

– Supporting Information –

**Towards Structurally Versatile Mesoionic N-Heterocyclic Olefin Ligands  
and their Coordination to Palladium, Gold, and Boron Hydride**

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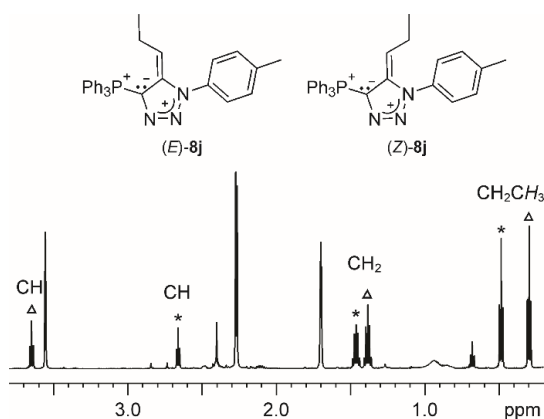
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<sup>#</sup> Disclaimer: The views expressed are purely those of the authors and may not in any circumstances be regarded as stating an official position of the ERCEA and the European Commission.

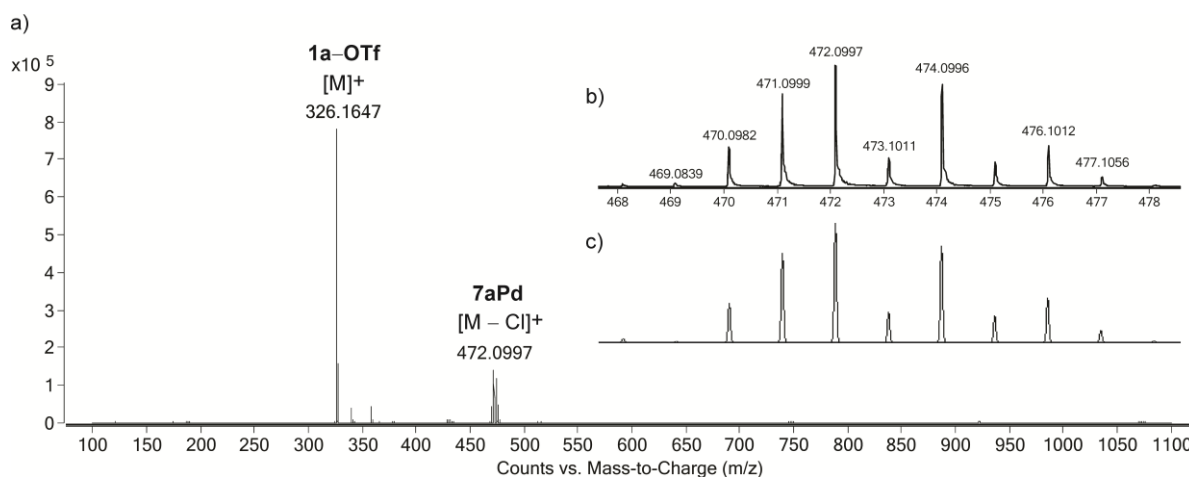
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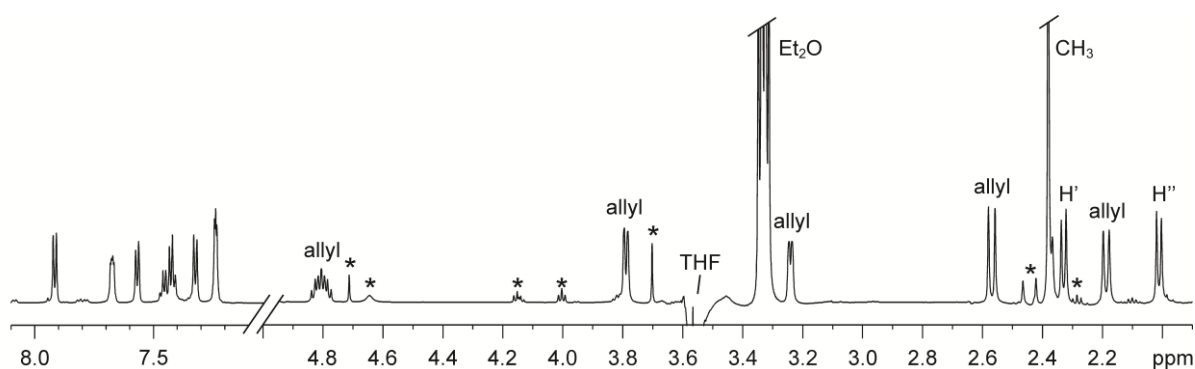
## 1. Figures S1–S6



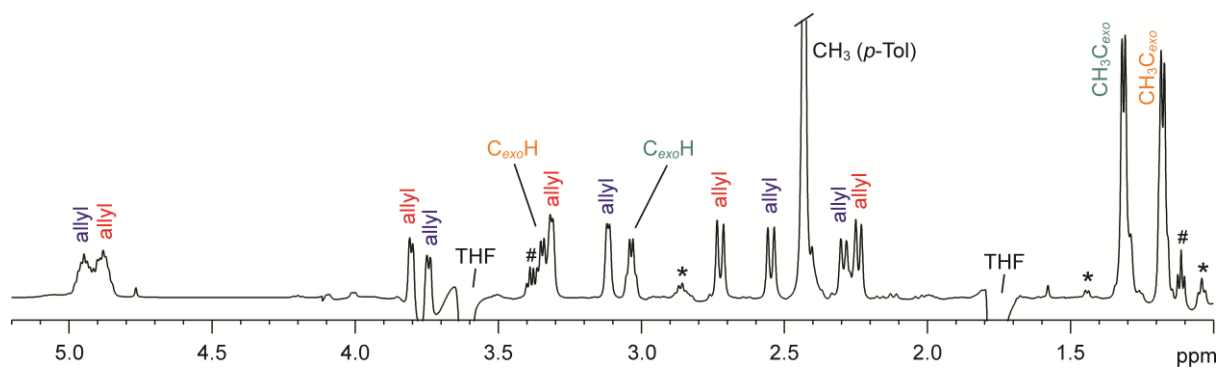
**Figure S1.** Selected region of <sup>1</sup>H NMR spectrum of *in situ* generated **8j** indicating *E* and *Z* geometric isomers. Spectra were recorded in THF-*d*<sub>8</sub>, Δ and \* denote major and minor isomer, respectively.



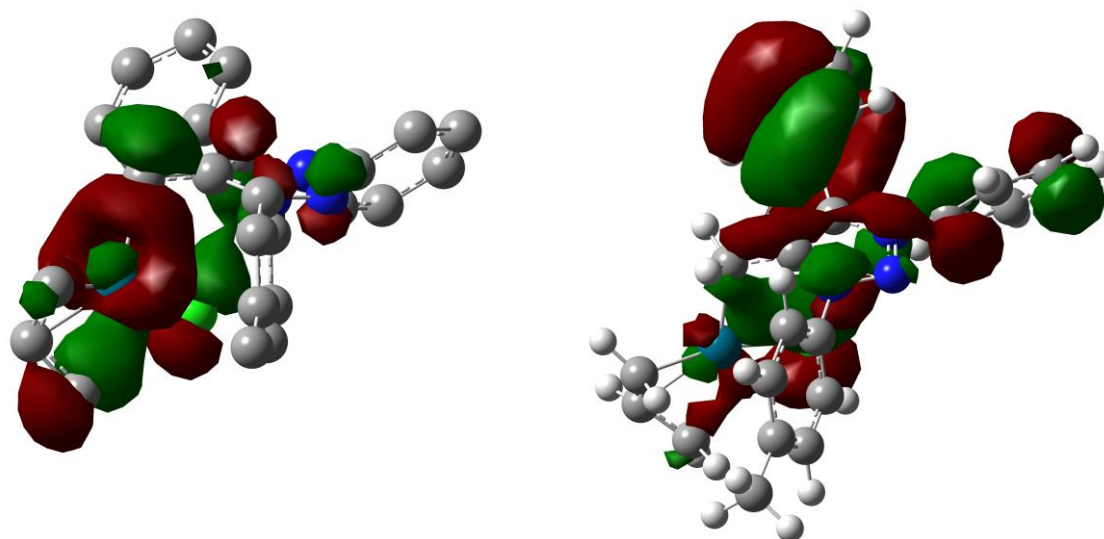
**Figure S2.** a) Positive-ion ESI-HRMS spectrum of complex **7aPd**:  $m/z$  472.0997 (calcd for  $C_{25}H_{24}N_3Pd^+$  [**7aPd** - Cl]<sup>+</sup> 472.1005),  $m/z$  326.1647 (calcd for  $C_{22}H_{20}N_3^+$  [(**1a**-OTf)]<sup>+</sup> 326.1652); b) inset showing the isotope distribution of [**7aPd** - Cl]<sup>+</sup> ion; and c) the corresponding calculated isotope distribution for  $C_{25}H_{24}N_3Pd^+$ .



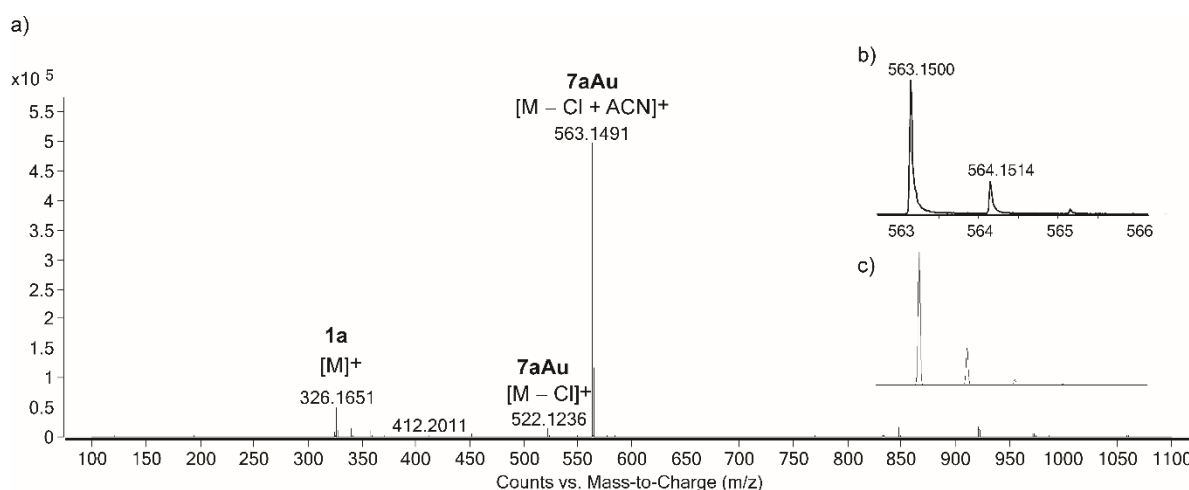
**Figure S3.** Selected regions of solvent suppression No-D <sup>1</sup>H NMR spectrum of **7aPd** in non-deuterated THF [for highly moisture-sensitive compounds like **7**, we found it experimentally convenient to conduct the reactions in a rigorously dried non-deuterated solvent, and record solvent suppression No-D NMR experiments of the aliquots without further manipulations]. THF denotes residual solvent resonance after solvent suppression. Resonances of residual Et<sub>2</sub>O ( $\delta$  = 3.34 ppm) are from the solvent system used for attempted recrystallization of **7aPd** (see above). H' and H'' are arbitrarily assigned. Asterisk denotes unidentified species.



**Figure S4.** Selected regions of solvent suppression No-D  $^1\text{H}$  NMR spectrum of **7bPd** in non-deuterated THF. Colour code denotes two different spin systems for the allyl and mNHO ligands in two diastereoisomers as extracted from  $^1\text{H}$ - $^1\text{H}$  *gs*-COSY spectrum. Asterisk denotes unidentified species. THF denotes residual solvent resonance after solvent suppression. Resonances marked by # belong to triazolium cation (**1b**-OTf), a product of hydrolytic decomposition of **7bPd**.



**Figure S5.** HOMO (left) and HOMO-6 (right) of **7aPd** showing  $\pi$ -type interaction contribution to the  $\text{C}_{\text{exo}}\text{-C}_{\text{endo}}$  bond of mNHO.



**Figure S6.** a) Positive-ion ESI-HRMS spectrum of complex **7aAu**:  $m/z$  at 563.1491 (calcd for  $\text{C}_{24}\text{H}_{22}\text{AuN}_4^+$  [**7aAu** - Cl +  $\text{CH}_3\text{CN}$ ] $^+$  563.1505),  $m/z$  at 522.1236 (calcd for  $\text{C}_{22}\text{H}_{19}\text{AuN}_3^+$  [**7aAu** - Cl] $^+$  522.1239),  $m/z$  326.1651 (calcd for  $\text{C}_{22}\text{H}_{20}\text{N}_3^+$  [**1a** - OTf] $^+$  326.1652); b) inset showing the isotope distribution of [**7aAu** - Cl +  $\text{CH}_3\text{CN}$ ] $^+$  ion; and c) the corresponding calculated isotope distribution for  $\text{C}_{24}\text{H}_{22}\text{AuN}_4^+$ .

## 2. Single-crystal X-ray diffraction

Crystal structure of **9hPd**·CDCl<sub>3</sub> was measured on a Rigaku OD XtaLAB Synergy-S diffractometer equipped with Cu and Ag PhotonJet micro-focus sealed X-ray tubes and an Eiger2 R CdTe 1M hybrid pixel detector, whereas the crystal structure of **10aBH<sub>3</sub>**·0.825(CH<sub>2</sub>Cl<sub>2</sub>) was measured on a Rigaku OD (Agilent) Gemini single-crystal X-ray diffractometer equipped with Cu and Mo Enhance fine-focus sealed X-ray tubes and an Atlas CCD detector. Both datasets were collected with Cu *K*α radiation at low temperatures. *CrysAlis<sup>Pro</sup>* software<sup>1</sup> was used for data collection and reduction. Crystal structures were solved and refined by *olex2.solve*<sup>2</sup> and *SHELXL*,<sup>3</sup> respectively, within the *Olex2* (v. 1.5)<sup>4</sup> software. *Diamond*<sup>5</sup> program was used for molecular graphics.

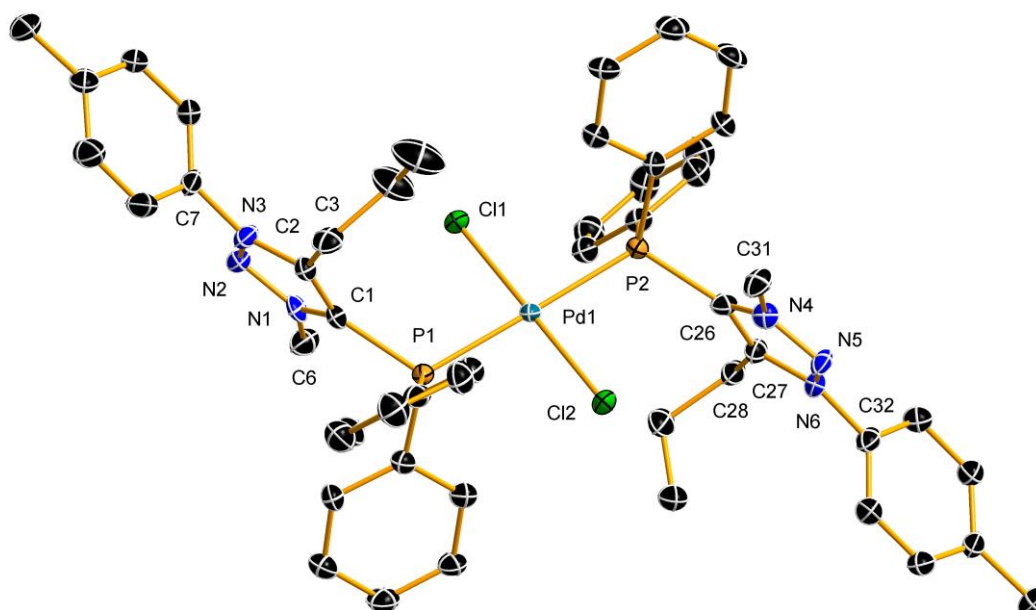
Crystals of **9hPd**, suitable for X-ray diffraction analysis were grown from a CDCl<sub>3</sub> solution by slow evaporation of the solvent and the complex crystallized as a CDCl<sub>3</sub> solvate. Crystals of **9hPd**·CDCl<sub>3</sub> were of low quality. Two full datasets were measured and both crystals were non-merohedrally twinned. Twin data processing and twin refinement using HKLF5-format file unfortunately did not improve the crystal structure model. Both crystal structures suffer from the same issues, namely, poor *R*-factors and high residual electron density peaks. In addition, one nitrogen atom (N4) in the triazole ring turns non-positive definite when refined anisotropically, which results in distorted bond distances, therefore, it was refined isotropically. Nevertheless, despite these shortcomings the crystal structure of **9hPd** complex is fully consistent with the spectroscopic data.

Hydrogen atoms in the crystal structure of **10aBH<sub>3</sub>**·0.825(CH<sub>2</sub>Cl<sub>2</sub>) were located in the difference Fourier map. The positions and isotropic thermal parameters of hydrogen atoms on CH<sub>2</sub> and BH<sub>3</sub> groups were freely refined.<sup>6</sup> Constrained refinement was employed for hydrogen atoms on methyl and aryl groups in the crystal structure of **10aBH<sub>3</sub>**·0.825(CH<sub>2</sub>Cl<sub>2</sub>) and for all hydrogen atoms in **9hPd**·CDCl<sub>3</sub>.

**Table S1.** Summary of the crystal data and structure refinements.

Compound	<b>9hPd</b> ·CDCl <sub>3</sub>	<b>10aBH<sub>3</sub></b> ·0.825(CH <sub>2</sub> Cl <sub>2</sub> )
Formula	[PdCl <sub>2</sub> (PC <sub>25</sub> H <sub>27</sub> N <sub>3</sub> ) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub> ·CDCl <sub>3</sub>	C <sub>22</sub> H <sub>22</sub> BN <sub>3</sub> ·0.825(CH <sub>2</sub> Cl <sub>2</sub> )
$F_w$	1272.22	409.30
$T$ [K]	100.0(1)	150.0(1)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
$a$ [Å]	18.7815(3)	9.8803(2)
$b$ [Å]	12.9118(2)	23.0698(3)
$c$ [Å]	23.7001(4)	10.6992(3)
$\alpha$ [°]	90	90
$\beta$ [°]	101.4136(16)	115.988(3)
$\gamma$ [°]	90	90
$V$ [Å <sup>3</sup> ]	5633.69(15)	2192.16(10)
$Z$	4	4
$\rho_{\text{calc}}$ [g/cm <sup>3</sup> ]	1.500	1.240
Crystal size [mm]	0.144 × 0.082 × 0.071	0.322 × 0.222 × 0.206
Radiation type	Cu $K\alpha$	Cu $K\alpha$
$\lambda$ [Å]	1.54184	1.54184
$\mu$ [mm <sup>-1</sup> ]	5.956	2.358
$F(000)$	2584	859
$\theta_{\text{max}}$ [°]	76.099	76.654
Index ranges	-23 ≤ $h$ ≤ 23 -10 ≤ $k$ ≤ 16 -29 ≤ $l$ ≤ 29	-12 ≤ $h$ ≤ 12 -28 ≤ $k$ ≤ 29 -11 ≤ $l$ ≤ 13
Reflections collected	41980	27485
Independent reflections	11392	4522
Reflections with [ $I > 2\sigma(I)$ ]	10029	4162
$R_{\text{int}}$	0.0572	0.0262
$R_{\text{sigma}}$	0.0357	0.0140
Data/restraints/parameters	11392/0/677	4522/6/312
$S$	1.060	1.058
$R_1, wR_2$ [ $I > 2\sigma(I)$ ]	0.0987, 0.2641	0.0429, 0.1161
$R_1, wR_2$ [all data]	0.1056, 0.2717	0.0461, 0.1192
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}}$ [eÅ <sup>-3</sup> ]	-2.683, 6.456	-0.199, 0.386
CCDC deposition number <sup>[a]</sup>	2297782	2297781

<sup>[a]</sup> The supplementary crystallographic data for this paper can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

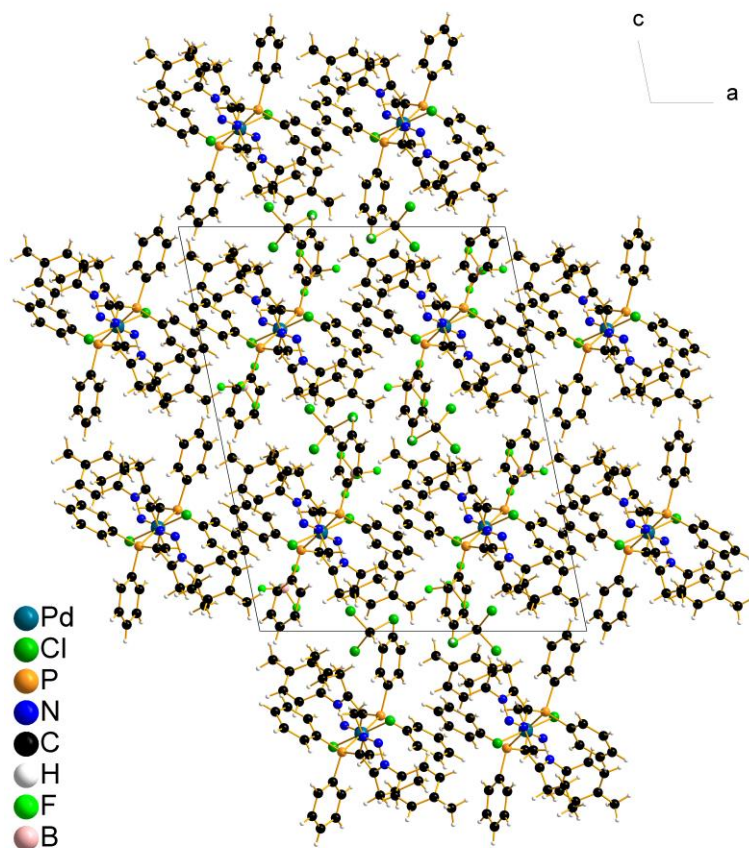


**Figure S7.** The asymmetric unit and selected atom labels of the **9hPd**·CDCl<sub>3</sub> crystal structure, the BF<sub>4</sub><sup>-</sup> anions, CDCl<sub>3</sub> molecule, and hydrogen atoms are omitted for clarity. Displacement ellipsoids are depicted at the 50% probability level.

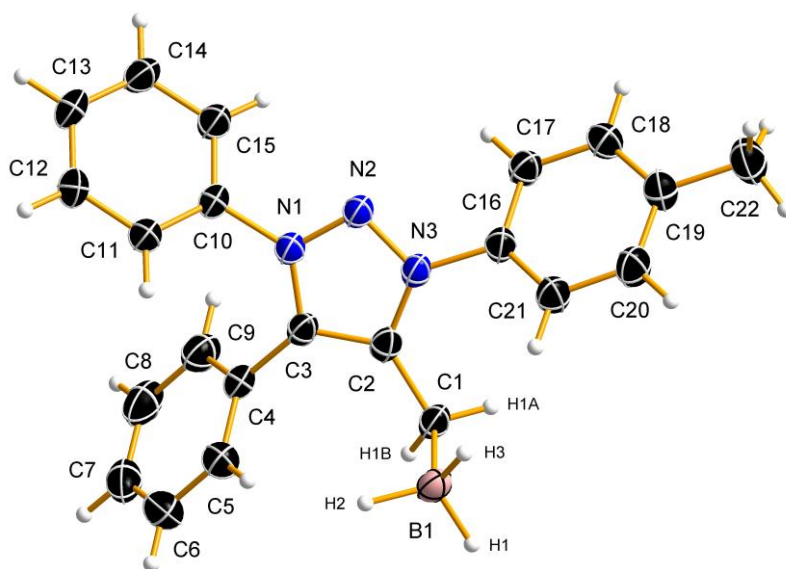
**Table S2.** Selected bond distances of **9hPd**·CDCl<sub>3</sub> crystal structure.

Bond Lengths [Å]							
Pd1–Cl1	2.2943(14)	P1–C1	1.841(6)	N1–N2	1.335(8)	N4–N5	1.304(7)
Pd1–Cl2	2.2955(14)	P1–C14	1.820(6)	N2–N3	1.318(8)	N5–N6	1.331(7)
Pd1–P1	2.3238(15)	P1–C20	1.819(6)	N1–C1	1.344(8)	N4–C26	1.358(8)
Pd1–P2	2.3331(15)	P2–C26	1.833(6)	N1–C6	1.471(8)	N4–C31	1.454(7)
		P2–C39	1.823(6)	N3–C2	1.367(8)	N6–C27	1.362(8)
		P2–C45	1.811(6)	N3–C7	1.450(7)	N6–C32	1.446(8)
				C1–C2	1.367(9)	C26–C27	1.393(8)
				C2–C3	1.488(9)	C27–C28	1.489(8)





**Figure S8.** The crystal packing and the unit cell of the **9hPd**·CDCl<sub>3</sub> crystal structure viewed along the *b*-crystallographic axis.

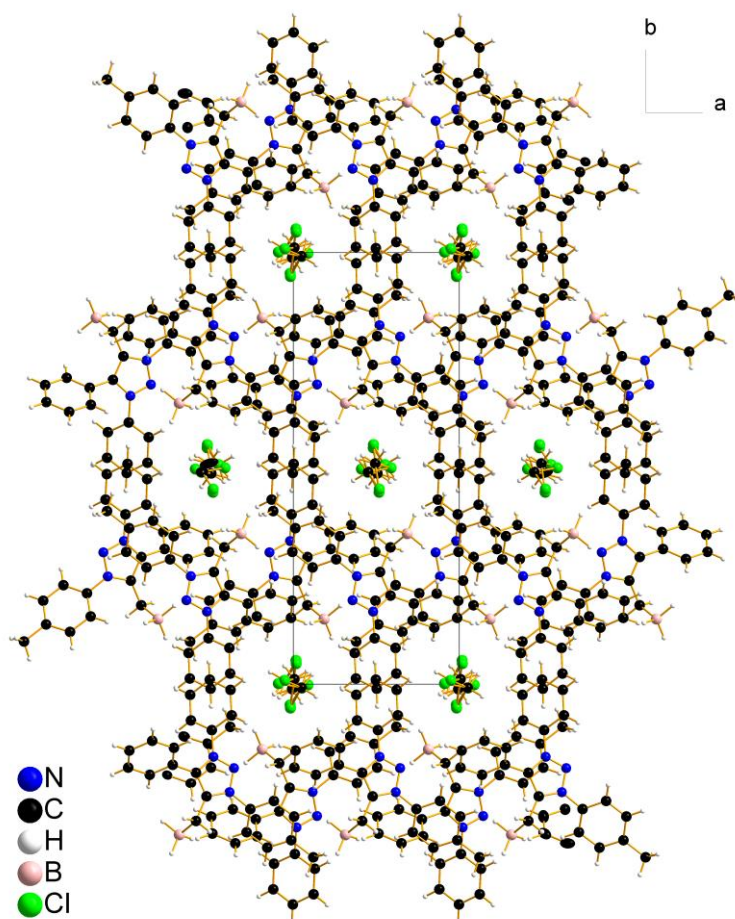


**Figure S9.** The asymmetric unit and selected atom labels of the **10aBH<sub>3</sub>**·0.825(CH<sub>2</sub>Cl<sub>2</sub>) crystal structure, the disordered CH<sub>2</sub>Cl<sub>2</sub> molecules are omitted for clarity. Displacement ellipsoids are depicted at the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius.

Compound **10aBH<sub>3</sub>** crystallized as dichloromethane solvate. In the crystal structure of **10aBH<sub>3</sub>·0.825(CH<sub>2</sub>Cl<sub>2</sub>)** dichloromethane molecule is disordered over two positions with partial occupancies of 0.555(10) and 0.269(10). The observed B–H distances [1.15(2)–1.17(2) Å], CH<sub>2</sub>–BH<sub>3</sub> bond distance [1.667(2) Å] and C–C–B angle [114.37(13)°] are similar to the values [1.132(13)–1.147(12) Å, 1.6767(19) Å and 109.68(10)°, respectively] reported for the crystal structure of NHO–BH<sub>3</sub> adduct, ((1,3-bis(2,6-diisopropylphenyl)-4,5-dihydro-1*H*-imidazol-3-ium-2-yl)methyl)(trihydrido)borate (Cambridge Structural Databases refcode AGUYAE).<sup>7</sup>

**Table S3.** Selected bond distances of **10aBH<sub>3</sub>·0.825(CH<sub>2</sub>Cl<sub>2</sub>)** crystal structure.

Bond Lengths [Å]							
B1–C1	1.667(2)	C1–C2	1.478(2)	C2–N3	1.367(2)	C3–C4	1.476(2)
B1–H1	1.15(2)	C2–C3	1.385(2)	C3–N1	1.3642(19)	N1–C10	1.4446(18)
B1–H2	1.17(2)	C1–H1a	0.96(2)	N1–N2	1.3166(18)	N3–C16	1.4442(19)
B1–H3	1.17(2)	C1–H1b	1.014(19)	N2–N3	1.3361(17)		



**Figure S10.** The crystal packing and the unit cell of **10aBH<sub>3</sub>·0.825(CH<sub>2</sub>Cl<sub>2</sub>)** crystal structure viewed along the *b*-crystallographic axis with channels that are occupied by disordered CH<sub>2</sub>Cl<sub>2</sub> molecules.

### 3. Experimental section

*General Considerations.* All reagents and solvents were used as obtained from the commercial sources (Fluka, Aldrich, Merck, Fluorochem, Honeywell), unless indicated otherwise. Tetrahydrofuran (THF) was dried using solvent purification system MBraun SPS5. For reactions performed in a nitrogen filled glovebox all solvents were purchased dry from Merck. All reactions were carried out in oven-dried glassware under argon atmosphere. All manipulations involving mNHOs were performed in a nitrogen filled glovebox. Preparation of **10aBH<sub>3</sub>** was performed using Schlenk techniques. Silica gel column chromatography was carried out on silica gel 60N. Analytical thin-layer chromatography (TLC) was carried out on Fluka Silica Gel TLC cards, visualized with a UV lamp (254 nm and/or 366 nm). Melting points were determined on a Kofler micro hot-stage microscope and are uncorrected. IR spectra were obtained with a PerkinElmer Spectrum 100, equipped with a Specac Golden Gate Diamond ATR as a solid sample support. An Agilent 6224 time-of-flight (TOF) mass spectrometer equipped with a double orthogonal electrospray source at atmospheric pressure ionization (ESI) coupled to an Agilent 1260 HLPC was used for recording HRMS spectra. Mobile phase composed of two solvents: A was 0.1% formic acid in Milli-Q water, and B was 0.1% formic acid in acetonitrile mixed in the ratio of 1:1. Compounds were prepared by dissolving the samples in acetonitrile. 0.1–10  $\mu\text{L}$  of each sample and injected into the LC-MS; flow rate 0.4 mL/min; fragmentor voltage 150 V; capillary voltage 4000 V; mass range 100–1700.

NMR spectra were recorded with a Bruker Avance III 500 MHz NMR instrument operating at 500 MHz ( $^1\text{H}$ ), 126 MHz ( $^{13}\text{C}$ ), 565 MHz ( $^{19}\text{F}$ ), and 160 MHz ( $^{11}\text{B}$ ) and Bruker Avance NEO 600 MHz NMR instrument operating at 600 MHz ( $^1\text{H}$ ), 151 MHz ( $^{13}\text{C}$ ) and 565 MHz ( $^{19}\text{F}$ ) at 296 K in  $\text{CDCl}_3$  and  $\text{THF-}d_8$  ( $\text{THF-}d_8$  was dried using 4 Å molecular sieves). For the (multiple) solvent suppression No-D  $^1\text{H}$  NMR spectra the samples were shimmed using Topshim unlocked and acquired by using standard *wetdc* pulse program (solvent suppression with shape pulse, with  $^{13}\text{C}$  low power decoupling) from the Bruker Topspin library. Proton and carbon spectra are referenced to the residual solvent shifts of  $\delta$  7.26 and  $\delta$  77.20 ppm for  $\text{CDCl}_3$  and 1.72 and 25.31 for  $\text{THF-}d_8$ , respectively.  $^{19}\text{F}$ ,  $^{11}\text{B}$  and  $^{15}\text{N}$  chemical shifts were determined with respect to external  $\text{CCl}_3\text{F}$ , 15%  $\text{BF}_3$  etherate in  $\text{CDCl}_3$ , and ammonia, respectively, as external standards at  $\delta$  0. Assignments of proton, carbon, and nitrogen resonances were performed by 2D NMR techniques ( $^1\text{H-}^1\text{H}$  *gs*-COSY,  $^1\text{H-}^{13}\text{C}$  *gs*-HSQC,  $^1\text{H-}^{13}\text{C}$  *gs*-HMBC and  $^1\text{H-}^{15}\text{N}$  *gs*-HMBC).  $^{13}\text{C}$  resonances for Pd-mNHO (**7aPd** and **7bPd**) and Au-mNHO complexes (**7aAu** and **7bAu**) were extracted from the  $^1\text{H-}^{13}\text{C}$  *gs*-HSQC and  $^1\text{H-}^{13}\text{C}$  *gs*-HMBC spectra. Coupling constants (*J*) are given in hertz. Multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet). The starting 4-methylphenyl azide<sup>8</sup> [**Caution!** The handling of azides is dangerous because of their explosive character and all reactions should be carried out on a small scale], triazoles [4-phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole (**2a**) and 2-(1-(*p*-tolyl)-1*H*-1,2,3-triazol-4-yl)pyridine (**2b**)],<sup>8,9</sup> diaryliodonium salts [diphenyliodonium triflate and bis(4-methoxyphenyl)iodonium hexafluorophosphate]<sup>Error!</sup> **Bookmark not defined.** and triazolium salts [5-methyl-4-phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole (**2a'**)],<sup>10</sup> 3,4-diphenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazolium trifluoromethanesulfonate (**3a**)<sup>9</sup> and 3-phenyl-4-(2-pyridinyl)-1-(*p*-tolyl)-1*H*-1,2,3-triazolium trifluoromethanesulfonate (**3b**)<sup>9</sup>] were prepared according to the known literature procedures.

*Computational Details.* Gas-phase geometry optimizations of the non-truncated species were performed using density functional theory (DFT) as implemented in ORCA 5.0.<sup>11</sup> The

hybrid functional PBE0<sup>12,13</sup> was employed, in combination with the double- $\zeta$  valence basis set def2-SV(p). The chain of spheres exchange algorithm combined with the resolution of identity for the Coulombic term (RIJCOSX)<sup>14</sup> was used to speed up equilibrium structure searches. A grid quality of DEFGRID2 and a tight convergence of the wavefunction were requested. Grimme's D3 method, in combination with the Becke-Johnson (D3BJ) damping scheme<sup>15</sup> to consider dispersion effects was employed in all calculations. To validate that the optimized equilibrium structures correspond to local minima of the potential energy surface (PES), analytical vibrational frequency calculations were carried out at the same level of theory as used for geometry optimizations. Subsequent single-point calculations at the TPSSh-D3/def2-TZVPP(DEFGRID3) level of theory were carried out to refine further the energy and electronic wavefunction of the studied complexes.

### Synthesis of triazolium salts 1

*General procedure 1 (GPI) for preparation of triazolium salts.* Alkylated triazolium salts **1a**, **1b**, **1e** and **1f** were synthesized according to a modified literature procedure.<sup>16</sup> Triazolium salt (1 equiv.) was dissolved in dry THF in an oven-dried round-bottomed flask and cooled to  $-78$  °C. *n*-BuLi (1.5 equiv.) was added dropwise to the stirred solution. After 5 min alkyl iodide (4 equiv.) was added. The reaction mixture was stirred at  $-78$  °C for 1 h. After it had been allowed to warm to room temperature it was stirred for 1 h. The precipitate was collected by filtration and dissolved in dichloromethane/MeOH 10:1. The crude product solution was filtered over a pad of silica and solvent was removed under reduced pressure. **1a** and **1e** were dissolved in a small amount of dichloromethane and triturated with diethyl ether to afford a white solid product. **1f** was purified using column chromatography on silica (dichloromethane/methanol = 20:1).

*5-Methyl-3,4-diphenyl-1-(p-tolyl)-1H-1,2,3-triazolium trifluoromethanesulfonate (1a).* Following **GPI**. Prepared from 3,4-diphenyl-1-(*p*-tolyl)-1H-1,2,3-triazolium trifluoromethanesulfonate (**3a**, 1.300 g, 2.817 mmol), *n*-BuLi (1.6 M in THF, 2.29 mL, 3.67 mmol) and MeI (0.53 mL, 8.46 mmol) in THF (45 mL). Product was obtained as white solid (1.100 g, 82%). mp 258–260 °C. IR: 3047, 3023, 2164, 1619, 1587, 1512, 1491, 1453, 1386, 1261, 1173, 1073, 834, 782, 697  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.99 (d,  $J = 8.4$  Hz, 2H), 7.72–7.71 (m, 4H), 7.55–7.42 (m, 8H), 2.59 (s, 3H), 2.49 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta$  142.7, 140.9, 140.1, 134.3, 131.6, 131.5, 131.3, 131.1, 130.6, 129.7, 129.3, 126.4, 122.9, 21.6, 11.0. <sup>15</sup>N NMR (61 MHz, CDCl<sub>3</sub>):  $\delta$  253, 250. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$   $-78.23$ . HRMS (ESI+): calcd for C<sub>22</sub>H<sub>20</sub>N<sub>3</sub><sup>+</sup> [M]<sup>+</sup>, 326.1652; found, 326.1647.

*5-Ethyl-3,4-diphenyl-1-(p-tolyl)-1H-1,2,3-triazolium trifluoromethanesulfonate (1b).* Following **GPI**. Prepared from 3,4-diphenyl-1-(*p*-tolyl)-1H-1,2,3-triazolium trifluoromethanesulfonate (**3a**, 1.00 g, 2.17 mmol), *n*-BuLi (1.6 M in THF, 2.03 mL, 3.25 mmol) and EtI (0.70 mL, 8.68 mmol) in THF (35 mL). Product was obtained as white solid (0.68 g, 64%). mp 77–79 °C. IR: 3056, 2981, 2165, 1613, 1594, 1514, 1494, 1262, 1223, 1178, 1030, 829, 692, 636  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.92 (d,  $J = 8.3$  Hz, 2H), 7.68–7.67 (m, 4H), 7.51–7.48 (m, 2H), 7.45–7.41 (m, 6H), 2.95 (q,  $J = 7.7$  Hz, 2H), 2.49 (s, 3H), 1.06 (t,  $J = 7.7$  Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta$  144.3, 142.8, 140.5, 134.2, 131.6, 131.5, 131.3, 131.0, 130.6, 129.6, 129.3, 126.53, 126.49, 123.0, 21.6, 17.9, 12.2. <sup>15</sup>N NMR (61 MHz, CDCl<sub>3</sub>):  $\delta$  252, 251.

$^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ ):  $\delta$  -78.19. HRMS (ESI+): calcd for  $\text{C}_{23}\text{H}_{22}\text{N}_3^+$   $[\text{M}]^+$ , 340.1808; found, 340.1811.

