Supplementary Information

Manganese-Mediated C(sp)–Si Cross-Electrophile Coupling of Alkynyl Halides with Chlorosilanes

Quan Lin, Liping Lin, Jingjing Wang, Daohong Yu*, Zhengwang Chen* and Zhong-Xia Wang*

Jiangxi Provincial Key Laboratory of Synthetic Pharmaceutical Chemistry, College of Chemistry and Materials Science, Gannan Normal University, Ganzhou 341000, P.R. China.

zhongxiawang@ncu.edu.cn, chenzwang2021@163.com, yudh@gnnu.edu.cn

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I. Experimental Section

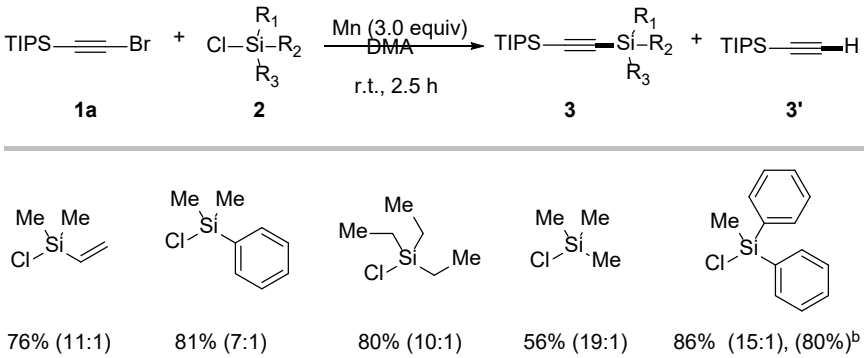
Part 1. General Information.

Unless otherwise mentioned, all reactions were performed under an atmosphere of argon using anhydrous solvents in a flame-dried Schlenk tube. THF was distilled under an argon atmosphere from sodium-benzophenone. DMA (*N,N*-dimethylacetamide, 99.5%, extra dry, Acros), DMF (*N,N*-dimethylformamide, 99.5%, extra dry, Across), NMP (N-Methyl-2-pyrrolidone, 99.5%, extra dry, Acros), MeCN (Acetonitrile, 99.5%, extra dry, Acros), DCE (1,2-Dichloroethane, 99.5%, extra dry, Acros), DME (1,2-Dimethoxyethane, 99.5%, extra dry, Acros), PhCl (chlorobenzene, 99.5%, extra dry, Acros), PC (Propylene carbonate, 99.5%, extra dry, Acros) and DMSO (Dimethyl sulfoxide, 99.5%, extra dry, Acros) were purchased and used directly. Deuterated solvents were used as received ($CDCl_3$ from Meryer Co., China, and DMSO-d_6 from Cambridge Isotope Laboratories). Mn powder (Energy Chemical Co., China) was purchased and stored under an argon atmosphere. Chlorosilanes or chlorogermanes (Adamas-beta Co., China) were purchased and used directly. Alkynyl bromides were either obtained from commercial suppliers or prepared according to literature procedures. Column chromatography was performed using silica gel 200-300 mesh (purchased from Qingdao-Haiyang Co., China) as the solid support. All NMR spectra were recorded on Bruker Avance 400 MHz spectrometers. ^{1}H NMR and ^{13}C NMR chemical shifts are reported in δ units, parts per million (ppm) relative to the chemical shift of residual solvent. Reference peaks for chloroform in ^{1}H NMR and ^{13}C NMR spectra were set at 7.260 ppm and 77.0 ppm, respectively. GC analyses were performed on a Shimadzu GC-2014 equipped with HP-5 columns (30 m × 320 μm × 0.25 μm), FID detectors, and hydrogen as the carrier gas. GC/MS analyses were performed on a Shimadzu GCMS-QP2010 equipped with an RTX-5MS column (30 m × 0.25 mm × 0.25 μm) with a quadrupole mass analyzer using helium as the carrier gas. High-resolution mass spectra (HRMS) were obtained using Bruker APEXIII 7.0 or IonSpec 4.7 TESLA FTMS instruments. Melting points were recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China).

Part 2. Optimization and Control Experiments

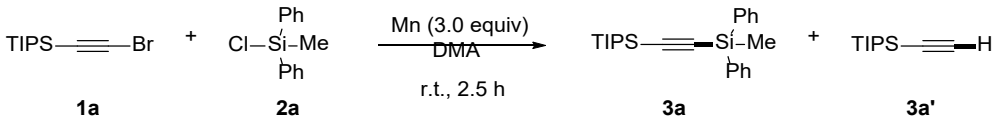
Typical procedure: A flame-dried tube equipped with a magnetic stir bar was loaded with alkynyl bromides (if solid), chlorosilanes (if solid), and manganese powder. Then was capped with a rubber septum, and it was evacuated and refilled with Ar three times. Solvent, alkynyl bromides (if liquid), and chlorosilanes (if liquid) were then added via a syringe. The reaction mixture was allowed to stir at room temperature for 2.5 h, after the reaction, the mixture was quenched by HCl (1M) aqueous, and extracted by EA. The yield of the target compound was determined using dodecane as the internal standard by GC analysis unless otherwise noted.

Table S1. Chlorosilanes attempting for this reductive cross-coupling reaction.[a]



[a] Reaction conditions: alkynyl bromide (0.15 mmol, 1 equiv.), chlorosilane (0.45 mmol, 3.0 equiv.), Mn (0.45 mmol, 3.0 equiv), DMA (1 mL), 25 ℃, Ar, yields, and the ratio of **3**/**3'** were determined by GC using dodecane as the internal standard. [b] Isolated yield.

Table S2. Variations and additives for this reductive cross-coupling reaction.[a]

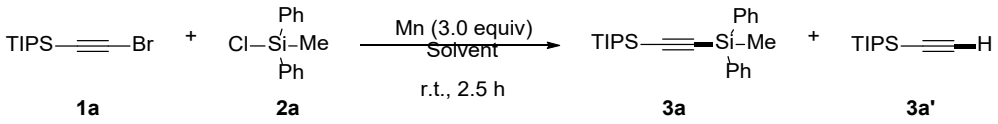


1a **2a** **3a** **3a'**

Entry	Conditions	**3a** (%)	**3a'** (%)
1	3.0 equiv. Cu instead of Mn	n.d.[b]	n.d.
2	3.0 equiv. In instead of Mn	n.d.	28
3	3.0 equiv. $MnCl_2$ instead of Mn	n.d.	n.d.
4	0.1 equiv. $MnCl_2$ instead of Mn	n.d.	n.d.
5	3.0 equiv. $MnBr_2$ instead of Mn	n.d.	n.d.
6	0.1 equiv. $MnBr_2$ instead of Mn	n.d.	n.d.
7	0.2 equiv. Mn	10	4
8	0.5 equiv. Mn	45	19
9	1 equiv. Mn	71	25
10	2 equiv. Mn	78	14
11	0.2 equiv. H_2O was added	62	30
12	0.5 equiv. H_2O was added	50	45
13	1 equiv. H_2O was added	13	69

[a] Reaction conditions: alkynyl bromide (0.15 mmol, 1 equiv.), chlorosilane (0.45 mmol, 3.0 equiv.), Mn (0.45 mmol, 3.0 equiv), DMA (1 mL), 25 ℃, Argon, yields were determined by GC using dodecane as the internal standard. [b] Isolated yield. n.d. = not detected.

Table S3. Solvent screening for this reductive cross-coupling reaction.[a]

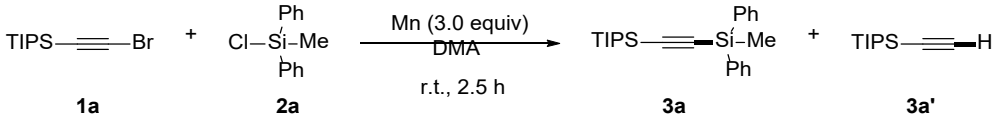


1a **2a** **3a** **3a'**

Entry	Solvent	**3a** (%)	**3a'** (%)
1	NMP	52	8
2	DMF	52	15
3	DME	n.d.	trace
4	DCE	n.d.	n.d.
5	DMSO	n.d.	trace
6	chlorobenzene	n.d.	n.d.
7	THF	n.d	trace
8	PC	n.d	trace
9	CH_3CN	n.d	trace
10	1,4-dioxane	n.d	trace
11	Toluene	n.d	n.d.

[a] Reaction conditions: alkynyl bromide (0.15 mmol, 1 equiv.), chlorosilane (0.45 mmol, 3.0 equiv.), Mn (0.45 mmol, 3.0 equiv), DMA (1 mL), 25 ℃, Argon, yields were determined by GC using dodecane as the internal standard. [b] Isolated yield. n.d. = not detected.

Table S4. Temperature screening for this reductive cross-coupling reaction.[a]



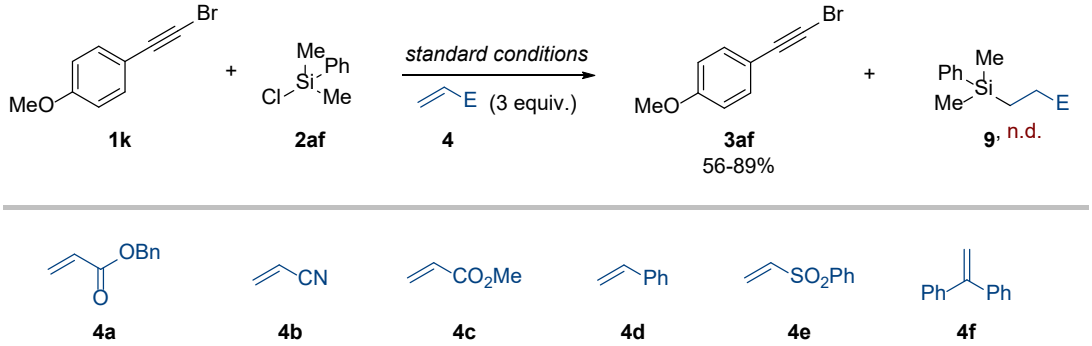
1a **2a** **3a** **3a'**

Entry	Conditions	**3a** (%)[a]	**3a'** (%)[a]
1	-10℃ instead of r.t	30	7
2	0℃ instead of r.t	46	15
3	10℃ instead of r.t	44	10
4	40℃ instead of r.t	81	36
5	60℃ instead of r.t	75	39

[a] Reaction conditions: alkynyl bromide (0.15 mmol, 1 equiv.), chlorosilane (0.45 mmol, 3.0 equiv.), Mn (0.45 mmol, 3.0 equiv), DMA (1 mL), 25 ℃, Argon, yields were determined by GC using dodecane as the internal standard. [b] Isolated yield.

Part 3. Mechanistic Studies

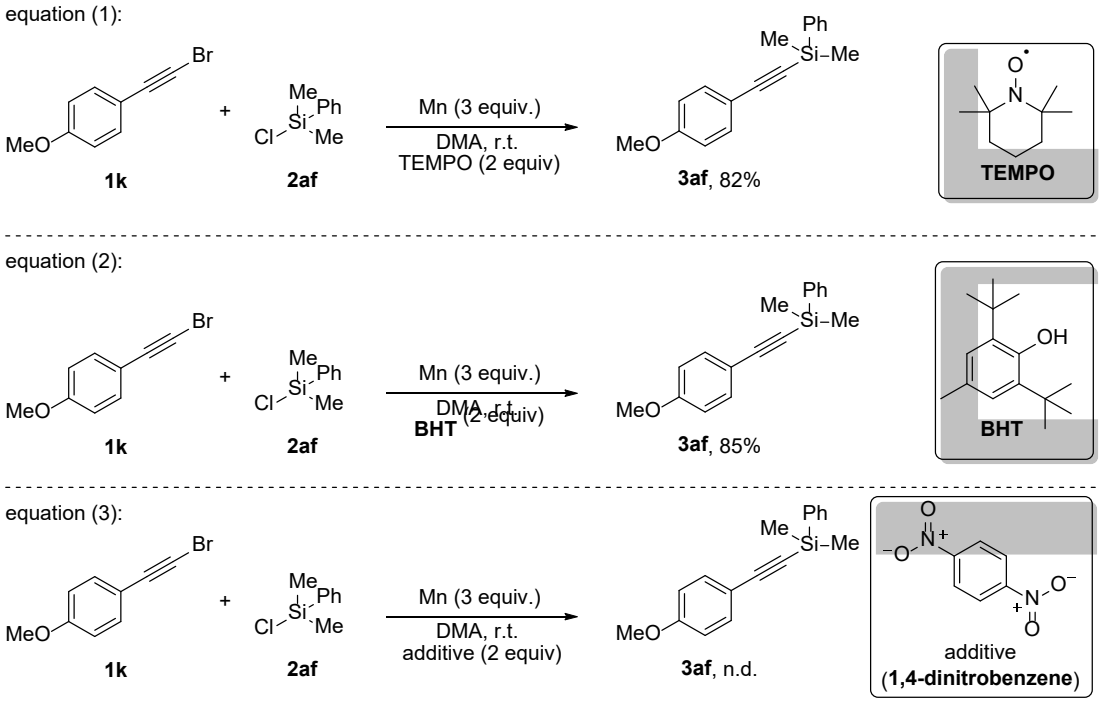
3.1 Radical trapping experiments



Scheme S1. Radical trapping experiments.

Experimental procedure: The procedure was conducted in an argon-filled glove box. To a flame-dried Schlenk tube equipped with a magnetic stir bar was added alkynyl bromide **1k** (31.7 mg, 0.15 mmol), chlorosilane **2af** (76.8 mg, 0.45 mmol), alkene **4** (if it is a solid, 0.45 mmol, 3 equiv.) and Mn (24.7 mg, 0.45 mmol). The tube was capped with a rubber septum and then evacuated and refilled with argon three times. Then alkene **4** (if it is a liquid, 0.45 mmol, 3 equiv.) and DMA (1.0 mL) were added via syringes. After stirring at room temperature for 2.5 h, the reaction mixture was diluted with ethyl acetate (5 mL) and washed with HCl (1M) aqueous. A 0.2 mL of solution was collected, diluted with ethyl acetate (1 mL), and used for GC analysis.

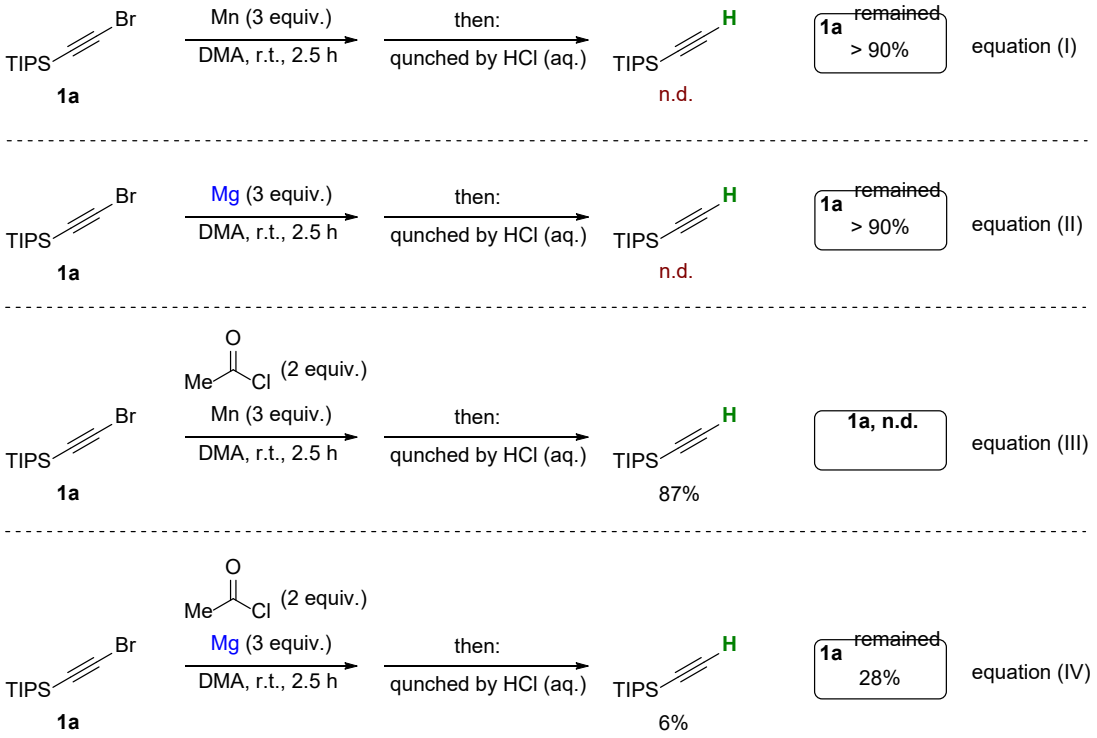
3.2 Radical trapping and SET inhibiting experiments



Scheme S2. Radical trapping and SET-inhibiting experiments

Experimental procedure: The procedure was conducted in an argon-filled glove box. To a flame-dried Schlenk tube equipped with a magnetic stir bar was added alkynyl bromide **1k** (31.7 mg, 0.15 mmol), chlorosilane **2af** (76.8 mg, 0.45 mmol), additives **TEMPO** or **BHT** or **9,10-dihydroanthracene** (0.3 mmol, 2 equiv.) and Mn (24.7 mg, 0.45 mmol). The tube was capped with a rubber septum and then evacuated and refilled with argon three times. Then DMA (1.0 mL) was added via syringes. After stirring at room temperature for 2.5 h, the reaction mixture was diluted with ethyl acetate (5 mL) and washed with HCl (1M) aqueous. A 0.2 mL of solution was collected, diluted with ethyl acetate (1 mL), and used for GC analysis.

3.3 Preparation and conversion experiments of alkynylmetallic species

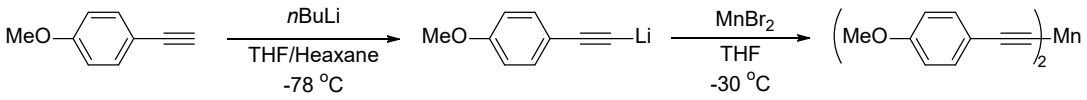


Scheme S3. Preparation and conversion experiments of alkynylmetallic species

Experimental procedure: The procedure was conducted in an argon-filled glove box. To a flame-dried Schlenk tube equipped with a magnetic stir bar was added alkynyl bromide **1a** (39.2 mg, 0.15 mmol), and Mn (24.7 mg, 0.45 mmol) or Mg (10.9 mg, 0.45 mmol). The tube was capped with a rubber septum and then evacuated and refilled with argon three times. Then AcCl (0.3 mmol, if needed) and DMA (1.0 mL) were added via syringes. After stirring at room temperature for 2.5 h, the reaction mixture was quenched with HCl (1M) aqueous and the reaction mixture was diluted with ethyl acetate (2 ~ 5 mL). A 0.2 mL of solution was collected, diluted with ethyl acetate (1 mL), and used for GC analysis.

3.4 Preparation and verification of alkynylmanganese compound

(I) the path for the synthesis of 1ki

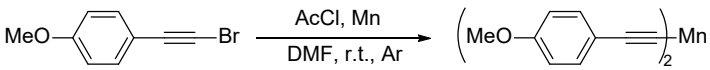


1kc **1kd** **1ki**

Experimental procedure: To a solution of manganese bromide (11.0 mmol, 1.1 equiv., in 6mL THF) was added **1kd** dropwise which was prepared from **1kc** (10.0 mmol, dissolved in THF 20 mL) and n-butyllithium (2.5 M solution in hexane, 4.0 mL, 10.0 mmol) under argon at -78 ℃. The resulting mixture was stirred for 6 h under argon at -30 ℃ until there was no more solid precipitation separated. Then remove the ice bath, the mixture was let sit for 10 minutes at room temperature to afford the organomanganese solution (**1ki**) as a clear solution. (The concentration was determined by iodine titration determined to be about 0.1 M).

HRMS (ESI) m/z ($[M+H]^+$) Calcd for $C_{18}H_{15}MnO_2$: 318.0447. Found: 318.0445.

(II) path b for the synthesis of 1ki

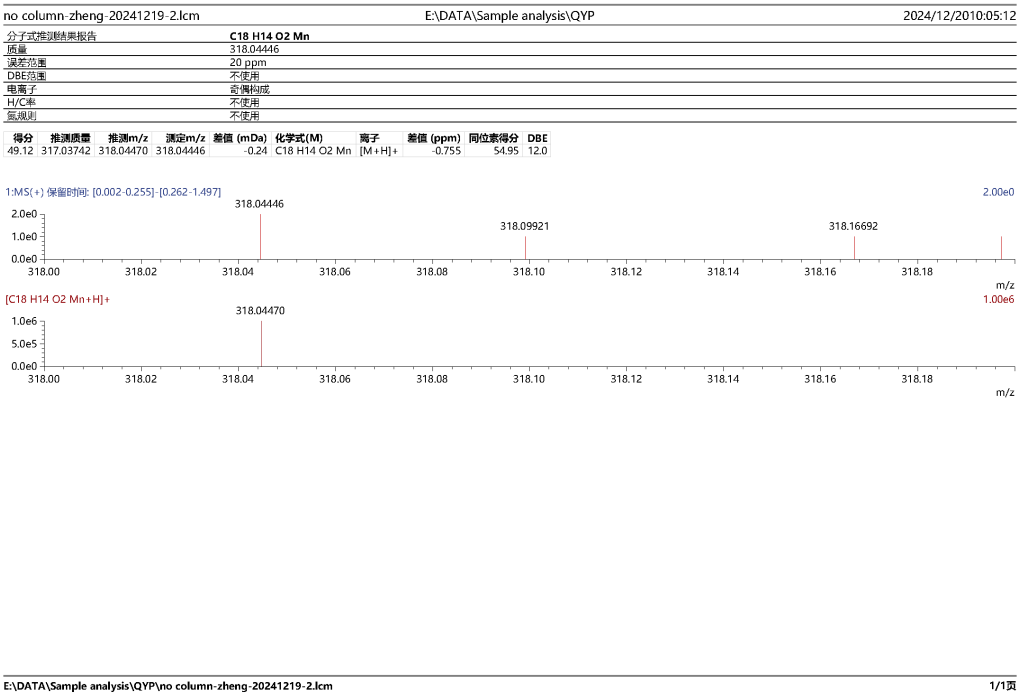


1k **1ki**

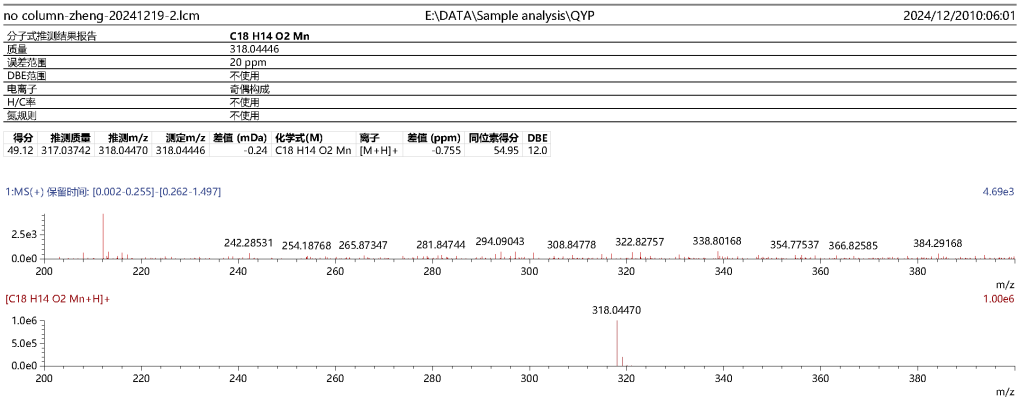
Experimental procedure: A flame-dried Schlenk tube equipped with a magnetic stir bar was added **1k** (0.15 mmol, 1.0 equiv.) and Mn (0.45 mmol, 3.0 equiv.). The tube was capped with a rubber septum and then evacuated and refilled with argon three times. Then AcCl (0.45 mmol, 3 equiv.), DMF (1.0 mL) was added via syringes. After stirring at room temperature for 6 h under Argon, the mixture was let sit for 10 minutes to afford the organomanganese solution (**1ki**) as a clear solution. The upper layer of the filtrate is then collected for the subsequent reaction.

HRMS (ESI) m/z ($[M+H]^+$) Calcd for $C_{18}H_{15}MnO_2$: 318.0447. Found: 318.0445.

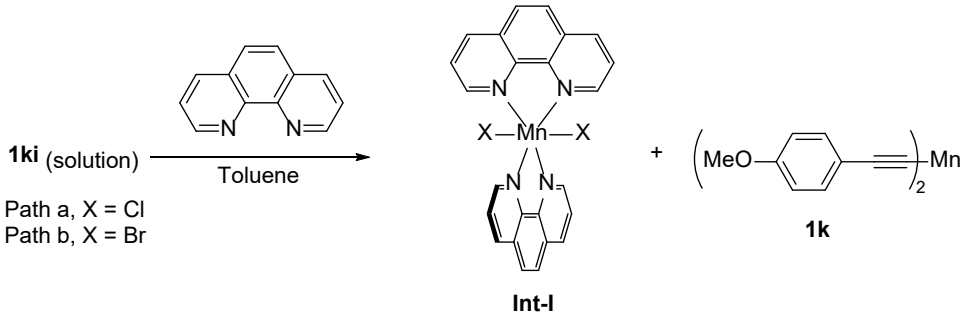
The partial mass spectroscopic figure of the sample (EIC-MS-data):



The full mass spectroscopic figure of the sample (TIC-MS-data):

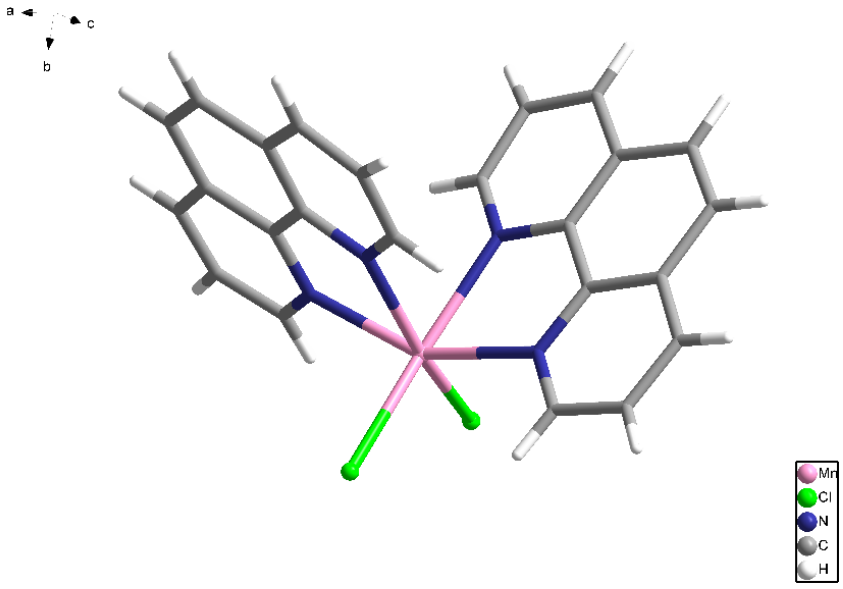


(III) synthesis of Int-I



Experimental procedure: A solution of Phen (0.15 mmol in toluene 0.5 mL) was added to **1ki** (0.15 mmol) solution in DMF (if obtained from path a) or THF (if obtained from path b), after stirring at room temperature under Argon until there is no more solid precipitation separated, then the mixture was filtered and washed with THF for three times, dried under vacuum for 30 min to afford pale yellow solid **Int-I** (X = Cl) or brown solid **Int-I** (X = Br).

Crystal structure of **Int-I** (X = Cl):

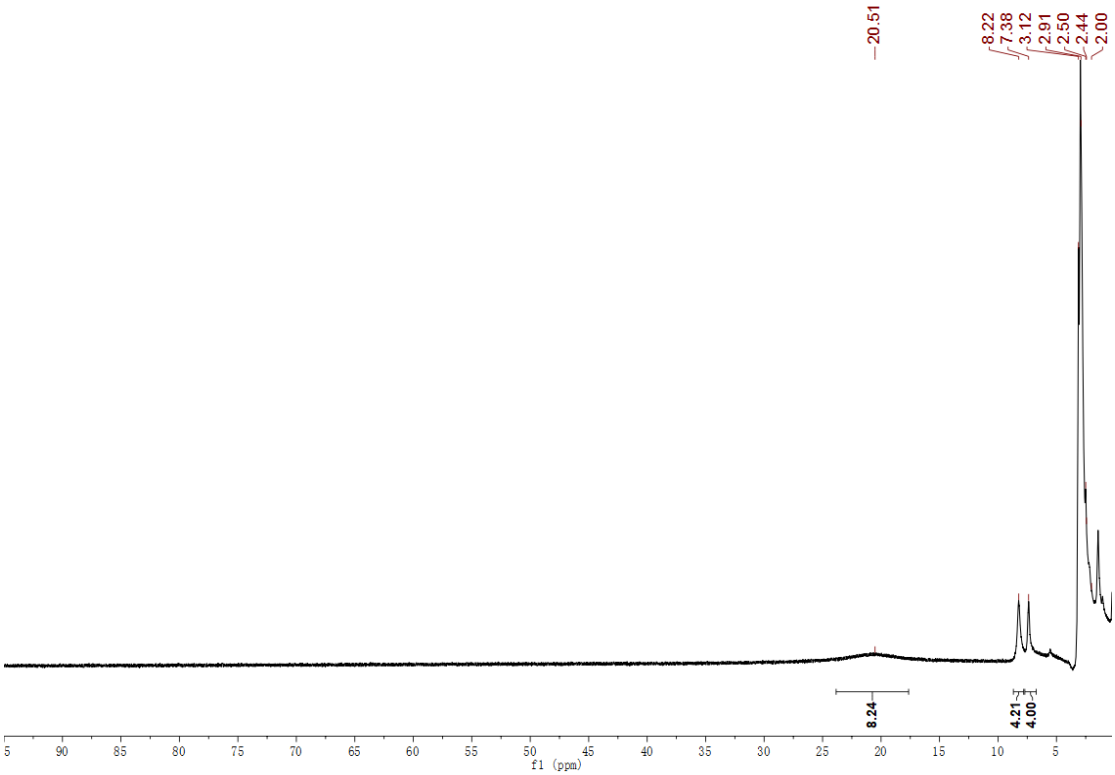


NMR:

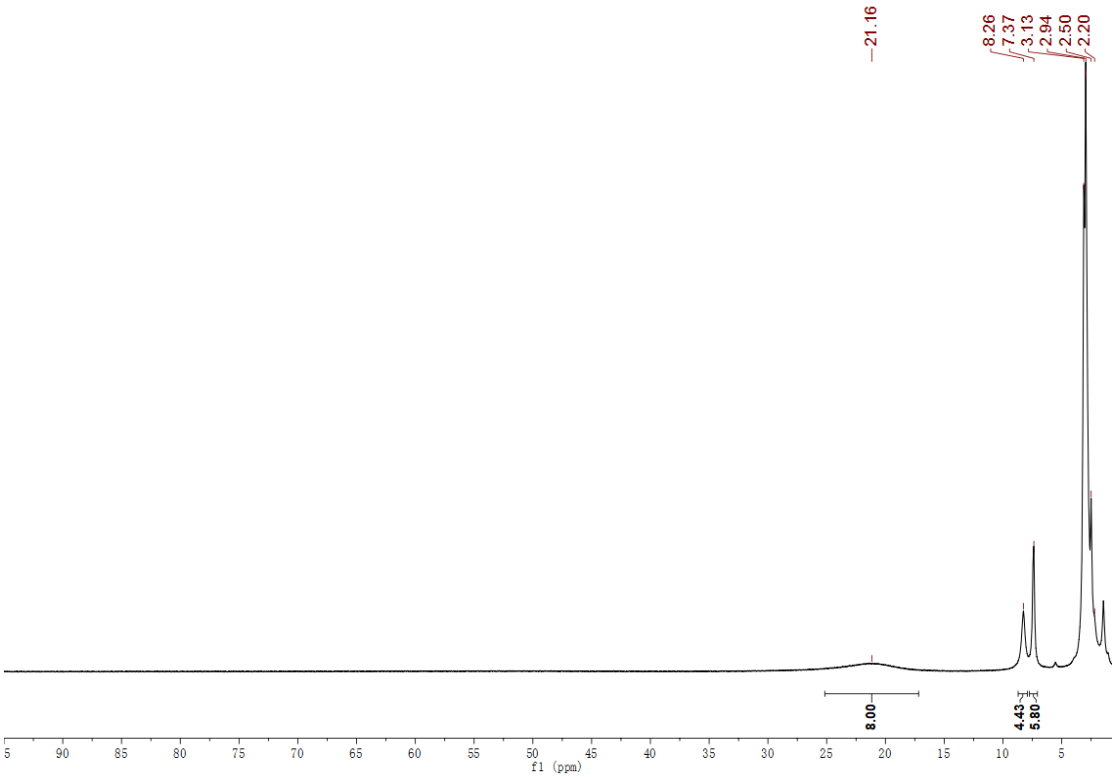
Path a: **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 20.51 (brs, 8H), 8.22 (s, 4H), 7.38 (s, 4H).

Path b: **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 21.16 (brs, 8H), 8.26 (s, 4H), 7.37 (s, 4H).

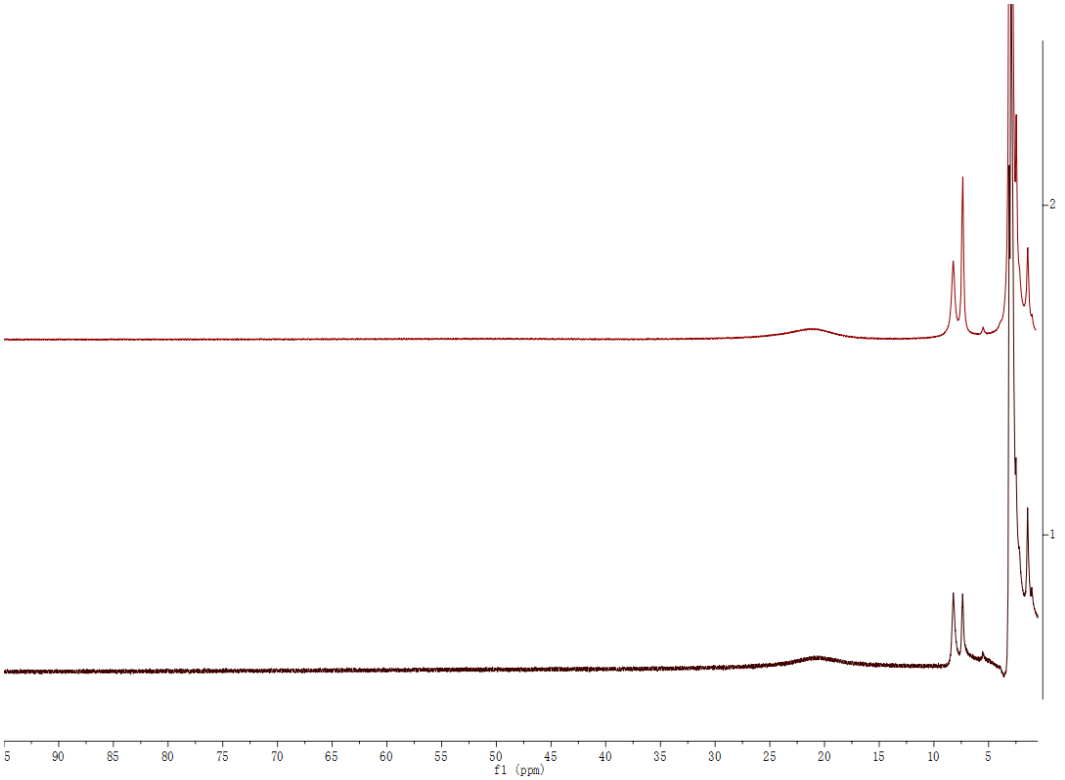
^{1}H NMR：400MHz, DMSO-d_6, the peak of DMSO in 2.500
(Full spectra, δ, obtained via **path a**)



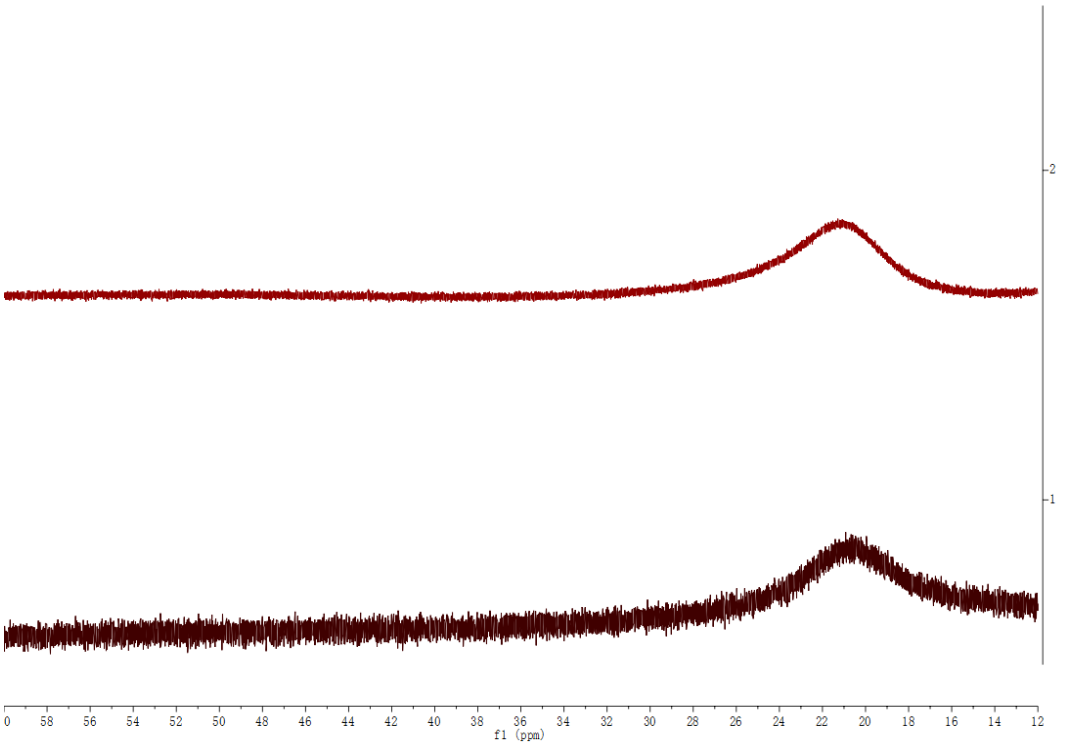
^{1}H NMR：400MHz, DMSO-d_6, the peak of DMSO in 2.500
(Full spectra, δ, obtained via **path b**)



^{1}H NMR：400MHz, DMSO-d_6, the peak of DMSO in 2.500
(Full stacked spectra, obtained via **path a** & **path b**)



^{1}H NMR：400MHz, DMSO-d_6, the peak of DMSO in 2.500
(Partial stacked spectra, obtained via **path a** & **path b**)



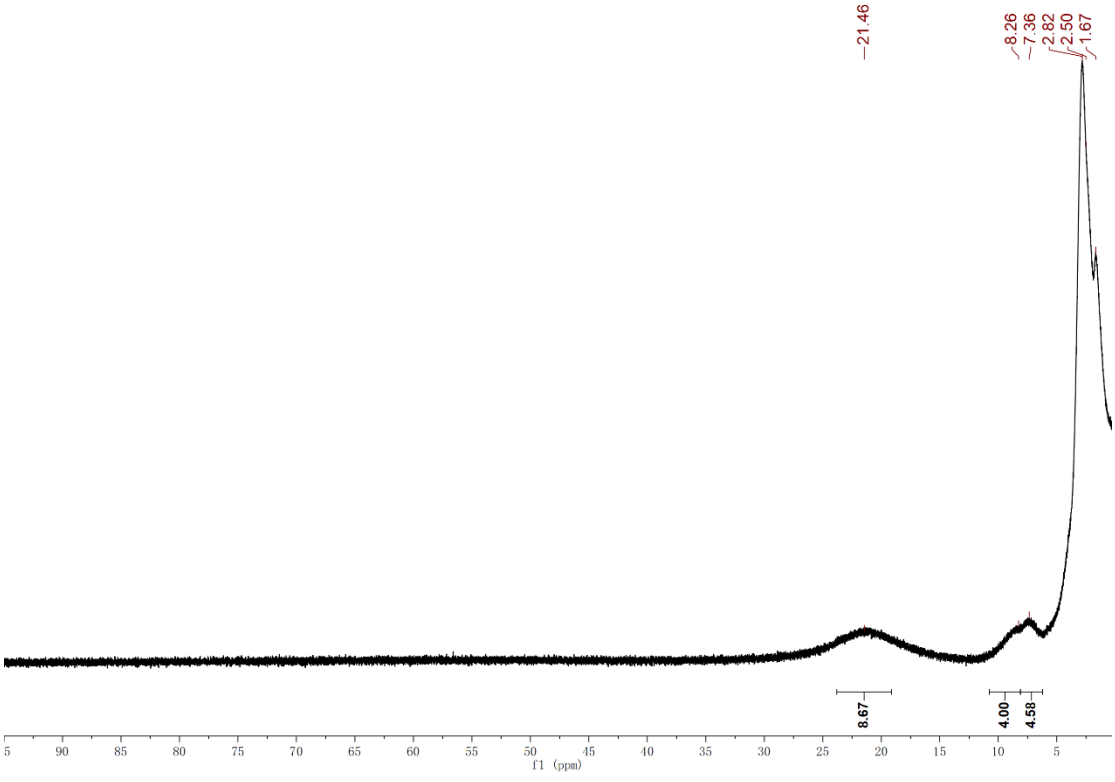
(IV) control experiment

equation (3):

Experimental procedure: Following a 2.5 h reaction of **1k** (0.15 mmol) with TMSCl (0.45 mmol, 3 equiv.) under standard conditions, the reaction mixture was filtered. Subsequently, Phen (0.15 mmol, 1 equiv.) and toluene (0.5 mL) were added to the filtrate. The solid residue was washed with toluene (3 x 1.5 mL) and THF (3 x 1.5 mL), then dried under vacuum for 30 minutes to yield a pale-yellow solid (72.2 mg, 99%). Comparative analysis of the NMR data and the characteristics confirmed the compound as Int-I (X = Cl).

^{1}H NMR (400 MHz, DMSO-d_6) δ 21.46 (s, 8H), 8.26 (s, 4H), 7.36 (s, 4H).

^{1}H NMR：400MHz, DMSO-d_6, the peak of DMSO in 2.500



Part 4. Crystallographic Data

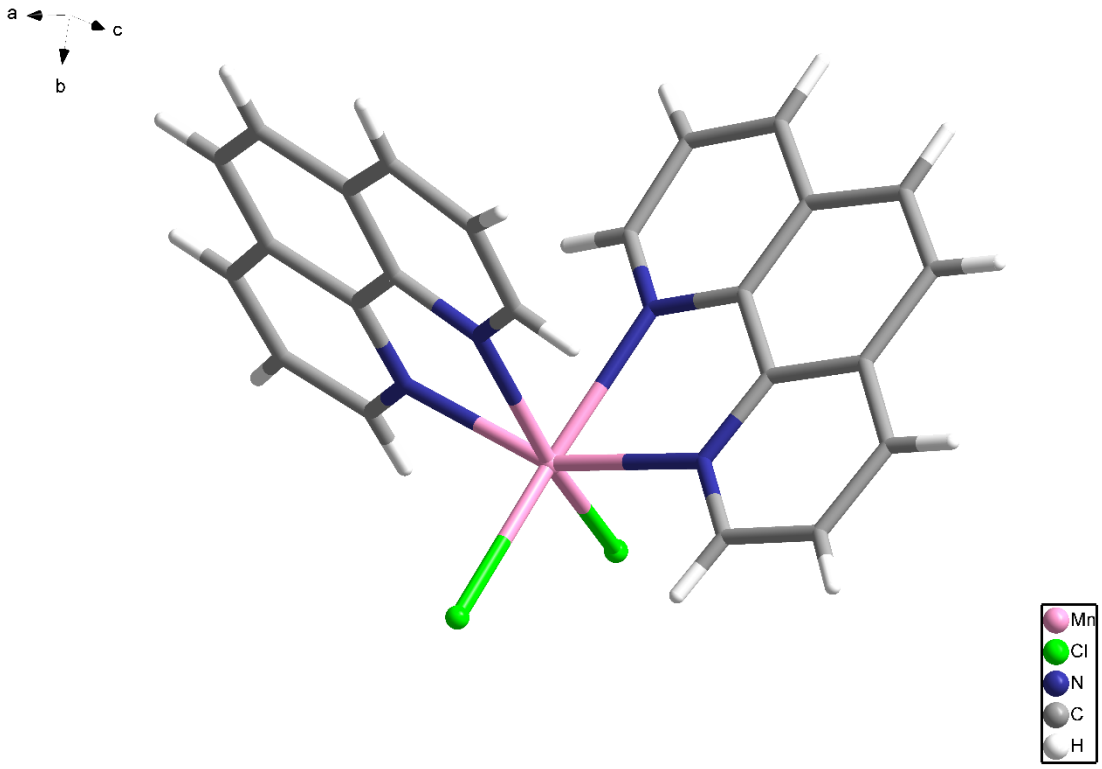
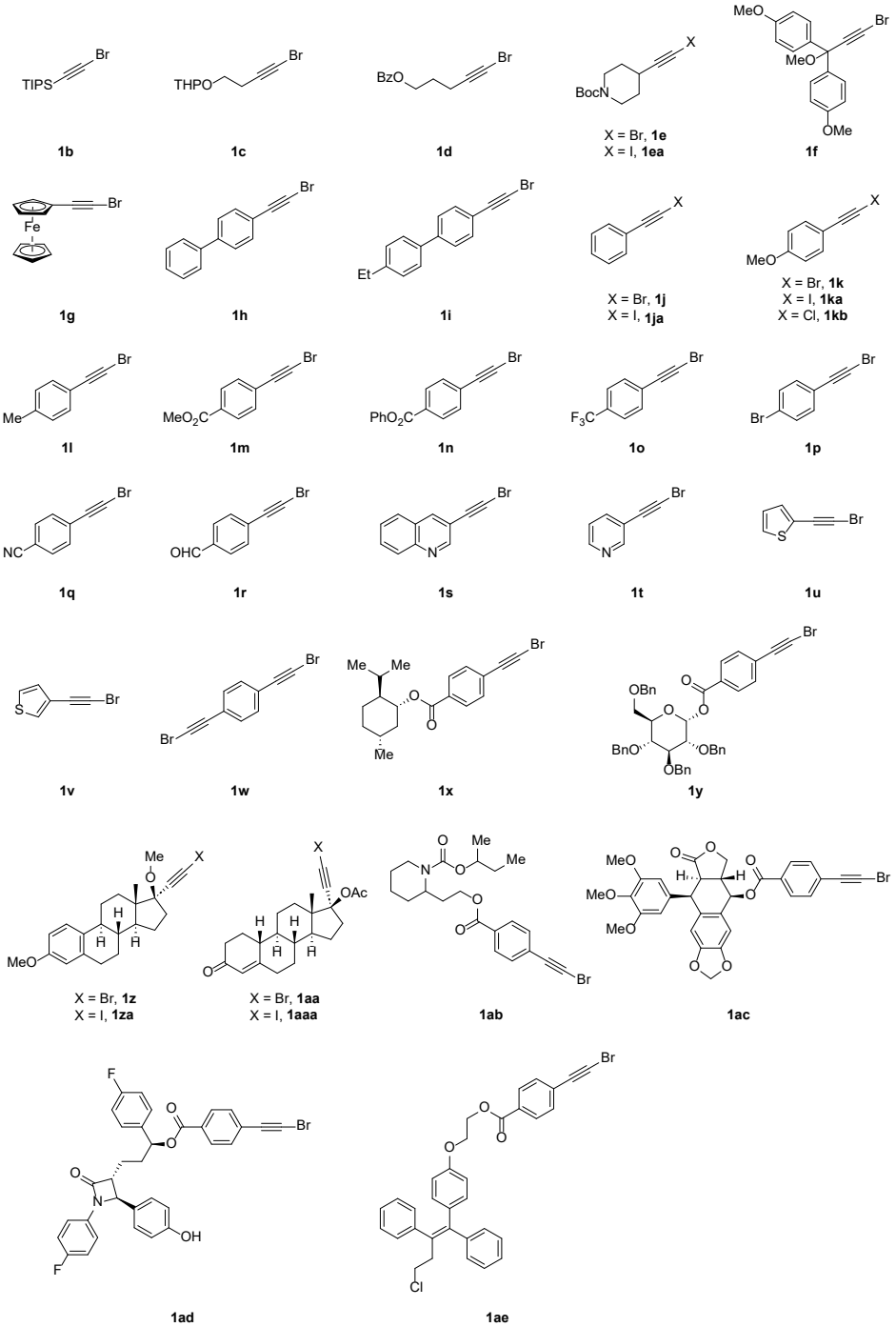


Table S5. Crystal data and structure refinement.

CSD number	2423603
Empirical formula	$C_{24}H_{16}Cl_2MnN_4$
Formula weight	486.25
Temperature/K	299.99(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.2331(6)
b/Å	17.0970(10)
c/Å	12.6421(7)
α/°	90
β/°	100.465(5)
γ/°	90
Volume/Å3	2175.0(2)
Z	4
ρcalcg/cm3	1.485
μ/mm-1	7.345
F(000)	988.0
Crystal size/mm3	0.1 × 0.1 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	8.794 to 148.242
Index ranges	-12 ≤ h ≤ 11, -21 ≤ k ≤ 20, -15 ≤ l ≤ 14
Reflections collected	16850
Independent reflections	4248 [R_{int} = 0.0828, R_{sigma} = 0.0675]
Data/restraints/parameters	4248/0/280
Goodness-of-fit on F2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.1305, wR_2 = 0.3044
Final R indexes [all data]	R_1 = 0.1676, wR_2 = 0.3278

Part 5. Preparation of Starting Materials

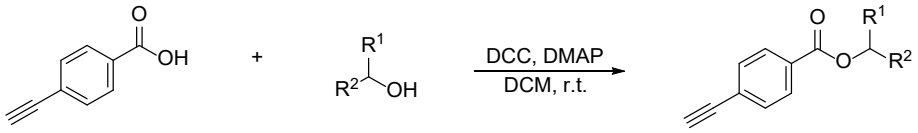
5.1 Synthesis of Alkynyl Bromides



Known alkynyl bromide **1c**[1], **1d**[2], **1e**[2], **1ea**[3], **1h**[4], **1i**[5], **1k**[5], **1ka**[6], **1kb**[7], **1l**[5], **1m**[5], **1o**[4], **1p**[5], **1q**[5], **1r**[8], **1s**[2], **1t**[9], **1u**[5], **1v**[10], **1w**[11], **1z**[12], **1za**,[13] **1aa**[14], **1ab**[14] were synthesized according to the literature procedure. Known alkynyl bromide **1b, 1j, 1ja** was purchased from Adamas-beta (www.tansoole.com). The preparation of new alkynyl bromide **1f, 1g, 1n, 1x, 1y, 1ab, 1ac, 1ad, 1ae** and their characterization data are provided as follows.

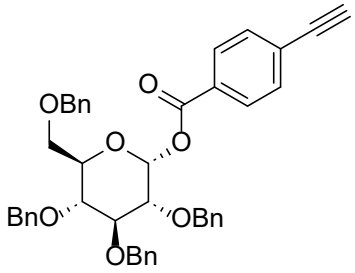
5.2 General procedure (I)

General Procedure for the synthesized of benzoates:



These compounds were prepared according to the literature procedure.[15] To a round-bottom flask equipped with magnetic bar were added 4-vinylbenzoic acid (1.64 g, 10 mmol, 1 equiv), alcohol (11 mmol, 1.1 equiv), *N,N*'-dicyclohexylcarbodiimide (DCC, 10 mmol, 1.5 equiv) and DMAP (2 mmol, 0.2 equiv). DCM (50 mL) was then added at room temperature. The mixture was stirred at room temperature until the acid was consumed as monitored by TLC. After the reaction, the mixture was quenched with water, and extracted with DCM three times, the combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography to give the desired benzoate.

Synthesis of (2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl 4-ethynylbenzoate (S-1).



This compound was synthesized from (2S,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-ol (5.95 g, 11 mmol) according to the *General procedure (I)* as a white solid (4.41 g, 66% yield). R_f =0.45 (Silica gel, hexane/ethyl acetate = 4:1).

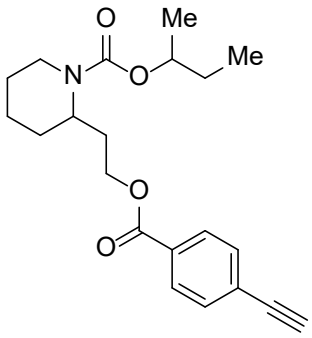
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.28 (m, 18H), 7.22 – 7.16 (m, 2H), 6.63 (d, *J* = 3.5 Hz, 1H), 5.02 (d, *J* = 10.9 Hz, 1H), 4.90 (dd, *J* = 10.7, 3.3 Hz, 2H), 4.80 – 4.68 (m, 1H), 4.67 – 4.55 (m, 2H), 4.51 (d, *J* = 12.1 Hz, 2H), 4.08 (t, *J* = 9.3 Hz, 1H), 4.00 (d, *J* = 10.1 Hz, 1H), 3.87 – 3.78 (m, 3H), 3.69 (dd, *J* = 10.9, 2.0 Hz, 1H), 3.28 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.2, 138.5, 137.9, 132.1, 129.8, 128.4, 127.9, 127.6, 127.2, 90.9, 82.7, 81.7, 80.4, 78.9, 75.6, 73.5, 68.0, 29.7.

HRMS (ESI) m/z ([M+Na]$^+$) Calcd for $C_{43}H_{40}O_7Na^+$: 691.2666. Found: 691.2728.

M.P. 92.6 ℃

sec-butyl 2-(2-((4-ethynylbenzoyl)oxy)ethyl)piperidine-1-carboxylate (S-2).



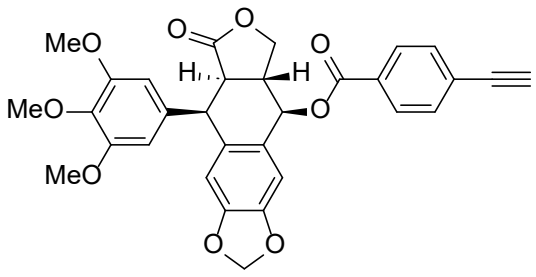
This compound was synthesized from sec-butyl 2-(2-hydroxyethyl)piperidine-1-carboxylate (*Icaridine*) (2.52 g, 11 mmol) according to the *General procedure (I)* as a pale-yellow oil (2.47 g, 69% yield). R_f =0.5 (Silica gel, hexane/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 4.75 – 4.65 (m, 1H), 4.49 (s, 1H), 4.34 – 4.24 (m, 2H), 4.06 (d, *J* = 12.8 Hz, 1H), 3.22 (s, 1H), 2.82 (t, *J* = 13.2 Hz, 1H), 2.25 – 2.12 (m,1H), 1.90 – 1.78 (m, 1H), 1.65 – 1.56 (m, 4H), 1.55 – 1.32 (m, 4H), 1.13 (d, *J* = 6.2 Hz, 3H), 0.83 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 165.7, 155.40 and 155.37, 131.9, 130.2, 129.4, 126.6, 82.7, 80.0, 72.89 and 72.84, 62.75 and 62.71, 47.83 and 47.80, 38.88 and 38.78, 29.0, 28.7, 28.5, 25.4, 19.7, 19.0, 9.62 and 9.59.

HRMS (ESI) m/z ($[M+H]^+$) Calcd for $C_{21}H_{27}NO_4H^+$: 358.2013. Found: 358.2013.

(5R,5aR,8aR,9R)-8-oxo-9-(3,4,5-trimethoxyphenyl)-5,5a,6,8,8a,9-hexahydrofuro[3',4':6,7]naphtho[2,3-d][1,3]dioxol-5-yl 4-ethynylbenzoate (S-3).



This compound was synthesized from (5R,5aR,8aR,9R)-9-hydroxy-5-(3,4,5-trimethoxyphenyl)-5,8,8a,9-tetrahydrofuro[3',4':6,7]naphtho[2,3-d][1,3]dioxol-6(5aH)-one (*Podophyllotoxin*) (4.56 g, 11 mmol) according to the *General procedure (I)* as a white solid (4.45 g, 82% yield). R_f =0.45 (Silica gel, hexane/ethyl acetate = 3:1).

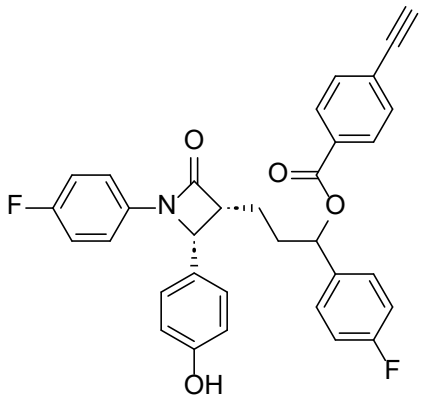
^{1}H NMR (400 MHz, Choroform-*d*) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 6.85 (s, 1H), 6.58 (s, 1H), 6.44 (s, 2H), 6.10 (d, *J* = 8.1 Hz, 1H), 5.99 (d, *J* = 7.0 Hz, 2H), 4.64 (d, *J* = 3.7 Hz, 1H), 4.44 (dd, *J* = 9.4, 6.4 Hz, 1H), 4.35 – 4.27 (m, 1H), 3.80 (s, 3H), 3.77 (s, 6H), 3.28 (s, 1H), 3.03 – 2.92 (m, 2H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 173.6, 166.1, 152.6, 148.2, 147.7, 137.1, 134.7, 132.5, 132.3, 129.5, 129.1, 128.1, 127.6, 109.8, 108.0, 107.0, 101.6, 82.5, 80.8, 74.5, 71.4, 60.7, 56.1, 45.6, 43.7, 38.8, 33.9, 25.6, 24.9.

HRMS (ESI) m/z ([M+K]$^+$) Calcd for $C_{31}H_{26}O_9K^+$: 581.1208. Found: 581.1204.

M.P. 174.9 ℃

1-(4-fluorophenyl)-3-((2R,3R)-1-(4-fluorophenyl)-2-(4-hydroxyphenyl)-4-oxoazetidin-3-yl)propyl 4-ethynylbenzoate (S-4).



This compound was synthesized from (3R,4R)-1-(4-fluorophenyl)-3-(3-(4-fluorophenyl)-3-hydroxypropyl)-4-(4-hydroxyphenyl)azetidin-2-one (*Ezetimibe*) (4.50 g, 11 mmol) according to the *General procedure (I)* as a white solid (4.09 g, 76% yield). R_f =0.4 (Silica gel, hexane/ethyl acetate = 3:2).

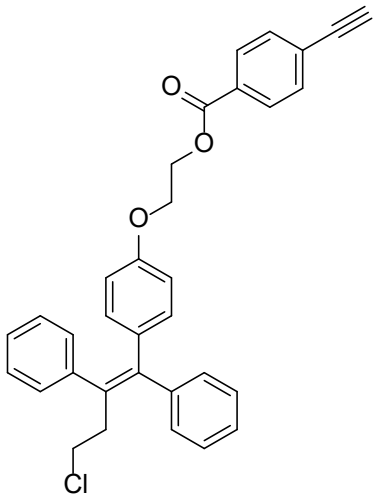
^{1}H NMR (400 MHz, Choroform-*d*) δ 8.13 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.30 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.26 – 7.21 (m, 4H), 7.02 (t, *J* = 8.7 Hz, 2H), 6.95 (dd, *J* = 9.4, 7.9 Hz, 2H), 4.72 (t, *J* = 6.0 Hz, 1H), 4.66 (d, *J* = 2.3 Hz, 1H), 3.29 (s, 1H), 3.15 – 3.08 (m, 1H), 2.38 (s, 1H), 2.03 – 1.83 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.3, 164.4, 161.0, 159.0 (d, *J* = 243.6 Hz), 150.9, 140.0 (d, *J* = 3.2 Hz), 135.3, 133.7, 132.3, 1fz30.0, 129.1, 127.7, 127.4 (d, *J* = 8.1 Hz), 127.0, 122.6, 118.4 (d, *J* = 7.8 Hz), 115.9 (d, *J* = 22.7 Hz), 115.4 (d, *J* = 21.4 Hz), 82.6, 80.8, 73.1, 60.8, 60.4, 36.6, 25.0.

HRMS (ESI) m/z ([M+H]$^+$) Calcd for $C_{33}H_{25}NO_4F_2H^+$: 538.1824. Found: 538.1825.

M.P. 85.0 ℃

(Z)-2-(4-(4-chloro-1,2-diphenylbut-1-en-1-yl)phenoxy)ethyl 4-ethynylbenzoate (S-5).



This compound was synthesized from (3R,4R)-1-(4-fluorophenyl)-3-(3-(4-fluorophenyl)-3-hydroxypropyl)-4-(4-hydroxyphenyl)azetidin-2-one (*Ospemifene*) (4.17 g, 11 mmol) according to the *General procedure (I)* as a white solid (4.72 g, 93% yield). R_f =0.45 (Silica gel, hexane/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.39 – 7.35 (m, 2H), 7.32 – 7.27 (m, 3H), 7.19 (d, *J* = 7.0 Hz, 2H), 7.17 – 7.12 (m, 3H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 8.8 Hz, 2H), 4.58 (dd, *J* = 5.5, 4.0 Hz, 2H), 4.17 (dd, *J* = 5.5, 4.1 Hz, 2H), 3.41 (t, *J* = 7.4 Hz, 2H), 3.23 (s, 1H), 2.92 (t, *J* = 7.5 Hz, 2H).

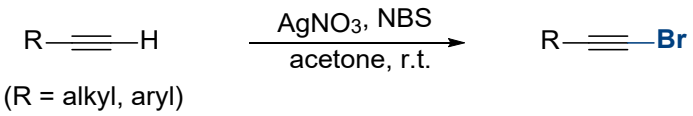
^{13}C NMR (101 MHz, Choroform-*d*) δ 165.7, 156.6, 142.8, 141.6, 140.9, 135.3, 132.0, 131.7, 129.8, 129.5, 129.5, 129.3, 128.3, 128.2, 126.9, 126.9, 126.6, 113.5, 82.7, 80.2, 65.6, 63.5, 42.8, 38.5.

HRMS (ESI) m/z ([M+K]$^+$) Calcd for $C_{33}H_{27}O_3ClK^+$: 545.1280. Found: 545.1277.

M.P. 101.3 ℃

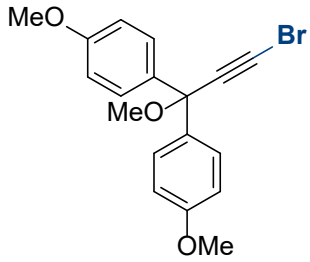
5.3 General procedure (II)

General Procedure for the synthesized of alkynyl bromides:



These compounds were prepared according to the literature procedure.[2] To a round bottom flask was charged with alkyne (20 mmol, 1.0 equiv), $AgNO_3$ (2.0 mmol, 0.1 equiv) and N-bromosuccinimide (NBS, 24 mmol, 1.1 equiv) in acetone (100 mL), the resulting reaction mixture was stirred at room temperature. Monitored by TLC, on completion, the reaction was quenched with H_2O (50 mL) and extracted with CH_2Cl_2 three times. The combined organic layers were dried with Na_2SO_4, then filtered and concentrated. The crude residue was purified by column chromatography to give desired alkynyl bromide.

4,4'-(3-bromo-1-methoxyprop-2-yne-1,1-diyl)bis(methoxybenzene) (1f).



This compound was synthesized from 4,4'-(1-methoxyprop-2-yne-1,1-diyl)bis(methoxybenzene)[16] (1 g, 3.5 mmol) according to the *General procedure (II)* as a pale-yellow solid (0.908 g, 71% yield). R_f = 0.5 (Silica gel, hexane/ethyl acetate = 19:1).

