Synthesis of Pentasubstituted 2-Aryl Pyrroles from Boryl and Stannyl Alkynes via One-Pot Sequential Ti-Catalyzed [2+2+1] Pyrrole Synthesis/Cross Coupling Reactions

Yukun Cheng, Channing K. Klein and Ian A. Tonks

Contribution from the Department of Chemistry, University of Minnesota – Twin Cities, 207 Pleasant St SE, Minneapolis MN 55455, United States. Email: itonks@umn.edu

Supporting Information

General Considerations

All air- and moisture-sensitive compounds were manipulated in a glovebox under nitrogen atmosphere. Solvents for air- and moisture-sensitive reactions ($PhCF_3$, $PhCH_3$, C_6H_6) were dried through activated alumina on a Pure Process Technology solvent purification system. $PhOCH_3$ and NMR solvents ($CDCl_3$ and C_6D_6) were dried over CaH_2 or Na^0/Ph_2CO and vacuum transferred before passing through activated alumina and storing over activated 3 Å molecular sieves in the glovebox. C_6D_5Br was synthesized following a reported procedure[1] and passed through activated alumina before storing over activated 3 Å molecular sieves in the glovebox. **1a-SnMe$_3$**, **1f-Sn^{n}Bu$_3$**, **1g-Sn^{n}Bu$_3$**, **2**, n-butyllithium, *B*-methoxy-9-borabicyclo[3,3,1]nonane solution in hexanes and Me_3SnCl solution in hexanes were purchased from Millipore-Sigma. Azobenzene was purchased from TCI Chemicals and purified by hexane/water extraction three times. Terminal alkynes were purchased from Oakwood Products, Inc. and Millipore-Sigma. **1a-BBN**,[2] **1e-BBN**,[3] **1g-BBN**,[4] **1a-Cu**,[5] and $[py_2TiCl_2(NPh)]_2$[6] were prepared following the reported procedures.

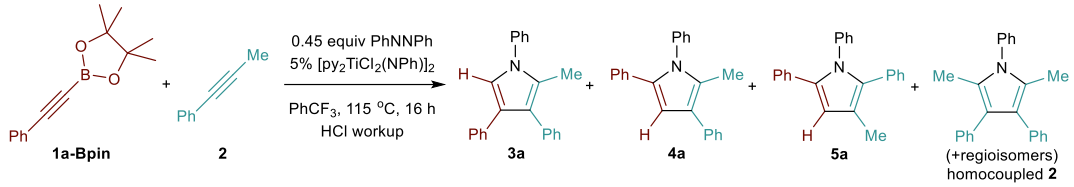
GC chromatographs were collected on Agilent 7890B GC system equipped with the HP-5 column (30 m, 0.32 mm, 0.25 μm, 7 inch cage), an oxidation-methanation reactor (Polyarc® System, Activated Research Company), and a FID detector for quantitative carbon detection.[7,8] ^1H, ^{11}B, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, $^{119}Sn\{^1H\}$, ^1H–^{13}C and ^1H–^{15}N HMBC, NOESY, and No-D ^1H NMR were collected on Bruker Avance III HD NanoBay 400 MHz or Bruker Avance III HD 500 MHz spectrometers. Chemical shifts are reported with respect to residual protio-solvent impurity for ^1H (s, 7.26 ppm for $CDCl_3$; s, 7.16 ppm for C_6D_6) and ^{13}C (t, 77.16 ppm for $CDCl_3$; t, 128.06 ppm for C_6D_6). ^{11}B NMR was externally referenced to $BF_3{\cdot}OEt_2$ in the corresponding solvent as 0.0 ppm. ^{119}Sn NMR in $CDCl_3$ was externally referenced to Me_4Sn in $CDCl_3$ as 0.00 ppm. ^{119}Sn NMR in toluene was referenced to the chemical shifts of the corresponding stannyl alkynes in C_6D_6 (**1a-SnMe$_3$**,[9] **1g-Sn^{n}Bu$_3$**[10]) or $CDCl_3$ (**1b-SnMe$_3$**, **1c-SnMe$_3$**, **1d-SnMe$_3$**). No-D ^1H NMR was referenced to the proton signal of the internal standard triphenylmethane (Ph_3CH, s, 5.54 ppm in $PhCF_3$; s, 5.34 ppm in $PhCH_3$). ^1H NMR of catalytic reactions in C_6D_5Br were referenced to the proton signal of the internal standard triphenylmethane (Ph_3CH, s, 5.45 ppm).

Initial Screening of Heteroatom-Substituted Alkynes (Table 1)

General Procedure for Initial Screening of Heteroatom-Substituted Alkynes as Heterocoupling Partner (Procedure A)

$[py_2TiCl_2(NPh)]_2$ (3.7 mg, 0.005 mmol, 0.05 equiv), heteroatom-substituted 2-phenylethyne (**1a-M**, 0.1 mmol, 1 equiv) and 0.5 mL of $PhCF_3$ stock solution containing 1-phenyl-1-propyne (**2**) (11.6 mg, 0.1 mmol, 1 equiv), azobenzene (8.2 mg, 0.045 mmol, 0.45 equiv) and triphenylmethane (4.9 mg, 0.02 mmol, 0.2 equiv, internal standard) were added to an NMR tube. The reaction was then sealed and heated in a preheated oil bath at 115 °C. No-D NMR spectra were collected before and after heating to monitor the reaction. The reaction was quenched with 5% HCl in methanol and extracted with $EtOAc/H_2O$. The organic phase was dried over $MgSO_4$ and evaporated under vacuum. The crude product mixture was characterized by GC-Polyarc®/FID to calculate the yield and selectivity.

Reaction of **1a-Bpin (Table 1, Entry 1)**



The reaction was performed following **Procedure A** using **1a-Bpin** (22.8 mg, 0.1 mmol, 1 equiv) with the reaction being heated for 16 h. Selectivity calculated for the major regioisomer of the heterocoupling, product **5a**.

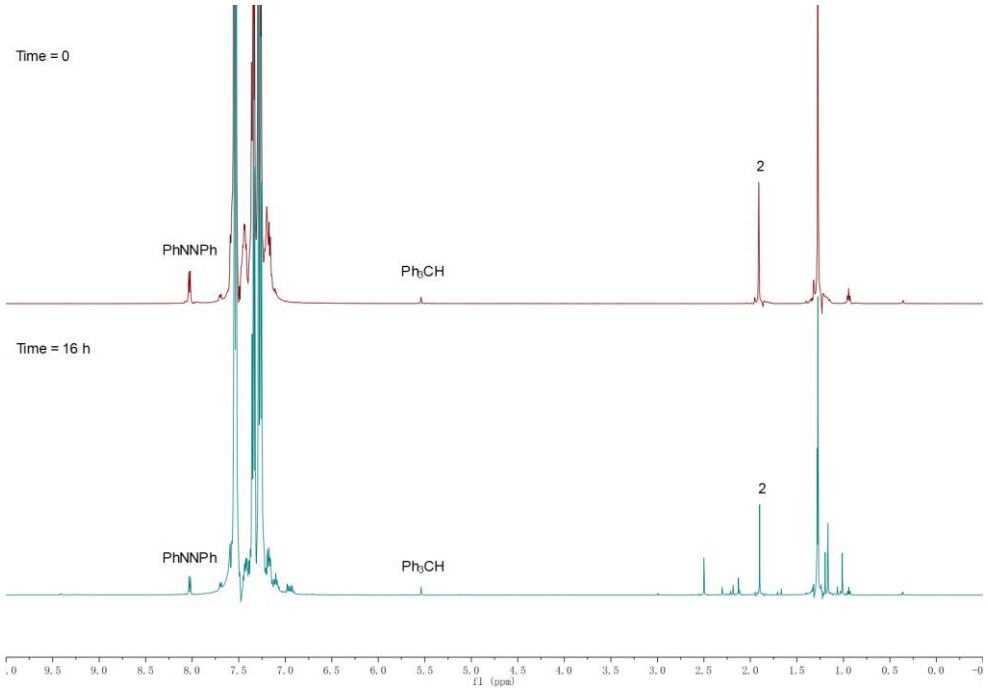


Figure S1. No-D ^1H NMR of the reaction of **1a-Bpin** at time = 0 (top), time = 16 h (bottom) in $PhCF_3$.

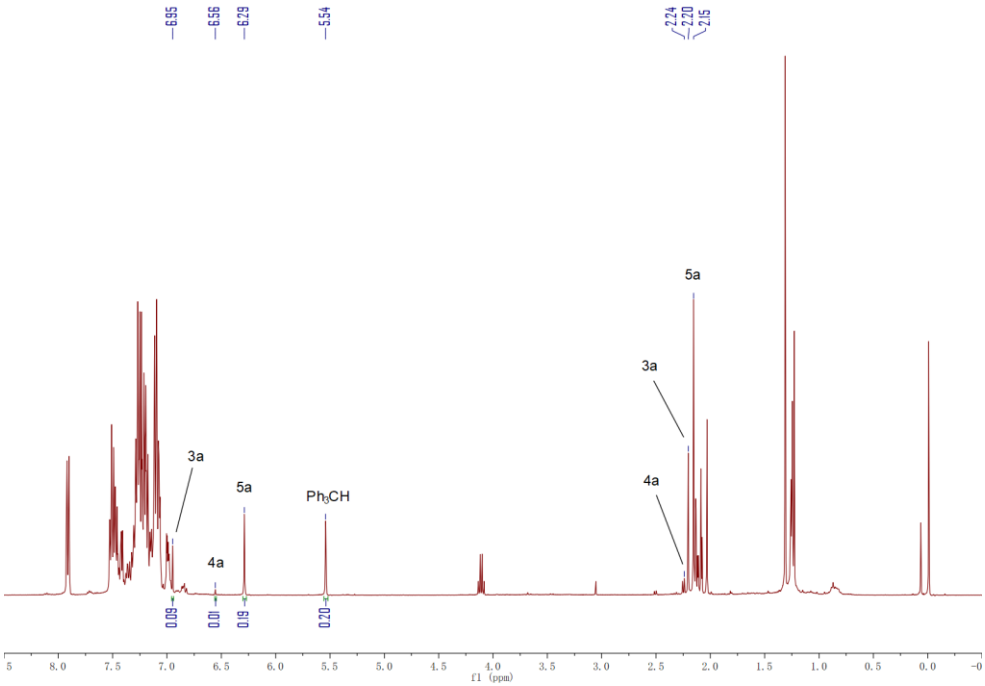


Figure S2. ^{1}H NMR of the reaction of **1a-Bpin** in $CDCl_3$ after HCl workup.

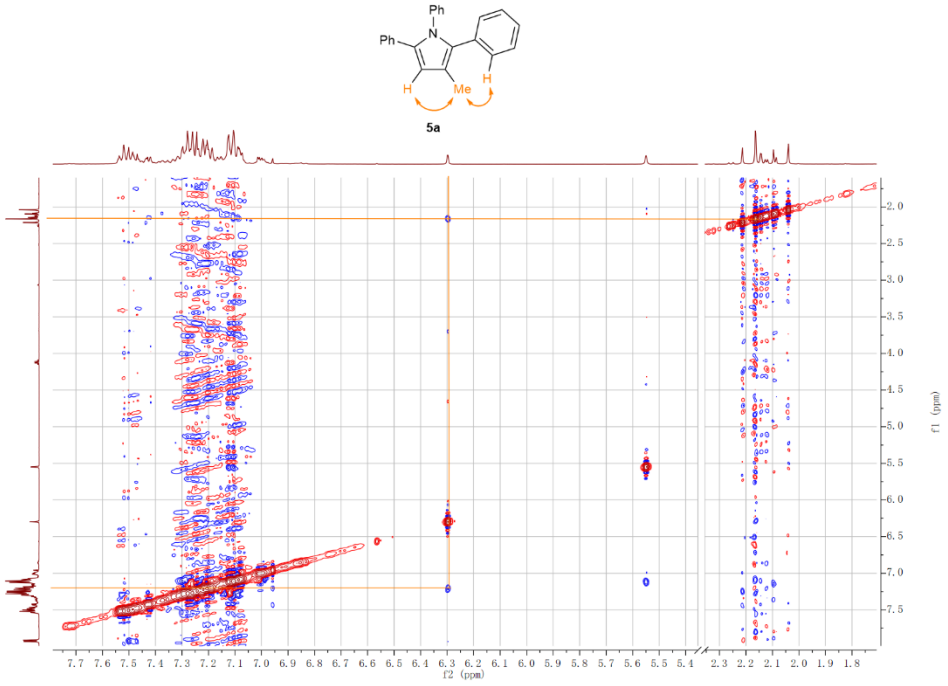
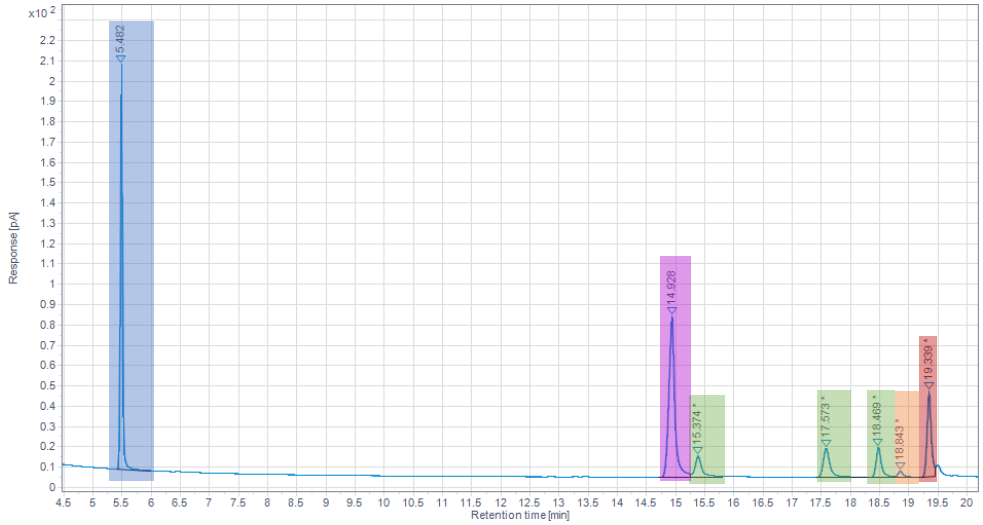


Figure S3. NOESY NMR spectrum of the reaction of **1a-Bpin** in $CDCl_3$ after HCl workup.



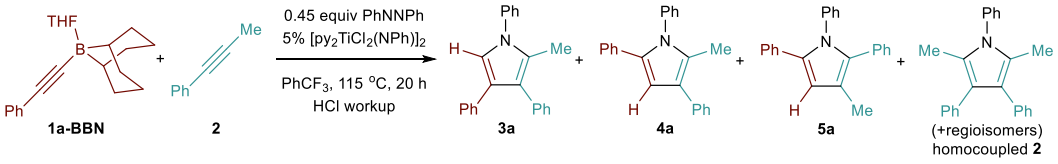
	Retention Time (min)	Surface Area	# of C	Yield (%)
Ph_3CH	5.48	479.301	19	n.a.
3a	19.34	208.919	23	9.1
4a	18.84	17.921	23	0.6
5a	14.93	560.266	23	19.3
homocoupled **2**	15.37, 17.57, 18.47	295.586	24	9.8

Figure S4. Quantitative GC-FID chromatograph of the reaction of **1a-Bpin** after HCl workup.

Sample yield calculation based on quantitative carbon detection:

$$Yield\ of\ \mathbf{3a} = \frac{Surface\ Area\ of\ \mathbf{3a}}{\#\ of\ C\ of\ \mathbf{3a}} \times \frac{\#\ of\ C\ of\ Ph_3CH}{Surface\ Area\ of\ Ph_3CH} \times equiv\ of\ Ph_3CH \times 100\%$$

Reaction of **1a-BBN (Table 1, Entry 2)**



The reaction was performed following **Procedure A** using **1a-BBN** (29.4 mg, 0.1 mmol, 1 equiv) with the reaction being heated for 20 h. Selectivity calculated for the major regioisomer of the heterocoupling, product **3a**.

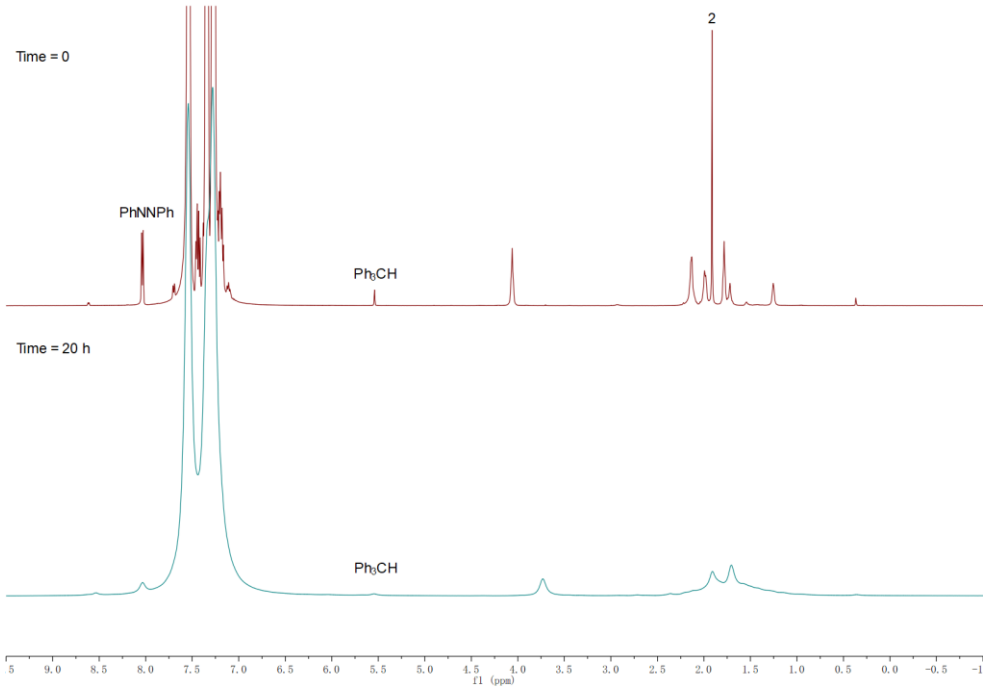
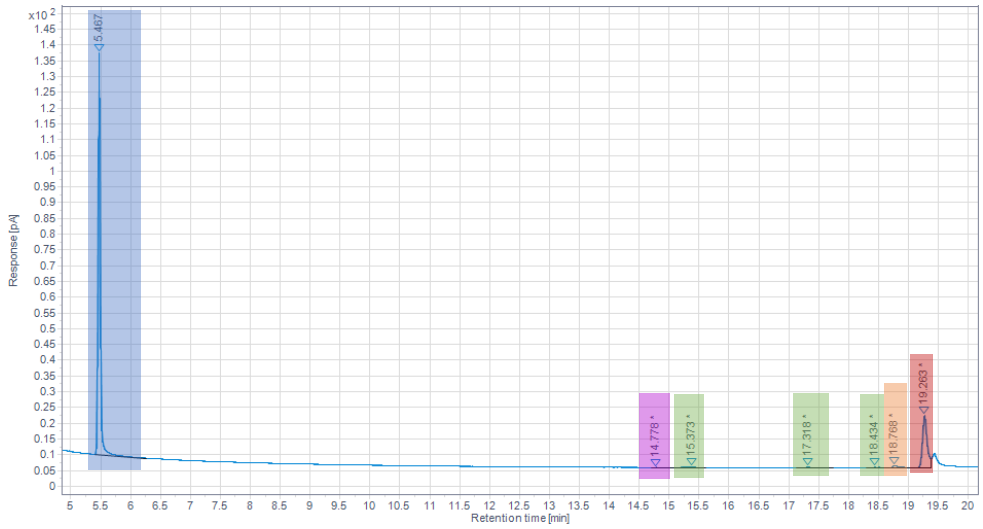


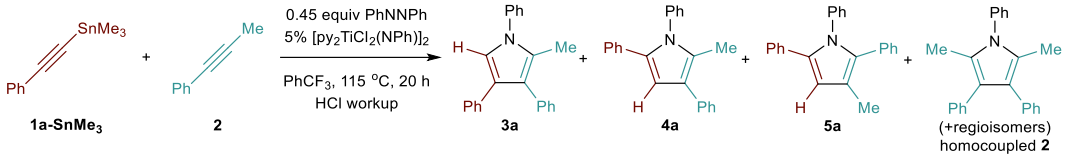
Figure S5. No-D ^{1}H NMR of the reaction of **1a-BBN** at time = 0 (top), time = 20 h (bottom) in $PhCF_3$.



	Retention Time (min)	Surface Area	# of C	Yield (%)
Ph_3CH	5.47	313.838	19	n.a.
3a	19.26	125.569	23	6.6
4a	18.77	5.332	23	0.3
5a	14.78	0.287	23	< 0.1
homocoupled **2**	15.37, 17.32, 18.43	4.602	24	0.2

Figure S6. Quantitative GC-FID chromatograph of the reaction of **1a-BBN** after HCl workup.

Reaction of **1a-SnMe$_3$ (Table 1, Entry 3)**



The reaction was performed following **Procedure A** using **1a-SnMe$_3$** (26.5 mg, 0.1 mmol, 1 equiv) with the reaction being heated for 20 h. Selectivity calculated for the major regioisomer of the heterocoupling, product **3a**.

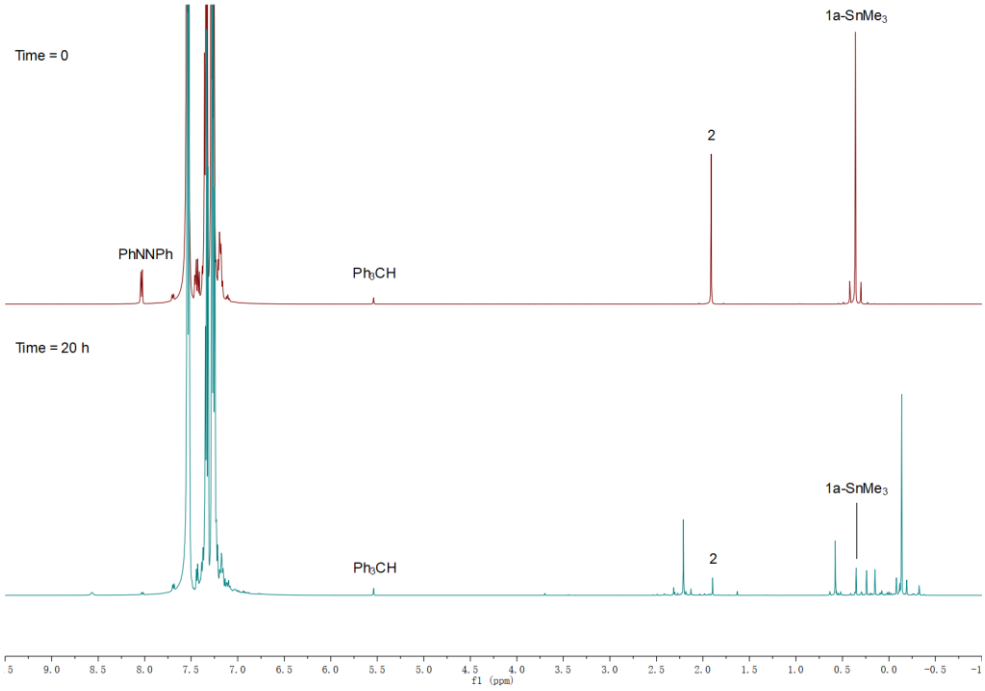
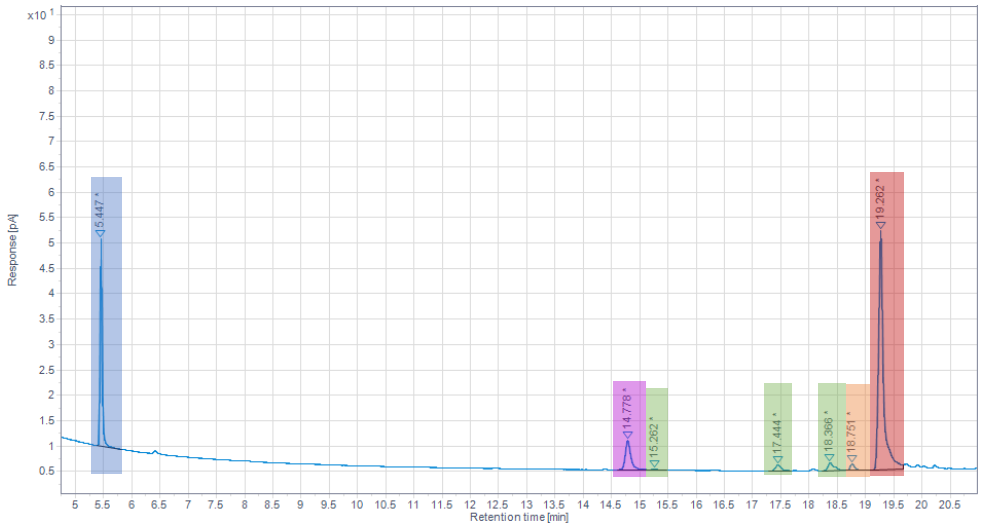


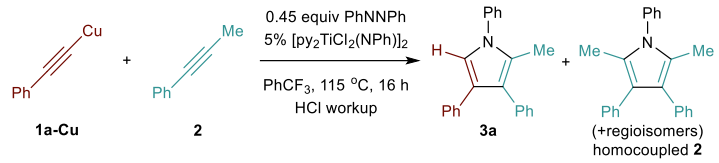
Figure S7. No-D ^{1}H NMR of the reaction of **1a-SnMe$_3$** at time = 0 (top), time = 20 h (bottom) in $PhCF_3$.



	Retention Time (min)	Surface Area	# of C	Yield (%)
Ph_3CH	5.45	97.101	19	n.a.
3a	19.26	297.256	23	50.6
4a	18.75	7.061	23	1.2
5a	14.78	39.048	23	6.6
homocoupled **2**	15.26, 17.44, 18.37	20.440	24	3.3

Figure S8. Quantitative GC-FID chromatograph of the reaction of **1a-SnMe$_3$** after HCl workup.

Reaction of **1a-Cu (Table 1, Entry 4)**



The reaction was performed following **Procedure A** using **1a-Cu** (16.5 mg, 0.1 mmol, 1 equiv) with the reaction being heated for 16 h. Yield of **3a** was found to be 7%. **4a** and **5a** were not found. Selectivity was not determined due to the peak overlapping with homocoupled **2**.

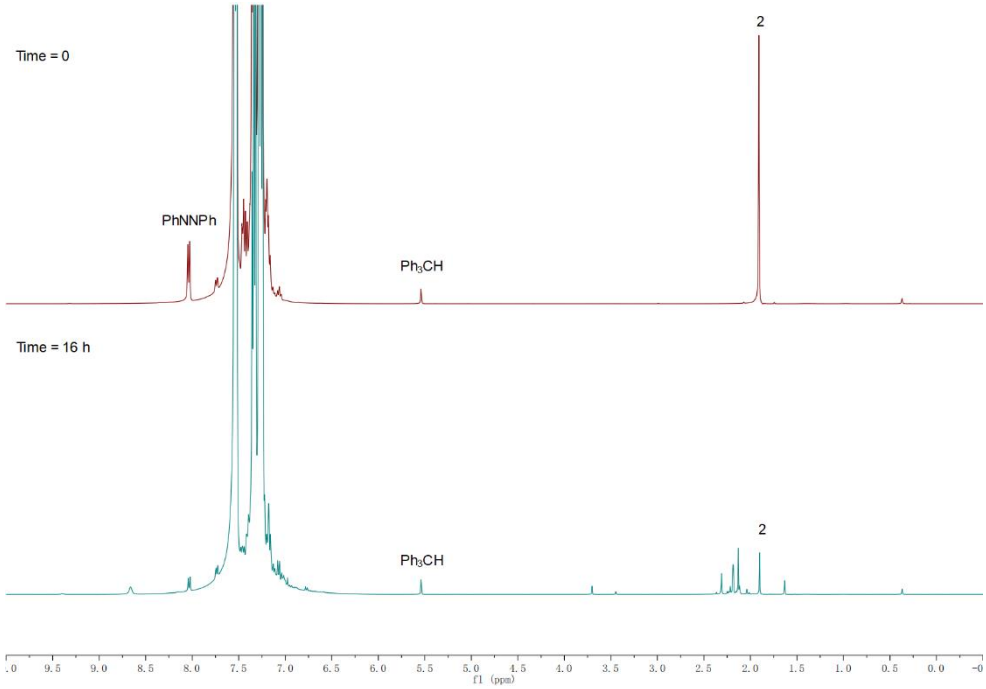


Figure S9. No-D ^{1}H NMR of the reaction of **1a-Cu** at time = 0 (top), time = 16 h (bottom) in $PhCF_3$.

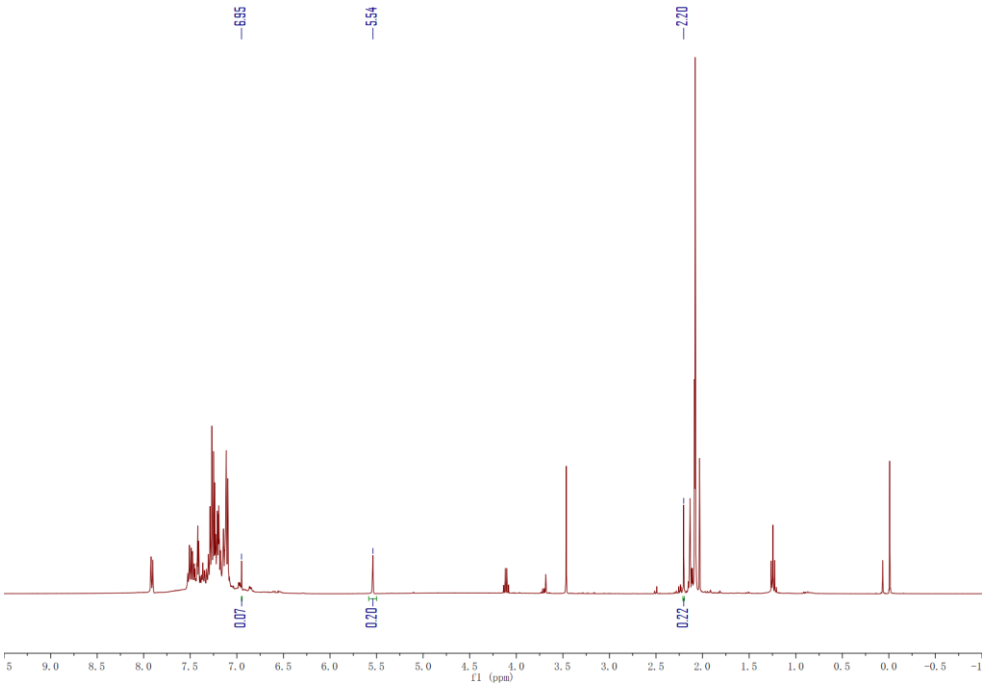
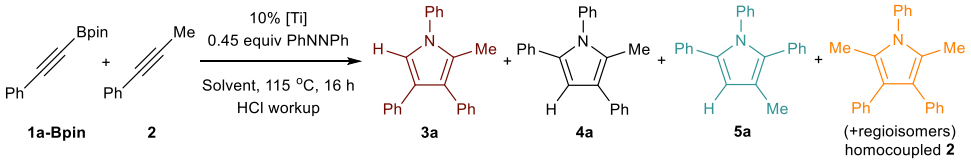


Figure S10. ^{1}H NMR of the reaction of **1a-Cu** after HCl workup.

Optimization of Reaction Conditions

Attempted Optimization of Catalysis with 1a-Bpin as Heterocoupling Partner



Ti catalyst (0.01 mmol, absolute quantity of titanium, 0.1 equiv), azobenzene (8.2 mg, 0.045 mmol, 0.45 equiv), 2-phenylethynyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a-Bpin**) (22.8 mg, 0.1 mmol, 1 equiv), 1-phenyl-1-propyne (**2**) (11.6 mg. 0.1 mmol, 1 equiv), triphenylmethane (4.9 mg, 0.02 mmol, 0.2 equiv, internal standard) and 0.5 mL of solvent were added to a 4 mL scintillation vial equipped with a stir bar in the glovebox. The vial was then sealed with a PTFE-lined Teflon screw cap, brought out of the glovebox and heated at 115 °C on an aluminum well plate for 16 h. After cooling down to room temperature, the reaction was quenched with 5% HCl in methanol and extracted with EtOAc/H_2O. The organic phase was dried over $MgSO_4$ and evaporated to yield a mixture containing **3a**, **5a** and the regioisomers from the homocoupling of **2**. The yields and selectivity were determined by GC-Polyarc®/FID. The yield of **4a** was lower than 1% throughout the whole optimization and was considered negligible.

A trend can be found that the sum yield of heterocoupling (**3a** and **5a**) as well as the yield of homocoupling of **2** are solvent dependent. Further, the ratio of the heterocoupling product (**3a**/**5a**) increases the catalyst ancillary halogen is changed from Cl, Br, to I, indicating that a more electron-deficient Ti center favors **3a** over **5a** (Figure S11 and S12). However, none of the attempted reactions ultimately led to high-yielding, selective outcomes.

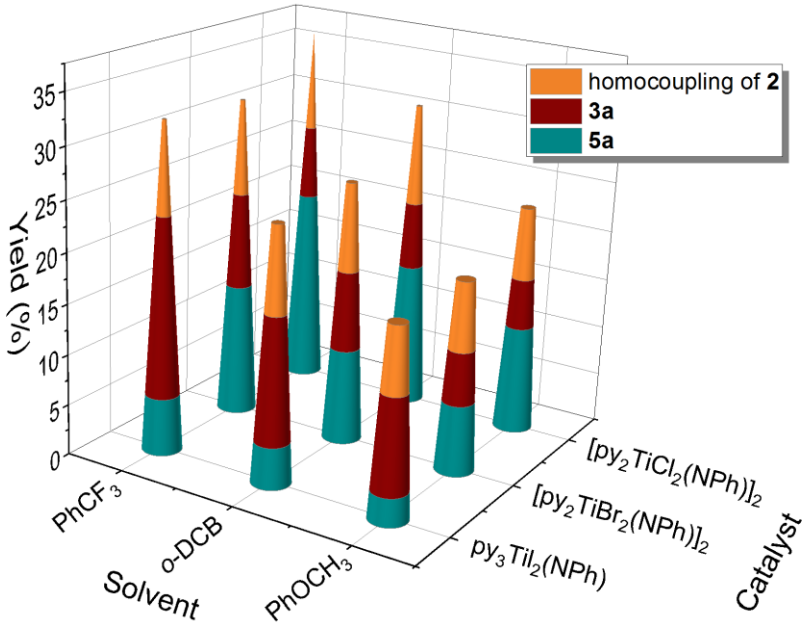


Figure S11. Scope of catalyst and solvent

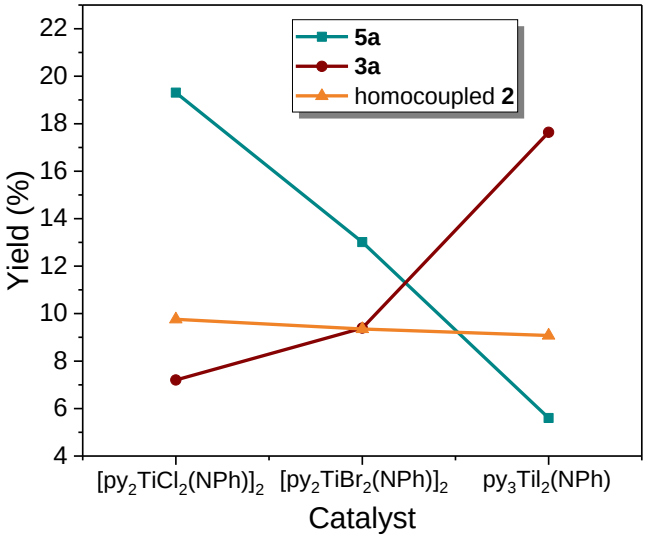
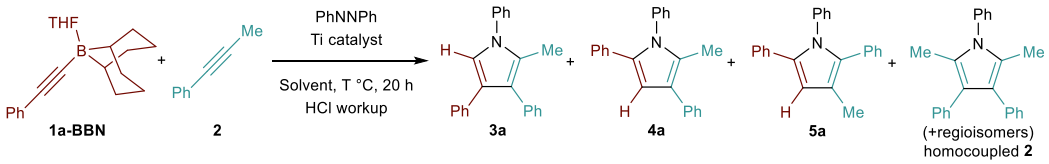


Figure S12. Yield distribution in $PhCF_3$.

Optimization of Catalysis with 1a-BBN as Heterocoupling Partner



$[py_2TiCl_2(NPh)]_2$, azobenzene, *B*-phenylethynyl-9-borabicyclo[3,3,1]nonane (**1a-BBN**, 29.4 mg, 0.1 mmol, 1 equiv), 1-phenyl-1-propyne (11.6 mg, 0.1 mmol, 1 equiv), triphenylmethane (4.9 mg, 0.02 mmol, 0.2 equiv, internal standard) and 0.5 mL solvent were added to an NMR tube. The total nitrene equivalent was kept as 1 by adjusting the molar quantity of azobenzene according to the Ti catalyst loading, following the relationship of:

$$Equiv_{nitrene} = Equiv_{[py_2TiCl_2(NPh)]_2} + Equiv_{azobenzene} \times 2$$

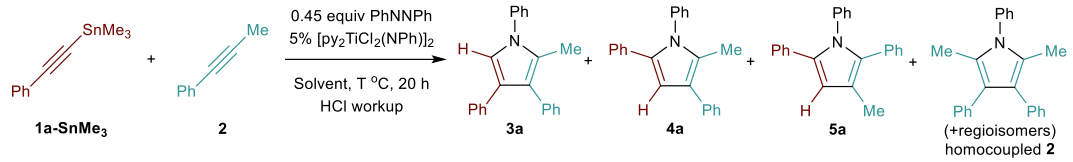
The reaction was then sealed and heated in a preheated oil bath for 20 h. The reaction was quenched with 5% HCl in methanol and extracted with $EtOAc/H_2O$. The organic phase was dried over $MgSO_4$ and evaporated under vacuum. The crude product mixture was characterized by GC-Polyarc®/FID to determine the yield and selectivity.

Table S1. Optimization of the catalysis using **1a-BBN** as heterocoupling partner.

Entry	%[Ti]	Solvent	T (°C)	**3a** (%)	**4a** (%)	**5a** (%)	homocoupled **2** (%)	Selectivity[a]
1	5	$PhCF_3$	115	**6.6**	0.3	< 0.1	0.2	22.3:1 (12.5:1)
2	5	C_6D_5Br	115	**21.8**	0.5	0.1	2.9	36.2:1 (6.2:1)
3	10	C_6D_5Br	115	**74.3**	1.2	0.1	3.0	55.8:1 (17.1:1)
4	15	C_6D_5Br	115	**64.9**	1.2	0.1	3.6	50.7:1 (13.2:1)
5	10	$PhCH_3$	115	**66.6**	2.0	0.1	1.3	31.5:1 (19.6:1)
6	10	$PhCF_3$	115	**54.6**	1.2	0.1	2.2	41.8:1 (15.7:1)
7	10	$PhOCH_3$	115	**20.0**	0.4	0.1	1.6	41.2:1 (9.6:1)
8	10[b]	C_6D_5Br	115	**3.3**	0.3	0.2	0.2	7.4:1 (4.9:1)
9	20[c]	C_6D_5Br	115	**3.2**	0.1	0.1	0.2	20.1:1 (9.2:1)
10	10	C_6D_5Br	90	**45.2**	0.9	0.1	3.1	48.5:1 (11.3:1)
11	10	C_6D_5Br	145	**60.5**	1.4	0.2	1.9	38.7:1 (17.6:1)
12[d]	10	C_6D_5Br	115	**65.9**	1.4	< 0.1	1.5	45.5:1 (22.7:1)

[a]Selectivity with respect to all heterocoupling pyrrole regioisomer products. Selectivity = **3a**/(**4a**+**5a**). In parenthesis: selectivity with respect to all possible pyrrole products. Selectivity in parenthesis = **3a**/(**4a**+**5a**+homocoupled **2**). [b]Ti catalyst = $[py_2TiBr_2(NPh)]_2$. [c]Ti catalyst = $py_3TiI_2(NPh)$. [d]Time = 0.5 h.

Catalysis with 1a-$SnMe_3$ as Heterocoupling Partner



$[py_2TiCl_2(NPh)]_2$ (3.7 mg, 0.005 mmol, 0.05 equiv), azobenzene (8.2 mg, 0.045 mmol, 0.45 equiv), phenylethynyl trimethylstannane (**1a-SnMe$_3$**, 26.5 mg, 0.1 mmol, 1 equiv), 1-phenyl-1-propyne (11.6 mg, 0.1 mmol, 1 equiv), triphenylmethane (4.9 mg, 0.02 mmol, 0.2 equiv, internal standard) and 0.5 mL solvent were added to an NMR tube. The reaction was then sealed and heated in a preheated oil bath for 20 h. The reaction was quenched with 10% HCl in methanol and extracted with EtOAc/H_2O. The organic phase was dried over $MgSO_4$ and evaporated under vacuum. The crude product mixture was characterized by GC-Polyarc®/FID to determine the yield and selectivity.

Precaution: Trialkyltin species are highly toxic. Proper PPE is required. All the chemical and labware waste should be handled separately from the normal waste stream and quenched thoroughly.

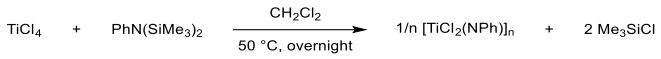
Table S2. Optimization of the catalysis using **1a-SnMe$_3$** as heterocoupling partner.

Entry	Solvent	T (°C)	Conc. (M)	**3a** (%)	**4a** (%)	**5a** (%)	homocoupled **2** (%)	Selectivity[a]
1	$PhCF_3$	115	0.2	**50.6**	1.2	6.6	3.3	6.4:1 (4.5:1)
2	C_6D_5Br	115	0.2	**47.5**	1.1	3.3	4.4	10.7:1 (5.4:1)
3	C_6D_5Br	60	0.2	**30.4**	0.7	2.0	0.9	11.1:1 (8.4:1)
4	$PhCH_3$	115	0.2	**51.1**	1.2	6.0	2.7	7.1:1 (5.1:1)
5[b]	$PhCH_3$	115	0.2	**46.2**	0.9	4.6	4.2	8.3:1 (4.7:1)
6	$PhCH_3$	90	0.2	**57.7**	1.3	4.9	2.6	9.3:1 (6.6:1)
7	$PhCH_3$	75	0.2	**41.4**	1.1	3.3	3.6	9.3:1 (5.2:1)
8	$PhCH_3$[c]	90	0.2	**28.1**	0.9	3.8	0.5	6.0:1 (5.4:1)
9	$PhCH_3$	90	0.07	**18.8**	0.5	1.8	0.4	8.3:1 (7.2:1)
10	$PhCH_3$	90	0.8	**66.0**	1.8	4.6	2.9	10.3:1 (7.1:1)
11	$PhCH_3$	90	2.0	**64.5**	2.0	3.9	2.8	10.9:1 (7.4:1)
12[d]	$PhCH_3$	90	0.8	**68.5**	2.1	4.5	1.5	10.4:1 (8.4:1)

[a]Selectivity with respect to all heterocoupling pyrrole regioisomer products. Selectivity = **3a**/(**4a**+**5a**). In parenthesis: selectivity with respect to all possible pyrrole products. Selectivity in parenthesis = **3a**/(**4a**+**5a**+homocoupled **2**). [b]10% $[py_2TiCl_2(NPh)]_2$. [c]2 equiv **1a-SnMe$_3$**. [d]Time = 9 h.

Catalyst Synthesis

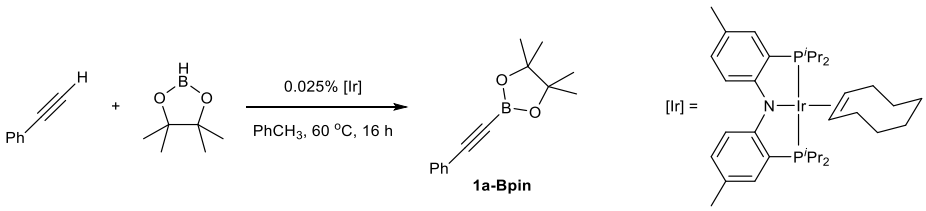
Synthesis of $[TiCl_2(NPh)]_n$



The synthesis of $[TiCl_2(NPh)]_n$ was modified from the synthetic procedure of $py_3TiBr_2(NTol)$.[6] $TiCl_4$ (2.000 g, 10.5 mmol), *N*-phenyl-*N*,*N*-bis(trimethylsilyl)amine (2.500 g, 10.5 mmol), 20 mL of CH_2Cl_2 and a stirbar were added to a 20 mL scintillation vial in the glovebox. The reaction was then sealed with a PTFE-lined Teflon screw cap and heated at 50 ℃ overnight while stirring. After cooling down, the suspension was filtered through a fine frit and washed with CH_2Cl_2 until the fresh filtrate changed from yellow to colorless. The precipitate was further washed by 20 mL of pentane twice to remove the remaining CH_2Cl_2. After drying under vacuum for 3 h, $[TiCl_2(NPh)]_n$ was obtained as black powder. Yield: 1.003 g (4.78 mmol, 45%). Attempts in characterizing the compound by ^1H NMR failed due to its low solubility in common organic solvents. Further addition of THF to the compound yielded $[(THF)_2TiCl_2(NPh)]_2$ in 95% yield.[11]

Substrate Syntheses

Synthesis of 2-phenylethynyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a-Bpin)



The synthesis was performed following a reported procedure using phenylacetylene (4.086 g, 40 mmol, limiting reagent) as the terminal alkyne reactant.[12,13] **1a-Bpin** was obtained as white needled-shaped crystals in 76% yield (6.900 g). Spectra data was consistent with literature values.[14]

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54-7.51 (m, 2H), 7.38-7.28 (m, 3H), 1.32 (s, 12H) ppm.

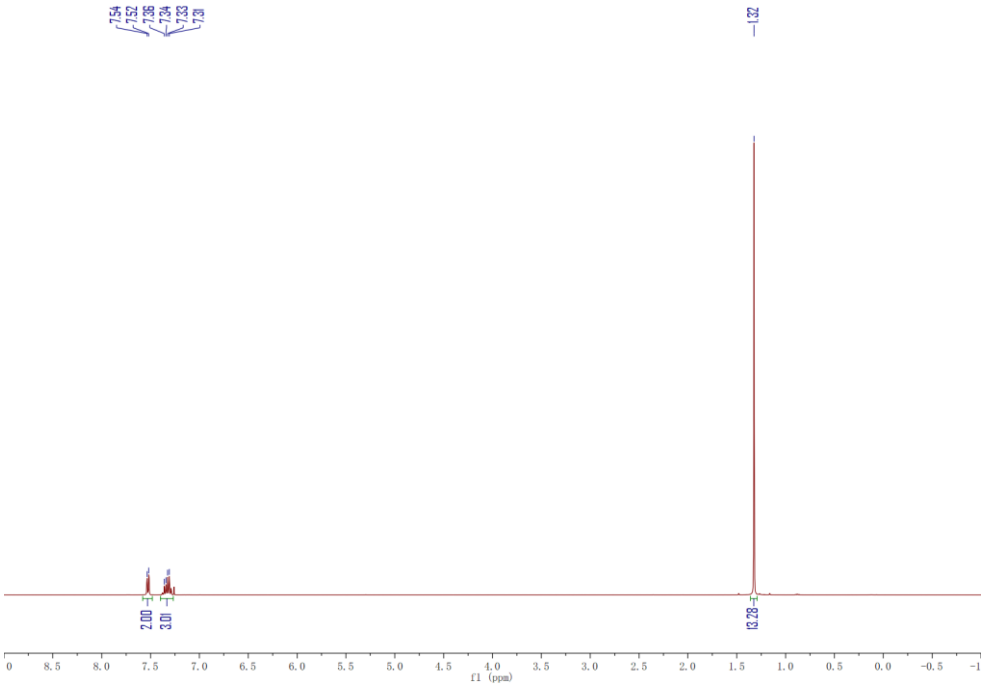
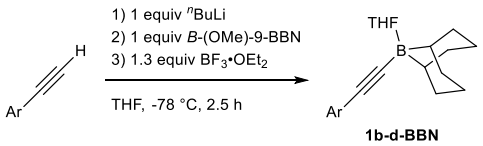


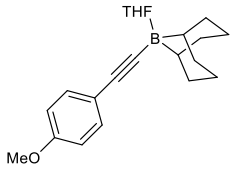
Figure S13. ^{1}H NMR spectrum of **1a-Bpin** in $CDCl_3$.

General Synthetic Procedure for *B*-Arylethynyl-9-Borabicyclo[3,3,1]nonanes (1b-d-BBN)



The synthesis was performed following a modification of the reported procedure.[2] Terminal aryl alkyne (10 mmol), dry THF (15 mL) and a stir bar were added to a N_2-filled 50 mL Schlenk flask and cooled at -78 °C. n-BuLi solution in hexanes (2.5 M, 4.0 mL, 10 mmol, 1.0 equiv) was slowly added to the mixture and stirred for 15 min at -78 °C. *B*-methoxy-9-BBN solution in hexanes (1.0 M, 10 mL, 10 mmol, 1.0 equiv) was added and the mixture was stirred for 1.5 h at -78 °C. $BF_3{\cdot}OEt_2$ (1.6 mL, 13 mmol, 1.3 equiv) was added, after which the reaction was further stirred at -78 °C for 0.5 h before warming up to room temperature. All volatiles were removed under vacuum, and the mixture was dissolved in

dry benzene (15 mL). The suspension was then filtered via cannula filtration into another N_2-filled 50 mL Schlenk flask. The resulting solution was concentrated under vacuum, yielding the white-pale yellow crude product. The Schlenk flask was then transferred into the glovebox, and the crude product was washed sequentially with pentane (3 x 10 mL). Redissolving the white solid in 30 mL of benzene separated the product from remaining $LiBF_4$ after filtration through a medium frit. The filtrate was concentrated to yield the *B*-arylethynyl-9-BBN after drying.



***B*-(*p*-methoxyphenyl)ethynyl-9-borabicyclo[3,3,1]nonane (1b-BBN)** off-white powder, 43% yield.

^{1}H NMR (C_6D_6, 400 MHz): δ 7.49 (d, *J* = 8.3 Hz, 2H), 6.65 (d, *J* = 8.3 Hz, 2H), 3.75-3.72 (br, 4H), 3.20 (s, 3H), 2.25-2.02 (m, 10H), 1.83-1.69 (m, 2H), 1.40 (s, 3H), 1.29-1.17 (br, 4H)

^{13}C{^{1}H} NMR (C_6D_6, 101 MHz): δ 159.48, 133.57, 118.48, 114.20, 104.44, 102.05 (br), 70.21, 54.75, 32.49, 26.96 (br), 25.08, 24.74 ppm.

^{11}B NMR (C_6D_6, 128 MHz): δ 22.8 ppm.

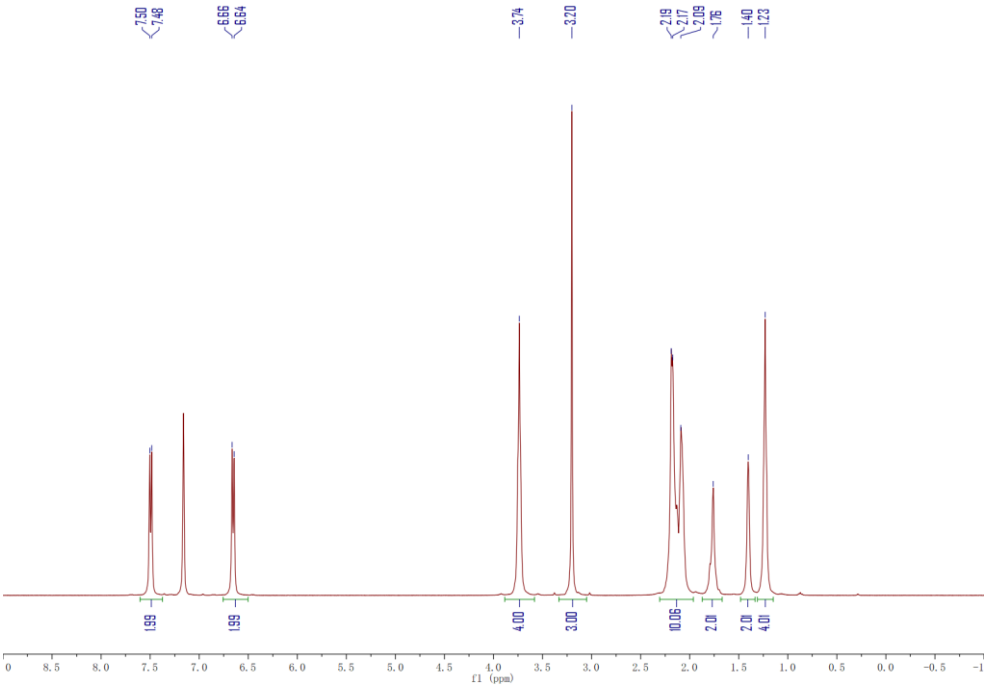


Figure S14. ^{1}H NMR spectrum of **1b-BBN** in C_6D_6.

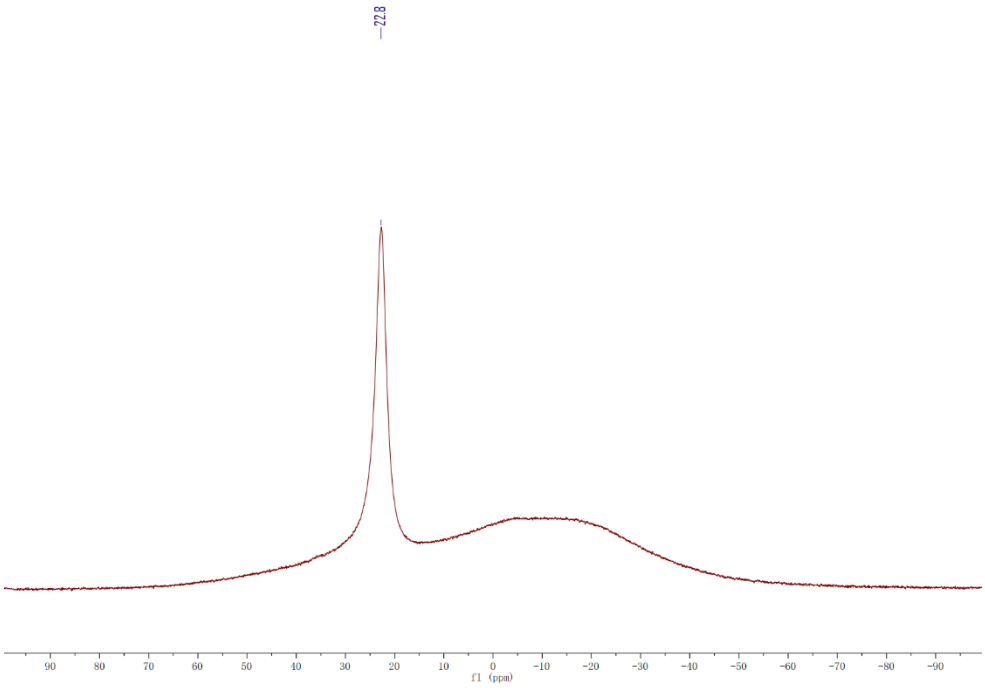


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of **1b-BBN** in C_6D_6.

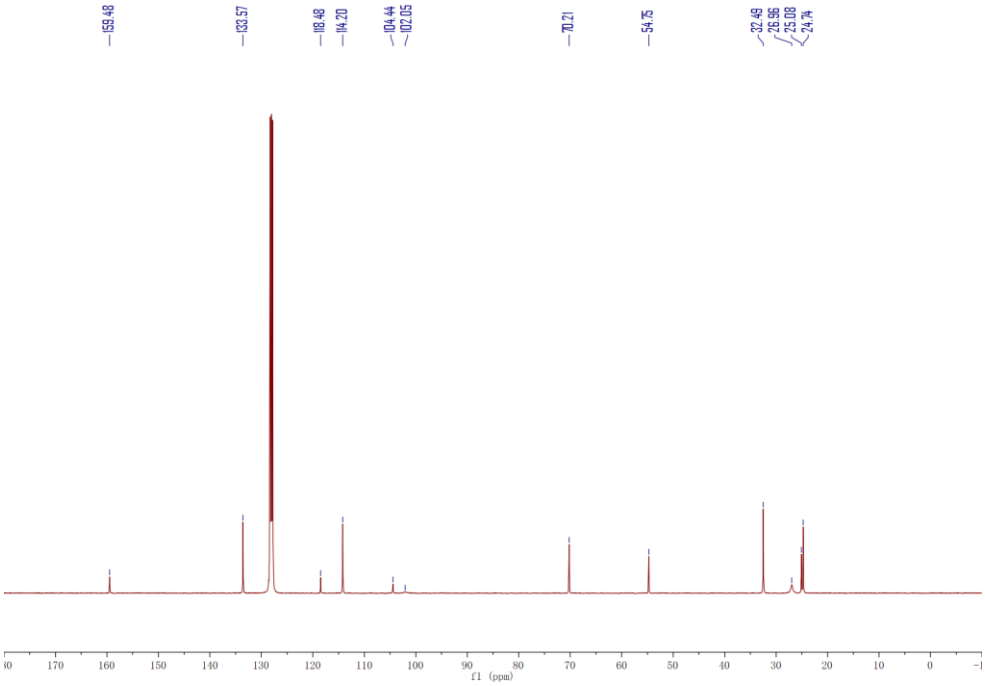
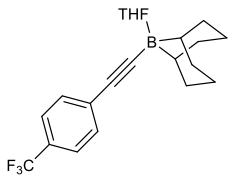


Figure S16. ^{11}B NMR spectrum of **1b-BBN** in C_6D_6.



***B*-(*p*-(trifluoromethyl)phenyl)ethynyl-9-borabicyclo[3,3,1]nonane (1c-BBN)** The crude product was further recrystallized from the saturated pentane solution at 0 °C overnight. Product was obtained as white crystalline solid after filtration and drying in 40% yield.

^{1}H NMR (C_6D_6, 500 MHz): δ 7.30 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 3.69-3.64 (m, 4H), 2.24-2.04 (m, 10H), 1.82-1.74 (m, 2H), 1.30 (s, 3H), 1.21-1.15 (m, 4H).

^{13}C{^{1}H} NMR (C_6D_6, 101 MHz): δ 131.98, 130.07 (q, *J* = 1.5 Hz), 128.75 (q, *J* = 32.4 Hz), 125.35 (q, *J* = 3.7 Hz), 124.94 (q, *J* = 271.9 Hz), 100.92, 70.72, 32.14, 25.93 (br), 25.11, 24.56 ppm.

^{11}B NMR (C_6D_6, 161 MHz): δ 19.4 ppm.

^{19}F{^{1}H} NMR (C_6D_6, 471 MHz): δ -62.31 ppm.

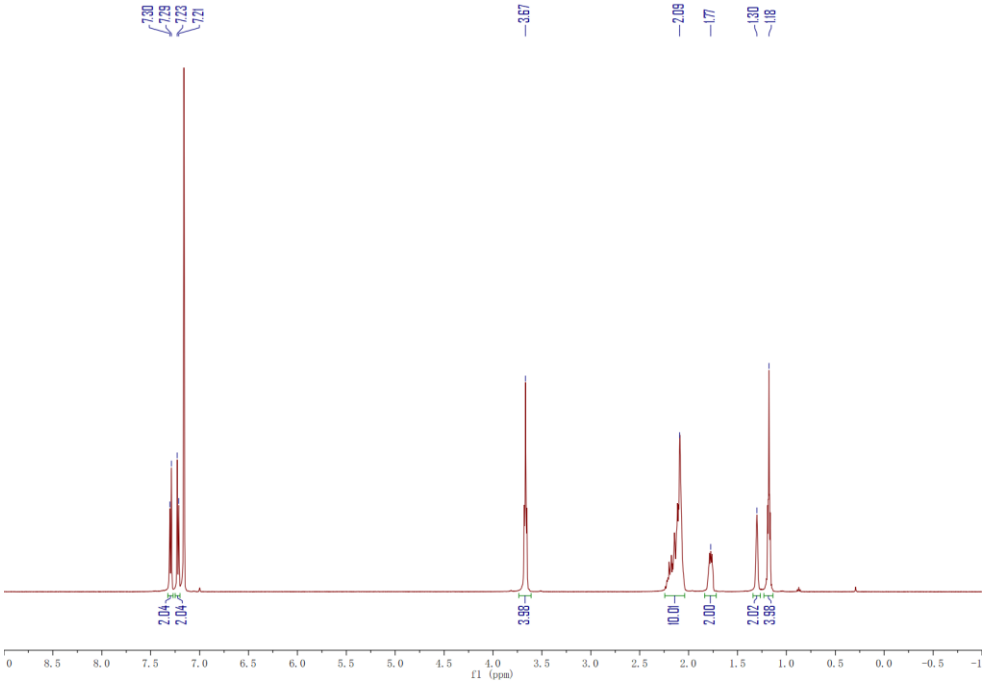


Figure S17. ^{1}H NMR spectrum of **1c-BBN** in C_6D_6.

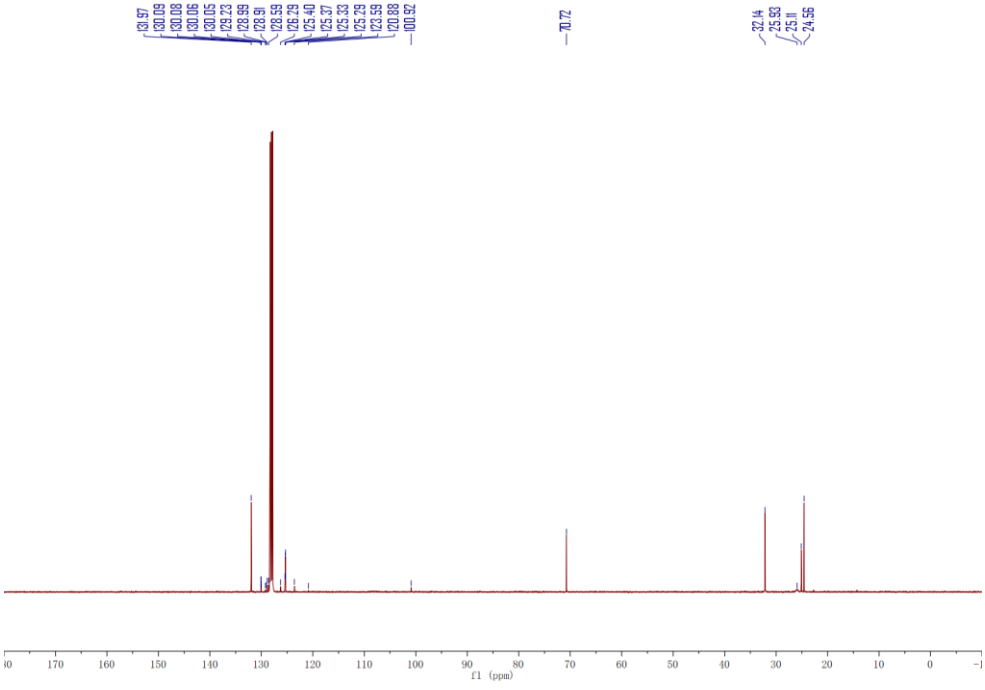


Figure S18. ^{13}C{^{1}H} NMR spectrum of **1c-BBN** in C_6D_6.

