Electronic Supplementary Information for Dalton Transactions


# *Supporting Information*

# Rare-Earth Metal Complexes Stabilized by Amino-Phosphine Ligand. Reaction with Mesityl Azide and Catalysis on Cycloadditon of Organic Azides and Aromatic Alkynes

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Legends

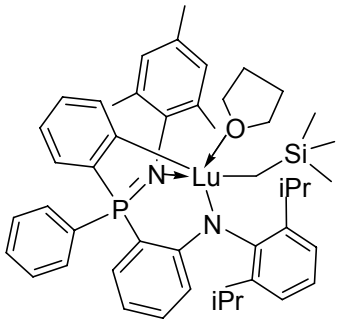
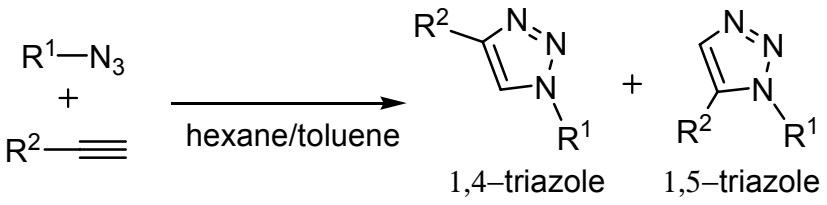



Chart S1 The structure of lutetium mono(alkyl) complex stabilized by anilido-phosphinimine ligand.

**A typical procedure for cycloaddition reaction:** To a toluene (7 mL) of mesityl azide (0.59 g, 3.66 mmol) and phenylacetylene (0.37 g, 3.66 mmol), complex **1a** (0.06 g, 0.07 mmol) was added. After 3 days, remove the volatiles and then the residue was chromatographed through silica gel with hexane/EtOAc (3:1) as the eluent to get **7a** (0.90 g, Yield: 94%).




1,4–triazole 1,5–triazole

**7a'**: $R^1$ = Mes, $R^2$ = $C_6H_5$.

**7a**: $R^1$ = Mes, $R^2$ = $C_6H_5$;
**7b**: $R^1$ = $C_6H_5$, $R^2$ = $C_6H_5$;
**7c**: $R^1$ = $C_6H_5CH_2$, $R^2$ = $C_6H_5$;
**7d**: $R^1$ = $(CH_2)CH$, $R^2$ = $C_6H_5$;
**7e**: $R^1$ = $CH_3(CH_2)_3$, $R^2$ = $C_6H_5$;
**7f**: $R^1$ = Mes, $R^2$ = *p*-$C_6H_4Me$;
**7g**: $R^1$ = Mes, $R^2$ = *m*-$C_6H_4F$.

**Note:** Approximately equivalent **7a'** and **7a** were obtained, when the cycloaddition was catalyzed by lutetium mono(alkyl) complex stabilized by anilido-phosphinimine ligand at room temperature or the mixture of mesityl azide and phenylacetylene was stirred at 60 ºC for 72 h.

**7a':** $^1$H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 2.02(s, 6H, *o*-$C_6H_2(CH_3)_3$), 2.37(s, 3H, *p*-$C_6H_2(CH_3)_3$), 7.01(s, 2H, *m*-$C_6H_2(CH_3)_3$), 7.36(t, $^3J$(H, H) = 9.6 Hz, 1H, *p*-$C_6H_5$), 7.46(t, $^3J$(H, H) = 7.2 Hz, 2H, *m*-$C_6H_5$), 7.83(s, 1H, PhC=C*H*N), 7.94 ppm(d, $^3J$(H, H) = 9.6 Hz, 2H, *o*-$C_6H_5$). $^{13}$C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 17.71(s, 2C, *o*-$C_6H_2(CH_3)_3$), 21.52(s, 1C, *p*-$C_6H_2(CH_3)_3$), 121.85, 126.15, 128.64,

129.30, 129.50, 130.93, 135.52, 140.46. Anal. Calc. for $C_{17}H_{17}N_3$: C, 77.54; H, 6.50; N, 15.96. Found: C, 77.53; H, 6.51; N, 15.96.

**7a:** $^1$H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 1.88(s, 6H, *o*-$C_6H_2(CH_3)_3$), 2.35(s, 3H, *p*-$C_6H_2(CH_3)_3$), 6.97(s, 2H, *m*-$C_6H_2(CH_3)_3$), 7.18(multi, 2H, *m*-$C_6H_5$), 7.30(multi, 1H, *p*-$C_6H_5$, 2H, *o*-$C_6H_5$), 8.00 ppm(s, 1H, PhC=C*H*N). $^{13}$C NMR (75 MHz, $CDCl_3$, 25 ºC): $\delta$ = 17.85(s, 2C, *o*-$C_6H_2(CH_3)_3$), 21.55(s, 1C, *p*-$C_6H_2(CH_3)_3$), 127.05, 127.29, 129.34, 129.48, 129.72, 132.51, 133.19, 135.81, 138.67, 140.43. Anal. Calc. for $C_{17}H_{17}N_3$: C, 77.54; H, 6.50; N, 15.96. Found: C, 77.54; H, 6.50; N, 15.96.

**7b:** $^1$H NMR (300 MHz, $CDCl_3$, 25 ºC): $\delta$= 7.15(t, 2H, $^3J$(H, H) = 7.2 Hz), 7.28 (multi, 4H), 7.15(d, 4H, $^3J$(H, H) = 7.6 Hz), 7.79(s, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$, 25 ºC): $\delta$= 125.61, 127.81, 129.00, 129.25, 129.62, 129.75, 133.78, 137.02, 138.13. Anal. Calc. for $C_{14}H_{11}N_3$: C, 76.00; H, 5.01; N, 18.99. Found: C, 75.99; H, 5.01; N, 19.00.

**7c:** $^1$H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 5.46(s, 2H), 6.98(t, 2H, $^3J$(H, H) = 5.0 Hz), 7.18(multi, 5H), 7.32(multi, 3H), 7.67(s, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$, 25 ºC): $\delta$ = 51.88, 127.18, 128.19, 128.92, 128.97, 129.56, 133.13, 135.44, 135.87, 138.25. Anal. Calc. for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.56; H, 5.57; N, 17.87.

**7d:** $^1$H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 1.59(multi, 2H), 2.00(multi, 4H), 2.14(multi, 2H), 4.67(multi, 1H), 7.28(multi, 2H), 7.40(multi, 3H), 7.60(s, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$, 25 ºC): $\delta$= 24.83, 33.94, 59.44, 127.46, 127.81, 128.13, 129.06, 129.12, 129.43, 132.57, 137.81. Anal. Calc. for $C_{13}H_{15}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.56; H, 5.57; N, 17.87. Anal. Calc. for $C_{13}H_{15}N_3$: C, 73.21; H, 7.09; N, 19.70. Found: C, 73.21; H, 7.09; N, 19.70.

**7e:** $^1$H NMR (300 MHz, $CDCl_3$, 25 ºC): $\delta$= 0.76(t, 3H, $^3J$(H,H) = 9.8 Hz), 1.18(multi, 2H), 1.71(multi, 2H), 4.25(t, 2H, $^3J$(H,H) = 9.8 Hz), 7.30(multi, 2H), 7.40(multi, 3H), 7.59(s, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$, 25 ºC): $\delta$=13.40, 19.67, 32.11, 48.08, 127.26, 128.76, 129.09, 129.43, 132.91, 137.75. Anal. Calc. for $C_{12}H_{15}N_3$: C, 71.61; H, 7.51; N, 20.88. Found: C, 71.60; H, 7.50; N, 20.90.

**7f:** $^1$H NMR (300 MHz, $CDCl_3$, 25 ºC): $\delta$= 1.78(s, 6H), 2.22(s, 3H), 2.26(s, 3H), 6.88(s, 2H), 6.99(multi, 4H), 7.89(s, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$, 25 ºC): δ =17.52, 21.26, 123.71, 126.80, 129.32, 129.67, 131.80, 132.86, 135.46, 138.46, 139.24, 140.02. Anal. Calc. for $C_{18}H_{19}N_3$: C, 77.95; H, 6.90; N, 15.15. Found: C, 77.95; H, 6.89; N, 15.16.

