Supporting Information

Palladium-Catalyzed Primary Amine-Directed Regioselective Mono- and Di-Alkynylation of Biaryl-2-Amines

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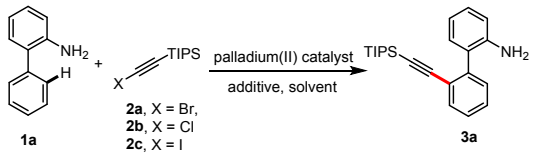
A. General Information

All purchased reagents and solvents were used without further purification unless otherwise noted. Melting points were measured with a melting point instrument and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker DRX-400 spectrometer using $CDCl_3$ or DMSO-d_6 as solvent. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. GC-MS was obtained using electron ionization. TLC was performed by using commercially prepared 100-400 mesh silica gel plates and visualization was effected at 254 nm. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker TENSOR 27 spectrometer.

B. Optimization of Reaction Conditions

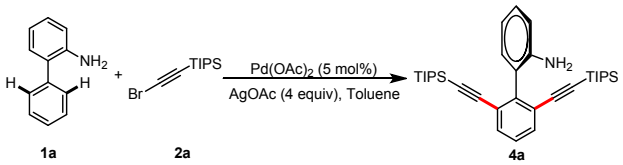
Table S1. Optimization of Reaction Conditions for Monoalkynylation[a]



entry	catalyst	additive	solvent	yield (%)[b]
1	$Pd(OAc)_2$	$Cu(OAc)_2$	toluene	n.d.
2	$Pd(OAc)_2$	AgOAc	toluene	76
3	$PdCl_2$	AgOAc	toluene	54
4	$Pd(PPh_3)_2Cl_2$	AgOAc	toluene	62
5	$Pd(OAc)_2$	AgOAc	DCE	53
6	$Pd(OAc)_2$	AgOAc	CH_3CN	trace
7	-	AgOAc	toluene	n.d.
8	$Pd(OAc)_2$	-	toluene	n.d.
9[c]	**$Pd(OAc)_2$**	**AgOAc**	**toluene**	**84(80)**
10[d]	$Pd(OAc)_2$	AgOAc	toluene	69(63)
11[e]	$Pd(OAc)_2$	AgOAc	toluene	37(31)

[a] Reaction conditions: a mixture of **1a** (0.2 mmol), **2a** (0.2 mmol), additive (0.4 mmol, 2 equiv), catalyst (0.01 mmol, 5 mol %) and solvent (1.5 mL) was sealed in a 25 mL Schlenk tube at 100 °C for 12 h under N_2. [b] Determined by GC using dodecane as an internal standard. Numbers in parentheses are yields of isolated products. n.d. = not detected. [c] **1a** (0.2 mmol), **2a** (0.14 mmol), AgOAc (0.28 mmol, 2 equiv) and catalyst (0.007 mmol, 5 mol %) were used. [d] Using the corresponding alkynyl chloride (**2b**). [e] Using the corresponding alkynyl iodide (**2c**).

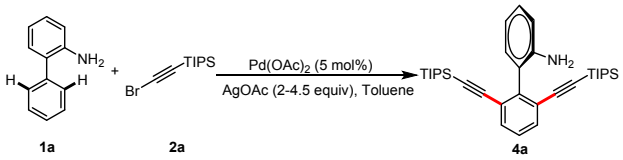
Table S2. Optimization of Reaction Conditions for Dialkynylation[a]



1a 2a 4a

entry	**1a** (mmol)	**2a** (mmol)	AgOAc (mmol)	solvent	yield[b] (%)
1	0.2	0.14	0.56	toluene	< 5
2	0.2	0.2	0.8	toluene	9
3	0.2	0.25	0.8	toluene	12
4	0.2	0.3	0.8	toluene	31
5	0.2	0.35	0.8	toluene	52
6	0.2	0.4	0.8	toluene	64
7	0.2	0.45	0.8	toluene	72
8	**0.2**	**0.5**	0.8	**toluene**	**82**
9	0.2	0.55	0.8	toluene	81

[a]Reaction conditions: a mixture of **1a** (0.2 mmol), **2a** (0.14-0.55 mmol), AgOAc (4 equiv), $Pd(OAc)_2$ (5 mol %) and toluene (1.5 mL) were sealed in a 25 mL Schlenk tube at 100 °C for 12 h under N_2. [b]isolated yield.



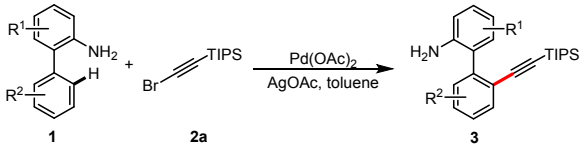
1a 2a 4a

entry	**1a** (mmol)	**2a** (mmol)	AgOAc (mmol)	solvent	yield[b] (%)
1	0.2	0.5	0.4	toluene	< 21
2	0.2	0.5	0.5	toluene	36
3	0.2	0.5	0.6	toluene	53
4	0.2	0.5	0.7	toluene	67
5	**0.2**	**0.5**	**0.8**	**toluene**	**82**
6	0.2	0.5	0.9	toluene	81

[a]Reaction conditions: a mixture of **1a** (0.2 mmol), **2a** (0.5 mmol), AgOAc (2-4.5 equiv), $Pd(OAc)_2$ (5 mol %) and toluene (1.5 mL) were sealed in a 25 mL Schlenk tube at 100 °C for 12 h under N_2. [b]isolated yield.

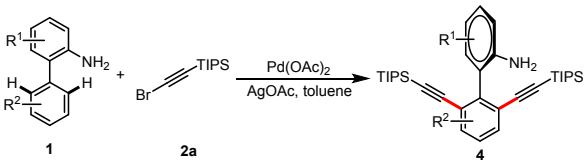
C. General Procedure for the Synthesis of 3 and 4

1. Monoalkynylation of Biaryl-2-amines



Biaryl-2-amines **1** (0.2 mmol), (bromoethynyl)triisopropylsilane **2a** (0.14 mmol), $Pd(OAc)_2$ (0.007 mmol, 5 mol %), AgOAc (0.28 mmol, 2 equiv) and toluene (1.5 mL) were sealed in a Schlenk tube under N_2 atmosphere. After this, the mixture was stirred at 100 ^oC (oil bath temperature) for 12 h. After the reaction was completed (monitored by TLC), the resulting mixture were cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired products **3** were obtained in the corresponding yields after purified by column chromatography on silica gel with mixture of petroleum ether and ethyl acetate.

2. Dialkynylation of Biaryl-2-amines



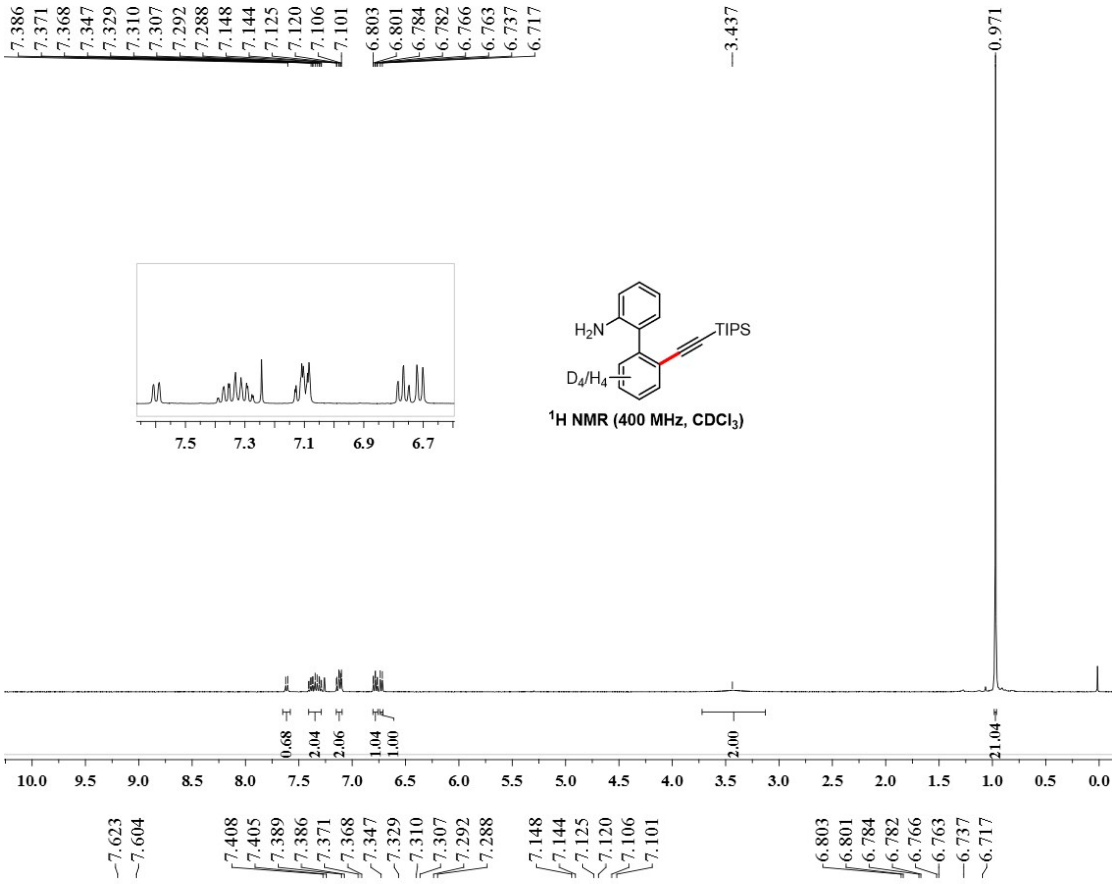
Biaryl-2-amines **1** (0.2 mmol), (bromoethynyl)triisopropylsilane **2a** (0.5 mmol), $Pd(OAc)_2$ (0.01 mmol, 5 mol %), AgOAc (0.8 mmol, 4 equiv) and toluene (1.5 mL) were sealed in a Schlenk tube under N_2 atmosphere. After this, the mixture was stirred at 100 ^oC (oil bath temperature) for 12 h. After the reaction was completed (monitored by TLC), the resulting mixture were cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired products **4** were obtained in the corresponding yields after purified by column chromatography on silica gel with mixture of petroleum ether and ethyl acetate.

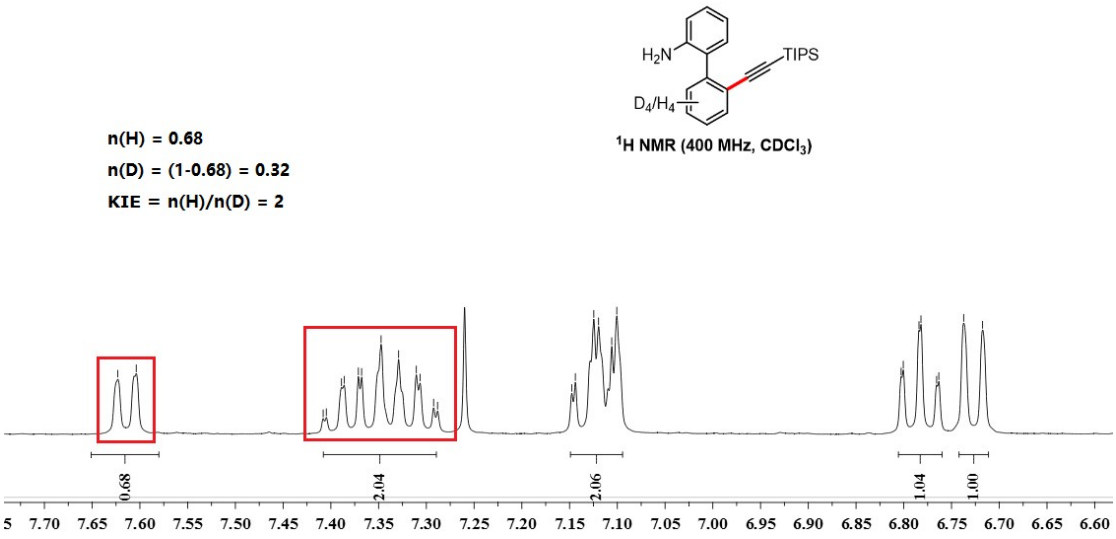
D. Intermolecular Kinetic Isotope Effect Experiment

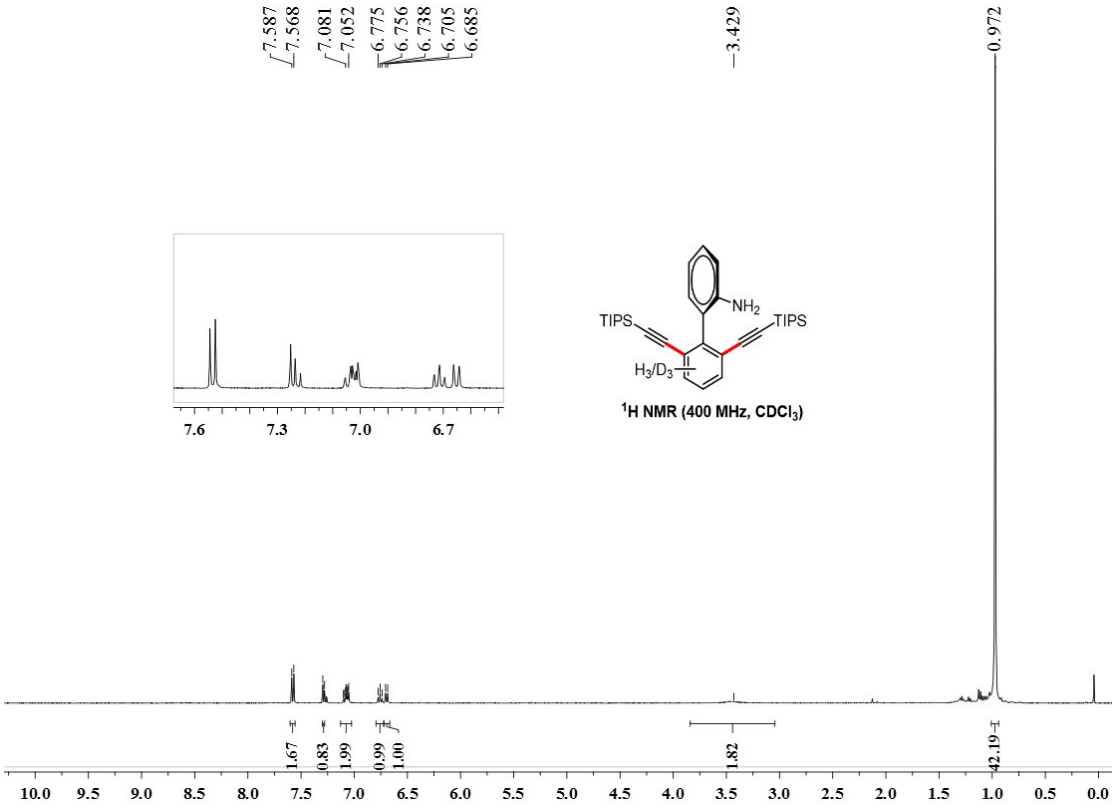
[1,1′-biphenyl]-2-amine **1a** (0.2 mmol), [1,1′-biphenyl]-2′,3′,4′,5′,6′-d_5-2-amine **1a-*d*$_5$** (0.2 mmol), (bromoethynyl)triisopropylsilane **2a** (0.14 mmol), $Pd(OAc)_2$ (0.007 mmol, 5 mol %), AgOAc (0.28 mmol, 2 equiv) and toluene (1.5 mL) were sealed in a Schlenk tube under N_2 atmosphere. After this, the mixture was stirred at 100 ^oC (oil bath temperature) for 1.5 h, the resulting mixture were cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. Then the resulting residue was purified by column chromatography on silica gel with petroleum ether/EtOAc (40/1) as eluent to afford a mixture of **3a** and **3a-*d*$_4$** in 25% isolated yield (12.2 mg). The KIE value (K_H/K_D = 2) was determined on the basis of ^1H NMR analysis. Data for compounds **3a**/**3a-*d*$_4$**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.8 Hz, 0.7H), 7.35 (m, J = 14.8, 7.4, 6.0 Hz, 2H), 7.15-7.09 (m, 2H), 6.78 (m, J = 7.6, 0.8 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 3.44 (s, 2H), 0.97 (s, 21H).

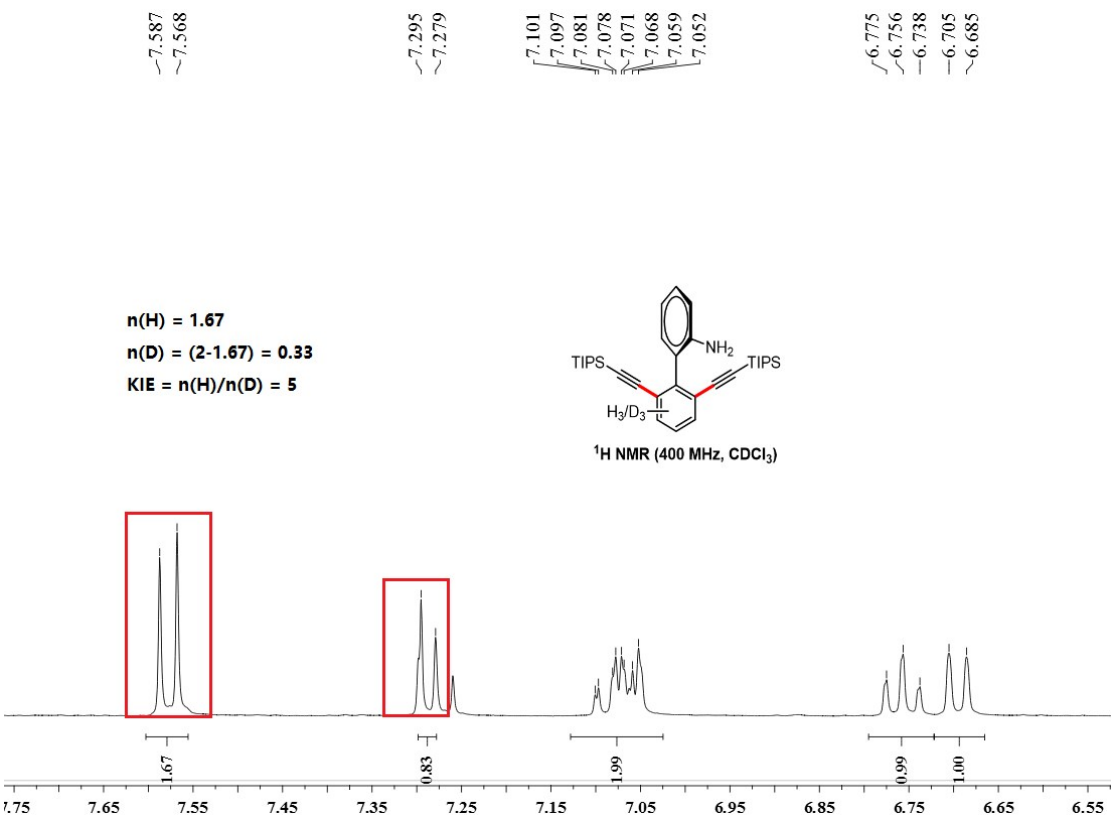
2′-((Triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine **3a** (0.2 mmol), 2′-((triisopropylsilyl)eth-ynyl)-[1,1'-biphenyl]-3′,4′,5′,6′-d_4-2-amine **3a-*d*$_4$** (0.2 mmol), (bromoethynyl)triisopropylsilane **2a** (0.5 mmol), $Pd(OAc)_2$ (0.01 mmol, 5 mol %), AgOAc (0.8 mmol, 4 equiv) and toluene (1.5 mL) were sealed in a Schlenk tube under N_2 atmosphere. After this, the mixture was stirred at 100 ^oC (oil bath temperature) for 1.5 h, the resulting mixture were cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. Then the resulting residue was purified by column chromatography on silica gel with petroleum ether/EtOAc (40/1) as eluent to afford a mixture of **4a** and **4a-*d*$_3$** in 21% isolated yield (15.6 mg). The KIE value (K_H/K_D = 5) was determined on the basis of ^1H NMR analysis. Data for compounds **4a**/**4a-*d*$_3$**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.8 Hz, 1.7H), 7.29 (d, J = 6.5

Hz, 0.8H), 7.08 (m, *J* = 7.6, 7.2, 2.2 Hz, 2H), 6.76 (t, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 3.43 (s, 2H), 0.97 (s, 42H).





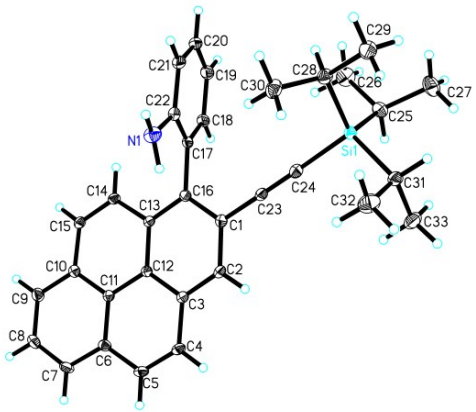

7.587
7.568
7.081
7.052
6.775
6.756
6.738
6.705
6.685
3.429
0.972
NH2
TIPS
TIPS
H3/D3
1H NMR (400 MHz, CDCl3)
1.67
0.83
1.99
0.99
1.00
1.82
42.19


7.587
7.568
7.295
7.279
7.101
7.097
7.081
7.078
7.071
7.068
7.059
7.052
6.775
6.756
6.738
6.705
6.685
n(H) = 1.67
n(D) = (2-1.67) = 0.33
KIE = n(H)/n(D) = 5
NH2
TIPS
TIPS
H3/D3
1H NMR (400 MHz, CDCl3)
1.67
0.83
1.99
0.99
1.00

E. X-ray Crystallographic Analysis

1. X-ray Crystallographic Analysis for Product 3o

The X-ray crystallographic structures for **3o**. ORTEP representation with 50% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 1560805.

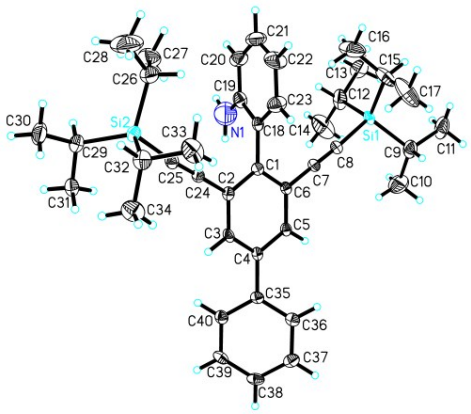


Empirical formula	$C_{33}H_{35}NSi$
Formula weight	473.71
Temperature	373(10) K
Wavelength	0.71073 *Å*
Crystal system, space group	Triclinic, *P-1*
Unit cell dimensions	a = 9.0089(6) (2) *Å* alpha = 98.702 (4) deg. b = 13.9567 (6) *Å* beta = 99.193 (4) deg. c = 22.3783 (10) *Å* gamma = 99.700 (4) deg.
Volume	2691.6 (2) *Å*^{3}
Z, Calculated density	4, 1.169 Mg/m^3
Absorption coefficient	0.109 mm^{-1}
F(000)	1016
Crystal size	0.14×0.12×0.10 mm
Theta range for data collection	3.315 to 29.544 deg.

Limiting indices	$-11 \leq h \leq 12$, $-17 \leq k \leq 17$, $-28 \leq l \leq 30$
Reflections collected / unique	25384 / 12544 [R(int) = 0.1029]
Completeness to theta = 25.00	99.8%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	25385 / 15 / 651
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	$R_1 = 0.0728$, $wR_2 = 0.1708$
R indices (all data)	$R_1 = 0.1029$, $wR_2 = 0.1909$

2. X-ray Crystallographic Analysis for Product 4b

The X-ray crystallographic structures for **4b**. ORTEP representation with 50% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 1560853.

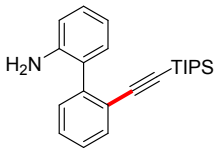


Empirical formula	$C_{40}\ H_{55}\ N\ Si_2$
Formula weight	606.03
Temperature	378(10) K
Wavelength	0.71073 *Å*
Crystal system, space group	Monoclinic, P_1

Unit cell dimensions	a = 15.3730 (8) (2) *Å* alpha = 90.000 (4) deg. b = 7.7388 (4) *Å* beta = 101.174 (4) deg. c = 32.2857 (16) *Å* gamma = 90.000 (4) deg.
Volume	3768.2 (3) $Å^3$
Z, Calculated density	4, 1.068 Mg/m^3
Absorption coefficient	0.120 mm^{-1}
F(000)	1320
Crystal size	0.18×0.16×0.12 mm
Theta range for data collection	3.264 to 24.999 deg.
Limiting indices	$-17 \leq h \leq 18$, $-9 \leq k \leq 8$, $-38 \leq l \leq 38$
Reflections collected / unique	16703 / 6618 [R(int) = 0.1200]
Completeness to theta = 25.00	99.6%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16703 / 0 / 400
Goodness-of-fit on F^2	1.014
Final R indices [I>2sigma(I)]	$R_1 = 0.0955$, $wR_2 = 0.2496$
R indices (all data)	$R_1 = 0.1200$, $wR_2 = 0.2730$

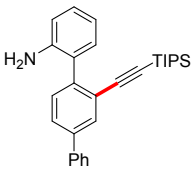
F. Characterization Date for All Products

2′-((Triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3a)



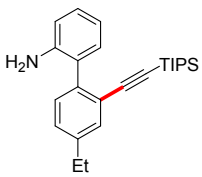
3a as a brown oil (39.1 mg, 80% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.8 Hz, 1H), 7.40-7.28 (m, 3H), 7.15-7.08 (m, 2H), 6.78 (m, J = 7.4, 3.8 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 3.11 (s, 2H), 0.96 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 142.3, 133.2, 130.6, 130.2, 128.7, 128.6, 127.2, 127.0, 123.3, 118.4, 115.7, 105.4, 94.0, 18.5, 11.2; ν_{max} (KBr)/cm^{-1} 3470, 3059, 2939, 2863, 2154, 1616, 1464, 1263, 752, 666, 454; HRMS (ESI) m/z: calcd for $C_{23}H_{32}NSi$ $[M+H]^+$ 350.2299; found 350.2304.

2′-((Triisopropylsilyl)ethynyl)-[1,1′:4′,1′′-terphenyl]-2-amine (3b)



3b as a brown oil (47.0 mg, 79% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 2.0 Hz, 1H), 7.66-7.60 (m, 3H), 7.49-7.37 (m, 4H), 7.14 (dd, J = 12.2, 4.5 Hz, 2H), 6.81 (t, J = 7.8 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H), 3.60 (s, 2H), 0.99 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 141.2, 140.3, 140.1, 140.0, 131.7, 130.6, 128.8, 128.7, 127.6, 127.5, 127.1, 126.6, 123.7, 118.4, 115.6, 105.4, 94.1, 18.5, 11.2; ν_{max} (KBr)/cm^{-1} 3472, 3306, 3029, 2933, 2863, 2152, 1674, 1546, 1383, 1304, 1257, 748, 667, 458; HRMS (ESI) m/z: calcd for $C_{29}H_{36}NSi$ $[M+H]^+$ 426.2621; found 426.2618.

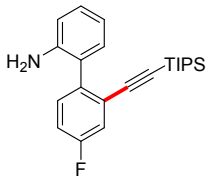
4′-Ethyl-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3c)



3c as a brown oil (39.6 mg, 75% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.25-7.19 (m, 2H), 7.10 (dd, J = 11.9, 4.5 Hz, 2H), 6.75 (t, J = 7.4 Hz, 1H), 6.70 (d, J = 7.8

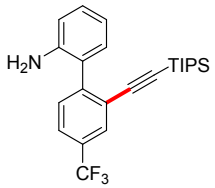
Hz, 1H), 3.38 (s, 2H), 2.66 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H), 0.96 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 143.3, 139.6, 132.4, 130.7, 130.1, 128.5, 128.4, 127.0, 123.1, 118.3, 115.5, 105.8, 93.3, 28.4, 18.5, 15.4, 11.2; ν_{max} (KBr)/cm^{-1} 3487, 3396, 2944, 2865, 2152, 1456, 1254, 1178, 980, 916, 881, 670, 459; HRMS (ESI) m/z: calcd for $C_{25}H_{36}NSi$ $[M+H]^+$ 378.2621; found 378.2616.

4′-Fluoro-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3d)



3d as a brown oil (42.1 mg, 82% yield); R_f = 0.2 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 2H), 7.10 (m, J = 10.5, 9.9, 7.2 Hz, 3H), 6.77 (t, J = 7.4 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 3.20 (s, 2H), 0.96 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 160.3, 143.8, 138.4, 131.8 (d, J = 8.6 Hz), 130.7 , 128.7, 125.9, 125.1 (d, J = 9.6 Hz), 119.5 (d, J = 22.6 Hz), 117.0 (d, J = 227.8 Hz), 116.1 (d, J = 22.0 Hz), 104.2, 95.4, 18.4, 11.1; ν_{max} (KBr)/cm^{-1} 3475, 3387, 2940, 2863, 2152, 1612, 1470, 1381, 1260, 1151, 999, 957, 751, 667, 460; HRMS (ESI) m/z: calcd for $C_{23}H_{31}FNSi$ $[M+H]^+$ 368.2204; found 368.2210.

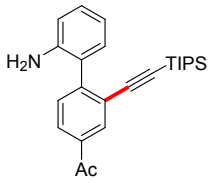
4′-(Trifluoromethyl)-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3e)



3e as a brown oil (49.6 mg, 85% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.62 (d, J = 8.6 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.16 (t, J = 7.8 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 6.80 (t, J = 7.6 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 3.20 (s, 2H), 0.97 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 143.5, 130.8, 130.3, 129.9 (q, J = 4.5 Hz), 129.6, 129.2, 127.8, 125.6, 125.1 (q, J = 3.5 Hz), 124.3, 122.4, 117.2 (d, J = 268.6 Hz), 103.8, 96.3, 18.4, 11.1; ν_{max}

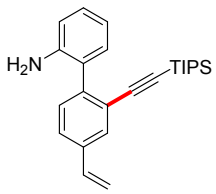
(KBr)/cm^{-1} 3390, 2943, 2865, 2156, 1617, 1460, 1404, 1330, 1169, 1130, 902, 751, 670, 457; HRMS (ESI) m/z: calcd for $C_{24}H_{31}F_3NSi$ $[M+H]^+$ 418.2172; found 418.2177.

1-(2′-Amino-2-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-4-yl)ethan-1-one (3f)



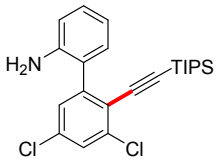
3f as a brown oil (41.6 mg, 76% yield); R_f = 0.2 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 1.8 Hz, 1H), 7.94 (dd, J = 8.0, 2.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.14 (m, J = 7.8, 1.5 Hz, 1H), 7.09 (dd, J = 7.6, 1.5 Hz, 1H), 6.79 (m, J = 7.6, 1.0 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 3.42 (s, 2H), 2.64 (s, 3H), 0.97 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 147.0, 143.4, 136.1, 133.1, 130.6, 130.2, 129.1, 128.2, 125.9, 124.0, 118.5, 115.9, 104.4, 95.5, 26.7, 18.5, 11.1; ν_{max} (KBr)/cm^{-1} 3473, 3372, 2932, 2863, 2153, 1687, 1617, 1459, 1358, 998, 885, 744, 673, 451; HRMS (ESI) m/z: calcd for $C_{25}H_{34}NOSi$ $[M+H]^+$ 392.2404; found 392.2406.

2′-((Triisopropylsilyl)ethynyl)-4′-vinyl-[1,1′-biphenyl]-2-amine (3g)



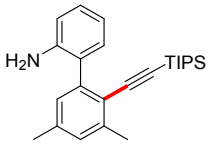
3g as a brown oil (43.6 mg, 83% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 1.8 Hz, 1H), 7.43 (dd, J = 8.0, 1.8 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.16-7.06 (m, 2H), 6.74 (m, J = 17.4, 8.6 Hz, 3H), 5.81 (d, J = 17.6 Hz, 1H), 5.31 (d, J = 11.1 Hz, 1H), 3.53 (s, 2H), 0.97 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 141.6, 136.7, 135.7, 130.9, 130.6, 130.4, 128.6, 126.6, 126.4, 123.5, 118.3, 115.6, 114.7, 105.3, 94.0, 18.5, 11.2; ν_{max} (KBr)/cm^{-1} 3473, 3385, 2936, 2863, 2150, 1616, 1459, 1382, 1296, 1155, 1069, 992, 749, 669, 458; HRMS (ESI) m/z: calcd for $C_{25}H_{34}NSi$ $[M+H]^+$ 376.2455; found 376.2452.

3′,5′-Dichloro-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3h)



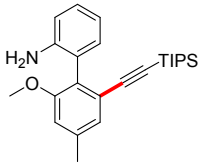
3h as a brown oil (44.4 mg, 76% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v)^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 2.2 Hz, 1H), 7.26 (s, 1H), 7.15 (m, J = 8.0, 1.4 Hz, 1H), 7.06 (dd, J = 7.6, 1.3 Hz, 1H), 6.78 (t, J = 7.4 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 3.30 (s, 2H), 0.97 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 143.4, 137.8, 134.2, 130.2, 129.3, 128.7, 128.2, 125.2, 122.1, 118.6, 115.9, 102.0, 100.5, 18.4, 11.1; ν_{max} (KBr)/cm^{-1} 3474, 3382, 2939, 2864, 2158, 1673, 1619, 1498, 1429, 1256, 881, 742, 672, 472; HRMS (ESI) m/z: calcd for $C_{23}H_{30}Cl_2NSi$ $[M+H]^+$ 418.1519; found 418.1523.

3′,5′-Dimethyl-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3i)



3i as a brown oil (41.2 mg, 78% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.07 (m, 2H), 7.05 (s, 1H), 6.99 (s, 1H), 6.77 (t, J = 7.4 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 3.35 (s, 2H), 2.51 (s, 3H), 2.35 (s, 3H), 0.97 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 142.5, 141.2, 138.3, 130.4, 129.3, 128.3, 128.1, 127.7, 120.23, 118.3, 115.6, 104.1, 97.5, 21.3, 18.5, 11.2; ν_{max} (KBr)/cm^{-1} 3472, 3382, 2942, 2864, 2149, 1613, 1497, 1460, 11217, 1157, 996, 799, 670, 604, 453; HRMS (ESI) m/z: calcd for $C_{25}H_{36}NSi$ $[M+H]^+$ 378.2621; found 378.2616.

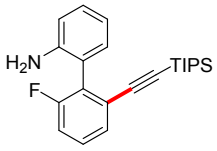
2′-Methoxy-4′-methyl-6′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3j)



3j as a yellow solid (40.2 mg, 73% yield); mp 82-83 ^{o}C; R_f = 0.2 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 8.4 Hz, 1H), 7.11 (m, J = 7.8, 1.6 Hz, 1H), 7.05 (dd, J = 7.6, 1.5 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H), 6.79 (m, J = 7.4, 1.0 Hz, 1H), 6.74 (dd, J = 8.0, 0.8 Hz, 1H), 3.72 (s, 3H), 3.51 (s, 2H), 2.46 (s, 3H), 0.95 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 144.1, 133.3, 131.0, 130.7,

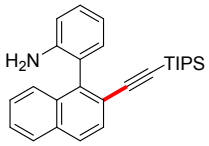
129.3, 128.4, 125.0, 123.7, 118.5, 115.6, 111.6, 103.8, 98.5, 56.1, 20.6, 18.5, 11.1; ν_{max} (KBr)/cm^{-1} 3470, 3379, 2941, 2864, 2149, 1677, 1616, 1499, 1384, 1164, 1108, 923, 742, 670, 476; HRMS (ESI) m/z: calcd for $C_{25}H_{36}NOSi$ $[M+H]^+$ 394.2561; found 394.2568.

2′-Fluoro-6′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3k)



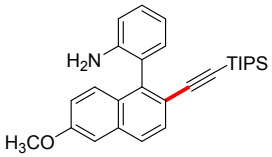
3k as a brown oil (44.7 mg, 87% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.4 Hz, 1H), 7.27 (m, J = 8.2, 5.6 Hz, 1H), 7.16-7.07 (m, 3H), 6.79 (m, J = 7.6, 0.9 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 3.38 (s, 2H), 0.94 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 158.9, 144.2, 131.0, 129.4, 129.3, 129.0, 128.9 (d, J = 2.8 Hz), 126.1 (d, J = 4.5 Hz), 120.0, 117.1 (d, J = 270.3 Hz), 116.2 (d, J = 22.9 Hz), 104.1 (d, J = 4.2 Hz), 95.3, 18.5, 11.1; ν_{max} (KBr)/cm^{-1} 3477, 3390, 3066, 2943, 2864, 2152, 1618, 1564, 1456, 1264, 987, 795, 745, 461; HRMS (ESI) m/z: calcd for $C_{23}H_{31}FNSi$ $[M+H]^+$ 368.2204; found 368.2208.

2-(2-((Triisopropylsilyl)ethynyl)naphthalen-1-yl)aniline (3l)



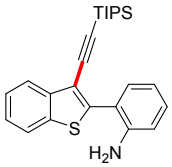
3l as a brown oil (46.4 mg, 83% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 17.4, 8.3 Hz, 2H), 7.67 (d, J = 8.6 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H), 7.51-7.46 (m, 1H), 7.44-7.38 (m, 1H), 7.23 (m, J = 8.0, 1.5 Hz, 1H), 7.12 (dd, J = 7.6, 1.4 Hz, 1H), 6.88 (m, J = 7.4, 0.8 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 3.27 (s, 2H), 1.00 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 140.4, 133.3, 132.1, 131.2, 129.2, 128.8, 128.0, 127.6, 126.8, 126.6, 126.5, 124.5, 121.2, 118.5, 115.6, 106.1, 94.6, , 18.5, 11.2; ν_{max} (KBr)/cm^{-1} 3474, 3383, 3057, 2943, 2864, 2147, 1615, 1497, 1458, 1070, 989, 926, 819, 747, 459; HRMS (ESI) m/z: calcd for $C_{27}H_{34}NSi$ $[M+H]^+$ 400.2455; found 400.2461.

2-(Methoxy-2-((triisopropylsilyl)ethynyl)naphthalen-1-yl)aniline (3m)



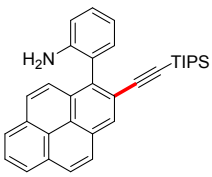
3m as a yellow solid (31.8 mg, 53% yield); mp 108-109 °C; R_f = 0.2 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.72-7.68 (m, 2H), 7.18-7.12 (m, 5H), 6.80 (m, J = 7.4, 0.8 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 3.93 (s, 3H), 3.50 (s, 2H), 0.99 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 144.1, 136.5, 133.4, 132.0, 130.9, 129.3, 128.8, 128.7, 128.5, 126.9, 121.9, 119.9, 118.3, 115.54, 105.8, 105.2, 93.9, 55.3, 18.5, 11.2; ν_{max} (KBr)/cm^{-1} 3462, 3372, 3056, 2932, 2861, 2146, 1617, 1494, 1457, 881, 807, 748, 671, 463; HRMS (ESI) m/z: calcd for $C_{28}H_{36}NOSi$ $[M+H]^+$ 430.2561; found 430.2563.

2-(3-((triisopropylsilyl)ethynyl)benzo[b]thiophen-2-yl)aniline (3n)



3n as a brown oil (28.9 mg, 51% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.39 (dd, J = 6.8, 5.6 Hz, 2H), 7.20 (t, J = 7.8 Hz, 1H), 6.79 (dd, J = 17.6, 8.0 Hz, 2H), 3.58 (s, 2H), 1.07 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 144.7, 140.2, 138.5, 131.8, 130.1, 125.0, 124.9, 123.1, 122.1, 118.7, 118.2, 116.8, 116.0, 99.7, 97.0, 18.6, 11.3; ν_{max} (KBr)/cm^{-1} 3488, 3374, 2944, 2864, 2155, 1702, 1620, 1466, 1368, 1306, 1109, 833, 670; HRMS (ESI) m/z: calcd for $C_{25}H_{32}NSSi$ $[M+H]^+$ 406.2019; found 406.2021.

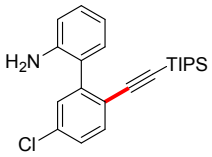
2-(2-((Triisopropylsilyl)ethynyl)pyren-1-yl)aniline (3o)



3o as a brown solid (47.7 mg, 72% yield); mp 113-114 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.11 (dd, J = 10.8, 7.6 Hz, 2H), 8.06-8.00 (m, 2H), 7.98-7.93 (m,

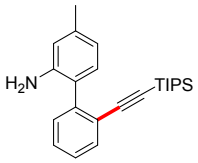
2H), 7.76 (d, J = 9.2 Hz, 1H), 7.25 (m, J = 7.8, 1.5 Hz, 1H), 7.21-7.18 (m, 1H), 6.90 (t, J = 7.4 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 3.40 (s, 2H), 1.01 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 136.7, 131.6, 131.4, 131.1, 130.5, 129.8, 128.9, 128.9, 128.1, 128.0, 126.7, 126.4, 125.5, 125.4, 125.3, 124.8, 124.6, 124.5, 121.7, 118.6, 115.6, 106.2, 94.3, 18.6, 11.2; ν_{max} (KBr)/cm^{-1} 3473, 3382, 3043, 2942, 2863, 2149, 1613, 1500, 1460, 1293, 1072, 993, 746, 683, 464; HRMS (ESI) m/z: calcd for $C_{33}H_{36}NSi$ $[M+H]^+$ 474.2612; found 474.2615.

5′-Chloro-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3p)



3p as a brown oil (32.7 mg, 61% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.4 Hz, 1H), 7.35 (d, J = 2.2 Hz, 1H), 7.29 (dd, J = 8.4, 2.2 Hz, 1H), 7.13 (m, J = 8.0, 1.6 Hz, 1H), 7.07 (dd, J = 7.6, 1.4 Hz, 1H), 6.78 (m, J = 7.5, 0.8 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 3.32 (s, 2H), 0.96 (s, 22H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 143.6, 134.4, 134.2, 130.4, 130.3, 129.0, 127.5, 125.6, 121.9, 118.4, 115.8, 104.3, 95.2, 18.5, 11.1; ν_{max} (KBr)/cm^{-1} 3475, 3386, 3027, 2944, 2864, 2155, 1616, 1583, 1230, 1206, 1012, 921, 883, 823, 747, 675, 466; HRMS (ESI) m/z: calcd for $C_{23}H_{31}NClSi$ $[M+H]^+$ 384.1909; found 384.1915.

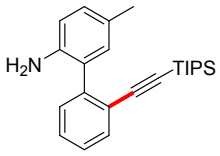
4-Methyl-2'-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3q)



3q as a brown oil (38.6 mg, 76% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 7.6, 0.6 Hz, 1H), 7.39-7.27 (m, 3H), 7.00 (d, J = 7.6 Hz, 1H), 6.61 (d, J = 7.8 Hz, 1H), 6.56 (s, 1H), 3.53 (s, 2H), 2.29 (s, 3H), 0.98 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 142.4, 138.3, 133.1, 130.4, 130.2, 128.6, 127.1, 124.3, 123.5, 119.3, 116.3, 105.6, 93.8, 21.2, 18.4, 11.2; ν_{max} (KBr)/cm^{-1} 3473,

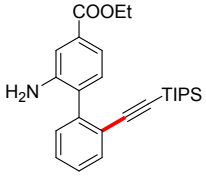
3383, 2941, 2864, 2154, 1618, 1514, 1466, 1381, 1300, 1071, 998, 801, 700, 454; HRMS (ESI) m/z: calcd for $C_{24}H_{34}NSi$ $[M+H]^+$ 364.2455; found 364.2460.

5-Methyl-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3r)



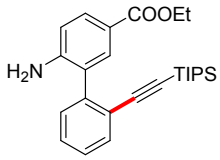
3r as a brown oil (37.1 mg, 73% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (t, J = 6.0 Hz, 1H), 7.36-7.23 (m, 3H), 6.91 (t, J = 6.0 Hz, 2H), 6.67-6.57 (m, 1H), 3.18 (s, 2H), 2.21 (s, 3H), 0.96 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 141.1, 133.1, 131.0, 130.1, 129.1, 128.6, 127.4, 127.1, 127.1, 123.3, 115.9, 105.6, 93.8, 20.4, 18.5, 11.2; ν_{max} (KBr)/cm^{-1} 3468, 3380, 3017, 2940, 2863, 2154, 1621, 1504, 1468, 918, 882, 825, 757, 669, 460; HRMS (ESI) m/z: calcd for $C_{24}H_{34}NSi$ $[M+H]^+$ 364.2455; found 364.2462.