*5-Methyl-3-phenyl-4-(2-pyridinyl)-1-(p-tolyl)-1H-1,2,3-triazolium trifluoromethanesulfonate (1e)*. Following **GP1**. Prepared from 3-phenyl-4-(2-pyridinyl)-1-(p-tolyl)-1H-1,2,3-triazolium trifluoromethanesulfonate (**3b**, 1.000 g, 2.162 mmol), *n*-BuLi (1.6 M in THF, 2.0 mL, 3.2 mmol) and MeI (0.5 mL, 8.6 mmol) in THF (36 mL). Product was obtained as white solid (0.728 g, 71%). mp 287–288 °C. IR: 3374, 2920, 1580, 1493, 1460, 1348, 1234, 1176, 836, 806, 693  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.65–8.64 (m, 1H), 8.22–8.20 (m, 1H), 7.93–7.91 (m, 2H), 7.80–7.76 (m, 3H), 7.56–7.53 (m, 1H), 7.48–7.44 (m, 4H), 7.42–7.39 (m, 1H), 2.62 (s, 3H), 2.48 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.3, 143.3, 143.1, 141.3, 139.9, 137.8, 134.4, 131.9, 131.2, 130.8, 129.8, 128.7, 126.4, 126.3, 125.7, 21.7, 11.0.  $^{15}\text{N}$  NMR (61 MHz,  $\text{CDCl}_3$ ):  $\delta$  253, 251. HRMS (ESI+): calcd for  $\text{C}_{21}\text{H}_{19}\text{N}_4^+$   $[\text{M}]^+$ , 327.1604; found, 327.1597.

*5-Ethyl-3-phenyl-4-(2-pyridinyl)-1-(p-tolyl)-1H-1,2,3-triazolium trifluoromethanesulfonate (1f)*. Following **GP1**. Prepared from 3-phenyl-4-(2-pyridinyl)-1-(p-tolyl)-1H-1,2,3-triazolium trifluoromethanesulfonate (**3b**, 0.973 g, 2.104 mmol), *n*-BuLi (1.6 M in THF, 1.7 mL, 2.7 mmol) and EtI (0.7 mL, 8.4 mmol) in THF (30 mL). Product was obtained as yellow solid (0.512 g, 50%). mp 240–241 °C. IR: 3732, 2018, 1574, 1511, 1262, 1018, 785, 695,  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.69–8.68 (m, 1H), 8.33 (d,  $J = 7.9$  Hz, 1H), 7.97 (d,  $J = 8.3$  Hz, 2H), 7.82–7.78 (m, 3H), 7.55–7.52 (m, 1H), 7.48–7.41 (m, 5H), 3.00 (q,  $J = 7.6$  Hz, 2H), 2.51 (s, 3H), 1.15 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.3, 145.6, 143.5, 143.2, 139.5, 137.8, 134.4, 131.8, 131.4, 130.8, 129.8, 128.9, 126.6, 126.5, 125.7, 21.7, 18.2, 12.4.  $^{15}\text{N}$  NMR (61 MHz,  $\text{CDCl}_3$ ):  $\delta$  252, 251. HRMS (ESI+): calcd for  $\text{C}_{22}\text{H}_{21}\text{N}_4^+$   $[\text{M}]^+$ , 341.1761; found, 341.1760.

*General procedure 2 (GP2) for preparation of triazolium salts*. Alkylated triazolium salts **1d** and **1g** were synthesized from corresponding triazolium salts according to a following procedure. Triazolium salt (1 equiv.) was combined with KO*t*-Bu (1 equiv.) and cooled to -78 °C. THF was added, and the mixture was stirred for 10 min. After the addition of *N,N*-dimethylmethyleammonium iodide (1 equiv.) the reaction mixture was warmed to room temperature and stirred overnight. The precipitate was filtered off and the solvent was evaporated. Crude products were purified using column chromatography on silica (dichloromethane/methanol = 20:1 → 10:1).

*5-((Dimethylamino)methyl)-3,4-diphenyl-1-(p-tolyl)-1H-1,2,3-triazolium trifluoromethanesulfonate (1d)*. Following **GP2**. Prepared from 3,4-diphenyl-1-(p-tolyl)-1H-1,2,3-triazolium trifluoromethanesulfonate (**3a**, 0.500 g, 1.084 mmol), KO*t*-Bu (0.122 g, 1.084 mmol) and *N,N*-dimethylmethyleammonium iodide (0.200 g, 1.084 mmol) in THF (10 mL). Product was obtained as white solid (0.243 g, 43%). mp 64–66 °C. IR: 3055, 2826, 2774, 1513, 1494, 1452, 1260, 1147, 1029, 826, 765, 692, 636  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.00–7.98 (m, 2H), 7.64–7.60 (m, 4H), 7.54–7.48 (m, 2H), 7.46–7.41 (m, 6H), 3.69 (s, 2H), 2.49 (s, 3H), 2.05 (s, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.9, 134.3, 132.1, 131.8, 131.5, 131.0, 130.5, 129.9, 129.5, 126.4, 126.3, 122.8, 121.9, 119.8, 50.9, 45.2, 21.6.  $^{15}\text{N}$  NMR (61 MHz,  $\text{CDCl}_3$ ):  $\delta$  251.0, 251.4, 256.  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ ):  $\delta$  -78.27. HRMS (ESI+): calcd for  $\text{C}_{24}\text{H}_{25}\text{N}_4^+$   $[\text{M}]^+$ , 369.2074; found, 369.2077.

*5-((Dimethylamino)methyl)-3-phenyl-4-(2-pyridinyl)-1-(p-tolyl)-1H-1,2,3-triazolium trifluoromethanesulfonate (1g)*. Following **GP2**. Prepared from 3-phenyl-4-(2-pyridinyl)-1-(p-tolyl)-1H-1,2,3-triazolium trifluoromethanesulfonate (**3b**, 0.518 g, 1.120 mmol), KO*t*-Bu (0.126 g, 1.120 mmol) and *N,N*-dimethylmethyleammonium iodide (0.207 g, 1.120 mmol) in THF (10 mL). Product was obtained as white solid (0.502 g, 86%). mp 115–118 °C. IR: 1578, 1513, 1494, 1456, 1342, 1261, 1225, 1149, 1032, 819, 798, 773, 691, 636 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.60–8.59 (m, 1H), 8.34–8.33 (m, 1H), 8.04–8.02 (m, 2H), 7.85–7.82 (m, 1H), 7.72–7.71 (m, 2H), 7.52–7.50 (m, 1H), 7.45–7.39 (m, 5H), 3.71 (s, 2H), 2.48 (s, 3H), 2.07 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 150.1, 143.2, 142.9, 141.2, 140.9, 137.7, 134.5, 131.9, 131.7, 130.4, 129.7, 128.5, 126.4, 126.3, 125.7, 51.4, 45.3, 21.6. <sup>15</sup>N NMR (61 MHz, CDCl<sub>3</sub>): δ 28, 251, 255, 318. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>): δ -78.30. HRMS (ESI+): calcd for C<sub>23</sub>H<sub>24</sub>N<sub>5</sub><sup>+</sup> [M]<sup>+</sup>, 370.2026; found, 370.2027.

*3-(4-Methoxyphenyl)-5-methyl-4-phenyl-1-(p-tolyl)-1H-1,2,3-triazolium hexafluorophosphate (1c)*. **1c** was prepared according to a slightly modified literature procedure.<sup>9</sup> In a high pressure tube 5-methyl-4-phenyl-1-(p-tolyl)-1H-1,2,3-triazole (**2a'**, 85 mg, 0.341 mmol) was combined with di-(4-methoxyphenyl)iodonium hexafluorophosphate (298 mg, 0.614 mmol) and CuSO<sub>4</sub> (5 mg, 0.0341 mmol). The reaction mixture was stirred overnight at 130 °C. The crude product was dissolved in acetone and triturated with light petroleum. It was filtered and purified using column chromatography on silica (dichloromethane/methanol = 30:1 → 10:1). **1c** was obtained as a white solid (95 mg, 56%). mp 83–85 °C. IR: 1605, 1509, 1257, 1174, 1056, 1026, 833, 774, 697 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.68–7.66 (m, 2H), 7.47–7.44 (m, 3H), 7.41–7.35 (m, 6H), 6.84–6.83 (m, 2H), 3.78 (s, 3H), 2.44 (s, 3H), 2.40 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 161.8, 142.8, 140.6, 139.2, 131.5, 131.3, 130.8, 130.6, 129.5, 127.4, 126.9, 125.9, 123.0, 115.0, 55.8, 21.6, 10.0. <sup>15</sup>N NMR (51 MHz, CDCl<sub>3</sub>): δ 253, 250. <sup>31</sup>P NMR (243 MHz, CDCl<sub>3</sub>): δ -144.7. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>): δ -73.65. HRMS (ESI+): calcd for C<sub>23</sub>H<sub>22</sub>N<sub>3</sub>O<sup>+</sup> [M]<sup>+</sup>, 356.1757; found 356.1758.

*4-(Diphenylphosphino)-5-propyl-1-(p-tolyl)-1H-1,2,3-triazole (5)*. Prepared according to a literature procedure.<sup>17</sup> In an oven-dried round-bottomed flask ethylmagnesium bromide (15.0 mmol, 1 M solution in THF) was diluted in 30 mL THF. Pentyne (1.48 mL, 15.0 mmol) was added dropwise. The reaction mixture was heated to 50 °C and stirred for 15 min. After cooling to room temperature 4-methylphenyl azide (2.197 g, 16.50 mmol) was added. The reaction was stirred for 30 min at room temperature and for 1 h at 50 °C. After cooling to room temperature, a solution of PPh<sub>2</sub>Cl (3.23 mL, 18.0 mmol) in THF (15 mL) was added and the mixture was stirred for 5 h at room temperature. The reaction was quenched with water (100 mL) and the product was extracted with ethyl acetate. Combined organic phases were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure and the product was purified using column chromatography on silica (light petroleum/ethyl acetate = 10:1 → 1:1). The product **5** was obtained as a yellowish solid (2.958 g, 51%). mp 96–97 °C. IR: 3060, 2959, 2927, 1518, 1478, 1434, 1246, 1177, 1091, 998, 821, 742, 695, 629 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.62–7.59 (m, 4H), 7.36–7.31 (m, 10H), 2.85–2.82 (m, 2H), 2.45 (s, 3H), 1.47–1.40 (m, 2H), 0.78 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 144.8 (d, *J* = 40.3 Hz), 140.0, 139.7 (d, *J* = 9.9 Hz), 136.9 (d, *J* = 4.3 Hz), 134.2, 133.9 (d, *J* = 20.4 Hz) 130.2, 128.8, 128.5 (d, *J* = 7.2 Hz), 125.5, 25.3 (d, *J* = 6.5 Hz), 23.1 (d, *J* = 2.7 Hz), 21.4, 13.9. <sup>15</sup>N NMR (61 MHz, CDCl<sub>3</sub>): δ 254. <sup>31</sup>P{H} NMR (243 MHz, CDCl<sub>3</sub>): δ -37.9. HRMS (ESI+): calcd for C<sub>24</sub>H<sub>25</sub>N<sub>3</sub>P<sup>+</sup> [M + H]<sup>+</sup>, 368.1781; found, 368.1776.

[4-(Diphenylphosphino)-1-phenyl-5-propyl-1*H*-1,2,3-triazole]trihydroboron (**6**). In an oven-dried round-bottomed flask triazole **5** (700 mg, 1.816 mmol) was dissolved in dry THF (4 mL). BH<sub>3</sub>·THF solution (1 M, 3.1 mL, 3.1 mmol) was added and the reaction mixture was stirred for 1 h at room temperature. Reaction was quenched with the addition of water (10 mL) and the product was extracted with dichloromethane. Combined organic phases were dried over sodium sulphate and the solvent was evaporated under reduced pressure. Isolated product (666 mg, 92%) was used in the next step without further purification. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.83–7.79 (m, 4H), 7.51–7.43 (m, 6H), 7.36–7.34 (m, 2H), 7.31–7.30 (m, 2H), 2.97–2.93 (m, 2H), 2.46 (s, 3H), 1.35–1.29 (m, 2H), 0.73 (t, *J* = 7.3 Hz, 3H). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>): δ 3.4 (br). <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>): δ –38.3.

4-(Diphenylphosphino)-3-methyl-5-propyl-1-(*p*-tolyl)-1*H*-1,2,3-triazolium tetrafluoroborate (**1h**). An oven-dried round-bottomed flask was charged with 4-(diphenylphosphino)-5-propyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole (**5**, 1.005 g, 2.607 mmol) and cooled to 0 °C. Trimethyloxonium tetrafluoroborate (0.386 g, 2.607 mmol) and dry dichloromethane (8 mL) were added and reaction mixture was stirred at room temperature for 3 h. The solvent was evaporated and products were separated using column chromatography on silica (ethyl acetate). The product **1h** was obtained as a slightly yellow solid (0.575 g, 45%). mp 65–66 °C. IR: 2964, 1512, 1436, 1378, 1047, 1033, 833, 747, 729, 695 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.53–7.48 (m, 10H), 7.36 (d, *J* = 8.1 Hz, 2H), 4.11 (s, 3 H), 2.44 (s, 3H), 2.23–2.19 (m, 2H), 1.11–1.03 (m, 2H), 0.42 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 148.6 (d, *J* = 6.2 Hz), 141.9, 135.9, 135.5, 132.9, 132.7, 130.2, 129.9, 129.8, 128.94, 128.88, 127.83, 127.78, 125.3, 39.2 (d, *J* = 9.2 Hz), 24.5, 21.1, 20.6, 12.8. <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>): δ –28.5. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): δ –153.9. HRMS (ESI+): calcd for C<sub>25</sub>H<sub>27</sub>N<sub>3</sub>P<sup>+</sup> [M]<sup>+</sup>, 400.1937; found, 400.1929.

Triphenyl(5-propyl-1-(*p*-tolyl)-1*H*-1,2,3-triazol-4-yl)phosphonium trifluoromethanesulfonate (**1j**). An oven-dried round-bottomed flask was charged with [4-(diphenylphosphino)-1-phenyl-5-propyl-1*H*-1,2,3-triazole]trihydroboron (**6**, 0.666 g, 1.668 mmol), diphenyliodonium triflate (1.292 g, 3.002 mmol) and CuSO<sub>4</sub> (27 mg, 0.167 mmol). *N,N*-Dimethylformamide (4 mL) was added, and the reaction mixture was stirred overnight at 100 °C under Ar. The solvent was evaporated and the product **1j** was purified using column chromatography on silica (dichloromethane/methanol = 20:1 → 10:1). The product was obtained as an off-white solid (0.532 g, 52%). mp 62–63 °C. IR: 3064, 2965, 1511, 1438, 1259, 1222, 1146, 1108, 1028, 996, 824, 753, 724, 688, 635 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.89–7.76 (m, 15H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 2.46 (s, 3H), 2.28–2.25 (m, 2H), 0.92–0.84 (m, 2H), 0.34 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 150.0 (d), 141.6, 135.9 (d), 134.6 (d), 132.4, 130.8 (d), 130.7, 126.0, 123.9, 122.8, 122.4, 119.8, 118.0, 117.3, 25.4, 22.5, 21.5, 13.8. <sup>15</sup>N NMR (CDCl<sub>3</sub>): δ 261. <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ 9.6. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>): δ –78.14. HRMS (ESI+): calcd for C<sub>30</sub>H<sub>29</sub>N<sub>3</sub>P<sup>+</sup> [M]<sup>+</sup>, 462.2094; found, 462.2095.

## Synthesis of mNHOs

*General procedure 3 (GP3) for preparation of mNHOs 7.* mNHOs **7** were prepared according to a slightly modified literature procedure.<sup>18</sup> In a Schlenk tube triazolium salts **1** (1 equiv.) were combined with KHMDS (1.05 equiv.) and dissolved in THF. Reaction mixture instantly turned dark blue (**7d**, **7e**, **7f**), green (**7g**) purple (**7a**, **7b**, **7c**) or red (**8j**) colour. It was left stirring at room temperature for 15 min.

**7a.** Prepared from **1a** according to **GP3**. <sup>1</sup>H NMR (600 MHz, THF-*d*<sub>8</sub>): δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.45–7.39 (m, 5H), 7.24–7.18 (m, 6H), 7.13–7.10 (m, 1H), 3.25 (d, *J* = 2.1 Hz, 1H), 3.18 (d, *J* = 2.1 Hz, 1H), 2.34 (s, 3H). <sup>13</sup>C NMR (151 MHz, THF-*d*<sub>8</sub>): δ 146.1, 138.0, 137.9, 135.7, 130.6, 130.22, 130.20, 130.0, 129.1, 129.0, 127.5, 126.2, 121.7, 120.1, 46.8, 21.1. <sup>15</sup>N NMR (61 MHz, THF-*d*<sub>8</sub>): δ 291, 241, 192.

**7b.** Prepared from **1b** according to **GP3**. In <sup>1</sup>H NMR spectra all resonances for the two isomers are overlapping. <sup>1</sup>H NMR (600 MHz, THF-*d*<sub>8</sub>): δ 7.56–7.55 (m, 2H), 7.37–7.30 (m, 6H), 7.19–7.17 (m, 4H), 7.14–7.09 (m, 3H), 3.88–3.82 (m, 1H), 2.33 (s, 3H), 1.27–1.24 (m, 3H). <sup>13</sup>C NMR (151 MHz, THF-*d*<sub>8</sub>): δ 141.7, 141.5, 138.7, 138.12, 138.10, 137.8, 135.0, 134.9, 131.4, 130.8, 130.33, 130.27, 130.2, 130.1, 129.9, 129.7, 129.4, 129.3, 129.1, 128.3, 127.7, 127.5, 126.6, 126.1, 123.1, 122.0, 121.4, 119.4, 61.9, 58.5, 21.0, 14.8, 13.2. <sup>15</sup>N NMR (61 MHz, THF-*d*<sub>8</sub>): δ 183, 242, 292.

**7c.** Prepared from **1c** according to **GP3**. <sup>1</sup>H NMR (600 MHz, THF-*d*<sub>8</sub>): δ 7.62–7.61 (m, 2H), 7.33–7.31 (m, 2H), 7.24–7.19 (m, 6H), 7.12–7.10 (m, 1H), 6.93–6.92 (m, 2H), 3.78 (s, 3H), 3.23 (d, *J* = 1.9 Hz, 1H), 3.16 (d, *J* = 1.9 Hz, 1H), 2.34 (s, 3H). <sup>13</sup>C NMR (151 MHz, THF-*d*<sub>8</sub>): δ 161.6, 146.0, 137.9, 135.6, 130.6, 130.4, 130.2, 129.1, 127.4, 127.3, 121.7, 120.0, 115.0, 55.8, 46.6, 21.1. <sup>15</sup>N NMR (61 MHz, THF-*d*<sub>8</sub>): δ 290, 240, 191.

**7d.** Prepared from **1d** according to **GP3**. Two isomeric products in a 1:0.45 (A:B) ratio. Resonances for aromatic protons of the different isomers cannot be separated. A: <sup>1</sup>H NMR (600 MHz, THF-*d*<sub>8</sub>): δ 7.53–7.07 (m, 14H), 4.84 (s, 1H), 2.31 (s, 3H), 2.03 (s, 6H). <sup>15</sup>N NMR (61 MHz, THF-*d*<sub>8</sub>): δ 25, 182, 240, 289. B: <sup>1</sup>H NMR (600 MHz, THF-*d*<sub>8</sub>): δ 7.53–7.07 (m, 14H), 4.67 (s, 1H), 2.33 (s, 3H), 1.96 (s, 6H). <sup>15</sup>N NMR (61 MHz, THF-*d*<sub>8</sub>): δ 20, 242. <sup>13</sup>C NMR (151 MHz, THF-*d*<sub>8</sub>): δ 138.9 (B), 138.1 (B), 137.0 (A), 134.9 (B), 133.0 (A), 132.84, 132.77, 132.6 (A), 131.4, 130.3, 130.1 (B), 129.9, 129.90, 129.86, 129.75, 129.4 (A), 129.1 (A), 128.0 (A), 127.6, 126.90, 126.87, 126.5, 126.2, 122.9, 121.9 (A), 121.7 (B), 120.0 (A), 119.7 (B), 92.7 (A), 90.2 (B), 47.7 (B), 45.0 (A), 21.1 (A), 21.0 (B). Some resonances could not be unambiguously assigned to isomer A or B.

**7e.** Prepared from **1e** according to **GP3**. <sup>1</sup>H NMR (600 MHz, THF-*d*<sub>8</sub>): δ 8.22–8.21 (m, 1H), 7.62–7.61 (m, 2H), 7.55–7.52 (m, 1H), 7.44–7.39 (m, 5H), 7.27–7.26 (m, 3H), 6.88–6.86 (m, 1H), 3.54 (d, *J* = 1.8 Hz, 1H), 3.34 (d, *J* = 1.9 Hz, 1H), 2.36 (s, 3H). <sup>13</sup>C NMR (151 MHz, THF-*d*<sub>8</sub>): δ 149.7, 148.9, 145.6, 139.4, 137.2, 136.7, 136.2, 130.4, 130.2, 129.6, 126.1, 122.9, 121.6, 120.1, 118.8, 45.5, 21.1. <sup>15</sup>N NMR (61 MHz, THF-*d*<sub>8</sub>): δ 196, 242, 300, 312.

**7f.** Prepared from **1f** according to **GP3**. Two isomeric products in 1:0.5 ratio, all proton resonances except for olefinic -CH- are overlapping. <sup>1</sup>H NMR (600 MHz, THF-*d*<sub>8</sub>): δ 8.25–8.24 (m, 1H), 7.56–7.52 (m, 1H), 7.47–7.32 (m, 7H), 7.22–7.20 (m, 2H), 7.10–7.08 (m, 1H), 6.94–6.84 (m, 1H), 4.40 (A, q, *J* = 7.3 Hz, 1H), 3.89 (B, q, *J* = 7.2 Hz, 1H), 2.34 (s, 3H), 1.27–1.24 (m, 3H). <sup>13</sup>C NMR (151 MHz, THF-*d*<sub>8</sub>): δ 149.8, 149.4, 149.3, 149.0, 141.6, 140.4, 139.4,



138.6, 138.5, 137.7, 135.9, 135.7, 135.62, 135.60, 130.3, 130.2, 129.7, 129.5, 129.4, 129.3, 126.7, 126.1, 125.5, 123.6, 122.5, 122.0, 121.1, 120.2, 120.0, 119.0, 63.9, 59.3, 21.1, 14.7, 13.9. <sup>15</sup>N NMR (61 MHz, THF-*d*<sub>8</sub>): δ 319, 251.

**7g.** Prepared from **1g** according to **GP3**. Two isomeric products in a 1:0.6 (A:B) ratio. Resonances for aromatic protons of different isomers cannot be separated. A: <sup>1</sup>H NMR (600 MHz, THF-*d*<sub>8</sub>): δ 8.30–6.83 (m, 13H), 5.45 (s, 1H), 2.32 (s, 3H), 2.05 (s, 6H). <sup>15</sup>N NMR (61 MHz, THF-*d*<sub>8</sub>): δ 26, 186, 243, 299. B: <sup>1</sup>H NMR (600 MHz, THF-*d*<sub>8</sub>): δ 8.02–6.83 (m, 13H), 4.69 (s, 1H), 2.34 (s, 3H), 2.01 (s, 6H). <sup>13</sup>C NMR (151 MHz, THF-*d*<sub>8</sub>): δ 149.7 (A), 148.8 (B), 148.4 (A), 147.8, 139.3, 138.3 (B), 137.7, 136.9, 135.6 (B), 134.1, 133.9 (A), 131.4 (A), 130.3 (B), 130.2, 129.81, 129.76, 129.2, 128.0 (A), 127.6, 126.7, 126.4, 126.3, 122.4 (A), 122.3, 122.1, 120.5, 119.7, 119.0 (B), 118.9 (A), 94.5 (A), 90.1(B), 47.4 (B), 44.9 (A), 21.10 (A), 21.06 (B).

**8j.** Prepared from **1j** according to **GP3**. Two isomeric products in a 1:0.9 (A:B) ratio. Resonances for phenyl protons of different isomers cannot be separated. A: <sup>1</sup>H NMR (600 MHz, THF-*d*<sub>8</sub>): δ 7.79–7.71 (m, 6H), 7.66–7.62 (m, 3H), 7.57–7.53 (m, 6H), 7.48–7.46 (m, 2H), 7.11–7.10 (m, 2H), 3.67 (t, *J* = 7.2 Hz, 1H), 2.29 (s, 3H), 1.43–1.38 (m, 2H), 0.32 (t, *J* = 7.2 Hz, 3H). B: <sup>1</sup>H NMR (600 MHz, THF-*d*<sub>8</sub>): δ 7.79–7.71 (m, 6H), 7.66–7.62 (m, 3H), 7.57–7.53 (m, 6H), 7.23–7.21 (m, 2H), 7.08–7.06 (m, 2H), 2.68 (t, *J* = 6.4 Hz, 1H), 2.28 (s, 3H), 1.51–1.46 (m, 2H), 0.51 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (151 MHz, THF-*d*<sub>8</sub>): δ 141.5 (B, d, *J* = 28.9 Hz, C5), 141.1 (A, d, *J* = 29.0 Hz, C5), 140.5 (B), 139.8 (A), 135.05, 135.01, 134.98, 134.94, 133.7 (d, *J* = 2.5 Hz), 133.5 (d, *J* = 3.0 Hz), 133.23, 133.20, 130.0, 129.9, 129.8, 129.7, 129.1 (B), 127.8 (d, *J* = 93.6 Hz), 126.5, 124.5 (d, *J* = 92.7 Hz), 123.5 (B), 122.7 (A), 89.0 (B, C4)\*, 88.0 (A, d, *J* = 152.8 Hz, C4), 75.0 (B), 69.2 (A), 26.1 (A) 24.0 (B), 21.1, 21.0, 17.2 (A), 16.5 (B). Not all doublets resulting from carbon-phosphorous coupling could be identified. Some resonances are listed as read from the spectrum. \*Coupling constant *J*<sub>CP</sub> could not be determined from the spectra due to insufficient signal/noise ratio.

## Synthesis of mNHO complexes

*General procedure 4 (GP4) for preparation of palladium complexes.* In a Schlenk tube triazolium salt **1** (1 equiv.) was combined with KHMDS (1.05 equiv.). THF was added and the solution was stirred for 10 min. [Pd(allyl)Cl]<sub>2</sub> (0.5 equiv.) was dissolved in THF and the solution was added dropwise to mNHO. After 15 min of stirring the solvent was evaporated and the product extracted into diethyl ether. Solvent was removed to afford product as a light yellow solid.

**7aPd.** Prepared from **1a** according to **GP4**. The product was dissolved in Et<sub>2</sub>O and layered with pentane to afford pure **7aPd**. <sup>1</sup>H NMR (600 MHz, THF): δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.69–7.68 (m, 2H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.49–7.42 (m, 3H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.26–7.25 (m, 3H), 4.84–4.77 (m, 1H), 3.79–3.78 (m, 1H), 3.25–3.24 (m, 1H), 2.57 (d, *J* = 13.2 Hz, 2H), 2.38 (s, 3H), 2.33 (d, *J* = 9.6 Hz, 1H), 2.19 (d, *J* = 11.8 Hz, 1H), 2.01 (d, *J* = 9.6 Hz, 1H). <sup>13</sup>C NMR (151 MHz, THF): δ 161.6, 140.6, 135.8, 133.4, 130.9, 130.2, 130.6, 129.4, 129.3, 128.9, 128.0, 126.4, 125.7, 109.9, 63.6, 53.7, 20.2, –1.6. <sup>13</sup>C chemical shifts are extracted from <sup>1</sup>H–<sup>13</sup>C *gs*-HSQC and <sup>1</sup>H–<sup>13</sup>C *gs*-HMBC spectra. HRMS (ESI+): calcd for C<sub>25</sub>H<sub>24</sub>N<sub>3</sub>Pd<sup>+</sup> [M – Cl]<sup>+</sup>, 472.1005; found, 472.1008.

**7bPd.** Prepared from **1b** according to **GP4**. Two isomeric products in a 1:0.9 (A:B) ratio. Resonances for aromatic protons of different isomers cannot be separated.  $^1\text{H}$  NMR (600 MHz, THF):  $\delta$  8.00–7.97 (m, H), 7.91 (d,  $J = 5.9$  Hz, H), 7.86 (d,  $J = 6.6$  Hz, H), 7.56–7.55 (m, H), 7.42–7.31 (m, H), 7.25–7.22 (m, H), 4.93–4.88 (m, 1H), 4.87–4.80 (m, 1H), 3.75 (d,  $J = 6.5$  Hz, 1H), 3.69 (d,  $J = 6.9$  Hz, 1H), 3.31–3.29 (m, 1H, B), 3.26 (d,  $J = 5.3$  Hz, 1H), 3.06 (d,  $J = 5.2$  Hz, 1H), 2.98 (q,  $J = 6.9$  Hz, 1H, A), 2.67 (d,  $J = 13.3$  Hz, 1H), 2.50 (d,  $J = 13.3$  Hz, 1H), 2.24 (d,  $J = 11.7$  Hz, 1H), 2.19 (d,  $J = 11.5$  Hz, 1H), 1.26 (d,  $J = 6.8$  Hz, 3H, A), 1.13 (d,  $J = 6.9$  Hz, 3H, B).  $^{13}\text{C}$  NMR (151 MHz, THF):  $\delta$  162.3, 162.2, 140.5, 135.4, 135.3, 133.4, 133.3, 132.0, 131.9, 130.7 (A and B), 130.2, 128.9, 127.3, 126.9, 125.7, 111.4, 109.8, 63.4, 62.4, 56.1, 56.0, 20.1, 18.6, 18.1, 10.9, 10.7.  $^{13}\text{C}$  chemical shifts are extracted from  $^1\text{H}$ - $^{13}\text{C}$  *gs*-HSQC and  $^1\text{H}$ - $^{13}\text{C}$  *gs*-HMBC spectra.

*General procedure 5 (GP5) for preparation of gold complexes.* In a Schlenk tube triazolium salt **1** (1 equiv.) was combined with KHMDS (1.05 equiv.). THF was added and purple solution was stirred for 10 min. AuCl(SMe<sub>2</sub>) (1 equiv.) was mixed with THF and the mNHO solution was added dropwise to the mixture. Reaction mixture was stirred for 10 minutes as it turned dark yellow and the solvent was evaporated.

**7aAu.** Prepared from **1a** according to **GP5**.  $^1\text{H}$  NMR (500 MHz, THF):  $\delta$  8.00–7.99 (m, 2H), 7.63–7.62 (m, 2H), 7.55–7.52 (m, 3H), 7.48–7.45 (m, 4H), 7.39–7.38 (m, 3H), 2.43 (s, 3H), 2.15 (s, 2H).  $^{13}\text{C}$  NMR (151 MHz, THF):  $\delta$  152.6, 141.5, 132.4, 131.4, 131.1, 130.0, 129.9, 128.9, 125.5, 125.2, 125.0, 20.3, 15.2.  $^{13}\text{C}$  chemical shifts are extracted from  $^1\text{H}$ - $^{13}\text{C}$  *gs*-HSQC and  $^1\text{H}$ - $^{13}\text{C}$  *gs*-HMBC spectra. HRMS (ESI<sup>+</sup>): calcd for C<sub>22</sub>H<sub>19</sub>AuN<sub>3</sub><sup>+</sup> [M – Cl]<sup>+</sup>, 522.1239; found, 522.1234.

**7bAu.** Prepared from **1b** according to **GP5**. Two isomeric products in A:B = 1:0.7 ratio. Resonances for aromatic protons of different isomers cannot be separated.  $^1\text{H}$  NMR (600 MHz, THF):  $\delta$  8.05–8.03 (m, 2H), 7.72 (m, 2H), 7.51–7.37 (m, 10H), 2.84 (q,  $J = 7.2$  Hz, 1H, B), 2.79 (q,  $J = 7.2$  Hz, 1H, A), 2.42 (s, 3H), 2.41 (s, 3H), 1.23 (d,  $J = 7.0$  Hz, 3H, A), 1.18 (d,  $J = 7.2$  Hz, 3H, B).  $^{13}\text{C}$  NMR (151 MHz, THF):  $\delta$  155.3 (B), 154.8 (A), 141.8, 135.1, 133.3 (B), 133.1 (A), 131.2, 131.0, 130.3, 130.1, 129.8, 128.9, 126.0, 125.9, 125.5, 26.0 (A), 20.7, 17.5 (B), 17.0 (A), 15.6 (B).  $^{15}\text{N}$  NMR (61 MHz, THF):  $\delta$  250, 249, 241 (B), 242 (A).  $^{13}\text{C}$  chemical shifts are extracted from  $^1\text{H}$ - $^{13}\text{C}$  *gs*-HSQC and  $^1\text{H}$ - $^{13}\text{C}$  *gs*-HMBC spectra.

**Synthesis of palladium complex 9hPd.** In a round bottomed flask **1h** (100 mg, 0.205 mmol) was combined with PdCl<sub>2</sub> (18 mg, 0.103 mmol). Dichloromethane (3 mL) was added, and the reaction mixture was stirred overnight at room temperature. Solvent was evaporated to afford a light yellow solid (225 mg, 95%). Crystals appropriate for X-ray diffraction analysis were obtained from a CDCl<sub>3</sub> solution. mp 210–211 °C. IR: 2966, 1510, 1437, 1372, 1059, 1016, 997, 835, 759, 694 cm<sup>-1</sup>.  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.44–8.40 (m, 4H), 7.74–7.70 (m, 6H), 7.57 (d,  $J = 8.3$  Hz, 2H), 7.37 (d,  $J = 8.2$  Hz, 2H), 4.06 (s, 3H), 2.44 (s, 3H), 1.88–1.85 (m, 2H), 1.19–1.11 (m, 2H), 0.40 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  150.4, 143.3, 136.5 (t), 134.1, 130.9, 130.7, 130.6, 130.4 (t), 126.5, 122.4 (t), 42.3, 25.5, 22.3, 21.6, 14.0.  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>):  $\delta$  11.2.  $^{19}\text{F}$  NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -151.17.

**Synthesis of mNHO-borane adduct 10aBH<sub>3</sub>.** In a Schlenk flask **1a** (685 mg, 1.44 mmol) was dried under vacuum for 2 h. After filling the flask with nitrogen, KHMDS (315 mg, 1.58 mmol) was added. The solid mixture was cooled to  $-78\text{ }^{\circ}\text{C}$  and dry THF (27 mL) was added. The reaction mixture instantly turned deep purple, indicating mNHO formation. After stirring for 20 min BH<sub>3</sub>·THF (1 M, 1.44 mL, 1.44 mmol) was added. The reaction mixture was stirred for 2 h at  $-78\text{ }^{\circ}\text{C}$ . After it had been allowed to warm to room temperature it was stirred overnight and filtered. Volatiles were removed under reduced pressure to afford yellow solid. The crude product was dissolved in dichloromethane, top-layered with hexane and left at  $-22\text{ }^{\circ}\text{C}$  overnight. The supernatant was decanted off to obtain crystalline **10aBH<sub>3</sub>** (262 mg, 53%). mp 97–99  $^{\circ}\text{C}$ . IR: 3056, 2250, 1582, 1512, 1493, 1437, 1376, 1346, 1263, 1208, 1119, 823, 768, 693  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.94–7.92 (m, 2H), 7.67–7.66 (m, 2H), 7.57–7.54 (m, 1H), 7.50–7.47 (m, 2H), 7.43–7.38 (m, 7H), 2.47 (s, 3H), 2.08 (br, 2H), 1.28–0.76 (br q, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  157.2, 141.8, 135.1, 135.0, 132.7, 131.4, 130.7, 130.5, 130.4, 130.1, 129.2, 125.8, 125.2, 124.6, 21.6, 14.3 (br). <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>):  $\delta$   $-26.8$  (q,  $J = 86.1$  Hz).

**Details on optimization of the reaction conditions for reduction of 3-phenylpropionaldehyde (11a) with 10aBH<sub>3</sub>.** Stirring a solution of **11a** (0.058 M) with **10aBH<sub>3</sub>** (1 equiv.) in acetonitrile for 3 h resulted in the quantitative formation of 3-phenylpropanol (**12a**). Other reaction solvents such as ethyl acetate, methanol, THF, and toluene were tested and found to be equally effective. Reducing the molar ratio of **10aBH<sub>3</sub>**/aldehyde from 1 to 0.5 and 0.33 also had no effect on the conversion (>90%).

**General procedure 7 (GP7) for reduction of aldehydes.** A round-bottomed flask was charged with aldehyde (0.1 mmol), **10aBH<sub>3</sub>** (0.05 mmol) and trimethoxybenzene (0.05 mmol). Acetonitrile (0.5 mL) was added, and the reaction mixture was stirred in the presence of air at room temperature. The conversion to product after 1, 4 and 24 h was determined by <sup>1</sup>H NMR analysis. The products were identified by comparison of the spectra with those for authentic samples of alcohols **12**.

**General procedure 8 (GP8) for reduction of ketones.** A round-bottomed flask was charged with **10aBH<sub>3</sub>** (0.05 mmol), silica gel (100 mg), trimethoxybenzene (0.05 mmol) and ketone (0.1 mmol). Acetonitrile (0.5 mL) was added, and the reaction mixture was stirred in the presence of air at room temperature. The conversion to product after 1, 4 and 24 h was determined by <sup>1</sup>H NMR analysis. The products were identified by comparison of the spectra with those for authentic samples of alcohols **14**.

**Table S4.** Reduction of aldehydes **11** into primary alcohols **12**.

Product	Conversion after 4 h (%) <sup>#</sup>	Conversion after 24 h (%) <sup>#</sup>
4-bromobenzyl alcohol, <b>12b</b>	25	61
3-nitrobenzyl alcohol, <b>12c</b>	44	44
3,4,5-methoxybenzyl alcohol, <b>12d</b>	8	21

<sup>#</sup> Conversion was determined by <sup>1</sup>H NMR with 1,3,5-trimethoxybenzene as internal standard. For copies of <sup>1</sup>H NMR spectra, see below.