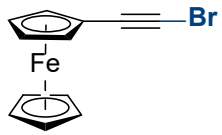
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.9 Hz, 4H), 6.85 (d, *J* = 8.9 Hz, 4H), 3.79 (s, 6H), 3.31 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.1, 135.2, 128.0, 113.4, 81.1, 80.1, 55.2, 52.4, 48.9.

HRMS (ESI) m/z ([M+Na]$^+$) Calcd for $C_{18}H_{17}O_3BrNa^+$: 383.0253. Found: 383.0256.

M.P. 85.8 ℃

Ferrocenyl acetylene bromide (1g).



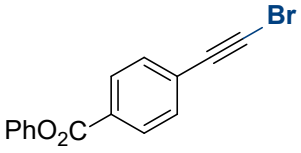
This compound was synthesized from acetylidene ferrocene (1 g, 4.8 mmol) according to the *General procedure (II)* as a deep-red oil (0.660 g, 48% yield). R_f = 0.7 (Silica gel, hexane/ethyl acetate = 99:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.81 (s, 1H), 4.44 (s, 1H), 4.37 (s, 1H), 4.27 (s, 2H), 4.23 (s, 3H), 4.18 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 72.0, 71.5, 70.3, 69.9, 69.2, 68.6.

HRMS (ESI) m/z ([M+H]$^+$) Calcd for $C_{12}H_9FeBrH^+$: 288.9310. Found: 288.9315.

Phenyl 4-(bromoethynyl)benzoate (1n).



This compound was synthesized from phenyl 4-ethynylbenzoate[17] (1 g, 4.5 mmol) according to the *General procedure (II)* as a pale-yellow solid (1.29 g, 95% yield). R_f = 0.55 (Silica gel, hexane/ethyl acetate = 9:1).

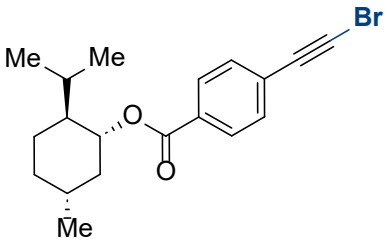
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 7.44 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.21 (dd, *J* = 8.6, 1.2 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.5, 150.8, 132.1, 130.0, 129.5, 129.4, 128.0, 126.0, 121.6, 79.3, 54.0.

HRMS (ESI) m/z ([M+Na]$^+$) Calcd for $C_{15}H_9O_2BrNa^+$: 322.9678. Found: 322.9690.

M.P. 93.4 ℃

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-(bromoethynyl)benzoate (1x).



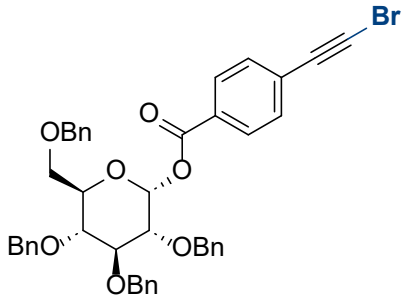
This compound was synthesized from phenyl (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-ethynylbenzoate[18] (1 g, 3.5 mmol) according to the *General procedure (II)* as a colorless liquid (1.07 g, 84% yield). R_f = 0.6 (Silica gel, hexane/ethyl acetate = 9:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 4.97 – 4.87 (m, 1H), 2.16 – 2.06 (m, 1H), 1.98 – 1.88 (m, 1H), 1.76 – 1.66 (m, 2H), 1.59 – 1.48 (m, 2H), 1.15 – 1.02 (m, 2H), 0.91 (dd, *J* = 6.9, 4.0 Hz, 7H), 0.78 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.2, 131.8, 130.7, 129.4, 127.0, 79.5, 75.1, 53.1, 47.2, 40.9, 34.2, 31.4, 26.5, 23.6, 22.0, 20.7, 16.5.

HRMS (ESI) m/z ([M+Na]$^+$) Calcd for $C_{19}H_{23}O_2BrNa^+$: 385.0774. Found: 385.0784.

(2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl 4-(bromoethynyl)benzoate (1y).



This compound was synthesized from **S-1** (1 g, 1.5 mmol) according to the *General procedure (II)* as a pale-yellow solid (1.08 g, 97% yield). R_f = 0.55 (Silica gel, hexane/ethyl acetate = 4:1).

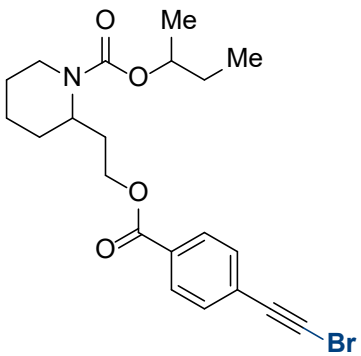
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.28 (m, 18H), 7.19 – 7.15 (m, 2H), 6.61 (d, *J* = 3.5 Hz, 1H), 5.01 (d, *J* = 10.9 Hz, 1H), 4.89 (dd, *J* = 10.7, 2.6 Hz, 2H), 4.79 – 4.66 (m, 1H), 4.65 – 4.53 (m, 2H), 4.50 (d, *J* = 12.1 Hz, 2H), 4.06 (t, *J* = 9.3 Hz, 1H), 4.01 – 3.95 (m, 1H), 3.86 – 3.77 (m, 3H), 3.67 (dd, *J* = 10.9, 2.0 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.2, 138.5, 137.9, 137.7, 137.6, 132.0, 129.8, 129.5, 128.5, 128.4, 128.4, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 90.9, 81.7, 79.4, 78.9, 77.2, 76.9, 75.7, 75.5, 73.6, 73.1, 68.0, 53.8.

HRMS (ESI) m/z ([M+Na]$^+$) Calcd for $C_{43}H_{39}O_7BrNa^+$: 769.1771. Found: 769.1841.

M.P. 91.3 ℃

sec-butyl 2-(2-((4-(bromoethynyl)benzoyl)oxy)ethyl)piperidine-1-carboxylate (1ab).



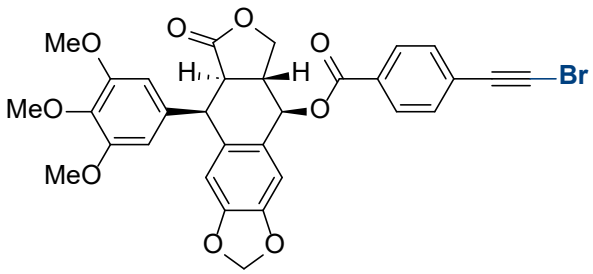
This compound was synthesized from **S-2** (1 g, 2.8 mmol) according to the *General procedure (II)* as a pale-yellow oil (1.10 g, 90% yield). R_f =0.5 (Silica gel, hexane/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 4.75 – 4.67 (m, 1H), 4.50 (s, 1H), 4.33 – 4.21 (m, 2H), 4.06 (s, 1H), 2.83 (t, *J* = 13.2 Hz, 1H), 2.24 – 2.14 (m, 1H), 1.89 – 1.81 (m, 1H), 1.68 – 1.58 (m, 4H), 1.56 – 1.37 (m, 4H), 1.14 (d, *J* = 6.2 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 165.7, 155.44 and 155.41, 131.8, 130.1, 129.4, 127.2, 79.3, 72.93 and 72.89, 62.78 and 62.74, 53.3, 47.84 and 47.81, 38.9, 29.0, 28.8, 28.5, 25.4, 19.7, 19.0, 9.66 and 9.63.

HRMS (ESI) m/z ([M+H]$^+$) Calcd for $C_{21}H_{26}NO_4BrH^+$: 436.1118. Found: 436.1120.

(5R,5aR,8aR,9R)-8-oxo-9-(3,4,5-trimethoxyphenyl)-5,5a,6,8,8a,9-hexahydrofuro[3',4':6,7]naphtho[2,3-d][1,3]dioxol-5-yl 4-(bromoethynyl)benzoate (1ac).



This compound was synthesized from **S-3** (1 g, 1.8 mmol) according to the *General procedure (II)* as a yellow solid (0.97 g, 85% yield). R_f =0.45 (Silica gel, hexane/ethyl acetate = 3:1).

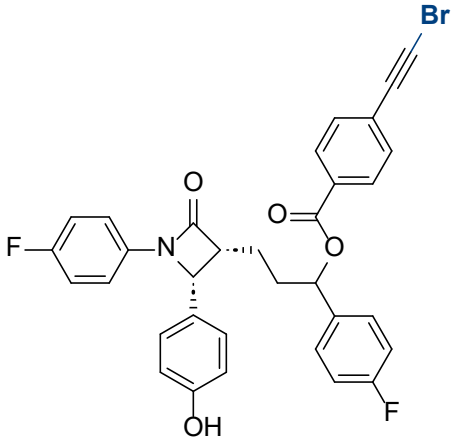
^{1}H NMR (400 MHz, Choroform-*d*) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.56 – 7.47 (m, 2H), 6.83 (s, 1H), 6.55 (s, 1H), 6.41 (s, 2H), 6.07 (d, *J* = 8.1 Hz, 1H), 5.96 (d, *J* = 6.3 Hz, 2H), 4.61 (d, *J* = 3.6 Hz, 1H), 4.41 (dd, *J* = 9.3, 6.4 Hz, 1H), 4.32 – 4.23 (m, 1H), 3.77 (s, 3H), 3.75 (s, 6H), 3.01 – 2.89 (m, 2H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 173.5, 166.0, 152.5, 148.1, 147.6, 137.0, 134.7, 132.4, 132.1, 129.4, 128.8, 128.1, 128.0, 109.7, 107.9, 106.9, 101.5, 79.1, 77.2, 74.3, 71.3, 60.6, 56.0, 54.3, 45.4, 43.6, 38.7.

HRMS (ESI) m/z ([M+Na]$^+$) Calcd for $C_{31}H_{25}O_9BrNa^+$: 643.0574. Found: 643.0583.

M.P. 129.5 ℃

1-(4-fluorophenyl)-3-((2R,3R)-1-(4-fluorophenyl)-2-(4-hydroxyphenyl)-4-oxoazetidin-3-yl)propyl 4-(bromoethynyl)benzoate (1ad).



This compound was synthesized from **S-4** (1 g, 1.9 mmol) according to the *General procedure (II)* as a pale-yellow solid (0.95 g, 83% yield). R_f =0.4 (Silica gel, hexane/ethyl acetate = 3:2).

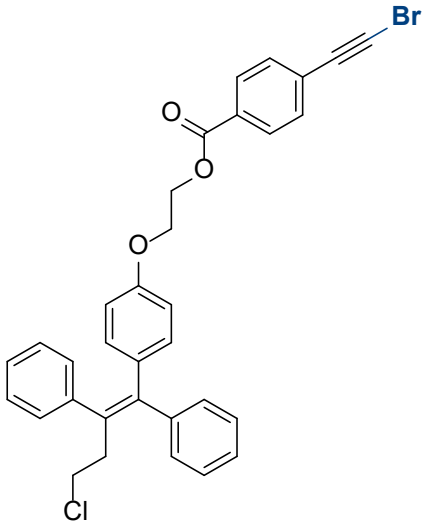
^{1}H NMR (400 MHz, Choroform-*d*) δ 8.12 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.29 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.26 – 7.20 (m, 4H), 7.01 (t, *J* = 8.7 Hz, 2H), 6.94 (t, *J* = 8.7 Hz, 2H), 4.71 (t, *J* = 5.9 Hz, 1H), 4.66 (d, *J* = 2.3 Hz, 1H), 3.14 – 3.08 (m, 1H), 2.53 (s, 1H), 2.02 – 1.88 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.3, 164.3, 162.1 (d, *J* = 245.5 Hz), 159.0 (d, *J* = 243.8 Hz), 150.9, 140.0 (d, *J* = 3.1 Hz), 135.2, 133.6 (d, *J* = 2.6 Hz), 132.1, 130.0, 128.9, 128.2, 127.4 (d, *J* = 8.1 Hz), 127.0, 122.5, 118.3 (d, *J* = 7.8 Hz), 115.9 (d, *J* = 22.8 Hz), 115.3 (d, *J* = 21.3 Hz), 79.2, 73.0, 60.8, 60.4, 54.3, 36.5, 25.0.

HRMS (ESI) m/z ($[M+H]^+$) Calcd for $C_{33}H_{24}NO_4F_2BrH^+$: 616.0930. Found: 616.0934.

M.P. 68.7 ℃

(Z)-2-(4-(4-chloro-1,2-diphenylbut-1-en-1-yl)phenoxy)ethyl 4-(bromoethynyl)benzoate (1ae).



This compound was synthesized from **S-5** (1 g, 2.0 mmol) according to the *General procedure (II)* as a white solid (0.83 g, 72% yield). R_f=0.45 (Silica gel, hexane/ethyl acetate = 5:1).

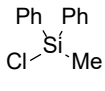
^{1}H NMR (400 MHz, Choroform-*d*) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.33 – 7.27 (m, 3H), 7.23 – 7.18 (m, 2H), 7.17 – 7.13 (m, 3H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 8.8 Hz, 2H), 4.61 – 4.55 (m, 2H), 4.19 – 4.14 (m, 2H), 3.42 (t, *J* = 7.4 Hz, 2H), 2.93 (t, *J* = 7.4 Hz, 2H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 165.8, 156.7, 142.8, 141.6, 140.9, 135.4, 131.9, 131.7, 129.6, 129.6, 129.5, 129.4, 128.4, 128.2, 127.4, 127.0, 126.6, 113.6, 79.4, 65.6, 63.5, 53.5, 42.8, 38.6.

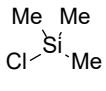
HRMS (ESI) m/z ($[M+H]^+$) Calcd for $C_{33}H_{26}O_3ClBrH^+$: 585.0827. Found: 585.0832.

M.P. 115.4 ℃

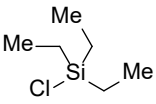
5.4 Synthesis of chlorosilane and chlorogermane



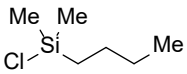
2a



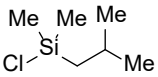
2b



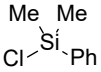
2c



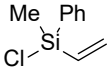
2d



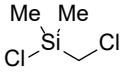
2e



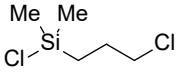
2f



2g



2h

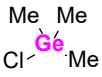


2i

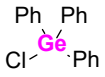
2j

2k

2l

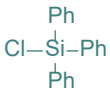


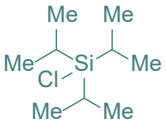
2m

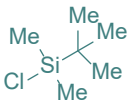


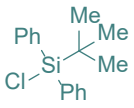
2n

Unreactive Substrates





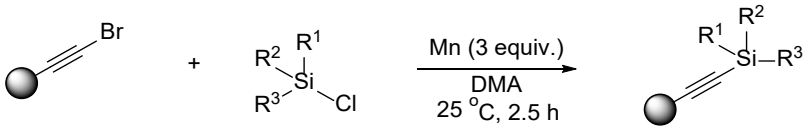




Known alkynyl bromide **2a-2m** are commercially available from Adamas-beta (www.tansoole.com).

Part 6. Cross-Electrophile Coupling of Alkynyl Bromides with Chlorosilanes

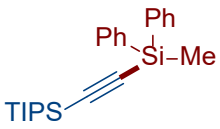
6.1 General procedure (III)



General Procedure for the cross-electrophile coupling of alkynyl bromides with chlorosilanes: To a flame-dried Schlenk tube equipped with a magnetic stir bar was added alkynyl bromide (if it is a solid, 0.15 mmol, 100 mol%), chlorosilane/germane (if it is a solid, 0.45 mmol, 300 mol%) and Mn (24.7 mg, 0.45 mmol, 300 mol%). The tube was capped with a rubber septum and then evacuated and refilled with argon three times. Then alkynyl bromide (if it is a liquid, 0.3 mmol, 100 mol%), chlorosilane/germane (if it is a liquid, 0.45 mmol, 300 mol%), DMA (1.0 mL) was added via syringes. After stirring at room temperature for 2.5 hours under an Argon atmosphere, the reaction mixture was directly loaded onto a silica gel column. The residue was rinsed with a small amount of DCM and loaded onto the same column, and the pure product was obtained after flash column chromatography.

6.2 Details of the Experimental Data

triisopropyl((methyldiphenylsilyl)ethynyl)silane (3a).



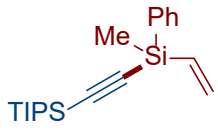
This compound was prepared according to *General procedure (III)* using (bromoethynyl)triisopropylsilane (39.2 mg, 0.15 mmol, 100 mol%) and chloro(methyl)diphenylsilane (104.7 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: hexane), the title compound was isolated in 80 % yield (45.4 mg, 0.12 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.73 (dd, *J* = 7.5, 2.1 Hz, 4H), 7.44 – 7.38 (m, 6H), 1.21 – 1.12 (m, 21H), 0.74 (s, 3H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 135.6, 134.5, 129.5, 127.8, 114.6, 111.5, 18.6, 11.2, -1.8.

HRMS (ESI) m/z ([M+H]$^+$) Calcd for $C_{24}H_{34}Si_2H^+$: 379.2271. Found: 379.2267.

triisopropyl((methyl(phenyl)(vinyl)silyl)ethynyl)silane (3b).[19]

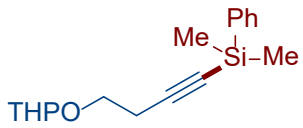


This compound was prepared according to *General procedure (III)* using (bromoethynyl)triisopropylsilane (35.0 mg, 0.15 mmol, 100 mol%) and chloro(methyl)(phenyl)(vinyl)silane (82.2 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: hexane), the title compound was isolated in 67 % yield (33.0 mg, 0.101 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.70 – 7.65 (m, 2H), 7.39 (dd, *J* = 5.5, 1.8 Hz, 3H), 6.26 (dd, *J* = 19.7, 14.4 Hz, 1H), 6.12 (dd, *J* = 14.4, 4.1 Hz, 1H), 5.98 (dd, *J* = 19.7, 4.0 Hz, 1H), 1.12 (d, *J* = 1.5 Hz, 21H), 0.50 (s, 3H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 135.4, 135.0, 134.5, 134.2, 129.5, 127.8, 114.0, 111.1, 18.6, 11.1, -2.3.

dimethyl(phenyl)(4-((tetrahydro-2H-pyran-2-yl)oxy)but-1-yn-1-yl)silane (3c).[20]

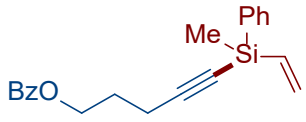


This compound was prepared according to *General procedure (III)* using 2-((4-bromobut-3-yn-1-yl)oxy)tetrahydro-2H-pyran (35.0 mg, 0.15 mmol, 100 mol%) and chlorodimethyl(phenyl)silane (76.8 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 3% ethyl acetate in hexane), the title compound was isolated in 37 % yield (16.0 mg, 0.055 mmol) as a colorless oil. This compound can also prepared according to *General procedure (III)* using 2-((4-bromobut-3-yn-1-yl)oxy)tetrahydro-2H-pyran (35.0 mg, 0.15 mmol, 100 mol%), chlorodimethyl(phenyl)silane (128.0 mg, 0.75 mmol, 500 mol%) and Mn (41.2 mg, 0.75 mmol, 500mol%). After purification by flash column chromatography, the title compound was isolated in 70 % yield (30.3 mg, 0.105 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.65 – 7.60 (m, 2H), 7.37 (dd, *J* = 5.0, 1.9 Hz, 3H), 4.67 (t, *J* = 3.5 Hz, 1H), 3.91 – 3.82 (m, 2H), 3.57 (dd, *J* = 9.7, 7.1 Hz, 1H), 3.53 - 3.46 (m, 1H), 2.59 (t, *J* = 7.1 Hz, 2H), 1.86 - 1.80 (m, 1H), 1.72 – 1.67 (m, 1H), 1.59 – 1.45 (m, 4H), 0.39 (s, 6H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 137.3, 133.6, 129.3, 127.8, 105.9, 98.6, 83.6, 65.5, 62.0, 30.5, 25.4, 21.5, 19.2, -0.8.

5-(methyl(phenyl)(vinyl)silyl)pent-4-yn-1-yl benzoate (3d).



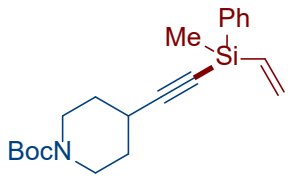
This compound was prepared according to *General procedure (III)* using 5-bromopent-4-yn-1-yl benzoate (40.1 mg, 0.15 mmol, 100 mol%) and chloro(methyl)(phenyl)(vinyl)silane (82.2 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 5% ethyl acetate in hexane), the title compound was isolated in 31 % yield (15.6 mg, 0.047 mmol) as a colorless oil. This compound can also prepared according to *General procedure (III)* using 5-bromopent-4-yn-1-yl benzoate (40.1 mg, 0.15 mmol, 100 mol%), chloro(methyl)(phenyl)(vinyl)silane (137.0 mg, 0.75 mmol, 500 mol%) and Mn (41.2 mg, 0.75 mmol, 500mol%). After purification by flash column chromatography, the title compound was isolated in 68 % yield (34.1 mg, 0.102 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 8.08 – 8.02 (m, 2H), 7.65 – 7.60 (m, 2H), 7.58 – 7.53 (m, 1H), 7.47 – 7.42 (m, 2H), 7.40 – 7.34 (m, 3H), 6.24 (dd, *J* = 19.7, 14.5 Hz, 1H), 6.11 (dd, *J* = 14.4, 4.0 Hz, 1H), 5.91 (dd, *J* = 19.8, 4.0 Hz, 1H), 4.44 (t, *J* = 6.2 Hz, 2H), 2.51 (t, *J* = 7.1 Hz, 2H), 2.09 – 2.02 (m, 2H), 0.47 (s, 3H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 135.1, 134.5, 134.1, 132.9, 130.2, 129.6, 129.5, 128.4, 127.9, 108.8, 63.6, 27.8, 17.0, -2.5.

HRMS (ESI) m/z ([M+H]$^{+}$) Calcd for $C_{21}H_{22}O_2SiH^{+}$: 335.1462. Found: 335.1466.

***tert*-butyl 4-((methyl(phenyl)(vinyl)silyl)ethynyl)piperidine-1-carboxylate (3e).**



This compound was prepared according to *General procedure (III)* using *tert*-butyl 4-(bromoethynyl)piperidine-1-carboxylate (43.2 mg, 0.15 mmol, 100 mol%) and chloro(methyl)(phenyl)(vinyl)silane (82.2 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 5% ethyl acetate in hexane), the title compound was isolated in 75 % yield (40.0 mg, 0.113 mmol) as a colorless oil.

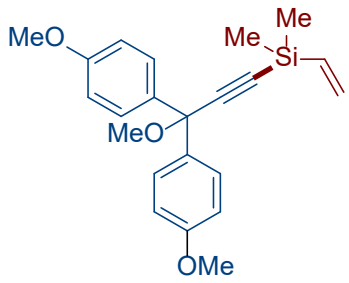
Alkynyl iodide was used instead of alkynyl bromide: this compound was also prepared according to *General procedure (III)* using *tert*-butyl 4-(iodoethynyl)piperidine-1-carboxylate (50.3 mg, 0.15 mmol, 100 mol%), the title compound was isolated in 87 % yield (46.4 mg, 0.131 mmol).

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.64 – 7.59 (m, 2H), 7.40 – 7.35 (m, 3H), 6.23 (dd, *J* = 19.7, 14.4 Hz, 1H), 6.10 (dd, *J* = 14.4, 4.0 Hz, 1H), 5.90 (dd, *J* = 19.8, 4.0 Hz, 1H), 3.71 – 3.64 (m, 2H), 3.26 – 3.21 (m, 2H), 2.73 – 2.65 (m, 1H), 1.81 – 1.76 (m, 2H), 1.67 – 1.60 (m, 2H), 1.45 (s, 9H), 0.47 (s, 3H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 154.7, 135.5, 135.1, 134.4, 134.1, 129.5, 127.8, 112.0, 81.7, 79.4, 69.5, 31.2, 28.4, 27.9, 26.7, -2.4.

HRMS (ESI) m/z ([M+H]$^+$) Calcd for $C_{21}H_{29}NO_2SiH^+$: 356.2040. Found: 356.2041.

(3-methoxy-3,3-bis(4-methoxyphenyl)prop-1-yn-1-yl)dimethyl(vinyl)silane (3f).



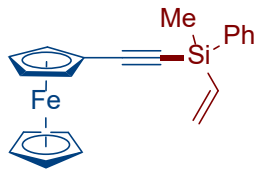
This compound was prepared according to *General procedure (III)* using **1f** (54.2 mg, 0.15 mmol, 100 mol%) and chlorodimethyl(vinyl)silane (54.3 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 5% ethyl acetate in hexane), the title compound was isolated in 87 % yield (47.8 mg, 0.131 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.44 (d, *J* = 8.8 Hz, 4H), 6.84 (d, *J* = 8.8 Hz, 4H), 6.18 (dd, *J* = 19.8, 14.5 Hz, 1H), 6.03 (dd, *J* = 14.5, 3.9 Hz, 1H), 5.89 (dd, *J* = 19.9, 3.9 Hz, 1H), 3.79 (s, 6H), 3.32 (s, 3H), 0.30 (s, 6H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 158.9, 136.4, 135.5, 133.3, 128.0, 113.4,106.0, 92.0, 80.5, 55.2, 52.3, -1.4.

HRMS (ESI) m/z ([M+H]$^+$) Calcd for $C_{22}H_{26}O_3SiH^+$: 367.1724. Found: 367.1724.

(methyl(phenyl)(vinyl)silyl)ethynyl ferrocene (3g).



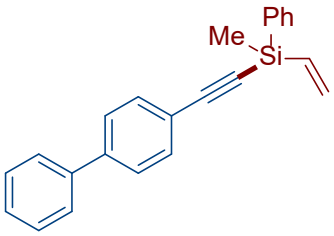
This compound was prepared according to *General procedure (III)* using **1g** (43.3 mg, 0.15 mmol, 100 mol%) and chloro(methyl)(phenyl)(vinyl)silane (82.2 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 1% ethyl acetate in hexane), the title compound was isolated in 58 % yield (31.0 mg, 0.087 mmol) as an orange-yellow oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.74 – 7.69 (m, 2H), 7.44 – 7.39 (m, 3H), 6.32 (dd, *J* = 19.9, 14.4 Hz, 1H), 6.17 (dd, *J* = 14.4, 3.9 Hz, 1H), 6.00 (dd, *J* = 19.9, 3.9 Hz, 1H), 4.51 (t, *J* = 1.9 Hz, 2H), 4.23 (d, *J* = 3.5 Hz, 7H), 0.55 (s, 3H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 135.7, 135.2, 134.5, 134.2, 129.5, 127.9, 107.4, 86.3, 71.9, 70.1, 68.9, 64.2, -2.3.

HRMS (ESI) m/z ([M+H]$^+$) Calcd for $C_{21}H_{20}FeSiH^+$: 357.0756. Found: 357.0748.

([1,1'-biphenyl]-4-ylethynyl)(methyl)(phenyl)(vinyl)silane (3h).



This compound was prepared according to *General procedure (III)* using 4-(bromoethynyl)-1,1'-biphenyl (38.6 mg, 0.15 mmol, 100 mol%) and chloro(methyl)(phenyl)(vinyl)silane (82.2 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: hexane), the title compound was isolated in a 73 % yield (35.5 mg, 0.110 mmol) as a white solid.

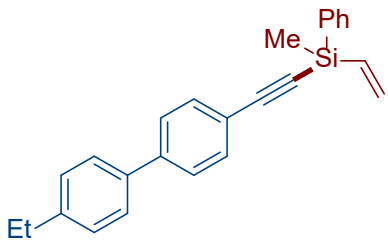
^{1}H NMR (400 MHz, Choroform-*d*) δ 7.77 – 7.71 (m, 2H), 7.63 – 7.56 (m, 6H), 7.49 – 7.37 (m, 6H), 6.36 (dd, *J* = 19.8, 14.4 Hz, 1H), 6.20 (dd, *J* = 14.4, 3.8 Hz, 1H), 6.04 (dd, *J* = 19.9, 3.8 Hz, 1H), 0.62 (s, 3H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 141.5, 140.2, 135.2, 134.9, 134.8, 134.3, 132.5, 129.6, 128.9, 128.0, 127.7, 127.0, 126.9, 121.6, 107.7, 90.7, -2.5.

HRMS (ESI) m/z ([M+NH4]$^+$) Calcd for $C_{23}H_{20}SiNa^+$: 342.1673. Found: 342.1671.

M.P. 94.7 °C

((4'-ethyl-[1,1'-biphenyl]-4-yl)ethynyl)(methyl)(phenyl)(vinyl)silane (3i).



This compound was prepared according to *General procedure (III)* using 4-(bromoethynyl)-4'-ethyl-1,1'-biphenyl (42.8 mg, 0.15 mmol, 100 mol%) and chloro(methyl)(phenyl)(vinyl)silane (82.2 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: hexane), the title compound was isolated in 56 % yield (29.6 mg, 0.084 mmol) as a white solid.

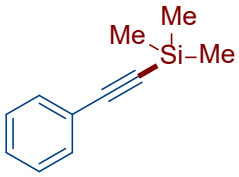
^{1}H NMR (400 MHz, Choroform-*d*) δ 7.77 – 7.72 (m, 2H), 7.63 – 7.52 (m, 6H), 7.44 (dd, *J* = 4.9, 1.9 Hz, 3H), 7.31 (d, *J* = 8.3 Hz, 2H), 6.37 (dd, *J* = 19.8, 14.4 Hz, 1H), 6.21 (dd, *J* = 14.4, 3.8 Hz, 1H), 6.04 (dd, *J* = 19.8, 3.8 Hz, 1H), 2.76 – 2.68 (m, 2H), 1.30 (t, *J* = 7.6 Hz, 3H), 0.62 (s, 3H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 144.0, 141.5, 137.5, 135.2, 134.9, 134.8, 134.3, 132.5, 129.6, 128.4, 127.9, 126.9, 126.7, 121.3, 107.8, 90.5, 28.5, 15.6, -2.5.

HRMS (ESI) m/z ([M+Na]$^+$) Calcd for $C_{25}H_{24}SiNa^+$: 375.1540. Found: 375.1542.

M.P. 50.5 ℃

trimethyl(phenylethynyl)silane (3j).[21]



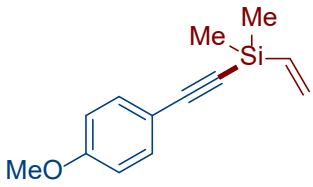
This compound was prepared according to *General procedure (III)* using (bromoethynyl)benzene (27.2 mg, 0.15 mmol, 100 mol%) and TMSCl (48.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: hexane), the title compound was isolated in 95 % yield (24.8 mg, 0.084 mmol) as a colorless oil.

Alkynyl iodide was used instead of alkynyl bromide: this compound was also prepared according to *General procedure (III)* using (iodoethynyl)benzene (34.2 mg, 0.15 mmol, 100 mol%), the title compound was isolated in 49 % yield (12.8 mg, 0.074 mmol).

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.49 – 7.44 (m, 2H), 7.30 (dd, *J* = 5.2, 2.1 Hz, 3H), 0.25 (s, 9H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 131.9, 128.5, 128.2, 123.1, 105.1, 94.1, 0.0.

((4-methoxyphenyl)ethynyl)dimethyl(vinyl)silane (3k).[22]



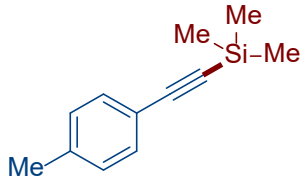
This compound was prepared according to *General procedure (III)* using 1-(bromoethynyl)-4-methoxybenzene (31.7 mg, 0.15 mmol, 100 mol%) and chlorodimethyl(vinyl)silane (54.3 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 1% ethyl acetate in hexane), the title compound was isolated in a 59 % yield (19.1 mg, 0.089 mmol) as a colorless oil.

Alkynyl iodide was used instead of alkynyl bromide: this compound was also prepared according to General procedure (III) using 1-(iodoethynyl)-4-methoxybenzene (38.7 mg, 0.15 mmol, 100 mol%), the title compound was isolated in 99 % yield (32.1 mg, 0.149 mmol).

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.42 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.21 (dd, *J* = 19.9, 14.5 Hz, 1H), 6.04 (dd, *J* = 14.5, 3.9 Hz, 1H), 5.90 (dd, *J* = 19.9, 3.9 Hz, 1H), 3.81 (s, 3H), 0.31 (s, 6H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 159.8, 136.7, 133.5, 133.0, 115.1, 113.8, 106.3, 90.3, 55.2, -1.4.

trimethyl(p-tolylethynyl)silane (3l).[23]

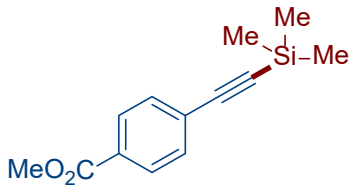


This compound was prepared according to *General procedure (III)* using 1-(bromoethynyl)-4-methylbenzene (29.3 mg, 0.15 mmol, 100 mol%) and TMSCl (48.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: hexane), the title compound was isolated in 58 % yield (16.4 mg, 0.087 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.38 – 7.33 (m, 2H), 7.12 – 7.07 (m, 2H), 2.34 (s, 3H), 0.24 (s, 9H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 138.6, 131.8, 128.9, 120.0, 105.3, 93.2, 21.5, 0.0.

methyl 4-((trimethylsilyl)ethynyl)benzoate (3m).[24]

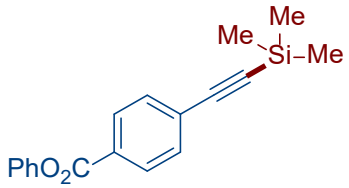


This compound was prepared according to *General procedure (III)* using methyl 4-(bromoethynyl)benzoate (36.0 mg, 0.15 mmol, 100 mol%) and TMSCl (48.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 5% ethyl acetate in hexane), the title compound was isolated in 46 % yield (16.0 mg, 0.069 mmol) as a white solid.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.54 – 7.48 (m, 2H), 3.90 (s, 3H), 0.25 (s, 9H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 166.5, 131.8, 129.6, 129.3, 127.7, 104.0, 97.7, 52.2, -0.2.

phenyl 4-((trimethylsilyl)ethynyl)benzoate (3n).



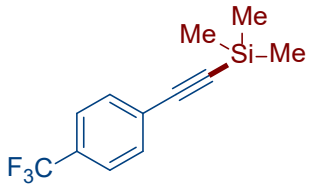
This compound was prepared according to *General procedure (III)* using **1n** (45.2 mg, 0.15 mmol, 100 mol%) and TMSCl (48.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 5% ethyl acetate in hexane), the title compound was isolated in a 73 % yield (32.2 mg, 0.110 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 8.19 – 8.10 (m, 2H), 7.63 – 7.57 (m, 2H), 7.44 (dd, *J* = 8.5, 7.4 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.22 (dd, *J* = 8.5, 1.2 Hz, 2H), 0.30 (s, 9H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 164.6, 150.8, 132.0, 129.9, 129.5, 129.0, 128.4, 125.9, 121.6, 103.9, 98.3, -0.2.

HRMS (ESI) m/z ([M+H]$^+$) Calcd for $C_{18}H_{18}O_2SiH^+$: 295.1149. Found: 295.1136.

trimethyl((4-(trifluoromethyl)phenyl)ethynyl)silane (3o).[25]

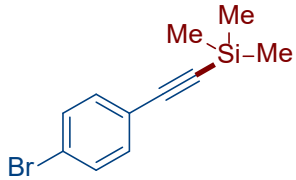


This compound was prepared according to *General procedure (III)* using 1-(bromoethynyl)-4-(trifluoromethyl)benzene (37.4 mg, 0.15 mmol, 100 mol%) and TMSCl (48.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: hexane), the title compound was isolated in 69 % yield (25.1 mg, 0.104 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.56 (s, 4H), 0.28 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 132.17, 130.15 (q, *J* = 32.7 Hz), 126.95 (d, *J* = 1.8 Hz), 125.13 (q, *J* = 3.8 Hz), 123.9z0 (q, *J* = 272.1 Hz), 103.41, 97.16, -0.23.

((4-bromophenyl)ethynyl)trimethylsilane (3p).[26]

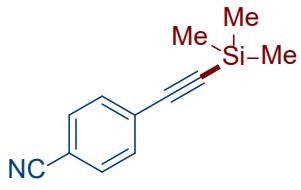


This compound was prepared according to *General procedure (III)* using 1-bromo-4-(bromoethynyl)benzene (39.0 mg, 0.15 mmol, 100 mol%) and TMSCl (48.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: hexane), the title compound was isolated in a 91 % yield (34.6 mg, 0.137 mmol) as a colorless solid.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 0.25 (s, 9H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 133.4, 131.4, 122.7, 122.1, 103.8, 95.6, 29.7, -0.1.

4-((trimethylsilyl)ethynyl)benzonitrile (3q).[27]

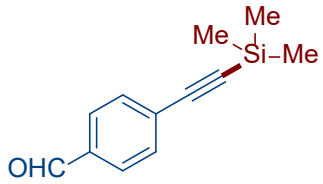


This compound was prepared according to *General procedure (III)* using 4-(bromoethynyl)benzonitrile (30.9 mg, 0.15 mmol, 100 mol%) and TMSCl (48.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 5% ethyl acetate in hexane), the title compound was isolated in a 91 % yield (27.2 mg, 0.137 mmol) as a white solid.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.60 – 7.51 (m, 4H), 0.26 (s, 9H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 132.4, 131.9, 128.0, 118.4, 111.7, 102.9, 99.5 , -0.3.

4-((trimethylsilyl)ethynyl)benzaldehyde (3r).[28]

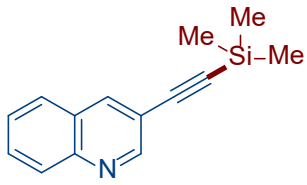


This compound was prepared according to *General procedure (III)* using 4-(bromoethynyl)benzaldehyde (31.4 mg, 0.15 mmol, 100 mol%) and TMSCl (48.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 5% ethyl acetate in hexane), the title compound was isolated in a 42 % yield (12.7 mg, 0.063 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 9.99 (s, 1H), 7.86 – 7.76 (m, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 0.26 (s, 9H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 191.4, 135.5, 132.4, 129.4, 129.3, 103.8, 99.0, -0.3.

3-((trimethylsilyl)ethynyl)quinoline (3s).[29]

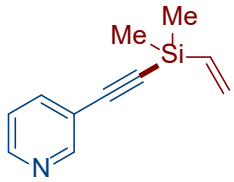


This compound was prepared according to *General procedure (III)* using 3-(bromoethynyl)quinoline (34.8 mg, 0.15 mmol, 100 mol%) and TMSCl (48.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 10 % ethyl acetate in hexane), the title compound was isolated in a 54 % yield (18.3 mg, 0.081 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 8.91 (d, *J* = 2.1 Hz, 1H), 8.25 (dd, *J* = 2.2, 0.9 Hz, 1H), 8.08 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.76 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.74 – 7.68 (m, 1H), 7.58 – 7.52 (m, 1H), 0.30 (s, 9H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 152.3, 146.8, 138.9, 130.2, 129.3, 127.6, 127.3, 127.1, 117.3, 102.0, 98.2, -0.2.

3-((dimethyl(vinyl)silyl)ethynyl)pyridine (3t).



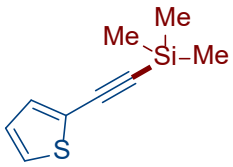
This compound was prepared according to *General procedure (III)* using 3-(bromoethynyl)pyridine (27.3 mg, 0.15 mmol, 100 mol%) and chlorodimethyl(vinyl)silane (54.3 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 10% ethyl acetate in hexane), the title compound was isolated in a 48 % yield (13.5 mg, 0.072 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 8.70 – 8.67 (m, 1H), 8.51 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.19 (m, 1H), 6.18 (dd, *J* = 19.8, 14.5 Hz, 1H), 6.05 (dd, *J* = 14.5, 4.0 Hz, 1H), 5.89 (dd, *J* = 19.8, 4.0 Hz, 1H), 0.31 (s, 6H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 152.6, 148.8, 138.8, 135.9, 133.5, 122.8, 120.1, 102.4, 96.2, -1.7.

HRMS (ESI) m/z ([M+H]$^+$) Calcd for $C_{11}H_{13}NSiH^+$: 188.0890. Found: 188.0895.

trimethyl(thiophen-2-ylethynyl)silane (3u).[30]

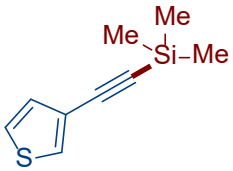


This compound was prepared according to *General procedure (III)* using 2-(bromoethynyl)thiophene (28.1 mg, 0.15 mmol, 100 mol%) and TMSCl (48.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 3% ethyl acetate in hexane), the title compound was isolated in 95 % yield (25.7 mg, 0.143 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.48 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.24 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.13 (dd, *J* = 5.0, 1.2 Hz, 1H), 0.25 (s, 9H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 130.1, 129.6, 125.1, 122.3, 99.9, 93.8, -0.1.

trimethyl(thiophen-3-ylethynyl)silane (3v).[31]

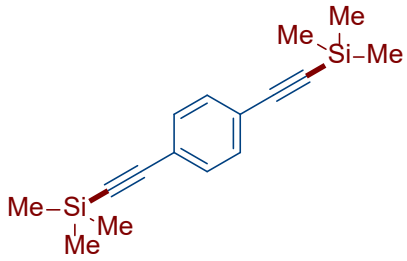


This compound was prepared according to *General procedure (III)* using 3-(bromoethynyl)thiophene (28.1 mg, 0.15 mmol, 100 mol%) and TMSCl (48.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 3 % ethyl acetate in hexane), the title compound was isolated in 95 % yield (25.7 mg, 0.143 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.25 – 7.22 (m, 2H), 6.95 (dd, *J* = 5.1, 3.7 Hz, 1H), 0.26 (s, 9H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 132.6, 127.2, 126.8, 123.2, 98.7, 97.5, -0.2.

1,4-bis((trimethylsilyl)ethynyl)benzene (3w).[32]

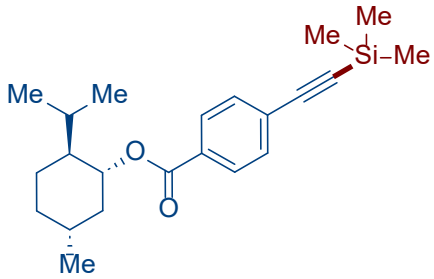


This compound was prepared according to *General procedure (III)* using 1,4-bis(bromoethynyl)benzene (42.6 mg, 0.15 mmol, 100 mol%) and TMSCl (97.8 mg, 0.9 mmol, 600 mol%). After purification by flash column chromatography (Silica gel: hexane), the title compound was isolated in a 73 % yield (29.6 mg, 0.110 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.39 (s, 4H), 0.24 (s, 18H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 131.7, 123.1, 104.5, 96.3, -0.1.

(1R,2R,5R)-2-isopropyl-5-methylcyclohexyl-4-((trimethylsilyl)ethynyl)benzoate (3x).[33]

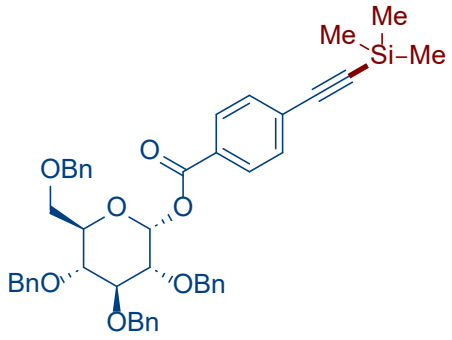


This compound was prepared according to *General procedure (III)* using **1x** (54.5 mg, 0.15 mmol, 100 mol%) and TMSCl (48.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 3 % ethyl acetate in hexane), the title compound was isolated in 52 % yield (27.8 mg, 0.110 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 4.96 – 4.80 (m, 1H), 2.10 (d, *J* = 11.3 Hz, 1H), 1.97 – 1.89 (m, 1H), 1.70 (d, *J* = 11.6 Hz, 2H), 1.57 – 1.48 (m, 2H), 1.09 (t, *J* = 11.5 Hz, 2H), 0.90 (dd, *J* = 7.0, 4.4 Hz, 6H), 0.78 (d, *J* = 7.0 Hz, 3H), 0.25 (s, 9H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 165.3, 131.7, 130.3, 129.3, 127.5, 104.1, 97.3, 74.9, 47.2, 40.9, 34.2, 31.4, 26.4, 23.6, 22.0, 20.7, 16.5, -0.2.

(2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl-4-((trimethylsilyl)ethynyl)benzoate (3y).



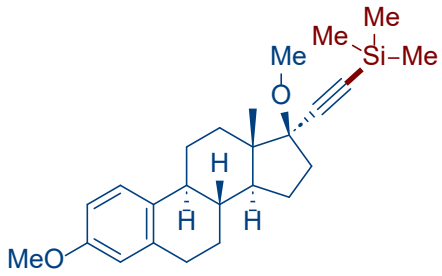
This compound was prepared according to *General procedure (III)* using **1y** (112.2 mg, 0.15 mmol, 100 mol%) and TMSCl (48.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 5 % ethyl acetate in hexane), the title compound was isolated in 24 % yield (26.7 mg, 0.036 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.29 (m, 18H), 7.21 – 7.19 (m, 2H), 6.64 (d, *J* = 3.5 Hz, 1H), 5.04 (d, *J* = 10.9 Hz, 1H), 4.93 – 4.90 (m, 2H), 4.87 – 4.77 (m, 2H), 4.73 – 4.64 (m, 2H), 4.61 – 4.57 (m, 1H), 4.54 – 4.50 (m, 1H), 4.05 – 3.98 (m, 1H), 3.86 – 3.80 (m, 3H), 3.72 – 3.68 (m, 1H), 0.32 (s, 9H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 164.3, 138.5, 137.6, 131.9, 129.7, 128.3, 128.1, 128.0, 127.9, 104.0, 98.1, 90.9, 81.7, 79.0, 75.6, 73.5, 73.1, 68.1, -0.2.

HRMS (ESI) m/z ([M+Na]$^{+}$) Calcd for $C_{46}H_{48}O_7SiNa^{+}$: 763.3062. Found: 763.3090.

(((8R,9S,13S,14S,17S)-3,17-dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)ethynyl)trimethylsilane (3z).



This compound was prepared according to *General procedure (III)* using (8R,9S,13S,14S,17S)-17-(bromoethynyl)-3,17-dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene (60.5 mg, 0.15 mmol, 100 mol%) and TMSCl (48.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 3 % ethyl acetate in hexane), the title compound was isolated in 81 % yield (48.2 mg, 0.122 mmol) as a white solid.

Alkynyl iodide was used instead of alkynyl bromide: this compound was also prepared according to General procedure (III) using (8R,9S,13S,14S,17S)-17-(iodoethynyl)-3,17-dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene (67.6 mg, 0.15 mmol, 100 mol%), the title compound was isolated in 81 % yield (48.2 mg, 0.122 mmol).

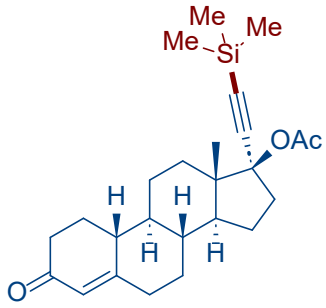
^{1}H NMR (400 MHz, Choroform-*d*) δ 7.24 (d, *J* = 8.6 Hz, 1H), 6.73 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.64 (d, *J* = 2.8 Hz, 1H), 3.79 (s, 3H), 3.42 (s, 3H), 2.90 – 2.83 (m, 2H), 2.39 – 2.31 (m, 1H), 2.29 – 2.19 (m, 2H), 2.04 – 1.95 (m, 2H), 1.91 – 1.86 (m, 1H), 1.83 – 1.73 (m, 3H), 1.48 – 1.35 (m, 4H), 0.88 (s, 3H), 0.22 (s, 9H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 157.4, 137.9, 132.5, 126.3, 113.7, 111.4, 106.8, 92.1, 86.0, 55.1, 53.2, 49.6, 47.5, 43.6, 39.2, 36.7, 34.2, 29.8, 27.3, 26.6, 22.7, 12.7, 0.1.

HRMS (ESI) m/z ([M+Na]$^+$) Calcd for $C_{25}H_{36}O_2SiNa^+$: 419.2377. Found: 419.2393.

M.P. 107.8 °C

(8R,9S,10R,13S,14S,17S)-13-methyl-3-oxo-17-((trimethylsilyl)ethynyl)-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl-acetate (3aa).



This compound was prepared according to *General procedure (III)* using (8R,9S,10R,13S,14S,17S)-17-(bromoethynyl)-13-methyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl acetate (62.9 mg, 0.15 mmol, 100 mol%) and TMSCl (48.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 5 % ethyl acetate in hexane), the title compound was isolated in 66 % yield (40.9 mg, 0.099 mmol) as a white solid.

Alkynyl iodide was used instead of alkynyl bromide: this compound was also prepared according to General procedure (III) using (8R,9S,10R,13S,14S,17S)-17-(iodoethynyl)-13-methyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl acetate (70.0 mg, 0.15 mmol, 100 mol%), the title compound was isolated in 41 % yield (25.4 mg, 0.062 mmol).

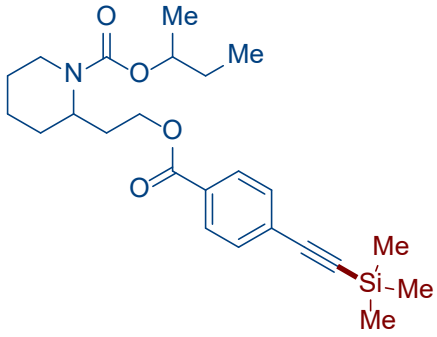
^{1}H NMR (400 MHz, Choroform-*d*) δ 5.81 (s, 1H), 2.72 -2.63 (m, 1H), 2.48 – 2.35 (m, 2H), 2.31 – 2.22 (m, 3H), 2.11 – 2.04 (m, 1H), 2.00 (s, 4H), 1.93 – 1.66 (m, 6H), 1.59 – 1.47 (m, 2H), 1.36 – 1.28 (m, 2H), 1.13 – 1.05 (m, 1H), 0.88 (s, 3H), 0.85 – 0.80 (m, 1H), 0.13 (s, 9H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 199.8, 169.1, 166.4, 124.6, 104.9, 91.2, 84.6, 49.2, 47.6, 47.6, 42.5, 40.7, 37.1, 36.5, 35.4, 32.8, 30.7, 26.5, 26.2, 23.3, 21.4, 13.4, -0.1.

HRMS (ESI) m/z ([M+H]$^+$) Calcd for $C_{25}H_{36}O_3SiH^+$: 413.2507. Found: 413.2543.

M.P. 165.3 °C

sec-butyl 2-(2-((4-((trimethylsilyl)ethynyl)benzoyl)oxy)ethyl)piperidine-1-carboxylate (3ab).



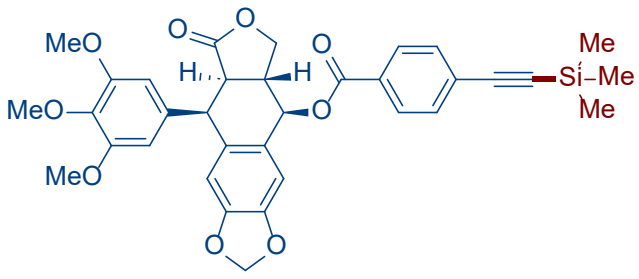
This compound was prepared according to *General procedure (III)* using **1ab** (65.5 mg, 0.15 mmol, 100 mol%) and TMSCl (48.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 15 % ethyl acetate in hexane), the title compound was isolated in 82 % yield (52.8 mg, 0.123 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 4.76 – 4.70 (m, 1H), 4.52 (s, 1H), 4.34 – 4.27 (m, 2H), 4.08 (s, 1H), 2.85 (t, *J* = 13.3 Hz, 1H), 2.25 – 2.17 (m, 1H), 1.92 – 1.83 (m, 1H), 1.61 (d, *J* = 11.0 Hz, 6H), 1.55 – 1.46 (m, 2H), 1.17 (d, *J* = 6.3 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H), 0.26 (s, 9H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 165.9, 155.53 and 155.50, 131.8, 129.9, 129.4, 127.7, 104.1, 97.6, 73.01 and 72.96, 62.82 and 62.77, 47.94 and 47.90, 38.99 and 38.90, 29.1, 28.87 and 28.60, 25.52 and 25.47, 19.8, 19.1, 9.72 and 9.69, -0.2.

HRMS (ESI) m/z ([M+H]$^+$) Calcd for $C_{24}H_{35}NO_4SiH^+$: 430.2408. Found: 430.2416.

(5R,5aR,8aR,9R)-8-oxo-9-(3,4,5-trimethoxyphenyl)-5,5a,6,8,8a,9-hexahydrofuro[3',4':6,7]naphtho[2,3-d][1,3]dioxol-5-yl-4-((trimethylsilyl)ethynyl)benzoate (3ac).



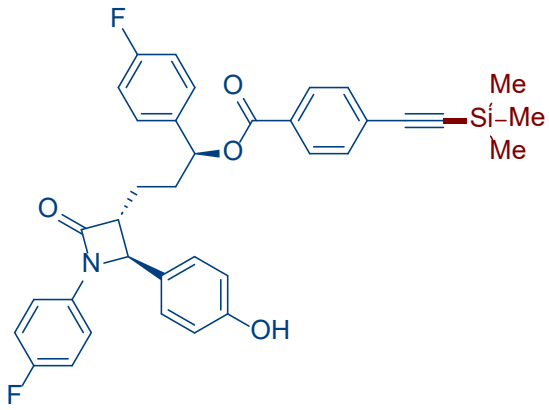
This compound was prepared according to *General procedure (III)* using **1ac** (93.2 mg, 0.15 mmol, 100 mol%) and TMSCl (48.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 20 % ethyl acetate in hexane), the title compound was isolated in 81 % yield (74.7 mg, 0.122 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 6.85 (s, 1H), 6.58 (s, 1H), 6.44 (s, 2H), 6.10 (d, *J* = 8.1 Hz, 1H), 6.02 – 5.97 (m, 2H), 4.64 (d, *J* = 3.5 Hz, 1H), 4.49 – 4.40 (m, 1H), 4.31 (t, *J* = 9.7 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 6H), 2.97 (dd, *J* = 8.7, 3.2 Hz, 2H), 0.27 (s, 9H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 173.6, 166.2, 152.6, 148.2, 147.7, 137.1, 134.7, 132.5, 132.1, 129.4, 128.7, 128.6, 128.2, 109.8, 108.1, 107.1, 103.7, 101.6, 98.6, 77.2, 74.4, 71.5, 60.7, 56.1, 45.6, 43.7, 38.8, 33.8, -0.2.

HRMS (ESI) m/z ([M+H]$^+$) Calcd for $C_{34}H_{34}O_9SiH^+$: 615.2045. Found: 615.2042.

(S)-1-(4-fluorophenyl)-3-((2S,3R)-1-(4-fluorophenyl)-2-(4-hydroxyphenyl)-4-oxoazetidin-3-yl)propyl-4-((trimethylsilyl)ethynyl)benzoate (3ad).



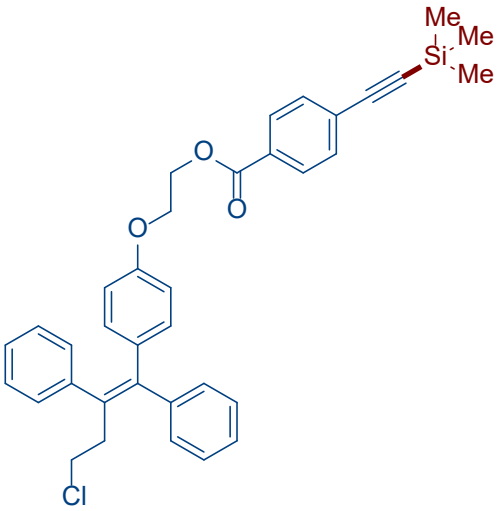
This compound was prepared according to *General procedure (III)* using **1ad** (92.5 mg, 0.15 mmol, 100 mol%) and TMSCl (48.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 25 % ethyl acetate in hexane), the title compound was isolated in 11 % yield (10.1 mg, 0.017 mmol) as a yellow oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 8.13 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.25 – 7.21 (m, 4H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.95 (dd, *J* = 9.1, 8.4 Hz, 2H), 4.65 (t, *J* = 3.8 Hz, 2H), 3.28 (s, 1H), 3.11 – 3.04 (m, 1H), 1.97 – 1.89 (m, 2H), 1.84 (dd, *J* = 8.3, 5.6 Hz, 2H), 0.02 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.18, 164.33, 160.72, 159.00 (d, *J* = 243.6 Hz), 150.83, 140.50, 135.43, 133.80, 132.28, 130.03, 129.14, 127.67, 127.27 (d, *J* = 7.9 Hz), 126.99, 122.52, 118.31 (d, *J* = 7.9 Hz), 115.88 (d, *J* = 22.7 Hz), 115.05 (d, *J* = 21.3 Hz), 82.58, 80.73, 73.81, 60.70 (d, *J* = 13.2 Hz), 31.53 (d, *J* = 1296.1 Hz), 31.42, 29.93 (d, *J* = 49.1 Hz), 0.05.

HRMS (ESI) m/z ([M+Na]$^+$) Calcd for $C_{36}H_{33}NO_4F_2SiNa^+$: 632.2039. Found: 632.2022.

(Z)-2-(4-(4-chloro-1,2-diphenylbut-1-en-1-yl)phenoxy)ethyl-4-((trimethylsilyl)ethynyl)benzoate (3ae).



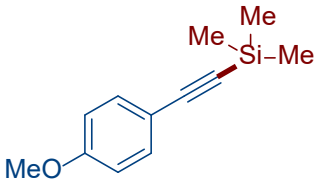
This compound was prepared according to *General procedure (III)* using **1ae** (87.9 mg, 0.15 mmol, 100 mol%) and TMSCl (48.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 10 % ethyl acetate in hexane), the title compound was isolated in 55 % yield (47.8 mg, 0.083 mmol) as a white solid.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.96 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.42 – 7.36 (m, 2H), 7.34 – 7.28 (m, 3H), 7.25 – 7.20 (m, 2H), 7.19 – 7.14 (m, 3H), 6.86 – 6.81 (m, 2H), 6.64 – 6.59 (m, 2H), 4.58 (t, *J* = 4.7 Hz, 2H), 4.21 – 4.13 (m, 2H), 3.48 – 3.39 (m, 2H), 2.99 – 2.91 (m, 2H), 0.29 (s, 9H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 165.8, 156.7, 142.8, 141.6, 140.9, 135.3, 131.8, 131.7, 129.5, 129.5, 129.3, 128.3, 128.2, 127.9, 126.9, 126.6, 113.6, 104.0, 97.8, 65.6, 63.5, 42.8, 38.5, -0.2.

HRMS (ESI) m/z ([M+H]$^+$) Calcd for $C_{36}H_{35}O_3ClSiH^+$: 579.2117. Found: 579.2118.

((4-methoxyphenyl)ethynyl)trimethylsilane (3af).[34]



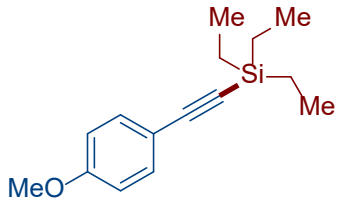
This compound was prepared according to *General procedure (III)* using 1-(bromoethynyl)-4-methoxybenzene (31.7 mg, 0.15 mmol, 100 mol%) and TMSCl (48.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 1 % ethyl acetate in hexane), the title compound was isolated in 84 % yield (25.7 mg, 0.126 mmol) as a colorless oil.

Alkynyl iodide was used instead of alkynyl bromide: this compound was also prepared according to General procedure (III) using 1-(iodoethynyl)-4-methoxybenzene (38.7 mg, 0.15 mmol, 100 mol%), the title compound was isolated in 90 % yield (27.6 mg, 0.135 mmol).

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.43 – 7.38 (m, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 0.24 (s, 9H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 159.7, 133.4, 115.2, 113.8, 105.2, 92.4, 55.2, 0.1.

triethyl((4-methoxyphenyl)ethynyl)silane (3ag).[35]

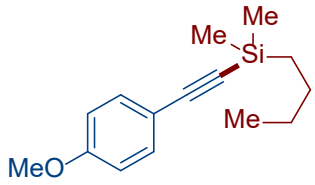


This compound was prepared according to *General procedure (III)* using 1-(bromoethynyl)-4-methoxybenzene (31.7 mg, 0.15 mmol, 100 mol%) and TESCl (67.8 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 1 % ethyl acetate in hexane), the title compound was isolated in 93 % yield (34.4 mg, 0.140 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.42 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.9 Hz, 2H), 3.80 (s, 3H), 1.05 (t, *J* = 7.9 Hz, 9H), 0.71 – 0.63 (m, 6H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 159.6, 133.5, 115.5, 113.8, 106.4, 89.8, 55.2, 7.5, 4.5.

butyl((4-methoxyphenyl)ethynyl)dimethylsilane (3ah).



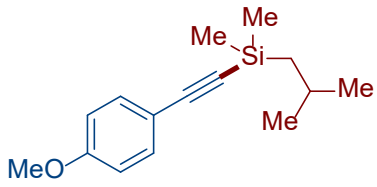
This compound was prepared according to *General procedure (III)* using 1-(bromoethynyl)-4-methoxybenzene (31.7 mg, 0.15 mmol, 100 mol%) and butylchlorodimethylsilane (67.8 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 1 % ethyl acetate in hexane), the title compound was isolated in 95 % yield (35.1 mg, 0.143 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.40 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.9 Hz, 2H), 3.80 (s, 3H), 1.44 – 1.37 (m, 4H), 0.95 – 0.89 (m, 3H), 0.71 – 0.65 (m, 2H), 0.21 (s, 6H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 159.7, 133.5, 115.3, 113.8, 105.5, 91.8, 55.2, 26.3, 26.0, 16.0, 13.8, -1.6.

HRMS (ESI) m/z ([M+Na]$^{+}$) Calcd for $C_{15}H_{22}OSiNa^{+}$: 269.1332. Found: 269.1343.

isobutyl((4-methoxyphenyl)ethynyl)dimethylsilane (3ai).



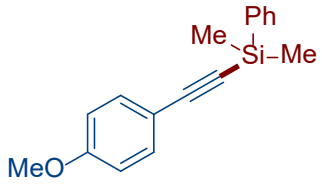
This compound was prepared according to *General procedure (III)* using 1-(bromoethynyl)-4-methoxybenzene (31.7 mg, 0.15 mmol, 100 mol%) and chloro(isobutyl)dimethylsilane (67.8 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 1 % ethyl acetate in hexane), the title compound was isolated in a 69 % yield (25.5 mg, 0.104 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.40 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 2.02 – 1.84 (m, 1H), 1.02 (d, *J* = 6.5 Hz, 6H), 0.71 (d, *J* = 7.0 Hz, 2H), 0.24 (s, 6H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 159.7, 133.4, 115.4, 113.8, 105.6, 92.2, 55.2, 26.8, 26.1, 25.1, -0.7.

HRMS (ESI) m/z ([M+H]$^{+}$) Calcd for $C_{15}H_{22}OSiH^{+}$: 247.1513. Found: 247.1511.

((4-methoxyphenyl)ethynyl)dimethyl(phenyl)silane (3aj).



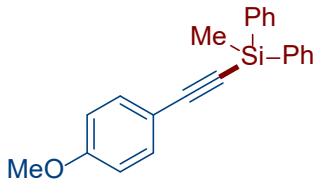
This compound was prepared according to *General procedure (III)* using 1-(bromoethynyl)-4-methoxybenzene (31.7 mg, 0.15 mmol, 100 mol%) and chlorodimethyl(phenyl)silane (76.8 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 1 % ethyl acetate in hexane), the title compound was isolated in 68 % yield (27.2 mg, 0.102 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.73 – 7.69 (m, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.42 – 7.39 (m, 3H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 0.50 (s, 6H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 159.9, 137.3, 133.7, 133.6, 129.3, 127.9, 115.1, 113.8, 106.9, 90.3, 55.3, -0.7.

