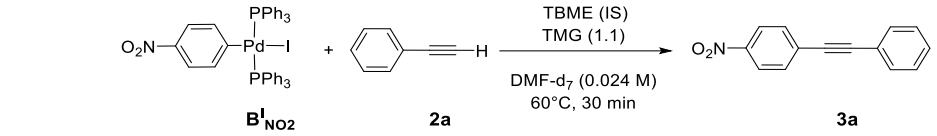


Figure S73. ^{1}H NMR spectrum of the stoichiometric reaction between $\mathbf{B^{I}_{NO_2}}$ and **2a** with TMG in $CDCl_3$ after 30 minutes at rt.

Entry 8, Table S3



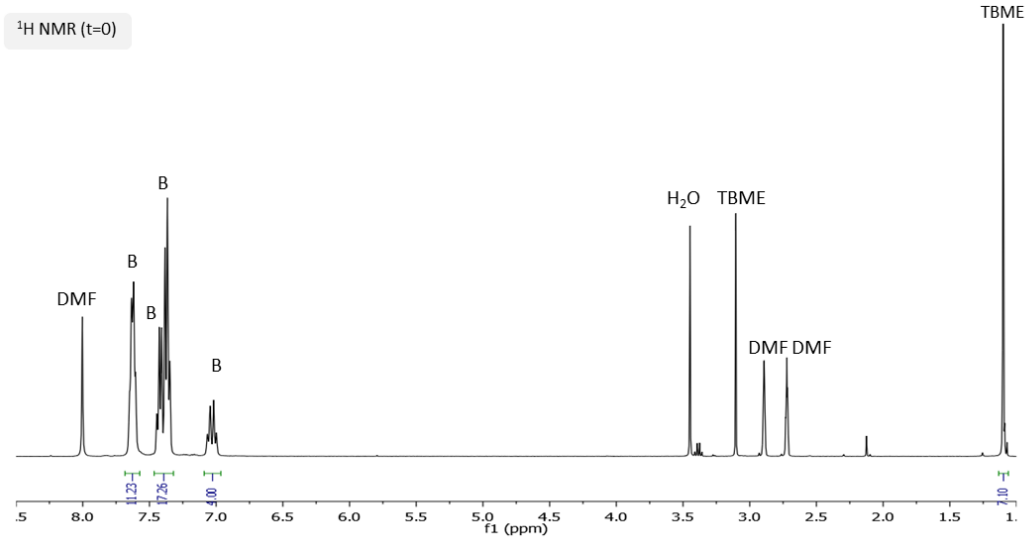


Figure S74. ^{1}H NMR spectrum in DMF-d_7 before the addition of **2a** and TMG.

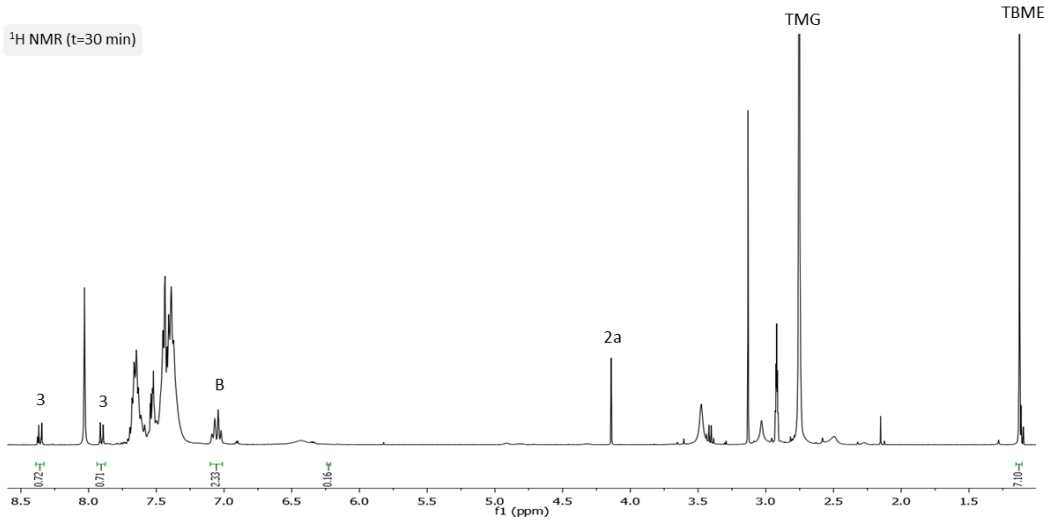


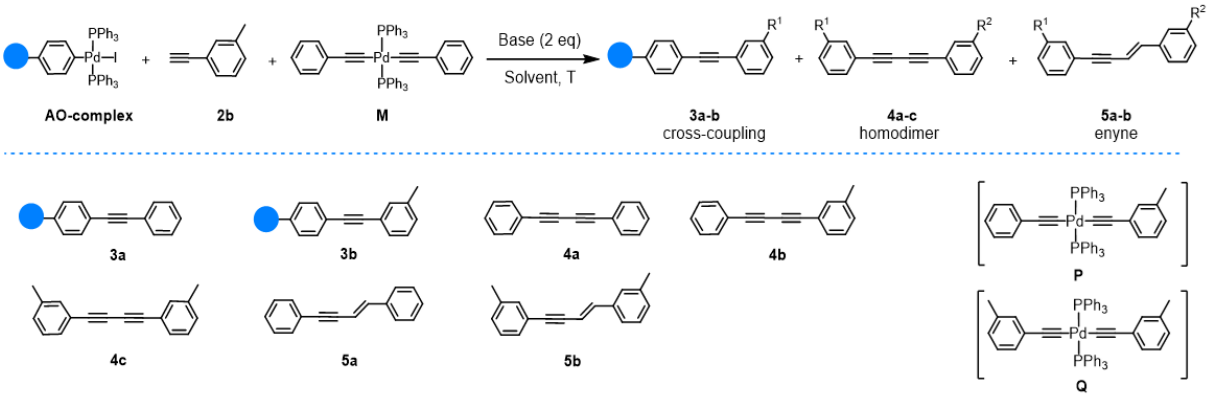
Figure S75. ^{1}H NMR spectrum of the stoichiometric reaction between $\mathbf{B^{I}_{NO_2}}$ and **2a** with TMG in DMF-d_7 after 30 minutes at 60°C.

8. Simultaneous competition reaction

Procedure:

To an oven-dried 10 mL Schlenk purged under N_2 atmosphere, **AO-complex** (0.05 mmol, 1 eq), **M** (43.9 mg, 0.05 mmol, 1 eq), and **2b** were dissolved in the solvent (0.375 mL). After the addition of the base (0.1 mmol, 2 eq), the reaction was stirred for 1 h and monitored by HPLC-MS and GC-MS technique.

Scheme S1. The competition between **M** and **2b** in the reaction with the **AO-complex**.



Supplementary Table 4. Simultaneous competition reactions at several conditions.

Entry	●	2b (eq)	Solvent	Base	T(°C)	3a/3b (1h)[a]	%Conv (1h)[b]
1	NO_2	1	$CDCl_3$	TMG	25	0/100	73
2	NO_2	1	$CDCl_3$	PYR	25	0/100	60
3	Me	1	$CDCl_3$	TMG	25	2/98	66
4	Me	1	$CDCl_3$	PYR	25	3/97	41
5	NO_2	10	$CDCl_3$	TMG	25	0/100	60
6	Me	10	$CDCl_3$	PYR	25	0/100	59
7[c]	NO_2	1	DMF	TMG	25	-	-
8	NO_2	1	DMF	TMG	40	0/100	100
9	NO_2	1	DMF	TMG	60	0/100	100
10	NO_2	1	$CDCl_3$	TMG	60	0/100	100
11	NO_2	1	NMP	TMG	60	0/100	100
12	NO_2	1	NBP	TMG	60	0/100	100
13	NO_2	1	HEP	TMG	60	0/100	100
14	NO_2	1	THF	TMG	60	0/100	100
15	NO_2	1	EtOH	TMG	60	0/100	100
16	NO_2	1	Toluene	TMG	60	0/100	100

[a] Calculated by GC-MS

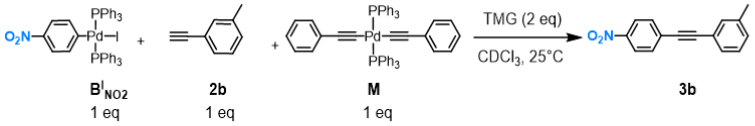
[b] Conversions calculated by comparing the integrated peak areas of **2b** and **3b** using HPLC-MS with Relative Response Factor (RRF) = 3.96

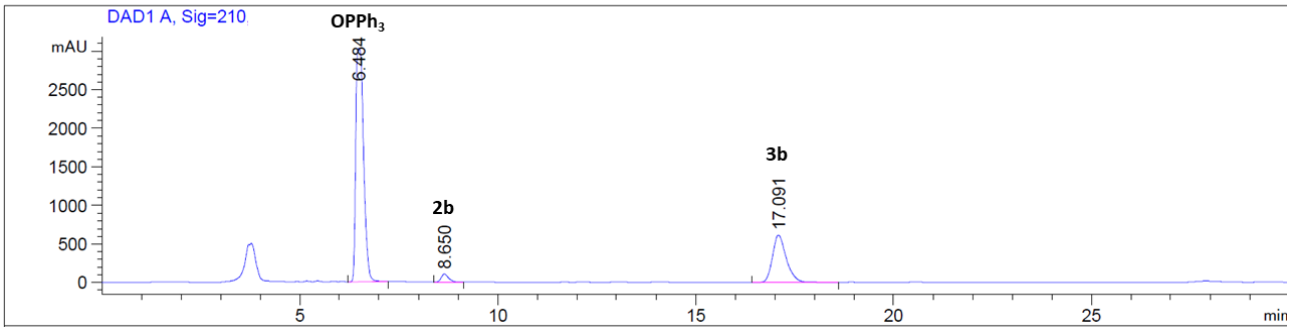
[c] Complex **M** is not soluble in DMF at 25°C

8.1. Competition reactions under stoichiometric condition at 25°C (Entries 1-4; Table S4)

To an oven-dried 10 mL Schlenk purged under N_2 atmosphere, **AO-complex** (0.05 mmol, 1 eq), **M** (43.9 mg, 0.05 mmol, 1 eq), and **2b** (6.5 µL, 0.05 mmol, 1 eq) were dissolved in $CDCl_3$ (0.375 mL). After the addition of the base (0.1 mmol, 2 eq), the reaction was stirred at 25°C for 1 h and monitored by HPLC-MS and GC-MS technique.

Entry 1, Table S4





Peak	specie	time (min)	Area [mAU*s]
1	**2b**	8,650	1391,4
2	**3b**	17,091	14807,8

Figure S76. HPLC chromatogram of $\mathbf{B^{I}_{NO_2}}$ (1eq) + **2b** (1eq) + **M** (1eq) with TMG in $CDCl_3$ at 25°C. Peak at 6.484 min = $OPPh_3$, peak at 8.650 min = **2b**; peak at 17.091 min = **3b**. Calculated conversion (RRF=3.96) of **2b** into **3b** = 73%.

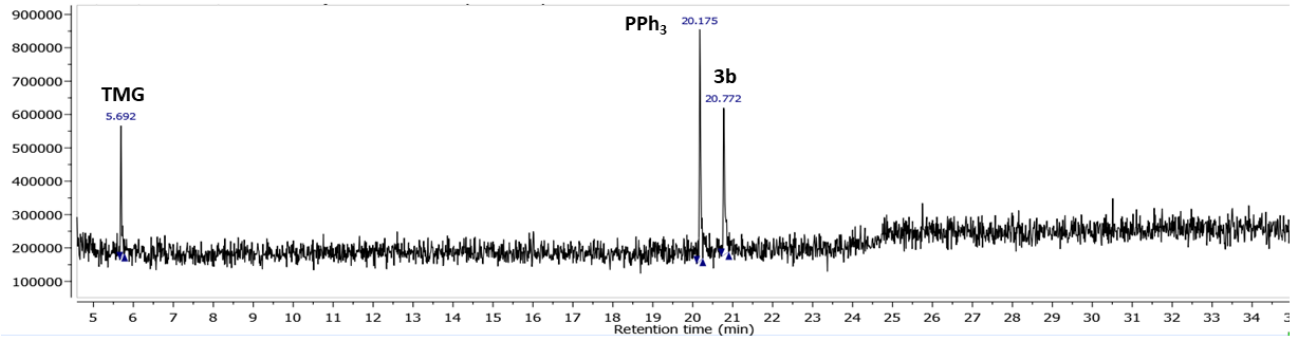


Figure S77. GC chromatogram of $\mathbf{B^{I}_{NO_2}}$ (1eq) + **2b** (1eq) + **M** (1eq) with TMG in $CDCl_3$ at 25°C. Peak at 5.692 min = TMG, peak at 20.175 min PPh_3 and peak at 20.772 min = **3b**.

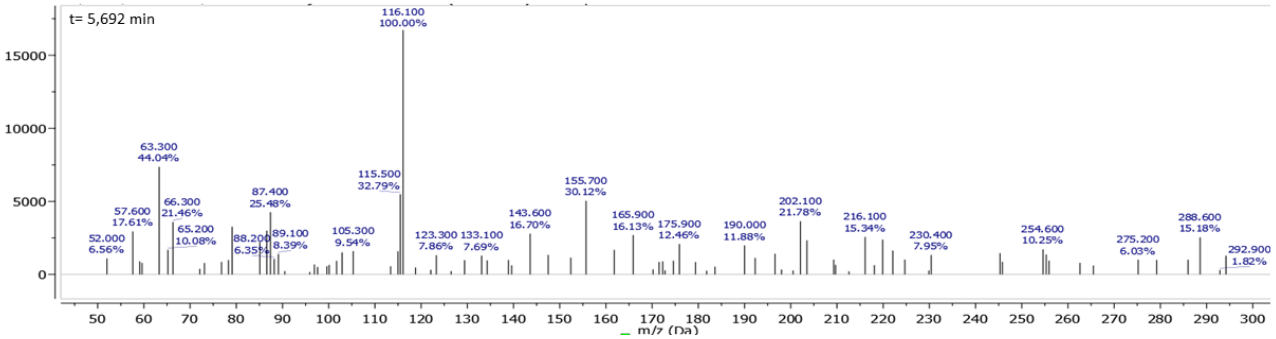


Figure S78. Mass spectrum of **TMG** (Exact Mass= 115.17 g mol^{-1}; t=5.692 min)

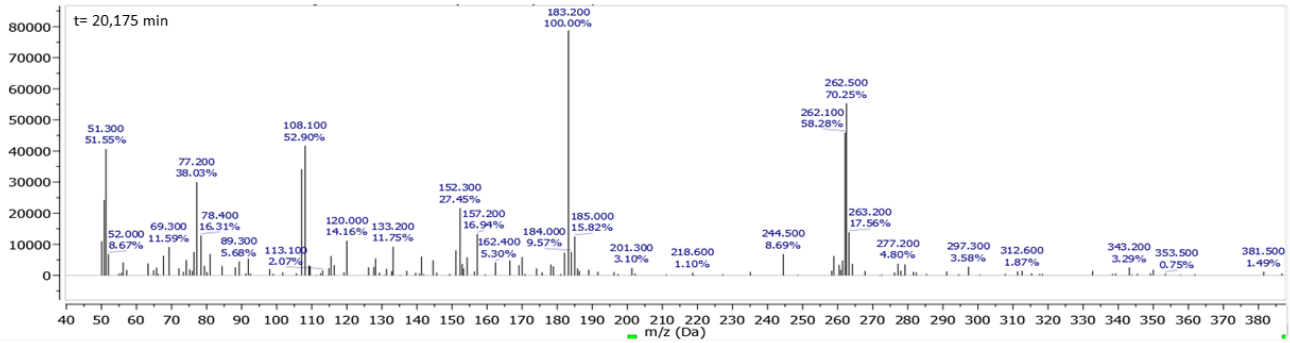


Figure S79. Mass spectrum of **PPh_3** (Exact Mass= 262.09 g mol^{-1}; t=20.64 min)

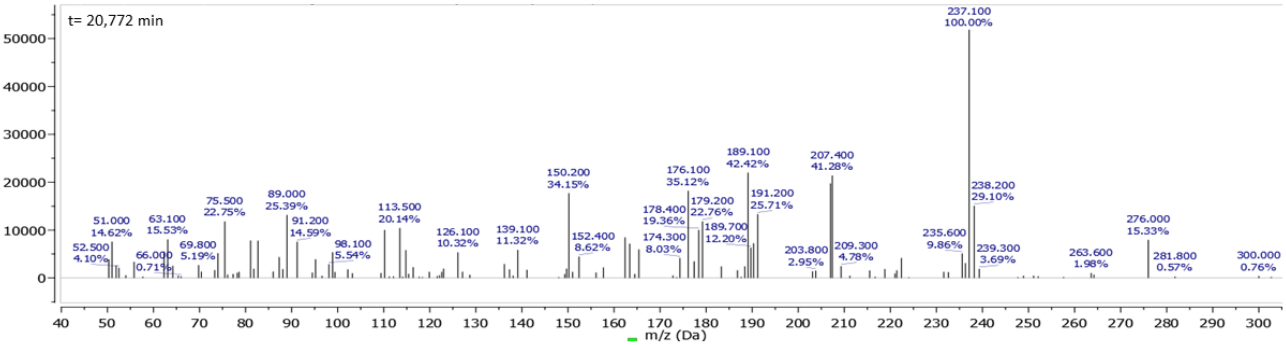
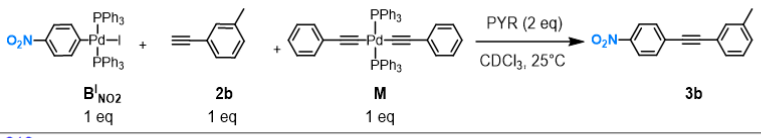
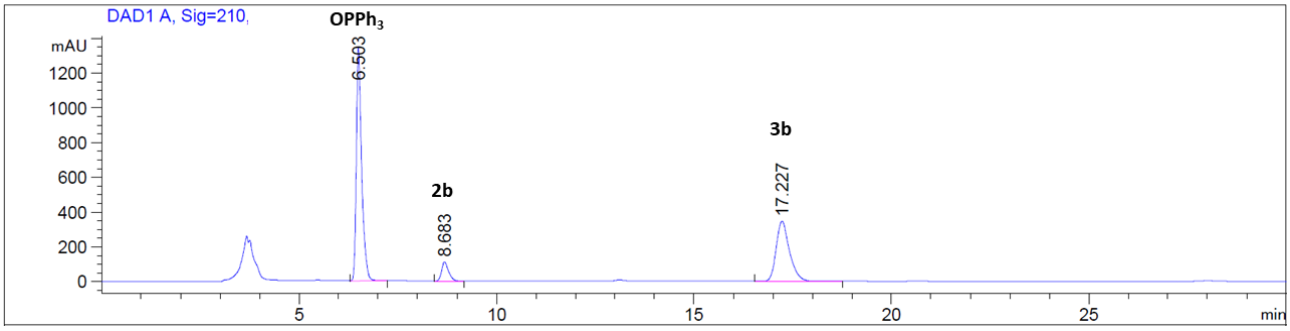


Figure S80. Mass spectrum of **3b** (Exact Mass= 237.08 g mol^{-1} t=21.26 min)

Entry 2, Table S4





Peak	specie	time (min)	Area [mAU*s]
1	**2b**	8,683	1368
2	**3b**	17,227	8094,7

Figure S81. HPLC chromatogram of $\mathbf{B^{I}_{NO_2}}$ (1eq) + **2b** (1eq) + **M** (1eq) with PYR in $CDCl_3$ at 25°C. Peak at 6.503 min = $OPPh_3$, peak at 8.683 min = **2b**; peak at 17.227 min = **3b**. Calculated conversion (RRF=3.96) of **2b** into **3b** = 60%.

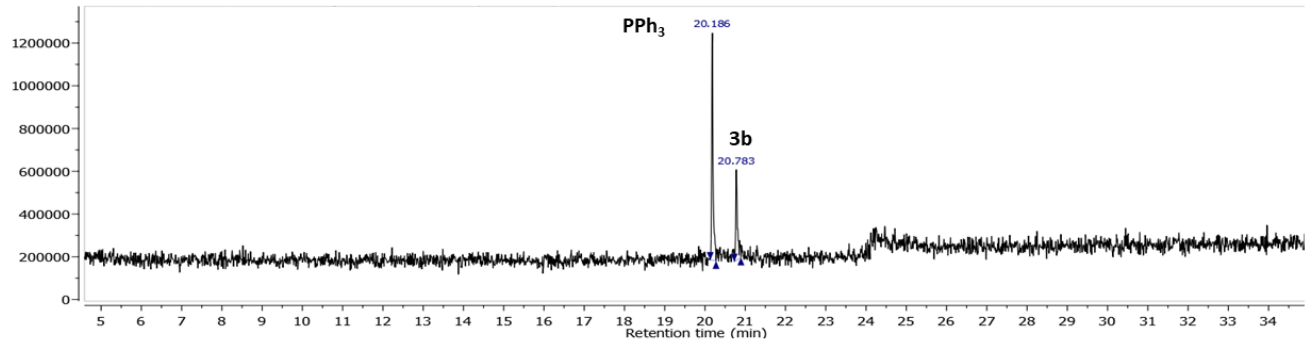
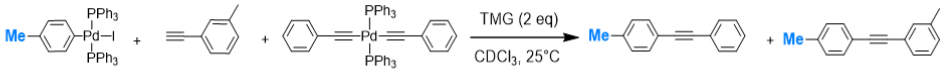
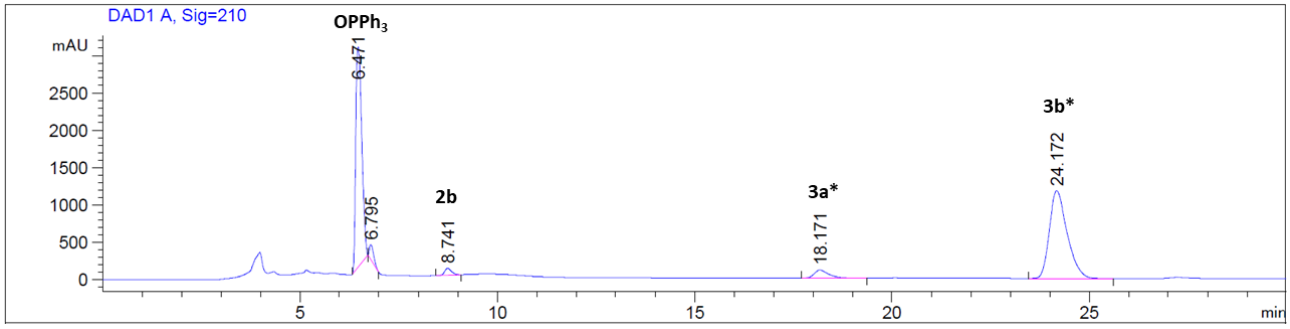


Figure S82. GC chromatogram of $\mathbf{B^{I}_{NO_2}}$ (1eq) + **2b** (1eq) + **M** (1eq) with PYR in $CDCl_3$ at 25°C. Peak at 20.196 min = PPh_3 and peak at 20.783 min = **3b**.

Entry 3, Table S4





Peak	specie	time (min)	Area [mAU*s]
1	**2b**	8,741	1102,8
2	**3b***	24,172	36799,4

Figure S83. HPLC chromatogram of $\mathbf{B^{I}_{Me}}$ (1eq) + **2b** (1eq) + **M** (1eq) with TMG in $CDCl_3$ at 25°C. Peak at 6.471 min = $OPPh_3$, peak at 8.741 min = **2b**; peak at 18.171 min = **3a*** and peak at 24.172 min = **3b***. Calculated conversion (RRF=3.96) of **2b** into **3b*** = 66%.

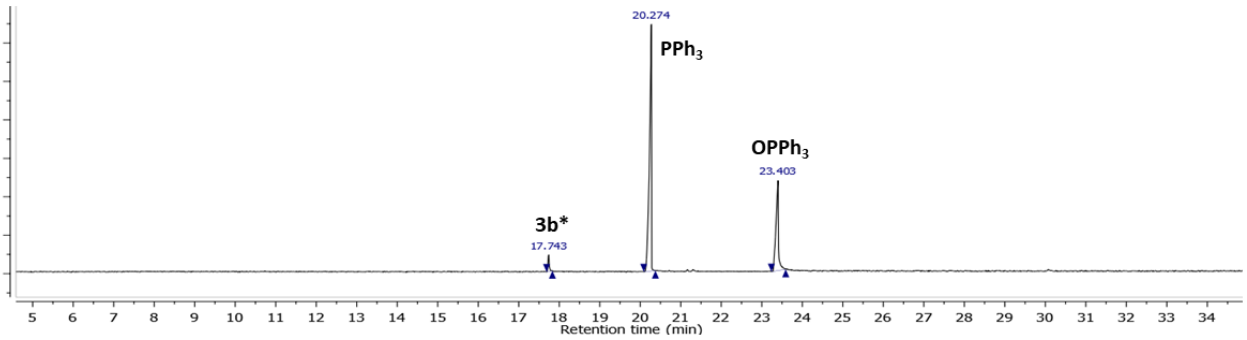


Figure S84. GC chromatogram of $\mathbf{B^{I}_{Me}}$ (1eq) + **2b** (1eq) + **M** (1eq) with TMG in $CDCl_3$ at 25°C. Peak at 17.743 min= **3b***, peak at 20.274 min = PPh_3 and peak at 23.403 min = $OPPh_3$.

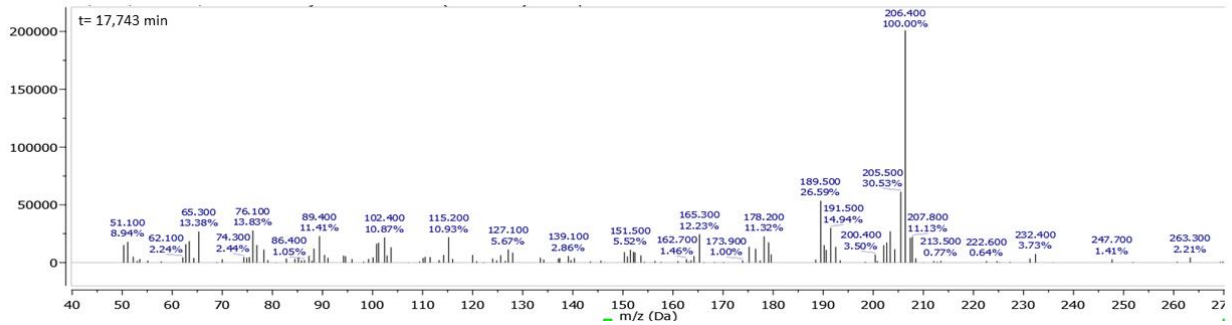


Figure S85. Mass spectrum of **3b*** (Exact Mass= 206.11 g mol^{-1} t=17.743 min)

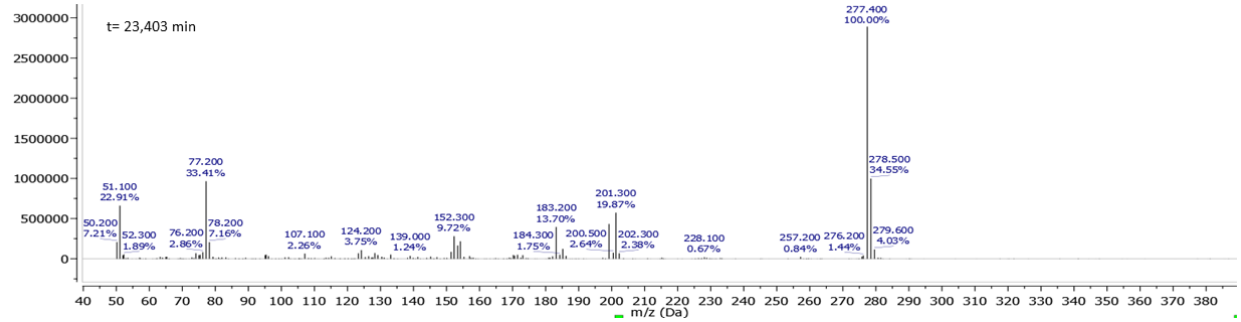
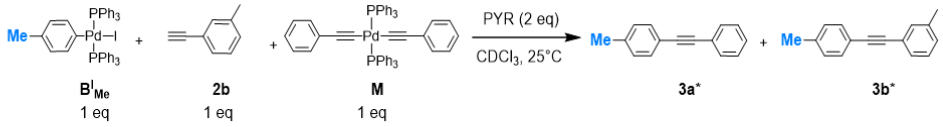
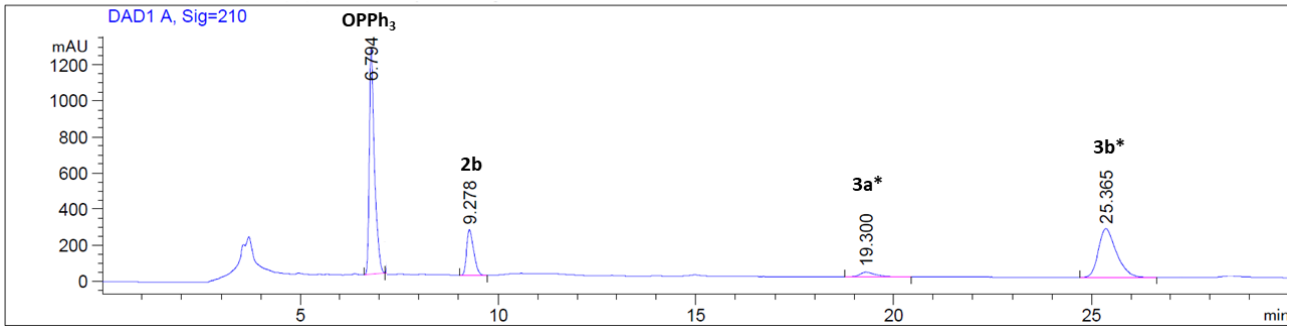


Figure S86. Mass spectrum of **$OPPh_3$** (Exact Mass= 278.08 g mol^{-1} t=23.043 min)

Entry 4, Table S4





Peak	specie	time (min)	Area [mAU*s]
1	**2b**	9,278	3153,1
2	**3b***	25,365	8513,7

Figure S87. HPLC chromatogram of $\mathbf{B^{I}_{Me}}$ (1eq) + **2b** (1eq) + **M** (1eq) with PYR in $CDCl_3$ at 25°C. Peak at 6.794 min = $OPPh_3$, peak at 9.278 min = **2b**; peak at 19.300 min = **3a*** and peak at 25.365 min = **3b***. Calculated conversion (RRF=3.96) of **2b** into **3b*** = 41%.

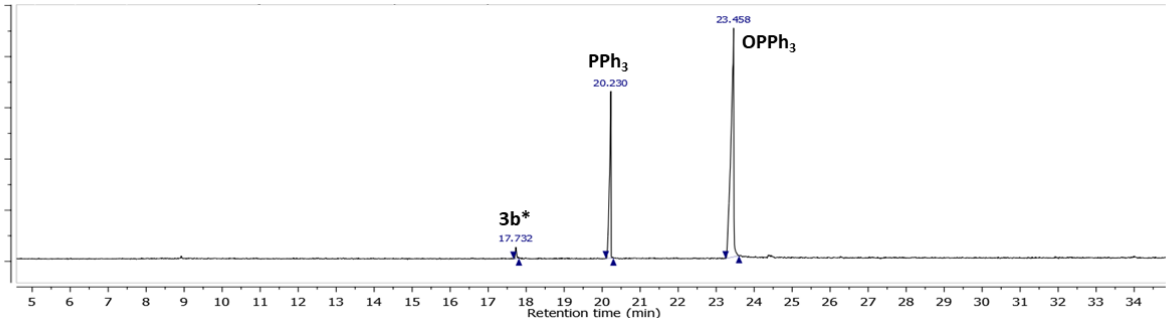
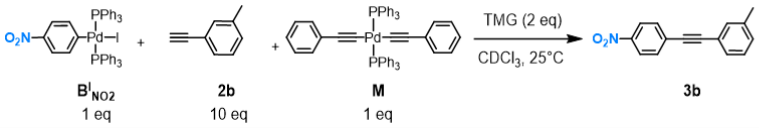


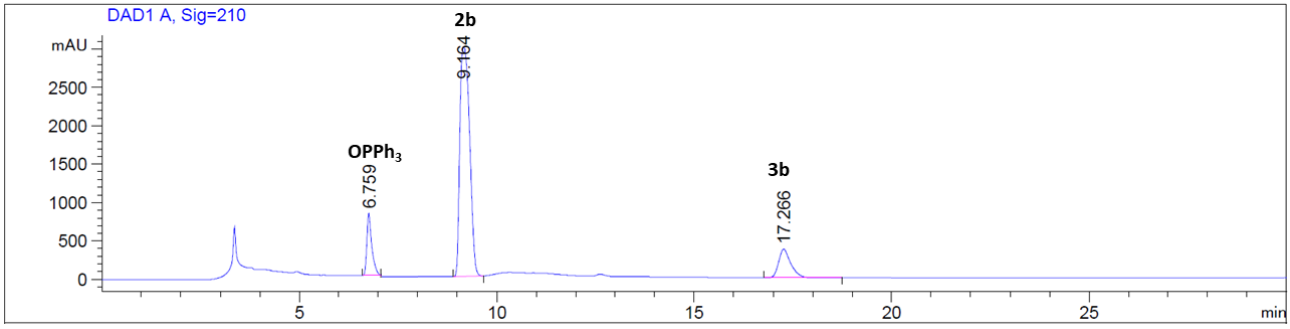
Figure S88. GC chromatogram of $\mathbf{B^{I}_{Me}}$ (1eq) + **2b** (1eq) + **M** (1eq) with PYR in $CDCl_3$ at 25°C. Peak at 17.732 min= **3b***, peak at 20.220 min = PPh_3 and peak at 23.458 min = $OPPh_3$.

8.2. Competition reactions with 10 eq of the alkyne (Entries 5-6; Table S4)

To an oven-dried 10 mL Schlenk purged under N_2 atmosphere, **AO-complex** (0.05 mmol, 1 eq), **M** (43.95 mg, 0.05 mmol, 1 eq), and **2b** (65 µL, 0.5 mmol, 10 eq) were dissolved in $CDCl_3$ (0.375 mL). After the addition of the base (0.1 mmol, 2 eq), the reaction was stirred at 25°C for 1 h and monitored by HPLC-MS and GC-MS technique.

Entry 5, Table S4





Peak	specie	time (min)	Area [mAU*s]
1	**2b**	9,164	29124,8
2	**3b**	17,266	17621,9

Figure S89. HPLC chromatogram of $\mathbf{B^{I}_{NO_2}}$ (1eq) + **2b** (10eq) + **M** (1eq) with TMG in $CDCl_3$ at 25°C. Peak at 6.759 min = $OPPh_3$, peak at 9.164 min= **2b** and peak at 17.266 min = **3b.** Calculated conversion (RRF=3.96) of **2b** into **3b** = 60%.

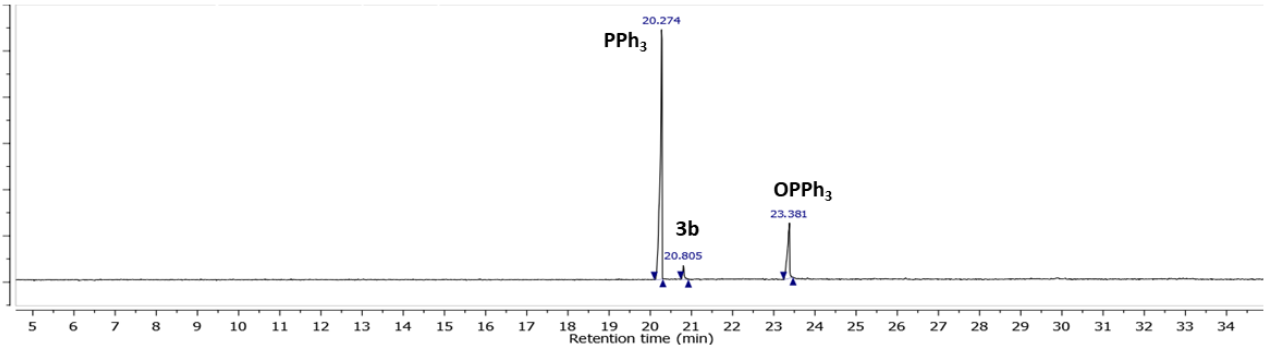
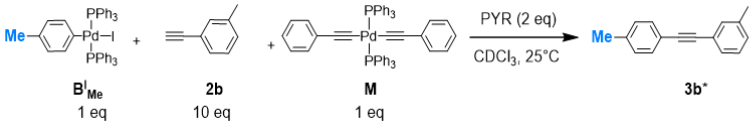
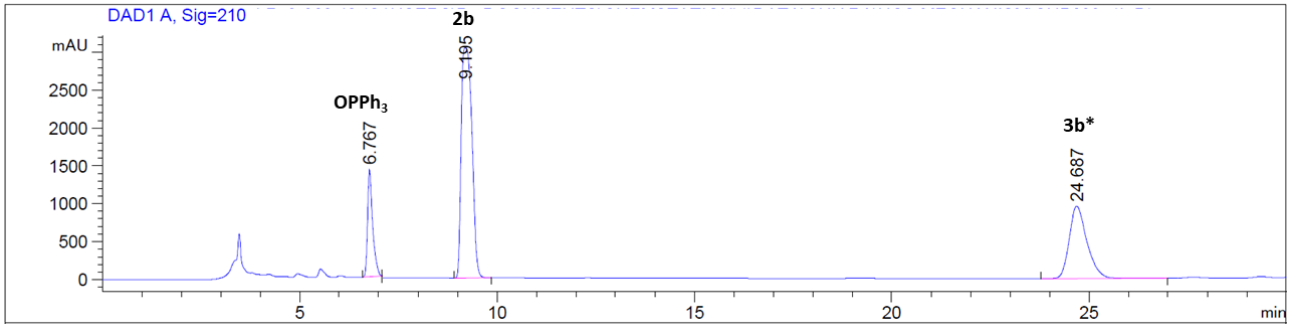


Figure S90. GC chromatogram of $\mathbf{B^{I}_{NO_2}}$ (1eq) + **2b** (10eq) + **M** (1eq) with TMG in $CDCl_3$ at 25°C. Peak at 20.274 min= PPh_3, peak at 20.805 min = **3b** and peak at 23.381 min = $OPPh_3$.

Entry 6, Table S4





Peak	specie	time (min)	Area [mAU*s]
1	**2b**	9,195	31321,7
2	**3b***	24,687	20173,9

Figure S91. HPLC chromatogram of $\mathbf{B^{I}_{Me}}$ (1eq) + **2b** (10eq) + **M** (1eq) with PYR in $CDCl_3$ at 25°C. Peak at 6.767 min = $OPPh_3$, peak at 9.195 min = **2b** and peak at 24.687 min = **3b***. Calculated conversion (RRF=3.96) of **2b** into **3b*** = 59%.

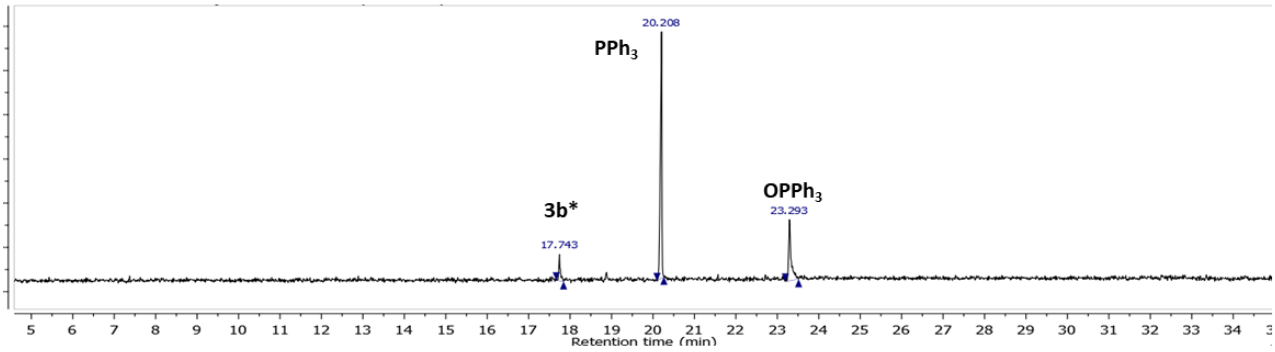


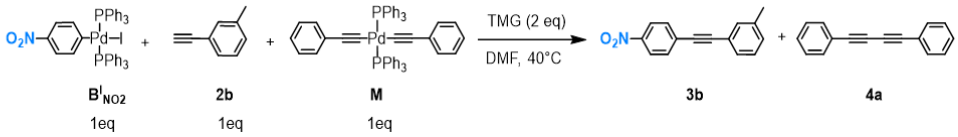
Figure S92. GC chromatogram of $\mathbf{B^{I}_{Me}}$ (1eq) + **2b** (10eq) + **M** (1eq) with PYR in $CDCl_3$ at 25°C. Peak at 17.743 min= **3b*,** peak at 20.208 min =PPh_3, peak at 23.293 min = $OPPh_3$**.**

8.3. Competition reactions in several solvents (Entries 8-16; Table S4)

General procedure:

To an oven-dried 10 mL Schlenk purged under N_2 atmosphere, AO complex $\mathbf{B^{I}_{NO_2}}$ (43.9 mg, 0.05 mmol, 1 eq), **M** (43.9 mg, 0.05 mmol, 1 eq), and **2b** (6.5 µL, 0.05 mmol, 1 eq) were dissolved in solvent (0.375 mL). After the addition of TMG (12.5 µL, 0.1 mmol, 2 eq), the reaction was stirred at several temperature for 1 h and monitored by HPLC-MS and GC-MS technique.

Entry 8, Table S4



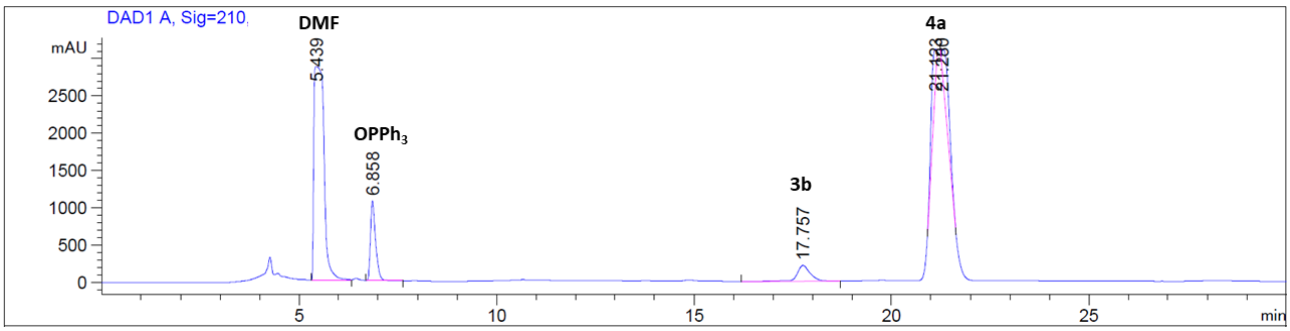


Figure S93. HPLC chromatogram of $\mathbf{B^{I}_{NO_2}}$ (1eq) + **2b** (10eq) + **M** (1eq) with TMG in DMF at 40°C. Peak at 5.439 min = DMF, peak at 6.858 min = $OPPh_3$, peak at 17.757 min= **2b** and peak at 21.268 min = **4a.**

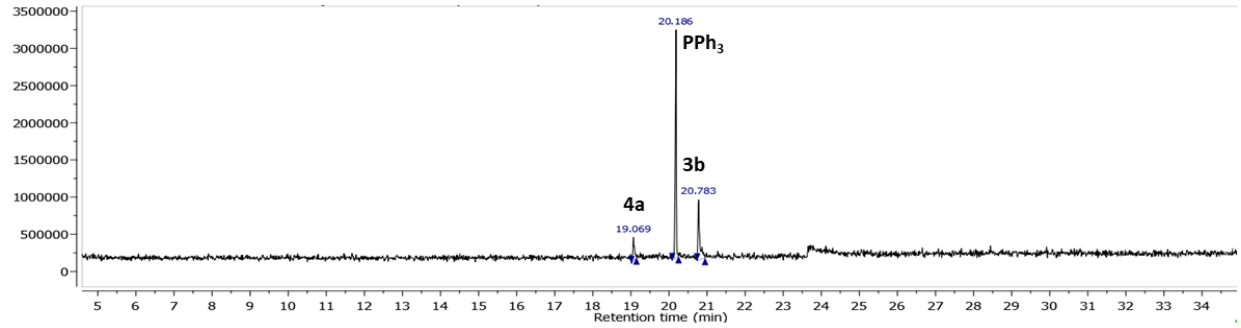


Figure S94. GC chromatogram of $\mathbf{B^{I}_{NO_2}}$ (1eq) + **2b** (1eq) + **M** (1eq) with TMG in DMF at 40°C. Peak at 19.069 min = **4a**, peak at 20.186 min = **PPh_3** and peak at 20.783 min = **3b**

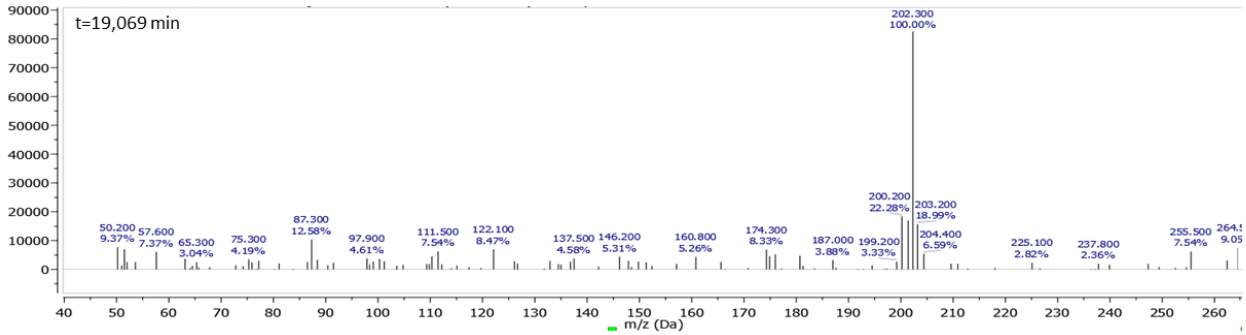
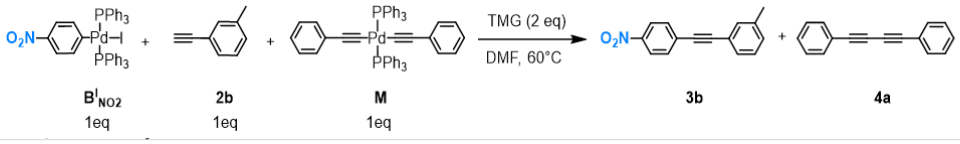


Figure S95. Mass spectrum of **4a** (Exact Mass= 202.08 g mol^{-1}t=19.069 min)

Entry 9, Table S4



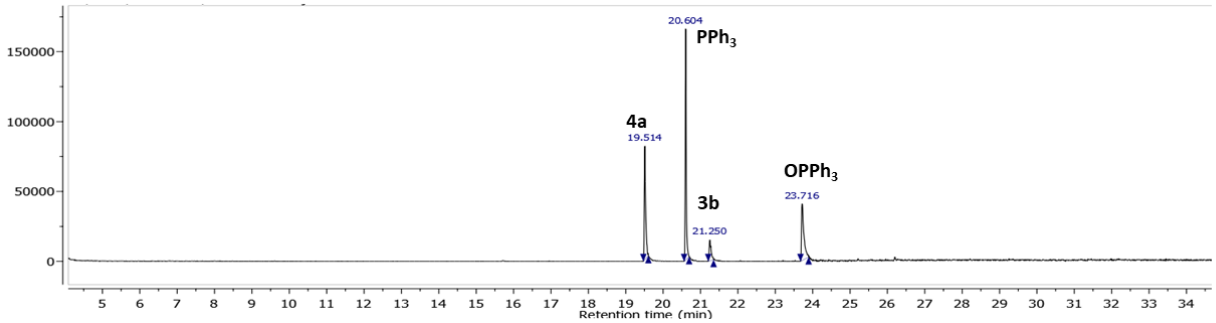
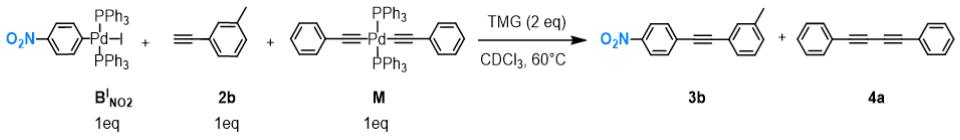


Figure S96. GC chromatogram of $\mathbf{B^{I}_{NO_2}}$ (1eq) + **2b** (1eq) + **M** (1eq) with TMG in DMF at 60°C. Peak at 19.514 min = **4a**, peak at 20.604 min = PPh_3, peak at 21.250 min = **3b** and peak at 23.716 min $OPPh_3$

Entry 10, Table S4



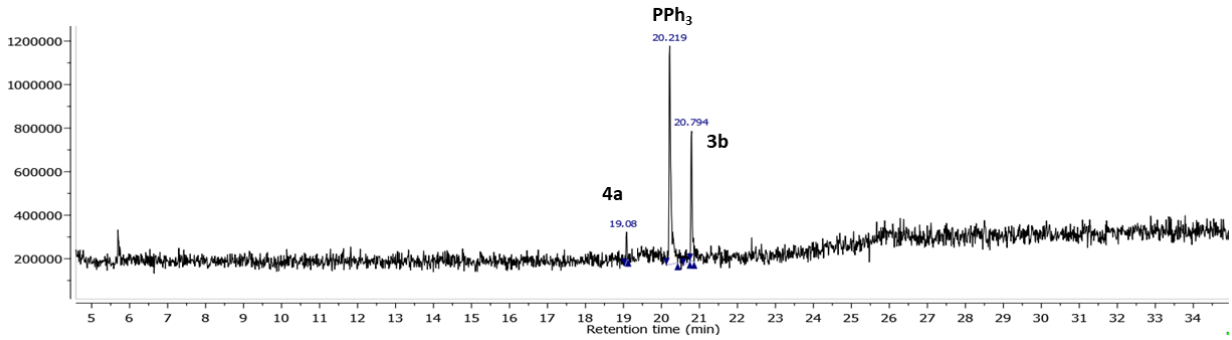
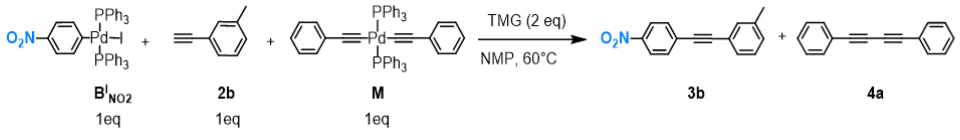


Figure S97. GC chromatogram of $\mathbf{B^{I}_{NO_2}}$ (1eq) + **2b** (1eq) + **M** (1eq) with TMG in $CDCl_3$ at 60°C. Peak at 19.08 min = **4a**, peak at 20.219 min = **PPh_3** and peak at 20.794 min = **3b.**

Entry 11, Table S4



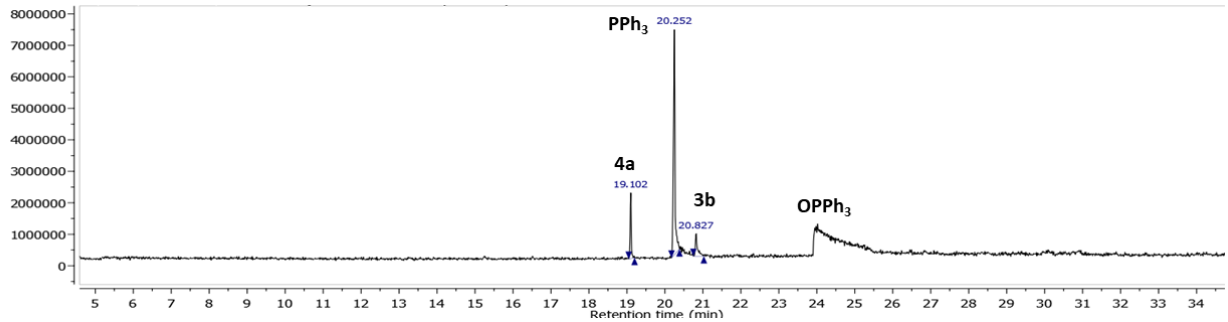
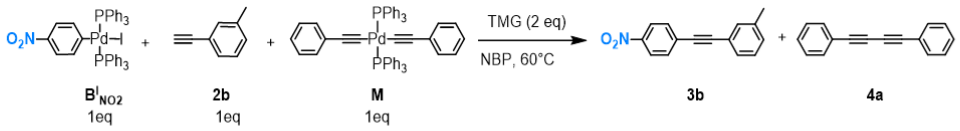


Figure S98. GC chromatogram of $\mathbf{B^{I}_{NO_2}}$ (1eq) + **2b** (1eq) + **M** (1eq) with TMG in NMP at 60°C. Peak at 19.102 min = **4a**, peak at 20.252 min = **PPh_3**, peak at 20.827 min = **3b.**

Entry 12, Table S4



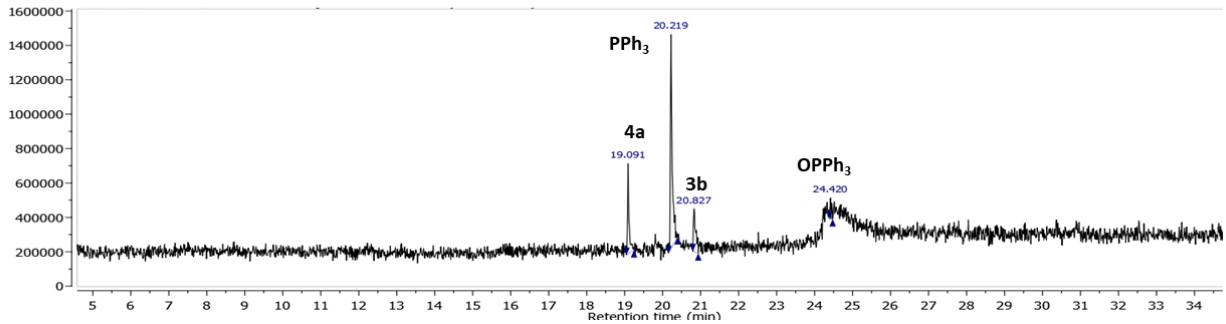
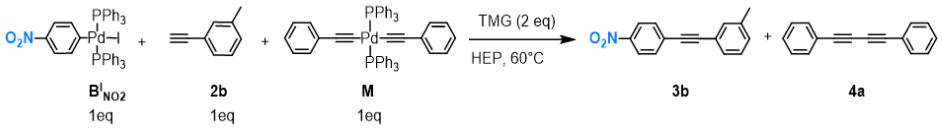


Figure S99. GC chromatogram of $\mathbf{B^{I}_{NO_2}}$ (1eq) + **2b** (1eq) + **M** (1eq) with TMG in NBP at 60°C. Peak at 19.091 min = **4a**, peak at 20.219 min = **PPh$_3$**, peak at 20.827 min = **3b** and peak at 24.420 min= OPPh$_3$

Entry 13, Table S4



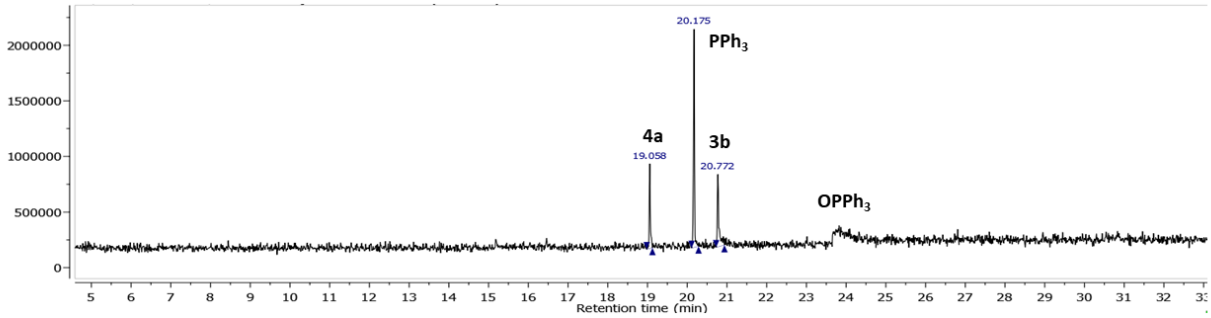
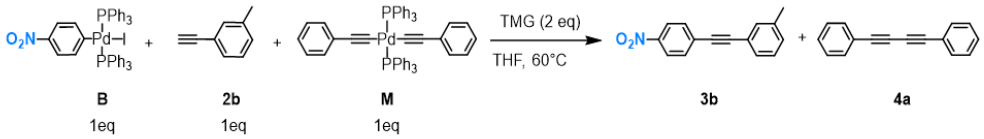


Figure S100. GC chromatogram of $\mathbf{B^{I}_{NO_2}}$ (1eq) + **2b** (1eq) + **M** (1eq) with TMG in HEP at 60°C. Peak at 19.058 min = **4a**, peak at 20.175 min = **PPh$_3$**, peak at 20.772 min = **3b**

Entry 14, Table S4



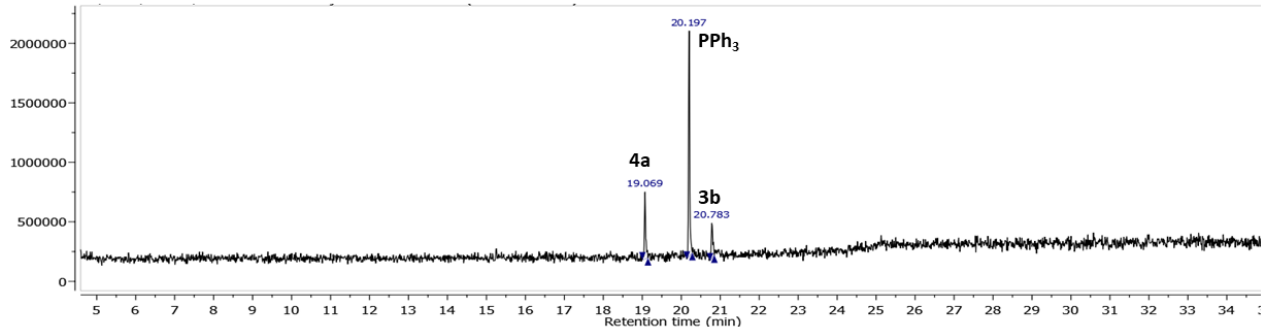


Figure S101. GC chromatogram of $\mathbf{B^{I}_{NO_2}}$ (1eq) + **2b** (1eq) + **M** (1eq) with TMG in THF at 60°C. Peak at 19.069 min = **4a**, peak at 20.197 min = **PPh$_3$**, peak at 20.783 min = **3b**

Entry 15, Table S4

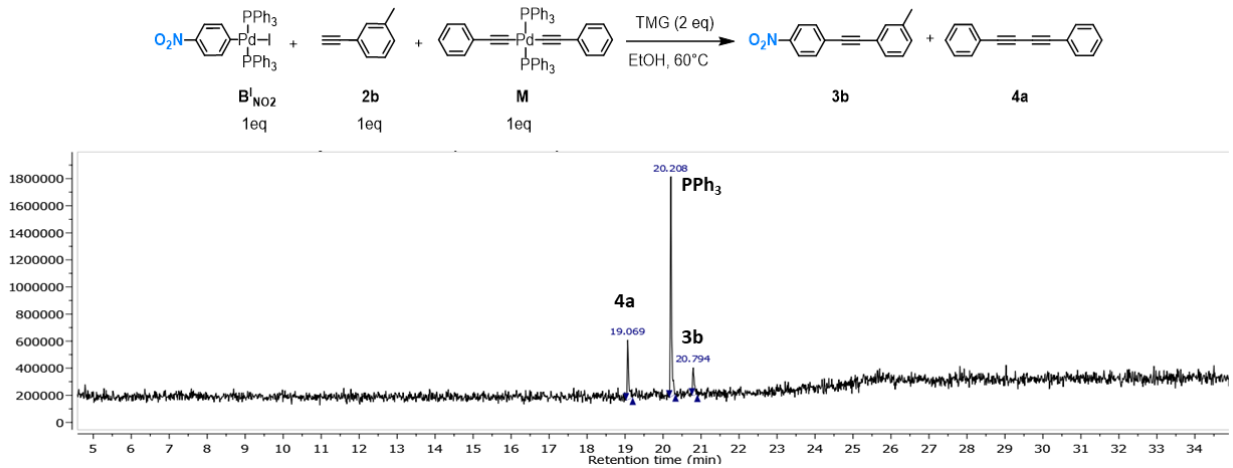


Figure S102. GC chromatogram of $\mathbf{B^{I}_{NO_2}}$ (1eq) + **2b** (1eq) + **M** (1eq) with TMG in EtOH at 60°C. Peak at 19.069 min = **4a**, peak at 20.208 min = $\mathbf{PPh_3}$, peak at 20.794 min = **3b**

Entry 16, Table S4

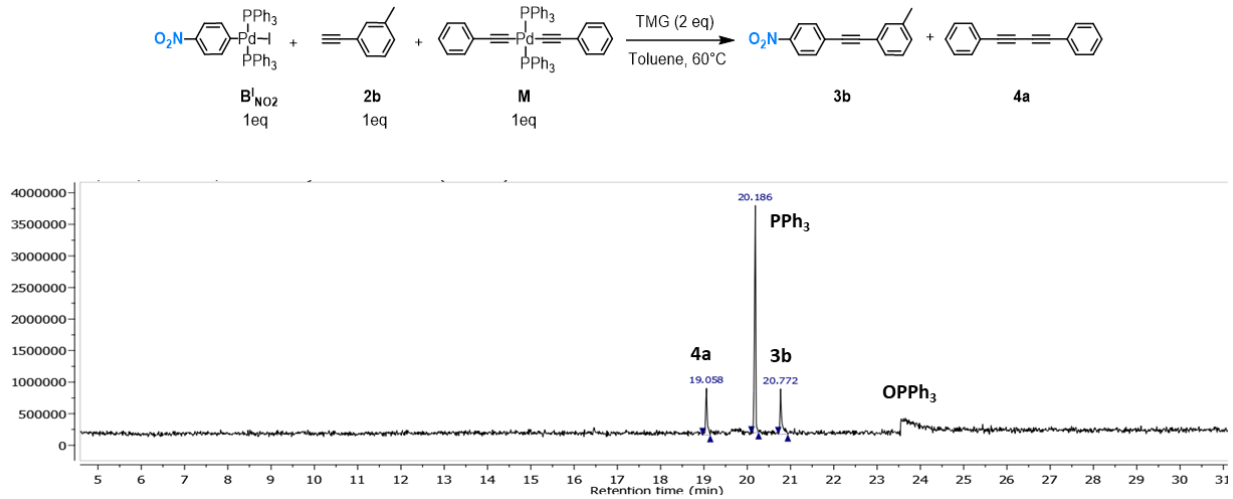


Figure S103. GC chromatogram of $\mathbf{B^{I}_{NO_2}}$ (1eq) + **2b** (1eq) + **M** (1eq) with TMG in Toluene at 60°C. Peak at 19.058 min = **4a**, peak at 20.186 min = $\mathbf{PPh_3}$, peak at 20.772 min = **3b**

9. Base effect on AO-complex B^x

General Procedure:

The reaction was performed in an oven-dried NMR tube purged under nitrogen atmosphere. The complex $\mathbf{B^X_{R1}}$ (0.026 mmol, 1 eq) was dissolved in DMF-d_7 (0.60 mL) followed by the addition of the base (10-20-50 eq). The base effect was evaluated using ^{31}P NMR technique. The spectra were collected as soon as after the addition and after 30 minutes, but the provided the same results.

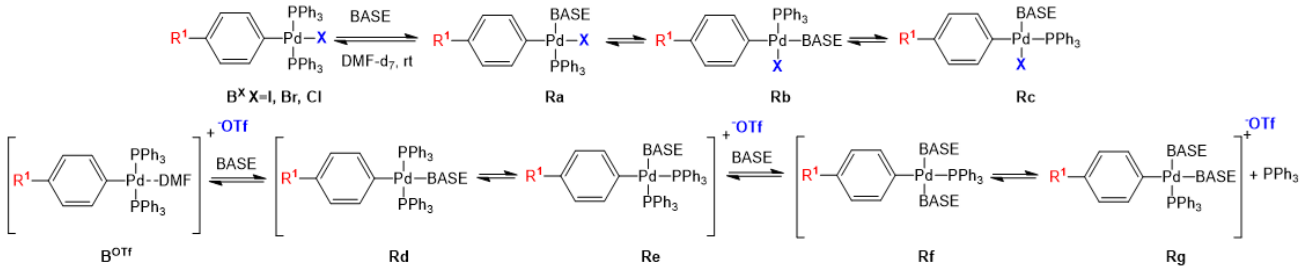


Table S5. Base effect on the oxidative addition complexes $\mathbf{B^X_{R1}}$

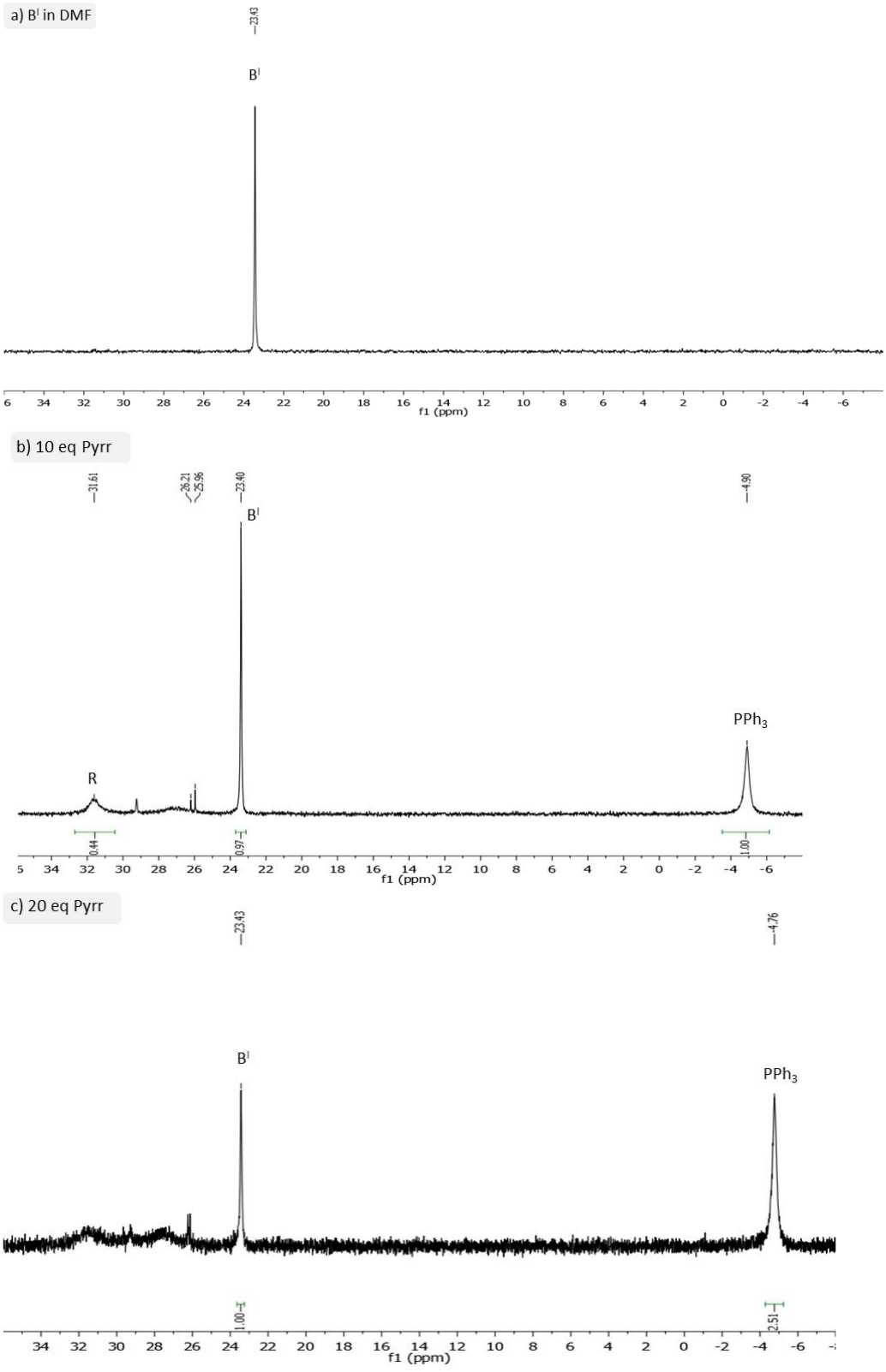
Entry	X	R_1	Base	50 eq R/B[a]	20 eq R/B[a]	10 eq R/B[a]	keq[b]
1	I	NO_2	Pyr	93/7	85/15	68/32	0.182
2	Br	NO_2	Pyr	91/9	78/22	68/32	0.099
3	Cl	NO_2	Pyr	93/7	82/18	70/30	0.134
4	I	NO_2	TMG	100/0	97/3	93/7	0.910
5	Br	NO_2	TMG	96/4	85/15	74/26	0.122
6	Cl	NO_2	TMG	87/13	71/29	63/37	0.074
7	I	NO_2	TEA	0/100	0/100	0/100	-
8	Br	NO_2	TEA	0/100	0/100	0/100	-
9	Cl	NO_2	TEA	0/100	0/100	0/100	-
10	I	OCH_3	TMG	>99/1	99/1	94/6	0.306
11	OTf	NO_2	TMG	-	100/0	-	-

[a]The ratio **R**/**B** was determined with ^{31}P NMR spectroscopy by using the respective integration of the singlets of complex **B** (z_B) and ligand (z_L): **B**(%)= [z_B /(z_B + 2z_L)]x100

[b]The equilibrium constant was calculated by using ^{31}P NMR spectroscopy (see the following Section 10 *"Evaluation of the Kinetic Constants")*

9.1. Pyrrolidine ($B^{X}_{NO_2}$):

X= Iodide. Entry 1, Table S4



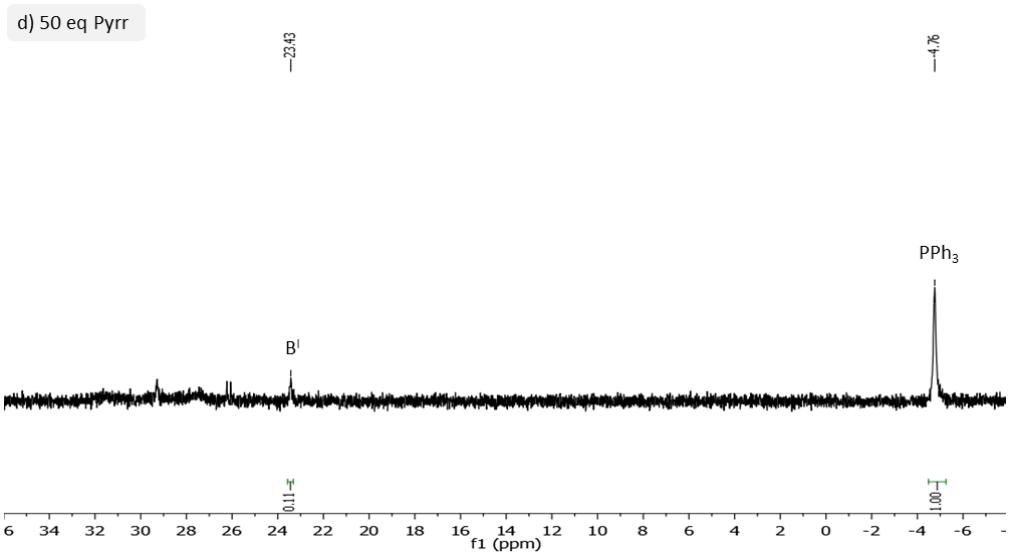
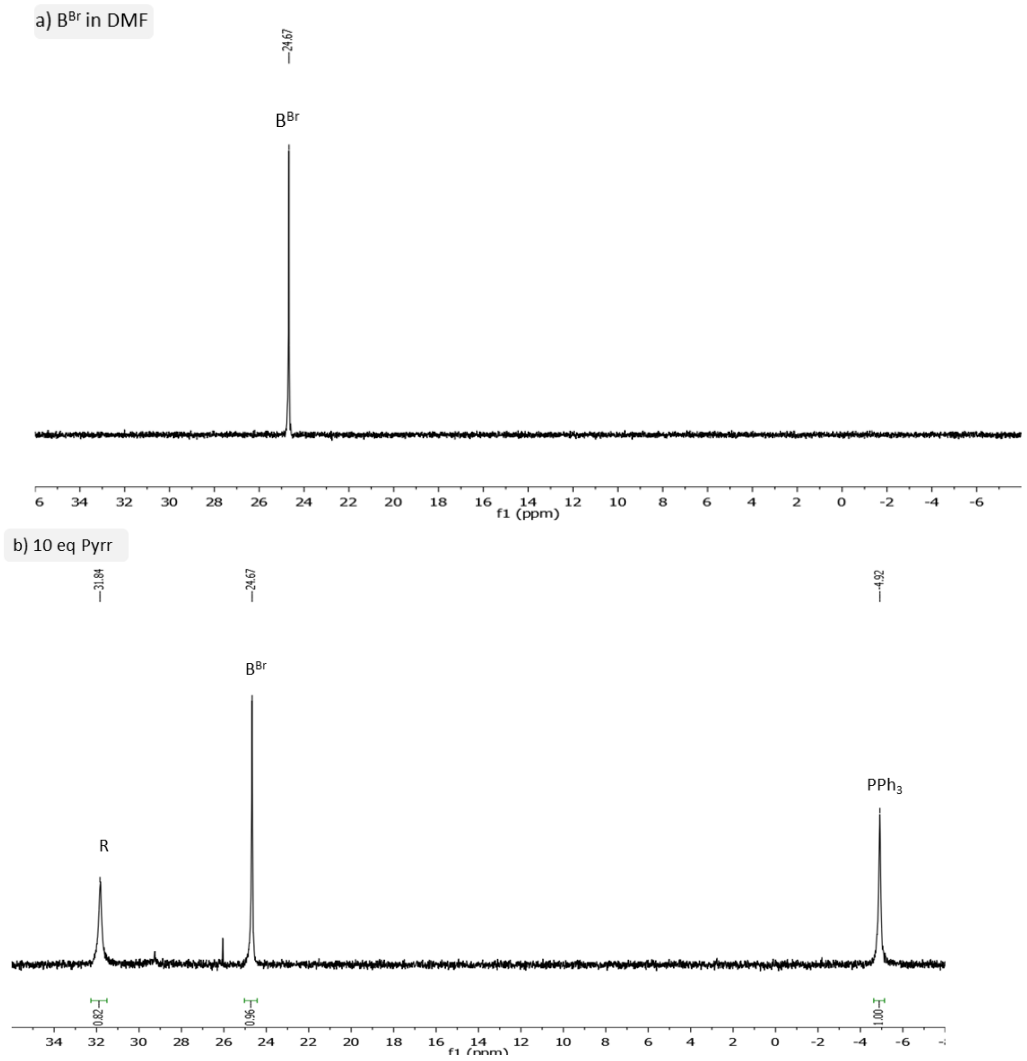


Figure S104. ^{31}P NMR spectra in DMF-d_7 of $\mathbf{B^{I}_{NO_2}}$ (a); with PYR 10 eq (b); PYR 20 eq (c) and PYR 50 eq (d).