**7g:** $^1$H NMR (300 MHz, $CDCl_3$, 25 ºC): $\delta$= 1.79(s, 6H), 2.27(s, 3H), 6.76(multi, 1H), 6.90(multi, 4H), 7.17(multi, 1H), 7.93(s, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$, 25 ºC): $\delta$=17.80, 21.56, 114.25(d), 116.50(d),

123.04(d), 128.96(d), 129.86, 131.09(d), 132.82, 137.45, 140.74, 161.44, 164.71. Anal. Calc. for $C_{17}H_{16}N_3F$: C, 72.58; H, 5.73; N, 14.94. Found: C, 72.57; H, 5.73; N, 14.94.

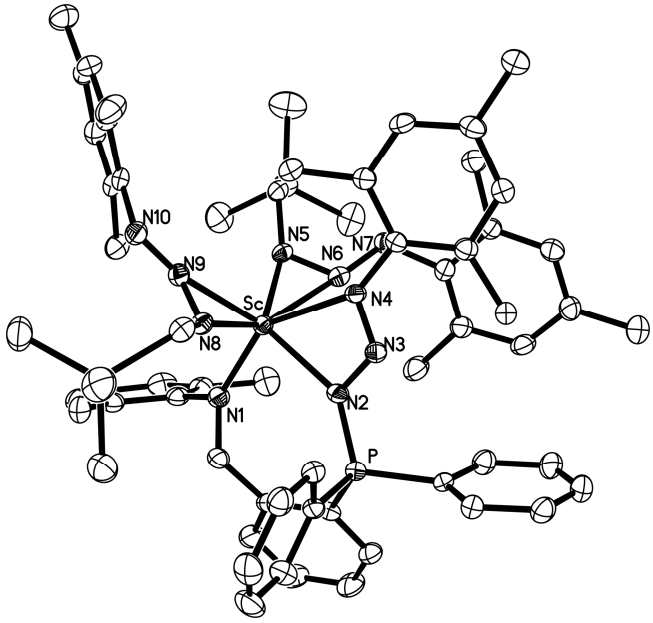



Figure S1. Molecular structure of **3b** (hydrogen atoms are omitted for clarity, thermal ellipsoids with 50% probability). Selected bond distances (Å) and angles (deg): Sc–N(1) 2.071(2), Sc–N(2) 2.276(2), Sc–N(4) 2.528(2), N(2)–N(3) 1.380(3), N(3)–N(4) 1.269(3), Sc–N(5) 2.126(2), Sc–N(6) 2.301(2), Sc–N(8) 2.143(2), Sc–N(9) 2.265(2), N(5)–N(6) 1.323(3), N(6)–N(7) 1.292(3), N(8)–N(9) 1.310(3), N(9)–N(10) 1.289(3); N(2)–Sc–N(4) 53.16(7), N(5)–Sc–N(6) 34.50(8), N(8)–Sc–N(9) 34.44(8).

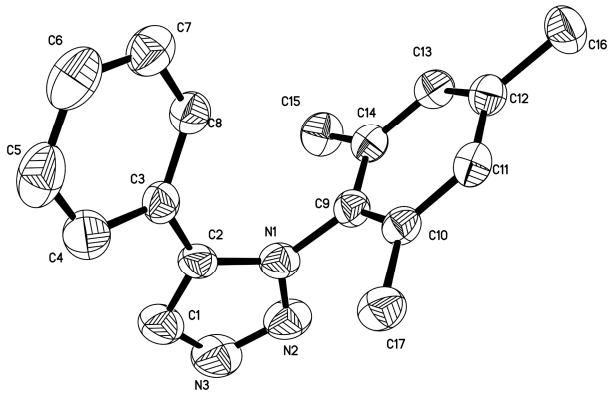



Figure S2. Molecular structure of **7a** (hydrogen atoms are omitted for clarity, thermal ellipsoids with 50% probability).

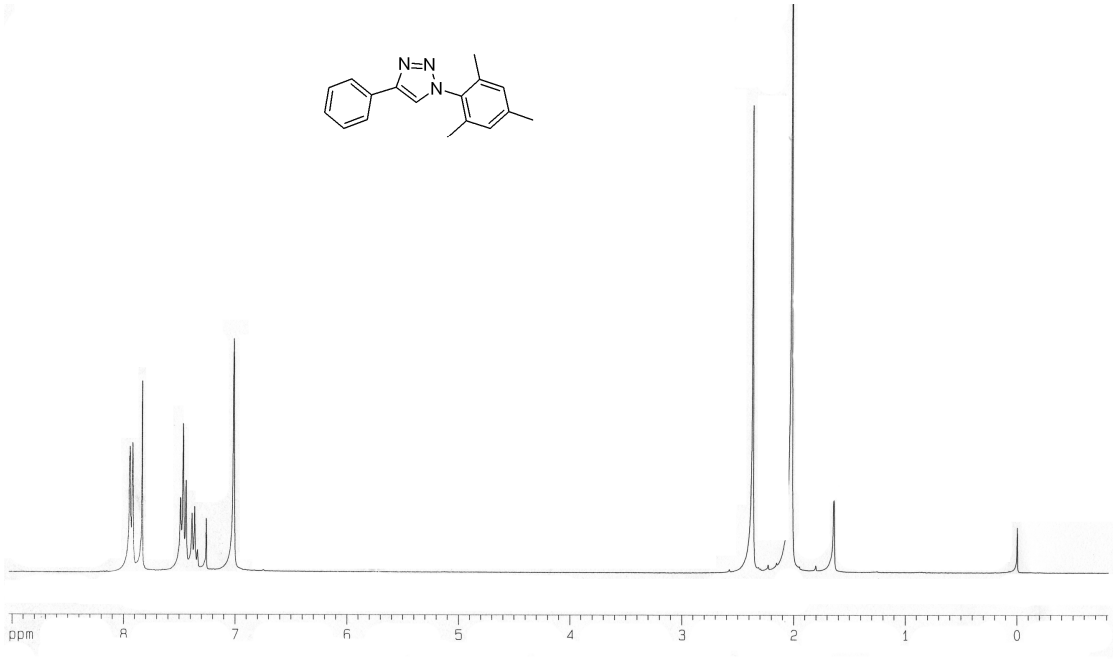



Figure S3. $^{1}$H NMR spectrum of **7a'**.

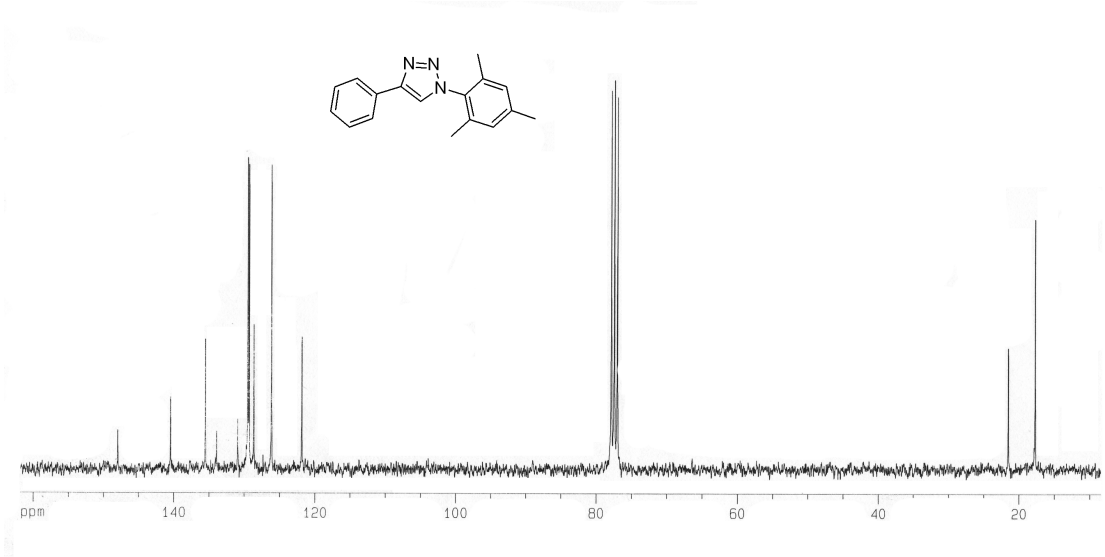



Figure S4. $^{13}$C NMR spectrum of **7a'**.

