Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Palladium-Catalyzed Regioselective C−H Alkynylation of Indoles with Bromoalkynes in Water

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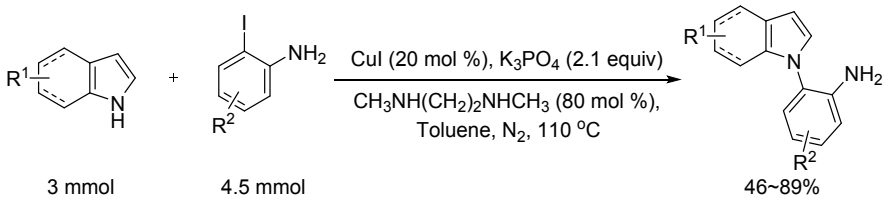
A. General Information

All purchased reagents and solvents were used without further purification unless otherwise noted. Analytical thin layer chromatography was performed by using commercially prepared 100-400 mesh silica gel plates (GF_{254}) and visualization was effected at 254 nm. All the haloalkynes were prepared according to known procedures. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker DRX-400 spectrometer using $CDCl_3$ as solvent. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. 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. Melting points were determined with a Büchi Melting Point B-545 instrument.

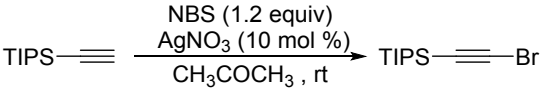
B. General Procedure for Synthesis of Starting Materials

(a) General Procedure for Synthesis of Starting Materials 1 [1]



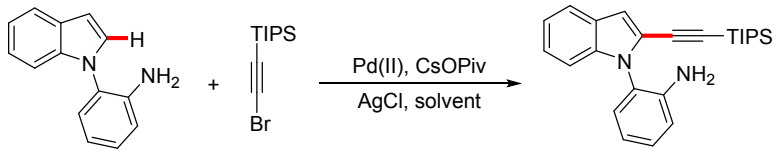
To a resealable Schlenk tube or alternatively, a screw-cap pressure tube, were added indole (3.0 mmol, 1.0 equiv), CuI (20 mol %), aromatic iodide (4.5 mmol, 1.5 equiv), *N,N′*-dimethylethylenediamine (80 mol %), K_3PO_4 (6.3 mmol, 2.1 equiv), toluene (5.0 mL) and a stir bar. The reaction vessel was fitted with a rubber septum, and was evacuated and back-filled with nitrogen. The reaction tube was sealed and immersed in a preheated oil bath at 110 °C for 24 h and the solution was stirred with the aid of a magnetic stirrer. After attaining ambient temperature, the reaction mixture was diluted with ethyl acetate and filtered through a plug of silica gel. The filtrate was concentrated and the resulting residue was purified by column chromatography (silica gel, petroleum ether /EtOAc) to give the desired substrates.

(b) General Procedure for Synthesis of Starting Material 2a



The ethynyltriisopropylsilane (20 mmol, 1.0 equiv) is dissolved in acetone (40.0 mL). *N*-bromosuccinimide (1.2 equiv) and $AgNO_3$ (10 mol %) are added to the resulting solution in this order and the mixture is stirred at rt for 4-8 h. The reaction mixture was filtered and the filtrate was concentrated. The residue was dissolved in 40.0 mL hexane and filtered again. The filtrate was concentrated under reduced pressure. The bromoalkyne **2a** was obtained as a colorless liquid (4.96 g, 95%) without further purification.

C. Optimization of Reaction Conditions[a]

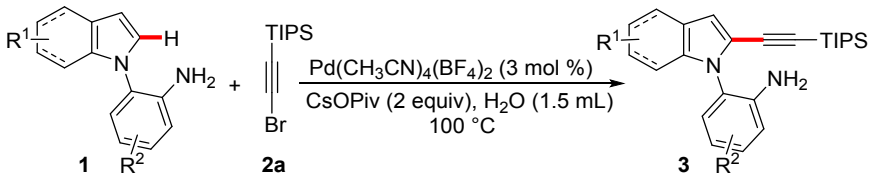


1a **2a** **3a**

entry	catalyst (mol %)	solvent (mL)		yield[b] (%)
		toluene	H_2O	
1	$Pd(CH_3CN)_4(BF_4)_2$ (10)	1.0	-	62
2	$Pd(CH_3CN)_4(BF_4)_2$ (5)	1.0	-	61
3	$Pd(CH_3CN)_4(BF_4)_2$ (5)	0.5	-	52
4	$Pd(CH_3CN)_4(BF_4)_2$ (5)	1.5	-	62
5	$Pd(CH_3CN)_4(BF_4)_2$ (5)	2.0	-	64
6	$Pd(CH_3CN)_4(BF_4)_2$ (5)	2.5	-	66
7	$Pd(CH_3CN)_4(BF_4)_2$ (5)	3.0	-	60
8	$Pd(CH_3CN)_4(BF_4)_2$ (5)	3.5	-	60
9	$Pd(CH_3CN)_4(BF_4)_2$ (5)	2.4	0.1	66
8	$Pd(CH_3CN)_4(BF_4)_2$ (5)	2.3	0.2	70
9	$Pd(CH_3CN)_4(BF_4)_2$ (5)	2.2	0.3	70
10	$Pd(CH_3CN)_4(BF_4)_2$ (5)	2.1	0.4	66
11	$Pd(CH_3CN)_4(BF_4)_2$ (5)	2.0	0.5	68
12	$Pd(CH_3CN)_4(BF_4)_2$ (5)	0.88	0.12	72
13	$Pd(CH_3CN)_4(BF_4)_2$ (4)	0.88	0.12	70
14	$Pd(CH_3CN)_4(BF_4)_2$ (3)	0.88	0.12	74
15	$Pd(CH_3CN)_4(BF_4)_2$ (1)	0.88	0.12	52
16[c]	$Pd(CH_3CN)_4(BF_4)_2$ (3)	1.32	0.18	76

[a] Conditions: Unless otherwise noted, all reactions were performed with **1a** (0.1 mmol, 1 equiv), **2a** (1.6 equiv), $Pd(CH_3CN)_4(BF_4)_2$, AgCl (2 equiv) and CsOPiv (2 equiv) in solvent under air at 100 °C for 24 h. [b] Determined by NMR using CH_2Br_2 as the internal standard. [c] **1a** (0.2 mmol), **2a** (0.32 mmol).

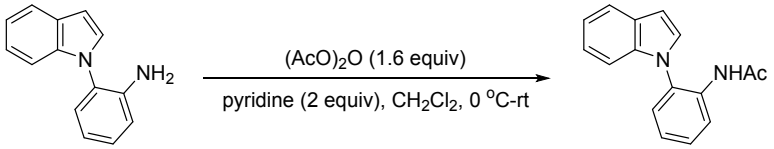
D. General Procedure for the Synthesis of 3



A mixture of *o*-indolylarylamines (**1**, 0.2 mmol), (bromoethynyl)triisopropylsilane (**2a**, 0.32 mmol), $Pd(CH_3CN)_4(BF_4)_2$ (3 mol %), CsOPiv (2.0 equiv) and 1.5 mL of H_2O was added to a test tube equipped with a magnetic stirring bar. The mixture was then stirred at 100 °C under air for 20~24 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.

E. The Reaction of *N*-Ac Type Substrate

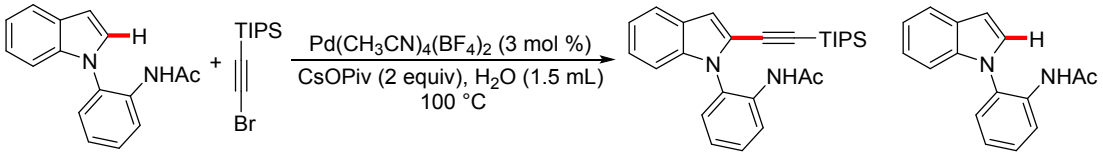
(a) Typical Procedure for the Synthesis of Starting Material 1am



1a, 3 mmol **1am**, 90%

A round-bottomed flask was added **1a** (3.0 mmol, 1.0 equiv), pyridine (6 mmol, 2 equiv), CH_2Cl_2 (5.0 mL) and a stir bar. Subsequently, $(AcO)_2O$ (4.8 mmol, 1.6 equiv) was added dropwise at 0 °C, and the resulting mixture was stirred for 4 h at room temperature. Then, the reaction mixture was diluted with ethyl acetate and washed with brine. The filtrate was concentrated and the resulting residue was purified by column chromatography (silica gel, petroleum ether/EtOAc = 15:1) to give the desired substrate **1am** in 90% yield.

(b) The Reaction of 1am and Bromoalkyne

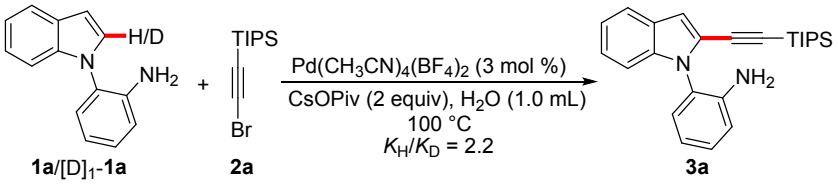


1am, 0.2 mmol **2a**, 0.32 mmol **3am**, 8% **1am**, 70%

A mixture of *N*-(2-(1*H*-indol-1-yl)phenyl)acetamide (**1am**, 0.2 mmol), (bromoethynyl)triisopropylsilane (**2a**, 0.32 mmol), $Pd(CH_3CN)_4(BF_4)_2$ (3 mol %), CsOPiv (2.0 equiv) and 1.5 mL of H_2O was added to a test tube equipped with a magnetic stirring bar. The mixture was stirred at 100 °C under air for 24 h. Then, the resulting mixture were cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired product **3am** and the starting material **1am** were obtained respectivly in 8%

and 70% yields after purification by column chromatography on silica gel with a mixture of petroleum ether and ethyl acetate (20: 1).

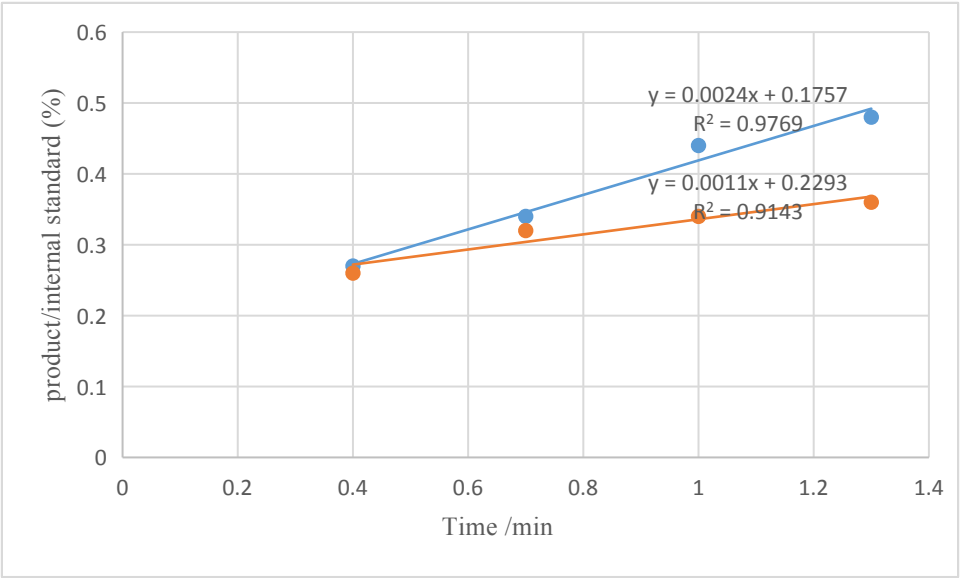
F. Mechanistic Studies



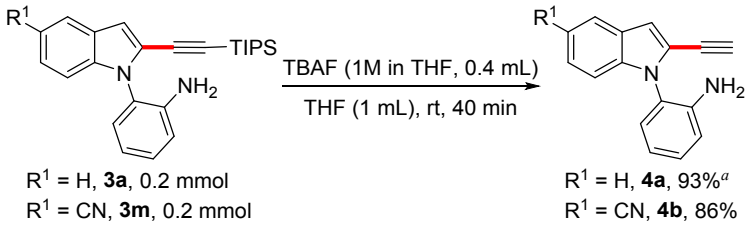
1a/[D]$_1$-**1a** **2a** **3a**

2-(1*H*-indol-1-yl)aniline (**1a**, 0.05 mmol) or 2-(1*H*-indol-1-yl-2-*d*)aniline ([D]$_1$-**1a**, 0.05 mmol) were added to two separate dried 25 mL test tube equipped with a magnetic stir bar along with (bromoethynyl)triisopropylsilane (**2a**, 0.08 mmol), $Pd(CH_3CN)_4(BF_4)_2$ (3 mol %), CsOPiv (2 equiv), H_2O (1.0 mL) at 100 °C. Each of the reaction was stirred at 100 °C under air atmosphere for a selected period of time. Then, the reaction mixture was cooled to the room temperature, diluted with water (20 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and then analyzed by NMR using CH_2Br_2 as internal standard:

Time [min]	40	70	100	130
3a /%	0.27	0.34	0.44	0.48
[D]$_1$-**3a** /%	0.26	0.32	0.34	0.36



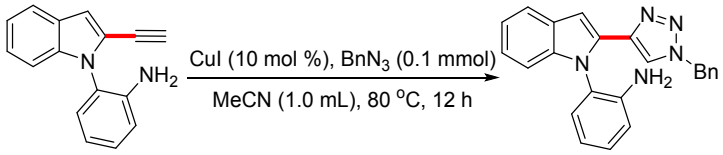
G. Futher Synthetic Applications



R^1 = H, **3a**, 0.2 mmol
R^1 = CN, **3m**, 0.2 mmol

R^1 = H, **4a**, 93%[a]
R^1 = CN, **4b**, 86%

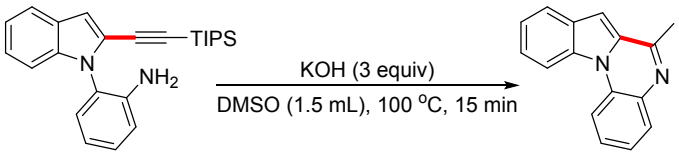
(a) 2-(2-((Triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (**3a**, 0.2 mmol) or 1-(2-aminophenyl)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-5-carbonitrile (**3m**, 0.2 mmol), TBAF (1 M in THF, 0.4 mL) and THF (1.0 mL) were added in a test tube under air atmosphere. Then the mixture was stirred at room temperature for 40 min. 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 product **4a** was obtained in 91% yield after purified by column chromatography on silica gel with a mixture of petroleum ether/ethyl acetate (v/v = 50/1), while **4b** was obtained in 86% yield after purified by column chromatography on silica gel with a mixture of petroleum ether/ethyl acetate (v/v = 30/1).



4a, 0.15 mmol

5a, 78%

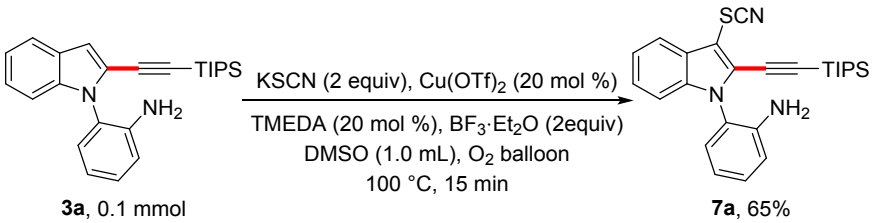
(b) **4a** (0.15 mmol), benzylazide (0.1 mmol, 1 equiv), CuI (10 mol %) and MeCN (1.0 mL) were added in a test tube under air atmosphere. Then the mixture was stirred at 80 °C for 12 h. After the reaction was completed (monitored by TLC), the resulting mixture was cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired product **5a** was obtained in 78% yield after purified by column chromatography on silica gel with a mixture of petroleum ether/ethyl acetate (v/v = 20/1).



3a, 0.2 mmol

6a, 79%

(c) 2-(2-((Triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (**3a**, 0.2 mmol), KOH (3 equiv) and DMSO (1.5 mL) were added in a test tube under air atmosphere. After this, the mixture was stirred at 100 °C for 15 min. 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 product **6a** was obtained in 79% yield after purified by column chromatography on silica gel with a mixture of petroleum ether/ethyl acetate (v/v = 5/1).



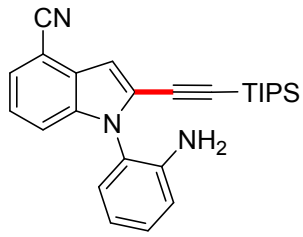
3a, 0.1 mmol **7a**, 65%

(d) 2-(2-((Triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (**3a**, 0.1 mmol), KSCN (2 equiv), $Cu(OTf)_2$ (20 mol %), TMEDA (20 mol %) and $BF_3{\cdot}Et_2O$ were mixed in DMSO and stirred under an O_2 balloon at 100 °C for 15 min. 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 product **7a** was obtained in 65% yield after purified by column chromatography on silica gel with a mixture of petroleum ether/ethyl acetate (v/v = 50/1).

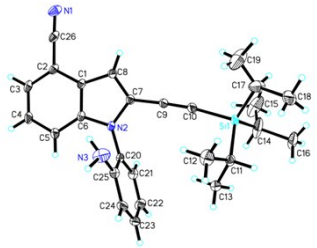
H. Reference

[1] N. T. Patil, R. D. Kavthe, V. S. Shinde, B. Sridhar, *J. Org. Chem.*, 2010, **75**, 3371.

I. X-ray Crystallographic Analysis



3g

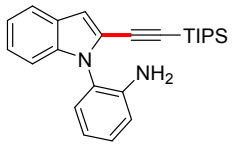


CCDC: 1857021

Empirical formula	$C_{26}H_{31}N_3Si$
Formula weight	413.63
Temperature	100.00(10) K
Wavelength	0.71073 *Å*
Crystal system, space group	monoclinic, C2/c
Unit cell dimensions	a = 41.982 (2) *Å* alpha = 90 deg. b = 8.4505(2) *Å* beta = 123.085(8) deg. c = 16.3226(9) *Å* gamma = 90 deg.
Volume	4851.9(5) *Å*^{3}
Z, Calculated density	8, 1.133 g/cm^3
Absorption coefficient	0.113 mm^{-1}
F(000)	1776.0
Crystal size	0.12 × 0.11 × 0.1 mm^3
Theta range for data collection	4.462 to 49.998 deg.
Limiting indices	-49 ≤ h ≤ 49, -10 ≤ k ≤ 10, -19 ≤ l ≤ 19
Reflections collected / unique	24245 / 4265 [R(int) = 0.1763]
Completeness to theta = 26.32	99.94%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4265/7/278
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R_1 = 0.0955, wR_2 = 0.2461
R indices (all data)	R_1 = 0.1040, wR_2 = 0.2565

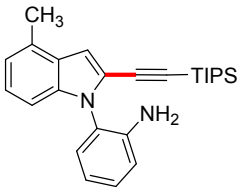
J. Characterization Data for All Products

2-(2-((Triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3a)



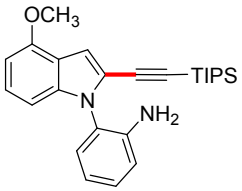
Brown solid (80%, 62.1 mg); mp: 57-58 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 3380, 2942, 2151, 1615, 1456, 1311, 1227, 799, 713 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.6 Hz, 1H), 7.26-7.08 (m, 4H), 7.00 (d, J = 8.0 Hz, 1H), 6.94 (s, 1H), 6.86-6.75 (m, 2H), 3.28 (s, 2H), 0.96 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 137.2, 130.0, 129.6, 127.3, 123.6, 123.1, 122.5, 121.0, 120.8, 118.4, 116.1, 110.7, 109.0, 97.7, 97.4, 18.4, 11.1; HRMS (ESI) m/z: calcd for $C_{25}H_{33}N_2Si$ $[M+H]^+$, 389.2408; found 389.2412.

2-(4-Methyl-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3b)



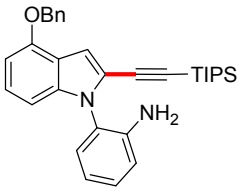
Brown solid (67%, 53.8 mg); mp: 75-76 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 3670, 2941, 2150, 1619, 1504, 1308, 1228, 796, 713 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.21 (m, 1H), 7.17 (dd, J = 7.7 Hz, 1H), 7.14-7.10 (t, J = 7.8 Hz, 1H), 7.00 (s, 1H), 6.97 (d, J = 7.2 Hz, 1H), 6.87 - 6.80 (m, 3H), 3.50 (s, 2H), 2.58 (s, 3H), 0.98 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 137.0, 130.6, 130.0, 129.6, 127.2, 123.8, 123.3, 121.9, 120.9, 118.4, 116.1, 108.4, 107.6, 97.8, 97.2, 18.6, 18.4, 11.1; HRMS (ESI) m/z: calcd for $C_{26}H_{35}N_2Si$ $[M+H]^+$, 403.2564, found 403.2566.

2-(4-Methoxy-2-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)aniline (3c)



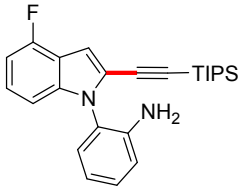
Brown oil (56%, 46.8 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 60/1); IR: ν = 3378, 2940, 2149, 1610, 1494, 1313, 1250, 798, 675 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.19 (m, 1H), 7.16 (d, J = 7.7 Hz, 1H), 7.11 (t, J = 8.0 Hz, 1H), 7.05 (s, 1H), 6.83-6.78 (m, 2H), 6.62 (d, J = 8.4 Hz, 1H), 6.53 (d, J = 7.6 Hz, 1H), 3.96 (s, 3H), 3.49 (s, 2H), 0.96 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 144.0, 138.5, 129.9, 129.6, 124.6, 123.2, 121.1, 118.4, 118.2, 116.1, 106.6, 104.0 100.4, 97.8, 96.8, 55.4, 18.4, 11.1; HRMS (ESI) m/z: calcd for $C_{26}H_{35}N_2OSi$ $[M+H]^+$, 419.2513, found 419.2514.

2-(4-(Benzyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3d)



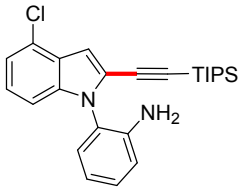
Brown oil (72%, 71.1 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 2946, 1578, 1497, 1305, 1232, 794, 717 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.2 Hz, 2H), 7.38 (t, J = 7.4 Hz, 2H), 7.31 (t, J = 7.3 Hz, 1H), 7.23-7.12 (m, 3H), 7.08 (t, J = 8.0, 1H), 6.79 (t, J = 7.4 Hz, 2H), 6.63 (d, J = 8.3 Hz, 1H), 6.58 (d, J = 7.8 Hz, 1H), 5.21 (s, 2H), 3.25 (s, 2H), 0.96 (s, 21H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 144.0, 138.6, 137.4, 129.9, 129.6, 128.5, 127.8, 127.3, 124.5, 123.2, 121.1, 118.5, 118.3, 116.1, 106.8, 104.2, 101.7, 97.7, 96.8, 69.9, 18.4, 11.1.; HRMS (ESI) m/z: calcd for $C_{32}H_{39}N_2OSi$ $[M+H]^+$, 495.2826, found 495.2832.

2-(4-Fluoro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3e)



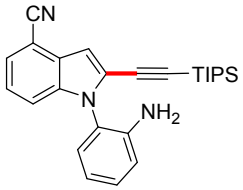
Brown solid (74%, 60.1 mg); mp: 75-76 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 3388, 2945, 2154, 1687, 1488, 1313, 1234, 788, 675 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 - 7.21 (m, 1H), 7.17-7.15 (m, 1H), 7.12-7.07 (m, 1H), 7.01 (s, 1H), 6.85-6.77 (m, 4H), 3.34 (s, 2H), 0.96 (d, J = 2.4 Hz, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1 (d, J = 248.8 Hz), 143.9, 139.4 (d, J = 10.5 Hz), 129.9 (d, J = 4.7 Hz), 124.1 (d, J = 7.7 Hz), 122.8, 122.6, 118.6, 116.6 (d, J = 22.8 Hz), 116.3, 106.8 (d, J = 3.8 Hz), 105.5, 105.3, 104.8, 97.9, 97.0, 18.4, 11.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -121.52 (dd, J = 10.1, 5.2 Hz); HRMS (ESI) m/z: calcd for $C_{25}H_{32}FN_2Si$ $[M+H]^+$, 407.2313, found 407.2319.

2-(4-Chloro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3f)



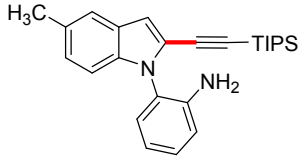
Brown solid (82%, 69.2mg); mp: 88-89 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 2946, 2154, 1613, 1503, 1309, 1228, 796, 713 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.20 (m, 1H), 7.15-7.12 (m, 2H), 7.08 (t, J = 7.8 Hz, 1H), 7.04 (s, 1H), 6.89 (d, J = 8.0 Hz, 1H), 6.83-6.78 (m, 2H), 3.44 (s, 2H), 0.96 (d, J = 2.3 Hz, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 137.8, 129.9, 129.8, 126.2, 126.1, 124.1, 123.2, 122.6, 120.5, 118.5, 116.2, 109.4, 107.3, 98.3, 97.0, 18.4, 11.1.; HRMS (ESI) m/z: calcd for $C_{25}H_{32}ClN_2Si$ $[M+H]^+$, 423.2018, found 423.2024.

1-(2-Aminophenyl)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-4-carbonitrile (3g)



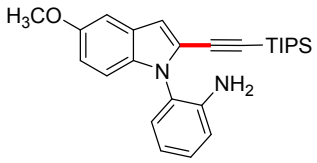
Brown solid (85%, 70.2 mg); mp: 175-176 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 50/1); IR: ν = 3372, 2943, 2223, 1622, 1507, 1314, 1229, 793, 671 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.48 (m, 1H), 7.28-7.22 (m, 3H), 7.15-7.13 (m, 2H), 6.87-6.81 (m, 2H), 3.11 (s, 2H), 0.97 (t, J = 4.0 Hz, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 136.7, 130.3, 129.7, 128.5, 126.3, 125.2, 123.1, 121.9, 118.6, 118.2, 116.4, 115.5, 107.2, 103.2, 100.2, 96.3, 18.4, 11.0; HRMS (ESI) m/z: calcd for $C_{26}H_{32}N_3Si$ $[M+H]^+$, 414.2360, found 414.2365.

2-(5-Methyl-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3h)



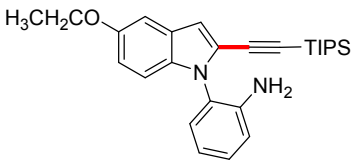
Brown oil (76%, 61.1 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 2945, 2150, 1615, 1458, 1308, 1228, 797, 716 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.22-7.17 (m, 1H), 7.16-7.14 (m, 1H), 7.03-7.00 (m, 1H), 6.89 (d, J = 8.4 Hz, 1H), 6.85 (s, 1H), 6.81-6.77 (m, 2H), 3.46 (s, 2H), 2.43 (s, 3H), 0.96 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 135.6, 130.1, 130.0, 129.5, 127.5, 125.4, 123.2, 122.4, 120.5, 118.4, 116.1, 110.4, 108.5, 97.8, 97.1, 21.4, 18.4, 11.1; HRMS (ESI) m/z: calcd for $C_{26}H_{35}N_2Si$ $[M+H]^+$, 403.2564, found 403.2568.

2-(5-Methoxy-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3i)



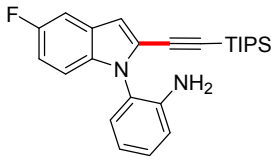
Brown oil (67%, 56.1 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 60/1); IR: ν = 3373, 2941, 2149, 1617, 1458, 1306, 1218, 798, 716 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.17 (m, 1H), 7.15 (dd, J = 7.7, 1.2 Hz, 1H), 7.04 (d, J = 2.1 Hz, 1H), 6.90 (d, J = 8.9 Hz, 1H), 6.86-6.83 (m, 2H), 6.81-6.77 (m, 2H), 3.84 (s, 3H), 3.39 (s, 2H), 0.96 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 144.0, 132.5, 123.0, 129.5, 127.6, 123.2, 122.8, 118.44, 116.1, 114.3, 111.5, 108.5, 102.0, 97.8, 97.2, 55.8, 18.4, 11.1; HRMS (ESI) m/z: calcd for $C_{26}H_{35}N_2OSi$ $[M+H]^+$, 419.2513, found 419.2519.

2-(5-Ethoxy-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3j)



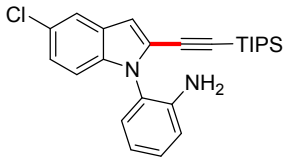
Brown oil (58%, 50.1 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 60/1); IR: ν = 3363, 2938, 2149, 1616, 1457, 1304, 1199, 796, 717 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.18 (m, 1H), 7.15 (dd, J = 7.7 Hz, 1.3, 1H), 7.04 (d, J = 2.0, 1H), 6.90 (d, J = 8.9 Hz, 1H), 6.8-6.84 (m, 2H), 6.82-6.77 (m, 2H), 4.06 (q, J = 7.0 Hz, 2H), 3.26 (s, 2H), 1.42 (t, J = 6.8 Hz, 3H), 0.96 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 144.0, 132.5, 123.0, 129.5, 127.6, 123.2, 122.7, 118.4, 116.1, 114.8, 111.5, 108.5, 103.1, 97.8, 97.2, 64.0, 18.4, 15.0, 11.1; HRMS (ESI) m/z: calcd for $C_{27}H_{37}N_2OSi$ $[M+H]^+$, 433.2670, found 433.2676.

2-(5-Fluoro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3k)



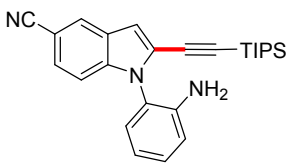
Brown solid (80%, 65.1 mg); mp: 59-60 ^{o}C; Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 2946, 2152, 1617, 1459, 1308, 1228, 795, 717 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.19 (m, 2H), 7.14 (dd, J = 7.7 Hz, 1.3, 1H), 6.90-6.90 (m, 2H), 6.88 (s, 1H), 6.83-6.78 (m, 2H), 3.44 (s, 2H), 0.96 (d, J = 2.2 Hz, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6 (d, J = 234.6 Hz), 143.0, 133.7, 129.8 (d, J = 10.1 Hz), 127.4 (d, J = 10.5 Hz), 124.0, 122.8, 118.5, 116.2, 112.3, 112.0, 111.5 (d, J = 9.5 Hz), 108.7 (d, J = 4.9 Hz), 105.5 (d, J = 23.6 Hz), 98.0, 97.2, 18.4, 11.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -123.47 (td, J = 8.9, 5.4 Hz); HRMS (ESI) m/z: calcd for $C_{25}H_{32}FN_2Si$ $[M+H]^+$, 407.2313, found 407.2320.

2-(5-Chloro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3l)



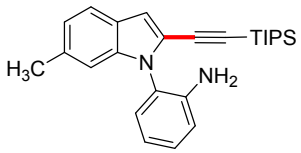
Brown oil (78%, 65.9 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 3379, 2941, 2152, 1616, 1451, 1311, 1228, 796, 717 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 2.0 Hz, 1H), 7.24-7.20 (m, 1H), 7.14-7.11 (m, 2H), 6.91 (d, J = 8.4 Hz, 1H), 6.86 (s, 1H), 6.83-6.78 (m, 2H), 3.45 (s, 2H), 0.95 (d, J = 2.0 Hz, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 135.5, 129.9, 129.8, 128.2, 126.5, 123.9, 123.8, 122.6, 120.2, 118.5, 116.2, 111.8, 108.3, 98.3, 97.0, 18.4, 11.1; HRMS (ESI) m/z: calcd for $C_{25}H_{32}ClN_2Si$ $[M+H]^+$, 423.2018, found 423.2012.

1-(2-Aminophenyl)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-5-carbonitrile (3m)



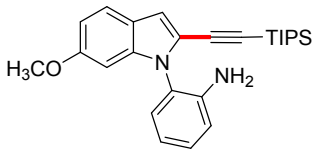
Brown solid (71%, 58.7 mg); mp: 141-142 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 50/1); IR: ν = 3373, 2942, 2222, 1615, 1460, 1312, 1230, 797, 719 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 0.6 Hz, 1H), 7.39-7.39 (m, 1H), 7.29-7.22 (m, 1H), 7.16-7.11 (m, 1H), 7.05 (d, J = 8.6 Hz, 1H), 6.98 (s, 1H), 6.88-6.80 (m, 2H), 3.33 (s, 2H), 0.96 (d, J = 3.0 Hz, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 138.6, 130.3, 129.6, 127.0, 126.4, 126.2, 125.0, 121.8, 120.2, 118.6, 116.4, 111.6, 109.0, 104.0, 99.7, 96.2, 18.3, 11.0; HRMS (ESI) m/z: calcd for $C_{26}H_{32}N_3Si$ $[M+H]^+$, 414.2360, found 414.2361.

2-(6-Methyl-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3n)



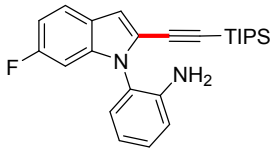
Brown oil (66%, 53.1 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 2947, 2149, 1606, 1505, 1305, 1230, 795, 718 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.1 Hz, 1H), 7.24-7.20 (m, 1H), 7.15 (dd, J = 7.7 Hz, 1.3, 1H), 6.97 (d, J = 8.0 Hz, 1H), 6.89 (d, J = 0.4 Hz, 1H), 6.84-6.79 (m, 1H), 3.43 (s, 2H), 2.38 (s, 3H), 0.96 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 137.6, 133.8, 130.0, 129.5, 125.1, 123.2, 122.7, 121.8, 120.6, 118.4, 116.1, 110.5, 108.9, 97.9, 97.0, 21.8, 18.4, 11.1; HRMS (ESI) m/z: calcd for $C_{26}H_{35}N_2Si$ $[M+H]^+$, 403.2564, found 403.2566.

2-(6-Methoxy-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3o)



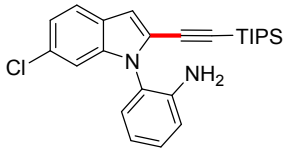
Brown solid (58%, 48.5 mg); mp: 57-58 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 60/1); IR: ν = 3378, 2945, 2147, 1616, 1498, 1306, 1237, 798, 717 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.4, 1H), 7.24-7.20 (m, 1H), 7.17 (dd, J = 7.6, 1.2 Hz, 1H), 6.87 (s, 1H), 6.85-6.79 (m, 3H), 6.44 (d, J = 2.0, 1H), 3.74 (s, 3H), 3.30 (s, 2H), 0.96 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 144.1, 138.1, 130.0, 129.6, 123.1, 121.6, 121.3, 118.5, 116.2, 111.5, 109.2, 97.9, 96.7, 93.4, 55.6, 18.5, 11.1; HRMS (ESI) m/z: calcd for $C_{26}H_{35}N_2OSi$ $[M+H]^+$, 419.2513, found 419.2519.

2-(6-Fluoro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3p)



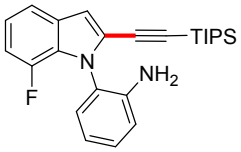
Brown solid (85%, 69.2 mg); mp: 48-49 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 2944, 2150, 1612, 1496, 1307, 1230, 799, 716 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.50 (m, 1H), 7.24-7.20 (m, 1H), 7.15-7.13 (m, 1H), 6.93-6.87 (m, 2H), 6.83-6.78 (m, 2H), 6.70-6.67 (m, 1H), 3.48 (s, 2H), 0.96 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, J = 240.7 Hz), 143.9,137.4 (d, J = 12.3 Hz), 129.8 (d, J = 8.1 Hz), 123.6, 123.1 (d, J = 4.1 Hz), 122.6, 121.8 (d, J = 10.0 Hz), 118.5, 116.2, 109.8 (d, J = 24.9 Hz), 108.9, 97.6, 97.3, 92,2, 97.0, 18.4, 11.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.00 – -118.16 (m); HRMS (ESI) m/z: calcd for $C_{25}H_{32}FN_2Si$ $[M+H]^+$, 407.2313, found 407.2318.

2-(6-Chloro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3q)



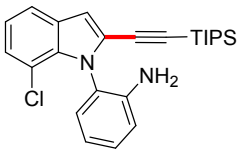
Brown oil (88%, 74.3 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 2944, 2151, 1609, 1452, 1311, 1224, 801, 711 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.8 Hz, 1H), 7.25-7.20 (m, 1H), 7.14-7.10 (m, 2H), 7.00 (s, 1H), 6.89 (s, 1H), 6.83-6.79 (m, 2H), 3.47 (s, 2H), 0.96 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 137.5, 129.9, 129.8, 125.7, 123.3, 122.4, 121.8, 121.6, 118.5, 116.2, 110.6, 108.8, 98.1, 97.1, 18.4, 11.1; HRMS (ESI) m/z: calcd for $C_{25}H_{32}ClN_2Si$ $[M+H]^+$, 423.2018, found 423.2012.

2-(7-Fluoro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3r)



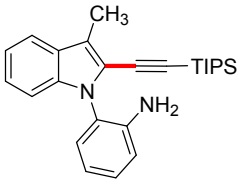
Brown solid (78%, 63.3 mg); mp: 68-69 ^{o}C; Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 2946, 2153, 1577, 1501, 1302, 1231, 795, 718 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.0 Hz, 1H), 7.22-7.17 (m, 2H), 7.04-7.00 (m, 1H), 6.93 (d, J = 2.3 Hz, 1H), 6.88-6.84 (m, 1H), 6.80-6.76 (m, 2H), 3.33 (s, 2H), 0.95 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5 (d, J = 245.2 Hz), 144.1, 131.0 (d, J = 4.5 Hz), 129.7, 129.5, 125.2 (d, J = 9.2 Hz), 124.6 (d, J = 0.9 Hz), 124.1, 120.8 (d, J = 6.3 Hz), 118.1, 116.8 (d, J = 3.9 Hz), 115.8, 109.4 (d, J = 1.9 Hz), 109.1 (d, J = 17.2 Hz), 98.1, 96.7, 18.4, 11.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -134.97– -135.01 (m); HRMS (ESI) m/z: calcd for $C_{25}H_{32}FN_2Si$ $[M+H]^+$, 407.2313, found 407.2321.