X= Bromide. Entry 2, Table S4



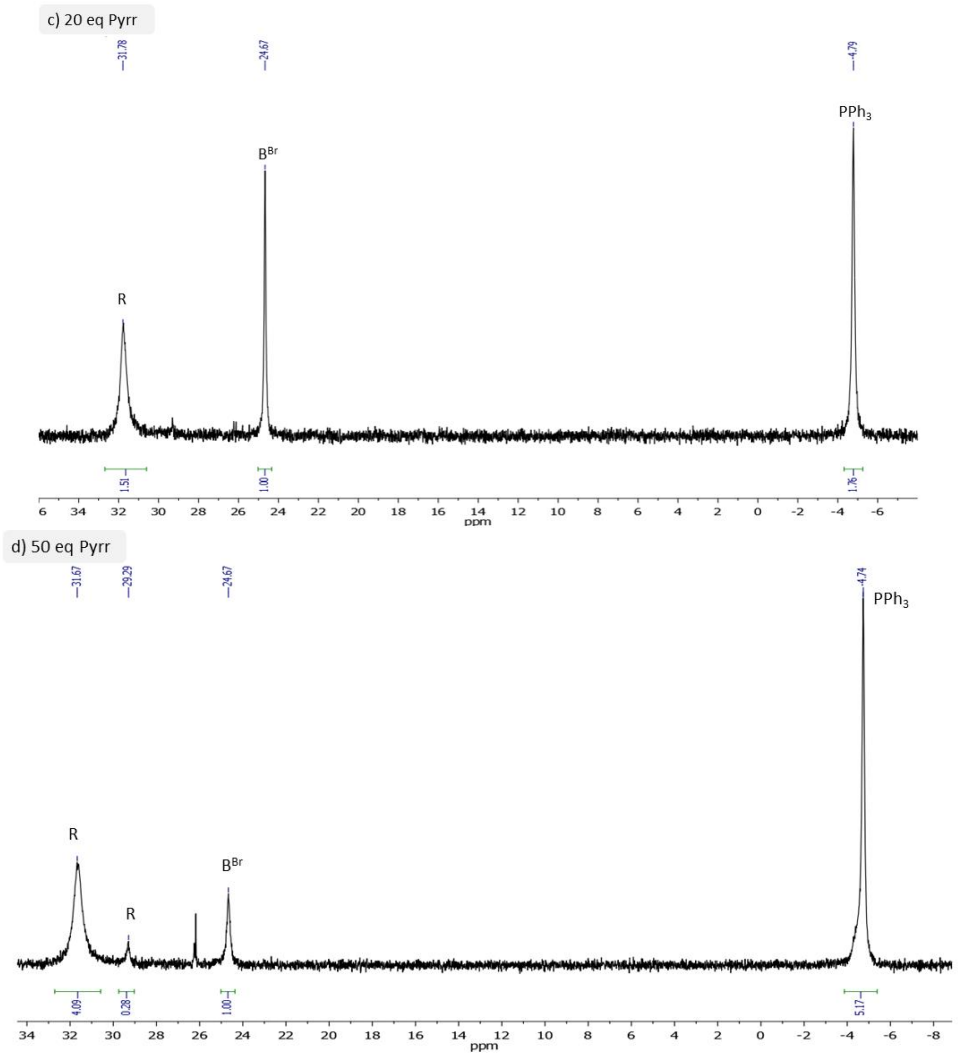
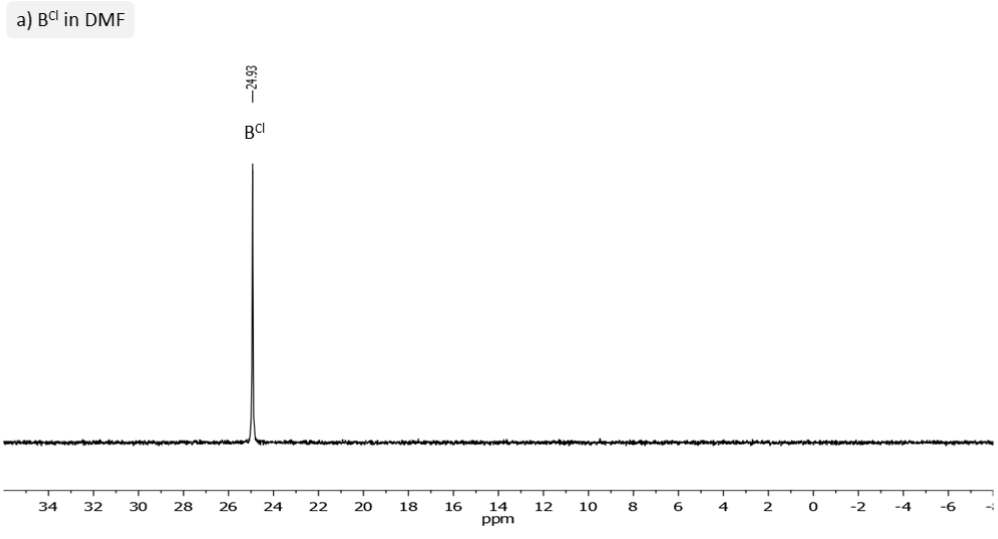


Figure S105. ^{31}P NMR spectra in DMF-d_7 of $\mathbf{B^{Br}_{NO_2}}$ (a); with PYR 10 eq (b); PYR 20 eq (c) and PYR 50 eq (d).

X=Chloride. Entry 3, Table S4



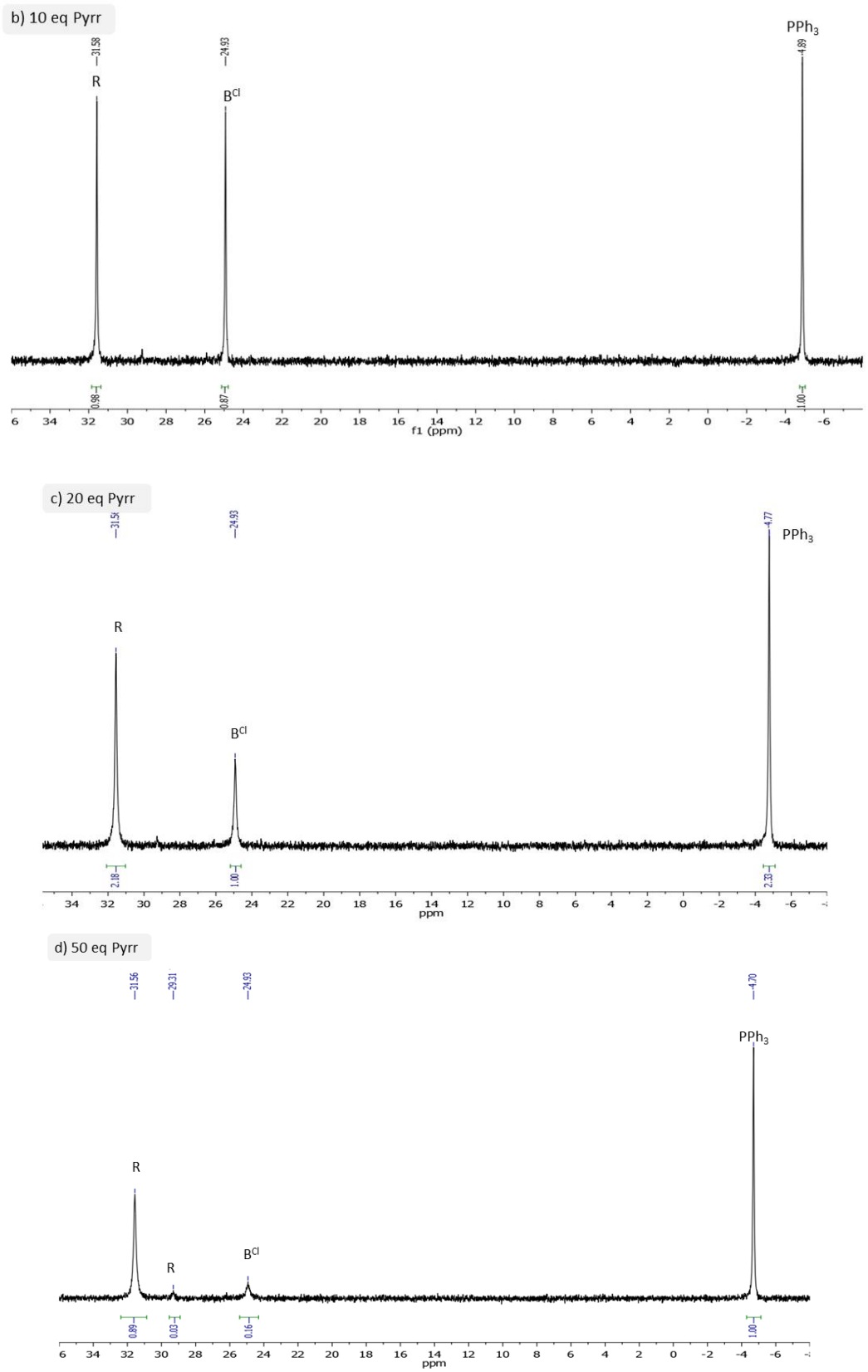


Figure S106. ^{31}P NMR spectra in DMF-d_7 of $\mathbf{B^{Cl}_{NO_2}}$ (a); with PYR 10 eq (b); PYR 20 eq (c) and PYR 50 eq (d).

9.2. TMG ($B^{X}_{NO_2}$)

X=Iodide. Entry 4, Table S4

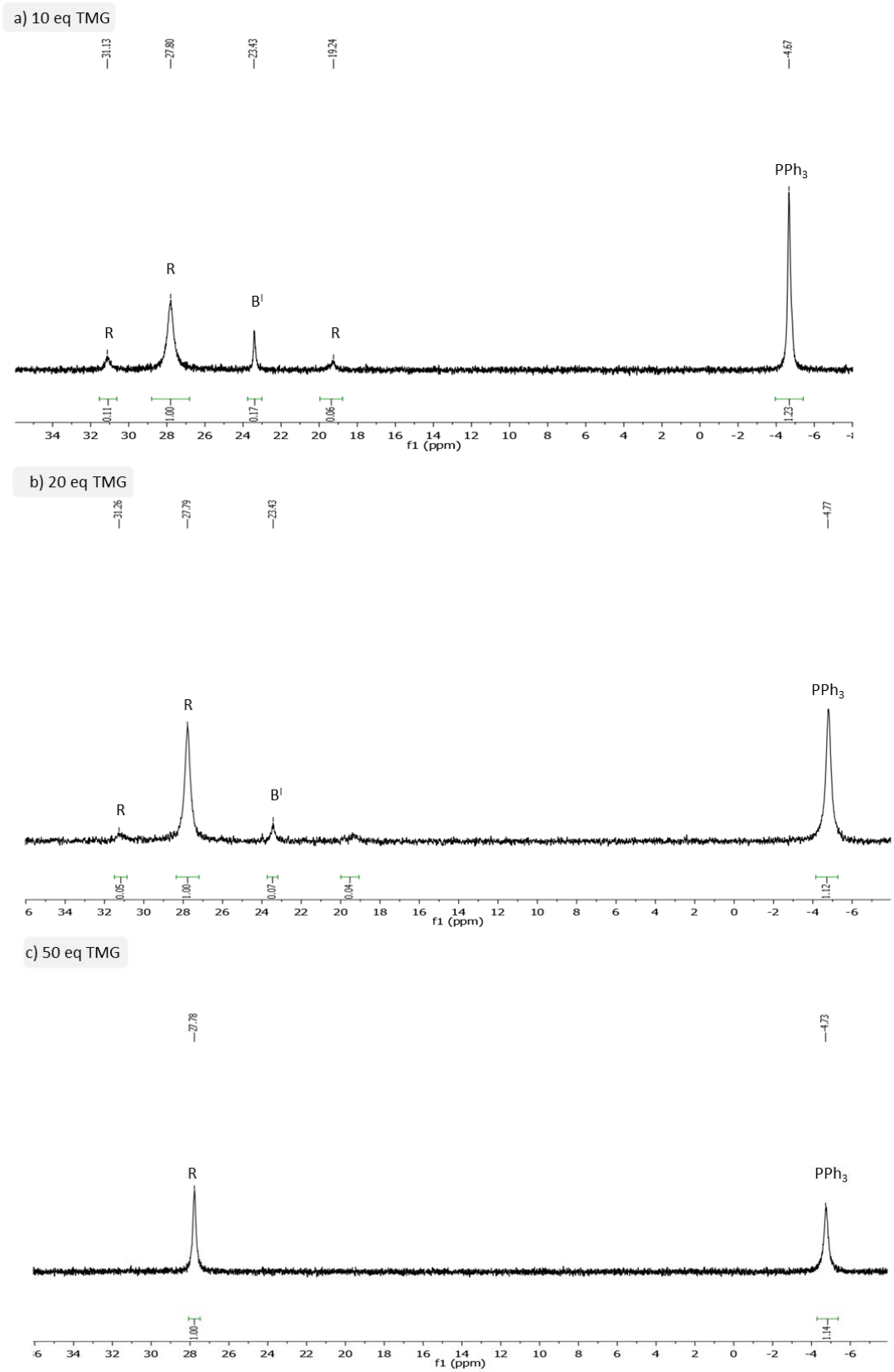


Figure S107. ^{31}P NMR spectra in DMF-d_7 of $\mathbf{B^{I}_{NO_2}}$ with TMG 10 eq (a); TMG 20 eq (b) and TMG 50 eq (c).

X=Bromide. Entry 5, Table S4

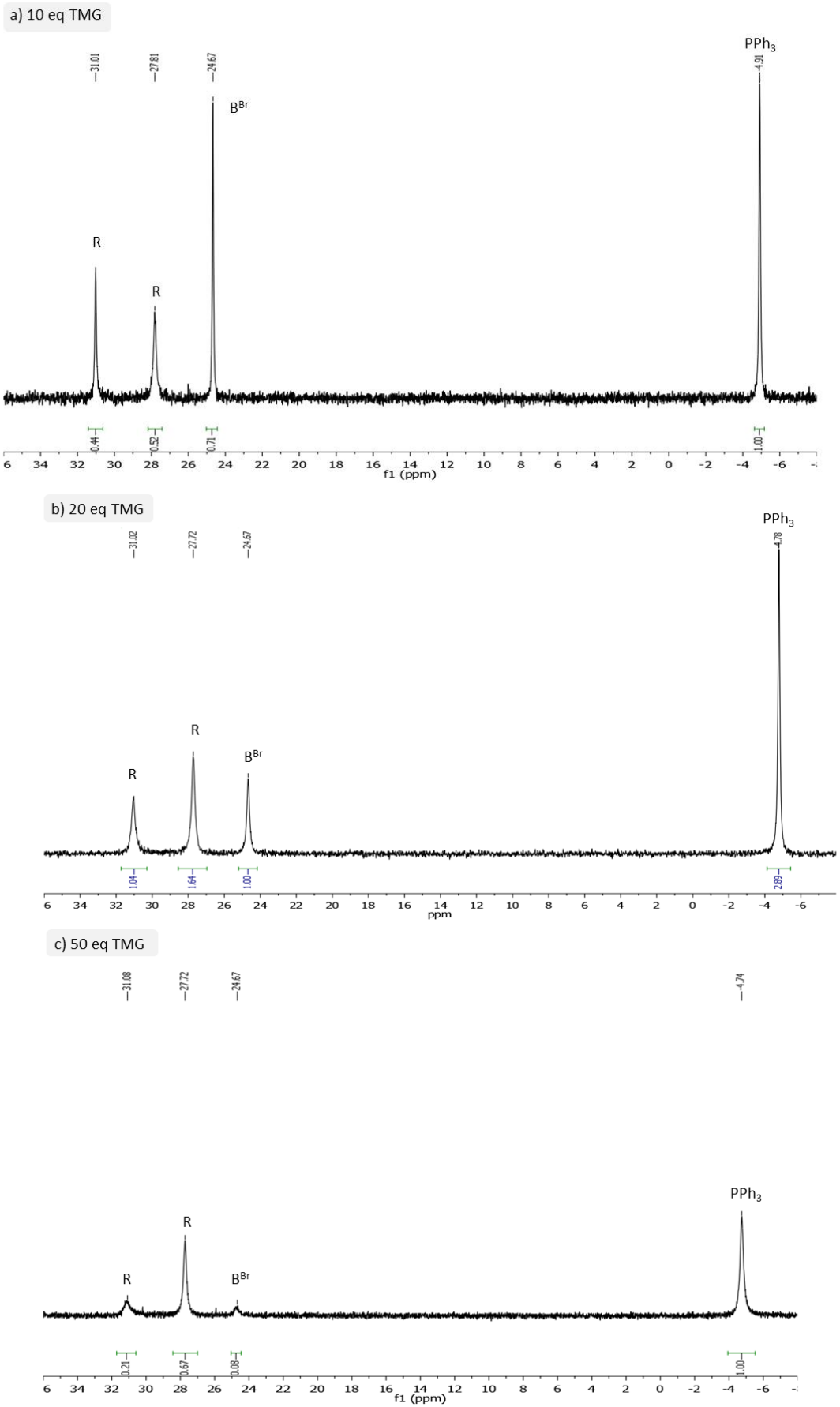


Figure S108. ^{31}P NMR spectra in DMF-d_7 of $\mathbf{B^{Br}_{NO_2}}$ with TMG 10 eq (a); TMG 20 eq (b) and TMG 50 eq (c).

X=Chloride. Entry 6, Table S4

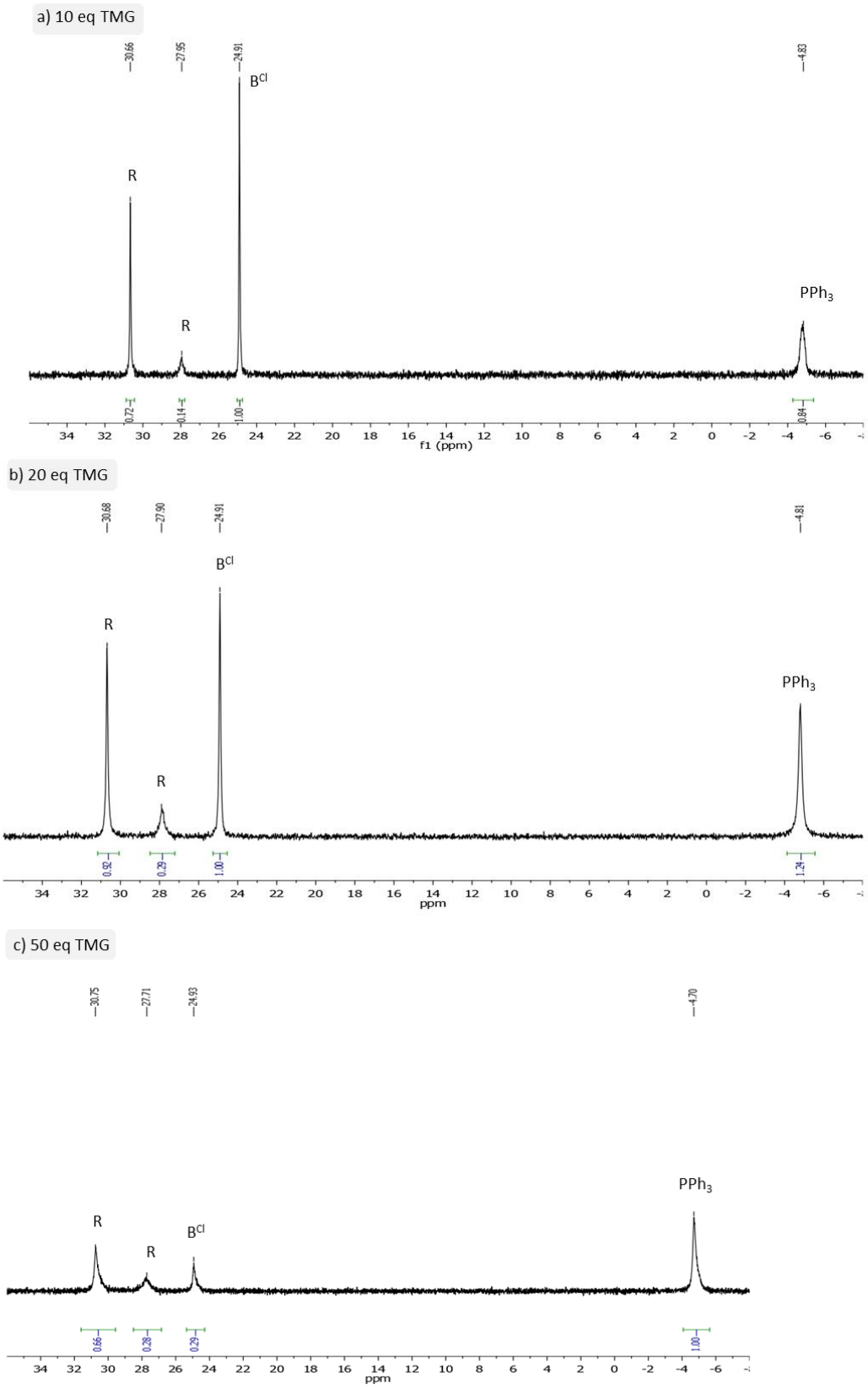


Figure S109. ^{31}P NMR spectra in DMF-d_7 of $\mathbf{B^{Cl}_{NO_2}}$ with TMG 10 eq (a); TMG 20 eq (b) and TMG 50 eq (c).

9.3. TEA ($B^{X}_{NO_2}$). Entries 7-9, Table S4

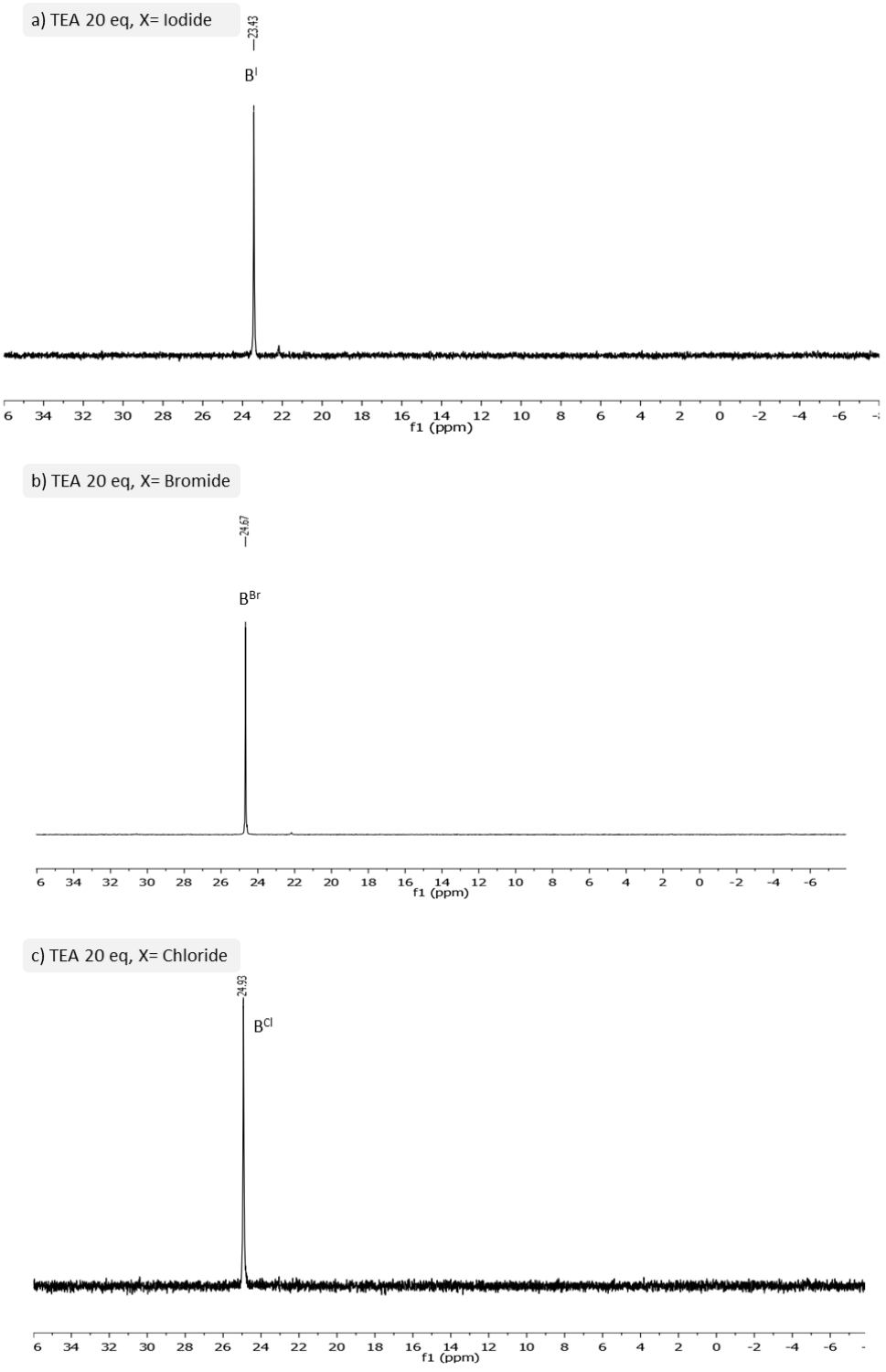
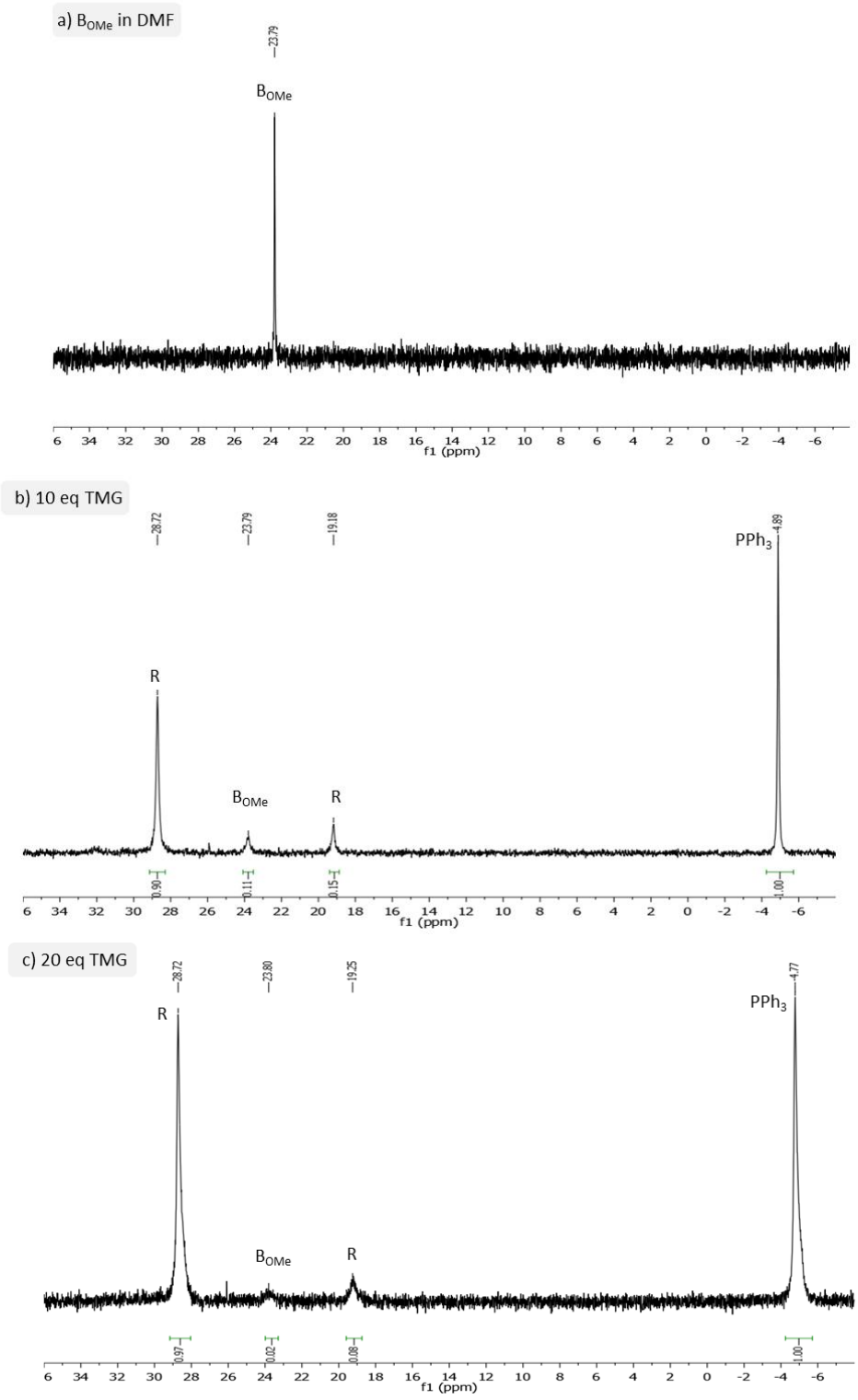


Figure S110. ^{31}P NMR spectra in DMF-d_7 TEA 20 eq of $\mathbf{B^{I}_{NO_2}}$(a); $\mathbf{B^{Br}_{NO_2}}$ (b); $\mathbf{B^{Cl}_{NO_2}}$ (c).

9.4. TMG (B^{I}_{OMe}). Entry 10, Table S4



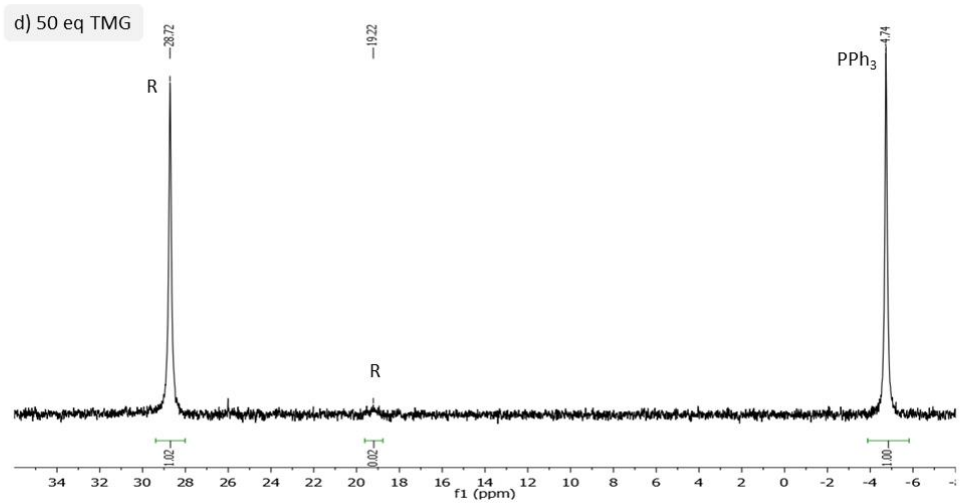


Figure S111. ^{31}P NMR spectra in DMF-d_7 of $\mathbf{B^{I}_{OMe}}$(a); with TMG 10 eq (b); TMG 20 eq (c) and TMG 50 eq (d).

10. Evaluation of the Kinetic Constants

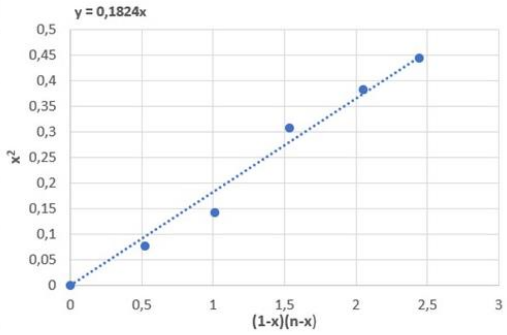
General procedure[7]

The equilibrium constant Keq=[Ligand][Σ**R**]/[**B**][base] was determined in DMF-d_7 by ^{31}P NMR spectroscopy. To evaluate Keq for the compounds $\mathbf{B^{Br}}$ and $\mathbf{B^{Cl}}$, the amine was added in the range of 10-50 equivalents, whereas the amount of base was lowered in case of $\mathbf{B^{I}}$, due to the high tendency to produce **R**. By considering [Ligand]=[Σ**R**], the formula becomes $Keq= x^2/(1-x)(n-x)$ where n is the number of equivalents of base added to **B**, x is the molar fraction of **R** in the equilibrium $x=2z_L/(z_B + 2z_L)$ and z_L and z_B are the magnitude of the ligand and **B** respectively. Keq was determined from the slope of the straight line obtained by the plot of x^2 versus $(1-x)(n-x)$. All experiments were repeated three times.

10.1. Pyrrolidine ($\mathbf{B^{X}_{NO_2}}$)

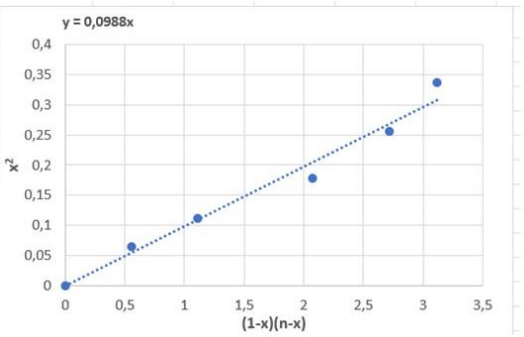
X=Iodide (**Table S5**, Entry 1)

eq	$x=2z_L/(z_B+2z_L)$	x^2	1-x	n-x	(1-x)(n-x)	Keq
		0			0	
1	0,275862069	0,07609988	0,72414	0,72414	0,5243757	0,14512
2	0,37530463	0,14085357	0,6247	1,6247	1,0149397	0,13878
4	0,553868402	0,30677021	0,44613	3,44613	1,5374282	0,19953
6	0,61878453	0,3828943	0,38122	5,38122	2,0514026	0,18665
8	0,666666667	0,44444444	0,33333	7,33333	2,4444444	0,18182



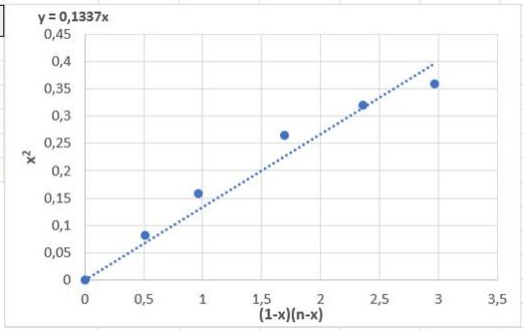
X=Bromide (**Table S5**, Entry 2)

eq	x=2z$_L$/(z$_B$+2z$_L$)	x^2	1-x	n-x	(1-x)(n-x)	Keq
		0			0	
1	0,253275109	0,06414828	0,74672	0,74672	0,5575981	0,11504
2	0,333333333	0,11111111	0,66667	1,66667	1,1111111	0,1
4	0,421234201	0,17743825	0,57877	3,57877	2,0712672	0,08567
6	0,505231689	0,25525906	0,49477	5,49477	2,7186372	0,09389
8	0,579545455	0,33587293	0,42045	7,42045	3,1199638	0,10765



X=Chloride (**Table S5** ,Entry 3)

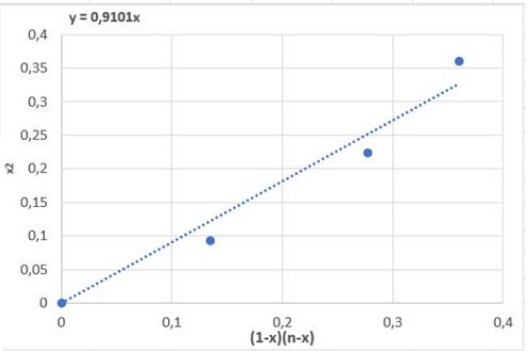
eq	x=2z$_L$/(z$_B$+2z$_L$)	x^2	1-x	n-x	(1-x)(n-x)	Keq
		0			0	
1	0,286203942	0,0819127	0,7138	0,7138	0,5095048	0,16077
2	0,397435897	0,15795529	0,60256	1,60256	0,9656476	0,16357
4	0,514629437	0,26484346	0,48537	3,48537	1,6916963	0,15655
6	0,56527977	0,31954122	0,43472	5,43472	2,3625828	0,13525
8	0,599439776	0,35932804	0,40056	7,40056	2,9643701	0,12122



10.2. TMG ($B^{X}_{NO_2}$)

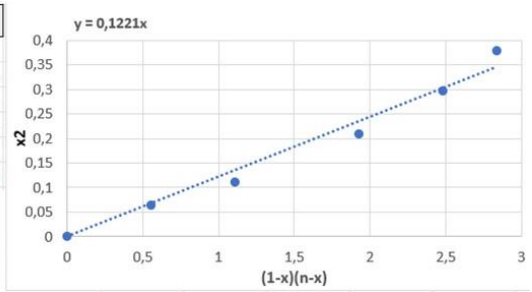
2a. X=Iodide (**Table S5**, Entry 4)

eq	x=2z$_L$/(z$_B$+2z$_L$)	x^2	1-x	n-x	(1-x)(n-x)	Keq
		0			0	
0,5	0,305659099	0,09342748	0,69434	0,19434	0,1349388	0,69237
1	0,473631993	0,22432726	0,52637	0,52637	0,2770633	0,80966
1,5	0,600027999	0,3600336	0,39997	0,89997	0,3599636	1,00019



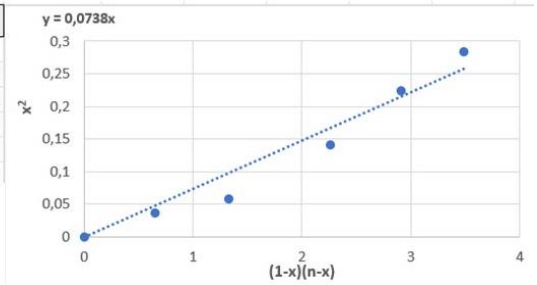
2b. X=Bromide (**Table S5**, Entry 5)

eq	x=2z$_L$/(z$_B$+2z$_L$)	x^2	1-x	n-x	(1-x)(n-x)	Keq
0		0			0	
1	0,253275109	0,06414828	0,74672	0,74672	0,5575981	0,11504
2	0,333333333	0,11111111	0,66667	1,66667	1,1111111	0,1
4	0,456790123	0,20865722	0,54321	3,54321	1,9247066	0,10841
6	0,545454545	0,29752066	0,45455	5,45455	2,4793388	0,12
8	0,615916955	0,3793537	0,38408	7,38408	2,8361011	0,13376



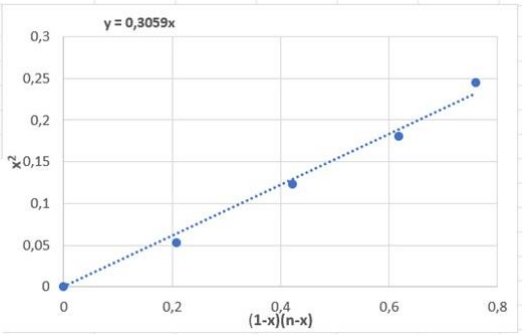
2c. X=Chloride (**Table S5**, Entry 6)

eq	$x=2z_L/(z_B+2z_L)$	x^2	1-x	n-x	(1-x)(n-x)	Keq
		0			0	
1	0,193315266	0,03737079	0,80668	0,80668	0,6507403	0,05743
2	0,242530756	0,05882117	0,75747	1,75747	1,3312289	0,04419
4	0,37530463	0,14085357	0,6247	3,6247	2,2643304	0,06221
6	0,473748474	0,22443762	0,52625	5,52625	2,9081983	0,07717
8	0,532648569	0,2837145	0,46735	7,46735	3,4898774	0,0813



10.3. TMG (B^{I}_{OMe}). (Table S5, Entry 10)

eq	$x=2z_L/(z_B+2z_L)$	x^2	1-x	n-x	(1-x)(n-x)	Keq
		0			0	
0,5	0,230714791	0,05322931	0,76929	0,26929	0,2071571	0,25695
1	0,350651493	0,12295647	0,64935	0,64935	0,4216535	0,29161
1,5	0,42519685	0,18079236	0,5748	1,0748	0,6178002	0,29264
2	0,495109105	0,24513303	0,50489	1,50489	0,7598057	0,32263



11. Base effect on Triflate-OA complex

Procedure: The reaction was performed in an oven-dried NMR tube purged under nitrogen atmosphere. The complex $\mathbf{B_{NO_2}^{OTf}}$ (11.7 mg mg, 0.013 mmol, 1 eq) was dissolved in DMF-d_7 (0.60 mL) followed by the addition of the base. The base effect was evaluated using ^{31}P NMR technique.

11.1. TMG

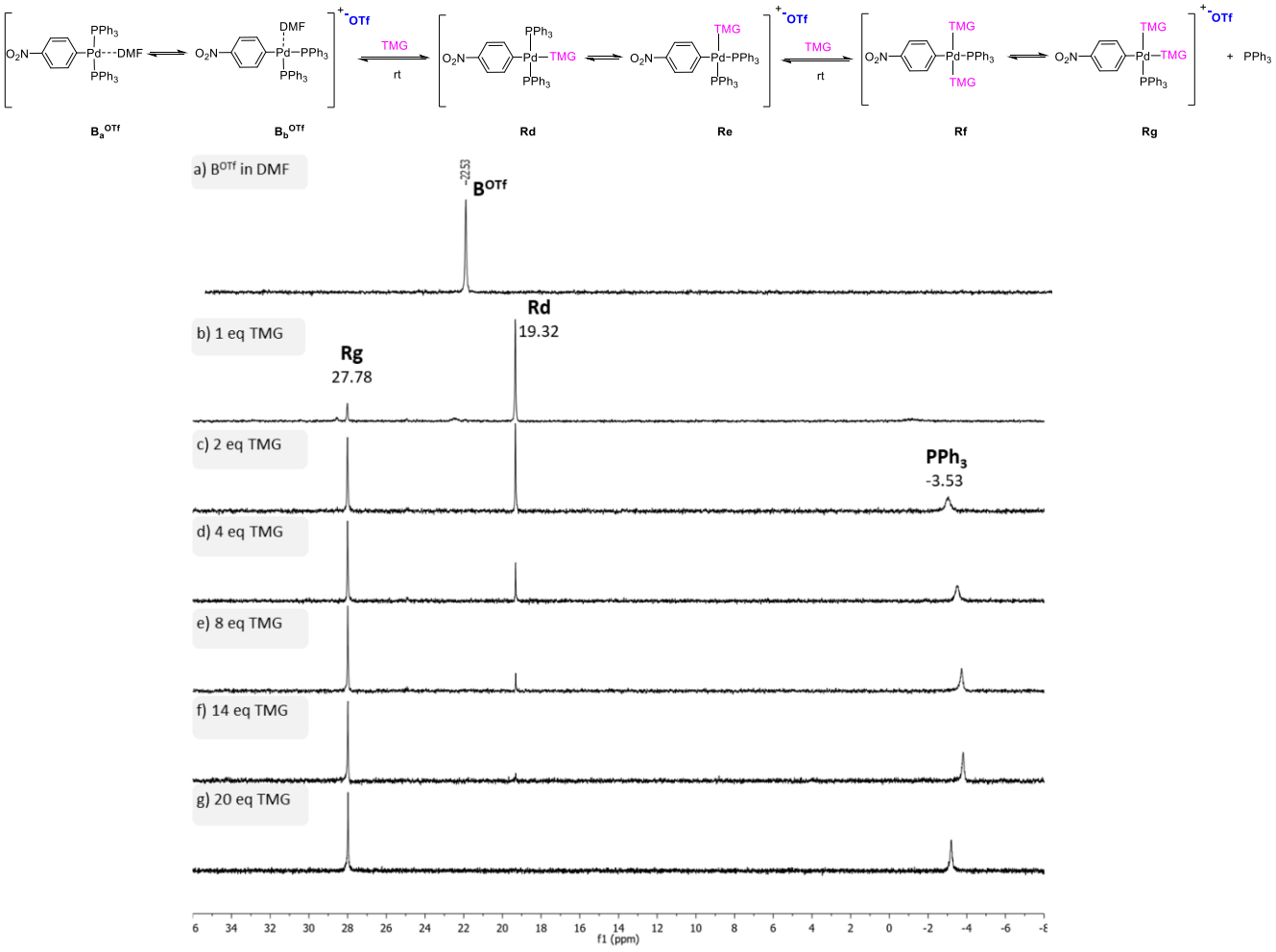
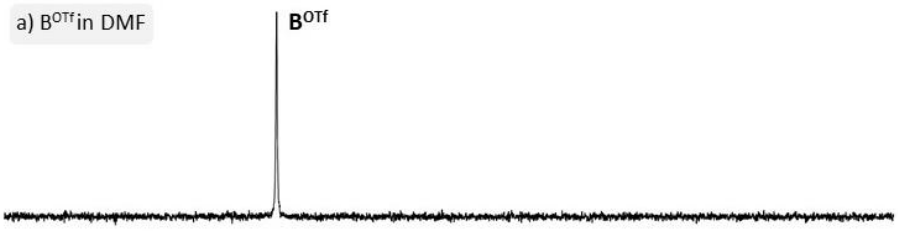


Figure S112. Stacking of ^{31}P NMR spectra in DMF-d_7 of $\mathbf{B_{NO_2}^{OTf}}$ (a); with the addition of TMG 1 eq (b); 2 eq (c); TMG 4 eq (d); TMG 8 eq (e); TMG 14 eq (f); TMG 20 eq (g).

11.2. TEA



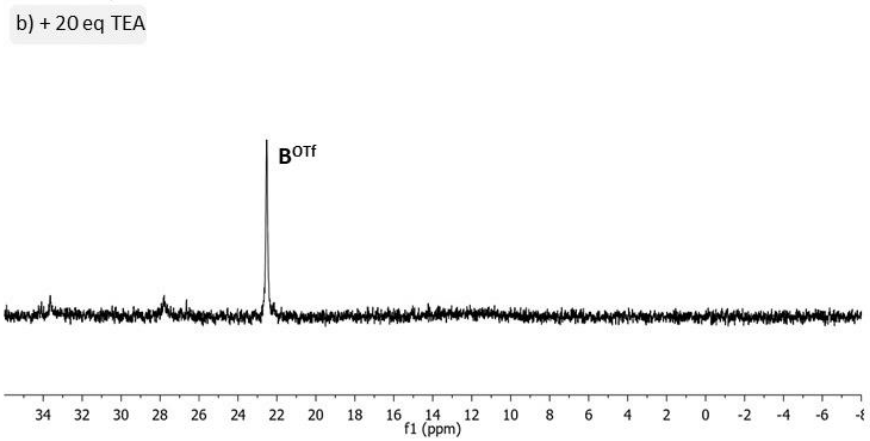
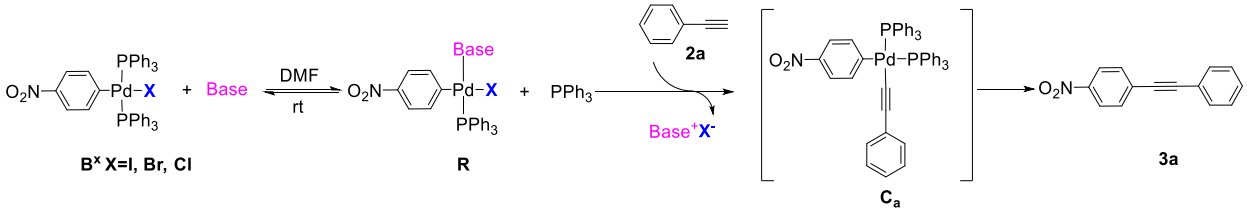


Figure S113. ^{31}P NMR spectra in DMF-d$_7$ of $\mathbf{B^{OTf}_{NO_2}}$ (a) and after the addition of 20 eq TEA (b).

12. The Addition of phenylacetylene

General procedure: The reaction was performed in an oven-dried NMR tube purged under nitrogen atmosphere. The complex $\mathbf{B^{X}_{NO_2}}$ (0.026 mmol, 1 eq) was dissolved in DMF-d$_7$ (0.60 mL) followed by the addition of the base (20-50 eq). The ^{31}P NMR were collected as soon as after the addition of **2a** (20-50eq) and after 10 minutes.



12.1. TMG

X=Iodide

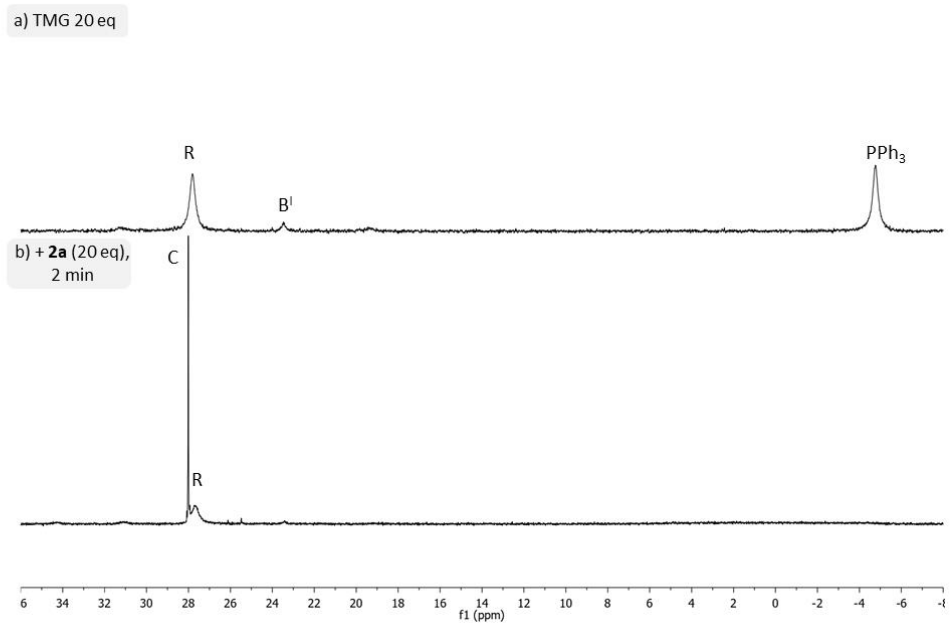


Figure S114. Stacking of ^{31}P NMR spectra in DMF-d_7 of $\mathbf{B^{I}_{NO_2}}$ after the addition of TMG 20 eq (a) and immediately after the following addition of **2a** 20eq (b).

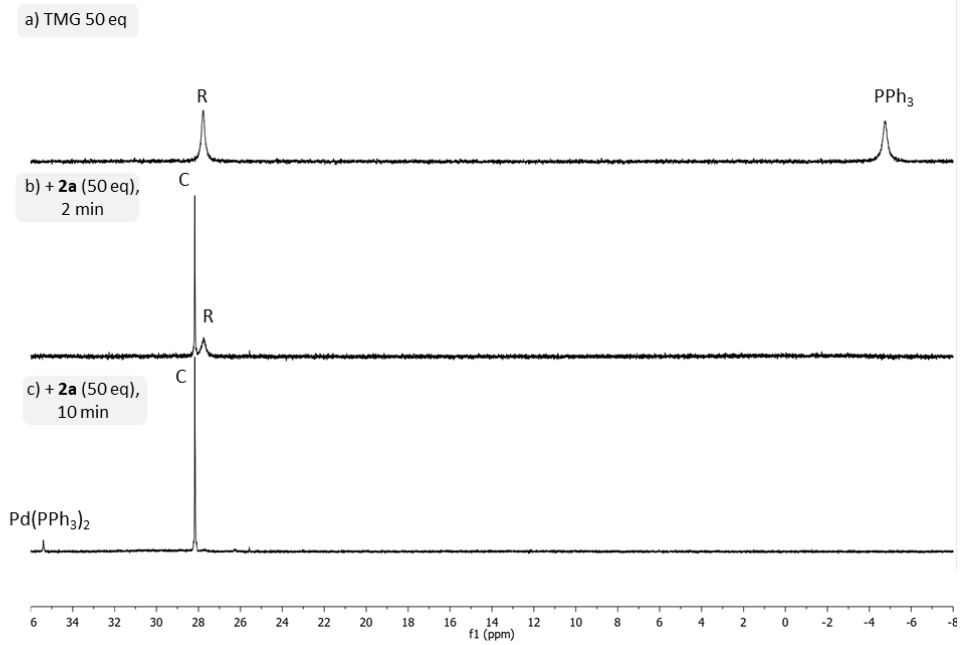


Figure S115. Stacking of ^{31}P NMR spectra in DMF-d_7 of $\mathbf{B^{I}_{NO_2}}$ after the addition of TMG 50 eq (a), immediately after the following addition of **2a** 50 eq (b) and after 10 minutes (c).

X=Bromide

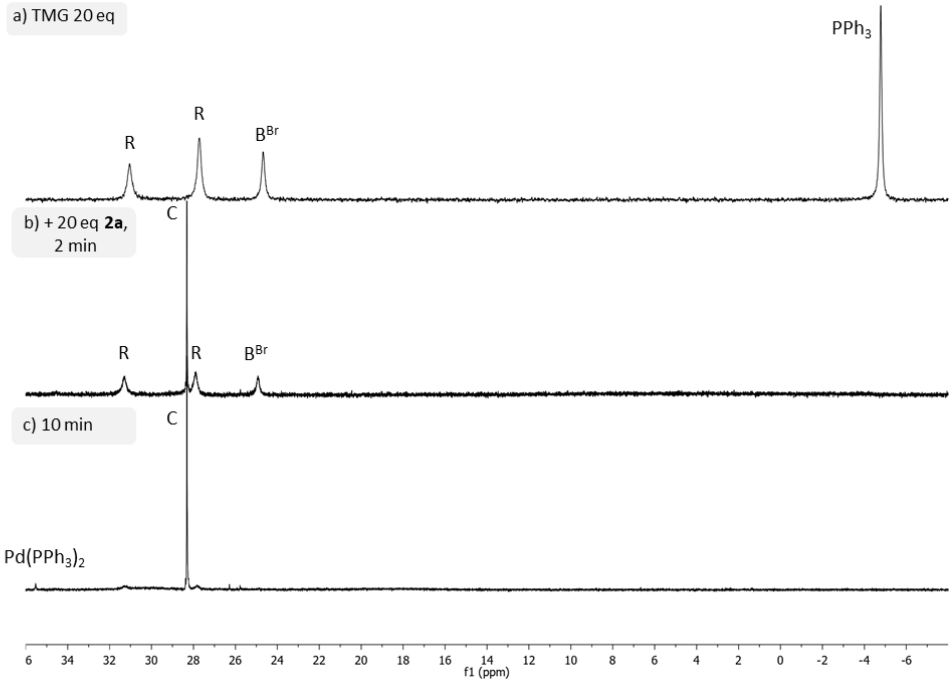


Figure S116. Stacking of ^{31}P NMR spectra in DMF-d_7 of $\mathbf{B^{Br}_{NO_2}}$ after the addition of TMG 20 eq (a), immediately after the following addition of **2a** 20 eq (b) and after 10 minutes (c).

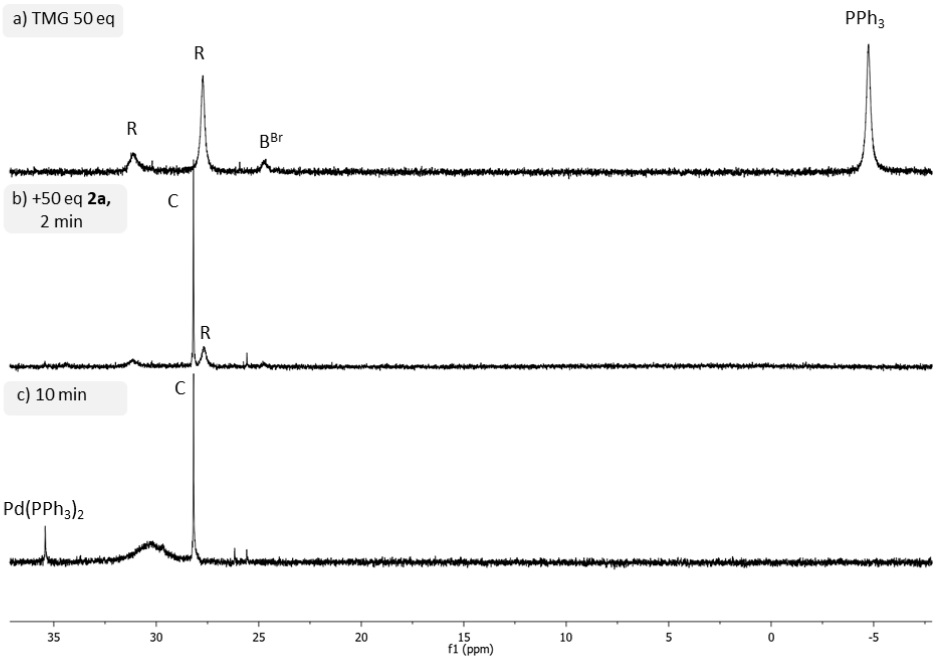


Figure S117. Stacking of ^{31}P NMR spectra in DMF-d_7 of $\mathbf{B^{Br}_{NO_2}}$ after the addition of TMG 50 eq (a), immediately after the following addition of **2a** 50 eq (b) and after 10 minutes (c).

X=Chloride

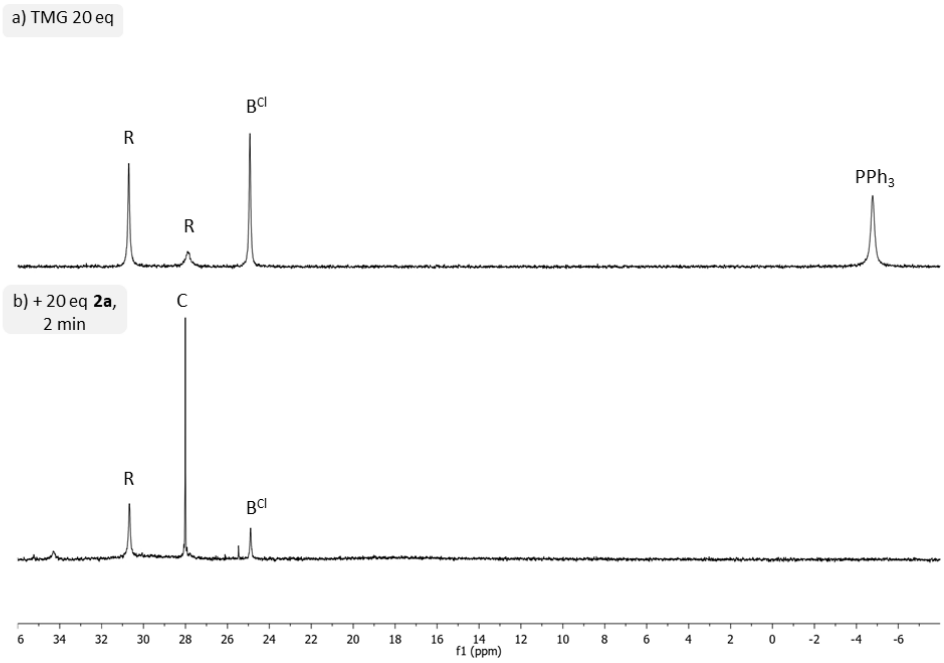


Figure S118. Stacking of ^{31}P NMR spectra in DMF-d$_7$ of $\mathbf{B^{Cl}_{NO_2}}$ after the addition of TMG 20 eq (a), and immediately after the following addition of **2a** 20 eq (b).

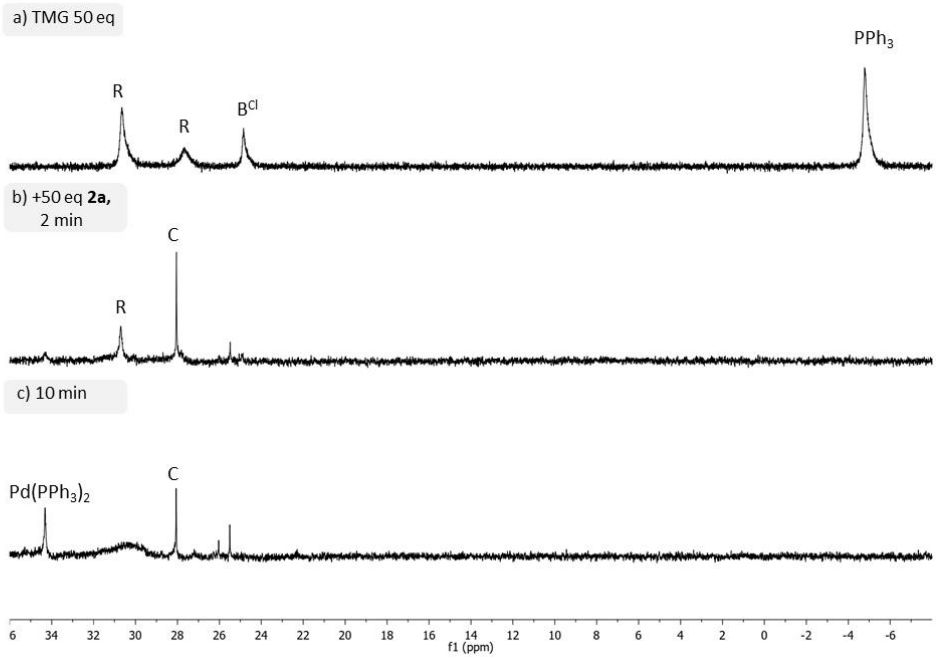


Figure S119. Stacking of ^{31}P NMR spectra in DMF-d$_7$ of $\mathbf{B^{Cl}_{NO_2}}$ after the addition of TMG 50 eq (a), immediately after the following addition of **2a** 50 eq (b) and after 10 minutes (c).

12.2. Pyrrolidine

X= Iodide

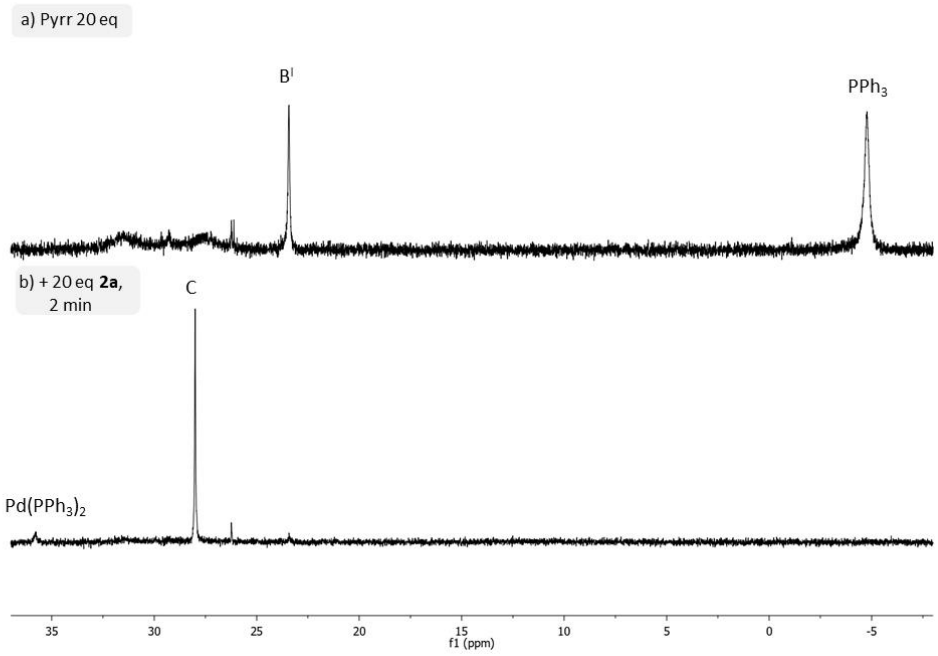


Figure S120. Stacking of ^{31}P NMR spectra in DMF-d$_7$ of $\mathbf{B^{I}_{NO_2}}$ after the addition of pyrrolidine 20 eq (a) and immediately after the following addition of **2a** 20 eq (b).

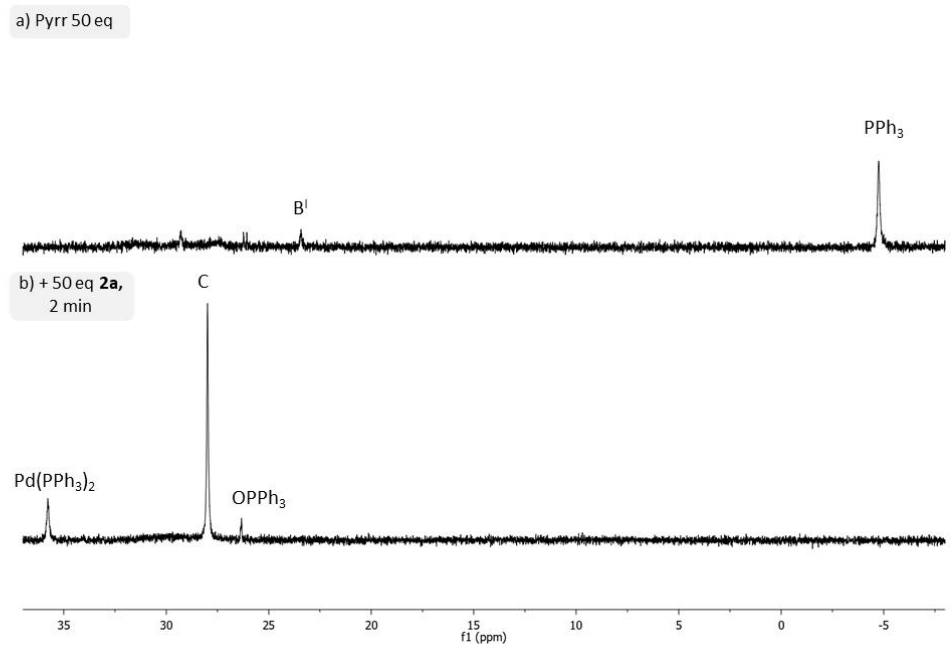


Figure S121. Stacking of ^{31}P NMR spectra in DMF-d$_7$ of $\mathbf{B^{I}_{NO_2}}$ after the addition of pyrrolidine 50 eq (a) and immediately after the following addition of **2a** 50 eq (b).

X= Bromide

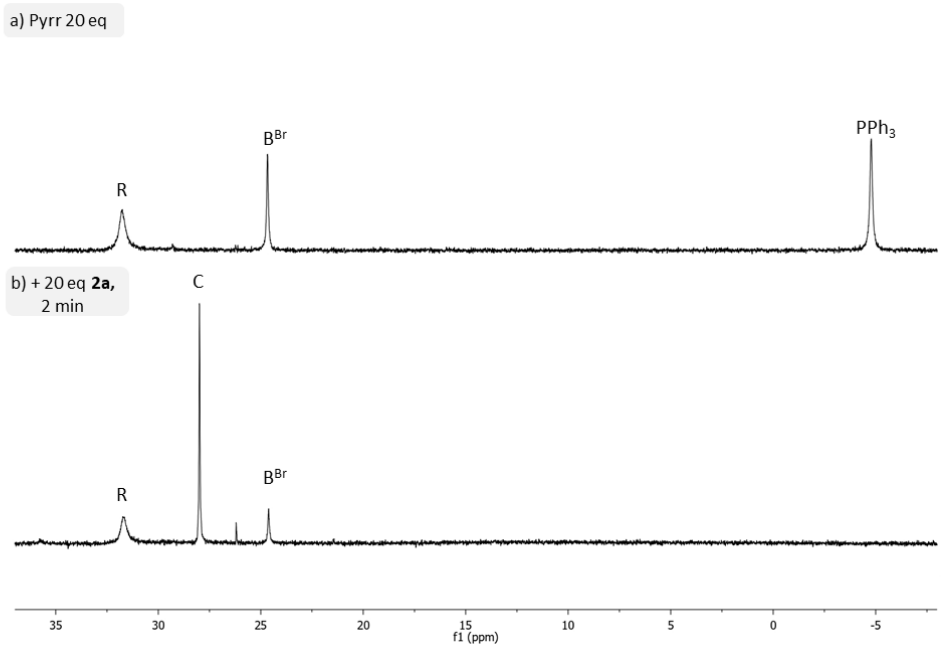


Figure S122. Stacking of ^{31}P NMR spectra in DMF-d_7 of $\mathbf{B^{Br}_{NO_2}}$ after the addition of pyrrolidine 20 eq (a) and immediately after the following addition of **2a** 20 eq (b).

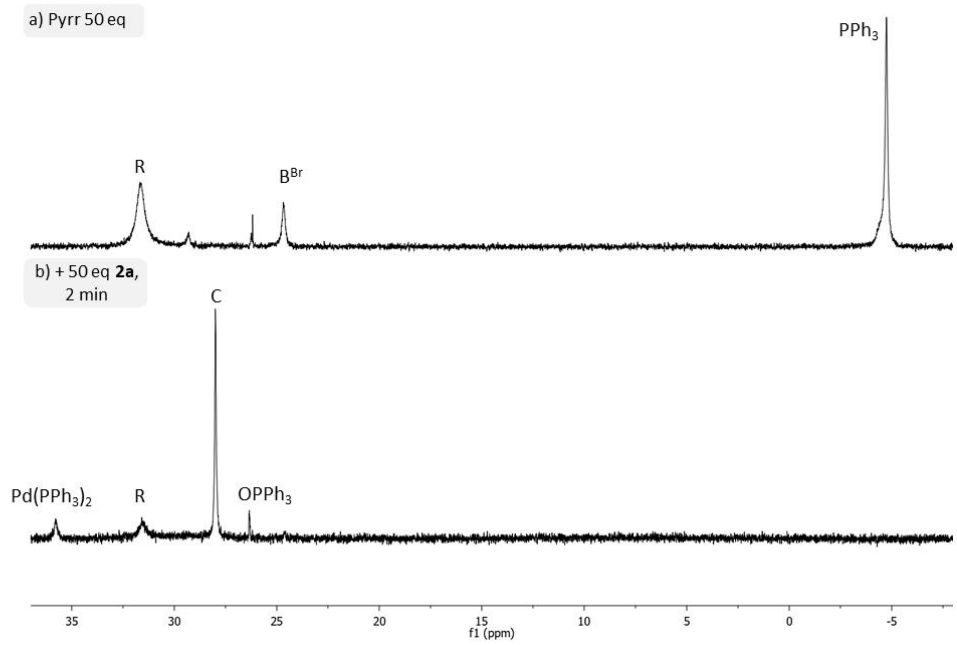


Figure S123. Stacking of ^{31}P NMR spectra in DMF-d_7 of $\mathbf{B^{Br}_{NO_2}}$ after the addition of pyrrolidine 50 eq (a) and immediately after the following addition of **2a** 50 eq (b).

X= Chloride

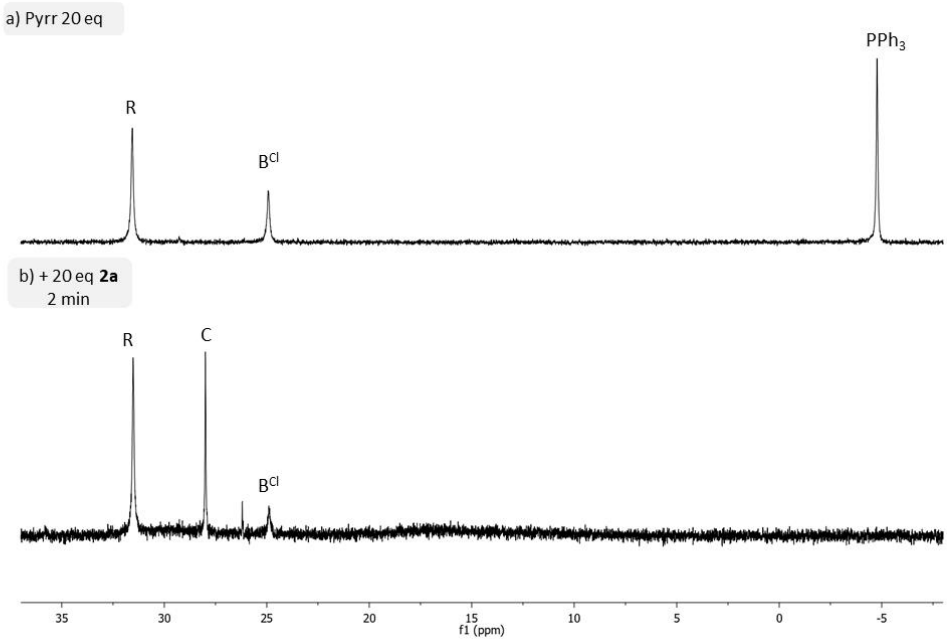


Figure S124. Stacking of ^{31}P NMR spectra in DMF-d$_7$ of $\mathbf{B^{Cl}_{NO_2}}$ after the addition of pyrrolidine 20 eq (a) and immediately after the following addition of **2a** 20 eq (b).

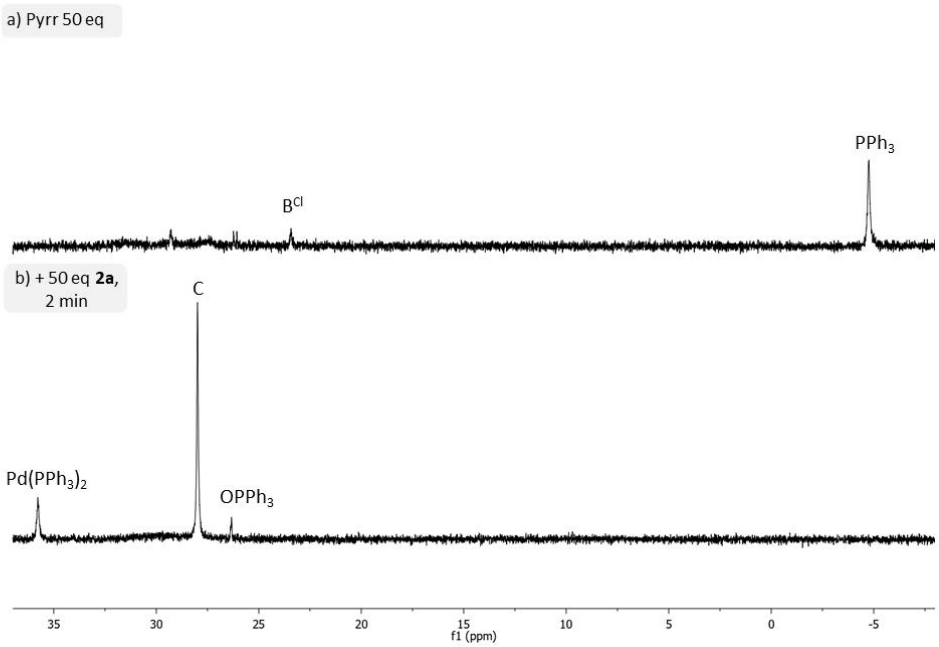


Figure S125. Stacking of ^{31}P NMR spectra in DMF-d$_7$ of $\mathbf{B^{Cl}_{NO_2}}$ after the addition of pyrrolidine 50 eq (a) and immediately after the following addition of **2a** 50 eq (b).

12.3. TEA (20 eq)

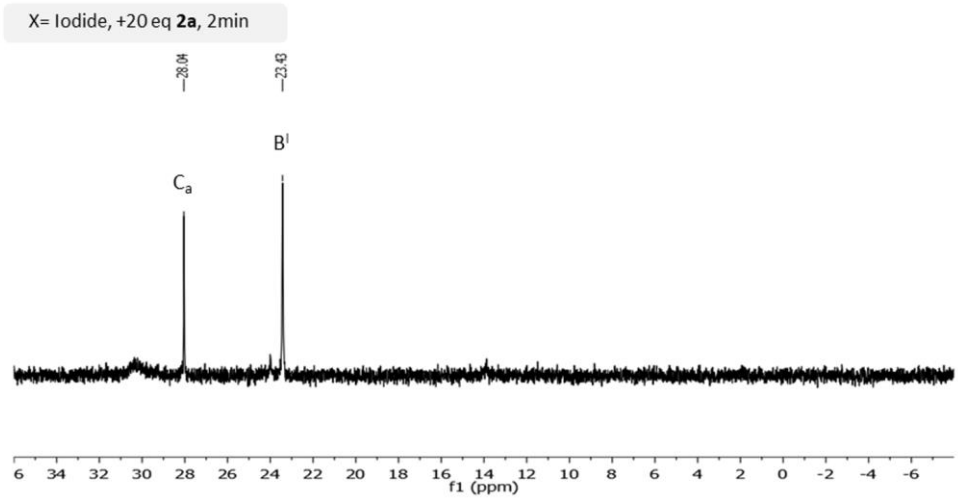


Figure S126. ^{31}P NMR spectra in DMF-d_7 of $\mathbf{B^{I}_{NO_2}}$ after the addition of TEA 20 eq immediately after the addition of **2a** 20 eq.

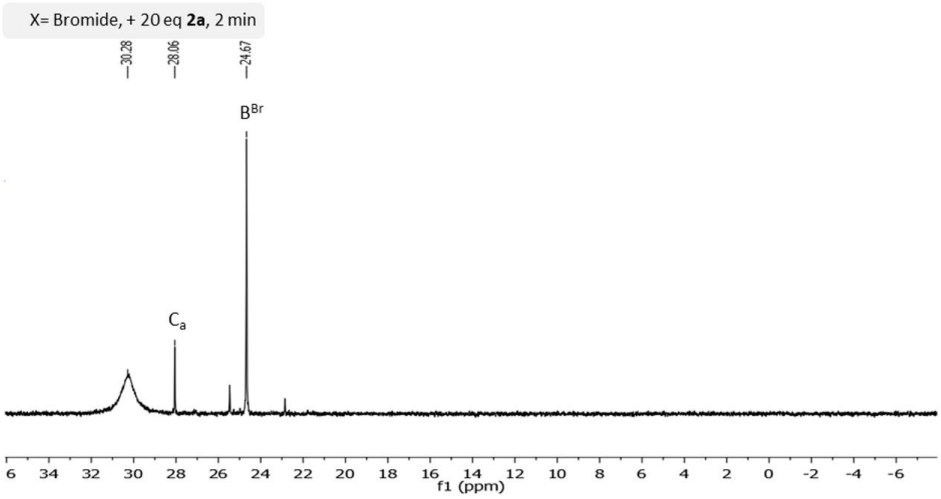


Figure S127. ^{31}P NMR spectra in DMF-d_7 of $\mathbf{B^{Br}_{NO_2}}$after the addition of TEA 20 eq immediately after the addition of **2a** 20 eq.