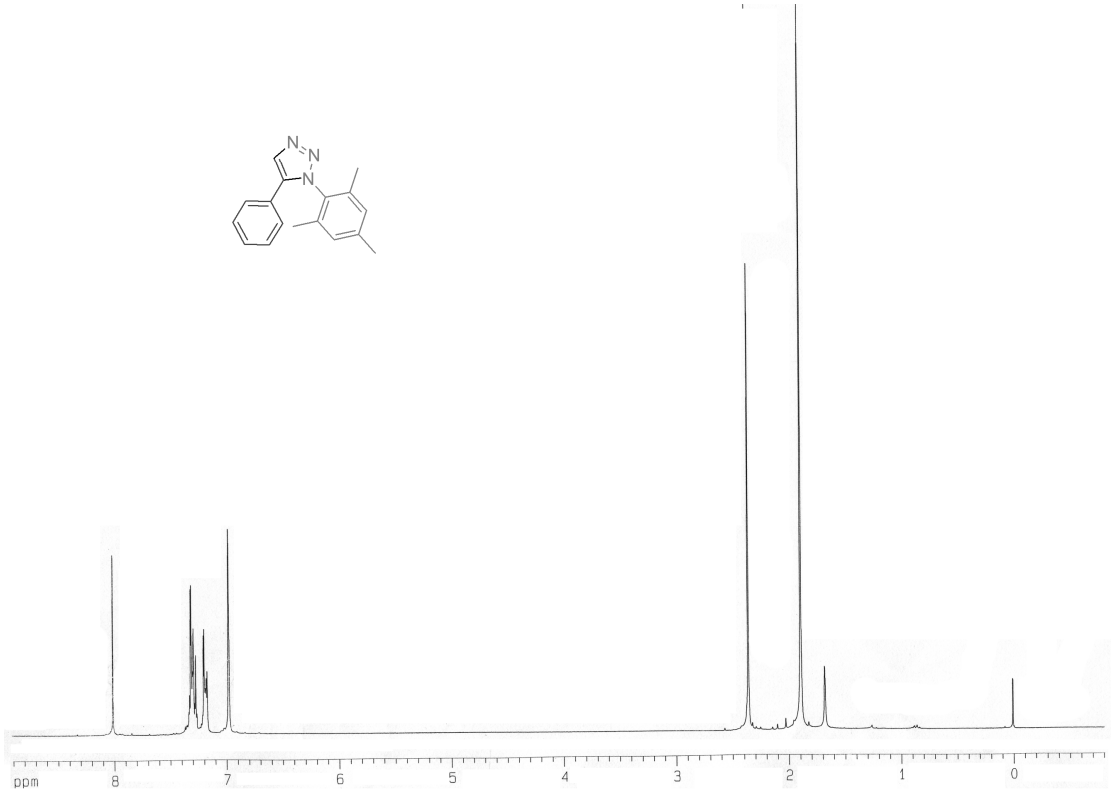



Figure S5. $^{1}$H NMR spectrum of **7a**.

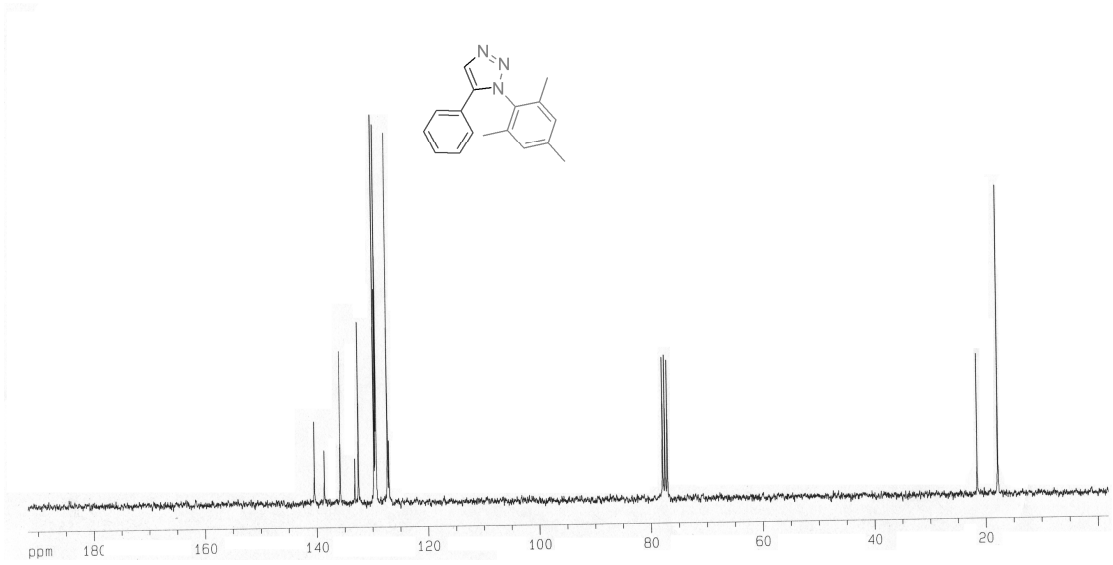



Figure S6. $^{13}$C NMR spectrum of **7a**.

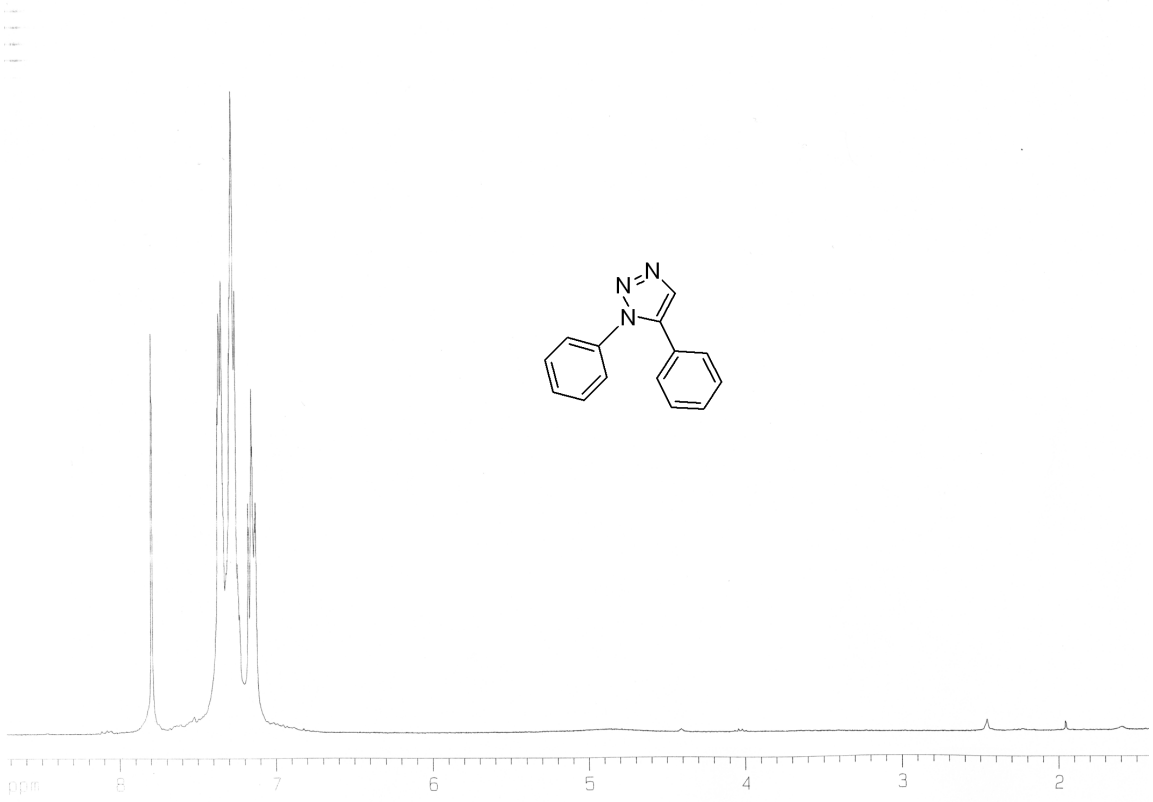



Figure S7. $^{1}$H NMR spectrum of **7b**.

