

Substituent-Controlled Site-Selective Silylation of 2*H*-indazoles to Access Silylated 1*H*-indazoles and 2*H*-indazoles under Transition Metal Free Conditions

Jia Jia,^{a#} Shuai Chen,^{b#} Ting Mao,^a Jinlan Li,^a Weipiao Li,^a An-Jun Wang,^a Dezhi Yang,^a Zhengli Liu,^{b,c*} Chun-Yang He,^{a*} and Zhang Feng^{b,c*}

^aKey Laboratory of Biocatalysis & Chiral Drug Synthesis of Guizhou Province, School of Pharmacy, Zunyi Medical University, Zunyi, Guizhou, 563003, P.R. China

^bChongqing Key Laboratory of Natural Product Synthesis and Drug Research, School of Pharmaceutical Sciences, Chongqing University, Chongqing 401331, P. R. China

^cAffiliated Hospital of North Sichuan Medical College and Medical Imaging Key Laboratory of Sichuan Province, Nanchong 637503, China.

List of Contents

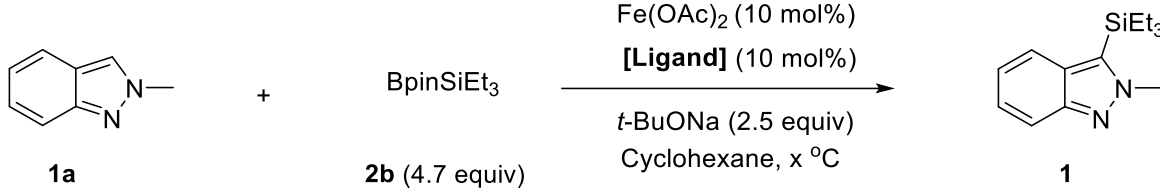
General Information and Materials.....	S2
Optimization of Transition-Metal-Free Selective Silylation of Indazoles.....	S3
Optimization of Transition-Metal-Free Selective Silylation of Indazoles protected by SEM	S 5
Preparation of Indazole Substrates.....	S7
General Procedure for Regioselective Silylation of Indazoles.....	S9
Gram-scale experimental procedures.....	S10
Experimental Procedures for Transformations.....	S11
Experimental Procedures and Characterization Data for Products.....	S12
References.....	S33
Spectra of Products 1-49.....	S34

General information: ^1H NMR and ^{13}C NMR spectra were recorded on Agilent 400MR DD2 (400 MHz) or 600MR DD2 (600 MHz) spectrometer at ambient temperature. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, sept = septet. NMR yield was determined by ^1H NMR using mesitylene as an internal standard before working up the reaction.

Materials: All reagents that used were from commercial sources, unless otherwise specified. *t*-BuONa (99%) was purchased from TCI. Diglyme and DMF were distilled under reduced pressure from CaH_2 . Cyclohexane, THF, MTBE, DME, and CPME were distilled from sodium immediately before used.

Optimization of Transition-Metal-Free Selective Silylation of Indazoles (Table S1-S4):

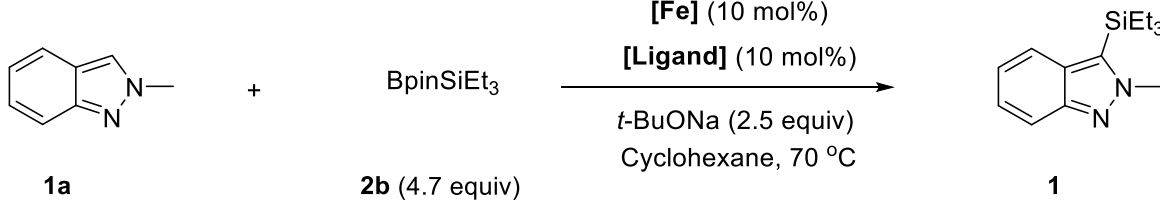
Table S1. Screening of Ligand and Temperature.^a



Entry	[Fe]	Ligand	Temp (°C)	Yield ^b
1	Fe(OAc) ₂	dppe	135	71%
2	Fe(OAc) ₂	BINAP	135	30%
3	Fe(OAc) ₂	dpppe	135	32%
4	Fe(OAc) ₂	dppe	130	78%
5	Fe(OAc) ₂	dppe	120	74%
6	Fe(OAc) ₂	dppe	100	73%
7	Fe(OAc) ₂	dppe	90	79%
8	Fe(OAc) ₂	dppe	80	85%
9	Fe(OAc)₂	dppe	70	93%(87%)
10	Fe(OAc) ₂	dppe	60	87%

^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2b** (4.7 equiv), *t*-BuONa (2.5 equiv), Fe(OAc)₂ (10 mol%), ligand (10 mol%), cyclohexane (1.0 mL), 16 h, under argon atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard.

Table S2. Control Experiments of Iron-Catalyzed Silylation of Indazoles.^a

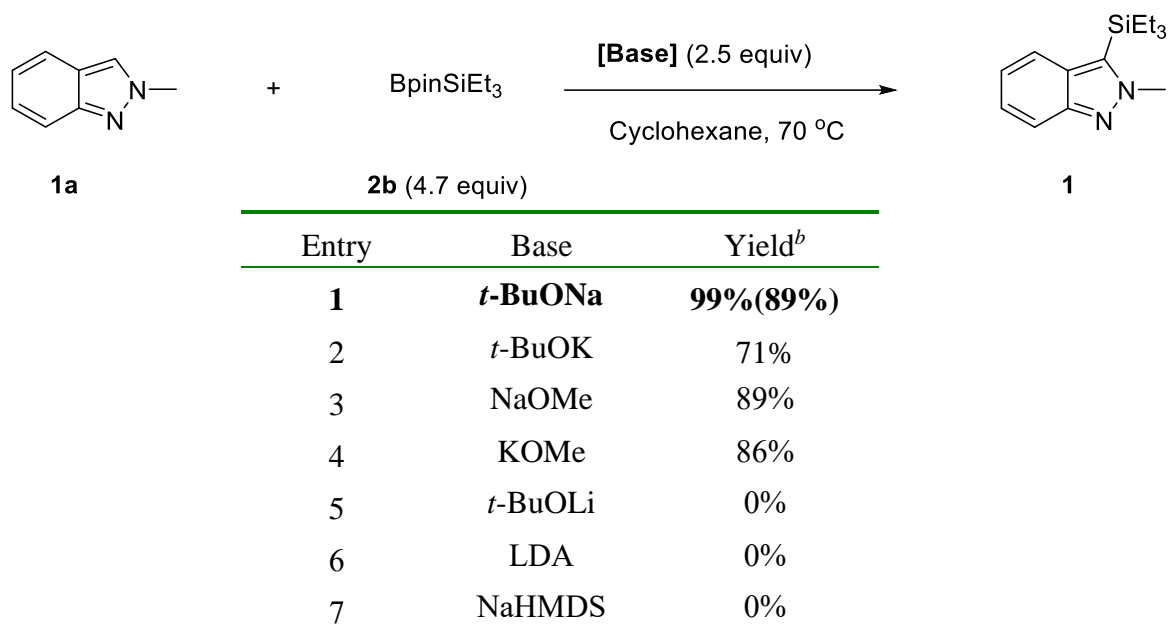


Entry	[Fe]	Ligand	Base	Yield ^b
1	-	dppe	<i>t</i> -BuONa	88%
2	Fe(OAc) ₂	-	<i>t</i> -BuONa	59%
3	Fe(OAc) ₂	dppe	-	2%
4	-	-	<i>t</i>-BuONa	99%(89%)

^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2b** (4.7 equiv), Fe(OAc)₂ (10 mol%), dppe (10 mol%), *t*-BuONa (2.5 equiv), cyclohexane (1.0 mL), 70 °C, 16 h,

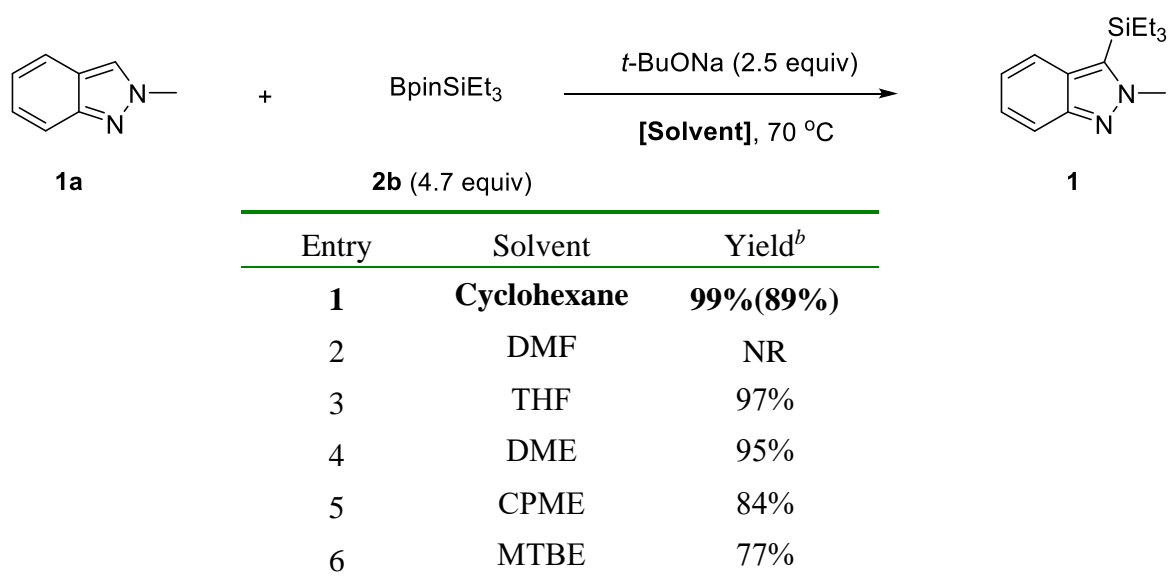
under argon atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard.

Table S3. Screening of Bases.^a



^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2b** (4.7 equiv), Base (2.5 equiv), cyclohexane (1.0 mL), 70 °C, 16 h, under argon atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard.

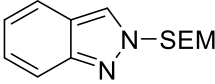
Table S4. Screening of Solvents.^a



^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2b** (4.7 equiv), *t*-BuONa (2.5 equiv), Solvent (1.0 mL), 70 °C, 16 h, under argon atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard.

Optimization of Transition-Metal-Free Selective Silylation of Indazoles Protected by SEM (Table S5-S9):

Table S5. Screening of Solvents and Bases.^a

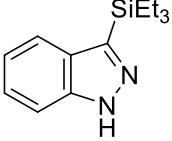


37a

+

2b (4.7 equiv)

$\xrightarrow[\text{[Solvent], 70 }^\circ\text{C}]{\text{[Base] (2.5 equiv)}}$

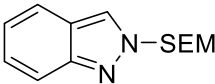


37

Entry	Base	Solvent	Yield ^b
1	<i>t</i> -BuONa	Cyclohexane	9%
2	<i>t</i> -BuOK	Cyclohexane	NR
3	KOMe	Cyclohexane	NR
4	NaOMe	Cyclohexane	NR
5	<i>t</i>-BuONa	THF	(22%)
6	<i>t</i> -BuONa	DME	10%
7	<i>t</i> -BuONa	MTBE	NR
8	<i>t</i> -BuONa	Diglyme	18%

^aReaction conditions (unless otherwise specified): **37a** (0.2 mmol, 1.0 equiv), **2b** (4.7 equiv), Base (2.5 equiv), Solvent (1.0 mL), 70 °C, 16 h, under argon atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard.

Table S6. Screening of Temperature.^a

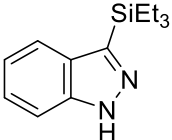


37a

+

2b (4.7 equiv)

$\xrightarrow[\text{THF, x } ^\circ\text{C}]{t\text{-BuONa (2.5 equiv)}}$



37

Entry	Temp (°C)	Yield ^b
1	60	8%
2	70	18%
3	90	19%
4	100	21%
5	110	24%
6	130	35%

^aReaction conditions (unless otherwise specified): **37a** (0.2 mmol, 1.0 equiv), **2b** (4.7 equiv), *t*-BuONa (2.5 equiv), THF (1.0 mL), 16 h, under argon atmosphere. ^bDetermined by ¹H NMR using

mesitylene as an internal standard.

Table S7. Evaluation of the Amount of Bases.^a

Entry	<i>t</i> -BuONa (equiv)	Yield ^b
1	1.0	6%
2	2.0	32%
3	2.5	35%
4	3.0	32%
5	4.0	42%
6	5.0	43%
7	6.0	48%(43%)
8	7.0	32%
9	8.0	33%

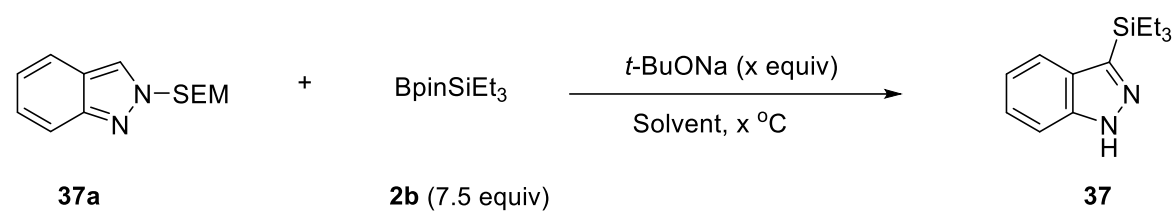
^aReaction conditions (unless otherwise specified): **37a** (0.2 mmol, 1.0 equiv), **2b** (4.7 equiv), *t*-BuONa (x equiv), THF (1.0 mL), 130 °C, 16 h, under argon atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard.

Table S8. Evaluation of the Amount of BpinSiEt₃ 2a.^a

Entry	2b (equiv)	Yield ^b
1	4.7	48%
2	5.7	45%
3	6.6	50%
4	7.5	(75%)

^aReaction conditions (unless otherwise specified): **37a** (0.2 mmol, 1.0 equiv), **2b** (x equiv), *t*-BuONa (6.0equiv), THF (1.0 mL), 130 °C, 16 h, under an argon atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard.

Table S9. Optimization of Silylation of Indazoles Protected by SEM.^a

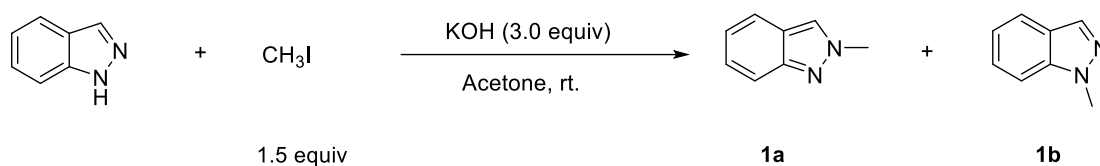


Entry	<i>t</i> -BuONa (equiv)	Temp (°C)	Solvent	Yield ^b
1	4.0	130	THF	52%
2	5.0	130	THF	52%
3	6.0	130	THF	(75%)
4	7.0	130	THF	67%
5	6.0	120	THF	59%
6	6.0	110	THF	63%
7	6.0	130	2-Methoxyethyl ether	63%
8	6.0	130	Cyclohexane	40%

^aReaction conditions (unless otherwise specified): **37a** (0.2 mmol, 1.0 equiv), **2b** (7.5 equiv), *t*-BuONa, Solvent (1.0 mL), 16 h, under an argon atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard.

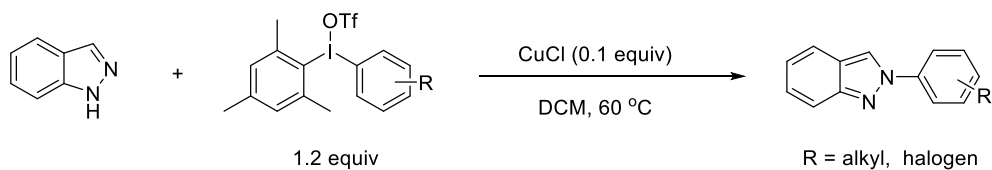
Preparation of Indazoles

General Procedure for the Synthesis of Indazoles Protected by Methyl:



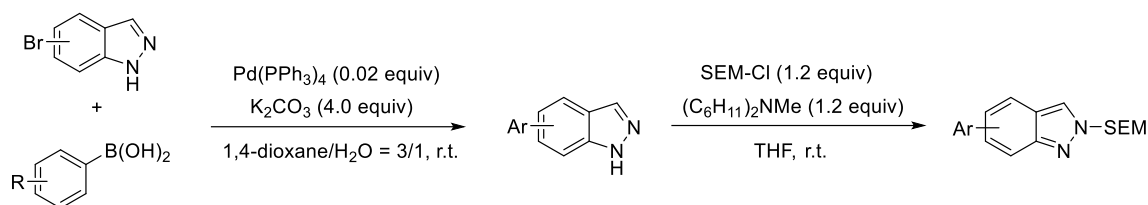
General procedure:^[1] To a stirred of 1*H*-indazole (0.591 g, 5.0 mmol) in acetone (10.0 mL) at 0 °C was added potassium hydroxide (0.842 g, 15.0 mmol). After stirring for 1 h at 0 °C, MeI (0.47 mL, 7.5 mmol) was added to the flask, and the mixture was stirred for 15 h at 25 °C. The reaction mixture was filtered and extracted with ethyl acetate. Then the organic phase was dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford the substrates **1a**.

General Procedure for the Synthesis of *N*-Aryl-protected Indolines:



General procedure:^[2] A mixture of corresponding Indazole (2.0 mmol, 1.0 equiv), the hypervalent iodine reagents (1.2 equiv), CuCl (0.1 equiv) in DCM (10.0 mL) under argon atmosphere was stirred for 24 h at 60 °C. The reaction mixture was filtered by diatomite with ethyl acetate. Then the organic phase was concentrated in vacuo and purified by silica gel flash chromatography to afford the substrates.

General Procedure for the Synthesis of Indazoles protected by SEM with Substituents



General procedure: A mixture of corresponding Bromoindazole (5.0 mmol, 1.0 equiv), Arylboronic acid (1.3 equiv), Pd(PPh₃)₄ (0.02 equiv) and K₂CO₃ (4.0 equiv) in 1,4-dioxane/H₂O = 3/1 under argon atmosphere was stirred for 24 h at 100 °C. The reaction mixture was filtered and extracted with ethyl acetate. Then the organic phase was dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford aryl-indazoles.

Dicyclohexyl methylamine (1.2 equiv) was added to the solution of aryl-indazole (1.5 mmol, 1.0 equiv) in THF (15 mL) in an oven-dried flask, followed by SEM-Cl (1.2 equiv) via syringe. The mixture was stirred at room temperature for 3 h and then diluted with ethyl acetate and quenched with 0.5 N NaOH. The organic layer was washed with brine and dried over Na₂SO₄. The residue which was concentrated in vacuo was purified by silica gel flash chromatography to obtain the substrates.

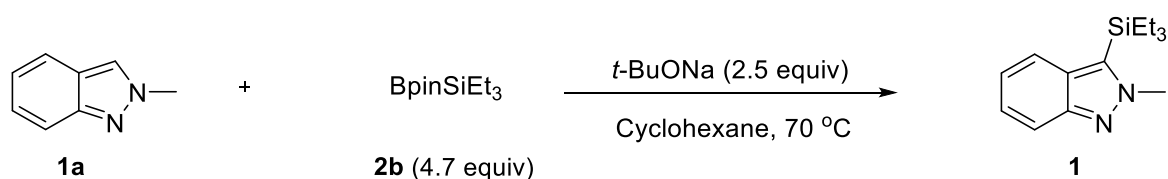
General Procedure for Selective Silylation of Indazoles

A 25 mL flame-dried Schlenk tube equipped with a magnetic stir bar was charged with

t-BuONa (48.1 mg, 0.5 mmol, 2.5 equiv) in glove box. 2-Methylindazole (0.2 mmol), fresh distilled silylborane **2b** (250 μ L, 0.94 mmol, 4.7 equiv), fresh distilled cyclohexane (1.0 mL) was then added under argon atmosphere. The reaction mixture was allowed to stir at 70 $^{\circ}$ C for 16 h. The cooled solution was quenched with saturated NH₄Cl aqueous solution, then diluted with ethyl acetate and washed with brine. The organic phase was dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford the corresponding compound (**1-36**).

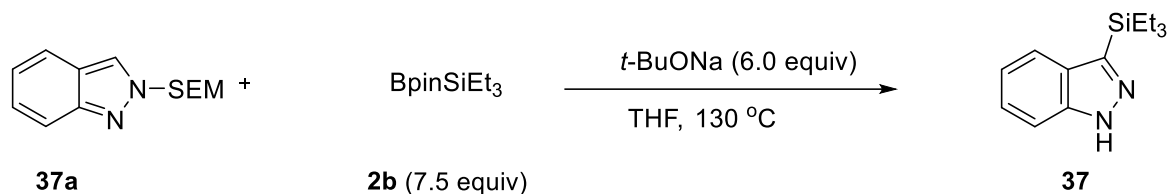
Procedure for The Silylation of Indazoles Protected by SEM: A 25 mL flame-dried Schlenk tube equipped with a magnetic stir bar was charged with *t*-BuONa (115.3 mg, 1.2 mmol, 6.0 equiv) in glove box. 2-((2-(trimethylsilyl)ethoxy)methyl)-2*H*-indazole (0.2 mmol), fresh distilled silylborane **2b** (400 μ L, 1.5 mmol, 7.5 equiv), fresh distilled THF (1.0 mL) were then added under argon atmosphere. The reaction mixture was allowed to stir at 130 $^{\circ}$ C for 16 h. The cooled solution was quenched with saturated NH₄Cl aqueous solution, then diluted with ethyl acetate and washed with brine. The organic phase was dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford the corresponding compound (**37-41**).

Gram-scale experimental procedures



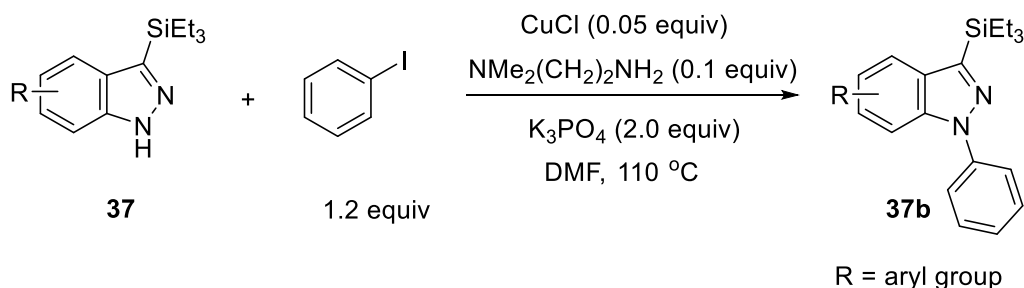
Procedure: To a 100 mL of Schlenk tube equipped with a magnetic stir bar, *t*-BuONa (1.826 g, 19.0 mmol) was added in glove box, followed by **1a** (1.0 g, 7.6 mmol) and BpinSiEt₃ (9.5 mL, 35.72 mmol), then fresh distilled cyclohexane (38.0 mL). The reaction mixture was heated at 70 $^{\circ}$ C for 16 h. The cooled solution was quenched with saturated NH₄Cl aqueous solution, then diluted with ethyl acetate and washed with brine. The organic phase was dried over Na₂SO₄ and concentrated in vacuum. The crude

mixture can be isolated by silica gel flash chromatography to afford the corresponding products **1** (1.68 g, 90%).

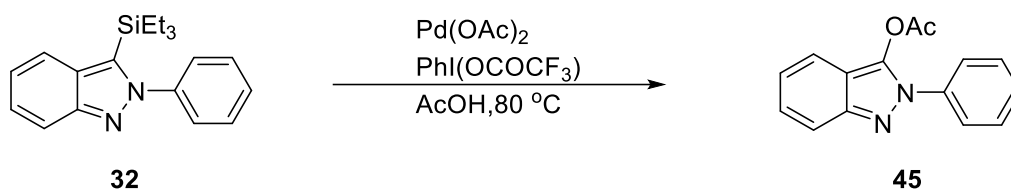


Procedure: To a 100 mL of Schlenk tube equipped with a magnetic stir bar, *t*-BuONa (2.324 g, 24.2 mmol) was added in glove box, followed by **37a** (1.0 g, 4.0 mmol) and BpinSiEt₃ (8.0 mL, 30.0 mmol), then fresh distilled THF (20.0 mL). The reaction mixture was heated at 130 °C for 16 h. The cooled solution was quenched with saturated NH₄Cl aqueous solution, then diluted with ethyl acetate and washed with brine. The organic phase was dried over Na₂SO₄ and concentrated in vacuum. The crude mixture can be isolated by silica gel flash chromatography to afford the corresponding products **37** (0.648 g, 69%).

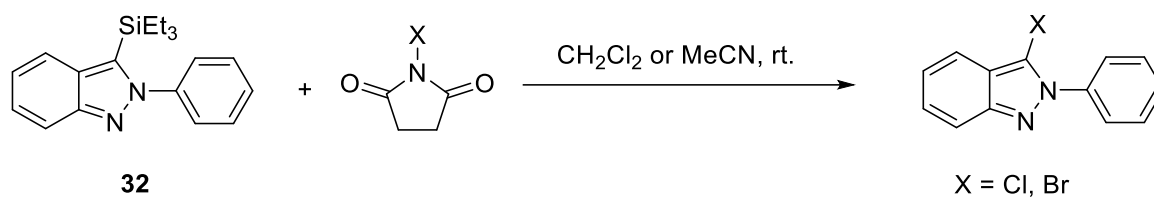
Experimental Procedures for Transformations.



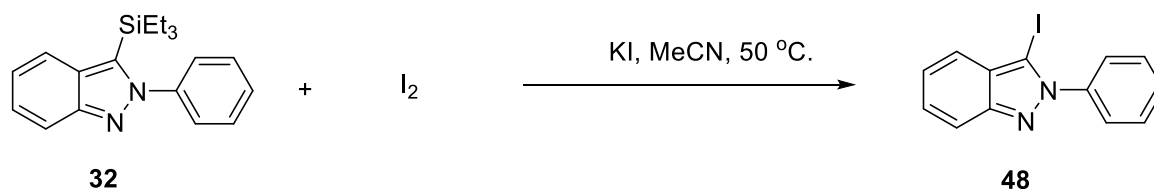
General Procedure: To a 25 mL of Schlenk tube equipped with a magnetic stir bar, CuCl (1.0 mg, 0.01 mmol), K₃PO₄ (84.9 mg, 0.4 mmol) were added in glove box. **37** (46.5 mg, 0.2 mmol), iodobenzene (49.0 mg, 0.24 mmol), N,N-Dimethylethylenediamine (1.8 mg, 0.02 mmol), dry solvent DMF (1.0 mL) were then added under argon atmosphere. The reaction mixture was stirred at 110 °C for 16 h. The cooled solution was quenched with saturated NH₄Cl aqueous solution, then diluted with ethyl acetate and washed with brine. The organic phase was dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford the corresponding compound **37b** in 85% yield.



General Procedure:^[3] A 25 mL flame-dried Schlenk tube equipped with a magnetic stir bar was charged with Pd(OAc)₂ (5 mmol%), PhI(OCOCF₃) (1.5 equiv). **32** (30.8 mg, 0.1 mmol), AcOH (0.5 mL) were then added under argon atmosphere. The reaction mixture was allowed to stir at 80 °C for 17 h. The reaction mixture was poured into aqueous NaHCO₃ solution and extract with ethyl acetate (20 mL×3). The combined organic extract was dried over anhydrous Na₂SO₄ and concentrated under a reduced pressure. The product **45** was separated by column chromatography on silica gel with petroleum ether/AcOEt eluent (46% yield).



General Procedure:^[4] A 25 mL flame-dried Schlenk tube equipped with a magnetic stir bar was charged with NXS (0.5 mmol, 5.0 equiv). **32** (30.8 mg, 0.1 mmol), fresh distilled CH₂Cl₂ or MeCN (1.0 mL) were then added under argon atmosphere. The reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was diluted with ethyl acetate. The residue was purified by silica gel flash chromatography to afford the corresponding compound **46** in 57% yield and **47** in 89% yield.

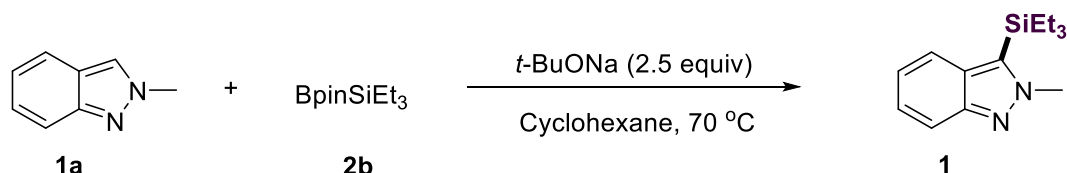


General Procedure: A 25 mL flame-dried Schlenk tube equipped with a magnetic stir bar was charged with I₂ (0.5 mmol, 5.0 equiv) and KI (0.2 mmol, 2 equiv). **32** (30.8 mg, 0.1 mmol), fresh distilled MeCN (1.0 mL) were then added under argon atmosphere.

The reaction mixture was allowed to stir at 50 °C for 12 h. The reaction mixture was diluted with ethyl acetate. The residue was purified by silica gel flash chromatography to afford the corresponding compound **48** in 50% yield.

Mechanistic studies

Radical inhibition experiments

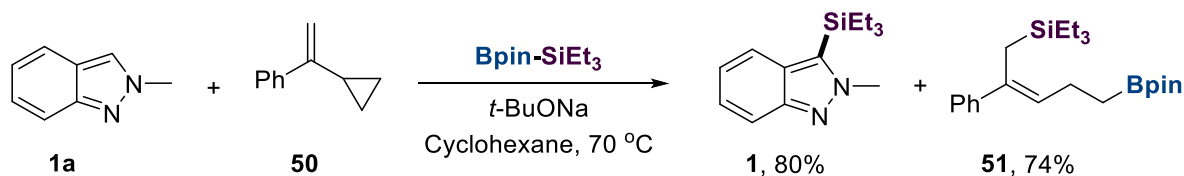


Entry	Additive (equiv)	Yield ^b
1	TEMPO (2.0)	13%
2	BHT (1.0)	trace

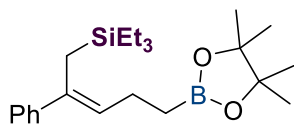
^aReaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2b** (4.7 equiv), TEMPO (2.0 equiv) or BHT (1.0 equiv), *t*-BuONa (2.5 equiv), Cyclohexane (1.0 mL), 70 °C, 16 h, under an argon atmosphere.

^bDetermined by ¹H NMR using mesitylene as an internal standard.

Radical clock experiments



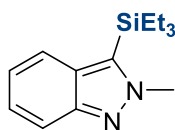
A 25 mL flame-dried Schlenk tube equipped with a magnetic stir bar was charged with *t*-BuONa (48.1 mg, 0.5 mmol, 2.5 equiv) in glove box. 2-Methylindazole (0.2 mmol), (1-Cyclopropylvinyl)benzene **50** (31 μL, 0.2 mmol, 1.0 equiv), fresh distilled silylborane **2b** (250 μL, 0.94 mmol, 4.7 equiv), fresh distilled cyclohexane (1.0 mL) were then added under argon atmosphere. The reaction mixture was allowed to stir at 70 °C for 16 h. The cooled solution was quenched with saturated NH₄Cl aqueous solution, then diluted with ethyl acetate and washed with brine. The organic phase was dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford the silylated ring-opening product **51**.



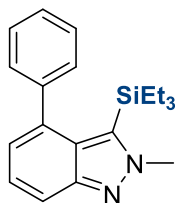
(Z)-triethyl(2-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-en-1-yl)silane (51). This compound is known^[7]. The product **51** (57.1mg, 74% yield) as a light yellow oil was purified with silica gel chromatography. ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, *J* = 6.8 Hz, 2 H), 7.21 (t, *J* = 7.2 Hz, 2 H), 7.18 (t, *J* = 7.6 Hz, 1 H), 5.43 (t, *J* = 7.2 Hz, 1 H), 2.24 (q, *J* = 8.0 Hz, 2 H), 1.99 (s, 2 H), 1.24 (s, 12 H), 0.93 (t, *J* = 7.8 Hz, 2 H), 0.81 (t, *J* = 8.0 Hz, 9 H), 0.35 (q, *J* = 8.0 Hz, 6 H).

Conclusion: When the radical scavenger TEMPO, or radical inhibitor BHT was added under the standard silylation reaction conditions, drastically diminished yields were observed. These results suggest that a radical pathway might be involved.

Characterization Data for Silylated Products:

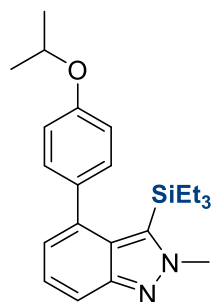


2-Methyl-3-(triethylsilyl)-2H-indazole (1). The product **1** (43.9 mg, 89% yield) as a yellow oil was purified with silica gel chromatography. ¹H NMR (400 MHz, CDCl₃) δ 7.77-7.74 (m, 2 H), 7.31-7.27 (m, 1 H), 7.10-7.06 (m, 1 H), 4.31 (s, 3 H), 1.09-0.97 (m, 15 H). ¹³C NMR (100 MHz, CDCl₃) δ 148.6, 132.9, 130.7, 125.3, 121.4, 121.3, 117.3, 41.5, 7.3, 4.1. FTMS (ESI): Calculated for C₁₄H₂₃N₂Si (M+H⁺): 247.1625; Found: 247.1619.

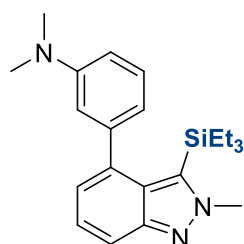


2-Methyl-4-phenyl-3-(triethylsilyl)-2H-indazole (2). The product **2** (53.5 mg, 83% yield) as a white solid was purified with silica gel chromatography. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.8 Hz, 1 H), 7.49 (d, *J* = 6.8 Hz, 2 H), 7.43-7.35 (m, 3 H), 7.32-7.28 (m, 1 H), 6.95 (d, *J* = 6.8 Hz, 1 H), 4.35 (s, 3 H), 0.79 (t, *J* = 8.0 Hz, 9 H), 0.48 (q,

$J = 8.0$ Hz, 6 H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.5, 143.7, 136.7, 133.8, 129.5, 129.1, 128.4, 127.3, 125.1, 124.0, 116.4, 42.9, 7.8, 4.5. FTMS (ESI): Calculated for $\text{C}_{20}\text{H}_{27}\text{N}_2\text{Si}$ ($\text{M}+\text{H}^+$): 323.1938; Found: 323.1936.

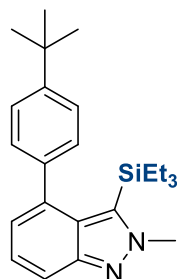


4-(4-Isopropoxyphenyl)-2-methyl-3-(triethylsilyl)-2H-indazole (3). The product **3** (57.9 mg, 76% yield) as a white solid was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.70 (dd, $J = 8.8$ Hz, $J = 0.8$ Hz, 1 H), 7.39-7.36 (m, 2 H), 7.28 (dd, $J = 8.4$ Hz, $J = 7.2$ Hz, 1 H), 6.96-6.91 (m, 3 H), 4.64-4.58 (m, 1 H), 4.34 (s, 3 H), 1.37 (d, $J = 6.0$ Hz, 6 H), 0.80 (t, $J = 8.0$ Hz, 9 H), 0.51 (q, $J = 8.0$ Hz, 6 H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.3, 149.5, 136.5, 136.2, 133.9, 130.0, 129.7, 125.1, 123.7, 116.1, 115.9, 70.1, 42.8, 21.9, 7.8, 4.6. FTMS (ESI): Calculated for $\text{C}_{23}\text{H}_{33}\text{N}_2\text{OSi}$ ($\text{M}+\text{H}^+$): 381.2356; Found: 381.2344.

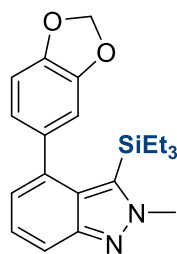


***N,N*-dimethyl-3-(2-methyl-3-(triethylsilyl)-2H-indazol-4-yl)aniline (4).** The product **4** (60.7 mg, 83% yield) as a yellow oil was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 8.4$ Hz, 1 H), 7.31-7.24 (m, 2 H), 7.00 (d, $J = 6.8$ Hz, 1 H), 6.88-6.84 (m, 2 H), 6.77 (dd, $J = 8.0$ Hz, $J = 2.4$ Hz, 1 H), 4.35 (s, 3 H), 2.97 (s, 6 H), 0.81 (t, $J = 8.0$ Hz, 9 H), 0.52 (q, $J = 8.0$ Hz, 6 H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.7, 149.4, 144.3, 137.6, 133.9, 129.6, 128.8, 125.0, 123.5,

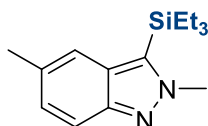
118.1, 116.1, 113.3, 111.7, 42.9, 40.7, 7.9, 4.4. FTMS (ESI): Calculated for $C_{22}H_{32}N_3Si$ ($M+H^+$): 366.2360; Found: 366.2349.



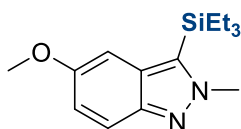
4-(4-(*Tert*-butyl)phenyl)-2-methyl-3-(triethylsilyl)-2*H*-indazole (5). The product **5** (53.8 mg, 71% yield) as a yellow solid was purified with silica gel chromatography. 1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, $J = 8.8$ Hz, 1 H), 7.43 (dd, $J = 14.4$ Hz, $J = 8.4$ Hz, 4 H), 7.31-7.27 (m, 1 H), 6.96 (d, $J = 6.8$ Hz, 1 H), 4.35 (s, 3 H), 1.39 (s, 9 H), 0.79 (t, $J = 8.0$ Hz, 9 H), 0.48 (q, $J = 8.0$ Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 149.5, 140.8, 136.7, 133.9, 129.8, 128.7, 125.3, 125.0, 123.5, 116.1, 42.8, 34.6, 31.4, 7.8, 4.4. FTMS (ESI): Calculated for $C_{24}H_{35}N_2Si$ ($M+H^+$): 379.2564; Found: 379.2549.



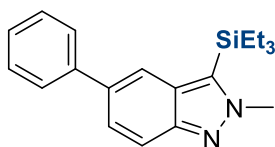
4-(Benzo[*d*][1,3]dioxol-5-yl)-2-methyl-3-(triethylsilyl)-2*H*-indazole (6). The product **6** (51.3 mg, 70% yield) as a yellow solid was purified with silica gel chromatography. 1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, $J = 8.4$ Hz, 1 H), 7.30-7.27 (m, 1 H), 6.97-6.92 (m, 3 H), 6.87 (d, $J = 7.6$ Hz, 1 H), 6.02 (s, 2 H), 4.35 (s, 3 H), 0.83 (t, $J = 8.0$ Hz, 9 H), 0.57 (q, $J = 8.0$ Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 147.6, 147.0, 137.8, 136.2, 133.8, 129.6, 125.1, 123.6, 122.3, 116.2, 109.6, 108.4, 101.1, 42.9, 7.8, 4.6. FTMS (ESI): Calculated for $C_{21}H_{27}N_2O_2Si$ ($M+H^+$): 367.1836; Found: 367.1836.



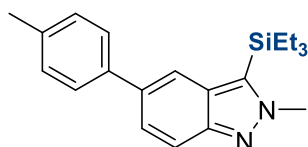
2,5-Dimethyl-3-(triethylsilyl)-2H-indazole (7). The product **7** (49.5 mg, 95% yield) as a colourless oil was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 8.8$ Hz, 1 H), 7.49 (s, 1 H), 7.11 (d, $J = 8.8$ Hz, 1 H), 4.26 (s, 3 H), 2.43 (s, 3 H), 1.07-0.98 (m, 15 H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.4, 131.8, 131.1, 130.5, 128.0, 119.6, 116.9, 41.4, 22.0, 7.3, 4.0. FTMS (ESI): Calculated for $\text{C}_{15}\text{H}_{25}\text{N}_2\text{Si}$ ($\text{M}+\text{H}^+$): 261.1781; Found: 261.1771.



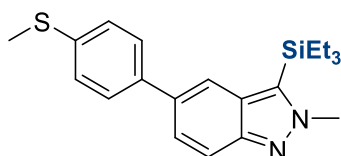
5-Methoxy-2-methyl-3-(triethylsilyl)-2H-indazole (8). The product **8** (47.0 mg, 85% yield) as a yellow oil was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 9.6$ Hz, 1 H), 7.00-6.97 (m, 2 H), 4.23 (s, 3 H), 3.83 (s, 3 H), 1.05-0.99 (m, 15 H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.8, 145.1, 131.3, 130.8, 119.4, 118.5, 98.6, 55.3, 41.4, 7.3, 4.1. FTMS (ESI): Calculated for $\text{C}_{15}\text{H}_{25}\text{N}_2\text{OSi}$ ($\text{M}+\text{H}^+$): 277.1730; Found: 277.1720.



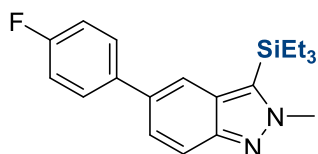
2-Methyl-5-phenyl-3-(triethylsilyl)-2H-indazole (9). The product **9** (47.1 mg, 73% yield) as a yellow oil was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.95 (s, 1 H), 7.83 (d, $J = 8.8$ Hz, 1 H), 7.65 (d, $J = 7.2$ Hz, 2 H), 7.57 (dd, $J = 8.8$ Hz, $J = 1.6$ Hz, 1 H), 7.47 (t, $J = 7.6$ Hz, 2 H), 7.35 (t, $J = 7.4$ Hz, 1 H), 4.32 (s, 3 H), 1.12-1.01 (m, 15 H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.1, 142.2, 134.6, 133.6, 131.2, 128.7, 127.3, 126.7, 125.9, 119.4, 117.6, 41.5, 7.4, 4.1. FTMS (ESI): Calculated for $\text{C}_{20}\text{H}_{27}\text{N}_2\text{Si}$ ($\text{M}+\text{H}^+$): 323.1938; Found: 323.1937.



2-Methyl-5-(*p*-tolyl)-3-(triethylsilyl)-2*H*-indazole (10). The product **10** (54.5 mg, 81% yield) as a colourless oil was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.92 (s, 1 H), 7.81 (d, $J = 9.2$ Hz, 1 H), 7.57-7.53 (m, 3 H), 7.28 (d, $J = 7.6$ Hz, 2 H), 4.31 (s, 3 H), 2.42 (s, 3 H), 1.12-1.00 (m, 15 H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.0, 139.3, 136.4, 134.5, 133.4, 131.2, 129.4, 127.1, 126.0, 119.0, 117.5, 41.5, 21.1, 7.4, 4.1. FTMS (ESI): Calculated for $\text{C}_{21}\text{H}_{29}\text{N}_2\text{Si}$ ($\text{M}+\text{H}^+$): 337.2094; Found: 337.2097.

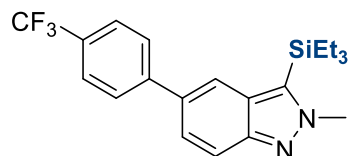


2-Methyl-5-(4-(methylthio)phenyl)-3-(triethylsilyl)-2*H*-indazole (11). The product **11** (61.9 mg, 84% yield) as a yellow solid was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.90 (s, 1 H), 7.81 (d, $J = 8.8$ Hz, 1 H), 7.56 (d, $J = 8.4$ Hz, 2 H), 7.53 (d, $J = 9.2$ Hz, 1 H), 7.36 (d, $J = 8.4$ Hz, 2 H), 4.31 (s, 3 H), 2.53 (s, 3 H), 1.11-1.01 (m, 15 H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.1, 139.1, 136.8, 133.9, 133.5, 131.2, 127.6, 127.1, 125.6, 119.0, 117.7, 41.5, 16.1, 7.4, 4.1. FTMS (ESI): Calculated for $\text{C}_{21}\text{H}_{29}\text{N}_2\text{SSi}$ ($\text{M}+\text{H}^+$): 369.1815; Found: 369.1811.

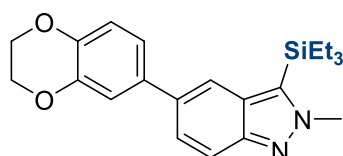


5-(4-Fluorophenyl)-2-methyl-3-(triethylsilyl)-2*H*-indazole (12). The product **12** (59.2 mg, 87% yield) as a yellow oil was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.87 (s, 1 H), 7.81 (d, $J = 8.8$ Hz, 1 H), 7.59-7.56 (m, 2 H), 7.51-7.48 (m, 1 H), 7.15 (t, $J = 8.6$ Hz, 2 H), 4.31 (s, 3 H), 1.12-1.00 (m, 15 H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.1 (d, $J = 244.0$ Hz), 147.9, 138.3, 133.6, 131.1, 128.7

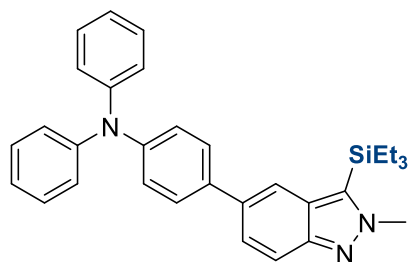
(d, $J = 8.0$ Hz), 125.8, 119.2, 117.7, 115.6, 115.4, 41.5, 7.4, 4.1. FTMS (ESI): Calculated for $C_{20}H_{26}FN_2Si$ ($M+H^+$): 341.1843; Found: 341.1843.



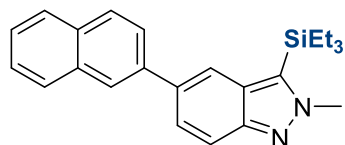
2-Methyl-3-(triethylsilyl)-5-(4-(trifluoromethyl)phenyl)-2H-indazole (13). The product **13** (35.1 mg, 45% yield) as a yellow oil was purified with silica gel chromatography. 1H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1 H), 7.84 (d, $J = 9.2$ Hz, 1 H), 7.71 (t, $J = 9.4$ Hz, 4 H), 7.54 (dd, $J = 9.2$ Hz, $J = 1.6$ Hz, 1 H), 4.32 (s, 3 H), 1.12-1.00 (m, 15 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 145.7, 134.3, 133.2, 131.0, 128.7 (d, $J = 33.0$ Hz), 127.5, 125.7 (q, $J = 3.3$ Hz), 124.4 (q, $J = 243$ Hz), 123.0, 120.1, 117.9, 41.6, 7.4, 4.1. FTMS (ESI): Calculated for $C_{21}H_{26}F_3N_2Si$ ($M+H^+$): 391.1811; Found: 391.1810.



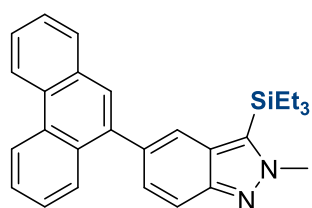
5-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-2-methyl-3-(triethylsilyl)-2H-indazole (14). The product **14** (70.8 mg, 93% yield) as a yellow oil was purified with silica gel chromatography. 1H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1 H), 7.78 (d, $J = 8.8$ Hz, 1 H), 7.50 (d, $J = 8.8$ Hz, 1 H), 7.15 (d, $J = 2.0$ Hz, 1 H), 7.13 (dd, $J = 8.4$ Hz, $J = 2.0$ Hz, 1 H), 6.96 (d, $J = 8.4$ Hz, 1 H), 4.31 (s, 4 H), 4.30 (s, 3 H), 1.11-0.99 (m, 15 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 143.5, 142.7, 135.8, 133.9, 133.3, 131.1, 125.8, 120.3, 118.7, 117.5, 115.9, 64.4, 64.3, 41.5, 7.3, 4.0. FTMS (ESI): Calculated for $C_{22}H_{29}N_2O_2Si$ ($M+H^+$): 381.1992; Found: 381.1995.