2-(7-Chloro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3s)



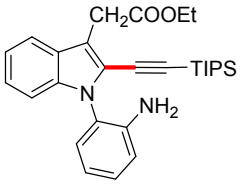
Brown solid (70%, 59.0 mg); mp: 89-90 ^{o}C; Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 2945, 2154, 1693, 1606, 1308, 1226, 796, 713 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.6 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.12-7.17 (m, 2H), 7.03 (t, J = 7.8 Hz, 1H), 6.93 (s, 1H), 6.77 (t, J = 7.8 Hz, 2H), 3.43 (s, 2H), 0.95 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 132.4, 130.5, 130.0, 129.8, 125.0, 124.6, 124.5, 121.3, 119.7, 117.9, 117.1, 115.5, 109.2, 98.3, 96.8, 18.4, 11.0; HRMS (ESI) m/z: calcd for $C_{25}H_{32}ClN_2Si$ $[M+H]^+$, 423.2018, found 423.2021.

2-(3-Methyl-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3t)



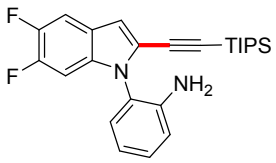
Brown solid (86%, 69.1 mg); mp: 80-81 ^{o}C; Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 2945, 2148, 1597, 1454, 1308, 1225, 797, 718 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.7 Hz, 1H), 7.22-7.11 (m, 4H), 6.99 (d, J = 8.0 Hz, 1H), 6.82-6.77 (m, 2H), 3.28 (s, 2H), 2.47 (s, 3H), 0.98 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 136.9, 130.0, 129.3, 127.6, 123.8, 123.4, 120.7, 120.1, 119.3, 118.7, 118.4, 116.1, 110.6, 99.6, 97.3, 18.5, 11.1, 9.9; HRMS (ESI) m/z: calcd for $C_{26}H_{35}N_2Si$ $[M+H]^+$, 403.2564, found 403.2569.

Ethyl 2-(1-(2-aminophenyl)-2-((triisopropylsilyl)ethynyl)-1*H*-indol-3-yl)acetate (3u)



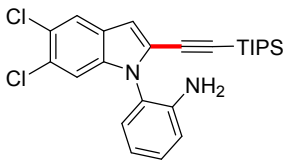
Brown solid (73%, 69.2 mg); mp: 67-68 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 60/1); IR: ν = 2940, 2150, 1733, 1505, 1308, 1158, 796, 717 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.64 (m, 1H), 7.23-7.13 (m, 4H), 7.01-6.99 (m, 1H), 6.82-6.77 (m, 2H), 4.17 (q, J = 7.1 Hz, 2H), 3.93 (s, 2H), 3.48 (s, 2H), 1.25 (t, J = 7.2 Hz, 3H), 0.98 (d, J = 2.4 Hz, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 143.9, 136.8, 129.9, 129.5, 126.8, 123.9, 123.0, 122.0, 120.6, 119.6, 118.2, 116.1, 115.0, 110.8, 100.5, 96.4, 60.7, 31.6, 18.4, 14.2, 11.1; HRMS (ESI) m/z: calcd for $C_{29}H_{39}N_2O_2Si$ $[M+H]^+$, 475.2775, found 475.2782.

2-(5,6-Difluoro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3v)



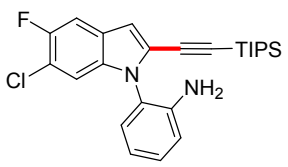
Brown oil (85%, 72.2 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 3726, 2953, 1303, 1229, 793, 717 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, J = 10.4, 7.7 Hz, 1H), 7.25-7.21 (m, 1H), 7.12 (dd, J = 7.7, 1.2 Hz, 1H), 6.87-6.73 (m, 4H), 3.48 (s, 2H), 0.95 (d, J = 2.4 Hz, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5 (dd, J = 199.0, 15.6 Hz), 147.1 (dd, J = 194.5, 15.5 Hz), 143.9, 132.6 (d, J = 10.0 Hz), 130.0, 129.7, 123.9 (d, J = 4.2 Hz), 122.4, 122.2-122.2 (m), 118.6, 116.3, 108.7 (dd, J = 4.4, 1.7 Hz), 107.2 (d, J = 19.5 Hz), 98.8 (d, J = 22.3 Hz), 98.1, 96.9, 18.4, 11.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -140.62– -140.73 (m), -145.98– -146.08 (m); HRMS (ESI) m/z: calcd for $C_{25}H_{31}F_2N_2Si$ $[M+H]^+$, 425.2219, found 425.2217.

2-(5,6-Dichloro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3w)



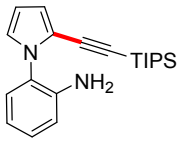
Brown oil (71%, 64.7 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 2950, 1612, 1306, 1227, 795, 716 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.26-7.22 (m, 1H), 7.13-7.10 (m, 2H), 6.84-6.79 (m, 3H), 3.47 (s, 2H), 0.95 (d, J = 2.4 Hz, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 135.9, 130.1, 129.7, 127.7, 126.7, 125.0, 124.5, 122.1, 121.7, 118.6, 116.3, 112.2, 108.0, 99.0, 96.6, 18.4, 11.0; HRMS (ESI) m/z: calcd for $C_{25}H_{31}Cl_2N_2Si$ $[M+H]^+$, 457.1628, found 457.1621.

2-(6-Chloro-5-fluoro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3x)



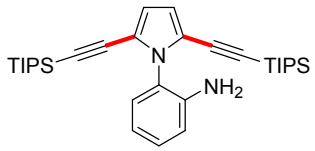
Brown solid (88%, 77.5 mg); mp: 71-72 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 3393, 2944, 2153, 1615, 1455, 1314, 1227, 796, 720 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 9.2 Hz, 1H), 7.26-7.22 (m, 1H), 7.14-7.11 (m, 1H), 7.02 (d, J = 6.0 Hz, 1H), 6.86-6.80 (m, 3H), 3.48 (s, 2H), 0.95 (d, J = 2.4 Hz, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7 (d, J = 239.3 Hz), 143.9, 133.5, 130.1, 129.8, 125.9 (d, J = 9.2 Hz), 124.5, 122.3, 118.6, 117.8 (d, J = 21.3 Hz), 116.3, 111.9, 108.6 (d, J = 4.8 Hz), 106.6 (d, J = 23.6 Hz), 98.8, 96.7, 18.4, 11.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.53– -125.57 (m); HRMS (ESI) m/z: calcd for $C_{25}H_{31}ClFN_2Si$ $[M+H]^+$, 441.1924, found 441.1927.

2-(2-((Triisopropylsilyl)ethynyl)-1*H*-pyrrol-1-yl)aniline (3y)



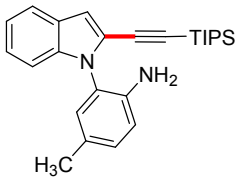
Brown oil (25%, 17.0 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 3356, 2926, 2145, 1624, 1458, 1161, 747, 468 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, J = 7.2, 2H), 6.75 (t, J = 7.8, 3H), 6.60 (d, J = 3.6, 1H), 6.25 (t, J = 3.2 Hz, 1H), 3.60 (s, 2H), 0.93 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 129.3, 128.7, 125.9, 123.9, 118.2, 116.6, 116.0, 115.7, 109.1, 97.8, 94.2, 18.4, 11.1; HRMS (ESI) m/z: calcd for $C_{21}H_{31}N_2Si$ $[M+H]^+$, 339.2251, found 339.2256.

2-(2,5-Bis((triisopropylsilyl)ethynyl)-1*H*-pyrrol-1-yl)aniline (3z)



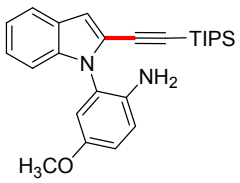
Brown oil (33%, 34.2 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 2944, 2145, 1460, 1306, 1229, 794, 716 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.08 (m, 2H), 6.73-6.69 (m, 2H), 6.49 (s, 2H), 3.50 (s, 2H), 0.92 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 129.6, 129.5, 124.3, 118.1, 118.0, 116.0, 115.0, 97.5, 94.8, 18.4, 11.1; HRMS (ESI) m/z: calcd for $C_{35}H_{51}N_2Si_2$ $[M+H]^+$, 519.3585, found 519.3591.

4-Methyl-2-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3aa)



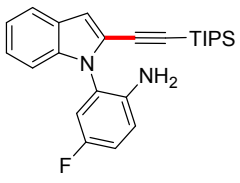
Brown oil (60%, 48.2 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 3673, 1695, 1306, 1226, 796, 715 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.8, 1H), 7.19 (t, J = 7.5 Hz, 1H), 7.13 (t, J = 7.3 Hz, 1H), 7.03-6.98 (m, 3H), 6.92 (s, 1H), 6.74 (d, J = 8.4 Hz, 1H), 3.07 (s, 2H), 2.24 (s, 3H), 0.97 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 137.1, 130.2, 127.8, 127.2, 123.6, 123.1, 122.5, 121.0, 120.7, 116.3, 110.8, 108.9, 97.8, 97.3, 20.2, 18.4, 11.1; HRMS (ESI) m/z: calcd for $C_{26}H_{35}N_2Si$ $[M+H]^+$, 403.2564, found 403.2569.

4-Methoxy-2-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3ab)



Brown oil (45%, 37.6 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 60/1); IR: ν = 3354, 2945, 1709, 1509, 1309, 797, 714 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.15 (t, J = 7.4 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 6.94 (s, 1H), 6.88-6.85 (m, 1H), 6.81 (d, J = 8.8 Hz, 1H), 6.76 (d, J = 2.4 Hz, 1H), 3.72 (s, 3H), 2.93 (s, 2H), 0.97 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 137.7, 137.1, 127.2, 123.7, 122.3, 121.0, 120.8, 117.5, 116.5, 114.5, 110.7, 109.0, 97.6, 97.5, 55.7, 18.4, 11.1; HRMS (ESI) m/z: calcd for $C_{26}H_{35}N_2OSi$ $[M+H]^+$, 419.2513, found 419.2518.

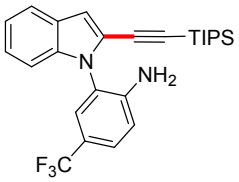
4-Fluoro-2-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3ac)



Brown oil (63%, 51.2 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 2946, 1587, 1507, 1309, 1224, 798, 713 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.6 Hz, 1H), 7.21 (t, J = 7.4 Hz, 1H), 7.15 (t, J = 7.4 Hz, 1H), 7.01-6.94 (m, 4H), 6.79-6.75 (m, 1H), 3.27 (s, 2H), 0.98 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3 (d, J = 236.4 Hz),

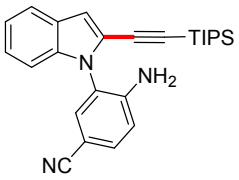
140.5 (d, J = 2.5 Hz), 136.9, 127.3, 123.9, 123.3 (d, J = 9.6 Hz), 122.2, 121.1, 121.0, 116.8 (d, J = 7.1), 116.6, 116.49 (d, J = 15.1 Hz), 110.6, 109.4, 98.0, 97.3, 18.4, 11.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.19 – -126.37 (m); HRMS (ESI) m/z: calcd for $C_{25}H_{32}FN_2Si$ $[M+H]^+$, 407.2313, found 407.2319.

4-(Trifluoromethyl)-2-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3ad)



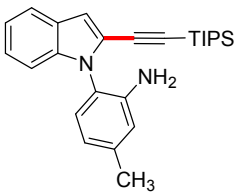
Brown solid (44%, 40.2 mg); mp: 60-61 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 50/1); IR: v = 2946, 1587, 1507, 1309, 1224, 798, 713 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.8 Hz, 1H), 7.47 (d, J = 9.2 Hz, 2H), 7.22 (t, J = 8.0 Hz, 1H), 7.16 (t, J = 7.2 Hz, 1H), 6.97 (d, J = 7.2, 2H), 6.87 (d, J = 8.0, 1H), 3.81 (s, 2H), 0.96 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 137.0, 127.7-127.6 (m), 127.5, 127.0 (q, J = 3.3 Hz), 125.6, 124.0, 122.9, 122.3, 122.2, 121.2, 120.3 (q, J = 33.2 Hz), 115.6, 110.5, 109.6, 98.2, 97.1, 18.4, 11.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.21 (s); HRMS (ESI) m/z: calcd for $C_{26}H_{32}F_3N_2Si$ $[M+H]^+$, 457.2281, found 457.2286.

4-Amino-3-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)benzonitrile (3ae)



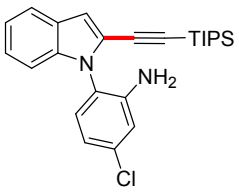
Brown oil (45%, 37.2 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 50/1); IR: v = 3061, 2951, 2221, 1697, 1511, 1308, 796, 715 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.6 Hz, 1H), 7.51-7.49 (m, 2H), 7.25-7.16 (m, 2H), 6.95 (d, J = 9.2 Hz, 2H), 6.84 (d, J = 8.8 Hz, 1H), 4.06 (s, 2H), 0.98 (d, J = 3.2 Hz, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 136.7, 134.5, 133.6, 127.4, 124.2, 122.5, 122.1, 121.4, 121.3, 119.0, 115.7, 110.3, 109.8, 100.3, 98.6, 96.8, 18.4, 11.0; HRMS (ESI) m/z: calcd for $C_{26}H_{32}N_3Si$ $[M+H]^+$, 414.2360, found 414.2357.

5-Methyl-2-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3af)



Brown oil (61%, 49.1 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: v = 3657, 2938, 2860, 1307, 795, 715 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 1H), 7.18 (t, J = 7.4 Hz, 1H), 7.13 (t, J = 7.2 Hz, 1H), 7.02 (t, J = 7.6, 2H), 6.92 (s, 1H), 6.65-6.59 (m, 2H), 3.35 (s, 2H), 2.31 (s, 3H), 0.96 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 139.6, 137.3, 129.7, 127.2, 123.5, 122.6, 120.9, 120.7, 120.6, 119.4, 116.6, 110.7, 108.7, 97.8, 97.2, 21.3, 18.4, 11.1; HRMS (ESI) m/z: calcd for $C_{26}H_{35}N_2Si$ $[M+H]^+$, 403.2564, found 403.2561.

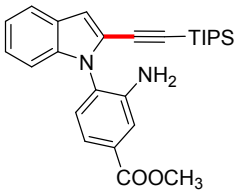
5-Chloro-2-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3ag)



Brown oil (56%, 47.2 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: v = 2949, 1588, 1500, 1307, 1226, 796, 715 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 1H), 7.24-7.18 (m, 1H), 7.14 (t, J = 7.4 Hz, 1H), 7.08 (d, J = 8.4 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.93 (s, 1H), 6.81 (s, 1H), 6.77 (d, J = 8.4 Hz, 1H), 3.42 (s, 2H), 0.98 (s, 21H);

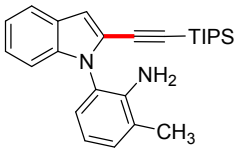
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 137.1, 135.2, 131.1, 127.3, 123.9, 122.4, 121.5, 121.1, 121.0, 118.3, 115.6, 110.5, 109.2, 97.9, 97.3, 18.4, 11.1; HRMS (ESI) m/z: calcd for $C_{25}H_{32}ClN_2Si$ $[M+H]^+$, 423.2018, found 423.2012.

Methyl 3-amino-4-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)benzoate (3ah)



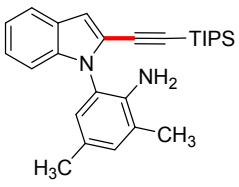
Brown solid (50%, 44.8 mg); mp: 104-105 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 50/1); IR: ν = 3378, 2946, 2150, 1720, 1444, 1308, 1234, 796, 715 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.6 Hz, 1H), 7.54 (s, 1H), 7.48 (d, J = 8.2 Hz, 1H), 7.25-7.19 (m, 2H), 7.16 (t, J = 7.4 Hz, 1H), 6.97 (d, J = 8.0 Hz, 2H), 3.94 (s, 3H), 3.67 (s, 2H), 0.95 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 144.0, 136.7, 131.1, 130.1, 127.4, 126.8, 123.9, 122.1, 121.1, 121.1, 119.3, 117.1, 110.6, 109.6, 98.0, 97.2, 52.2, 18.4, 11.0; HRMS (ESI) m/z: calcd for $C_{27}H_{35}N_2O_2Si$ $[M+H]^+$, 447.2462, found 447.2468.

2-Methyl-6-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3ai)



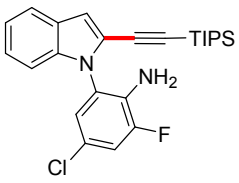
Brown solid (66%, 53.2 mg); mp: 89-90 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 3391, 2942, 2150, 1686, 1612, 1311, 1227, 795, 718 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 1H), 7.22-7.10 (m, 3H), 7.01 (m, 2H), 6.94 (s, 1H), 6.73 (t, J = 7.6 Hz, 1H), 3.36 (s, 2H), 2.20 (s, 3H), 0.94 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 137.4, 130.6, 127.5, 127.2, 123.6, 123.3, 122.7, 122.5, 120.9, 120.7, 117.7, 110.7, 108.8, 97.7, 97.2, 18.4, 18.4, 17.5, 11.1; HRMS (ESI) m/z: calcd for $C_{26}H_{35}N_2Si$ $[M+H]^+$, 403.2564, found 403.2569.

2,4-Dimethyl-6-(2-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)aniline (3aj)



Brown solid (73%, 60.7 mg); mp: 83-84 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 3385, 2941, 2151, 1694, 1599, 1312, 1228, 797, 717 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 1H), 7.18 (t, J = 7.4 Hz, 1H), 7.12 (t, J = 7.2 Hz, 1H), 6.99 (d, J = 8.0 Hz, 1H), 6.94 (s, 1H), 6.92 (s, 1H), 6.85 (s, 1H), 3.04 (s, 2H), 2.22 (s, 3H), 2.17 (s, 3H), 0.95 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 137.4, 131.4, 127.7, 127.2, 127.0, 123.5, 123.4, 122.9, 122.6, 120.9, 120.7, 110.8, 108.7, 97.9, 97.1, 20.2, 18.4, 17.5, 11.1; HRMS (ESI) m/z: calcd for $C_{27}H_{37}N_2Si$ $[M+H]^+$, 417.2721, found 417.2727.

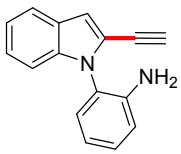
4-Chloro-2-fluoro-6-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3ak)



Brown solid (70%, 61.7 mg); mp: 85-86 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 100/1); IR: ν = 2947, 1700, 1580, 1498, 1305, 793, 718 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.6 Hz, 1H), 7.25-7.21 (m, 1H), 7.18-7.11 (m, 2H)., 7.04 (s, 1H), 7.00 (d, J = 8.0, 1H), 6.95 (s, 1H), 3.61 (s, 2H), 1.00 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$)

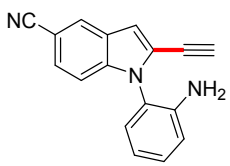
δ 151.4 (d, J = 240.8 Hz), 136.7, 132.4, 132.2, 127.4, 125.5 (d, J = 3.2), 124.7 (d, J = 6.3 Hz), 124.1, 122.1, 121.3 (d, J = 5.5 Hz), 121.1 (d, J = 11.7 Hz), 116.0 (d, J = 22.0 Hz), 110.5, 109.8, 98.5, 97.0, 18.4, 11.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -131.29 (d, J = 10.4 Hz); HRMS (ESI) m/z: calcd for $C_{25}H_{31}ClFN_2Si$ $[M+H]^+$, 441.1924, found 441.1927.

2-(2-Ethynyl-1*H*-indol-1-yl)aniline (4a)



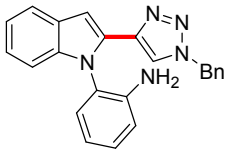
Brown solid (91%, 42.2 mg); mp: 90-91 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 50/1); IR: v = 3283, 3052, 1689, 1611, 1311, 1227, 796, 717 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 7.8 Hz, 1H), 7.31-7.26 (m, 1H), 7.25-7.15 (m, 3H), 7.02 (d, J = 6.4 Hz, 2H), 6.90-6.84 (m, 2H), 3.52 (s, 2H), 3.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 137.1, 129.8, 129.8, 127.1, 123.9, 122.1, 121.0, 121.0, 120.9, 118.3, 116.2, 110.8, 110.2, 82.9, 75.2; HRMS (ESI) m/z: calcd for $C_{16}H_{13}N_2$ $[M+H]^+$, 233.1073, found 233.1076.

1-(2-Aminophenyl)-2-ethynyl-1*H*-indole-5-carbonitrile (4b)



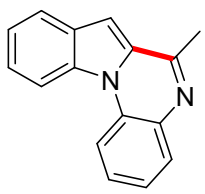
Brown solid (86%, 44.3 mg); mp: 153-154 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); IR: v = 3289, 3054, 2223, 1309, 798, 713 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 1.2Hz, 1H), 7.44-7.41 (m, 1H), 7.34-7.30 (m, 1H), 7.15 (dd, J = 7.8, 1.3 Hz, 1H), 7.07 (d, J = 8.8 Hz, 2H), 6.93-6.86 (m, 2H), 3.41 (s, 2H), 3.26 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 138.5, 130.5, 129.5, 126.8, 126.6, 126.5, 123.7, 121.5, 120.1, 118.7, 116.5, 111.9, 110.4, 104.3, 84.4, 73.9; HRMS (ESI) m/z: calcd for $C_{17}H_{12}N_3$ $[M+H]^+$, 258.1026, found 258.1022.

2-(2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)-1*H*-indol-1-yl)aniline (5a)



Brown solid (78%, 42.7 mg); mp: 185-186 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 20/1); IR: v = 3671, 3348, 3052, 1599, 1504, 1308, 1223, 798, 714 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.70 (m, 1H), 7.32 (d, J = 4.8 Hz, 4H), 7.25-7.22 (m, 1H), 7.18-7.10 (m, 4H), 7.05-7.00 (m, 2H), 6.79-6.73 (m, 2H), 6.57 (s, 1H), 5.42-5.33 (m, 2H), 2.81 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 140.4, 138.2, 134.4, 131.0, 130.2, 130.1, 129.0, 128.6, 128.3, 127.9, 122.9, 122.7, 121.0, 120.8, 119.8, 118.6, 116.1, 110.4, 102.7, 53.9; HRMS (ESI) m/z: calcd for $C_{23}H_{20}N_5$ $[M+H]^+$, 366.1713, found 366.1715.

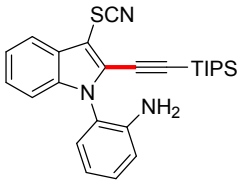
6-Methylindolo[1,2-*a*]quinoxaline (6a)



Brown solid (79%, 36.7 mg); mp: 112-113 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 5/1); IR: v = 3053, 1688, 1534, 1307, 1209, 798, 716 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (t, J = 7.8 Hz, 2H), 7.91 (t, J = 7.8 Hz, 2H), 7.54-7.47 (m, 2H), 7.42-7.36 (m, 2H), 7.08 (s, 1H), 2.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 135.7, 132.9, 130.2, 129.6, 129.4,

128.9, 127.7, 124.1, 123.9, 122.6, 122.5, 114.5, 114.5, 100.0, 22.2; HRMS (ESI) m/z: calcd for $C_{16}H_{13}N_2$ $[M+H]^+$, 233.1073, found 233.1075.

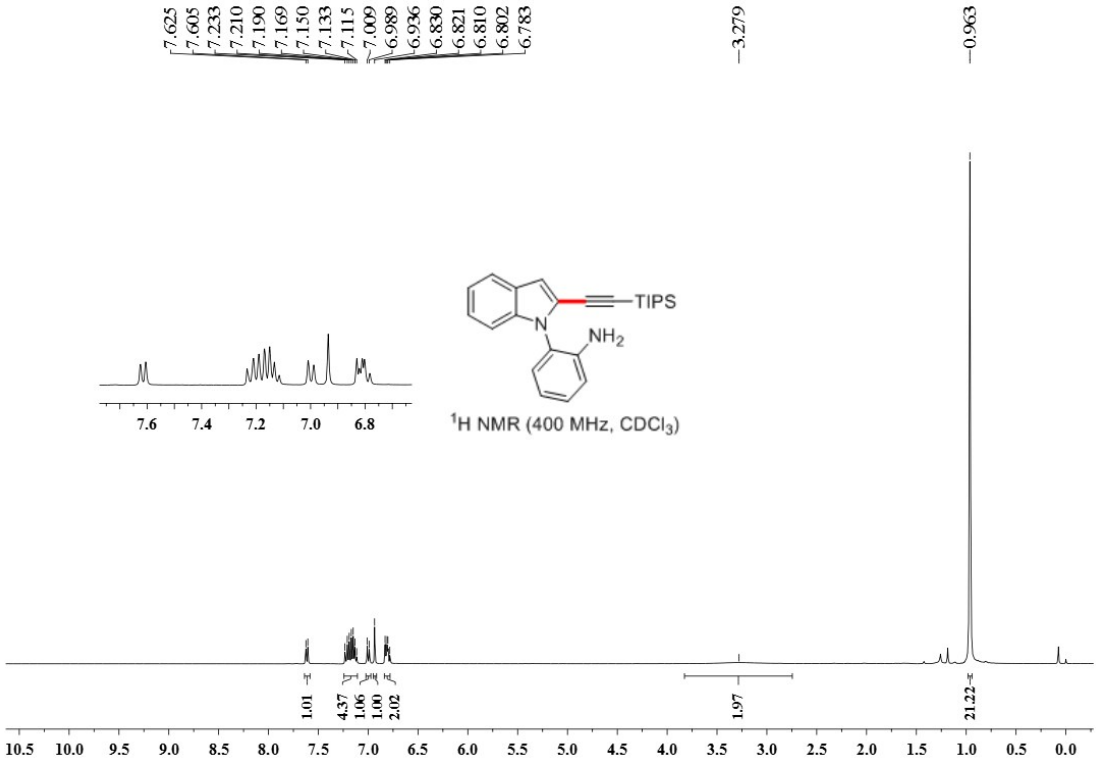
2-(3-Thiocyanato-2-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)aniline (7a)

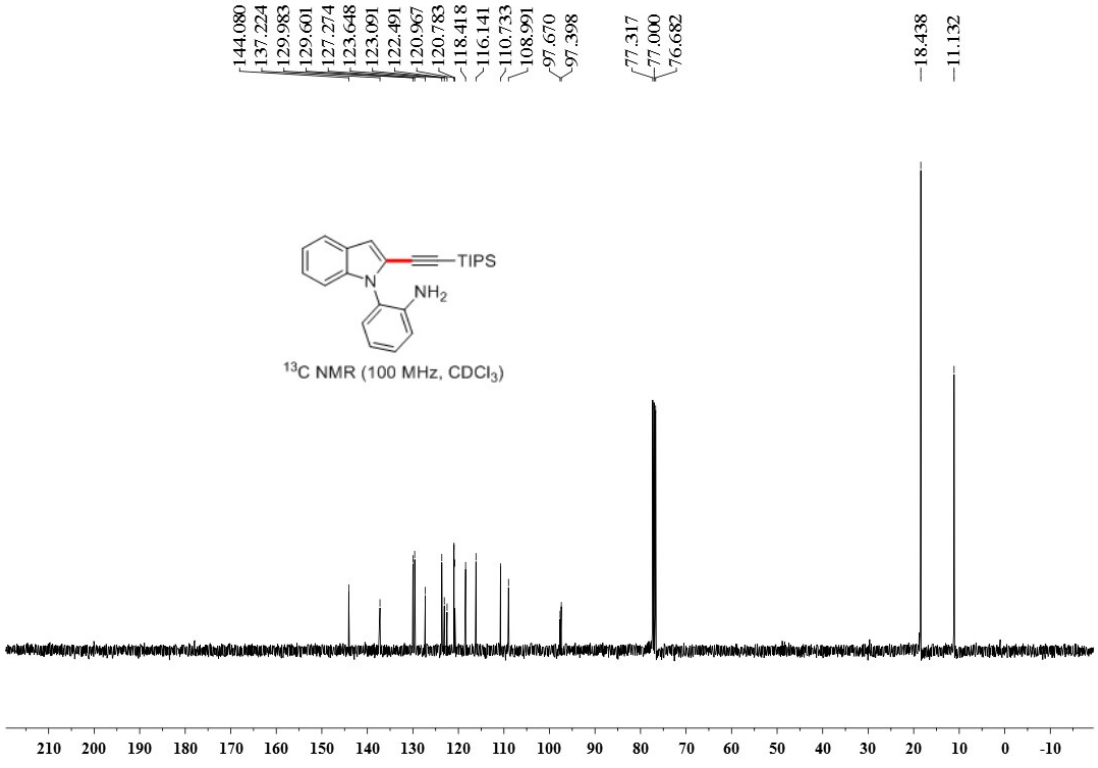


Brown solid (65%, 28.9 mg); mp: 100-101 ^oC; Isolation by column chromatography (petroleum ether/ethyl acetate: 50/1); IR: ν = 3364, 2937, 2154, 1604, 1505, 1368, 1319, 740, 663 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, J = 6.5, 2.1 Hz, 1H), 7.36-7.31 (m, 2H), 7.28 (dd, J = 11.7, 3.8 Hz, 1H), 7.15 (dd, J = 7.8, 1.3 Hz, 1H), 7.08 (dd, J = 6.7, 1.8 Hz, 1H), 6.88-6.82 (m, 2H), 2.90 (s, 2H), 1.01 (t, J = 6.0 Hz, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 136.9, 130.4, 129.6, 128.5, 127.4, 125.2, 122.8, 121.9, 119.2, 118.6, 116.4, 111.6, 110.6, 105.4, 97.3, 93.8, 18.4, 11.0; HRMS (ESI) m/z: calcd for $C_{26}H_{31}N_3NaSSi$ $[M+Na]^+$, 468.1900, found 468.1902.

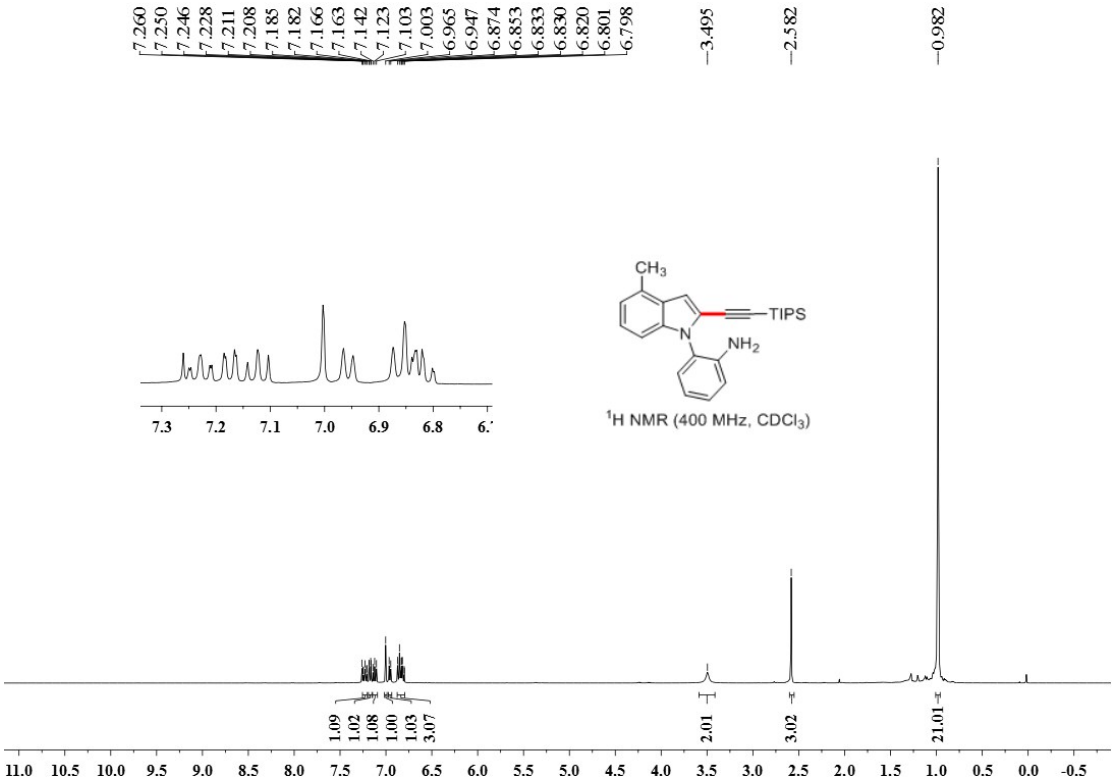
K. Copies of ^{1}H and ^{13}C NMR Spectra

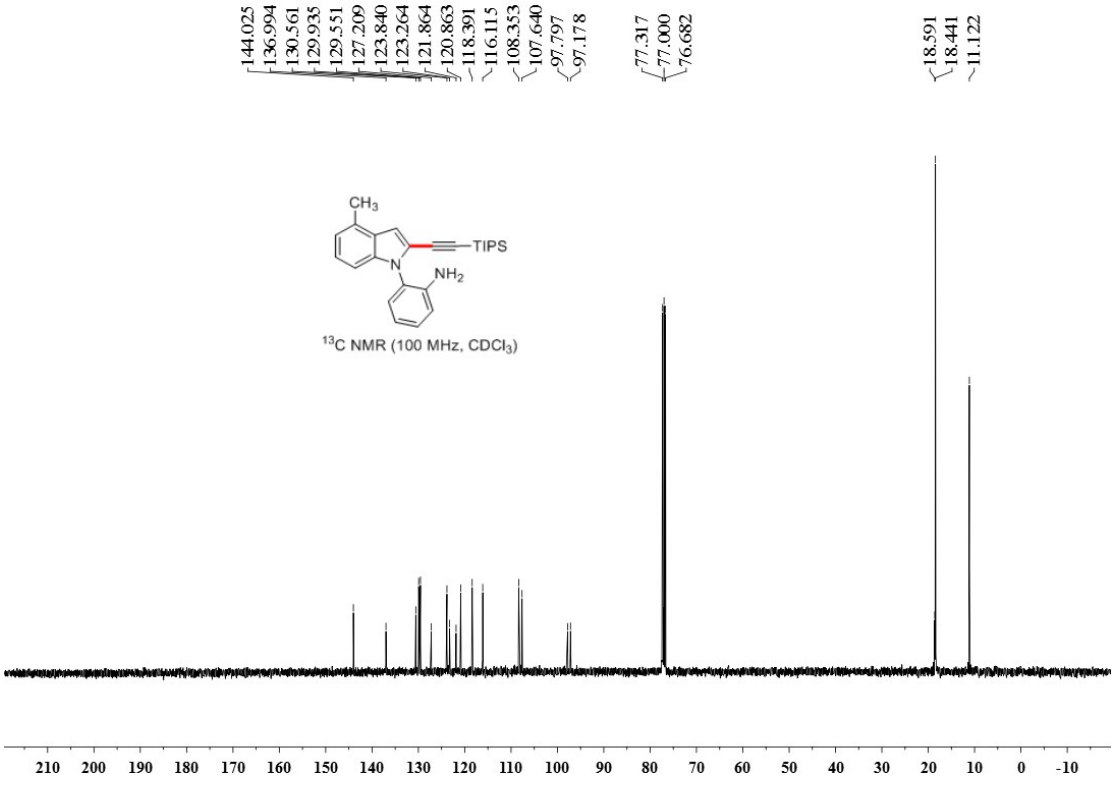
2-(2-((Triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3a)



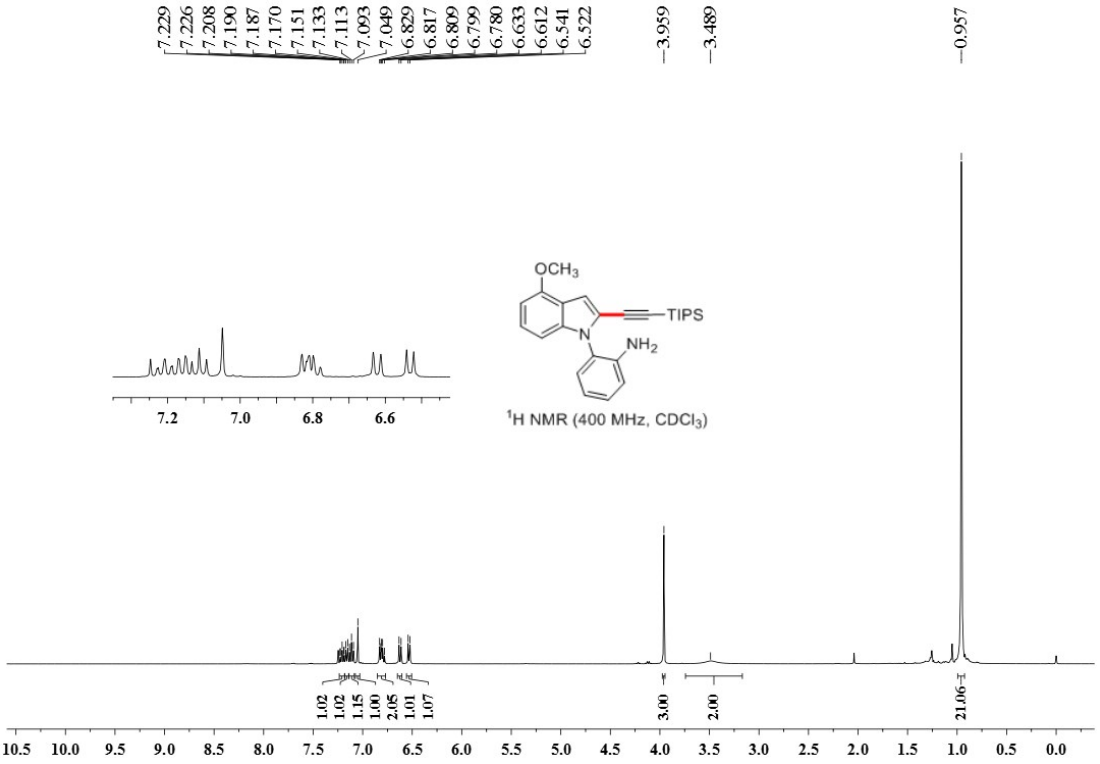


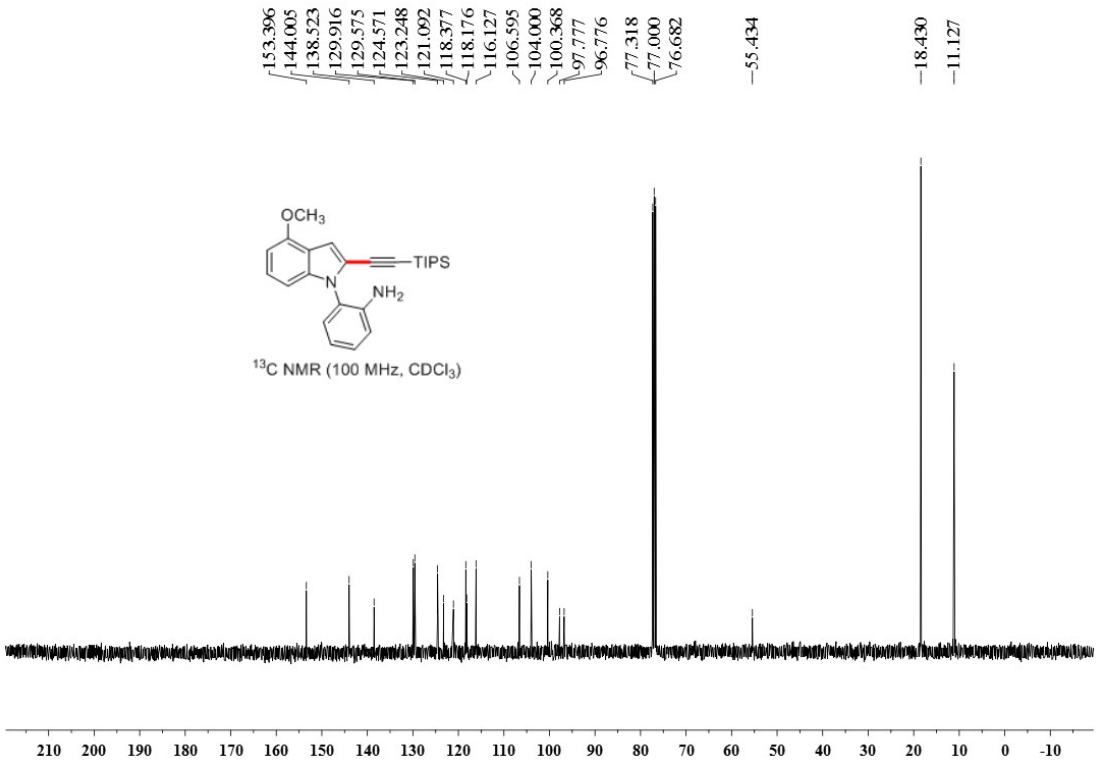
2-(4-Methyl-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3b)