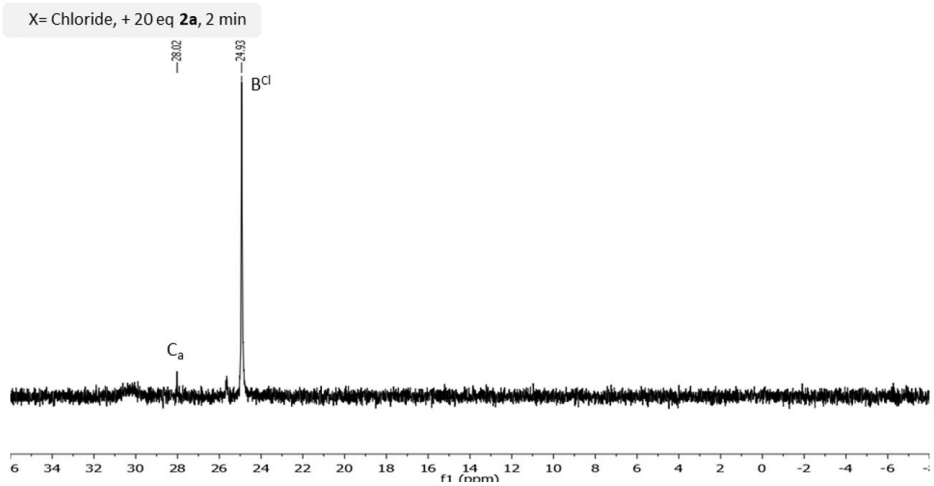


Figure S128. ^{31}P NMR spectra in DMF-d_7 of $\mathbf{B^{Cl}_{NO_2}}$ after the addition of TEA 20 eq immediately after the addition of **2a** 20 eq.

13. Scope of alkynes for the Direct Coordination step

General procedure: The reaction was performed in an oven-dried NMR tube purged under nitrogen atmosphere. The complex $\mathbf{B^{Br}_{NO_2}}$ (21.6 mg, 0.026 mmol, 1 eq) was dissolved in DMF-d_7 (0.60 mL) followed by the addition of TMG (65 µL, 0.52 mmol, 20 eq). The ^{31}P NMR were collected as soon as after the addition of **2a-l** (0.052 mmol, 20 eq). After 24h of stirring, the mixture was quenched with H_2O (1 mL) and extracted with cyclohexane or ethyl acetate (3x1 mL, ethyl acetate was used to extract product with hydroxyl group). Then, the collected organic phases were washed with brine, dried over anhydrous sodium sulfate (Na_2SO_4) and concentrated under reduced pressure. Finally, the crude was purified by flash chromatography (the eluent is specified below in Section 17 *"Compounds Characterization"*).

Scheme S2. Direct Coordination step with alkynes **2a-l**

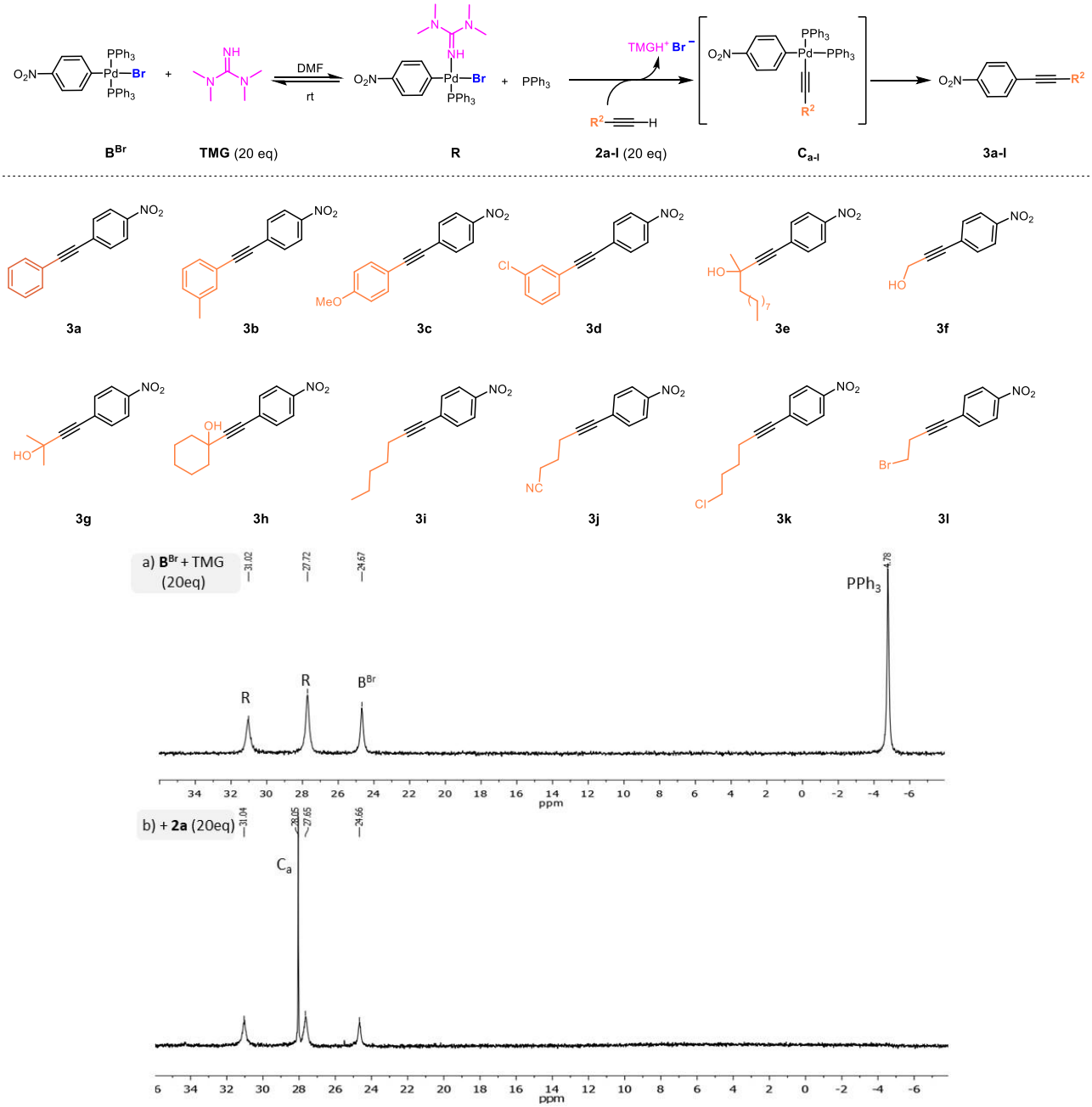


Figure S129. ^{31}P NMR spectra of $\mathbf{B^{Br}_{NO_2}}$ with TMG 20 eq (a) and immediately after the addition of phenylacetylene **2a** 20 eq.

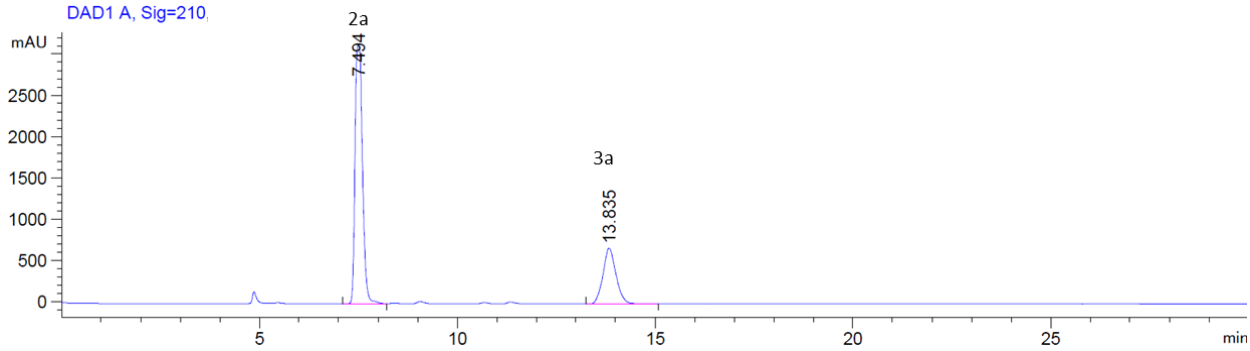


Figure S130. HPLC chromatogram after the extraction with cyclohexane of **3a**. Peak at 7,494 min = **2a**; peak at 13,835 min = **3a.**

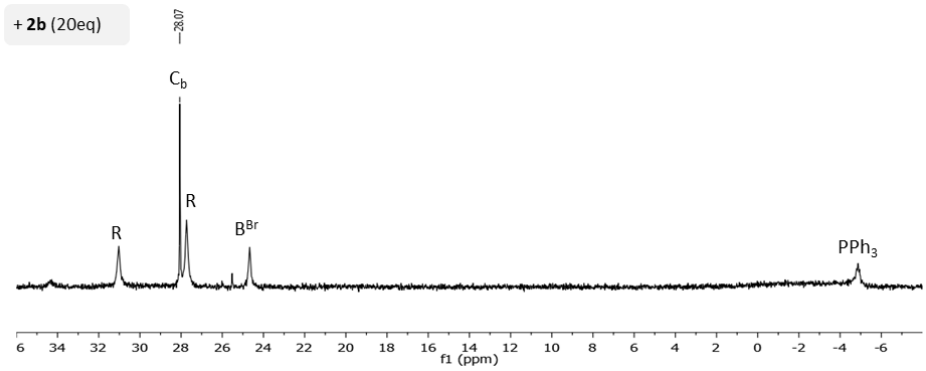


Figure S131. ^{31}P NMR spectrum of $\mathbf{B^{Br}_{NO_2}}$ with TMG 20 eq immediately after the addition of 3-Methylphenylacetylene **2b** 20 eq.

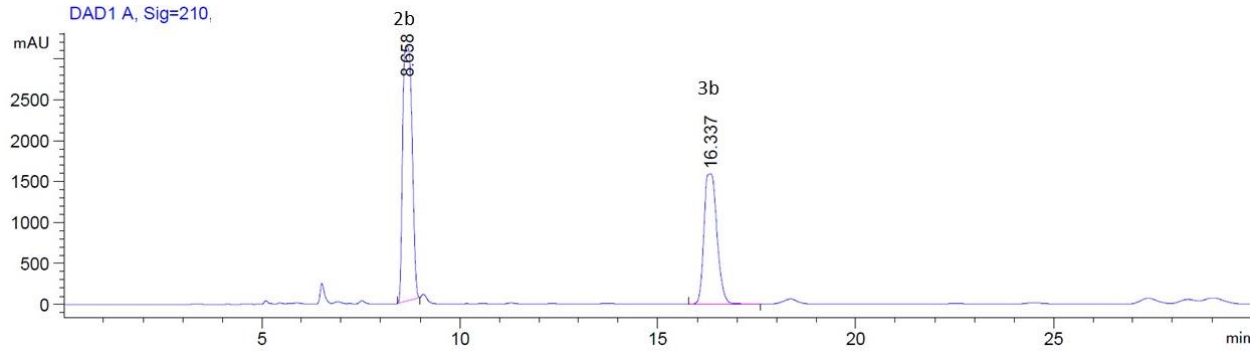


Figure S132. HPLC chromatogram after the extraction with cyclohexane of **3b**. Peak at 8.658 min = **2b**; peak at 16,337 min = **3b**.

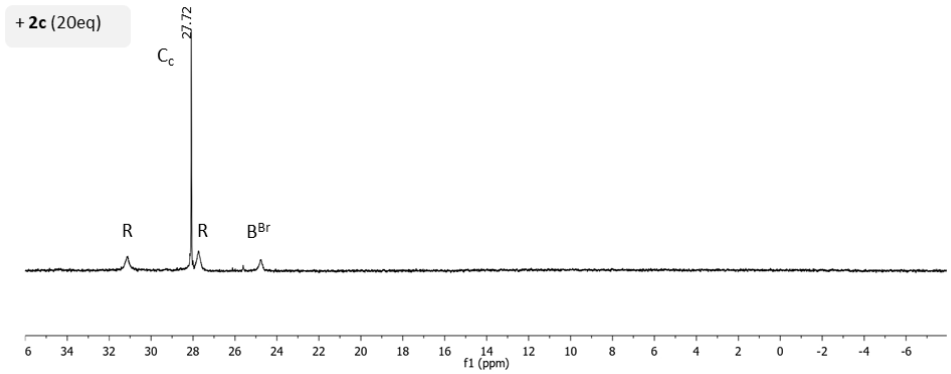


Figure S133. ^{31}P NMR spectrum of $\mathbf{B^{Br}_{NO_2}}$ with TMG 20 eq immediately after the addition of 4-ethynylanisole **2c** 20 eq.

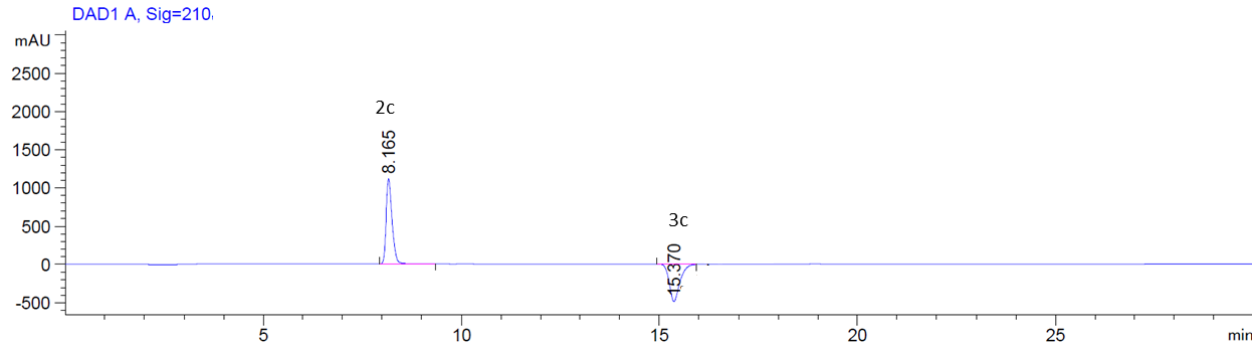


Figure S134. HPLC chromatogram after the extraction with cyclohexane of **3c**. Peak at 8.165 min = **2c**, peak at 15.370 min = **3c.**

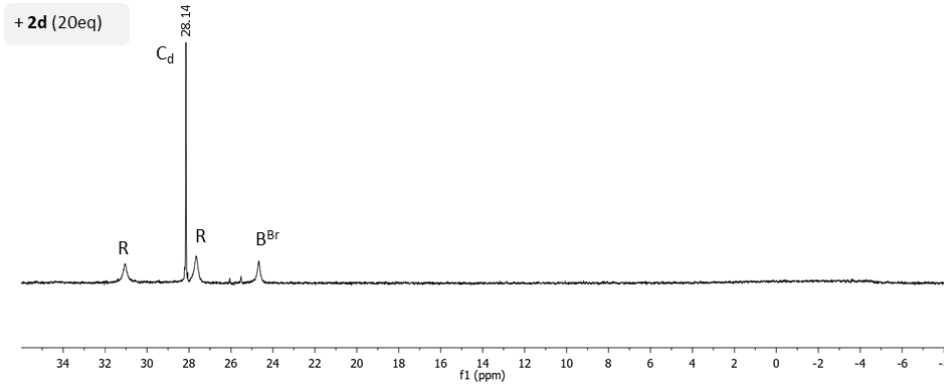


Figure S135. ^{31}P NMR spectrum of $\mathbf{B^{Br}_{NO_2}}$ with TMG 20 eq immediately after the addition of 3-Cloro-1-ethynylbenzene **2d** 20 eq.

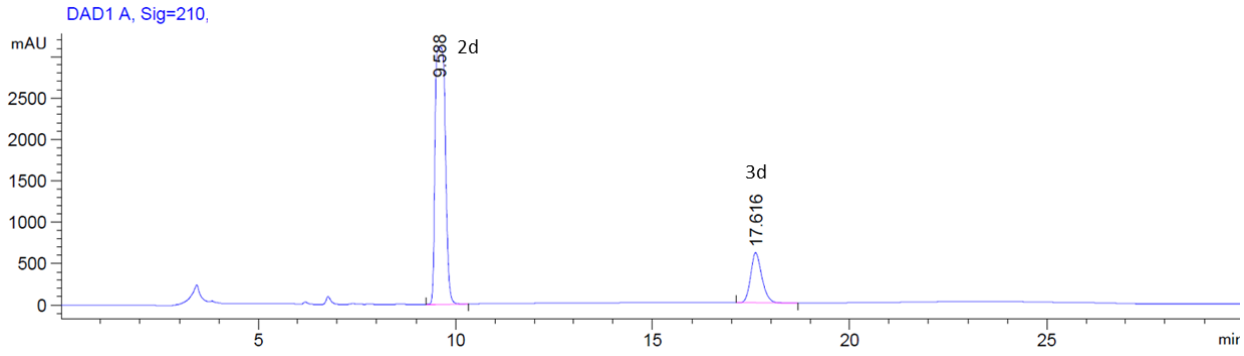


Figure S136. HPLC chromatogram after the extraction with cyclohexane of **3d**. Peak at 9,588 min = **2d**; peak at 17.616 min = **3d**.

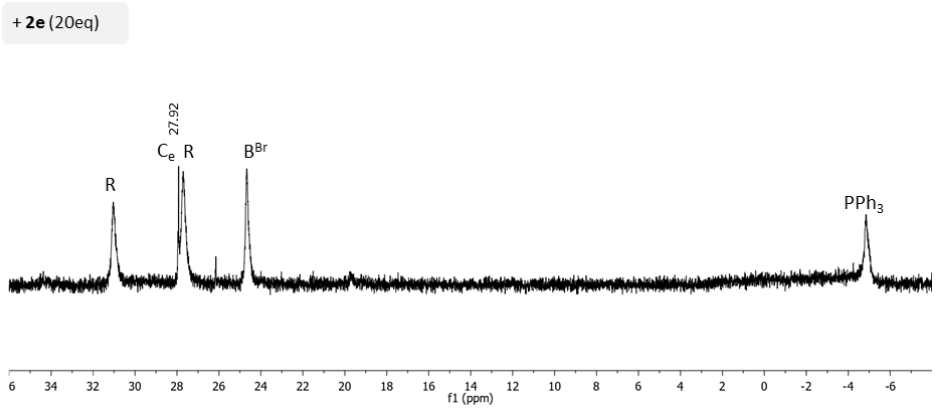


Figure S137. ^{31}P NMR spectrum of $\mathbf{B^{Br}_{NO_2}}$ with TMG 20 eq immediately after the addition of 3-Methyl-1-dodecyn-3-ol **2e** 20 eq.

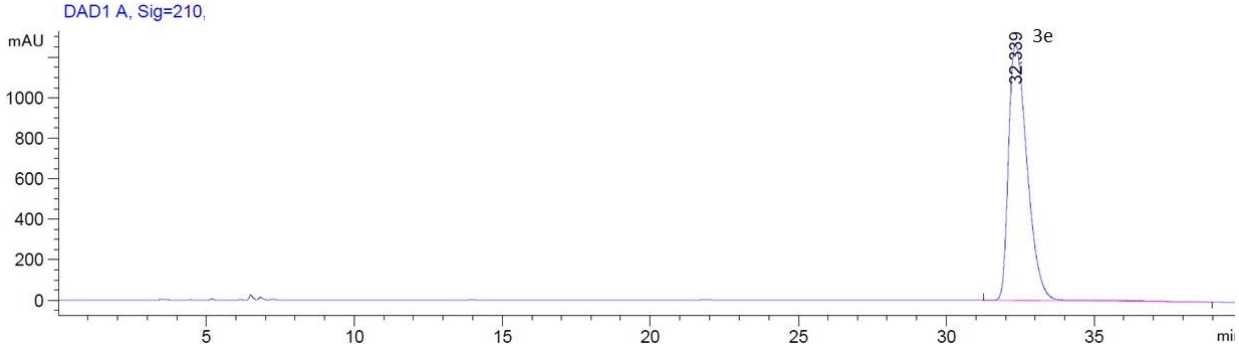


Figure S138. HPLC chromatogram after the extraction with ethyl acetate of **3e**. Peak at 32.339 min = **3e**. Mobile phase A: H_2O, mobile phase B: ACN. Gradient (Time(min), %B): 0, 80; 30, 80; 32, 10; 40, 10; flow 0.5 mL min^{-1} .

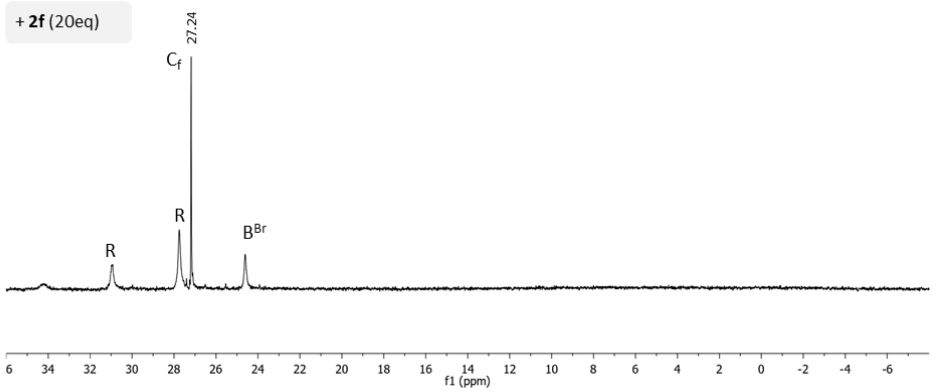


Figure S139. ^{31}P NMR spectrum of $\mathbf{B^{Br}_{NO_2}}$ with TMG 20 eq immediately after the addition of propargyl alcohol **2f** 20 eq.

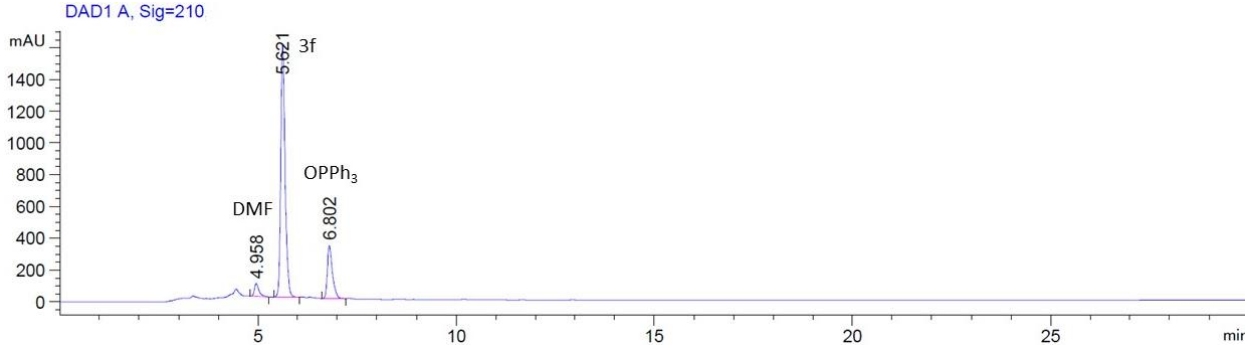


Figure S140. HPLC chromatogram after the extraction with ethyl acetate of **3f**. Peak at 4,958 min = DMF; peak at 5.621 min = **3f**; peak at 6.802 min = $OPPh_3$.

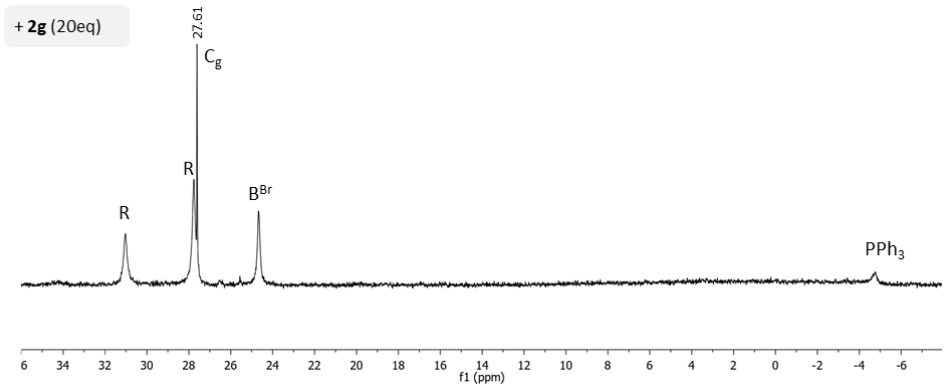


Figure S141. ^{31}P NMR spectrum of $\mathbf{B^{Br}_{NO_2}}$ with TMG 20 eq immediately after the addition of 2-Methyl-3-butyn-2-ol **2g** 20 eq.

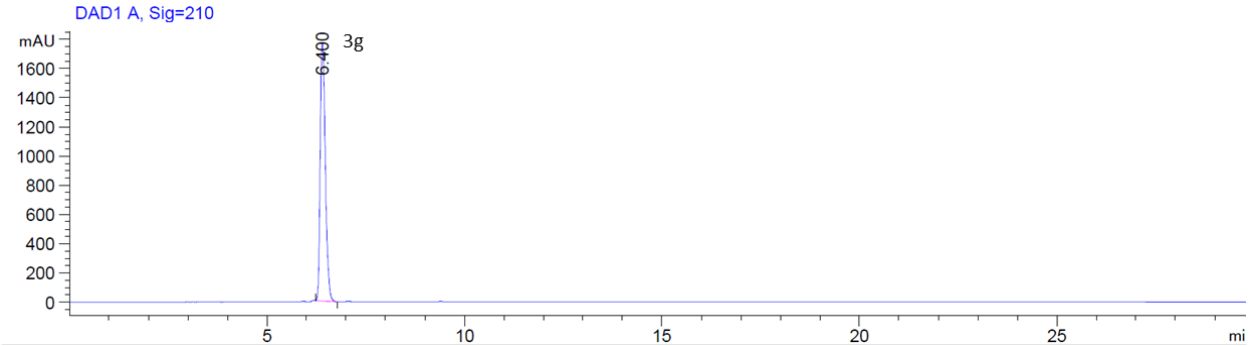


Figure S142. HPLC chromatogram after the extraction with ethyl acetate of **3g**. Peak at 6.400 min = **3g.**

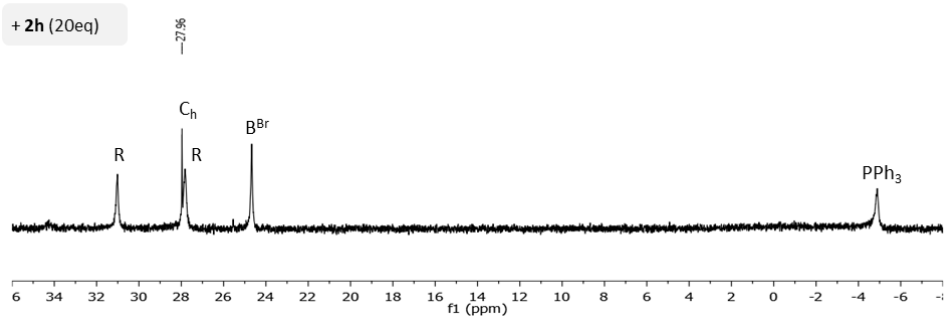


Figure S143. ^{31}P NMR spectrum of $\mathbf{B^{Br}_{NO_2}}$ with TMG 20 eq immediately after the addition of 1-ethynylcyclohexan-1-ol **2h** 20 eq.

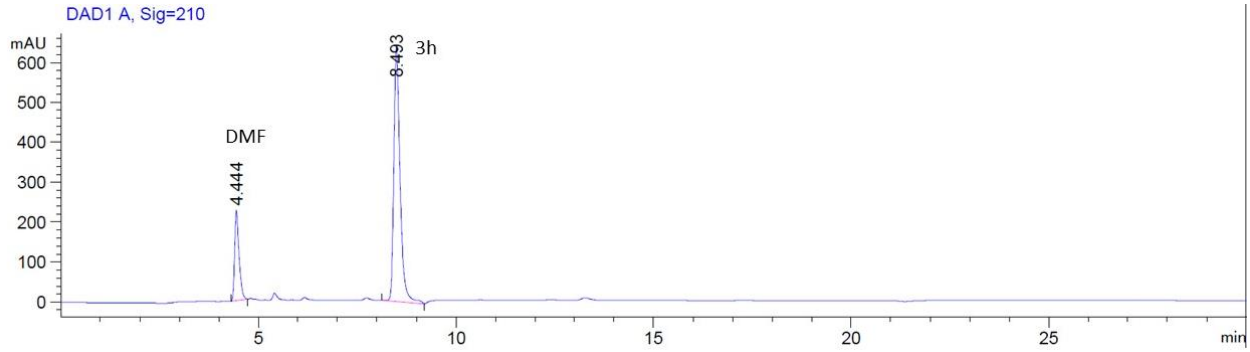


Figure S144. HPLC chromatogram after the extraction with ethyl acetate of **3h**. Peak at 4.444 min = DMF; peak at 8.493 min = **3h**.

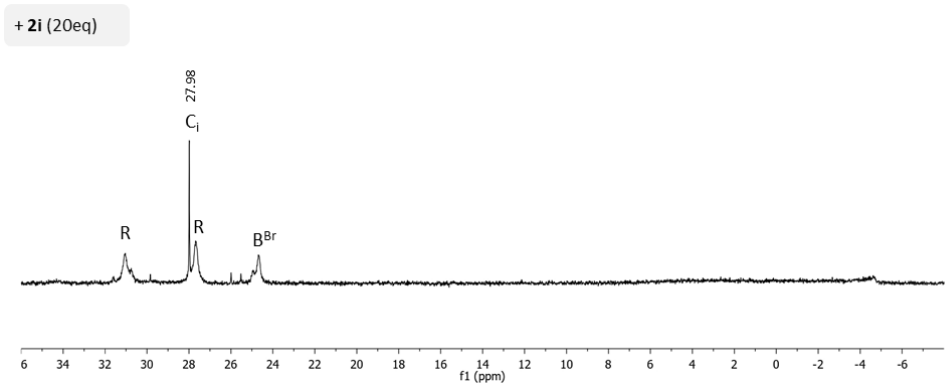


Figure S145. ^{31}P NMR spectrum of $\mathbf{B^{Br}_{NO_2}}$ with TMG 20 eq immediately after the addition of 1-Heptyne **2i** 20 eq.

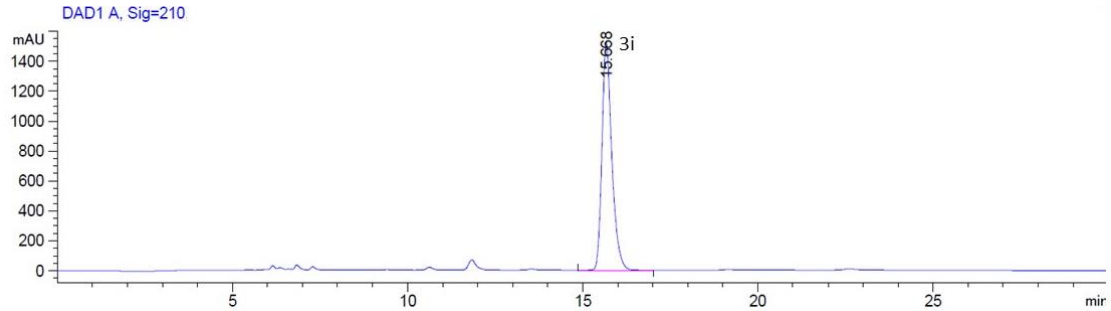


Figure S146. HPLC chromatogram after the extraction cyclohexane of **3i**. Peak at 15.668 min = **3i**.

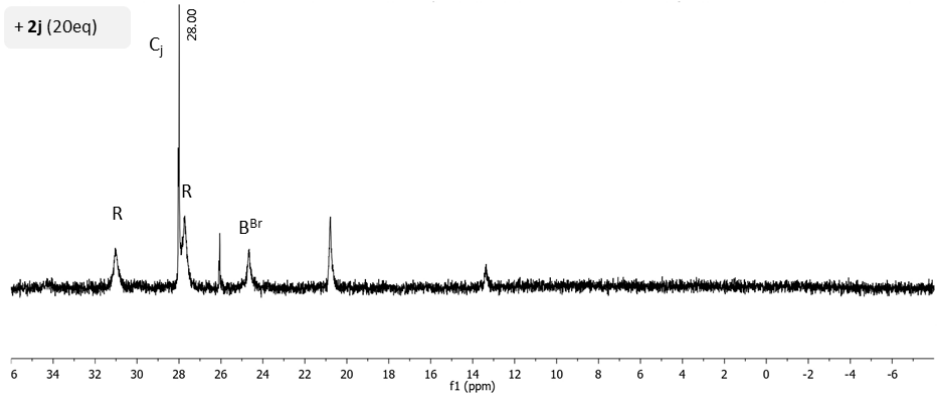


Figure S147. ^{31}P NMR spectrum of $\mathbf{B^{Br}_{NO_2}}$ with TMG 20 eq immediately after the addition of 5-Hexynenitrile **2j** 20 eq.

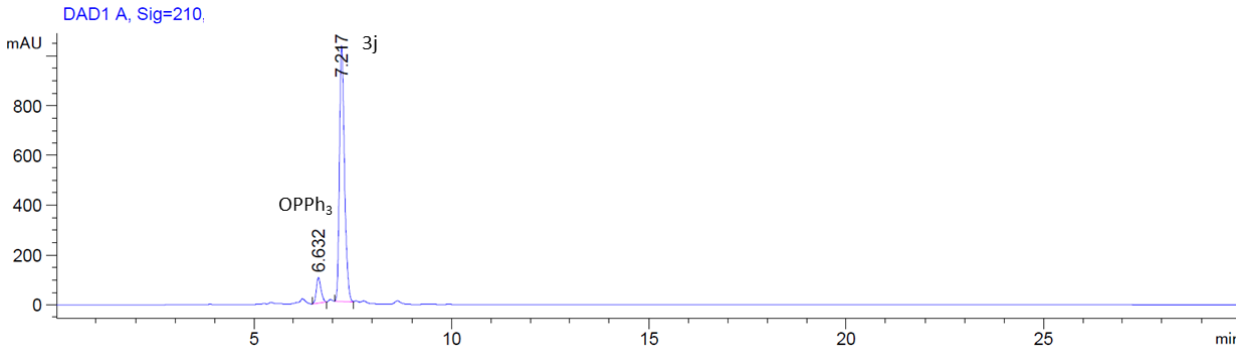


Figure S148. HPLC chromatogram after the extraction cyclohexane of **3j**. Peak at 6.632 min= $OPPh_3$, peak at 7.217 min = **3j.**

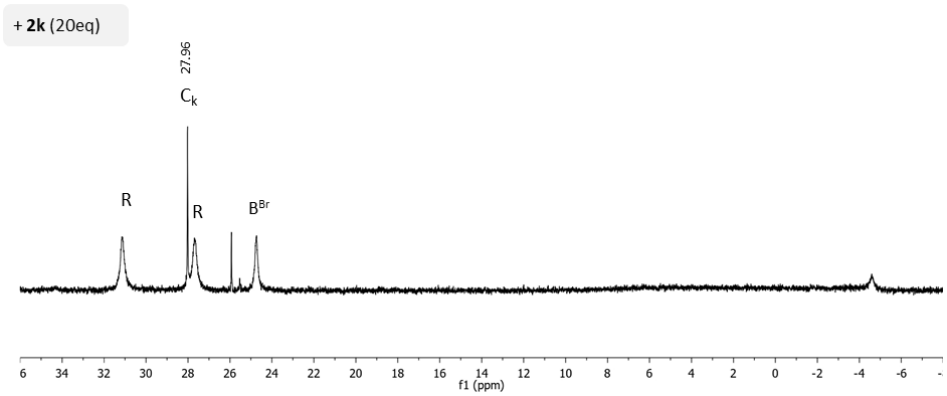


Figure S149. ^{31}P NMR spectrum of $\mathbf{B^{Br}_{NO_2}}$ with TMG 20 eq immediately after the addition of 6-Chloro-1-hexyne **2k** 20 eq.

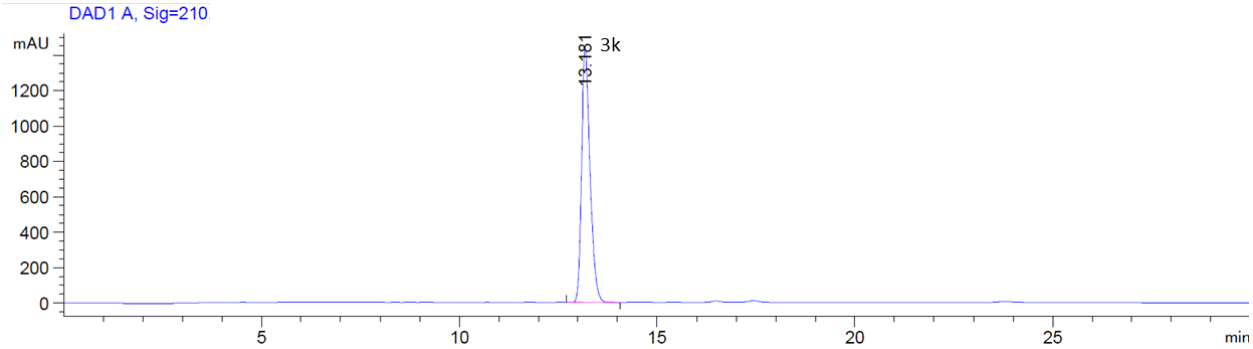


Figure S150. HPLC chromatogram after the extraction cyclohexane of **3k**. Peak at 13.181 min= **3k.**

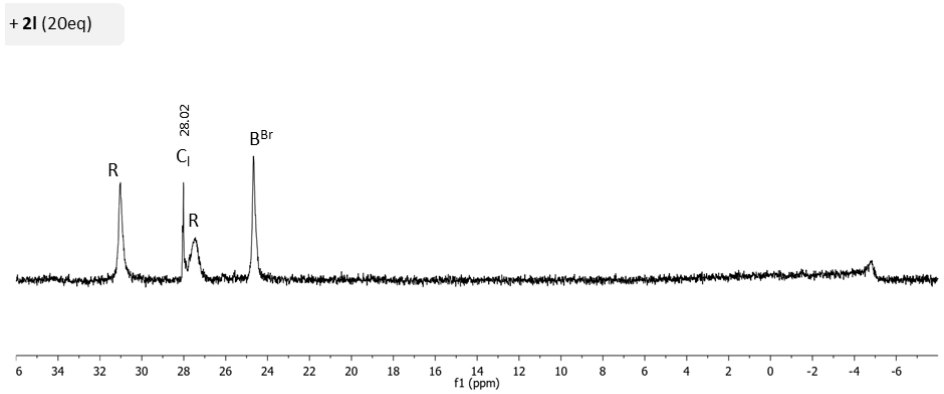


Figure S151. ^{31}P NMR spectrum of $\mathbf{B^{Br}_{NO_2}}$ with TMG 20 eq immediately after the addition of 4-Bromo-1-butyne **2l** 20 eq.

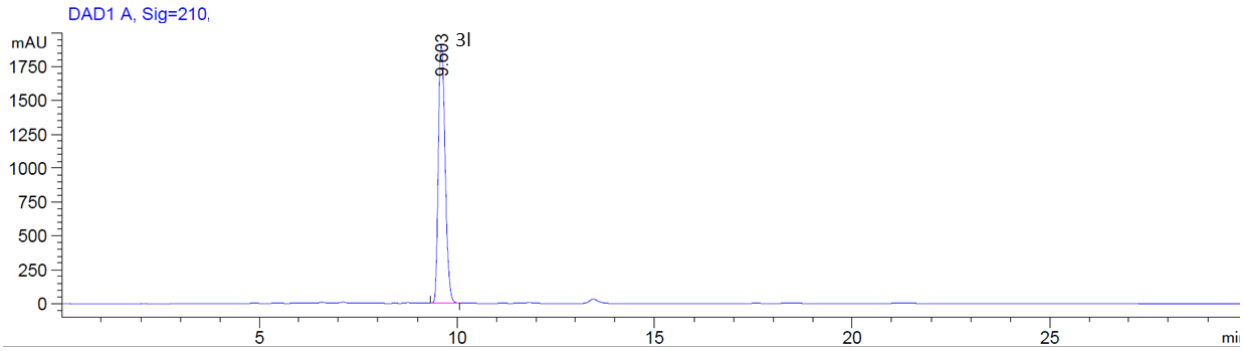
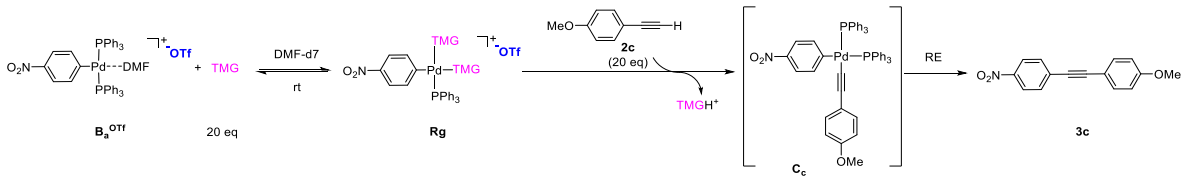


Figure S152. HPLC chromatogram after the extraction cyclohexane of **3l**. Peak at 9.603 min= **3l.**

14. Direct coordination step with the Triflate-AO complex

General procedure: The reaction was performed in an oven-dried NMR tube purged under nitrogen atmosphere. The complex $\mathbf{B_{NO_2}^{OTf}}$ (11.7 mg mg, 0.013 mmol, 1 eq) was dissolved in DMF-d_7 (0.60 mL) followed by the addition of TMG (33 µL, 0.26 mmol, 20 eq) and the following addition of 4-ethynylanisole **2c** (34 µL, 0.26 mmol, 20 eq). **2c** was chosen in this case, rather than phenylacetylene **2a** as in previous cases, to obtain a better separation between the peaks related to **C** and **Rg**. The ^{31}P NMR were collected immediately after the addition of **2c**.

Scheme S3. Direct coordination of **2c** onto AO-complex $\mathbf{B_{NO_2}^{OTf}}$



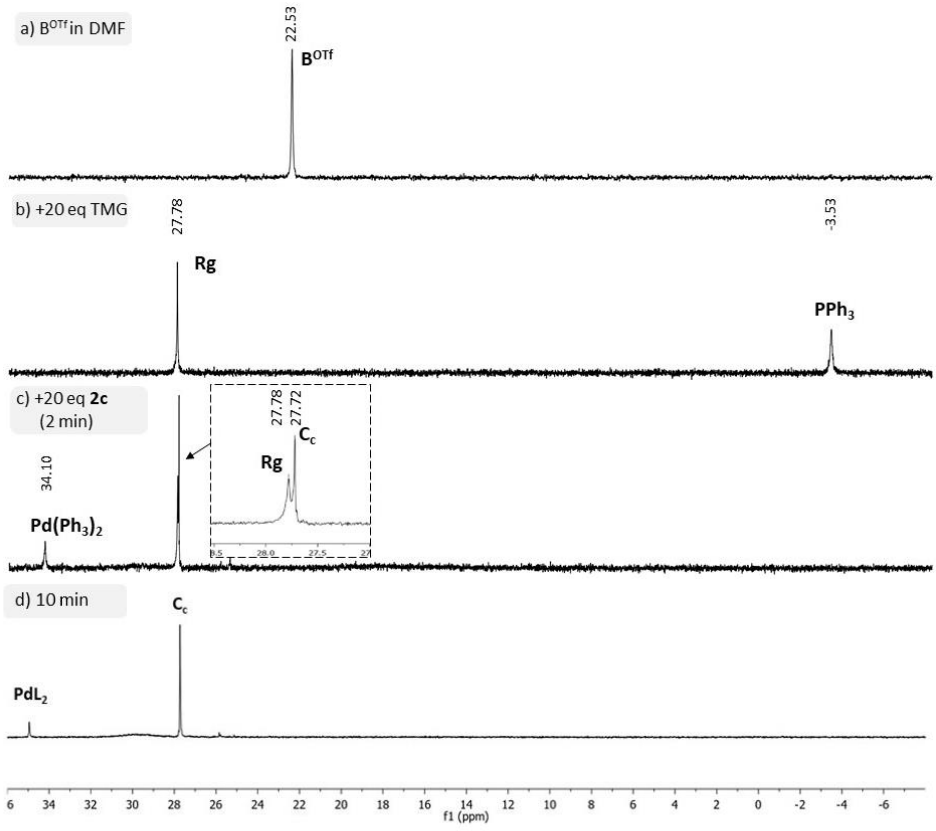
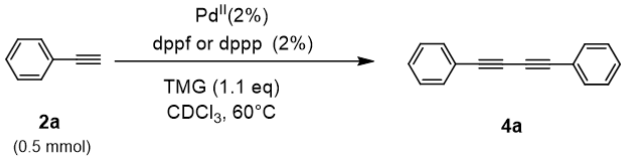


Figure S153. Stacking of ^{31}P NMR spectra in DMF-d_7 of $\mathbf{B_{NO_2}^{OTf}}$ (a); after the addition of TMG 20 eq, (b); immediately after the following addition of **2c** 20 eq (c) and after 10 minutes (d).

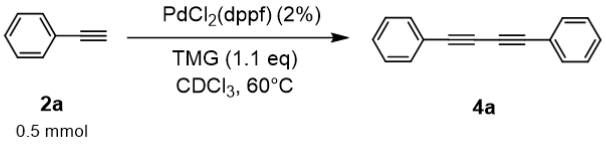
15. Bidentate Ligands

15.1. The pre-catalyst reduction with phenylacetylene



General procedure:

To an oven-dried 20 mL Schlenk purged under argon atmosphere, the phenylacetylene **2a** (55 µL, 0.5 mmol, 1 eq), the pre-catalyst (0.01 mmol, 0.02 eq), the bidentate ligand (0.01 mmol, 0.02 eq) and TMG (69 µL, 0.55 mmol, 1.1 eq) were dissolved in degassed $CDCl_3$ (1 mL). The reaction was stirred at 60°C for 1 hour and analyzed by HPLC-MS.



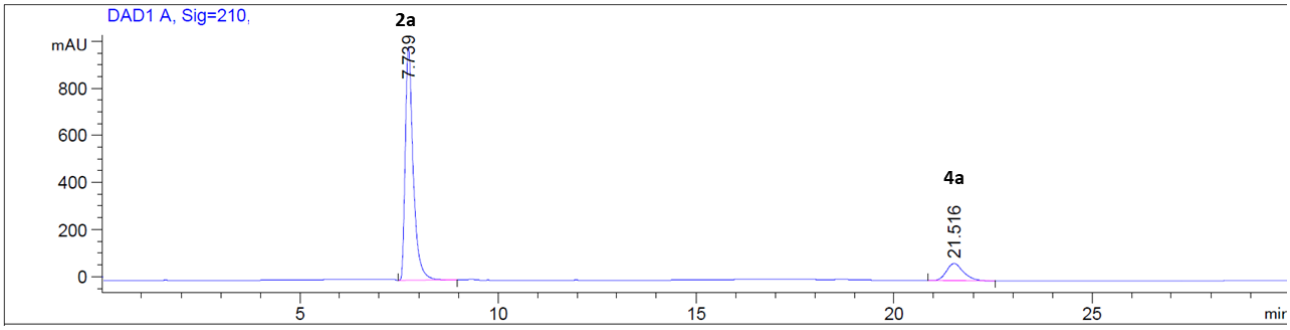
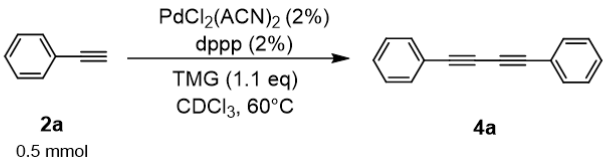


Figure S154. HPLC chromatogram of the $PdCl_2$(dppf) reduction with **2a**. The reduction goes through complex **M** followed by the formation of **4a**. Peak at 7.739 min= **2a** and peak at 21.516 min**=4a.**



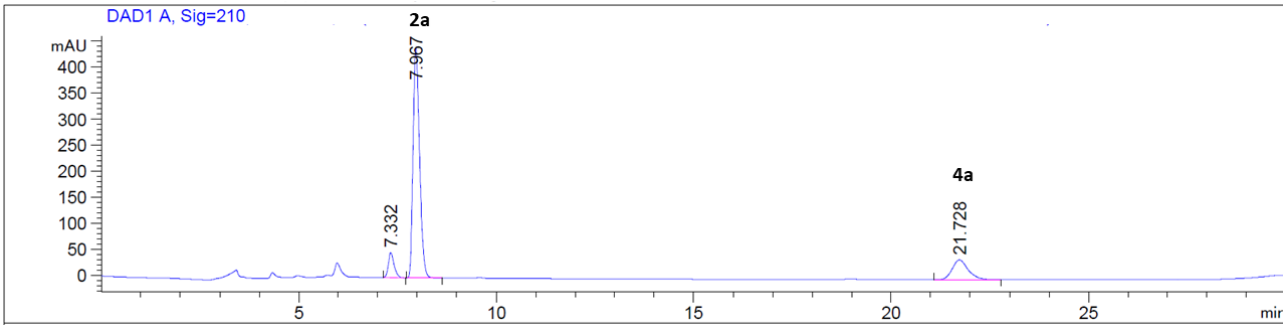
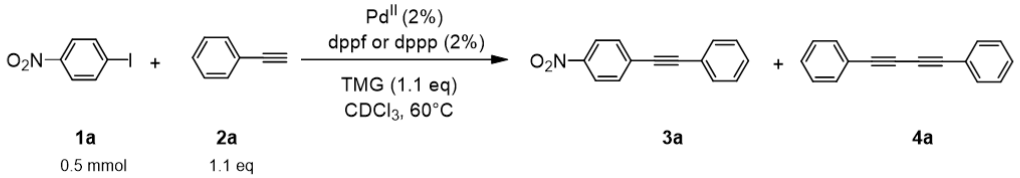


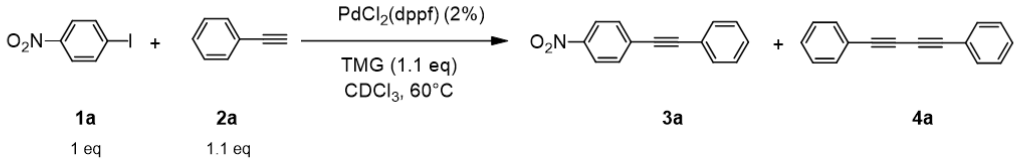
Figure S155. HPLC chromatogram of the $PdCl_2(ACN)_2$ reduction with **2a** and dppp as ligand. The reduction goes through complex **M** followed by the formation of **4a**. Peak at 7.967 min= **2a** and peak at 21.728 min**=4a.**

15.2. The HCS reaction with bidentate ligands



General procedure:

To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst (0.01 mmol, 0.02 eq), the bidentate ligand (0.02 mmol, 0.02 eq) were dissolved in degassed $CDCl_3$ (1 mL). Then, **1a** (124.5 mg, 0.5 mmol, 1 eq), **2a** (60 µL, 0.55 mmol, 1.1 eq), and TMG (69 µL, 0.55 mmol, 1.1 eq) were added. The reaction was stirred at 60°C and analyzed by HPLC-MS



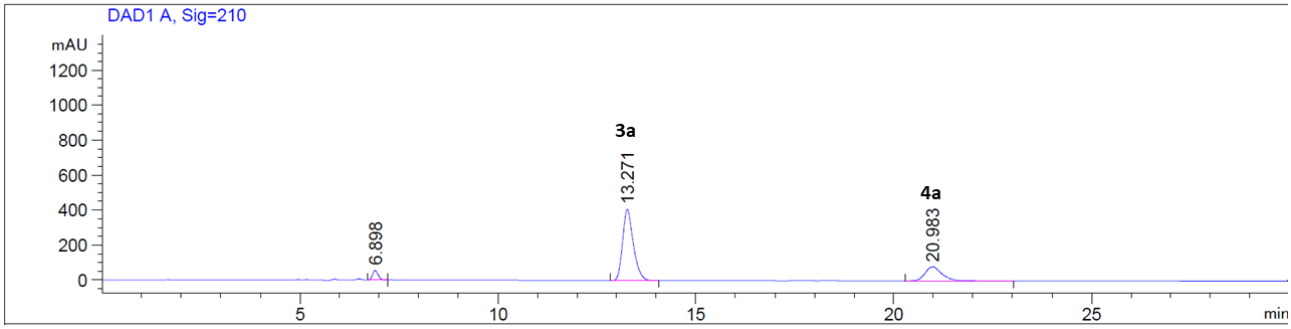
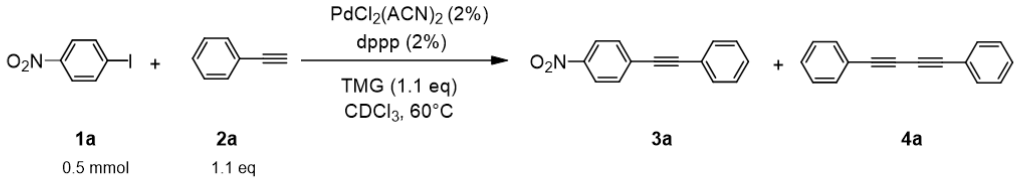


Figure S156. HPLC chromatogram of the reaction between **1a** and **2a** with $PdCl_2$(dppf) after 2h. Without further addition of ligand, the reduction goes through complex **M**. Peak at 13.271 min= **3a** and peak at 20.983 min=**4a**



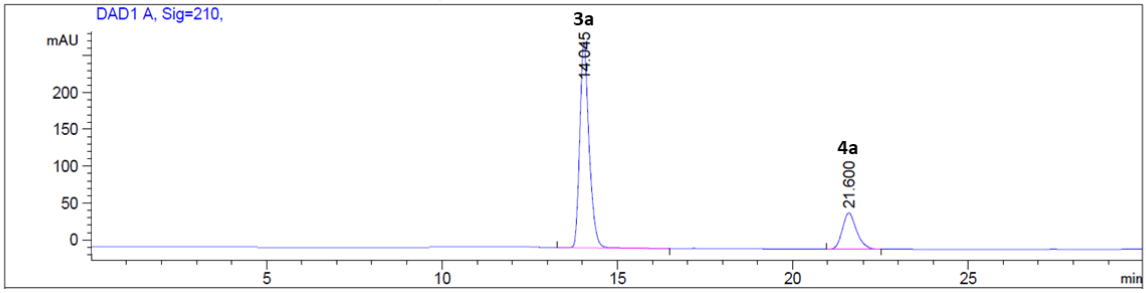
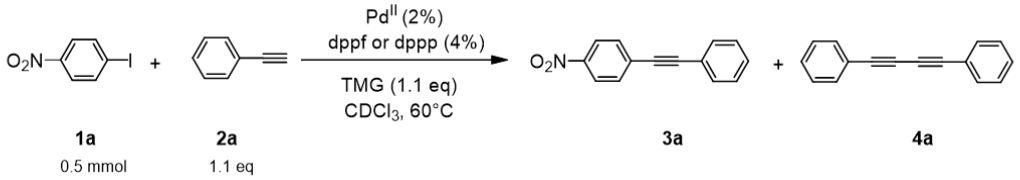
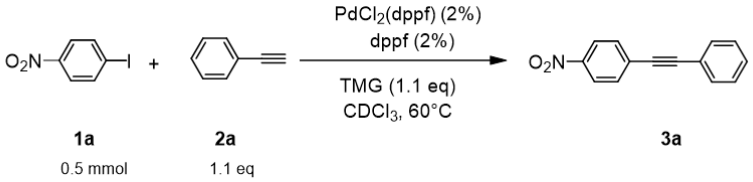


Figure S157. HPLC chromatogram of the reaction between **1a** and **2a** with $PdCl_2(ACN)_2$ after 2h. Without further addition of ligand, the reduction goes through complex **M**. Peak at 14.045 min= **3a** and peak at 21.600 min=**4a**

15.3. Excess of bidentate Ligand



General procedure: To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst (0.01 mmol, 0.02 eq), the bidentate ligand (0.02 mmol, 0.04 eq) were dissolved in degassed $CDCl_3$ (1 mL). Then, **1a** (124.5 mg, 0.5 mmol, 1 eq), **2a** (60 µL, 0.55 mmol, 1.1 eq), and TMG (69 µL, 0.55 mmol, 1.1 eq) were added. The reaction was stirred at 60°C and analyzed by HPLC-MS.



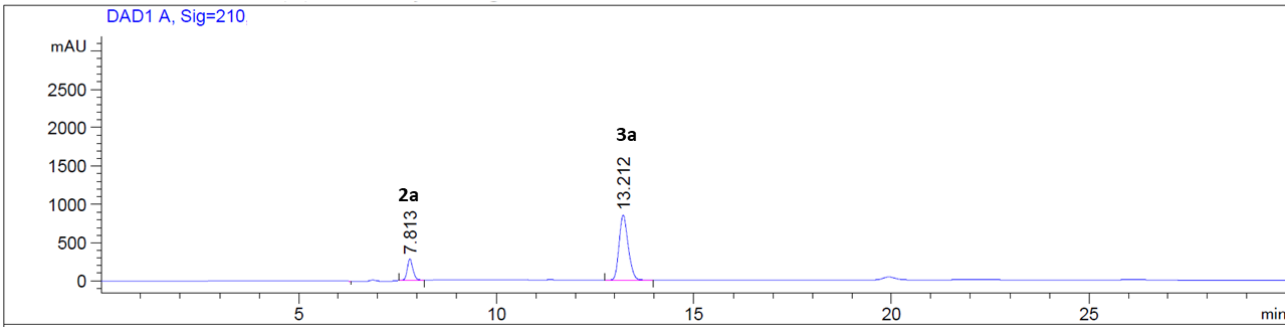
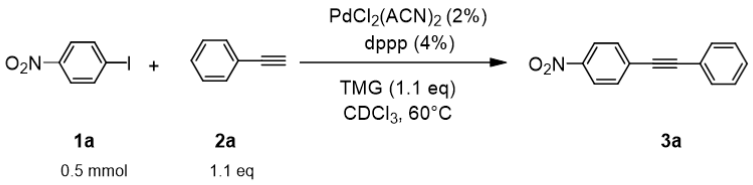


Figure S158. HPLC chromatogram of the reaction between **1a** and **2a** with $PdCl_2$(dppf) and dppf (2%) after 2h. With additional dppf, the reduction does not proceed through complex **M**. Peak at 7.813 min = **2a** and peak at 13.212 min=**3a**



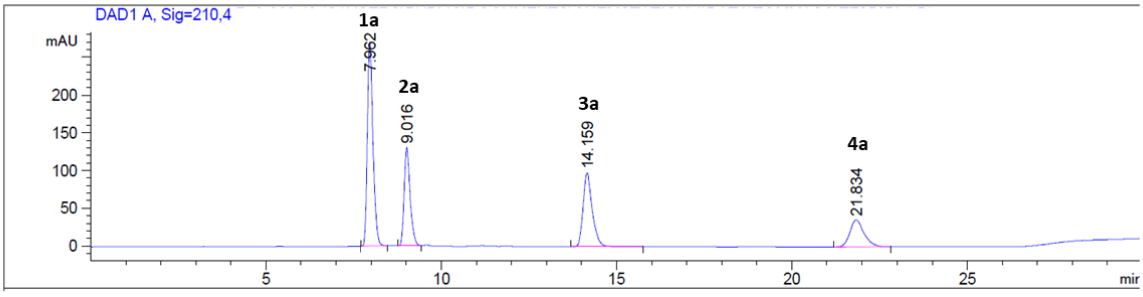


Figure S159. HPLC chromatogram of the reaction between **1a** and **2a** with $PdCl_2(ACN)_2$ and dppp (4%) after 2h. Even with additional dppp, the reduction proceeds through complex **M** because dppp is more electron donor than the dppf and the base is unable to displace it. Peak at 7.962 min = **1a**, peak at 9.016 min=**2a,** peak at 14.159 min=**3a** and peak at 21.834 min=**4a**.

15.4. The HCS reaction in alcohol as solvent with dppp

Procedure: To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $PdCl_2(ACN)_2$ (5.2 mg, 0.01 mmol, 0.02 eq), dppp (8.3 mg, 0.02 mmol, 0.02 eq) were dissolved in degassed EtOH (1 mL). Then, iodobenzene (56 µL mg, 0.5 mmol, 1 eq), 2a (60 µL, 0.55 mmol, 1.1 eq), and TMG (69 µL, 0.55 mmol, 1.1 eq) were added. The reaction was stirred at 60°C and analyzed by HPLC-MS.

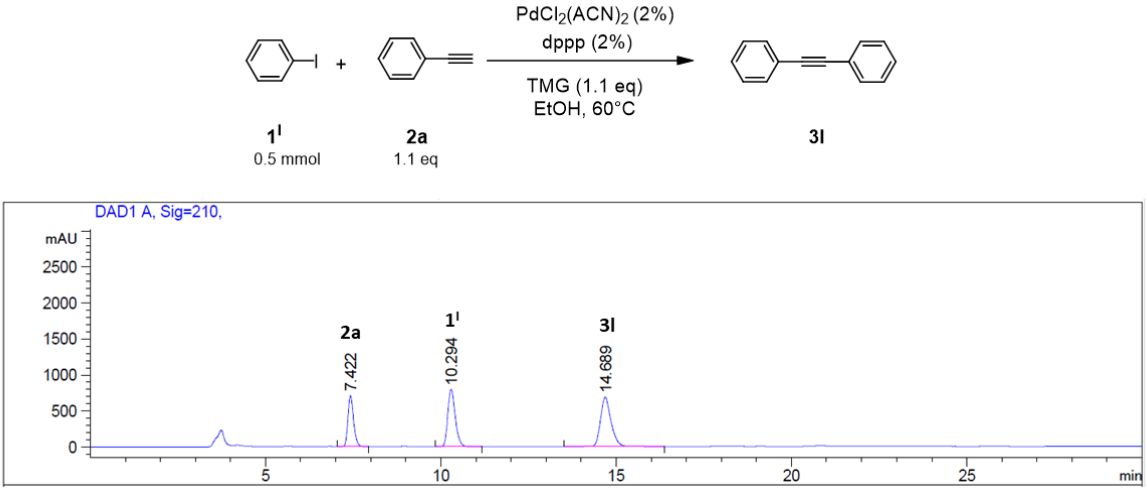
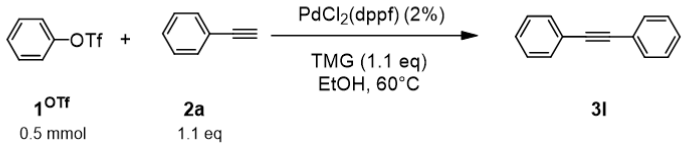


Figure S160. HPLC chromatogram of the reaction between **1^I** and **2a** with $PdCl_2(ACN)_2$ and TMG after 2h in EtOH. With EtOH aging as reducing agent, the reduction does not proceed through complex **M.** Peak at 7.422 min = **2a**, peak at 10.294 min=**1^I** and peak at 14.689 min=**3l**.

15.4. Triflate as leaving group.

15.4.1. Dppf



To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $PdCl_2(dppf)$ (8.2 mg, 0.01 mmol, 0.02 eq), was dissolved in degassed EtOH (1 mL). Then, phenyl trifluoromethanesulfonate (80 µL mg, 0.5 mmol, 1 eq), **2a** (60 µL, 0.55 mmol, 1.1 eq), and TMG (69 µL, 0.55 mmol, 1.1 eq) were added. The reaction was stirred at 60°C and analyzed by HPLC-MS.

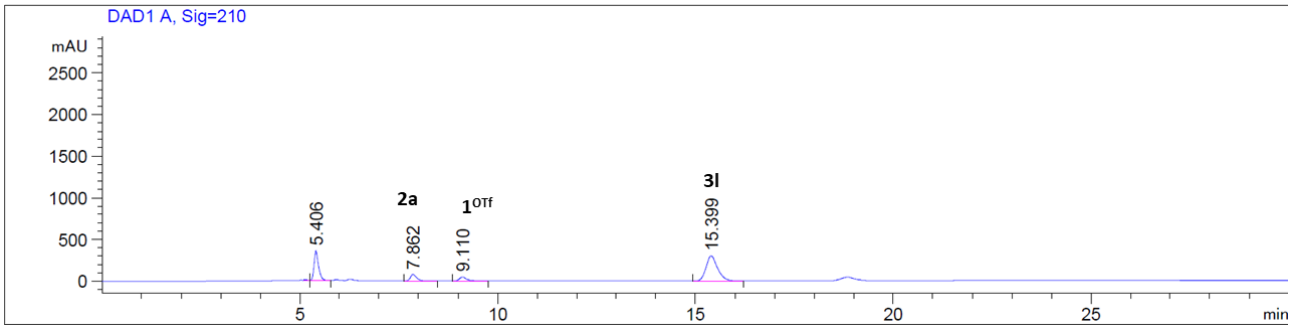
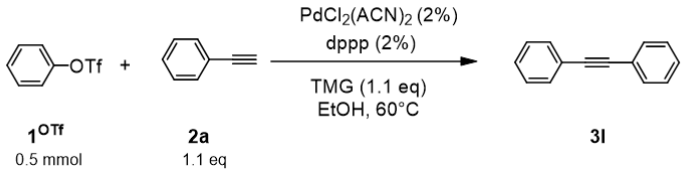


Figure S161. HPLC chromatogram of the reaction between $\mathbf{1^{OTf}}$ and **2a** with $PdCl_2(dppf)$ and after 2h. Peak at 7.862 min = **2a**, peak at 9.110 min=$\mathbf{1^{OTf}}$ and peak at 15.339 min=**3l**.

15.4.1. Dppp



To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $PdCl_2(ACN)_2$ (5.2 mg, 0.01 mmol, 0.02 eq) and dppp (8.3 mg, 0.02 mmol, 0.02 eq), were dissolved in degassed EtOH (1 mL). Then, phenyl trifluoromethanesulfonate (80 µL mg, 0.5 mmol, 1 eq), **2a** (60 µL, 0.55 mmol, 1.1 eq), and TMG (69 µL, 0.55 mmol, 1.1 eq) were added. The reaction was stirred at 60°C and analyzed by HPLC-MS.

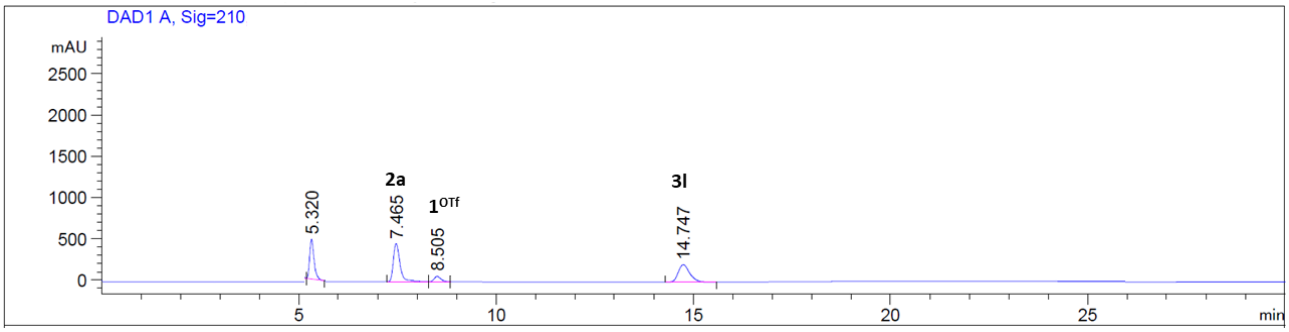


Figure S162. HPLC chromatogram of the reaction between $\mathbf{1^{OTf}}$ and **2a** with $PdCl_2(ACN)_2$ and dppp after 2h. Peak at 7.465 min = **2a**, peak at 8.505 min=$\mathbf{1^{OTf}}$ and peak at 14.747 min=**3l**.

16. Palladium nanoparticles (Pd-NPs)

16.1. Synthesis

The solution of H_2PdCl_4 (2mM) was obtained by mixing $PdCl_2$ (178 mg), 0.2M HCl (12 mL) and distilled H_2O (500 mL). Subsequently, the solution was left under reflux for 3 hours and allowed to age for 2 days. The colour of the product was pale-yellow according to the procedure in literature.[8] Then, deionized H_2O (20 mL), polyvinylpyrrolidone (PVP, 67 mg) and 4 drops of 1M HCl were added to 15 mL of the H_2PdCl_4 solution. The mixture was heated at 120°C and EtOH (14 mL) was added to perform the reduction of H_2PdCl_4. The solution was refluxed for 3h to obtain a dark brown solution. The mixture was centrifugated at 60000 RPM by Andreas Hettich GmbH & Co. KG for 2 h. The palladium nanoparticles stabilized by PVP (PVP Pd-NPs) were isolated taking the supernatant and analyzed by TEM.

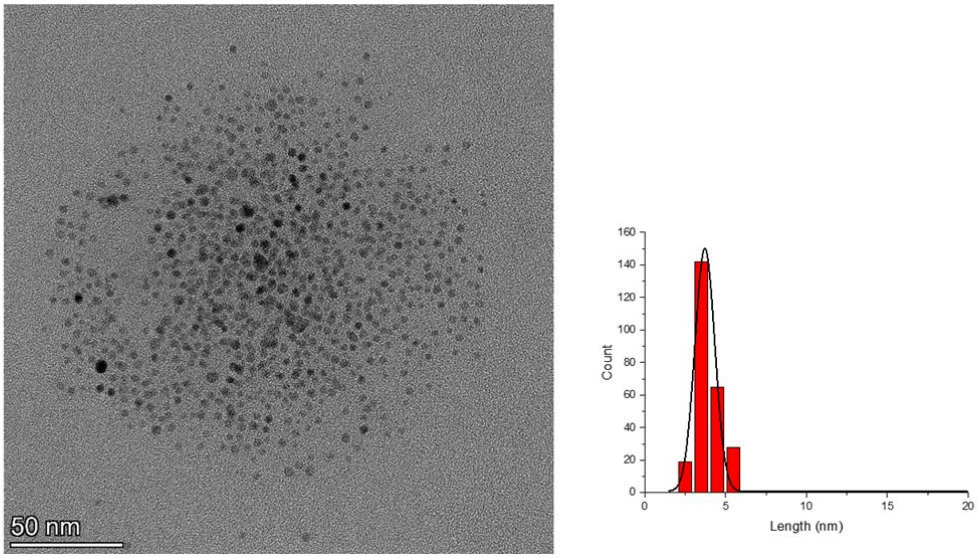


Figure S 163. TEM images of PVP-Pd-NPs (left) and particle size distribution: mean diameter 3.72 ± 0.03 nm (right)

16.2. Investigation of the possible Pd-NPs

16.2.1. Reduction process

To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol, 1eq) and PPh_3 (10.5 mg, 0.04 mmol, 2 eq) were dissolved in degassed DMF (0.5 µL), followed by the addition TMG (65 µL from a stock solution of 0.66 M, 0.04 mmol, 2eq). After 1h, the solution was maintained under inert atmosphere, transferred into a falcon with silicon septum and centrifugated. The particles obtained were isolated by taking the supernatant and analyzed by TEM.
The analysis did not show the formation of palladium nanoparticles.

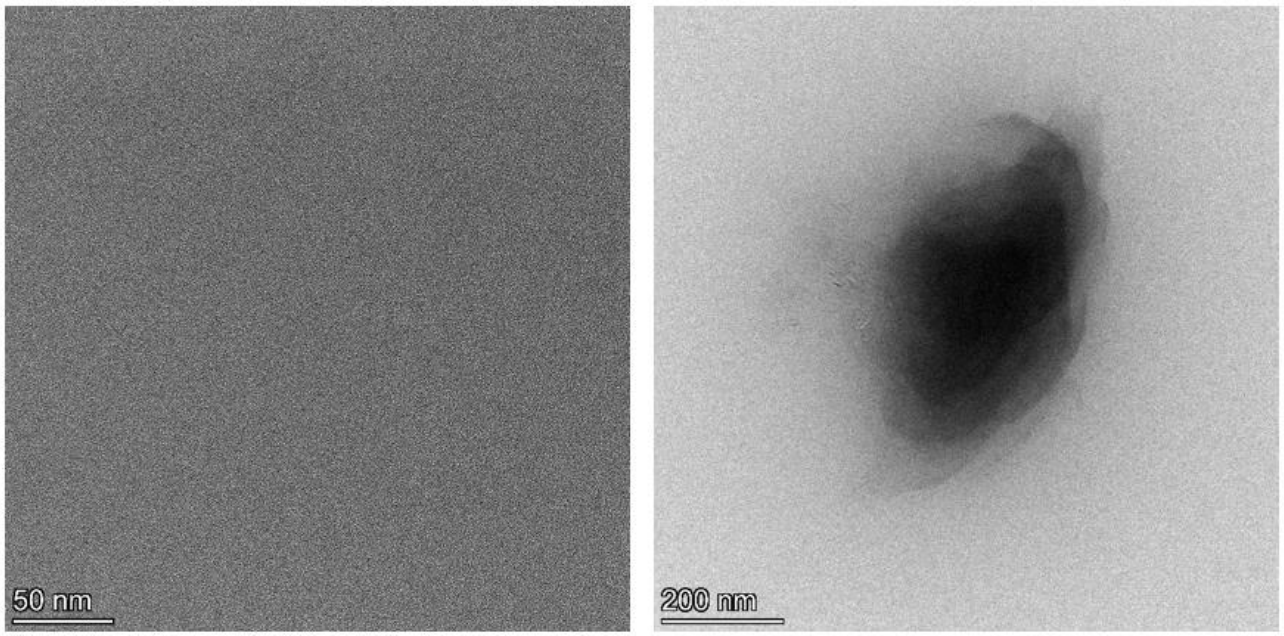
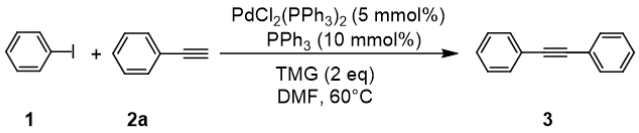


Figure S164. TEM images of $PdCl_2(PPh_3)_2$ reduction with PPh_3 (2eq) and TMG as base in DMF. Pd-NPs not detected (left), unreacted organic material (right).

16.2.2. HCS reaction

A)



To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $PdCl_2(PPh_3)_2$ (17.5 mg, 0.025 mmol, 0.05 eq) and PPh_3 (13 mg, 0.05 mmol, 0.1 eq) were dissolved in degassed DMF (1 mL). Then, iodobenzene (56 µL, 0.5 mmol, 1 eq), **2a** (60 µL, 0.55 mmol, 1.1 eq) and TMG (125 µL, 1 mmol, 2 eq) were added and the reaction was stirred at 60°C. After 1h, the solution was maintained under inert atmosphere, transferred into a falcon with silicon septum and centrifugated. The particles obtained were isolated by taking the supernatant and analyzed by TEM. The analysis does not show the formation of palladium nanoparticles

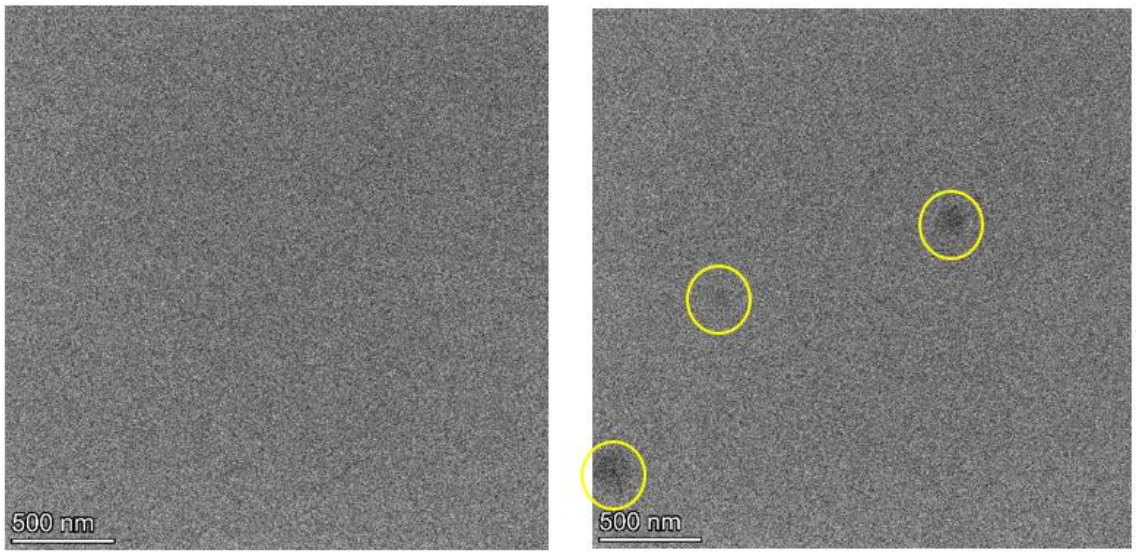


Figure S165. TEM Analysis of HCS reaction between **1** and **2a** with $PdCl_2(PPh_3)_2$, PPh_3 (2eq) and TMG as base in DMF. Pd-NPs not detected (left), unreacted organic material (right).

B) According to the literature[9] PVP palladium nanoparticles are soluble in ethanol and precipitate with the addition of diethyl ether (Et_2O). To further investigate the possibility that the reaction proceeds through the formation of palladium nanoparticles, the HCS reaction was performed in EtOH at 60°C. After 1 h, PVP (200 mg) was added to stabilize any palladium nanoparticles and Et_2O was added dropwise at 0°C. The solution was clear and no precipitated was formed. (**Figure S166**, left). For comparison, the reaction was repeated in the same conditions but, in that case, after 1 h PVP-Pd-NPs were added. Et_2O was added dropwise at 0°C and, dark brown precipitates appeared (**Figure S166**, right), confirming that the HCS coupling does not proceed through palladium nanoparticles.