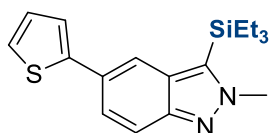
4-(2-Methyl-3-(triethylsilyl)-2H-indazol-5-yl)-N, N-diphenylaniline (15). The product **15** (82.3 mg, 84% yield) as a yellow solid was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.90 (s, 1 H), 7.79 (d, $J = 8.8$ Hz, 1 H), 7.55-7.50 (m, 3 H), 7.26 (t, $J = 7.8$ Hz, 4 H), 7.17-7.14 (m, 6 H), 7.02 (t, $J = 7.4$ Hz, 2 H), 4.29 (s, 3 H), 1.11-0.99 (m, 15 H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.9, 147.7, 146.6, 136.1, 134.0, 133.4, 131.2, 129.2, 127.8, 125.7, 124.2, 124.1, 122.7, 118.5, 117.5, 41.5, 7.4, 4.1. FTMS (ESI): Calculated for $\text{C}_{32}\text{H}_{36}\text{N}_3\text{Si}$ ($\text{M}+\text{H}^+$): 490.2673; Found: 490.2672.



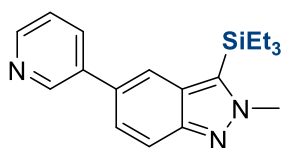
2-Methyl-5-(naphthalen-2-yl)-3-(triethylsilyl)-2H-indazole (16). The product **16** (70.0 mg, 94% yield) as a yellow oil was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 8.08 (s, 2 H), 7.97-7.94 (m, 2 H), 7.91 (s, 1 H), 7.88 (s, 1 H), 7.82 (dd, $J = 8.4$ Hz, $J = 1.6$ Hz, 1 H), 7.72 (dd, $J = 8.8$ Hz, $J = 1.2$ Hz, 1 H), 7.55-7.48 (m, 2 H), 4.34 (s, 3 H), 1.16-1.04 (m, 15 H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.1, 139.5, 134.5, 133.7, 133.6, 132.3, 131.2, 128.3, 128.1, 127.6, 126.2, 126.1, 125.9, 125.7, 125.6, 119.7, 117.7, 41.5, 7.4, 4.1. FTMS (ESI): Calculated for $\text{C}_{24}\text{H}_{29}\text{N}_2\text{Si}$ ($\text{M}+\text{H}^+$): 373.2094; Found: 373.2096.



2-Methyl-5-(phenanthren-9-yl)-3-(triethylsilyl)-2H-indazole (17). The product **17** (70.2 mg, 83% yield) as a white solid was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 8.81 (d, $J = 8.0$ Hz, 1 H), 8.75 (d, $J = 8.4$ Hz, 1 H), 8.02 (d, $J = 8.4$ Hz, 1 H), 7.95 (d, $J = 7.2$ Hz, 2 H), 7.90 (d, $J = 8.8$ Hz, 1 H), 7.79 (s, 1 H), 7.71-7.62 (m, 3 H), 7.56 (t, $J = 7.6$ Hz, 1 H), 7.50 (d, $J = 8.8$ Hz, 1 H), 4.37 (s, 3 H), 1.08-1.01 (m, 15 H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.0, 139.5, 133.9, 133.5, 131.6, 131.5, 130.9, 130.6, 129.8, 128.6, 128.5, 127.6, 127.1, 126.8, 126.4, 126.3, 122.8, 122.5, 122.1, 116.8, 41.6, 7.4, 4.1. FTMS (ESI): Calculated for $\text{C}_{28}\text{H}_{31}\text{N}_2\text{Si}$ ($\text{M}+\text{H}^+$): 423.2251; Found: 423.2255.

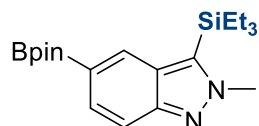


2-Methyl-5-(thiophen-2-yl)-3-(triethylsilyl)-2H-indazole (18). The product **18** (48.0 mg, 73% yield) as a yellow oil was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.98 (s, 1 H), 7.75 (d, $J = 8.8$ Hz, 1 H), 7.57 (dd, $J = 8.8$ Hz, $J = 1.6$ Hz, 1 H), 7.29 (d, $J = 2.8$ Hz, 1 H), 7.25 (d, $J = 5.6$ Hz, 1 H), 7.08 (dd, $J = 5.2$ Hz, $J = 3.6$ Hz, 1 H), 4.28 (s, 3 H), 1.11-0.99 (m, 15 H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.1, 145.6, 133.7, 130.9, 127.9, 127.8, 125.0, 124.0, 122.5, 118.1, 117.8, 41.5, 7.4, 4.1. FTMS (ESI): Calculated for $\text{C}_{18}\text{H}_{25}\text{N}_2\text{SSi}$ ($\text{M}+\text{H}^+$): 329.1502; Found: 329.1489.

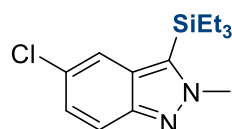


2-Methyl-5-(pyridin-3-yl)-3-(triethylsilyl)-2H-indazole (19). The product **19** (50.5 mg, 78% yield) as a yellow solid was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 8.90 (s, 1 H), 8.58 (d, $J = 4.0$ Hz, 1 H), 7.93-7.91 (m, 2 H), 7.85 (d, $J = 8.8$ Hz, 1 H), 7.50 (dd, $J = 8.8$ Hz, $J = 1.6$ Hz, 1 H), 7.40 (dd, $J = 7.6$ Hz, $J = 4.8$ Hz, 1 H), 4.31 (s, 3 H), 1.11-0.97 (m, 15 H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.2,

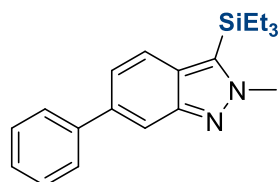
148.1, 147.6, 137.7, 134.6, 134.1, 131.1, 130.9, 125.2, 123.6, 119.9, 118.2, 41.6, 7.3, 4.0. FTMS (ESI): Calculated for $C_{19}H_{26}N_3Si$ ($M+H^+$): 324.1890; Found: 324.1882.



2-Methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(triethylsilyl)-2H-indazole (20). The product **20** (31.9 mg, 65% yield) as a brown solid was purified with silica gel chromatography. 1H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1 H), 7.71-7.64 (m, 2 H), 4.29 (s, 3 H), 1.35 (s, 12 H), 1.11-1.05 (m, 6 H), 1.01-0.97 (m, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 134.6, 130.5, 130.3, 130.2, 116.1, 83.5, 41.4, 24.8, 7.3, 3.9. FTMS (ESI): Calculated for $C_{20}H_{34}BN_2O_2Si$ ($M+H^+$): 373.2481; Found: 373.2465.

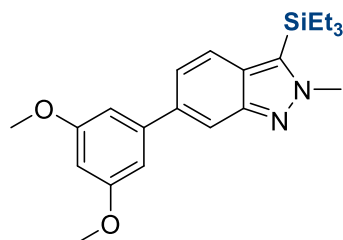


5-Chloro-2-methyl-3-(triethylsilyl)-2H-indazole (21). The product **21** (24.2 mg, 43% yield) as a brown solid was purified with silica gel chromatography. 1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, $J = 1.6$ Hz, 1 H), 7.67 (d, $J = 8.8$ Hz, 1 H), 7.20 (dd, $J = 9.2$ Hz, $J = 2.0$ Hz, 1 H), 4.27 (s, 3 H), 1.06-0.96 (m, 15 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 132.9, 131.1, 127.0, 126.6, 120.2, 118.8, 41.6, 7.3, 3.9. FTMS (ESI): Calculated for $C_{14}H_{22}ClN_2Si$ ($M+H^+$): 281.1235; Found: 281.1235.

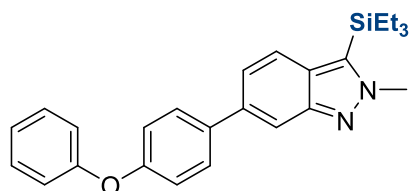


2-Methyl-6-phenyl-3-(triethylsilyl)-2H-indazole (22). The product **22** (61.3 mg, 95% yield) as a yellow oil was purified with silica gel chromatography. 1H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1 H), 7.85 (d, $J = 9.2$ Hz, 1 H), 7.70 (d, $J = 7.6$ Hz, 2 H), 7.47 (t, $J = 7.6$ Hz, 2 H), 7.39-7.35 (m, 2 H), 4.32 (s, 3 H), 1.12-1.01 (m, 15 H). ^{13}C NMR (100

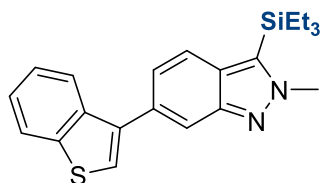
MHz, CDCl₃) δ 149.1, 141.7, 138.4, 133.0, 130.0, 128.7, 127.3, 127.0, 121.9, 121.7, 115.0, 41.5, 7.3, 4.0. FTMS (ESI): Calculated for C₂₀H₂₇N₂Si (M+H⁺): 323.1938; Found: 323.1926.



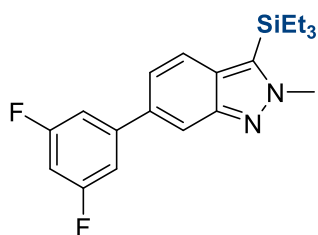
6-(3,5-Dimethoxyphenyl)-2-methyl-3-(triethylsilyl)-2H-indazole (23). The product **23** (68.7 mg, 90% yield) as a yellow oil was purified with silica gel chromatography. ¹H NMR (400 MHz, CDCl₃) δ 7.94 (s, 1 H), 7.81 (d, *J* = 8.8 Hz, 1 H), 7.34 (d, *J* = 8.8 Hz, 1 H), 6.83 (d, *J* = 2.0 Hz, 2 H), 6.48 (s, 1 H), 4.31 (s, 3 H), 3.86 (s, 6 H), 1.11-0.99 (m, 15 H). ¹³C NMR (100 MHz, CDCl₃) δ 160.9, 149.0, 143.9, 138.4, 133.1, 130.2, 121.9, 121.6, 115.1, 105.5, 99.1, 55.4, 41.5, 7.3, 4.0. FTMS (ESI): Calculated for C₂₂H₃₁N₂O₂Si (M+H⁺): 383.2149; Found: 383.2139.



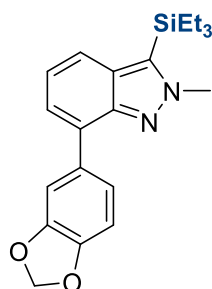
2-Methyl-6-(4-phenoxyphenyl)-3-(triethylsilyl)-2H-indazole (24). The product **24** (67.2 mg, 81% yield) as a yellow oil was purified with silica gel chromatography. ¹H NMR (400 MHz, CDCl₃) δ 7.92 (s, 1 H), 7.83 (d, *J* = 8.8 Hz, 1 H), 7.64 (d, *J* = 8.8 Hz, 2 H), 7.39-7.33 (m, 3 H), 7.15-7.08 (m, 5 H), 4.31 (s, 1 H), 1.12-1.00 (m, 15 H). ¹³C NMR (100 MHz, CDCl₃) δ 157.1, 156.7, 149.1, 137.8, 136.7, 133.2, 129.8, 129.7, 128.6, 123.3, 121.8, 121.7, 119.0, 118.9, 114.5, 41.5, 7.3, 4.0. FTMS (ESI): Calculated for C₂₆H₃₁N₂O₂Si (M+H⁺): 415.2200; Found: 415.2209.



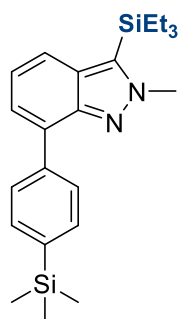
6-(Benzo[*b*]thiophen-3-yl)-2-methyl-3-(triethylsilyl)-2*H*-indazole (25). The product **25** (56.8 mg, 75% yield) as a yellow solid was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 8.06-8.03 (m, 1 H), 7.98 (s, 1 H), 7.95-7.93 (m, 1 H), 7.87 (d, $J = 8.4$ Hz, 1 H), 7.48 (s, 1 H), 7.41-7.39 (m, 2 H), 7.34 (d, $J = 8.8$ Hz, 1 H), 4.34 (s, 3 H), 1.14-1.02 (m, 15 H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.9, 140.6, 138.5, 138.0, 133.3, 133.1, 130.1, 124.3, 124.2, 123.3, 123.2, 122.8, 121.7, 116.6, 41.5, 7.4, 4.0. FTMS (ESI): Calculated for $\text{C}_{22}\text{H}_{27}\text{N}_2\text{SSi}$ ($\text{M}+\text{H}^+$): 379.1658; Found: 379.1658.



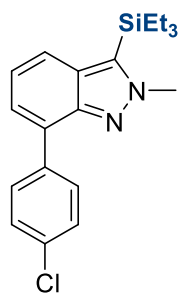
6-(3,5-Difluorophenyl)-2-methyl-3-(triethylsilyl)-2*H*-indazole (26). The product **26** (45.2 mg, 63% yield) as a light yellow solid was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.91 (s, 1 H), 7.83 (d, $J = 8.8$ Hz, 1 H), 7.27 (d, $J = 8.4$ Hz, 1 H), 7.18 (d, $J = 6.8$ Hz, 2 H), 6.78 (t, $J = 8.0$ Hz, 1 H), 4.31 (s, 3 H), 1.11-1.00 (m, 15 H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.2 (dd, $J = 246.0$, $J = 13.0$), 148.8, 145.1 (t, $J = 9.5$), 136.1, 133.4, 130.4, 122.2, 121.1, 115.5, 110.1 (dd, $J = 18.0$, $J = 7.0$), 102.2 (t, $J = 26.0$), 41.6, 7.3, 4.0. FTMS (ESI): Calculated for $\text{C}_{20}\text{H}_{25}\text{F}_2\text{N}_2\text{Si}$ ($\text{M}+\text{H}^+$): 359.1749; Found: 359.1734.



7-(Benzo[*d*][1,3]dioxol-5-yl)-2-methyl-3-(triethylsilyl)-2*H*-indazole (27). The product **27** (41.8 mg, 57% yield) as a yellow oil was purified with silica gel chromatography. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.4 Hz, 1 H), 7.58 (d, *J* = 1.6 Hz, 1 H), 7.48 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1 H), 7.33 (d, *J* = 6.8 Hz, 1 H), 7.13 (dd, *J* = 8.4 Hz, *J* = 7.2 Hz, 1 H), 6.94 (d, *J* = 8.0 Hz, 1 H), 6.01 (s, 2 H), 4.32 (s, 3 H), 1.11-0.99 (m, 15 H). ¹³C NMR (100 MHz, CDCl₃) δ 147.5, 146.9, 146.8, 133.0, 131.6, 130.2, 123.6, 122.4, 121.7, 120.3, 109.6, 108.3, 100.9, 41.7, 7.4, 4.1. FTMS (ESI): Calculated for C₂₁H₂₇N₂O₂Si (M+H⁺): 367.1836; Found: 367.1831.

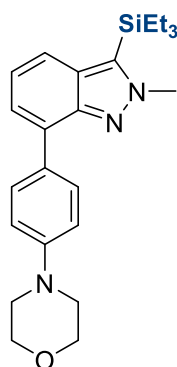


2-Methyl-3-(triethylsilyl)-7-(4-(trimethylsilyl)phenyl)-2*H*-indazole (28). The product **28** (62.3 mg, 79% yield) as a white solid was purified with silica gel chromatography. ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.4 Hz, 2 H), 7.76 (d, *J* = 8.4 Hz, 1 H), 7.65 (d, *J* = 8.0 Hz, 2 H), 7.41 (d, *J* = 7.6 Hz, 1 H), 7.17 (dd, *J* = 8.8 Hz, *J* = 7.2 Hz, 1 H), 4.34 (s, 3 H), 1.11-0.99 (m, 15 H), 0.31 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ 139.2, 139.1, 133.5, 131.5, 130.5, 128.2, 124.6, 121.9, 120.7, 41.7, 7.4, 4.1, -1.1. FTMS (ESI): Calculated for C₂₃H₃₅N₂Si₂ (M+H⁺): 395.2333; Found: 395.2322.

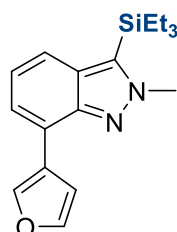


7-(4-Chlorophenyl)-2-methyl-3-(triethylsilyl)-2*H*-indazole (29). The product **29** (37.1 mg, 52% yield) as a white solid was purified with silica gel chromatography. ¹H

NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 8.8 Hz, 2 H), 7.77 (d, J = 8.4 Hz, 1 H), 7.45 (d, J = 8.4 Hz, 2 H), 7.38 (d, J = 6.8 Hz, 1 H), 7.16 (dd, J = 8.4 Hz, J = 7.2 Hz, 1 H), 4.32 (s, 3 H), 1.11-0.99 (m, 15 H). ¹³C NMR (100 MHz, CDCl₃) δ 146.6, 137.3, 133.4, 133.1, 131.6, 130.1, 129.2, 128.5, 124.1, 121.7, 121.1, 41.8, 7.4, 4.1. FTMS (ESI): Calculated for C₂₀H₂₆ClN₂Si (M+H⁺): 357.1548; Found: 357.1544.

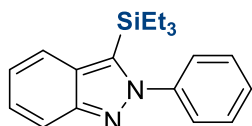


4-(4-(2-Methyl-3-(triethylsilyl)-2H-indazol-7-yl)phenyl)morpholine (30). The product **30** (33.4 mg, 41% yield) as a light yellow solid was purified with silica gel chromatography. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 8.8 Hz, 2 H), 7.71 (dd, J = 8.8 Hz, J = 0.8 Hz, 1 H), 7.36 (dd, J = 6.8 Hz, J = 0.8 Hz, 1 H), 7.14 (dd, J = 8.4 Hz, J = 6.8 Hz, 1 H), 7.05 (d, J = 8.4 Hz, 2 H), 4.32 (s, 3 H), 3.90 (t, J = 4.6 Hz, 4 H), 3.23 (t, J = 4.8 Hz, 4 H), 1.10-0.98 (m, 15 H). ¹³C NMR (100 MHz, CDCl₃) δ 146.9, 132.8, 131.7, 130.2, 129.6, 123.1, 121.8, 119.9, 115.7, 66.9, 49.4, 41.8, 7.4, 4.1. FTMS (ESI): Calculated for C₂₄H₃₄N₃OSi (M+H⁺): 408.2465; Found: 408.2452.

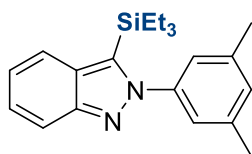


7-(Furan-3-yl)-2-methyl-3-(triethylsilyl)-2H-indazole (31). The product **31** (29.4 mg, 47% yield) as a brown oil was purified with silica gel chromatography. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 7.2 Hz, 1 H), 7.69 (d, J = 8.4 Hz, 1 H), 7.54-7.53 (m, 1 H), 7.50 (d, J = 3.6 Hz, 1 H), 7.13 (dd, J = 8.4 Hz, J = 7.2 Hz, 1 H), 6.57 (q, J = 1.6 Hz, 1 H), 4.35 (s, 3 H), 1.09-0.97 (m, 15 H). ¹³C NMR (100 MHz, CDCl₃) δ 151.6, 144.4,

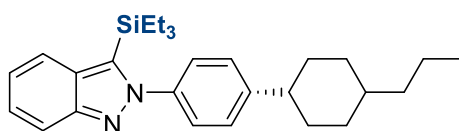
141.7, 133.3, 131.5, 121.5, 120.5, 120.1, 119.8, 111.8, 109.8, 41.7, 7.3, 4.0. FTMS (ESI): Calculated for C₁₈H₂₅N₂OSi (M+H⁺): 313.1730; Found: 313.1722.



2-Phenyl-3-(triethylsilyl)-2H-indazole (32). The product **32** (54.9 mg, 89% yield) as a yellow oil was purified with silica gel chromatography. ¹H NMR (400 MHz, CDCl₃) δ 7.88-7.83 (m, 2 H), 7.53-7.48 (m, 5 H), 7.37-7.33 (m, 1 H), 7.16-7.12 (m, 1 H), 0.86 (t, *J* = 8.0 Hz, 9 H), 0.69 (q, *J* = 8.0 Hz, 6 H). ¹³C NMR (100 MHz, CDCl₃) δ 149.1, 142.8, 134.9, 130.7, 129.4, 128.7, 126.9, 126.0, 121.9, 121.8, 117.8, 7.3, 3.9. FTMS (ESI): Calculated for C₁₉H₂₅N₂Si (M+H⁺): 309.1781; Found: 309.1782.

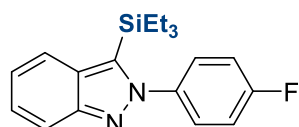


2-(3,5-Dimethylphenyl)-3-(triethylsilyl)-2H-indazole (33). The product **33** (41.1 mg, 61% yield) as a yellow oil was purified with silica gel chromatography. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (dd, *J* = 11.2 Hz, *J* = 8.4 Hz, 2 H), 7.35-7.31 (m, 1 H), 7.14-7.11 (m, 4 H), 2.39 (s, 6 H), 0.87 (t, *J* = 8.0 Hz, 9 H), 0.71 (q, *J* = 8.0 Hz, 6 H). ¹³C NMR (100 MHz, CDCl₃) δ 149.0, 142.5, 138.4, 134.5, 130.8, 130.7, 125.8, 124.8, 121.8, 121.6, 117.8, 21.1, 7.3, 4.0. FTMS (ESI): Calculated for C₂₁H₂₉N₂Si (M+H⁺): 337.2094; Found: 337.2091.

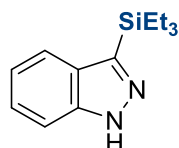


2-(4-(4-Propylcyclohexyl)phenyl)-3-(triethylsilyl)-2H-indazole (34). The product **34** (70.1 mg, 81% yield) as a yellow oil was purified with silica gel chromatography. ¹H NMR (400 MHz, CDCl₃) δ 7.86-7.81 (m, 2 H), 7.38 (d, *J* = 8.0 Hz, 2 H), 7.35-7.30 (m, 3 H), 7.13 (t, *J* = 7.6 Hz, 1 H), 2.58 (t, *J* = 12.2 Hz, 1 H), 1.92 (t, *J* = 15.0 Hz, 4 H),

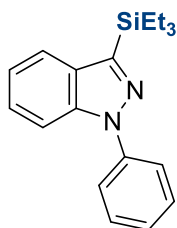
1.54-1.45 (m, 2 H), 1.40-1.32 (m, 2 H), 1.26-1.22 (m, 3 H), 1.13-1.04 (m, 2 H), 0.92 (t, $J = 7.2$ Hz, 3 H), 0.85 (t, $J = 8.0$ Hz, 9 H), 0.69 (q, $J = 8.0$ Hz, 6 H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.6, 148.9, 140.4, 135.0, 130.6, 127.0, 126.7, 126.0, 121.8, 121.7, 117.8, 44.4, 39.6, 37.0, 34.3, 33.4, 20.0, 14.4, 7.3, 4.0. FTMS (ESI): Calculated for $\text{C}_{28}\text{H}_{41}\text{N}_2\text{Si}$ ($\text{M}+\text{H}^+$): 433.3033; Found: 433.3021.



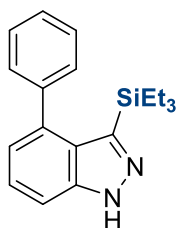
2-(4-Fluorophenyl)-3-(triethylsilyl)-2H-indazole (35). The product **35** (49.0 mg, 75% yield) as a white solid was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.84 (dd, $J = 13.6$ Hz, $J = 8.8$ Hz, 2 H), 7.50-7.45 (m, 2 H), 7.37-7.33 (m, 1 H), 7.20 (t, $J = 8.0$ Hz, 2 H), 7.16-7.12 (m, 1 H), 0.87 (t, $J = 8.0$ Hz, 9 H), 0.71 (q, $J = 8.0$ Hz, 6 H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.9 (d, $J = 249.0$ Hz), 149.1, 139.0, 135.2, 130.7, 128.7, 128.6, 126.2, 122.0, 121.8, 117.8, 115.8, 115.5, 7.2, 3.9. FTMS (ESI): Calculated for $\text{C}_{19}\text{H}_{24}\text{FN}_2\text{Si}$ ($\text{M}+\text{H}^+$): 327.1687; Found: 327.1678.



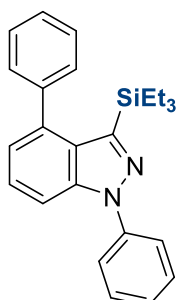
3-(Triethylsilyl)-1H-indazole (36). The product **36** (46.5 mg, 75% yield) as a brown solid was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 8.0$ Hz, 1 H), 7.56 (d, $J = 8.4$ Hz, 1 H), 7.38 (t, $J = 7.6$ Hz, 1 H), 7.16 (t, $J = 7.6$ Hz, 1 H), 1.08-0.97 (m, 15 H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.1, 140.7, 129.3, 126.2, 121.9, 120.6, 110.2, 7.5, 3.8. FTMS (ESI): Calculated for $\text{C}_{13}\text{H}_{21}\text{N}_2\text{Si}$ ($\text{M}+\text{H}^+$): 233.1468; Found: 233.1477.



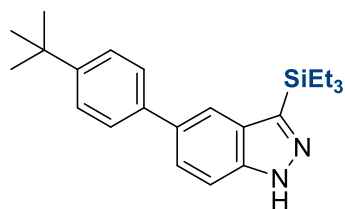
1-Phenyl-3-(triethylsilyl)-1H-indazole (36b). The product **36b** (52.4 mg, 85% yield) as a yellow oil was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, $J = 9.2$ Hz, 1 H), 7.81-7.78 (m, 3 H), 7.55 (t, $J = 8.0$ Hz, 2 H), 7.44-7.40 (m, 1 H), 7.36 (t, $J = 7.4$ Hz, 1 H), 7.24-7.20 (m, 1 H), 1.12-1.02 (m, 15 H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.5, 140.4, 138.9, 131.7, 129.3, 126.4, 126.3, 122.7, 122.3, 121.0, 110.3, 7.6, 3.9. FTMS (ESI): Calculated for $\text{C}_{19}\text{H}_{25}\text{N}_2\text{Si}$ ($\text{M}+\text{H}^+$): 309.1781; Found: 309.1774.



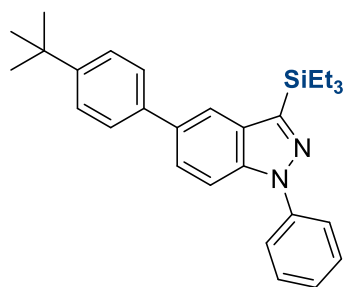
4-Phenyl-3-(triethylsilyl)-1H-indazole (37). The reaction was carried out according to the general procedure on 0.4 mmol scale. The product **37** (62 mg, 50% yield) as a brown solid was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J = 8.4$ Hz, 1 H), 7.50-7.44 (m, 5 H), 7.40 (t, $J = 7.6$ Hz, 1 H), 7.01 (d, $J = 6.8$ Hz, 1 H), 0.82 (t, $J = 8.0$ Hz, 9 H), 0.49 (q, $J = 8.0$ Hz, 6 H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.3, 142.1, 137.5, 129.4, 128.8, 128.5, 128.2, 127.6, 125.7, 122.2, 109.7, 7.7, 3.4. FTMS (ESI): Calculated for $\text{C}_{19}\text{H}_{25}\text{N}_2\text{Si}$ ($\text{M}+\text{H}^+$): 309.1781; Found: 309.1790.



1,4-Diphenyl-3-(triethylsilyl)-1H-indazole (37b). The reaction was carried out according to the general procedure on 0.1 mmol scale. The product **37b** (17.1 mg, 44% yield) as a white solid was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.79-7.77 (m, 3 H), 7.56 (t, $J = 7.8$ Hz, 2 H), 7.52-7.43 (m, 5 H), 7.41-7.35 (m, 2 H), 7.05 (d, $J = 7.2$ Hz, 1 H), 0.83 (t, $J = 8.0$ Hz, 9 H), 0.47 (q, $J = 8.0$ Hz, 6 H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.5, 142.1, 140.4, 139.7, 137.8, 130.4, 129.5, 129.4, 128.3, 127.7, 126.5, 125.8, 123.1, 122.7, 109.2, 7.8, 3.6. FTMS (ESI): Calculated for $\text{C}_{25}\text{H}_{29}\text{N}_2\text{Si}$ ($\text{M}+\text{H}^+$): 385.2094; Found: 385.2093.

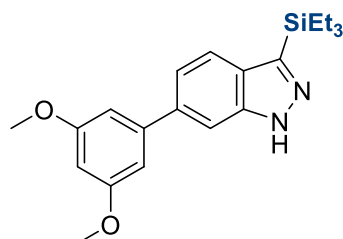


5-(4-(tert-Butyl)phenyl)-3-(triethylsilyl)-1H-indazole (38). The product **38** (51.2 mg, 70% yield) as a yellow oil was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.99 (s, 1 H), 7.64 (s, 2 H), 7.59 (d, $J = 8.4$ Hz, 2 H), 7.52 (d, $J = 8.4$ Hz, 2 H), 1.40 (s, 9 H), 1.08-1.05 (m, 15 H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.8, 145.2, 138.9, 134.2, 132.1, 129.9, 127.1, 126.6, 125.8, 119.9, 110.6, 83.7, 31.4, 7.5, 3.8. FTMS (ESI): Calculated for $\text{C}_{19}\text{H}_{25}\text{N}_2\text{Si}$ ($\text{M}+\text{H}^+$): 365.2407; Found: 365.2398.

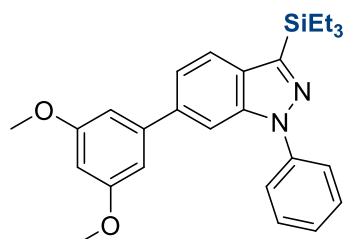


5-(4-(tert-Butyl)phenyl)-1-phenyl-3-(triethylsilyl)-1H-indazole (38b). The reaction was carried out according to the general procedure on 0.1 mmol scale. The product **38b** (34.9 mg, 79% yield) as a colourless oil was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 8.02 (s, 1 H), 7.84-7.79 (m, 3 H), 7.66 (dd, $J = 8.8$ Hz, $J = 1.6$ Hz, 1 H), 7.61 (d, $J = 8.4$ Hz, 2 H), 7.57-7.52 (m, 4 H), 7.36 (t, $J = 7.4$ Hz, 1 H),

1.40 (s, 9 H), 1.12-1.03 (m, 15 H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.9, 146.9, 140.3, 138.7, 138.3, 134.5, 132.4, 129.4, 127.1, 126.5, 126.4, 125.8, 122.7, 120.2, 110.6, 34.5, 31.4, 7.6, 3.9. FTMS (ESI): Calculated for $\text{C}_{29}\text{H}_{37}\text{N}_2\text{Si}$ ($\text{M}+\text{H}^+$): 441.2720; Found: 441.2730.

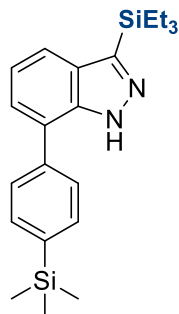


6-(3,5-Dimethoxyphenyl)-3-(triethylsilyl)-1H-indazole (39). The reaction was carried out according to the general procedure on 0.4 mmol scale. The product **39** (61.9 mg, 42% yield) as a yellow oil was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, $J = 8.4$ Hz, 1 H), 7.72 (s, 1 H), 7.39 (dd, $J = 8.4$ Hz, $J = 1.2$ Hz, 1 H), 6.80 (d, $J = 2.0$ Hz, 2 H), 6.50 (t, $J = 2.2$ Hz, 1 H), 3.86 (s, 6 H), 1.08-1.01 (m, 15 H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.0, 145.1, 143.7, 141.3, 139.7, 128.8, 122.0, 121.0, 108.4, 105.9, 99.3, 55.4, 7.5, 3.8. FTMS (ESI): Calculated for $\text{C}_{21}\text{H}_{29}\text{N}_2\text{O}_2\text{Si}$ ($\text{M}+\text{H}^+$): 369.1992; Found: 369.1995.

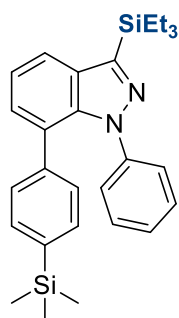


6-(3,5-Dimethoxyphenyl)-1-phenyl-3-(triethylsilyl)-1H-indazole (39b). The reaction was carried out according to the general procedure on 0.1 mmol scale. The product **39b** (32.5 mg, 73% yield) as a yellow oil was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 8.0$ Hz, 2 H), 7.81-7.78 (m, 2 H), 7.56 (t, $J = 7.6$ Hz, 2 H), 7.45-7.43 (m, 1 H), 7.37 (t, $J = 7.4$ Hz, 1 H), 6.79 (d, $J = 2.4$ Hz, 2 H), 6.51 (t, $J = 2.2$ Hz, 1 H), 3.87 (s, 6 H), 1.14-1.02 (m, 15 H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.0, 146.5, 143.8, 140.3, 140.0, 139.5, 131.1, 129.4, 126.5,

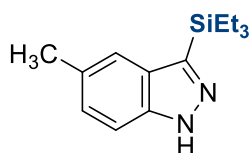
122.9, 122.3, 121.3, 108.7, 106.1, 99.1, 55.4, 7.6, 3.9. FTMS (ESI): Calculated for $C_{27}H_{33}N_2O_2Si$ ($M+H^+$): 445.2305; Found: 445.2303.



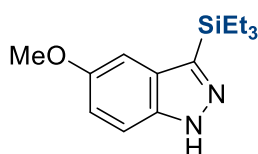
3-(Triethylsilyl)-7-(4-(trimethylsilyl)phenyl)-1H-indazole (40). The product **40** (61.7 mg, 81% yield) as a yellow oil was purified with silica gel chromatography. 1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, $J = 7.6$ Hz, 1 H), 7.70 (dd, $J = 10.8$ Hz, $J = 8.4$ Hz, 4 H), 7.44 (d, $J = 6.4$ Hz, 1 H), 7.30-7.28 (m, 1 H), 1.11-1.00 (m, 15 H), 0.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 140.2, 138.9, 138.7, 134.3, 129.9, 127.1, 125.6, 124.9, 121.4, 121.1, 7.5, 3.8, 1.1. FTMS (ESI): Calculated for $C_{22}H_{33}N_2Si_2$ ($M+H^+$): 381.2176; Found: 381.2175.



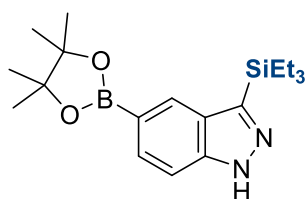
1-Phenyl-3-(triethylsilyl)-7-(4-(trimethylsilyl)phenyl)-1H-indazole (40b). The reaction was carried out according to the general procedure on 0.1 mmol scale. The product **40b** (19.8 mg, 43% yield) as a light yellow oil was purified with silica gel chromatography. 1H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, $J = 8.8$ Hz, $J = 0.8$ Hz, 1 H), 7.37 (dd, $J = 8.2$ Hz, $J = 1.0$ Hz, 1 H), 7.29 (t, $J = 7.6$ Hz, 1 H), 7.15 (d, $J = 8.0$ Hz, 2 H), 7.05-7.01 (m, 1 H), 6.99-6.97 (m, 6 H), 1.10-1.06 (m, 15 H), 0.24 (s, 9 H). FTMS (ESI): Calculated for $C_{28}H_{37}N_2Si_2$ ($M+H^+$): 457.2489; Found: 457.2488.



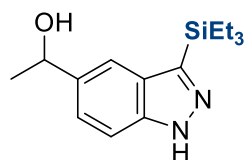
5-Methyl-3-(triethylsilyl)-3a,7a-dihydro-1H-indazole (41). The product **41** (36.3 mg, 73% yield) as a brown oil was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.56 (s, 1H), 7.43 (d, $J = 8.4$ Hz, 1H), 7.19 (d, $J = 8.3$ Hz, 1H), 2.47 (s, 3H), 1.07-0.95 (m, 15H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.3, 139.6, 129.9, 129.8, 128.3, 120.9, 109.9, 21.5, 7.5, 3.8. HRMS (ESI): Calculated for $\text{C}_{27}\text{H}_{45}\text{Si}$ ($\text{M}+\text{H}$) $^+$:247.1625; Found: 247.1631.



5-Methoxy-3-(triethylsilyl)-3a,7a-dihydro-1H-indazole (42). The product **42** (36.3 mg, 61% yield) as a brown oil was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, $J = 8.9$ Hz, 1H), 7.14 (s, 1H), 7.05 (d, $J = 9.1$ Hz, 1H), 3.86 (s, 3H), 1.07-0.96 (m, 15H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.5, 142.9, 137.6, 129.7, 118.3, 111.9, 101.3, 55.7, 7.5, 3.8. HRMS (ESI): Calculated for $\text{C}_{27}\text{H}_{45}\text{Si}$ ($\text{M}+\text{H}$) $^+$:263.1574; Found: 263.1580.

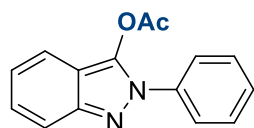


5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(triethylsilyl)-1H-indazole(43). The product **43** (39.4 mg, 55% yield) as a brown oil was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 8.28 (s, 1H), 7.14 (s, 1H), 7.78 (d, $J = 8.4$ Hz, 1H), 1.36 (s, 12H), 1.02 (s, 15H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.5, 142.3, 132.0, 129.9, 129.2, 109.2, 83.7, 24.9, 7.5, 3.8. HRMS (ESI): Calculated for $\text{C}_{27}\text{H}_{45}\text{Si}$ ($\text{M}+\text{H}$) $^+$:359.2321; Found: 359.2326.

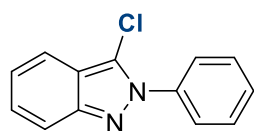


5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(triethylsilyl)-1H-indazole(44).

The product **44** (35.4 mg, 64% yield) as a brown oil was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) 7.76 (s, 1H), 7.52 (d, $J = 8.6$ Hz, 1H), 7.42 (d, $J = 8.5$ Hz, 1H), 5.02 (q, $J = 6.4$ Hz, 1H), 1.56 (d, $J = 6.4$ Hz, 3H), 1.04-0.94 (m, 15H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.9, 138.4, 129.3, 124.5, 118.2, 116.4, 110.6, 75.1, 24.8, 7.4, 3.8. HRMS (ESI): Calculated for $\text{C}_{27}\text{H}_{45}\text{Si}$ ($\text{M}+\text{H}$) $^+$:277.1731; Found: 277.1736.

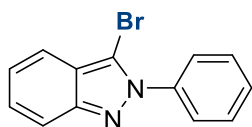


2-Phenyl-2H-indazol-3-yl acetate (45). The reaction was carried out according to the general procedure on 0.1 mmol scale. The product **45** (11.9 mg, 46% yield) as a light yellow oil was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 8.24 (s, 1 H), 7.78 (d, $J = 8.8$ Hz, 1 H), 7.73 (t, $J = 8.6$ Hz, 2 H), 7.49 (t, $J = 8.0$ Hz, 1 H), 7.42 (t, $J = 7.6$ Hz, 1 H), 7.34 (d, $J = 7.2$ Hz, 1 H), 7.30 (d, $J = 8.4$ Hz, 1 H), 7.13 (t, $J = 7.6$ Hz, 1 H), 2.16 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.7, 149.5, 143.8, 129.5, 126.8, 126.7, 124.1, 124.0, 122.4, 122.1, 120.4, 117.9, 20.8. FTMS (ESI): Calculated for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{NaO}_2$ ($\text{M}+\text{Na}^+$): 275.0791; Found: 275.0799.

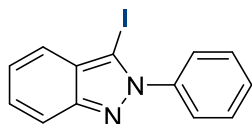


3-Chloro-2-phenyl-2H-indazole (46). This compound is known^[5]. The reaction was carried out according to the general procedure on 0.1 mmol scale. The product **46** (13.1 mg, 57% yield) as a light yellow solid was purified with silica gel chromatography. ^1H NMR (400 MHz, CDCl_3) δ 7.68 (t, $J = 8.6$ Hz, 1H), 7.62 (s, 1H), 7.59-7.50 (m, 4 H), 7.29 (dd, $J = 9.2$ Hz, $J = 1.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.8, 138.1,

129.4, 129.2, 129.1, 128.5, 125.6, 120.2, 119.8, 117.74, 117.68.



3-Bromo-2-phenyl-2H-indazole (47). This compound is known^[5]. The reaction was carried out according to the general procedure on 0.1 mmol scale. The product **47** (24.2 mg, 89% yield) as a light yellow solid was purified with silica gel chromatography. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 8.8 Hz, 1 H), 7.69-7.65 (m, 2 H), 7.61-7.50 (m, 4 H), 7.40-7.36 (m, 1 H), 7.21-7.17 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 149.0, 139.1, 129.3, 129.1, 127.7, 126.2, 123.0, 122.8, 119.7, 118.1, 106.4.



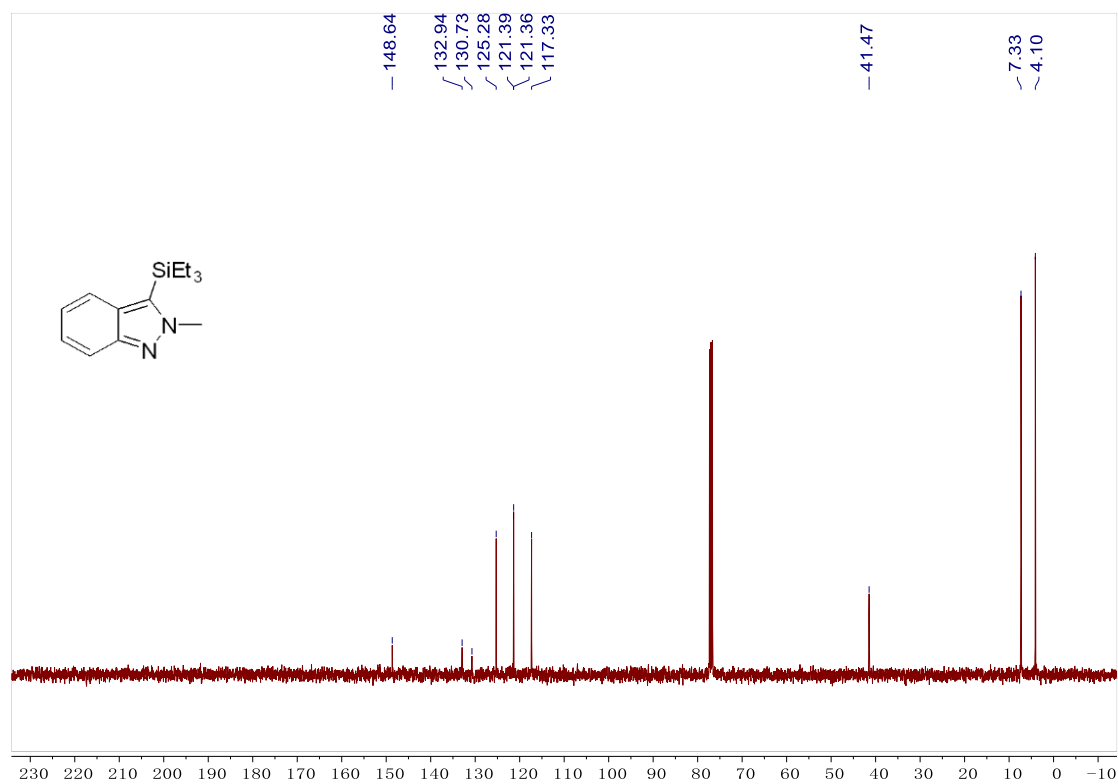
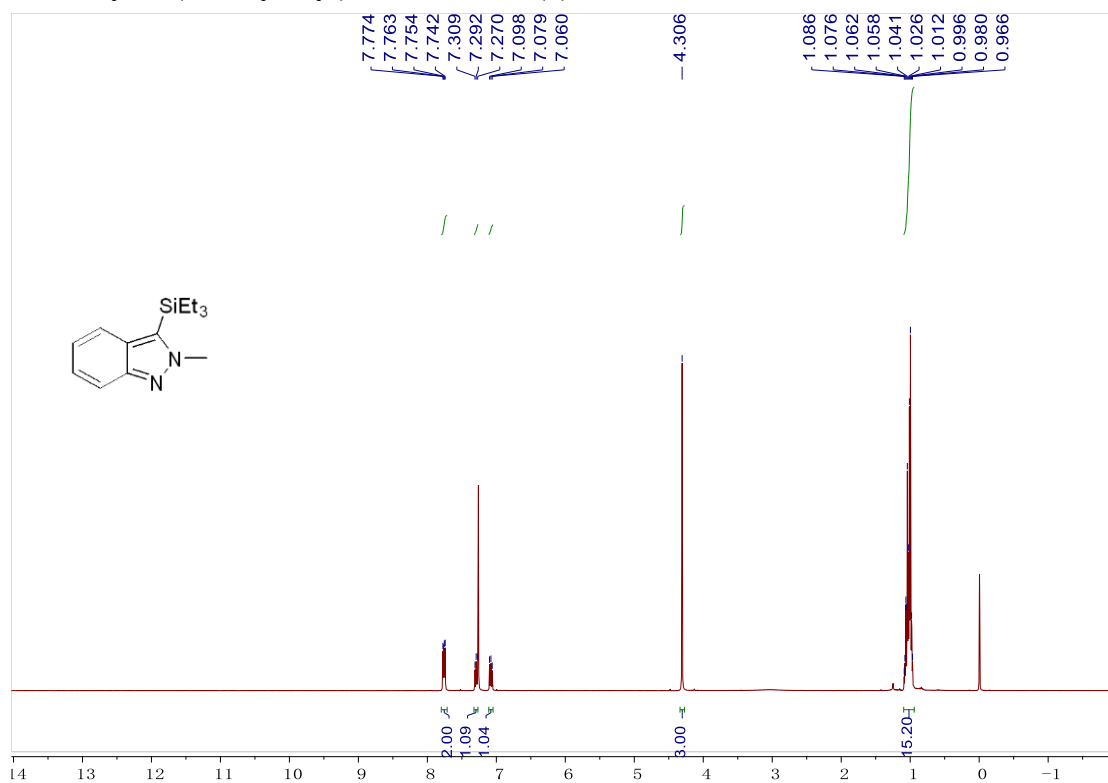
3-Iodo-2-phenyl-2H-indazole (48). This compound is known^[6]. The reaction was carried out according to the general procedure on 0.1 mmol scale. The product **48** (15.9 mg, 50% yield) as a reddish-brown oil was purified with silica gel chromatography. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 8.8 Hz, 1 H), 7.66-7.64 (m, 2 H), 7.59-7.53 (m, 3 H), 7.50 (d, *J* = 8.4 Hz, 1 H), 7.39 (t, *J* = 7.8 Hz, 1 H), 7.19 (t, *J* = 7.2 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 150.0, 140.5, 129.4, 129.0, 128.2, 127.6, 126.7, 123.2, 121.1, 118.3.

