Supporting Information

Hydroamination of Diphenylbutadiyne with Secondary *N*-Methyl-anilines Using the Dipotassium Tetrakis(2,6-diisopropylanilino)calciate Precatalyst

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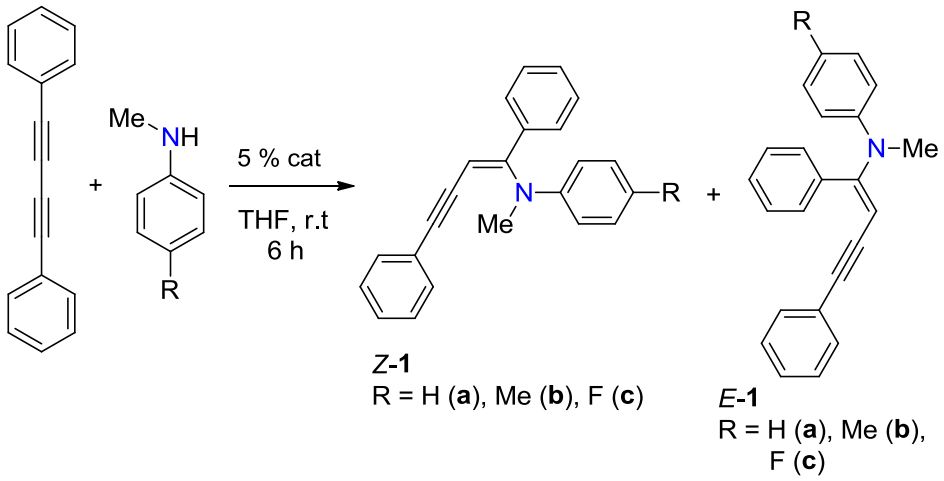
Singly hydroaminated diphenylbutadiyne



Z-**1**
R = H (**a**), Me (**b**), F (**c**)

E-**1**
R = H (**a**), Me (**b**), F (**c**)

(*N*-Methyl)-1,4-diphenylbut-1-ene-3-yne-1-ylaniline (**1a**):

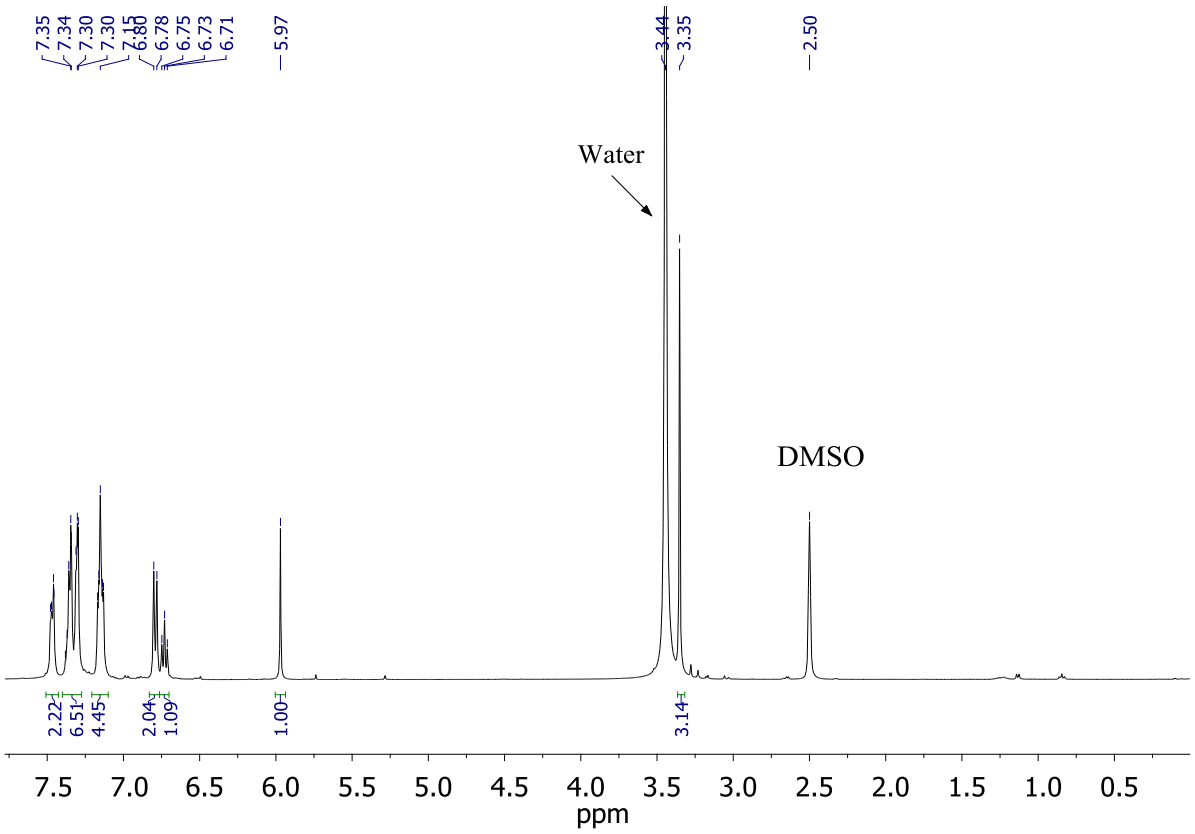


Figure S1: ^{1}H NMR spectrum of *E*-**1a** (400.08 MHz, [D_6]DMSO).

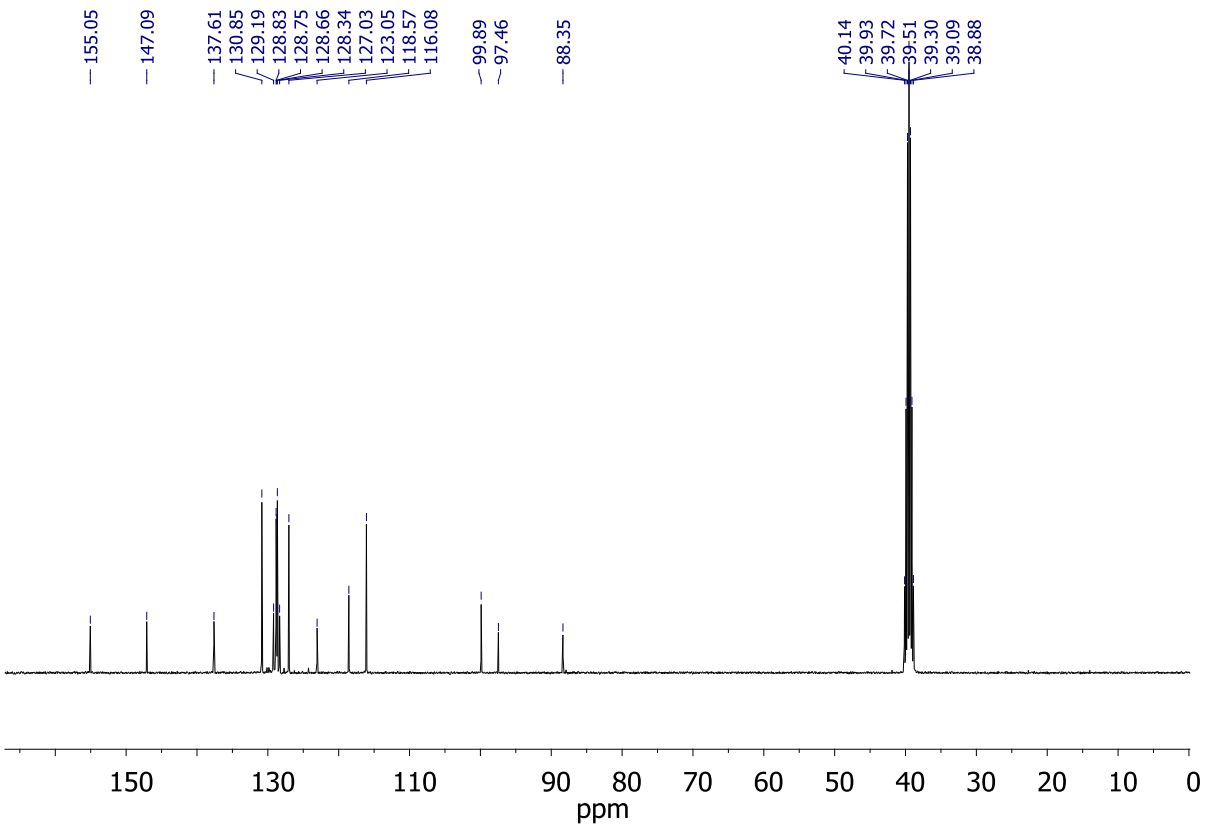


Figure S2: ^{13}C NMR spectrum of *E*-**1a** (100.60 MHz, [D_6]DMSO).