Ethyl 2-amino-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-4-carboxylate (3s)



3s as a brown oil (48.3 mg, 82% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.8 Hz, 1H), 7.45 (dd, J = 7.8, 1.6 Hz, 1H), 7.42-7.37 (m, 2H), 7.32 (ddd, J = 12.4, 7.5, 1.2 Hz, 2H), 7.16 (d, J = 7.8 Hz, 1H), 4.37 (q, J = 7.2 Hz, 2H), 3.49 (s, 2H), 1.39 (t, J = 7.2 Hz, 3H), 0.94 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 143.9, 141.3, 133.2, 131.2, 130.7, 130.6, 129.6, 128.8, 127.7, 123.1, 119.3, 116.3, 104.9, 94.6, 60.7, 18.4, 14.3, 11.1; ν_{max} (KBr)/cm^{-1} 3479, 3380, 2943, 2865, 2154, 1716, 1622, 1466, 1426,, 1296, 1233, 1106, 831, 722, 461; HRMS (ESI) m/z: calcd for $C_{26}H_{36}NO_2Si$ $[M+H]^+$ 422.2510; found 422.2515.

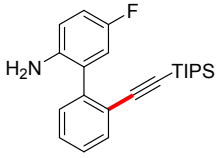
Ethyl 6-amino-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-3-carboxylate (3t)



3t as a brown oil (49.5 mg, 84% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.80 (m, 2H), 7.62

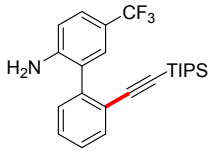
(d, J = 7.6 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H), 7.32 (dd, J = 9.0, 7.8 Hz, 2H), 6.69 (d, J = 8.4 Hz, 1H), 4.29 (dd, J = 7.1, 4.6 Hz, 2H), 3.98 (s, 2H), 1.33 (t, J = 7.1 Hz, 3H), 0.94 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 148.2, 141.0, 133.2, 132.6, 130.8, 130.1, 128.8, 127.7, 125.5, 123.5, 119.8, 114.3, 105.0, 94.5, 60.2, 18.4, 14.4, 11.1; ν_{max} (KBr)/cm^{-1} 3487, 3374, 2944, 2865, 2155, 1703, 1620, 1465, 1369, 1237, 1151, 1109, 833, 670, 460; HRMS (ESI) m/z: calcd for $C_{26}H_{36}NO_2Si$ $[M+H]^+$ 422.2510; found 422.2513.

5-Fluoro-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3u)



3u as a brown oil (37.5 mg, 73% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, J = 6.6, 2.4 Hz, 1H), 7.41-7.37 (m, 1H), 7.33 (t, J = 6.8 Hz, 2H), 6.86 (m, J = 11.2, 4.3 Hz, 2H), 6.66 (dd, J = 8.3, 4.8 Hz, 1H), 3.25 (s, 2H), 0.98 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 154.9, 141.1, 139.9, 133.2, 128.8, 128.7 (d, J = 222.5 Hz), 127.9 (d, J = 7.5 Hz), 123.2, 117.0 (d, J = 22.5 Hz), 116.5 (d, J = 7.7 Hz), 115.0 (d, J = 22.2 Hz), 105.0, 94.5, 18.4, 11.2; ν_{max} (KBr)/cm^{-1} 3469, 3382, 3061, 2942, 2864, 2154, 1614, 1501, 1471, 1264, 1177, 995, 879, 827, 704, 459; HRMS (ESI) m/z: calcd for $C_{23}H_{31}FNSi$ $[M+H]^+$ 368.2204; found 368.2211.

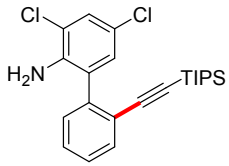
5-(Trifluoromethyl)-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3v)



3v as a brown oil (37.4 mg, 64% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, J = 7.5, 1.2 Hz, 1H), 7.43-7.29 (m, 5H), 6.75 (d, J = 8.2 Hz, 1H), 3.75 (s, 2H), 0.96 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 140.6, 133.3, 128.8 (d, J = 207 Hz), 128.9, 127.7 (q, J = 3.8 Hz), 126.2, 125.9 (q, J = 3.7 Hz), 123.5, 123.4, 120.8, 119.9 (q, J = 32.4 Hz), 114.7, 104.7, 94.7, 18.4, 11.1; ν_{max}

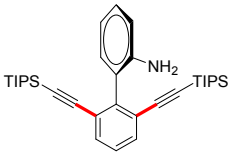
(KBr)/cm^{-1} 3494, 3401, 2946, 2866, 2156, 1625, 1464, 1332, 1273, 1244, 1151, 1115, 880, 760, 670, 459; HRMS (ESI) m/z: calcd for $C_{24}H_{31}F_3NSi$ $[M+H]^+$ 418.2172; found 418.2177.

3,5-Dichloro-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3w)



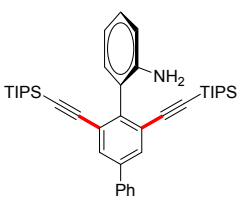
3w as a brown oil (40.9 mg, 70% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, J = 7.6, 1.4 Hz, 1H), 7.38 (ddd, J = 12.8, 7.4, 1.6 Hz, 2H), 7.29-7.25 (m, 2H), 7.01 (d, J = 2.4 Hz, 1H), 3.97 (s, 2H), 0.98 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 139.6, 133.2, 129.7, 128.9, 128.8, 128.7, 128.2, 128.1, 123.3, 122.1, 119.7, 104.5, 95.3, 18.4, 11.1; ν_{max} (KBr)/cm^{-1} 3489, 3394, 3063, 2944, 2864, 2155, 1612, 1459, 1107, 920, 880, 759, 718, 467; HRMS (ESI) m/z: calcd for $C_{23}H_{30}Cl_2NSi$ $[M+H]^+$ 418.1519; found 418.1523.

2′,6′-Bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4a)



4a as a brown oil (86.7 mg, 82% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.8 Hz, 2H), 7.24 (d, J = 6.4 Hz, 1H), 7.06-6.99 (m, 2H), 6.71 (t, J = 7.4 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 3.42 (s, 2H), 0.93 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 143.7, 132.8, 130.3, 128.6, 127.1, 125.8, 124.5, 118.5, 115.7, 104.8, 94.4, 18.5, 11.1; ν_{max} (KBr)/cm^{-1} 3478, 3390, 2942, 2864, 2151, 1617, 1458, 1069, 978, 922, 881, 744, 709, 671, 459; HRMS (ESI) m/z: calcd for $C_{34}H_{52}NSi_2$ $[M+H]^+$ 530.3633; found 530.3639.

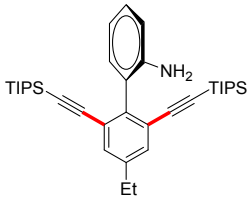
2′,6′-Bis((triisopropylsilyl)ethynyl)-[1,1′:4′,1″-terphenyl]-2-amine (4b)



4b as a yellow solid (89.5 mg, 74% yield); mp 128-129 ^{o}C; R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 2H), 7.64-7.61 (m, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.39 (dd, J = 8.3,

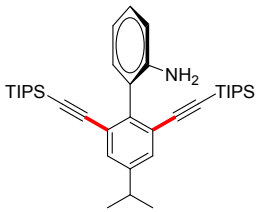
6.3 Hz, 1H), 7.07 (dd, J = 10.2, 4.1 Hz, 2H), 6.77-6.73 (m, 1H), 6.69 (dd, J = 8.4, 0.8 Hz, 1H), 3.45 (s, 2H), 0.95 (s, 51H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 143.7, 140.5, 139.5, 131.5, 130.4, 128.9, 128.6, 127.8, 127.1, 125.5, 124.9, 118.5, 115.8, 104.9, 94.5, 18.5, 11.2; ν_{max} (KBr)/cm^{-1} 3479, 3389, 3029, 2941, 2863, 2152, 1615, 1501, 1460, 1251, 1070, 1003, 920, 745, 672, 461; HRMS (ESI) m/z: calcd for $C_{40}H_{56}NSi_2$ $[M+H]^+$ 606.3946; found 606.3950.

4′-Ethyl-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4c)



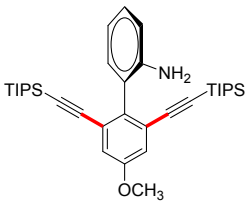
4c as a brown oil (88.1 mg, 79% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 2H), 7.05-6.99 (m, 2H), 6.71 (t, J = 7.2 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 3.17 (s, 2H), 2.63 (t, J = 7.6 Hz, 2H), 1.28 (t, J = 7.6 Hz, 3H), 0.94 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 143.2, 142.3, 132.4, 130.5, 128.4, 125.8, 124.2, 118.5, 115.7, 105.2, 93.7, 28.2, 18.5, 15.3, 11.2; ν_{max} (KBr)/cm^{-1} 3478, 3389, 2940, 2864, 2153, 1616, 1501, 1461, 1068, 997, 881, 743, 718, 458; HRMS (ESI) m/z: calcd for $C_{36}H_{56}NSi_2$ $[M+H]^+$ 558.3946; found 558.3952.

4′-Isopropyl-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4d)



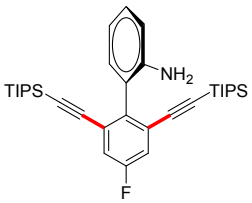
4d as a brown oil (82.2 mg, 72% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 2H), 7.05-7.00 (m, 2H), 6.71 (t, J = 7.2 Hz, 1H), 6.66 (d, J = 7.8 Hz, 1H), 3.17 (s, 2H), 1.29 (d, J = 6.8 Hz, 6H), 1.06 (d, J = 5.6 Hz, 1H), 0.93 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 143.8, 142.5, 131.1, 130.5, 128.4, 125.9, 124.2, 118.5, 115.7, 105.3, 93.7, 33.7, 23.7, 18.5, 11.2; ν_{max} (KBr)/cm^{-1} 3477, 3389, 2949, 2865, 2151, 1616, 1502, 1461, 1298, 1073, 1000, 882, 744, 672, 461; HRMS (ESI) m/z: calcd for $C_{37}H_{58}NSi_2$ $[M+H]^+$ 572.4102; found 572.4104.

4′-Methoxy-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4e)



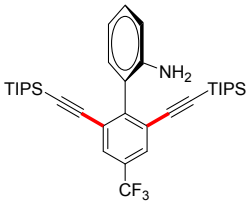
4e as a brown solid (63.7 mg, 57% yield); mp 83-84 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 2H), 7.04-6.99 (m, 2H), 6.71-6.67 (m, 1H), 6.64 (d, J = 8.0 Hz, 1H), 3.84 (s, 3H), 3.31 (s, 2H), 0.93 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 144.1, 137.6, 130.8, 128.4, 125.5, 125.3, 118.5, 118.4, 115.6, 104.8, 94.2, 55.6, 18.5, 11.1; ν_{max} (KBr)/cm^{-1} 3476, 3387, 2941, 2863, 2150, 1615, 1501, 1461, 1194, 1153, 1061, 1003, 921, 743, 671, 463; HRMS (ESI) m/z: calcd for $C_{35}H_{54}NSi_2$ $[M+H]^+$ 560.3738; found 560.3743.

4′-Fluoro-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4f)



4f as a brown oil (72.2 mg, 66% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 2.6 Hz, 2H), 7.10-7.05 (m, 1H), 7.02 (d, J = 7.6 Hz, 1H), 6.74 (t, J = 7.4 Hz, 1H), 6.68 (d, J = 8.0 Hz, 1H), 3.42 (s, 2H), 0.96 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 159.7, 143.9, 141.1, 130.5, 128.8, 126.1 (d, J = 10.2 Hz), 124.8, 119.6 (d, J = 22.5 Hz), 117.1 (d, J = 279.1 Hz), 103.7 (d, J = 3.1 Hz), 95.8, 18.4, 17.7, 11.1; ν_{max} (KBr)/cm^{-1} 3478, 3392, 2942, 2864, 2159, 1617, 1579, 1312, 1131, 1070, 1000, 744, 670, 460; HRMS (ESI) m/z: calcd for $C_{34}H_{51}FNSi_2$ $[M+H]^+$ 548.3539; found 548.3533.

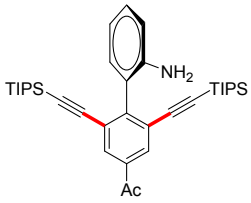
4′-(Trifluoromethyl)-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4g)



4g as a brown oil (95.5 mg, 80% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 2H), 7.107.05 (m, 1H), 6.99 (dd, J = 7.6, 1.3 Hz, 1H), 6.74 (t, J = 7.4 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 2.87 (s, 2H), 0.94 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 143.5, 130.0 (q, J = 32.9 Hz), 129.9, 129.0, 129.0 (q, J = 3.7 Hz), 125.5, 124.6, 123.4 (q, J = 271.0 Hz), 118.6,

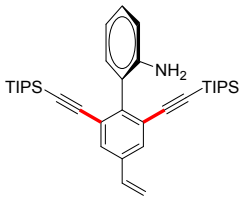
115.9, 103.3, 96.7, 18.4, 11.1; ν_{max} (KBr)/cm^{-1} 3479, 3392, 2946, 2865, 2155, 1618, 1502, 1462, 1233, 1169, 1136, 889, 739, 672, 464; HRMS (ESI) m/z: calcd for $C_{35}H_{51}F_3NSi_2$ $[M+H]^+$ 598.3507; found 598.3515.

1-(2′-Amino-2,6-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-4-yl)ethan-1-one (4h)



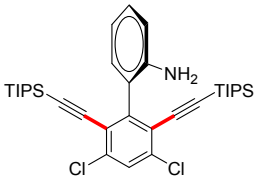
4h as a yellow solid (87.9 mg, 77% yield); mp 99-100 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 15/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 3H), 7.06 (dd, J = 10.9, 4.5 Hz, 1H), 7.00 (dd, J = 7.6, 1.3 Hz, 1H), 6.73 (t, J = 7.6 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 3.25 (s, 2H), 2.64 (s, 3H), 0.94 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 149.3, 143.4, 136.1, 132.2, 129.9, 129.0, 125.2, 124.9, 118.6, 115.9, 103.85, 95.9, 26.7, 18.5, 11.1; ν_{max} (KBr)/cm^{-1} 3475, 3381, 2939, 2864, 2152, 1691, 1619, 1461, 1306, 1070, 1006, 884, 744, 714, 672, 462; HRMS (ESI) m/z: calcd for $C_{36}H_{54}NOSi_2$ $[M+H]^+$ 572.3788; found 572.3741.

2′,6′-Bis((triisopropylsilyl)ethynyl)-4′-vinyl-[1,1′-biphenyl]-2-amine (4i)



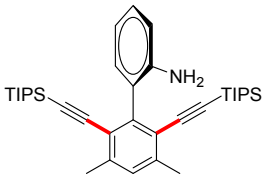
4i as a brown oil (93.2 mg, 84% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 2H), 7.06-7.00 (m, 2H), 6.74-6.64 (m, 3H), 5.82 (d, J = 17.6 Hz, 1H), 5.33 (d, J = 10.8 Hz, 1H), 3.43 (s, 2H), 0.94 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 142.8, 135.8, 134.1, 129.4, 129.3, 127.6, 124.5, 123.7, 117.4, 114.7, 114.4, 103.8, 93.3, 17.5, 10.1; ν_{max} (KBr)/cm^{-1} 3477, 3389, 2943, 2864, 2152, 1616, 1500, 1461, 1298, 1068, 916, 802, 671, 460; HRMS (ESI) m/z: calcd for $C_{36}H_{54}NSi_2$ $[M+H]^+$ 556.3789; found 556.3794.

3′,5′-Dichloro-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4j)



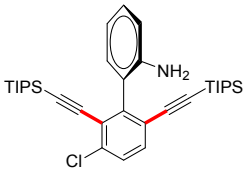
4j as a brown solid (85.9 mg, 72% yield); mp 103-104 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.08-7.04 (m, 1H), 6.98 (dd, J = 7.6, 1.4 Hz, 1H), 6.73 (t, J = 7.2 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 2.91 (s, 2H), 0.94 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 143.3, 136.6, 129.9, 129.1, 128.8, 125.1, 123.0, 118.8, 116.0, 102.1, 100.2, 18.4, 11.1; ν_{max} (KBr)/cm^{-1} 3463, 3383, 2940, 2862, 2160, 1618, 1497, 1459, 1148, 1067, 919, 790, 751, 672, 470; HRMS (ESI) m/z: calcd for $C_{34}H_{50}Cl_2NSi_2$ $[M+H]^+$ 530.3633; found 530.3639.

3′,5′-Dimethyl-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4k)



4k as a brown solid (76.9 mg, 69% yield); mp 137-138 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 3H), 7.09 (s, 1H), 7.04-6.99 (m, 2H), 6.71 (t, J = 7.4 Hz, 1H), 6.76-6.61 (m, 2H), 6.66 (d, J = 8.0 Hz, 1H), 2.87 (s, 2H), 2.47 (s, 6H), 0.93 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 143.5, 141.0, 130.3, 129.8, 128.3, 127.0, 121.6, 118.6, 115.8, 103.6, 97.9, 21.4, 18.5, 11.2; ν_{max} (KBr)/cm^{-1} 3374, 2940, 2864, 2150, 1615, 1459, 1378, 1074, 995, 883, 743, 672, 603, 463; HRMS (ESI) m/z: calcd for $C_{36}H_{56}NSi_2$ $[M+H]^+$ 558.3946; found 558.3940.

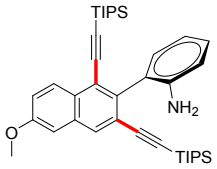
3′-Chloro-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4l)



4l as a yellow solid (38.3 mg, 34% yield); mp 79-80 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.077.02 (m, 1H), 6.99 (dd, J = 7.6, 1.3 Hz, 1H), 6.72 (t, J = 7.6 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 2.80 (s, 2H), 0.93 (d, J = 9.4 Hz, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 143.5, 136.9, 132.8, 130.1, 128.9, 128.2, 125.4, 124.4, 122.9, 118.6, 115.9, 103.9, 101.3, 101.0, 95.4, 18.5, 11.1; ν_{max} (KBr)/cm^{-1} 3479,

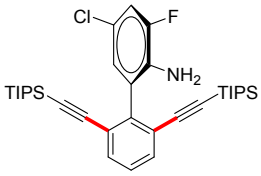
3389, 2940, 2864, 2153, 1679, 1616, 1547, 1460, 1259, 1071, 991, 921, 818, 742, 676, 470; HRMS (ESI) m/z: calcd for $C_{34}H_{51}ClNSi_2$ $[M+H]^+$ 564.3243; found 564.3239.

2-(6-Methoxy-1,3-bis((triisopropylsilyl)ethynyl)naphthalen-2-yl)aniline (4m)



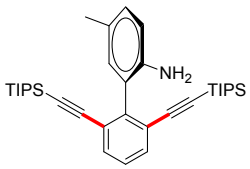
4m as a brown solid (57.2 mg, 47% yield); mp 111-112 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 9.2 Hz, 1H), 7.99 (s, 1H), 7.25-7.21 (m, 1H), 7.11-7.04 (m, 3H), 6.74 (t, J = 7.4 Hz, 1H), 6.68 (d, J = 8.0 Hz, 1H), 3.93 (s, 3H), 3.43 (s, 2H), 0.99 (s, 21H), 0.95 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 144.0, 140.5, 133.4, 132.0, 130.7, 128.9, 128.5, 128.2, 126.3, 122.4, 121.5, 120.3, 118.5, 115.7, 105.7, 105.3, 102.8, 99.9, 94.1, 55.4, 18.6, 18.5, 11.2, 11.2; ν_{max} (KBr)/cm^{-1} 3 76, 3383, 2939, 2864, 2150, 1686, 1496, 1459, 1230, 1164, 1000, 882, 822, 671, 462; HRMS (ESI) m/z: calcd for $C_{39}H_{56}NOSi_2$ $[M+H]^+$ 610.3895; found 610.3890.

5-Chloro-3-fluoro-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4n)



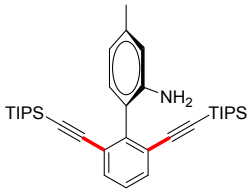
4n as a brown oil (87.2 mg, 75% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.8 Hz, 2H), 7.30 (t, J = 7.8 Hz, 1H), 6.96 (dd, J = 10.8, 2.3 Hz, 1H), 6.89-6.88 (m, 1H), 3.47 (s, 2H), 0.97 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 150.4, 141.9 (d, J = 3.1 Hz), 132.7, 131.6 (d, J = 12.8 Hz), 128.4 (d, J = 4.4 Hz), 126.1 (d, J = 374.7 Hz), 125.6 (d, J = 3.0 Hz), 121.8 (d, J = 10.6 Hz), 114.8 (d, J = 22.4 Hz), 104.0, 95.5, 18.4, 11.1; ν_{max} (KBr)/cm^{-1} 3488, 3396, 2945, 2865, 2152, 1573, 1456, 1255, 1178, 1074, 980, 916, 881, 803, 670, 461; HRMS (ESI) m/z: calcd for $C_{34}H_{50}ClFNSi_2$ $[M+H]^+$ 582.3149; found 582.3154.

5-Methyl-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4o)



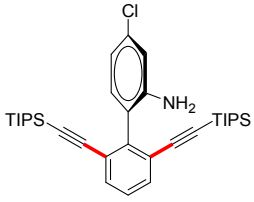
4o as a yellow solid (82.5 mg, 76% yield); mp 60-61 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.8 Hz, 2H), 7.25 (d, J = 4.0 Hz, 1H), 6.84 (d, J = 9.8 Hz, 2H), 6.57 (d, J = 8.0 Hz, 1H), 3.24 (s, 2H), 2.18 (s, 3H), 0.93 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 141.2, 132.7, 130.5, 129.1, 127.4, 127.0, 126.1, 124.4, 116.1, 104.9, 94.3, 20.3, 18.4, 11.2; ν_{max} (KBr)/cm^{-1} 3471, 3384, 2941, 2864, 2151, 1620, 1505, 1458, 1318, 979, 920, 882, 804, 741, 671, 459; HRMS (ESI) m/z: calcd for $C_{35}H_{54}NSi_2$ $[M+H]^+$ 544.3789; found 544.3785.

4-Methyl-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4p)



4p as a brown oil (79.3 mg, 73% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.8 Hz, 2H), 7.32-7.27 (m, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.59 (d, J = 7.8 Hz, 1H), 6.54 (s, 1H), 3.42 (s, 2H), 2.28 (s, 3H), 0.99 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 143.5, 138.1, 132.7, 130.2, 127.0, 124.6, 123.2, 119.5, 116.4, 105.0, 94.2, 21.1, 18.4, 11.2; ν_{max} (KBr)/cm^{-1} 3478, 3389, 2943, 2865, 2151, 1620, 1515, 1459, 1071, 978, 922, 882, 755, 671, 457; HRMS (ESI) m/z: calcd for $C_{35}H_{54}NSi_2$ $[M+H]^+$ 544.3789; found 544.3779.

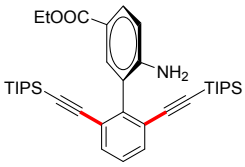
4-Chloro-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4q)



4q as a brown oil (79.9 mg, 71% yield); R_f = 0.5 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.8 Hz, 2H), 7.19 (d, J = 8.0 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H), 6.63 (dd, J = 8.2, 2.0 Hz, 1H), 6.59 (d, J = 1.8 Hz, 1H), 3.42 (s, 2H), 0.87 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 143.6, 134.1, 132.7, 131.5, 127.5, 124.5, 124.2, 118.3, 115.2, 104.4, 94.9, 18.4, 11.2; ν_{max}

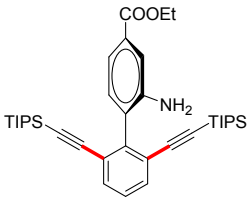
(KBr)/cm^{-1} 3483, 3393, 2944, 2865, 2151, 1615, 1567, 1497, 1238, 1070, 980, 883, 843, 754, 671, 460; HRMS (ESI) m/z: calcd for $C_{34}H_{51}ClNSi_2$ $[M+H]^+$ 564.3243; found 564.3243.

Ethyl 6-amino-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-3-carboxylate (4r)



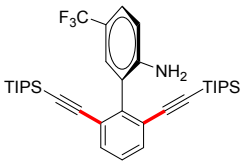
4r as a yellow solid (96.2 mg, 80% yield); mp 108-109 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 10/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.76 (m, 2H), 7.55 (d, J = 7.8 Hz, 2H), 7.28 (t, J = 7.6 Hz, 1H), 6.65 (d, J = 8.4 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 3.71 (s, 2H), 1.32 (t, J = 7.2 Hz, 4H), 0.91 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 148.3, 143.4, 132.8, 132.7, 130.9, 127.6, 124.6, 124.4, 120.0, 114.4, 104.4, 95.0, 60.0, 18.4, 14.4, 11.1; ν_{max} (KBr)/cm^{-1} 3490, 3375, 2944, 2865, 2151, 1705, 1620, 1573, 1459, 1368, 1298, 1150, 1109, 981, 917, 465; HRMS (ESI) m/z: calcd for $C_{37}H_{56}NO_2Si_2$ $[M+H]^+$ 602.3844; found 602.3850.

Ethyl 2-amino-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-4-carboxylate (4s)



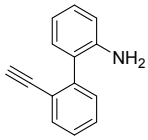
4s as a yellow solid (99.7 mg, 83% yield); mp 85-86 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 10/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.8 Hz, 2H), 7.43 (dd, J = 8.0, 1.6 Hz, 1H), 7.38 (d, J = 1.4 Hz, 1H), 7.28 (t, J = 6.2 Hz, 1H), 7.11 (d, J = 8.0 Hz, 1H), 4.37 (q, J = 7.2 Hz, 2H), 3.21 (s, 2H), 1.38 (t, J = 7.2 Hz, 3H), 0.92 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 144.0, 143.8, 132.7, 130.7, 130.5, 130.3, 127.6, 124.1, 119.6, 116.5, 104.3, 95.1, 60.5, 18.4, 14.4, 11.1; ν_{max} (KBr)/cm^{-1} 3480, 3381, 2943, 2865, 2151, 1719, 1622, 1569, 1460, 1431, 1369, 1297, 1232, 979, 714, 463; HRMS (ESI) m/z: calcd for $C_{37}H_{55}NNaO_2Si_2$ $[M+Na]^+$ 624.3664; found 624.3674.

5-(Trifluoromethyl)-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4t)



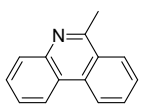
4t as a yellow solid (80.0 mg, 67% yield); mp 78-79 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.8 Hz, 2H), 7.34-7.27 (m, 3H), 6.71 (d, J = 8.2 Hz, 1H), 3.72 (s, 2H), 0.92 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 142.9, 132.9, 127.9, 127.6 (q, J = 4.1 Hz), 126.0 (q, J = 3.6 Hz), 125.0, 124.9 (q, J = 269.0 Hz), 124.6, 120.1 (q, J = 32.3 Hz), 114.8, 104.1, 95.2, 18.4, 11.1; ν_{max} (KBr)/cm^{-1} 3494, 3402, 2945, 2865, 2151, 1625, 1513, 1460, 1381, 1150, 1116, 980, 883, 670, 457; HRMS (ESI) m/z: calcd for $C_{35}H_{51}F_3NSi_2$ $[M+H]^+$ 598.3507; found 598.3512.

2′-Ethynyl-[1,1′-biphenyl]-2-amine (5a)



5a as a yellow oil (35.1 mg, 91% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.8 Hz, 1H), 7.41 (m, J = 7.6, 1.3 Hz, 1H), 7.36-7.30 (m, 2H), 7.18 (m, J = 7.8, 1.5 Hz, 1H), 7.12 (dd, J = 7.5, 1.6 Hz, 1H), 6.82 (m, J = 7.5, 0.8 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 3.38 (s, 2H), 2.99 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 142.2, 133.5, 130.6, 130.3, 129.2, 128.8, 127.4, 126.4, 121.9, 118.3, 115.6, 82.3, 80.2; ν_{max} (KBr)/cm^{-1} 3474, 3383,3301, 3060, 2939, 2864, 2150, 1676, 1617, 1500, 1462, 1381, 1253, 1077, 1000, 802, 670, 458; HRMS (ESI) m/z: calcd for $C_{14}H_{12}N$ $[M+H]^+$ 194.0964; found 194.0968.

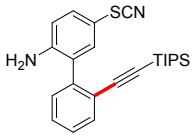
6-Methylphenanthridine (6a)



6a as a yellow solid (30.2 mg, 78% yield); mp 85-86 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 8.4 Hz, 1H), 8.55 (d, J = 8.2 Hz, 1H), 8.23 (d, J = 8.2 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H), 7.90-7.82 (m, 1H),

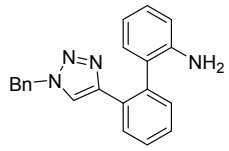
7.76-7.67 (m, 2H), 7.66-7.60 (m, 1H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 143.6, 132.6, 130.6, 129.3, 128.7, 127.3, 126.6, 126.4, 125.9, 123.8, 122.3, 122.0, 23.3; ν_{max} (KBr)/cm^{-1} 3307, 2926, 2859, 2312, 1675, 1636, 1599, 1544, 1308, 1253, 1087, 806, 753, 654, 576, 455; HRMS (ESI) m/z: calcd for $C_{14}H_{12}N$ $[M+H]^+$ 194.0964; found 194.0968.

5-Thiocyanato-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (7a)



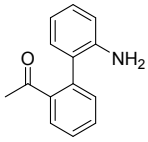
7a as a yellow oil (108.1 mg, 89% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, J = 7.4, 1.2 Hz, 1H), 7.41 (m, J = 7.5, 1.4 Hz, 1H), 7.38-7.33 (m, 2H), 7.32-7.27 (m, 2H), 6.74 (d, J = 8.4 Hz, 1H), 3.88 (s, 2H), 0.96 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 140.0, 135.01, 133.3, 133.3, 129.8, 128.9, 128.1, 123.4, 116.6, 112.1, 109.3, 104.7, 94.9, 18.5, 11.1; ν_{max} (KBr)/cm^{-1} 3484, 3383, 2941, 2863, 2154, 1620, 1495, 1468, 1402, 1306, 919, 882, 670; HRMS (ESI) m/z: calcd for $C_{24}H_{30}N_2NaSSi$ $[M+Na]^+$ 429.1791; found 429.1794.

2′-(1-Benzyl-1H-1,2,3-triazol-4-yl)-[1,1′-biphenyl]-2-amine (8a)



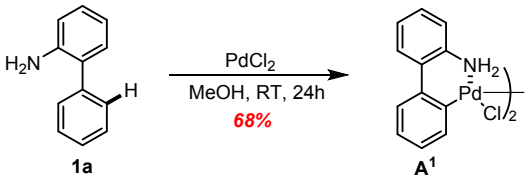
8a as a yellow oil (56.7 mg, 87% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, J = 7.8, 1.1 Hz, 1H), 7.48 (m, J = 7.6, 1.4 Hz, 1H), 7.41 (m, J = 7.6, 1.4 Hz, 1H), 7.30 (ddd, J = 9.0, 6.6, 1.8 Hz, 4H), 7.09 (ddd, J = 9.2, 7.8, 2.8 Hz, 3H), 6.95 (dd, J = 7.6, 1.4 Hz, 1H), 6.71 (t, J = 7.4 Hz, 1H), 6.56 (d, J = 8.0 Hz, 1H), 6.46 (s, 1H), 5.32 (s, 2H), 3.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 143.5, 136.4, 134.6, 130.5, 130.1, 130.0, 128.9, 128.8, 128.5, 128.4, 128.3, 128.2, 127.8, 126.7, 121.9, 118.5, 115.1, 53.8; ν_{max} (KBr)/cm^{-1} 3464, 3363, 3058, 2927, 2861, 2151, 1615, 1452, 1348, 1299, 1223, 1073, 1044, 809, 753, 507; HRMS (ESI) m/z: calcd for $C_{21}H_{18}N_4Na$ $[M+Na]^+$ 349.1424; found 349.1434.

1-(2′-Amino-[1,1'-biphenyl]-2-yl)ethan-1-one (9a)

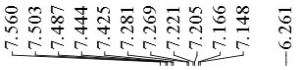


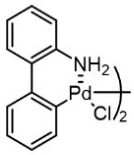
9a as a yellow oil (31.7 mg, 75% yield); R_f = 0.2 (petroleum ether/ethyl acetate = 10/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 8.4 Hz, 1H), 8.53 (d, J = 8.2 Hz, 1H), 8.21 (d, J = 8.2 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H), 7.87-7.81 (m, 1H), 7.70 (m, J = 8.2, 1.2 Hz, 2H), 7.65-7.58 (m, 1H), 3.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 143.6, 132.6, 130.5, 129.3, 128.6, 127.3, 126.5, 126.3, 125.9, 123.8, 122.3, 121.9, 23.3; ν_{max} (KBr)/cm^{-1} 3462, 3068, 2922, 2853, 2309, 1614, 1580, 1444, 1375, 1316, 860, 753, 720, 614, 436; HRMS (ESI) m/z: calcd for $C_{14}H_{13}NNaO$ $[M+Na]^+$ 234.0889; found 234.0891.

G. The Preparation of Palladacycle Intermediate A^1

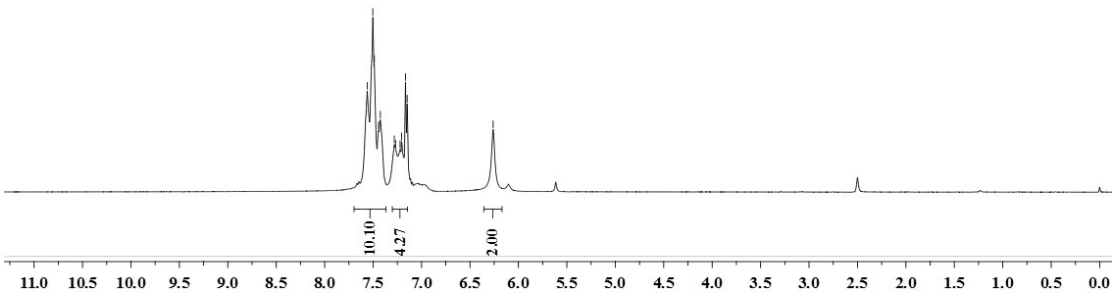


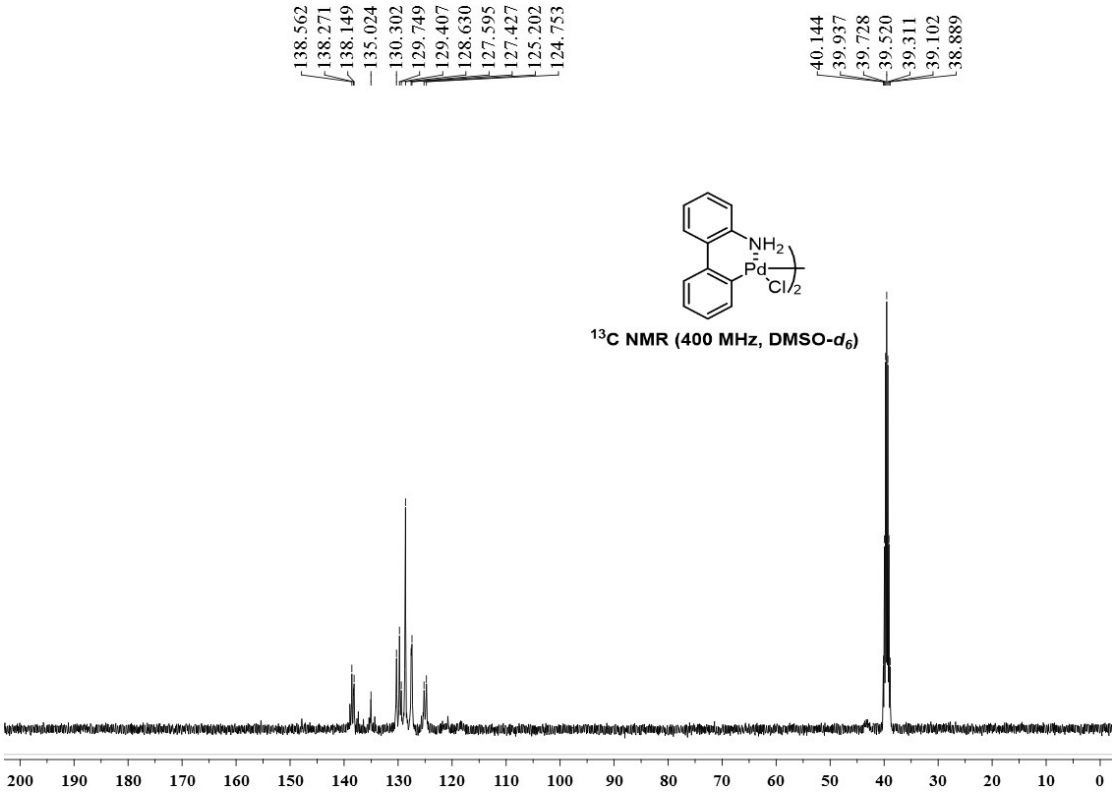
Palladacycle Intermediate A: [1,1′-biphenyl]-2-amine **1a** (0.6 mmol), $PdCl_2$ (0.6 mmol), and MeOH (4 mL) were sealed in a Schlenk tube under N_2 atmosphere. After this, the mixture was stirred at room temperature for 24 h. The precipitate was filtered, washed with 10 mL MeOH, 10 mL diethylether and dried under vacuum. Palladacycle $\mathbf{A^1}$ as a brown solid (119.3 mg, 68% yield); ^{1}H NMR (400 MHz, DMSO) δ 7.70-7.37 (m, 10H), 7.30-7.14 (m, 4H), 6.26 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 138.3, 138.2, 135.0, 130.3, 129.8, 129.4, 128.6, 127.6, 127.4, 125.2, 124.8; ν_{max} (KBr)/cm^{-1} 3241, 3183, 3096, 1567, 1480, 1453, 1314, 1287, 1129, 1178, 826, 760, 701, 520. HRMS (ESI) Calcd for $C_{24}H_{20}N_2ClPd_2$ $[M\text{-}Cl]^+$ 584.9388; Found, 584.9382.

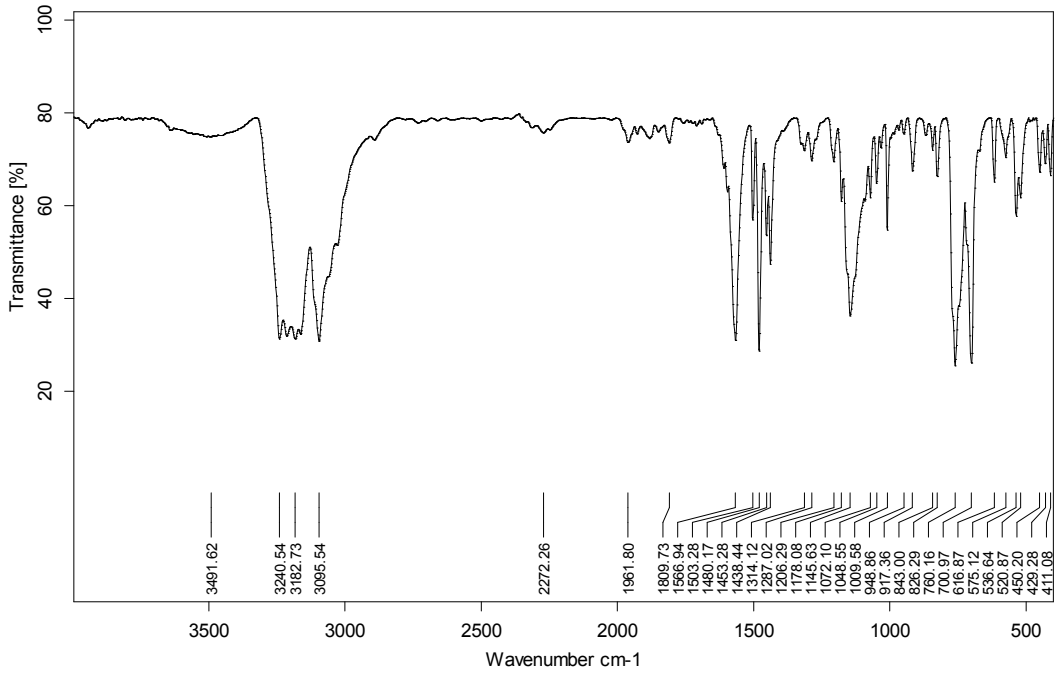


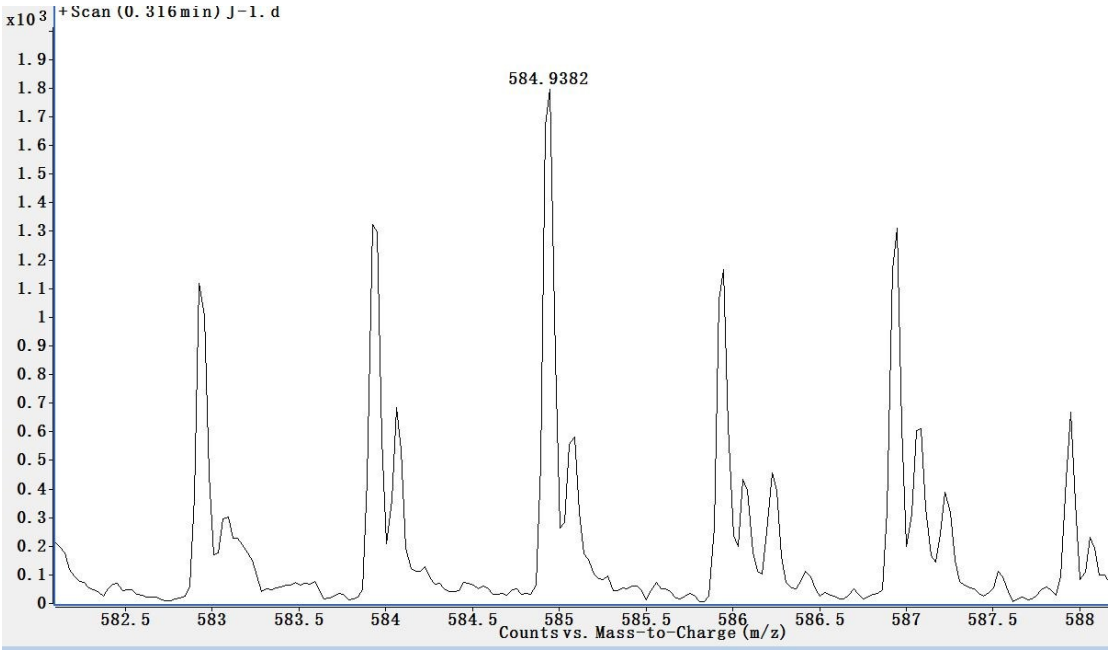


^{1}H NMR (400 MHz, DMSO-d_6)

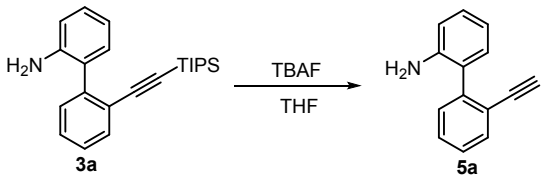



138.562
138.271
138.149
135.024
130.302
129.749
129.407
128.630
127.595
127.427
125.202
124.753
40.144
39.937
39.728
39.520
39.311
39.102
38.889
NH2
Pd
Cl2
13C NMR (400 MHz, DMSO-d6)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

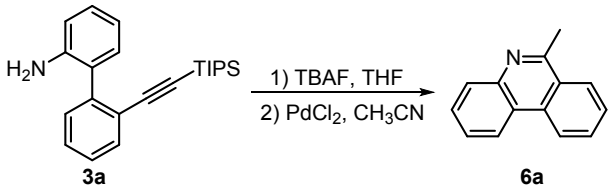

Transmittance [%]
100
80
60
40
20
3491.62
3240.54
3182.73
3095.54
2272.26
1961.80
1809.73
1566.94
1503.28
1480.17
1453.28
1438.44
1314.12
1287.02
1206.29
1178.08
1145.63
1072.10
1048.55
1009.58
948.86
917.36
843.00
826.29
760.16
700.97
616.87
575.12
536.64
520.87
450.20
429.28
411.08
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1


+Scan (0.316 min) J-1.d
x10 3
584.9382
Counts vs. Mass-to-Charge (m/z)

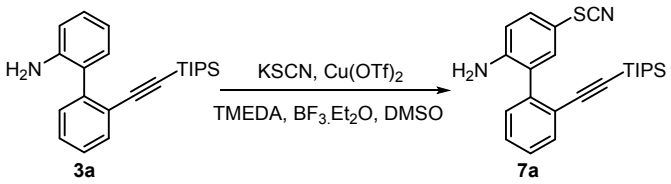
H. Further Synthetic Applications



(a) 2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine **3a** (0.2 mmol), TBFA (1 M in THF, 0.4 ML) and THF (1.0 mL) were sealed in a Schlenk tube under N_2 atmosphere. After this, the mixture was stirred at room temperature for 3 h. After the reaction was completed (monitored by TLC), the resulting mixture was extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired products **5a** were obtained after purified by column chromatography on silica gel with mixture of petroleum ether and ethyl acetate.