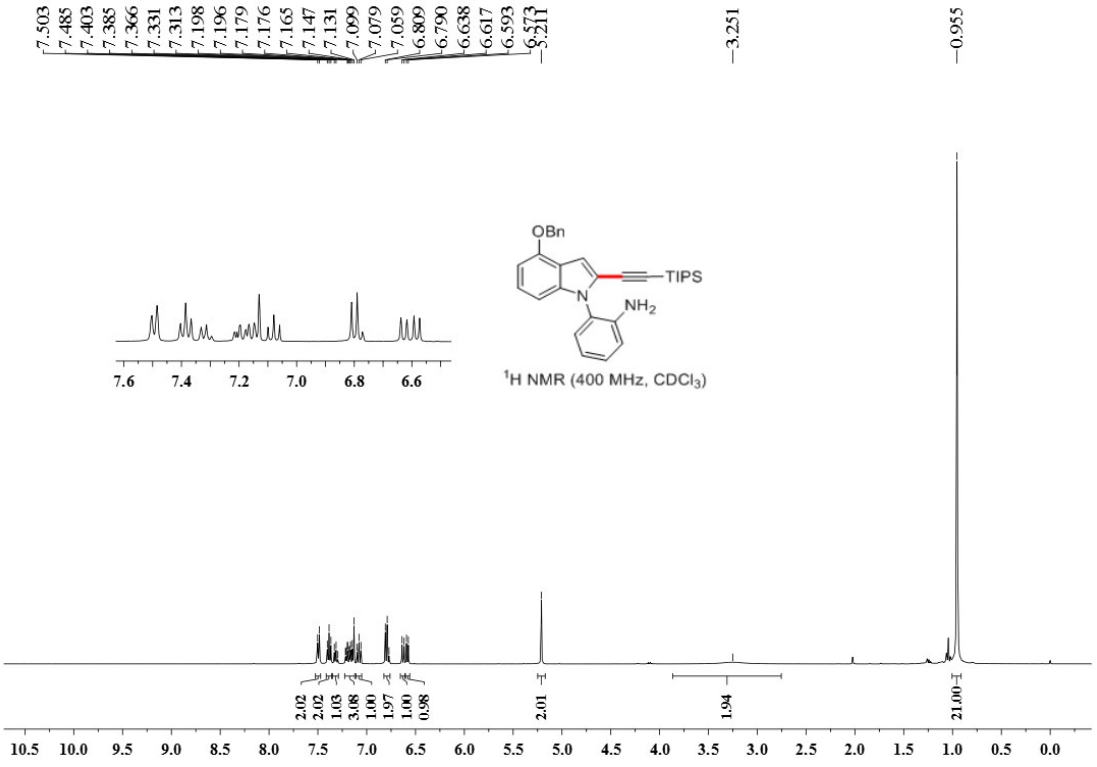


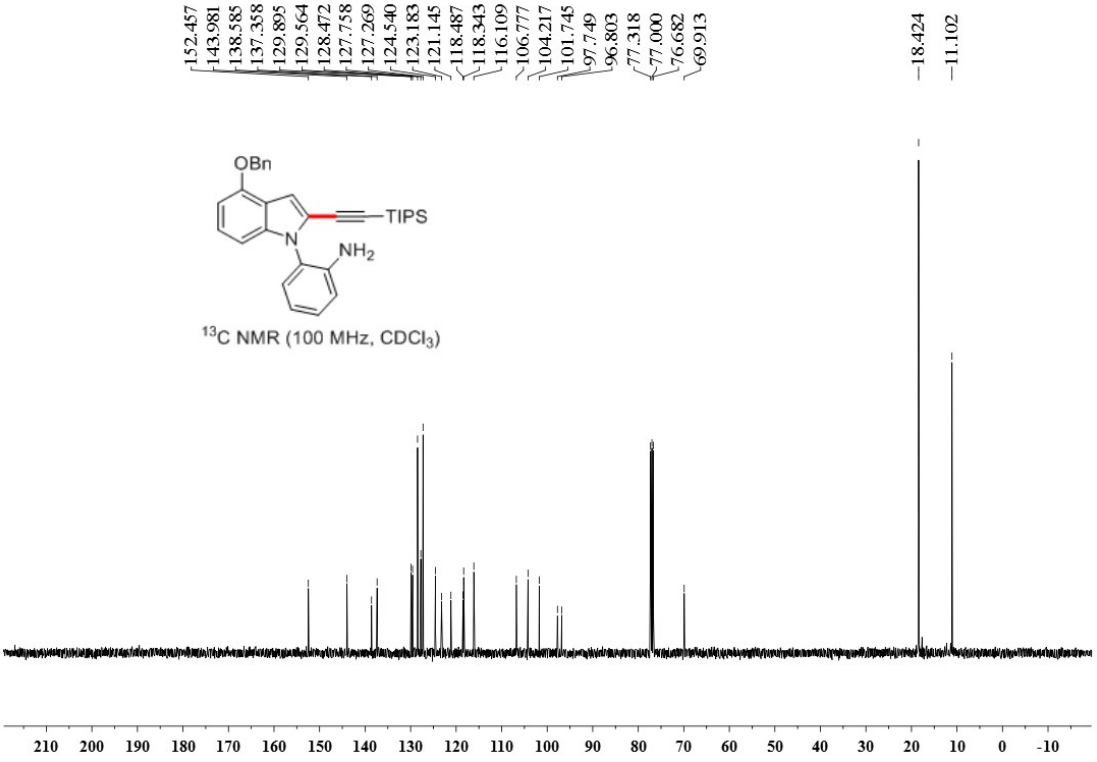
2-(4-Methoxy-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3c)



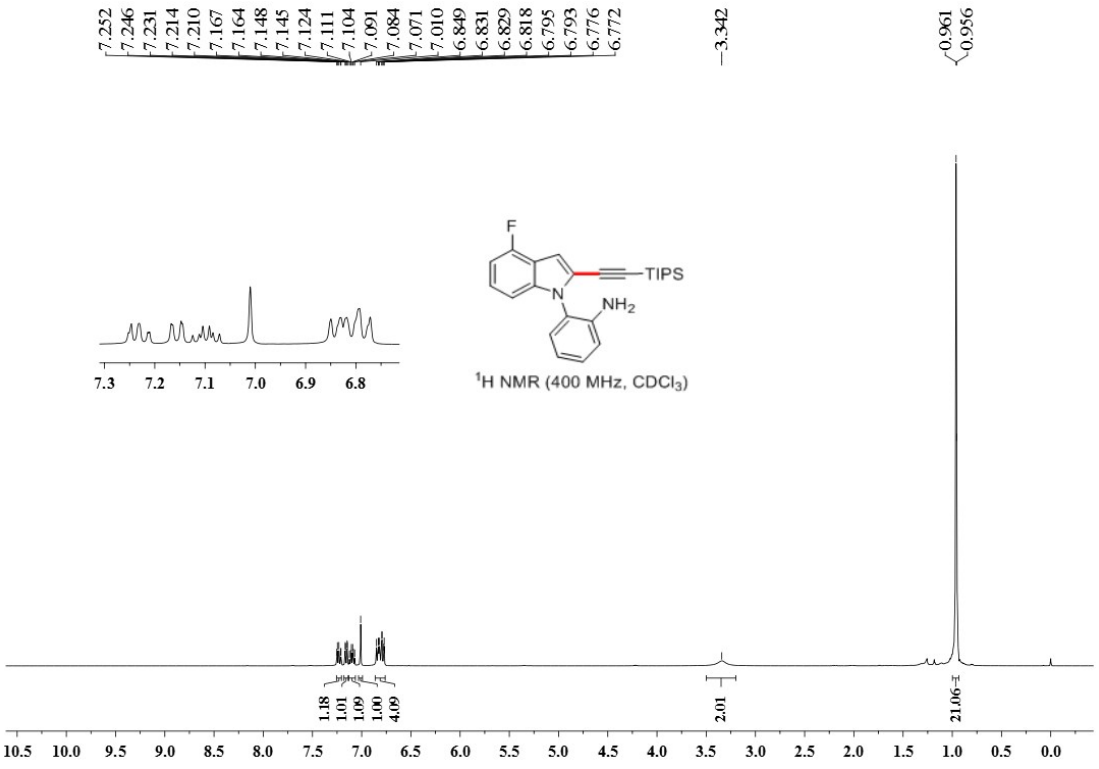


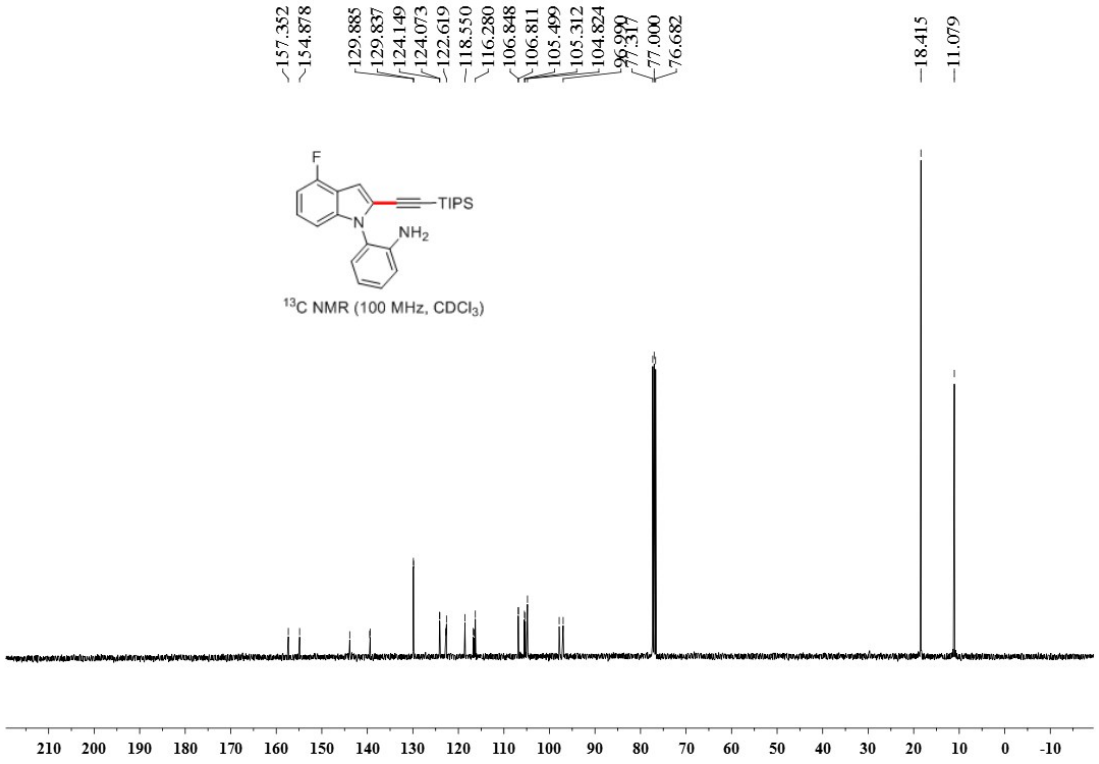
2-(4-(Benzyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3d)

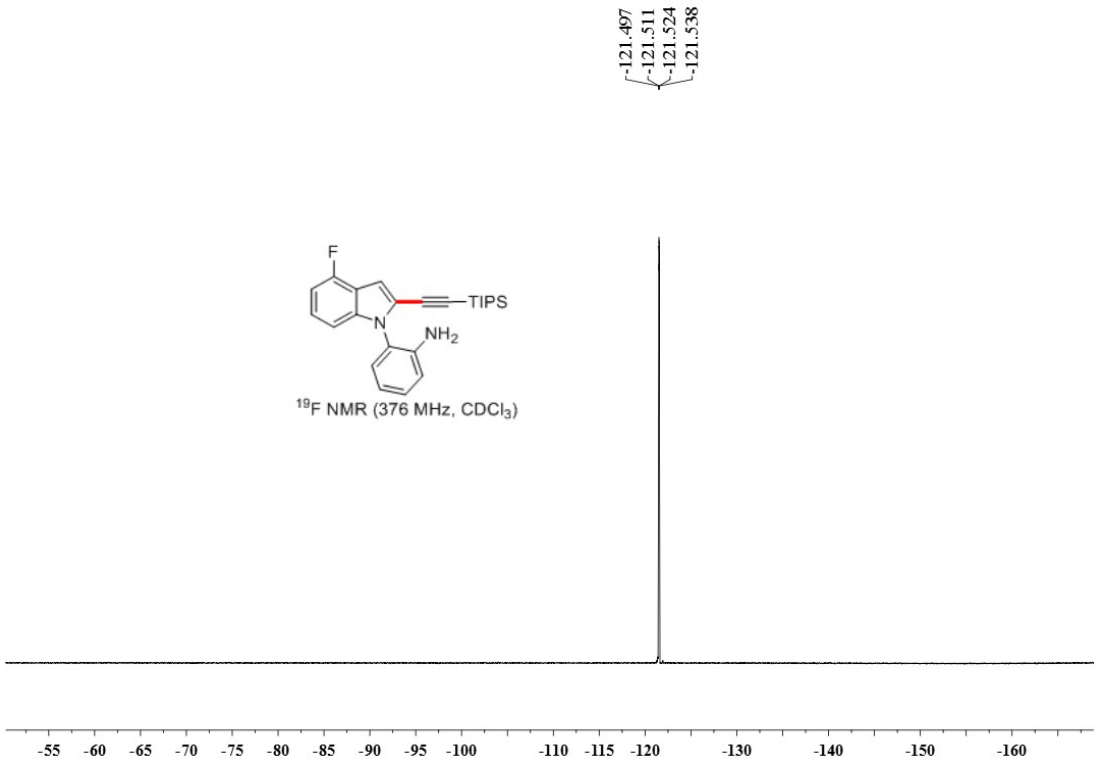




2-(4-Fluoro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3e)

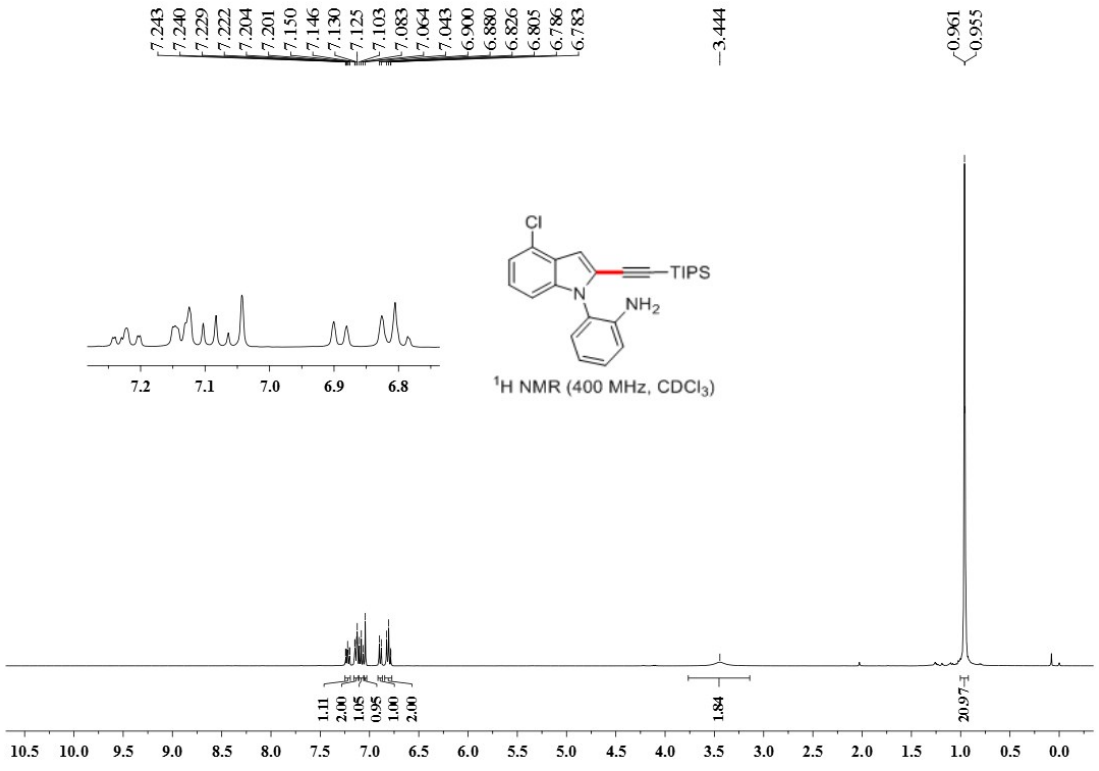


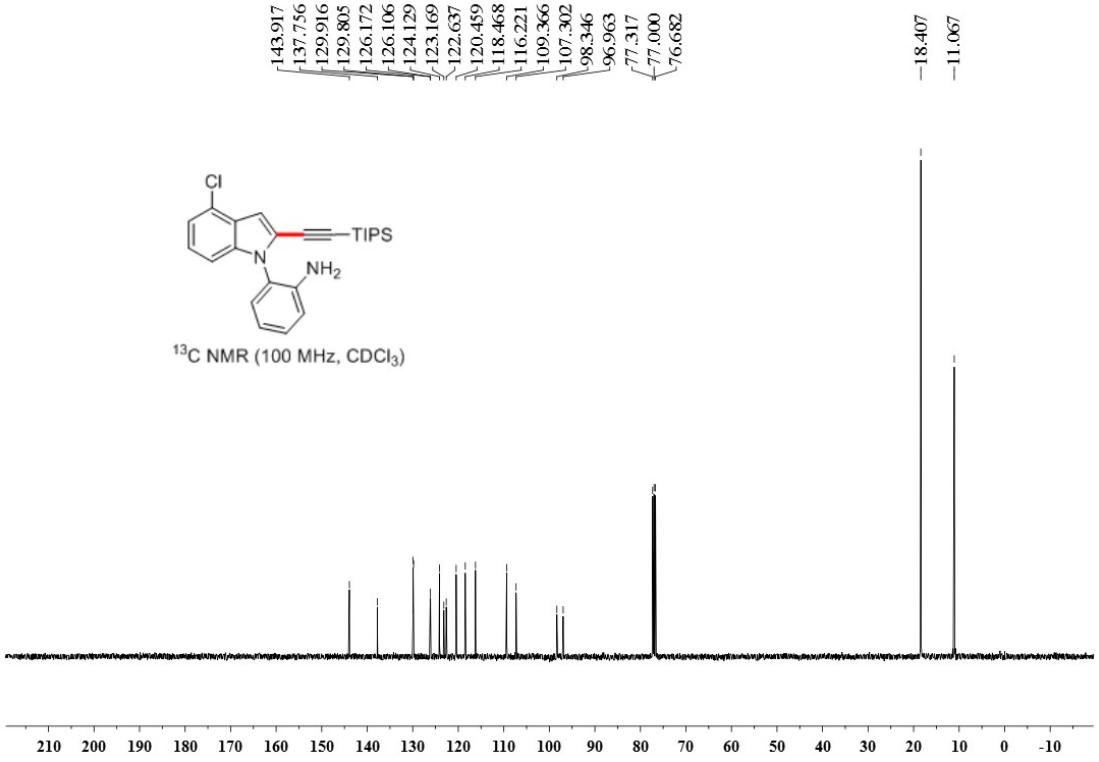




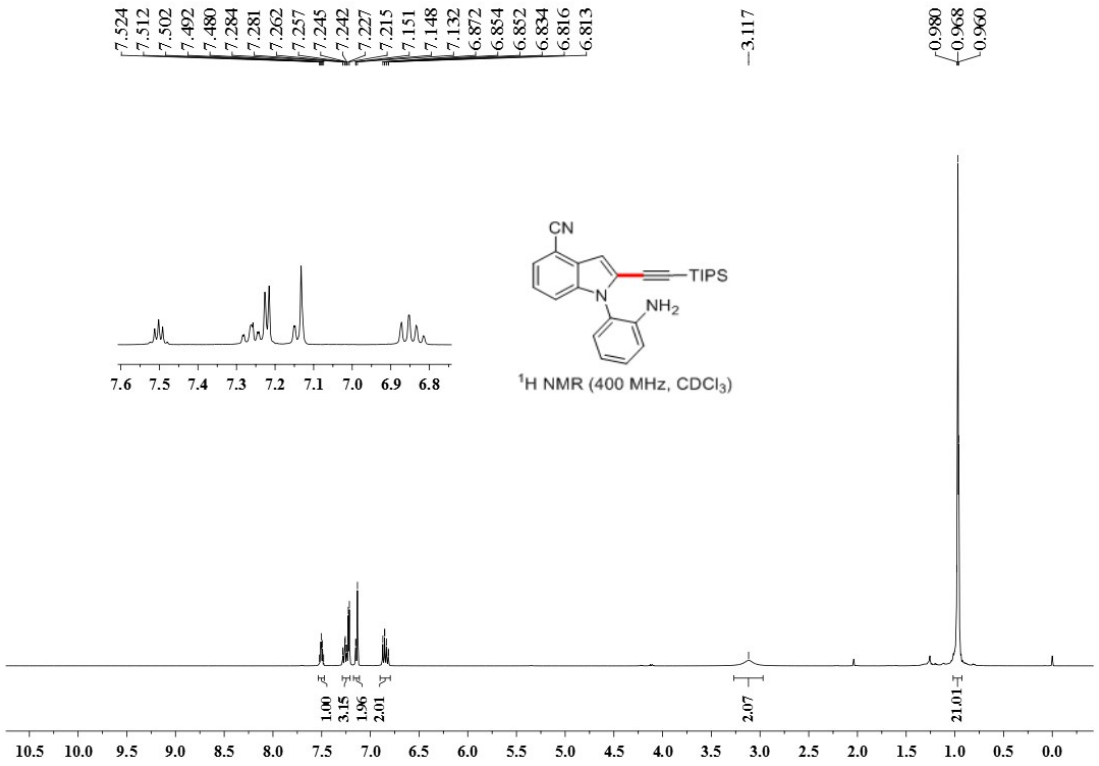
^{19}F NMR (376 MHz, $CDCl_3$)

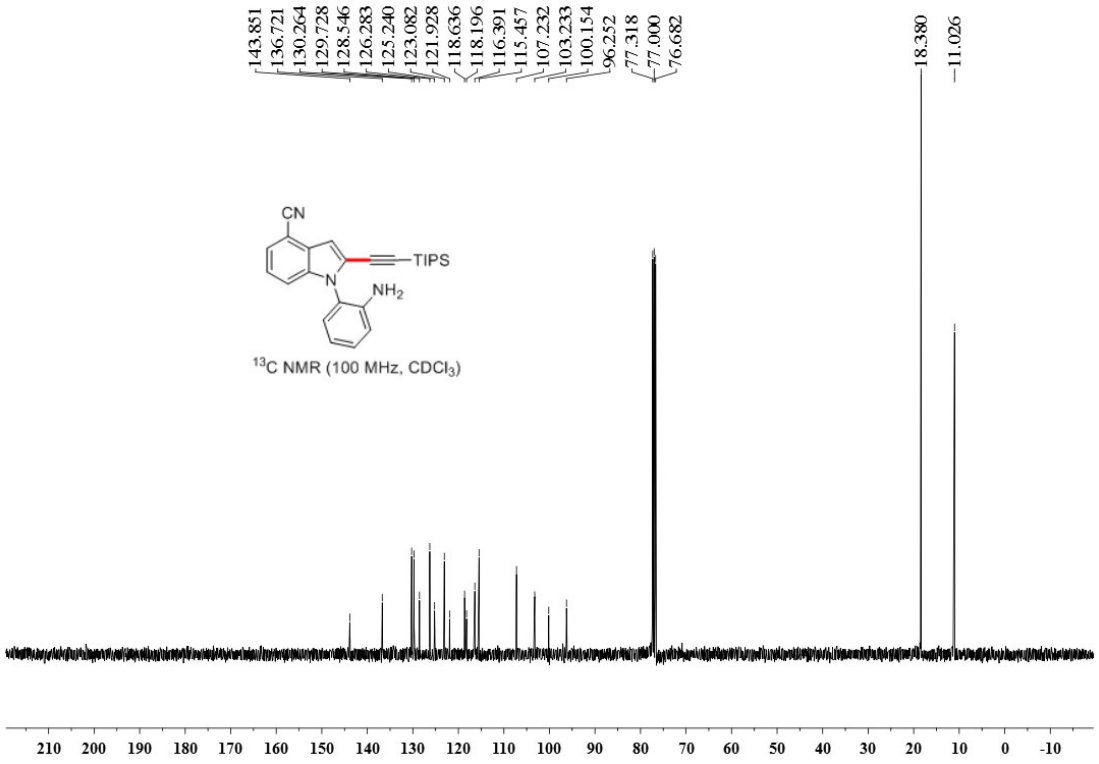
2-(4-Chloro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3f)



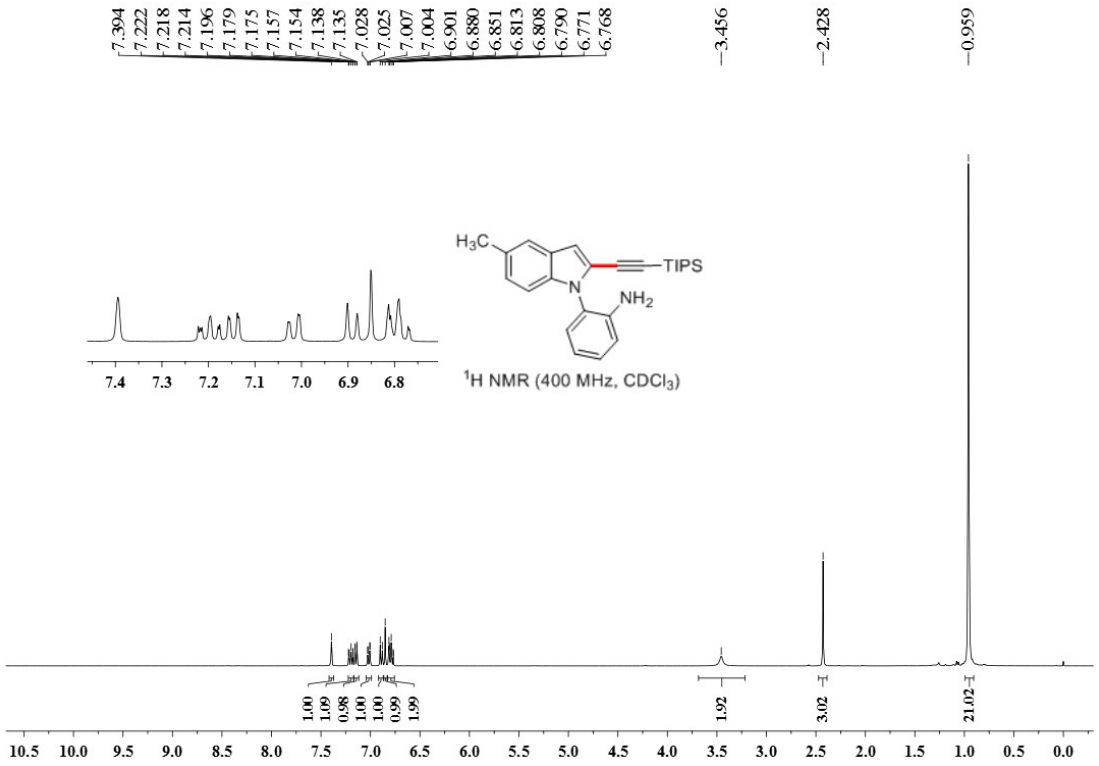


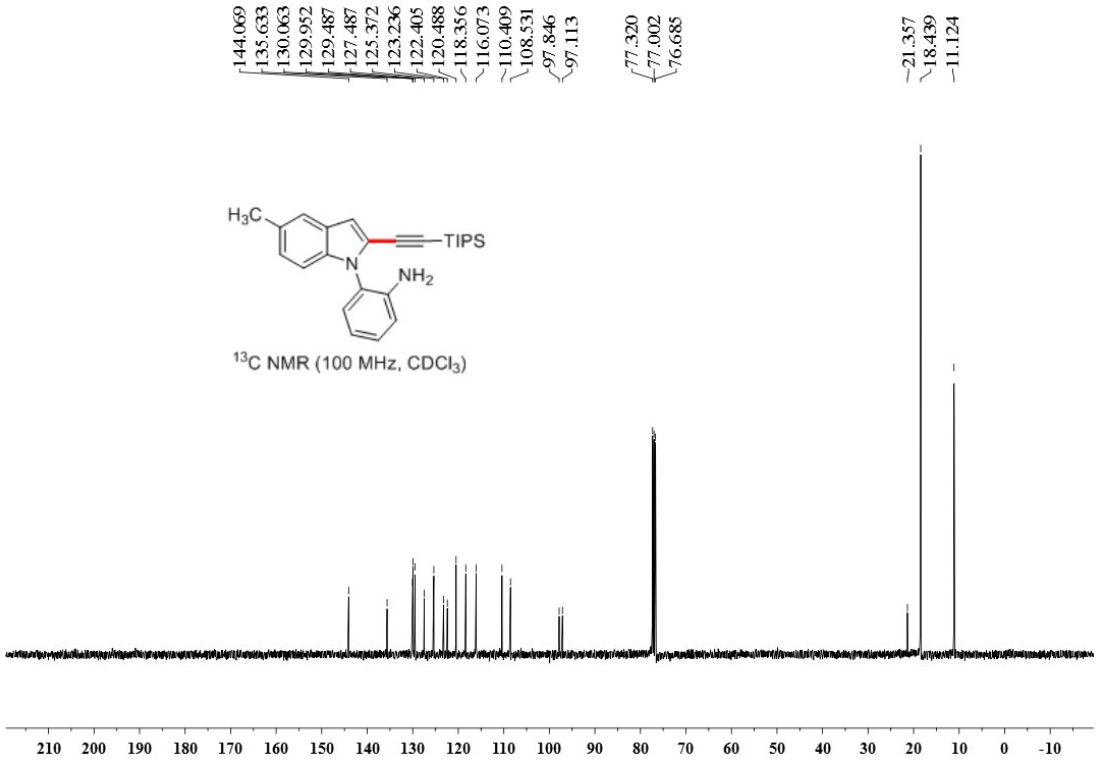
1-(2-Aminophenyl)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-4-carbonitrile (3g)



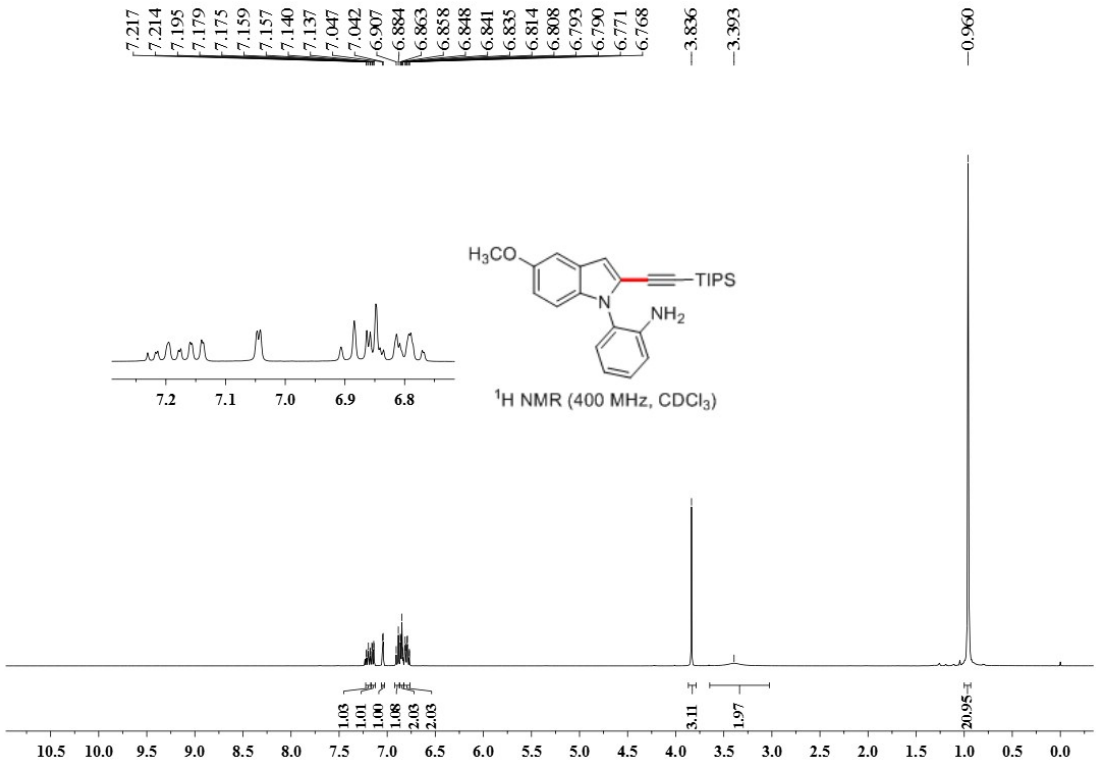


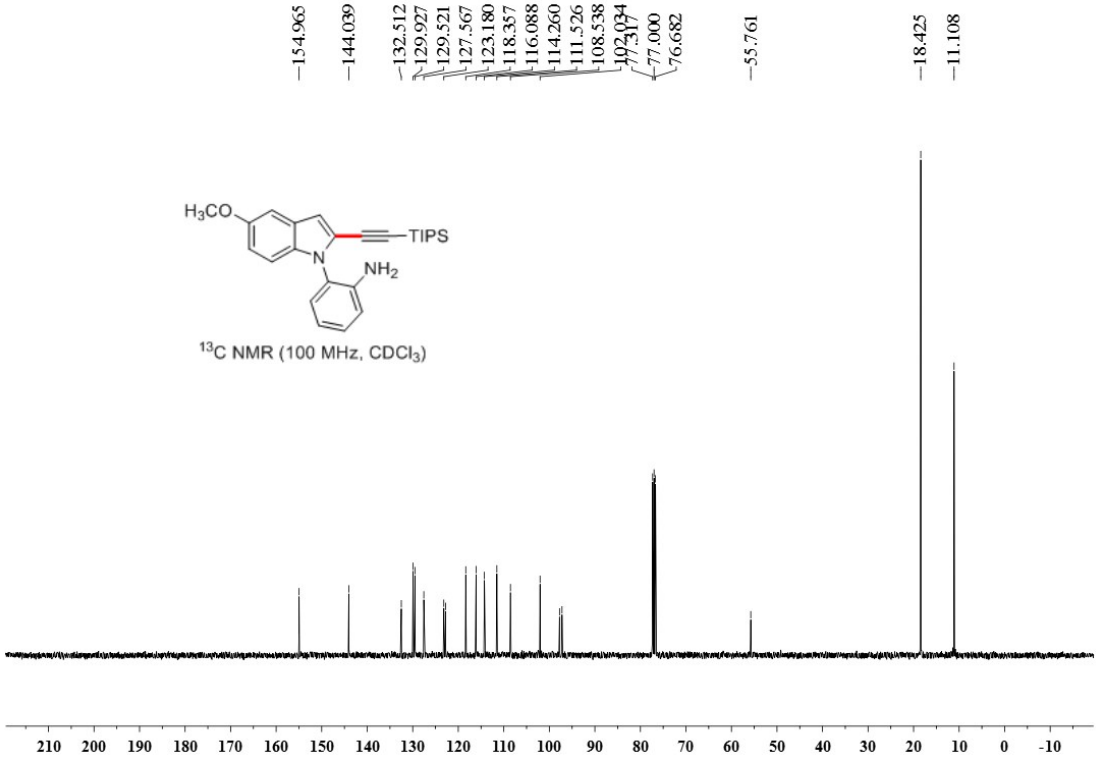
2-(5-Methyl-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3h)