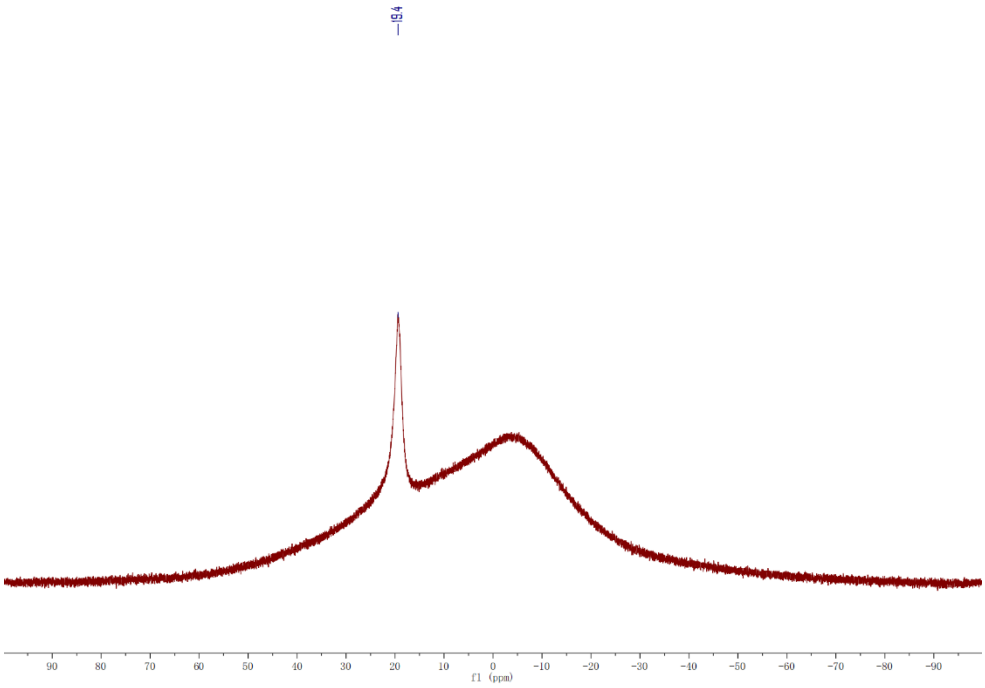


Figure S19. ^{11}B NMR spectrum of **1c-BBN** in C_6D_6.

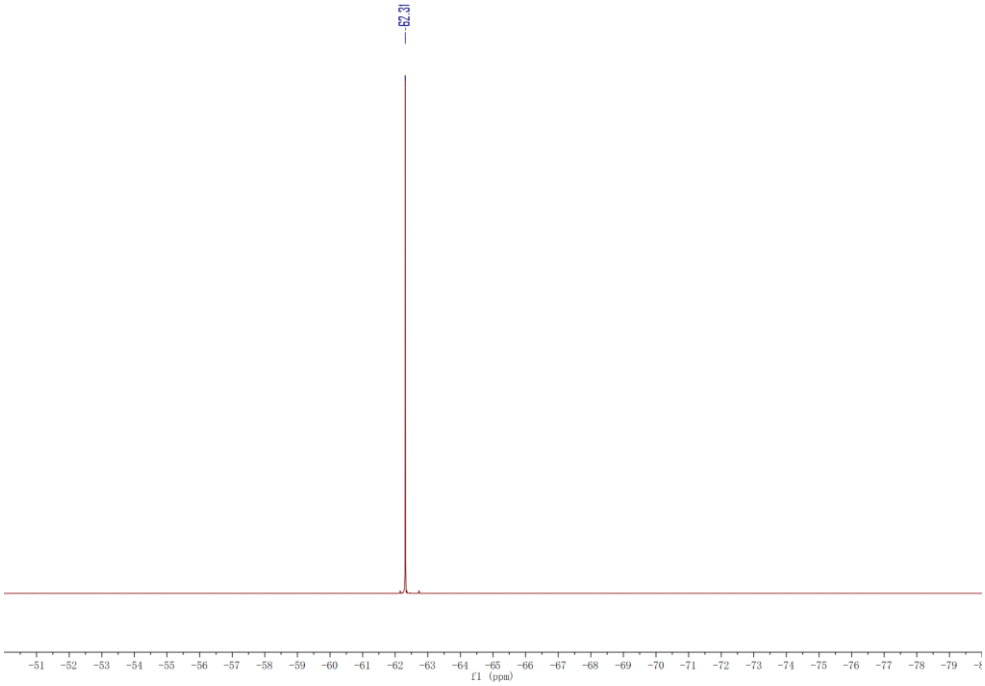
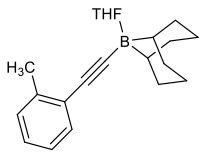


Figure S20. $^{19}F\{^1H\}$ NMR spectrum of **1c-BBN** in C_6D_6.



***B*-(*o*-tolyl)ethynyl-9-borabicyclo[3,3,1]nonane (1d-BBN)** isolated as alkynylborane:THF = 1/1.25 adduct, white powder, 46% yield.

^1H NMR (C_6D_6, 500 MHz): δ 7.54 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.04-6.91 (m, 3H), 3.70-3.62 (m, 5H), 2.49 (s,

3H), 2.21-2.00 (m, 10H), 1.77-1.67 (m, 2H), 1.43 (s, 2H), 1.30-1.18 (m, 5H) ppm.

$^{13}C\{^{1}H\}$ NMR (C_6D_6, 101 MHz): δ 139.74, 131.92, 129.31, 125.44, 69.24, 32.22, 24.62, 24.58, 20.89 ppm.

^{11}B NMR (C_6D_6, 161 MHz): δ 26.7 ppm.

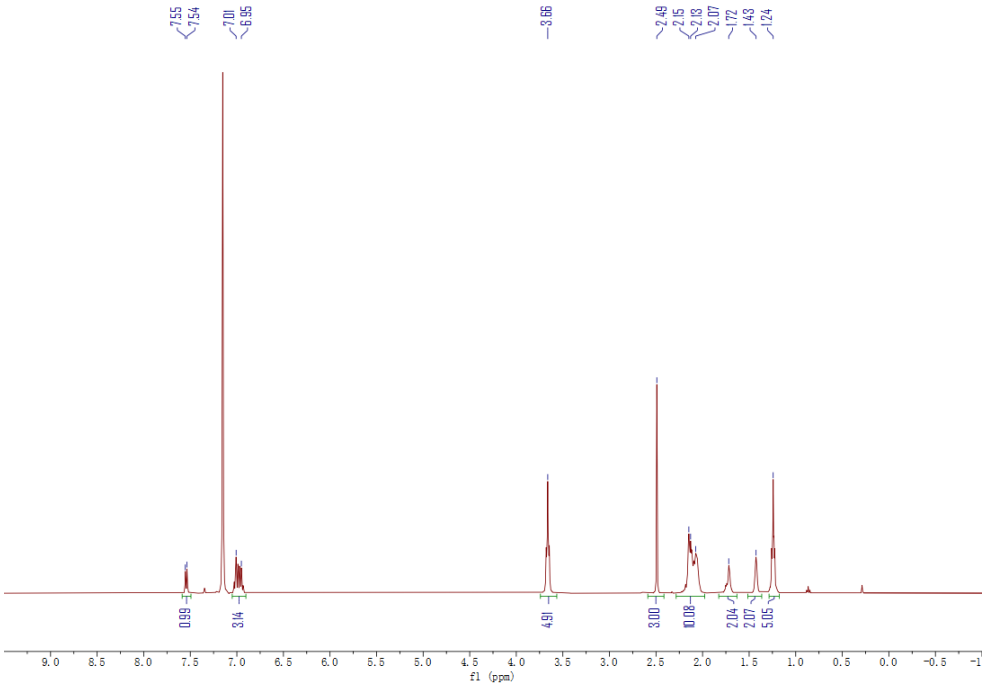


Figure S21. ^{1}H NMR spectrum of **1d-BBN** in C_6D_6.

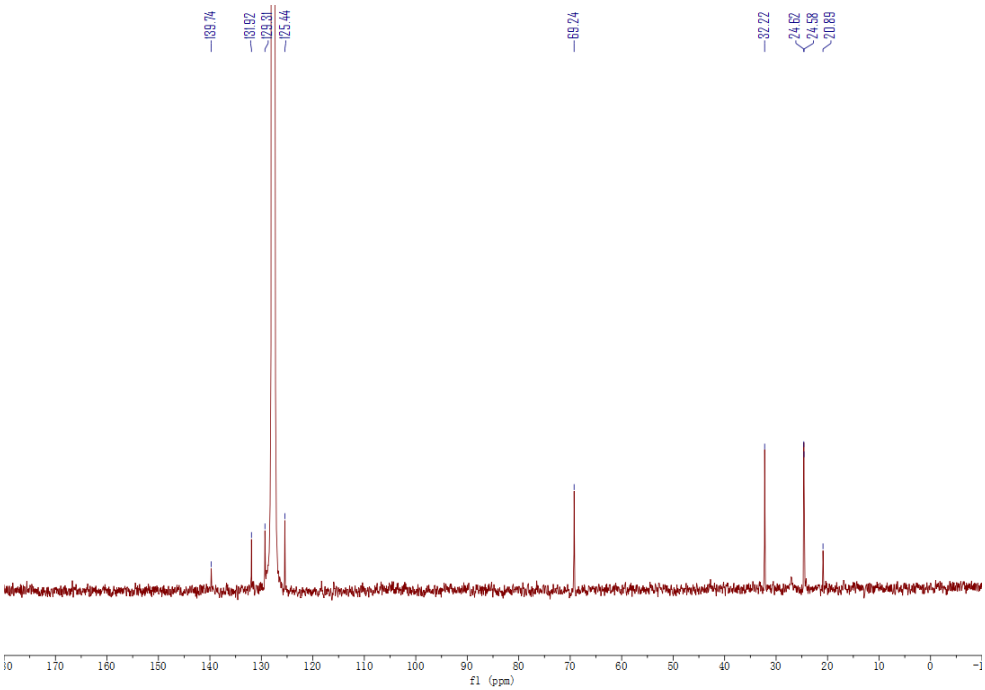


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of **1d-BBN** in C_6D_6.

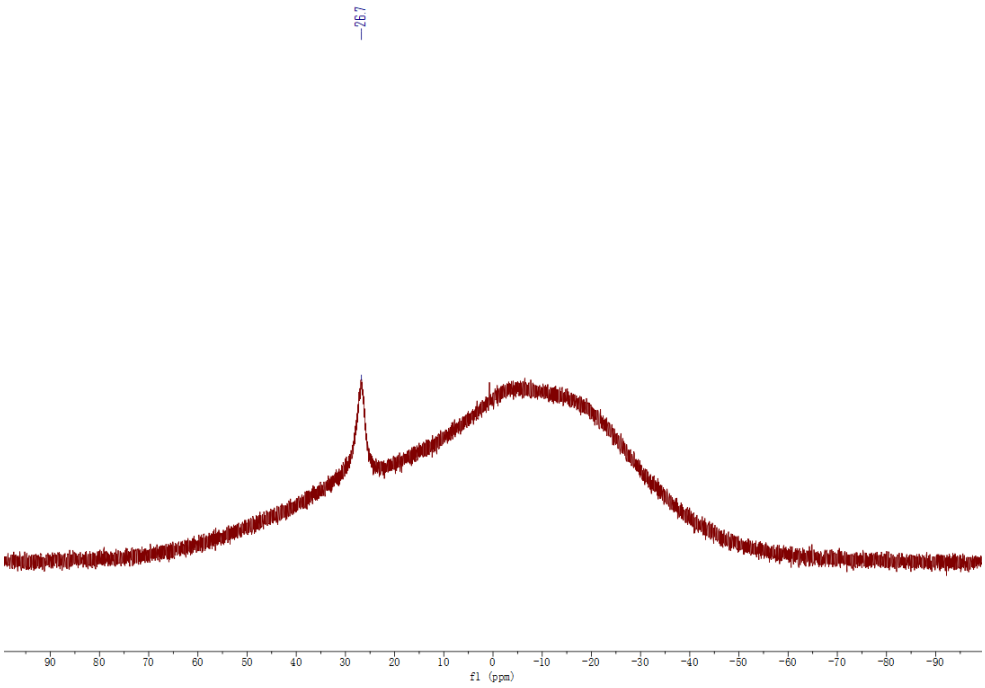
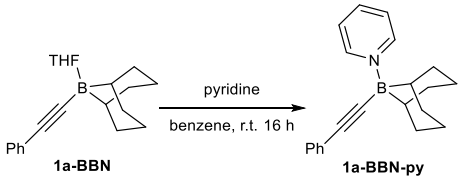


Figure S23. ^{11}B NMR spectrum of **1d-BBN** in C_6D_6.

Synthesis of Pyridine-Adduct of *B*-phenylethynyl-9-BBN (1a-BBN-py)



The synthesis of **1a-BBN-py** was adopted from the reported procedure for the synthesis of pyridine-adduct of *B*-(1-propynyl)-9-BBN, using 1a-BBN instead as the *B*-alkynyl-9-BBN reactant and benzene as solvent. **1a-BBN-py** was obtained in quantitative yield.

^{1}H NMR (C_6D_6, MHz): δ 8.29 (d, *J* = 5.0 Hz, 2H), 7.53 (d, *J* = 6.9 Hz, 2H), 6.97 (t, *J* = 7.3 Hz, 2H), 6.90 (t, , *J* = 7.3 Hz, 1H), 6.58 (t, *J* = 7.6 Hz, 1H), 6.28 (t, *J* = 7.1 Hz, 2H), 3.20-3.06 (br, 2H), 2.44-2.11 (m, 5H), 2.09-1.97 (m, 2H), 1.64 (s, 2H), 1.55-1.41 (m, 3H) ppm.

^{13}C{^{1}H} NMR (C_6D_6, MHz): δ 145.59, 138.94, 131.81, 128.59, 126.37, 125.10, 34.07, 29.89, 25.61, 25.02 ppm.

^{11}B NMR (C_6D_6, MHz): δ -3.2 ppm.

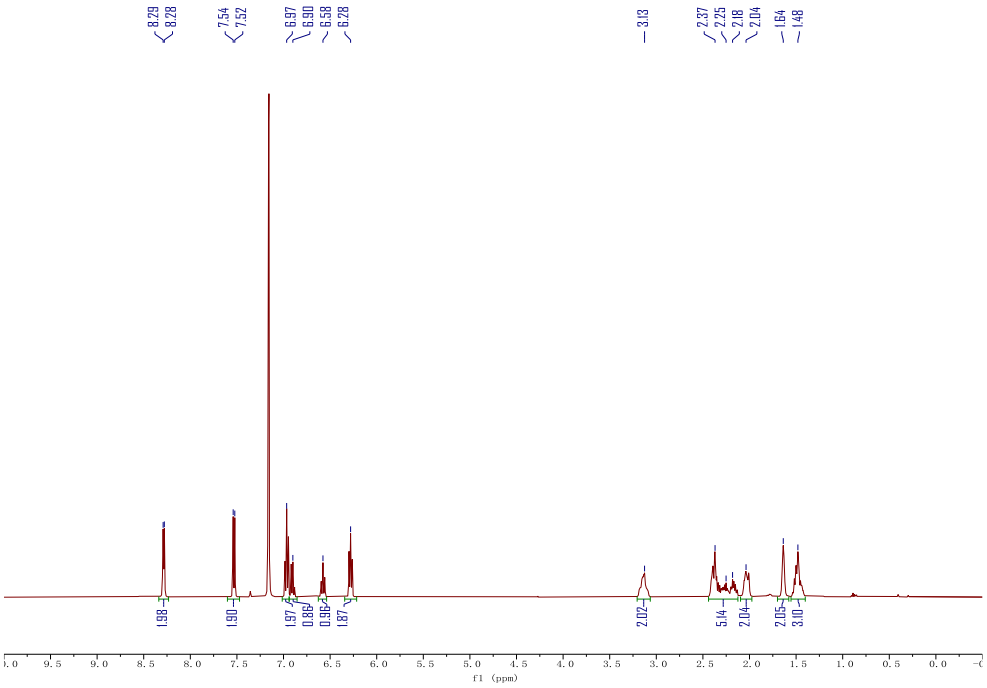


Figure S24. ^{1}H NMR spectrum of **1a-BBN-py** in C_6D_6.

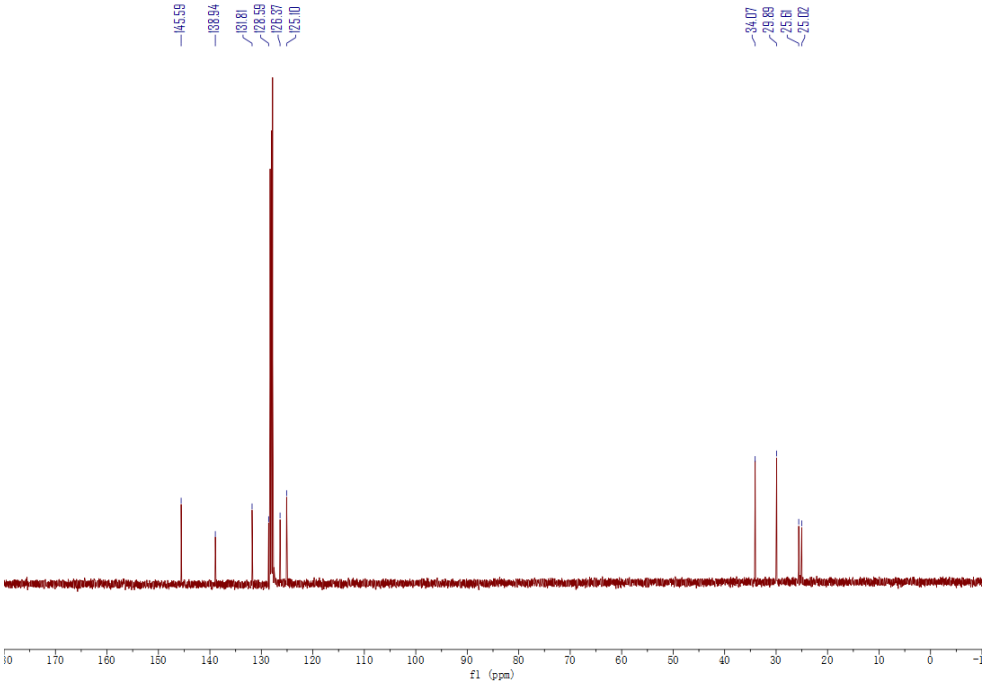


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of **1a-BBN-py** in C_6D_6.

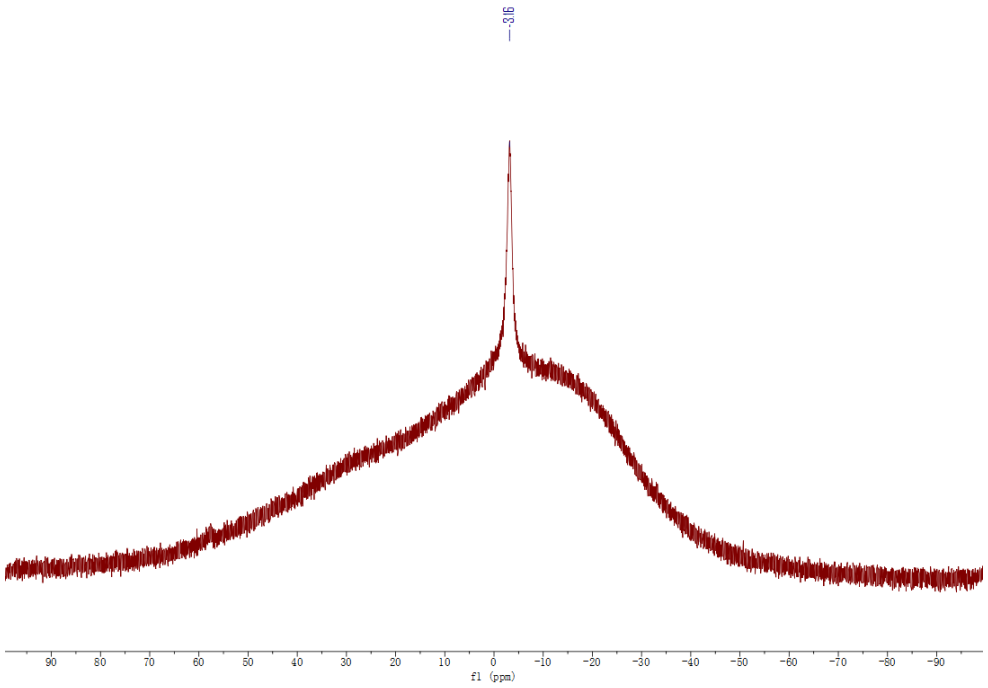
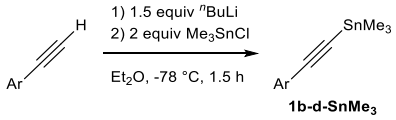


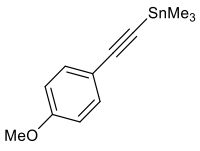
Figure S26. ^{11}B NMR spectrum of **1a-BBN-py** in C_6D_6.

General Synthetic Procedure for Arylethynyl Trimethylstannanes (1b-d-SnMe$_3$)



The synthesis was performed following a modification of the reported procedure.[15] Terminal aryl alkyne (2.5 mmol), dry diethyl ether (5 mL) and a stir bar were added to a N_2-filled 50 mL Schlenk flask and cooled at -78 ℃. n-BuLi solution in hexanes (2.5 M, 1.5 mL, 3.8 mmol, 1.5 equiv) was slowly added to the mixture and stirred for 15 min at -78 ℃. Trimethyltin chloride solution in hexanes (1.0 M, 5 mL, 5 mmol, 2.0 equiv) was added via syringe. The resulting white suspension was stirred for an hour at room temperature. All volatiles were carefully removed under vacuum. Pentane (5 mL) was added to the white mixture, and the resulting suspension was washed by 3 x 10 mL of water. After drying over $MgSO_4$ and evaporation under vacuum, arylethynyl trimethylstannane was obtained as yellow or colorless oil.

Precaution: Trialkyltin species are highly toxic. Proper PPE is required. A secondary cold trap is recommended for evacuation of the crude reaction mixture. All the chemical and labware waste should be handled separately from the normal waste stream and quenched thoroughly.



(*p*-methoxyphenyl)ethynyl trimethylstannane (1b-SnMe$_3$) 55% yield.

^1H NMR ($CDCl_3$, 500 MHz): δ 7.40 (d, 8.7 Hz, 2H), 6.81 (d, 8.7 Hz, 2H), 3.80 (s, 3H), 0.34 (s, 9H) ppm.

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 159.58, 133.54, 115.95, 113.92, 109.11, 91.54, 55.40, -7.50 ppm.

$^{119}Sn\{^{1}H\}$ NMR ($CDCl_3$, 187 MHz): δ -66.21 ppm.

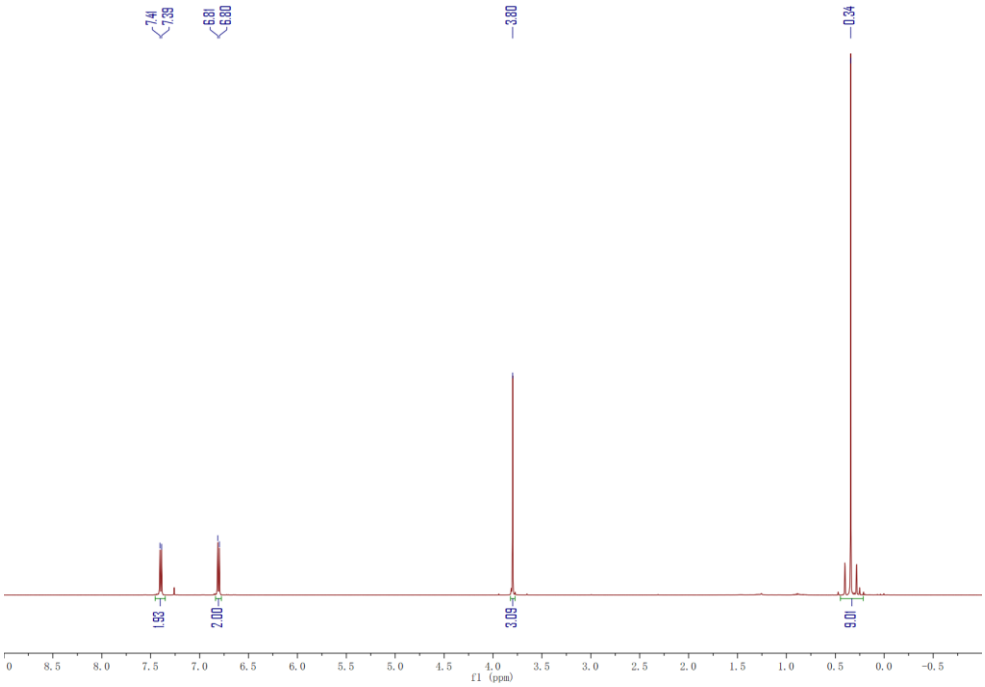


Figure S27. ^{1}H NMR spectrum of **1b-SnMe$_3$** in $CDCl_3$.

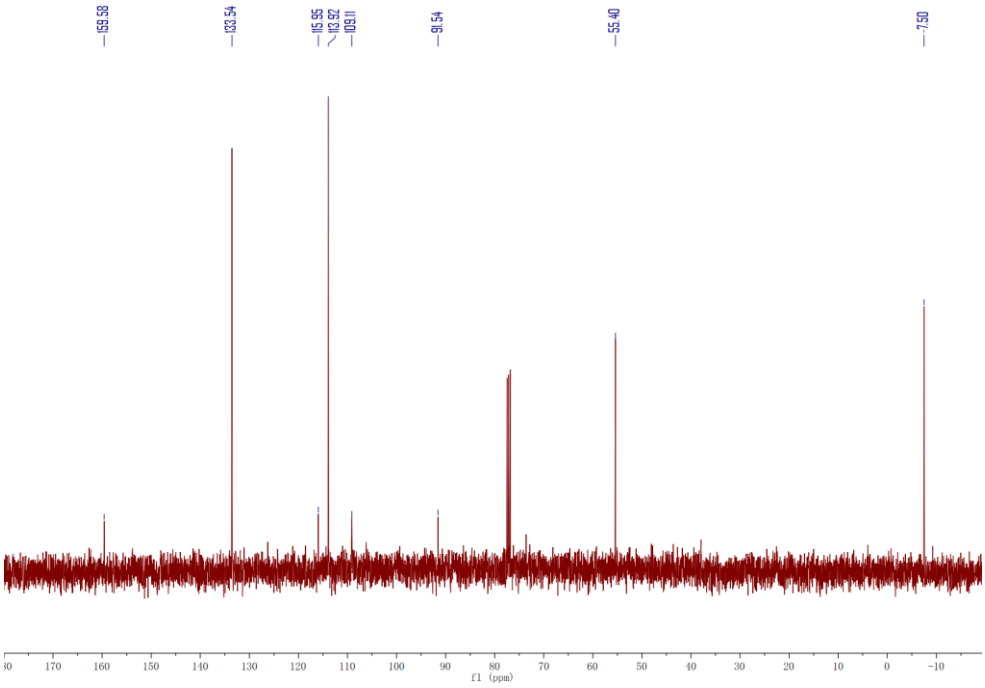


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of **1b-SnMe$_3$** in $CDCl_3$.

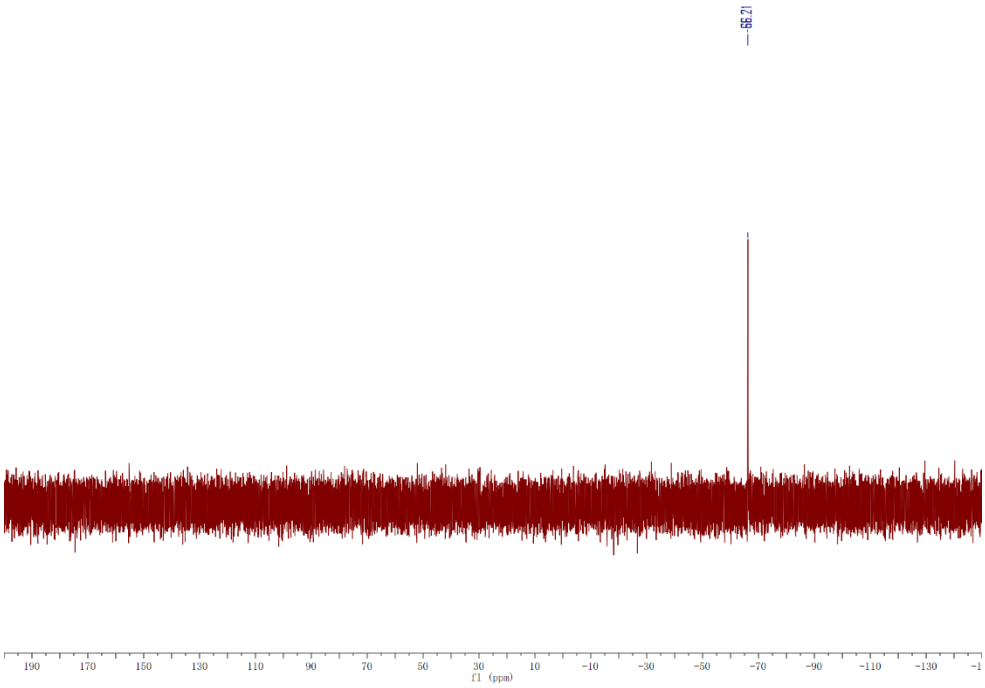
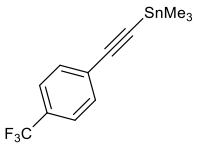


Figure S29. $^{119}Sn\{^{1}H\}$ NMR spectrum of **1b-SnMe$_3$** in $CDCl_3$.



(*p*-(trifluoromethyl)phenyl)ethynyl trimethylstannane (1c-SnMe$_3$) 59% yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (s, 4H), 0.37 (s, 9H) ppm.

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz): δ 132.26, 125.25, -7.55 ppm.

$^{119}Sn\{^{1}H\}$ NMR ($CDCl_3$, 187 MHz): δ -63.29 ppm.

$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, MHz): δ -62.79 ppm.

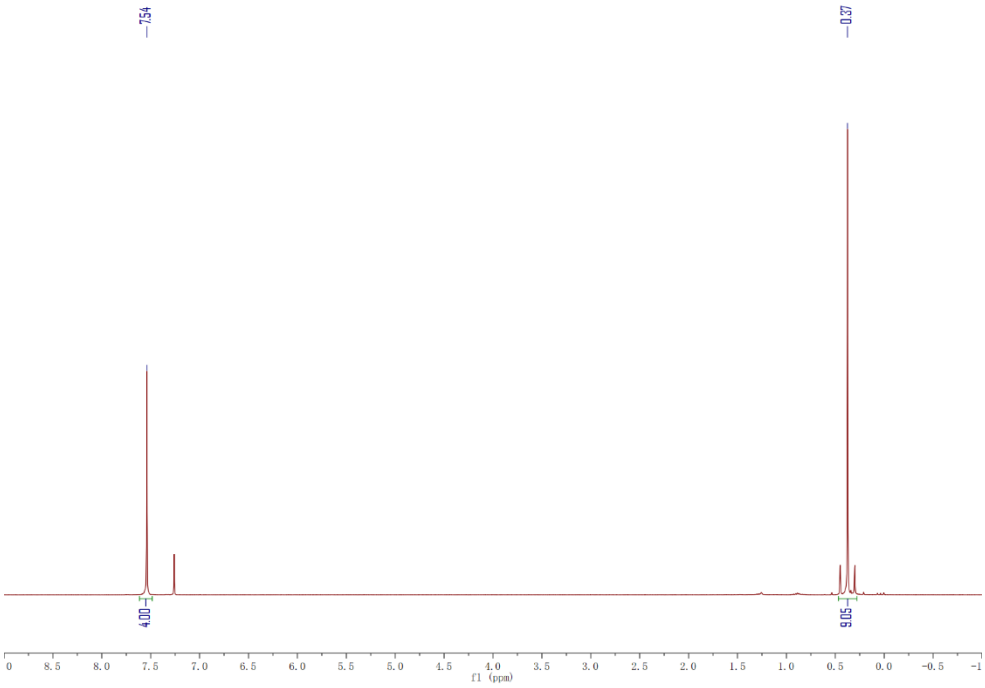


Figure S30. ^{1}H NMR spectrum of **1c-SnMe$_3$** in $CDCl_3$.

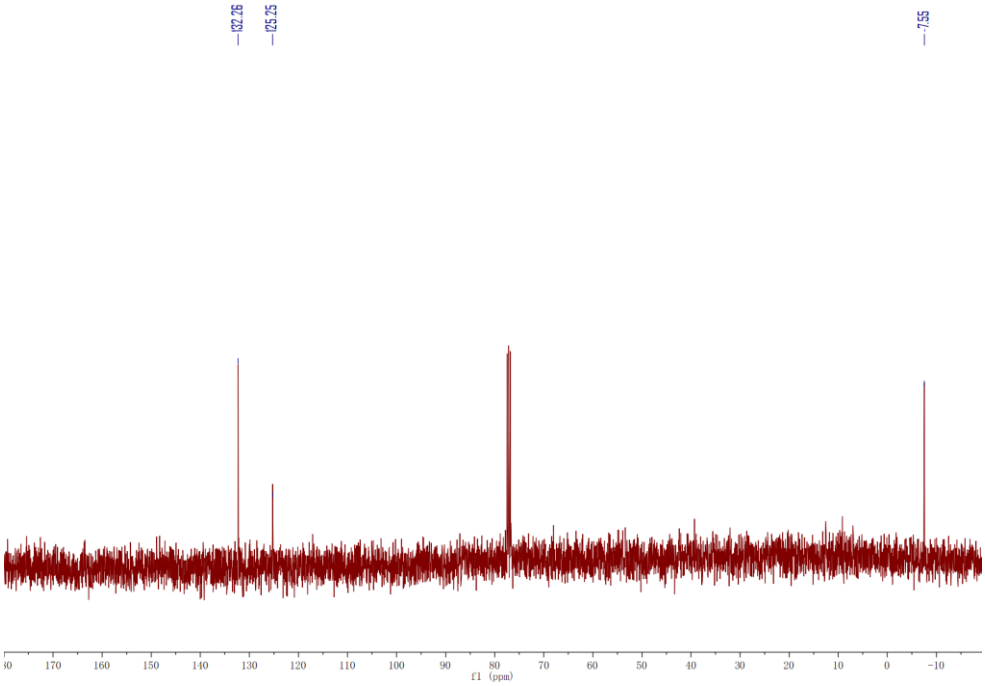


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of **1c-SnMe$_3$** in $CDCl_3$.

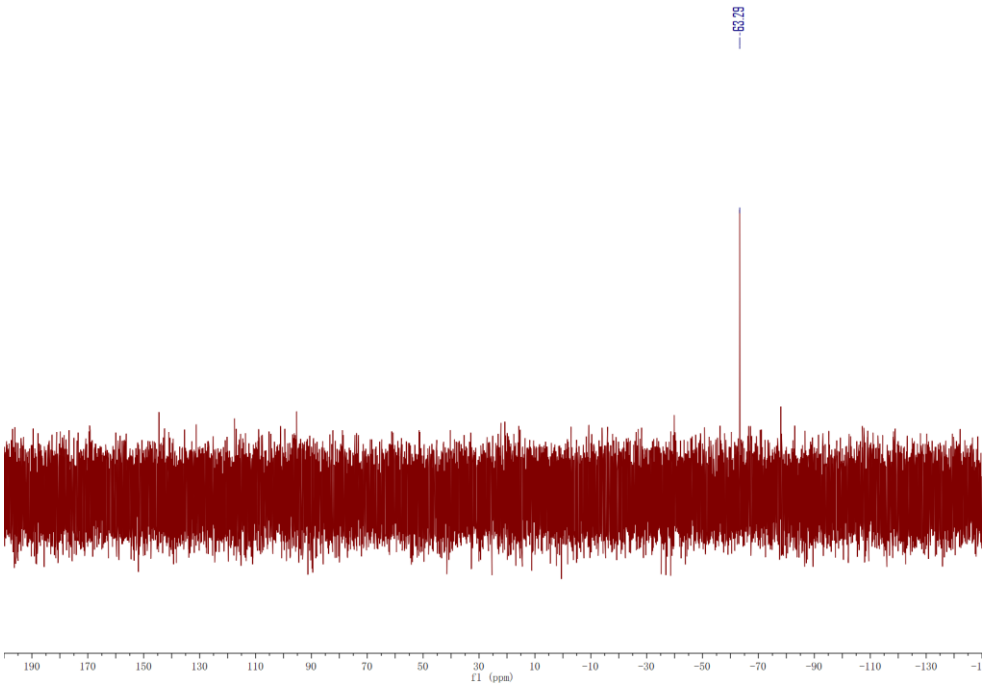


Figure S32. $^{119}Sn\{^{1}H\}$ NMR spectrum of **1c-SnMe$_3$** in $CDCl_3$.

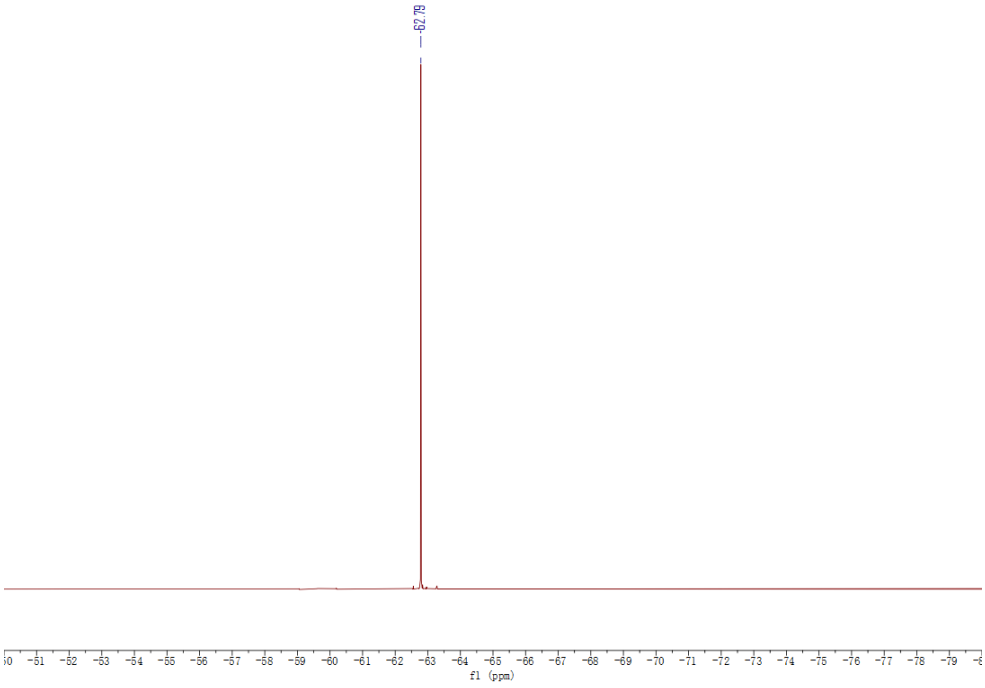
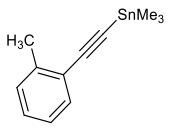


Figure S33. $^{19}F\{^{1}H\}$ NMR spectrum of **1c-SnMe$_3$** in $CDCl_3$.



(*o*-tolyl)ethynyl trimethylstannane (1d-SnMe$_3$) 40% yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.42 (d, 7.5 Hz, 1H), 7.20-7.14 (m, 2H), 7.13-7.07 (m, 1H), 2.44 (s, 3H), 0.36 (s, 9H) ppm.

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz): δ 140.52, 132.26, 129.43, 128.17, 125.53, 123.58, 107.97, 97.47, 20.93, -7.47 ppm.

$^{119}Sn\{^{1}H\}$ NMR ($CDCl_3$, 187 MHz): δ -65.64 ppm.

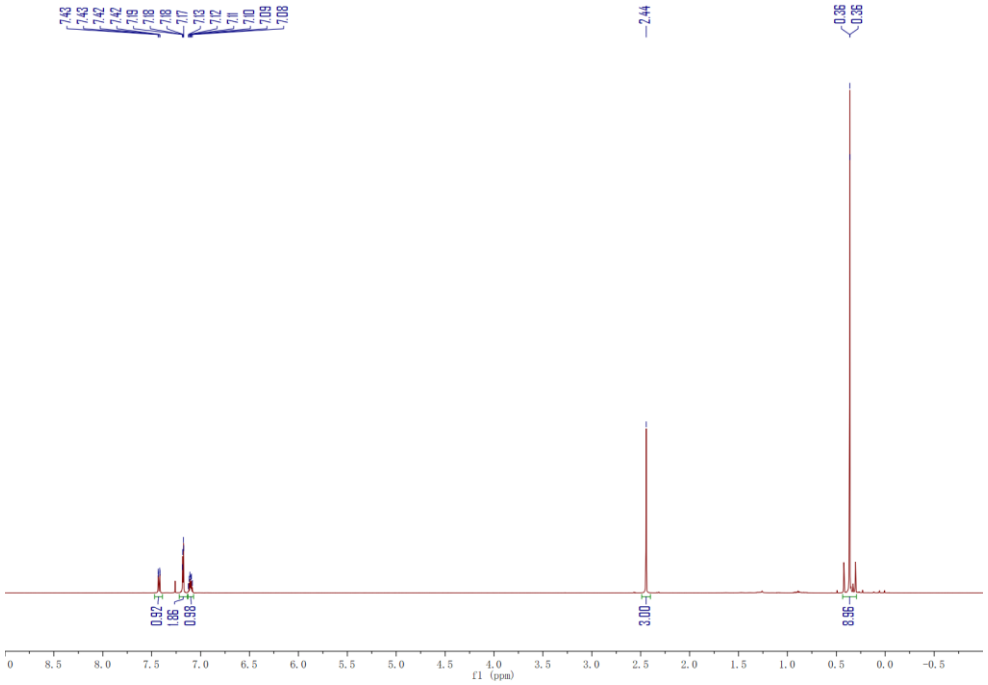


Figure S34. ^{1}H NMR spectrum of **1d-SnMe$_3$** in $CDCl_3$.

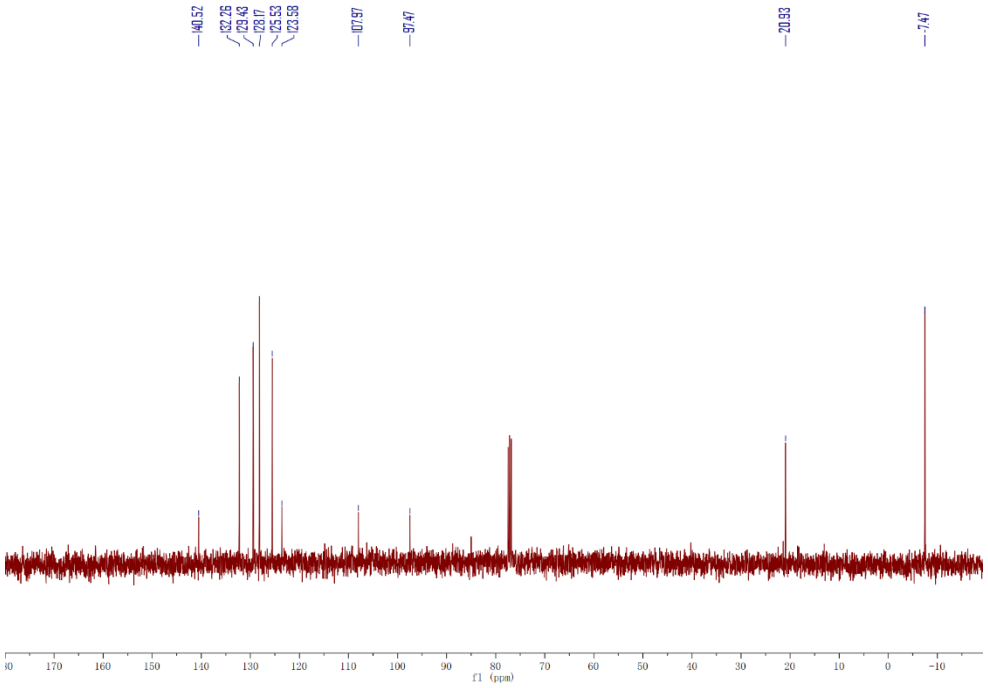


Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of **1d-SnMe$_3$** in $CDCl_3$.

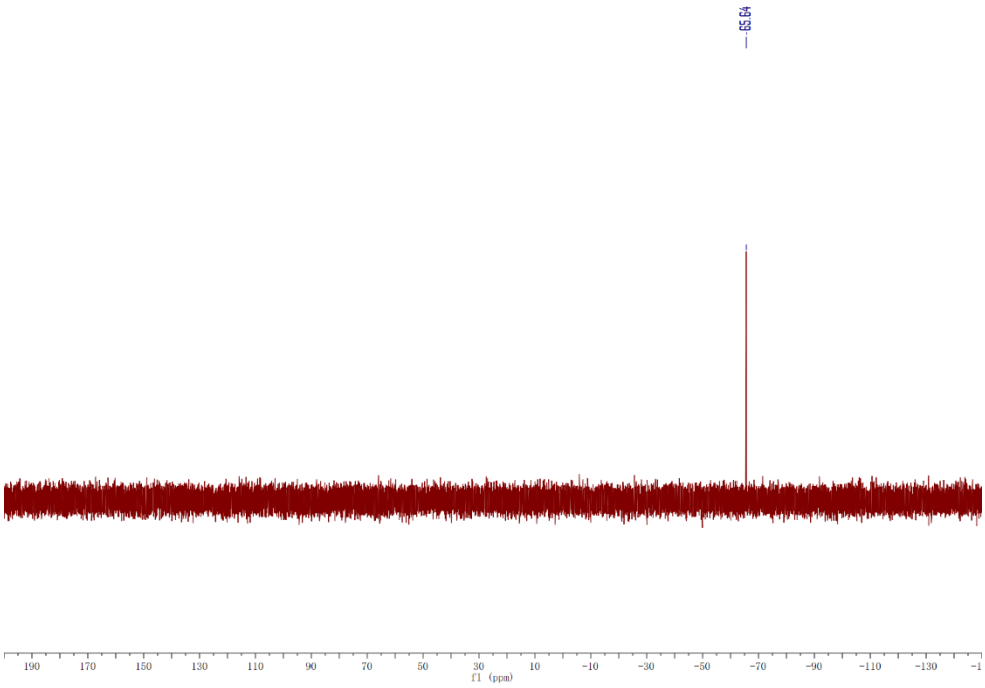


Figure S36. $^{119}Sn\{^{1}H\}$ NMR spectrum of **1d-SnMe$_3$** in $CDCl_3$.

Catalytic Pyrrole Syntheses: Alkynyl BBN and Alkynyl Stannanes Scopes (Table 3)

General Procedure for Catalysis with *B*-alkynyl-9-BBN as Substrate (Procedure B)

$[py_2TiCl_2(NPh)]_2$ (7.4 mg, 0.01 mmol, 0.1 equiv), *B*-alkynyl-9-BBN (0.1 mmol, 1 equiv) and 0.5 mL of C_6D_5Br stock solution containing 1-phenyl-1-propyne (11.6 mg, 0.1 mmol, 1 equiv), azobenzene (7.3 mg, 0.04 mmol, 0.4 equiv) and triphenylmethane (4.9 mg, 0.02 mmol, 0.2 equiv, internal standard) were added to an NMR tube. The reaction was then sealed and heated in a preheated oil bath at 115 °C for 0.5 h. NMR spectra were collected before and after heating to monitor the reaction. The reaction was quenched with 5% HCl in methanol and extracted with EtOAc/H_2O. The organic phase was dried over $MgSO_4$, evaporated and characterized by NMR. The peak assignment of pyrrole products were performed based on the reported chemical shifts,[16–18] and the yields were calculated by the comparison of peak area integral with respect to the internal standard. The peak area of selected ^1H NMR peaks were calculated by Gaussian-Lorentzian fitting to omit the influence from minor baseline overlapping.[19]

Catalytic Reaction of **1a-BBN** with 1-phenyl-1-propyne **(Table 3)**

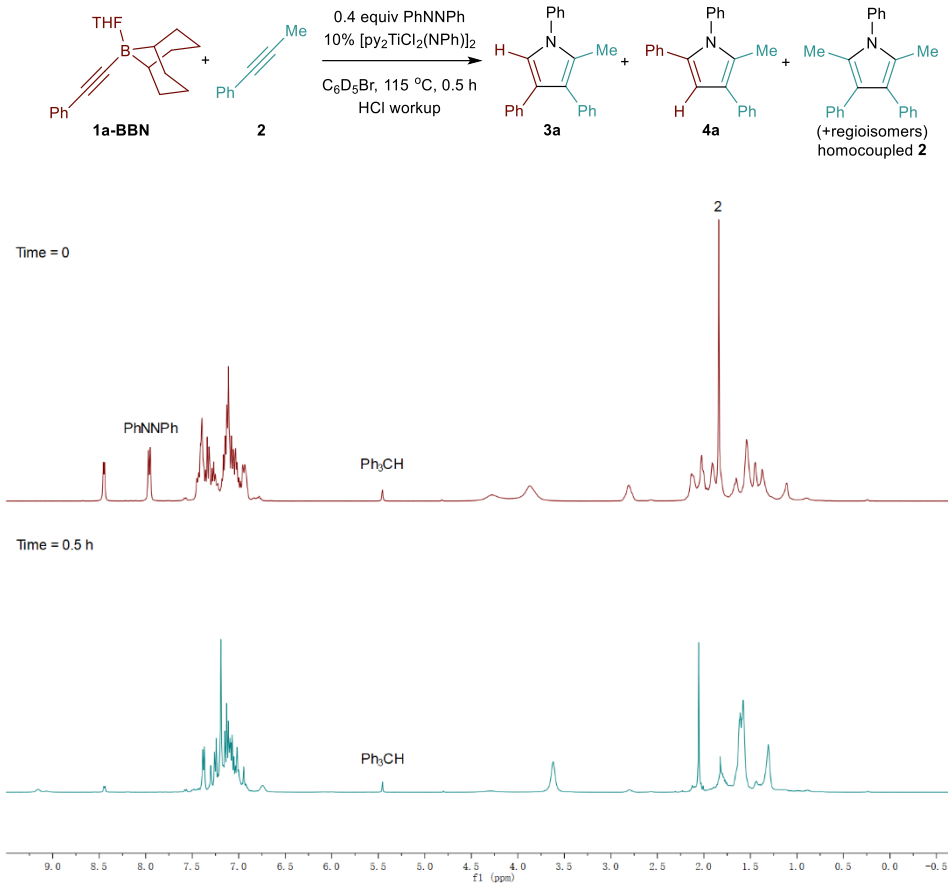


Figure S37. ^1H NMR of the reaction of **1a-BBN** with 1-phenyl-1-propyne at time = 0 (top), time = 0.5 h (bottom) in C_6D_5Br.

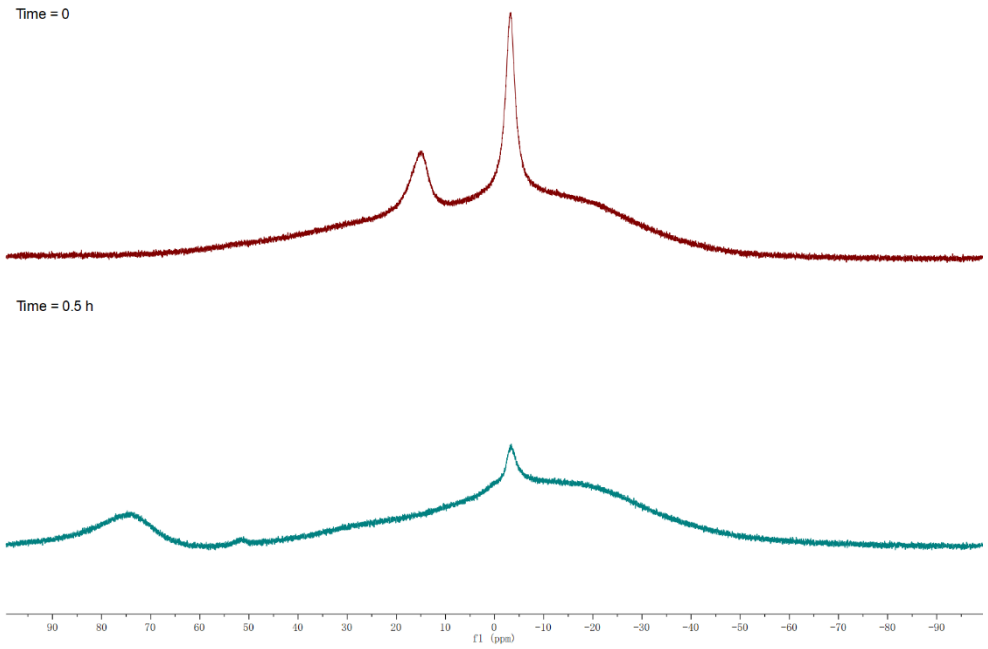
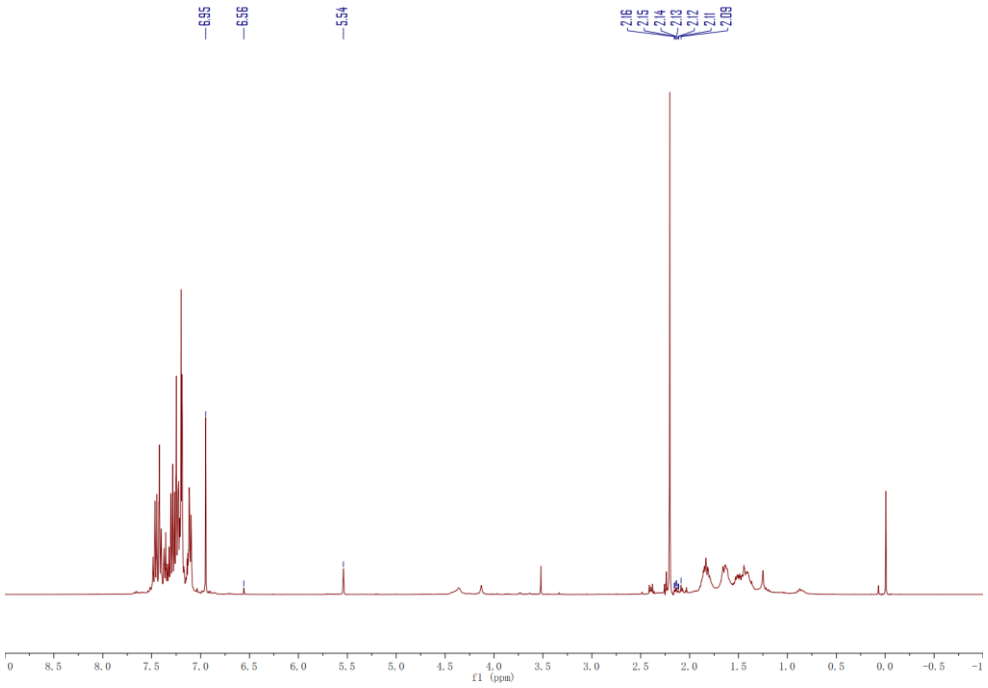


Figure S38. ^{11}B NMR of the reaction of **1a-BBN** with 1-phenyl-1-propyne at time = 0 (top), time = 0.5 h (bottom) in C_6D_5Br.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	3363.3	n.a.
3a	6.95	$H_{pyrrolyl}$	1	12234.0	72.8
4a	6.56	$H_{pyrrolyl}$	1	534.5	3.2
homocoupled **2**	2.16, 2.15, 2.14, 2.13, 2.12, 2.11, 2.09	$Me_{pyrrolyl}$ (2 per molecule)	6	3040.3	3.0

Figure S39. ^{1}H NMR of the reaction of **1a-BBN** with 1-phenyl-1-propyne in $CDCl_3$ after HCl workup.

Sample yield calculation based on ^{1}H NMR peak area:

$$Yield\ of\ \mathbf{3a} = \frac{Peak\ Area\ of\ \mathbf{3a}}{\#\ of\ H\ of\ \mathbf{3a}} \times \frac{\#\ of\ H\ of\ Ph_3CH}{Peak\ Area\ of\ Ph_3CH} \times equiv\ of\ Ph_3CH \times 100\%$$

Catalytic Reaction of **1b-BBN** with 1-phenyl-1-propyne **(Table 3)**

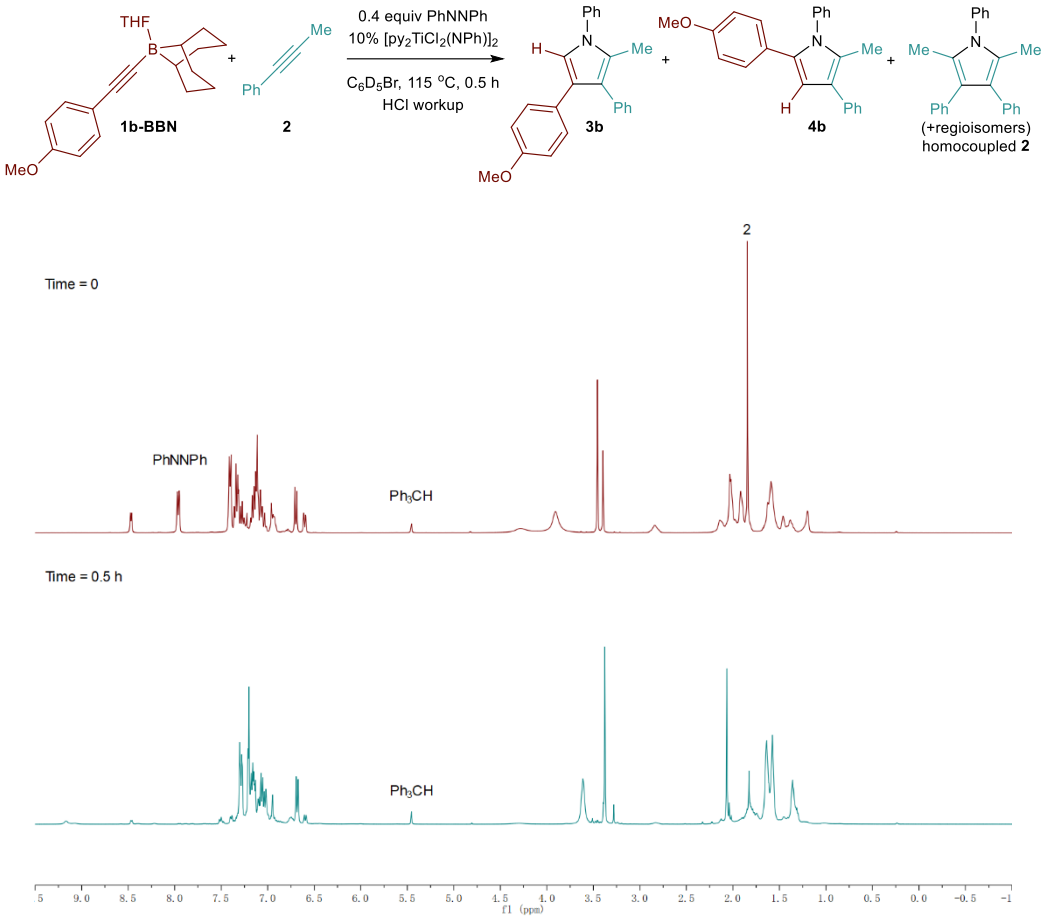


Figure S40. ^{1}H NMR of the reaction of **1b-BBN** with 1-phenyl-1-propyne at time = 0 (top), time = 0.5 h (bottom) in C_6D_5Br.

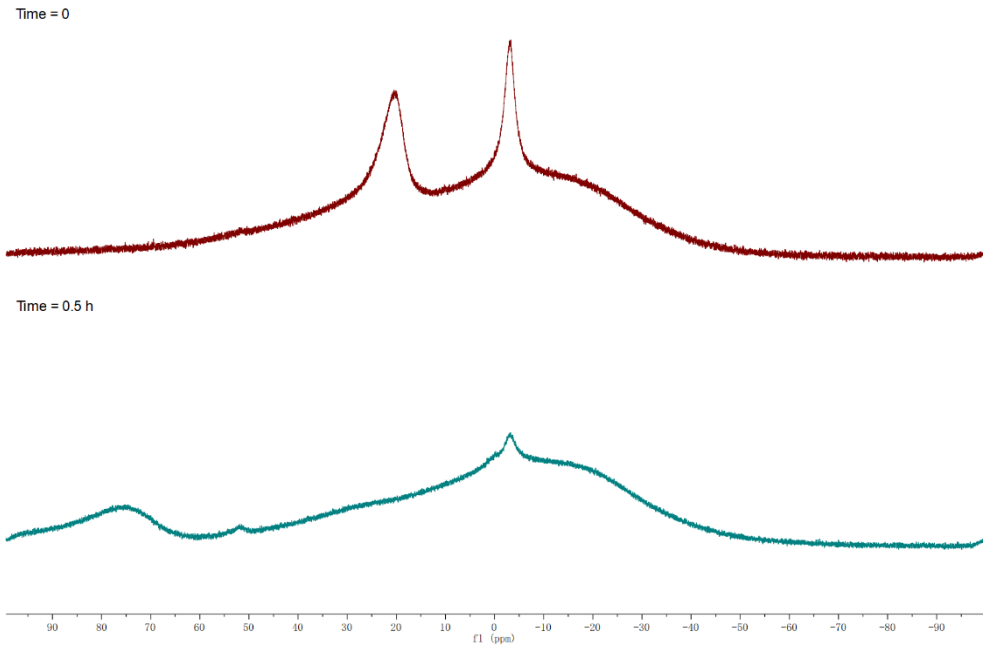
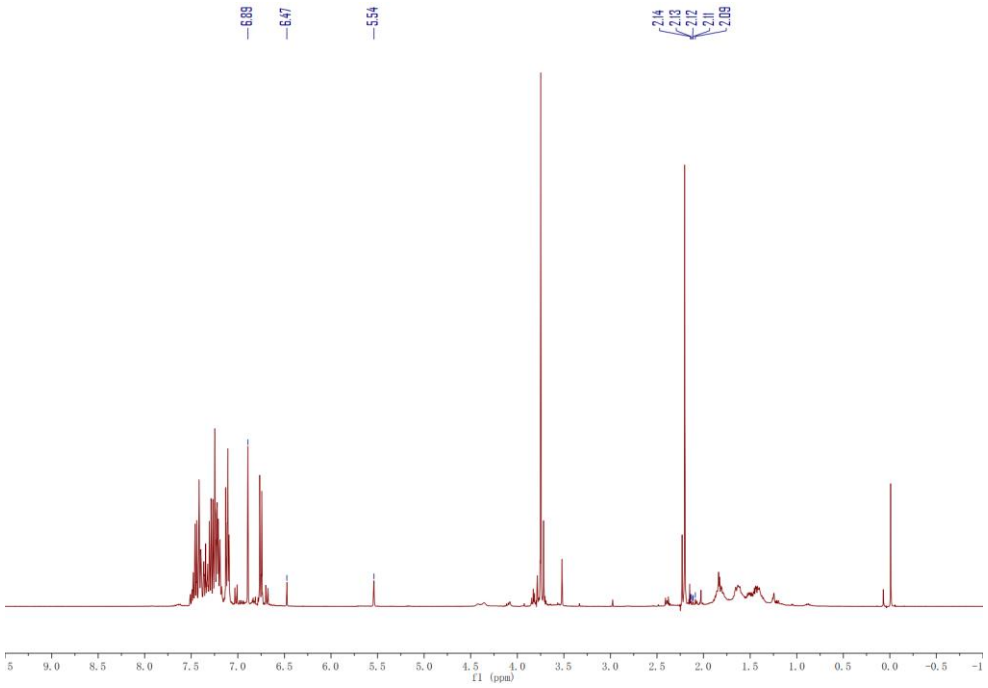


Figure S41. ^{11}B NMR of the reaction of **1b-BBN** with 1-phenyl-1-propyne at time = 0 (top), time = 0.5 h (bottom) in C_6D_5Br.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	3296.7	n.a.
3b	6.89	$H_{pyrrolyl}$	1	9824.6	59.6
4b	6.47	$H_{pyrrolyl}$	1	1560.1	9.5
homocoupled **2**	2.14, 2.13, 2.12, 2.11, 2.09	$Me_{pyrrolyl}$ (2 per molecule)	6	2025.7	2.1

Figure S42. ^{1}H NMR of the reaction of **1b-BBN** with 1-phenyl-1-propyne in $CDCl_3$ after HCl workup.