HRMS (ESI) m/z ([M+H]$^{+}$) Calcd for $C_{17}H_{18}OSiH^{+}$: 267.1200. Found: 267.1203.

((4-methoxyphenyl)ethynyl)(methyl)diphenylsilane (3ak).[36]

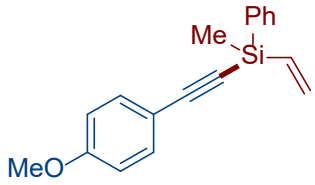


This compound was prepared according to *General procedure (III)* using 1-(bromoethynyl)-4-methoxybenzene (31.7 mg, 0.15 mmol, 100 mol%) and chloro(methyl)diphenylsilane (104.7 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 1 % ethyl acetate in hexane), the title compound was isolated in a 60 % yield (29.6 mg, 0.09 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.72 (dd, *J* = 7.2, 2.2 Hz, 4H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.43 – 7.38 (m, 6H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 0.77 (s, 3H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 160.0, 135.6, 134.5, 133.7, 129.6, 127.9, 114.9, 113.9, 108.5, 88.6, 55.3, -1.9.

((4-methoxyphenyl)ethynyl)(methyl)(phenyl)(vinyl)silane (3al).[37]

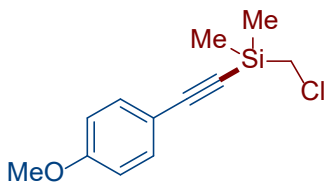


This compound was prepared according to *General procedure (III)* using 1-(bromoethynyl)-4-methoxybenzene (31.7 mg, 0.15 mmol, 100 mol%) and chloro(methyl)(phenyl)(vinyl)silane (82.2 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 2 % ethyl acetate in hexane), the title compound was isolated in a 78 % yield (32.6 mg, 0.117 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.71 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.48 (d, *J* = 8.9 Hz, 2H), 7.41 (dd, *J* = 4.9, 1.9 Hz, 3H), 6.85 (d, *J* = 8.9 Hz, 2H), 6.33 (dd, *J* = 19.9, 14.5 Hz, 1H), 6.17 (dd, *J* = 14.4, 3.9 Hz, 1H), 6.00 (dd, *J* = 19.9, 3.9 Hz, 1H), 3.82 (s, 3H), 0.58 (s, 3H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 160.0, 135.4, 135.0, 134.7, 134.3, 133.7, 129.6, 127.9, 114.9, 113.8, 108.0, 88.3, 55.3, -2.5.

(chloromethyl)((4-methoxyphenyl)ethynyl)dimethylsilane (3am).



This compound was prepared according to *General procedure (III)* using 1-(bromoethynyl)-4-methoxybenzene (31.7 mg, 0.15 mmol, 100 mol%) and chloro(chloromethyl)dimethylsilane (64.4 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica

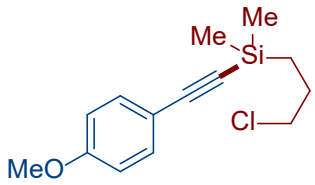
gel: 1 % ethyl acetate in hexane), the title compound was isolated in a 99 % yield (35.5 mg, 0.149 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.44 – 7.37 (m, 2H), 6.85 – 6.80 (m, 2H), 3.81 (s, 3H), 2.93 (s, 2H), 0.36 (s, 6H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 160.1, 133.6, 114.5, 113.9, 107.1, 88.6, 55.3, 30.2, -3.1.

HRMS (ESI) m/z ([M+NH_4]$^+$) Calcd for $C_{12}H_{15}OSiClNH_4^+$: 256.0919. Found: 256.0917.

(3-chloropropyl)((4-methoxyphenyl)ethynyl)dimethylsilane (3an).



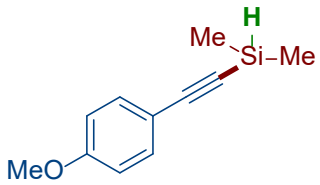
This compound was prepared according to *General procedure (III)* using 1-(bromoethynyl)-4-methoxybenzene (31.7 mg, 0.15 mmol, 100 mol%) and chloro(3-chloropropyl)dimethylsilane (77.0 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 1 % ethyl acetate in hexane), the title compound was isolated in 87 % yield (34.8 mg, 0.131 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.40 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 3.57 (t, *J* = 6.9 Hz, 2H), 1.97 – 1.86 (m, 2H), 0.82 – 0.74 (m, 2H), 0.24 (s, 6H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 159.8, 133.5, 115.0, 113.8, 106.2, 90.8, 55.2, 47.7, 27.6, 13.9, -1.7.

HRMS (ESI) m/z ([M+H]$^+$) Calcd for $C_{14}H_{19}ClOSiH^+$: 267.0967. Found: 267.0968.

((4-methoxyphenyl)ethynyl)dimethylsilane (3ao)[38]

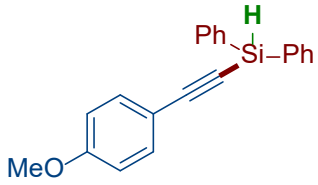


This compound was prepared according to *General procedure (III)* using 1-(bromoethynyl)-4-methoxybenzene (31.7 mg, 0.15 mmol, 100 mol%) and chlorodiphenylsilane (42.6 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 1 % ethyl acetate in hexane), the title compound was isolated in 96 % yield (27.4 mg, 0.144 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.42 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 4.30 – 4.20 (m, 1H), 3.81 (s, 3H), 0.31 (d, *J* = 3.7 Hz, 6H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 159.9, 133.5, 114.9, 113.8, 106.5, 89.4, 55.3, -2.9.

((4-methoxyphenyl)ethynyl)diphenylsilane (3ap).[39]

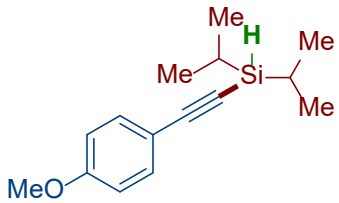


This compound was prepared according to *General procedure (III)* using 1-(bromoethynyl)-4-methoxybenzene (31.7 mg, 0.15 mmol, 100 mol%) and chlorodiphenylsilane (98.4 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 1 % ethyl acetate in hexane), the title compound was isolated in 70 % yield (33.0 mg, 0.105 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.76 – 7.72 (m, 4H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.45 – 7.40 (m, 6H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.31 (s, 1H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 160.2, 135.2 133.8 132.4 130.0, 128.1 114.5, 113.9, 109.8, 85.5 55.3.

diisopropyl((4-methoxyphenyl)ethynyl)silane (3aq).



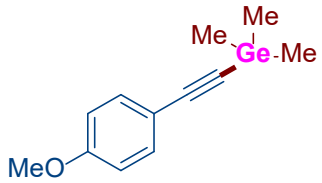
This compound was prepared according to *General procedure (III)* using 1-(bromoethynyl)-4-methoxybenzene (31.7 mg, 0.15 mmol, 100 mol%) and chlorodiisopropylsilane (67.8 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: hexane), the title compound was isolated in a 78 % yield (28.8 mg, 0.117 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 1H), 3.81 (s, 3H), 1.15 – 1.08 (m, 14H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 159.8, 133.6, 115.2, 113.8, 107.9, 86.1, 55.3, 18.5, 18.3, 10.9.

HRMS (ESI) m/z ([M+Na]$^+$) Calcd for $C_{15}H_{22}OSiNa^+$: 269.1332. Found: 269.1339.

((4-methoxyphenyl)ethynyl)trimethylgermane (3ar).[37]



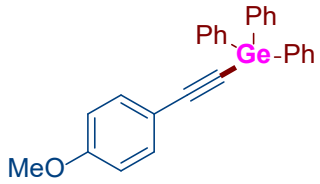
This compound was prepared according to *General procedure (III)* using 1-(bromoethynyl)-4-methoxybenzene (31.7 mg, 0.15 mmol, 100 mol%) and chlorotrimethylgermane (68.9 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 1 %

ethyl acetate in hexane), the title compound was isolated in a 43 % yield (16.1 mg, 0.065 mmol) as a colorless oil.

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.39 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 0.42 (s, 9H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 159.5, 133.3, 115.6, 113.8, 104.2, 92.7, 55.2, -0.1.

((4-methoxyphenyl)ethynyl)triphenylgermane (3as).



This compound was prepared according to *General procedure (III)* using 1-(bromoethynyl)-4-methoxybenzene (31.7 mg, 0.15 mmol, 100 mol%) and chlorotriphenylgermane (152.7 mg, 0.45 mmol, 300 mol%). After purification by flash column chromatography (Silica gel: 1 % ethyl acetate in hexane), the title compound was isolated in 34 % yield (22.2 mg, 0.051 mmol) as a colorless oil.

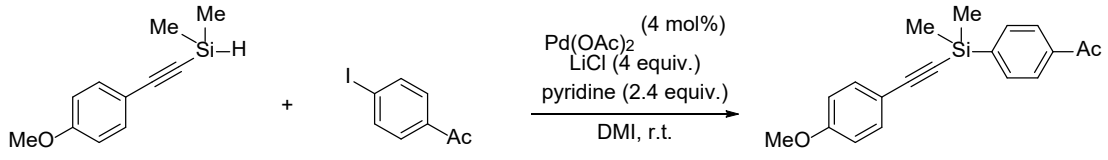
^{1}H NMR (400 MHz, Choroform-*d*) δ 7.71 – 7.65 (m, 6H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.41 (dd, *J* = 5.1, 1.9 Hz, 9H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 159.9, 135.4, 134.6, 133.7, 129.4, 128.4, 115.2, 113.8, 108.2, 86.8, 55.3.

HRMS (ESI) m/z ([M+H]$^{+}$) Calcd for $C_{21}H_{18}OSiH^{+}$: 315.1200. Found: 315.1192.

Part 7. Product Derivatizations

7.1 Cross-coupling:



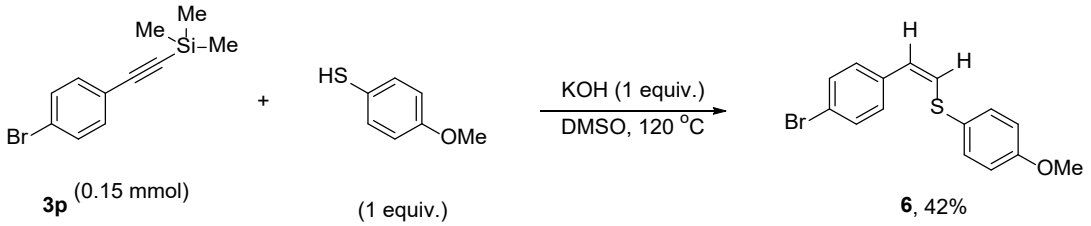
According to a literature procedure,[40] in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was added 1-(4-iodophenyl)ethan-1-one (36.9 mg, 0.15 mmol), LiCl (25.4 mg, 0.6 mmol), **3ao** (57.1 mg, 0.3 mmol), $Pd(OAc)_2$ (1.3 mg, 0.008 mmol), DMI (0.6 mL), and pyridine (28.4 mg, 0.36 mmol). The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at room temperature for 24 hours. The reaction was quenched with water (8.0 mL) and extracted with ethyl acetate (3 × 10.0 mL). The combined organic layer was washed with water (2 ×10.0 mL), and brine (15.0 mL), dried over anhydrous Na_2SO4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give compound **5** (36.1 mg, 78%, colorless oil).

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.61 (s, 3H), 0.50 (s, 6H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 198.3, 160.0, 143.9, 137.6, 134.0, 133.6, 127.3, 114.7, 113.9, 107.5, 89.4, 55.3, 26.6, -0.9.

HRMS (ESI) m/z ($[M+H]^+$) Calcd for $C_{19}H_{20}O_2SiH^+$: 309.1305. Found: 309.1312.

7.2 Nucleophilic addition:



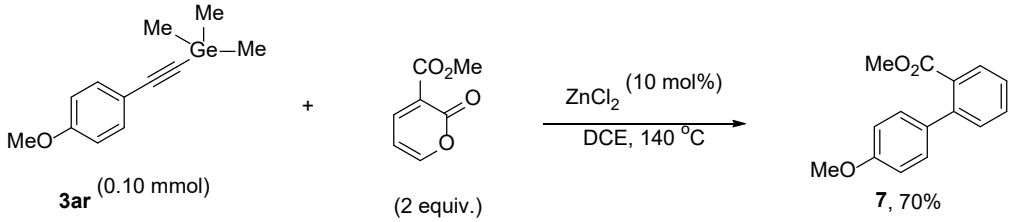
According to a literature procedure,[41] in an argon-filled glove box. To a solution of 4-methoxybenzenethiol (21.0 mg, 0.15 mmol) in DMSO (1 mL), finely crushed KOH (8.4 mg, 1.0 equiv.) and **3p** (38.0 mg, 0.15 mmol) were added under inert atmosphere. The resulting reaction

mixture was heated at 120 °C for 4 h. Progression of the reaction was monitored by TLC, while noticing complete consumption of alkynes, the reaction was brought to room temperature. The reaction mixture was diluted with ethyl acetate (5 mL) and water (5 mL). The organic layer was concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on silica gel to give compound **6** in 42% yield (20.2 mg, 42%, colorless oil).

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.50 (d, *J* = 8.6 Hz, 2H), 7.40 (dd, *J* = 12.4, 8.7 Hz, 4H), 6.90 (d, *J* = 8.7 Hz, 2H), δ 6.45 (d, *J* = 10.8 Hz, 1H), 6.40 (d, *J* = 10.8 Hz, 1H), 3.82 (s, 3H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 159.6, 135.5, 133.0, 131.4, 130.2, 129.5, 126.3, 124.4, 114.9, 55.4.

7.3 Diels-Alder reaction:



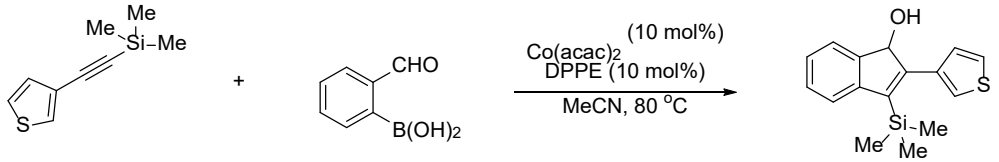
According to a literature procedure,[42] a 10 mL sealed tube equipped with a magnetic stirring bar was charged with $ZnCl_2$ (10 mol%), **3ar** (37.3 mg, 0.15 mmol), 2-pyrone (46.2 mg, 0.30 mmol, 2.0 equiv.) and DCE (1.0 mL). The reaction mixture was stirred at 140 °C for 12 h. The mixture was then filtered through a silica gel pad. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel to yield the desired product **7** as a colorless oil in 70% yield (25.4 mg).

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.81 – 7.77 (m, 1H), 7.54 – 7.48 (m, 1H), 7.41 – 7.33 (m, 2H), 7.26 – 7.23 (m, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H), 3.67 (s, 3H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 169.4, 158.9, 142.0, 133.6, 131.2, 130.8, 130.7, 129.7, 129.4, 126.8, 113.5, 55.2, 52.0.

HRMS (ESI) m/z ($[M+H]^+$) Calcd for $C_{15}H_{14}O_3H^+$: 243.1016. Found: 243.1025.

7.4 [3+2] annulation:



3v (0.15 mmol) (1.5 equiv.) **8**, 95%

According to a literature procedure,[43] a 5 mL sealed tube equipped with a magnetic stirring bar was charged with $Co(acac)_2$ (5.3 mg, 10 mol%), DPPE (6.0 mg, 10 mol%), ortho-formylphenylboronic acid (33.7mg, 0.225 mmol, 1.5 equiv.), **3v** (27.1 mg, 0.15 mmol), and MeCN (1 mL). The reaction mixture was stirred at 80 ℃ for 12 h. The mixture was then filtered through a silica gel pad. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel to yield the desired product **8** as a colorless oil in 95% yield (40.8 mg).

^{1}H NMR (400 MHz, Choroform-*d*) δ 7.54 (d, *J* = 7.3 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.37 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.25 – 7.19 (m, 2H), 7.11 (dd, *J* = 4.9, 1.3 Hz, 1H), 5.25 (s, 1H), 1.89 (s, 1H), 0.19 (s, 9H).

^{13}C NMR (101 MHz, Choroform-*d*) δ 155.7, 146.4, 144.5, 139.8, 137.5, 128.8, 128.5, 125.4, 125.3, 123.9, 123.6, 122.6, 80.6, 0.2.

HRMS (ESI) m/z ($[M+H]^+$) Calcd for $C_{16}H_{18}OSiSH^+$: 287.0920. Found: 287.0921.

Part 8. DFT Data

All DFT calculations were performed using Gaussian 09, and molecular structures were constructed using Gauss View 5.0. The geometry optimization calculations were performed using the B3LYP-D3 functional in combination with a mixed basis set. The basis set included the SDD pseudopotential basis set for Mn atoms and the def2-svp basis set for C, H, O, N, and Br atoms. Frequency analysis was conducted to confirm that all structures exhibited no imaginary frequencies. The solvent model employed was the IEFPCM model, with *N,N*-Dimethylacetamide (DMA) as the solvent, and a dielectric constant of 37.8. The self-consistent field (SCF) convergence threshold was set to 1×10^{-8} Hartree. The convergence thresholds for maximum force, root mean square (RMS) force, maximum displacement, and RMS displacement were set to 0.00045, 0.00030, 0.00180, and 0.00120, respectively.[44]

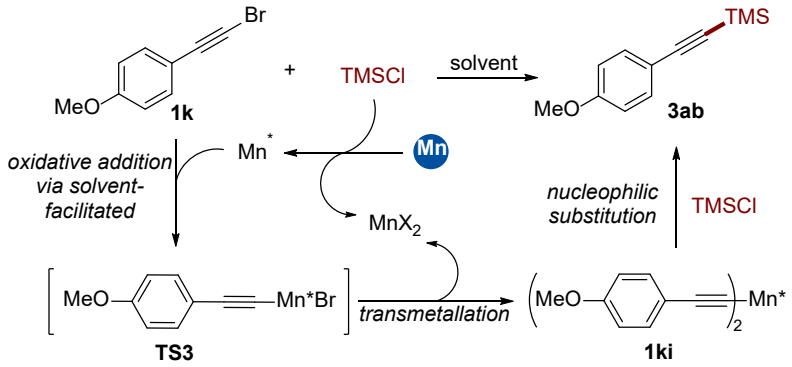


Figure S1. Proposed mechanism.

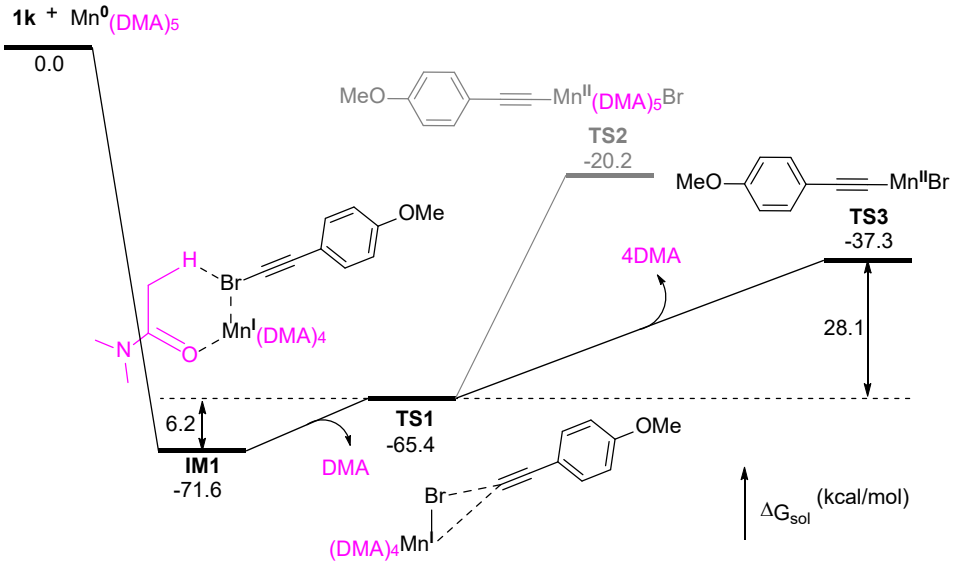


Figure S2. DFT computations for 1k to TS3.

Cartesian Coordinates, SCF Energies, and Free Energies of DFT-Computed Structures

IM1

E_{sol} single-point: -4536.779185 a.u.

G_{sol} thermo-corrected: -4536.873536 a.u.

Mn	-1.56268000	0.22334000	0.20762700
O	-3.04030300	1.43137300	0.95930500
C	-3.74648600	2.45379600	0.94558200
N	-3.25200800	3.69182800	0.82653300
C	-5.24250800	2.29931900	1.10178900
C	-1.82117100	3.95261400	0.82101500
C	-4.08507700	4.88356400	0.85356000
H	-5.61417800	2.88817200	1.95126600
H	-5.77084300	2.63673500	0.19921500
H	-5.45823900	1.23976500	1.26987100
H	-1.54319100	4.47569700	-0.10465000
H	-1.57239100	4.59431200	1.68111500
H	-1.26241600	3.01572500	0.87738600
H	-5.10475900	4.66960200	0.52259800
H	-4.11657100	5.31923600	1.86478100
H	-3.65334000	5.62540700	0.16944600
O	-2.93791600	-0.97769100	-0.73411800
C	-3.95769500	-0.85780600	-1.44247900
N	-4.54337400	-1.96173600	-1.92422200
C	-4.55259400	0.48617300	-1.76413200
C	-3.96416500	-3.25649000	-1.59826800
C	-5.78698700	-1.97713600	-2.67560200
H	-4.67282300	0.60858400	-2.84878800
H	-5.54196900	0.58604400	-1.29569600
H	-3.87154000	1.25752500	-1.39580900
H	-4.15331800	-3.52007200	-0.54650900
H	-4.41435600	-4.01546300	-2.24706700
H	-2.88081100	-3.23579300	-1.76298600
H	-6.53925400	-2.57177600	-2.13731700
H	-6.17880900	-0.96668700	-2.81118500
H	-5.62578900	-2.42876600	-3.66483300
O	-0.01044200	-1.00455100	-0.28180300
C	0.34216800	-1.74804100	-1.21944000
N	1.44140600	-2.49955300	-1.07136900
C	-0.41970600	-1.84965700	-2.50872800
C	2.26928500	-2.26109000	0.09870800
C	1.98857500	-3.29543700	-2.16115700
H	0.26185400	-1.56626900	-3.32448200

H	-0.76677700	-2.87930400	-2.67864800
H	-1.26651300	-1.15846600	-2.47625100
H	1.64503800	-2.23712700	1.00031400
H	3.00704300	-3.06565400	0.18985500
H	2.79238700	-1.29599700	0.00708300
H	1.19268100	-3.84296100	-2.67908800
H	2.51844000	-2.64731000	-2.87605200
H	2.68410900	-4.03116900	-1.74057100
O	-0.10527600	1.27063100	1.25002700
C	0.95885400	0.84630900	1.74618200
N	2.13641300	1.15176200	1.19801100
C	0.92948700	0.01587900	3.00620100
C	2.19733000	1.98945200	0.00799500
C	3.42154500	0.71803400	1.72117900
H	1.16341000	-1.03642600	2.78468500
H	1.64814600	0.37869400	3.75175300
H	-0.08610300	0.06636800	3.40606800
H	1.20608700	2.40797400	-0.19186800
H	2.93246700	2.79111900	0.17324500
H	2.51147700	1.38808200	-0.85964100
H	3.31286800	-0.14317000	2.38713700
H	4.06603800	0.42571300	0.87882900
H	3.91767400	1.53715000	2.26601500
O	-1.83041500	-0.93540700	1.92932600
C	-1.62794500	-2.12501800	2.21697700
N	-1.56944500	-2.51429500	3.50527600
C	-1.46132200	-3.18194400	1.15292200
C	-1.88252600	-1.58868600	4.58082000
C	-1.30861100	-3.88411600	3.91546000
H	-0.40121800	-3.45429000	1.03810200
H	-2.02563300	-4.08953900	1.40172900
H	-1.82586900	-2.76269500	0.21141800
H	-2.68007800	-2.01326900	5.20844800
H	-0.99809500	-1.41584000	5.21239400
H	-2.22131800	-0.63851600	4.15862800
H	-2.24415900	-4.44883500	4.05612800
H	-0.67858000	-4.40398900	3.18745800
H	-0.76957600	-3.86371600	4.87139900
C	6.37428900	1.41288100	-0.56413700
C	5.30446400	1.30214900	-1.45501300
C	4.73250600	0.06201500	-1.78911500
C	5.31059200	-1.08410300	-1.19824700
C	6.37118000	-0.98898100	-0.30898100
C	6.91104300	0.26249000	0.02407800

H	6.77413000	2.40023100	-0.33568700
H	4.88821700	2.20930500	-1.89715500
H	4.90043100	-2.06557600	-1.44442600
H	6.80660700	-1.87886600	0.14847500
O	7.93737100	0.26235100	0.90854100
C	8.50391400	1.49974500	1.26693200
H	9.30391500	1.28562000	1.98378600
H	8.93170400	2.01516000	0.39185800
H	7.76053000	2.16038900	1.74211400
C	3.59253200	-0.03385000	-2.66239400
C	2.58367800	-0.10801200	-3.38926800
Br	-1.21207800	1.74278400	-1.91968600

TS1

E_{sol} single-point: -4249.393092 a.u.

G_{sol} thermo-corrected: -4249.478868 a.u.

Mn	1.66499600	-0.35774500	0.57283600
O	3.29506700	-1.46748200	1.04943100
C	4.21525600	-2.13335300	0.52580500
N	3.99386200	-3.27729400	-0.11920500
C	5.63616100	-1.64483700	0.66668700
C	2.66317500	-3.85866700	-0.20170600
C	5.04660600	-4.06301100	-0.74376000
H	6.28515400	-2.41969000	1.09560700
H	6.04795300	-1.36140100	-0.31257200
H	5.63111900	-0.76665600	1.31963500
H	2.30299300	-3.81857700	-1.23964400
H	2.71602900	-4.90760600	0.12476600
H	1.97117500	-3.30068600	0.43435700
H	5.93416200	-3.45746500	-0.94395200
H	5.32465300	-4.91730700	-0.10768800
H	4.67191800	-4.44866800	-1.70102400
O	2.71366400	1.36581800	0.77353600
C	3.62937700	2.04852700	0.27195300
N	3.76193600	3.33243900	0.62521900
C	4.58963000	1.45034100	-0.71959600
C	2.85820800	3.92877000	1.59788100
C	4.83811200	4.19925600	0.17526200
H	4.57003400	2.00819600	-1.66582600
H	5.61555000	1.47518900	-0.32687300
H	4.28271300	0.41797300	-0.91304400
H	3.34544800	3.99910100	2.58260500
H	2.59411300	4.94142800	1.26442800

H	1.95175000	3.32274900	1.68730200
H	5.44679200	4.51333700	1.03602300
H	5.48352700	3.69211900	-0.54517100
H	4.41521700	5.09589200	-0.29932300
O	0.03031800	0.80767800	0.54553800
C	-0.21450700	1.96716500	0.13722600
N	-1.20880200	2.64749600	0.70790600
C	0.55434600	2.61136900	-0.97886300
C	-2.01366500	1.95599400	1.70511400
C	-1.59180100	3.97509600	0.24295600
H	-0.16201300	2.91537000	-1.75764100
H	1.09717800	3.49981400	-0.62284300
H	1.26033100	1.88028700	-1.38745700
H	-1.37076200	1.54725200	2.49602100
H	-2.72743400	2.66235600	2.14066400
H	-2.56441500	1.12262600	1.24207800
H	-0.71317700	4.63100900	0.18745000
H	-2.06987500	3.90833900	-0.74613900
H	-2.29408700	4.40675300	0.96419800
O	0.38009500	-1.87762800	1.02688100
C	-0.80519700	-1.91834500	1.43348500
N	-1.83806200	-1.60833700	0.65563500
C	-1.06528800	-2.35092400	2.85479800
C	-1.66016500	-1.28428400	-0.75240300
C	-3.21909600	-1.62567400	1.11462300
H	-1.37957900	-1.48481200	3.45608000
H	-1.84935500	-3.11527900	2.91887800
H	-0.13016000	-2.74344300	3.26540300
H	-0.60873600	-1.40169700	-1.03300500
H	-2.29136300	-1.95900400	-1.35100300
H	-1.97386000	-0.24680000	-0.94508000
H	-3.28165300	-1.50372100	2.19990500
H	-3.75346800	-0.79159700	0.63884700
H	-3.71840900	-2.56333800	0.82232400
C	-5.94020900	-0.91696900	-1.11049600
C	-4.93311000	-0.22866500	-1.79022100
C	-4.44491000	1.01420200	-1.34851200
C	-5.03077100	1.54739100	-0.17848000
C	-6.02860000	0.87191900	0.50997000
C	-6.49359600	-0.37041200	0.05256700
H	-6.27867700	-1.87839200	-1.49557800
H	-4.50542200	-0.67031300	-2.69225700
H	-4.68283000	2.51446900	0.19026600
H	-6.47127400	1.28957600	1.41564400

O	-7.46692200	-0.95990300	0.78760400
C	-7.92963400	-2.22613800	0.38290900
H	-8.69129200	-2.53122800	1.10853200
H	-8.38230500	-2.18821800	-0.62104100
H	-7.11477300	-2.96857400	0.37950500
C	-3.39682100	1.70751200	-2.04991500
C	-2.49571100	2.30490800	-2.66760000
Br	1.97871900	-0.79516400	-1.94037700

TS2

E_{sol} single-point: -4249.434808 a.u.

G_{sol} thermo-corrected: -4249.520735 a.u.

Mn	0.86922700	-0.21885000	-0.13019600
O	1.10935300	-2.26913300	-0.23500600
C	1.74218100	-3.31059700	-0.45827600
N	2.28995300	-3.59201300	-1.64968600
C	1.88109800	-4.32972700	0.65138600
C	2.11427200	-2.70649500	-2.78743500
C	3.00261600	-4.82303600	-1.94174900
H	1.49663200	-5.31064300	0.34110900
H	2.93309800	-4.45275400	0.94524700
H	1.30797400	-3.97010600	1.51145000
H	3.09288600	-2.34130900	-3.13138900
H	1.63482400	-3.26377100	-3.60766600
H	1.49807900	-1.84998400	-2.50316400
H	3.31040500	-5.33921000	-1.02912100
H	2.37777900	-5.50064900	-2.54484800
H	3.90492300	-4.58120700	-2.52020700
O	1.27220900	-0.17300300	1.89472100
C	2.10760800	-0.54509100	2.73265800
N	2.11026900	-0.00171500	3.96414400
C	3.12299100	-1.60918700	2.40696800
C	1.14160700	1.01839700	4.32605200
C	2.99390400	-0.40935400	5.04034400
H	4.14303300	-1.25828400	2.61156900
H	2.93952900	-2.51241900	3.00647700
H	3.03437800	-1.83085300	1.34055100
H	0.43441800	0.62375900	5.07207900
H	1.66373600	1.88081500	4.76576100
H	0.58988700	1.33364200	3.43623700
H	2.39839400	-0.75312600	5.89943900
H	3.65487200	-1.22127300	4.72918000
H	3.60945800	0.44275800	5.36545800

O	0.60128100	1.83185400	-0.05086200
C	1.10107500	2.83997200	0.46767900
N	0.51879900	4.04306000	0.28648300
C	2.35086700	2.76467900	1.30816200
C	-0.70209700	4.16243000	-0.49137800
C	0.99082500	5.28399500	0.87181700
H	3.11794700	3.45163700	0.92574900
H	2.13294500	3.04024600	2.34990800
H	2.73102500	1.74076300	1.25926300
H	-1.55228400	4.40226200	0.16617100
H	-0.59211500	4.97655700	-1.22358600
H	-0.89938300	3.21991200	-1.01150900
H	1.83058200	5.11422600	1.54925500
H	1.30702700	5.98215400	0.08186800
H	0.17562300	5.75456500	1.44116500
O	0.48335800	0.01450000	-2.16843300
C	-0.36827100	0.73059800	-2.72318000
N	-0.06437100	1.97234800	-3.12870200
C	-1.75872100	0.20838300	-2.98557700
C	1.28091100	2.49643500	-2.95341500
C	-0.98069800	2.81487600	-3.87866800
H	-2.49463400	0.77279000	-2.39486100
H	-2.02247900	0.29077000	-4.04884900
H	-1.79221800	-0.83638800	-2.66371900
H	1.89099900	1.76877700	-2.40656000
H	1.72783900	2.70523900	-3.93782900
H	1.23895800	3.43743900	-2.38288200
H	-2.02259000	2.59515900	-3.62522400
H	-0.78153200	3.86399000	-3.62374600
H	-0.83868500	2.68979800	-4.96391500
C	-5.96124800	-1.51951300	-0.07831100
C	-4.57210500	-1.44727200	-0.19718500
C	-3.80585200	-0.54413200	0.55803800
C	-4.50146100	0.29758100	1.45267100
C	-5.88100900	0.23652100	1.57919000
C	-6.62676900	-0.67258200	0.81401300
H	-6.50996500	-2.23836300	-0.68560600
H	-4.06429800	-2.11280600	-0.89766900
H	-3.93650600	1.01101800	2.05526700
H	-6.41456400	0.88943000	2.27162900
O	-7.96768800	-0.65961200	1.00042500
C	-8.75196400	-1.56637400	0.26256300
H	-9.79357400	-1.39086800	0.55233200
H	-8.64671900	-1.40025300	-0.82163700

H	-8.48354500	-2.61029000	0.49198000
C	-2.37501000	-0.47652800	0.41481400
C	-1.15284600	-0.41654900	0.24326300
Br	3.50328800	0.01385500	-0.75798200

TS3

E_{sol} single-point: -3099.862794 a.u.

G_{sol} thermo-corrected: -3099.904163 a.u.

C	4.20428400	0.99882700	-0.01150600
C	2.81265300	1.08923100	-0.02581300
C	2.00192700	-0.05731700	-0.03267100
C	2.63896900	-1.31373700	-0.01905000
C	4.02027800	-1.41437300	0.00179500
C	4.81730600	-0.25918000	0.00945700
H	4.79830300	1.91194400	-0.00569800
H	2.34225400	2.07370400	-0.02885500
H	2.02989300	-2.21923200	-0.02277100
H	4.51622100	-2.38583500	0.01178200
O	6.15393700	-0.45083600	0.03052700
C	6.99691500	0.67850500	0.06299600
H	8.02365600	0.30212100	0.12075100
H	6.88447200	1.28508600	-0.84986000
H	6.79673800	1.31337800	0.94080000
C	0.56458100	0.03302100	-0.04287600
C	-0.66365100	0.09522400	-0.05336300
Mn	-2.68245800	0.09717300	-0.05098900
Br	-5.19774700	-0.00585700	0.04373000

DMA

E_{sol} single-point: -287.352804 a.u.

G_{sol} thermo-corrected: -287.384848 a.u.

C	0.72301000	-0.29566800	0.00000000
O	1.06326000	-1.47098200	-0.00000100
N	-0.58689800	0.07824500	-0.00000100
C	1.76449700	0.80743500	0.00000100
H	1.67272600	1.44625200	-0.88895600
H	1.67273000	1.44624300	0.88896500
H	2.74833100	0.32846700	-0.00000300
C	-1.62485000	-0.93199200	0.00000100
H	-2.26259300	-0.82697200	0.89188400
H	-2.26259700	-0.82697500	-0.89188000
H	-1.15929000	-1.92110100	0.00000100

C	-1.06336300	1.44493600	-0.00000100
H	-0.23587200	2.15878800	0.00001600
H	-1.68348600	1.63359300	-0.89071300
H	-1.68351100	1.63358100	0.89069600

Mn(DMA)$_5$

E_{sol} single-point: -1541.070633 a.u.

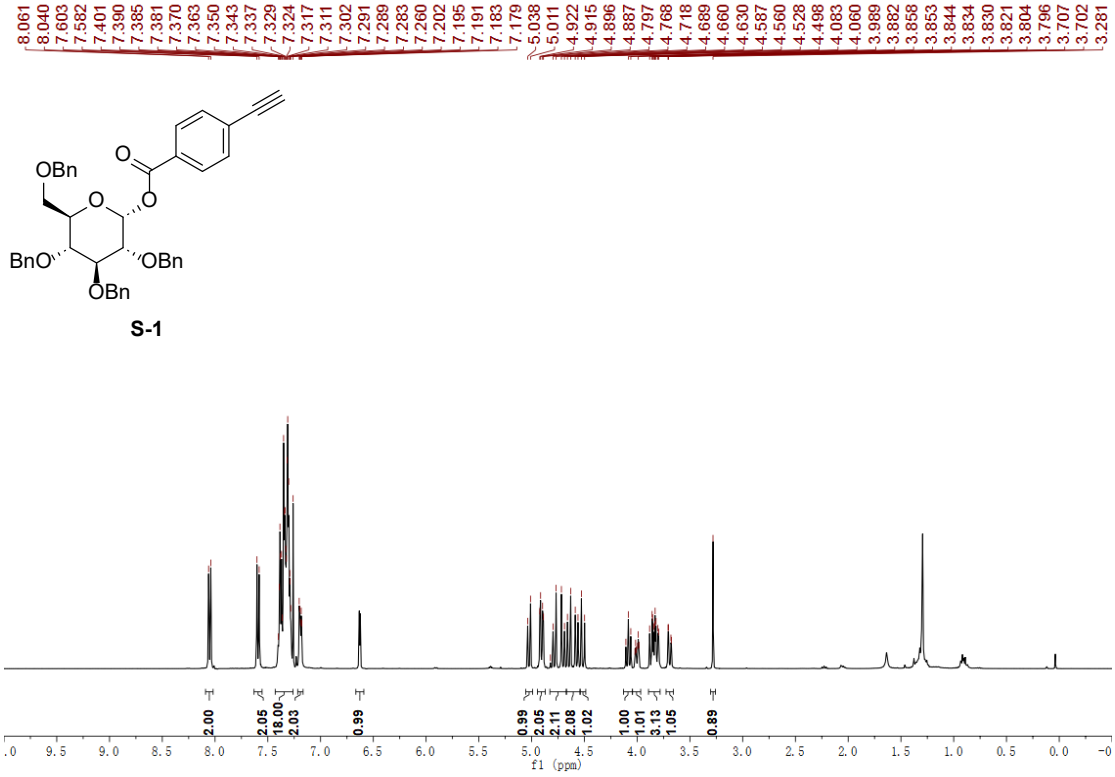
G_{sol} thermo-corrected: -1541.148729 a.u.

Mn	0.00882900	0.21037500	0.20908400
O	1.82660400	-0.51848300	0.28182200
C	2.49540900	-1.62737800	0.04356900
N	3.80917500	-1.67077100	0.60571700
C	1.75927800	-2.94619100	0.04663100
C	4.48896900	-0.40411700	0.65202000
C	4.65846900	-2.71549100	0.08779500
H	2.17786300	-3.67856300	-0.66056200
H	1.77622900	-3.41182600	1.05440100
H	0.70747300	-2.75926800	-0.20600800
H	3.83699100	0.35000700	1.10801600
H	5.41054800	-0.49742700	1.24632100
H	4.77776700	-0.04878600	-0.36817800
H	4.20110900	-3.70269500	0.22904300
H	4.86516200	-2.58201900	-0.99901000
H	5.61767800	-2.71163500	0.62535900
O	-1.04776800	-1.44690900	0.20940800
C	-1.86199800	-1.95691900	1.11118600
N	-1.44806600	-1.95289400	2.48623700
C	-2.55693900	-3.22954900	0.68925700
C	-0.28741400	-1.16506300	2.81385900
C	-2.51693900	-1.76086800	3.43738100
H	-1.81197900	-4.03915700	0.53846300
H	-3.28112800	-3.58583000	1.43455000
H	-3.09000300	-3.08644500	-0.26250400
H	0.56935200	-1.43500300	2.18473200
H	-0.46708900	-0.06529200	2.71642200
H	-0.01166100	-1.34552900	3.86316200
H	-3.38588200	-2.37744500	3.17197600
H	-2.18758400	-2.05595000	4.44604800
H	-2.85478300	-0.70140400	3.48009400
O	-1.75048600	1.24200500	0.78062400
C	-2.44545700	2.07584100	0.18927100
N	-3.79029800	2.02092100	0.29185800
C	-1.82208500	3.16306300	-0.65047700

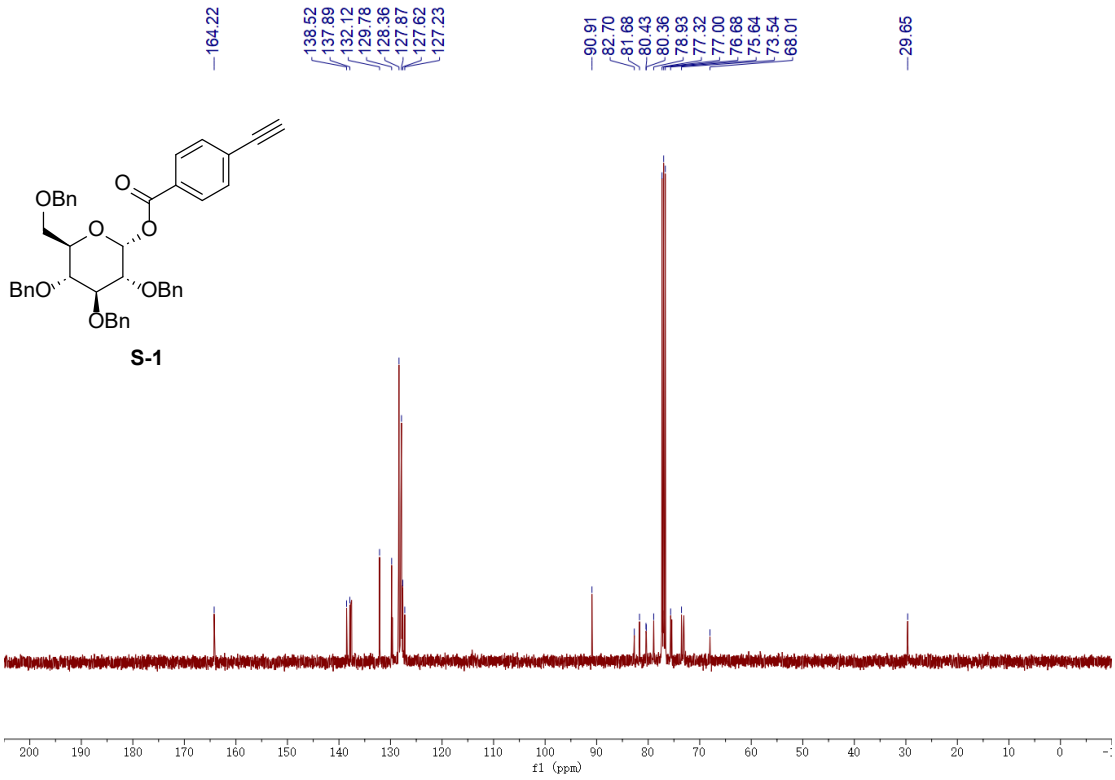
C	-4.41533300	0.93786600	1.03338600
C	-4.69771100	2.96966800	-0.31618700
H	-2.16689000	3.09526600	-1.69089000
H	-2.07534700	4.15561900	-0.25124600
H	-0.73865600	3.01755000	-0.62178900
H	-4.77877100	1.29247100	2.01154700
H	-5.27316700	0.55980900	0.45689100
H	-3.69001700	0.12702900	1.18841700
H	-5.39076600	3.36485300	0.44244300
H	-4.15802200	3.81034500	-0.76045700
H	-5.29657600	2.48122500	-1.10271700
O	1.05368600	2.03317200	0.30636600
C	2.14985000	2.13914300	-0.27077200
N	3.17416400	2.76562500	0.34110500
C	2.34282200	1.60918100	-1.66708400
C	3.02622900	3.25023400	1.70054800
C	4.50273800	2.89749800	-0.21804000
H	2.79380200	2.36025200	-2.32948700
H	2.97889300	0.70910700	-1.63413000
H	1.35709400	1.31899200	-2.05014700
H	3.62483200	2.63255600	2.38961600
H	3.37926100	4.29055000	1.76378800
H	1.97386300	3.19701200	1.99161100
H	4.59352100	2.34549200	-1.15704400
H	4.74826900	3.95729100	-0.39512900
H	5.23884100	2.48504600	0.48955100
O	-0.82105000	0.60517300	-1.95202800
C	-1.47136100	-0.41304400	-2.24384300
N	-0.86132600	-1.47705500	-2.79268000
C	-2.95764000	-0.44746200	-1.98878200
C	0.57422200	-1.38374500	-3.01380800
C	-1.41294400	-2.81634800	-2.75710000
H	-3.51882300	-1.00826900	-2.74564200
H	-3.11807400	-0.89443500	-0.99333800
H	-3.31229800	0.59013100	-1.96697400
H	1.14418200	-1.39433800	-2.06838400
H	0.88697200	-2.23814800	-3.62677600
H	0.80522500	-0.45314300	-3.54712900
H	-0.96626200	-3.37996500	-1.92241700
H	-2.49541300	-2.79063900	-2.60397800
H	-1.20286800	-3.33513000	-3.70367200

II. Spectral Data for New Compounds

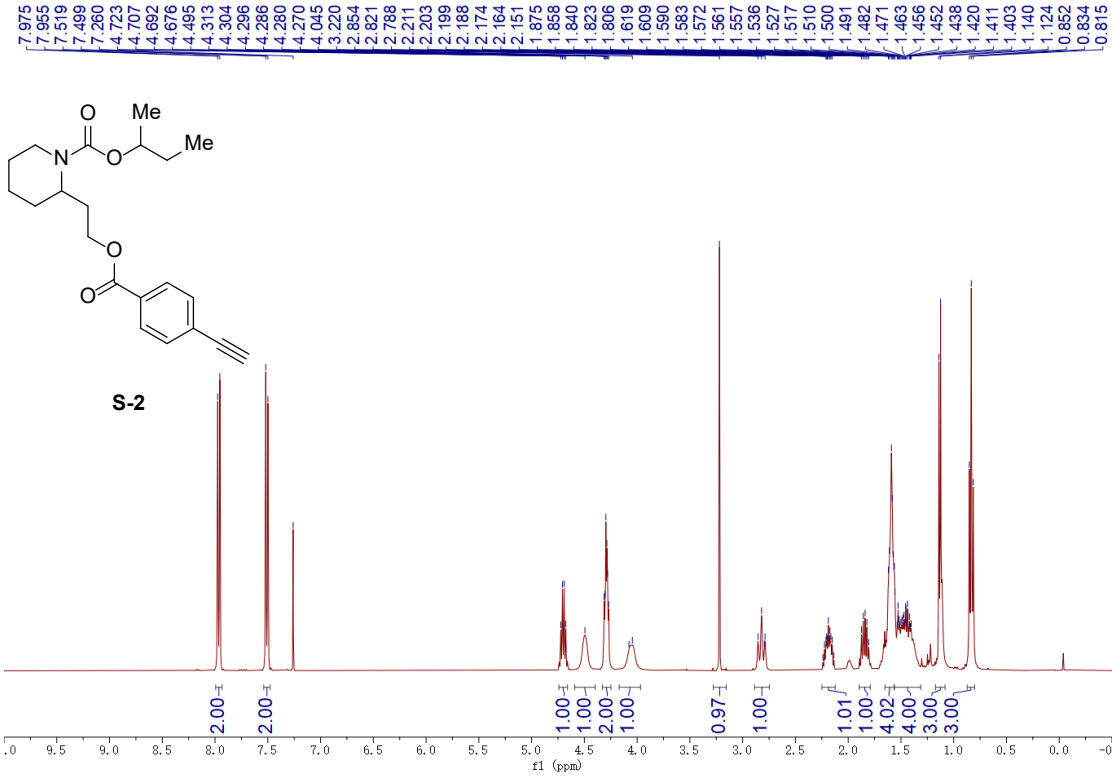
^{1}H NMR：400MHz, Choroform-*d*, peak of $CHCl_3$ in 7.260



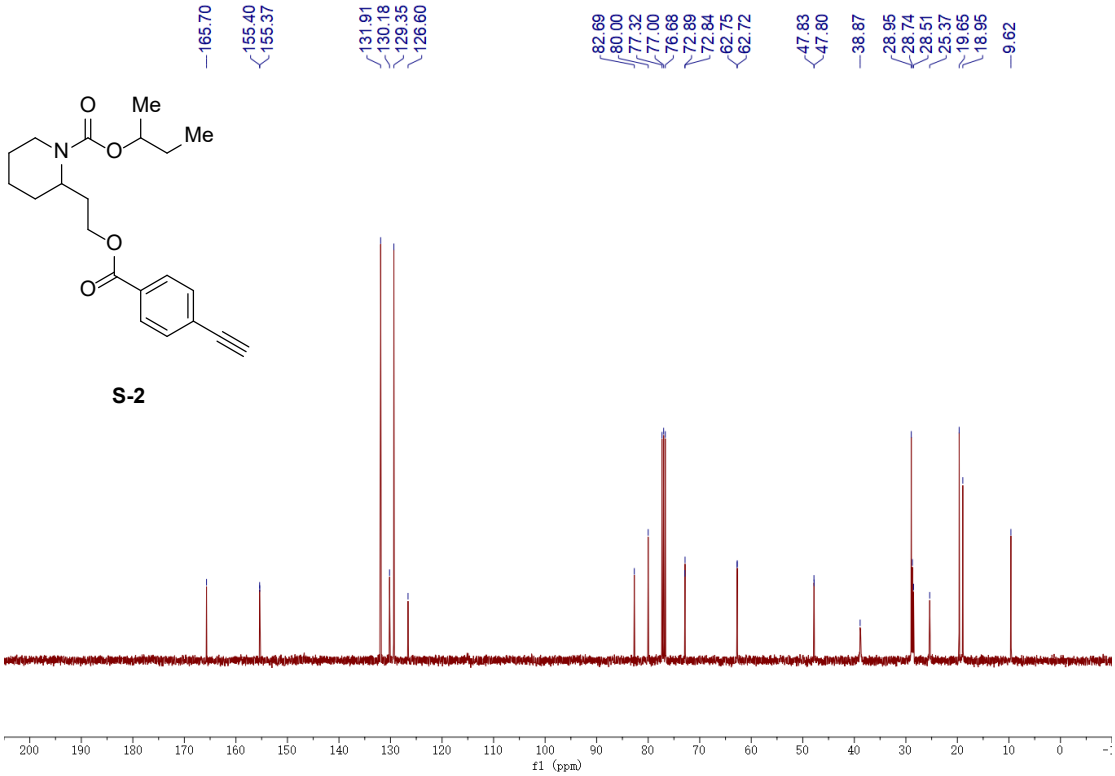
^{13}C NMR：101MHz, Choroform-*d*, peak of $CHCl_3$ in 77.0



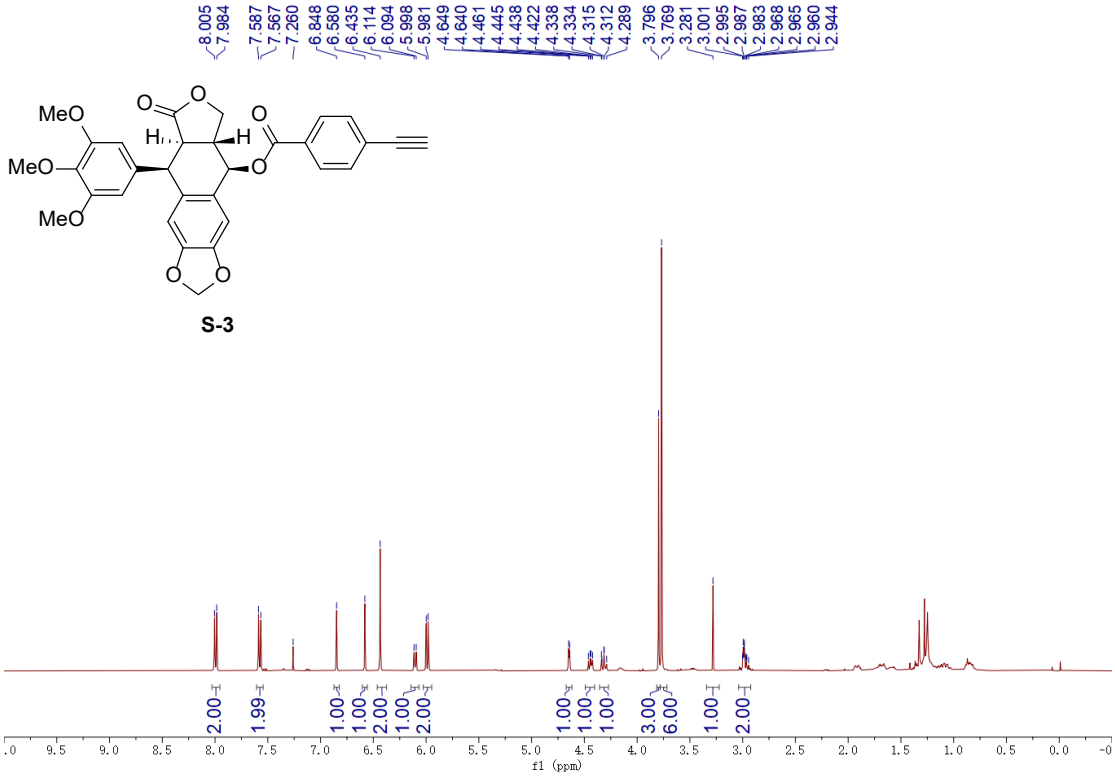
^{1}H NMR：400MHz, Choroform-*d*, peak of $CHCl_3$ in 7.260



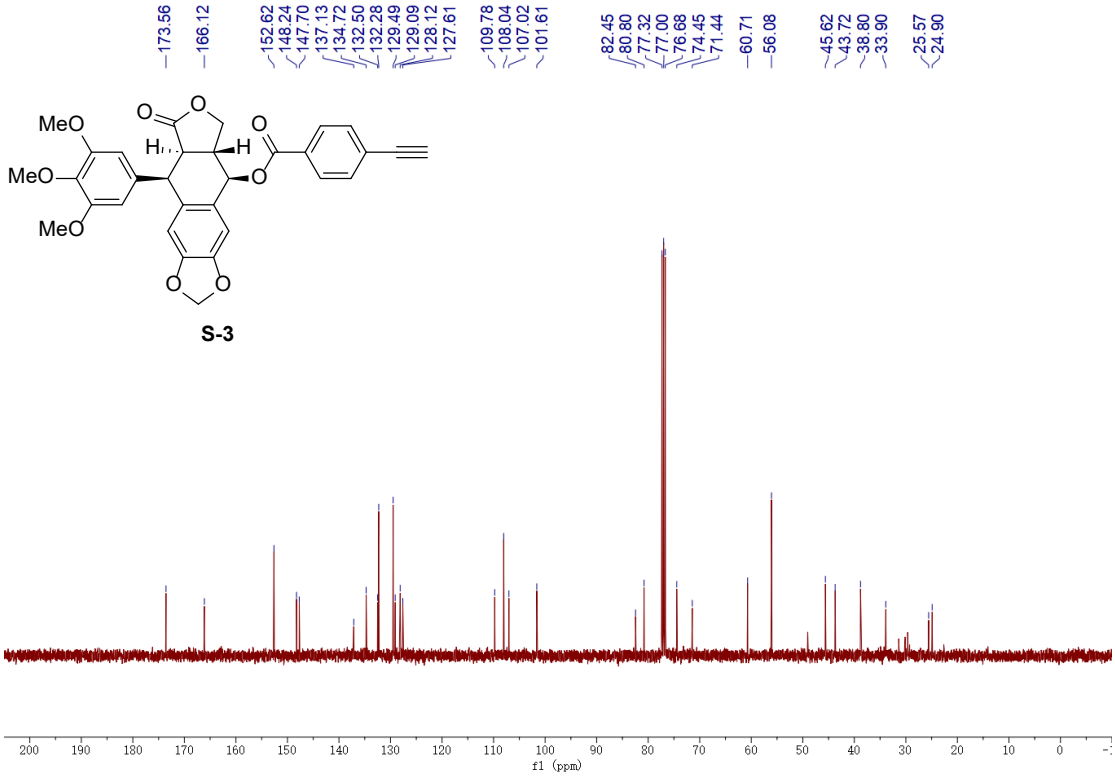
^{13}C NMR：101MHz, Choroform-*d*, peak of $CHCl_3$ in 77.0



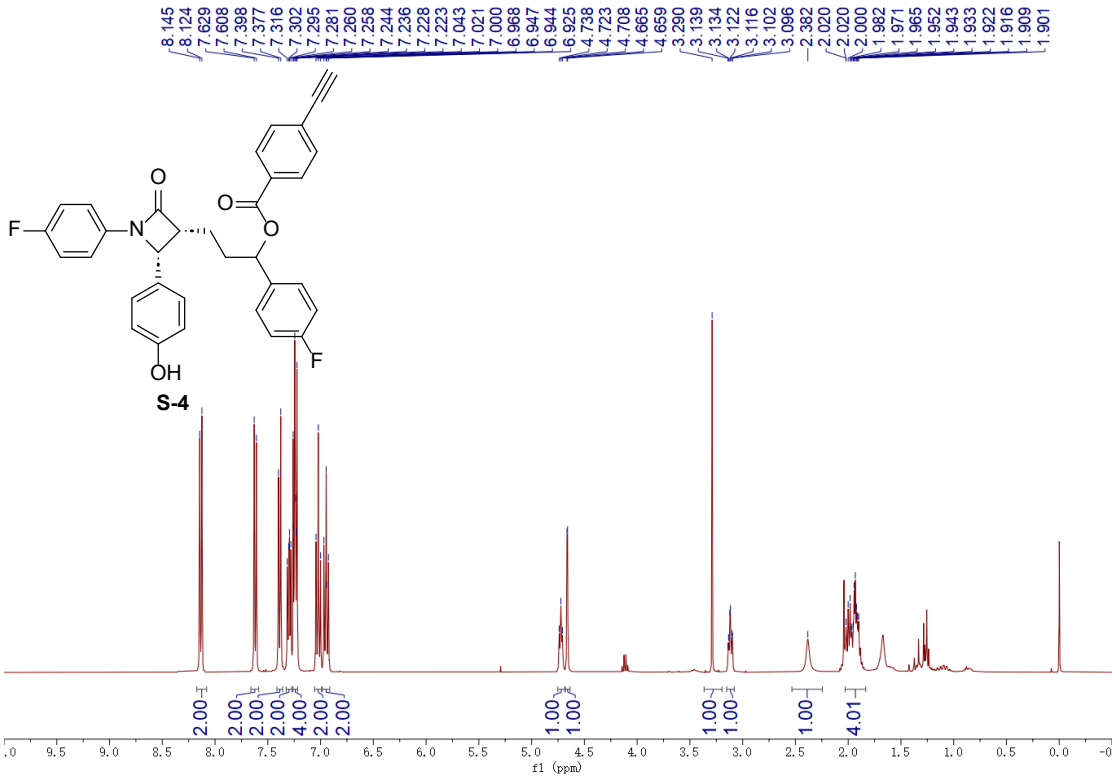
^{1}H NMR：400MHz, Choroform-*d*, peak of $CHCl_3$ in 7.260



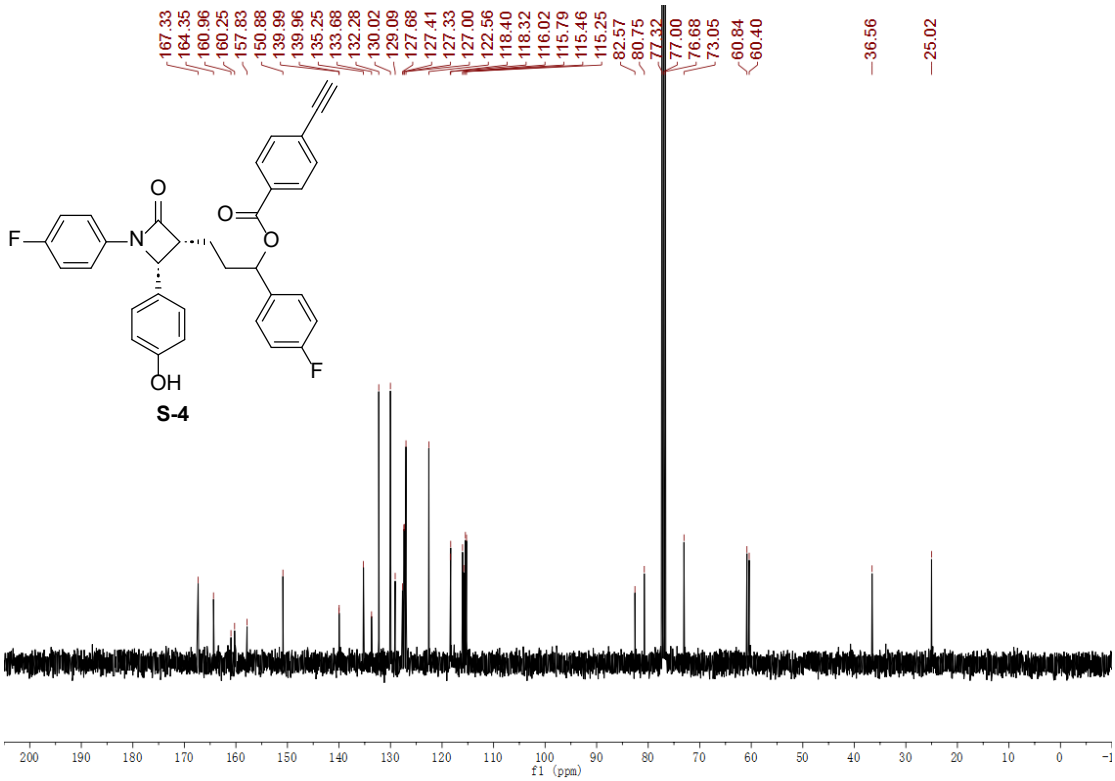
^{13}C NMR：101MHz, Choroform-*d*, peak of $CHCl_3$ in 77.0



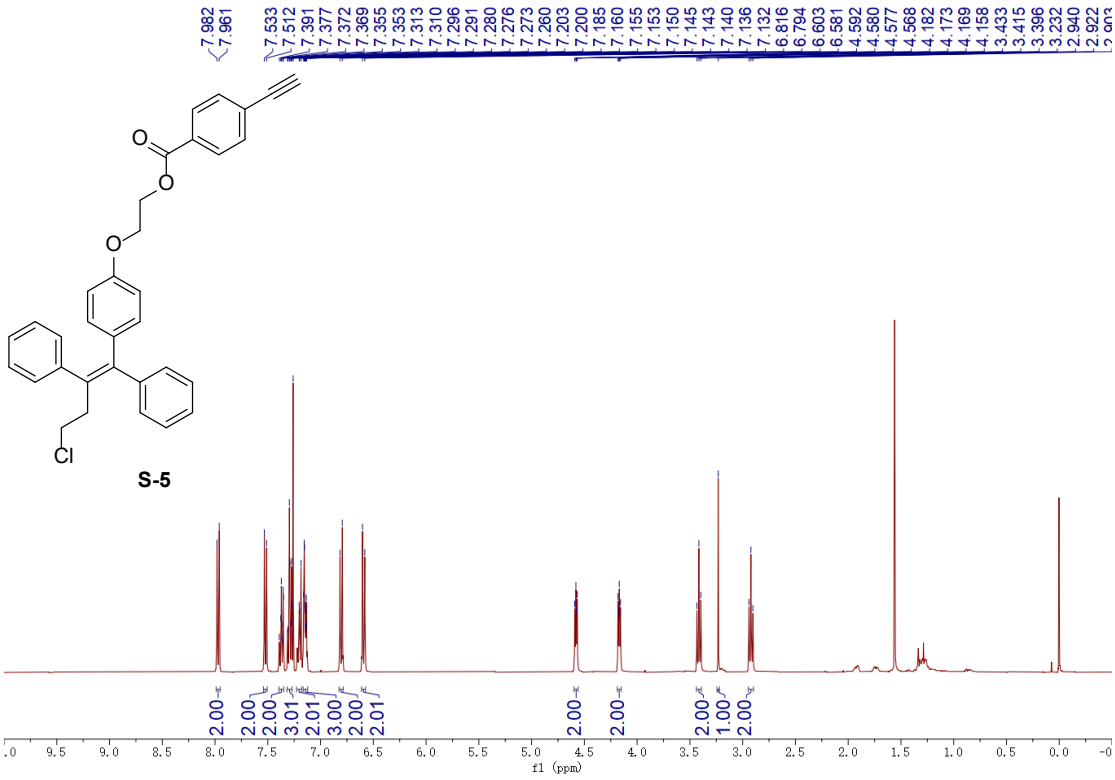
^{1}H NMR：400MHz, Choroform-*d*, peak of $CHCl_3$ in 7.260