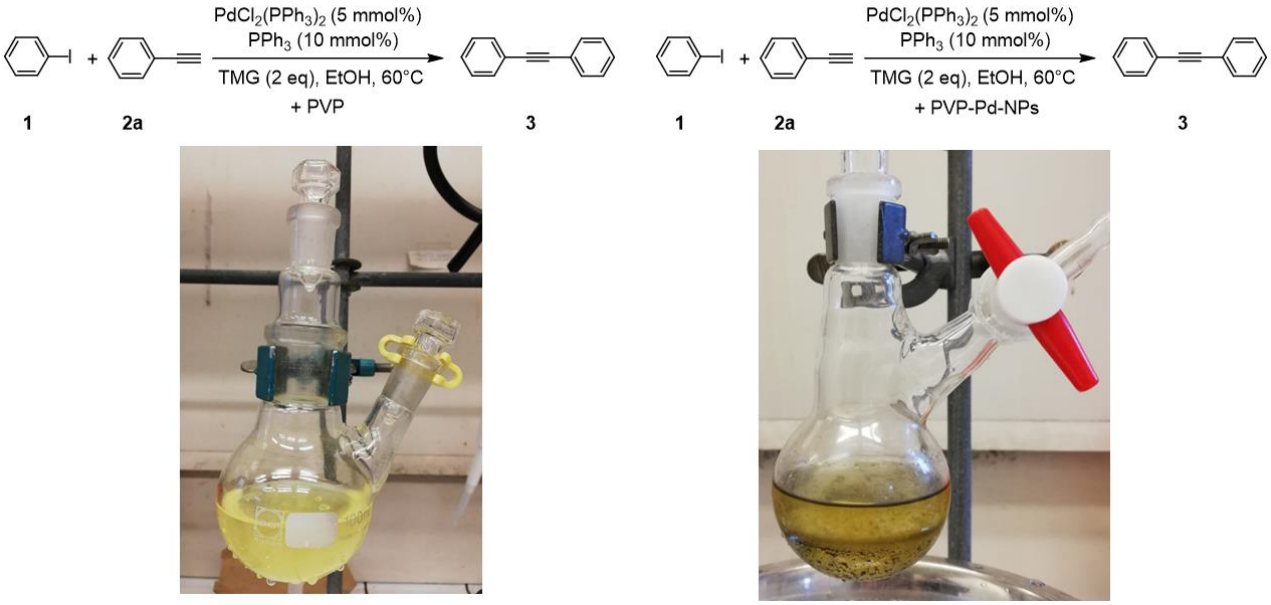


Figure S166. HCS reaction with **1** and **2a** in EtOH at 60°C with the addition of: PVP after 1 h (left); PVP-Pd-NPs (right)

Previously, the HCS reaction was performed in EtOH to evaluate the effectiveness of the solvent for the HCS coupling.

Procedure: To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $PdCl_2(PPh_3)_2$ (8.8 mg, 0.0125 mmol, 0.05 eq) and PPh_3 (6.6 mg, 0.025 mmol, 0.1 eq) were dissolved in degassed EtOH (0.5 mL). Then, iodobenzene (28 µL, 0.25 mmol, 1 eq), **2a** (30.2 µL, 0.27 mmol, 1.1 eq) and TMG (63 µL, 0.5 mmol, 2 eq) were added and the reaction was stirred for at 60°C. The reaction was analyzed by HPLC-MS.

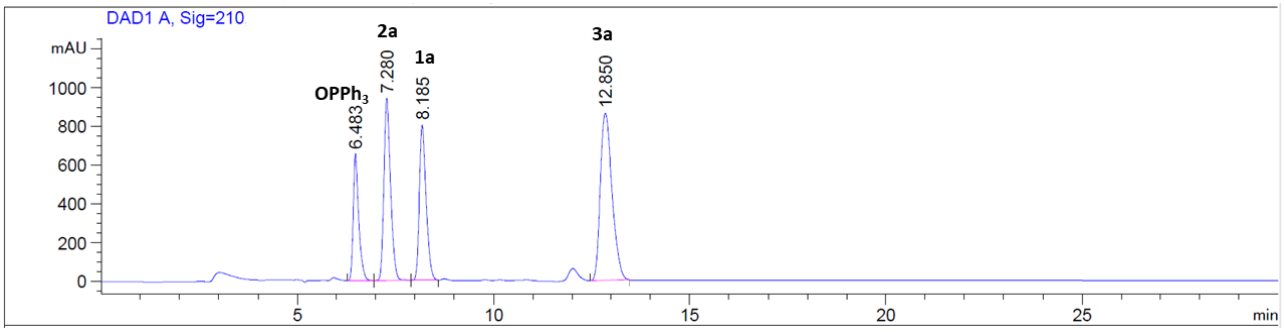
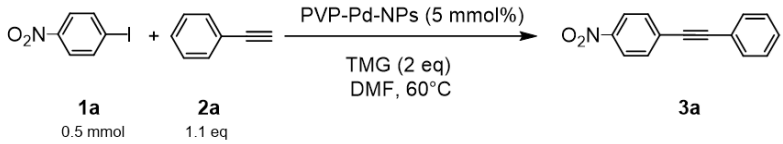


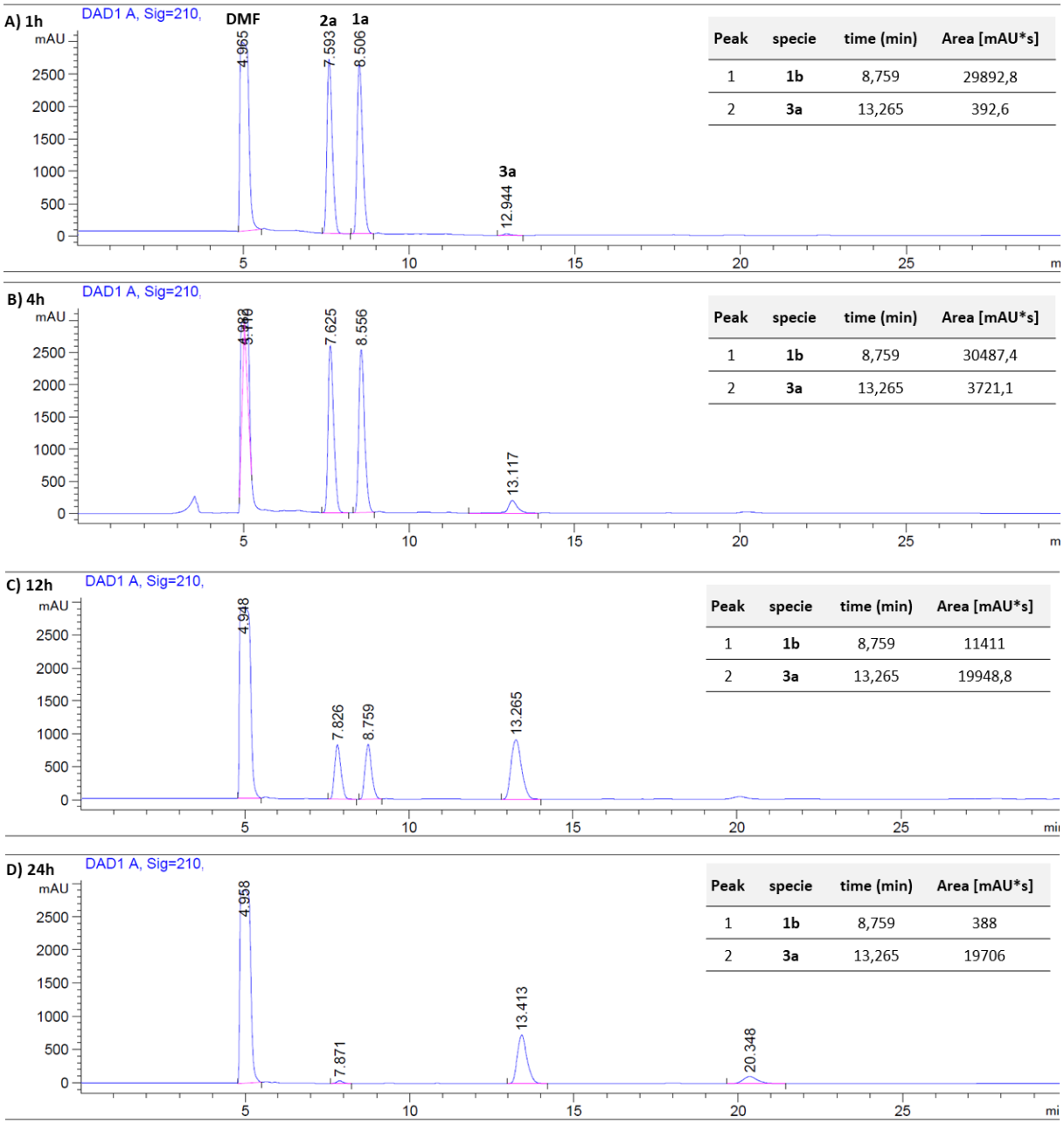
Figure S 167. HPLC chromatogram of the reaction between **1a** and **2a** with $PdCl_2(PPh_3)_2$ and PPh_3 in EtOH after 12h. Peak at 6.483 min = $OPPh_3$, peak at 7.280 min = **2a** and peak at 8.185 min=**1a** and peak at 12.850 min=**2a**.

16.2.3. Comparison between the HCS reaction with PVP-Pd-NPs and $PdCl_2(PPh_3)_2$

A) PVP-Pd-NPs:



To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-synthesized (see **paragraph 16.1.)** PVP-Pd-NPs (59 mg, 0.025 mmol of Pd, 0.05 eq) were solubilized in DMF (1 mL) at 60°C. **1a** (124.5mg, 0.5 mmol, 1 eq) and **2a** (61 µL, 0.55 mmol, 1.1 eq) and TMG (125 µL, 1 mmol, 2eq) were added. The reaction was analyzed by HPLC-MS.



Peak	specie	time (min)	Area [mAU*s]
1	**1b**	8,759	29892,8
2	**3a**	13,265	392,6

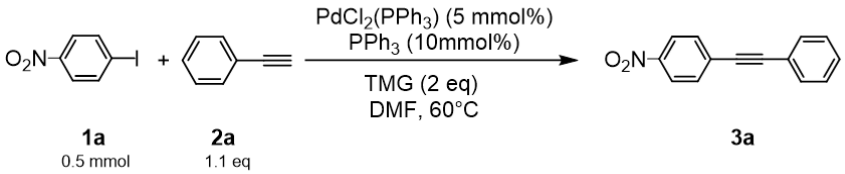
Peak	specie	time (min)	Area [mAU*s]
1	**1b**	8,759	30487,4
2	**3a**	13,265	3721,1

Peak	specie	time (min)	Area [mAU*s]
1	**1b**	8,759	11411
2	**3a**	13,265	19948,8

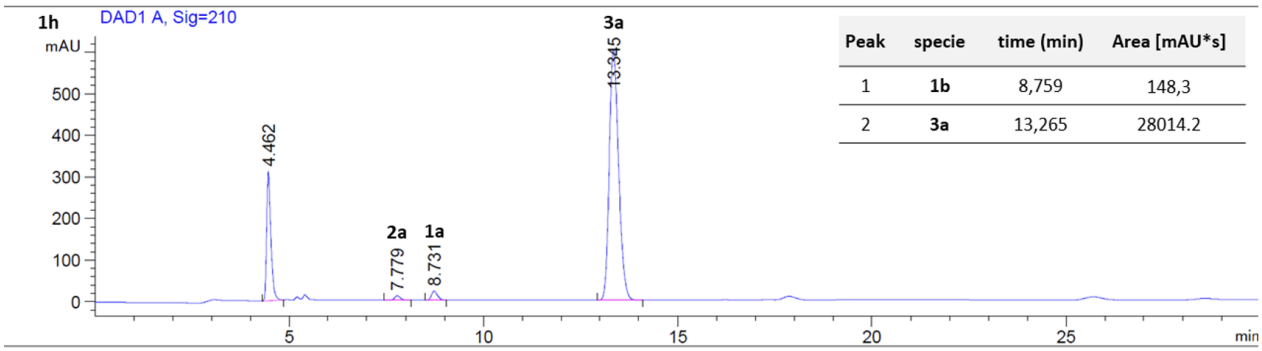
Peak	specie	time (min)	Area [mAU*s]
1	**1b**	8,759	388
2	**3a**	13,265	19706

Figure S168. HPLC chromatogram of HCS reaction between **1a** and **2a** with PVP-Pd-NPs (5 mmol% of Pd) in DMF at 60°C. Peak at 4.965 min=DMF, peak at 7.593 min=**2a**, peak at 8.506 min=**1a** and peak at 12.944 min=**3a**. Conversion at several times was calculated considering RRF of 3.05 between **1a** and **3a**: A) c=0.43% (1h); B) c=3.85% (4h); C) 36.43% (12h); D) 94.33% (24h).

B) $PdCl_2(PPh_3)_2$



To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $PdCl_2(PPh_3)_2$ (17.5 mg, 0.025 mmol, 0.05 eq) and PPh_3 (13 mg, 0.05 mmol, 0.1 eq) were dissolved in degassed DMF (1 mL). Then, **2a** (124.5 mg, 0.5 mmol, 1eq), **2a** (61 µL, 0.55 mmol, 1.1 eq) and TMG (125 µL, 1 mmol, 2eq) were added and the reaction was stirred for at 60°C. The reaction was analyzed by HPLC-MS.



Peak	specie	time (min)	Area [mAU*s]
1	**1b**	8,759	148,3
2	**3a**	13,265	28014.2

Figure S169. HPLC chromatogram of HCS reaction between **1a** and **2a** with $PdCl_2(PPh_3)_2$ and PPh_3. Peak at 7.779 min=**2a,** peak at 8.731 min=**1a** and peak at 13.345 min=**3a.** Conversion after 1h = 98.5% was calculated considering RRF of 3.05 between **1a** and **3a**.

17.HRMS spectra

Since it is not possible isolating complex **R**, ESI (+)-HRMS spectrum referred to this complex is shown below to identify the specie. The analysis was performed after the following procedure: complex $\mathbf{B^{Br}}$ (15 mg, 0.018 mmol, 1 eq) and TMG (45 µL, 0.36 mmol, 20 eq) were added to 600 µL of acetonitrile for HPLC (ACN ≥99.9%) and an aliquot of 10 µL was diluted in 0.5 mL of methanol for HPLC.

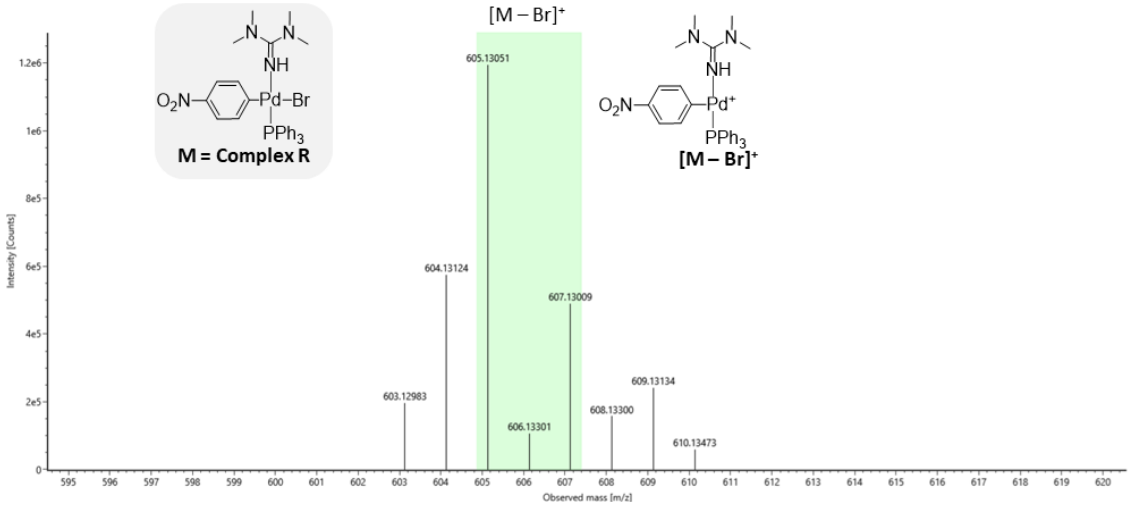


Figure S170. HRMS (ESI+) m/z of complex **R** upon a ionization with loss of Br^-. $[M\text{-}Br]^+$ calcd. for $C_{29}H_{32}N_4O_2PPd+$ 605,1298; found 605,1385.

The HRMS spectra of complex $\mathbf{B}_{\mathbf{NO_2}}^{\mathbf{Br}}$, complex **L** and **M** were analyzed too:

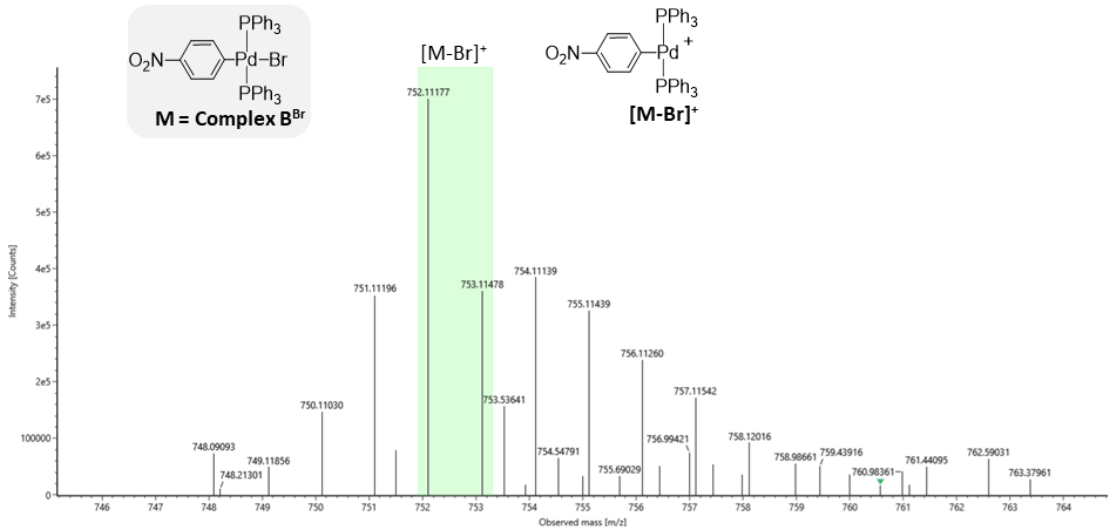


Figure S171 HRMS (ESI+) m/z of complex $\mathbf{B}_{\mathbf{NO_2}}^{\mathbf{Br}}$ upon a ionization with loss of Br^-. $[M\text{-}Br]^+$ calcd. for $C_{42}H_{34}NO_2P_2Pd^+$ 752,1100; found 752,1117.

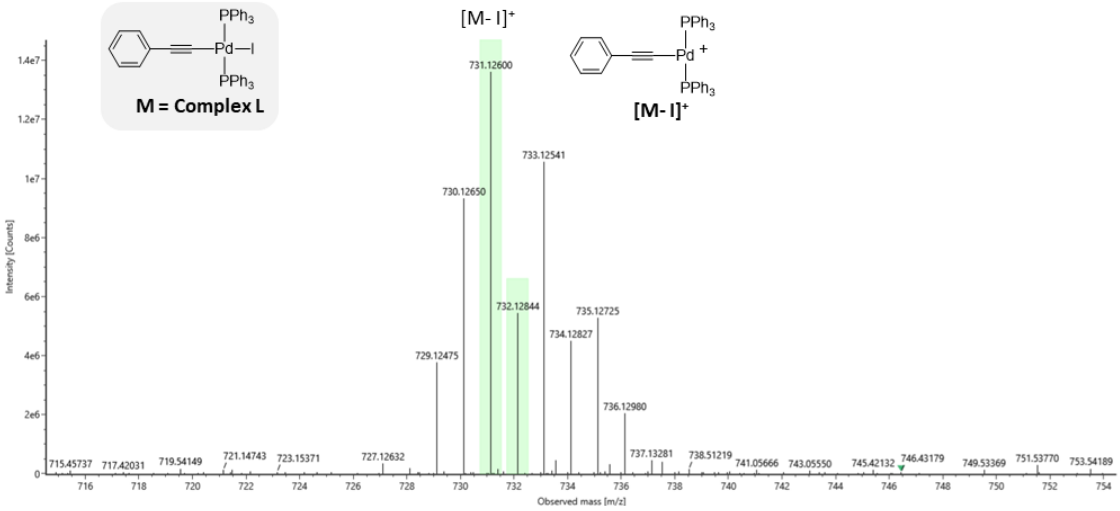


Figure S172. HRMS (ESI+) m/z of complex **L** upon a ionization with loss of Br^-. $[M\text{-}I]^+$ calcd. for $C_{44}H_{35}IP_2Pd+$ 731,1249; found 731,1260

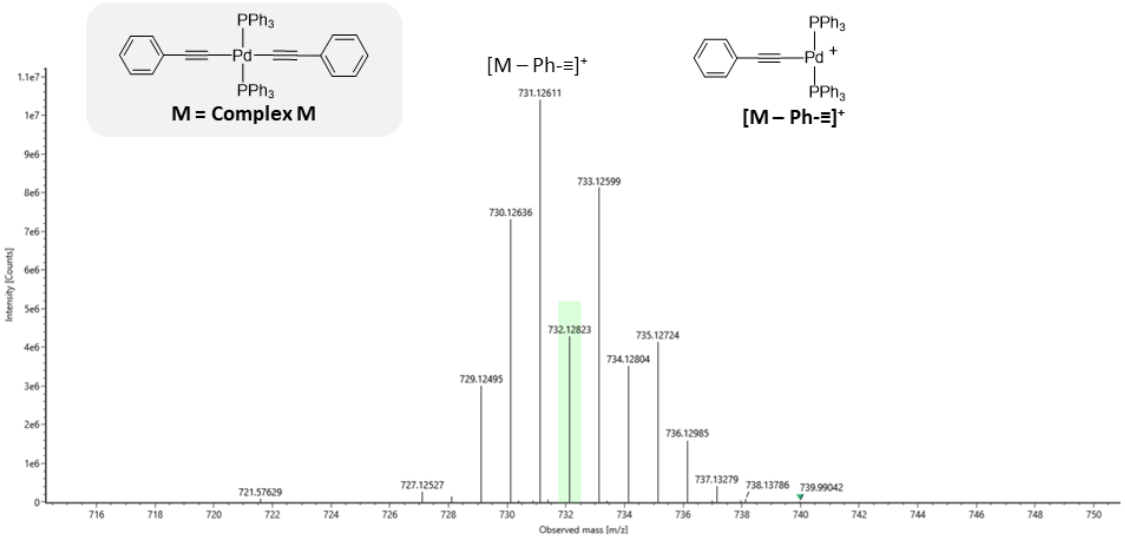
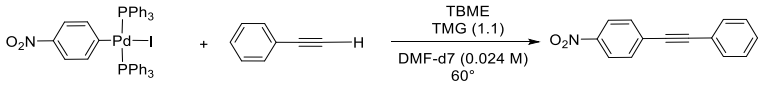


Figure S173. HRMS (ESI+) m/z of complex **M** upon a ionization with loss of Br^-. $[M\text{-}Ph\text{-}\equiv]^+$ calcd. for 731,1249; found 731,1261.

18. Control experiments:

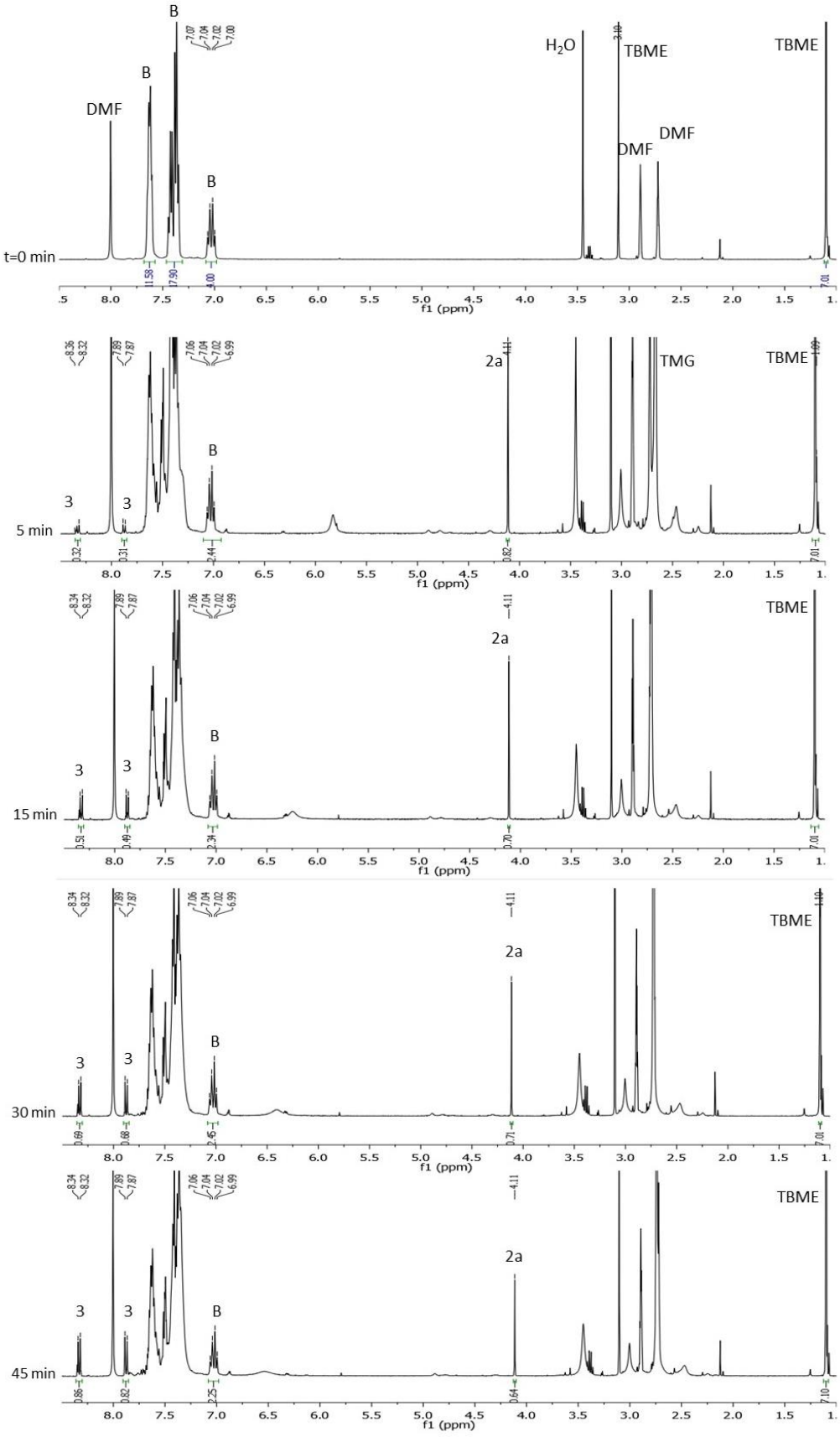
1. To demonstrate that during the reaction between complex $\mathbf{B^{I}_{NO_2}}$ and 2a no side reactions occurred.



B **2a** **3a**

The reaction was performed in an oven-dried NMR tube purged under nitrogen atmosphere. Complexes $\mathbf{B^{I}_{NO_2}}$ (8.8 mg, 0.01 mmol, 1 eq) was dissolved in in $CDCl_3$ (0.750 mL), followed by the addition of **2a** (13.6 µL from a stock solution of 0.73 M, 0.01 mmol, 1eq) and TMG (15 µL from a stock solution of 0.73 M, 0.02 mmol, 1.1 eq). Tert-butyl methyl ether (TBME) was used as internal standard. The mixture was let at room temperature and it was monitored by ^1H and ^{31}P NMR spectroscopy at several times.

^{1}H NMR spectra:



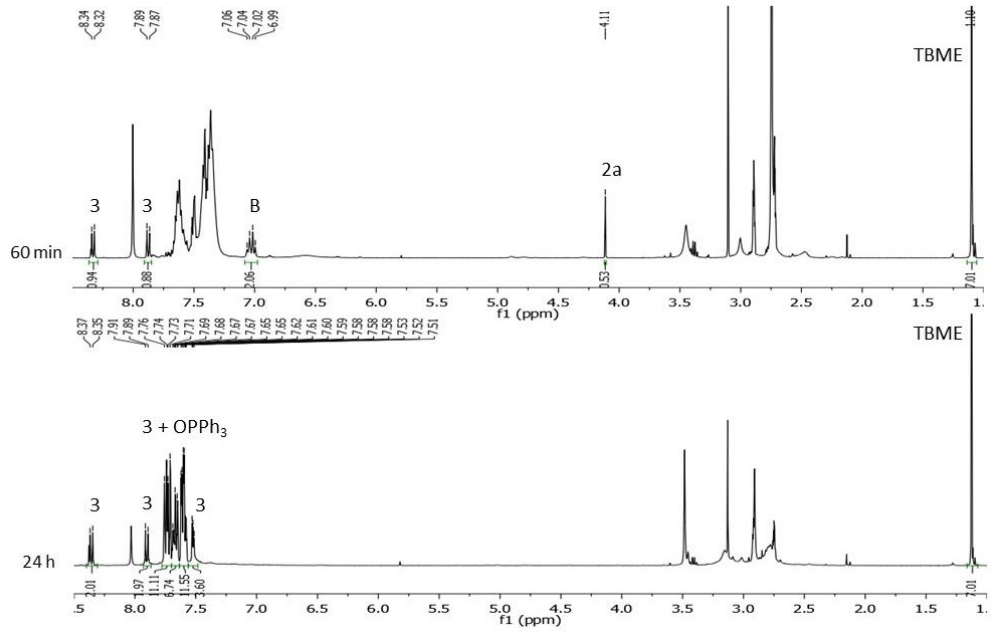
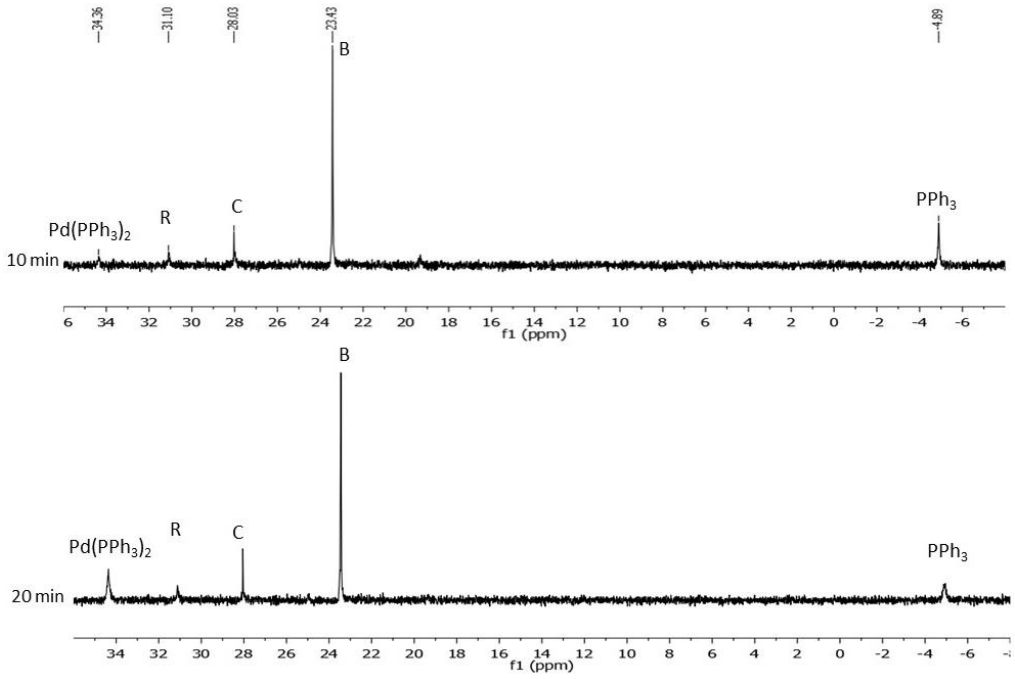


Figure S174. Stacking of ^{1}H NMR spectra of the stoichiometric reaction between $\mathbf{B^{I}_{NO_2}}$+ **2a** with TMG in DMF-d_7 at 60°C in presence of TBME as internal standard at: t=0 before the addition of 2a and TMG (a); t=5 min (Y= 16%) (b); t=15 min (Y= 25%) (c); d) t=30 min (Y= 34%) (d); t=45 min (Y= 43%) (e); t=60 min (Y= 50%) (f); t=24h (Y= 100%) (g).

^{31}P NMR spectra:



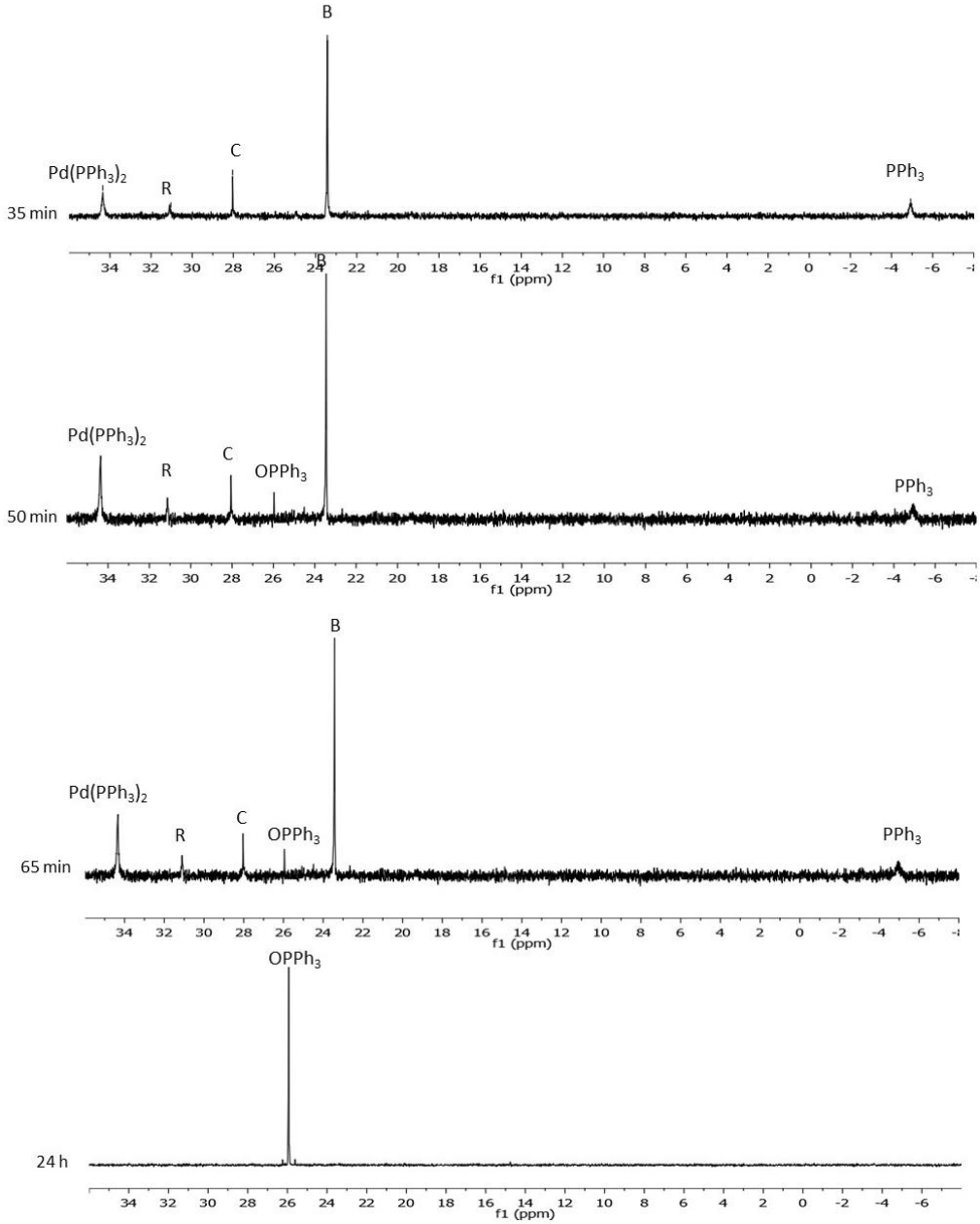
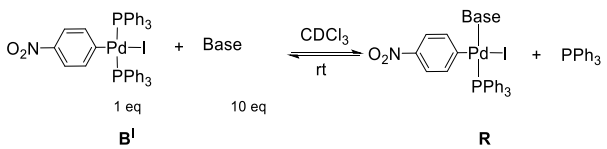


Figure S175. Stacking of ^{31} P NMR spectra of the stoichiometric reaction between $\mathbf{B^{I}_{NO_2}}$ + **2a** with **TMG** in DMF-d_7 at 60°C in presence of TBME as internal standard at t=10 min (a); t=20 min (b); t=35 min (c); t=50 min (d); t=65 min (e); t=24 h (f).

2. The Chemical shifts of R starting from $\mathbf{B^{X}_{NO_2}}$ (X=I) with the addition of TMG and pyrrolidine in $CDCl_3$.



$\mathbf{B^{I}}$ **R**

General procedure

The reaction was performed in an oven-dried NMR tube purged under nitrogen atmosphere. The complex $\mathbf{B^{I}_{NO_2}}$ (22.8 mg, 0.026 mmol, 1 eq) was dissolved in $CDCl_3$ (0.60 mL) followed by the addition of the base (0.26 mmol, 10 eq). The mixture was analyzed using ^{31}P NMR spectroscopy.

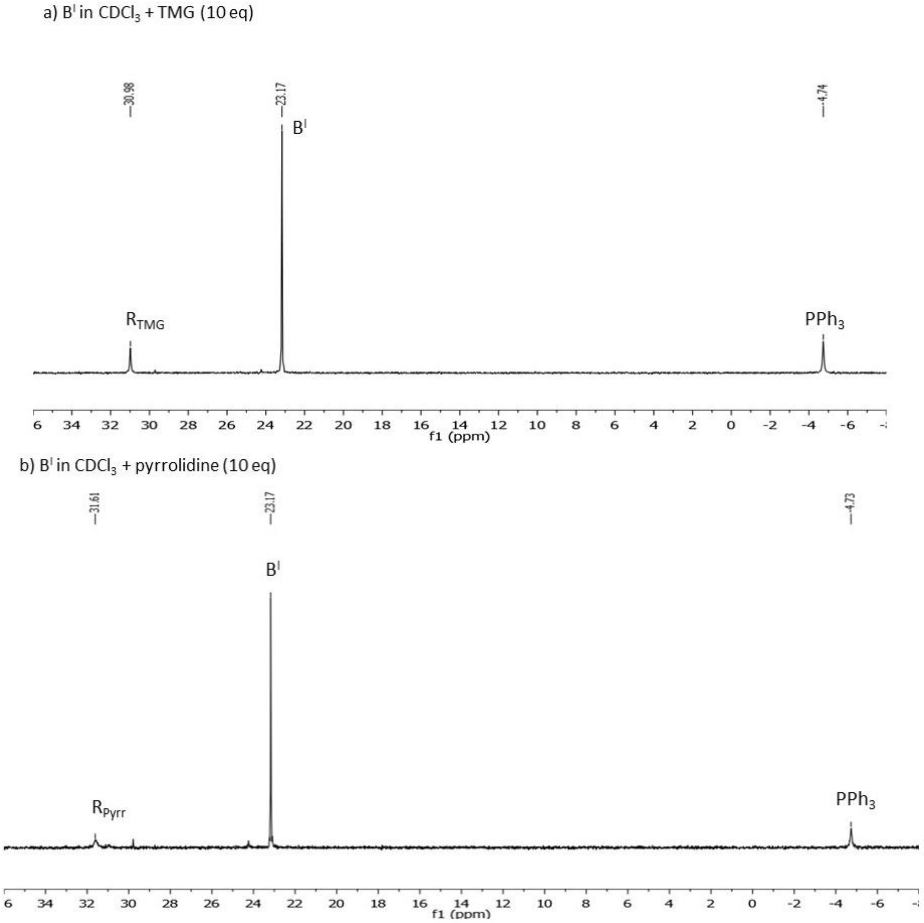
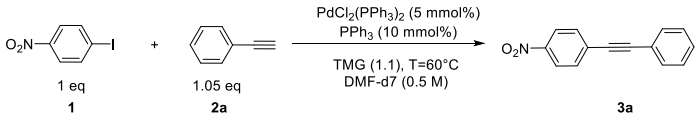


Figure S176. ^{31}P NMR spectra of B (X=I) in $CDCl_3$ with the addition of TMG 10 eq (a) and pyrrolidine 10 eq (b).

3. The HC reaction under operative conditions.



To an oven-dried 10 mL Schlenk purged under N_2 atmosphere, $PdCl_2(PPh_3)_2$ (17.55 mg, 0.025 mmol, 0.05 eq) and PPh_3 (26.2 mg, 0.1 mmol, 0.1 eq) were dissolved in the degassed DMF-d_7 (1 mL). After the addition of 1-Iodo-4-nitrobenzene **1** (124.5 mg, 0.5 mmol, 1 eq), phenylacetylene **2a** (60.4 µL, 0.55, 1.1 eq) and TMG (69 µL, 0.55 mmol, 1.1 eq), the reaction mixture was stirred at 60°C. After a given time, the ^{31}P NMR spectra were collected to detect which species were formed.

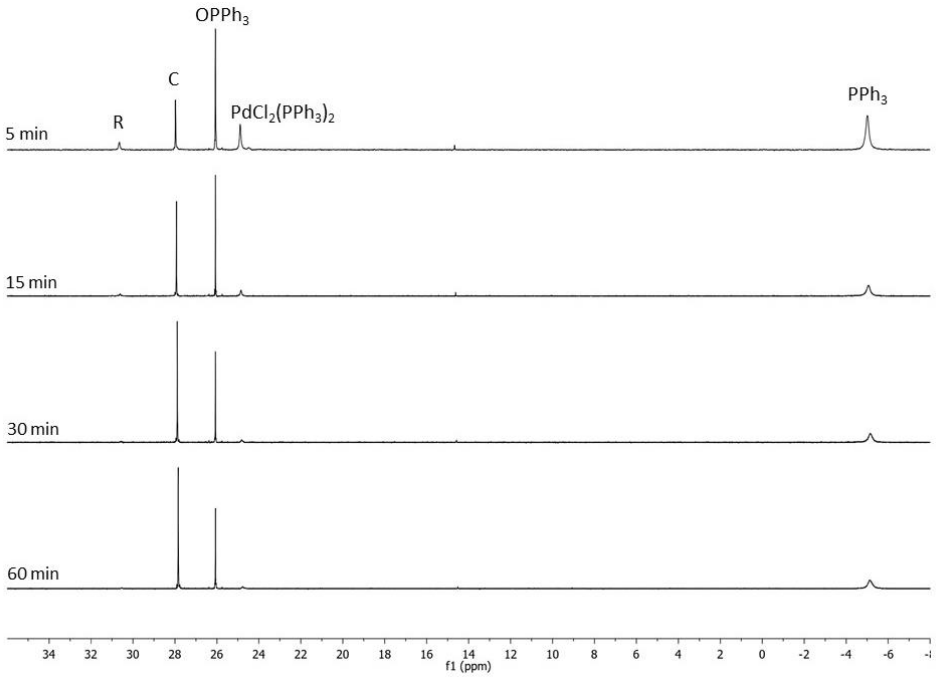
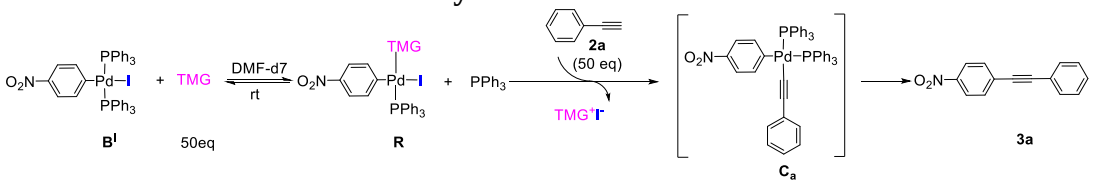
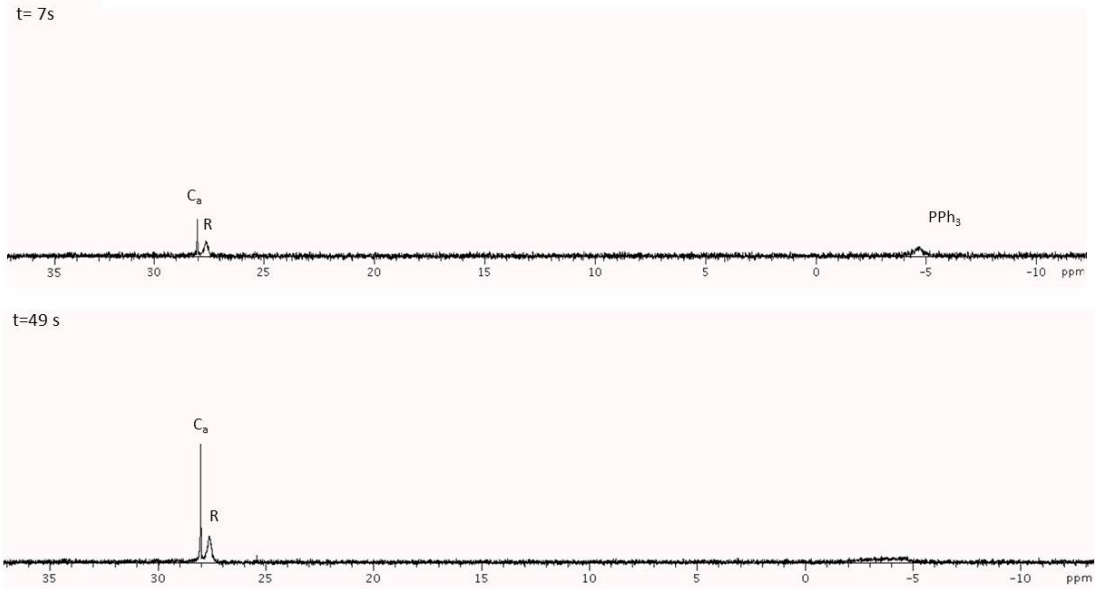


Figure S177. Stacking of ^{31}P NMR spectra of the catalytic reaction between $\mathbf{B^{I}_{NO_2}}$ and **2a** with TMG and PPh_3 in DMF-d_7 at 60°C after 5 min (a), 15 min (b), 30 min (c) and 60 min (d).

4. The fast direct coordination of the alkyne



The reaction was performed in an oven-dried NMR tube purged under nitrogen atmosphere. The complex $\mathbf{B^{I}_{NO_2}}$ (22.8 mg, 0.026 mmol, 1 eq) was dissolved in DMF-d_7 (0.60 mL) followed by the addition of the TMG (163 µL, 1.3 mmol, 50 eq) and **2a** (143 µL, 1.3 mmol, 50 eq). The ^{31}P NMR spectrum was immediately acquired and several scans were captured during the analysis, to show that the simultaneous disappearance of PPh_3 and appearance of complex **C** occurred very quickly.



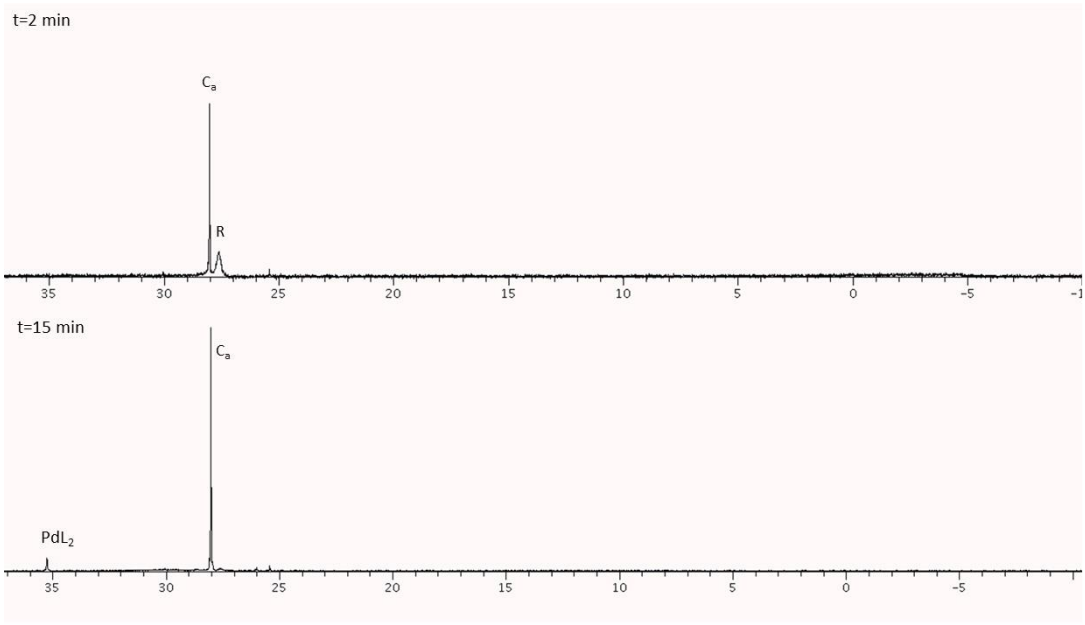
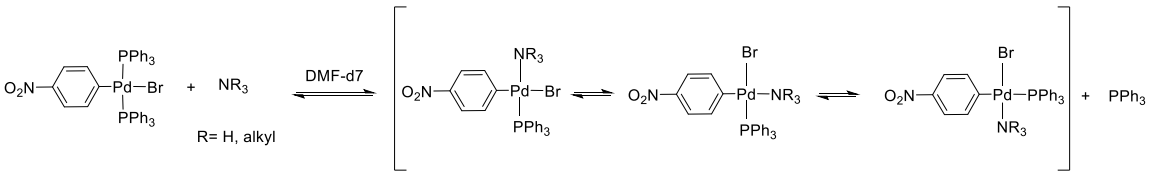


Figure S178. Acquisition of ^{31}P NMR spectrum of $\mathbf{B^{I}_{NO_2}}$ with TMG (50 eq) and **2a** (50 eq) at rt after 7s, 49s, 2 min, 15 min.

5. Study of the base effect on complex B using different bases

General procedure:

The reaction was performed in an oven-dried NMR tube purged under nitrogen atmosphere. The complex $\mathbf{B^{Br}_{NO_2}}$ (21.6 mg, 0.026 mmol, 1 eq) was dissolved in DMF-d_7 (0.60 mL) followed by the addition of the base (0.52 mmol, 20 eq). The reactions were analyzed using ^{31}P NMR spectroscopy.



1) Piperidine

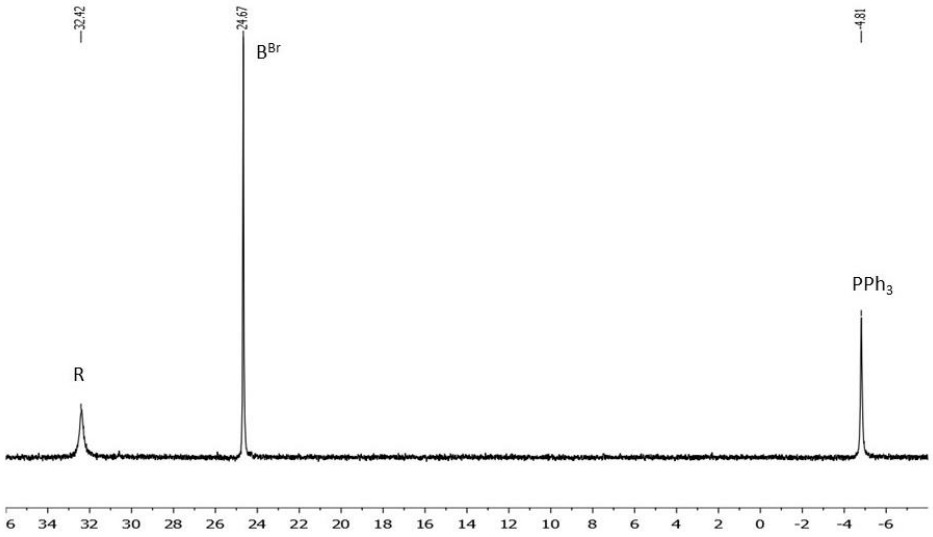


Figure S179. ^{31}P NMR spectrum of $\mathbf{B^{Br}_{NO_2}}$ after the addition of piperidine 20 eq.

2) Morpholine

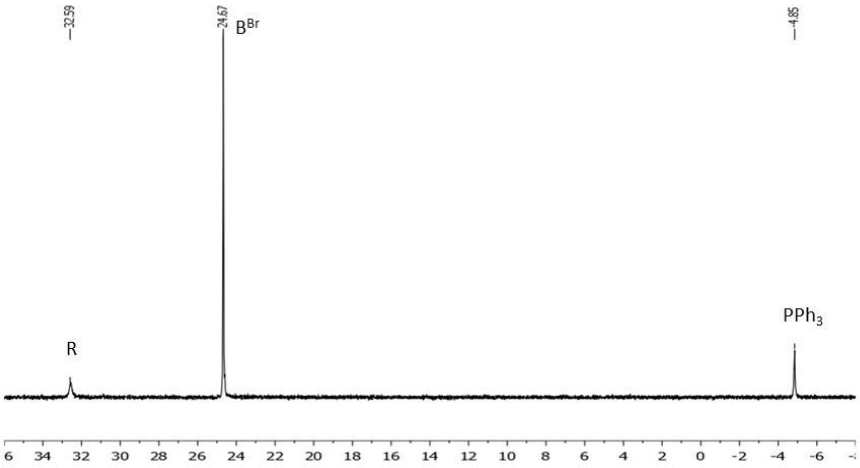


Figure S180. ^{31}P NMR spectrum of $\mathbf{B^{Br}_{NO_2}}$ after the addition of morpholine 20 eq.

3) 4-Methylmorpholine

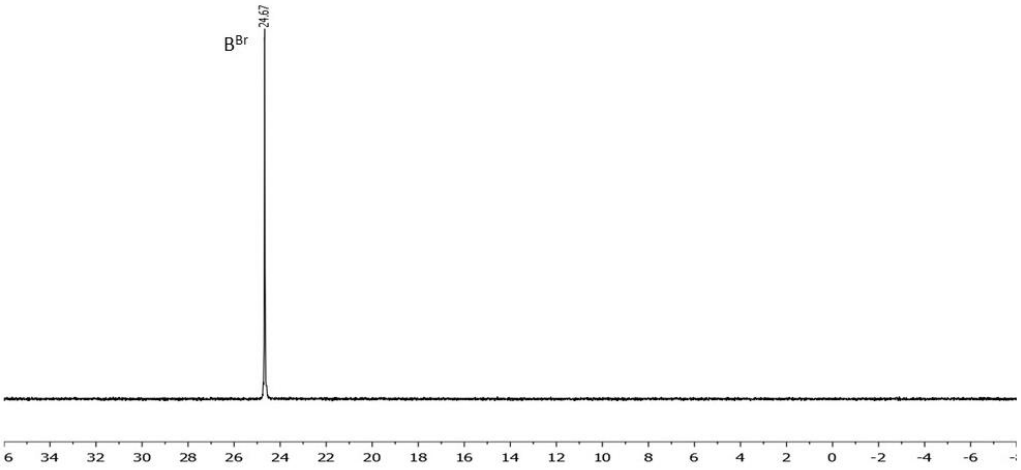
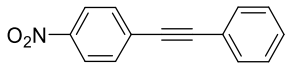


Figure S181. ^{31}P NMR spectrum of $\mathbf{B^{Br}_{NO_2}}$ after the addition of 4-methylmorpholine 20 eq.

19.Compounds Characterization

The products **3a-3l** were synthesized following the procedure described in the Section 12.

1-nitro-4-(phenylethynyl)benzene



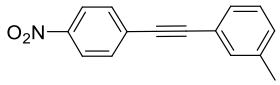
3a

Yellow solid; Purification by flash chromatography (Cy 100%)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.19 – 8.17 (d, J = 9.0 Hz, 2H), 7.64 – 7.62 (d, J = 9.0 Hz, 2H), 7.56 – 7.53 (m, 2H), 7.38 – 7.36 (m, 3H).

^{13}C NMR (100.8 MHz, $CDCl_3$): δ (ppm) 146.95, 132.27, 131.84, 130.22, 129.28, 128.57, 123.58, 122.10, 94.75, 87.59.

1-Methyl-3-(4-nitrophenyl)benzene



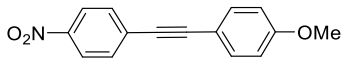
3b

Yellow solid; Purification by flash chromatography (Cy 100%)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.23-8.20 (d, J= 9 Hz, 2H); 7.66-7.64 (d, J= 9 Hz, 2H); 7.39-7.36 (m, 1H); 7.30-7.28 (m, 1H); 7.22-7.20 (m, 1H), 2.38 (s, 3H).

^{13}C NMR (100.8 MHz, $CDCl_3$): δ (ppm)147.02, 138.42, 132.52, 132.36, 130.33, 129.07, 128.57, 125.92, 123.76, 122.54, 122.01, 95.12, 87.38, 21.38.

1-Methoxy-4-((4-nitrophenyl)ethynyl)benzene



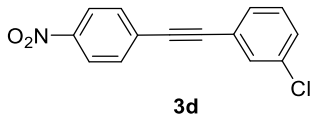
3c

Yellow solid; Purification by flash chromatography (Cy/EtOAc 95/5)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.22-8.20 (d, J= 9 Hz, 2H); 7.64-7.62 (d, J= 9 Hz, 2H); 7.51-7.49 (d, J=8.9 Hz, 2H), 6.92-6.90 (d, J=8.9 Hz, 2H); 3.85 (s, 3H)

^{13}C NMR (100.8 MHz, $CDCl_3$): δ (ppm) 160.54, 146.81, 133.59, 132.13, 130.84, 123.78, 114.35, 95.28, 86.78, 55.52.

1-Chloro-3-((4-nitrophenyl)ethynyl)benzene



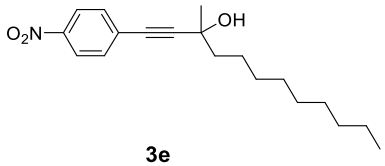
3d

Yellow solid; Purification by flash chromatography (Cy/EtOAc 90/10)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.24-8.22 (d, J= 8.8 Hz, 2H); 7.67-6.65 (d, J= 8.8 Hz, 2H); 7.54 (s, 1H); 7.45-7.43 (m, 2H) 7.38-7.30 (m, 2H).

^{13}C NMR (100.8 MHz, $CDCl_3$): δ (ppm) 147.33, 134.54, 132.51, 131.78, 130.07, 129.91, 129.77, 129.65, 123.92, 123.82, 93.09, 88.61

3-methyl-1-(4-nitrophenyl)dodec-1-yn-3-ol



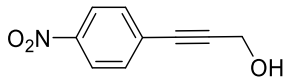
3e

Orange oil; Purification by flash chromatography (Cy/EtOAc 90/10)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.20 – 8.18 (d, J = 9.0 Hz, 2H), 7.57 – 7.55 (d, J = 9.0 Hz, 2H), 1.80 – 2.75 (m, 2H), 1.50 (s, 3H), 1.32 – 1.28 (m, 14H), 0.90 – 0.87 (m, 3H).

^{13}C NMR (100.8 MHz, $CDCl_3$) δ (ppm) 146.99, 132.36, 129.78, 123.50, 98.51, 83.12, 81.49, 68.67, 67.37, 43.53, 29.65, 29.53, 29.42, 29.27, 24.69, 22.64, 14.08

1-(hept-1-yn-1-yl)-4-nitrobenzene



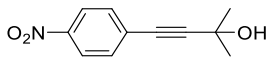
3f

Yellow oil; Purification by flash chromatography (Cy/EtOAc = 95/5).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.21 – 8.18 (d, J = 9.0 Hz, 2H), 7.60 – 7.57 (d, J = 9.0 Hz, 2H), 4.55 (s, 2H).

^{13}C NMR (100.8 MHz, $CDCl_3$) δ (ppm) 147.25, 132.39, 129.41, 123.57, 92.46, 83.81, 51.49.

2-methyl-4-(4-nitrophenyl)but-3-yn-2-ol

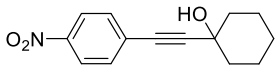


3g

Yellow solid; Purification by flash chromatography (Cy/EtOAc 90/10)
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.20 – 8.18 (d, J = 9.0 Hz, 2H), 7.58 – 7.56 (d, J = 9.0 Hz, 2H), 1.65 (s, 3H).

^{13}C NMR (100.8 MHz, $CDCl_3$) δ (ppm) 147.02, 132.34, 129.70, 123.46, 99.08, 80.38, 65.61, 31.20.

1-((4-nitrophenyl)ethynyl)cyclohexan-1-ol



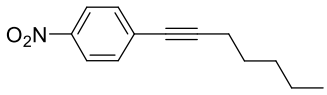
3h

White solid; Purification by flash chromatography (Cy/EtOAc 90/10)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19 – 8.17 (d, J = 9.0 Hz, 2H), 7.58 – 7.56 (d, J = 9.0 Hz, 2H) 2.19 (s, 1H), 2.04 – 2.03 (m, 2H), 1.78 – 1.55 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 147.02, 132.70, 129.81, 123.55, 98.29, 82.54, 69.12, 39.74, 25.04, 23.25

1-(hept-1-yn-1-yl)-4-nitrobenzene



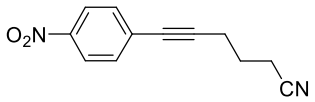
3i

Yellow oil; Purification by flash chromatography (Cy 100%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.16 – 8.14 (d, J = 9.0 Hz, 2H), 7.52 – 7.50 (d, J = 9.0 Hz, 2H), 2.46 – 2.43 (t, *J* = 12.0 Hz, 2H), 1.66 – 1.60 (m, 2H), 1.48 – 1.34 (m, 4H), 0.95 – 0.91 (t, *J* = 12.0 Hz, 3H).

^{13}C NMR (100.8 MHz, $CDCl_3$) δ (ppm) 146.53, 132.19, 131.20, 123.43, 96.79, 79.25, 31.08, 28.08, 22.16, 19.50, 13.93.

6-(4-nitrophenyl)hex-5-ynenitrile



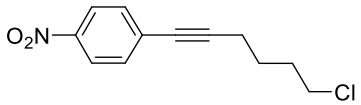
3j

Yellow oil; Purification by flash chromatography (Cy/EtOAc 95/5)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19 – 8.17 (d, J = 9.0 Hz, 2H), 7.55 – 7.53 (d, J = 9.0 Hz, 2H), 2.69 – 2.66 (t, J = 6.8 Hz, 2H), 2.59 – 2.56 (t, J = 7.1 Hz, 2H), 2.04 – 1.97 (p, J = 7.0 Hz, 2H).

^{13}C NMR (100.8 MHz, $CDCl_3$) δ (ppm) 146.87, 132.32, 130.12, 123.52, 118.88, 92.84, 80.82, 24.21, 18.63, 16.30.

1-(6-chlorohex-1-yn-1-yl)-4-nitrobenzene



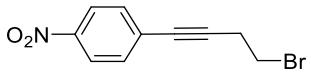
3k

Yellow solid; Purification by flash chromatography (Cy/EtOAc 95/5)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.16-8.14 (d, J= 8.9 Hz, 2H); 7.52-7.50 (d, J= 8.89 Hz, 2H); 3.62-3.59 (J=6.5 Hz, 2H); 2.52-2.49 (7 Hz, 2H); 1.99-1.92 (m, 2H); 1.83-1.76 (m, 2H).

^{13}C NMR (100.8 MHz, $CDCl_3$): δ (ppm) 146.80, 132.39, 130.95, 123.63, 95.61, 44.55, 31.73, 25.71, 19.03

1-(4-bromobut-1-yn-1-yl)-4-nitrobenzene



3l

Yellow solid; Purification by flash chromatography (Cy/EtOAc 95/5)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.21 – 8.18 (d, J = 9.0 Hz, 2H), 7.60 – 7.57 (d, J = 9.0 Hz, 2H), 6.08 – 6.01 (dd, J = 17.5, 11.2 Hz, 1H), 5.87 – 5.82 (dd, J = 17.6, 2.0 Hz, 1H), 5.70 – 5.66 (dd, J = 11.2, 2.0 Hz, 1H).

^{13}C NMR (100.8 MHz, $CDCl_3$) δ (ppm) 132.24, 130.06, 129.09, 123.57, 116.45, 93.15, 87.97.

20. Computational Studies

Computational Methods

DFT calculations were conducted through the Molecular Graphics and Computation Facility (MGCF) at the University of California, Berkeley using the Gaussian 16 software package[10].
Geometry optimizations for all reported structures were performed using the PBE0 functional (the hybrid functional based on the Perdew-Burke-Ernzerhof functional [PBE][11,12]) with Grimme's D3 dispersion correction with Becke Johnson damping (GD3-BJ)[13] and the basis sets def2-TZVP[14] (with effective core potential) for Pd, I, Br, Cl and def2-SVP for all the other atoms. Frequency calculations were performed on all optimized structures to ensure that each local minimum lacked imaginary frequencies and that each transition state contained exactly one imaginary frequency. Solvation in DMF were introduced through single point calculations at optimized gas-phase geometries for all the minima and transition state using the dispersion corrected PBE0 with def2-TZVP for all atoms and the SMD implicit solvation model.[15] The reported Gibbs free energies were corrected considering the thermal correction computed at 298.15 K.

Reaction coordinate in gas-phase

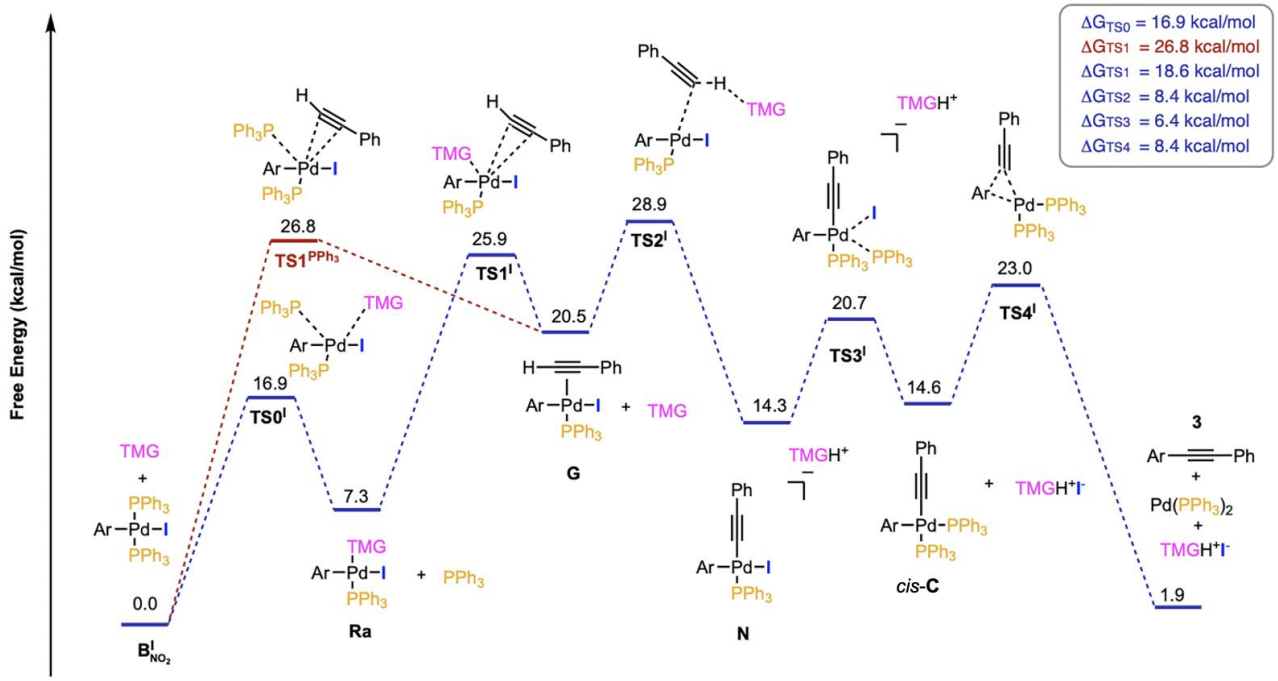


Figure S182. DFT-calculation-computed reaction profile and solution-state Gibbs free energies in gas-phase (ΔG kcal mol^{-1}) PBE/def2-TZVP level of theory at 298 K for stationary points of the Heck–Cassar protocol mechanism with $\mathbf{B^{I}_{NO_2}}$

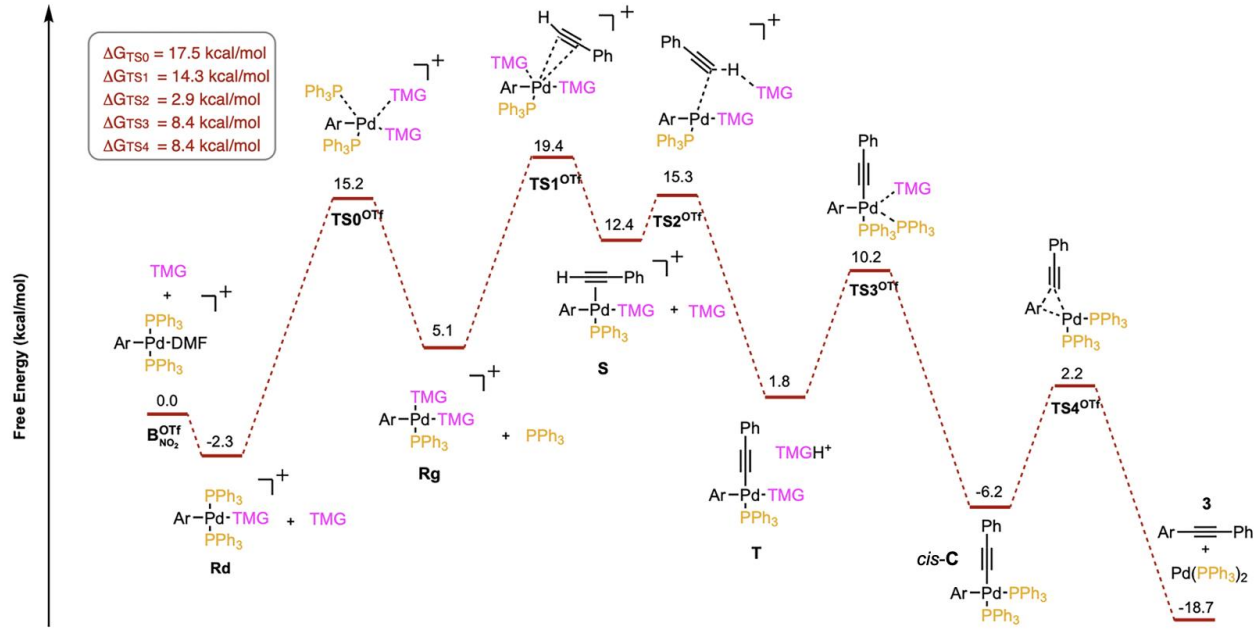


Figure S183. DFT-calculation-computed reaction profile and solution-state Gibbs free energies in gas-phase (ΔG kcal mol^{-1}) PBE/def2-TZVP level of theory at 298 K for stationary points of the Heck–Cassar protocol mechanism with $\mathbf{B^{OTf}_{NO_2}}$

Reaction coordinate for the isomerization mechanism

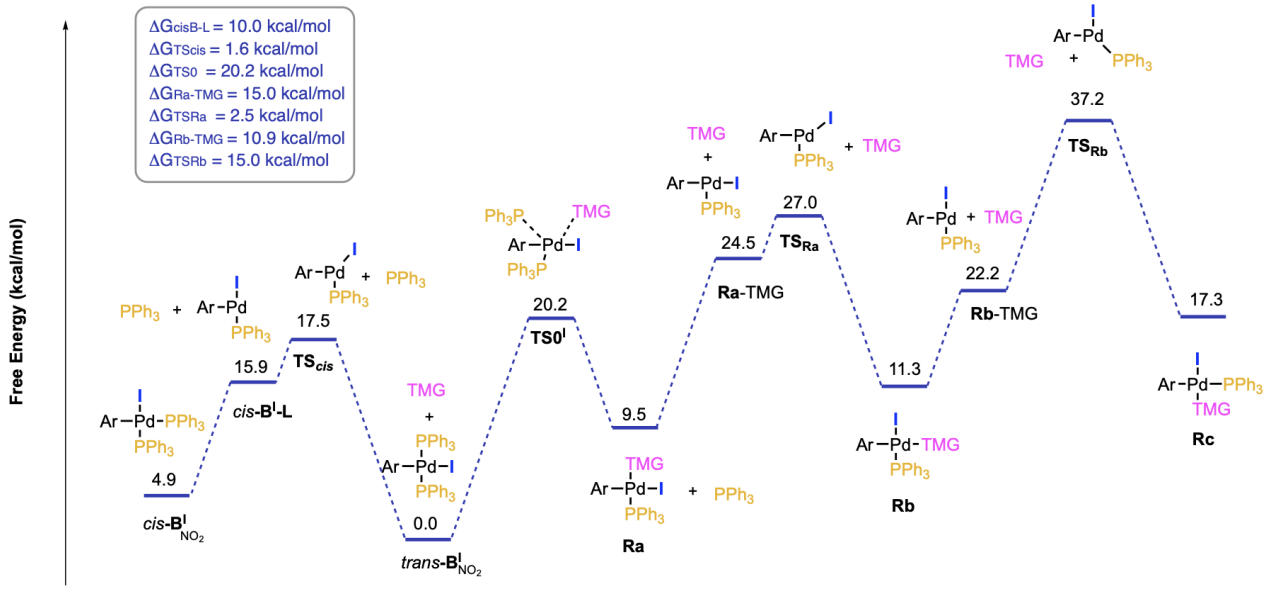


Figure S184. Isomerization from *cis*- $\mathbf{B^{I}_{NO_2}}$ to *trans*- $\mathbf{B^{I}_{NO_2}}$: dissociation pathway investigated but other possible isomerization mechanism can occur (see ref 10a in the main text).