Catalytic Reaction of **1c-BBN** with 1-phenyl-1-propyne **(Table 3)**

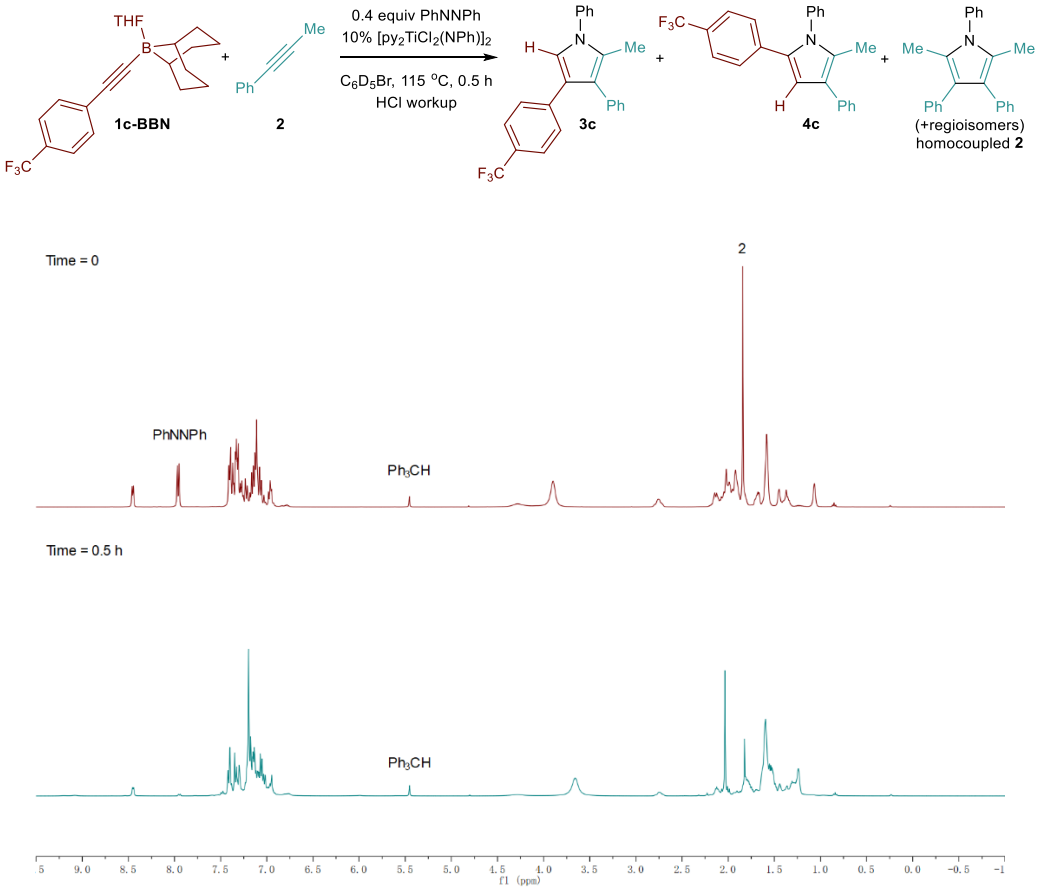


Figure S43. ^{1}H NMR of the reaction of **1c-BBN** with 1-phenyl-1-propyne at time = 0 (top), time = 0.5 h (bottom) in C_6D_5Br.

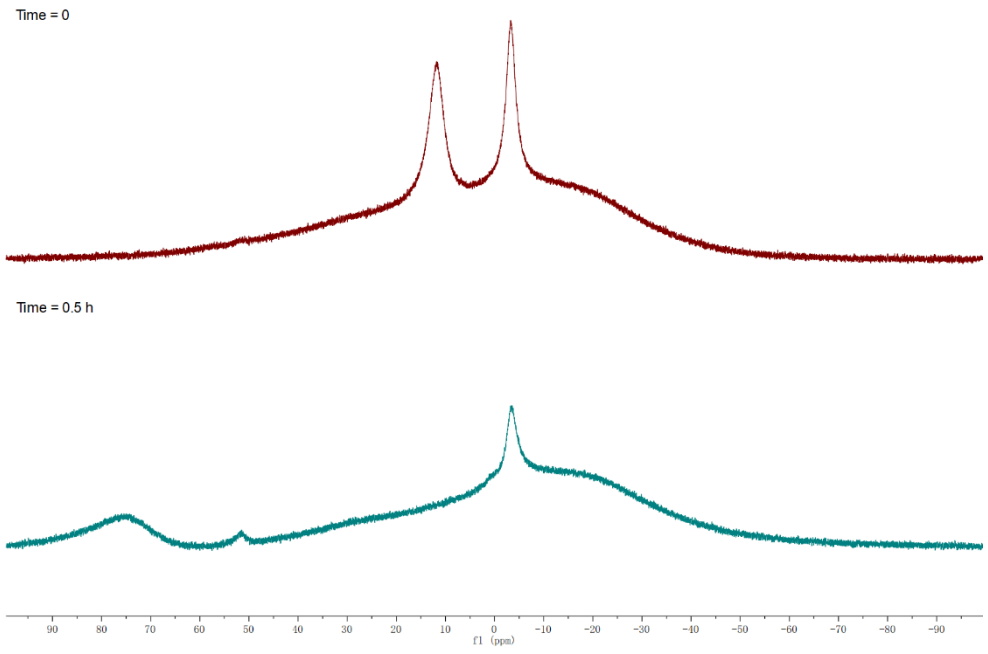


Figure S44. ^{11}B NMR of the reaction of **1c-BBN** with 1-phenyl-1-propyne at time = 0 (top), time = 0.5 h (bottom) in C_6D_5Br.

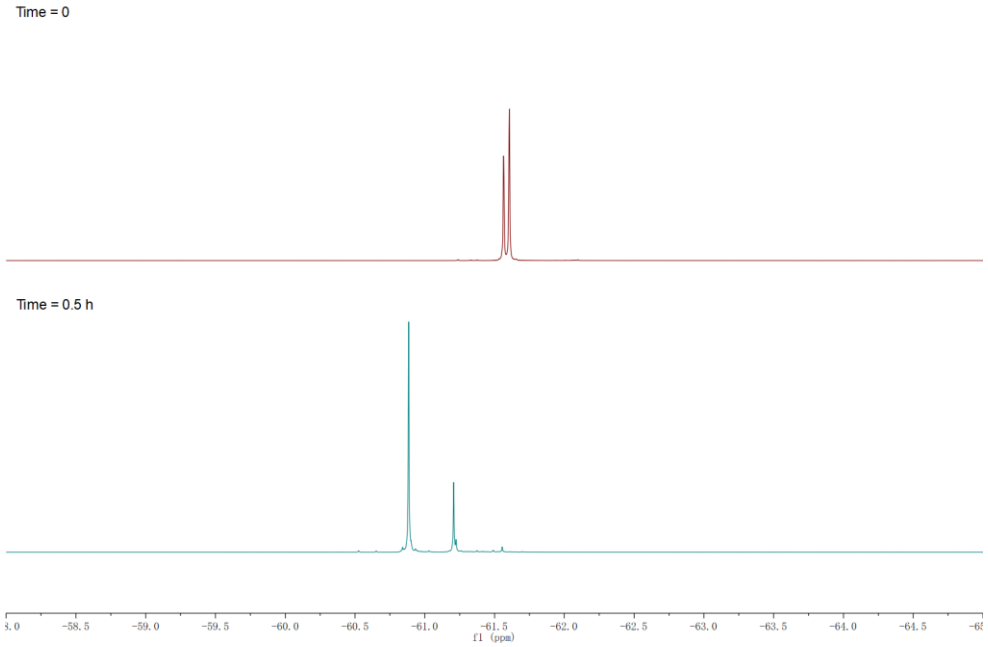
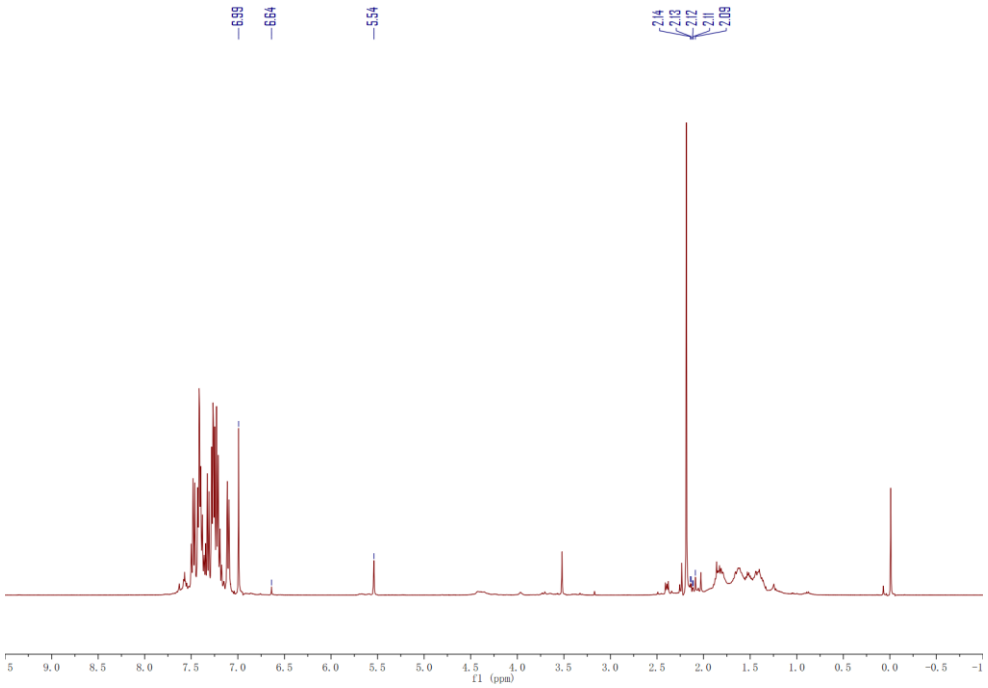


Figure S45. $^{19}F\{^1H\}$ NMR of the reaction of **1c-BBN** with 1-phenyl-1-propyne at time = 0 (top), time = 0.5 h (bottom) in C_6D_5Br.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	3643.1	n.a.
3c	6.99	$H_{pyrrolyl}$	1	11843.5	65.0
4c	6.64	$H_{pyrrolyl}$	1	605.9	3.3

homocoupled **2**	2.14, 2.13, 2.12, 2.11, 2.09	$Me_{pyrrolyl}$ (2 per molecule)	6	2869.3	2.6

Figure S46. ^{1}H NMR of the reaction of **1c-BBN** with 1-phenyl-1-propyne in $CDCl_3$ after HCl workup.

Catalytic Reaction of **1d-BBN** with 1-phenyl-1-propyne **(Table 3)**

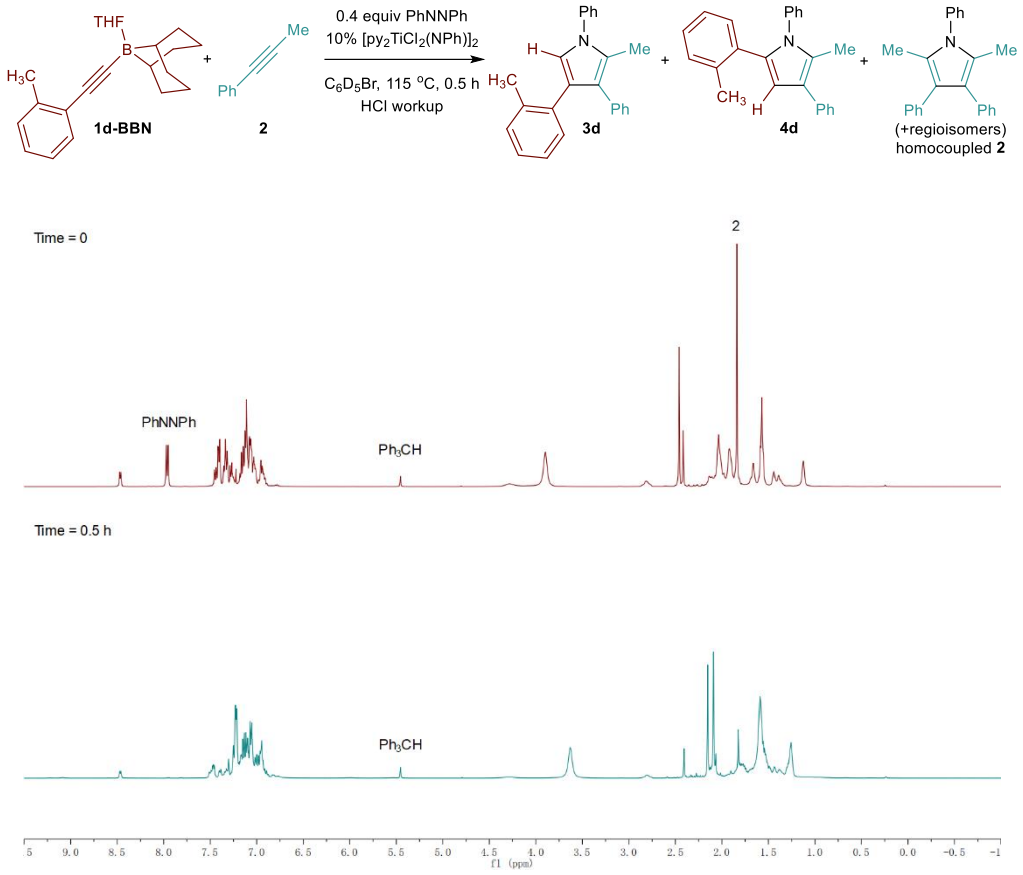


Figure S47. ^{1}H NMR of the reaction of **1d-BBN** with 1-phenyl-1-propyne at time = 0 (top), time = 0.5 h (bottom) in C_6D_5Br.

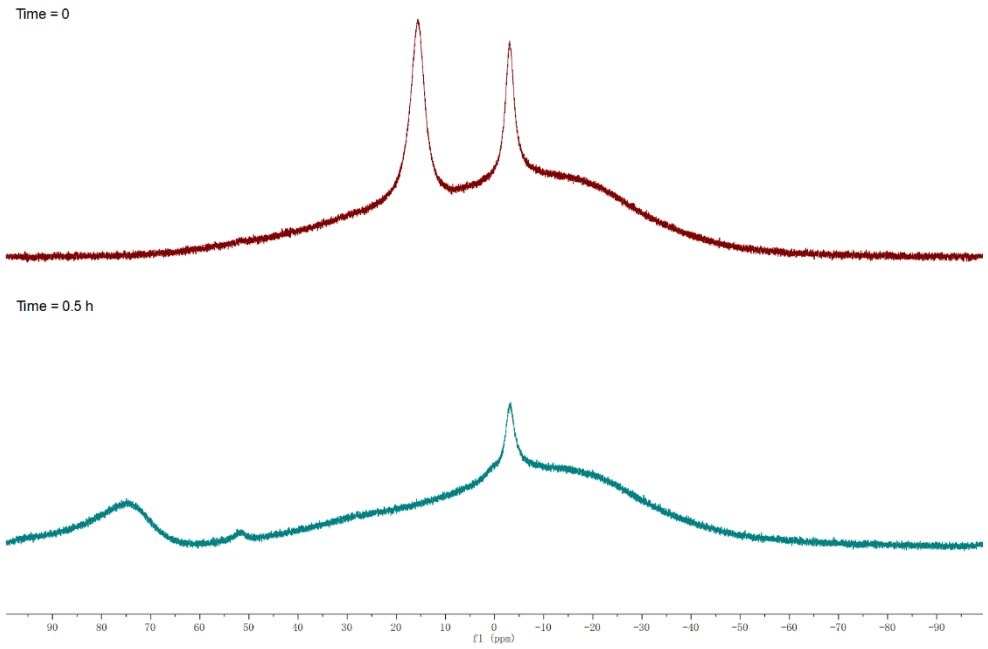
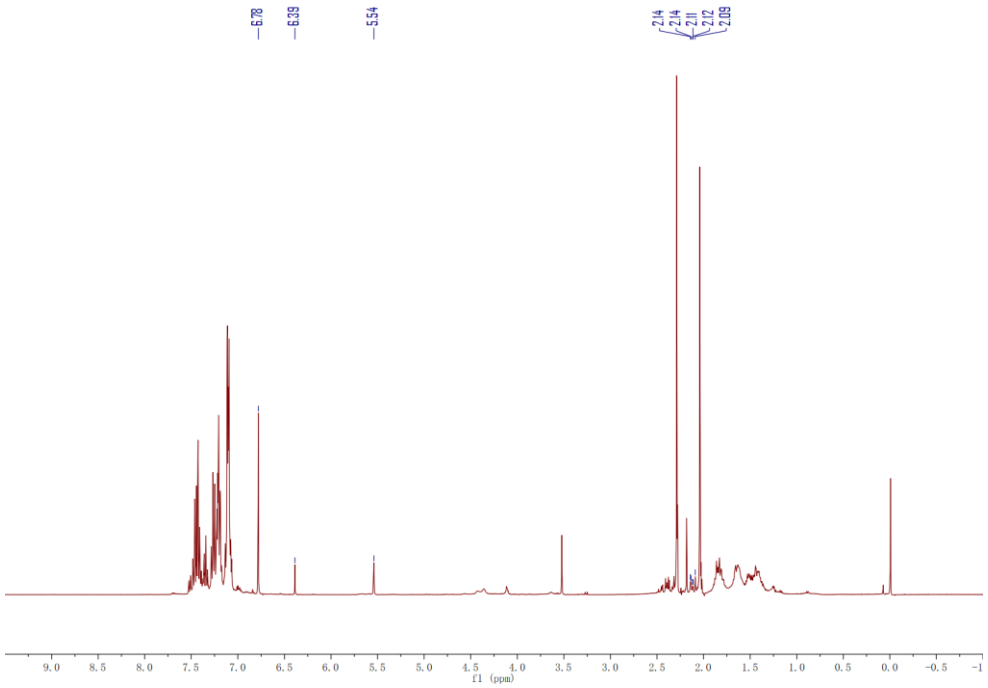


Figure S48. ^{11}B NMR of the reaction of **1d-BBN** with 1-phenyl-1-propyne at time = 0 (top), time = 0.5 h (bottom) in C_6D_5Br.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	3098.0	n.a.
3d	6.78	$H_{pyrrolyl}$	1	10013.2	64.6
4d	6.39	$H_{pyrrolyl}$	1	1831.5	11.8
homocoupled **2**	2.14, 2.13, 2.12, 2.11, 2.09	$Me_{pyrrolyl}$ (2 per molecule)	6	3011.5	3.2

Figure S49. ^1H NMR of the reaction of **1d-BBN** with 1-phenyl-1-propyne in $CDCl_3$ after HCl workup.

Catalytic Reaction of **1e-BBN** with 1-phenyl-1-propyne **(Table 3)**

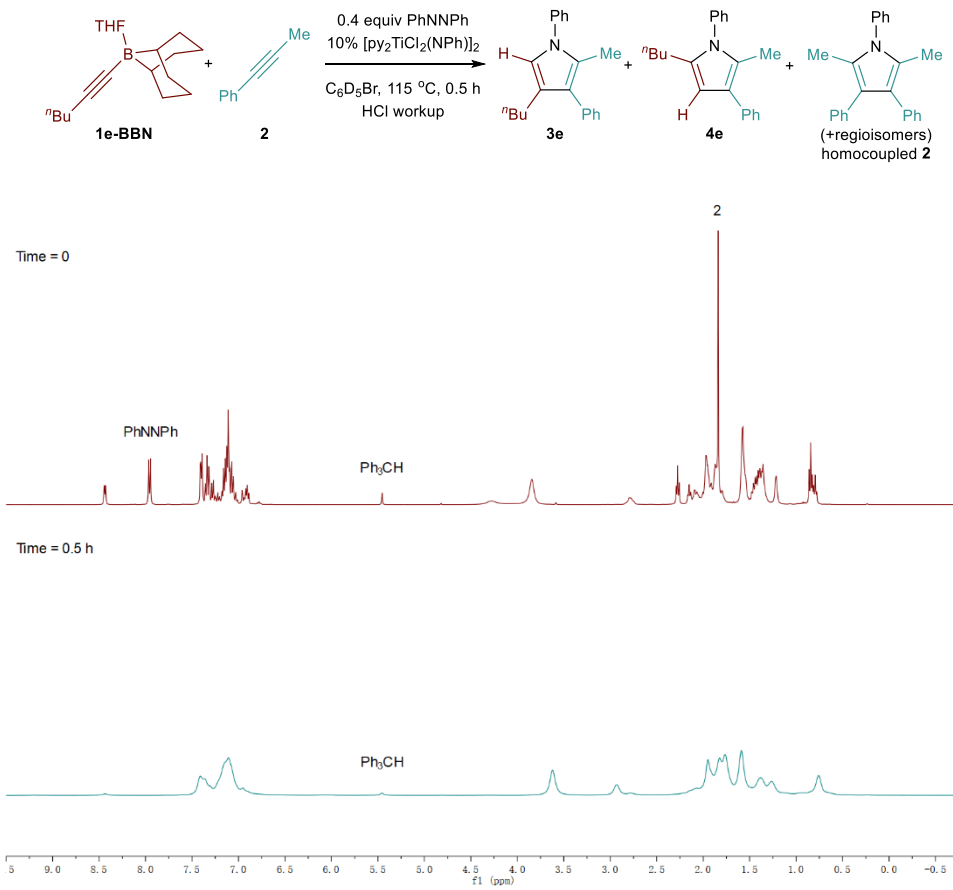


Figure S50. ^{1}H NMR of the reaction of **1e-BBN** with 1-phenyl-1-propyne at time = 0 (top), time = 0.5 h (bottom) in C_6D_5Br.

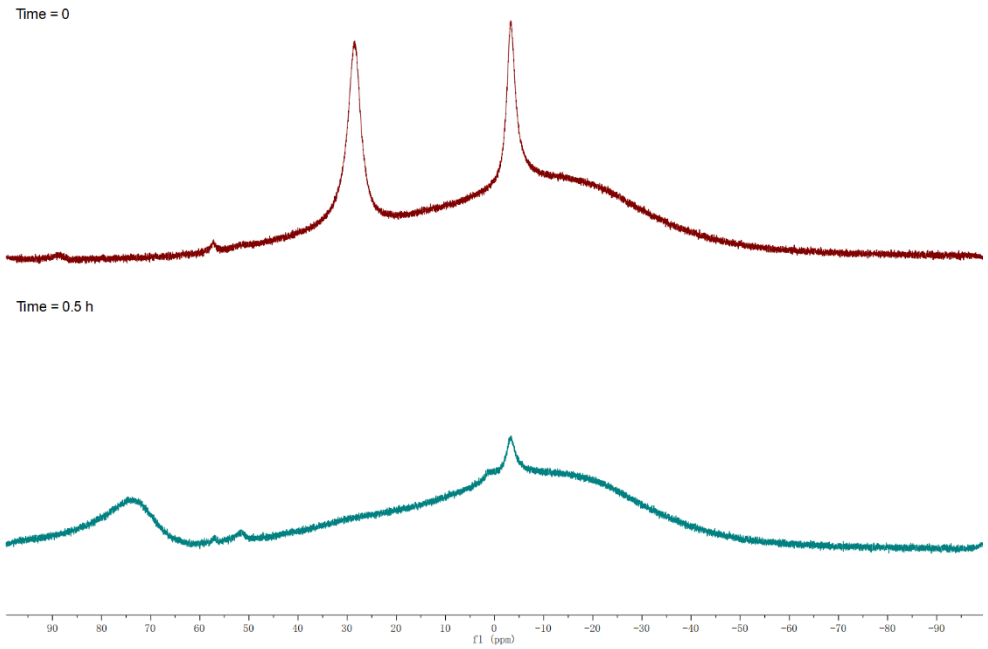
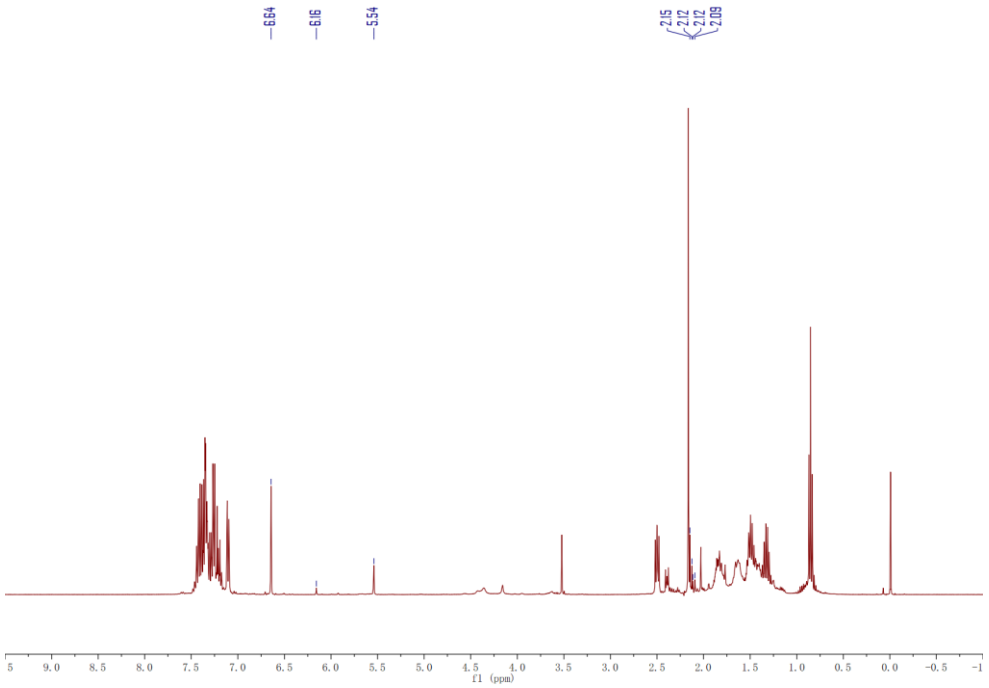


Figure S51. ^{11}B NMR of the reaction of **1e-BBN** with 1-phenyl-1-propyne at time = 0 (top), time = 0.5 h (bottom) in C_6D_5Br.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	3527.4	n.a.
3e	6.64	$H_{pyrrolyl}$	1	10587.6	60.0
4e	6.16	$H_{pyrrolyl}$	1	587.4	3.3
homocoupled **2**	2.15, 2.12, 2.12, 2.09	$Me_{pyrrolyl}$ (2 per molecule)	6	6246.3	5.9

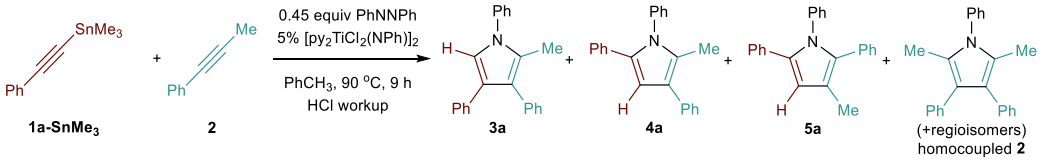
Figure S52. ^1H NMR of the reaction of **1e-BBN** with 1-phenyl-1-propyne in $CDCl_3$ after HCl workup.

General Procedure for Catalysis with Alkynyl Trialkylstannane as Substrate (Procedure C) (Table 3)

$[py_2TiCl_2(NPh)]_2$ (14.7 mg, 0.02 mmol, 0.05 equiv), alkynyl trialkylstannane (0.4 mmol, 1 equiv) and 0.5 mL of toluene stock solution containing 1-phenyl-1-propyne (46.5 mg, 0.4 mmol, 1 equiv), azobenzene (32.8 mg, 0.18 mmol, 0.45 equiv) and triphenylmethane (19.5 mg, 0.08 mmol, 0.2 equiv, internal standard) were added to an NMR tube. The reaction was then sealed and heated in a preheated oil bath at 90 °C for 9 h. No-D NMR spectra were collected before and after heating to monitor the reaction. The reaction was quenched with 10% HCl in methanol and extracted with EtOAc/H_2O. The organic phase was dried over $MgSO_4$, evaporated and characterized by NMR. The peak assignment of pyrrole products were performed based on the reported chemical shifts,[16–18,20–22] and the yields were calculated by the comparison of peak area integral with respect to the internal standard. The peak area of selected ^1H NMR peaks were calculated by Gaussian-Lorentzian fitting to omit the influence from minor baseline overlapping.[19]

Precaution: Trialkyltin species are highly toxic. Proper PPE is required. All the chemical and labware waste should be handled separately from the normal waste stream and quenched thoroughly.

Catalytic Reaction of **1a-SnMe$_3$** with 1-phenyl-1-propyne **(Table 3)**



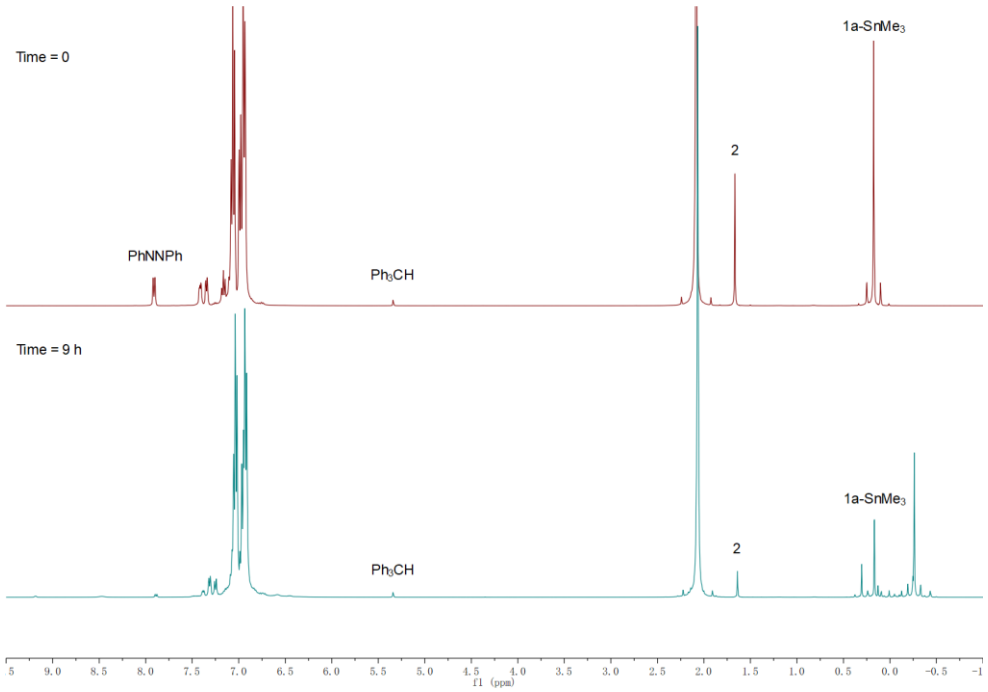


Figure S53. No-D ^{1}H NMR of the reaction of **1a-SnMe$_3$** with 1-phenyl-1-propyne at time = 0 (top), time = 9 h (bottom) in $PhCH_3$.

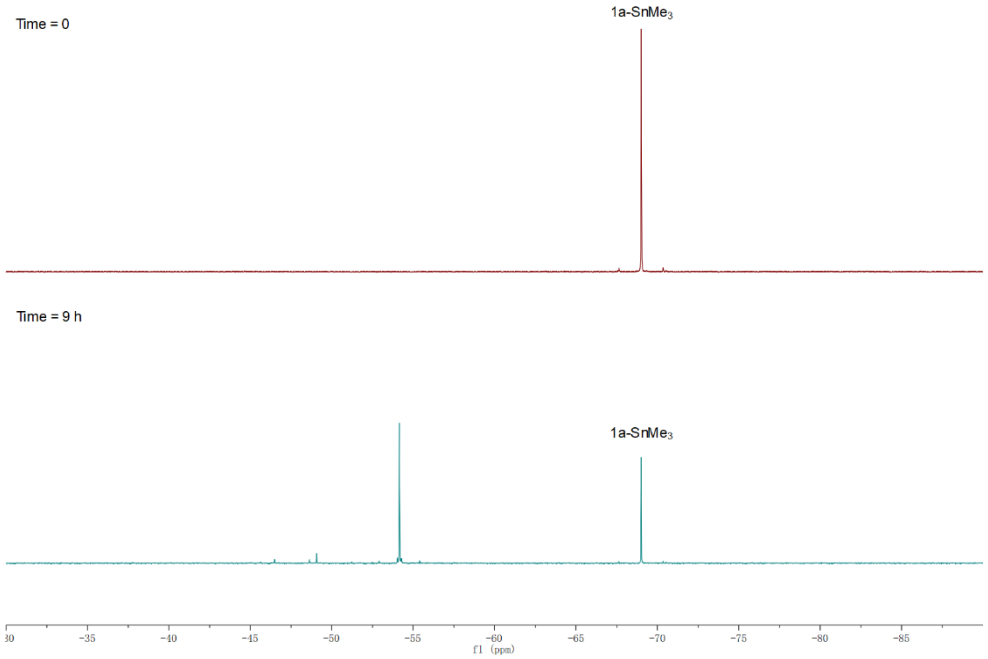
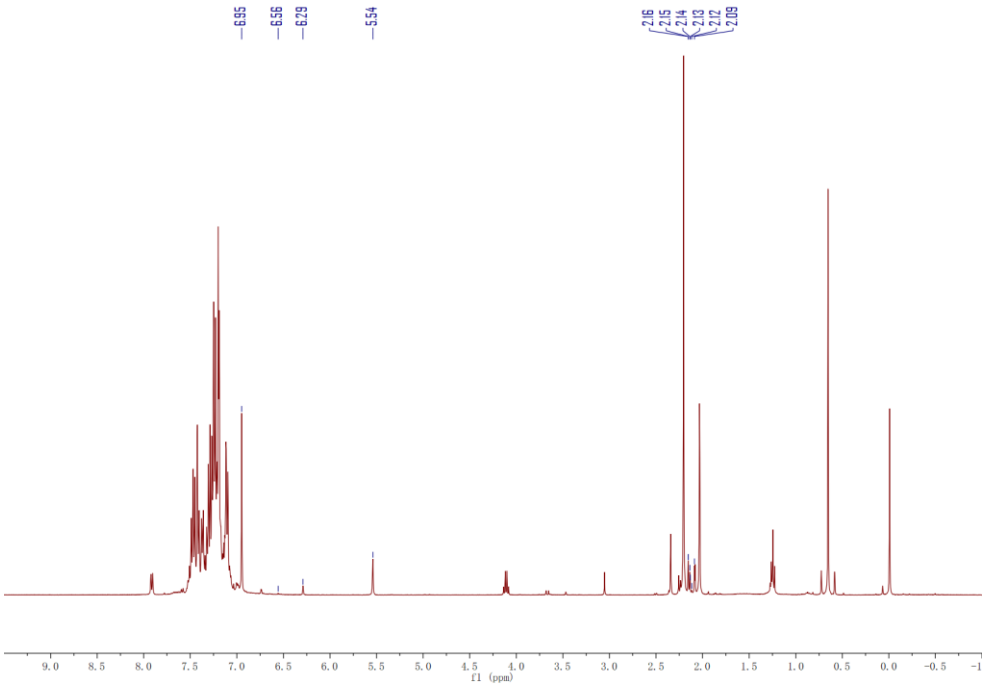


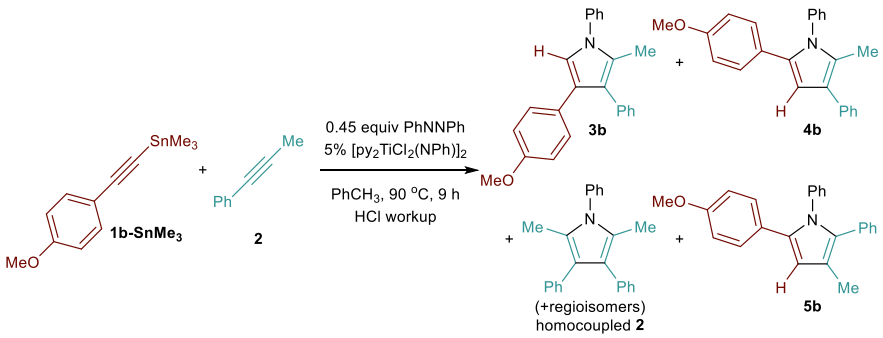
Figure S54. ^{119}Sn{^{1}H} NMR of the reaction of **1a-SnMe$_3$** with 1-phenyl-1-propyne at time = 0 (top), time = 9 h (bottom) in $PhCH_3$.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	5049.3	n.a.
3a	6.95	$H_{pyrrolyl}$	1	13354.3	52.9
4a	6.56	$H_{pyrrolyl}$	1	125.2	0.5
5a	6.29	$H_{pyrrolyl}$	1	1185.1	4.7
homocoupled **2**	2.16, 2.15, 2.14, 2.13 2.12, 2.09	$Me_{pyrrolyl}$ (2 per molecule)	6	7087.7	4.7

Figure S55. ^{1}H NMR of the reaction of **1a-SnMe$_3$** with 1-phenyl-1-propyne in $CDCl_3$ after HCl workup.

Catalytic Reaction of **1b-SnMe$_3$** with 1-phenyl-1-propyne **(Table 3)**



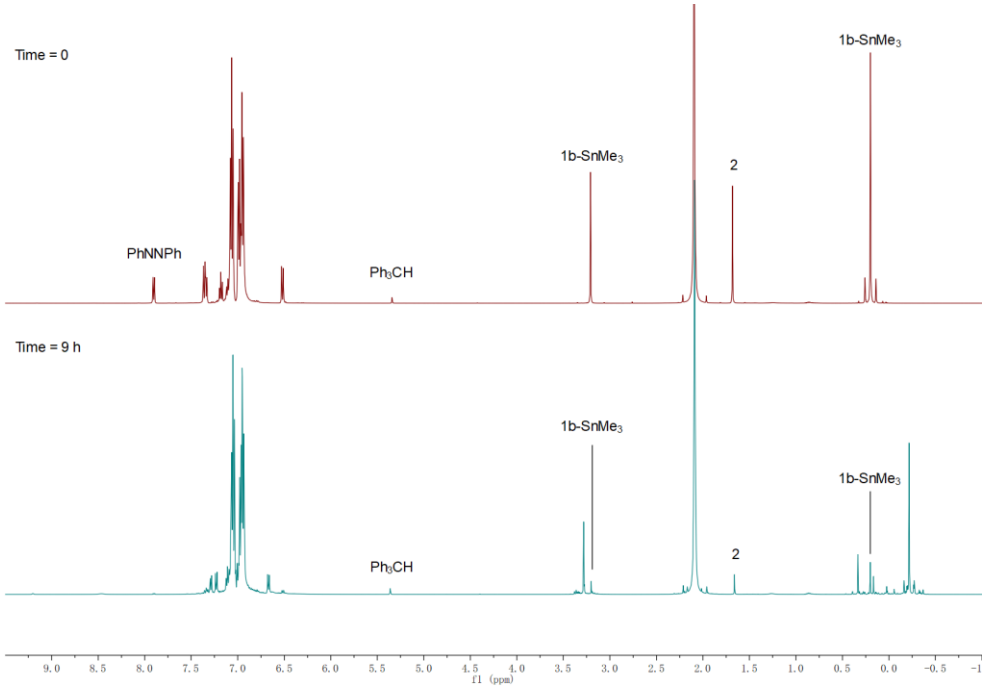


Figure S56. No-D ^{1}H NMR of the reaction of **1b-SnMe$_3$** with 1-phenyl-1-propyne at time = 0 (top), time = 9 h (bottom) in $PhCH_3$.

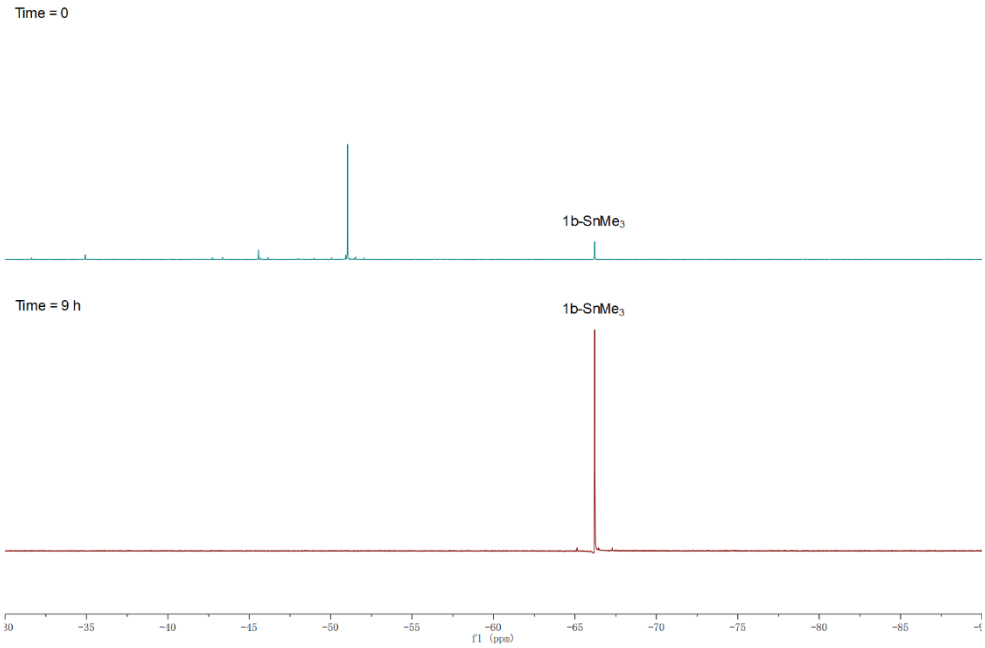
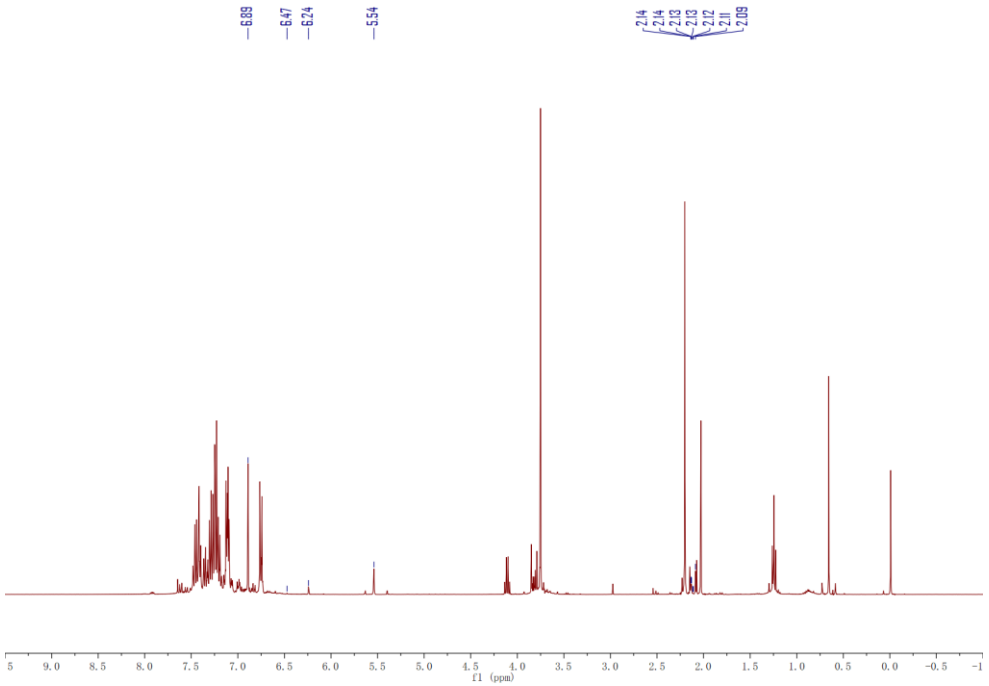


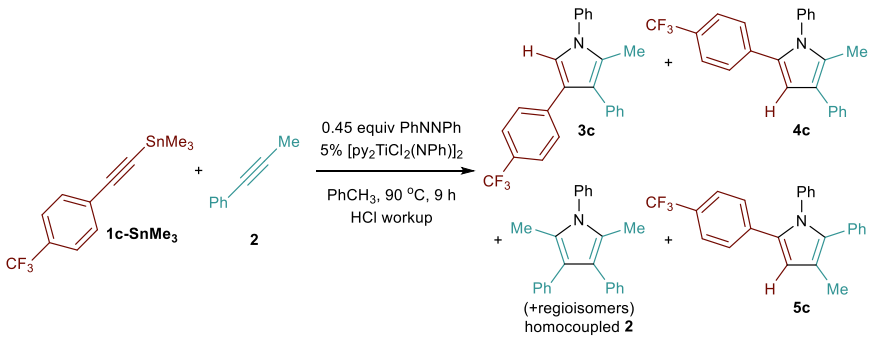
Figure S57. ^{119}Sn{^{1}H} NMR of the reaction of **1b-SnMe$_3$** with 1-phenyl-1-propyne at time = 0 (top), time = 9 h (bottom) in $PhCH_3$.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	3542.0	n.a.
3b	6.89	$H_{pyrrolyl}$	1	9469.0	53.5
4b	6.47	$H_{pyrrolyl}$	1	158.8	0.9
5b	6.24	$H_{pyrrolyl}$	1	980.0	5.5
homocoupled **2**	2.14, 2.14, 2.13, 2.13, 2.12, 2.11, 2.09	$Me_{pyrrolyl}$ (2 per molecule)	6	3861.5	3.6

Figure S58. ^{1}H NMR of the reaction of **1b-SnMe$_3$** with 1-phenyl-1-propyne in $CDCl_3$ after HCl workup.

Catalytic Reaction of **1c-SnMe$_3$** with 1-phenyl-1-propyne **(Table 3)**



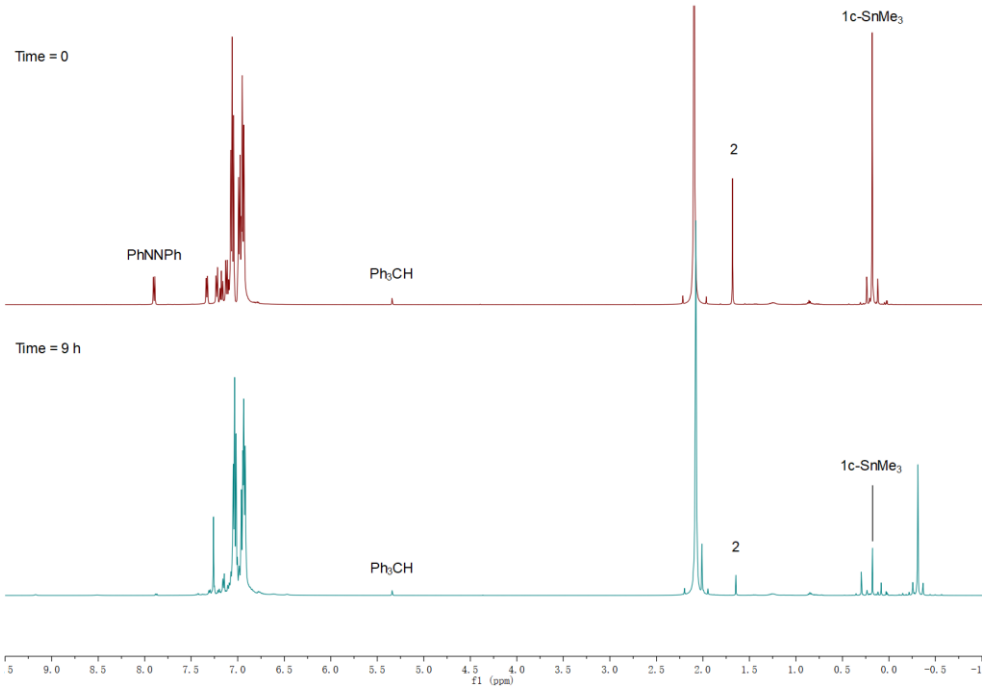


Figure S59. No-D ^{1}H NMR of the reaction of **1c-SnMe$_3$** with 1-phenyl-1-propyne at time = 0 (top), time = 9 h (bottom) in $PhCH_3$.

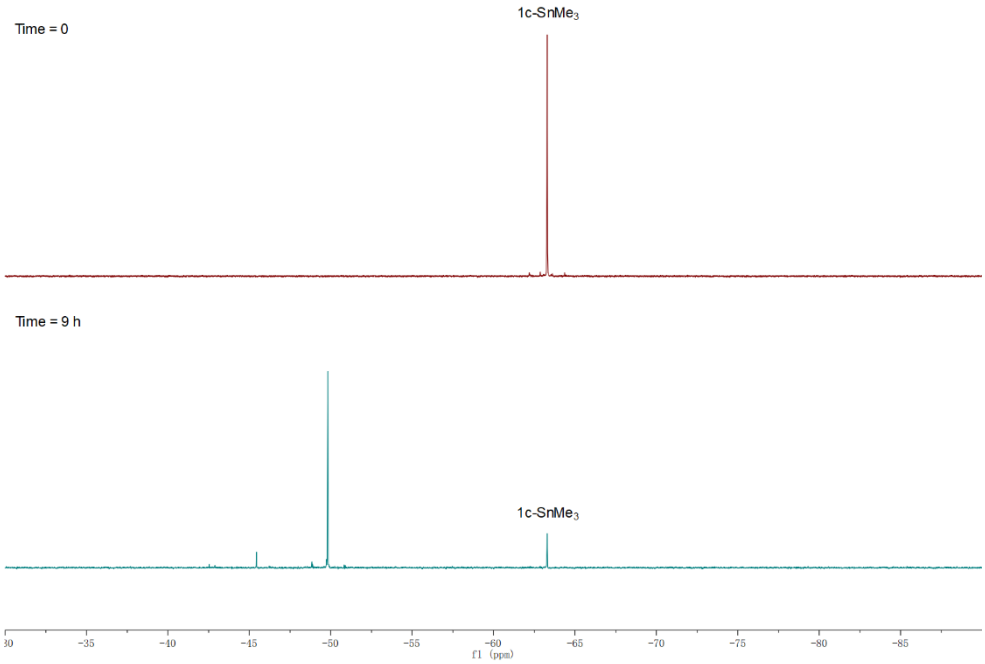


Figure S60. $^{119}Sn\{^{1}H\}$ NMR of the reaction of **1c-SnMe$_3$** with 1-phenyl-1-propyne at time = 0 (top), time = 9 h (bottom) in $PhCH_3$.

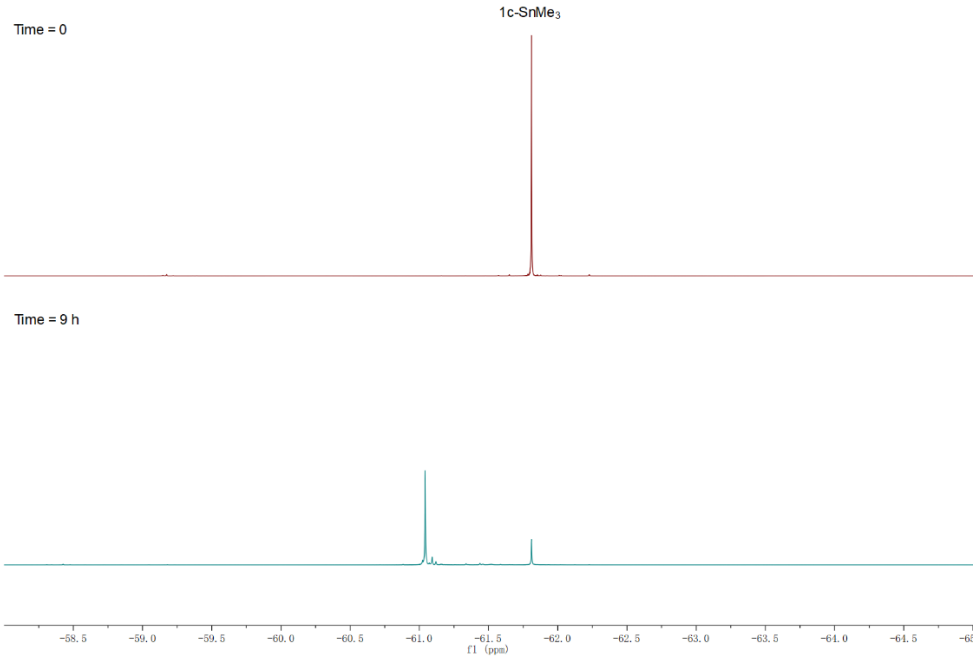
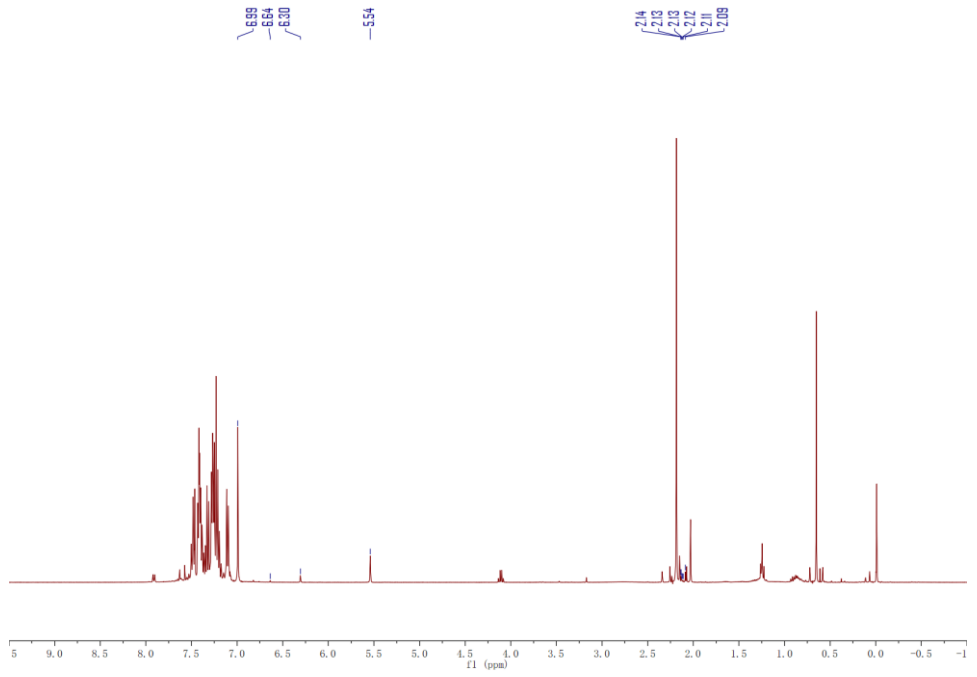


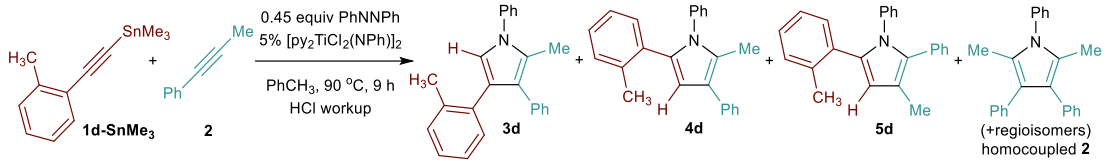
Figure S61. $^{19}F\{^{1}H\}$ NMR of the reaction of **1c-SnMe$_3$** with 1-phenyl-1-propyne at time = 0 (top), time = 9 h (bottom) in $PhCH_3$.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	5789.5	n.a.
3c	6.99	$H_{pyrrolyl}$	1	17397.6	60.1
4c	6.64	$H_{pyrrolyl}$	1	324.5	1.1
5c	6.30	$H_{pyrrolyl}$	1	1437.4	5.0
homocoupled **2**	2.14, 2.14, 2.13, 2.13, 2.12, 2.11, 2.09	$Me_{pyrrolyl}$ (2 per molecule)	6	3061.2	1.8

Figure S62. ^{1}H NMR of the reaction of **1c-SnMe$_3$** with 1-phenyl-1-propyne in $CDCl_3$ after HCl workup.

Catalytic Reaction of **1d-SnMe$_3$** with 1-phenyl-1-propyne **(Table 3)**



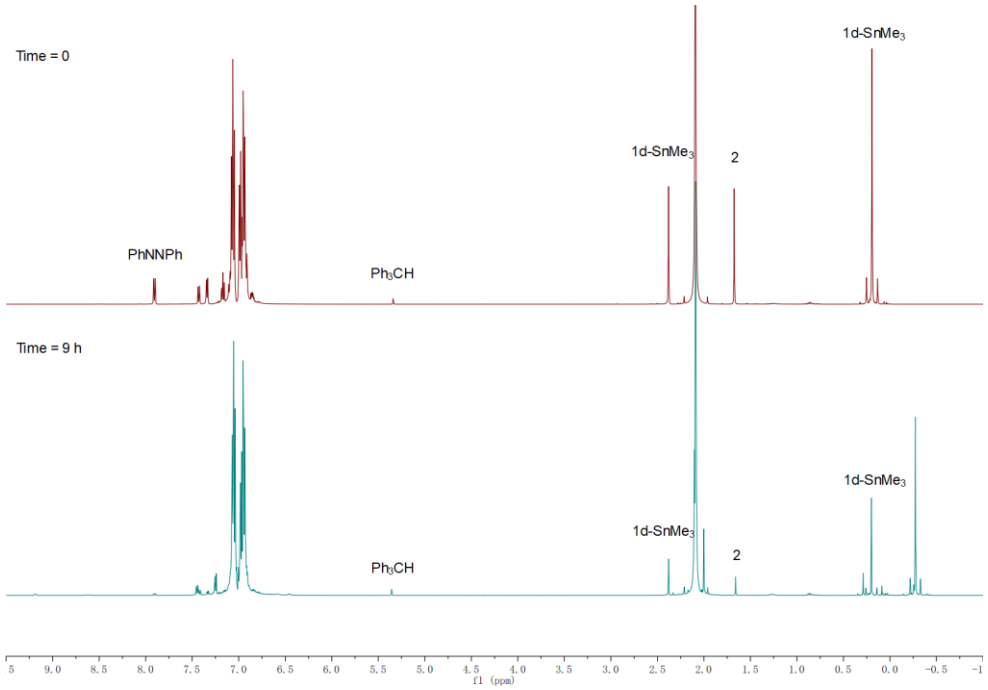


Figure S63. No-D ^{1}H NMR of the reaction of **1d-SnMe$_3$** with 1-phenyl-1-propyne at time = 0 (top), time = 9 h (bottom) in $PhCH_3$.

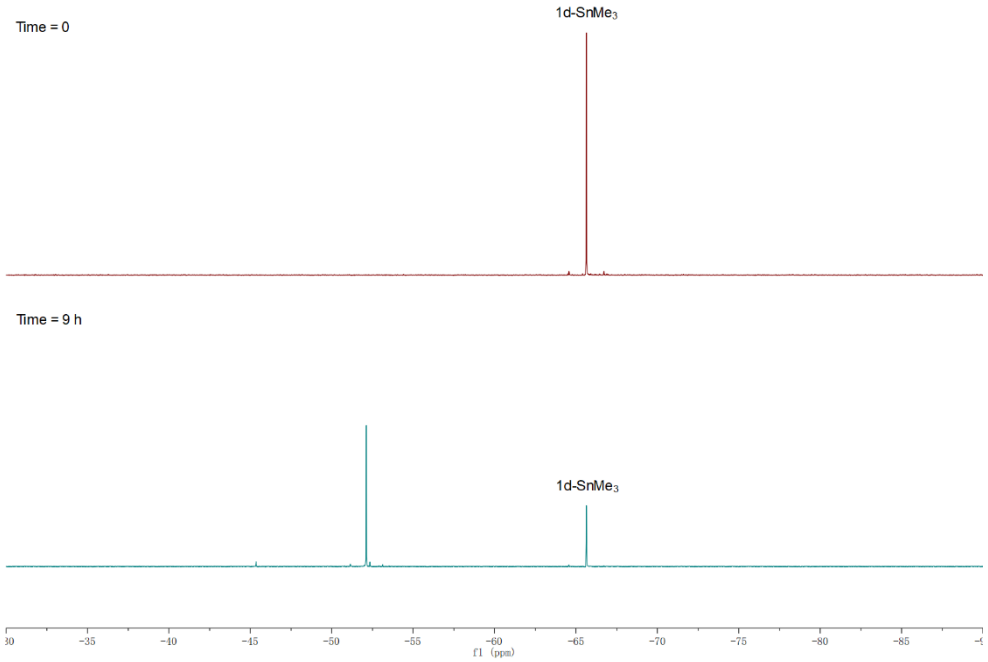
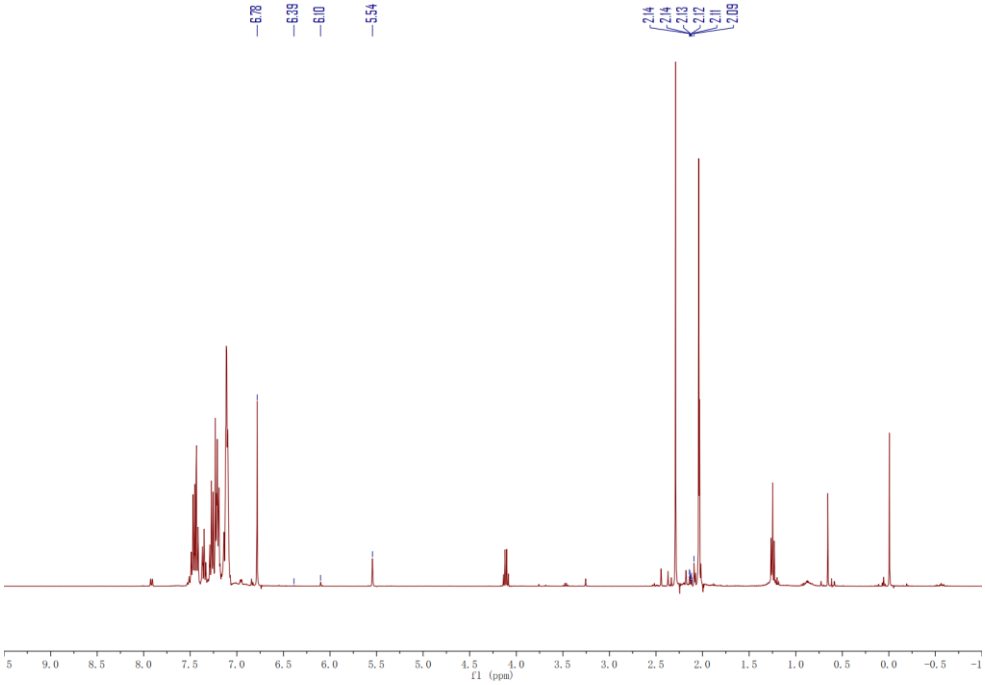


Figure S64. ^{119}Sn{^{1}H} NMR of the reaction of **1d-SnMe$_3$** with 1-phenyl-1-propyne at time = 0 (top),

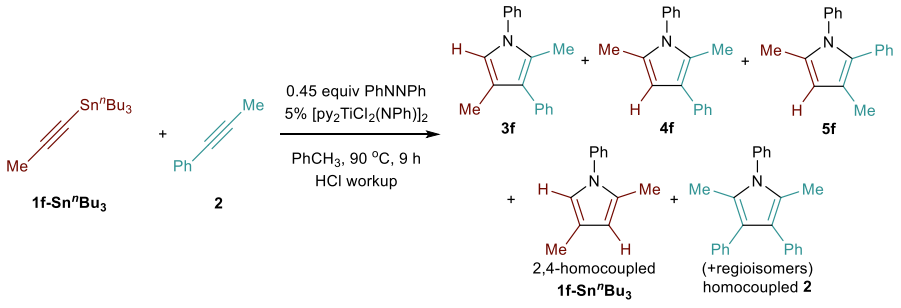
time = 9 h (bottom) in $PhCH_3$.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	5252.4	n.a.
3d	6.78	$H_{pyrrolyl}$	1	17946.9	68.3
4d	6.39	$H_{pyrrolyl}$	1	113.0	0.4
5d	6.10	$H_{pyrrolyl}$	1	662.8	2.5
homocoupled **2**	2.14, 2.14, 2.13, 2.12, 2.11, 2.09	$Me_{pyrrolyl}$ (2 per molecule)	6	4672.7	3.0

Figure S65. ^{1}H NMR of the reaction of **1d-SnMe$_3$** with 1-phenyl-1-propyne in $CDCl_3$ after HCl workup.