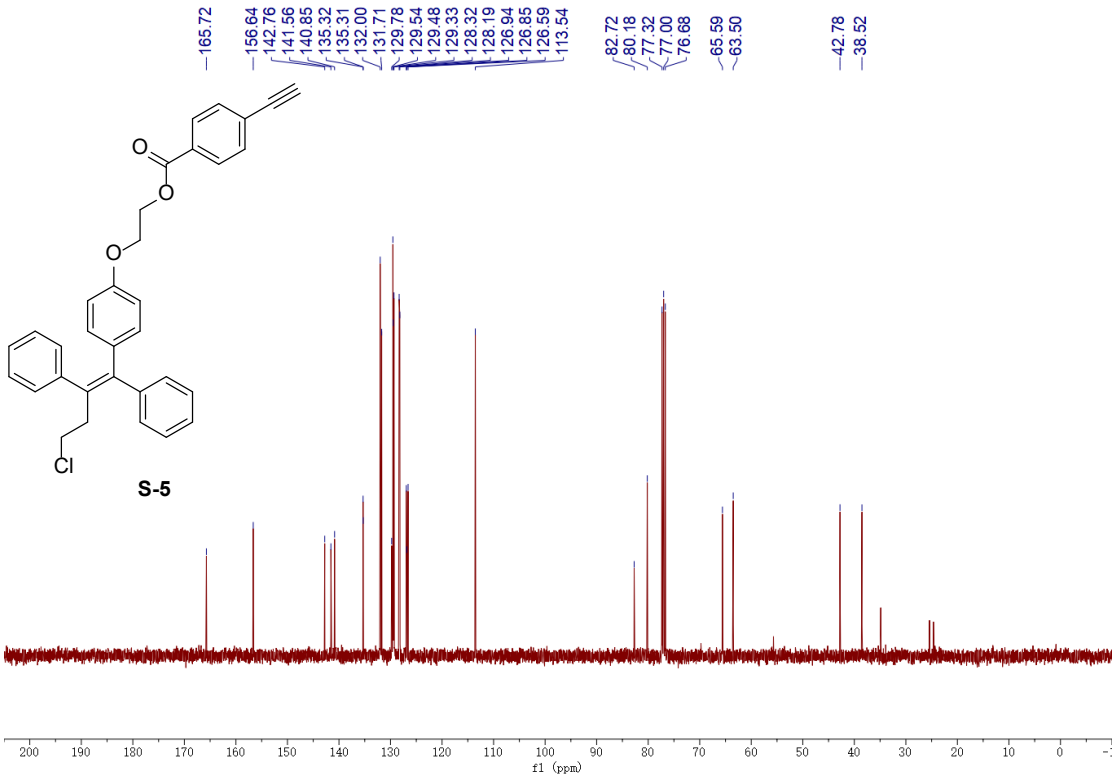
^{13}C NMR：101MHz, Choroform-*d*, peak of $CHCl_3$ in 77.0



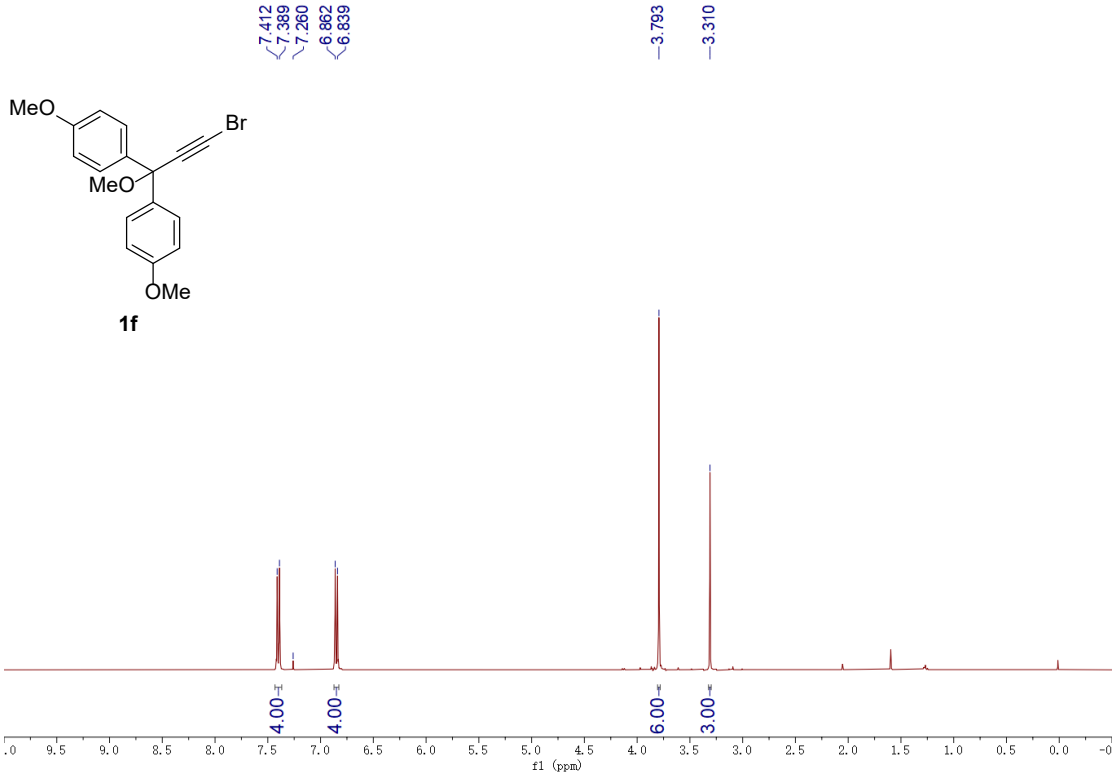
^{1}H NMR：400MHz, Choroform-*d*, peak of $CHCl_3$ in 7.260



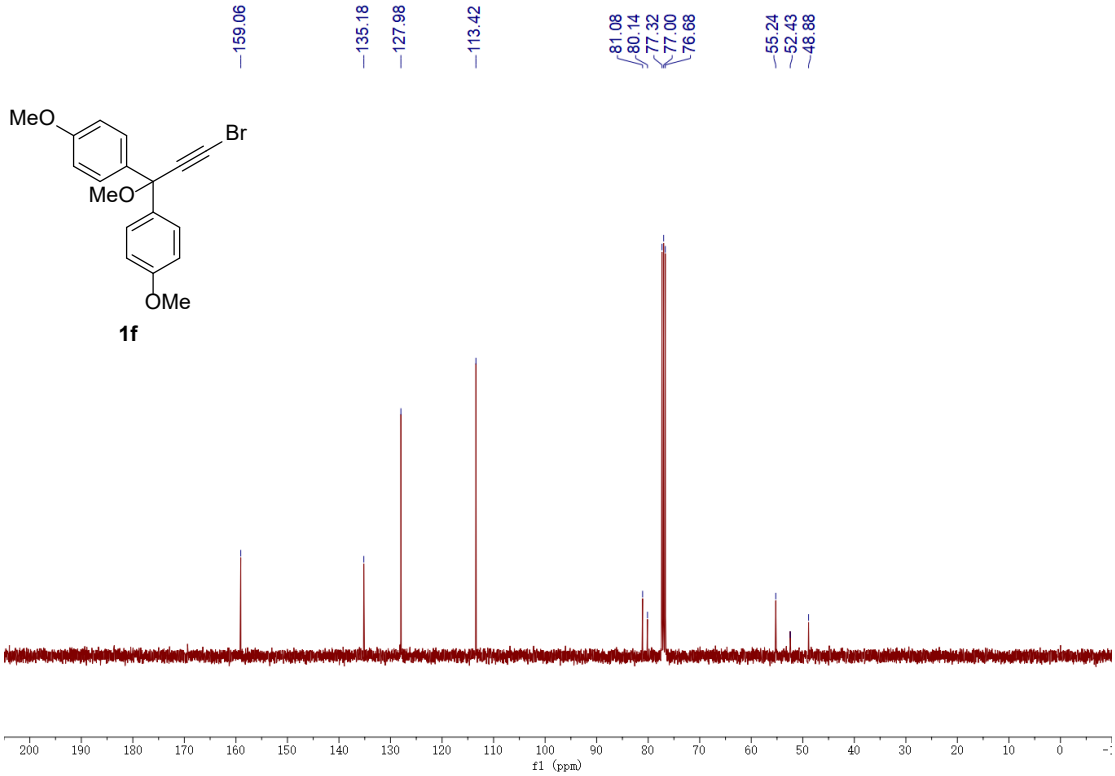
^{13}C NMR：101MHz, Choroform-*d*, peak of $CHCl_3$ in 77.0



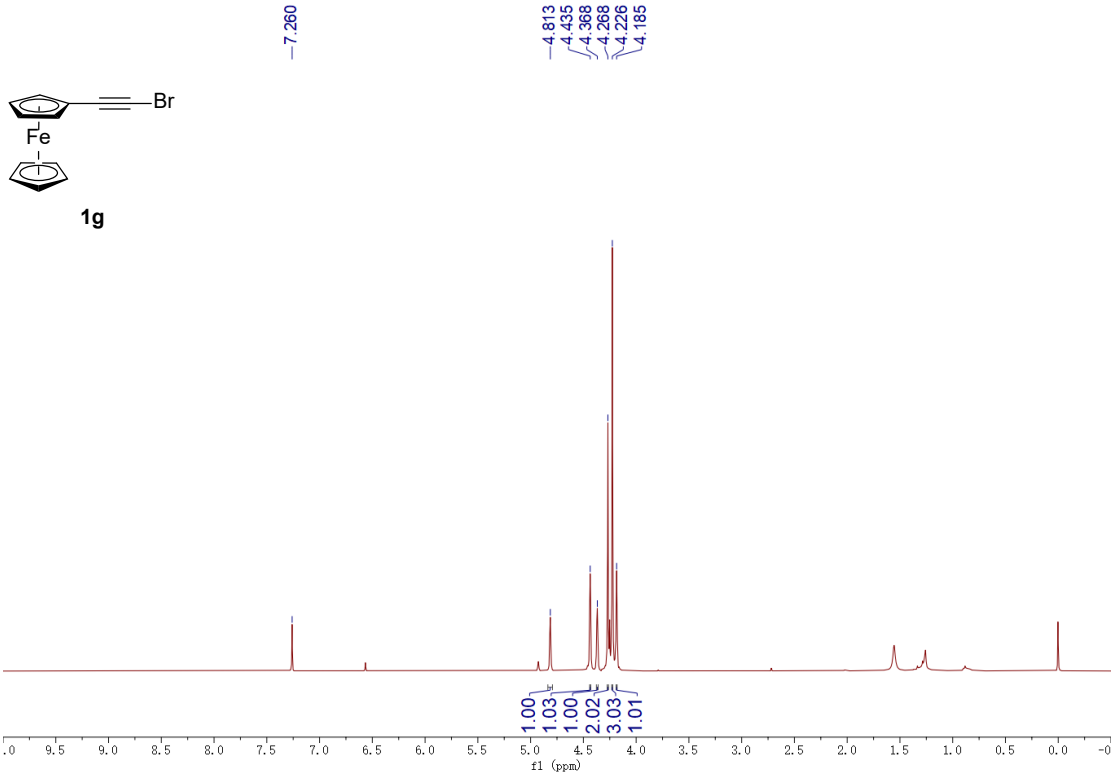
^{1}H NMR：400MHz, Choroform-*d*, peak of $CHCl_3$ in 7.260



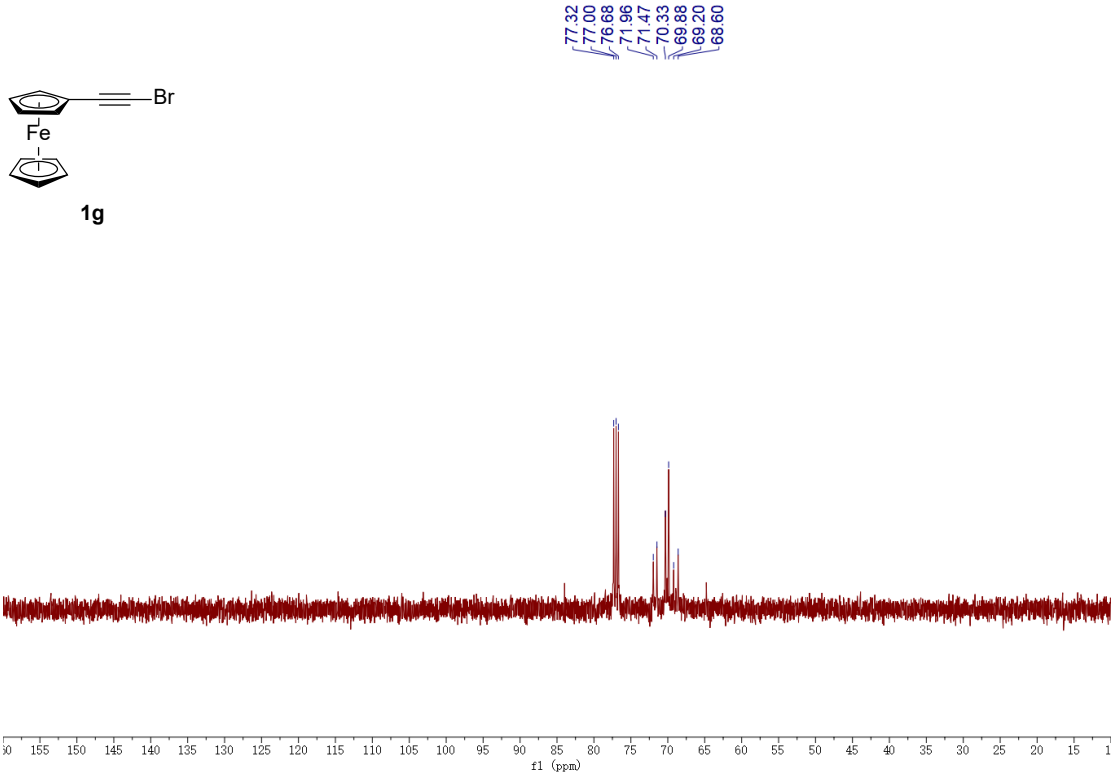
^{13}C NMR：101MHz, Choroform-*d*, peak of $CHCl_3$ in 77.0



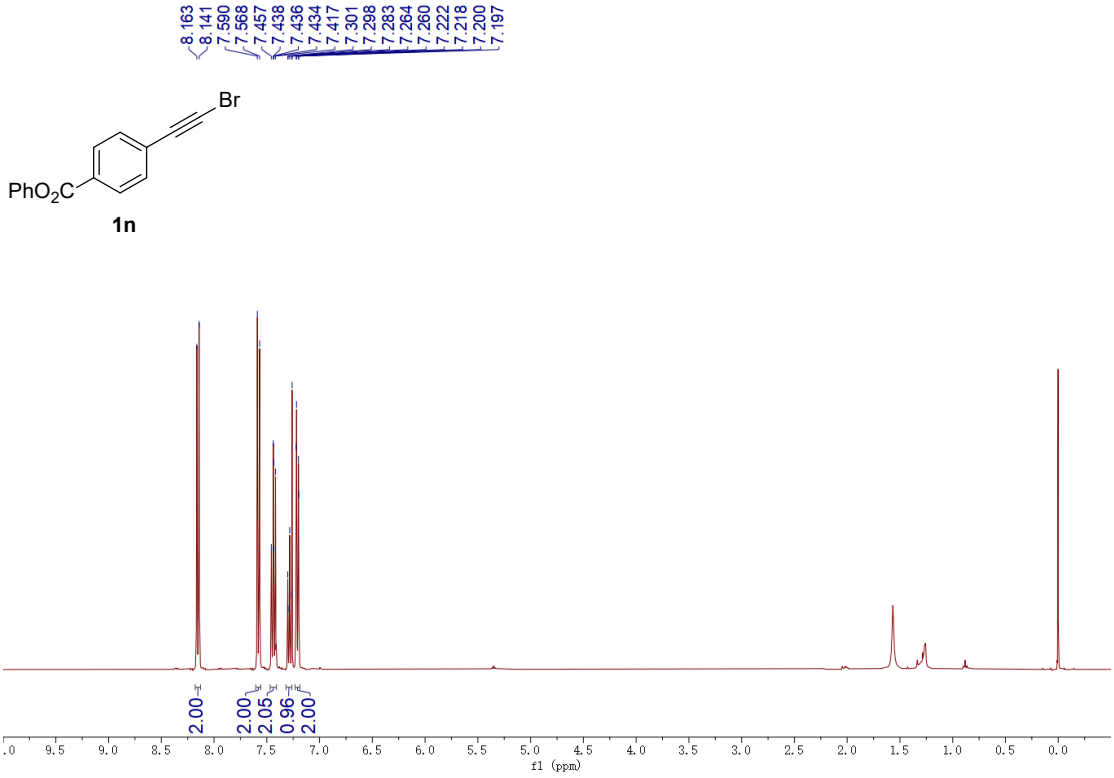
^{1}H NMR：400MHz, Choroform-*d*, peak of $CHCl_3$ in 7.260



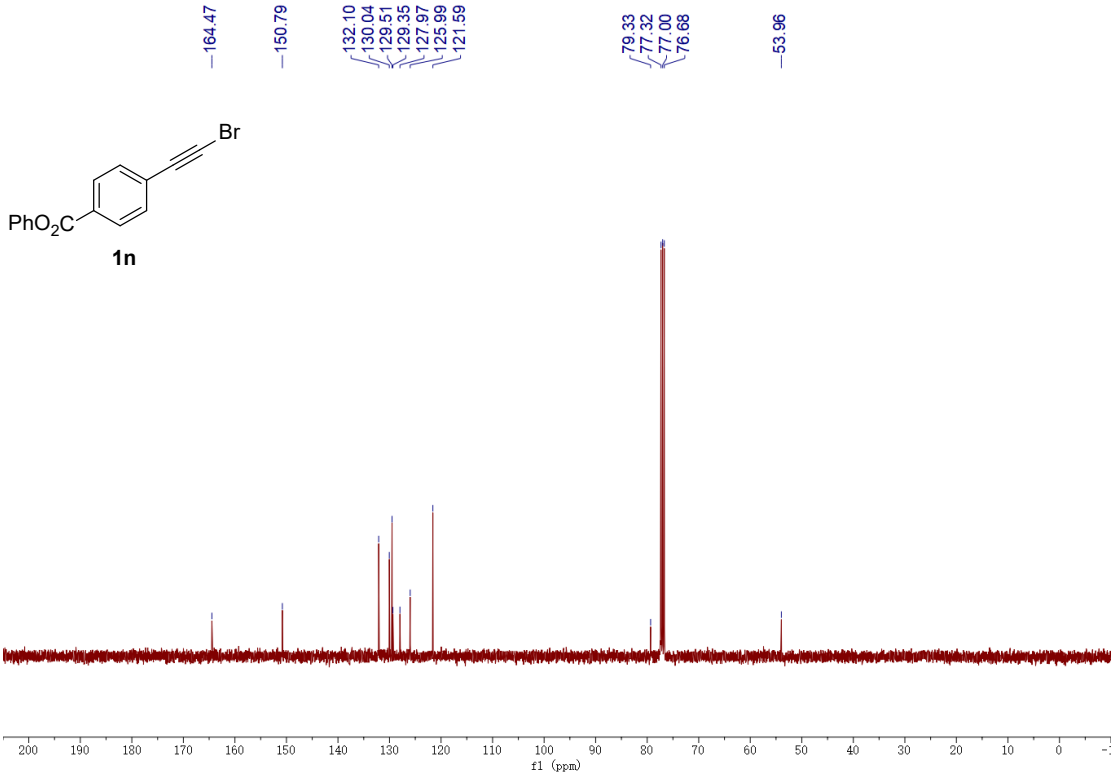
^{13}C NMR：101MHz, Choroform-*d*, peak of $CHCl_3$ in 77.0



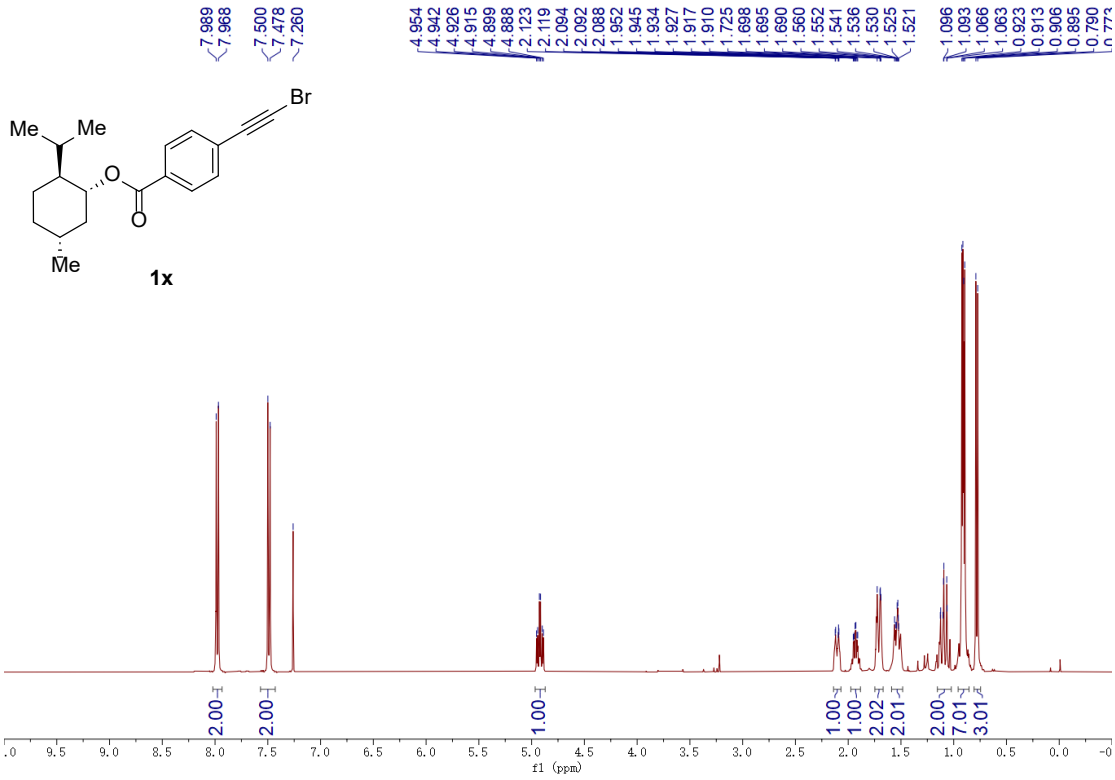
^{1}H NMR：400MHz, Choroform-*d*, peak of $CHCl_3$ in 7.260



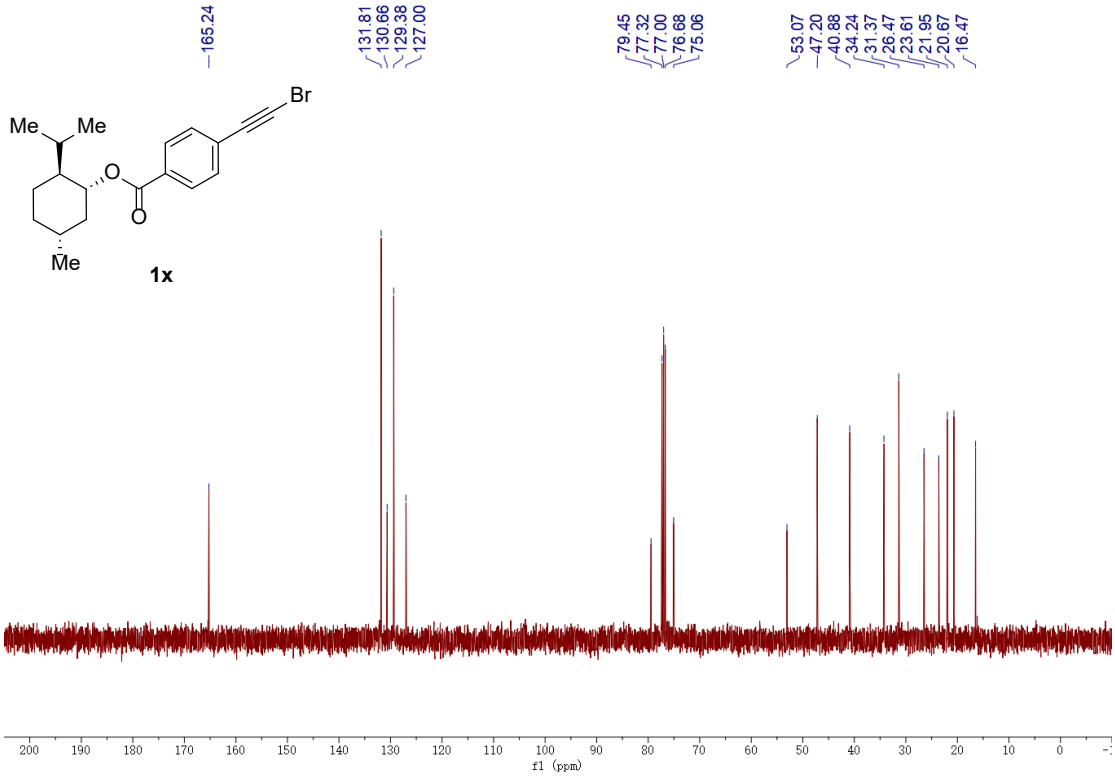
^{13}C NMR：101MHz, Choroform-*d*, peak of $CHCl_3$ in 77.0



^{1}H NMR：400MHz, Choroform-*d*, peak of $CHCl_3$ in 7.260



^{13}C NMR：101MHz, Choroform-*d*, peak of $CHCl_3$ in 77.0



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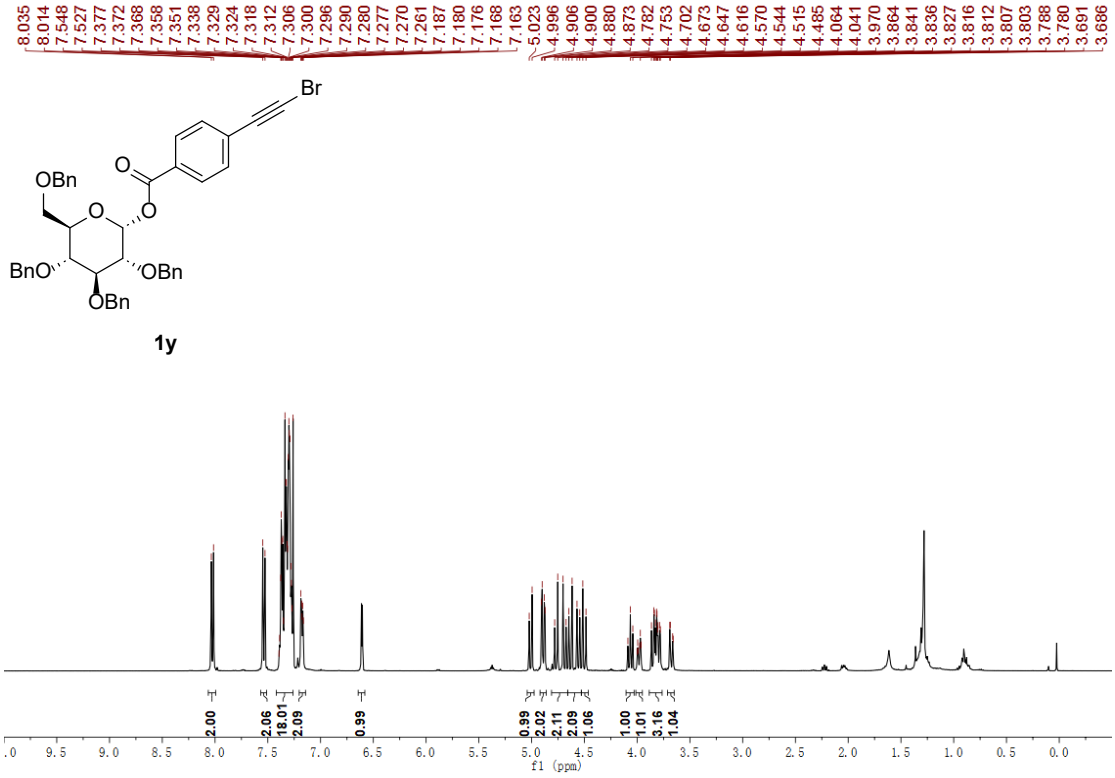
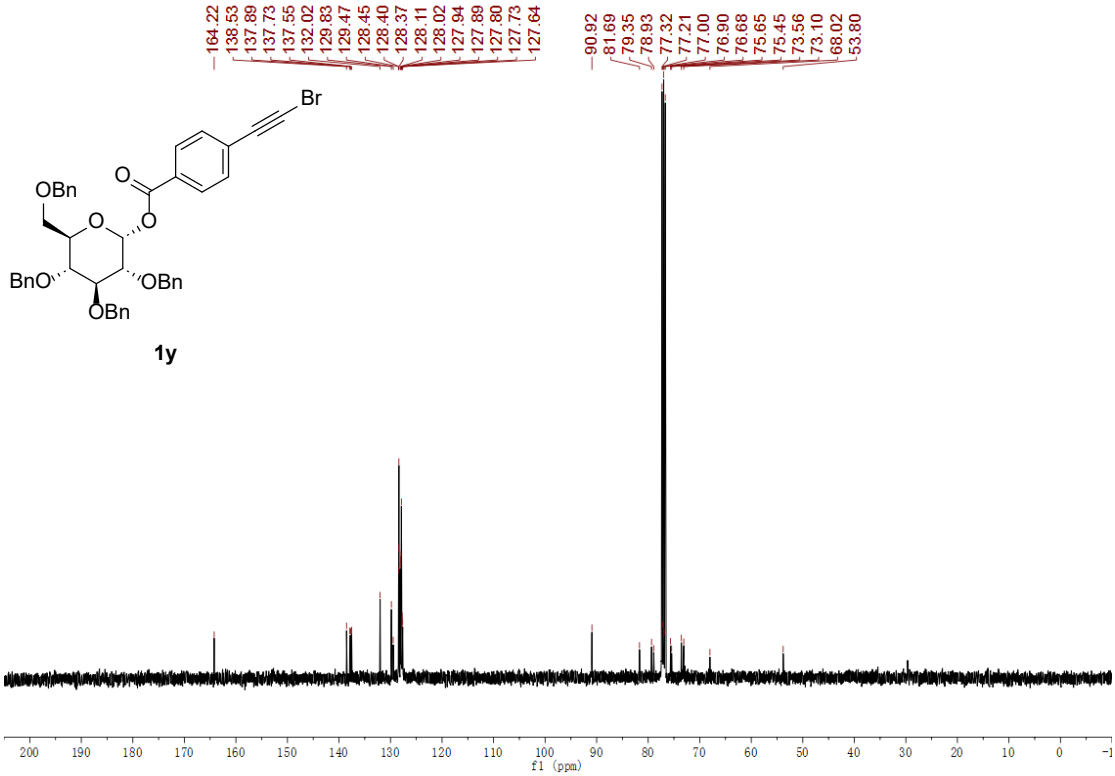


^{13}C NMR：101MHz, Choroform-*d*, peak of $CHCl_3$ in 77.0



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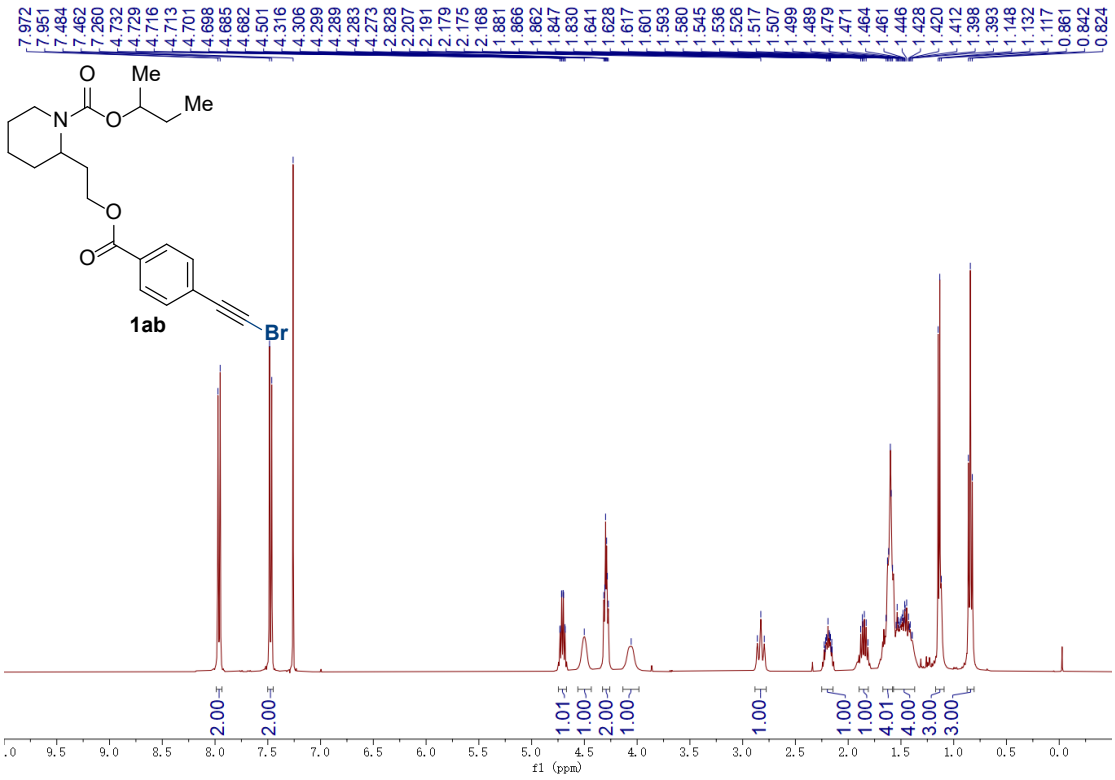

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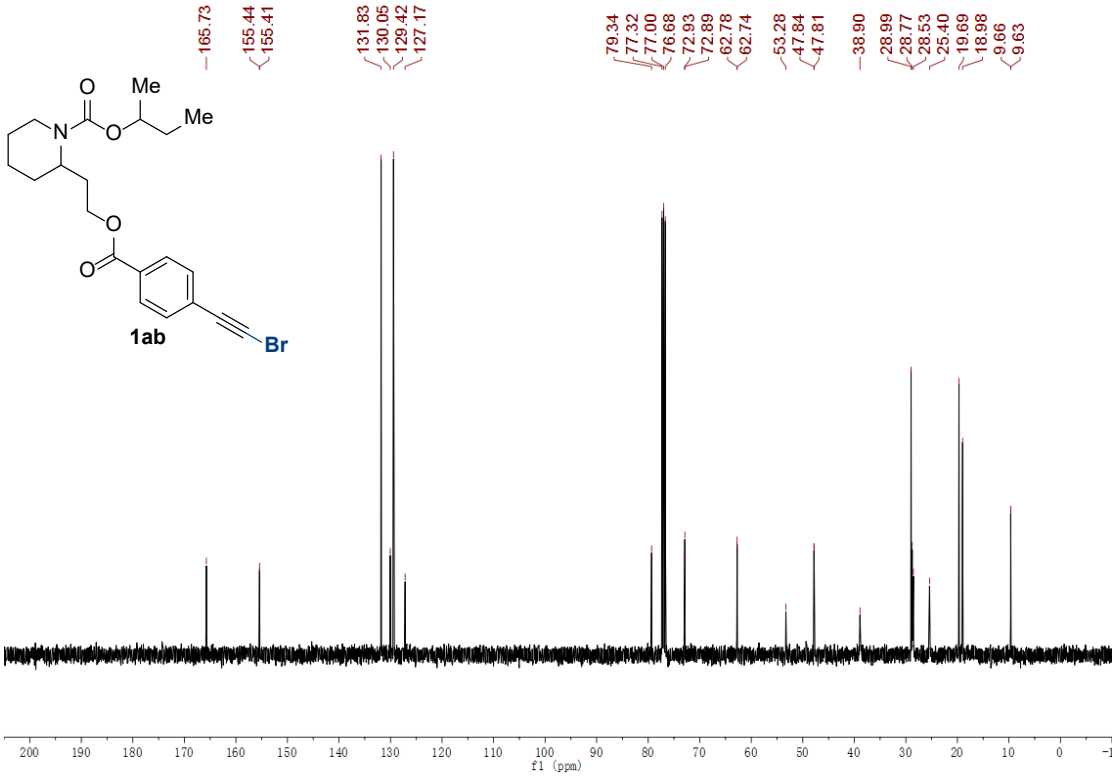

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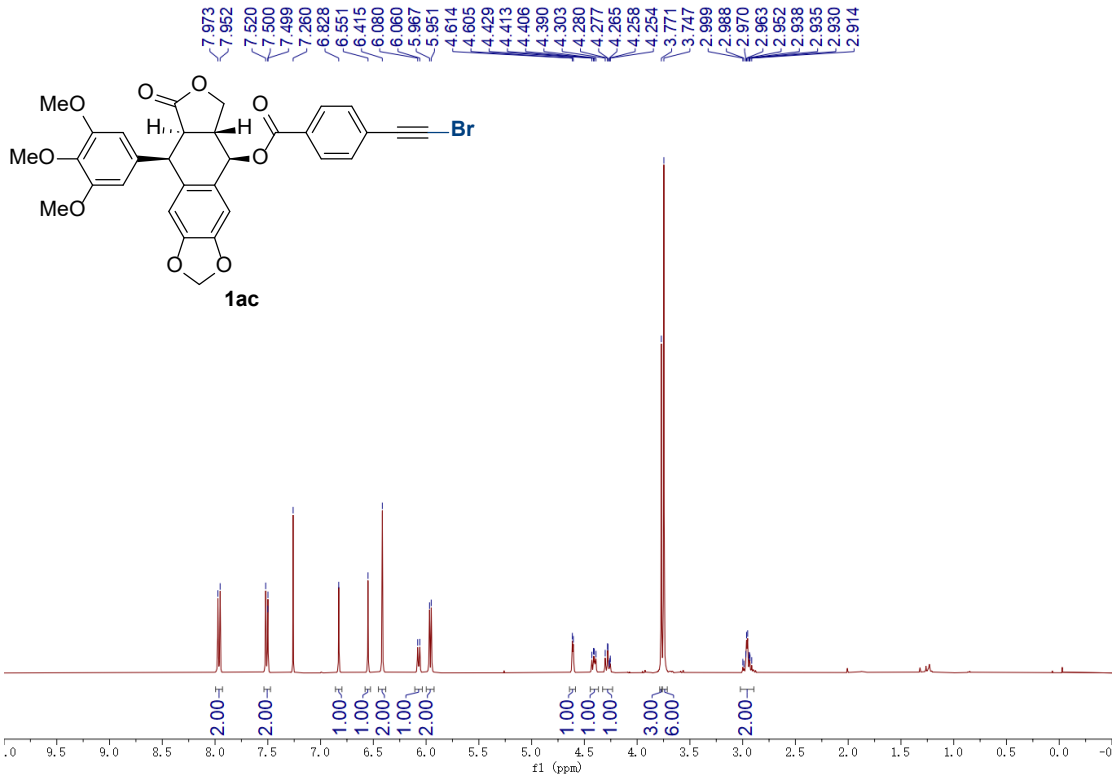

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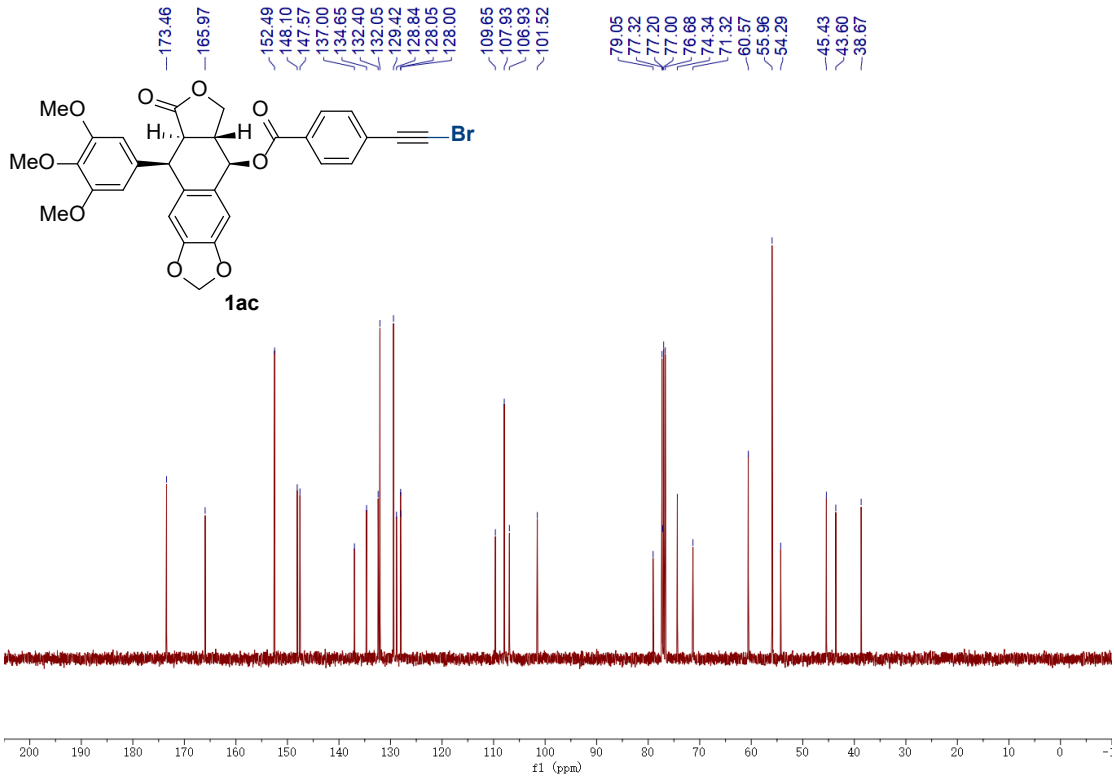

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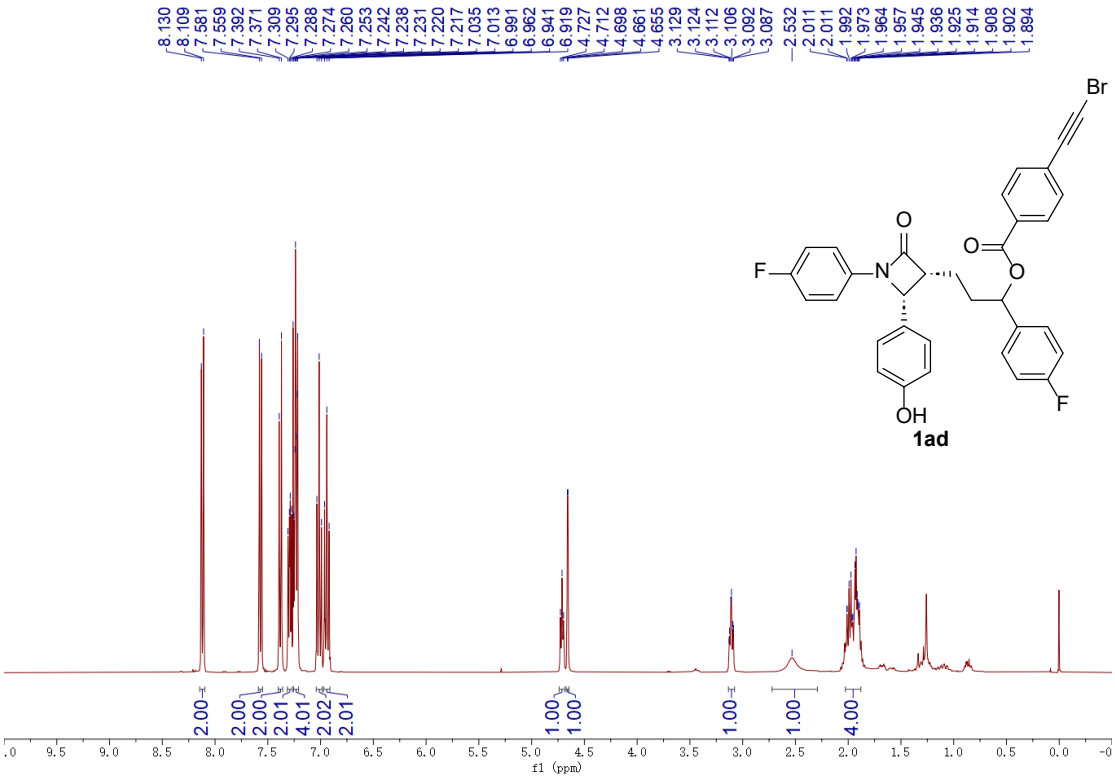

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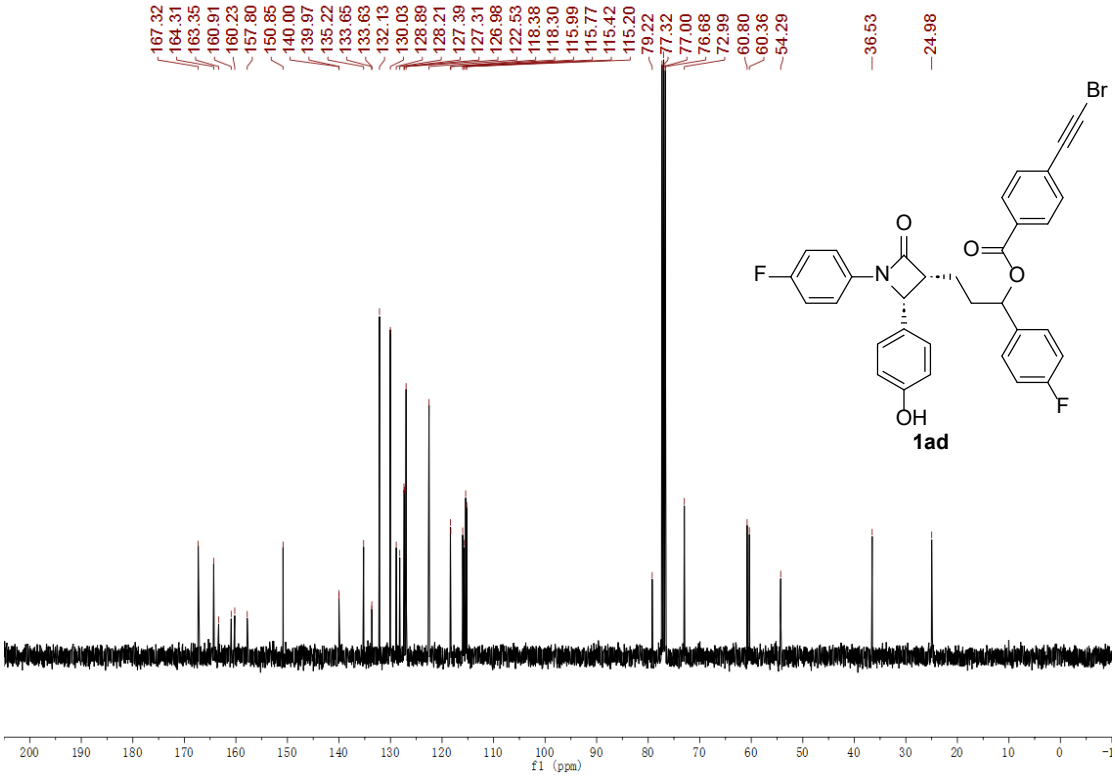

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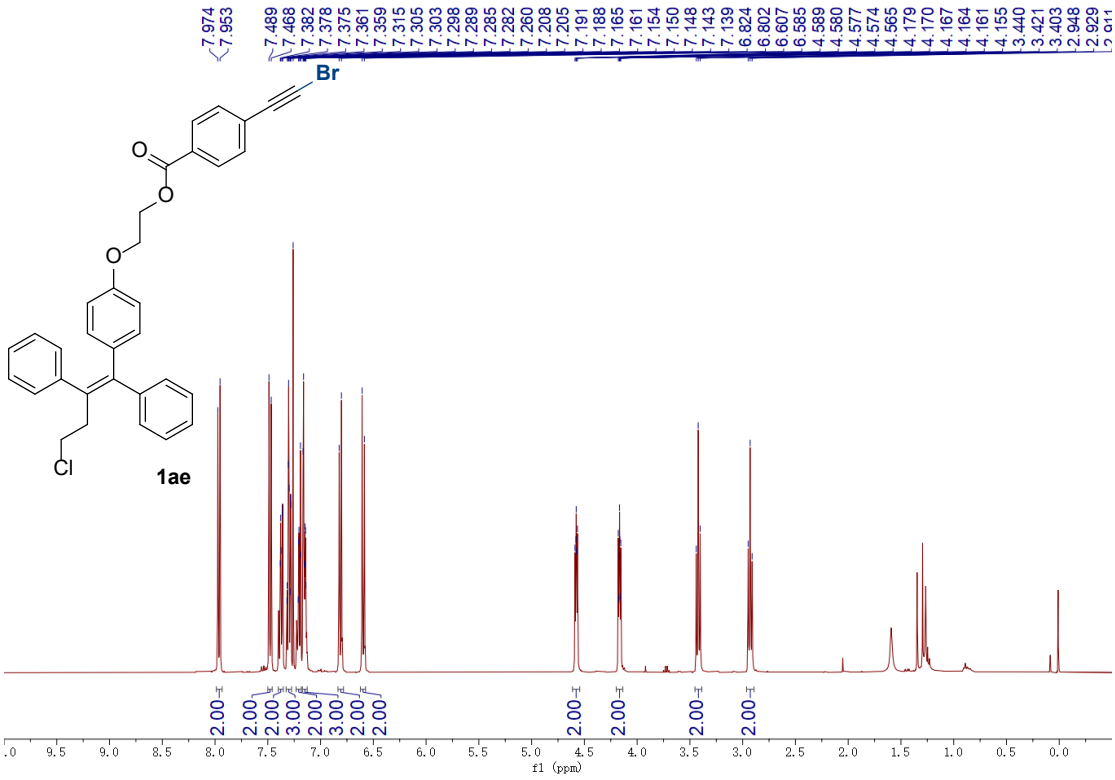

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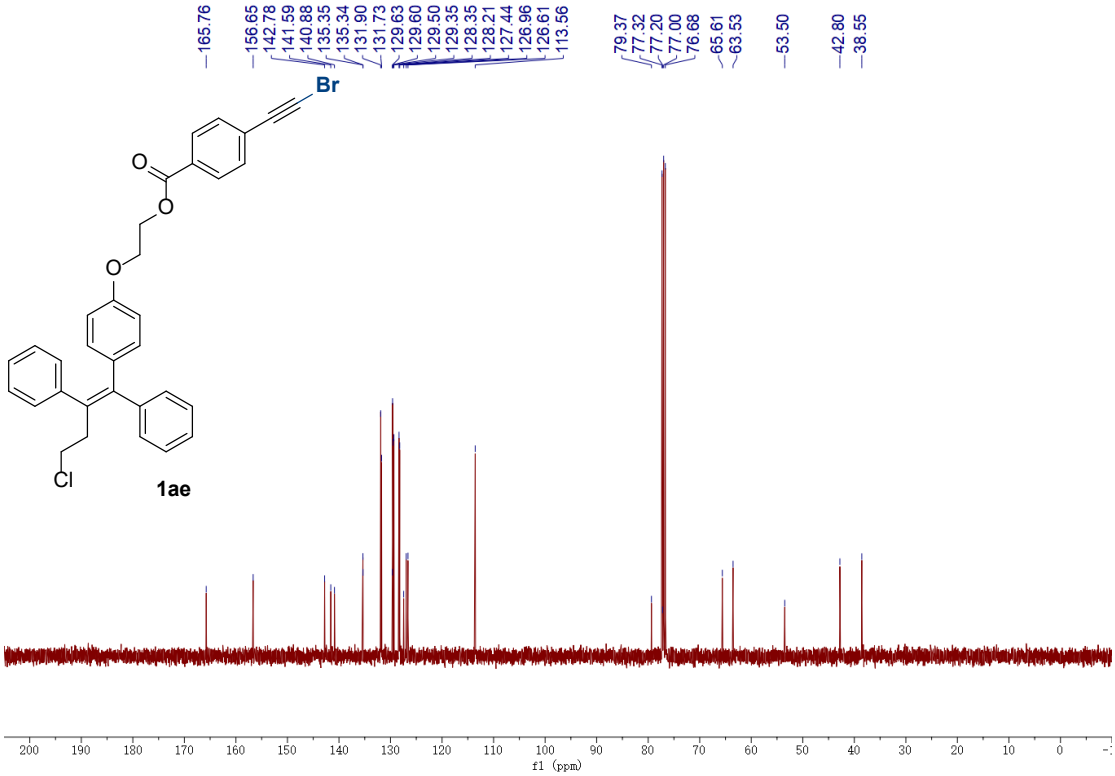

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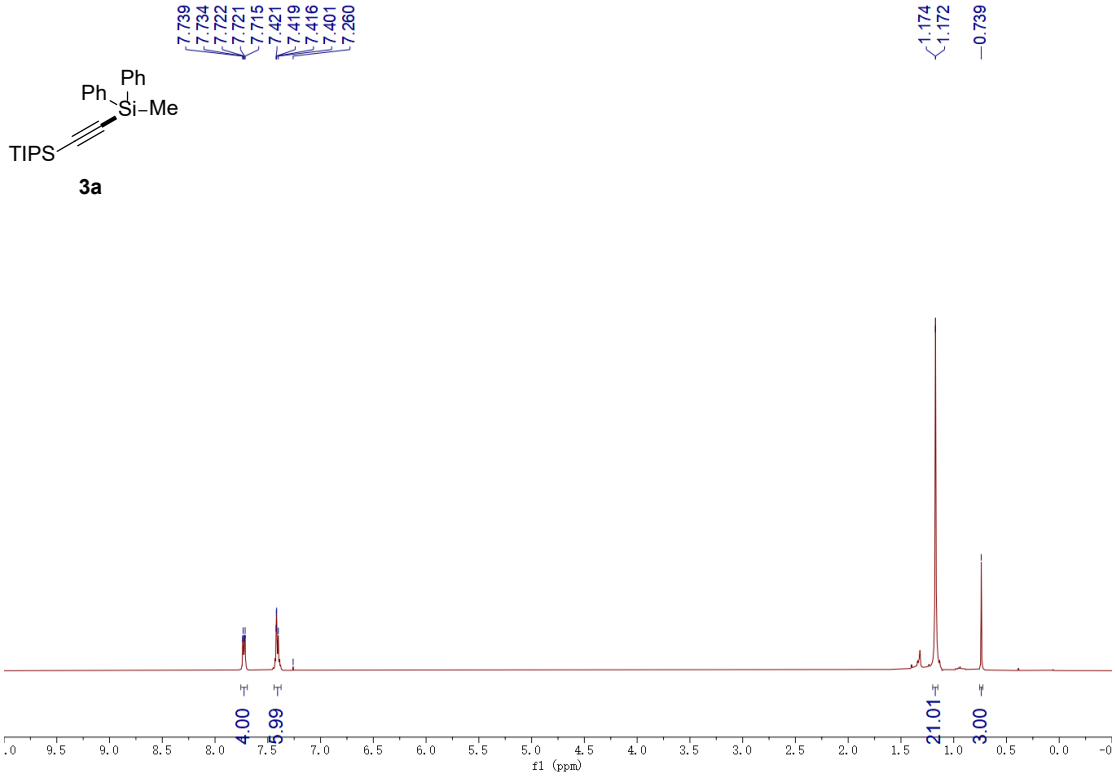

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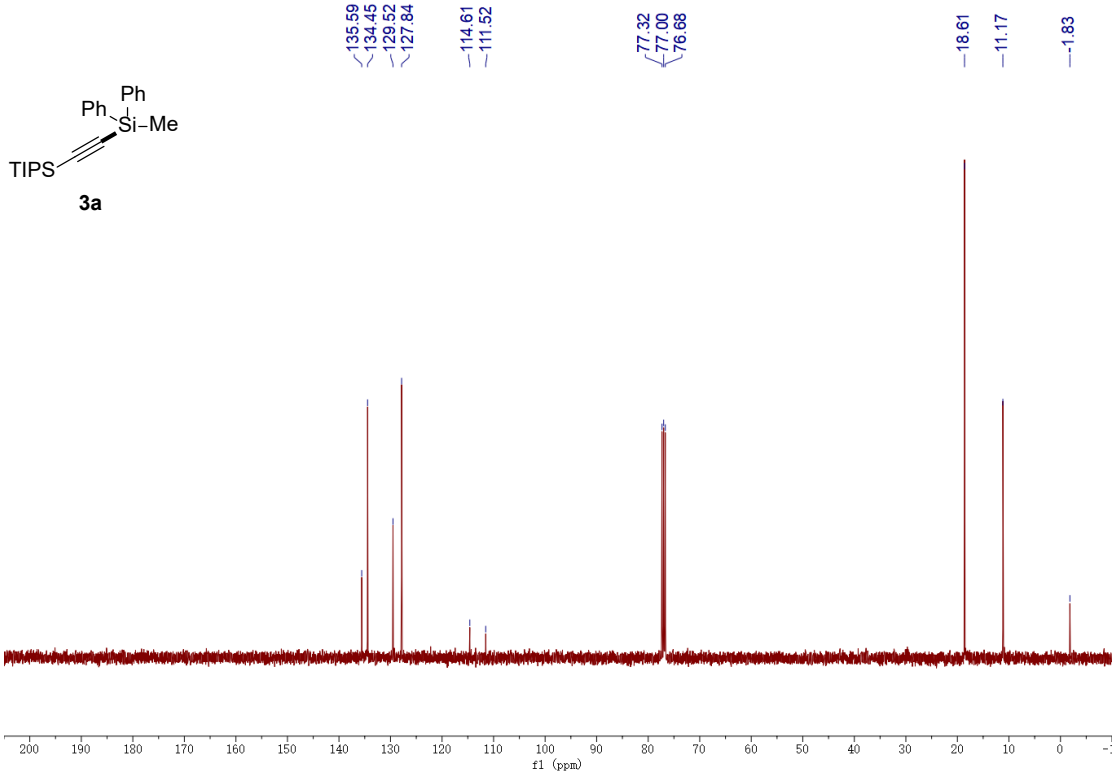

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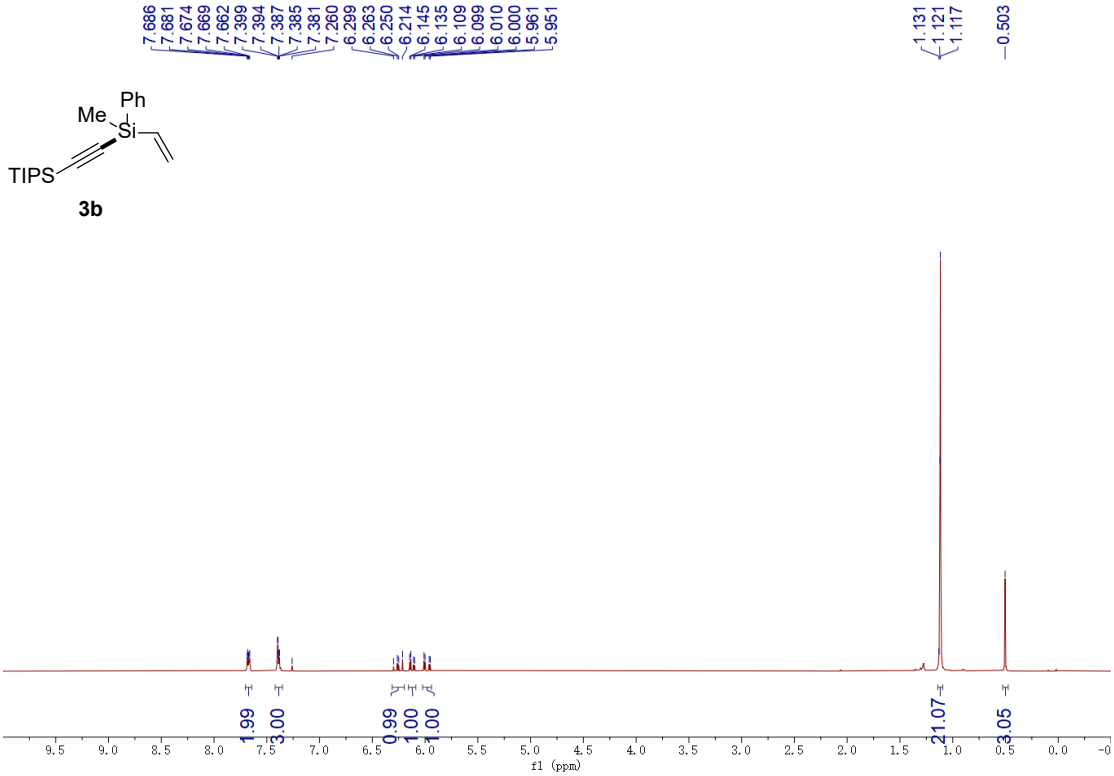

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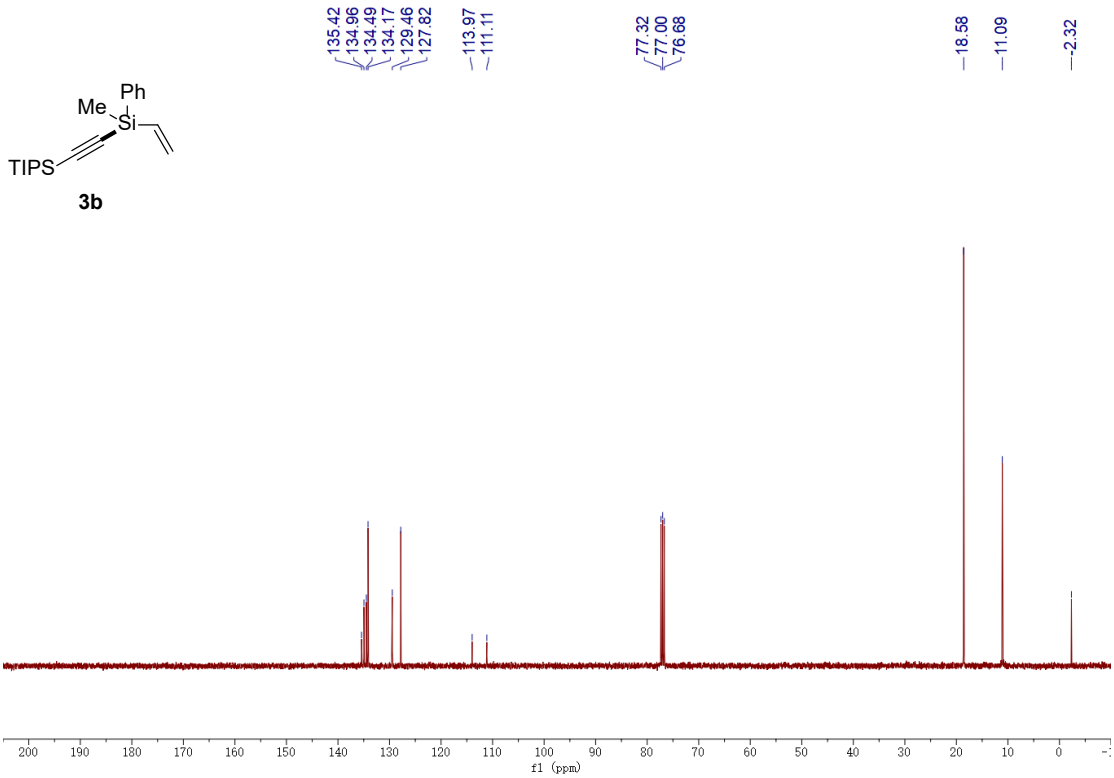