Alternative pathways

Dissociation of PPh_3 from $\mathbf{B^{I}_{NO_2}}$

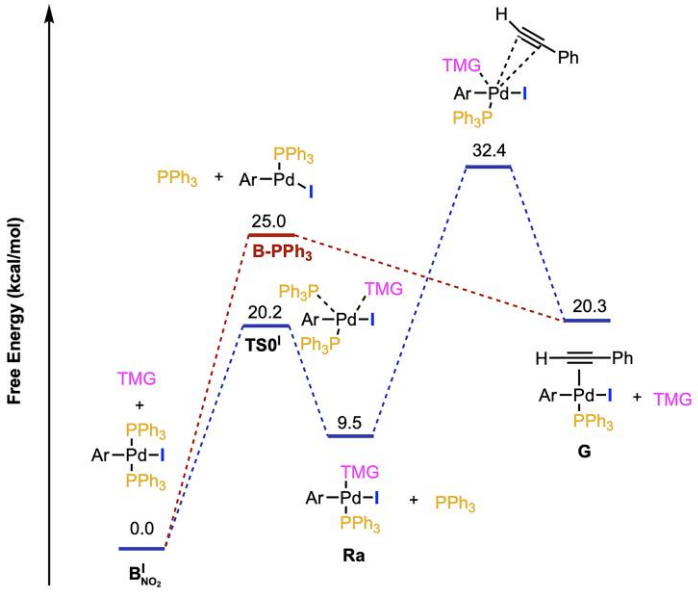


Figure S185. Dissociation of PPh_3 from $\mathbf{B^{I}_{NO_2}}$ to form complex **B-PPh$_3$** has an energy of 25.0 kcal/mol, therefore unfavored over the formation of **TS0^{I}** where the TMG displaces the phosphine giving intermediate **Ra**

Equilibrium between *cis*-**C** and *trans*-**C**

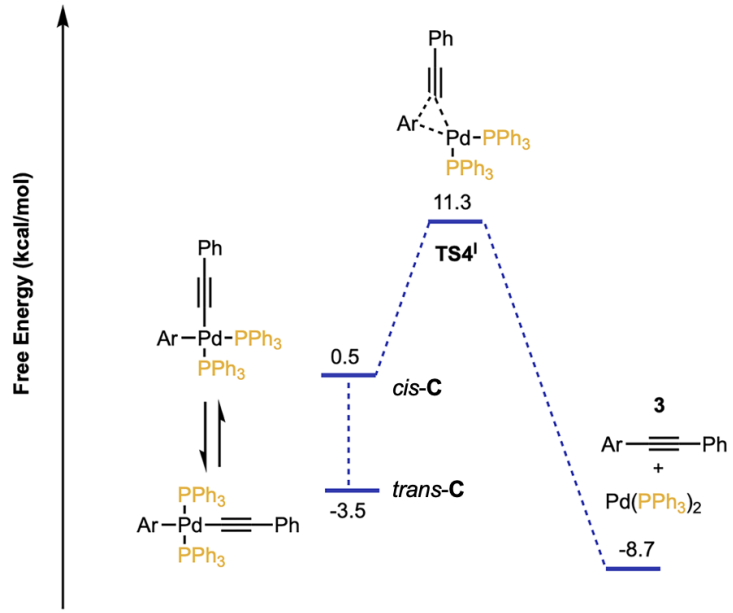


Figure S186. The equilibrium between *cis*-**C** and *trans*-**C** (4.0 kcal/mol more stable than *cis*-**C**) could slow down the reductive elimination step

Cartesian Coordinates (Å) of Optimized Structures

PPh_3

E (DMF) = -1035.420095

P	0.00101600	0.00053400	-1.26984500
C	-0.83277900	1.41650400	-0.44332900
C	-0.31770500	2.08992300	0.67065000
C	-2.05688100	1.83715900	-0.98289700
C	-1.01814300	3.15448600	1.23739100
H	0.63762300	1.77771400	1.09896700
C	-2.76193900	2.89116800	-0.40796400
H	-2.45978800	1.32834100	-1.86369000
C	-2.24193800	3.55459800	0.70374200
H	-0.60395200	3.67276600	2.10587400
H	-3.71775500	3.20350200	-0.83578700
H	-2.78940000	4.38800200	1.15059100
C	1.64391300	0.01373400	-0.44272400
C	1.96712600	-0.76789100	0.67288700
C	2.62301400	0.85925900	-0.98386000
C	3.23956300	-0.69688400	1.23924800
H	1.21698100	-1.43577400	1.10268800
C	3.88878800	0.93955000	-0.40932000
H	2.38576600	1.46186700	-1.86568300
C	4.20094000	0.15838600	0.70363300
H	3.47933400	-1.31388200	2.10887600
H	4.63934900	1.60772700	-0.83869700
H	5.19682100	0.21292900	1.14994500
C	-0.80982700	-1.42869800	-0.44274200
C	-1.63916200	-1.31830900	0.67981600
C	-0.57534900	-2.69836700	-0.98953100
C	-2.21276200	-2.45558500	1.24752900
H	-1.83603000	-0.33519000	1.11372300
C	-1.13779400	-3.83468800	-0.41385400
H	0.05772500	-2.79340600	-1.87676500
C	-1.96083500	-3.71506600	0.70616100
H	-2.85965000	-2.35541600	2.12270300
H	-0.94109900	-4.81816100	-0.84774000
H	-2.41055500	-4.60470400	1.15365900

2

E (DMF) = -308.065783

C	-1.51127400	-1.20691600	-0.00000600
C	-0.12048500	-1.21146000	0.00000700
C	0.59181300	-0.00002100	0.00001000
C	-0.12046300	1.21144800	0.00000600
C	-1.51124100	1.20693800	-0.00000400
C	-2.21047400	0.00001400	-0.00001300
H	-2.05504800	-2.15448300	-0.00001000
H	0.43179000	-2.15310300	0.00001300
H	0.43185500	2.15306600	0.00001100
H	-2.05500900	2.15450700	-0.00000900
H	-3.30297800	0.00003700	-0.00002400

C	2.02112500	-0.00001500	0.00003100
C	3.23445700	0.00000500	0.00001400
H	4.30864600	0.00002200	-0.00024900

cis-**B**$^{\mathbf{I}}$

E (DMF) = -2932,393507

Pd	0.19126000	-0.74938500	-0.01610900
C	2.13900900	-1.24867300	-0.05921500
C	2.92292400	-1.31059700	1.10130000
C	2.75359100	-1.46782500	-1.30070500
C	4.29361100	-1.51928200	1.02802400
H	2.46217400	-1.16867900	2.08155300
C	4.12568300	-1.67818200	-1.39191700
H	2.15758800	-1.46058800	-2.21687800
C	4.88290800	-1.67760900	-0.22407800
H	4.92352000	-1.53670600	1.91716500
H	4.62630100	-1.82158700	-2.34981100
N	6.33381700	-1.78916100	-0.31513600
O	6.96905400	-1.76976200	0.71933200
O	6.82676000	-1.87431300	-1.42185300
P	0.91820700	1.44693800	0.05579300
C	2.67255700	1.73999000	0.47501700
C	3.64648200	1.60385600	-0.52288900
C	3.06917900	1.97583400	1.79535200
C	4.99672900	1.67773200	-0.19744100
H	3.34832800	1.41921000	-1.55679300
C	4.42358100	2.05439400	2.11501300
H	2.31921100	2.08859000	2.58115400
C	5.38908700	1.89508500	1.12349100
H	5.74851800	1.54591600	-0.97908500
H	4.72472700	2.23260000	3.14989000
H	6.45047700	1.93252600	1.37833600
C	0.03762900	2.34775200	1.38348300
C	-0.44418000	1.58802000	2.45577000
C	-0.18521000	3.72908200	1.36540900
C	-1.16814100	2.19149400	3.48234300
H	-0.27697000	0.50755200	2.46565500
C	-0.90447000	4.33182900	2.39427100
H	0.16939100	4.33324300	0.52904700
C	-1.40463500	3.56442400	3.44815500
H	-1.56502700	1.57841300	4.29448900
H	-1.08714200	5.40875200	2.36726200
H	-1.98358400	4.03987700	4.24334700
C	0.70348600	2.39931600	-1.48424200
C	-0.06052500	1.84981900	-2.51720800
C	1.30269400	3.65480900	-1.66461700
C	-0.26150000	2.55979100	-3.69901600
H	-0.49318600	0.85563300	-2.38866800
C	1.10055000	4.36201900	-2.84597100
H	1.95038000	4.06791500	-0.88744000
C	0.31165100	3.81859000	-3.86111400
H	-0.86764200	2.12307100	-4.49537300
H	1.56984000	5.33945900	-2.97983000
H	0.15640900	4.37512400	-4.78843900

P	-2.20659300	-0.38753300	-0.09290700
C	-3.06970800	-1.66550400	-1.07543500
C	-4.34871700	-2.11724900	-0.74212600
C	-2.44222300	-2.15608400	-2.22687100
C	-4.99481500	-3.04643100	-1.55605200
H	-4.83920100	-1.75273700	0.16297400
C	-3.09613300	-3.07129500	-3.04638800
H	-1.42456800	-1.83658300	-2.46697400
C	-4.37325600	-3.51989000	-2.70996200
H	-5.99006000	-3.40477800	-1.28281900
H	-2.59655900	-3.45264800	-3.93970900
H	-4.88091200	-4.25017000	-3.34457300
C	-3.01488800	-0.42529500	1.55055500
C	-4.17973800	0.30015400	1.83009700
C	-2.44062000	-1.21342300	2.55661700
C	-4.74768500	0.25441700	3.10200300
H	-4.64336200	0.91178100	1.05346100
C	-3.01481800	-1.26071300	3.82462700
H	-1.54409200	-1.80033000	2.33499400
C	-4.16461400	-0.52163600	4.10261700
H	-5.65358100	0.82874700	3.31007800
H	-2.55852900	-1.88172300	4.59907000
H	-4.61092500	-0.55527100	5.09952800
C	-2.86029200	1.15083900	-0.86270500
C	-3.34018200	1.14940900	-2.17887200
C	-2.79089900	2.36856100	-0.17249500
C	-3.70928300	2.34167000	-2.79852600
H	-3.42603500	0.20957400	-2.72761300
C	-3.15744900	3.55801200	-0.79568200
H	-2.46059600	2.39056200	0.86563400
C	-3.60846700	3.55106300	-2.11452100
H	-4.08029400	2.32142700	-3.82609400
H	-3.08787600	4.49621100	-0.24016400
H	-3.89081400	4.48575500	-2.60444500
I	-0.16518300	-3.34004600	0.28770500

cis-**B^{I}-L**

E (DMF) = -1896,955683

Pd	-3.52996244	-1.10486890	0.00000000
C	-1.76742444	-1.92563990	0.02008200
C	-1.09096744	-2.10130790	-1.19206300
C	-1.19913444	-2.36394790	1.22087400
C	0.13885656	-2.74984390	-1.21011200
H	-1.52665944	-1.74484990	-2.12674100
C	0.03180556	-3.01349190	1.20678100
H	-1.71704444	-2.21669590	2.16986000
C	0.67691356	-3.20959290	-0.01133700
H	0.68541456	-2.91682190	-2.13838900
H	0.49894756	-3.37838090	2.12181400
N	1.95151056	-3.92895490	-0.03269700
O	2.46159456	-4.13339890	-1.11342700
O	2.41334756	-4.28416390	1.03021500
P	-4.42462344	-3.20880390	0.01538100
C	-3.77158344	-4.44397290	-1.15267800

C	-2.50691544	-5.00350390	-0.91691200
C	-4.47320944	-4.78822390	-2.31339700
C	-1.95672644	-5.89483190	-1.83260800
H	-1.94870344	-4.74295790	-0.01467100
C	-3.91441144	-5.67957690	-3.22791800
H	-5.46090944	-4.36273790	-2.50356400
C	-2.65728244	-6.23199390	-2.99083800
H	-0.96852444	-6.31989390	-1.64271700
H	-4.46902044	-5.94413690	-4.13107300
H	-2.22058844	-6.92826290	-3.71050800
C	-6.19682444	-3.05048890	-0.38440100
C	-6.57233644	-2.08911290	-1.33349800
C	-7.17651144	-3.84424490	0.22290600
C	-7.91239844	-1.93453990	-1.68124100
H	-5.80967144	-1.45831190	-1.80242100
C	-8.51524544	-3.68251390	-0.12555200
H	-6.89183044	-4.58461290	0.97389100
C	-8.88388944	-2.73132690	-1.07707400
H	-8.19767544	-1.18280690	-2.42040700
H	-9.27728444	-4.30219490	0.35263200
H	-9.93583044	-2.60568090	-1.34381000
C	-4.36608144	-4.01082690	1.64806800
C	-4.36863744	-3.18908490	2.78254600
C	-4.35842544	-5.40241490	1.80016400
C	-4.36834544	-3.75343390	4.05530800
H	-4.36208044	-2.10112490	2.66036100
C	-4.35327644	-5.96240990	3.07626900
H	-4.34883744	-6.04883790	0.91950600
C	-4.35864644	-5.14044490	4.20259800
H	-4.36752144	-3.10677690	4.93555500
H	-4.34220244	-7.04876390	3.19055200
H	-4.34974444	-5.58326490	5.20128500
I	-2.80215444	1.34195010	0.04077000

TS*cis*

E (DMF) = -1896,953133

Pd	0.50024800	-1.33429600	-0.22621500
P	0.50063000	0.86565400	0.03771200
C	-1.45612900	-1.11144300	-0.17422500
C	-2.17800400	-1.08496500	-1.37579900
C	-2.14089000	-1.15848900	1.04800200
C	-3.56776400	-1.12510800	-1.36203600
H	-1.65517800	-1.01681700	-2.33302000
C	-3.53278100	-1.19300000	1.07255600
H	-1.58998300	-1.15506700	1.99197000
C	-4.22481000	-1.16839800	-0.13495900
H	-4.15576200	-1.10571700	-2.27986100
H	-4.09386300	-1.22814100	2.00680600
N	-5.69027100	-1.17234200	-0.11337500
O	-6.26585600	-1.13640400	-1.17920800
O	-6.23425500	-1.20517900	0.96906900
C	-0.67754100	1.89120200	-0.90457900
C	-2.02221900	1.98202800	-0.51454200
C	-0.25459600	2.54150200	-2.06991700

C	-2.92221900	2.71970700	-1.27602400
H	-2.37169500	1.46757000	0.38272500
C	-1.16430800	3.27019800	-2.83442000
H	0.79032300	2.48283900	-2.38139800
C	-2.49687900	3.36166400	-2.43951900
H	-3.96669300	2.78306200	-0.96286100
H	-0.82431600	3.77181600	-3.74316800
H	-3.20826500	3.93376500	-3.03958200
C	2.13045300	1.55336200	-0.40961500
C	2.58814300	2.72333300	0.20914800
C	2.89548700	0.94999800	-1.41287700
C	3.80143300	3.28441500	-0.17978200
H	2.00269200	3.19228400	1.00295500
C	4.10585400	1.52010300	-1.80112700
H	2.55722300	0.01720800	-1.87053400
C	4.55944100	2.68547700	-1.18600300
H	4.15957000	4.19191100	0.31154000
H	4.70265000	1.03864900	-2.57873700
H	5.51401700	3.12498500	-1.48479700
C	0.26590900	1.28229100	1.79383700
C	-0.33768700	2.47508700	2.20953700
C	0.77111100	0.38852400	2.74827700
C	-0.44332400	2.76319200	3.56915400
H	-0.72892000	3.17996600	1.47291800
C	0.66581000	0.68520900	4.10414700
H	1.24731000	-0.54128100	2.42040100
C	0.05530300	1.87002000	4.51591200
H	-0.91991300	3.69265200	3.88889800
H	1.06061400	-0.01606000	4.84254500
H	-0.03297700	2.09770000	5.58076000
I	2.72276100	-2.66443200	-0.19025500

trans-**B**$^{\mathbf{I}}$

E (DMF) = -2932.401309

Pd	-0.00006600	0.43960600	0.07679900
I	-0.00038700	3.11385800	0.32066900
C	0.00003700	-1.55890600	0.06589400
C	0.00003800	-2.29803400	-1.12652100
C	0.00005700	-2.25249000	1.28639400
C	0.00010100	-3.68623800	-1.11071800
H	-0.00001600	-1.78304600	-2.09014800
C	0.00015600	-3.64382300	1.32134800
H	-0.00005500	-1.69943900	2.23017100
C	0.00019200	-4.34245300	0.11811200
H	0.00005300	-4.27558200	-2.02721400
H	0.00022500	-4.20050800	2.25894100
N	0.00039000	-5.80210700	0.14281200
O	0.00048300	-6.38527100	-0.92136100
O	0.00036300	-6.34891200	1.22681400
P	-2.32935800	0.35488400	-0.00545700
C	-3.01029400	-1.22804400	-0.62446200
C	-3.09140700	-2.33100900	0.23699700
C	-3.30344100	-1.39890100	-1.98114700
C	-3.44006600	-3.58382900	-0.25575700

H	-2.86389600	-2.21396500	1.29796700
C	-3.65359400	-2.65666700	-2.47092900
H	-3.25646100	-0.54684700	-2.66264500
C	-3.71483200	-3.75219000	-1.61317900
H	-3.48598400	-4.43745300	0.42440800
H	-3.87844500	-2.77827000	-3.53314400
H	-3.97715900	-4.73952300	-2.00002700
C	-3.04891500	1.59354500	-1.13708100
C	-2.33862500	1.91120400	-2.30116900
C	-4.28336500	2.20134300	-0.89543900
C	-2.86907700	2.80673100	-3.22461600
H	-1.35325200	1.46804100	-2.46763000
C	-4.80511400	3.10915500	-1.81544100
H	-4.83424400	1.98052000	0.02088700
C	-4.10359700	3.40834000	-2.98169100
H	-2.30661600	3.05142100	-4.12842600
H	-5.76554900	3.58952600	-1.61479600
H	-4.51447700	4.12253100	-3.69918300
C	-3.14930500	0.58383500	1.60753400
C	-2.46613500	1.24626200	2.63355800
C	-4.45482300	0.12331200	1.83205900
C	-3.08257700	1.44826000	3.86689800
H	-1.45550500	1.62044200	2.45011400
C	-5.06603300	0.32837600	3.06622800
H	-4.99054400	-0.40813900	1.04189600
C	-4.38050900	0.99051600	4.08503500
H	-2.54233900	1.96889600	4.66078400
H	-6.08282000	-0.03440000	3.23398000
H	-4.86105800	1.14750600	5.05375000
P	2.32926800	0.35519000	-0.00531900
C	3.01034900	-1.22775900	-0.62413200
C	3.30361200	-1.39872400	-1.98078300
C	3.09149300	-2.33063500	0.23743200
C	3.65396300	-2.65650300	-2.47039500
H	3.25656100	-0.54675300	-2.66238100
C	3.44036700	-3.58346700	-0.25514400
H	2.86385300	-2.21351100	1.29836700
C	3.71528000	-3.75193000	-1.61252000
H	3.87890800	-2.77820000	-3.53257900
H	3.48628500	-4.43700800	0.42512400
H	3.97778400	-4.73926000	-1.99925500
C	3.14927100	0.58452100	1.60759600
C	4.45463000	0.12370400	1.83240000
C	2.46627500	1.24768000	2.63327500
C	5.06584900	0.32915900	3.06650300
H	4.99022900	-0.40828100	1.04251400
C	3.08272900	1.45008000	3.86653900
H	1.45577600	1.62210600	2.44960900
C	4.38050200	0.99200800	4.08496100
H	6.08251000	-0.03387300	3.23447200
H	2.54263300	1.97129000	4.66014600
H	4.86106100	1.14931000	5.05362000
C	3.04880300	1.59368100	-1.13715300
C	4.28365200	2.20085400	-0.89597000
C	2.33828500	1.91160300	-2.30102400
C	4.80556500	3.10832500	-1.81621100

H	4.83472900	1.97980300	0.02018700
C	2.86889000	2.80679900	-3.22471100
H	1.35265400	1.46888800	-2.46712900
C	4.10380300	3.40778700	-2.98224800
H	5.76632300	3.58820100	-1.61593100
H	2.30625300	3.05171000	-4.12835100
H	4.51481200	4.12170100	-3.69994200

Ra^{I}

E (DMF) = -2259.136849

Pd	0.57943300	-0.45579600	-0.15970500
I	2.91628000	0.91585300	-0.28218900
C	-1.09404400	-1.53449900	-0.12029300
C	-1.86316700	-1.71083100	-1.28205300
C	-1.52956800	-2.15100100	1.06333200
C	-3.04703100	-2.43940200	-1.26155400
H	-1.55743100	-1.23680000	-2.21860600
C	-2.71218600	-2.88231900	1.10455400
H	-0.95337800	-2.03500100	1.98474300
C	-3.46426400	-3.00606100	-0.06015200
H	-3.66806000	-2.56048800	-2.14918900
H	-3.07580500	-3.34607700	2.02205400
N	-4.73619300	-3.72173100	-0.01485100
O	-5.36694600	-3.81847000	-1.04693800
O	-5.09341700	-4.17095400	1.05476800
P	-0.65992300	1.44078500	0.05039900
C	-2.45519000	1.22906300	-0.24647000
C	-3.24180300	0.59792400	0.72763100
C	-3.02587100	1.55092300	-1.48124100
C	-4.56738500	0.27530200	0.46057300
H	-2.80856100	0.34103500	1.69625100
C	-4.35668000	1.22625000	-1.74531100
H	-2.42761200	2.05085900	-2.24586300
C	-5.12655800	0.58107600	-0.78122400
H	-5.16444400	-0.23166100	1.22214000
H	-4.79088500	1.47779100	-2.71578800
H	-6.16379600	0.31301300	-0.99471200
C	-0.20725700	2.75057100	-1.13935000
C	0.26268700	2.36794300	-2.40095500
C	-0.37047300	4.10688000	-0.84511000
C	0.54622500	3.33170200	-3.36445300
H	0.42750600	1.30855800	-2.61416800
C	-0.07275400	5.06969400	-1.80761300
H	-0.71785600	4.41616500	0.14280900
C	0.38010100	4.68421900	-3.06819900
H	0.91658200	3.02515000	-4.34525200
H	-0.19189100	6.12884000	-1.56772500
H	0.61493400	5.44156500	-3.81994900
C	-0.58932300	2.21912800	1.70308200
C	0.55298900	2.04960100	2.49397700
C	-1.64577200	3.00811700	2.18007700
C	0.63632700	2.66110900	3.74313300
H	1.38610400	1.45364400	2.11143500
C	-1.55750400	3.61624000	3.43011100

H	-2.54572100	3.14046500	1.57524500
C	-0.41711600	3.44281200	4.21390400
H	1.53419800	2.52522000	4.35043400
H	-2.38670300	4.22758000	3.79394700
H	-0.35095300	3.91868600	5.19534600
C	2.78158900	-2.60014300	-0.01095200
N	1.60519700	-2.24368400	-0.45551500
N	3.70340300	-3.21302000	-0.81394700
N	3.13522200	-2.38984000	1.28483200
C	3.66213400	-3.00467700	-2.24009900
H	3.06610500	-3.77191100	-2.77091400
H	3.24977400	-2.00913200	-2.45456200
H	4.68673700	-3.04164300	-2.64143200
C	4.55051700	-4.28025800	-0.33858800
H	4.36081000	-5.20304200	-0.91472800
H	5.62180800	-4.03296700	-0.43502300
H	4.33232300	-4.48694600	0.71585400
C	2.11382000	-2.13957100	2.27125300
H	2.47602300	-2.47822400	3.25428300
H	1.85720000	-1.06655900	2.33780600
H	1.20557600	-2.69575400	2.01068600
C	4.46927800	-1.96203600	1.64627500
H	4.42959700	-0.94003500	2.05773500
H	4.92059700	-2.63533800	2.39491200
H	5.10803900	-1.92584800	0.75724900
H	1.35046900	-2.70973200	-1.32054400

Rb^{I}

E (DMF) = -2259.133976

Pd	0.66093900	-0.49539500	-0.20607300
P	-0.46996800	1.51013600	-0.05200000
C	0.34648600	3.02158100	0.60061700
C	1.69844100	3.23937200	0.30678700
C	-0.36244500	3.99944800	1.31182100
C	2.32875400	4.41207800	0.71659400
H	2.25864800	2.46666900	-0.22198800
C	0.27298000	5.17007200	1.72150100
H	-1.41640100	3.84562500	1.55206700
C	1.61862700	5.38004100	1.42507300
H	3.38491800	4.56782900	0.48360600
H	-0.29084600	5.92365900	2.27650400
H	2.11436500	6.29844800	1.74843800
C	-1.99803600	1.40624500	0.93880400
C	-1.87963000	1.33273900	2.33383900
C	-3.25229700	1.23554500	0.34679600
C	-3.00229600	1.10335500	3.12239500
H	-0.89902600	1.44471400	2.80514300
C	-4.37198800	0.98981700	1.14002100
H	-3.35337100	1.26525000	-0.73940700
C	-4.25088900	0.92408700	2.52582700
H	-2.90022700	1.04744900	4.20866500
H	-5.34418200	0.83524200	0.66650500
H	-5.12936900	0.71927200	3.14165100
C	-0.99954500	2.06218700	-1.71380000

C	-0.59430400	1.33135100	-2.83484500
C	-1.77013200	3.21936000	-1.88650800
C	-0.96400500	1.74419000	-4.11450200
H	0.01383500	0.43232400	-2.69204600
C	-2.14233400	3.62643200	-3.16386500
H	-2.08044100	3.80515700	-1.01772200
C	-1.74065700	2.88866600	-4.27912400
H	-0.64556200	1.16524800	-4.98440500
H	-2.74739900	4.52703300	-3.29171500
H	-2.03422600	3.21104200	-5.28096800
C	3.66905400	-0.23291400	0.31302800
N	2.66330000	0.24952600	-0.36936100
N	3.56767400	-0.42682200	1.66011700
N	4.86297500	-0.55943000	-0.26536700
H	2.93605500	0.50604200	-1.31363800
C	2.51323500	0.22904000	2.39414200
H	2.32388100	1.22514500	1.97750600
H	1.56726300	-0.34502700	2.36162100
H	2.82422700	0.33535400	3.44475800
C	4.07059900	-1.64140500	2.27004100
H	4.71116500	-1.41901000	3.14003300
H	3.22592600	-2.26959000	2.59913900
H	4.63852600	-2.22682200	1.53931200
C	6.12406600	-0.36730000	0.40964900
H	5.95403700	0.07657800	1.39768500
H	6.67396200	-1.31548800	0.53859300
H	6.76431400	0.31994500	-0.17096700
C	4.92470800	-0.85936200	-1.67491600
H	5.13953200	0.03303900	-2.29434000
H	5.72695000	-1.59136500	-1.85301000
H	3.97933200	-1.31903200	-1.99688400
C	-1.13982100	-1.33177600	-0.10229800
C	-1.95741100	-1.51038200	-1.22882800
C	-1.64846300	-1.70626300	1.15260500
C	-3.26098000	-1.98105300	-1.10533000
H	-1.58225300	-1.26818400	-2.22486100
C	-2.94596400	-2.17708900	1.29548300
H	-1.02590700	-1.60463400	2.04459800
C	-3.74767000	-2.28867800	0.16139300
H	-3.91516400	-2.10110500	-1.96926600
H	-3.36135900	-2.44144200	2.26767700
N	-5.13748600	-2.70191500	0.31221700
O	-5.81642700	-2.78591700	-0.69107700
O	-5.54312600	-2.92334000	1.43540700
I	1.60543100	-2.93556600	-0.51877800

Rc^{I}

E (DMF) = -2259.124437

Pd	-0.55816700	-0.34638000	0.03240700
I	-0.52857500	-2.89985600	-0.42825400
P	1.81994200	-0.22934700	0.16484800
C	2.54592200	1.45514500	0.07770300
C	2.20771600	2.37202700	1.08401100
C	3.41608500	1.85739300	-0.94071700

C	2.73400500	3.65959200	1.07555300
H	1.54450800	2.05635500	1.89278200
C	3.94565700	3.14951000	-0.94586000
H	3.69806900	1.15048600	-1.72424900
C	3.60819500	4.05218400	0.05959300
H	2.46992200	4.35945200	1.87237900
H	4.63457000	3.44663800	-1.74037800
H	4.02997300	5.06007600	0.05739300
C	2.78183700	-1.13703000	-1.09670100
C	2.20517100	-1.33062100	-2.35709600
C	4.07899200	-1.60166700	-0.85532700
C	2.92710600	-1.95472300	-3.37178000
H	1.17228500	-1.01945500	-2.52936600
C	4.79531800	-2.23472800	-1.86880800
H	4.52896500	-1.47898200	0.13223600
C	4.22330900	-2.40651000	-3.12903800
H	2.46546500	-2.10753500	-4.34989200
H	5.80500600	-2.60179000	-1.67015500
H	4.78552500	-2.90713800	-3.92100600
C	2.47419900	-0.81745000	1.77417100
C	1.78133500	-1.82631700	2.45472100
C	3.65330900	-0.29982700	2.32960000
C	2.26634200	-2.31351500	3.66706900
H	0.86451900	-2.23641600	2.02226300
C	4.13256900	-0.78946700	3.54238300
H	4.19726300	0.49656500	1.81631200
C	3.44021400	-1.79754900	4.21290400
H	1.71764800	-3.10216500	4.18704700
H	5.05233000	-0.37917600	3.96630500
H	3.81642700	-2.17921600	5.16521400
C	-0.71641600	2.78672000	-0.22983000
N	-0.90842400	1.66646900	0.40701200
N	-0.25173100	2.83741200	-1.50741900
N	-0.95689800	4.00230300	0.37335500
H	-1.52890600	1.77965400	1.20384400
C	-0.42654000	1.74711100	-2.43477400
H	0.51681100	1.20031100	-2.60041000
H	-1.17582400	1.04191500	-2.05597900
H	-0.76873900	2.14412300	-3.40527300
C	0.60598600	3.90387800	-1.96804500
H	0.89339500	4.54757900	-1.12955300
H	1.52780300	3.47323700	-2.39019800
H	0.12326200	4.51696700	-2.74939700
C	-1.65331800	5.05334600	-0.33798300
H	-1.11170700	6.01200700	-0.27702500
H	-1.77117400	4.78380500	-1.39324500
H	-2.66312700	5.20062300	0.08484500
C	-1.04922600	4.07670800	1.80912900
H	-0.32405500	3.39545800	2.27235800
H	-0.81328200	5.10141900	2.13390100
H	-2.05976600	3.82974900	2.19049800
C	-2.55784300	-0.49352300	0.06575900
C	-3.22267700	-0.37311400	1.29750100
C	-3.33495300	-0.59468600	-1.09886600
C	-4.61172000	-0.32974000	1.37110300
H	-2.64780200	-0.32528400	2.22767100

C	-4.72380500	-0.54427600	-1.04678400
H	-2.85035500	-0.73446700	-2.06854900
C	-5.34675800	-0.40564000	0.19138500
H	-5.14089900	-0.23952200	2.32029700
H	-5.33970900	-0.61621600	-1.94376000
N	-6.80445800	-0.33865300	0.25438900
O	-7.41859000	-0.40478500	-0.79003800
O	-7.31726800	-0.21460500	1.34753100

Ra^{Br}

E (DMF) = -4535.268146

Pd	0.75254000	-0.36582400	-0.18296600
C	-0.81447000	-1.58167100	-0.10914000
C	-1.61168100	-1.79669200	-1.24591900
C	-1.14891600	-2.26311500	1.07219400
C	-2.72878200	-2.62272200	-1.20086700
H	-1.38340100	-1.27688200	-2.18019100
C	-2.26517500	-3.09043000	1.13863800
H	-0.54434200	-2.12506800	1.97210500
C	-3.05075000	-3.24893200	0.00033000
H	-3.37160100	-2.77527600	-2.06786400
H	-2.55180700	-3.60540000	2.05610500
N	-4.25669600	-4.06842600	0.07459200
O	-4.92000200	-4.19034100	-0.93429700
O	-4.53150300	-4.57344600	1.14374600
P	-0.62916200	1.42822500	0.02926300
C	-2.41047300	1.06791000	-0.18010900
C	-3.09100700	0.36312100	0.82316300
C	-3.06387900	1.34402900	-1.38455500
C	-4.39472200	-0.07226700	0.61545000
H	-2.58946700	0.13566200	1.76595700
C	-4.37199700	0.90464000	-1.58956800
H	-2.54606500	1.89590400	-2.17200500
C	-5.03629500	0.19026000	-0.59617500
H	-4.90830600	-0.63485000	1.39848100
H	-4.87135300	1.12000200	-2.53713700
H	-6.05475200	-0.16733800	-0.76400500
C	-0.33019000	2.74055600	-1.20405500
C	0.23130400	2.39266500	-2.43687900
C	-0.71063100	4.06486900	-0.96508000
C	0.39377600	3.35771900	-3.42792400
H	0.56110900	1.36453100	-2.60467300
C	-0.53778700	5.02926800	-1.95509200
H	-1.13490100	4.34719500	0.00105100
C	0.01009200	4.67627700	-3.18801900
H	0.83732100	3.08024000	-4.38679500
H	-0.82962600	6.06389900	-1.76029600
H	0.14711500	5.43511200	-3.96221300
C	-0.53131300	2.25990300	1.65560500
C	0.69774300	2.29064000	2.32647900
C	-1.64257000	2.89813300	2.22317800
C	0.80888200	2.94836200	3.54939800
H	1.56988100	1.81537400	1.86757000
C	-1.52500400	3.55194700	3.44809100

H	-2.60660200	2.87865100	1.71014000
C	-0.30035800	3.57655500	4.11385200
H	1.77284400	2.97000400	4.06314800
H	-2.39766400	4.04403700	3.88406500
H	-0.21100700	4.08795400	5.07540700
C	3.17004900	-2.23368800	-0.02843700
N	1.93813300	-2.05769400	-0.42836000
N	4.12250800	-2.78704800	-0.83914400
N	3.55704000	-1.88875900	1.22876100
C	3.98261600	-2.70205700	-2.27138200
H	3.47247900	-3.58236800	-2.70767800
H	3.42498700	-1.79270400	-2.53370300
H	4.98119400	-2.63397400	-2.73038600
C	5.12896700	-3.69232500	-0.33930800
H	5.03780400	-4.67500900	-0.83475500
H	6.15083100	-3.31502700	-0.51730100
H	4.99308000	-3.84012100	0.73858300
C	2.56069100	-1.69135600	2.25257100
H	3.01100400	-1.90597800	3.23414400
H	2.17316000	-0.65654500	2.25762400
H	1.71953400	-2.37469400	2.08572800
C	4.83098700	-1.24744400	1.47385600
H	4.66260100	-0.20491400	1.79014500
H	5.40450800	-1.77617600	2.25400400
H	5.41988600	-1.21189300	0.55112700
H	1.69925500	-2.61386800	-1.24307700
Br	2.81066800	1.10208300	-0.37354700

Rb^{Br}

E (DMF) = -4535.264705

Pd	0.69533900	-0.66536700	-0.25810100
P	-0.27267900	1.39716400	-0.01807200
C	0.66399700	2.80916000	0.69263900
C	2.03250300	2.92214200	0.41820400
C	0.03011400	3.81939300	1.42917500
C	2.75284900	4.02493700	0.87209300
H	2.53255700	2.12157500	-0.12980400
C	0.75536800	4.91939200	1.88259200
H	-1.03537900	3.74557300	1.65631000
C	2.11720500	5.02576100	1.60506100
H	3.82108800	4.09926700	0.65443900
H	0.24975200	5.69894200	2.45745600
H	2.68364100	5.88887400	1.96285100
C	-1.79716600	1.36763500	0.98426000
C	-1.67416100	1.23541600	2.37431400
C	-3.06428300	1.30377400	0.39825200
C	-2.80430500	1.05245000	3.16456900
H	-0.68504600	1.26430100	2.84013300
C	-4.19239400	1.10505600	1.19240700
H	-3.17076100	1.37884400	-0.68524900
C	-4.06621000	0.97991900	2.57380100
H	-2.69863300	0.94987900	4.24708800
H	-5.17612200	1.03439800	0.72282300
H	-4.95219100	0.81296900	3.19035900

C	-0.77148700	2.06213800	-1.64798100
C	-0.41677700	1.36226500	-2.80526800
C	-1.46615700	3.27344600	-1.76048300
C	-0.76129000	1.86006600	-4.06150000
H	0.13184600	0.41993400	-2.70886400
C	-1.81378400	3.76554200	-3.01461700
H	-1.73700000	3.83472800	-0.86288200
C	-1.46260700	3.05891600	-4.16643900
H	-0.48276200	1.30496500	-4.96016700
H	-2.35991700	4.70826700	-3.09542900
H	-1.73665600	3.44806100	-5.14993300
C	3.69600200	-0.75141700	0.20253400
N	2.75560400	-0.08817800	-0.42054500
N	3.60358500	-0.99336400	1.54202800
N	4.80778900	-1.22491900	-0.43271100
H	3.03978700	0.17315300	-1.36022000
C	2.67175500	-0.23017600	2.33562800
H	2.61785000	0.80198400	1.97061100
H	1.65234600	-0.66063700	2.30282400
H	3.01674600	-0.22248900	3.38091000
C	3.92700200	-2.30151400	2.07564800
H	4.61026200	-2.22569800	2.93813100
H	3.00245600	-2.81164800	2.39361800
H	4.38406000	-2.92549200	1.30074700
C	6.10216800	-1.26851400	0.20301900
H	6.03569000	-0.84377300	1.21172800
H	6.49350900	-2.29782500	0.27886000
H	6.82884600	-0.67123800	-0.37524800
C	4.77077700	-1.48655300	-1.85082300
H	5.10050300	-0.62025600	-2.45637000
H	5.44120700	-2.32897600	-2.07931100
H	3.75321300	-1.78384100	-2.14182900
C	-1.15948300	-1.36647800	-0.17631400
C	-1.98520000	-1.44511300	-1.30747100
C	-1.68444800	-1.77283400	1.06099800
C	-3.31139300	-1.85345600	-1.20264600
H	-1.59930900	-1.17165900	-2.29132900
C	-3.00476300	-2.18203300	1.18520200
H	-1.05621200	-1.74534600	1.95435300
C	-3.81161800	-2.19745200	0.04928600
H	-3.97193800	-1.89769000	-2.06894600
H	-3.43288100	-2.47196100	2.14454100
N	-5.21973400	-2.55235100	0.18296700
O	-5.90310900	-2.54907700	-0.82073700
O	-5.63339000	-2.81728700	1.29357500
Br	1.42377200	-2.99903800	-0.60629000

Rc^{Br}

E (DMF) = -4535.256285

Pd	-0.60253500	-0.46894800	0.03576300
P	1.78339300	-0.37895100	0.12818100
C	2.53293600	1.29557800	0.11303400
C	2.21501700	2.16858000	1.16400800
C	3.39353000	1.73742400	-0.89719800

C	2.75110000	3.45149700	1.20697300
H	1.55972200	1.82094700	1.96631300
C	3.93306900	3.02437900	-0.85090600
H	3.65824200	1.06553100	-1.71668500
C	3.61507500	3.88341000	0.19822400
H	2.50277200	4.11657200	2.03792500
H	4.61341200	3.35251900	-1.64058700
H	4.04429900	4.88745900	0.23580100
C	2.69673000	-1.23989200	-1.19974000
C	2.05748800	-1.45046300	-2.42614800
C	4.02309500	-1.65472400	-1.03388500
C	2.74555200	-2.04322200	-3.48301600
H	1.00484300	-1.18091100	-2.53619400
C	4.70626100	-2.25326700	-2.08968100
H	4.52213800	-1.51767100	-0.07176300
C	4.07024000	-2.44311700	-3.31671100
H	2.23594800	-2.21111300	-4.43450600
H	5.73968600	-2.57967100	-1.95110600
H	4.60626200	-2.91747600	-4.14234600
C	2.46164900	-1.07604100	1.68289500
C	1.79815900	-2.16142900	2.26978100
C	3.62641100	-0.57592900	2.28164600
C	2.29900500	-2.73798500	3.43536000
H	0.89387600	-2.55784100	1.79878300
C	4.12025800	-1.15549200	3.44843400
H	4.14869200	0.27556400	1.83935700
C	3.45757900	-2.23733400	4.02707700
H	1.77441300	-3.58502000	3.88347000
H	5.02857400	-0.75795400	3.90777600
H	3.84511100	-2.68968100	4.94322800
C	-0.71443000	2.64675700	-0.15683700
N	-0.92918600	1.51975400	0.46176300
N	-0.28472000	2.70496200	-1.44621100
N	-0.89587200	3.85531300	0.47687100
H	-1.52784900	1.63359600	1.27490000
C	-0.56234600	1.65556300	-2.39661900
H	0.33149800	1.04318100	-2.60158700
H	-1.35473200	0.99942000	-2.01772500
H	-0.89643900	2.10555700	-3.34664100
C	0.61716200	3.73432900	-1.90611400
H	0.97350800	4.33155300	-1.05942300
H	1.49587200	3.26536100	-2.37641500
H	0.14469700	4.40077700	-2.64921600
C	-1.54091000	4.95885900	-0.20185800
H	-0.93672600	5.87980000	-0.14613500
H	-1.70623200	4.71093800	-1.25603400
H	-2.52614100	5.16525900	0.25244500
C	-0.95496800	3.90693200	1.91528600
H	-0.26177900	3.17596100	2.35024500
H	-0.65350800	4.90955200	2.25469700
H	-1.97059000	3.71073800	2.31178800
C	-2.59921400	-0.61878200	0.06617900
C	-3.29064000	-0.41808500	1.27193100
C	-3.34955200	-0.84943200	-1.09728000
C	-4.68153000	-0.42305500	1.32085200
H	-2.73691300	-0.26883300	2.20461500

C	-4.74023400	-0.84517300	-1.07173600
H	-2.83985700	-1.05627000	-2.04166800
C	-5.39059600	-0.62567200	0.14033100
H	-5.23167800	-0.27385000	2.25047400
H	-5.33636900	-1.01565200	-1.96875600
N	-6.85102000	-0.60897200	0.17510700
O	-7.44292200	-0.78399800	-0.86943300
O	-7.38811800	-0.41541600	1.24627700
Br	-0.53087200	-2.84599500	-0.46559900

Ra^{Cl}

E (DMF) = -2421.466958

Pd	-0.92293300	0.22493700	-0.20186800
C	0.49710000	1.60343900	-0.10219700
C	1.29541100	1.90333000	-1.21940600
C	0.72745700	2.31883300	1.08456700
C	2.31677800	2.84347400	-1.14915800
H	1.14727800	1.36190600	-2.15757900
C	1.74747000	3.25995300	1.17664700
H	0.11687600	2.11904900	1.96885300
C	2.54056800	3.50053400	0.05792000
H	2.96106000	3.06341000	-2.00045900
H	1.95414600	3.80329500	2.09922900
N	3.65028700	4.44334800	0.15976800
O	4.32343300	4.63332000	-0.83206300
O	3.84192600	4.97675100	1.23336400
P	0.63739500	-1.41427200	-0.00147000
C	2.37403300	-0.86568600	-0.15595100
C	2.94433200	-0.09937700	0.87085500
C	3.08709200	-1.05713700	-1.34289600
C	4.19829700	0.47679700	0.70415300
H	2.39326300	0.06601700	1.79891500
C	4.34482700	-0.47614800	-1.50681200
H	2.65387200	-1.65299800	-2.14921700
C	4.89885500	0.29659800	-0.48976100
H	4.62479000	1.08539000	1.50483000
H	4.89091000	-0.62582800	-2.44116500
H	5.87634700	0.76490500	-0.62573800
C	0.49673500	-2.71692400	-1.27199400
C	-0.15135200	-2.42723100	-2.47646200
C	1.07932600	-3.97486700	-1.08257000
C	-0.20053800	-3.38241300	-3.48969500
H	-0.63615100	-1.45649700	-2.60332800
C	1.02178400	-4.92937000	-2.09467600
H	1.57366100	-4.21238800	-0.13761600
C	0.38535400	-4.63273400	-3.30018700
H	-0.71237600	-3.15201800	-4.42680000
H	1.47337600	-5.91205500	-1.93974100
H	0.33886600	-5.38410300	-4.09223900
C	0.58048000	-2.30572900	1.59513800
C	-0.66883900	-2.53923300	2.18505100
C	1.73860000	-2.79599400	2.21264000
C	-0.75196300	-3.24974600	3.38018500
H	-1.57225400	-2.17776100	1.68348700

C	1.64736600	-3.50304500	3.41027700
H	2.71724500	-2.62084400	1.76052800
C	0.40326700	-3.72913900	3.99678700
H	-1.73028300	-3.43061700	3.83180600
H	2.55610000	-3.87870200	3.88662300
H	0.33438800	-4.28213900	4.93677800
C	-3.55077300	1.76169400	-0.06868900
N	-2.29492400	1.77115500	-0.43010000
N	-4.54539200	2.21794200	-0.88961200
N	-3.92599400	1.31230900	1.15900500
C	-4.34940200	2.22893200	-2.31745400
H	-3.95751200	3.19436200	-2.69139400
H	-3.65741100	1.42439400	-2.60081500
H	-5.31238000	2.04358000	-2.81839000
C	-5.68716800	2.94371500	-0.38778000
H	-5.72348000	3.95325100	-0.83380300
H	-6.63778600	2.43394900	-0.62181500
H	-5.60741300	3.05352700	0.70019700
C	-2.94523800	1.21068100	2.21187300
H	-3.45262400	1.32296400	3.18273100
H	-2.42066700	0.23856400	2.19503800
H	-2.20058300	2.00807400	2.10155700
C	-5.09364800	0.47303400	1.32312200
H	-4.77603400	-0.54994600	1.58352700
H	-5.75966500	0.86109300	2.11222200
H	-5.64785200	0.40753800	0.38069200
H	-2.10568700	2.39104900	-1.21114400
Cl	-2.69858800	-1.37086700	-0.39957600

Rb^{Cl}

E (DMF) = -2421.463228

Pd	0.72374900	-0.83873900	-0.33048400
P	-0.10658900	1.25985300	0.00926300
C	0.92479400	2.57035600	0.78007900
C	2.29970900	2.59569100	0.51696100
C	0.35854600	3.59267900	1.55412300
C	3.09301300	3.62567400	1.01825700
H	2.74498500	1.78246500	-0.05946100
C	1.15645600	4.61939300	2.05465900
H	-0.71090700	3.58465300	1.77475200
C	2.52446700	4.63947800	1.78751400
H	4.16555700	3.63203300	0.80927400
H	0.70340900	5.40916400	2.65867000
H	3.14805400	5.44516000	2.18232900
C	-1.62239500	1.27882700	1.02562500
C	-1.49703700	1.07794600	2.40707500
C	-2.89529800	1.31583700	0.44993300
C	-2.63027500	0.92565800	3.19954400
H	-0.50451800	1.02847900	2.86379300
C	-4.02732300	1.14792100	1.24548900
H	-3.00469700	1.44617800	-0.62803800
C	-3.89846900	0.95331400	2.61864900
H	-2.52298100	0.76893900	4.27540900
H	-5.01695600	1.15669500	0.78315900

H	-4.78814400	0.81138400	3.23619500
C	-0.57551100	2.03594000	-1.58019400
C	-0.27140900	1.37530800	-2.77436500
C	-1.19731900	3.29040300	-1.62585500
C	-0.59402600	1.95500600	-4.00093200
H	0.22028400	0.39839600	-2.73015900
C	-1.52326900	3.86467800	-2.85053800
H	-1.42870100	3.82106800	-0.69913200
C	-1.22290300	3.19721100	-4.03946400
H	-0.35546600	1.43004100	-4.92874500
H	-2.01264000	4.84101300	-2.87899700
H	-1.47989800	3.65077900	-4.99968700
C	3.68900700	-1.20335400	0.07290100
N	2.82180300	-0.39958100	-0.48929000
N	3.59549500	-1.50335700	1.40078400
N	4.72112800	-1.77164800	-0.61499500
H	3.11686200	-0.12228300	-1.42115500
C	2.77660500	-0.67679500	2.25322300
H	2.84700900	0.37319400	1.94663900
H	1.71070900	-0.97400100	2.21627400
H	3.13234400	-0.77216900	3.29048800
C	3.74991400	-2.87237600	1.85150100
H	4.43879200	-2.93611000	2.71028900
H	2.76797700	-3.27922400	2.14541100
H	4.12172800	-3.50103400	1.03604900
C	6.00990300	-2.01838400	-0.01605500
H	6.02000100	-1.63908100	1.01276600
H	6.26160300	-3.09307000	0.00198100
H	6.79842300	-1.49514200	-0.58479600
C	4.61578800	-1.96493500	-2.04073900
H	5.03604800	-1.12124200	-2.62136200
H	5.16941900	-2.87351600	-2.32266400
H	3.56173400	-2.12119900	-2.31053200
C	-1.16870100	-1.42672800	-0.26521300
C	-2.00074300	-1.40935100	-1.39393400
C	-1.70766400	-1.86735700	0.95385700
C	-3.34461800	-1.75913400	-1.30172300
H	-1.60594900	-1.10477200	-2.36508000
C	-3.04578900	-2.21864500	1.06563100
H	-1.07584700	-1.91286000	1.84391700
C	-3.85610800	-2.14049100	-0.06526600
H	-4.00963400	-1.72971800	-2.16523500
H	-3.48416100	-2.53490900	2.01196600
N	-5.27848200	-2.43901500	0.05780800
O	-5.96401400	-2.35444200	-0.94080700
O	-5.69989400	-2.74259200	1.15544900
Cl	1.28926700	-3.06683800	-0.74251500

Rc^{Cl}

E (DMF) = -2421.453969

Pd	-0.63690500	-0.59958100	0.01509600
P	1.75196800	-0.51835900	0.08804700
C	2.51406000	1.14777100	0.15604600
C	2.19608300	1.96996900	1.24733000

C	3.37606900	1.63661900	-0.83107900
C	2.73336400	3.24888700	1.35188400
H	1.53806800	1.58555200	2.03059400
C	3.91681600	2.91923100	-0.72301000
H	3.63939400	1.00528900	-1.68257400
C	3.59840000	3.72768500	0.36544700
H	2.48466800	3.87410000	2.21310700
H	4.59743400	3.28438200	-1.49602800
H	4.02797100	4.72864700	0.45093100
C	2.63695700	-1.32177000	-1.29365500
C	1.95774700	-1.53871600	-2.49694100
C	3.98219200	-1.69427300	-1.18397500
C	2.62450500	-2.09531000	-3.58710700
H	0.89298500	-1.30515000	-2.56134700
C	4.64435600	-2.25442700	-2.27322400
H	4.51238800	-1.55279700	-0.23905300
C	3.96744000	-2.45061000	-3.47757300
H	2.08448200	-2.26916600	-4.52059900
H	5.69298600	-2.54646300	-2.17927200
H	4.48693500	-2.89539900	-4.32983200
C	2.43832700	-1.31578800	1.58955400
C	1.79002000	-2.45636600	2.08210200
C	3.59013000	-0.84428500	2.23389000
C	2.29420700	-3.11430700	3.20203400
H	0.89559600	-2.82796600	1.57281000
C	4.08642900	-1.50592000	3.35540500
H	4.10067600	0.04767000	1.86347800
C	3.43953500	-2.64149200	3.84110700
H	1.78254700	-4.00341100	3.57783400
H	4.98451700	-1.13047600	3.85199200
H	3.82910000	-3.15811500	4.72172900
C	-0.72851100	2.50721900	-0.09395800
N	-0.95713800	1.36752400	0.49618700
N	-0.30233100	2.59164600	-1.38310900
N	-0.89150700	3.70084000	0.57122800
H	-1.55275100	1.46804100	1.31322800
C	-0.61159500	1.57776500	-2.36252000
H	0.26554900	0.95025200	-2.59210200
H	-1.41699500	0.92929500	-1.99769600
H	-0.94096800	2.06443700	-3.29604700
C	0.61801700	3.61528400	-1.81835300
H	0.99577600	4.17645500	-0.95622800
H	1.48146900	3.14254800	-2.31243000
H	0.15447600	4.31624300	-2.53494000
C	-1.51304000	4.83450500	-0.07885700
H	-0.88740700	5.73972800	-0.00483200
H	-1.68855800	4.61484200	-1.13765000
H	-2.49117400	5.05305700	0.38483400
C	-0.94719000	3.71764200	2.01056900
H	-0.26900800	2.96145700	2.42540300
H	-0.62403600	4.70475600	2.37464900
H	-1.96622600	3.53295100	2.40369000
C	-2.63198400	-0.76280000	0.03986000
C	-3.34680500	-0.52266200	1.22442800
C	-3.35847000	-1.07212000	-1.12050500
C	-4.73756900	-0.56557300	1.25564600

H	-2.81290500	-0.31272000	2.15725100
C	-4.74909600	-1.10498700	-1.11409900
H	-2.82774100	-1.31138500	-2.04531500
C	-5.42301200	-0.84530000	0.07700700
H	-5.30538100	-0.38784400	2.16949400
H	-5.32713100	-1.33538000	-2.00959100
N	-6.88382600	-0.86899300	0.09190100
O	-7.45556400	-1.11030400	-0.95059700
O	-7.44151700	-0.64068500	1.14560400
Cl	-0.53192100	-2.82892700	-0.53463700

Ra-TMG

E (DMF) = -1896,941498

Pd	0.41855800	-1.40106000	-0.14285100
I	2.80517700	-2.43634600	-0.14404900
C	-1.54440100	-1.19159700	-0.11534500
C	-2.27361000	-0.92532200	-1.28286800
C	-2.22691400	-1.44041400	1.08391800
C	-3.66311800	-0.90277500	-1.25804500
H	-1.75613100	-0.70717800	-2.22026800
C	-3.61857400	-1.41774400	1.12179500
H	-1.67199400	-1.64062900	2.00484800
C	-4.31479400	-1.13653500	-0.04971600
H	-4.25473200	-0.68937800	-2.14837100
H	-4.17606700	-1.59893400	2.04120800
N	-5.77689900	-1.06261600	-0.00649500
O	-6.35664900	-0.81486600	-1.04177600
O	-6.31646300	-1.24600800	1.06346600
P	0.53022000	0.80492100	0.06028700
C	-0.95265700	1.78226300	-0.34430200
C	-2.02313000	1.83857800	0.55999800
C	-1.08957200	2.35336400	-1.61333800
C	-3.21612300	2.44884500	0.19148100
H	-1.93076200	1.38493600	1.54867000
C	-2.28976300	2.96266200	-1.97792400
H	-0.25968600	2.31623000	-2.32256700
C	-3.35450800	3.00555000	-1.08138500
H	-4.04860000	2.47918300	0.89792300
H	-2.39133500	3.40322700	-2.97227100
H	-4.29759800	3.47341300	-1.37275200
C	1.81872900	1.47439300	-1.04172800
C	2.19095200	0.77288300	-2.19238600
C	2.39570300	2.72010800	-0.76608000
C	3.12591100	1.32001100	-3.06849600
H	1.76537700	-0.21469100	-2.38706700
C	3.33381800	3.25857200	-1.64212800
H	2.12214100	3.26669500	0.13911500
C	3.69720400	2.56108200	-2.79447000
H	3.41860000	0.76362600	-3.96145100
H	3.78863300	4.22644200	-1.41957500
H	4.43776100	2.98414900	-3.47726600
C	0.99907900	1.29020200	1.75179400
C	1.79838600	0.42509800	2.50964600
C	0.62973300	2.53648700	2.27757700

C	2.22206100	0.80600700	3.78036200
H	2.09383400	-0.54424100	2.09622200
C	1.05617900	2.90827400	3.55033700
H	0.00409100	3.21656700	1.69535400
C	1.85092000	2.04413400	4.30268400
H	2.84538500	0.12588900	4.36496600
H	0.76315000	3.87924500	3.95614600
H	2.18068300	2.33725000	5.30221100

TS_{Ra}

E (DMF) = -1896,937443

Pd	0.62501800	-1.23187300	-0.05811500
I	2.42398300	-3.07829300	-0.05892600
C	-1.32505000	-1.07626000	-0.03098400
C	-2.01188500	-1.22406500	-1.24380300
C	-2.03572900	-0.97749000	1.17152800
C	-3.40058500	-1.28522000	-1.25647300
H	-1.46364400	-1.28070500	-2.18696900
C	-3.42702200	-1.03296300	1.16526700
H	-1.51015000	-0.84477600	2.11946400
C	-4.08895200	-1.17763900	-0.05062400
H	-3.96382200	-1.39845700	-2.18297100
H	-4.01047300	-0.95697300	2.08319700
N	-5.55359000	-1.20350300	-0.06316000
O	-6.10231100	-1.31088800	-1.13843300
O	-6.12459100	-1.10913900	1.00170000
P	0.52621400	0.99181300	0.00369700
C	-0.57175600	1.87404700	-1.15088600
C	-1.95218300	1.94221100	-0.90884500
C	-0.05036300	2.42437800	-2.32782900
C	-2.79159000	2.56208000	-1.82876500
H	-2.37541200	1.50596000	-0.00155100
C	-0.89868900	3.03593400	-3.24911900
H	1.02274500	2.37791600	-2.52512200
C	-2.26780700	3.10696500	-3.00141400
H	-3.86477100	2.60963000	-1.63111300
H	-0.48294100	3.46126200	-4.16524900
H	-2.93098800	3.58721900	-3.72459300
C	2.19278300	1.63907500	-0.36382600
C	3.07599100	0.89082800	-1.14982100
C	2.57571800	2.90196900	0.10664800
C	4.32990300	1.40811900	-1.47028900
H	2.79283100	-0.10806800	-1.49404200
C	3.82977300	3.41164400	-0.21618800
H	1.89629700	3.48481500	0.73272900
C	4.70667100	2.66645600	-1.00572300
H	5.01724700	0.81545500	-2.07775900
H	4.12670700	4.39471200	0.15620200
H	5.69275700	3.06709500	-1.25232700
C	0.13961500	1.61425000	1.66965800
C	0.59732300	0.86390700	2.76158100
C	-0.53539400	2.82000100	1.89013100
C	0.37659600	1.31504500	4.05948200

H	1.12362100	-0.08001000	2.58635800
C	-0.75720800	3.26396900	3.19288800
H	-0.89255800	3.41281600	1.04534900
C	-0.30404900	2.51356900	4.27631600
H	0.73407400	0.72441100	4.90581600
H	-1.28945700	4.20308900	3.36031100
H	-0.48353900	2.86298900	5.29570900

Rb-TMG

E (DMF) = -1896,945405

Pd	0.40342600	1.45065500	-0.07428800
P	1.20957100	-0.70144600	-0.03020300
C	2.86035200	-0.85032000	-0.79436100
C	3.69599800	0.27295800	-0.77527000
C	3.32718800	-2.04794300	-1.35020400
C	4.98423300	0.20001100	-1.29982700
H	3.33940700	1.21536100	-0.34685800
C	4.61459100	-2.11626400	-1.87675900
H	2.67816500	-2.92623100	-1.38320100
C	5.44383500	-0.99486700	-1.85113800
H	5.62787800	1.08216900	-1.28226800
H	4.97225700	-3.05210100	-2.31234800
H	6.45224600	-1.05190600	-2.26744900
C	0.15857500	-1.91831400	-0.87871200
C	0.14892400	-1.94451600	-2.28002300
C	-0.77690500	-2.67770300	-0.16759200
C	-0.77873700	-2.73059200	-2.95719600
H	0.86243900	-1.33784200	-2.84415900
C	-1.71071400	-3.45337100	-0.85150000
H	-0.79299000	-2.64635200	0.92350500
C	-1.71392600	-3.48154500	-2.24447900
H	-0.77945500	-2.74722900	-4.04945700
H	-2.44760500	-4.03149600	-0.28937400
H	-2.45354200	-4.08387200	-2.77660900
C	1.43854800	-1.33289100	1.66549900
C	1.27692800	-0.45567400	2.74269200
C	1.81598300	-2.66105200	1.90392100
C	1.48264200	-0.90252200	4.04736400
H	0.99172200	0.58352500	2.55033600
C	2.01649800	-3.10449500	3.20719600
H	1.94909000	-3.35286800	1.06856600
C	1.84906400	-2.22613200	4.27959200
H	1.35426000	-0.21182900	4.88367600
H	2.30707800	-4.14173200	3.38890600
H	2.00730000	-2.57788500	5.30176100
C	-1.37670000	0.66340200	0.01324200
C	-1.95040600	0.31007400	1.23754900
C	-2.03746600	0.38747800	-1.18867100
C	-3.16196400	-0.37568300	1.25870000
H	-1.45435900	0.55089300	2.17861300
C	-3.24508900	-0.29904500	-1.17135200
H	-1.60064600	0.68537400	-2.14301500
C	-3.78184700	-0.68741300	0.05319900
H	-3.62958700	-0.68473100	2.19384500

H	-3.77270300	-0.55492500	-2.08994700
N	-5.01635600	-1.47053000	0.06976600
O	-5.46387500	-1.79250200	1.14990400
O	-5.50994900	-1.76300400	-0.99871700
I	-0.31857900	3.89380200	-0.05402500

TS_{Rb}

E (DMF) = -1896,91351

Pd	-0.45300200	-0.68317600	0.19852800
I	-1.35364900	-3.04437200	0.05686200
P	1.73958800	0.39604600	0.05179500
C	1.65626800	1.75655000	-1.16348600
C	0.51624100	2.57221900	-1.15074400
C	2.67261600	2.00553800	-2.09172000
C	0.40343700	3.63396300	-2.04363500
H	-0.29219400	2.36928200	-0.44087800
C	2.55186200	3.06546500	-2.98953000
H	3.55723600	1.36486200	-2.11664500
C	1.42179800	3.88116300	-2.96486300
H	-0.48860900	4.26422100	-2.02700700
H	3.34673200	3.25251800	-3.71533900
H	1.32953600	4.70899300	-3.67180900
C	3.07575000	-0.68931200	-0.55088800
C	2.73226300	-1.73938600	-1.41168300
C	4.41464500	-0.49389600	-0.19177200
C	3.72345700	-2.57149300	-1.92582000
H	1.68175900	-1.91284900	-1.66463200
C	5.40117300	-1.33386500	-0.70453500
H	4.68413600	0.31268000	0.49454100
C	5.05763800	-2.36903700	-1.57371700
H	3.44894400	-3.39058500	-2.59423000
H	6.44478500	-1.18033300	-0.42003900
H	5.83324400	-3.02831200	-1.97062200
C	2.42657000	1.17053400	1.55388100
C	2.35631200	0.44152100	2.74868800
C	3.01668500	2.43890100	1.55070600
C	2.88833600	0.96868500	3.92174900
H	1.87813800	-0.54272000	2.75548900
C	3.53942500	2.96668000	2.73075200
H	3.06358100	3.01647000	0.62440500
C	3.47958500	2.23273300	3.91407200
H	2.83266200	0.39418600	4.84920200
H	3.99587700	3.95927000	2.72396000
H	3.88903300	2.64977800	4.83713400
C	-2.34457800	-0.29595400	0.11743800
C	-3.03627400	-0.05884100	1.31133100
C	-2.87533200	0.09985200	-1.11654200
C	-4.22480600	0.66412300	1.27883600
H	-2.64764900	-0.42968300	2.26154400
C	-4.06345200	0.82272400	-1.14796500
H	-2.35949300	-0.14558000	-2.04680100
C	-4.71580600	1.10017300	0.05090300
H	-4.78612000	0.88898200	2.18609400
H	-4.50156500	1.16913700	-2.08432400

N	-5.96648900	1.86147100	0.01717000
O	-6.36795200	2.23128000	-1.06513700
O	-6.51952200	2.07775500	1.07364800

TMG

E (DMF) = -362.171147

C	0.01073000	-0.55683800	-0.01094800
N	-1.15875600	0.20439000	0.07565700
N	1.17108700	0.20186600	-0.08969900
N	0.08131400	-1.83613700	-0.01077600
H	-0.84116600	-2.25232200	-0.12845300
C	2.38438900	-0.50271200	-0.41726600
H	2.17857200	-1.25494900	-1.18792800
H	3.13086900	0.21636000	-0.79025100
H	2.81198500	-1.03465100	0.45424700
C	1.35686000	1.31902000	0.80683800
H	0.38627000	1.71485400	1.12756400
H	1.91652800	1.01959100	1.71529700
H	1.92321800	2.12729000	0.31478600
C	-2.36233700	-0.46784600	0.47938900
H	-2.14951800	-1.15928300	1.30704100
H	-3.09517400	0.27405900	0.83295000
H	-2.84208900	-1.04296600	-0.34076600
C	-1.36141000	1.30677400	-0.83647800
H	-1.87949000	2.14425400	-0.33910600
H	-0.39416700	1.66295000	-1.20970400
H	-1.97075100	1.00358900	-1.71117100

TMGH$^+$

E (Hartree) = -362.643586

C	0.00003500	-0.49916700	0.00000100
N	-1.16845200	0.15693400	-0.03240800
N	1.16844000	0.15704300	0.03244600
N	0.00017100	-1.83896100	-0.00016600
H	-0.80438600	-2.36354500	-0.31734500
C	2.40271400	-0.47653000	-0.40162600
H	2.19656500	-1.24271200	-1.15958600
H	3.04829400	0.28576400	-0.85952900
H	2.95413500	-0.92661000	0.44166400
C	1.31837900	1.43973800	0.70402900
H	1.53236700	2.25152300	-0.00770400
H	0.41437000	1.68278100	1.27277600
H	2.15733200	1.36977500	1.41272600
C	-2.40268600	-0.47660000	0.40179000
H	-2.19643000	-1.24333600	1.15915800
H	-3.04787900	0.28553000	0.86053200
H	-2.95458300	-0.92597900	-0.44155800
C	-1.31855100	1.43952500	-0.70414000
H	-1.53266100	2.25141400	0.00745000
H	-0.41458500	1.68261200	-1.27294700
H	-2.15750800	1.36932800	-1.41281100
H	0.80451600	-2.36345100	0.31773500

$TMGH^+$ I^-

E (DMF) = -660.55214

C	1.45598700	0.02596900	-0.55677500
N	1.25122800	1.28501500	-0.14603900
N	2.39026800	-0.73947000	0.04675600
N	0.73570700	-0.44382100	-1.57590900
H	-0.30084300	-0.29957300	-1.44188600
C	2.26283300	-2.18179200	0.07239900
H	2.87519600	-2.67142400	-0.70583000
H	2.59863600	-2.55315600	1.05208900
H	1.20896100	-2.46744000	-0.04479000
C	3.60000000	-0.18376300	0.61056900
H	3.69171600	0.87226000	0.33034700
H	3.62180900	-0.26364700	1.71003600
H	4.47172900	-0.72627400	0.20967000
C	0.55997300	2.23519000	-1.00075100
H	-0.52837100	2.18966800	-0.82373800
H	0.93508100	3.24365800	-0.77243800
H	0.76217600	2.00362100	-2.05332500
C	1.25402300	1.62690300	1.26492100
H	1.52550500	0.75678900	1.87100700
H	1.94684000	2.45781500	1.47300400
H	0.22896200	1.91280400	1.55081700
H	0.99423500	-1.34427900	-1.95804800
I	-2.06545200	-0.24448900	0.16957100

3

E (DMF) = -743.271941

C	5.40357700	-1.20764900	0.00053700
C	4.01362100	-1.21293200	0.00055900
C	3.30046500	-0.00007500	0.00002400
C	4.01342800	1.21289300	-0.00054900
C	5.40338700	1.20783600	-0.00057100
C	6.10205800	0.00015100	-0.00002600
H	5.94808000	-2.15466100	0.00096300
H	3.46189900	-2.15484300	0.00099600
H	3.46156200	2.15472000	-0.00097500
H	5.94773700	2.15493700	-0.00101800
H	7.19448100	0.00023700	-0.00004400
C	1.87690000	-0.00019300	0.00003300
C	0.65825500	-0.00014500	0.00002300
C	-0.76292400	-0.00008300	0.00001300
C	-1.47677900	1.21485900	0.00043300
C	-1.47686300	-1.21497800	-0.00041500
C	-2.86334100	1.21759200	0.00042400
H	-0.92586700	2.15659400	0.00077000
C	-2.86342500	-1.21761500	-0.00042300
H	-0.92601200	-2.15674900	-0.00074500
C	-3.53806800	0.00001200	-0.00000400
H	-3.43907800	2.14311600	0.00074200
H	-3.43922800	-2.14309700	-0.00074900

N	-5.00439900	0.00006100	-0.00001200
O	-5.56219400	-1.07521600	-0.00034800
O	-5.56212200	1.07537600	0.00032300

$Pd(PPh_3)_2$

E (DMF) = -2198.827392

Pd	0.00005900	0.00005800	1.14676800
P	2.14369900	0.00618700	0.42351700
C	3.64623500	0.11540700	1.47154300
C	4.77334700	0.86962500	1.12582300
C	3.64843000	-0.60761200	2.67123100
C	5.88728600	0.89169500	1.96440100
H	4.77772700	1.44441000	0.19643100
C	4.76612500	-0.59392700	3.50150800
H	2.75846100	-1.17926800	2.95158100
C	5.88761200	0.15794900	3.14974900
H	6.76149500	1.48660400	1.68839900
H	4.75849600	-1.16418200	4.43358100
H	6.76152500	0.17736600	3.80546300
C	2.36056300	1.41731100	-0.73386700
C	2.82583500	1.27078800	-2.04476400
C	1.98284800	2.69019500	-0.28171800
C	2.91181700	2.37951000	-2.88821500
H	3.11439900	0.28334300	-2.41194900
C	2.08224600	3.79615300	-1.11985600
H	1.58596200	2.80200800	0.73152200
C	2.54403300	3.64240500	-2.42879300
H	3.26959300	2.25191200	-3.91289700
H	1.78227300	4.78153600	-0.75536300
H	2.61153500	4.50851800	-3.09174500
C	2.50525000	-1.44462800	-0.64347200
C	3.77805400	-2.01317600	-0.76344700
C	1.44035300	-1.98687200	-1.37607300
C	3.98106500	-3.10412900	-1.60869700
H	4.61423000	-1.60454500	-0.19110500
C	1.64776900	-3.06934000	-2.22631800
H	0.44084100	-1.55774700	-1.25995500
C	2.91962000	-3.63149600	-2.34293800
H	4.97740100	-3.54543500	-1.69198300
H	0.80474300	-3.48040400	-2.78704400
H	3.08279200	-4.48772200	-3.00220300
P	-2.14356000	-0.00618900	0.42349400
C	-3.64589600	-0.11536300	1.47181500
C	-4.77316900	-0.86940900	1.12623600
C	-3.64775400	0.60750700	2.67159000
C	-5.88693400	-0.89145400	1.96504500
H	-4.77780400	-1.44409700	0.19678500
C	-4.76527800	0.59384800	3.50210200
H	-2.75765600	1.17901800	2.95182300
C	-5.88692500	-0.15785000	3.15048300
H	-6.76126900	-1.48623100	1.68915800
H	-4.75738200	1.16397600	4.43425000
H	-6.76070200	-0.17724800	3.80637900
C	-2.50526700	1.44459500	-0.64347800

C	-3.77804900	2.01324900	-0.76314700
C	-1.44051500	1.98669300	-1.37640700
C	-3.98120000	3.10415500	-1.60842700
H	-4.61410200	1.60472100	-0.19055300
C	-1.64807900	3.06910500	-2.22668600
H	-0.44099300	1.55752300	-1.26052700
C	-2.91991300	3.63136500	-2.34300300
H	-4.97752100	3.54554000	-1.69147000
H	-0.80517700	3.48005300	-2.78768200
H	-3.08318800	4.48754800	-3.00229900
C	-2.36069800	-1.41732700	-0.73382400
C	-2.82662300	-1.27088300	-2.04450000
C	-1.98266400	-2.69016400	-0.28181400
C	-2.91294300	-2.37964100	-2.88786500
H	-3.11542400	-0.28346800	-2.41158100
C	-2.08237900	-3.79616100	-1.11986900
H	-1.58525200	-2.80189400	0.73122900
C	-2.54483400	-3.64249200	-2.42857700
H	-3.27122900	-2.25211000	-3.91237700
H	-1.78213500	-4.78150400	-0.75549200
H	-2.61260000	-4.50863300	-3.09146700

DMF

E (DMF) = -248.261649

C	-0.82027500	-0.68599100	-0.00041900
O	-1.90970800	-0.15922900	0.00027700
N	0.35739300	-0.01216000	-0.00026100
H	-0.67588000	-1.79465800	0.00011900
C	0.30657000	1.43221000	0.00000700
H	-0.23033700	1.80843900	0.88508200
H	1.32813800	1.83320500	0.00403200
H	-0.22356900	1.80935600	-0.88880100
C	1.62572400	-0.68764600	0.00016100
H	2.22422900	-0.43650600	-0.89252000
H	2.22298100	-0.43804300	0.89413400
H	1.45823800	-1.77429200	-0.00092900

B-PPh$_3$

E (DMF) = -1896.941432

C	-1.45610900	-1.11154700	-0.17429000
C	-2.17804600	-1.08484800	-1.37582000
C	-2.14081100	-1.15882700	1.04796400
C	-3.56780300	-1.12502600	-1.36198500
H	-1.65527800	-1.01649800	-2.33305500
C	-3.53270200	-1.19335700	1.07257900
H	-1.58986700	-1.15557800	1.99190800
C	-4.22479500	-1.16855100	-0.13489200
H	-4.15583000	-1.10548500	-2.27979000
H	-4.09371200	-1.22866900	2.00686500
Pd	0.50028400	-1.33430300	-0.22625500
P	0.50053300	0.86563700	0.03771200
I	2.72300000	-2.66411500	-0.19022200

C	-0.67804100	1.89113200	-0.90415500
C	-0.25557400	2.54134900	-2.06971300
C	-2.02256500	1.98194500	-0.51359900
C	-1.16561300	3.26995200	-2.83391700
H	0.78922300	2.48269400	-2.38160200
C	-2.92289000	2.71953000	-1.27478600
H	-2.37167000	1.46753600	0.38383800
C	-2.49803000	3.36140400	-2.43850100
H	-0.82600100	3.77151500	-3.74283900
H	-3.96724400	2.78287600	-0.96122300
H	-3.20967200	3.93342600	-3.03833400
C	2.13017800	1.55343300	-0.41012900
C	2.58799800	2.72348100	0.20838000
C	2.89497100	0.94994800	-1.41350100
C	3.80116500	3.28455200	-0.18094900
H	2.00274100	3.19250500	1.00228800
C	4.10521100	1.52004800	-1.80215800
H	2.55661800	0.01708600	-1.87095100
C	4.55892100	2.68551200	-1.18729900
H	4.15941200	4.19212300	0.31015600
H	4.70181500	1.03851300	-2.57986400
H	5.51340500	3.12501600	-1.48639300
C	0.26634200	1.28222100	1.79391100
C	0.77175600	0.38842000	2.74820500
C	-0.33699500	2.47509400	2.20977800
C	0.66689200	0.68513400	4.10410200
H	1.24778400	-0.54142300	2.42018800
C	-0.44218800	2.76322800	3.56942100
H	-0.72838500	3.17999600	1.47326500
C	0.05664000	1.87001500	4.51603500
H	1.06184500	-0.01616300	4.84239500
H	-0.91857800	3.69274300	3.88930300
H	-0.03128500	2.09771700	5.58090800
N	-5.69026600	-1.17253100	-0.11324300
O	-6.23421700	-1.20538700	0.96922000
O	-6.26591100	-1.13663200	-1.17904600

TS0^{I}

E (DMF) = -3294.540265

Pd	0.07725100	-0.09438900	-0.65831800
C	0.79934300	1.70558500	-0.21478000
C	1.38584500	2.43666100	-1.26311700
C	0.75410500	2.29350200	1.05680800
C	1.88684700	3.71761200	-1.05984700
H	1.45918300	1.99216100	-2.25813500
C	1.23711500	3.57906000	1.27781200
H	0.33726800	1.74769200	1.90330900
C	1.79955300	4.27737300	0.21372500
H	2.34672700	4.29281500	-1.86395700
H	1.19792500	4.04518100	2.26239100
N	2.32664100	5.62136600	0.44041500
O	2.26717000	6.06787600	1.56715600
O	2.79331700	6.21175400	-0.51132100
P	2.22121200	-0.80354800	-0.28336700

C	2.44266600	-2.58937900	0.06407300
C	3.55719900	-3.29133200	-0.40266000
C	1.50728600	-3.24321500	0.87373200
C	3.73618300	-4.62943000	-0.05402700
H	4.28456100	-2.79990200	-1.05138700
C	1.69926500	-4.57250600	1.23674200
H	0.61816700	-2.71139700	1.21239200
C	2.81369700	-5.26971500	0.77102100
H	4.60404000	-5.17386700	-0.43366300
H	0.96186400	-5.06624200	1.87360800
H	2.95830400	-6.31800200	1.04351000
C	3.28096500	-0.48213600	-1.74229300
C	4.66329400	-0.28101000	-1.63608300
C	2.68147900	-0.47206900	-3.00757900
C	5.43028500	-0.06412100	-2.77920400
H	5.14411700	-0.28791900	-0.65556800
C	3.45285600	-0.26113100	-4.14787600
H	1.60349800	-0.64062800	-3.08750700
C	4.82686500	-0.05231800	-4.03594200
H	6.50673600	0.09780000	-2.68528000
H	2.97404700	-0.25807500	-5.12979800
H	5.42992800	0.12117000	-4.93050500
C	3.17163800	-0.05521500	1.10381500
C	3.35258800	-0.75628300	2.30269000
C	3.68949500	1.24395400	0.99782300
C	4.01437900	-0.16300000	3.37699300
H	2.98024800	-1.77751300	2.39846300
C	4.35698300	1.82986400	2.06908200
H	3.57078800	1.80641900	0.07032700
C	4.51492000	1.13219700	3.26594000
H	4.14862700	-0.72624100	4.30396900
H	4.74700400	2.84530000	1.96769500
H	5.03429900	1.59603500	4.10781700
P	-1.78437800	-0.36480000	1.19852900
C	-1.23063900	-1.44169100	2.57720600
C	0.00957500	-1.12274400	3.15052000
C	-1.95436900	-2.52212600	3.09176200
C	0.50832800	-1.85839200	4.22025800
H	0.60106500	-0.29756100	2.74385400
C	-1.44090000	-3.27429000	4.14934200
H	-2.92805900	-2.77802500	2.67011400
C	-0.21253900	-2.94425500	4.71827200
H	1.47315300	-1.58848300	4.65549800
H	-2.01407900	-4.12054900	4.53600100
H	0.18429900	-3.53287300	5.54871900
C	-3.40063600	-1.05970600	0.69154900
C	-4.55871200	-0.27101400	0.64985200
C	-3.46761000	-2.38397400	0.22880900
C	-5.75511700	-0.79528800	0.16383100
H	-4.52788800	0.75944100	1.00967700
C	-4.67021100	-2.90843400	-0.23934500
C	-5.81728100	-2.11675900	-0.27623300
H	-6.64912500	-0.16690500	0.14196400
H	-4.70245000	-3.94200400	-0.59191600
H	-6.75821600	-2.52884100	-0.64885200
C	-2.30031300	1.12585800	2.14072200

C	-2.34433700	2.34499100	1.45645600
C	-2.63010200	1.09597400	3.50146400
C	-2.71240100	3.51588100	2.11624600
H	-2.06771000	2.36305000	0.40130800
C	-2.99630200	2.26741500	4.16088200
H	-2.59490700	0.15182200	4.04947800
C	-3.03672400	3.47950200	3.47135300
H	-2.72434600	4.46567800	1.57554300
H	-3.24898100	2.23369900	5.22343900
H	-3.31358900	4.39832500	3.99375100
C	-2.55976700	1.38281900	-2.34395100
N	-3.67164200	0.81339900	-2.92437500
N	-2.72474300	2.67971200	-1.92391400
N	-1.42937000	0.75489600	-2.20474000
H	-1.43104900	-0.09597500	-2.76712600
C	-1.61547200	3.59794000	-1.90539900
H	-0.78252700	3.16666200	-2.46913200
H	-1.91554300	4.55395700	-2.36786400
H	-1.24872700	3.81117200	-0.88576300
C	-3.99290300	3.18855800	-1.46438900
H	-4.69519700	2.35931300	-1.31576200
H	-3.86545500	3.70216900	-0.49800300
H	-4.44179200	3.91157700	-2.16991700
C	-3.79227800	-0.62240100	-2.98649100
H	-3.31372700	-1.08536300	-2.11550000
H	-4.85806400	-0.89537300	-2.97872000
H	-3.33039200	-1.04970600	-3.89698000
C	-4.45613700	1.53568700	-3.89861500
H	-5.52834600	1.54756200	-3.63692700
H	-4.10553900	2.57065300	-3.98442200
H	-4.35592400	1.06450200	-4.89309300
H	-2.56937000	-3.00390200	0.21464600
I	-0.51054800	-2.48478000	-1.88755800