**Table S5.** Reduction of ketones **13** into secondary alcohols **14**.

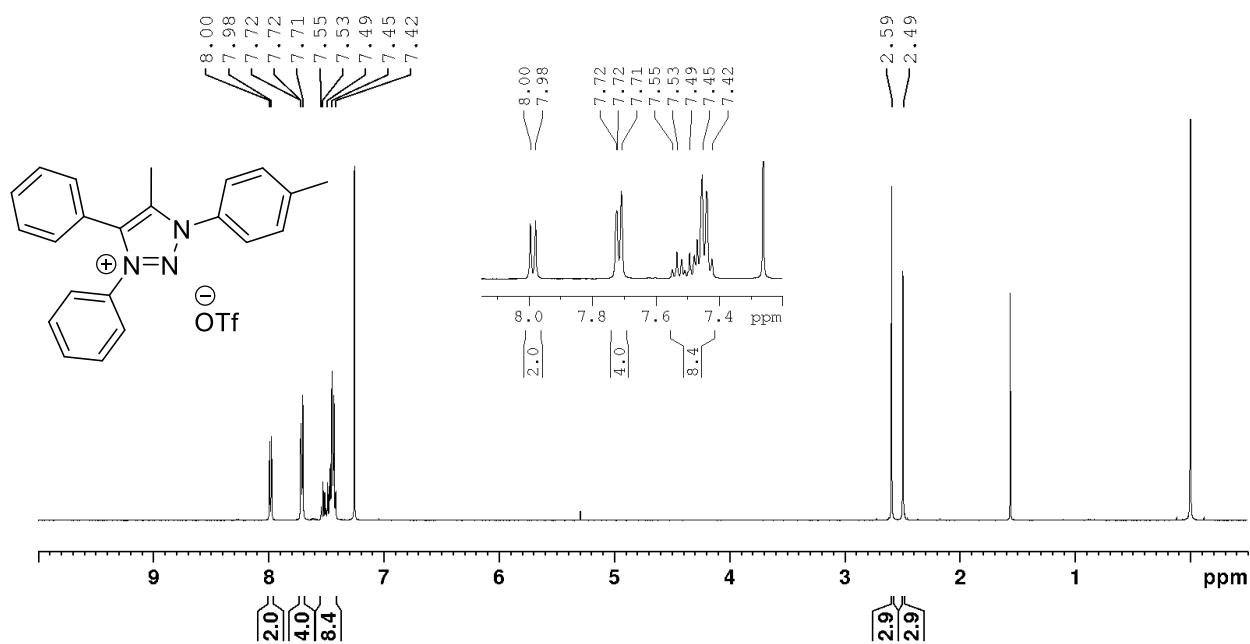
Product	Conversion after 4 h (%) <sup>#</sup>	Conversion after 24 h (%) <sup>#</sup>
1-(4-nitrophenyl)ethanol, <b>14a</b>	70	76
1-(4-bromophenyl)ethanol, <b>14b</b>	62	66
1-(3-aminophenyl)ethanol, <b>14c</b>	39	50
1-(4-methoxyphenyl)ethanol, <b>14d</b>	35	39
diphenylmethanol, <b>14e</b>	38	46

<sup>#</sup> Conversion was determined by <sup>1</sup>H NMR with 1,3,5-trimethoxybenzene as internal standard. For copies of <sup>1</sup>H NMR spectra, see below.

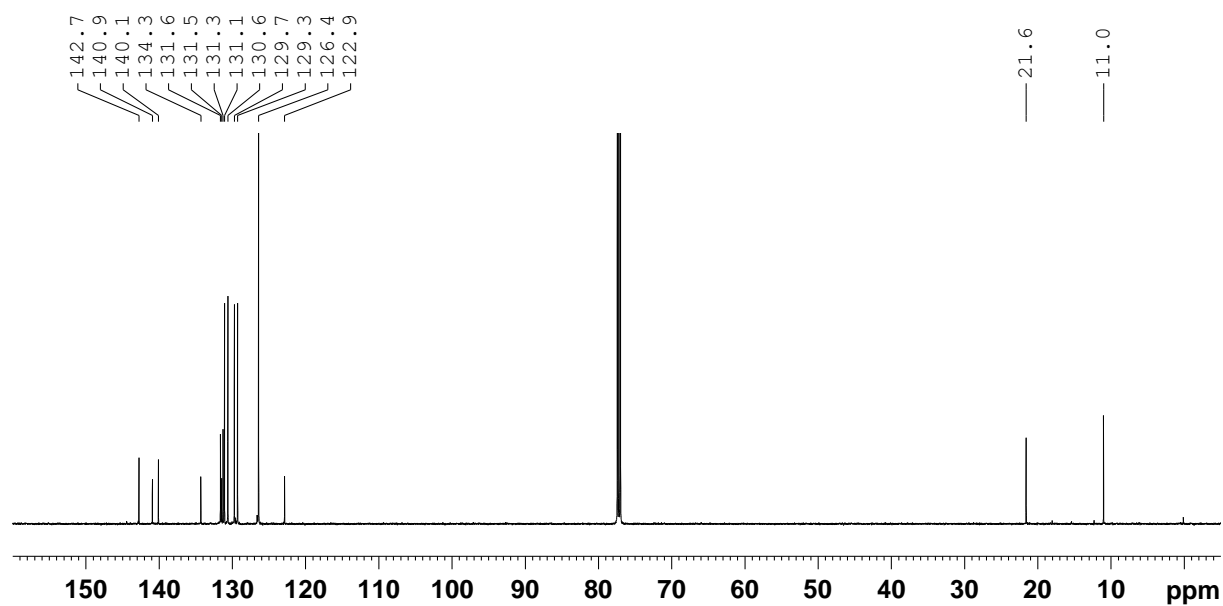
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## 5. Copies of NMR spectra



**Figure S11.**  $^1\text{H}$  NMR spectrum of **1a** in  $\text{CDCl}_3$ , 500 MHz.



**Figure S12.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1a** in  $\text{CDCl}_3$ , 151 MHz.

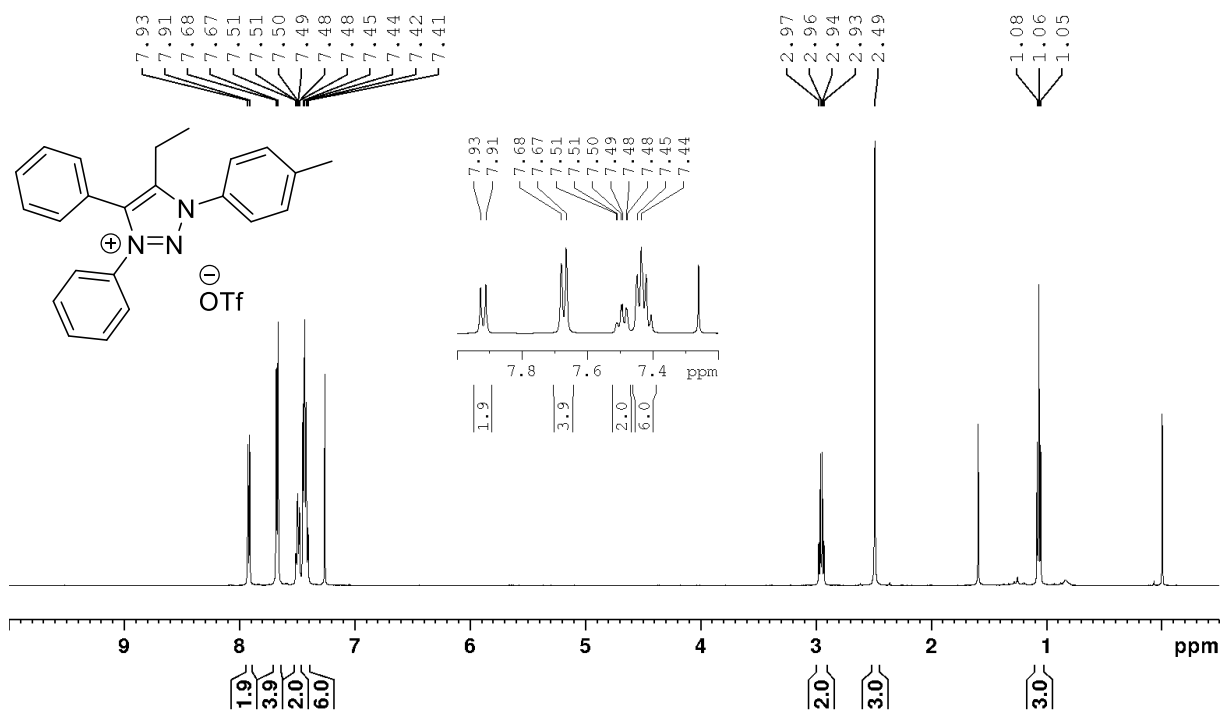


Figure S13. <sup>1</sup>H NMR spectrum of **1b** in CDCl<sub>3</sub>, 500 MHz.

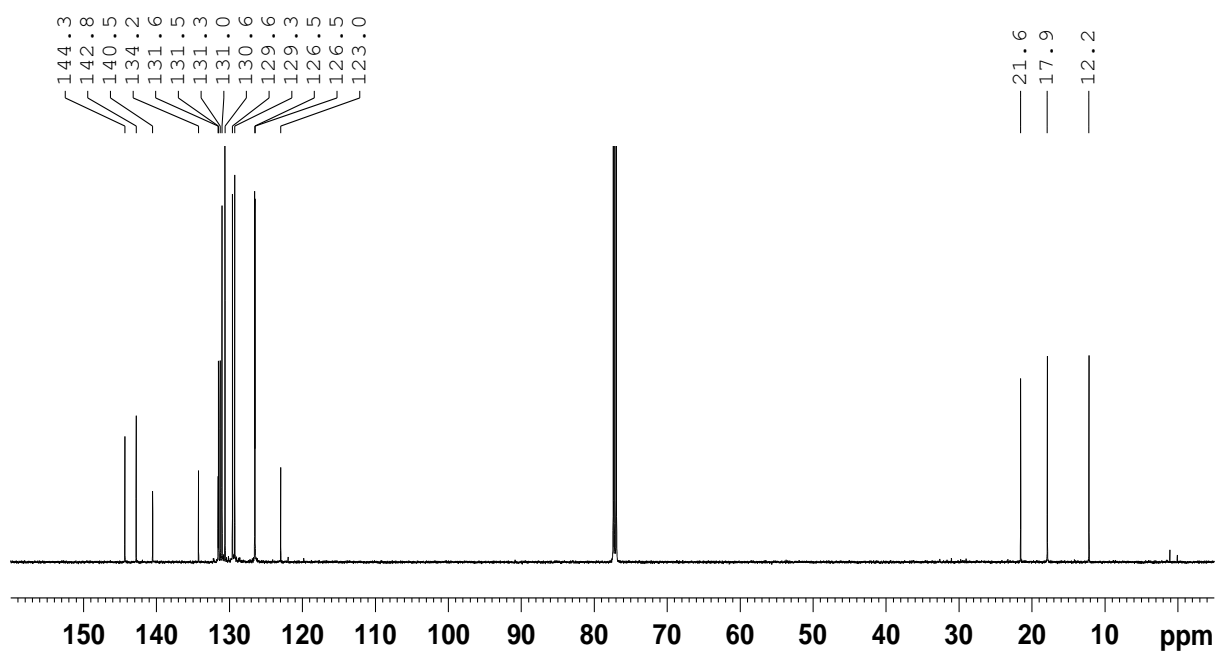


Figure S14. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **1b** in CDCl<sub>3</sub>, 151 MHz.

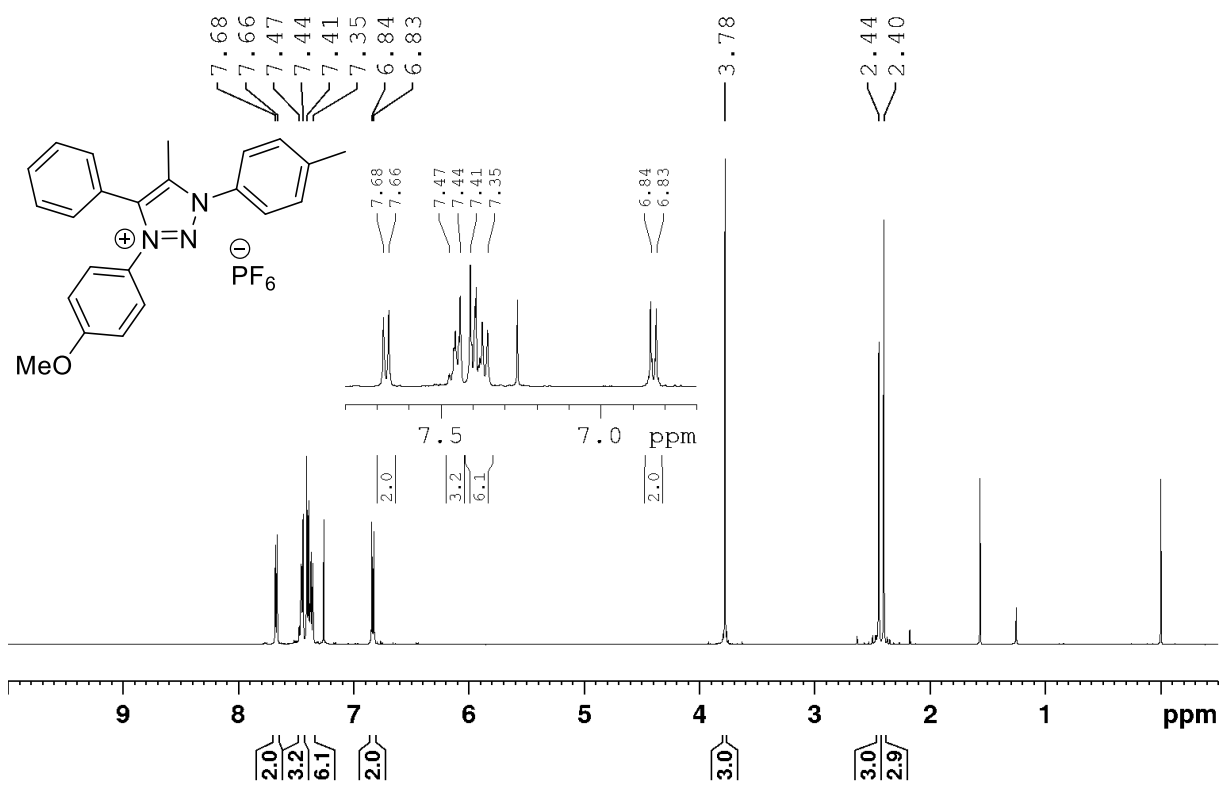


Figure S15. <sup>1</sup>H NMR spectrum of **1c** in CDCl<sub>3</sub>, 500 MHz.

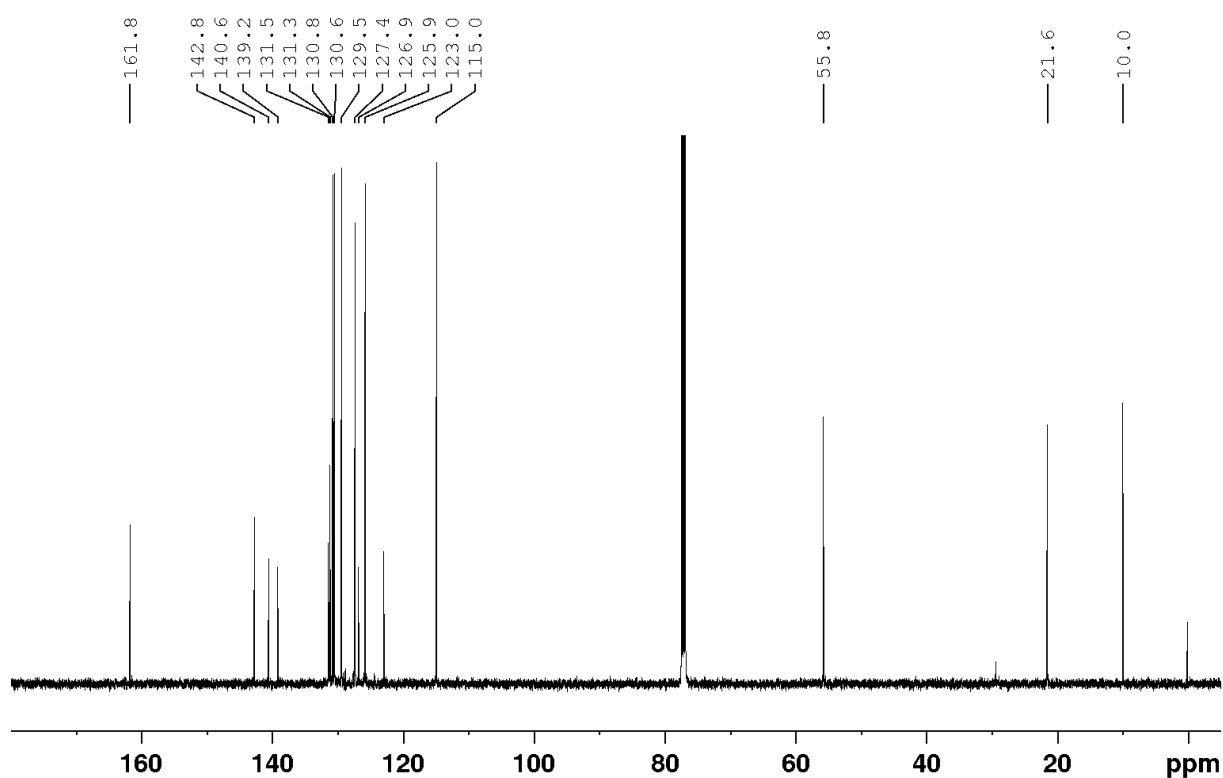


Figure S16. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **1c** in CDCl<sub>3</sub>, 126 MHz.



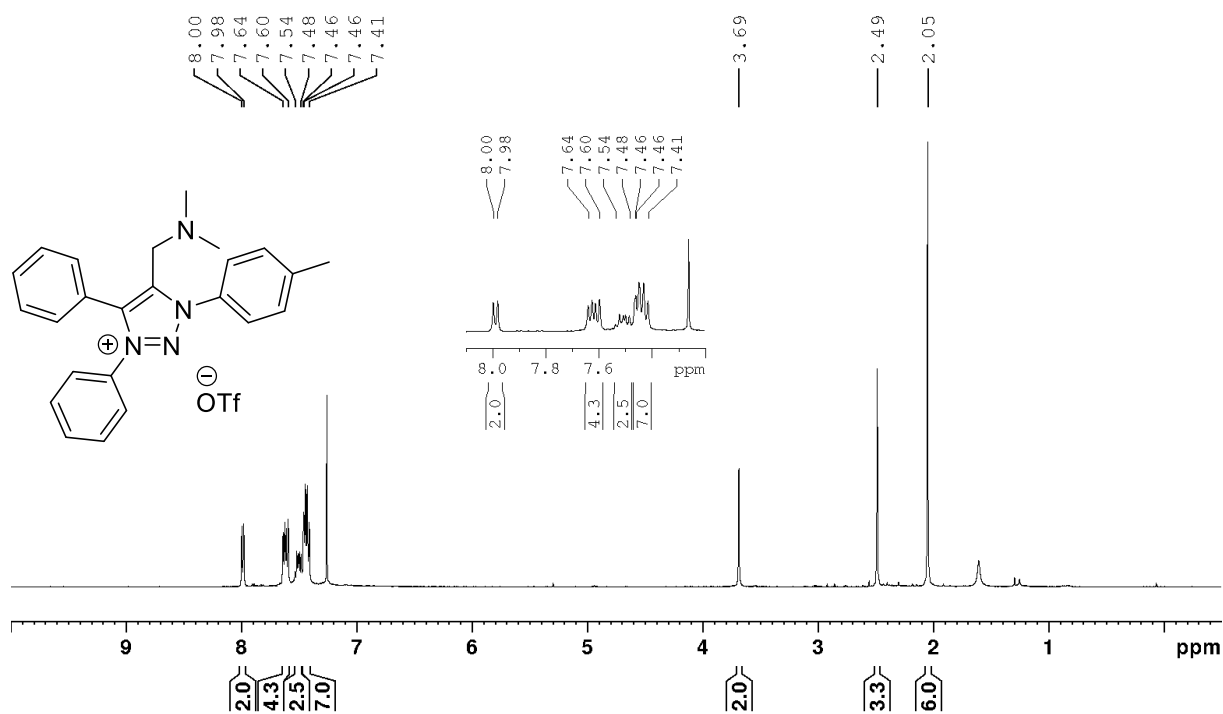


Figure S17.  $^1\text{H}$  NMR spectrum of **1d** in  $\text{CDCl}_3$ , 500 MHz.

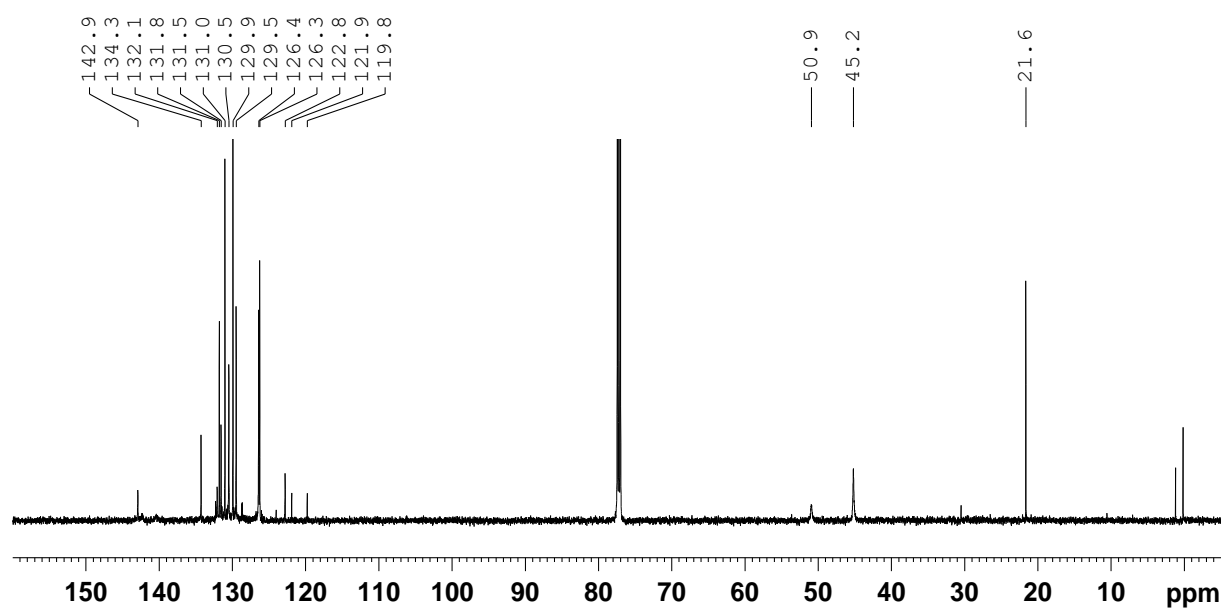
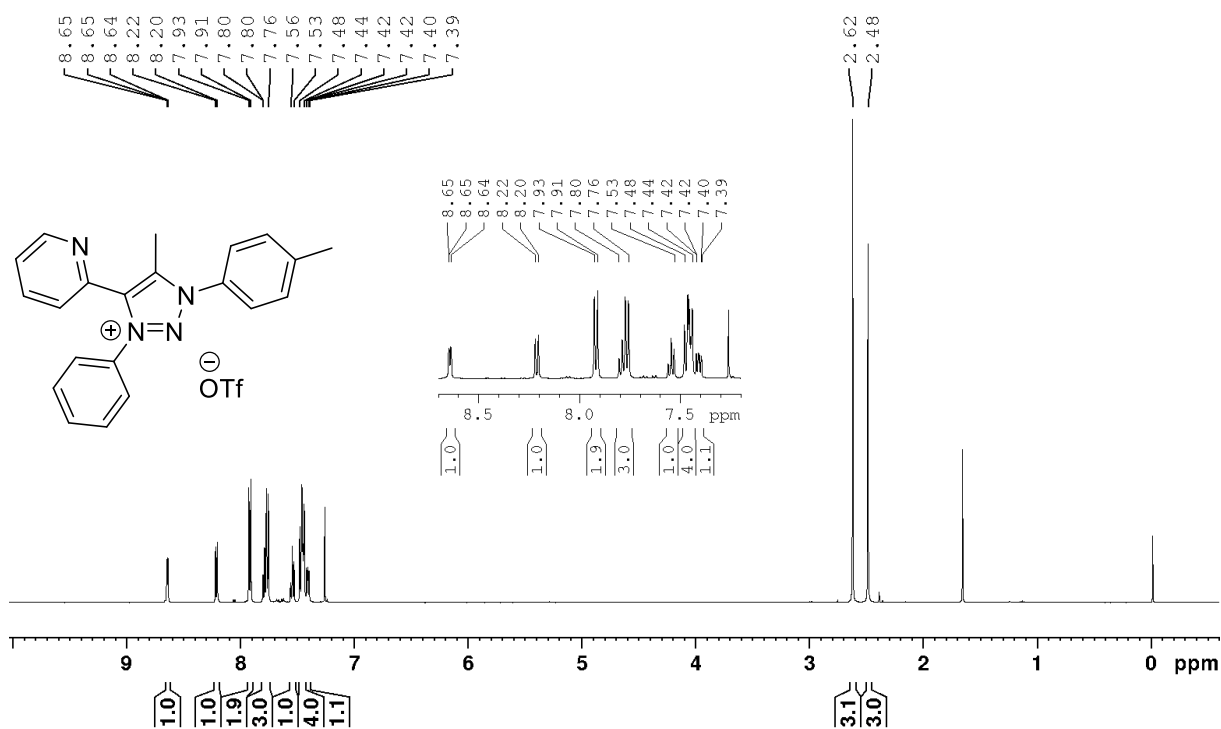
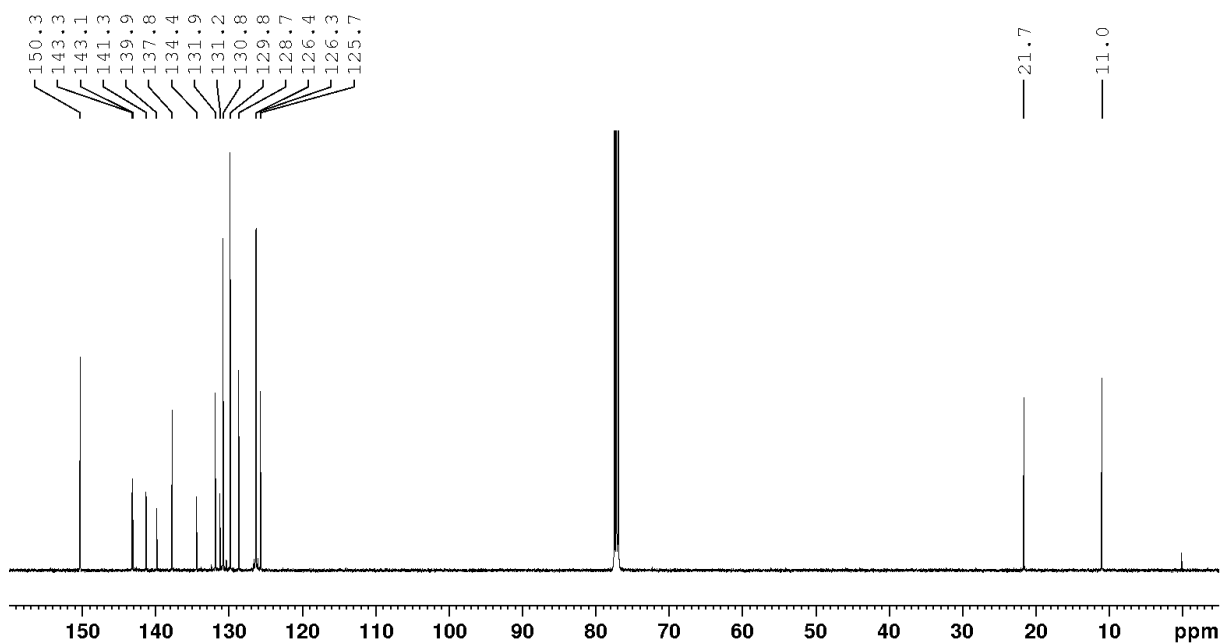


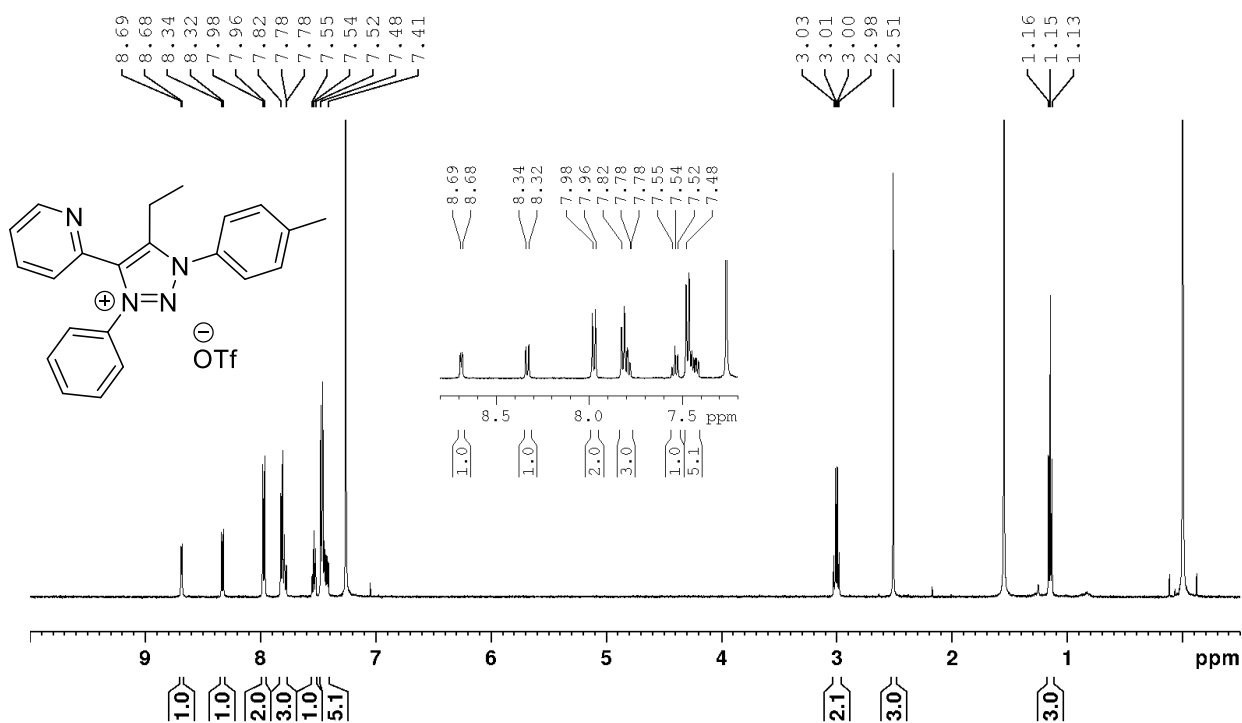
Figure S18.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1d** in  $\text{CDCl}_3$ , 151 MHz.



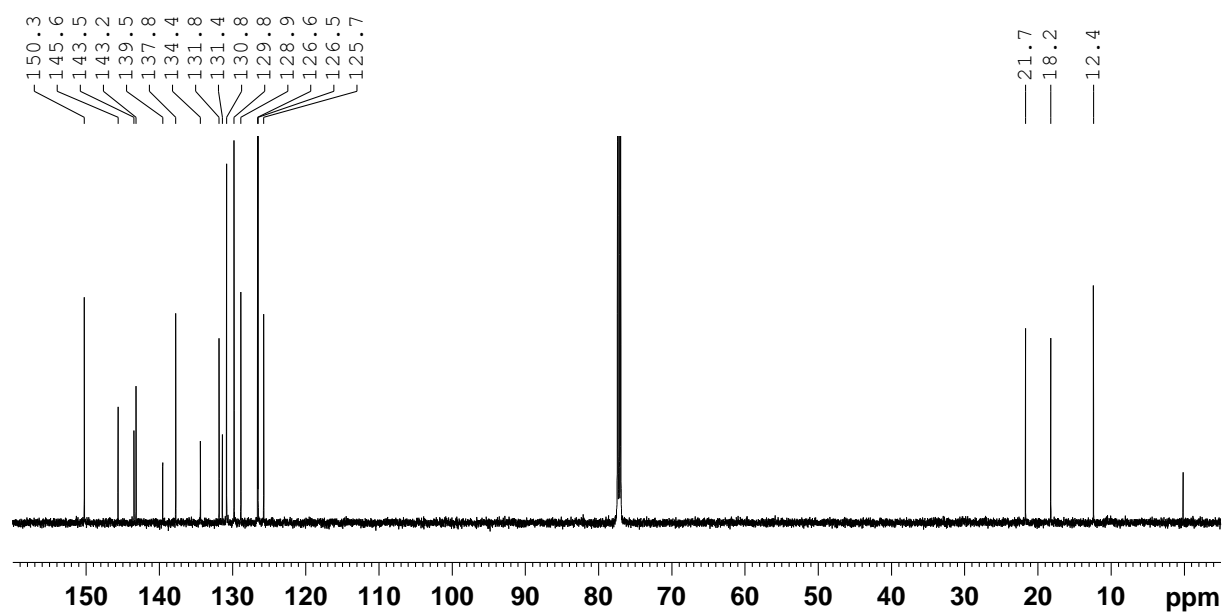
**Figure S19.** <sup>1</sup>H NMR spectrum of **1e** in CDCl<sub>3</sub>, 500 MHz.



**Figure S20.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **1e** in CDCl<sub>3</sub>, 126 MHz.



**Figure S21.**  $^1\text{H}$  NMR spectrum of **1f** in  $\text{CDCl}_3$ , 500 MHz.



**Figure S22.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1f** in  $\text{CDCl}_3$ , 151 MHz.

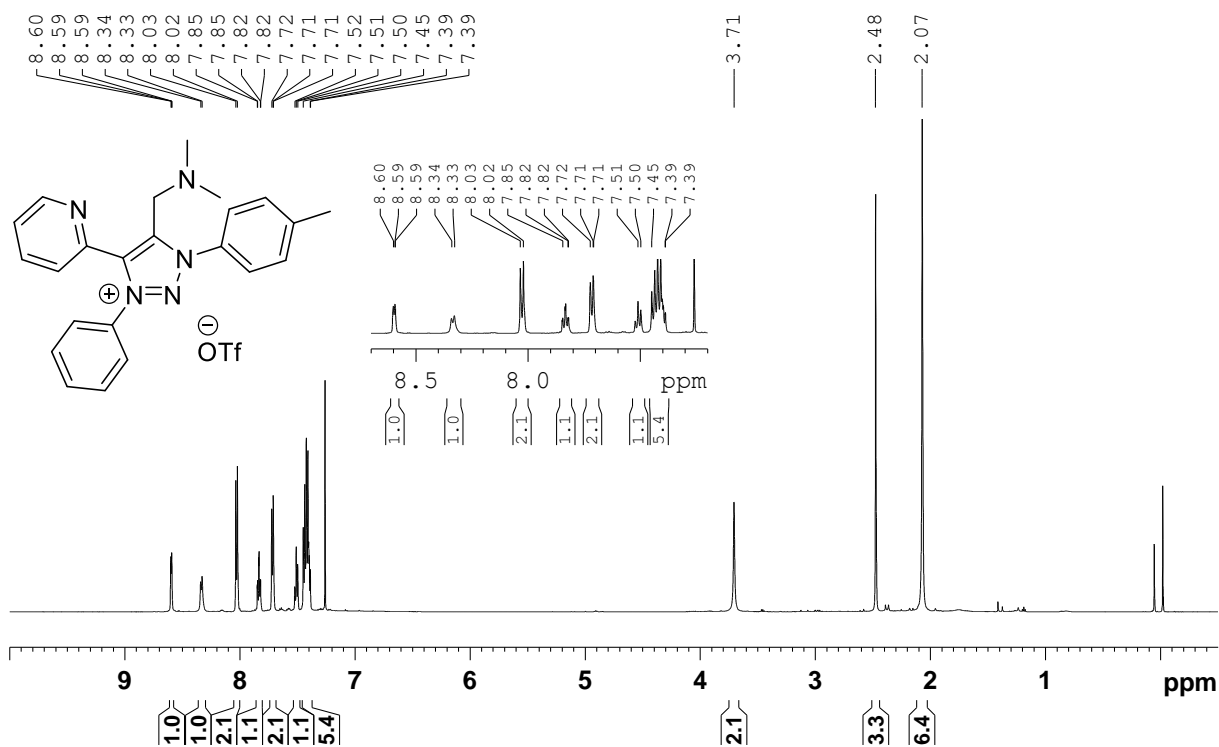


Figure S23.  $^1\text{H}$  NMR spectrum of **1g** in  $\text{CDCl}_3$ , 600 MHz.