Catalytic Reaction of **1f-Sn^{n}Bu$_3$** with 1-phenyl-1-propyne **(Table 3)**



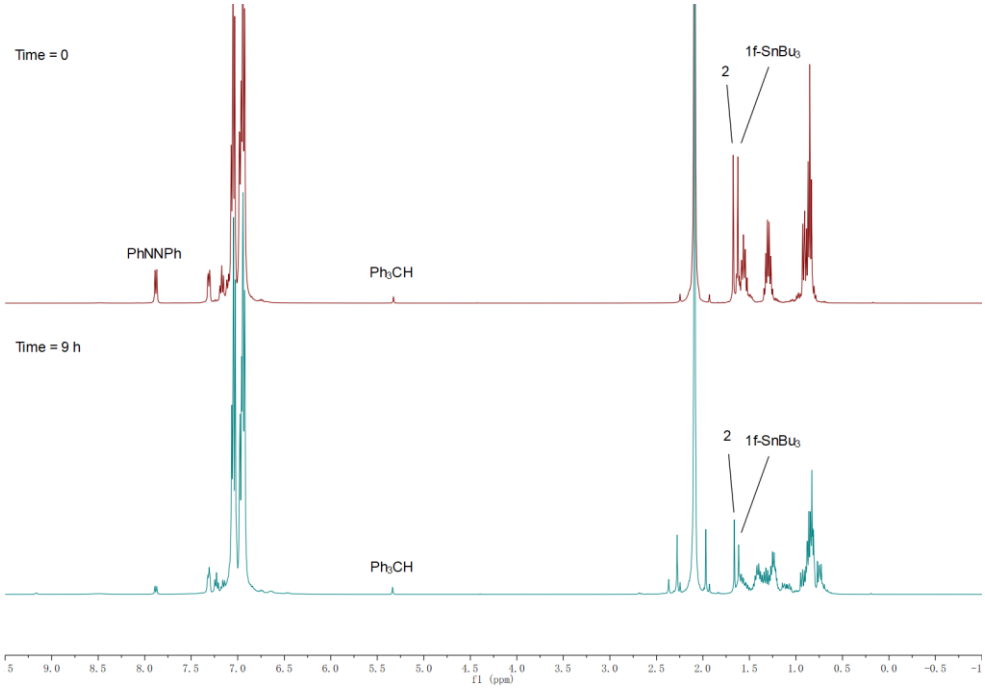


Figure S66. No-D ^{1}H NMR of the reaction of **1f-Sn^{n}Bu$_3$** with 1-phenyl-1-propyne at time = 0 (top), time = 9 h (bottom) in $PhCH_3$.

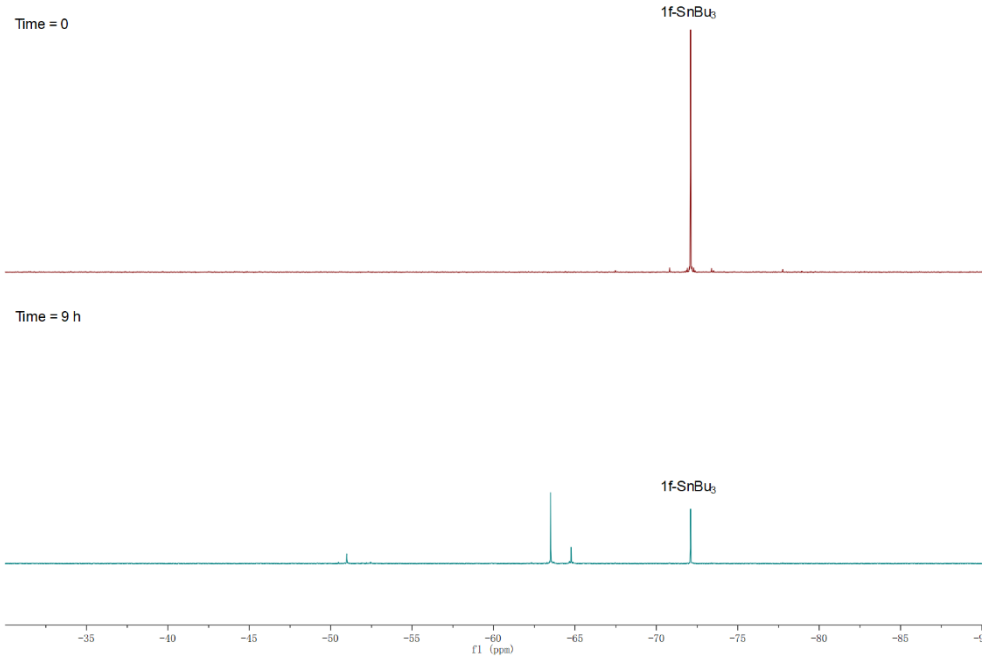
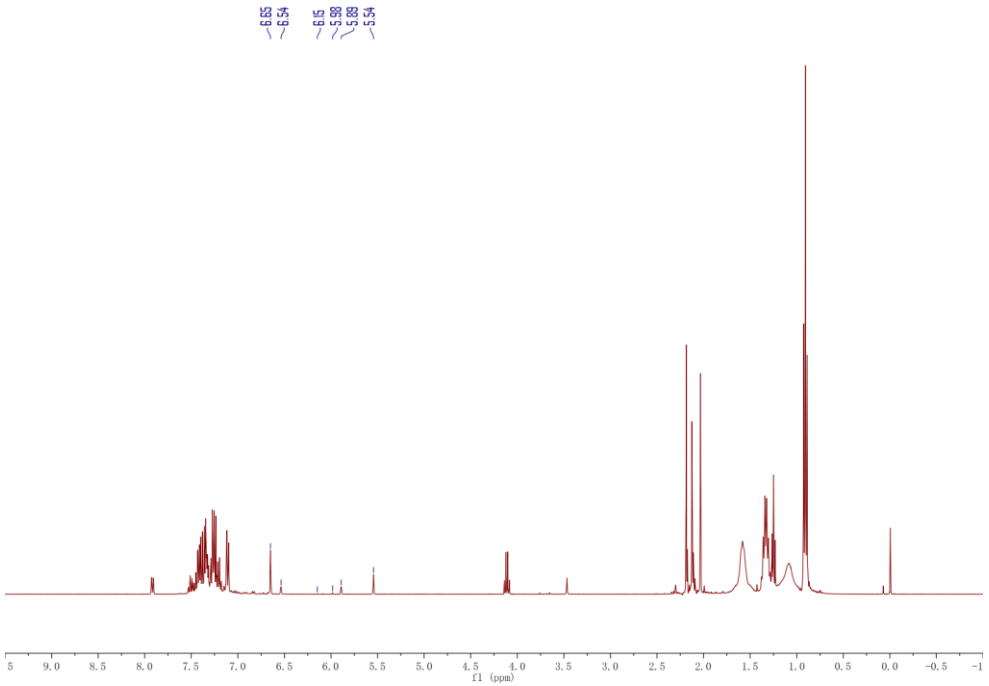


Figure S67. $^{119}Sn\{^{1}H\}$ NMR of the reaction of **1f-Sn^{n}Bu$_3$** with 1-phenyl-1-propyne at time = 0 (top), time = 9 h (bottom) in $PhCH_3$.



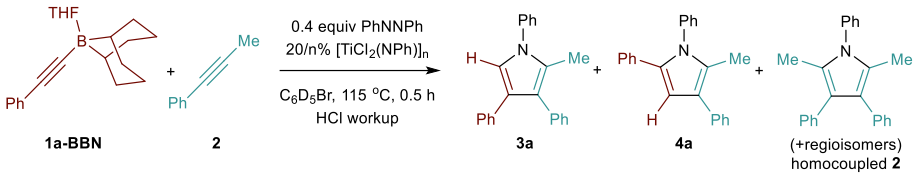
	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	3941.1	n.a.
3f	6.65	$H_{pyrrolyl}$	1	8607.3	43.7
4f	6.15	$H_{pyrrolyl}$	1	98.0	0.5
5f	5.98	$H_{pyrrolyl}$	1	282.9	1.4
2,4-homocoupled **1f-Sn^{n}Bu$_3$**	6.54, 5.89	$H_{pyrrolyl}$ (2 per molecule)	2	4117.4	10.4
homocoupled **2**	overlap[a]	$Me_{pyrrolyl}$ (2 per molecule)	6	n.d.	n.d.

[a]Peaks overlapped with the $Me_{pyrrolyl}$ peaks of **4f**, **4f'** and 2,4-homocoupled of **1f-Sn^{n}Bu$_3$**.

Figure S68. ^{1}H NMR of the reaction of **1f-Sn^{n}Bu$_3$** with 1-phenyl-1-propyne in $CDCl_3$ after HCl workup.

L Donor Effect Study

Reaction with No Pyridine (Figure 3A)



The reaction was performed following **Procedure B** using $[TiCl_2(NPh)]_n$ (4.2 mg, 0.02 mmol, absolute quantity of titanium, 0.2 equiv) as catalyst instead of $[py_2TiCl_2(NPh)]_2$.

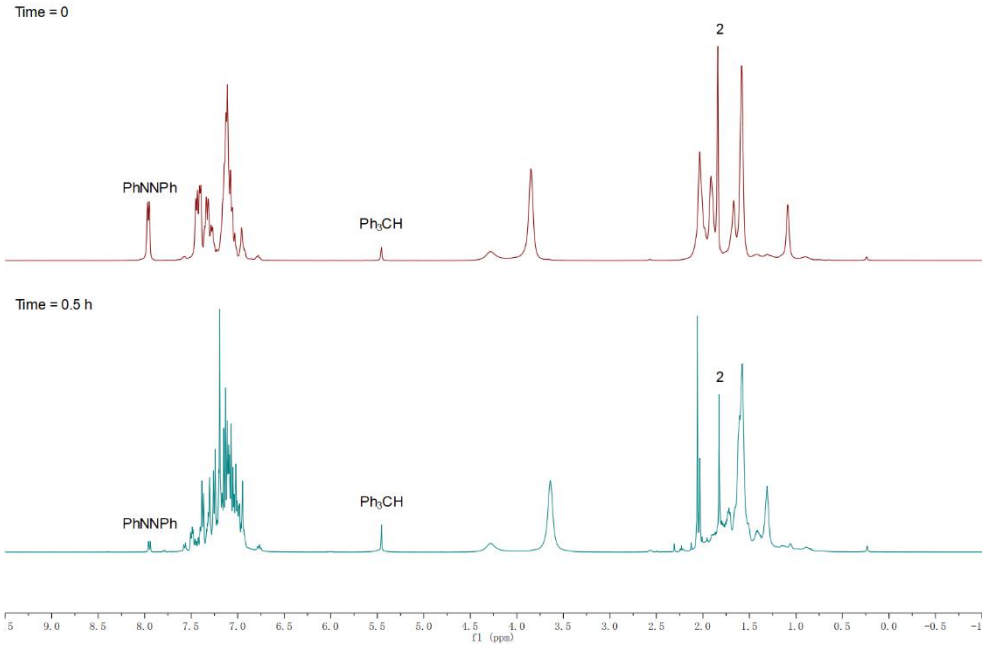


Figure S69. ^1H NMR of the reaction using $[TiCl_2(NPh)]_n$ at time = 0 (top), time = 0.5 h (bottom) in C_6D_5Br.

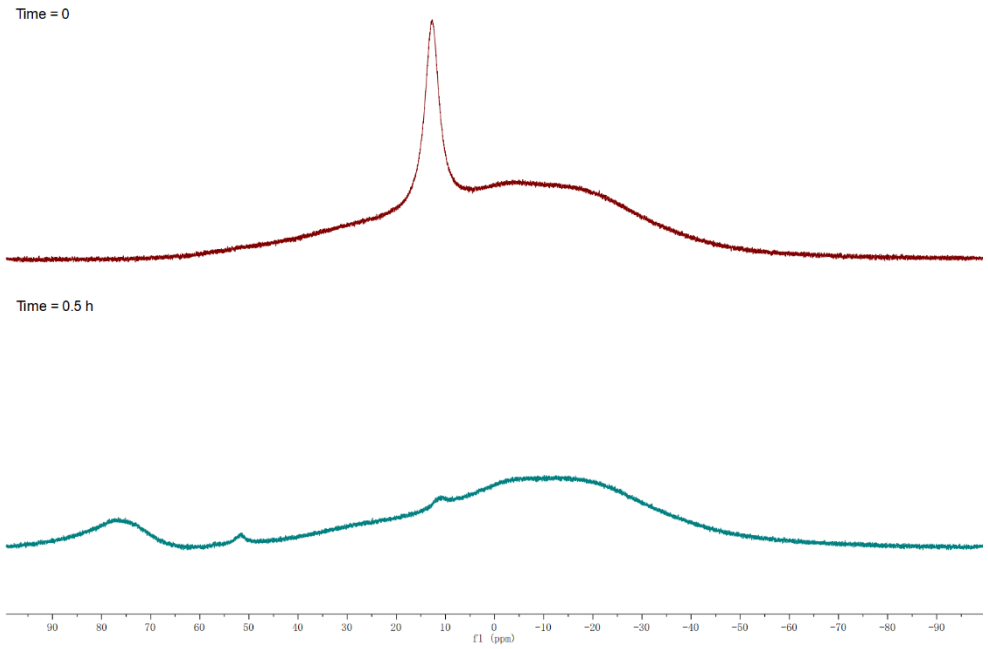
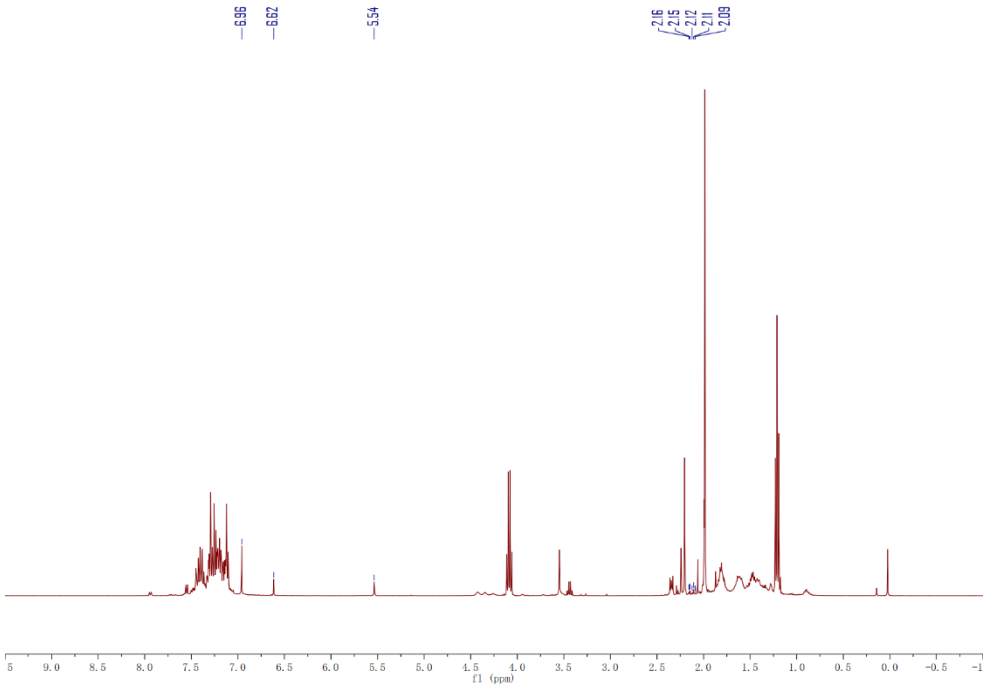


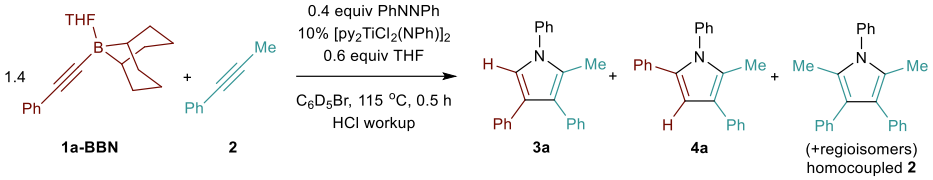
Figure S70. ^{11}B NMR of the reaction using $[TiCl_2(NPh)]_n$ at time = 0 (top), time = 0.5 h (bottom) in C_6D_5Br.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	2708.9	n.a.
3a	6.96	$H_{pyrrolyl}$	1	4589.7	33.9
4a	6.62	$H_{pyrrolyl}$	1	1765.2	13.0
homocoupled **2**	2.16, 2.15, 2.12, 2.11, 2.09	$Me_{pyrrolyl}$ (2 per molecule)	6	3603.2	4.4

Figure S71. ^1H NMR of the reaction using $[TiCl_2(NPh)]_n$ in $CDCl_3$ after HCl workup.

Reaction with Excess *B*-phenylethynyl-9-BBN as Pyridine Scavenger (Figure 3B)



The reaction was performed following **Procedure B** with higher 1a-BBN (41.2 mg, 0.14 mmol, 1.4 equiv) loading and THF (4.3 mg, 0.06 mmol, 0.6 equiv) as additive.

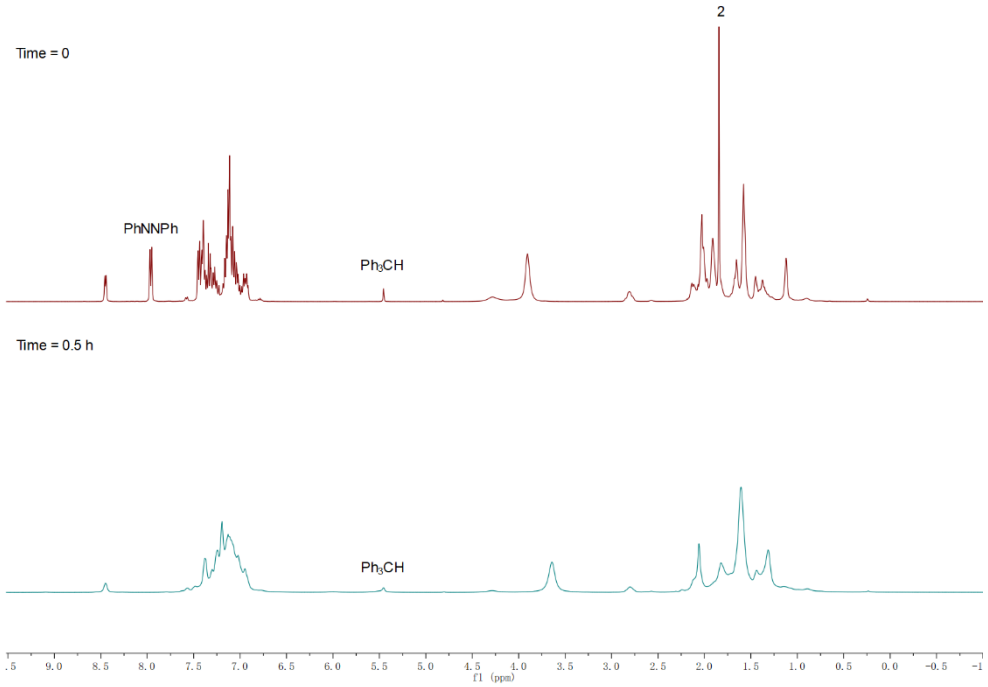


Figure S72. ^{1}H NMR of the reaction with excess **1a-BBN** at time = 0 (top), time = 0.5 h (bottom) in C_6D_5Br.

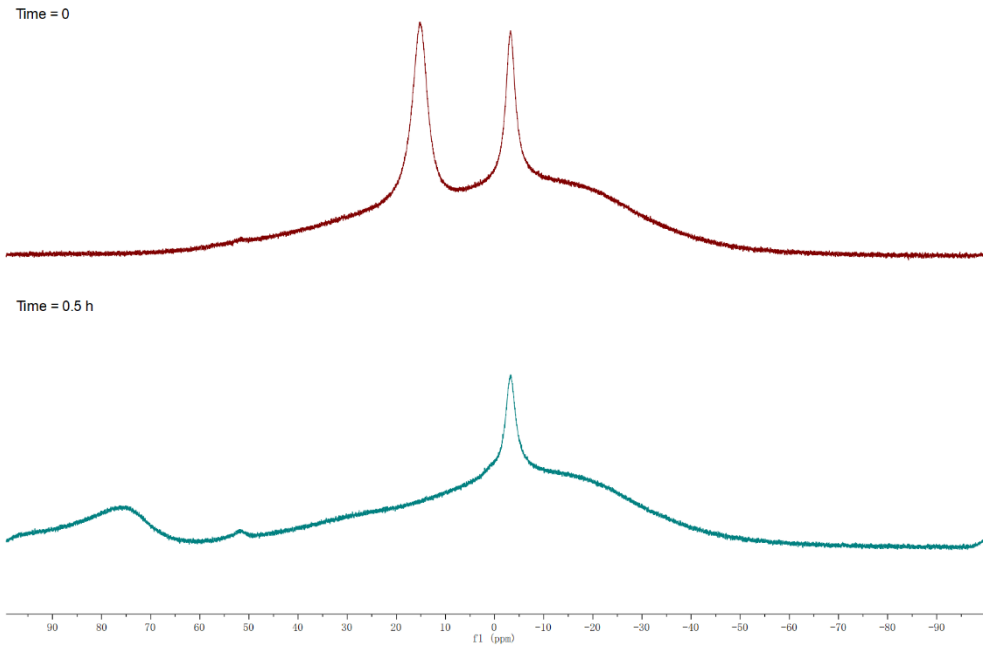
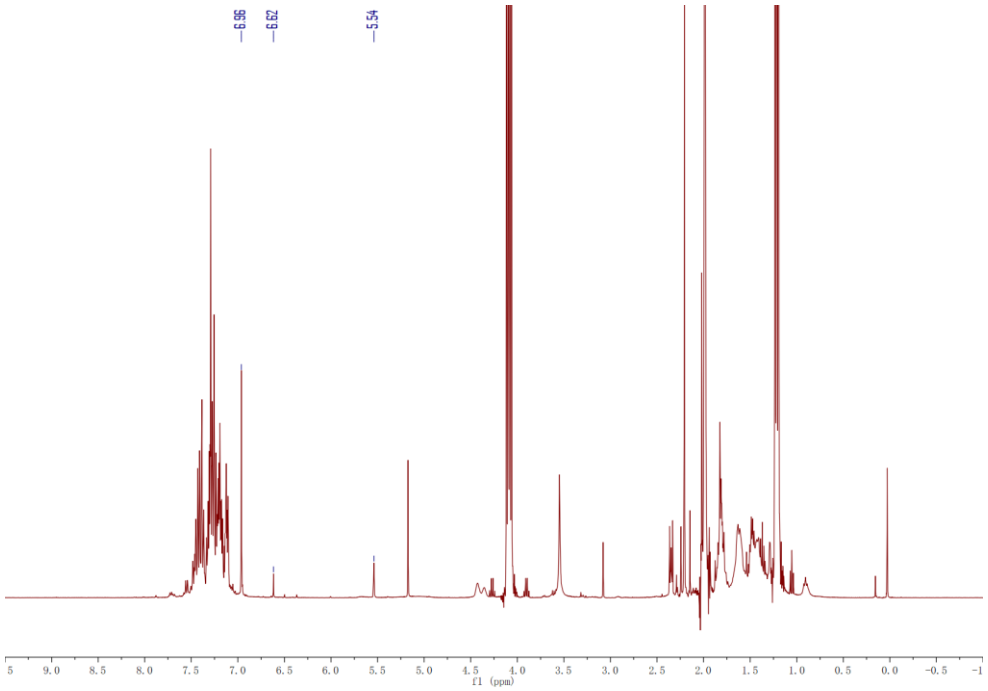


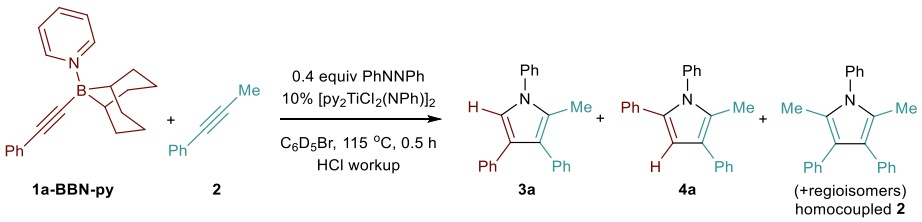
Figure S73. ^{11}B NMR of the reaction with excess **1a-BBN** at time = 0 (top), time = 0.5 h (bottom) in C_6D_5Br.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	1342.0	n.a.
3a	6.96	$H_{pyrrolyl}$	1	3910.8	58.3
4a	6.62	$H_{pyrrolyl}$	1	444.7	6.6
homocoupled **2**	not found	$Me_{pyrrolyl}$ (2 per molecule)	6	n.a.	n.d.

Figure S74. ^{1}H NMR of the reaction with excess **1a-BBN** in $CDCl_3$ after HCl workup.

Reaction with Pyridine-Adduct of *B*-phenylethynyl-9-BBN (Figure 3C)



The reaction was performed following **Procedure B** using **1a-BBN-py** (30.1 mg, 0.1 mmol, 1 equiv) as heterocoupling partner instead of **1a-BBN**.

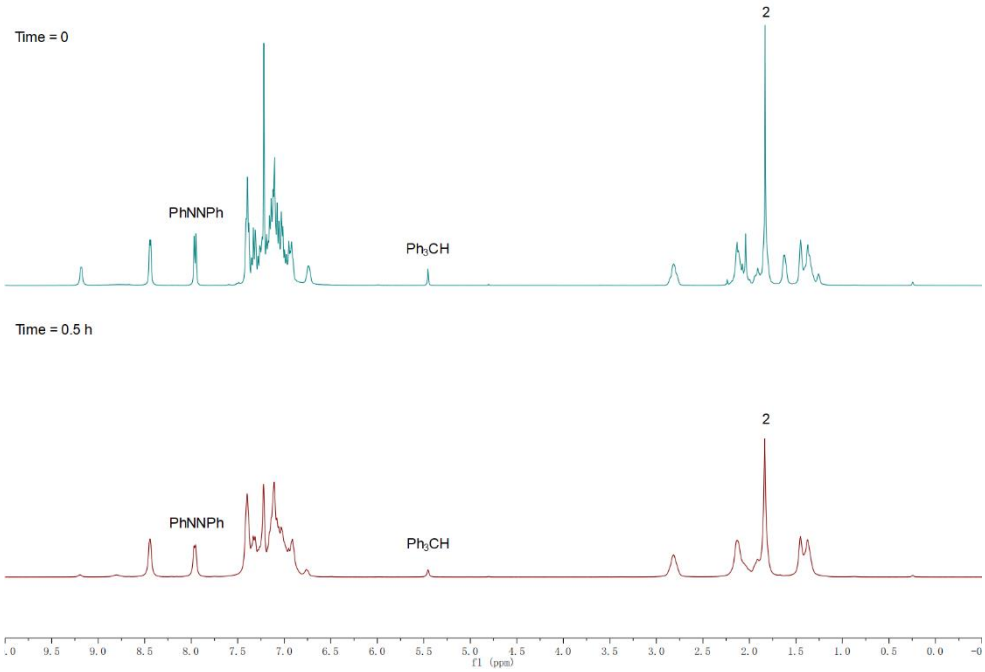


Figure S75. ^{1}H NMR of the reaction of **1a-BBN-py** at time = 0 (top), time = 0.5 h (bottom) in C_6D_5Br.

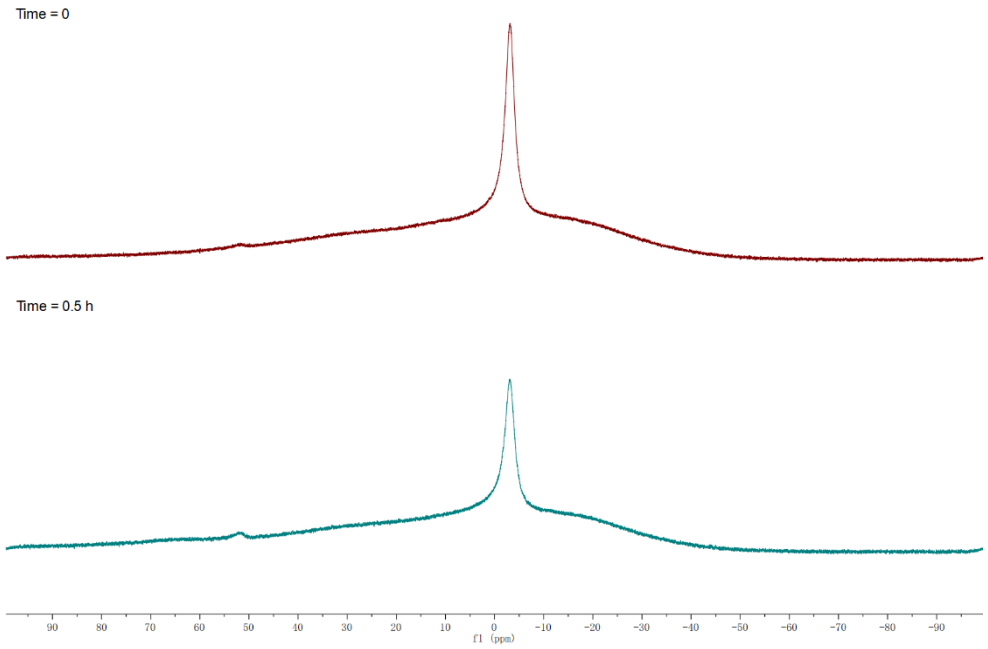
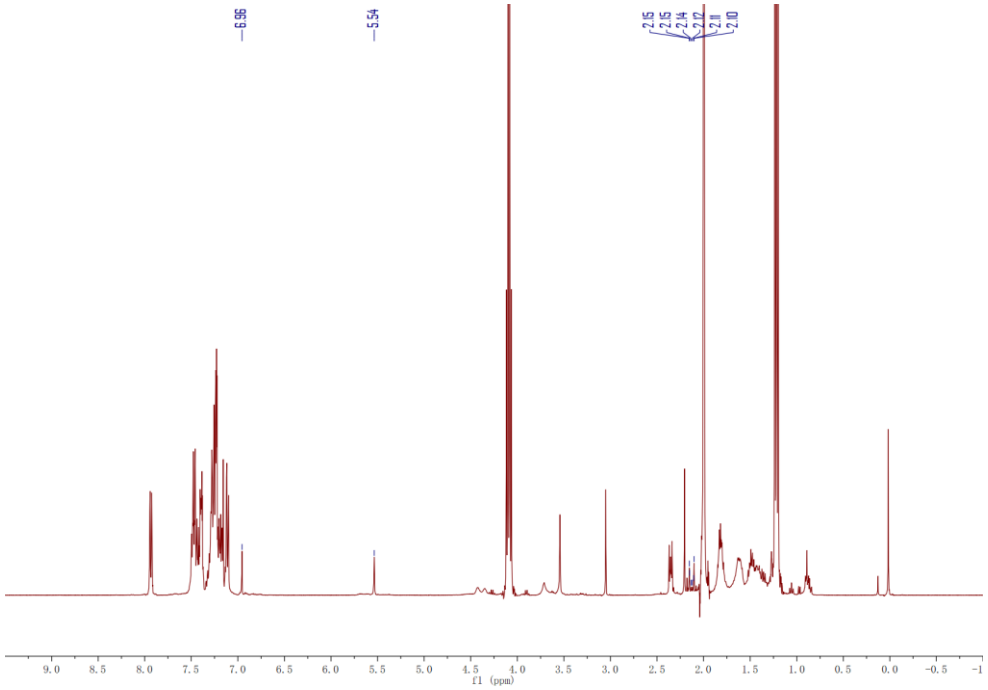


Figure S76. ^{11}B NMR of the reaction of **1a-BBN-py** at time = 0 (top), time = 0.5 h (bottom) in C_6D_5Br.

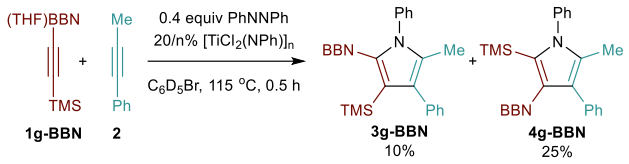


	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	2978.9	n.a.
3a	6.96	$H_{pyrrolyl}$	1	1654.2	11.1
4a	not found	$H_{pyrrolyl}$	1	n.a.	n.d.
homocoupled **2**	2.15, 2.15, 2.14, 2.12, 2.11, 2.10	$Me_{pyrrolyl}$ (2 per molecule)	6	2281.8	2.6

Figure S77. ^1H NMR of the reaction of **1a-BBN-py** in $CDCl_3$ after HCl workup.

Directing Group Strength Comparisons

Comparison Between TMS and 9-BBN (Figure 5, Top)



The reaction of **1g-BBN** was performed following **Procedure B** using $[TiCl_2(NPh)]_2$ as catalyst (4.2 mg, 0.02 mmol, absolute quantity of titanium, 0.2 equiv) as catalyst instead of $[py_2TiCl_2(NPh)]_2$, and the reaction was not quenched by the HCl workup. Instead the NMR tube was transferred into the glovebox after heating and taking t = 0.5 h NMR spectra. C_6D_6 (0.5 mL) was added to the reaction mixture, and the NMR tube was re-sealed and taken out of the glovebox. The reaction mixture was then characterized by ^1H NMR, ^1H–^{15}N HMBC and NOESY. **4g-BBN** was found to be the major product.

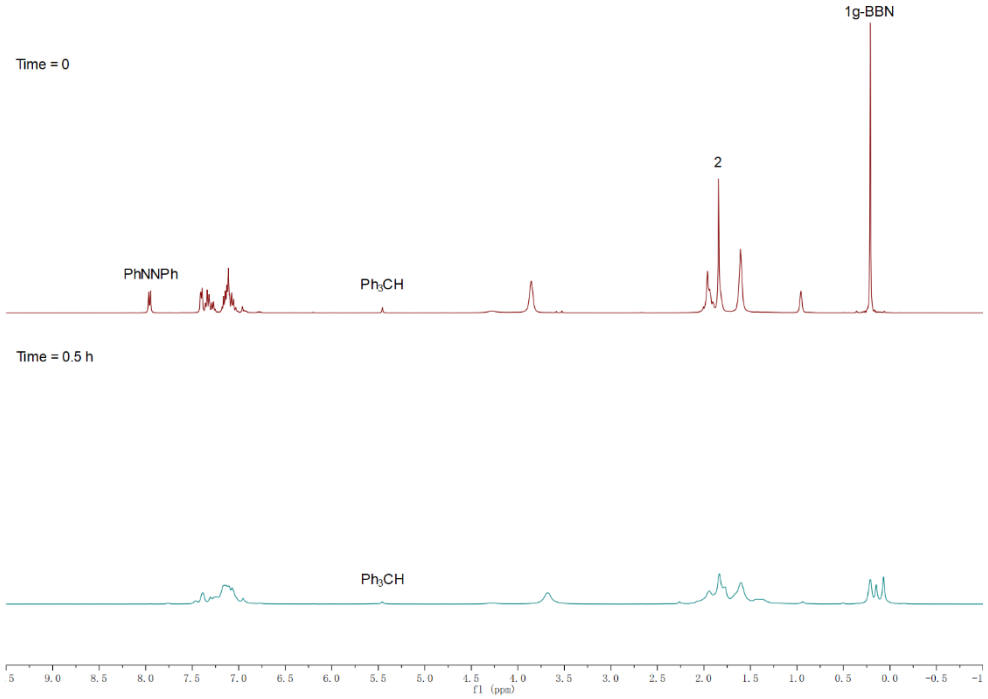


Figure S78. ^1H NMR in C_6D_5Br of the reaction of **1g-BBN** at time = 0 (top), time = 0.5 h (bottom).

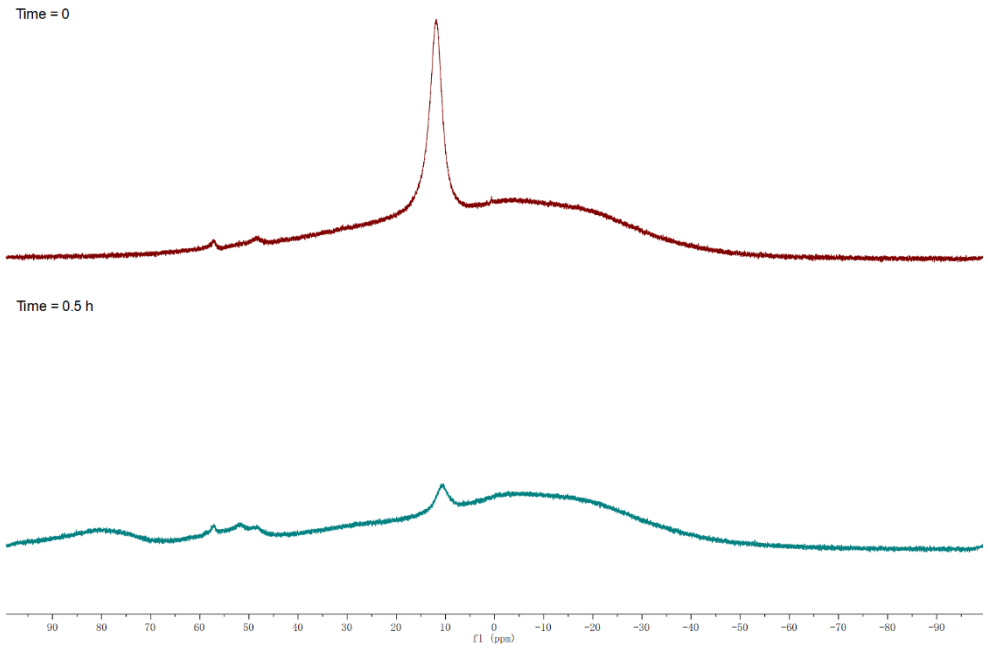
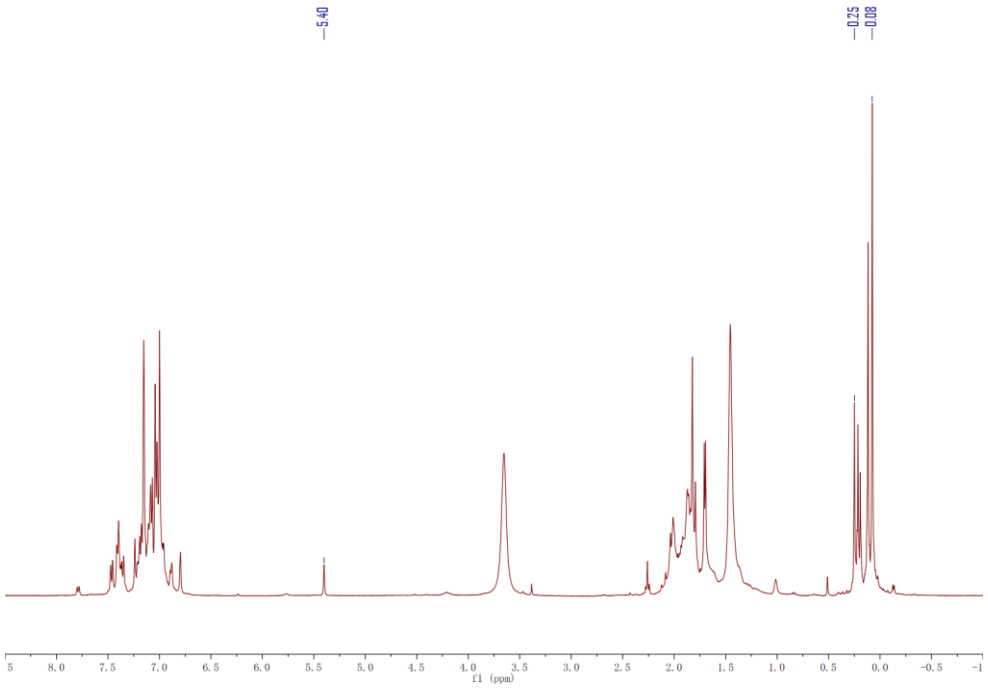


Figure S79. ^{11}B NMR in C_6D_5Br of the reaction of **1g-BBN** at time = 0 (top), time = 0.5 h (bottom).



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.40	Ph_3C-H	1	2637.0	n.a.
3g-BBN	0.25	$TMS_{pyrrolyl}$	9	11494.0	9.7
4g-BBN	0.08	$TMS_{pyrrolyl}$	9	30159.4	25.4

Figure S80. ^1H NMR of the reaction product mixture of **1g-BBN** in C_6D_5Br/C_6D_6 (1:1, v/v). Chemical shifts were referenced to the proton signal of the internal standard triphenylmethane (Ph_3CH, s, 5.40 ppm).

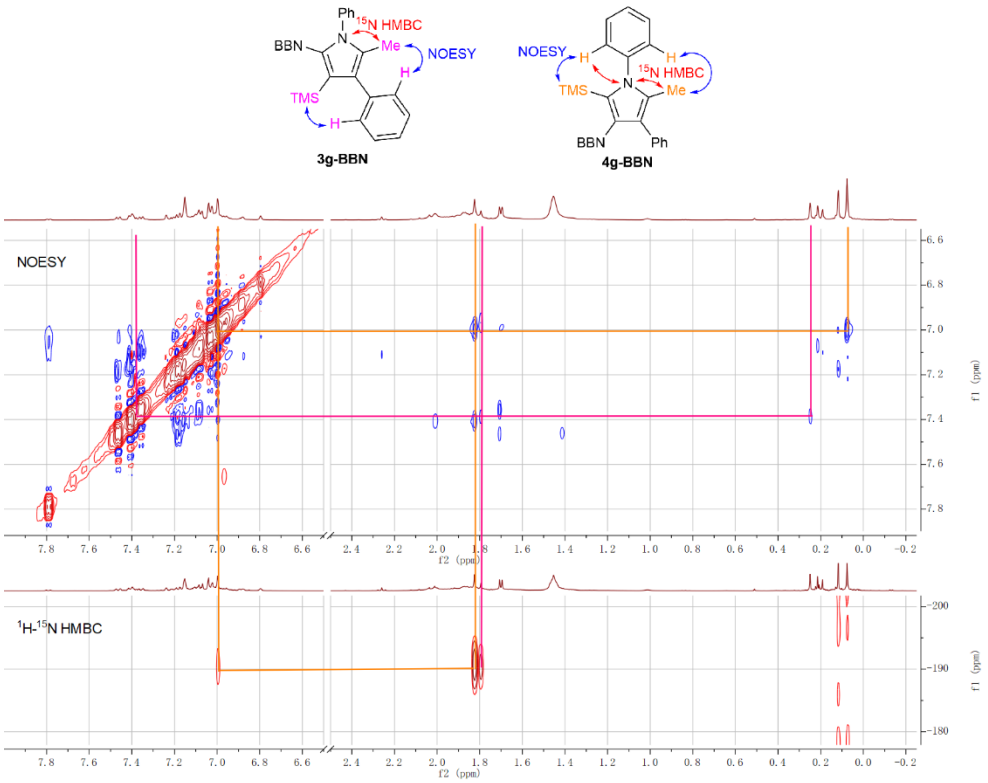
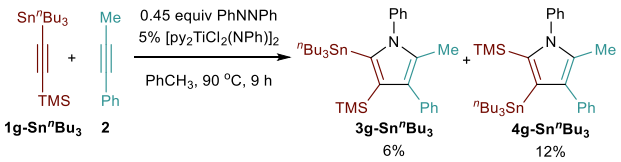


Figure S81. NOESY (top) and ^{1}H–^{15}N HMBC (bottom) NMR spectra of the reaction product mixture of **1g-BBN** in C_6D_5Br/C_6D_6 (1:1, v/v).

Comparison Between TMS and Sn^{n}Bu$_3$ (Figure 5, Bottom)



The reaction of **1g-Sn^{n}Bu$_3$** was performed following **Procedure C** without being quenched by the HCl workup. Instead the NMR tube was transferred into the glovebox after heating and taking t = 0.5 h NMR spectra. The reaction was diluted with toluene, filtered and evaporated under vacuum. The crude mixture was dissolved in CD_2Cl_2 and characterized by ^{1}H NMR and NOESY. The solution was then was extracted by EtOAc/H_2O, during which the Sn^{n}Bu$_3$ moiety was hydrolyzed while the TMS moiety remained. The organic phase was then dried by $MgSO_4$, evaporated, redissoved in $CDCl_3$ and characterized by ^{1}H NMR, ^{1}H–^{13}C and ^{1}H–^{15}N HMBC and NOESY. **4g-Sn^{n}Bu$_3$** was found to be the major product.

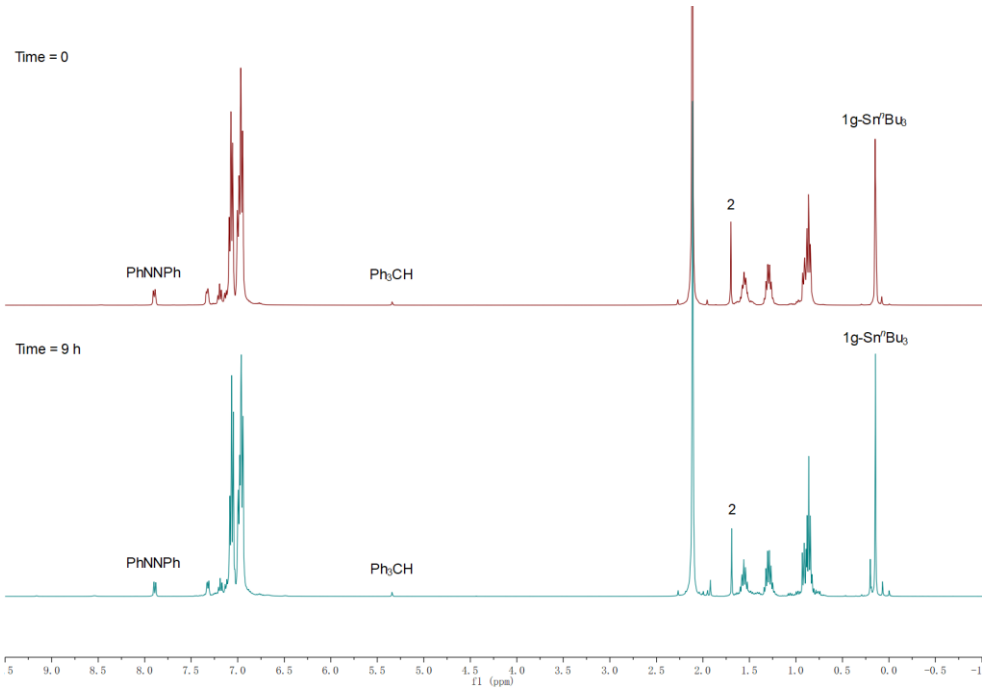


Figure S82. No-D ^{1}H NMR of the reaction of **1g-Sn^{n}Bu$_3$** at time = 0 (top), time = 9 h (bottom) in $PhCH_3$.

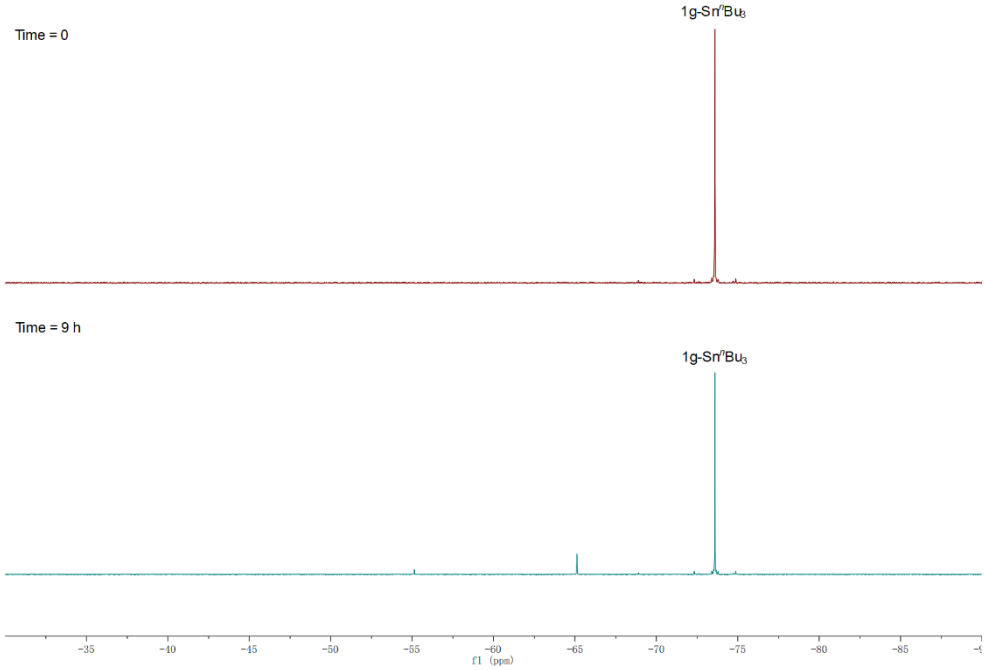


Figure S83. ^{119}Sn{^{1}H} NMR of the reaction of **1g-Sn^{n}Bu$_3$** at time = 0 (top), time = 9 h (bottom) in $PhCH_3$. Two new ^{119}Sn{^{1}H} signals observed

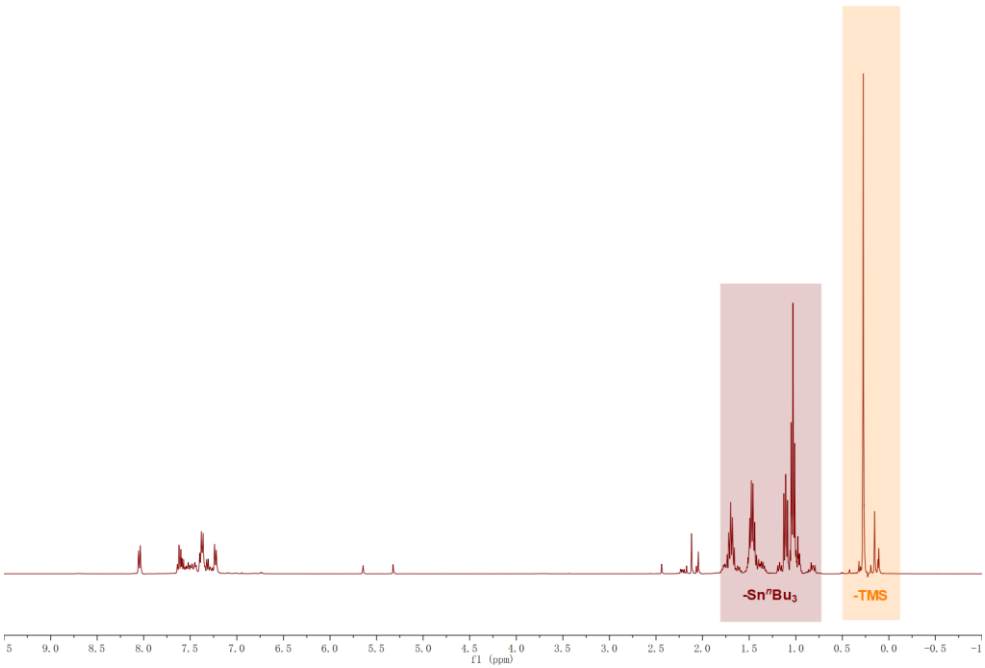


Figure S84. ^{1}H NMR of the reaction of **1g-Sn^{n}Bu$_3$** in CD_2Cl_2.

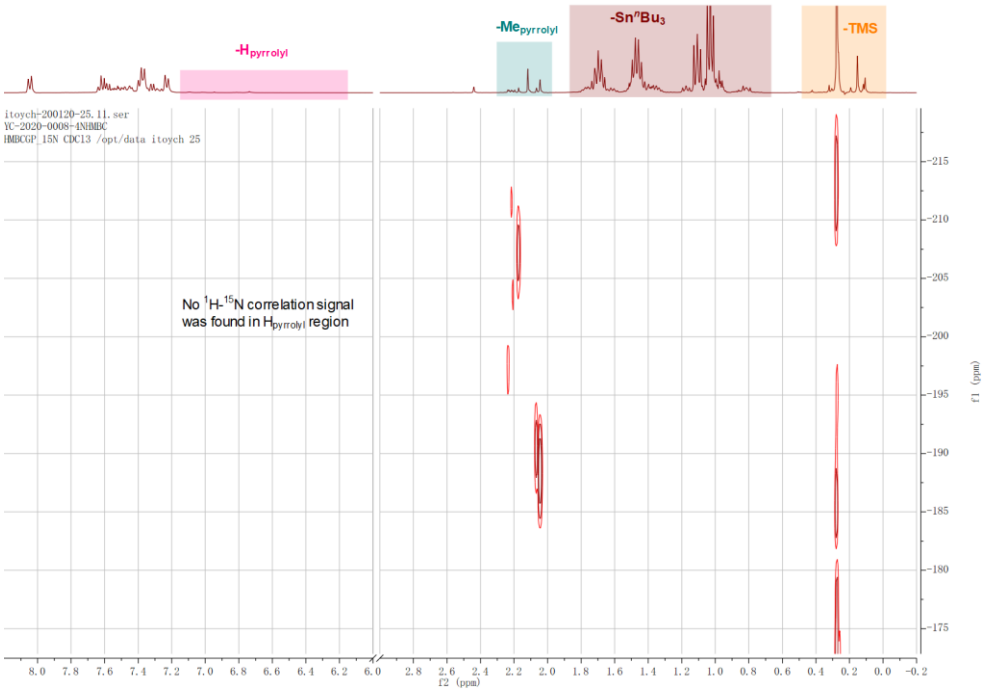


Figure S85. ^{1}H–^{15}N HMBC of the reaction of **1g-Sn^{n}Bu$_3$** in CD_2Cl_2.

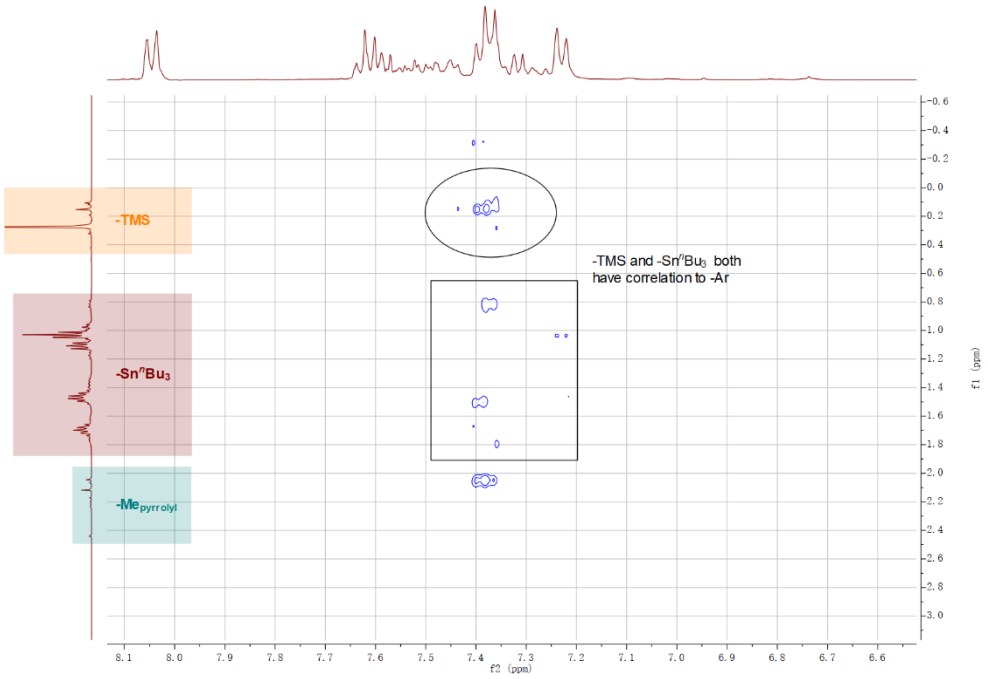


Figure S86. NOESY NMR spectrum of the reaction of **1g-Sn^{n}Bu$_3$** in CD_2Cl_2.

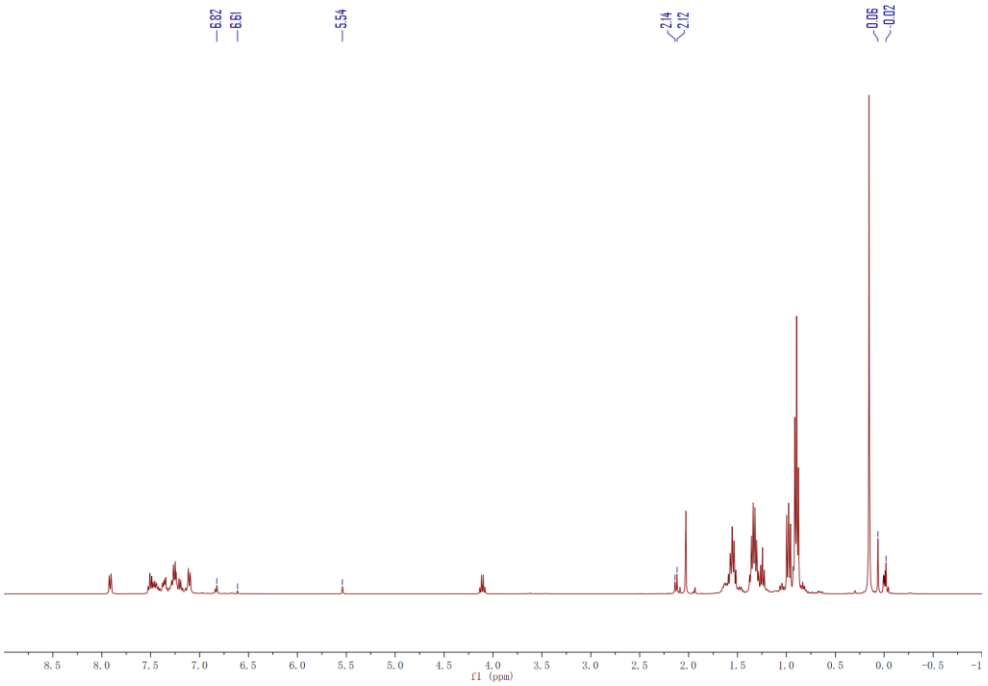


Figure S87. ^{1}H NMR of the reaction of **1g-Sn^{n}Bu$_3$** in $CDCl_3$ after extraction.

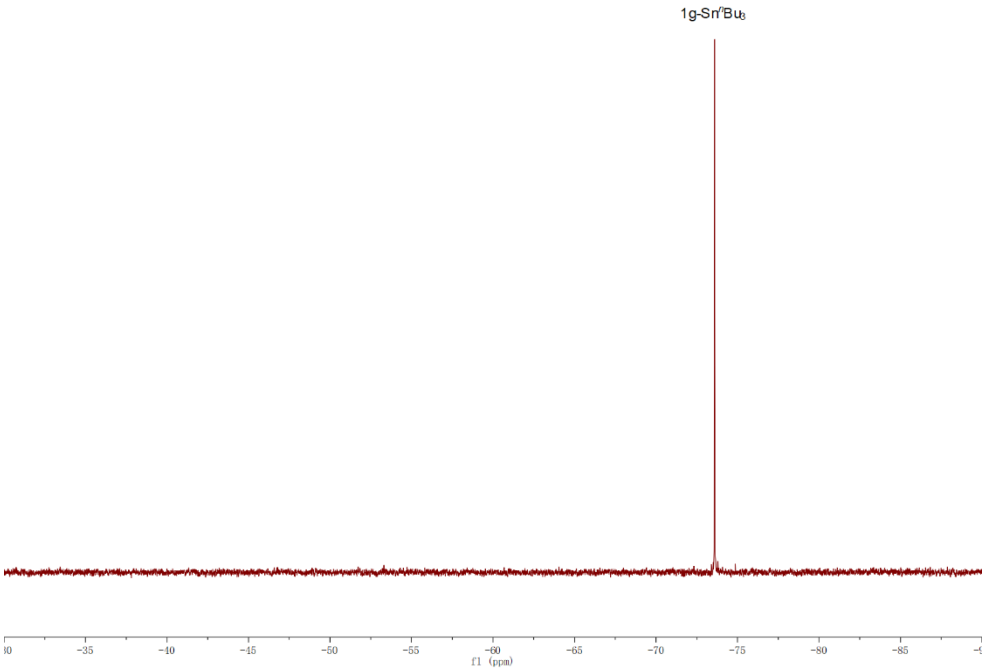


Figure S88. ^{119}Sn{^{1}H} NMR of the reaction of **1g-Sn^{n}Bu$_3$** in $CDCl_3$ after extraction.

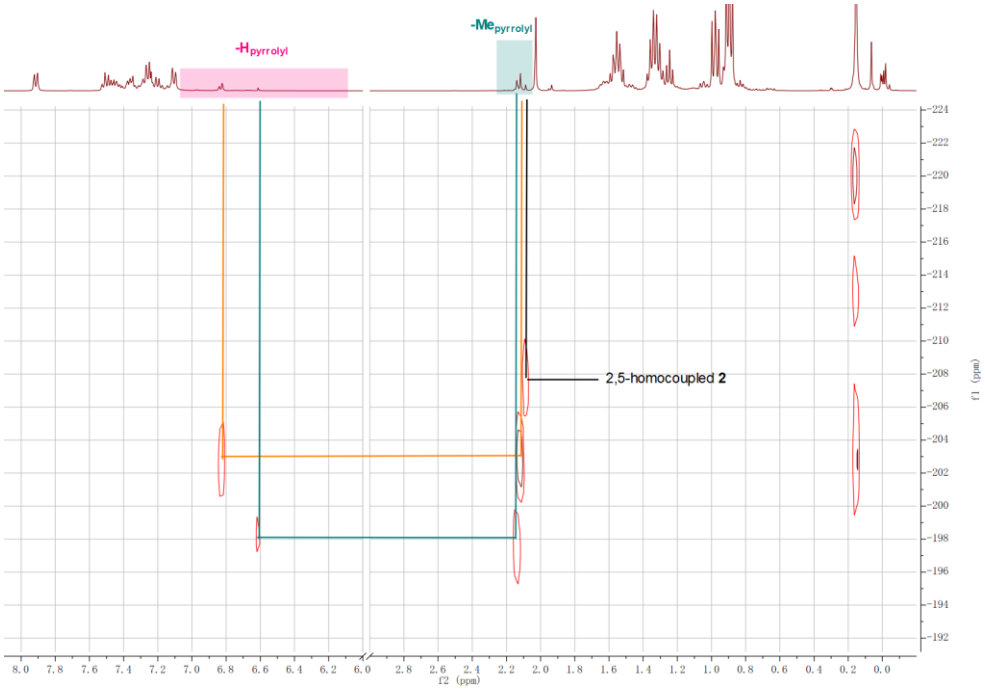
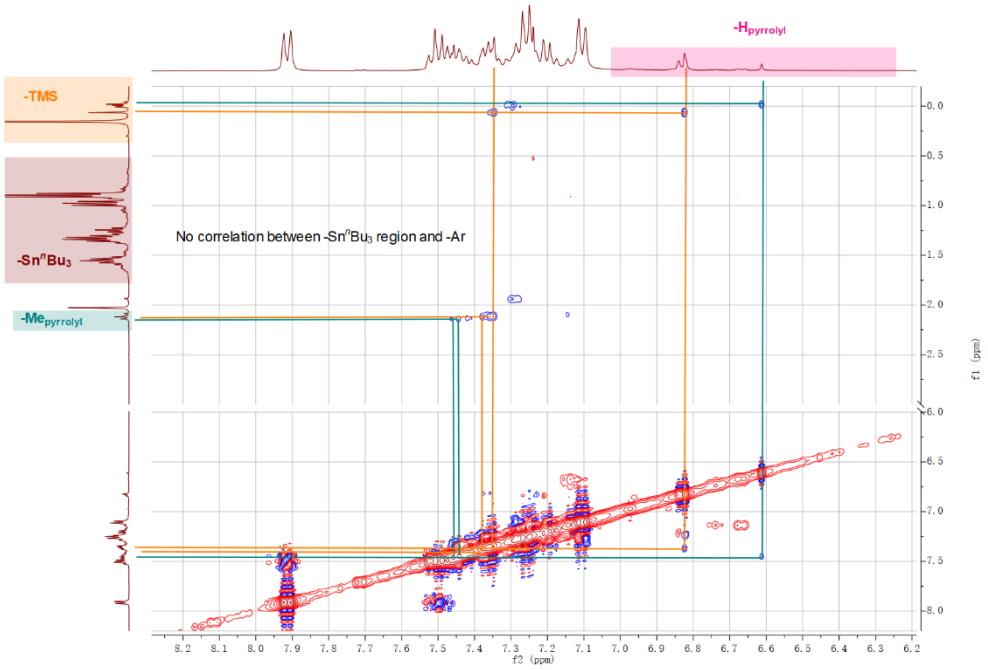


Figure S89. ^{1}H–^{15}N HMBC of the reaction of **1g-Sn^{n}Bu$_3$** in $CDCl_3$ after extraction.