References

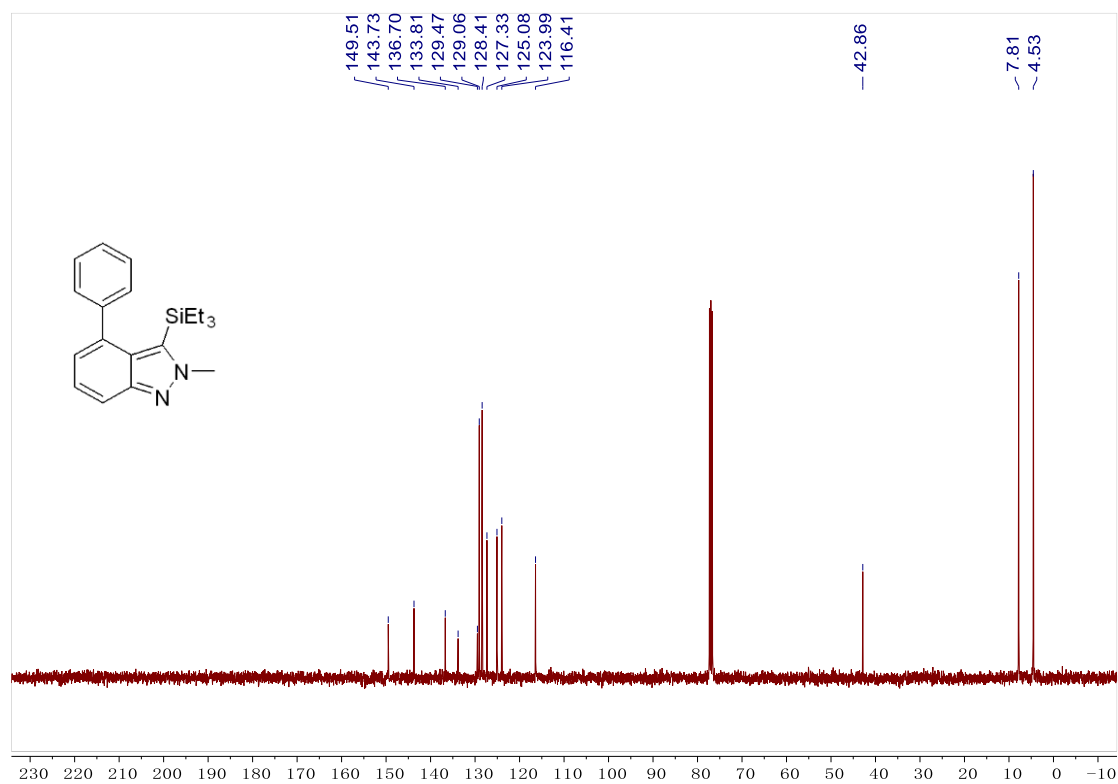
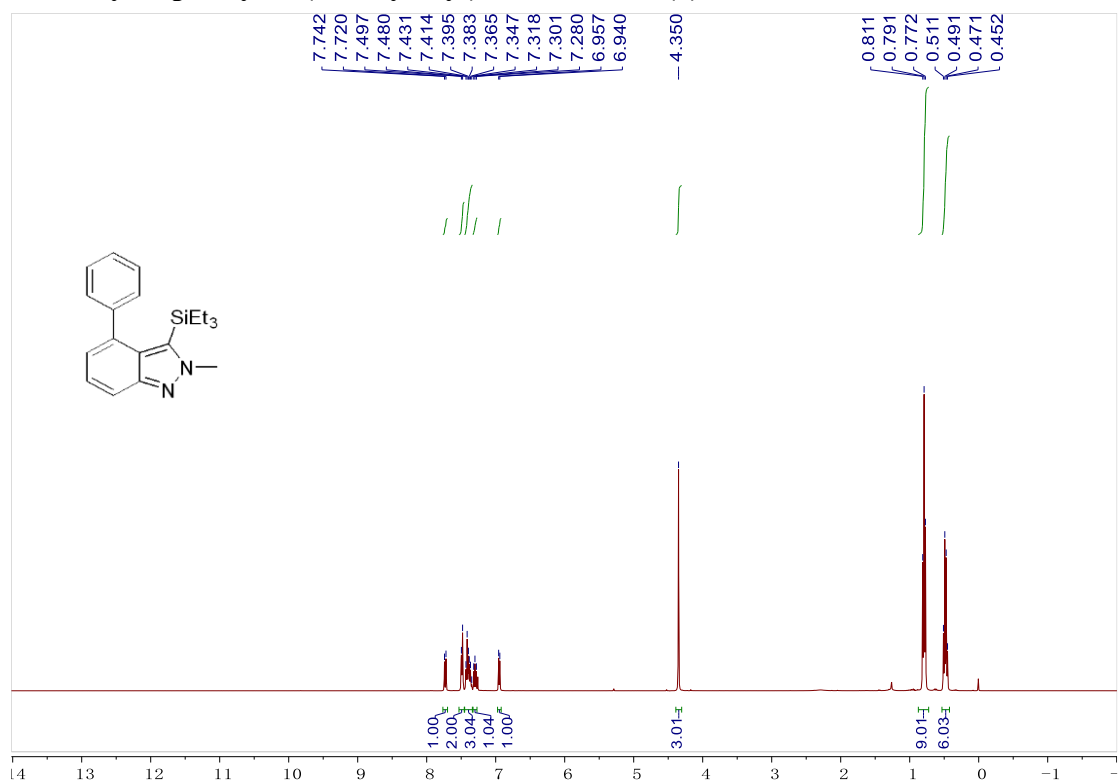
- [1] Han, S. J.; Kim, H. T.; Joo, J. M. Direct C-H alkenylation of functionalized pyrazoles. *J. Org. Chem.* **2016**, *81*, 689.
- [2] Zhang, R.; Liu, Z.; Peng, Q.; Zhou, Y.; Xu, L.; Pan, X. Access to 2-substituted-2H-indazoles via a copper-catalyzed regioselective cross-coupling reaction. *Org. Biomol. Chem.* **2018**, *16*, 1816.
- [3] Gondo, K.; Oyamada, J.; Kitamura, T. Palladium-catalyzed desilylative acyloxylation of silicon-carbon bonds on (trimethylsilyl) arenes: Synthesis of phenol derivatives from trimethylsilylarenes. *Org. Lett.* **2015**, *17*, 4778.

- [4] Zarate, C.; Nakajima, M.; Martin, R. A mild and ligand-free Ni-catalyzed silylation via C-OMe cleavage. *J. Am. Chem. Soc.* **2017**, *139*, 1191.
- [5] Liu, X.; Wu, Z.; Feng, C.; Liu, W.; Li, M.; Shen, Z. Catalyst-and Oxidant-Free Electrochemical Halogenation Reactions of 2H-Indazoles with NaX (X=Cl, Br). *Eur. J. Org. Chem.* **2022**, *2022*, e202200262.
- [6] Fang, Y.; Wu, C.; Larock, R. C.; Shi, F. Synthesis of 2H-indazoles by the [3+2] dipolar cycloaddition of sydnone with arynes. *J. Org. Chem.* **2011**, *76*, 8840.
- [7] Sun, M.; Tao, M.; Zhao, L.; Li, W.; Liu, Z.; He, C.-Y.; Feng, Z. Iron-catalyzed C–F bond silylation and borylation of fluoroarenes. *Org. Chem. Front.* **2011**, *8*, 5322.

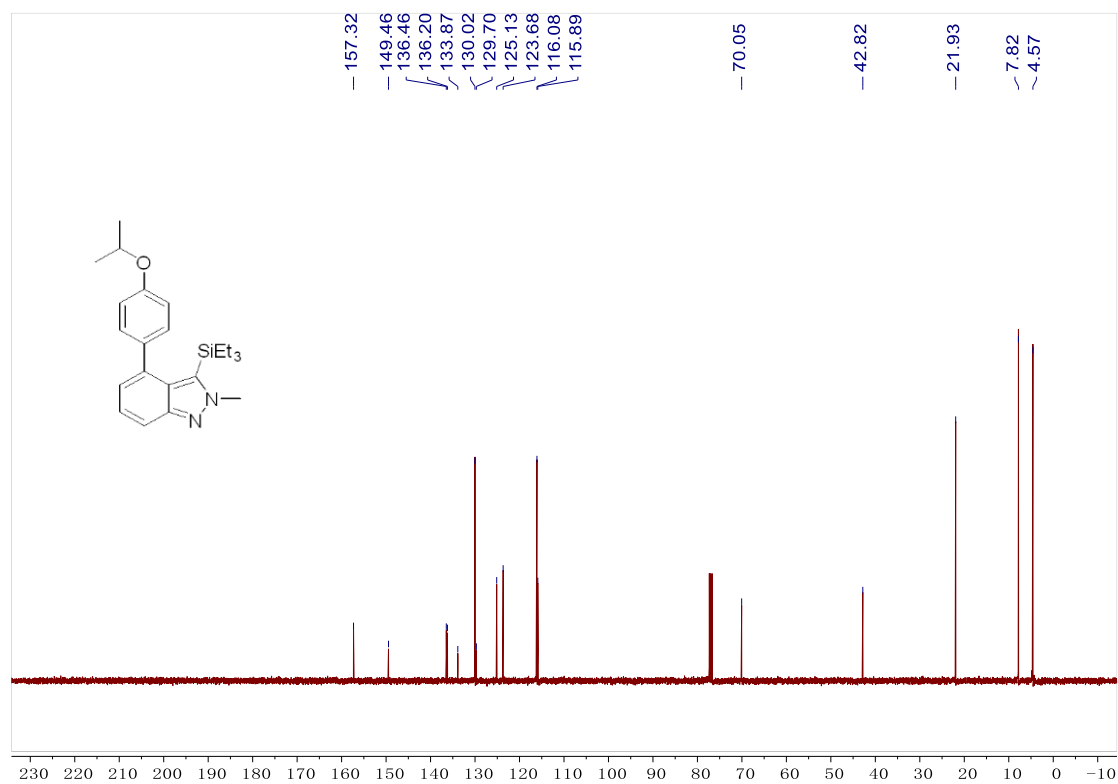
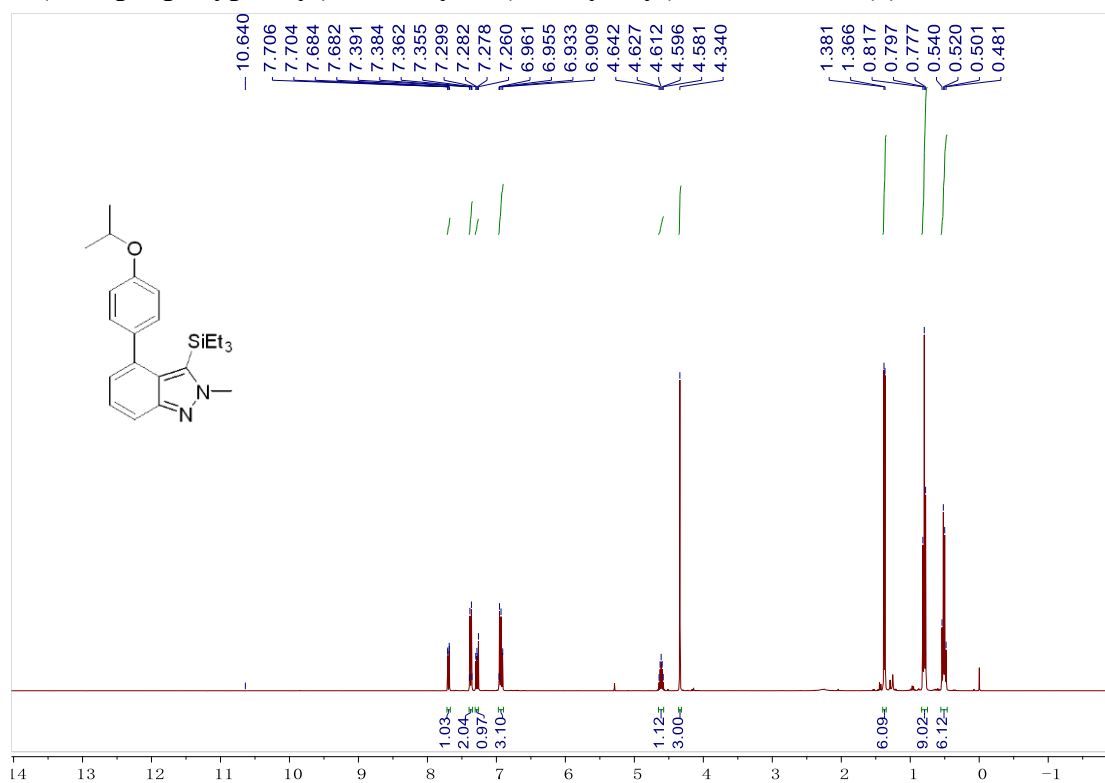
2-Methyl-3-(triethylsilyl)-2H-indazole (1)



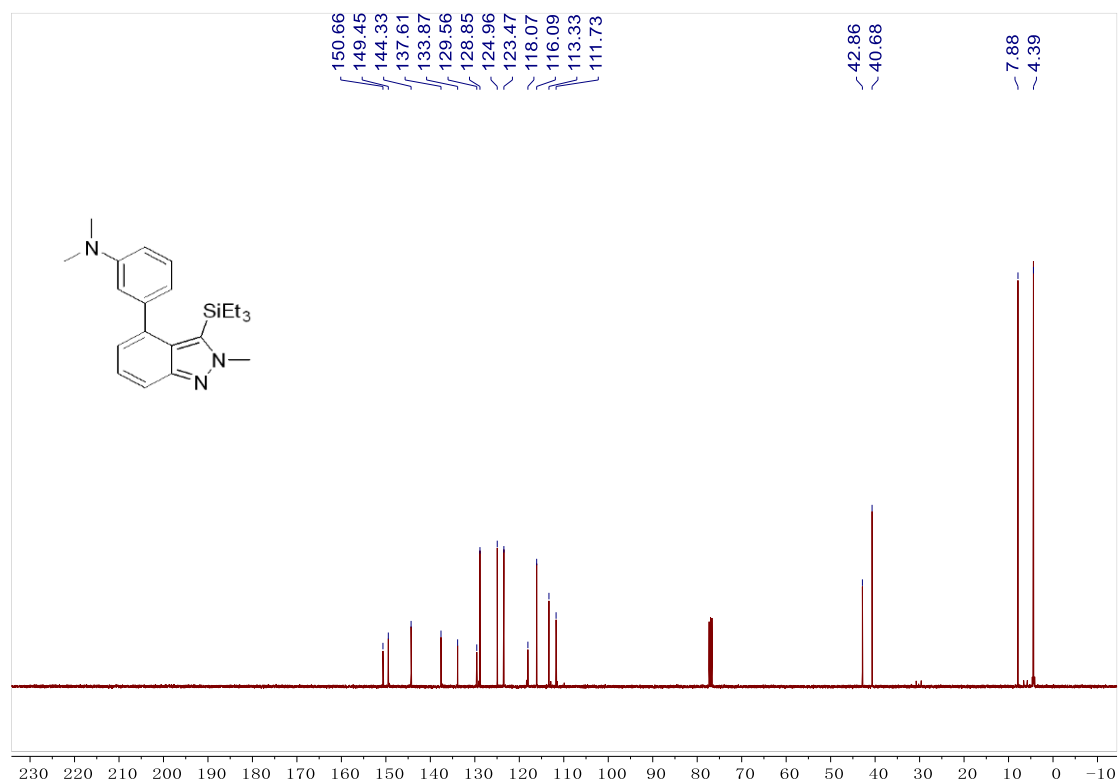
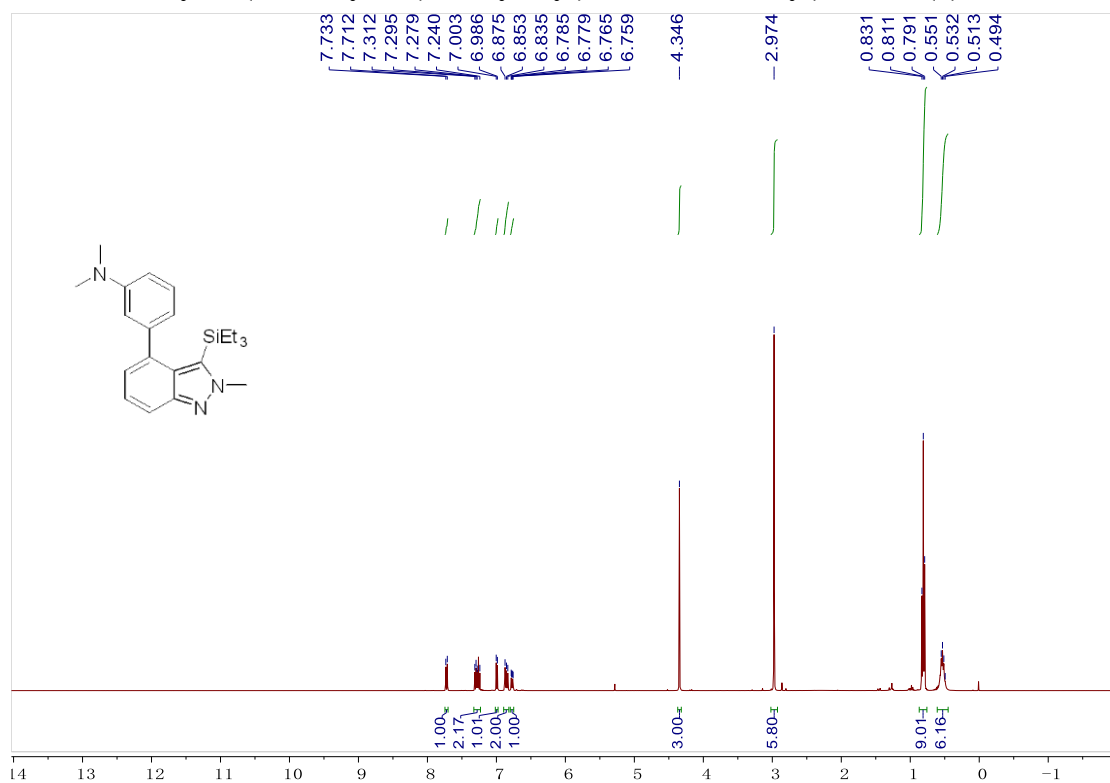
2-Methyl-4-phenyl-3-(triethylsilyl)-2H-indazole (2)



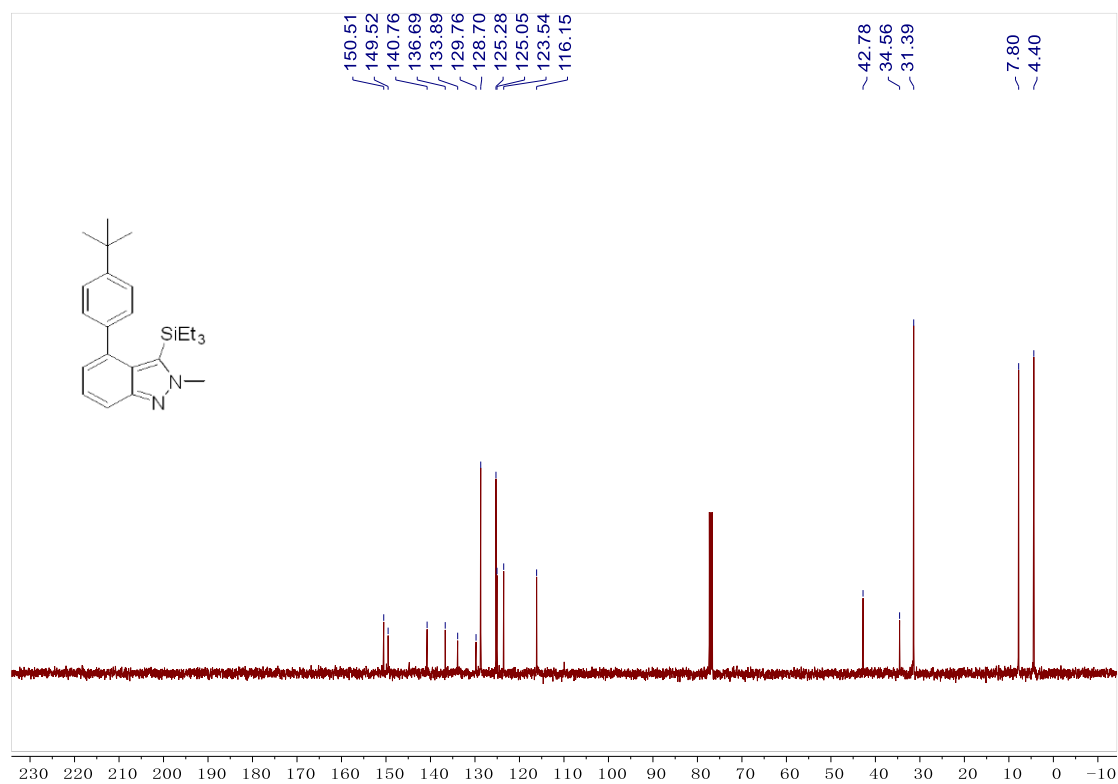
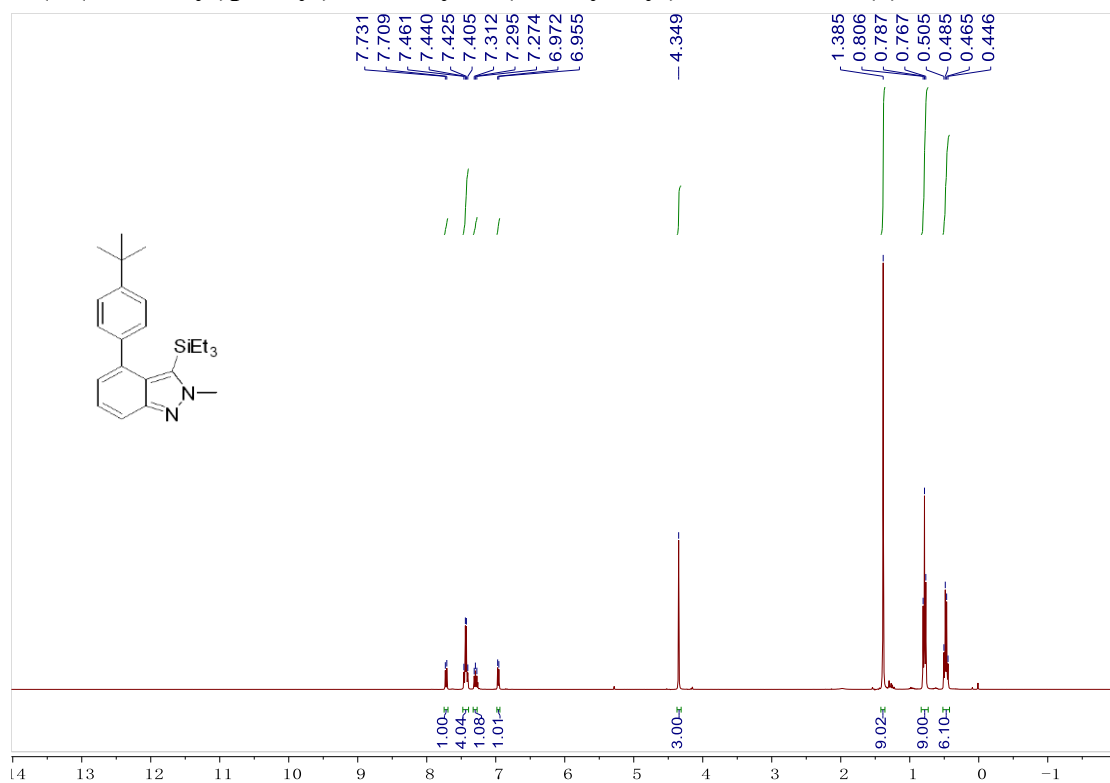
4-(4-Isopropoxyphenyl)-2-methyl-3-(triethylsilyl)-2H-indazole (3)



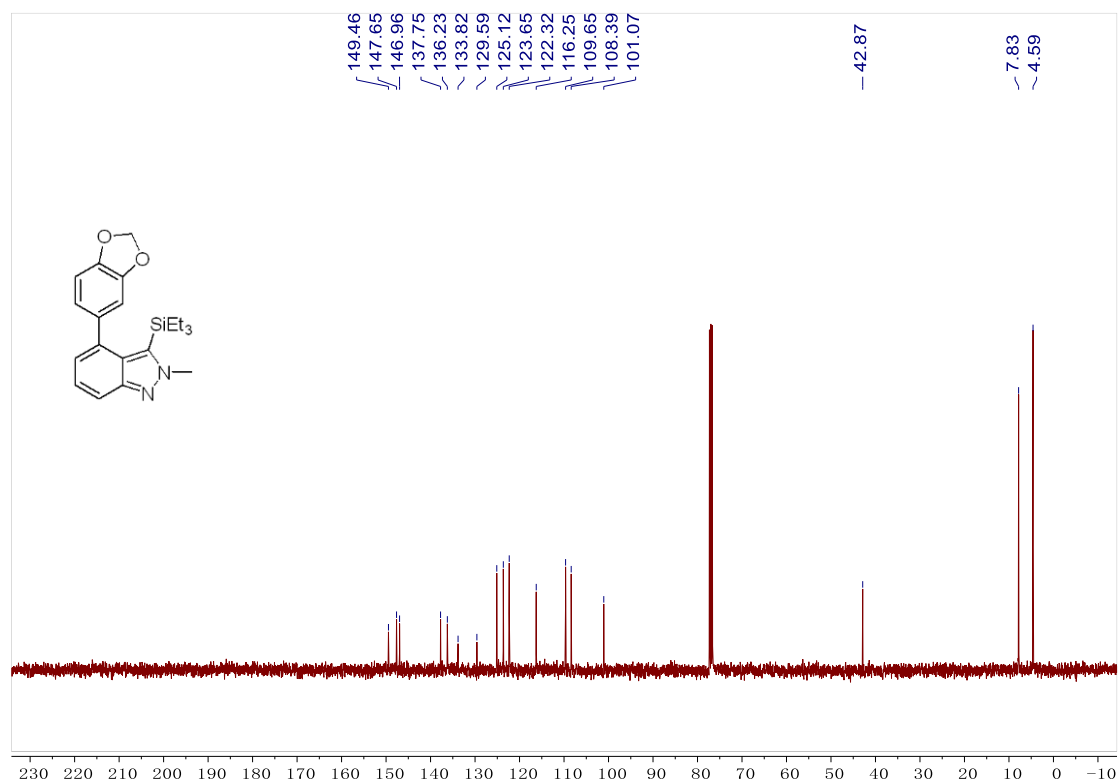
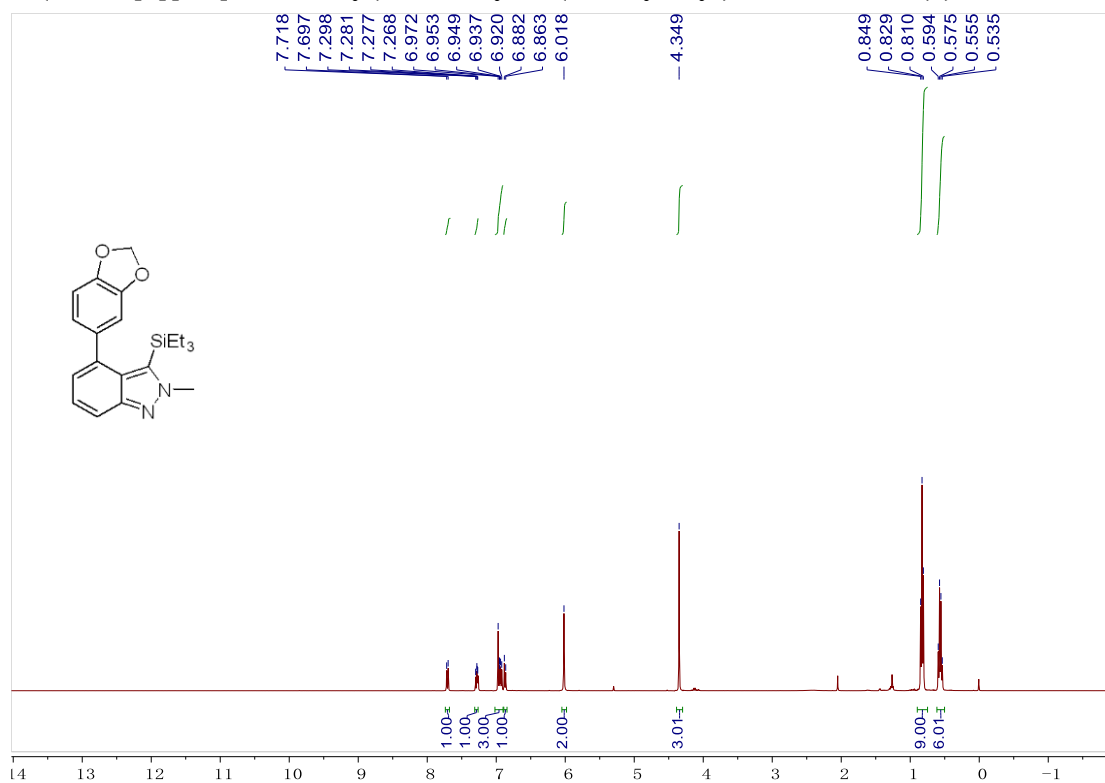
***N,N*-dimethyl-3-(2-methyl-3-(triethylsilyl)-2*H*-indazol-4-yl)aniline (4)**



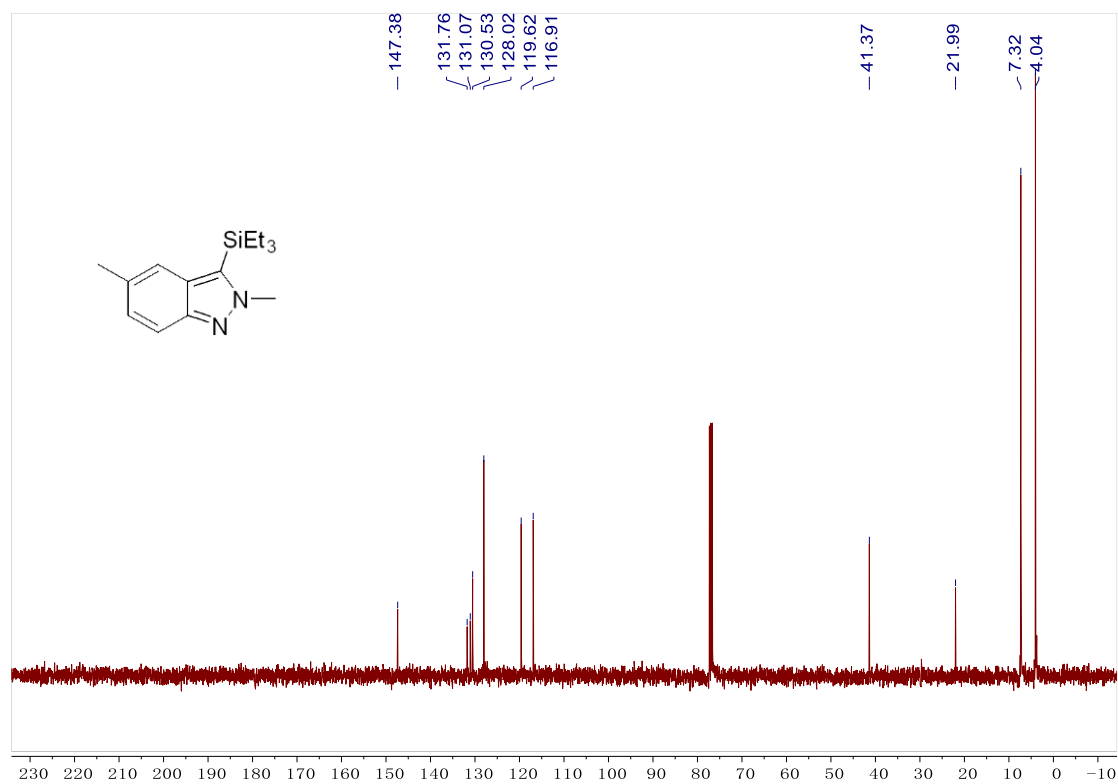
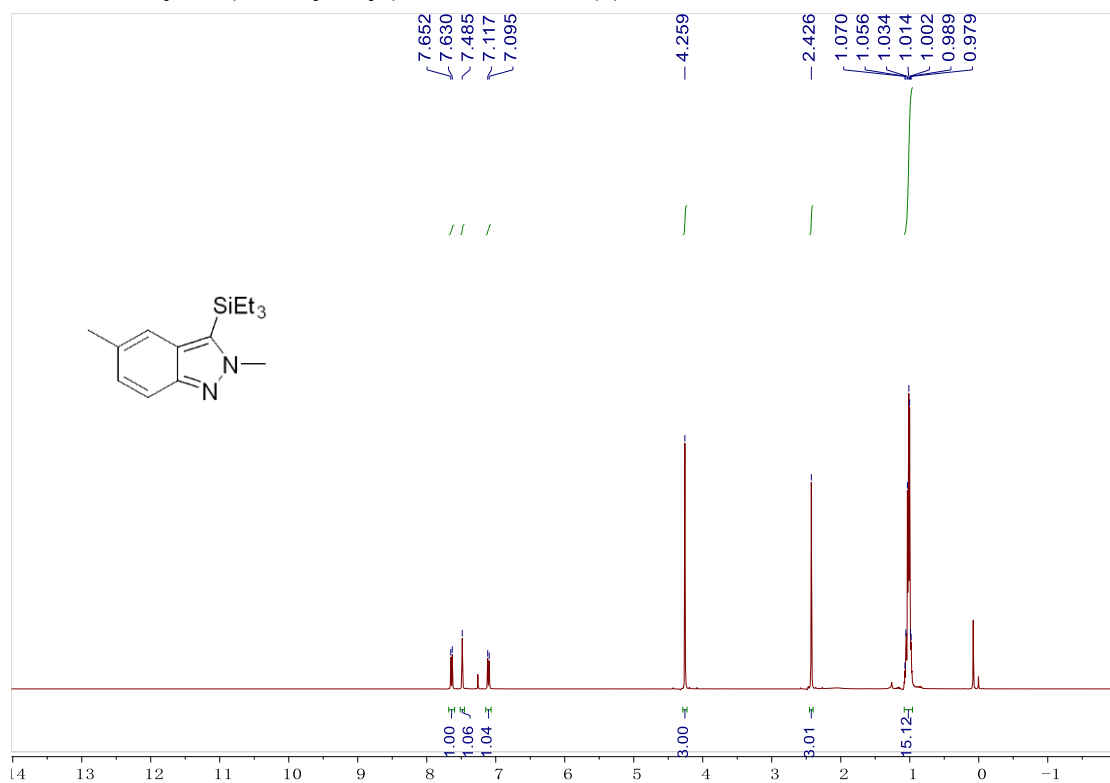
4-(4-(*Tert*-butyl)phenyl)-2-methyl-3-(triethylsilyl)-2*H*-indazole (5)



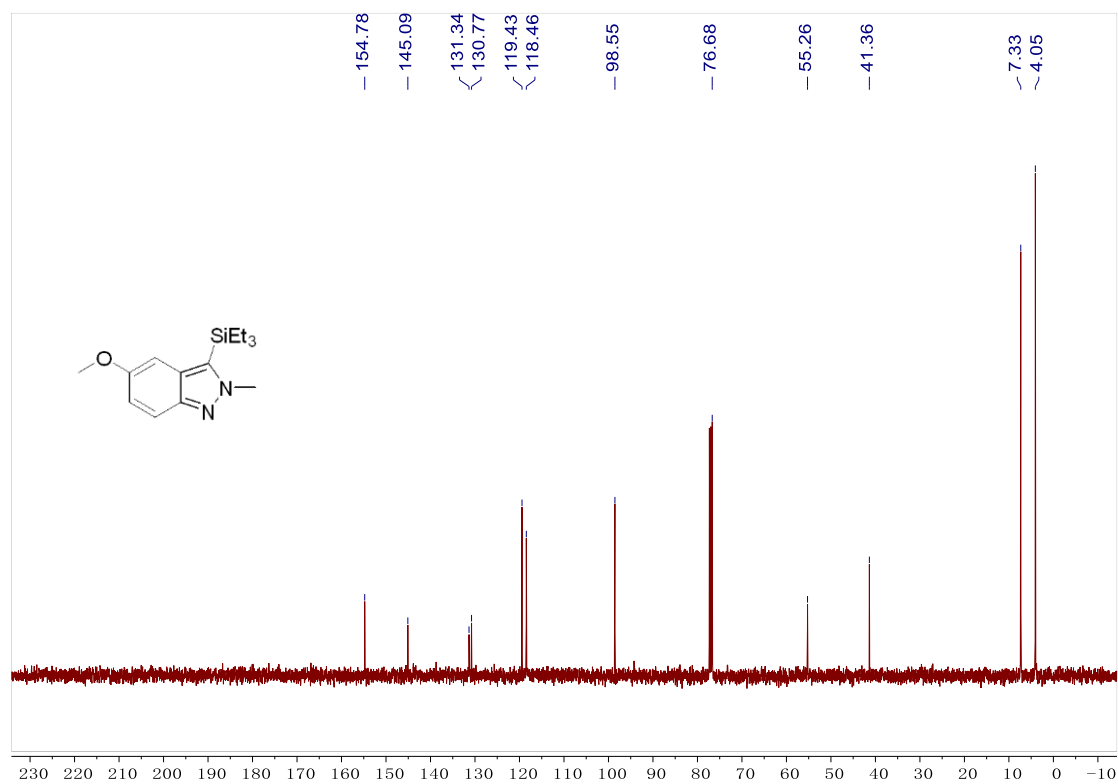
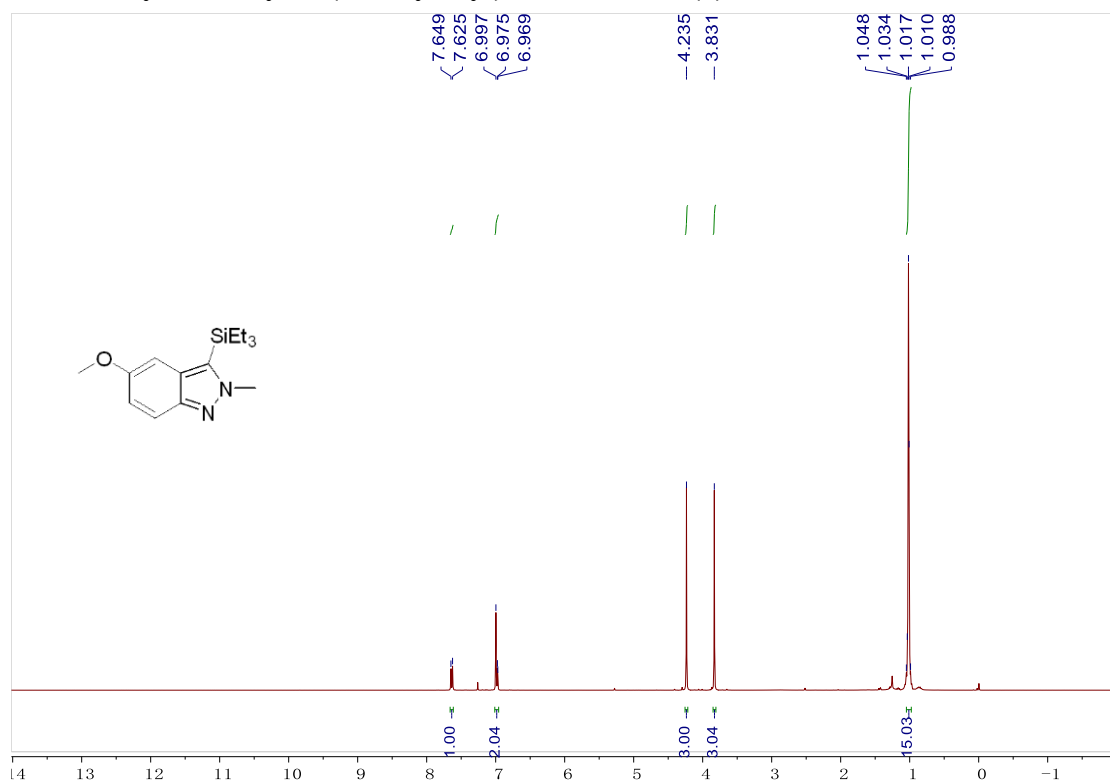
4-(Benzo[d][1,3]dioxol-5-yl)-2-methyl-3-(triethylsilyl)-2H-indazole (6)



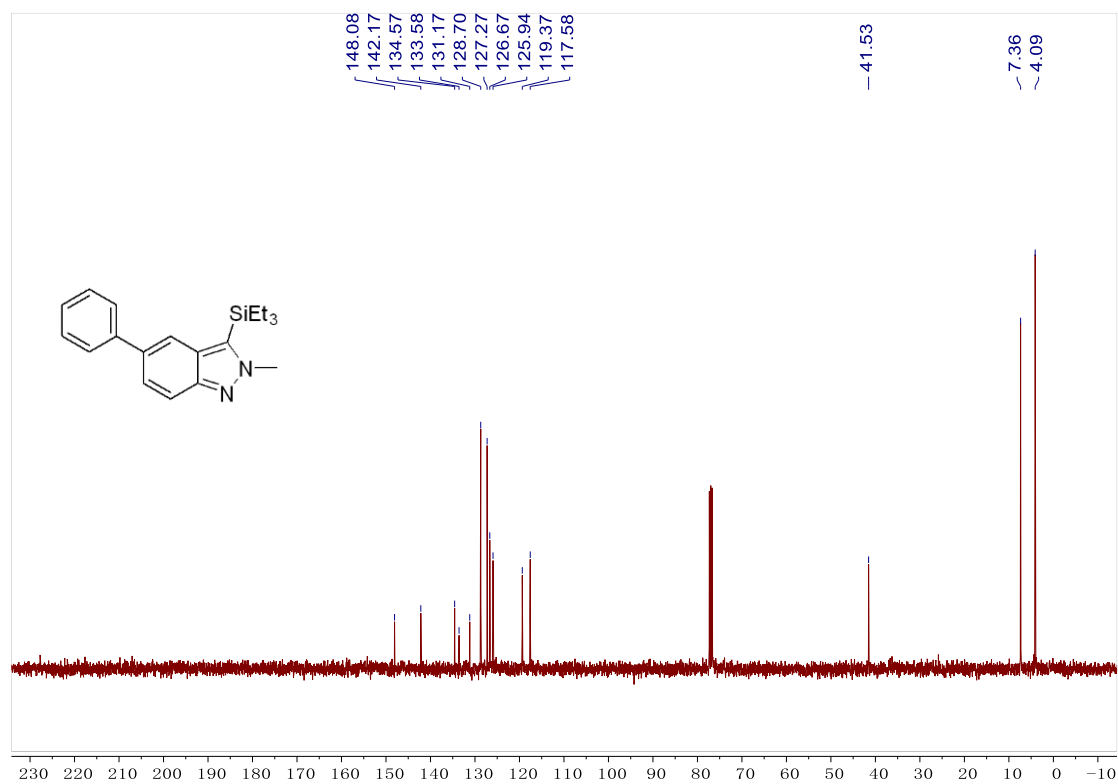
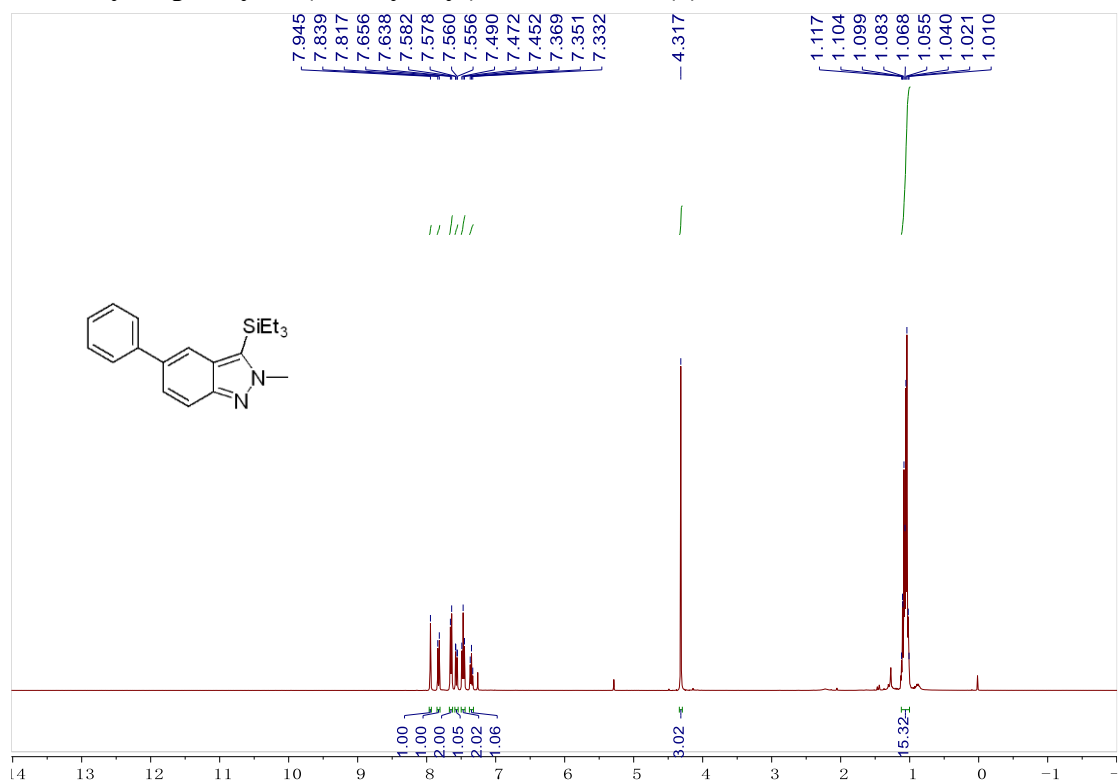
2,5-Dimethyl-3-(triethylsilyl)-2*H*-indazole (7)