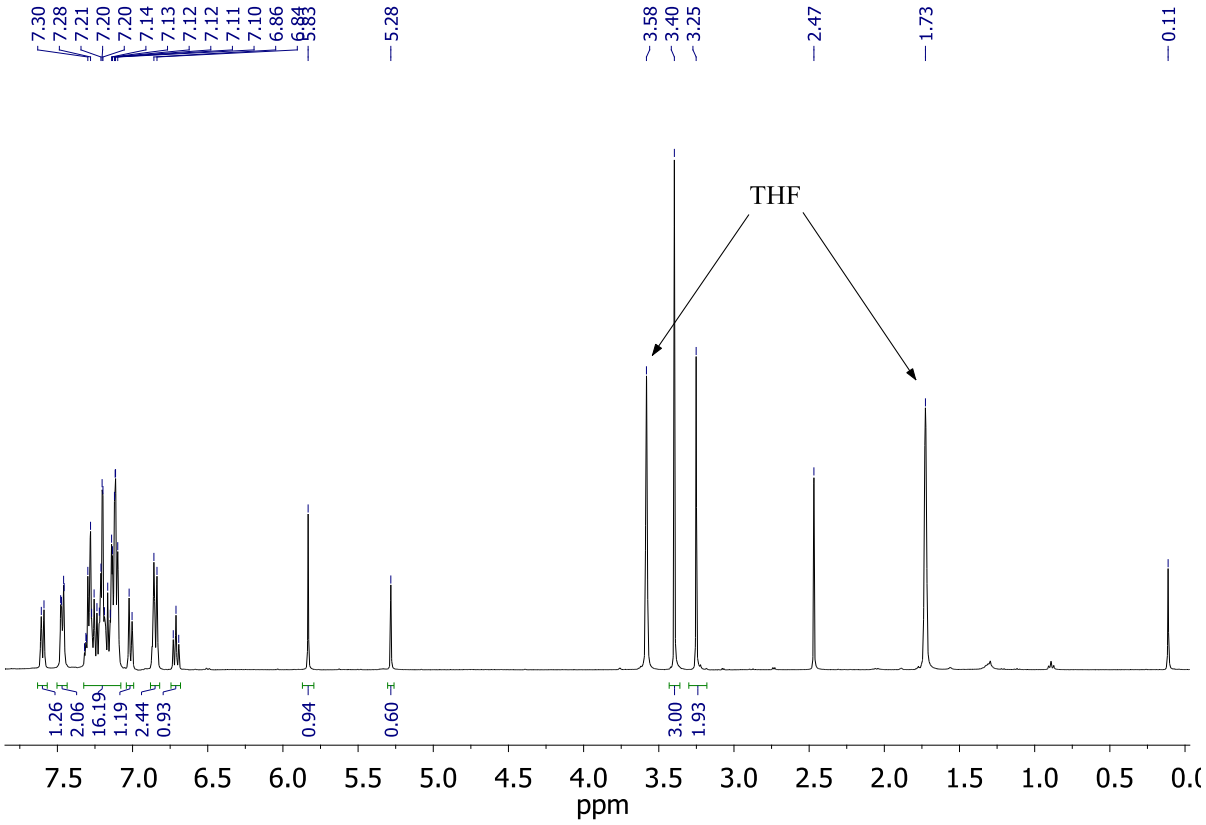


Figure S3: ^{1}H NMR spectrum of an *E*/*Z*-mixture of **1a** (400.08 MHz, [D_8]THF).

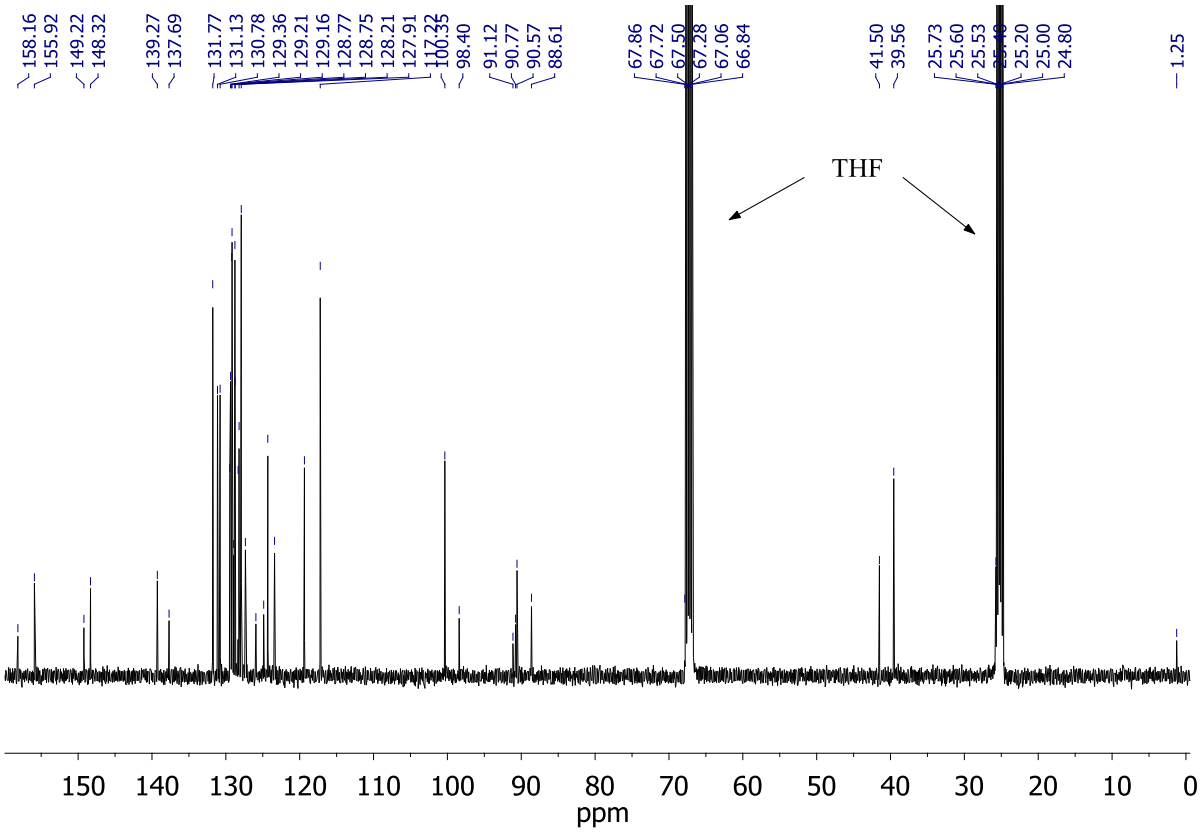


Figure S4: ^{13}C NMR spectrum of an *E*/*Z*-mixture of **1a** (100.60 MHz, [D_8]THF).

(N-Methyl)-(N-4-tolyl)-1,4-diphenylbut-1-ene-3-yne-1-ylamine (**1b**):