List of correlations (chemical shifts in ppm):

Peak — Peak		Peak — Peak	
6.82 (–H)	0.06 (–TMS)	6.61 (–H)	-0.02 (–TMS)
6.82 (–H)	7.38 (–Ph)	6.61 (–H)	7.45 (–Ph)
2.12 (–Me)	7.38 (–Ph)	2.14 (–Me)	7.45 (–Ph)
2.12 (–Me)	7.35 (–Ph)	2.14 (–Me)	7.46 (–Ph)
0.06 (–TMS)	7.35 (–Ph)		

Figure S90. NOESY NMR spectrum of the reaction of **1g-Sn^{n}Bu$_3$** in $CDCl_3$ after extraction.

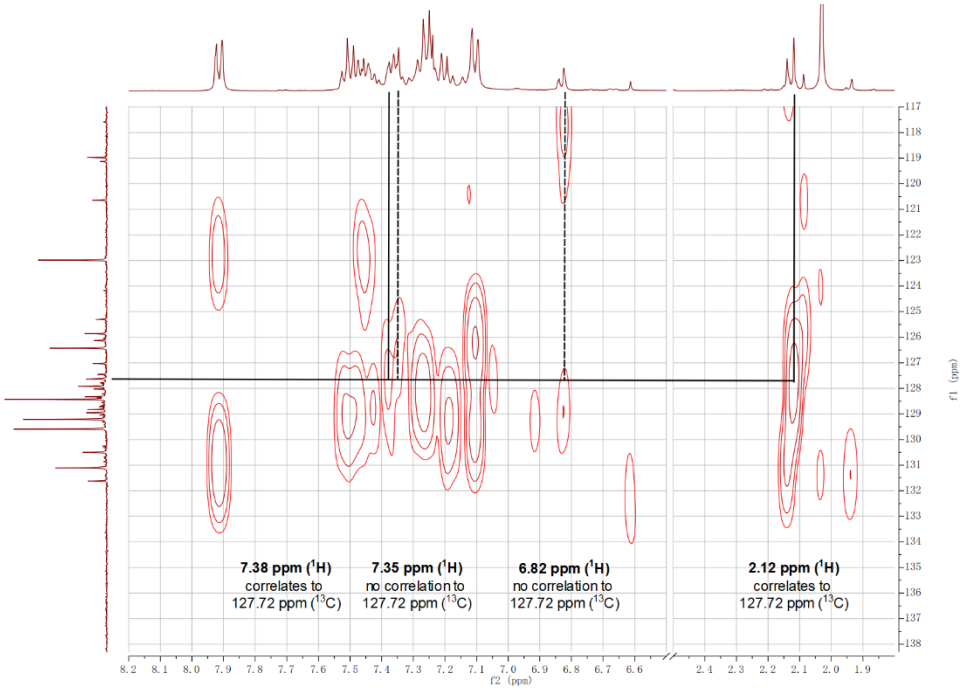
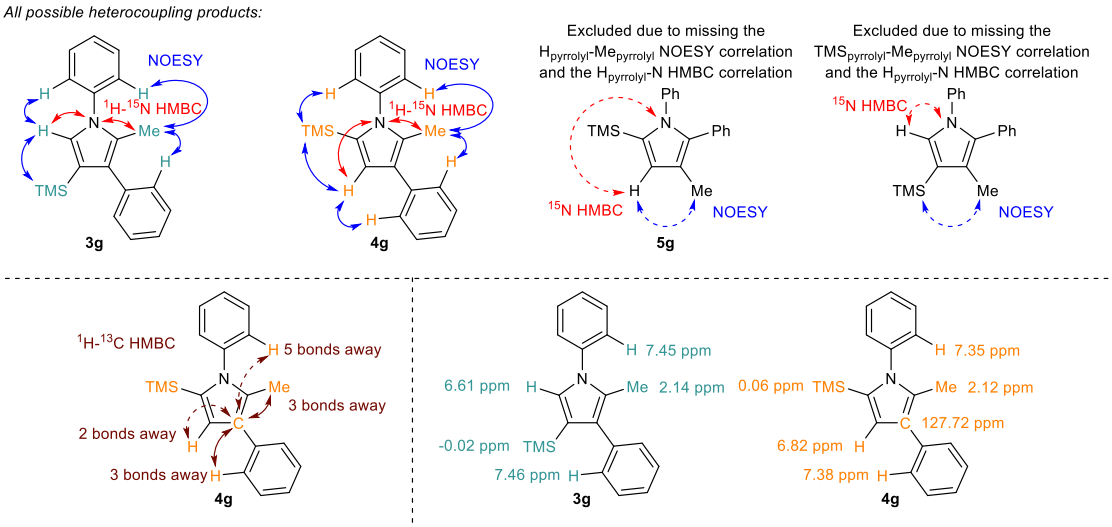


Figure S91. ^{1}H–^{13}C HMBC of the reaction of **1g-Sn^{n}Bu$_3$** in $CDCl_3$ after extraction.

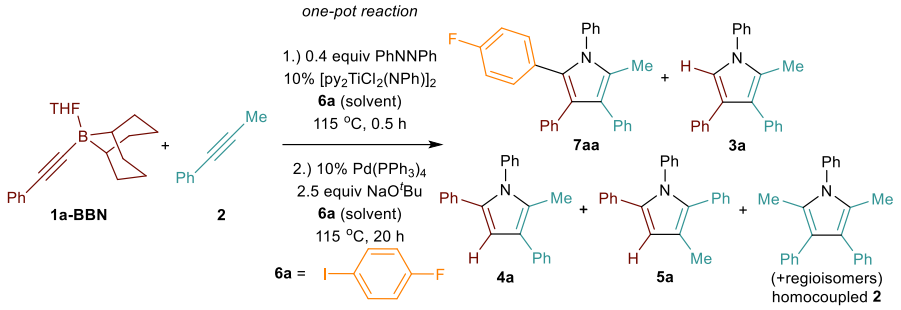


	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.40	Ph_3C-H	1	8903.9	n.a.
3g	6.61	$H_{pyrrolyl}$	1	2588.2	5.8
4g	2.12	$Me_{pyrrolyl}$	3	15998.7	12.0

Figure S92. Determination of regioisomers and yields.

One-Pot Reactions

One-Pot Pyrrole Synthesis/Arylation in *p*-Fluoroiodobenzene



$[py_2TiCl_2(NPh)]_2$ (7.4 mg, 0.01 mmol, 0.1 equiv), *B*-alkynyl-9-BBN (0.1 mmol, 1 equiv), 1-phenyl-1-propyne (11.6 mg, 0.1 mmol, 1 equiv), azobenzene (7.3 mg, 0.04 mmol, 0.4 equiv) and triphenylmethane (2.7 mg, 0.011 mmol, 0.11 equiv, internal standard) and 0.5 mL of *p*-fluoroiodobenzene (**6a**) were added to an NMR tube. The reaction was then sealed and heated in a preheated oil bath at 115 °C for 0.5 h. NMR spectra were collected before and after heating to monitor the reaction. The NMR tube was then transferred into the glovebox. $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.1 equiv) and NaO^{t}Bu (24.0 mg, 0.25 mmol, 2.5 equiv) were added to the reaction, the NMR tube was re-sealed and heated in a preheated oil bath at 115 °C for 20 h. NMR spectra were collected before and after the reaction. The reaction was then quenched with 5% HCl in methanol and extracted with EtOAc/H_2O. The organic phase was dried over $MgSO_4$ and evaporated under vacuum. The crude product mixture was characterized by NMR and GC-Polyarc®/FID to calculate the yield and selectivity.

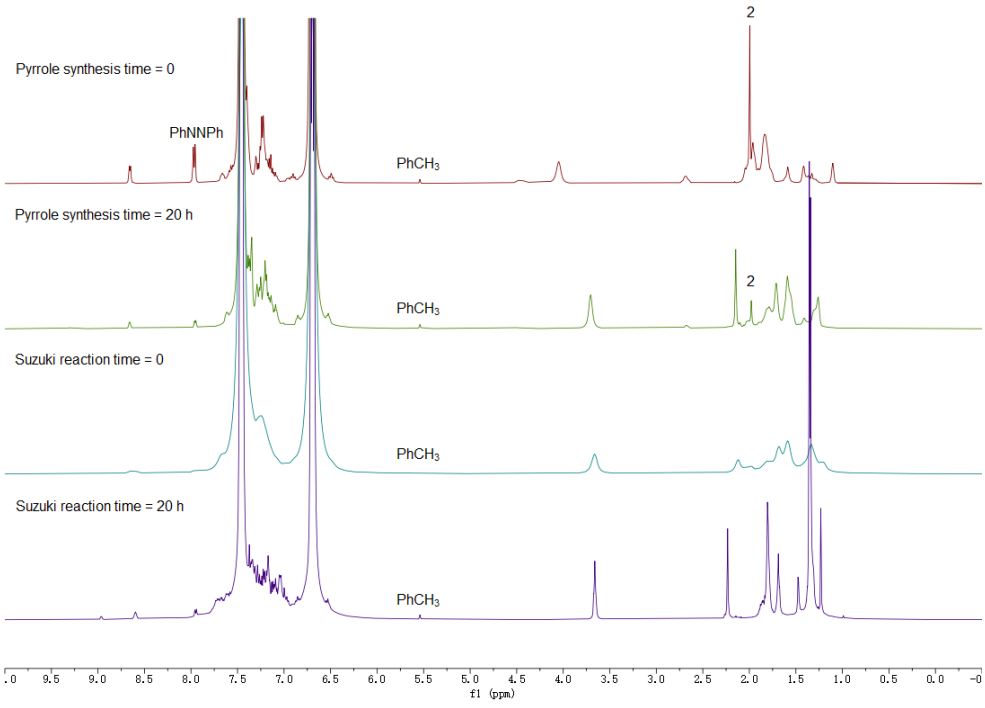


Figure S93. No-D ^{1}H NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6a** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in *p*-fluoroiodobenzene. Chemical shifts were referenced to the proton signal of the internal standard triphenylmethane (Ph_3CH, s, 5.40 ppm).

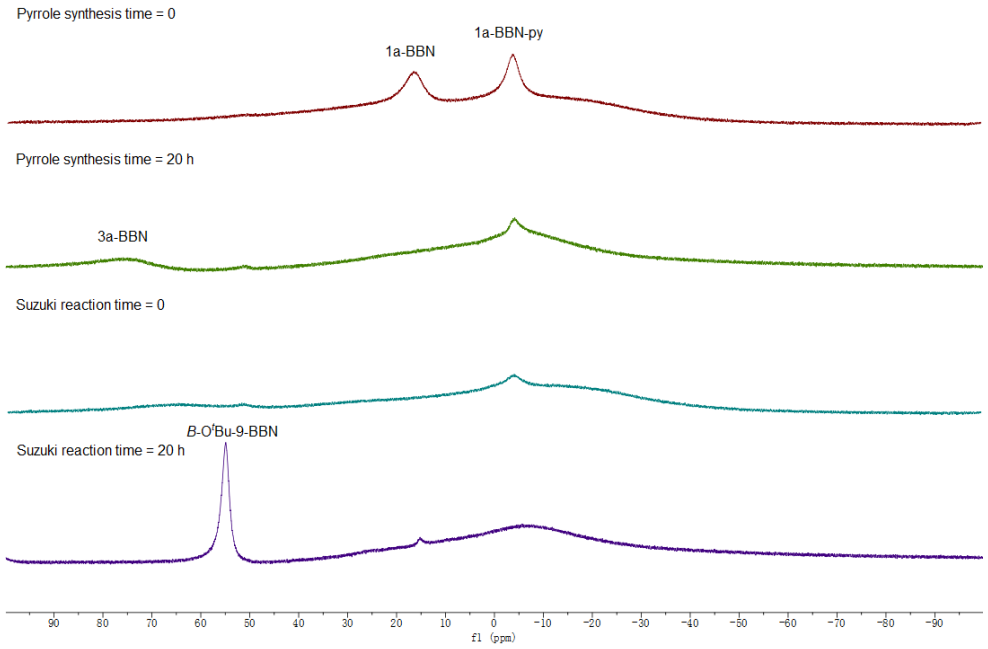


Figure S94. ^{11}B NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6a** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in *p*-fluoroiodobenzene.

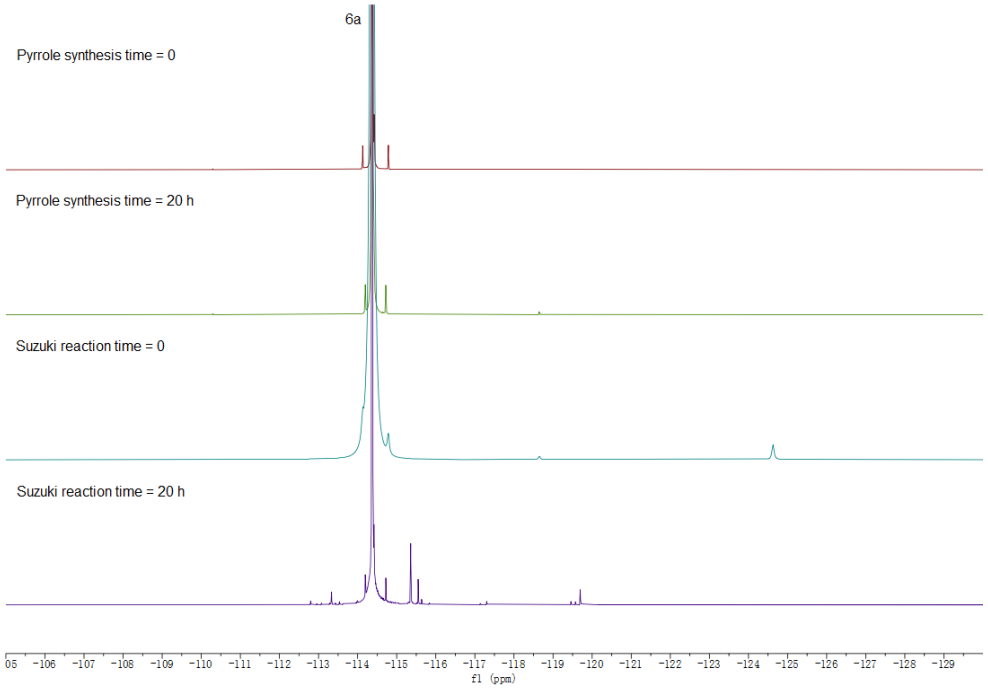
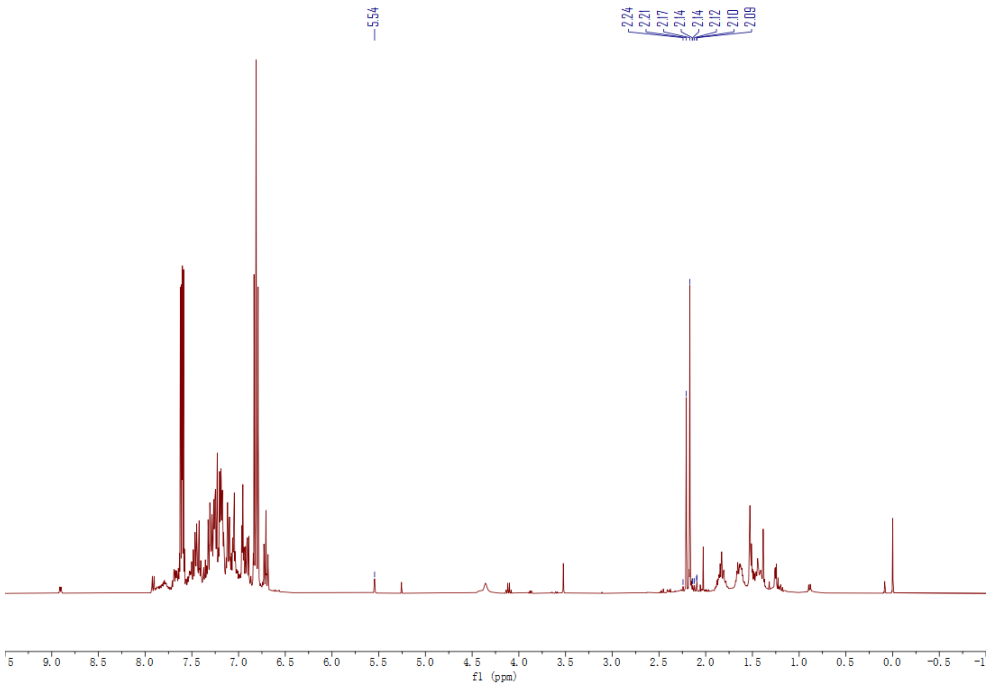


Figure S95. ^{19}F NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6a** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in *p*-fluoroiodobenzene.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	1945.8	n.a.
7aa	2.17	$Me_{pyrrolyl}$	3	21284.0	40.1
3a	2.21	$Me_{pyrrolyl}$	3	12903.9	24.3
4a	2.24	$Me_{pyrrolyl}$	3	700.8	1.3
5a	not found	$H_{pyrrolyl}$	1	n.a.	n.d.
homocoupled **2**	2.14, 2.14, 2.12, 2.10, 2.09	$Me_{pyrrolyl}$ (2 per molecule)	6	2941.0	2.8

Figure S96. ^1H NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6a** in $CDCl_3$ after HCl workup.

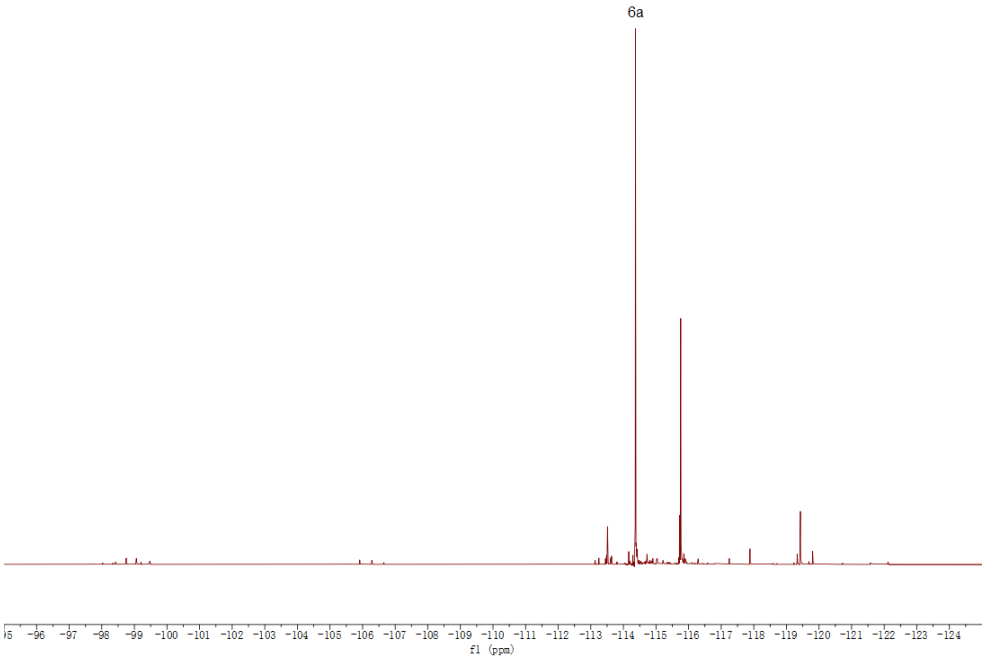


Figure S97. $^{19}F\{^{1}H\}$ NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6a** in $CDCl_3$ after HCl workup.

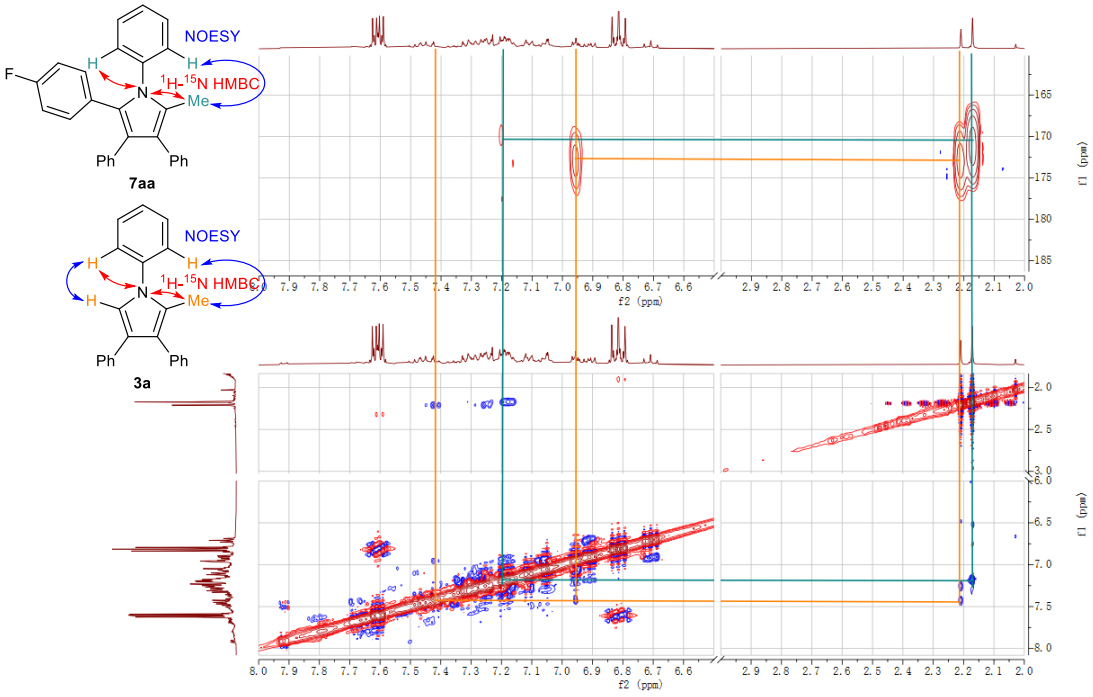
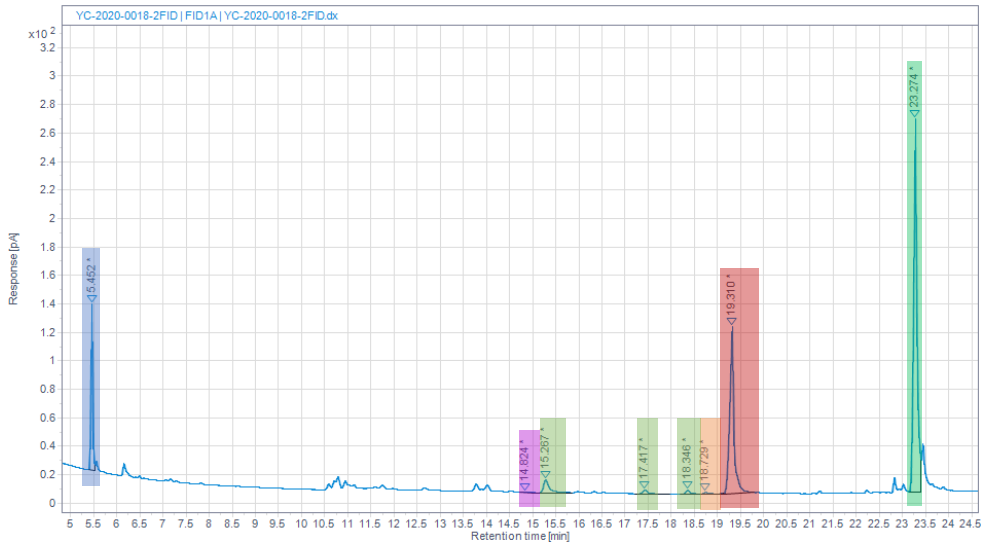


Figure S98. ^{1}H–^{15}N HMBC (top) and NOESY (bottom) NMR spectra of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6a** in $CDCl_3$ after HCl workup.



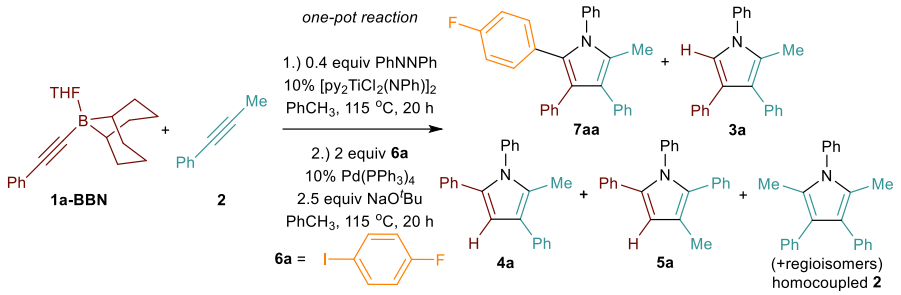
	Retention Time (min)	Surface Area	# of C	Yield (%)
Ph_3CH	5.45	281.717	19	n.a.
7aa	23.27	1508.02	29	38.6
3a	19.31	736.615	23	23.8
4a	18.73	11.991	23	0.4
5a	14.82	1.801	23	0.1
homocoupled **2**	15.27, 17.42, 18.35	116.179	24	3.6

Figure S99. Quantitative GC-FID chromatograph of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6a** after HCl workup.

General Procedure for One-Pot Pyrrole Synthesis/Arylation in Toluene (Procedure D) (Table 4)

$[py_2TiCl_2(NPh)]_2$ (7.4 mg, 0.01 mmol, 0.1 equiv), *B*-alkynyl-9-BBN (0.1 mmol, 1 equiv) and 0.5 mL of $PhCH_3$ stock solution containing 1-phenyl-1-propyne (11.6 mg, 0.1 mmol, 1 equiv), azobenzene (7.3 mg, 0.04 mmol, 0.4 equiv) and triphenylmethane (4.9 mg, 0.02 mmol, 0.2 equiv, internal standard) were added to an NMR tube. The reaction was then sealed and heated in a preheated oil bath at 115 °C for 20 h. NMR spectra were collected before and after heating to monitor the reaction. The NMR tube was then transferred into the glovebox. $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.1 equiv), aryl iodide (0.2 mmol, 2 equiv), NaO^{t}Bu (24.0 mg, 0.25 mmol, 2.5 equiv) and 0.2 mL of $PhCH_3$ were added to the reaction, the NMR tube was re-sealed and heated in a preheated oil bath at 115 °C for 20 h. NMR spectra were collected before and after the reaction. The reaction was then quenched with 5% HCl in methanol and extracted with EtOAc/H_2O. The organic phase was dried over $MgSO_4$ and evaporated under vacuum. The crude product mixture was characterized by NMR and GC-Polyarc®/FID to calculate the yield and selectivity.

One-Pot Pyrrole Synthesis/Arylation for 1a-BBN and *p*-Fluoroiodobenzene



The reaction was performed following **Procedure D** using **1a-BBN** (29.4 mg, 0.1 mmol, 1 equiv) as alkynylborane and *p*-fluoroiodobenzene (**6a**, 44.4 mg, 0.2 mmol, 2 equiv) as aryl iodide.

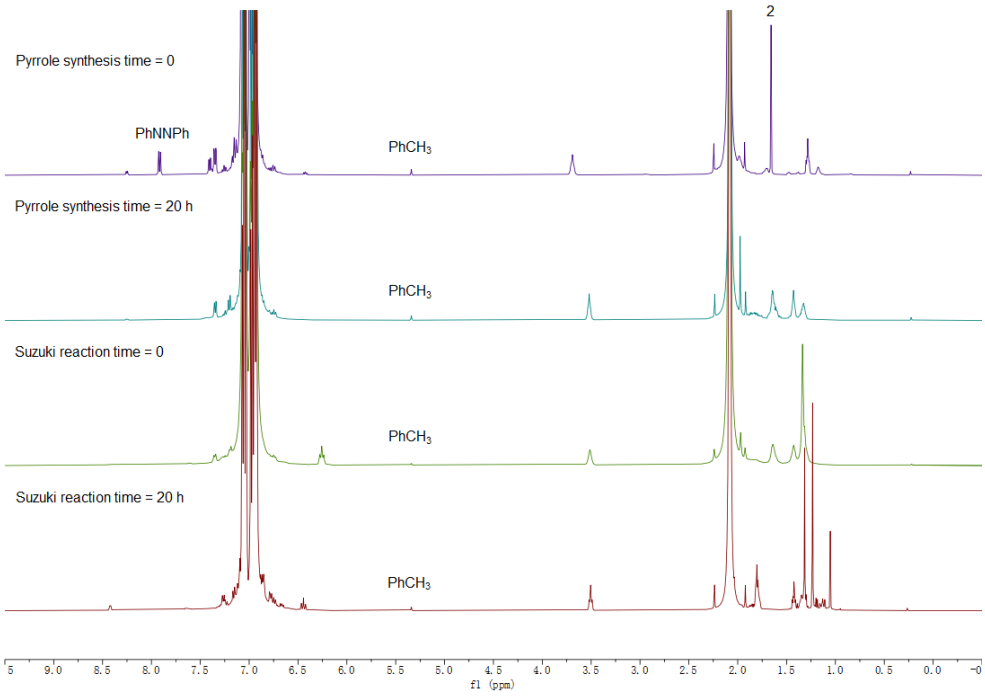


Figure S100. No-D ^{1}H NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6a** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.

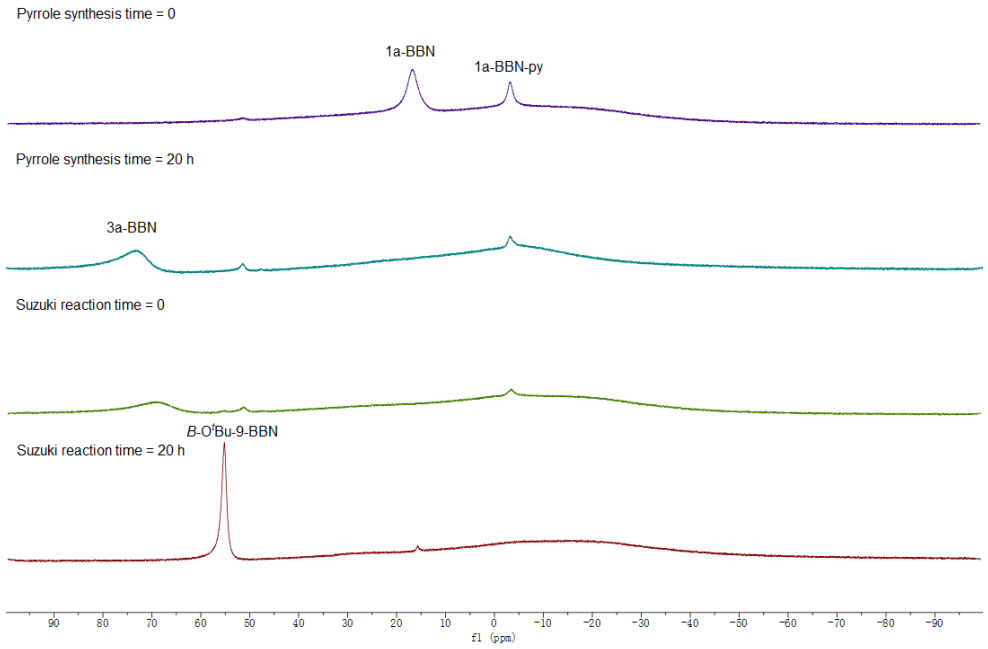


Figure S101. ^{11}B NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6a** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.

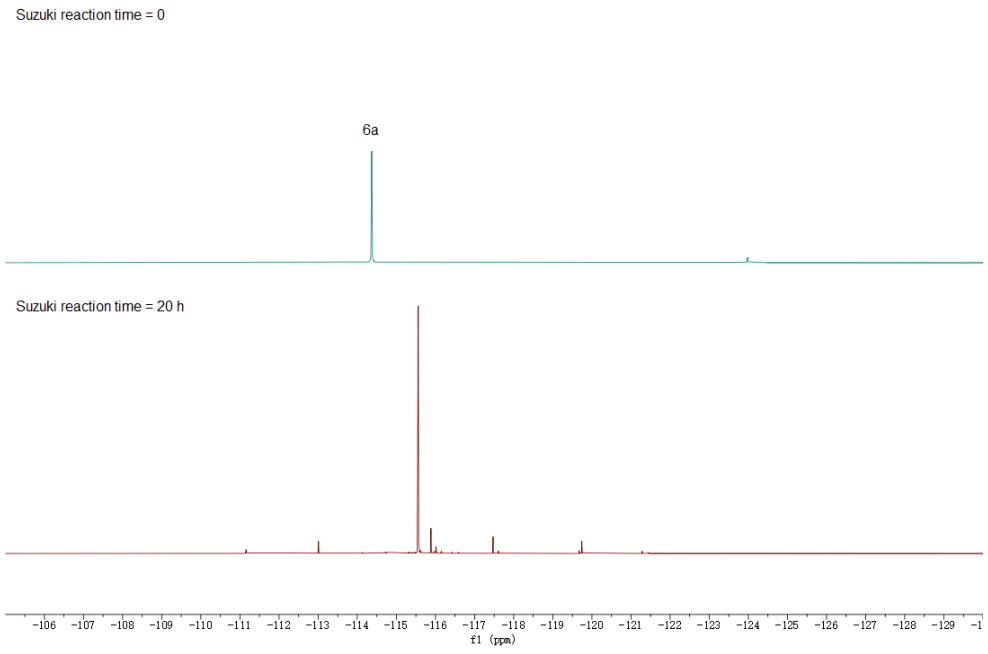
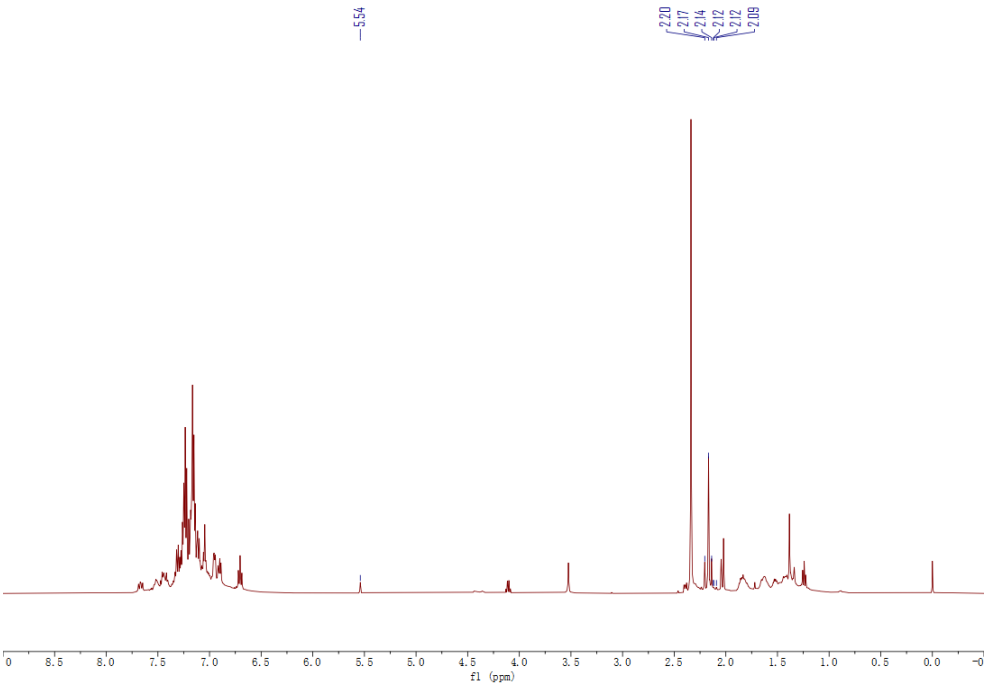


Figure S102. ^{19}F NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6a** at time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	1745.7	n.a.
7aa	2.17	$Me_{pyrrolyl}$	3	15242.5	58.2
3a	2.20	$Me_{pyrrolyl}$	3	2800.3	10.7
4a	not found	$H_{pyrrolyl}$	1	n.a.	n.d.
5a	not found	$H_{pyrrolyl}$	1	n.a.	n.d.
homocoupled **2**	2.14, 2.12, 2.12, 2.09	$Me_{pyrrolyl}$ (2 per molecule)	6	4165.5	8.0

Figure S103. ^1H NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6a** in $CDCl_3$ after HCl workup.

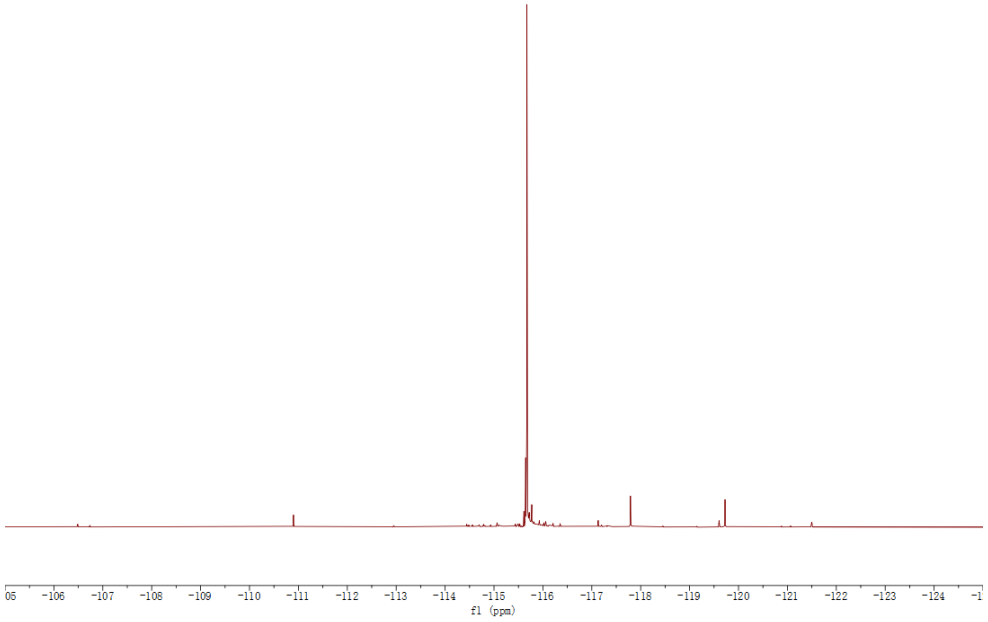
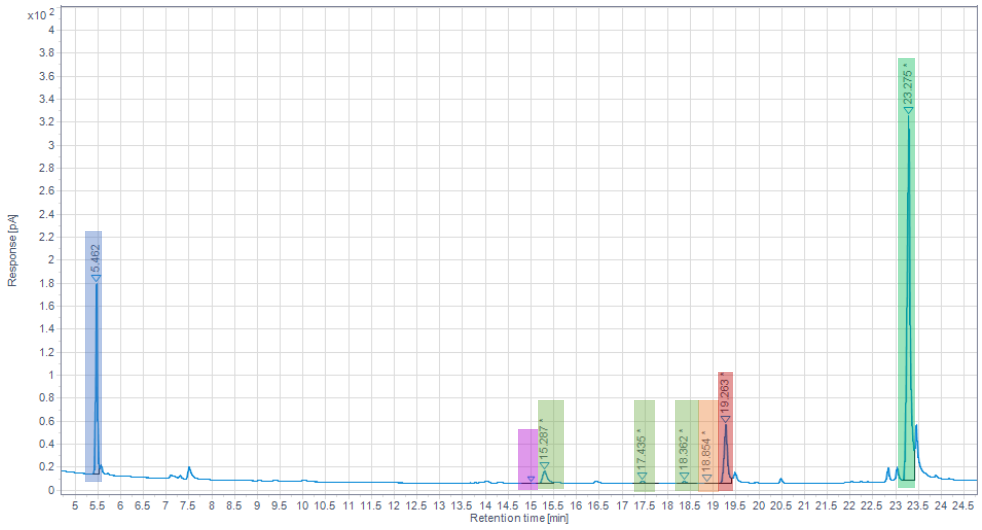


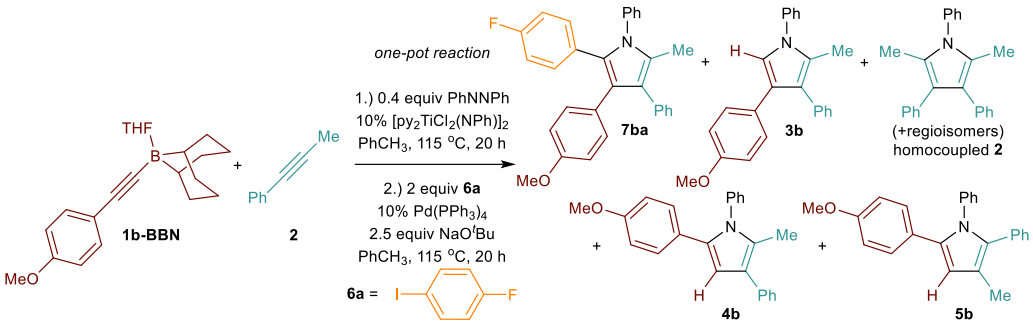
Figure S104. $^{19}F\{^{1}H\}$ NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6a** in $CDCl_3$ after HCl workup.



	Retention Time (min)	Surface Area	# of C	Yield (%)
Ph_3CH	5.46	394.879	19	n.a.
7aa	23.28	1732.741	29	57.5
3a	19.26	258.055	23	10.8
4a	18.85	1.164	23	< 0.1
5a	14.99	0.022	23	< 0.1
homocoupled **2**	15.29, 17.44, 18.36	109.487	24	4.4

Figure S105. Quantitative GC-FID chromatograph of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6a** after HCl workup.

One-Pot Pyrrole Synthesis/Arylation for 1b-BBN and *p*-Fluoroiodobenzene



The reaction was performed following **Procedure D** using **1b-BBN** (32.4 mg, 0.1 mmol, 1 equiv) as alkynylborane and *p*-fluoroiodobenzene (**6a**, 44.4 mg, 0.2 mmol, 2 equiv) as aryl iodide.

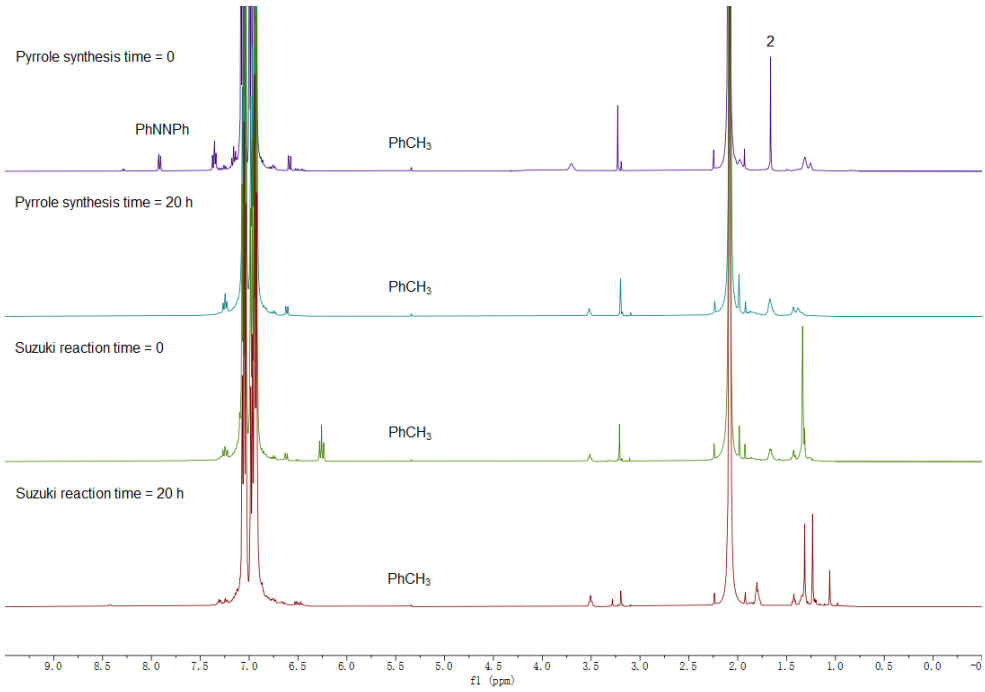


Figure S106. No-D ^{1}H NMR of the one-pot pyrrole synthesis/arylation of **1b-BBN** and **6a** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.

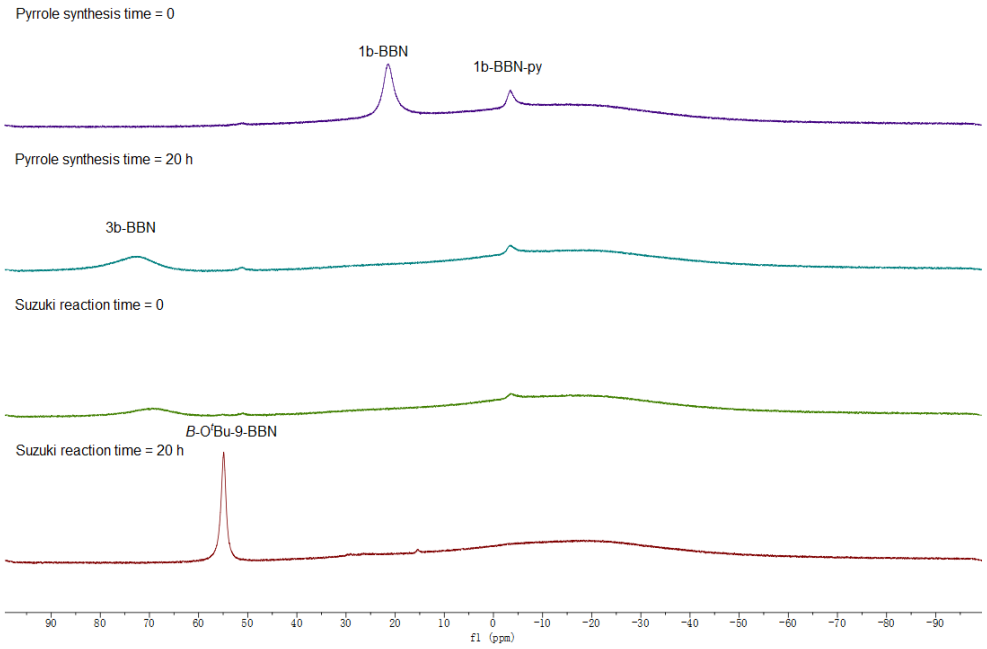


Figure S107. ^{11}B NMR of the one-pot pyrrole synthesis/arylation of **1b-BBN** and **6a** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.

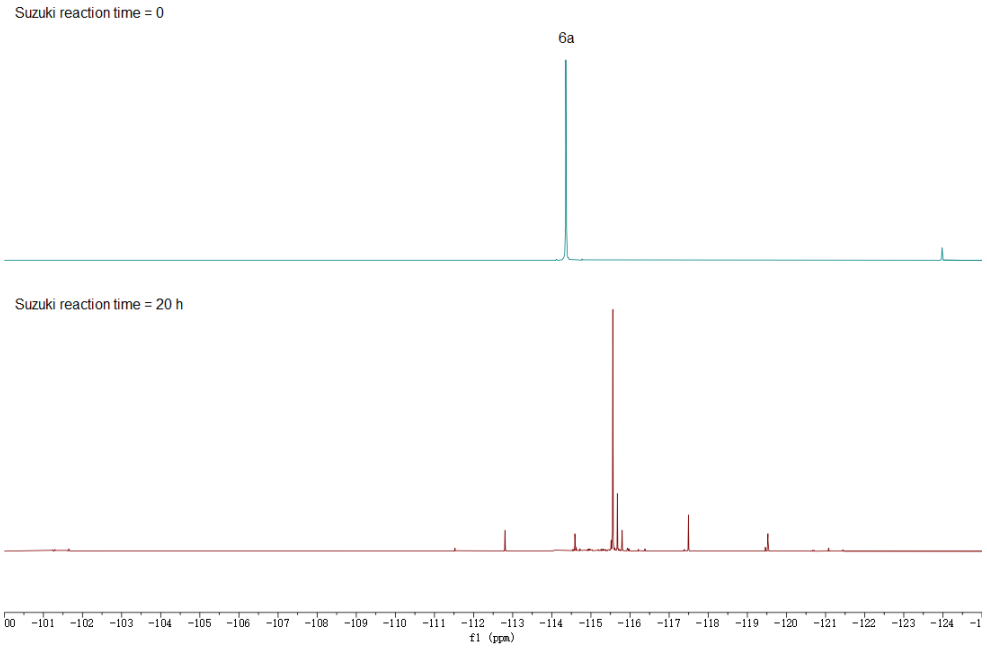
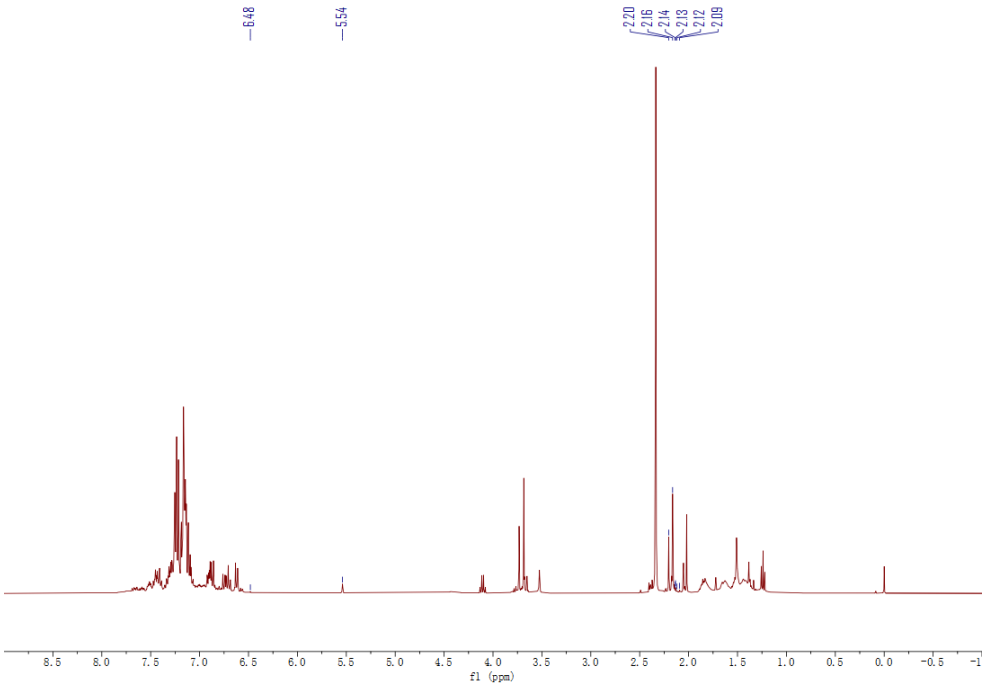


Figure S108. ^{19}F NMR of the one-pot pyrrole synthesis/arylation of **1b-BBN** and **6a** at time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	1956.4	n.a.
7ba	2.16	$Me_{pyrrolyl}$	3	9315.6	31.7
3b	2.20	$Me_{pyrrolyl}$	3	6711.6	22.9
4b	6.48	$H_{pyrrolyl}$	1	80.5	0.8
5b	not found	$H_{pyrrolyl}$	1	n.a.	n.d.
homocoupled **2**	2.14, 2.13, 2.12, 2.09	$Me_{pyrrolyl}$ (2 per molecule)	6	1959.8	3.3

Figure S109. ^1H NMR of the one-pot pyrrole synthesis/arylation of **1b-BBN** and **6a** in $CDCl_3$ after HCl workup.

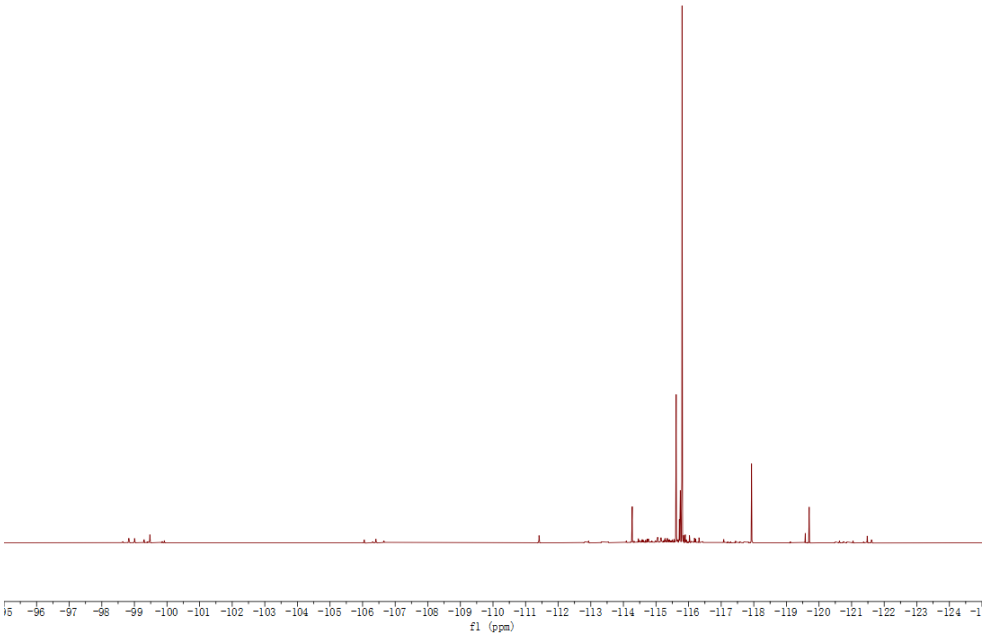


Figure S110. $^{19}F\{^{1}H\}$ NMR of the one-pot pyrrole synthesis/arylation of **1b-BBN** and **6a** in $CDCl_3$ after HCl workup.

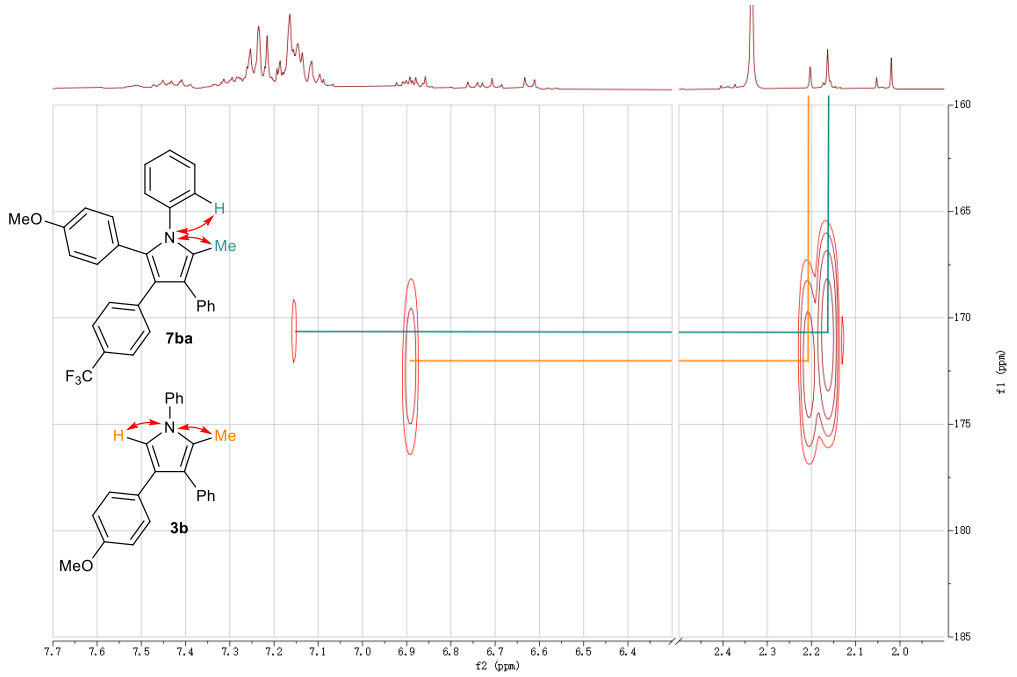
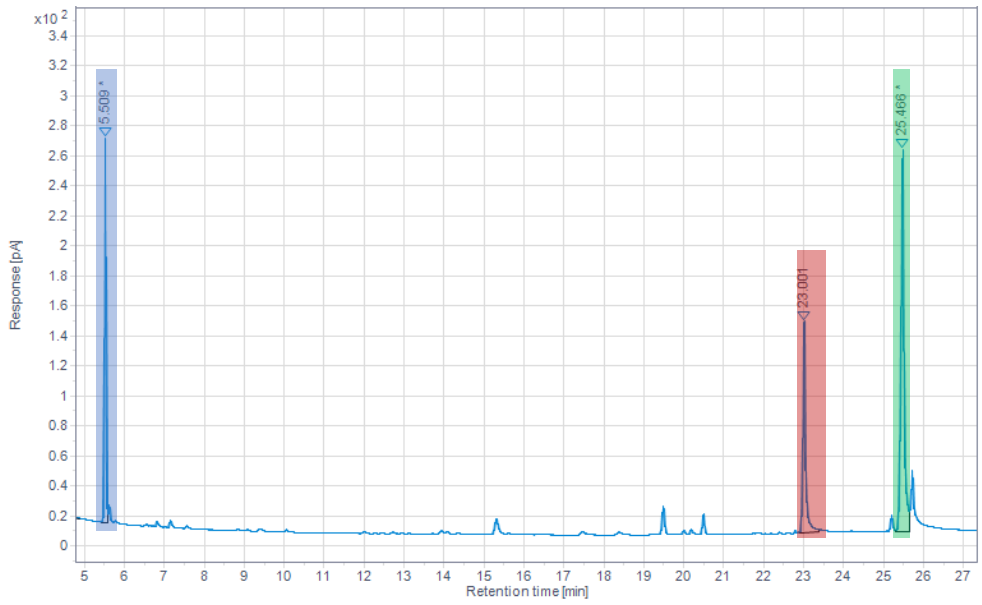


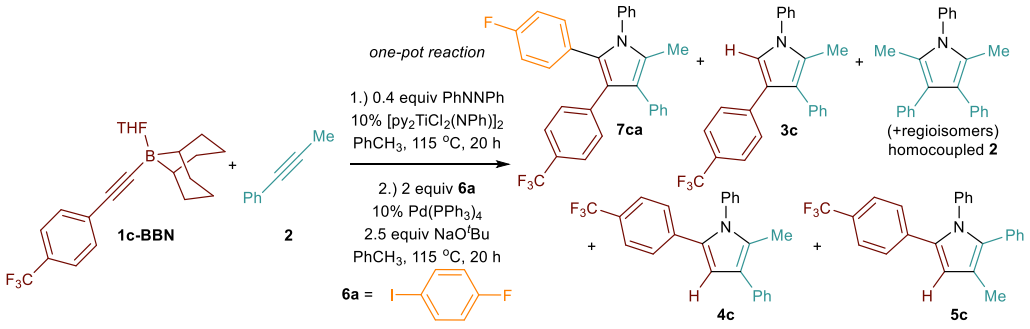
Figure S111. $^{1}H–^{15}N$ HMBC of the one-pot pyrrole synthesis/arylation of **1b-BBN** and **6a** in $CDCl_3$ after HCl workup.



	Retention Time (min)	Surface Area	# of C	Yield (%)
Ph_3CH	5.51	603.790	19	n.a.
7ba	25.47	1336.157	30	28.0
3b	23.00	598.320	24	15.7

Figure S112. Quantitative GC-FID chromatograph of the one-pot pyrrole synthesis/arylation of **1b-BBN** and **6a** after HCl workup.

One-Pot Pyrrole Synthesis/Arylation for 1c-BBN and *p*-Fluoroiodobenzene



The reaction was performed following **Procedure D** using **1c-BBN** (36.2 mg, 0.1 mmol, 1 equiv) as alkynylborane and *p*-fluoroiodobenzene (**6a**, 44.4 mg, 0.2 mmol, 2 equiv) as aryl iodide.

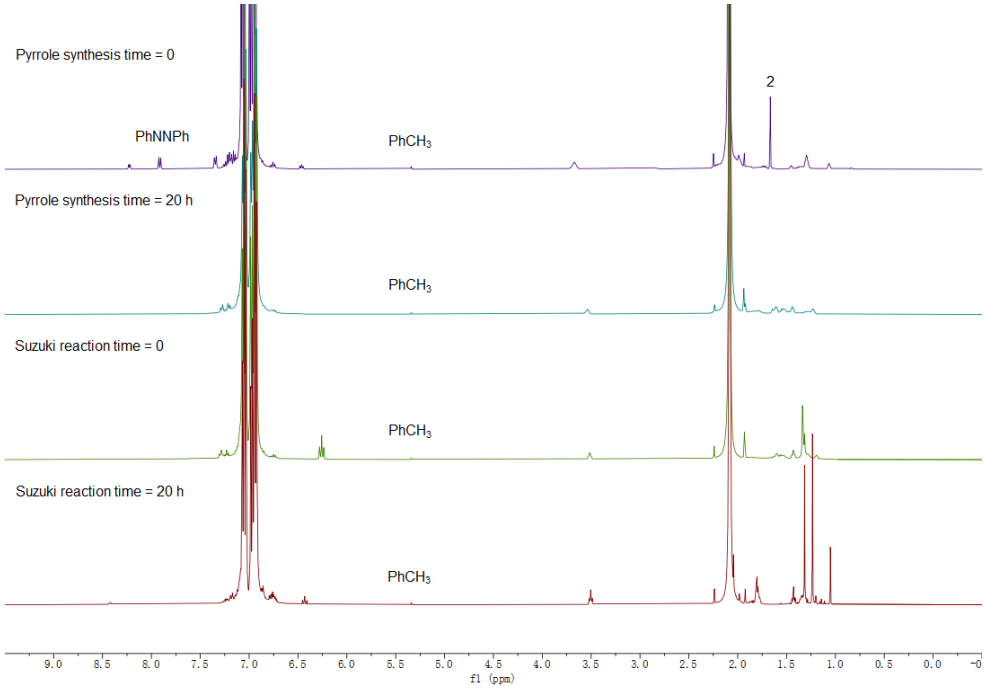


Figure S113. No-D ^{1}H NMR of the one-pot pyrrole synthesis/arylation of **1c-BBN** and **6a** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.

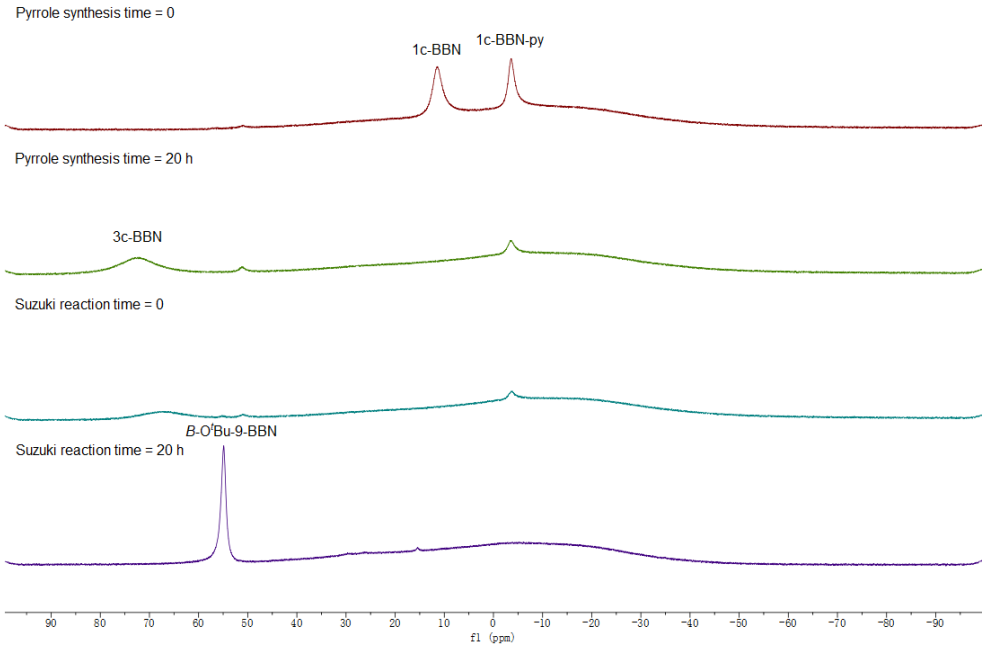


Figure S114. ^{11}B NMR of the one-pot pyrrole synthesis/arylation of **1c-BBN** and **6a** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.