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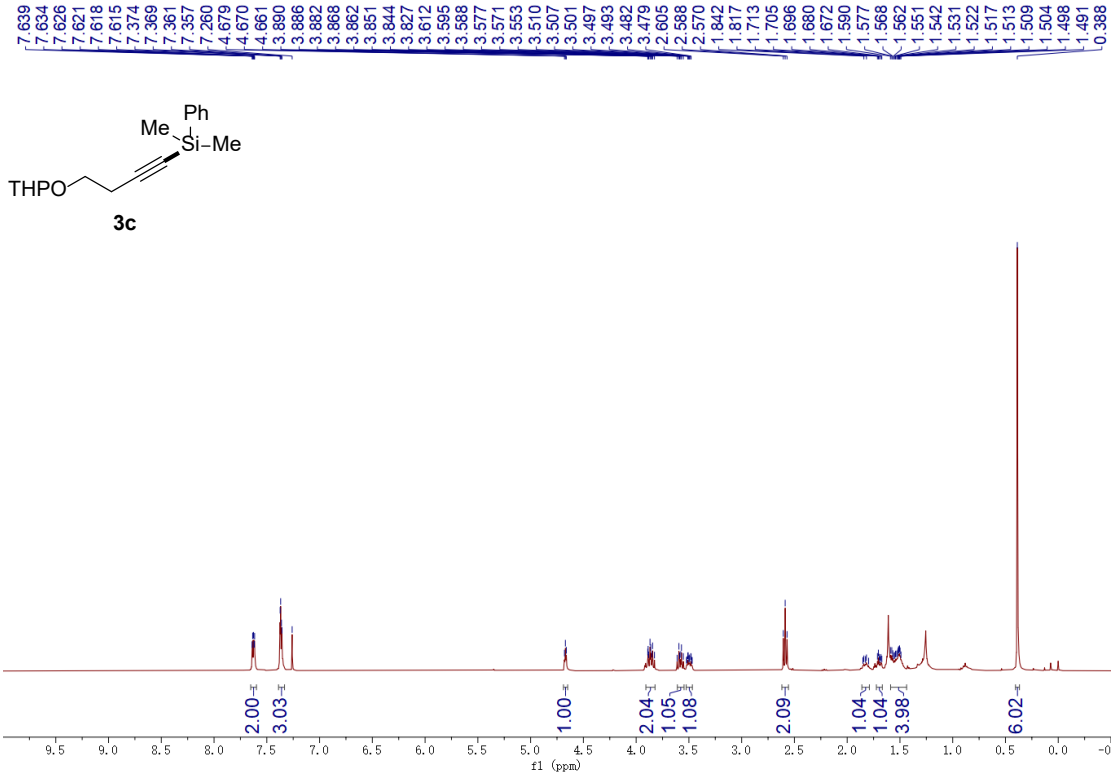

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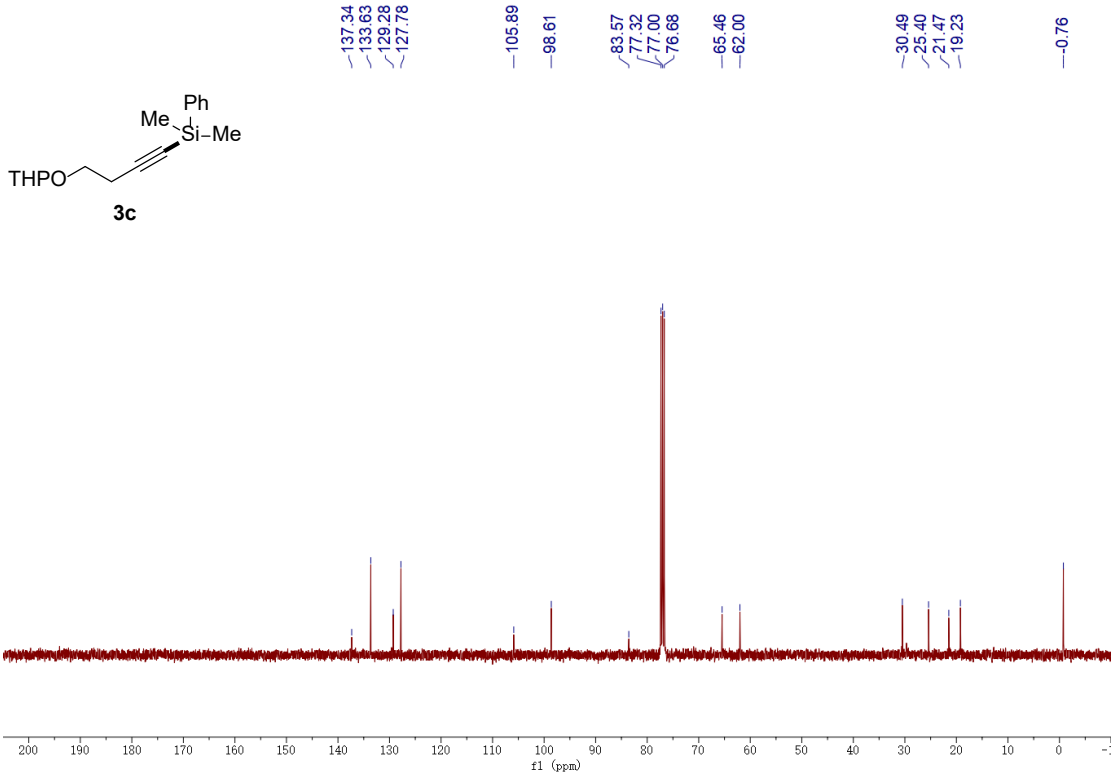

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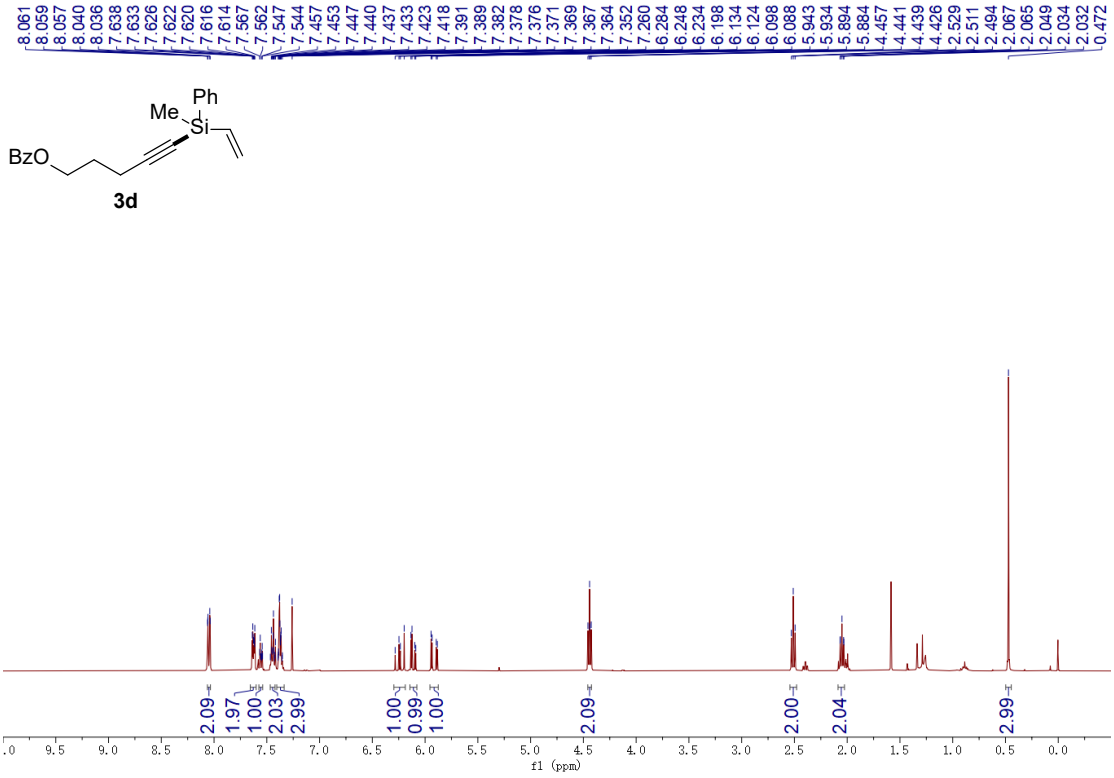

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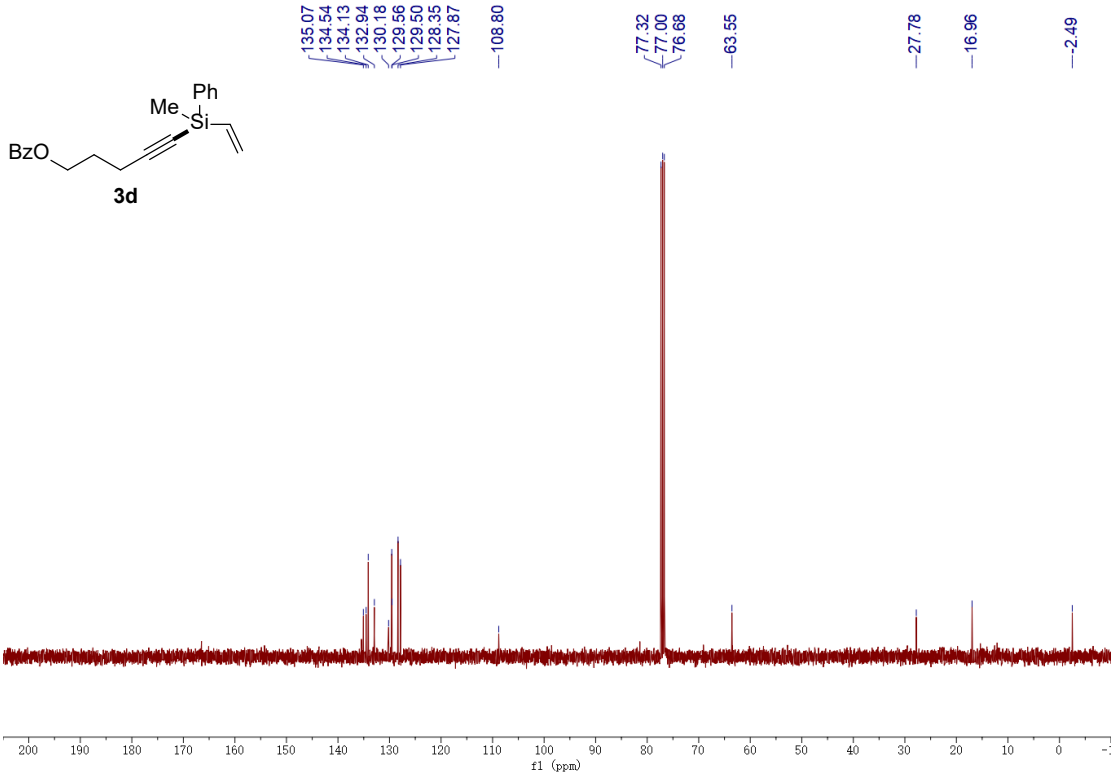

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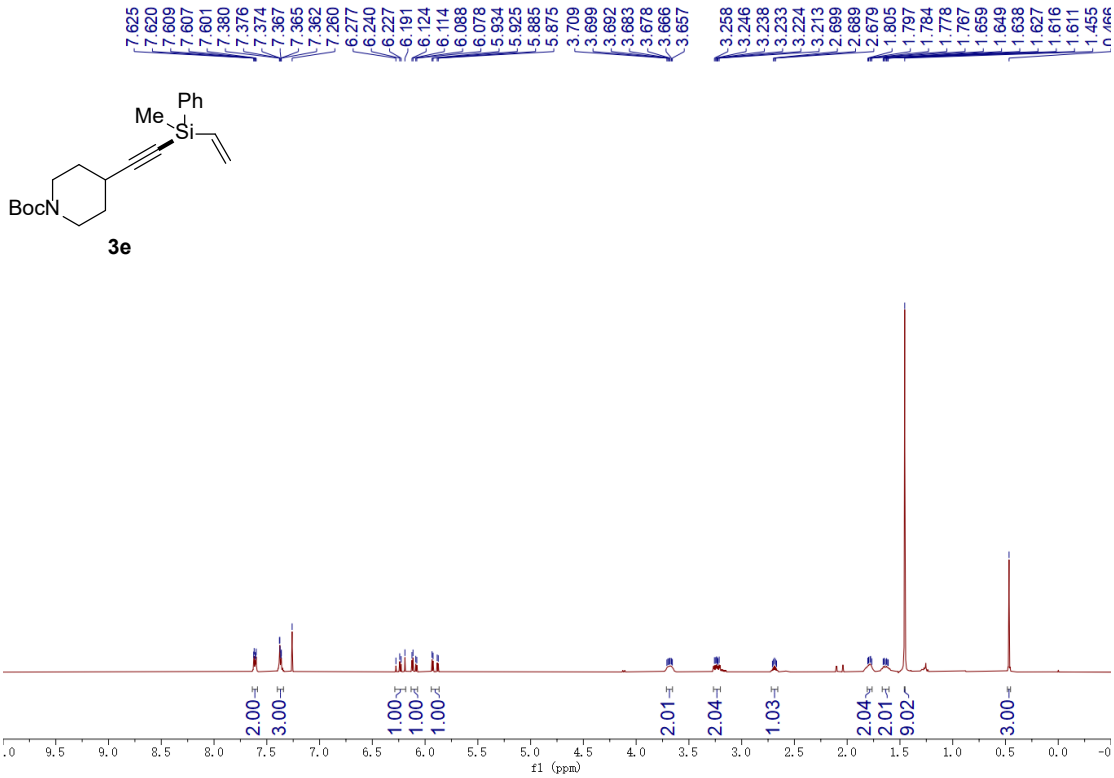

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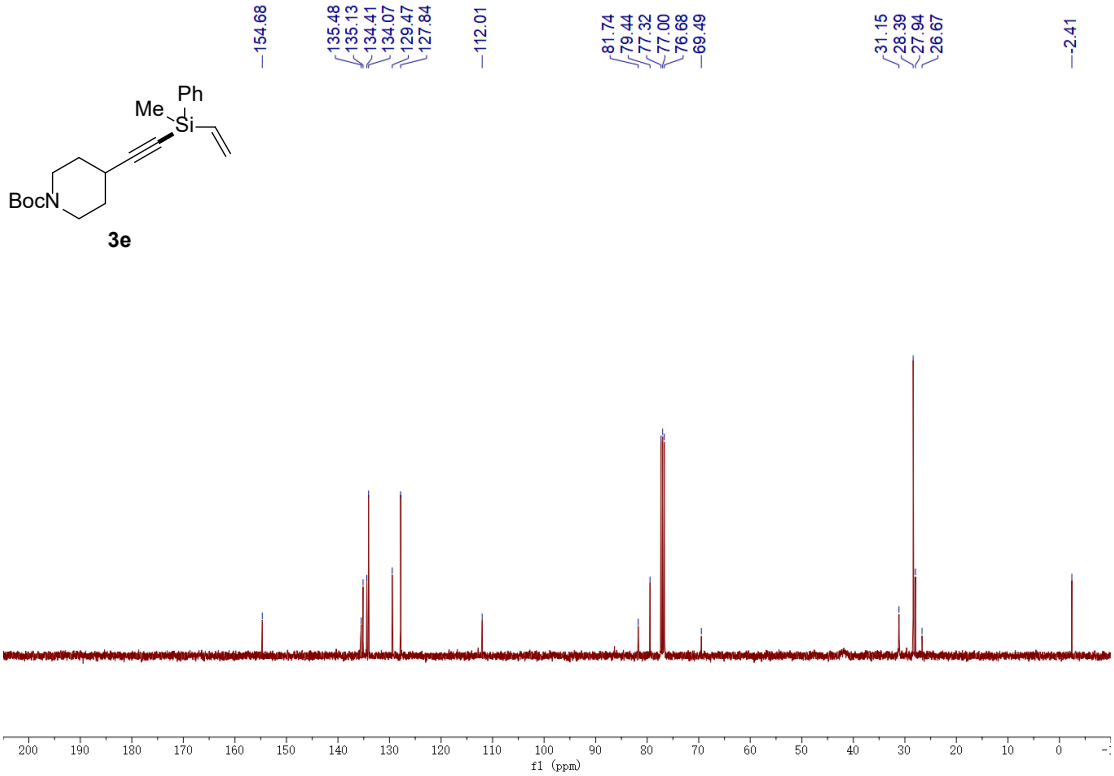

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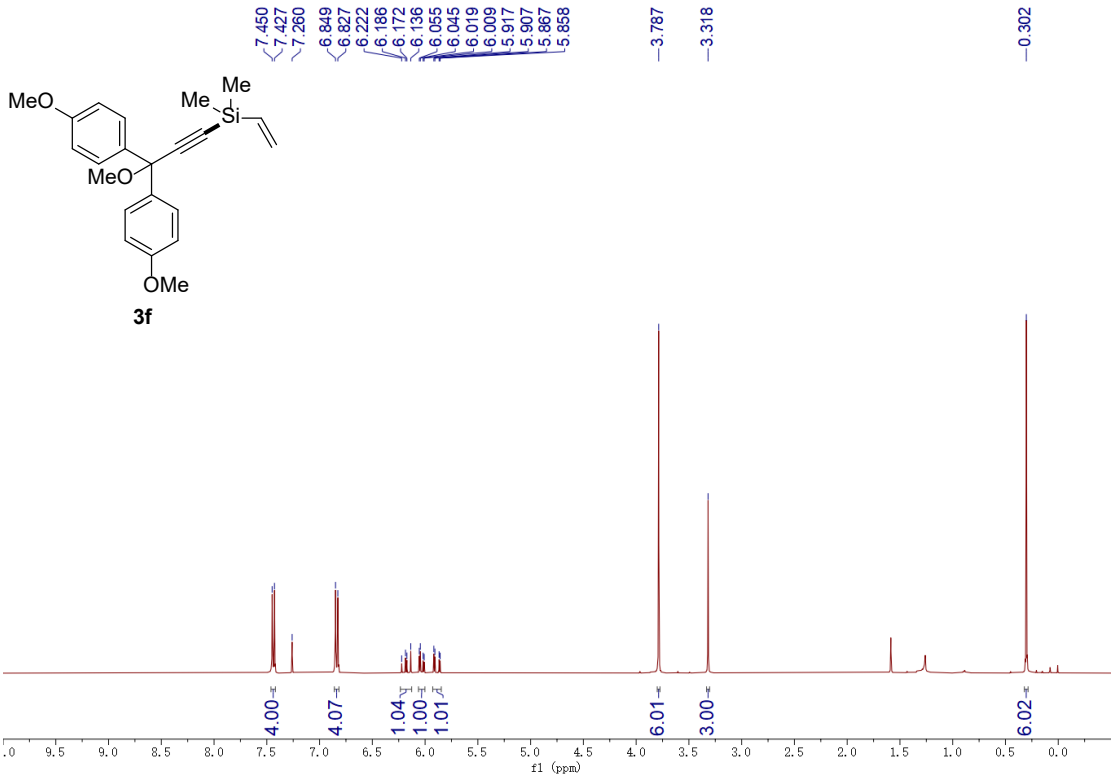

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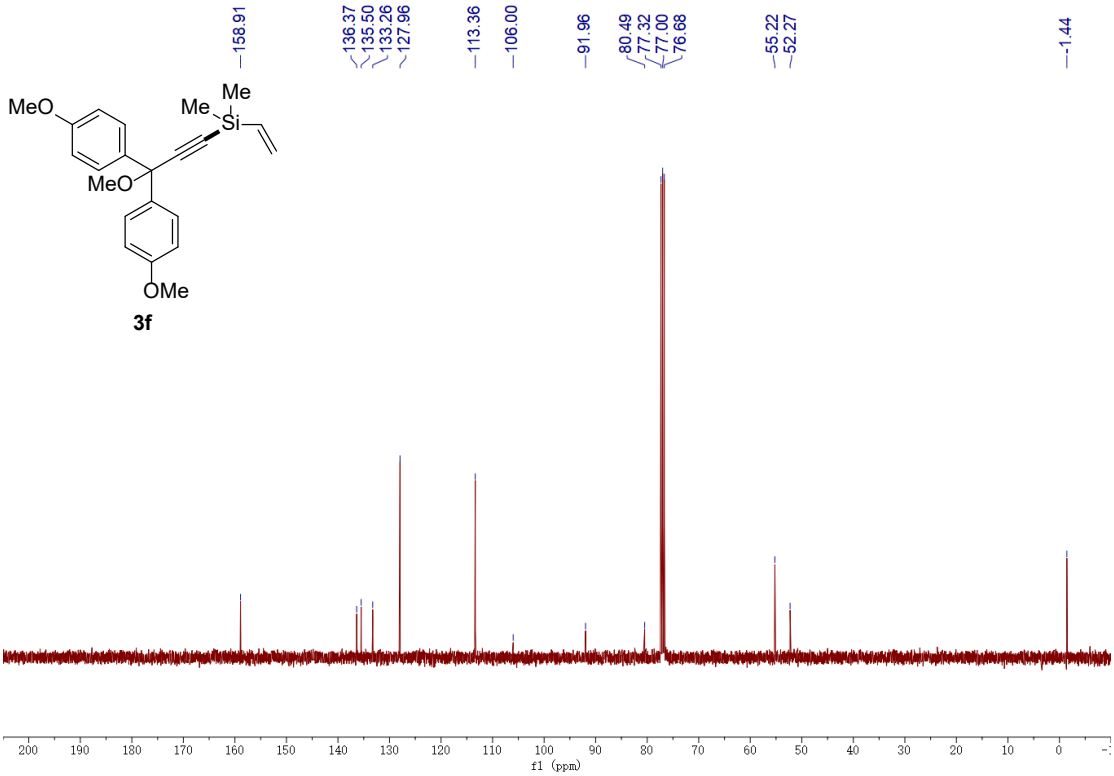

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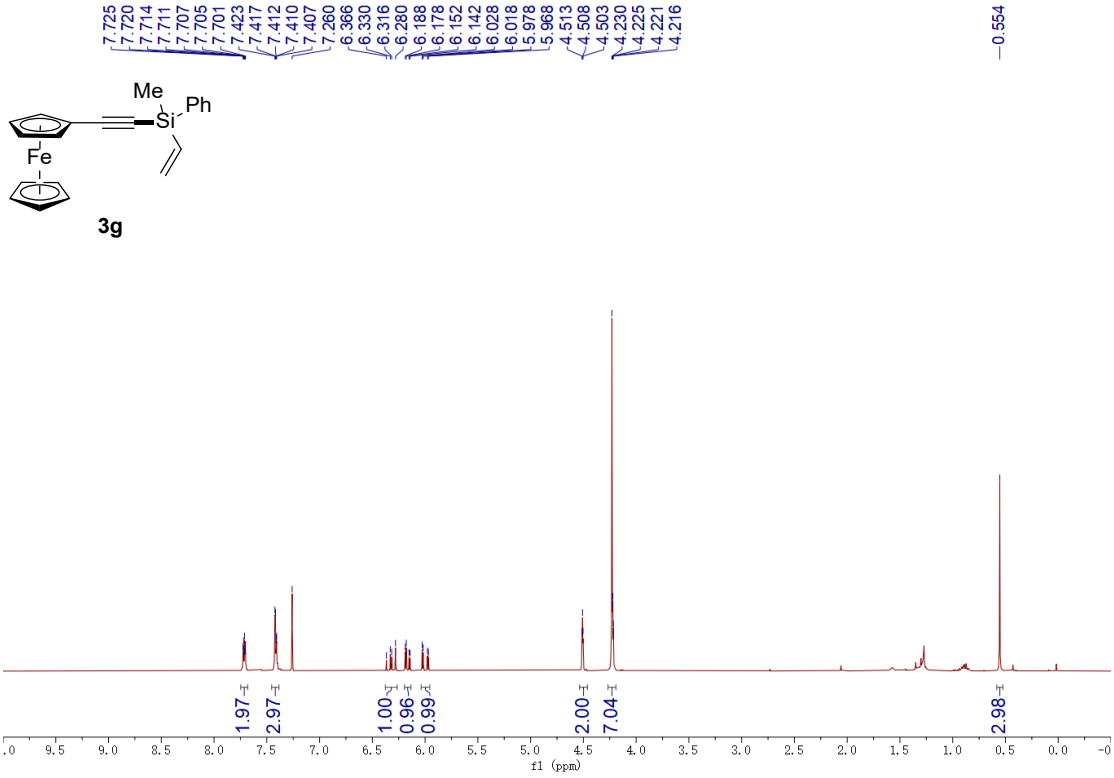

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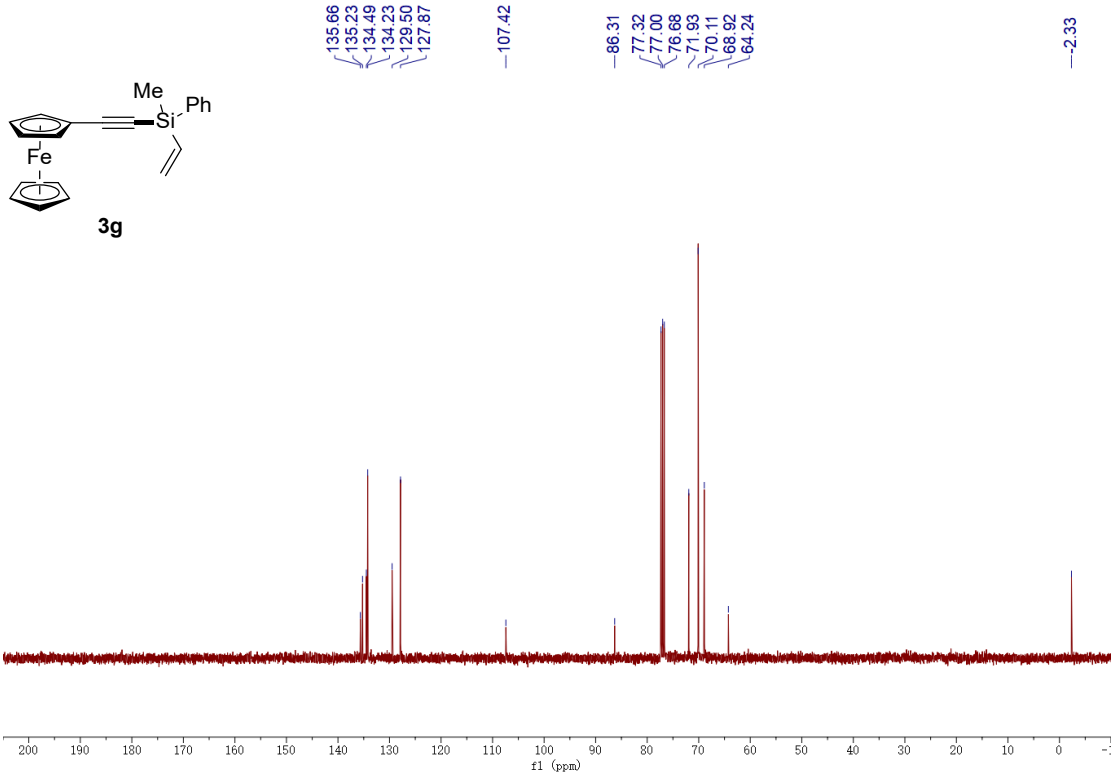

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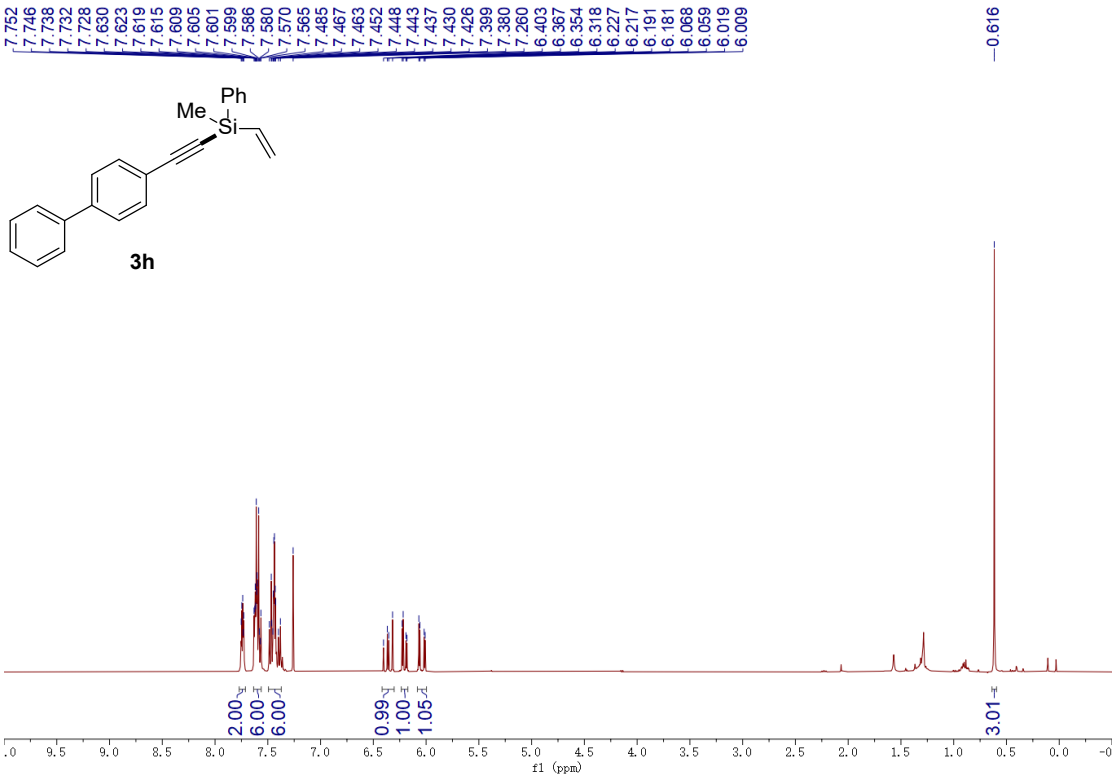

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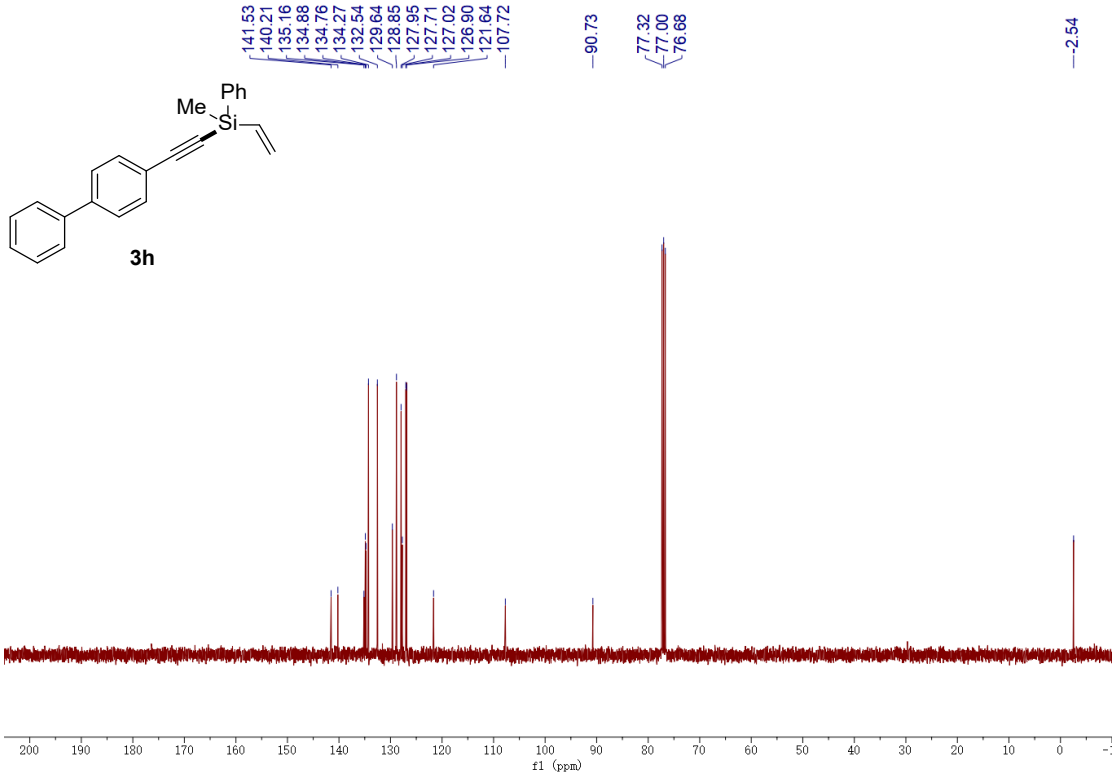

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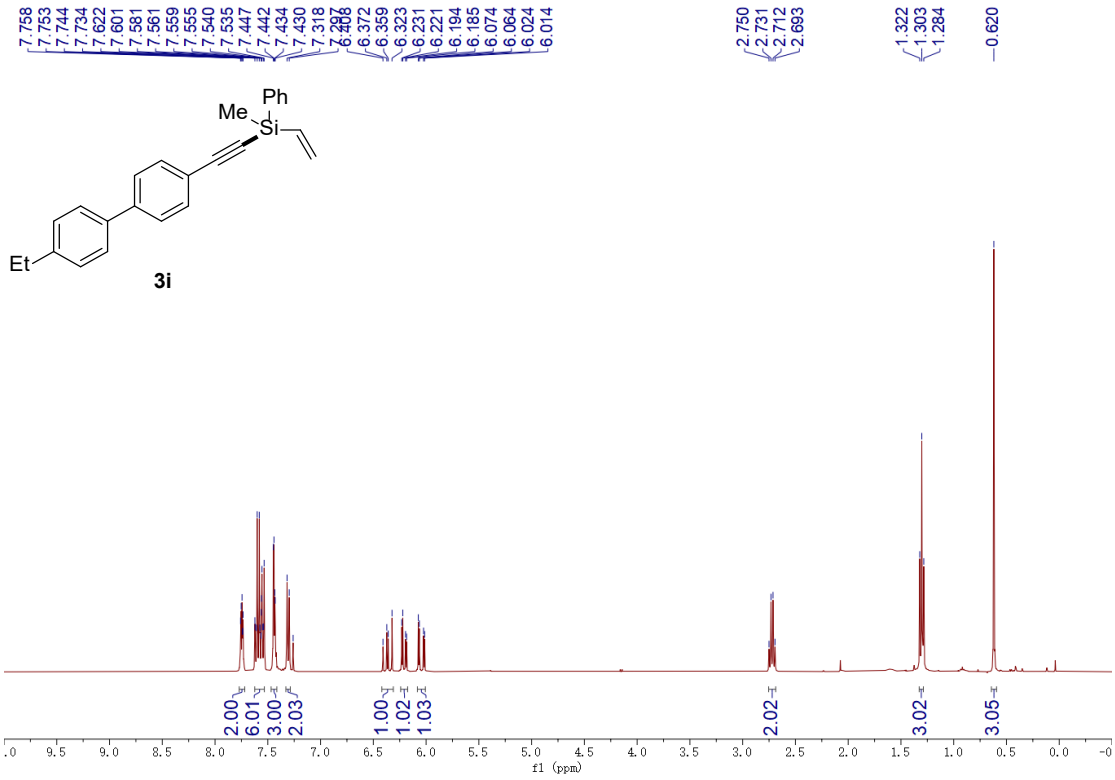

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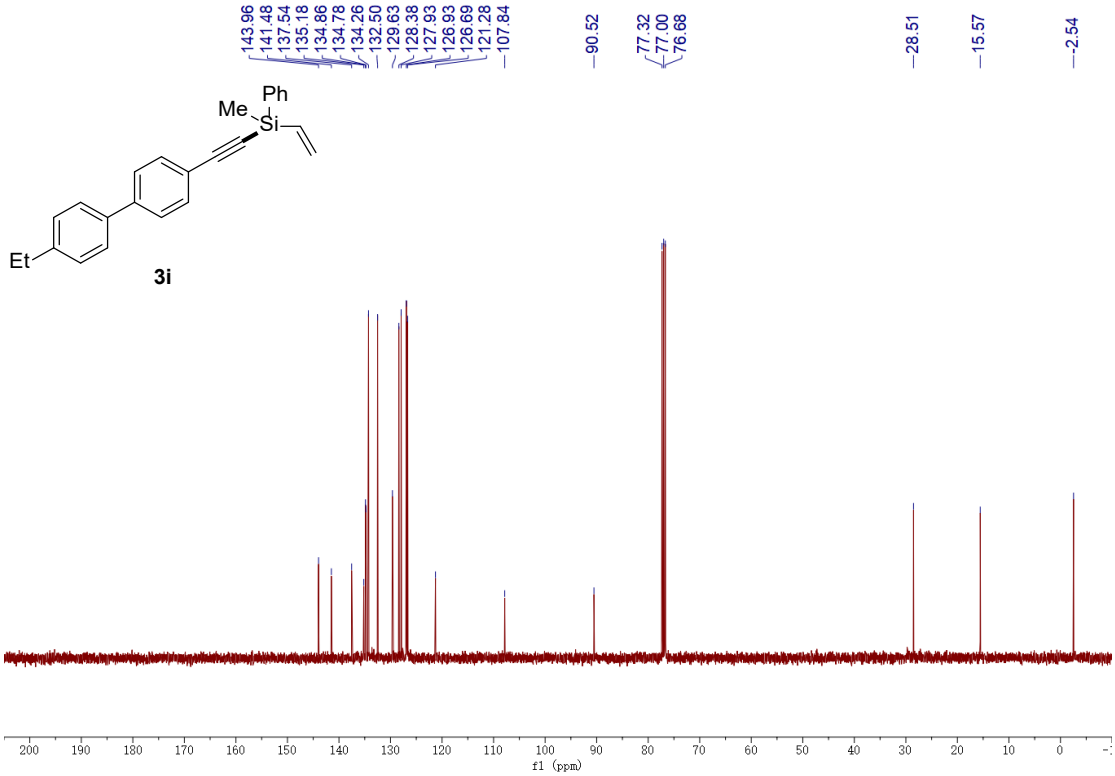

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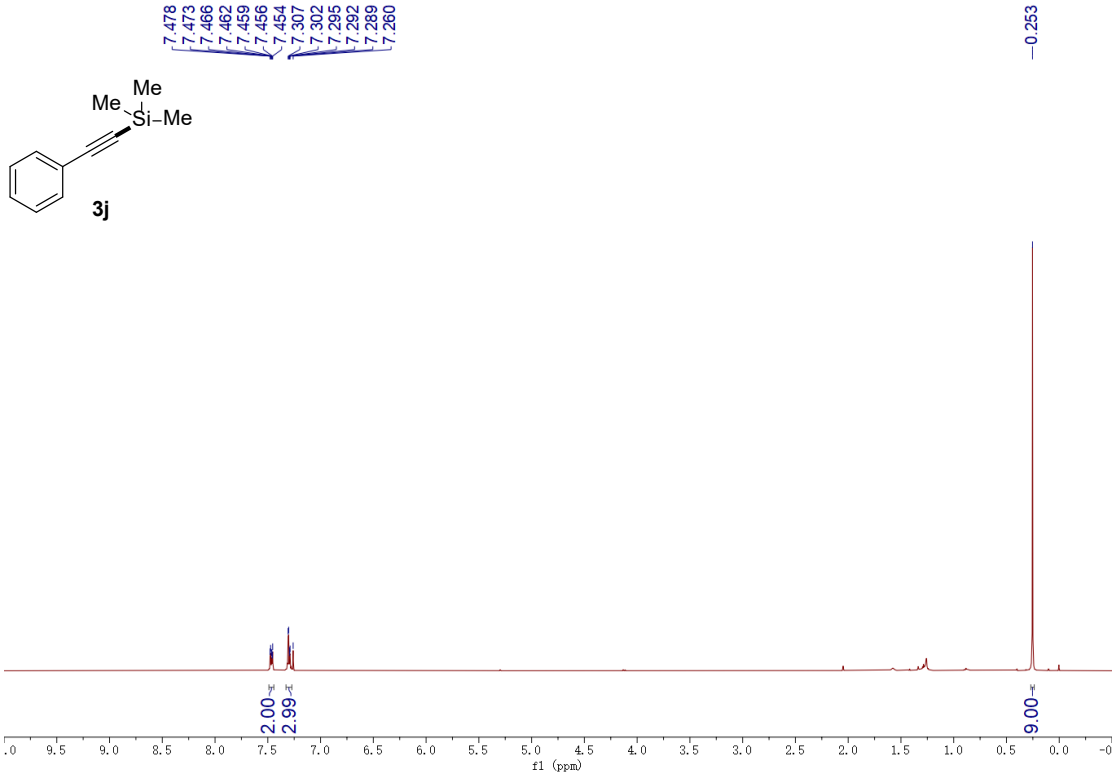

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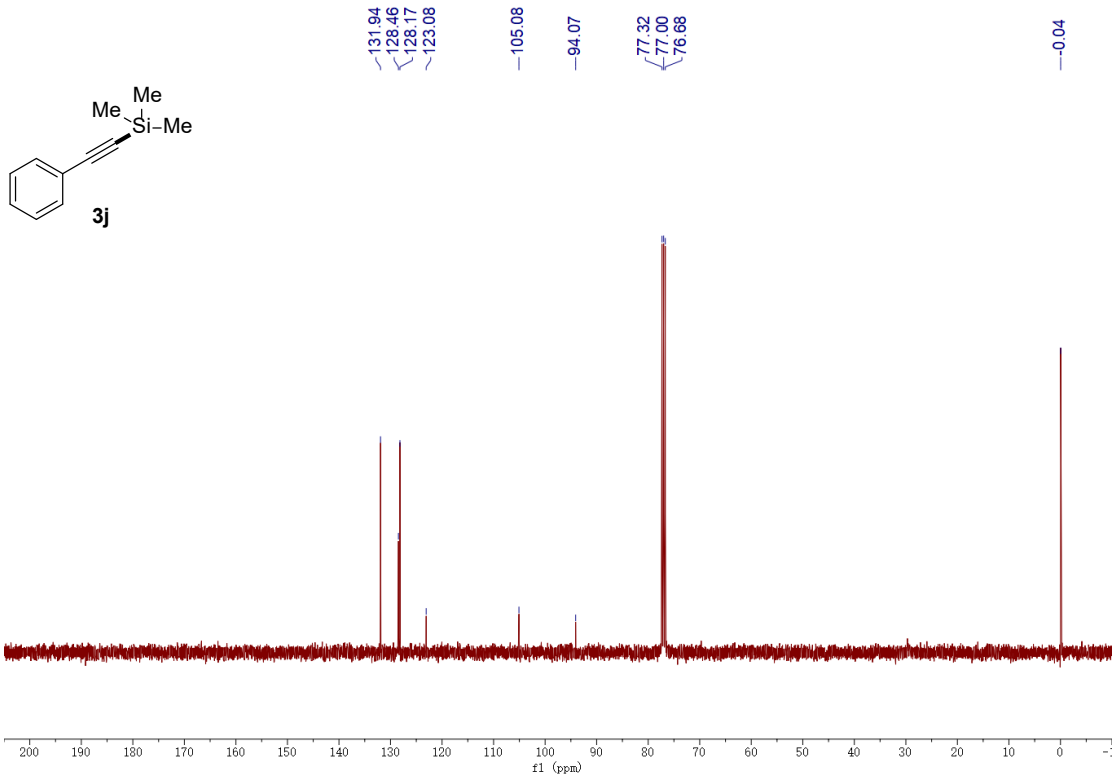

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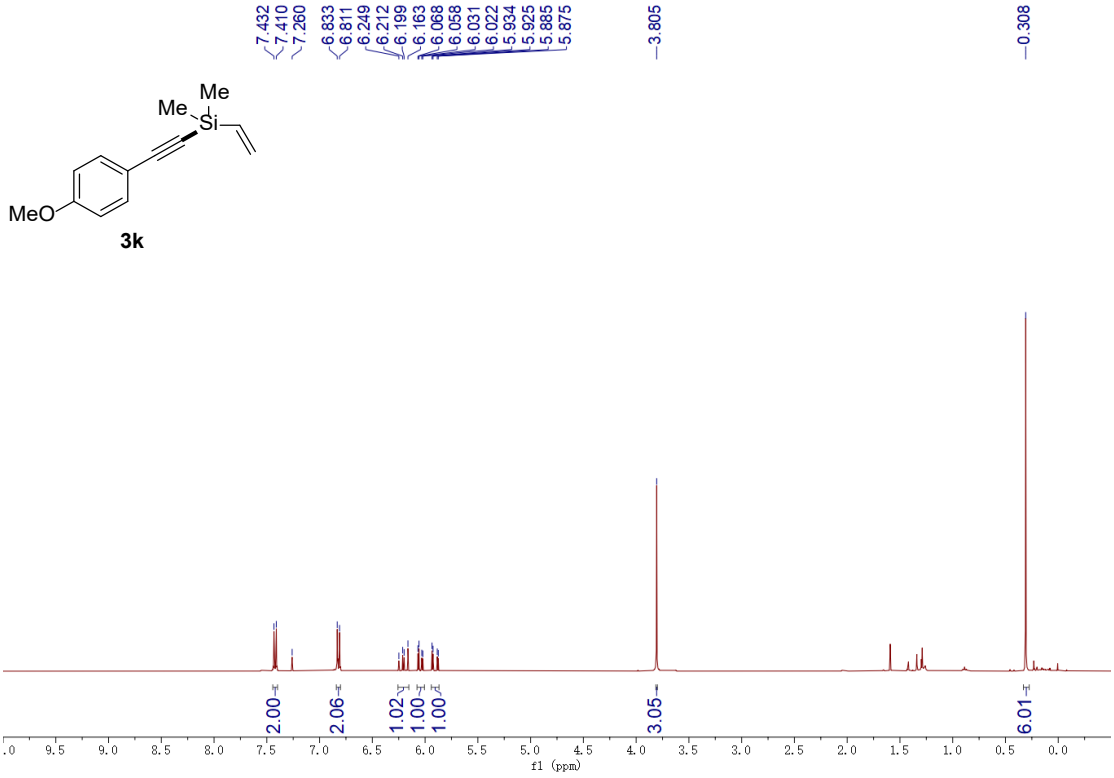

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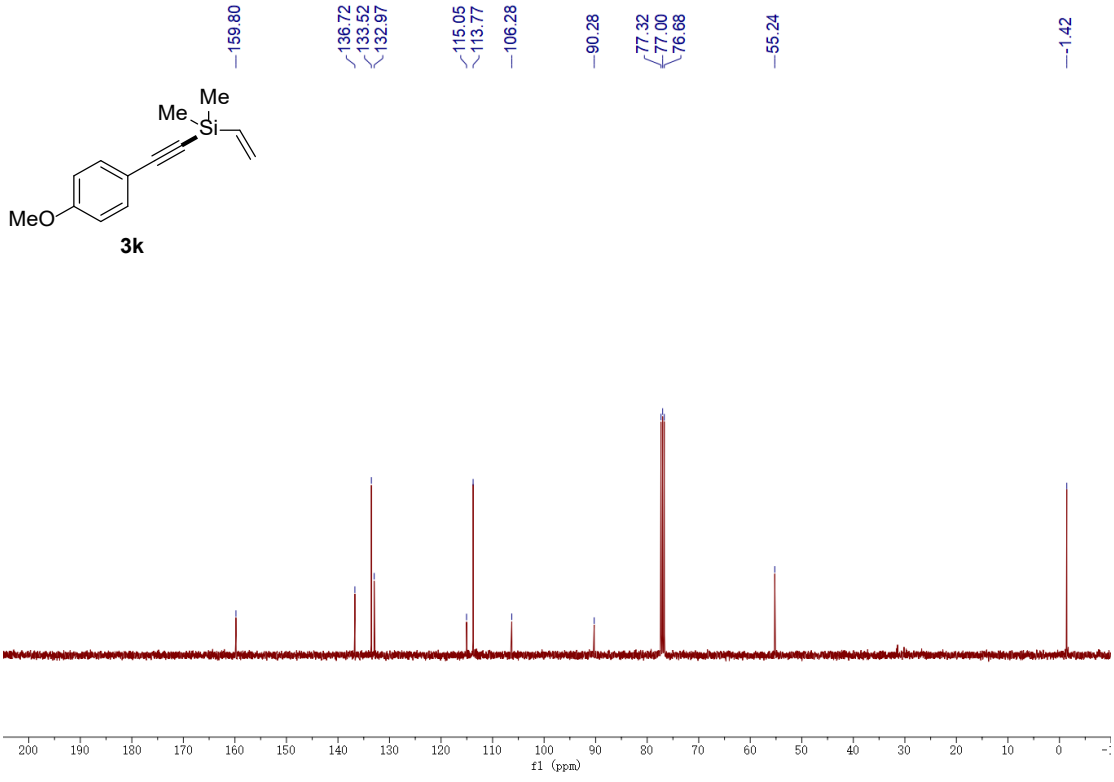

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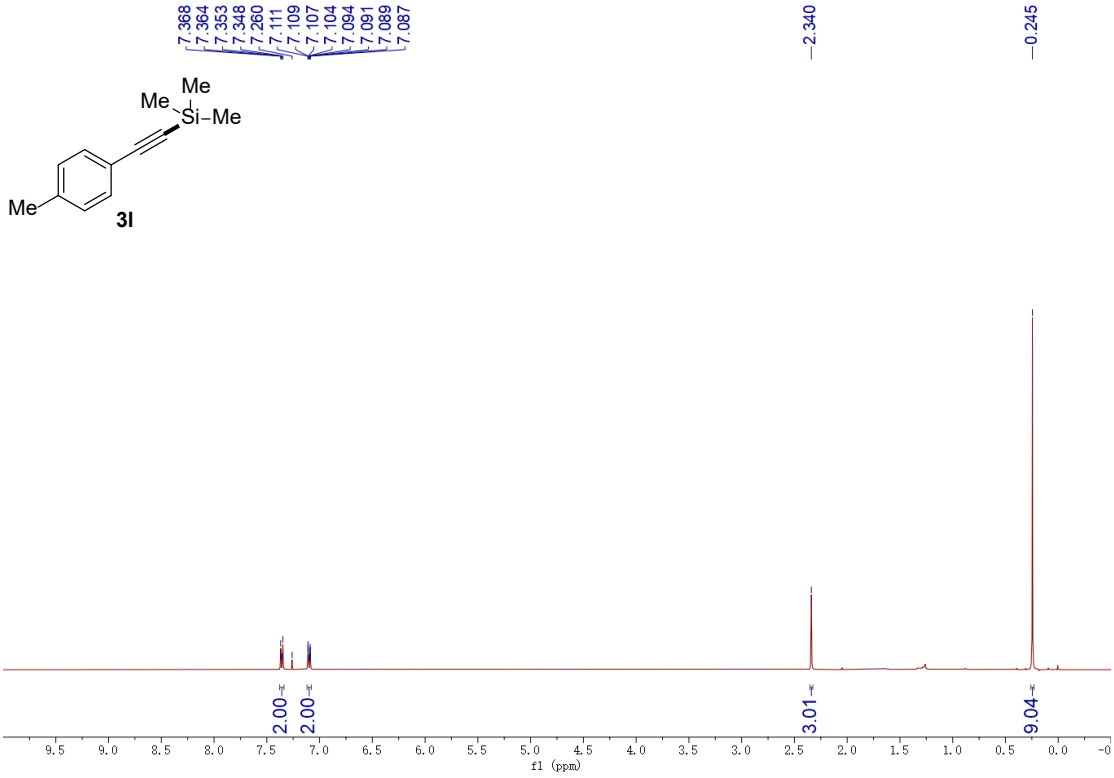

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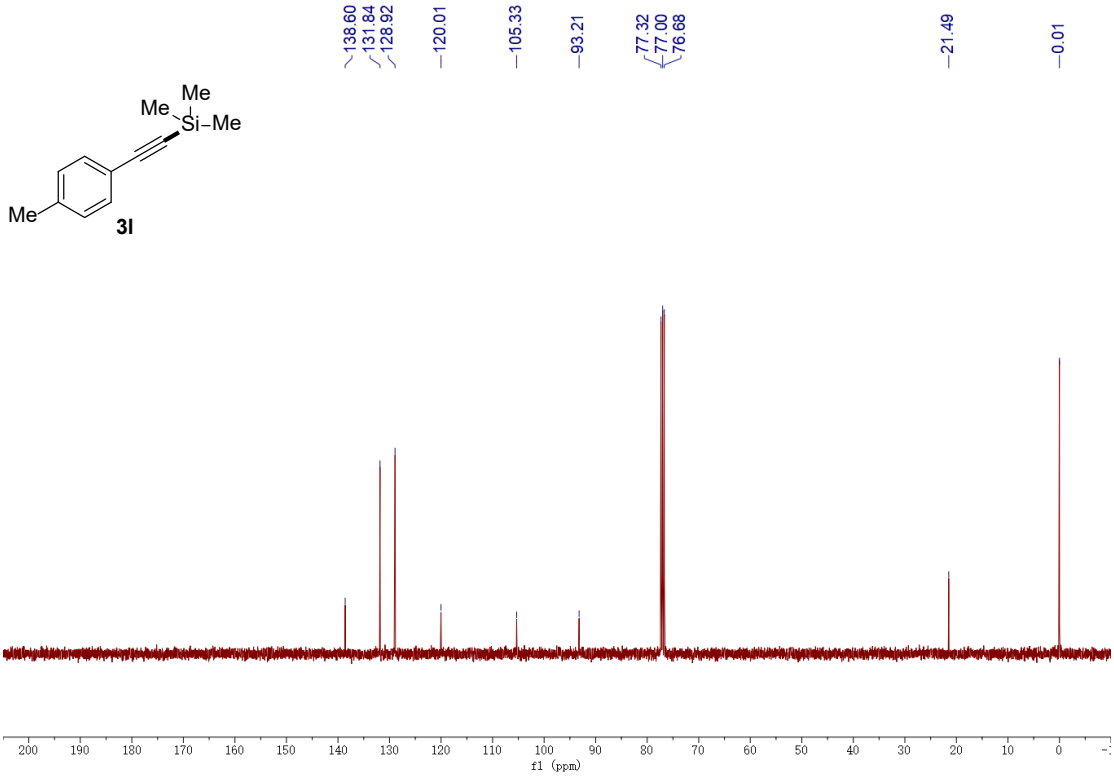

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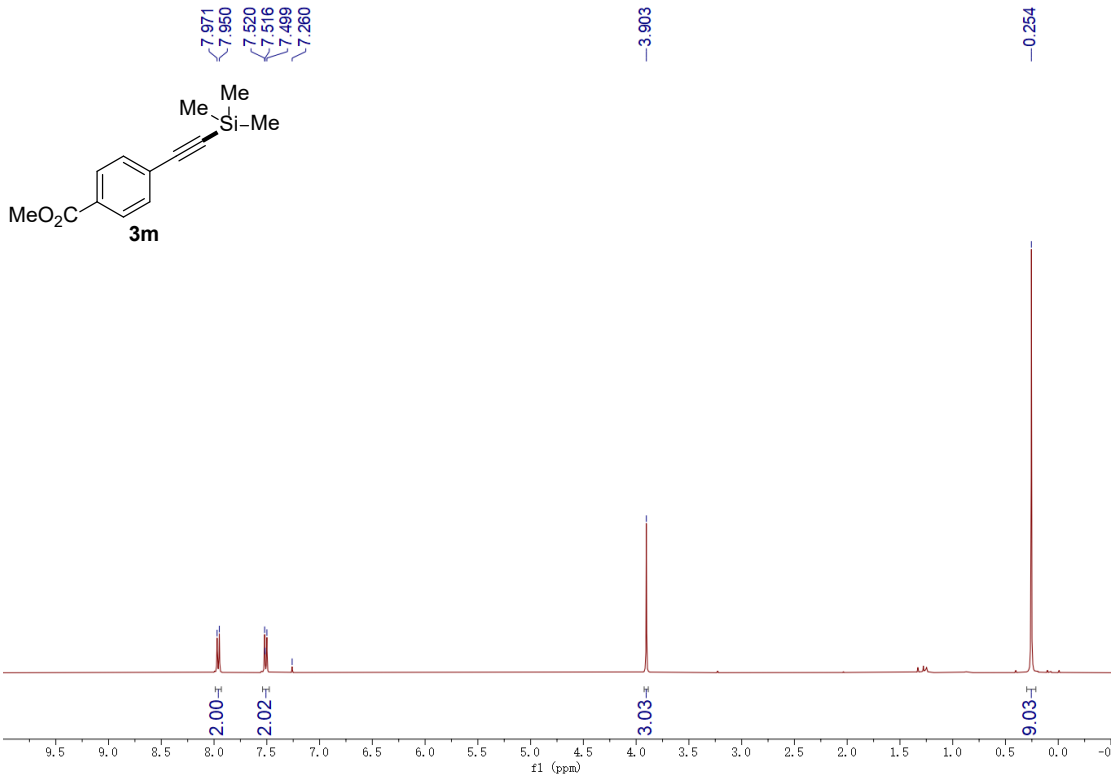

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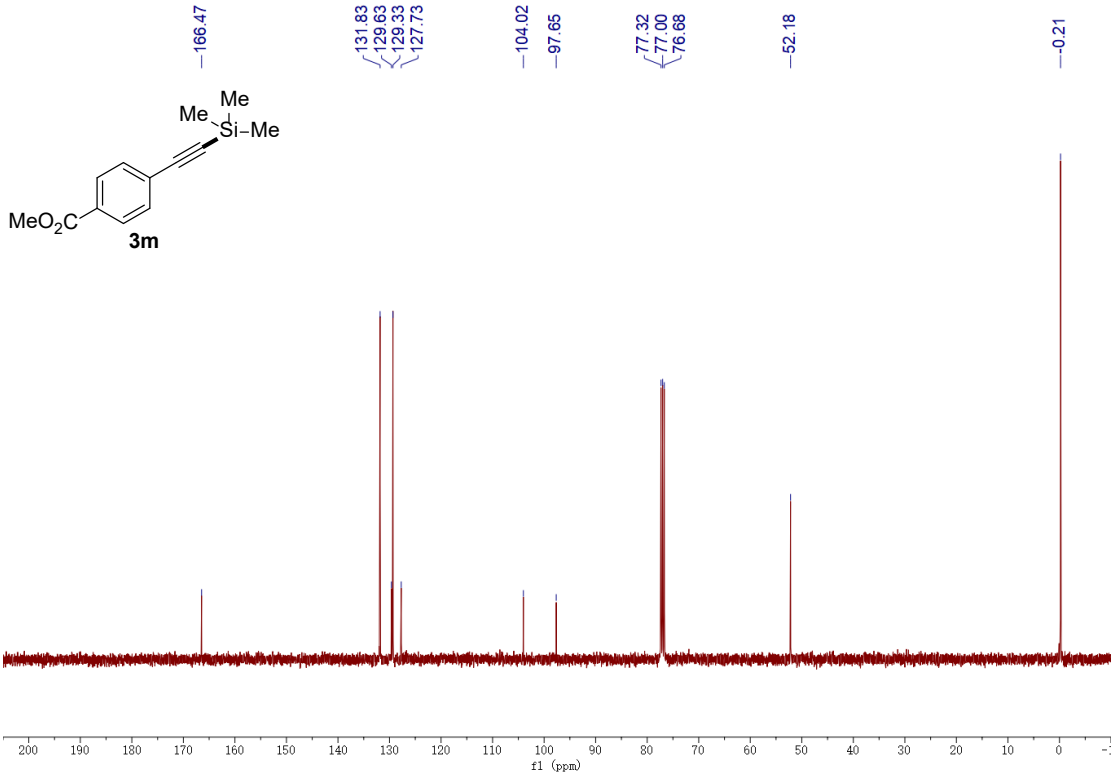

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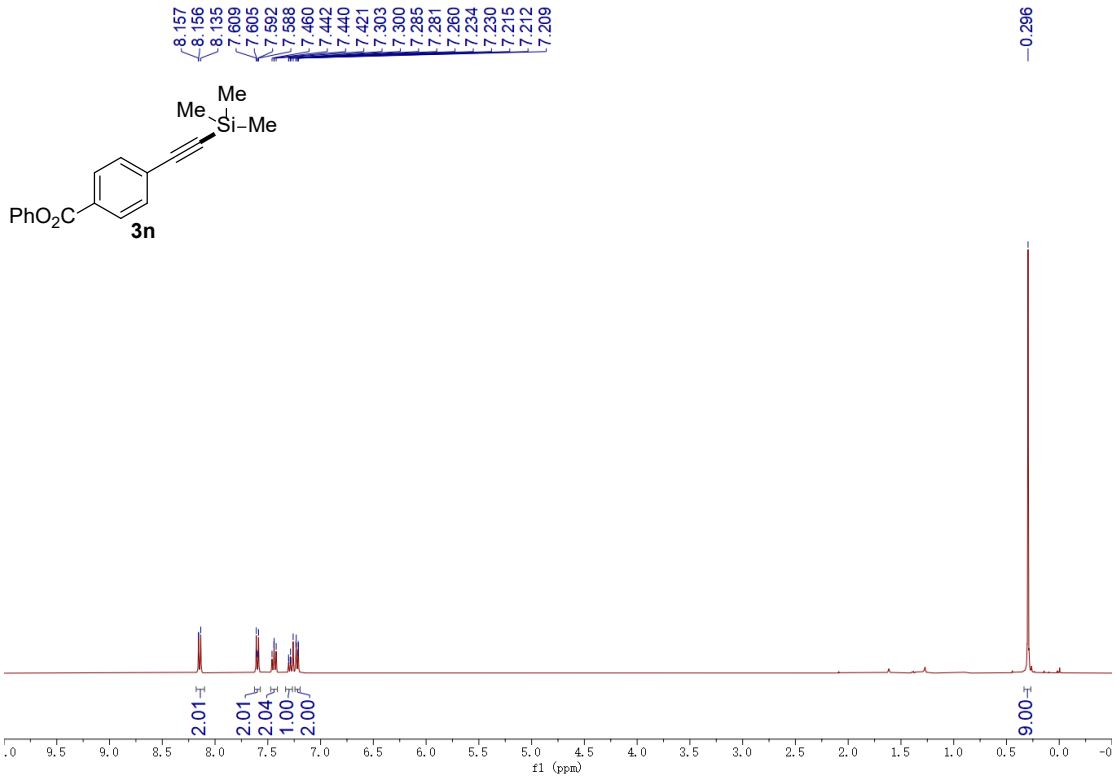

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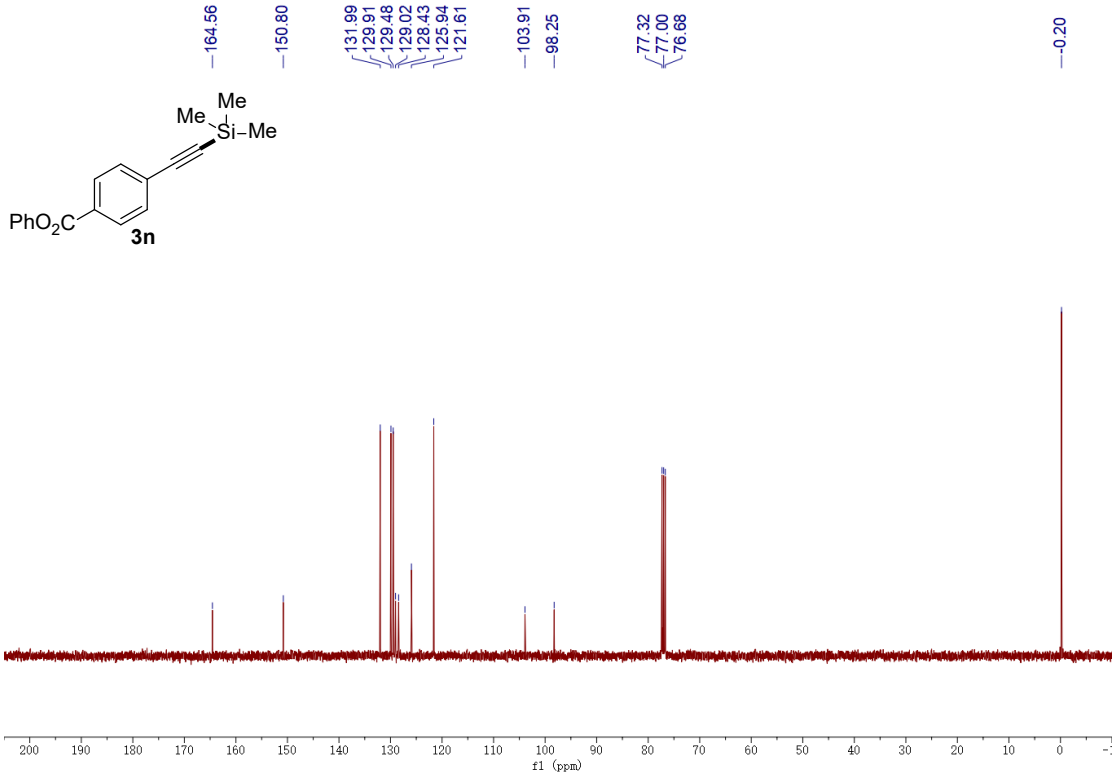

