Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Copper-Catalyzed Desymmetric Silylative-Cyclization of 1,6-Diynes for Syntheis of Spirocyclic Compounds

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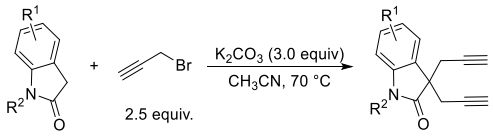
I. General Information

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification (such as Shanghai Titan Scientific Co., Ltd., Energy Chemical Corporation, J&K Scientific, Sinopharm Chemical Reagent Corporation etc.). ^{1}H NMR, ^{13}C NMR and ^{13}F NMR spectra were recorded at 25 °C on a Bruker Advance 400M NMR spectrometers ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.00) and relative to the signal of $SiMe_4$ (δ 0.00 singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets) *etc*. Coupling constants are reported as a *J* value in Hz. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.00) and relative to the signal of chloroform-*d* (δ 77.16 triplet). High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF using electrospray ionization (ESI) (Waters Corporation). Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system. Enantiomeric excesses of chiral compounds were determined by chiral high-performance liquid chromatography analyses which were performed on an Agilent 1260. Infinity equipped with a Daicel Chiralpak IB, IC-3 or Chiralcel OJ-3 column. Optical rotations were recorded on an Anton Paar MCP 200 polarimeter at 589 nm in chloroform. Single crystal X-ray diffraction data was collected on the Rigaku Oxford Diffraction (ROD) SuperNova Diffraction System.

II. Experimental Procedures

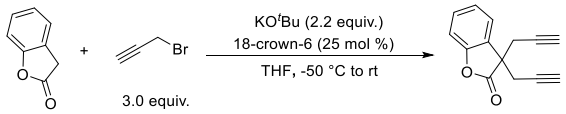
Method A: Synthesis of oxindole-derivated 1,6-diynes



The 1,6-diynes were prepared according to the reported literature.[1]

3-Bromoprop-1-yne (5.0 mmol) was added dropwise to a mixture of *N*-protected 2-oxindole (2.0 mmol), potassium carbonate (6.0 mmol) in anhydrous acetonitrile (6.0 mL). Then, the mixture was stirred at 70 °C for 6 h. After completion, the reaction mixture was cooled to room temperature and ethyl acetate was added, then the precipitate was removed by filtration. The resultant solution was concentrated, and the crude products were purified by column chromatography to give the desired products.

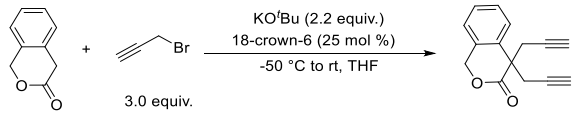
Method B: Synthesis of 3,3-di(prop-2-yn-1-yl)benzofuran-2(3*H*)-one (**1ak**)



The 1,6-diyne **1ak** were prepared according to the reported literature.[2]

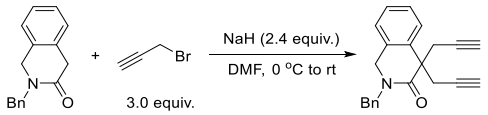
The mixture of benzofuran-2(3*H*)-one (5.0 mmol, 670.7 mg), 3-bromoprop-1-yne (15 mmol, 1.784 g) and 18-crown-6 (1.25 mmol, 646.8 mg) in THF (60 mL) was cooled to –50 °C, ^{t}BuOK (11 mmol, 1.234 g) was added slowly and the mixture was stirred at the same temperature for 1 h. Then, the mixture was warmed to room temperature and stirred for another 1 h. After completion, ethyl acetate was added, and the precipitate was removed by filtration. The resultant solution was concentrated, and the crude products were purified by column chromatography to give the desired product as white solid in 68% yield (0.715 g).

Synthesis of 4,4-di(prop-2-yn-1-yl)isochroman-3-one (**1al**)



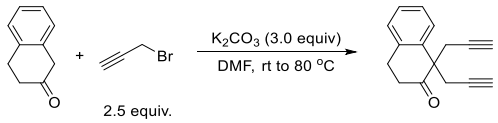
The mixture of isochroman-3-one (5.0 mmol, 740.8 mg), 3-bromoprop-1-yne (15 mmol, 1.784 g) and 18-crown-6 (1.25 mmol, 646.8 mg) in THF (60 mL) was cooled to –50 °C, ^{t}BuOK (11 mmol, 1.234 g) was added slowly and the mixture was stirred at the same temperature for 1 h. Then, the mixture was warmed to room temperature and stirred for another 1 h. After completion, ethyl acetate was added, and the precipitate was removed by filtration. The resultant solution was concentrated, and the crude product was purified by column chromatography to give the desired product as white solid in 20% yield (0.224 g).

Method C: Synthesis of substituted 1,4-dihydroisoquinolin-3(2*H*)-one (**1w**)



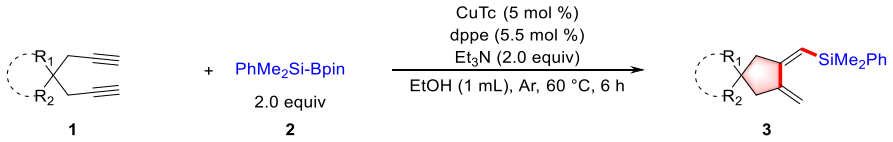
NaH (60 wt% dispersion in mineral oil, 12 mmol, 172.8 mg) was added to the mixture of 2-benzyl-1,4-dihydroisoquinolin-3(2*H*)-one (5.0 mmol, 1.187 g) in DMF (0.75 M) at 0 °C. After 15 min, 3-bromoprop-1-yne (15 mmol, 1.784 g) was added. Then the mixture was allowed to warm up to room temperature and stirred at room temperature until complete consumption of the starting material (monitored by TLC). The reaction mixture was quenched with saturated NH_4Cl (5 mL), extracted with ethyl acetate (20 mL×3). The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography and afforded the desired product as colorless crystal in 88% yield (1.376 g).

Method D: Synthesis of 1,1-di(prop-2-yn-1-yl)-3,4-dihydronaphthalen-2(1*H*)-one (**1s**)



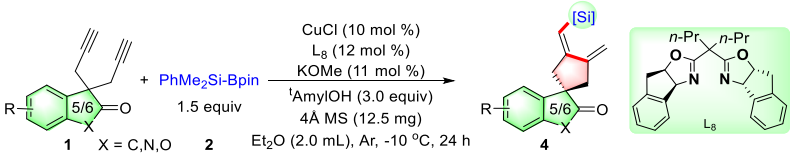
3,4-Dihydronaphthalen- 2(1*H*)-one (5.0 mmol, 730.9 mg) was added to the mixture of K_2CO_3 (15 mmol, 2.073 g) in DMF (25 mL) under argon atmosphere and the resulting solution was stirred at room temperature for 10 min. Then, a solution of 3-bromoprop-1-yne (12.5 mmol, 1.487 g) in DMF (5 mL) was added dropwise, the resultant mixture was stirred at 80 °C for 6 h. The reaction was quenched with saturated NH_4Cl (10 mL), extracted with ethyl acetate (20 mL×3). The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography and afforded the desired product as yellow solid in 32% yield (354 mg).

Method E: Synthesis of products **3**



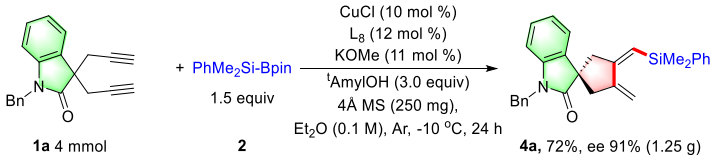
An oven dried 10-mL Schlenk tube equipped with a stirring bar, was charged with CuTc (0.01 mmol, 1.9 mg), dppe (0.011 mmol, 4.4 mg), EtOH (1.0 mL), Et_3N (0.4 mmol. 40.5 mg) and 1,6-diynes (0.2 mmol), in sequence. The reaction mixture was stirred at room temperature for 15 min. Then Me_2PhSi–Bpin (0.4 mmol, 104.9 mg) was added. The mixture was stirred at 60 °C for 6 h. Then, saturated NH_4Cl (5 mL) was added and extracted with ethyl acetate (20 mL×3). The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography and afforded the desired product **3**.

Method F: Synthesis of chiral products **4**



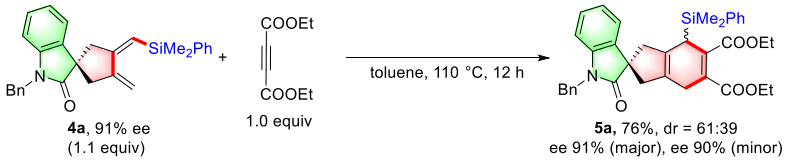
An oven dried 10-mL Schlenk tube equipped with a stirring bar, was charged with CuCl (0.02 mmol, 2.0 mg), KOMe (0.022 mmol, 1.5 mg), 4Å MS (12.5 mg), L_8 (0.024 mmol, 9.9 mg), Et_2O (2.0 mL) and ^{t}AmylOH (0.6 mmol, 52.9 mg). The mixture was stirred for 1 h at room temperature. Then 1,6-diynes (0.2 mmol), Me_2PhSi–Bpin (0.3 mmol, 78.7 mg) were added. The solution was stirred at –10 °C until the complete consumption of the starting material. Then, saturated NH_4Cl (5 mL) was added and extracted with ethyl acetate (20 mL×3). The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography and afforded the desired product **4**.

Gram-Scaled Experiment



An oven dried 10-mL Schlenk tube equipped with a stirring bar, was charged with CuCl (0.4 mmol, 39.6 mg), KOMe (0.44 mmol, 30.9 mg), 4Å MS (250 mg), L_8 (0.48 mmol, 199 mg), Et_2O (40 mL) and ^{t}AmylOH (12.0 mmol, 1.058 g). The mixture was stirred for 1 h at room temperature. Then **1a** (4.0 mmol, 1.197 g) and **2** (6.0 mmol, 1.573 g) were added. The solution was stirred at –10 °C for 24 h. Then, saturated NH_4Cl (20 mL) was added and extracted with ethyl acetate (40 mL×3). The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography and afforded the desired product **4a** in 72% yield and 91% ee (1.25 g).

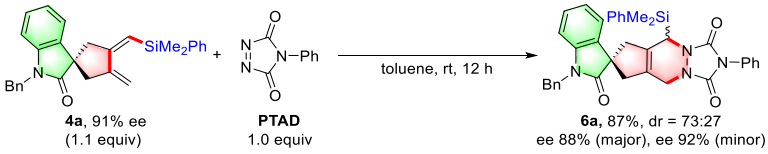
Method G: Synthesis of product **5a**



4a, 91% ee (1.1 equiv) | 1.0 equiv | **5a**, 76%, dr = 61:39, ee 91% (major), ee 90% (minor)

An oven dried 10-mL Schlenk tube equipped with a stirring bar, was charged with **4a** (0.22 mmol, 95.8 mg), diethyl but-2-ynedioate (0.2 mmol, 34.0 mg) and toluene (1.0 mL). The mixture was stirred at 110 °C for 12 h under argon atmosphere. Then, saturated NH_4Cl (5 mL) was added and extracted with ethyl acetate (20 mL×3). The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography and afforded the desired product **5a** in 76% yield (91.9 mg, dr = 61:39).

Method H: Synthesis of product **6a**

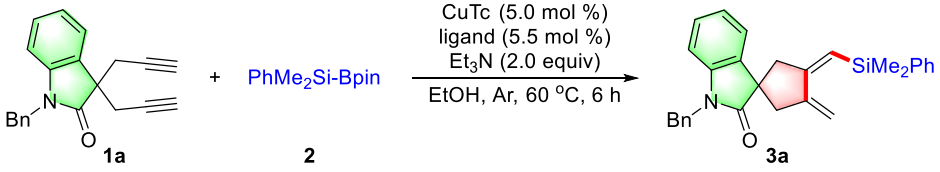


4a, 91% ee (1.1 equiv) | **PTAD** 1.0 equiv | **6a**, 87%, dr = 73:27, ee 88% (major), ee 92% (minor)

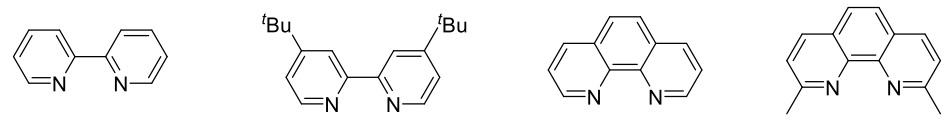
An oven dried 10-mL Schlenk tube equipped with a stirring bar, was charged with **4a** (0.22 mmol, 95.8 mg), PTAD (0.2 mmol, 34.0 mg) and toluene (1.0 mL). The mixture was stirred room temperature for 12 h under argon atmosphere. Then, saturated NH_4Cl (5 mL) was added and extracted with ethyl acetate (20 mL×3). The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography and afforded the desired product **6a** in 87% yield (106.2 mg, dr = 27:73).

III. Screening of ligands

Screening of nitrogen ligands for racemic reaction:

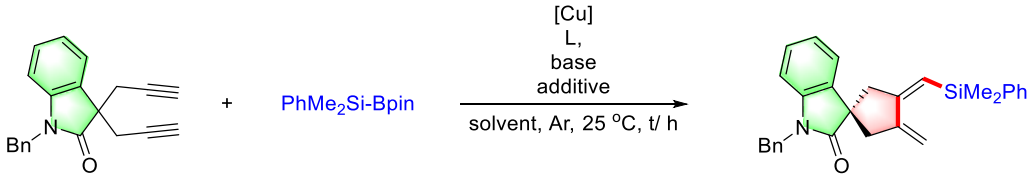


1a | **2** | **3a**



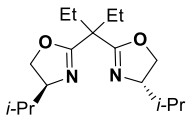
14% | 16% | 11% | 34%

Screening of chiral ligands for asymmetric reaction:

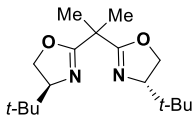


1a **2** **4a**

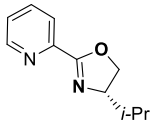
entry	[Cu] (10 mol %)	ligand (mol %)	base (22 mol%)	additive (equiv)	solvent (1 mL)	T/°C	t/h	yield (%)[b]	ee %
1	CuCl	L_1 (12)	NaO^{t}Bu	MeOH (2.0)	THF	25	20	41	66
2	CuCl	L_2 (12)	NaO^{t}Bu	MeOH (2.0)	THF	25	20	0	--
3	CuCl	L_3 (12)	NaO^{t}Bu	MeOH (2.0)	THF	25	20	20	10
4	CuCl	L_4 (12)	NaO^{t}Bu	MeOH (2.0)	THF	25	20	24	0
5	CuCl	L_5 (12)	NaO^{t}Bu	MeOH (2.0)	THF	25	20	19	7
6	CuCl	L_6 (12)	NaO^{t}Bu	MeOH (2.0)	THF	25	20	32	76
7	CuCl	L_7 (20)	KO^{t}Bu	--	MeOH:THF (1:5)	25	20	52	74
8	CuCl	L_8 (20)	KO^{t}Bu	--	MeOH:THF (1:5)	25	20	58	77
9	CuCl	L_9 (20)	KO^{t}Bu	--	MeOH:THF (1:5)	25	20	47	76
10	CuBr	L_{10} (20)	KO^{t}Bu	--	MeOH:THF (1:5)	25	20	42	66
11	CuTc	L_{11} (20)	KO^{t}Bu	--	MeOH:THF (1:5)	25	20	37	58
12	CuCl	L_{12} (20)	KO^{t}Bu (10)	--	MeOH:THF (1:5)	25	3	37	72



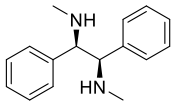
L_1



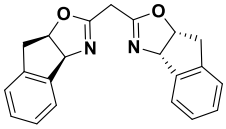
L_2



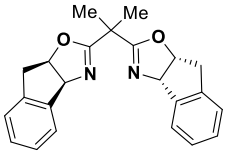
L_3



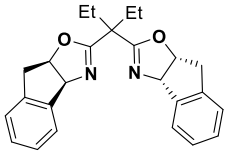
L_4



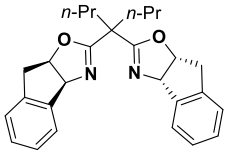
L_5



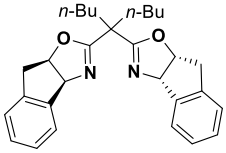
L_6



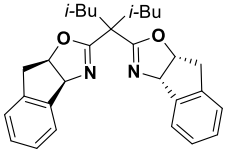
L_7



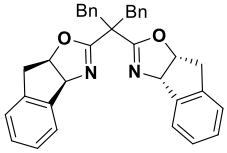
L_8



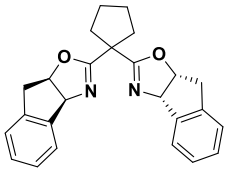
L_9



L_{10}



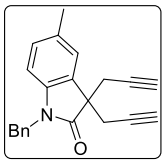
L_{11}



L_{12}

IV. Characterization Data and Spectrums of Substrates and Products

1-benzyl-5-methyl-3,3-di(prop-2-yn-1-yl)indolin-2-one (1b)

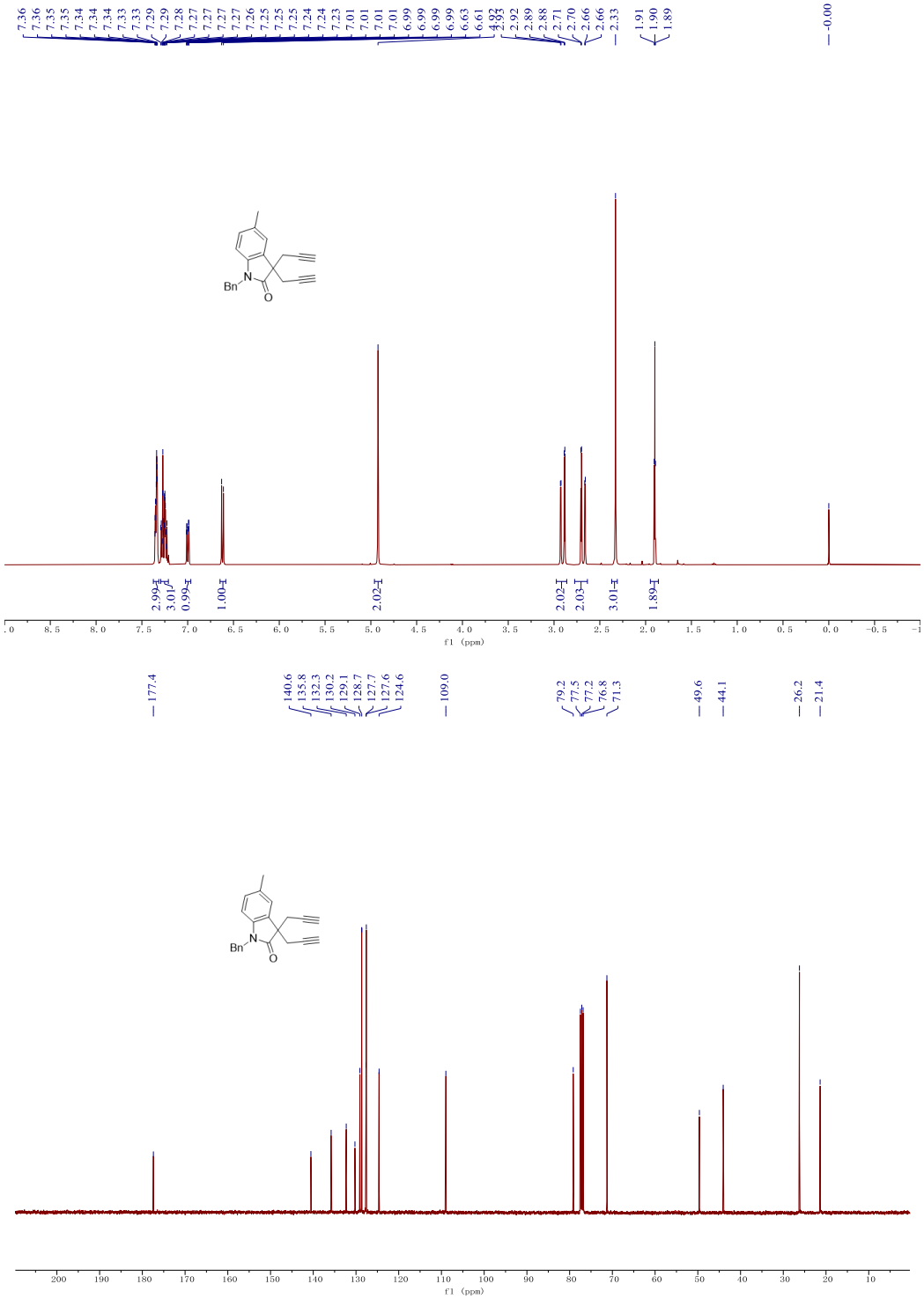


Prepared according to method **A**. The substrate **1b** was obtained as colorless crystal in 46% yield (0.287 g).

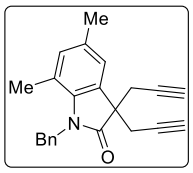
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 3H), 7.30 – 7.17 (m, 3H), 7.00 (ddd, *J* = 7.9, 1.7, 0.8 Hz, 1H), 6.62 (d, *J* = 7.9 Hz, 1H), 4.92 (s, 2H), 2.91 (dd, *J* = 16.8, 2.6 Hz, 2H), 2.68 (dd, *J* = 16.8, 2.6 Hz, 2H), 2.33 (s, 3H), 1.90 (t, *J* = 2.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 140.6, 135.8, 132.3, 130.3, 129.1, 128.7, 127.7, 127.6, 124.6, 109.0, 79.2, 71.3, 49.6, 44.1, 26.2, 21.4.

HRMS (ESI): m/z Calcd. for $C_{22}H_{20}NO$ $[M+H]^+$: 314.1545, found: 314.1541.



1-benzyl-5,7-dimethyl-3,3-di(prop-2-yn-1-yl)indolin-2-one (1c)

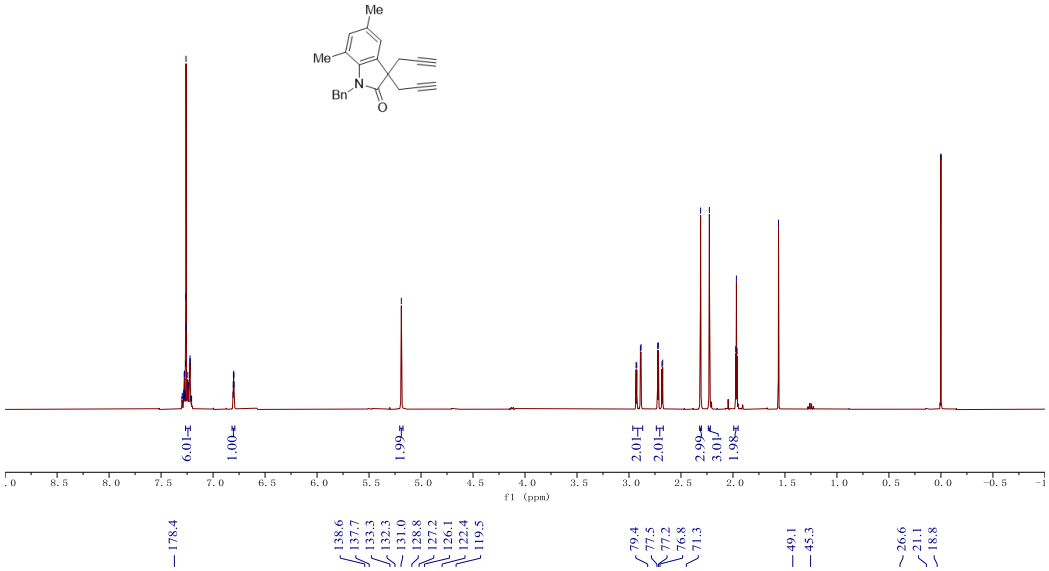


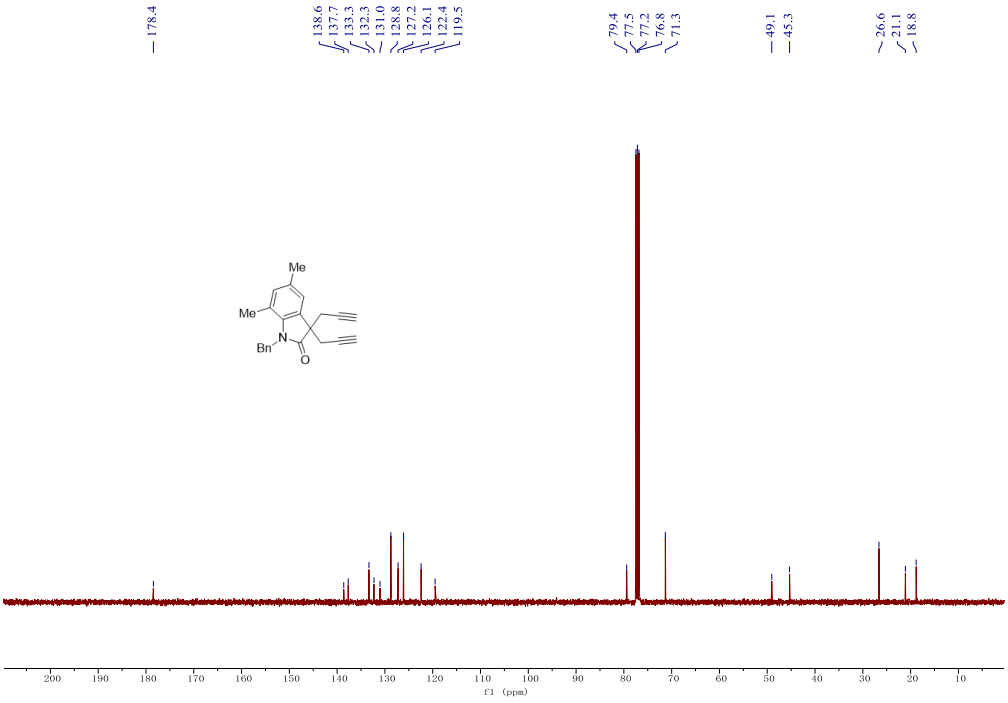
Prepared according to method **A**. The substrate **1c** was obtained as light red solid in 70% yield (0.457 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.18 (m, 6H), 6.80 (td, *J* = 1.5, 0.7 Hz, 1H), 5.19 (s, 2H), 2.91 (dd, *J* = 16.8, 2.6 Hz, 2H), 2.70 (dd, *J* = 16.8, 2.6 Hz, 2H), 2.31 (s, 3H), 2.23 (s, 3H), 1.97 (t, *J* = 2.6 Hz, 2H).

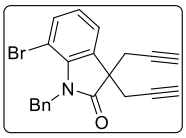
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 138.6, 137.7, 133.3, 132.3, 131.0, 128.8, 127.3, 126.1, 122.4, 119.5, 79.4, 71.3, 49.1, 45.3, 26.6, 21.1, 18.8.

HRMS (ESI): m/z Calcd. for $C_{23}H_{22}NO$ $[M+H]^+$: 328.1701, found: 328.1696.





1-benzyl-7-bromo-3,3-di(prop-2-yn-1-yl)indolin-2-one (1g)

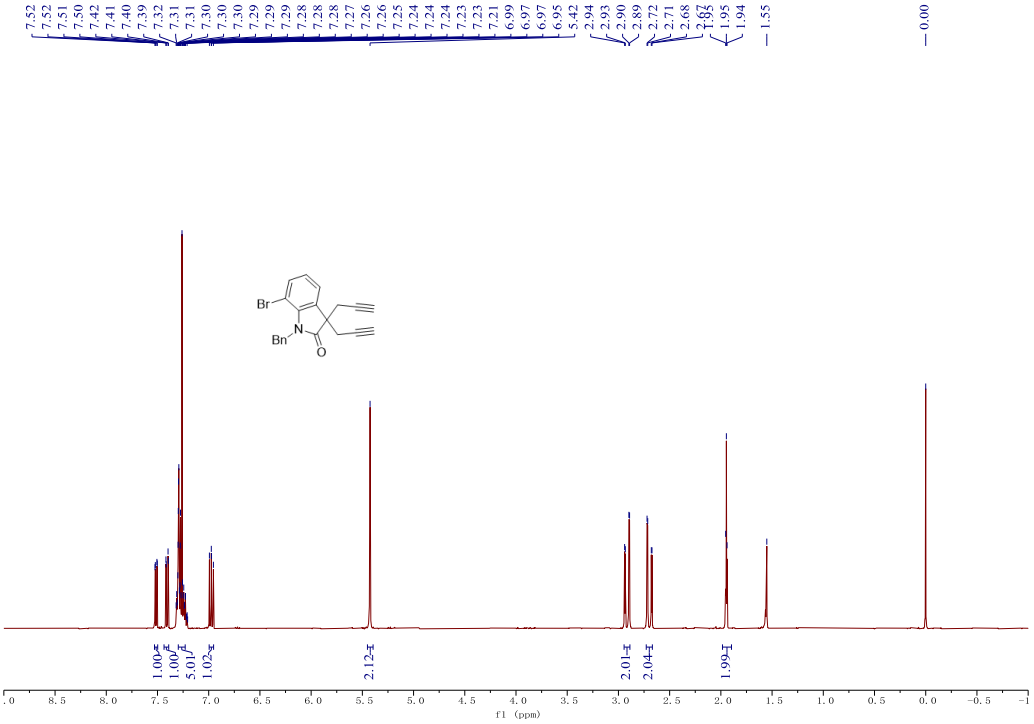


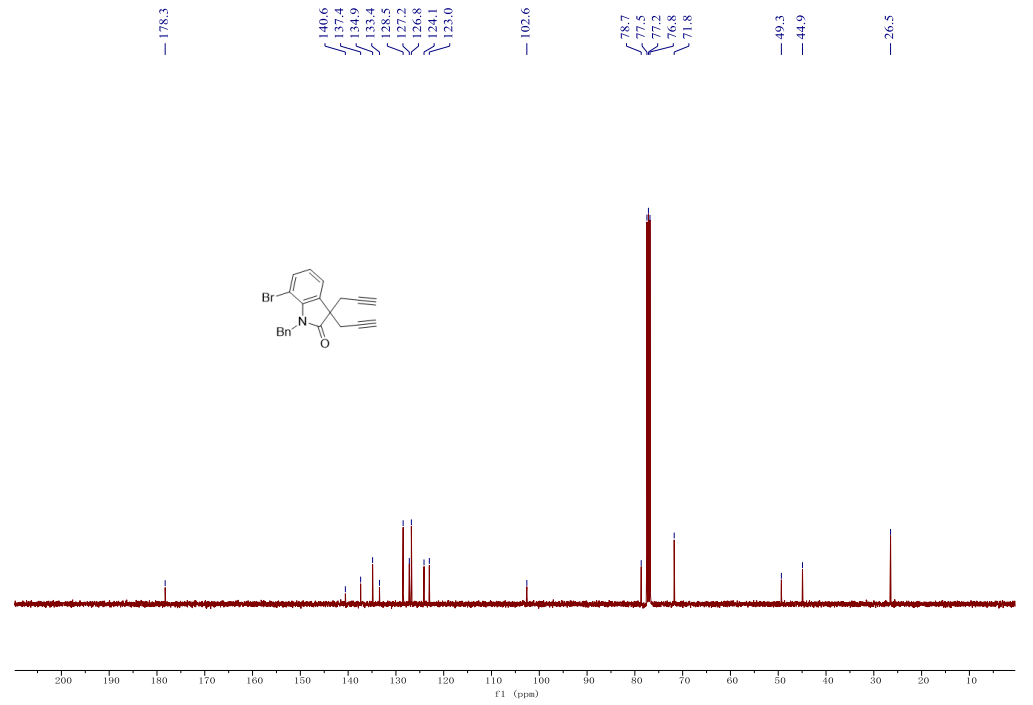
Prepared according to method **A**. The substrate **1g** was obtained as yellow solid in 67% yield (0.504 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.41 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.34 – 7.18 (m, 5H), 6.97 (dd, *J* = 8.2, 7.4 Hz, 1H), 5.42 (s, 2H), 2.92 (dd, *J* = 16.8, 2.6 Hz, 2H), 2.70 (dd, *J* = 16.8, 2.6 Hz, 2H) 1.95 (t, *J* = 2.6 Hz, 2H).

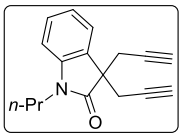
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 140.6, 137.4, 134.9, 133.4, 128.5, 127.2, 126.8, 124.1, 123.0, 102.6, 78.7, 71.8, 49.3, 44.9, 26.5.

HRMS (ESI): m/z Calcd. for $C_{21}H_{17}NOBr$ $[M+H]^+$: 378.0494, found: 378.0493.





3,3-di(prop-2-yn-1-yl)-1-propylindolin-2-one (1j)

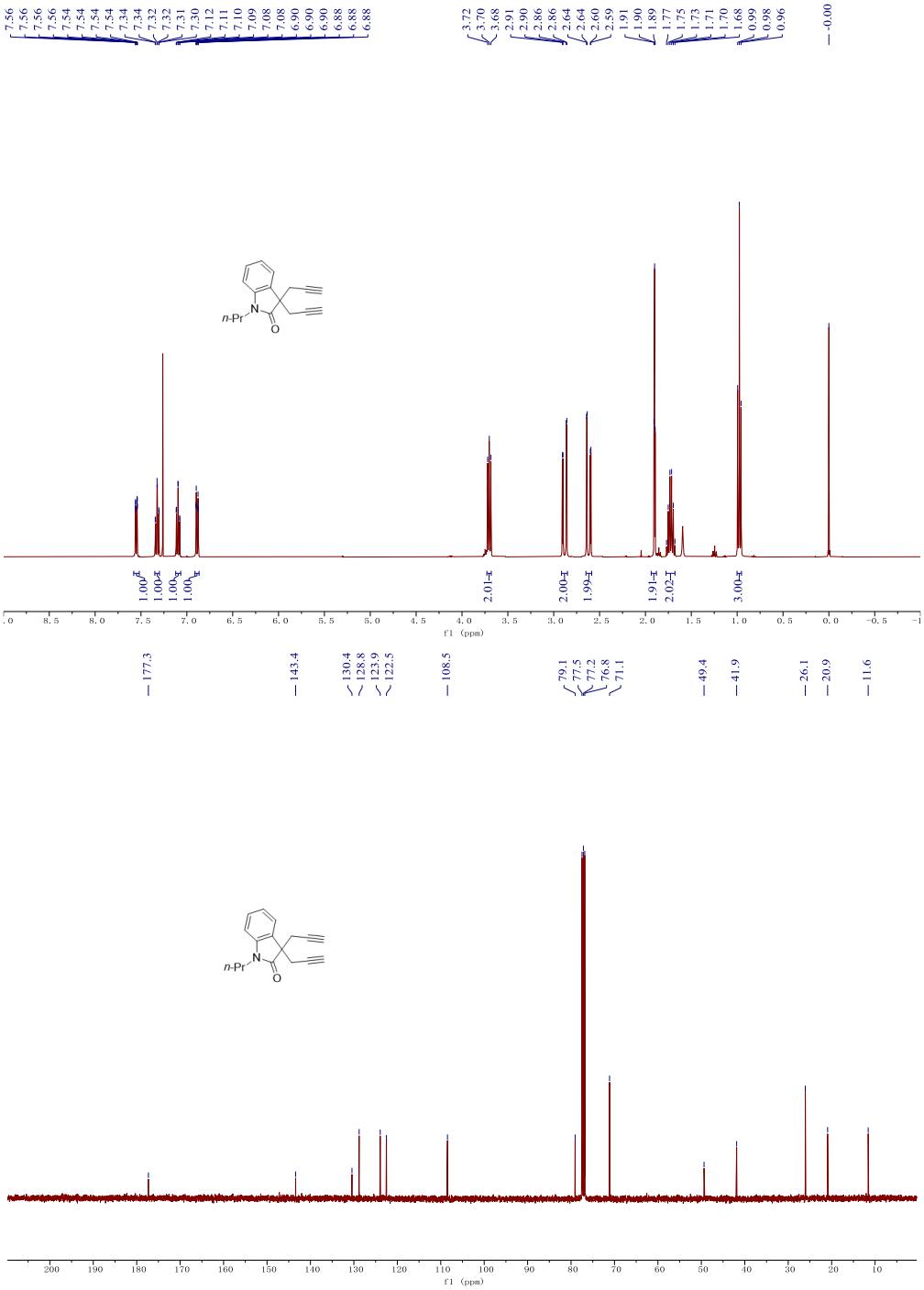


Prepared according to method **A**. The substrate **1j** was obtained as yellow solid in 78% yield (0.391 g).