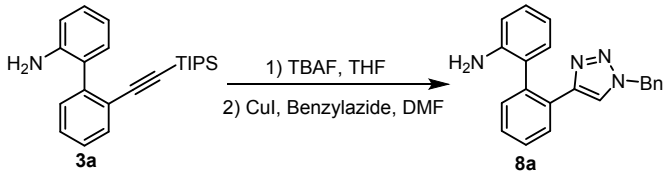


(b) i) 2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine **3a** was hydrolyzed to **5a**. ii) **5a** (0.1 mmol), $PdCl_2$ (5 mol %) and CH_3CN (1 mL) were sealed in a Schlenk tube under N_2 atmosphere . After this, the mixture was stirred at 100 ^oC for 12 h. Aftre the reaction was completed (monitored by TLC), the resulting mixture were cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired products **6a** were obtained in the corresponding yields after purified by column chromatography on silica gel with mixture of petroleum ether and ethyl acetate.



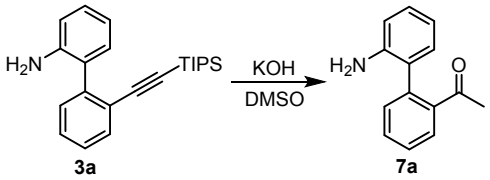
3a 7a

(c) 2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine **3a** (0.3 mmol), KSCN (2 equiv), $Cu(OTf)_2$ (20 mol%), TMEDA (20 mol%) and $BF_3.Et_2O$ were mixed in DMSO to stir under an O_2 balloon at 80 °C. Aftre the reaction was completed (monitored by TLC), the resulting mixture were cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired products **7a** were obtained in the corresponding yields after purified by column chromatography on silica gel with mixture of petroleum ether and ethyl acetate.



3a 8a

(d) i) 2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine **3a** was hydrolyzed to **5a**. ii) **5a** (0.2 mmol), Benzylazide (0.2 mmol), CuI (10 mol %) and DMF (1 mL) were sealed in a Schlenk tube under N_2 atmosphere . After this, the mixture was stirred at 80 ^oC for 12 h. Aftre the reaction was completed (monitored by TLC), the resulting mixture were cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired products **8a** were obtained in the corresponding yields after purified by column chromatography on silica gel with mixture of petroleum ether and ethyl acetate.

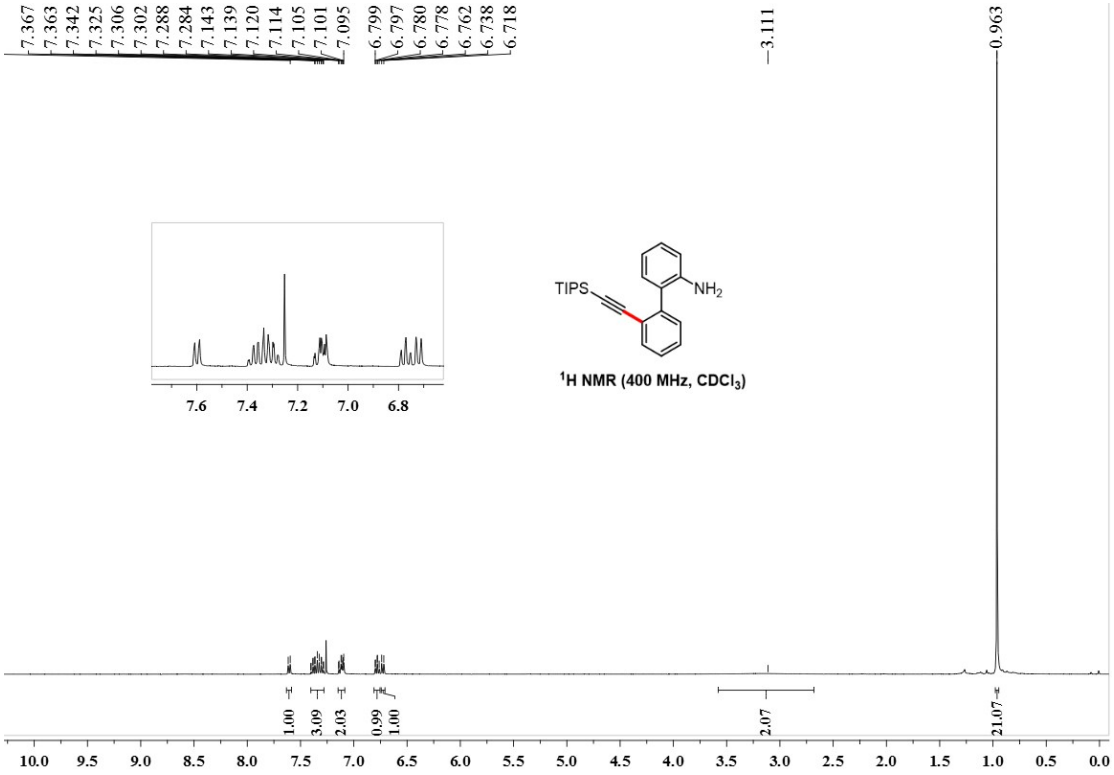


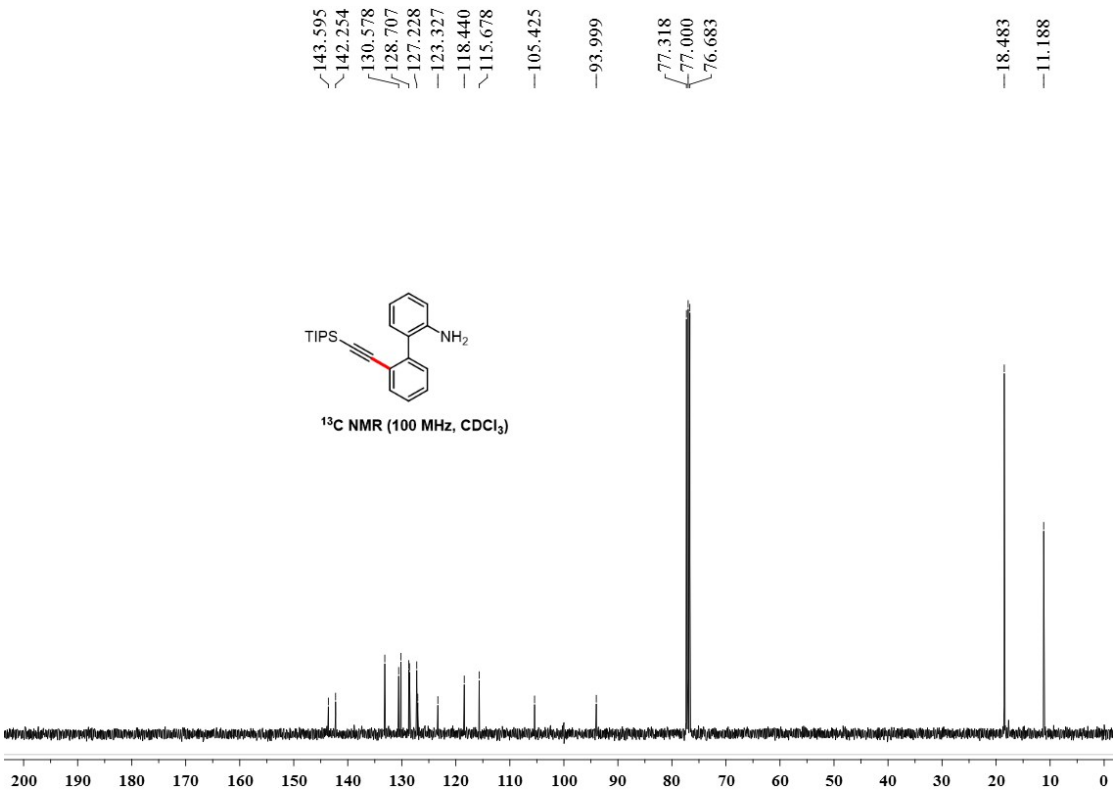
3a 7a

(e) 2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine **3a** (0.2 mmol) and KOH (3 equiv) were sealed in a Schlenk tube under N_2 atmosphere. After this, the mixture was stirred at 100 ^oC for 12 h. Aftre the reaction was completed (monitored by TLC), the resulting mixture were cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired products **9a** were obtained in the corresponding yields after purified by column chromatography on silica gel with mixture of petroleum ether and ethyl acetate.

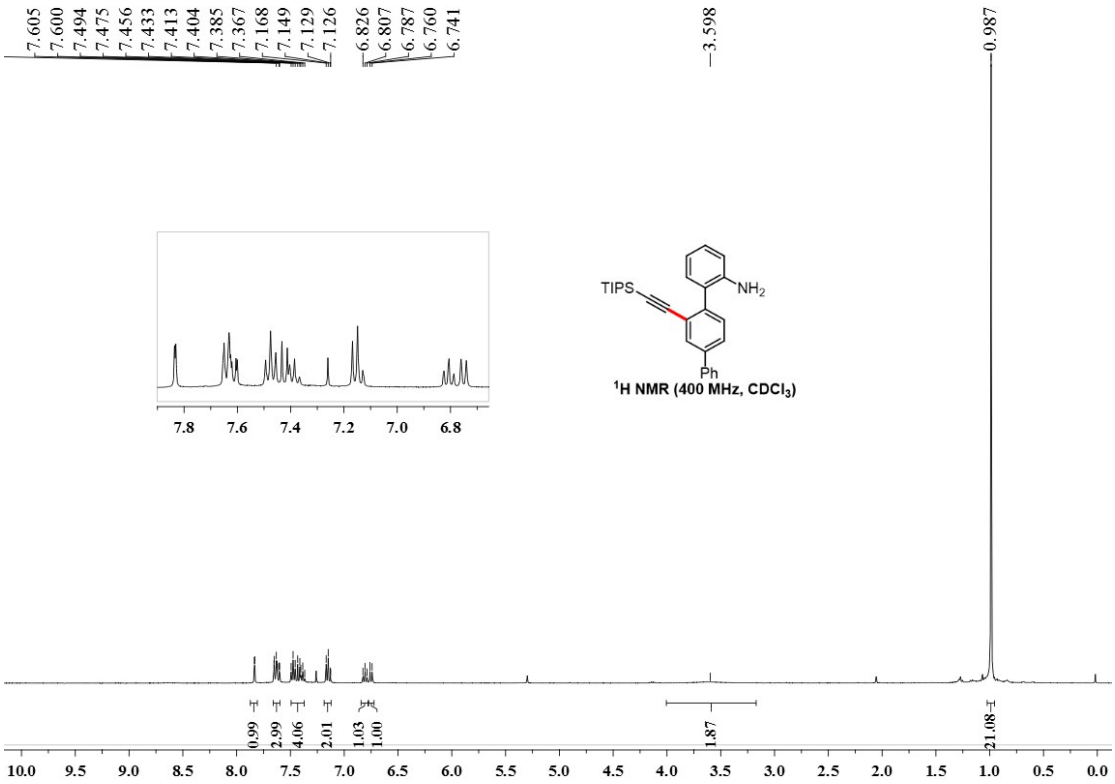
I. Copies of ^{1}H and ^{13}C NMR Spectra

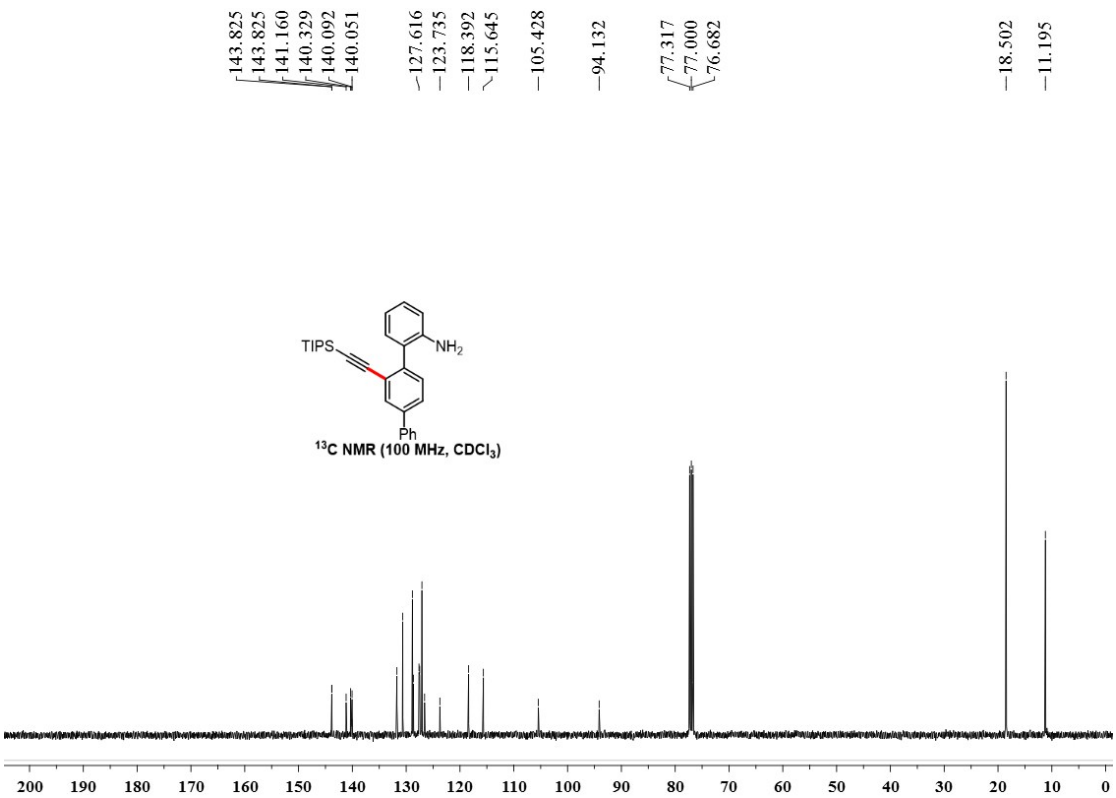
2′-((Triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3a)



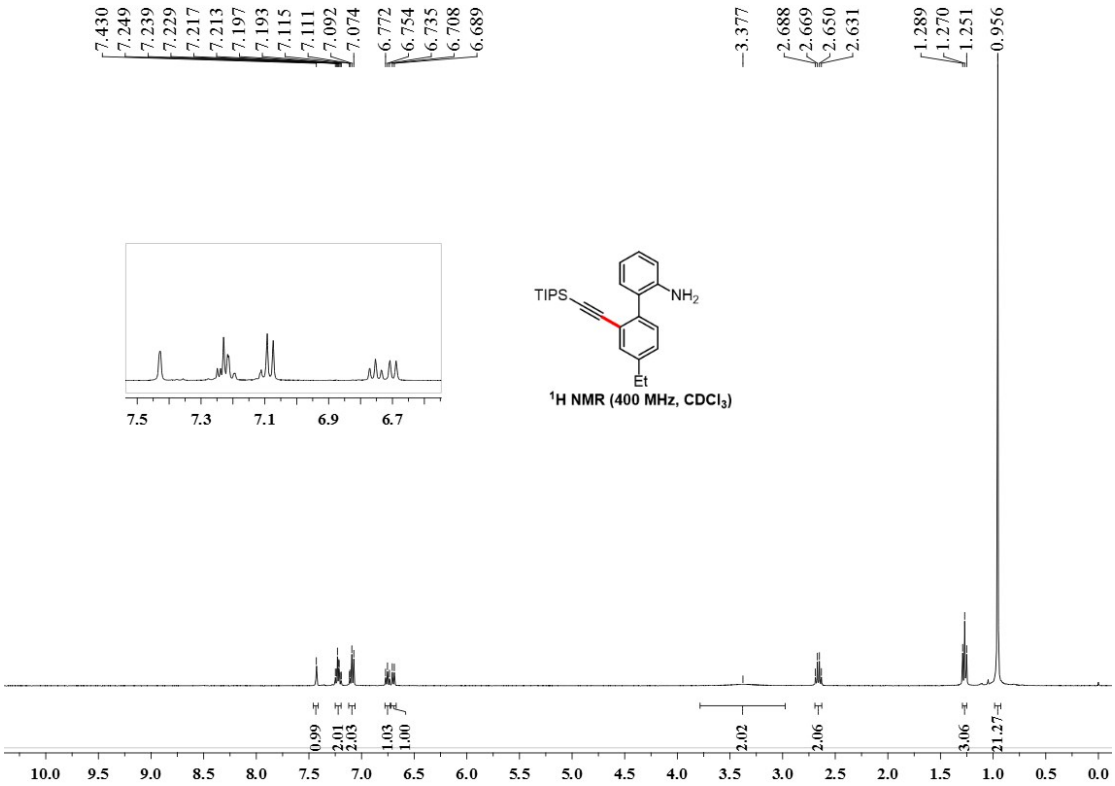


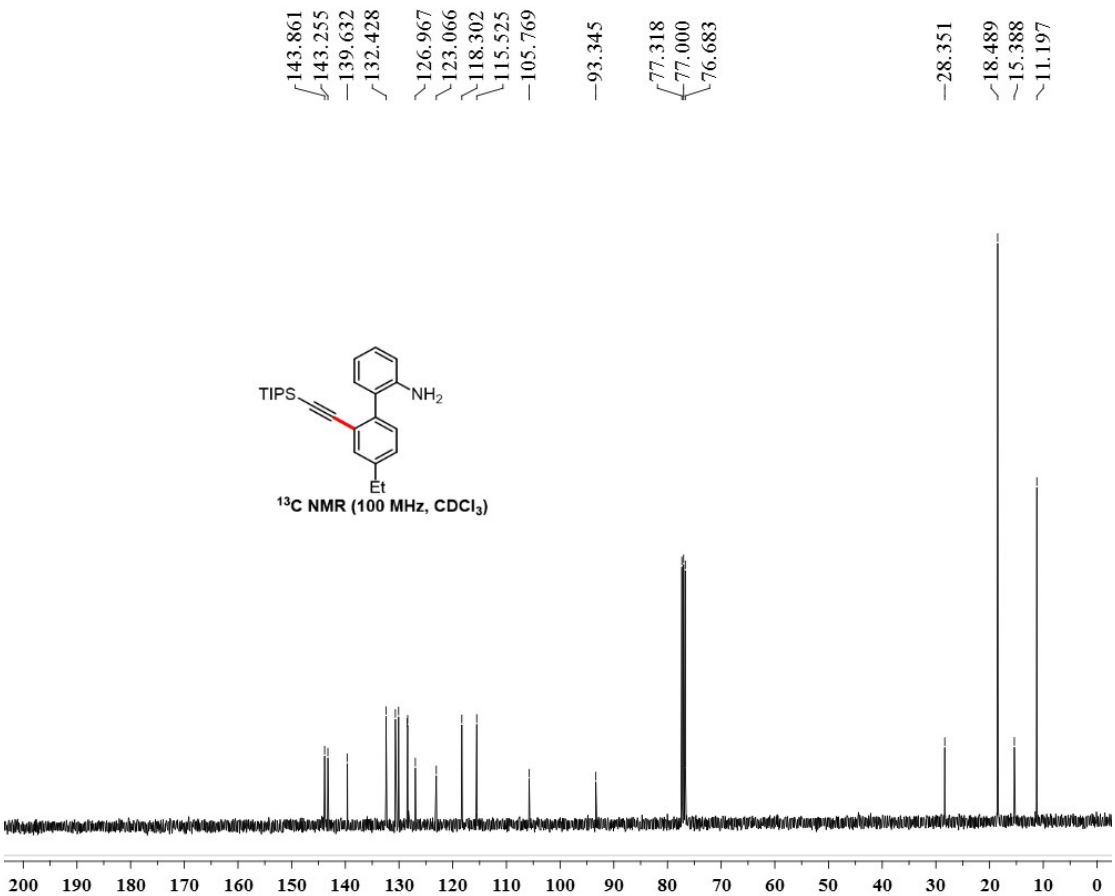
2′-((Triisopropylsilyl)ethynyl)-[1,1′:4′,1′′-terphenyl]-2-amine (3b)



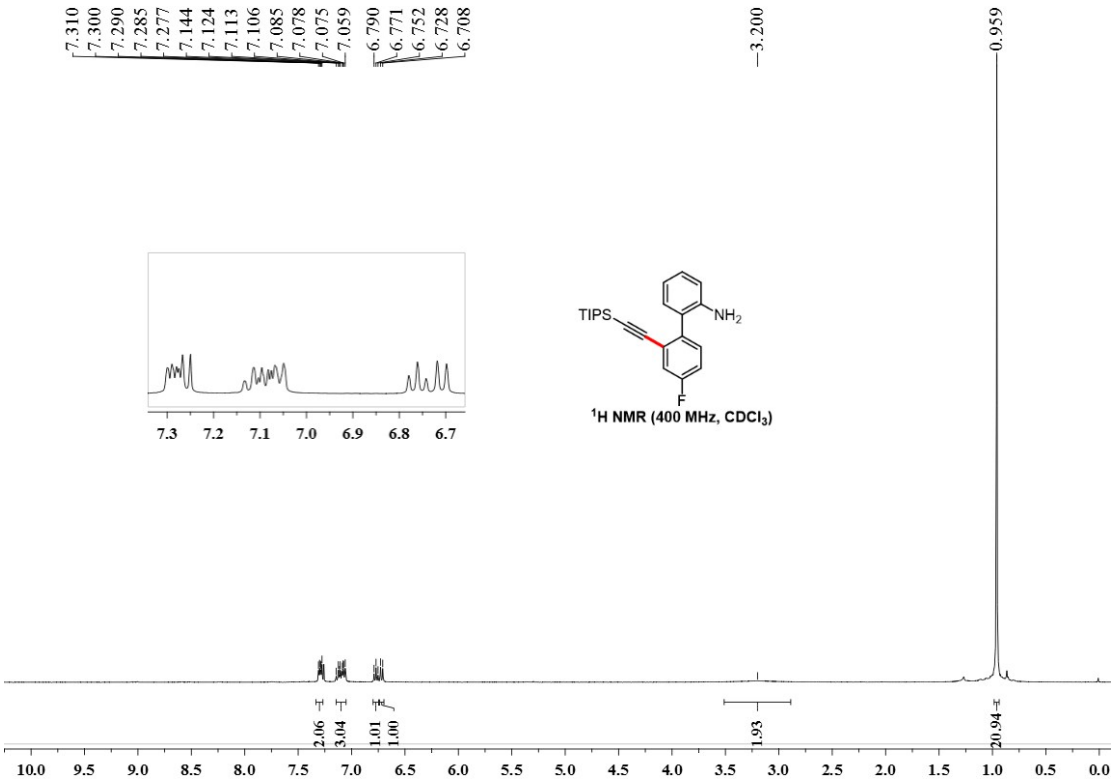


4′-Ethyl-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3c)

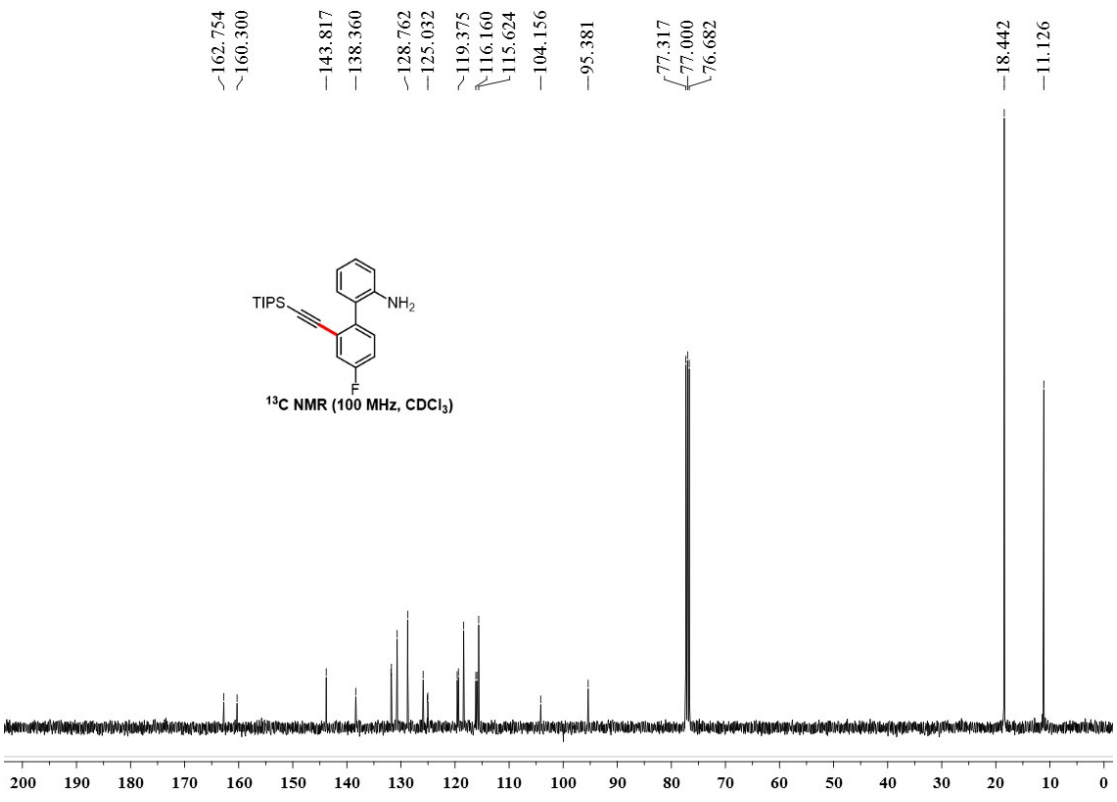




4′-Fluoro-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3d)

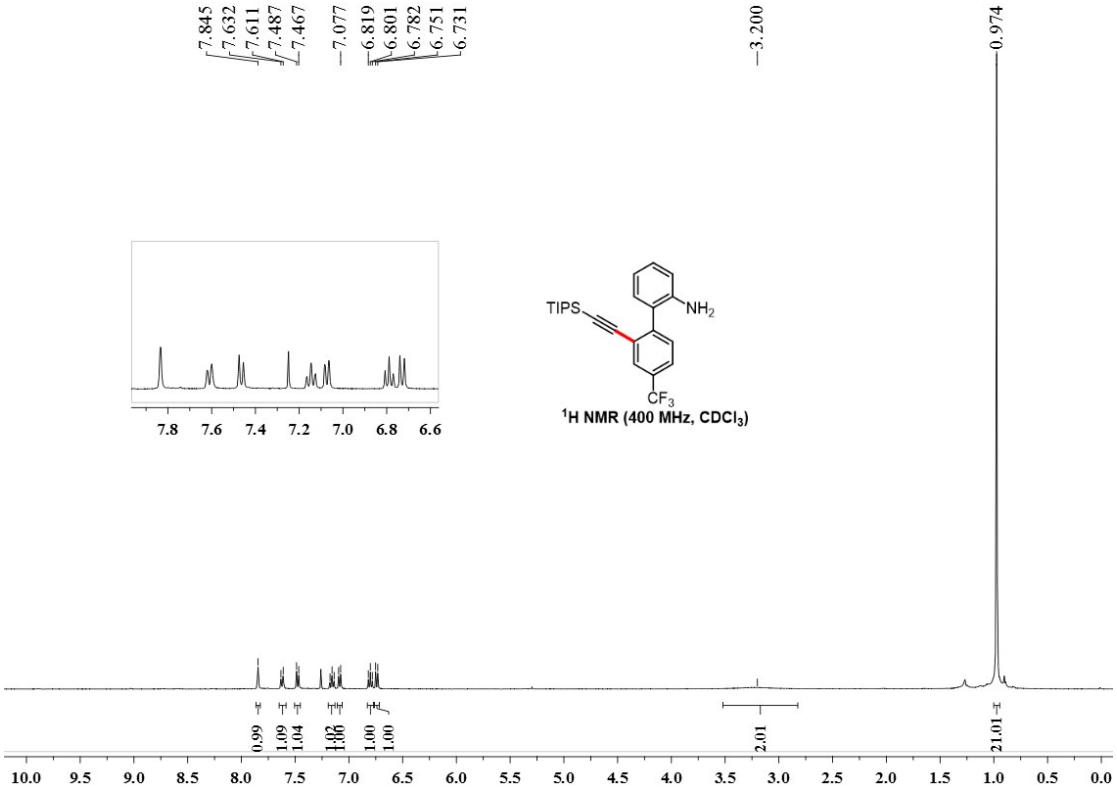


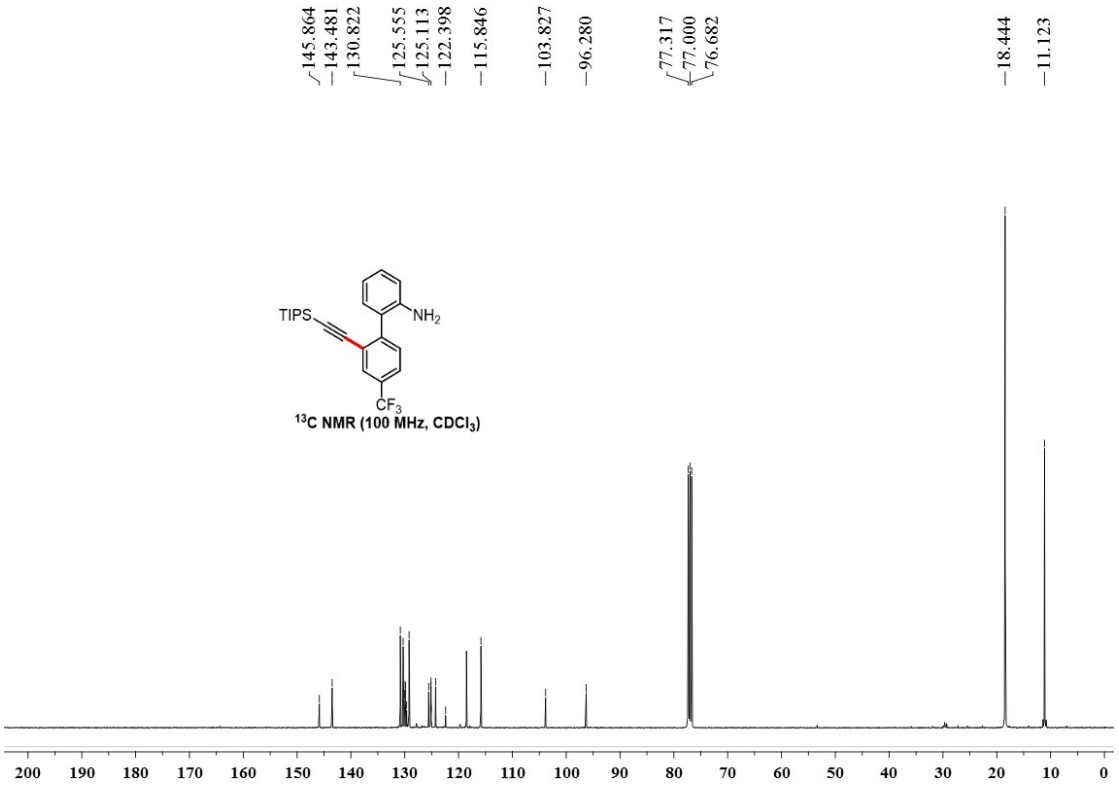
^{1}H NMR (400 MHz, $CDCl_3$)



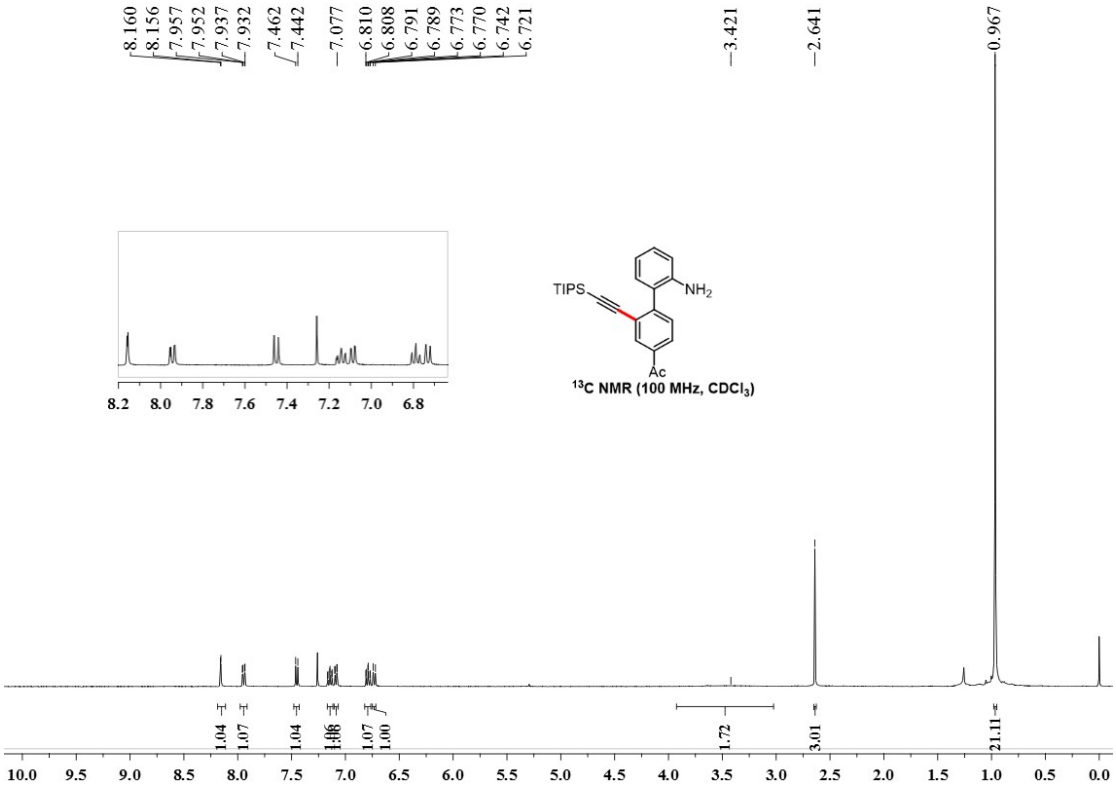
^{13}C NMR (100 MHz, $CDCl_3$)

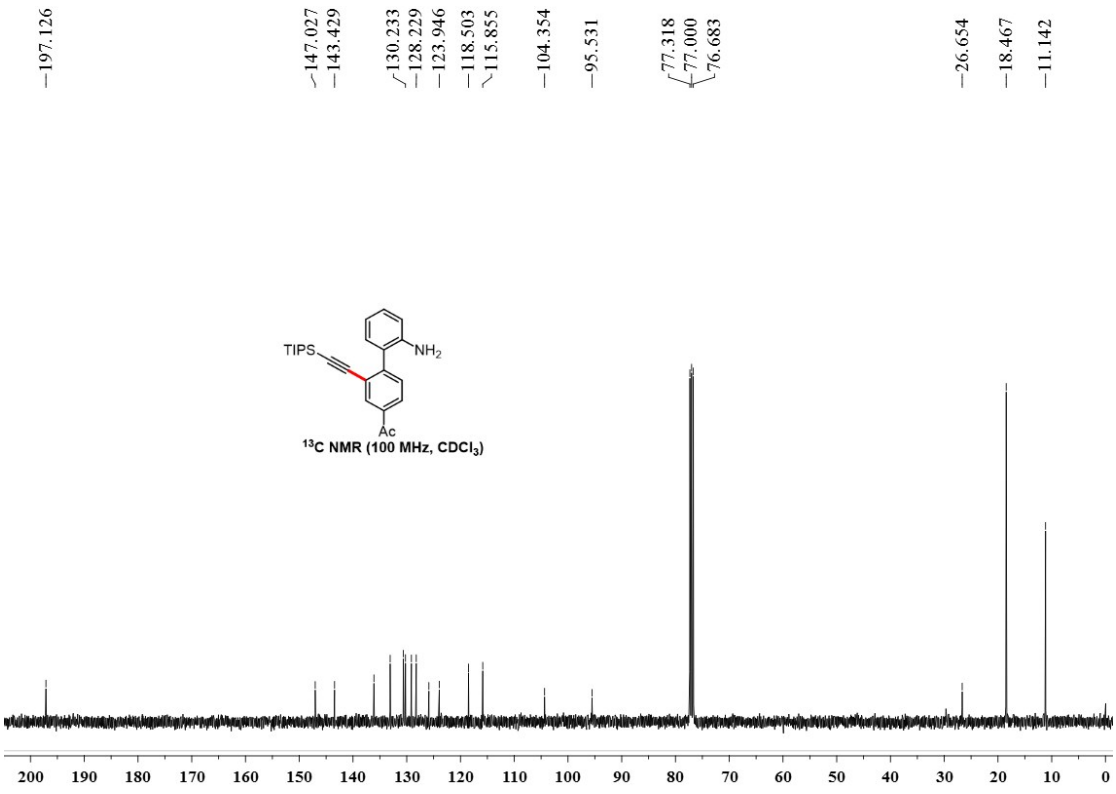
4′-(Trifluoromethyl)-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3e)



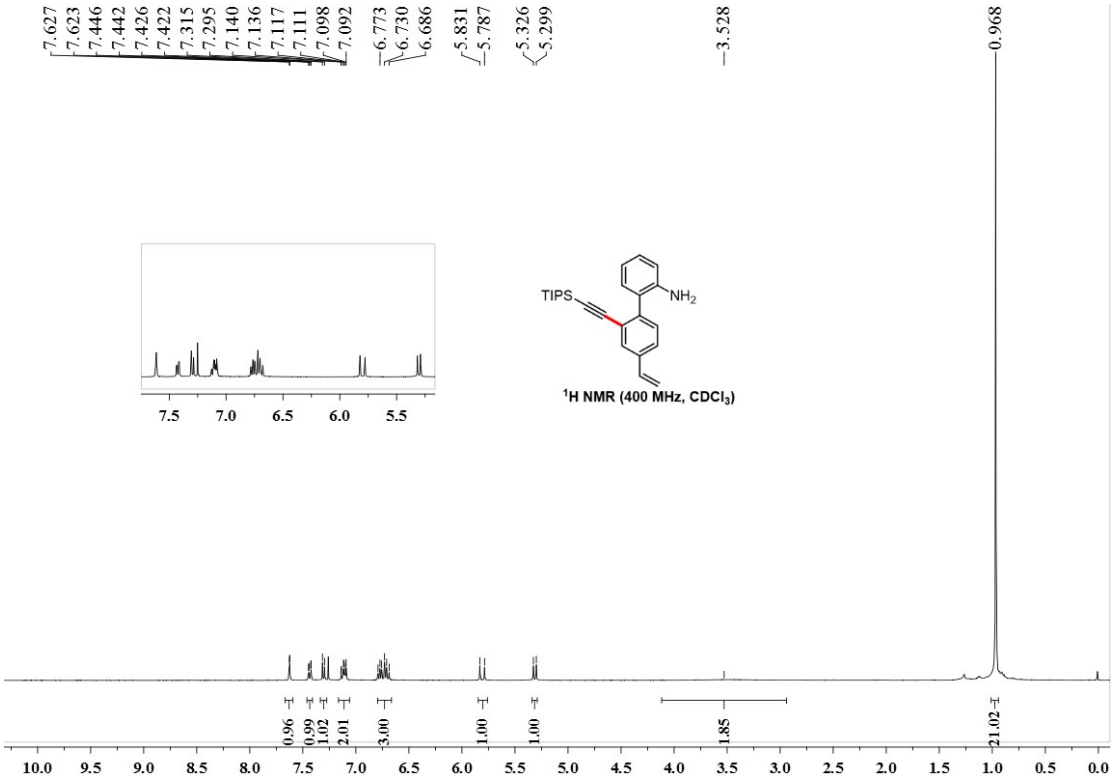


1-(2′-Amino-2-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-4-yl)ethan-1-one (3f)

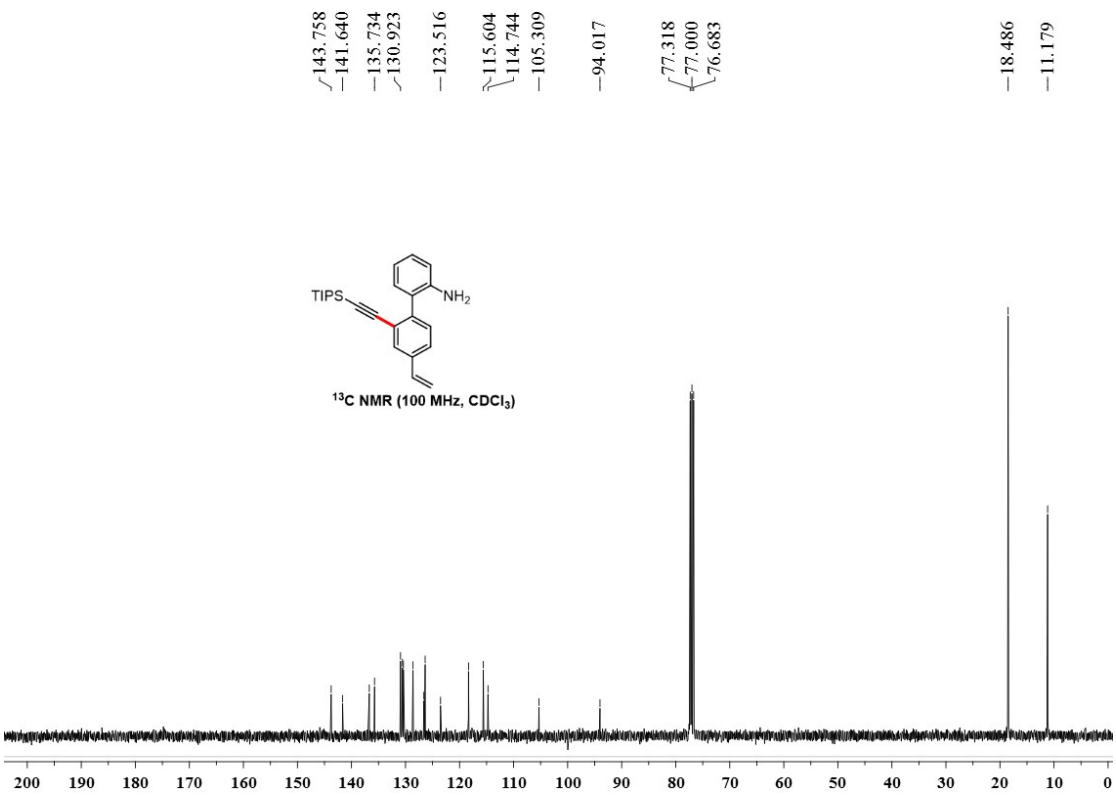




2′-((Triisopropylsilyl)ethynyl)-4′-vinyl-[1,1′-biphenyl]-2-amine (3g)