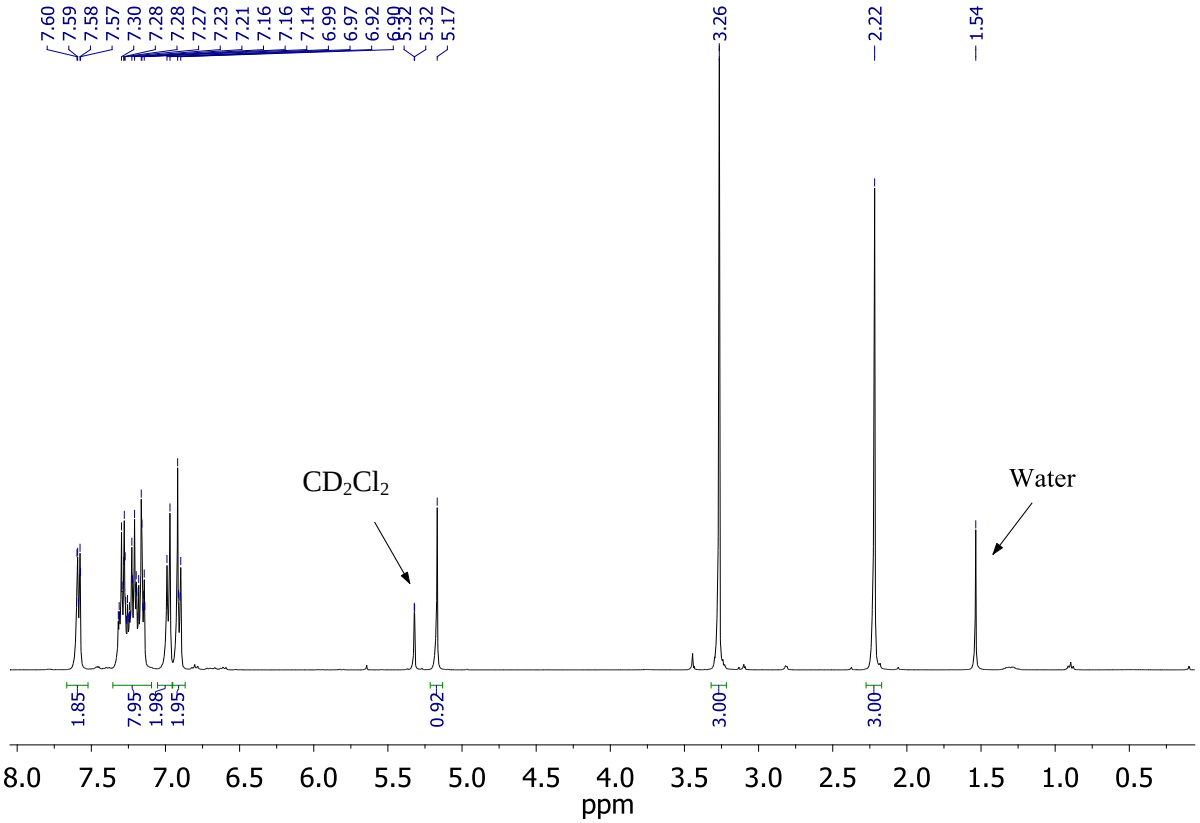


Figure S5: ^{1}H NMR spectrum of *E*-**1b** (400.08 MHz, CD_2Cl_2)**.**

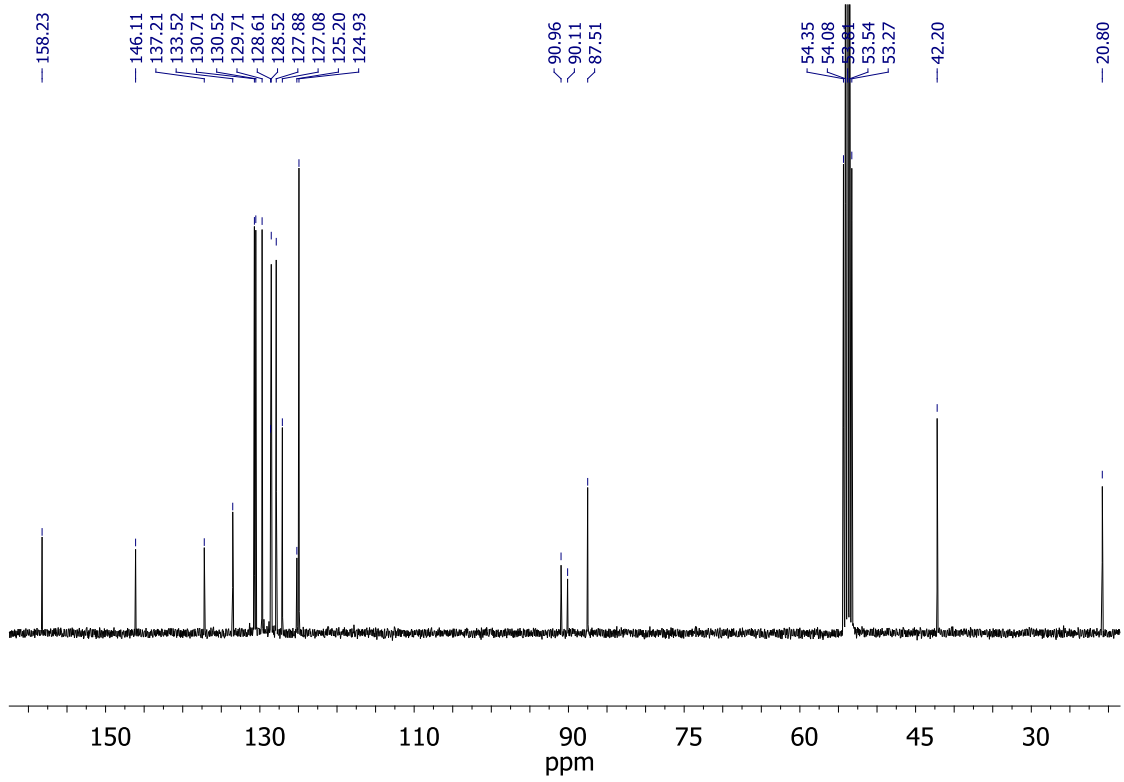


Figure S6: ^{13}C NMR spectrum of *E*-**1b** (100.60 MHz, CD_2Cl_2)**.**

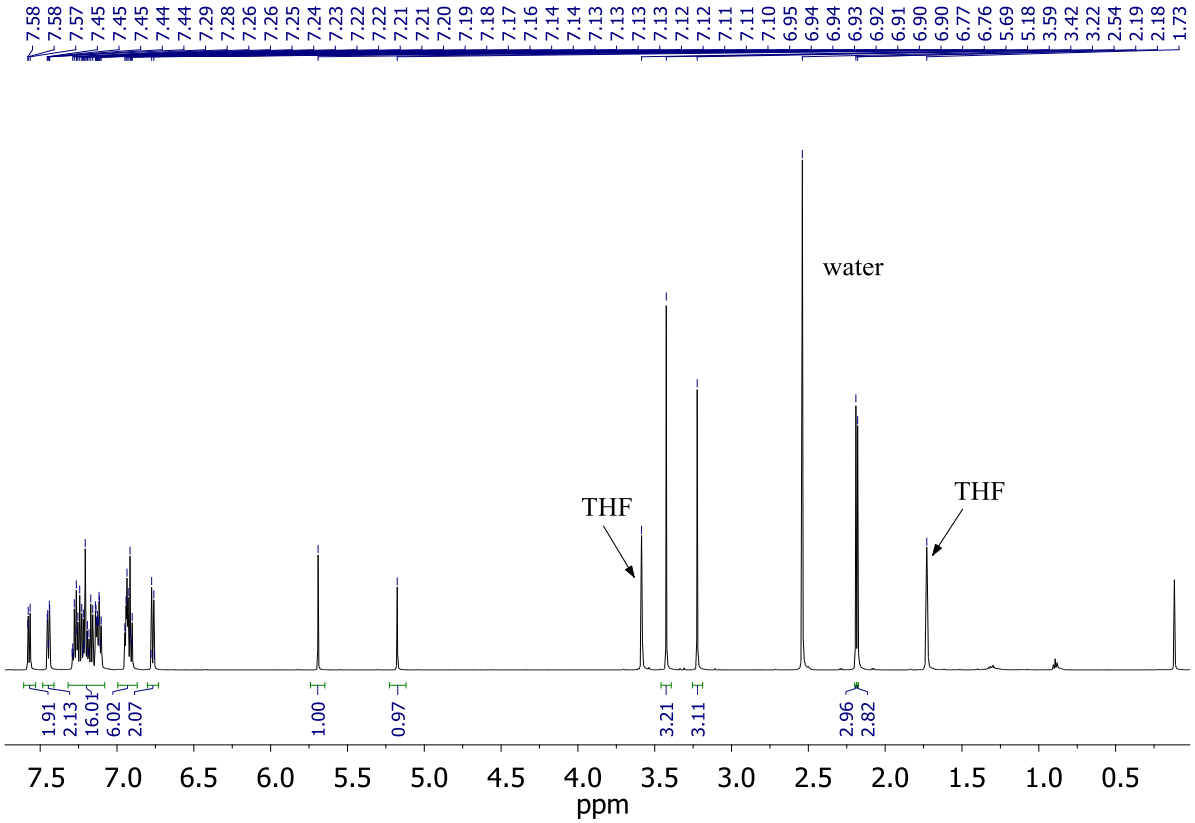


Figure S7: ^{1}H-NMR spectrum of an *E/Z*-mixture of **1b** (600.15 MHz, [D_8]THF).