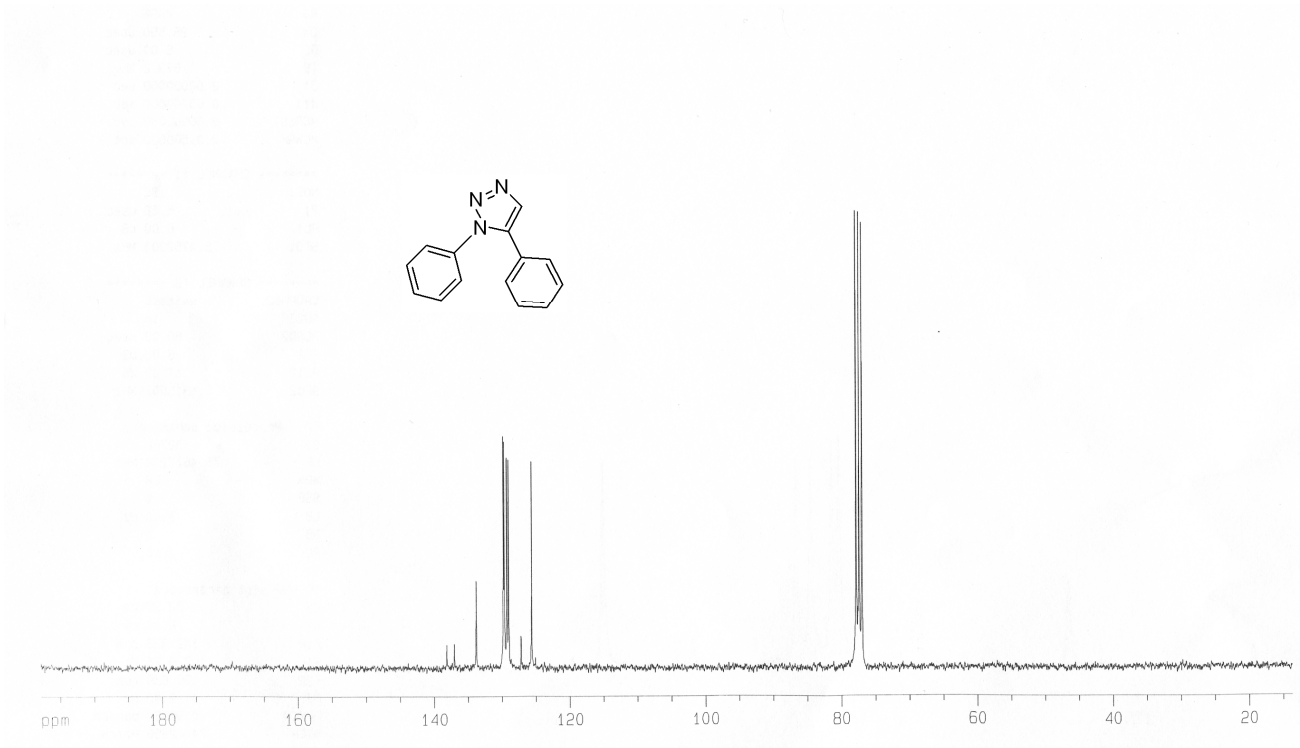



Figure S8. $^{13}$C NMR spectrum of **7b**.

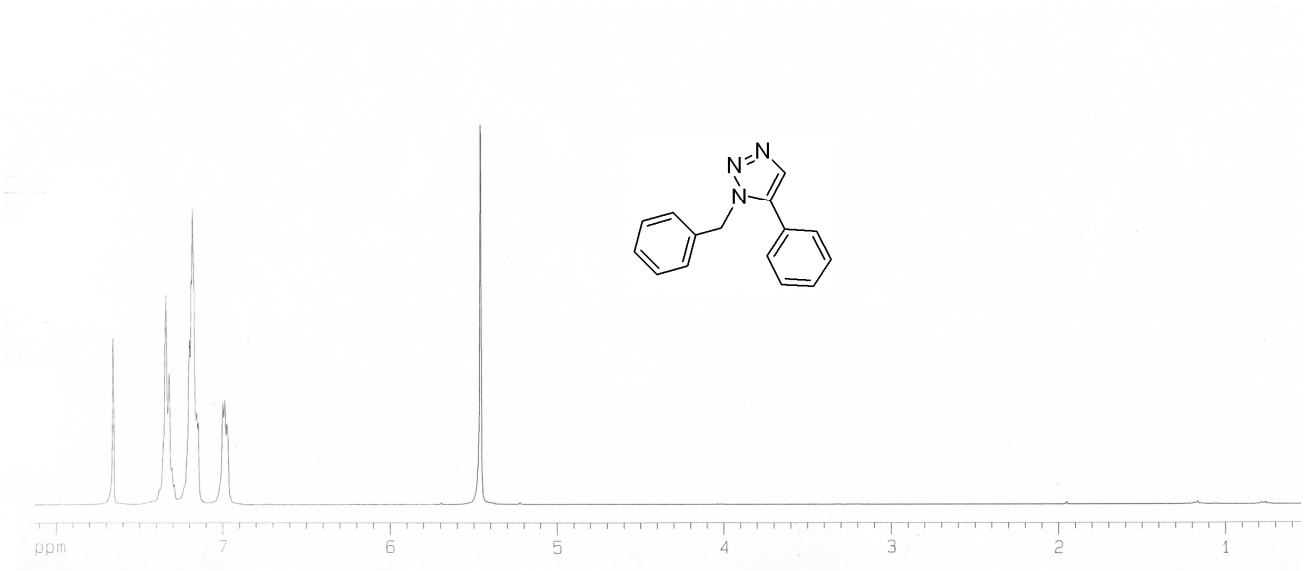



Figure S9. $^{1}$H NMR spectrum of **7c**.