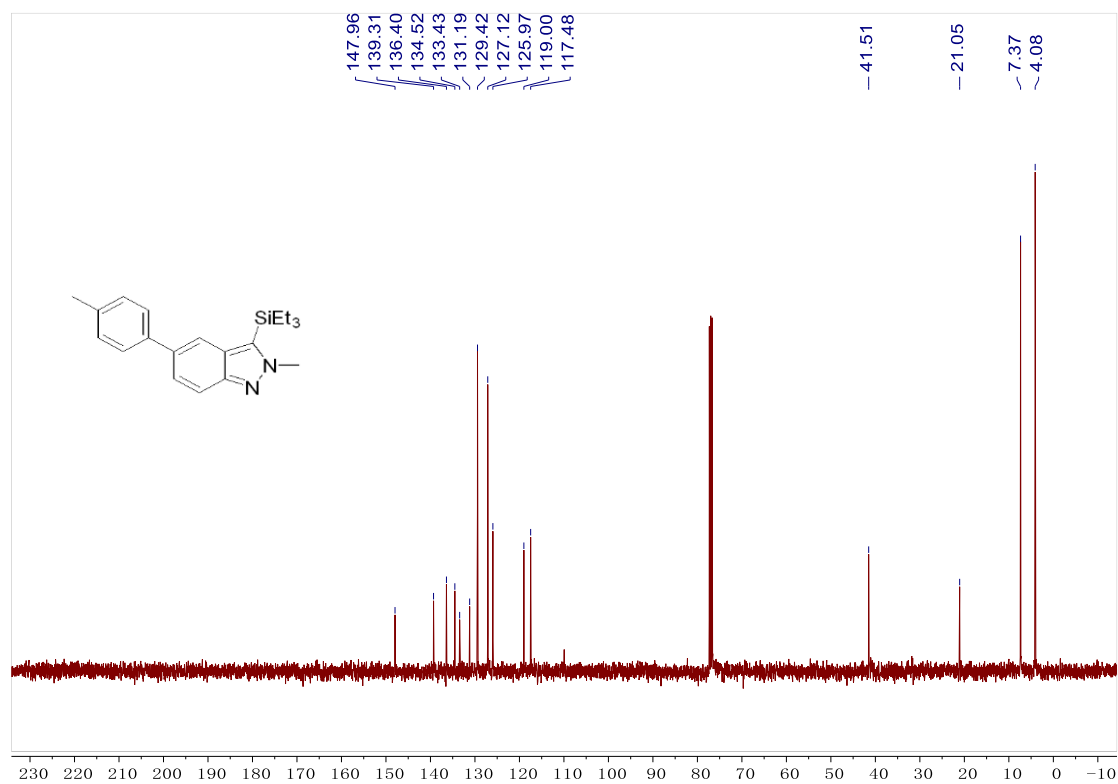
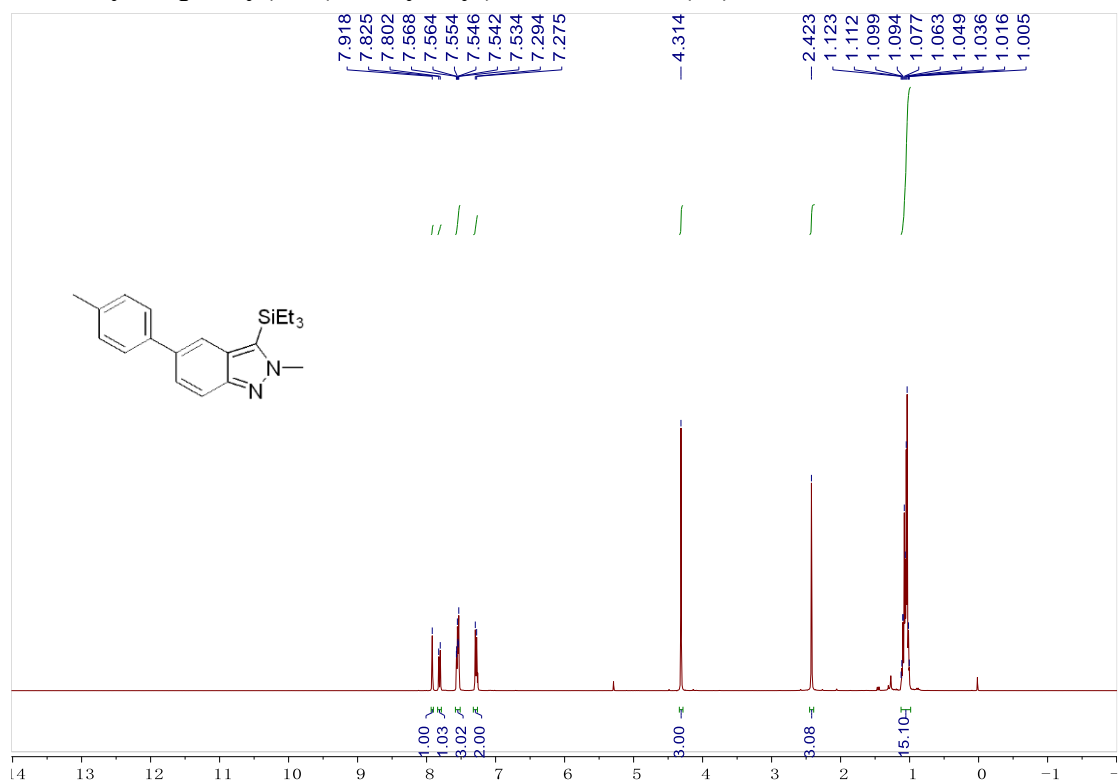
5-Methoxy-2-methyl-3-(triethylsilyl)-2H-indazole (8)



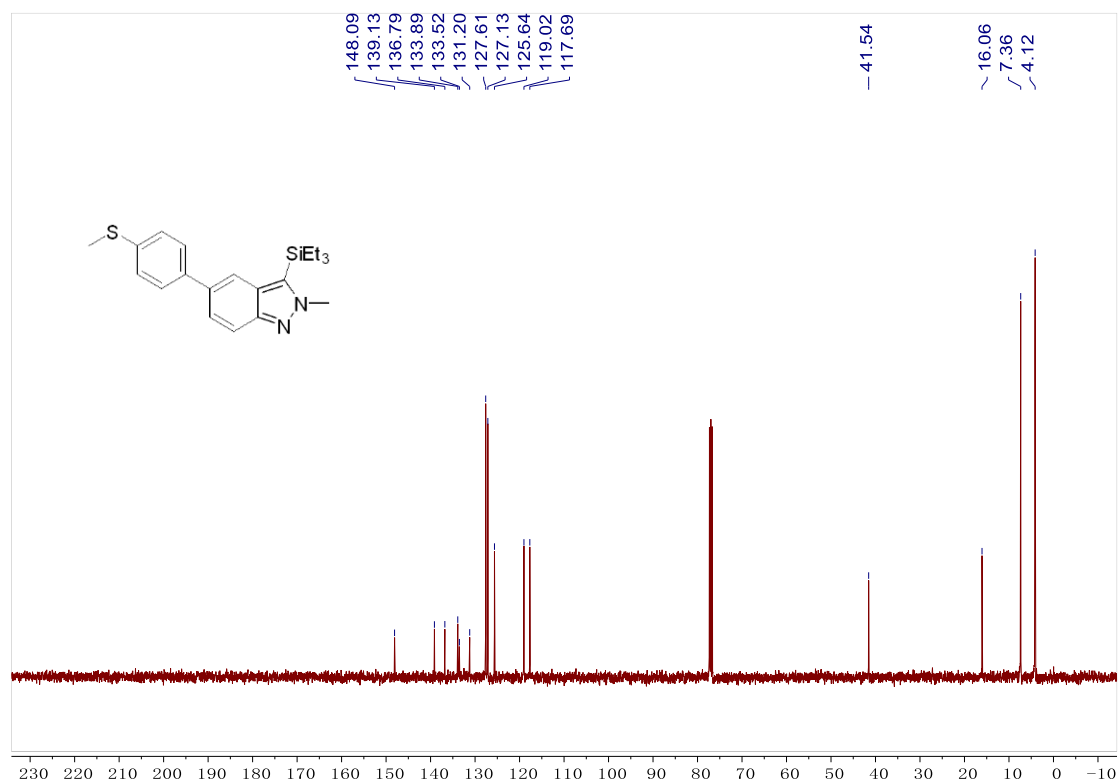
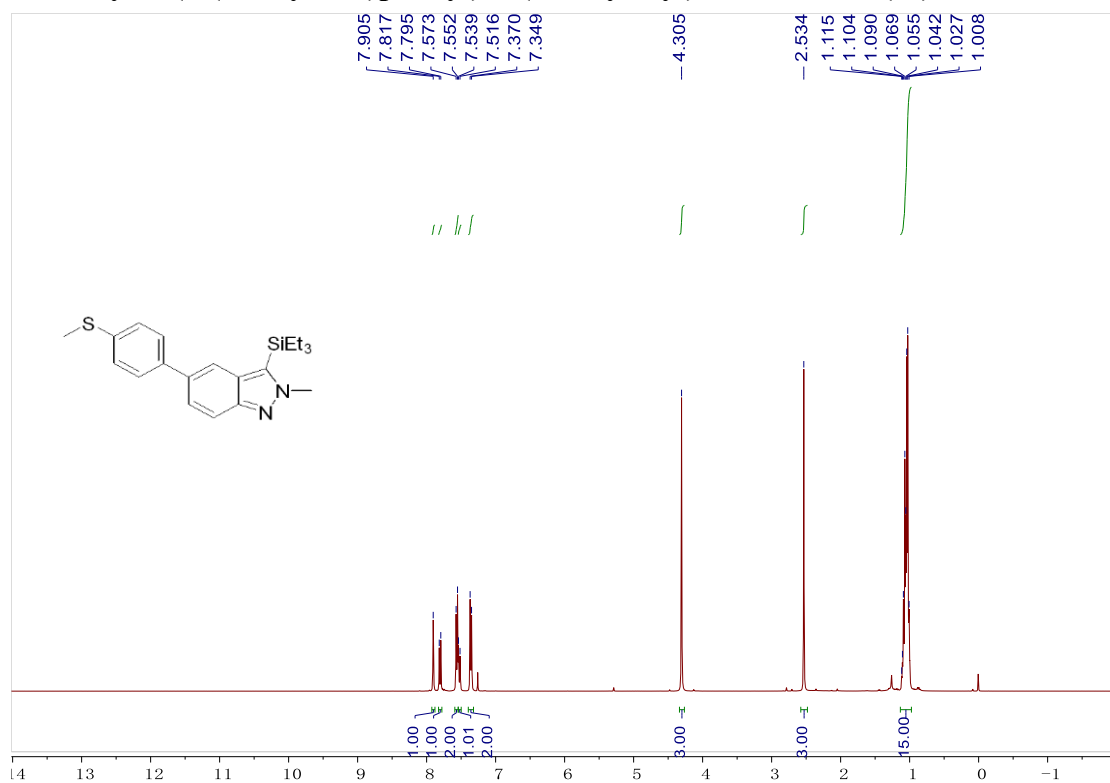
2-Methyl-5-phenyl-3-(triethylsilyl)-2H-indazole (9)



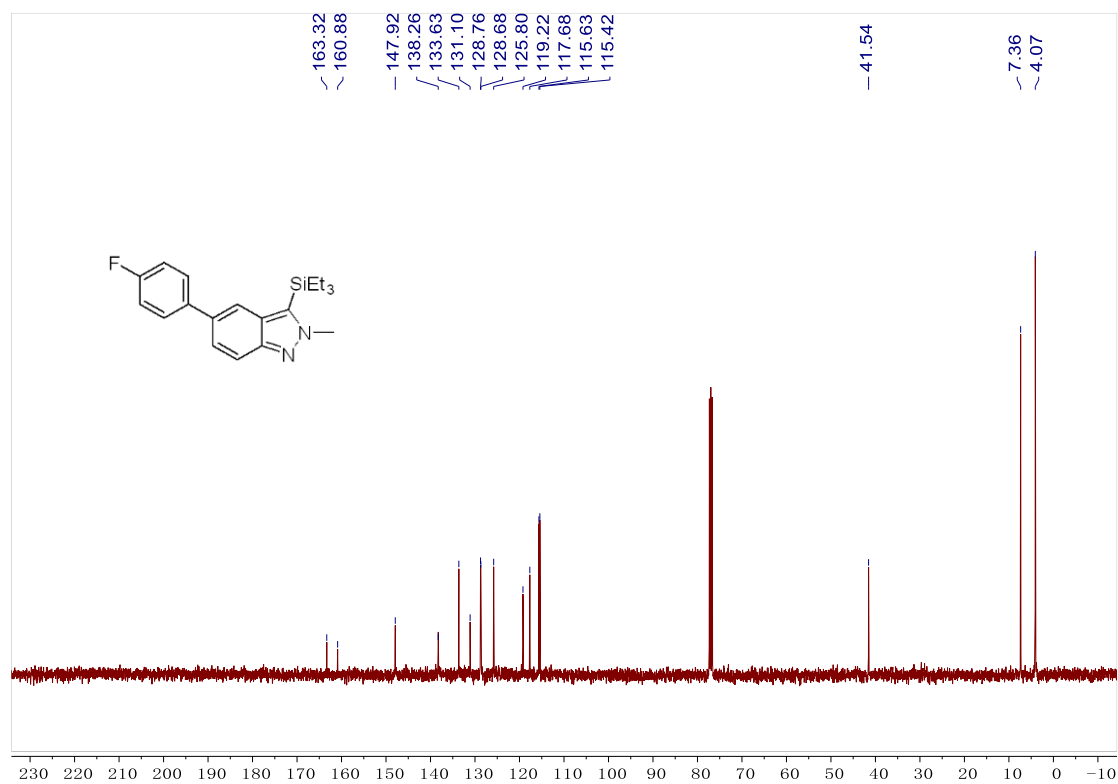
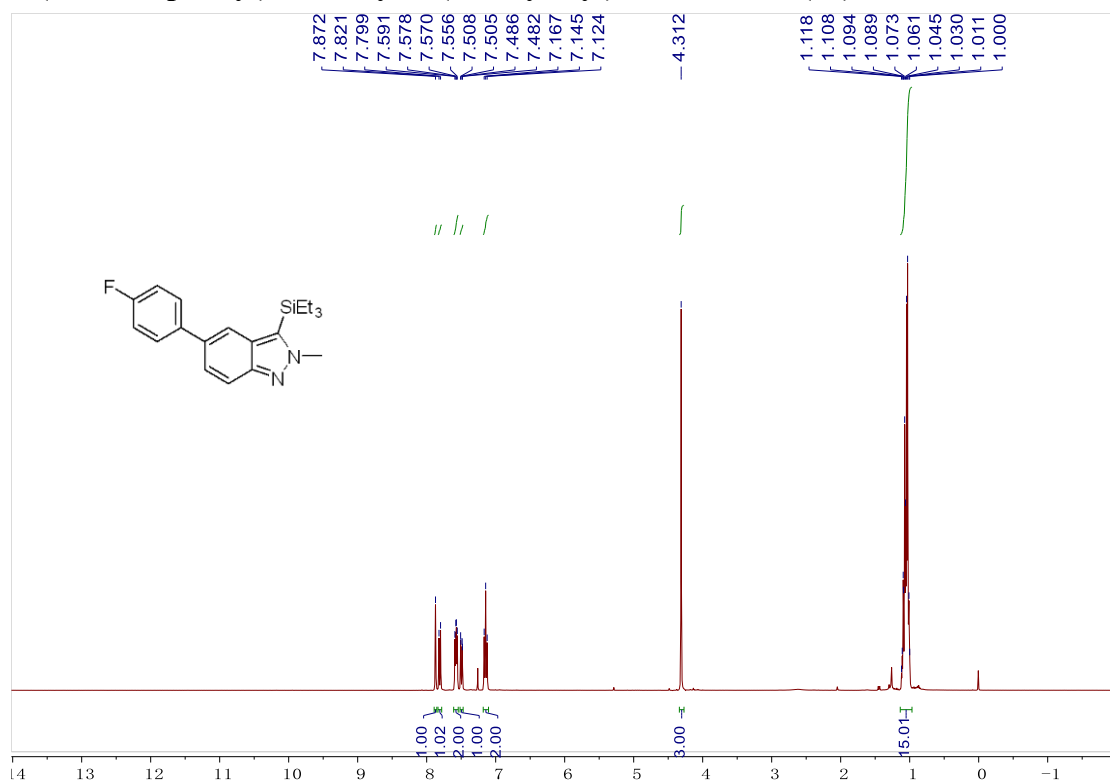
2-Methyl-5-(*p*-tolyl)-3-(triethylsilyl)-2*H*-indazole (10)



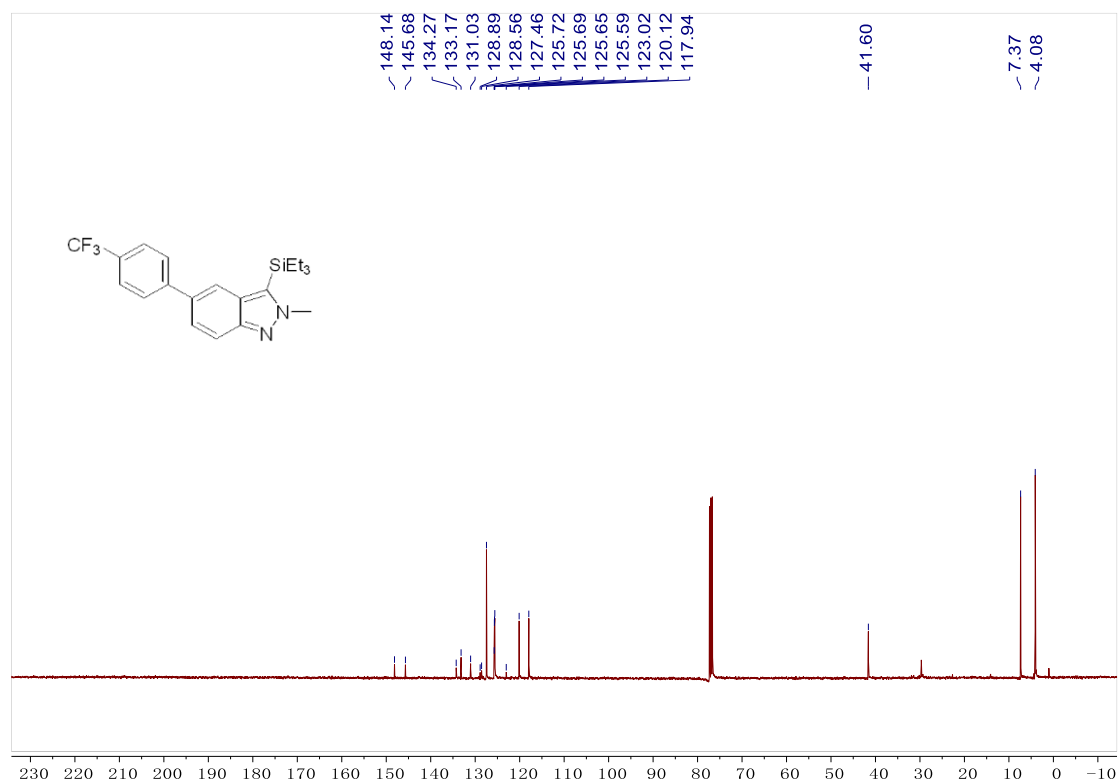
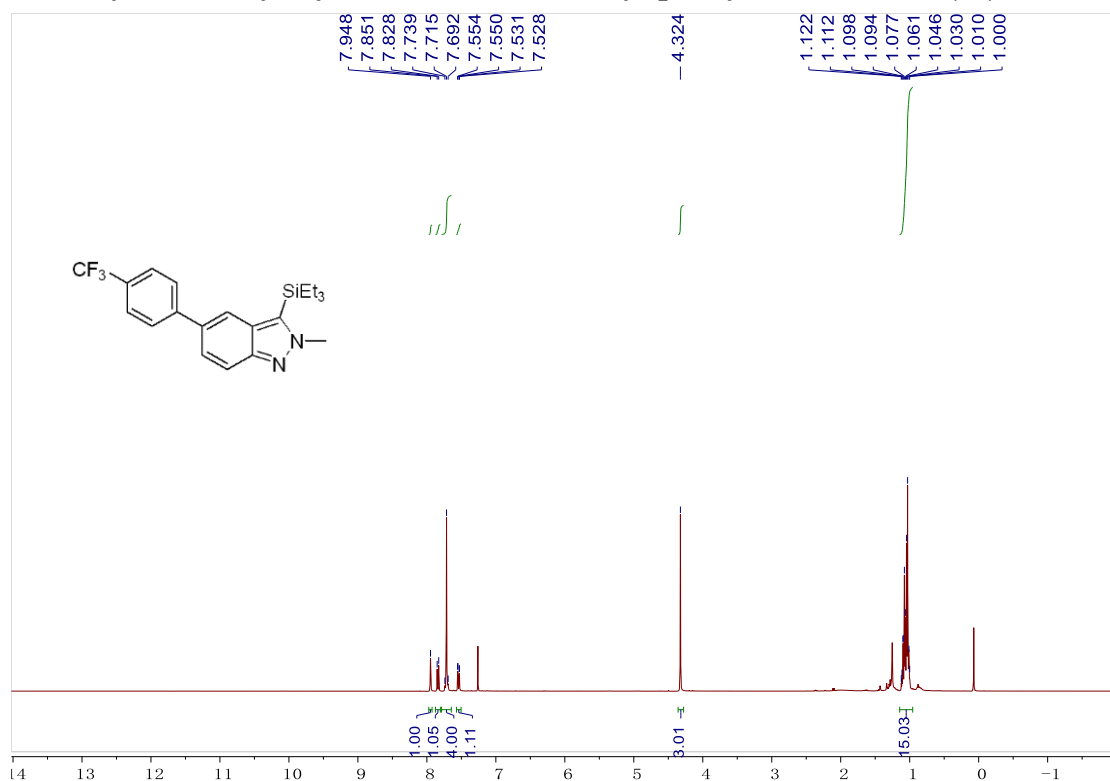
2-Methyl-5-(4-(methylthio)phenyl)-3-(triethylsilyl)-2H-indazole (11)



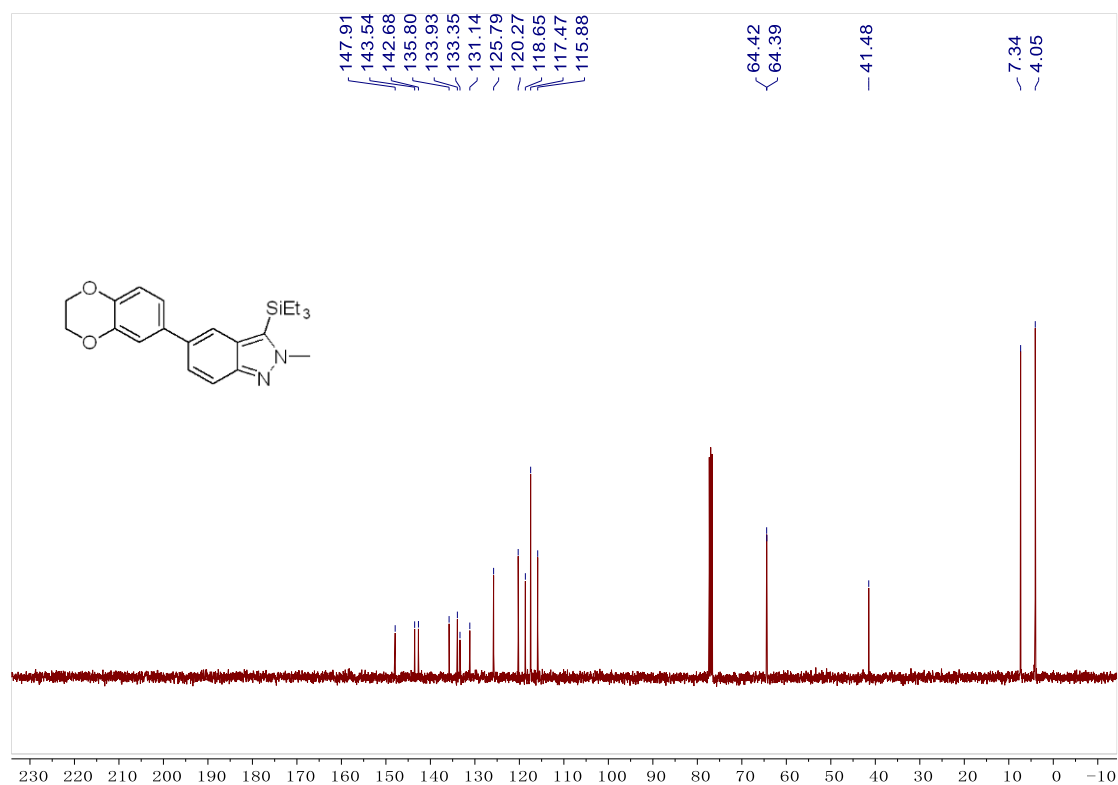
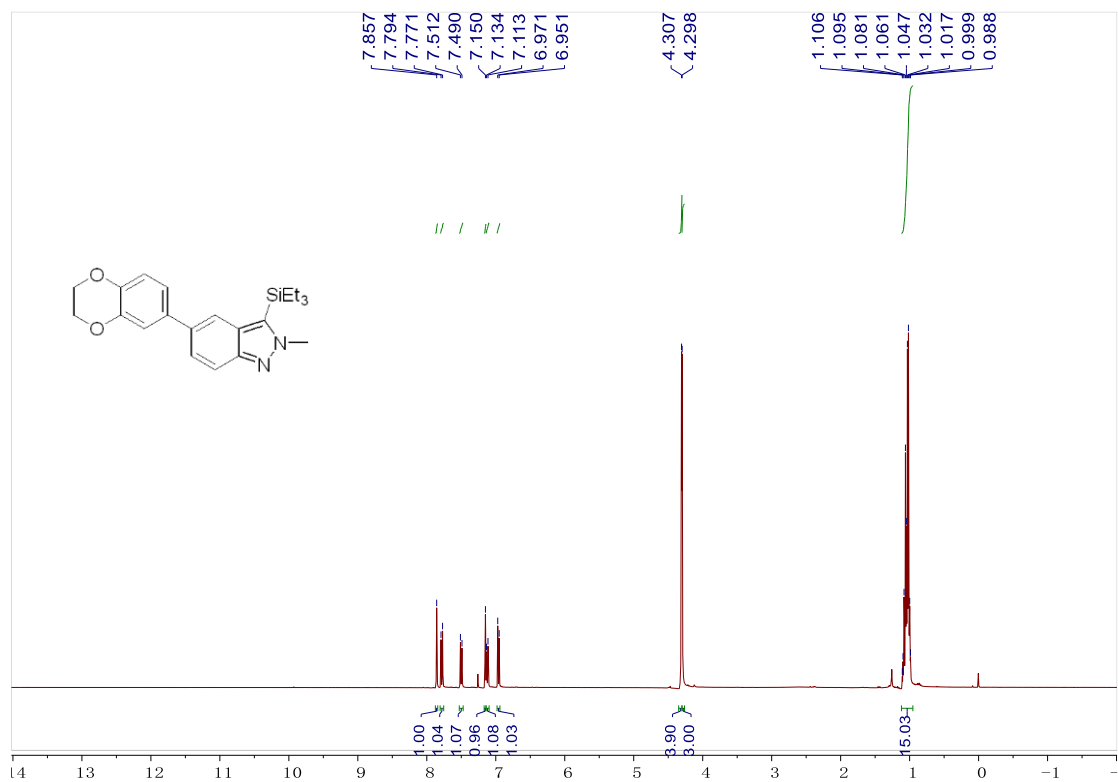
5-(4-Fluorophenyl)-2-methyl-3-(triethylsilyl)-2H-indazole (12)



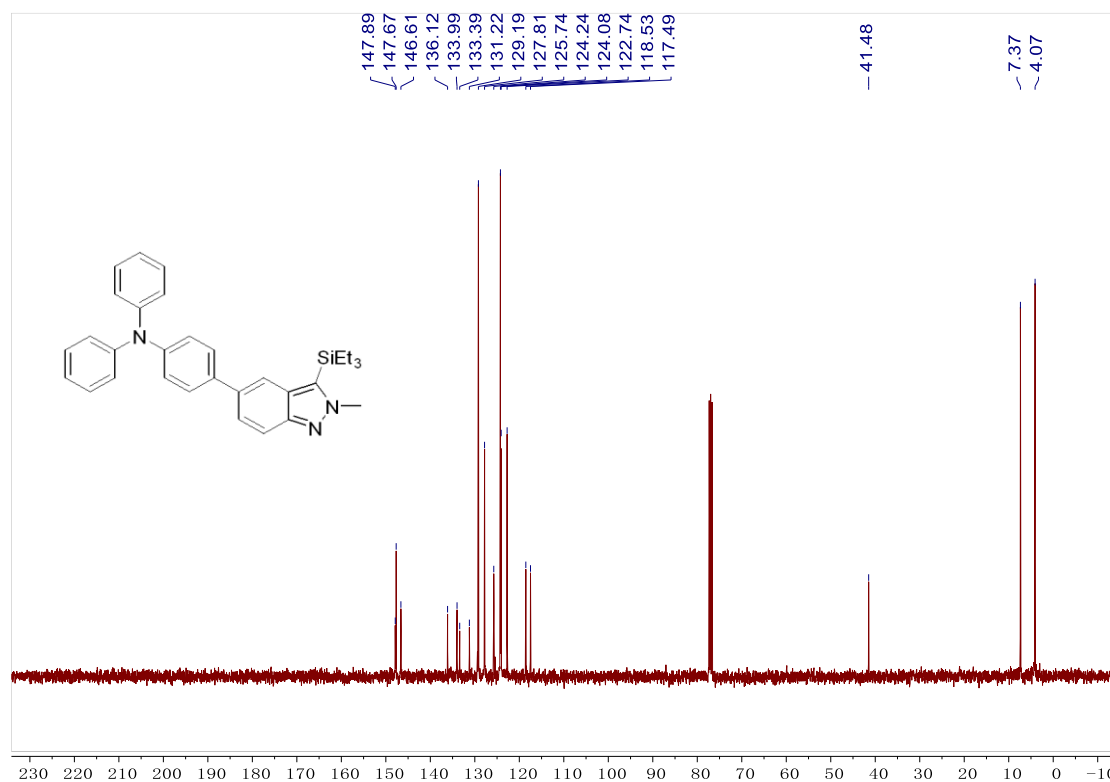
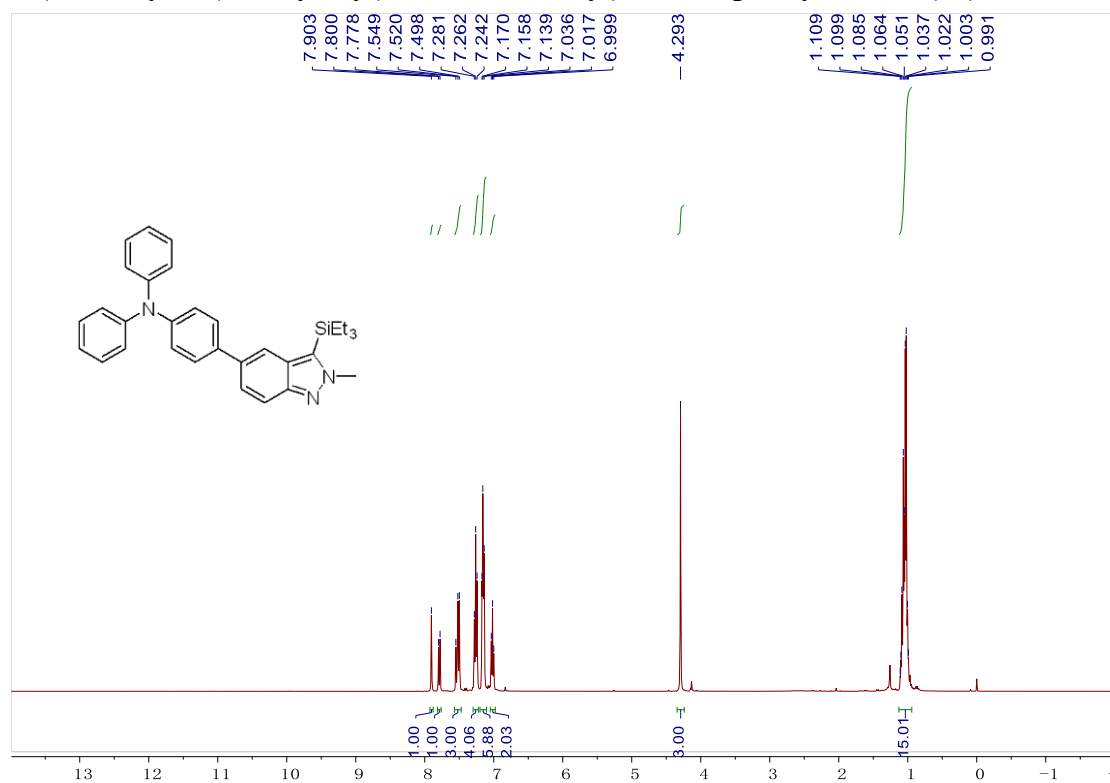
2-Methyl-3-(triethylsilyl)-5-(4-(trifluoromethyl)phenyl)-2H-indazole (13)



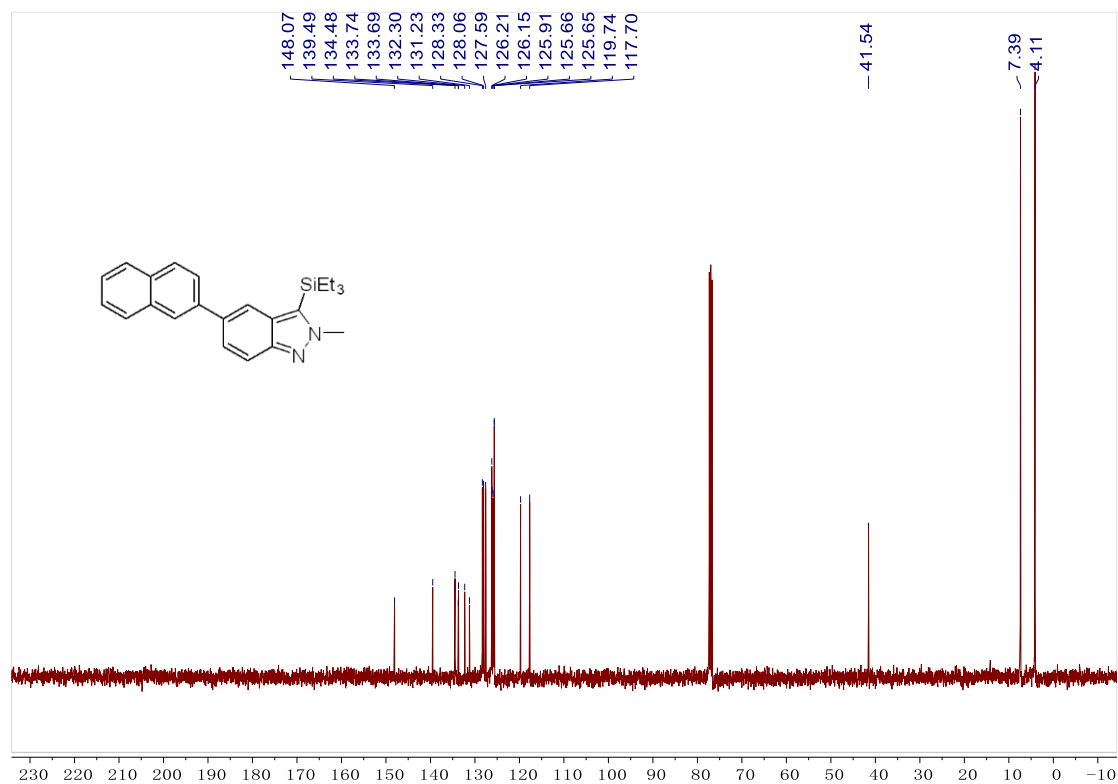
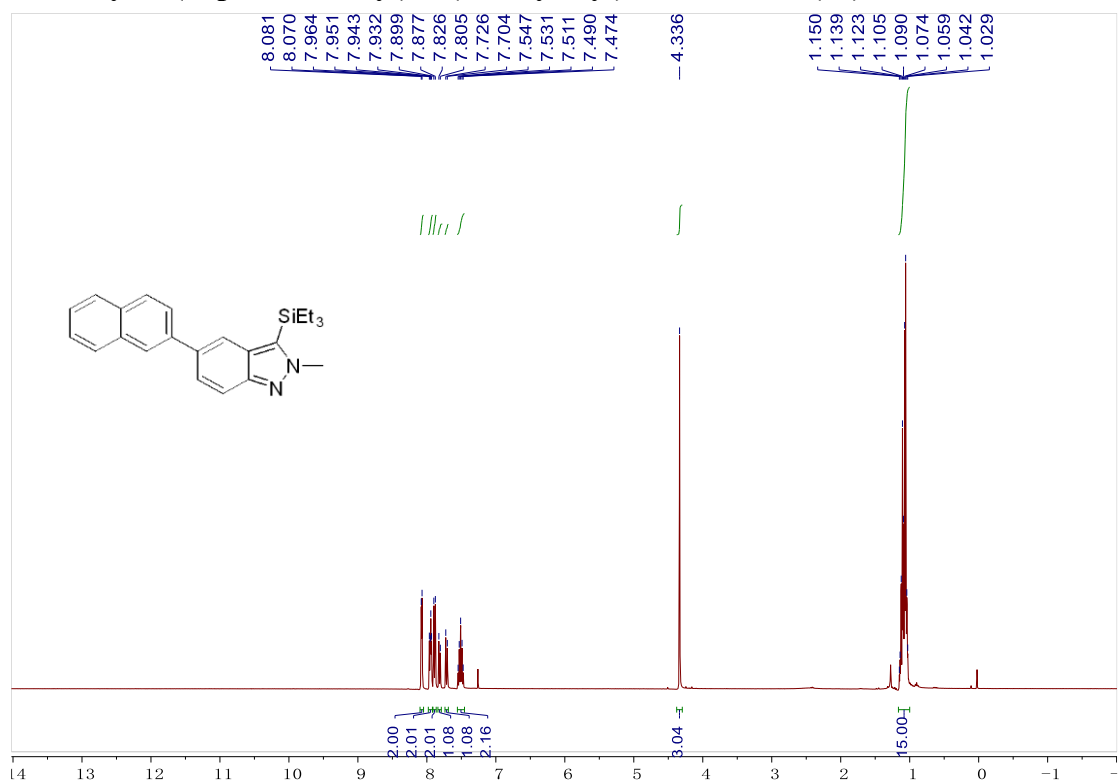
5-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-2-methyl-3-(triethylsilyl)-2*H*-indazole
(14)



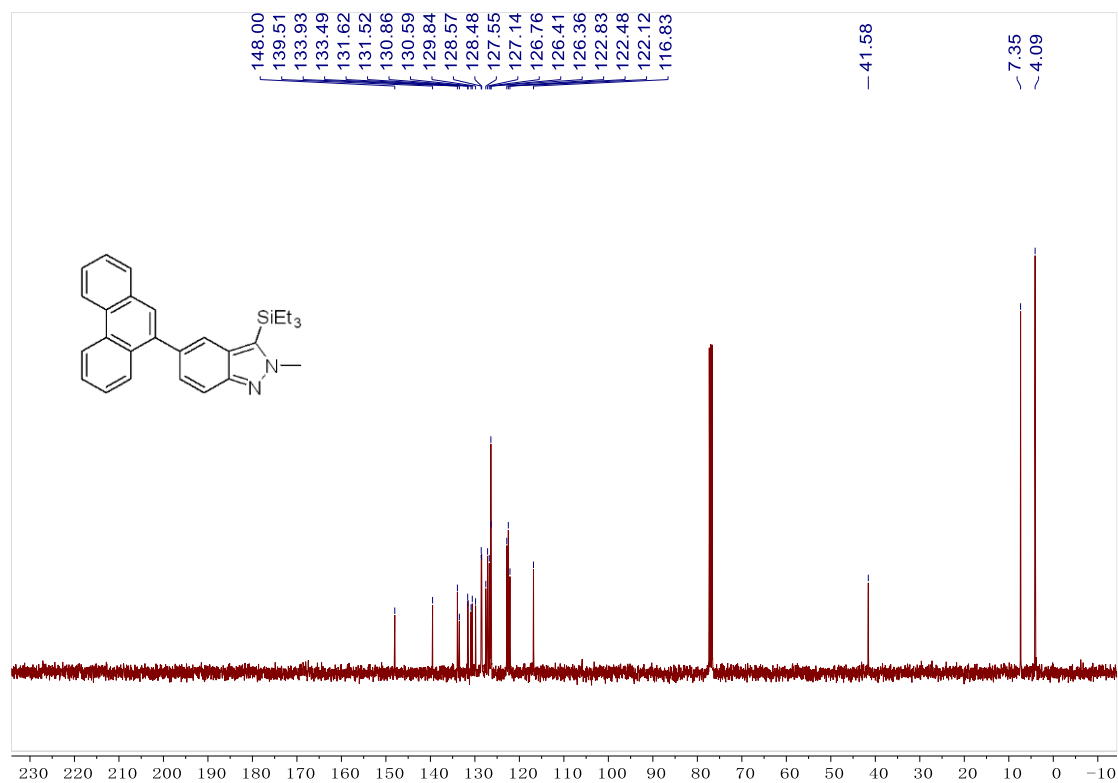
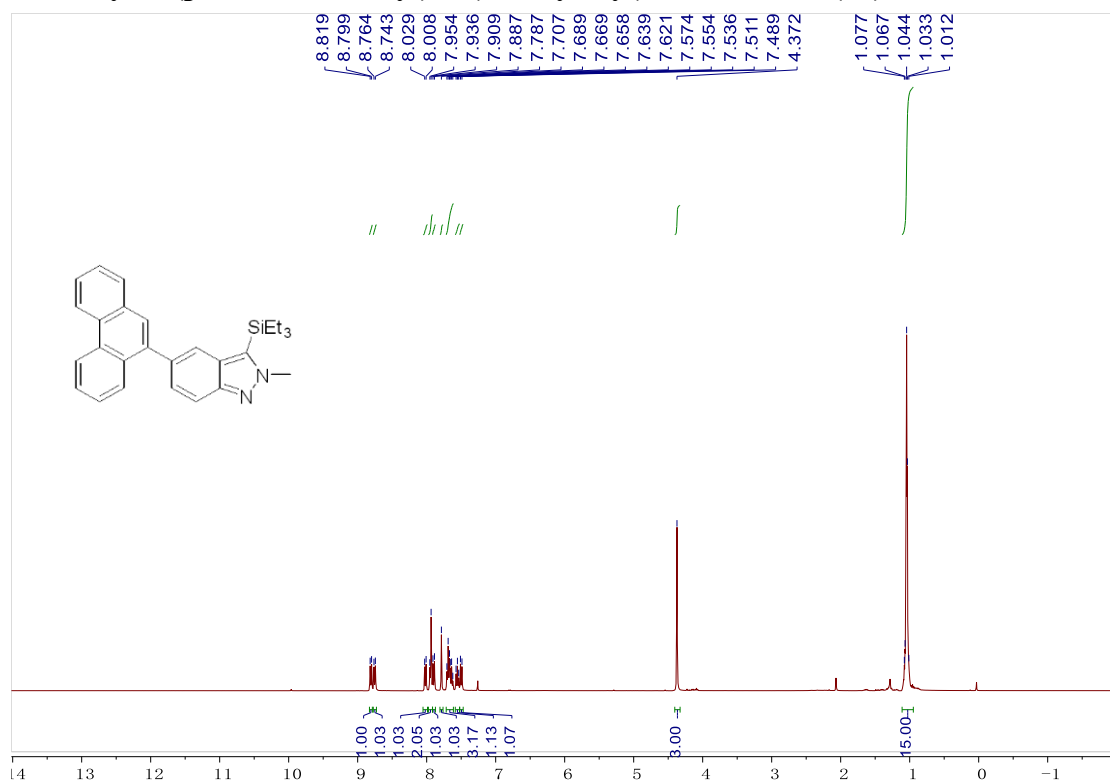
4-(2-Methyl-3-(triethylsilyl)-2H-indazol-5-yl)-N,N-diphenylaniline (15)



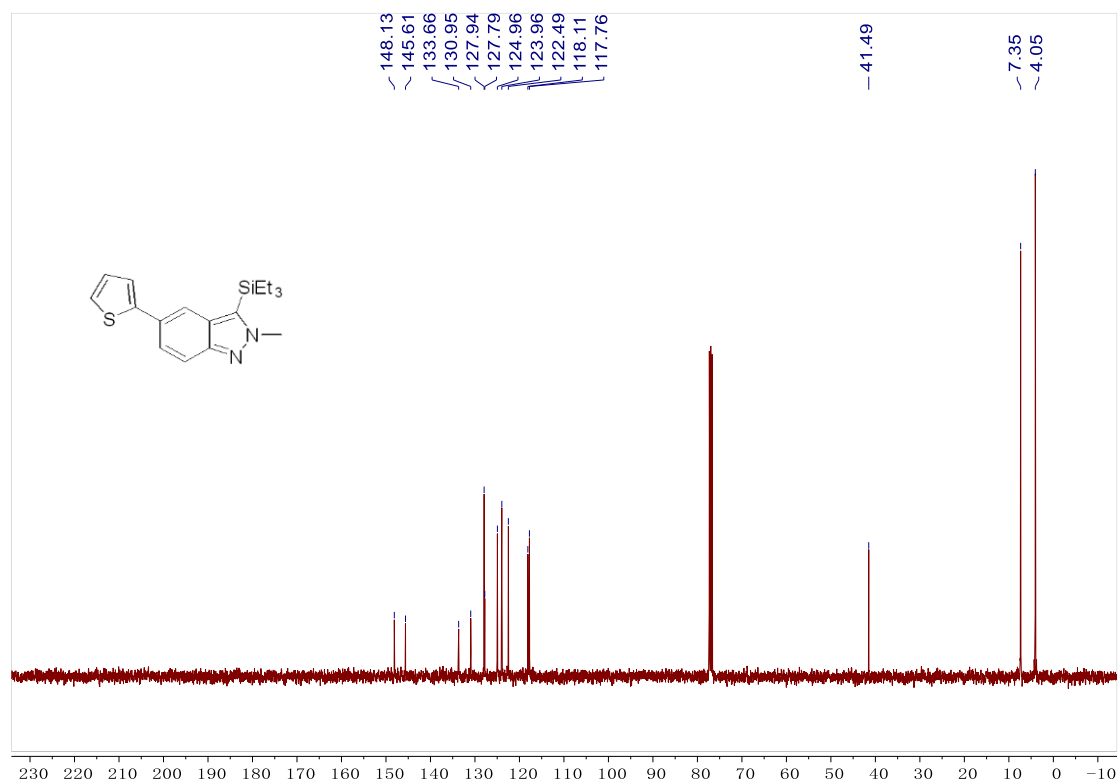
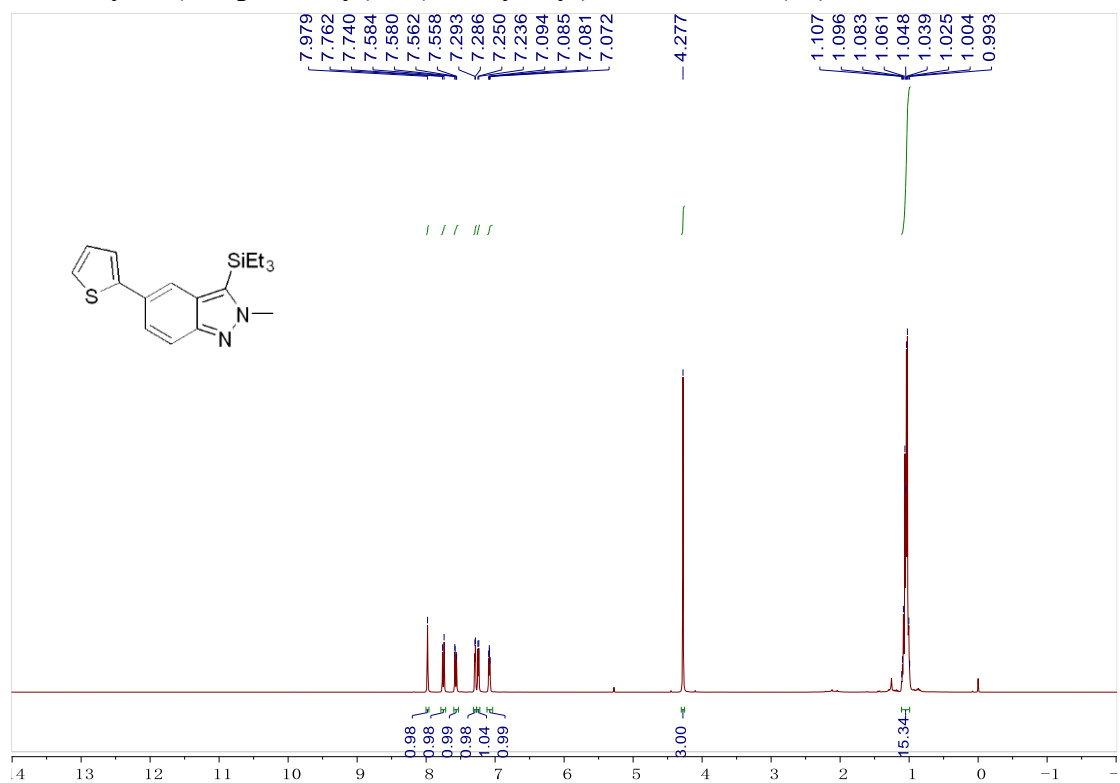
2-Methyl-5-(naphthalen-2-yl)-3-(triethylsilyl)-2H-indazole (16)