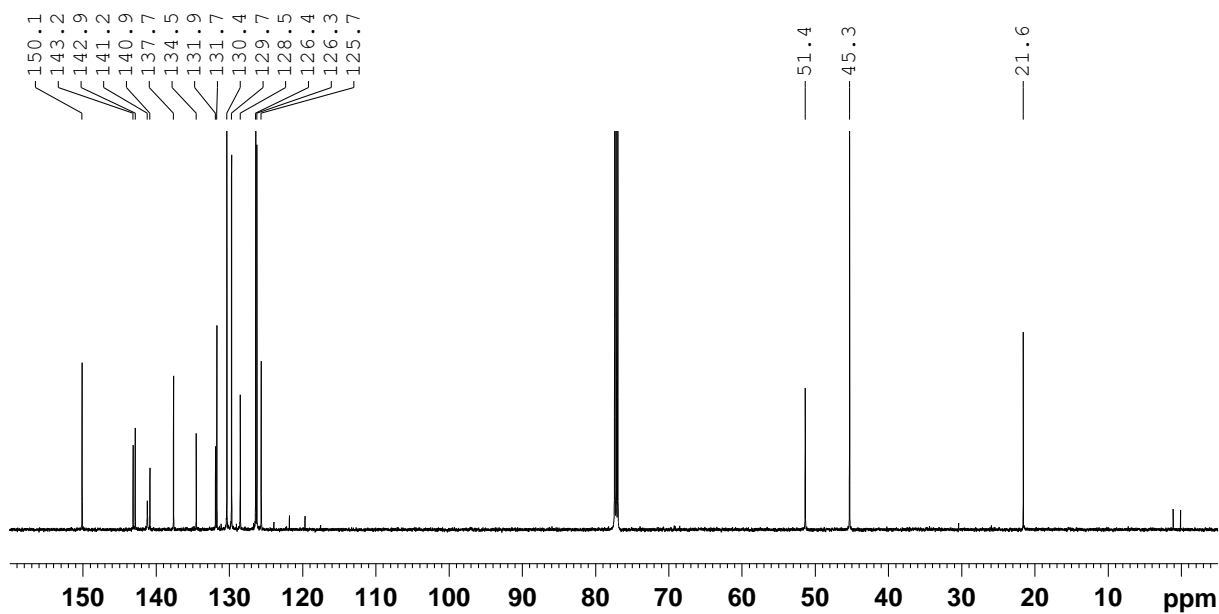
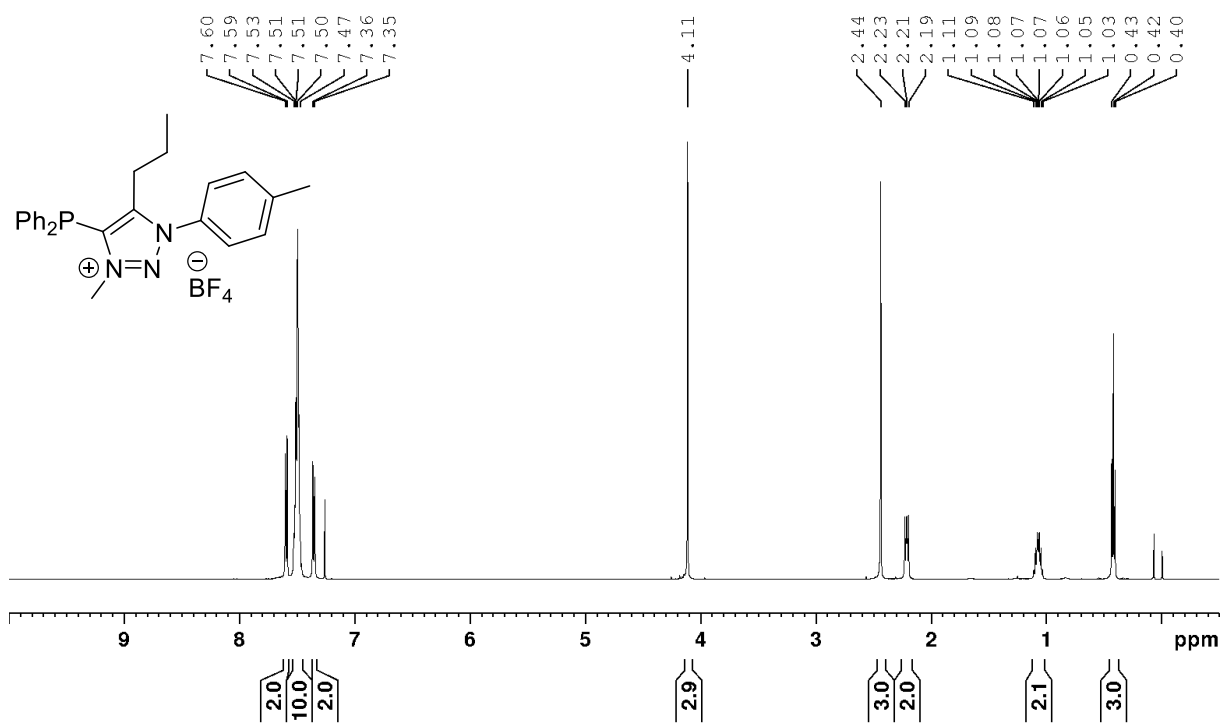
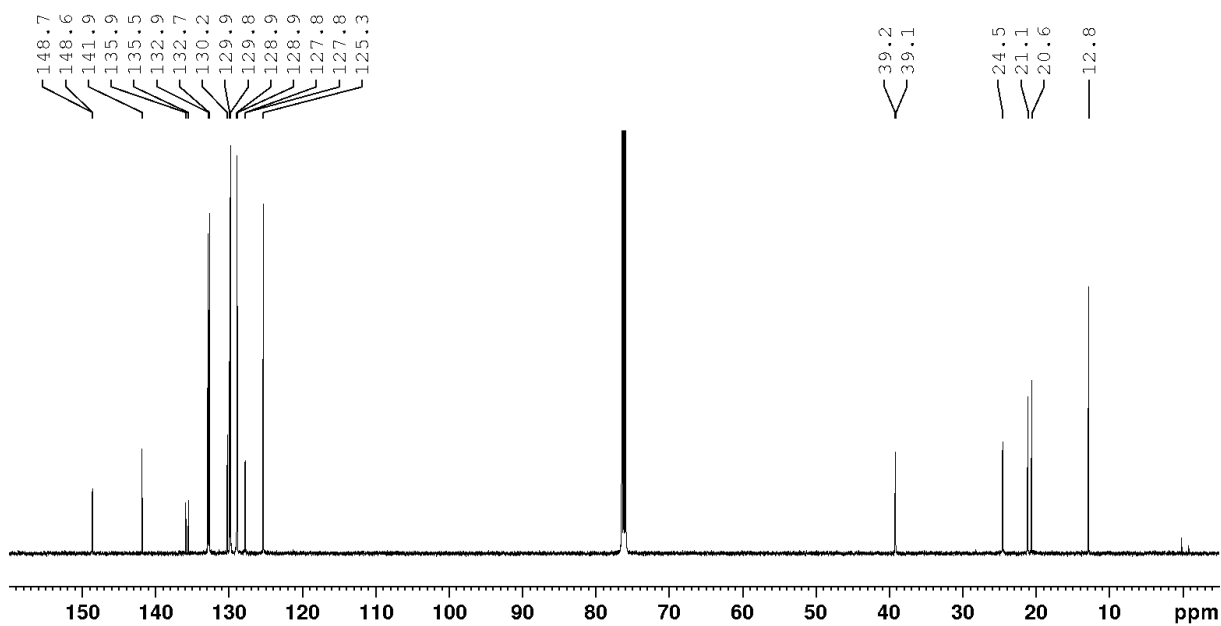


Figure S24.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1g** in  $\text{CDCl}_3$ , 151 MHz.



**Figure S25.**  $^1\text{H}$  NMR spectrum of **1h** in  $\text{CDCl}_3$ , 500 MHz.



**Figure S26.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1h** in  $\text{CDCl}_3$ , 126 MHz.

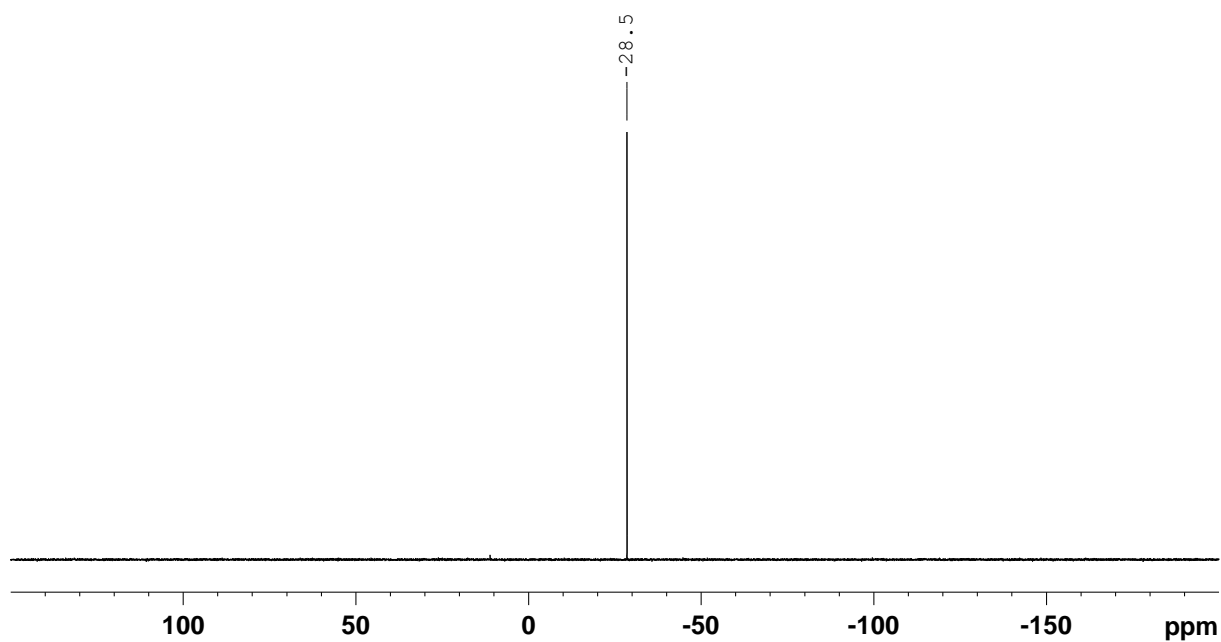


Figure S27.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **1h** in  $\text{CDCl}_3$ , 202 MHz.

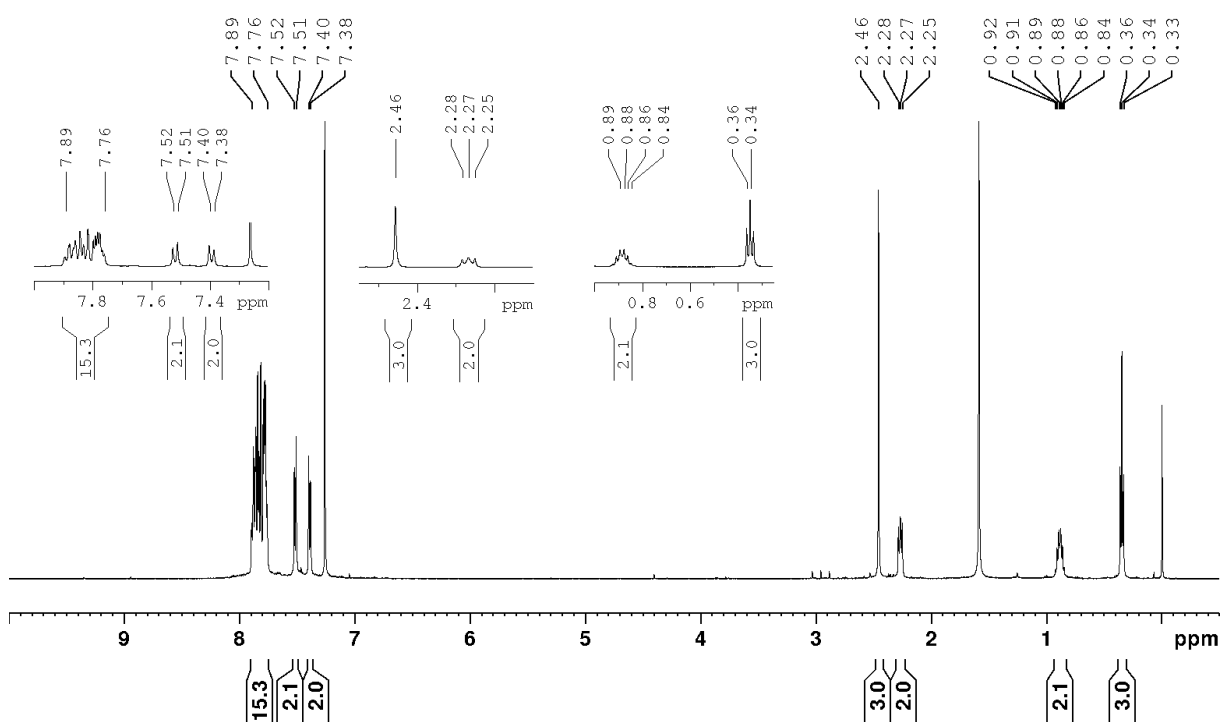


Figure S28.  $^1\text{H}$  NMR spectrum of **1j** in  $\text{CDCl}_3$ , 500 MHz.

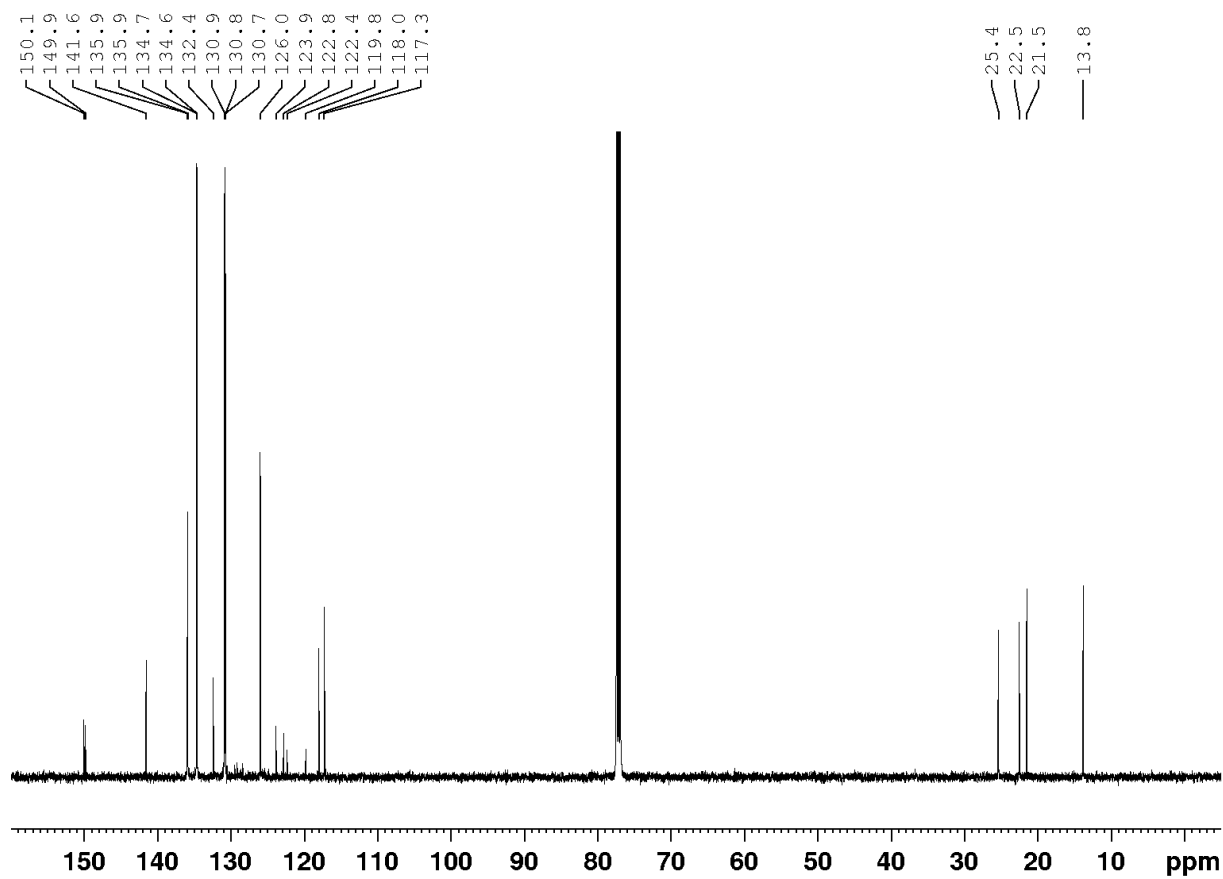


Figure S29.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1j** in  $\text{CDCl}_3$ , 126 MHz.

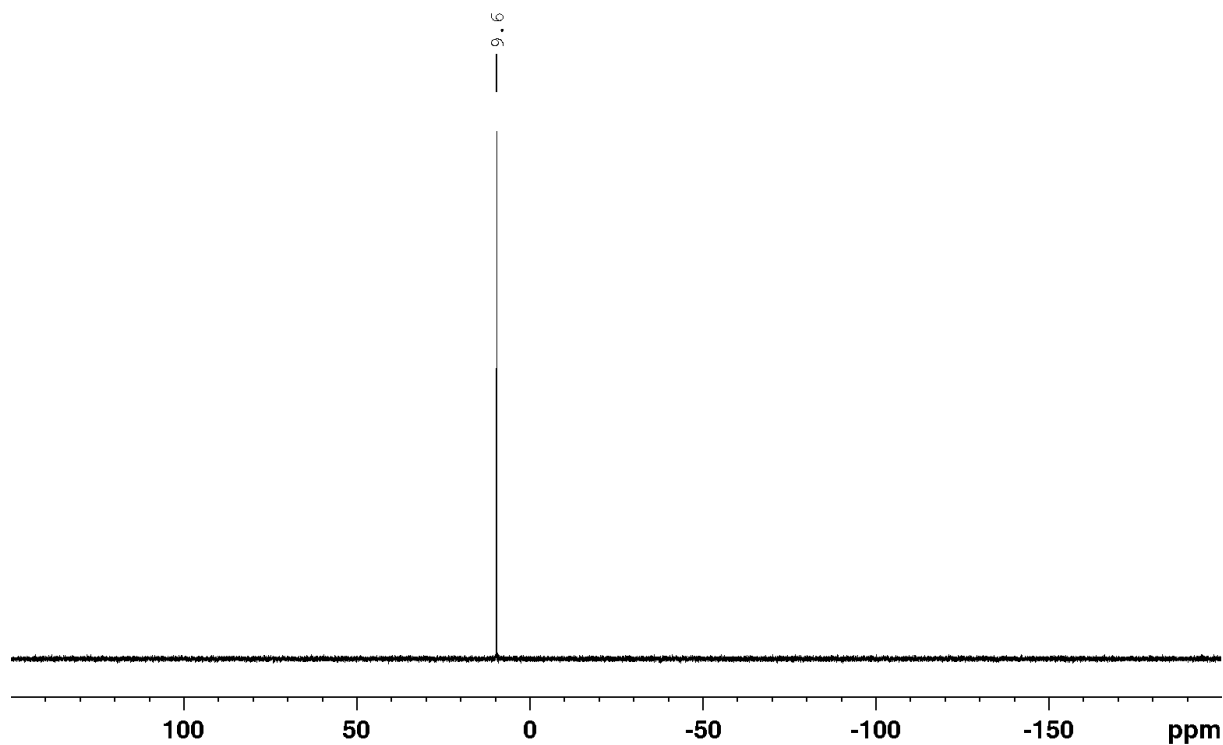
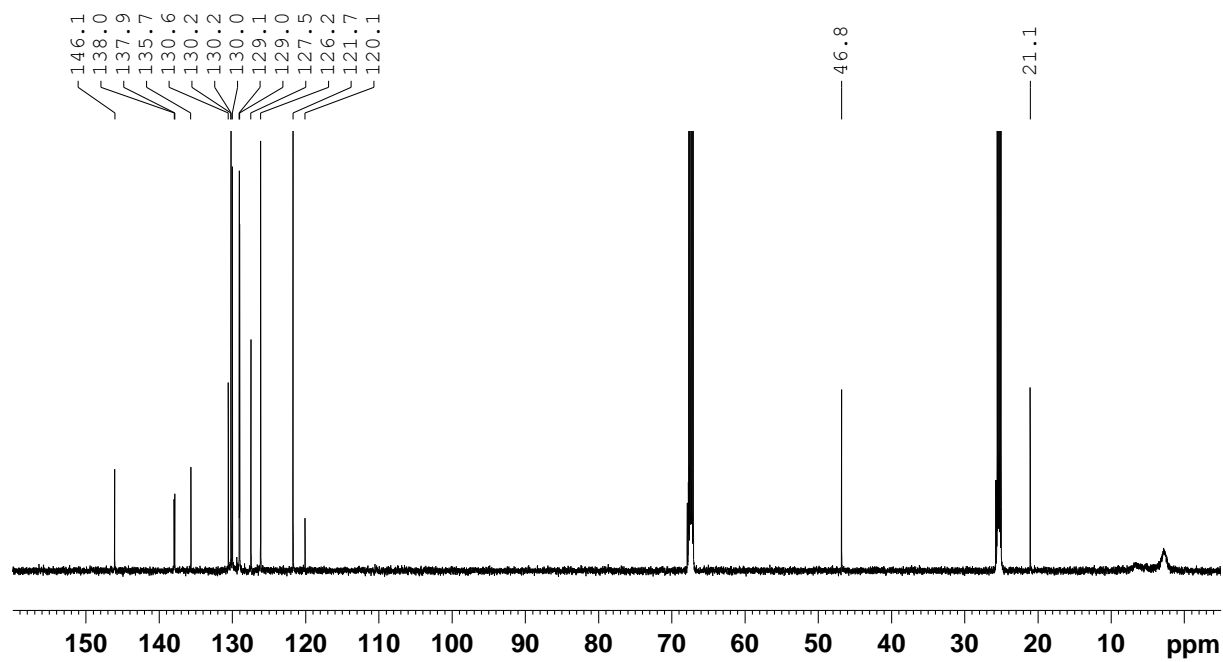
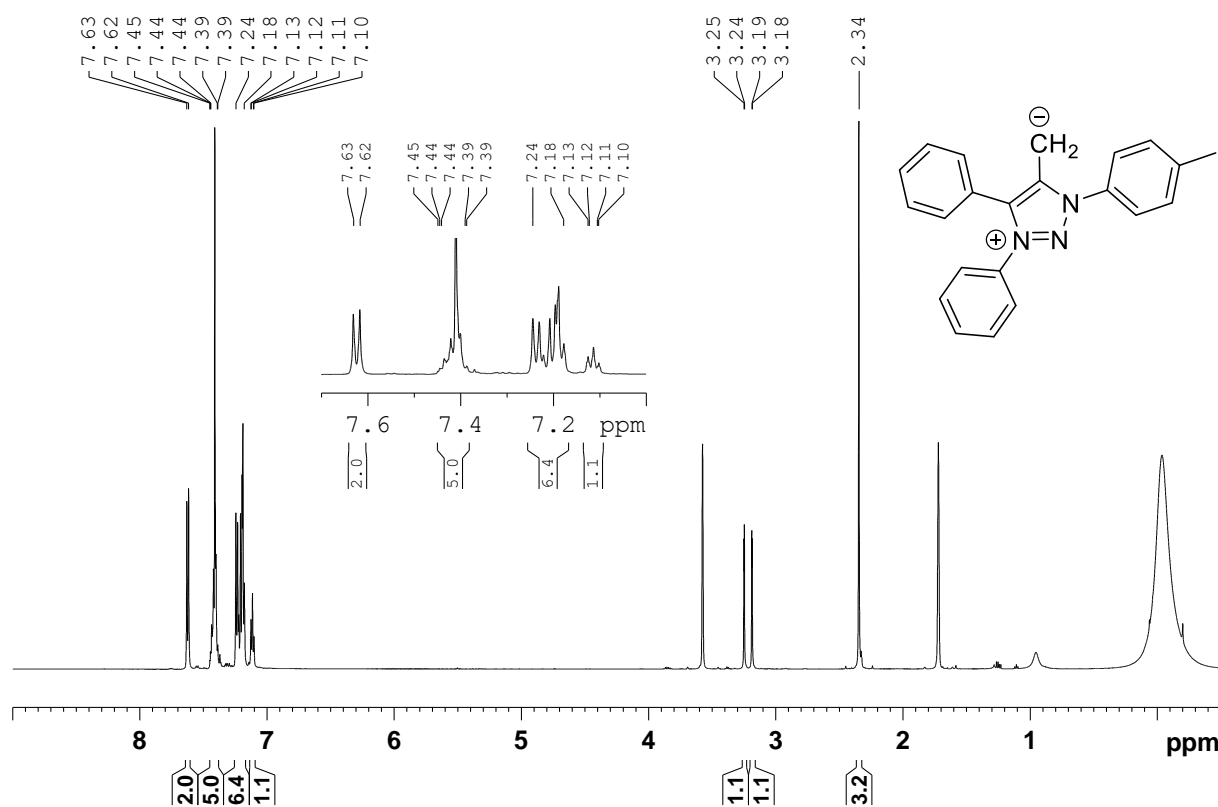


Figure S30.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **1j** in  $\text{CDCl}_3$ , 202 MHz.





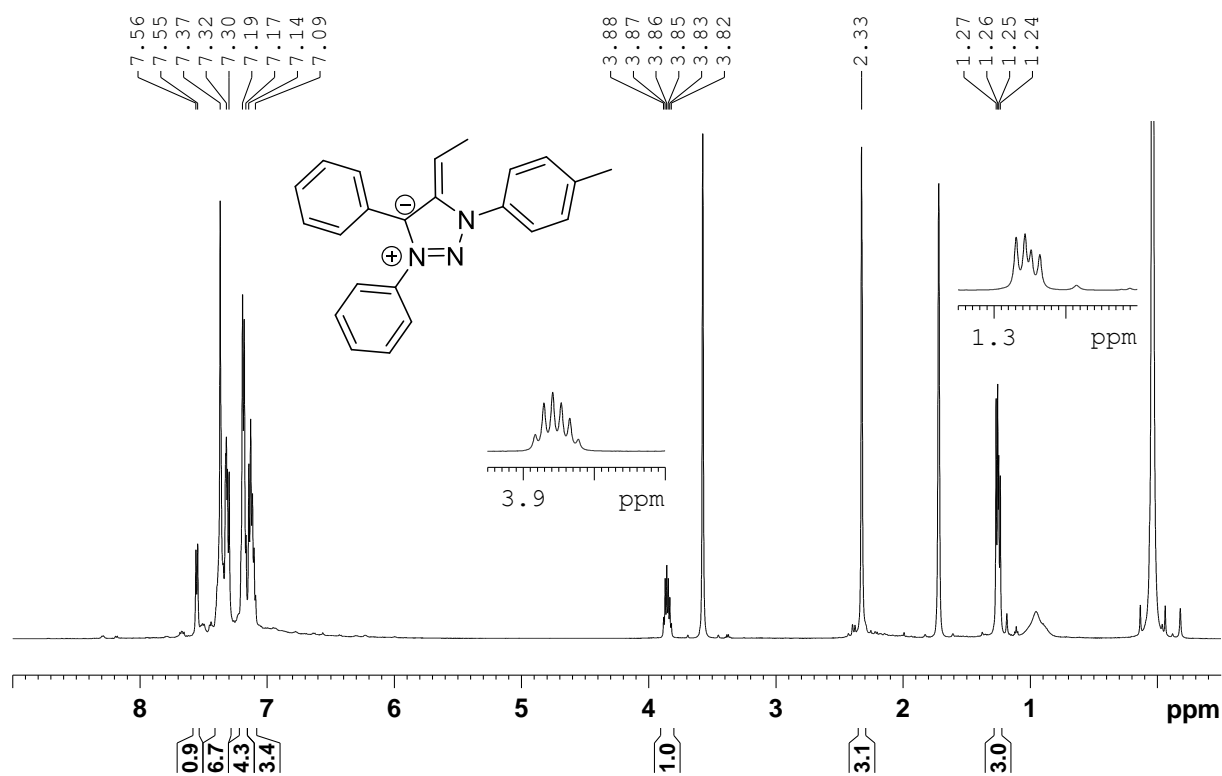


Figure S33. <sup>1</sup>H NMR spectrum of **7b** in THF-*d*<sub>8</sub>, 600 MHz.

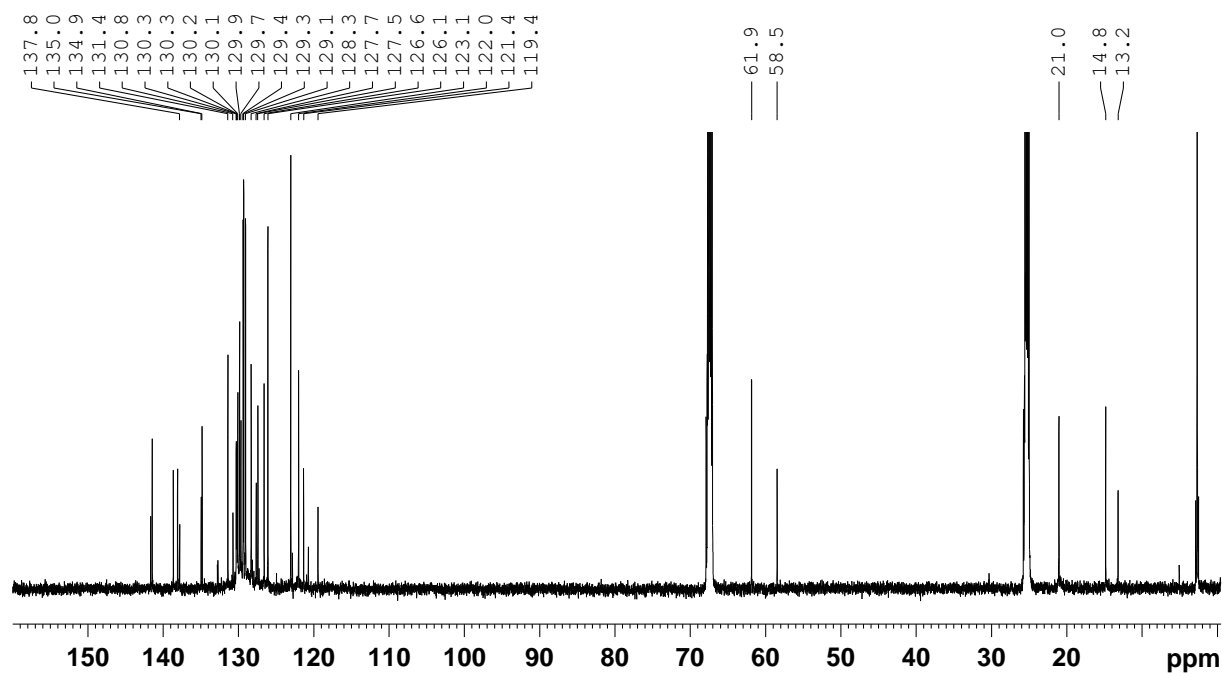


Figure S34. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **7b** in THF-*d*<sub>8</sub>, 151 MHz.

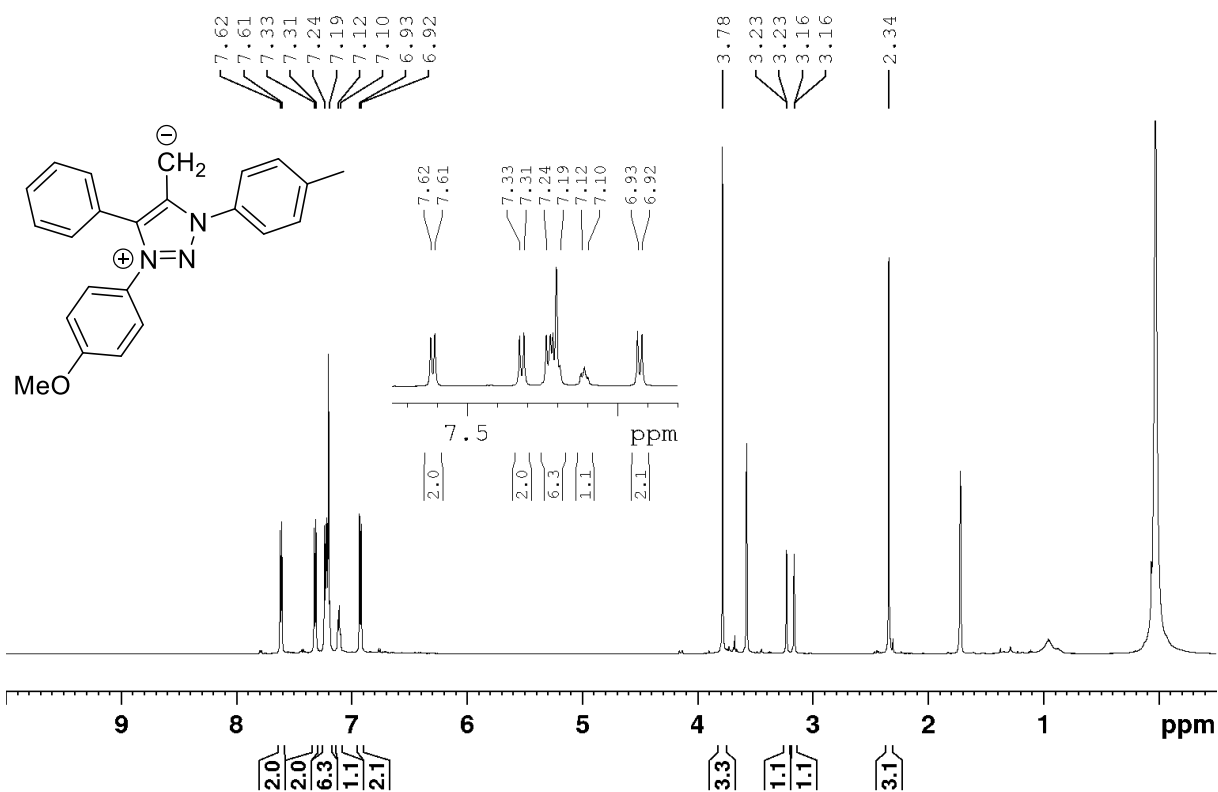


Figure S35.  $^1\text{H}$  NMR spectrum of **7c** in  $\text{THF-}d_8$ , 600 MHz.

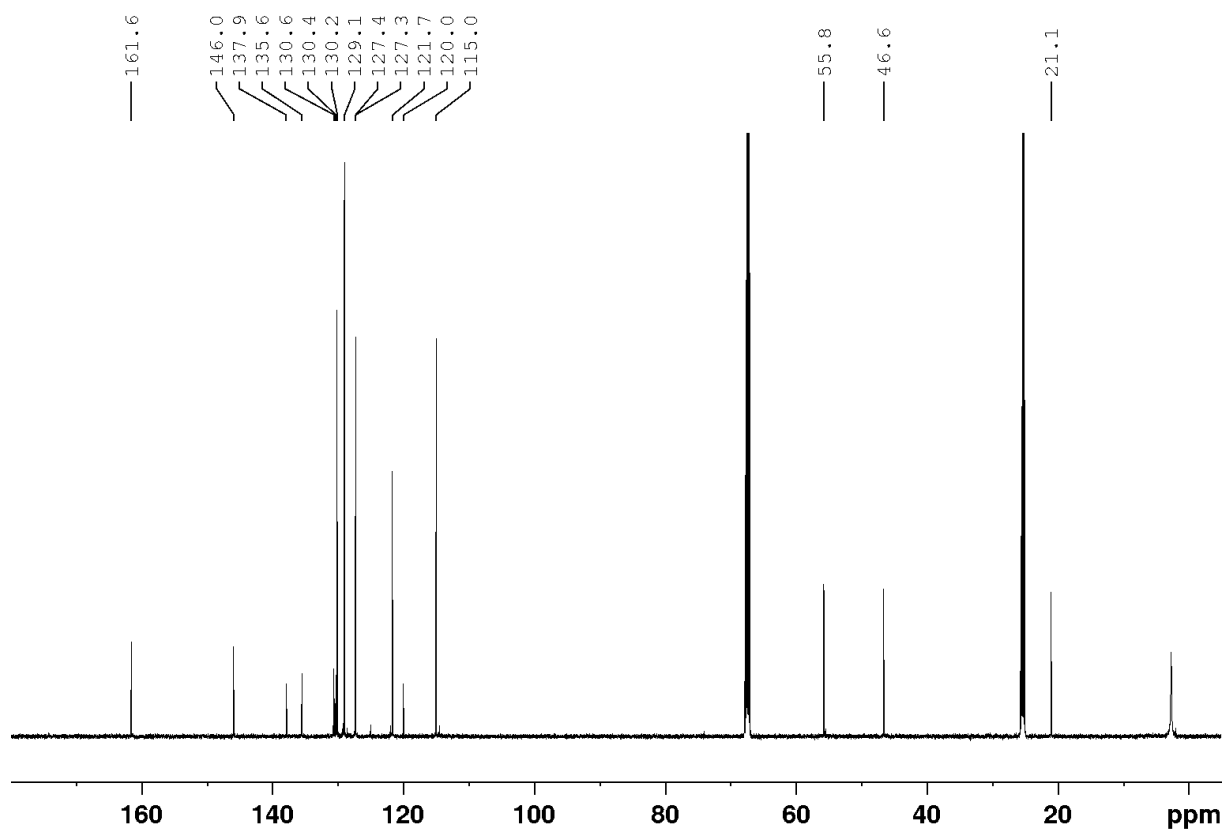


Figure S36.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **7c** in  $\text{THF-}d_8$ , 151 MHz.

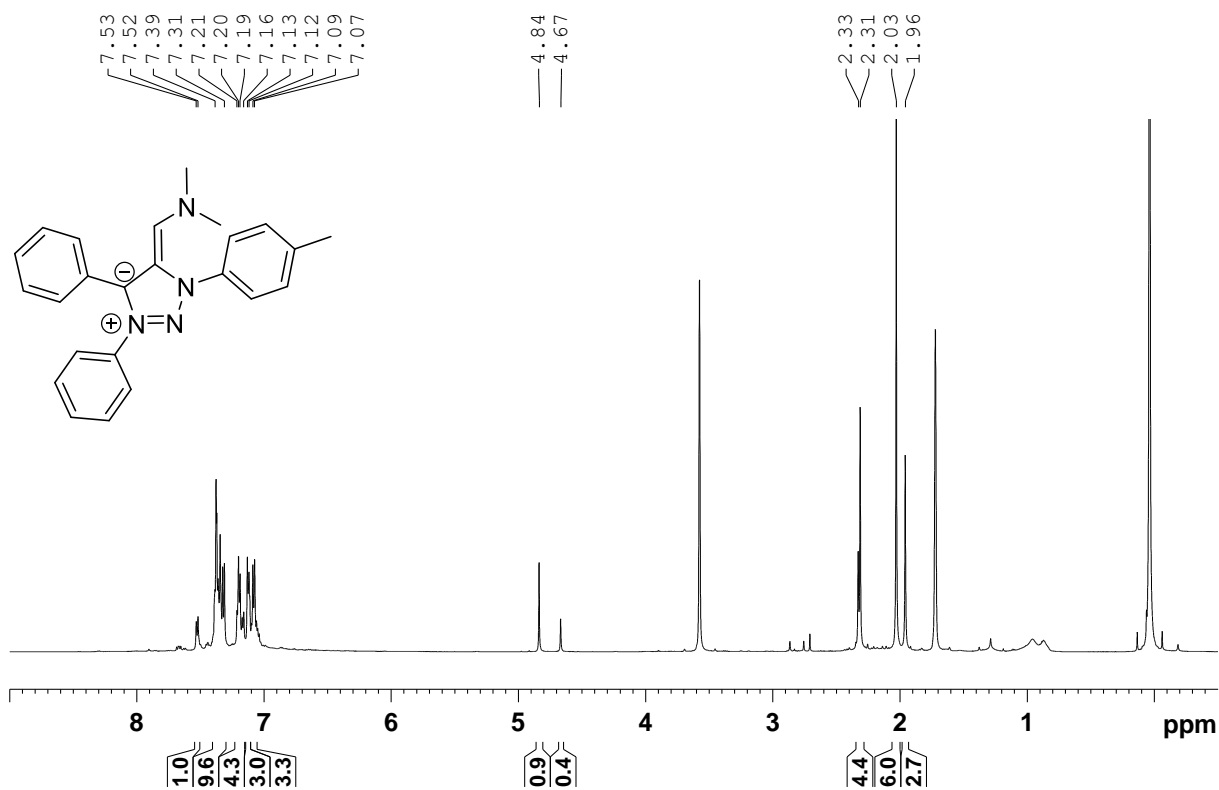


Figure S37.  $^1\text{H NMR}$  spectrum of **7d** in  $\text{THF-}d_8$ , 600 MHz.

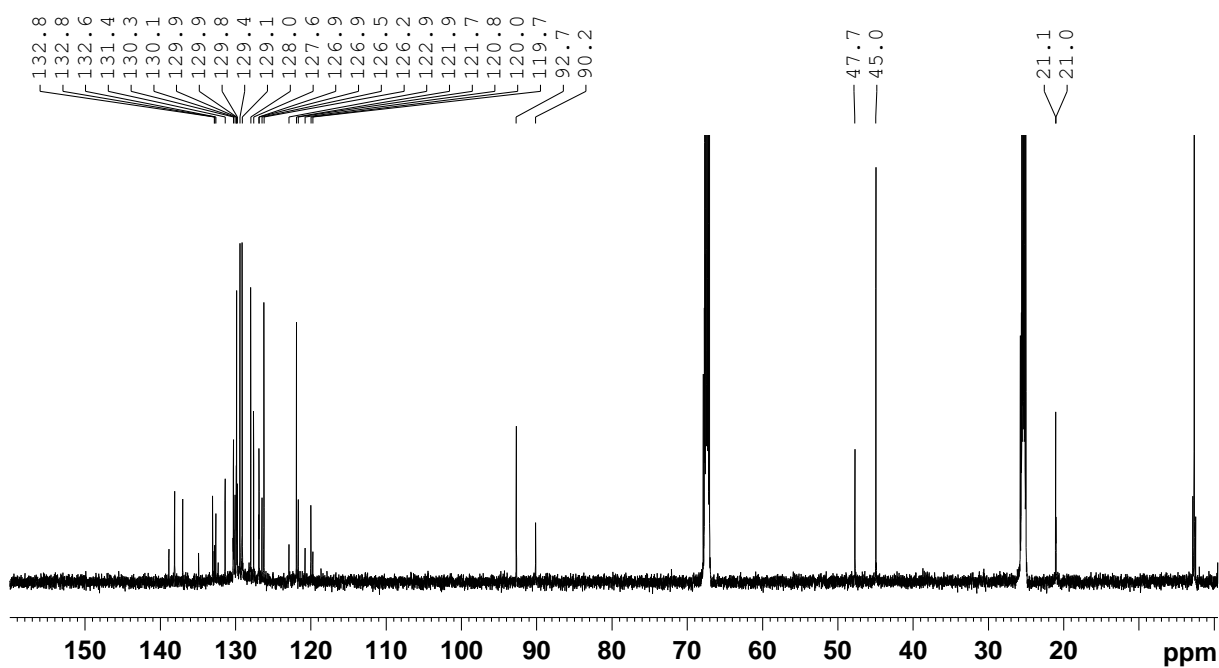


Figure S38.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **7d** in  $\text{THF-}d_8$ , 151 MHz.

