## **Supporting Information**

## Facile synthesis of 1,5-disubstituted tetrazoles by reacting a ruthenium acetylide complex with trimethylsilyl azide

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## Content:

- 1. Fig. S1 ORTEP drawing of 4c
- 2. NMR spectra of all relevant compounds



**Fig. S1** ORTEP drawing of **4c** with thermal ellipsoids shown at a 50% probability level. Hydrogen atoms and counter ions have been omitted for clarity. Selected distances (Å) and angles (°): Ru–N2 2.0749(19), N1–N2 1.363(3), N2–N3 1.304(3), N3–N4 1.342(3), N4–C1 1.347(3), N1–C1 1.319(3); N1–N2–N3 111.93(19), N2–N3–N4 105.21(18), N3–N4–C1 109.24(19), N4–C1–N1 108.6(2), C1–N1–N2 104.98(19).



Fig. S3 <sup>1</sup>H , <sup>31</sup>P and <sup>13</sup>C NMR spectra of compound 1.



Fig. S4 <sup>1</sup>H , <sup>31</sup>P and <sup>13</sup>C NMR spectra of compound 2.



Fig. S5 <sup>1</sup>H , <sup>31</sup>P and <sup>13</sup>C NMR spectra of compound **3**.



Fig. S6  ${}^{1}$ H ,  ${}^{31}$ P and  ${}^{13}$ C NMR spectra of compound 4a·[PF<sub>6</sub>].



Fig. S7  ${}^{1}$ H ,  ${}^{31}$ P and  ${}^{13}$ C NMR spectra of compound 4b·[PF<sub>6</sub>].



Fig. S8 <sup>1</sup>H , <sup>31</sup>P and <sup>13</sup>C NMR spectra of compound 4c·[PF<sub>6</sub>].



**Fig. S9** <sup>1</sup>H , <sup>31</sup>P and <sup>13</sup>C NMR spectra of compound  $4d \cdot [PF_6]$ .



Fig. S10 <sup>1</sup>H , <sup>31</sup>P and <sup>13</sup>C NMR spectra of compound 4e·[PF<sub>6</sub>].



Fig. S11 <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound 5a.



Fig. S12 <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound 5b.





Fig. S13 <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound 5c.



Fig. S14 <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound 5d.



Fig. S15 <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound 5e.

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50

0

ppm

10

40

30 20



Fig. S16 <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound 6.