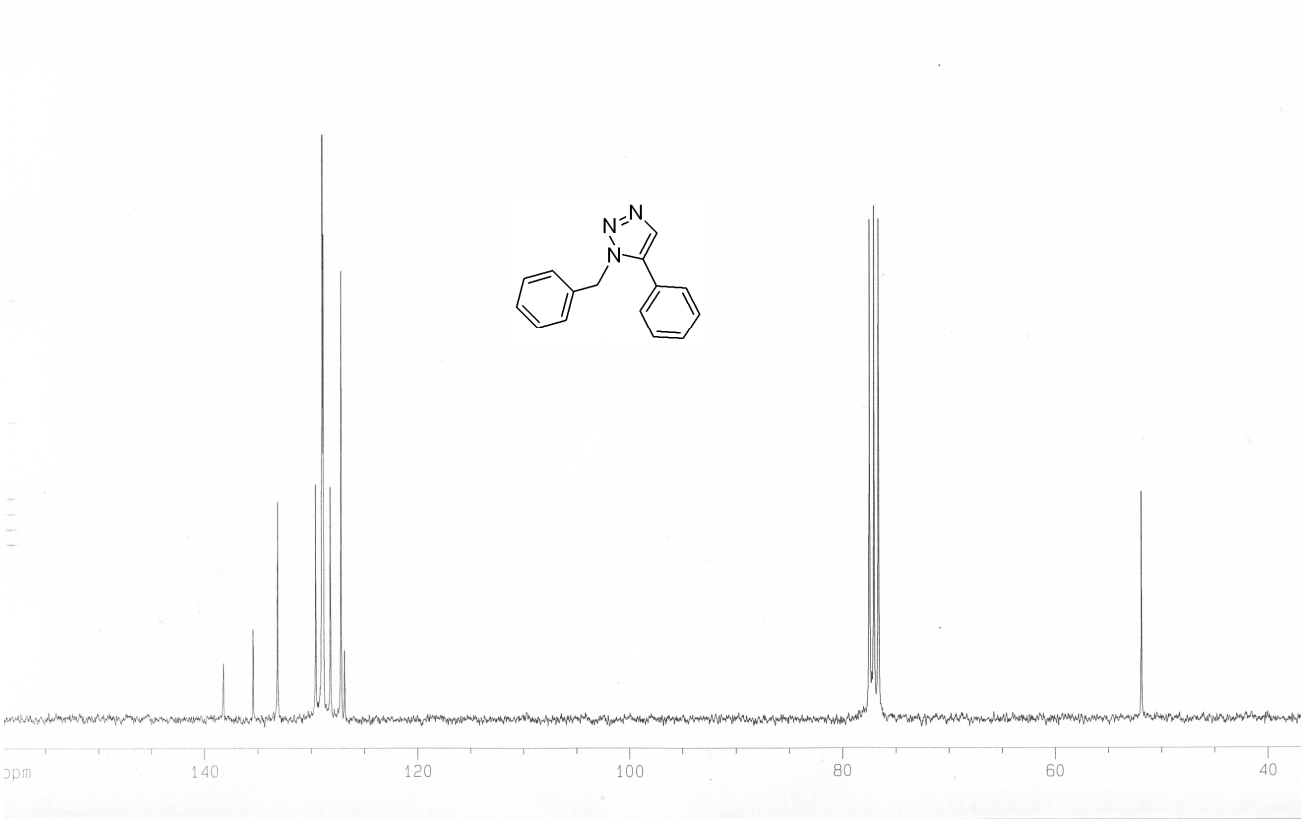



Figure S10. $^{13}$C NMR spectrum of **7c**.

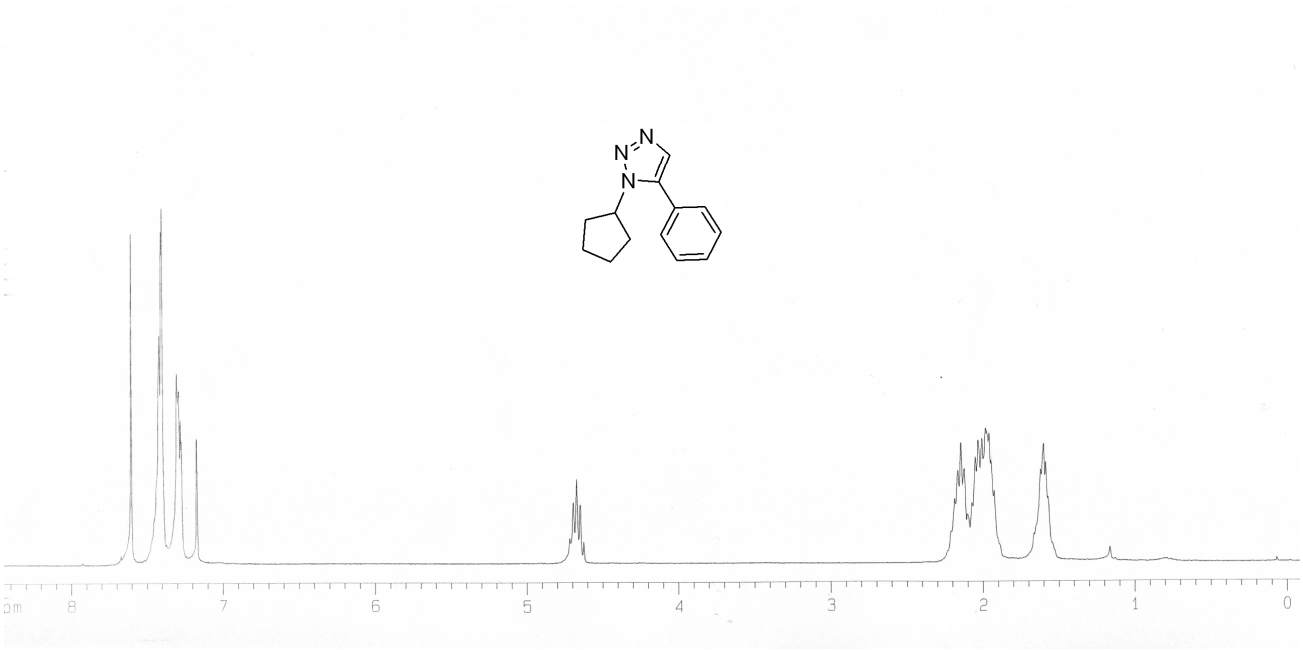



Figure S11. $^{1}$H NMR spectrum of **7d**.

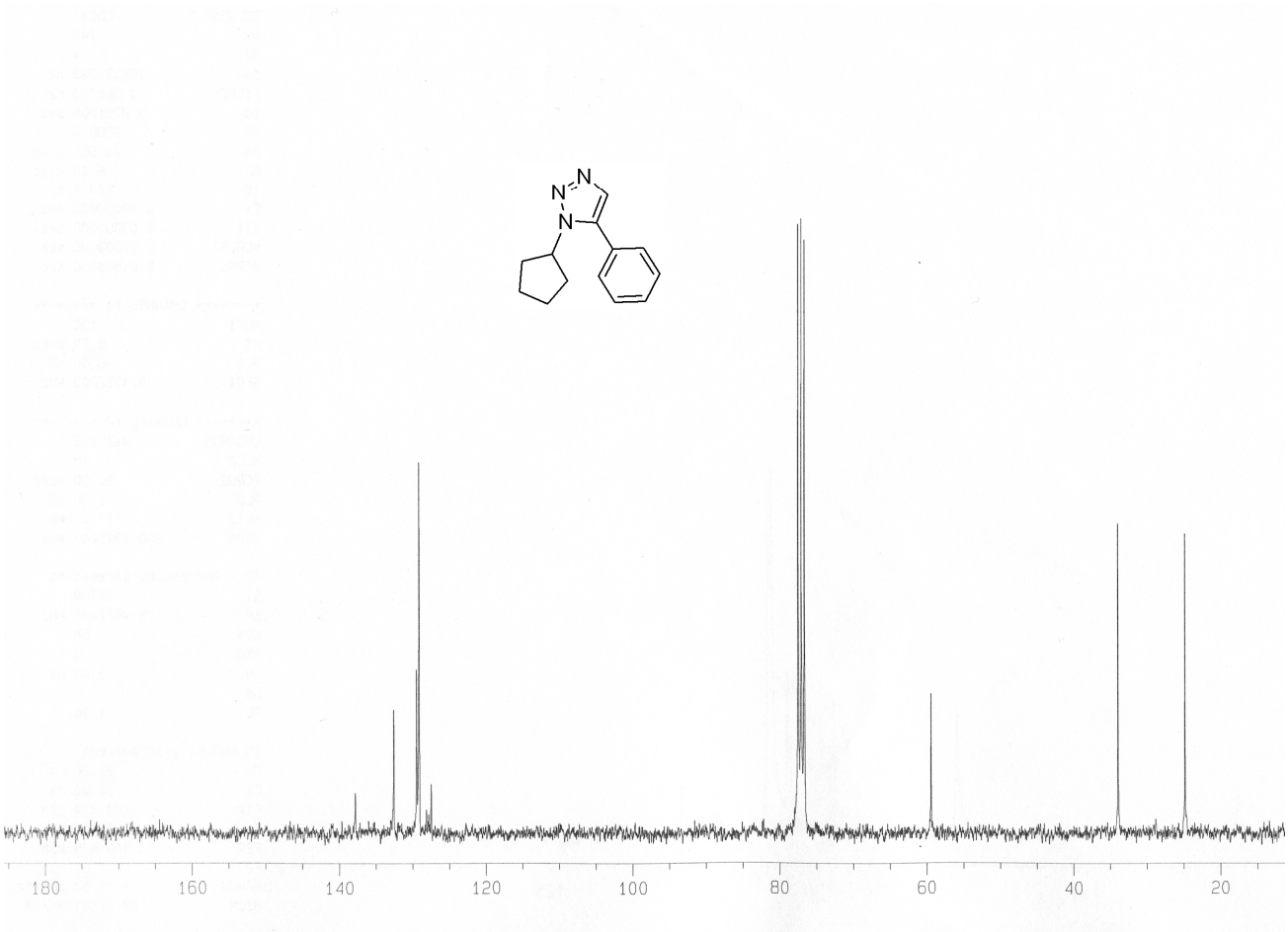



Figure S12. $^{13}$C NMR spectrum of **7d**.