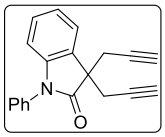
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (ddd, *J* = 7.4, 1.3, 0.5 Hz, 1H), 7.32 (td, *J* = 7.7, 1.3 Hz, 1H), 7.10 (td, *J* = 7.6, 1.0 Hz, 1H), 6.89 (dt, *J* = 7.8, 0.8 Hz, 1H), 3.70 (t, *J* = 7.2 Hz, 2H), 2.88 (dd, *J* = 16.8, 2.6 Hz, 2H), 2.62 (dd, *J* = 16.8, 2.6 Hz, 2H), 1.90 (t, *J* = 2.7 Hz, 2H), 1.72 (h, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 143.4, 130.4, 128.8, 123.9, 122.5, 108.5, 79.1, 71.1, 49.4, 41.9, 26.1, 20.9, 11.6.

HRMS (ESI): m/z Calcd. for $C_{17}H_{18}NO$ $[M+H]^+$: 252.1388, found: 252.1388.



1-phenyl-3,3-di(prop-2-yn-1-yl)indolin-2-one (1k)

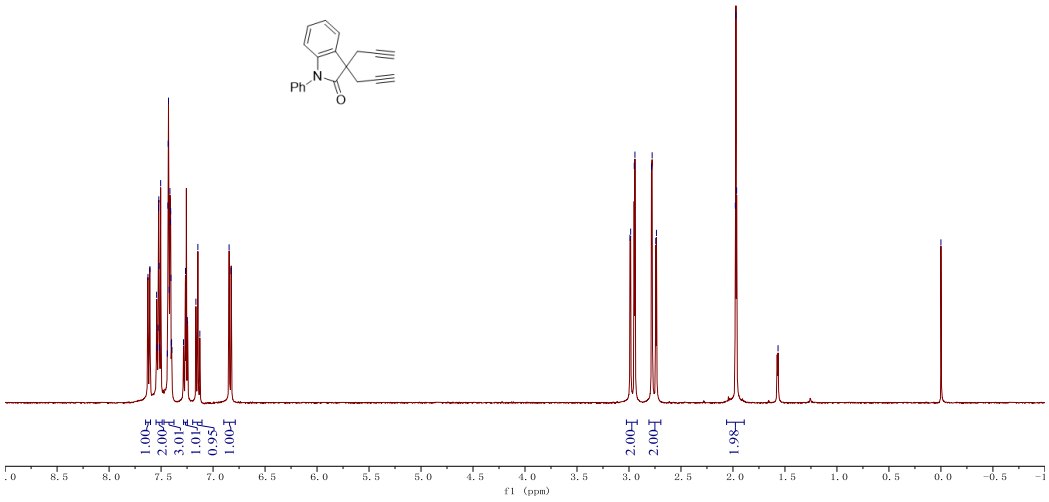


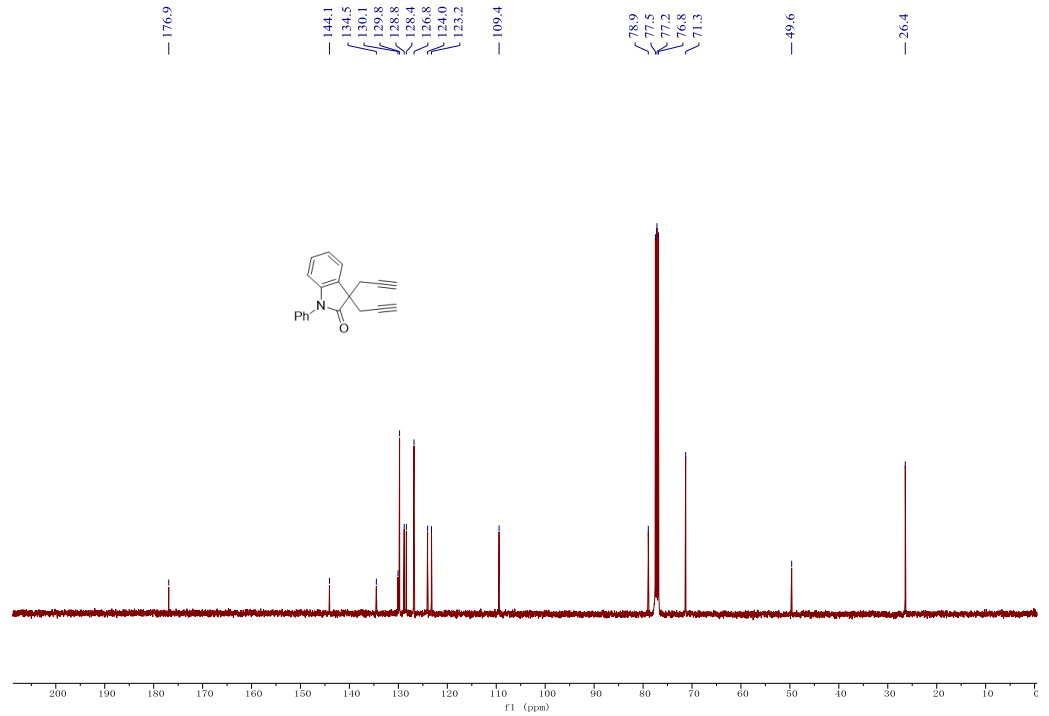
Prepared according to method **A**. The substrate **1k** was obtained as yellow solid in 72% yield (0.411 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.4 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.46 – 7.39 (m, 3H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 2.97 (dd, *J* = 16.8, 2.6 Hz, 2H), 2.76 (dd, *J* = 16.8, 2.6 Hz, 2H), 1.97 (t, *J* = 2.6 Hz, 2H).

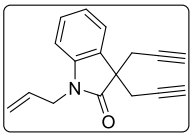
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 144.1, 134.5, 130.1, 129.8, 128.8, 128.4, 126.8, 124.0, 123.2, 109.4, 78.9, 71.3, 49.6, 26.4.

HRMS (ESI): m/z Calcd. for $C_{20}H_{16}NO$ $[M+H]^+$: 286.1232, found: 286.1230.





1-allyl-3,3-di(prop-2-yn-1-yl)indolin-2-one (1m)

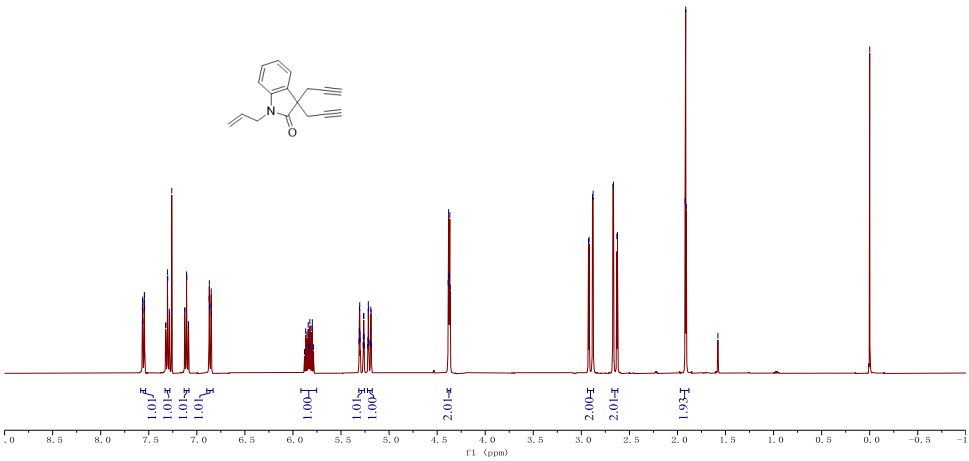


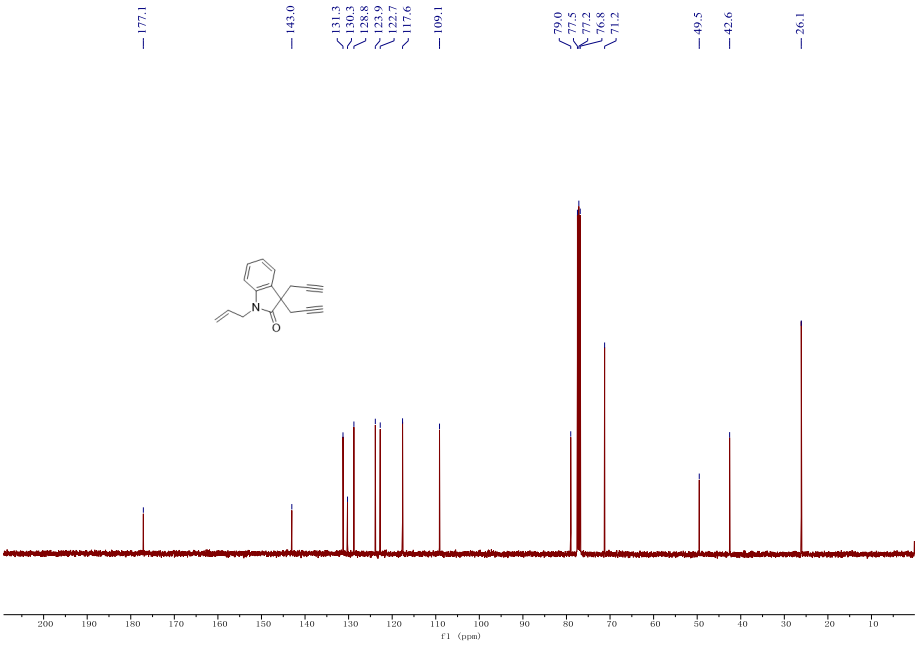
Prepared according to method **A**. The substrate **1m** was obtained as white plate crystal in 45% yield (0.225 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (ddd, *J* = 7.4, 1.3, 0.6 Hz, 1H), 7.30 (td, *J* = 7.8, 1.3 Hz, 1H), 7.11 (td, *J* = 7.6, 1.0 Hz, 1H), 6.86 (dt, *J* = 7.8, 0.8 Hz, 1H), 5.83 (ddt, *J* = 17.2, 10.3, 5.1 Hz, 1H), 5.29 (dtd, *J* = 17.2, 1.8, 1.1 Hz, 1H), 5.20 (dq, *J* = 10.3, 1.5 Hz, 1H), 4.37 (dt, *J* = 5.1, 1.8 Hz, 2H), 2.90 (dd, *J* = 16.8, 2.6 Hz, 2H), 2.65 (dd, *J* = 16.8, 2.6 Hz, 2H), 1.91 (t, *J* = 2.6 Hz, 2H).

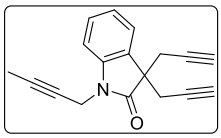
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 143.0, 131.3, 130.3, 128.8, 123.9, 122.7, 117.6, 109.1, 79.0, 71.2, 49.5, 42.6, 26.1.

HRMS (ESI): m/z Calcd. for $C_{17}H_{16}NO$ $[M+H]^+$: 250.1232, found: 250.1235.





1-(but-2-yn-1-yl)-3,3-di(prop-2-yn-1-yl)indolin-2-one (1n)

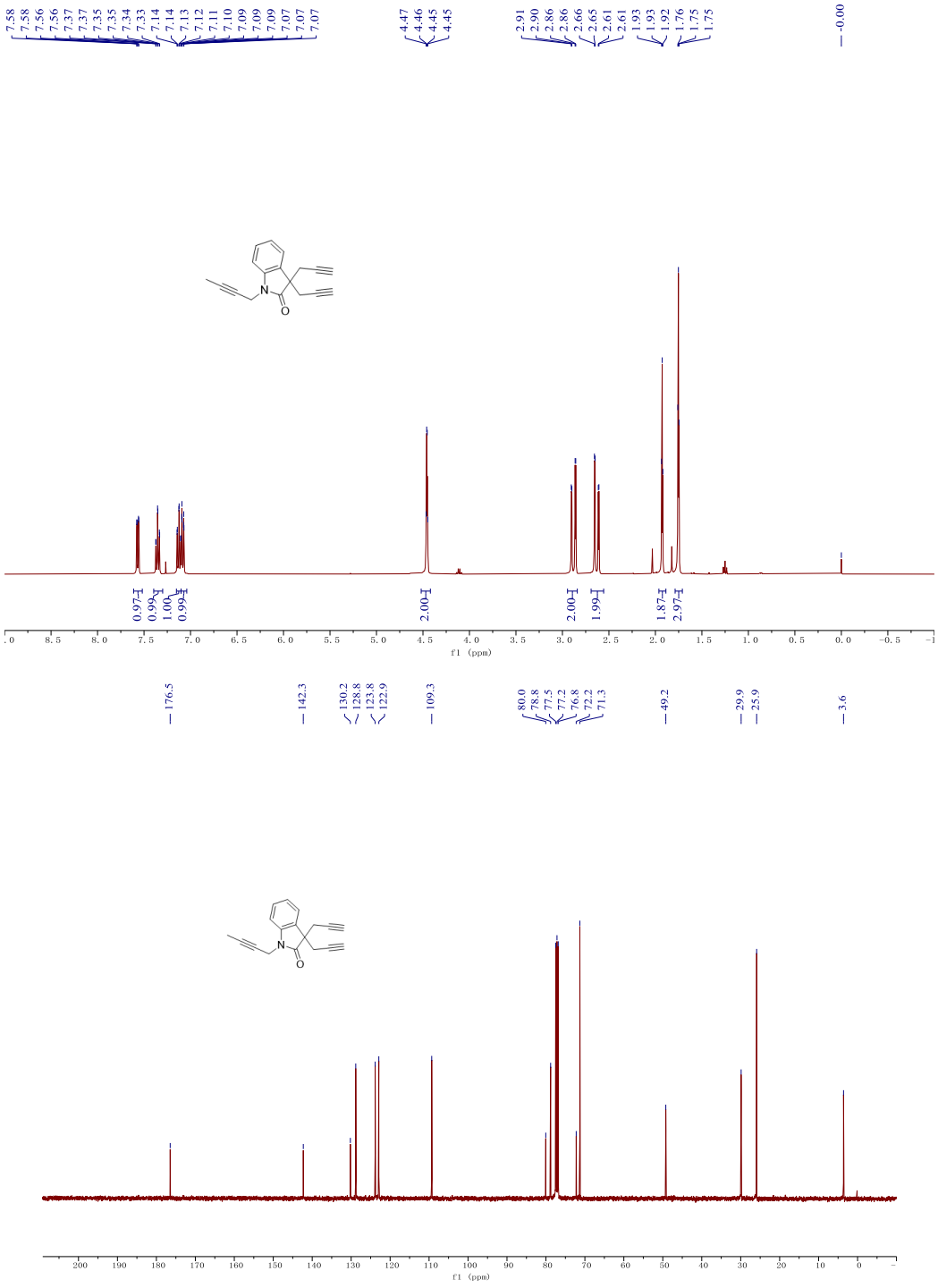


Prepared according to method **A**. The substrate **1n** was obtained as colorless crystal in 51% yield (0.266 g).

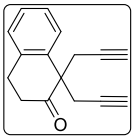
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.35 (td, *J* = 7.7, 1.2 Hz, 1H), 7.12 (td, *J* = 7.6, 1.1 Hz, 1H), 7.08 (dt, *J* = 7.9, 0.7 Hz, 1H), 4.46 (q, *J* = 2.4 Hz, 2H), 2.88 (dd, *J* = 16.6, 2.7 Hz, 2H), 2.63 (dd, *J* = 16.6, 2.7 Hz, 2H), 1.93 (t, *J* = 2.7 Hz, 2H), 1.75 (t, *J* = 2.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 142.3, 130.2, 128.8, 123.8, 122.9, 109.3, 80.0, 78.8, 72.2, 71.3, 49.2, 29.9, 25.9, 3.6.

HRMS (ESI): m/z Calcd. for $C_{18}H_{16}NO$ $[M+H]^+$: 262.1232, found: 262.1234.



1,1-di(prop-2-yn-1-yl)-3,4-dihydronaphthalen-2(1*H*)-one (1s)

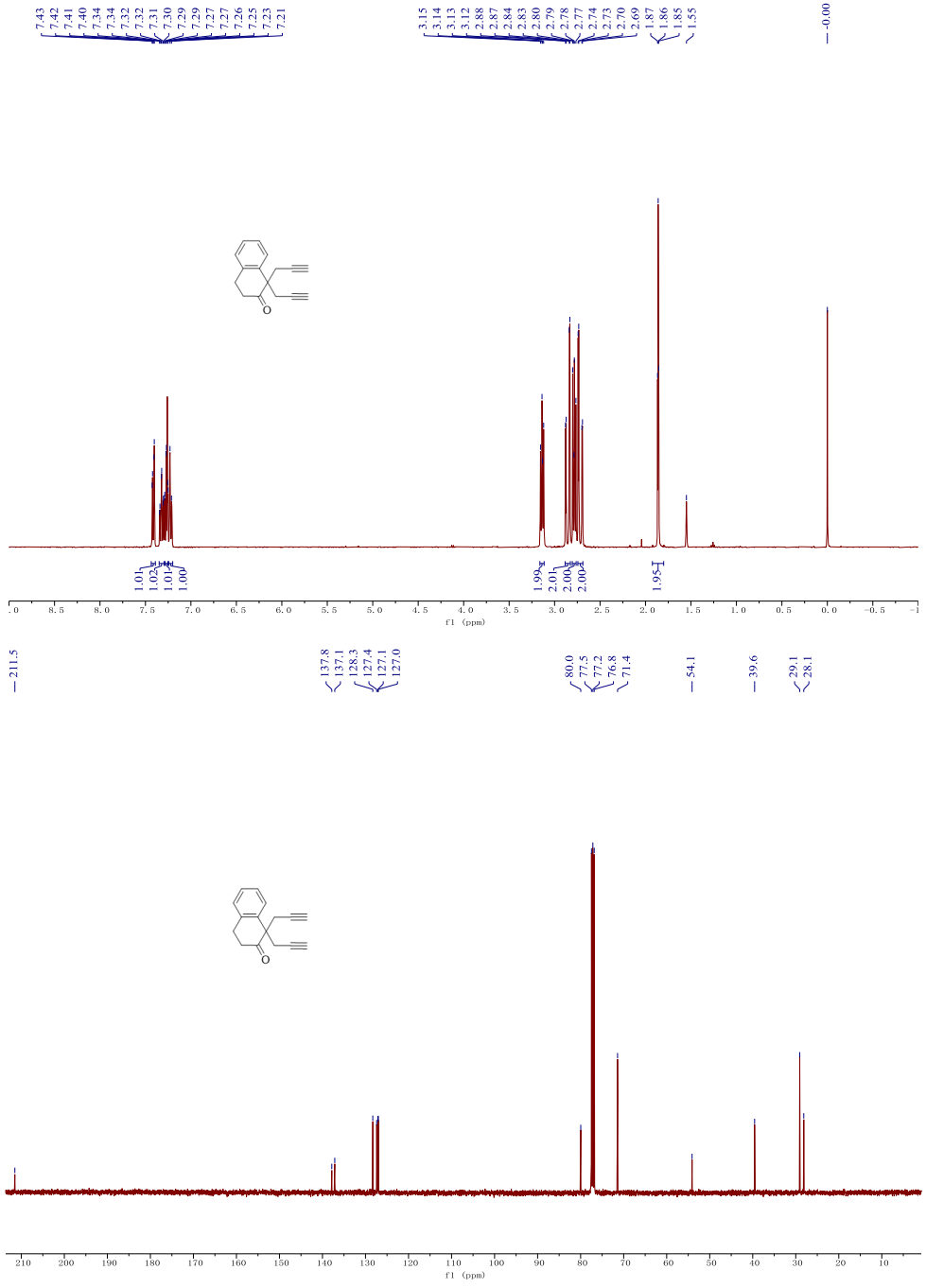


Prepared according to method **D**. The substrate **1s** was obtained as yellow solid in 32% yield (0.354 g).

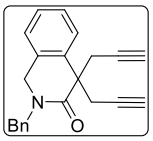
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.32 (td, *J* = 7.7, 1.7 Hz, 1H), 7.27 (td, *J* = 7.3, 1.5 Hz, 1H), 7.22 (d, *J* = 6.6 Hz, 1H), 3.14 (dd, *J* = 7.9, 5.9 Hz, 2H), 2.86 (dd, *J* = 16.8, 2.6 Hz, 2H), 2.72 (dd, *J* = 16.8, 2.6 Hz, 2H), 2.78 (dd, *J* = 7.9, 5.9 Hz, 2H), 1.86 (t, *J* = 2.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 211.5, 137.8, 137.2, 128.3, 127.4, 127.1, 127.0, 80.0, 71.4, 54.1, 39.6, 29.1, 28.1.

HRMS (ESI): m/z Calcd. for $C_{16}H_{15}O$ $[M+H]^+$: 223.1123, found: 223.1123.



2-benzyl-4,4-di(prop-2-yn-1-yl)-1,4-dihydroisoquinolin-3(2*H*)-one (1w)

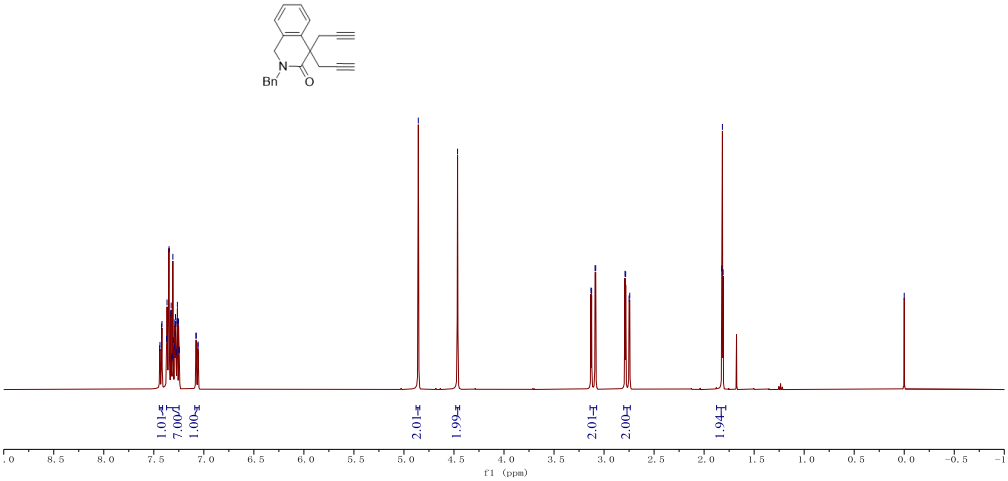


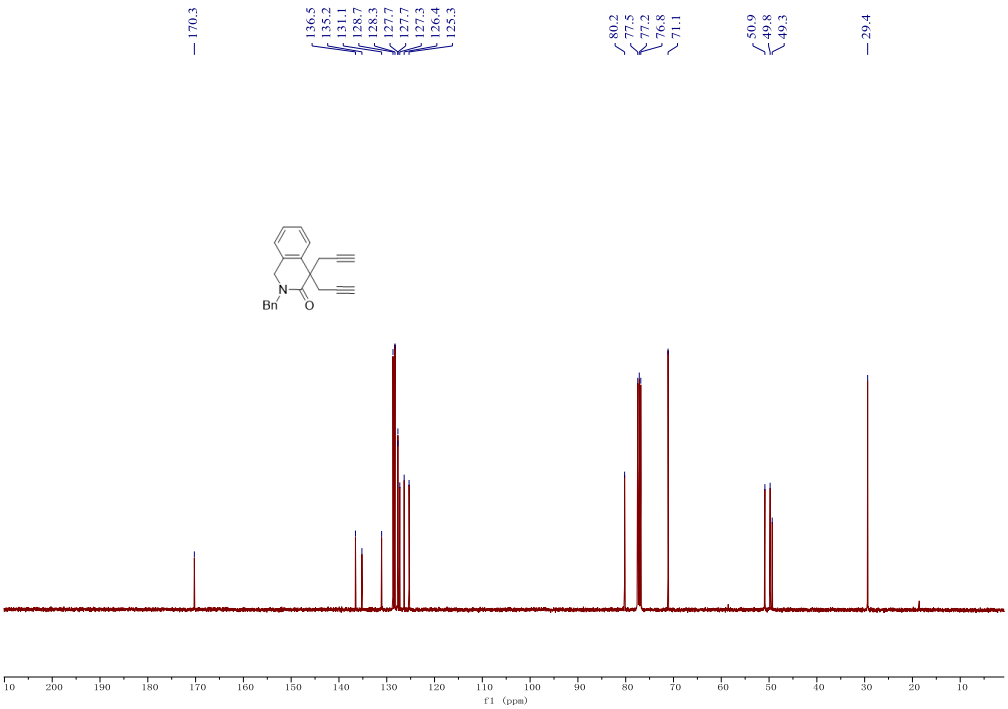
Prepared according to method **C**. The substrate **1w** was obtained as colorless crystal in 88% yield (1.376 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.40 – 7.22 (m, 7H), 7.10 – 7.03 (m, 1H), 4.86 (s, 2H), 4.46 (s, 2H), 3.11 (dd, *J* = 16.4, 2.7 Hz, 2H), 2.77 (dd, *J* = 16.4, 2.7 Hz, 2H), 1.82 (t, *J* = 2.6 Hz, 2H).

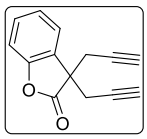
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 136.6, 135.2, 131.1, 128.7, 128.3, 127.7, 127.7, 127.3, 126.4, 125.3, 80.2, 71.1, 50.9, 49.8, 49.3, 29.4.

HRMS (ESI): m/z Calcd. for $C_{22}H_{20}NO$ $[M+H]^+$: 314.1545, found: 314.1541.





3,3-di(prop-2-yn-1-yl)benzofuran-2(3*H*)-one (1ak)

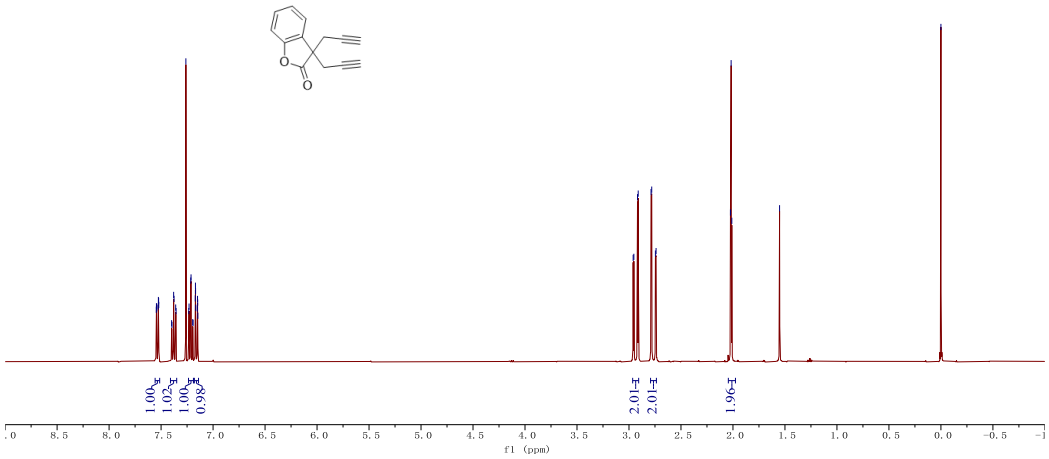


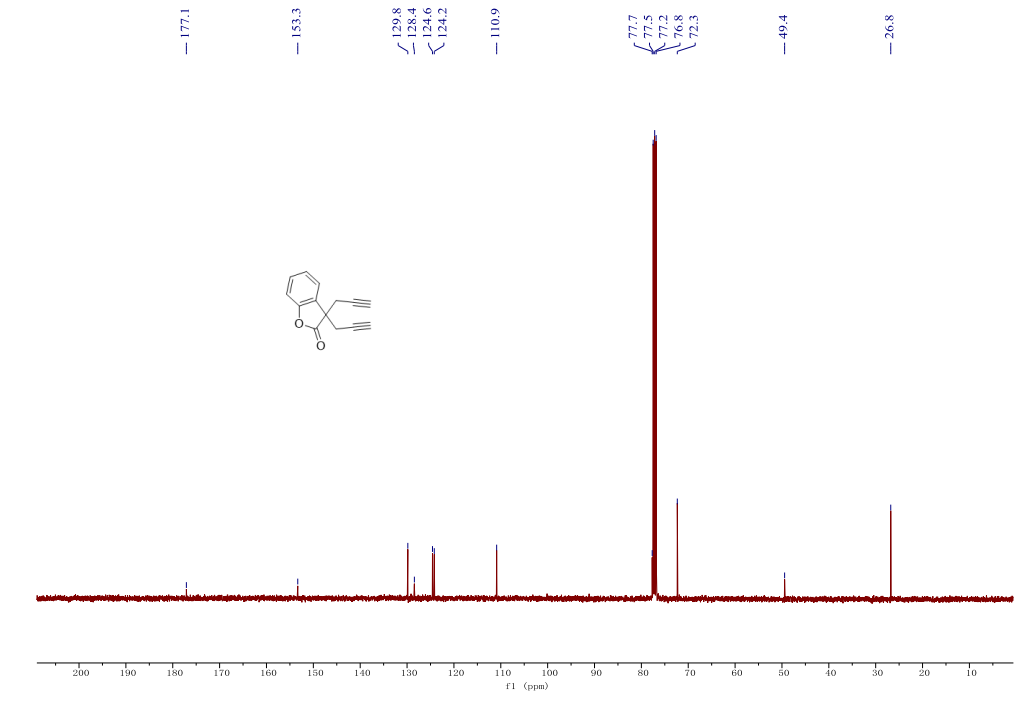
Prepared according to method **B**. The substrate **1ak** was obtained as white solid in 68% yield (0.715 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (ddd, *J* = 7.5, 1.4, 0.5 Hz, 1H), 7.38 (td, *J* = 7.8, 1.4 Hz, 1H), 7.21 (td, *J* = 7.6, 1.0 Hz, 1H), 7.16 (ddd, *J* = 8.0, 1.1, 0.6 Hz, 1H), 2.94 (dd, *J* = 16.8, 2.6 Hz, 2H), 2.76 (dd, *J* = 16.8, 2.6 Hz, 2H), 2.02 (t, *J* = 2.7 Hz, 2H).

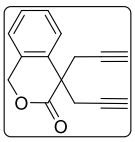
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 153.3, 129.8, 128.4, 124.6, 124.2, 110.9, 77.7, 72.3, 49.4, 26.8.

HRMS (ESI): m/z Calcd. for $C_{14}H_{11}O_2$ $[M+H]^+$: 211.0759, found: 211.0753.





4,4-di(prop-2-yn-1-yl)isochroman-3-one (1al)

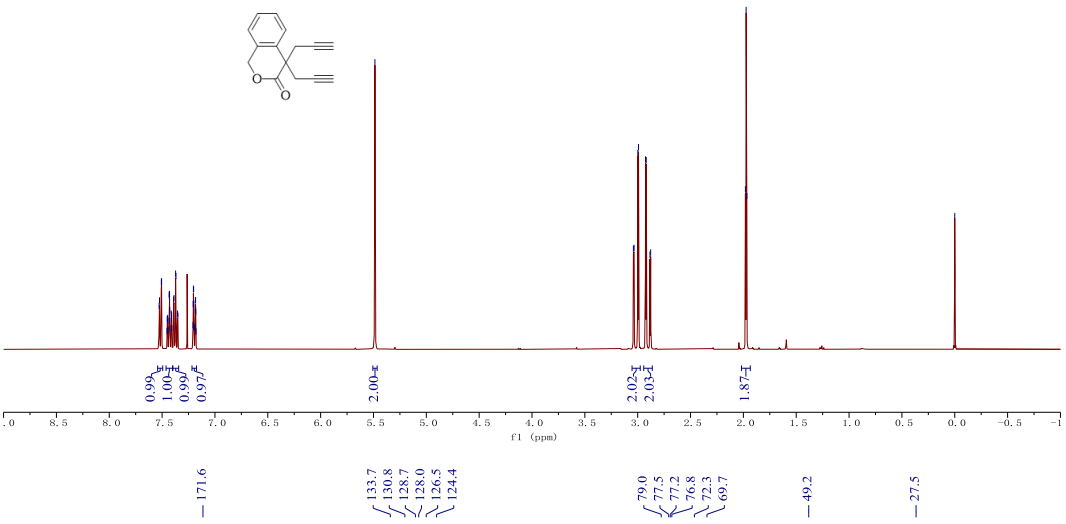


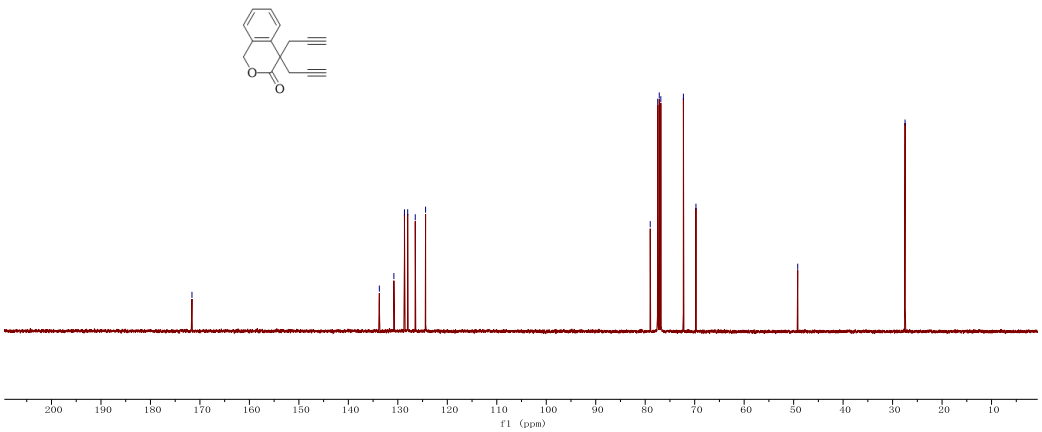
Prepared according to method **B**. The substrate **1al** was obtained as white solid in 20% yield (0.224 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.43 (tdd, *J* = 7.8, 1.4, 0.7 Hz, 1H), 7.37 (td, *J* = 7.4, 1.4 Hz, 1H), 7.19 (ddq, *J* = 7.5, 1.6, 0.8 Hz, 1H), 5.49 (s, 2H), 3.02 (dd, *J* = 16.8, 2.6 Hz, 2H), 2.90 (dd, *J* = 16.8, 2.6 Hz, 2H), 1.97 (t, *J* = 2.7 Hz, 2H).

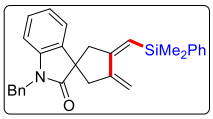
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 133.7, 130.8, 128.7, 128.0, 126.5, 124.4, 79.0, 72.3, 69.7, 49.2, 27.5.

HRMS (ESI): m/z Calcd. for $C_{15}H_{13}O_2$ $[M+H]^+$: 225.0916, found: 225.0913.