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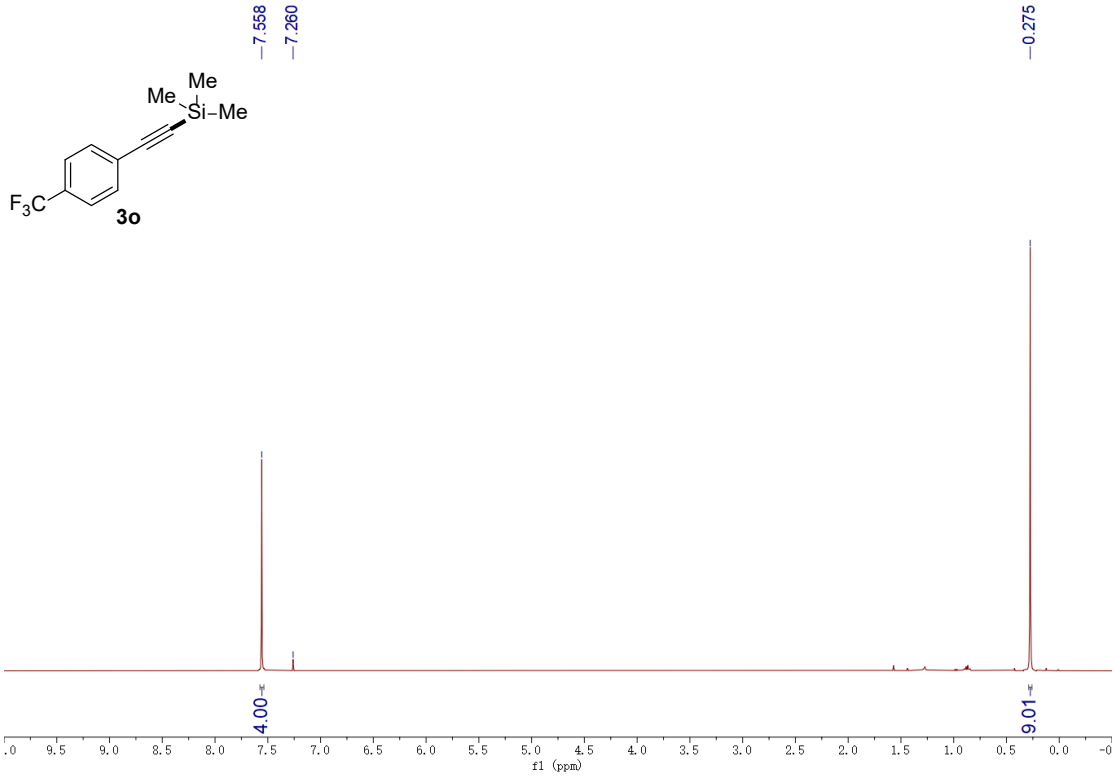

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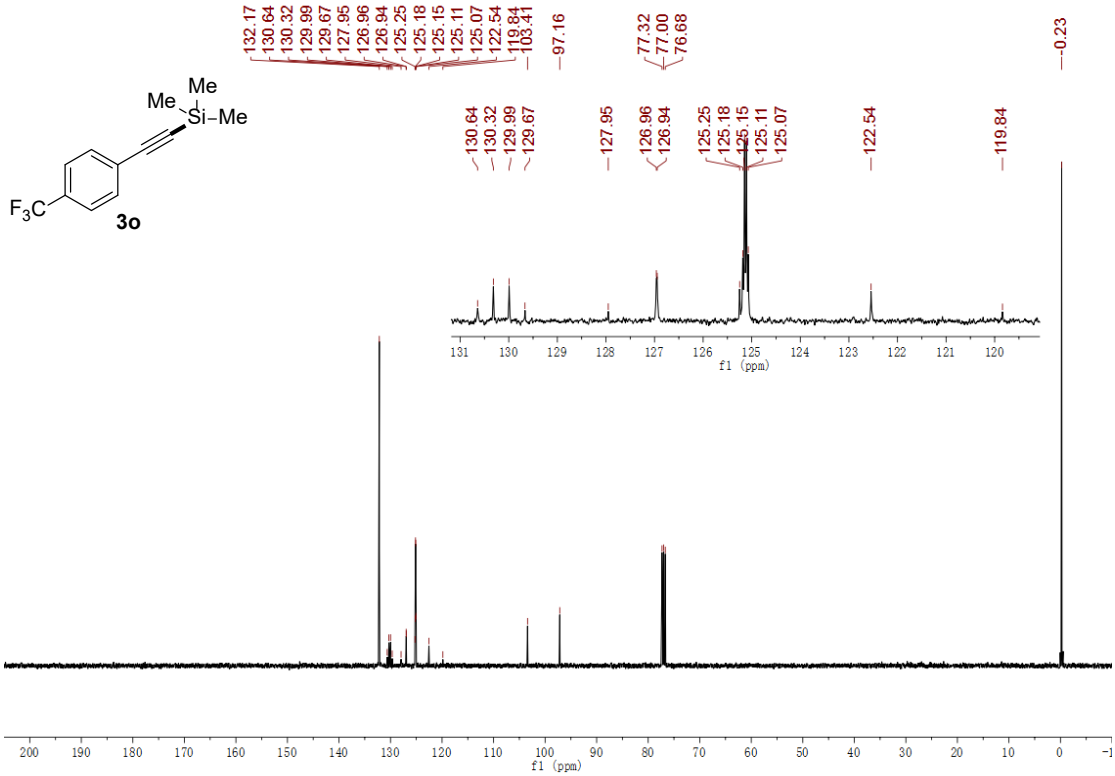
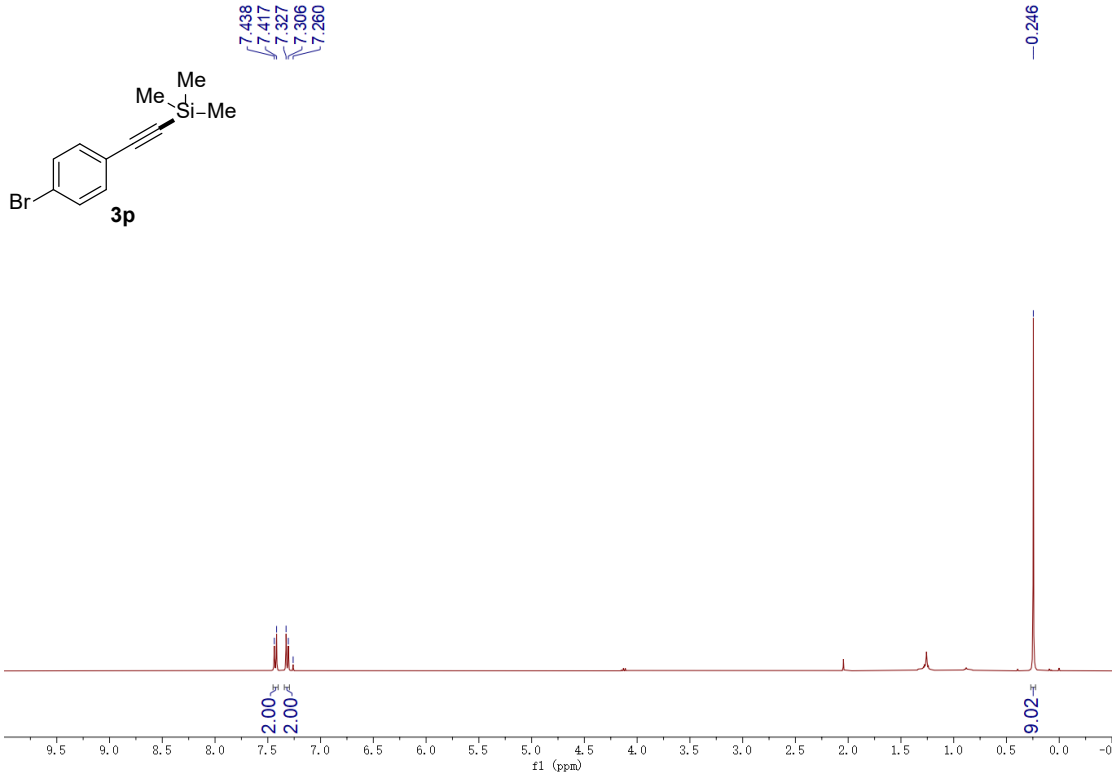
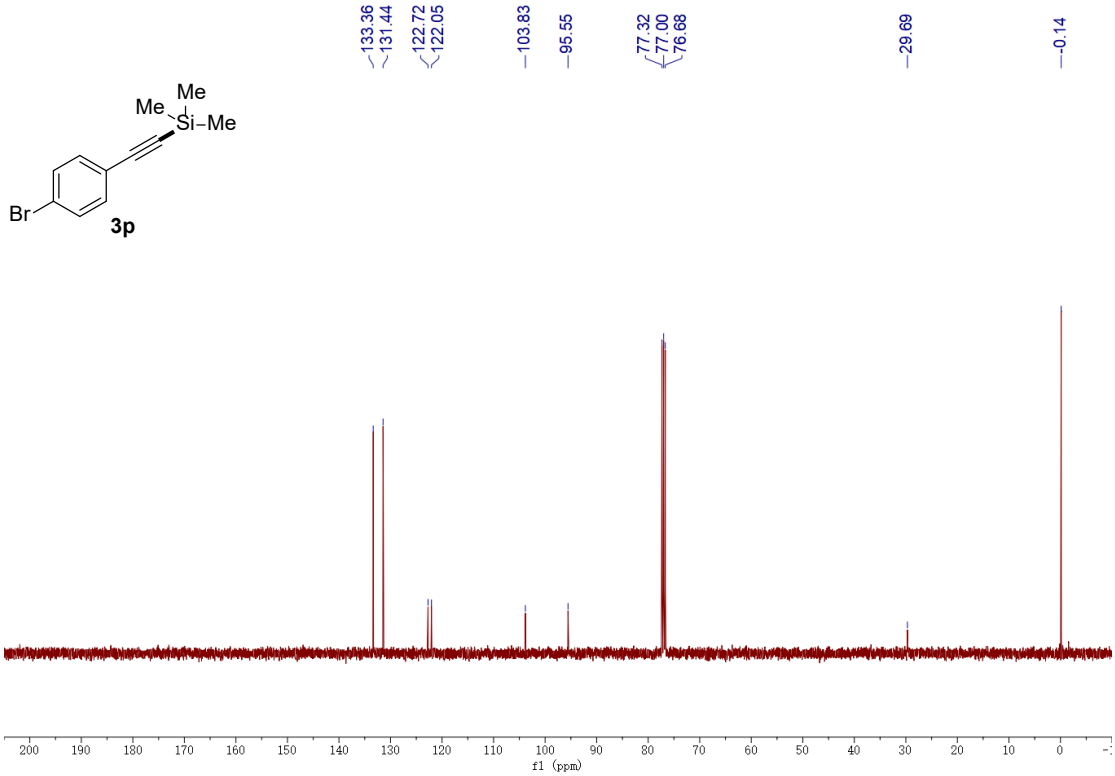


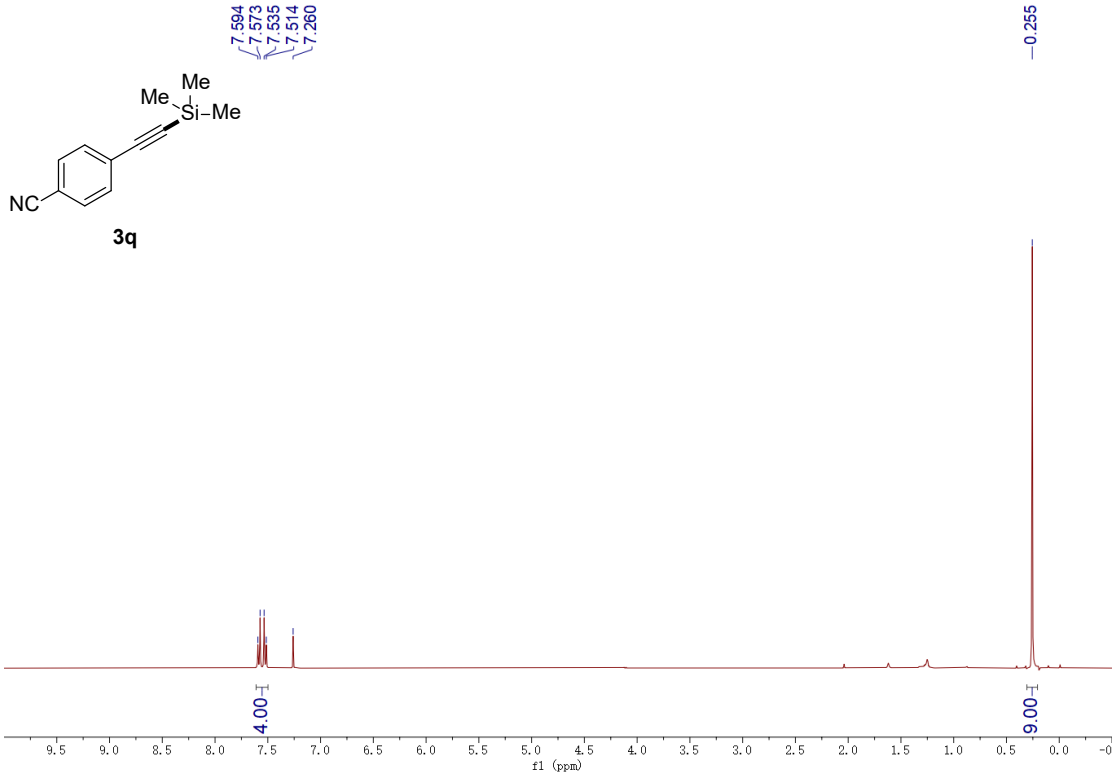
^{1}H NMR：400MHz, Choroform-*d*, peak of $CHCl_3$ in 7.260



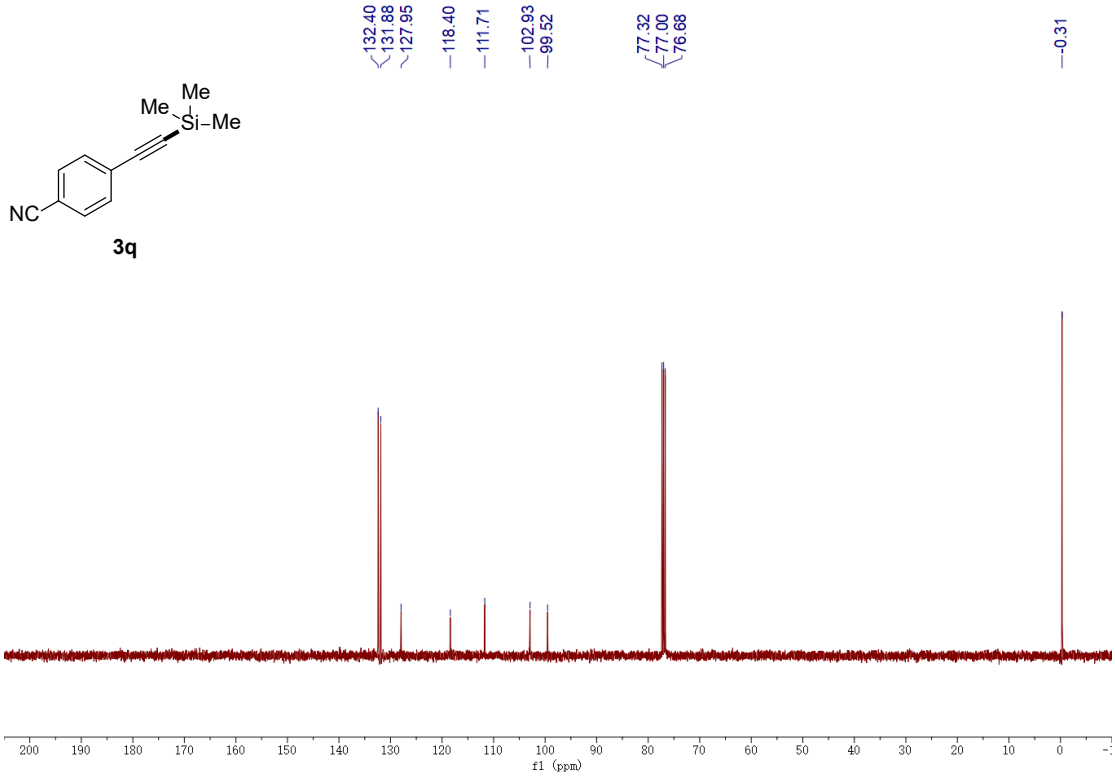
^{13}C NMR：101MHz, Choroform-*d*, peak of $CHCl_3$ in 77.0



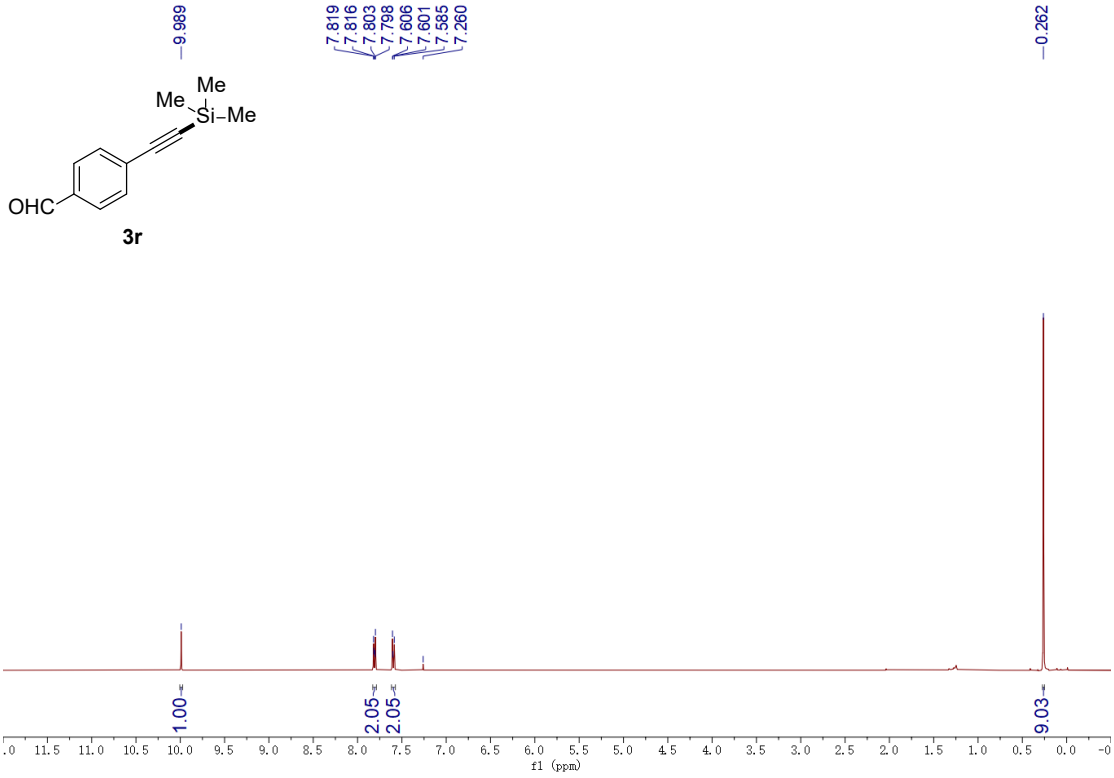
^{1}H NMR：400MHz, Choroform-*d*, peak of $CHCl_3$ in 7.260



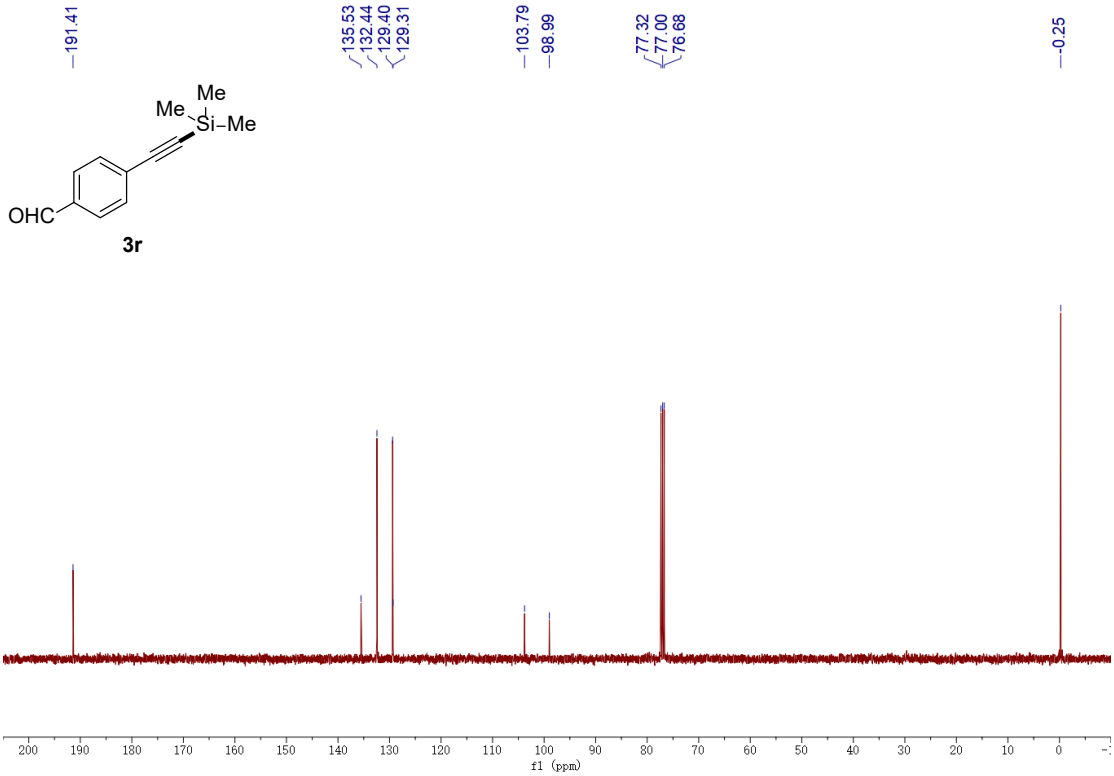
^{13}C NMR：101MHz, Choroform-*d*, peak of $CHCl_3$ in 77.0



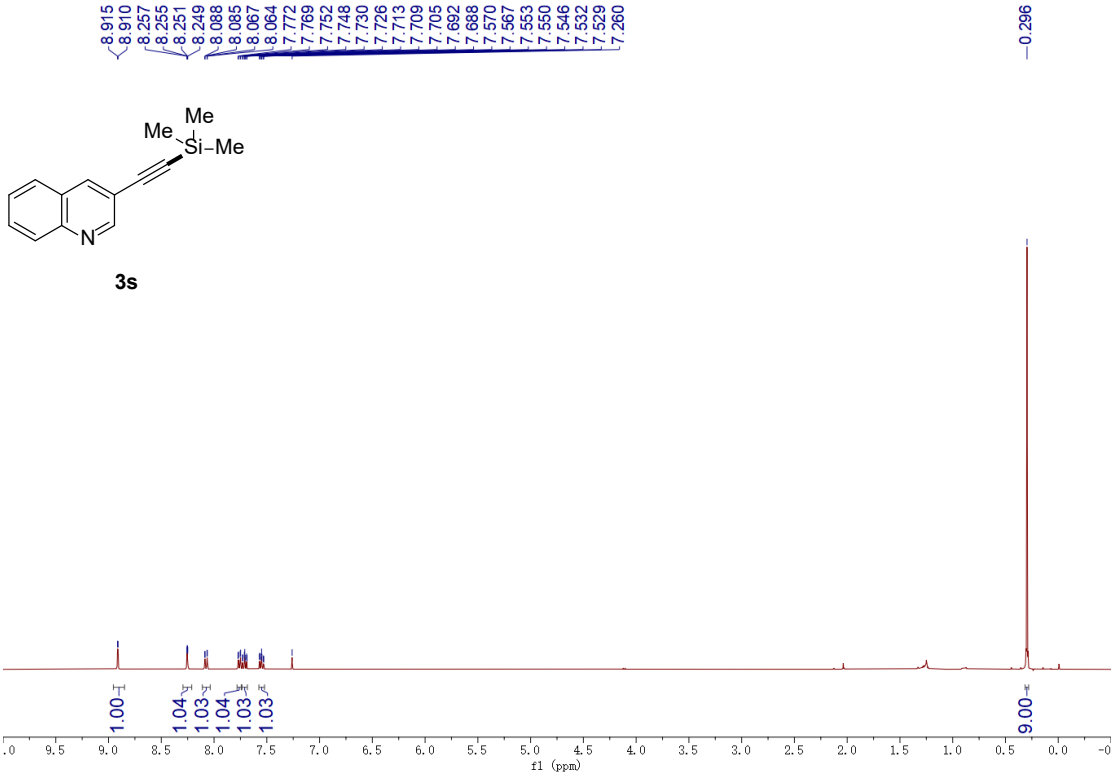
^{1}H NMR：400MHz, Choroform-*d*, peak of $CHCl_3$ in 7.260



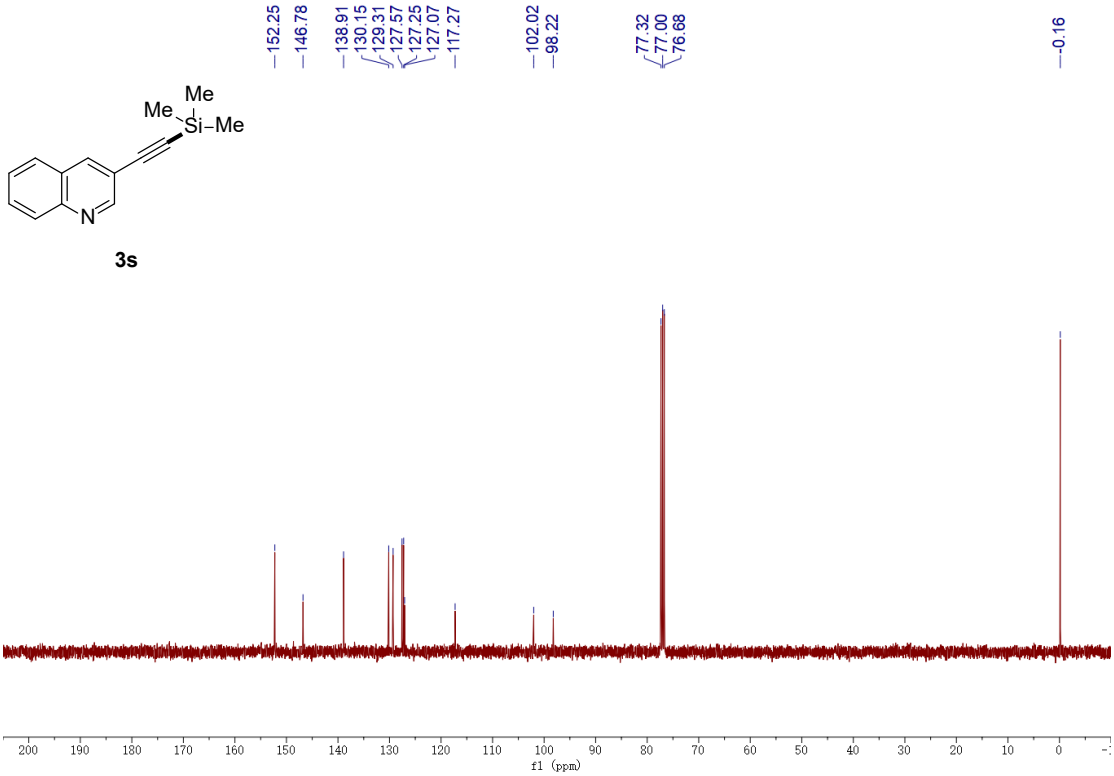
^{13}C NMR：101MHz, Choroform-*d*, peak of $CHCl_3$ in 77.0



^{1}H NMR：400MHz, Choroform-*d*, peak of $CHCl_3$ in 7.260



^{13}C NMR：101MHz, Choroform-*d*, peak of $CHCl_3$ in 77.0



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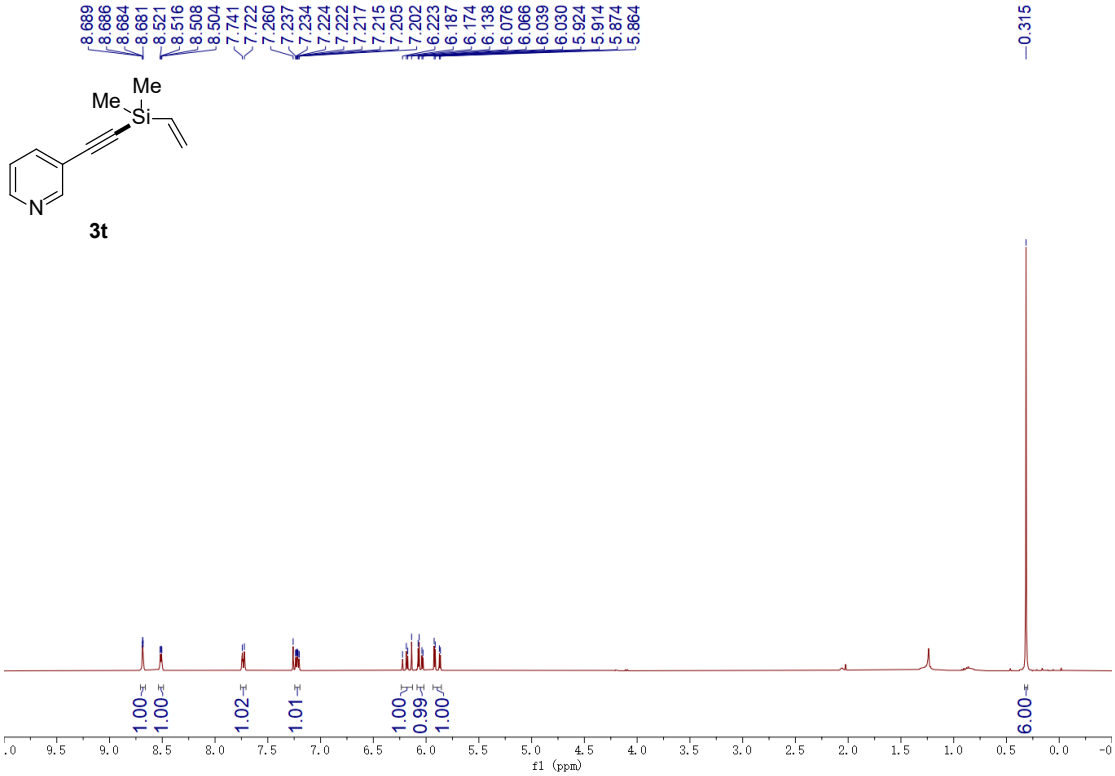

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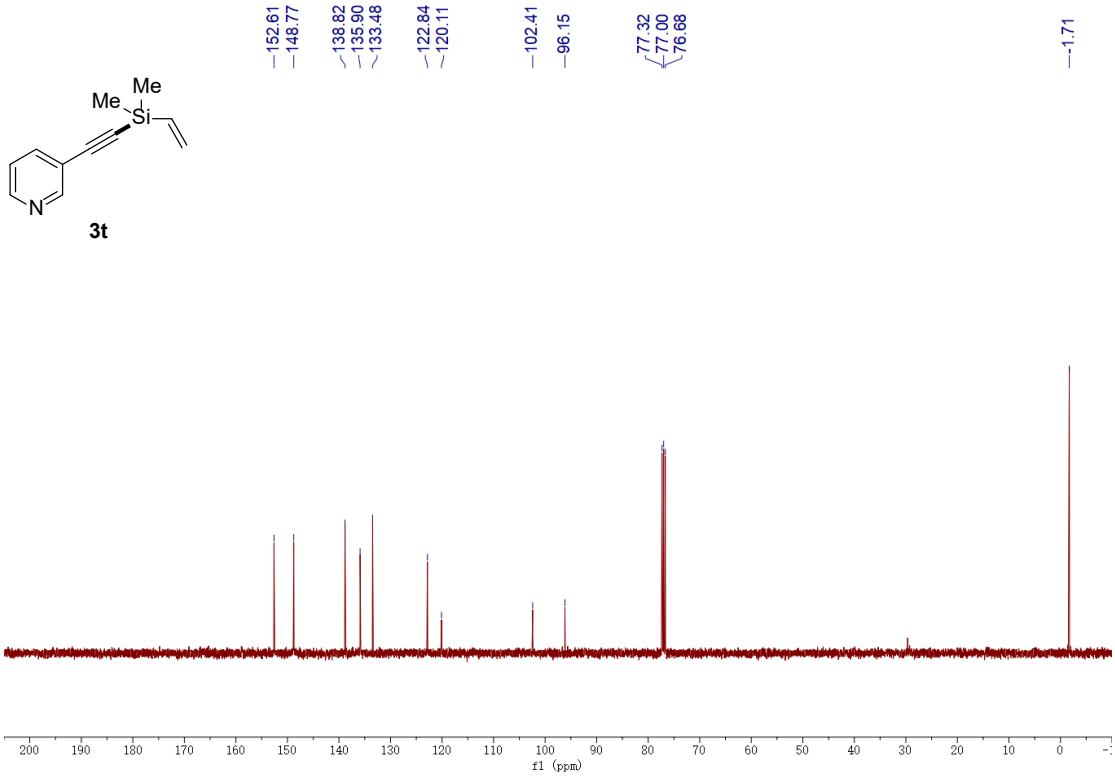
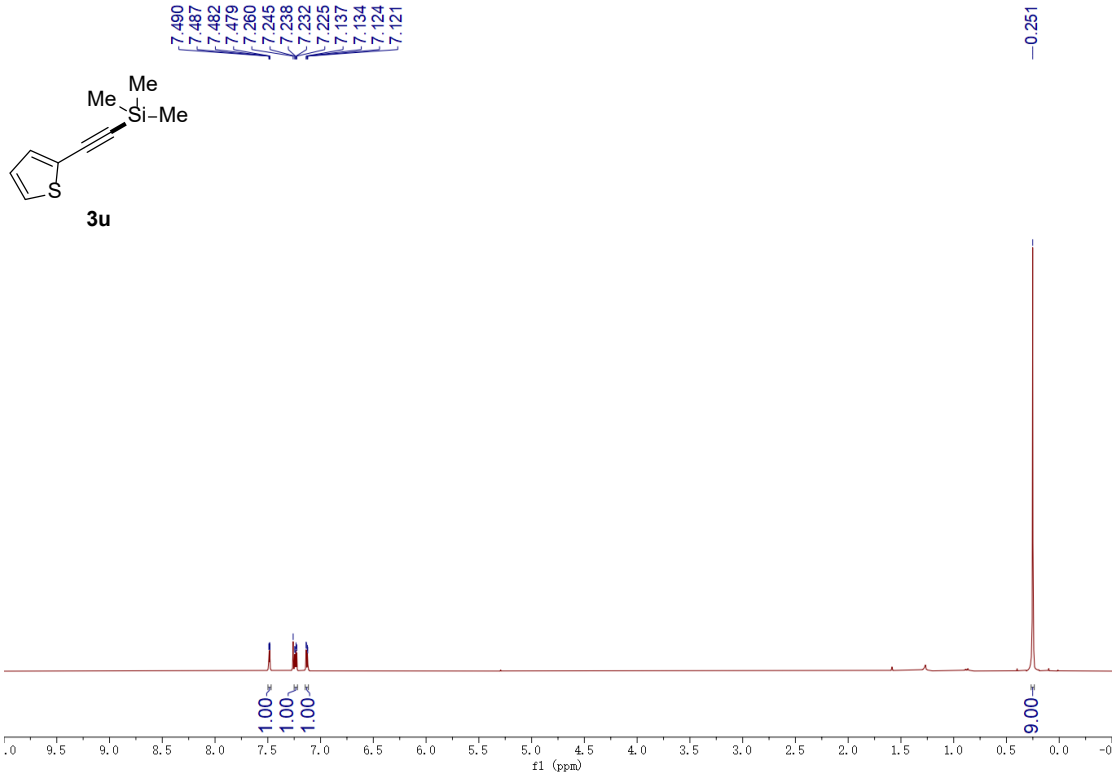


^{1}H NMR：400MHz, Choroform-*d*, peak of $CHCl_3$ in 7.260



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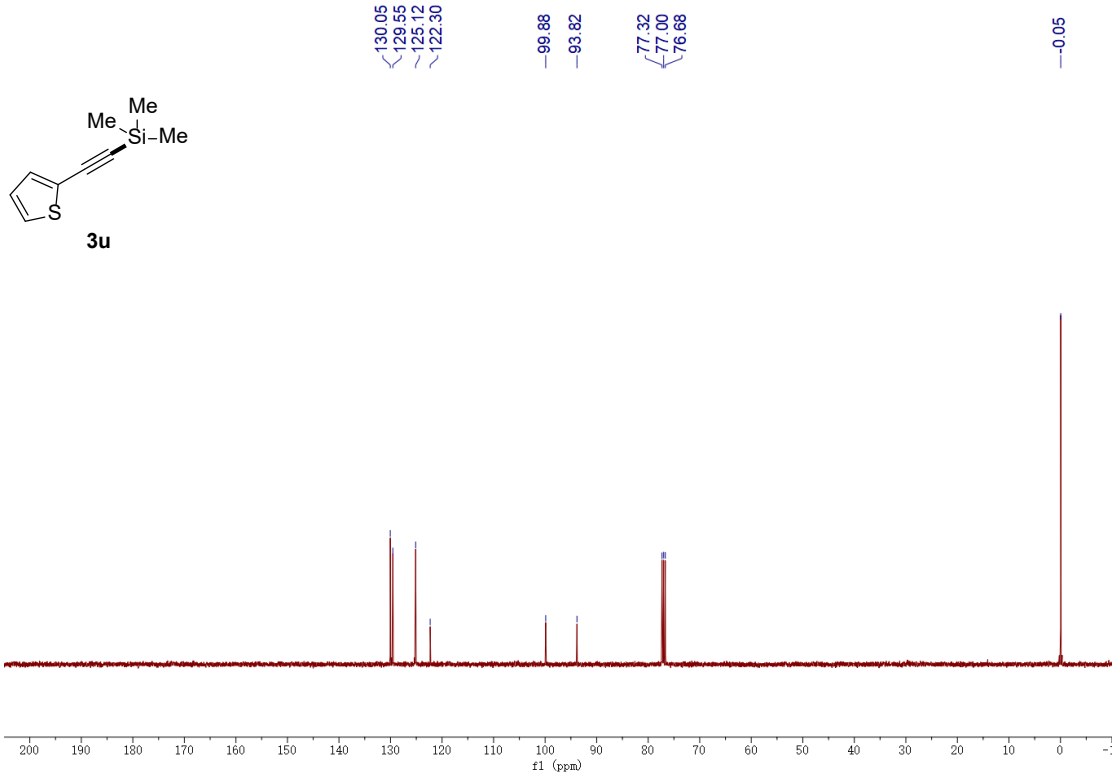

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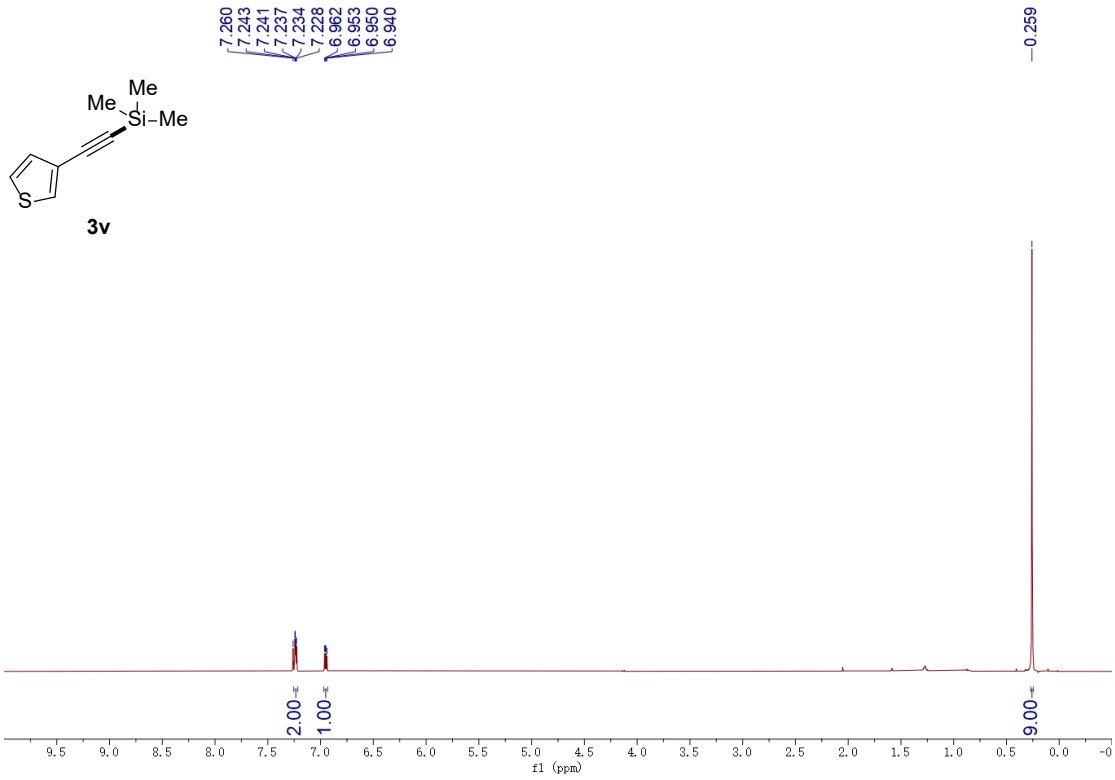

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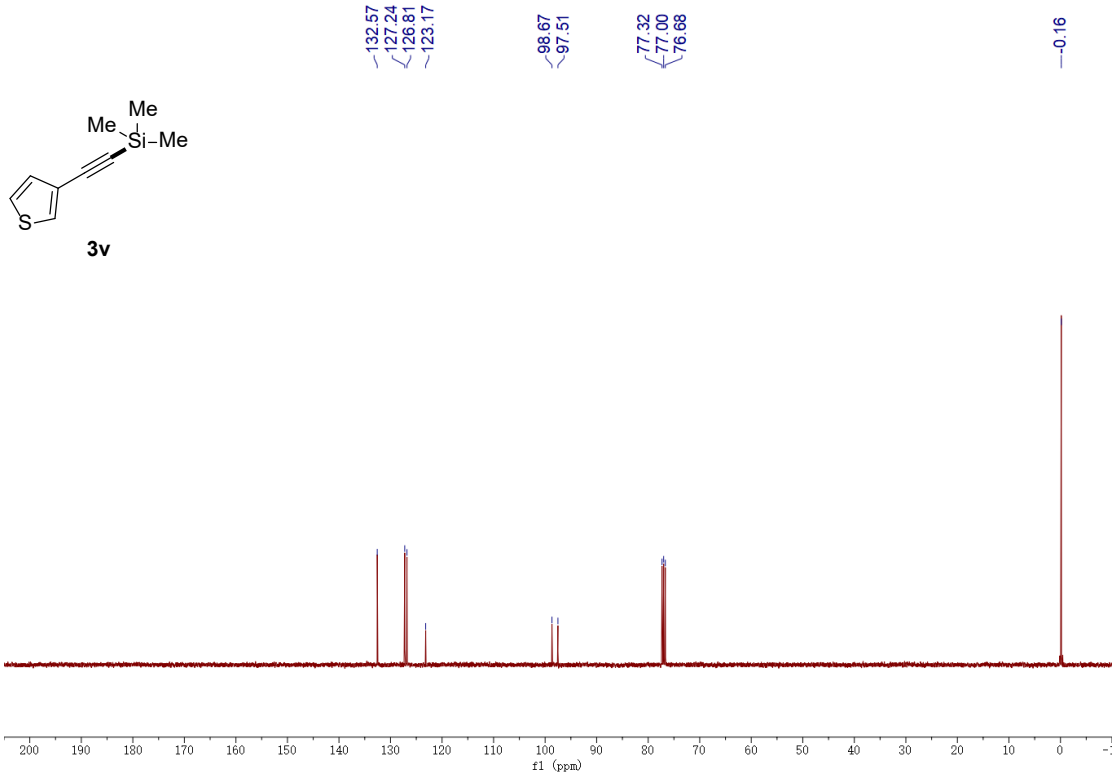

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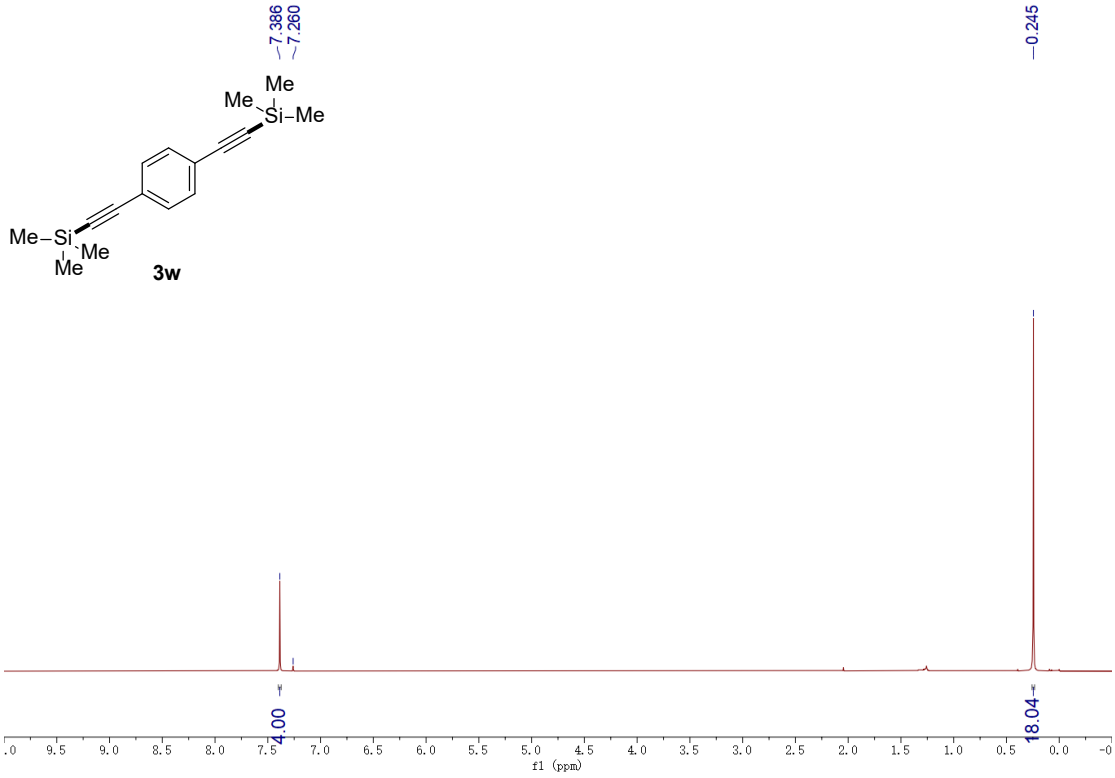

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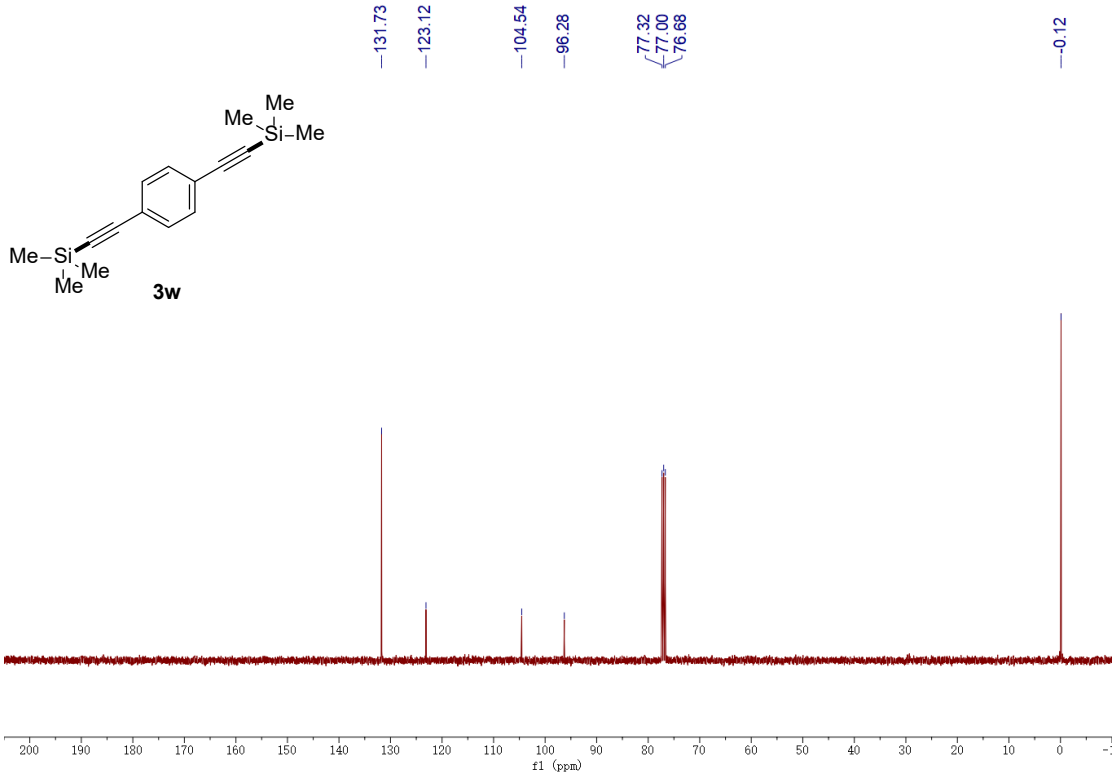

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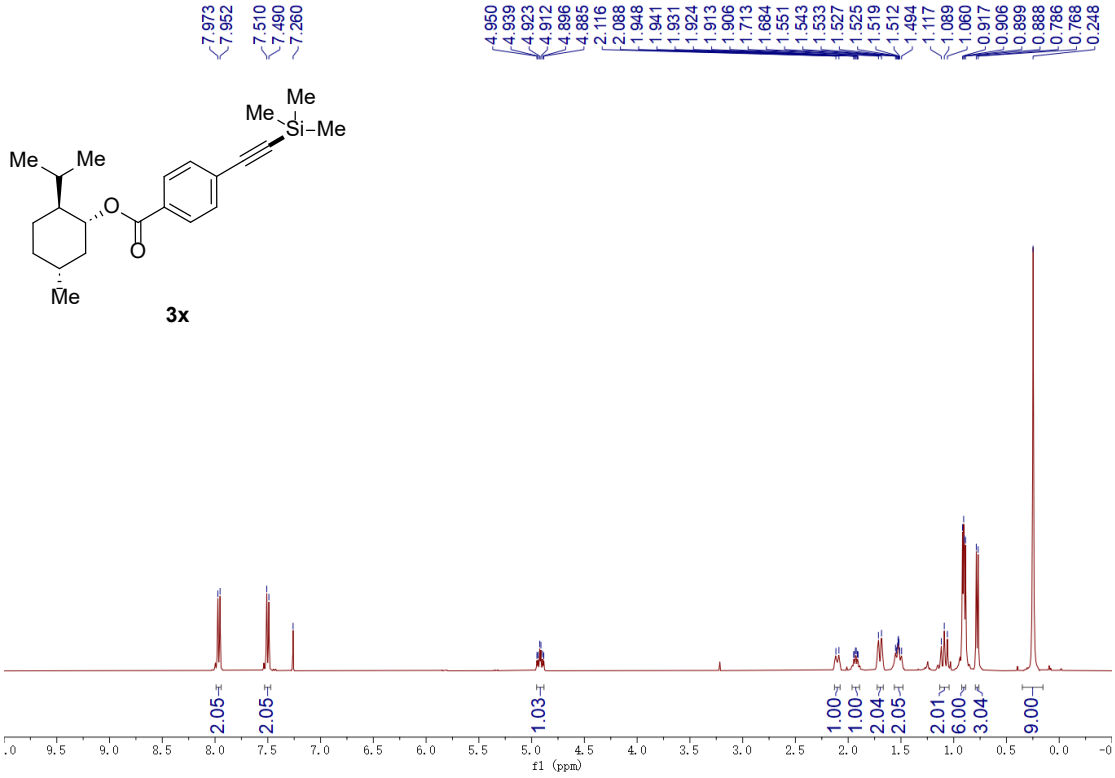

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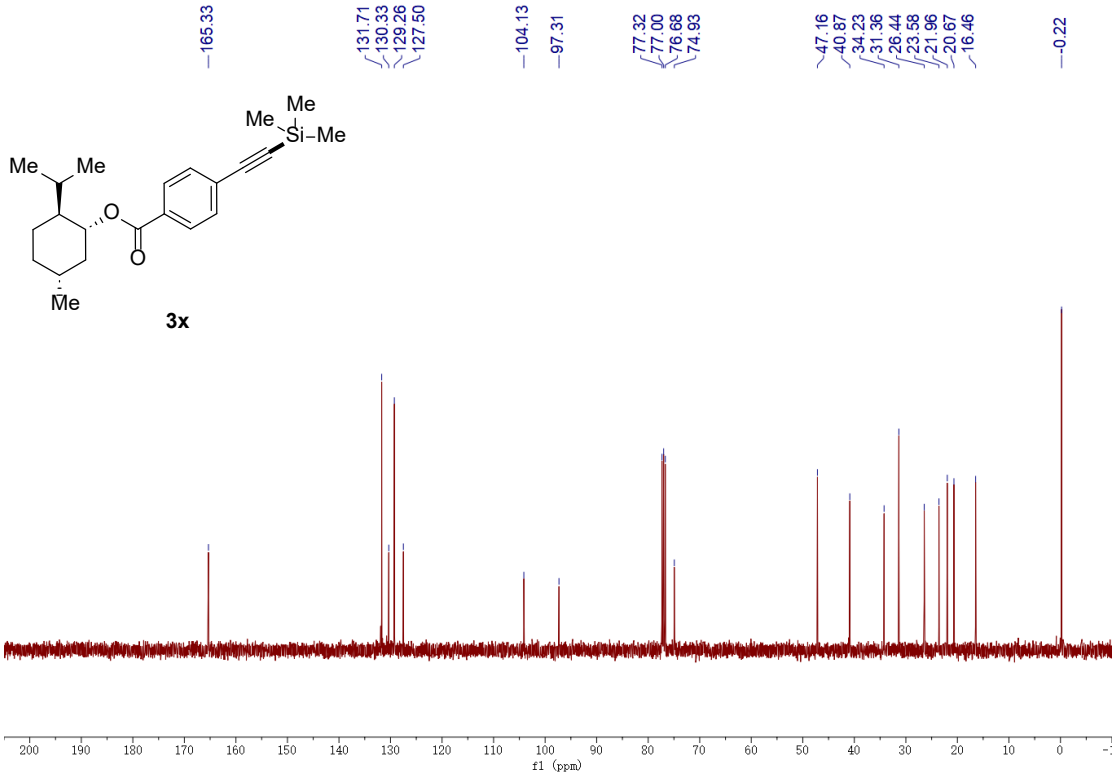

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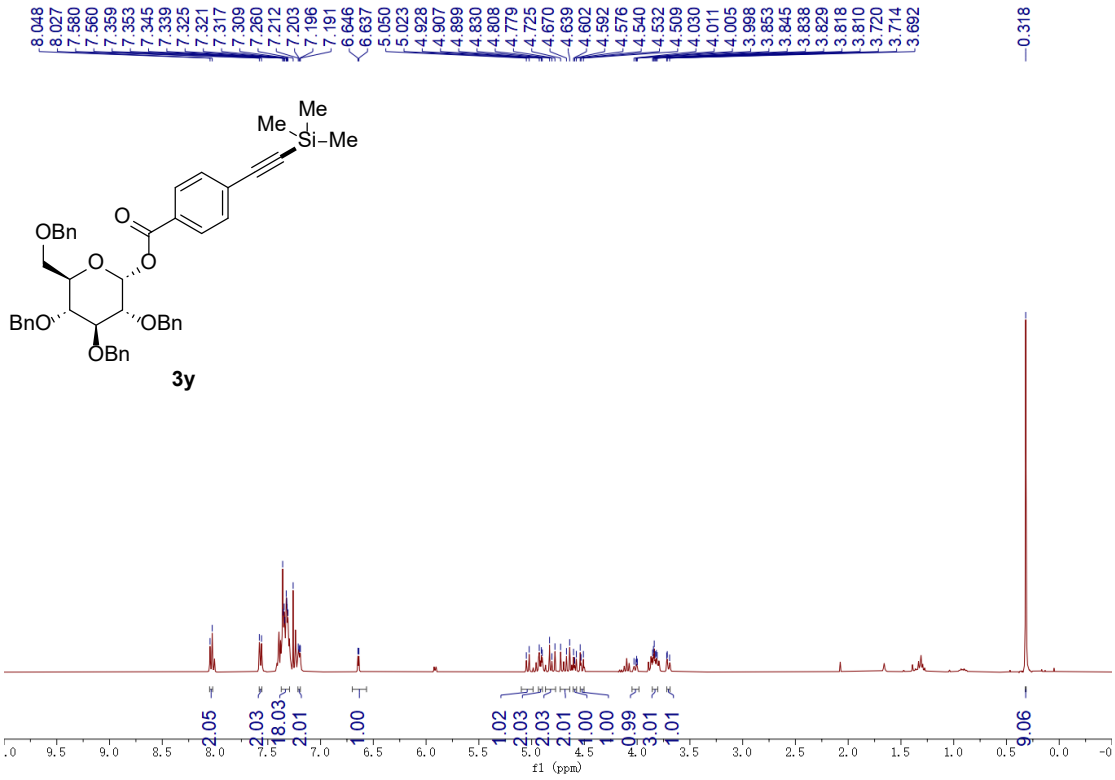

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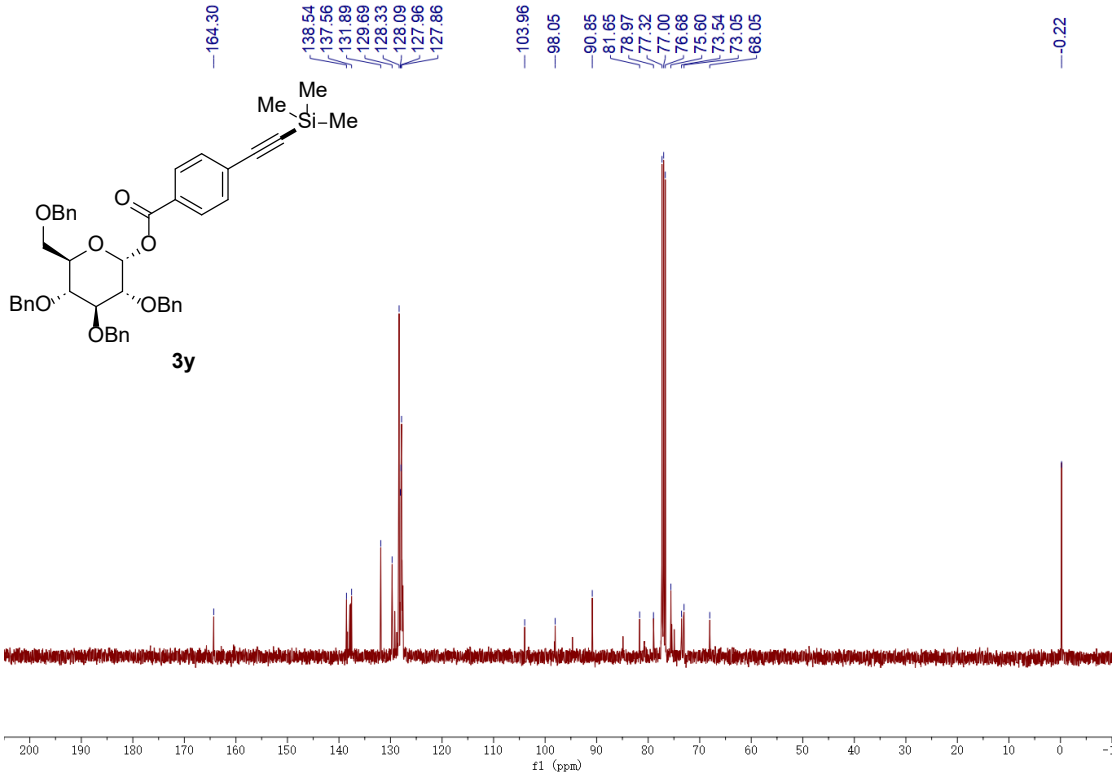

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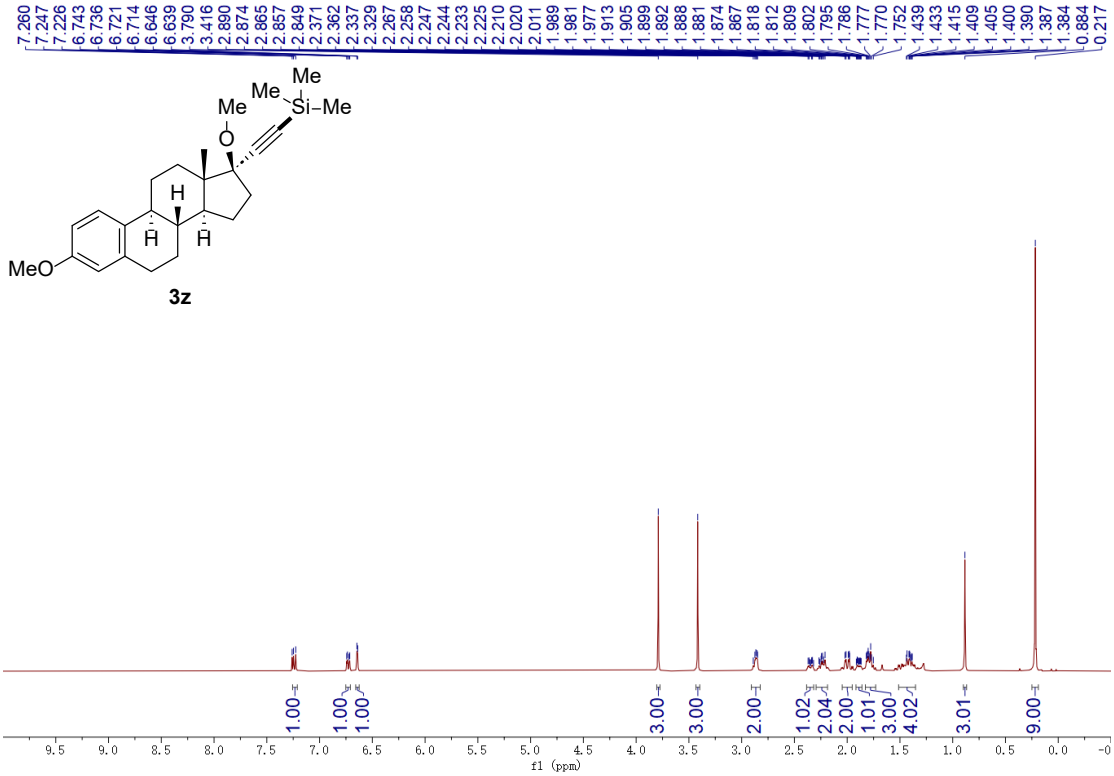