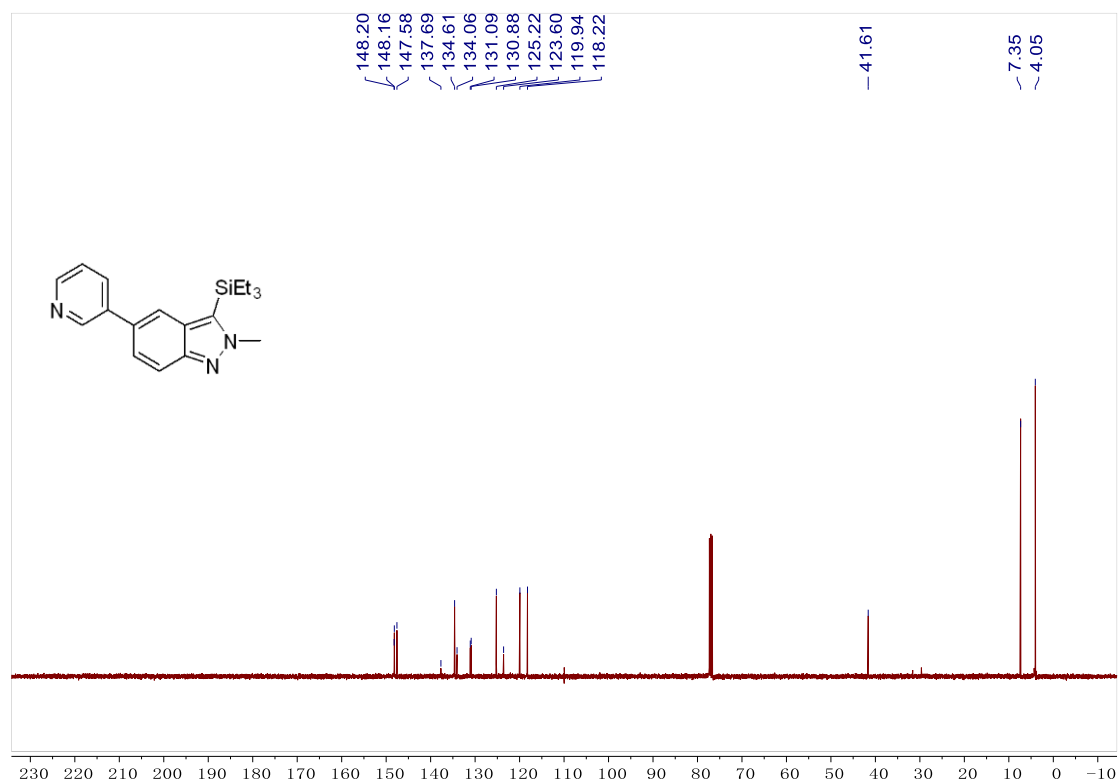
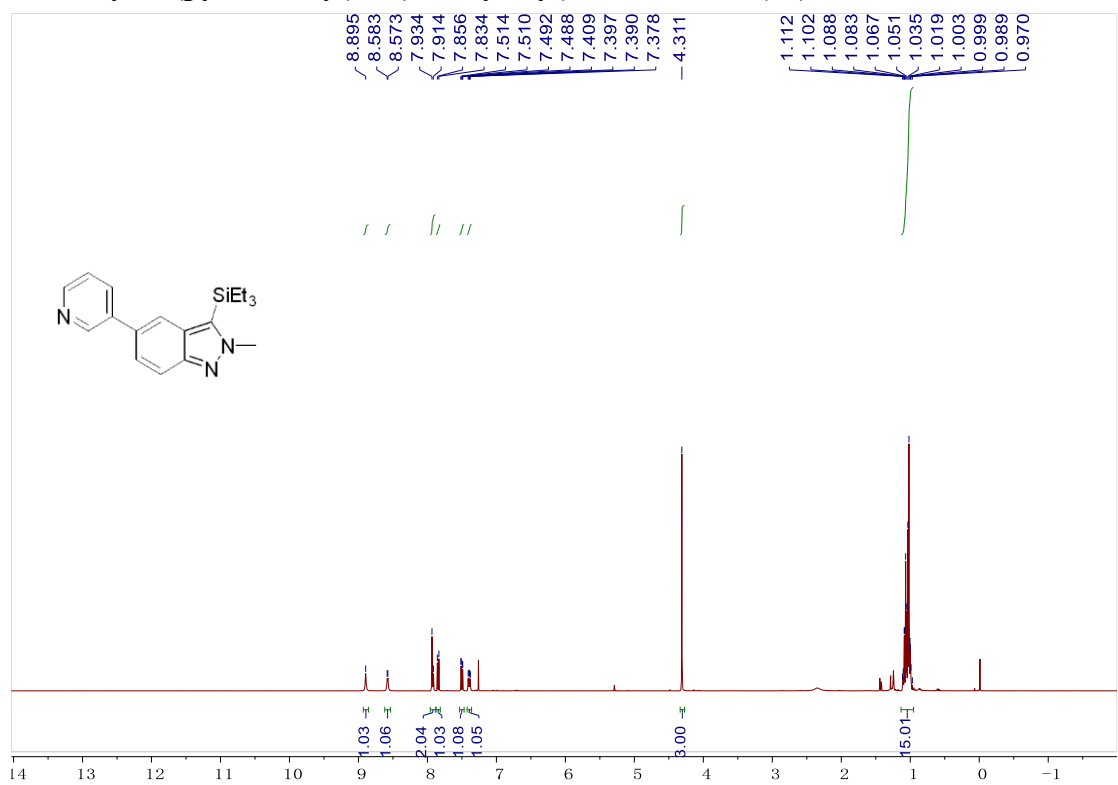
2-Methyl-5-(phenanthren-9-yl)-3-(triethylsilyl)-2H-indazole (17)



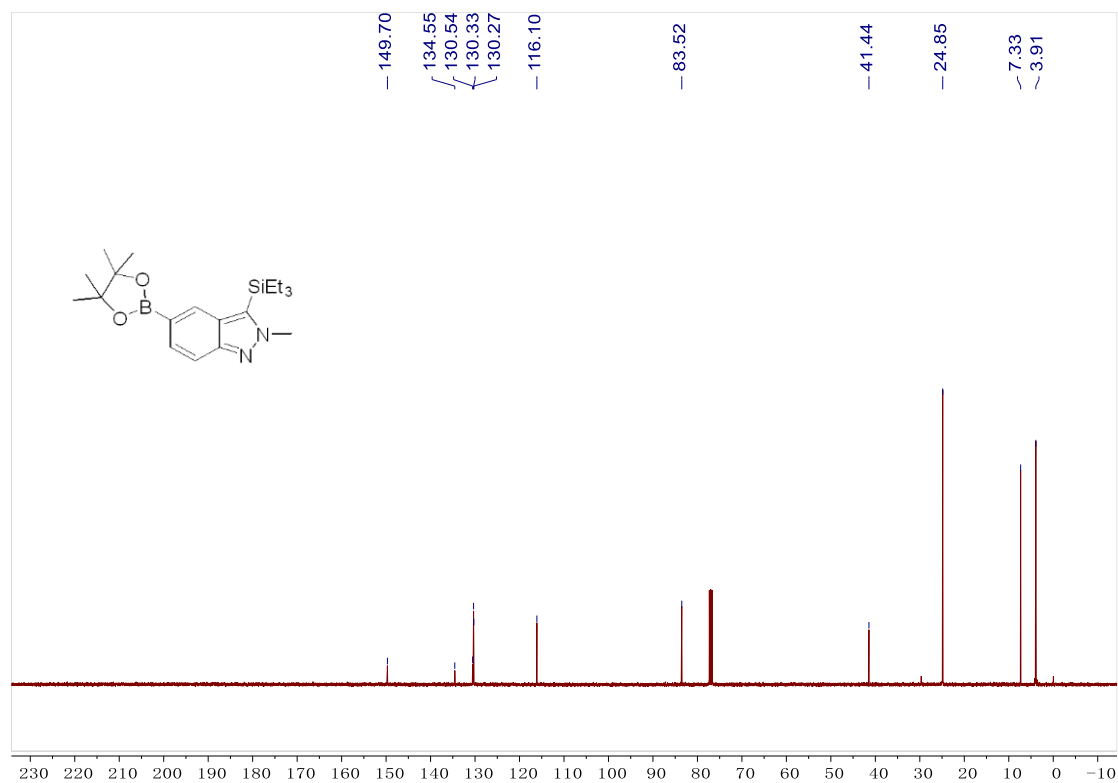
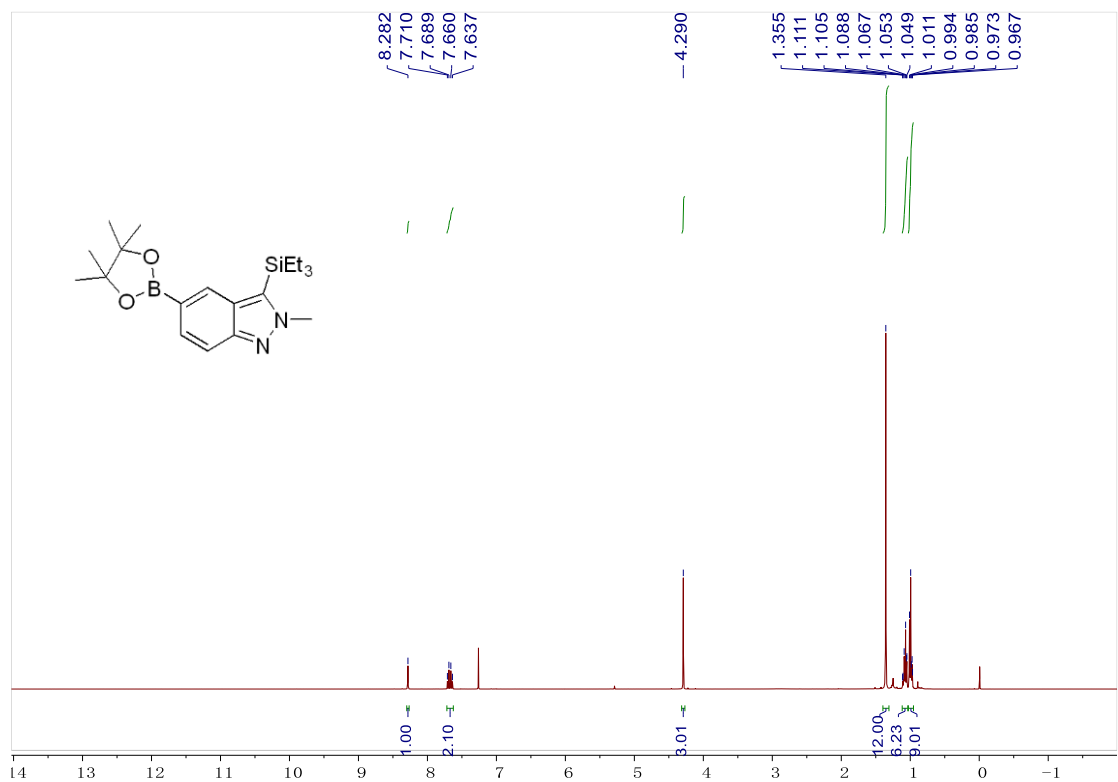
2-Methyl-5-(thiophen-2-yl)-3-(triethylsilyl)-2H-indazole (18)



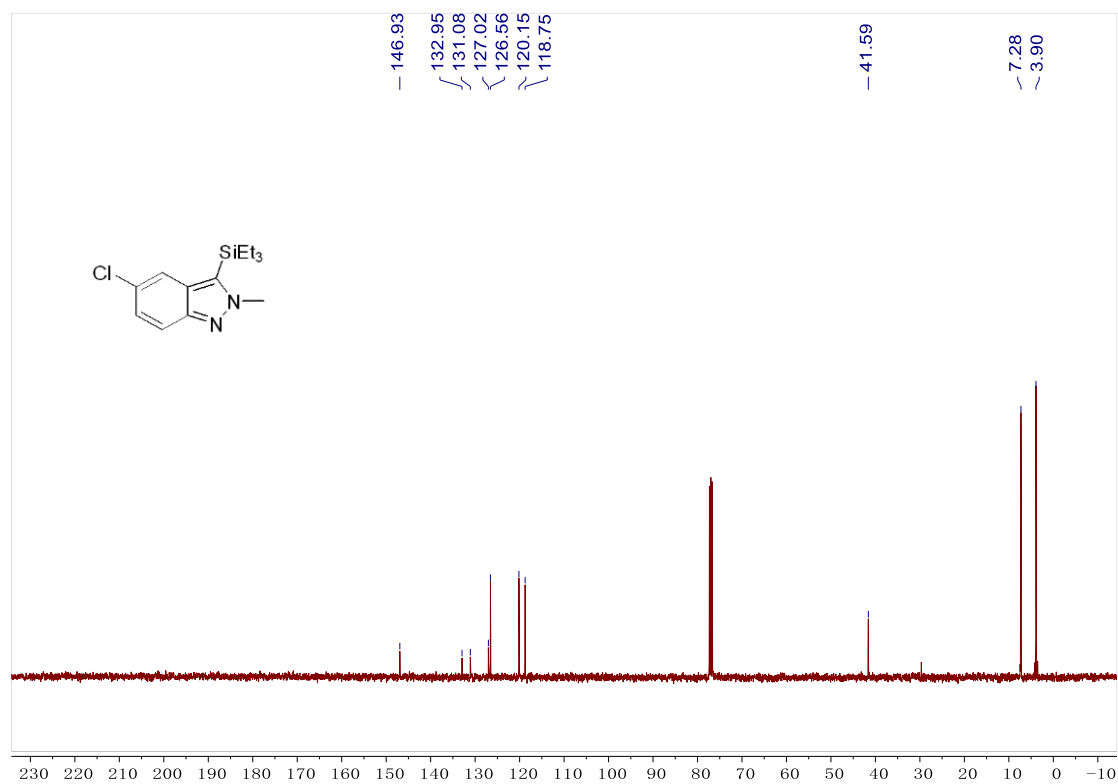
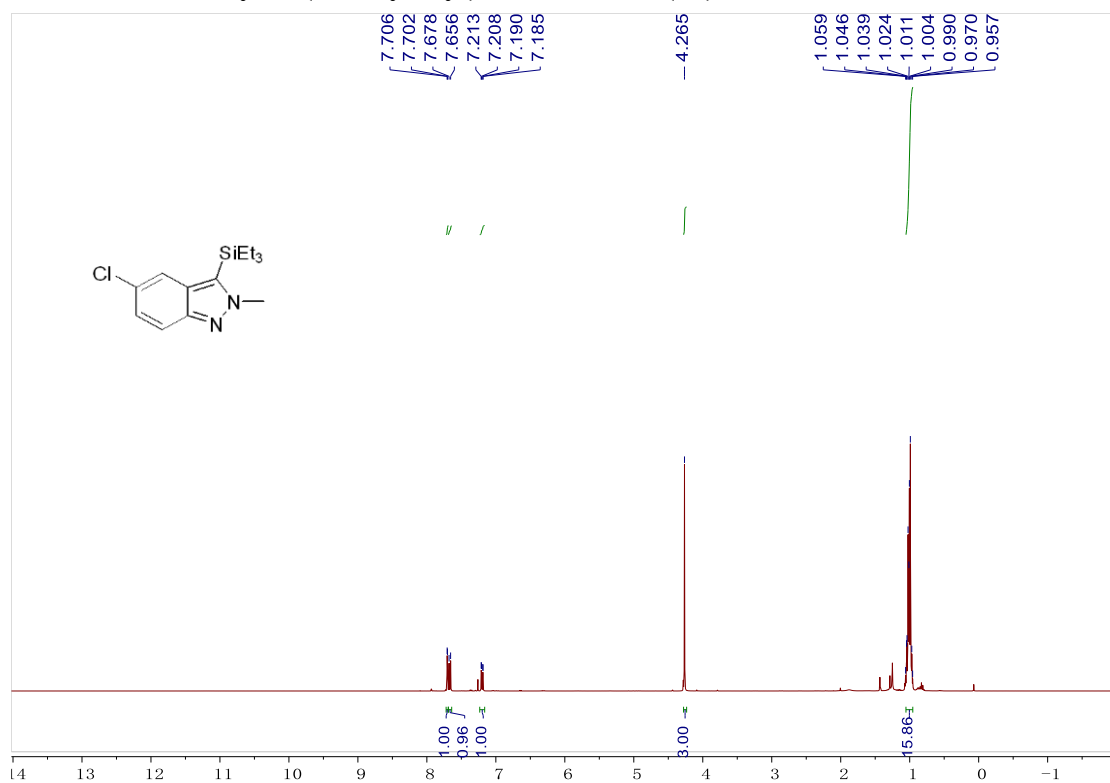
2-Methyl-5-(pyridin-3-yl)-3-(triethylsilyl)-2H-indazole (19)



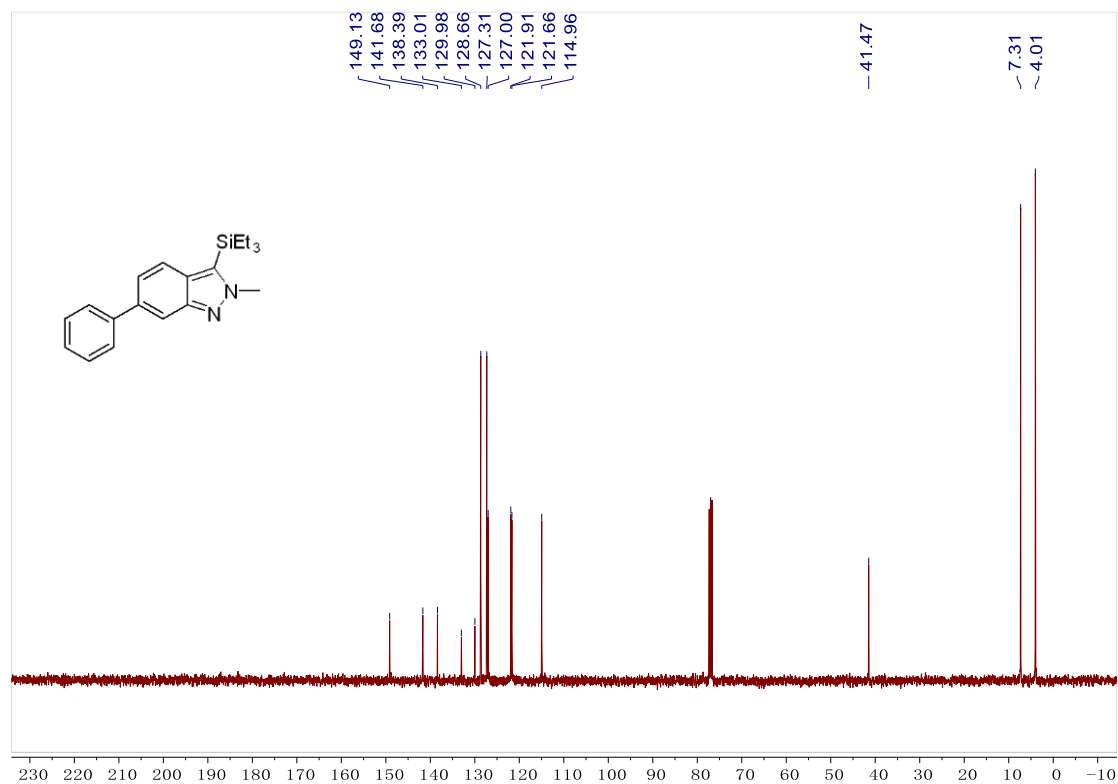
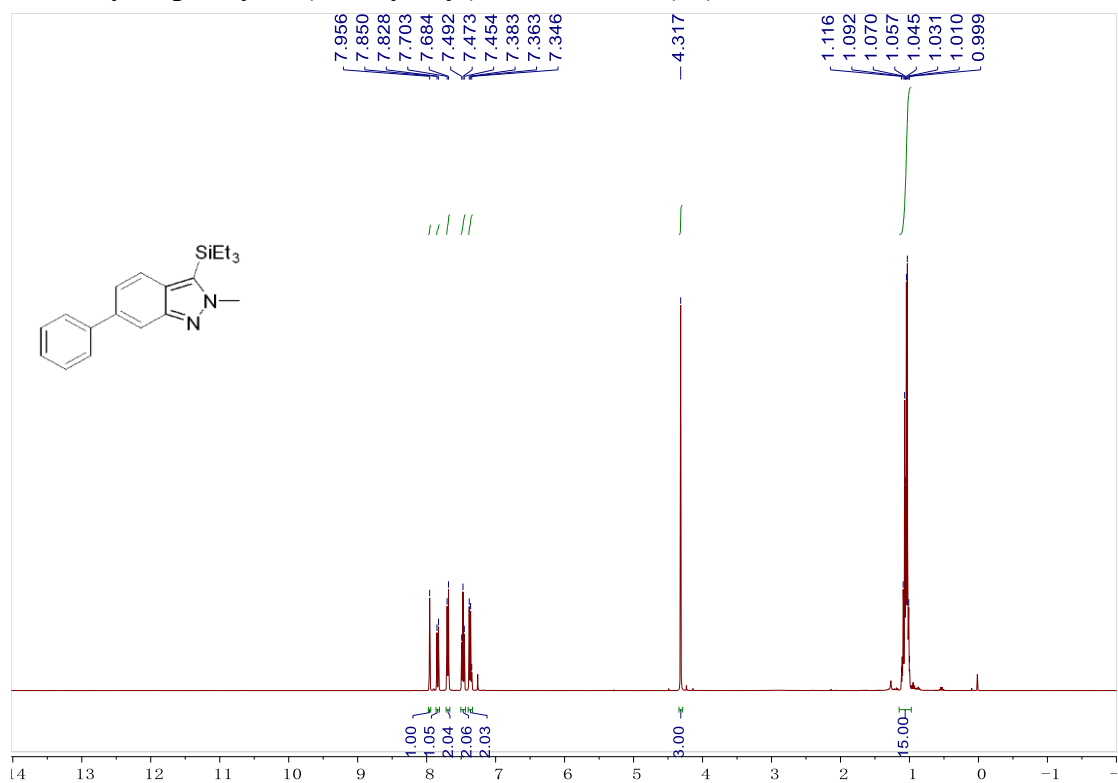
2-Methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(triethylsilyl)-2H-indazole (20)



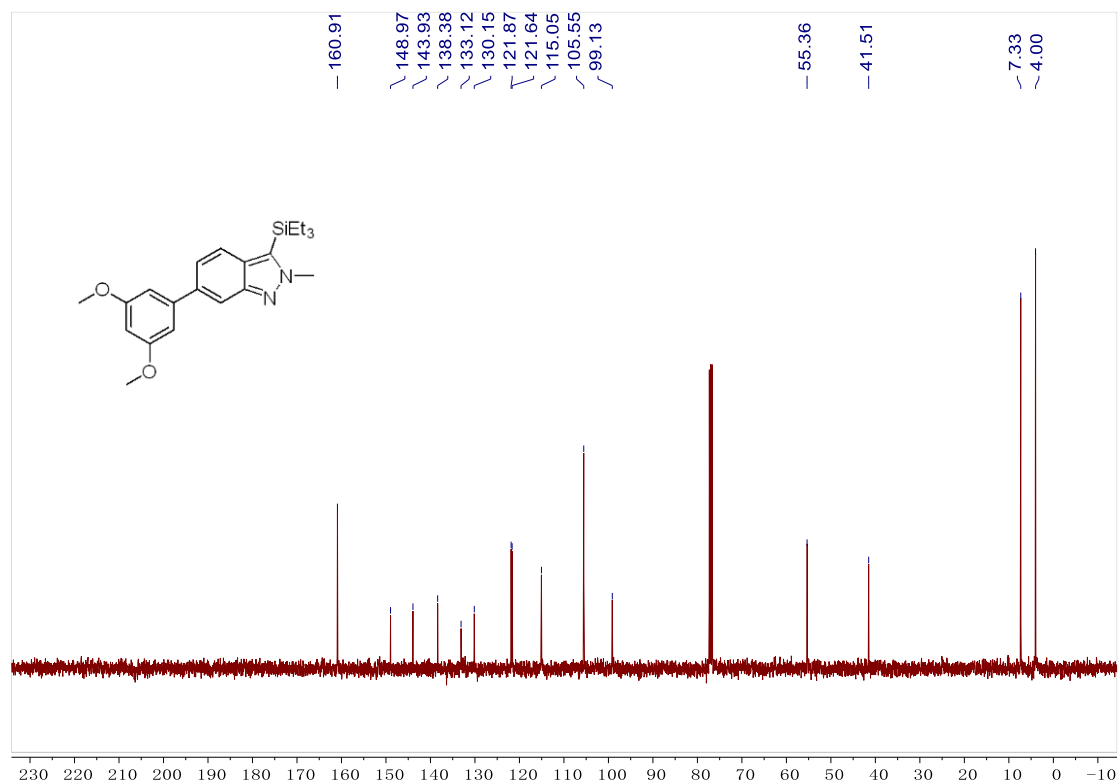
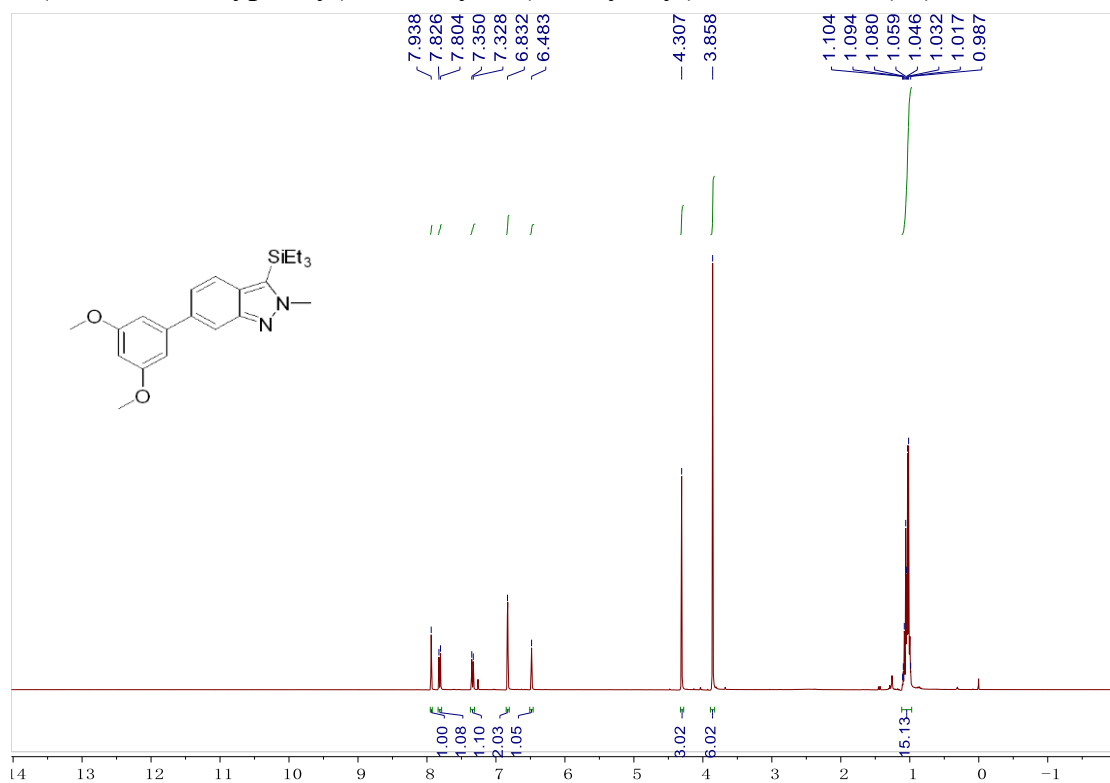
5-Chloro-2-methyl-3-(triethylsilyl)-2H-indazole (21)



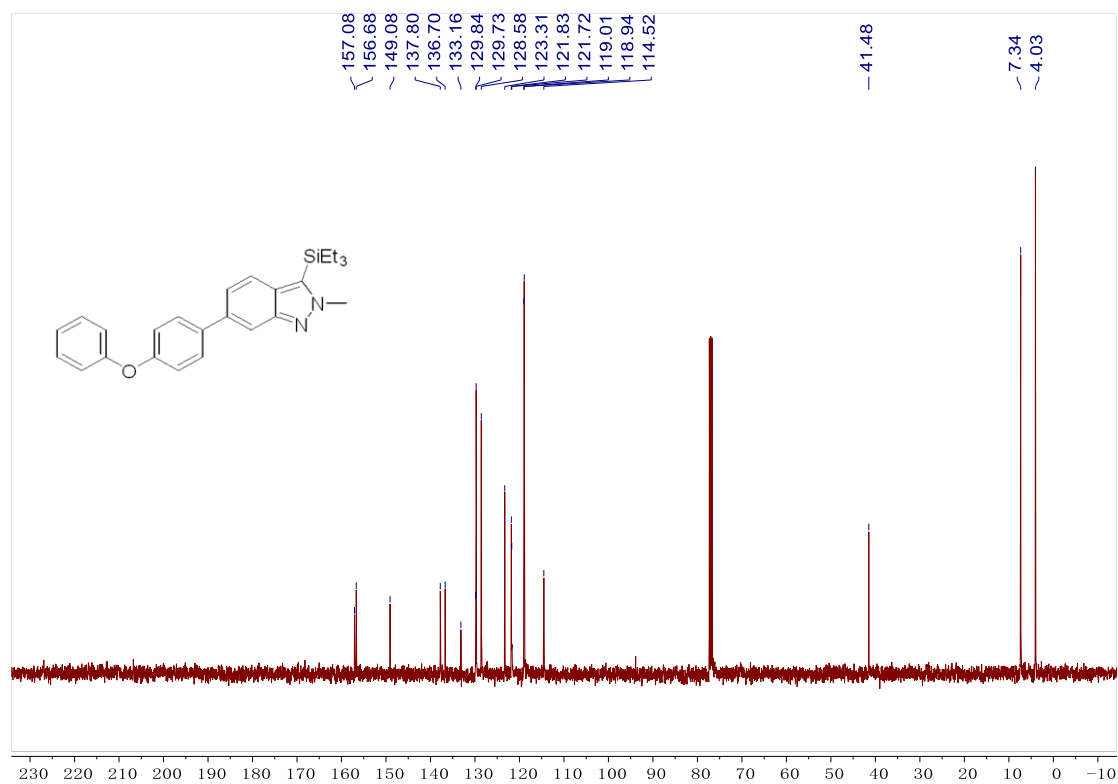
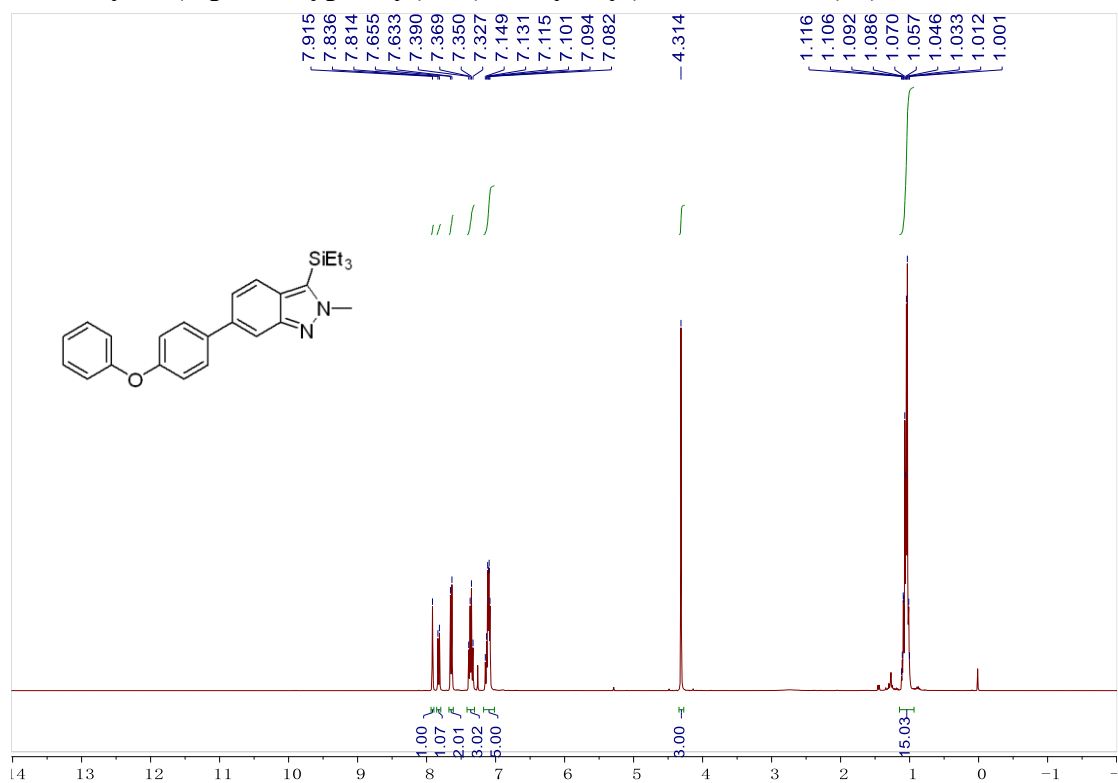
2-Methyl-6-phenyl-3-(triethylsilyl)-2H-indazole (22)



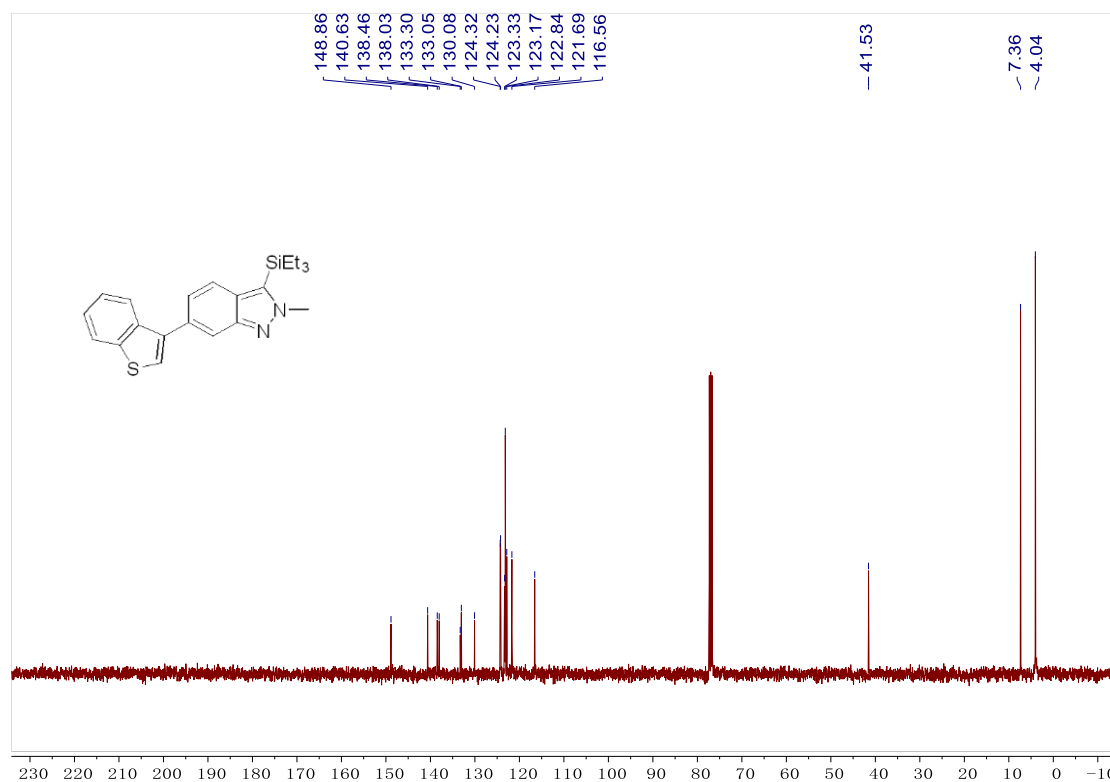
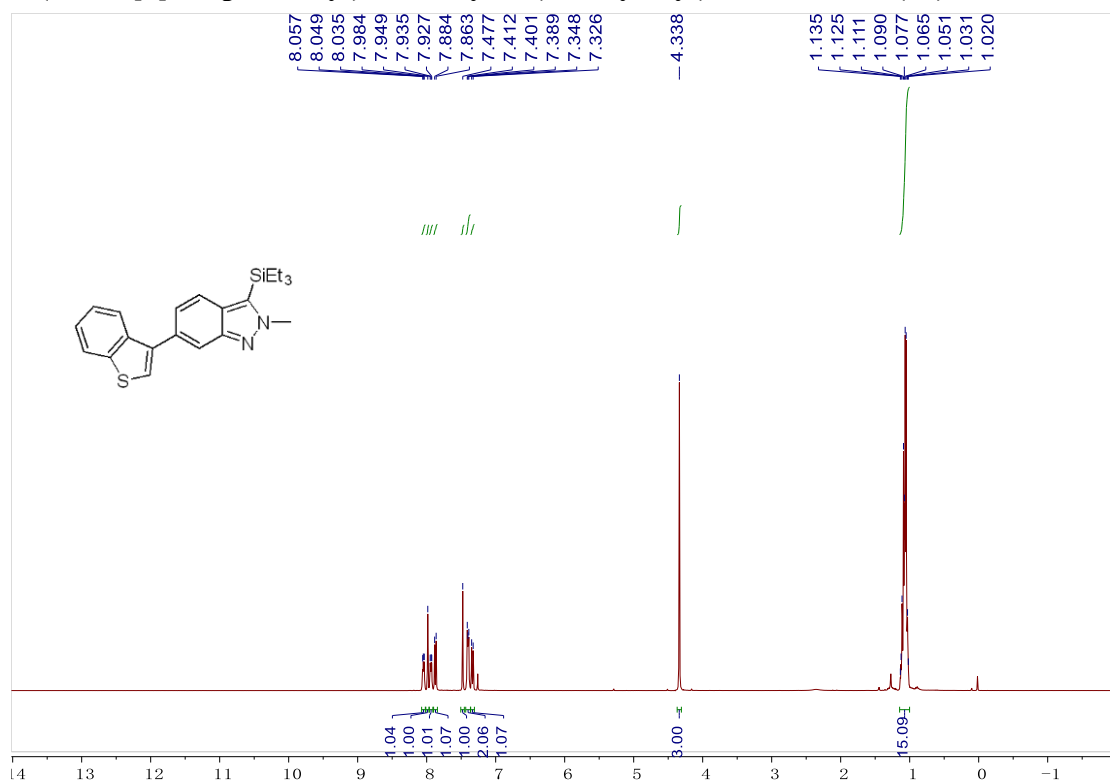
6-(3,5-Dimethoxyphenyl)-2-methyl-3-(triethylsilyl)-2H-indazole (23)



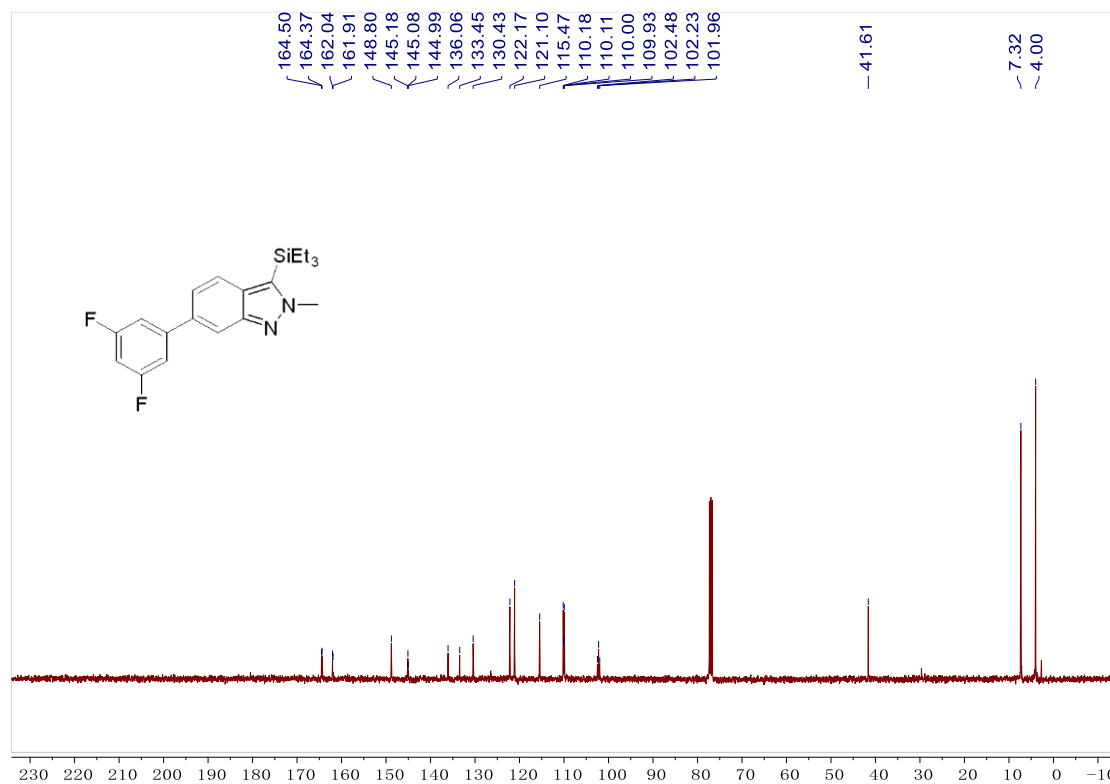
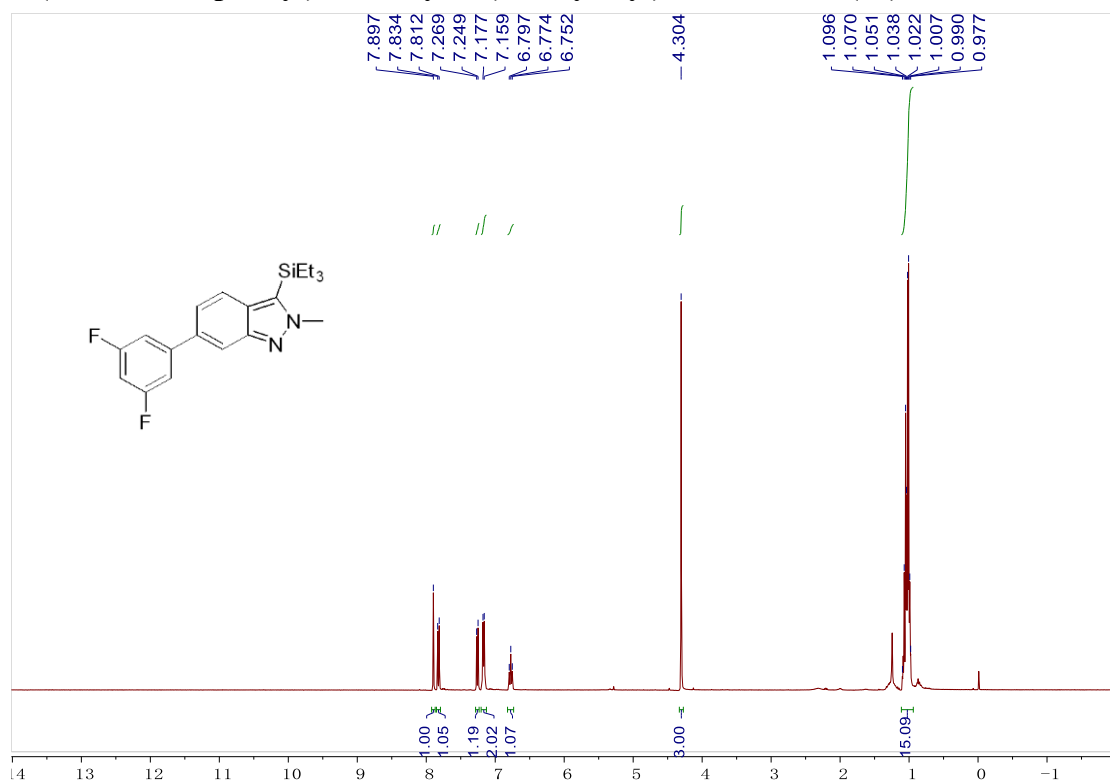
2-Methyl-6-(4-phenoxyphenyl)-3-(triethylsilyl)-2H-indazole (24)