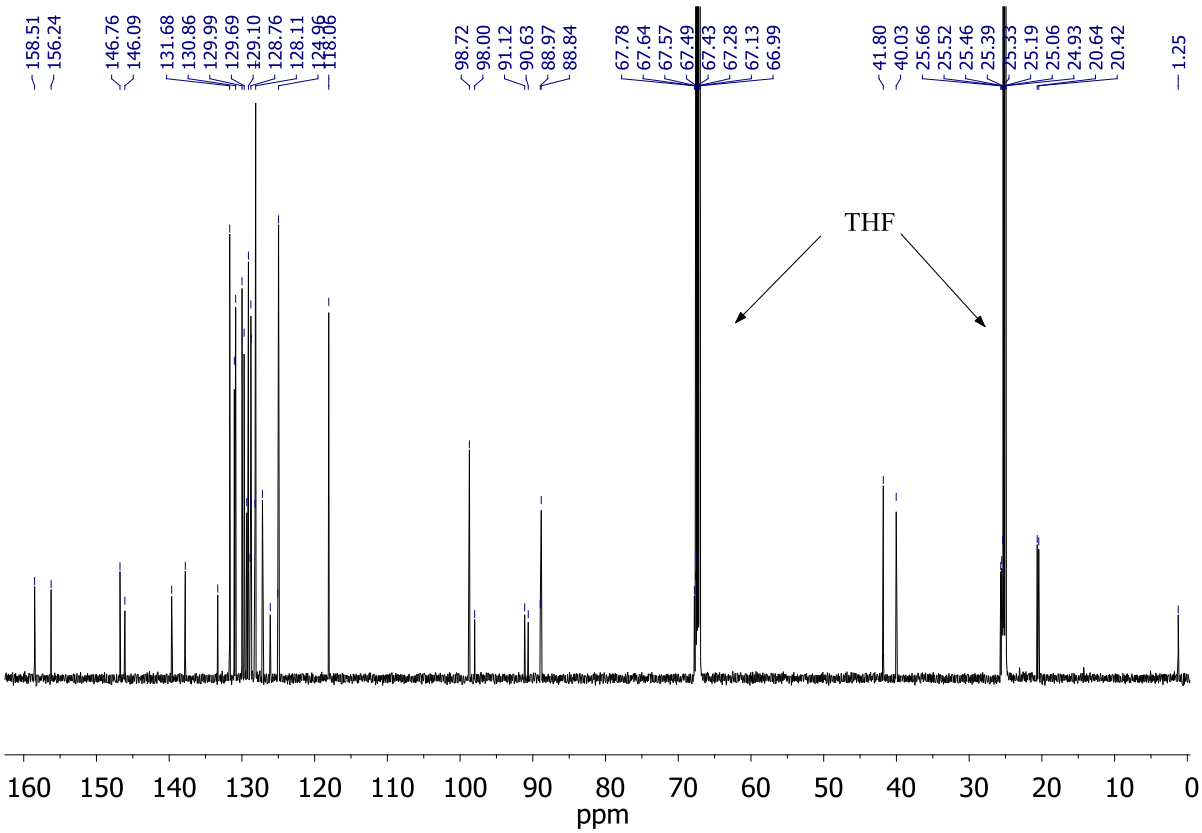


Figure S8: ^{13}C NMR spectrum of an *E/Z*-mixture of **1b** (150.91 MHz, [D_8]THF)**.**

(N-Methyl)-(N-4-fluorophenyl)-1,4-diphenylbut-1-ene-3-yne-1-ylamine (**1c**):

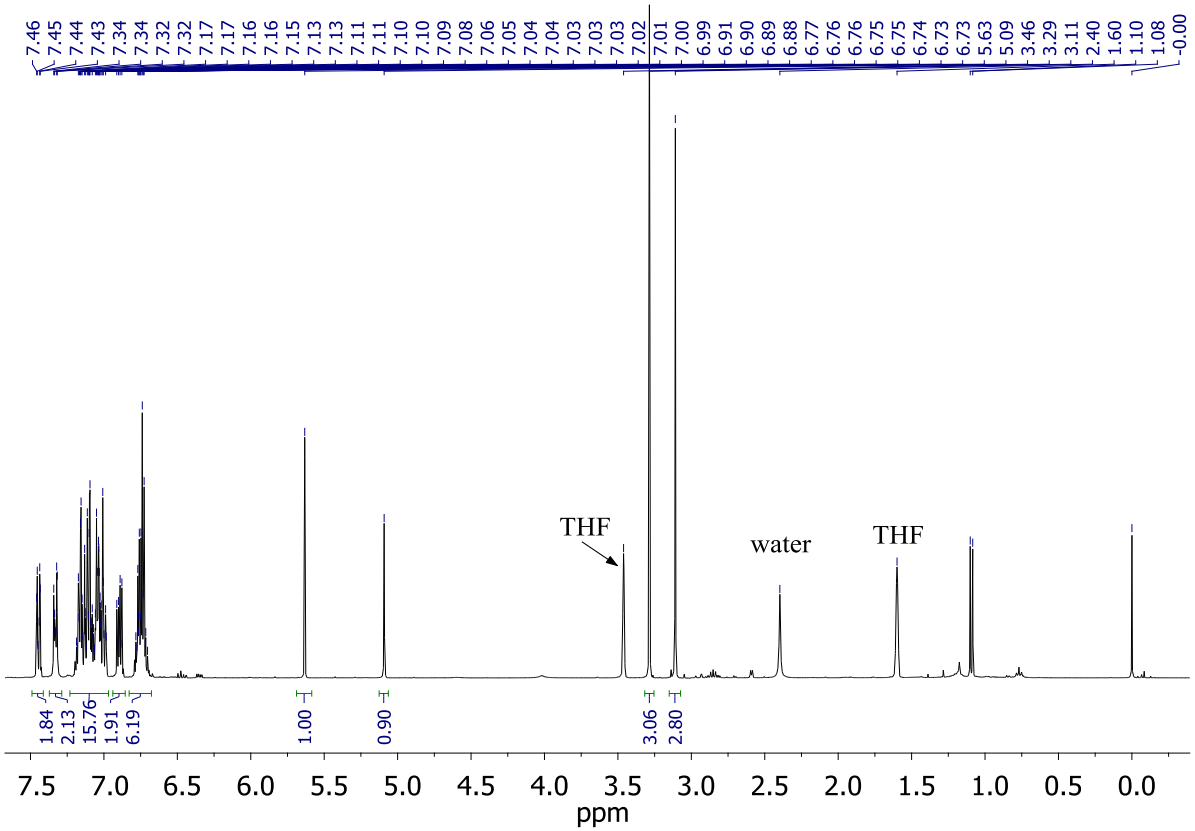


Figure S9: ^{1}H NMR spectrum of an *E/Z*-mixture of **1c** (400.13 MHz, [D_8]THF).

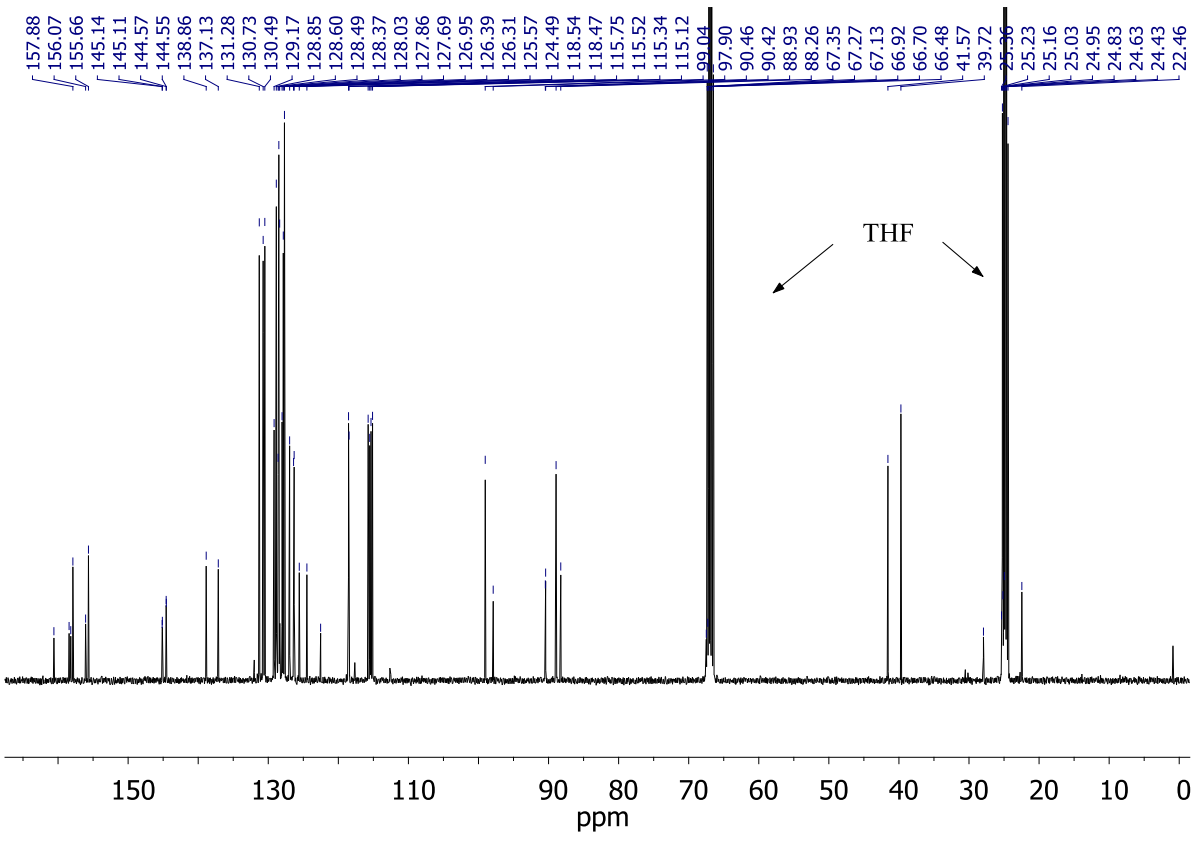


Figure S10: ^{13}C NMR spectrum of an *E/Z*-mixture of **1c** (100.61 MHz, [D_8]THF).