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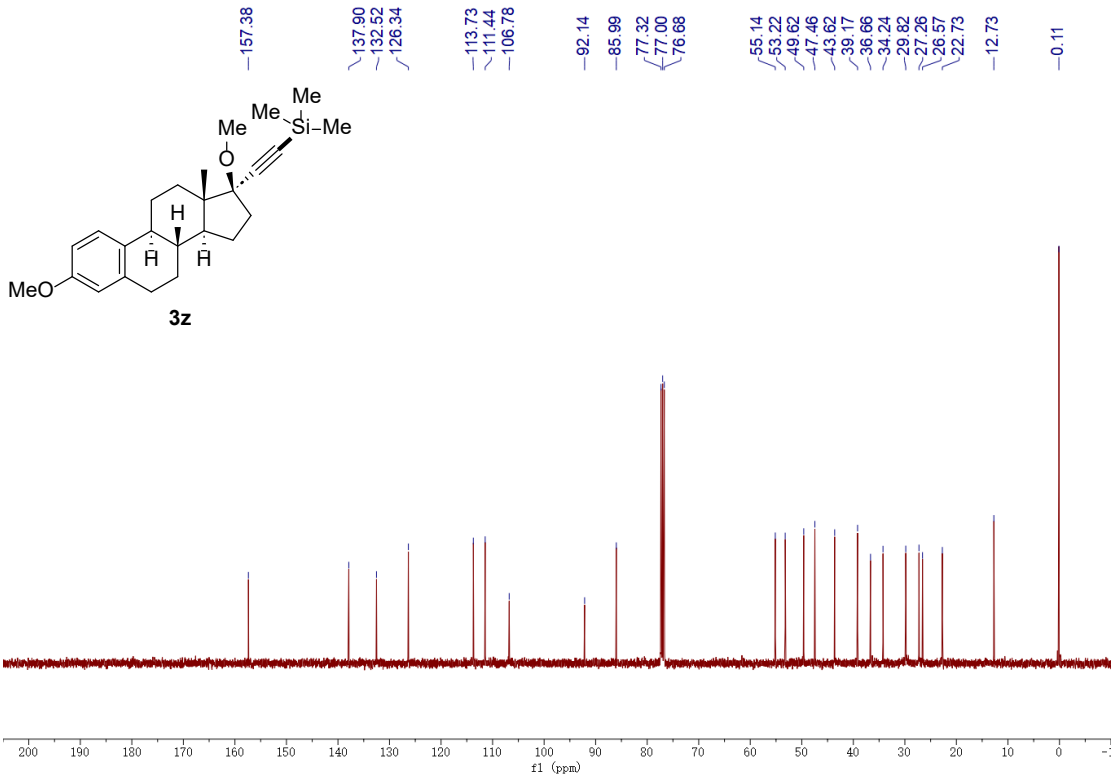

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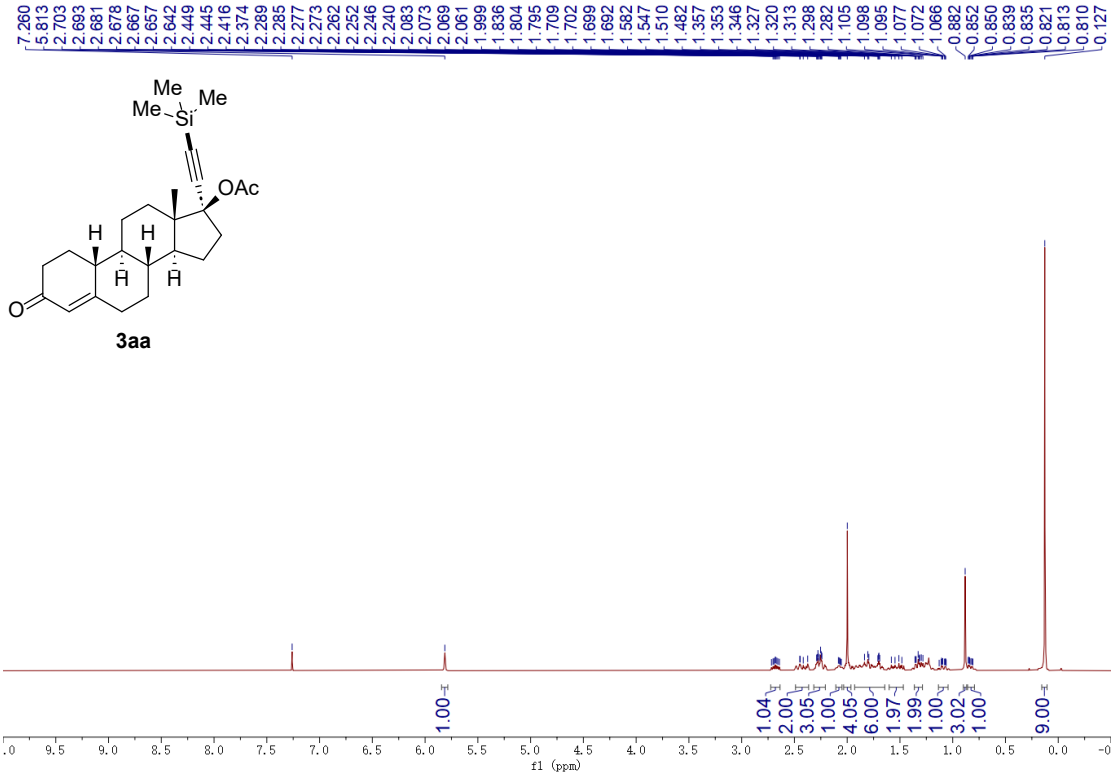

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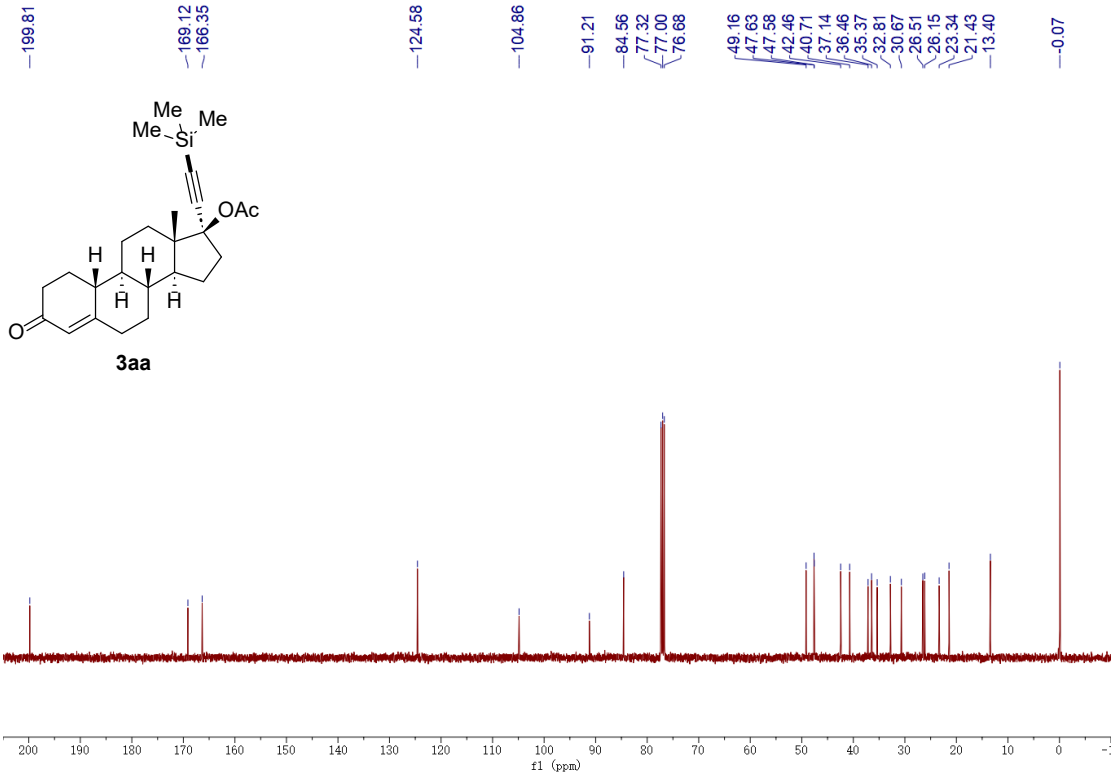

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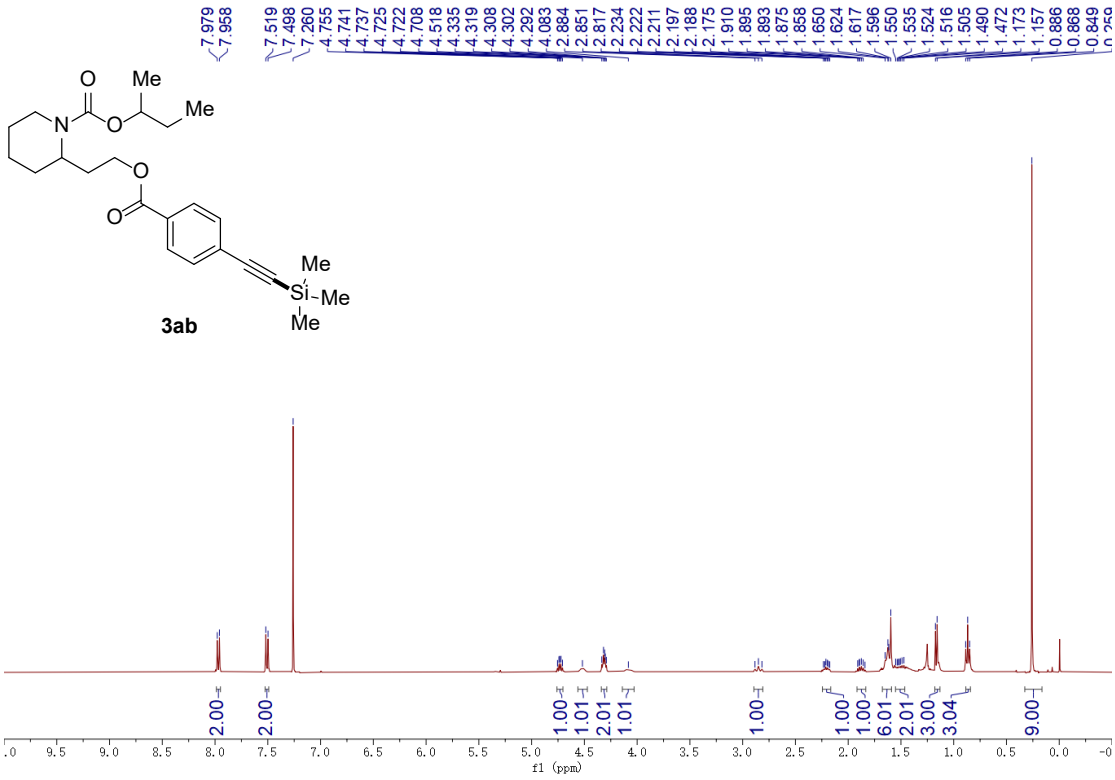

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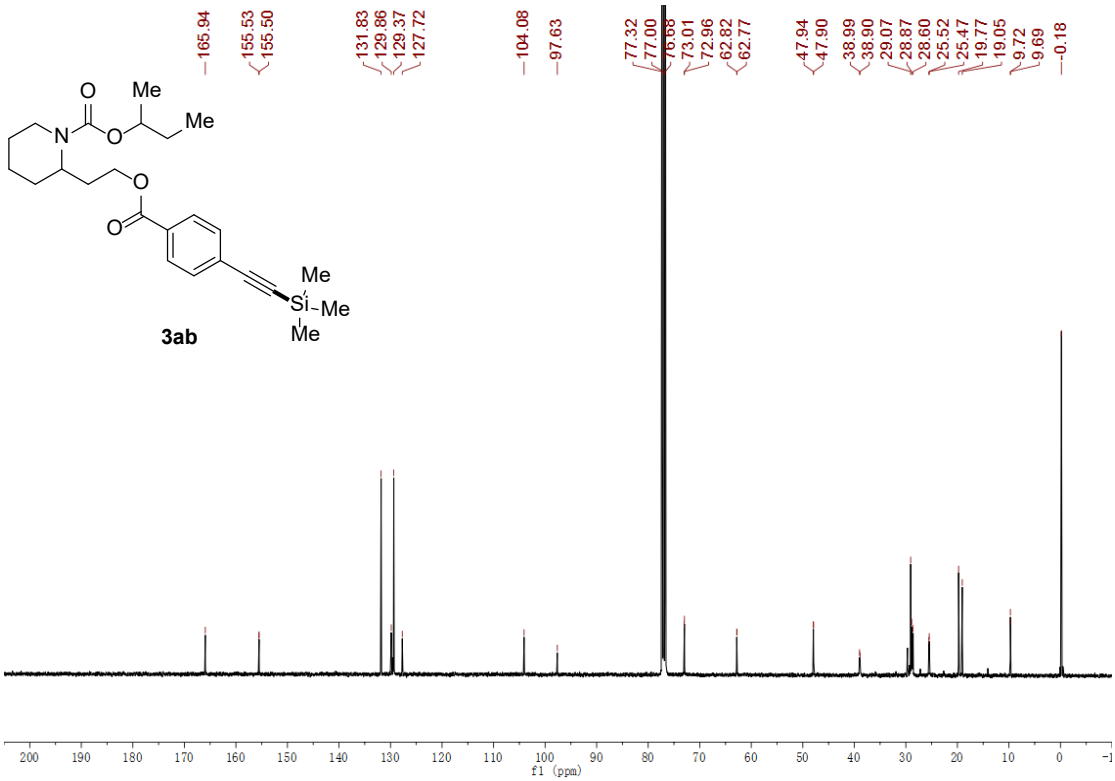

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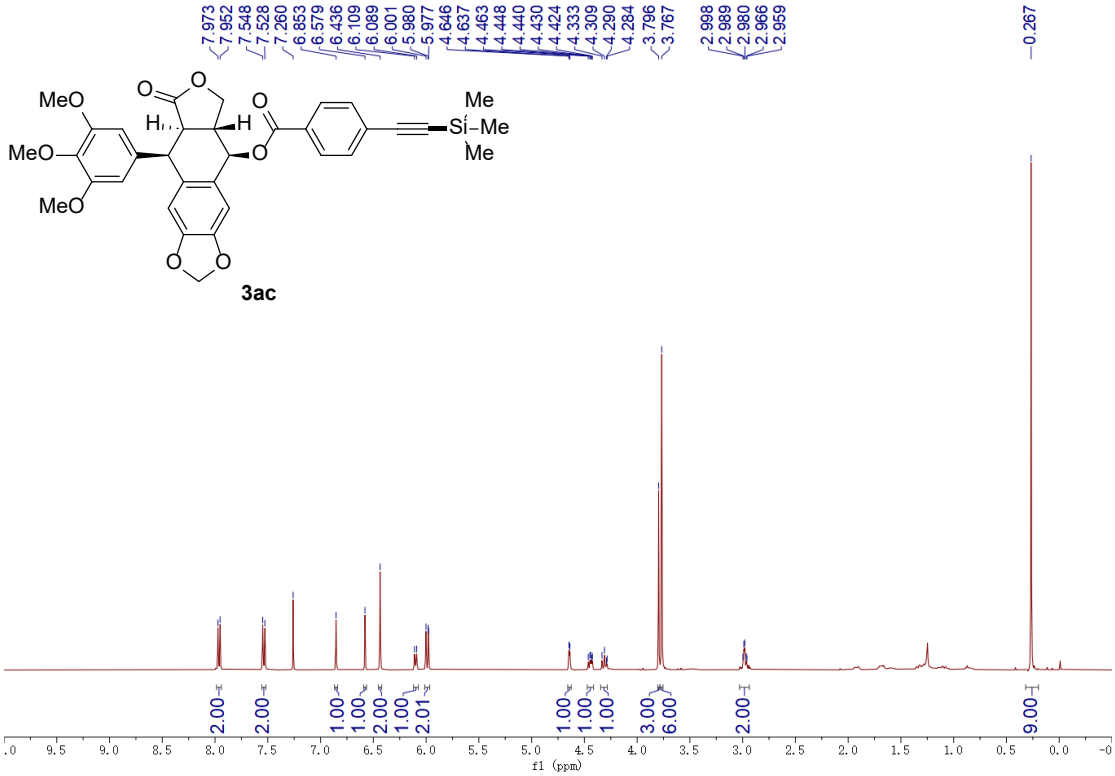

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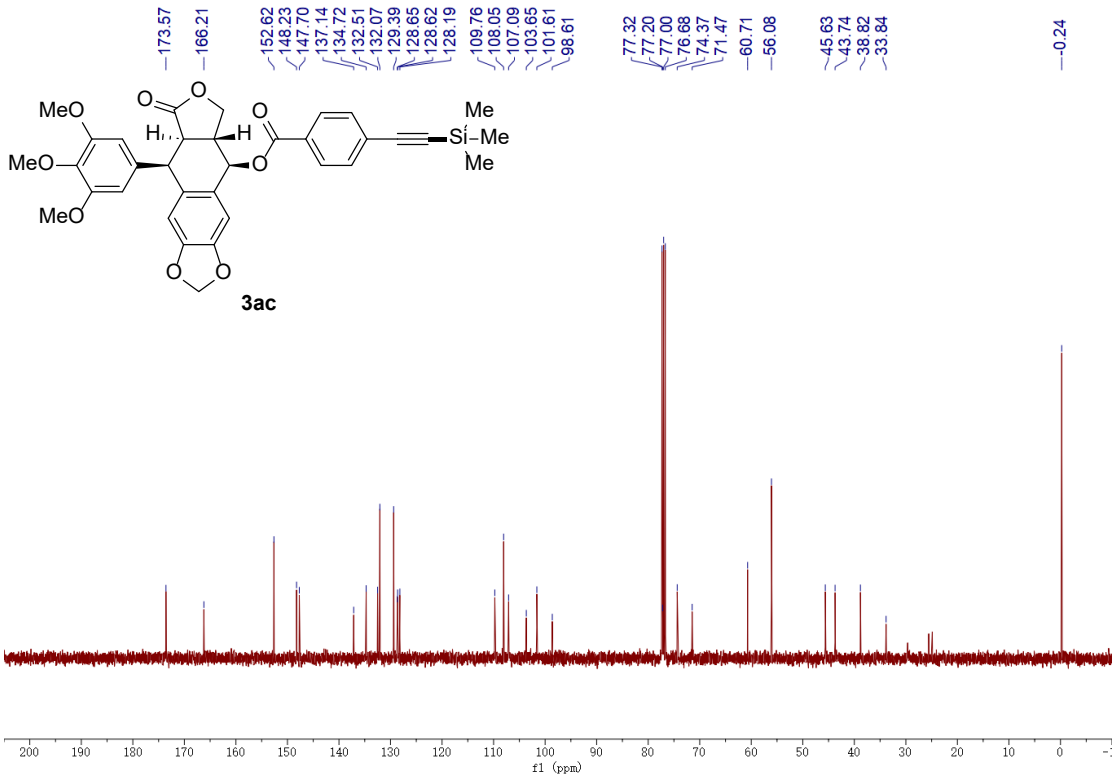

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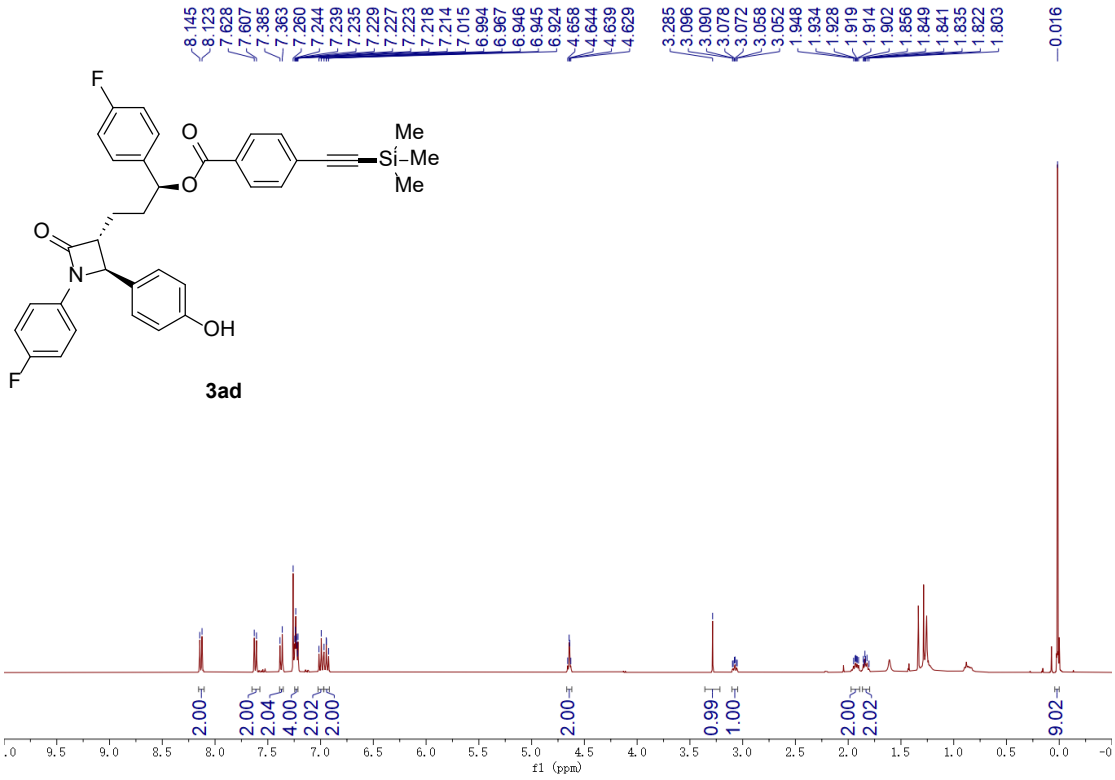

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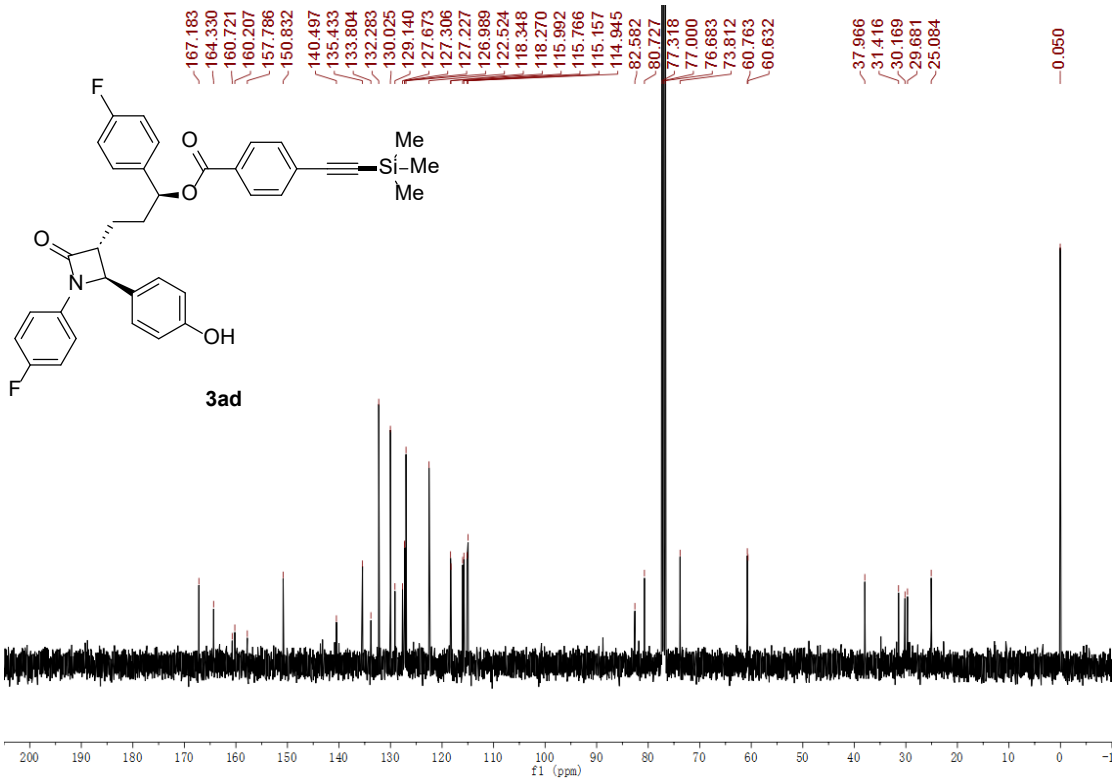

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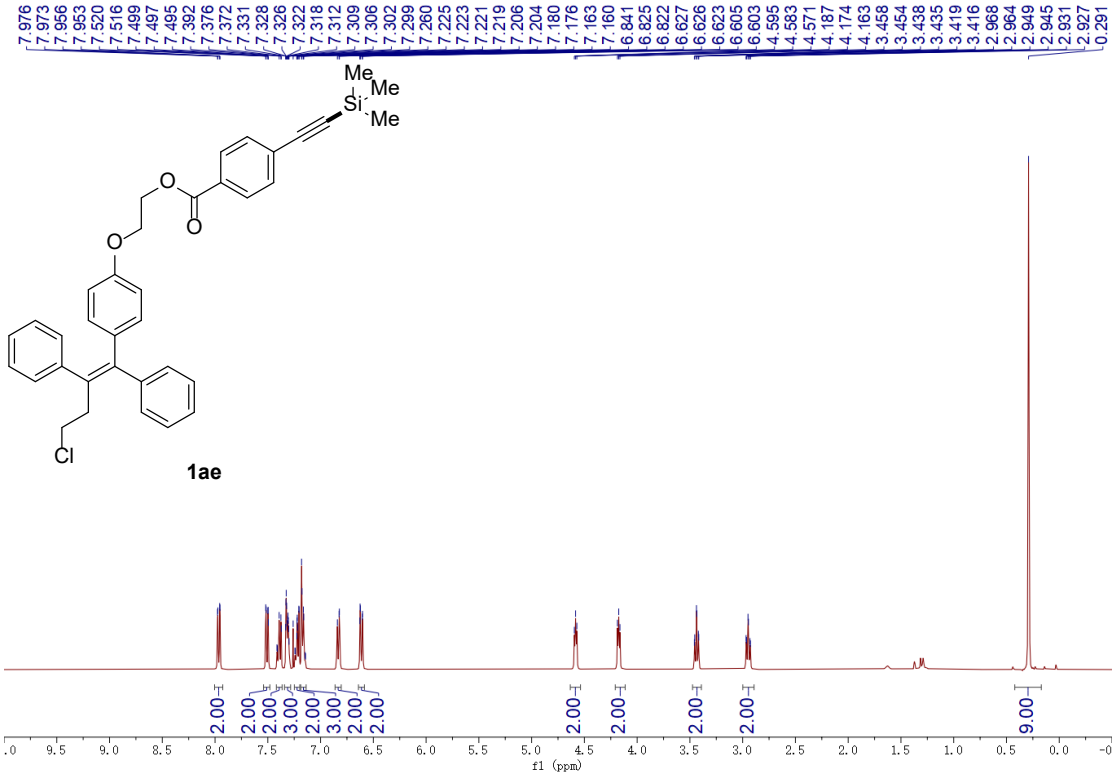

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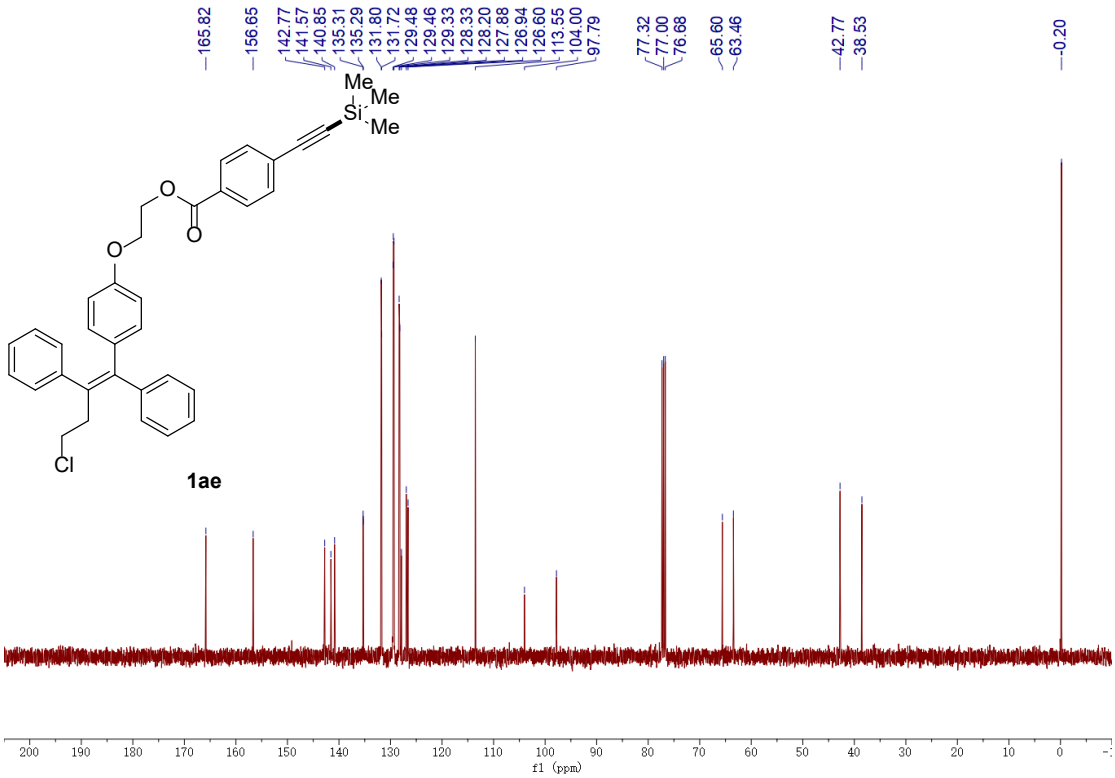

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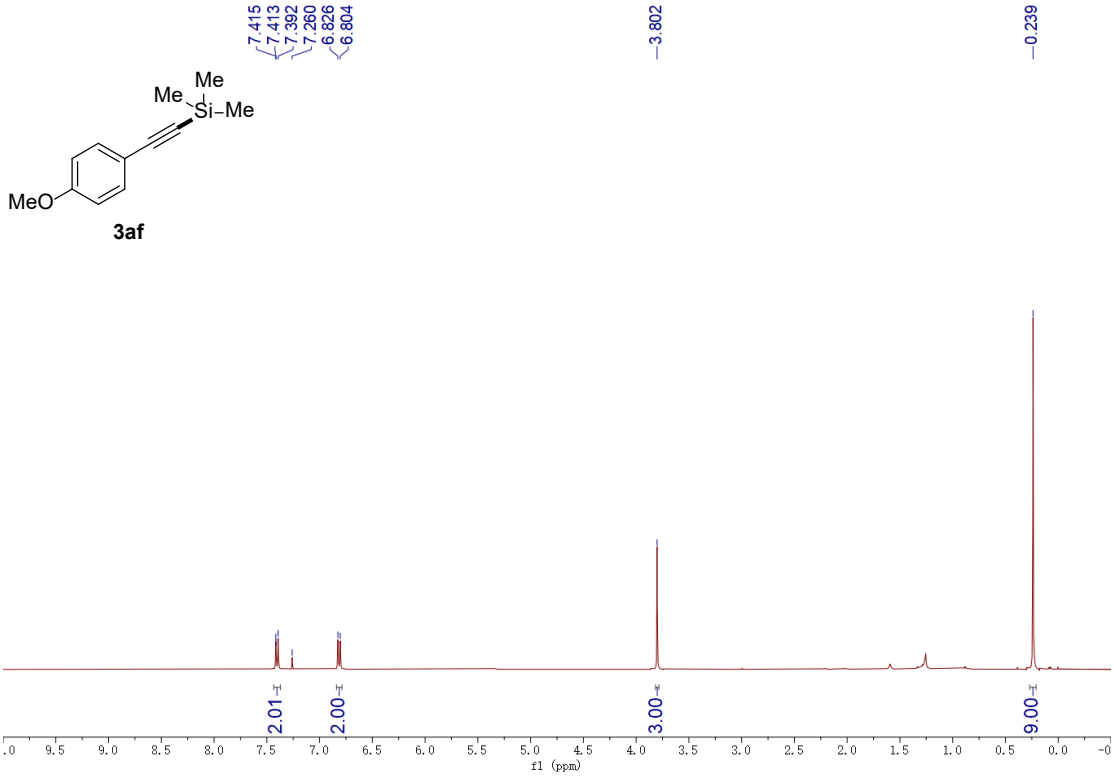

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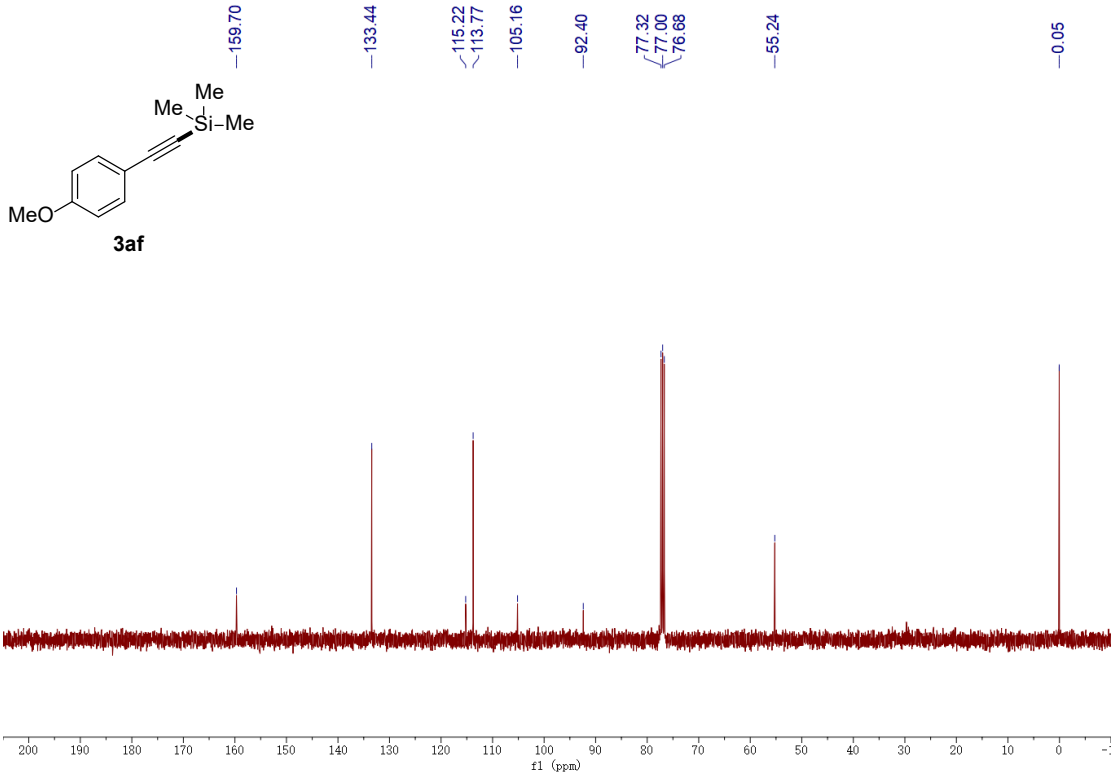

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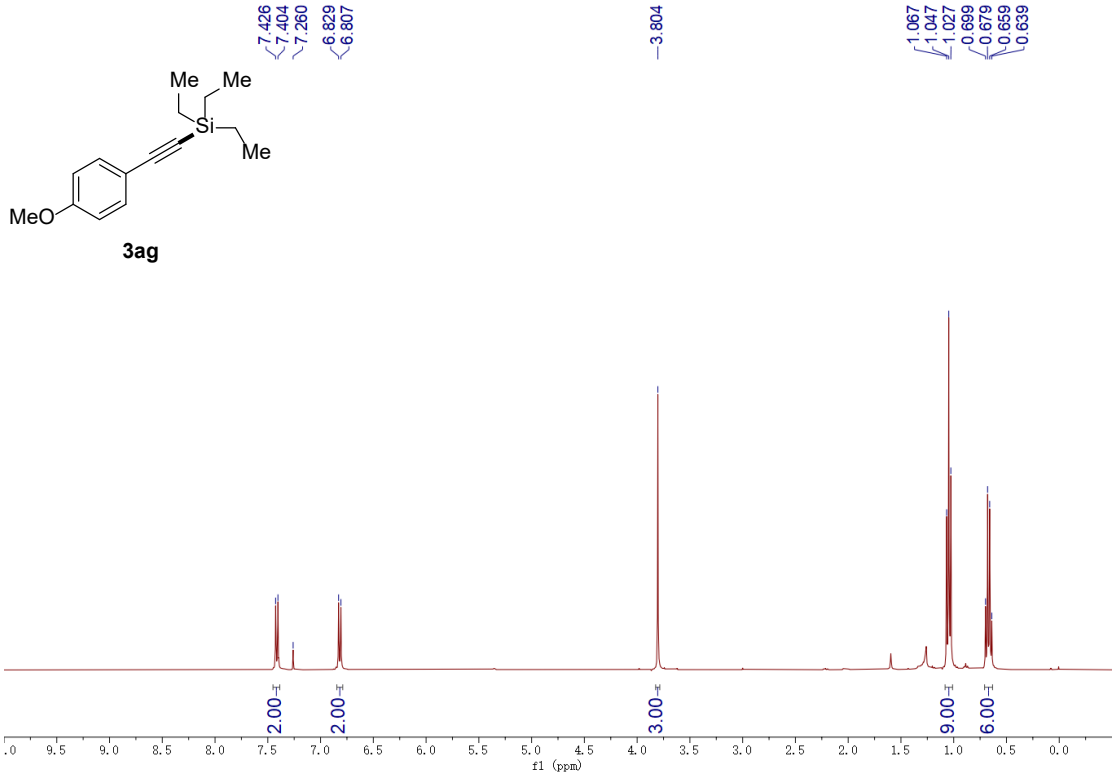

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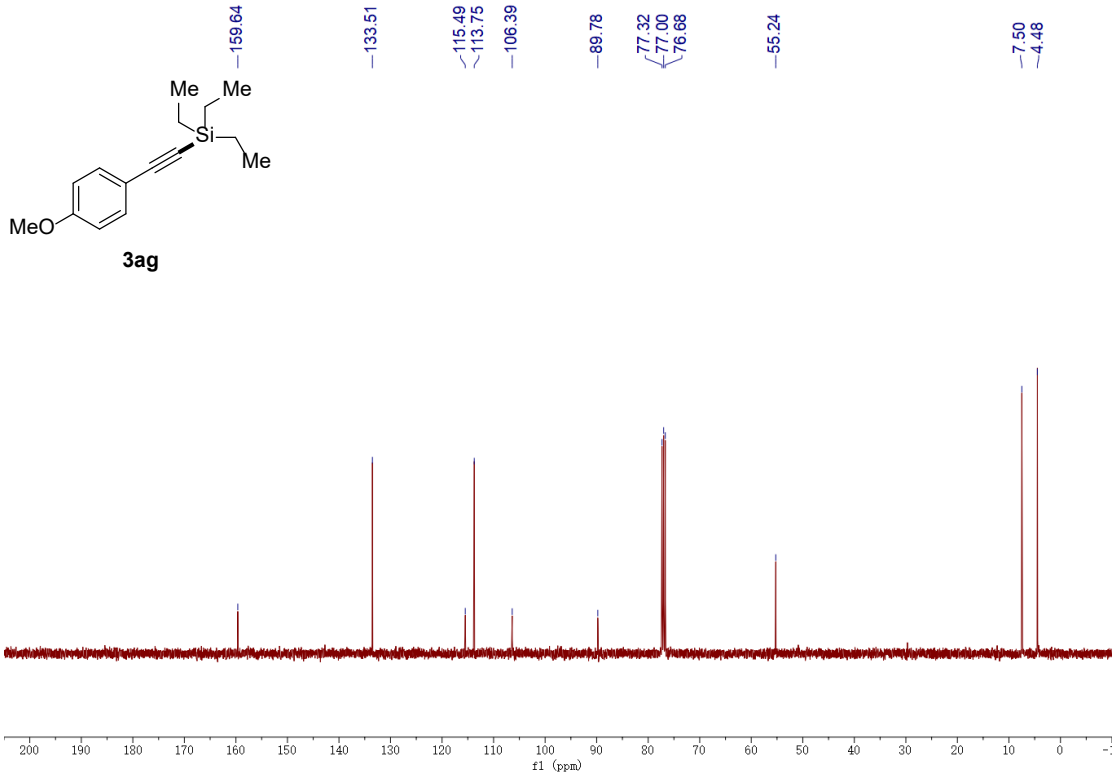

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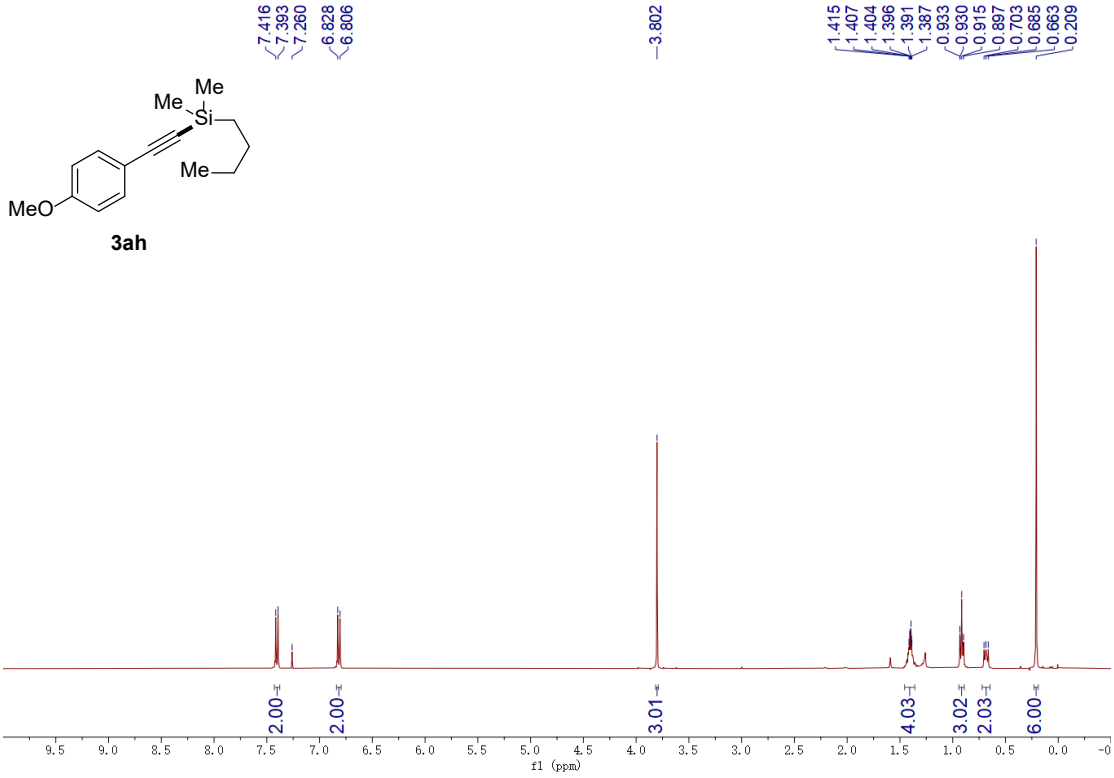

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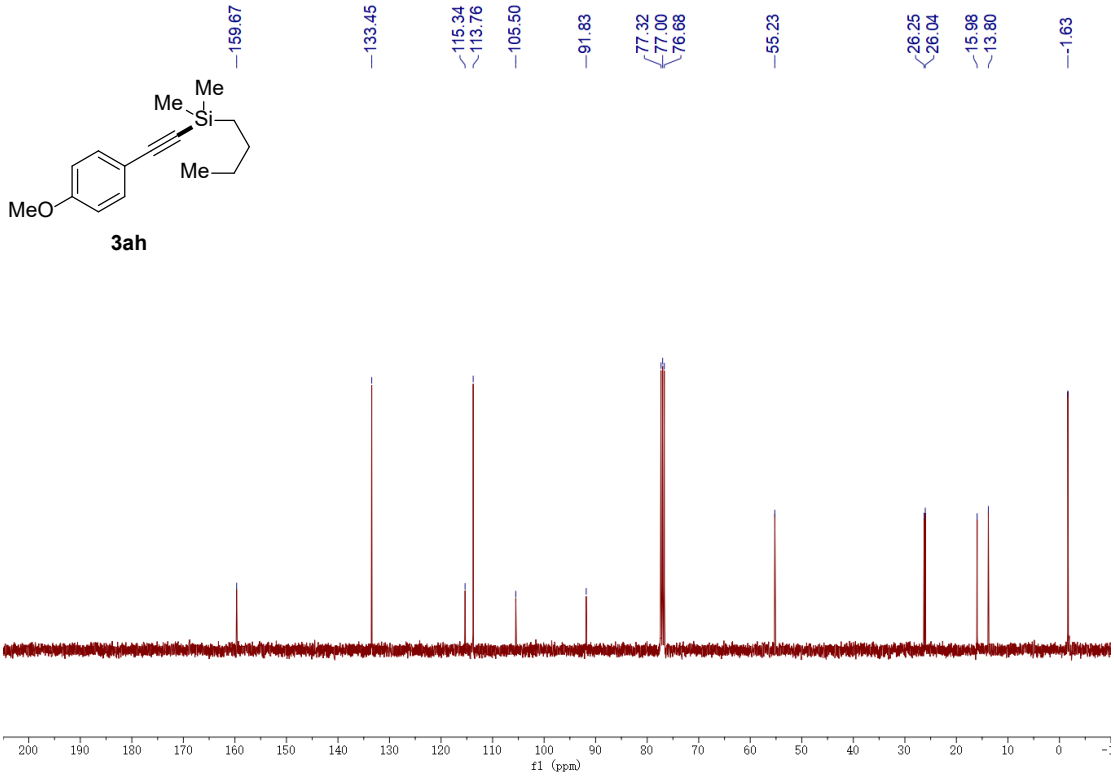

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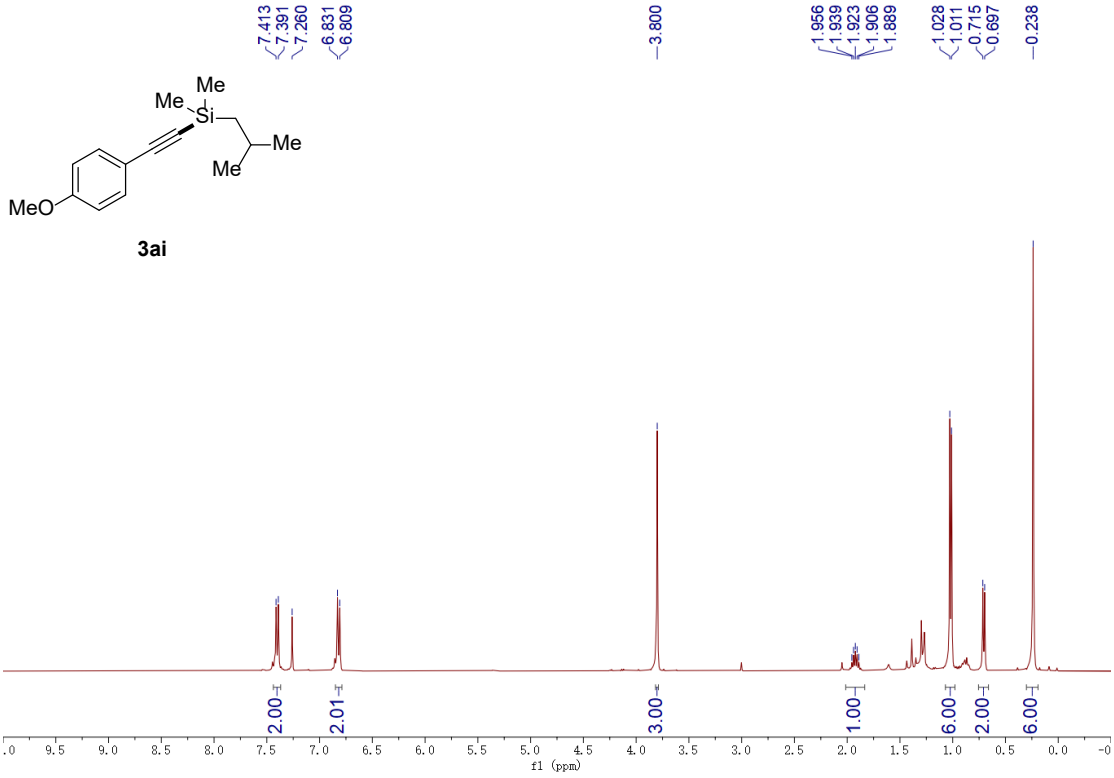

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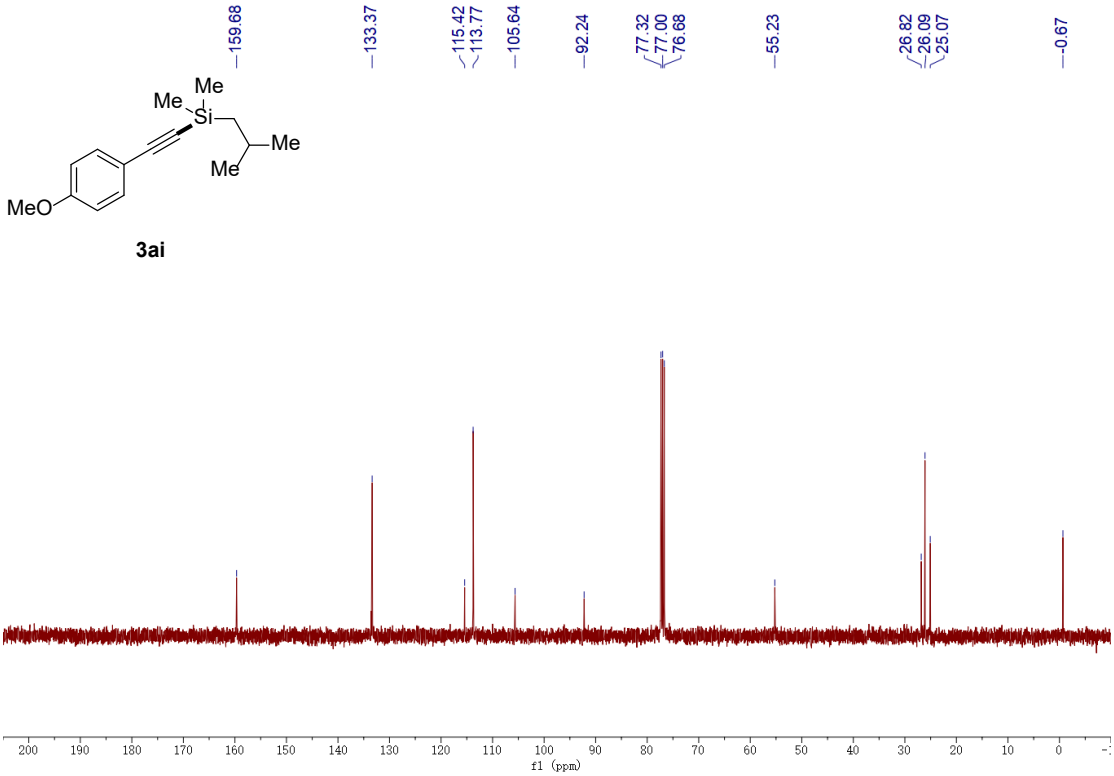

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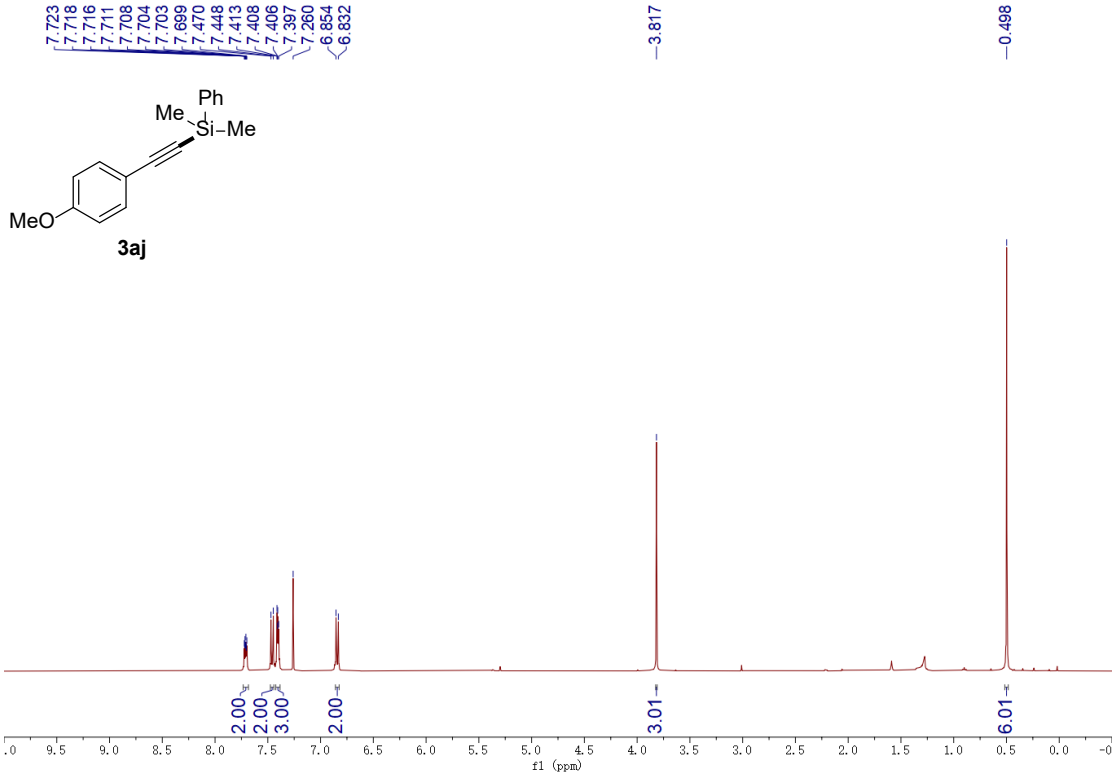

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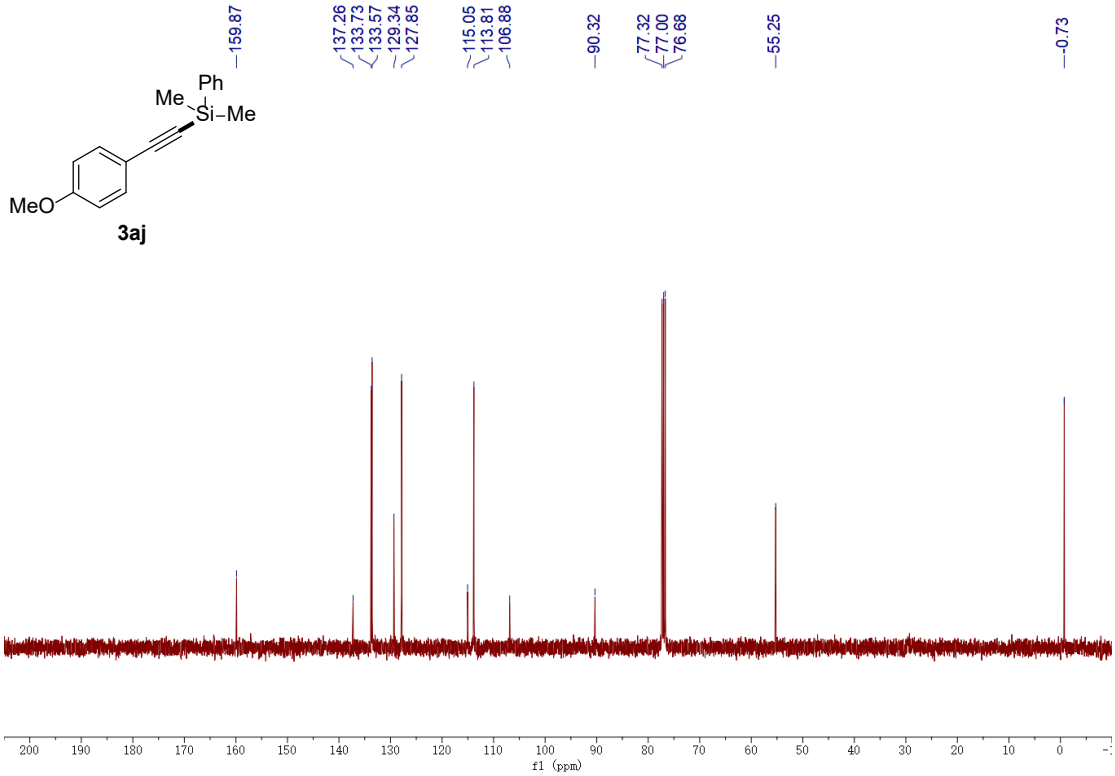

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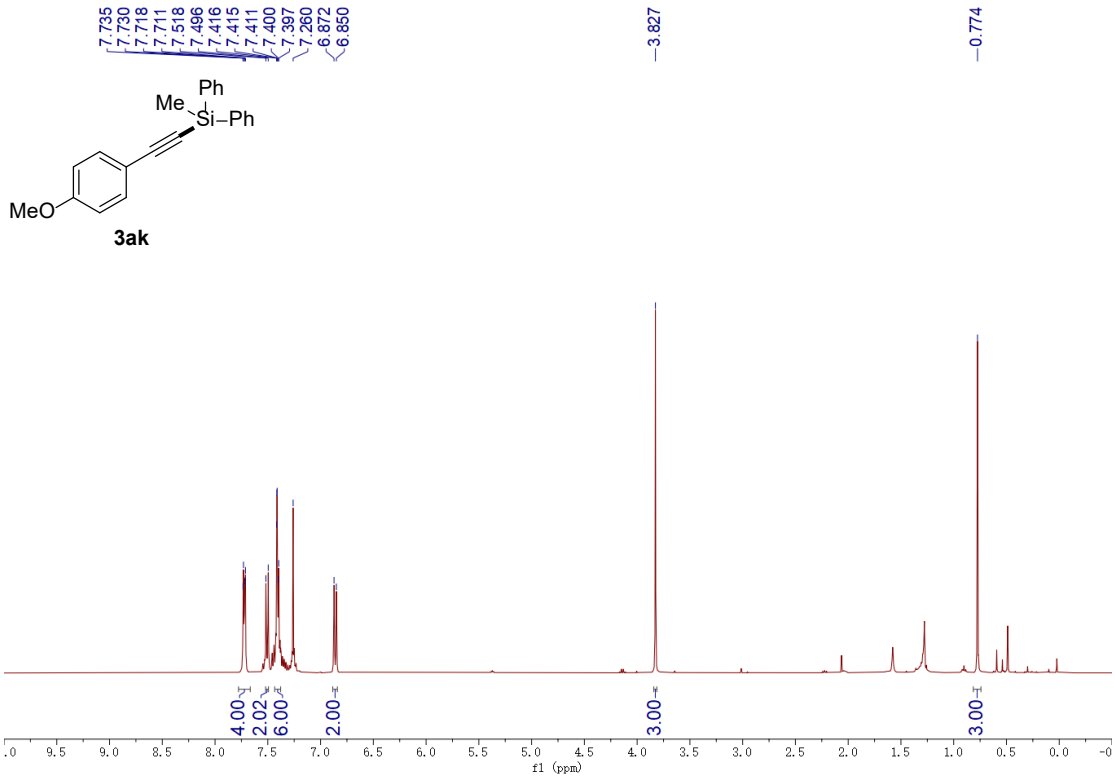

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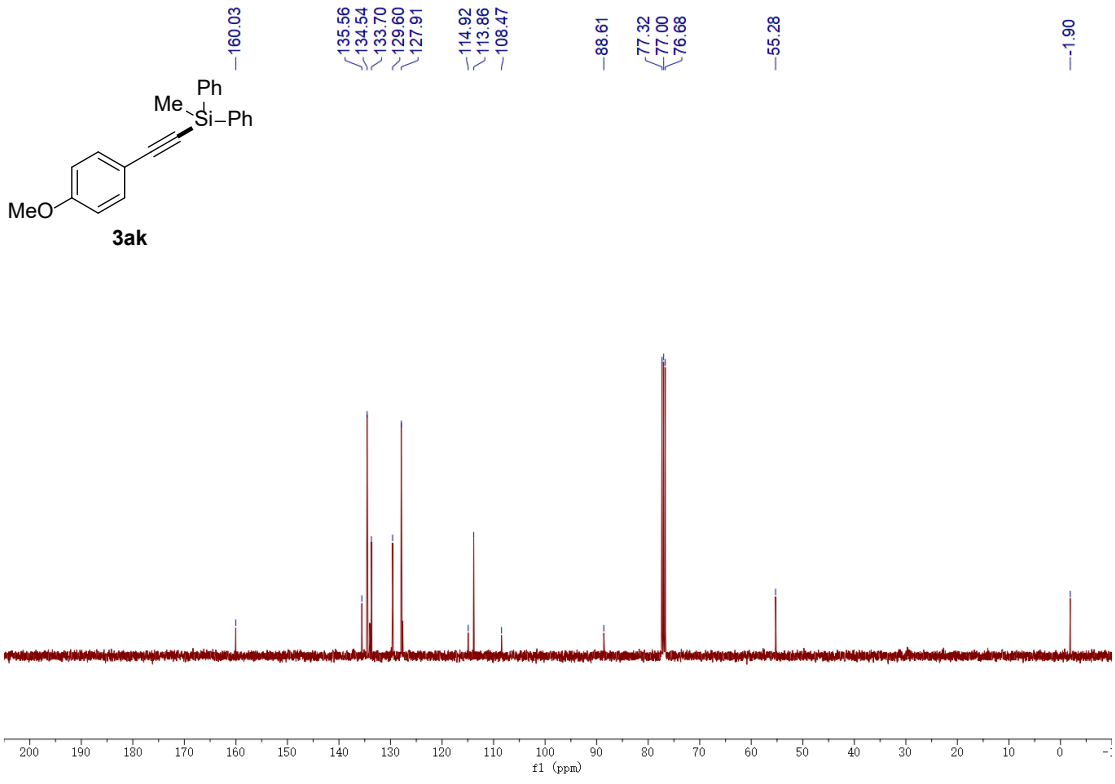