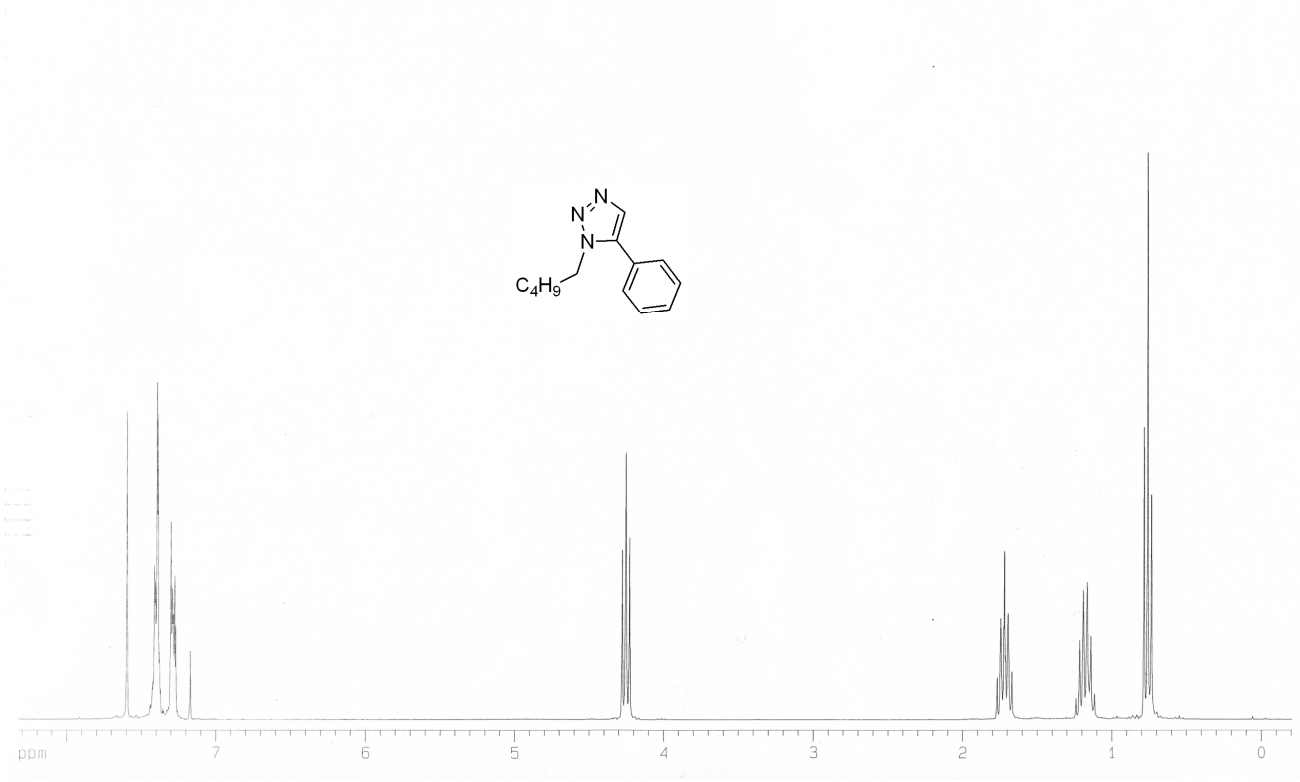



Figure S13. $^{1}$H NMR spectrum of **7e**.

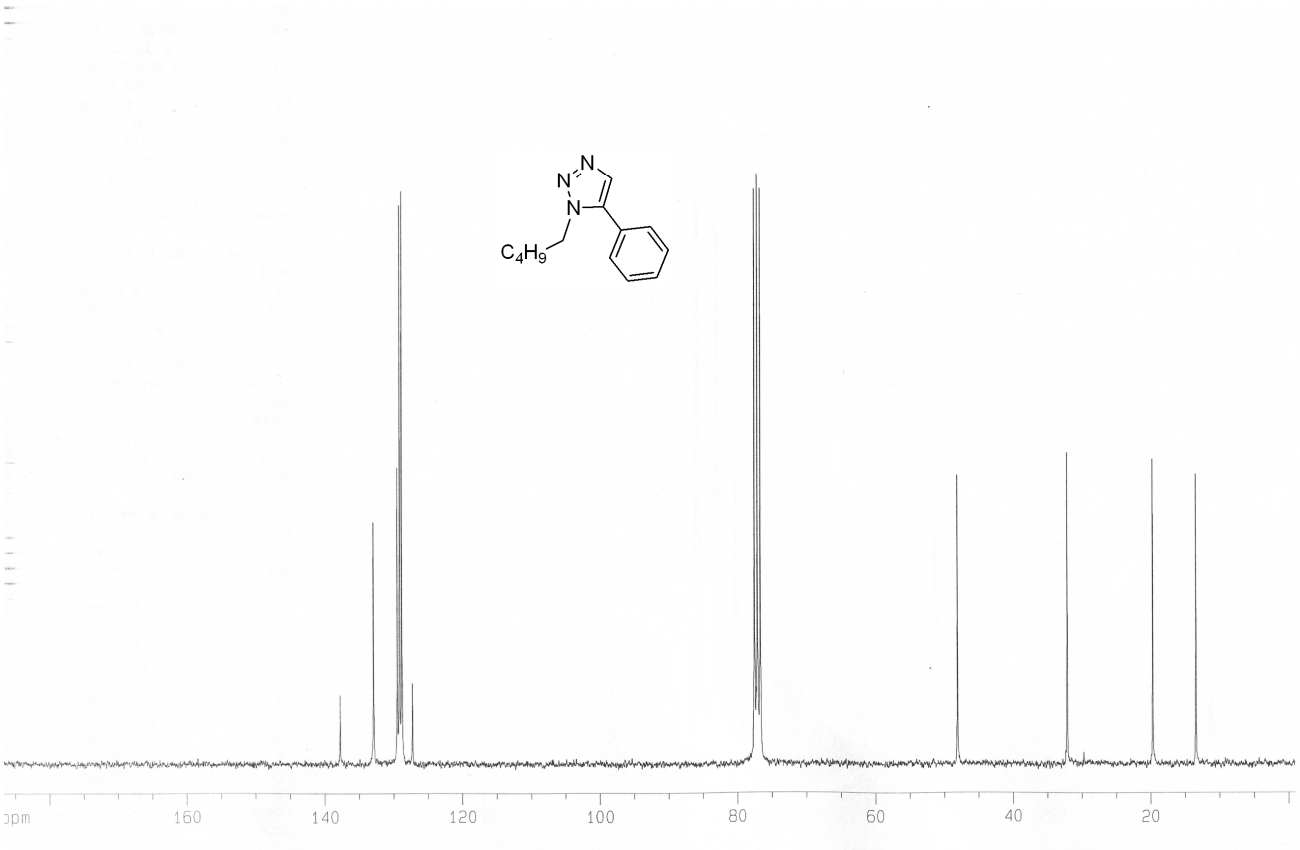



Figure S14. $^{13}$C NMR spectrum of **7e**.

