Supplementary Information

Formation of bicyclic pyrroles from the catalytic coupling reaction of 2,5-disubstituted pyrroles with terminal alkynes involving multiple C-H bond activation

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Experimental details

General information. All operations were carried out in an inert-atmosphere glove box or by using standard high vacuum and Schlenk techniques. Tetrahydrofuran, benzene, hexanes were distilled from purple solutions of sodium and benzophenone immediately prior to use. CH_2Cl_2 was distilled from CaH_2. The NMR solvents were dried from activated molecular sieves (4 Å). Pyrrole and alkyne substrates were received from commercial sources and used without further purification. The ^{1}H, ^{2}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 MHz or 400 MHz FT-NMR spectrometer. Mass spectra were recorded from a Hewlett-Packard HP5970 GC/MS spectrometer. Elemental analyses were performed at the Midwest Microlab, Indianapolis, Indiana, USA.

Typical procedure of the catalytic reaction. In a glove box, $Ru_3(CO)_{12}$ (0.03 mmol), NH_4PF_6 (0.1 mmol), 2,5-dimethylpyrrole (1.0 mmol) and an alkyne (2.0 mmol) were dissolved in 5 mL benzene solution in a medium-walled 25 mL Schlenk tube equipped with teflon stopcock and a magnetic stirring bar. The tube was sealed and was brought out of the box. The reaction tube was heated in an oil bath at 95 °C for 36-48 h. The tube was opened to air at room temperature, and the crude product mixture was analysed by GC/MS. The solvent was removed under a rotary evaporator, and the organic product was isolated by a column chromatography on silica gel (hexane/CH_2Cl_2) under nitrogen. For the combined catalyst system: 2,5-dimethylpyrrole (1.0 mmol), phenylacetylene (2.0 mmol), $Ru_3(CO)_{12}$ (0.03 mmol), NH_4PF_6 (0.1 mmol), $Au(PPh_3)Cl$ (0.05 mmol) and AgOTf (0.05 mmol) were used under otherwise same reaction conditions.

For **1a**: δ_H(300 MHz; C_6D_6) 7.60-6.83 (8 H, m, Ar), 6.25 (1 H, br s, NH), 6.13 (1 H, s, C=C*H*), 3.33 (3 H, s, OCH_3), 3.32 (3 H, s, OCH_3), 2.10 (3 H, s, CH_3), 1.92 (3 H, s, CH_3), 1.87 (3 H, s, CH_3); δ_C(75 MHz, C_6D_6) 159.6, 158.5, 141.1, 138.6, 138.1, 135.4, 130.2, 129.2, 127.8, 127.4, 117.2, 114.2, 114.1, 114.0, 54.8 (OCH_3), 54.7 (OCH_3), 50.3 (*C*CH_3), 24.7 (CH_3), 13.0 (CH_3), 11.8 (CH_3); *m/z* (GC-MS) 359 (M^+); Found: C, 79.62; H, 7.34; N, 3.25. Calc. for $C_{24}H_{25}NO_2$: C, 80.19; H, 7.01; N, 3.90%.

For **1b**: δ_H(400 MHz; C_6D_6) 7.58-7.03 (8 H, m, Ar), 6.20 (1 H, br s, NH), 6.17 (1 H, s, C=CH), 2.15 (6 H, s, CH_3), 2.08 (3 H, s, CH_3), 1.90 (3 H, s, CH_3), 1.86 (3 H, s, CH_3); δ_C(75 MHz, C_6D_6) 142.9, 141.4, 138.9, 136.6, 135.1, 135.0, 134.7, 129.1, 127.9, 126.7, 117.0, 114.1, 50.6 (*C*CH_3), 24.3 (CH_3), 21.1 (CH_3), 20.9 (CH_3), 12.8 (CH_3), 11.6 (CH_3); *m/z* (GC-MS) 327 (M^+); Found: C, 88.02; H, 7.62; N, 4.31. Calc. for $C_{24}H_{25}N$: C, 88.03; H, 7.70; N, 4.28%.