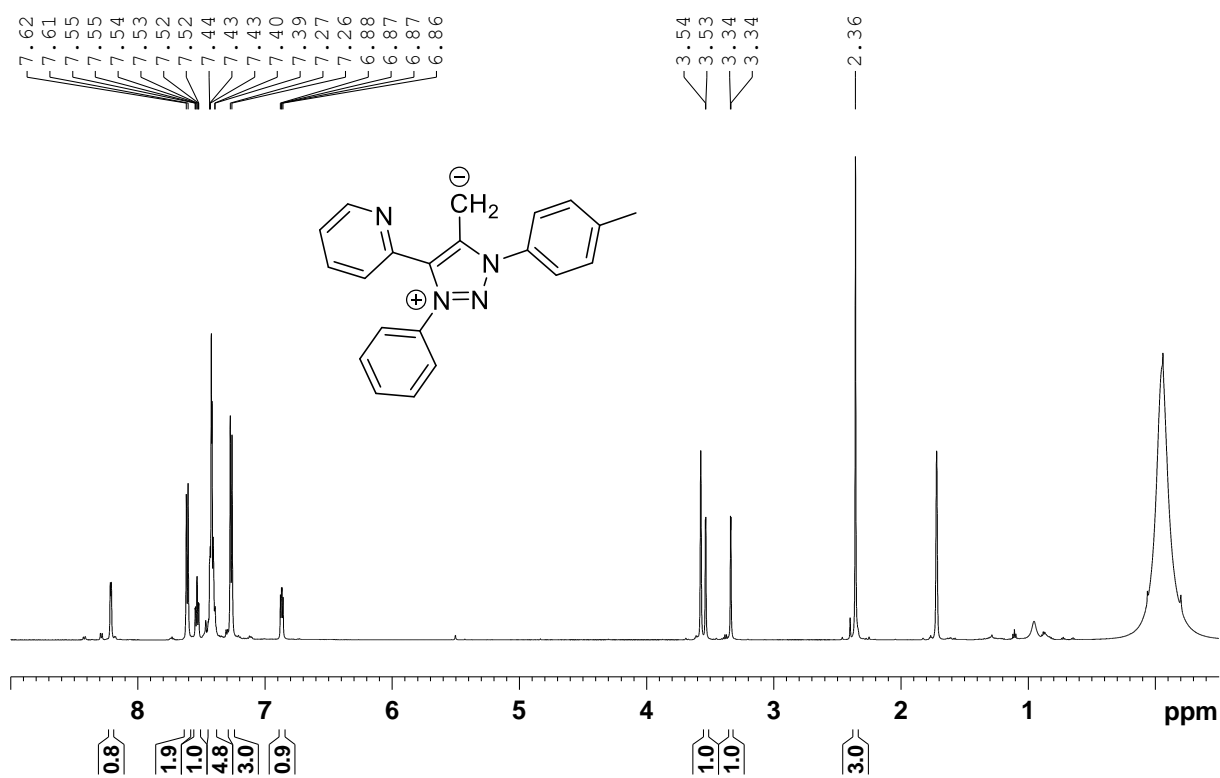


Figure S39. <sup>1</sup>H NMR spectrum of 7e in THF-*d*<sub>8</sub>, 600 MHz.

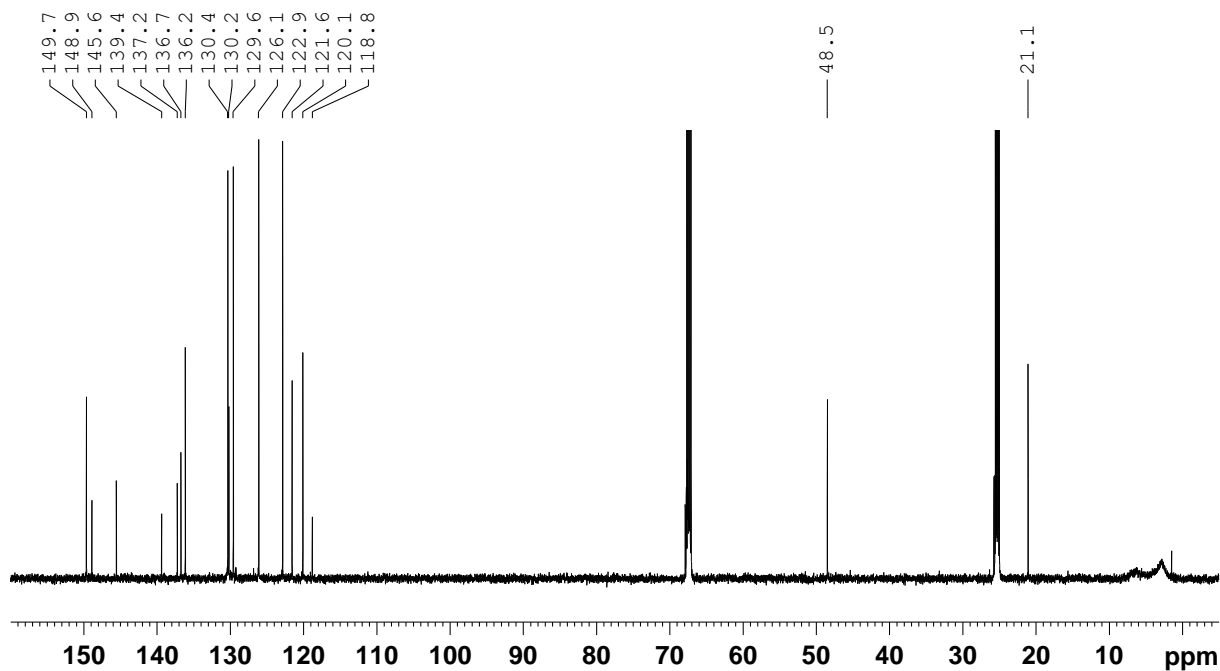


Figure S40. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 7e in THF-*d*<sub>8</sub>, 151 MHz.

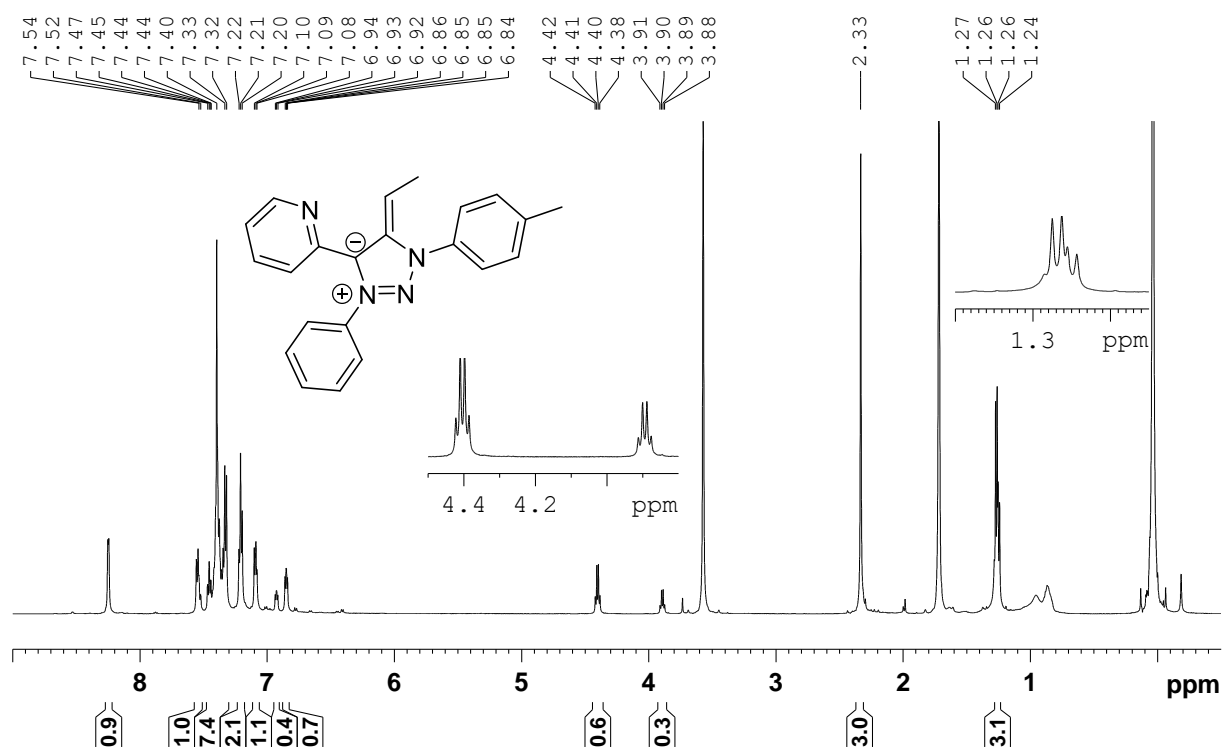


Figure S41.  $^1\text{H}$  NMR spectrum of **7f** in  $\text{THF-}d_8$ , 600 MHz.

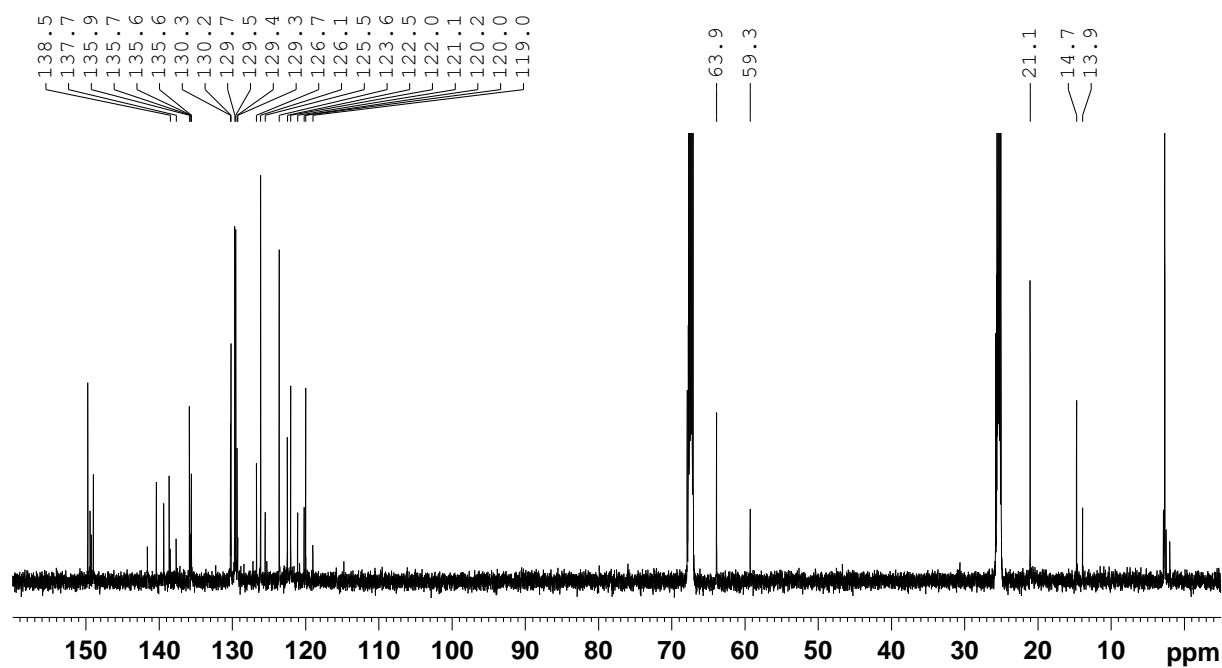


Figure S42.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **7f** in  $\text{THF-}d_8$ , 151 MHz.

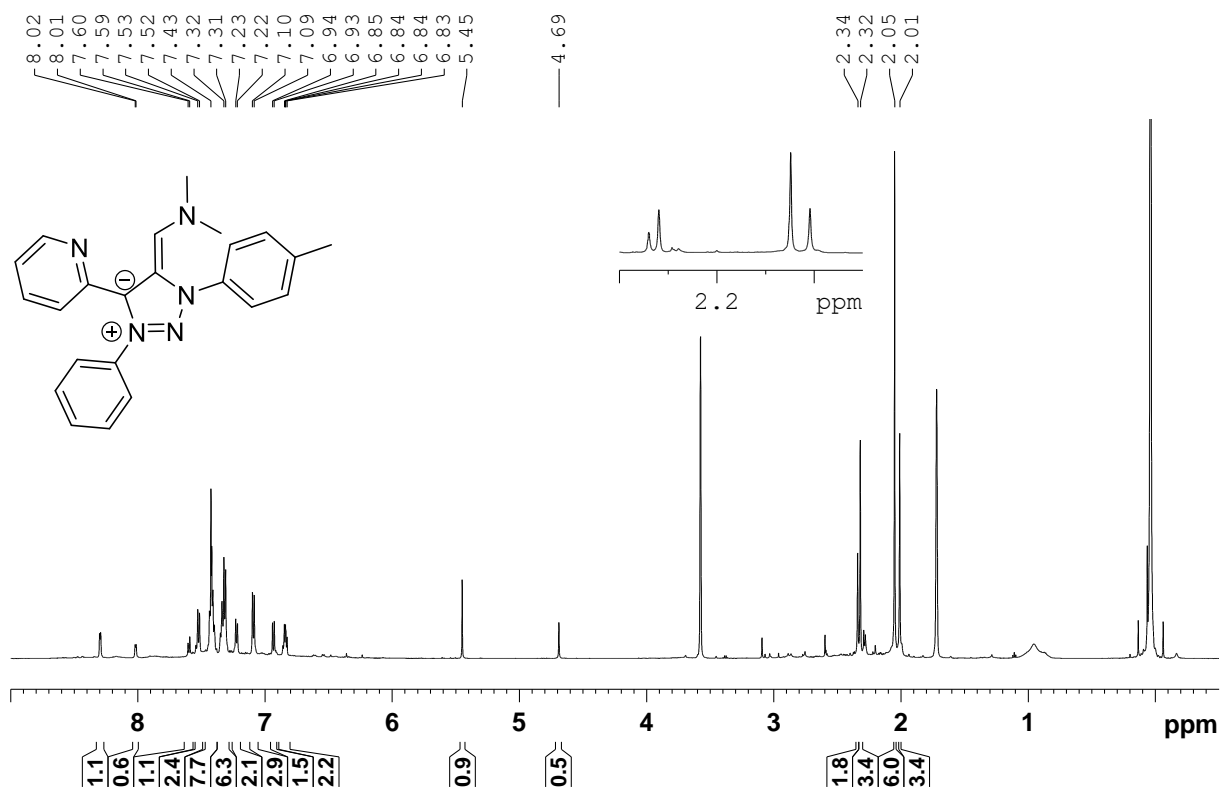


Figure S43.  $^1\text{H}$  NMR spectrum of **7g** in  $\text{THF-}d_8$ , 600 MHz.

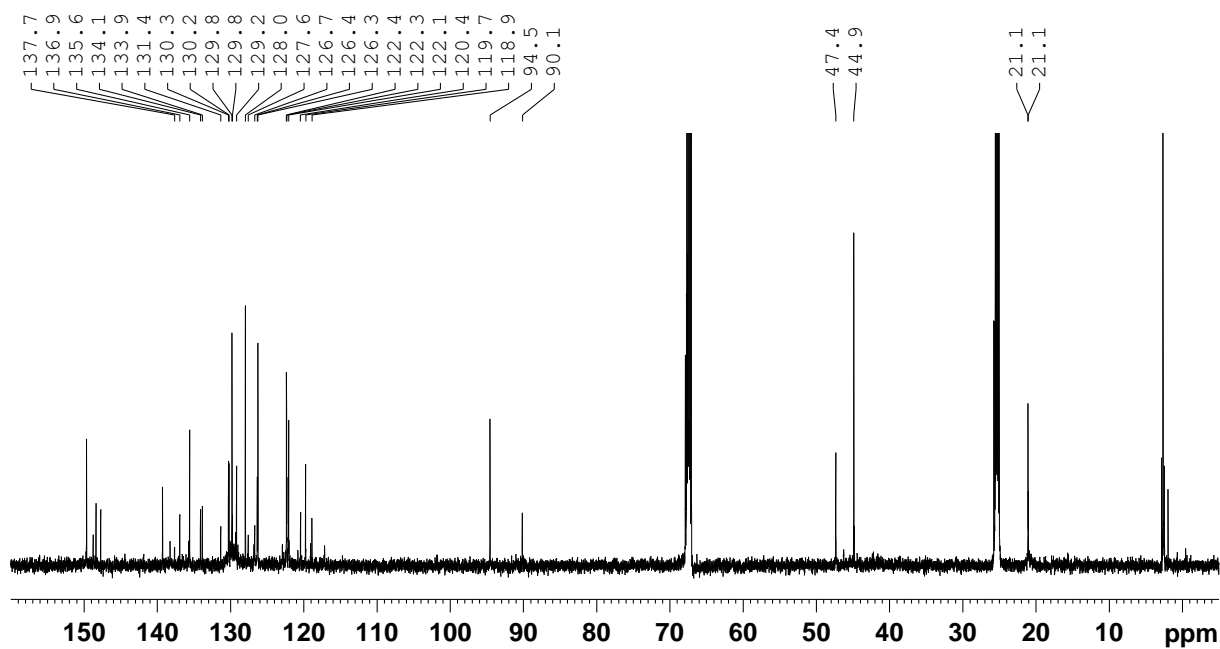


Figure S44.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **7g** in  $\text{THF-}d_8$ , 151 MHz.

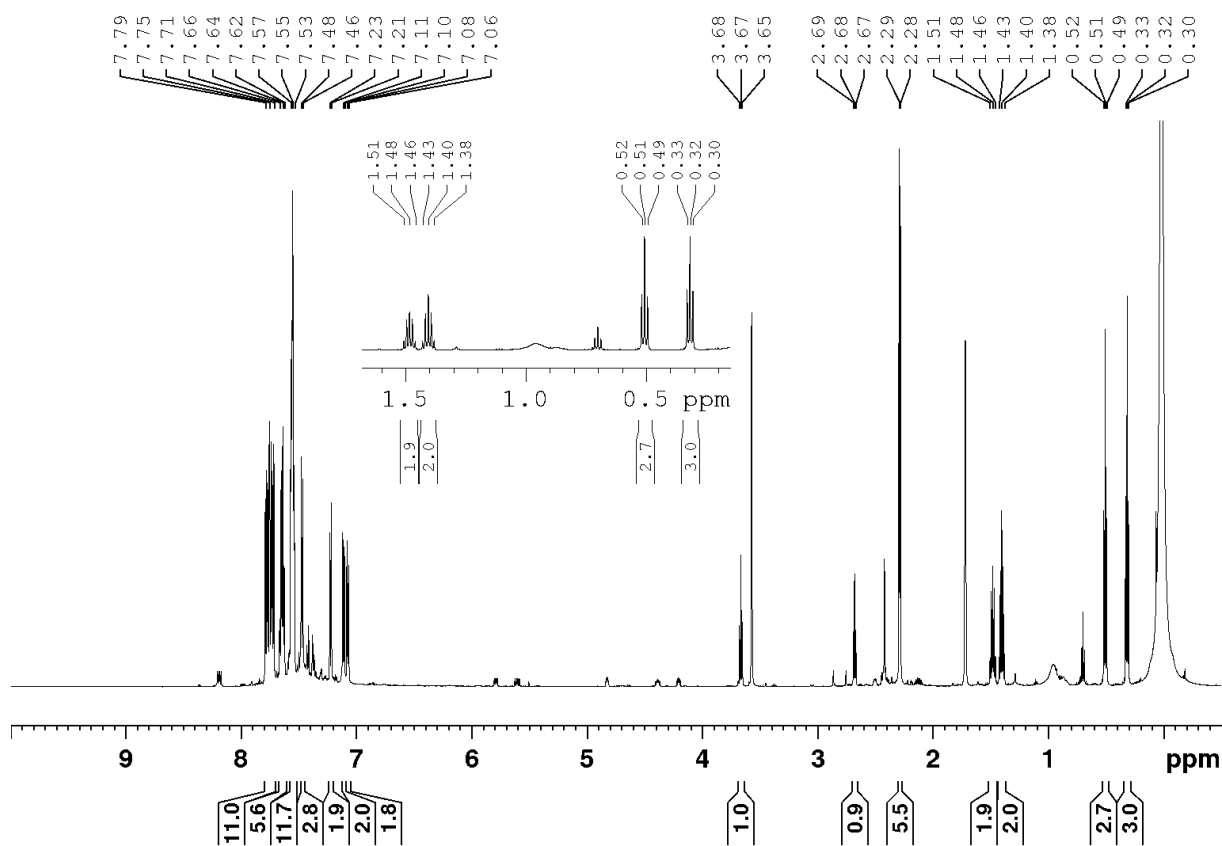


Figure S45.  $^1\text{H}$  NMR spectrum of **8j** in  $\text{THF-}d_8$ , 600 MHz.

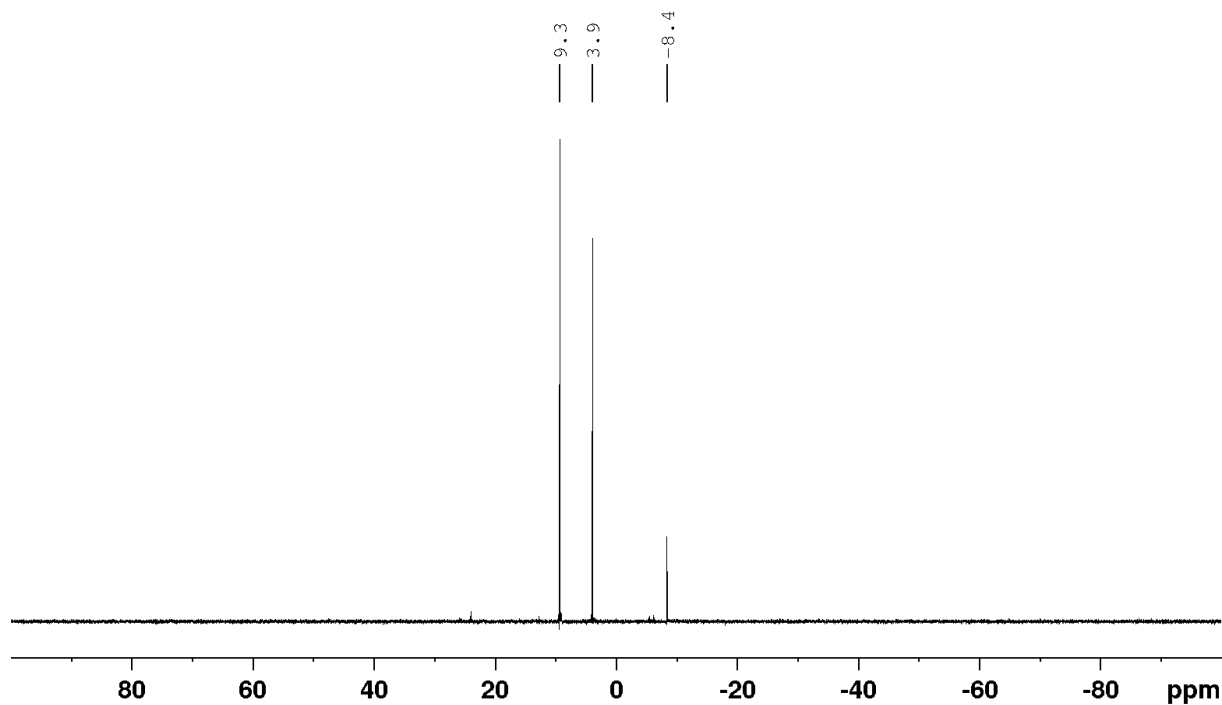


Figure S46.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **8j** in  $\text{THF-}d_8$ , 243 MHz.

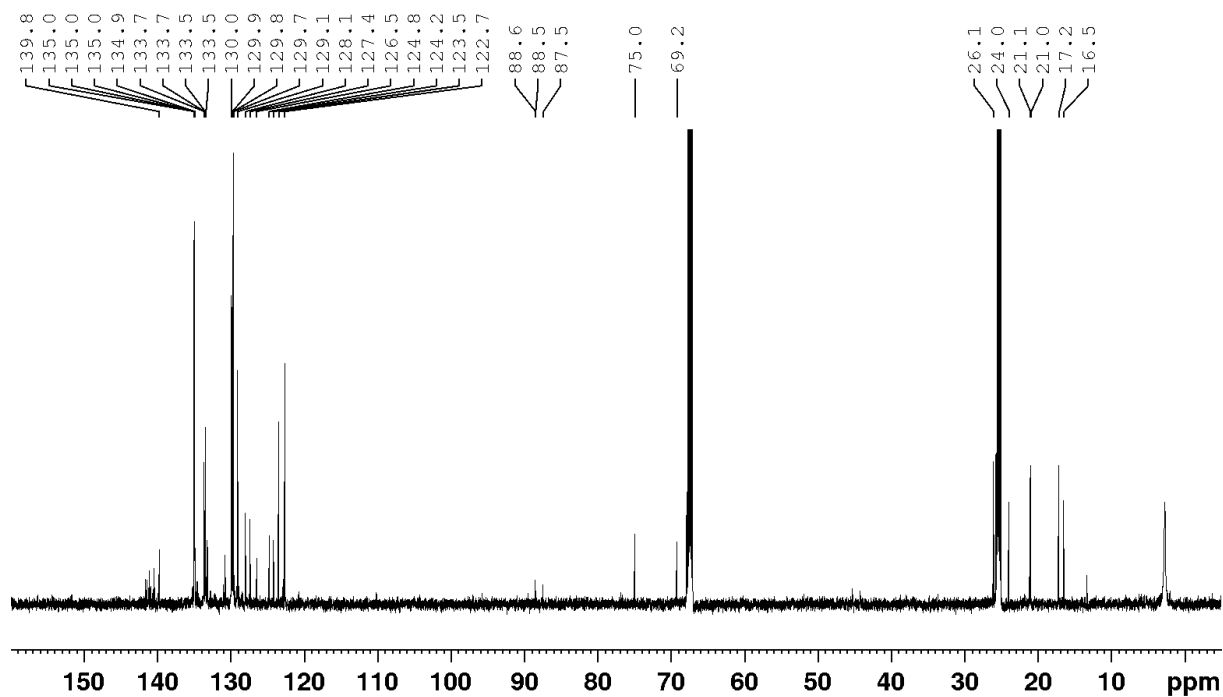


Figure S47.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **8j** in THF- $d_8$ , 151 MHz.

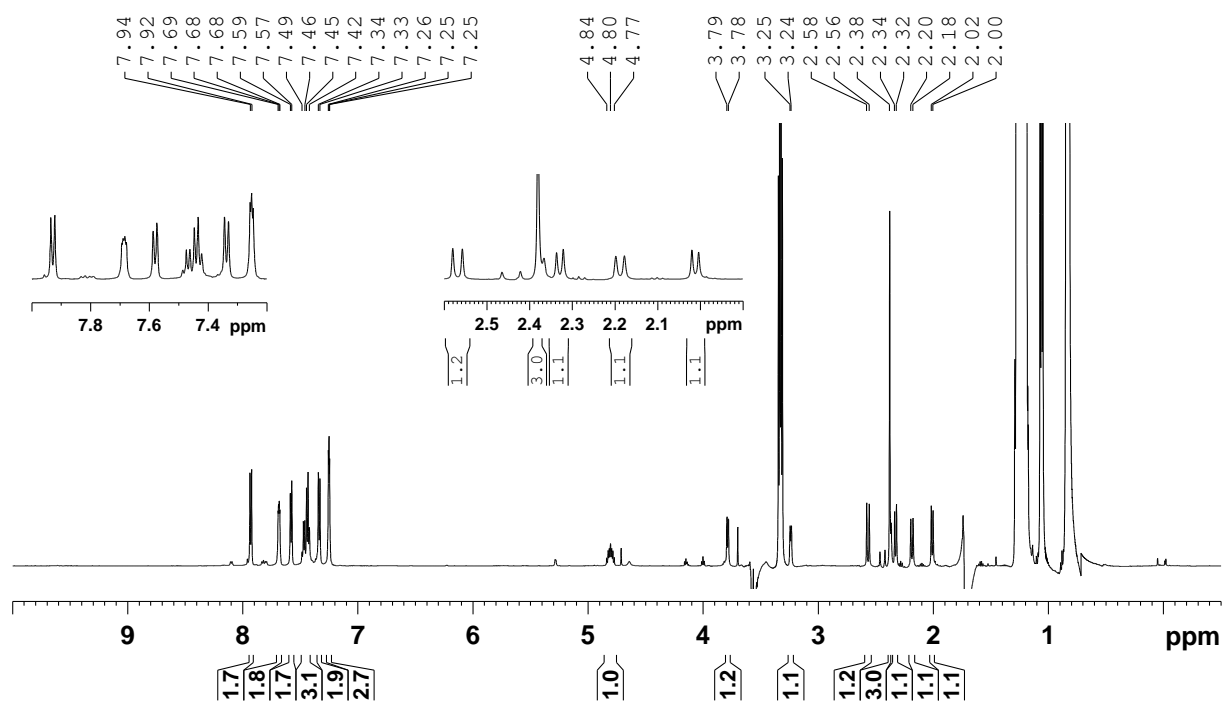
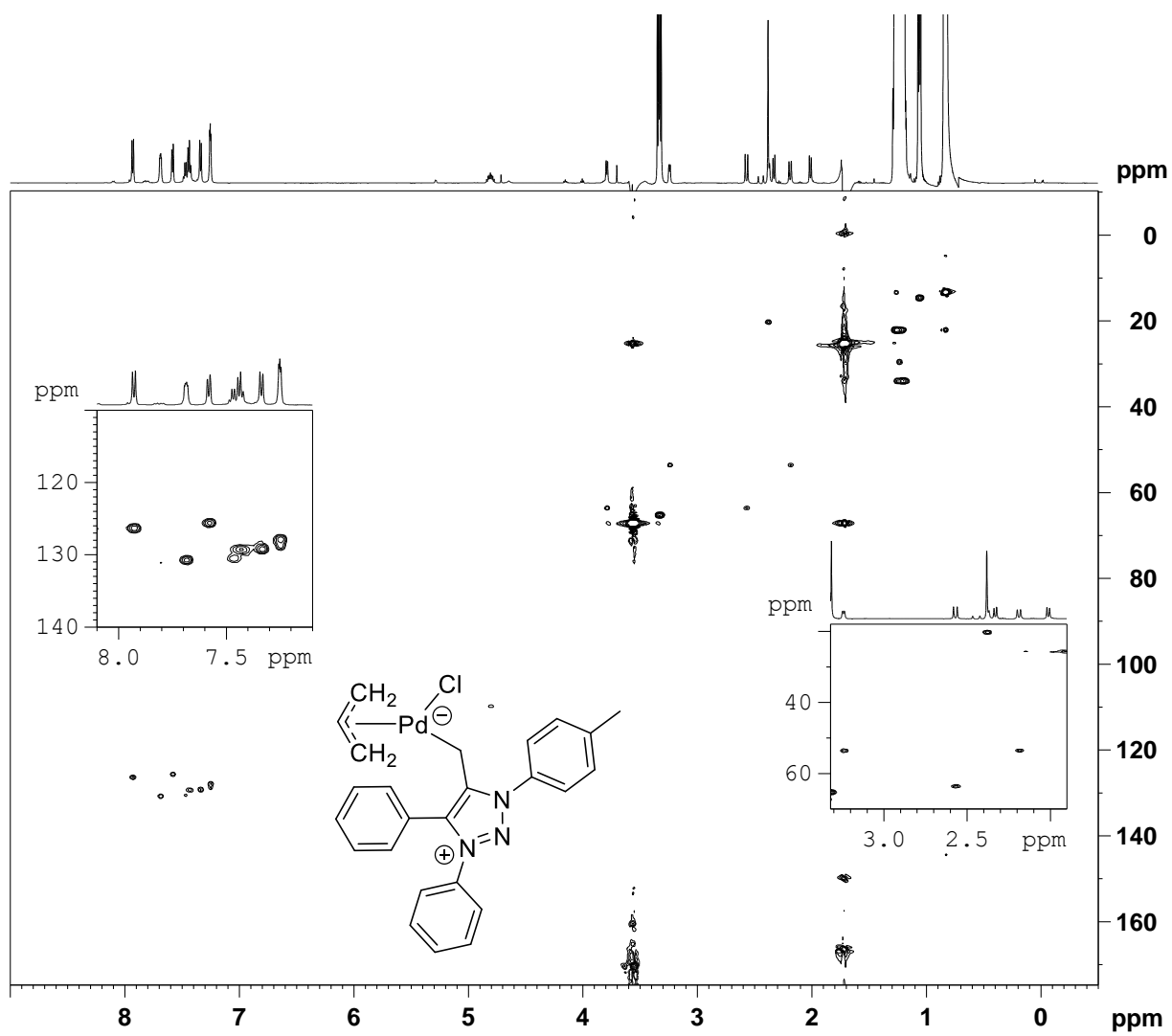
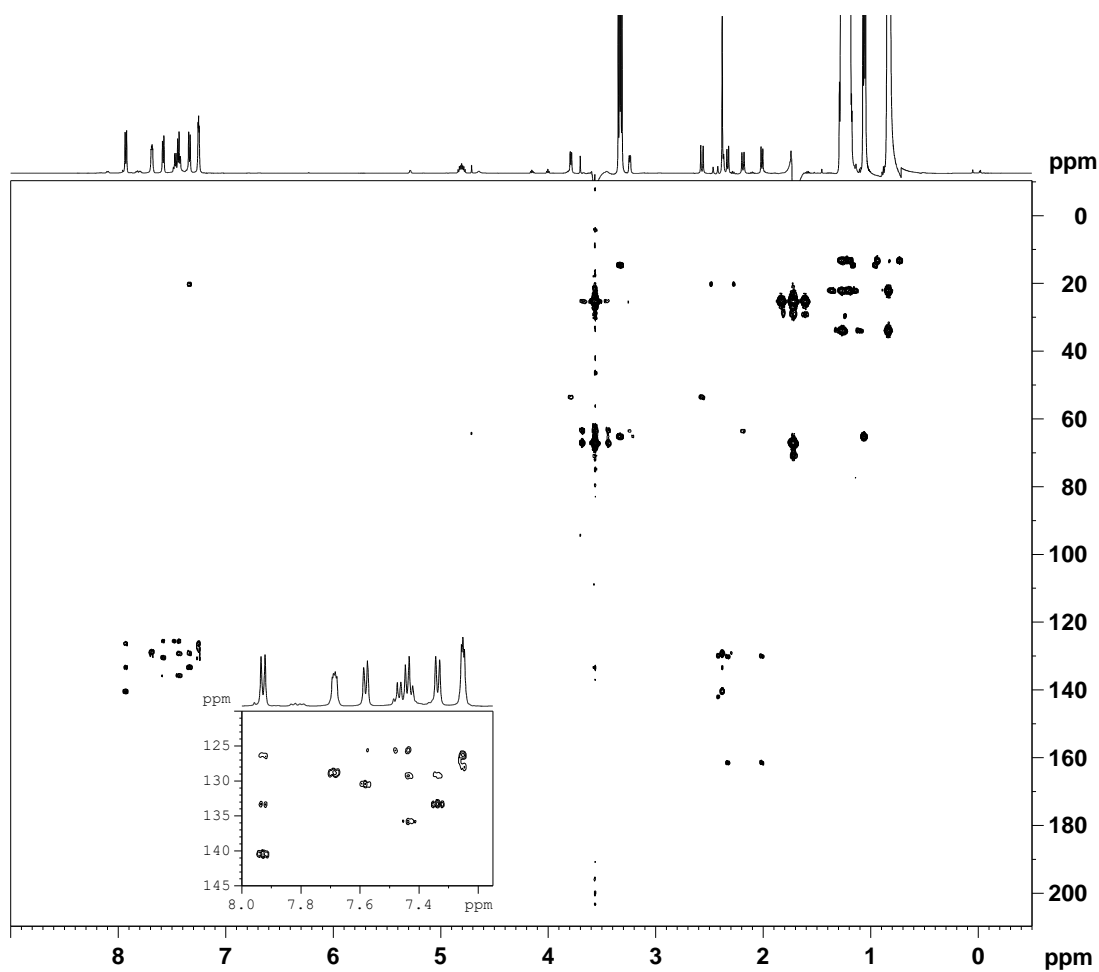


Figure S48. Solvent suppression No-D  $^1\text{H}$  NMR spectrum of **7aPd** in THF, 600 MHz.