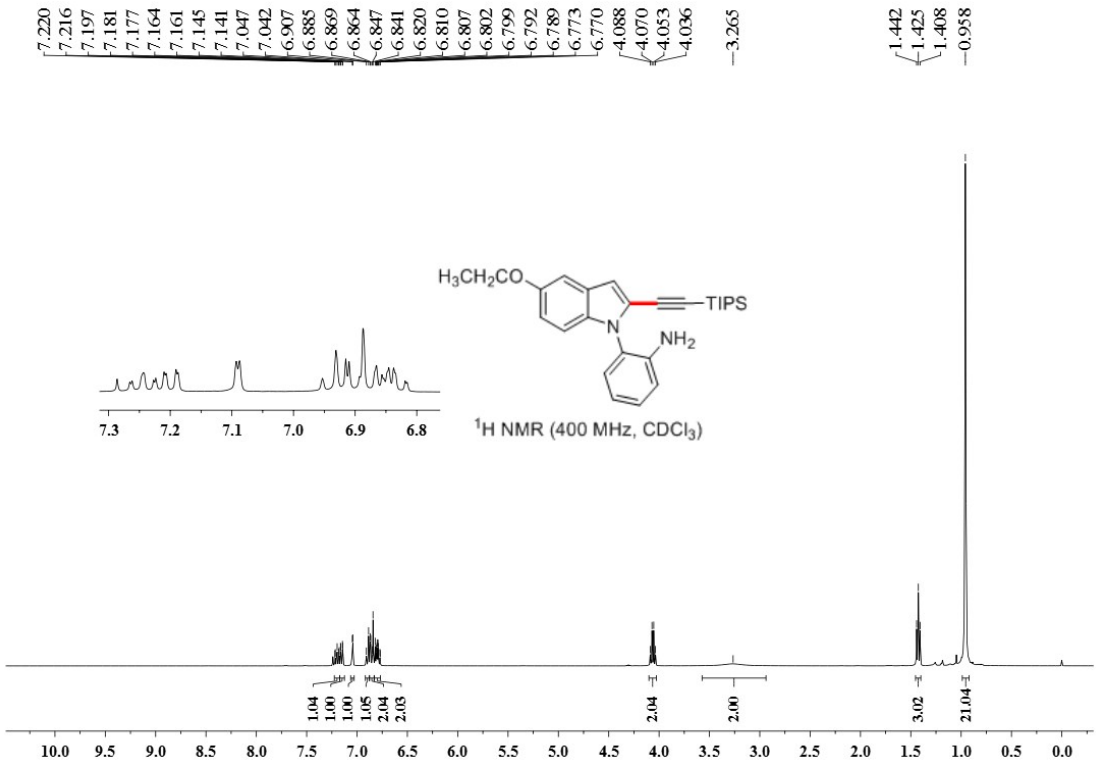


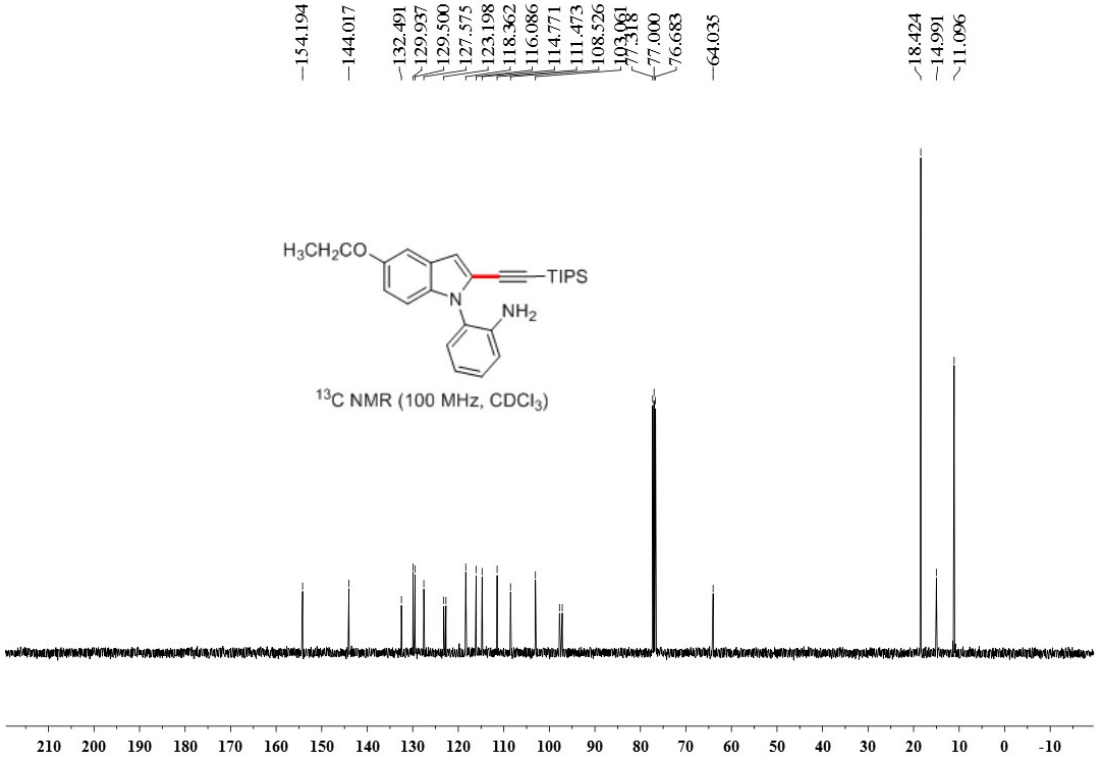
2-(5-Methoxy-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3i)



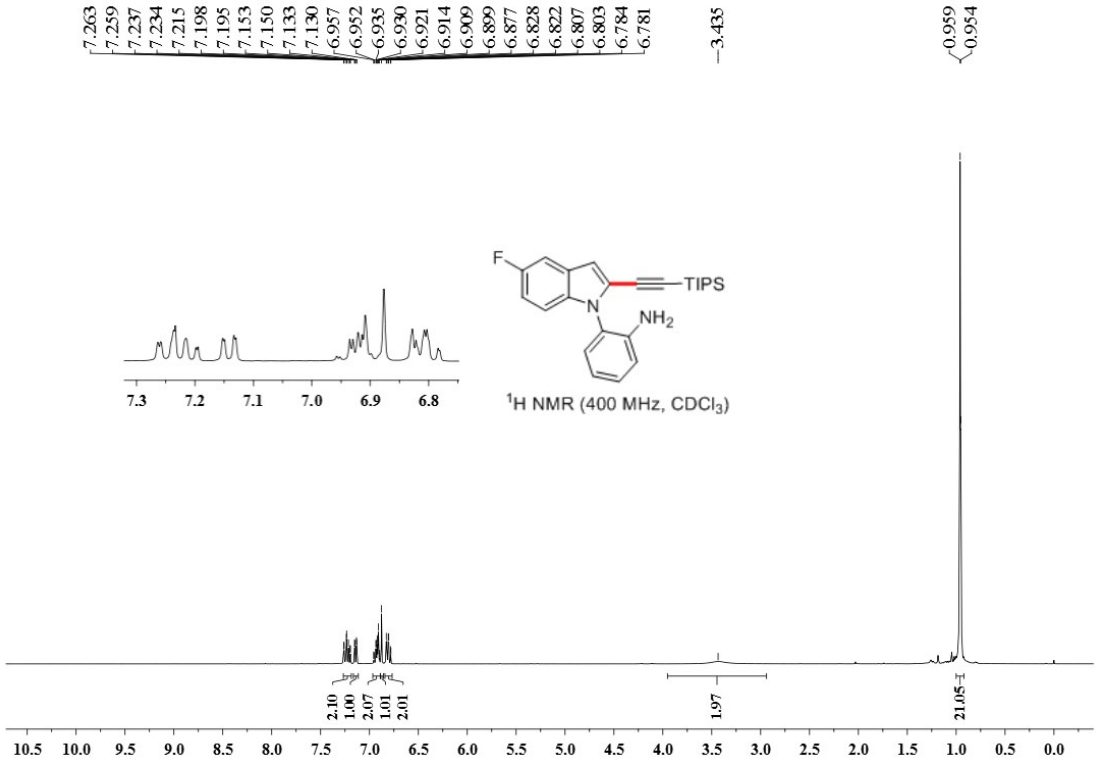


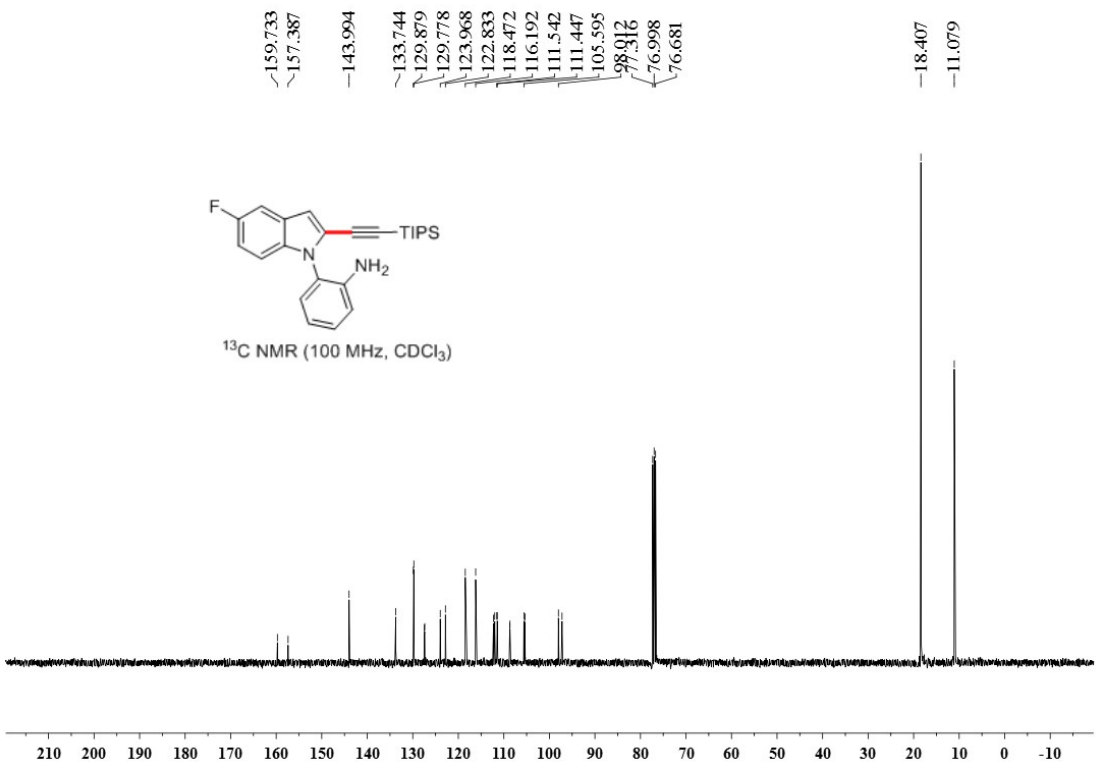
2-(5-Ethoxy-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3j)

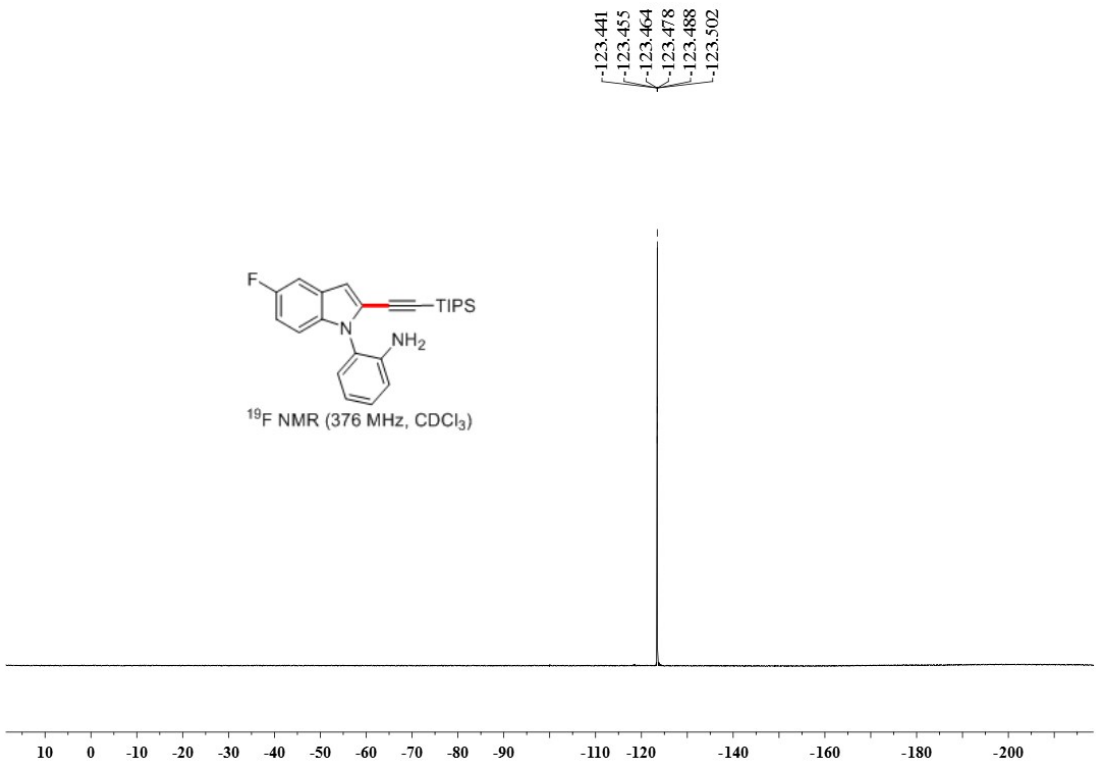




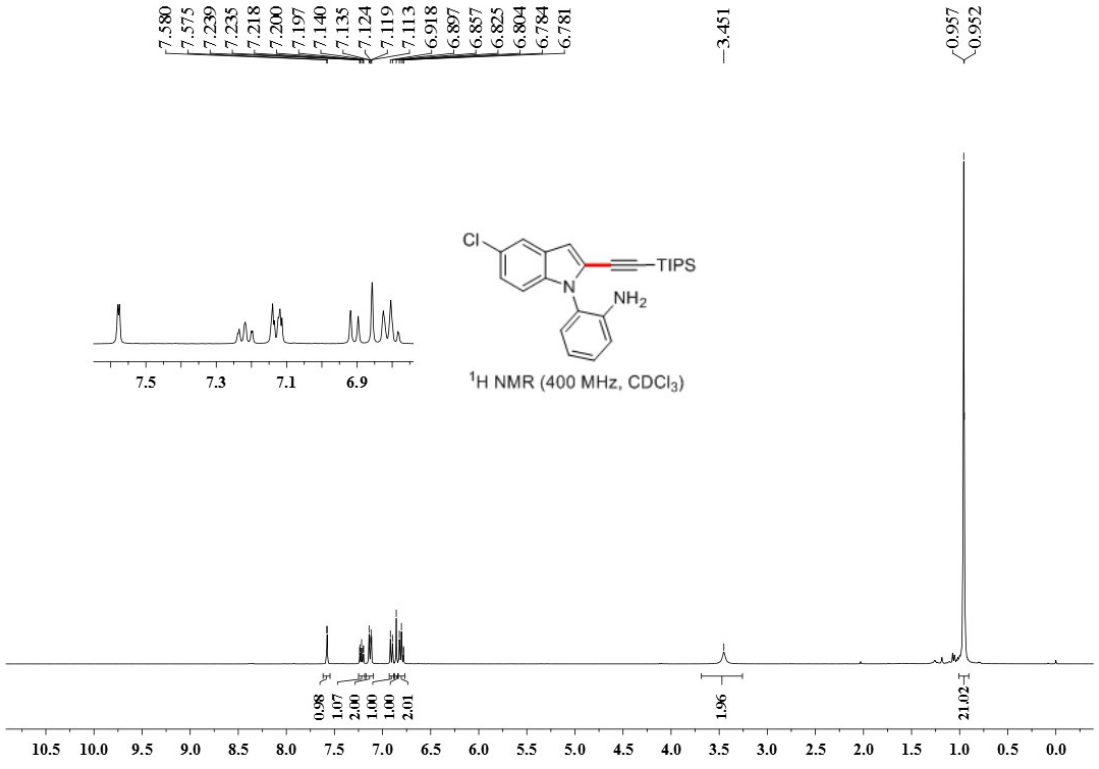
2-(5-Fluoro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3k)

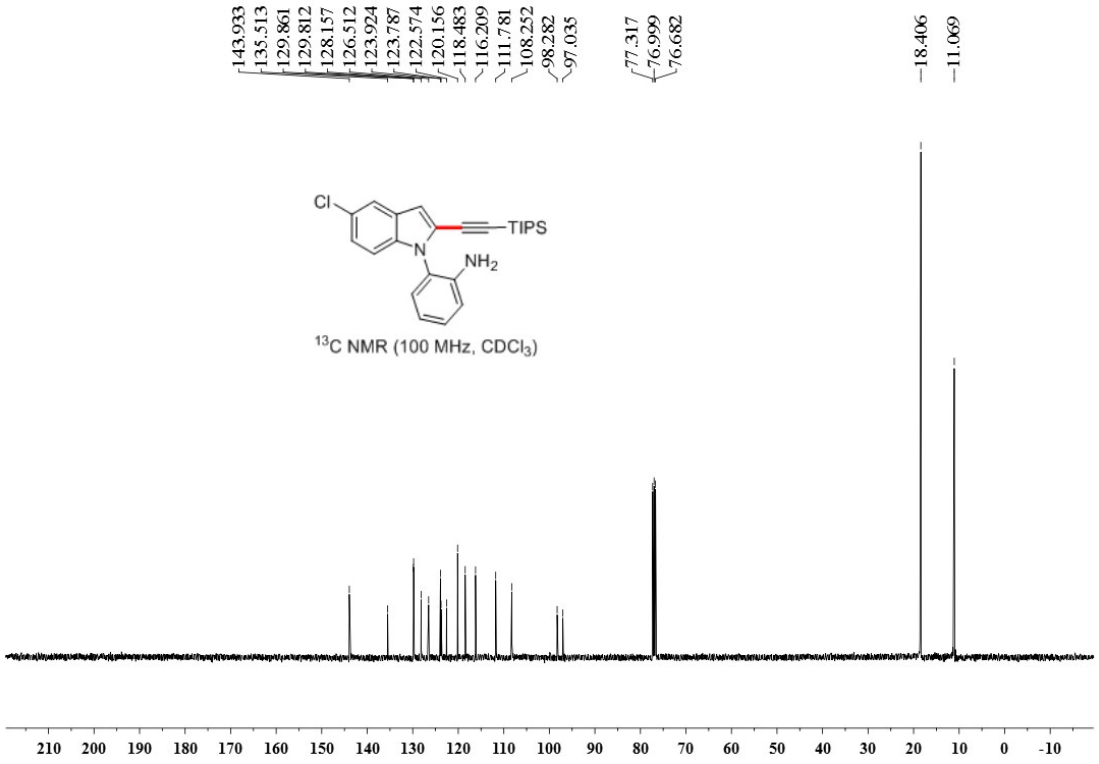




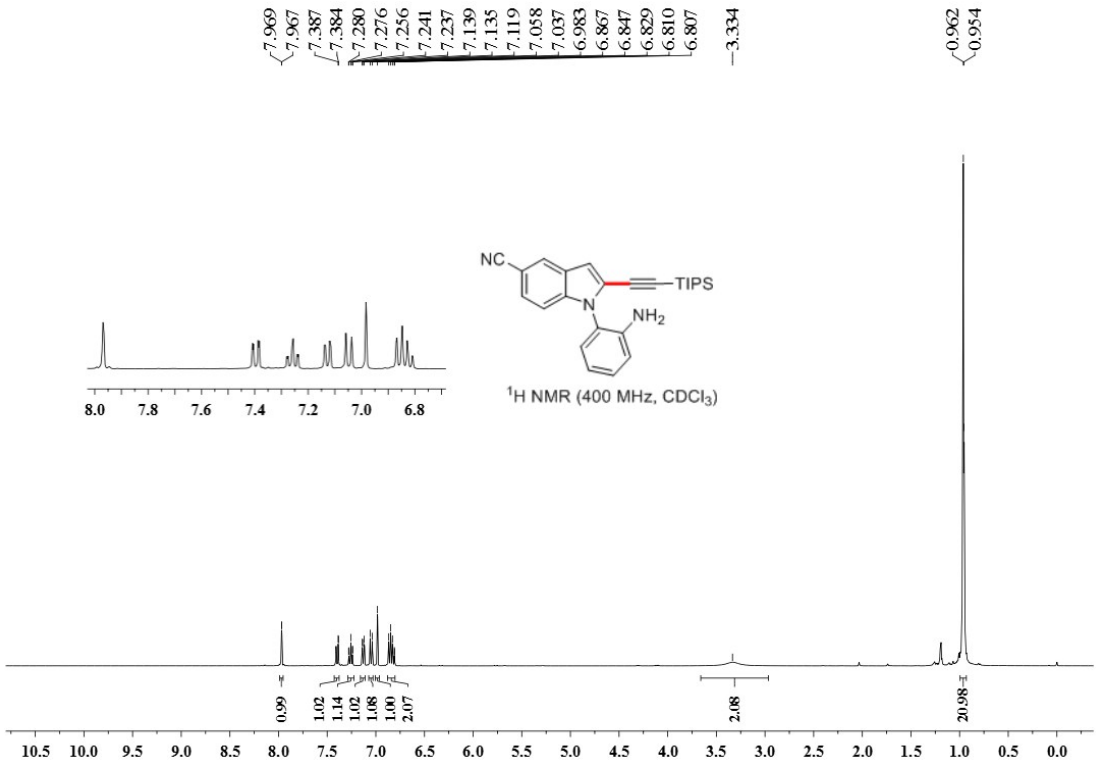

-123.441
-123.455
-123.464
-123.478
-123.488
-123.502
F
TIPS
N
NH2
19F NMR (376 MHz, CDCl3)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-120
-140
-160
-180
-200

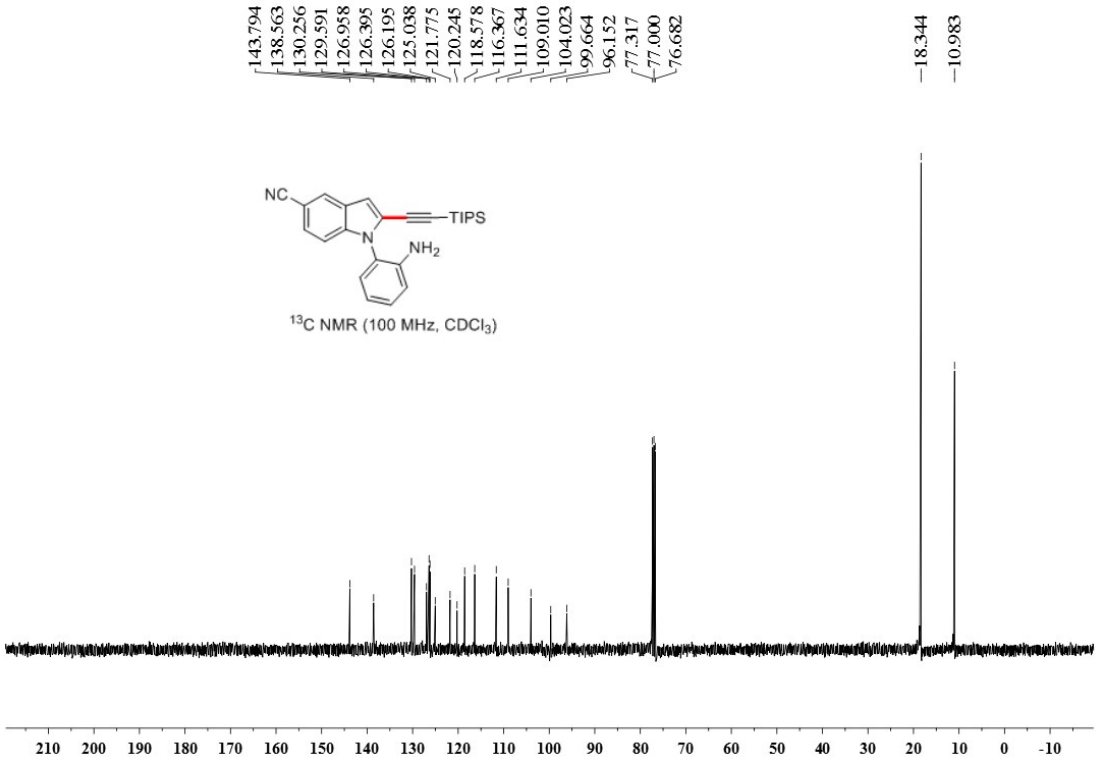
2-(5-Chloro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3l)



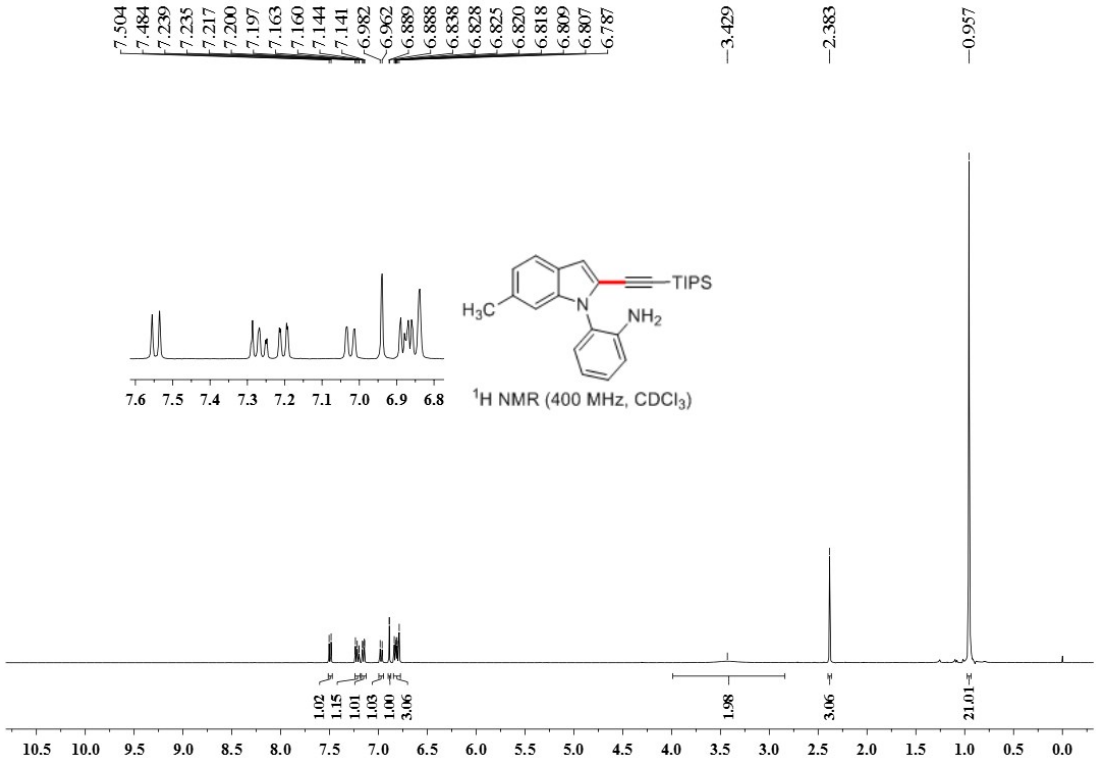


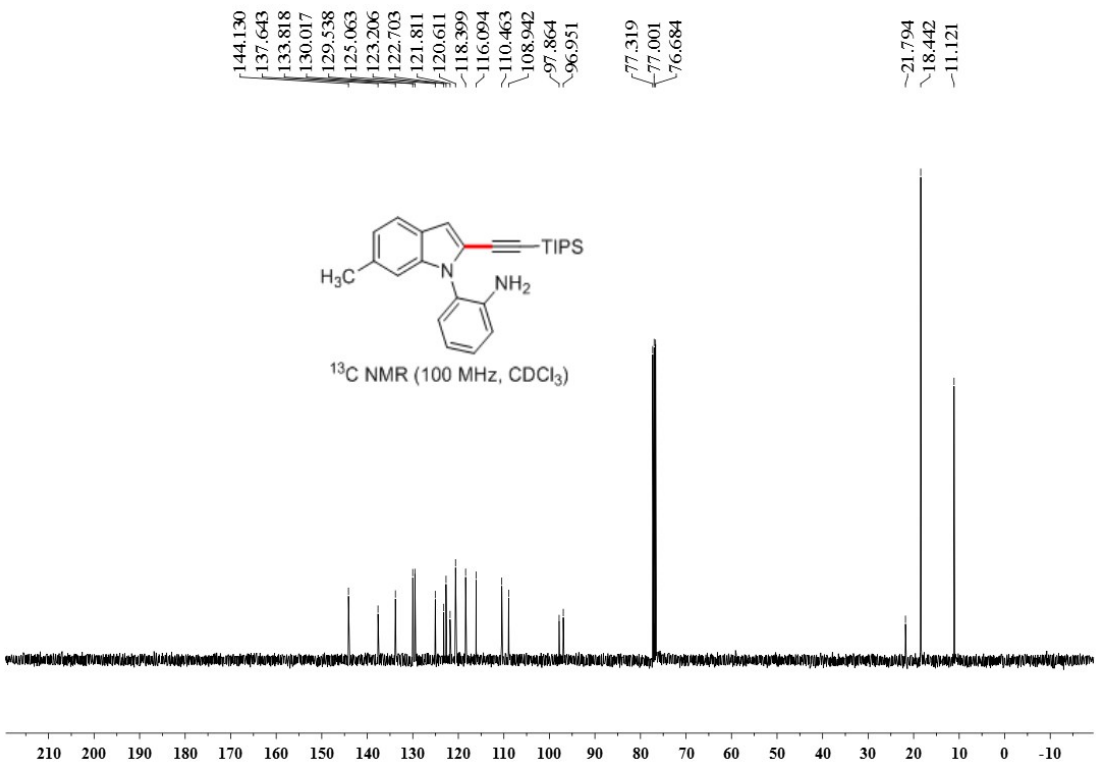
1-(2-Aminophenyl)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-5-carbonitrile (3m)



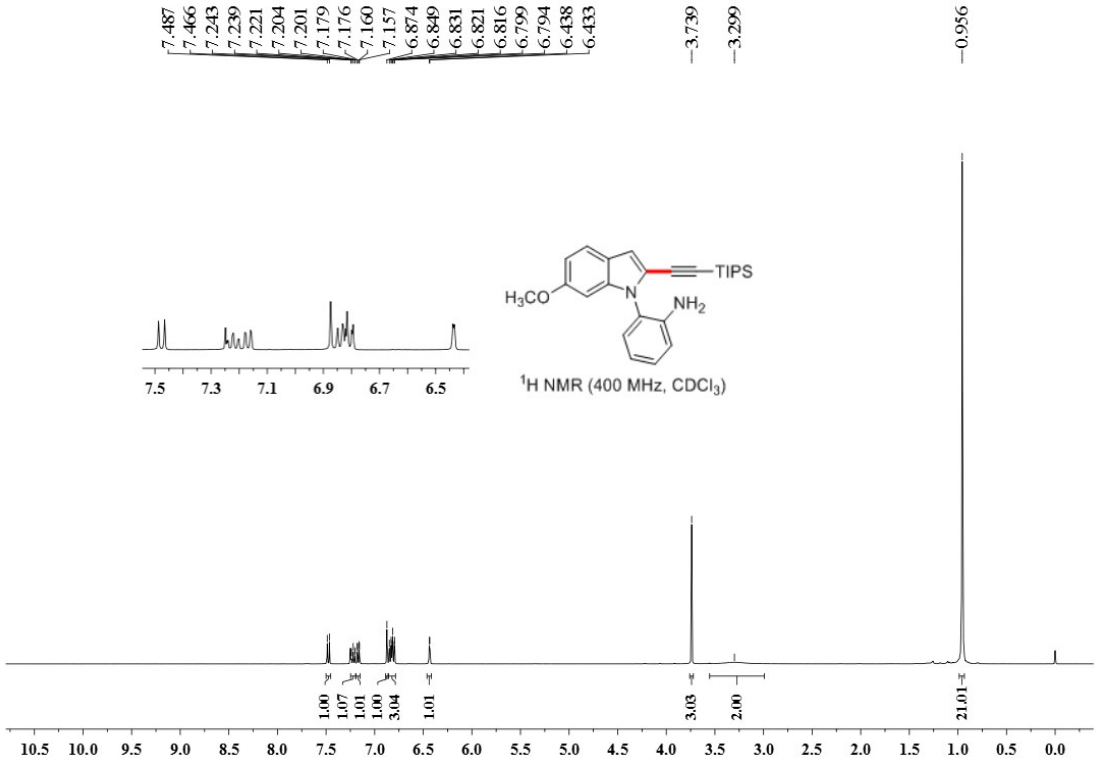


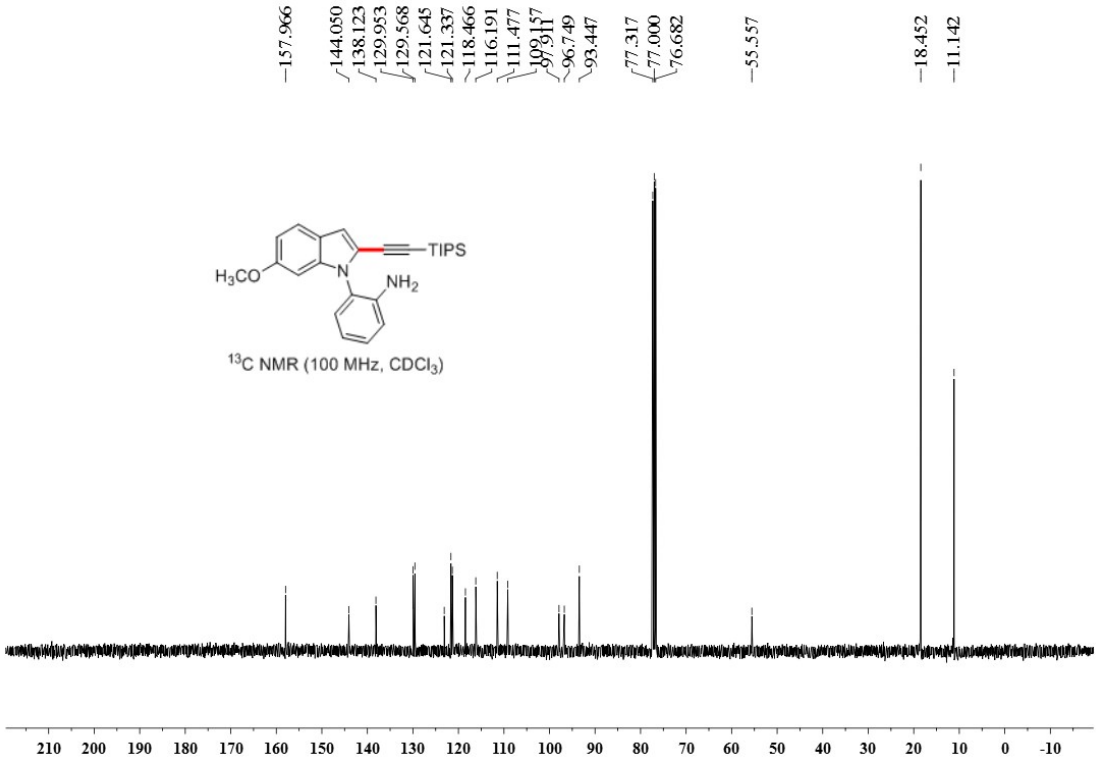
2-(6-Methyl-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3n)



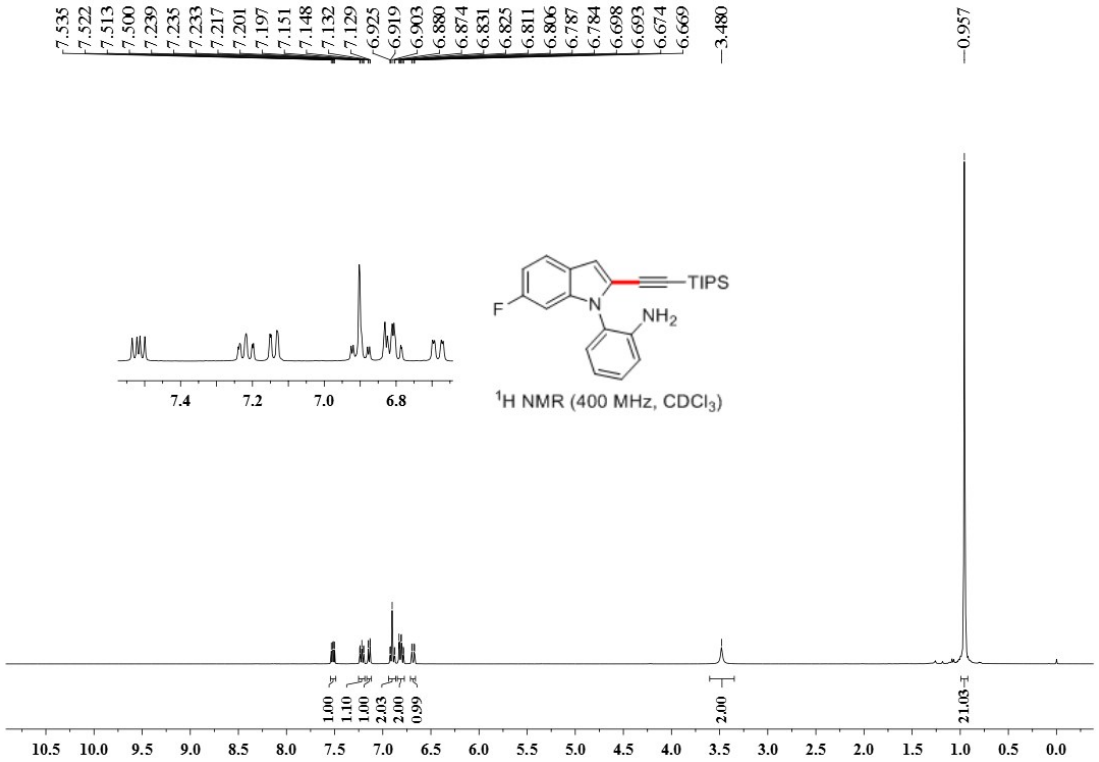


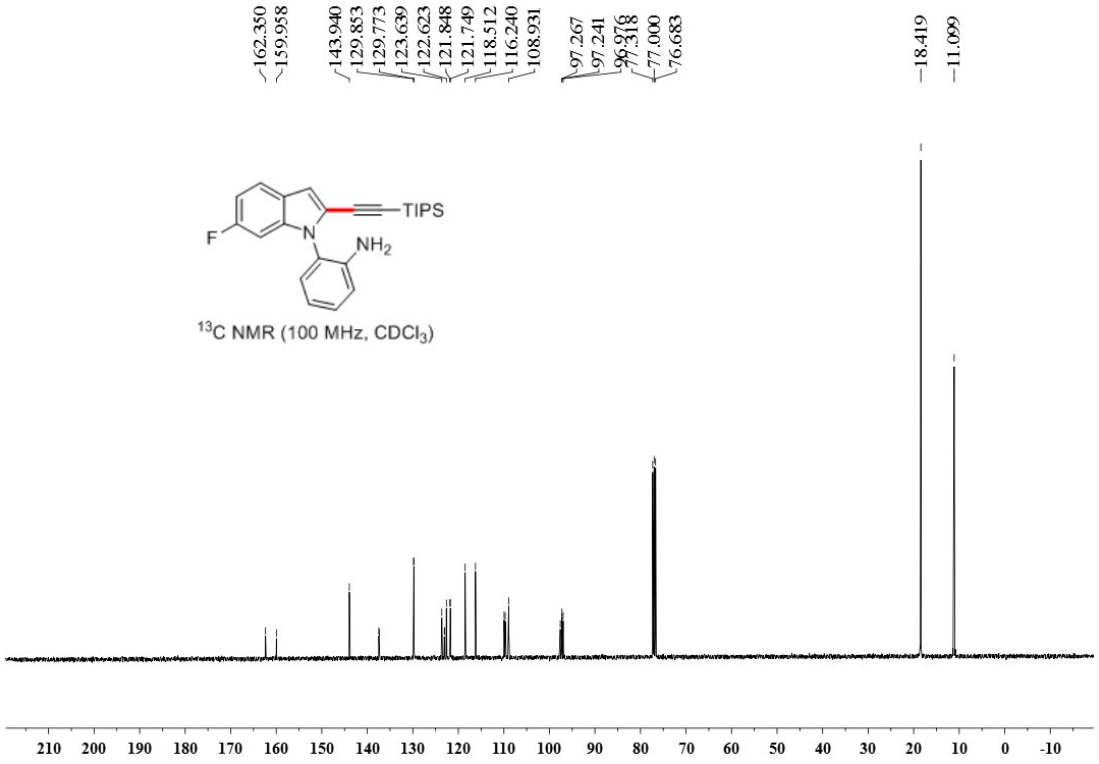
2-(6-Methoxy-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3o)