For **1c**: δ_H(400 MHz; C_6D_6) 7.61-6.85 (8 H, m, Ar), 6.12 (1 H, s, C=C*H*), 3.34 (6 H, s, OCH_3), 2.74 (3 H, s, NCH_3), 2.12 (3 H, s, CH_3), 1.94 (3 H, s, CH_3), 1.90 (3 H, s, CH_3); δ_C(100 MHz, C_6D_6) 159.4, 158.3, 140.9, 138.7, 138.0, 134.6, 130.3, 129.2, 127.7, 126.4, 119.2, 116.2, 113.9, 113.8, 54.7 (OCH_3), 54.6 (OCH_3), 50.5 (*C*CH_3), 29.4 (NCH_3), 24.6 (CH_3), 11.7 (CH_3), 11.0 (CH_3); *m/z* (GC-MS) 373 (M^+); Found: C, 79.87; H, 7.16; N, 3.68. Calc. for $C_{25}H_{27}NO_2$: C, 80.40; H, 7.29; N, 3.75%.

For **1d**: δ_H(300 MHz; acetone-d_6) 7.42-7.04 (8 H, m, Ar), 5.93 (1 H, s, C=CH), 3.39 (3 H, s, NCH_3), 2.34 (3 H, s, CH_3), 2.26 (3 H, s, CH_3), 2.20 (3 H, s, CH_3), 2.08 (3 H, s, CH_3), 1.67 (3 H, s, CH_3); δ_C(75 MHz; acetone-d_6) 143.4, 141.0, 139.6, 137.4, 135.5, 135.2, 134.2, 129.7, 129.5, 128.3, 127.1, 126.3, 120.1, 117.0, 51.2 (*C*CH_3), 30.2 (NCH_3), 24.8 (CH_3), 21.2 (CH_3), 20.9 (CH_3), 11.8 (CH_3), 11.2 (CH_3); *m/z* (GC-MS) 341 (M^+); Found: C, 88.08; H, 8.03; N, 4.02. Calc. for $C_{25}H_{27}N$: C, 87.93; H, 7.97; N, 4.10%.

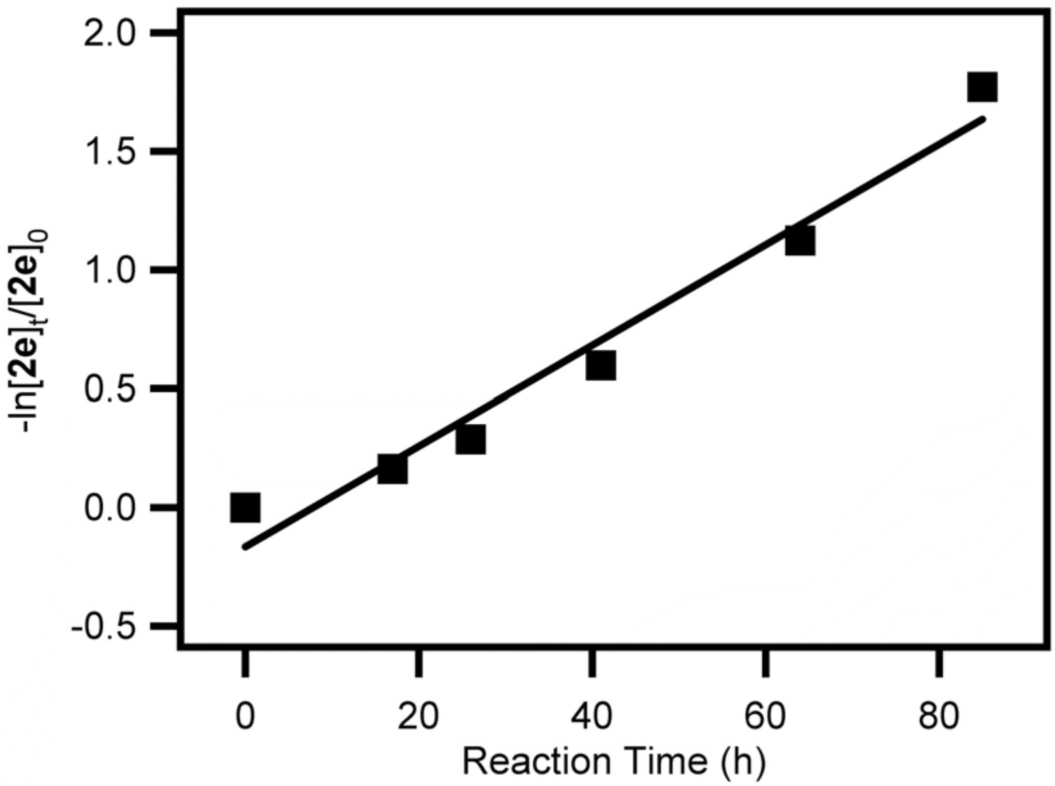
For **1e**: δ_H(400 MHz; C_6D_6) 7.68-7.01 (10 H, m, Ar), 6.24 (1 H, br s, NH), 6.19 (1 H, s, C=C*H*), 2.10 (3 H, s, CH_3), 1.92 (3 H, s, CH_3), 1.89 (3 H, s, CH_3); δ_C(100 MHz; C_6D_6) 145.8, 139.3, 137.5, 134.9, 128.5, 128.4, 127.4, 127.0, 126.1, 121.2, 117.3, 114.3, 51.0 (*C*CH_3), 24.3 (CH_3), 12.9 (CH_3), 11.7 (CH_3); *m/z* (GC-MS) 299 (M^+).