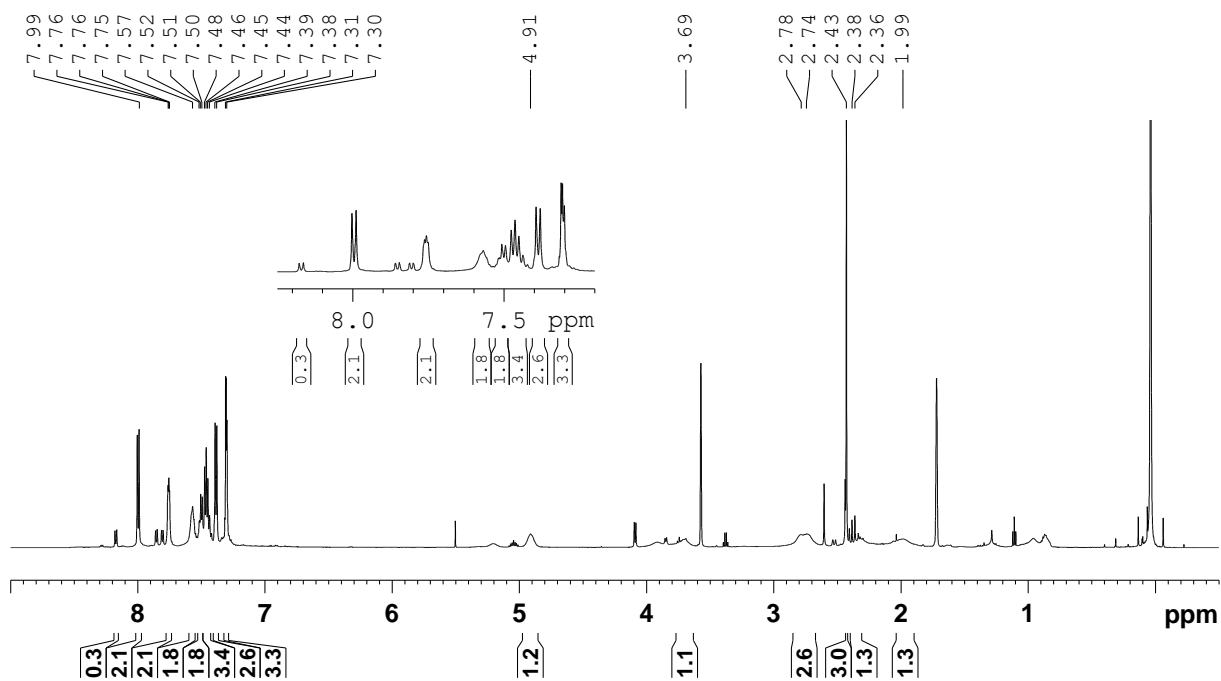




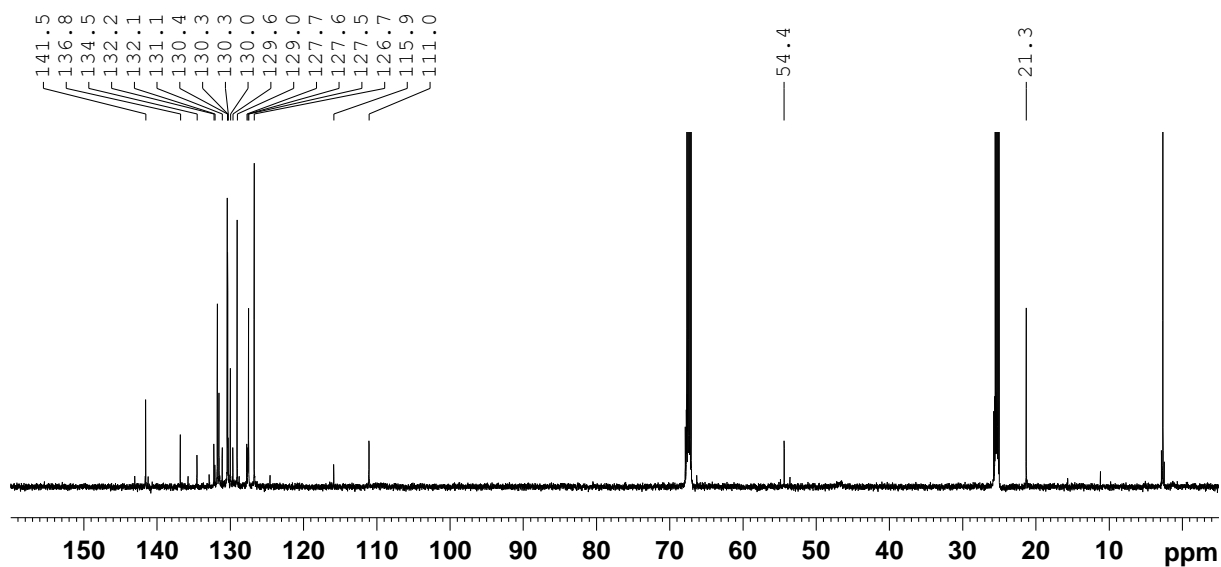
**Figure S49.**  $^1\text{H}$ - $^{13}\text{C}$  *gs*-HSQC NMR spectrum of **7aPd** in THF, 600 MHz NMR instrument.



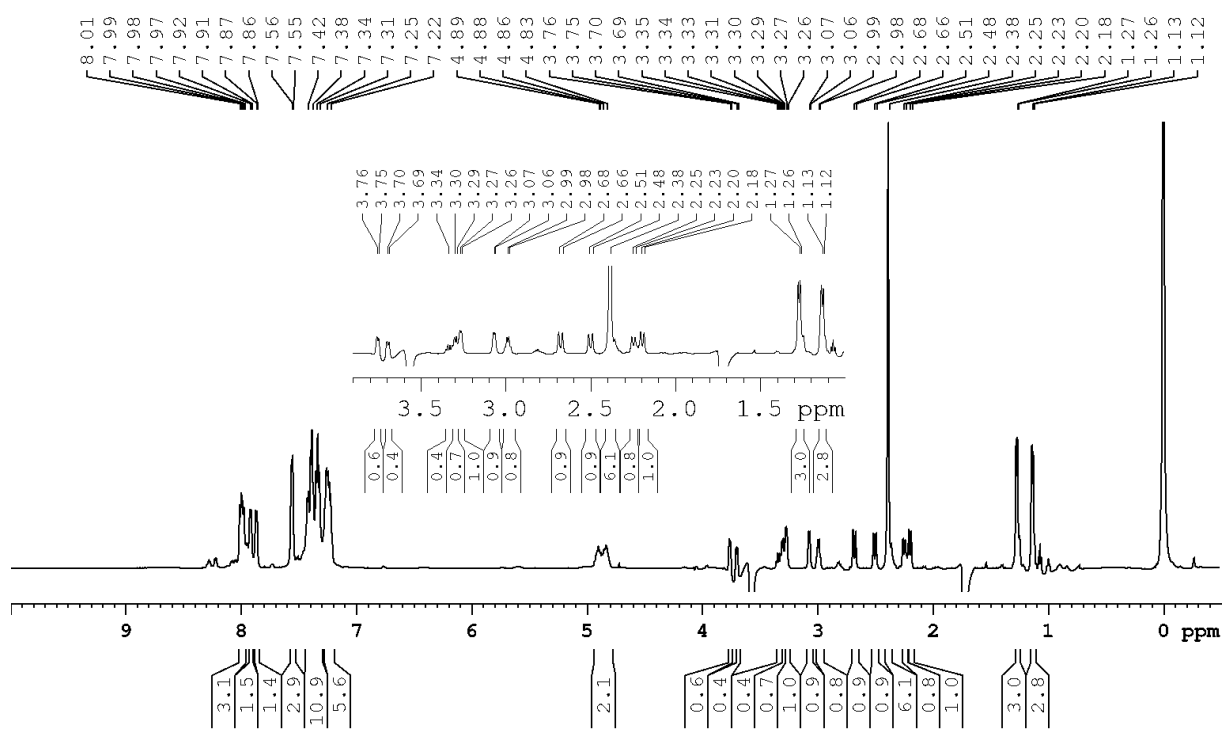
**Figure S50.**  $^1\text{H}$ - $^{13}\text{C}$  *gs*-HMBC NMR spectrum of **7aPd** in THF, 600 MHz NMR instrument.



**Figure S51.**  $^1\text{H}$  NMR spectrum of **7aPd** in THF- $d_8$ , 600 MHz. Contains 13% of **1a** as well as residues of allyl ligand and KHMDS.



**Figure S52.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **7aPd** in  $\text{THF-}d_8$ , 600 MHz. Contains 13% of **1a** as well as residues of KHMDS.



**Figure S53.** Solvent suppression No-D  $^1\text{H}$  NMR spectrum of **7bPd** in THF, 600 MHz.

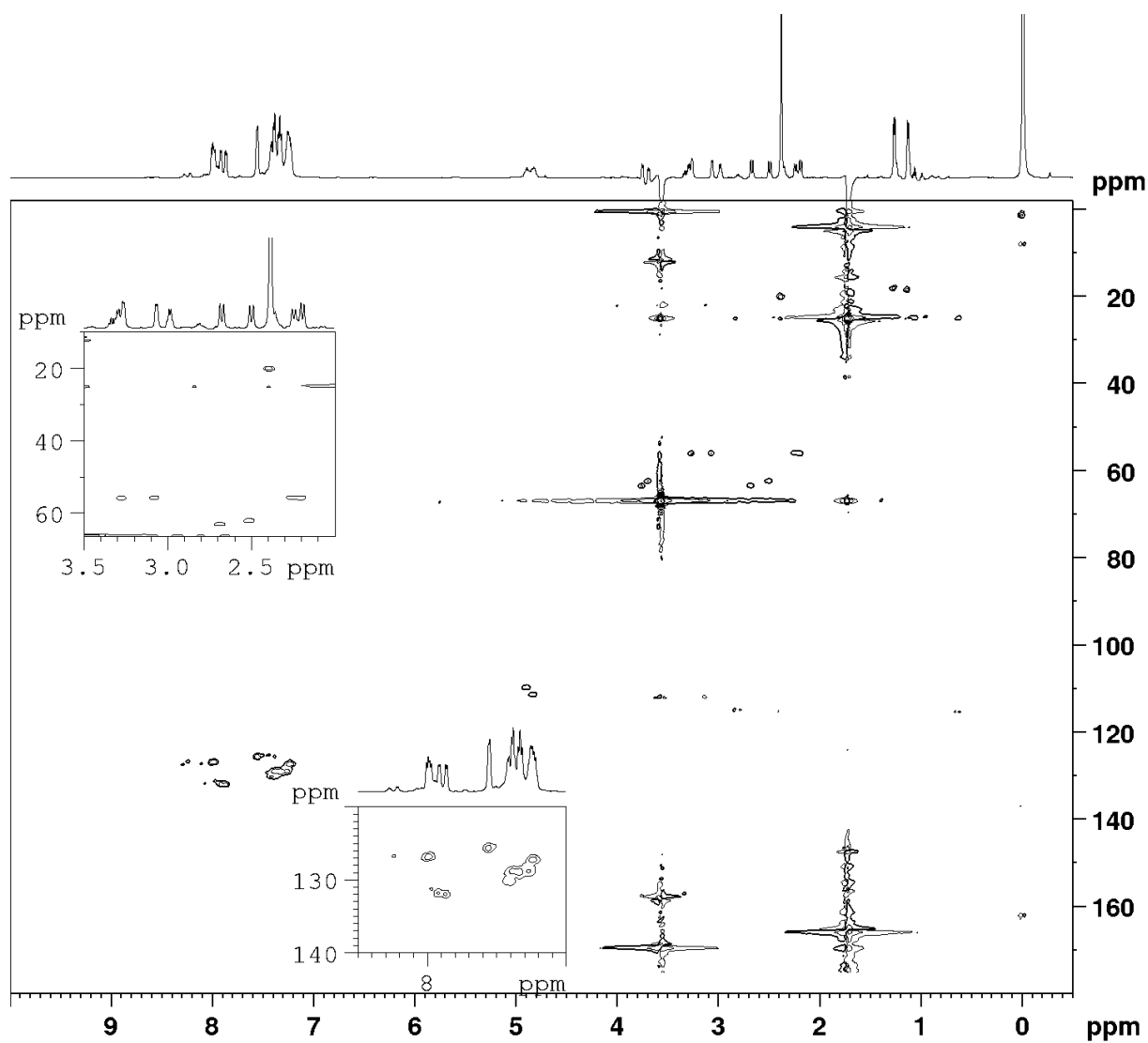
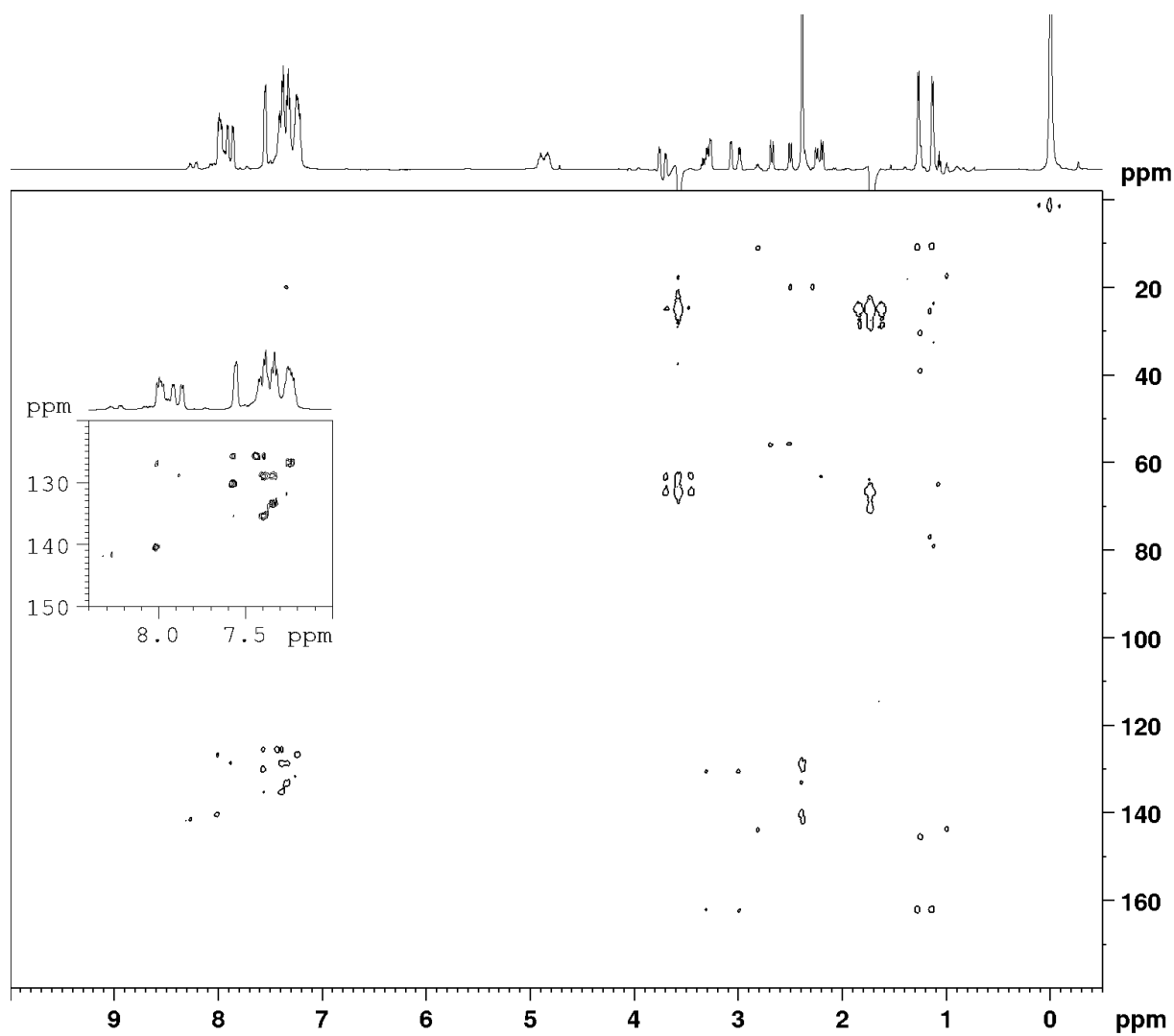
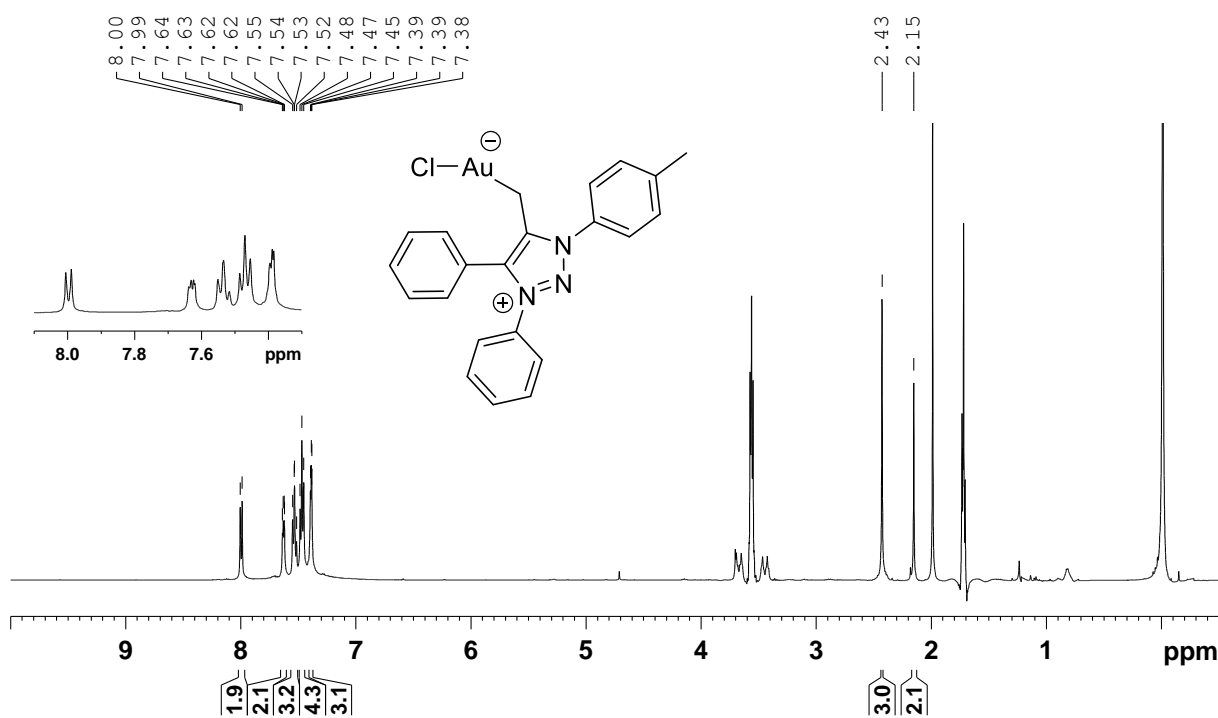


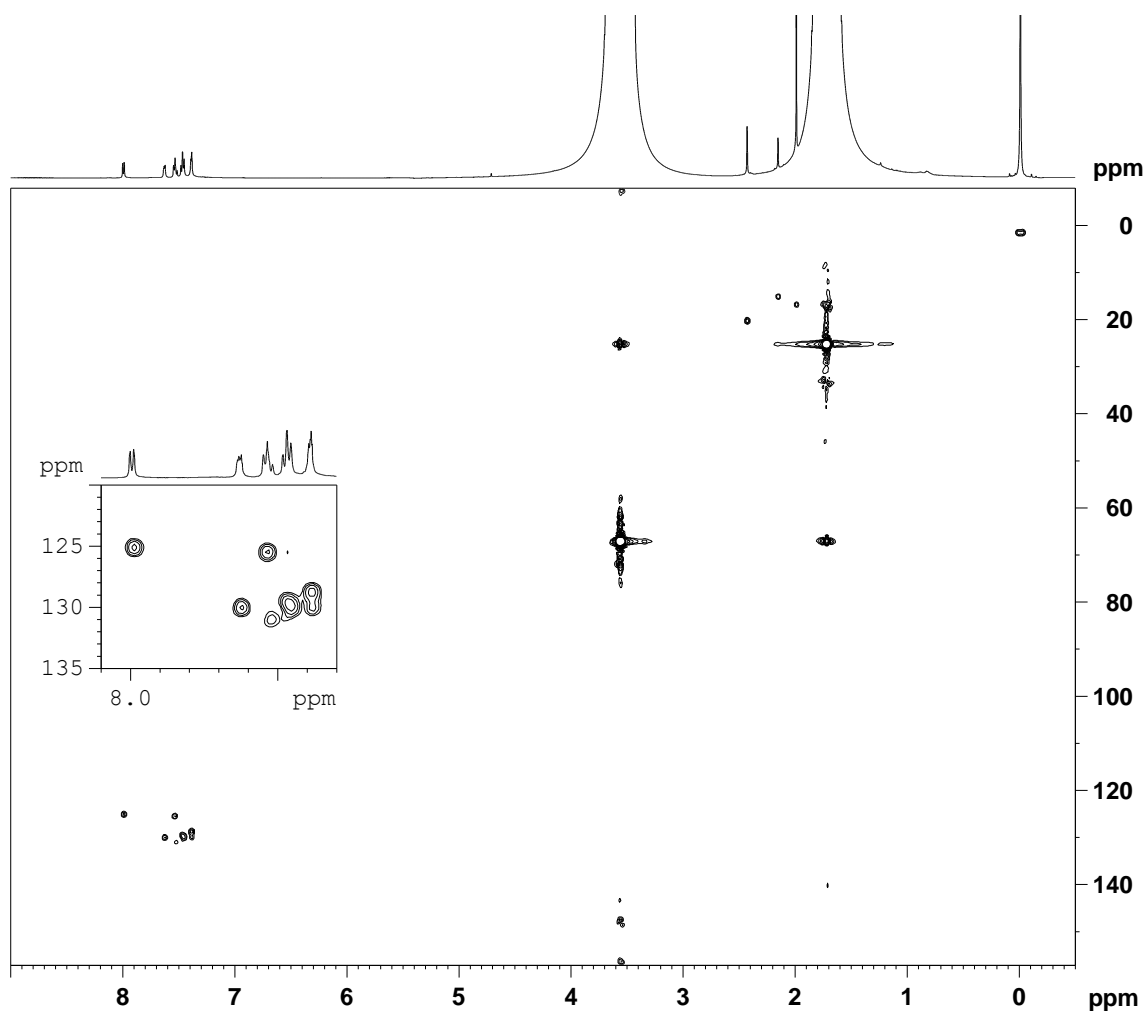
Figure S54.  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of **7bPd** in THF, 600 MHz NMR instrument.



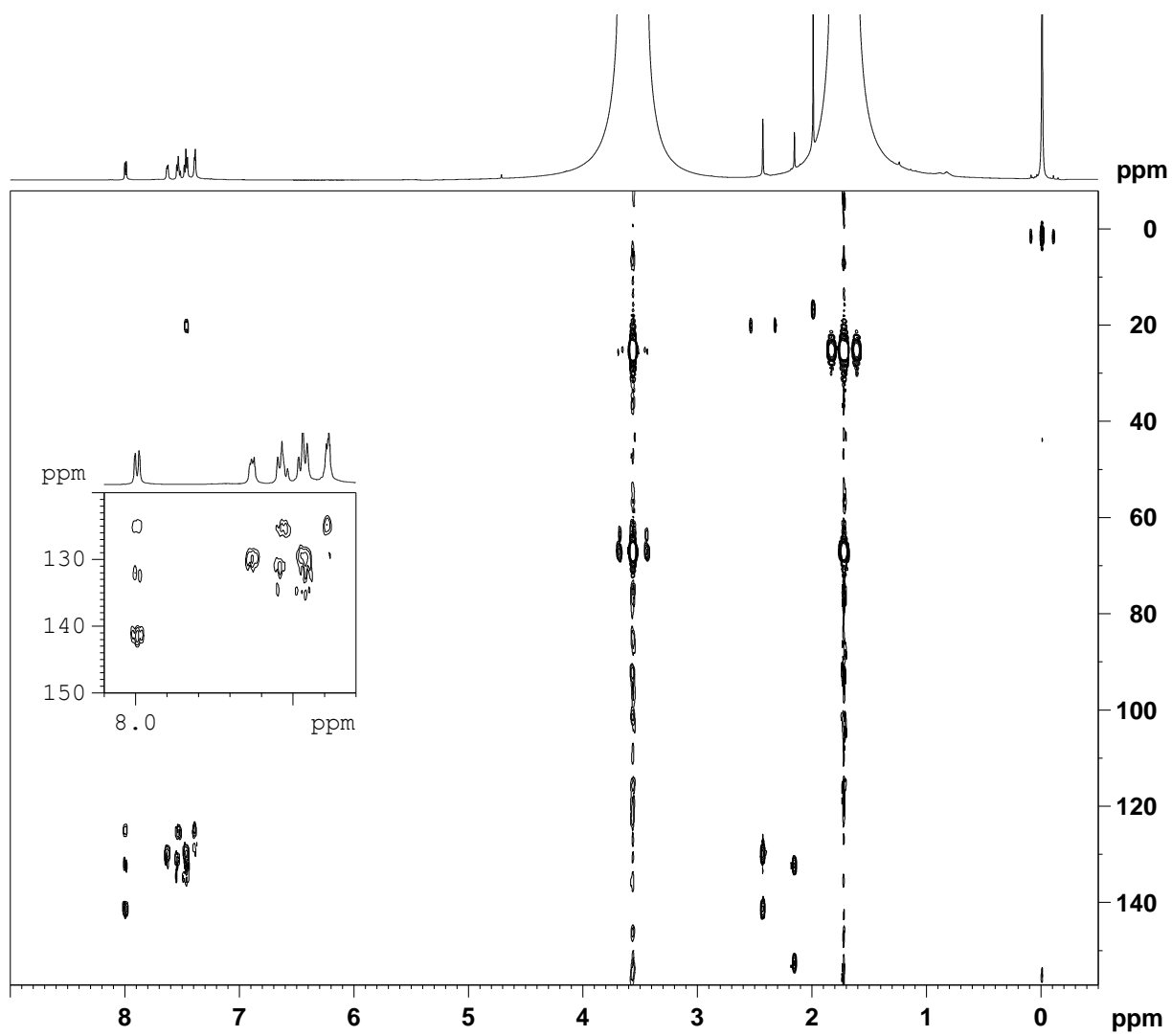
**Figure S55.**  $^1\text{H}$ - $^{13}\text{C}$  *gs*-HMBC NMR spectrum of **7bPd** in THF, 600 MHz NMR instrument.



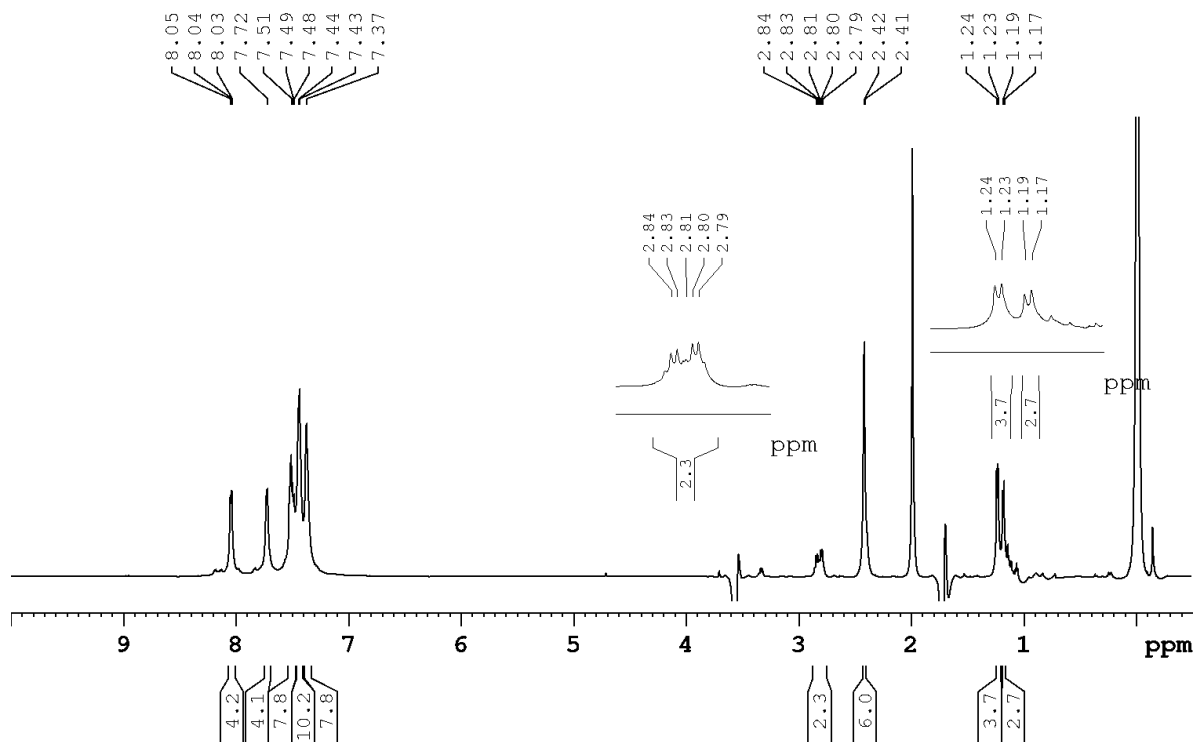
**Figure S56.** Solvent suppression No-D  $^1\text{H}$  NMR spectrum of **7aAu** in THF, 600 MHz NMR instrument.



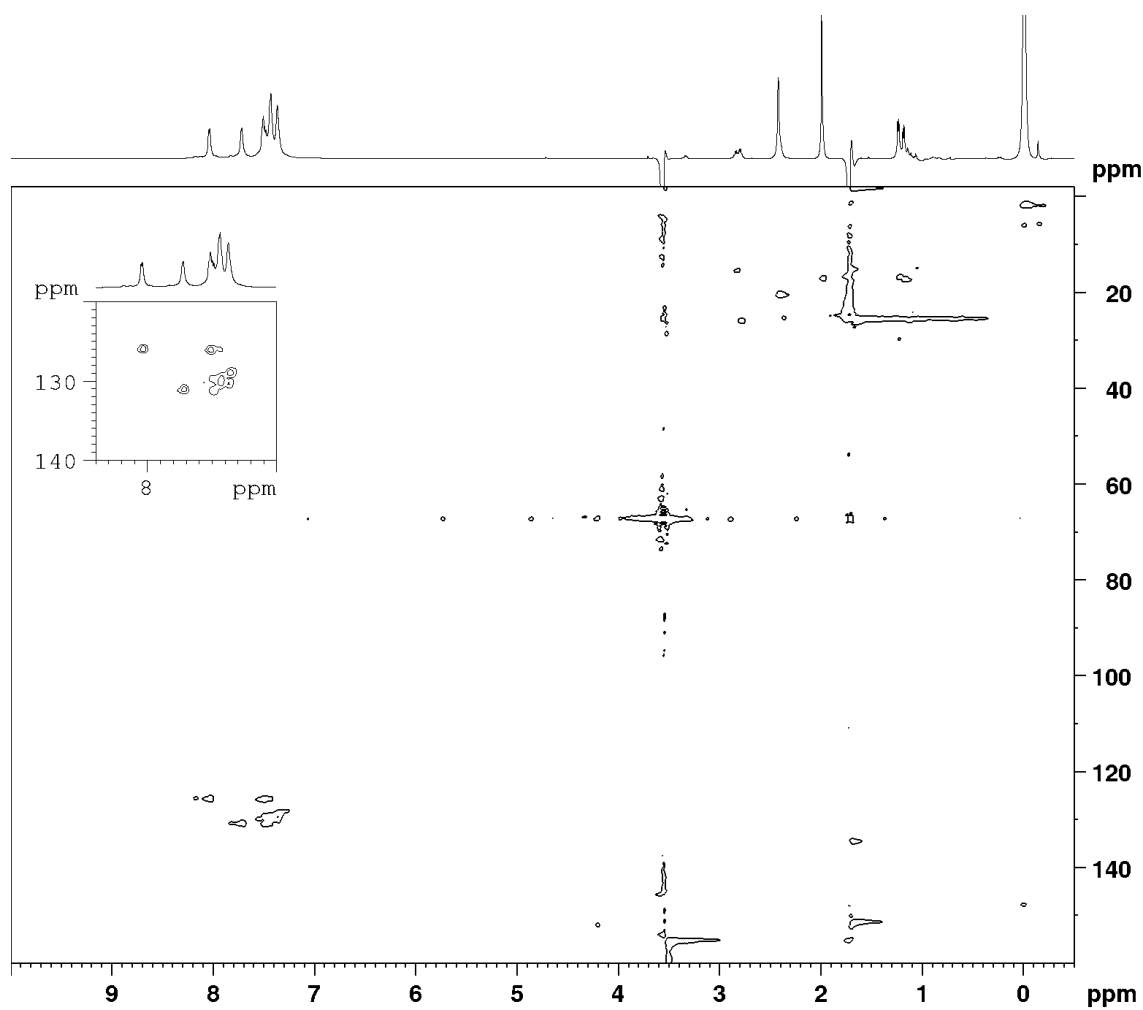
**Figure S57.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of **7aAu** in THF, 600 MHz NMR instrument.



**Figure S58.**  $^1\text{H}$ - $^{13}\text{C}$  *gs*-HMBC NMR spectrum of **7aAu** in THF, 600 MHz NMR instrument.

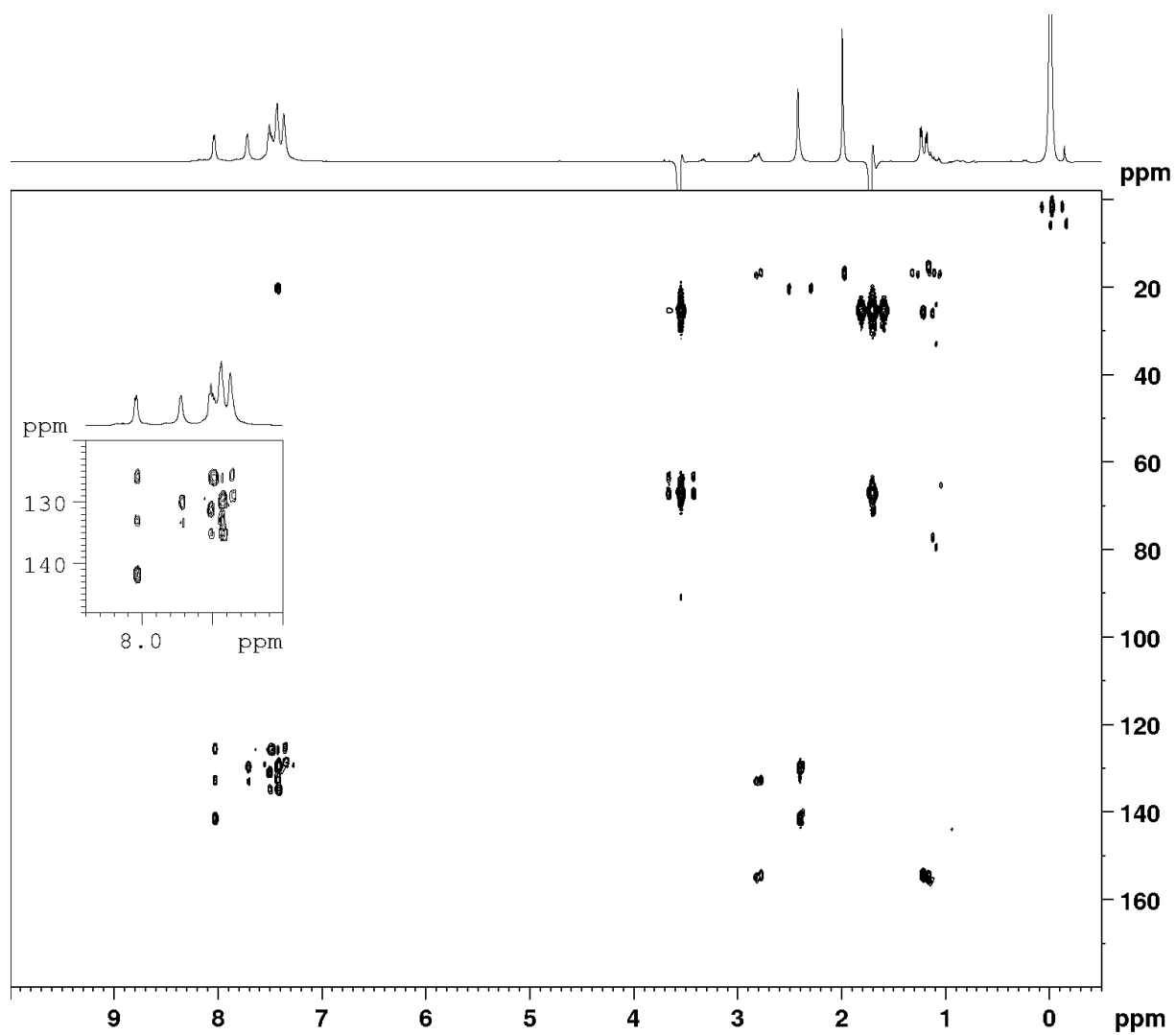


**Figure S59.** Solvent suppression No-D  $^1\text{H}$  NMR spectrum of **7bAu** in THF, 600 MHz.



**Figure S60.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of **7bAu** in THF, 600 MHz NMR instrument.





**Figure S61.**  $^1\text{H}$ - $^{13}\text{C}$  *gs*-HMBC NMR spectrum of **7bAu** in THF, 600 MHz NMR instrument.

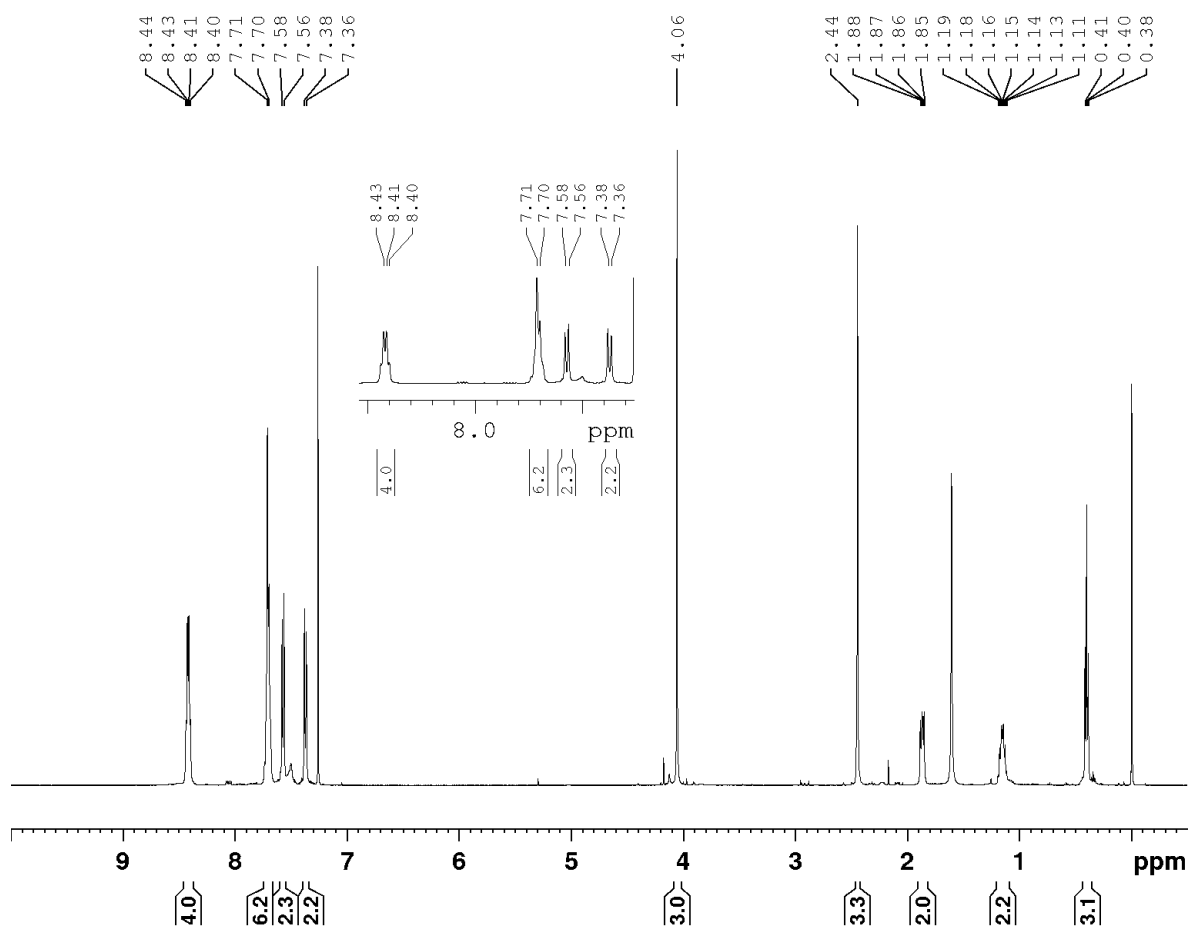


Figure S62.  $^1\text{H}$  NMR spectrum of **9hPd** in  $\text{CDCl}_3$ , 500 MHz.