TS1^{PPh3}

E (DMF) = -3240.416052

Pd	-0.48627000	-0.14466300	-1.19014200
C	-0.65315500	1.79487300	-0.73777300
C	-1.43727700	2.65961900	-1.51406600
C	0.06490700	2.32649700	0.33947400
C	-1.51520300	4.01749100	-1.21101100
H	-2.00339300	2.27937100	-2.36682300
C	0.01023500	3.67720600	0.65208700
H	0.66103700	1.65568800	0.95661500
C	-0.78881000	4.50788900	-0.12946100
H	-2.12718500	4.70495000	-1.79563700
H	0.56364900	4.10156900	1.48952600
N	-0.87283000	5.92885300	0.20159200
O	-0.19964900	6.33106800	1.12775700
O	-1.61079600	6.62146000	-0.46675800
P	2.20133300	-0.80652100	0.48335100
C	1.45312900	-1.47598000	2.02226900
C	0.46374400	-2.45967000	1.86275500
C	1.75603000	-1.01894200	3.30983100

C	-0.20305100	-2.97594000	2.96938000
H	0.21332500	-2.82025200	0.85969700
C	1.07161700	-1.52713600	4.41555300
H	2.53312900	-0.26537600	3.45428200
C	0.09117100	-2.50391000	4.24950100
H	-0.97244200	-3.73752900	2.82487200
H	1.31612600	-1.16036300	5.41581900
H	-0.44405500	-2.89919600	5.11607000
C	3.01454300	-2.30640800	-0.19063700
C	3.51136300	-3.32713200	0.63064300
C	3.15276500	-2.42118500	-1.57816000
C	4.15268600	-4.42992600	0.07248000
H	3.39218000	-3.25604000	1.71468600
C	3.80377500	-3.52033200	-2.13584400
H	2.71357200	-1.66250000	-2.22988900
C	4.30516300	-4.52502500	-1.31155800
H	4.53447900	-5.22170700	0.72169700
H	3.89600200	-3.60137100	-3.22124000
H	4.80539800	-5.39288800	-1.74823200
C	3.64810500	0.14416900	1.12084800
C	4.96875100	-0.30825800	1.00305300
C	3.42799600	1.41652700	1.67043400
C	6.03358800	0.48577200	1.42786900
H	5.16913400	-1.29043100	0.57092400
C	4.48985700	2.20415300	2.10559200
H	2.41302600	1.80855800	1.75319700
C	5.79993000	1.74255100	1.98227200
H	7.05612500	0.11327900	1.32621300
H	4.29147500	3.19098600	2.53066400
H	6.63577800	2.36241200	2.31536900
P	-2.32437900	-0.34524500	0.22384500
C	-2.86762300	-1.86371800	1.11202500
C	-2.93914800	-3.07525900	0.41478800
C	-3.32918200	-1.81075200	2.43442900
C	-3.42903500	-4.21896000	1.04026200
H	-2.59448900	-3.12871500	-0.61959200
C	-3.82800200	-2.95594200	3.05204300
H	-3.30066100	-0.87545500	2.99364600
C	-3.87179600	-4.16526200	2.36135200
H	-3.46560500	-5.15831200	0.48377200
H	-4.18170000	-2.89780800	4.08416600
H	-4.25731800	-5.06359500	2.84962600
C	-3.82058600	0.00687700	-0.76730900
C	-5.06829500	0.14264100	-0.14361000
C	-3.73693800	0.07129400	-2.16057800
C	-6.20809800	0.37616500	-0.90634500
H	-5.14862600	0.05918600	0.94316700
C	-4.88228500	0.29609100	-2.92318300
C	-6.11596400	0.45657800	-2.29705900
H	-7.17672500	0.48754400	-0.41358900
H	-4.80822800	0.33983000	-4.01214000
H	-7.01352700	0.63488300	-2.89401100
C	-2.29706500	0.90052300	1.56041300
C	-3.02429300	2.09238500	1.49531200
C	-1.39925700	0.69633000	2.61809500
C	-2.85047900	3.06989400	2.47351200

H	-3.70710200	2.27466500	0.66384200
C	-1.23885600	1.67065600	3.59805100
H	-0.81217900	-0.22293700	2.67210300
C	-1.95908900	2.86322000	3.52473900
H	-3.41053000	4.00536200	2.40542200
H	-0.53544100	1.49557300	4.41547000
H	-1.82182700	3.63606800	4.28457800
H	-2.76558600	-0.07754600	-2.64071400
I	-0.40509900	-2.69761100	-2.10484700
C	1.31441100	0.94609400	-2.70680200
C	0.43304500	0.24986600	-3.21607100
H	-0.13213100	-0.26860200	-3.97370100
C	2.34670900	1.80025300	-2.22046000
C	2.08878600	3.16656200	-2.00772000
C	3.63662200	1.29503200	-1.98006500
C	3.09858900	4.00012400	-1.54381000
H	1.08978600	3.55847700	-2.20272000
C	4.64265500	2.14005100	-1.52935700
H	3.84133200	0.23670500	-2.14418400
C	4.37403200	3.48892400	-1.30166100
H	2.88570900	5.05657500	-1.36610200
H	5.63680400	1.73646800	-1.32985400
H	5.16415800	4.14522400	-0.92974200

TS1[I]

E (DMF) = -2567.166

Pd	0.18576000	-0.53286900	-0.62486100
I	1.47668700	-2.87786100	-0.38408300
C	-1.21458700	0.87389000	-0.60111700
C	-1.30887400	1.93815600	-1.50644200
C	-2.24164700	0.69335100	0.33997300
C	-2.39923900	2.80191200	-1.48441500
H	-0.52883200	2.09573500	-2.25224600
C	-3.33796600	1.54611800	0.37468700
H	-2.18531700	-0.11962100	1.06851600
C	-3.40579500	2.58848000	-0.54625700
H	-2.49066300	3.63462700	-2.18241500
H	-4.14036600	1.42355100	1.10184400
N	-4.57194100	3.46656000	-0.53415100
O	-4.52976000	4.47226800	-1.20934900
O	-5.51938100	3.13134200	0.14880200
P	1.06915000	0.51171300	1.17636300
C	1.07294000	2.34100000	1.04415400
C	-0.08323300	3.09301100	1.29933400
C	2.21700200	2.99654900	0.57194500
C	-0.09161800	4.46833300	1.08694000
H	-0.99167600	2.60278900	1.65190700
C	2.20048700	4.37260900	0.35083700
H	3.12823500	2.43017400	0.37197000
C	1.04787000	5.11235700	0.60628100
H	-1.00258400	5.03698400	1.28710100
H	3.10140600	4.86866300	-0.01843200
H	1.03649500	6.19092700	0.43270600
C	2.83482600	0.13542400	1.45632300

C	3.66812700	-0.11199400	0.36026300
C	3.37489800	0.16410800	2.74607500
C	5.03216400	-0.31113700	0.55266100
H	3.24768600	-0.16321000	-0.64535300
C	4.73877700	-0.05025700	2.93436800
H	2.72948600	0.34476700	3.60832800
C	5.56894700	-0.28375500	1.83905800
H	5.67113800	-0.50496700	-0.31143000
H	5.15322100	-0.03772200	3.94508900
H	6.63762700	-0.45412000	1.99020300
C	0.25968200	0.11109700	2.76053000
C	-0.12741900	-1.22200300	2.95182100
C	0.06386500	1.04230400	3.78663300
C	-0.71801400	-1.61308500	4.14989300
H	0.05931100	-1.95089900	2.15614900
C	-0.53533100	0.64600400	4.98172800
H	0.38033600	2.07899600	3.65603400
C	-0.93051000	-0.67825000	5.16344700
H	-1.01371100	-2.65532700	4.29107100
H	-0.69160200	1.37904900	5.77659600
H	-1.40158700	-0.98395800	6.10070900
C	-3.38050200	-2.28319200	-0.80219300
N	-2.23806900	-2.27372500	-1.40440900
N	-3.67267000	-3.02977700	0.33532100
N	-4.40457700	-1.49763900	-1.26888800
C	-2.56170000	-3.56675400	1.07869700
H	-2.15046700	-4.49778100	0.63969500
H	-1.74743100	-2.83243200	1.12552600
H	-2.88848700	-3.79329200	2.10535600
C	-4.86099000	-3.85476900	0.36348400
H	-4.61807100	-4.90784800	0.12368000
H	-5.33737400	-3.83432100	1.35789700
H	-5.58874400	-3.50631600	-0.37777100
C	-4.22972100	-0.83743300	-2.53865100
H	-5.21578500	-0.57194300	-2.94751100
H	-3.62376200	0.08325200	-2.44905500
H	-3.72211000	-1.51040500	-3.24149400
C	-5.43506200	-0.96027000	-0.41163000
H	-5.47504600	0.13715300	-0.50241300
H	-6.43691000	-1.35235600	-0.66395400
H	-5.21838200	-1.20514300	0.63553200
H	-1.61635300	-3.01187500	-1.07592300
C	0.84265900	-0.29973200	-2.99883800
C	-0.26039700	-0.83367900	-2.97002400
H	-1.22318400	-1.33810900	-2.85577700
C	2.16921800	0.23596900	-3.05970200
C	2.41879300	1.59559100	-2.80696600
C	3.24841000	-0.62814100	-3.31321300
C	3.72242600	2.07846900	-2.80985400
H	1.58749700	2.26523200	-2.58238100
C	4.54879500	-0.13378900	-3.31929500
H	3.04984200	-1.68862000	-3.47579700
C	4.78977700	1.21722600	-3.06689500
H	3.90577800	3.13525100	-2.60304500
H	5.38217500	-0.81274100	-3.51366900
H	5.81315700	1.59961700	-3.06524700

G

E (DMF) = -2205.014041

Pd	0.32072200	0.60317300	-1.05671500
C	-1.62640200	0.17759500	-0.90057300
C	-2.26177500	-0.52454100	-1.93451500
C	-2.38286400	0.56825200	0.21336800
C	-3.60793000	-0.86814300	-1.84462000
H	-1.69833100	-0.82928800	-2.82075900
C	-3.72844700	0.23641900	0.31852700
H	-1.91346300	1.11598500	1.03407600
C	-4.31995600	-0.49249100	-0.70950200
H	-4.11585100	-1.43155200	-2.62792300
H	-4.32516000	0.50950500	1.18879600
I	2.94808900	1.14393900	-1.32843000
P	0.77050300	-1.11571100	0.39379000
C	-0.35230900	2.74531400	-1.62201500
C	-0.06909700	2.13314900	-2.65272800
H	0.15811200	1.84761500	-3.66664600
C	-0.65849400	3.51255300	-0.45467100
C	-1.98641800	3.85384200	-0.15268300
C	0.38182700	3.89556700	0.41106800
C	-2.26741200	4.57139700	1.00540100
H	-2.78624300	3.54074200	-0.82558900
C	0.08655500	4.61094300	1.56567700
H	1.40727500	3.60704600	0.16587400
C	-1.23513000	4.94768000	1.86514900
H	-3.30072400	4.83520400	1.24098600
H	0.89475300	4.90921400	2.23747100
H	-1.46208900	5.50820600	2.77511200
C	1.56246900	-2.58863500	-0.33045900
C	2.19980500	-2.51564700	-1.57316900
C	1.53289400	-3.80789300	0.36327700
C	2.80809300	-3.64814900	-2.11169400
H	2.23449600	-1.56260100	-2.10642700
C	2.14700100	-4.93381200	-0.17762600
H	1.01777700	-3.87834900	1.32431200
C	2.78501800	-4.85497200	-1.41600500
H	3.30480300	-3.58164800	-3.08216400
H	2.12189900	-5.87944300	0.36881000
H	3.26253000	-5.74109900	-1.84110700
C	-0.68198100	-1.81887700	1.25532900
C	-1.00779900	-1.45829700	2.56543400
C	-1.55466500	-2.64288800	0.53023100
C	-2.20410700	-1.89675700	3.13415000
H	-0.33121100	-0.82640500	3.14431100
C	-2.74639800	-3.07461000	1.09985800
H	-1.30731100	-2.93308300	-0.49328500
C	-3.07887600	-2.69437000	2.40156000
H	-2.45308300	-1.60632400	4.15745600
H	-3.42714500	-3.70220500	0.52020300
H	-4.02317900	-3.02214200	2.84208100
C	1.83428400	-0.51927900	1.74866600
C	2.84974100	-1.29956600	2.30517600

C	1.59074700	0.76552800	2.25051200
C	3.61055300	-0.79848600	3.36068000
H	3.06261500	-2.29241800	1.90412100
C	2.34268300	1.25523600	3.31295700
H	0.82278100	1.39338800	1.78955500
C	3.35620400	0.47371400	3.86857300
H	4.41308200	-1.40706900	3.78360700
H	2.14703200	2.25918700	3.69678400
H	3.95723900	0.86308200	4.69363800
N	-5.71855800	-0.89728900	-0.57872100
O	-6.31181400	-0.55648200	0.42307200
O	-6.20032200	-1.55754900	-1.47499800

TS2^{I}

E (DMF) = -2567.169631

C	1.99447000	-0.01705100	0.21283900
C	2.68473900	-0.51802400	1.11044600
C	-0.26087600	1.61151000	0.37615700
C	-0.18363500	2.56102600	-0.65629200
C	-0.46296700	2.06534800	1.68825600
C	-0.33397000	3.91994400	-0.39792200
H	-0.02339300	2.23052700	-1.68655900
C	-0.61953600	3.41826700	1.96442700
H	-0.52475200	1.34772900	2.50980100
C	-0.56056400	4.33091700	0.91322300
H	-0.29884900	4.66984100	-1.18909500
H	-0.80074900	3.78517200	2.97478800
Pd	-0.06341600	-0.31916000	-0.06481900
C	3.46333800	-1.22920300	2.06000200
C	4.04347000	-0.58426800	3.16853900
C	3.65931200	-2.61428300	1.88510300
C	4.81234500	-1.30751100	4.07275800
H	3.87923200	0.48659400	3.30446800
C	4.41985400	-3.32988500	2.80246700
H	3.18314900	-3.10553900	1.03255300
C	5.00109600	-2.67903400	3.89217400
H	5.26355900	-0.80184900	4.92965000
H	4.56079800	-4.40482700	2.66786300
H	5.60204100	-3.24479200	4.60833500
P	-2.34078900	-0.51524000	-0.15505600
H	2.19615100	0.70924200	-0.80057600
C	-3.24701800	0.86150000	0.64230000
C	-3.36861400	2.08557400	-0.03042800
C	-3.68114300	0.76441000	1.96766700
C	-3.89750000	3.19525300	0.61929900
H	-3.03125000	2.17531700	-1.06488500
C	-4.21232300	1.87958900	2.61548600
H	-3.59842900	-0.18515700	2.50087500
C	-4.31410200	3.09732200	1.94763100
H	-3.97323500	4.14712200	0.08852400
H	-4.54521200	1.79328100	3.65252600
H	-4.71673500	3.97379800	2.46049800
C	-3.05609900	-0.58204500	-1.83390500
C	-2.26168800	-1.02001400	-2.89932500

C	-4.38991200	-0.21874400	-2.07033700
C	-2.79818100	-1.10043400	-4.18302600
H	-1.22533500	-1.31340900	-2.71037500
C	-4.92025700	-0.30081900	-3.35534800
H	-5.01253200	0.14167100	-1.24800600
C	-4.12508700	-0.74220800	-4.41311800
H	-2.17094900	-1.44674100	-5.00762500
H	-5.95993300	-0.01474600	-3.53142500
H	-4.54238200	-0.80337400	-5.42123800
C	-2.96064100	-1.98600800	0.73240900
C	-2.23526900	-2.44156100	1.83958500
C	-4.14740900	-2.62954600	0.37117800
C	-2.70564900	-3.51503600	2.59072400
H	-1.28522800	-1.96384300	2.09407500
C	-4.60780000	-3.71259500	1.11749100
H	-4.70838600	-2.29672300	-0.50439500
C	-3.89208900	-4.15257900	2.22976500
H	-2.13119400	-3.86689400	3.45053700
H	-5.53027100	-4.21865100	0.82327300
H	-4.25443600	-5.00379500	2.81120400
I	0.34585300	-2.88628700	-0.79841000
N	-0.76207100	5.74945100	1.18899700
O	-0.97872300	6.07789700	2.33701800
O	-0.70565300	6.52113600	0.25268500
C	4.06251500	1.24583100	-1.90661000
N	5.06091400	2.18105700	-1.81178500
N	4.44262400	-0.04792000	-2.09505400
N	2.79327300	1.52557400	-1.78973200
H	2.56842400	2.51590800	-1.80326300
C	3.49958000	-1.01431400	-2.62196100
H	2.73292900	-0.49558600	-3.20888700
H	4.03866600	-1.72227700	-3.27137700
H	2.98516000	-1.58221600	-1.82841700
C	5.59533600	-0.60795000	-1.42615600
H	6.10589100	0.16131900	-0.83517600
H	5.27033500	-1.40384600	-0.73426200
H	6.31337100	-1.04569000	-2.14072300
C	4.79135100	3.45585400	-1.19446500
H	4.04020600	3.34115400	-0.40136800
H	5.71460200	3.84094100	-0.73523400
H	4.43274800	4.21502500	-1.91588600
C	6.24692700	2.11402800	-2.63443300
H	7.16923400	2.09458400	-2.02904600
H	6.21834900	1.21355800	-3.25891200
H	6.29697300	2.99138400	-3.30321100

N

E (DMF) = -2567.199329

Pd	0.10873700	-0.30701400	0.51792900
C	0.15720800	1.67402400	0.28251900
C	0.38971400	2.23172300	-0.98773800
C	0.00259800	2.55352600	1.36727400
C	0.51382100	3.60363900	-1.17144100
H	0.53174500	1.58076200	-1.85493100

C	0.13980600	3.92835100	1.20710100
H	-0.21930500	2.15328300	2.35872900
C	0.40312900	4.43772300	-0.06256600
H	0.72656500	4.04122700	-2.14681300
H	0.05167300	4.61891000	2.04651500
N	0.59354800	5.87369200	-0.23365400
O	0.82315800	6.28428200	-1.35343900
O	0.51872400	6.57653900	0.75313000
P	2.40960900	-0.47297700	0.08863400
C	3.21244200	1.09376500	-0.41537700
C	3.28666300	2.12492700	0.53245600
C	3.62097100	1.34067600	-1.72822700
C	3.73951000	3.38615500	0.16474700
H	2.96474400	1.94272400	1.56056100
C	4.07459100	2.60916700	-2.09398900
H	3.57601900	0.54346600	-2.47350100
C	4.12559700	3.63478300	-1.15396300
H	3.77525000	4.18633200	0.90756500
H	4.38577700	2.79490200	-3.12481600
H	4.46237400	4.63199500	-1.44626500
C	2.83041400	-1.61920300	-1.27088600
C	1.96095300	-1.66995500	-2.36744100
C	3.97658300	-2.41755200	-1.26727100
C	2.24644600	-2.48774500	-3.45625600
H	1.04407100	-1.07443100	-2.35263300
C	4.25374300	-3.24730400	-2.35290600
H	4.64937600	-2.40357500	-0.40738800
C	3.39469100	-3.27983200	-3.44954100
H	1.56153000	-2.52014800	-4.30683200
H	5.14687000	-3.87635800	-2.33779600
H	3.61455200	-3.93238100	-4.29787700
C	3.42376700	-0.99000600	1.51862400
C	2.83246500	-1.70442100	2.56644500
C	4.78956400	-0.67730600	1.58108100
C	3.60107700	-2.11098900	3.65590800
H	1.76841500	-1.94912700	2.52058100
C	5.55302000	-1.08758900	2.67074800
H	5.25338000	-0.09899100	0.77820500
C	4.95960500	-1.80611700	3.70910900
H	3.12958000	-2.66806800	4.46864600
H	6.61630600	-0.83945700	2.71175300
H	5.55912800	-2.12362300	4.56580500
C	-1.79424400	-0.03662200	0.96547400
C	-2.97135300	0.16474700	1.25957700
C	-4.34064300	0.40504800	1.57222500
C	-4.82545900	1.71918600	1.72605500
C	-5.25961000	-0.65737600	1.68522400
C	-6.17765500	1.95880600	1.94841000
H	-4.11726200	2.54807100	1.65810300
C	-6.61199300	-0.41170200	1.90446100
H	-4.88744200	-1.68032300	1.60642400
C	-7.08053000	0.89727400	2.02855700
H	-6.53251400	2.98637000	2.06183700
H	-7.30760000	-1.25073100	1.99101300
H	-8.14203400	1.08861900	2.20189200
I	-0.14511800	-3.02393600	0.57314700

C	-3.31332600	-0.93184800	-1.83371200
N	-3.67876000	0.31570200	-2.17171700
N	-4.23559500	-1.87687600	-1.57804900
N	-2.01319200	-1.23852500	-1.82112900
H	-1.39462000	-0.54971500	-1.37482200
C	-3.89965000	-3.04217300	-0.78197800
H	-3.08029000	-2.81592200	-0.08399100
H	-4.78168000	-3.32806900	-0.19143200
H	-3.61187300	-3.90233000	-1.41137900
C	-5.52927700	-1.90297400	-2.22614300
H	-6.34874400	-1.70568100	-1.51585400
H	-5.56913900	-1.16474200	-3.03511900
H	-5.68603100	-2.90012600	-2.66776400
C	-2.69044800	1.23305700	-2.70585100
H	-1.98497900	0.69576800	-3.35210600
H	-3.20575000	1.99576000	-3.30547500
H	-2.12836800	1.73440500	-1.89894400
C	-4.88741600	0.94118300	-1.66572300
H	-5.58143100	1.19646200	-2.48269500
H	-5.38817500	0.29569200	-0.93774600
H	-4.61203400	1.86273800	-1.13327200
H	-1.73058000	-2.17459000	-1.52481800

TS3^{I}

E (DMF) = -3602.59912

Pd	-0.25205100	0.27391300	-0.40143300
C	-0.51275100	2.21242400	0.12272300
C	-0.76285800	3.21404400	-0.82955700
C	-0.46887600	2.59871000	1.47438100
C	-1.06610900	4.51930300	-0.45176200
H	-0.74703600	2.97660500	-1.89259600
C	-0.77230700	3.89349500	1.87412300
H	-0.18732500	1.87131500	2.23475900
C	-1.09412400	4.83928400	0.90268500
H	-1.29089000	5.29206400	-1.18738300
H	-0.76644800	4.18742100	2.92402300
P	-2.57016600	0.19246200	-0.93326100
C	2.67514500	1.20036900	0.46089900
C	1.56678700	0.80355500	0.10060300
I	0.75927300	-1.64144100	-2.30629700
P	-0.28475400	-1.66216600	1.47730900
C	3.95344400	1.72314400	0.80137900
C	4.46487900	2.85229300	0.12511400
C	4.74344400	1.16005000	1.82506600
C	5.69659300	3.39843700	0.47164500
H	3.85644800	3.30887400	-0.65832900
C	5.97388900	1.71289100	2.16904300
H	4.35795900	0.29748500	2.37055200
C	6.45854900	2.83622100	1.49775100
H	6.05960600	4.28548700	-0.05424200
H	6.55505900	1.27005900	2.98251600
H	7.41809200	3.27665400	1.77847200
C	-3.51801800	0.59765500	0.57600300

C	-3.64667800	1.92366300	1.01165700
C	-3.97921400	-0.43786100	1.40315100
C	-4.25006000	2.20592800	2.23629000
H	-3.26196800	2.74270500	0.40102400
C	-4.58692400	-0.15008900	2.62204000
H	-3.85077600	-1.47977600	1.10407000
C	-4.72879400	1.17251400	3.04032200
H	-4.33590700	3.24503200	2.56265200
H	-4.93449300	-0.97056800	3.25392400
H	-5.20235000	1.39767100	3.99897900
C	-3.50001400	-1.22261000	-1.66950600
C	-2.87414800	-1.98897300	-2.65759300
C	-4.85354600	-1.45205200	-1.39115700
C	-3.57396100	-2.99039700	-3.32671900
H	-1.82382200	-1.81040400	-2.89860100
C	-5.54830300	-2.46138200	-2.05363100
H	-5.37762300	-0.84033700	-0.65522300
C	-4.91049700	-3.23792200	-3.01986200
H	-3.06339400	-3.58089300	-4.09139800
H	-6.60097300	-2.63422700	-1.81689100
H	-5.45906600	-4.02727400	-3.53980400
C	-3.03391500	1.43001700	-2.20423300
C	-4.21675900	2.17267500	-2.17369500
C	-2.18075000	1.53437600	-3.31023400
C	-4.52552200	3.03705400	-3.22294000
H	-4.90262900	2.07978400	-1.32894100
C	-2.50099800	2.38624400	-4.36370900
H	-1.25515000	0.94874100	-3.33051700
C	-3.66929100	3.14714300	-4.31727200
H	-5.44542200	3.62549300	-3.18574100
H	-1.82937500	2.46227000	-5.22216700
H	-3.91508500	3.82531000	-5.13797200
C	-0.46133300	-1.13211800	3.22654700
C	-1.29482800	-0.03938400	3.48942700
C	0.13911700	-1.80002700	4.30380700
C	-1.51871200	0.38610800	4.79787300
H	-1.77657300	0.48111800	2.66087000
C	-0.07859100	-1.36959500	5.61042200
H	0.77844000	-2.66603600	4.11860200
C	-0.90626500	-0.27393700	5.86067700
H	-2.17343200	1.24175100	4.97838000
H	0.39799600	-1.89702900	6.44057000
H	-1.07332000	0.06336200	6.88658700
C	1.31387900	-2.55323800	1.50674300
C	1.49864400	-3.78760000	0.87282200
C	2.42370100	-1.92596300	2.09643800
C	2.75230000	-4.39750400	0.85520900
H	0.65335600	-4.28551700	0.39496100
C	3.67029900	-2.54979300	2.09970500
H	2.30097800	-0.95019600	2.57104900
C	3.84053000	-3.79018400	1.47886000
H	2.87245400	-5.36340100	0.35911000
H	4.51273400	-2.06973200	2.60562000
H	4.81537000	-4.28438800	1.49123600
C	-1.53937700	-2.99826600	1.37291500
C	-1.82611600	-3.52474600	0.10507200

C	-2.30665400	-3.41469600	2.46978100
C	-2.85193500	-4.45240400	-0.06105800
H	-1.25248200	-3.18366200	-0.76163500
C	-3.33943900	-4.33423800	2.29730500
H	-2.10820500	-3.00416800	3.46162400
C	-3.61636600	-4.85423700	1.03288500
H	-3.07126100	-4.83617700	-1.05959800
H	-3.93501200	-4.64412100	3.15987000
H	-4.43352500	-5.56719100	0.89916600
N	-1.44837100	6.19411100	1.31166700
O	-1.51266200	6.42677300	2.50196400
O	-1.66488300	7.01127200	0.44025900
C	4.96450800	-0.57091400	-1.55970400
N	6.20509700	-0.74219700	-1.04442300
N	4.80197800	0.25280200	-2.61114800
N	3.94533400	-1.24160700	-1.05707600
H	3.94139200	-1.53413200	-0.08299100
C	3.52457300	0.87575500	-2.91088100
H	2.88987000	0.90679300	-2.01513400
H	3.71223000	1.90926200	-3.23963900
H	2.98540600	0.33547900	-3.70516800
C	5.82468300	0.40414600	-3.62292600
H	6.25589400	1.41883400	-3.62637200
H	6.62839300	-0.32532600	-3.47037100
H	5.37634300	0.21919400	-4.61210800
C	6.51182400	-1.89758600	-0.23350300
H	5.87851600	-2.74482500	-0.52482200
H	7.56491600	-2.17601300	-0.38842100
H	6.36182800	-1.69603800	0.84179500
C	7.14762700	0.35577300	-0.96227000
H	8.03514200	0.18822500	-1.59454100
H	6.66081800	1.29430800	-1.24952100
H	7.47198400	0.47270600	0.08228900
H	3.01880000	-1.27011900	-1.51945500

cis-**C**

E (DMF) = -2942.084651

Pd	-0.05675500	0.48315700	-0.12334500
C	-1.38050200	1.99941700	-0.12791000
C	-2.02566300	2.41097200	1.04798900
C	-1.74191500	2.61474000	-1.33624500
C	-3.05834900	3.33934200	1.01610700
H	-1.74711100	1.97089000	2.00865800
C	-2.77517800	3.54447400	-1.38882800
H	-1.22245700	2.34931500	-2.26017500
C	-3.43888900	3.87650700	-0.21092800
H	-3.59789200	3.63563700	1.91550700
H	-3.09318700	4.00445400	-2.32488200
N	-4.59173700	4.76728300	-0.26786300
O	-5.17029700	5.01214100	0.77143500
O	-4.92115800	5.19932700	-1.35401100
P	-1.85162900	-1.02703600	0.00625200
C	-3.49119900	-0.29059400	0.33445300
C	-4.13658500	0.39093300	-0.70620700

C	-4.04837800	-0.27501800	1.61619000
C	-5.30925900	1.09609300	-0.45963600
H	-3.70638700	0.38836200	-1.71025400
C	-5.22707800	0.43049900	1.85737600
H	-3.55450500	-0.80365000	2.43440500
C	-5.85302700	1.12507400	0.82535200
H	-5.79147800	1.64486100	-1.27190100
H	-5.65183800	0.44462800	2.86382500
H	-6.76116200	1.69952700	1.02087000
C	-1.60821400	-2.15257000	1.42987400
C	-0.82717800	-1.67249900	2.48867100
C	-2.12019700	-3.45327000	1.48931000
C	-0.53728400	-2.48754600	3.58096000
H	-0.41430700	-0.66112100	2.43660400
C	-1.83171500	-4.26646400	2.58308600
H	-2.71615500	-3.84672700	0.66385000
C	-1.03463300	-3.78903000	3.62516200
H	0.09800500	-2.10705600	4.38391000
H	-2.22345500	-5.28594500	2.61738900
H	-0.79807000	-4.43674800	4.47262400
C	-2.16262700	-2.08957300	-1.44366000
C	-1.17388800	-2.19292500	-2.42645300
C	-3.36318400	-2.79746400	-1.59756100
C	-1.36086700	-3.02458200	-3.52840300
H	-0.25527300	-1.61248200	-2.32351600
C	-3.54883200	-3.62590700	-2.70086000
H	-4.16172900	-2.68279000	-0.86005500
C	-2.54466000	-3.74662900	-3.66270500
H	-0.57686700	-3.10375100	-4.28437700
H	-4.48651500	-4.17483900	-2.81542000
H	-2.69377000	-4.39693000	-4.52803200
C	1.27017800	1.93553600	-0.04857400
C	2.15331100	2.78598200	0.00437500
C	3.24420500	3.70412200	0.03358200
C	4.56634300	3.22899900	-0.06481500
C	3.03475300	5.09035200	0.15175400
C	5.63889100	4.11393800	-0.04683700
H	4.73414500	2.15457100	-0.16003200
C	4.11293000	5.96933000	0.16988100
H	2.01134400	5.46339900	0.22711900
C	5.41842400	5.48682600	0.07062600
H	6.65852900	3.72802800	-0.12591700
H	3.93315100	7.04346500	0.26185700
H	6.26274700	6.18037100	0.08474800
P	1.80926500	-1.02065700	-0.08334700
C	3.25251700	-0.40221300	-1.02243900
C	4.55782200	-0.74073100	-0.65207800
C	3.03903500	0.38469100	-2.15955600
C	5.63804500	-0.29882100	-1.41438500
H	4.73334300	-1.34285800	0.24239700
C	4.11989300	0.81887600	-2.92307200
H	2.02240900	0.68258800	-2.42592400
C	5.42018800	0.47909300	-2.55094500
H	6.65565200	-0.55925700	-1.11390100
H	3.94564600	1.44409800	-3.80139600
H	6.26783400	0.83297700	-3.14247300

C	2.43842900	-1.22003100	1.62479500
C	2.98070900	-2.41866700	2.10219600
C	2.36991100	-0.10753700	2.47590600
C	3.42775400	-2.51063700	3.41955500
H	3.04927300	-3.28922400	1.44687200
C	2.82379500	-0.20384300	3.78884700
H	1.96469300	0.83542900	2.09589100
C	3.34607200	-1.40653200	4.26618700
H	3.84408300	-3.45279800	3.78407400
H	2.76837900	0.66977400	4.44254400
H	3.69609600	-1.48095800	5.29870300
C	1.65533500	-2.73252300	-0.72670400
C	2.16092800	-3.07013000	-1.98893000
C	0.91416800	-3.68749200	-0.01702000
C	1.90960800	-4.32706900	-2.53637100
H	2.75268000	-2.34461000	-2.55104100
C	0.66674300	-4.94185400	-0.56673100
H	0.52942600	-3.45445300	0.97572300
C	1.15579600	-5.26356100	-1.83190200
H	2.30987900	-4.57457000	-3.52256200
H	0.08137700	-5.66887900	0.00101000
H	0.95452000	-6.24577600	-2.26565600

trans-**C**

E (DMF) = -2942.090687

Pd	-0.04795900	-0.00001200	0.16651200
C	-2.07213400	-0.00021400	0.00674700
C	-2.71199400	-0.00037300	-1.24493200
C	-2.88759400	-0.00016100	1.15350900
C	-4.09634800	-0.00043700	-1.35949000
H	-2.11471000	-0.00044300	-2.16098500
C	-4.27615700	-0.00020000	1.06504400
H	-2.42749700	-0.00007100	2.14677100
C	-4.86418400	-0.00032700	-0.19703000
H	-4.59938400	-0.00055000	-2.32645800
H	-4.91610400	-0.00012100	1.94812500
N	-6.31967700	-0.00031000	-0.30458300
O	-6.80552500	-0.00064800	-1.41686600
O	-6.96318300	0.00006200	0.72545900
P	-0.00671700	2.31075100	0.10432000
C	-1.50319500	3.10405300	-0.57212200
C	-2.68015300	3.11860500	0.19007900
C	-1.54079400	3.54470800	-1.89871000
C	-3.87434100	3.55721800	-0.37090300
H	-2.66763900	2.76617900	1.22280000
C	-2.74148900	3.98134900	-2.45790000
H	-0.62962500	3.54179100	-2.50115700
C	-3.90945200	3.98299700	-1.69930600
H	-4.78687300	3.55145500	0.22947700
H	-2.76142100	4.31991600	-3.49644900
H	-4.85127400	4.31471800	-2.14238100
C	1.35779600	2.97008800	-0.91650700
C	1.80184600	2.22479000	-2.01455600
C	1.96882200	4.19206800	-0.62016100

C	2.83983000	2.69930000	-2.81118600
H	1.34783300	1.25334700	-2.22132100
C	3.01366900	4.66134000	-1.41494400
H	1.64033000	4.77294500	0.24463200
C	3.44971400	3.91680300	-2.50989200
H	3.18885900	2.10513700	-3.65850400
H	3.49319500	5.61243800	-1.17184600
H	4.27515800	4.28149400	-3.12583900
C	0.25167800	3.05689700	1.74900700
C	1.08894500	2.38536200	2.64986600
C	-0.31103900	4.28701000	2.11111800
C	1.35553000	2.94085400	3.89862500
H	1.53983200	1.43412300	2.35248500
C	-0.04472300	4.83397700	3.36513600
H	-0.96195000	4.81777700	1.41273500
C	0.78696800	4.16212700	4.25980000
H	2.01142800	2.41334300	4.59504500
H	-0.49044600	5.79197100	3.64316000
H	0.99268000	4.59243400	5.24290200
C	1.95494000	0.00016800	0.29147000
C	3.17863600	0.00024300	0.17709200
C	4.58243600	0.00029900	-0.06364800
C	5.28633000	-1.21063000	-0.20780300
C	5.28634800	1.21129700	-0.20716000
C	6.65006100	-1.20594900	-0.48151100
H	4.73969100	-2.15128000	-0.11075200
C	6.65007500	1.20674700	-0.48087400
H	4.73971400	2.15190000	-0.10962200
C	7.33831800	0.00043000	-0.61787100
H	7.18258600	-2.15413900	-0.59175300
H	7.18261500	2.15498700	-0.59061100
H	8.40975200	0.00048000	-0.83252200
P	-0.00628000	-2.31076400	0.10441000
C	-1.50263700	-3.10439600	-0.57189300
C	-2.67954500	-3.11905100	0.19038000
C	-1.54022300	-3.54523000	-1.89842100
C	-3.87368800	-3.55793400	-0.37047900
H	-2.66702000	-2.76650400	1.22306500
C	-2.74087600	-3.98214800	-2.45748600
H	-0.62908600	-3.54223100	-2.50091500
C	-3.90879700	-3.98389000	-1.69882800
H	-4.78618900	-3.55224800	0.22994800
H	-2.76081000	-4.32085500	-3.49598900
H	-4.85059000	-4.31582000	-2.14181000
C	1.35828000	-2.96970200	-0.91659500
C	1.96991700	-4.19136100	-0.62021900
C	1.80165800	-2.22441600	-2.01493000
C	3.01471300	-4.66033800	-1.41525200
H	1.64196600	-4.77220300	0.24480500
C	2.83956100	-2.69864800	-2.81182200
H	1.34719800	-1.25318400	-2.22170900
C	3.45006000	-3.91584100	-2.51050100
H	3.49473800	-5.61117400	-1.17211400
H	3.18805600	-2.10450800	-3.65937600
H	4.27542800	-4.28032000	-3.12667600
C	0.25244700	-3.05690500	1.74903400

C	-0.31007100	-4.28710600	2.11116700
C	1.08975600	-2.38530400	2.64980000
C	-0.04351800	-4.83408600	3.36512800
H	-0.96099900	-4.81792500	1.41283900
C	1.35657900	-2.94081100	3.89850200
H	1.54048600	-1.43399800	2.35239000
C	0.78821100	-4.16216600	4.25970500
H	-0.48907600	-5.79215100	3.64317300
H	2.01250900	-2.41324800	4.59485100
H	0.99411400	-4.59248600	5.24276200

TS4

E (DMF) = -2942.067384

P	-1.73936400	-1.19191400	-0.04918300
C	-1.59581900	-2.85335000	-0.79853300
C	-2.24398200	-3.16843500	-1.99863100
C	-0.69491500	-3.77669100	-0.24650800
C	-1.98497600	-4.37994900	-2.63977600
H	-2.95345100	-2.46169200	-2.43534000
C	-0.44715800	-4.98726400	-0.88503900
H	-0.17649700	-3.54584100	0.68560900
C	-1.08569800	-5.29034700	-2.08787000
H	-2.49650700	-4.61370500	-3.57669800
H	0.26061300	-5.69191000	-0.44224600
H	-0.88303300	-6.23723600	-2.59371700
C	-3.28596600	-0.50959800	-0.74541900
C	-3.20415300	0.27172100	-1.90448600
C	-4.52673000	-0.69110700	-0.12592400
C	-4.34774600	0.85899500	-2.43832300
H	-2.22925000	0.45179500	-2.36474600
C	-5.66786700	-0.09227000	-0.65656200
H	-4.59904500	-1.28575800	0.78754400
C	-5.57984800	0.68554900	-1.80923100
H	-4.27160800	1.48150600	-3.33229000
H	-6.63013700	-0.22306500	-0.15613500
H	-6.47103200	1.17388100	-2.20972400
C	-2.16534600	-1.49815500	1.70461800
C	-2.06140600	-0.41228900	2.58670100
C	-2.58846800	-2.73882200	2.19134100
C	-2.36553700	-0.57287700	3.93568300
H	-1.73739600	0.56027400	2.20284100
C	-2.88415600	-2.89729400	3.54518400
H	-2.68264700	-3.58896600	1.51257800
C	-2.77075500	-1.81810200	4.41956200
H	-2.28117800	0.27930400	4.61434300
H	-3.20772300	-3.87255500	3.91677500
H	-3.00207300	-1.94519700	5.47992800
C	-1.11007600	1.96973200	-0.05589200
C	-2.12032200	2.67692300	-0.05061100
C	-3.37666100	3.33420400	-0.10756200
C	-3.71566800	4.15328000	-1.20265200
C	-4.34309900	3.11979000	0.89503500
C	-4.97938200	4.72541400	-1.29331500
H	-2.97099900	4.32545800	-1.98231300

C	-5.60346200	3.69668800	0.79684500
H	-4.09222100	2.47638900	1.74064800
C	-5.93029600	4.49923800	-0.29731700
H	-5.22594600	5.35678100	-2.15072000
H	-6.34293800	3.51408500	1.58060000
H	-6.92259200	4.95032700	-0.37169700
C	0.83842000	2.25915900	-0.05545800
C	1.26624900	2.91851000	-1.22806800
C	1.40663900	2.65063000	1.17550700
C	2.27682600	3.86473000	-1.18585100
H	0.80370700	2.66554500	-2.18446600
C	2.42067000	3.59225800	1.22682700
H	1.06893700	2.17796600	2.10034800
C	2.86501600	4.17678300	0.04073600
H	2.64834700	4.34999400	-2.08873900
H	2.90740600	3.86290800	2.16365600
P	2.00167800	-0.90202700	-0.10976200
Pd	0.03017300	0.38181000	-0.16754000
C	2.45982500	-1.84828300	-1.60193300
C	1.44181500	-2.22097300	-2.48693000
C	3.78041000	-2.23417100	-1.86893000
C	1.73358500	-2.99199300	-3.61010800
H	0.41524400	-1.90545000	-2.28884200
C	4.07004900	-2.99842900	-2.99685700
H	4.58357500	-1.92524800	-1.19499900
C	3.04693700	-3.38277300	-3.86479700
H	0.92801600	-3.28404800	-4.28740000
H	5.10193800	-3.29391500	-3.20125600
H	3.27801400	-3.98277500	-4.74835700
C	1.94698500	-2.14901600	1.23007400
C	2.54993000	-3.40815000	1.13921800
C	1.19207900	-1.83001900	2.36637900
C	2.38309000	-4.33722200	2.16494000
H	3.12742100	-3.67429100	0.25134100
C	1.02844200	-2.75798800	3.39195200
H	0.70085700	-0.85533000	2.42800100
C	1.61928300	-4.01697800	3.28810500
H	2.84724600	-5.32305000	2.08240000
H	0.41700700	-2.50086800	4.25983000
H	1.48049800	-4.75391000	4.08274500
C	3.48933000	0.08905500	0.26241900
C	4.05670300	0.12959100	1.54017500
C	3.97998200	0.94467100	-0.73363400
C	5.09269500	1.02076600	1.81814800
H	3.68312800	-0.53179200	2.32521600
C	5.01794400	1.82755800	-0.45292700
H	3.53548300	0.93101700	-1.73182400
C	5.57109800	1.87489400	0.82693800
H	5.52402900	1.05125800	2.82152000
H	5.37749900	2.50711100	-1.22927300
H	6.36482800	2.59033700	1.05259700
N	4.01425800	5.05986700	0.07375800
O	4.50445000	5.31833600	1.15629900
O	4.44216700	5.47564900	-0.98710900

B^{OTf}

E (DMF) = -2882.736925

Pd	-0.18891500	-0.12342900	0.31753500
C	1.64871700	0.56483800	0.19370000
C	2.27977500	0.75189300	-1.04262000
C	2.34018900	0.88279000	1.37091300
C	3.57968600	1.23893000	-1.11002500
H	1.75771900	0.51996800	-1.97397200
C	3.64234200	1.37224000	1.31738200
H	1.86358200	0.74927000	2.34583500
C	4.24296100	1.54098100	0.07478300
H	4.09245900	1.39175000	-2.05964100
H	4.20327800	1.62594000	2.21756100
N	5.61423000	2.05475300	0.01037400
O	6.16523700	2.30508700	1.05974300
O	6.10590000	2.19525100	-1.08744500
P	0.62673000	-2.30222300	0.11870000
C	2.35550400	-2.52161700	-0.38910100
C	3.34889200	-2.15850100	0.53225200
C	2.71998700	-2.93689900	-1.67313100
C	4.68806900	-2.18887200	0.16187600
H	3.07334700	-1.84014800	1.53999300
C	4.06590200	-2.96560100	-2.03809400
H	1.95896800	-3.24249900	-2.39358100
C	5.04816300	-2.58306600	-1.12800200
H	5.45559600	-1.89528300	0.88125500
H	4.34594400	-3.29065700	-3.04248300
H	6.10029400	-2.59632100	-1.42082700
C	-0.41475400	-3.00294800	-1.20706800
C	-0.49440600	-2.30767100	-2.42470900
C	-1.22169300	-4.12637800	-1.00337500
C	-1.36120300	-2.73820300	-3.42535300
H	0.12484000	-1.42031800	-2.58439300
C	-2.09854400	-4.54746800	-2.00473000
H	-1.17068700	-4.66979100	-0.05718800
C	-2.17004500	-3.85767600	-3.21382400
H	-1.40663800	-2.19964400	-4.37488500
H	-2.72468700	-5.42706500	-1.83863100
H	-2.85125700	-4.19620700	-3.99795800
C	0.38357500	-3.37761400	1.56050100
C	-0.62643400	-3.06248100	2.47919600
C	1.16266800	-4.52713000	1.74444200
C	-0.85593200	-3.89638300	3.57102100
H	-1.23574100	-2.16764300	2.32878100
C	0.92938600	-5.35374100	2.84093800
H	1.95558800	-4.77064600	1.03319800
C	-0.07812200	-5.03969000	3.75310100
H	-1.64153600	-3.64909300	4.28846900
H	1.54041300	-6.24748500	2.98520200
H	-0.25467700	-5.68838400	4.61411600
P	-0.97807700	2.06232400	0.09241900
C	0.15576500	3.29121700	-0.61584600
C	0.11637700	3.64678200	-1.96754000
C	1.18088200	3.78664000	0.20320700
C	1.10481800	4.47554000	-2.49742800

H	-0.68647400	3.28392800	-2.61227400
C	2.16365400	4.61139800	-0.33213200
H	1.21771500	3.51843100	1.26111400
C	2.13233400	4.95030900	-1.68564300
H	1.06808500	4.75264200	-3.55327200
H	2.96318600	4.98703800	0.31014100
H	2.90996200	5.59186500	-2.10585300
C	-1.61310100	2.78965700	1.62898300
C	-1.79385000	4.17297300	1.75930100
C	-1.95648300	1.93844700	2.68731000
C	-2.31988400	4.69527600	2.93845700
H	-1.51457400	4.84108000	0.94079400
C	-2.48309100	2.46752200	3.86363400
H	-1.80777400	0.86061600	2.58294900
C	-2.66516800	3.84446300	3.98892500
H	-2.45662100	5.77418000	3.03973800
H	-2.74393900	1.80306100	4.69038700
H	-3.07173600	4.25904800	4.91419200
C	-2.40659700	1.94539100	-1.03889200
C	-3.65560200	2.49102700	-0.72853300
C	-2.25247600	1.20673900	-2.22176600
C	-4.73204500	2.31005400	-1.59770200
H	-3.78986200	3.05741000	0.19569500
C	-3.32637600	1.03518700	-3.09050100
H	-1.28550100	0.75077600	-2.45338300
C	-4.56978500	1.58816300	-2.77898400
H	-5.70316100	2.74634900	-1.35200300
H	-3.19361900	0.46636200	-4.01383700
H	-5.41297300	1.45798300	-3.46145900
C	-3.03757500	-1.16201500	-0.24675200
O	-2.24735200	-0.76726900	0.62588200
N	-4.35795500	-1.13085000	-0.11759900
H	-2.68124800	-1.57415300	-1.20647200
C	-5.21714400	-1.66416500	-1.14950900
H	-5.83324100	-2.48649500	-0.75307300
H	-5.88309200	-0.87742100	-1.53585700
H	-4.60663400	-2.04891100	-1.97694000
C	-4.98356700	-0.57006500	1.05950200
H	-4.21649400	-0.09141000	1.67828700
H	-5.72945200	0.18069900	0.75929100
H	-5.48788800	-1.35612600	1.64373100

Rd

E (DMF) = -2996.651025

Pd	0.21820000	-0.19697700	-0.04413100
C	3.14473000	-1.16078800	0.68748000
N	2.09583200	-1.21292600	-0.09767700
N	4.37414800	-1.60417300	0.28132600
N	3.06516500	-0.65689900	1.94644000
C	4.66873500	-1.74523100	-1.12451600
H	4.32407900	-2.71105900	-1.54217700
H	4.21334900	-0.92436600	-1.69211200
H	5.75722100	-1.68965000	-1.27031700

C	5.23840000	-2.34606000	1.17770700
H	5.40461200	-3.36254000	0.78247300
H	6.22042400	-1.86040200	1.29883400
H	4.76885500	-2.44250100	2.16293400
C	1.85105100	-0.75675100	2.71883600
H	2.10214800	-1.03788600	3.75435600
H	1.29750100	0.19526200	2.74817100
H	1.20482500	-1.53453200	2.30116900
C	4.14508100	0.09055700	2.55120000
H	3.75381600	1.04315500	2.93942500
H	4.61494400	-0.45489100	3.38768000
H	4.91154700	0.31933300	1.80157600
H	2.23468000	-1.86831500	-0.86187500
C	-1.58635200	0.59713900	0.22890300
C	-2.46571400	0.91211500	-0.81418100
C	-2.00727600	0.81660300	1.55005500
C	-3.72533100	1.43848300	-0.55701900
H	-2.16882800	0.74559100	-1.85129700
C	-3.26634900	1.34378300	1.82763500
H	-1.34799300	0.56826100	2.38768900
C	-4.10782900	1.64778500	0.76433500
H	-4.42150800	1.68936600	-1.35700400
H	-3.61185700	1.52258500	2.84638900
N	-5.43607900	2.19848300	1.04239900
O	-5.74113300	2.36135400	2.20381900
O	-6.14386400	2.45469700	0.09329300
P	1.01625600	2.00121800	-0.32463300
P	-0.87146200	-2.25754100	-0.14370600
C	-0.28834100	3.20229200	-0.77958500
C	-0.99219700	3.95014600	0.16877100
C	-0.68359200	3.25295000	-2.12370700
C	-2.08447700	4.72302700	-0.21962300
H	-0.69717200	3.93872200	1.21815200
C	-1.76933500	4.03434800	-2.50783800
H	-0.14277500	2.67566300	-2.87772200
C	-2.47934800	4.76352400	-1.55520700
H	-2.63007600	5.29895900	0.53101900
H	-2.06568900	4.06916100	-3.55862200
H	-3.33888300	5.36742300	-1.85395300
C	1.85491800	2.69625300	1.14302500
C	3.15942400	3.20233800	1.10385300
C	1.15780900	2.70240500	2.36160400
C	3.74011600	3.73621900	2.25389200
H	3.72949800	3.18301600	0.17370800
C	1.73911400	3.24294500	3.50590500
H	0.14883600	2.28644400	2.41433800
C	3.03070100	3.76709200	3.45311400
H	4.75620400	4.13477700	2.20843600
H	1.17940900	3.25465200	4.44387200
H	3.48559000	4.19522100	4.34907000
C	2.18235300	2.19587100	-1.71424700
C	2.61616100	3.47574500	-2.09352600
C	2.57896700	1.08857500	-2.46782900
C	3.45909900	3.63178500	-3.18935700
H	2.27814700	4.35467700	-1.53875800
C	3.41640500	1.24803300	-3.57191000

H	2.22072500	0.10060900	-2.17829200
C	3.86245300	2.51819300	-3.92883800
H	3.79450500	4.63071100	-3.47680500
H	3.71554500	0.37727900	-4.16033800
H	4.51704300	2.64580900	-4.79397300
C	-2.66108900	-2.25357800	-0.50851200
C	-3.65179200	-2.19976100	0.47744600
C	-3.03239300	-2.14496400	-1.85671000
C	-4.98622100	-2.01988800	0.12073500
H	-3.39986100	-2.30087400	1.53175900
C	-4.36783000	-1.97124200	-2.20730300
H	-2.27462700	-2.19265600	-2.64205400
C	-5.34772500	-1.89657500	-1.21905800
H	-5.74919200	-1.97524500	0.90090800
H	-4.64321600	-1.89052700	-3.26117700
H	-6.39453600	-1.74809000	-1.49254000
C	-0.55647000	-3.14928900	1.41421600
C	0.38244300	-4.18660800	1.48474000
C	-1.12186200	-2.66272000	2.60442500
C	0.71793700	-4.74933600	2.71552500
H	0.86308500	-4.55611800	0.57758500
C	-0.79400400	-3.23814500	3.82860800
H	-1.79583800	-1.80478500	2.58410800
C	0.12472500	-4.28579900	3.88772200
H	1.44713400	-5.56178000	2.75478600
H	-1.25209400	-2.85697400	4.74401300
H	0.38330900	-4.73521000	4.84901500
C	-0.20715200	-3.28371000	-1.49644400
C	-0.52960100	-4.64443700	-1.59335800
C	0.53502000	-2.67960200	-2.51860900
C	-0.07483200	-5.39380300	-2.67469700
H	-1.14794000	-5.11713900	-0.82620000
C	0.98358000	-3.43136400	-3.60419000
H	0.73148900	-1.60412000	-2.47482100
C	0.68720800	-4.79093800	-3.67692200
H	-0.32658100	-6.45448000	-2.74247800
H	1.55480800	-2.94998300	-4.40125900
H	1.03684800	-5.38227200	-4.52617100

Re

E (DMF) = -2996.649237

Pd	-0.18604600	0.51431100	0.02705300
C	-2.09931200	1.15256800	0.07931200
C	-2.68467200	1.35441300	1.33831800
C	-2.84708400	1.45774600	-1.06458200
C	-3.98754800	1.82497300	1.46000800
H	-2.13556800	1.10376200	2.25087500
C	-4.15373000	1.93046900	-0.96251800
H	-2.43310300	1.29930100	-2.06371500
C	-4.70712800	2.09793700	0.30106700
H	-4.46672900	1.96700100	2.42888400
H	-4.75884400	2.15746200	-1.84100300
N	-6.09702600	2.55208000	0.41677000
O	-6.54450400	2.69542900	1.53277600

O	-6.70673500	2.74658600	-0.61138500
P	-1.12217900	-1.58405400	-0.11088500
C	-2.74915300	-1.75699500	0.71831500
C	-3.91693800	-1.45320900	0.00517400
C	-2.84254100	-2.06554200	2.07969100
C	-5.14981300	-1.43598500	0.64965800
H	-3.86590200	-1.21260000	-1.05736400
C	-4.08010700	-2.04826800	2.72035800
H	-1.95341500	-2.33210400	2.65196600
C	-5.23458700	-1.72494000	2.01096100
H	-6.05028300	-1.18970100	0.08251100
H	-4.14000200	-2.29412000	3.78290900
H	-6.20253100	-1.70410500	2.51639800
C	-0.12559700	-2.94698200	0.59211200
C	0.36084600	-2.79416600	1.89712500
C	0.14824600	-4.12993200	-0.10165200
C	1.07608800	-3.81679600	2.51310700
H	0.19098100	-1.86418100	2.44005500
C	0.86645100	-5.15103600	0.51709200
H	-0.18260100	-4.25582500	-1.13301300
C	1.32232700	-5.00365900	1.82560500
H	1.44536900	-3.67905400	3.53189400
H	1.07599400	-6.06940800	-0.03564700
H	1.88089400	-5.81040800	2.30551800
C	-1.48395700	-2.03071900	-1.83787100
C	-1.05622500	-1.19948800	-2.87721500
C	-2.21937100	-3.18603000	-2.14094500
C	-1.33223800	-1.52542500	-4.20363100
H	-0.51157700	-0.28433900	-2.63430100
C	-2.49067800	-3.51278900	-3.46646500
H	-2.59472900	-3.82361100	-1.33679200
C	-2.04433400	-2.68632000	-4.49880200
H	-0.99721600	-0.86728100	-5.00847100
H	-3.06276100	-4.41453600	-3.69551100
H	-2.26471800	-2.94351300	-5.53729400
P	2.12225800	-0.11458600	0.20606100
C	3.40466900	1.04845200	-0.42117700
C	3.69630000	2.19003400	0.33991500
C	4.13984200	0.80377500	-1.58642500
C	4.71338000	3.05704900	-0.04718200
H	3.14925400	2.37742400	1.26579500
C	5.15795400	1.67727400	-1.97249100
H	3.94939700	-0.09202400	-2.18048900
C	5.45180400	2.80052800	-1.20306200
H	4.94162800	3.93112000	0.56743100
H	5.73715800	1.46284400	-2.87356200
H	6.26084300	3.47222300	-1.49861200
C	2.58304600	-0.16567800	1.97252500
C	3.90185000	-0.41203400	2.37999200
C	1.61631200	0.14041700	2.93744200
C	4.22981700	-0.40302200	3.73282500
H	4.68153300	-0.59083200	1.63570900
C	1.94815400	0.15949900	4.29123700
H	0.59519200	0.37030400	2.61655900
C	3.25319200	-0.12351200	4.69004100
H	5.25780300	-0.60403200	4.04259200

H	1.18584700	0.39919500	5.03602000
H	3.51562200	-0.11203800	5.75036400
C	2.60113200	-1.69399800	-0.57302800
C	2.18145900	-1.88113900	-1.89748400
C	3.35398200	-2.69179400	0.05109400
C	2.52963600	-3.03279700	-2.59679700
H	1.56821800	-1.12143500	-2.38625000
C	3.69810900	-3.84590500	-0.65041000
H	3.65646600	-2.58621600	1.09335000
C	3.29640100	-4.01650200	-1.97373800
H	2.19225500	-3.16363000	-3.62743100
H	4.28090100	-4.62322400	-0.15135200
H	3.57157200	-4.92322600	-2.51710600
C	0.82974500	3.49284300	-0.44777900
N	1.10472700	4.71251000	0.11414800
N	1.16505400	3.33358000	-1.75357300
N	0.28092000	2.53599200	0.25874600
H	-0.18723200	2.90256400	1.08233900
C	0.56807300	2.30892800	-2.56961400
H	-0.39843300	2.01104200	-2.14850300
H	0.39933300	2.70395400	-3.58387700
H	1.21870700	1.41997000	-2.65177800
C	2.29744400	4.00696200	-2.35260800
H	2.85125500	4.56795500	-1.59383200
H	2.98139200	3.25706700	-2.78006600
H	1.98595800	4.69338100	-3.15755100
C	1.17360000	4.83925200	1.55012700
H	1.61635100	3.93769100	1.99399500
H	1.81352900	5.69659900	1.80568200
H	0.18343200	5.01329900	2.01398300
C	0.83239900	5.94675900	-0.59804300
H	1.72164300	6.59617800	-0.64238600
H	0.50021600	5.73304500	-1.61972400
H	0.02454900	6.50281600	-0.09250100

TS0^{OTf}

E (DMF) = -3358.783977

Pd	0.29200500	-0.16685100	-0.61371100
C	1.27508700	1.54786900	-0.48678200
C	1.90443700	2.05459600	-1.63481800
C	1.39081200	2.26904500	0.70960000
C	2.60414300	3.25350400	-1.60506600
H	1.86436800	1.48796700	-2.56763500
C	2.08490400	3.47627500	0.75896700
H	0.93611600	1.88997300	1.62634900
C	2.68290700	3.95106200	-0.40239800
H	3.10547900	3.65442600	-2.48610100
H	2.17929200	4.05146200	1.68050700
N	3.44133400	5.20384800	-0.35312200
O	3.47039900	5.79824700	0.70215000
O	3.99249800	5.56216600	-1.37085700
P	2.31490300	-0.99365500	0.03820700
C	2.71309900	-0.94510700	1.81737400
C	4.00661300	-1.24736600	2.27222100

C	1.72722700	-0.59627300	2.74465600
C	4.29331500	-1.22654800	3.63394800
H	4.79843400	-1.48207300	1.55699200
C	2.01627000	-0.57813400	4.10758900
H	0.72488500	-0.33937500	2.39462700
C	3.29686900	-0.89700300	4.55355500
H	5.30261300	-1.46239500	3.97853000
H	1.23121700	-0.31371300	4.81800600
H	3.52416500	-0.88044300	5.62191800
C	2.52761400	-2.73806900	-0.49089800
C	2.09223900	-3.08364700	-1.77790900
C	3.16749900	-3.70542400	0.29113200
C	2.31189600	-4.36318100	-2.28066400
H	1.56887300	-2.33704500	-2.38005600
C	3.38571600	-4.98694500	-0.21448100
H	3.50104000	-3.46421500	1.30171600
C	2.96454600	-5.31794700	-1.50044600
H	1.97730500	-4.61633200	-3.28958200
H	3.89241400	-5.73099200	0.40451400
H	3.14407800	-6.32038500	-1.89560000
C	3.77718100	-0.17502200	-0.71268600
C	4.42234000	0.86517500	-0.03062900
C	4.18716000	-0.49670800	-2.01101100
C	5.45115300	1.57475900	-0.64234000
H	4.10669500	1.14173100	0.97647800
C	5.21651300	0.21781400	-2.62033400
H	3.70948700	-1.31204700	-2.55672400
C	5.84770200	1.25783100	-1.94061200
H	5.93946700	2.38919100	-0.10258100
H	5.52951400	-0.04499200	-3.63334000
H	6.65131600	1.82031800	-2.42094200
P	-2.04856500	0.52654100	1.11352800
C	-2.12872900	0.03839700	2.89288000
C	-1.33289600	0.78775200	3.77460000
C	-2.89875700	-1.00724100	3.41192200
C	-1.31168700	0.49947300	5.13577400
H	-0.74717800	1.63103600	3.39682300
C	-2.86406200	-1.30466900	4.77511900
H	-3.55651600	-1.58438200	2.76058100
C	-2.07139500	-0.55628000	5.64126000
H	-0.70635400	1.11201800	5.80861800
H	-3.47952800	-2.11973500	5.16334700
H	-2.05613600	-0.78365400	6.70939000
C	-3.55569700	-0.23394300	0.39032000
C	-4.58303800	0.54011900	-0.16511300
C	-3.66628000	-1.63310500	0.32121700
C	-5.69559800	-0.06343100	-0.75049600
H	-4.52145700	1.62856100	-0.12257200
C	-4.78542300	-2.23479500	-0.25008300
H	-2.87504300	-2.26170600	0.73003600
C	-5.80627500	-1.45174000	-0.78880300
H	-6.48982700	0.56087200	-1.16718300
H	-4.86279300	-3.32459400	-0.26962900
H	-6.68628300	-1.92283000	-1.23250500
C	-2.52765600	2.28658000	1.31109300
C	-1.75421400	3.26968600	0.69345000

C	-3.60378900	2.67222500	2.12651400
C	-2.04240300	4.62271500	0.88248600
H	-0.91215000	2.96745200	0.07239300
C	-3.90198800	4.01925800	2.30056300
H	-4.20356400	1.91157500	2.63309400
C	-3.11849400	4.99777700	1.68209000
H	-1.41682600	5.38350400	0.40895700
H	-4.74262500	4.31187900	2.93392500
H	-3.34546800	6.05544100	1.83510200
C	-2.02641000	1.24751500	-2.78550000
N	-3.09956800	0.71604900	-3.46098800
N	-2.06842900	2.59409500	-2.58012200
N	-1.02164900	0.50909000	-2.37998700
H	-1.01502800	-0.35240200	-2.92245800
C	-0.87518500	3.39886100	-2.67675900
H	-0.03664400	2.76774600	-2.98067800
H	-1.02590000	4.19400700	-3.42744000
H	-0.60868300	3.88145200	-1.72428900
C	-3.30598100	3.31661600	-2.39667200
H	-4.13242700	2.61290900	-2.24811300
H	-3.22988900	3.95342400	-1.50148500
H	-3.54258300	3.96576700	-3.25797000
C	-3.41502300	-0.68162100	-3.33492500
H	-3.24179000	-1.01801000	-2.30411000
H	-4.48249400	-0.83309800	-3.54894700
H	-2.84144300	-1.31697700	-4.03899200
C	-3.66864800	1.37638800	-4.61734800
H	-4.74515000	1.57786900	-4.48870400
H	-3.15466600	2.32506900	-4.80699000
H	-3.54362600	0.74368900	-5.51289500
C	-0.86186800	-3.28162800	-0.63855100
N	-1.39848500	-4.19406300	-1.51839900
N	-0.45828500	-3.78253500	0.55598700
C	-0.33412100	-2.95588900	1.72929700
H	-0.64339700	-1.93192200	1.49983600
H	-0.96263400	-3.34672000	2.54716900
H	0.70724700	-2.93024800	2.08397400
C	-0.00960400	-5.14760300	0.71612600
H	0.16439700	-5.60746500	-0.26287500
H	0.94513300	-5.14693000	1.26257300
H	-0.72813600	-5.76110200	1.28587500
C	-1.37449600	-3.94604200	-2.93695800
H	-0.51798100	-3.31139800	-3.19623100
H	-1.26545600	-4.90136100	-3.47386500
H	-2.30070700	-3.46432200	-3.30264700
C	-2.35180600	-5.19392600	-1.08740800
H	-2.01338800	-6.21804000	-1.31706000
H	-2.52368200	-5.11737400	-0.00771800
H	-3.31901800	-5.03365200	-1.59473500
N	-0.76719600	-2.01377800	-0.94876500
H	-1.40595200	-1.80981000	-1.71093600

Rf

E (DMF) = -2323.389711

Pd	0.08714900	-0.00874300	0.13555500
C	0.98510300	-2.93182700	0.20744100
N	0.09082400	-2.02650100	-0.12608700
N	1.20635300	-4.02577900	-0.57412200
N	1.72060600	-2.81902500	1.34117500
C	0.81833500	-4.02712600	-1.96465100
H	-0.20600200	-4.41399600	-2.12025500
H	0.87760000	-3.01073800	-2.37597000
H	1.50790100	-4.66795500	-2.53406600
C	1.53607900	-5.31938100	-0.01155400
H	0.77953600	-6.06170200	-0.31533200
H	2.52261500	-5.67519800	-0.35072300
H	1.53727300	-5.26339700	1.08262400
C	1.20503500	-2.13902200	2.50466100
H	1.44538000	-2.73047800	3.40320300
H	1.64111500	-1.13403200	2.62161200
H	0.11727800	-2.04365300	2.42127700
C	3.12858000	-3.15161700	1.37749700
H	3.70487800	-2.25766000	1.66818300
H	3.34450400	-3.95543500	2.10078600
H	3.47097200	-3.46123200	0.38390400
H	-0.60565400	-2.39331600	-0.76828000
P	-2.28845700	-0.00146000	0.01866800
C	-3.14544800	1.42480700	0.77124200
C	-3.90596000	1.32023300	1.94084700
C	-2.97209400	2.68399200	0.17418400
C	-4.47660700	2.45906900	2.50927400
H	-4.06834900	0.34582900	2.40589600
C	-3.54758900	3.81616900	0.74371900
H	-2.39616700	2.77442900	-0.75004200
C	-4.29674400	3.70678100	1.91636700
H	-5.07449400	2.36553900	3.41858700
H	-3.41820400	4.78943800	0.26448500
H	-4.75003300	4.59526800	2.36158100
C	-3.04432400	-1.48627500	0.75671400
C	-3.92813600	-2.31652800	0.06019900
C	-2.66551500	-1.82647400	2.06396300
C	-4.43157200	-3.46677600	0.66869800
H	-4.22524100	-2.06815900	-0.96093300
C	-3.18186800	-2.96584600	2.67278900
H	-1.96181500	-1.18923300	2.60726600
C	-4.06422800	-3.79059600	1.97281200
H	-5.12089900	-4.11093000	0.11814300
H	-2.89034300	-3.21677900	3.69525400
H	-4.46505400	-4.68923700	2.44708000
C	-2.84594100	0.01799100	-1.71614100
C	-4.15107600	0.39207800	-2.06400800
C	-1.94970200	-0.37331900	-2.71905500
C	-4.55212100	0.36399400	-3.39710100
H	-4.85225000	0.71162100	-1.28881100
C	-2.35575800	-0.40274700	-4.05211700
H	-0.92290900	-0.63795800	-2.44860700
C	-3.65696300	-0.03521300	-4.39079300
H	-5.56987700	0.65767600	-3.66366500
H	-1.65155300	-0.70531200	-4.83044900
H	-3.97504600	-0.05315600	-5.43565900

C	2.10447600	0.00723700	0.08650700
C	2.80070000	-0.59850900	-0.97446400
C	2.86955200	0.64323800	1.07977400
C	4.19108700	-0.57157700	-1.05346300
H	2.24846300	-1.11113300	-1.76677000
C	4.26137300	0.67369000	1.02947000
H	2.37184200	1.13365300	1.92046900
C	4.90470800	0.06570000	-0.04364700
H	4.73760300	-1.03404700	-1.87648300
H	4.86180200	1.15989100	1.79955500
N	6.36932000	0.09764200	-0.11253000
O	6.95516200	0.68177800	0.77170500
O	6.89432600	-0.46203000	-1.04938200
C	0.91868500	2.92345900	-0.00441600
N	1.52367100	2.82674000	-1.21626200
N	1.19334800	4.02695800	0.74546700
N	0.09472700	1.99512200	0.42488700
H	-0.52552800	2.32168900	1.16070700
C	0.93484900	4.03190900	2.16645800
H	-0.08619600	4.37997100	2.40984800
H	1.07224800	3.02473300	2.58155000
H	1.64813100	4.70644300	2.66252500
C	1.43319500	5.32390000	0.14630400
H	0.68992100	6.04929000	0.51685000
H	2.43749700	5.70787200	0.38871300
H	1.33321300	5.25952300	-0.94286000
C	0.90627900	2.11397500	-2.30868400
H	1.35265200	1.11668000	-2.45443400
H	-0.16624200	1.98886400	-2.12061200
H	1.03974700	2.69255900	-3.23716000
C	2.91537000	3.17940200	-1.40271800
H	3.47549700	2.28834000	-1.73203800
H	3.04235400	3.97083500	-2.15982900
H	3.35141700	3.51582300	-0.45557700

Rg

E (DMF) = -2323.389799

Pd	0.39441500	0.50006400	-0.09521900
C	3.13184300	1.85152000	0.30812700
N	2.48456800	0.84297300	-0.21689700
N	4.15917000	2.47580400	-0.33895700
N	2.80153500	2.32689000	1.54149600
C	4.30093400	2.33479900	-1.76793200
H	4.90860600	1.45539500	-2.05376700
H	3.31112100	2.24874300	-2.23625400
H	4.79662500	3.22890300	-2.17422100
C	5.31998700	2.98079400	0.36494500
H	6.22851200	2.46550200	0.01044000
H	5.45743400	4.06332700	0.20791100
H	5.22035600	2.78927000	1.43929100
C	2.17805900	1.46363800	2.51305000
H	2.54496100	1.72291300	3.51857800
H	1.07555100	1.55236900	2.52120600
H	2.42826800	0.41776200	2.30302400

C	2.76872800	3.74212500	1.82837400
H	1.74472100	4.04333400	2.10926200
H	3.44202000	4.01325500	2.65867200
H	3.05122500	4.31531500	0.93819800
H	3.00634300	0.39450600	-0.96346600
C	-1.56477500	0.22489800	0.09142000
C	-2.39921800	-0.11443500	-0.98402700
C	-2.15712100	0.42096900	1.35054800
C	-3.76966900	-0.28189800	-0.81263900
H	-1.97548600	-0.28365300	-1.97694600
C	-3.52671300	0.25881600	1.54359400
H	-1.54078700	0.69733100	2.21229300
C	-4.31424900	-0.09686600	0.45405800
H	-4.42680300	-0.56491300	-1.63544100
H	-3.99872100	0.39429700	2.51749300
N	-5.75466300	-0.28832200	0.64739400
O	-6.19833400	-0.09118100	1.75722300
O	-6.40529700	-0.62958400	-0.31520400
P	0.67199900	-1.73707800	-0.00821200
C	-0.81045400	-2.78001900	-0.22696700
C	-1.66901100	-3.10680200	0.82804900
C	-1.17312400	-3.12242800	-1.53719500
C	-2.87907000	-3.74716800	0.57252300
H	-1.40381000	-2.86820000	1.85758300
C	-2.38169700	-3.76680800	-1.78608300
H	-0.51018100	-2.88264200	-2.37188800
C	-3.24280400	-4.07105600	-0.73334800
H	-3.54275500	-3.99489400	1.40376200
H	-2.65254700	-4.03108900	-2.81070700
H	-4.19572300	-4.56740100	-0.92914900
C	1.41481900	-2.08780600	1.62029600
C	2.72545300	-2.55779800	1.75937900
C	0.69171700	-1.72941400	2.76947700
C	3.28867000	-2.69889300	3.02759800
H	3.31894300	-2.80552700	0.87800200
C	1.25282900	-1.88695400	4.03300200
H	-0.30665200	-1.29688500	2.67592500
C	2.55324900	-2.37490900	4.16530900
H	4.31218500	-3.06809900	3.12365600
H	0.67484700	-1.61670400	4.91963200
H	2.99565000	-2.49429700	5.15676400
C	1.79826700	-2.39406900	-1.27985800
C	2.20481100	-3.73565800	-1.23925000
C	2.17412200	-1.59538500	-2.36562500
C	3.00997900	-4.25181200	-2.25020900
H	1.87868900	-4.38276900	-0.42103600
C	2.97516000	-2.11744200	-3.38090800
H	1.81168000	-0.56558600	-2.42566100
C	3.40053600	-3.44262100	-3.31850700
H	3.32636900	-5.29645500	-2.21067100
H	3.25927600	-1.48960200	-4.22843600
H	4.02799100	-3.85338000	-4.11266900
C	-1.02409500	3.13585300	-0.68701700
N	-1.06591400	3.04488500	-2.03956100
N	-2.03796500	3.84467400	-0.09018000
H	-0.23476900	2.71677900	0.99400500

N	-0.03427500	2.60054100	0.00374000
C	-3.42102000	3.58921300	-0.46536500
H	-3.94195400	3.08529000	0.36615300
H	-3.95894500	4.52032600	-0.70428500
H	-3.46721400	2.91475600	-1.32705800
C	-1.86258100	4.30631900	1.26531800
H	-2.02615200	3.50770600	2.01527500
H	-0.85871600	4.73274500	1.40170400
H	-2.59097000	5.10455600	1.46550200
C	-1.71671900	4.05590000	-2.85244400
H	-2.57609000	3.64986000	-3.41010900
H	-2.05858100	4.88653800	-2.22580700
H	-0.99367300	4.45605900	-3.58076300
C	-0.13448300	2.20376700	-2.74962700
H	0.86125600	2.67431100	-2.83690200
H	-0.01100800	1.23865000	-2.23272700
H	-0.52645600	2.00932400	-3.75692500

TS1^{OTf}

E (DMF) = -2631.422834

Pd	0.42587400	0.24540400	0.39837400
C	-1.51317700	0.32586200	-0.06658300
C	-2.07419600	1.54662700	-0.47512500
C	-2.37604200	-0.77530000	0.06262300
C	-3.43800200	1.67267900	-0.72651200
H	-1.44263800	2.42308100	-0.60826700
C	-3.74020800	-0.66830100	-0.17564500
H	-1.99365200	-1.75341600	0.35405500
C	-4.25647700	0.56216100	-0.56393200
H	-3.88205500	2.61701500	-1.04399600
H	-4.41223500	-1.51836600	-0.06035800
P	0.65391300	-1.46399000	-1.06190000
C	-0.89524300	0.66005200	2.97570700
C	0.19585000	1.19131200	2.83715100
H	1.12058900	1.73649900	2.87176800
C	-2.18091500	0.06228500	3.11527000
C	-3.33489600	0.82311900	2.86562000
C	-2.30418200	-1.29413600	3.46043900
C	-4.58791300	0.22737300	2.93923900
H	-3.23438400	1.87412400	2.59059500
C	-3.56208700	-1.88134700	3.53082000
H	-1.40615500	-1.87797900	3.67354500
C	-4.70369400	-1.12439800	3.26400400
H	-5.48355200	0.81559400	2.72913700
H	-3.65558200	-2.93663200	3.79620400
H	-5.69079000	-1.58954600	3.30870900
C	2.22665700	-1.35181800	-1.99080300
C	3.43555500	-1.62221800	-1.33137700
C	2.25484900	-0.95779900	-3.33365400
C	4.64735900	-1.48462400	-2.00143600
H	3.42625500	-1.94978500	-0.29116000
C	3.47234300	-0.81559300	-3.99859200
H	1.32314900	-0.77359100	-3.87152900
C	4.66962800	-1.07255300	-3.33465500