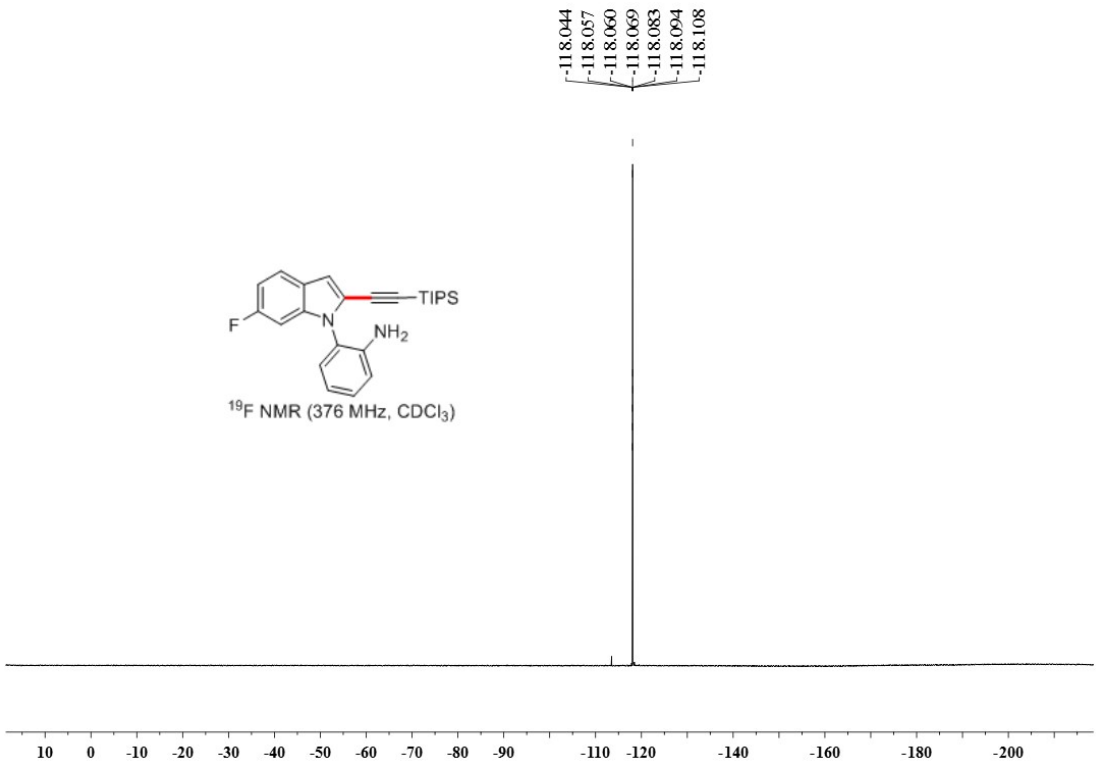




2-(6-Fluoro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3p)

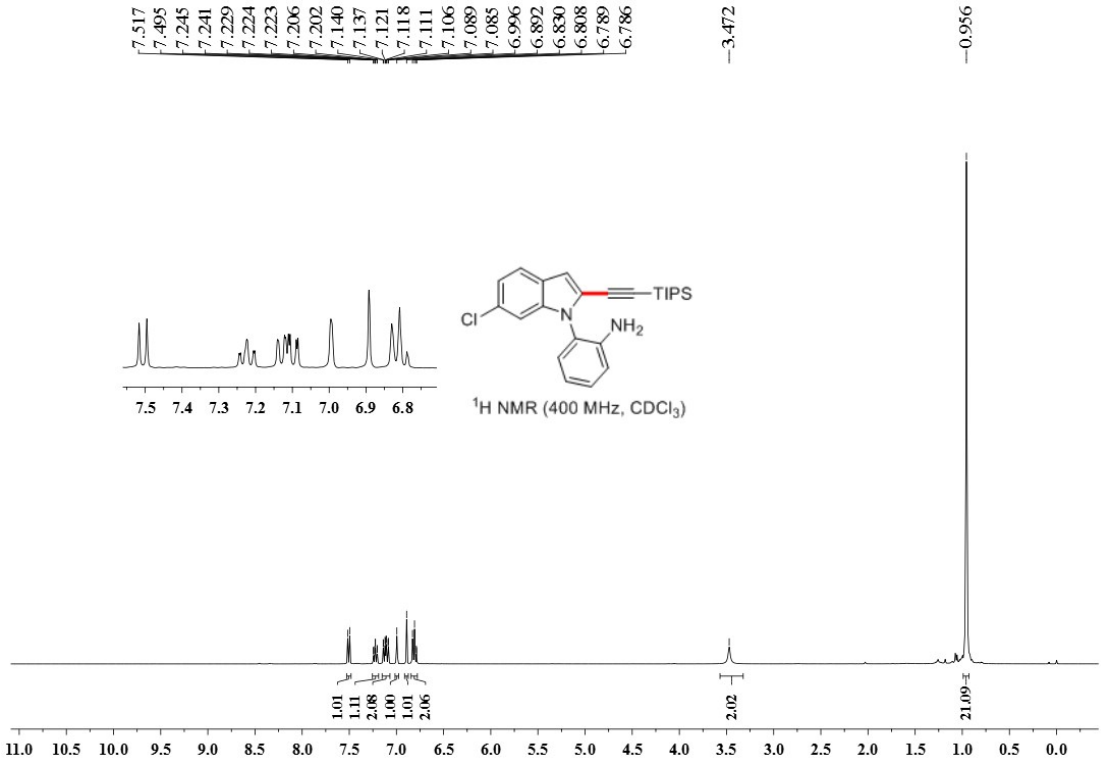


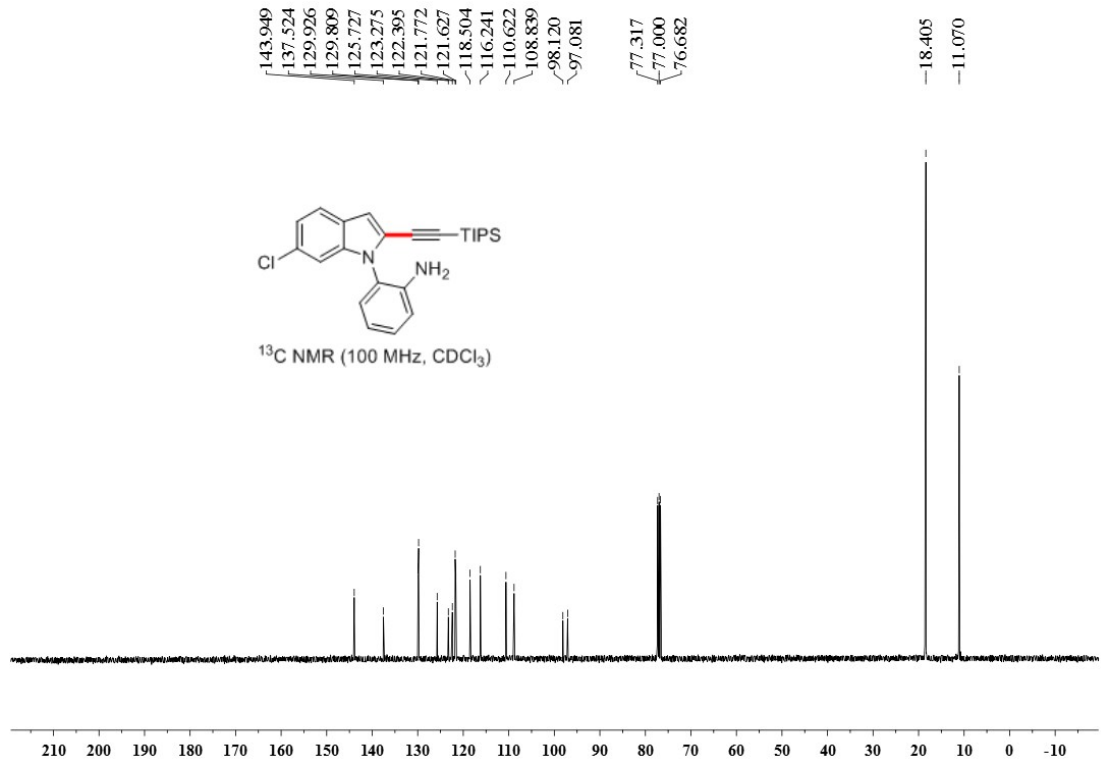




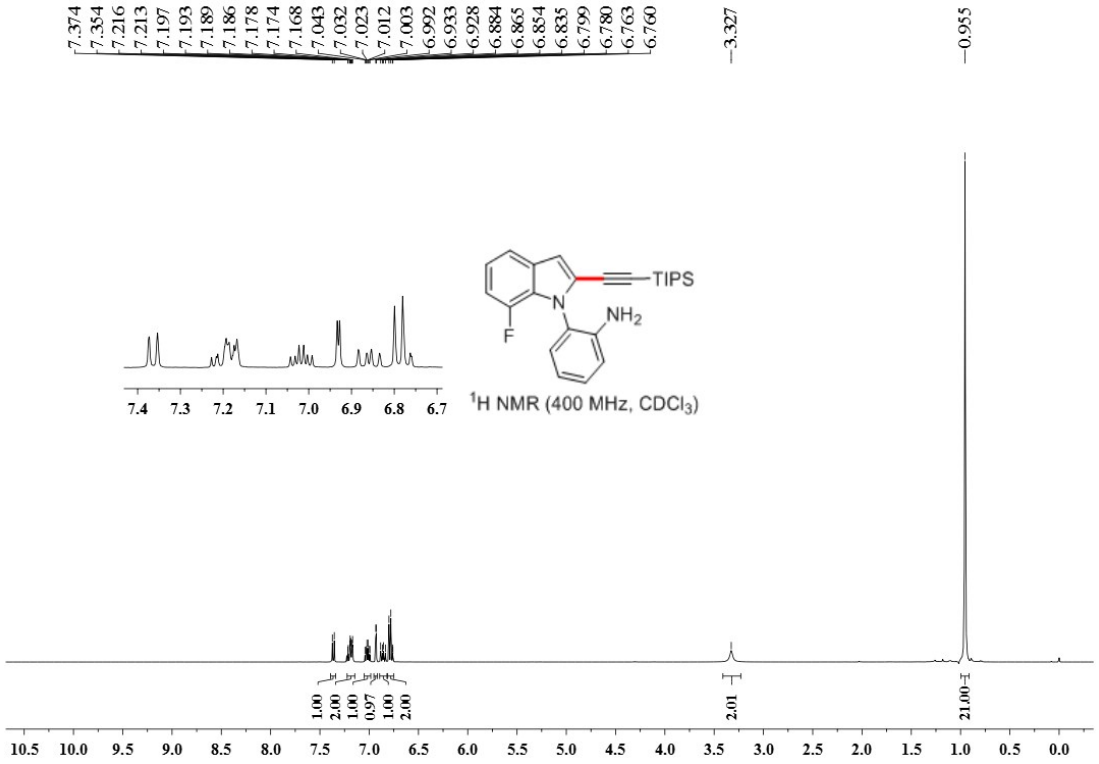
^{19}F NMR (376 MHz, $CDCl_3$)

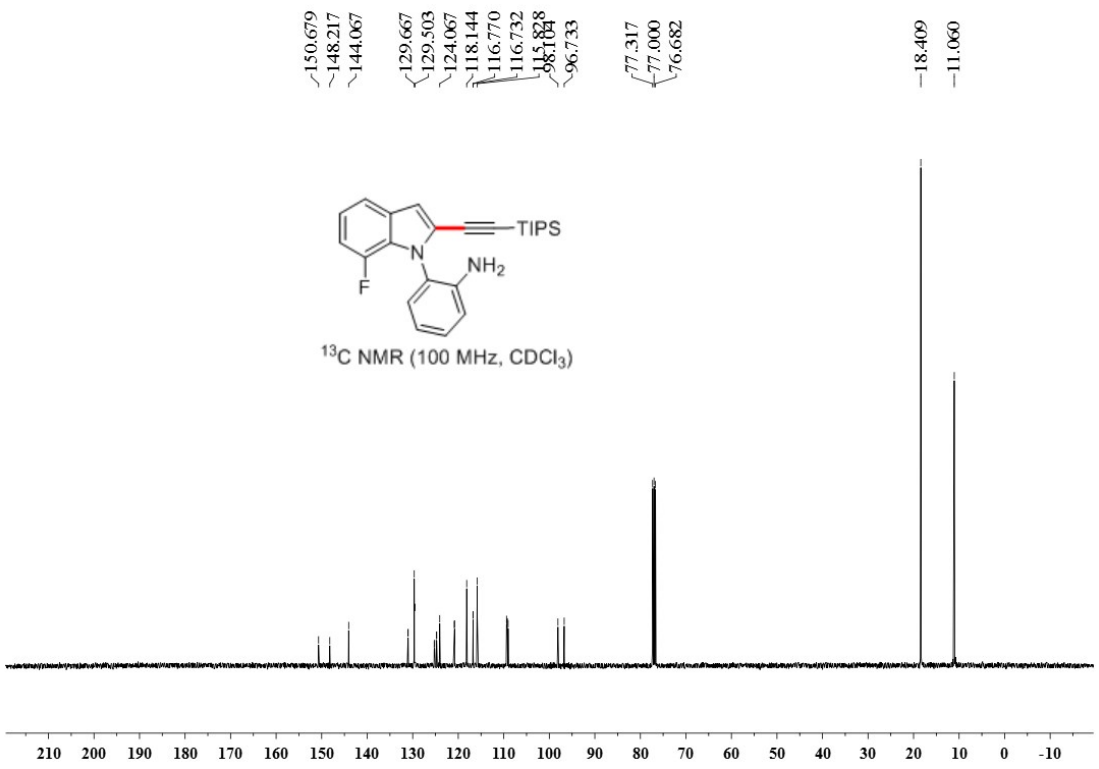
2-(6-Chloro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3q)

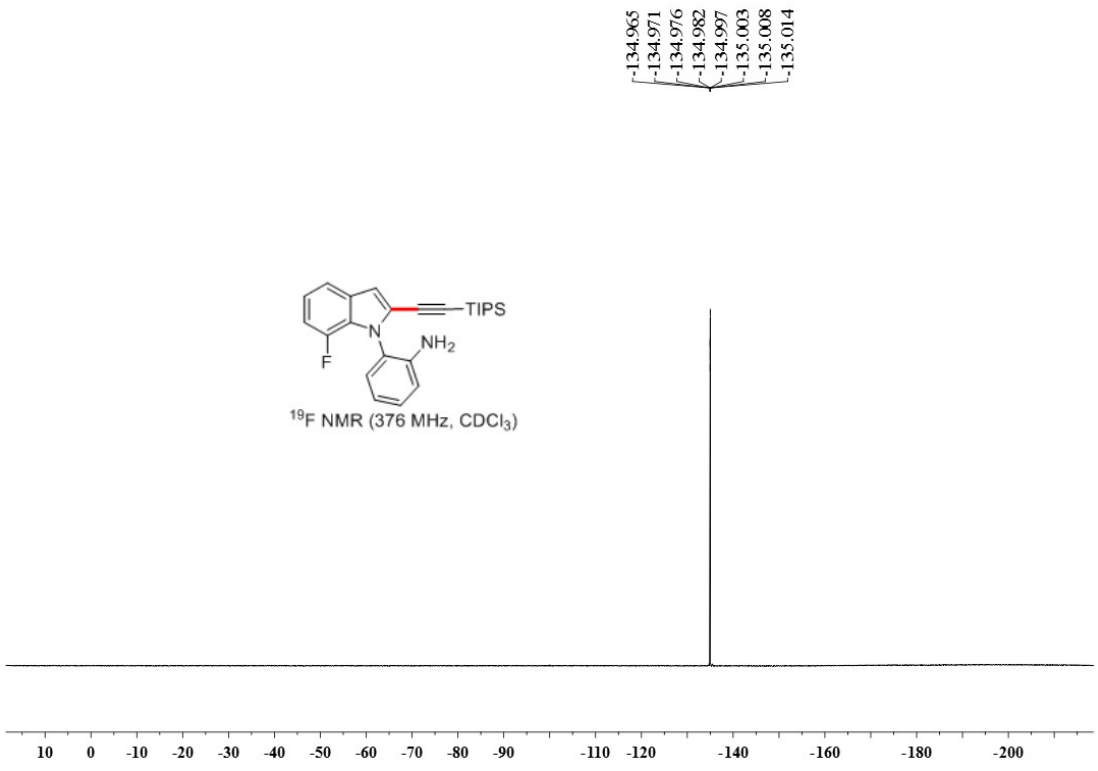




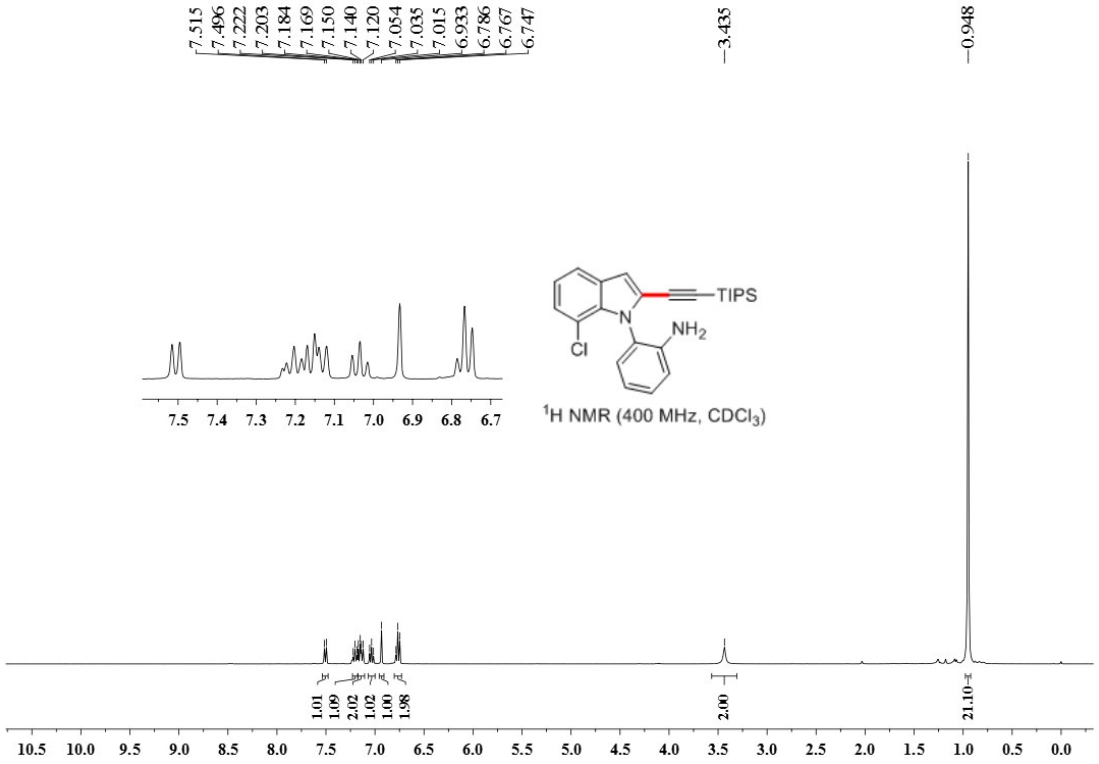
2-(7-Fluoro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3r)

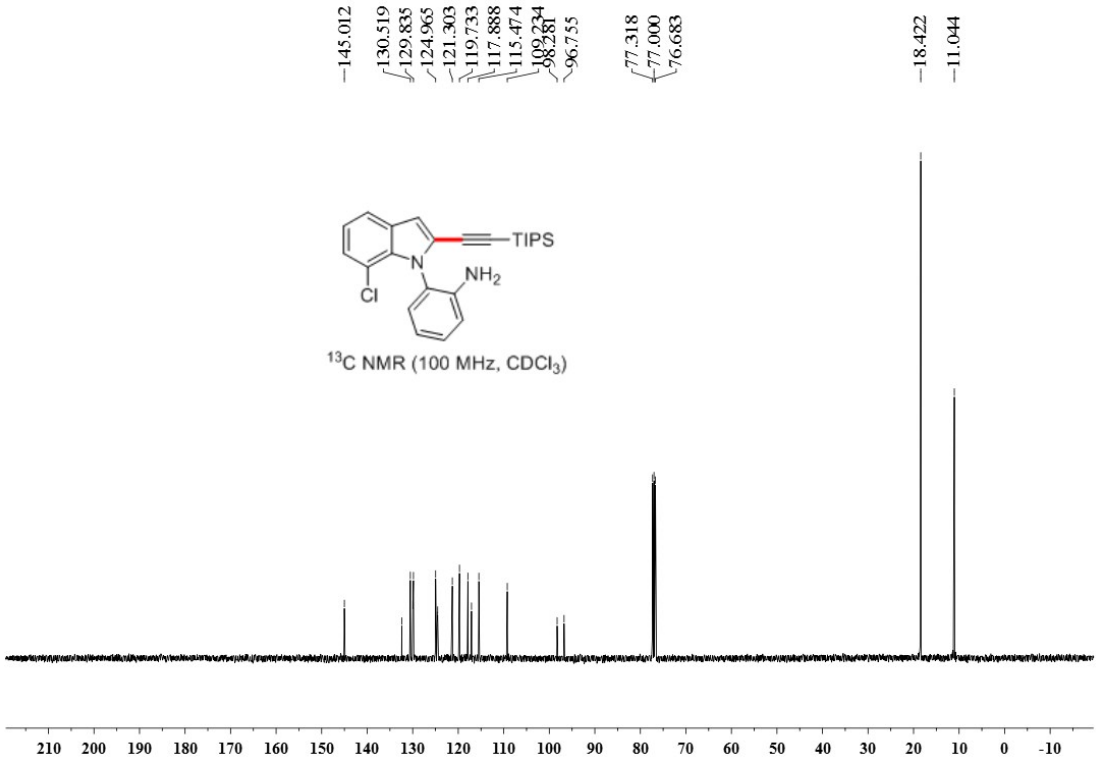




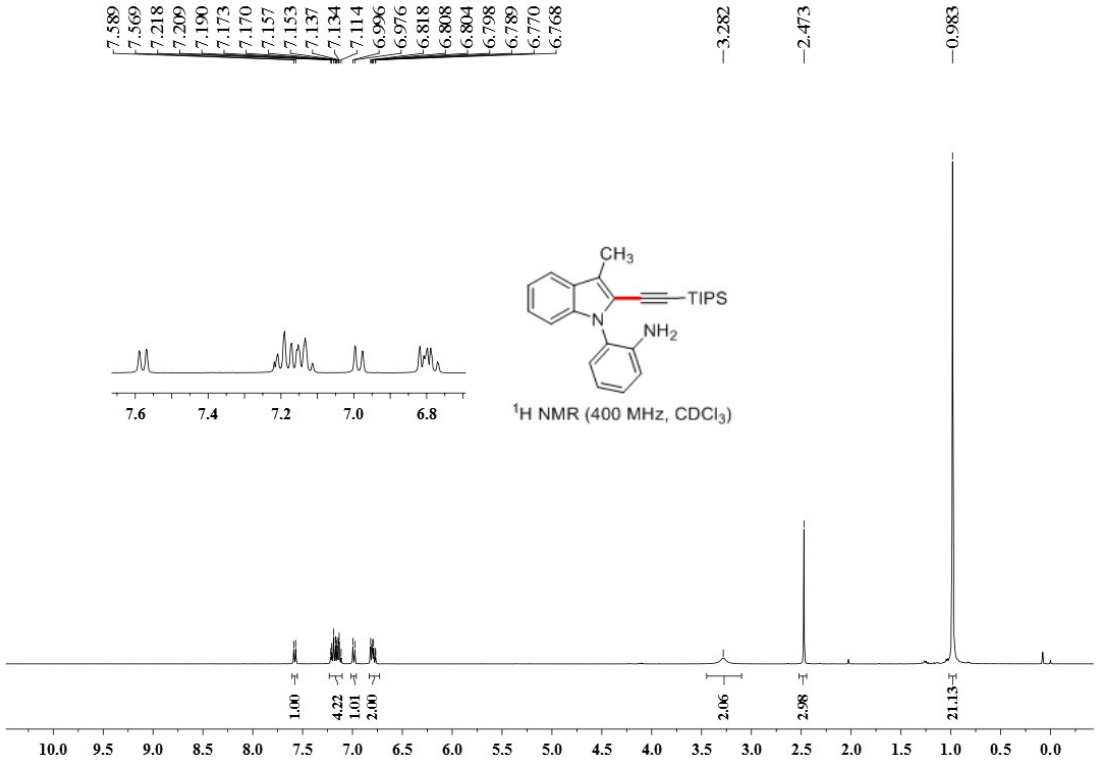

-134.965
-134.971
-134.976
-134.982
-134.997
-135.003
-135.008
-135.014
TIPS
N
NH2
F
19F NMR (376 MHz, CDCl3)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-120
-140
-160
-180
-200

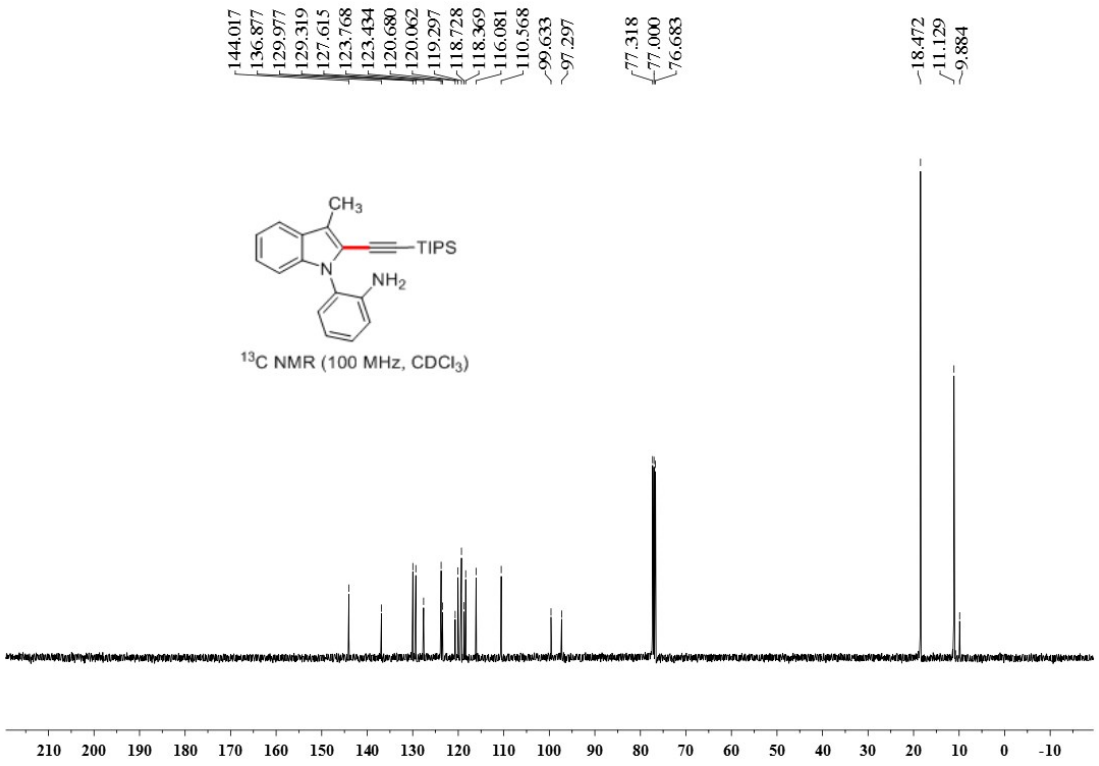
2-(7-Chloro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3s)



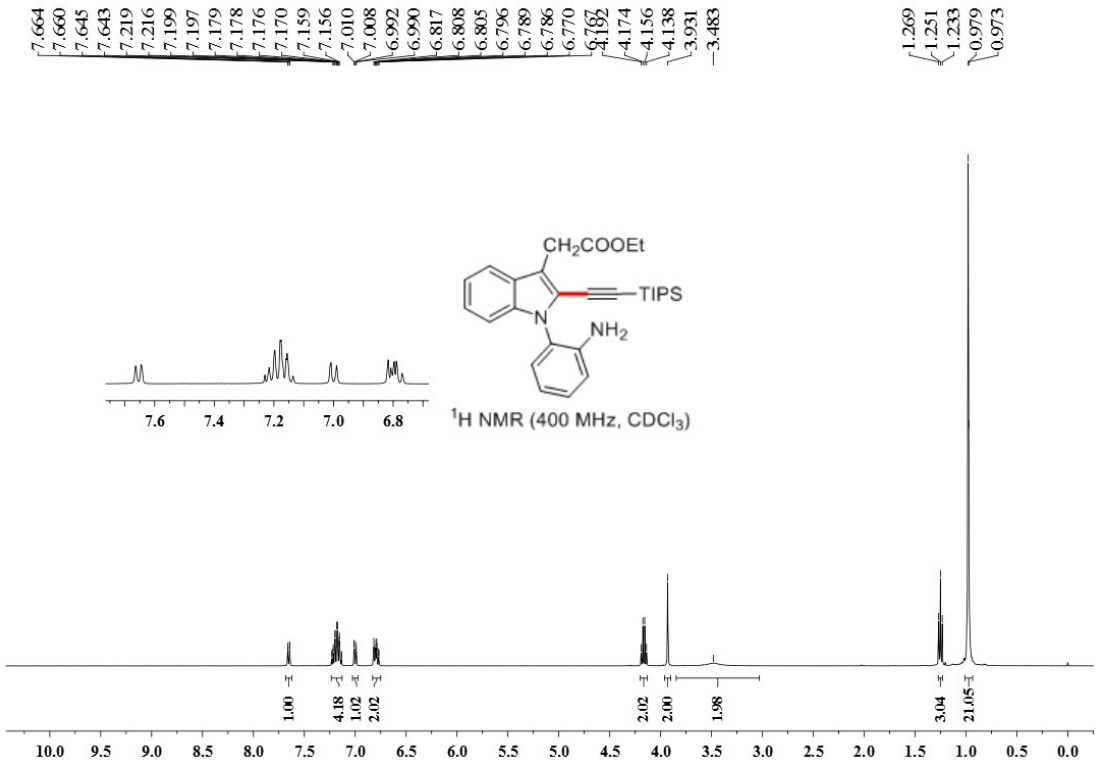


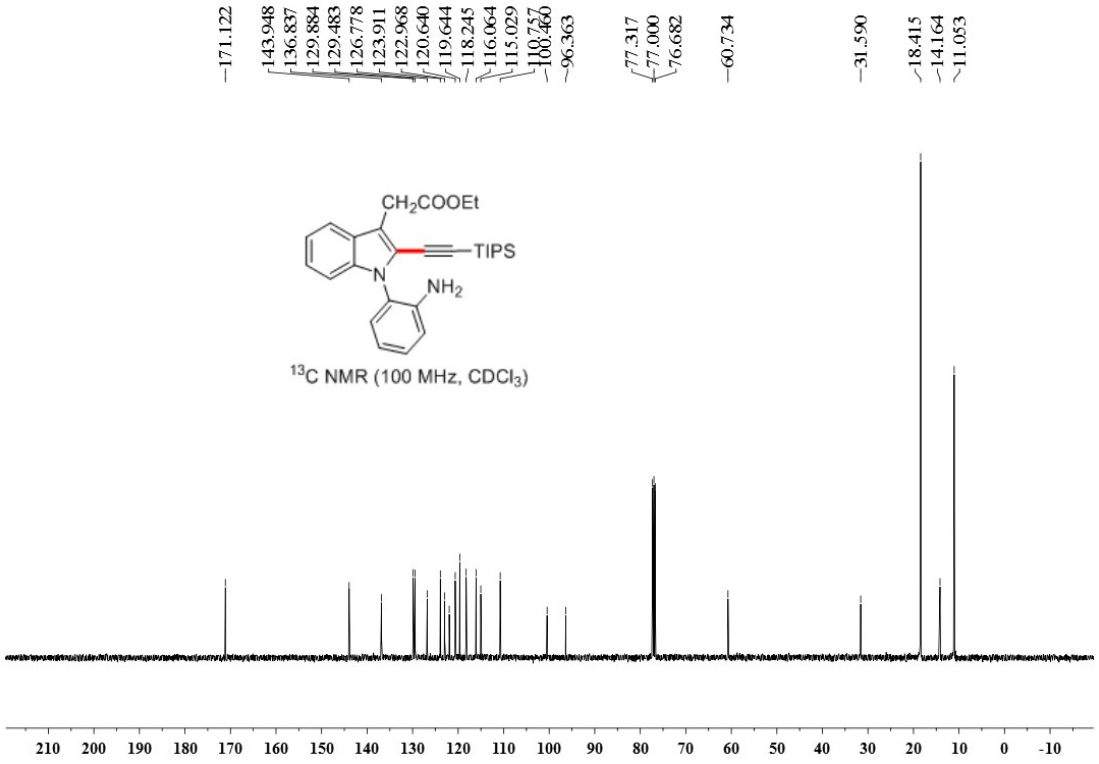
2-(3-Methyl-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3t)



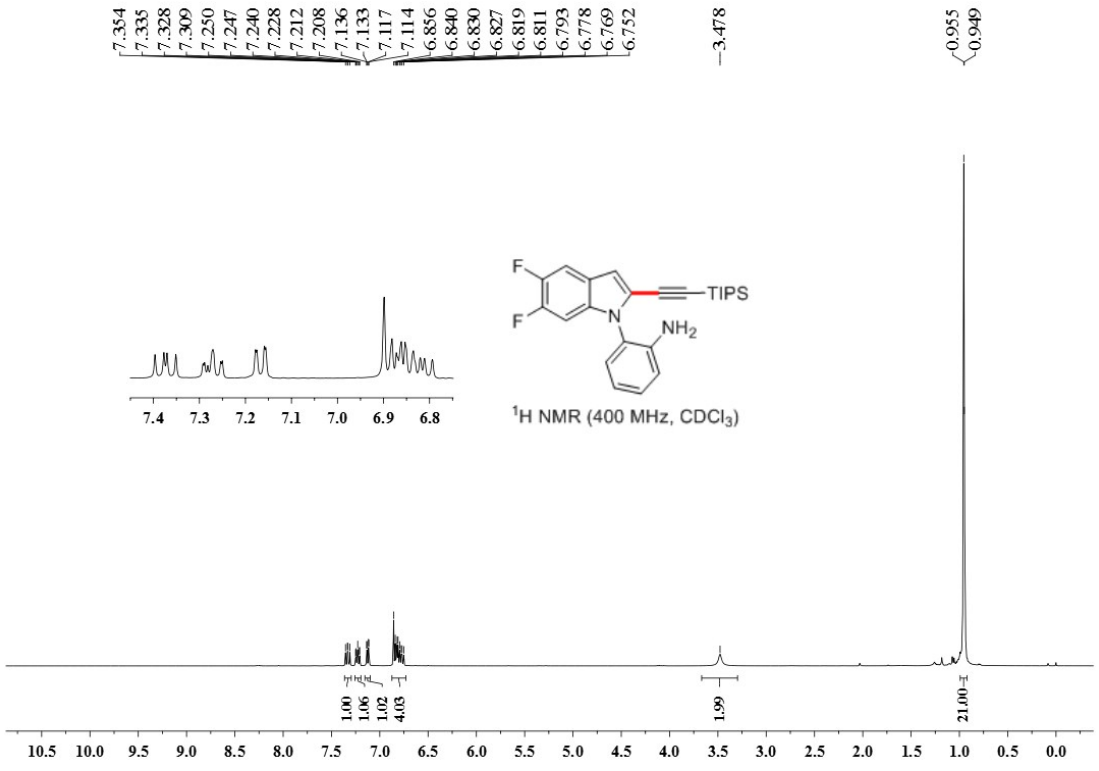


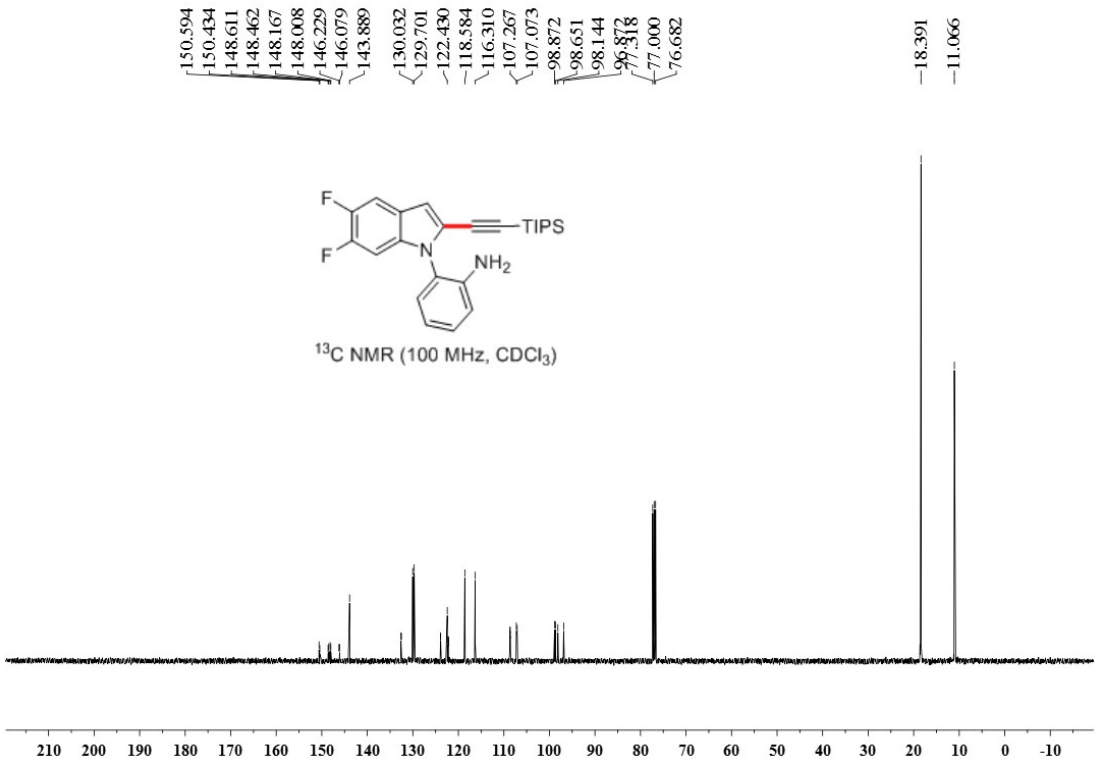
Ethyl 2-(1-(2-aminophenyl)-2-((triisopropylsilyl)ethynyl)-1*H*-indol-3-yl)acetate (3u)