(*Z*)-1'-benzyl-3-((dimethyl(phenyl)silyl)methylene)-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (3a)

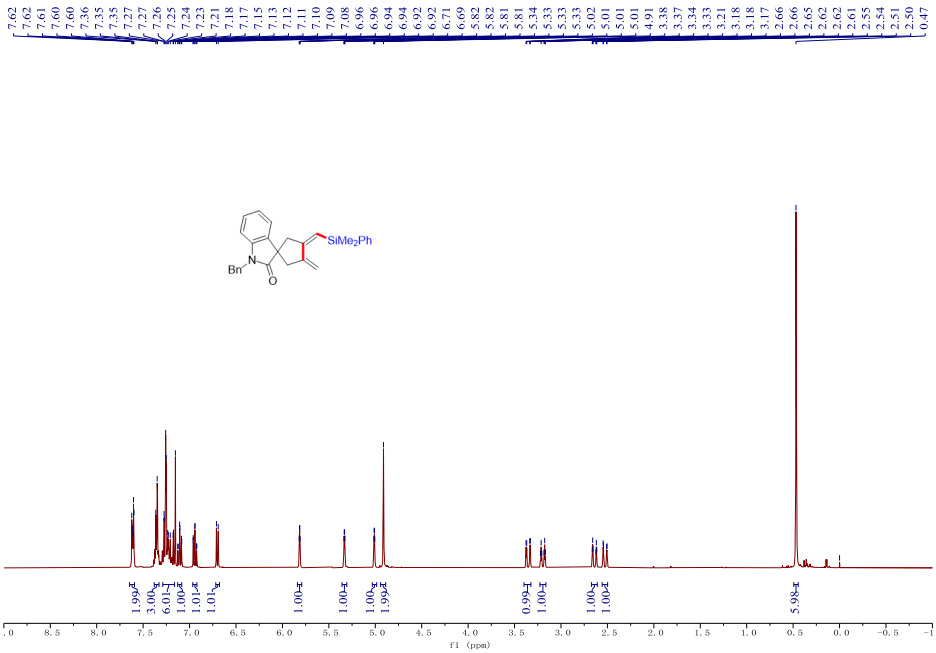


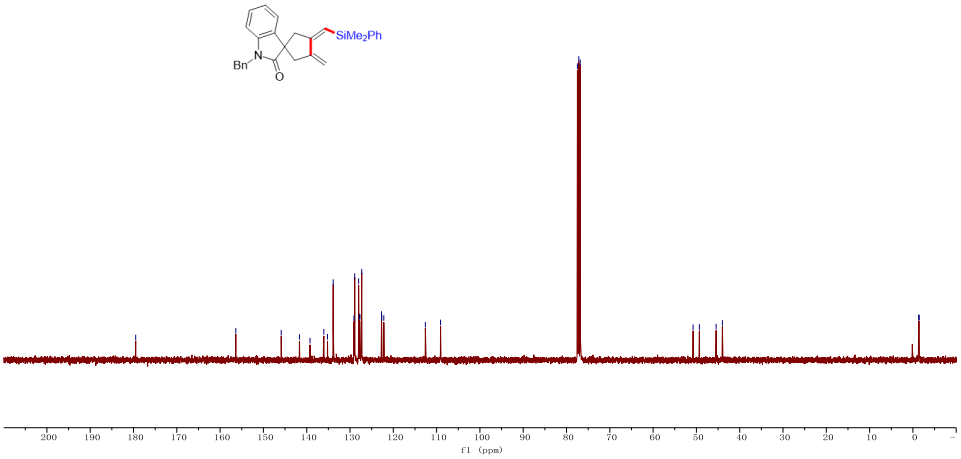
Prepared according to method **E**. The product **3a** was obtained as yellow oil in 77% yield (67.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 2H), 7.41 – 7.30 (m, 3H), 7.30 – 7.13 (m, 6H), 7.11 (td, *J* = 7.7, 1.3 Hz, 1H), 6.94 (td, *J* = 7.6, 1.0 Hz, 1H), 6.70 (d, *J* = 7.7 Hz, 1H), 5.81 (dd, *J* = 2.6, 1.5 Hz, 1H), 5.33 (dd, *J* = 3.0, 1.4 Hz, 1H), 5.01 (dd, *J* = 2.7, 1.4 Hz, 1H), 4.91 (s, 2H), 3.35 (dd, *J* = 15.8, 2.7 Hz, 1H), 3.19 (dt, *J* = 15.3, 2.8 Hz, 1H), 2.64 (dt, *J* = 15.8, 1.9 Hz, 1H), 2.53 (dd, *J* = 15.1, 1.9 Hz, 1H), 0.47 (s, 6H).

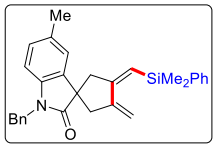
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 156.4, 145.9, 141.7, 139.2, 136.0, 135.2, 133.9, 129.1, 128.9, 128.0, 127.8, 127.7, 127.3, 122.7, 122.7, 122.2, 112.6, 109.1, 50.8, 49.3, 45.5, 44.0, -1.3, -1.5.

HRMS (ESI): m/z Calcd. for $C_{29}H_{30}NOSi$ $[M+H]^+$: 436.2097, found: 436.2097.





(*Z*)-1'-benzyl-3-((dimethyl(phenyl)silyl)methylene)-5'-methyl-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (3b)

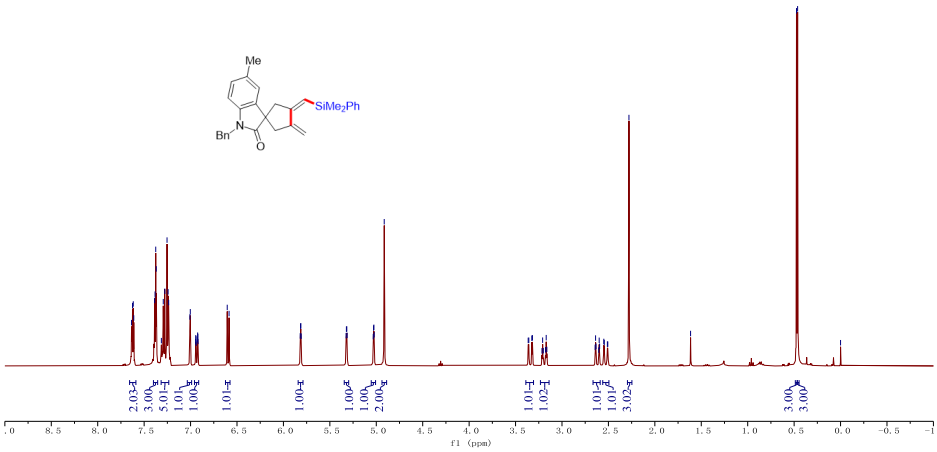


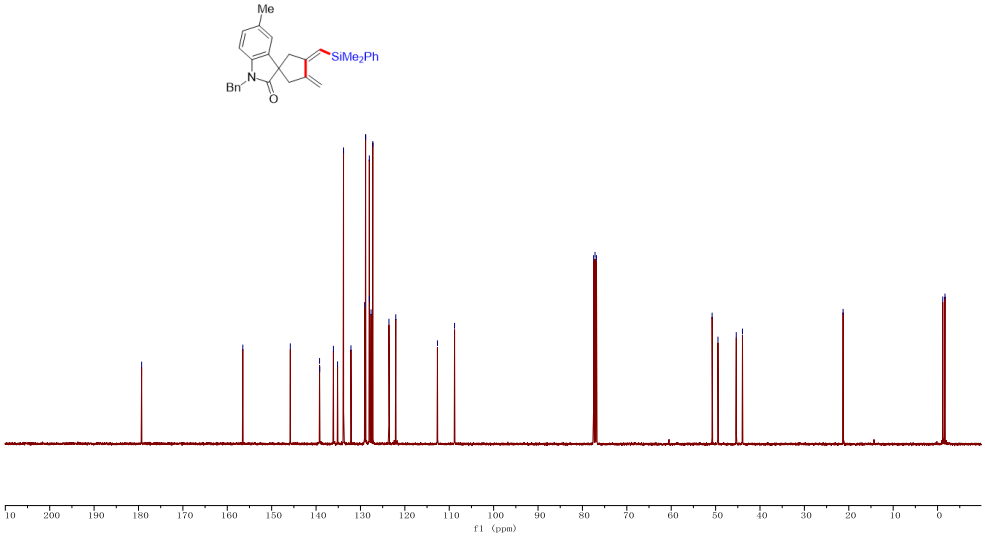
Prepared according to method **E**. The product **3b** was obtained as colorless oil in 71% yield (63.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.41 – 7.36 (m, 3H), 7.32 – 7.23 (m, 5H), 7.01 (d, *J* = 1.7 Hz, 1H), 6.93 (ddd, *J* = 7.9, 1.8, 0.8 Hz, 1H), 6.60 (d, *J* = 7.9 Hz, 1H), 5.81 (dd, *J* = 2.7, 1.5 Hz, 1H), 5.32 (dd, *J* = 3.1, 1.5 Hz, 1H), 5.03 (dd, *J* = 2.7, 1.4 Hz, 1H), 4.91 (s, 2H), 3.34 (dd, *J* = 15.7, 2.7 Hz, 1H), 3.19 (dt, *J* = 15.3, 2.8 Hz, 1H), 2.62 (dt, *J* = 15.6, 1.9 Hz, 1H), 2.53 (dd, *J* = 15.2, 1.9 Hz, 1H), 2.28 (s, 3H), 0.47 (s, 3H), 0.46 (s, 3H).

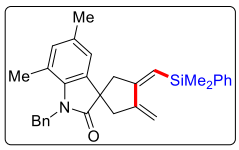
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.3, 156.5, 145.8, 139.2, 139.2, 136.1, 135.2, 133.8, 132.1, 129.1, 128.8, 128.0, 128.0, 127.6, 127.2, 123.6, 122.0, 112.7, 108.8, 50.8, 49.5, 45.4, 44.0, 21.3, -1.2, -1.7.

HRMS (ESI): m/z Calcd. for $C_{30}H_{32}NOSi$ $[M+H]^+$: 450.2253, found: 450.2252.





(*Z*)-1'-benzyl-3-((dimethyl(phenyl)silyl)methylene)-5',7'-dimethyl-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (3c)

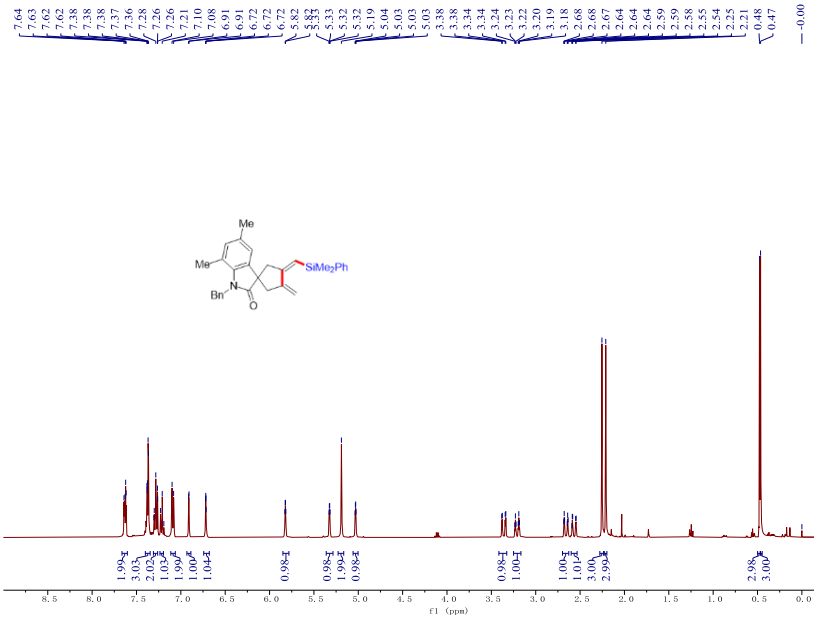


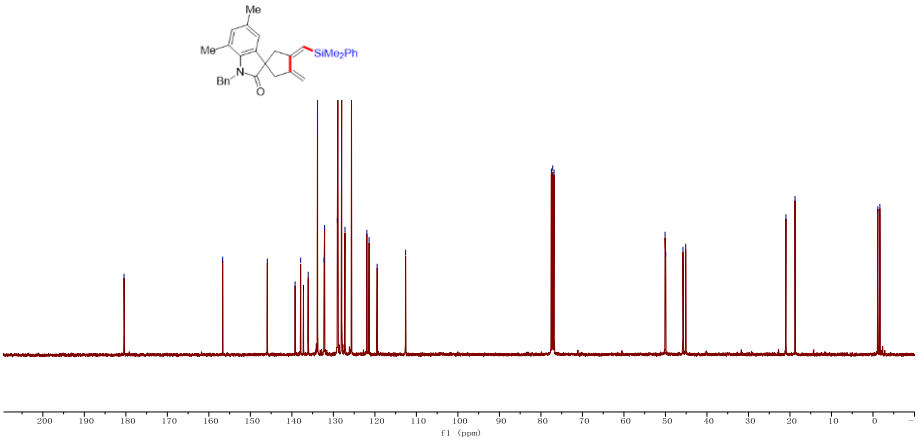
Prepared according to method **E**. The product **3c** was obtained as yellow oil in 71% yield (65.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 2H), 7.41 – 7.35 (m, 3H), 7.31 – 7.25 (m, 2H), 7.25 – 7.16 (m, 1H), 7.11 – 7.05 (m, 2H), 6.91 (d, *J* = 1.8 Hz, 1H), 6.72 (dd, *J* = 1.9, 0.9 Hz, 1H), 5.82 (dd, *J* = 2.6, 1.5 Hz, 1H), 5.32 (dd, *J* = 3.1, 1.6 Hz, 1H), 5.19 (s, 2H), 5.03 (dd, *J* = 2.8, 1.4 Hz, 1H), 3.36 (dd, *J* = 15.7, 2.7 Hz, 1H), 3.21 (dt, *J* = 15.4, 2.8 Hz, 1H), 2.66 (dt, *J* = 15.6, 1.8 Hz, 1H), 2.56 (dd, *J* = 15.4, 1.8 Hz, 1H), 2.25 (s, 3H), 2.21 (s, 3H), 0.48 (s, 3H), 0.47 (s, 3H).

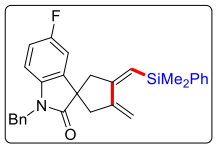
^{13}C NMR (101 MHz, $CDCl_3$) δ 180.4, 156.7, 145.9, 139.2, 137.9, 137.2, 136.1, 133.8, 132.2, 132.1, 129.0, 128.9, 128.0, 127.2, 125.6, 121.9, 121.4, 119.5, 112.6, 50.1, 49.9, 45.8, 45.1, 21.0, 18.8, -1.2, -1.7.

HRMS (ESI): m/z Calcd. for $C_{31}H_{34}NOSi$ $[M+H]^+$: 464.2410, found: 464.2414.





(*Z*)-1'-benzyl-3-((dimethyl(phenyl)silyl)methylene)-5'-fluoro-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (3d)



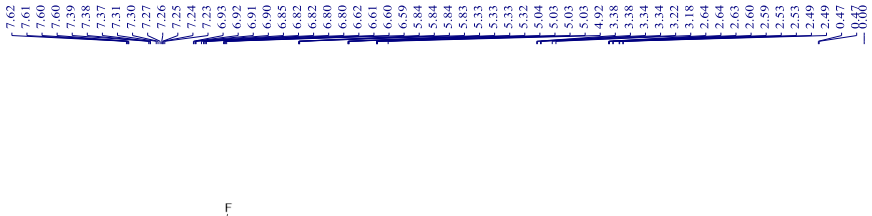
Prepared according to method **E**. The product **3d** was obtained as colorless oil in 59% yield (53.5 mg).

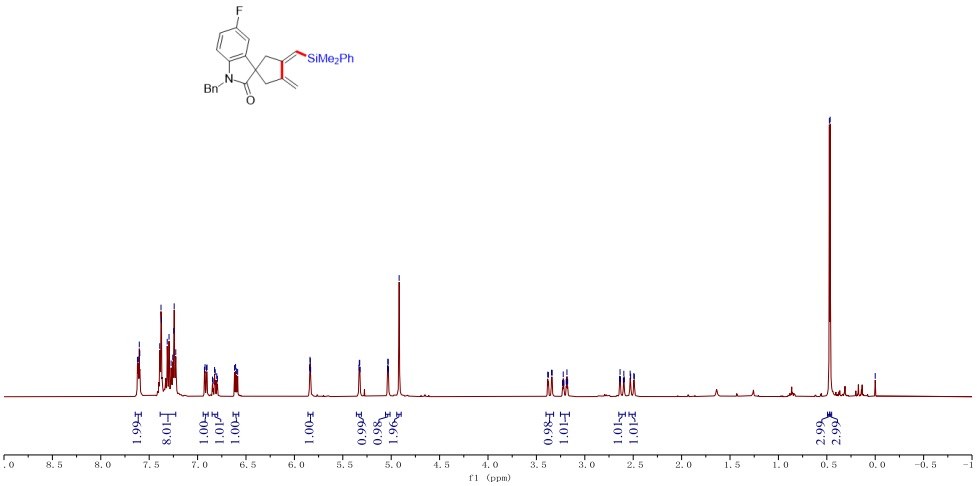
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 2H), 7.42 – 7.20 (m, 8H), 6.92 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.82 (td, *J* = 8.9, 2.6 Hz, 1H), 6.60 (dd, *J* = 8.5, 4.2 Hz, 1H), 5.84 (dd, *J* = 2.6, 1.4 Hz, 1H), 5.33 (dd, *J* = 3.1, 1.4 Hz, 1H), 5.03 (dd, *J* = 2.8, 1.4 Hz, 1H), 4.92 (s, 2H), 3.36 (dd, *J* = 15.7, 2.7 Hz, 1H), 3.20 (dt, *J* = 15.3, 2.9 Hz, 1H), 2.62 (dt, *J* = 15.6, 1.9 Hz, 1H), 2.51 (dd, *J* = 15.1, 1.9 Hz, 1H), 0.47 (s, 3H), 0.46 (s, 3H).

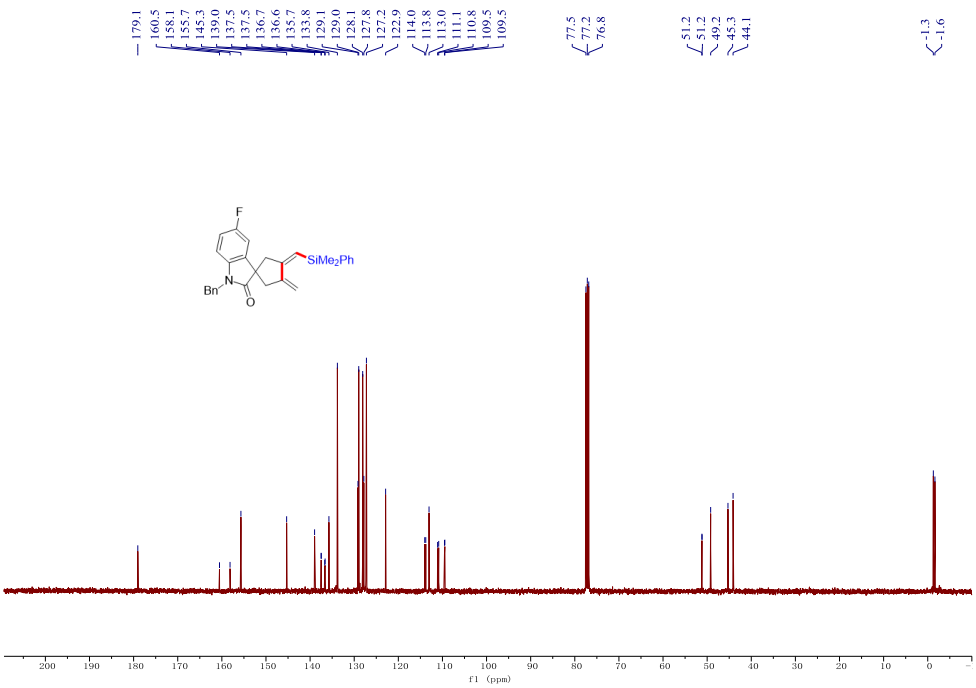
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.1, 159.3 (d, *J* = 240.6 Hz), 155.7, 145.3, 139.0, 137.5 (d, *J* = 2.0 Hz), 136.6 (d, *J* = 8.3 Hz), 135.7, 133.8, 129.2, 129.0, 128.1, 127.8, 127.2, 122.9, 113.9 (d, *J* = 23.5 Hz), 113.0, 111.0 (d, *J* = 25.1 Hz), 109.5 (d, *J* = 8.1 Hz), 51.2 (d, *J* = 1.9 Hz), 49.2, 45.3, 44.1, -1.3, -1.6.

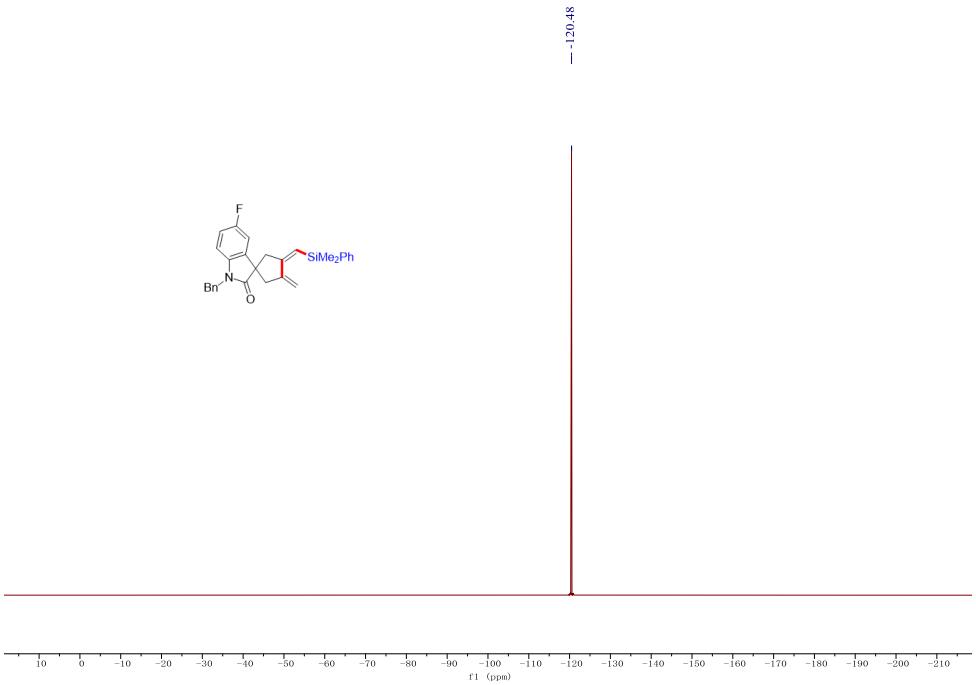
^{19}F NMR (376 MHz, $CDCl_3$) δ -120.48.

HRMS (ESI): m/z Calcd. for $C_{29}H_{29}NOFSi$ $[M+H]^+$: 454.2002, found: 454.2000.

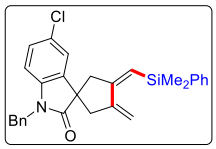





179.1
160.5
158.1
155.7
145.3
139.0
137.5
137.5
136.7
136.6
135.7
133.8
129.1
129.0
128.1
127.8
127.2
122.9
114.0
113.8
113.0
111.1
110.8
109.5
109.5
77.5
77.2
76.8
51.2
51.2
49.2
45.3
44.1
1.3
-1.6
F
SiMe2Ph
Bn
N
O
f1 (ppm)


-120.48
F
SiMe2Ph
Bn
N
O
f1 (ppm)

(*Z*)-1'-benzyl-5'-chloro-3-((dimethyl(phenyl)silyl)methylene)-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (3e)

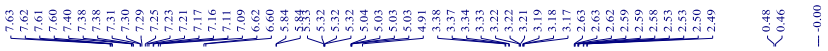


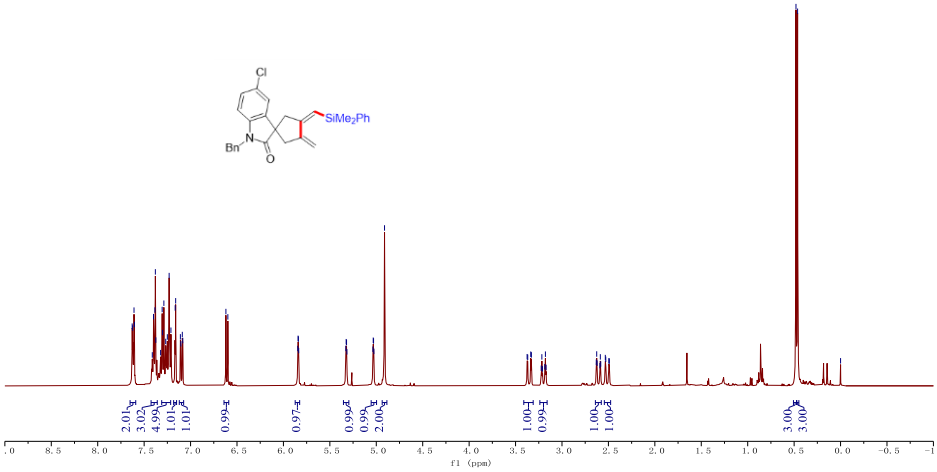
Prepared according to method **E**. The product **3e** was obtained as yellow oil in 80% yield (75.4 mg).

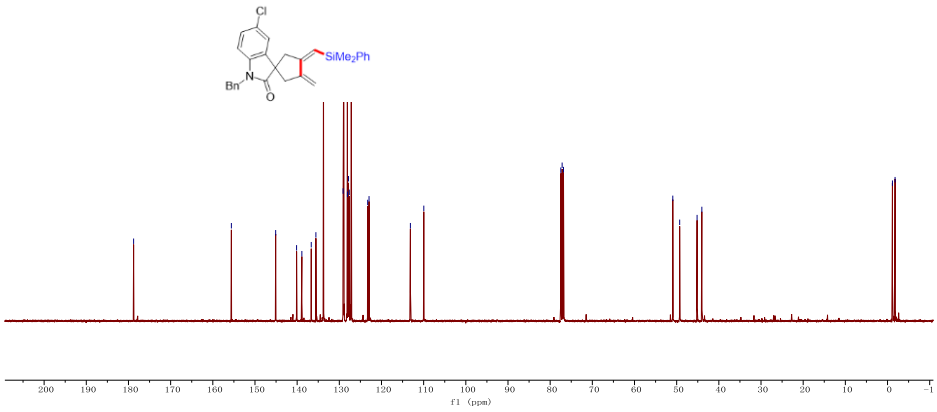
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.42 – 7.35 (m, 3H), 7.33 – 7.20 (m, 5H), 7.16 (d, *J* = 2.1 Hz, 1H), 7.09 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.61 (d, *J* = 8.3 Hz, 1H), 5.84 (dd, *J* = 2.6, 1.4 Hz, 1H), 5.32 (dd, *J* = 3.1, 1.5 Hz, 1H), 5.03 (dd, *J* = 2.8, 1.4 Hz, 1H), 4.91 (s, 2H), 3.35 (dd, *J* = 15.7, 2.7 Hz, 1H), 3.19 (dt, *J* = 15.4, 2.9 Hz, 1H), 2.60 (dt, *J* = 15.7, 1.8 Hz, 1H), 2.51 (dd, *J* = 15.2, 2.0 Hz, 1H), 0.48 (s, 3H), 0.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 155.6, 145.1, 140.1, 138.9, 136.7, 135.6, 133.8, 129.1, 129.0, 128.1, 128.1, 127.8, 127.6, 127.2, 123.3, 123.0, 113.1, 110.0, 50.9, 49.3, 45.2, 44.0, -1.2, -1.8.

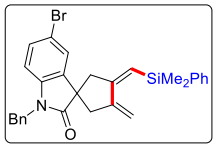
HRMS (ESI): m/z Calcd. for $C_{29}H_{29}NOClSi$ $[M+H]^+$: 470.1707, found: 470.1729.







(*Z*)-1'-benzyl-5'-bromo-3-((dimethyl(phenyl)silyl)methylene)-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (3f)

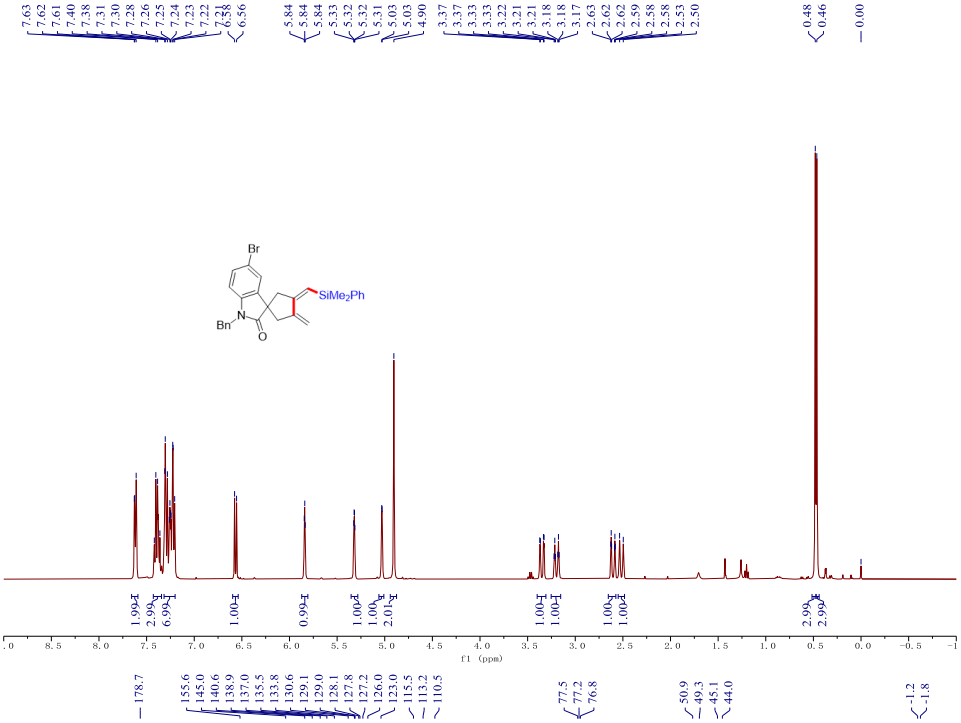


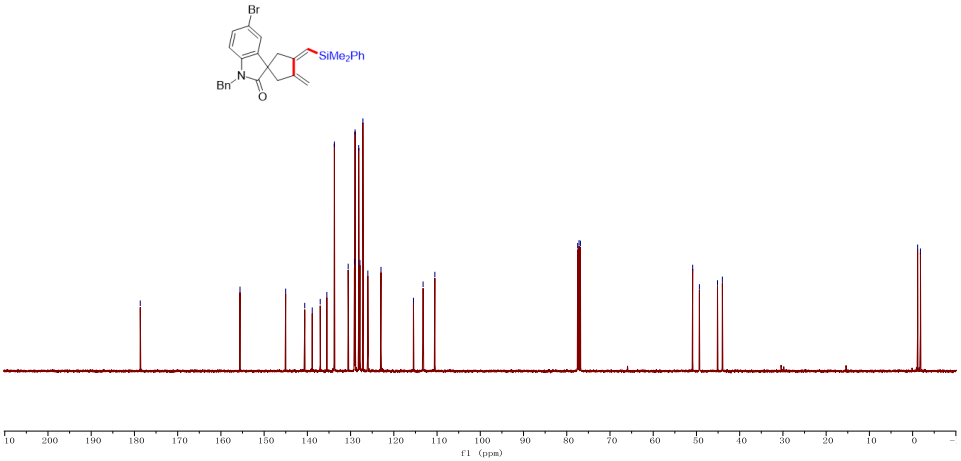
Prepared according to method **E**. The product **3f** was obtained as white solid in 64% yield (65.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 2H), 7.45 – 7.34 (m, 3H), 7.33 – 7.18 (m, 7H), 6.57 (d, *J* = 8.3 Hz, 1H), 5.84 (t, *J* = 1.9 Hz, 1H), 5.32 (dd, *J* = 3.0, 1.4 Hz, 1H), 5.03 (d, *J* = 1.4 Hz, 1H), 4.90 (s, 2H), 3.35 (dd, *J* = 15.5, 2.6 Hz, 1H), 3.20 (dt, *J* = 15.4, 2.9 Hz, 1H), 2.60 (dt, *J* = 15.5, 1.8 Hz, 1H), 2.52 (d, *J* = 15.4 Hz, 1H), 0.48 (s, 3H), 0.46 (s, 3H).

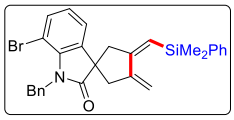
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 155.6, 145.0, 140.6, 138.9, 137.0, 135.5, 133.8, 130.6, 129.1, 129.0, 128.1, 127.8, 127.2, 126.0, 123.0, 115.5, 113.2, 110.5, 50.9, 49.3, 45.1, 44.0, -1.2, -1.8.

HRMS (ESI): m/z Calcd. for $C_{29}H_{29}NOBrSi$ $[M+H]^+$: 514.1202, found: 514.1199.





(*Z*)-1'-benzyl-7'-bromo-3-((dimethyl(phenyl)silyl)methylene)-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (3g)

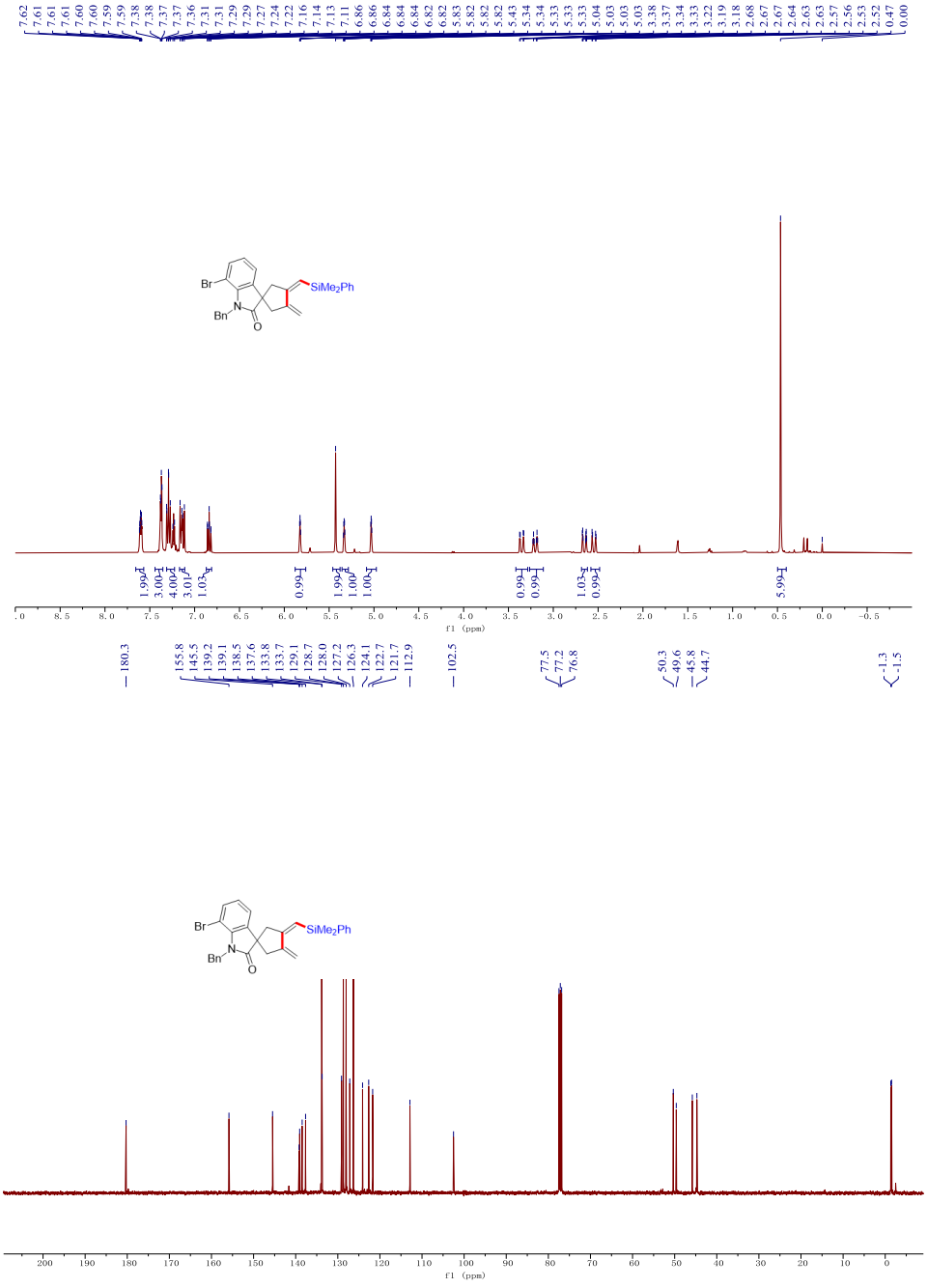


Prepared according to method **E**. The product **3g** was obtained as colorless oil in 61% yield (62.7 mg).