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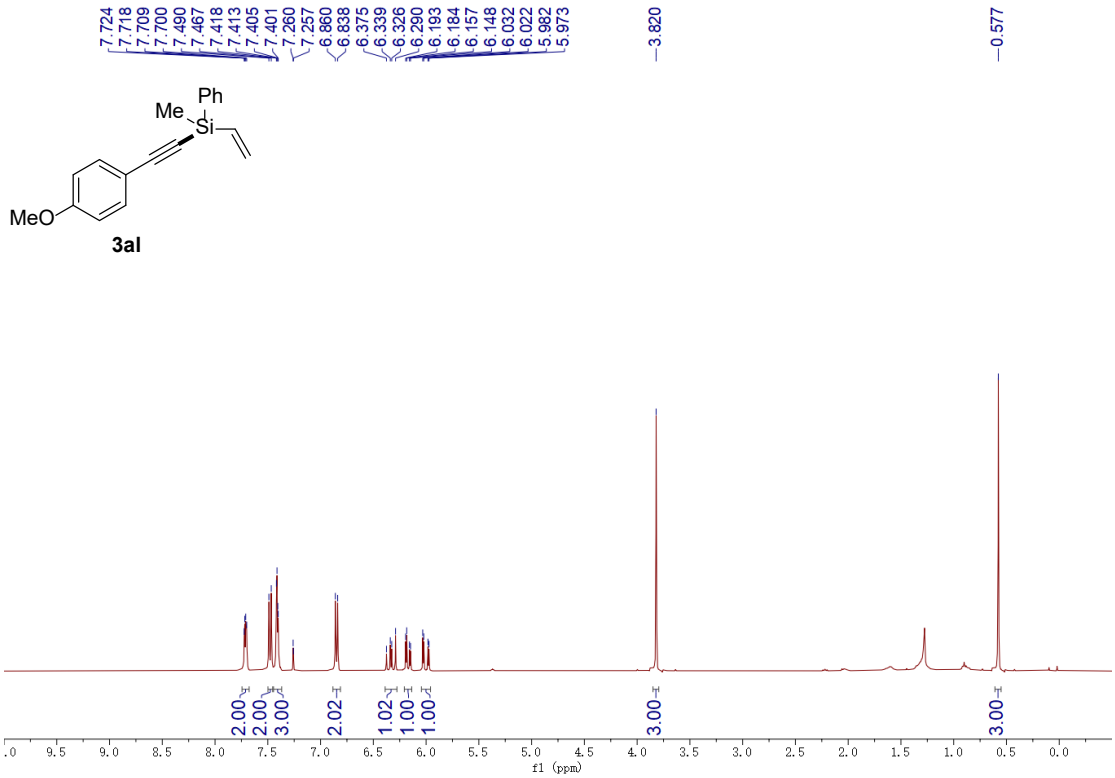

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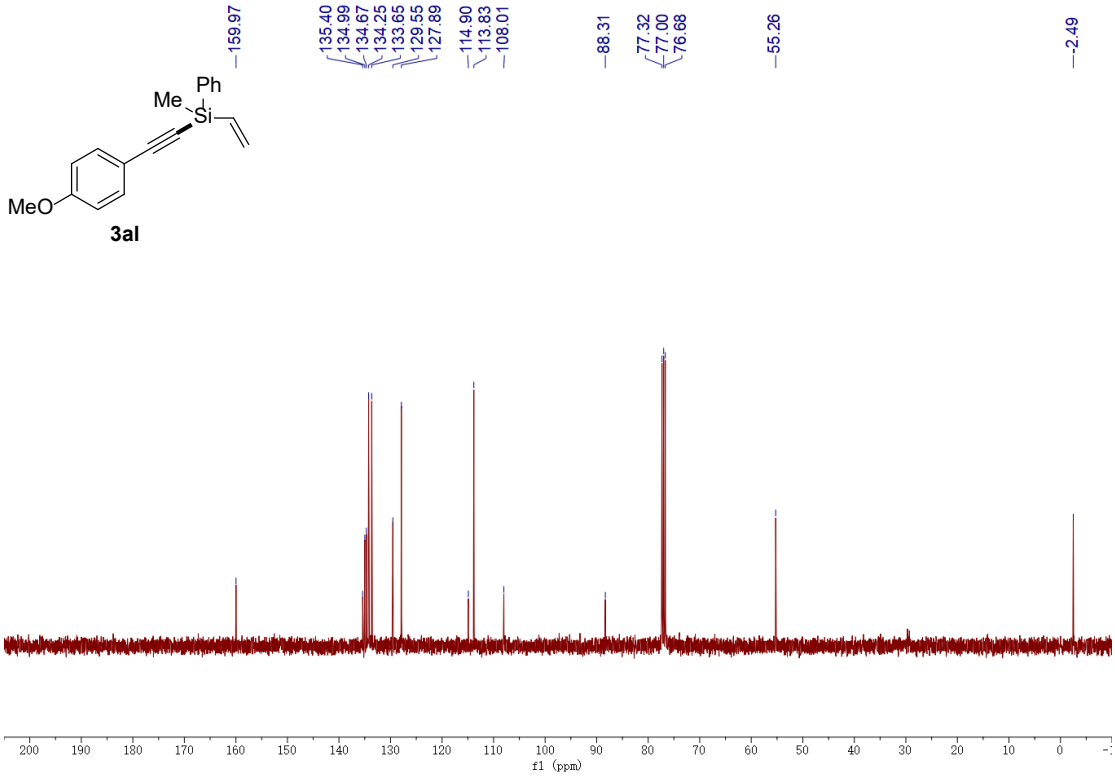

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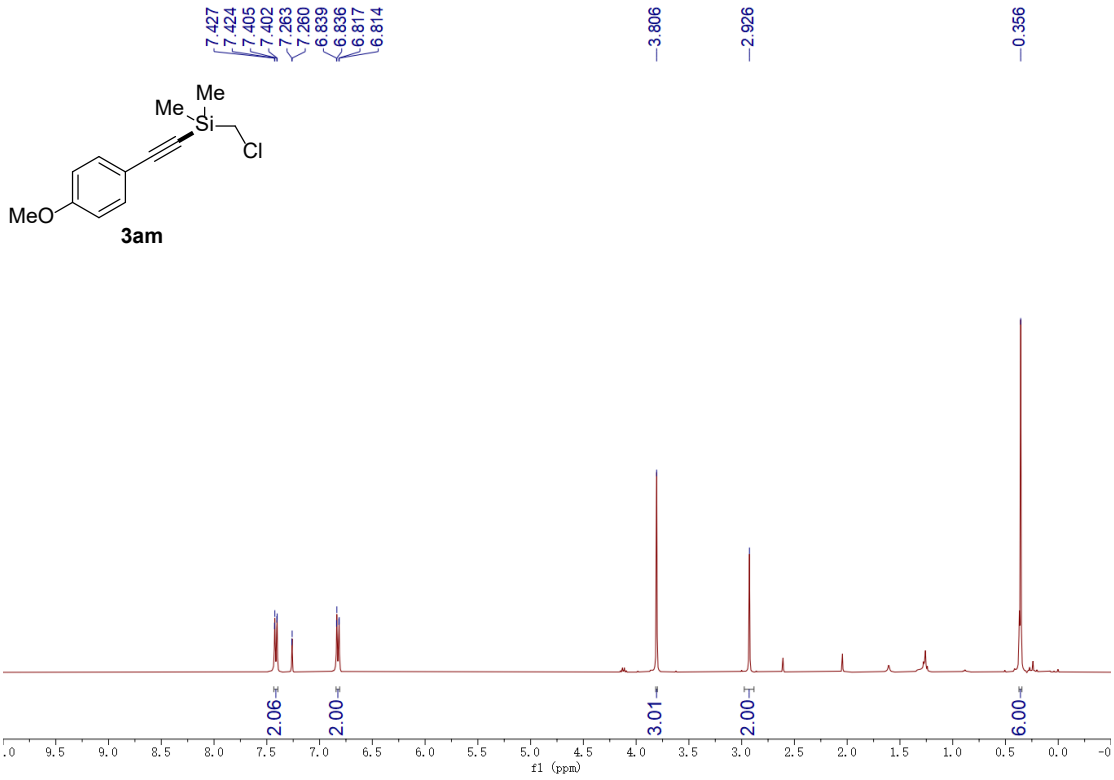

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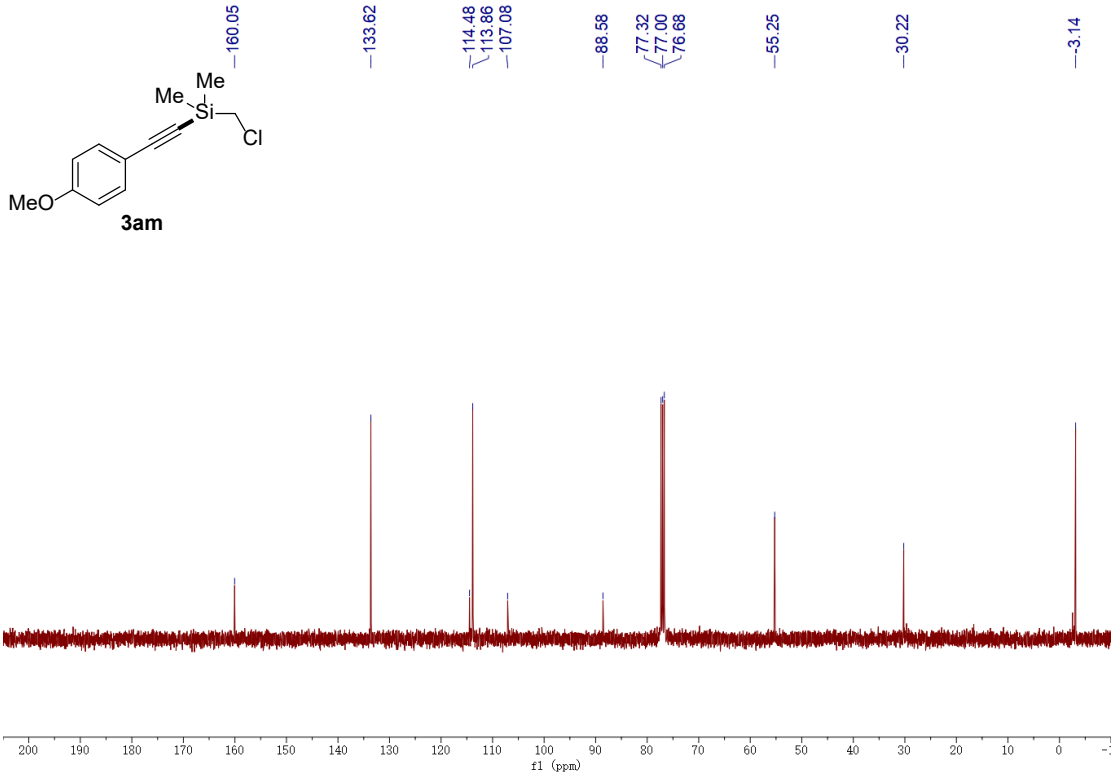

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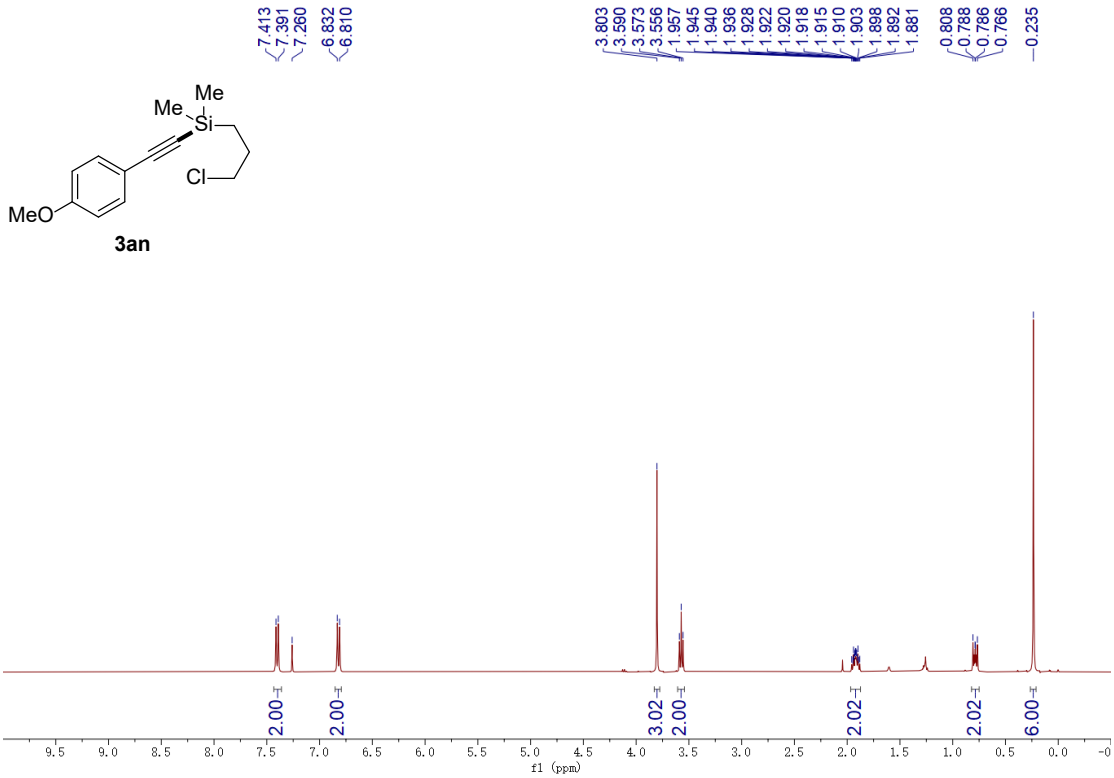
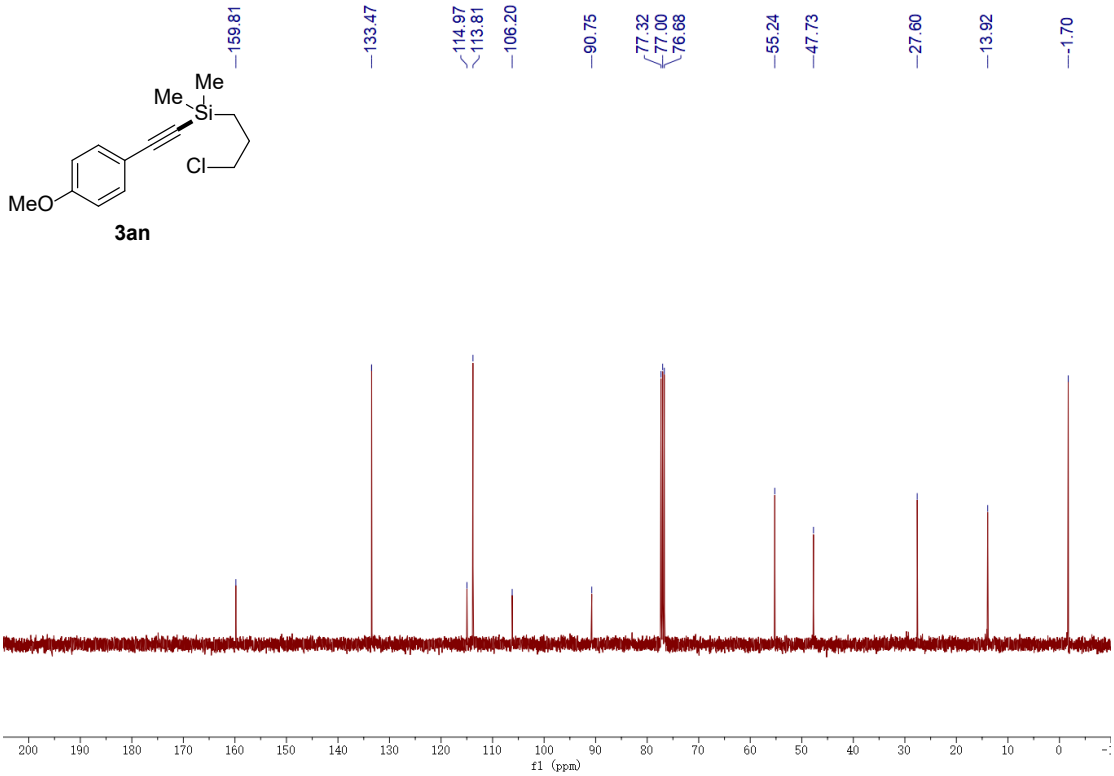
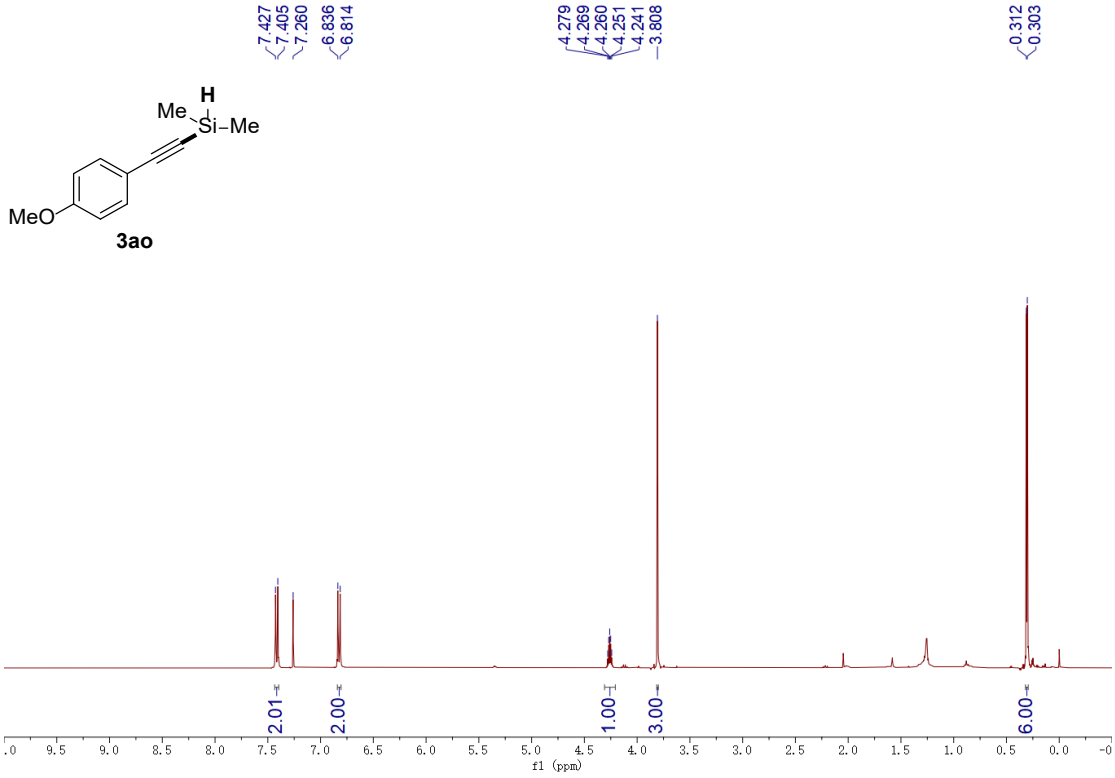


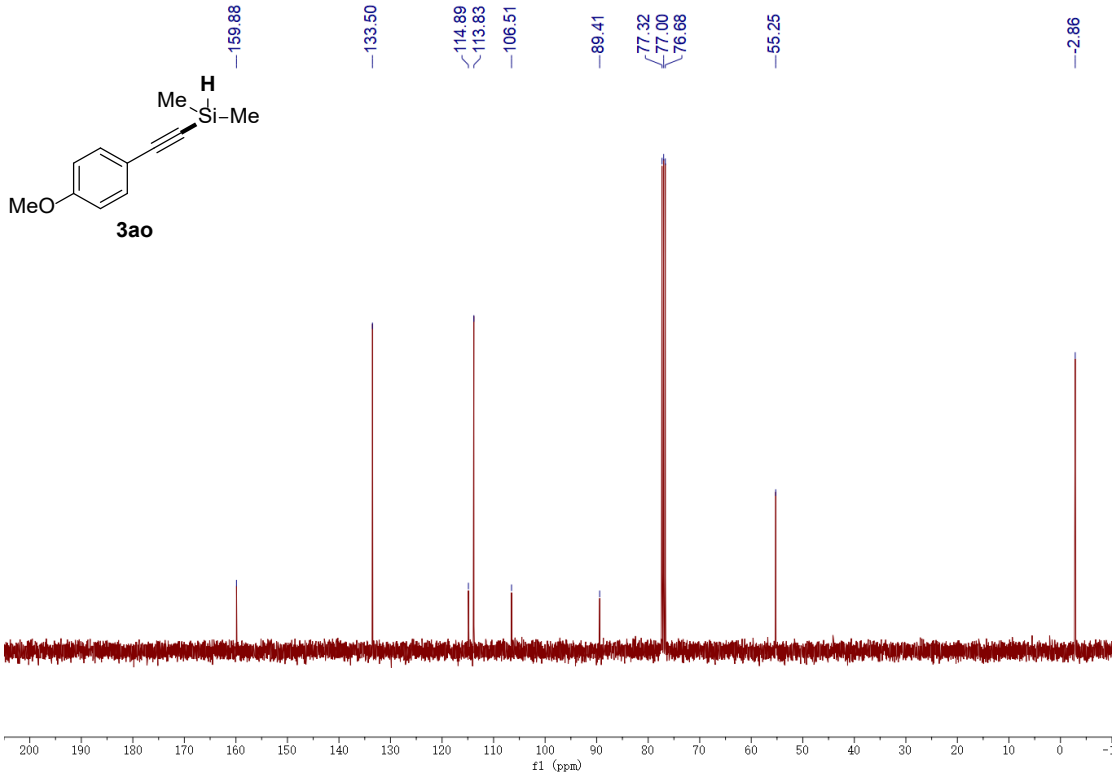
^{13}C NMR：101MHz, Choroform-*d*, peak of $CHCl_3$ in 77.0



^{1}H NMR：400MHz, Choroform-*d*, peak of $CHCl_3$ in 7.260



^{13}C NMR：101MHz, Choroform-*d*, peak of $CHCl_3$ in 77.0



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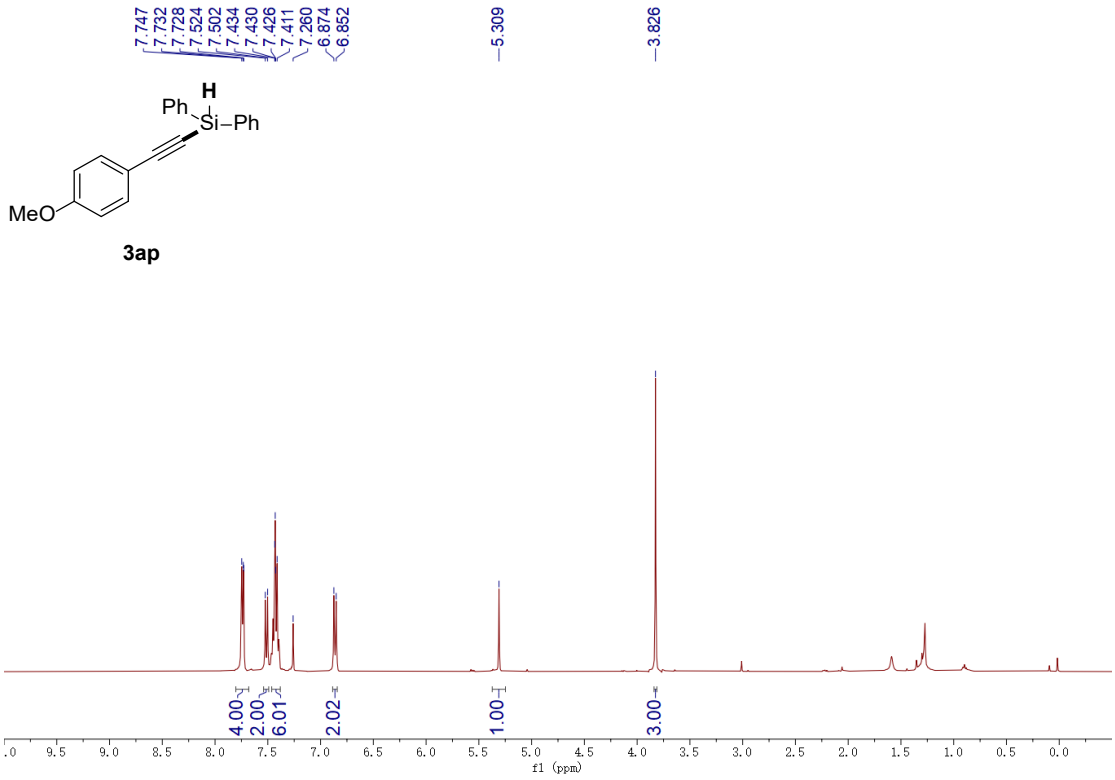

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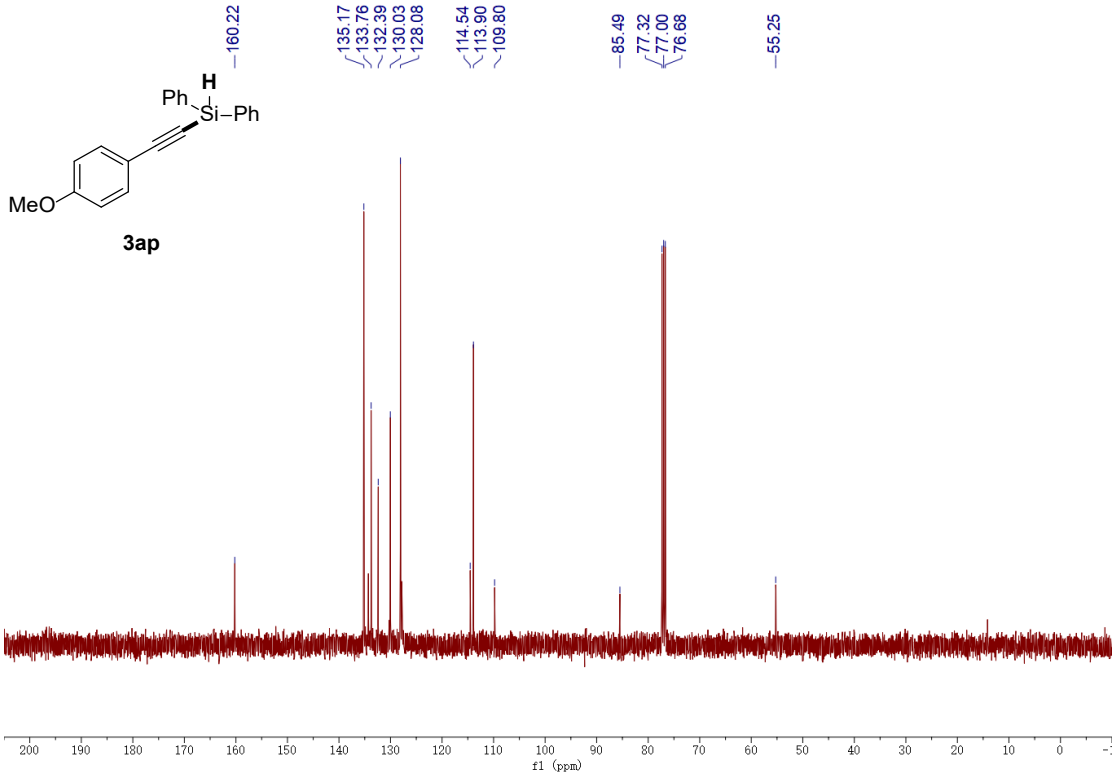

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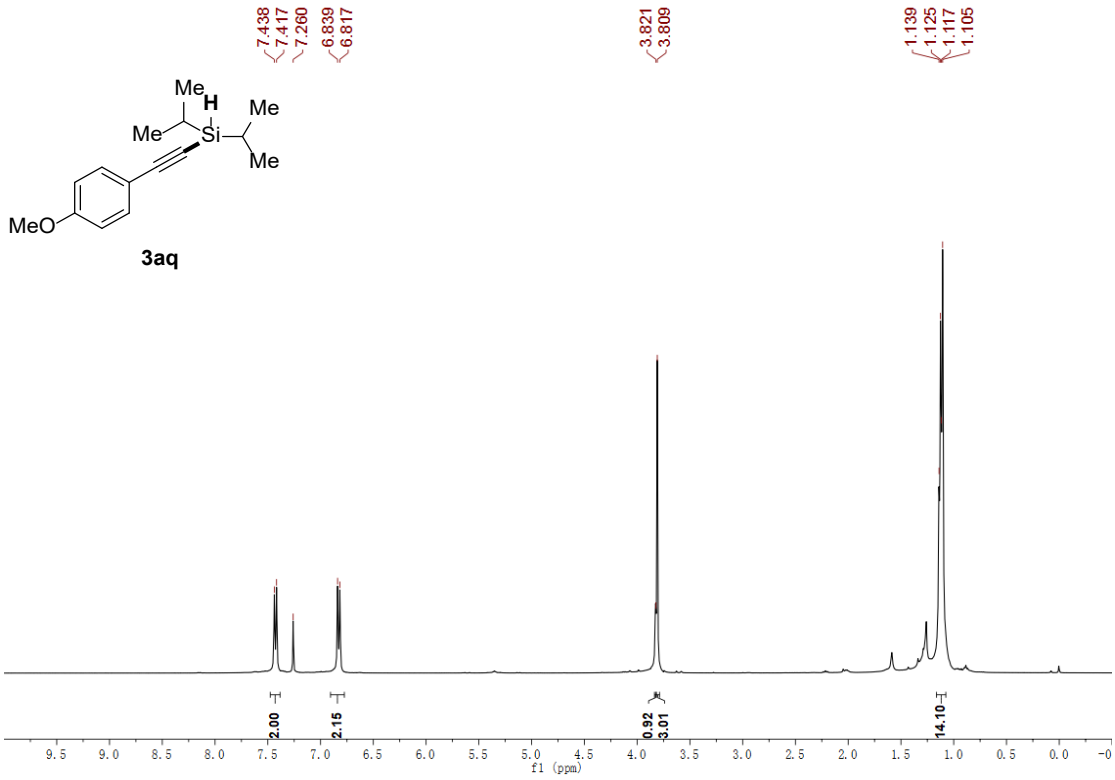

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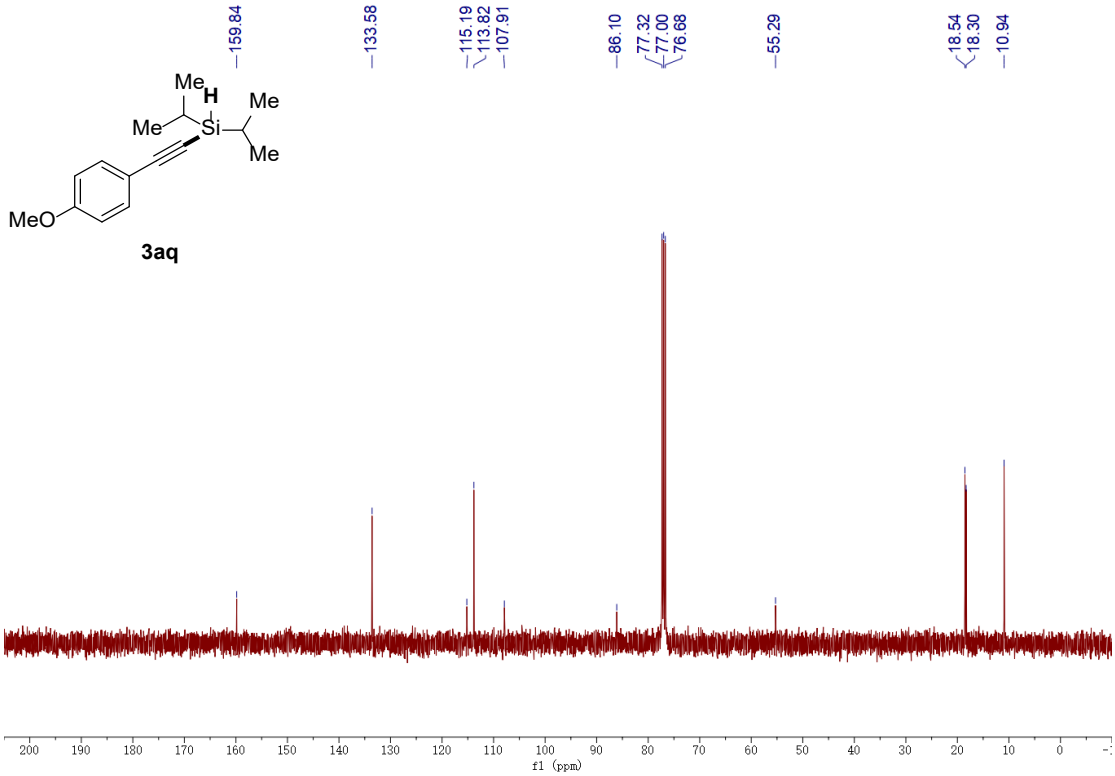

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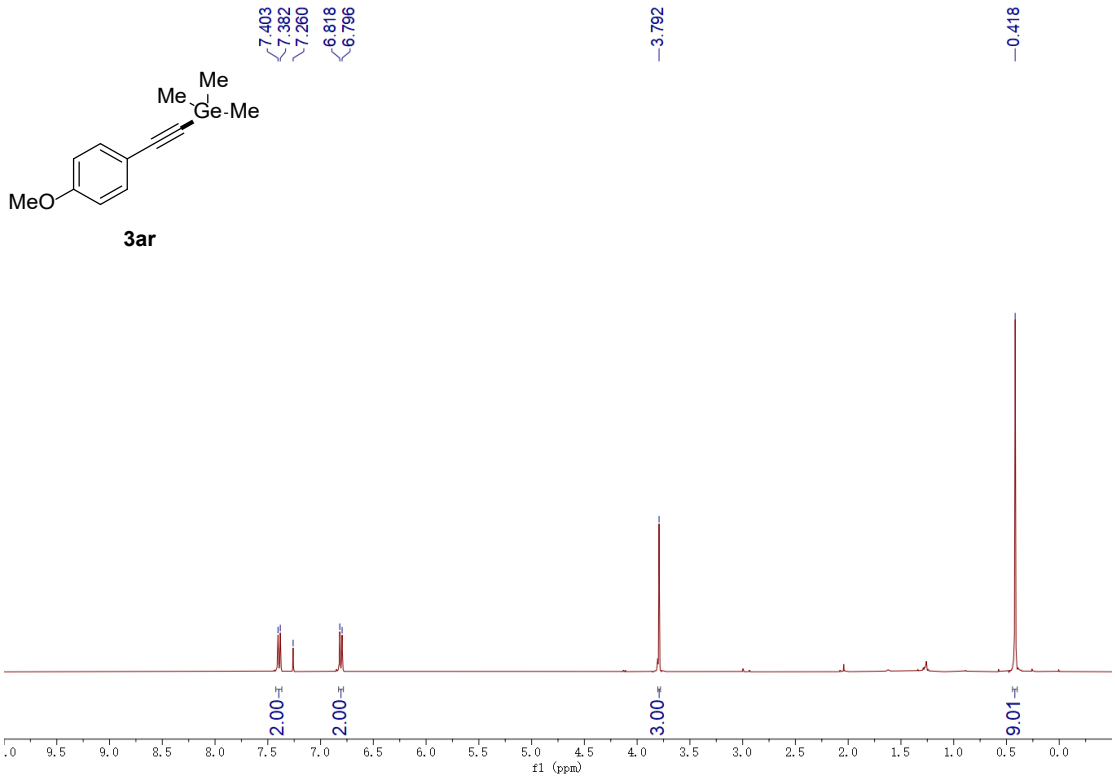

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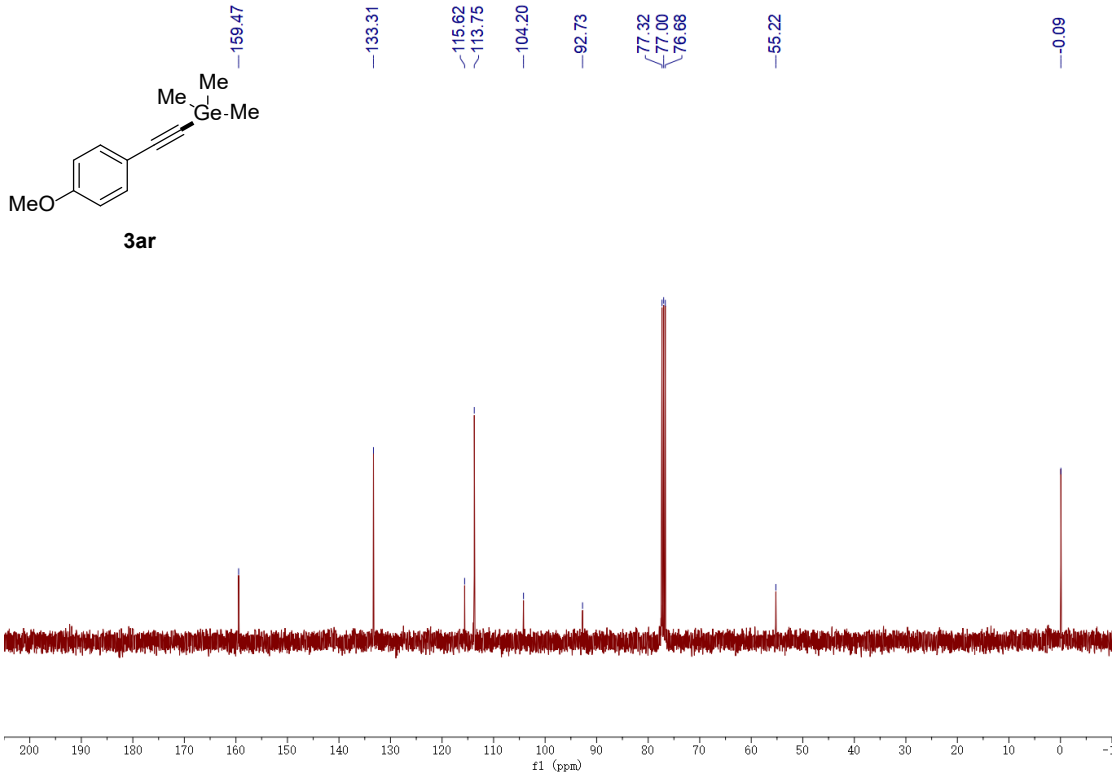

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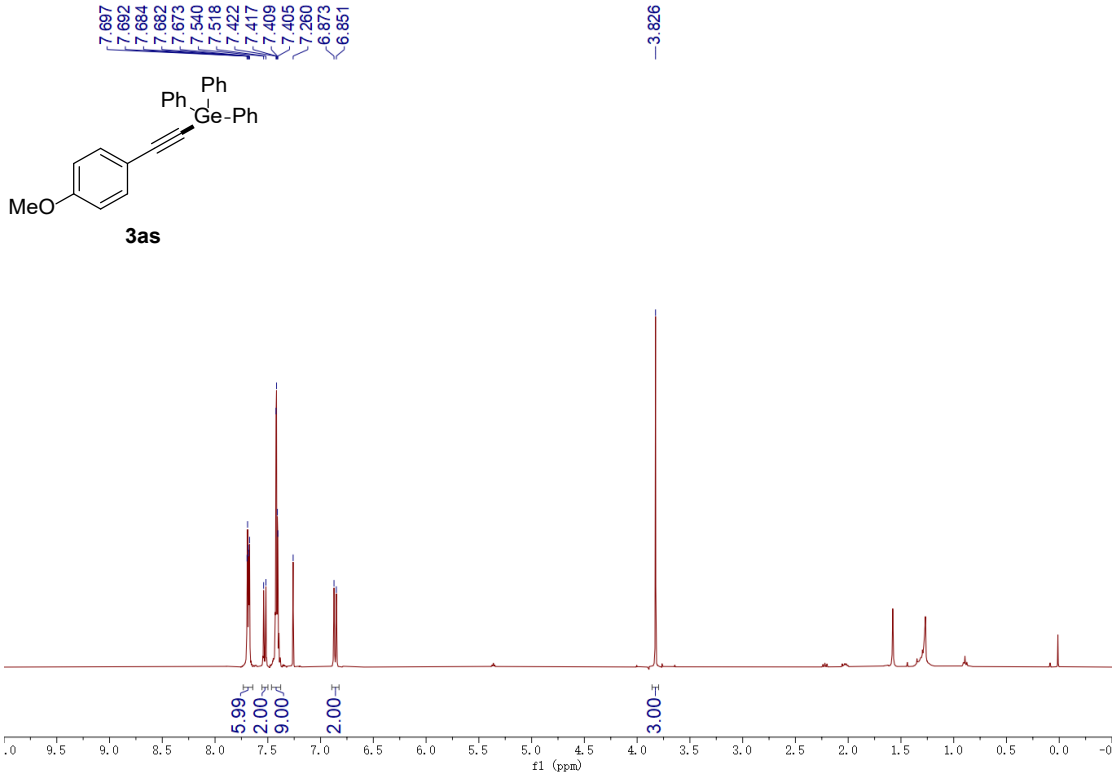

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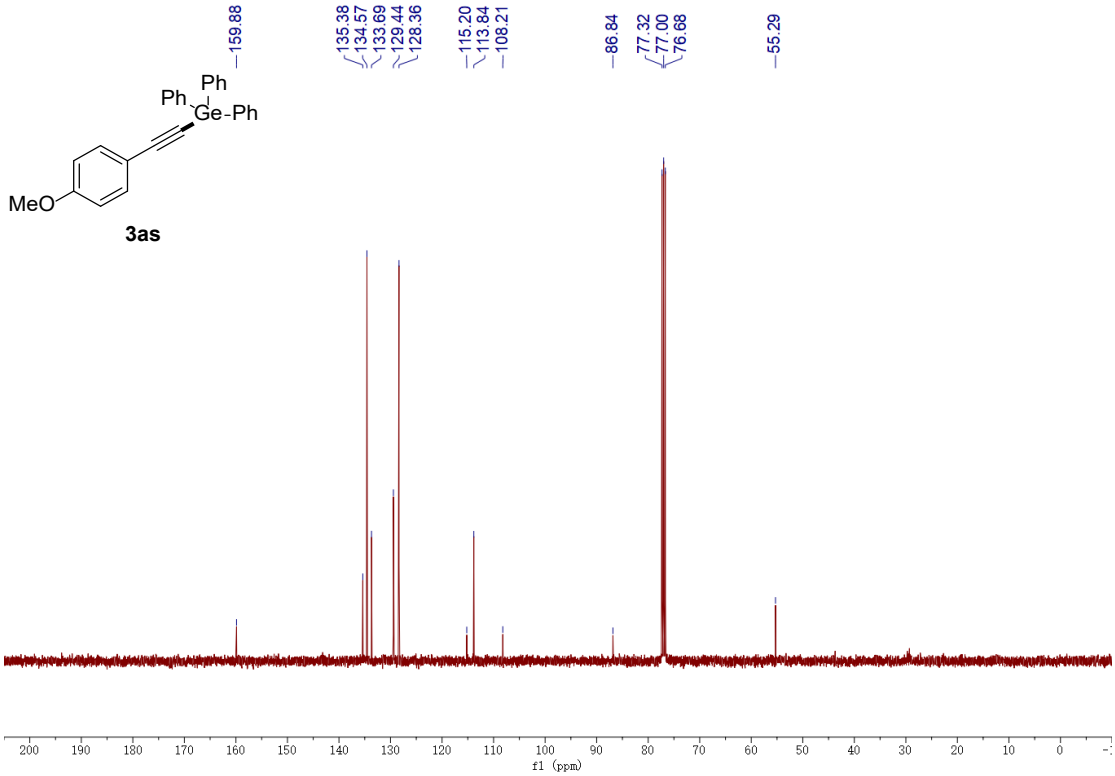

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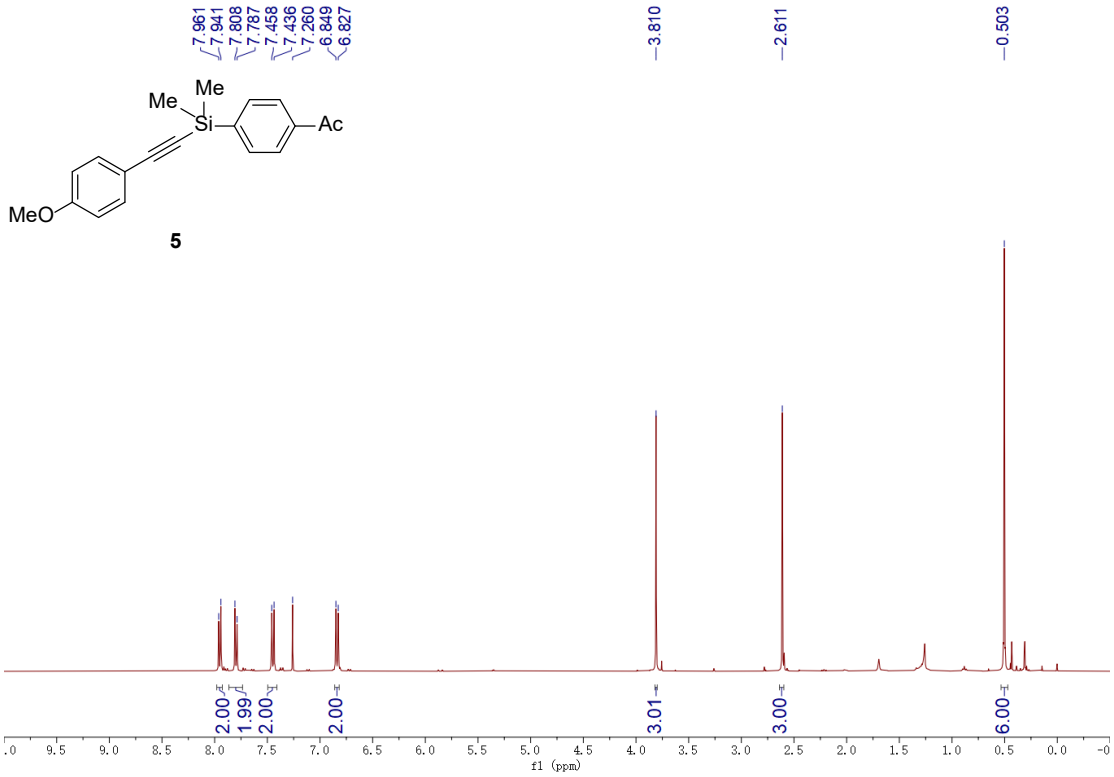

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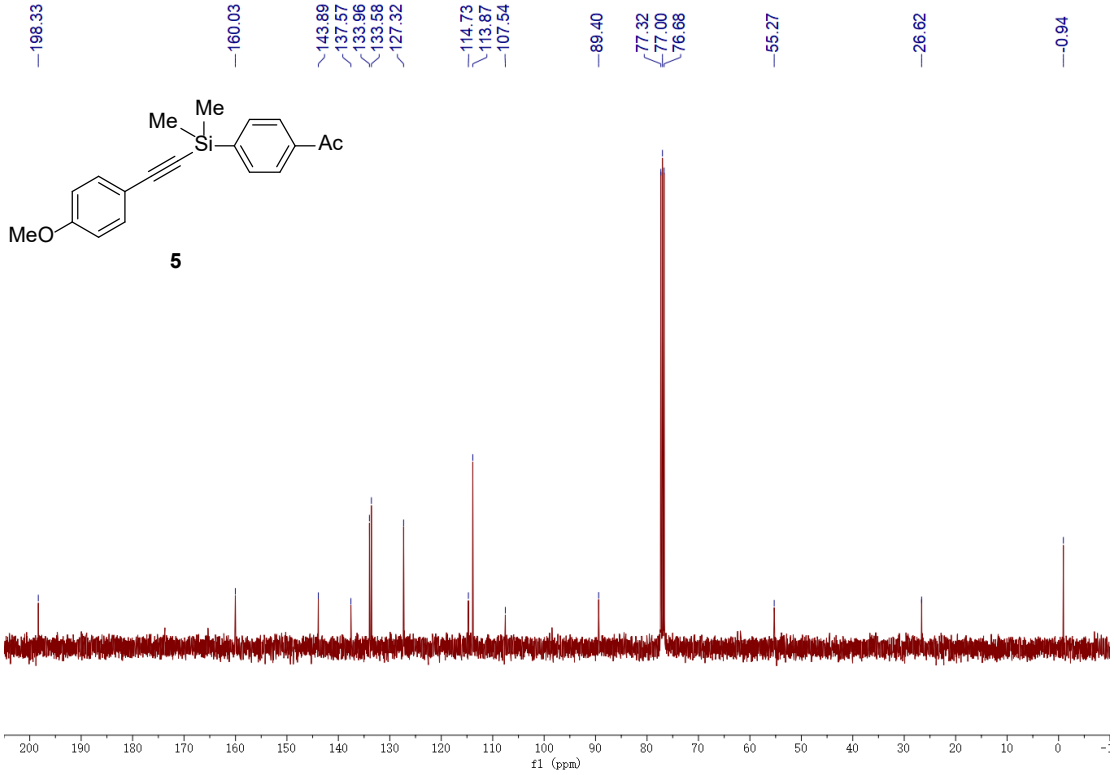

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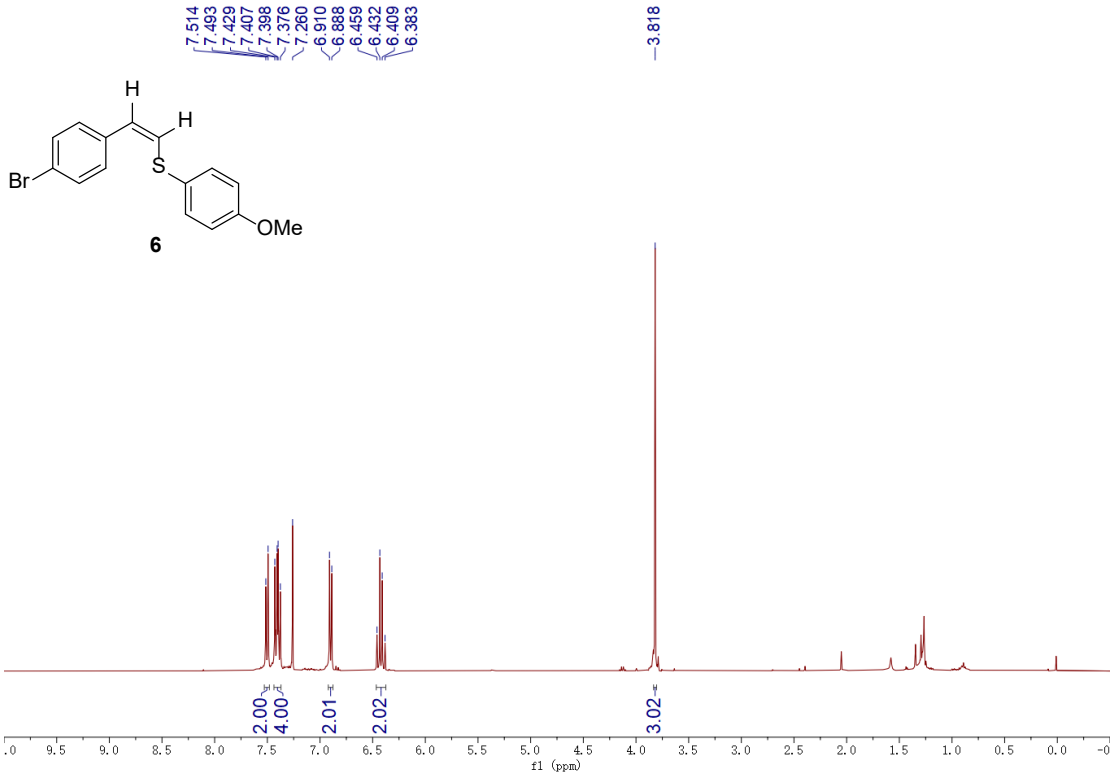

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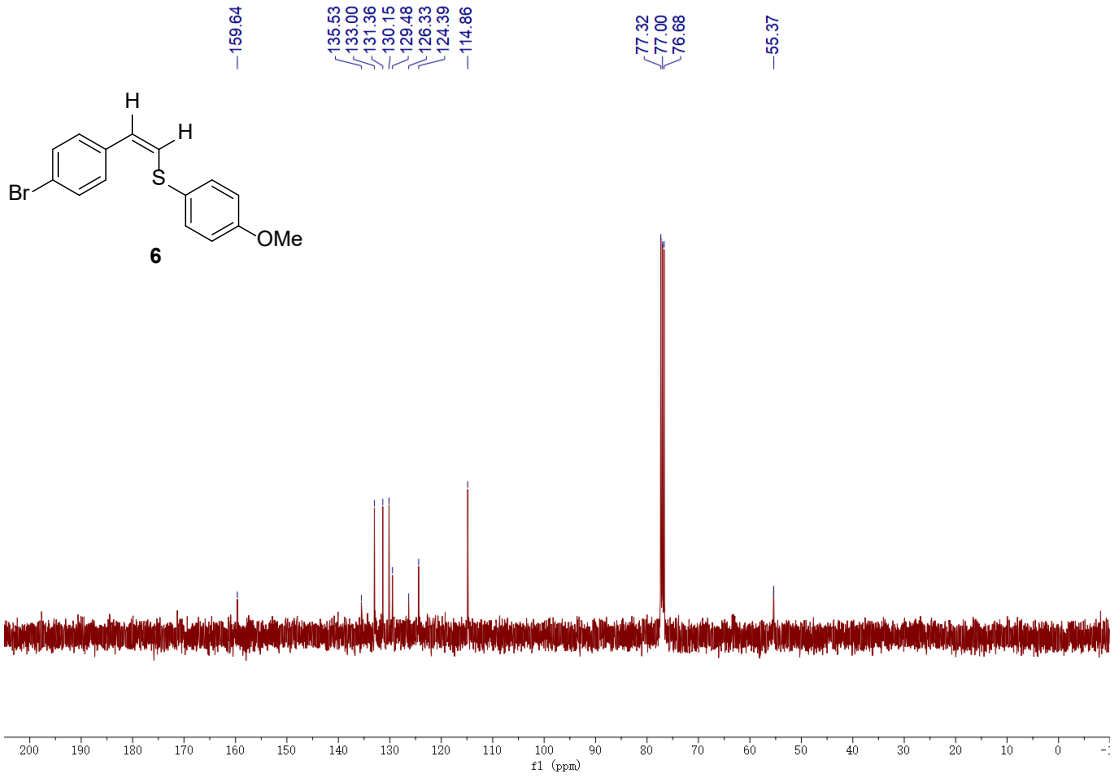

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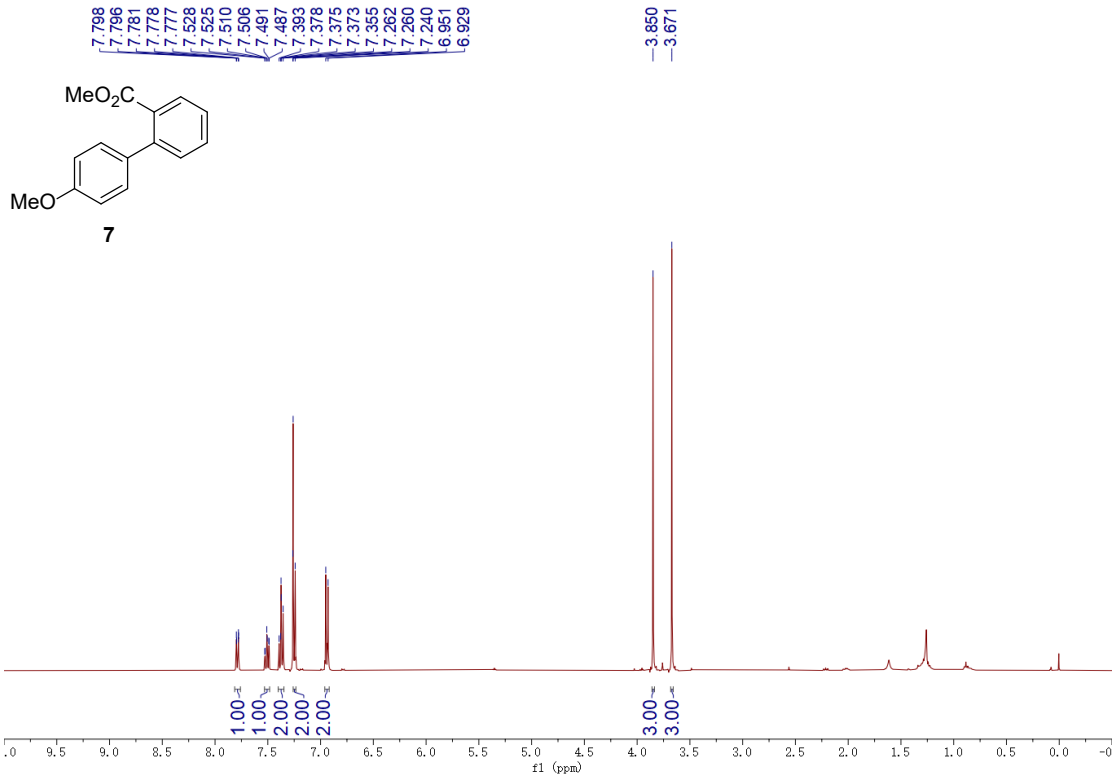

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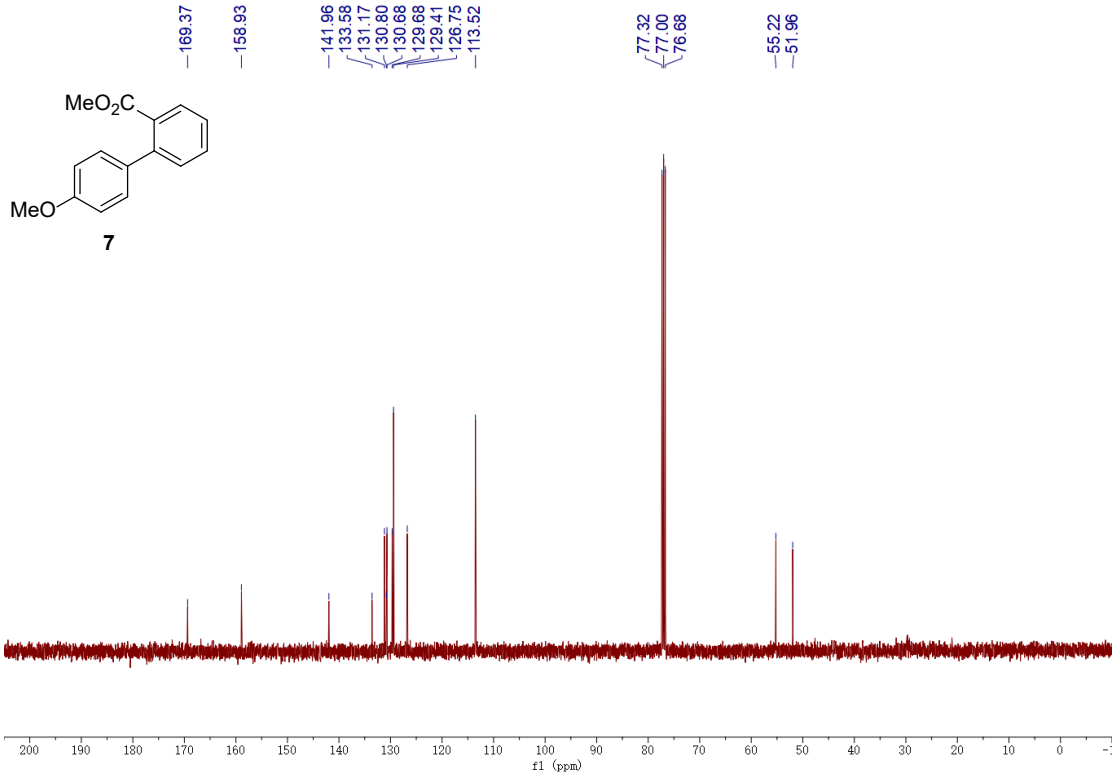

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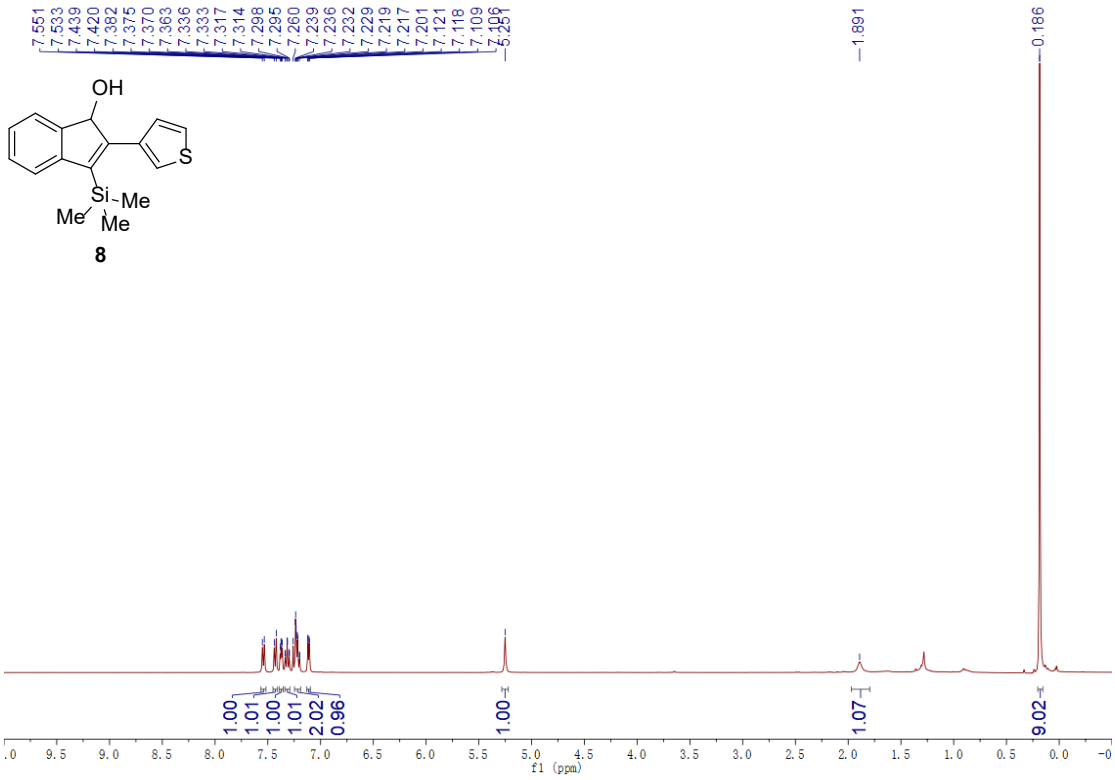

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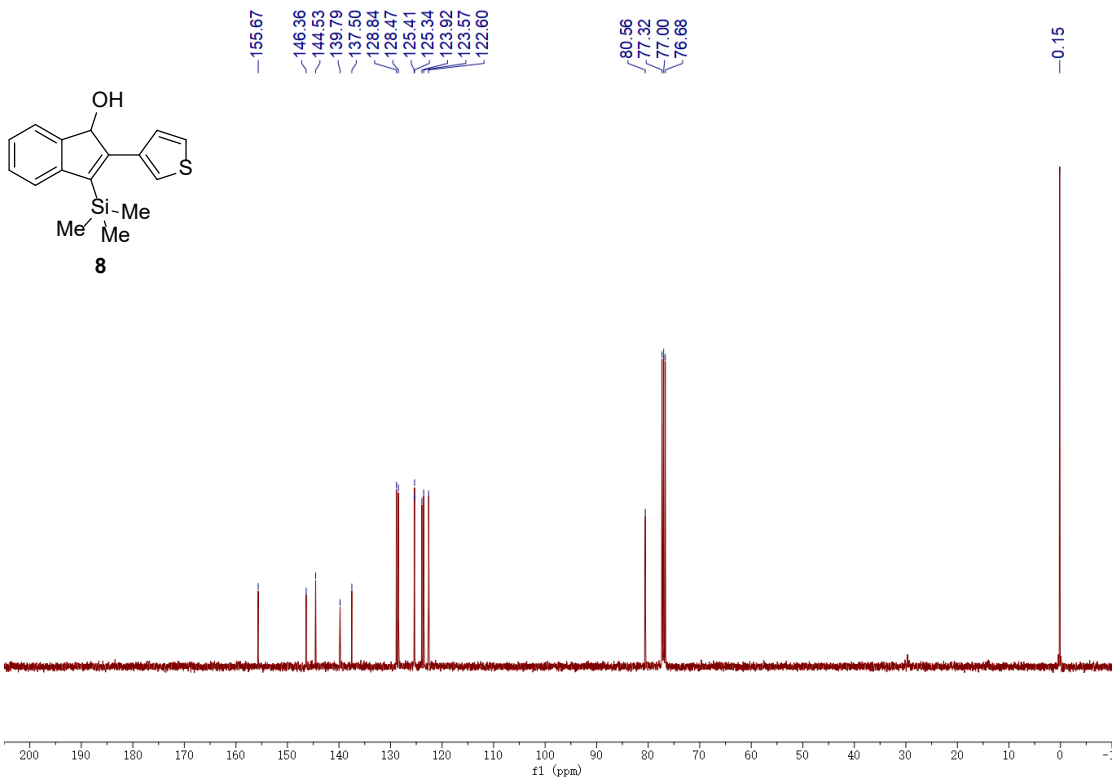

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