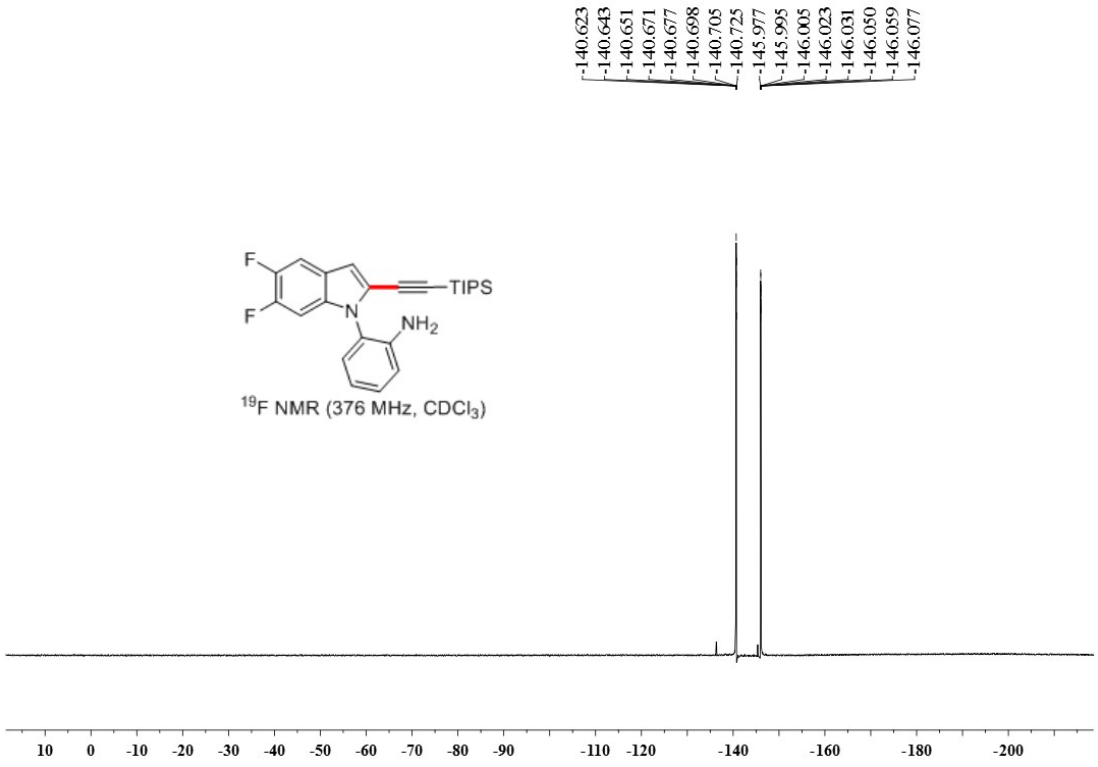




2-(5,6-Difluoro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3v)

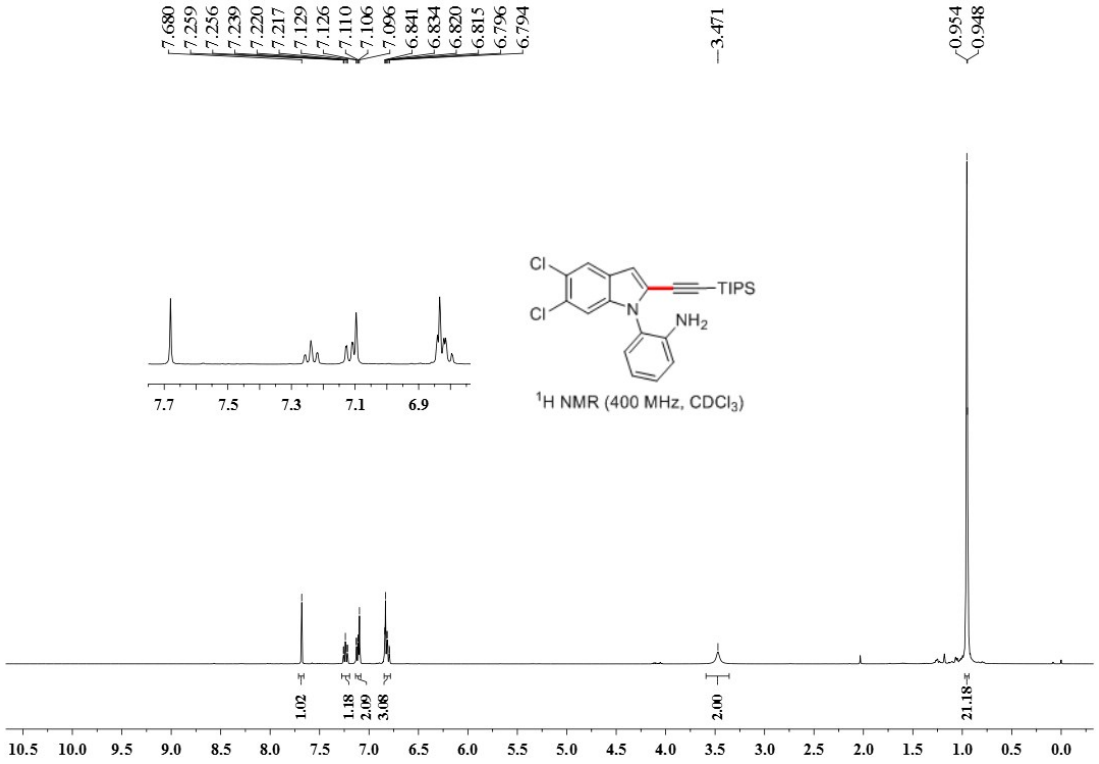


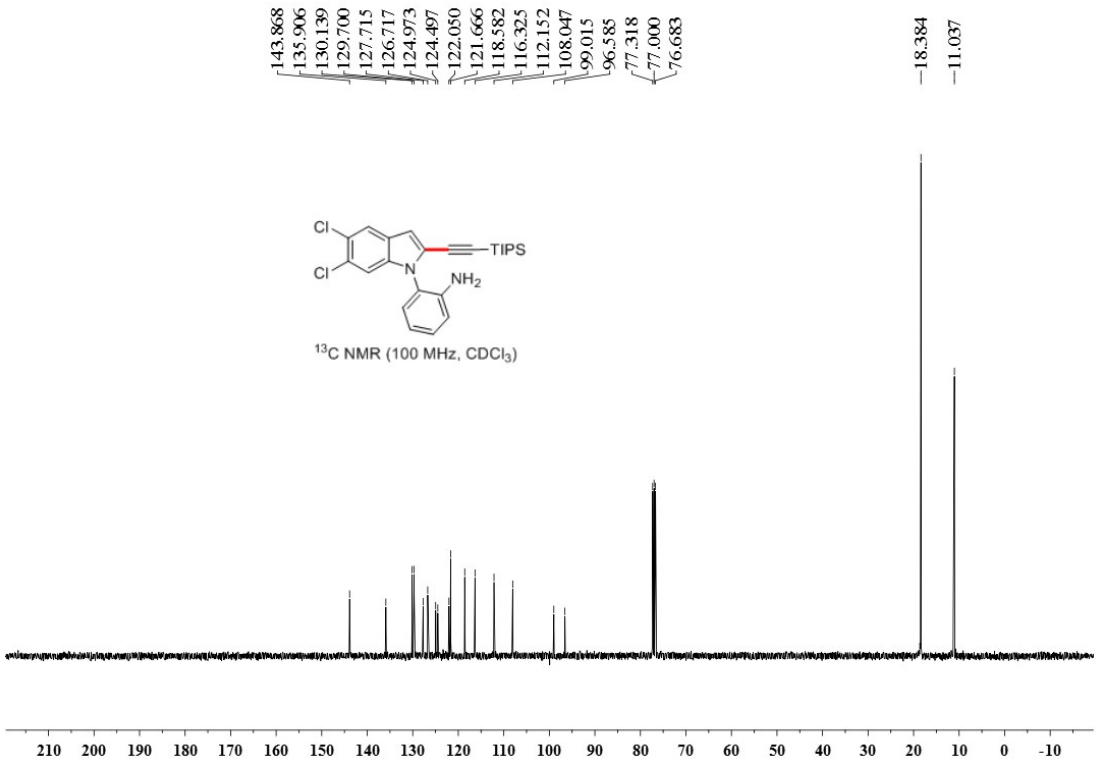




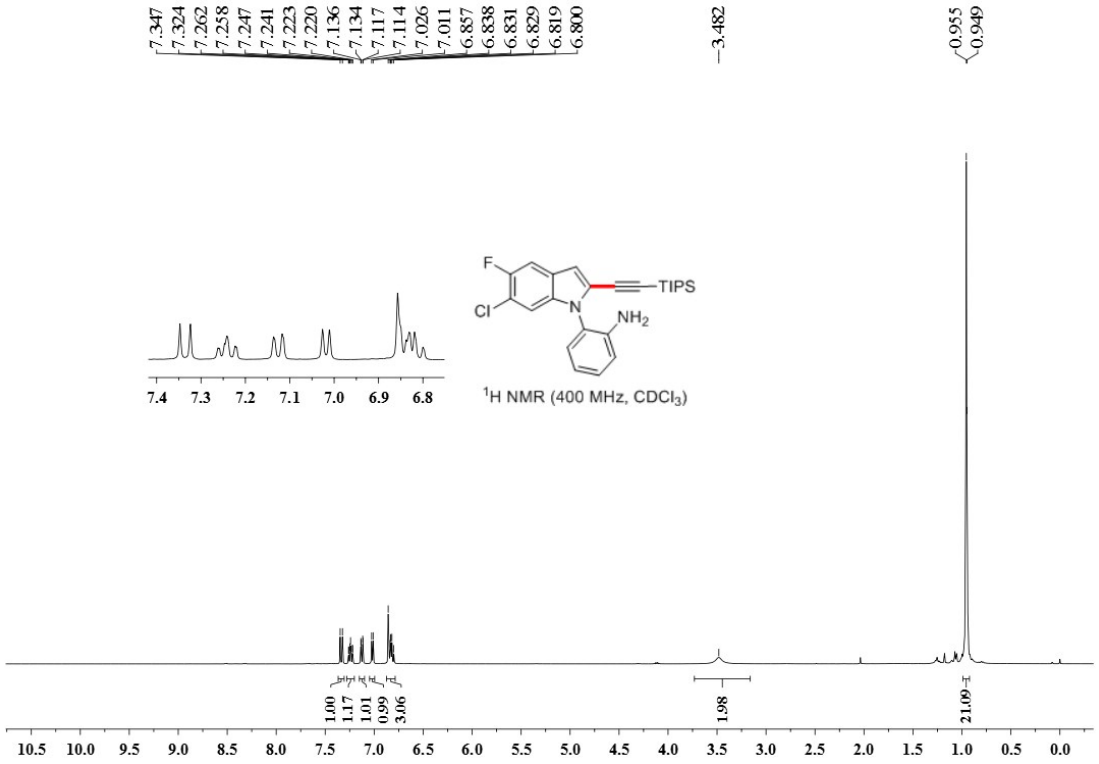
^{19}F NMR (376 MHz, $CDCl_3$)

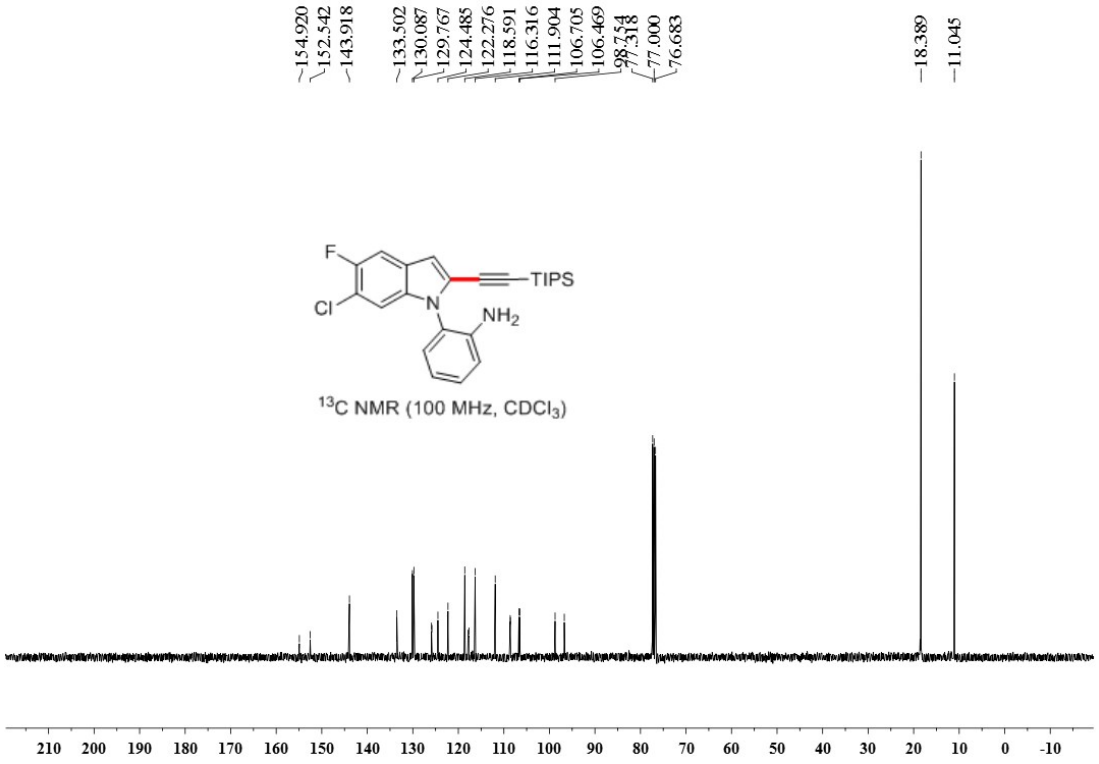
2-(5,6-Dichloro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3w)

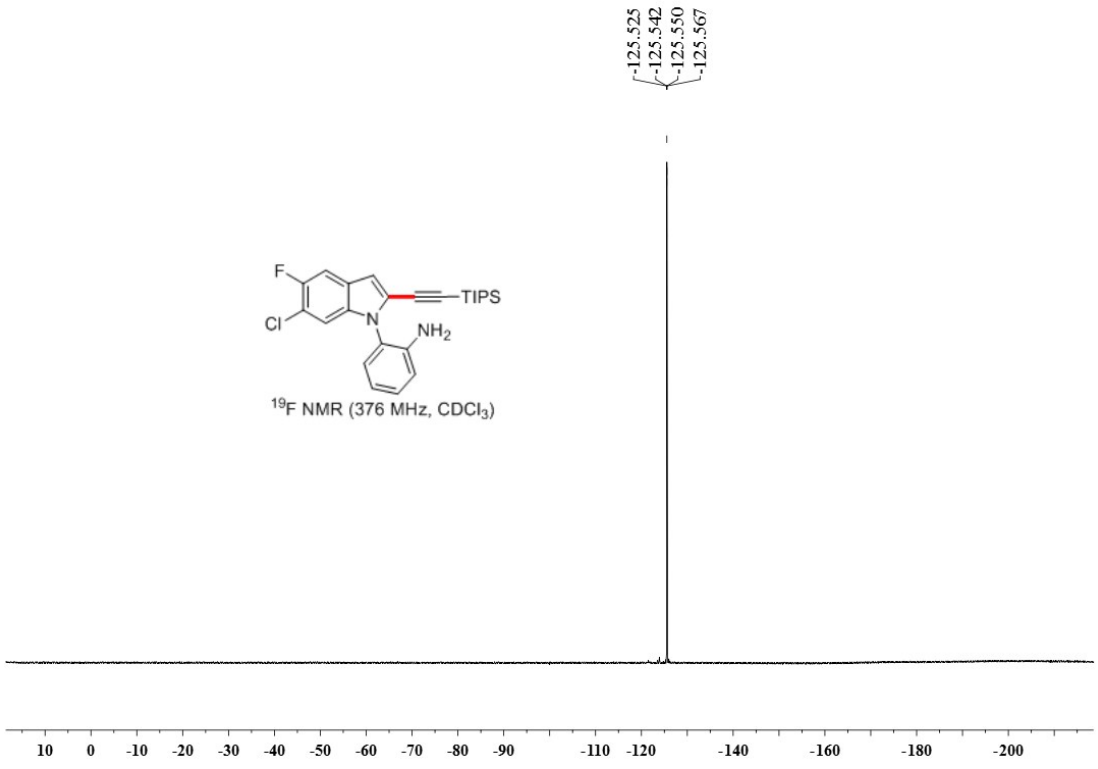




2-(6-Chloro-5-fluoro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3x)

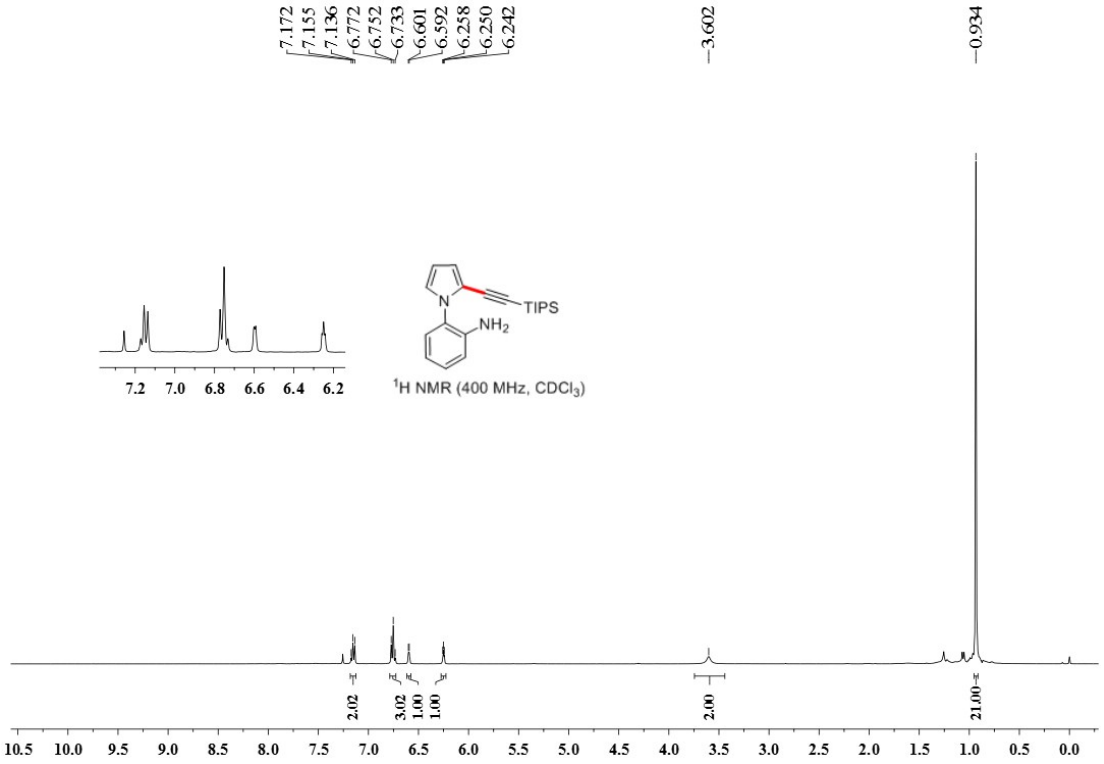


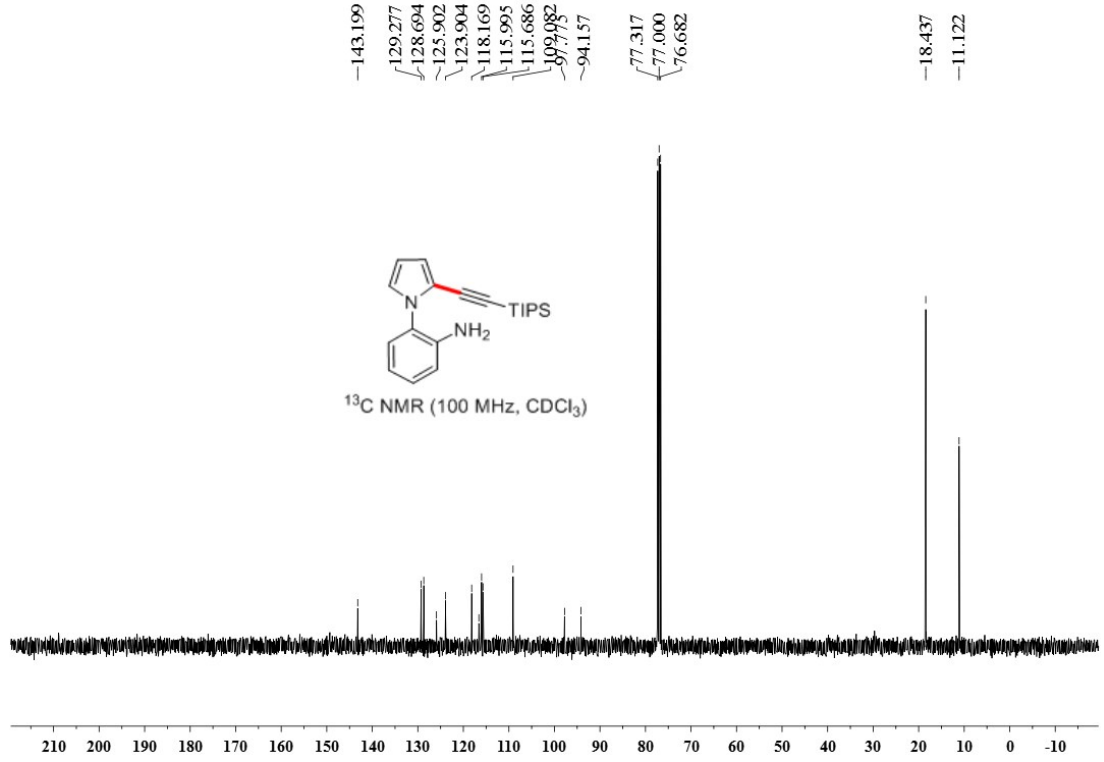




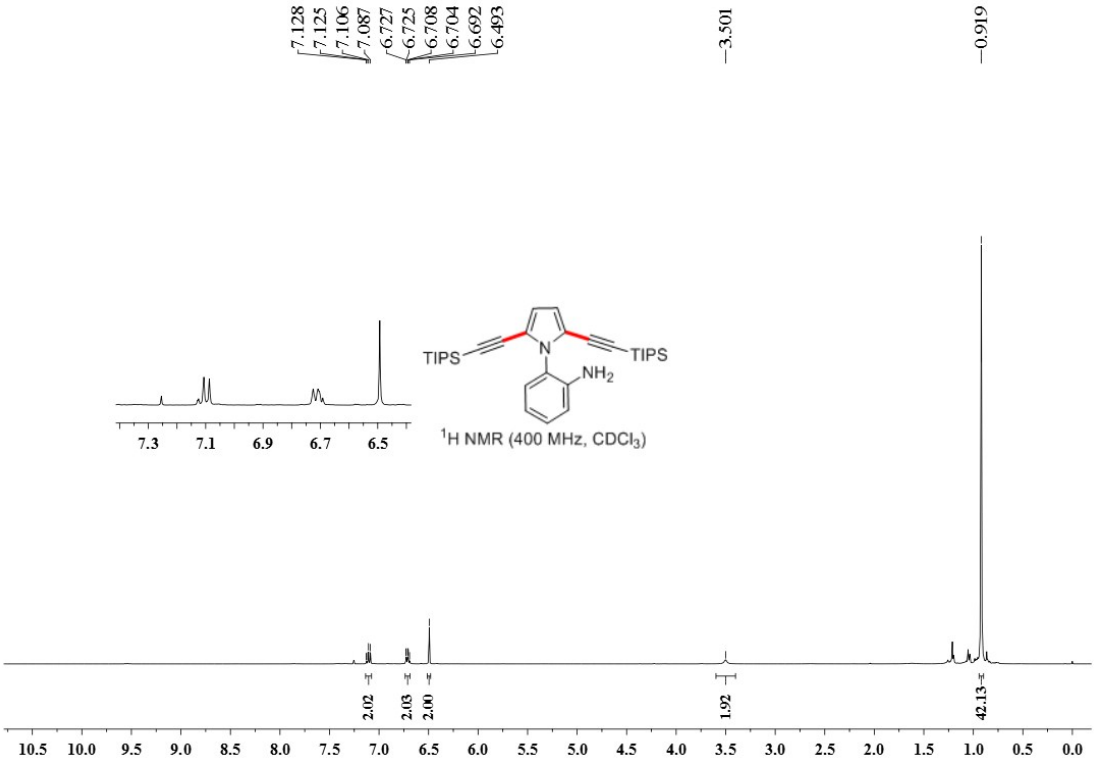
^{19}F NMR (376 MHz, $CDCl_3$)

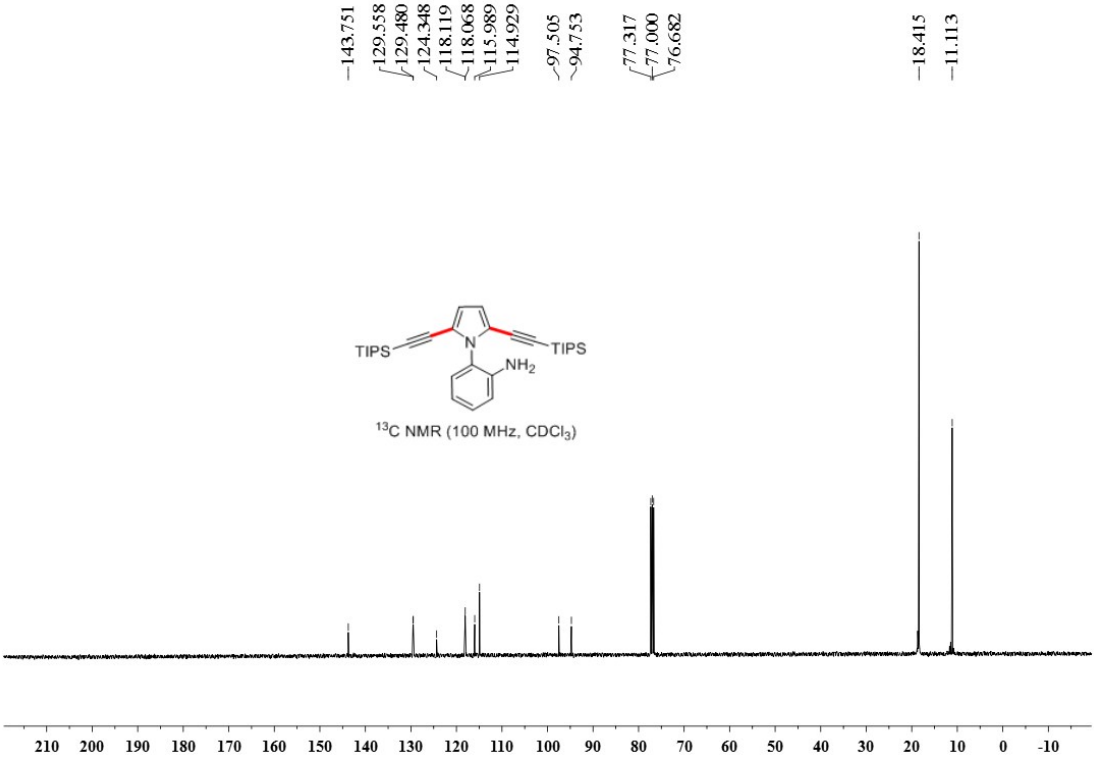
2-(2-((Triisopropylsilyl)ethynyl)-1*H*-pyrrol-1-yl)aniline (3y)



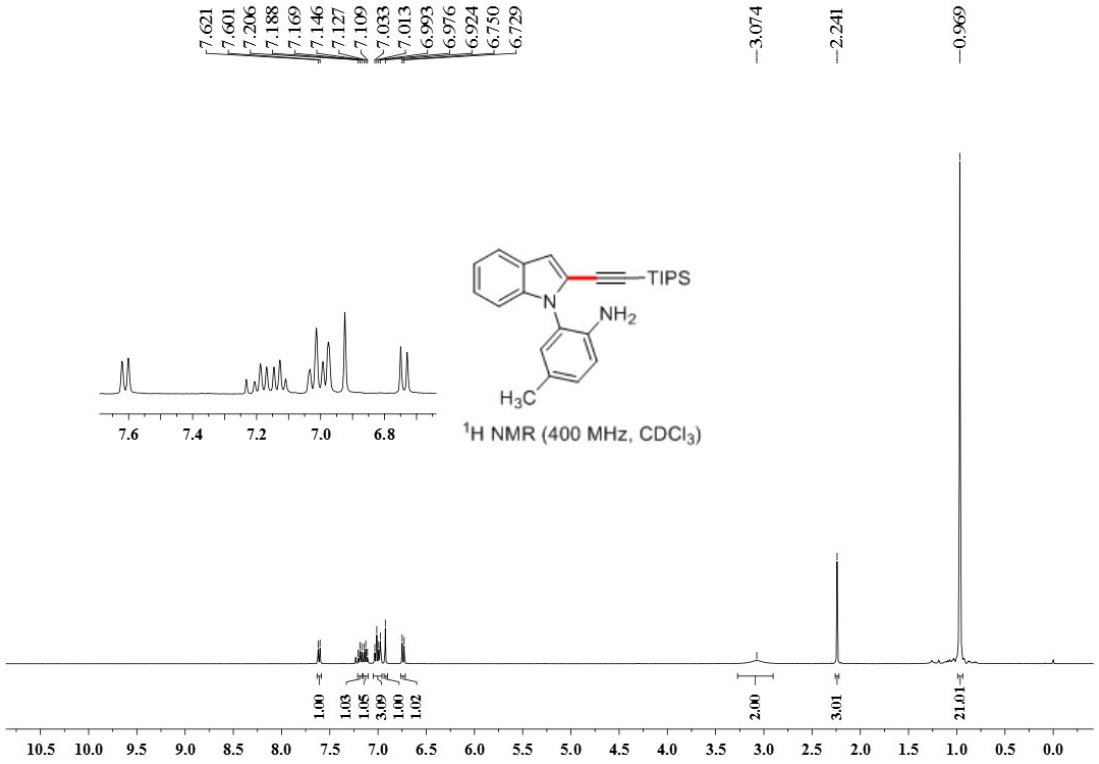


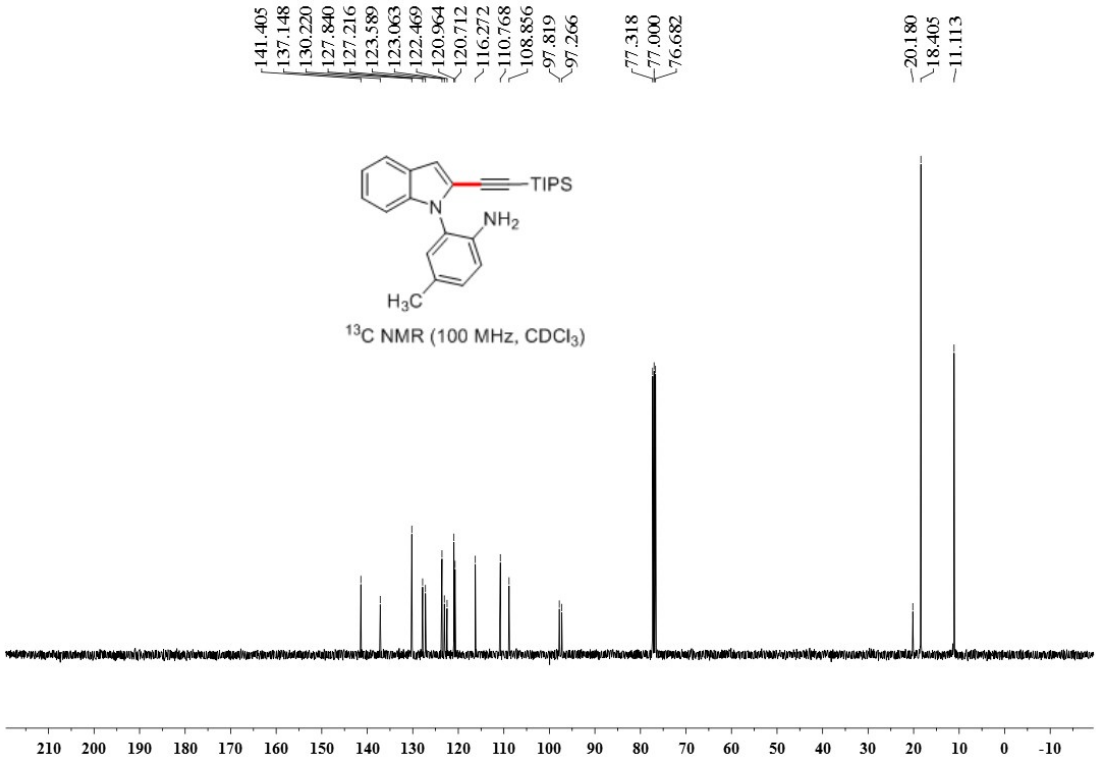
2-(2,5-Bis((triisopropylsilyl)ethynyl)-1*H*-pyrrol-1-yl)aniline (3z)



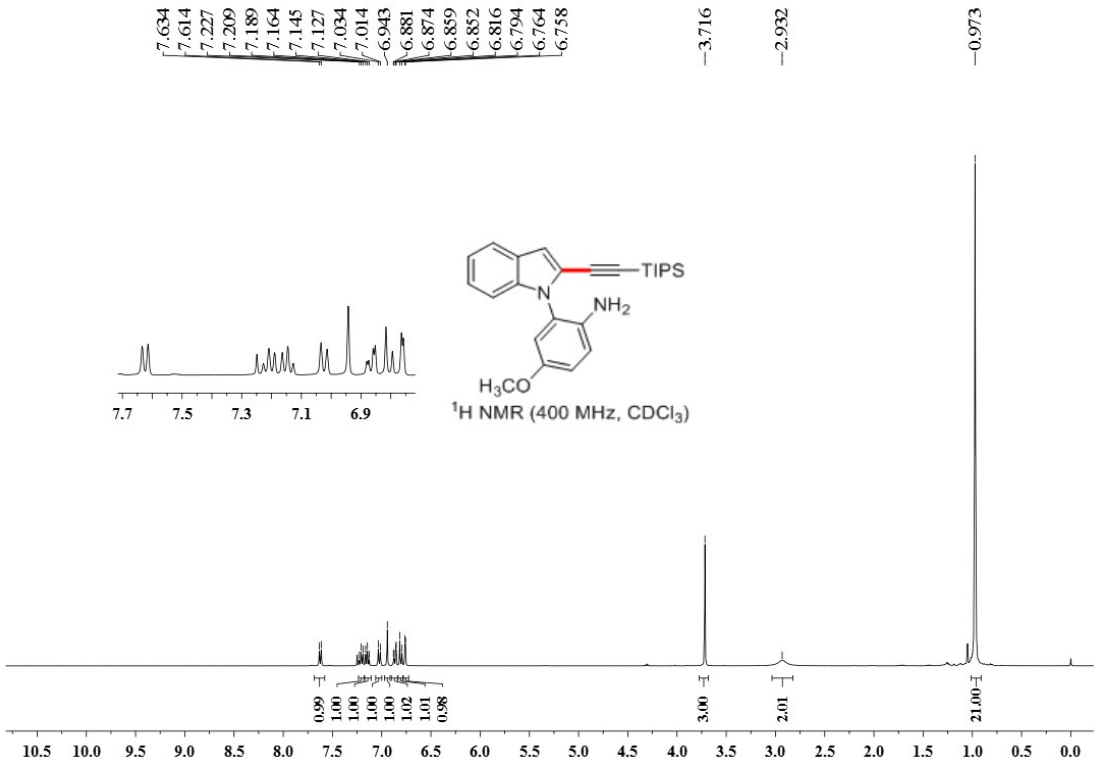


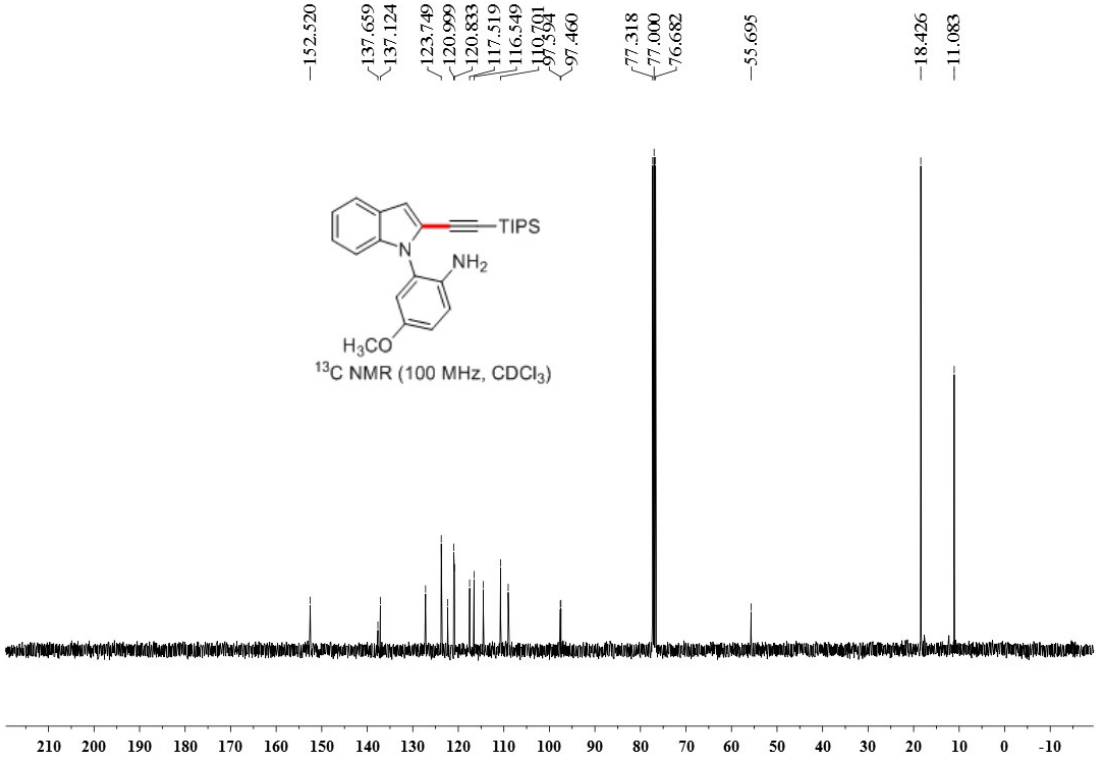
4-Methyl-2-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3aa)