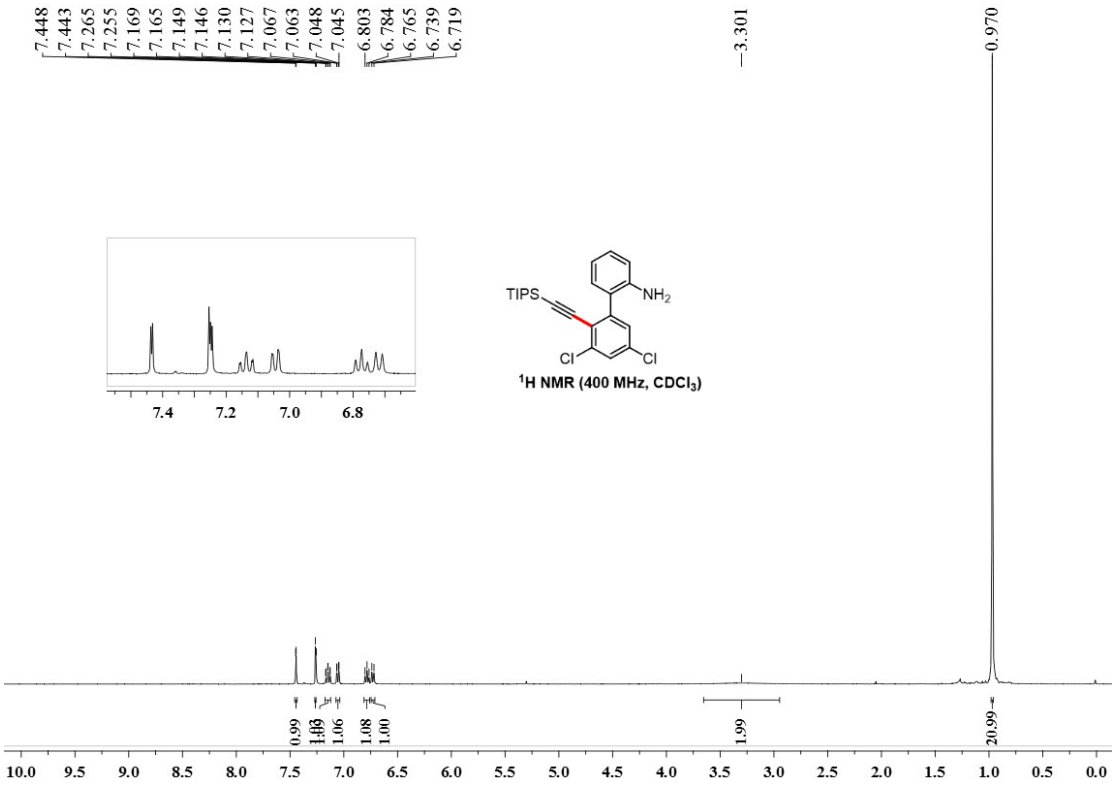


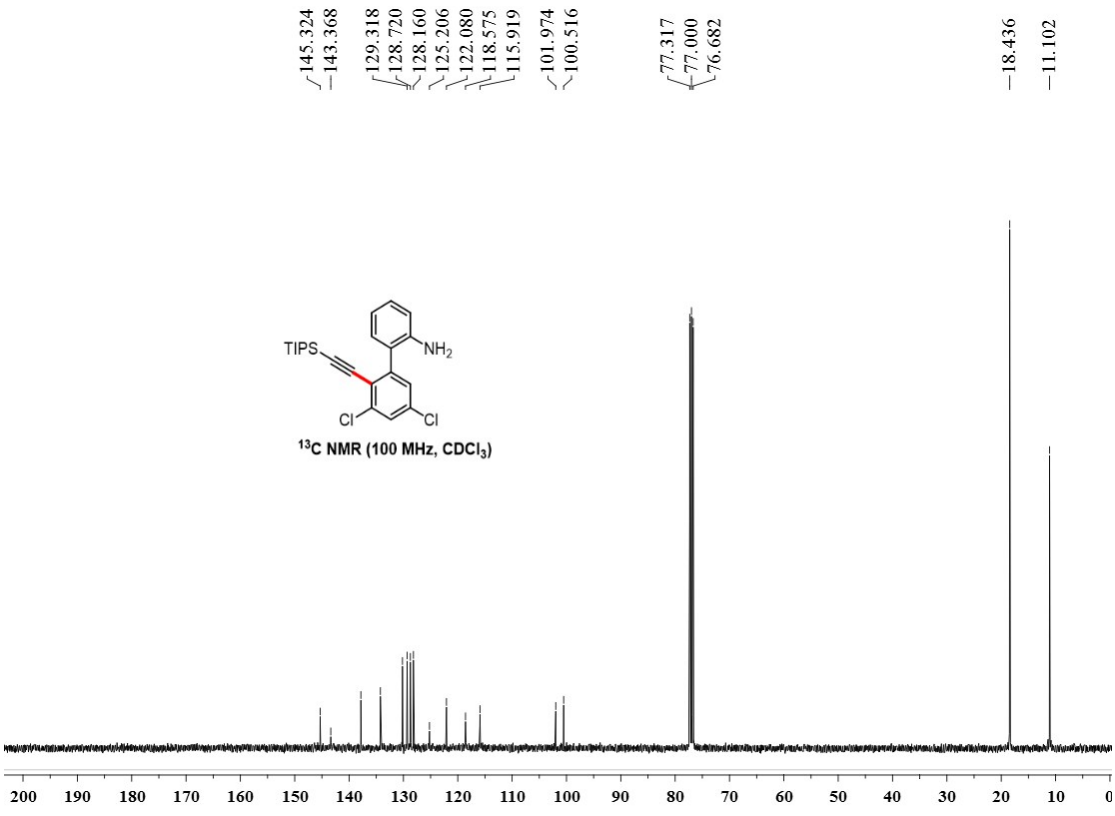
^{1}H NMR (400 MHz, $CDCl_3$)



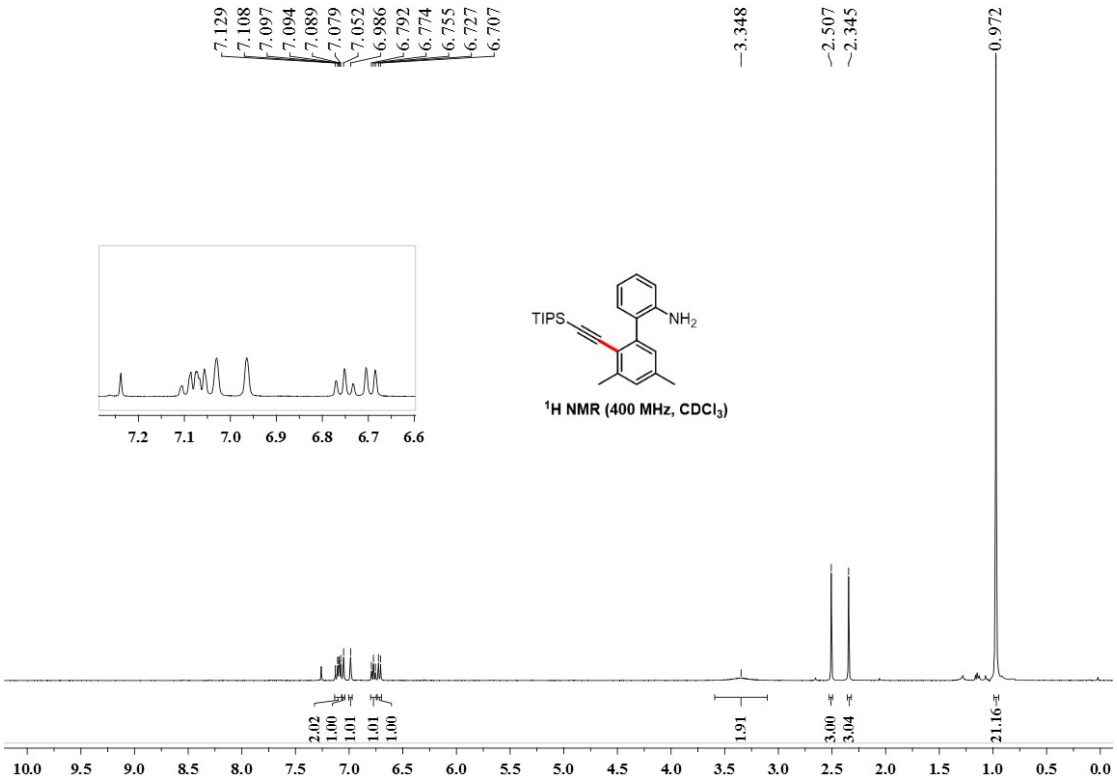
^{13}C NMR (100 MHz, $CDCl_3$)

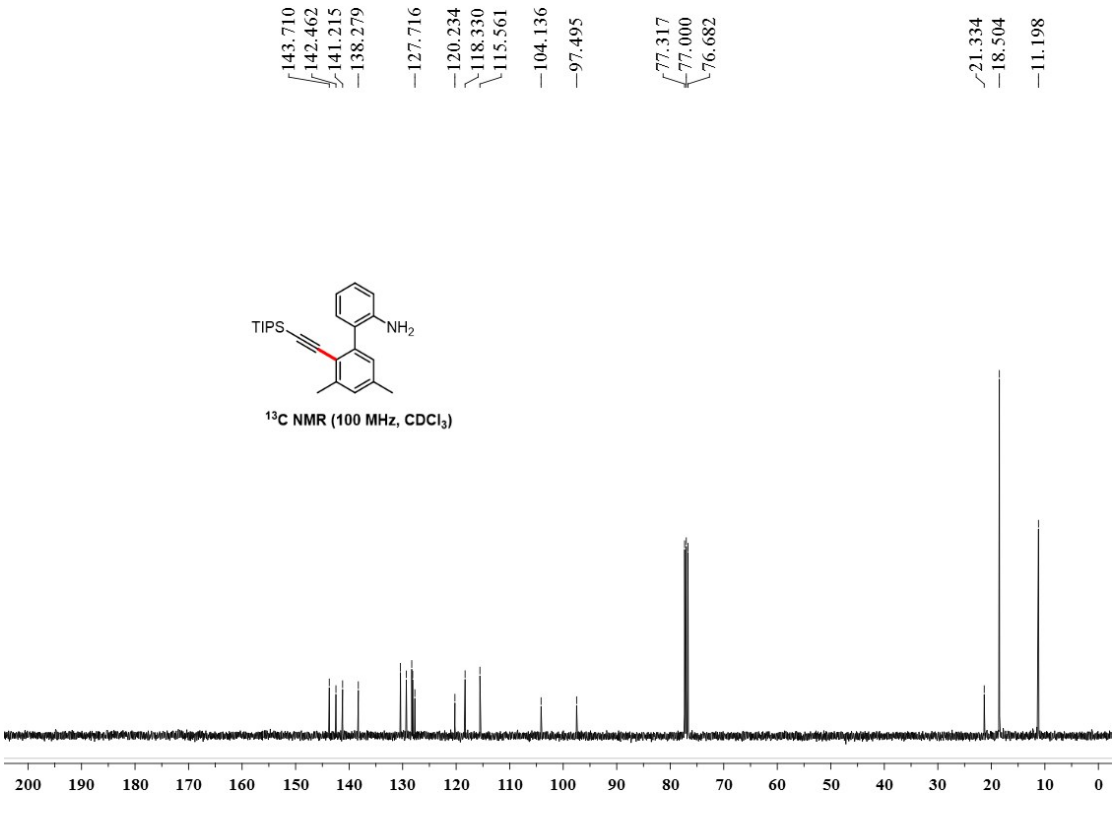
3′,5′-Dichloro-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3h)



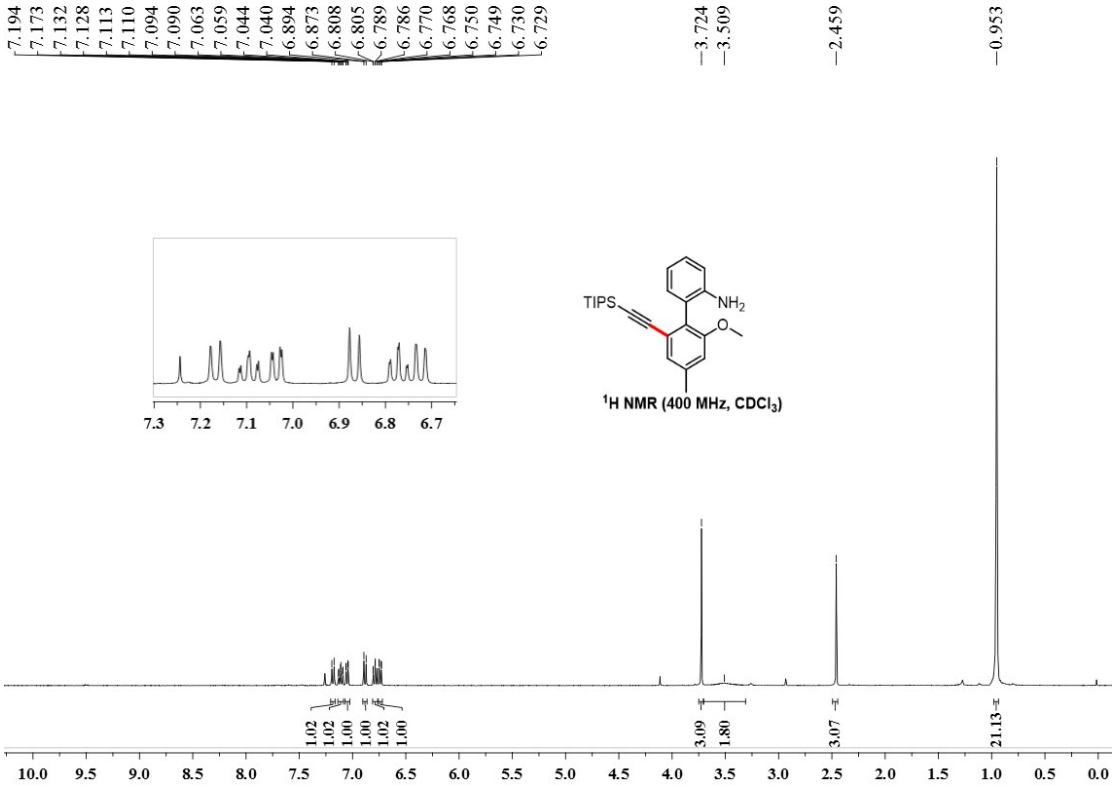


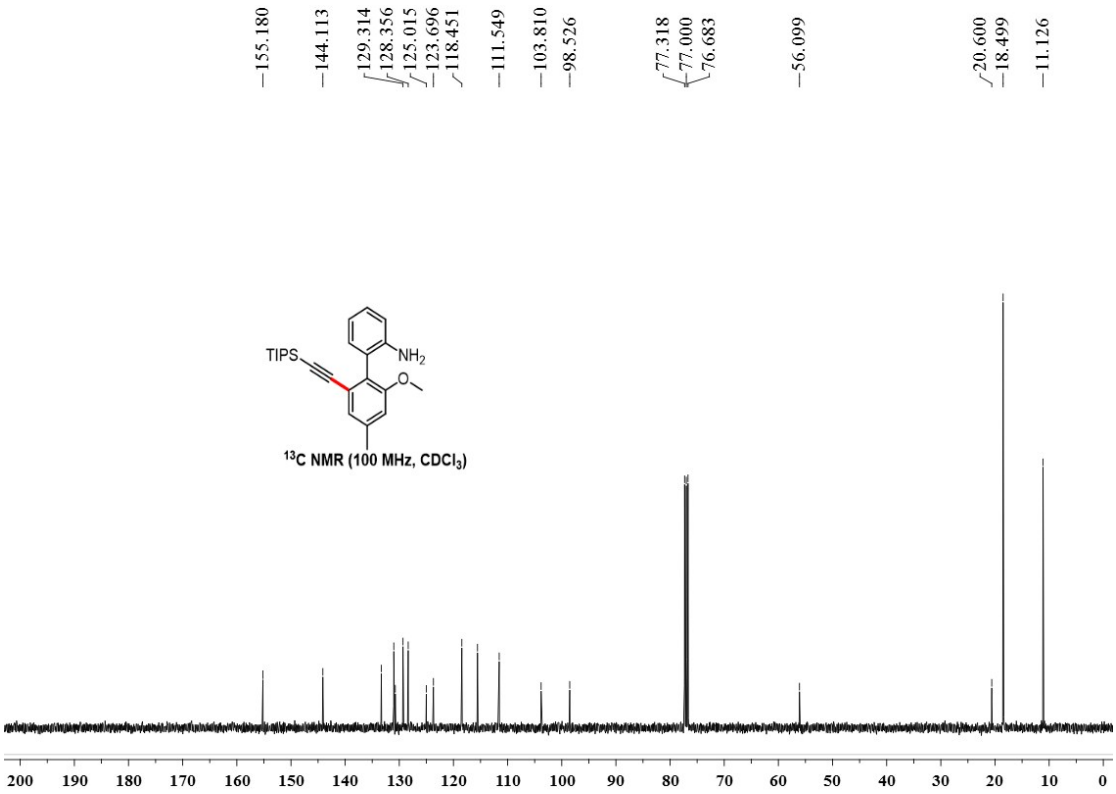
3′,5′-Dimethyl-2'-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3i)



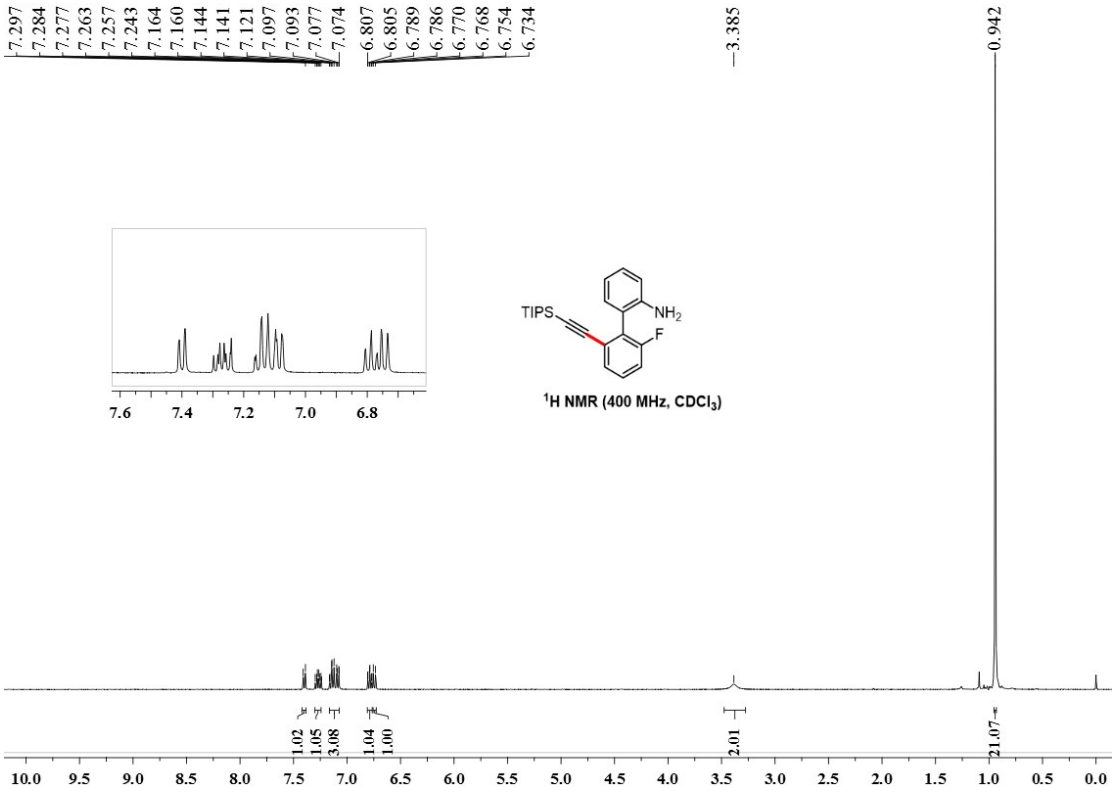


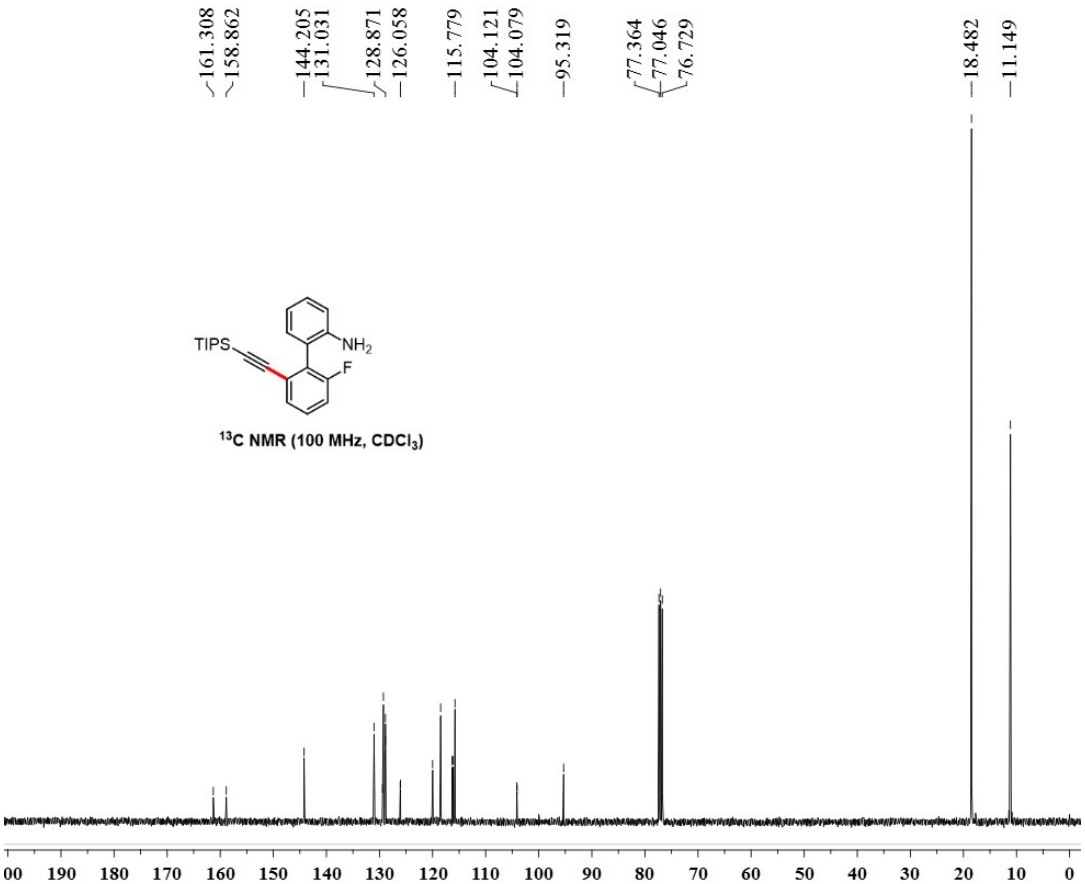
2′-Methoxy-4′-methyl-6′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3j)



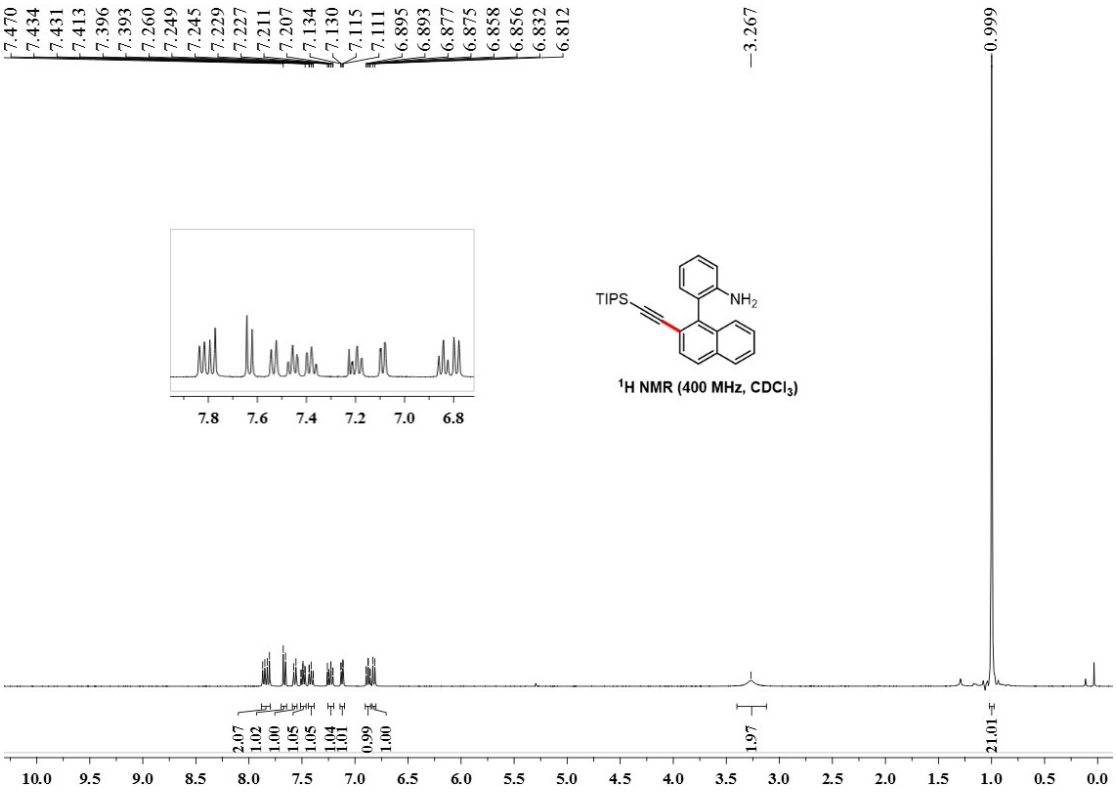


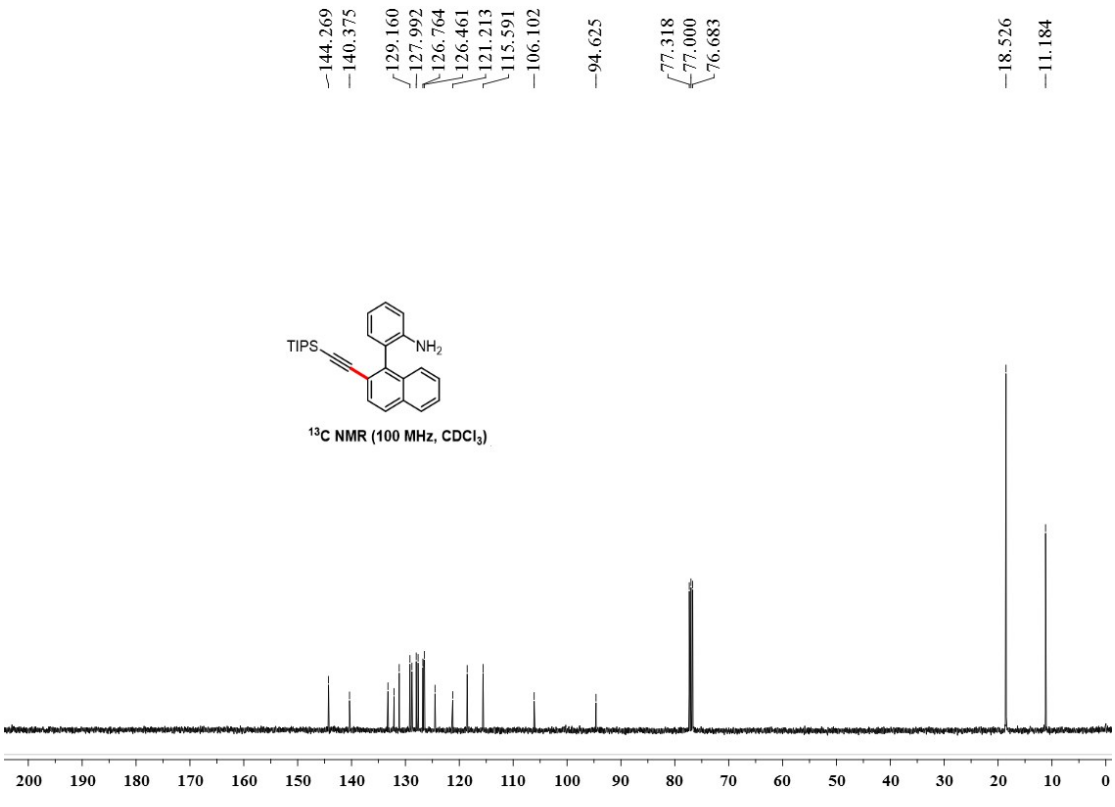
2′-Fluoro-6′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3k)



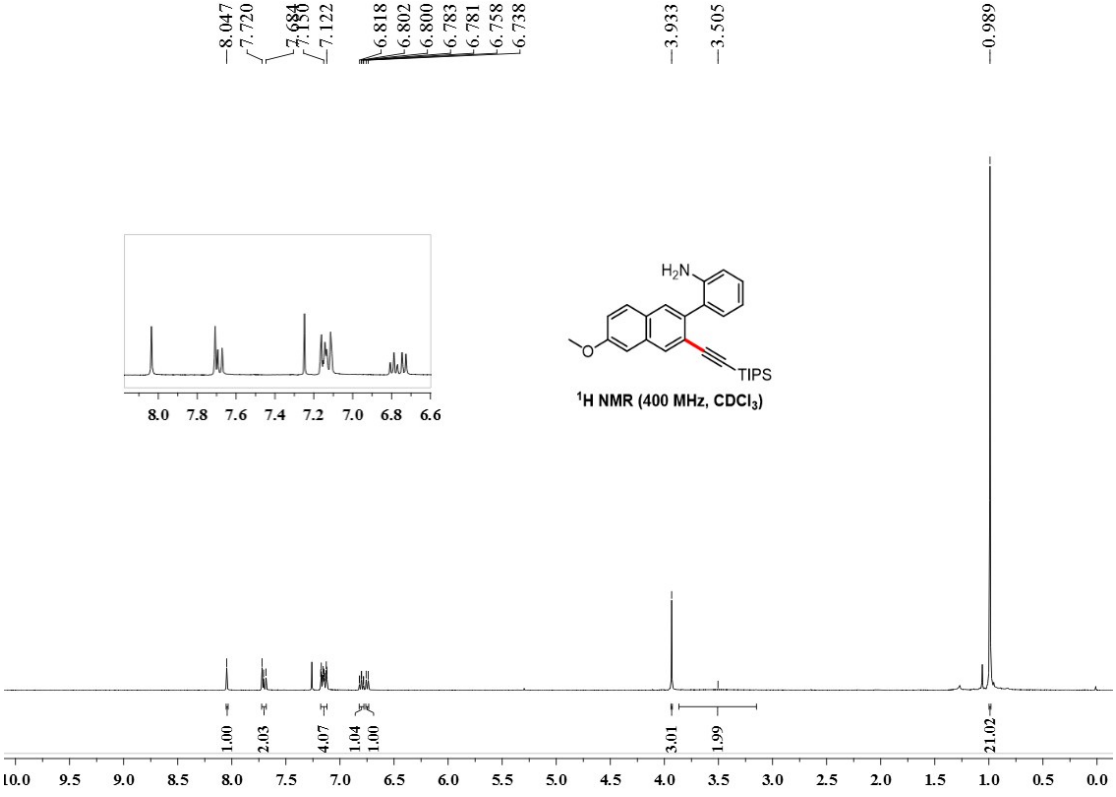


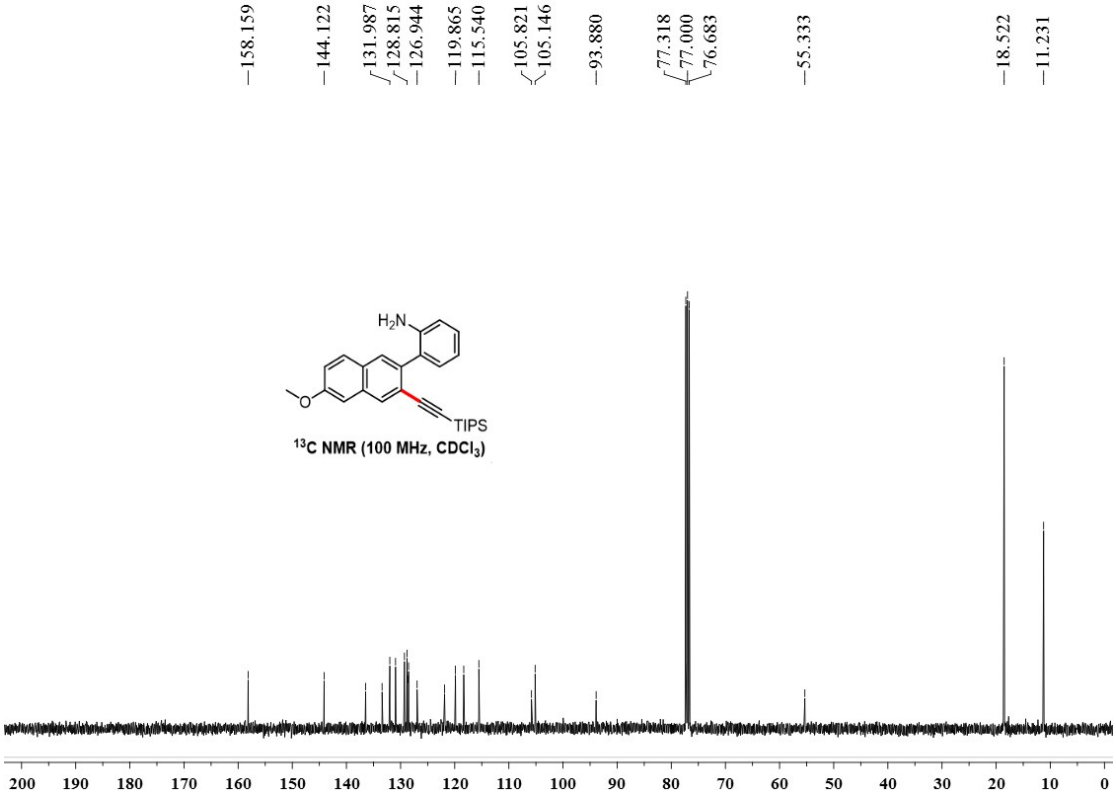
2-(2-((Triisopropylsilyl)ethynyl)naphthalen-1-yl)aniline (3l)



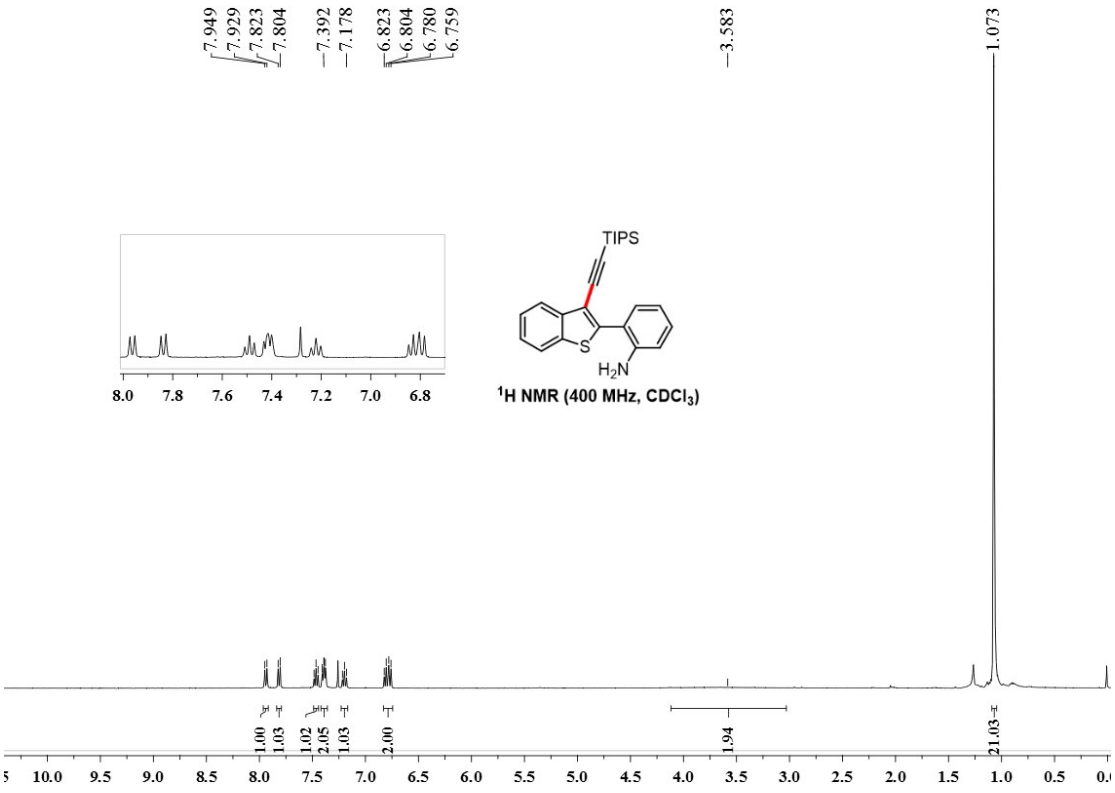


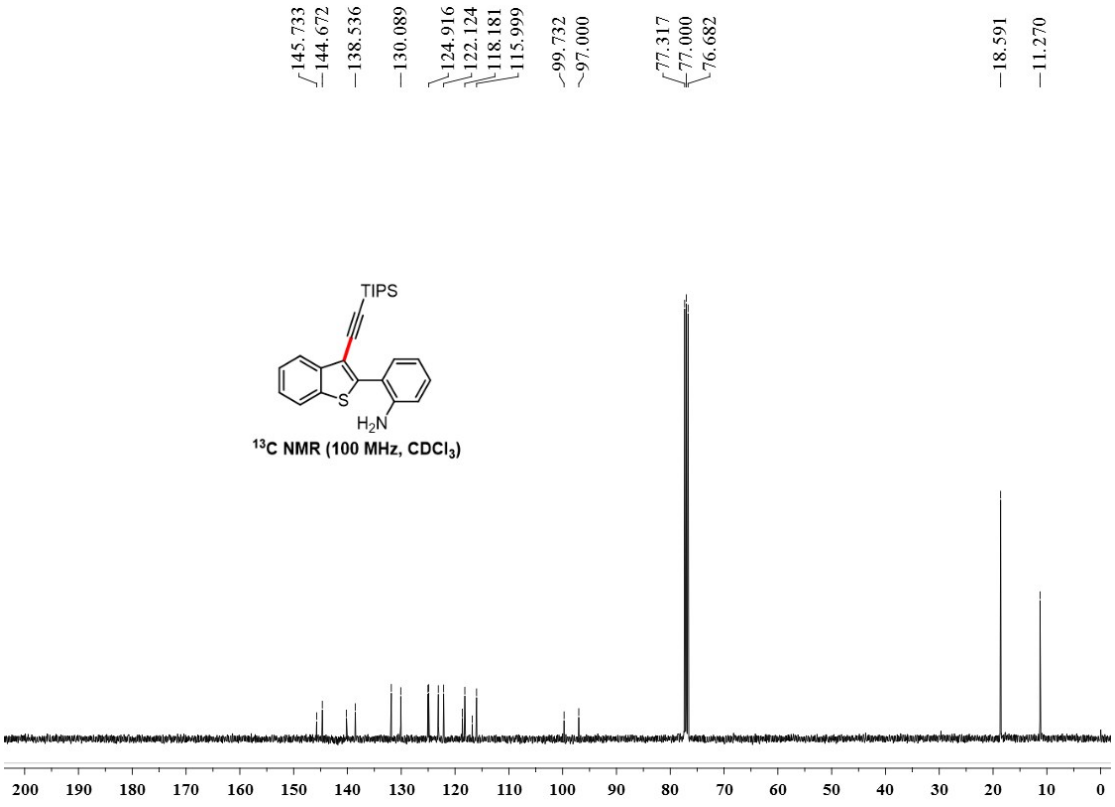
2-(Methoxy-2-((triisopropylsilyl)ethynyl)naphthalen-1-yl)aniline (3m)



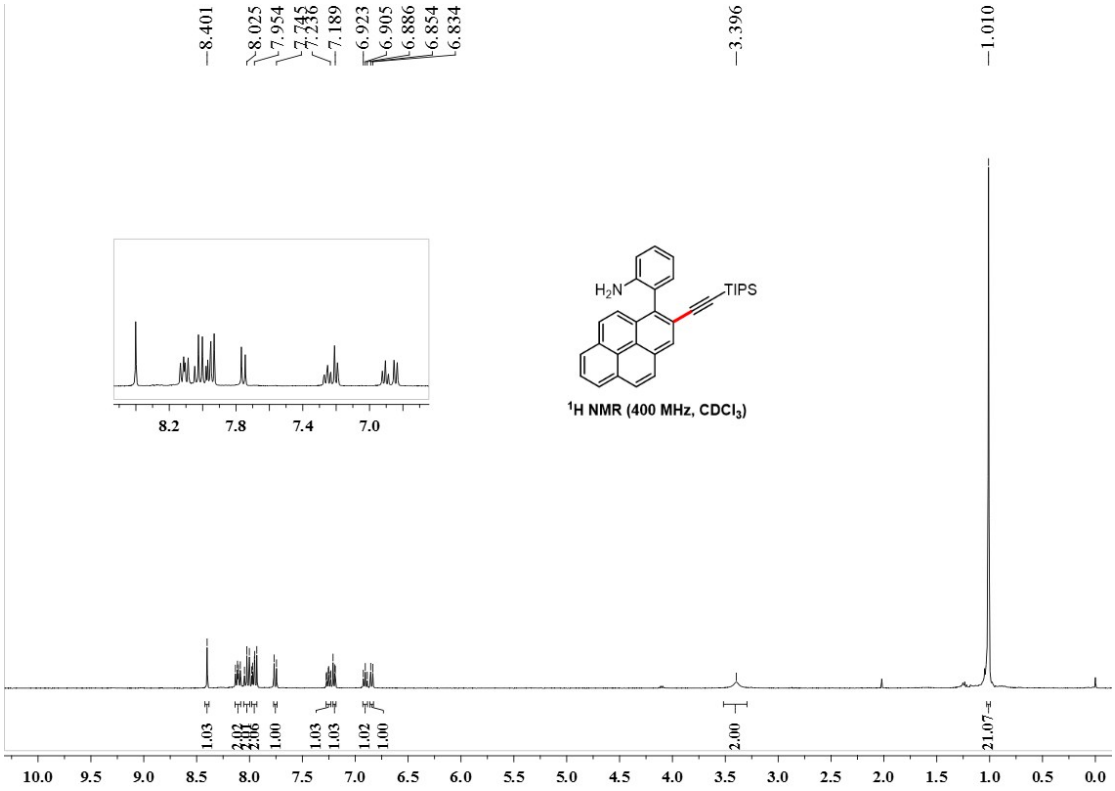


2-(3-((triisopropylsilyl)ethynyl)benzo[b]thiophen-2-yl)aniline (3n)