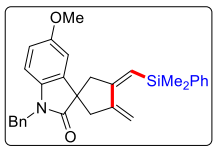
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 2H), 7.42 – 7.34 (m, 3H), 7.34 – 7.20 (m, 4H), 7.14 (dd, *J* = 11.2, 7.7 Hz, 3H), 6.84 (ddd, *J* = 8.1, 7.2, 0.7 Hz, 1H), 5.82 (dd, *J* = 2.6, 1.4 Hz, 1H), 5.43 (s, 2H), 5.33 (dt, *J* = 2.8, 1.3 Hz, 1H), 5.03 (dd, *J* = 2.7, 1.4 Hz, 1H), 3.35 (dd, *J* = 15.9, 2.6 Hz, 1H), 3.20 (dt, *J* = 15.4, 2.9 Hz, 1H), 2.65 (dt, *J* = 16.0, 1.7 Hz, 1H), 2.55 (dd, *J* = 15.5, 1.9 Hz, 1H), 0.47 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.3, 155.9, 145.5, 139.2, 139.1, 138.5, 137.7, 133.8, 133.7, 129.1, 128.7, 128.0, 127.2, 126.3, 124.1, 122.7, 121.7, 112.9, 102.5, 50.3, 49.6, 45.8, 44.7, -1.3, -1.5.

HRMS (ESI): m/z Calcd. for $C_{29}H_{29}NOBrSi$ $[M+H]^+$: 514.1202, found: 514.1201.



(*Z*)-1'-benzyl-3-((dimethyl(phenyl)silyl)methylene)-5'-methoxy-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (3h)

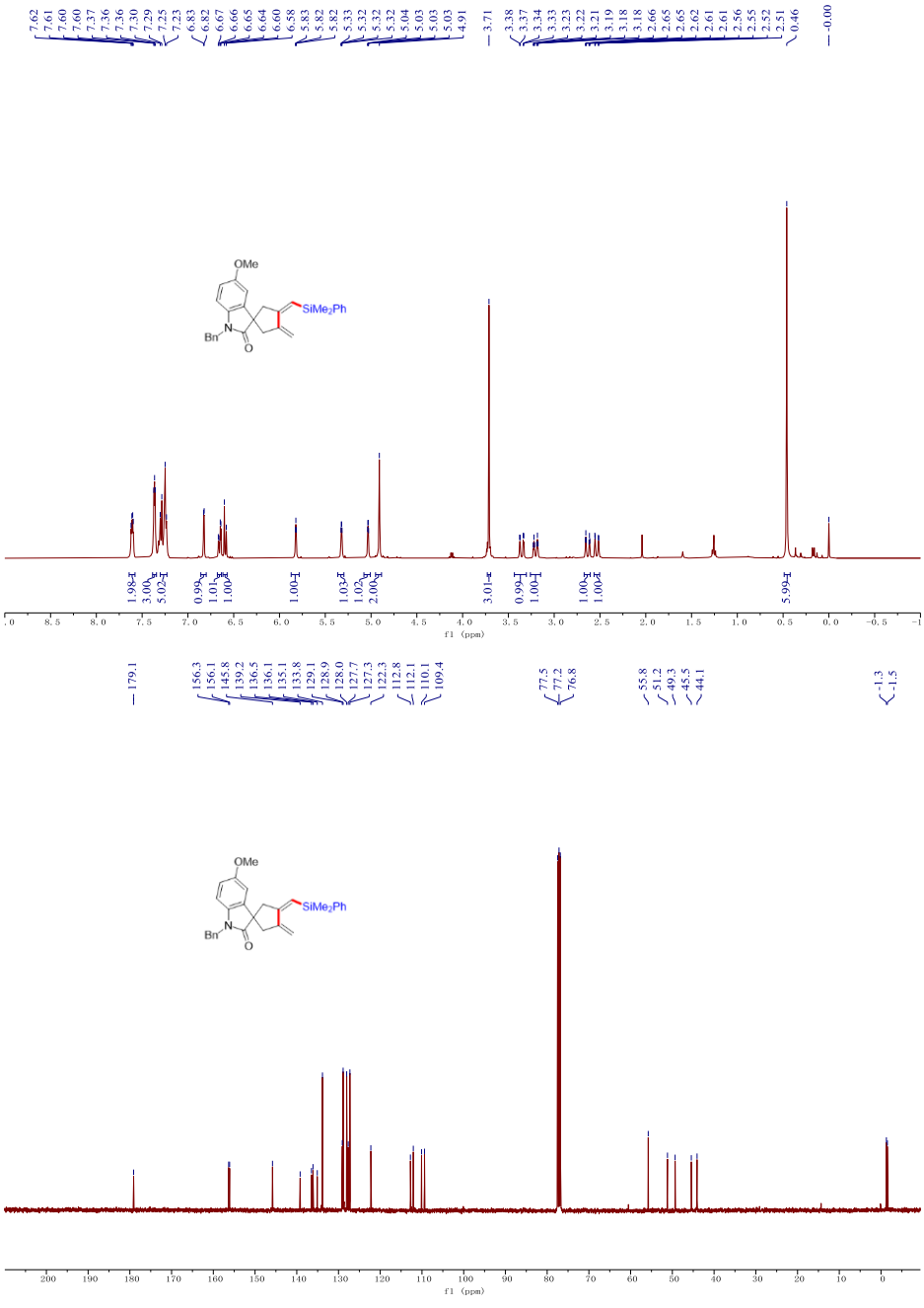


Prepared according to method **E**. The product **3h** was obtained as yellow oil in 70% yield (65.1 mg).

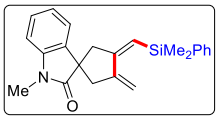
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 2H), 7.40 – 7.33 (m, 3H), 7.33 – 7.21 (m, 5H), 6.83 (d, *J* = 2.5 Hz, 1H), 6.65 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.59 (d, *J* = 8.5 Hz, 1H), 5.82 (t, *J* = 2.0 Hz, 1H), 5.32 (dd, *J* = 3.1, 1.4 Hz, 1H), 5.03 (dd, *J* = 2.7, 1.4 Hz, 1H), 4.91 (s, 2H), 3.71 (s, 3H), 3.35 (dd, *J* = 15.8, 2.7 Hz, 1H), 3.20 (dt, *J* = 15.3, 2.9 Hz, 1H), 2.63 (dt, *J* = 15.8, 1.8 Hz, 1H), 2.53 (dd, *J* = 15.2, 1.9 Hz, 1H), 0.46 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.1, 156.3, 156.1, 145.8, 139.2, 136.5, 136.1, 135.1, 133.8, 129.1, 128.9, 128.0, 127.7, 127.3, 122.3, 112.8, 112.1, 110.1, 109.4, 55.8, 51.2, 49.3, 45.5, 44.1, -1.3, -1.5.

HRMS (ESI): m/z Calcd. for $C_{30}H_{32}NO_2Si$ $[M+H]^+$: 466.2202, found: 466.2198.



(*Z*)-3-((dimethyl(phenyl)silyl)methylene)-1'-methyl-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (3i)

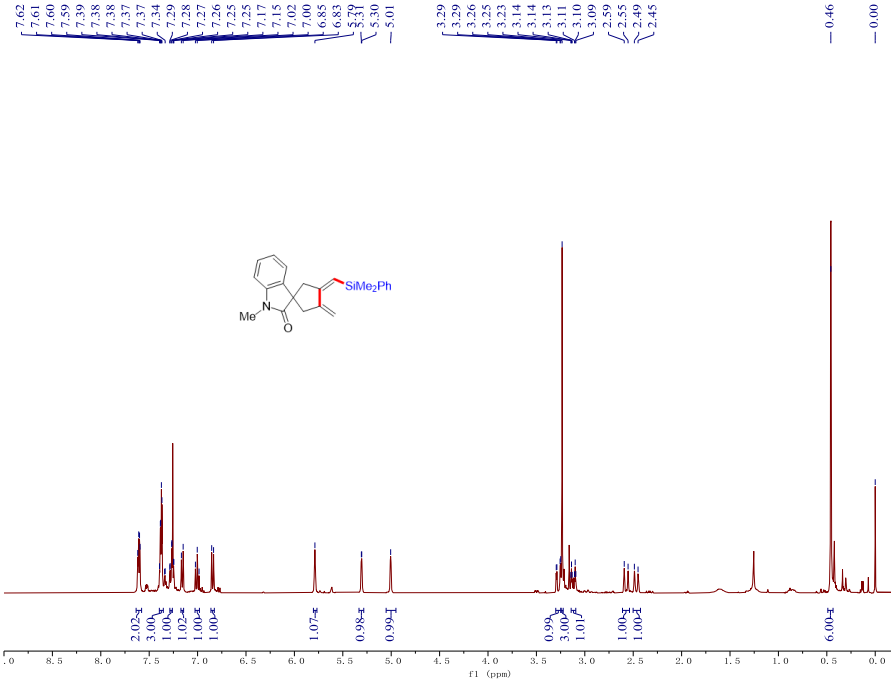


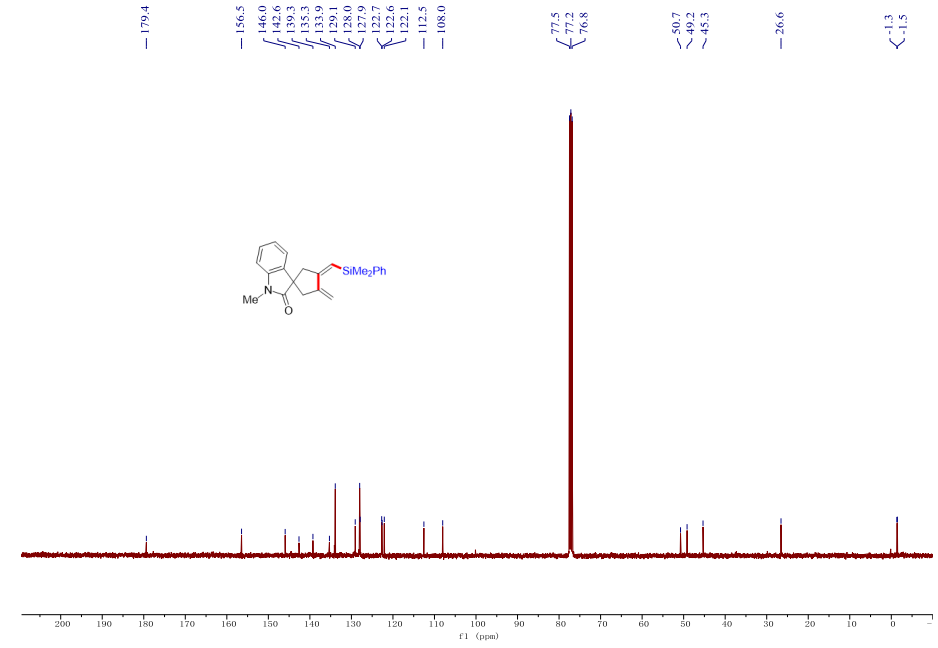
Prepared according to method **E**. The product **3i** was obtained as yellow oil in 53% yield (38.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.40 – 7.35 (m, 3H), 7.27 (td, *J* = 7.7, 1.1 Hz, 1H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 5.79 (s, 1H), 5.31 (d, *J* = 1.5 Hz, 1H), 5.01 (s, 1H), 3.27 (dd, *J* = 15.9, 2.6 Hz, 1H), 3.23 (s, 3H), 3.12 (dt, *J* = 15.3, 2.8 Hz, 1H), 2.57 (d, *J* = 15.8 Hz, 1H), 2.47 (d, *J* = 15.2 Hz, 1H), 0.46 (s, 6H).

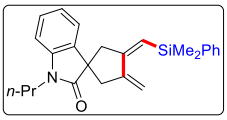
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.4, 156.5, 146.0, 142.6, 139.3, 135.3, 133.9, 129.1, 128.0, 127.9, 122.7, 122.6, 122.1, 112.6, 108.0, 50.8, 49.2, 45.3, 26.6, -1.3, -1.5.

HRMS (ESI): m/z Calcd. for $C_{23}H_{26}NOSi$ $[M+H]^+$: 360.1784, found: 360.1781.





(*Z*)-3-((dimethyl(phenyl)silyl)methylene)-4-methylene-1'-propylspiro[cyclopentane-1,3'-indolin]-2'-one (3j)

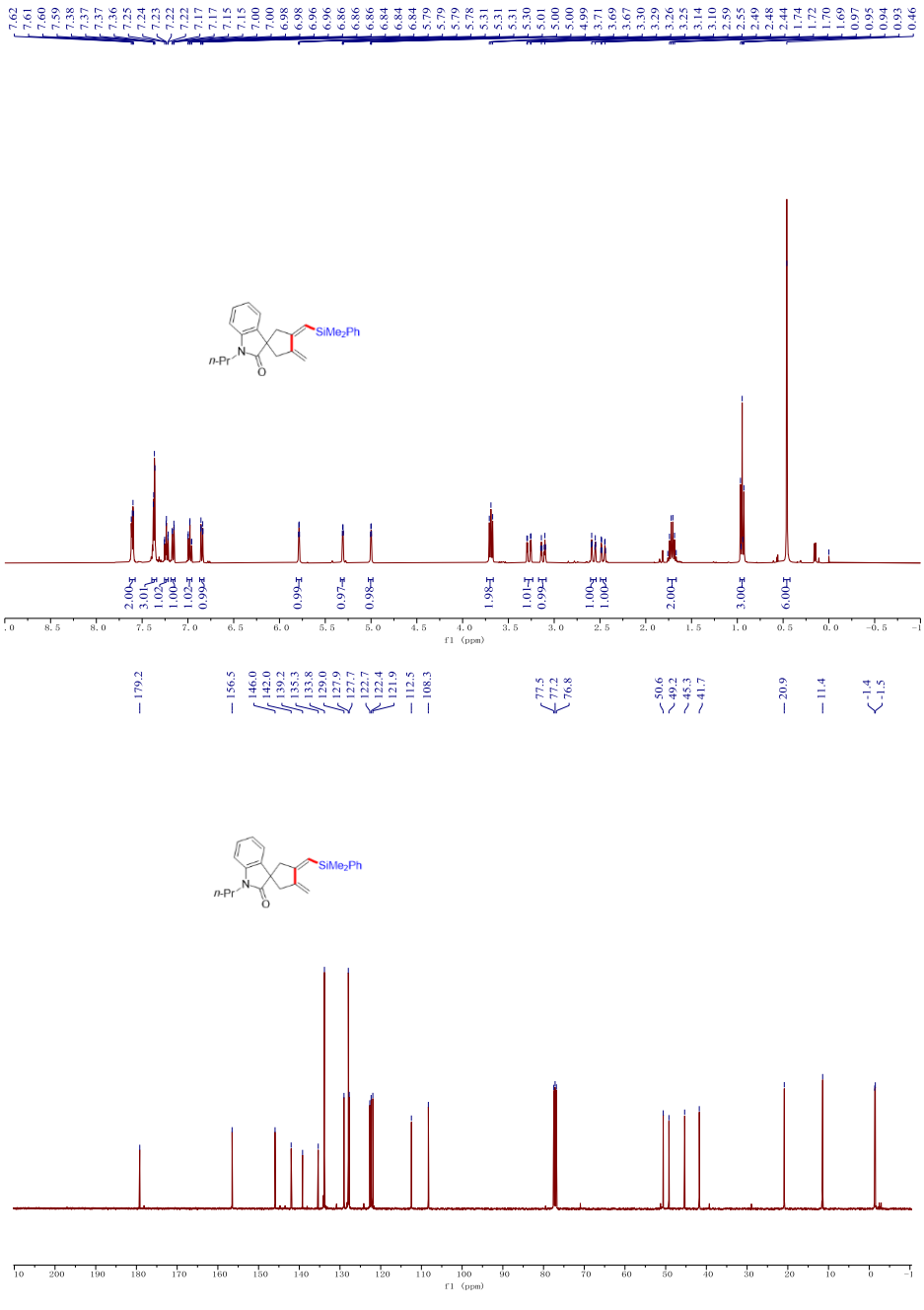


Prepared according to method **E**. The product **3j** was obtained as yellow oil in 76% yield (58.3 mg).

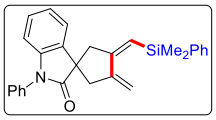
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.40 – 7.34 (m, 3H), 7.27 – 7.21 (m, 1H), 7.16 (dd, *J* = 7.4, 1.2 Hz, 1H), 6.98 (td, *J* = 7.5, 1.0 Hz, 1H), 6.85 (dt, *J* = 7.8, 0.7 Hz, 1H), 5.79 (dd, *J* = 2.7, 1.5 Hz, 1H), 5.31 (dd, *J* = 3.1, 1.4 Hz, 1H), 5.00 (dd, *J* = 2.8, 1.4 Hz, 1H), 3.69 (t, *J* = 7.3 Hz, 2H), 3.28 (dd, *J* = 15.8, 2.7 Hz, 1H), 3.12 (dt, *J* = 15.3, 2.8 Hz, 1H), 2.57 (dt, *J* = 15.8, 1.8 Hz, 1H), 2.46 (dt, *J* = 15.2, 1.7 Hz, 1H), 1.71 (h, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.46 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.2, 156.5, 146.0, 142.0, 139.2, 135.4, 133.8, 129.0, 128.0, 127.7, 122.7, 122.4, 121.9, 112.5, 108.3, 50.6, 49.2, 45.3, 41.7, 20.9, 11.4, -1.4, -1.5.

HRMS (ESI): m/z Calcd. for $C_{25}H_{30}NOSi$ $[M+H]^+$: 388.2097, found: 388.2093.



(*Z*)-3-((dimethyl(phenyl)silyl)methylene)-4-methylene-1'-phenylspiro[cyclopentane-1,3'-indolin]-2'-one (3k)

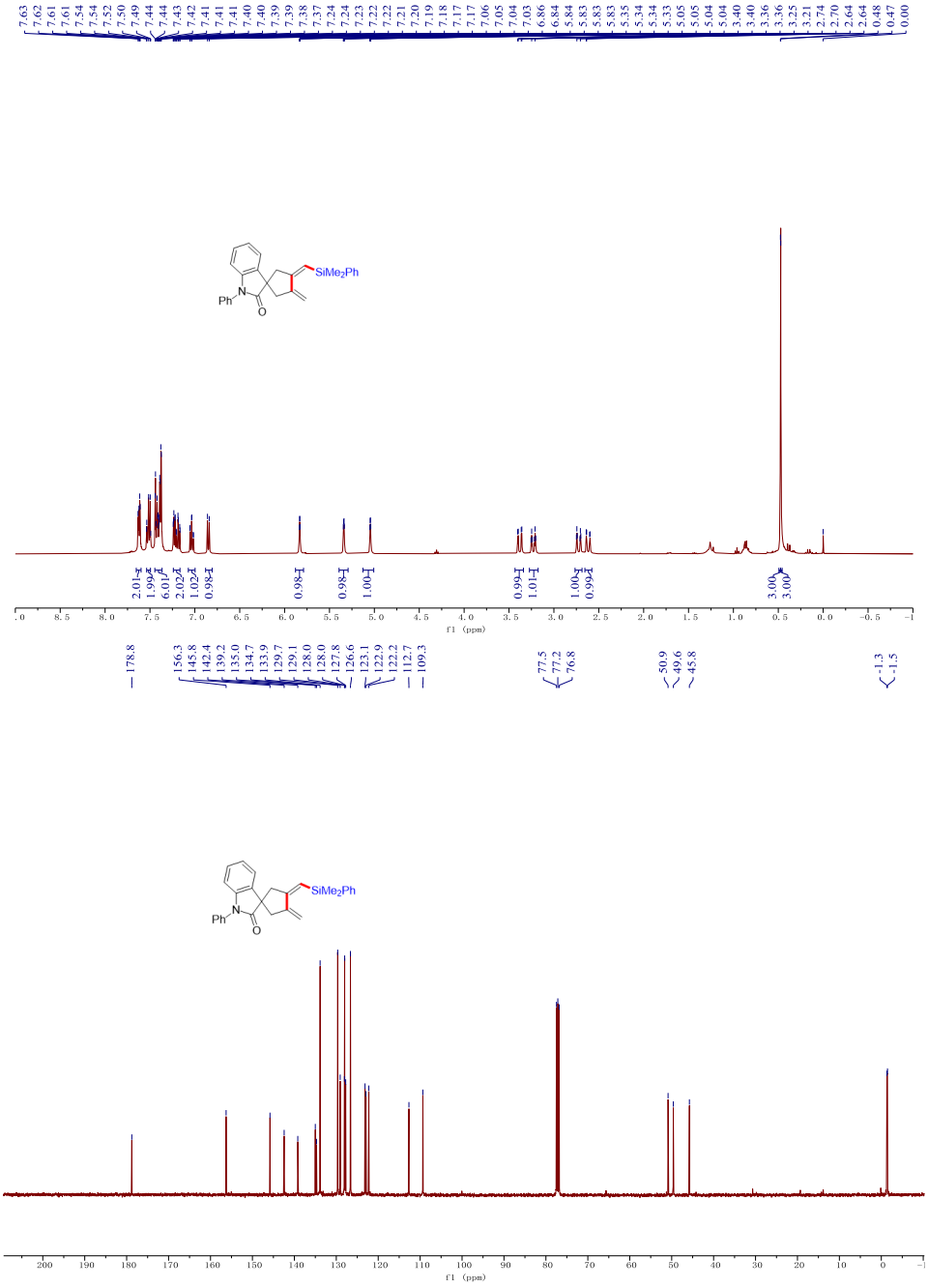


Prepared according to method **E**. The product **3k** was obtained as white solid in 69% yield (58.0 mg).

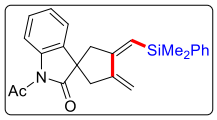
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.58 (m, 2H), 7.55 – 7.48 (m, 2H), 7.45 – 7.36 (m, 6H), 7.26 – 7.16 (m, 2H), 7.04 (td, *J* = 7.5, 1.1 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 5.83 (dd, *J* = 2.6, 1.5 Hz, 1H), 5.34 (dd, *J* = 3.1, 1.4 Hz, 1H), 5.05 (dd, *J* = 2.7, 1.4 Hz, 1H), 3.38 (dd, *J* = 15.8, 2.7 Hz, 1H), 3.23 (dt, *J* = 15.3, 2.8 Hz, 1H), 2.72 (dt, *J* = 15.8, 1.9 Hz, 1H), 2.62 (dd, *J* = 15.2, 1.7 Hz, 1H), 0.48 (s, 3H), 0.47 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 156.3, 145.8, 142.4, 139.2, 135.0, 134.7, 133.9, 129.7, 129.1, 128.1, 128.0, 127.8, 126.6, 123.2, 122.9, 122.2, 112.7, 109.3, 50.9, 49.6, 45.8, -1.3, -1.5.

HRMS (ESI): m/z Calcd. for $C_{28}H_{28}NOSi$ $[M+H]^+$: 422.1940, found: 422.1939.



(*Z*)-1'-acetyl-3-((dimethyl(phenyl)silyl)methylene)-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (3l)

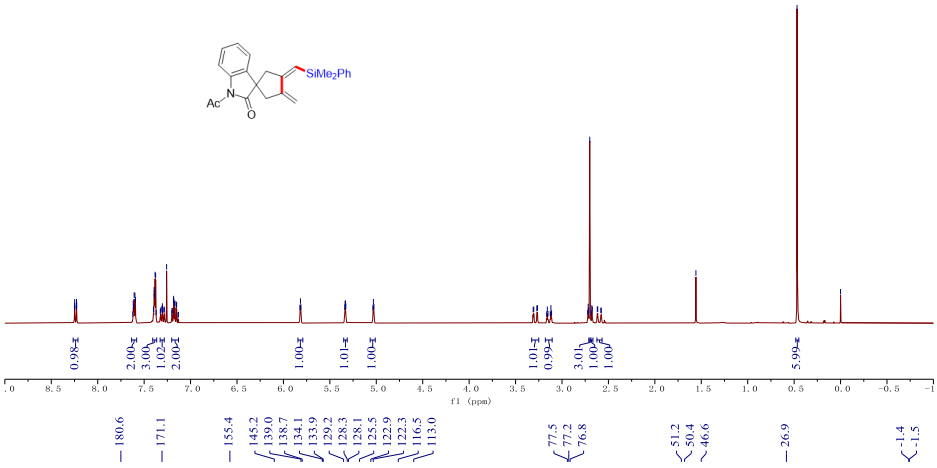


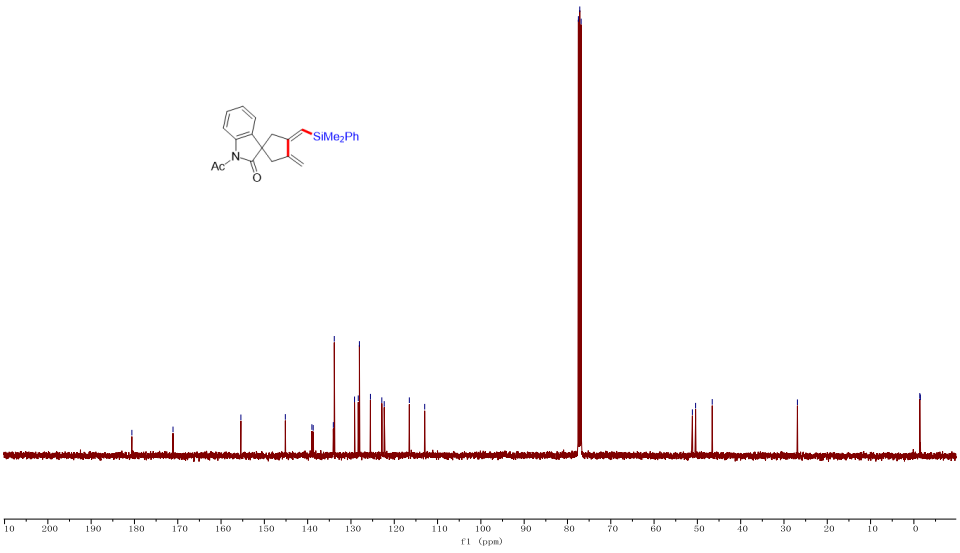
Prepared according to method **E**. The product **3l** was obtained as white solid in 49% yield (37.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dt, *J* = 8.1, 0.8 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.42 – 7.37 (m, 3H), 7.31 (ddd, *J* = 8.3, 7.2, 1.9 Hz, 1H), 7.21 – 7.13 (m, 2H), 5.82 (t, *J* = 2.1 Hz, 1H), 5.34 (dd, *J* = 3.0, 1.6 Hz, 1H), 5.03 (t, *J* = 2.1 Hz, 1H), 3.29 (dd, *J* = 15.9, 2.6 Hz, 1H), 3.14 (dt, *J* = 15.4, 2.8 Hz, 1H), 2.70 (s, 3H), 2.69 (dt, *J* = 15.7, 1.9 Hz, 1H), 2.60 (dd, *J* = 15.4, 1.8 Hz, 1H), 0.47 (s, 6H).

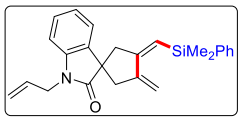
^{13}C NMR (101 MHz, $CDCl_3$) δ 180.6, 171.1, 155.4, 145.2, 139.0, 138.7, 134.1, 133.9, 129.2, 128.3, 128.1, 125.5, 122.9, 122.3, 116.5, 113.0, 51.2, 50.4, 46.6, 26.9, -1.4, -1.5.

HRMS (ESI): m/z Calcd. for $C_{24}H_{26}NO_2Si$ $[M+H]^+$: 388.1733, found: 388.1724.





(*Z*)-1'-allyl-3-((dimethyl(phenyl)silyl)methylene)-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (3m)

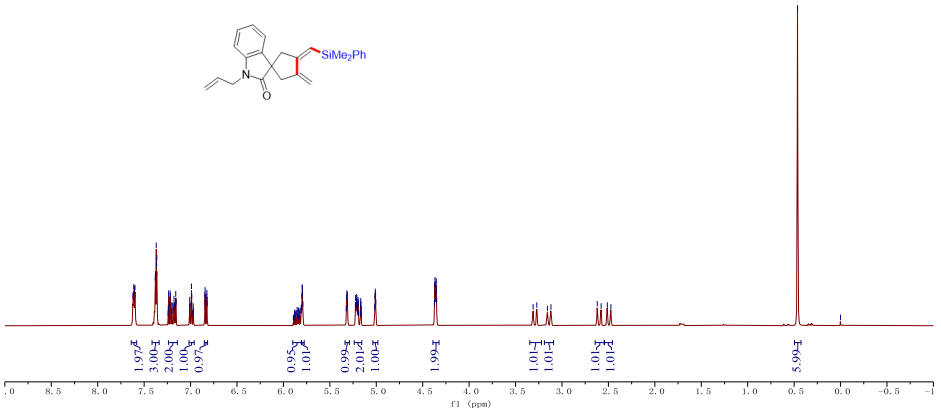


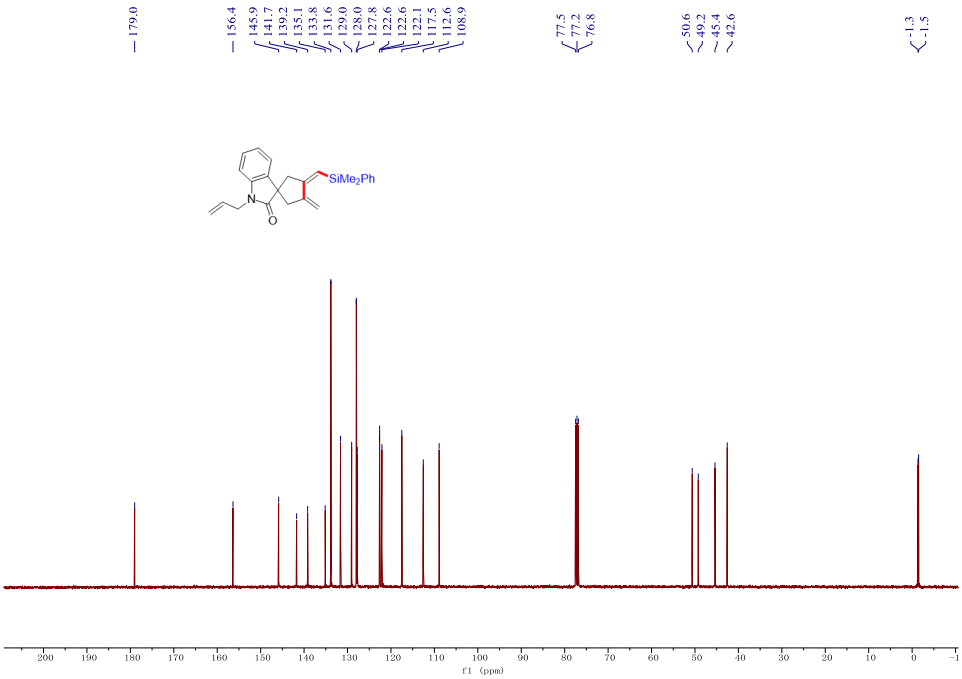
Prepared according to method **E**. The product **3m** was obtained as colorless crystal in 65% yield (50.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.40 – 7.34 (m, 3H), 7.24 – 7.13 (m, 2H), 6.98 (tt, *J* = 7.5, 1.0 Hz, 1H), 6.83 (dt, *J* = 7.7, 0.8 Hz, 1H), 5.89 – 5.80 (m, 1H), 5.80 – 5.78 (m, 1H), 5.31 (dt, *J* = 2.9, 1.4 Hz, 1H), 5.24 – 5.14 (m, 2H), 5.00 (dt, *J* = 2.5, 1.2 Hz, 1H), 4.36 (ddd, *J* = 5.3, 2.2, 1.2 Hz, 2H), 3.29 (d, *J* = 15.9 Hz, 1H), 3.13 (d, *J* = 15.3 Hz, 1H), 2.60 (d, *J* = 17.0 Hz, 1H), 2.49 (d, *J* = 15.4 Hz, 1H), 0.46 (s, 6H).

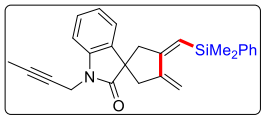
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 156.4, 145.9, 141.7, 139.2, 135.1, 133.8, 131.6, 129.1, 128.0, 127.8, 122.6, 122.6, 122.1, 117.5, 112.6, 108.9, 50.6, 49.2, 45.4, 42.6, -1.4, -1.5.

HRMS (ESI): m/z Calcd. for $C_{25}H_{28}NOSi$ $[M+H]^+$: 386.1940, found: 386.1942.





(*Z*)-1'-(but-2-yn-1-yl)-3-((dimethyl(phenyl)silyl)methylene)-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (3n)

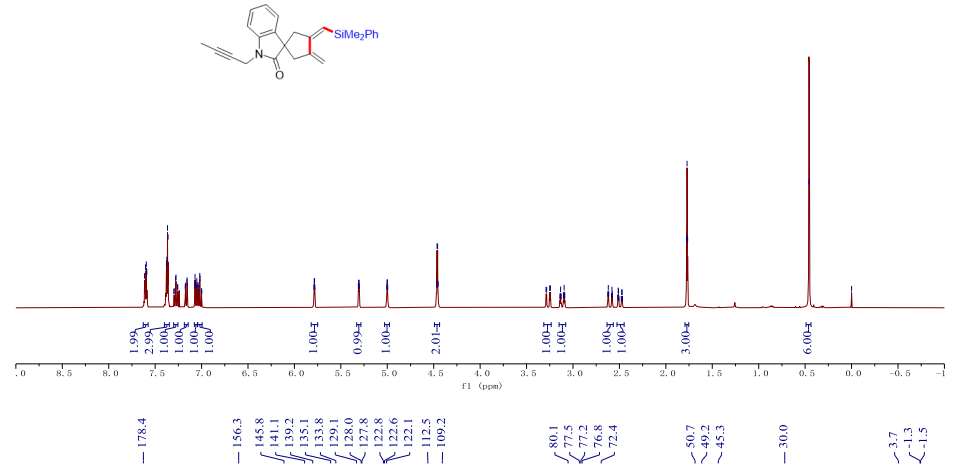


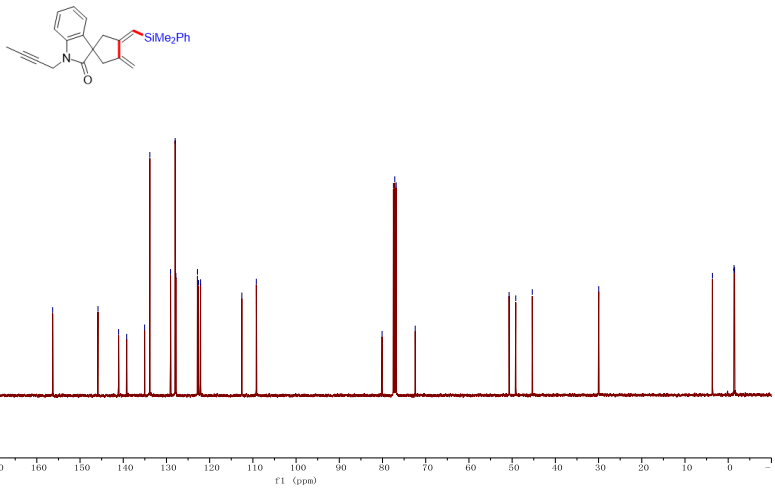
Prepared according to method **E**. The product **3n** was obtained as yellow oil in 78% yield (62.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.39 – 7.34 (m, 3H), 7.28 (td, *J* = 7.7, 1.3 Hz, 1H), 7.18 – 7.15 (m, 1H), 7.06 (dt, *J* = 7.7, 0.8 Hz, 1H), 7.02 (td, *J* = 7.5, 1.0 Hz, 1H), 5.78 (dd, *J* = 2.6, 1.5 Hz, 1H), 5.30 (dd, *J* = 3.0, 1.5 Hz, 1H), 5.00 (dd, *J* = 2.8, 1.4 Hz, 1H), 4.46 (q, *J* = 2.4 Hz, 2H), 3.27 (dd, *J* = 15.8, 2.7 Hz, 1H), 3.11 (dt, *J* = 15.3, 2.8 Hz, 1H), 2.60 (dt, *J* = 15.8, 1.9 Hz, 1H), 2.49 (dq, *J* = 15.3, 1.7 Hz, 1H), 1.77 (t, *J* = 2.4 Hz, 3H), 0.46 (s, 6H).