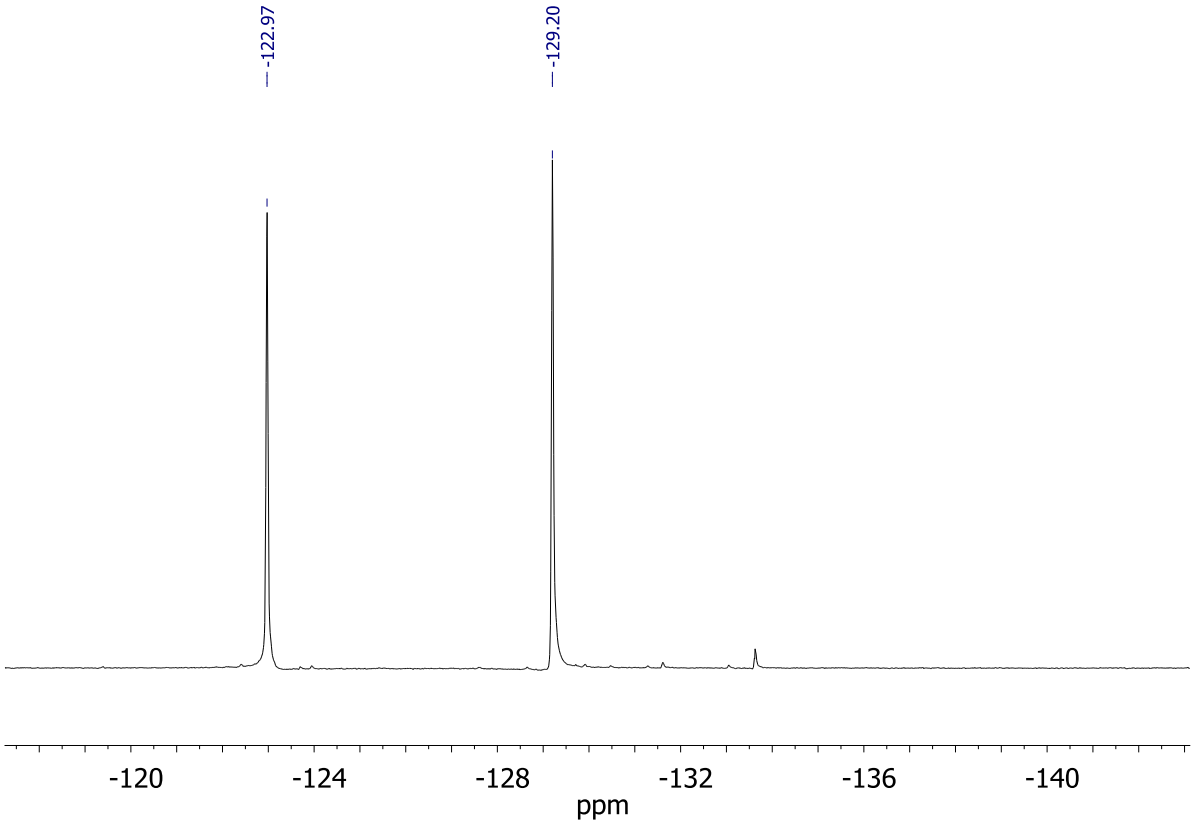
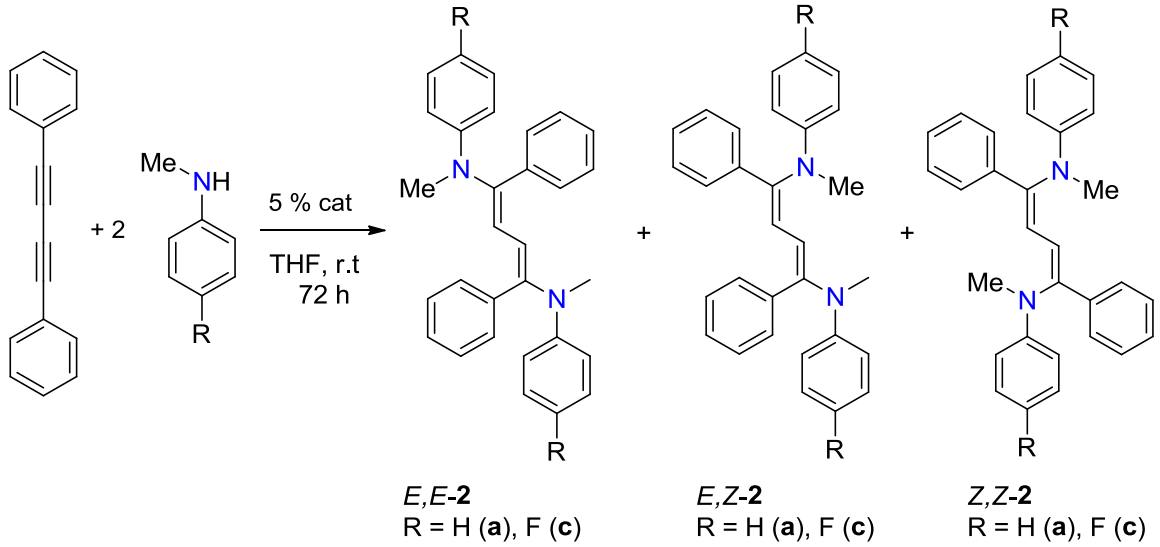


Figure S11: ^{19}F-NMR spectrum of an *E/Z*-mixture of **1c** (188.31 MHz, [D_8]THF).

Doubly hydroaminated diphenylbutadiyne

Mixture of 1,4-diphenyl-1,4-bis(*N*-methylanilino)buta-1,3-diene (**2a**) with (*N*-methyl)-1,4-diphenylbut-1-ene-3-yne-1-ylaniline (**1a**):



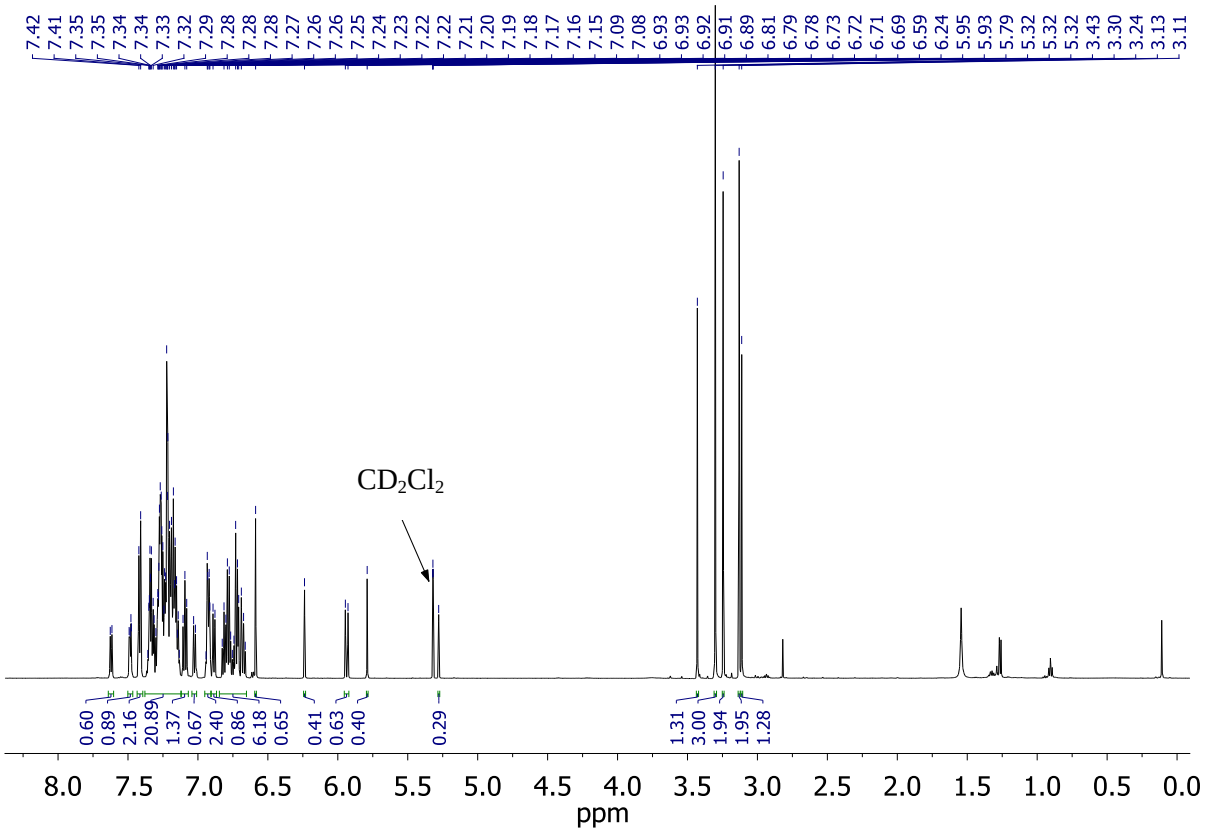


Figure S12: ^{1}H-NMR spectrum of a mixture of **1a** and **2a** (600.13 MHz, CD_2Cl_2).