For **2e**: δ_H(400 MHz; C_6D_6) 7.68-7.01 (10 H, m, Ar), 6.44 (1 H, br s, NH), 5.53 (2 H, d, *J* = 1.6 Hz, C=CH*H*), 5.27 (2 H, d, *J* = 1.6 Hz, C=CH*H*), 1.92 (6 H, s, CH_3); δ_C(100 MHz, C_6D_6) 144.4, 142.9, 141.8, 128.0, 127.6, 127.2, 126.8, 123.6, 114.4, 12.0 (CH_3); *m/z* (GC-MS) 299 (M^+).

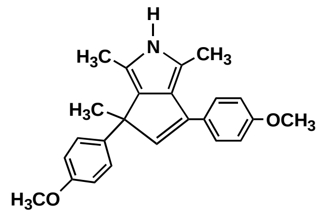
For **2f**: δ_H(300 MHz; C_6D_6) 7.17-6.95 (8 H, m, Ar), 6.25 (1 H, br s, NH), 5.40 (2 H, d, *J* = 2.4 Hz, C=CH*H*), 5.16 (2 H, d, *J* = 2.4 Hz, C=C*H*H), 2.07 (6 H, s, CH_3), 1.69 (6 H, s, CH_3); δ_H(400 MHz; acetone-d_6) 9.58 (1 H, br s, NH), 7.05-6.94 (8 H, m, Ar), 5.21 (2 H, d, *J* = 2.7 Hz, C=CH*H*), 5.98 (2 H, d, *J* = 2.7 Hz, C=C*H*H), 1.99 (6 H, s, CH_3), 1.92 (6 H, s, CH_3); δ_C(75 MHz, C_6D_6) 144.5, 143.2, 135.8, 130.6, 130.4, 126.9, 125.4, 123.4, 121.3, 117.0 (C=*C*H_2), 20.6 (CH_3), 11.9 (CH_3); δ_C(100 MHz; acetone-d_6) 145.6, 143.9, 136.4, 130.0, 130.9, 127.4, 125.9, 124.6, 121.3, 116.6 (C=*C*H_2), 20.7 (CH_3), 12.0 (CH_3); *m/z* (GC-MS) 327 (M^+); Found C, 87.26; H, 7.70; N, 4.32. Calc. for $C_{24}H_{25}N$: C, 88.03; H, 7.70; N, 4.28%.