H	5.58163600	-1.70883600	-1.48144800
H	3.48077600	-0.51386000	-5.04840200
H	5.62158700	-0.96694200	-3.85985300
C	-0.62903200	-1.62725100	-2.34805800
C	-1.21947700	-2.85791800	-2.64773000
C	-1.05907900	-0.47328500	-3.01815000
C	-2.23084600	-2.93103500	-3.60527700
H	-0.90672600	-3.76248500	-2.12314700
C	-2.06157500	-0.55235100	-3.97763400
H	-0.63196100	0.49844100	-2.76050400
C	-2.65345200	-1.78250300	-4.26924700
H	-2.69539800	-3.89442400	-3.82635400
H	-2.39769600	0.35311000	-4.48733100
H	-3.45275600	-1.84203300	-5.01121800
C	0.73322200	-3.09839700	-0.25644500
C	1.39187400	-4.17338800	-0.86886800
C	0.07708000	-3.29819900	0.96326000
C	1.39000900	-5.42821700	-0.26376100
H	1.90921200	-4.02904600	-1.82027400
C	0.07115500	-4.55548200	1.56178600
H	-0.41710000	-2.45450200	1.45027300
C	0.72865500	-5.62157500	0.94912200
H	1.90752700	-6.26136200	-0.74442900
H	-0.44563200	-4.70278200	2.51293700
H	0.72847400	-6.60746200	1.41946700
N	-5.69733600	0.69801200	-0.77958900
O	-6.39688700	-0.24458000	-0.47762600
O	-6.09867900	1.74727400	-1.23367100
C	3.20465600	0.36669400	1.96327000
N	4.21828900	1.27853200	2.09677600
N	2.93957200	-0.41790500	3.04454200
N	2.51508200	0.25572100	0.85862700
H	2.98477900	0.72123000	0.08796800
C	2.20602000	-1.64753800	2.88560000
H	2.34528600	-2.04136800	1.87370400
H	2.57373400	-2.38906500	3.61107600
H	1.12445700	-1.50187600	3.04849000
C	3.07049500	0.06125100	4.40378700
H	3.39348800	1.10878800	4.41031500
H	2.09442900	0.00052200	4.91405000
H	3.79593600	-0.53461800	4.98219100
C	4.26220800	2.42509200	1.21808200
H	3.23996900	2.72282800	0.94145000
H	4.74369800	3.26384700	1.74338700
H	4.84671200	2.23001100	0.29789200
C	5.46177200	0.94381700	2.75975400
H	5.69968500	1.65513300	3.56760700
H	5.40685800	-0.06519600	3.18401200
H	6.29333500	0.96221300	2.03410300
C	0.70849400	3.65825400	-0.56080900
N	1.42692300	3.52507900	-1.71955300
N	-0.04861400	4.80713100	-0.46411200
H	0.04507500	2.94830100	1.07370000
N	0.76510400	2.75706900	0.37981400
C	-0.81036300	5.30352500	-1.59424100
H	-1.89242100	5.18815800	-1.40528800

H	-0.61130500	6.37077800	-1.78552800
H	-0.56729500	4.73296000	-2.49754000
C	-0.54174200	5.21179900	0.82928300
H	-1.45836700	4.66761400	1.13191800
H	0.22844300	5.05789400	1.59772000
H	-0.78378600	6.28402700	0.80382200
C	2.03794300	4.66484000	-2.36981200
H	1.72079300	4.75826700	-3.42187400
H	1.78207400	5.58933400	-1.84043900
H	3.13689100	4.55909900	-2.35706200
C	1.97359400	2.24770900	-2.08945300
H	3.00910100	2.10592700	-1.72462200
H	1.35263100	1.44267500	-1.67758400
H	1.99646200	2.15655400	-3.18584200

S

E (DMF) = -2269.267732

Pd	-0.36126900	-0.35746500	-0.67014700
C	1.55221200	-0.95006500	-0.64423400
C	2.13953700	-1.29703400	-1.87055500
C	2.36130300	-0.96937700	0.50299500
C	3.49385200	-1.60529900	-1.96379700
H	1.54465100	-1.31460600	-2.78650900
C	3.71356000	-1.28772300	0.43190700
H	1.95697100	-0.69384000	1.47965500
C	4.26484900	-1.58548600	-0.80809000
H	3.96656500	-1.85529500	-2.91421700
H	4.35474800	-1.28631600	1.31365200
P	0.29899100	1.62505400	0.31883100
C	-0.91303600	-2.57231100	-1.15323600
C	-0.98820300	-1.87962000	-2.17079400
H	-1.08202000	-1.48227600	-3.16811700
C	-0.96390900	-3.57707400	-0.13344900
C	-0.11959100	-3.55263000	0.98760500
C	-1.89576800	-4.62074000	-0.27956700
C	-0.21784600	-4.55048900	1.95111900
H	0.62234600	-2.75932000	1.07897100
C	-1.98468400	-5.61277000	0.69057100
H	-2.53777400	-4.64921500	-1.16203300
C	-1.15130000	-5.57715800	1.80920100
H	0.44738200	-4.53123800	2.81696900
H	-2.70553300	-6.42427500	0.56974100
H	-1.22343100	-6.35913800	2.56824100
C	-0.66216100	3.04378900	-0.31441900
C	-1.97406300	3.24417400	0.14292200
C	-0.13648200	3.89902200	-1.28968700
C	-2.74494800	4.28164600	-0.37429400
H	-2.38839000	2.59382700	0.91594800
C	-0.91572000	4.93285600	-1.80744300
H	0.89095400	3.77371600	-1.63643000
C	-2.21943400	5.12450400	-1.35478900
H	-3.75956000	4.43991500	-0.00135700
H	-0.49339400	5.59929100	-2.56261300
H	-2.82397600	5.94074600	-1.75657000

C	2.05043700	2.07801900	0.12774800
C	2.83322900	2.47256000	1.21695900
C	2.63871400	1.94846100	-1.13839500
C	4.19136700	2.73164300	1.03891700
H	2.39431300	2.55697600	2.21259400
C	3.99260600	2.21349200	-1.31084100
H	2.04446800	1.60069900	-1.98675900
C	4.77253500	2.60001000	-0.21994900
H	4.80053400	3.02862300	1.89528400
H	4.44654700	2.09836000	-2.29737900
H	5.83991000	2.78994200	-0.35208500
C	-0.03853700	1.60610900	2.10649800
C	-0.13174500	2.80601100	2.82637600
C	-0.16660400	0.38576900	2.78029900
C	-0.34480000	2.77770200	4.20195700
H	-0.04170900	3.76448600	2.30929000
C	-0.37826100	0.36215600	4.15715400
H	-0.11238200	-0.55103100	2.21983400
C	-0.46611700	1.55764200	4.86830200
H	-0.41658500	3.71508300	4.75787700
H	-0.47753400	-0.59426700	4.67511700
H	-0.63313100	1.54019000	5.94760900
N	5.70164600	-1.87032000	-0.90081200
O	6.33973500	-1.84599500	0.12770100
O	6.15206100	-2.10189500	-2.00015000
C	-3.51654200	-0.17701700	-0.76637400
N	-4.54848800	0.13023600	-1.60729300
N	-3.75906200	-1.09625600	0.20429700
N	-2.33777000	0.38557600	-0.88434800
H	-2.37808800	1.24765900	-1.42157700
C	-3.03009800	-1.07409600	1.45031600
H	-2.53813000	-0.10362500	1.57467400
H	-3.73185200	-1.22437200	2.28656500
H	-2.26517000	-1.86647800	1.50093200
C	-4.65224500	-2.21666300	0.00958600
H	-4.94406100	-2.28822000	-1.04494400
H	-4.13100400	-3.14641400	0.28805200
H	-5.56343900	-2.14110100	0.62699400
C	-4.27925200	0.74459500	-2.88671200
H	-3.33500500	0.36555600	-3.29925900
H	-5.08613400	0.48773200	-3.58851200
H	-4.22215500	1.84776400	-2.82663400
C	-5.91126300	0.25779300	-1.12944000
H	-6.59590900	-0.43311400	-1.64766700
H	-5.95664600	0.05851800	-0.05308000
H	-6.27109200	1.28671800	-1.29745900

TS2^{OTf}

E (DMF) = -2631.43209

Pd	0.38372100	-0.38165100	-0.41412300
C	-0.17973800	1.50335700	-0.15352600
C	-0.50090800	2.03110700	1.10596100
C	-0.34753300	2.32082400	-1.28284200
C	-0.98020700	3.33168700	1.24198900

H	-0.36216100	1.42691700	2.00568400
C	-0.83484300	3.61820700	-1.16834500
H	-0.09441000	1.94190300	-2.27638000
C	-1.14493700	4.10716800	0.09765000
H	-1.22966800	3.76095000	2.21296000
H	-0.98078400	4.26068200	-2.03706200
P	2.50553000	0.32851600	0.05465200
C	-2.59472600	-0.26634200	-1.04269700
C	-1.68386800	-0.84813400	-0.43468800
H	-1.61328300	-1.62023700	0.57526200
C	-3.59154300	0.53018400	-1.65903100
C	-3.87270900	1.80189700	-1.11754800
C	-4.28609500	0.09879400	-2.80567000
C	-4.81811400	2.62191600	-1.71950500
H	-3.32260300	2.13250600	-0.23425700
C	-5.23947500	0.92113400	-3.39316500
H	-4.06452500	-0.88347800	-3.22832500
C	-5.50300200	2.18216400	-2.85411600
H	-5.01974000	3.61295000	-1.30712500
H	-5.77737100	0.58373000	-4.28166000
H	-6.24675700	2.82924800	-3.32480100
C	-2.94864500	-1.96803700	2.34579200
N	-3.11035400	-1.39745400	3.57482300
N	-4.07063600	-2.22160500	1.62057700
N	-1.77715900	-2.24335600	1.82255900
H	-1.00887700	-2.17866500	2.48462600
C	-4.05430900	-3.20492200	0.56108300
H	-3.19556700	-3.87281600	0.69564600
H	-4.98474700	-3.79408400	0.59484400
H	-3.97436600	-2.73251400	-0.43165000
C	-5.21529800	-1.33558900	1.63558000
H	-5.01594200	-0.46767800	2.27421100
H	-5.40410400	-0.96471900	0.61426100
H	-6.12775400	-1.84153100	1.99264800
C	-2.01430000	-0.68982400	4.19188300
H	-1.40006800	-0.19670500	3.42662400
H	-2.41508000	0.09092900	4.85486100
H	-1.36940400	-1.34950300	4.80321900
C	-4.20912300	-1.75114300	4.45038400
H	-4.83593700	-0.87920700	4.69950600
H	-4.83751900	-2.51435000	3.97761900
H	-3.81634400	-2.17079000	5.39166400
C	3.15146600	1.84387300	-0.72794000
C	2.63211000	3.09003500	-0.34362000
C	4.12737500	1.78592600	-1.72996700
C	3.08237100	4.25385700	-0.95854000
H	1.87852700	3.15541200	0.44326400
C	4.56795000	2.95580000	-2.34666600
H	4.55849000	0.82801800	-2.02613400
C	4.04586100	4.18958500	-1.96508800
H	2.67259100	5.21805500	-0.64974800
H	5.33132900	2.89948300	-3.12577200
H	4.39431200	5.10512000	-2.44833500
C	3.75484600	-0.95769500	-0.29469800
C	4.70912700	-1.34598000	0.65216100
C	3.74317300	-1.57657700	-1.55323600

C	5.64198500	-2.33446500	0.33950000
H	4.72629800	-0.87605600	1.63764800
C	4.68437500	-2.55272900	-1.86601700
H	2.98742700	-1.29195200	-2.28875700
C	5.63400700	-2.93535900	-0.91762700
H	6.38350000	-2.63171200	1.08442500
H	4.67420900	-3.02139600	-2.85271600
H	6.36983200	-3.70538500	-1.16043700
C	2.64517600	0.61392500	1.85039600
C	3.55166600	1.52908500	2.39613300
C	1.84578700	-0.15690900	2.70448400
C	3.64909900	1.67329100	3.77952700
H	4.18075100	2.13414900	1.73947800
C	1.95208100	-0.01734100	4.08527700
H	1.13153700	-0.86136000	2.26622800
C	2.85230900	0.90239700	4.62440300
H	4.35438700	2.39387000	4.19940300
H	1.32885300	-0.62404600	4.74668800
H	2.93207200	1.01965000	5.70747200
N	-1.67641400	5.46610800	0.22948400
O	-1.86324600	6.09382100	-0.78979100
O	-1.90134300	5.87175400	1.34899800
C	0.20550900	-3.34205800	-1.31257400
N	0.17097600	-4.63958000	-0.87922900
N	-0.50825500	-3.05454200	-2.43609400
N	0.88055700	-2.41604100	-0.68353800
H	1.59861300	-2.80312300	-0.07820200
C	-0.16280800	-1.93855200	-3.28361700
H	0.86442600	-1.61868100	-3.07579000
H	-0.23341800	-2.24716400	-4.33954300
H	-0.83241300	-1.07752000	-3.12233200
C	-1.78989800	-3.66253500	-2.70439800
H	-2.05864800	-4.35182200	-1.89603900
H	-2.56321500	-2.87699200	-2.75244400
H	-1.79515000	-4.21296500	-3.66037600
C	0.48651600	-4.93943300	0.49695700
H	0.08676500	-4.15096500	1.14873100
H	0.00479400	-5.88804300	0.77645700
H	1.57277800	-5.05169100	0.67695100
C	0.22786400	-5.75415900	-1.80176900
H	-0.62427300	-6.44087900	-1.66780700
H	0.22539200	-5.38867800	-2.83494300
H	1.15739800	-6.32856000	-1.64722700

T

E (DMF) = -2631.456576

Pd	-0.67601500	-0.45822400	-0.17288600
C	0.08383300	1.37868900	-0.25750300
C	-0.07435200	2.34440600	0.75445300
C	0.79653400	1.76828000	-1.41348900
C	0.45356300	3.62825600	0.63719000
H	-0.64183300	2.10453900	1.65741900
C	1.33884600	3.04305100	-1.54711100
H	0.93731800	1.04866600	-2.22317800

C	1.17438800	3.95481600	-0.50635900
H	0.32816300	4.37935900	1.41840100
H	1.89899300	3.34365400	-2.43388200
N	1.82204800	5.25954300	-0.59523100
O	1.44260900	6.13025900	0.15347300
O	2.72023800	5.37765900	-1.40676800
P	-2.83818300	0.40690800	0.01429200
C	-3.02993400	2.15012300	-0.48606600
C	-2.47621200	2.54157300	-1.71363500
C	-3.61108400	3.11411000	0.34276100
C	-2.51576800	3.87421200	-2.10975300
H	-1.98228900	1.80161700	-2.34870800
C	-3.63907300	4.45092300	-0.05328600
H	-4.02828100	2.82891000	1.31030300
C	-3.09300200	4.83306400	-1.27626000
H	-2.07800900	4.16955300	-3.06586400
H	-4.08690200	5.19939100	0.60421600
H	-3.10961300	5.88235100	-1.57917400
C	-3.42348100	0.32274900	1.73913300
C	-2.48651000	0.15698800	2.76563500
C	-4.78365600	0.43526300	2.05838400
C	-2.90084600	0.11513700	4.09599900
H	-1.42876500	0.04740100	2.50780300
C	-5.19422600	0.39187900	3.38806400
H	-5.52368100	0.55035500	1.26231100
C	-4.25403300	0.23402100	4.40744400
H	-2.16495800	-0.01632500	4.89256200
H	-6.25552500	0.47975500	3.63118700
H	-4.58050000	0.19847800	5.44932200
C	-4.11834900	-0.51768200	-0.91166800
C	-4.53390300	-1.76591300	-0.42132200
C	-4.63566000	-0.05380100	-2.12615700
C	-5.44463100	-2.53540400	-1.14130600
H	-4.15073600	-2.13054900	0.53457300
C	-5.54565600	-0.82943900	-2.84330000
H	-4.34173600	0.92499400	-2.51021900
C	-5.94890100	-2.07119600	-2.35656900
H	-5.77049000	-3.49997100	-0.74473300
H	-5.94831300	-0.45330600	-3.78645000
H	-6.66629400	-2.67356800	-2.91842000
C	1.19284200	-1.12578500	-0.27884500
C	2.33943400	-1.54876800	-0.43429800
C	3.64972000	-2.05073500	-0.69976200
C	4.41789500	-2.69148800	0.29340300
C	4.20773300	-1.93356500	-1.98940300
C	5.68528100	-3.19311000	0.00817800
H	3.99840800	-2.81077100	1.29408100
C	5.47175100	-2.44260900	-2.27087600
H	3.61996500	-1.44992100	-2.77244800
C	6.21991200	-3.07253900	-1.27513300
H	6.25594500	-3.69796800	0.79188700
H	5.87626800	-2.35316700	-3.28221500
H	7.20890300	-3.47721500	-1.50071100
C	-0.91838300	-3.56812100	-0.09510700
N	-1.07815000	-4.61953900	-0.95346500
N	-0.16840200	-3.79074600	1.01807300

N	-1.47042200	-2.40354600	-0.31854000
H	-2.21086600	-2.46293900	-1.01266400
C	-0.31451100	-2.94585900	2.17678800
H	-1.32080600	-2.51099400	2.19618800
H	-0.16788200	-3.55194000	3.08519100
H	0.41845100	-2.12006600	2.17410800
C	1.04112400	-4.58016500	0.96949900
H	1.19652600	-4.97660100	-0.03994400
H	1.90623900	-3.93984300	1.20649500
H	1.01441800	-5.41808000	1.68636700
C	-1.47381700	-4.37419600	-2.32018900
H	-1.03819800	-3.42992900	-2.67378500
H	-1.09401300	-5.18648000	-2.95744200
H	-2.57230200	-4.33056900	-2.44690700
C	-1.23146000	-5.97931000	-0.48325300
H	-0.45895400	-6.64818100	-0.89785400
H	-1.17140600	-6.00762500	0.61073200
H	-2.21864700	-6.37278900	-0.78068300
C	4.34289200	1.08392300	0.88893700
N	5.20704000	1.38199900	-0.09279600
N	4.72290200	0.36275800	1.95931500
N	3.09737100	1.54364600	0.81967600
H	2.63090000	1.65764600	-0.07973500
C	3.73300800	-0.31904700	2.76996400
H	2.88750300	-0.64135300	2.14460800
H	4.19351700	-1.21643300	3.20562000
H	3.37194300	0.31192000	3.60207200
C	6.06799300	0.41590000	2.49850800
H	6.59965800	-0.53972400	2.36590700
H	6.64125300	1.21656700	2.01854900
H	6.01352700	0.63895200	3.57533400
C	4.92412500	2.45458500	-1.03007300
H	4.30528100	3.23415400	-0.56977500
H	5.87397000	2.91033900	-1.34223500
H	4.40899500	2.07835300	-1.93003200
C	6.29099900	0.49004500	-0.46578200
H	7.27679100	0.92501600	-0.23788100
H	6.18308900	-0.47815400	0.03508200
H	6.23258700	0.30104800	-1.54693600
H	2.46573600	1.43440200	1.60007500

T-TMGH$^+$

E (DMF) = -2268.821321

Pd	0.36345300	-0.01117300	-0.03430900
C	-0.51161100	1.77144300	0.09159100
C	-1.39863900	2.11094700	1.12848800
C	-0.35390100	2.69627000	-0.95755500
C	-2.16775300	3.26748600	1.08301900
H	-1.53994800	1.43581000	1.97589200
C	-1.11816100	3.85530100	-1.02575400
H	0.37071800	2.49335400	-1.74882700
C	-2.03816300	4.11564300	-0.01295500
H	-2.89007300	3.51218400	1.86183700
H	-1.02842000	4.55883200	-1.85402400

N	-2.90628800	5.28209200	-0.11696700
O	-3.70884500	5.47295000	0.77443300
O	-2.78903400	5.99032600	-1.09656600
P	-1.71408200	-1.09185700	-0.09488000
C	-3.15734400	-0.01613300	-0.40018300
C	-3.08868300	0.87620500	-1.47972000
C	-4.24999000	0.04285700	0.46935500
C	-4.09356800	1.81656400	-1.67941000
H	-2.21858700	0.86445300	-2.14043400
C	-5.25287300	0.99077000	0.26856400
H	-4.30805100	-0.63449100	1.32360500
C	-5.17395900	1.88186800	-0.79877900
H	-4.01660600	2.52373100	-2.50823300
H	-6.09468300	1.04152200	0.96300400
H	-5.94765500	2.64021900	-0.93827800
C	-2.10498700	-1.93080300	1.48218000
C	-1.52292700	-1.44494100	2.65846400
C	-2.99261800	-3.01220400	1.55031800
C	-1.82726400	-2.02690100	3.88770900
H	-0.81839900	-0.61084600	2.59942400
C	-3.29178900	-3.59521900	2.77941300
H	-3.44800900	-3.40044800	0.63596500
C	-2.71115300	-3.10300200	3.94886100
H	-1.36751800	-1.64017400	4.80015700
H	-3.98362900	-4.43964500	2.82490900
H	-2.94728100	-3.56299100	4.91141200
C	-1.86372200	-2.44712900	-1.31934500
C	-1.06903600	-3.59083200	-1.14409300
C	-2.70584300	-2.36580000	-2.43294700
C	-1.11667100	-4.62844700	-2.07063700
H	-0.41297400	-3.66406100	-0.27395200
C	-2.74543700	-3.40604400	-3.36153100
H	-3.34303600	-1.49016000	-2.57244400
C	-1.95185300	-4.53699100	-3.18500800
H	-0.49909400	-5.51732800	-1.91979300
H	-3.40913000	-3.33098800	-4.22616500
H	-1.98783400	-5.35166600	-3.91211700
C	2.09771600	0.92300900	0.01671600
C	3.23729800	1.38263200	-0.01817800
C	4.57368700	1.88046000	-0.03638600
C	5.57500800	1.22801500	-0.78316800
C	4.93669300	3.02232200	0.70329100
C	6.88471500	1.69677200	-0.78578800
H	5.30121300	0.34654100	-1.36718800
C	6.24836900	3.48540700	0.69825800
H	4.16733600	3.53837500	1.28098300
C	7.22943600	2.82676100	-0.04382900
H	7.64502400	1.17717800	-1.37484100
H	6.50869600	4.37380500	1.27929900
H	8.25811200	3.19474100	-0.04642300
C	2.67337200	-2.01867400	0.02121100
N	3.67013300	-2.33700200	-0.86038100
N	3.02023500	-1.90494000	1.33132100
N	1.43316800	-1.84043400	-0.36045100
H	1.27394600	-2.19611000	-1.29923500
C	1.98355400	-1.88553800	2.33337300

H	1.14050400	-2.51018500	2.01632400
H	2.39069700	-2.27439900	3.27964700
H	1.60719400	-0.86050300	2.50103500
C	4.26382700	-1.28213200	1.73498100
H	4.88345900	-1.05366400	0.86219200
H	4.05100600	-0.32271100	2.23384200
H	4.83009400	-1.92786200	2.42717900
C	3.52303400	-1.98840700	-2.25188200
H	2.94456700	-1.05814800	-2.33935700
H	4.51878000	-1.81241600	-2.68733400
H	3.03372300	-2.78272000	-2.84830900
C	4.73688400	-3.25093200	-0.53007500
H	5.72973400	-2.77477000	-0.60711500
H	4.60608600	-3.62217700	0.49325300
H	4.72085400	-4.11830000	-1.21347400

TS3^{OTf}

E (DMF) = -3304.216142

Pd	-0.16328100	0.36118400	-0.44603300
C	-1.43667500	1.86664600	-0.17517600
C	-2.14226100	2.45345500	-1.23793500
C	-1.68508700	2.32362500	1.12891500
C	-3.11880200	3.41615200	-1.00386200
H	-1.94463900	2.13939200	-2.26392600
C	-2.66098400	3.28169800	1.37946100
H	-1.13136000	1.90539000	1.97095000
C	-3.38115000	3.80463300	0.30848900
H	-3.69168600	3.86477800	-1.81584300
H	-2.88652100	3.62114600	2.39059500
P	-2.01486500	-1.08835900	-0.59988800
C	1.88015000	2.71962200	-1.10806100
C	1.06723200	1.85473800	-0.79095200
P	1.46364300	-0.49892000	1.54860800
C	2.85830100	3.70498100	-1.43432900
C	4.22410000	3.47385500	-1.17852600
C	2.48542700	4.93440200	-2.01002800
C	5.17813000	4.43677100	-1.49118800
H	4.52245000	2.53263800	-0.71386100
C	3.44467200	5.89282600	-2.31972000
H	1.42795700	5.12210700	-2.20669100
C	4.79480600	5.64981400	-2.06355700
H	6.23268000	4.23938800	-1.28152400
H	3.13558900	6.84174100	-2.76536500
H	5.54557000	6.40525000	-2.30761400
C	-3.38152000	-0.97814200	0.61984600
C	-4.13249100	0.20346200	0.70954700
C	-3.64340600	-2.01962300	1.51933700
C	-5.11637000	0.34046600	1.68468900
H	-3.95405600	1.02059500	0.00910000
C	-4.63172500	-1.87871200	2.49297600
H	-3.07053800	-2.94747500	1.46380800
C	-5.36771600	-0.69831500	2.58074400
H	-5.68350700	1.27230100	1.74535600
H	-4.82559800	-2.70071300	3.18626500

H	-6.13996000	-0.58778500	3.34576000
C	-1.67132600	-2.88671300	-0.62393600
C	-2.51998600	-3.80490300	-1.25558800
C	-0.53707500	-3.34921300	0.04531200
C	-2.23183200	-5.16652400	-1.20704900
H	-3.40235500	-3.45232500	-1.79462200
C	-0.25455300	-4.71327500	0.10569500
H	0.13698700	-2.63113200	0.51084900
C	-1.10205700	-5.62317500	-0.52383000
H	-2.89372900	-5.87818400	-1.70635300
H	0.63419700	-5.05226600	0.64351000
H	-0.88309900	-6.69315800	-0.48643900
C	-2.84363800	-0.78462300	-2.20338300
C	-4.22561200	-0.90846800	-2.38379600
C	-2.03311400	-0.42036000	-3.28716000
C	-4.79067000	-0.67192100	-3.63643300
H	-4.86670700	-1.17778900	-1.54132700
C	-2.60329100	-0.19184500	-4.53710800
H	-0.95335400	-0.31525300	-3.13107000
C	-3.98178400	-0.31434900	-4.71365600
H	-5.87150900	-0.76271500	-3.76816400
H	-1.96581900	0.09534600	-5.37687900
H	-4.42831500	-0.12336900	-5.69251100
C	0.49334700	-0.18844900	3.07695300
C	-0.87173000	-0.49045100	3.06081100
C	1.06345100	0.31381300	4.25432000
C	-1.66135400	-0.29470000	4.19140500
H	-1.32765700	-0.85998400	2.14270900
C	0.27373200	0.51546800	5.38447700
H	2.12822900	0.55496100	4.28356200
C	-1.08862400	0.21409500	5.35567900
H	-2.72792200	-0.52562200	4.14508900
H	0.72663700	0.91538300	6.29501000
H	-1.70512300	0.38320400	6.24187400
C	2.91427900	0.59033900	1.82429000
C	4.22899200	0.12545300	1.93292200
C	2.67106700	1.97032200	1.90820300
C	5.28158600	1.02312800	2.11912900
H	4.43829300	-0.94490000	1.88573000
C	3.72085900	2.86023300	2.11014700
H	1.65238700	2.35056600	1.81186400
C	5.03069700	2.39010500	2.21170800
H	6.30327000	0.64471300	2.20502200
H	3.51479300	3.93108100	2.16725500
H	5.85473000	3.09250700	2.35776800
C	2.15469600	-2.17199600	1.88919800
C	2.94321800	-2.77683100	0.89777700
C	1.86558600	-2.89443500	3.05339000
C	3.46197800	-4.05547800	1.08802500
H	3.15239300	-2.24448600	-0.03432000
C	2.36746400	-4.18338700	3.23024900
H	1.24227800	-2.44577700	3.82941400
C	3.17428200	-4.76519000	2.25424100
H	4.08871300	-4.50719800	0.31528300
H	2.13068500	-4.73294300	4.14461100
H	3.57487000	-5.77137600	2.39877400

N	-4.44022900	4.77619900	0.56700400
O	-4.71009800	5.02160300	1.72514400
O	-4.99597100	5.27512600	-0.38922900
C	2.11510800	-1.63602500	-2.51220600
N	3.48133900	-1.41255600	-2.41269200
N	1.75628300	-2.91709300	-2.85014900
N	1.21926400	-0.72191200	-2.31109700
H	1.63915100	0.20760500	-2.32724400
C	0.46366300	-3.18036500	-3.42840600
H	0.02784500	-2.24312400	-3.78887900
H	0.57373500	-3.88100100	-4.27412600
H	-0.23534800	-3.62588500	-2.70337200
C	2.48977700	-4.08258300	-2.43072800
H	3.39234000	-3.78936100	-1.88450600
H	1.86948900	-4.70310900	-1.76014500
H	2.78839600	-4.70820900	-3.29128800
C	3.93291600	-0.19744500	-1.77666800
H	3.27969600	0.07322700	-0.93752500
H	4.95226600	-0.34587300	-1.38856500
H	3.95378600	0.66428000	-2.47145300
C	4.38456900	-1.92038000	-3.42255200
H	5.28046900	-2.37795100	-2.96997500
H	3.88321600	-2.67048000	-4.04437200
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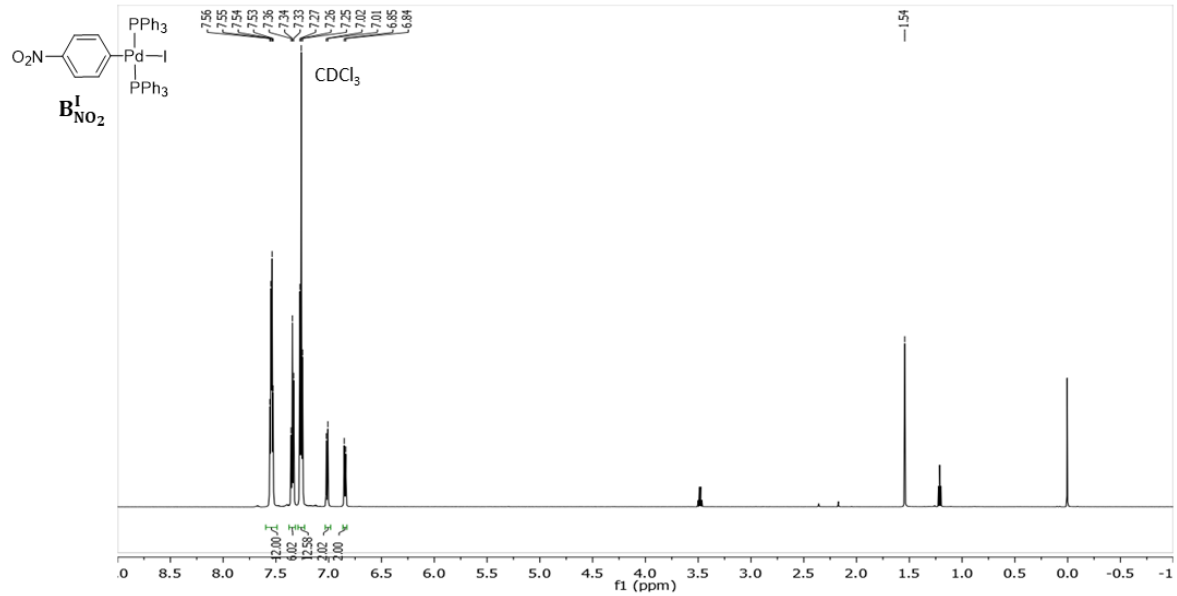
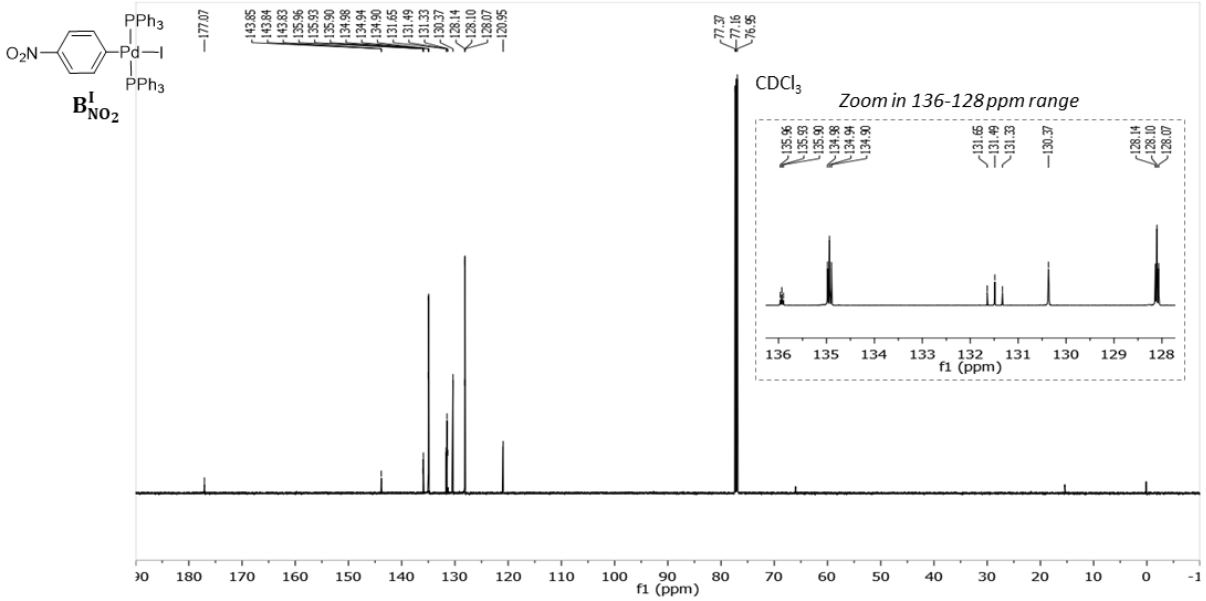
21.NMR spectra

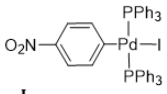
^{1}H-NMR (600 MHz-$CDCl_3$)



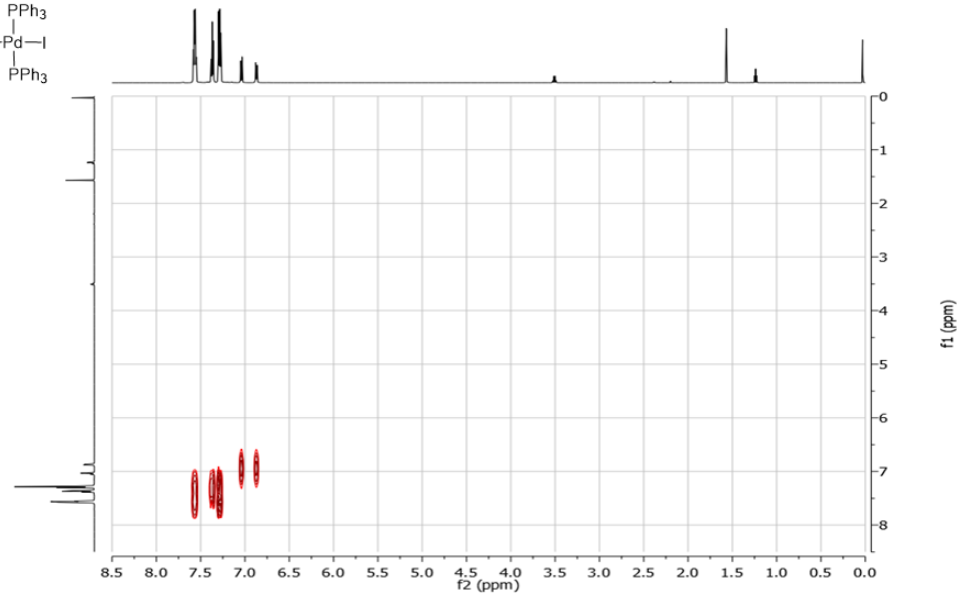
^{13}C-NMR (151.2 MHz-$CDCl_3$)



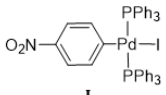
^{1}H-^{1}H gs-COSY



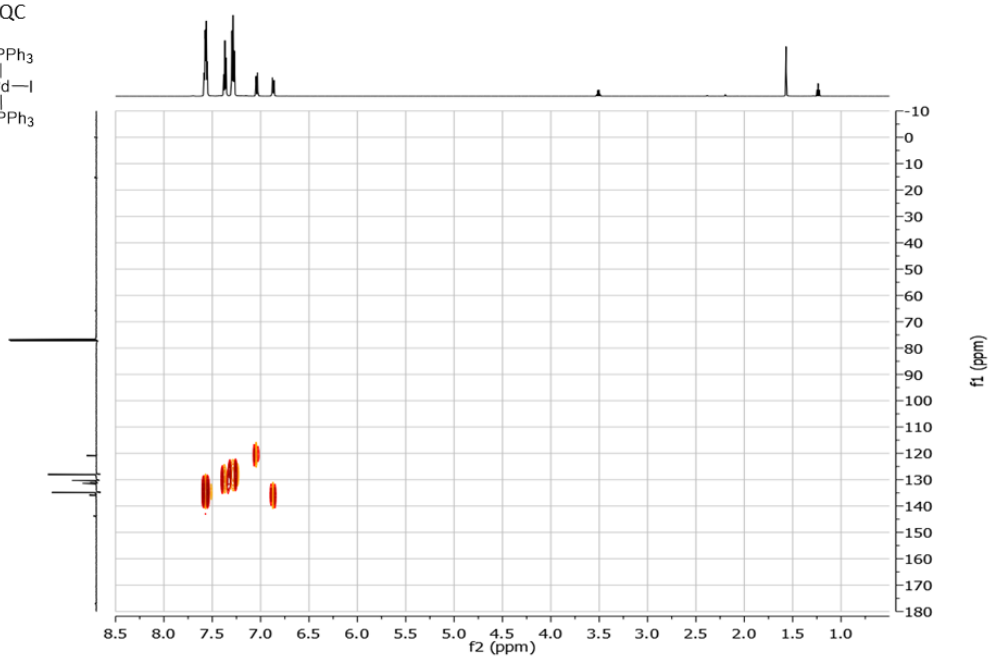
$\mathbf{B^{I}_{NO_2}}$



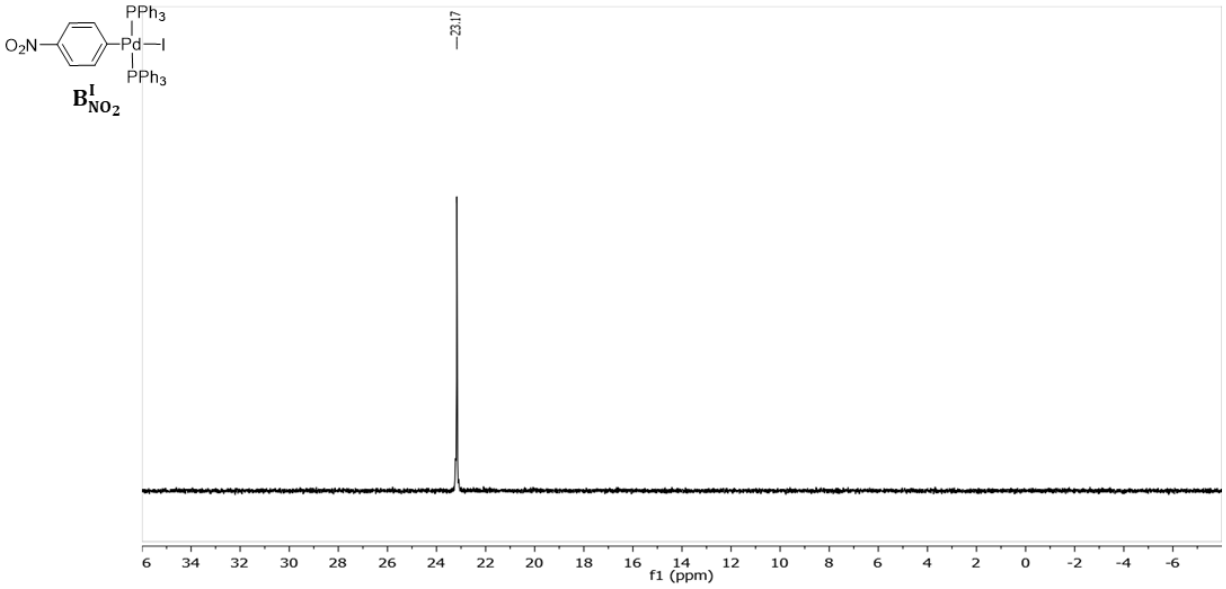
^{1}H-^{13}C gs-HSQC



$\mathbf{B^{I}_{NO_2}}$

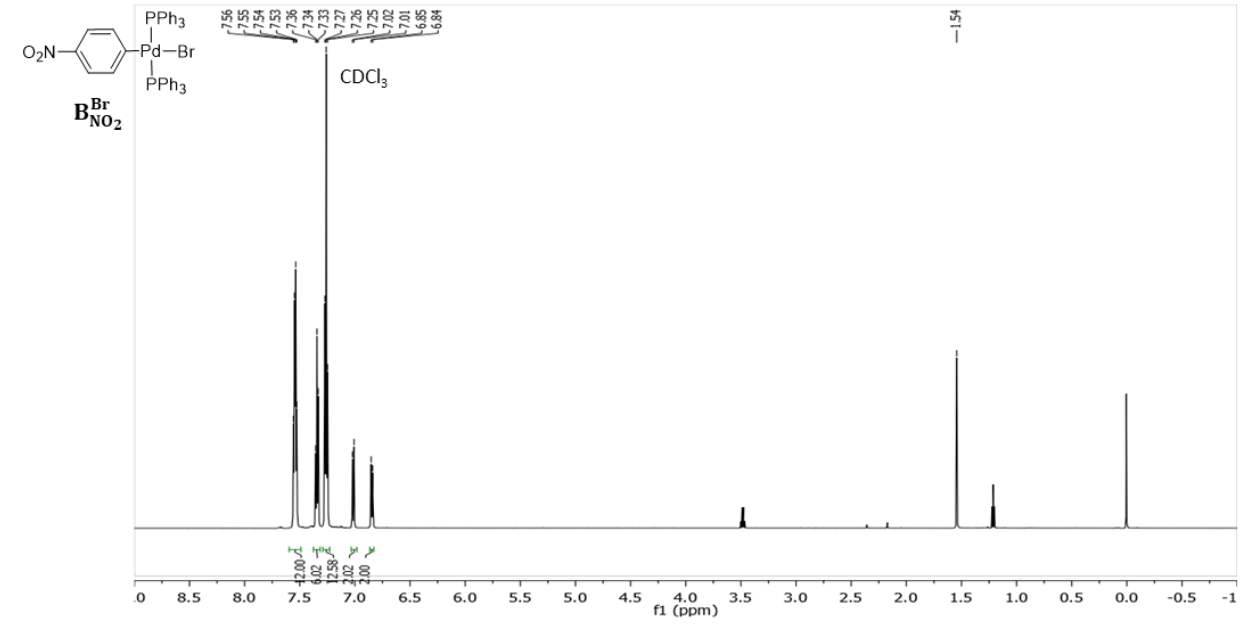


^{31}P-NMR (242.4 MHz-$CDCl_3$)



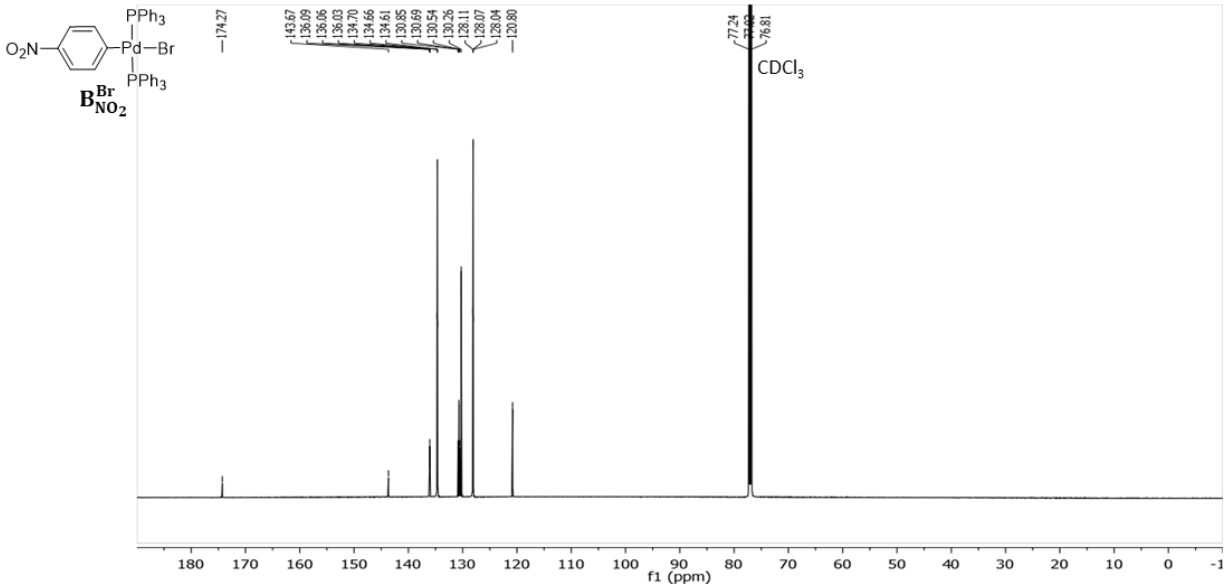
$\mathbf{B^{I}_{NO_2}}$

^{1}H-NMR (600 MHz-$CDCl_3$)

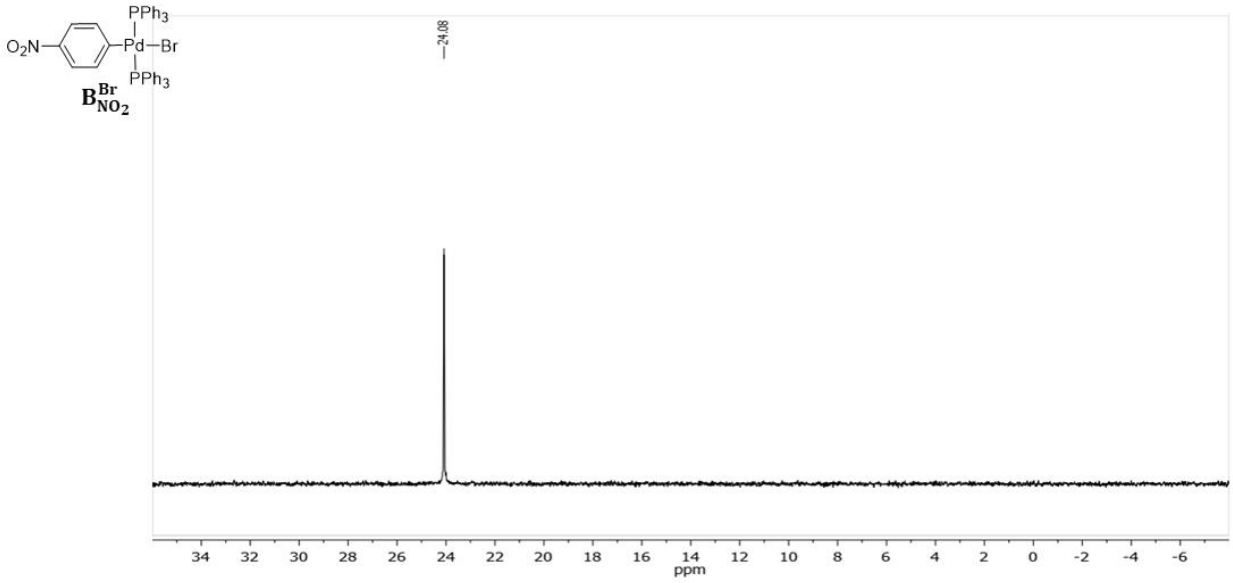


$\mathbf{B^{Br}_{NO_2}}$

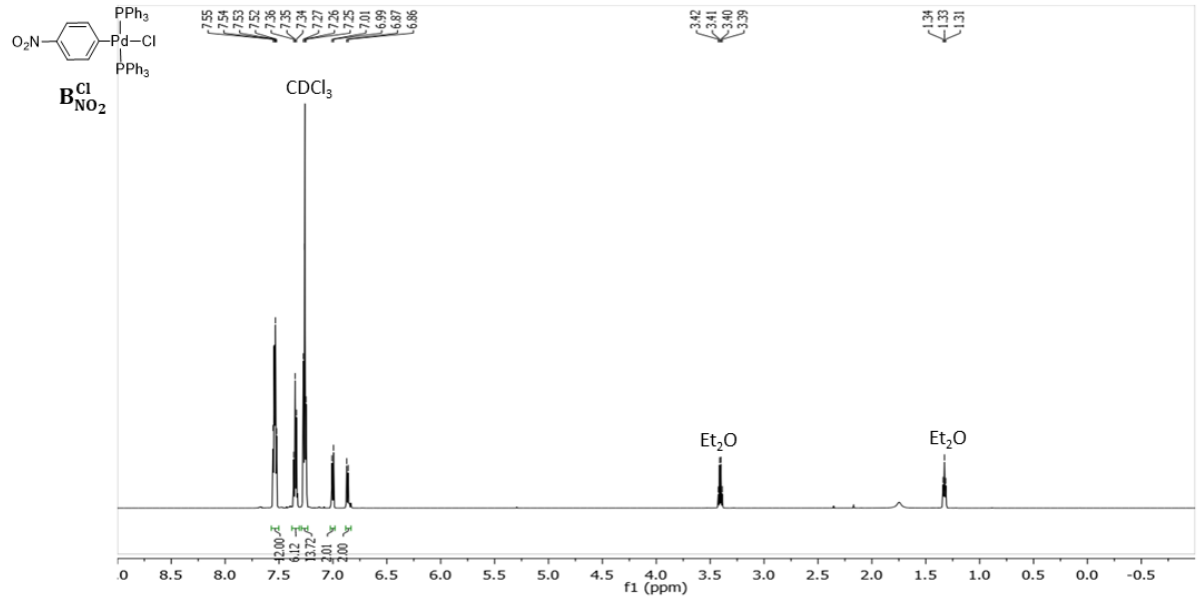
^{13}C-NMR (151.2 MHz-$CDCl_3$)



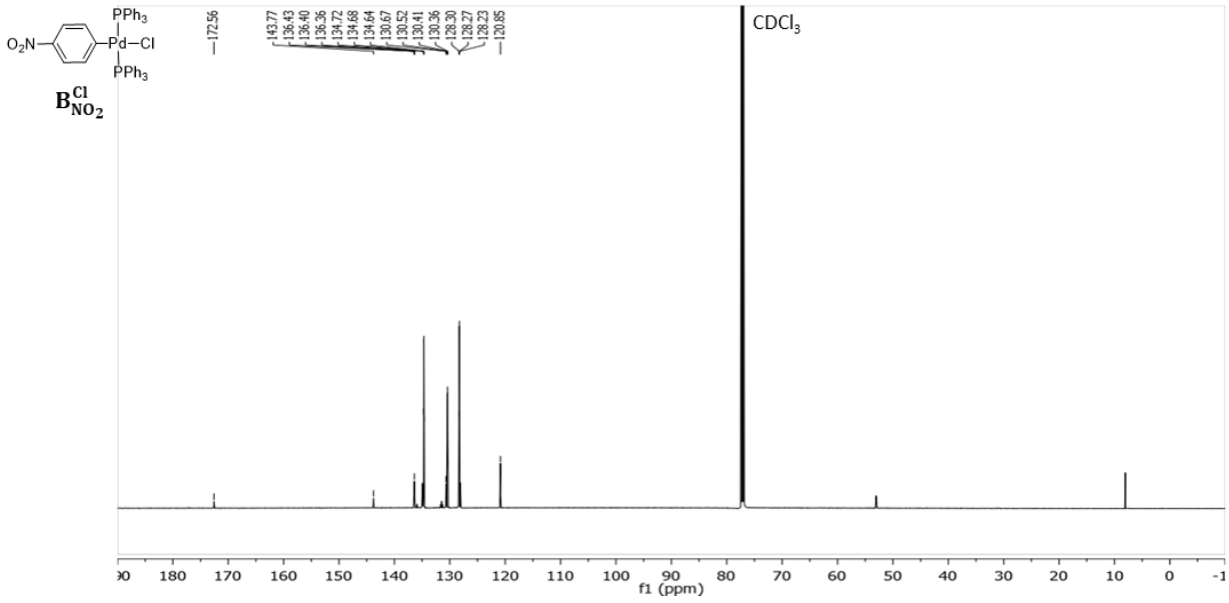
^{31}P-NMR (242.4 MHz-$CDCl_3$)



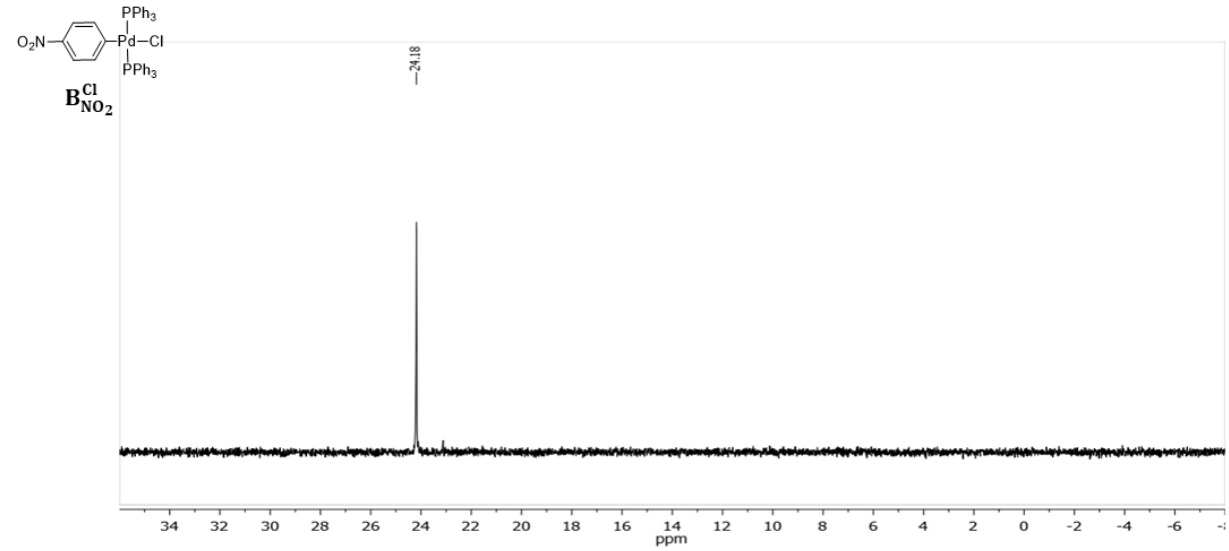
^{1}H-NMR (600 MHz-$CDCl_3$)



^{13}C-NMR (151.2 MHz-$CDCl_3$)

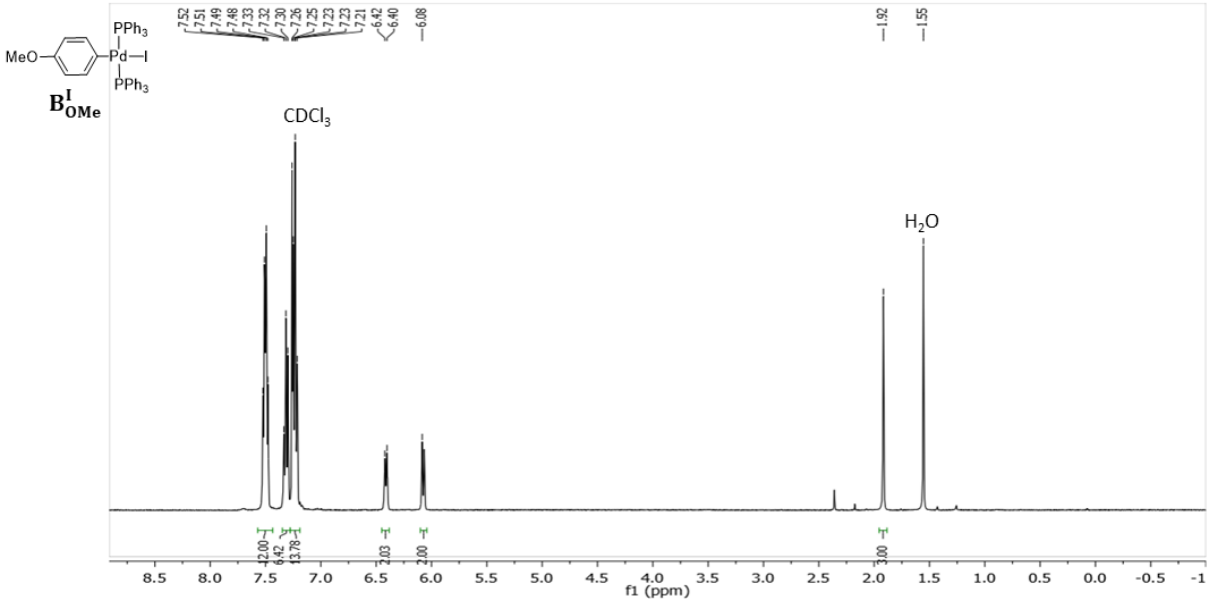


^{31}P-NMR (242.4 MHz-$CDCl_3$)



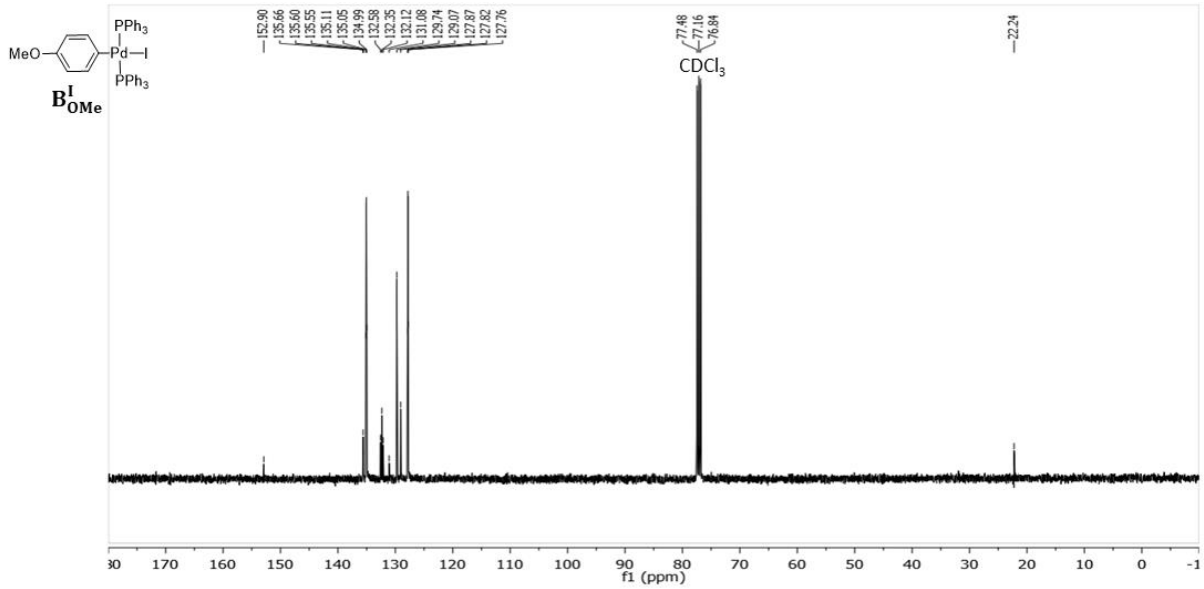
$\mathbf{B^{Cl}_{NO_2}}$

^{1}H-NMR (400 MHz-$CDCl_3$)

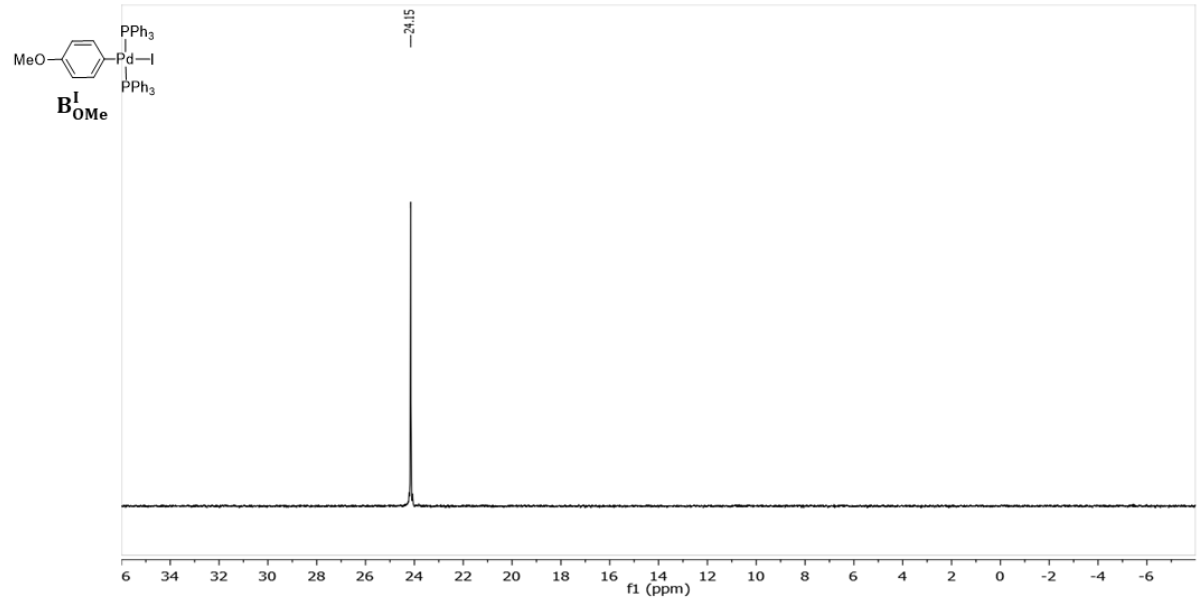


$\mathbf{B^{I}_{OMe}}$

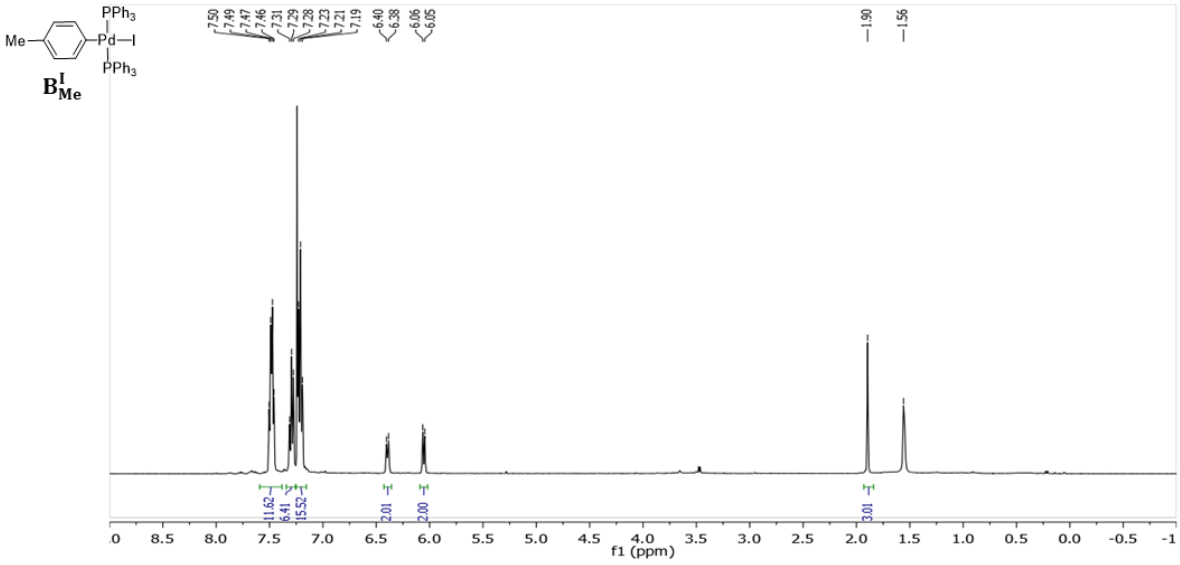
^{13}C-NMR (100.8 MHz-$CDCl_3$)



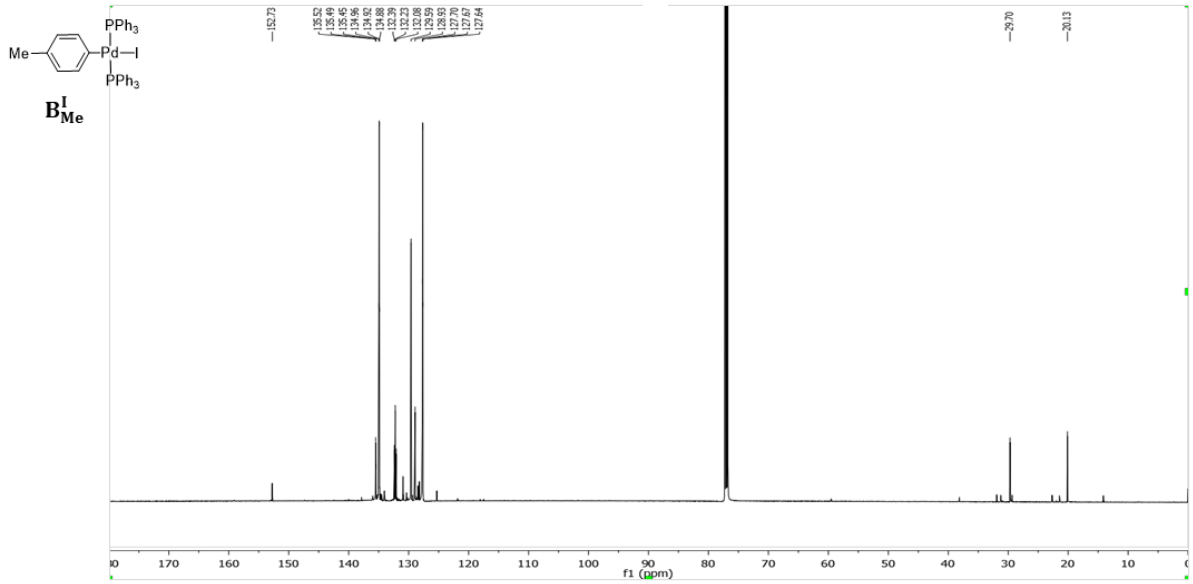
^{31}P-NMR (161.6 MHz-$CDCl_3$)



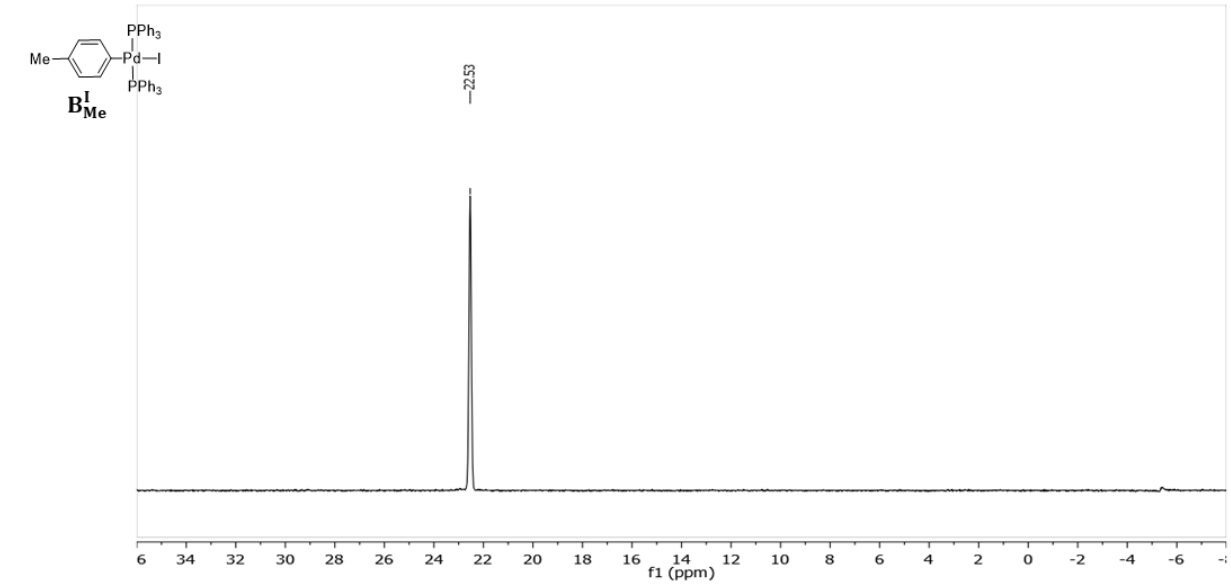
^{1}H-NMR (400 MHz-$CDCl_3$)



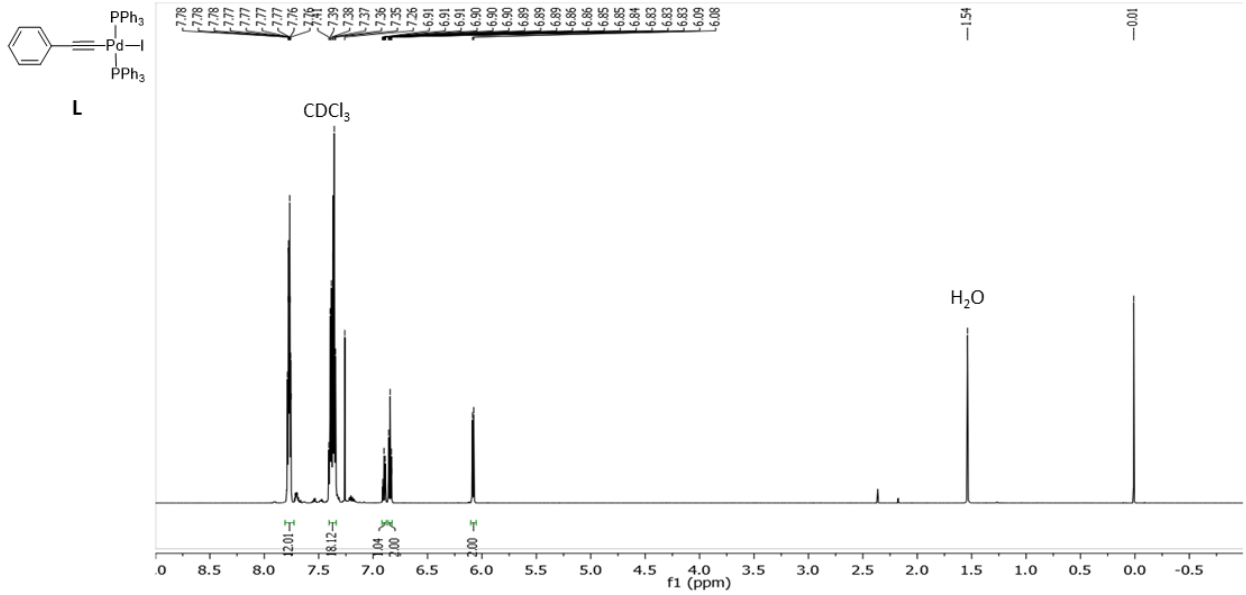
^{13}C-NMR (100.8 MHz-$CDCl_3$)



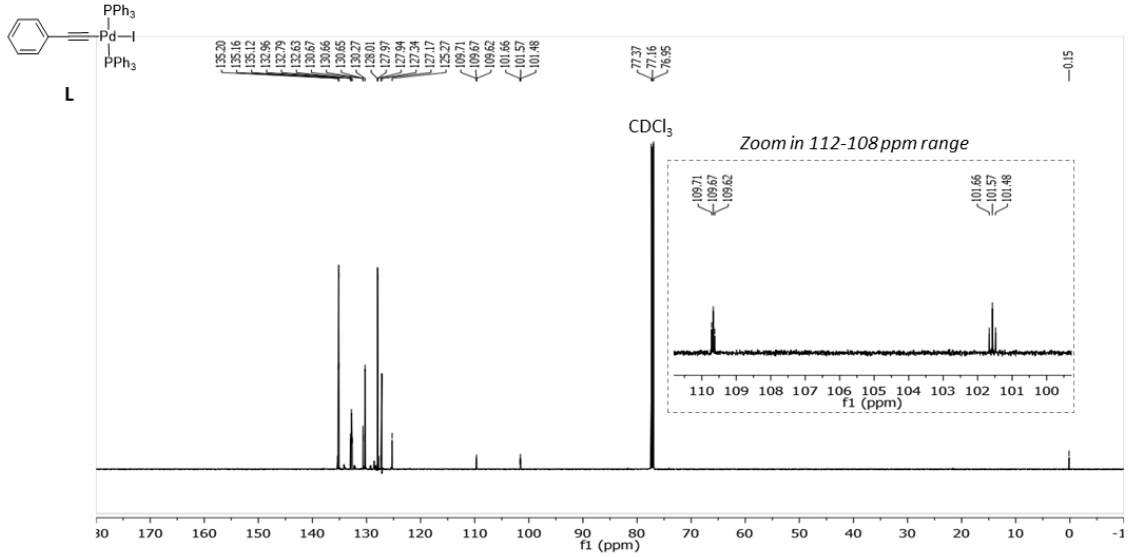
^{31}P-NMR (161.6 MHz-$CDCl_3$)



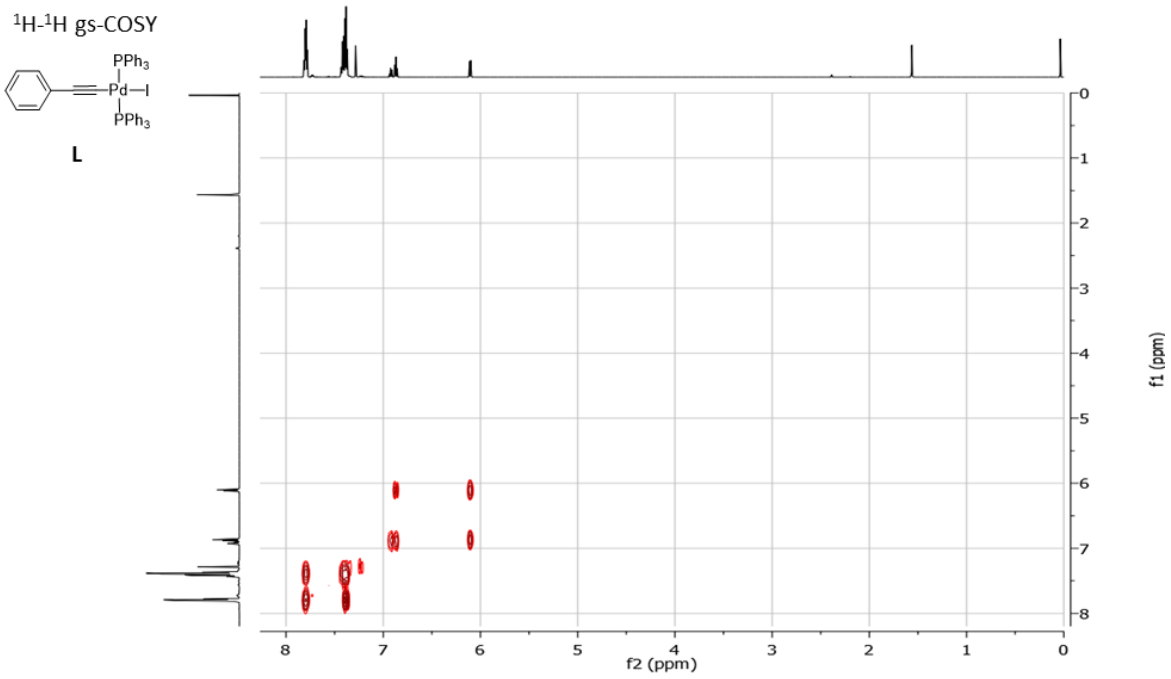
^{1}H-NMR (600 MHz-$CDCl_3$)



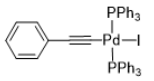
^{13}C-NMR (151.2 MHz-$CDCl_3$)



^{1}H-^{1}H gs-COSY

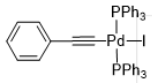


^{1}H-^{13}C gs-HSQC

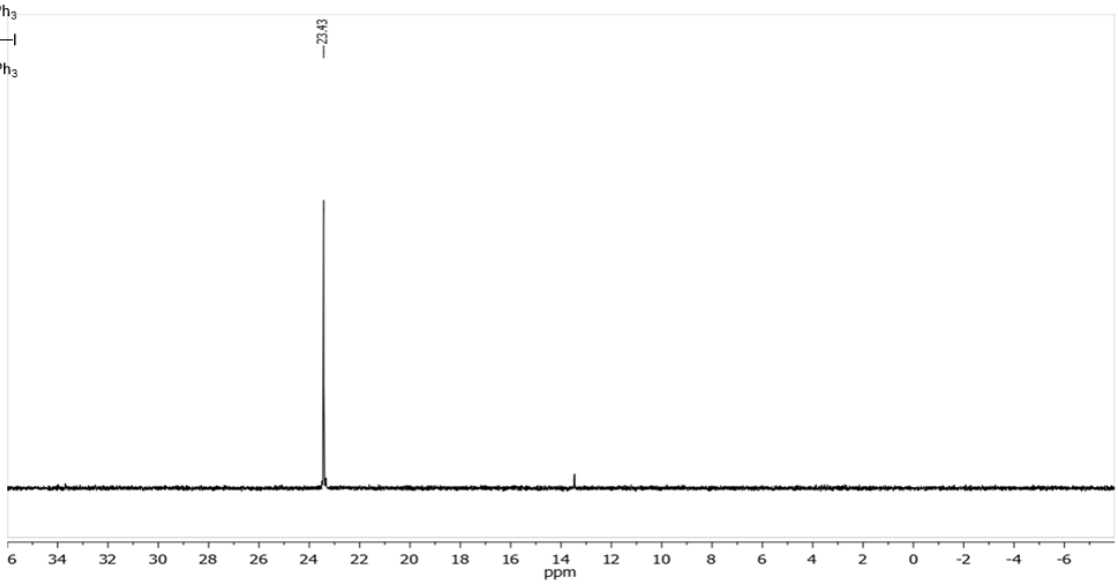


L

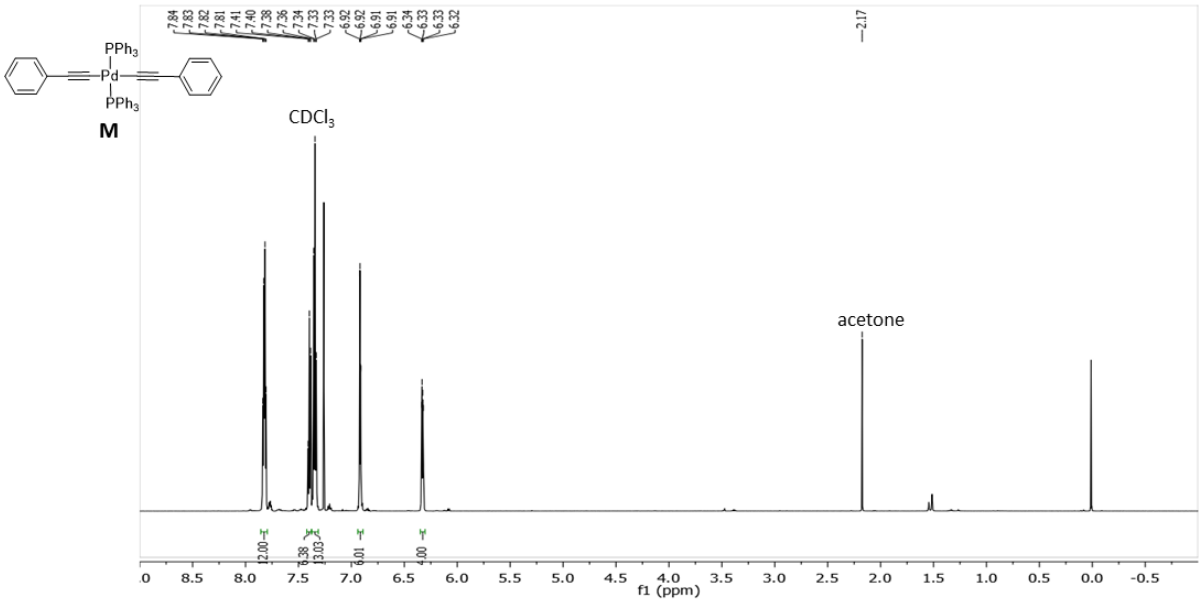
^{31}P-NMR (242.4 MHz-$CDCl_3$)