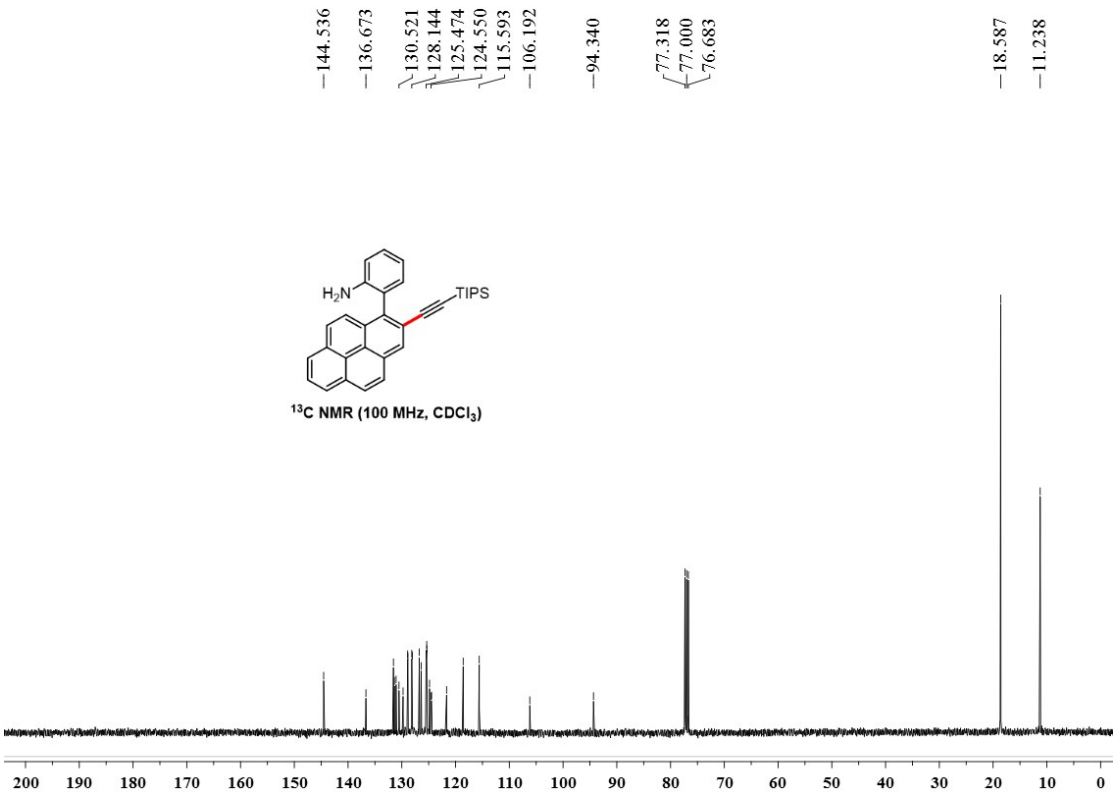




2-(2-((Triisopropylsilyl)ethynyl)pyren-1-yl)aniline (3o)

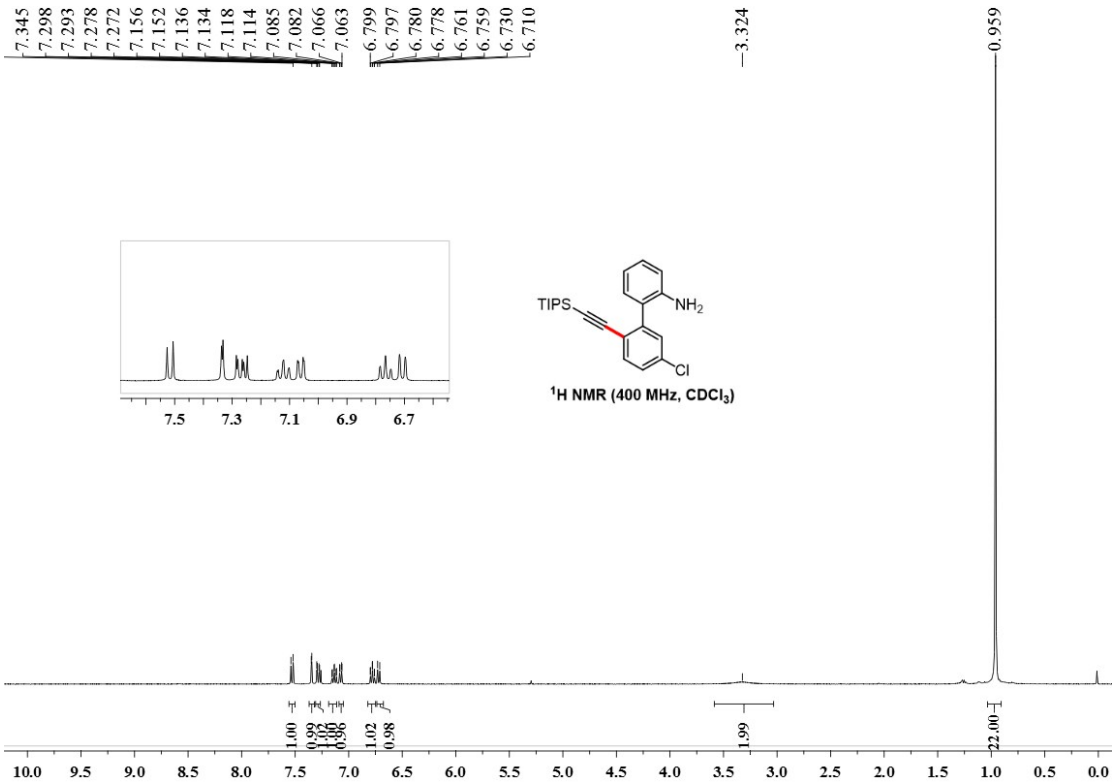


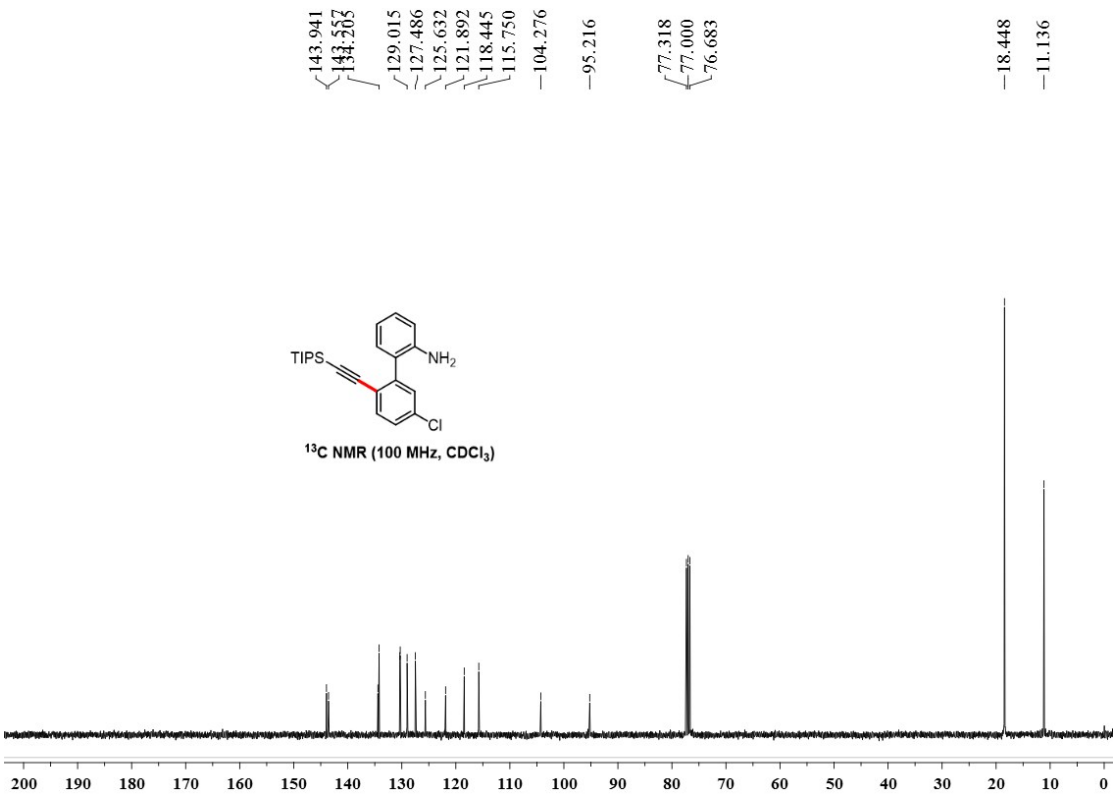
^{1}H NMR (400 MHz, $CDCl_3$)



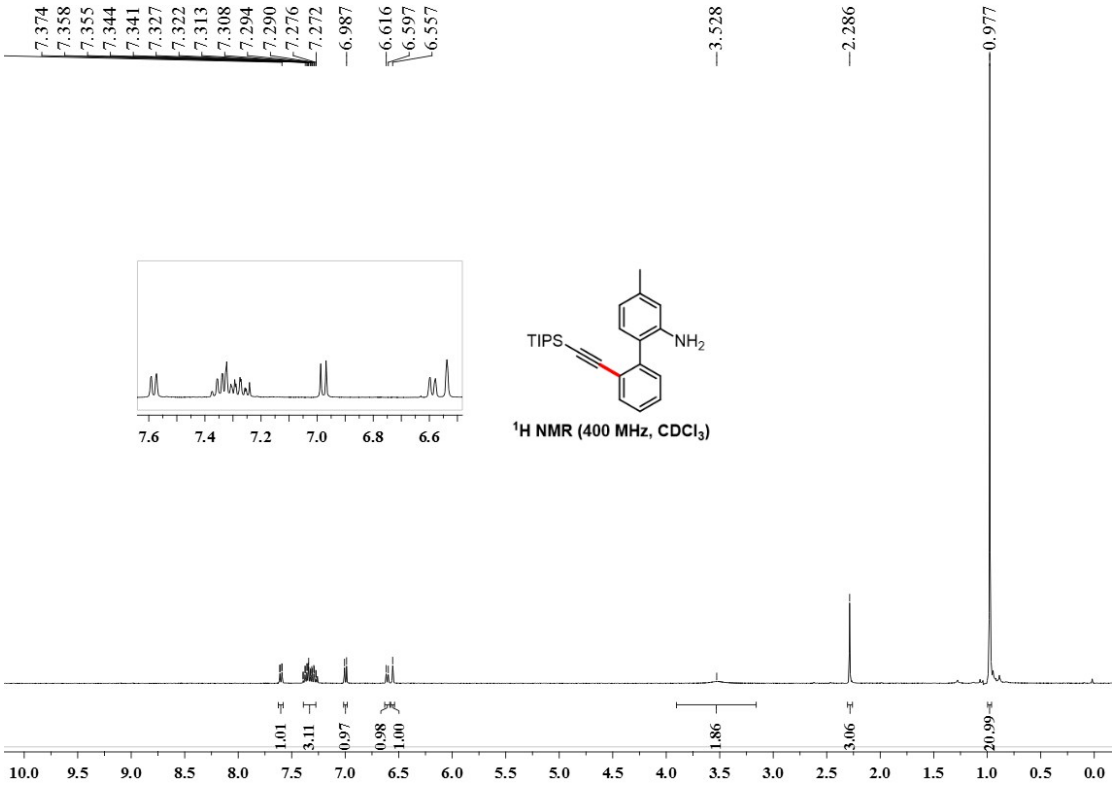
^{13}C NMR (100 MHz, $CDCl_3$)

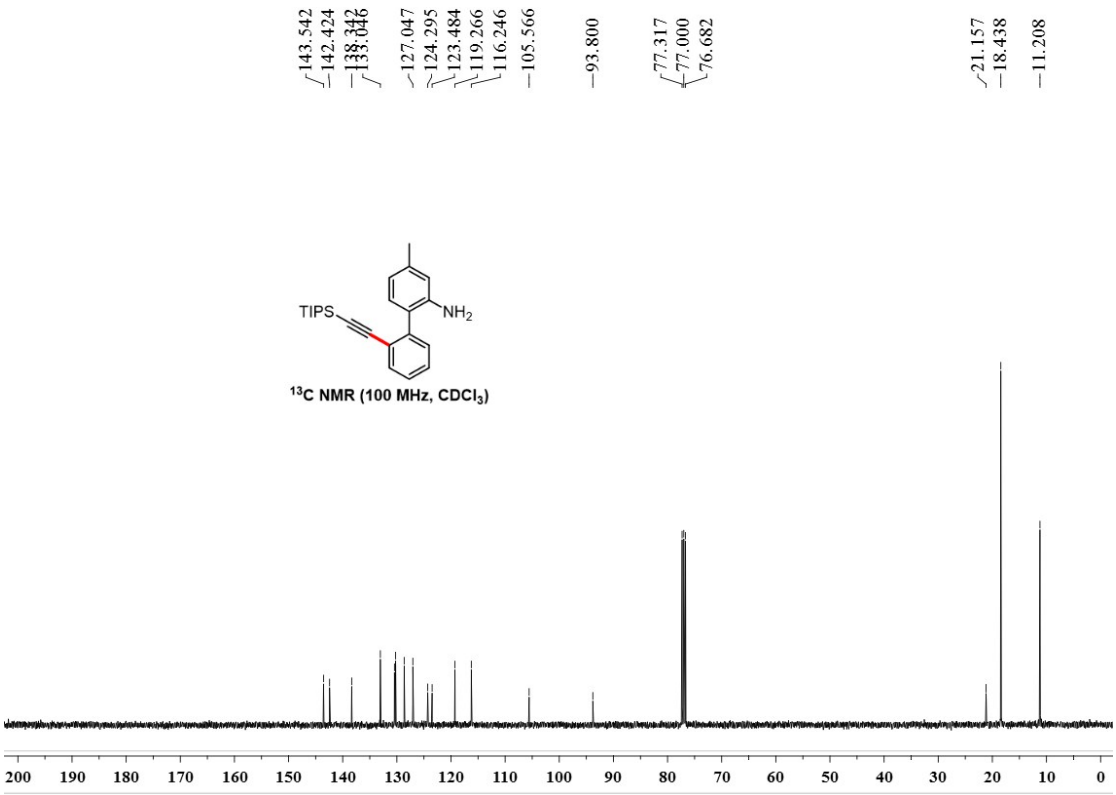
5′-Chloro-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3p)



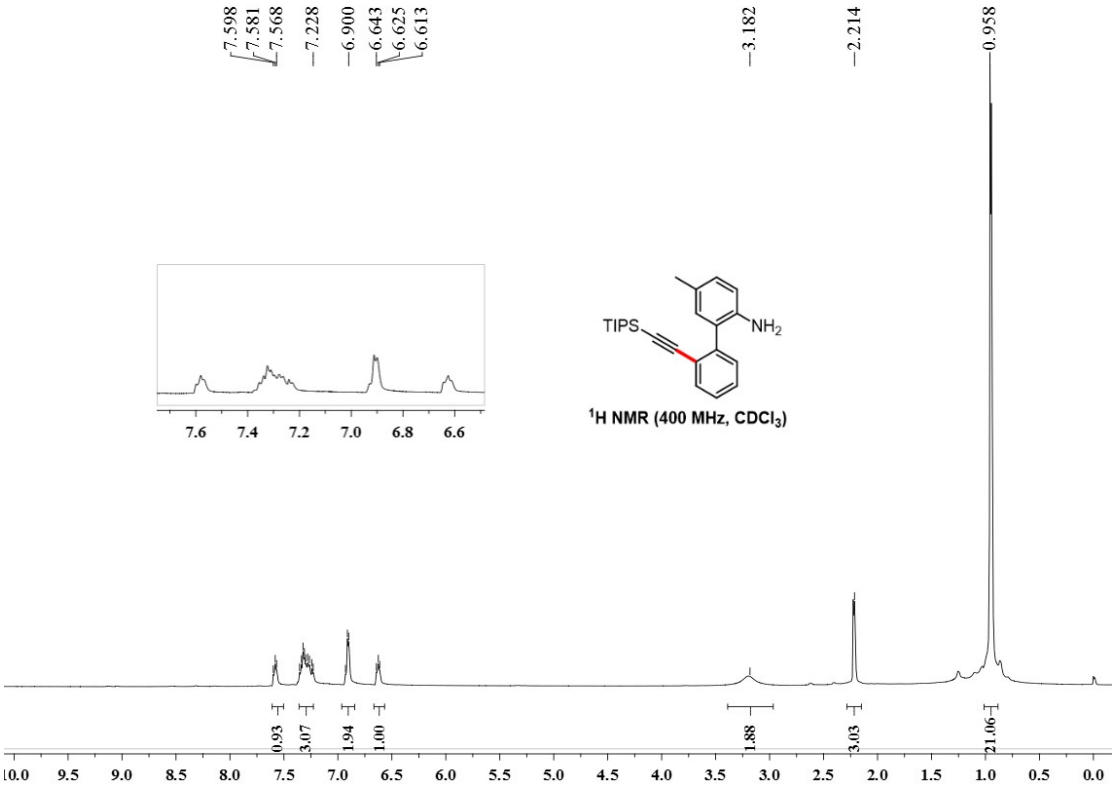


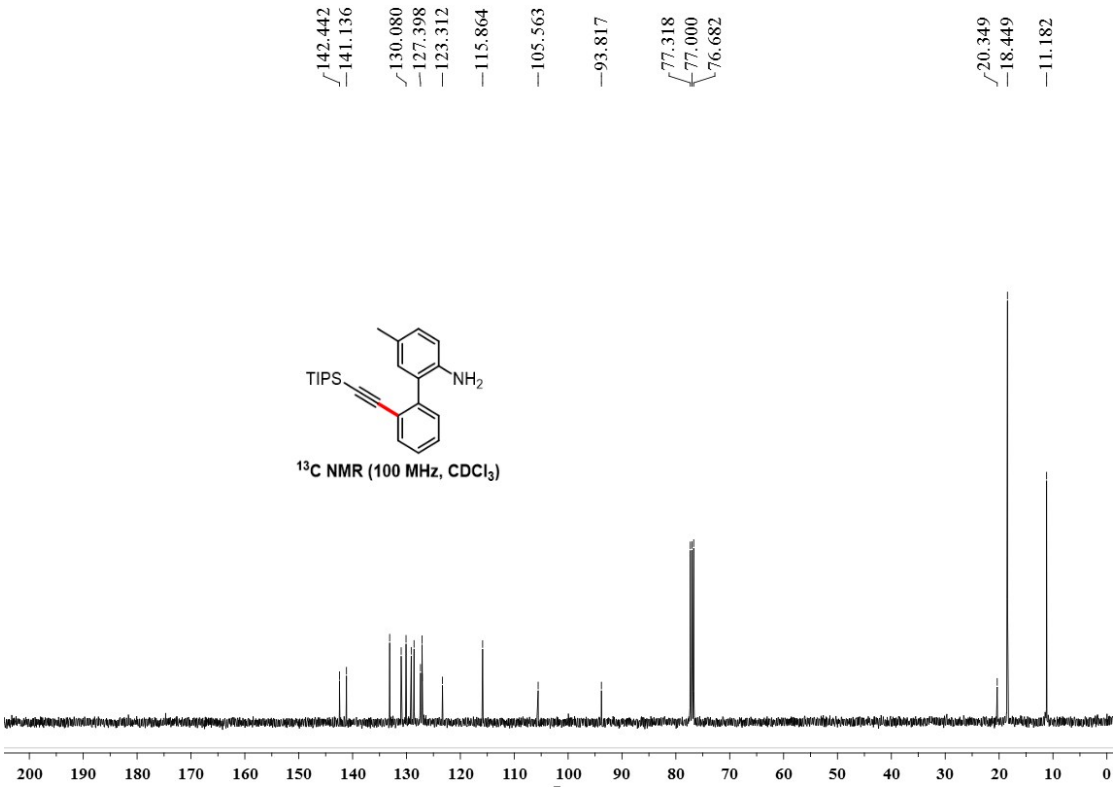
4-Methyl-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3q)



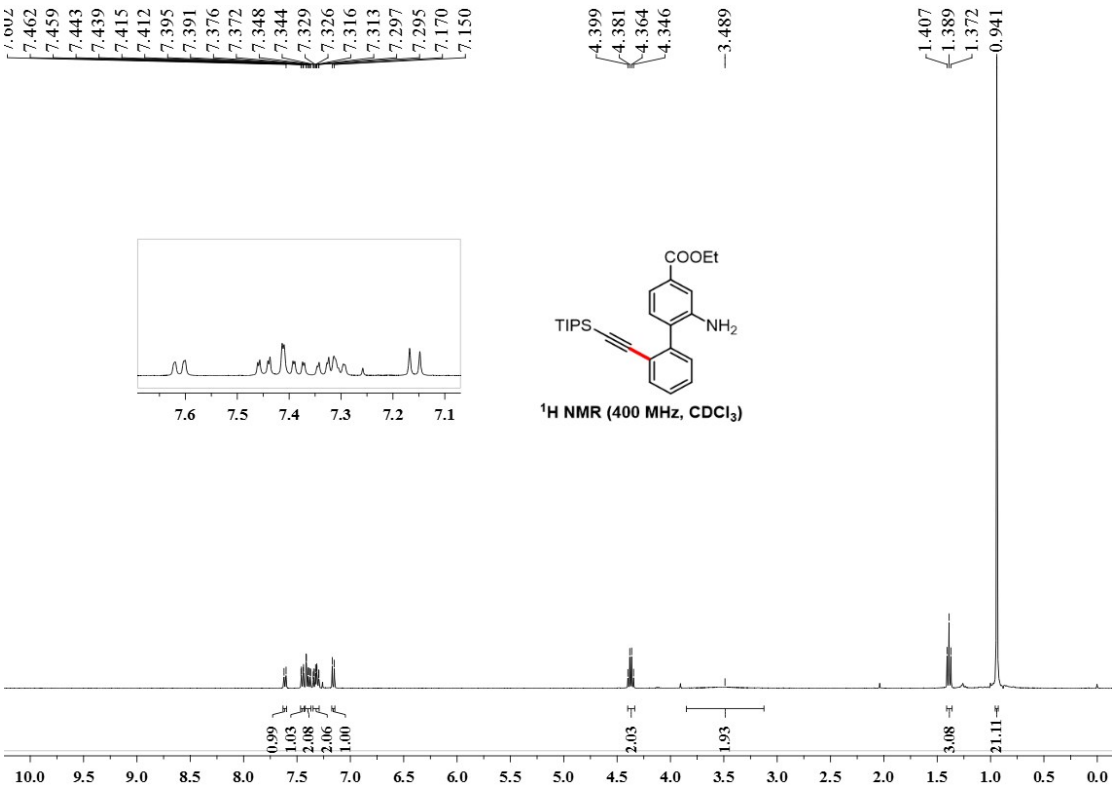


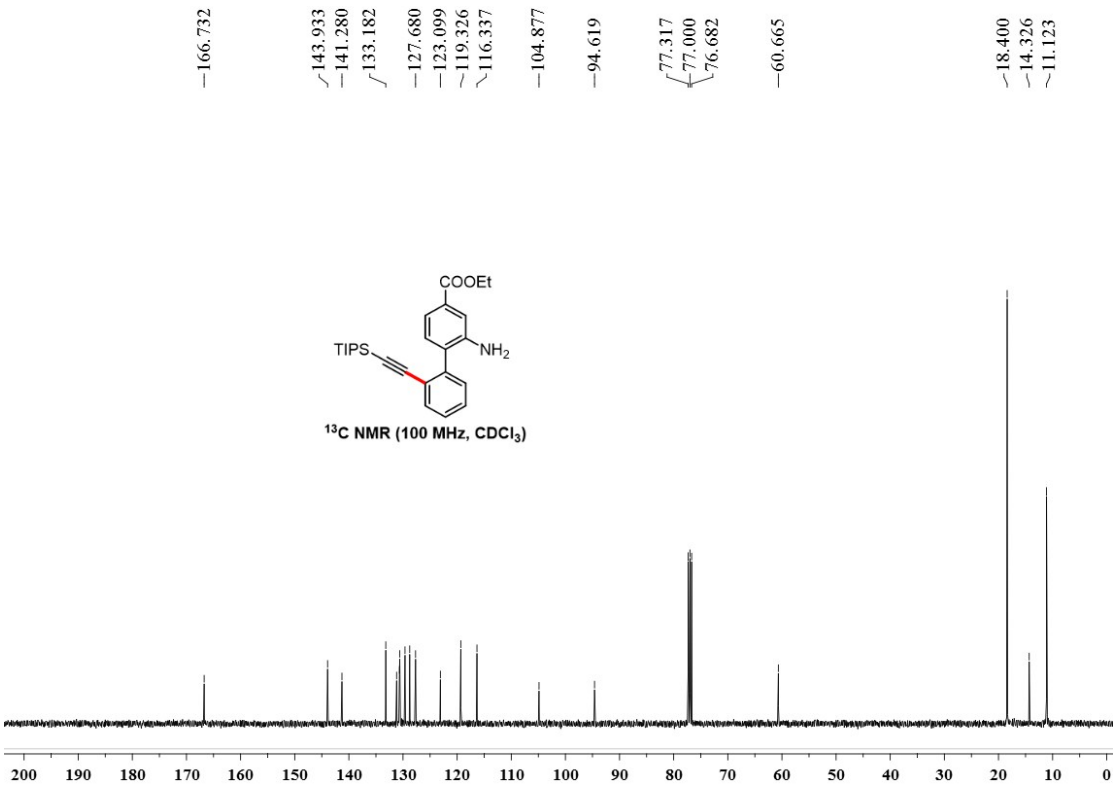
5-Methyl-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3r)



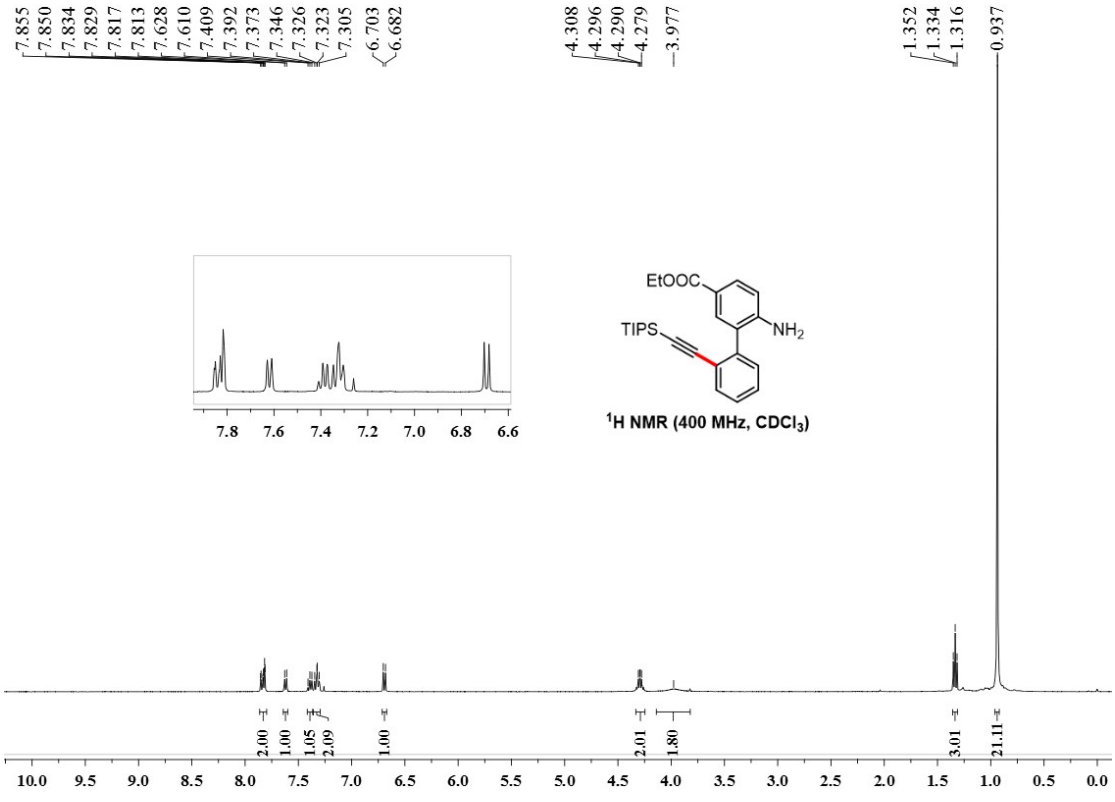


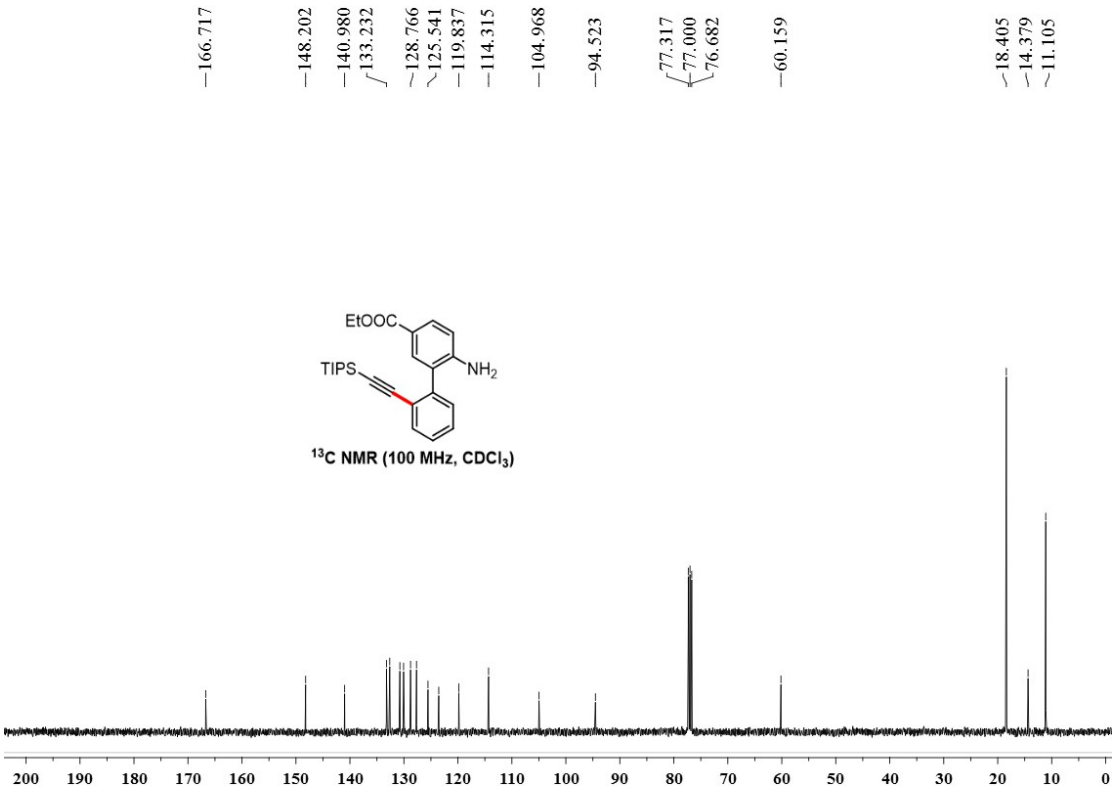
Ethyl 2-amino-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-4-carboxylate (3s)



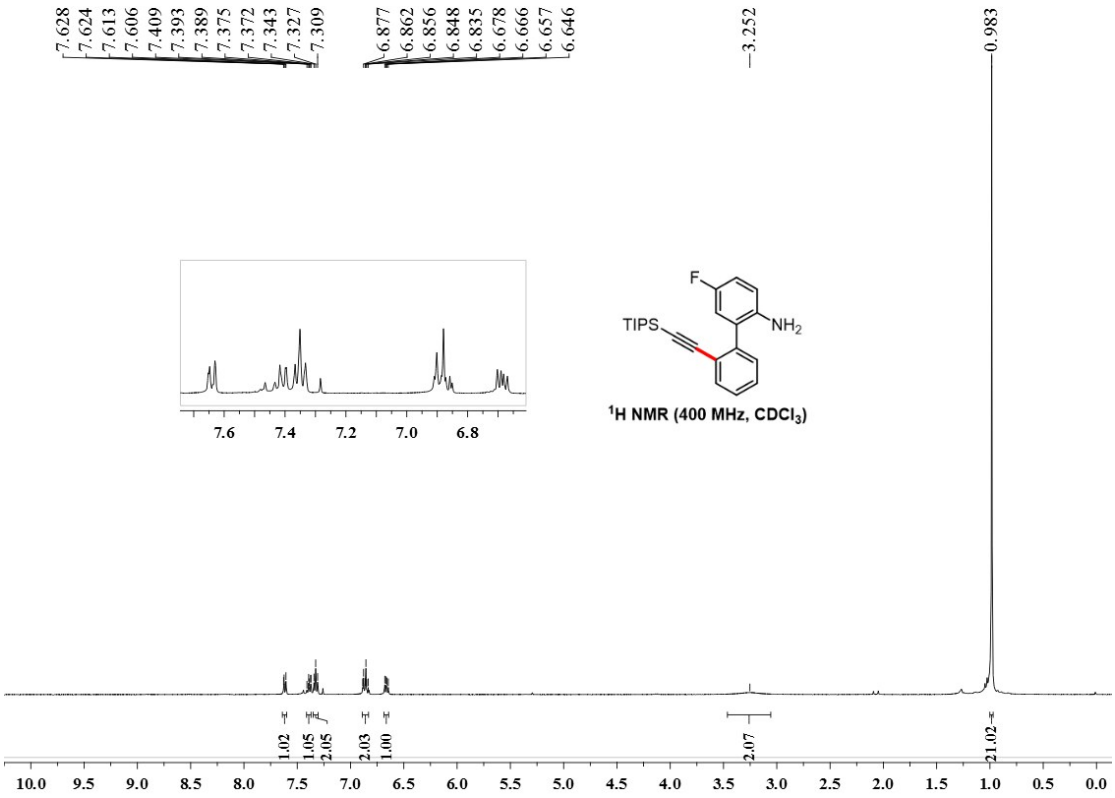


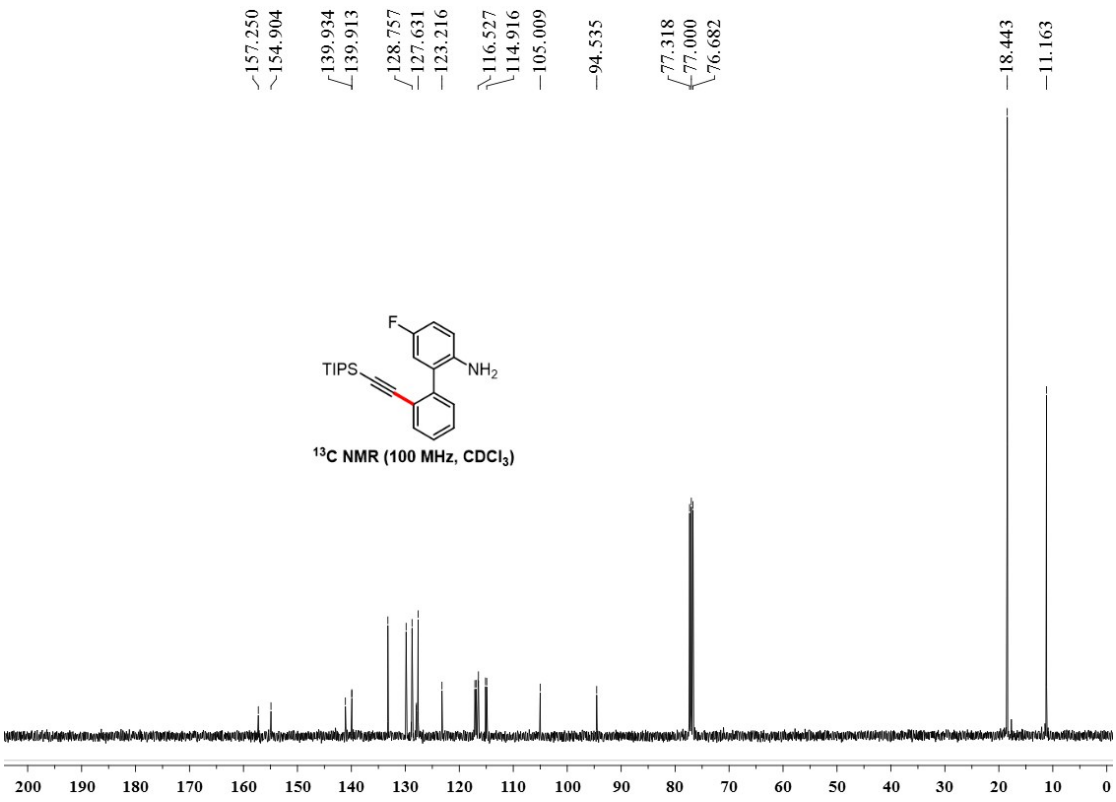
Ethyl 6-amino-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-3-carboxylate (3t)



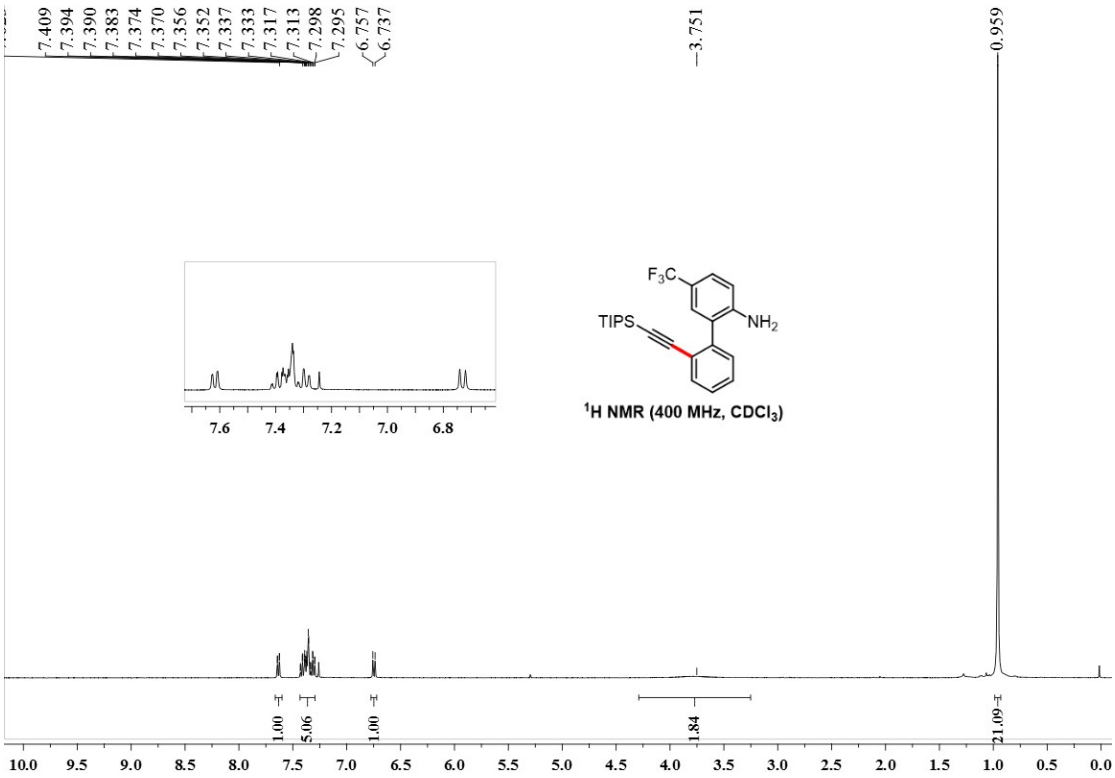


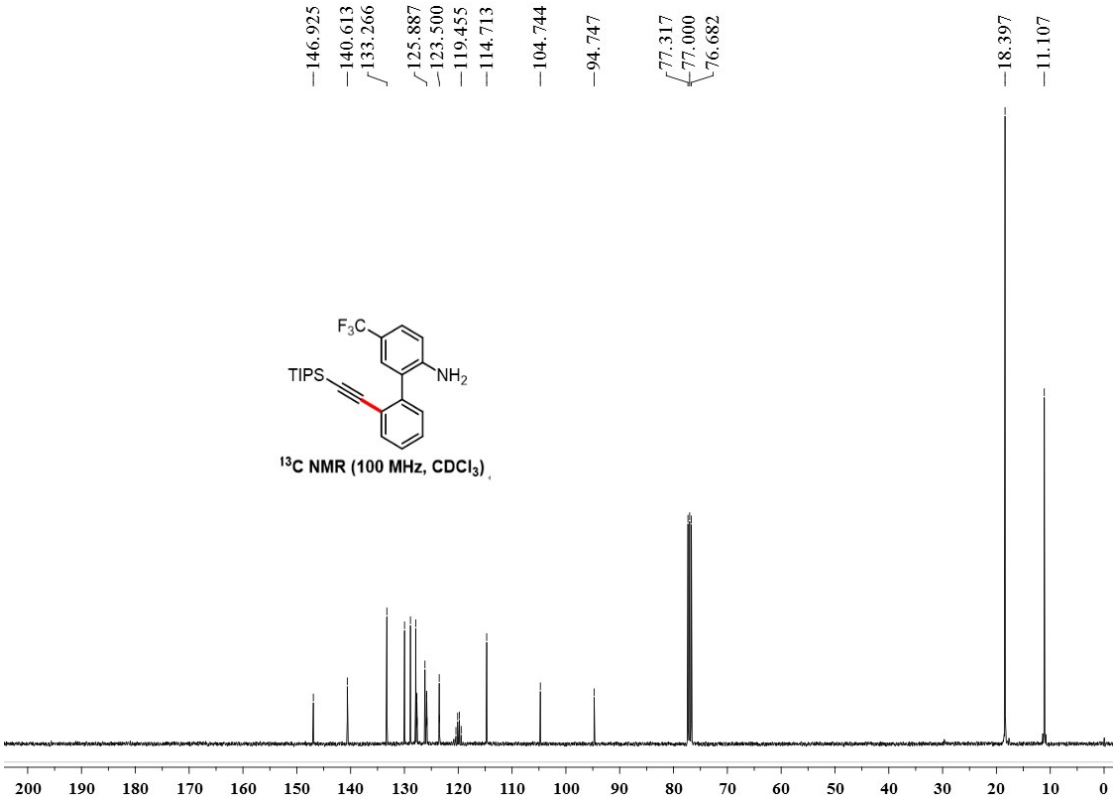
5-Fluoro-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3u)



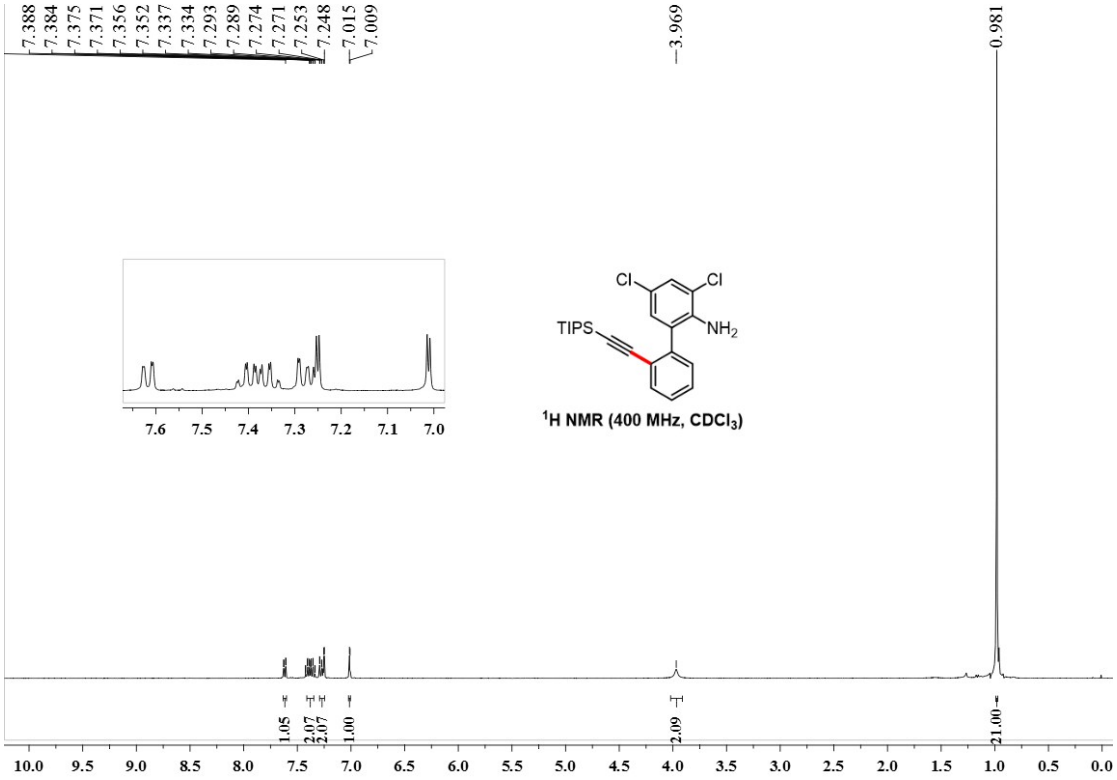


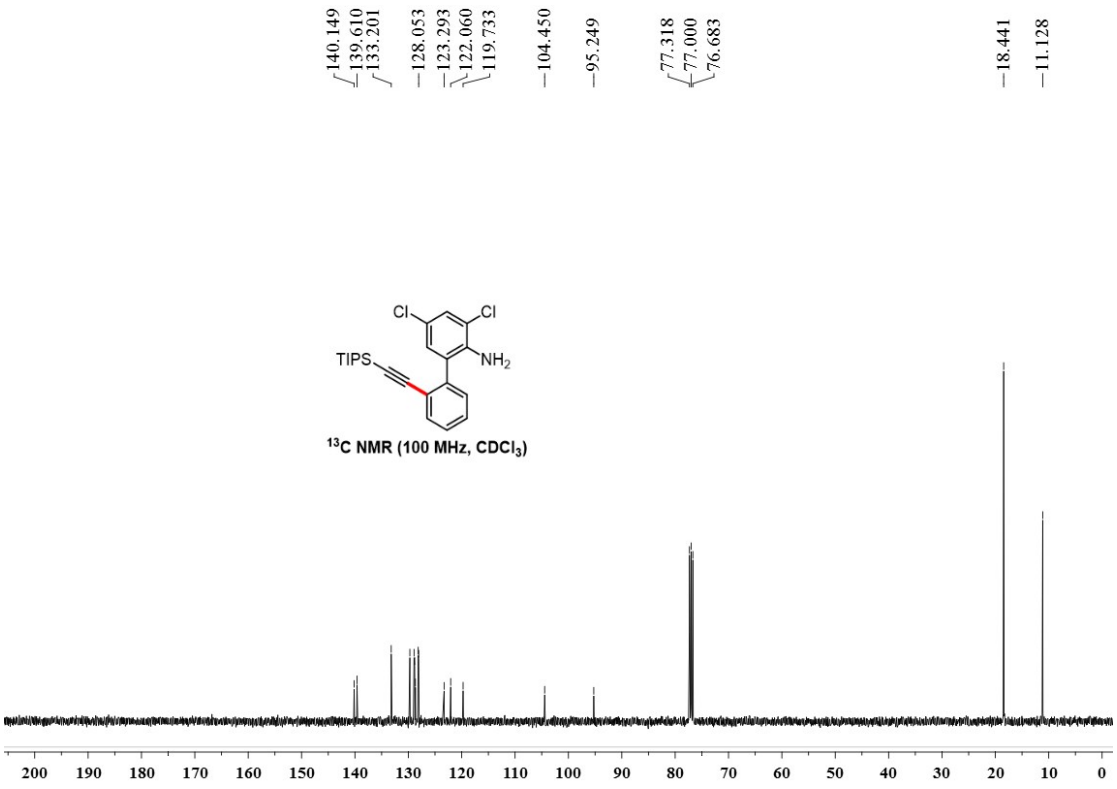
5-(Trifluoromethyl)-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3v)