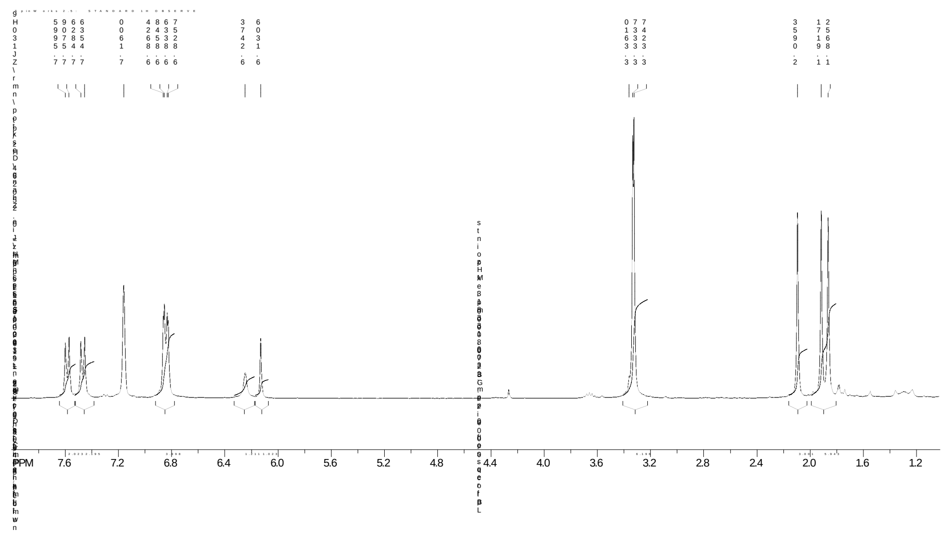
For **3f**: δ_H(300 MHz; C_6D_6) 7.41-7.11 (4 H, m, Ar), 6.25 (1 H, br s, NH), 5.91 (1 H, s, C=C*H*), 5.51 (1 H, d, *J* = 1.8 Hz, C=CH*H*), 5.05 (1 H, d, *J* = 1.8 Hz, C=C*H*H), 2.27 (3 H, s, CH_3), 1.81 (3 H, s, CH_3), 1.64 (3 H, s, CH_3); δ_C(75 MHz, C_6D_6) 145.9, 144.3, 136.1, 130.1, 129.8, 125.9, 124.6, 123.3, 121.0, 20.1 (CH_3), 12.7 (CH_3), 12.6 (CH_3); *m/z* (GC-MS) 211 (M^+).

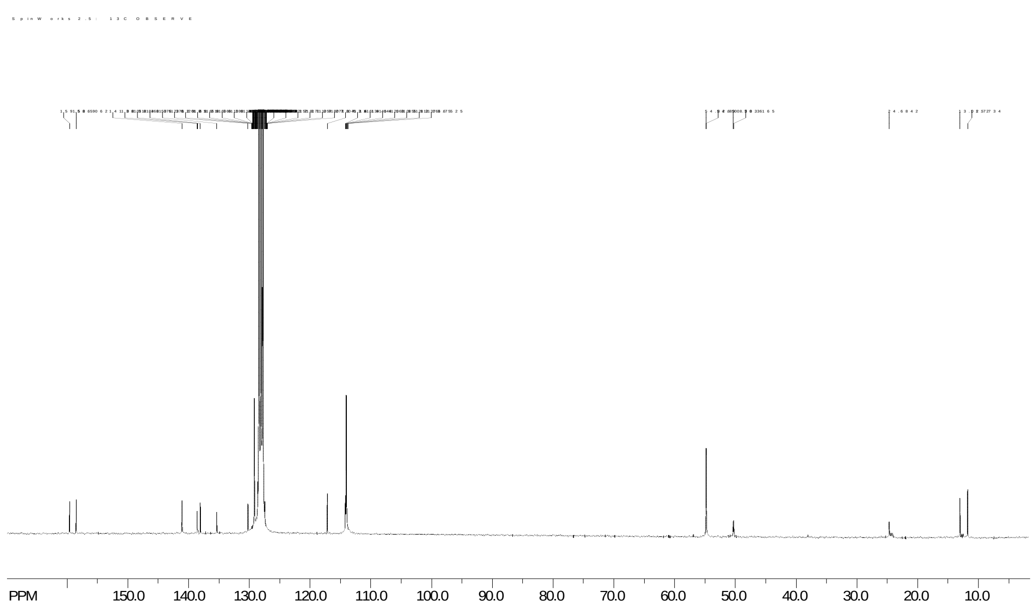
Figure S1. Pseudo first order plot of ln([**2e**]$_t$/[**2e**]$_0$) vs time