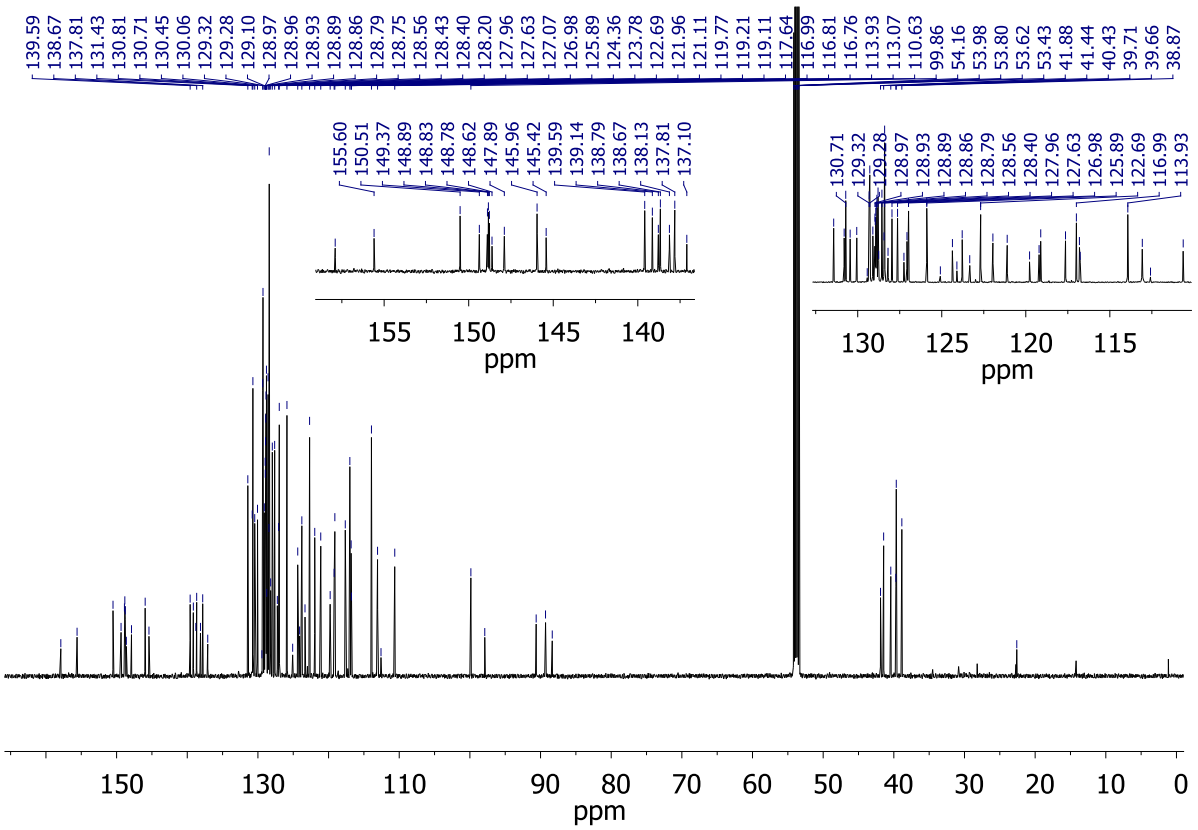


Figure S13: ^{13}C-NMR spectrum of a mixture of **1a** and **2a** (150.90 MHz, CD_2Cl_2).

1,4-Diphenyl-1,4-bis(*N*-methyl-4-fluoroanilino)buta-1,3-diene (**2c**):

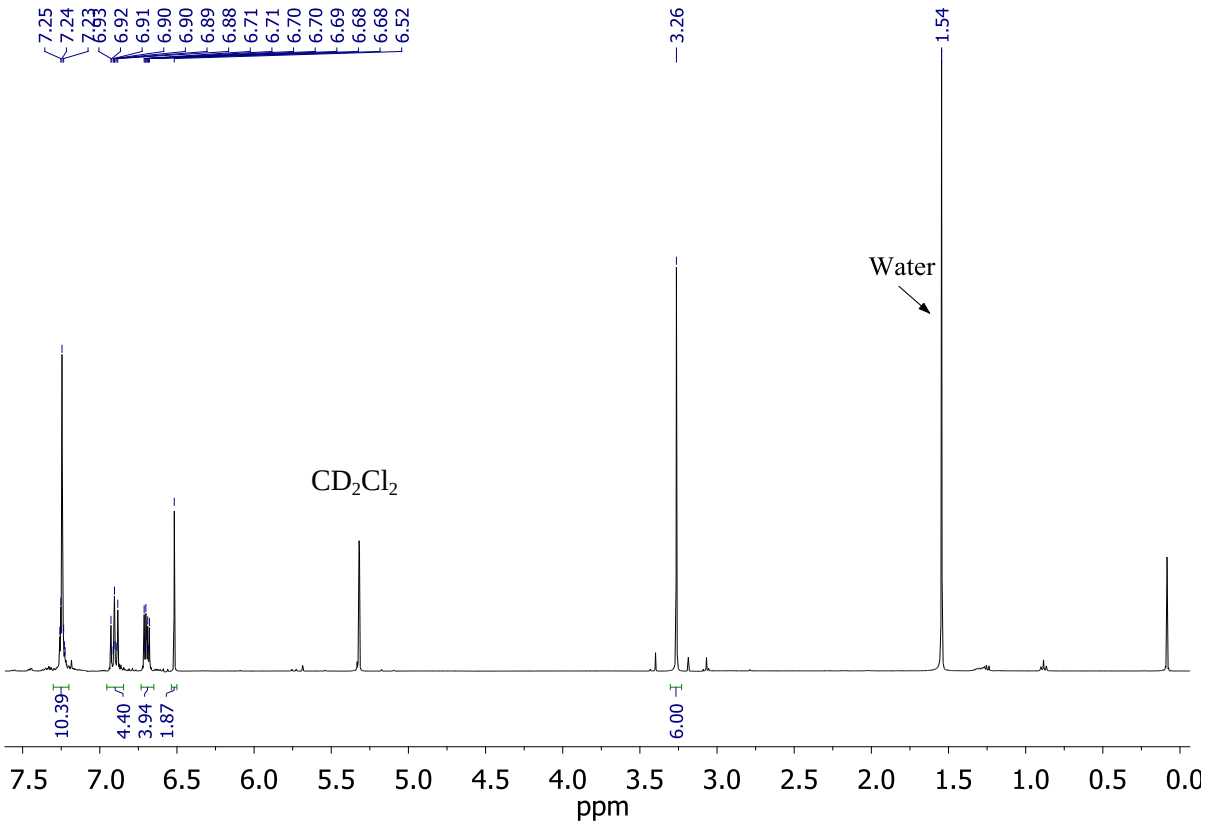


Figure S14: ^{1}H NMR spectrum of **2c** (400.13 MHz, CD_2Cl_2).