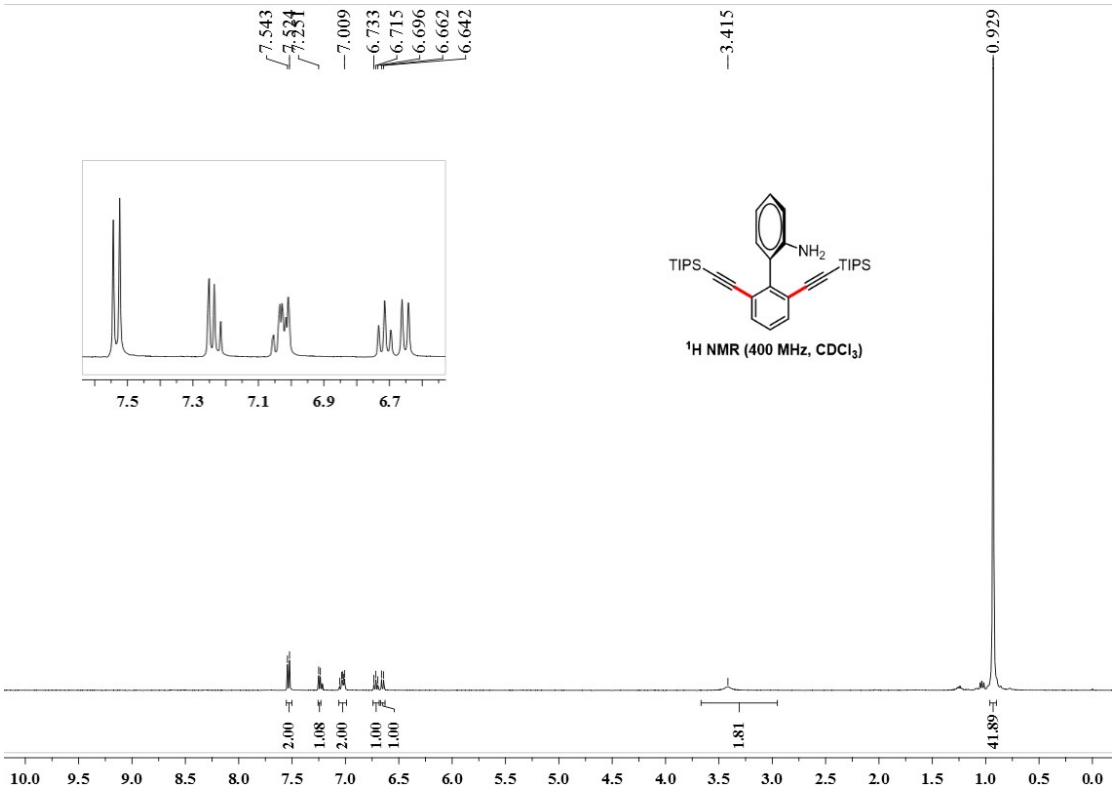


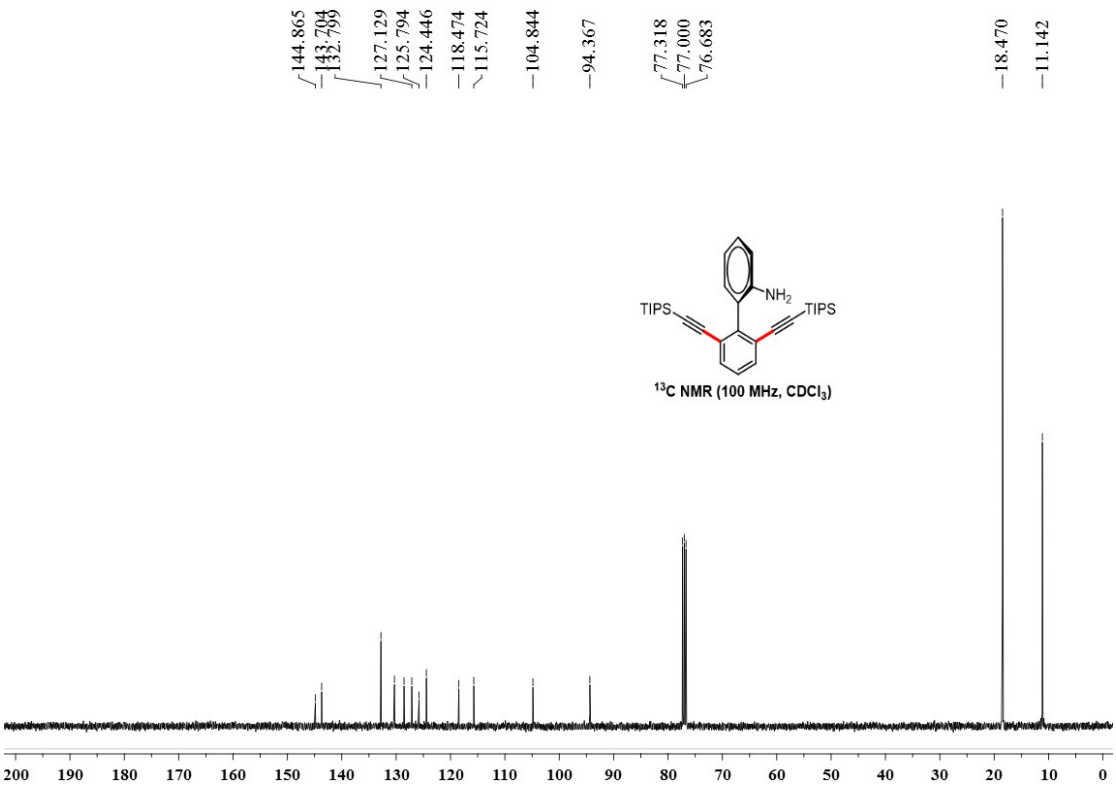
3,5-Dichloro-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3w)



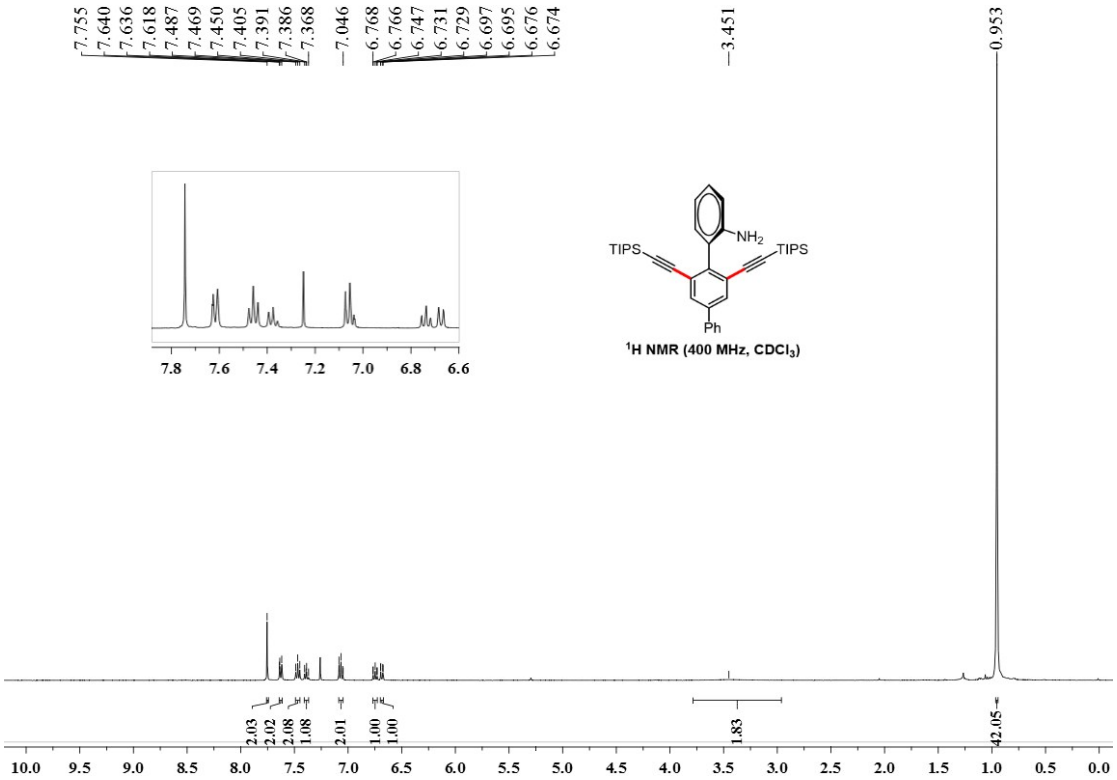


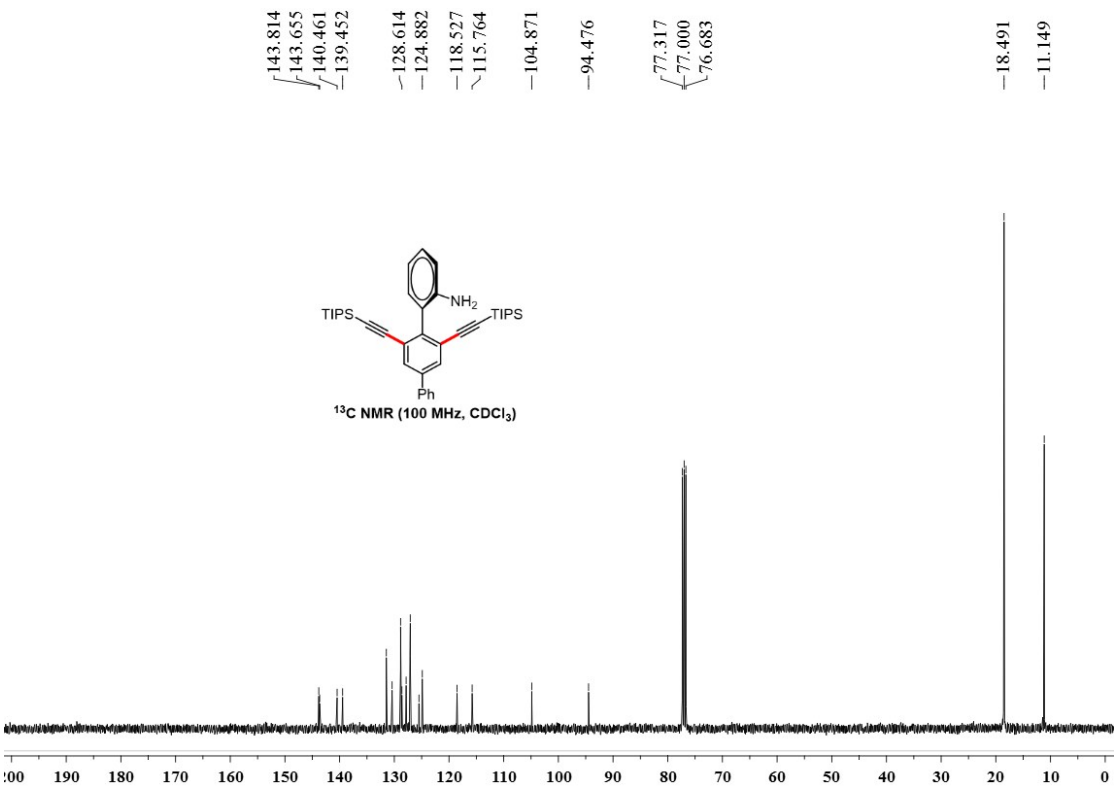
2′,6′-Bis((triisopropylsilyl)ethynyl)-[1,*1′*-biphenyl]-2-amine (4a)



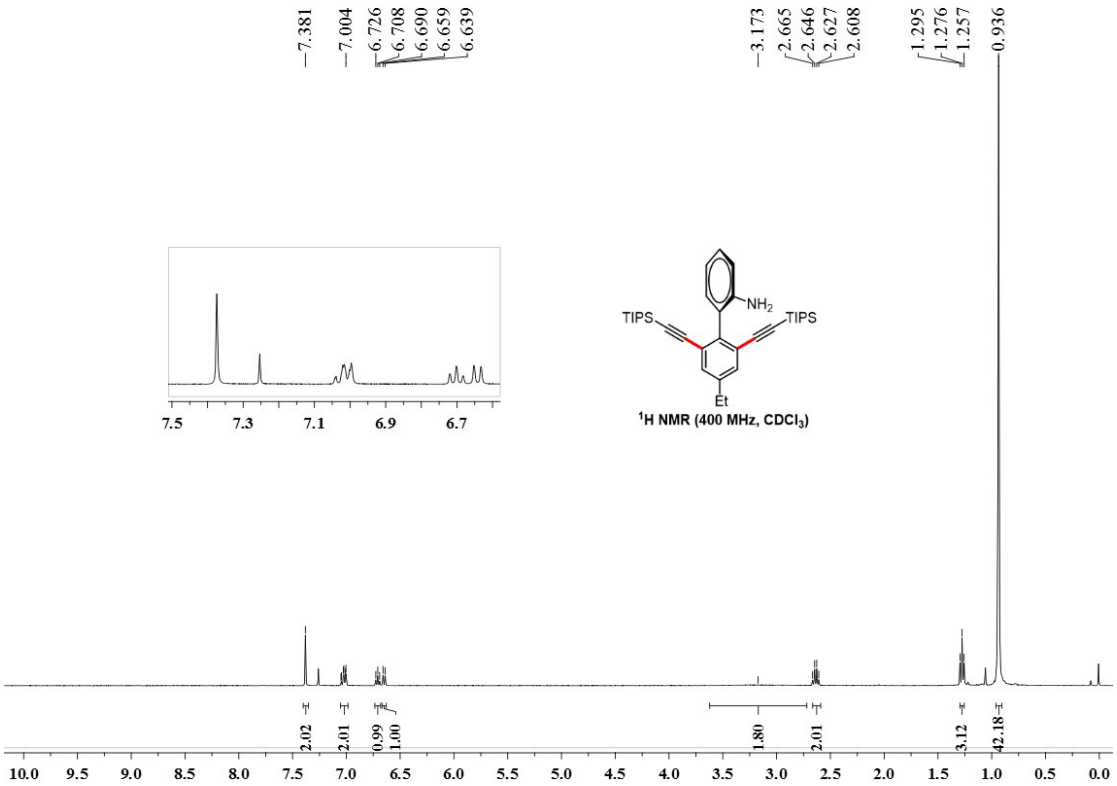


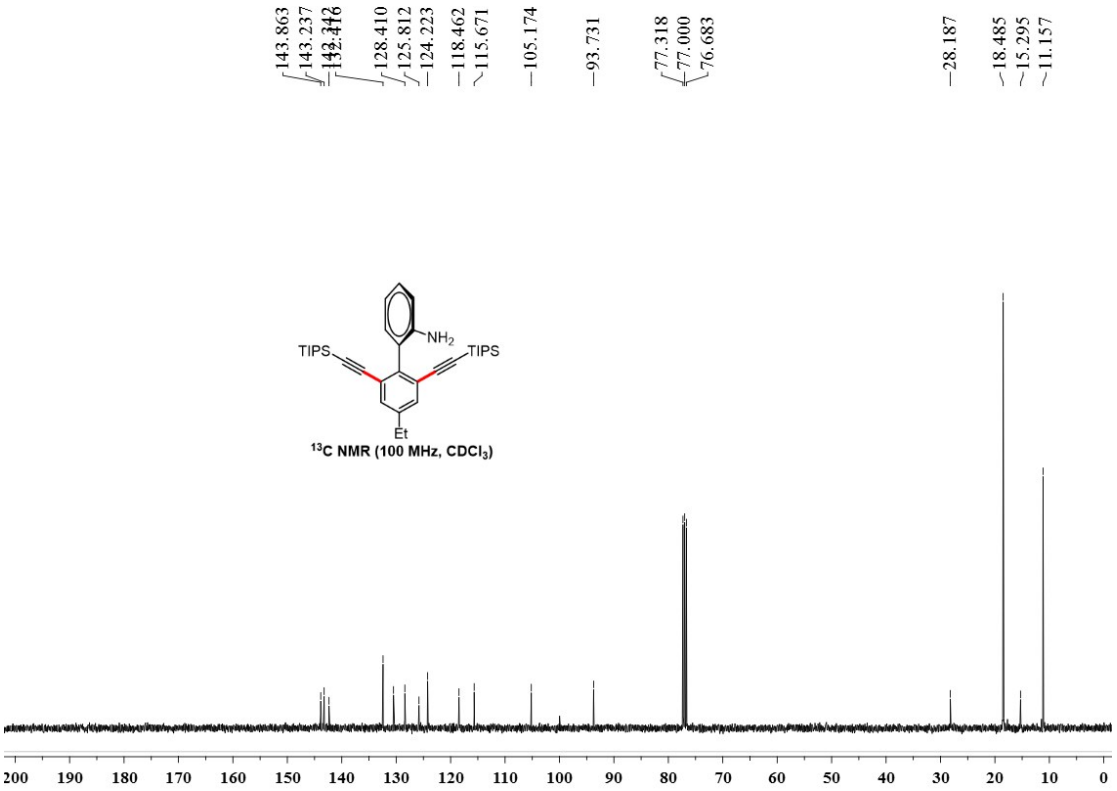
2′,6′-Bis((triisopropylsilyl)ethynyl)-[1,1′:4′,1″-terphenyl]-2-amine (4b)



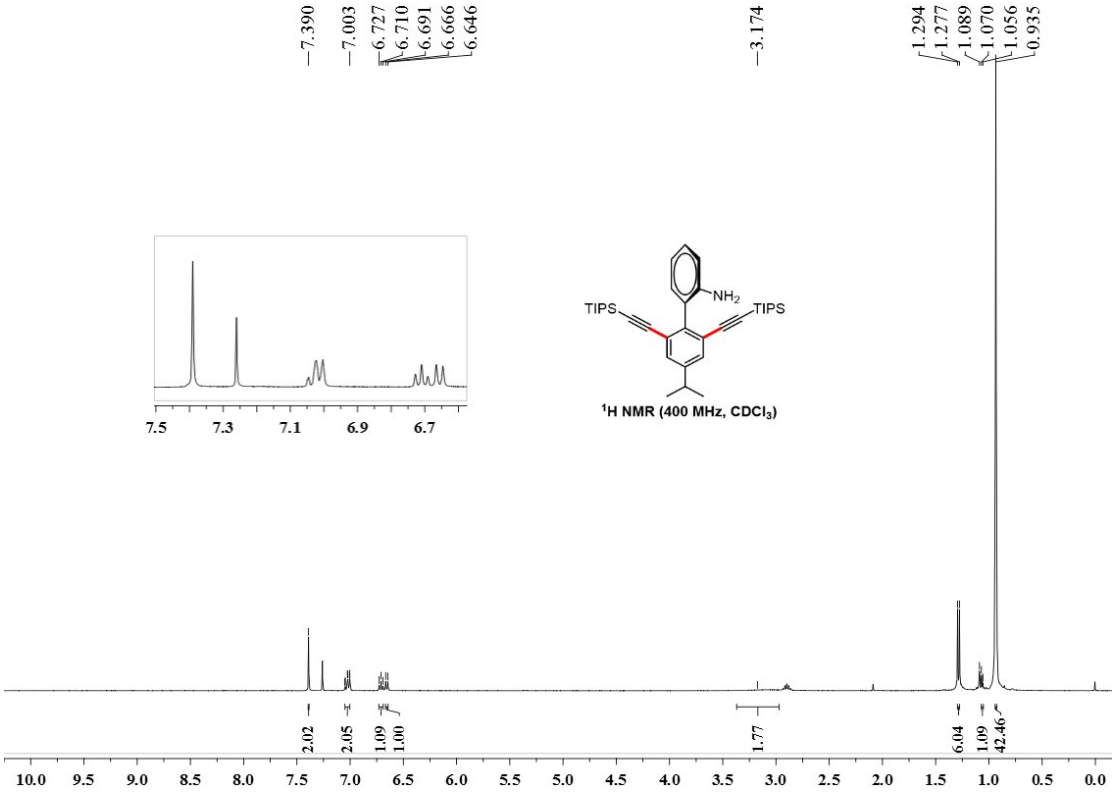


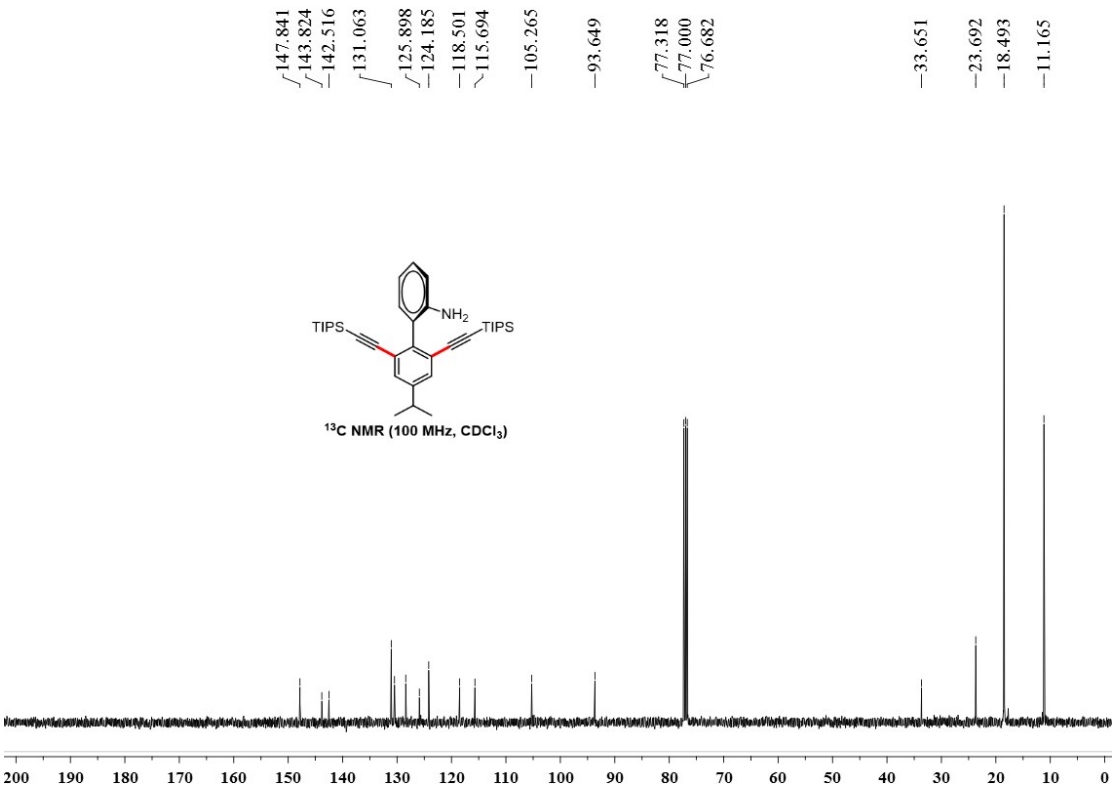
4′-Ethyl-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4c)



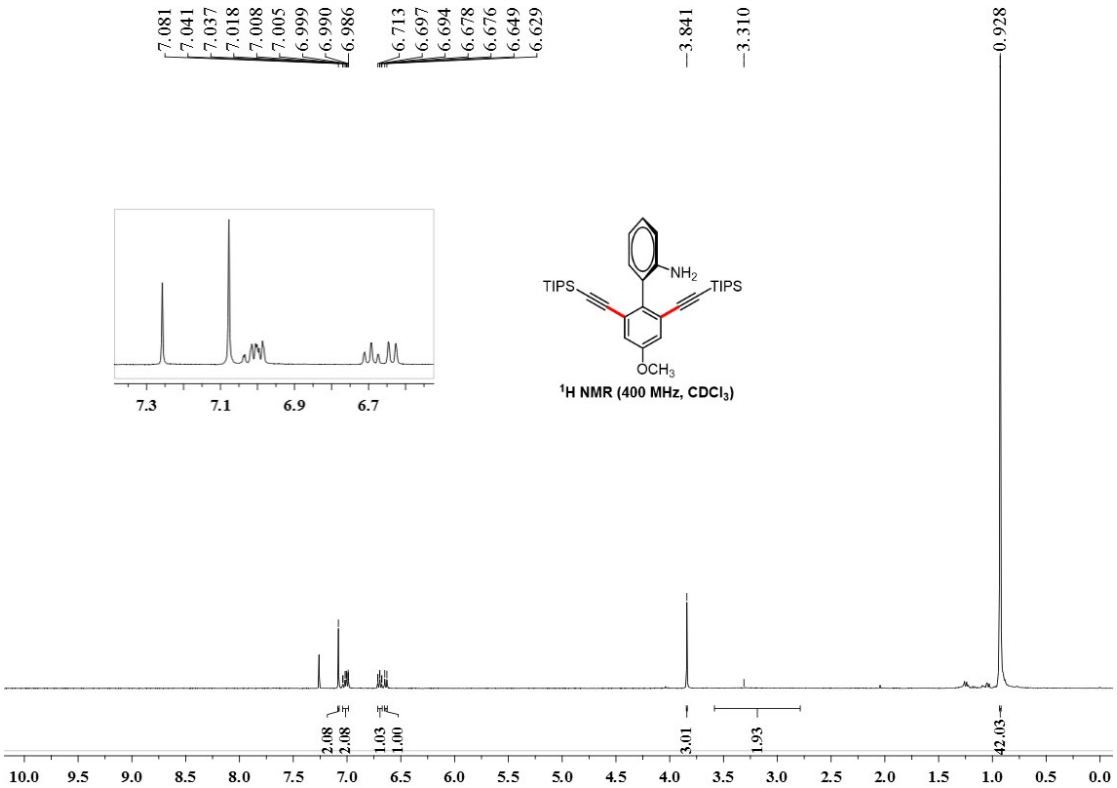


4′-Isopropyl-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4d)

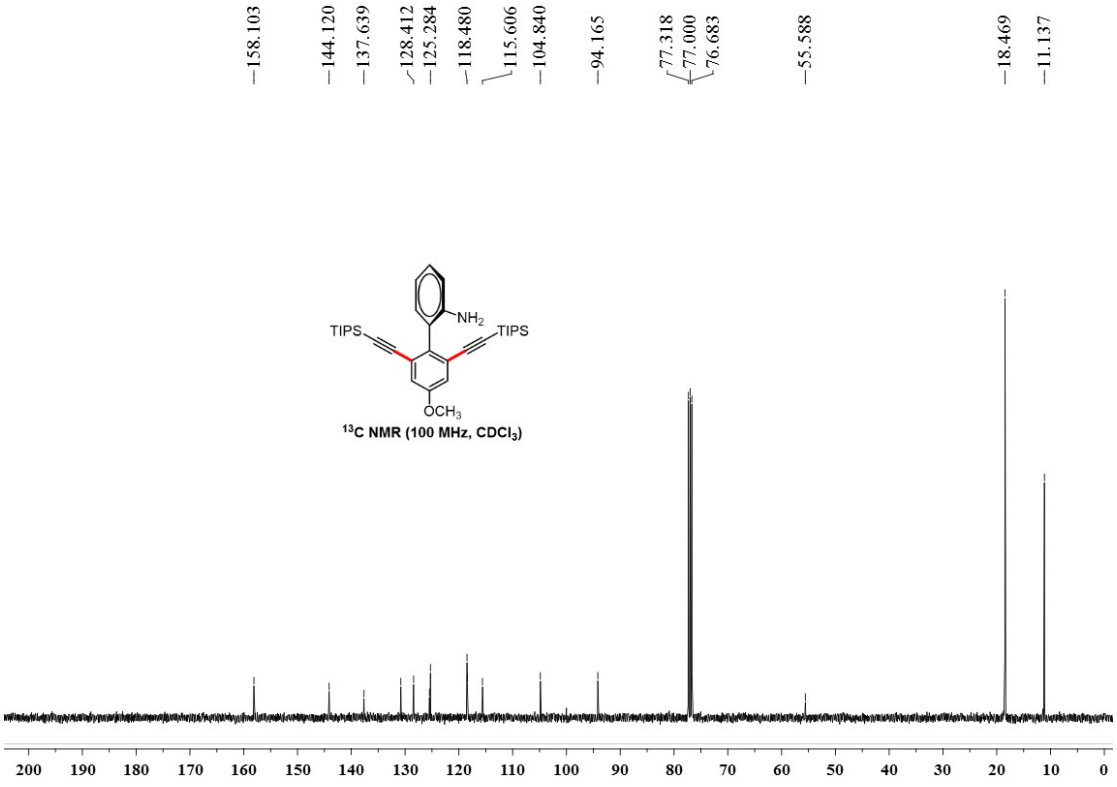




4′-Methoxy-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4e)

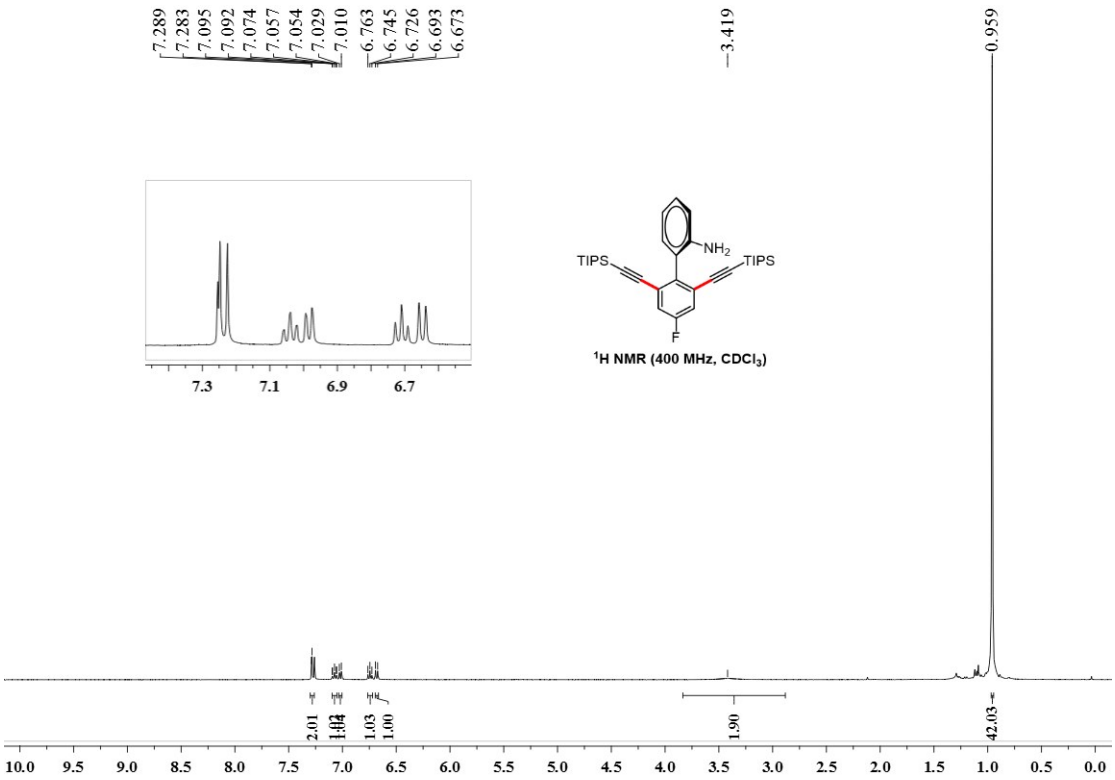


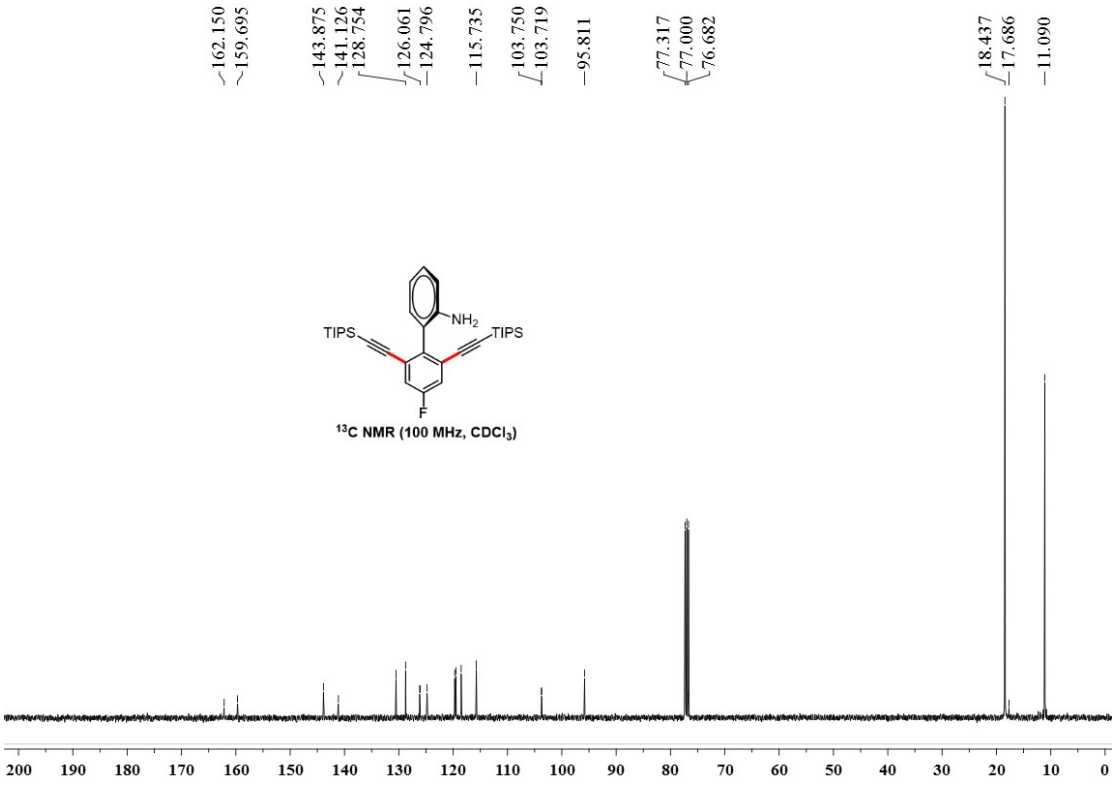
^{1}H NMR (400 MHz, $CDCl_3$)



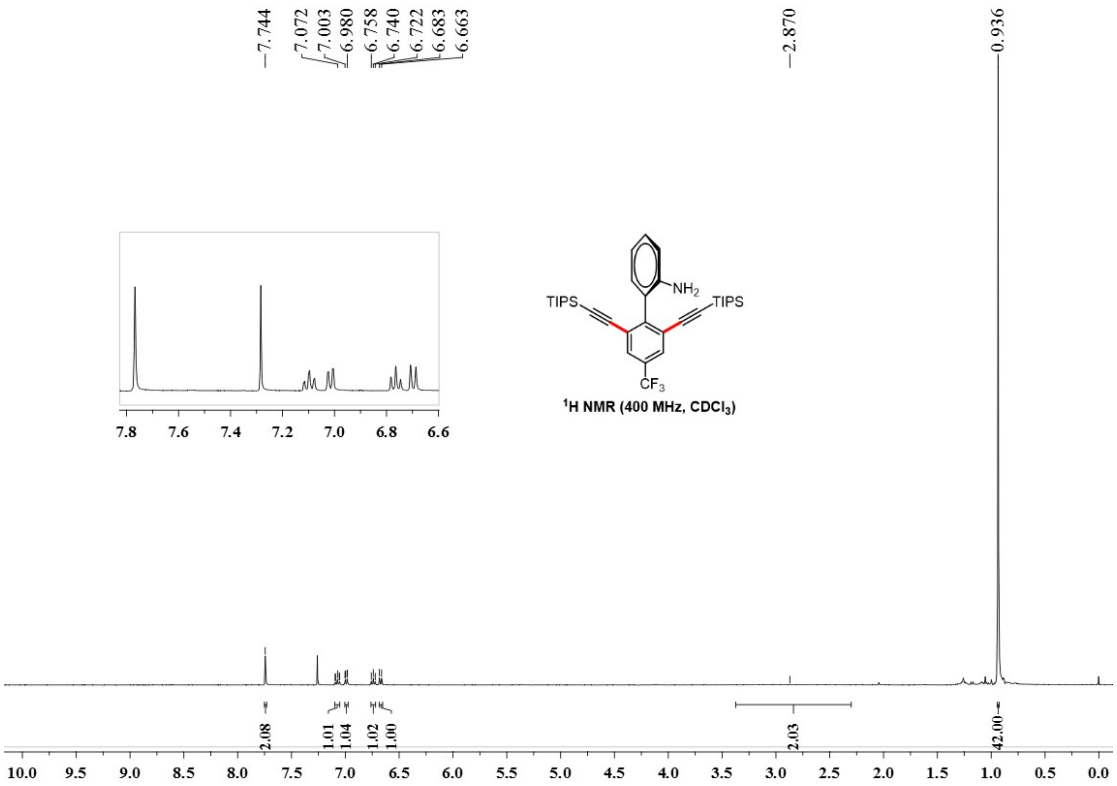
^{13}C NMR (100 MHz, $CDCl_3$)

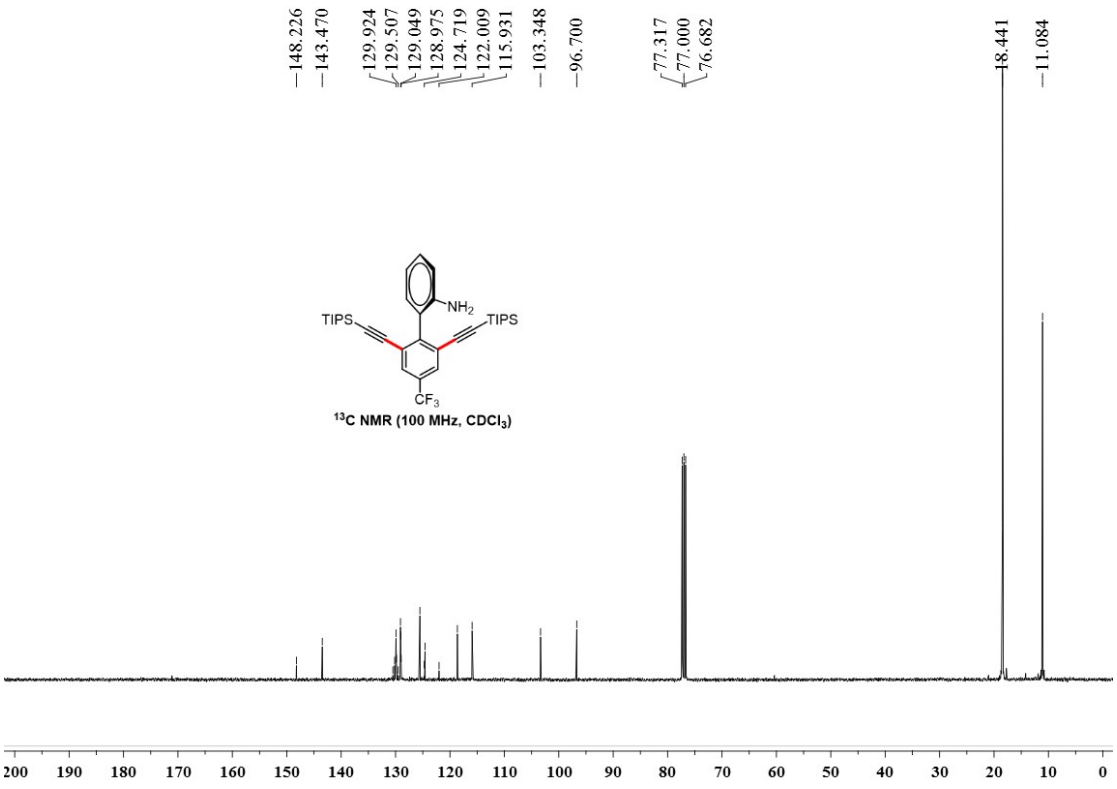
4′-Fluoro-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4f)