^{1}H and $^{13}C\{^{1}H\}$ NMR of **1a** in C_6D_6

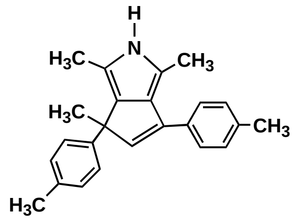


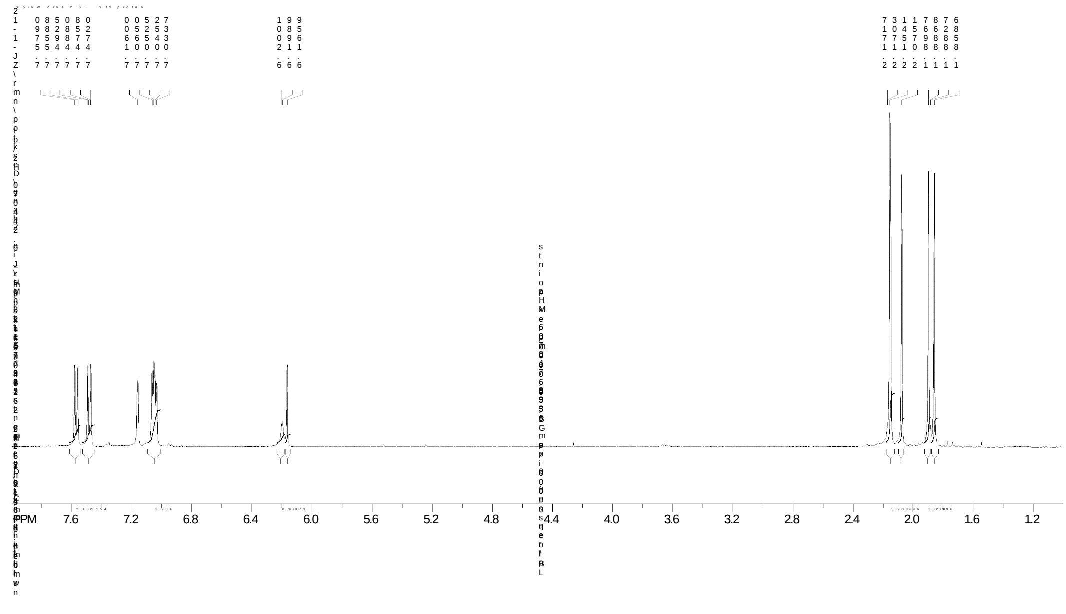


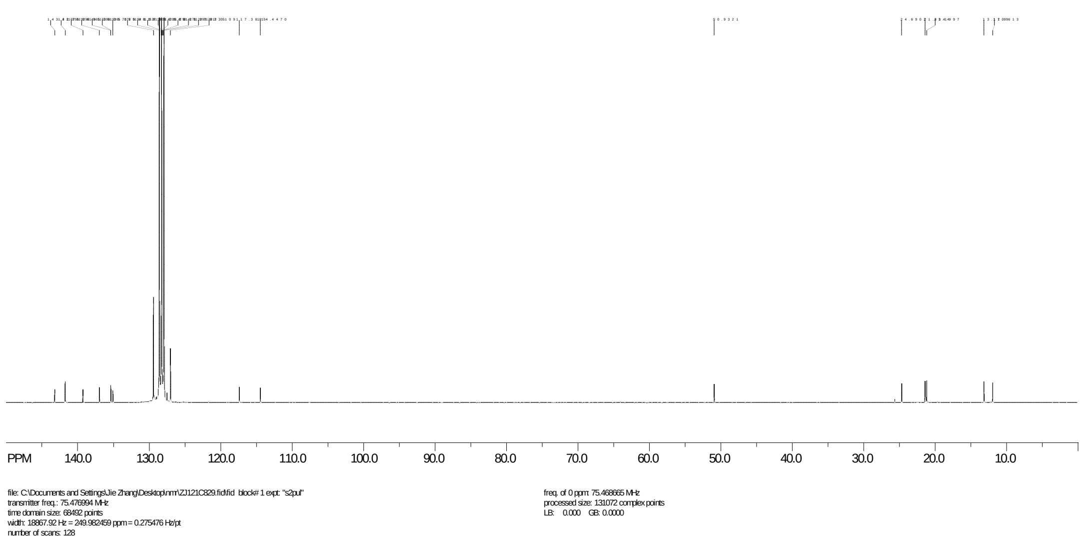


Supplementary Material (ESI) for Chemical Communications

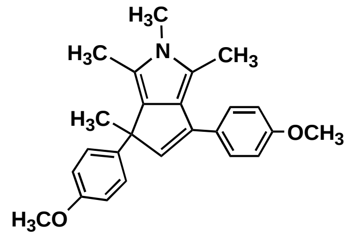
^{1}H and $^{13}C\{^{1}H\}$ NMR of **1b** in C_6D_6