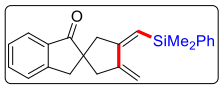
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 156.3, 145.8, 141.1, 139.2, 135.1, 133.9, 129.1, 128.0, 127.8, 122.8, 122.6, 122.1, 112.6, 109.2, 80.1, 72.4, 50.7, 49.2, 45.3, 30.0, 3.7, -1.4, -1.5.

HRMS (ESI): m/z Calcd. for $C_{26}H_{28}NOSi$ $[M+H]^+$: 398.1940, found: 398.1940.





(*Z*)-3-((dimethyl(phenyl)silyl)methylene)-4-methylenespiro[cyclopentane-1,2'-inden]-1'(3'*H*)-one (3o)

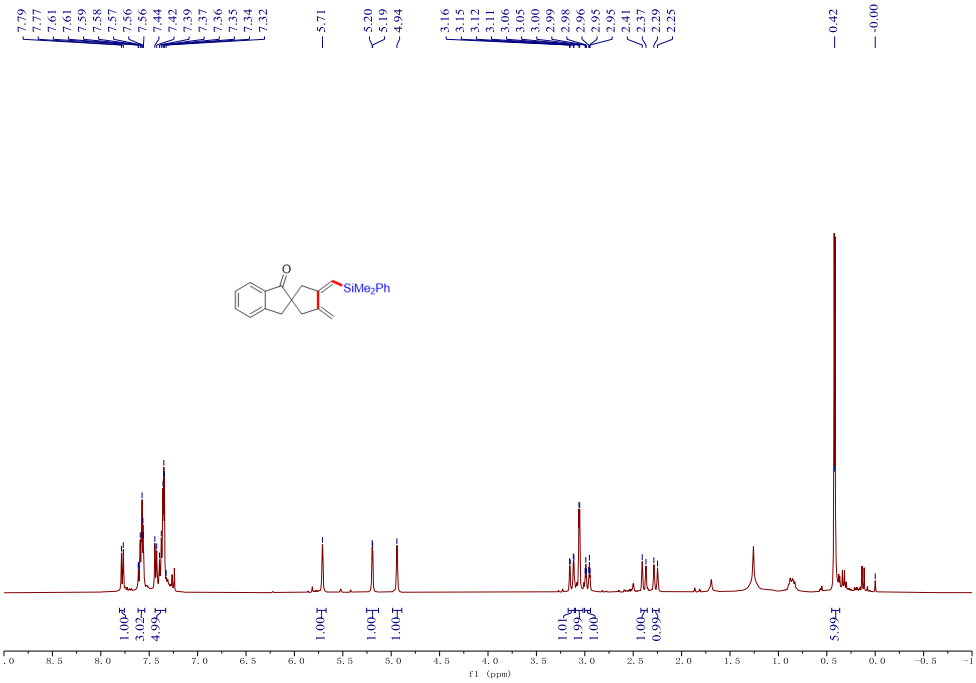


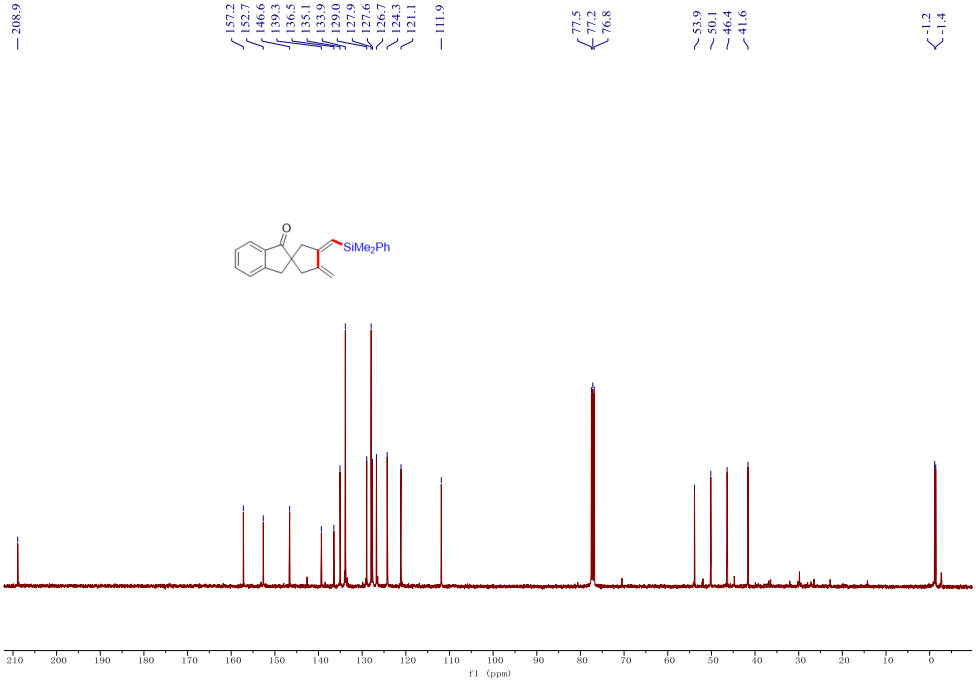
Prepared according to method **E**. The product **3o** was isolated in 79% yield (54.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.62 – 7.54 (m, 3H), 7.45 – 7.32 (m, 5H), 5.71 (s, 1H), 5.19 (d, *J* = 1.8 Hz, 1H), 4.94 (s, 1H), 3.13 (dd, *J* = 15.6, 2.5 Hz, 1H), 3.06 (d, *J* = 3.0 Hz, 2H), 2.97 (dt, *J* = 14.9, 2.7 Hz, 1H), 2.39 (d, *J* = 15.5 Hz, 1H), 2.27 (d, *J* = 15.2 Hz, 1H), 0.42 (s, 6H).

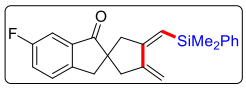
^{13}C NMR (101 MHz, $CDCl_3$) δ 208.9, 157.2, 152.7, 146.6, 139.4, 136.5, 135.1, 133.9, 129.0, 127.9, 127.6, 126.7, 124.3, 121.1, 111.9, 53.9, 50.1, 46.4, 41.6, -1.2, -1.4.

HRMS (ESI): m/z Calcd. for $C_{23}H_{25}OSi$ $[M+H]^+$: 345.1675, found: 345.1674.





(*Z*)-3-((dimethyl(phenyl)silyl)methylene)-6'-fluoro-4-methylenespiro[cyclopentane-1,2'-inden]-1'(3'*H*)-one (3p)



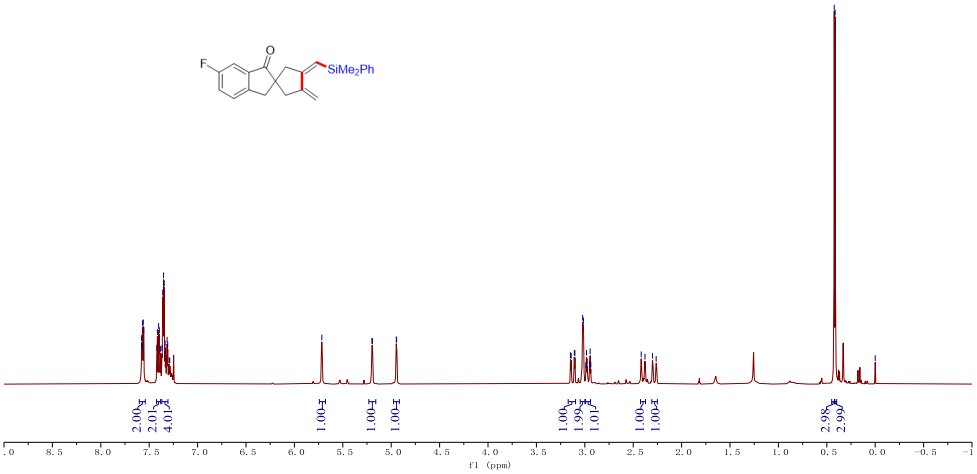
Prepared according to method **E**, and the product **3p** was obtained as yellow oil in 72% yield (51.9 mg).

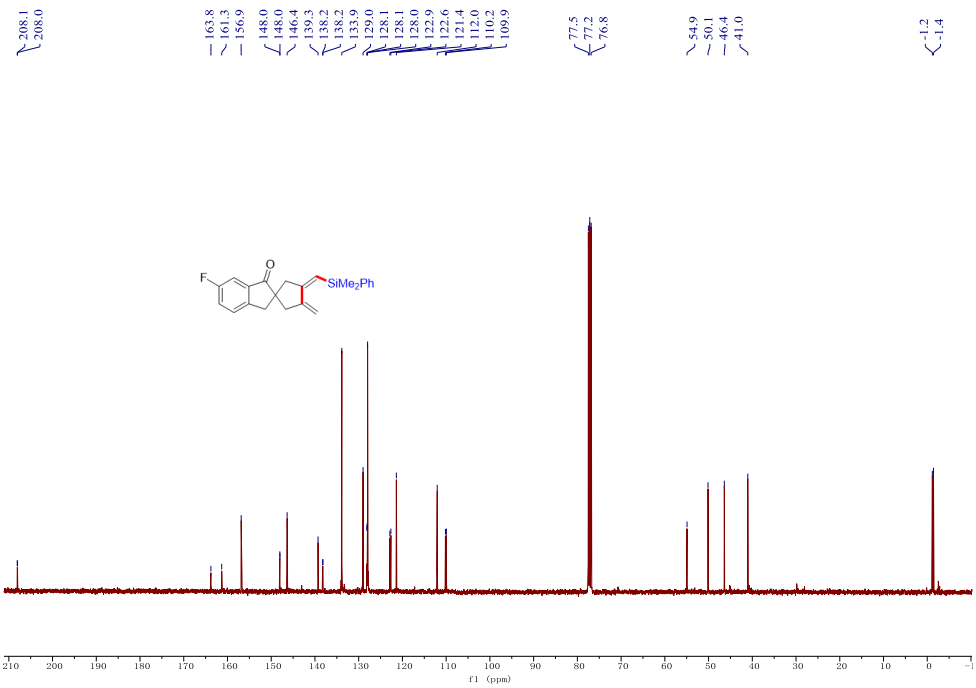
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.43 – 7.37 (m, 2H), 7.37 – 7.30 (m, 4H), 5.72 (s, 1H), 5.20 (d, *J* = 1.9 Hz, 1H), 4.95 (d, *J* = 1.1 Hz, 1H), 3.12 (dd, *J* = 15.6, 2.6 Hz, 1H), 3.02 (d, *J* = 3.2 Hz, 2H), 2.96 (dt, *J* = 14.9, 2.8 Hz, 1H), 2.40 (d, *J* = 15.5 Hz, 1H), 2.28 (d, *J* = 15.0 Hz, 1H), 0.42 (s, 3H), 0.41 (s, 3H).

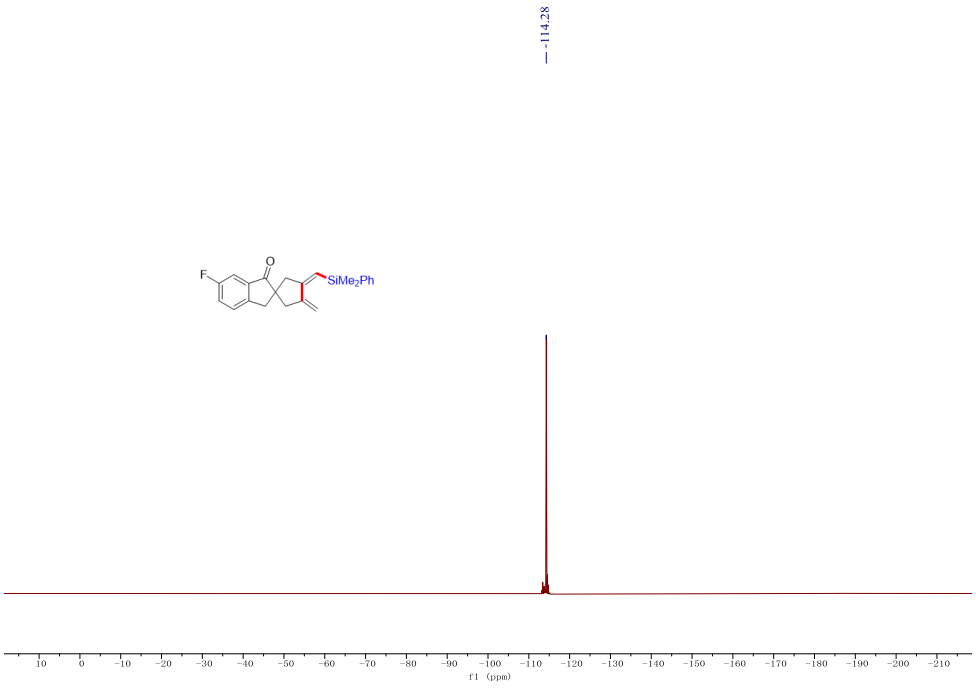
^{13}C NMR (101 MHz, $CDCl_3$) δ 208.0 (d, *J* = 2.7 Hz), 162.6 (d, *J* = 248.2 Hz), 156.9, 148.0 (d, *J* = 2.0 Hz), 146.4, 139.3, 138.2 (d, *J* = 7.1 Hz), 133.9, 129.0, 128.1 (d, *J* = 7.9 Hz), 128.0, 122.8 (d, *J* = 23.7 Hz), 121.4, 112.0, 110.1 (d, *J* = 21.7 Hz), 54.9, 50.1, 46.4, 41.0, -1.2, -1.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.28.

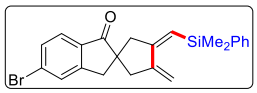
HRMS (ESI): m/z Calcd. for $C_{23}H_{24}FOSi$ $[M+H]^+$: 363.1580, found: 363.1583.




208.1
208.0
163.8
161.3
156.9
148.0
148.0
146.4
139.3
138.2
138.2
133.9
129.0
128.1
128.1
128.0
122.9
122.6
121.4
112.0
110.2
109.9
77.5
77.2
76.8
54.9
50.1
46.4
41.0
-1.2
-1.4
F
O
SiMe2Ph
f1 (ppm)


-114.28
F
O
SiMe2Ph
f1 (ppm)

(*Z*)-5'-bromo-3-((dimethyl(phenyl)silyl)methylene)-4-methylenespiro[cyclopentane-1,2'-inden]-1'(3'*H*)-one (3q)

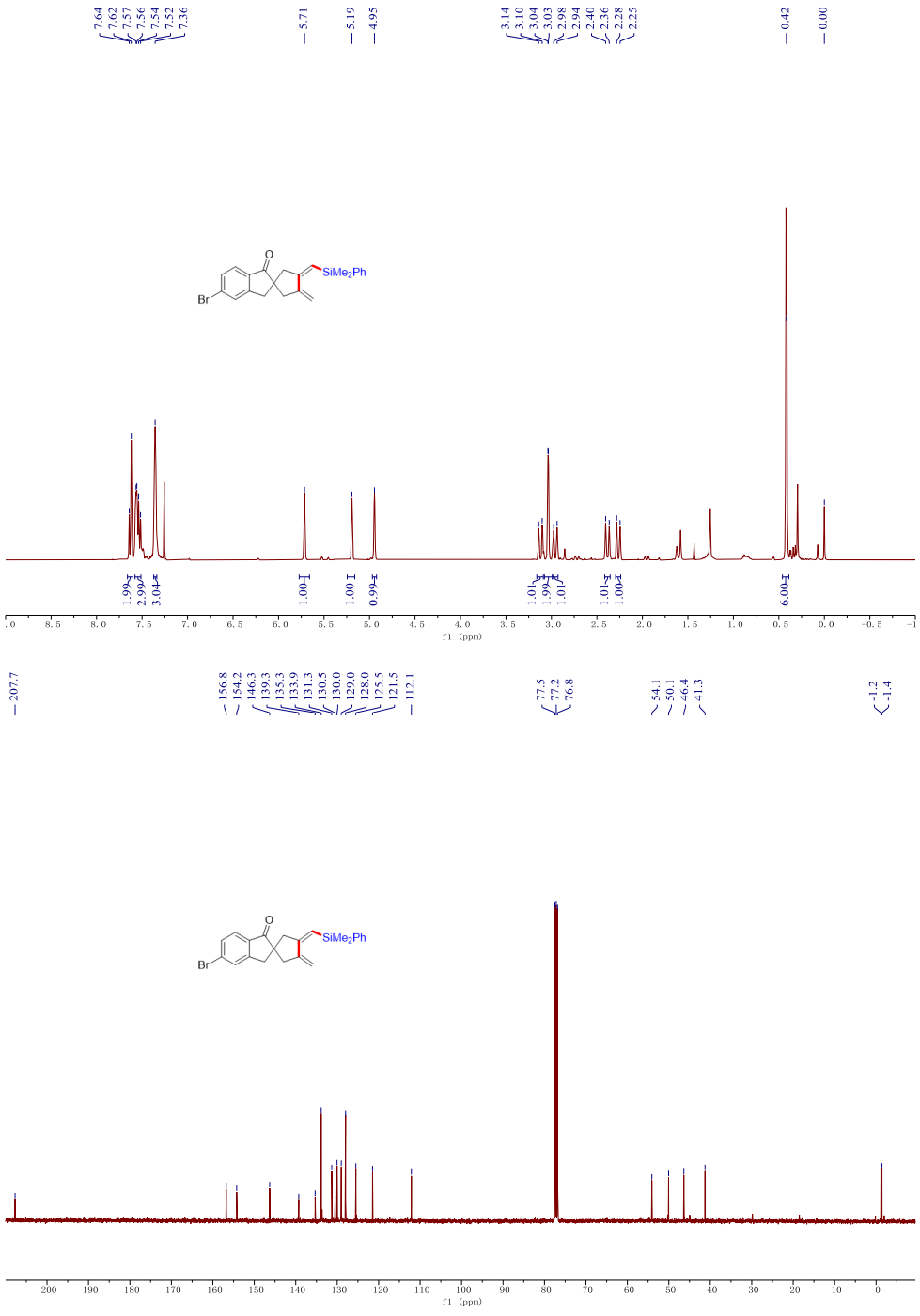


Prepared according to method **E**, and the product **3q** was obtained as yellow oil in 65% yield (55.0 mg).

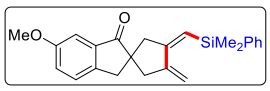
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 2H), 7.59 – 7.48 (m, 3H), 7.38 – 7.33 (m, 3H), 5.71 (s, 1H), 5.19 (s, 1H), 4.95 (s, 1H), 3.12 (d, *J* = 15.5 Hz, 1H), 3.04 (d, *J* = 1.8 Hz, 2H), 2.96 (d, *J* = 15.1 Hz, 1H), 2.38 (d, *J* = 15.8 Hz, 1H), 2.26 (d, *J* = 15.0 Hz, 1H), 0.42 (s, 6H),.

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.7, 156.8, 154.3, 146.3, 139.3, 135.3, 133.9, 131.3, 130.5, 130.0, 129.0, 128.0, 125.5, 121.5, 112.1, 54.1, 50.1, 46.4, 41.3, -1.2, -1.4.

HRMS (ESI): m/z Calcd. for $C_{23}H_{24}OBrSi$ $[M+H]^+$: 423.0780, found: 423.0780.



(*Z*)-3-((dimethyl(phenyl)silyl)methylene)-6'-methoxy-4-methylenespiro[cyclopentane-1,2'-inden]-1'(3'*H*)-one (3r)

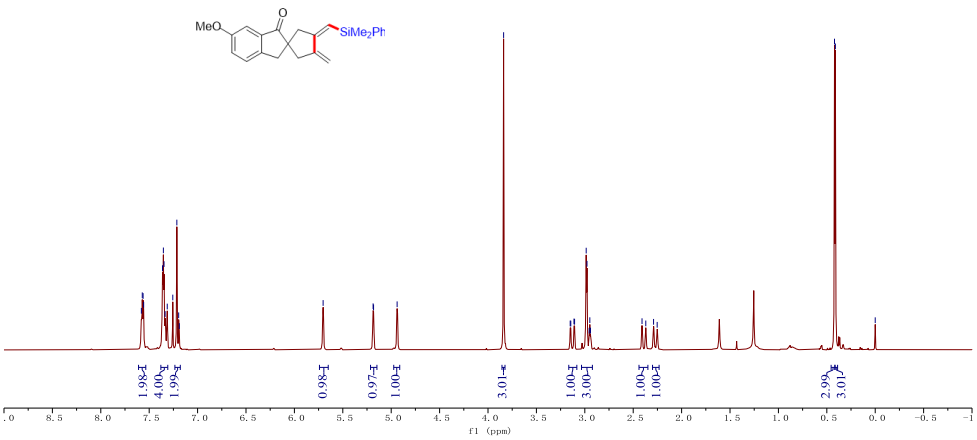


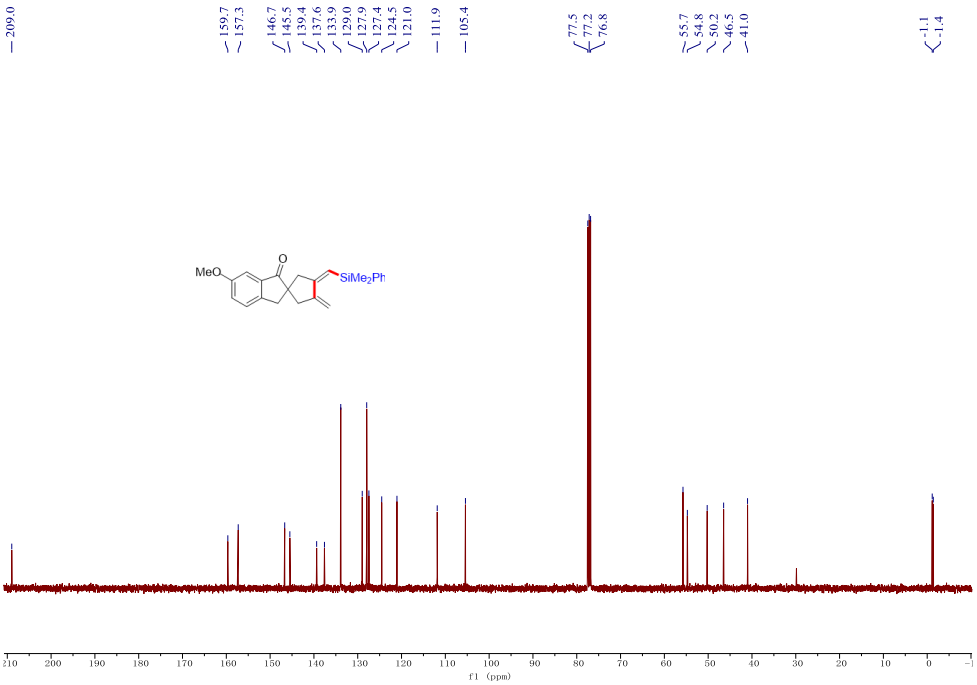
Prepared according to method **E**, and the product **3r** was obtained as yellow oil in 75% yield (55.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H), 7.38 – 7.30 (m, 4H), 7.23 – 7.18 (m, 2H), 5.70 (s, 1H), 5.18 (d, *J* = 1.9 Hz, 1H), 4.94 (s, 1H), 3.84 (s, 3H), 3.13 (dd, *J* = 15.7, 2.4 Hz, 1H), 3.01 – 2.92 (m, 3H), 2.39 (d, *J* = 15.5 Hz, 1H), 2.27 (d, *J* = 14.9 Hz, 1H), 0.42 (s, 3H), 0.41 (s, 3H).

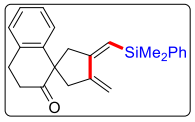
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.0, 159.7, 157.3, 146.7, 145.5, 139.4, 137.6, 133.9, 129.0, 128.0, 127.5, 124.5, 121.0, 111.9, 105.4, 55.8, 54.8, 50.2, 46.5, 41.0, -1.2, -1.4.

HRMS (ESI): m/z Calcd. for $C_{24}H_{27}O_2Si$ $[M+H]^+$: 375.1780, found: 375.1782.





(*Z*)-3-((dimethyl(phenyl)silyl)methylene)-4-methylene-3',4'-dihydro-2'*H*-spiro[cyclopentane-1,1'-naphthalen]-2'-one (3s)

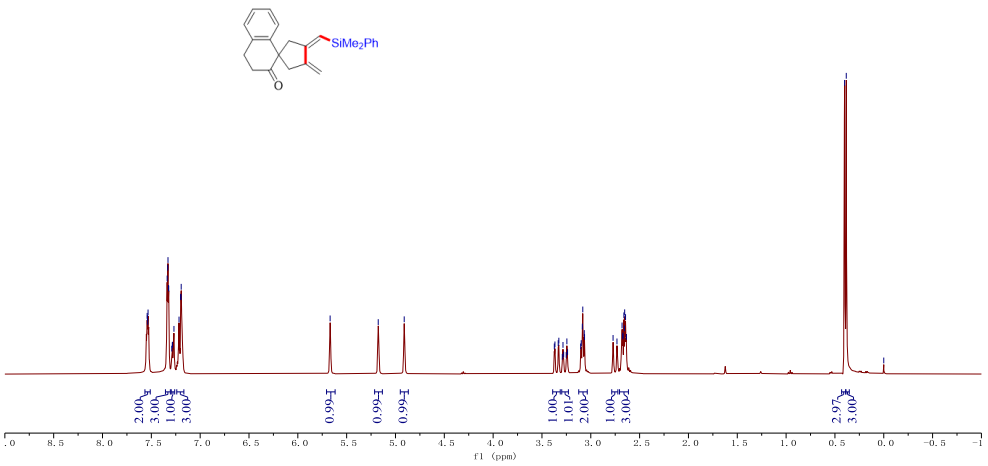


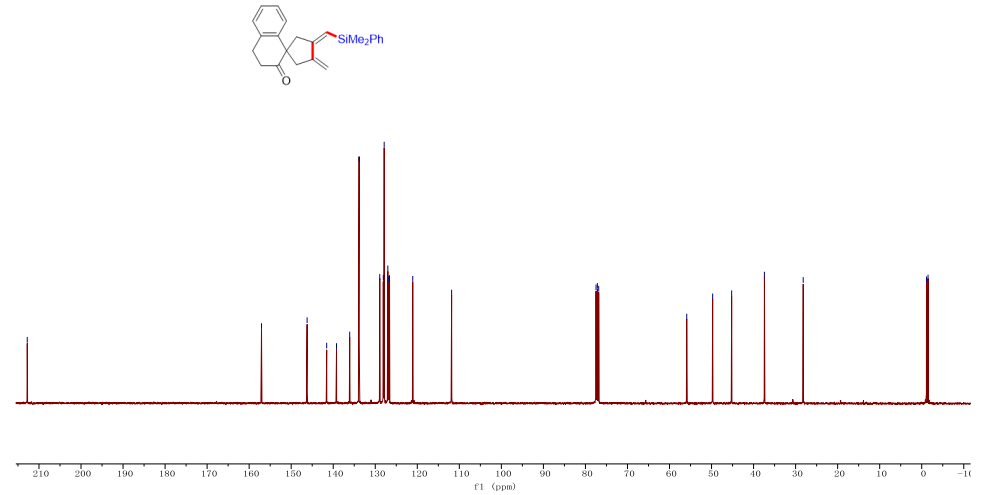
Prepared according to method **E**, and the product **3s** was obtained as yellow solid in 81% yield (58.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.37 – 7.31 (m, 3H), 7.30 – 7.26 (m, 1H), 7.24 – 7.17 (m, 3H), 5.67 (d, *J* = 2.1 Hz, 1H), 5.18 (s, 1H), 4.91 (d, *J* = 2.2 Hz, 1H), 3.35 (dd, *J* = 16.0, 2.6 Hz, 1H), 3.26 (dt, *J* = 15.9, 2.8 Hz, 1H), 3.12 – 3.04 (m, 2H), 2.75 (d, *J* = 16.0 Hz, 1H), 2.70 – 2.62 (m, 3H), 0.40 (s, 3H), 0.38 (s, 3H).

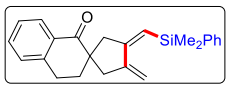
^{13}C NMR (101 MHz, $CDCl_3$) δ 212.8, 157.1, 146.2, 141.6, 139.2, 136.1, 133.9, 128.9, 128.1, 127.9, 127.0, 126.8, 126.6, 121.1, 111.8, 55.9, 49.7, 45.2, 37.4, 28.2, -1.1, -1.5.

HRMS (ESI): m/z Calcd. for $C_{24}H_{27}OSi$ $[M+H]^+$: 359.1831, found: 359.1830.





(*Z*)-3-((dimethyl(phenyl)silyl)methylene)-4-methylene-3',4'-dihydro-1'*H*-spiro[cyclopentane-1,2'-naphthalen]-1'-one (3t)

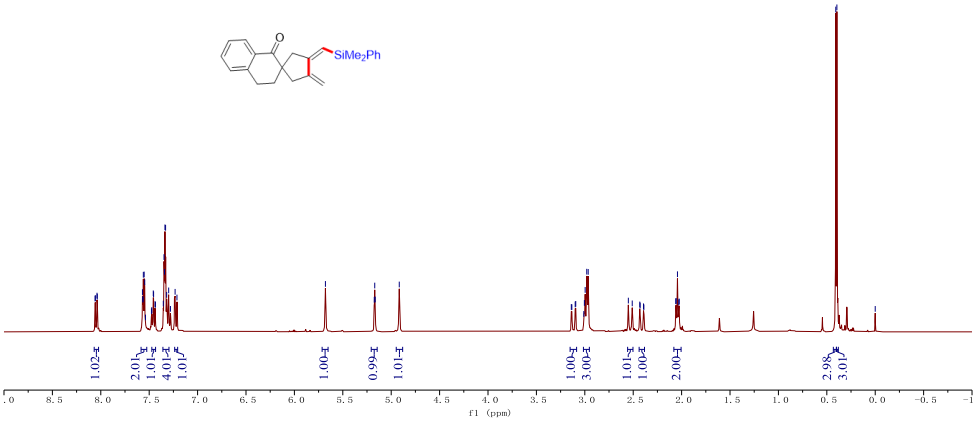


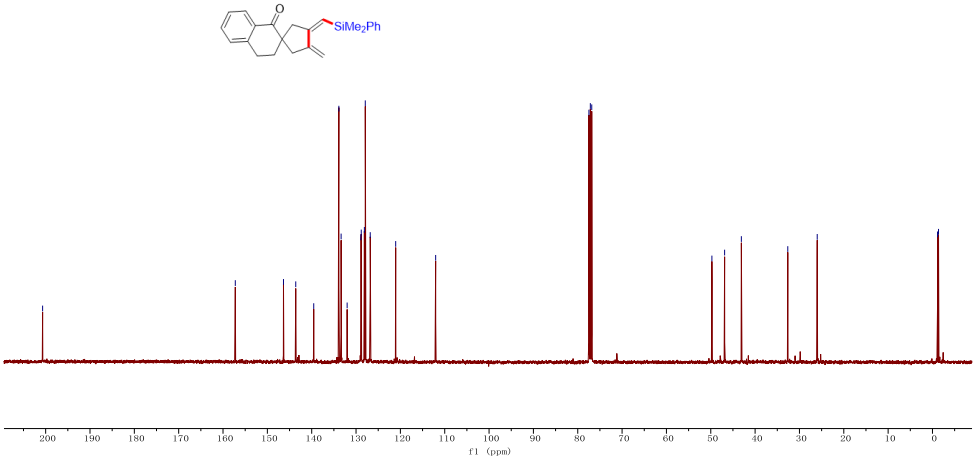
Prepared according to **E**, and the product **3t** was obtained as yellow oil in 94% yield (67.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.46 (td, *J* = 7.5, 1.4 Hz, 1H), 7.36 – 7.27 (m, 4H), 7.22 (d, *J* = 7.7 Hz, 1H), 5.68 (s, 1H), 5.17 (t, *J* = 2.0 Hz, 1H), 4.92 (s, 1H), 3.12 (dd, *J* = 16.1, 2.2 Hz, 1H), 3.02 – 2.95 (m, 3H), 2.53 (d, *J* = 16.1 Hz, 1H), 2.41 (dd, *J* = 15.5, 1.4 Hz, 1H), 2.08 – 2.02 (m, 2H), 0.41 (s, 3H), 0.40 (s, 3H).

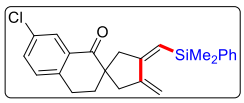
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.7, 157.2, 146.4, 143.6, 139.5, 133.9, 133.4, 132.0, 128.9, 128.8, 128.1, 127.9, 126.8, 121.1, 112.0, 49.8, 46.9, 43.1, 32.6, 26.0, -1.2, -1.4.

HRMS (ESI): m/z Calcd. for $C_{24}H_{27}OSi$ $[M+H]^+$: 359.1831, found: 359.1831.





(*Z*)-7'-chloro-3-((dimethyl(phenyl)silyl)methylene)-4-methylene-3',4'-dihydro-1'*H*-spiro[cyclopentane-1,2'-naphthalen]-1'-one (3u)

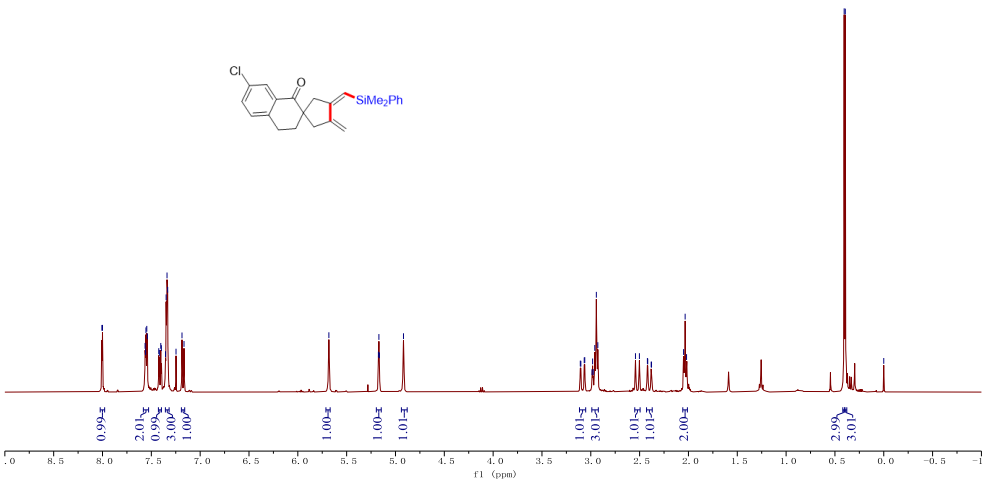


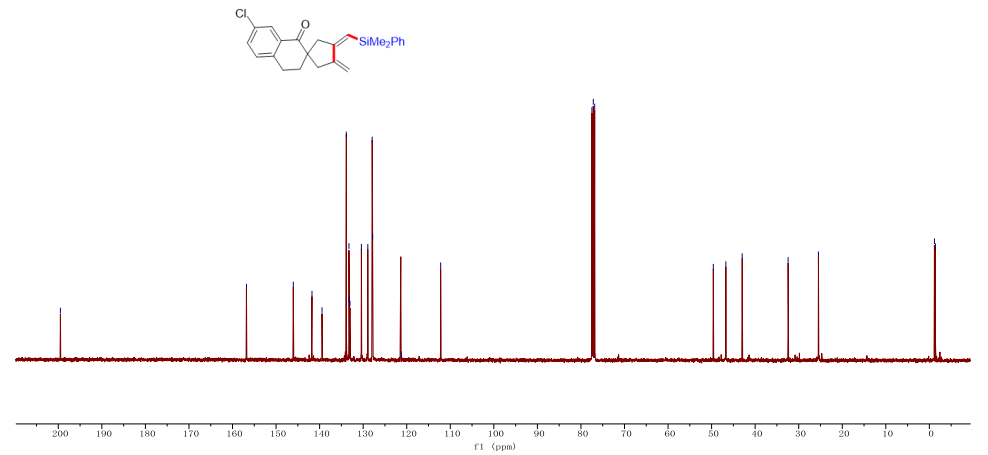
Prepared according to method **E**, and the product **3u** was obtained as yellow oil in 92% yield (71.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 2.3 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.41 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.36 – 7.32 (m, 3H), 7.18 (d, *J* = 8.2 Hz, 1H), 5.68 (s, 1H), 5.17 (t, *J* = 2.0 Hz, 1H), 4.92 (s, 1H), 3.08 (dd, *J* = 16.1, 2.2 Hz, 1H), 2.99 – 2.91 (m, 3H), 2.52 (d, *J* = 16.2 Hz, 1H), 2.40 (dd, *J* = 15.5, 1.4 Hz, 1H), 2.06 – 2.01 (m, 2H), 0.41 (s, 3H), 0.39 (s, 3H).