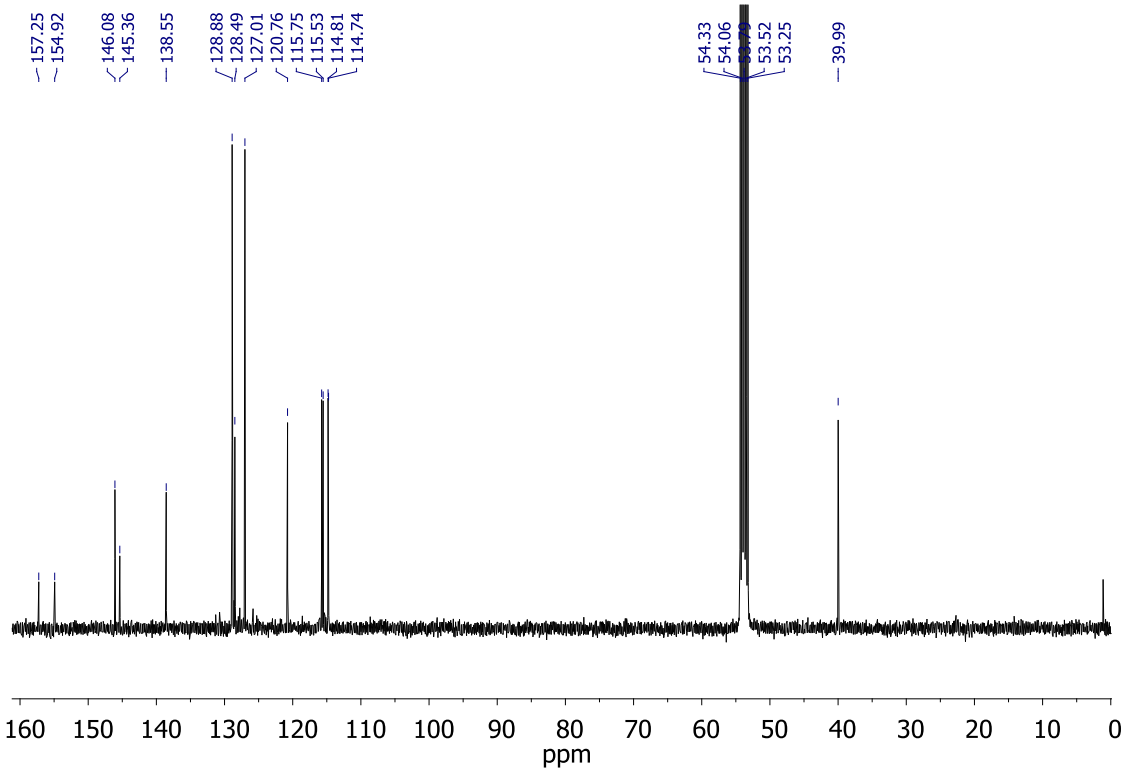


Figure S15: ^{13}C NMR spectrum of **2c** (100.61 MHz, CD_2Cl_2).

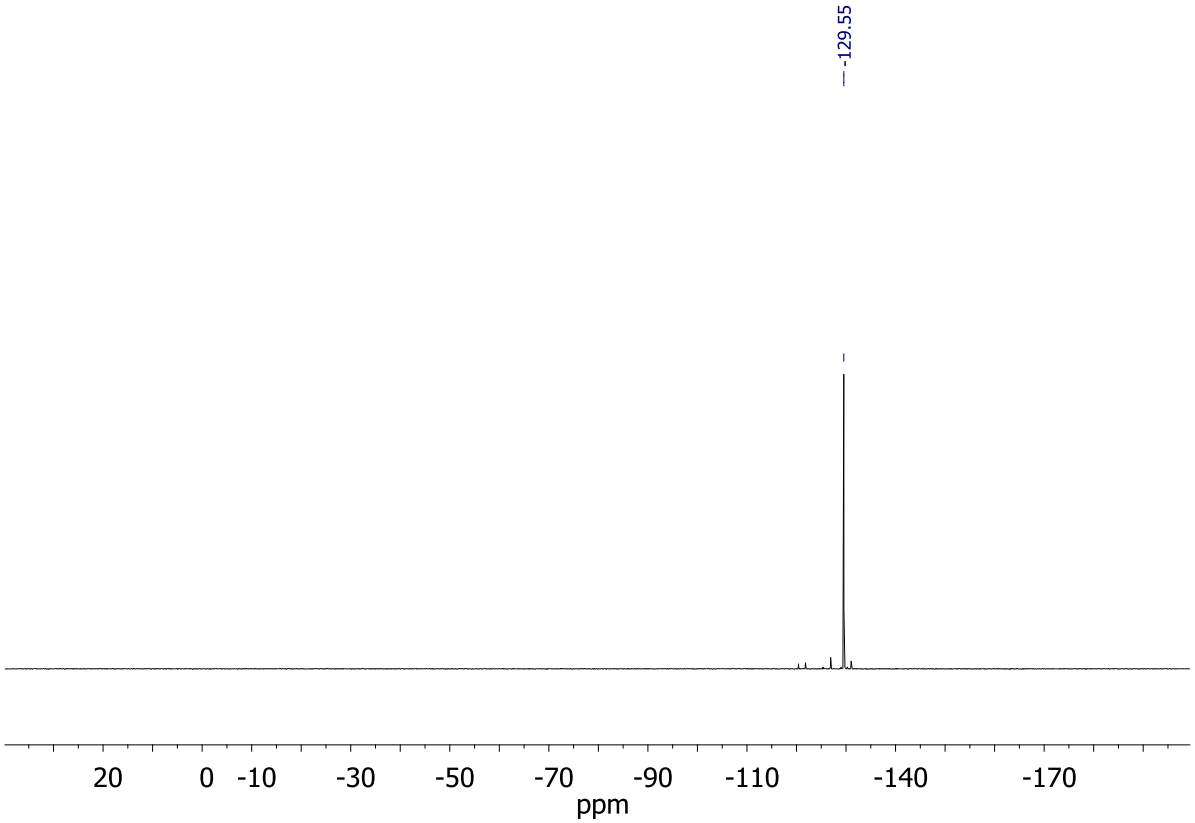
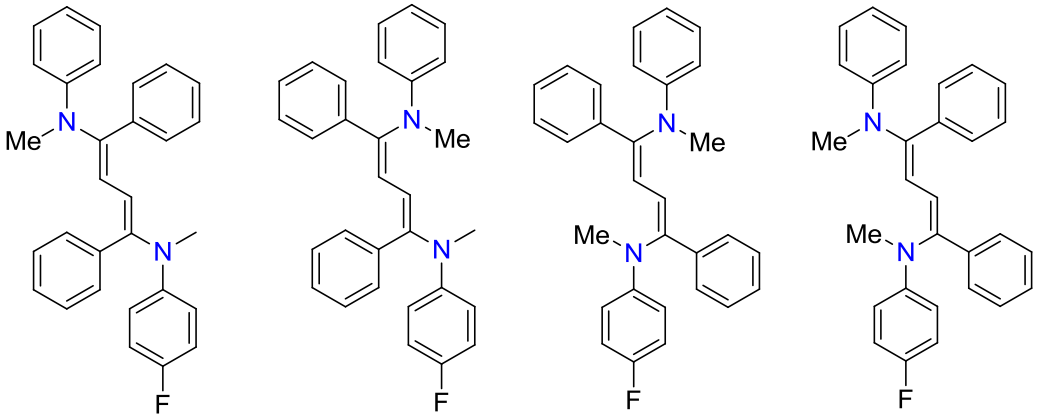


Figure S16: ^{19}F-NMR spectrum of **2c** (188.31 MHz, CD_2Cl_2).

1,4-Diphenyl-1-(N-methyl-anilino)-4-(N-methyl-4-fluoroanilino)buta-1,3-diene (**3**):