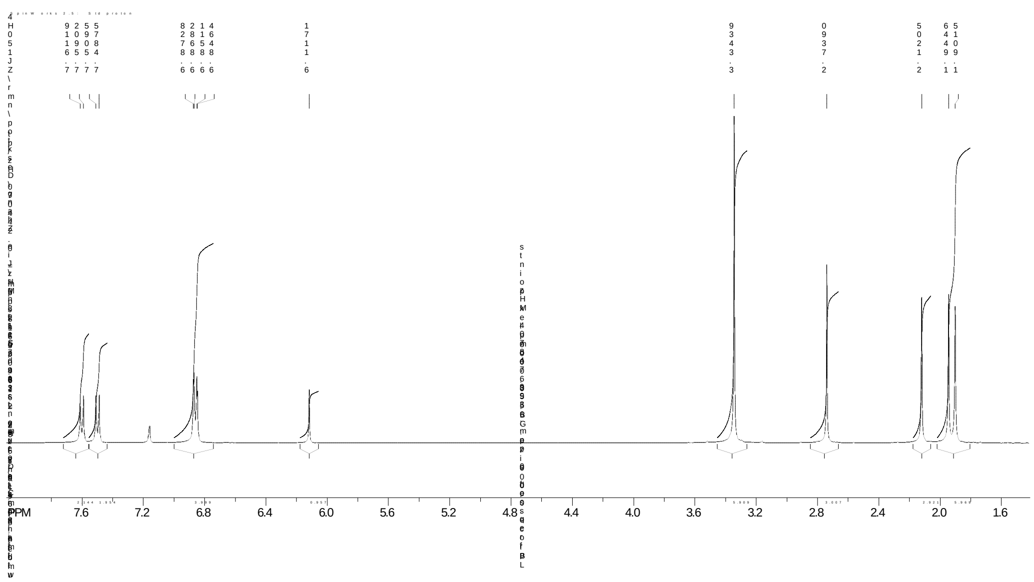


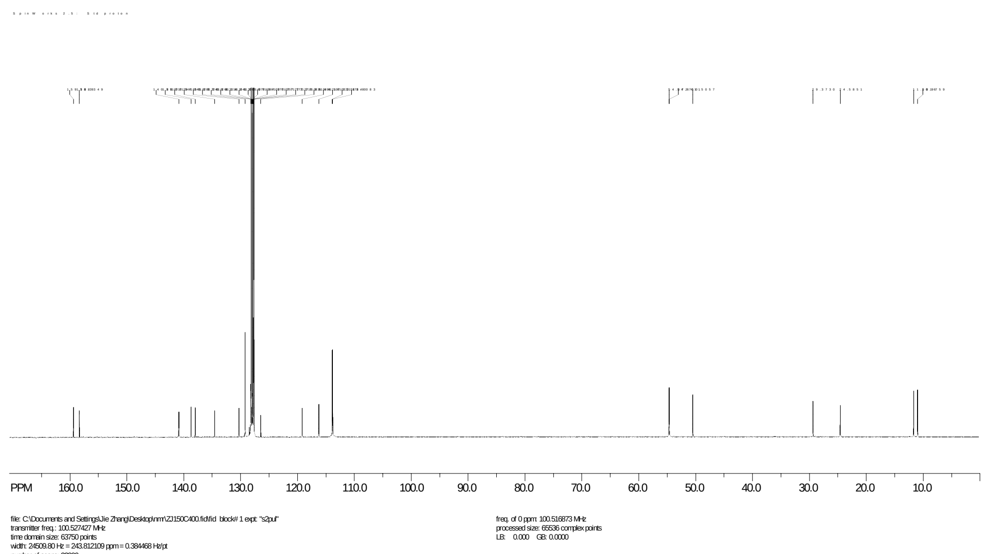




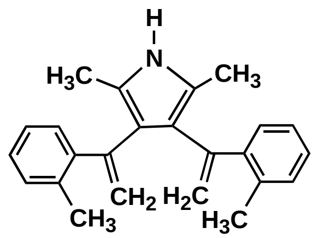
^{1}H and $^{13}C\{^{1}H\}$ NMR of **1c** in C_6D_6