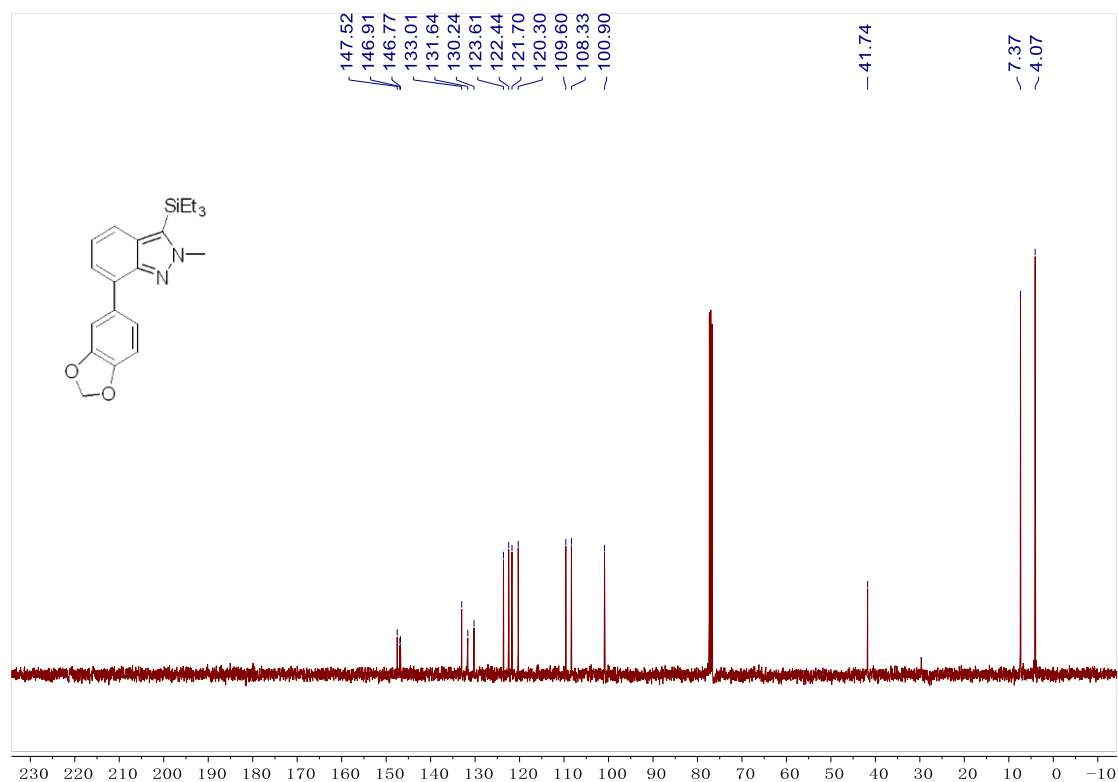
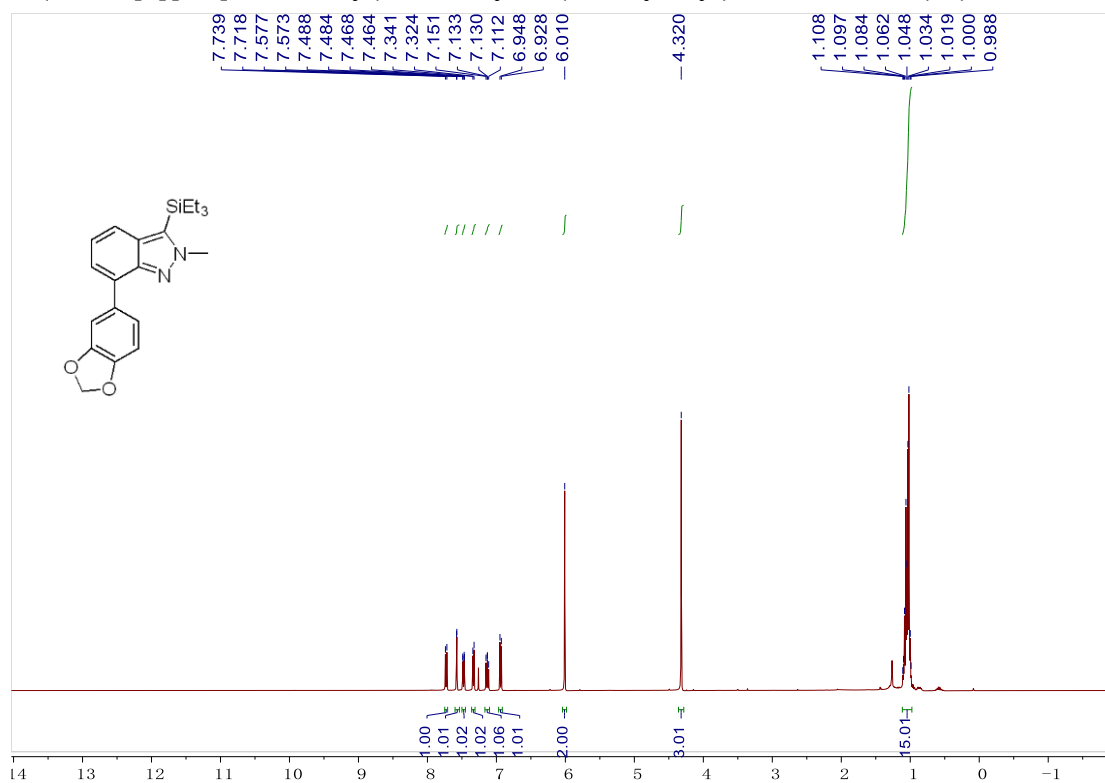
6-(Benzo[b]thiophen-3-yl)-2-methyl-3-(triethylsilyl)-2H-indazole (25)



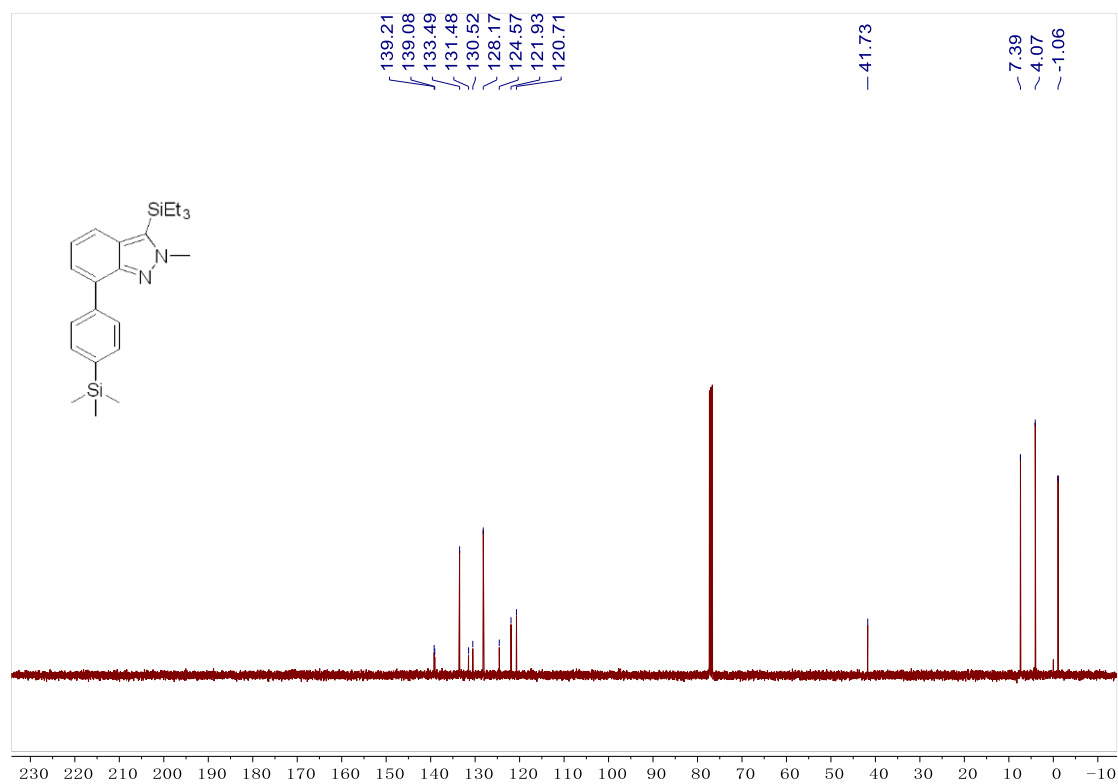
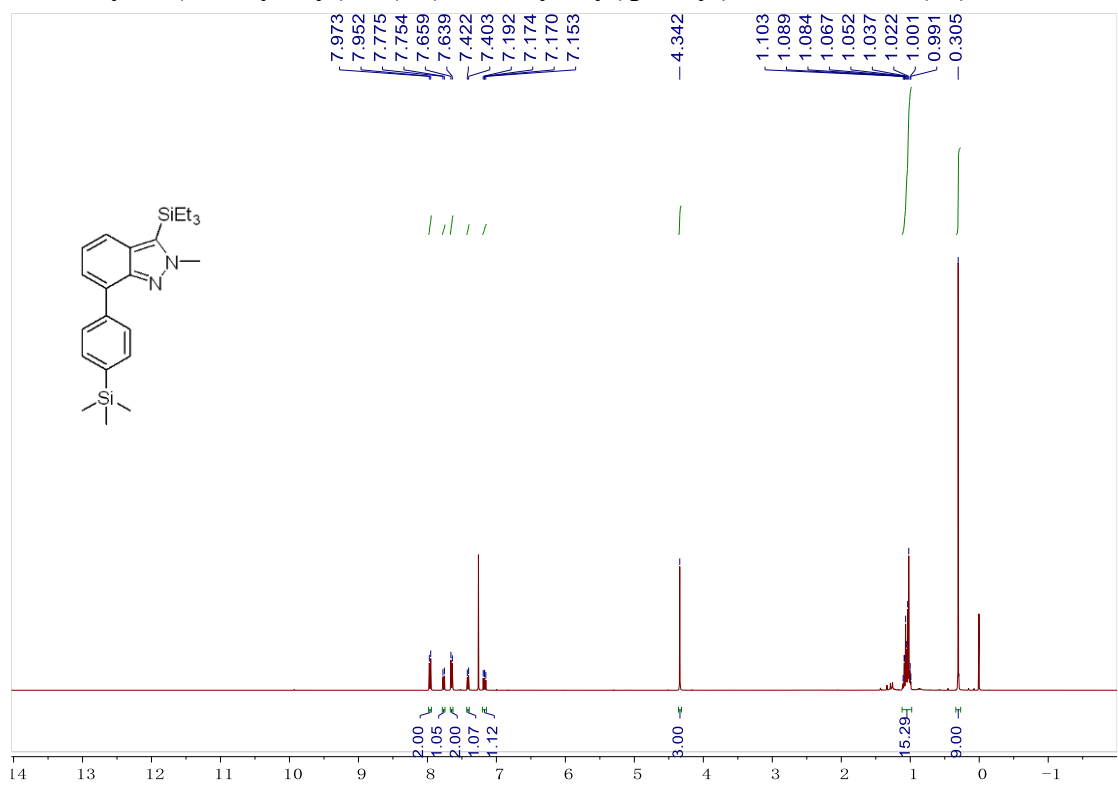
6-(3,5-Difluorophenyl)-2-methyl-3-(triethylsilyl)-2H-indazole (26)



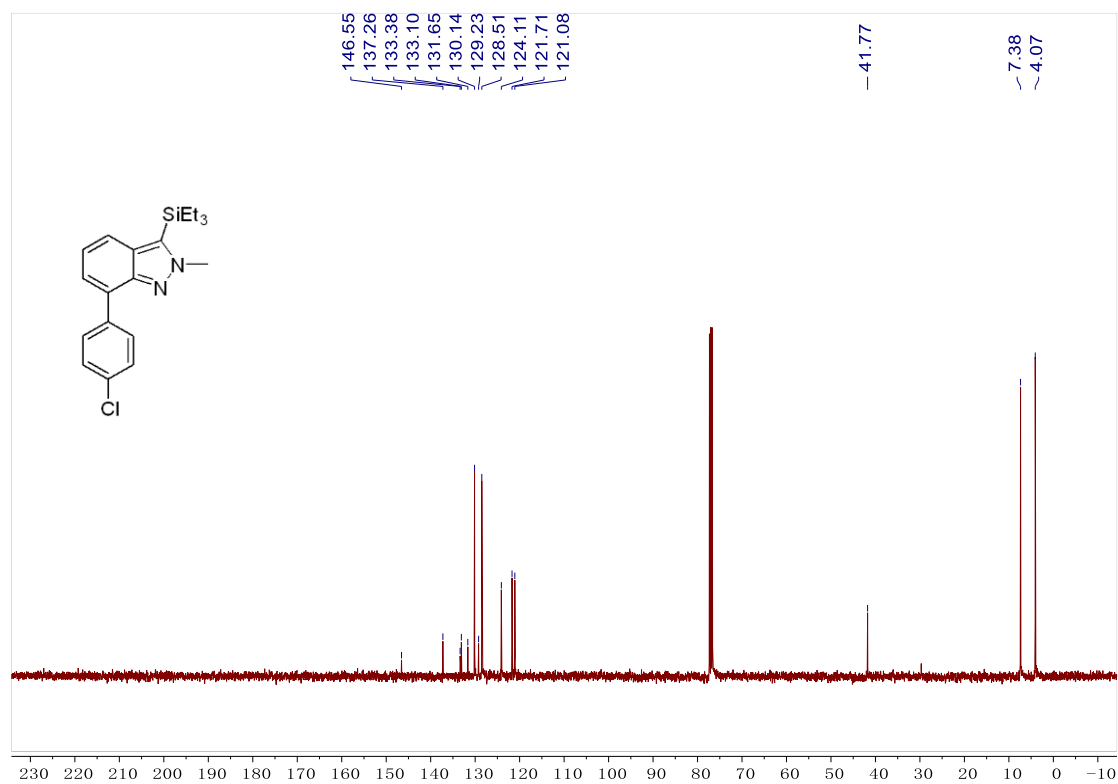
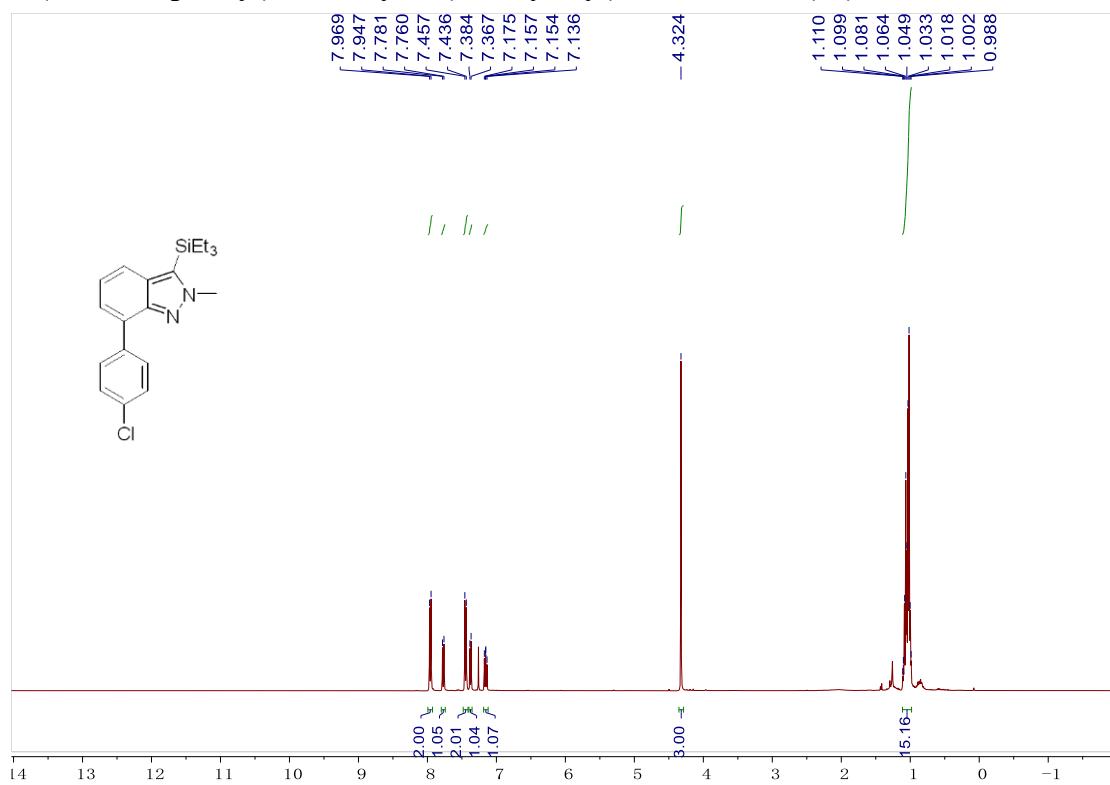
7-(Benzo[d][1,3]dioxol-5-yl)-2-methyl-3-(triethylsilyl)-2H-indazole (27)



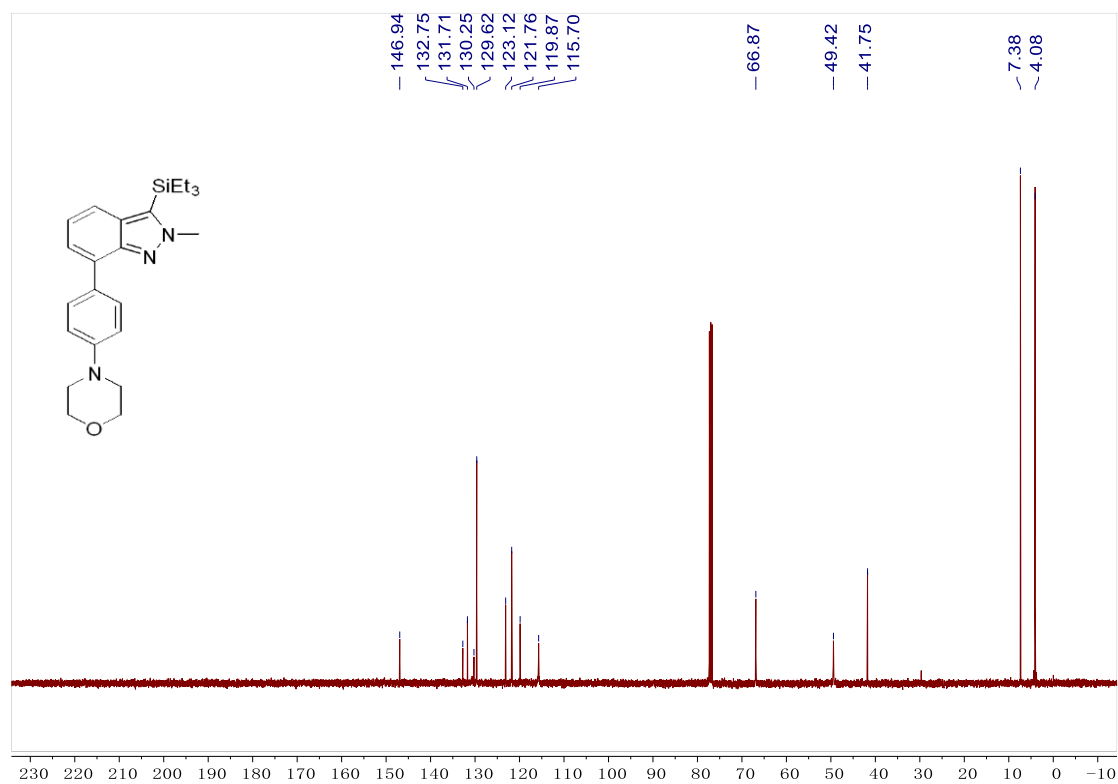
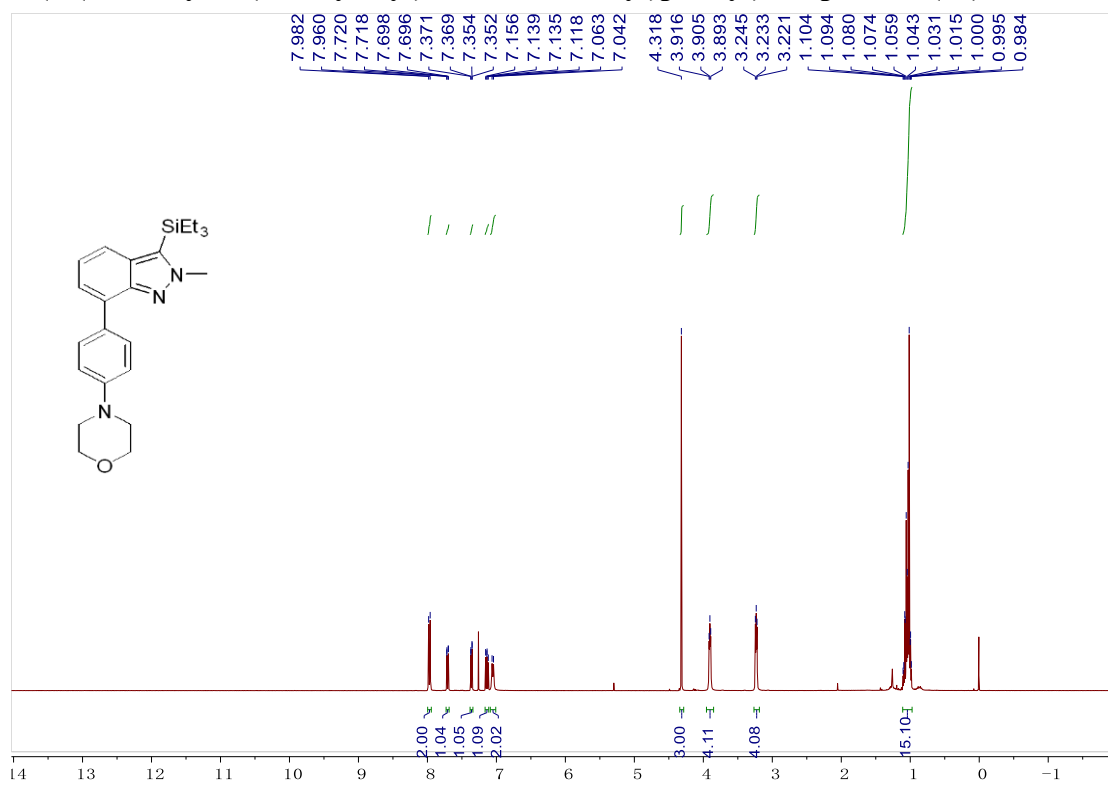
2-Methyl-3-(triethylsilyl)-7-(4-(trimethylsilyl)phenyl)-2H-indazole (28)



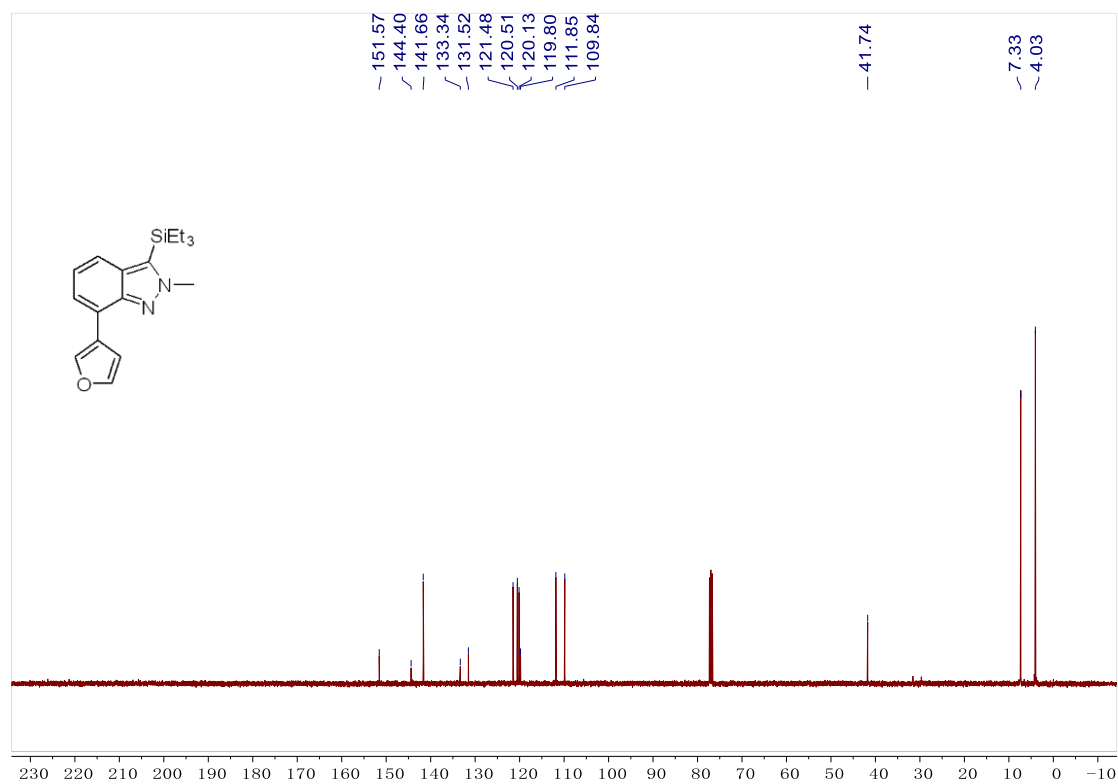
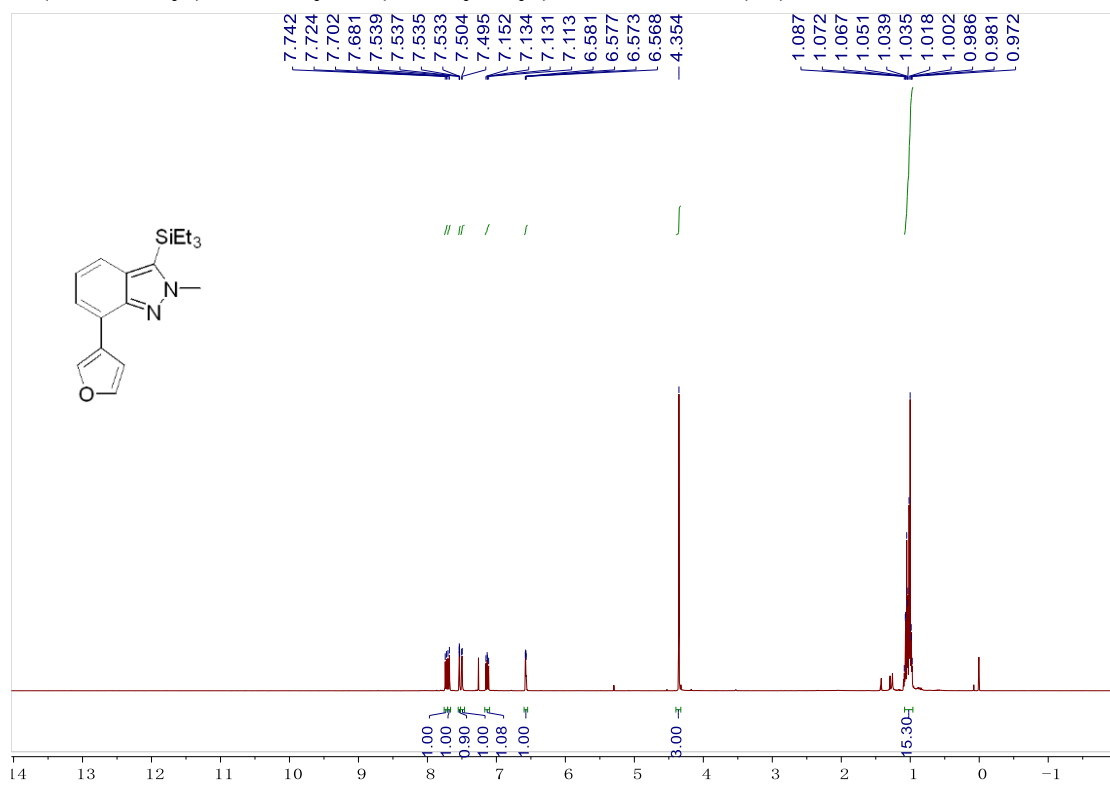
7-(4-Chlorophenyl)-2-methyl-3-(triethylsilyl)-2H-indazole (29)



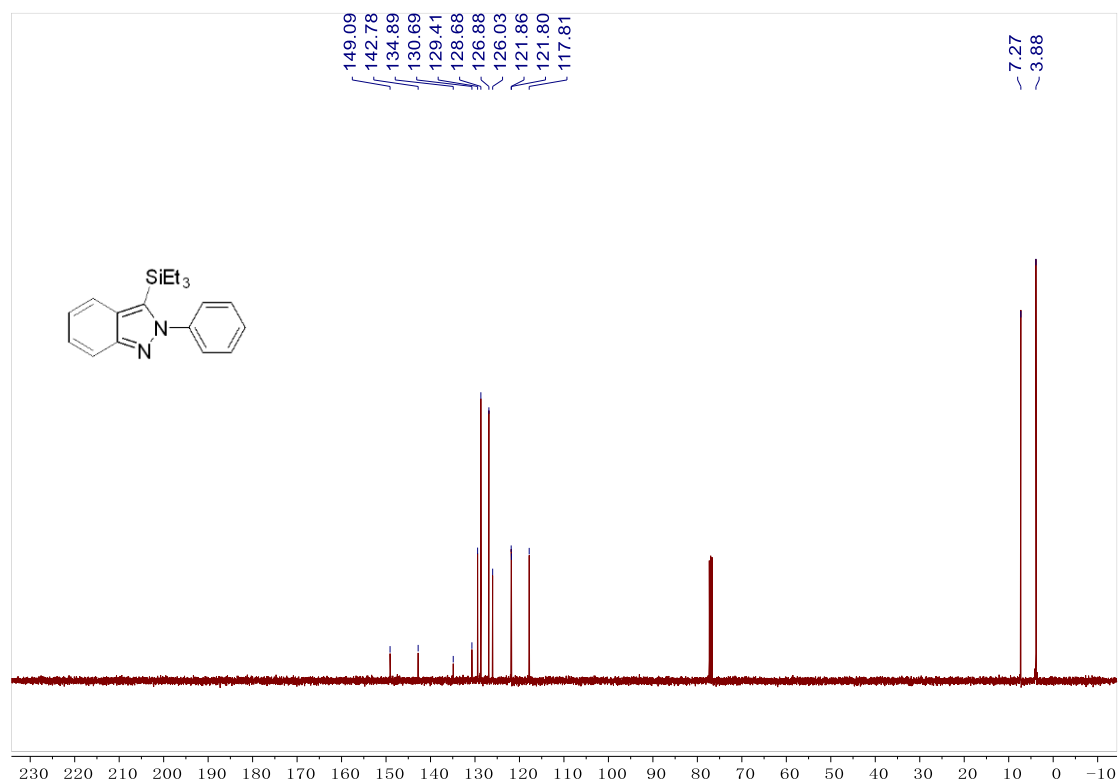
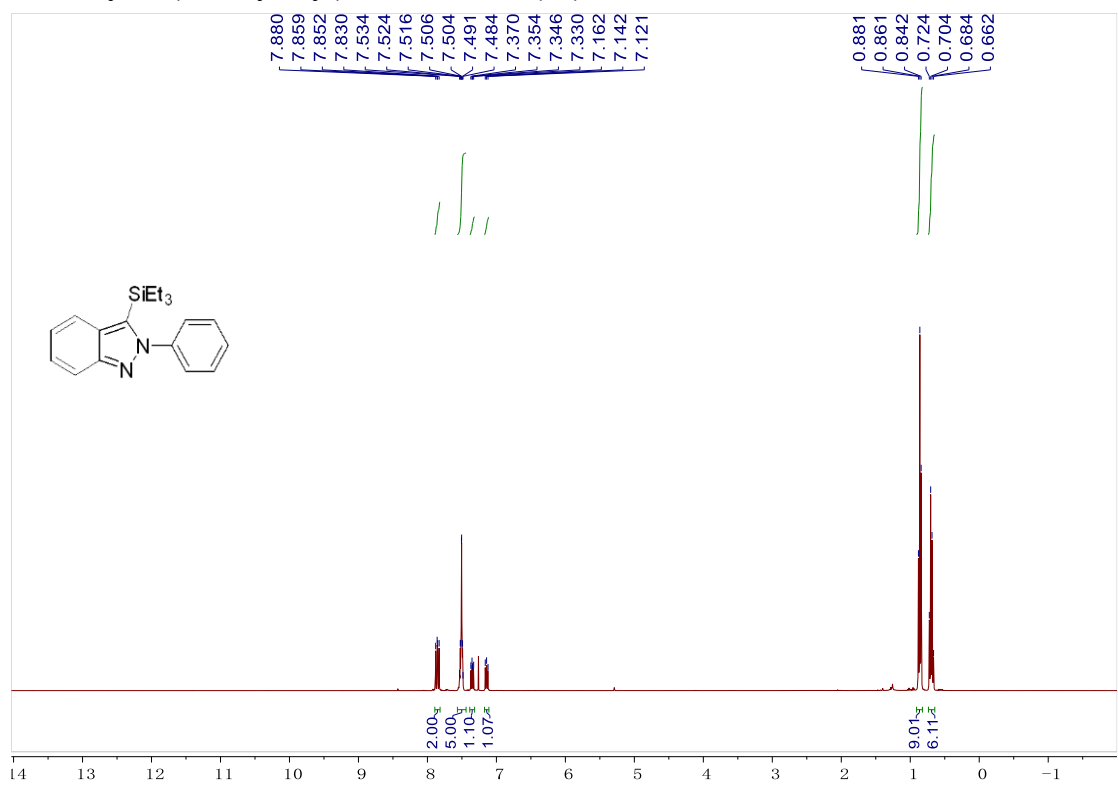
4-(4-(2-Methyl-3-(triethylsilyl)-2H-indazol-7-yl)phenyl)morpholine (30)



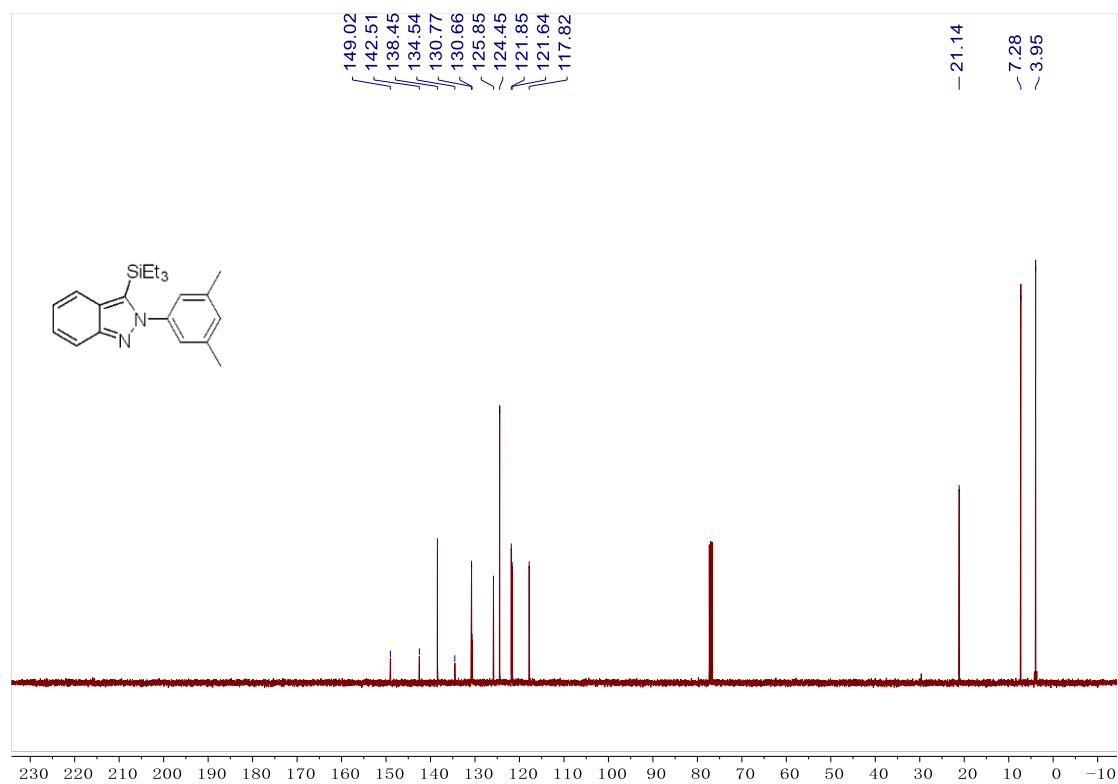
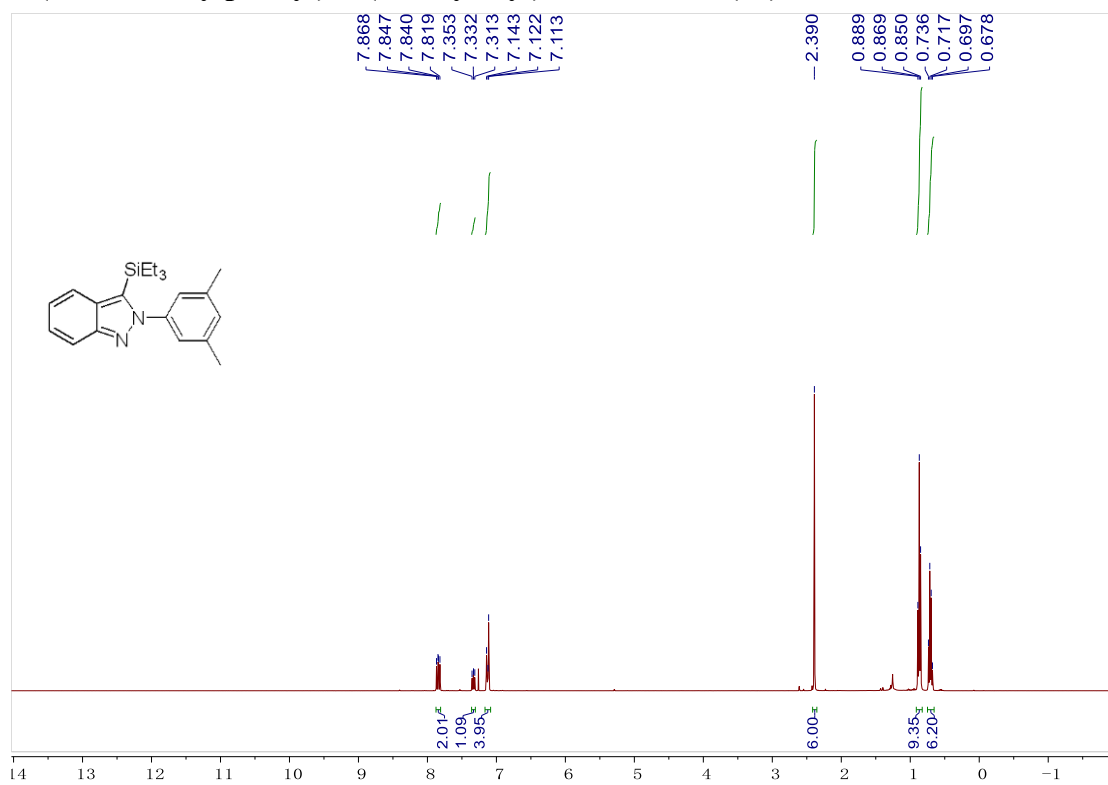
7-(Furan-3-yl)-2-methyl-3-(triethylsilyl)-2H-indazole (31)



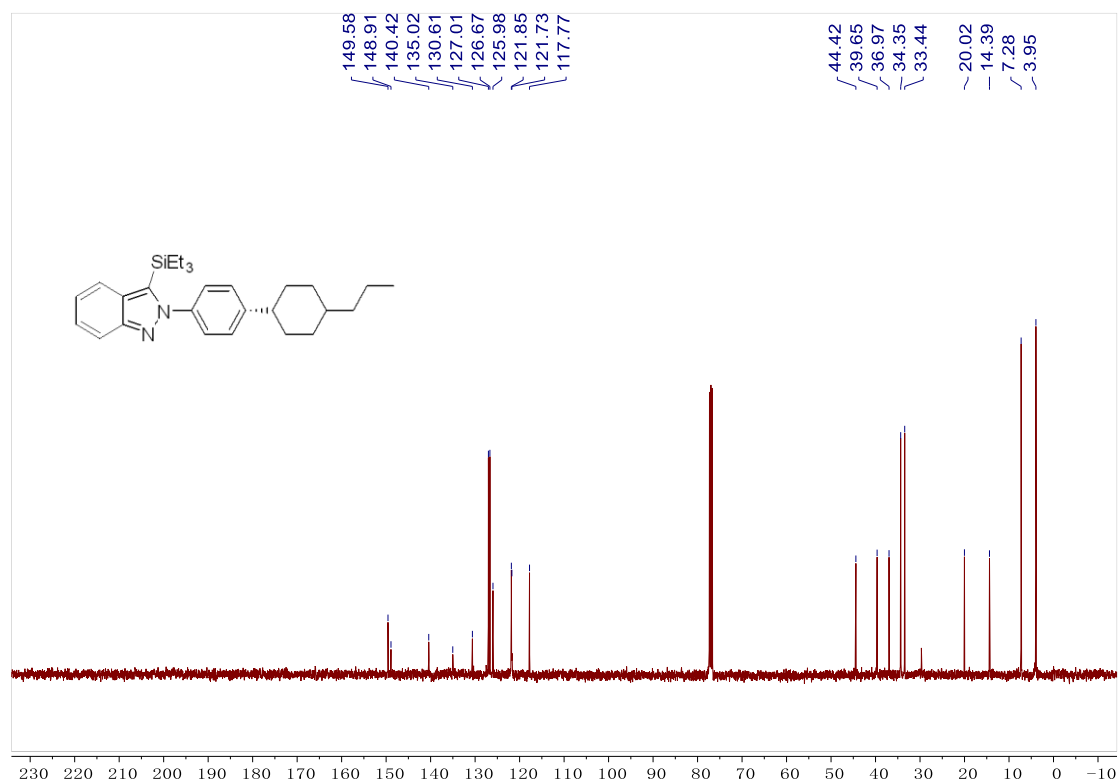
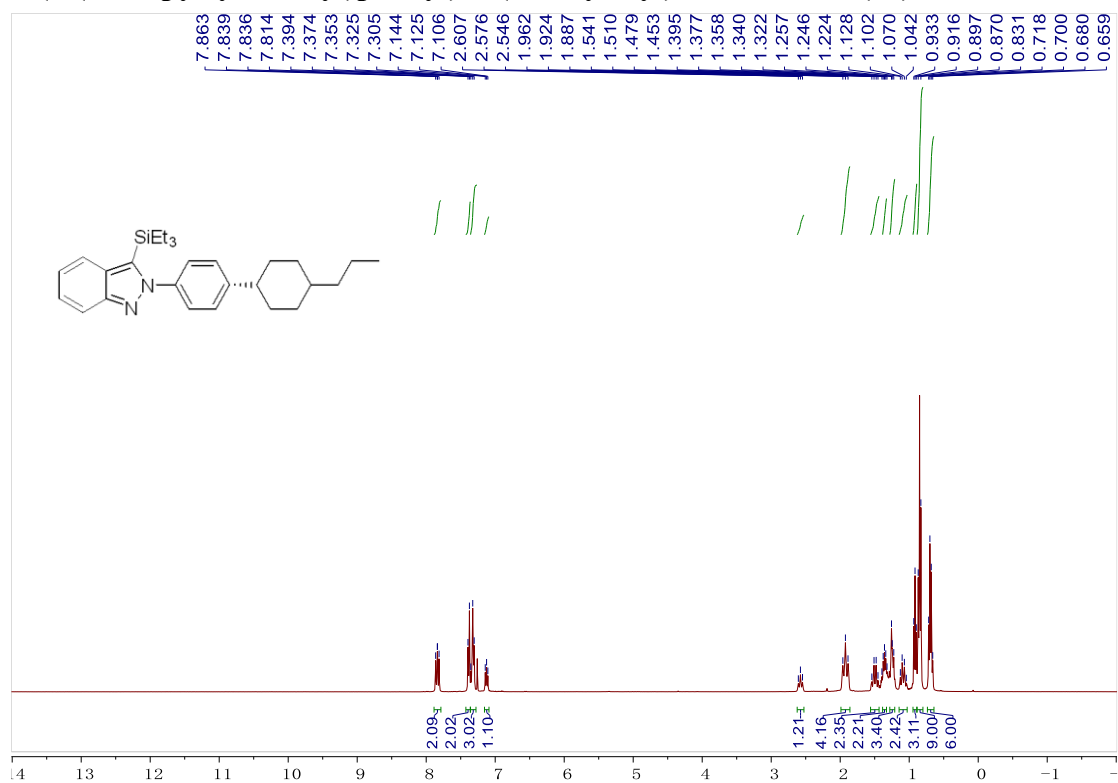
2-Phenyl-3-(triethylsilyl)-2H-indazole (32)



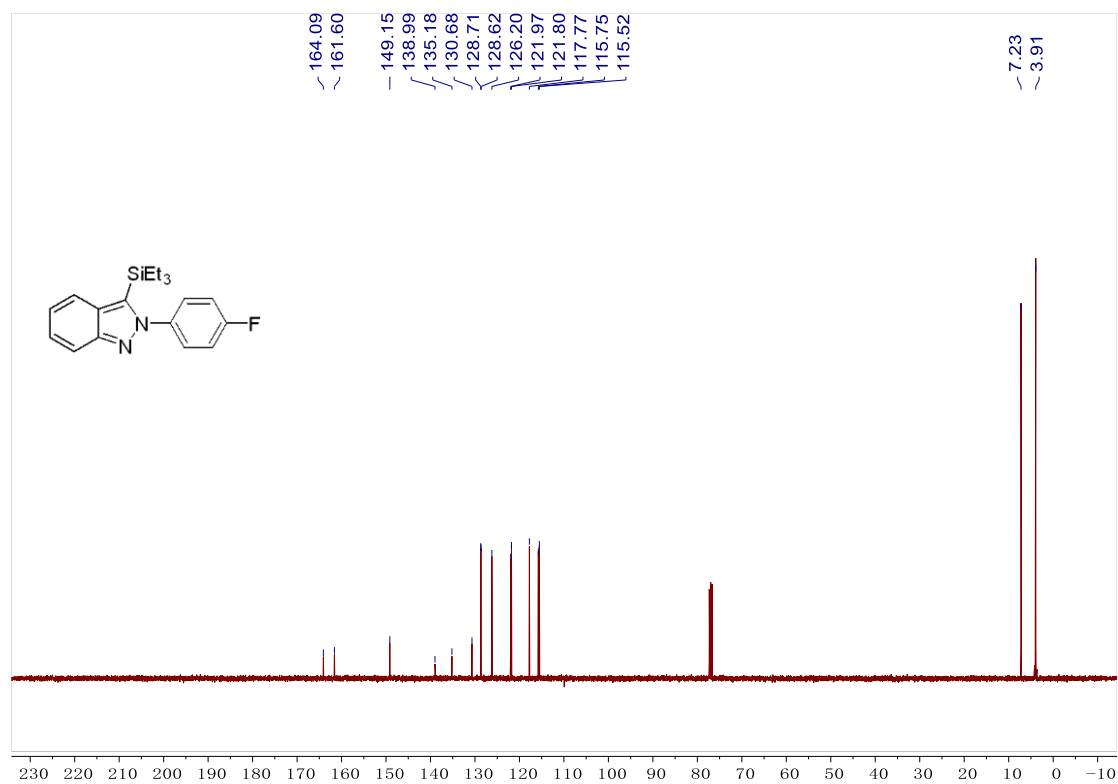
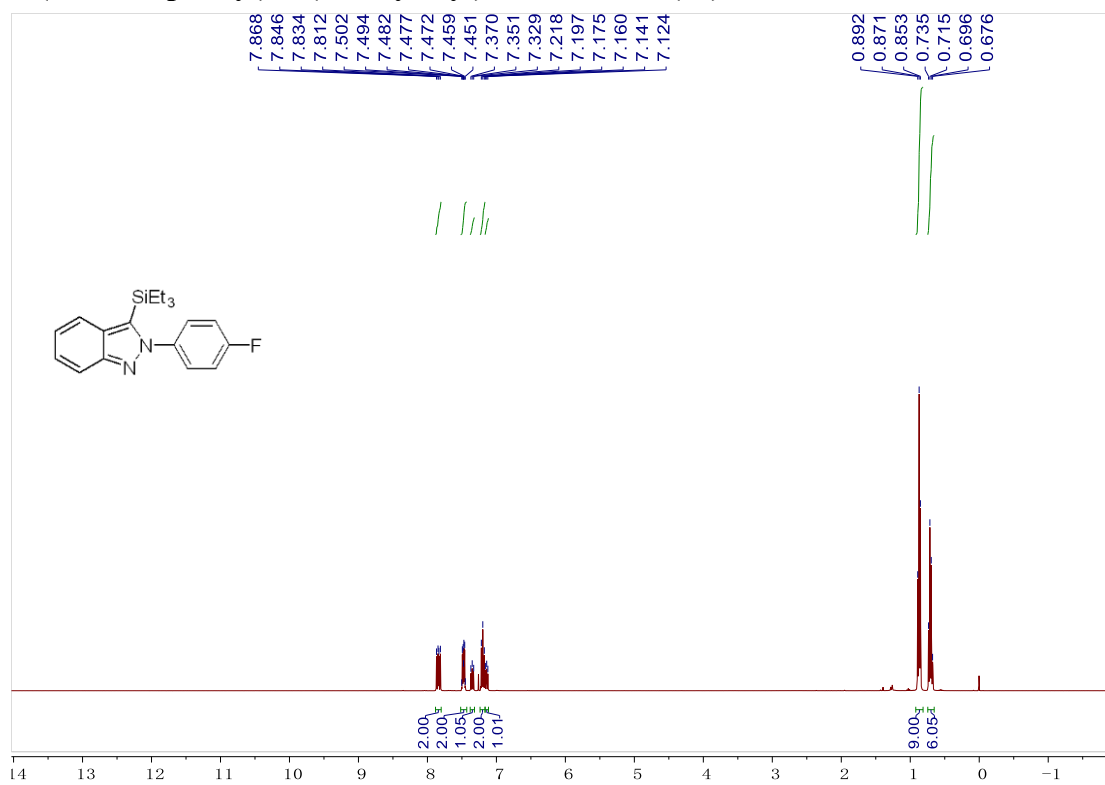
2-(3,5-Dimethylphenyl)-3-(triethylsilyl)-2H-indazole (33)