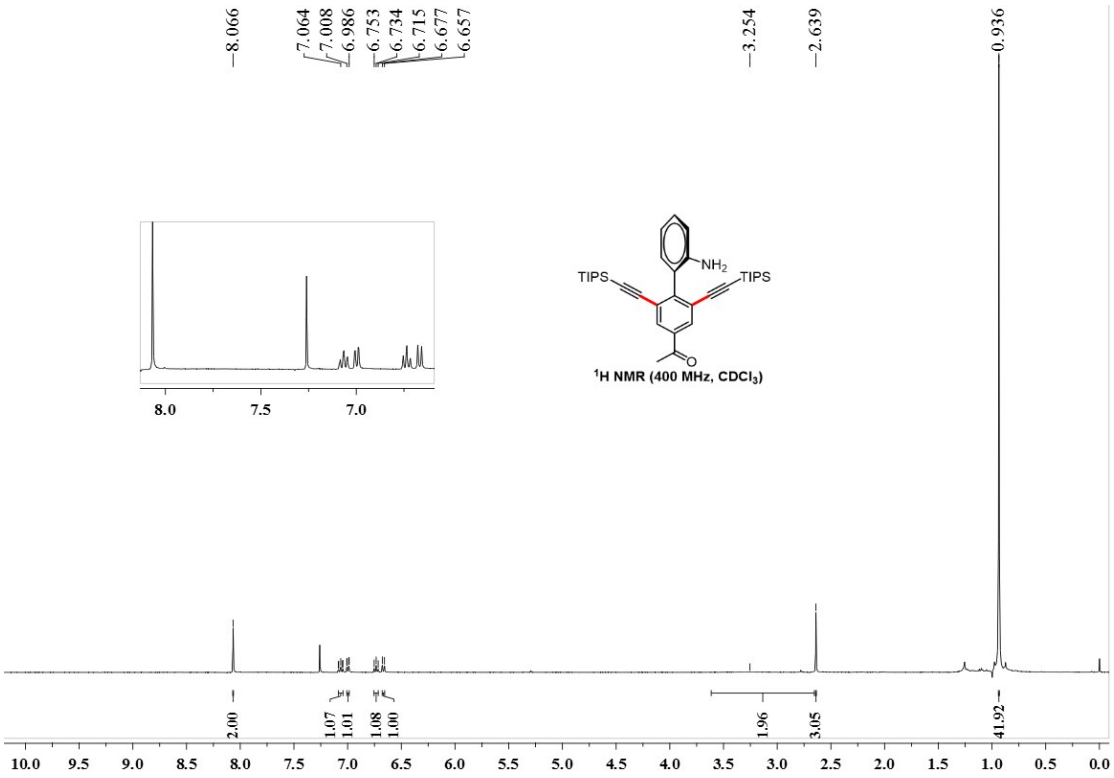


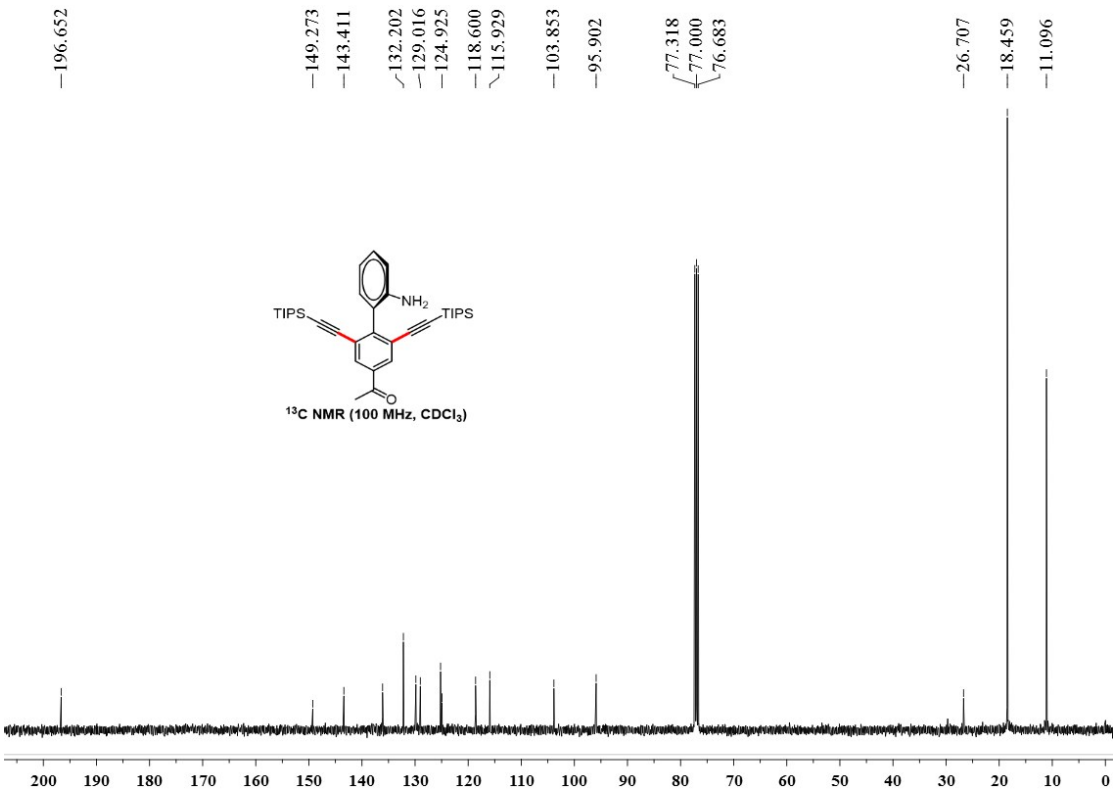
4′-(Trifluoromethyl)-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4g)



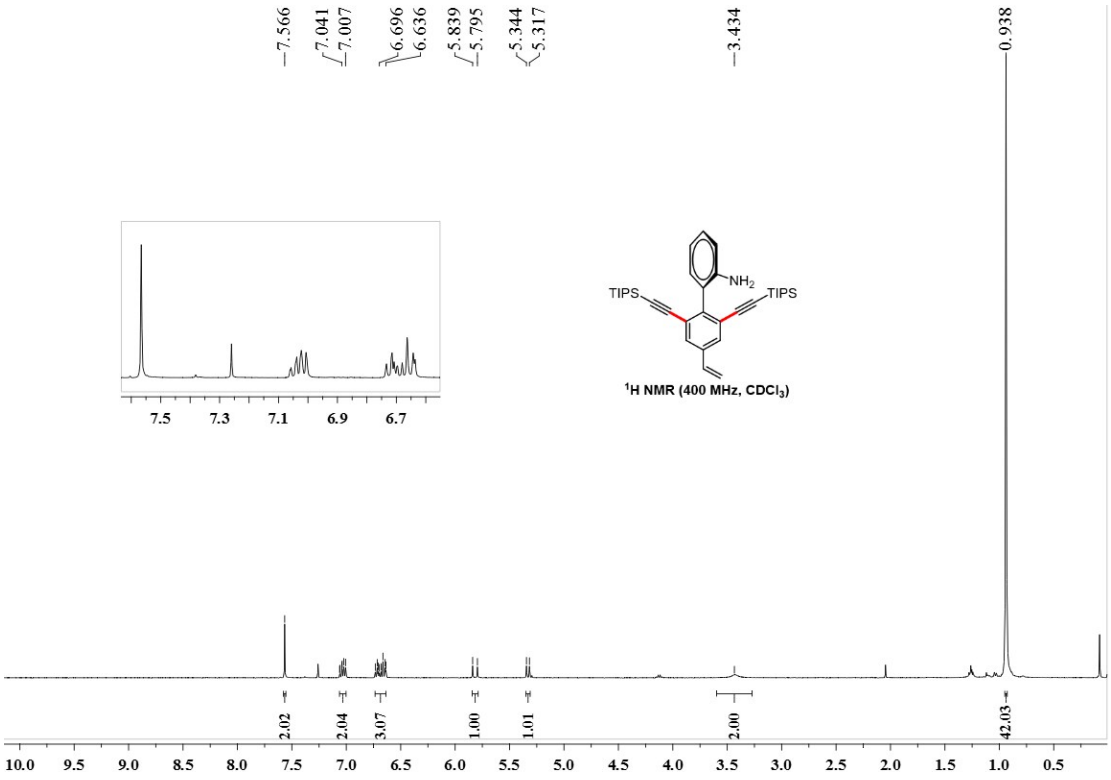


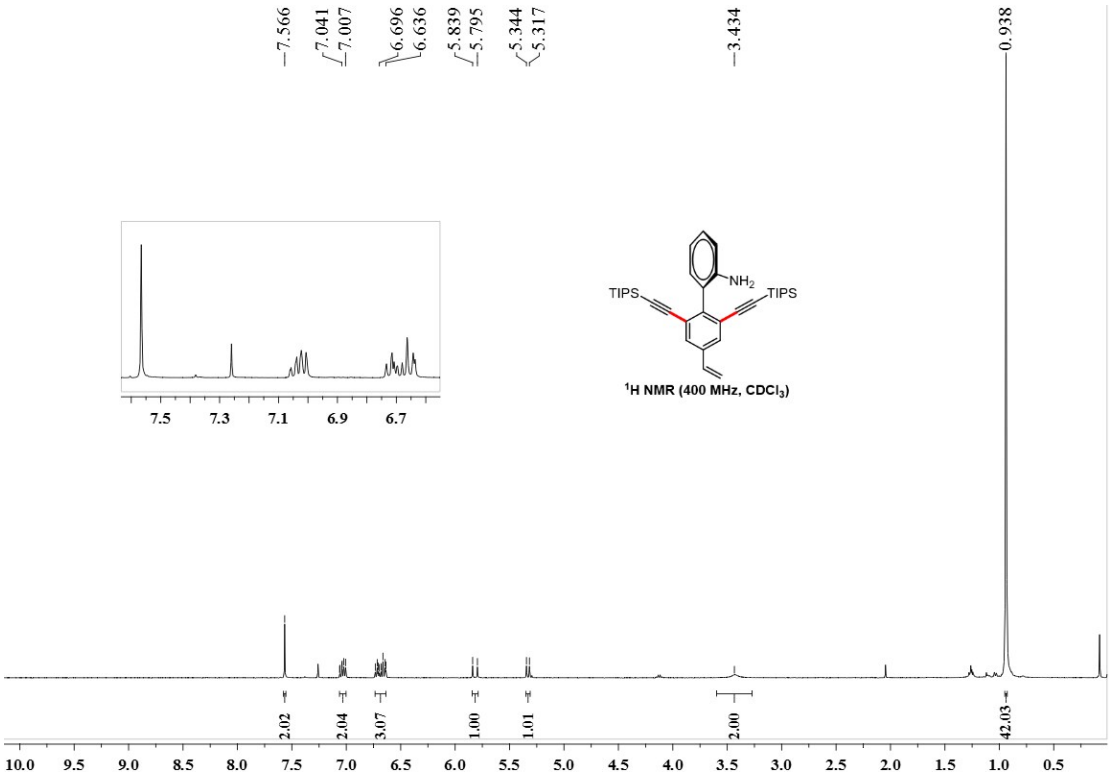
1-(2′-Amino-2,6-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-4-yl)ethan-1-one (4h)



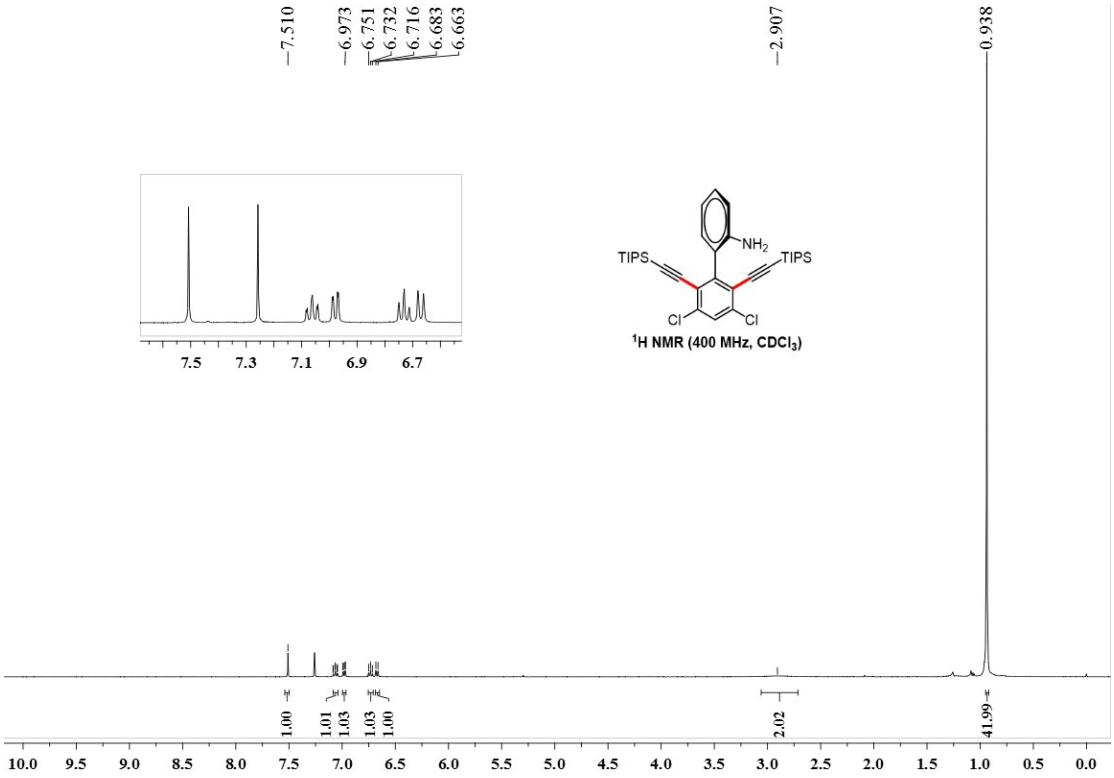


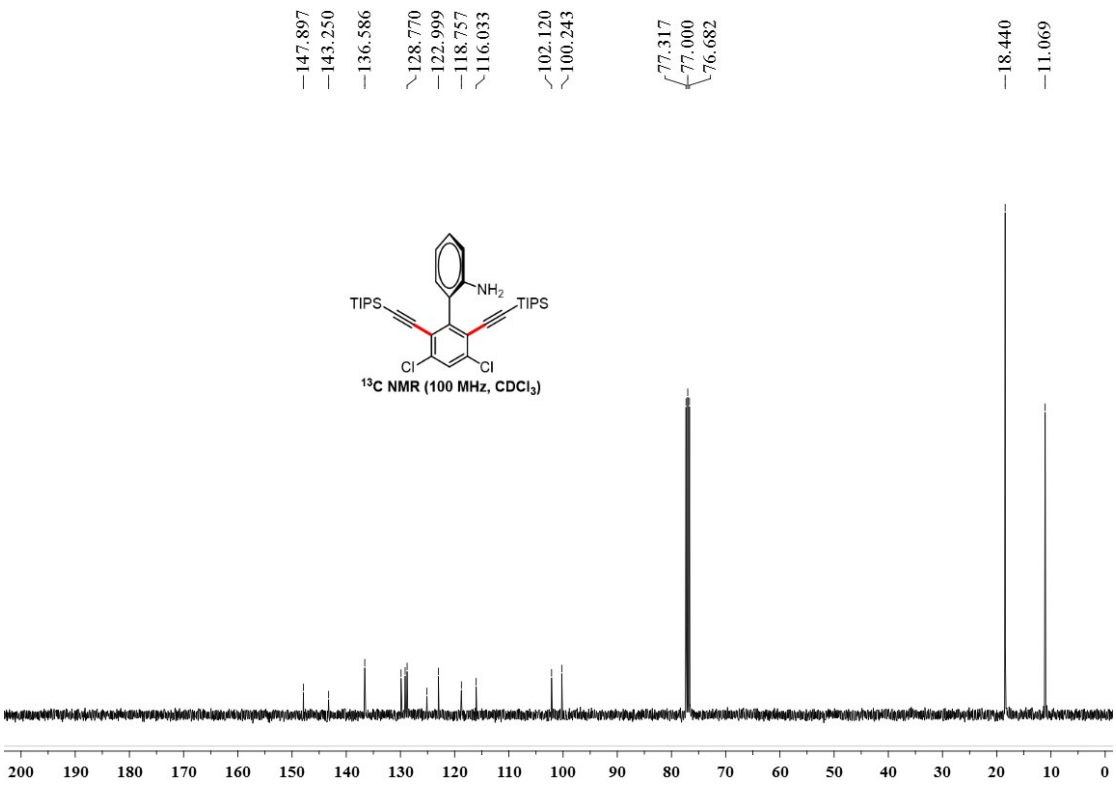
2′,6′-Bis((triisopropylsilyl)ethynyl)-4′-vinyl-[1,1′-biphenyl]-2-amine (4i)



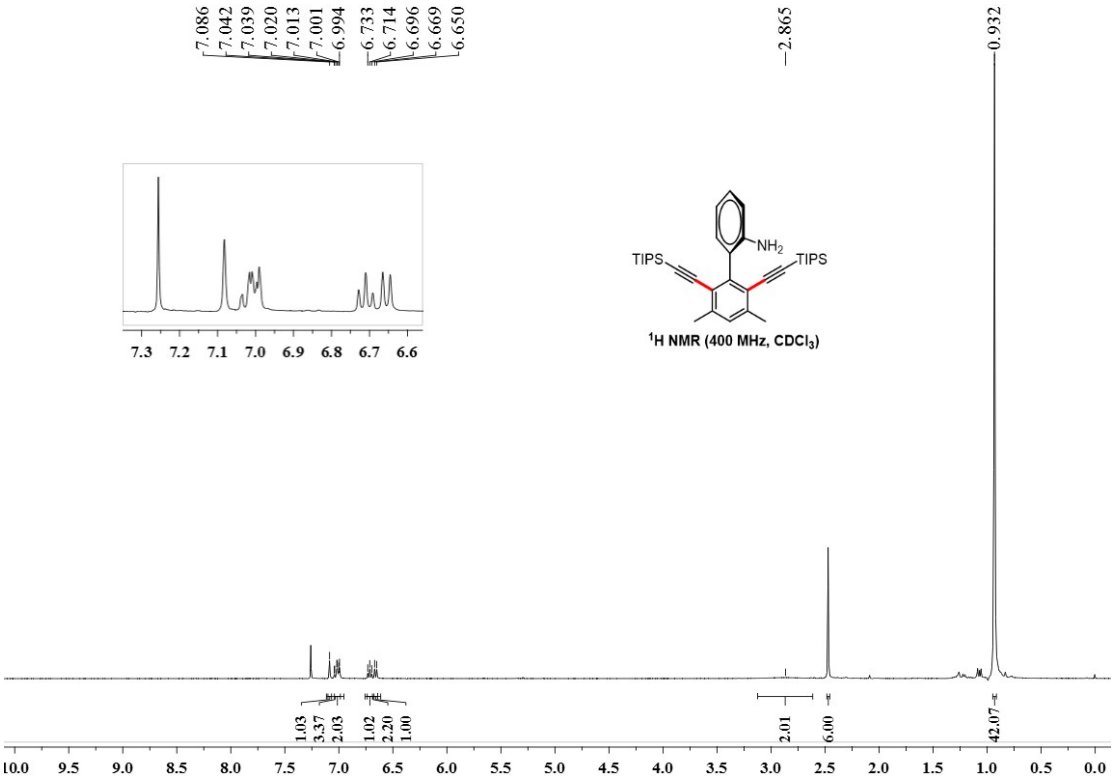


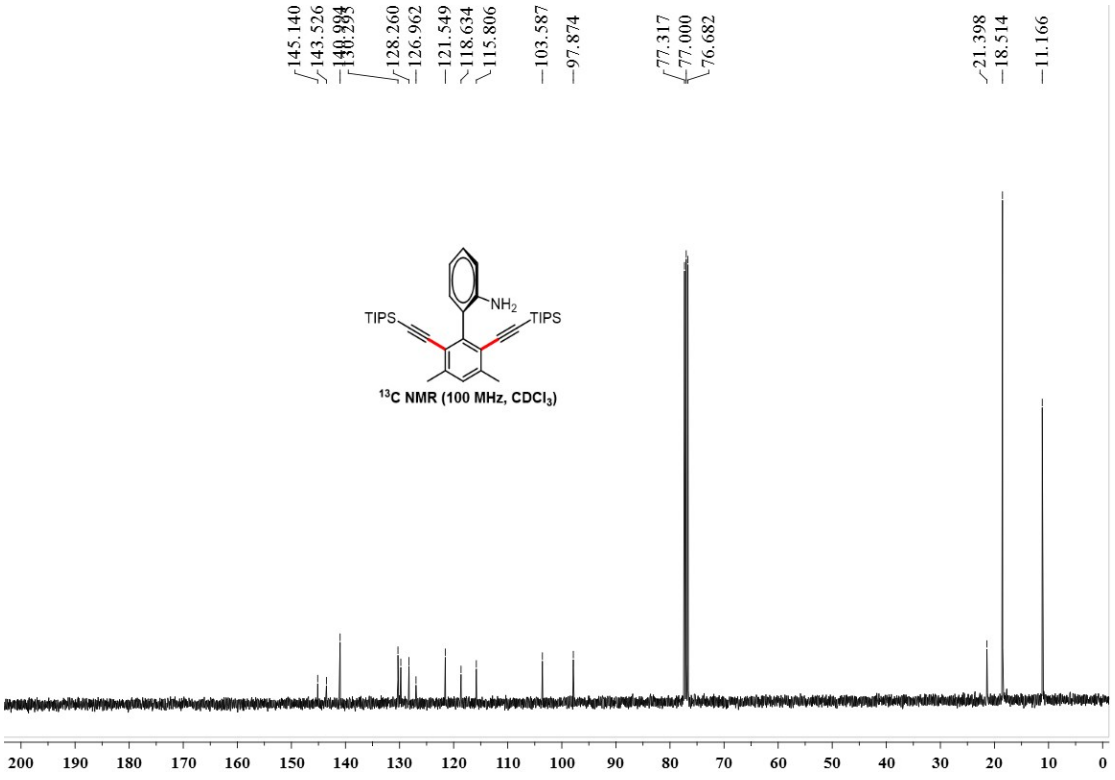
3′,5′-Dichloro-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4j)



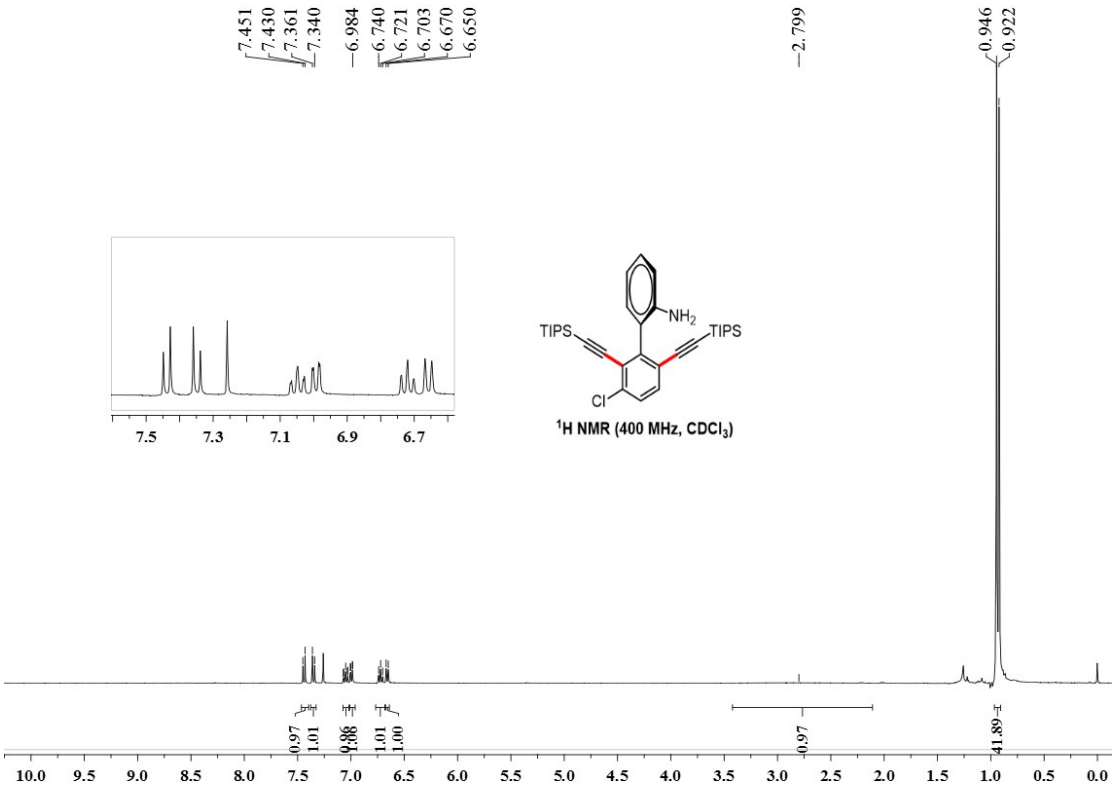


3′,5′-Dimethyl-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4k)

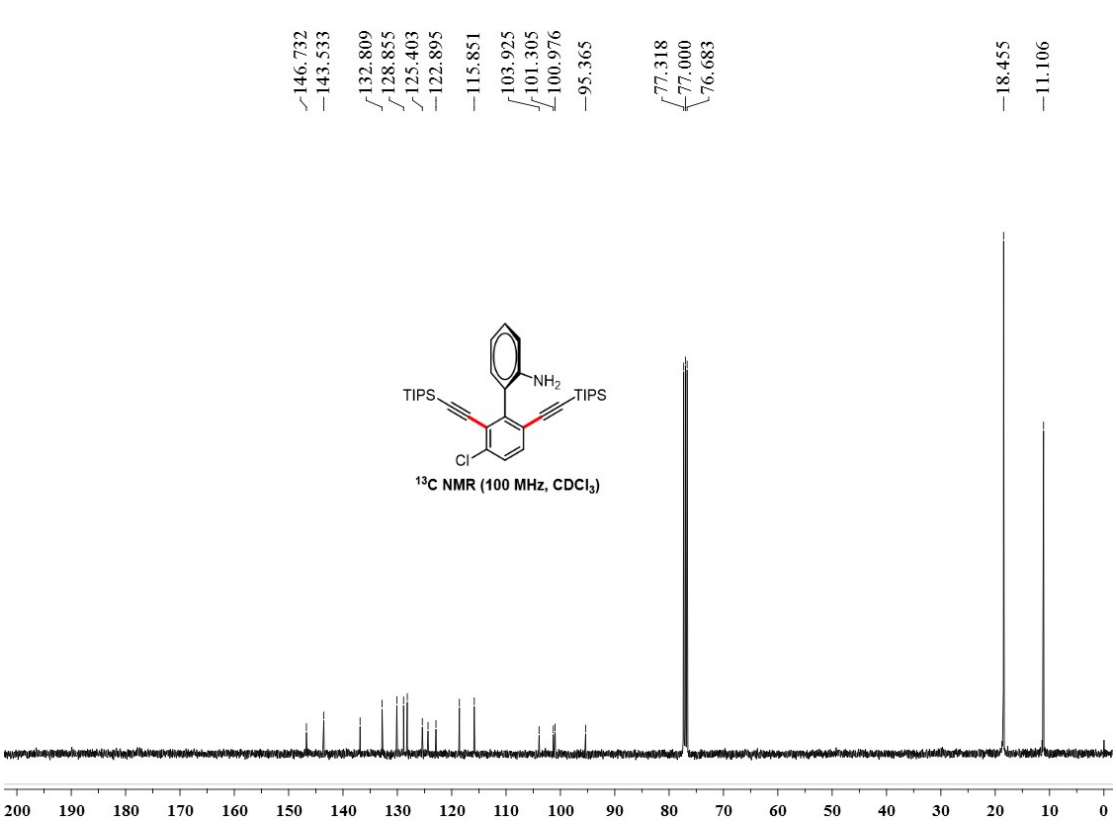




3′-Chloro-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4l)

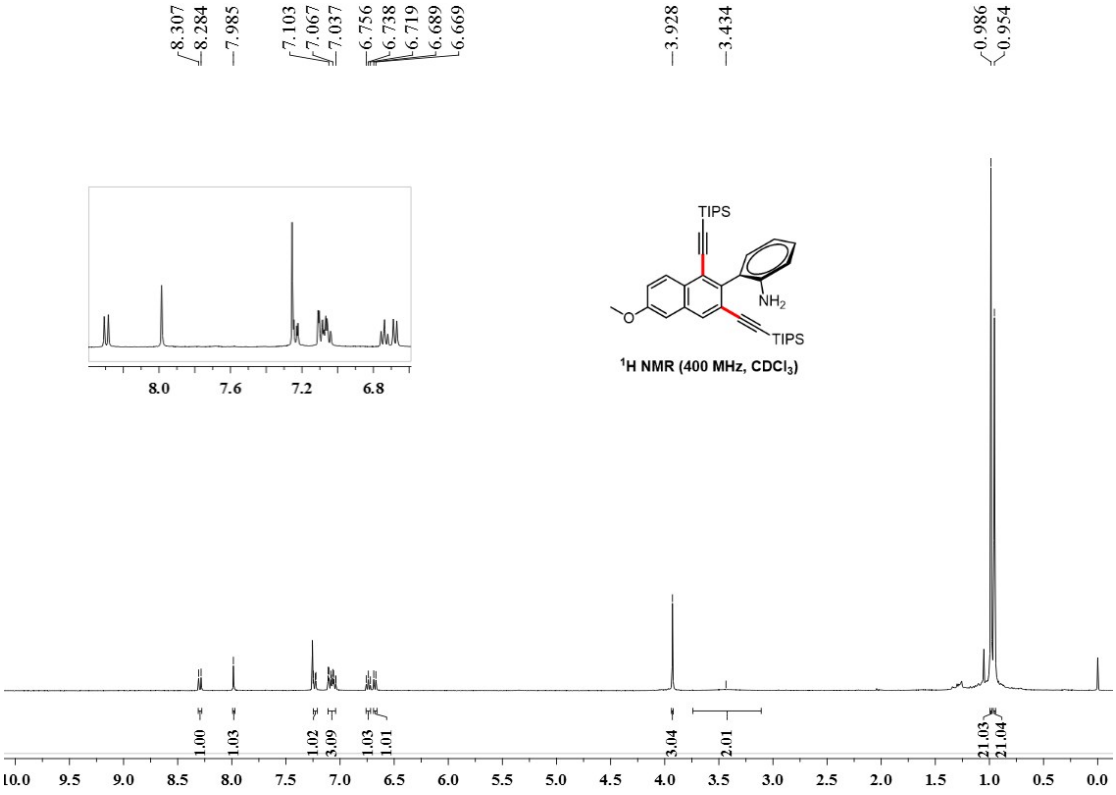


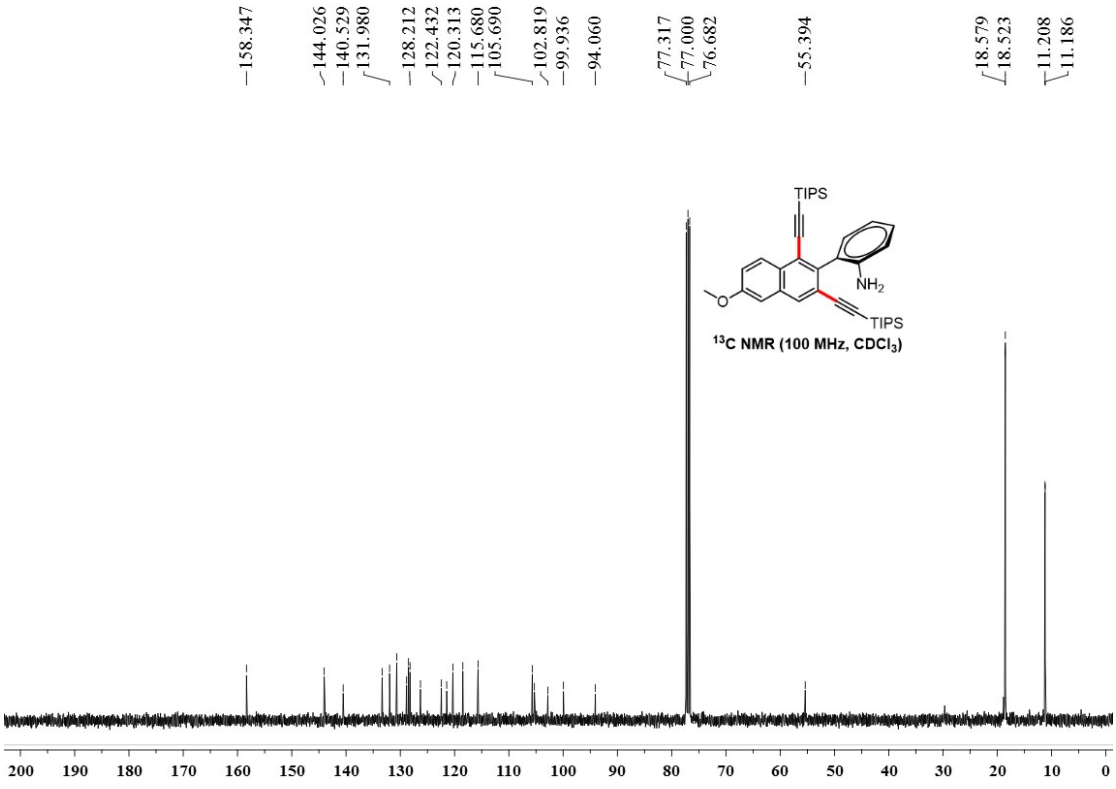
^{1}H NMR (400 MHz, $CDCl_3$)



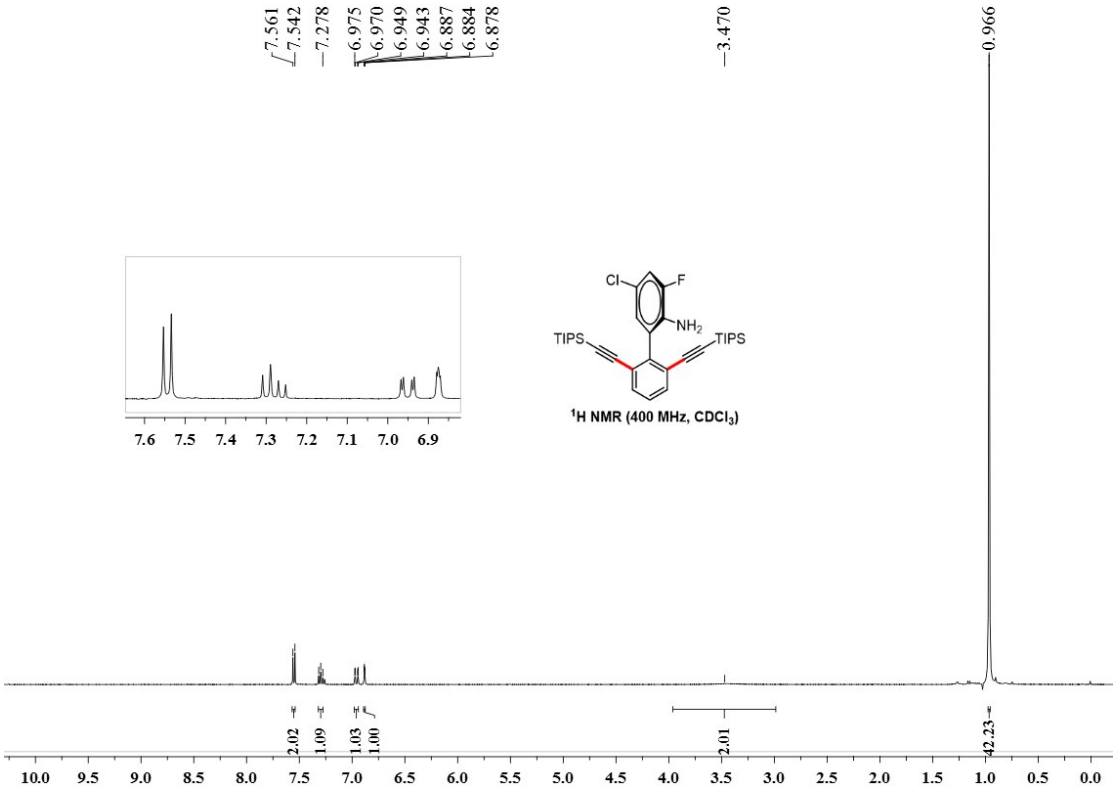
^{13}C NMR (100 MHz, $CDCl_3$)

2-(6-Methoxy-1,3-bis((triisopropylsilyl)ethynyl)naphthalen-2-yl)aniline (4m)

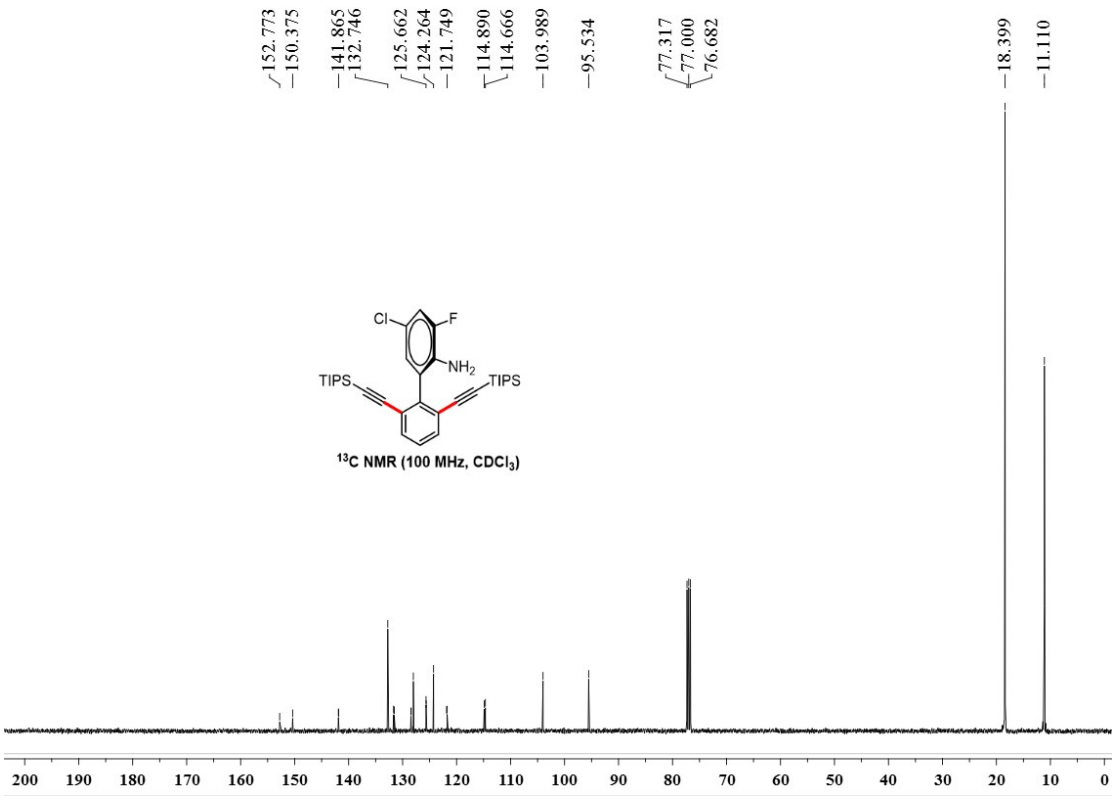




5-Chloro-3-fluoro-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4n)

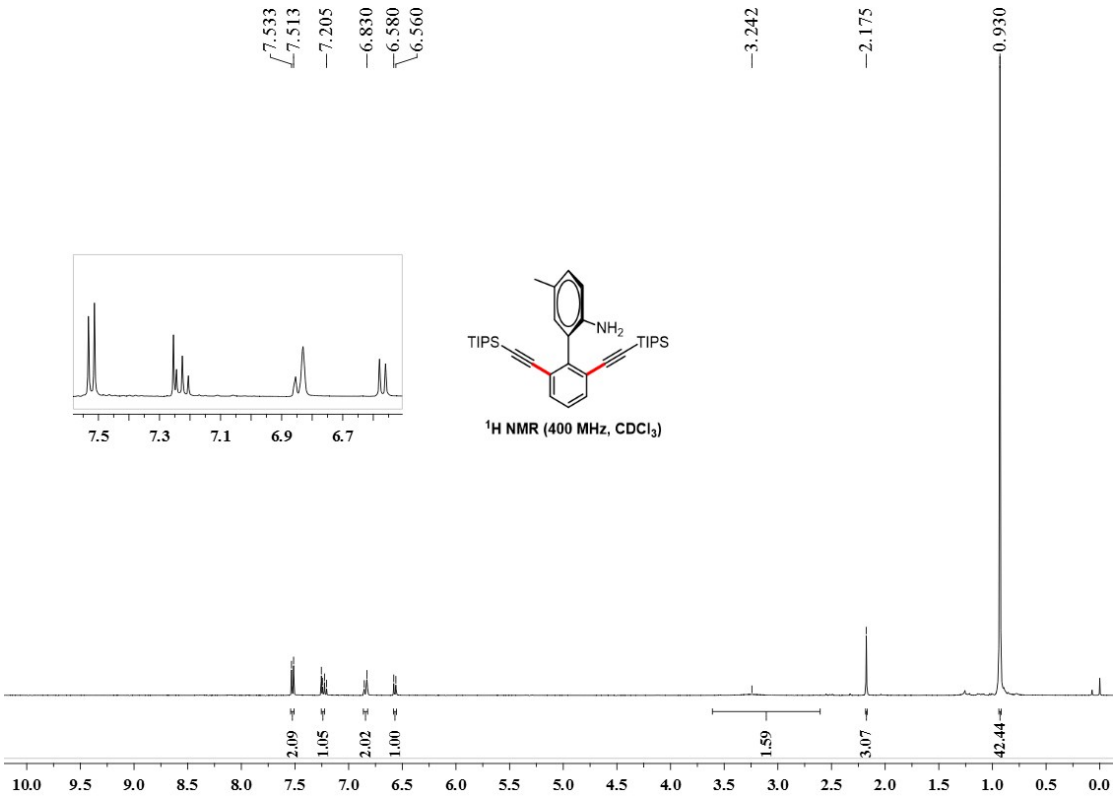


^{1}H NMR (400 MHz, $CDCl_3$)

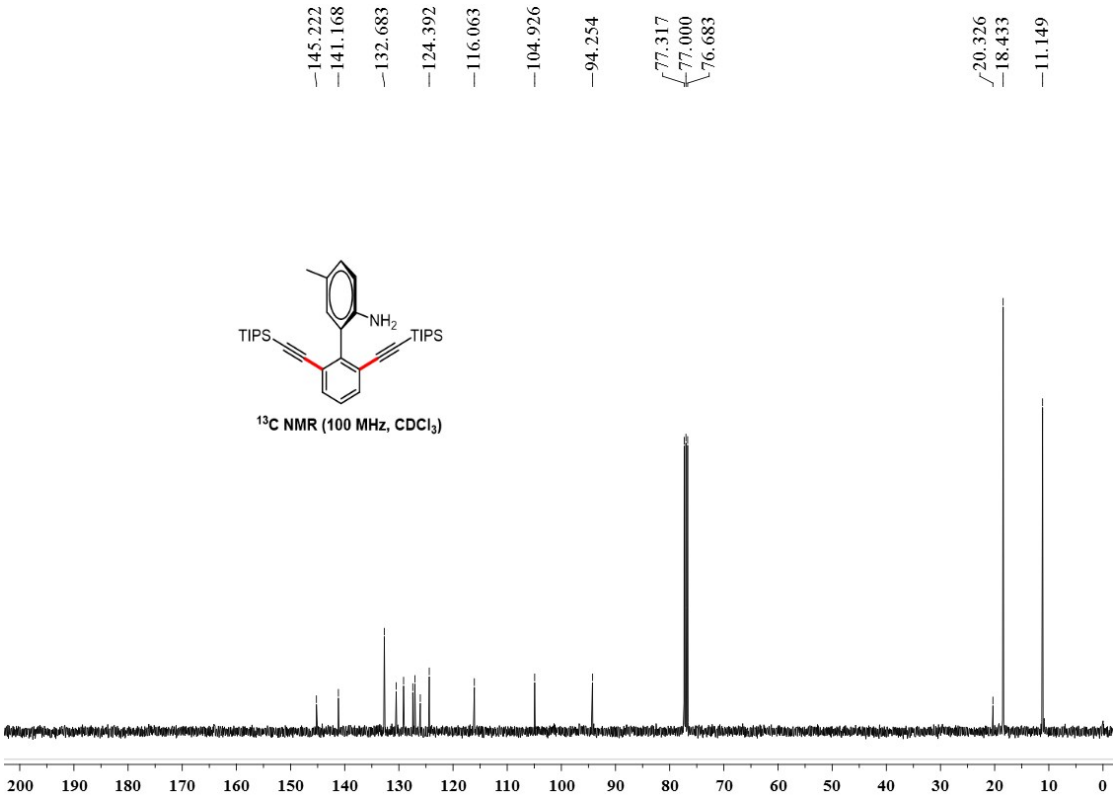


^{13}C NMR (100 MHz, $CDCl_3$)

5-Methyl-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4o)