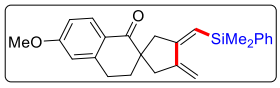
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 156.8, 146.1, 141.8, 139.5, 133.9, 133.3, 133.2, 133.0, 130.4, 128.9, 127.9, 127.8, 121.3, 112.2, 49.6, 46.7, 43.0, 32.4, 25.5, -1.2, -1.4.

HRMS (ESI): m/z Calcd. for $C_{24}H_{26}OClSi$ $[M+H]^+$: 393.1441, found: 393.1432.





(*Z*)-3-((dimethyl(phenyl)silyl)methylene)-6'-methoxy-4-methylene-3',4'-dihydro-1'*H*-spiro[cyclopentane-1,2'-naphthalen]-1'-one (3v)

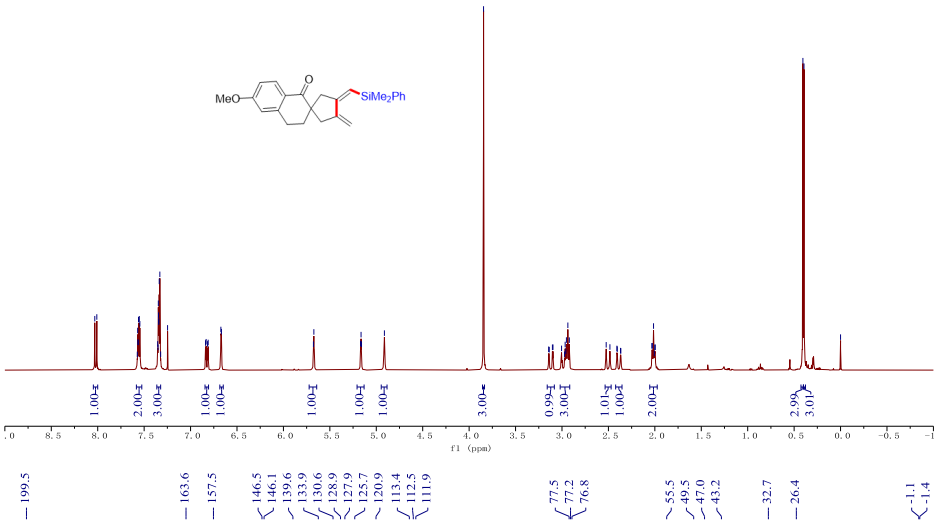


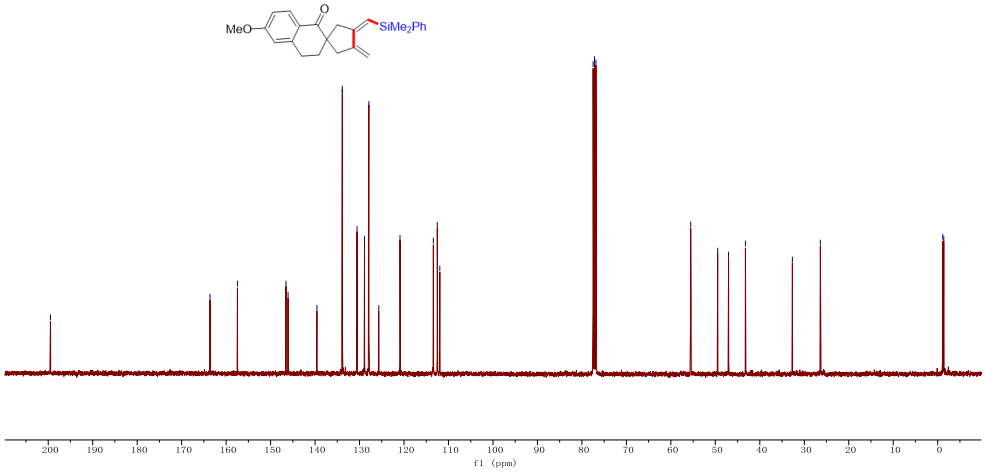
Prepared according to method **E**, and the product **3v** was obtained as yellow oil in 89% yield (69.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.8 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.37 – 7.29 (m, 3H), 6.82 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.67 (d, *J* = 2.5 Hz, 1H), 5.67 (d, *J* = 1.9 Hz, 1H), 5.16 (t, *J* = 2.1 Hz, 1H), 4.91 (s, 1H), 3.84 (s, 3H), 3.12 (dd, *J* = 16.1, 2.4 Hz, 1H), 3.02 – 2.91 (m, 3H), 2.50 (d, *J* = 16.1 Hz, 1H), 2.39 (dd, *J* = 15.5, 1.5 Hz, 1H), 2.04 – 1.98 (m, 2H), 0.41 (s, 3H), 0.39 (s, 3H).

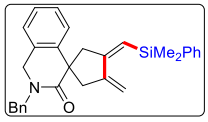
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 163.6, 157.5, 146.5, 146.1, 139.6, 133.9, 130.6, 128.9, 127.9, 125.7, 120.9, 113.4, 112.5, 112.0, 55.5, 49.5, 47.0, 43.2, 32.7, 26.4, -1.1, -1.4.

HRMS (ESI): m/z Calcd. for $C_{25}H_{29}O_2Si$ $[M+H]^+$: 389.1937, found: 389.1937.





(*Z*)-2'-benzyl-3-((dimethyl(phenyl)silyl)methylene)-4-methylene-1',2'-dihydro-3'*H*-spiro[cyclopentane-1,4'-isoquinolin]-3'-one (3w)

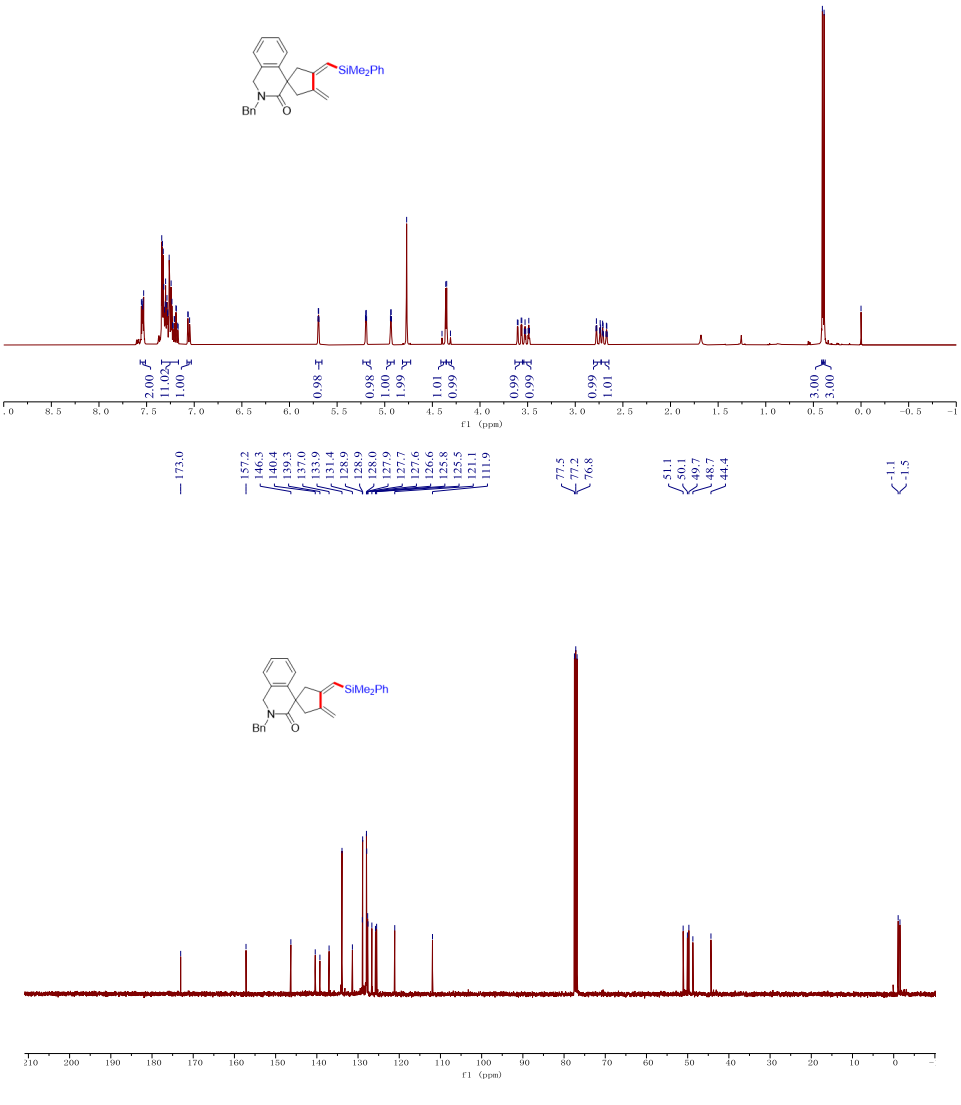


Prepared according to method **E**. The product **3w** was obtained as colorless oil in 67% yield (60.2 mg).

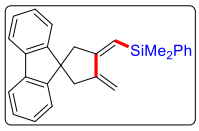
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.36 – 7.16 (m, 11H), 7.08 – 7.03 (m, 1H), 5.74 – 5.66 (m, 1H), 5.20 (dd, *J* = 3.2, 1.5 Hz, 1H), 4.93 (dd, *J* = 2.8, 1.4 Hz, 1H), 4.77 (s, 2H), 4.38 (d, *J* = 15.7 Hz, 1H), 4.33 (d, *J* = 15.8 Hz, 1H), 3.58 (dd, *J* = 15.9, 2.7 Hz, 1H), 3.51 (dt, *J* = 15.8, 2.9 Hz, 1H), 2.76 (dt, *J* = 15.9, 1.8 Hz, 1H), 2.69 (dq, *J* = 15.8, 1.7 Hz, 1H), 0.41 (s, 3H), 0.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 157.2, 146.3, 140.4, 139.3, 137.0, 133.9, 131.4, 129.0, 128.9, 128.0, 127.9, 127.7, 127.6, 126.7, 125.8, 125.5, 121.1, 111.9, 51.1, 50.1, 49.7, 48.7, 44.4, -1.1, -1.5.

HRMS (ESI): m/z Calcd. for $C_{30}H_{32}NOSi$ $[M+H]^+$: 450.2253, found: 450.2256.



(*Z*)-dimethyl((3-methylenespiro[cyclopentane-1,9'-fluoren]-4-ylidene)methyl)(phenyl)silane (3x)

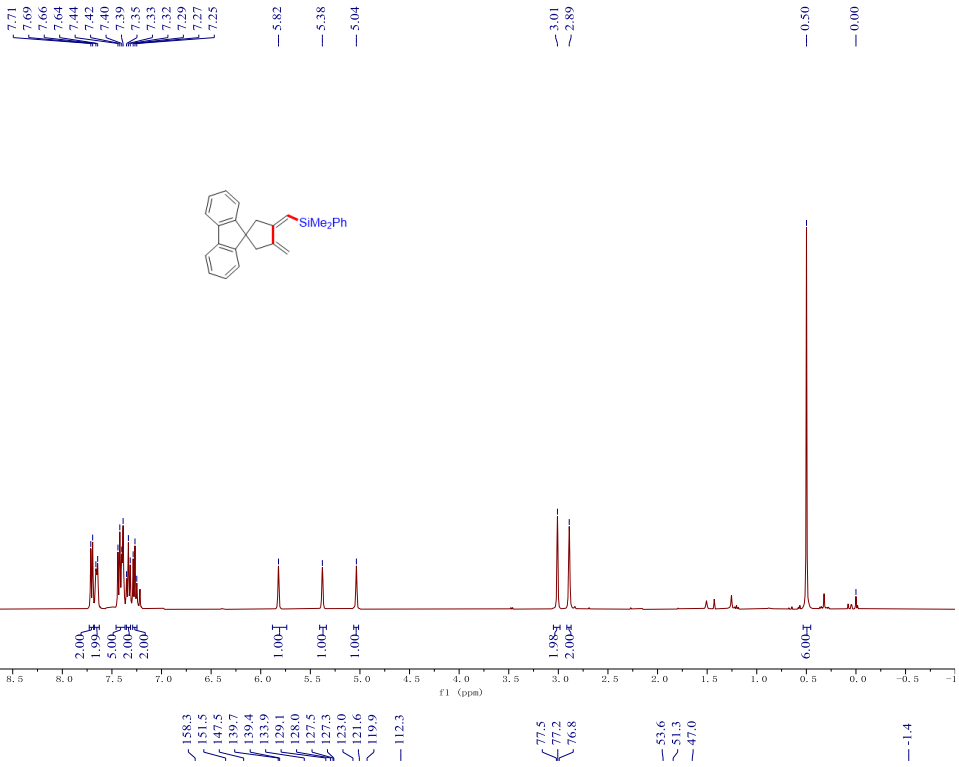


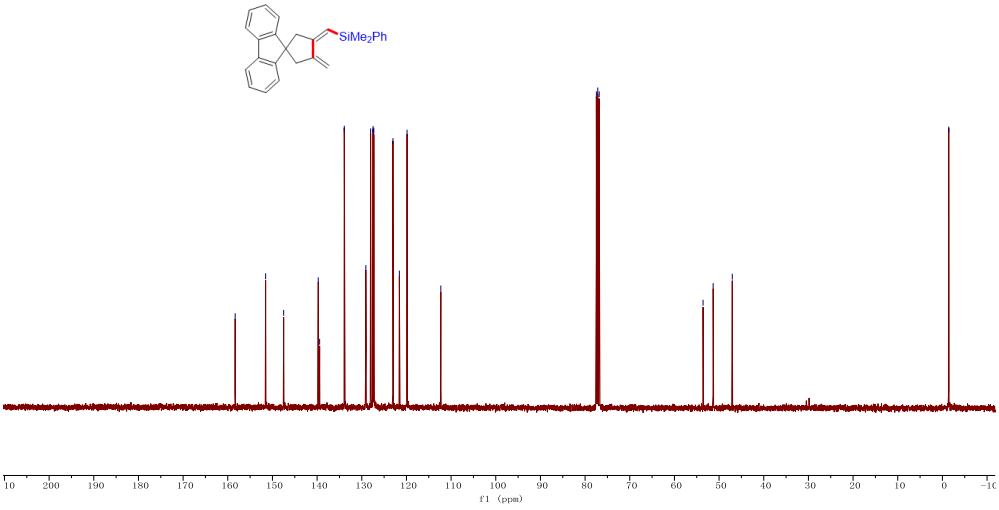
Prepared according to method **E**. The product **3x** was obtained as yellow oil in 99% yield (74.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.4 Hz, 2H), 7.67 – 7.62 (m, 2H), 7.45 – 7.37 (m, 5H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 2H), 5.82 (s, 1H), 5.38 (s, 1H), 5.04 (s, 1H), 3.01 (s, 2H), 2.89 (s, 2H), 0.50 (s, 6H).

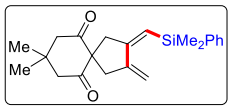
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 151.5, 147.5, 139.8, 139.4, 133.9, 129.1, 128.0, 127.5, 127.3, 123.0, 121.6, 119.9, 112.3, 53.6, 51.3, 47.1, -1.4.

HRMS (ESI): m/z Calcd. for $C_{27}H_{27}Si$ $[M+H]^+$: 379.1882, found: 379.1890.





(*Z*)-2-((dimethyl(phenyl)silyl)methylene)-8,8-dimethyl-3-methylenespiro[4.5]decane-6,10-dione (3y)

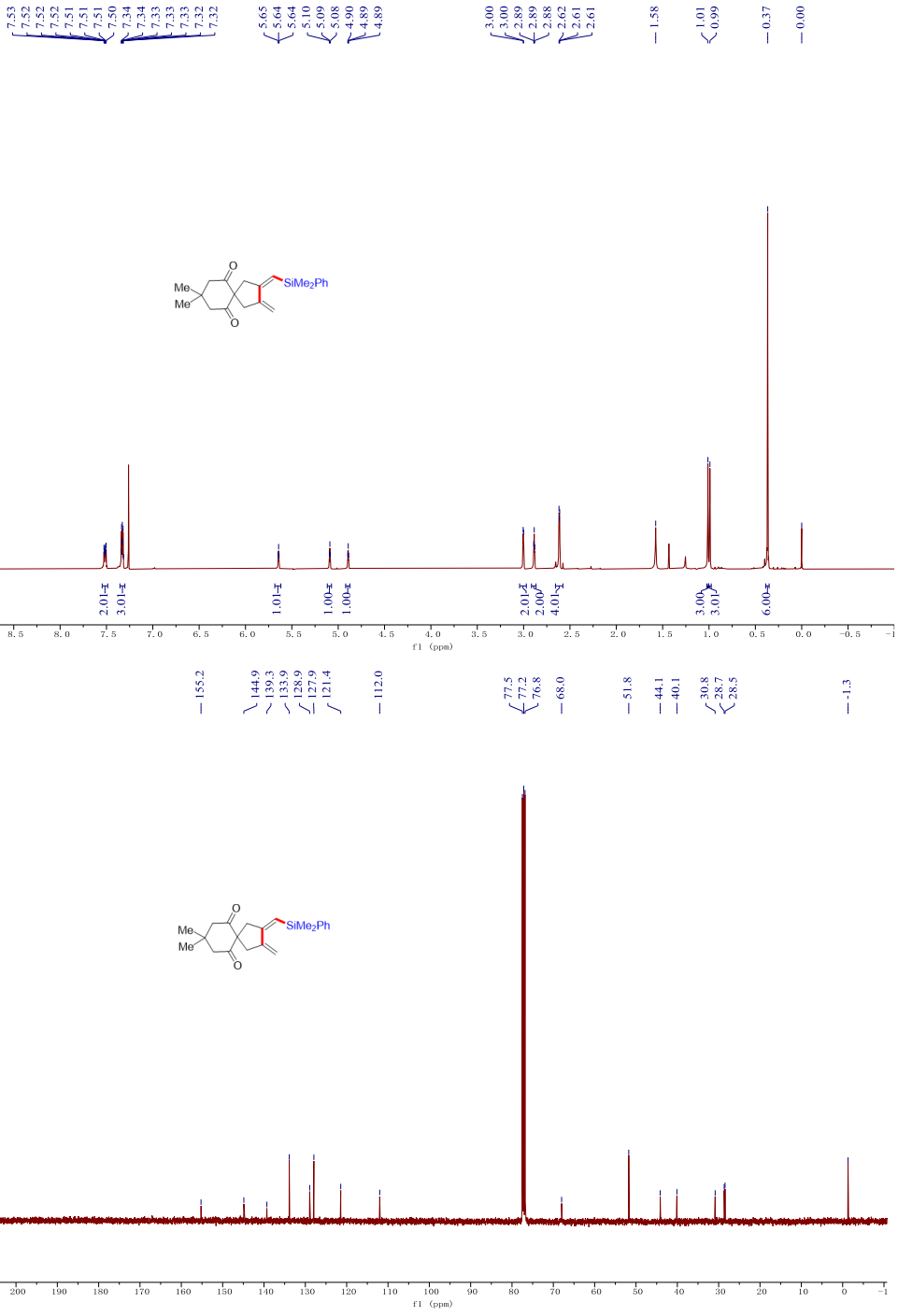


Prepared according to method **E**, and the product **3y** was obtained as white solid in 96% yield (67.6 mg).

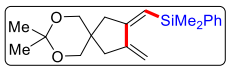
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.35 – 7.31 (m, 3H), 5.64 (t, *J* = 1.9 Hz, 1H), 5.09 (t, *J* = 2.2 Hz, 1H), 4.89 (t, *J* = 1.9 Hz, 1H), 3.00 (d, *J* = 1.9 Hz, 2H), 2.89 (t, *J* = 2.0 Hz, 2H), 2.64 – 2.60 (m, 4H), 1.01 (s, 3H), 0.99 (s, 3H), 0.37 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.1, 155.2, 144.9, 139.3, 133.9, 129.0, 127.9, 121.4, 112.0, 68.0, 51.8, 44.1, 40.1, 30.9, 28.7, 28.5, -1.3.

HRMS (ESI): m/z Calcd. for $C_{22}H_{29}O_2Si$ $[M+H]^+$: 353.1937, found: 353.1940.



(*Z*)-((8,8-dimethyl-3-methylene-7,9-dioxaspiro[4.5]decan-2-ylidene)methyl)dimethyl(phenyl)silane (3z)

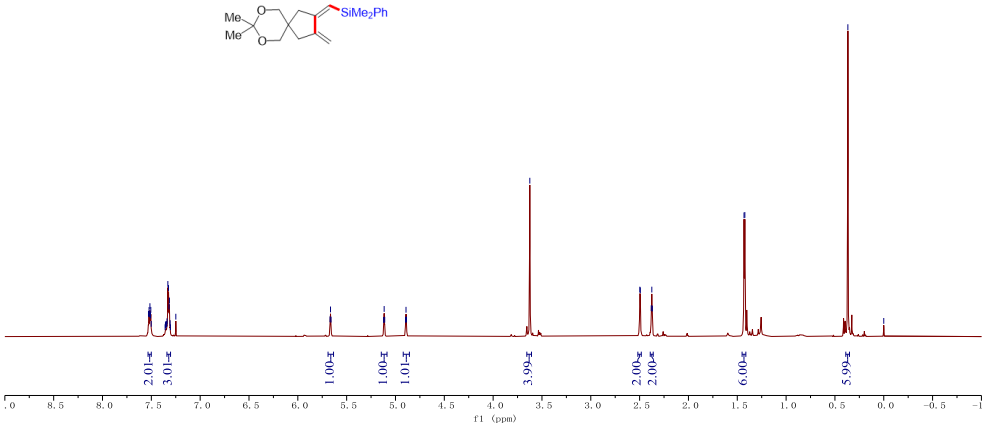


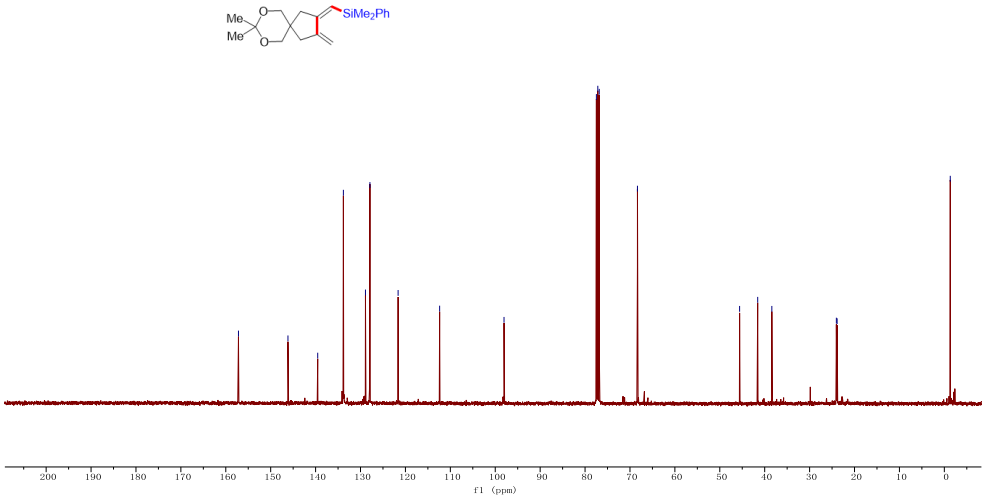
Prepared according to method **E**. The product **3z** was obtained as yellow oil in 82% yield (53.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.36 – 7.29 (m, 3H), 5.67 (t, *J* = 2.0 Hz, 1H), 5.12 (t, *J* = 2.3 Hz, 1H), 4.89 (t, *J* = 2.0 Hz, 1H), 3.62 (s, 4H), 2.50 (d, *J* = 2.0 Hz, 2H), 2.38 (d, *J* = 2.3 Hz, 2H), 1.43 (d, *J* = 3.3 Hz, 6H), 0.37 (s, 6H).

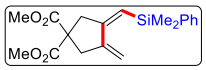
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 146.2, 139.5, 133.8, 128.9, 127.9, 121.6, 112.4, 98.0, 68.3, 45.6, 41.6, 38.4, 24.0, 23.9, -1.3.

HRMS (ESI): m/z Calcd. for $C_{20}H_{29}O_2Si$ $[M+H]^+$: 329.1937, found: 329.1922.





dimethyl (*Z*)-3-((dimethyl(phenyl)silyl)methylene)-4-methylenecyclopentane-1,1-dicarboxylate (3aa)

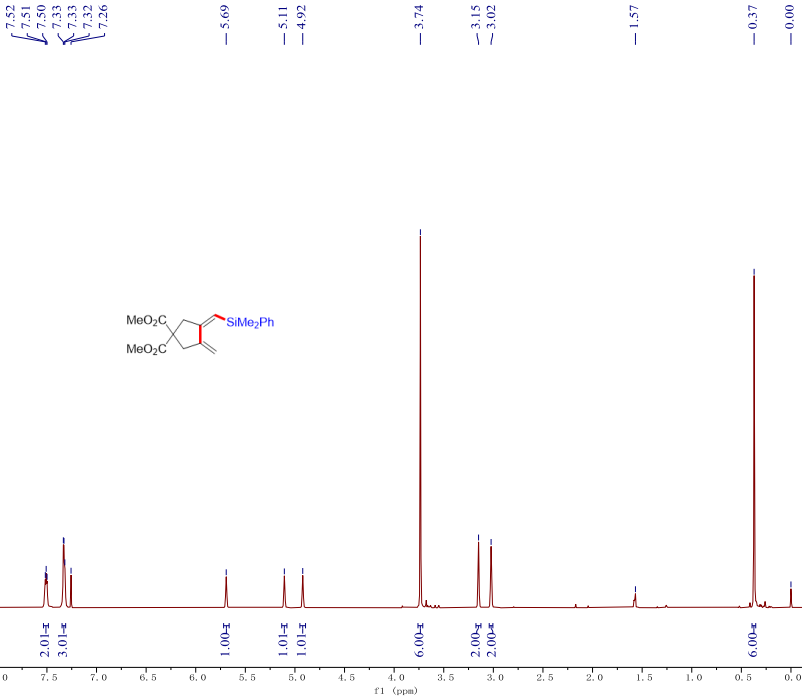


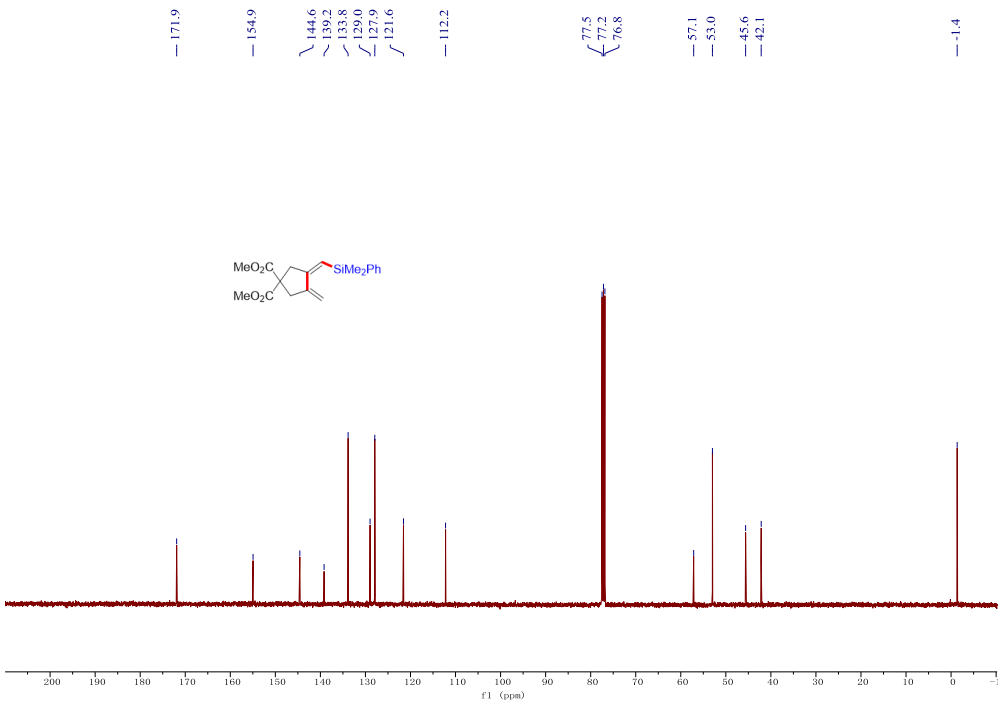
Prepared according to method **E** and the product **3aa** was obtained as colorless oil in 90% yield (61.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.36 – 7.31 (m, 3H), 5.69 (s, 1H), 5.11 (s, 1H), 4.92 (s, 1H), 3.74 (s, 6H), 3.15 (s, 2H), 3.02 (s, 2H), 0.37 (s, 6H).

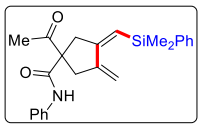
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 155.0, 144.6, 139.2, 133.9, 129.0, 127.9, 121.6, 112.2, 57.1, 53.0, 45.6, 42.2, -1.4.

HRMS (ESI): m/z Calcd. for $C_{19}H_{25}O_4Si$ $[M+H]^+$: 345.1522, found: 345.1523.





(*Z*)-1-acetyl-3-((dimethyl(phenyl)silyl)methylene)-4-methylene-*N*-phenylcyclopentane-1-carboxamide (3ab)

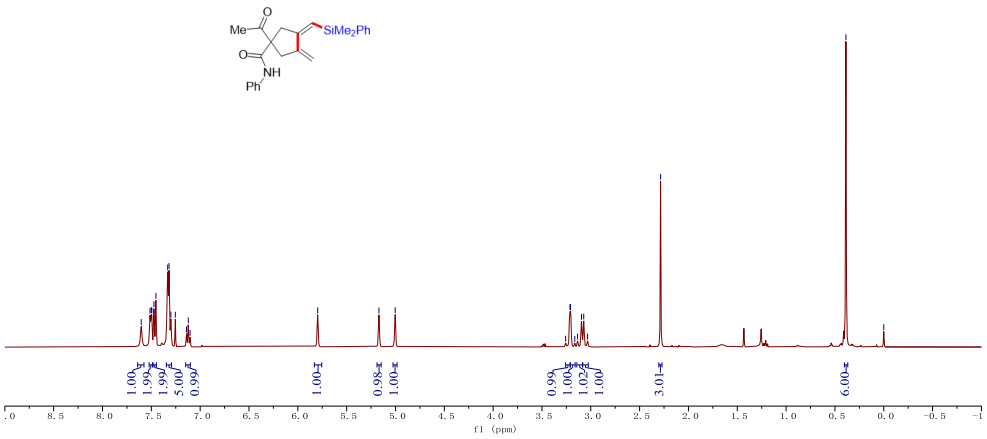


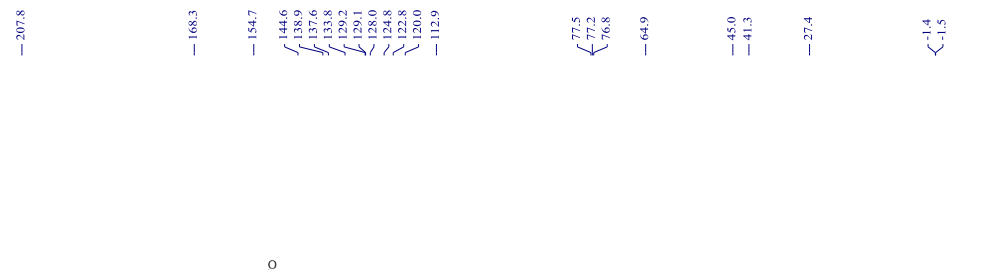
Prepared according to method **E**. The product **3ab** was obtained as white solid in 92% yield (71.4 mg).

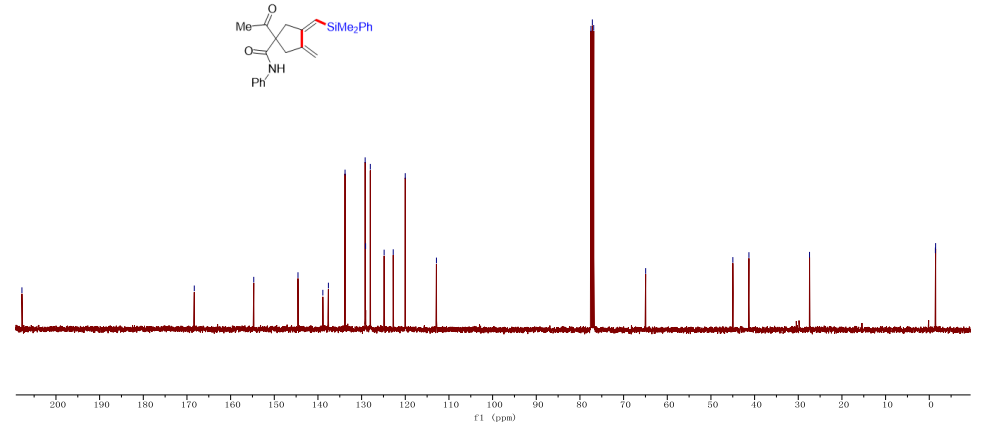
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.53 – 7.49 (m, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.29 (m, 5H), 7.12 (t, *J* = 7.3 Hz, 1H), 5.80 (s, 1H), 5.17 (s, 1H), 5.00 (s, 1H), 3.24 (d, *J* = 18.3 Hz, 1H), 3.19 (d, *J* = 17.4 Hz, 1H), 3.12 (d, *J* = 16.1 Hz, 1H), 3.05 (d, *J* = 15.8 Hz, 1H), 2.29 (s, 3H), 0.39 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.8, 168.3, 154.7, 144.6, 138.9, 137.6, 133.8, 129.2, 129.1, 128.0, 124.8, 122.8, 120.0, 112.9, 65.0, 45.0, 41.3, 27.4, -1.4, -1.5.