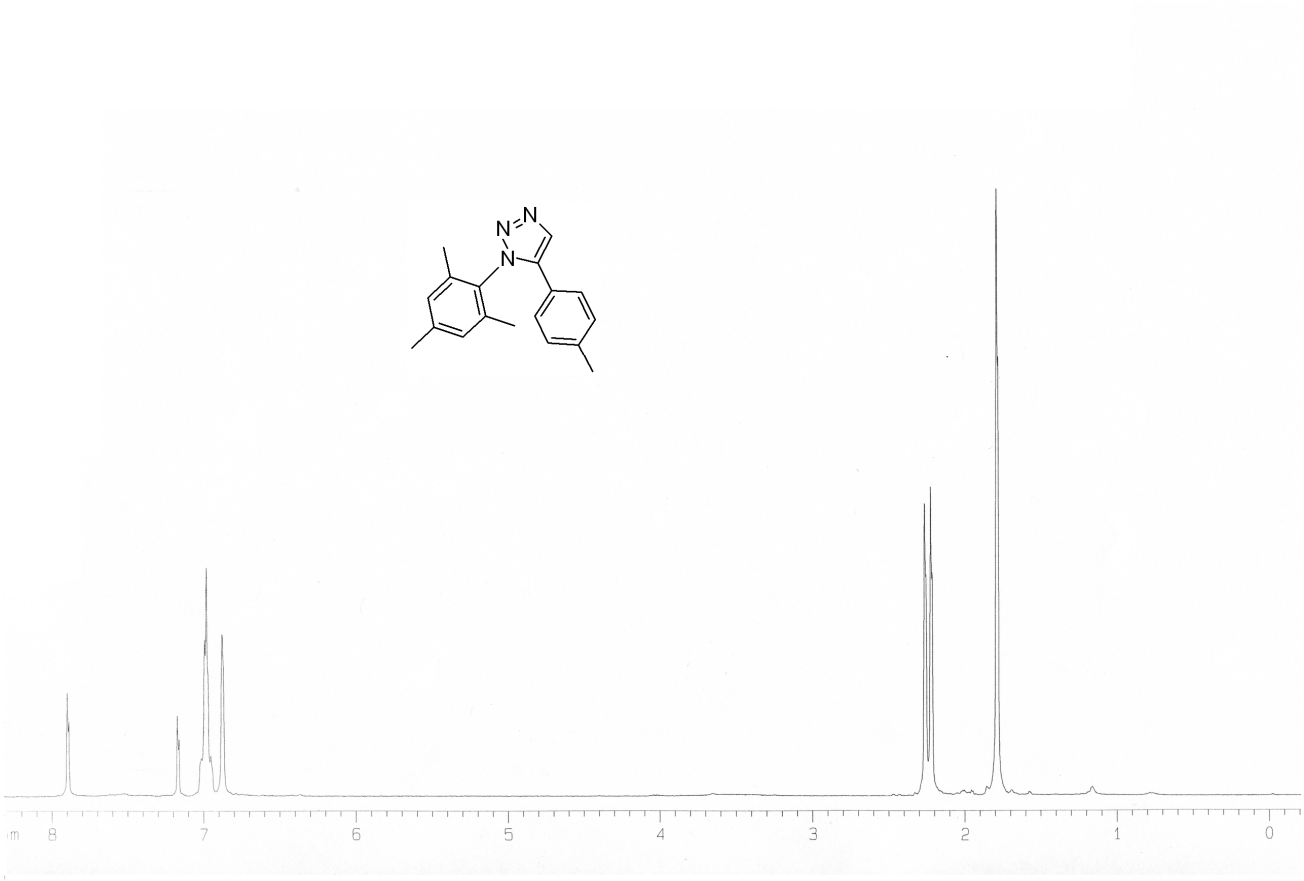



Figure S15. $^{1}$H NMR spectrum of **7f**.

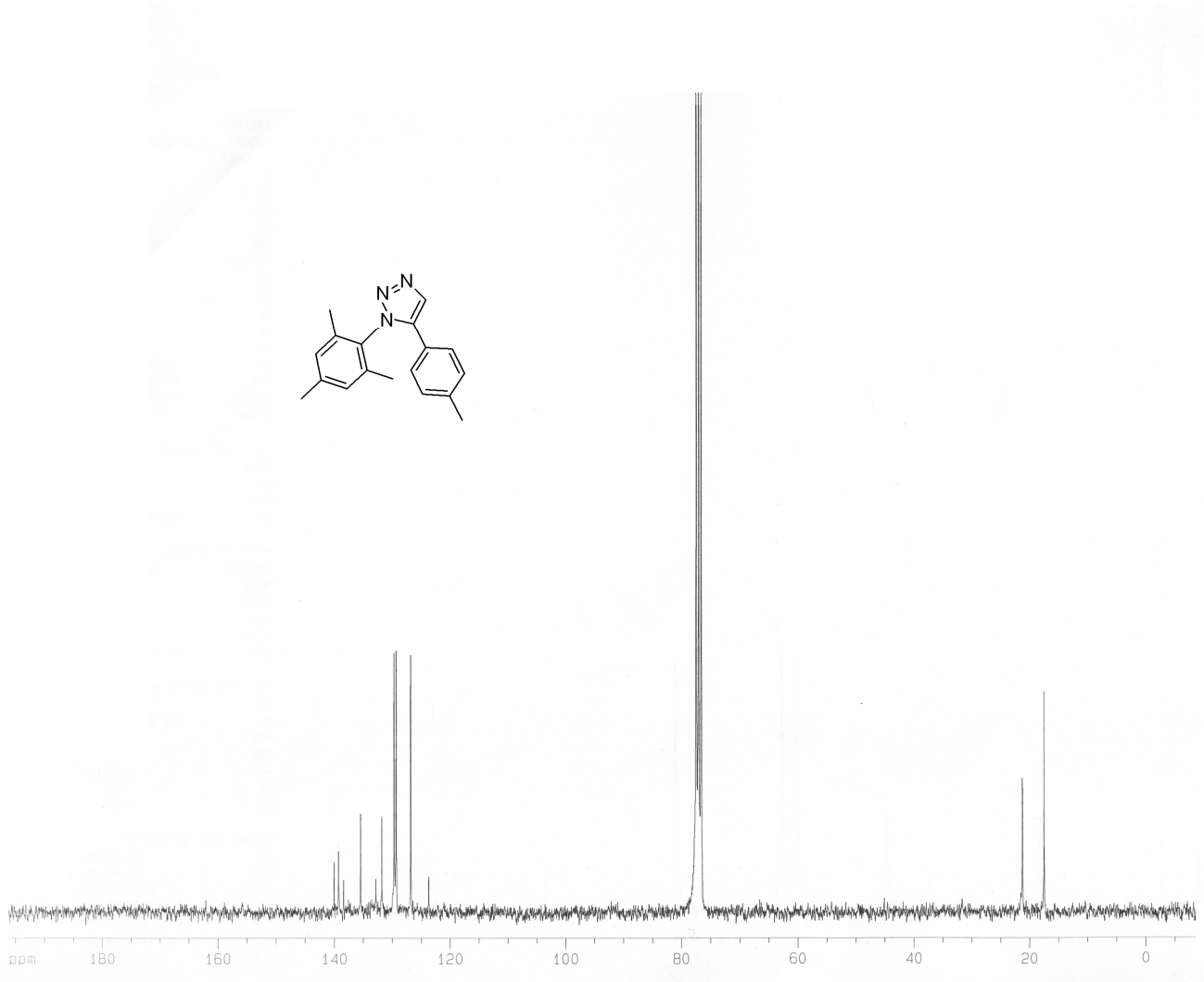



Figure 16. $^{13}$C NMR spectrum of **7f**.