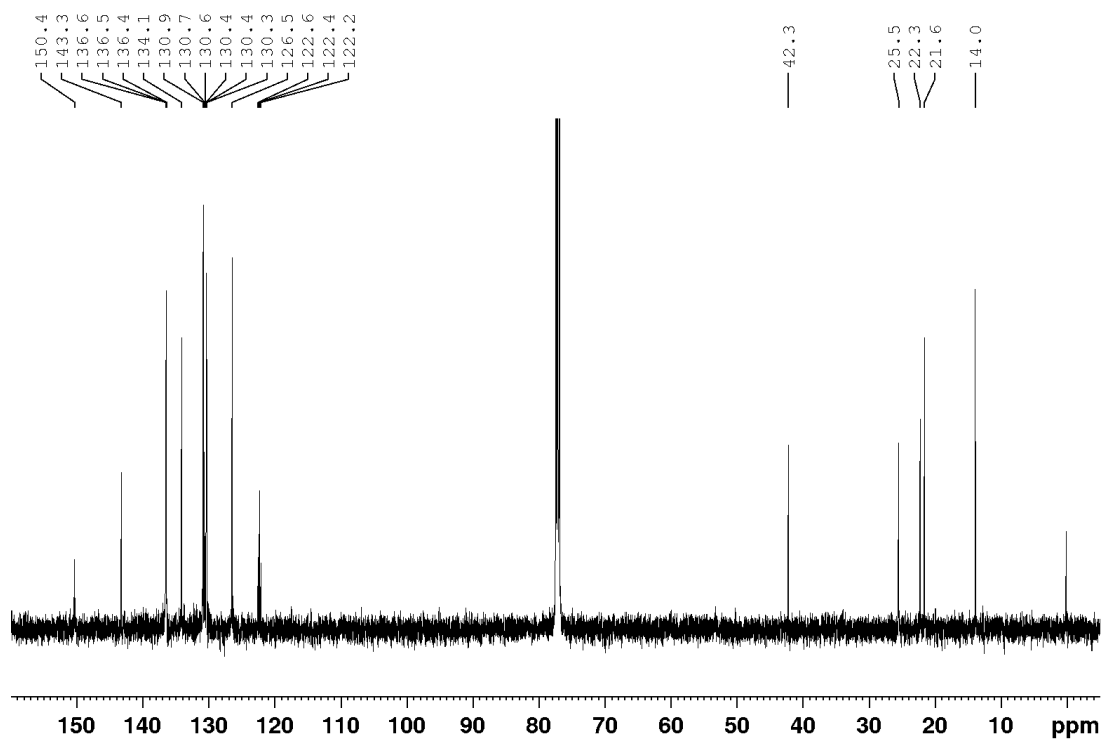


Figure S63.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **9hPd** in  $\text{CDCl}_3$ , 126 MHz.

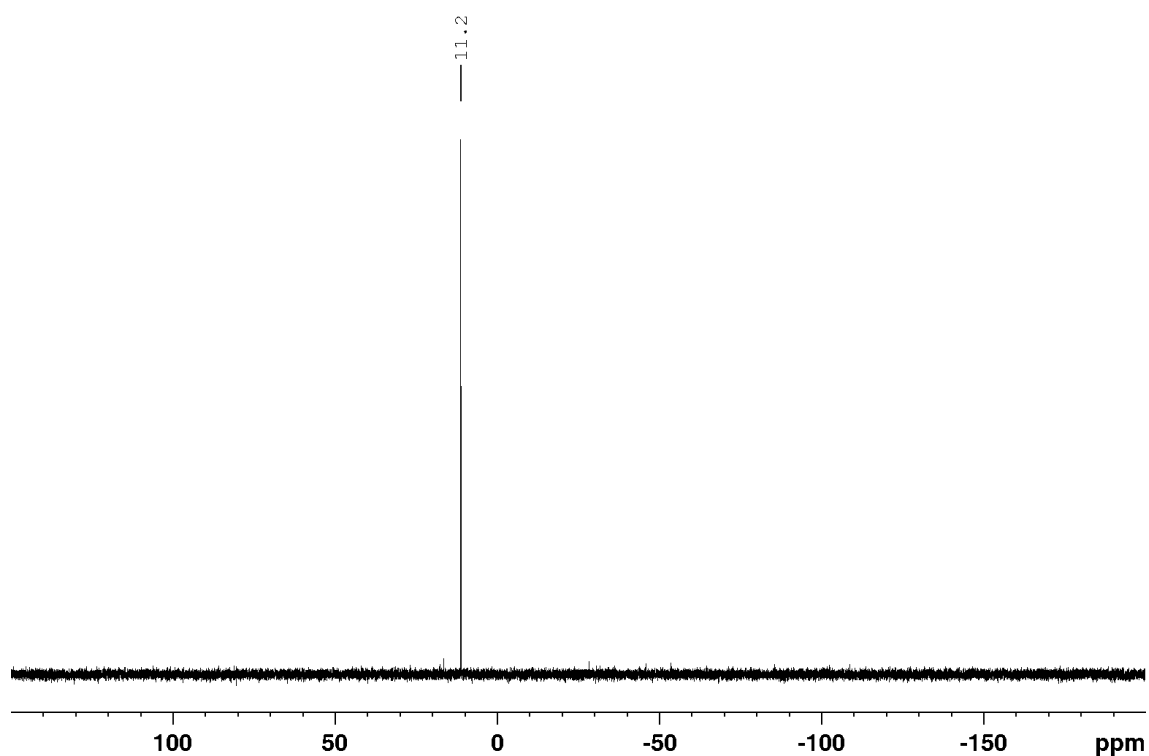


Figure S64.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **9hPd** in  $\text{CDCl}_3$ , 151 MHz.

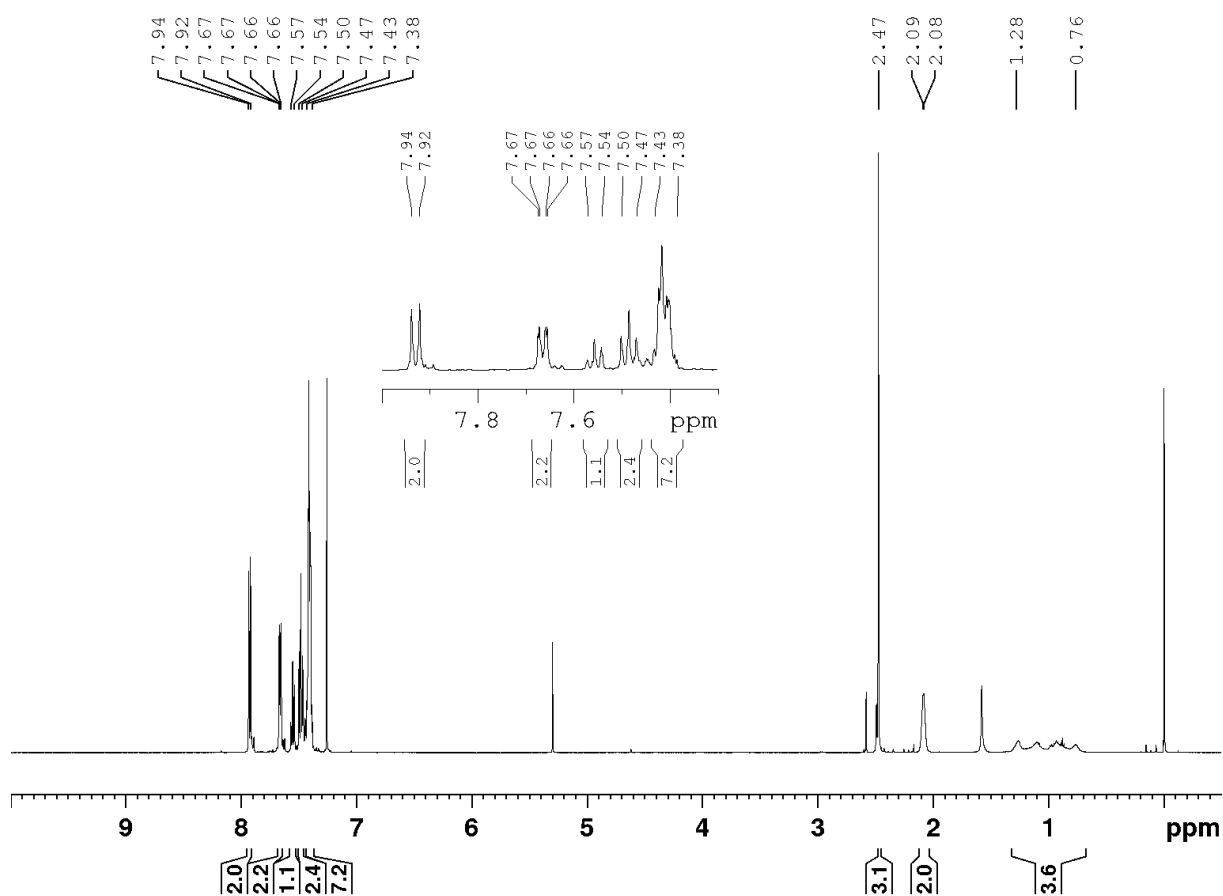


Figure S65.  $^1\text{H}$  NMR spectrum of **10aBH<sub>3</sub>** in  $\text{CDCl}_3$ , 500 MHz.

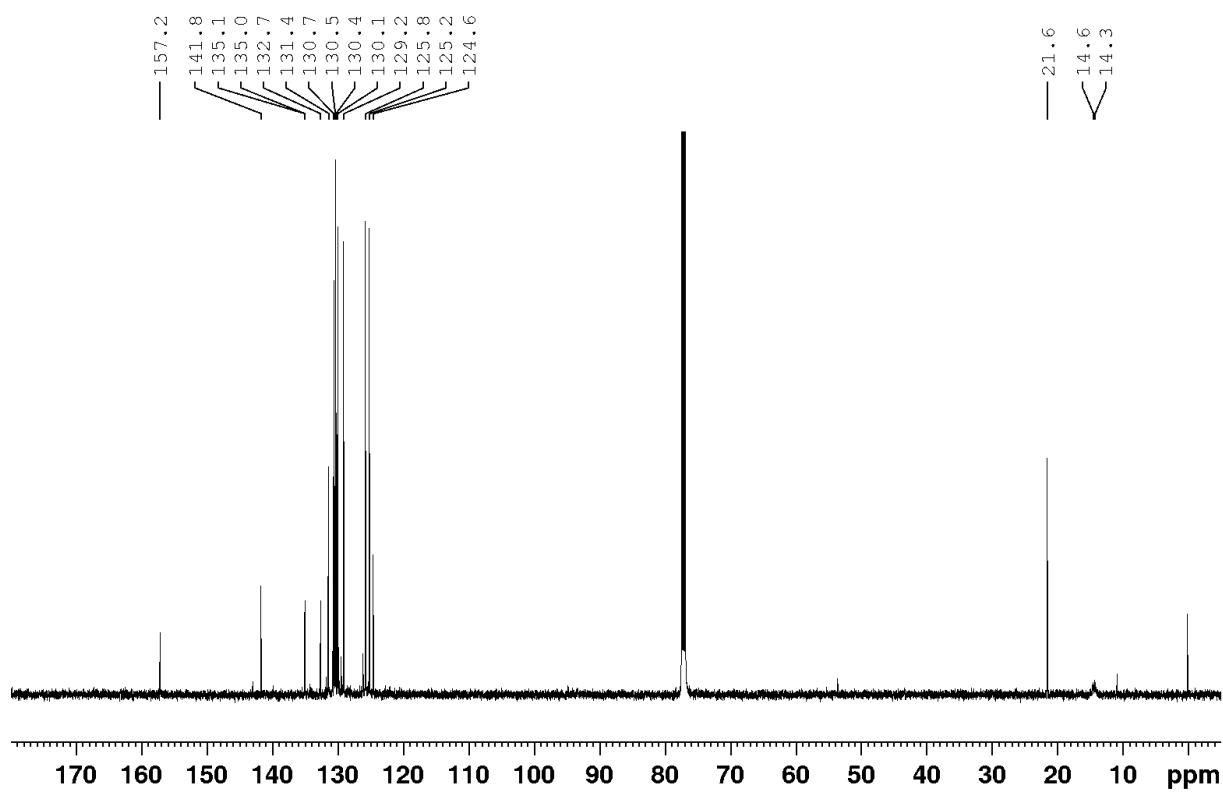


Figure S66.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $10\text{aBH}_3$  in  $\text{CDCl}_3$ , 126 MHz.

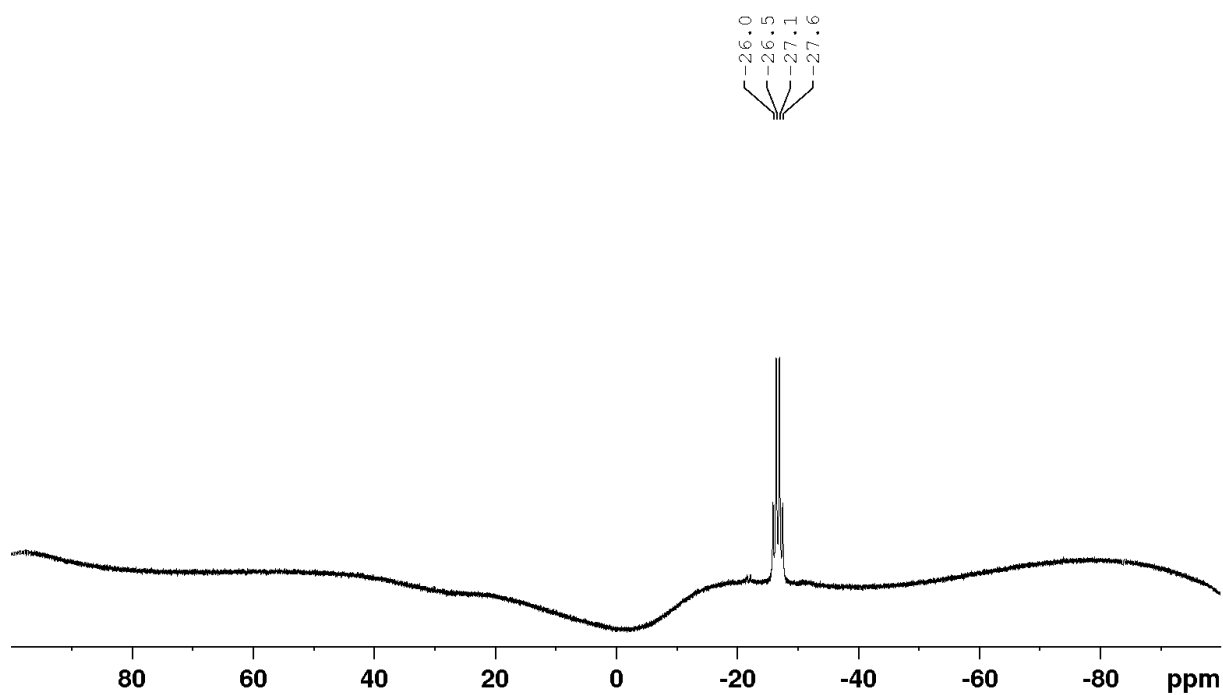


Figure S67.  $^{11}\text{B}$  NMR spectrum of  $10\text{aBH}_3$  in  $\text{CDCl}_3$ , 160 MHz.

### NMR spectra of aldehyde reductions

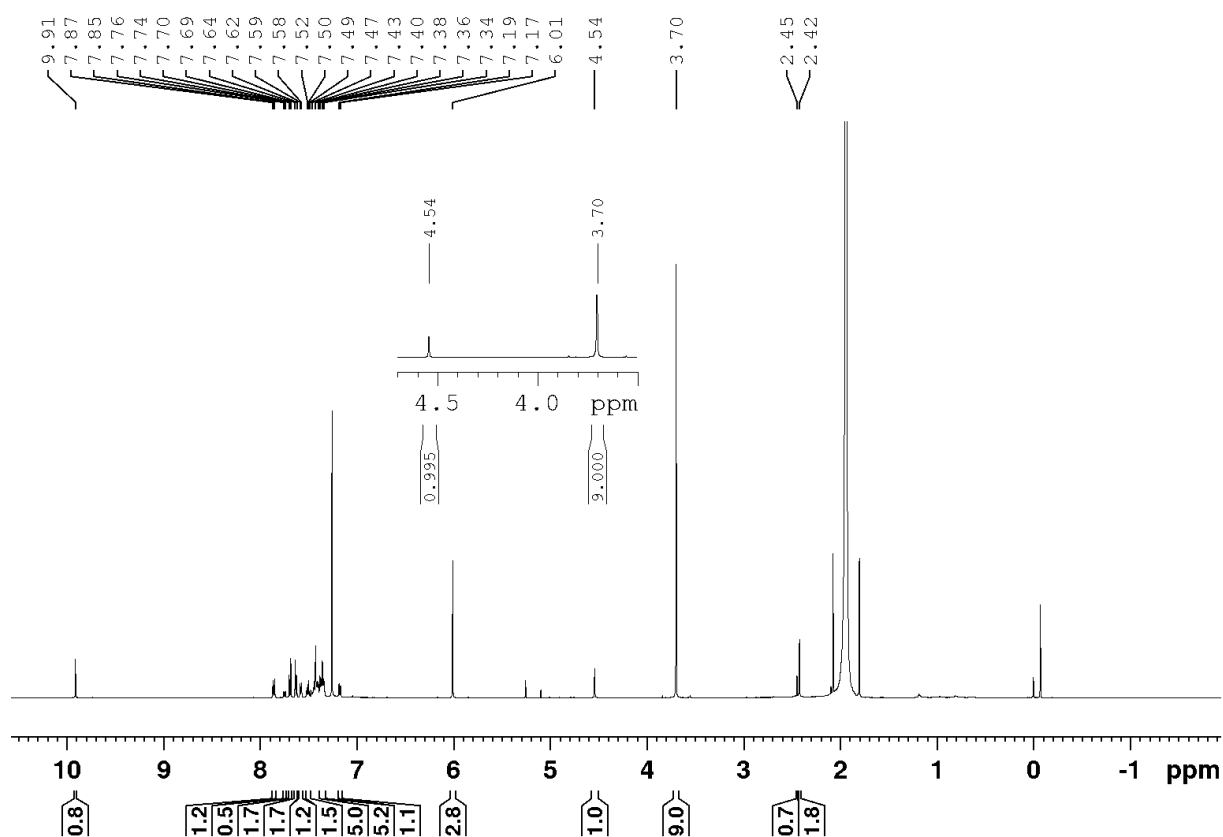


Figure S68. <sup>1</sup>H NMR spectrum of 4-bromobenzaldehyde (**11b**) reduction after 4 h.

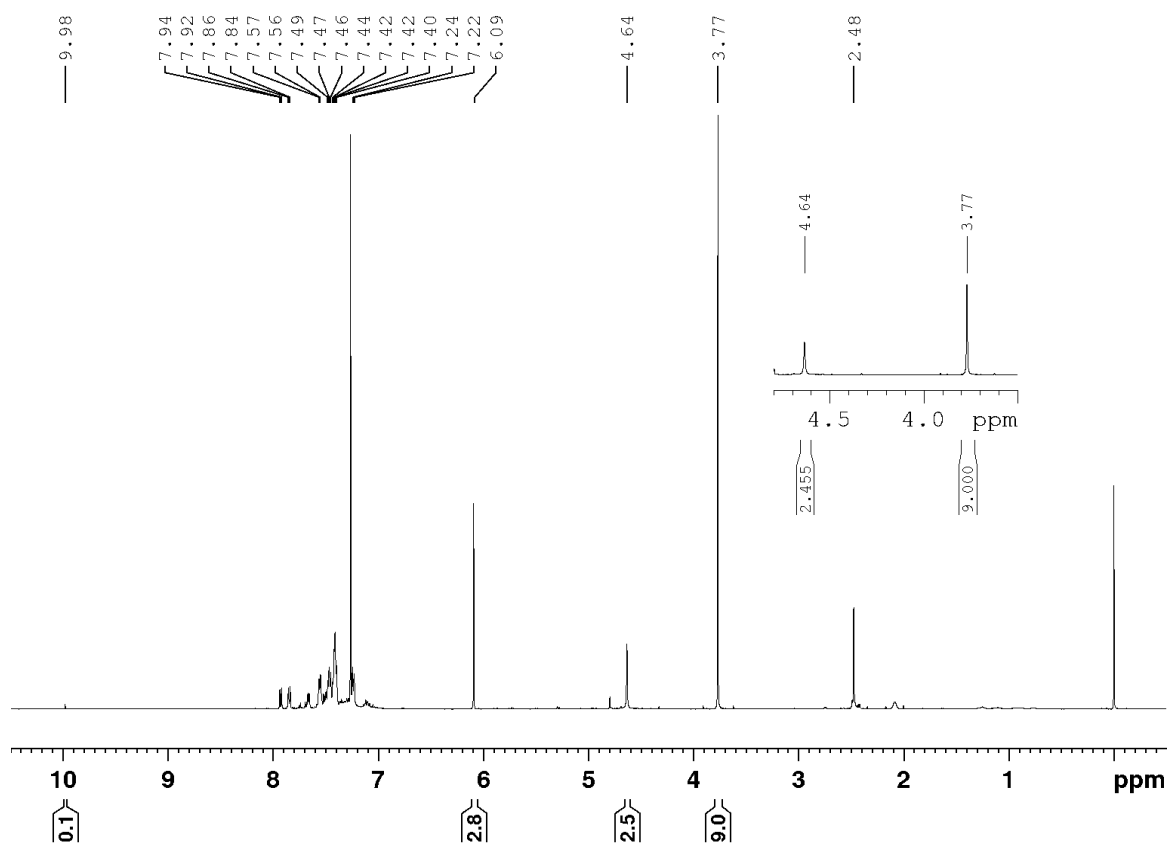


Figure S69. <sup>1</sup>H NMR spectrum of 4-bromobenzaldehyde (**11b**) reduction after 24 h.

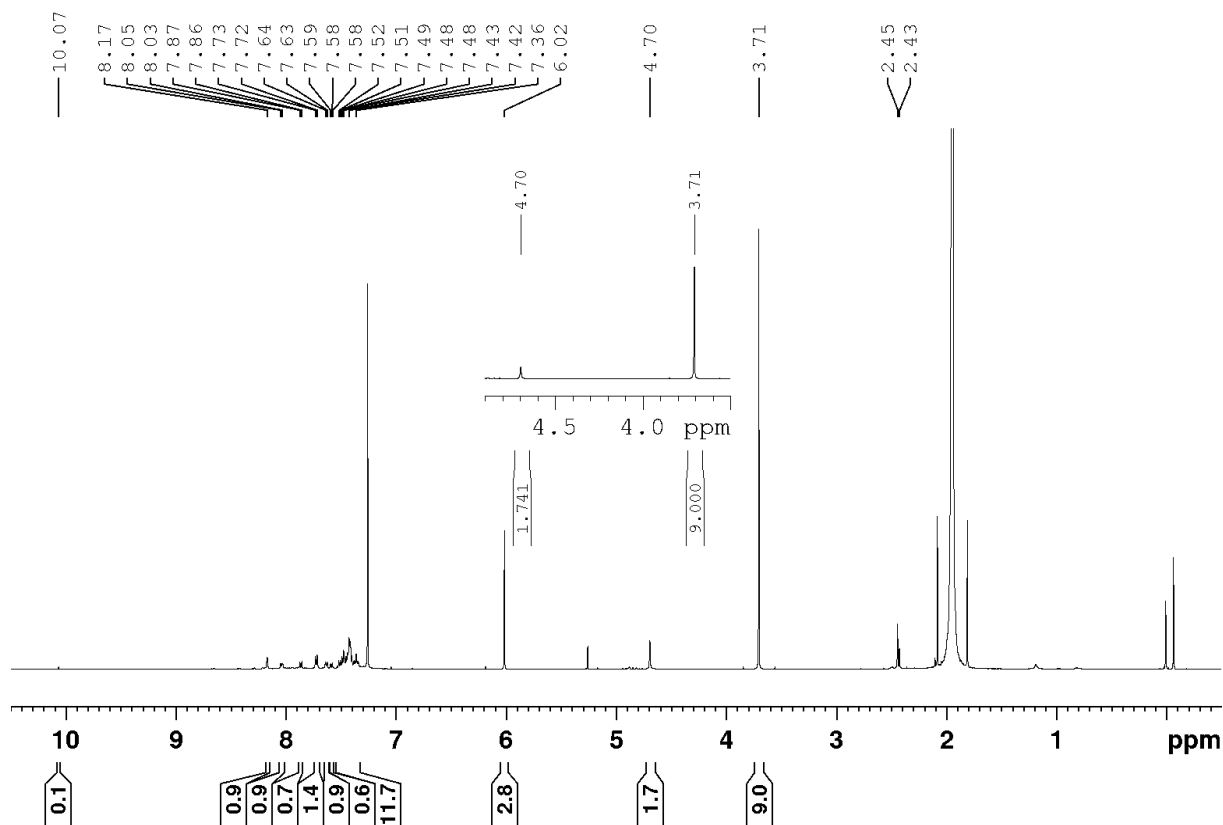


Figure S70.  $^1\text{H}$  NMR spectrum of 3-nitrobenzaldehyde (**11c**) reduction after 4 h.

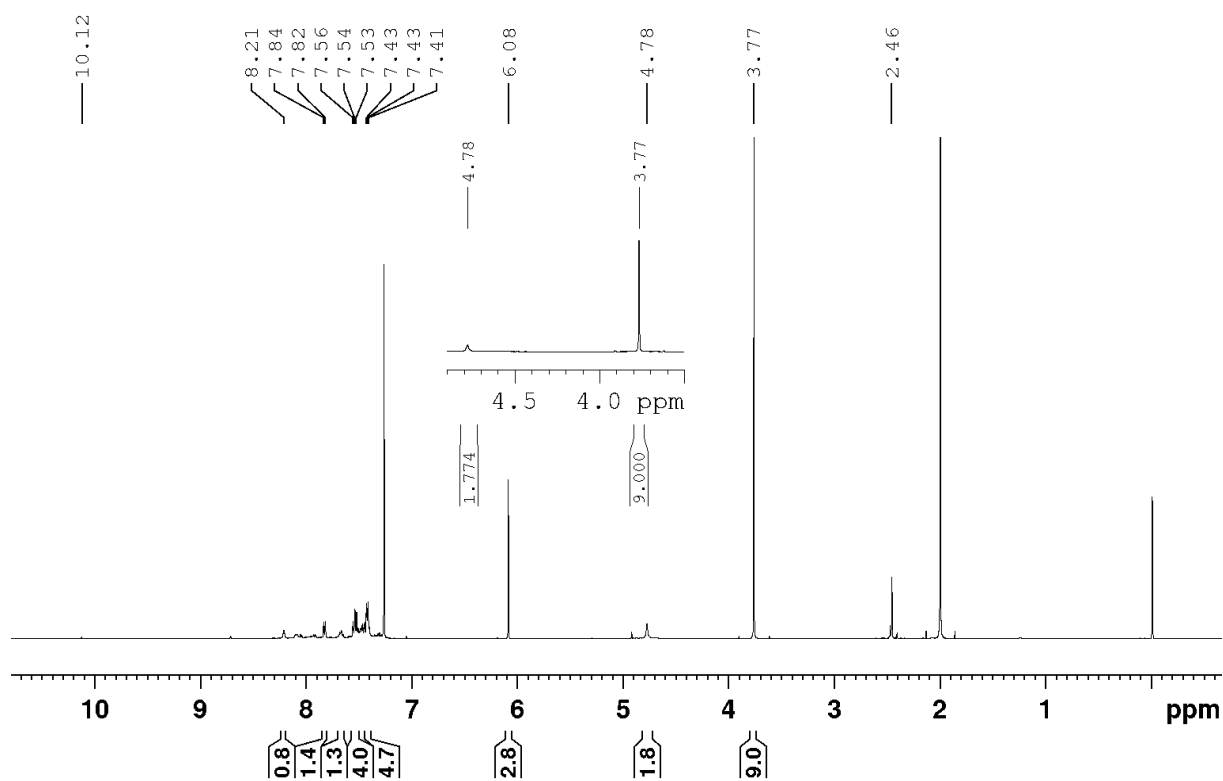


Figure S71.  $^1\text{H}$  NMR spectrum of 3-nitrobenzaldehyde (**11c**) reduction after 24 h.

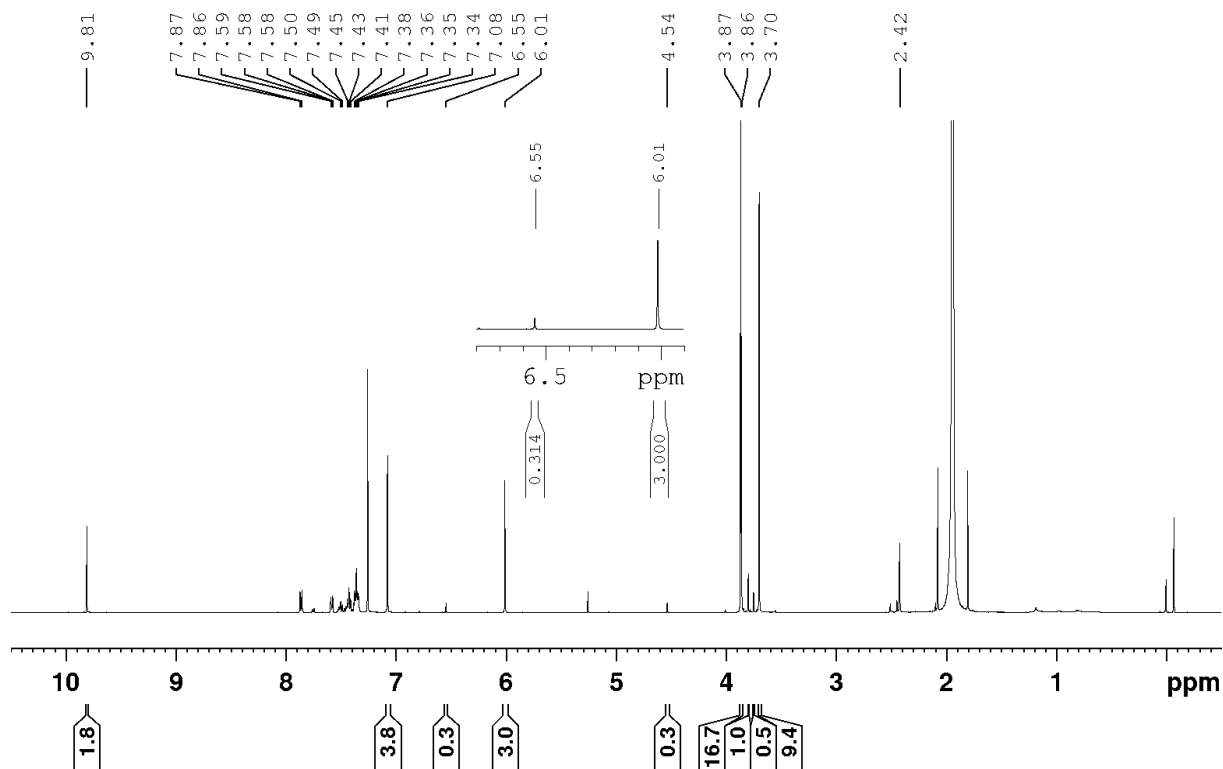


Figure S72. <sup>1</sup>H NMR spectrum of 2,3,4-trimethoxybenzaldehyde (**11d**) reduction after 4 h.

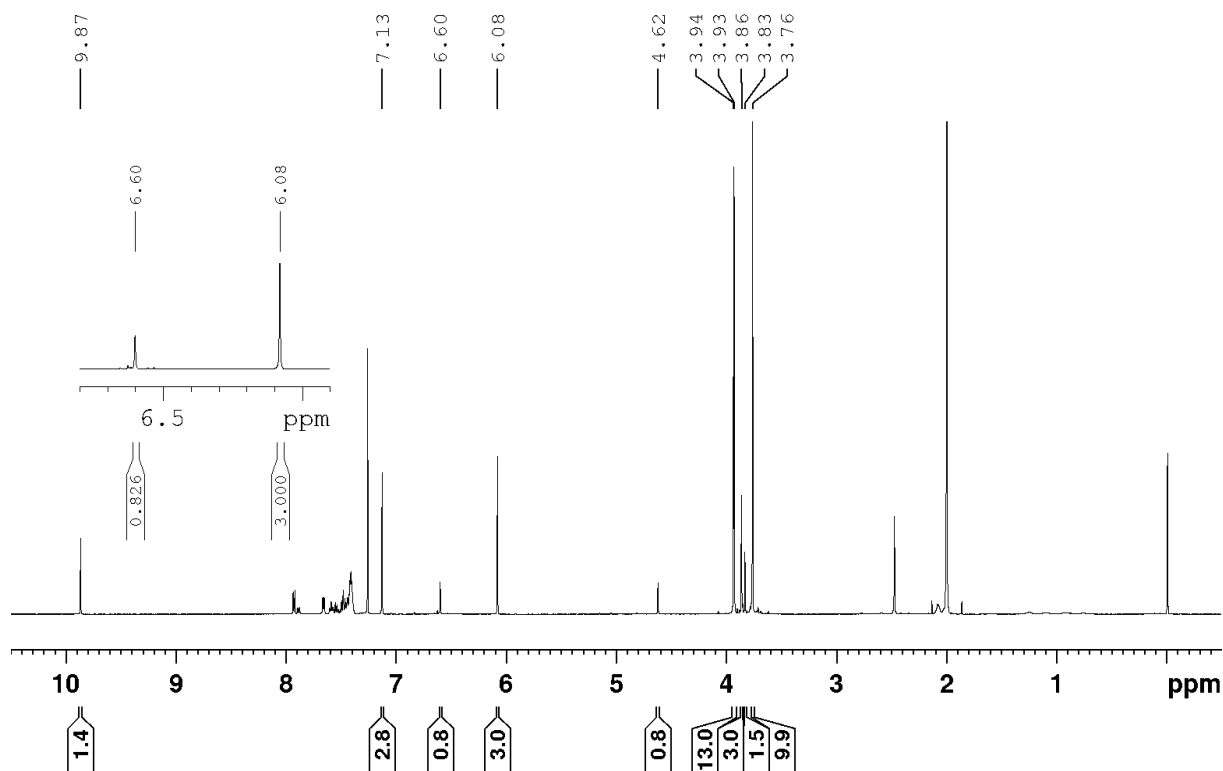


Figure S73. <sup>1</sup>H NMR spectrum of 2,3,4-trimethoxybenzaldehyde (**11d**) reduction after 24 h.

### NMR spectra of ketone reductions

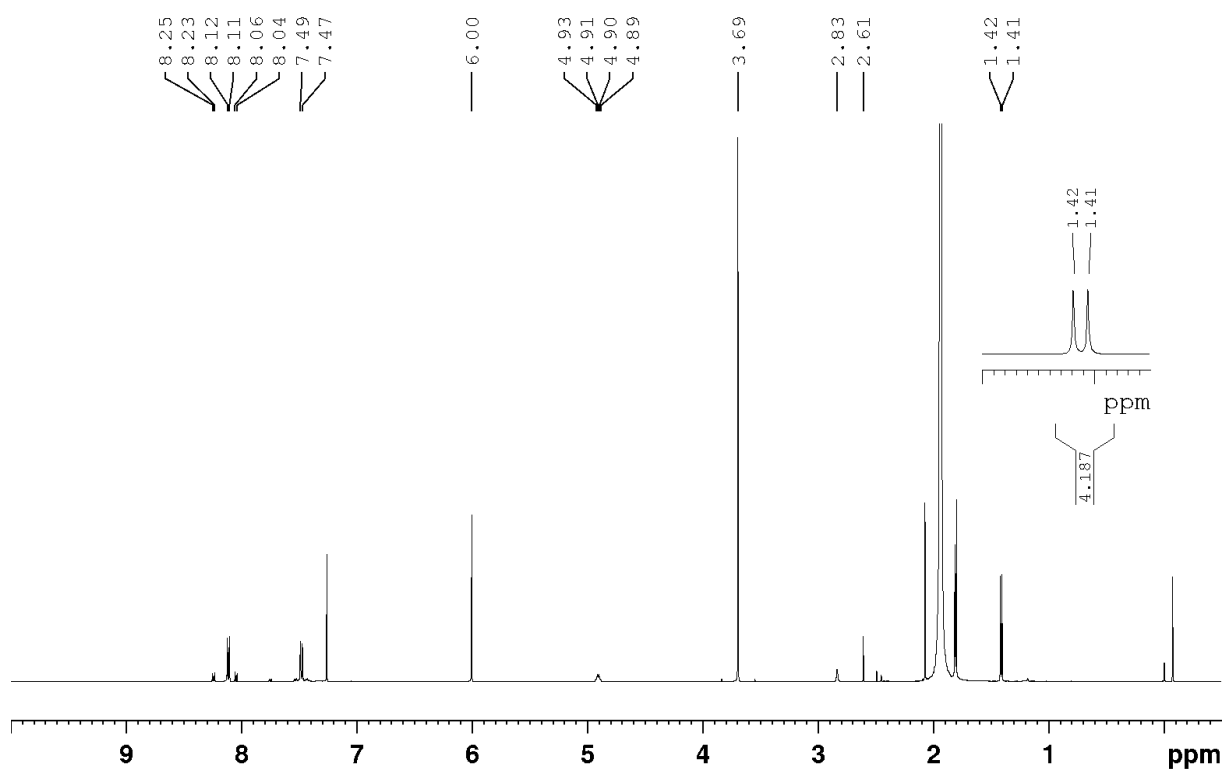


Figure S74. <sup>1</sup>H NMR spectrum of 4-nitroacetophenone (13a) reduction after 4 h.