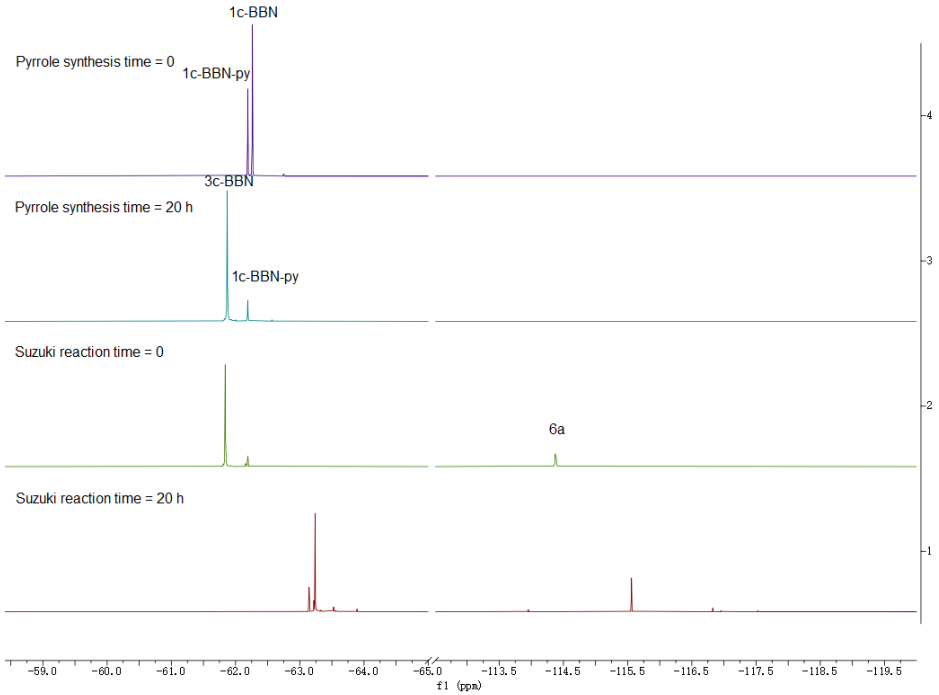
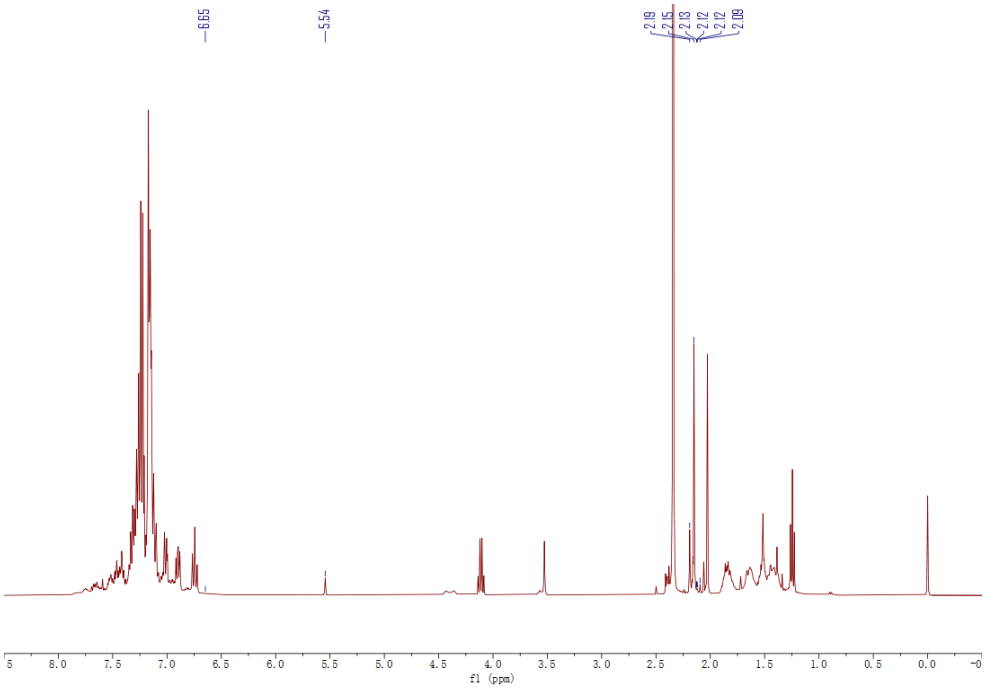


Figure S115. ^{19}F NMR of the one-pot pyrrole synthesis/arylation of **1c-BBN** and **6a** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	2089.5	n.a.
7ca	2.15	$Me_{pyrrolyl}$	3	17925.1	57.2
3c	2.19	$Me_{pyrrolyl}$	3	4156.4	13.3
4c	6.65	$H_{pyrrolyl}$	1	44.7	0.4
5c	not found	$H_{pyrrolyl}$	1	n.a.	n.d.
homocoupled **2**	2.13, 2.12, 2.12, 2.09	$Me_{pyrrolyl}$ (2 per molecule)	6	1043.1	1.7

Figure S116. ^1H NMR of the one-pot pyrrole synthesis/arylation of **1c-BBN** and **6a** in $CDCl_3$ after HCl workup.

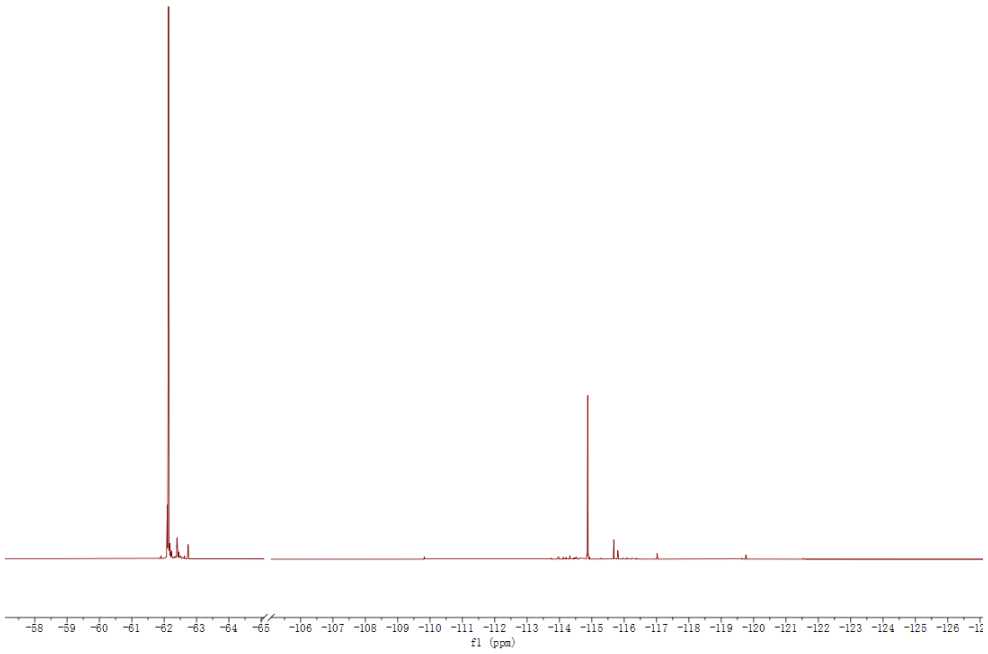


Figure S117. $^{19}F\{^{1}H\}$ NMR of the one-pot pyrrole synthesis/arylation of **1c-BBN** and **6a** in $CDCl_3$ after HCl workup.

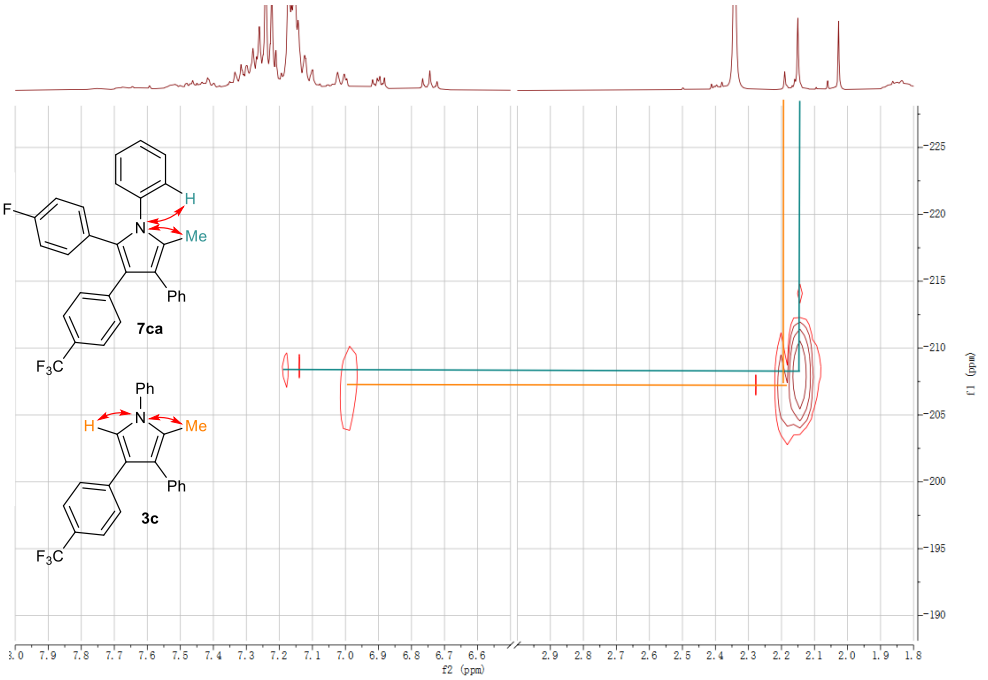
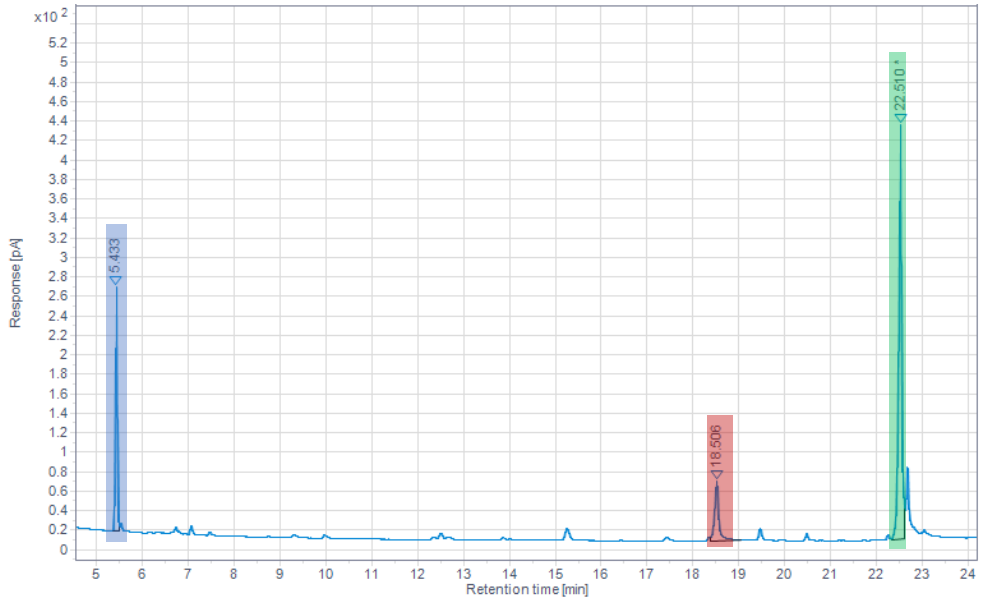


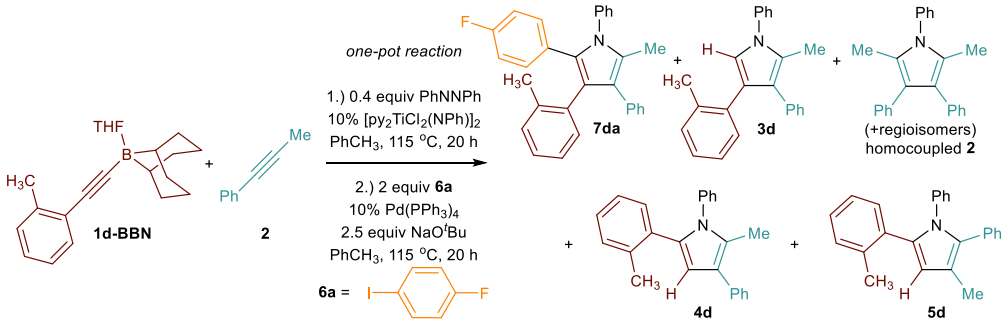
Figure S118. $^{1}H–^{15}N$ HMBC of the one-pot pyrrole synthesis/arylation of **1c-BBN** and **6a** in $CDCl_3$ after HCl workup.



	Retention Time (min)	Surface Area	# of C	Yield (%)
Ph_3CH	5.43	593.967	19	n.a.
7ca	22.51	2204.875	30	47.0
3c	18.51	388.869	24	10.4

Figure S119. Quantitative GC-FID chromatograph of the one-pot pyrrole synthesis/arylation of **1c-BBN** and **6a** after HCl workup.

One-Pot Pyrrole Synthesis/Arylation for 1d-BBN and *p*-Fluoroiodobenzene



The reaction was performed following **Procedure D** using **1d-BBN** (30.8 mg, 0.1 mmol, 1 equiv) as alkynylborane and *p*-fluoroiodobenzene (**6a**, 44.4 mg, 0.2 mmol, 2 equiv) as aryl iodide.

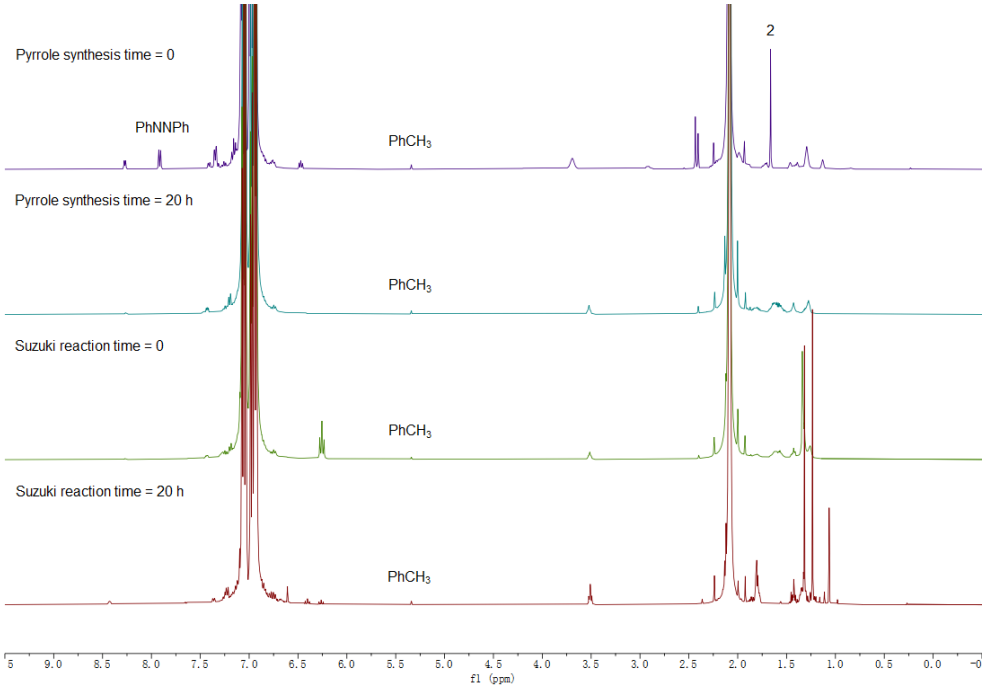


Figure S120. No-D ^{1}H NMR of the one-pot pyrrole synthesis/arylation of **1d-BBN** and **6a** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.

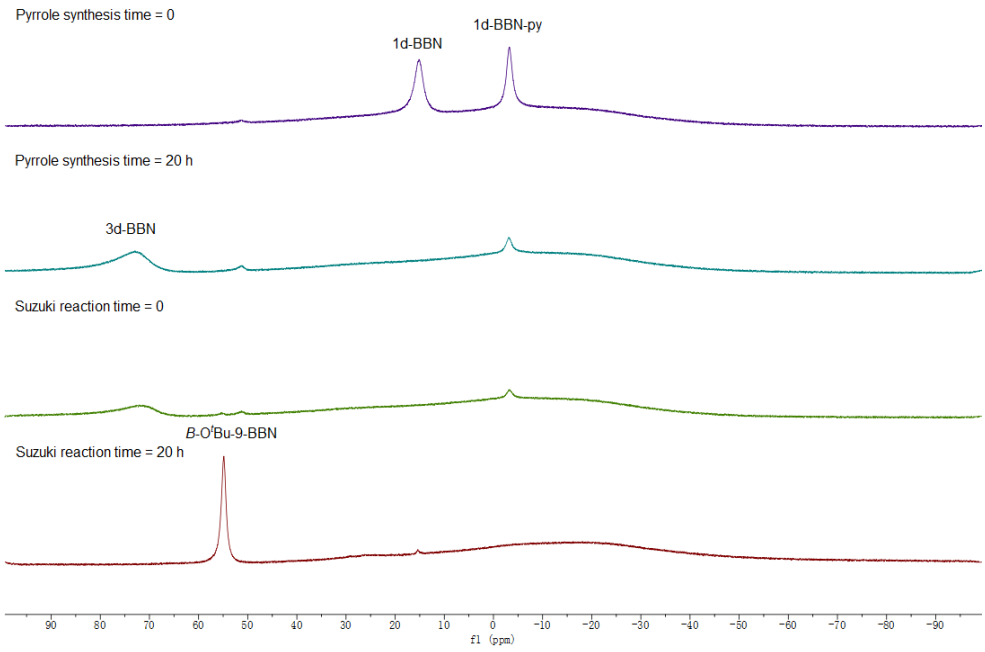


Figure S121. ^{11}B NMR of the one-pot pyrrole synthesis/arylation of **1d-BBN** and **6a** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.

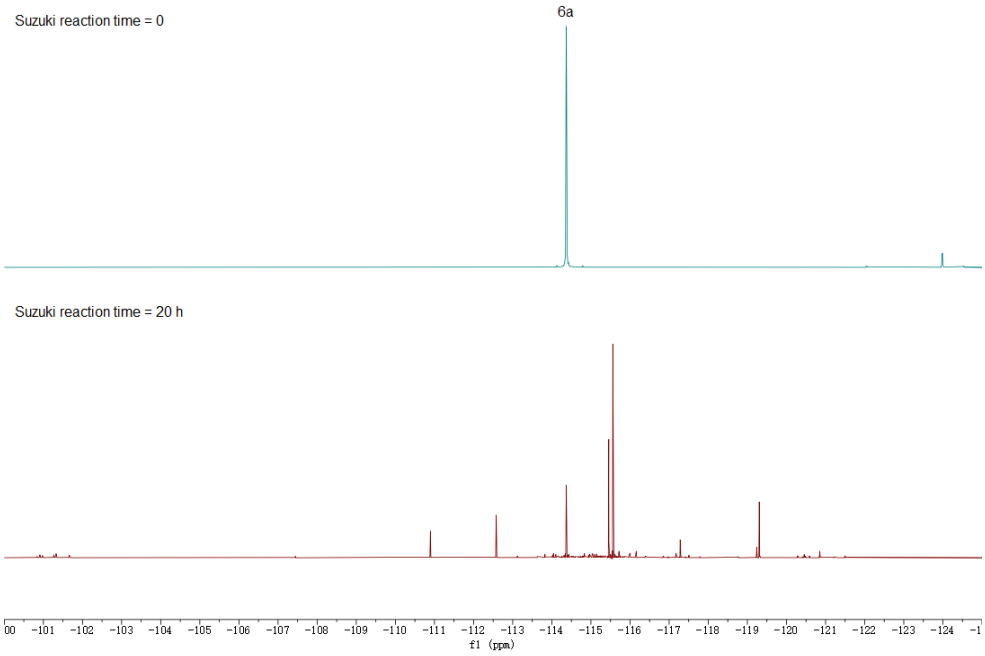
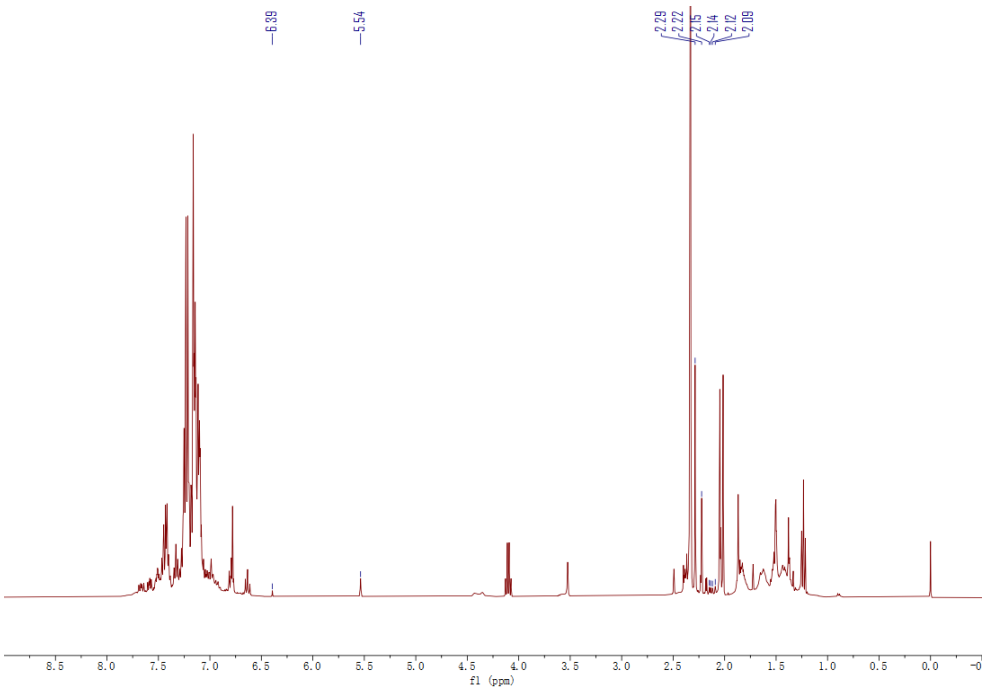


Figure S122. ^{19}F NMR of the one-pot pyrrole synthesis/arylation of **1d-BBN** and **6a** at time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	1645.6	n.a.
7da	2.22	$Me_{pyrrolyl}$	3	4649.1	18.8
3d	2.29	$Me_{pyrrolyl}$	3	11361.0	46.0
4d	6.39	$H_{pyrrolyl}$	1	273.2	3.3
5d	not found	$H_{pyrrolyl}$	1	n.a.	n.d.
homocoupled **2**	2.15, 2.14, 2.12, 2.09	$Me_{pyrrolyl}$ (2 per molecule)	6	1477.0	3.0

Figure S123. ^1H NMR of the one-pot pyrrole synthesis/arylation of **1d-BBN** and **6a** in $CDCl_3$ after HCl workup.

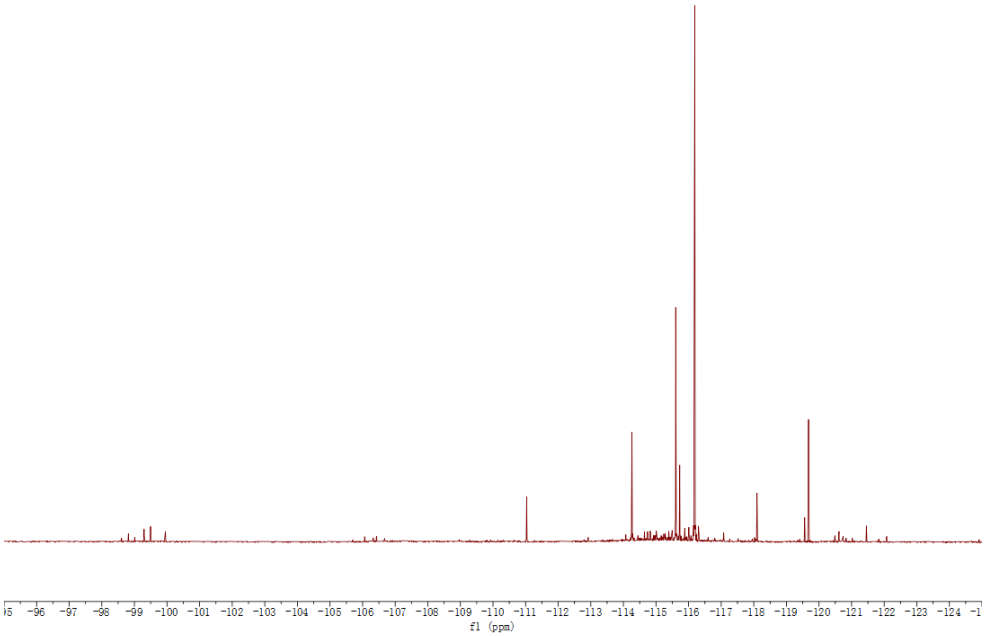


Figure S124. $^{19}F\{^{1}H\}$ NMR of the one-pot pyrrole synthesis/arylation of **1d-BBN** and **6a** in $CDCl_3$ after HCl workup.

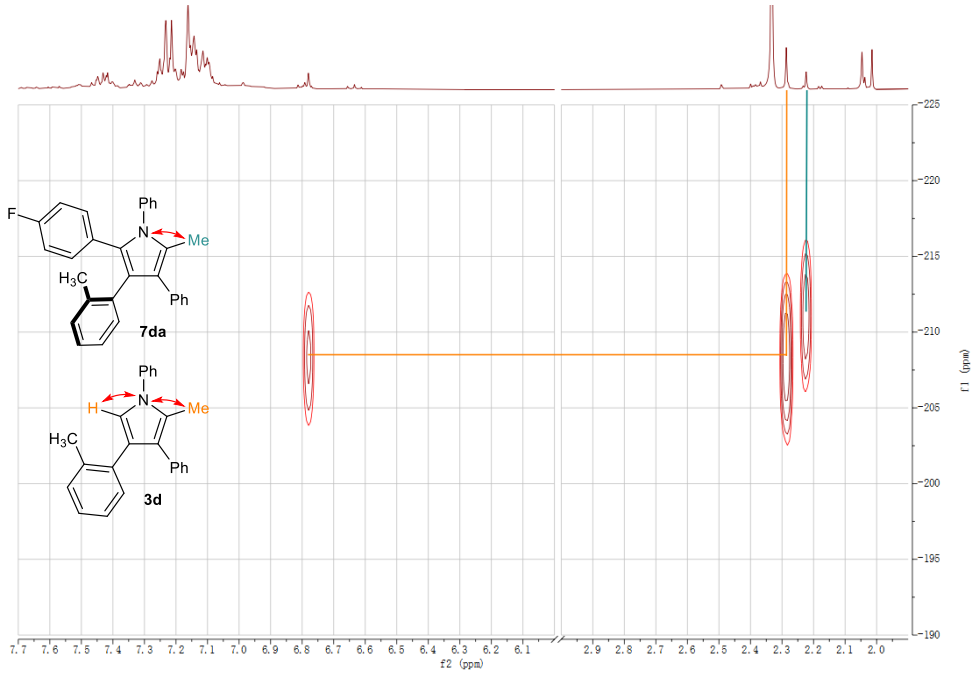
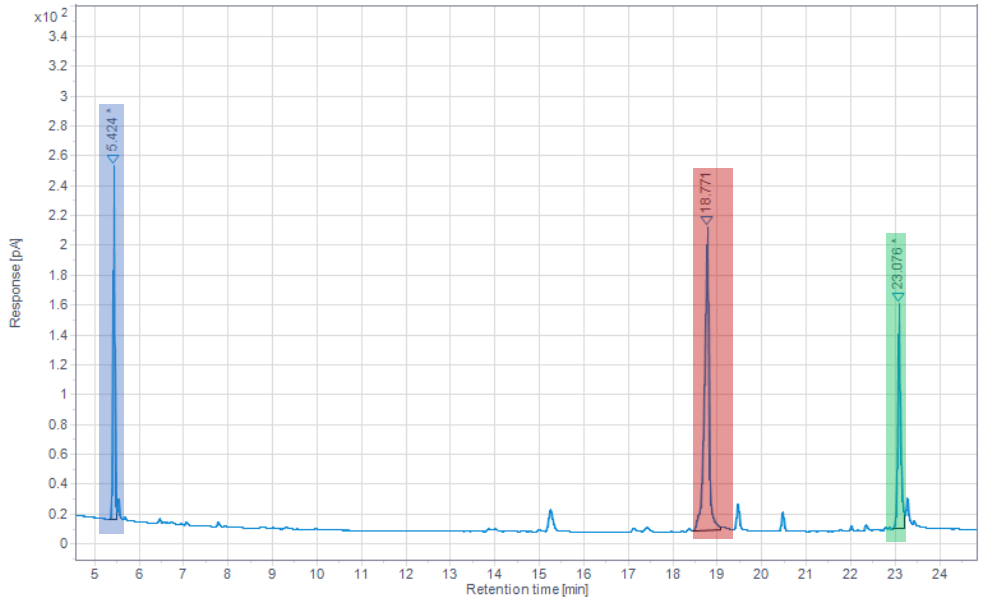


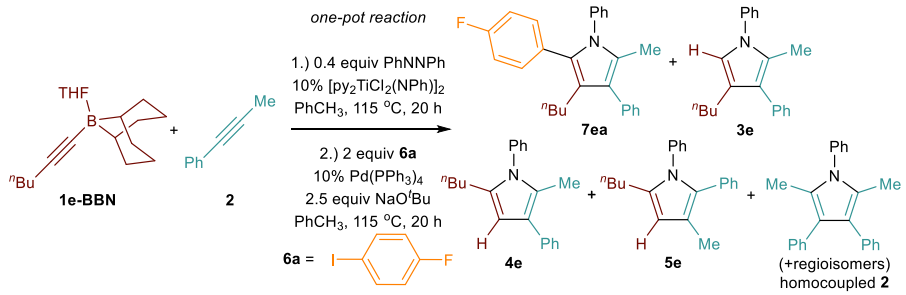
Figure S125. $^{1}H–^{15}N$ HMBC of the one-pot pyrrole synthesis/arylation of **1d-BBN** and **6a** in $CDCl_3$ after HCl workup.



	Retention Time (min)	Surface Area	# of C	Yield (%)
Ph_3CH	5.42	555.761	19	n.a.
7da	23.08	710.741	30	16.2
3d	18.77	1403.187	24	40.0

Figure S126. Quantitative GC-FID chromatograph of the one-pot pyrrole synthesis/arylation of **1d-BBN** and **6a** after HCl workup.

One-Pot Pyrrole Synthesis/Arylation for 1e-BBN and *p*-Fluoroiodobenzene



The reaction was performed following **Procedure D** using **1e-BBN** (27.4 mg, 0.1 mmol, 1 equiv) as alkynylborane and *p*-fluoroiodobenzene (**6a**, 44.4 mg, 0.2 mmol, 2 equiv) as aryl iodide.

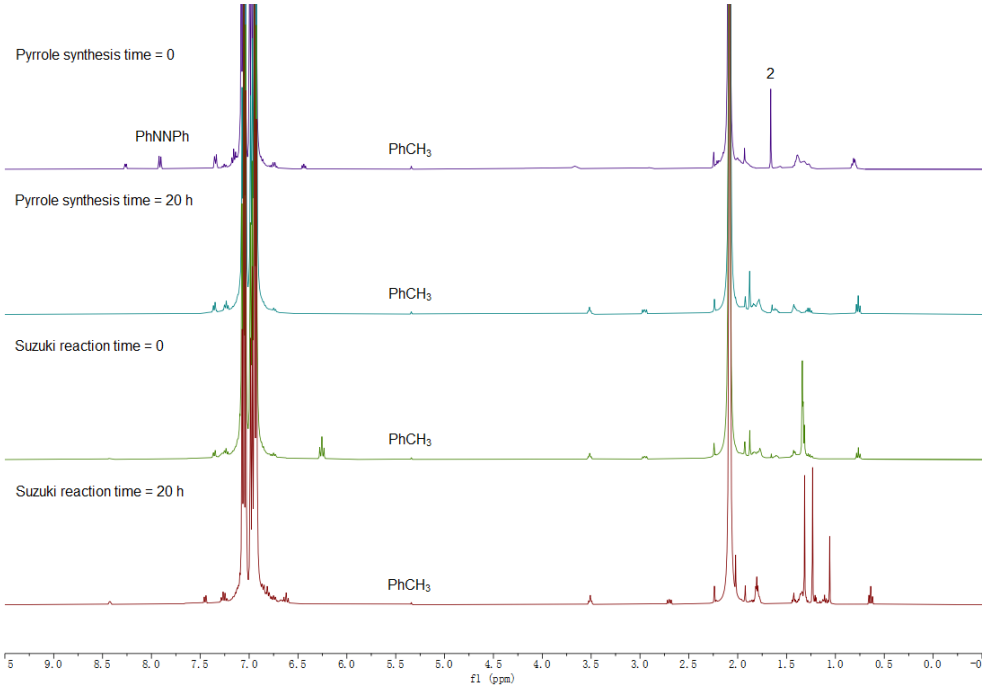


Figure S127. No-D ^{1}H NMR of the one-pot pyrrole synthesis/arylation of **1e-BBN** and **6a** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.

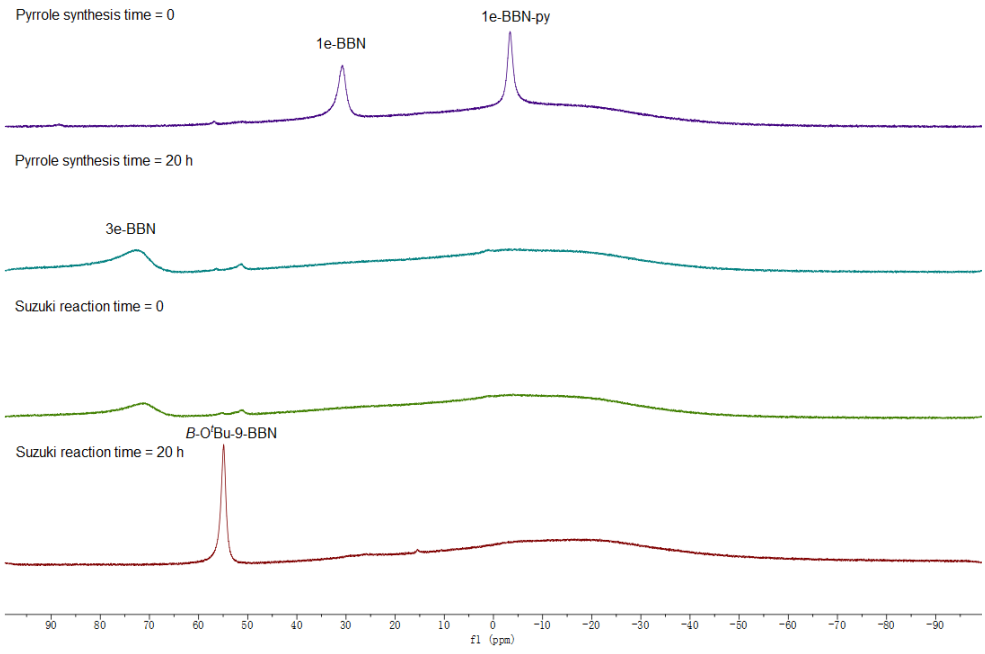


Figure S128. ^{11}B NMR of the one-pot pyrrole synthesis/arylation of **1e-BBN** and **6a** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.

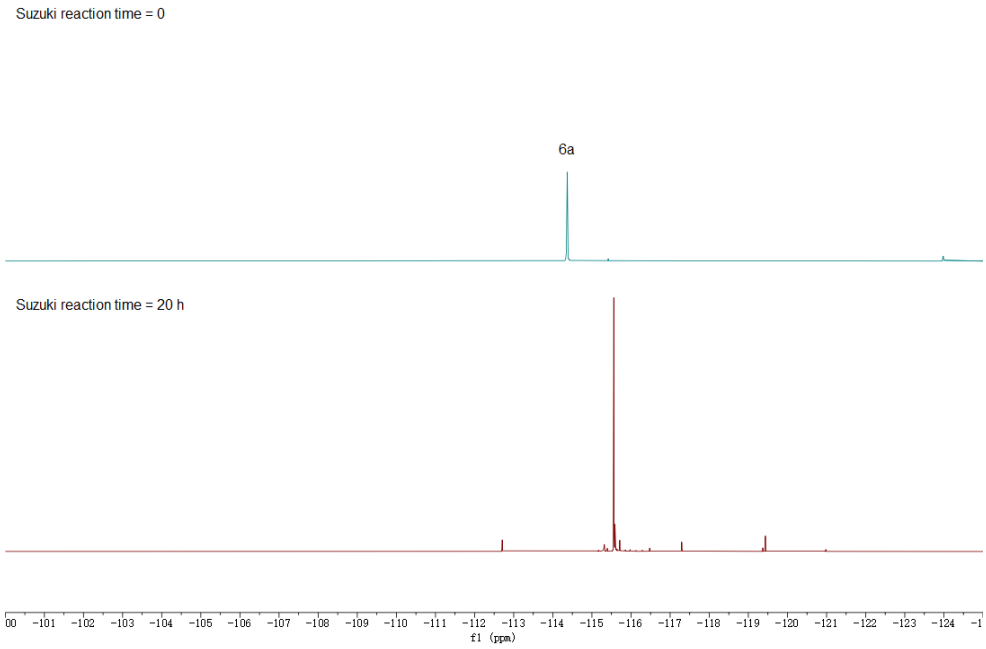
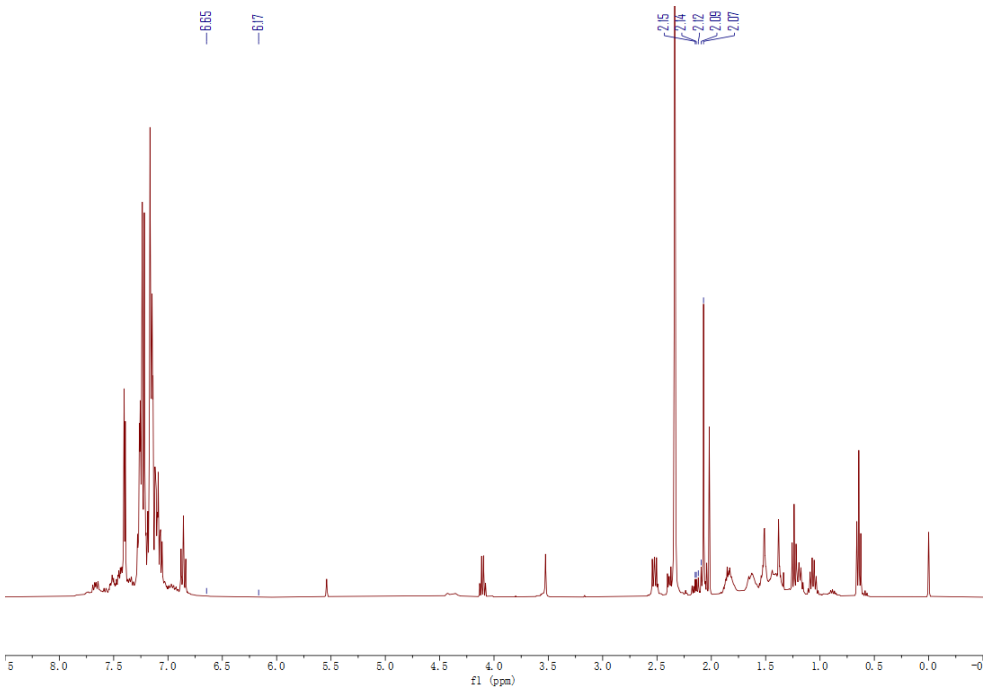


Figure S129. ^{19}F NMR of the one-pot pyrrole synthesis/arylation of **1e-BBN** and **6a** at time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	1777.6	n.a.
7ea	2.07	$Me_{pyrrolyl}$	3	16573.1	62.2
3e	6.65	$H_{pyrrolyl}$	1	93.6	1.1
4e	6.17	$H_{pyrrolyl}$	1	54.8	0.6
5e	not found	$H_{pyrrolyl}$	1	n.a.	n.d.
homocoupled **2**	2.15, 2.14, 2.12, 2.09	$Me_{pyrrolyl}$ (2 per molecule)	6	5062.5	9.5

Figure S130. ^1H NMR of the one-pot pyrrole synthesis/arylation of **1e-BBN** and **6a** in $CDCl_3$ after HCl workup.

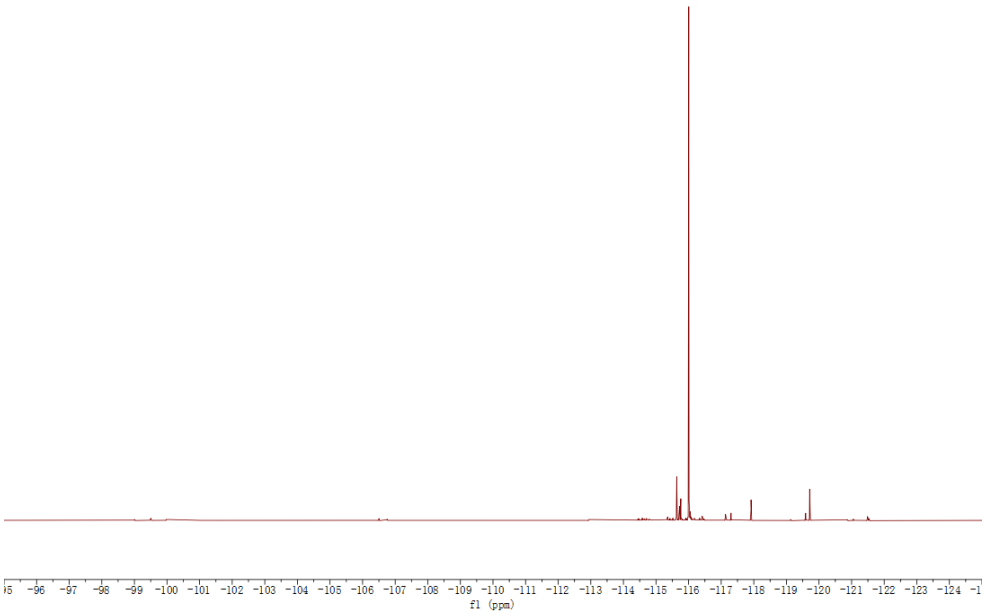


Figure S131. $^{19}F\{^{1}H\}$ NMR of the one-pot pyrrole synthesis/arylation of **1e-BBN** and **6a** in $CDCl_3$ after HCl workup.

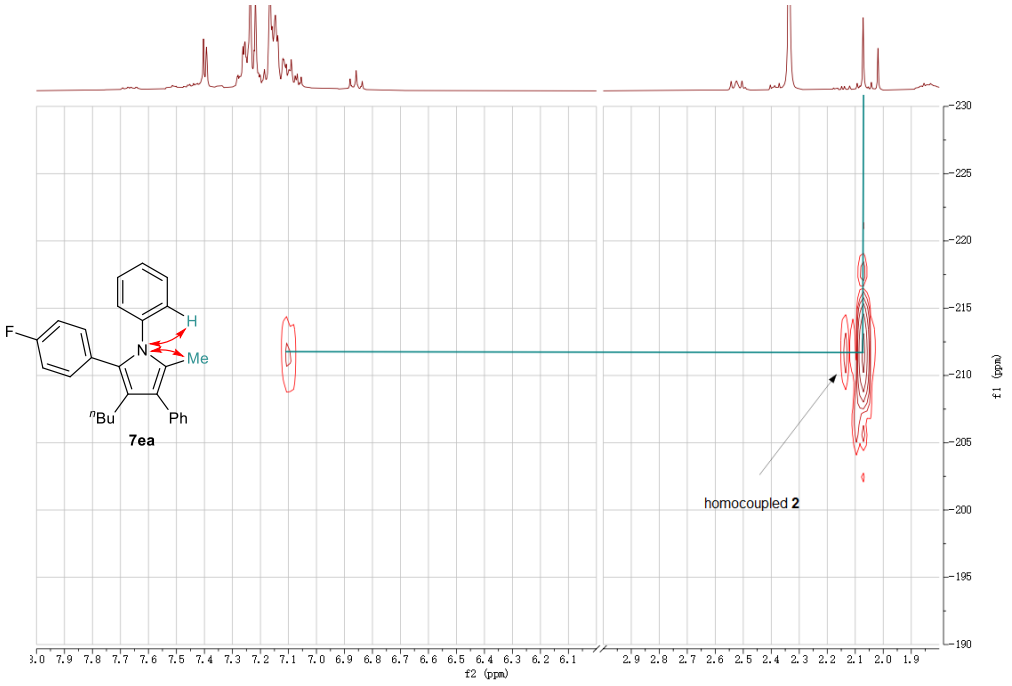
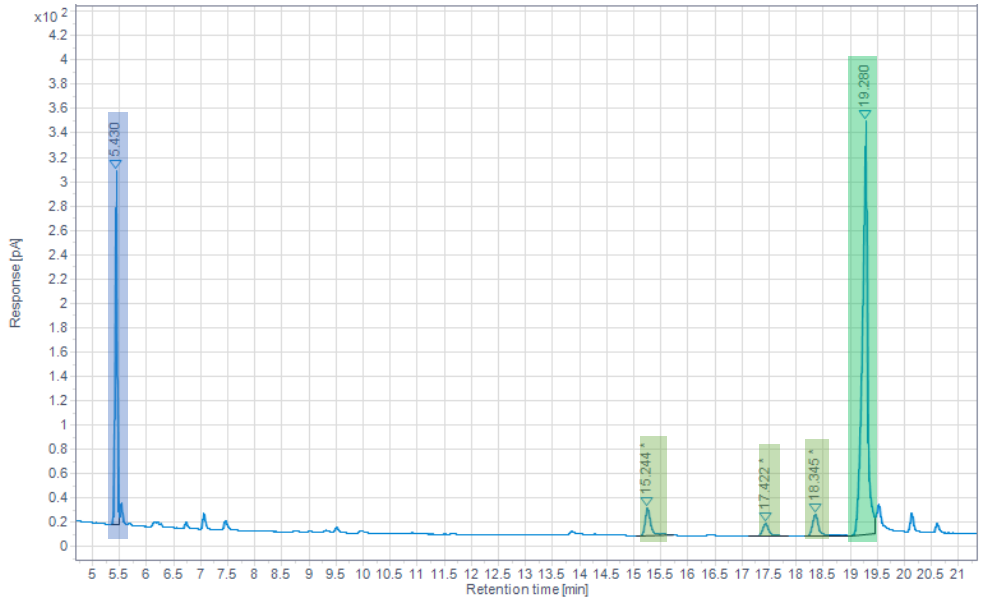


Figure S132. $^{1}H–^{15}N$ HMBC of the one-pot pyrrole synthesis/arylation of **1e-BBN** and **6a** in $CDCl_3$ after HCl workup.

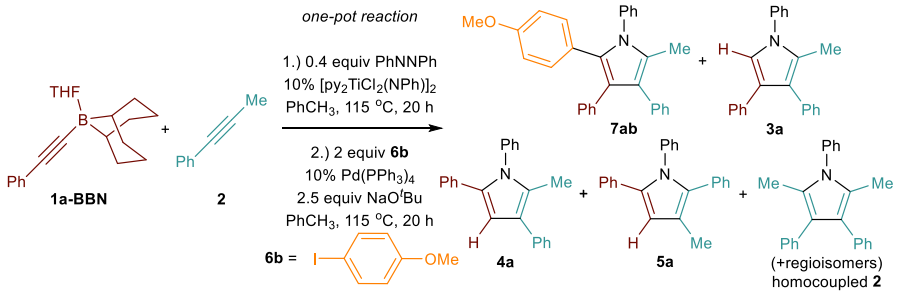


	Retention Time (min)	Surface Area	# of C	Yield (%)
Ph_3CH	5.43	705.418	19	n.a.
7ea	19.28	2349.471	27	46.9
3e	not found[a]	n.d.	21	n.a.
homocoupled **2**	15.24, 17.42, 18.35	385.400	24	8.7

[a]The yield was too low to be identified.

Figure S133. Quantitative GC-FID chromatograph of the one-pot pyrrole synthesis/arylation of **1e-BBN** and **6a** after HCl workup.

One-Pot Pyrrole Synthesis/Arylation for 1a-BBN and *p*-Iodoanisole



The reaction was performed following **Procedure D** using **1a-BBN** (29.4 mg, 0.1 mmol, 1 equiv) as alkynylborane and *p*-iodoanisole (**6b**, 46.8 mg, 0.2 mmol, 2 equiv) as aryl iodide. The extraction was performed with CH_2Cl_2/H_2O.

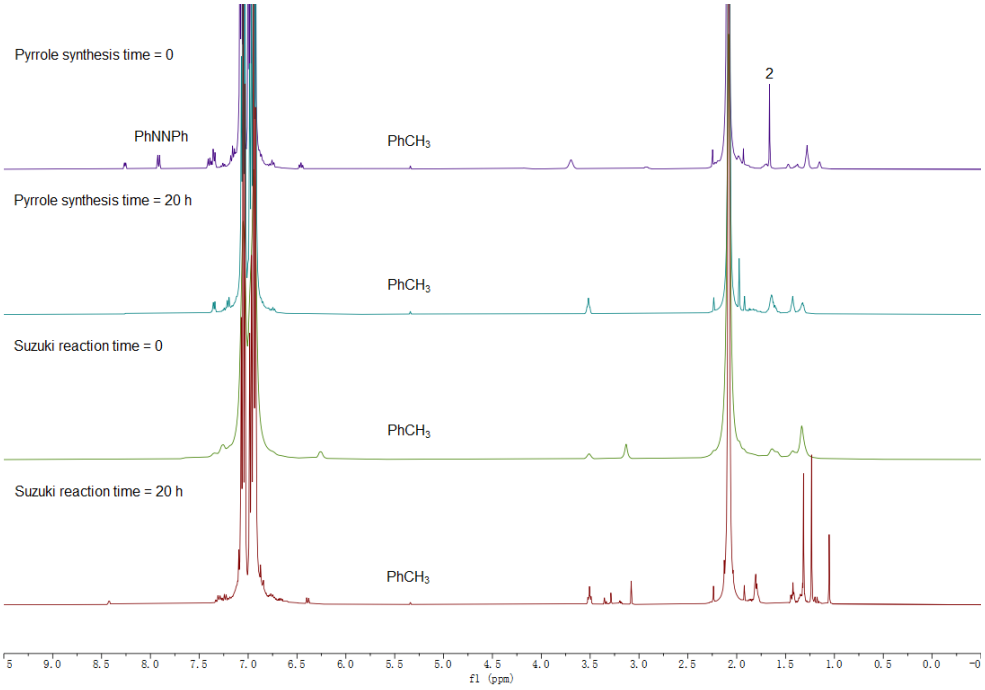


Figure S134. No-D ^{1}H NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6b** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.

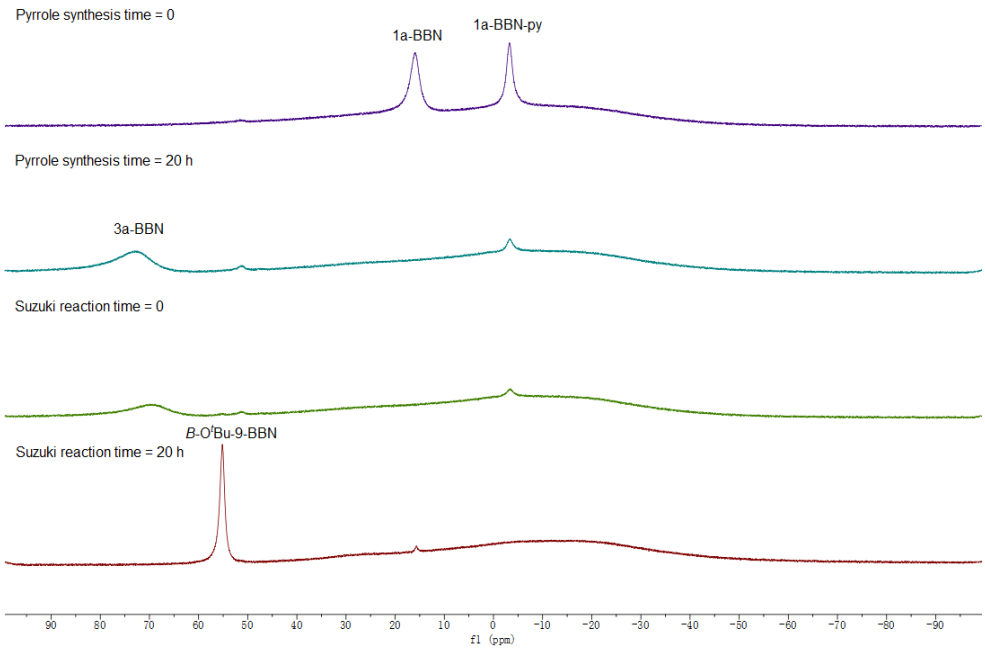
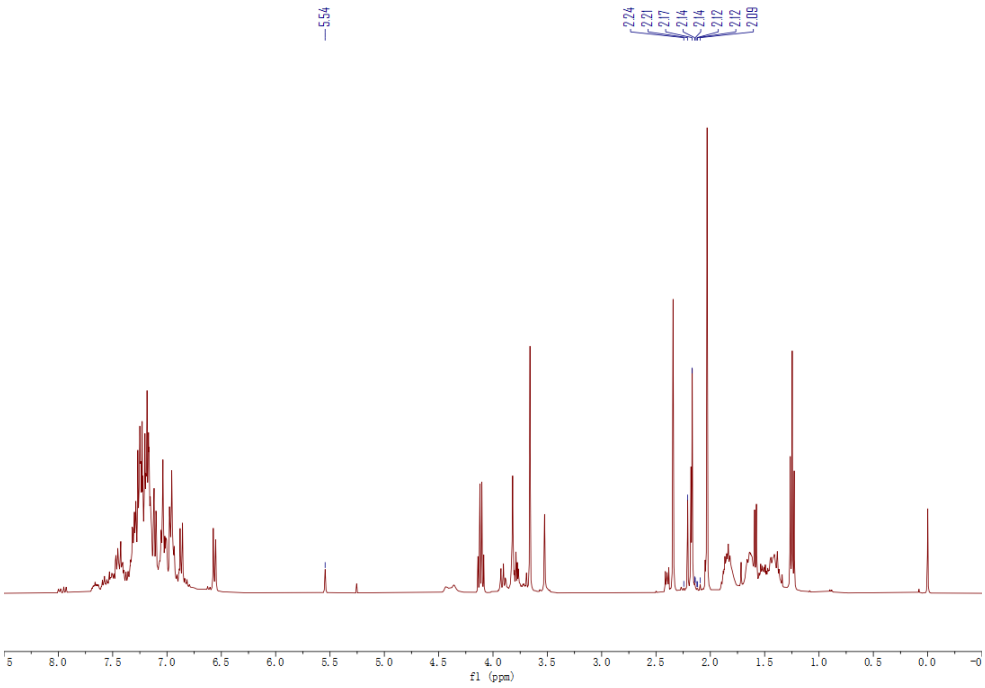


Figure S135. ^{11}B NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6b** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	3010.6	n.a.
7ab	2.17	$Me_{pyrrolyl}$	3	17318.6	38.4
3a	2.20	$Me_{pyrrolyl}$	3	6484.8	14.4
4a	2.24	$Me_{pyrrolyl}$	3	309.1	0.7
5a	not found	$H_{pyrrolyl}$	1	n.a.	n.d.
homocoupled **2**	2.14, 2.14, 2.12, 2.12, 2.09	$Me_{pyrrolyl}$ (2 per molecule)	6	1213.1	1.3

Figure S136. ^{1}H NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6b** in $CDCl_3$ after HCl workup.

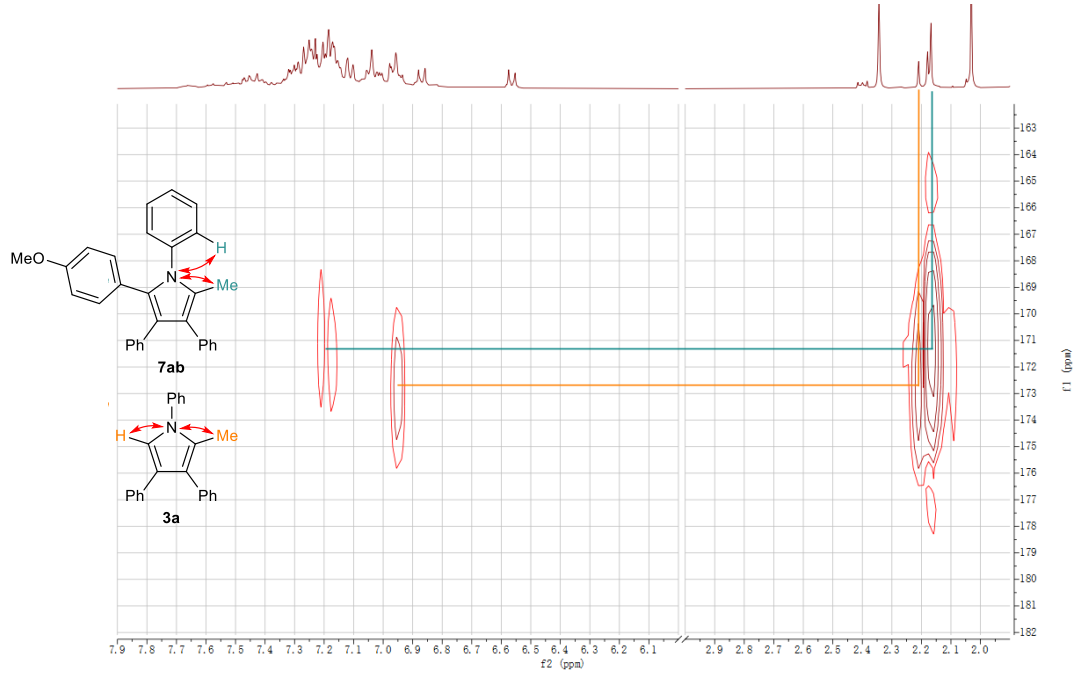
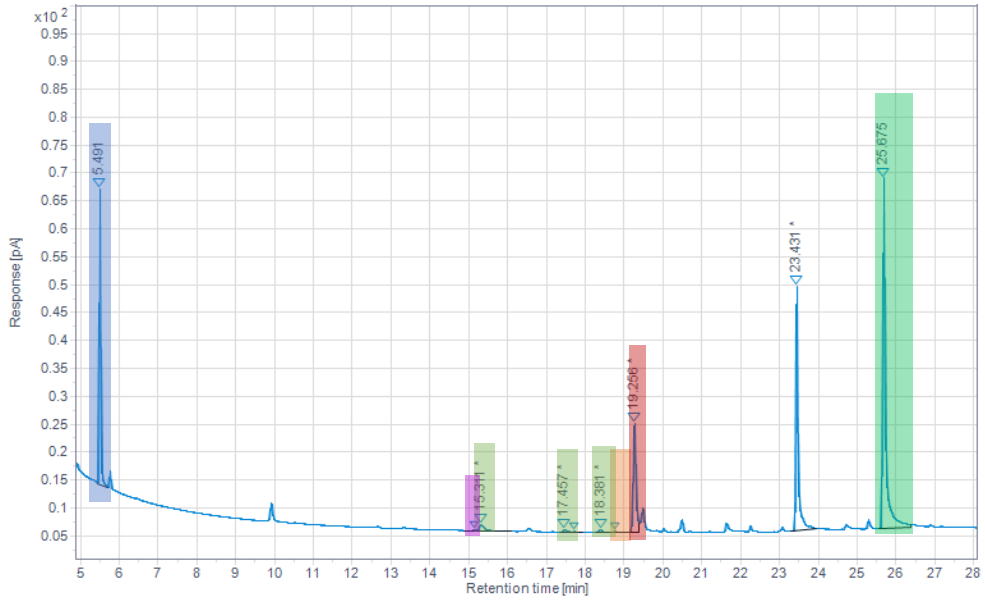


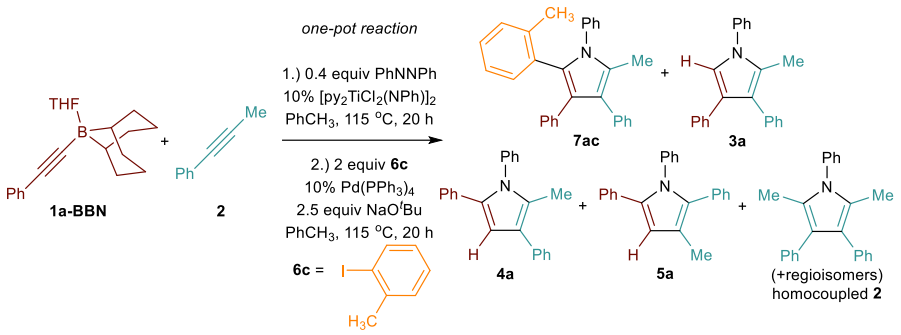
Figure S137. $^{1}H–^{15}N$ HMBC of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6b** in $CDCl_3$ after HCl workup.



	Retention Time (min)	Surface Area	# of C	Yield (%)
Ph_3CH	5.49	127.128	19	n.a.
7ab	25.68	306.060	30	30.5
3a	19.26	96.947	23	12.6
4a	18.76	1.783	23	0.2
5a	15.14	1.131	23	0.1
homocoupled **2**	15.31, 17.46, 18.38	17.406	24	2.2

Figure S138. Quantitative GC-FID chromatograph of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6b** after HCl workup.

One-Pot Pyrrole Synthesis/Arylation for 1a-BBN and *o*-Iodotoluene



The reaction was performed following **Procedure D** using **1a-BBN** (29.4 mg, 0.1 mmol, 1 equiv) as alkynylborane and *o*-iodotoluene (**6c**, 43.6 mg, 0.2 mmol, 2 equiv) as aryl iodide.

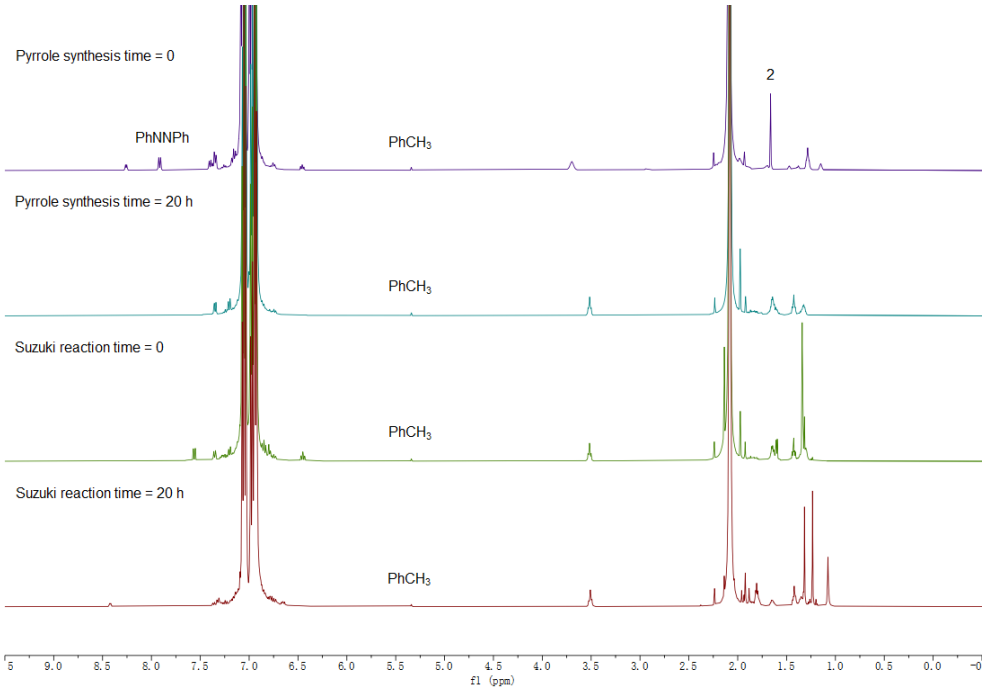


Figure S139. No-D ^{1}H NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6c** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.