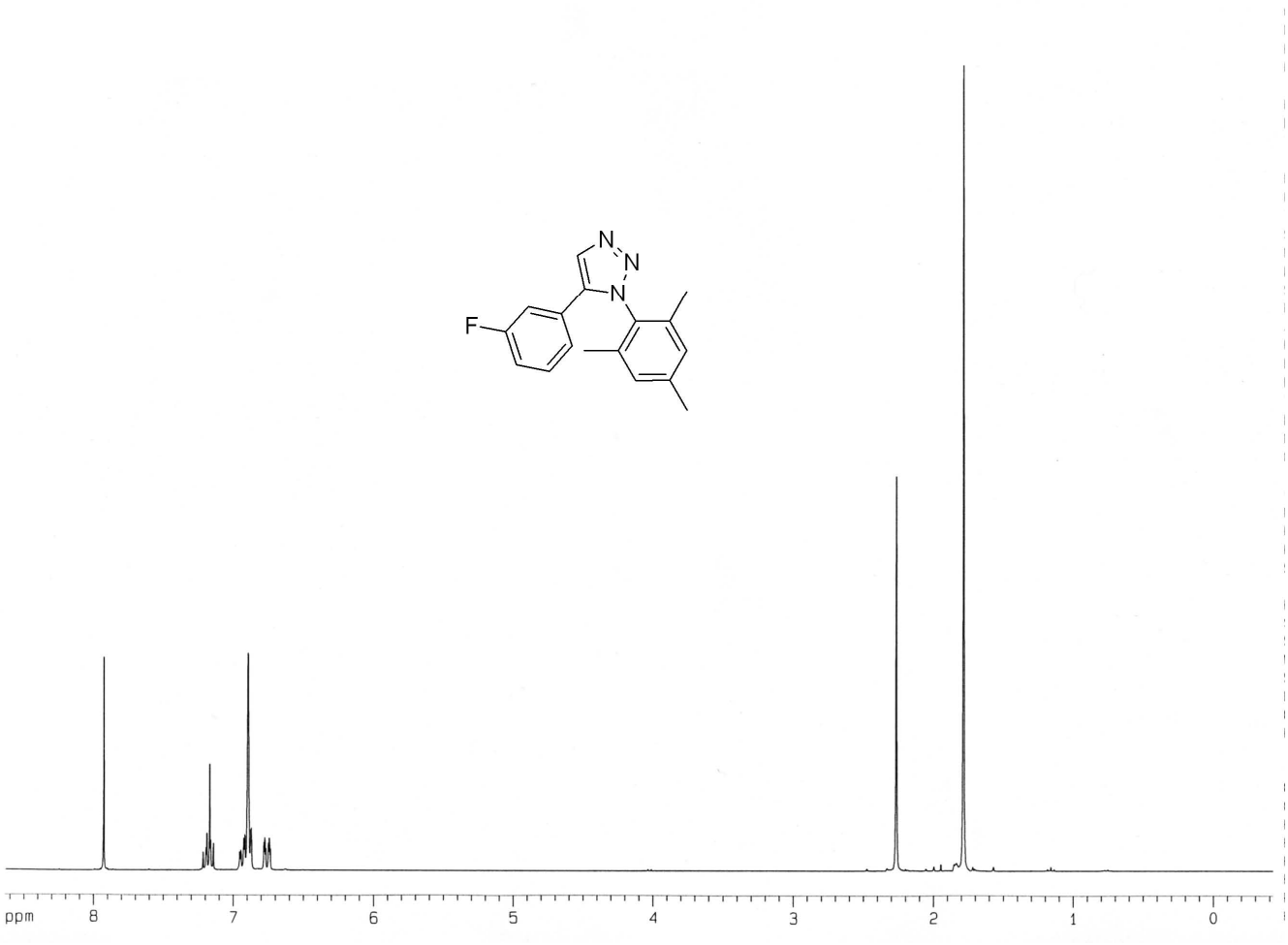



Figure S17. $^{1}$H NMR spectrum of **7g**.

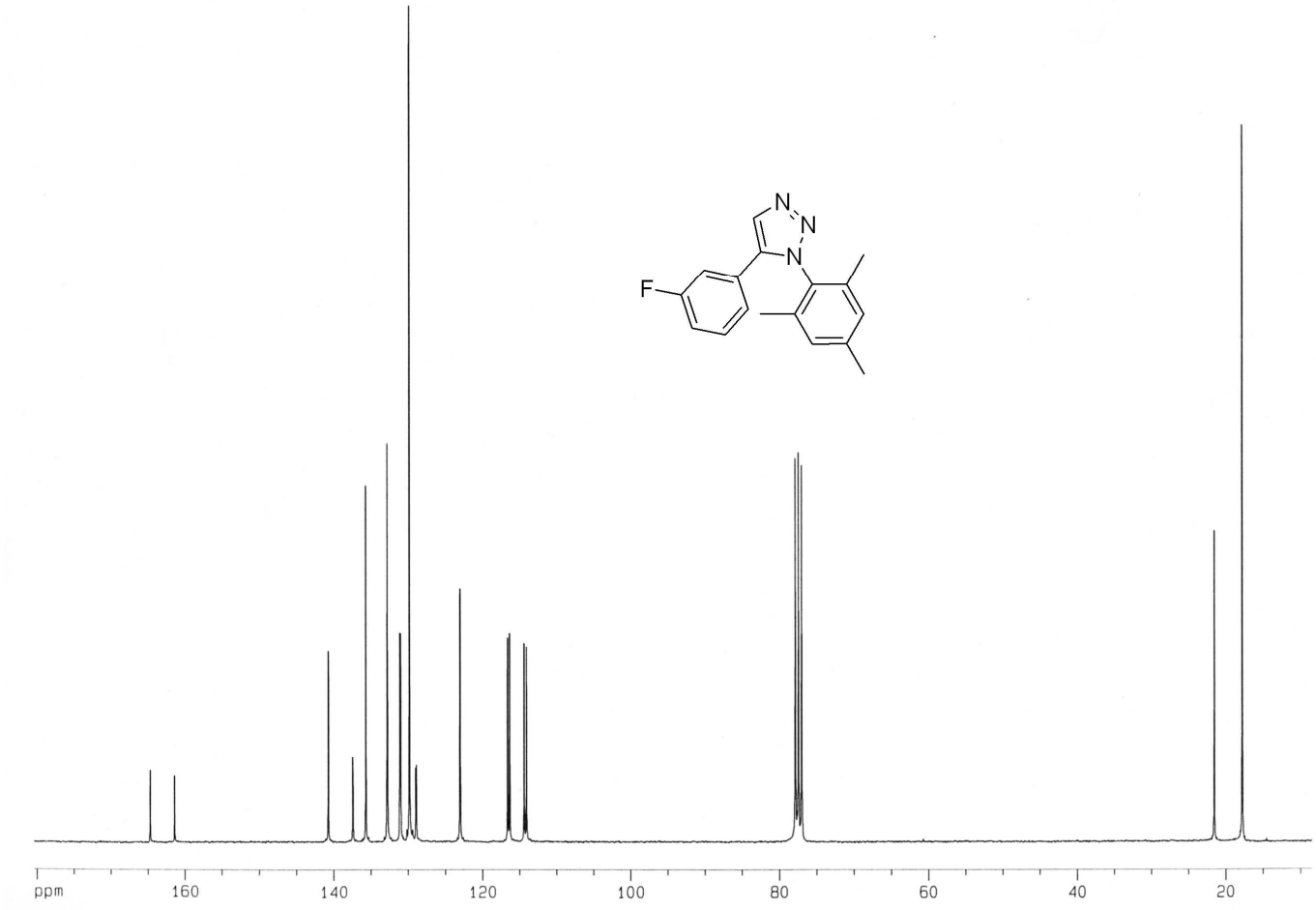



Figure S18. $^{13}$C NMR spectrum of **7g**.