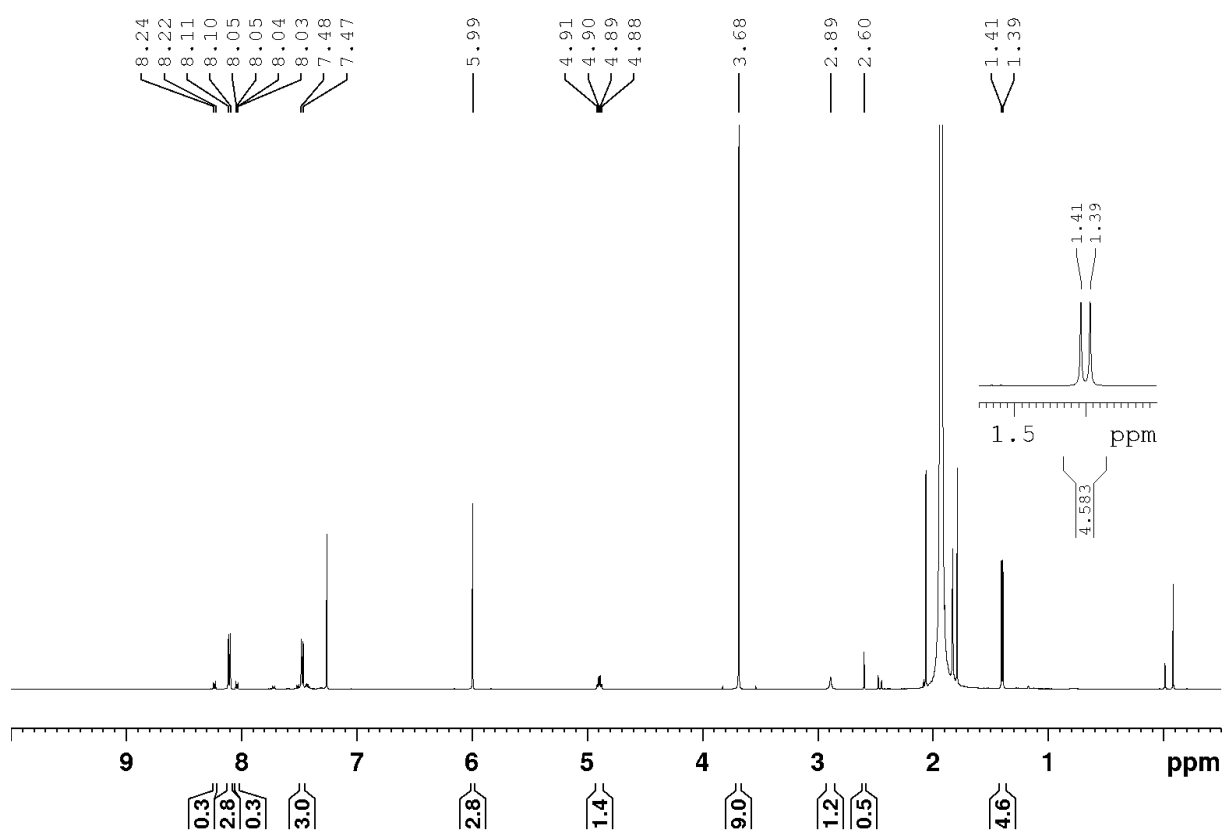


Figure S75. <sup>1</sup>H NMR spectrum of 4-nitroacetophenone (13a) reduction after 24 h.



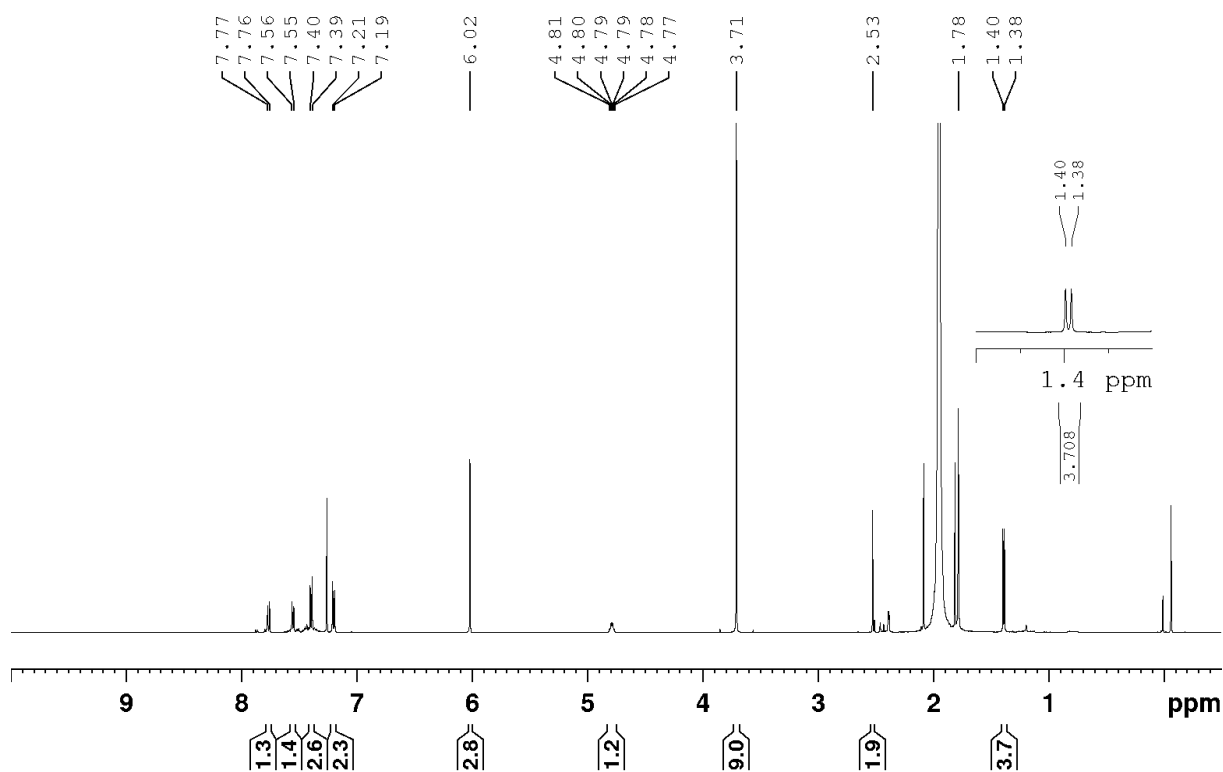


Figure S76.  $^1\text{H}$  NMR spectrum of 4-bromoacetophenone (**13b**) reduction after 4 h.

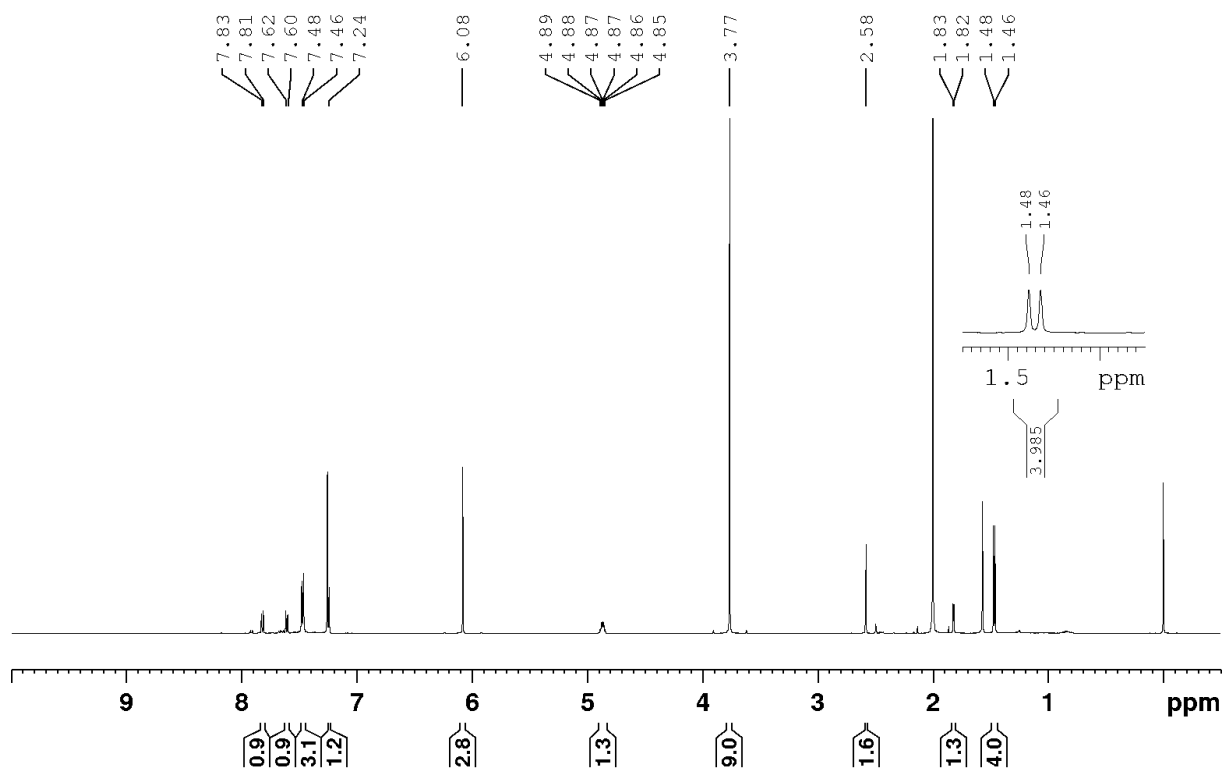


Figure S77.  $^1\text{H}$  NMR spectrum of 4-bromoacetophenone (**13b**) reduction after 24 h.

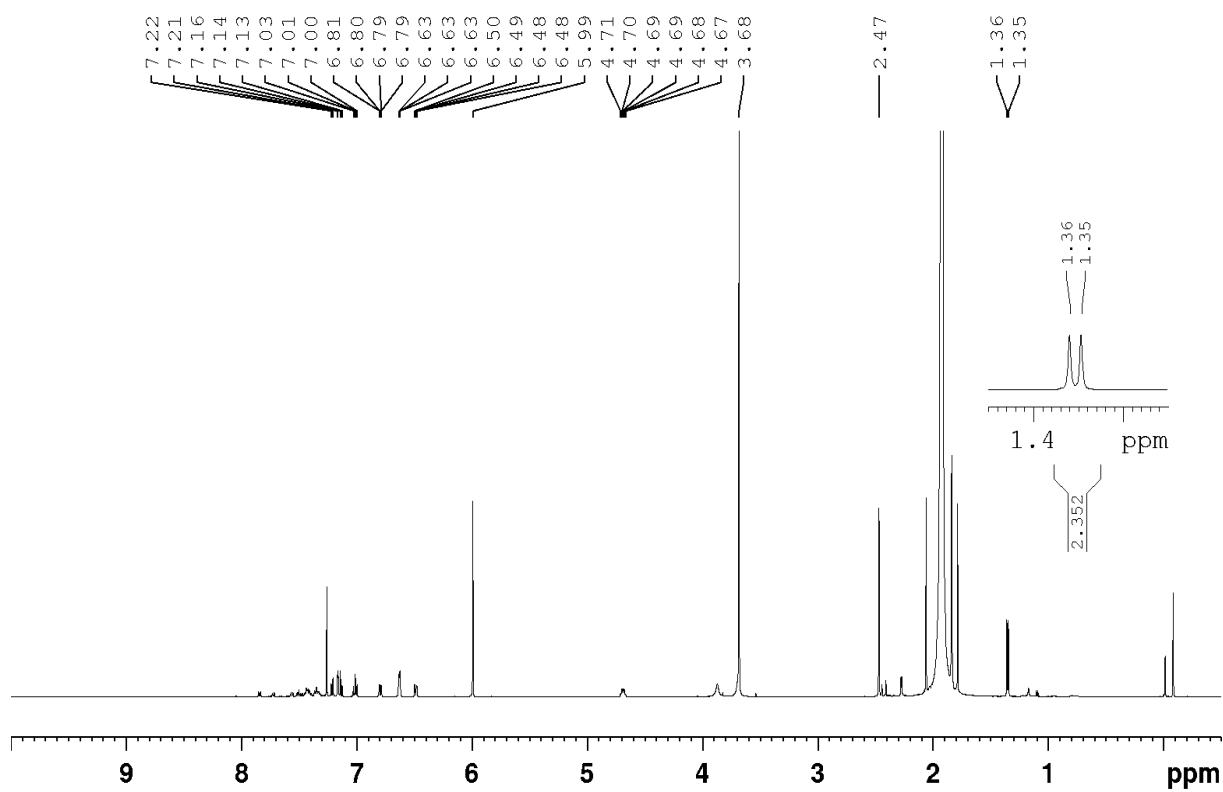


Figure S78.  $^1\text{H}$  NMR spectrum of 3-aminoacetophenone (**13c**) reduction after 4 h.

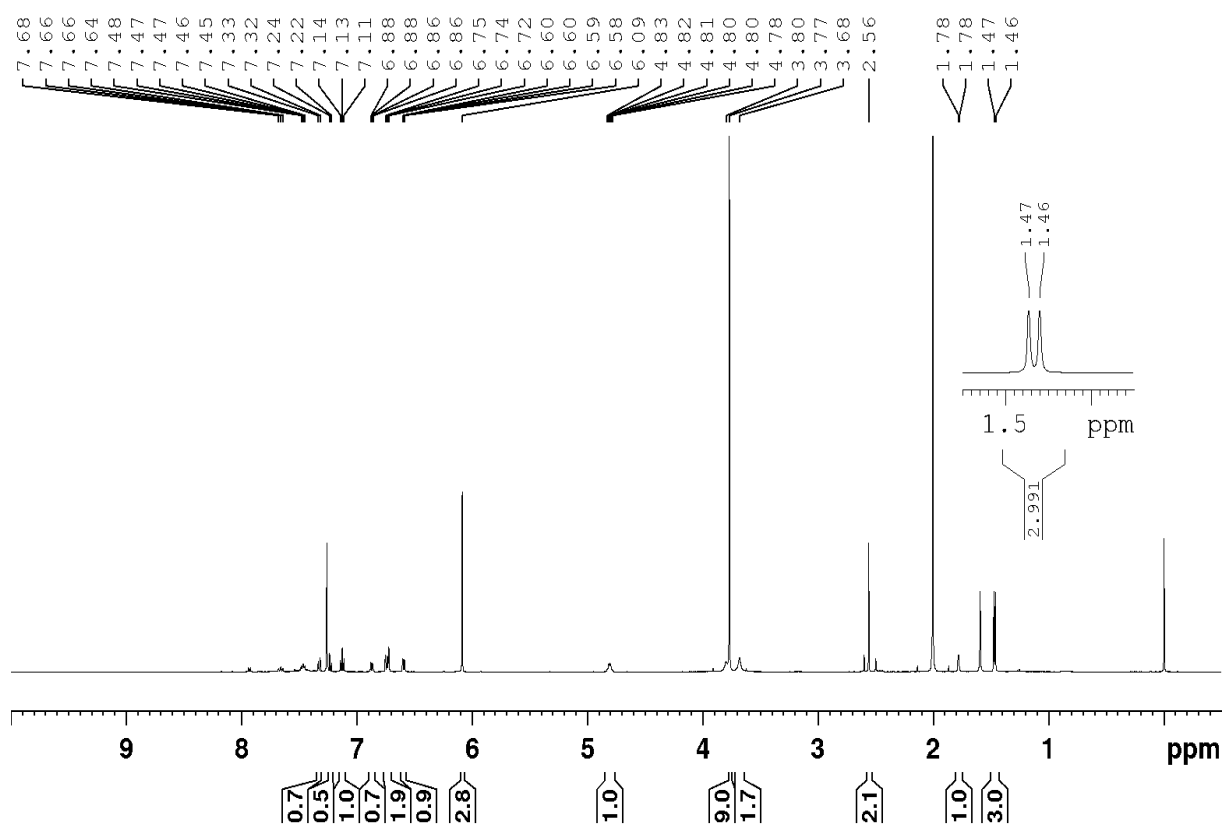


Figure S79.  $^1\text{H}$  NMR spectrum of 3-aminoacetophenone (**13c**) reduction after 24 h.

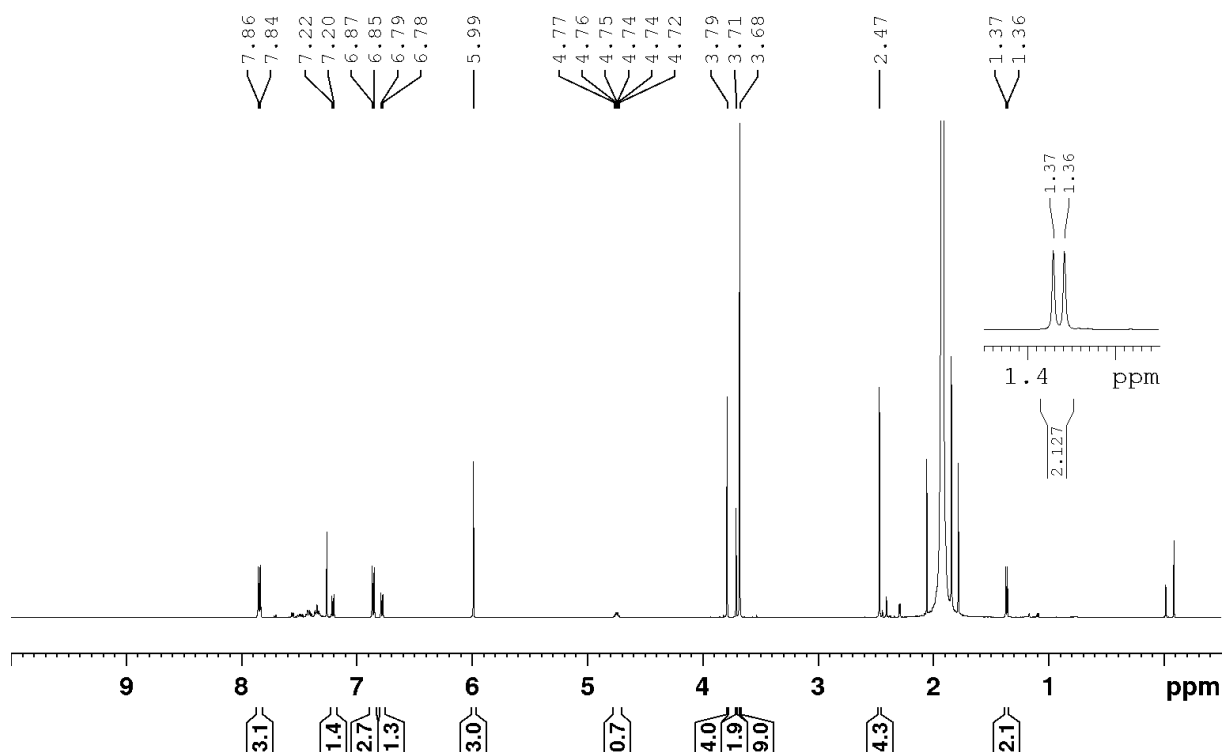


Figure S80.  $^1\text{H}$  NMR spectrum of 4-methoxyacetophenone (**13d**) reduction after 4 h.

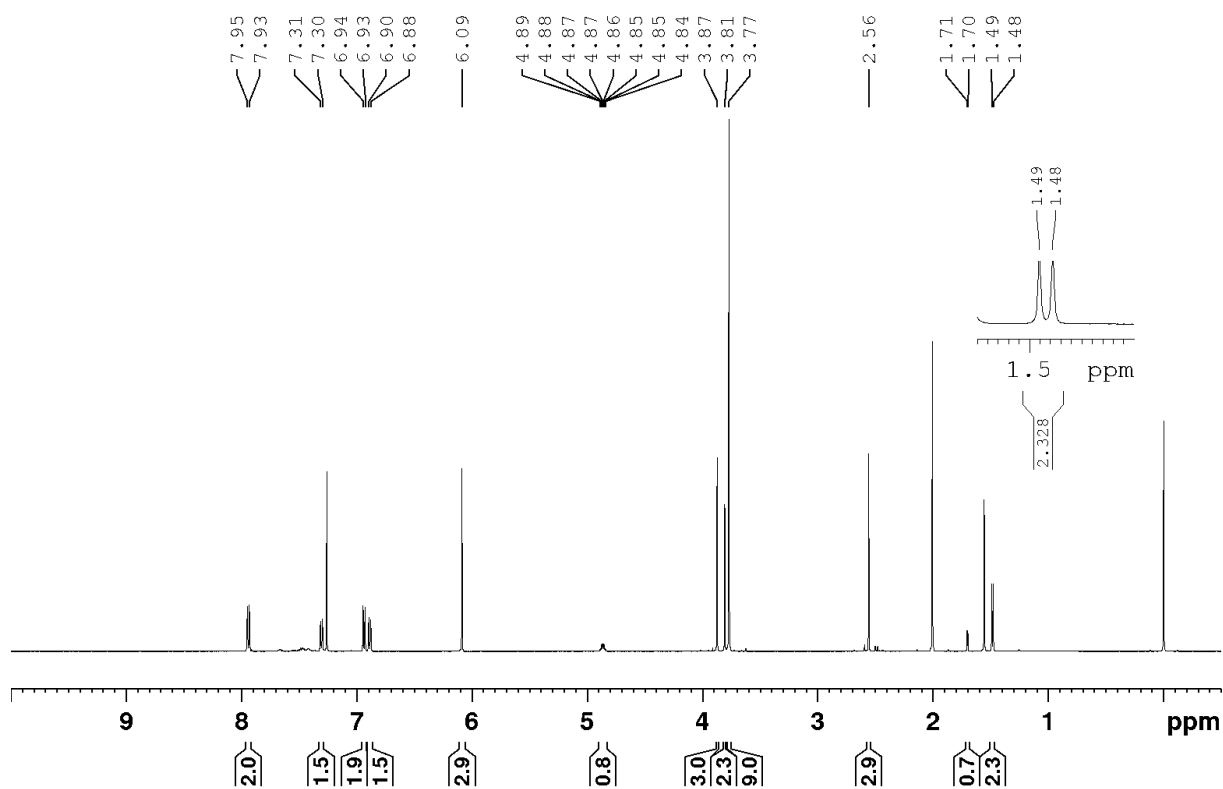


Figure S81.  $^1\text{H}$  NMR spectrum of 4-methoxyacetophenone (**13d**) reduction after 24 h.

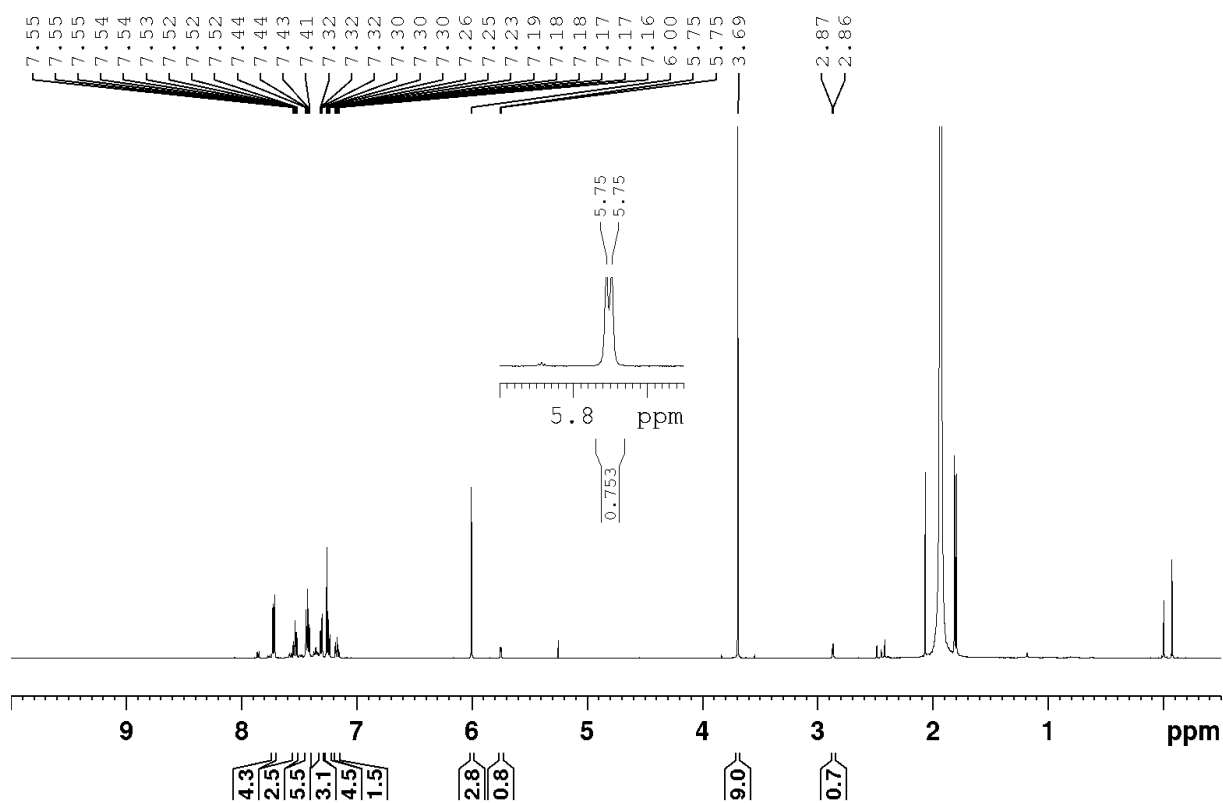


Figure S82. <sup>1</sup>H NMR spectrum of benzophenone (**13e**) reduction after 4 h.

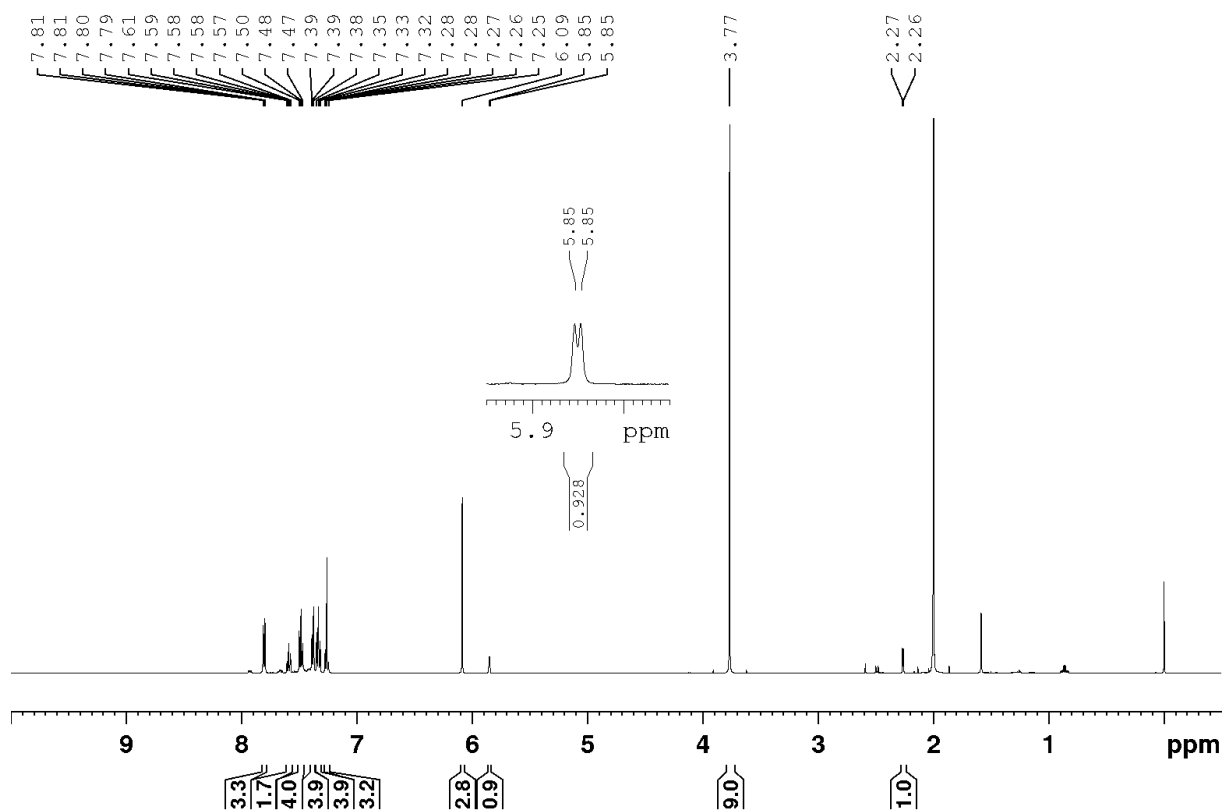


Figure S83. <sup>1</sup>H NMR spectrum of benzophenone (**13e**) reduction after 24 h.

## 6. Cartesian coordinates of optimized structures

Cartesian coordinates of the gas-phase optimized equilibrium structures (in Å) at PBE0-D3/ def2-SV(p) level of theory

### 7aPd

Cl	6.032294000	4.502272000	8.202767000
N	4.239495000	7.404991000	7.579150000
N	3.173223000	6.658568000	7.534851000
N	3.392796000	5.850730000	6.517116000
C	5.169118000	5.127106000	4.941955000
H	6.056507000	5.550987000	4.451931000
H	4.435002000	4.782318000	4.200636000
C	4.614786000	6.025431000	5.916651000
C	5.163623000	7.103911000	6.622234000
C	6.444144000	7.789102000	6.453807000
C	7.614338000	7.031728000	6.301779000
H	7.552391000	5.942513000	6.377261000
C	8.838062000	7.672325000	6.124566000
H	9.747659000	7.074745000	6.014343000
C	8.908822000	9.065300000	6.104614000
H	9.872877000	9.564347000	5.967599000
C	7.747721000	9.822636000	6.264757000
H	7.797143000	10.915378000	6.250653000
C	6.520309000	9.189613000	6.434744000
H	5.610217000	9.785345000	6.548474000
C	2.539588000	4.733628000	6.294328000
C	2.565317000	3.689507000	7.217027000
C	1.797313000	2.555841000	6.969722000
H	1.812127000	1.733824000	7.692240000
C	1.023235000	2.439700000	5.807766000
C	1.021102000	3.506413000	4.899622000
H	0.415675000	3.439967000	3.990381000
C	1.774617000	4.652789000	5.135638000
C	4.415893000	8.300058000	8.675767000
C	5.510039000	8.091274000	9.512695000
C	5.702594000	8.958565000	10.584216000
H	6.554713000	8.807128000	11.252444000
C	4.807639000	10.005623000	10.810750000
H	4.964449000	10.683123000	11.655084000
C	3.708666000	10.187147000	9.970407000
H	3.004182000	11.003007000	10.154661000
C	3.506429000	9.330741000	8.889662000
C	6.343635000	1.474471000	5.414834000
H	7.390419000	1.412039000	5.090167000
Pd	5.754177000	3.409143000	6.078915000
C	6.044077000	1.333843000	6.775869000
H	5.018139000	1.129856000	7.106503000
H	6.839412000	1.103395000	7.491329000
C	5.377658000	2.037895000	4.533181000
H	5.677917000	2.279803000	3.506892000
H	4.313551000	1.791023000	4.659230000
H	3.209840000	3.771737000	8.096002000
H	1.773655000	5.482516000	4.424105000
C	0.242726000	1.188058000	5.524632000
H	0.859812000	0.460838000	4.964662000
H	-0.081169000	0.694615000	6.455704000
H	-0.651917000	1.397300000	4.915098000
H	2.654654000	9.452795000	8.216331000
H	6.173514000	7.242885000	9.320631000

### 7aPd – isomer 2

Cl	8.076521000	4.643865000	6.051961000
N	2.005475000	4.078397000	3.723597000
N	2.733653000	3.668337000	2.722641000

N	3.945926000	4.119679000	2.996514000
C	5.254980000	5.207259000	4.813667000
H	5.111132000	5.951803000	5.606296000
H	6.056582000	5.493112000	4.125432000
C	4.038553000	4.783264000	4.201995000
C	2.702954000	4.794437000	4.656156000
C	2.137815000	5.407530000	5.854683000
C	2.848376000	5.339715000	7.063842000
H	3.805510000	4.810310000	7.100480000
C	2.331333000	5.931028000	8.214054000
H	2.895275000	5.871469000	9.149275000
C	1.105856000	6.595029000	8.175012000
H	0.704643000	7.062086000	9.079238000
C	0.396725000	6.670934000	6.974958000
H	-0.559259000	7.201084000	6.933699000
C	0.908439000	6.086682000	5.821452000
H	0.356221000	6.168797000	4.881369000
C	5.041659000	3.725286000	2.182946000
C	5.290648000	2.368933000	1.986335000
C	6.396459000	1.982019000	1.236815000
H	6.592210000	0.916292000	1.083845000
C	7.271641000	2.929384000	0.691702000
C	6.989520000	4.285980000	0.896242000
H	7.653188000	5.044776000	0.471150000
C	5.882114000	4.689613000	1.633132000
C	0.637623000	3.675782000	3.764514000
C	0.133437000	3.095381000	4.927244000
C	-1.198268000	2.692005000	4.954672000
H	-1.603340000	2.234831000	5.861429000
C	-2.007459000	2.860770000	3.830304000
H	-3.052799000	2.540580000	3.857377000
C	-1.483814000	3.431360000	2.670370000
H	-2.114800000	3.558452000	1.786419000
C	-0.154507000	3.846103000	2.631940000
C	5.705072000	1.373869000	5.785538000
H	6.037091000	0.856996000	4.875576000
Pd	6.075539000	3.463226000	5.738915000
C	6.637606000	1.632757000	6.800288000
H	6.307645000	1.897593000	7.812570000
H	7.666135000	1.272224000	6.705027000
C	4.462580000	2.068573000	5.775384000
H	3.801062000	1.945063000	4.908226000
H	3.940976000	2.257727000	6.724521000
H	4.619823000	1.626811000	2.424981000
H	5.671294000	5.750491000	1.785845000
C	8.499588000	2.505828000	-0.060630000
H	9.368300000	2.444634000	0.620905000
H	8.369947000	1.513296000	-0.522741000
H	8.755291000	3.226970000	-0.854539000
H	0.276796000	4.294592000	1.734369000
H	0.781340000	2.960571000	5.796255000

### 7aAu

Cl	6.279574000	1.222364000	7.471506000
N	2.015962000	4.094215000	3.662732000
N	2.765011000	3.705772000	2.668972000
N	3.998579000	3.938711000	3.075185000
C	5.283416000	4.790467000	5.071527000
H	5.089261000	5.626591000	5.762734000
H	6.113732000	5.044220000	4.393486000
C	4.072287000	4.465956000	4.342976000
C	2.727312000	4.583027000	4.721637000
C	2.142479000	5.141927000	5.942462000
C	2.651670000	4.761097000	7.192032000
H	3.482698000	4.047958000	7.245444000
C	2.098869000	5.283089000	8.358916000
H	2.501513000	4.974751000	9.327822000
C	1.040908000	6.188725000	8.291260000

H	0.610392000	6.598397000	9.209769000
C	0.535745000	6.577694000	7.049351000
H	-0.287297000	7.295656000	6.990921000
C	1.082753000	6.060225000	5.879867000
H	0.689859000	6.375151000	4.909055000
C	5.070074000	3.636818000	2.183935000
C	6.164869000	2.900237000	2.631198000
C	7.187903000	2.602686000	1.737931000
H	8.043561000	2.020609000	2.093549000
C	7.138509000	3.021925000	0.402243000
C	6.017898000	3.748396000	-0.020372000
H	5.951362000	4.080647000	-1.060883000
C	4.986804000	4.061495000	0.859107000
C	0.604146000	3.913359000	3.564311000
C	-0.079245000	3.302689000	4.614283000
C	-1.456402000	3.131354000	4.509063000
H	-2.002149000	2.652449000	5.326403000
C	-2.133344000	3.557540000	3.365797000
H	-3.215253000	3.418349000	3.288803000
C	-1.432181000	4.155794000	2.318815000
H	-1.960265000	4.486232000	1.420230000
C	-0.054868000	4.339973000	2.413931000
H	6.213990000	2.559833000	3.671439000
H	4.115899000	4.628733000	0.523227000
C	8.268750000	2.720437000	-0.538567000
H	9.095629000	3.441515000	-0.400769000
H	8.681850000	1.713591000	-0.360187000
H	7.947793000	2.781029000	-1.591202000
H	0.513225000	4.807847000	1.606958000
H	0.463698000	2.963260000	5.499030000
Au	5.775684000	3.104847000	6.211452000

### mNHO-RhCO

Rh	6.504049000	2.771132000	5.569368000
Cl	4.434432000	1.592257000	5.866265000
O	9.011801000	4.305418000	5.103694000
O	7.847887000	0.361327000	6.822329000
N	2.051567000	4.016642000	3.882624000
N	2.648053000	3.712616000	2.763644000
N	3.925731000	3.896503000	3.012851000
C	5.518321000	4.551497000	4.803794000
H	5.475477000	5.237809000	5.664154000
H	6.149031000	4.986178000	4.014486000
C	4.187785000	4.305763000	4.292370000
C	2.915051000	4.403928000	4.870233000
C	7.348572000	1.264488000	6.334083000
C	8.053832000	3.702931000	5.296790000
C	2.514648000	4.836445000	6.209306000
C	3.292506000	4.460458000	7.314837000
H	4.153848000	3.805250000	7.165321000
C	2.926469000	4.861078000	8.596614000
H	3.536364000	4.549820000	9.449375000
C	1.785040000	5.636758000	8.795238000
H	1.497717000	5.944574000	9.805052000
C	1.009965000	6.019101000	7.699849000
H	0.116206000	6.632781000	7.844379000
C	1.372664000	5.627073000	6.415258000
H	0.762417000	5.943093000	5.566892000
C	4.885401000	3.753051000	1.957545000
C	5.364082000	2.468305000	1.658052000
C	6.314502000	2.371004000	0.638000000
H	6.715990000	1.390036000	0.372929000
C	6.760103000	3.502472000	-0.038587000
H	7.509187000	3.402536000	-0.829682000
C	6.258169000	4.759907000	0.281148000
H	6.612127000	5.638494000	-0.265564000
C	5.302958000	4.914989000	1.289540000
C	4.727562000	6.284332000	1.595420000

H	4.062309000	6.189454000	2.469868000
C	3.872933000	6.776371000	0.424785000
H	4.490750000	6.945251000	-0.474987000
H	3.378775000	7.731093000	0.679238000
H	3.094325000	6.040798000	0.164837000
C	5.808313000	7.301314000	1.961353000
H	6.488795000	7.492904000	1.113143000
H	6.417265000	6.954652000	2.813052000
H	5.346458000	8.264207000	2.241521000
C	4.832095000	1.244951000	2.370113000
H	4.437969000	1.568114000	3.346967000
C	3.673664000	0.631361000	1.577986000
H	2.864955000	1.364571000	1.417968000
H	3.253305000	-0.228450000	2.128894000
H	4.011891000	0.272947000	0.588406000
C	5.912348000	0.213318000	2.676872000
H	6.300484000	-0.276163000	1.765265000
H	5.492908000	-0.572322000	3.327532000
H	6.754570000	0.676943000	3.219141000
C	0.623093000	3.897260000	3.960757000
C	0.088538000	2.850046000	4.725946000
C	-1.305227000	2.772550000	4.803246000
H	-1.761363000	1.969772000	5.388876000
C	-2.113764000	3.691959000	4.144203000
H	-3.202289000	3.610947000	4.217669000
C	-1.546510000	4.714583000	3.388931000
H	-2.194924000	5.428210000	2.873400000
C	-0.159720000	4.845105000	3.282129000
C	0.445584000	5.957614000	2.448649000
H	1.527518000	5.993055000	2.658553000
C	-0.123912000	7.330984000	2.804106000
H	-1.194651000	7.412792000	2.548288000
H	0.409402000	8.117841000	2.242626000
H	-0.015163000	7.549917000	3.880619000
C	0.279089000	5.649763000	0.958813000
H	0.774289000	4.699955000	0.697121000
H	0.719589000	6.453677000	0.344083000
H	-0.789372000	5.564511000	0.691764000
C	0.959448000	1.821297000	5.410419000
H	2.009956000	2.138765000	5.340845000
C	0.647989000	1.696946000	6.900629000
H	0.700147000	2.679450000	7.400815000
H	1.393333000	1.037216000	7.376169000
H	-0.354097000	1.267867000	7.082855000
C	0.871457000	0.474506000	4.690034000
H	-0.143397000	0.041163000	4.754845000
H	1.583633000	-0.236171000	5.143420000
H	1.131502000	0.577793000	3.622356000