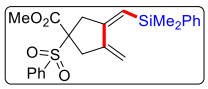
HRMS (ESI): m/z Calcd. for $C_{24}H_{28}NO_2Si$ $[M+H]^+$: 390.1889, found: 390.1891.







methyl (*Z*)-3-((dimethyl(phenyl)silyl)methylene)-4-methylene-1-(phenylsulfonyl) cyclopentane-1-carboxylate (3ac)

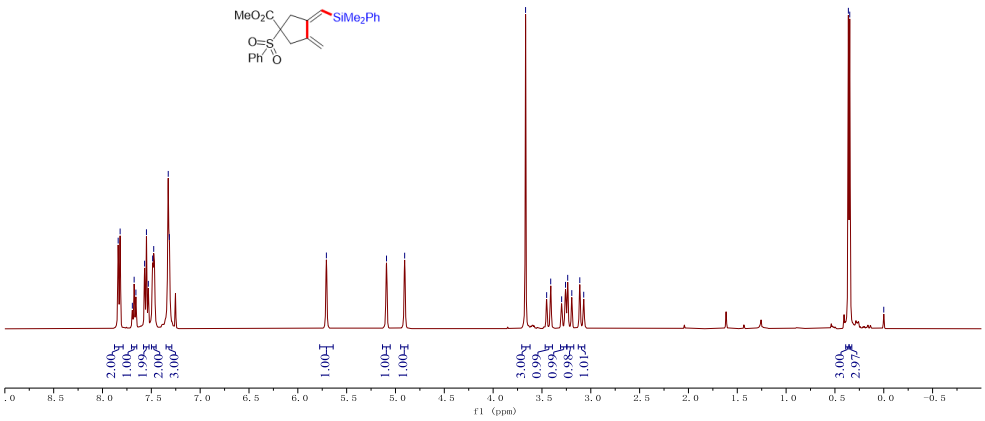


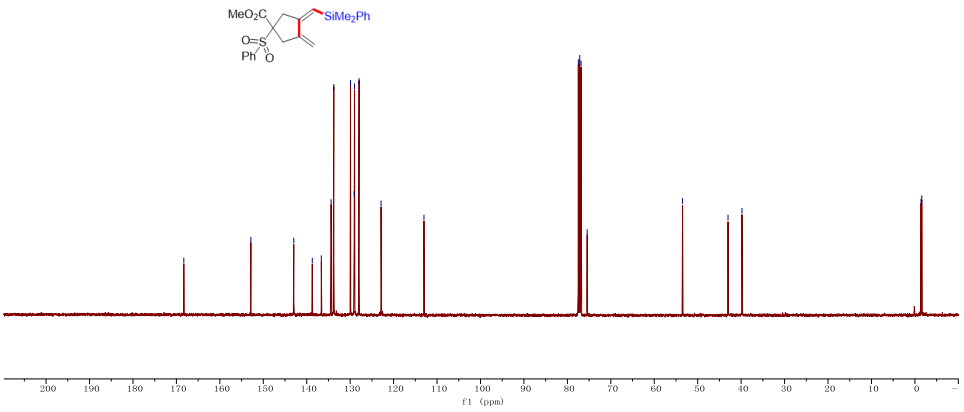
Prepared according to method **E**. The product **3ac** was obtained as colorless oil in 92% yield (78.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.68 (t, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.51 – 7.46 (m, 2H), 7.35 – 7.30 (m, 3H), 5.71 (s, 1H), 5.09 (s, 1H), 4.91 (s, 1H), 3.67 (s, 3H), 3.43 (d, *J* = 16.6 Hz, 1H), 3.28 (d, *J* = 15.9 Hz, 1H), 3.22 (d, *J* = 16.7 Hz, 1H), 3.09 (d, *J* = 16.1 Hz, 1H), 0.36 (s, 3H), 0.35 (s, 3H).

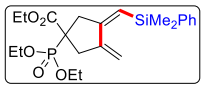
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 152.9, 143.0, 138.7, 136.6, 134.4, 133.8, 129.9, 129.1, 129.0, 128.0, 122.9, 113.0, 75.4, 53.5, 43.0, 39.8, -1.4, -1.6.

HRMS (ESI): m/z Calcd. for $C_{23}H_{27}SO_4Si$ $[M+H]^+$: 427.1399, found: 427.1395.





ethyl (*Z*)-1-(diethoxyphosphoryl)-3-((dimethyl(phenyl)silyl)methylene)-4-methylenecyclo-pentane-1-carboxylate (3ad)

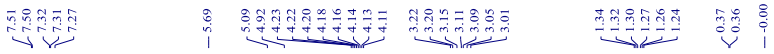


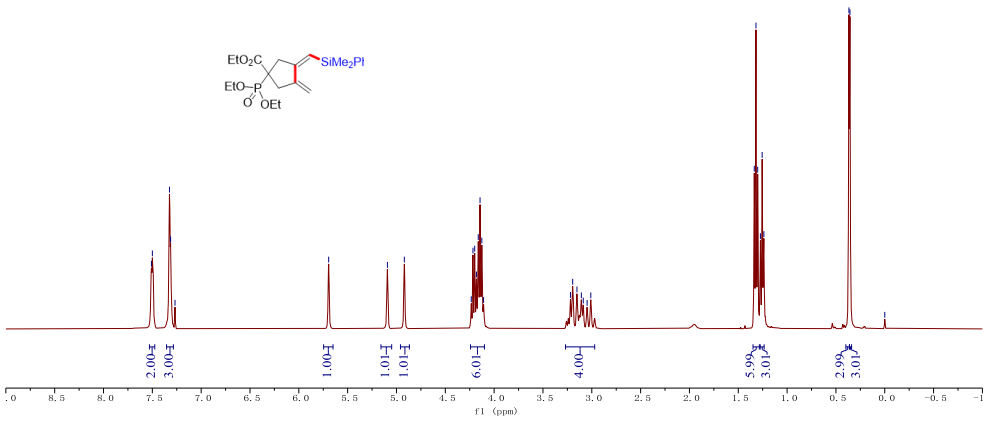
Prepared according to method **E**. The product **3ad** was obtained as colorless oil in 88% yield (76.9 mg).

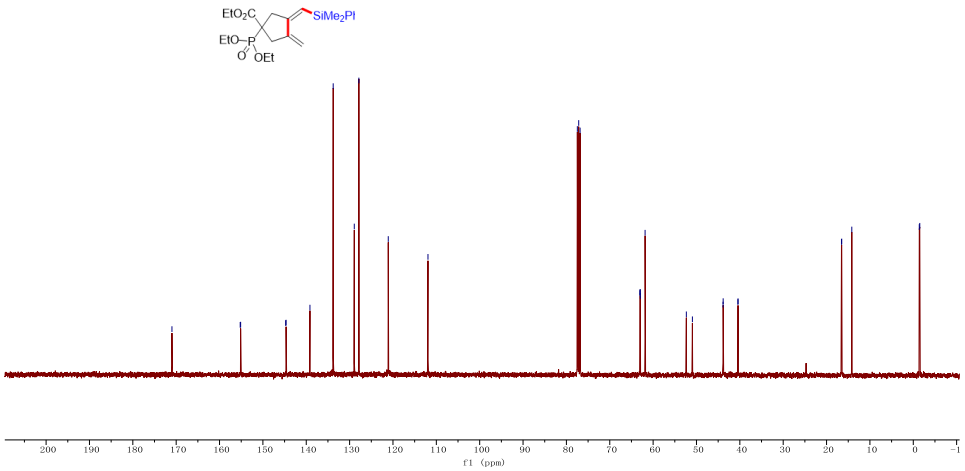
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.35 – 7.29 (m, 3H), 5.69 (s, 1H), 5.09 (s, 1H), 4.92 (s, 1H), 4.25 – 4.09 (m, 6H), 3.30 – 2.94 (m, 4H), 1.32 (t, *J* = 7.0 Hz, 6H), 1.26 (t, *J* = 7.0 Hz, 3H), 0.37 (s, 3H), 0.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 155.2 (d, *J* = 9.7 Hz), 144.7 (d, *J* = 9.6 Hz), 139.2, 133.8, 128.9, 127.9, 121.1, 111.9, 63.0 (d, *J* = 2.5 Hz), 63.0 (d, *J* = 2.5 Hz), 61.9, 51.6 (d, *J* = 141.2 Hz), 43.9 (d, *J* = 2.4 Hz), 40.4 (d, *J* = 2.4 Hz), 16.6, 16.5, 14.2, -1.4, -1.5.

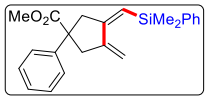
HRMS (ESI): m/z Calcd. for $C_{22}H_{34}O_5PSi$ $[M+H]^+$: 437.1913, found: 437.1912.







ethyl (*Z*)-3-((dimethyl(phenyl)silyl)methylene)-4-methylene-1-phenylcyclopentane-1-carboxylate (3ae)

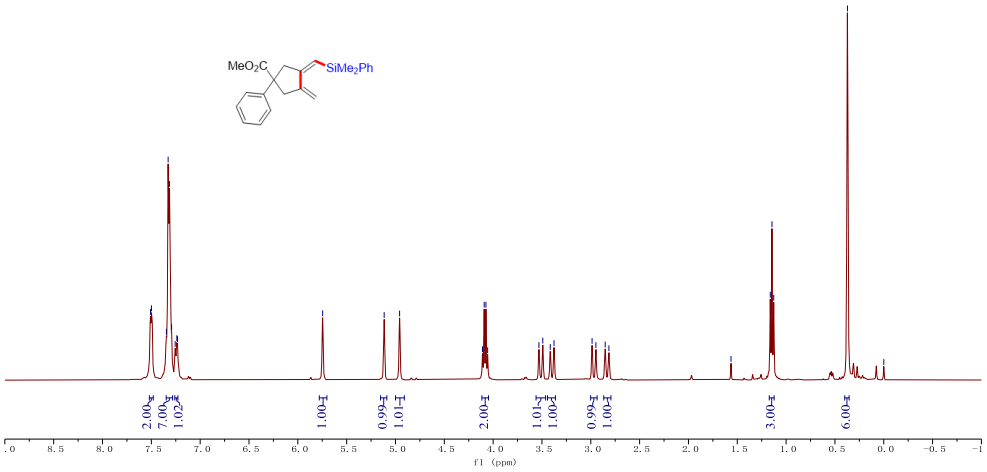


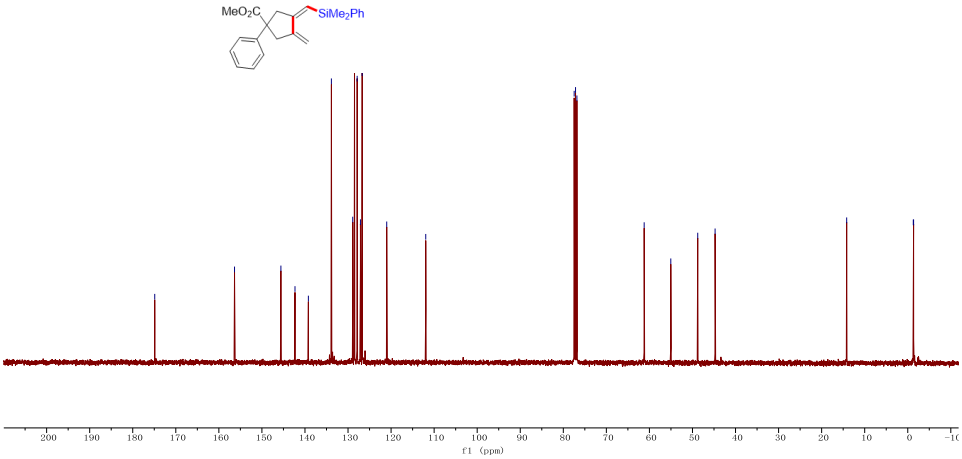
Prepared according to method **E**. The product **3ae** was obtained as colorless oil in 97% yield (73.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 4.1 Hz, 2H), 7.37 – 7.28 (m, 7H), 7.27 – 7.22 (m, 1H), 5.75 (s, 1H), 5.12 (s, 1H), 4.96 (s, 1H), 4.08 (q, *J* = 7.0 Hz, 2H), 3.51 (d, *J* = 15.7 Hz, 1H), 3.40 (d, *J* = 15.4 Hz, 1H), 2.97 (d, *J* = 15.6 Hz, 1H), 2.83 (d, *J* = 15.2 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H), 0.37 (s, 6H).

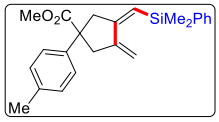
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 156.4, 145.6, 142.3, 139.2, 133.9, 128.9, 128.5, 127.9, 127.1, 126.7, 121.0, 112.0, 61.2, 55.0, 48.8, 44.8, 14.2, -1.3, -1.4.

HRMS (ESI): m/z Calcd. for $C_{24}H_{29}O_2Si$ $[M+H]^+$: 377.1937, found: 377.1942.





methyl (*Z*)-3-((dimethyl(phenyl)silyl)methylene)-4-methylene-1-(*p*-tolyl)cyclopentane-1-carboxylate (3af)

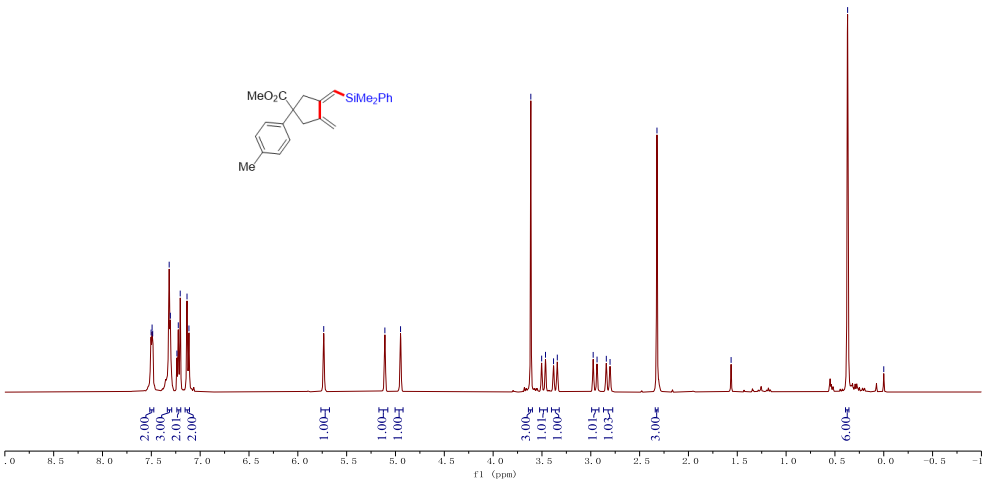


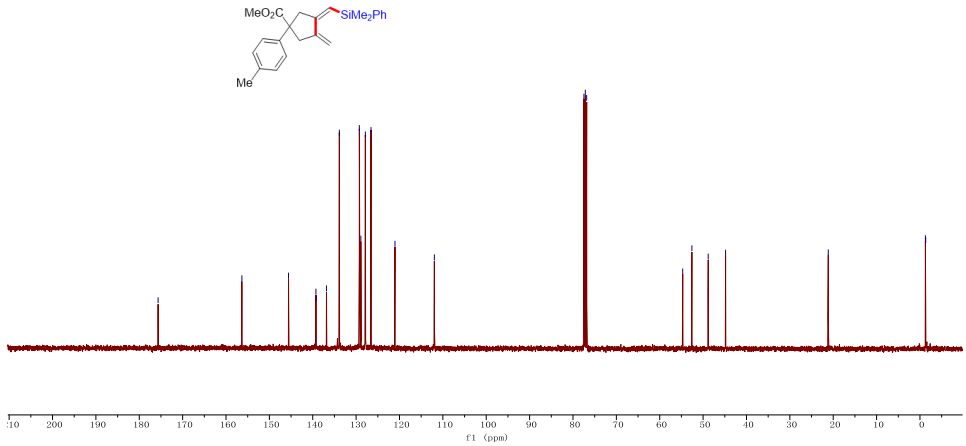
Prepared according to method **E**. The product **3af** was obtained as yellow oil in 95% yield (71.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.34 – 7.28 (m, 3H), 7.25 – 7.18 (m, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 5.73 (s, 1H), 5.11 (s, 1H), 4.95 (s, 1H), 3.61 (s, 3H), 3.48 (d, *J* = 15.8 Hz, 1H), 3.36 (d, *J* = 15.4 Hz, 1H), 2.96 (d, *J* = 15.9 Hz, 1H), 2.82 (d, *J* = 15.3 Hz, 1H), 2.32 (s, 3H), 0.37 (s, 6H).

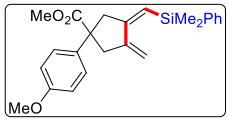
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 156.3, 145.6, 139.3, 139.2, 136.8, 133.9, 129.3, 128.9, 127.9, 126.6, 121.0, 112.0, 54.7, 52.6, 48.8, 44.8, 21.1, -1.3, -1.3.

HRMS (ESI): m/z Calcd. for $C_{24}H_{29}O_2Si$ $[M+H]^+$: 377.1937, found: 377.1945.





methyl (*Z*)-3-((dimethyl(phenyl)silyl)methylene)-1-(4-methoxyphenyl)-4-methylenecyclopentane-1-carboxylate (3ag)

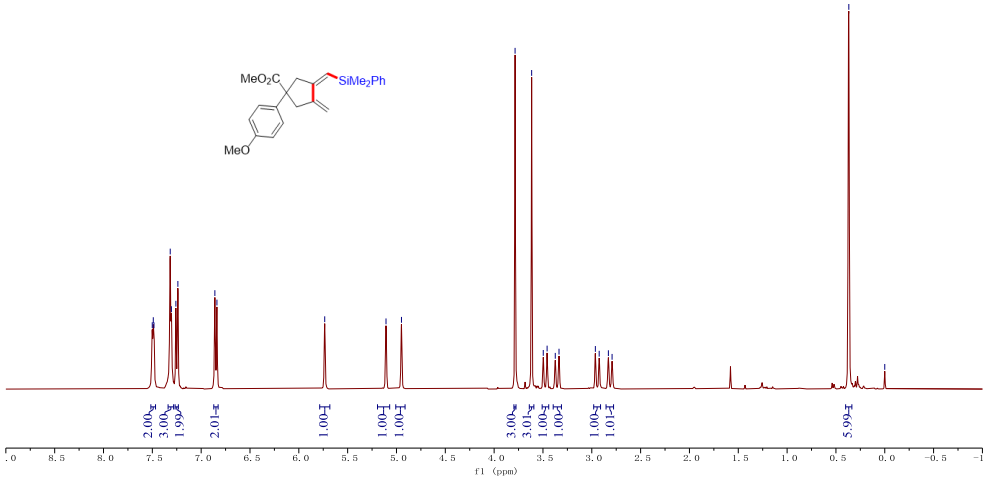


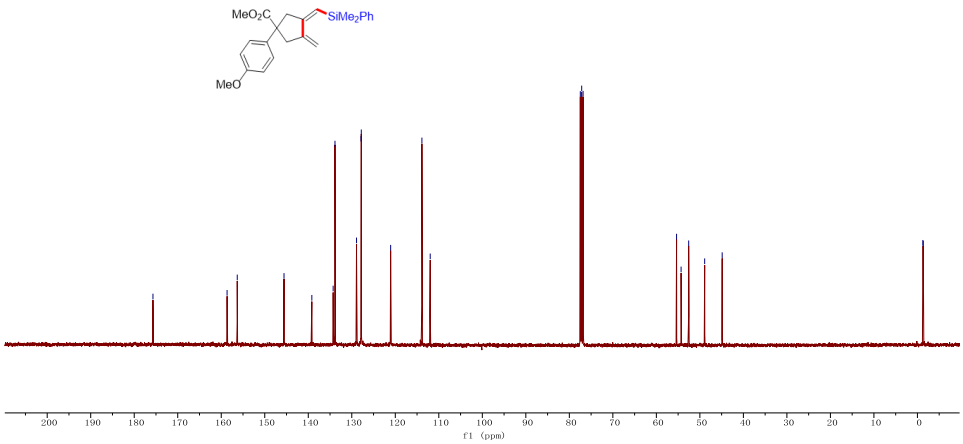
Prepared according to method **E**. The product **3ag** was obtained as yellow oil in 80% yield (62.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.34 – 7.29 (m, 3H), 7.25 (d, *J* = 8.1 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.73 (s, 1H), 5.11 (s, 1H), 4.95 (s, 1H), 3.79 (s, 3H), 3.62 (s, 3H), 3.48 (d, *J* = 15.7 Hz, 1H), 3.35 (d, *J* = 15.4 Hz, 1H), 2.94 (d, *J* = 15.7 Hz, 1H), 2.81 (d, *J* = 15.1 Hz, 1H), 0.37 (s, 6H).

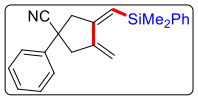
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 158.7, 156.3, 145.6, 139.2, 134.3, 133.9, 128.9, 127.9, 127.8, 121.1, 113.9, 112.0, 55.4, 54.3, 52.6, 48.9, 44.9, -1.3, -1.3.

HRMS (ESI): m/z Calcd. for $C_{24}H_{29}O_3Si$ $[M+H]^+$: 393.1886, found: 393.1884.





(*Z*)-3-((dimethyl(phenyl)silyl)methylene)-4-methylene-1-phenylcyclopentane-1-carbonitrile (3ah)

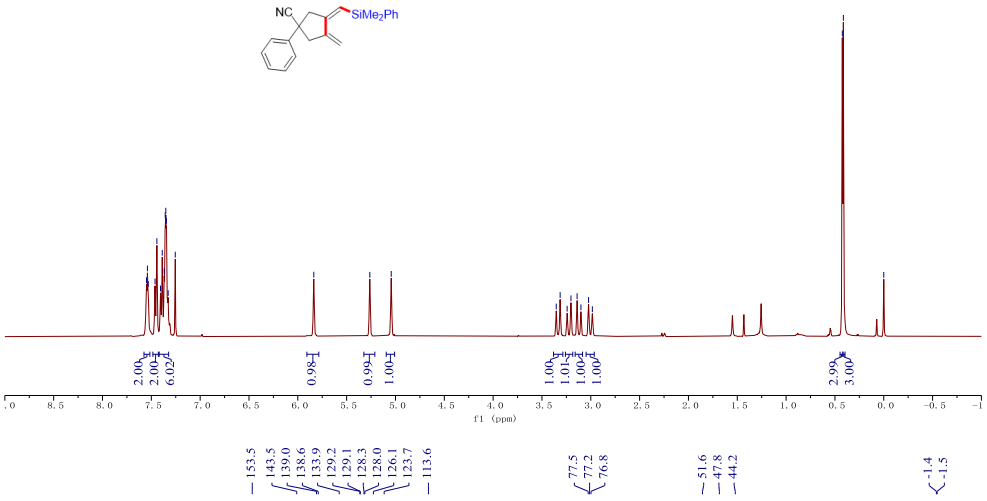


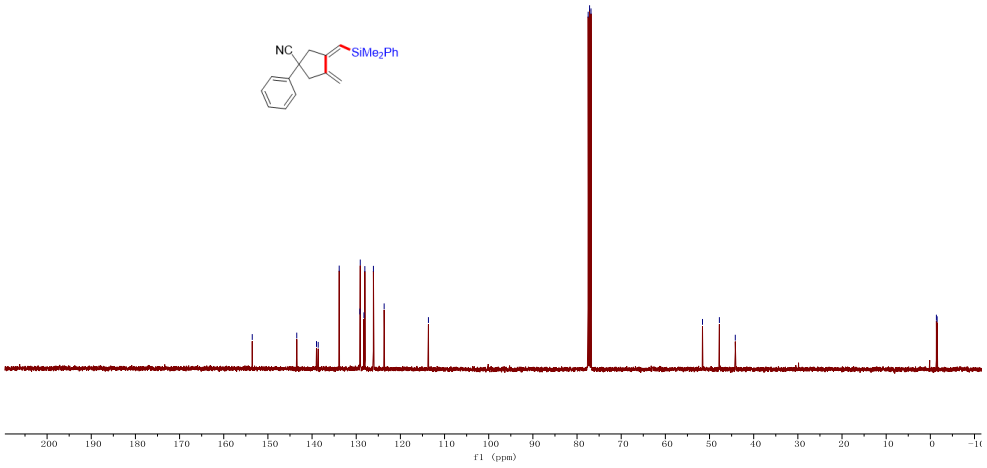
Prepared according to method **E**. The product **3ah** was obtained as yellow oil in 85% yield (55.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.42 – 7.32 (m, 6H), 5.84 (s, 1H), 5.26 (s, 1H), 5.04 (s, 1H), 3.33 (d, *J* = 15.9 Hz, 1H), 3.22 (d, *J* = 15.7 Hz, 1H), 3.12 (d, *J* = 15.8 Hz, 1H), 3.00 (d, *J* = 15.5 Hz, 1H), 0.42 (s, 3H), 0.41 (s, 3H).

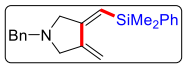
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 143.5, 139.0, 138.6, 133.9, 129.2, 129.1, 128.3, 128.1, 126.1, 123.7, 113.7, 51.6, 47.8, 44.2, -1.4, -1.5.

HRMS (ESI): m/z Calcd. for $C_{22}H_{24}NSi$ $[M+H]^+$: 330.1678, found: 330.1679.





(*E*)-1-benzyl-3-((dimethyl(phenyl)silyl)methylene)-4-methylenepyrrolidine (3ai)

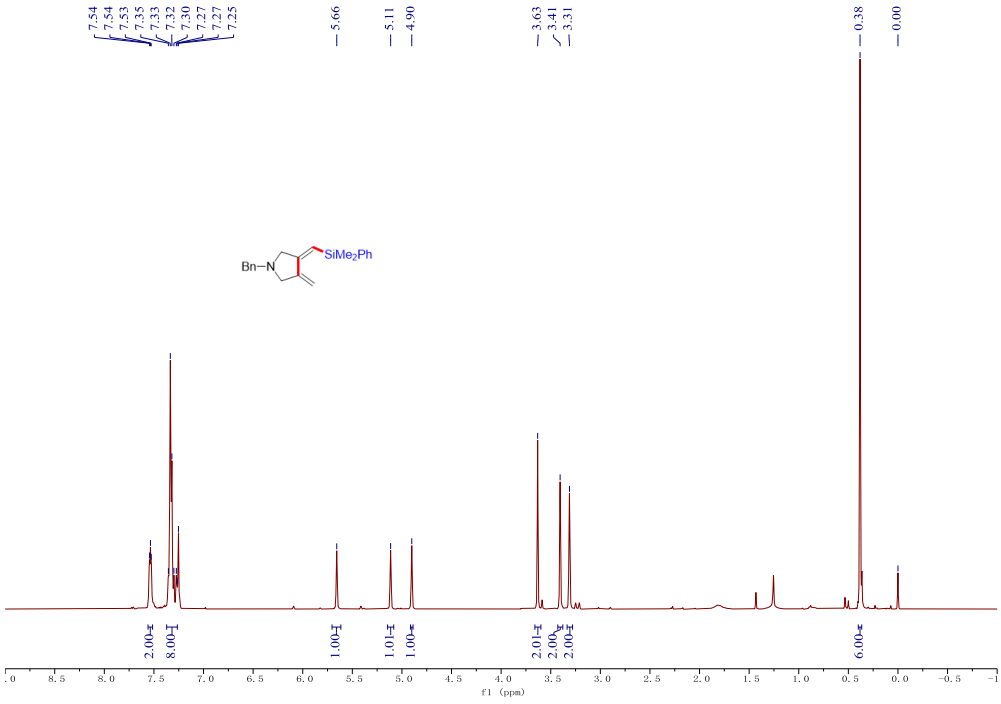


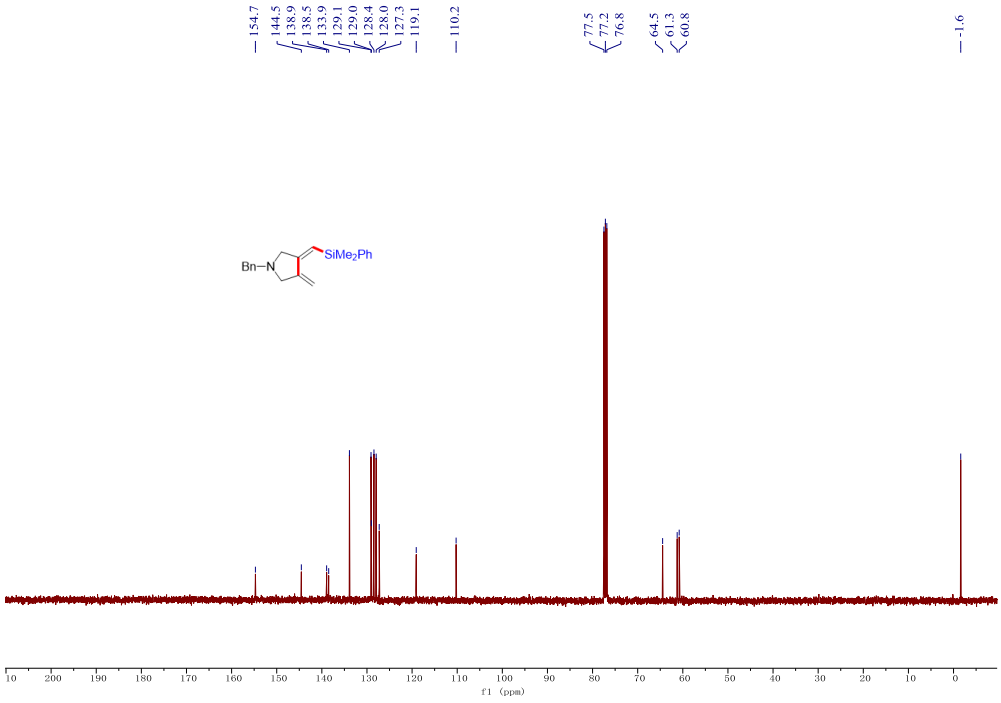
Prepared according to method **E**. The product **3ai** was obtained as colorless oil in 93% yield (59.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.38 – 7.26 (m, 8H), 5.66 (s, 1H), 5.11 (s, 1H), 4.90 (s, 1H), 3.63 (s, 2H), 3.41 (s, 2H), 3.31 (s, 2H), 0.38 (s, 6H).

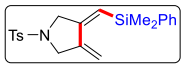
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 144.5, 138.9, 138.5, 133.9, 129.1, 129.0, 128.5, 128.0, 127.3, 119.1, 110.2, 64.5, 61.3, 60.8, -1.6.

HRMS (ESI): m/z Calcd. for $C_{21}H_{26}NSi$ $[M+H]^+$: 320.1835, found: 320.1836.





(*E*)-3-((dimethyl(phenyl)silyl)methylene)-4-methylene-1-tosylpyrrolidine (3aj)

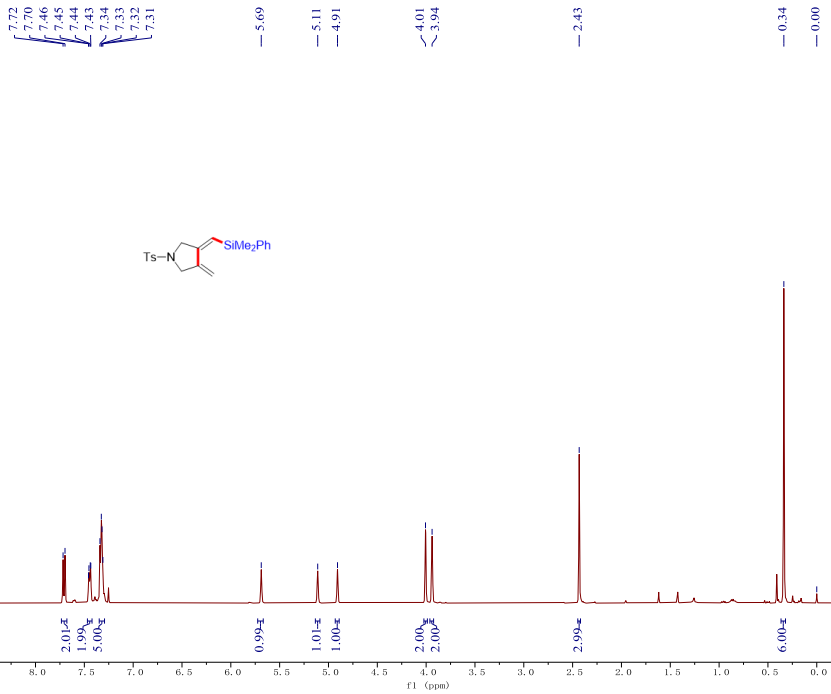


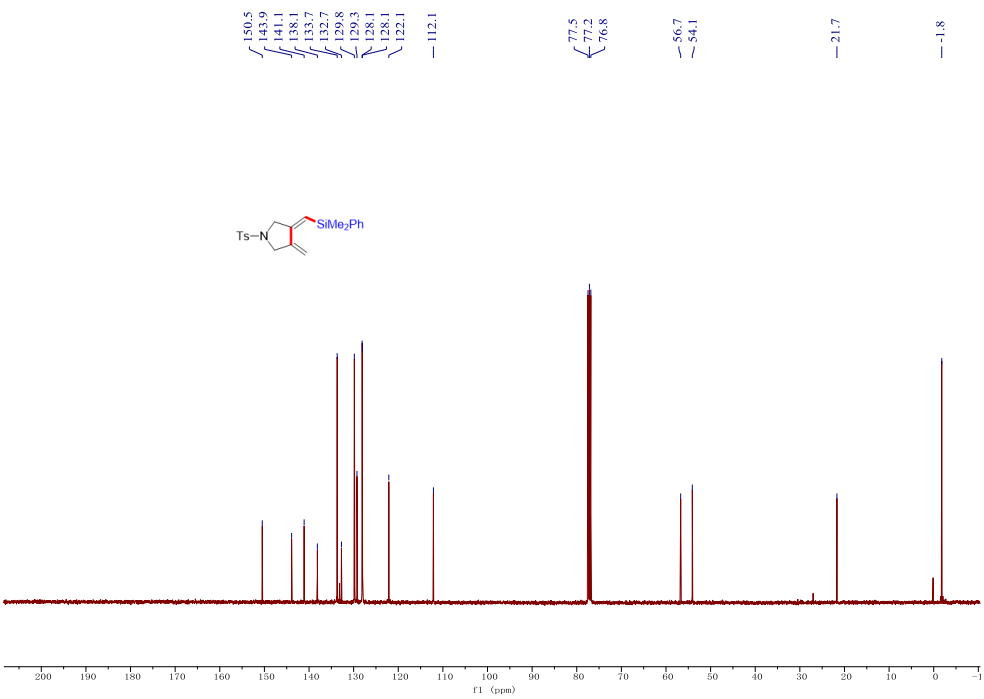
Prepared according to method **E**. The product **3aj** was obtained as colorless oil in 72% yield (55.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.42 (m, 2H), 7.37 – 7.28 (m, 5H), 5.69 (s, 1H), 5.11 (s, 1H), 4.91 (s, 1H), 4.01 (s, 2H), 3.94 (s, 2H), 2.43 (s, 3H), 0.34 (s, 6H).

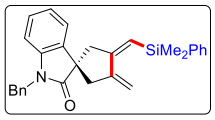
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 143.9, 141.1, 138.1, 133.7, 132.7, 129.8, 129.3, 128.1, 128.1, 122.1, 112.1, 56.7, 54.1, 21.7, -1.8.

HRMS (ESI): m/z Calcd. for $C_{21}H_{26}NO_2SSi$ $[M+H]^+$: 384.1454, found: 384.1458.





(*S*,*Z*)-1'-benzyl-3-((dimethyl(phenyl)silyl)methylene)-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (4a)

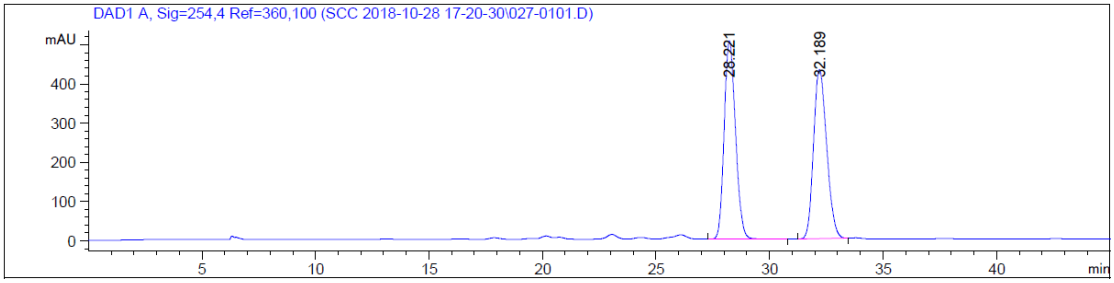


Prepared according to method **F**. The product **4a** was isolated in 74% yield (64.5 mg) with 92% ee.