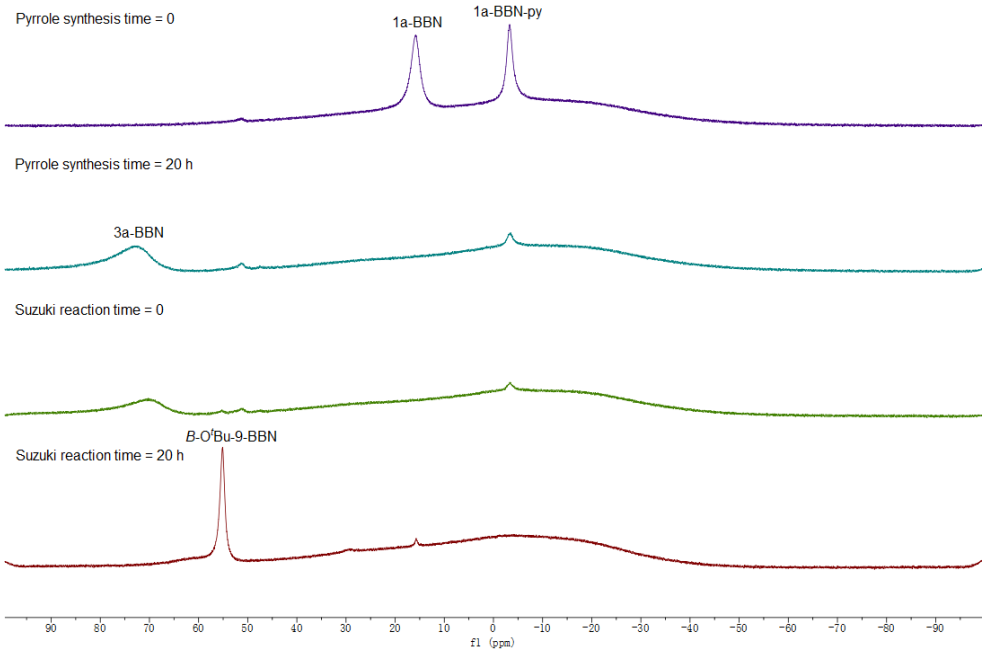
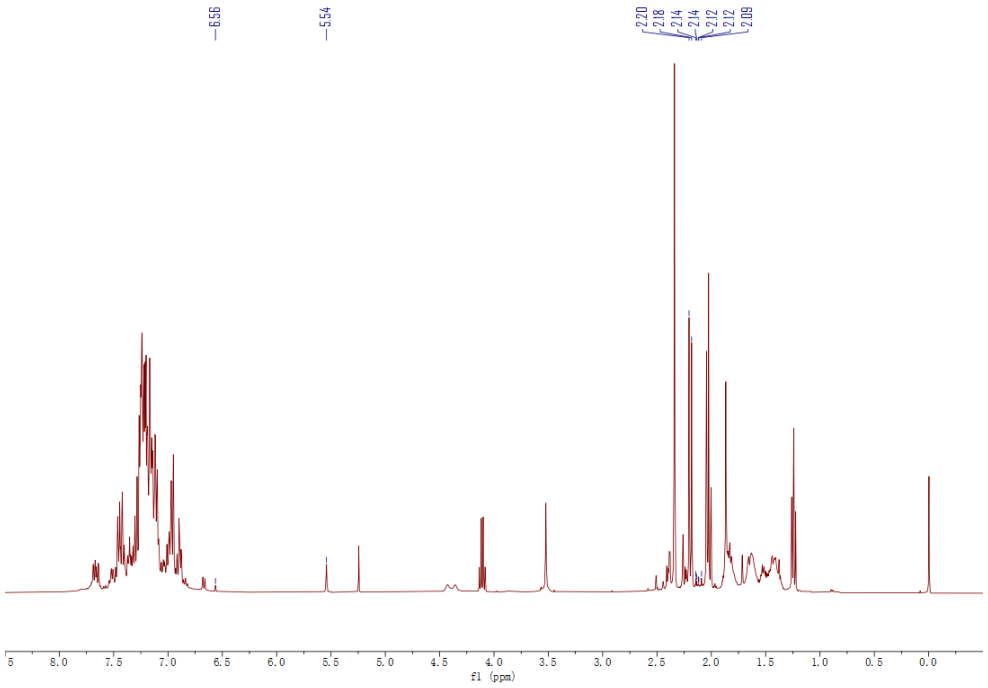


Figure S140. ^{11}B NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6c** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	2996.5	n.a.
7ac	2.17	$Me_{pyrrolyl}$	3	14251.9	31.7
3a	2.20	$Me_{pyrrolyl}$	3	15108.3	33.6
4a	6.56	$H_{pyrrolyl}$	1	356.2	2.4
5a	not found	$H_{pyrrolyl}$	1	n.a.	n.d.
homocoupled **2**	2.14, 2.14, 2.12, 2.12, 2.09	$Me_{pyrrolyl}$ (2 per molecule)	6	2009.3	2.2

Figure S141. ^{1}H NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6c** in $CDCl_3$ after HCl workup.

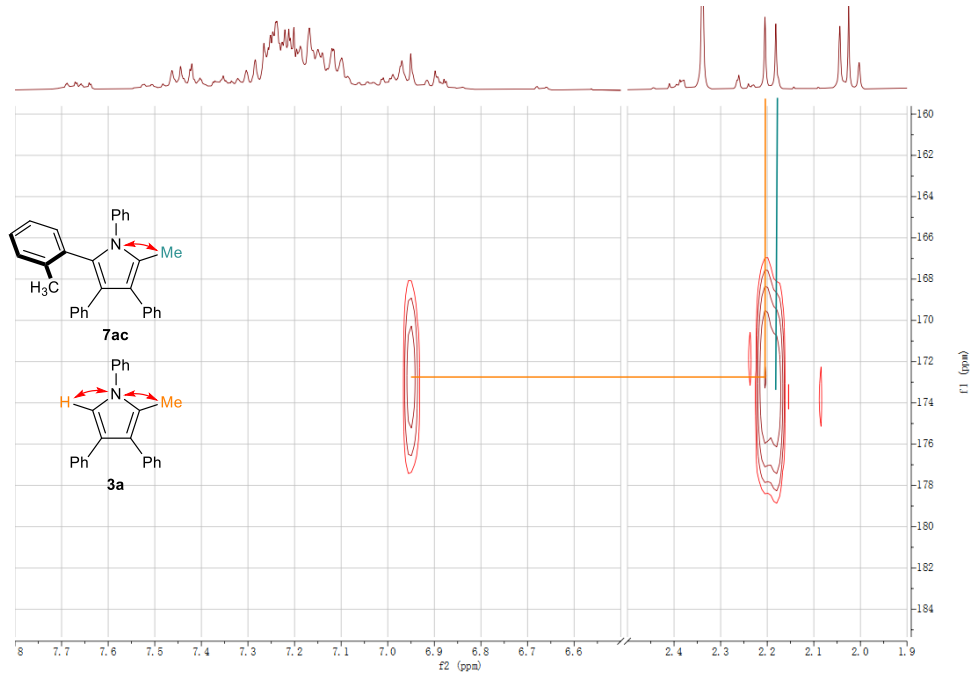
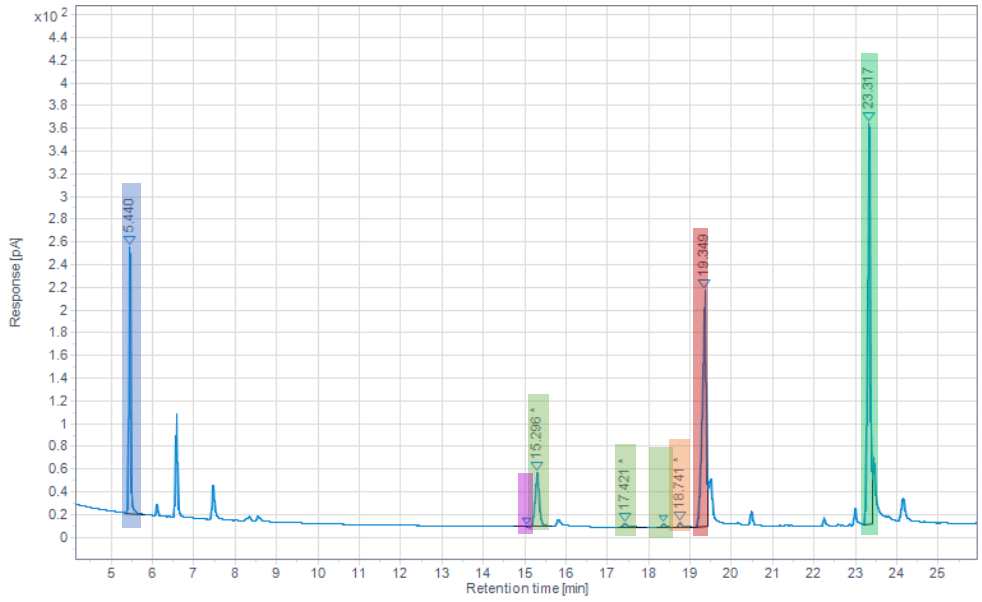


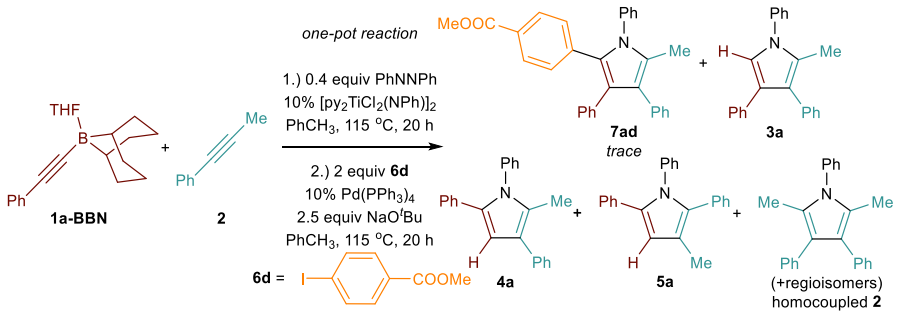
Figure S142. $^{1}H–^{15}N$ HMBC of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6c** in $CDCl_3$ after HCl workup.



	Retention Time (min)	Surface Area	# of C	Yield (%)
Ph_3CH	5.44	602.354	19	n.a.
7ac	23.32	1431.650	30	30.1
3a	19.35	1285.246	23	35.3
4a	18.74	27.693	23	0.8
5a	15.04	2.29	23	0.1
homocoupled **2**	15.30, 17.42, 18.35	363.792	24	9.6

Figure S143. Quantitative GC-FID chromatograph of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6c** after HCl workup.

One-Pot Pyrrole Synthesis/Arylation for 1a-BBN and Methyl *p*-Iodobenzoate



The reaction was performed following **Procedure D** using **1a-BBN** (29.4 mg, 0.1 mmol, 1 equiv) as alkynylborane and methyl *p*-iodobenzoate (**6d**, 52.4 mg, 0.2 mmol, 2 equiv) as aryl iodide.

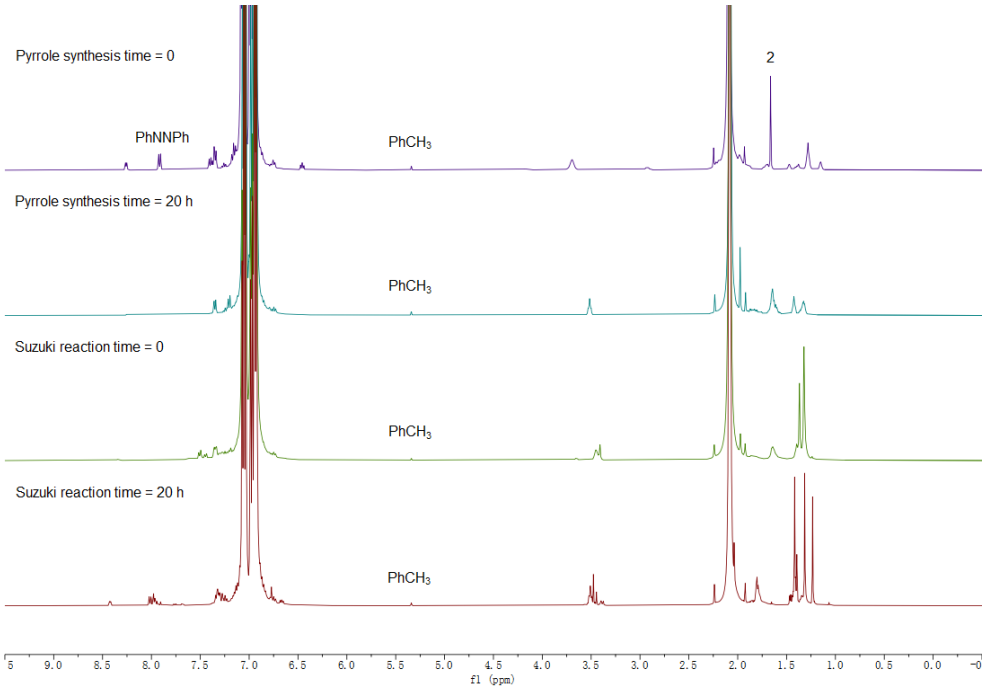


Figure S144. No-D ^{1}H NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6d** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.

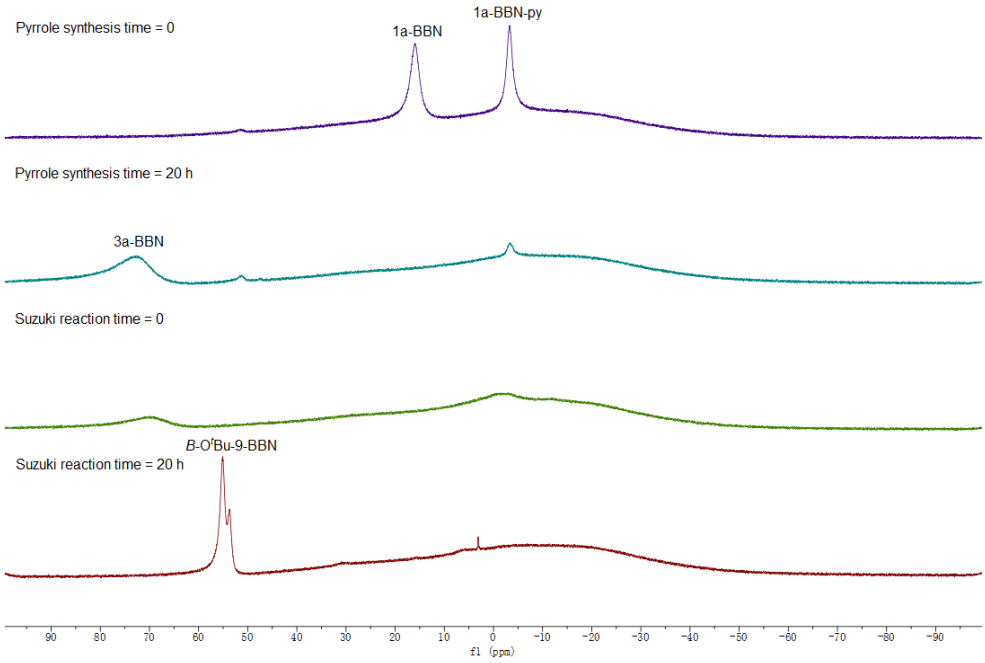
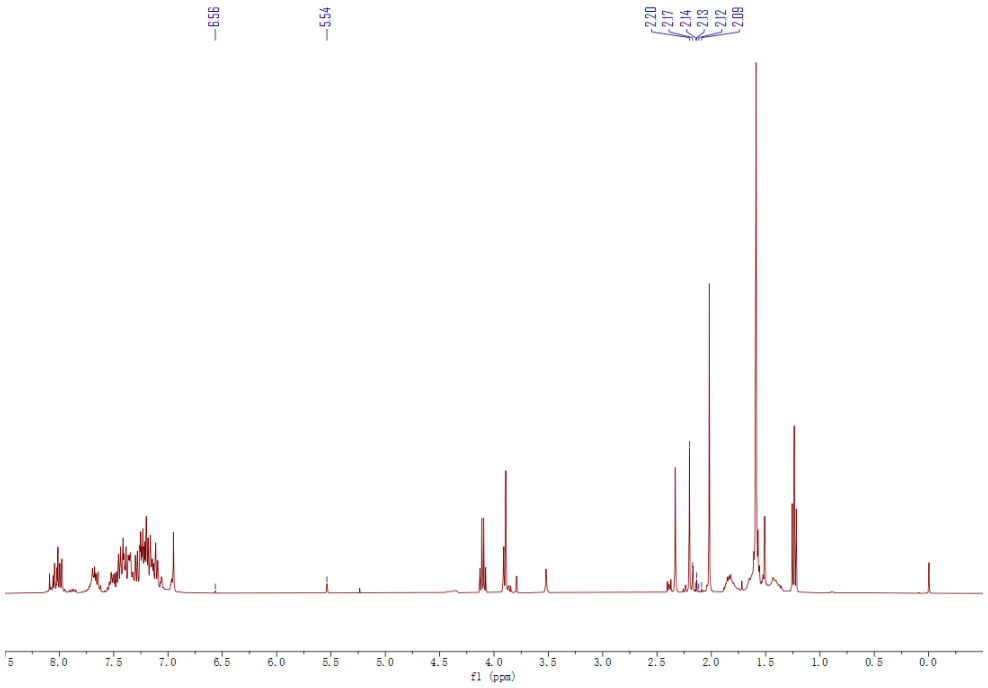


Figure S145. ^{11}B NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6d** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	1904.2	n.a.
7ad	2.17	$Me_{pyrrolyl}$	3	1954.3	6.8
3a	2.20	$Me_{pyrrolyl}$	3	15225.7	53.4
4a	5.56	$H_{pyrrolyl}$	1	230.1	2.4
5a	not found	$H_{pyrrolyl}$	1	n.a.	n.d.
homocoupled **2**	2.14, 2.13, 2.12, 2.09	$Me_{pyrrolyl}$ (2 per molecule)	6	1414.6	2.5

Figure S146. ^{1}H NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6d** in $CDCl_3$ after HCl workup.

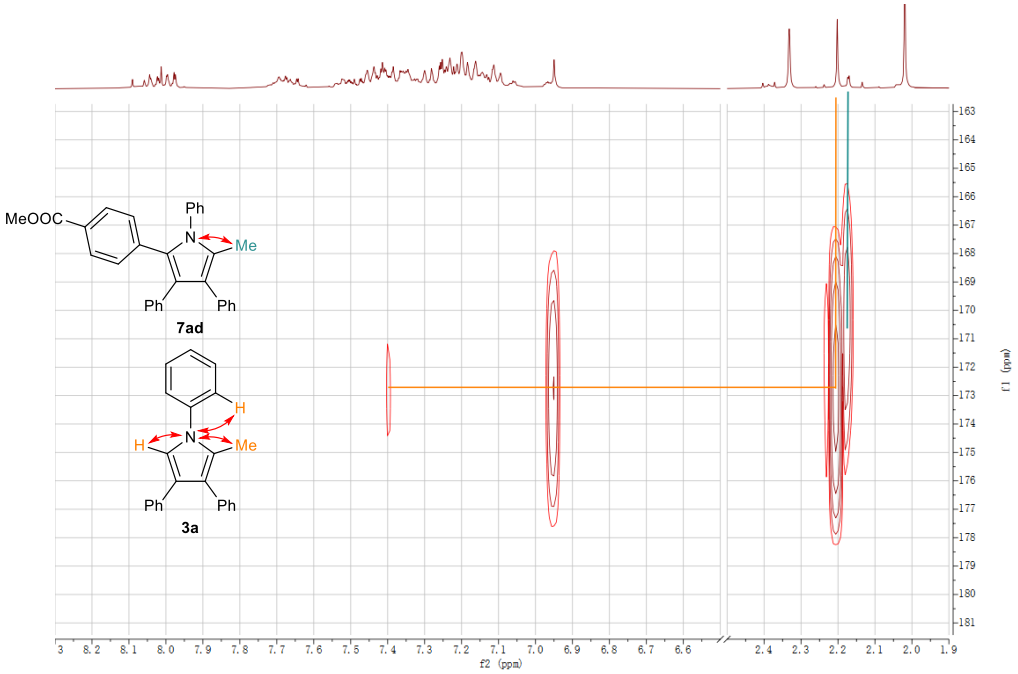
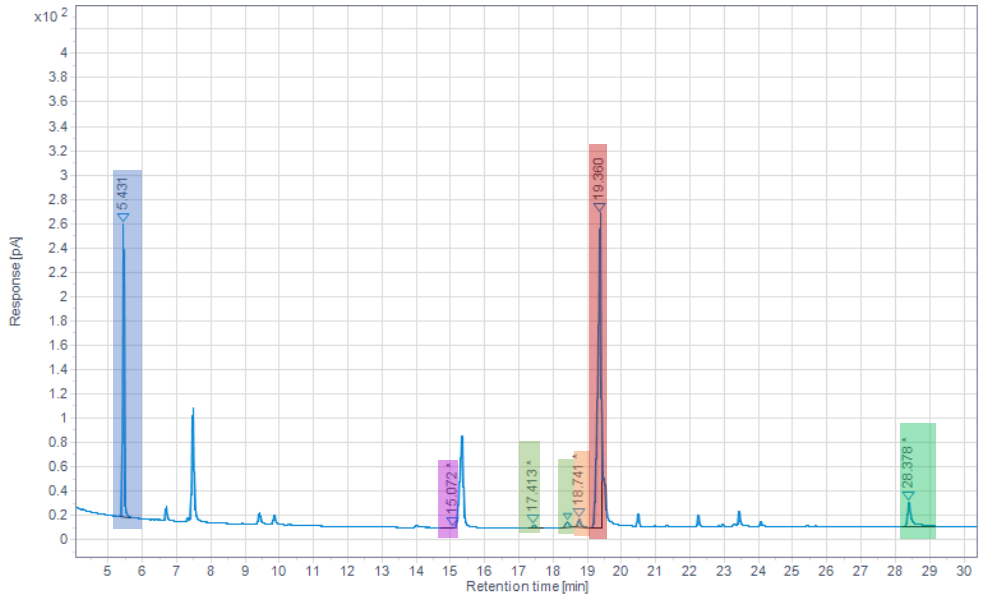


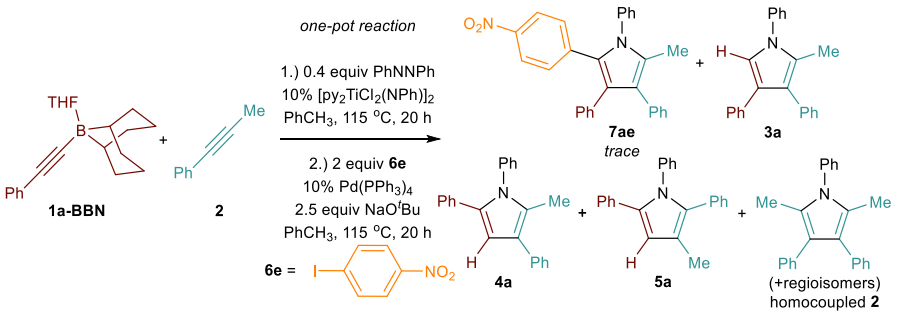
Figure S147. $^{1}H–^{15}N$ HMBC of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6d** in $CDCl_3$ after HCl workup.



	Retention Time (min)	Surface Area	# of C	Yield (%)
Ph_3CH	5.43	596.253	19	n.a.
7ad	28.38	171.625	31	3.5
3a	19.36	1666.566	23	46.2
4a	18.74	42.820	23	1.2
5a	15.07	0.184	23	< 0.1
homocoupled **2**	17.41, 18.36	59.168	24	1.6

Figure S148. Quantitative GC-FID chromatograph of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6d** after HCl workup.

One-Pot Pyrrole Synthesis/Arylation for 1a-BBN and *p*-Iodonitrobenzene



The reaction was performed following **Procedure D** using **1a-BBN** (29.4 mg, 0.1 mmol, 1 equiv) as alkynylborane and *p*-iodonitrobenzene (**6e**, 49.8 mg, 0.2 mmol, 2 equiv) as aryl iodide. The extraction was performed with CH_2Cl_2/H_2O.

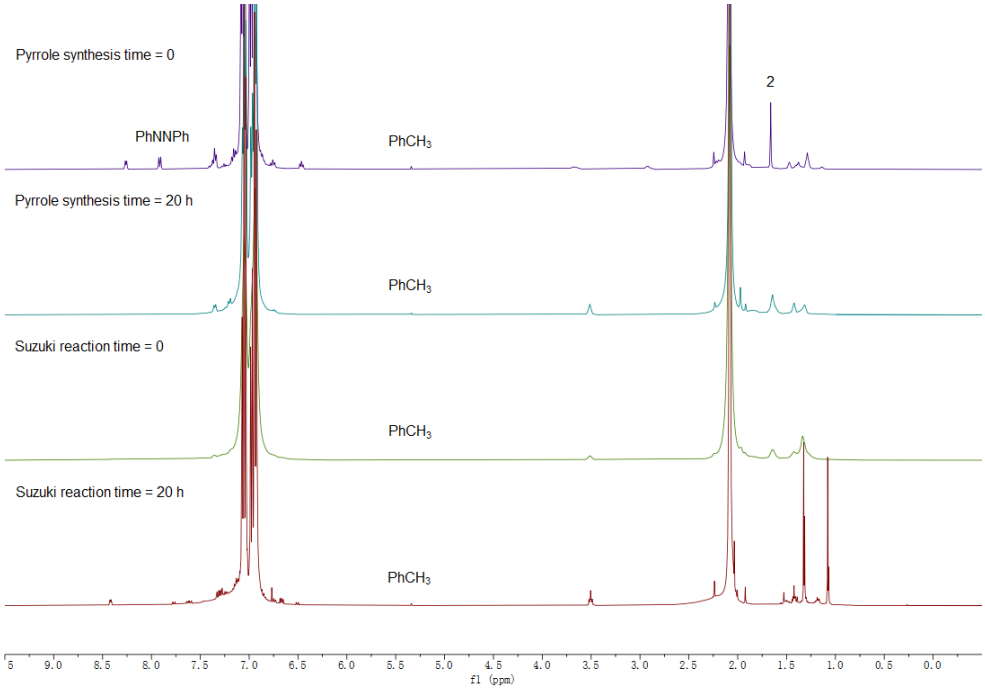


Figure S149. No-D ^{1}H NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6e** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.

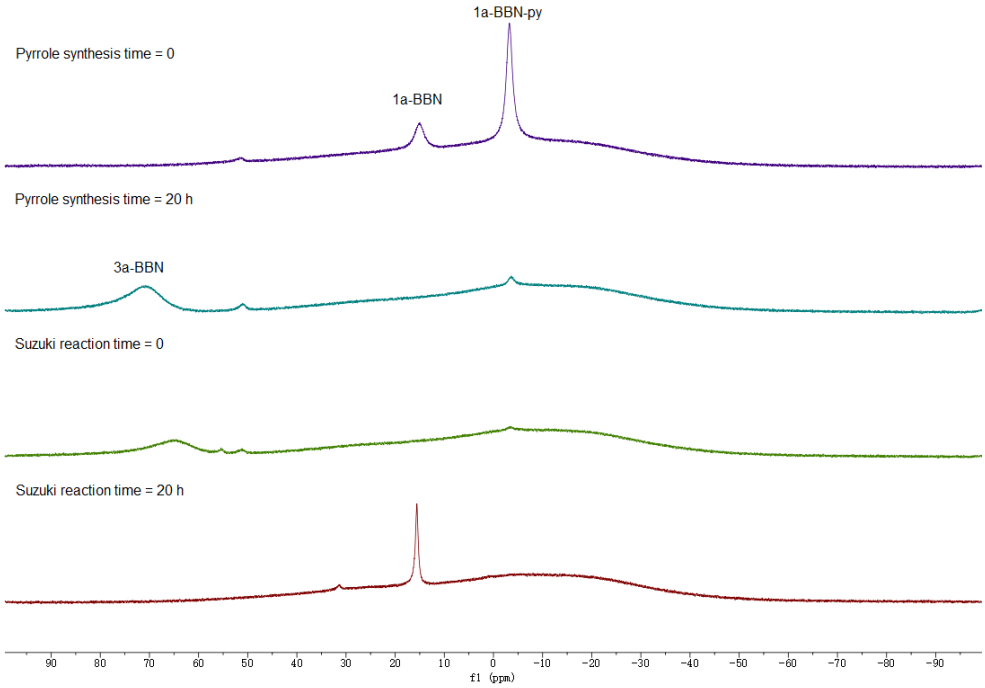
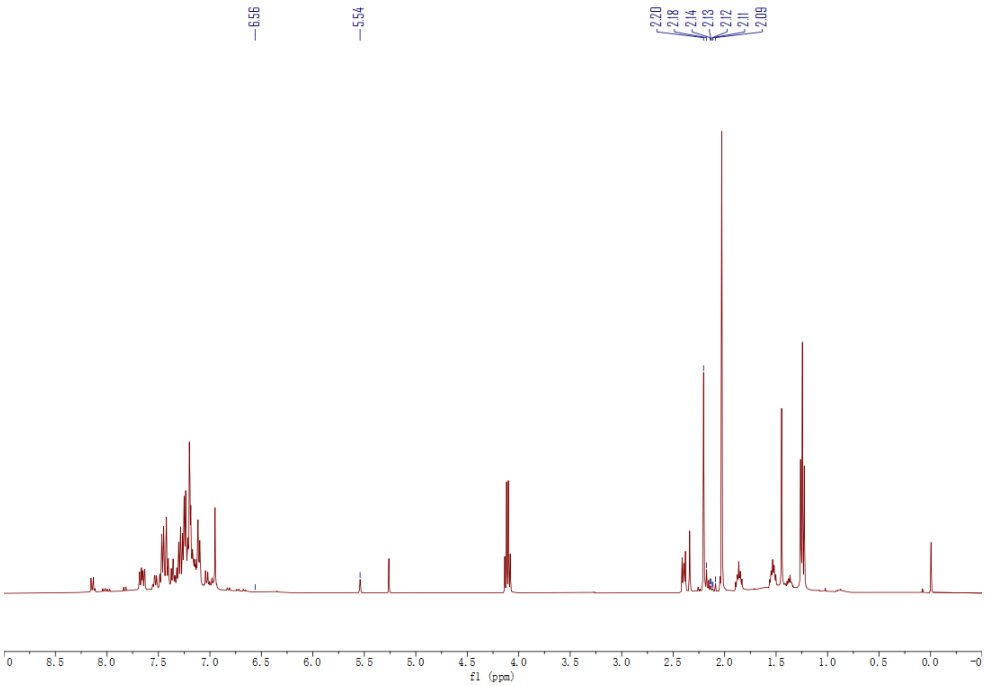


Figure S150. ^{11}B NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6e** at time = 0, time = 20 h of pyrrole synthesis, time = 0 and time = 20 h of Suzuki reaction in $PhCH_3$.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	3084.0	n.a.
7ae	2.18	$Me_{pyrrolyl}$	3	2120.5	4.6
3a	2.20	$Me_{pyrrolyl}$	3	28226.0	61.0
4a	6.56	$H_{pyrrolyl}$	1	111.6	0.7
5a	not found	$H_{pyrrolyl}$	1	n.a.	n.d.
homocoupled **2**	2.14, 2.13, 2.12, 2.11, 2.09	$Me_{pyrrolyl}$ (2 per molecule)	6	2539.1	2.7

Figure S151. ^1H NMR of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6e** in $CDCl_3$ after HCl workup.

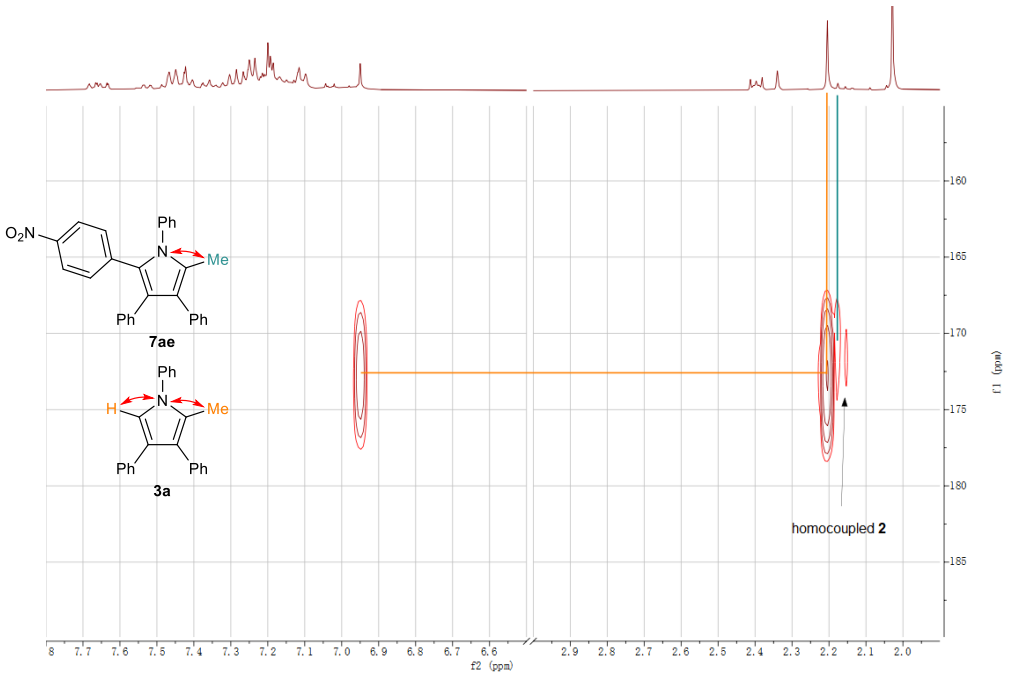
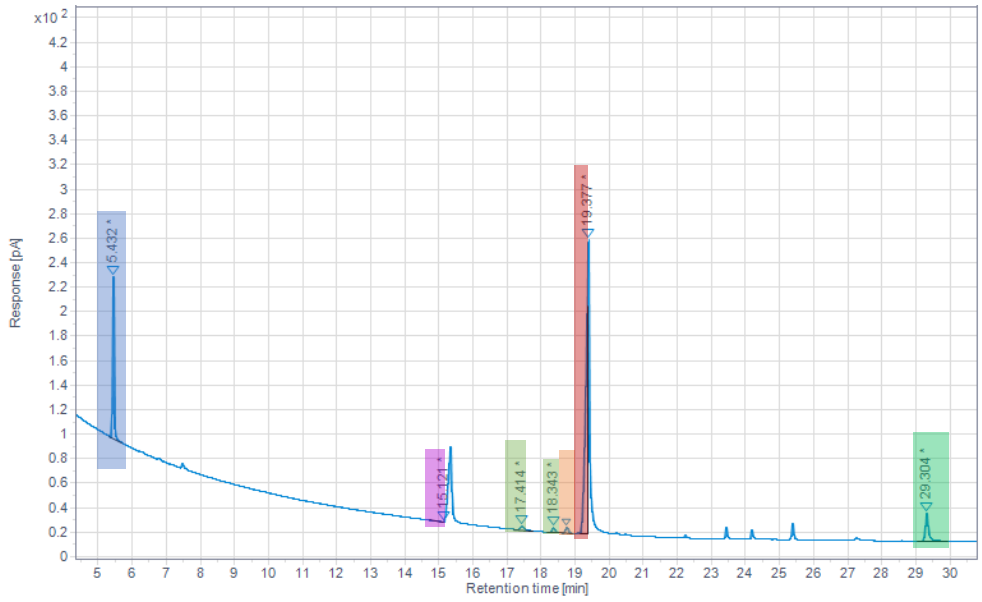


Figure S152. $^{1}H–^{15}N$ HMBC of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6e** in $CDCl_3$ after HCl workup.

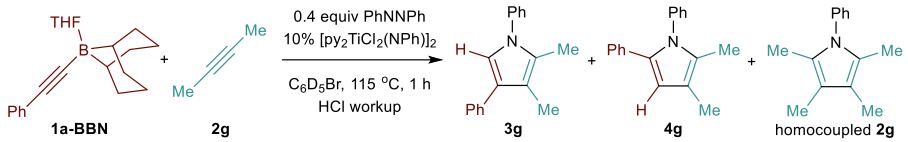


	Retention Time (min)	Surface Area	# of C	Yield (%)
Ph_3CH	5.43	336.796	19	n.a.
7ae	29.30	148.209	29	5.8
3a	19.38	1396.794	23	68.5
4a	18.74	27.707	23	1.4
5a	15.12	0.107	23	< 0.1
homocoupled **2**	17.41, 18.34	48.556	24	2.3

Figure S153. Quantitative GC-FID chromatograph of the one-pot pyrrole synthesis/arylation of **1a-BBN** and **6e** after HCl workup.

Catalytic Pyrrole Syntheses: Hydrocarbon Alkyne Scopes (Table 4)

Catalytic reaction of **1a-BBN** with 2-butyne **(Table 4)**



The reaction was performed following **Procedure B** using **1a-BBN** (29.4 mg, 0.1 mmol, 1 equiv) and 2-butyne (**2g**, 5.4 mg, 0.1 mmol, 1 equiv) with the reaction being heated for 1 h.

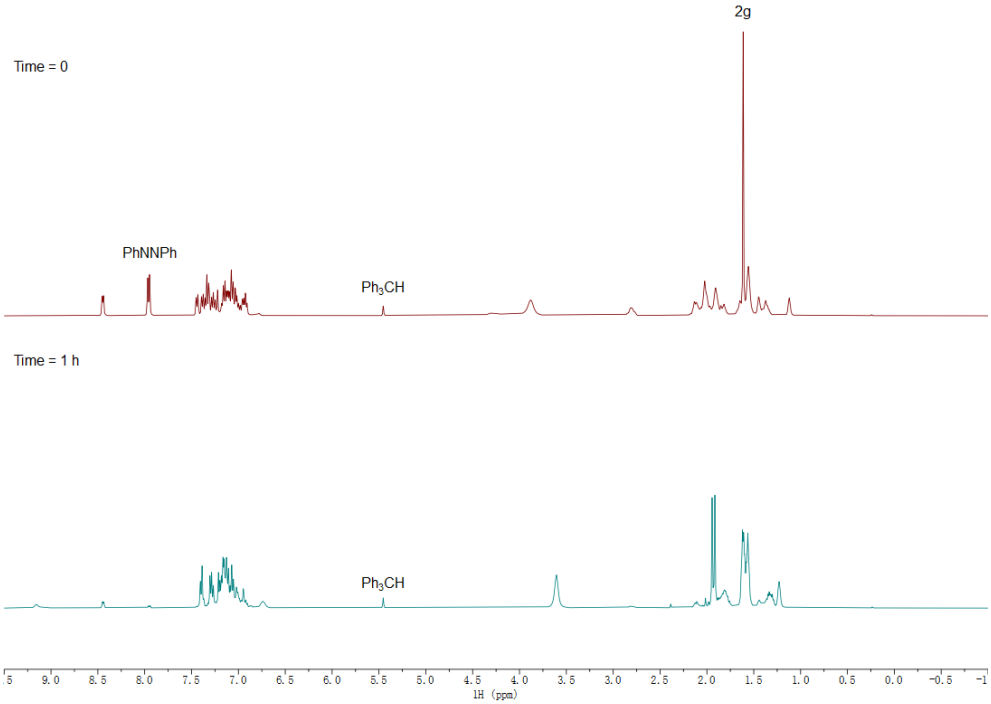


Figure S154. ^{1}H NMR of the reaction of **1a-BBN** with **2g** at time = 0 (top), time = 1 h (bottom) in C_6D_5Br.

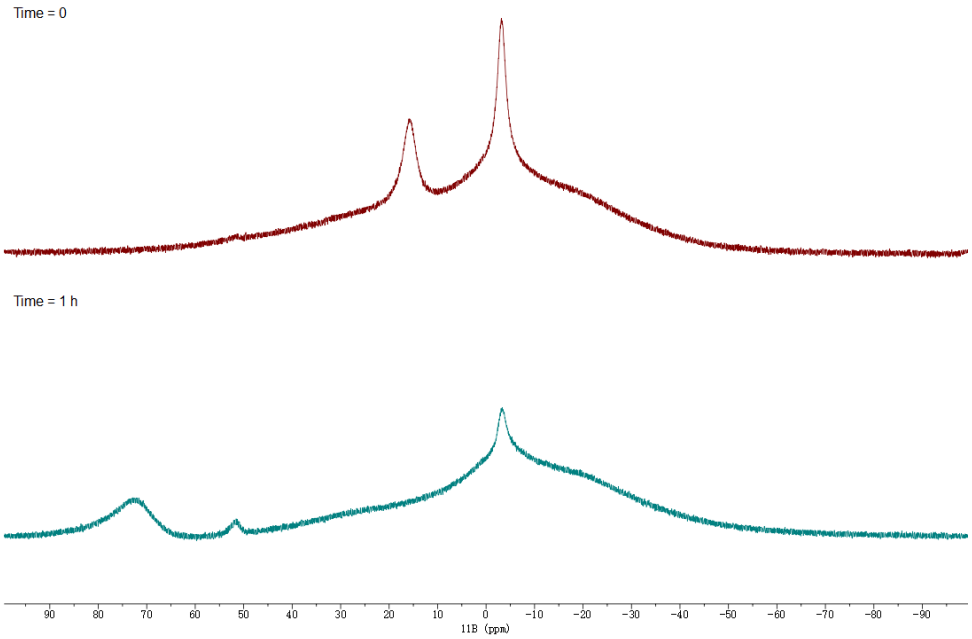
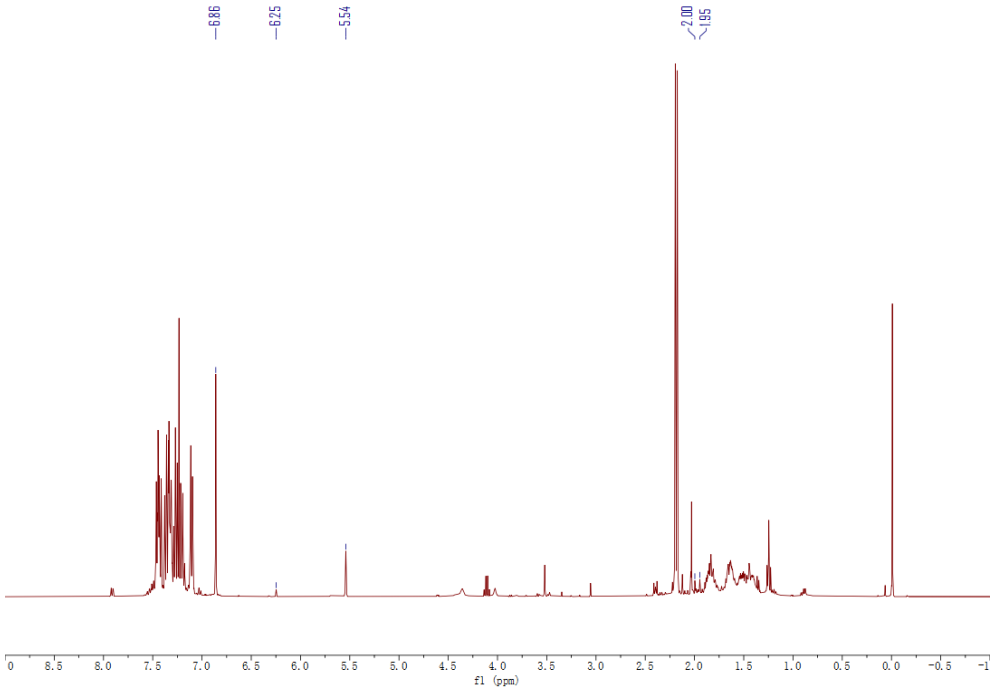


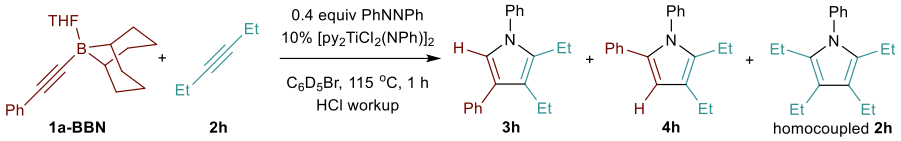
Figure S155. ^{11}B NMR of the reaction of **1a-BBN** with **2g** at time = 0 (top), time = 1 h (bottom) in C_6D_5Br.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	5760.5	n.a.
3g	6.86	$H_{pyrrolyl}$	1	15151.4	52.6
4g	6.25	$H_{pyrrolyl}$	1	597.5	2.1
homocoupled **2g**	2.00, 1.95	$Me_{pyrrolyl}$ (4 per molecule)	12	2685.6	0.8

Figure S156. ^{1}H NMR of the reaction of **1a-BBN** with **2g** in $CDCl_3$ after HCl workup.

Catalytic reaction of **1a-BBN** with 3-hexyne **(Table 4)**



The reaction was performed following **Procedure B** using **1a-BBN** (29.4 mg, 0.1 mmol, 1 equiv) and 3-hexyne (**2h**, 8.2 mg, 0.1 mmol, 1 equiv) with the reaction being heated for 1 h.

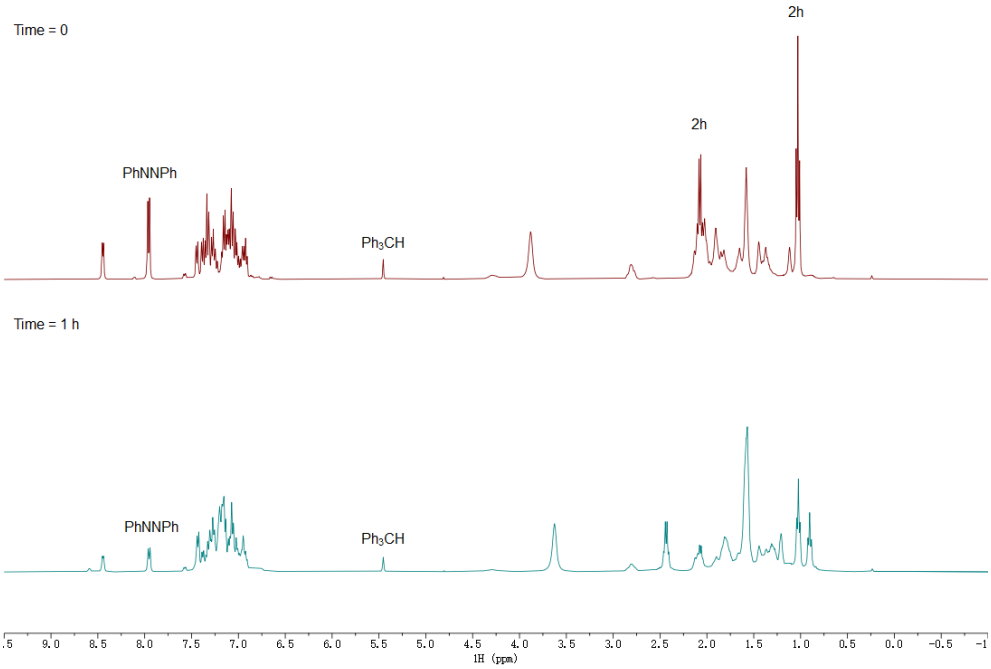


Figure S157. ^{1}H NMR of the reaction of **1a-BBN** with **2h** at time = 0 (top), time = 1 h (bottom) in C_6D_5Br.

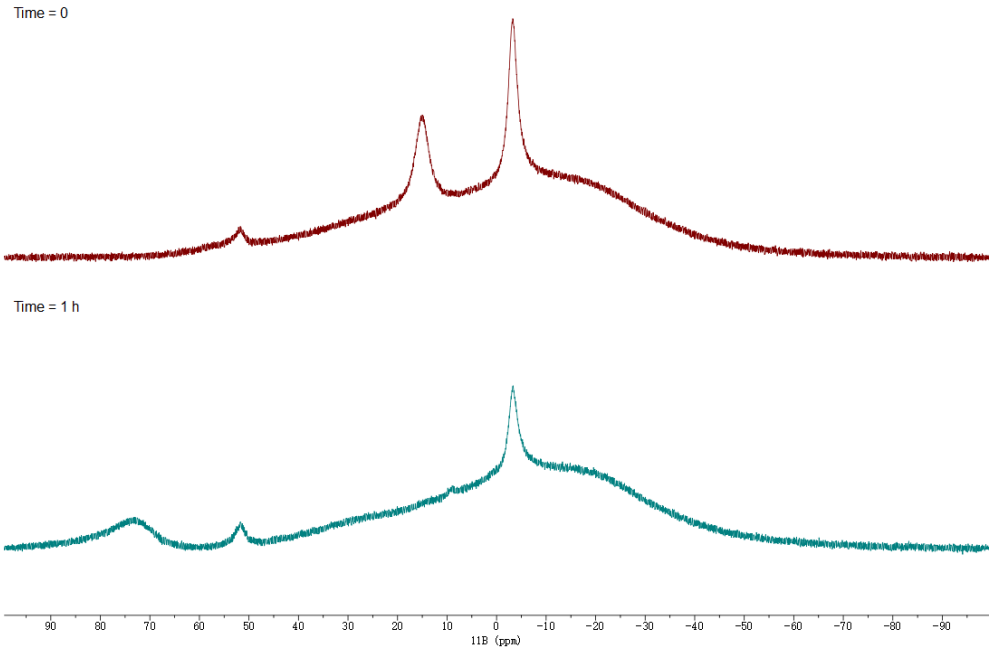
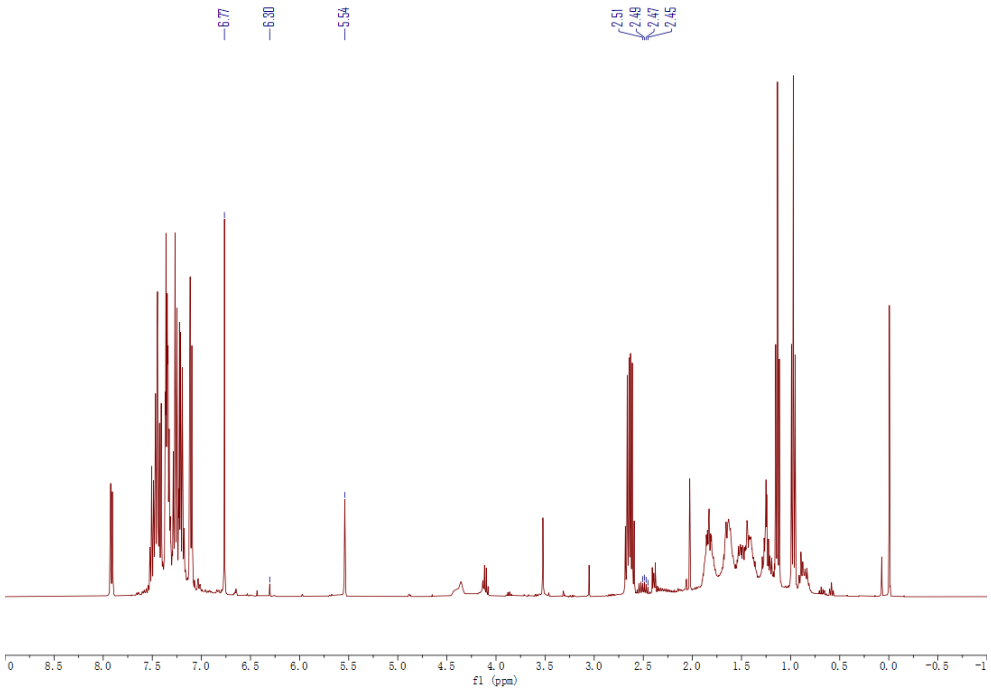


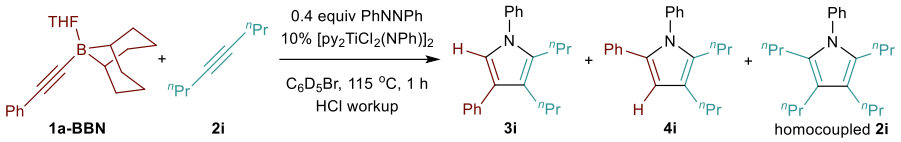
Figure S158. ^{11}B NMR of the reaction of **1a-BBN** with **2h** at time = 0 (top), time = 1 h (bottom) in C_6D_5Br.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	4143.2	n.a.
3h	6.77	$H_{pyrrolyl}$	1	7107.0	34.3
4h	6.30	$H_{pyrrolyl}$	1	348.0	1.7
homocoupled **2h**	2.51, 2.49, 2.47, 2.45	3,4-CH_2CH_3 (2 per molecule)	4	904.8	1.1

Figure S159. ^1H NMR of the reaction of **1a-BBN** with **2h** in $CDCl_3$ after HCl workup.

Catalytic reaction of **1a-BBN** with 4-octyne **(Table 4)**



The reaction was performed following **Procedure B** using **1a-BBN** (29.4 mg, 0.1 mmol, 1 equiv) and 4-octyne (**2i**, 11.0 mg, 0.1 mmol, 1 equiv) with the reaction being heated for 1 h.

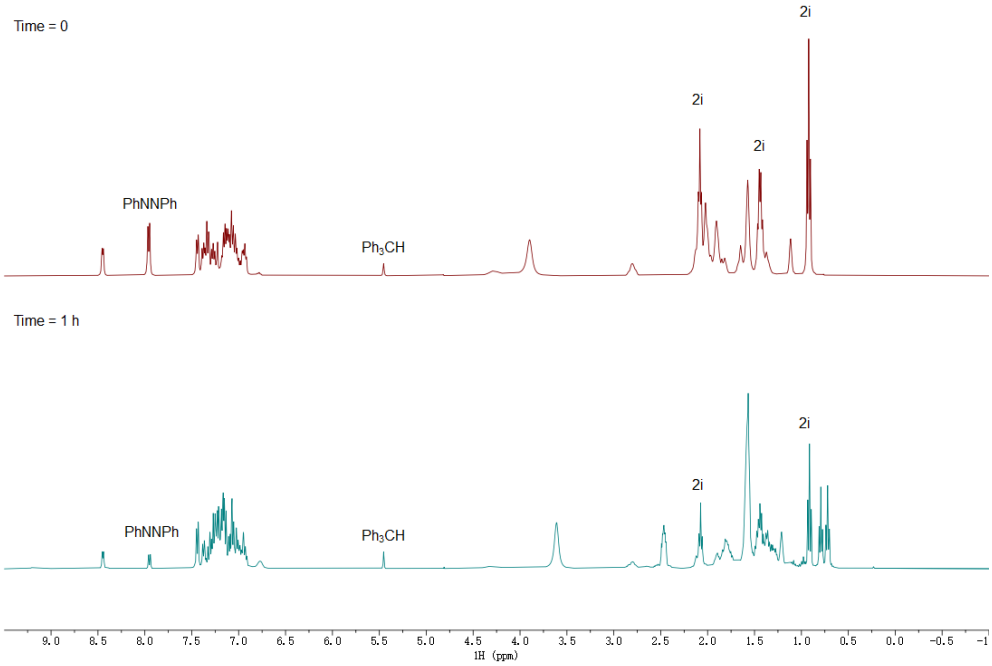


Figure S160. ^{1}H NMR of the reaction of **1a-BBN** with **2i** at time = 0 (top), time = 1 h (bottom) in C_6D_5Br.

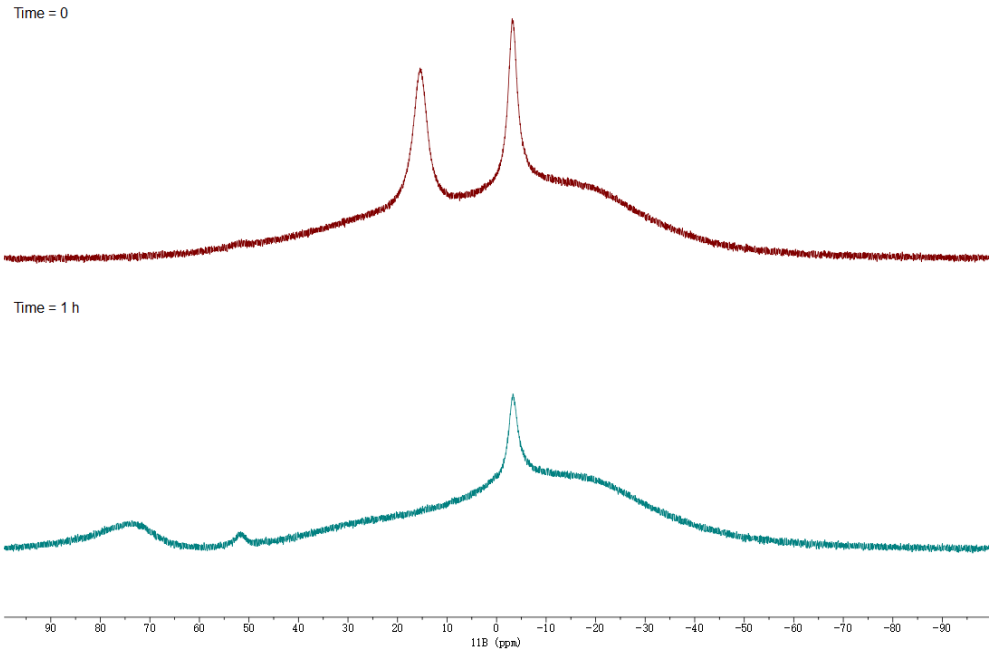
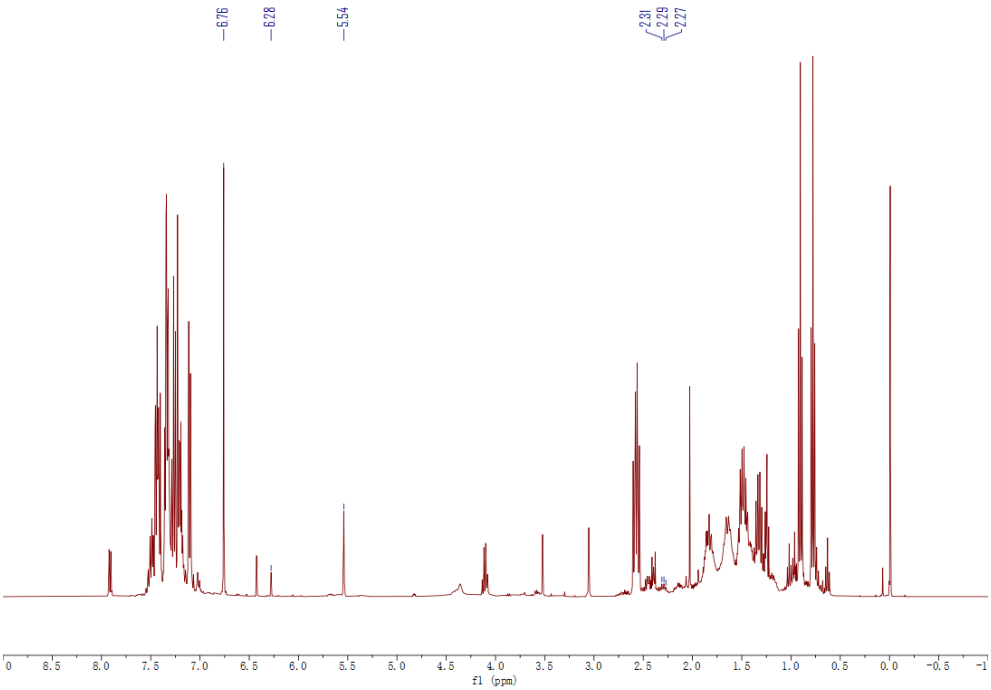


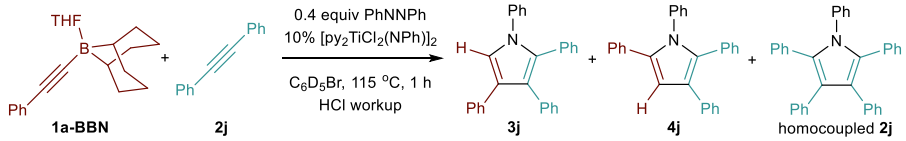
Figure S161. ^{11}B NMR of the reaction of **1a-BBN** with **2i** at time = 0 (top), time = 1 h (bottom) in C_6D_5Br.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	4788.6	n.a.
3i	6.76	$H_{pyrrolyl}$	1	10643.2	44.5
4i	6.28	$H_{pyrrolyl}$	1	808.8	3.4
homocoupled **2i**	2.30, 2.29, 2.27	2,5-CH_2CH_3 (2 per molecule)	4	948.7	1.0

Figure S162. ^{1}H NMR of the reaction of **1a-BBN** with **2i** in $CDCl_3$ after HCl workup.

Catalytic reaction of **1a-BBN** with diphenylacetylene **(Table 4)**



The reaction was performed following **Procedure B** using **1a-BBN** (29.4 mg, 0.1 mmol, 1 equiv) and diphenylacetylene (**2j**, 17.8 mg, 0.1 mmol, 1 equiv) with the reaction being heated for 1 h. Yields were determined by GC due to peak overlapping in ^{1}H NMR spectrum after HCl workup.

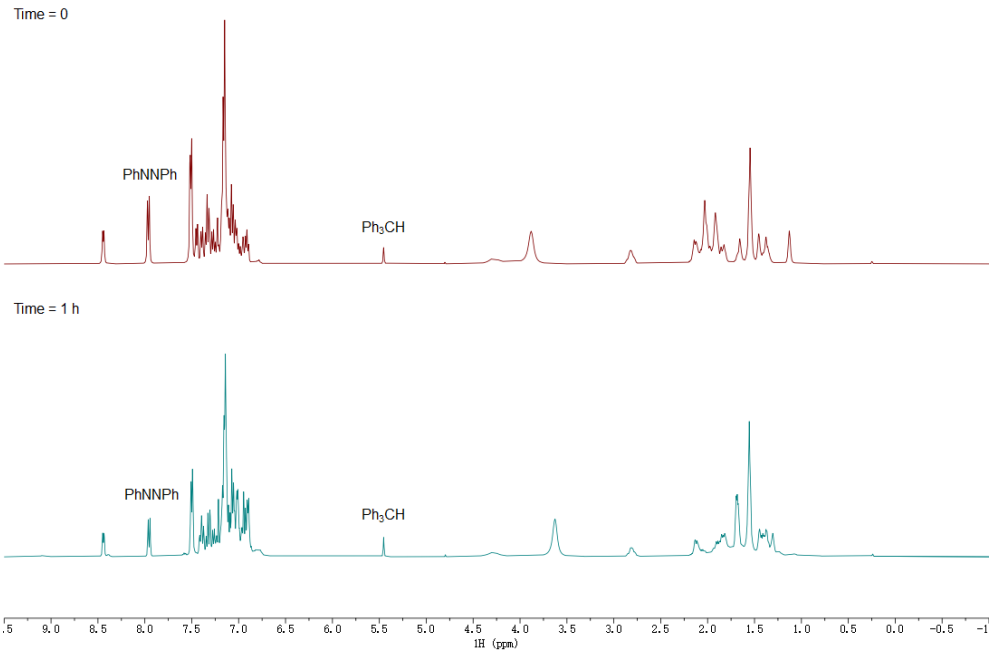


Figure S163. ^{1}H NMR of the reaction of **1a-BBN** with **2j** at time = 0 (top), time = 1 h (bottom) in C_6D_5Br.