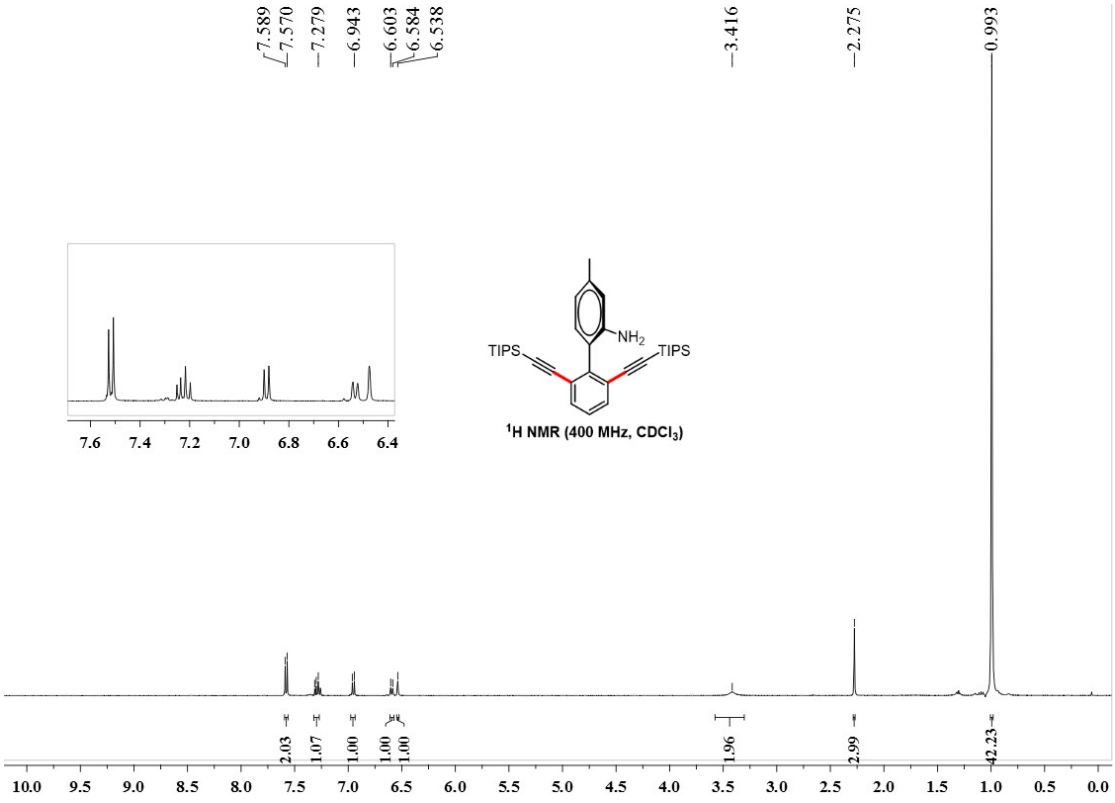


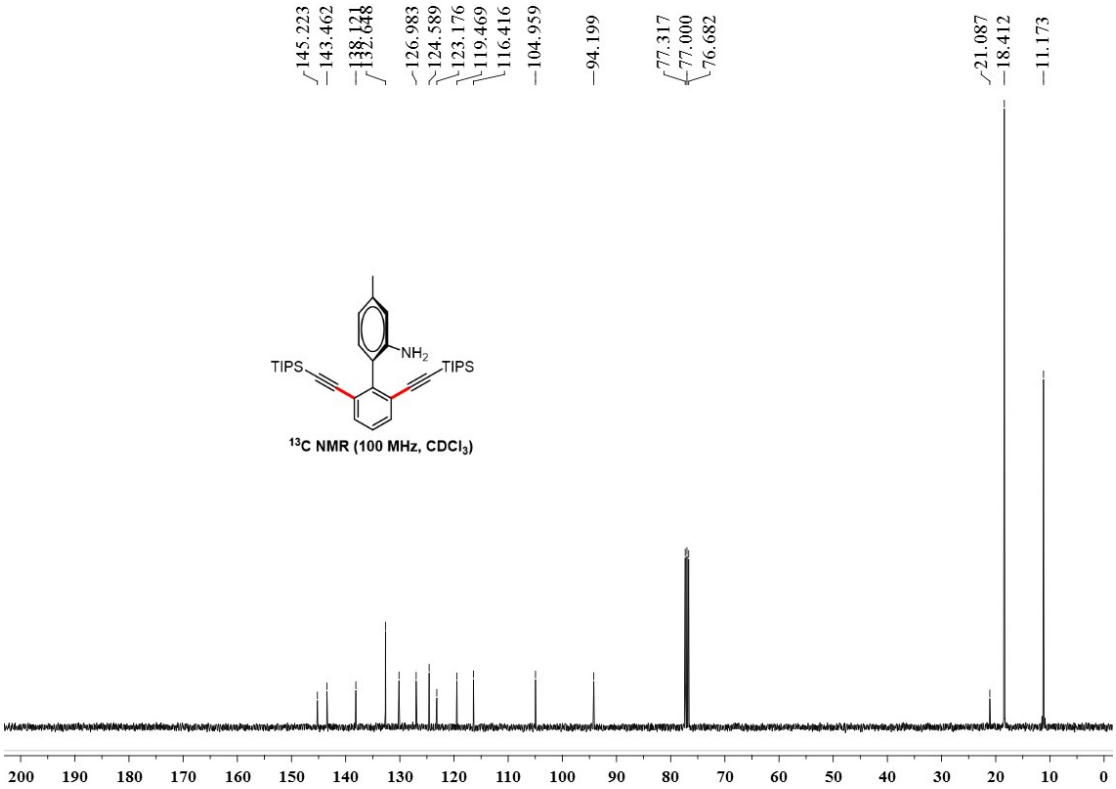
^{1}H NMR (400 MHz, $CDCl_3$)



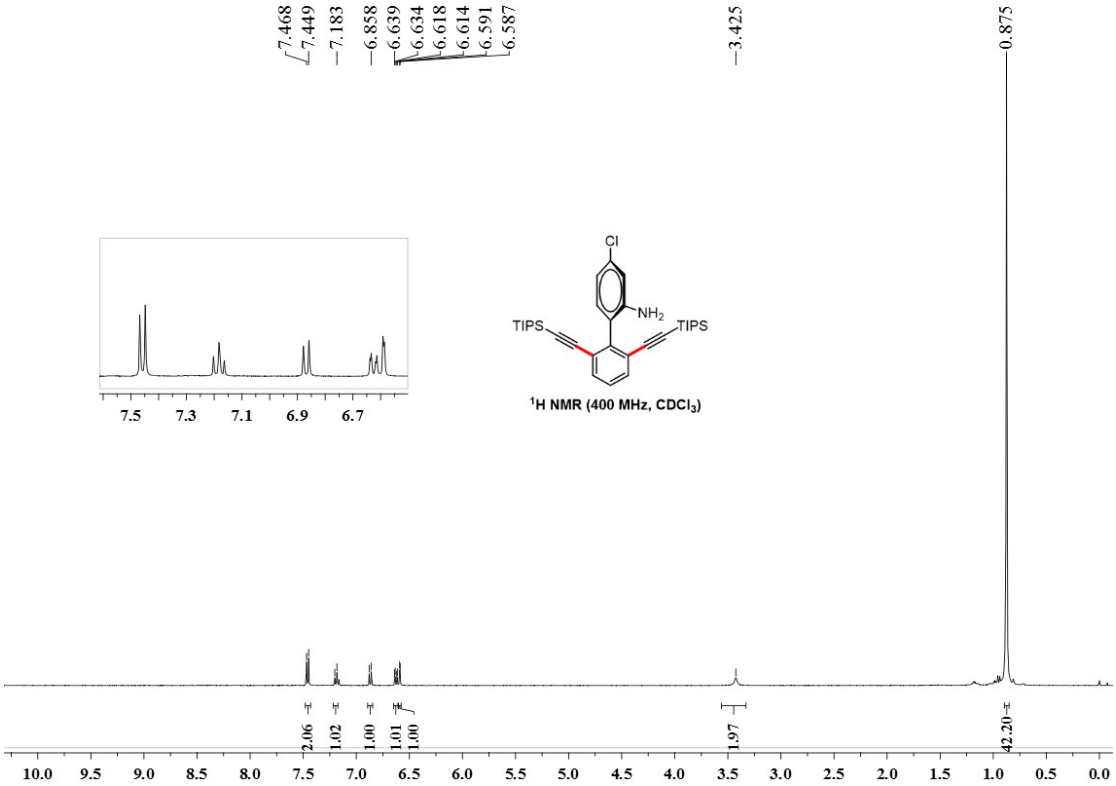
^{13}C NMR (100 MHz, $CDCl_3$)

4-Methyl-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4p)

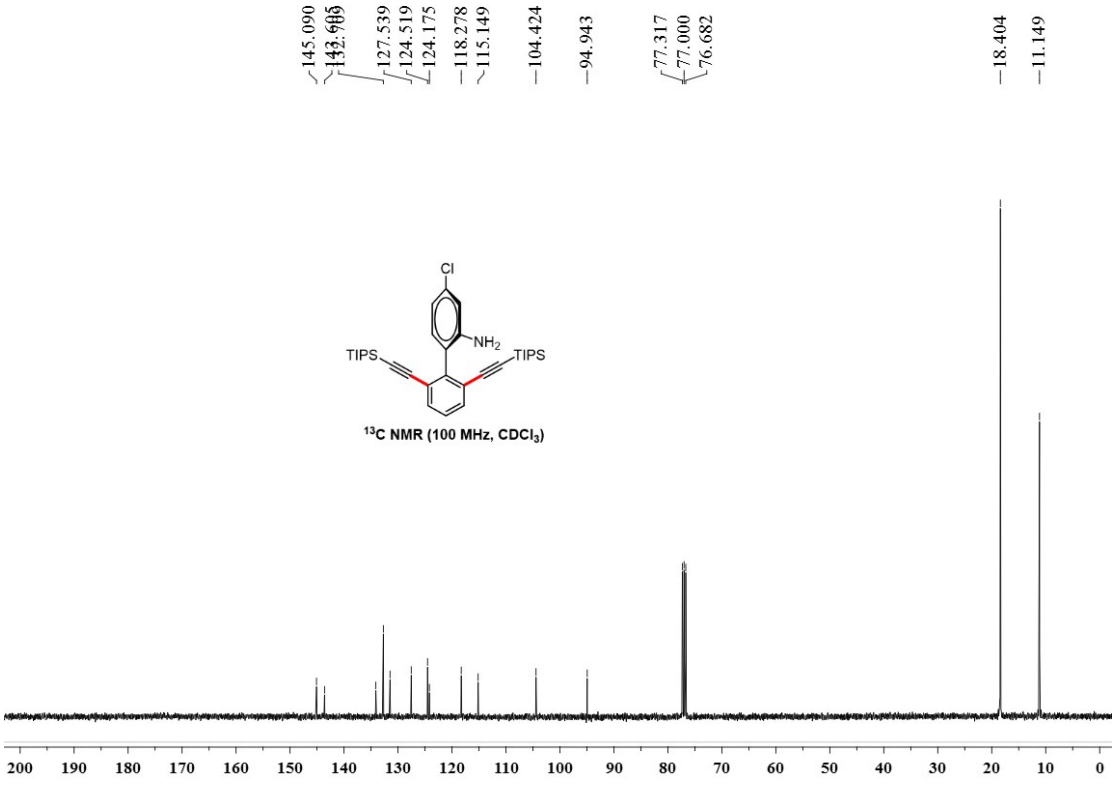




4-Chloro-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4q)

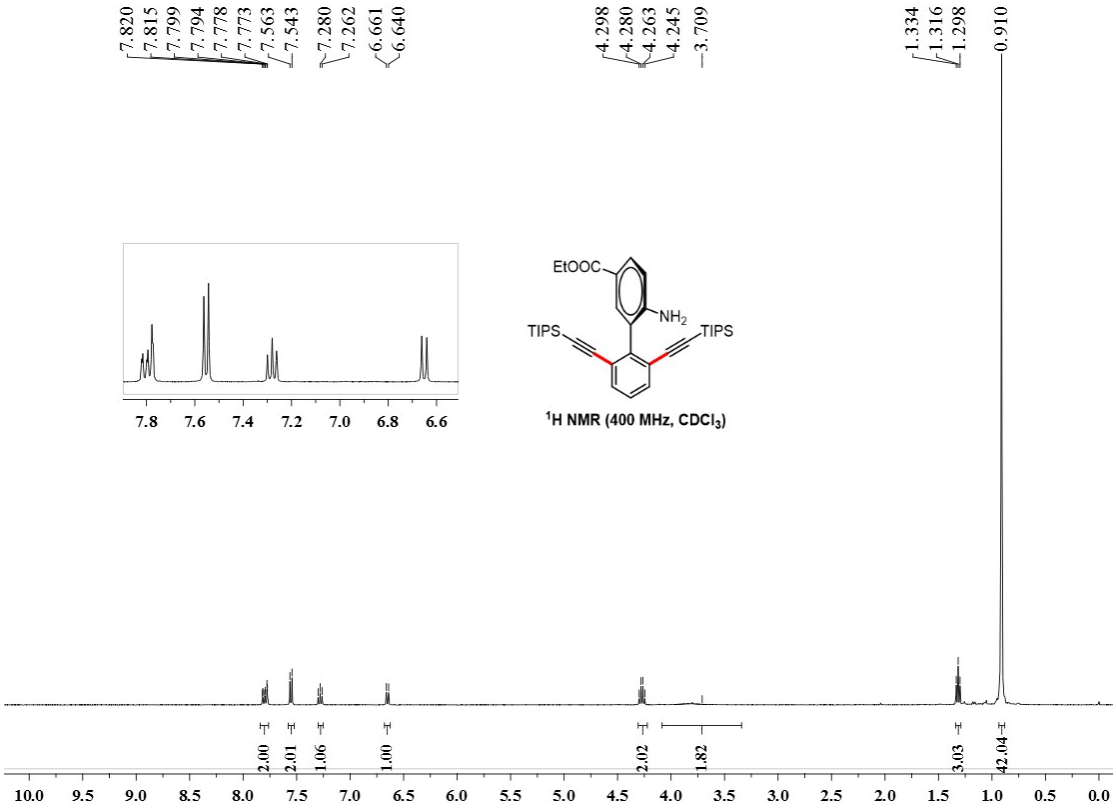


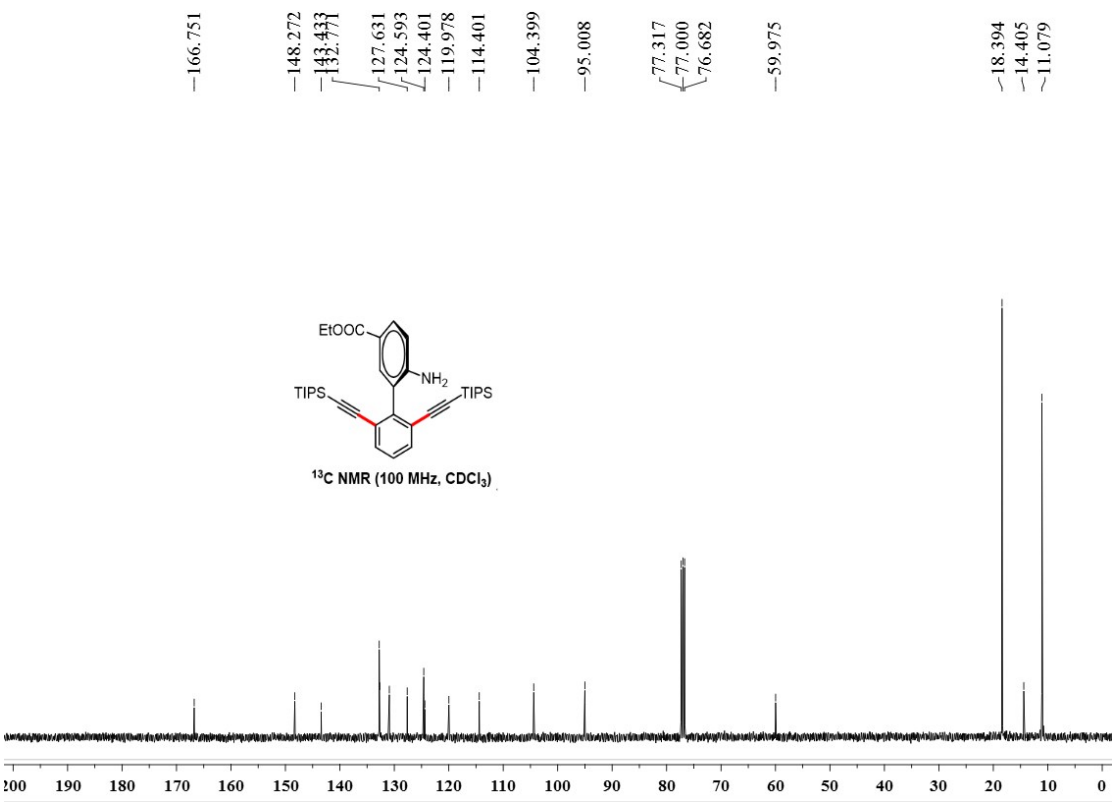
¹H NMR (400 MHz, $CDCl_3$)



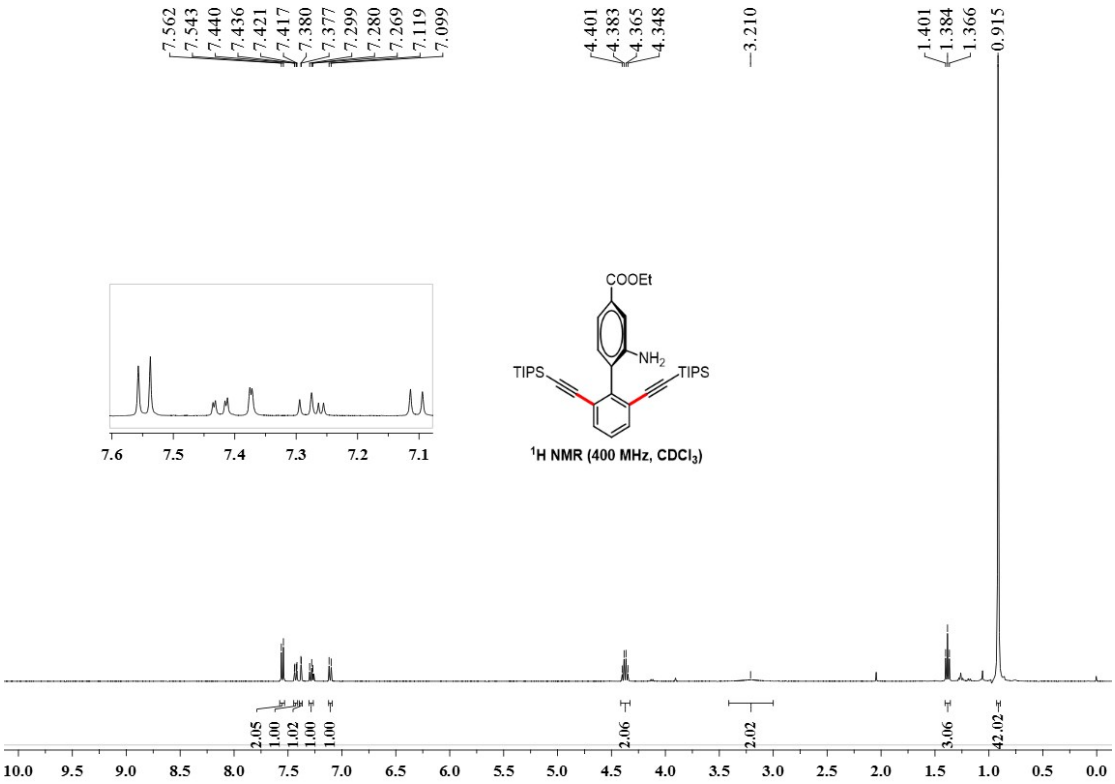
¹³C NMR (100 MHz, $CDCl_3$)

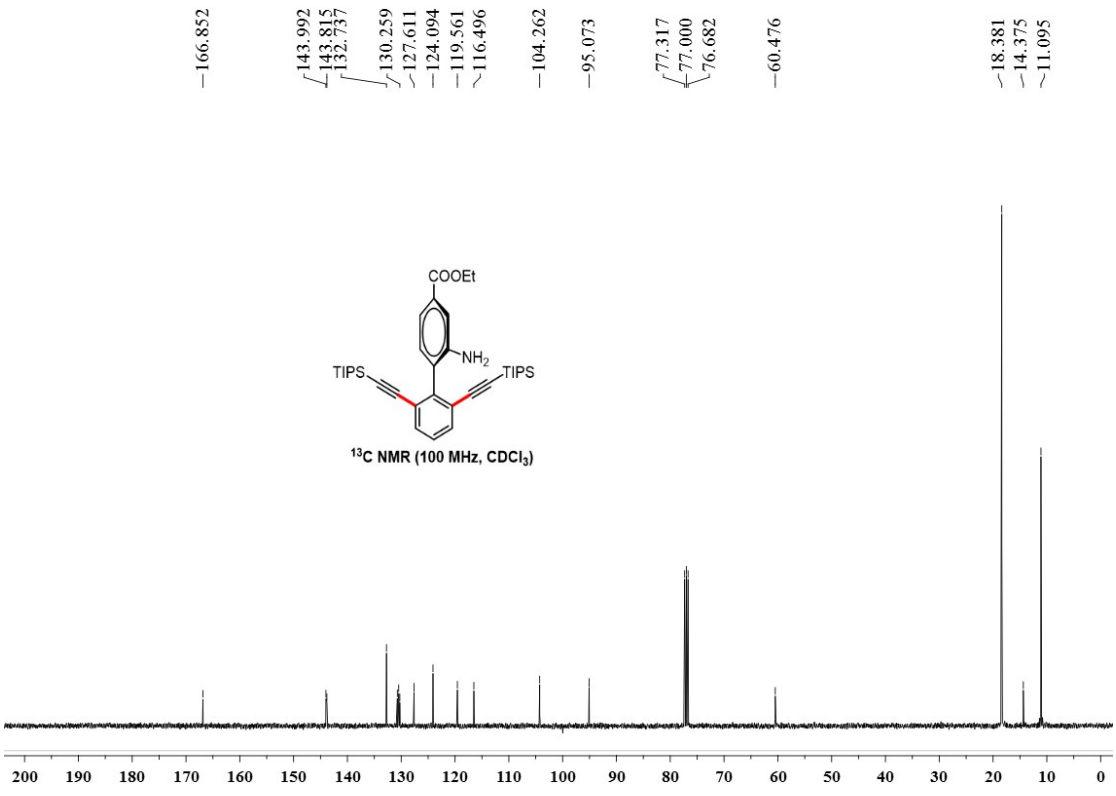
Ethyl 6-amino-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-3-carboxylate (4r)



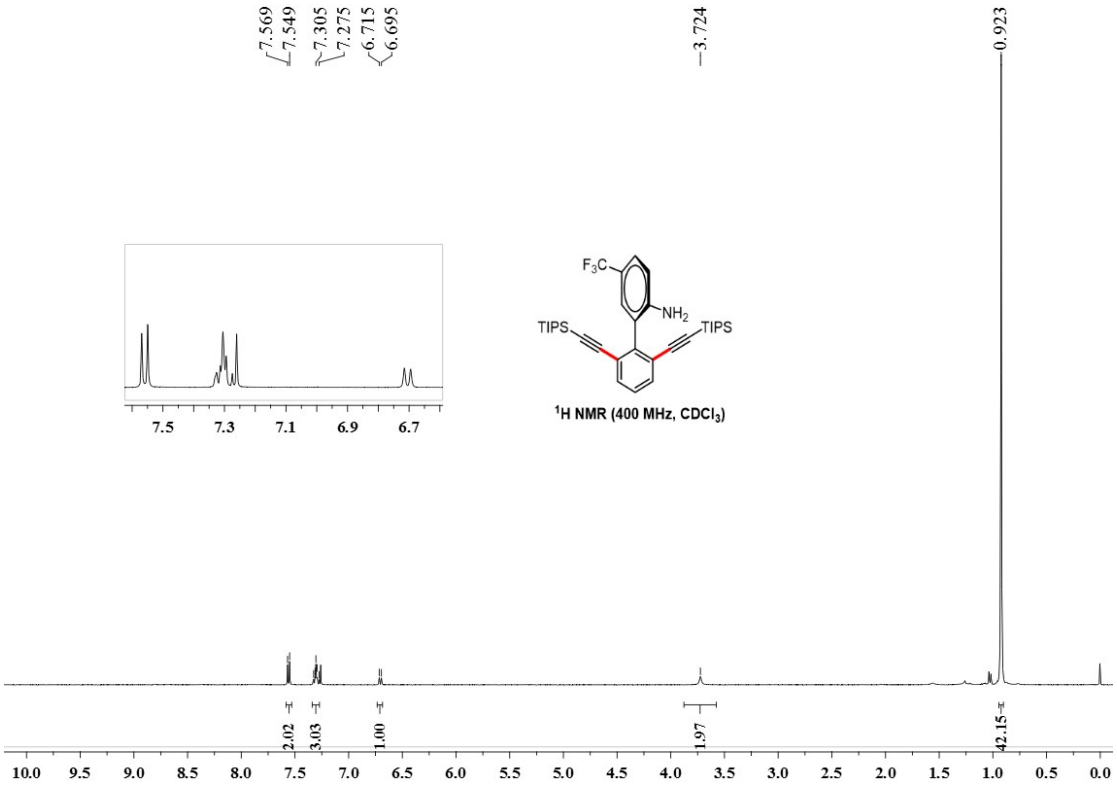


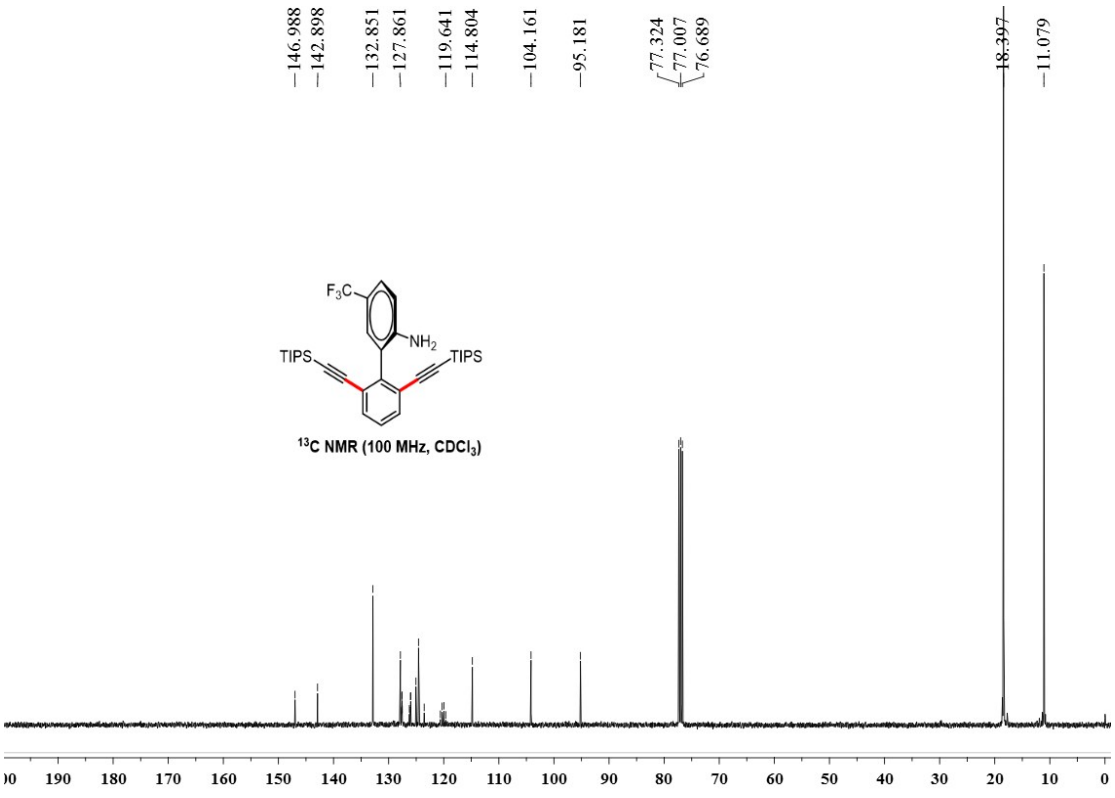
Ethyl 2-amino-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-4-carboxylate (4s)



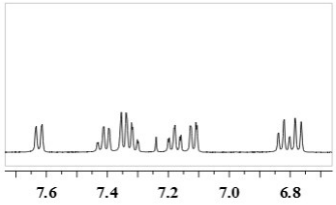


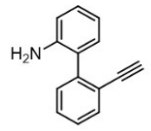
5-(Trifluoromethyl)-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4t)



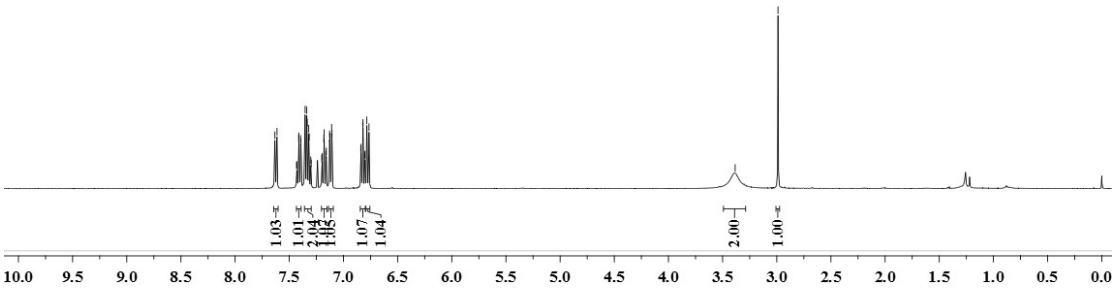


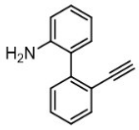
2′-Ethynyl-[1,1′-biphenyl]-2-amine (5a)



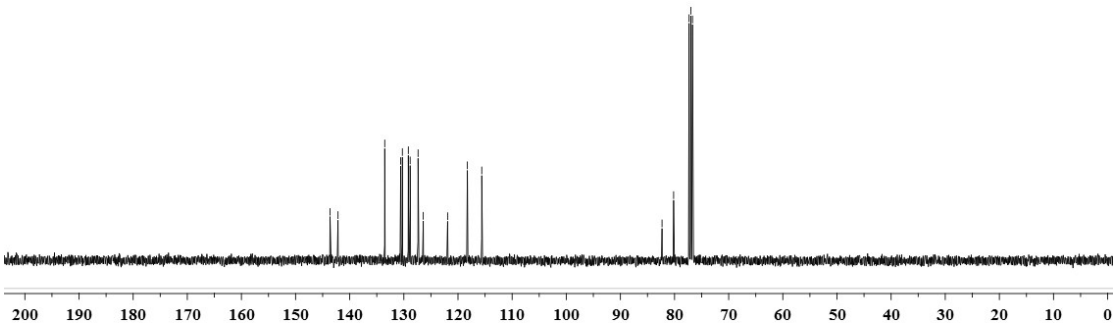


^{1}H NMR (400 MHz, $CDCl_3$)

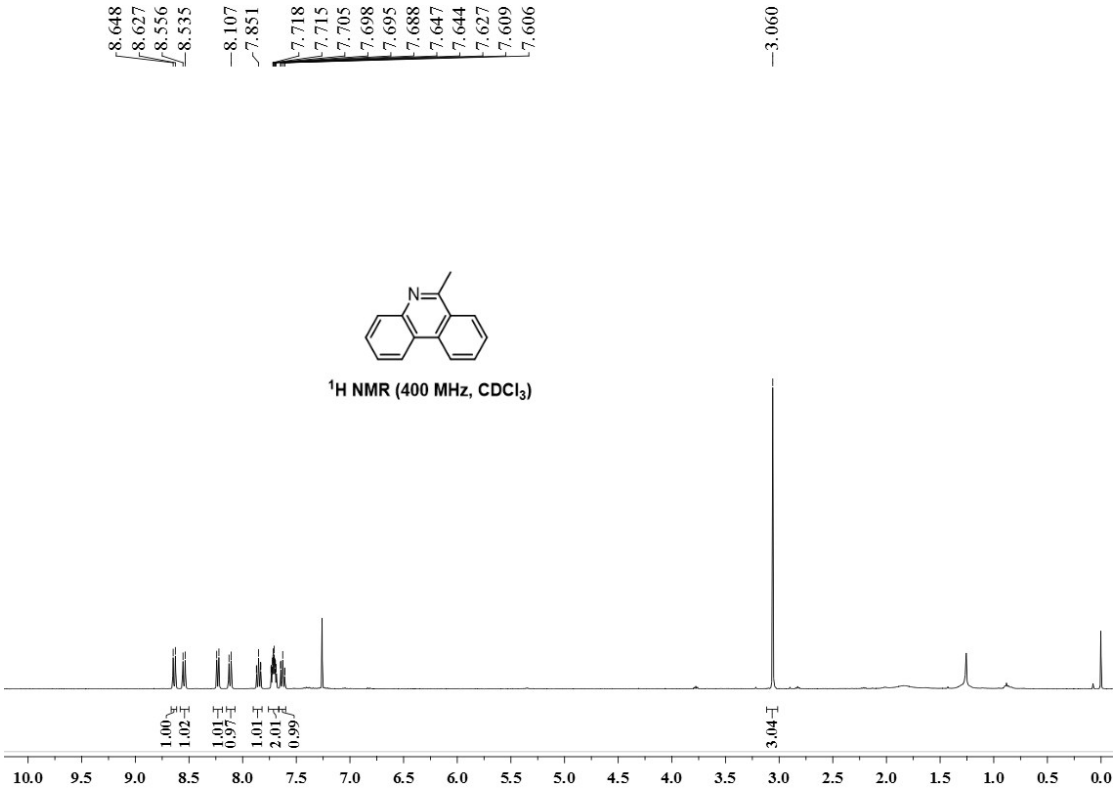


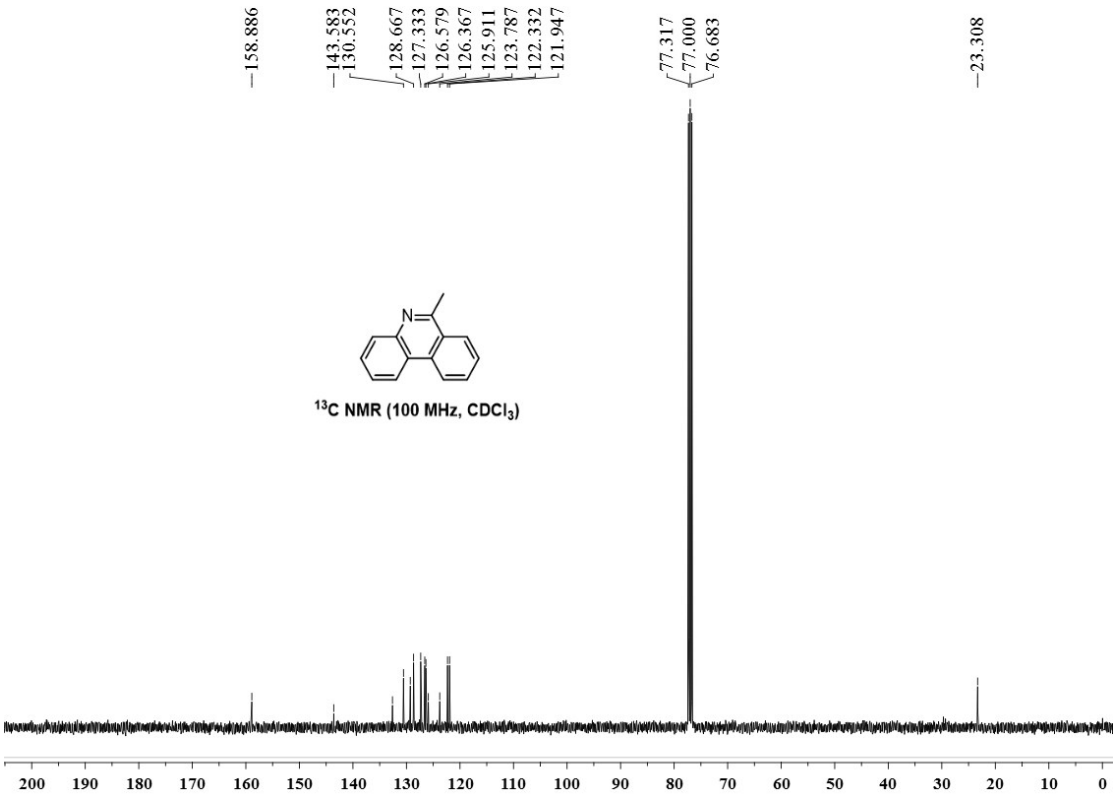


^{13}C NMR (100 MHz, $CDCl_3$)

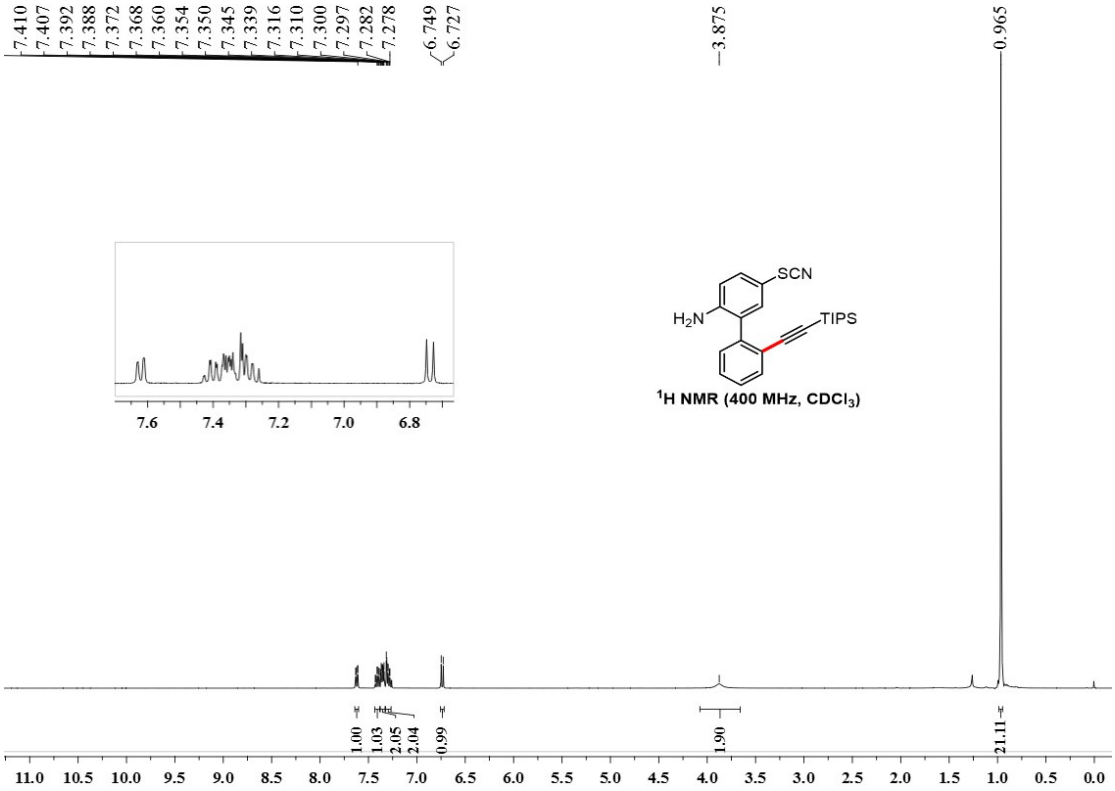


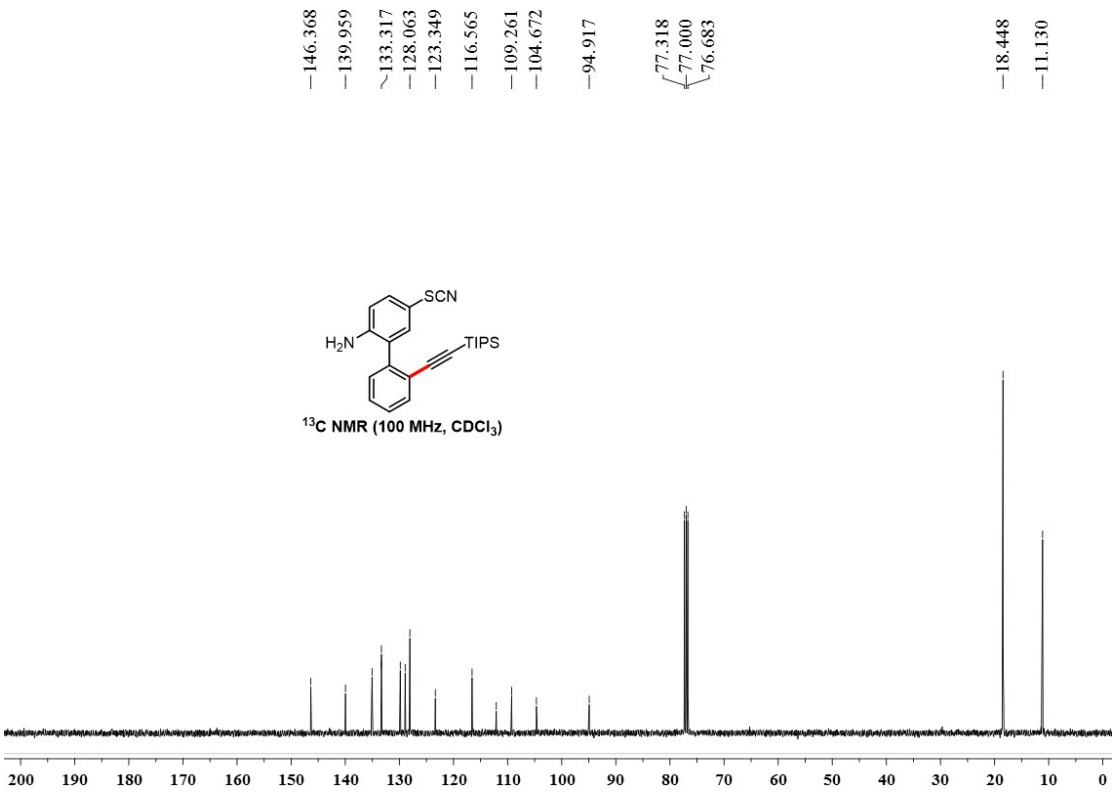
6-Methylphenanthridine (6a)



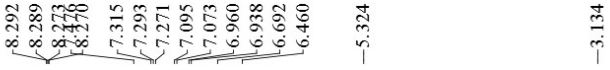


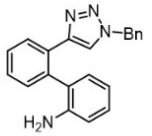
5-Thiocyanato-2'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (7a)



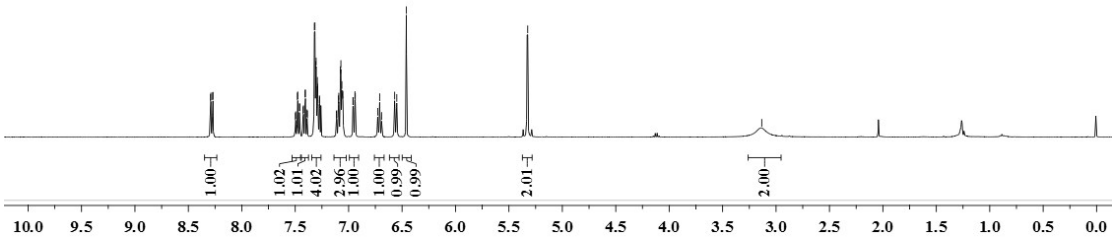


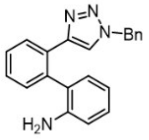
2′-(1-Benzyl-1H-1,2,3-triazol-4-yl)-[1,1′-biphenyl]-2-amine (8a)



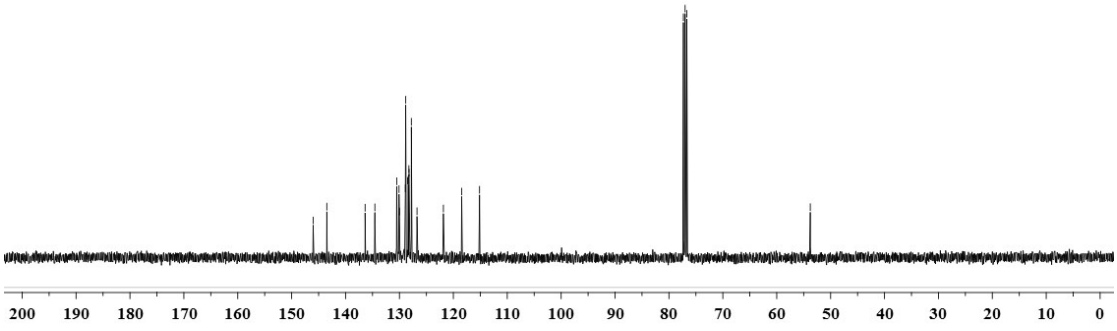


^{1}H NMR (400 MHz, $CDCl_3$)





^{13}C NMR (100 MHz, $CDCl_3$)



1-(2′-Amino-[1,1′-biphenyl]-2-yl)ethan-1-one (9a)