E,E-**3** *E,Z*-**3** *Z,Z*-**3** *Z,E*-**3**

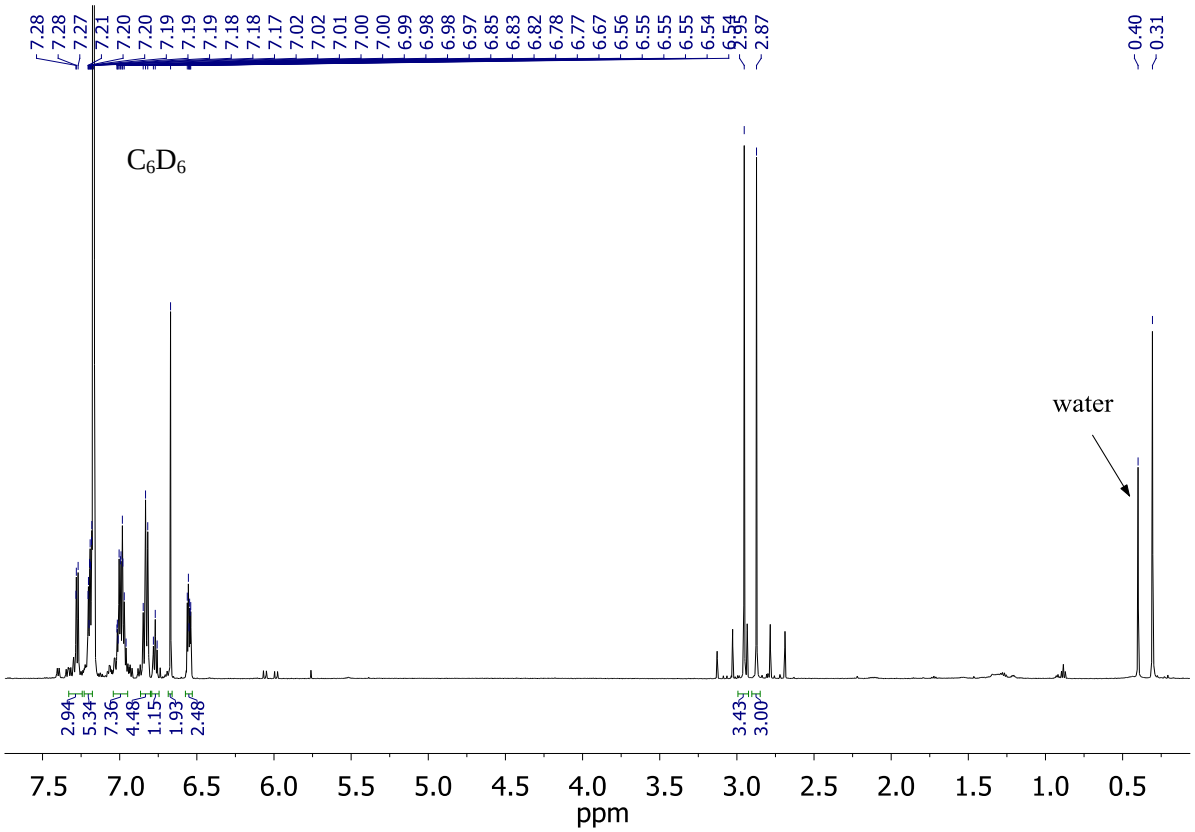


Figure S17: ^{1}H-NMR spectrum of **3** (600.15 MHz, C_6D_6).

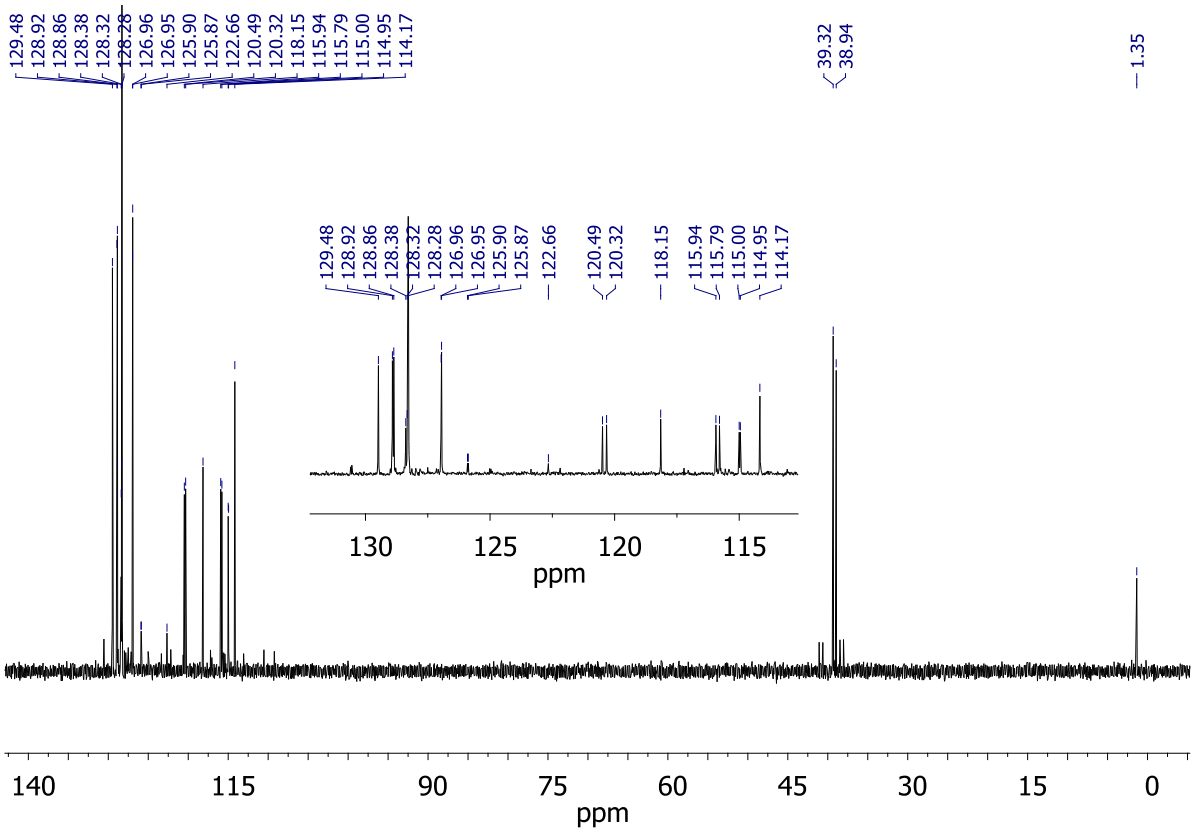


Figure S18: ^{13}H-NMR spectrum of **3** (150.91 MHz, C_6D_6).

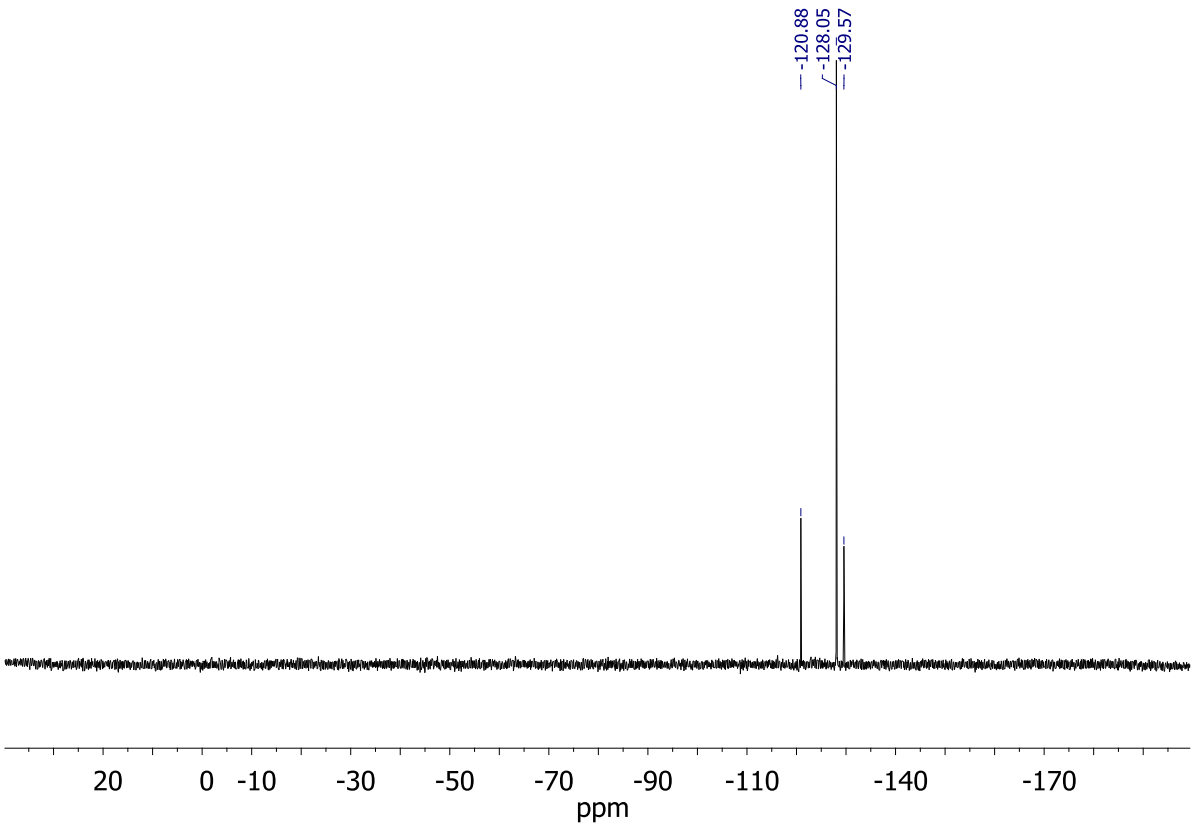


Figure S19: ^{19}F-NMR spectrum of **3** (188.31 MHz, C_6D_6)**.**

Molecular structures

Figure S20: Molecular structures and numbering schemes of *E*-**1a** (top) and *E*-**1b** (bottom). The ellipsoids represent a probability of 30 %, H atoms are drawn with arbitrary radii. Selected bond lengths and angles are listed in Table 1.