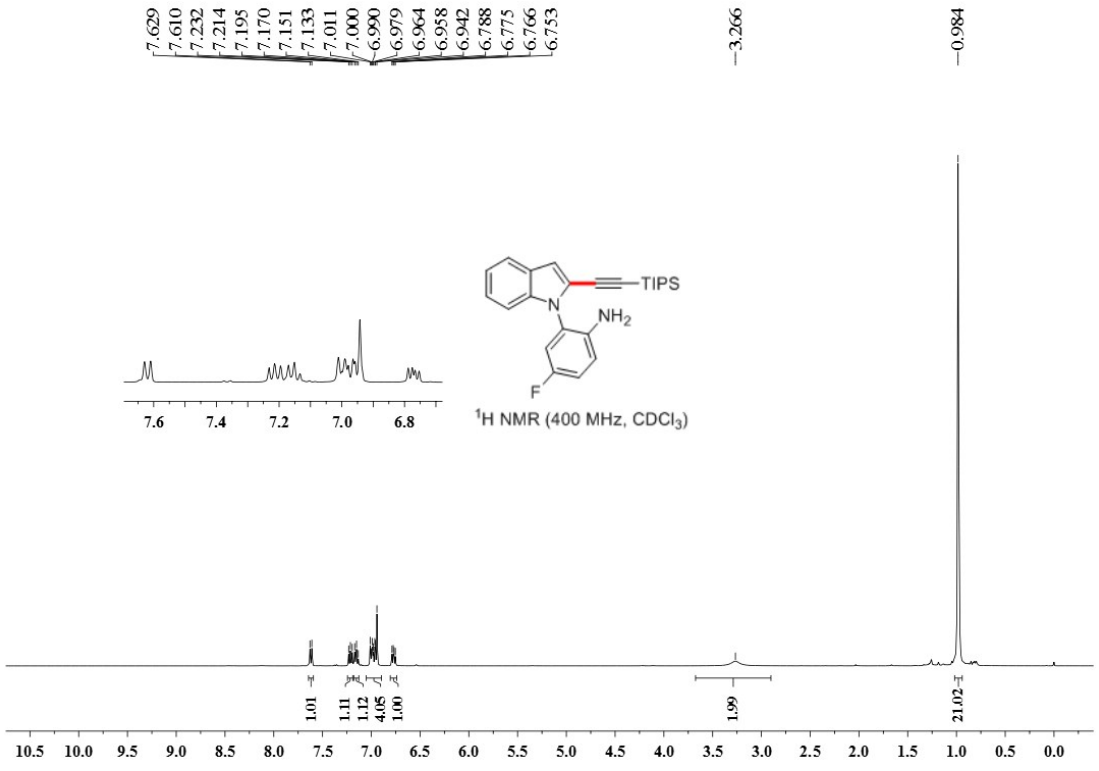


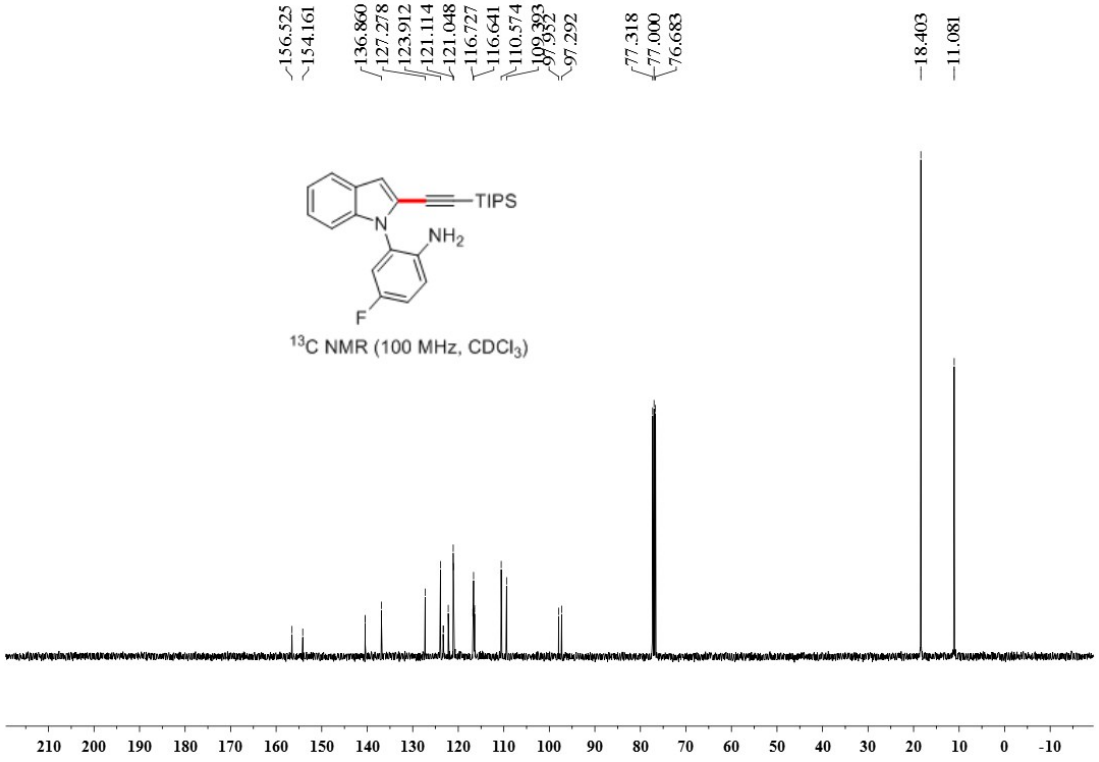
4-Methoxy-2-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3ab)

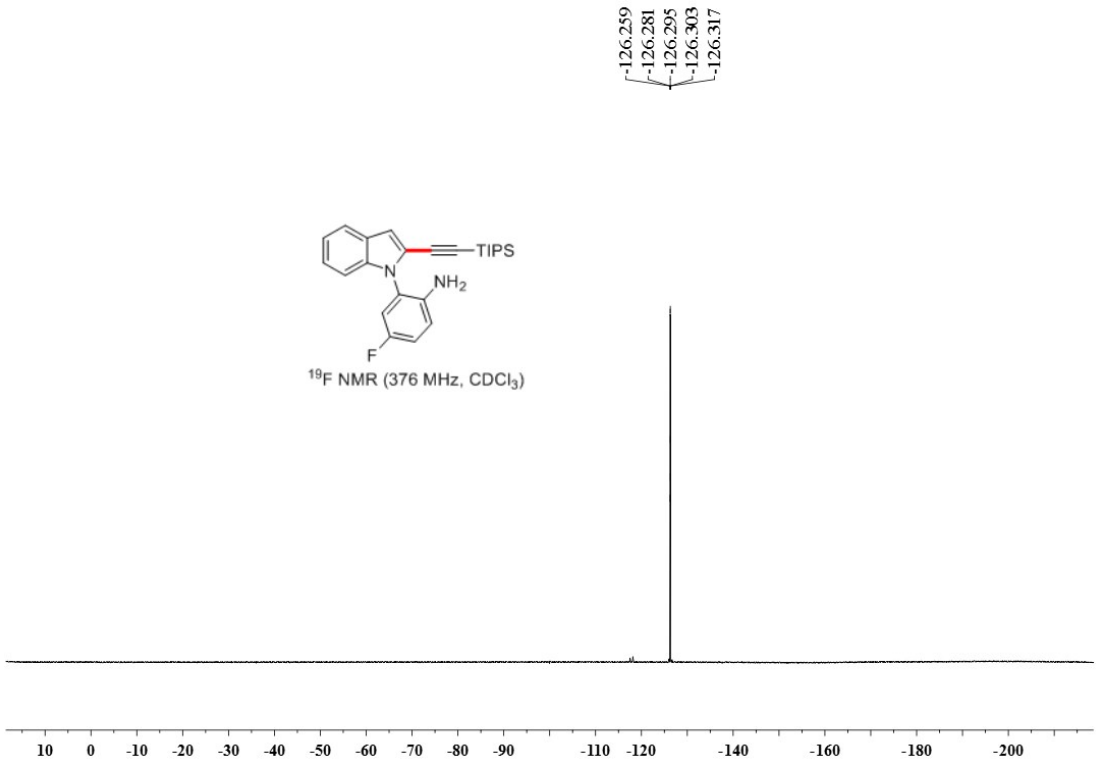




4-Fluoro-2-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3ac)

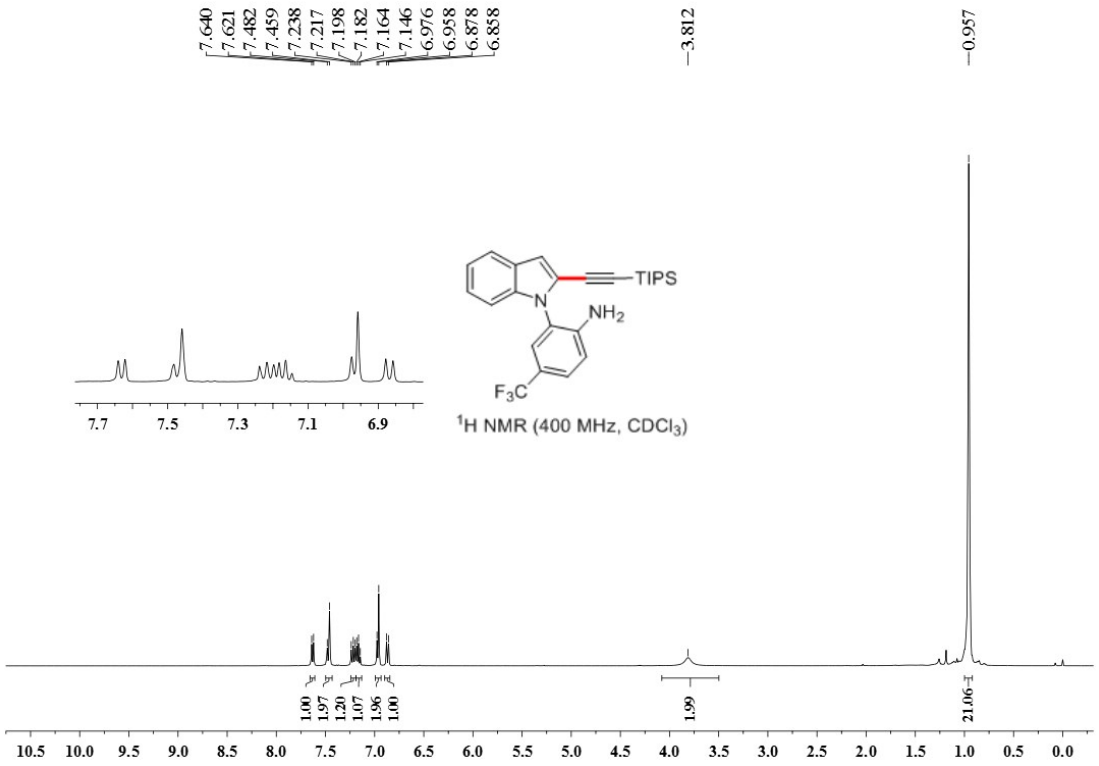


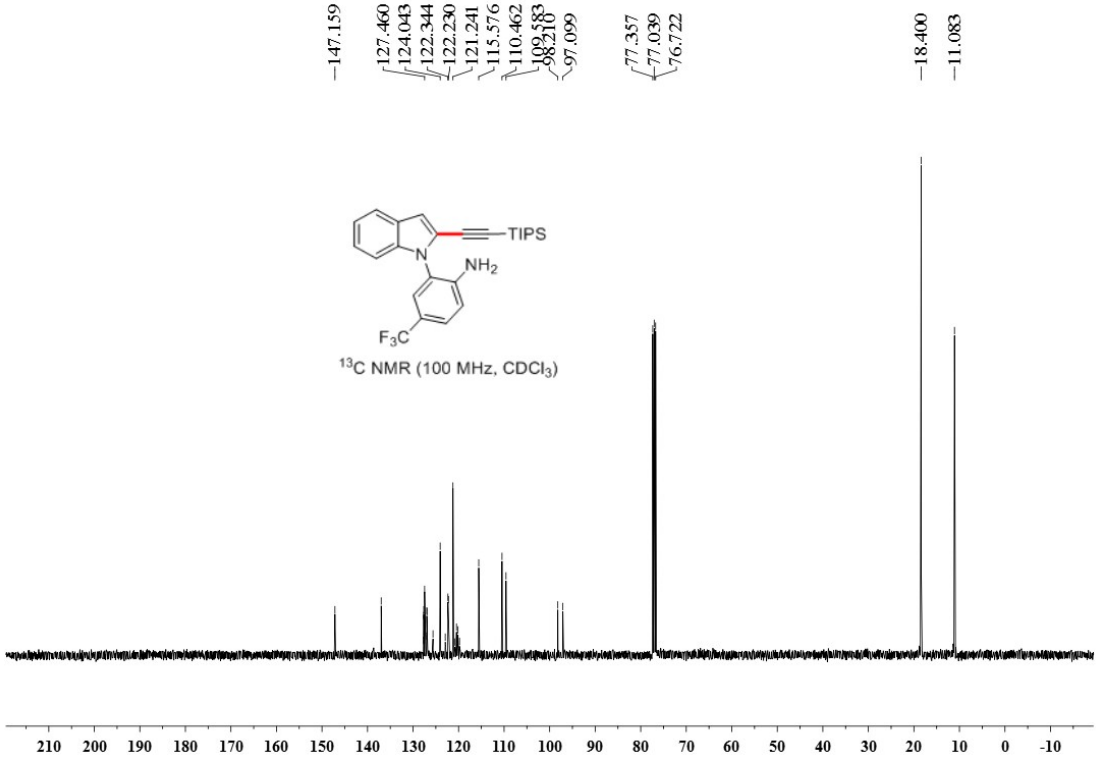


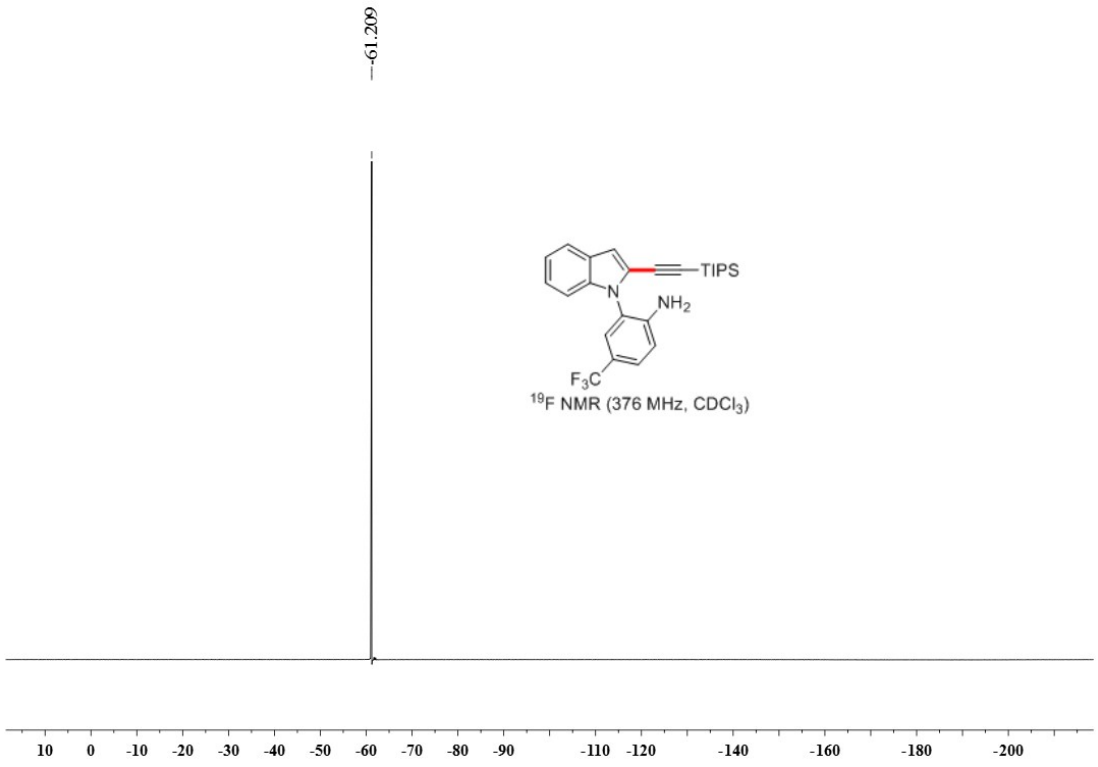


^{19}F NMR (376 MHz, $CDCl_3$)

4-(Trifluoromethyl)-2-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3ad)

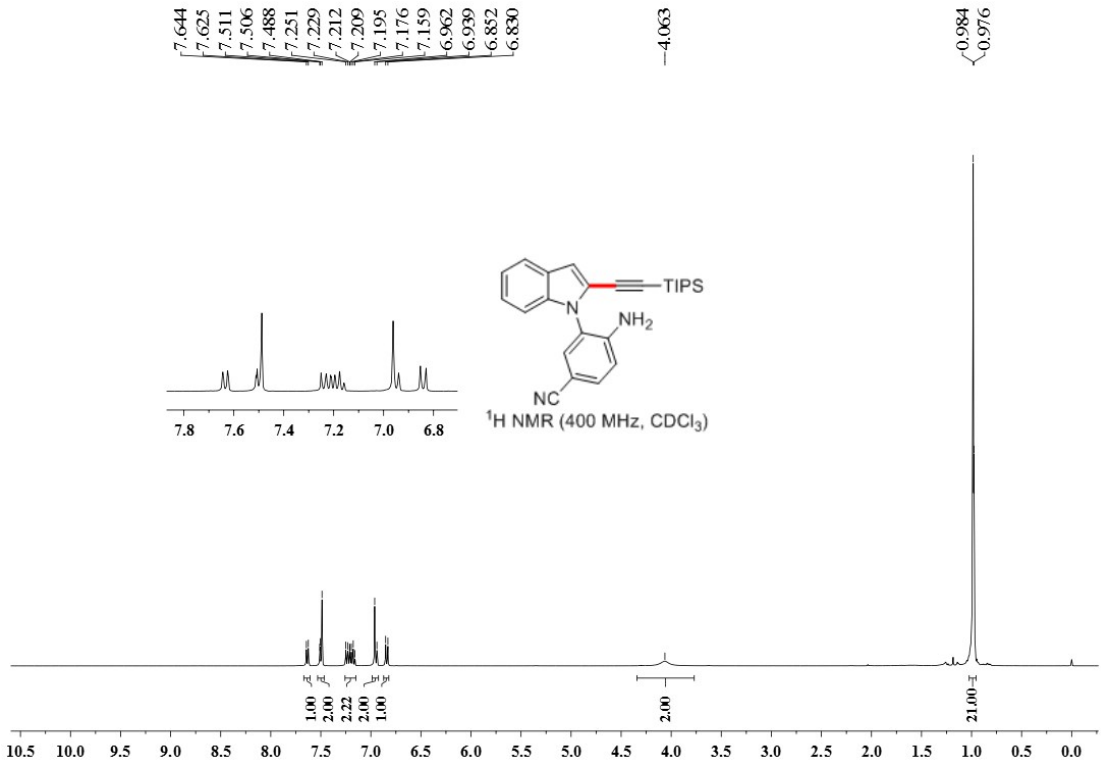


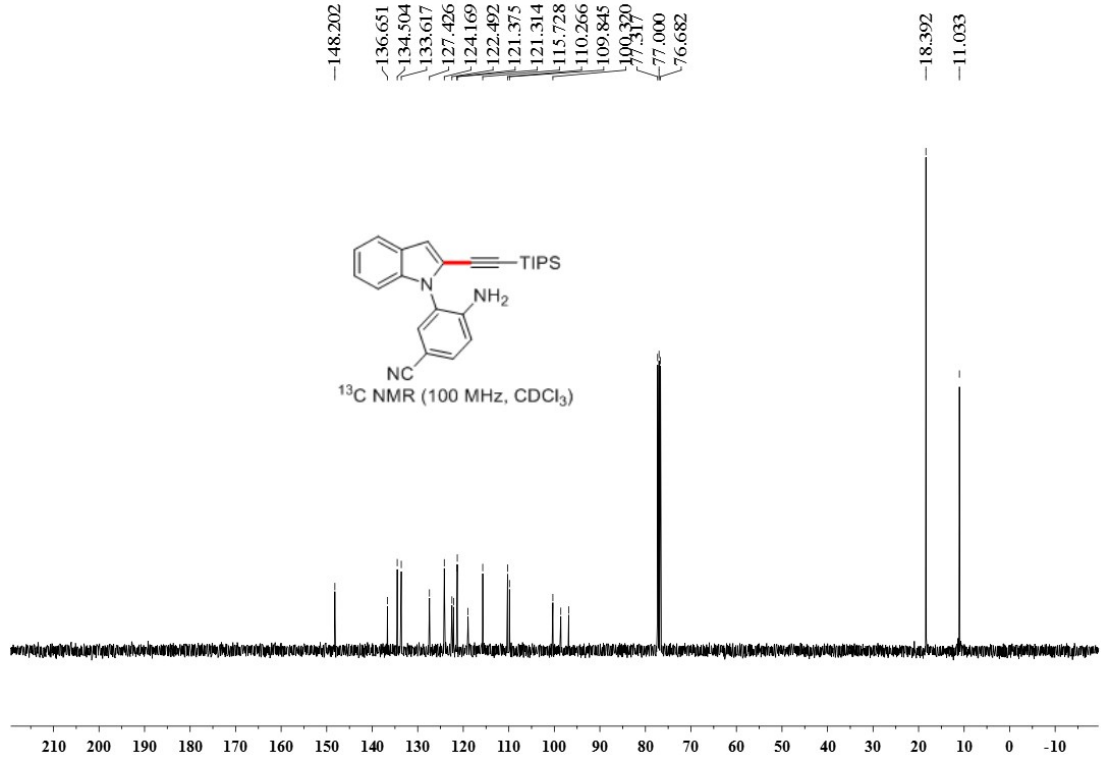




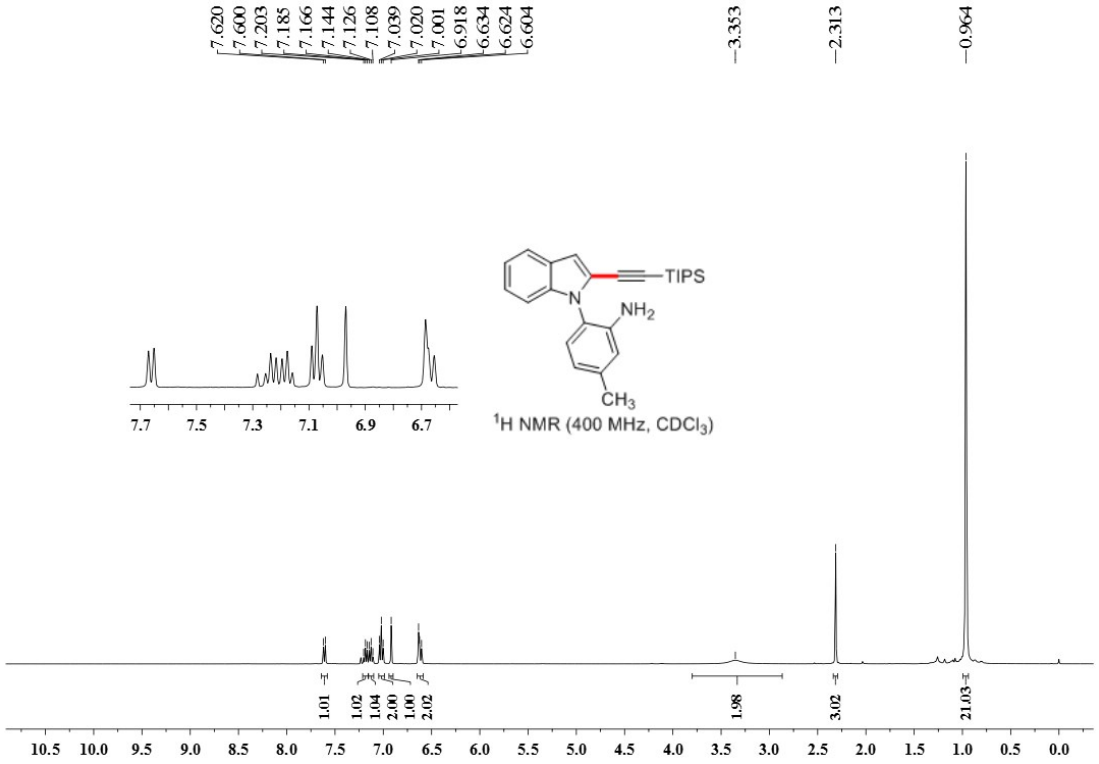
^{19}F NMR (376 MHz, $CDCl_3$)

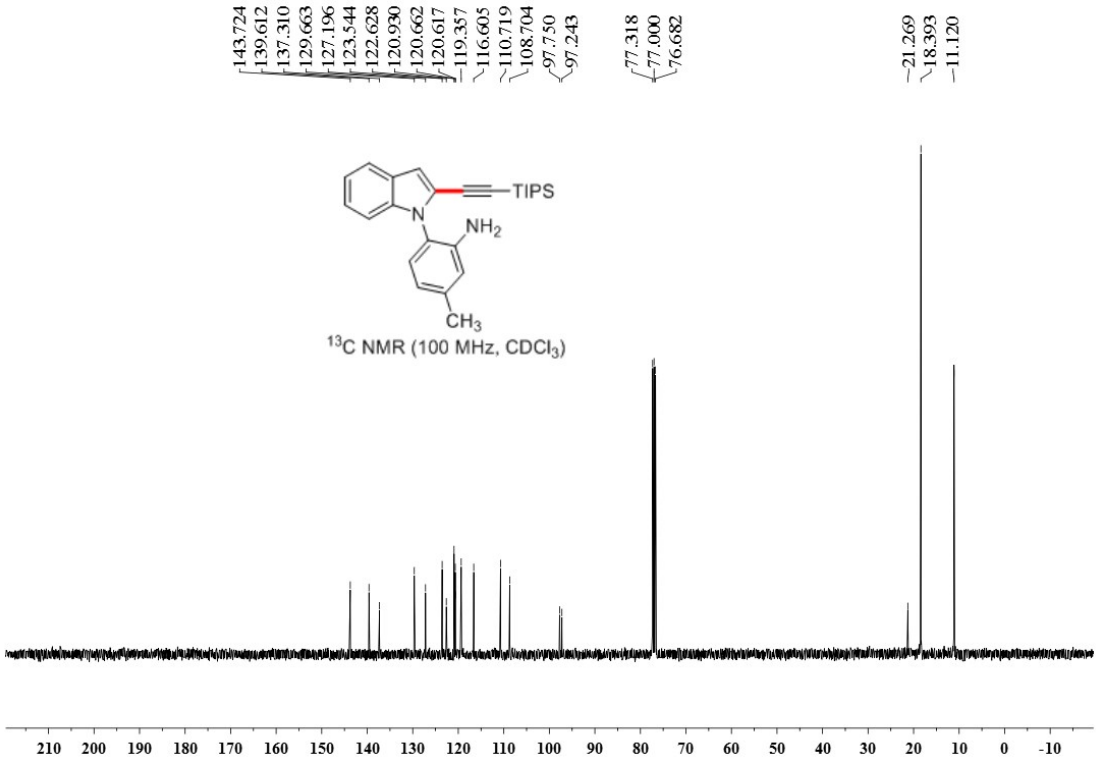
4-Amino-3-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)benzonitrile (3ae)



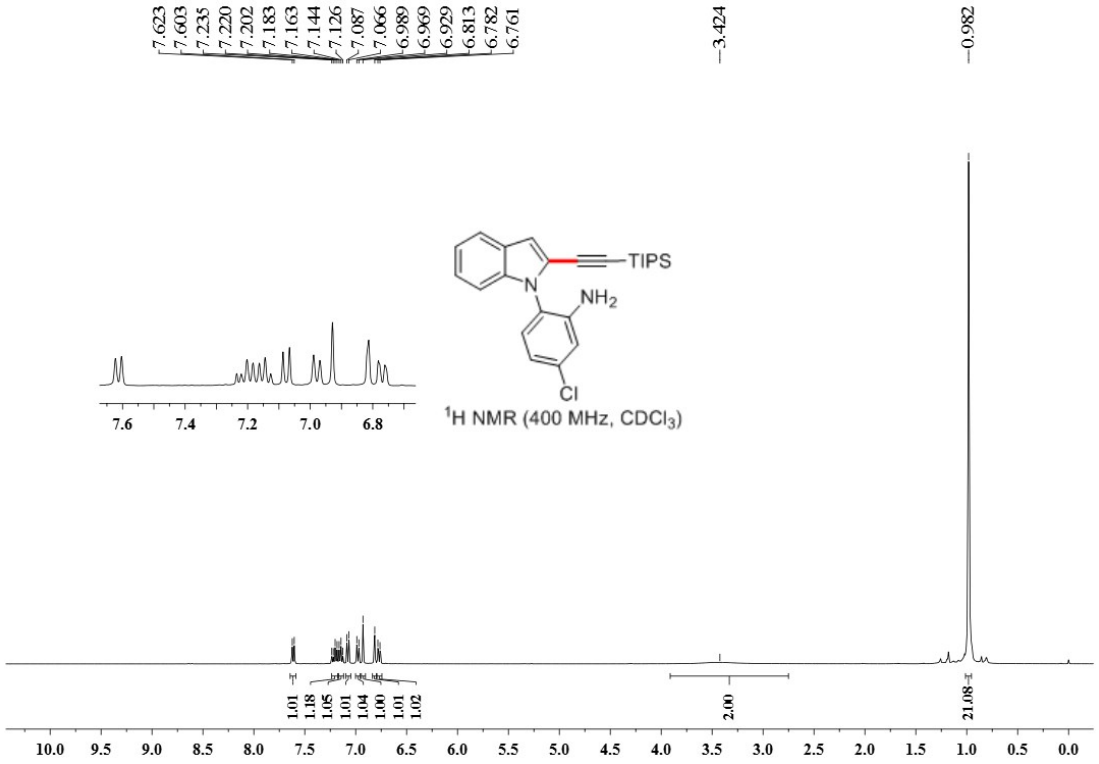


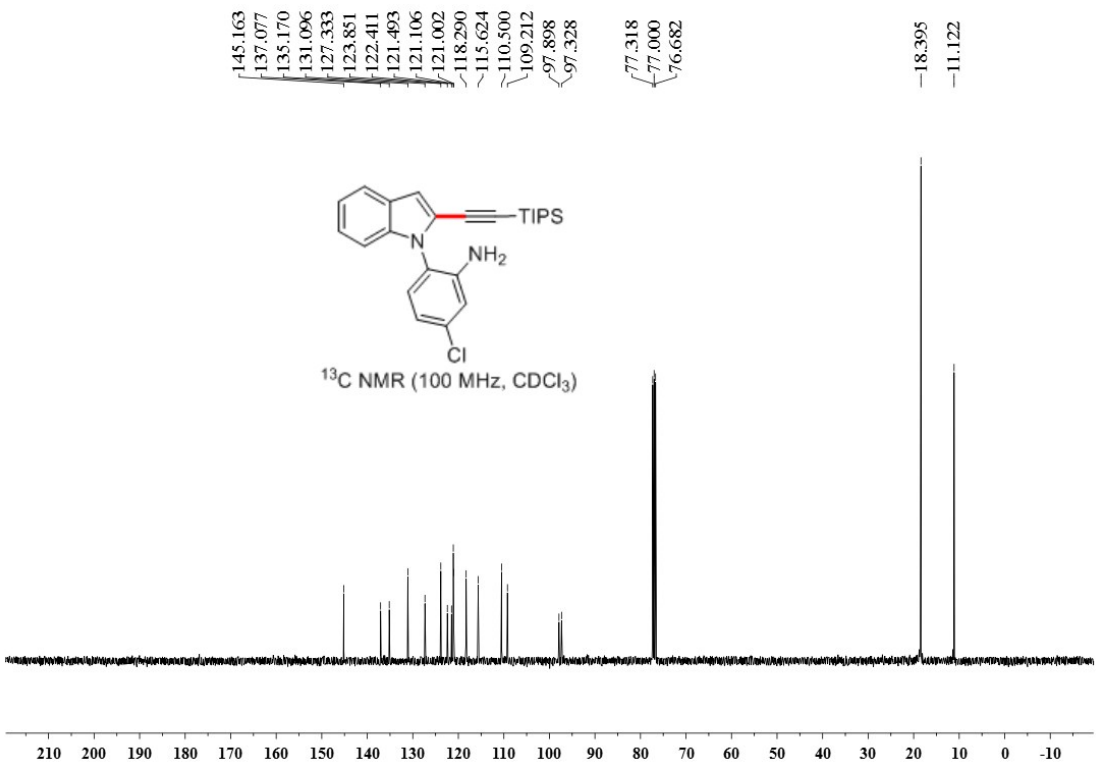
5-Methyl-2-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3af)



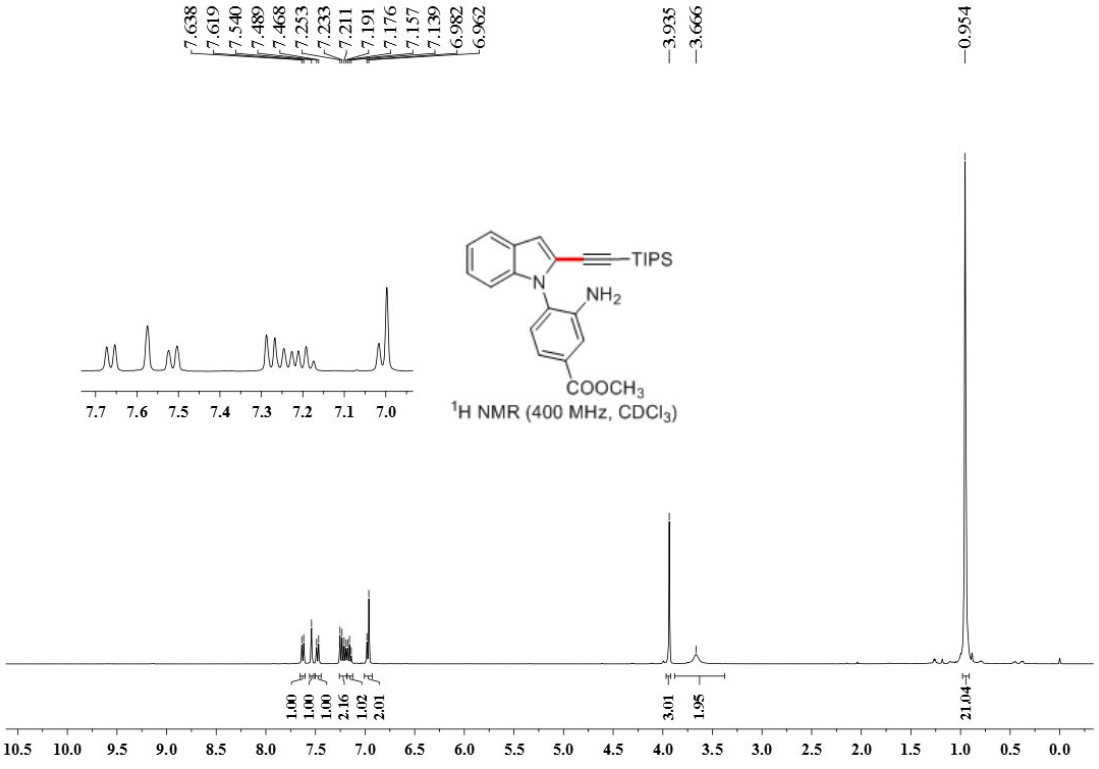


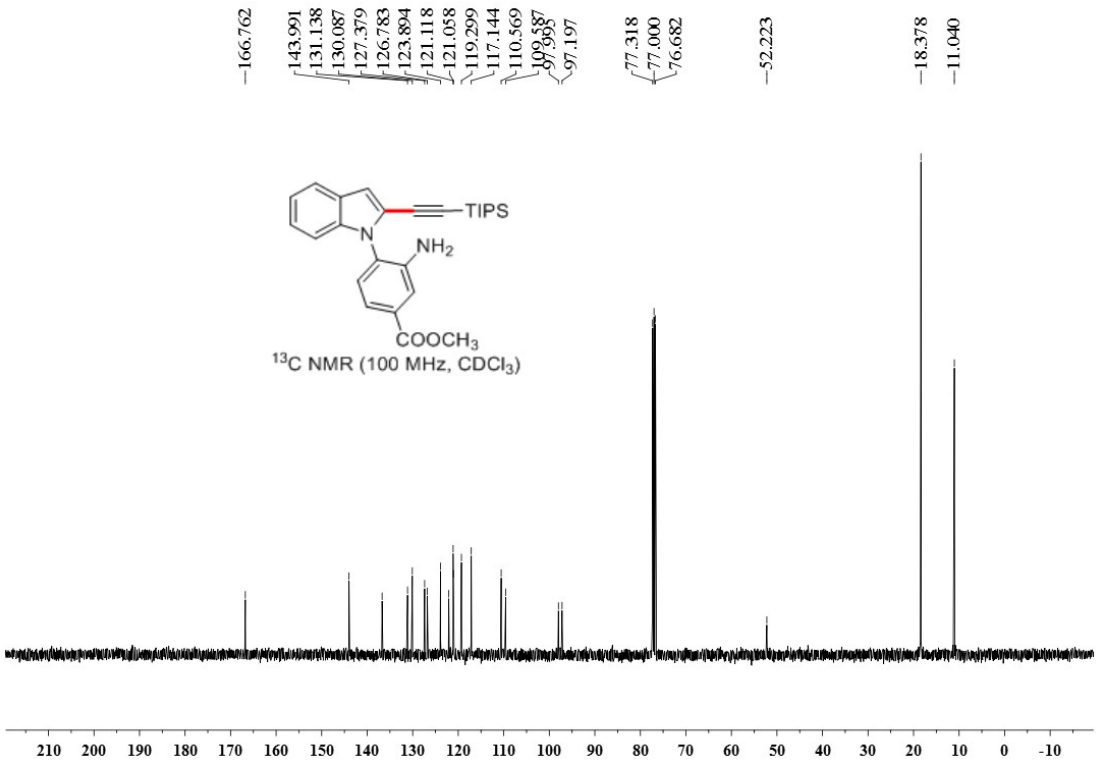
5-Chloro-2-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3ag)