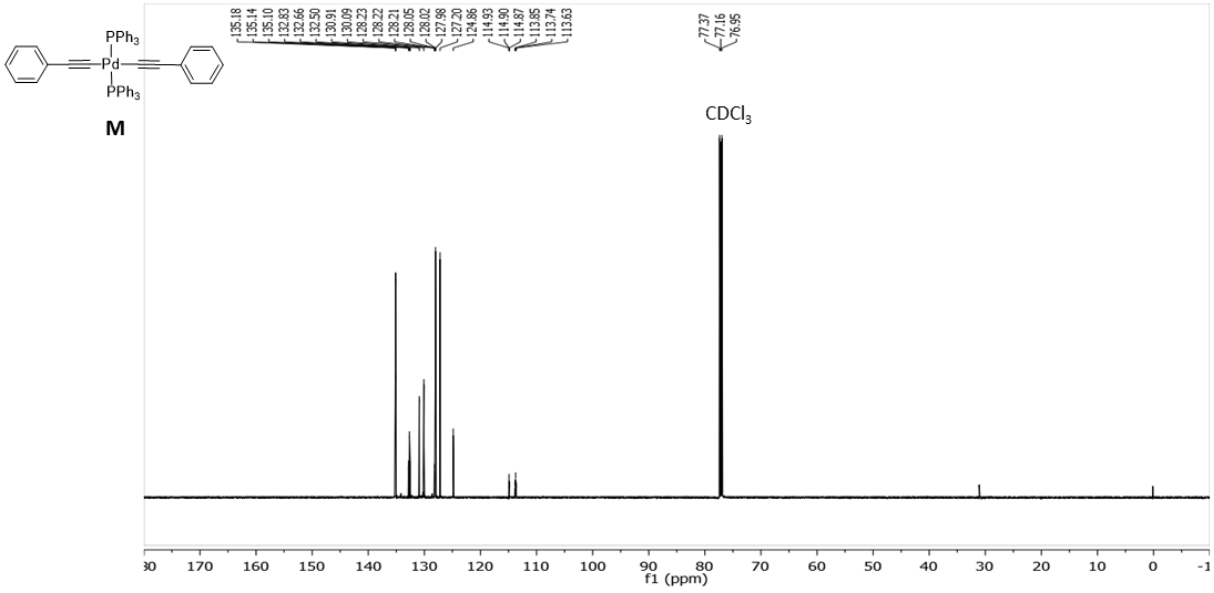
L



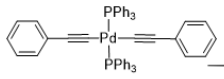
^{1}H-NMR (600 MHz-$CDCl_3$)



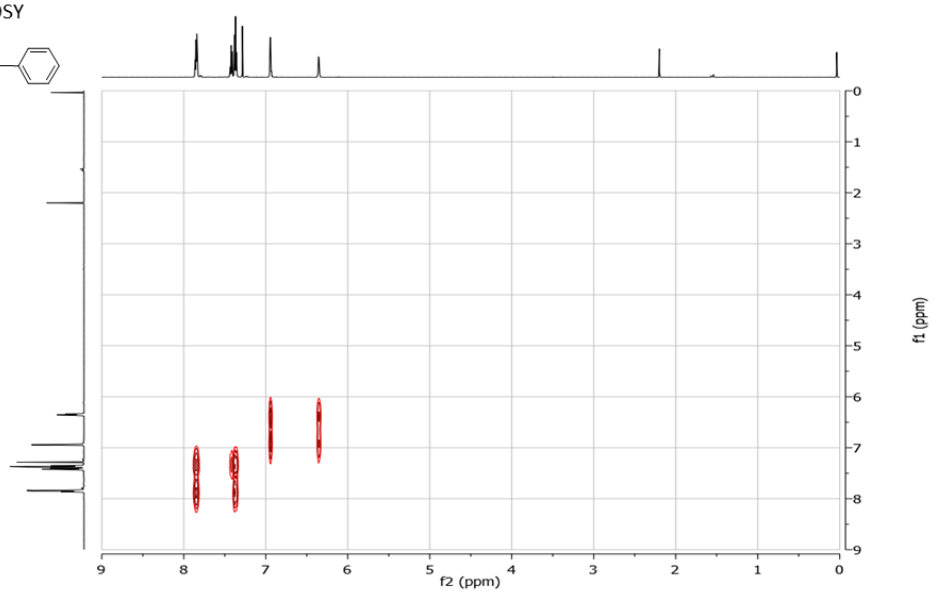
^{13}C-NMR (151.2 MHz-$CDCl_3$)



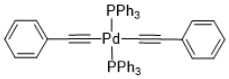
^{1}H-^{1}H gs-COSY



M



^{1}H-^{13}C gs-HSQC



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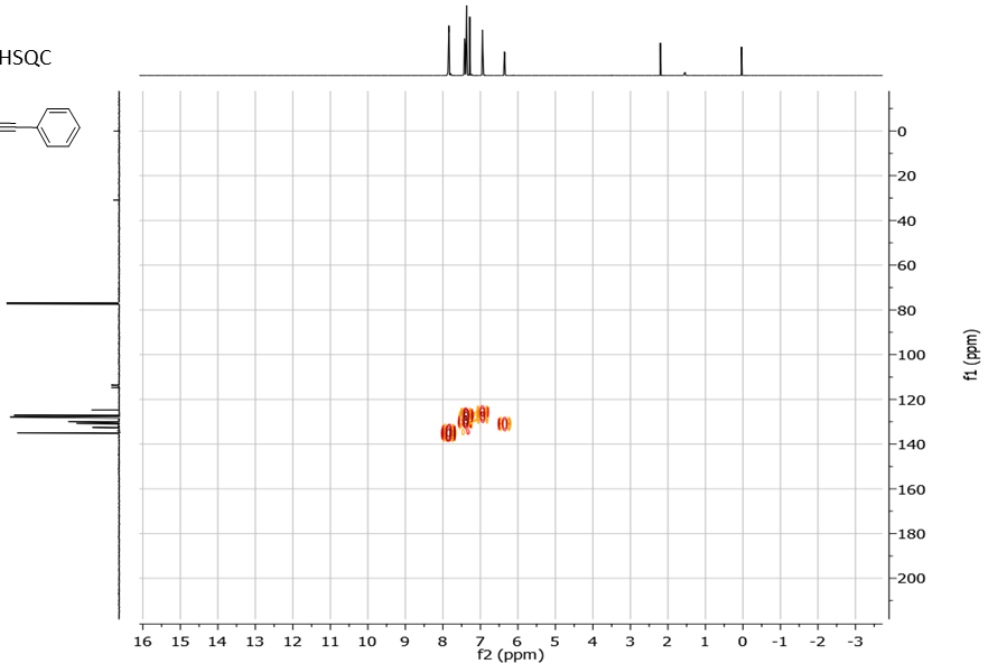
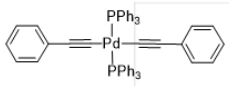


^{31}P-NMR (242.4 MHz-$CDCl_3$)



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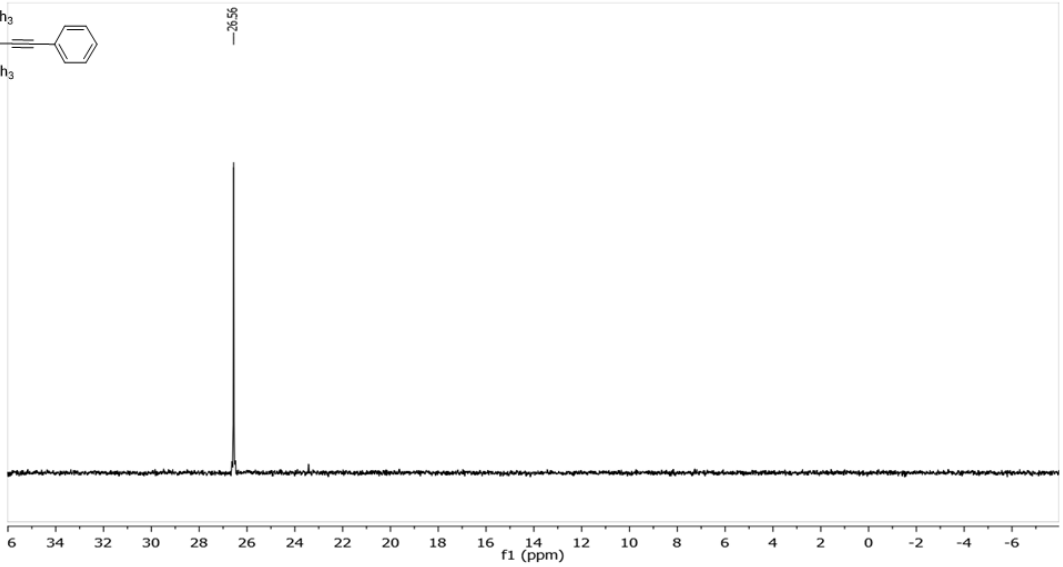
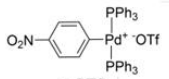
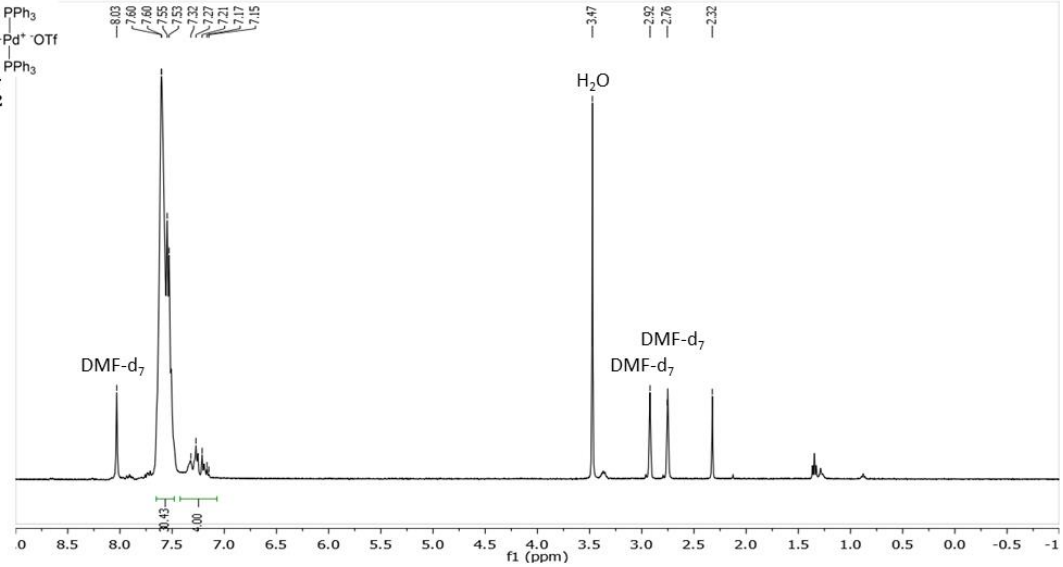


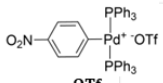
^{1}H-NMR (400 MHz-DMF-d_7)



$\mathbf{B^{OTf}_{NO2}}$



^{19}F-NMR (377 MHz-DMF-d_7)



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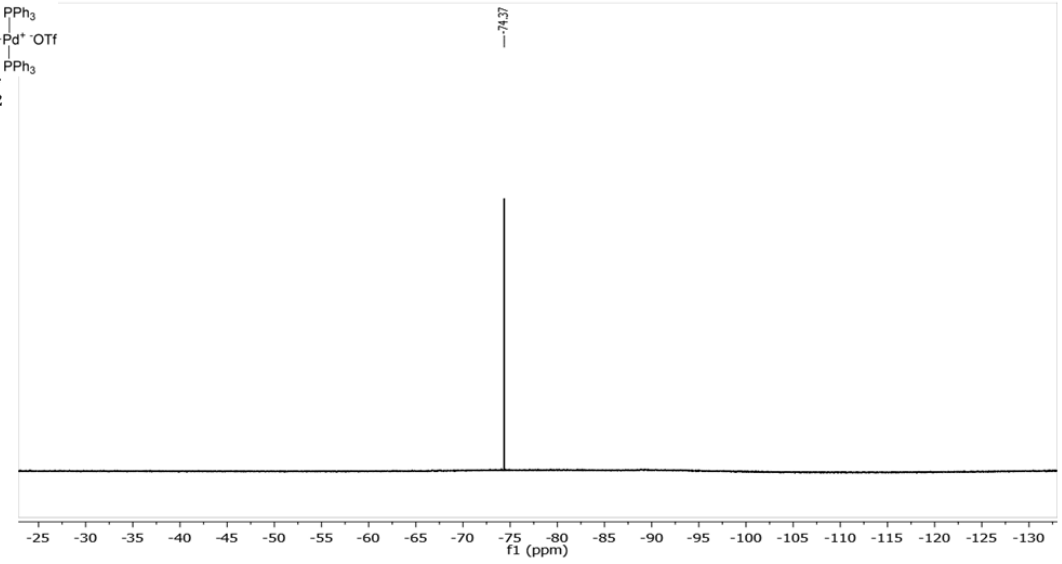
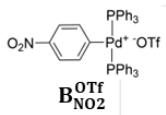
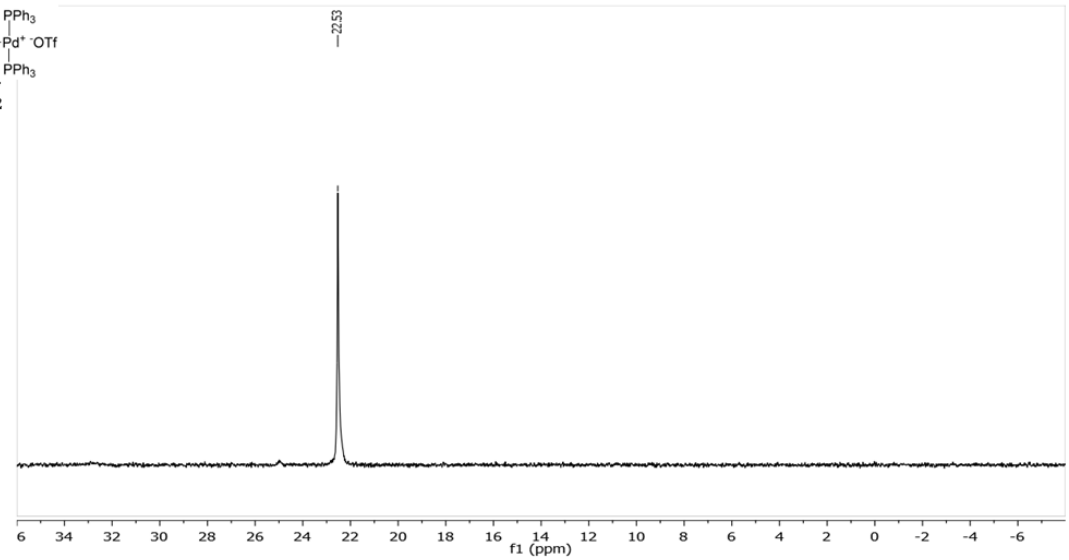


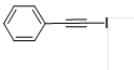
^{31}P-NMR (161.6 MHz-DMF-d_7)



$\mathbf{B_{NO2}^{OTf}}$



^{1}H-NMR (600 MHz-$CDCl_3$)



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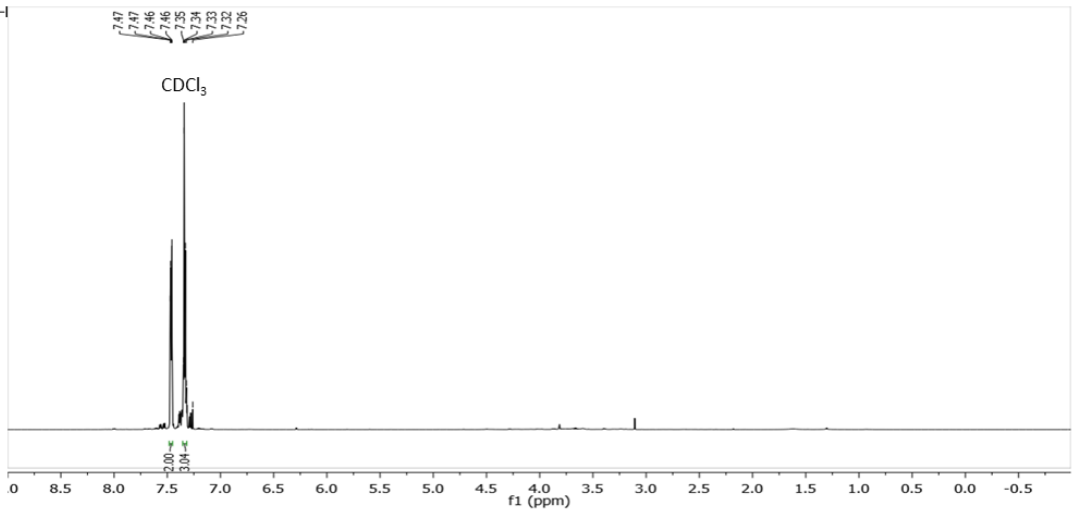
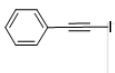


^{13}C-NMR (151.2 MHz-$CDCl_3$)



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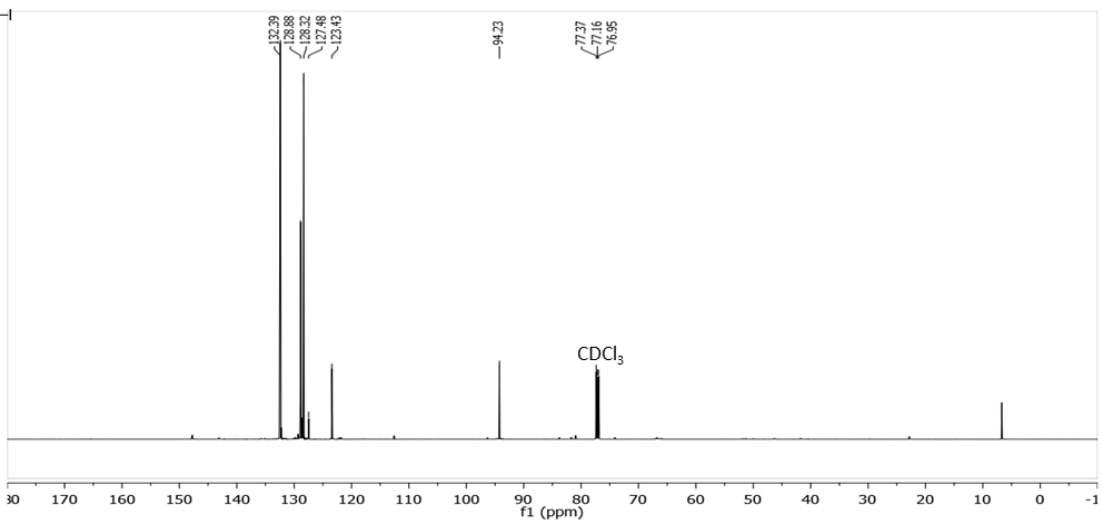
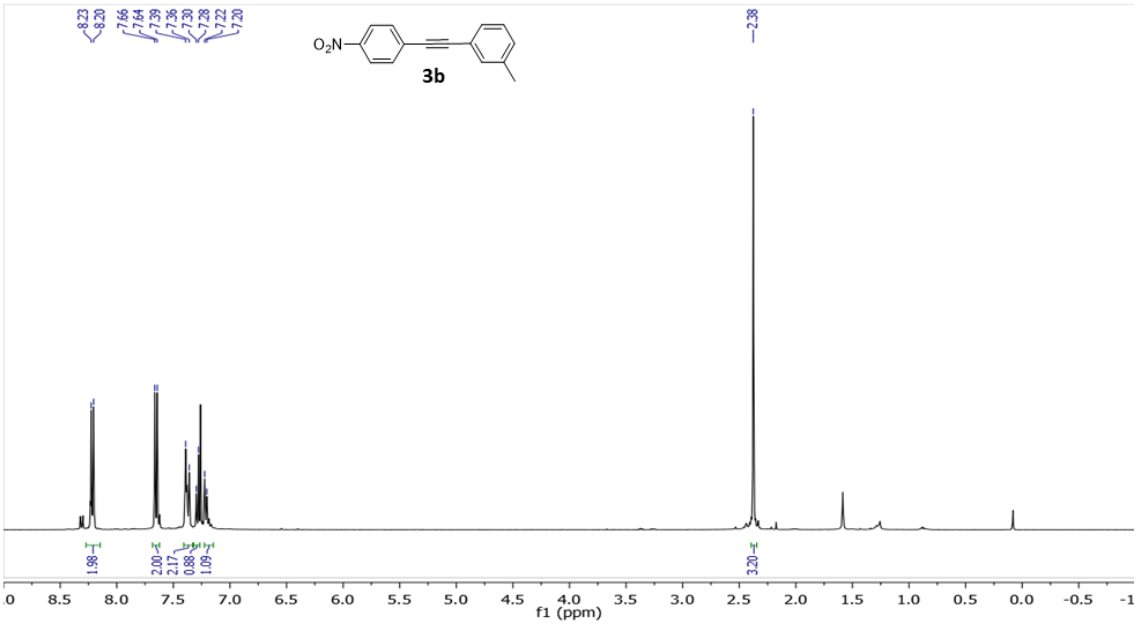
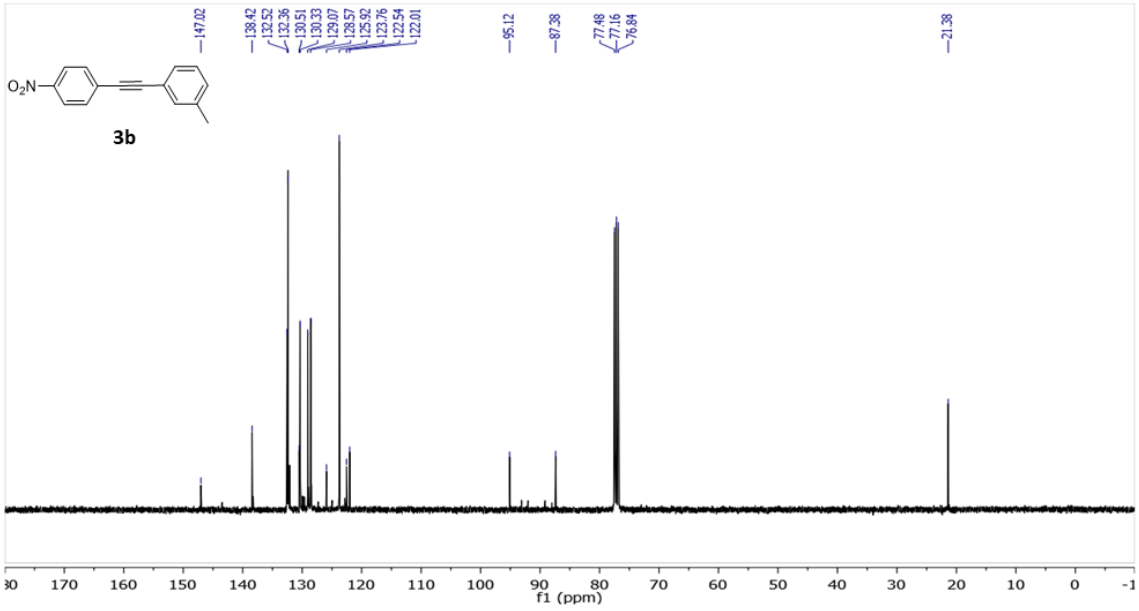


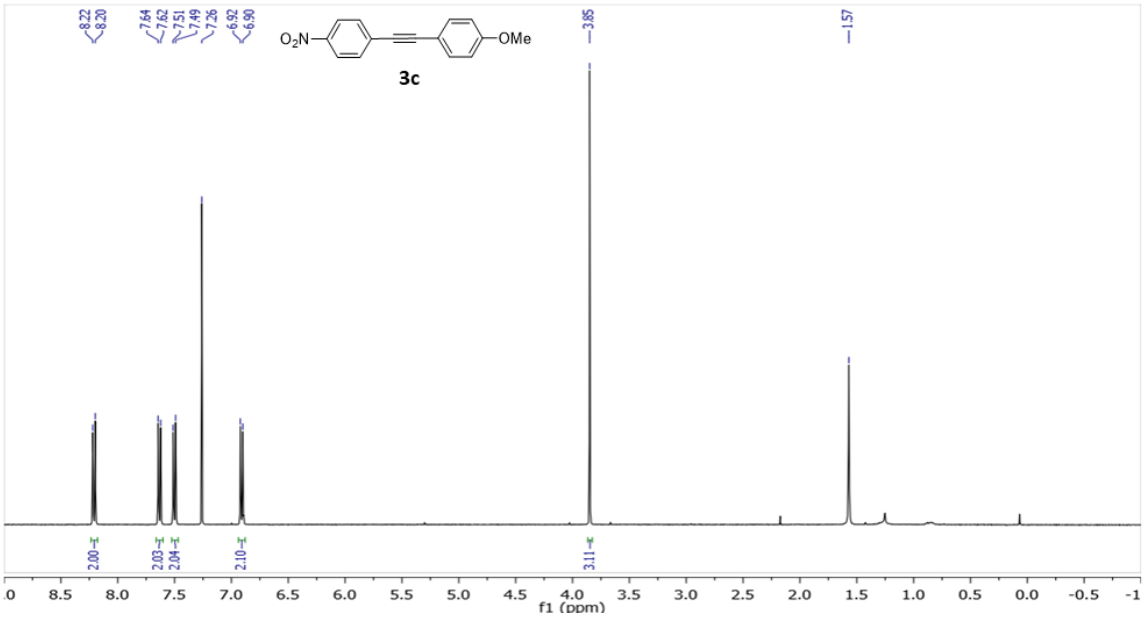
^{1}H-NMR (400 MHz-$CDCl_3$)



^{13}C-NMR (100.8 MHz-$CDCl_3$)



¹H-NMR (400 MHz-$CDCl_3$)



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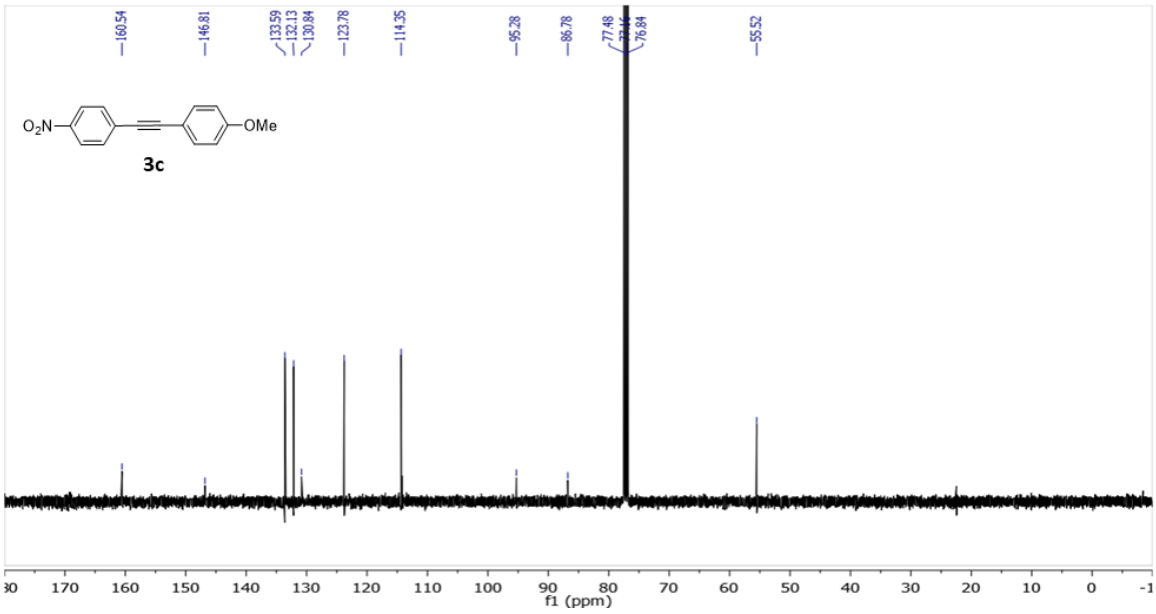

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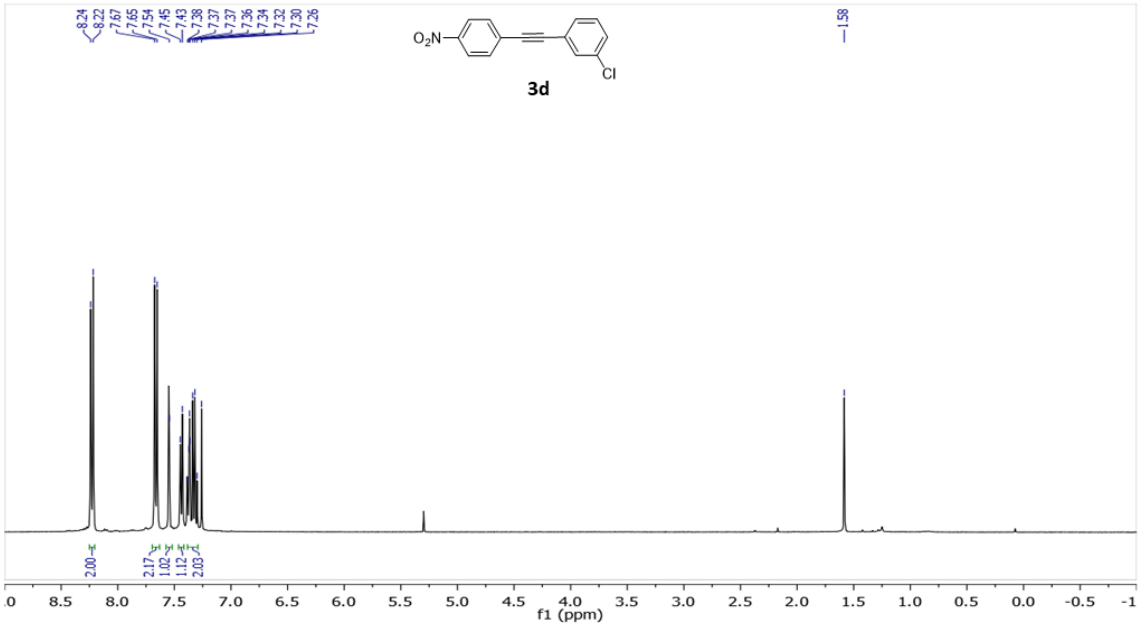

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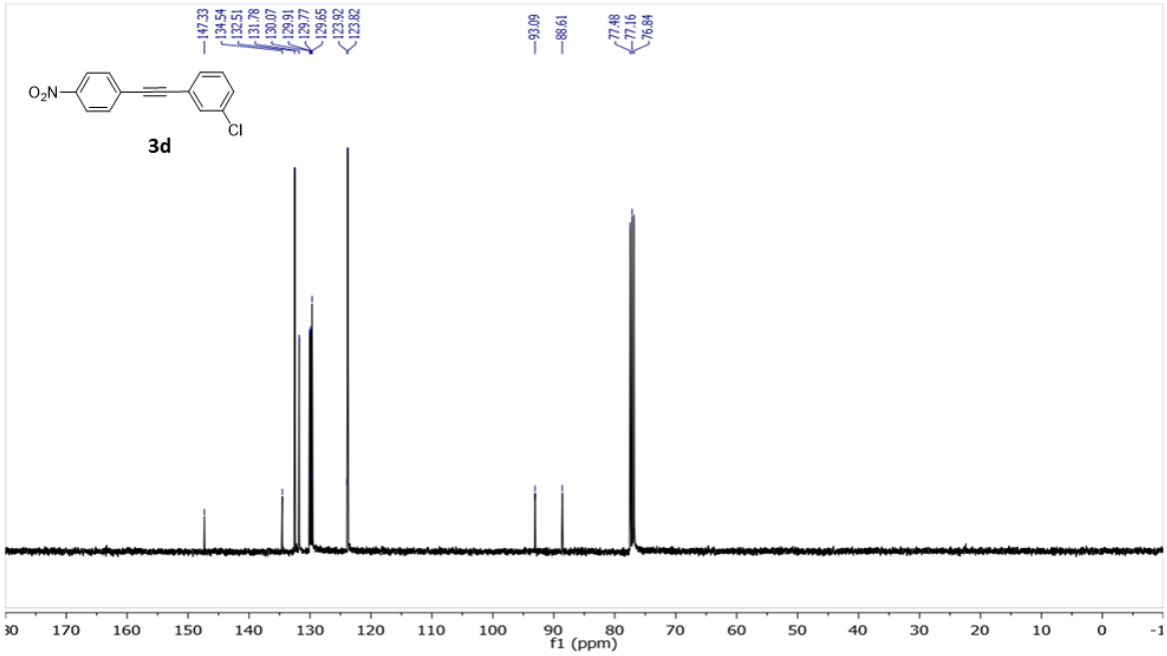

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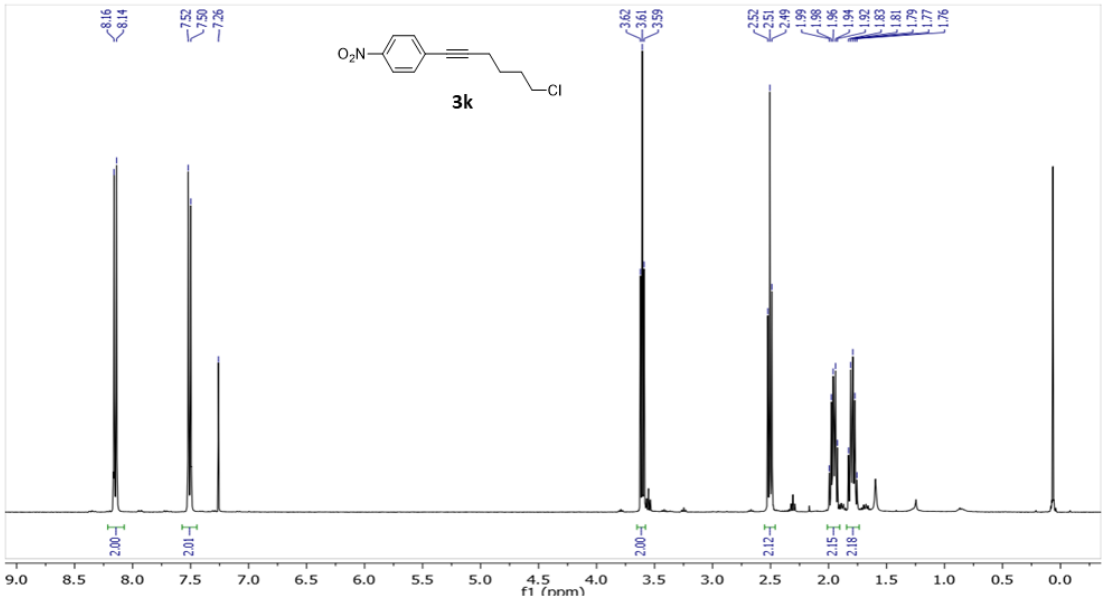
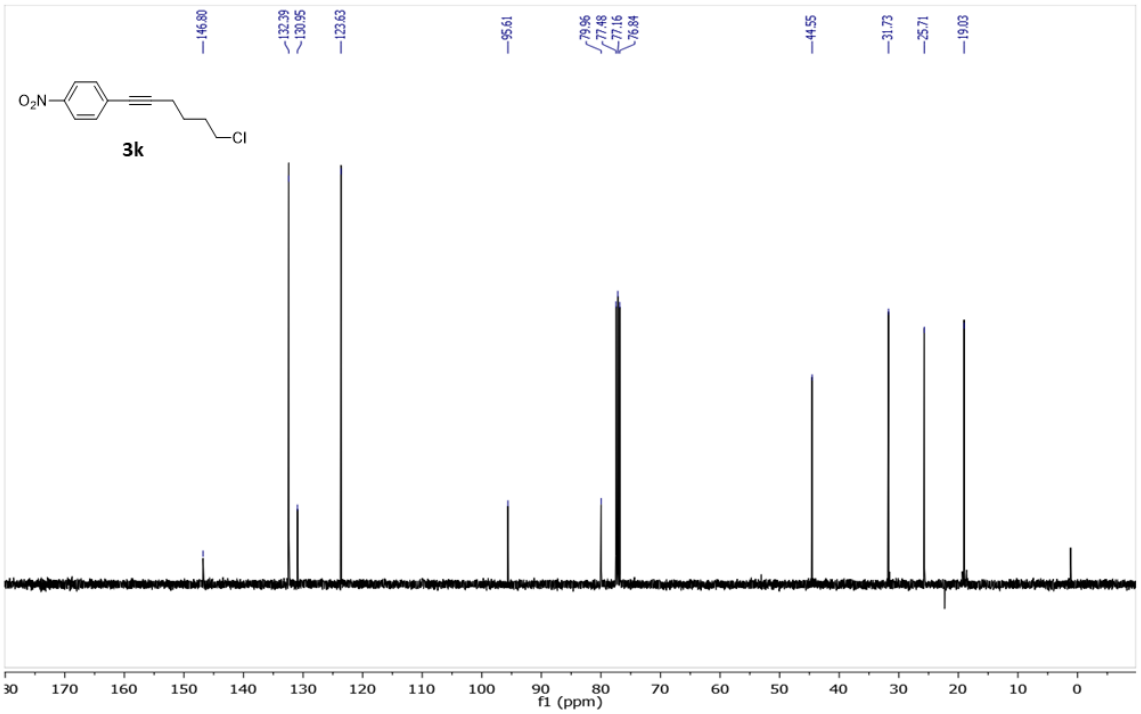


^{13}C-NMR (100.8 MHz-$CDCl_3$)



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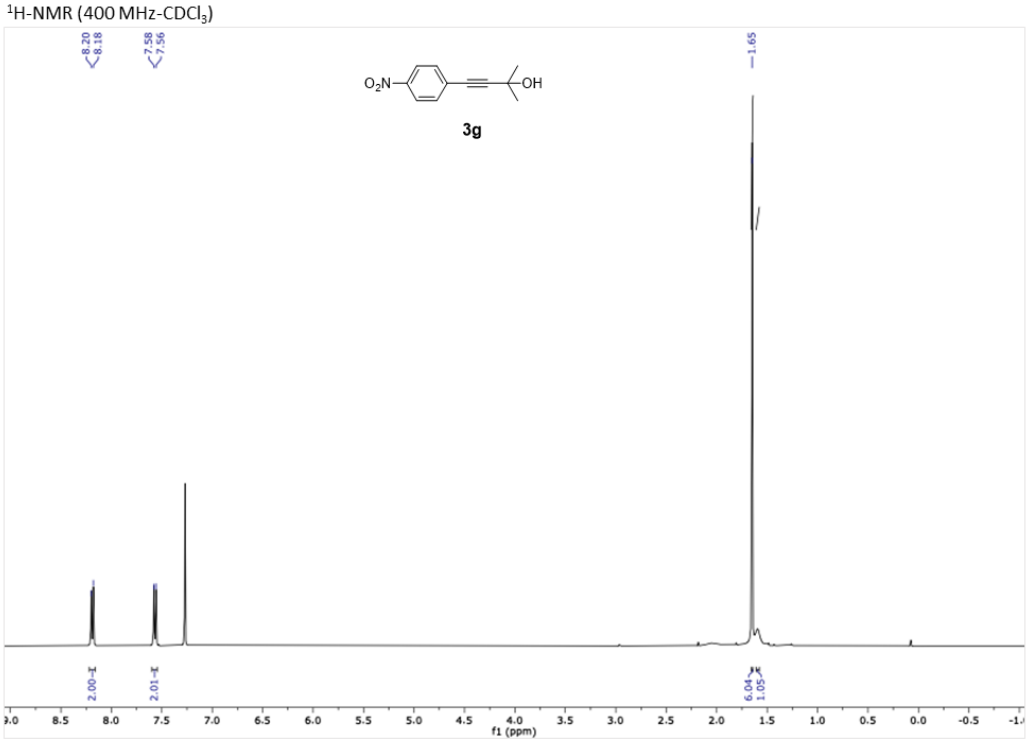

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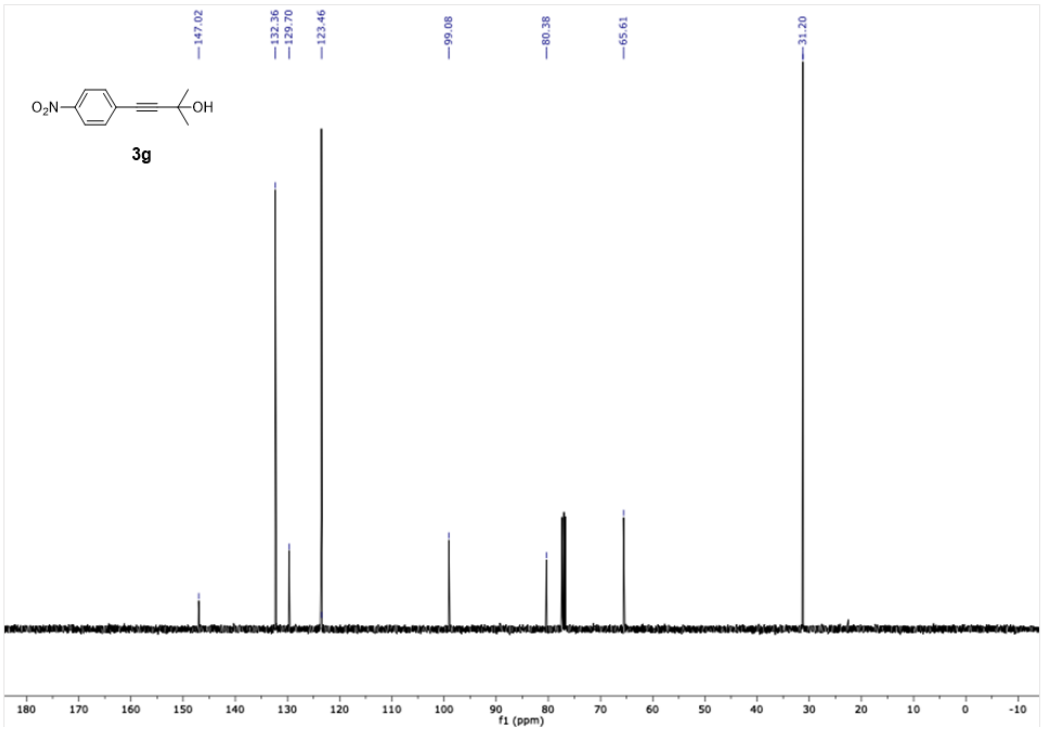

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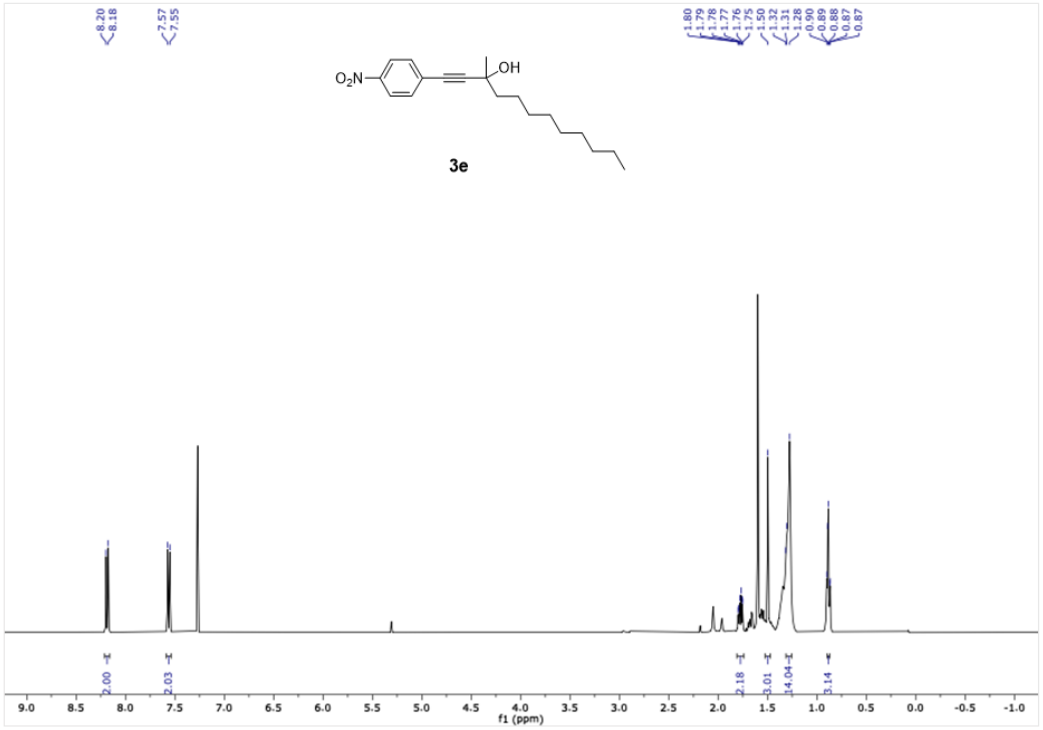

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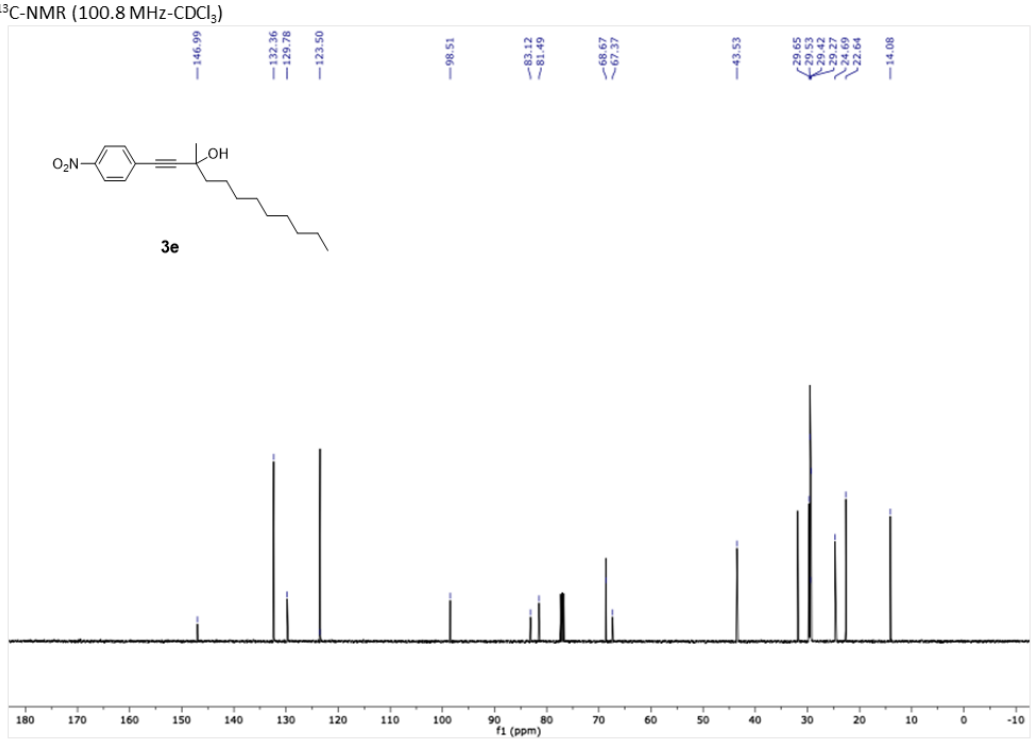

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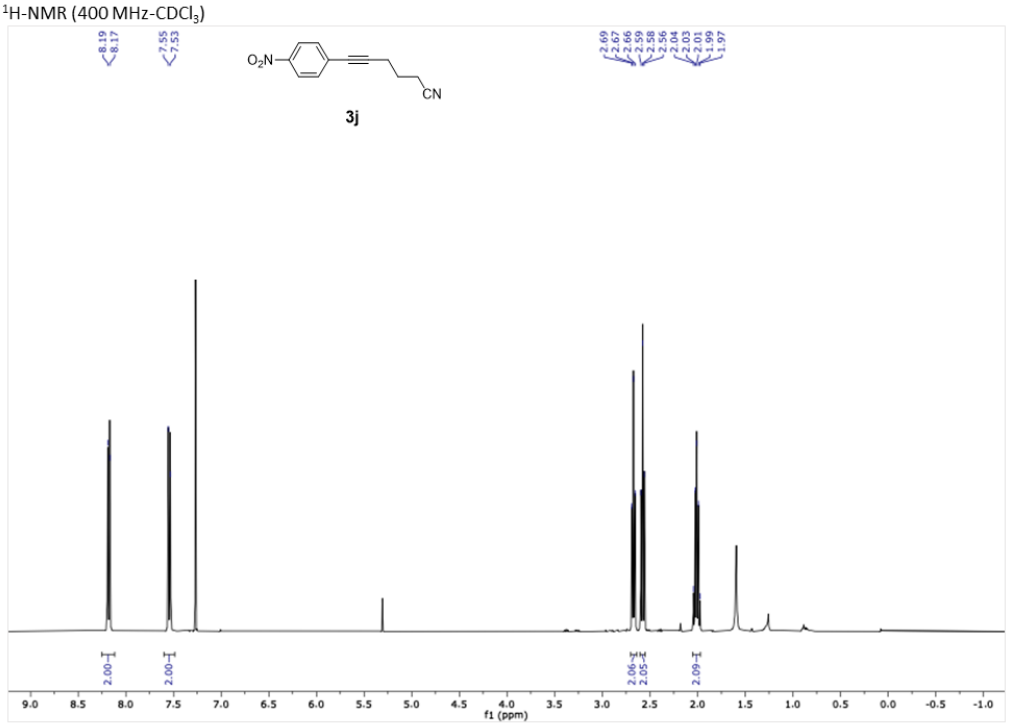

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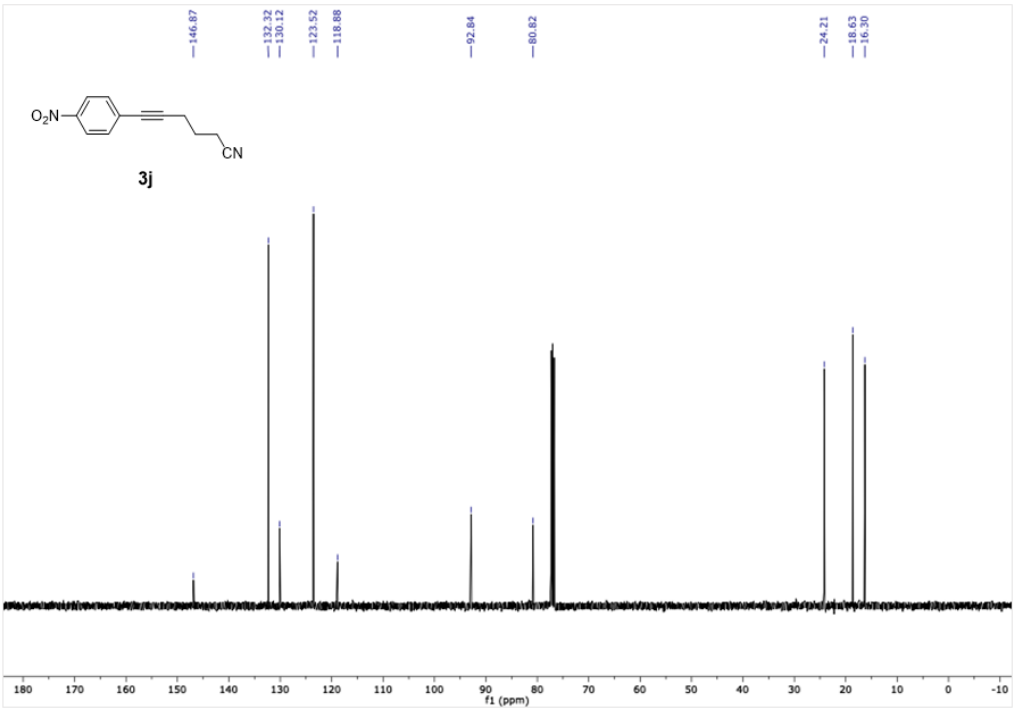

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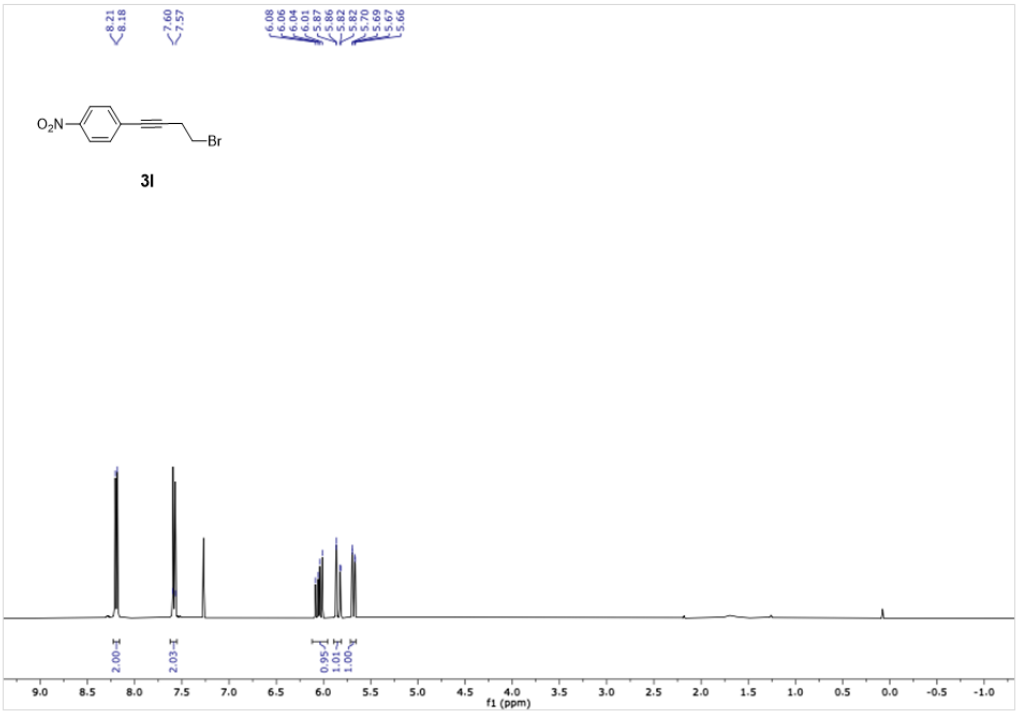

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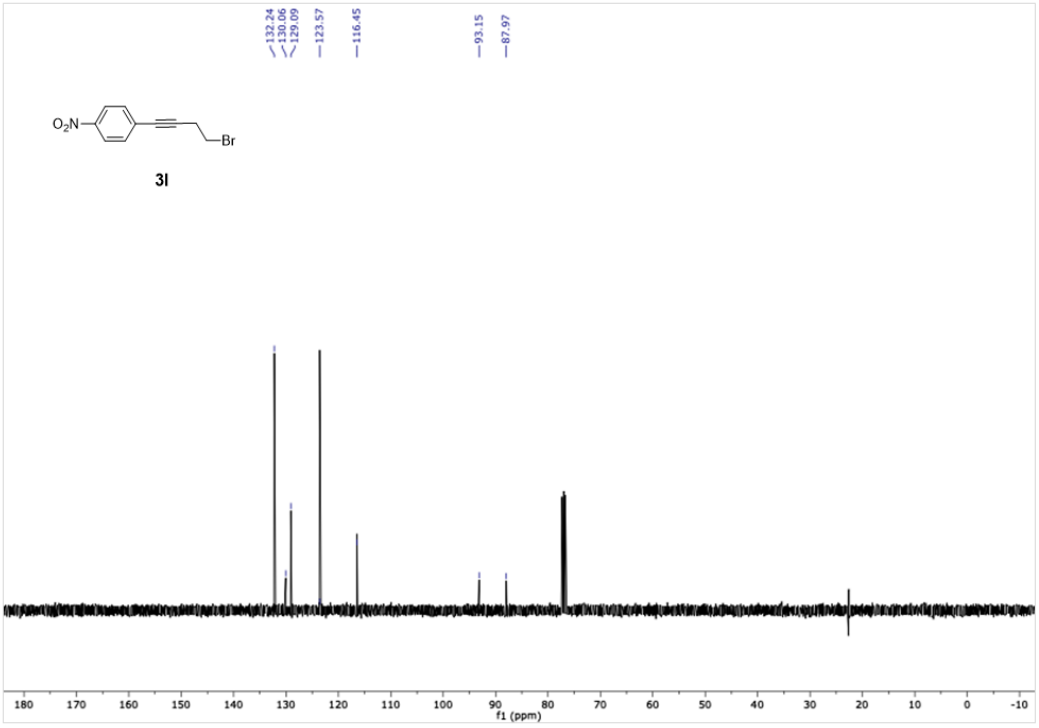

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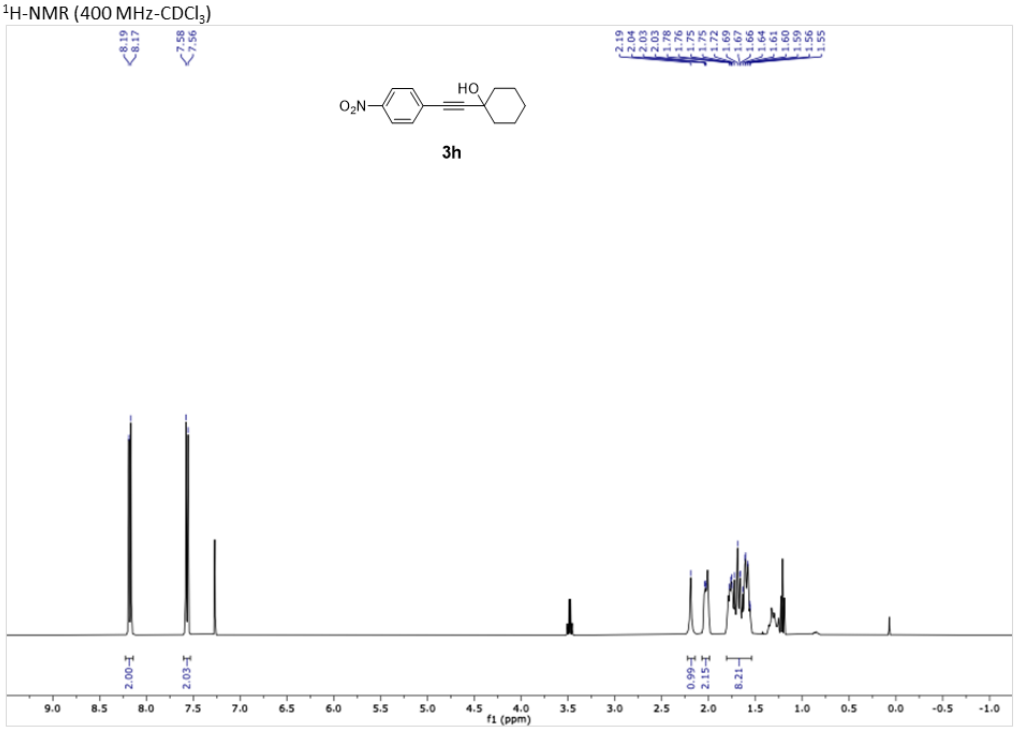

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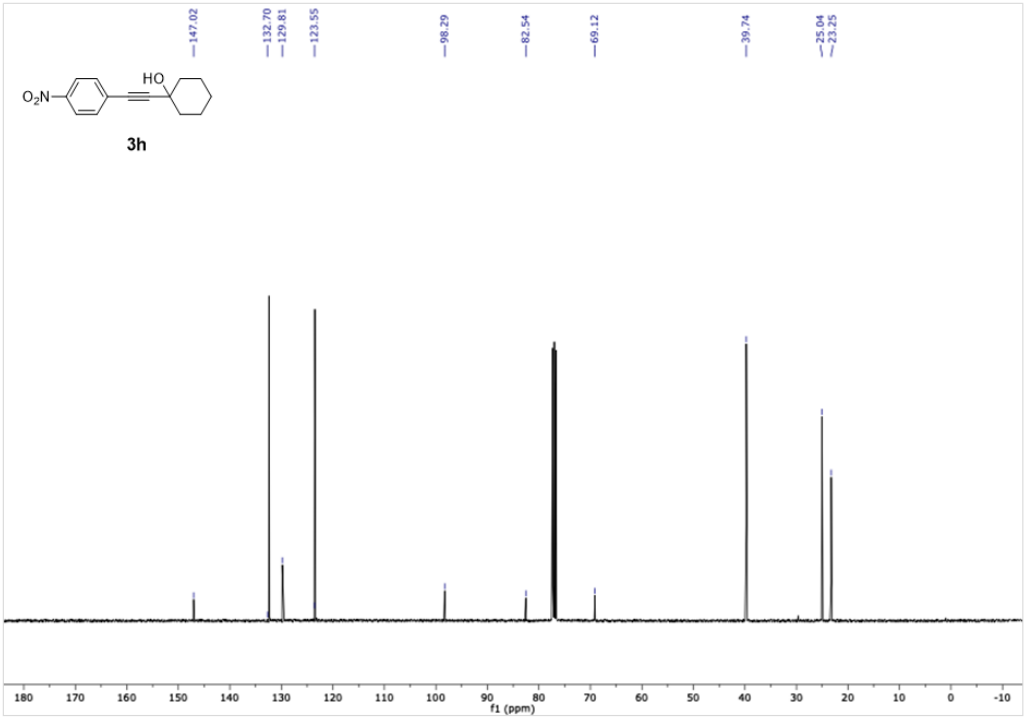

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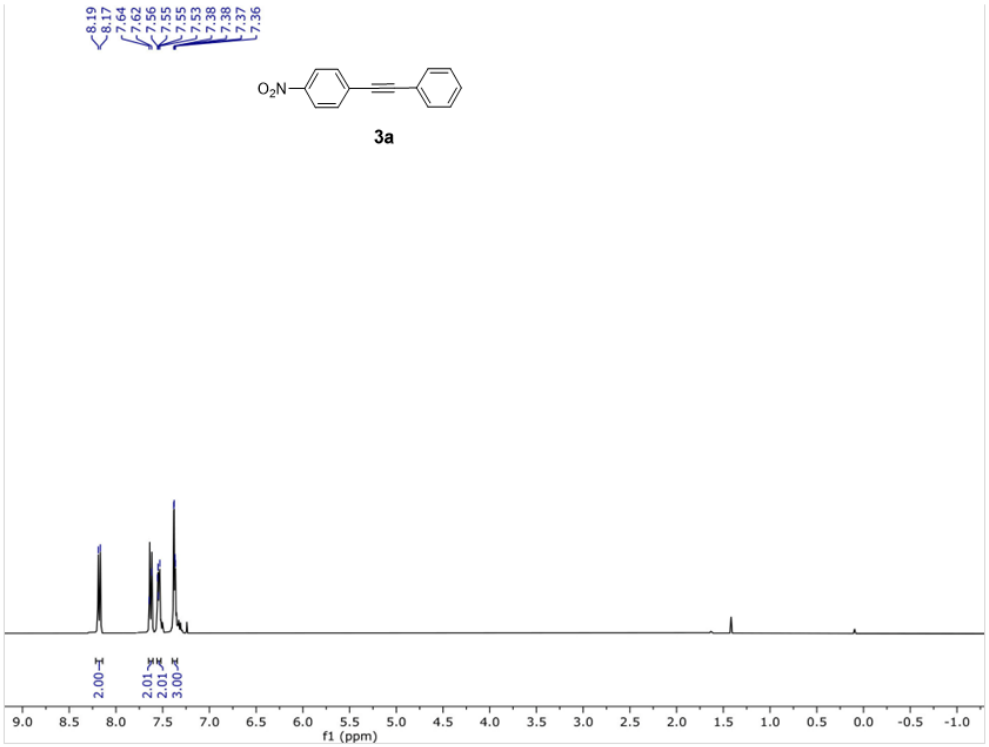

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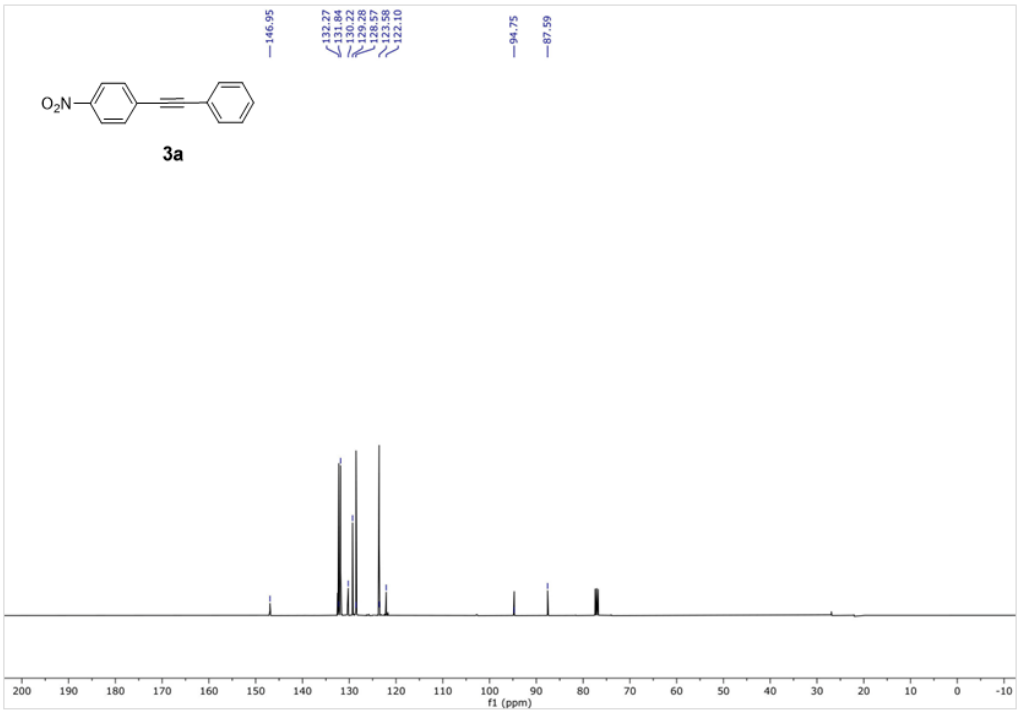

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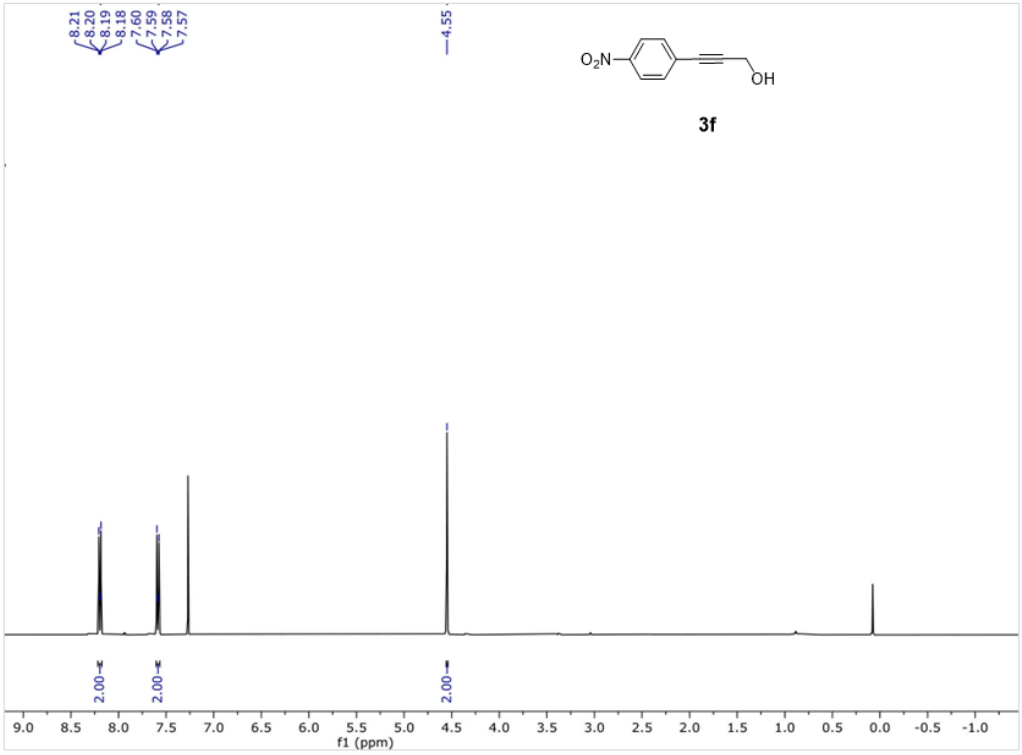

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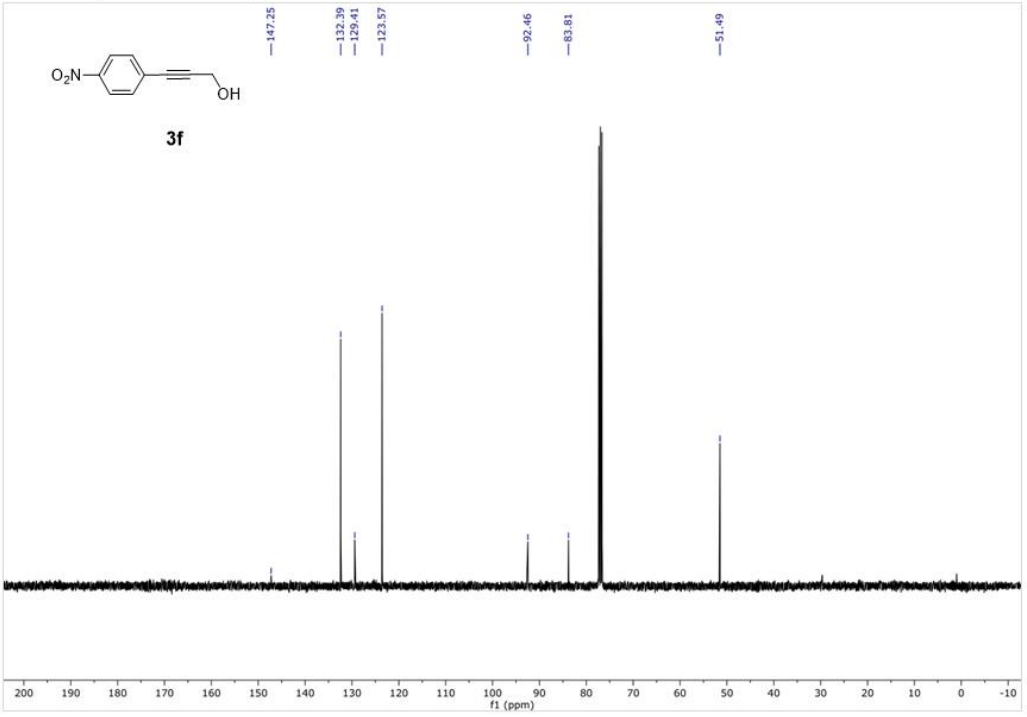

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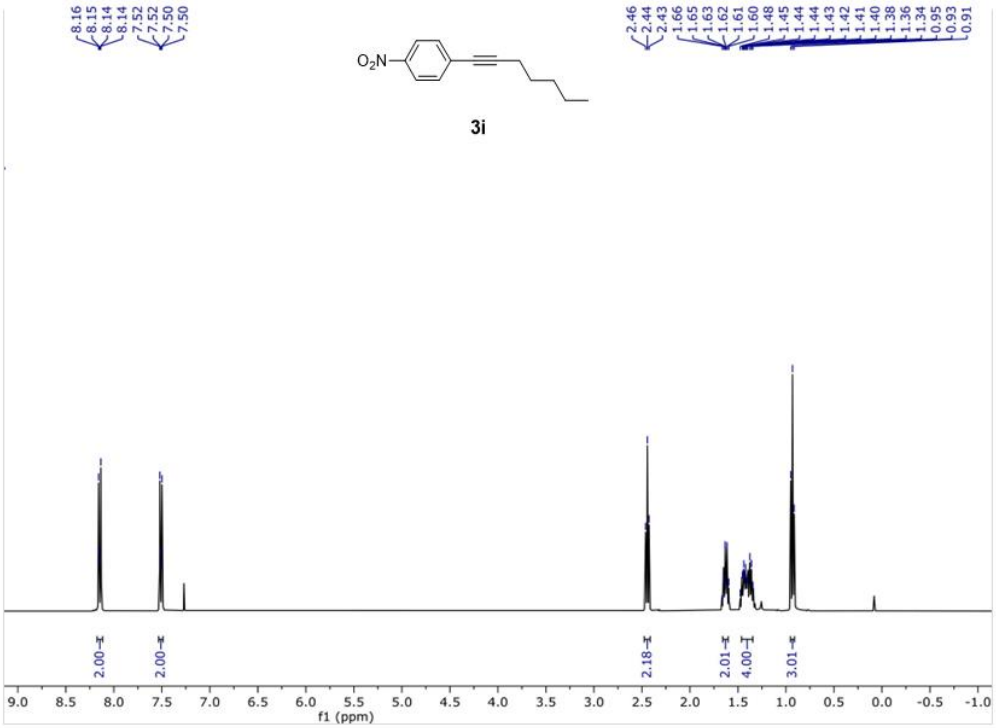

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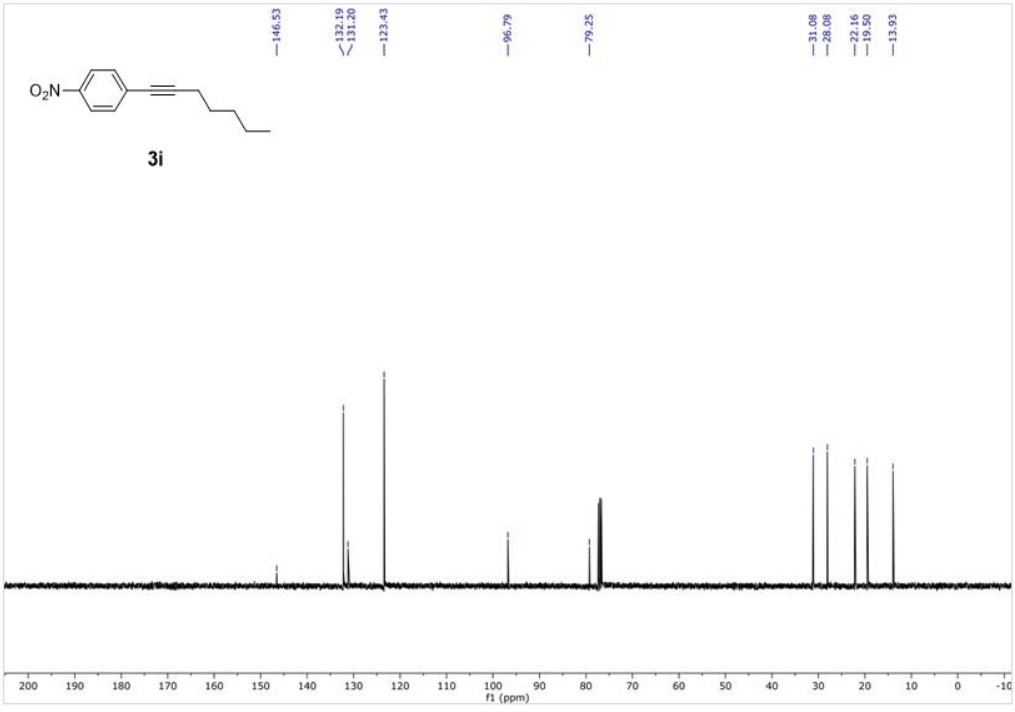

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