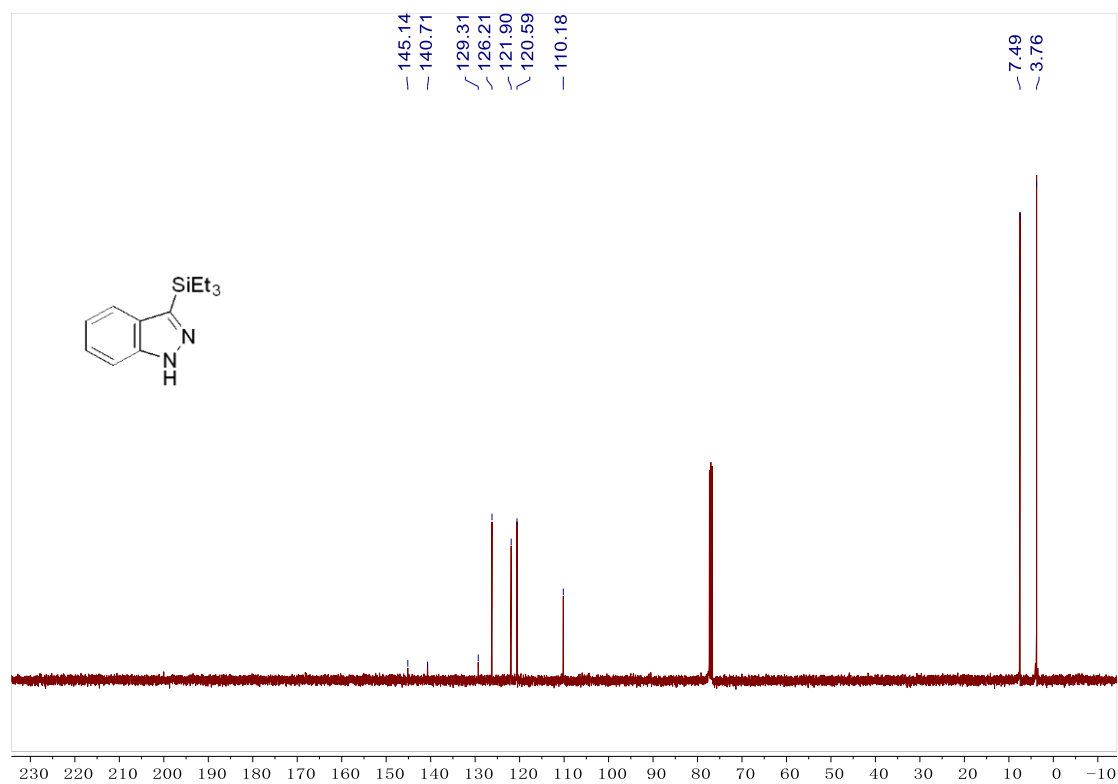
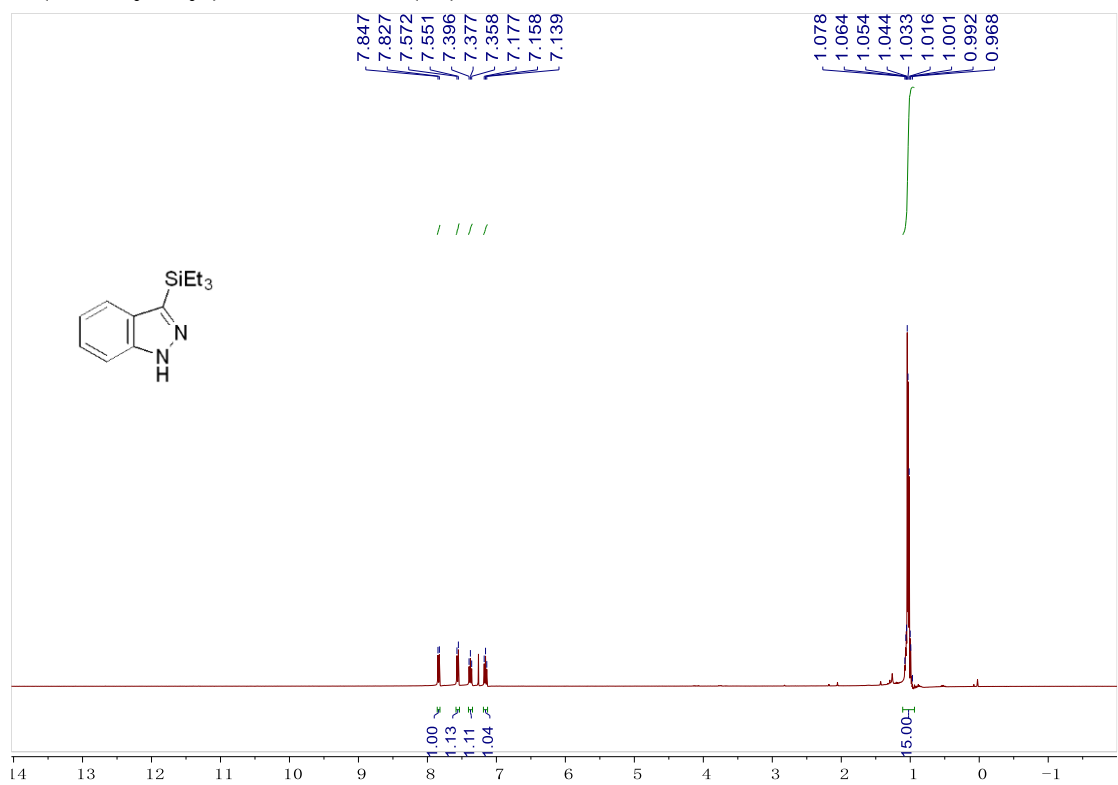
2-(4-(4-Propylcyclohexyl)phenyl)-3-(triethylsilyl)-2H-indazole (34)



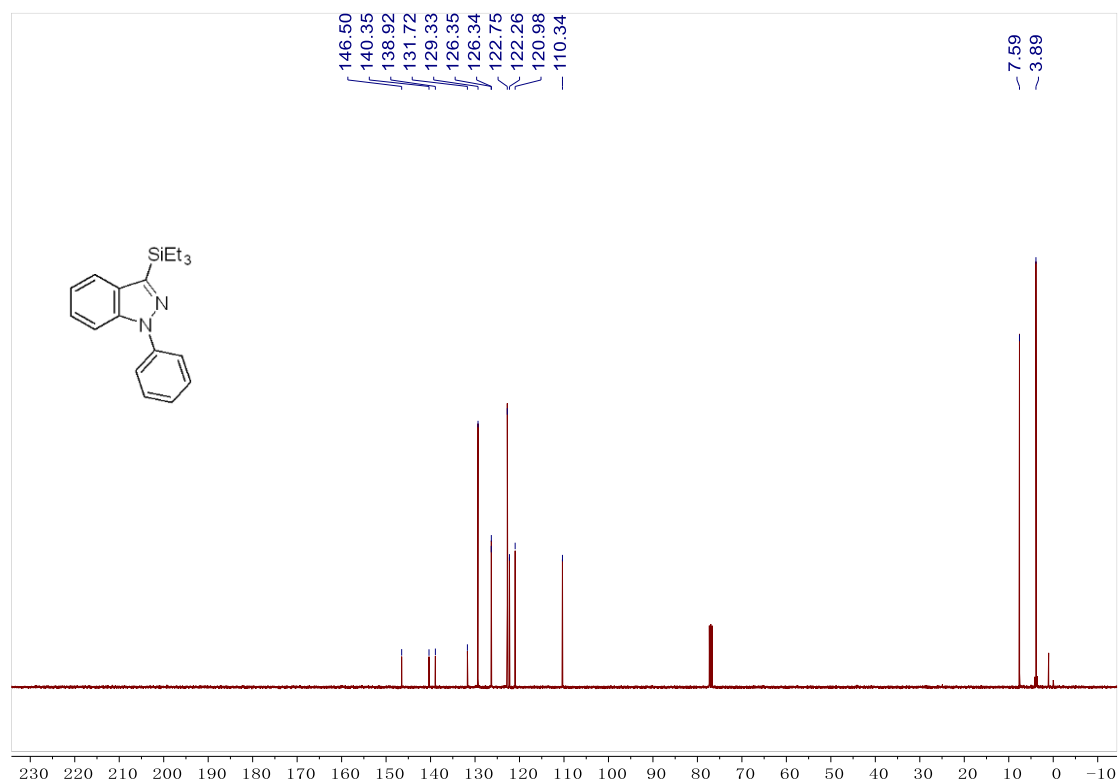
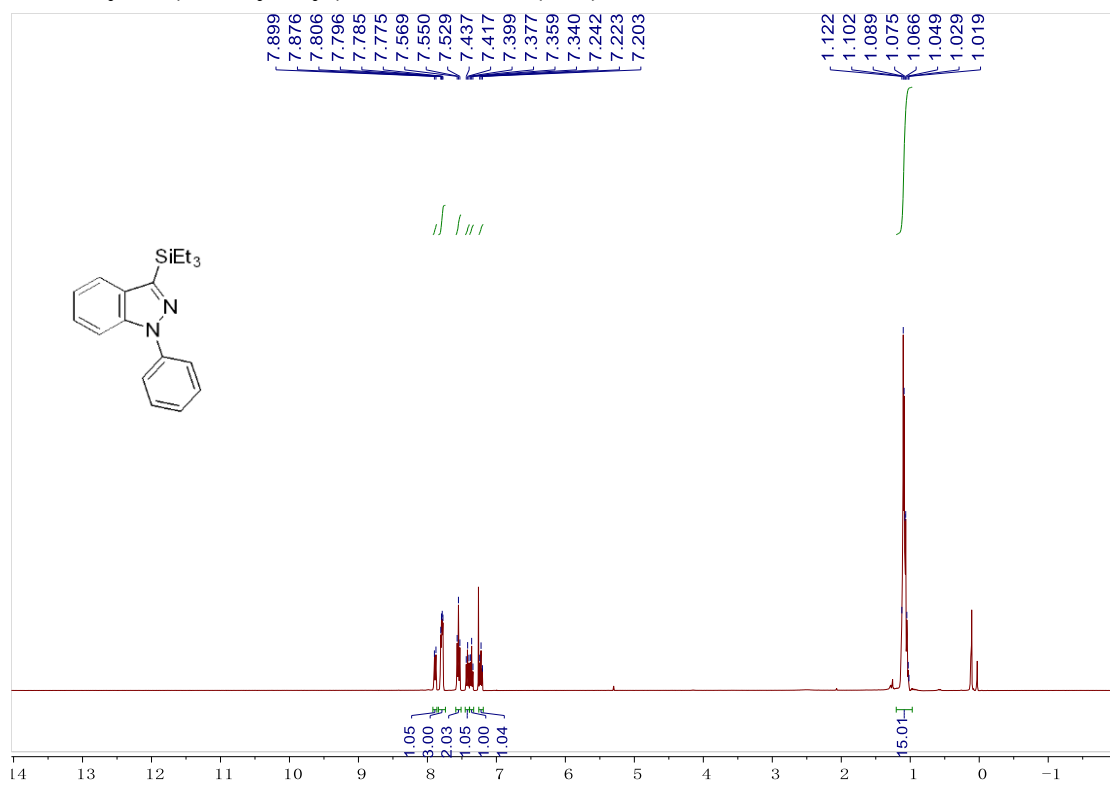
2-(4-Fluorophenyl)-3-(triethylsilyl)-2H-indazole (35)



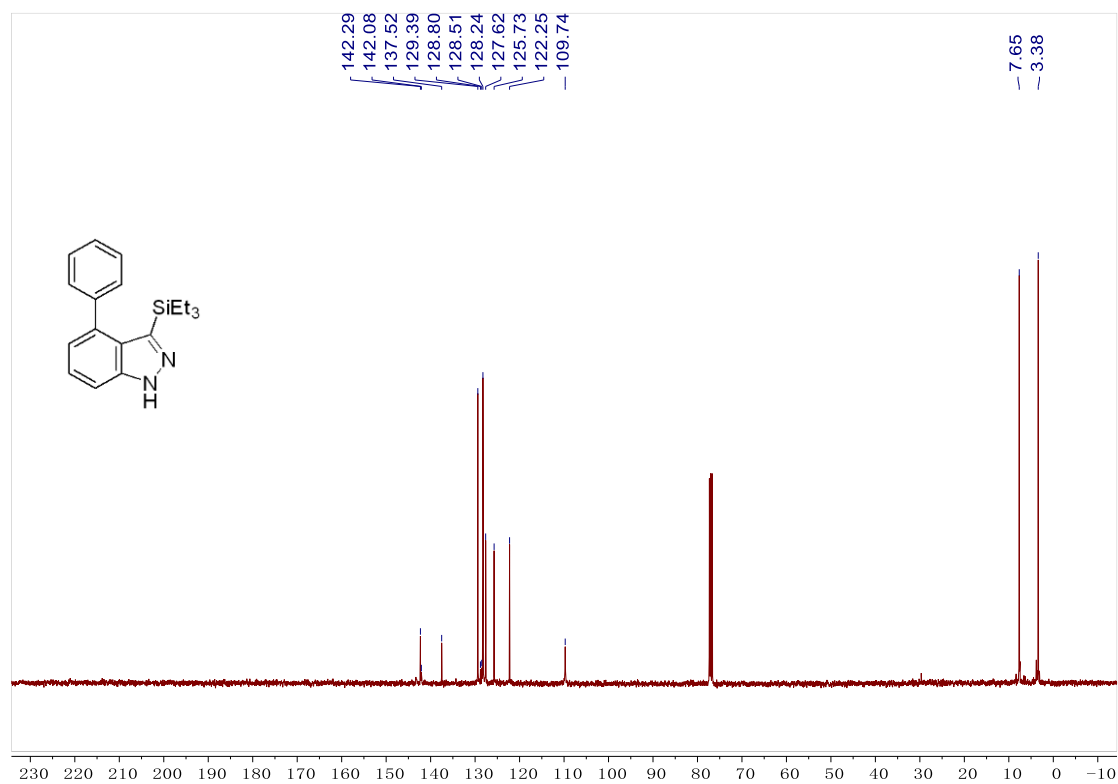
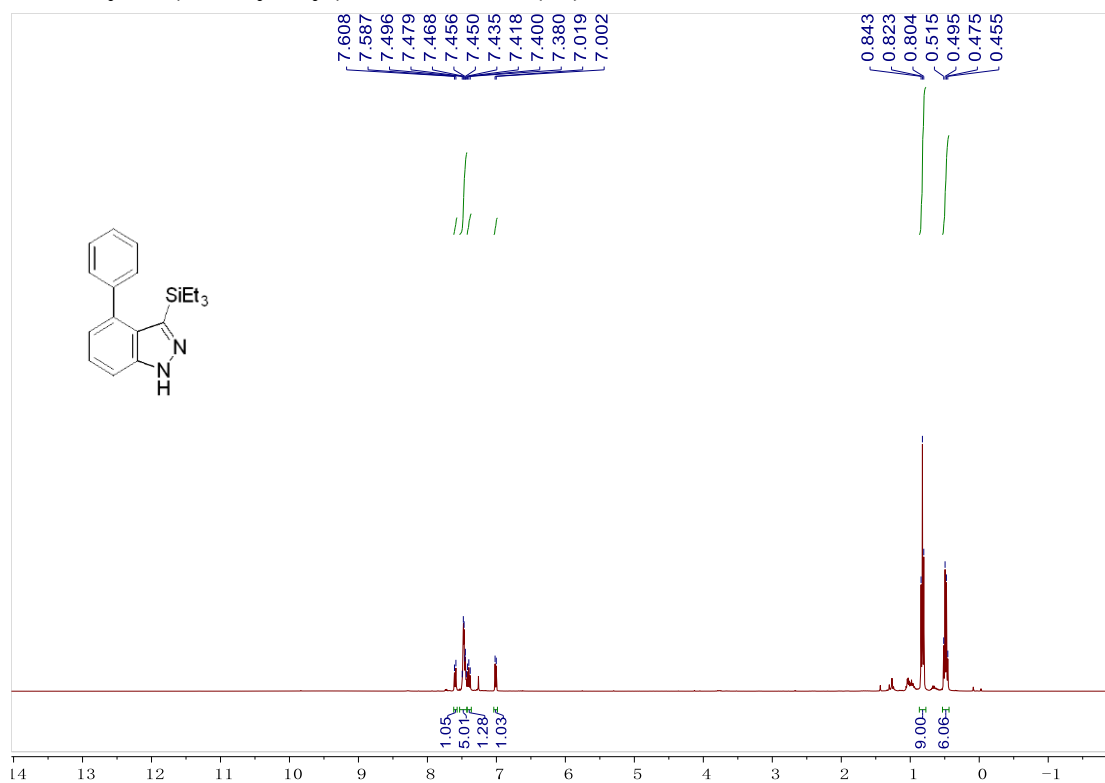
3-(Triethylsilyl)-1H-indazole (36)



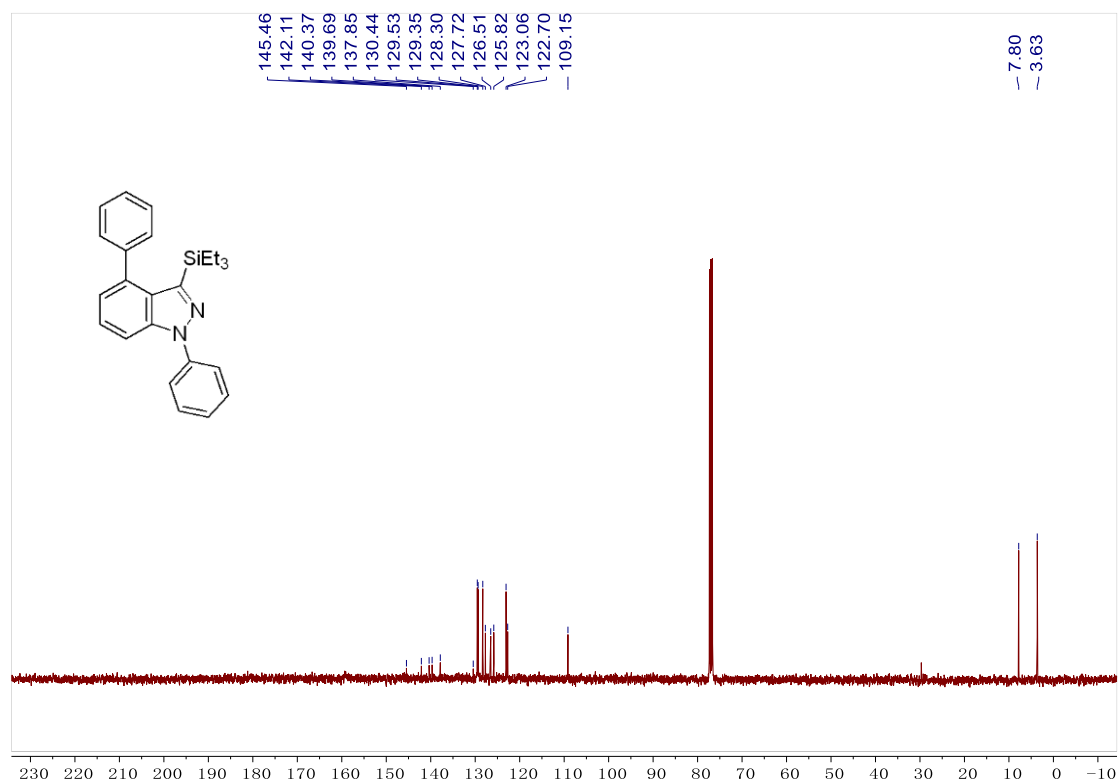
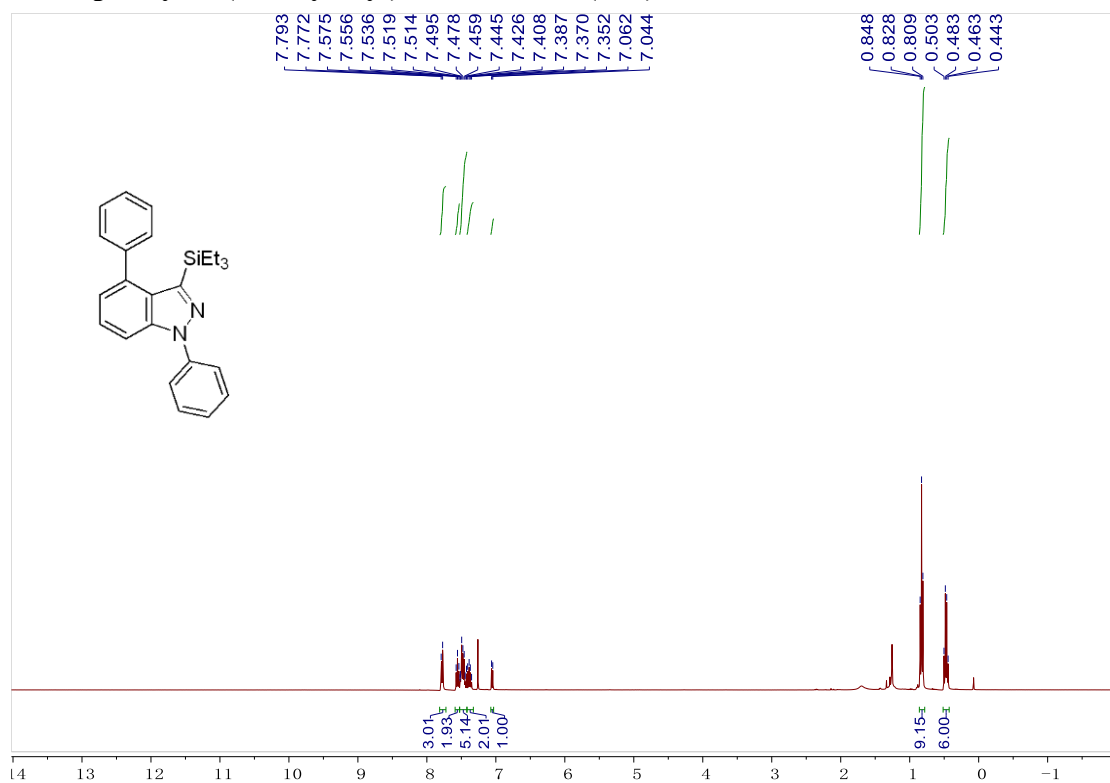
1-Phenyl-3-(triethylsilyl)-1H-indazole (36b)



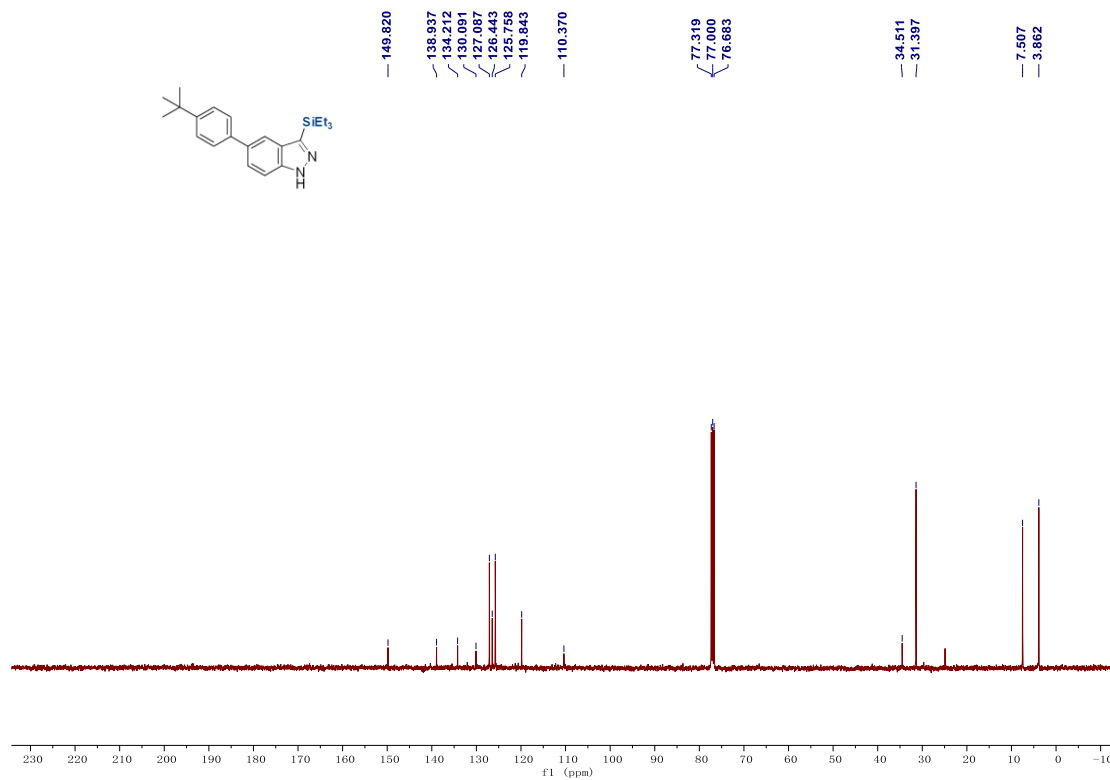
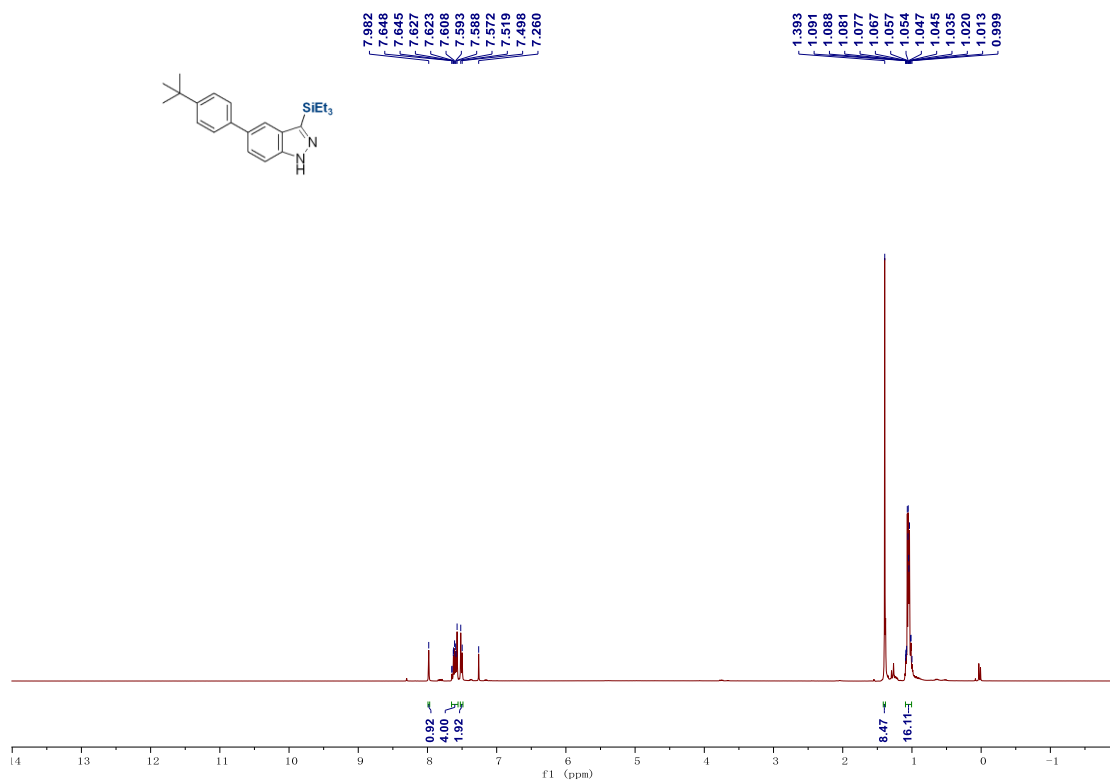
4-Phenyl-3-(triethylsilyl)-1H-indazole (37)



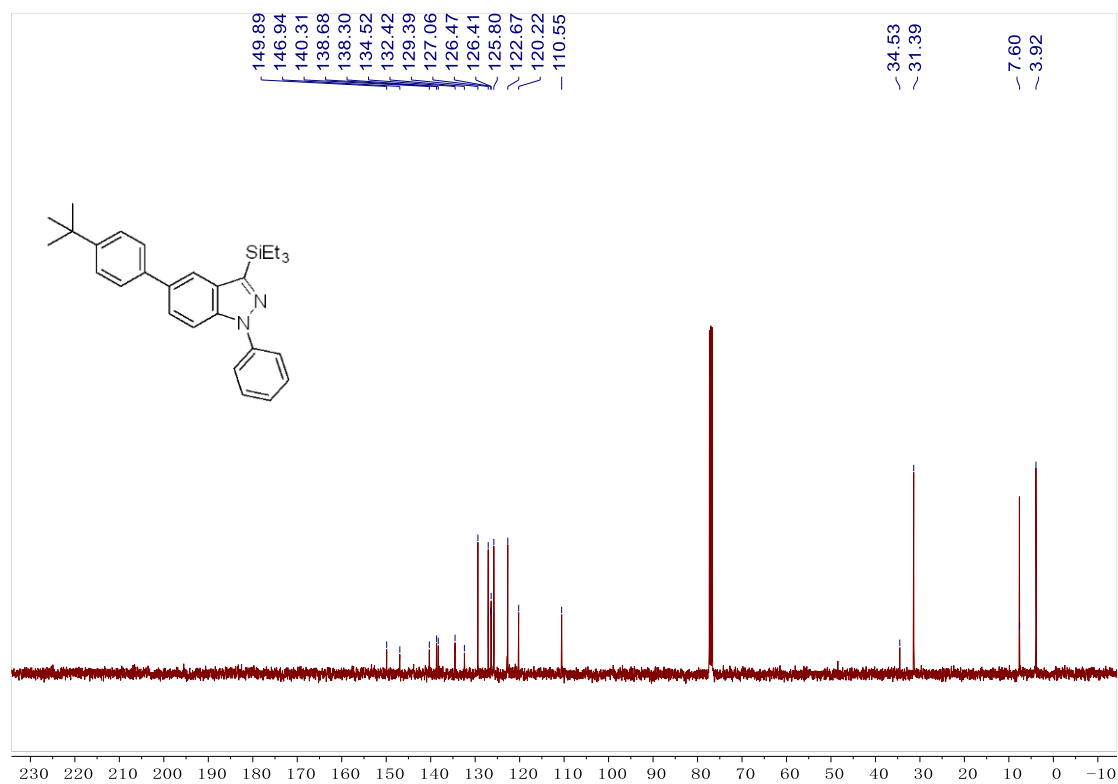
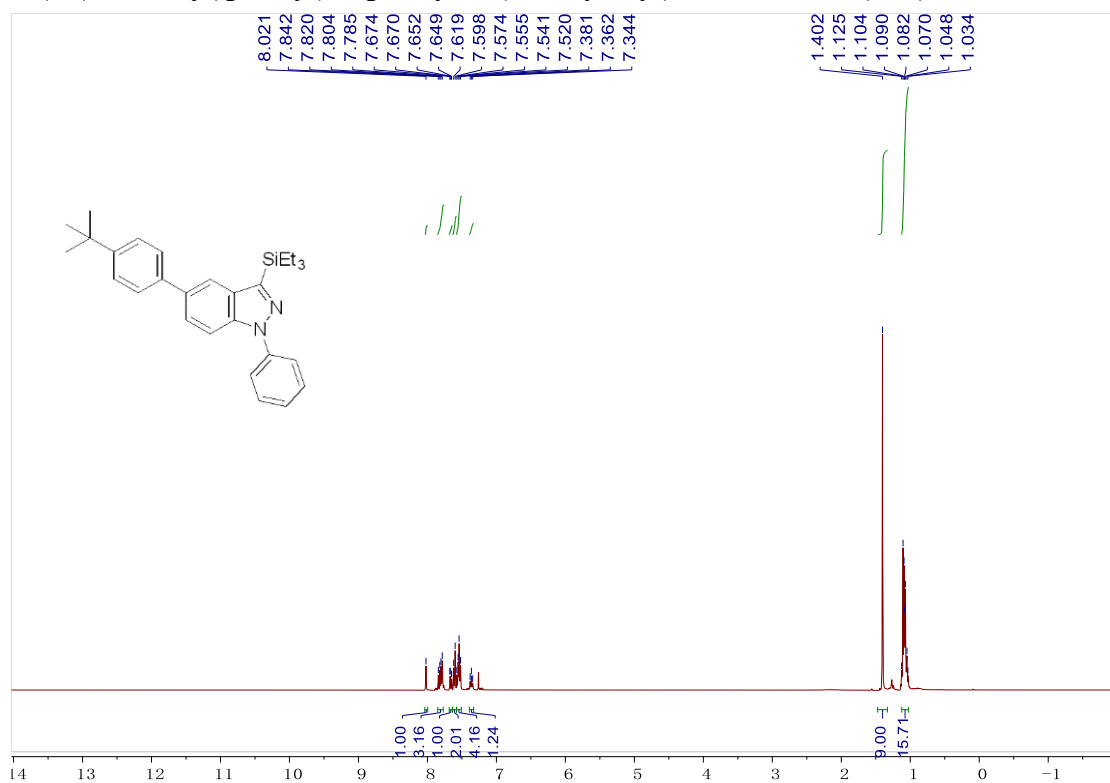
1,4-Diphenyl-3-(triethylsilyl)-1*H*-indazole (37b)



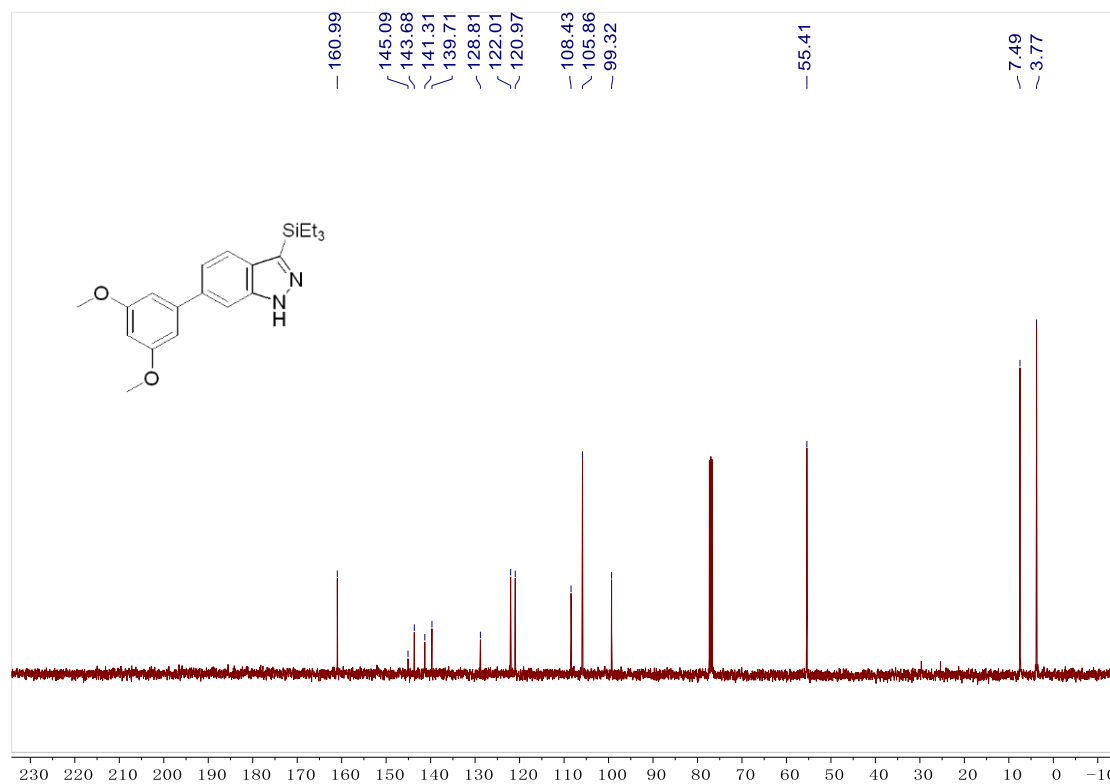
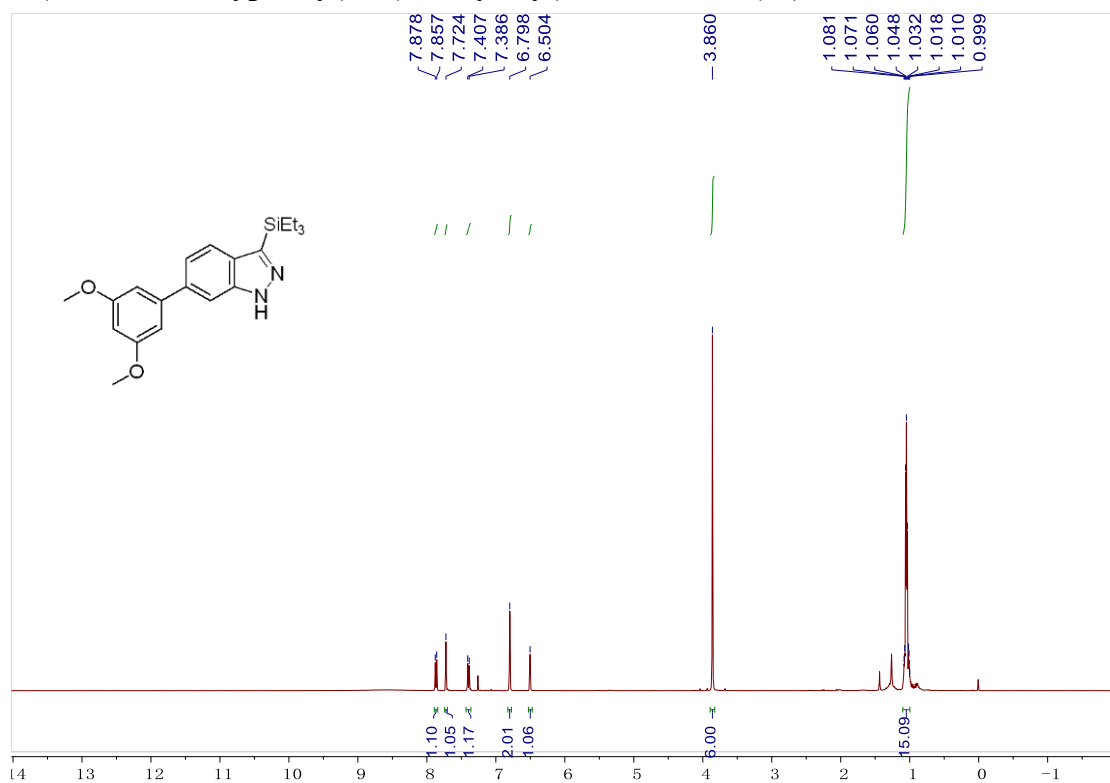
5-(4-(*tert*-Butyl)phenyl)-3-(triethylsilyl)-1*H*-indazole (38)



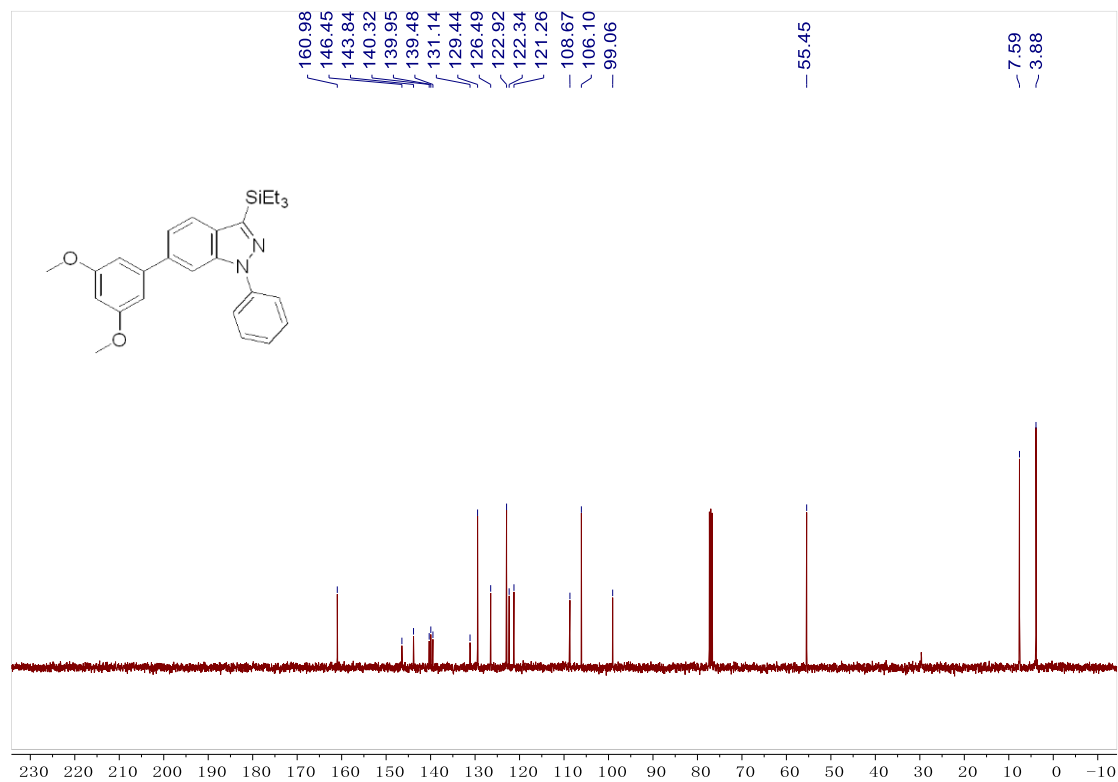
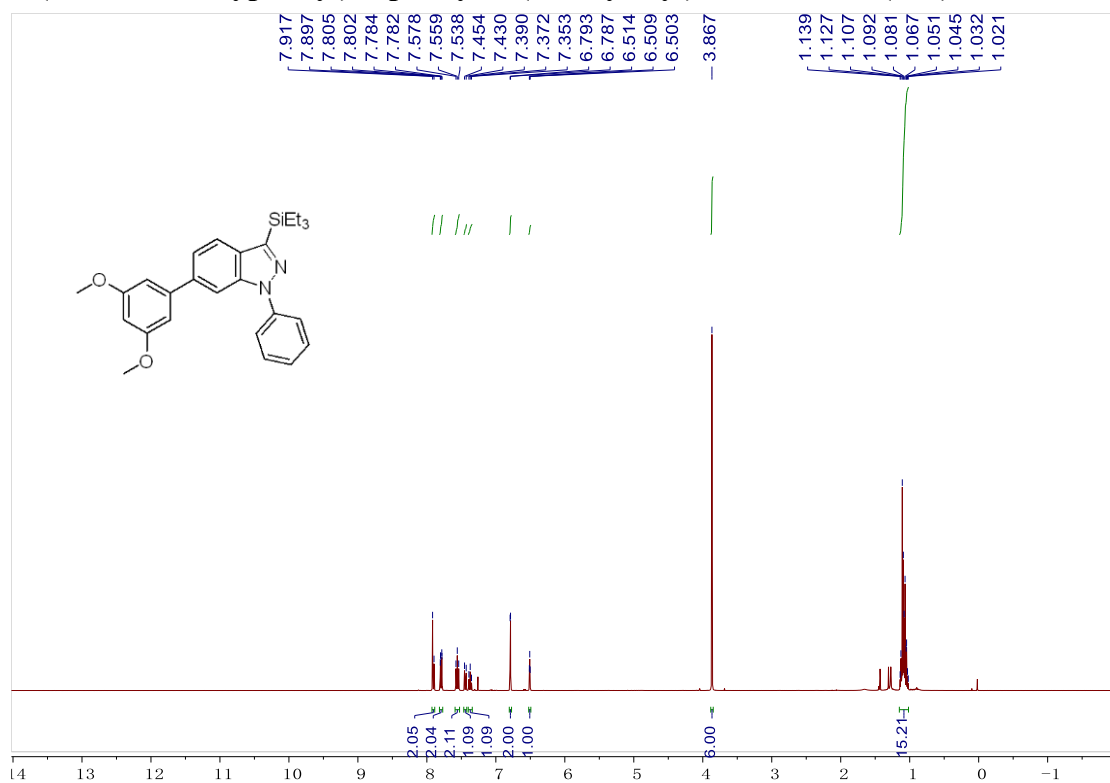
5-(4-*tert*-Butylphenyl)-1-phenyl-3-(triethylsilyl)-1*H*-indazole (38b)