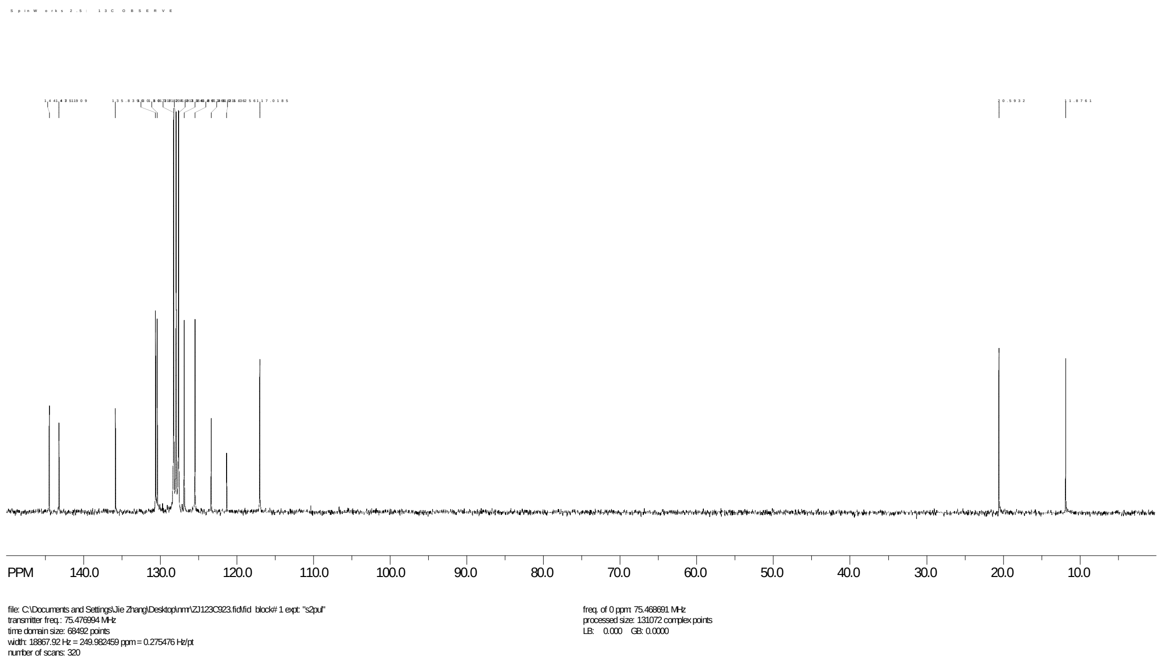






$^{13}C\{^{1}H\}$ NMR of **2f** in C_6D_6





^{1}H and $^{13}C\{^{1}H\}$ NMR of **3f** in C_6D_6