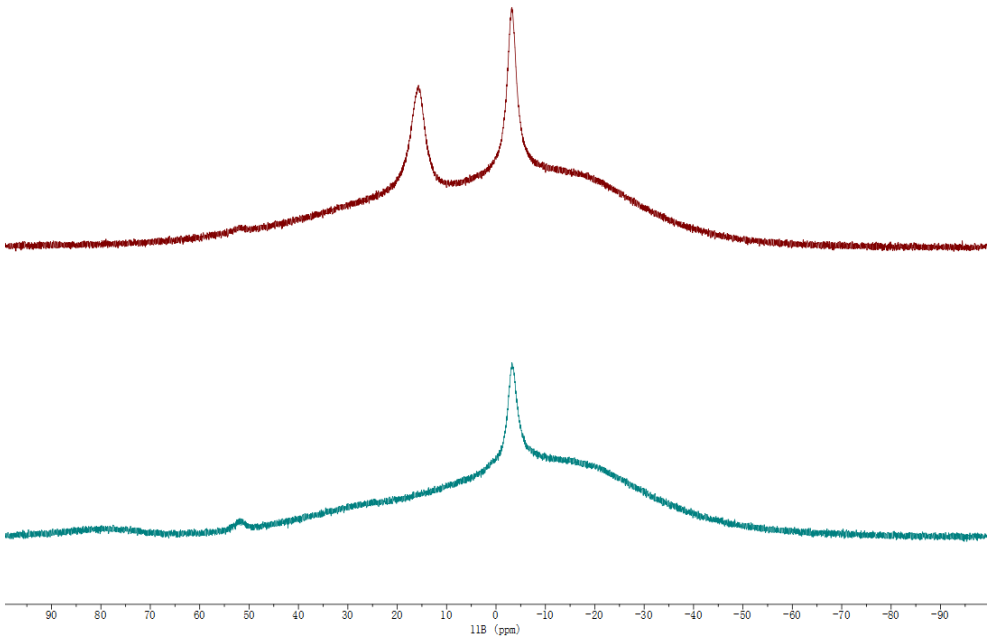
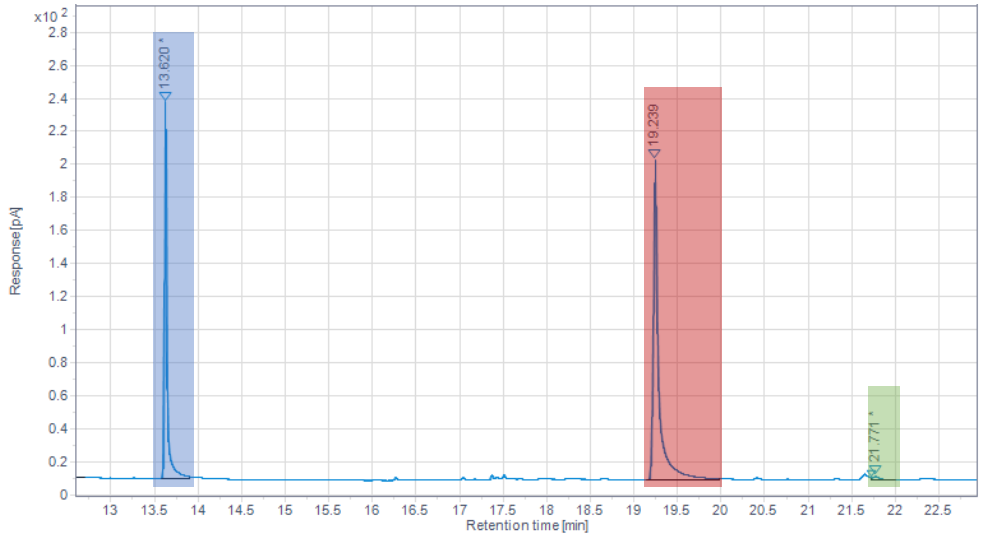


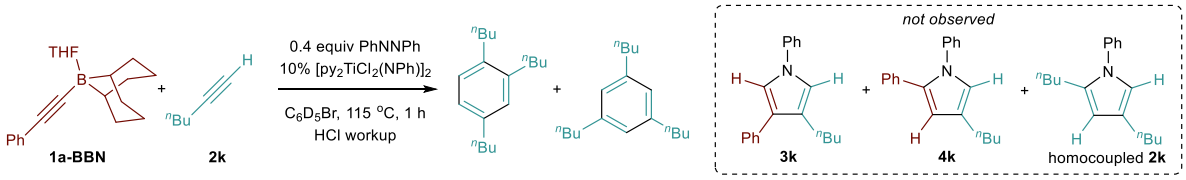
Figure S164. ^{11}B NMR of the reaction of **1a-BBN** with **2j** at time = 0 (top), time = 1 h (bottom) in C_6D_5Br.



	Retention Time (min)	Surface Area	# of C	Yield (%)
Ph_3CH	13.620	434.769	19	n.a.
3j	19.239	791.935	28	24.7
4j	not found	n.a.	28	n.d.
homocoupled **2j**	21.771	10.684	34	0.3

Figure S165. Quantitative GC-FID chromatograph of the reaction of **1a-BBN** with **2j** after HCl workup.

Catalytic reaction of **1a-BBN** with 1-hexyne **(Table 4)**



The reaction was performed following **Procedure B** using **1a-BBN** (29.4 mg, 0.1 mmol, 1 equiv) and 1-hexyne (**2k**, 8.2 mg, 0.1 mmol, 1 equiv) with the reaction being heated for 1 h.

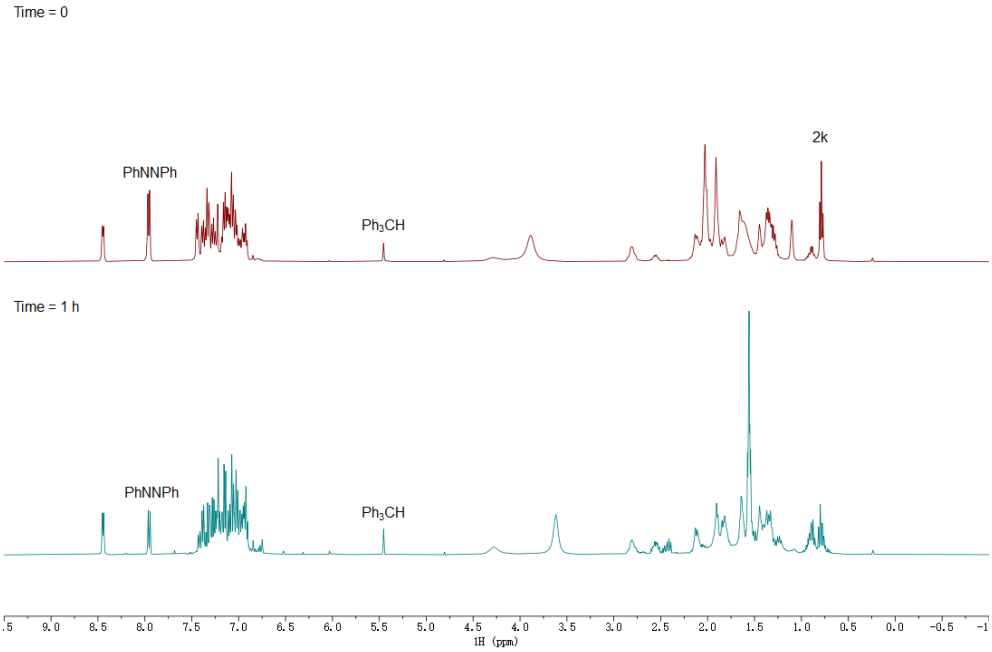


Figure S166. ^{1}H NMR of the reaction of **1a-BBN** with **2k** at time = 0 (top), time = 1 h (bottom) in C_6D_5Br.

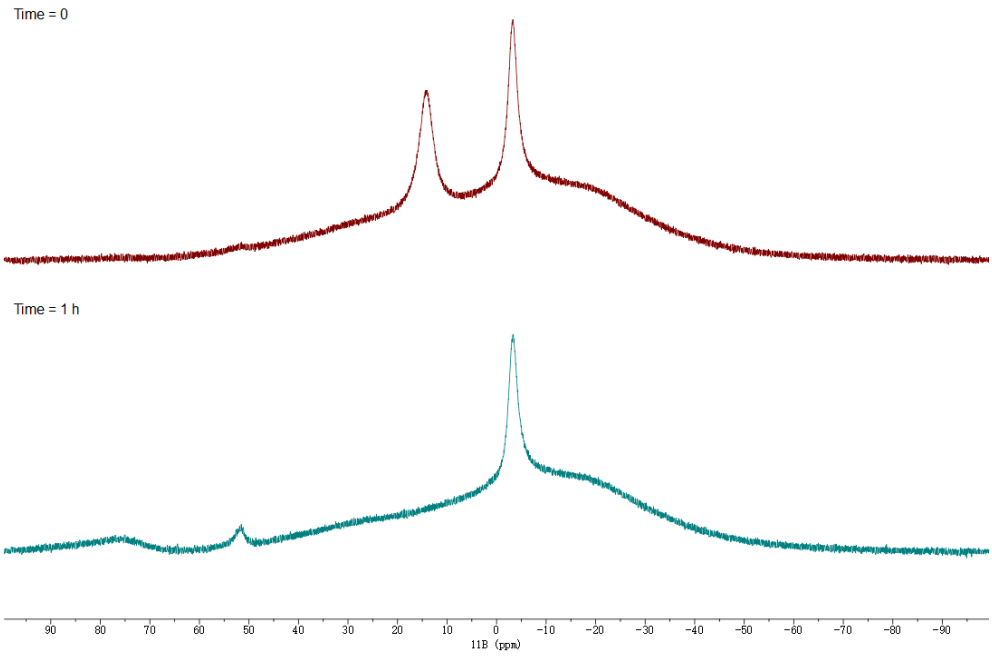


Figure S167. ^{11}B NMR of the reaction of **1a-BBN** with **2k** at time = 0 (top), time = 1 h (bottom) in C_6D_5Br.

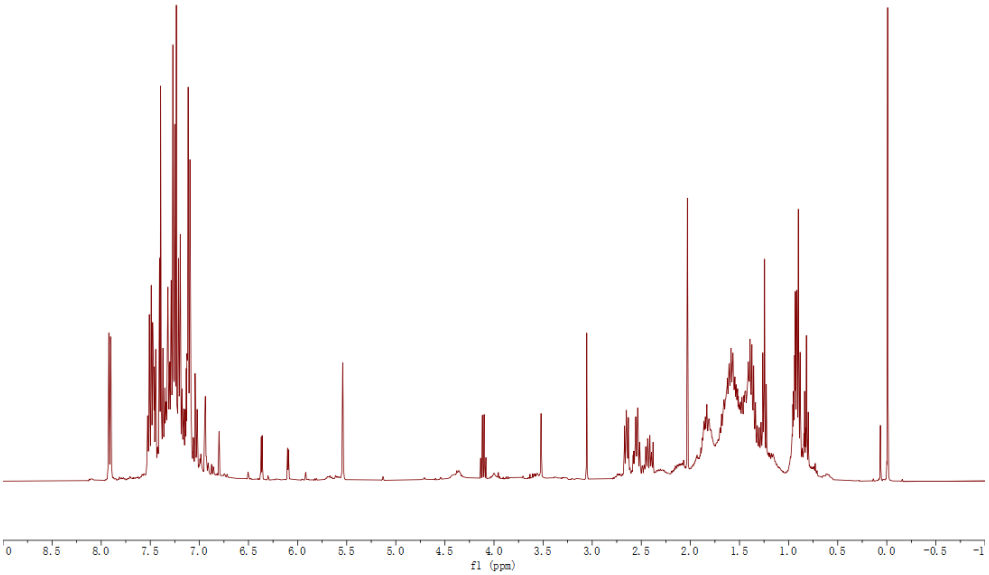


Figure S168. ^{1}H NMR of the reaction of **1a-BBN** with **2k** in $CDCl_3$ after HCl workup.

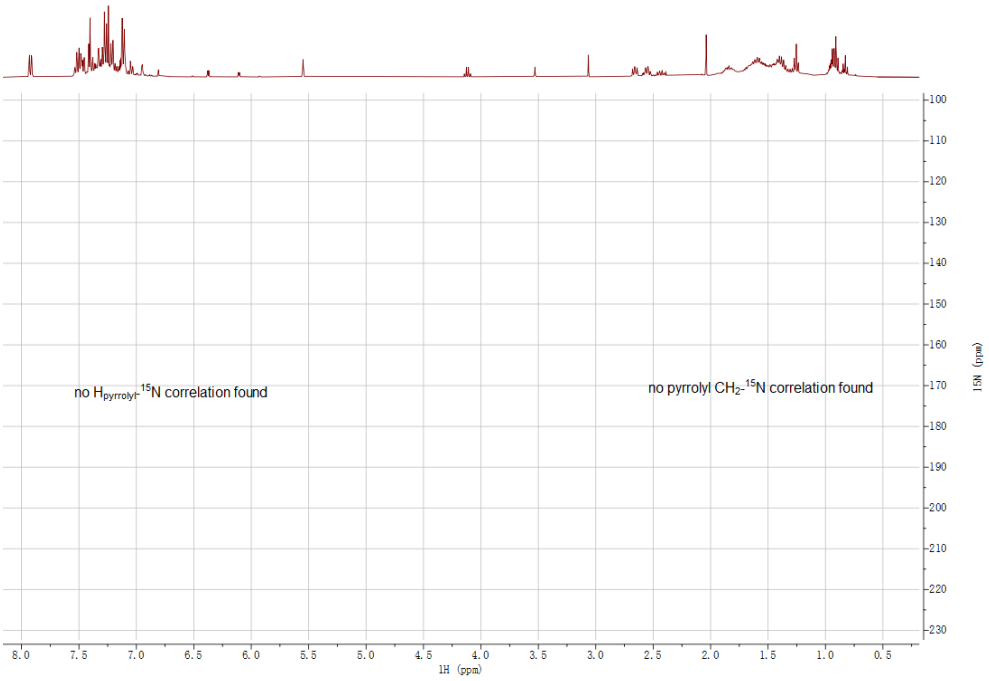


Figure S169. ^{1}H–^{15}N HMBC of the reaction of **1a-BBN** with **2k** in $CDCl_3$ after HCl workup.

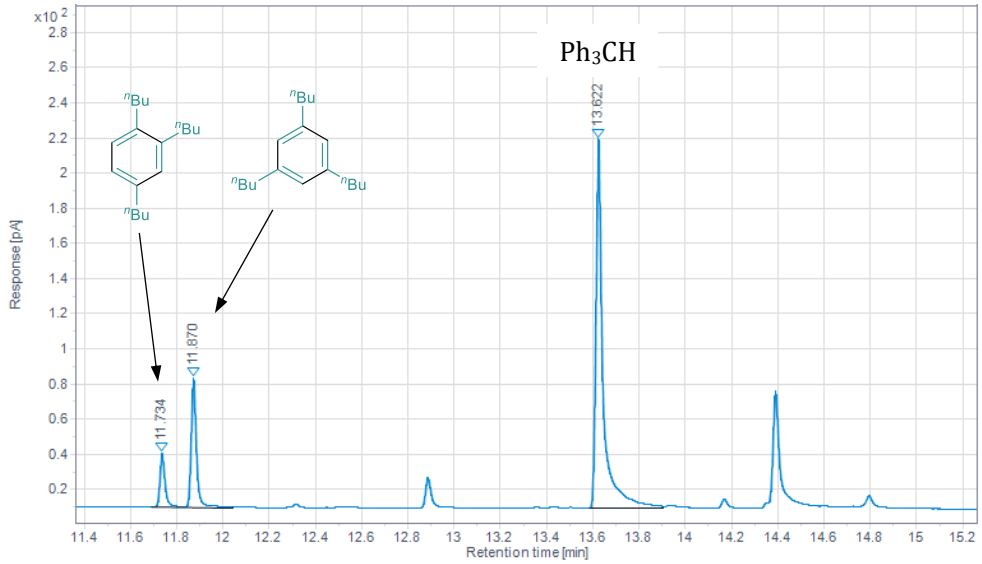
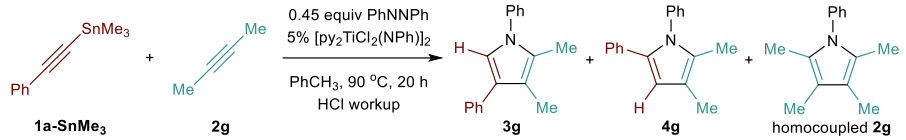


Figure S170. GC-FID chromatograph of the reaction of **1a-BBN** with **2k** after HCl workup.

Catalytic reaction of **1a-SnMe$_3$** with 2-butyne **(Table 4)**



The reaction was performed following **Procedure B** using **1a-SnMe$_3$** (26.5 mg, 0.1 mmol, 1 equiv) and 2-butyne (**2g**, 5.4 mg, 0.1 mmol, 1 equiv) with the reaction being heated for 20 h.

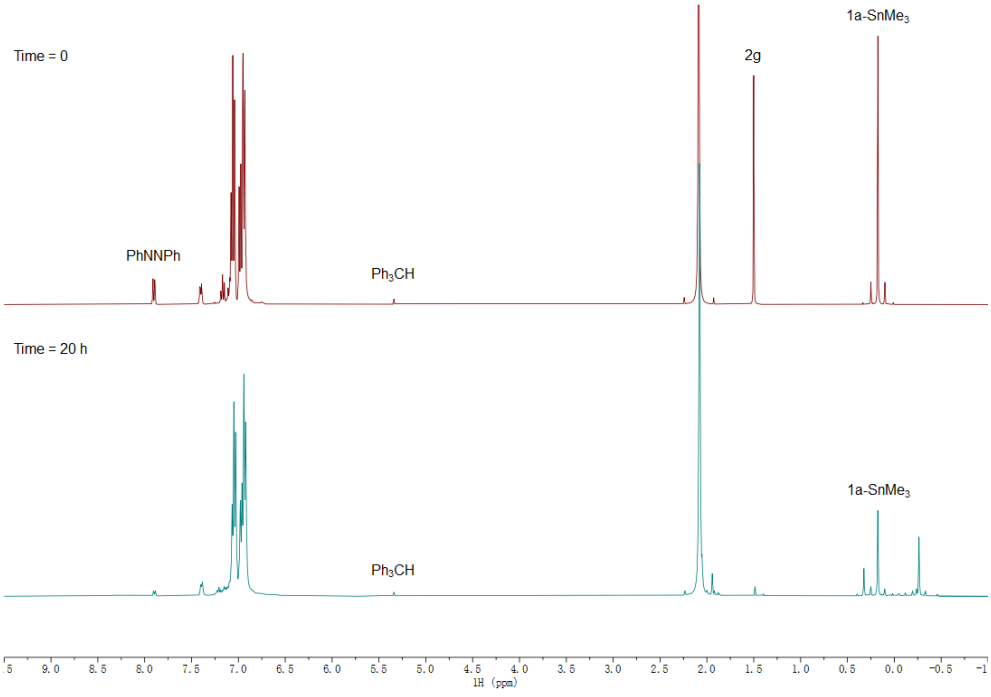


Figure S171. No-D ^{1}H NMR of the reaction of **1a-SnMe$_3$** with **2g** at time = 0 (top), time = 20 h (bottom) in $PhCH_3$.

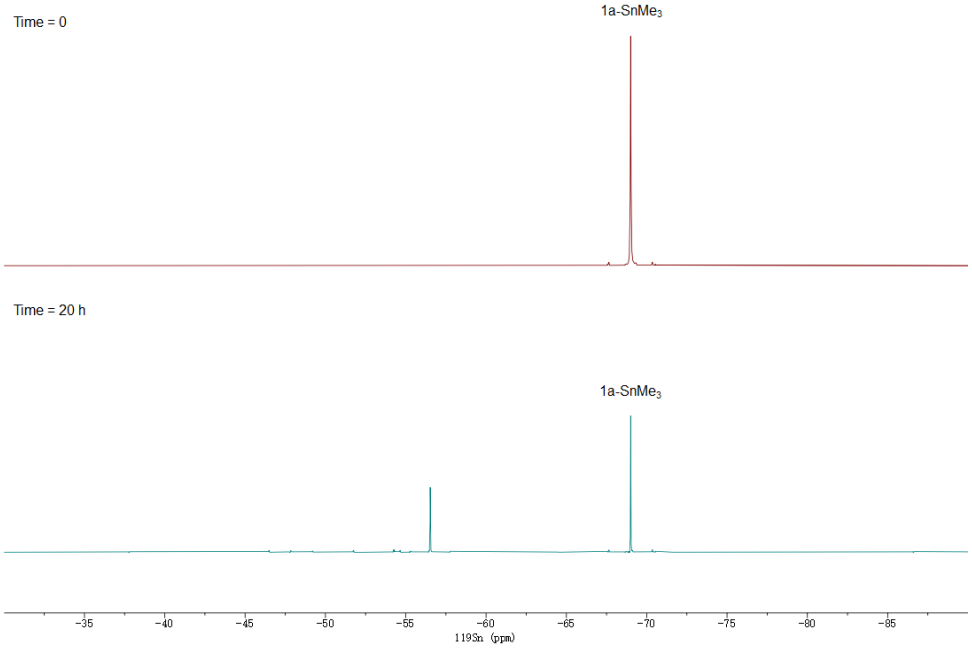
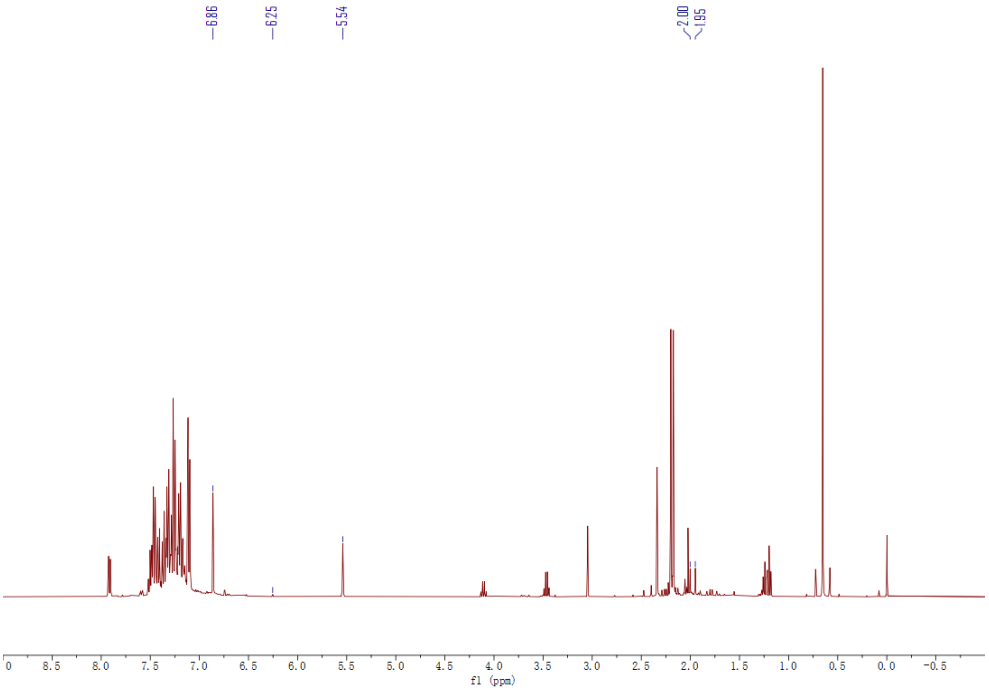


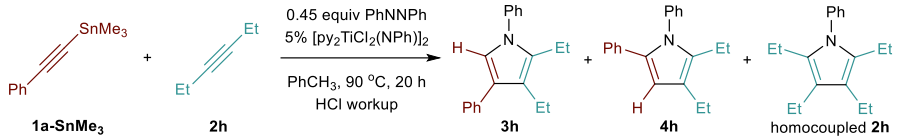
Figure S172. $^{119}Sn\{^{1}H\}$ NMR of the reaction of **1a-SnMe$_3$** with **2g** at time = 0 (top), time = 20 h (bottom) in $PhCH_3$.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	10245.3	n.a.
3g	6.86	$H_{pyrrolyl}$	1	10562.7	20.6
4g	6.25	$H_{pyrrolyl}$	1	401.1	0.8
homocoupled **2g**	2.00, 1.95	$Me_{pyrrolyl}$ (4 per molecule)	12	7329.5	1.2

Figure S173. ^{1}H NMR of the reaction of **1a-SnMe$_3$** with **2g** in $CDCl_3$ after HCl workup.

Catalytic reaction of **1a-SnMe$_3$** with 3-hexyne **(Table 4)**



The reaction was performed following **Procedure B** using **1a-SnMe$_3$** (26.5 mg, 0.1 mmol, 1 equiv) and 3-hexyne (**2h**, 8.2 mg, 0.1 mmol, 1 equiv) with the reaction being heated for 20 h.

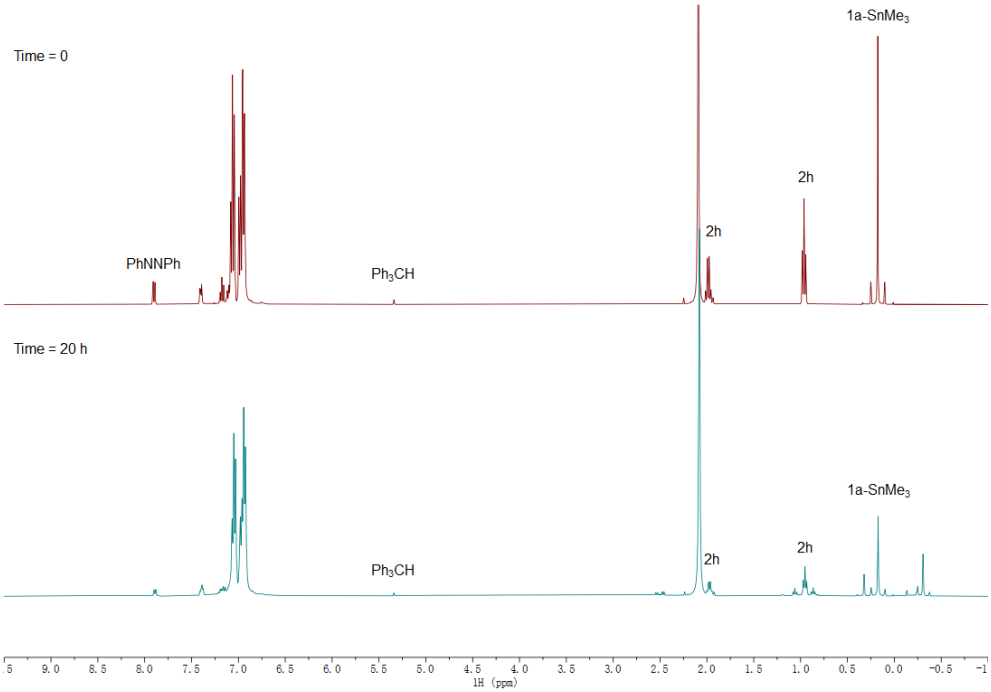


Figure S174. No-D ^{1}H NMR of the reaction of **1a-SnMe$_3$** with **2h** at time = 0 (top), time = 20 h (bottom) in $PhCH_3$.

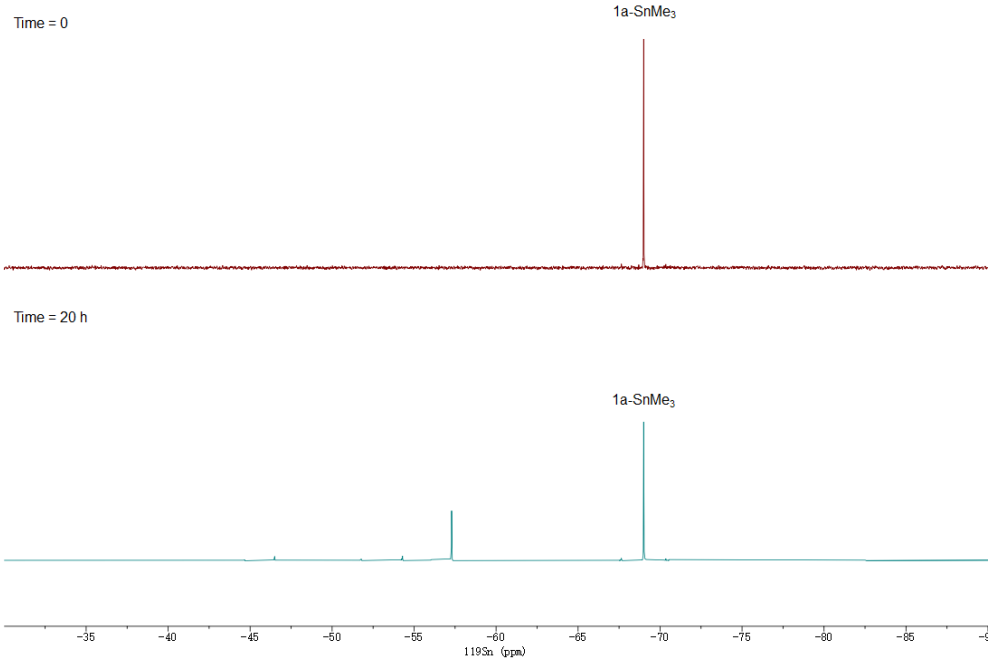
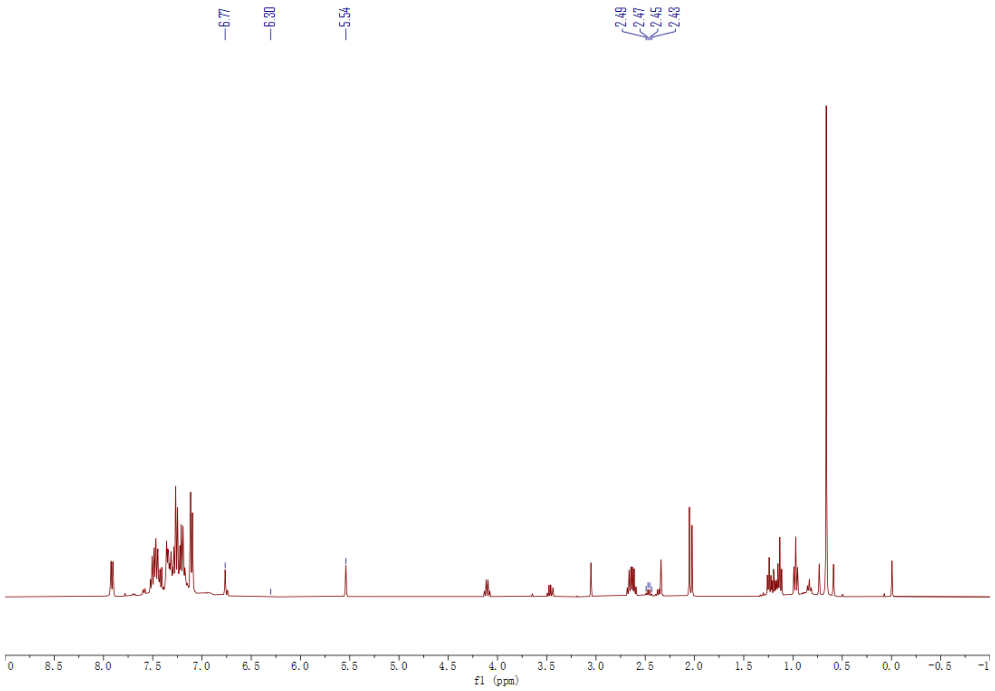


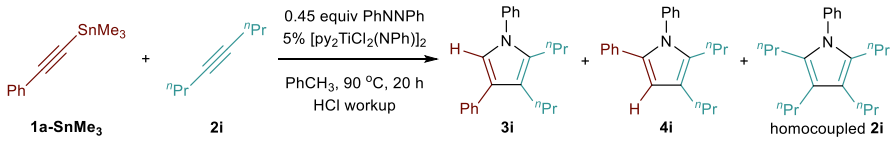
Figure S175. $^{119}Sn\{^{1}H\}$ NMR of the reaction of **1a-SnMe$_3$** with **2h** at time = 0 (top), time = 20 h (bottom) in $PhCH_3$.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	8048.1	n.a.
3h	6.77	$H_{pyrrolyl}$	1	6337.5	15.7
4h	6.30	$H_{pyrrolyl}$	1	240.8	0.6
homocoupled **2h**	2.49, 2.47, 2.45, 2.43	3,4-CH_2CH_3 (2 per molecule)	4	4087.2	2.5

Figure S176. ^{1}H NMR of the reaction of **1a-SnMe$_3$** with **2h** in $CDCl_3$ after HCl workup.

Catalytic reaction of **1a-SnMe$_3$** with 4-octyne **(Table 4)**



The reaction was performed following **Procedure B** using **1a-SnMe$_3$** (26.5 mg, 0.1 mmol, 1 equiv) and 4-octyne (**2i**, 11.0 mg, 0.1 mmol, 1 equiv) with the reaction being heated for 20 h.

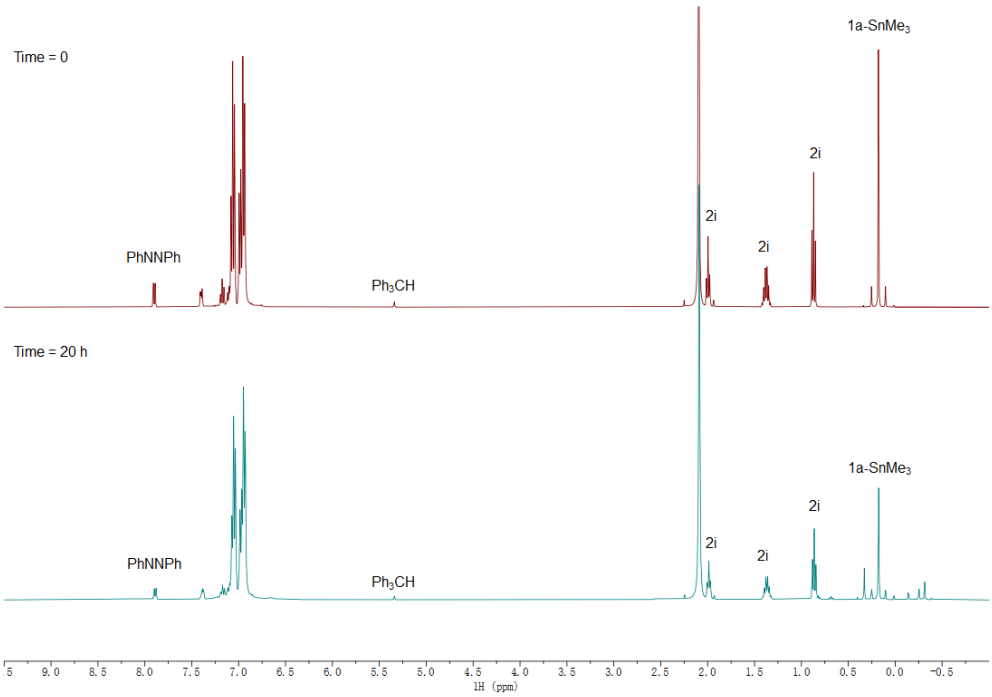


Figure S177. No-D ^{1}H NMR of the reaction of **1a-SnMe$_3$** with **2i** at time = 0 (top), time = 20 h (bottom) in $PhCH_3$.

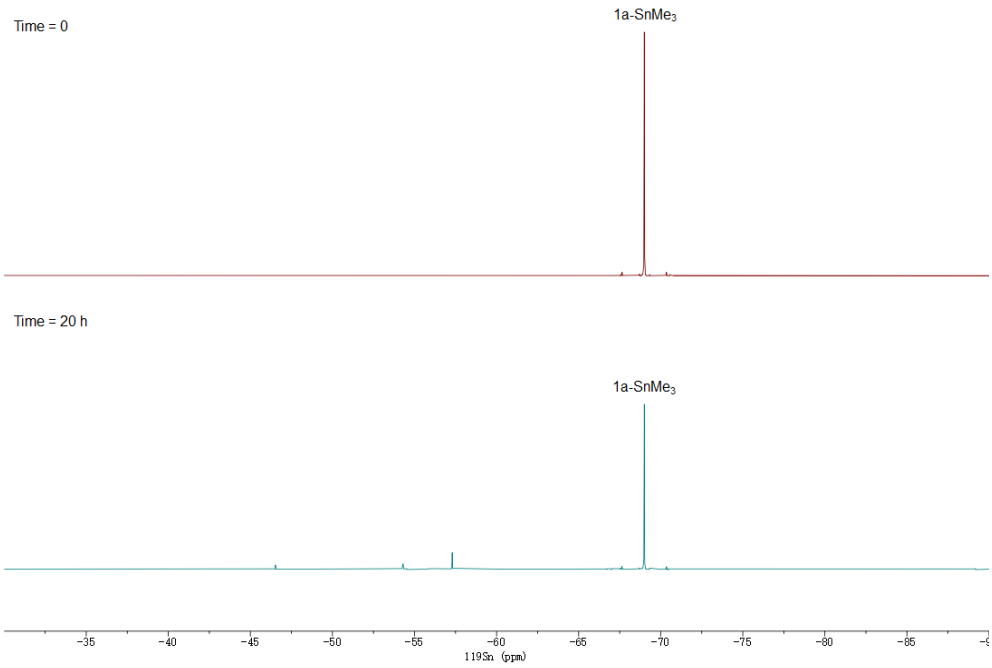
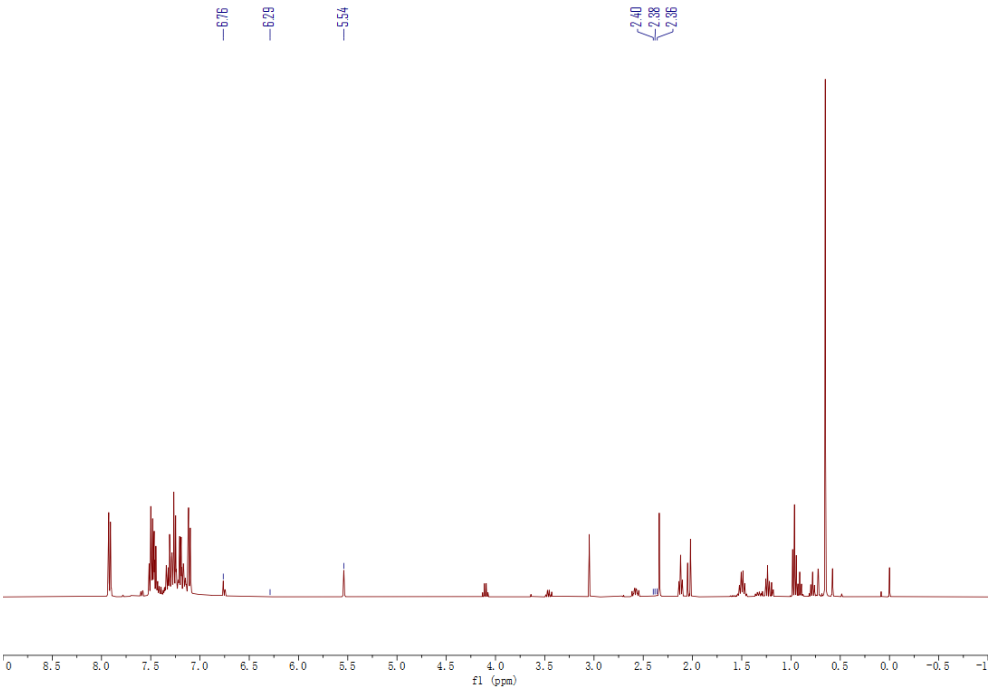


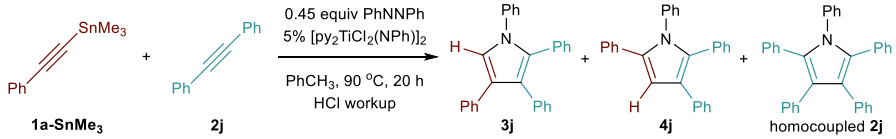
Figure S178. $^{119}Sn\{^{1}H\}$ NMR of the reaction of **1a-SnMe$_3$** with **2i** at time = 0 (top), time = 20 h (bottom) in $PhCH_3$.



	δ (ppm)	Assignment	# of H	Peak Area	Yield (%)
Ph_3CH	5.54	Ph_3C-H	1	12272.0	n.a.
3i	6.76	$H_{pyrrolyl}$	1	3508.8	5.7
4i	6.29	$H_{pyrrolyl}$	1	81.5	0.1
homocoupled **2i**	2.40, 2.38, 2.36	3,4-CH_2CH_3 (2 per molecule)	4	621.2	0.3

Figure S179. ^{1}H NMR of the reaction of **1a-SnMe$_3$** with **2i** in $CDCl_3$ after HCl workup.

Catalytic reaction of **1a-SnMe$_3$** with diphenylacetylene **(Table 4)**



The reaction was performed following **Procedure B** using **1a-SnMe$_3$** (26.5 mg, 0.1 mmol, 1 equiv) and diphenylacetylene (**2j**, 17.8 mg, 0.1 mmol, 1 equiv) with the reaction being heated for 20 h. Yields were determined by GC due to peak overlapping in ^{1}H NMR spectrum after HCl workup.

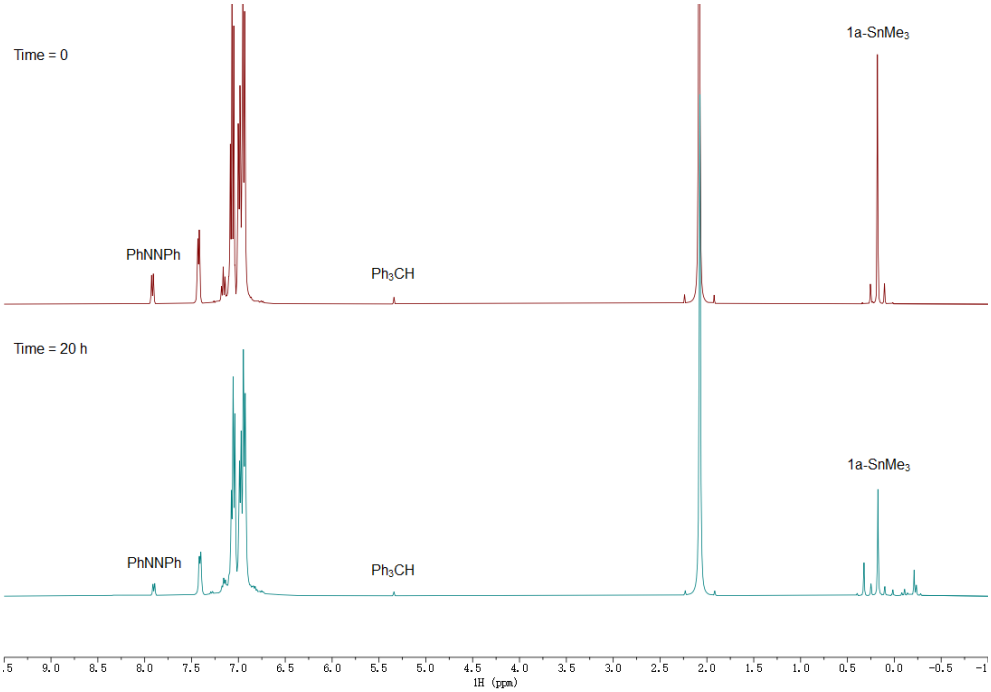


Figure S180. No-D ^{1}H NMR of the reaction of **1a-SnMe$_3$** with **2j** at time = 0 (top), time = 20 h (bottom) in $PhCH_3$.

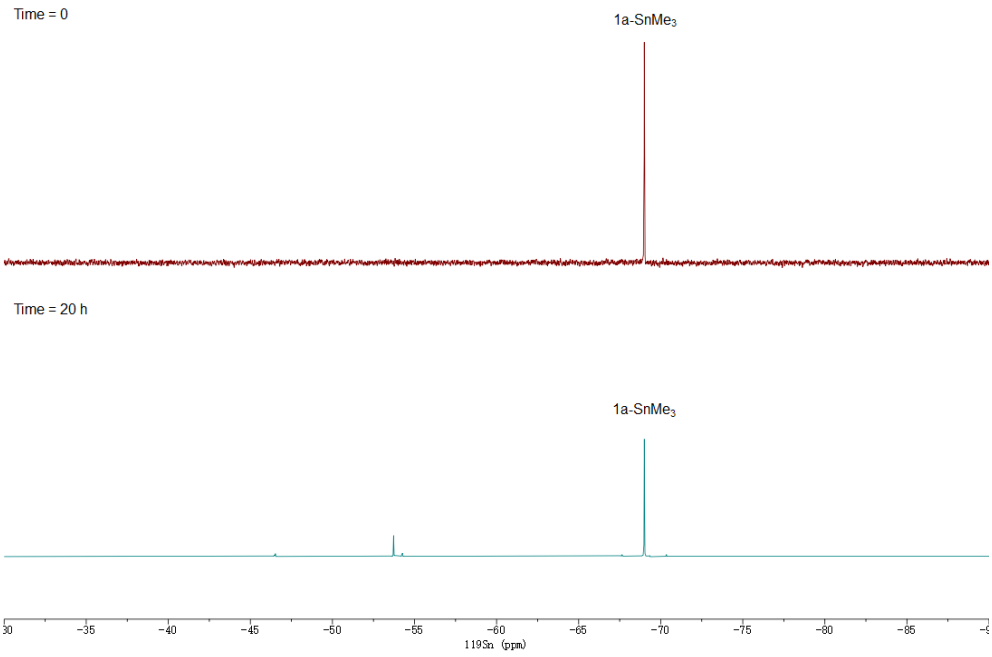
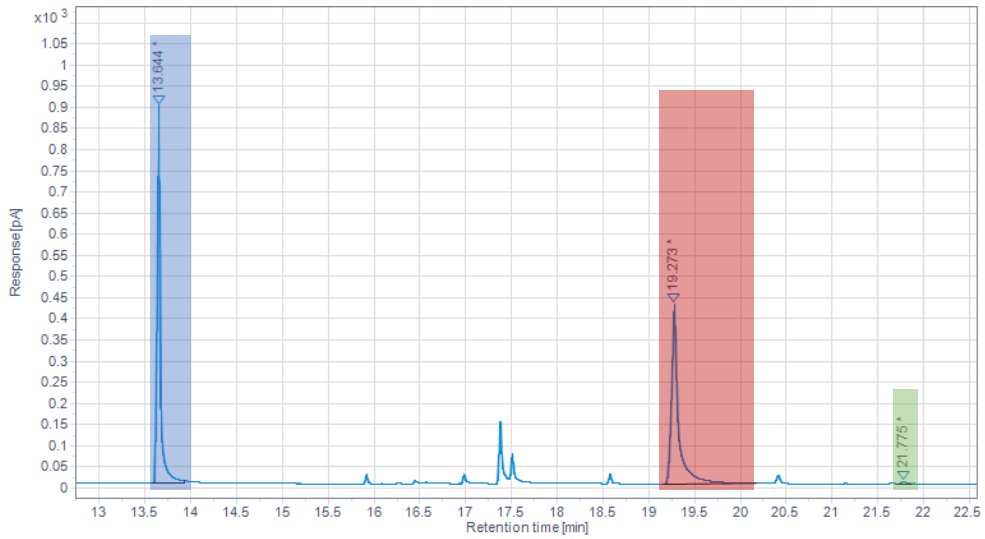


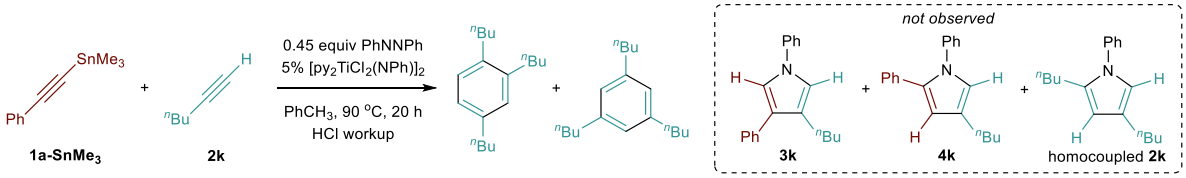
Figure S181. $^{119}Sn\{^{1}H\}$ NMR of the reaction of **1a-SnMe$_3$** with **2j** at time = 0 (top), time = 20 h (bottom) in $PhCH_3$.



	Retention Time (min)	Surface Area	# of C	Yield (%)
Ph_3CH	13.644	2087.757	19	n.a.
3j	19.273	2196.968	28	14.3
4j	not found	n.a.	28	n.d.
homocoupled **2j**	21.775	25.834	34	0.1

Figure S182. Quantitative GC-FID chromatograph of the reaction of **1a-SnMe$_3$** with **2j** after HCl workup.

Catalytic reaction of **1a-SnMe$_3$** with 1-hexyne **(Table 4)**



The reaction was performed following **Procedure B** using **1a-SnMe$_3$** (26.5 mg, 0.1 mmol, 1 equiv) and 1-hexyne (**2k**, 8.2 mg, 0.1 mmol, 1 equiv) with the reaction being heated for 20 h.

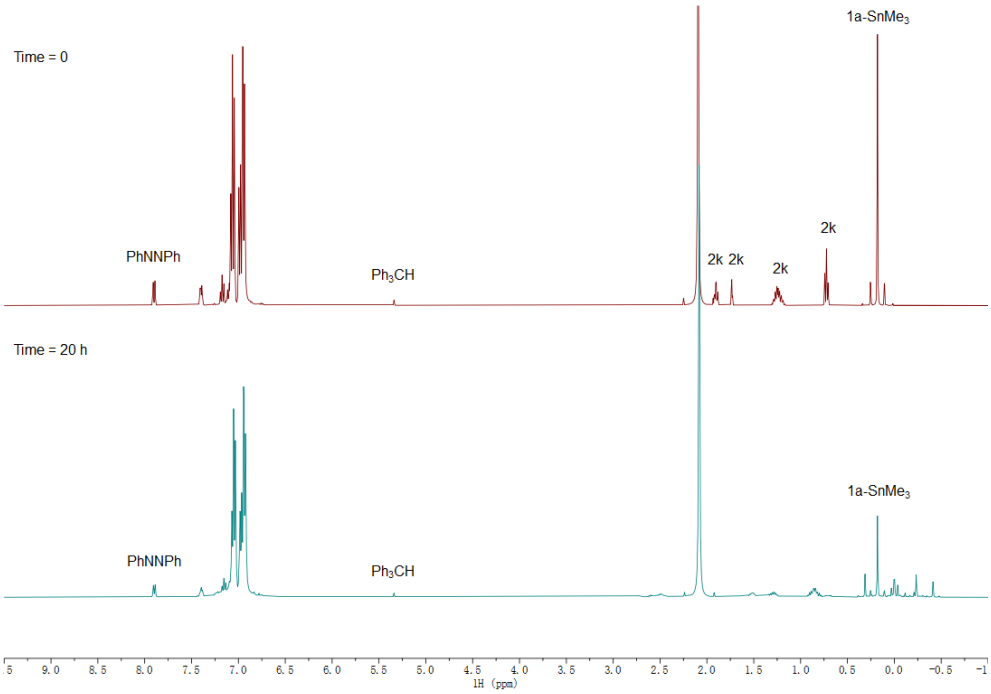


Figure S183. No-D ^{1}H NMR of the reaction of **1a-SnMe$_3$** with **2k** at time = 0 (top), time = 20 h (bottom) in $PhCH_3$.

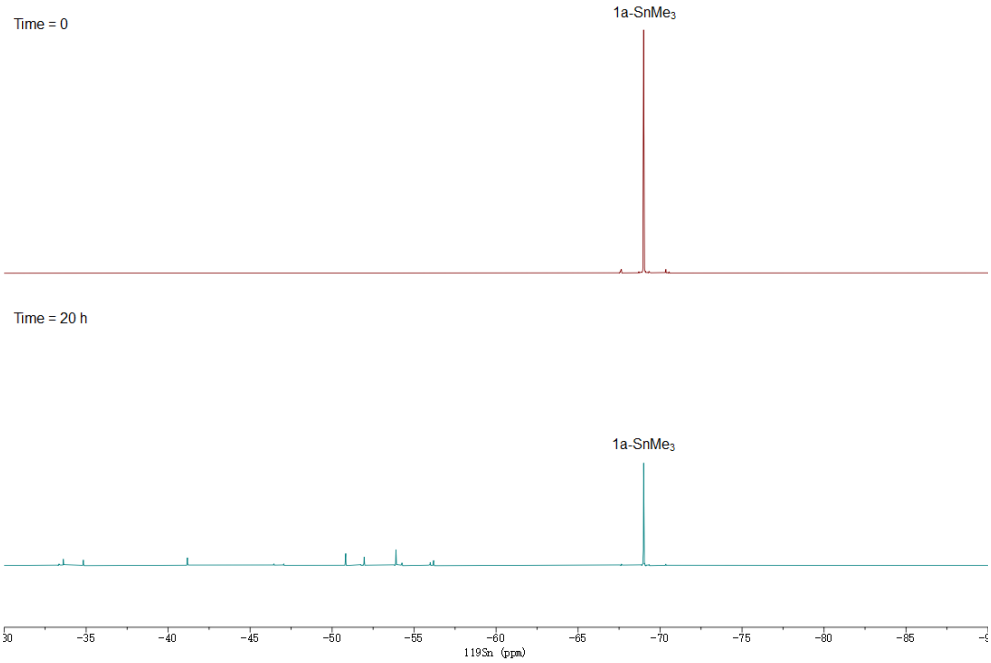


Figure S184. $^{119}Sn\{^{1}H\}$ NMR of the reaction of **1a-SnMe$_3$** with **2k** at time = 0 (top), time = 20 h (bottom) in $PhCH_3$.

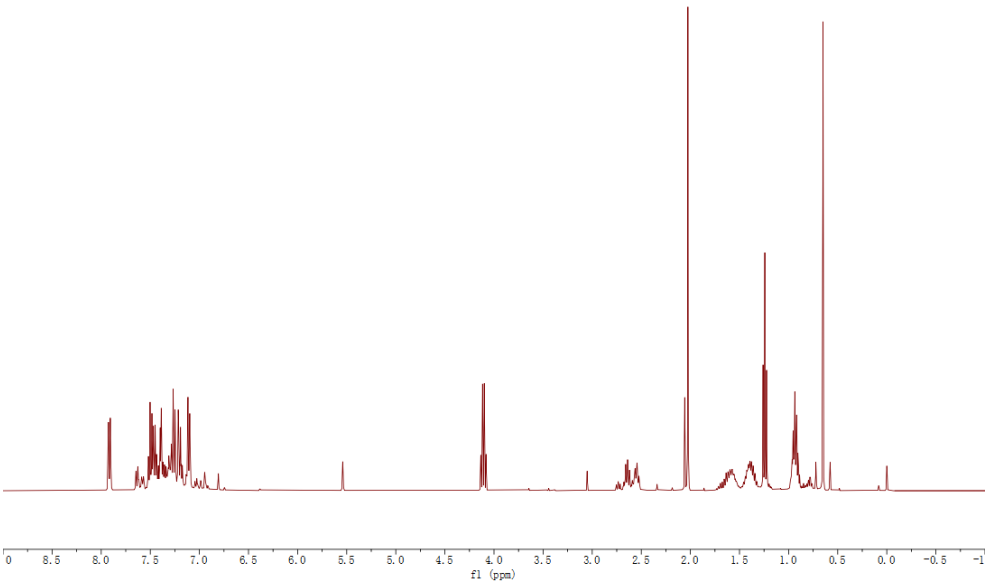


Figure S185. ^{1}H NMR of the reaction of **1a-SnMe$_3$** with **2k** in $CDCl_3$ after HCl workup.

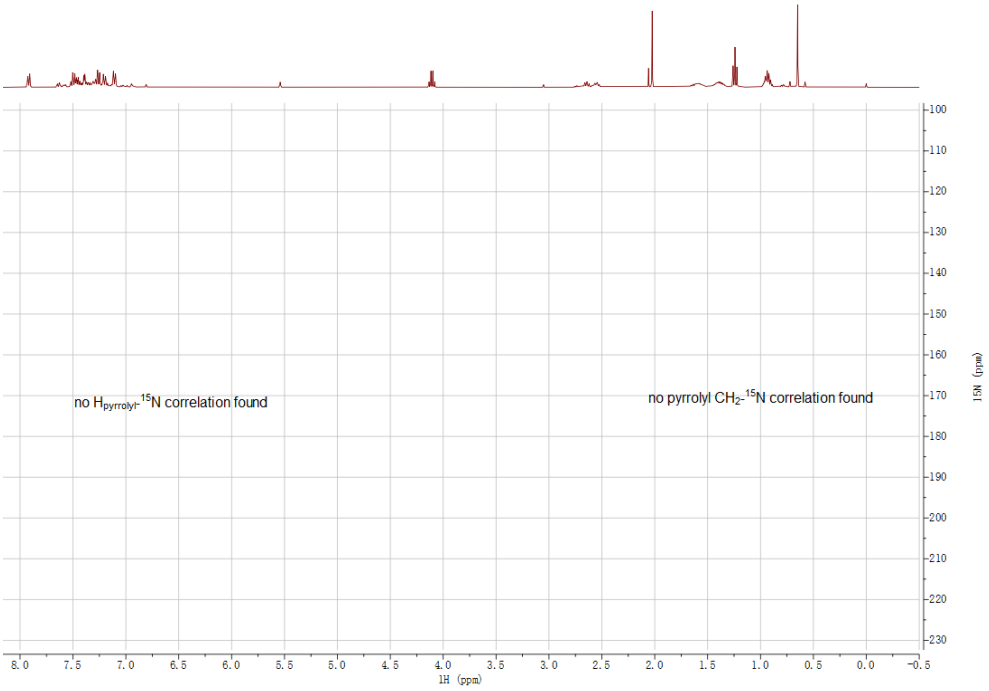


Figure S186. ^{1}H–^{15}N HMBC of the reaction of **1a-SnMe$_3$** with **2k** in $CDCl_3$ after HCl workup.

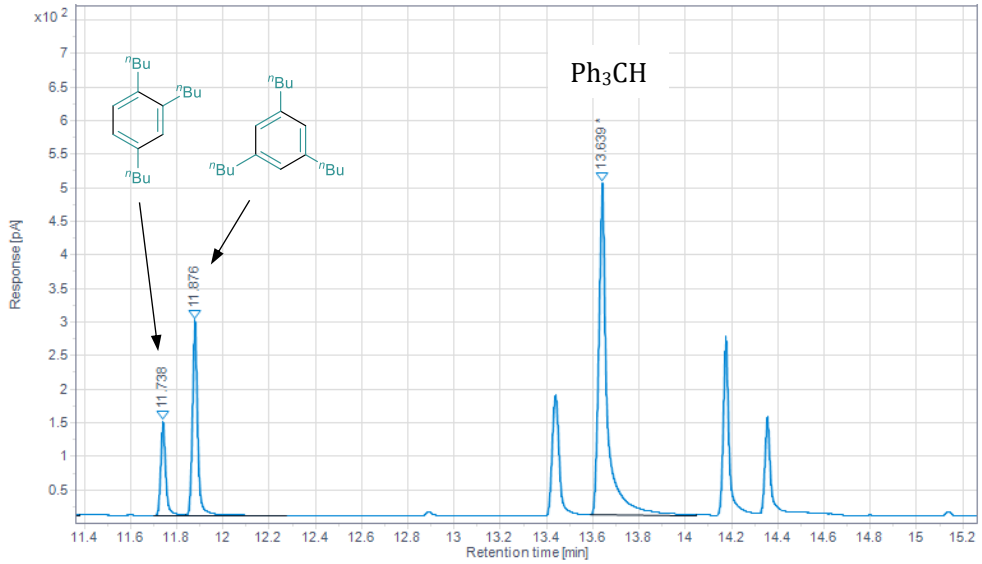


Figure S187. GC-FID chromatograph of the reaction of **1a-SnMe$_3$** with **2k** after HCl workup.

Reference

1 G. M. Whitesides and W. J. Ehmann, Mechanism of formation of 1,2,3,4-tetramethylnaphthalene from 2-butyne and triphenyltris(tetrahydrofuran) chromium(III), *J. Am. Chem. Soc.*, 1970, **92**, 5625–5640.

2 H. C. Brown and J. A. Sinclair, Organoboranes. XVIII. Reaction of lithium alkynes with methyl dialkylborinates: The synthesis of B-1-alkynyldialkylboranes, *J. Organomet. Chem.*, 1977, **131**, 163–169.

3 G. Y. Fang, O. A. Wallner, N. Di Blasio, X. Ginesta, J. N. Harvey and V. K. Aggarwal, Asymmetric Sulfur Ylide Reactions with Boranes: Scope and Limitations, Mechanism and Understanding, *J. Am. Chem. Soc.*, 2007, **129**, 14632–14639.

4 J. C. Evans, C. T. Goralski and D. L. Hasha, B-[2-(Trimethylsilyl)ethynyl]-9-borabicyclo[3.3.1]nonane. A new organoboron reagent for the preparation of propargylic alcohols, *J. Org. Chem.*, 1992, **57**, 2941–2943.

5 W. Shi, Y. Luo, X. Luo, L. Chao, H. Zhang, J. Wang and A. Lei, Investigation of an Efficient Palladium-Catalyzed C(sp)−C(sp) Cross-Coupling Reaction Using Phosphine−Olefin Ligand: Application and Mechanistic Aspects, *J. Am. Chem. Soc.*, 2008, **130**, 14713–14720.

6 X. Y. See, E. P. Beaumier, Z. W. Davis-Gilbert, P. L. Dunn, J. A. Larsen, A. J. Pearce, T. A. Wheeler and I. A. Tonks, Generation of TiIIalkyne trimerization catalysts in the absence of strong metal reductants, *Organometallics*, 2017, **36**, 1383–1390.

7 C. A. Beach, K. E. Joseph, P. J. Dauenhauer, C. S. Spanjers, A. J. Jones and T. J. Mountziaris, Complete carbon analysis of sulfur-containing mixtures using postcolumn reaction and flame ionization detection, *AIChE J.*, 2017, **63**, 5438–5444.

8 C. S. Spanjers, C. A. Beach, A. J. Jones and P. J. Dauenhauer, Increasing flame ionization detector (FID) sensitivity using post-column oxidation–methanation, *Anal. Methods*, 2017, **9**, 1928–1934.

9 P. G. Harrison, S. E. Ulrich and J. J. Zuckerman, Tin-119 chemical shifts by the double resonance of organotin compounds, *J. Am. Chem. Soc.*, 1971, **93**, 5398–5402.

10 F. Forster, V. M. Rendón López and M. Oestreich, Catalytic Dehydrogenative Stannylation of C(sp)–H Bonds Involving Cooperative Sn–H Bond Activation of Hydrostannanes, *J. Am. Chem. Soc.*, 2018, **140**, 1259–1262.

11 D. A. Pennington, P. N. Horton, M. B. Hursthouse, M. Bochmann and S. J. Lancaster, Synthesis and catalytic activity of dinuclear imido titanium complexes: The molecular structure of [Ti(NPh)Cl(μ-Cl)(THF)2]2, *Polyhedron*, 2005, **24**, 151–156.

12 C. Lee, J. Zhou and O. V Ozerov, Catalytic Dehydrogenative Borylation of Terminal Alkynes by a SiNN Pincer Complex of Iridium, *J. Am. Chem. Soc.*, 2013, **135**, 3560–3566.

13 C.-I. Lee, J. C. DeMott, C. J. Pell, A. Christopher, J. Zhou, N. Bhuvanesh and O. V. Ozerov, Ligand survey results in identification of PNP pincer complexes of iridium as long-lived and chemoselective catalysts for dehydrogenative borylation of terminal alkynes, *Chem. Sci.*, 2015, **6**, 6572–6582.

14 H. E. Ho, N. Asao, Y. Yamamoto and T. Jin, Carboxylic Acid-Catalyzed Highly Efficient and Selective Hydroboration of Alkynes with Pinacolborane, *Org. Lett.*, 2014, **16**, 4670–4673.

15 D. Unseld, V. V. Krivykh, K. Heinze, F. Wild, G. Artus, H. Schmalle and H. Berke, Versatile Routes to Mono- and Bis(alkynyl) Manganese(II) and Manganese(III) Complexes via Manganocenes, *Organometallics*, 1999, **18**, 1525–1541.

16 H. C. Chiu and I. A. Tonks, Trimethylsilyl-Protected Alkynes as Selective Cross-Coupling Partners in Titanium-Catalyzed [2+2+1] Pyrrole Synthesis, *Angew. Chemie - Int. Ed.*, 2018, **57**, 6090–6094.

17 Z. W. Gilbert, R. J. Hue and I. A. Tonks, Catalytic formal [2+2+1] synthesis of pyrroles from alkynes and diazenes via TiII/TiIVredox catalysis, *Nat. Chem.*, 2016, **8**, 63–68.

18 X. Li, M. Chen, X. Xie, N. Sun, S. Li and Y. Liu, Synthesis of Multiple-Substituted Pyrroles via Gold(I)-Catalyzed Hydroamination/Cyclization Cascade, *Org. Lett.*, 2015, **17**, 2984–2987.

19 L. Petrakis, Spectral line shapes: Gaussian and Lorentzian functions in magnetic resonance, *J. Chem. Educ.*, 1967, **44**, 432.

20 G.-Z. Wang, R. Shang, W.-M. Cheng and Y. Fu, Decarboxylative 1,4-Addition of α-Oxocarboxylic Acids with Michael Acceptors Enabled by Photoredox Catalysis, *Org. Lett.*, 2015, **17**, 4830–4833.

21 T. N. Danks and S. E. Thomas, Nucleophilic addition to tricarbonyliron(0) complexes of 1-aza-1,3-dienes and the production of pyrroles, *J. Chem. Soc. Perkin Trans. 1*, 1990, 761.

22 A. S. Demir, I. M. Akhmedov and Ö. Sesenoglu, Synthesis of 1,2,3,5-tetrasubstituted pyrrole derivatives from 2-(2-bromoallyl)-1,3-dicarbonyl compounds, *Tetrahedron*, 2002, **58**, 9793–9799.