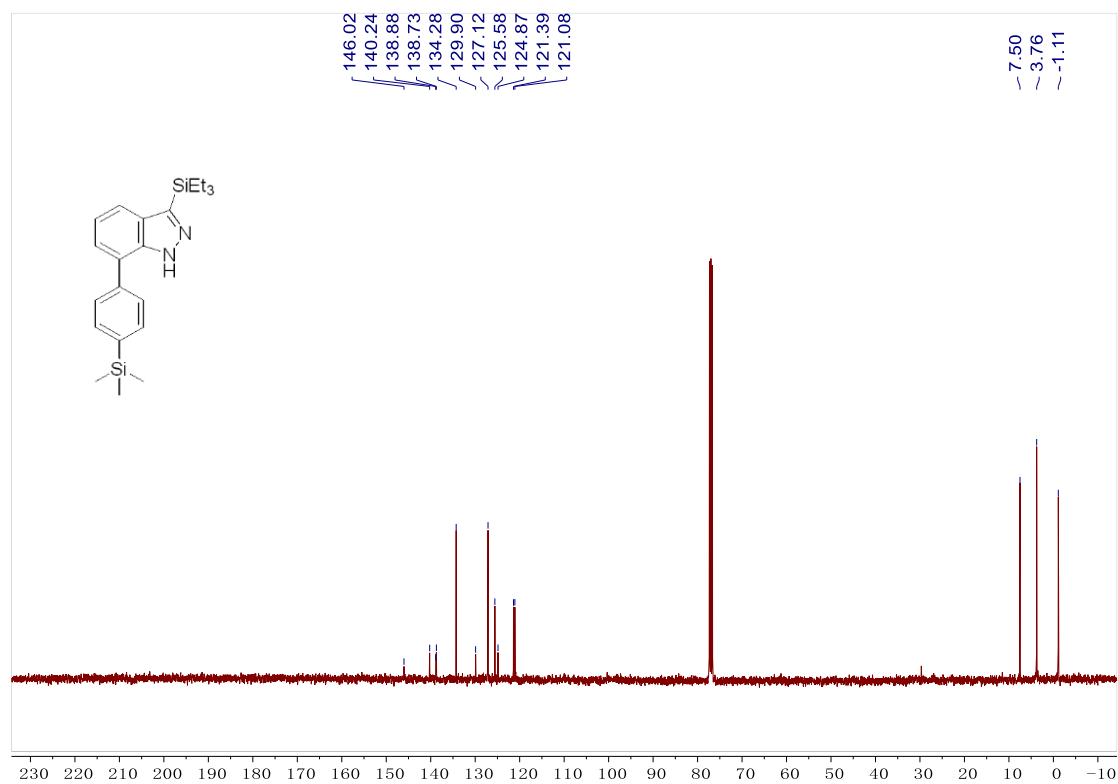
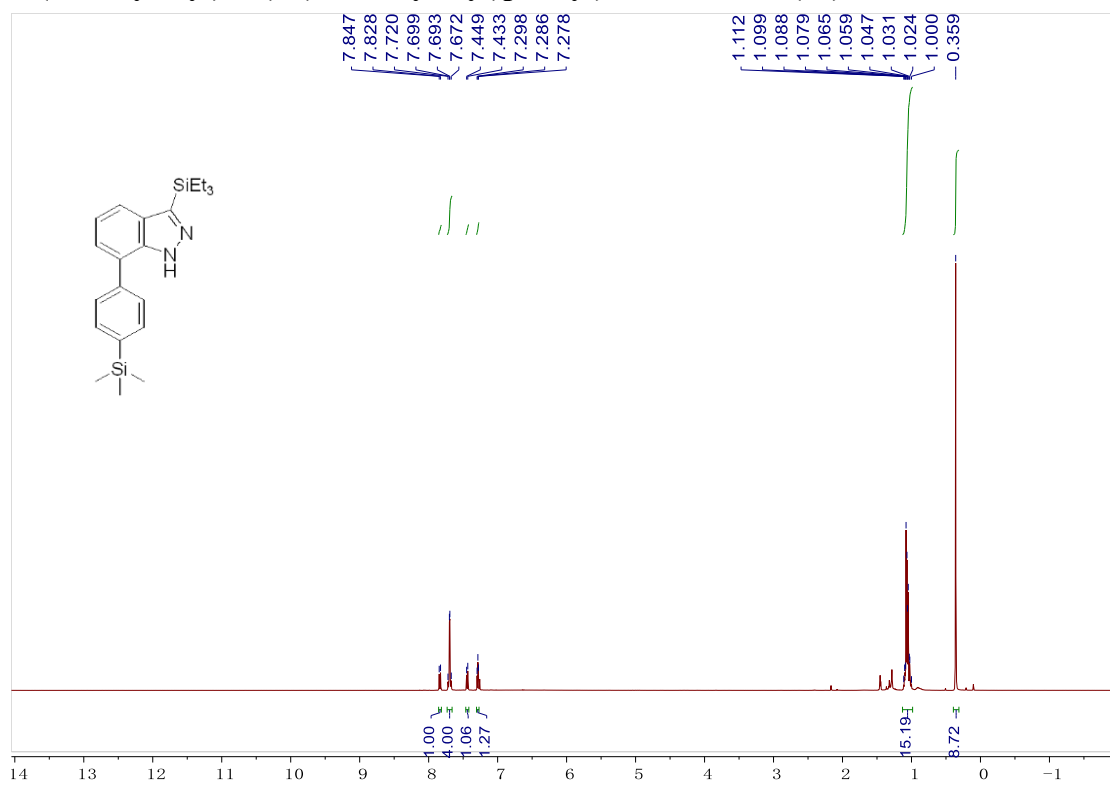
6-(3,5-Dimethoxyphenyl)-3-(triethylsilyl)-1H-indazole (39)



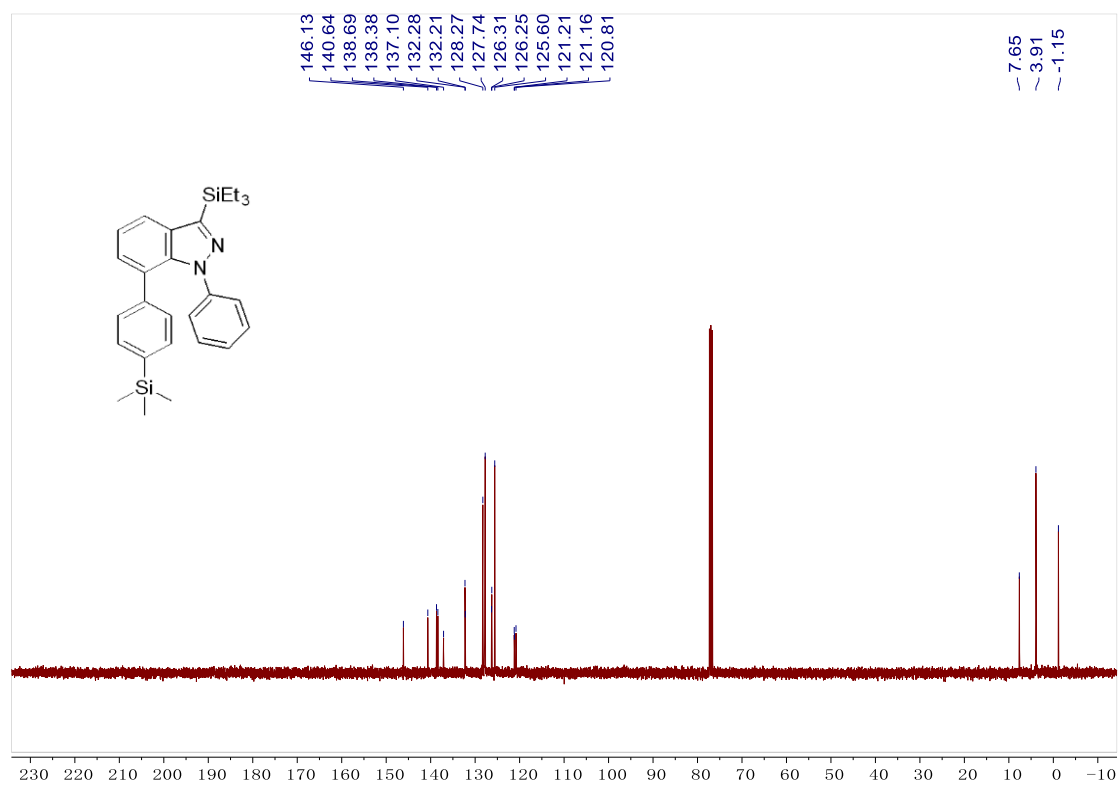
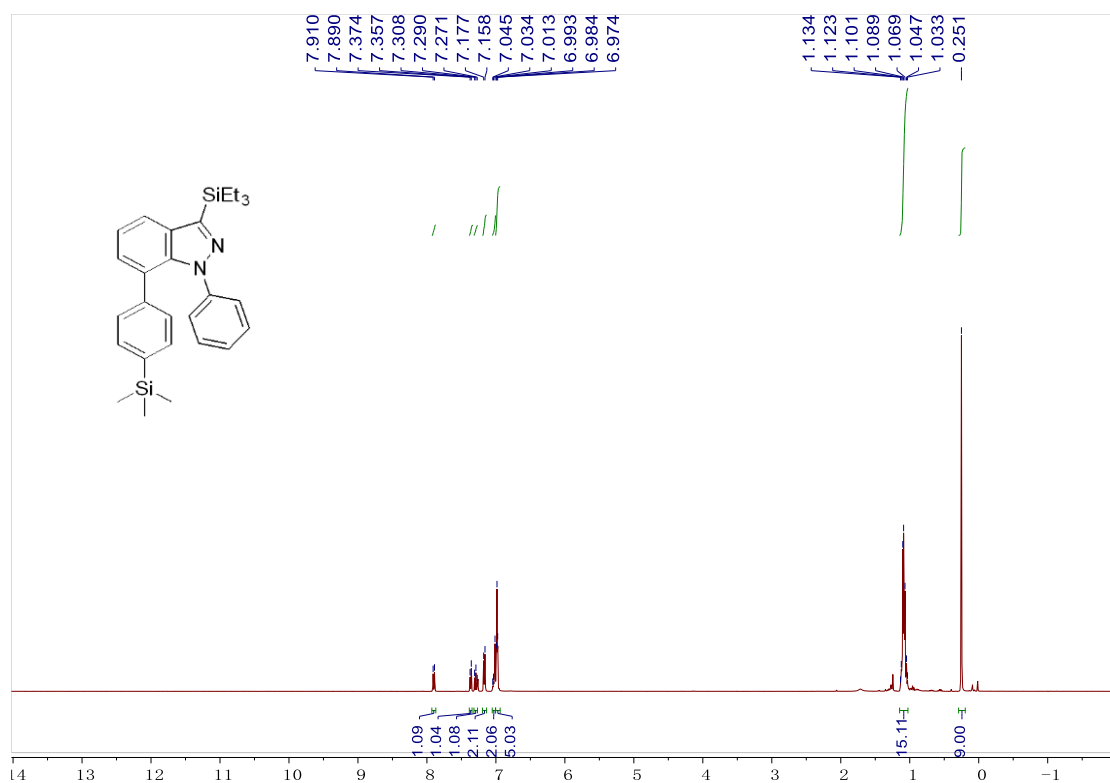
6-(3,5-Dimethoxyphenyl)-1-phenyl-3-(triethylsilyl)-1H-indazole (39b)



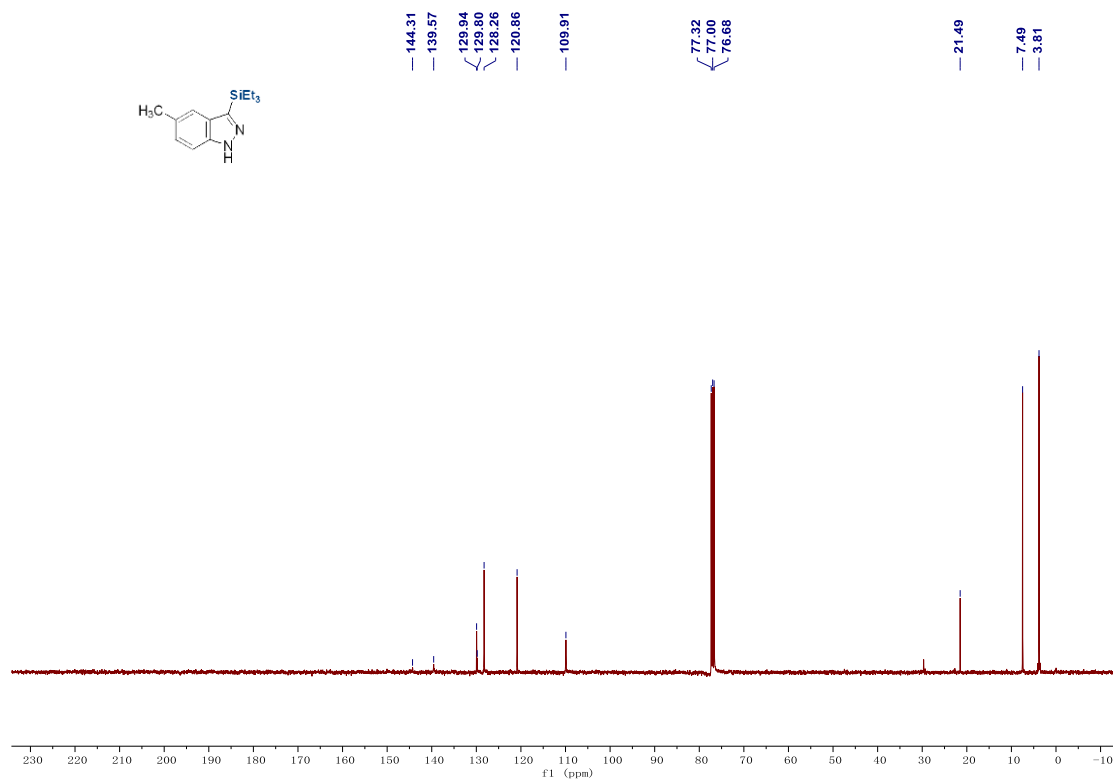
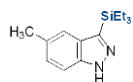
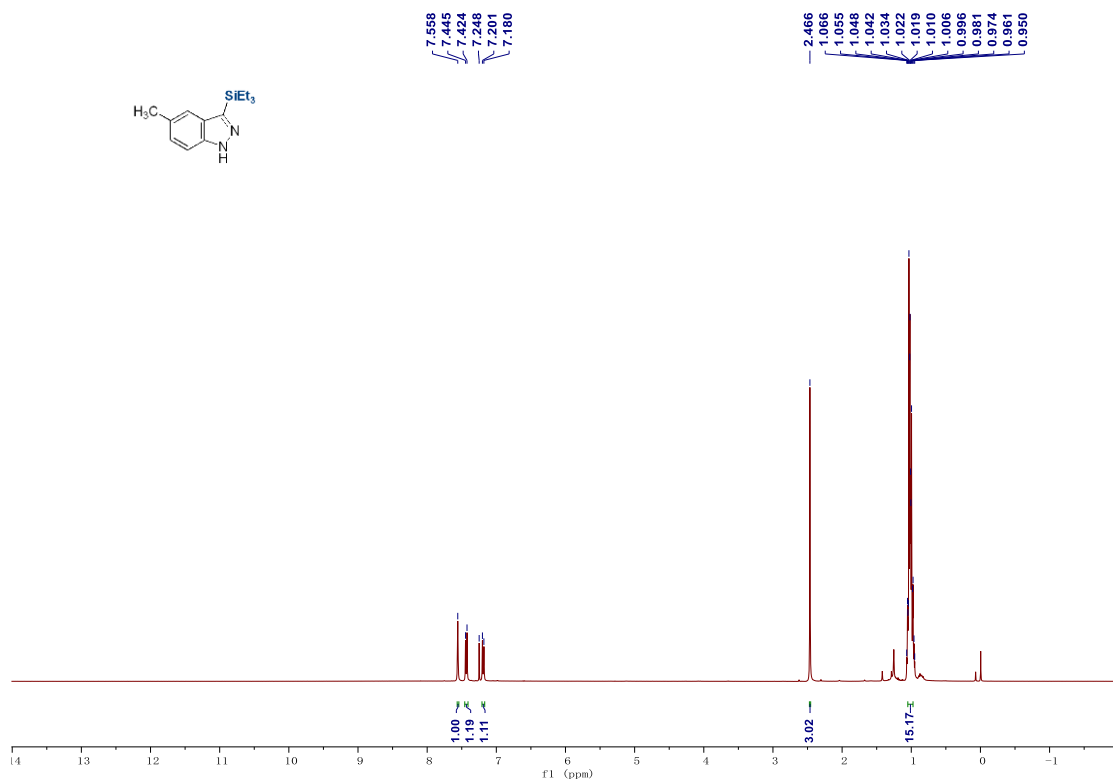
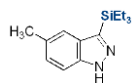
3-(Triethylsilyl)-7-(4-(trimethylsilyl)phenyl)-1H-indazole (40)



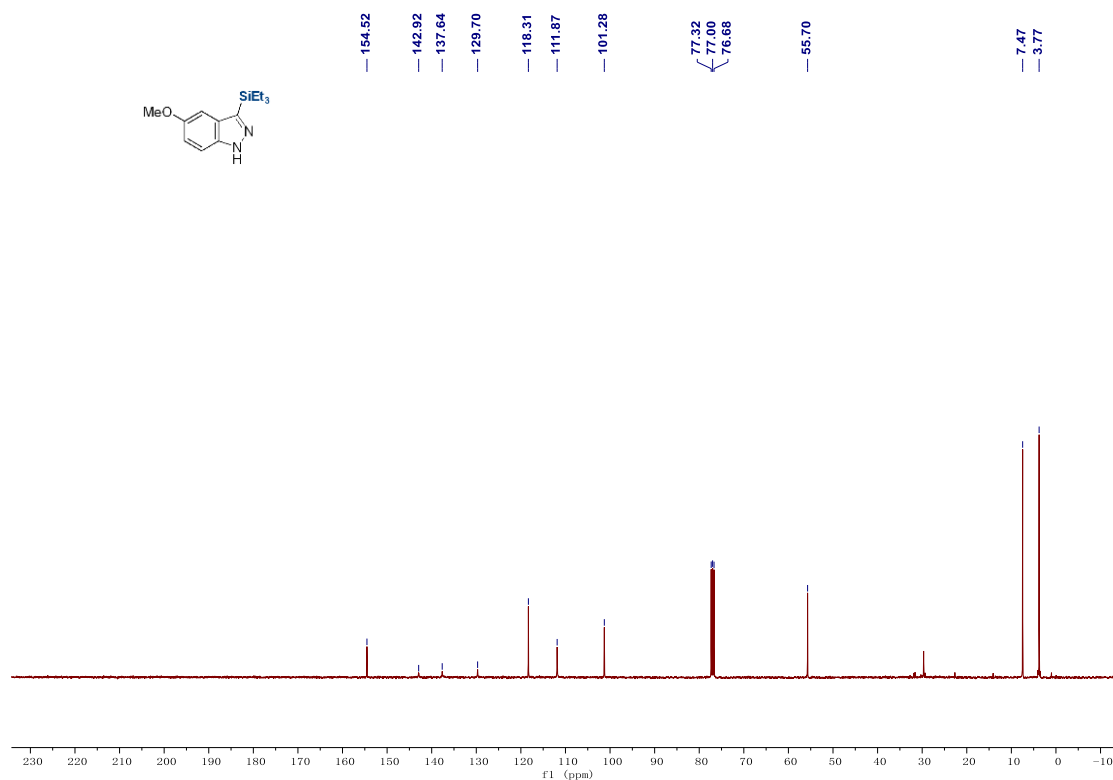
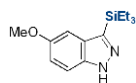
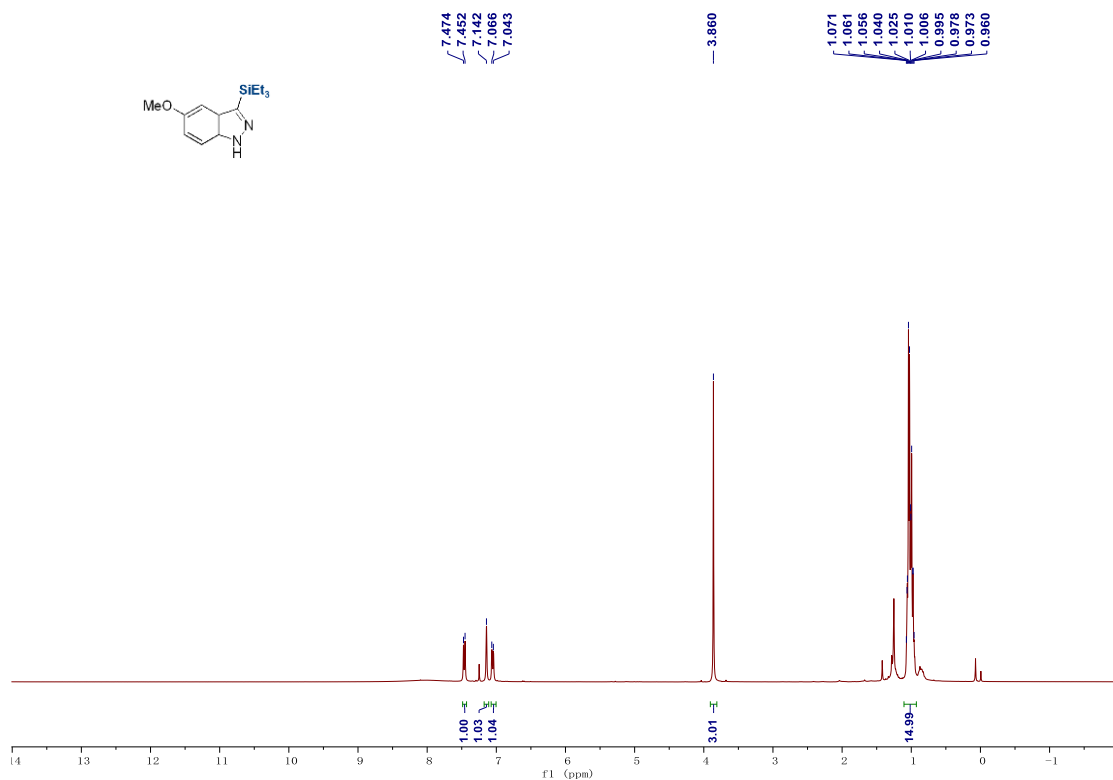
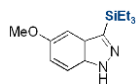
1-phenyl-3-(triethylsilyl)-7-(4-(trimethylsilyl)phenyl)-1H-indazole (40b).



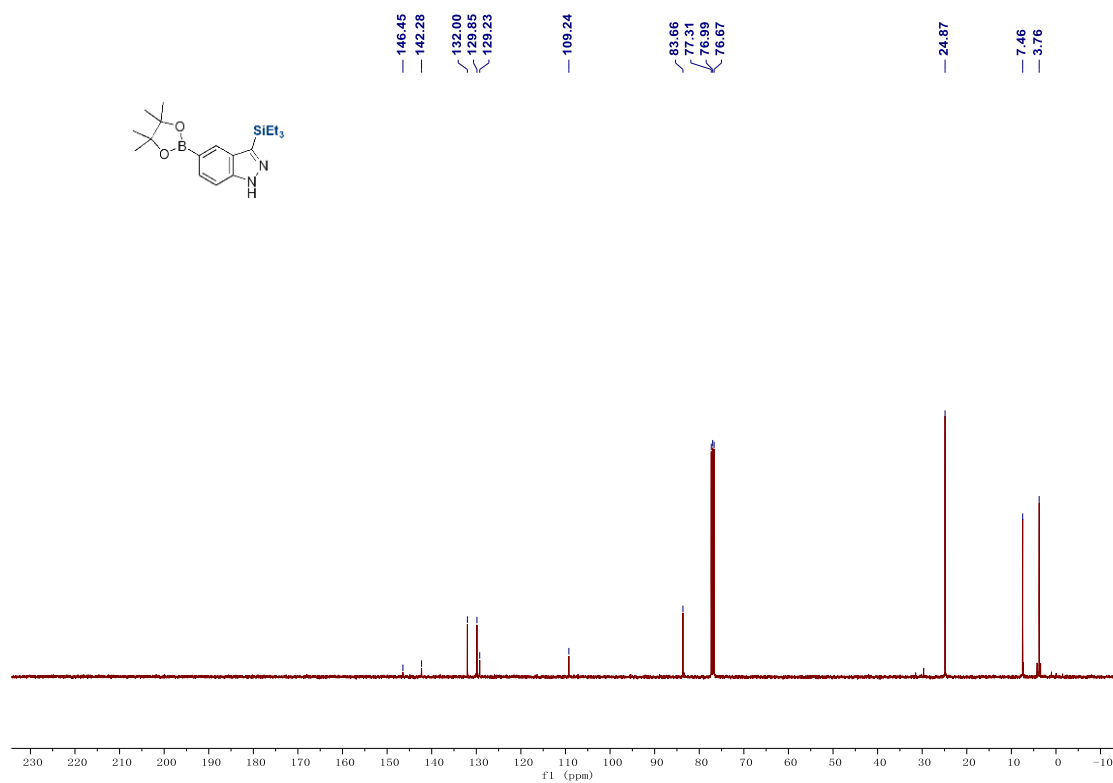
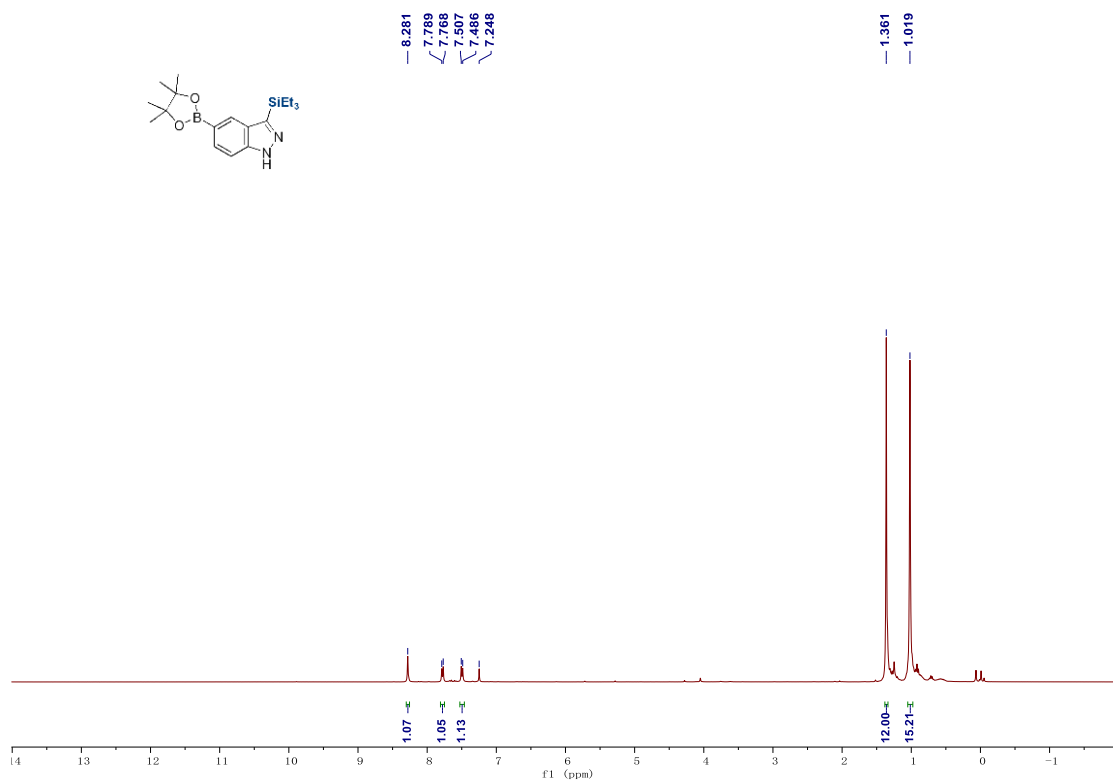
5-Methyl-3-(triethylsilyl)-3a,7a-dihydro-1H-indazole (41)



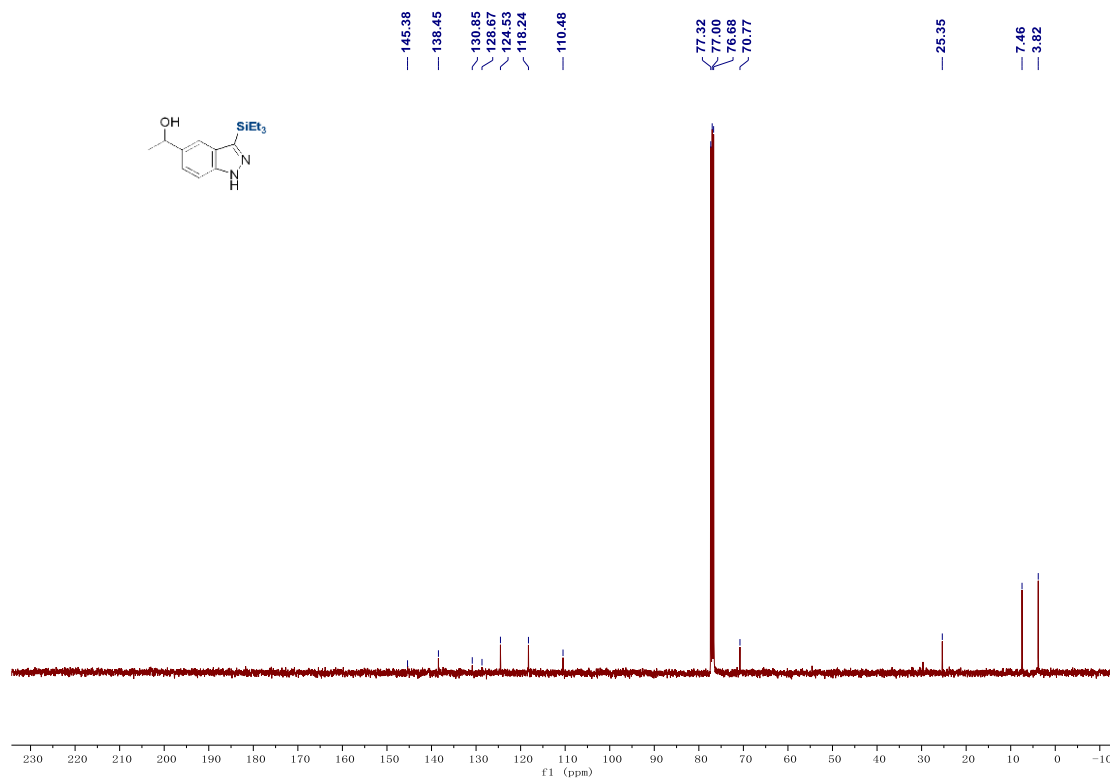
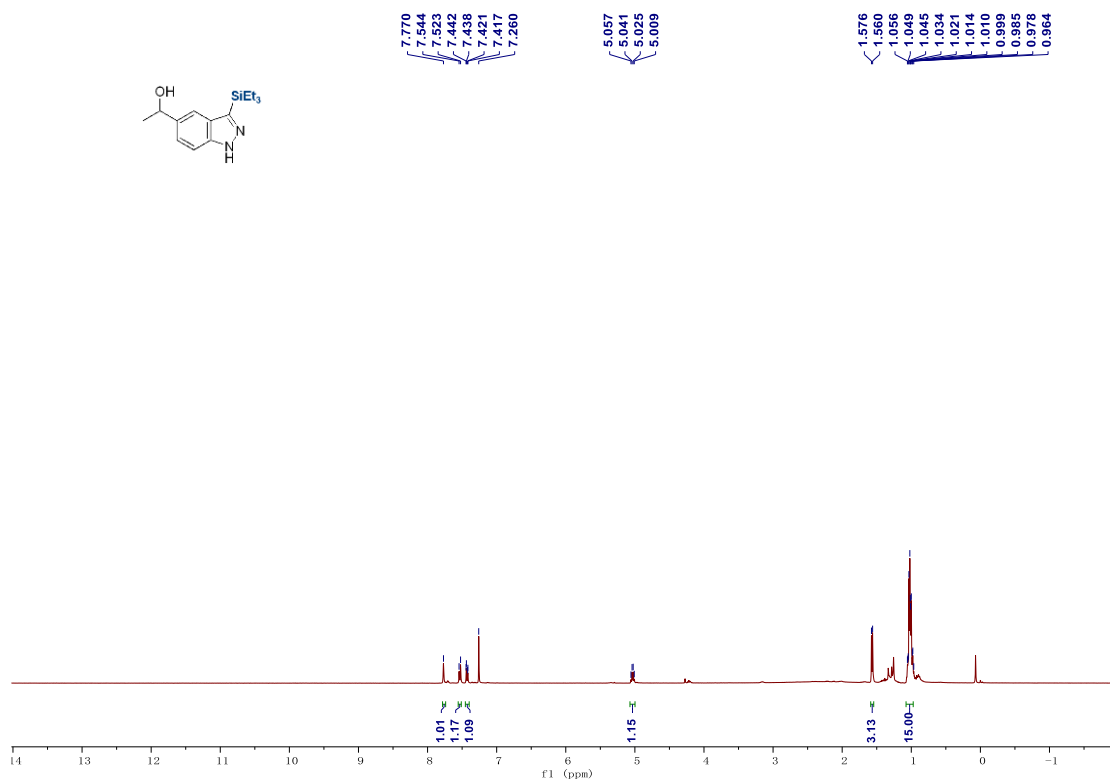
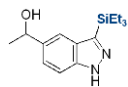
5-Methoxy-3-(triethylsilyl)-3a,7a-dihydro-1H-indazole (42)



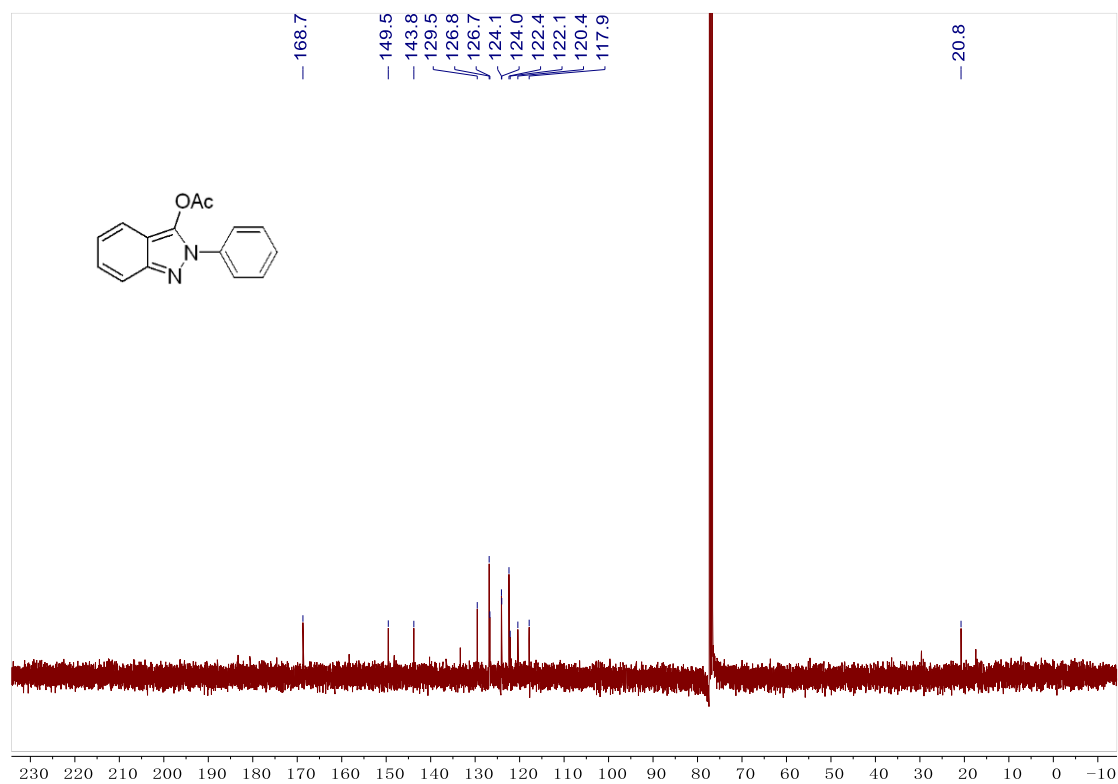
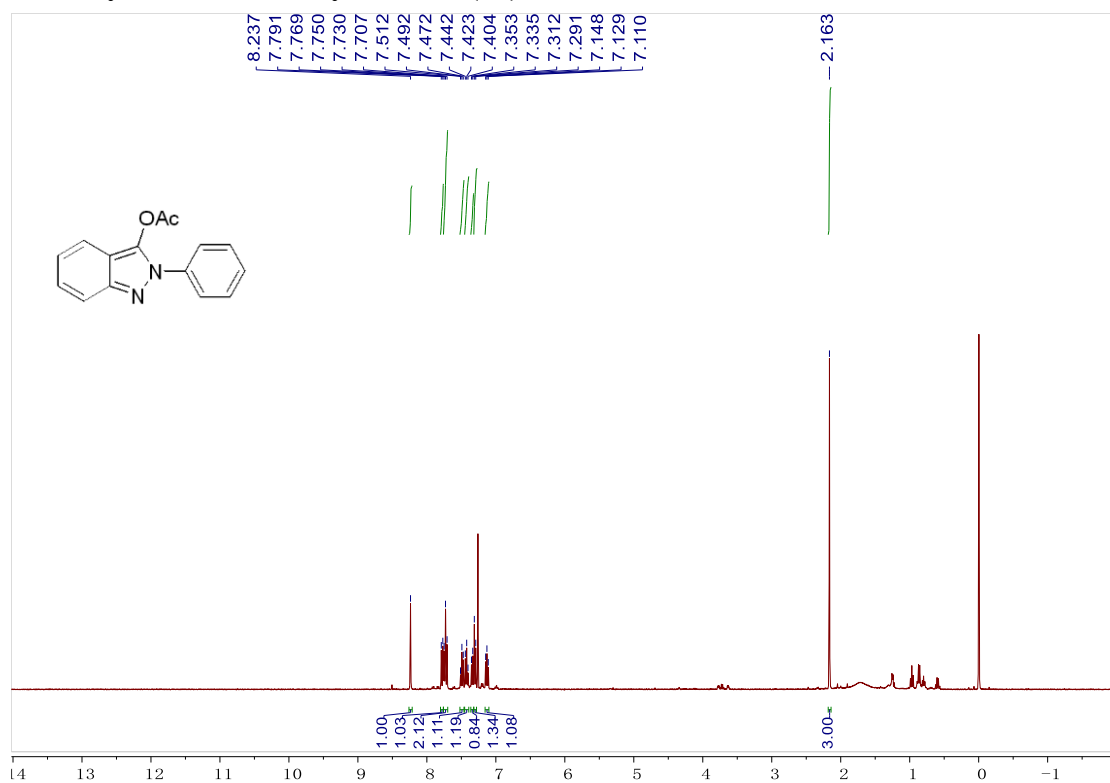
5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(triethylsilyl)-1H-indazole(43)



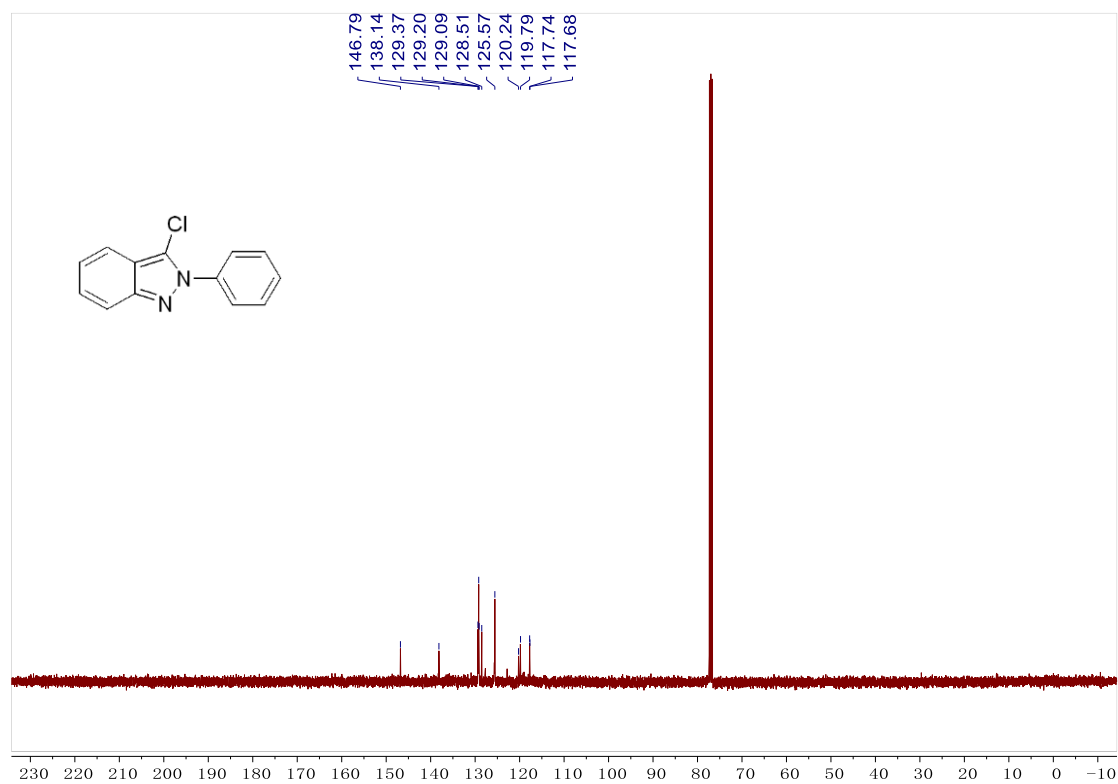
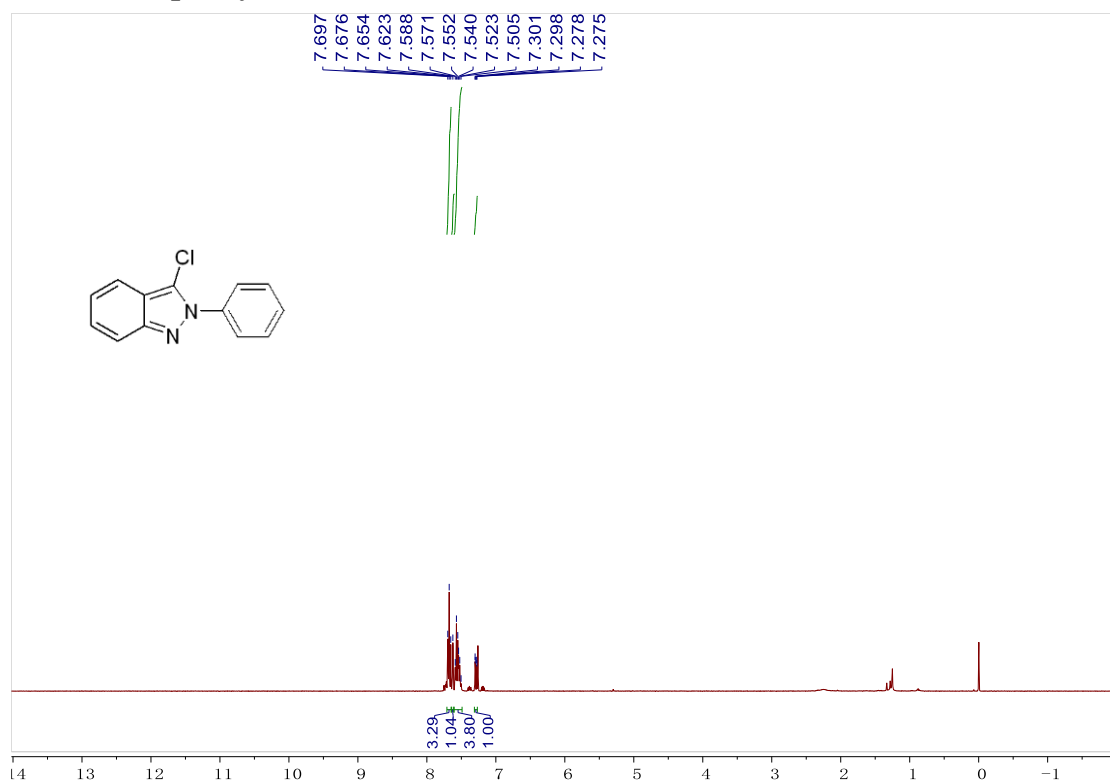
5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(triethylsilyl)-1H-indazole(44)



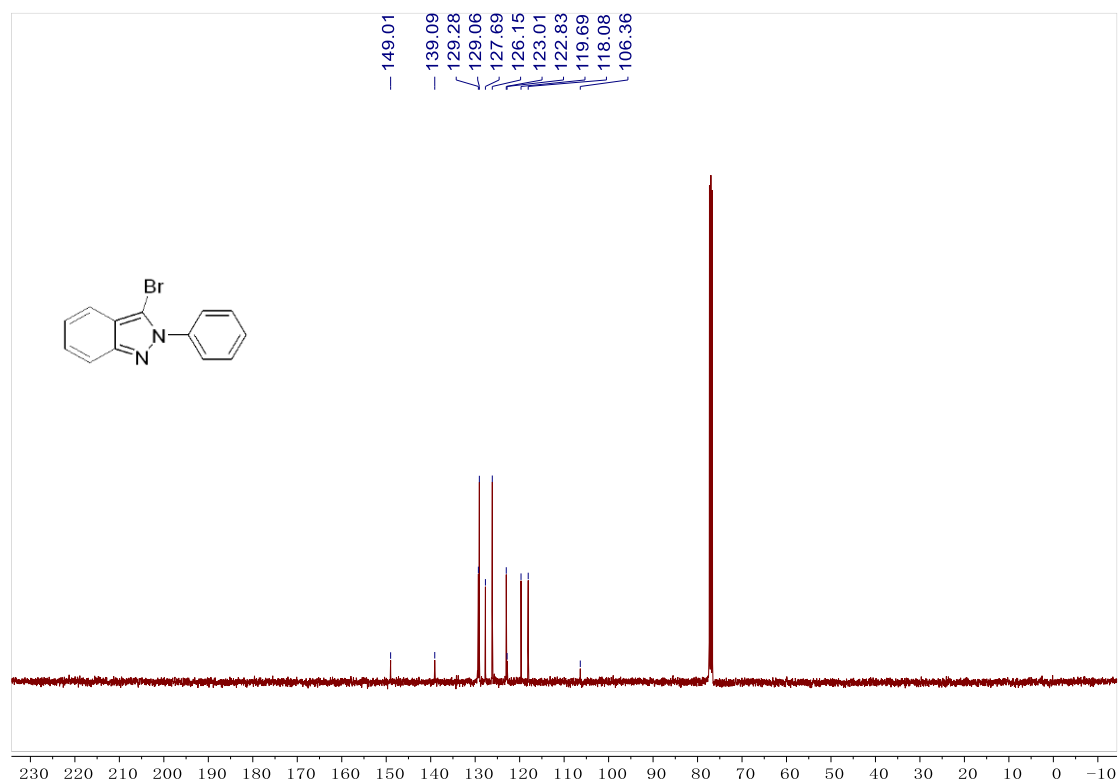
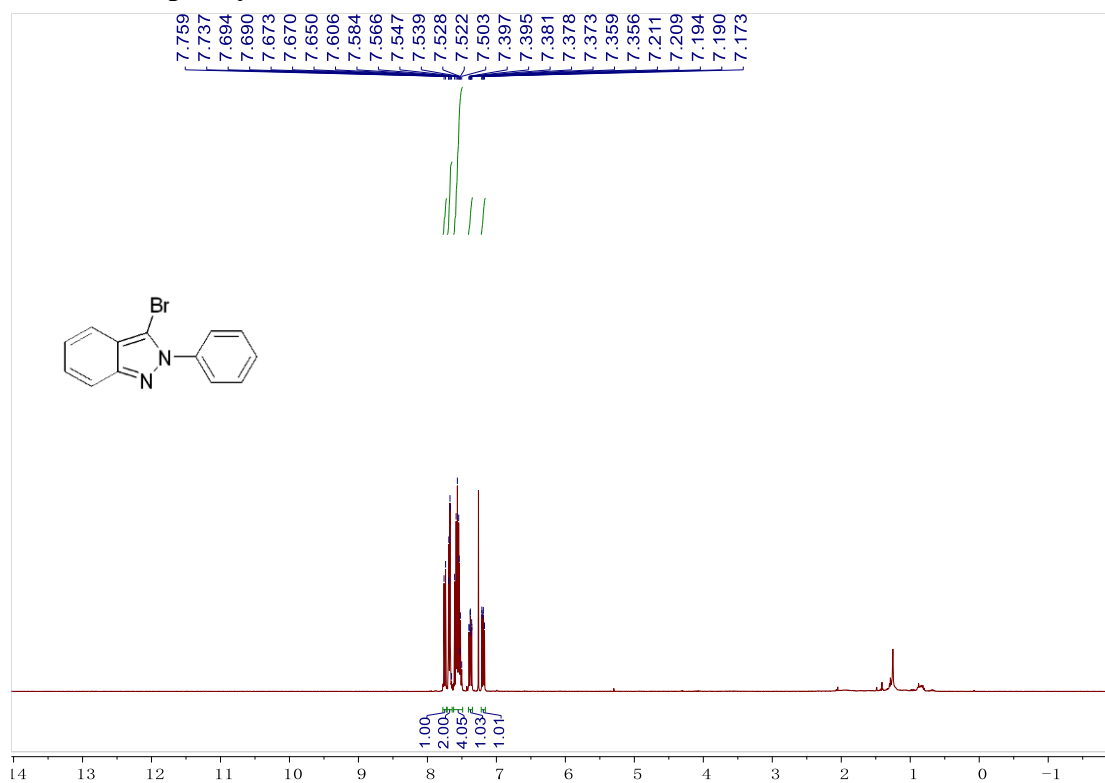
2-Phenyl-2H-indazol-3-yl acetate (45)



3-Chloro-2-phenyl-2H-indazole (46)



3-Bromo-2-phenyl-2H-indazole (47)



3-Iodo-2-phenyl-2H-indazole (48)