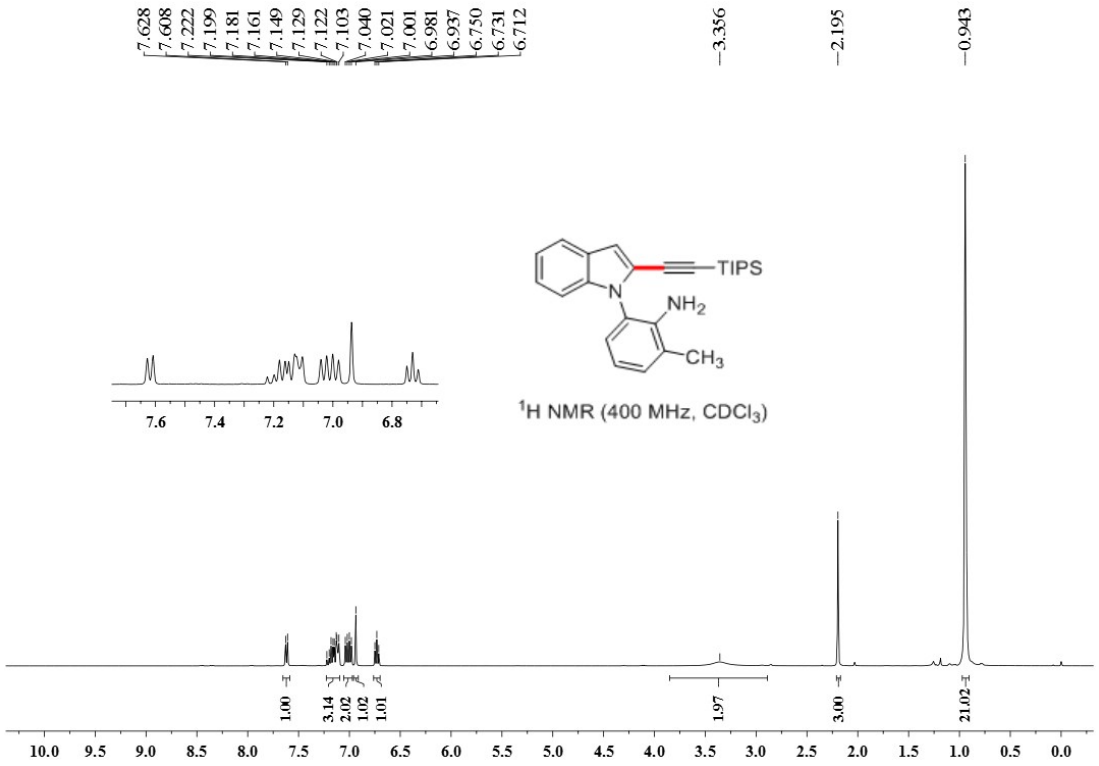


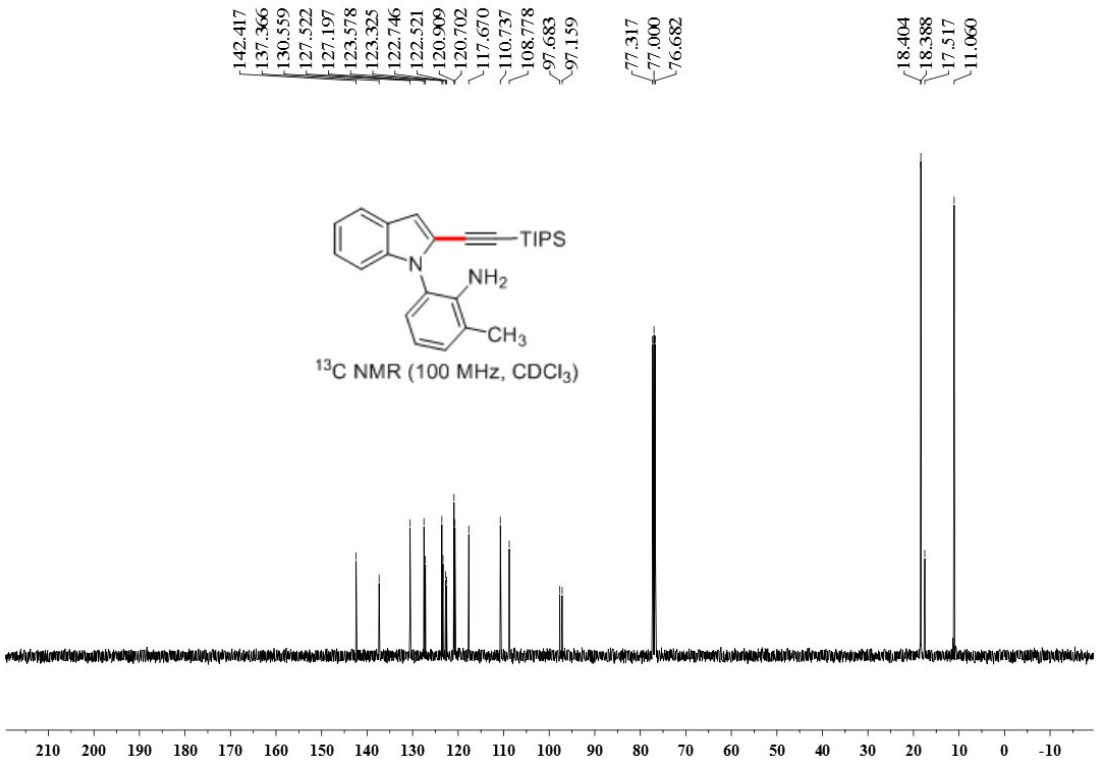
Methyl 3-amino-4-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)benzoate (3ah)



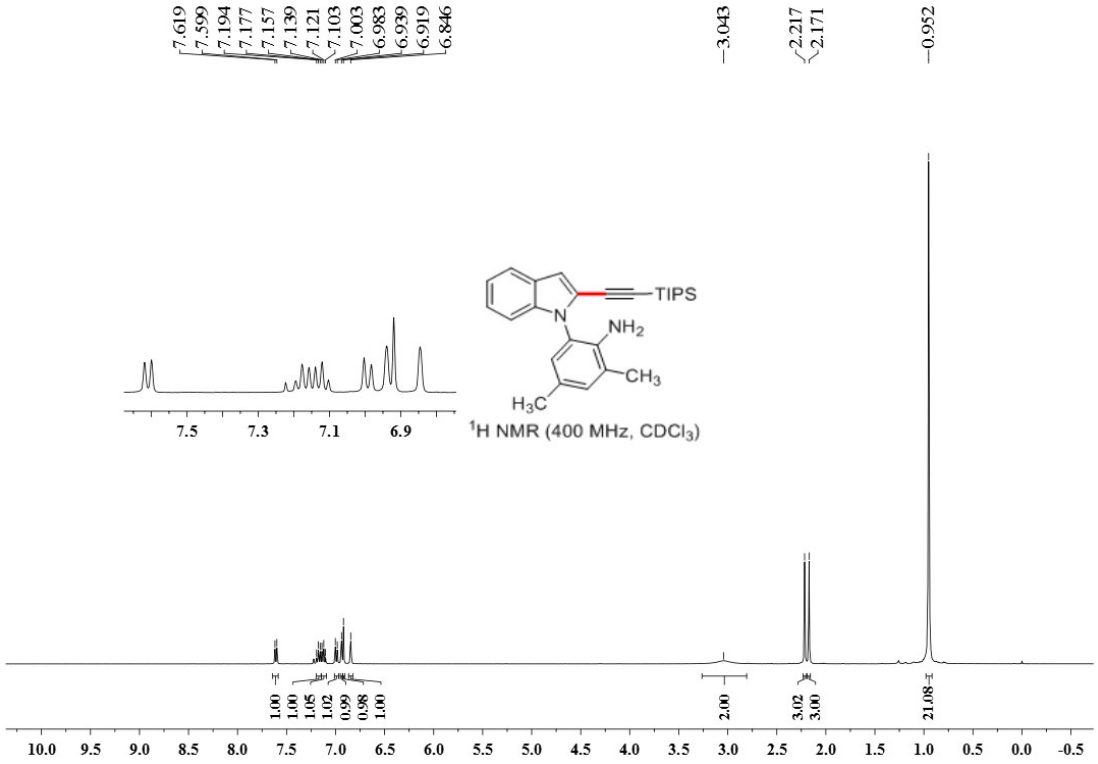


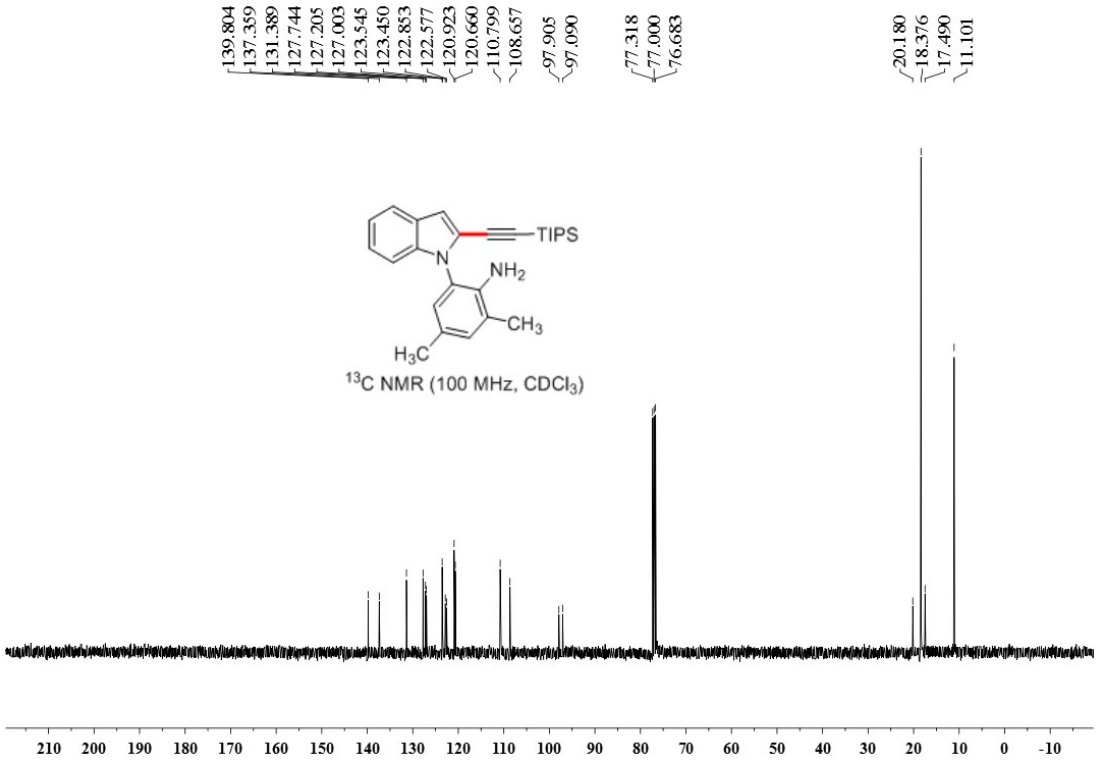
2-Methyl-6-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3ai)



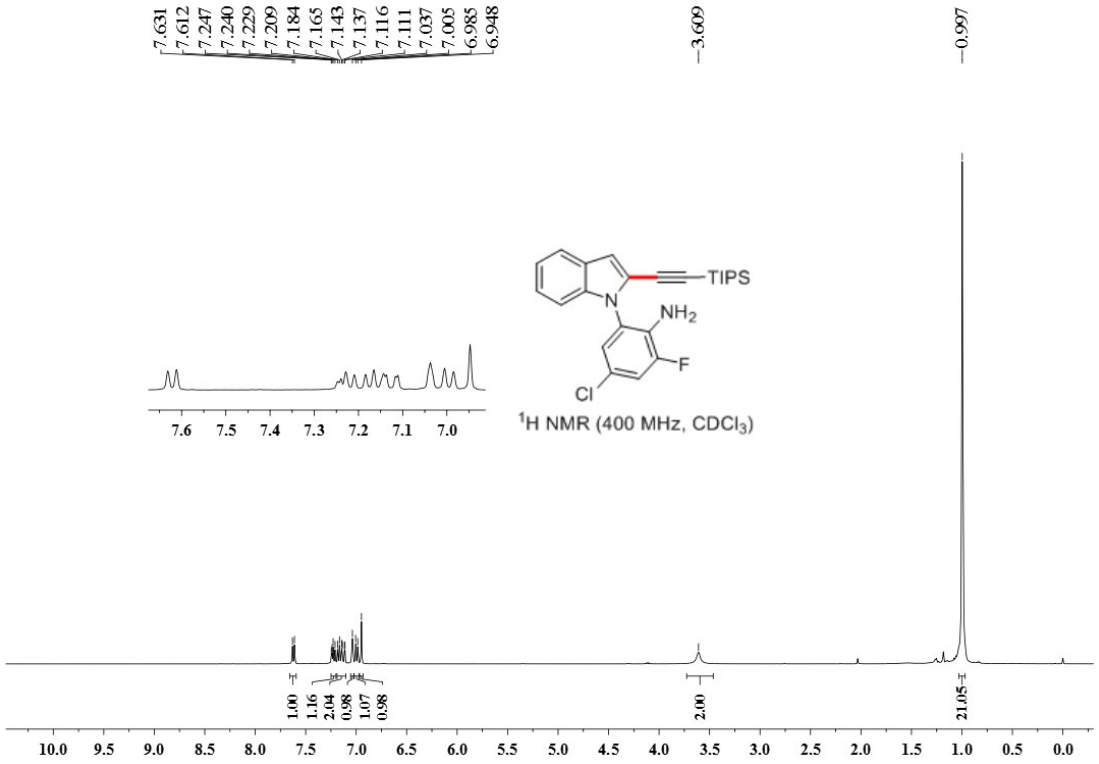


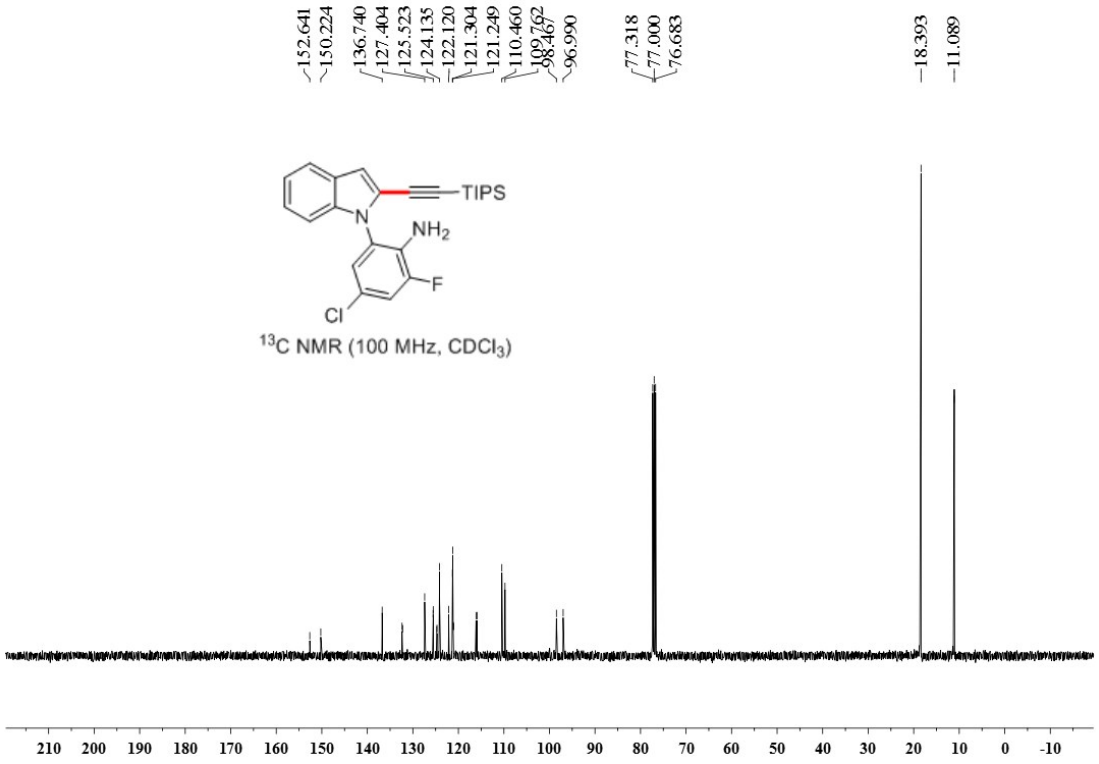
2,4-Dimethyl-6-(2-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)aniline (3aj)

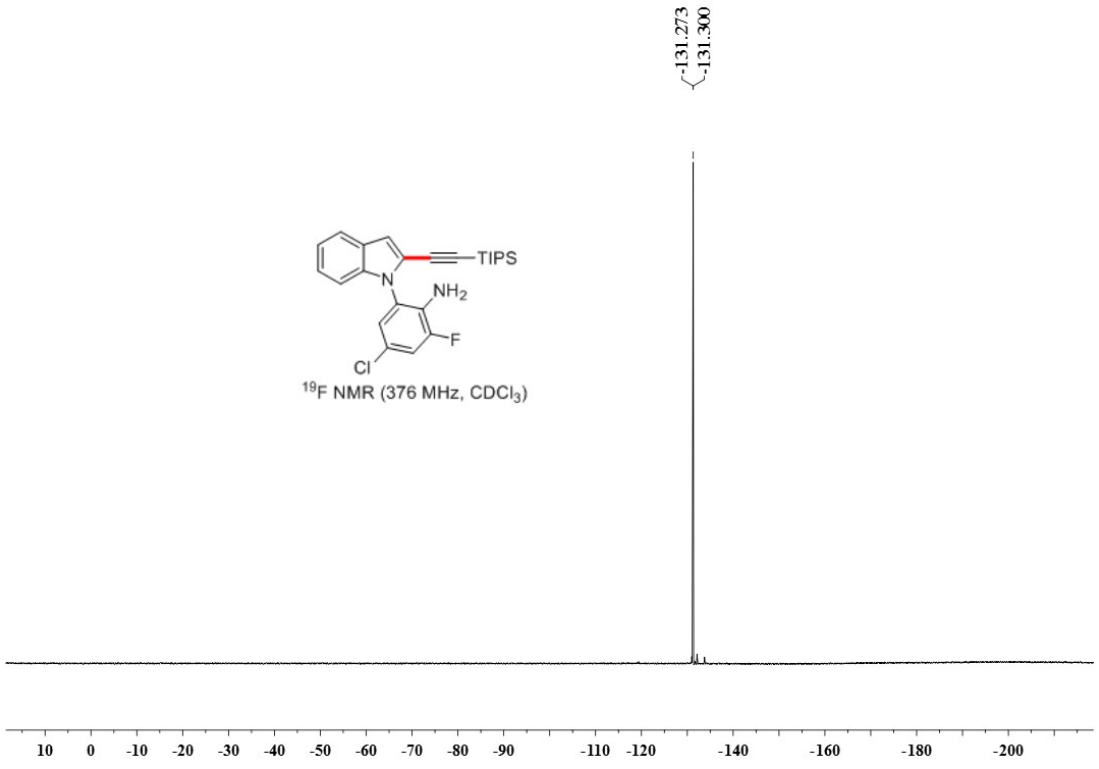




4-Chloro-2-fluoro-6-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3ak)

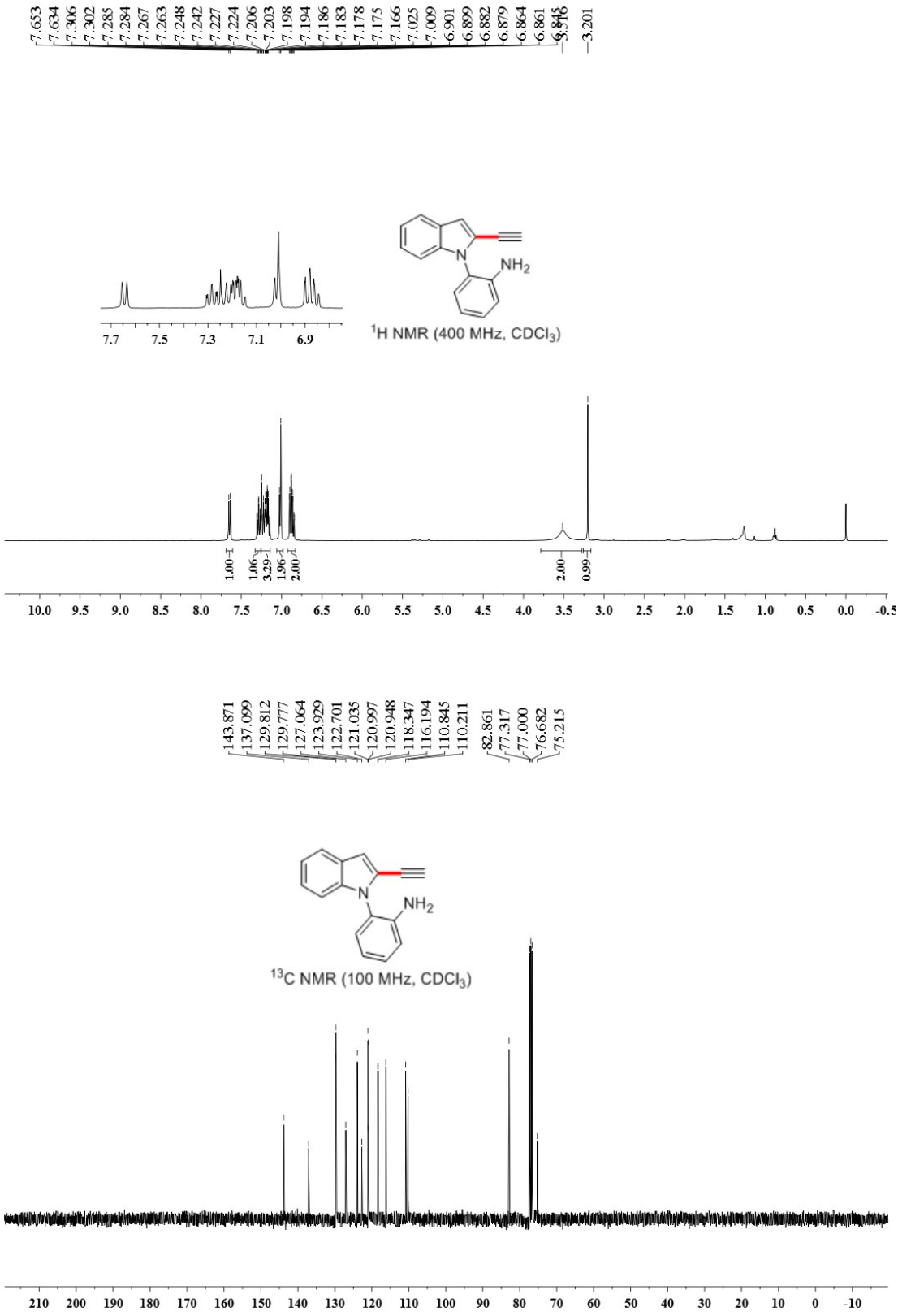




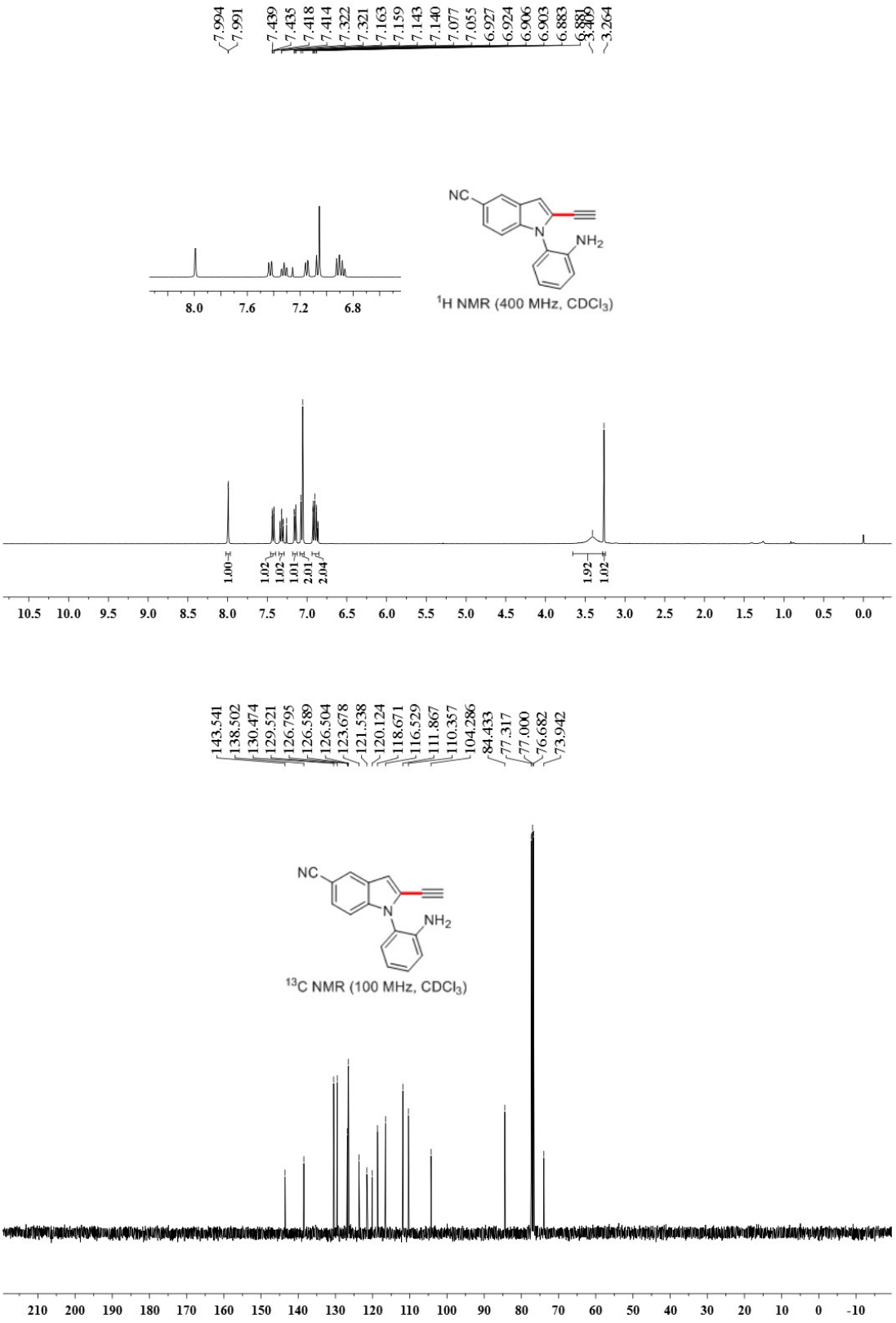


^{19}F NMR (376 MHz, $CDCl_3$)

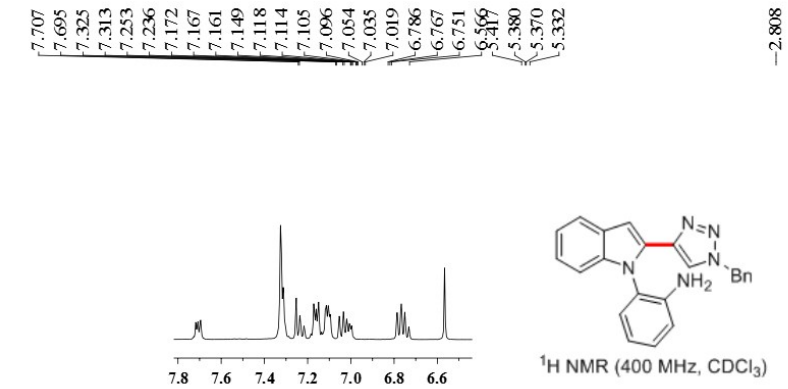
2-(2-Ethynyl-1*H*-indol-1-yl)aniline (4a)

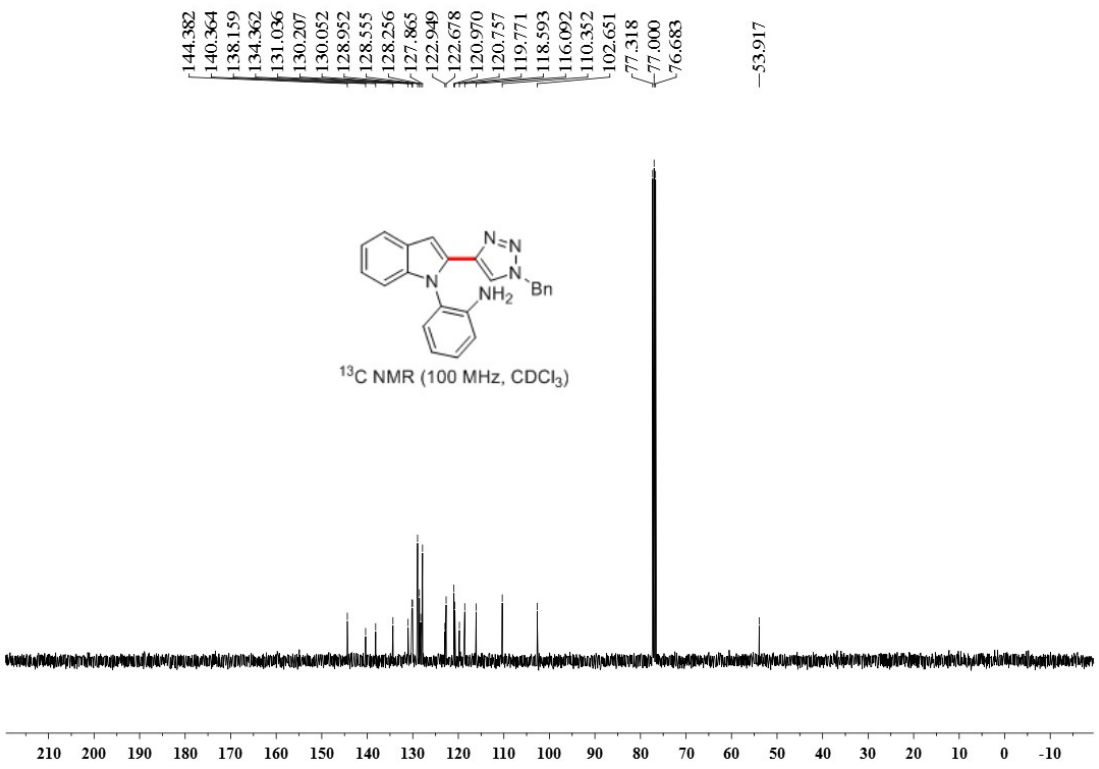


1-(2-Aminophenyl)-2-ethynyl-1*H*-indole-5-carbonitrile (4b)

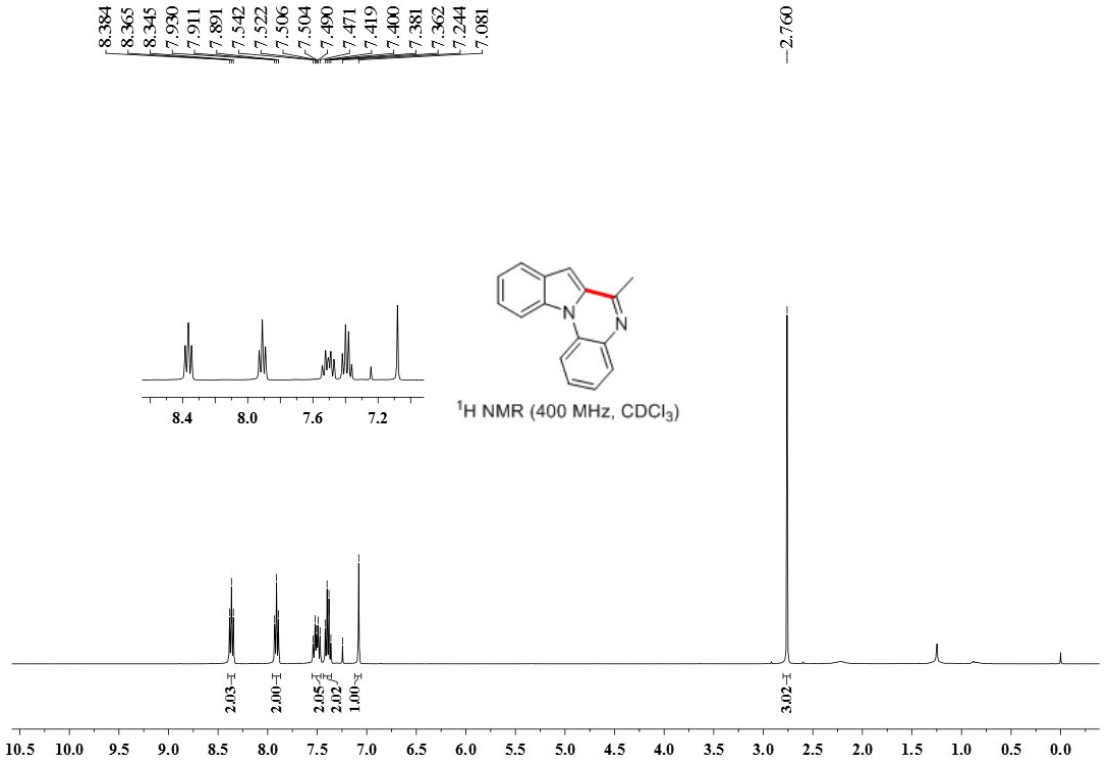


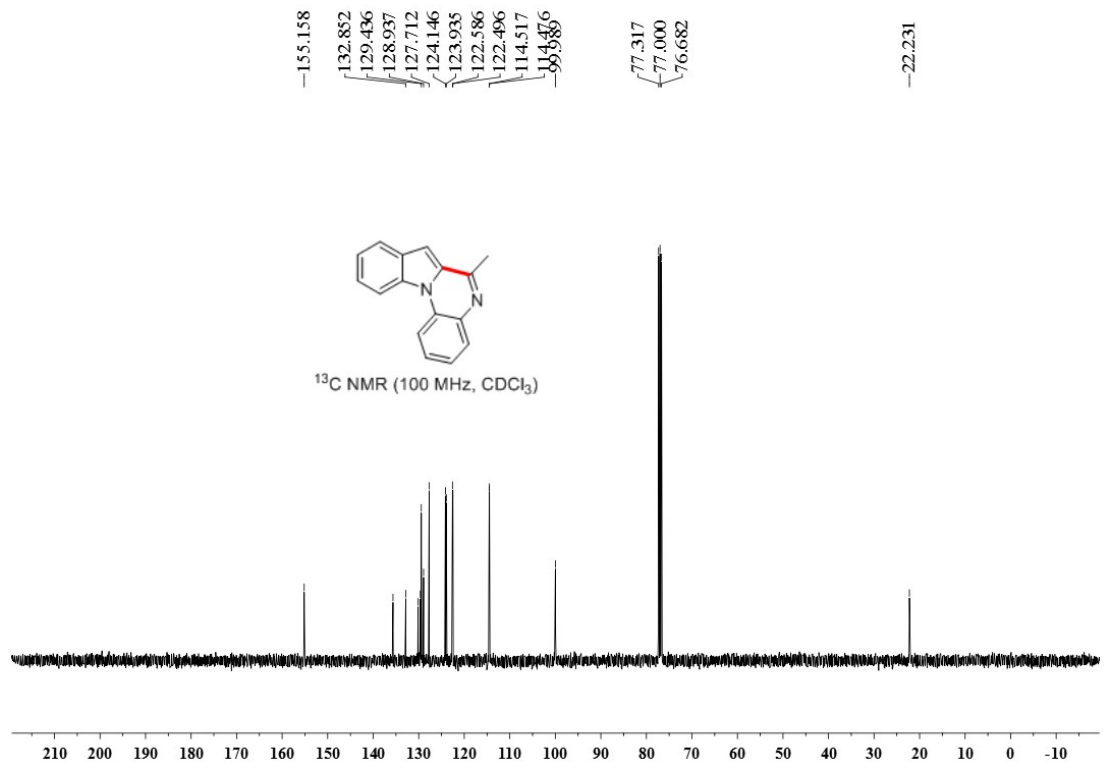
2-(2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)-1*H*-indol-1-yl)aniline (5a)





6-Methylindolo[1,2-*a*]quinoxaline (6a)





2-(3-Thiocyanato-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (7a)