The characterization data and spectrums of **4a** are same to **3a**

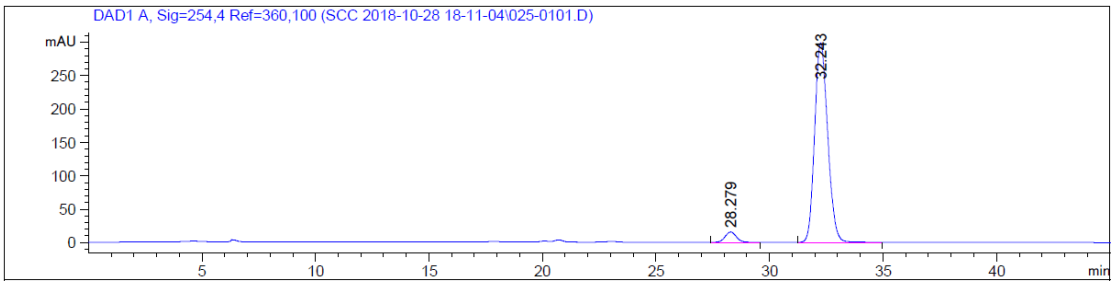
$[\alpha]_D^{20}$ +7.9° (*c* 1.35, $CHCl_3$)

The enantiomeric excess of **4a** was determined by chiral HPLC analysis on IC-3 column. Conditions: hexane/isopropanol = 95:5, flow rate = 0.5 mL/min, T = 25 °C, UV-Vis detection at λ = 254 nm, t_{R1} = 28.3 min (minor), t_{R2} = 32.2 min (major).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

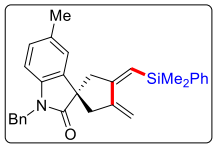
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.221	BB	0.5405	1.75231e4	505.45673	50.2562
2	32.189	BB	0.6272	1.73445e4	431.28418	49.7438
Totals :				3.48676e4	936.74091	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.279	BB	0.5288	523.55487	15.54896	4.2113
2	32.243	BB	0.6213	1.19086e4	298.59094	95.7887
Totals :				1.24322e4	314.13990	

(*S*,*Z*)-1'-benzyl-3-((dimethyl(phenyl)silyl)methylene)-5'-methyl-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (4b)

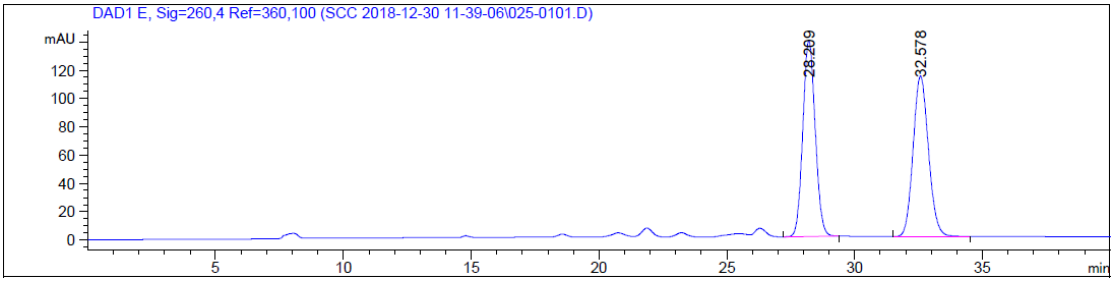


Prepared according to method **F**. The product **4b** was isolated in 80% yield (71.9 mg) and 94% ee.

The characterization data and spectrums of **4b** are same to **3b**.

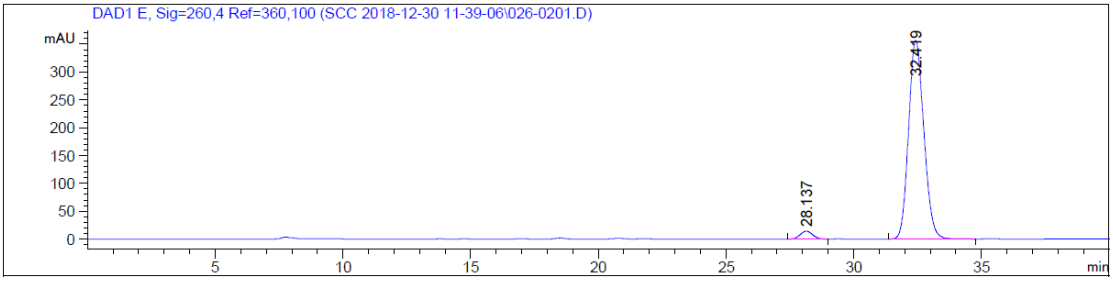
$[\alpha]_D^{20}$ +12.6° (*c* 1.14, $CHCl_3$)

The enantiomeric excess of **4b** was determined by chiral HPLC analysis on IC-3 column. Conditions: hexane/isopropanol = 90:10, flow rate = 0.4 mL/min, T = 25 °C, UV-Vis detection at λ = 260 nm, t_{R1} = 28.1 min (minor), t_{R2} = 32.4 min (major).



Signal 5: DAD1 E, Sig=260,4 Ref=360,100

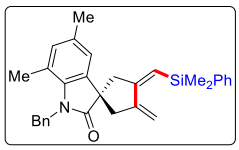
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.209	BB	0.5252	4672.03516	138.63710	49.6211
2	32.578	BB	0.6475	4743.39258	113.52082	50.3789
Totals :				9415.42773	252.15792	



Signal 5: DAD1 E, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.137	BB	0.5125	471.56274	14.16234	3.0847
2	32.419	BB	0.6445	1.48155e4	356.72794	96.9153
Totals :				1.52871e4	370.89027	

(*S*,*Z*)-1'-benzyl-3-((dimethyl(phenyl)silyl)methylene)-5',7'-dimethyl-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (4c)

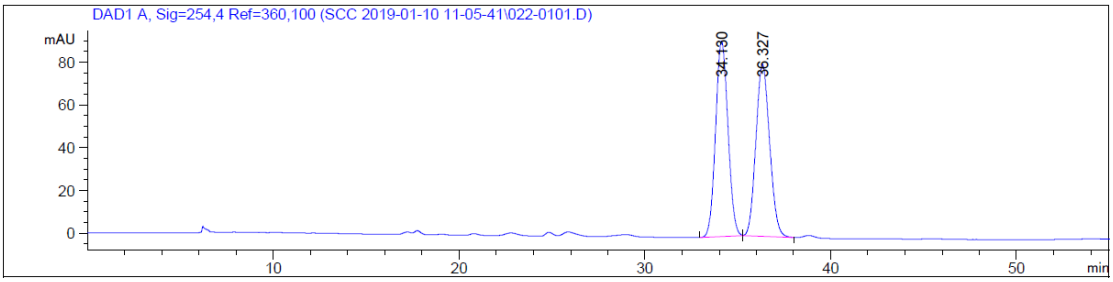


Prepared according to method **F**. The product **4c** was isolated in 72% yield (66.4 mg) and 96% ee.

The characterization data and spectrums of **4c** are same to **3c**.

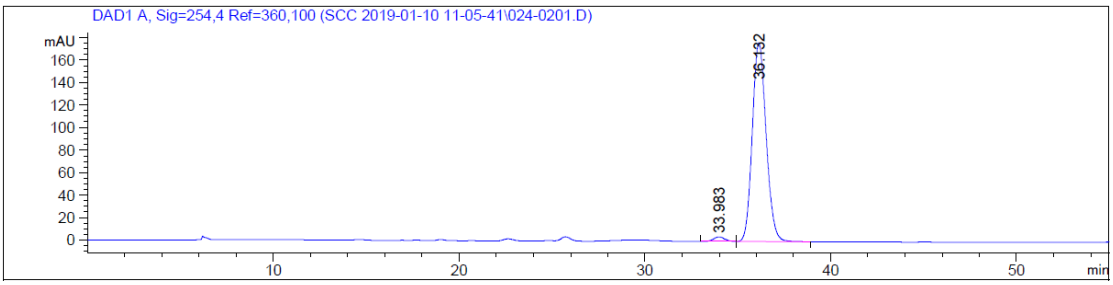
$[\alpha]_D^{20}$ +8.7° (*c* 2.30, $CHCl_3$)

The enantiomeric excess of **4c** was determined by chiral HPLC analysis on Chiralpak IC-3 column. Conditions: hexane/isopropanol = 92:8, flow rate = 0.5 mL/min, T = 25 °C, UV-Vis detection at λ = 254 nm, t_{R1} = 34.0 min (minor), t_{R2} = 36.1 min (major).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

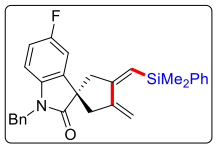
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.130	BB	0.7170	4220.34033	91.34421	50.5122
2	36.327	BB	0.8073	4134.75879	80.22382	49.4878
Totals :				8355.09912	171.56802	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.983	BB	0.6166	176.31381	3.95137	1.8932
2	36.132	BB	0.8031	9136.66113	176.75449	98.1068
Totals :				9312.97495	180.70585	

(*S*,*Z*)-1'-benzyl-3-((dimethyl(phenyl)silyl)methylene)-5'-fluoro-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (4d)

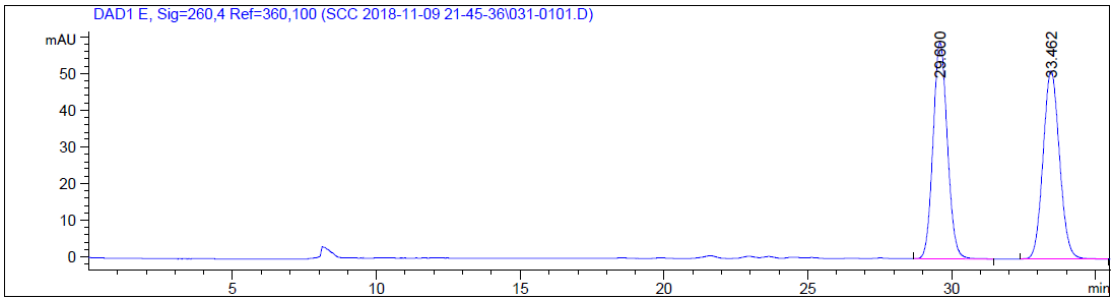


Prepared according to method **F**. The product **4d** was isolated in 67% yield (60.4 mg) with 91% ee.

The characterization data and spectrums of **4d** are same to **3d**.

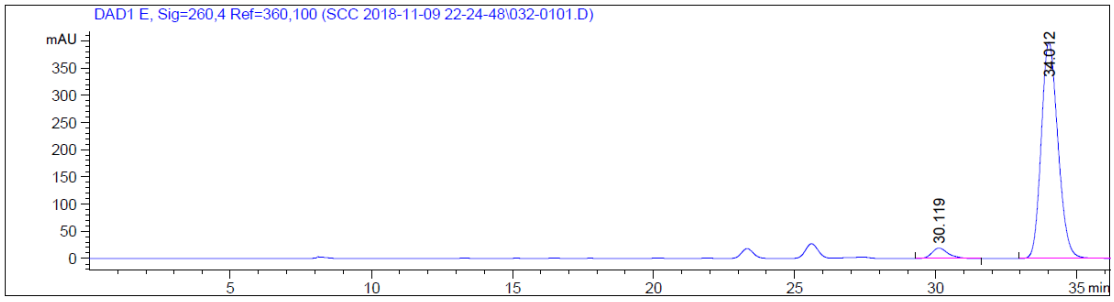
$[\alpha]_D^{20}$ +27.3° (*c* 3.20, $CHCl_3$)

The enantiomeric excess of **4d** was determined by chiral HPLC analysis on IC-3 column. Conditions: hexane/isopropanol = 95:5, flow rate = 0.4 mL/min, T = 25 °C, UV-Vis detection at λ = 260 nm, t_{R1} = 30.1 min (minor), t_{R2} = 34.0 min (major).



Signal 5: DAD1 E, Sig=260,4 Ref=360,100

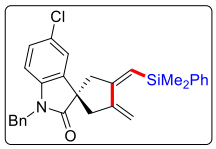
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.600	BB	0.5357	2044.32739	59.07508	50.0249
2	33.462	BBA	0.6223	2042.29297	51.31702	49.9751
Totals :				4086.62036	110.39211	



Signal 5: DAD1 E, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.119	BB	0.6049	767.74963	19.10295	4.4870
2	34.012	BBA	0.6372	1.63429e4	397.92712	95.5130

(*S*,*Z*)-1'-benzyl-5'-chloro-3-((dimethyl(phenyl)silyl)methylene)-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (4e)



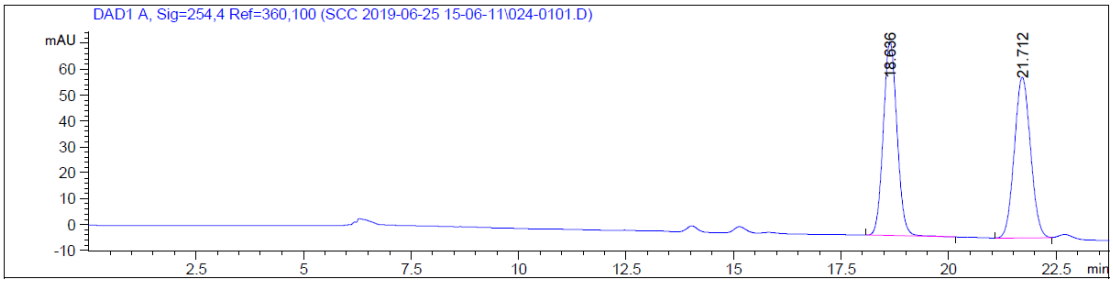
Prepared according to method **F**. The product **4e** was isolated in 56% yield (52.4 mg) and 92% ee.

The characterization data and spectrums of **4e** are same to **3e**.

$[\alpha]_D^{20}$ +28.9° (*c* 1.01, $CHCl_3$)

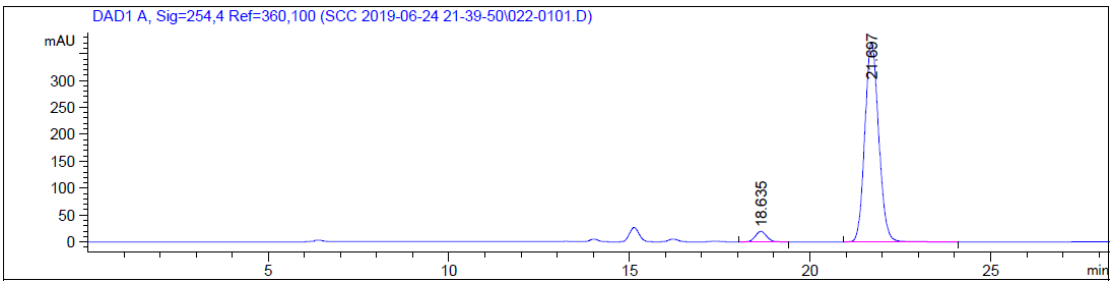
The enantiomeric excess of **4e** was determined by chiral HPLC analysis on IC-3 column.

Conditions: hexane/isopropanol = 94:6, flow rate = 0.5 mL/min, T = 25 °C, UV-Vis detection at λ = 254 nm, t_{R1} = 18.6 min (minor), t_{R2} = 21.7 min (major).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

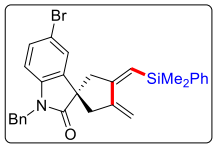
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.636	BB	0.3449	1661.94470	74.88974	50.5844
2	21.712	BB	0.4072	1623.54663	62.05556	49.4156
Totals :				3285.49133	136.94530	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.635	BB	0.3444	430.87222	19.60421	4.1824
2	21.697	BB	0.4131	9871.22949	370.15411	95.8176
Totals :				1.03021e4	389.75833	

(*S*,*Z*)-1'-benzyl-5'-bromo-3-((dimethyl(phenyl)silyl)methylene)-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (4f)

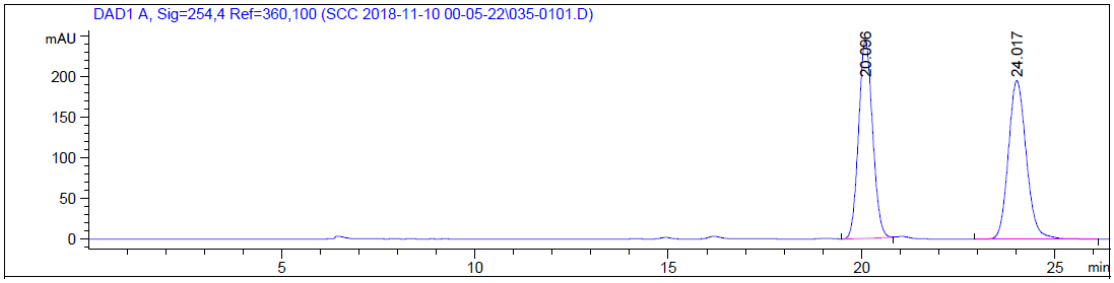


Prepared according to method **F**. The product **4f** was isolated in 72% yield (73.7 mg) and 91% ee.

The characterization data and spectrums of **4f** are same to **3f**.

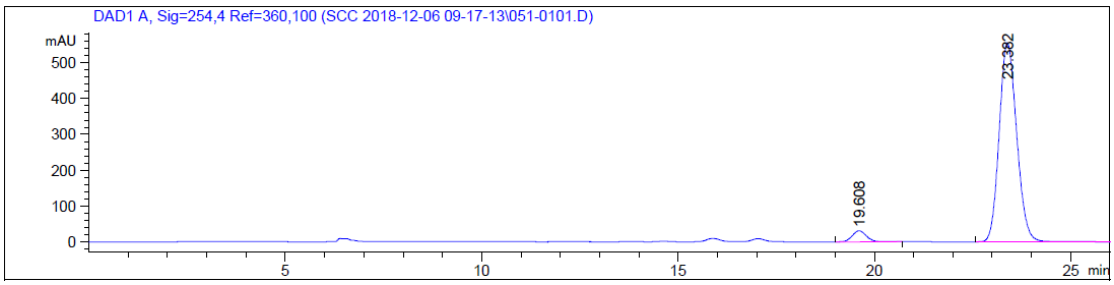
$[\alpha]_D^{20}$ +32.9° (*c* 2.03, $CHCl_3$)

The enantiomeric excess of **4f** was determined by chiral HPLC analysis on IC-3 column. Conditions: hexane/isopropanol = 94:6, flow rate = 0.5 mL/min, T = 25 °C, UV-Vis detection at λ = 254 nm, t_{R1} = 19.6 min (minor), t_{R2} = 23.4 min (major).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

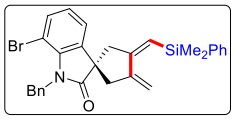
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.096	BB	0.3906	6106.10498	243.43355	49.2254
2	24.017	BB	0.4984	6298.26660	195.21004	50.7746
Totals :				1.24044e4	438.64359	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.608	BB	0.3947	779.69208	30.86169	4.3450
2	23.382	BBA	0.4830	1.71647e4	554.77472	95.6550
Totals :				1.79444e4	585.63641	

(*S*,*Z*)-1'-benzyl-7'-bromo-3-((dimethyl(phenyl)silyl)methylene)-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (4g)

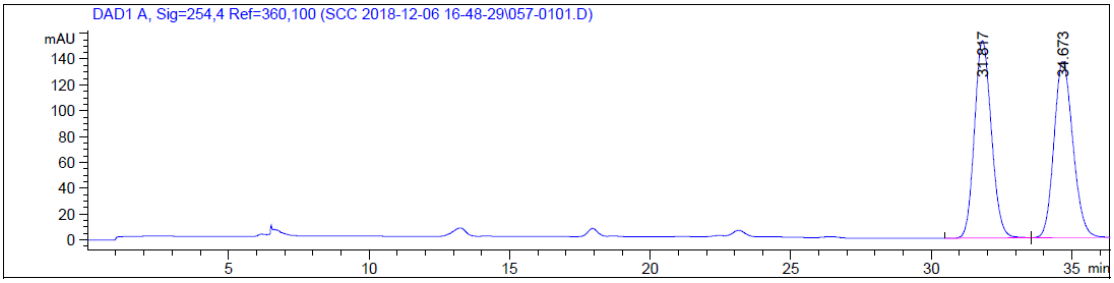


Prepared according to method **F**. The product **4g** was isolated in 62% yield (63.7 mg) and 94% ee.

The characterization data and spectrums of **4g** are same to **3g**.

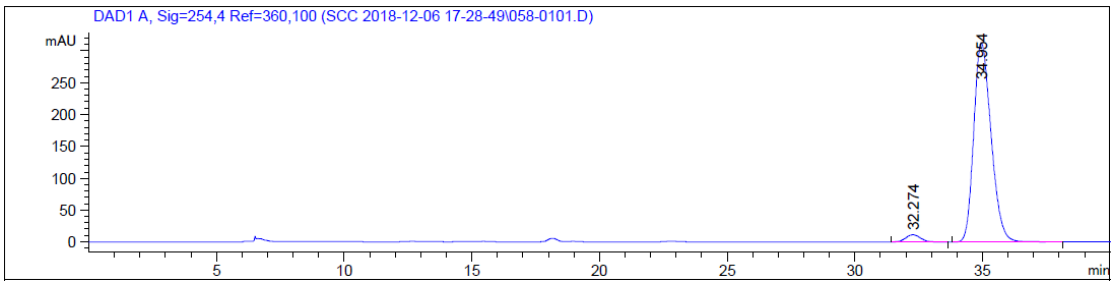
$[\alpha]_D^{20}$ +26.4° (*c* 3.10, $CHCl_3$)

The enantiomeric excess of **4g** was determined by chiral HPLC analysis on IC-3 column. Conditions: hexane/isopropanol = 98.8:1.2, flow rate = 0.5 mL/min, T = 25 °C, UV-Vis detection at λ = 254 nm, t_{R1} = 32.3 min (minor), t_{R2} = 35.0 min (major).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

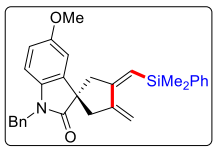
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.817	BB	0.6536	6388.25830	152.85295	50.0958
2	34.673	BBA	0.7240	6363.81348	136.46954	49.9042
Totals :				1.27521e4	289.32249	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.274	BB	0.6384	464.55576	11.47335	3.0475
2	34.954	BB	0.7314	1.47791e4	312.70972	96.9525
Totals :				1.52436e4	324.18307	

(*S*,*Z*)-1'-benzyl-3-((dimethyl(phenyl)silyl)methylene)-5'-methoxy-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (4h)



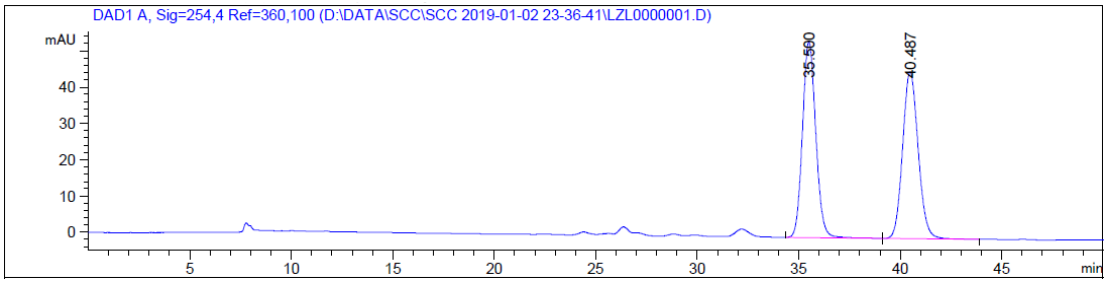
Prepared according to method **F**. The product **4h** was isolated in 68% yield (63.2 mg) and 92% ee.

The characterization data and spectrums of **4h** are same to **3h**.

$[\alpha]_D^{20}$ +16.3° (*c* 2.06, $CHCl_3$)

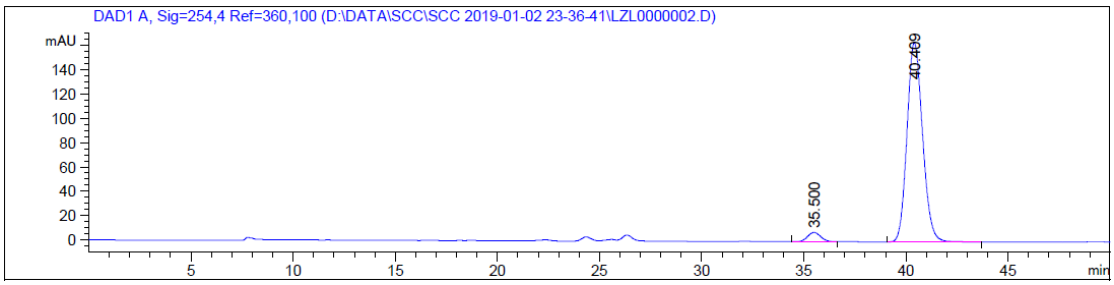
The enantiomeric excess of **4h** was determined by chiral HPLC analysis on IC-3 column.

Conditions: hexane/isopropanol = 90:10, flow rate = 0.4 mL/min, T = 25 °C, UV-Vis detection at λ = 254 nm, t_{R1} = 35.5 min (minor), t_{R2} = 40.4 min (major).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

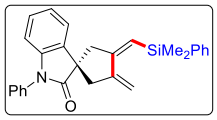
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.500	BB	0.7028	2456.62573	53.99958	50.1020
2	40.487	BB	0.8185	2446.62012	46.00107	49.8980
Totals :				4903.24585	100.00065	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.500	BB	0.6890	343.56180	7.69335	3.8135
2	40.409	BB	0.8171	8665.59375	163.82230	96.1865
Totals :				9009.15555	171.51564	

(*S*,*Z*)-3-((dimethyl(phenyl)silyl)methylene)-4-methylene-1'-phenylspiro[cyclopentane-1,3'-indolin]-2'-one (4i)



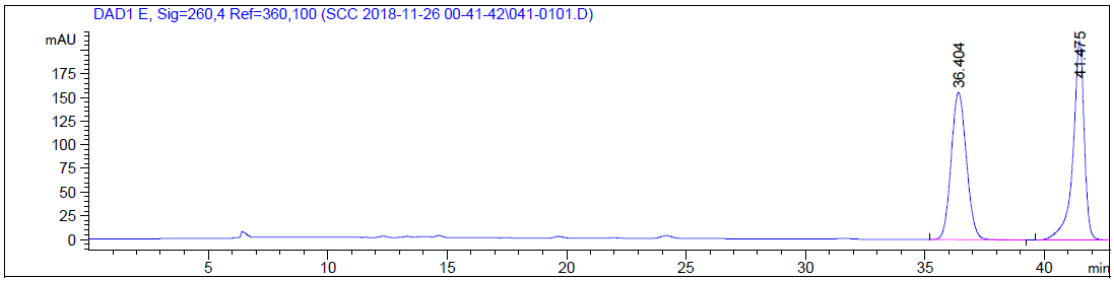
Prepared according to method **F**. The product **4i** was isolated in 70% yield (58.9 mg) and 92% ee. (ee value improved to 95% after recrystallization in Et_2O at room temperature)

The characterization data and spectrums of **4i** are same to **3k**.

$[\alpha]_D^{20}$ +10.8° (*c* 1.28, $CHCl_3$)

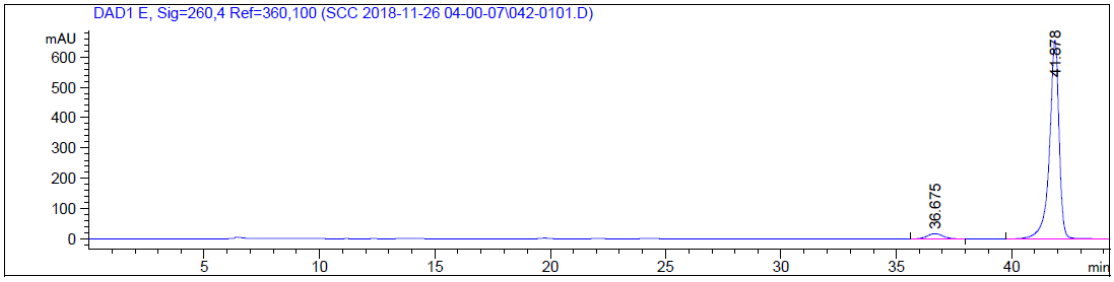
The enantiomeric excess of **4i** was determined by chiral HPLC analysis on IC-3 column.

Conditions: hexane/isopropanol = 95:5, flow rate = 0.5 mL/min, T = 25 °C, UV-Vis detection at λ = 260 nm, t_{R1} = 36.7 min (minor), t_{R2} = 41.9 min (major).



Signal 5: DAD1 E, Sig=260,4 Ref=360,100

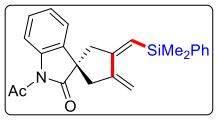
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.404	BB	0.6891	6897.40137	155.60748	50.1393
2	41.475	BBA	0.4809	6859.08838	210.09293	49.8607
Totals :				1.37565e4	365.70041	



Signal 5: DAD1 E, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.675	BB	0.6939	779.98395	17.23628	3.9409
2	41.878	BBA	0.4350	1.90122e4	654.36096	96.0591
Totals :				1.97921e4	671.59725	

(*S*,*Z*)-1'-acetyl-3-((dimethyl(phenyl)silyl)methylene)-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (4j)

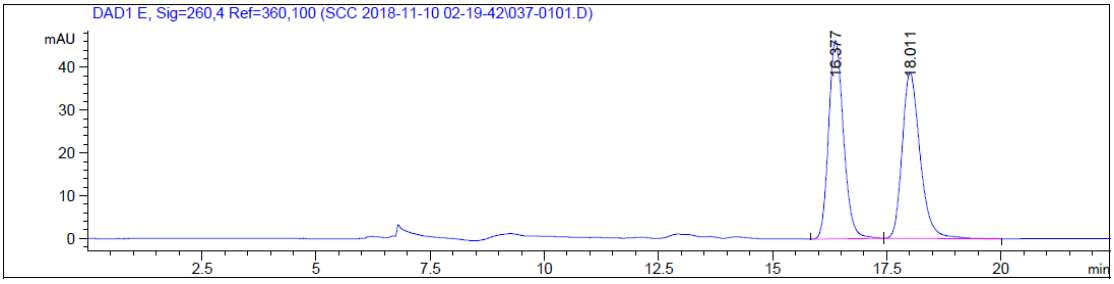


Prepared according to method **F**. The product **4j** was isolated in 42% yield (32.5 mg) and 69% ee.

The characterization data and spectrums of **4j** are same to **3l**.

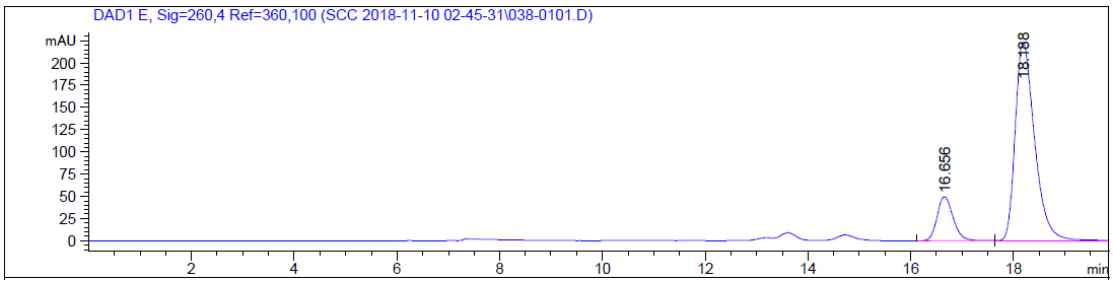
$[\alpha]_D^{20}$ +8.0° (*c* 1.04, $CHCl_3$)

The enantiomeric excess of **4j** was determined by chiral HPLC analysis on IC-3 column. Conditions: hexane/isopropanol = 99:1, flow rate = 0.5 mL/min, T = 25 °C, UV-Vis detection at λ = 260 nm, t_{R1} = 16.7 min (minor), t_{R2} = 18.2 min (major).



Signal 5: DAD1 E, Sig=260,4 Ref=360,100

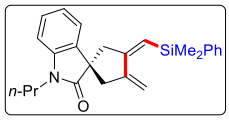
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.377	BB	0.3506	1050.74756	46.32187	49.9254
2	18.011	BB	0.4160	1053.88916	38.66420	50.0746
Totals :				2104.63672	84.98607	



Signal 5: DAD1 E, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.656	BB	0.3307	1069.39160	49.75622	15.4793
2	18.188	BBA	0.3992	5839.15283	223.22215	84.5207
Totals :				6908.54443	272.97837	

(*S*,*Z*)-3-((dimethyl(phenyl)silyl)methylene)-4-methylene-1'-propylspiro[cyclopentane-1,3'-indolin]-2'-one (4k)

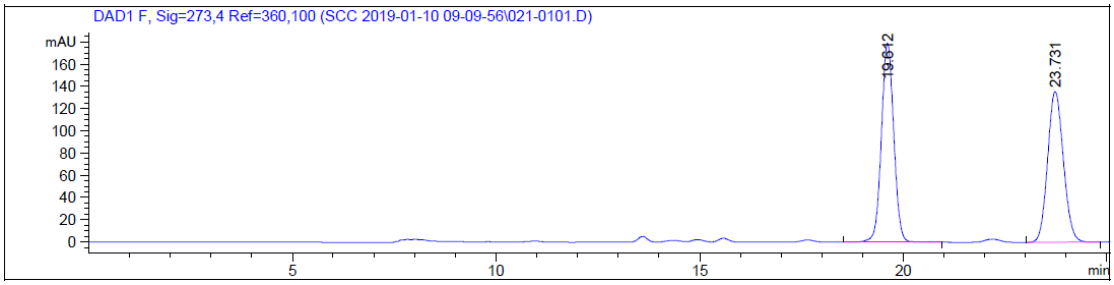


Prepared according to method **F**. The product **4k** was isolated in 79% yield (60.9 mg) and 85% ee.

The characterization data and spectrums of **4k** are same to **3j**.

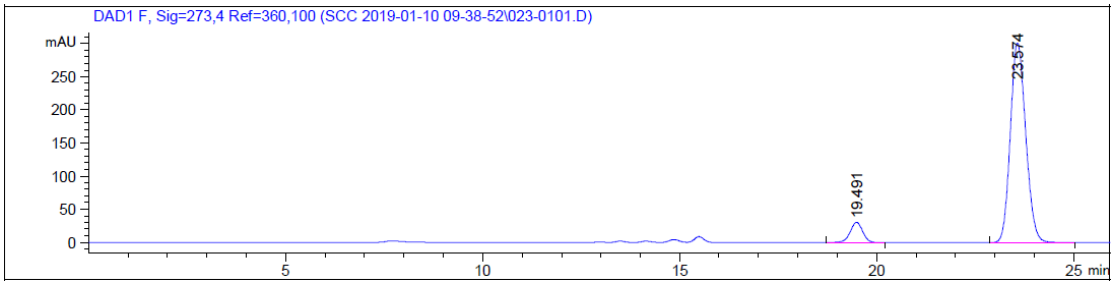
$[\alpha]_D^{20}$ +13.8° (*c* 1.85, $CHCl_3$)

The enantiomeric excess of **4k** was determined by chiral HPLC analysis on IC-3 column. Conditions: hexane/isopropanol = 90:10, flow rate = 0.4 mL/min, T = 25 °C, UV-Vis detection at λ = 273 nm, t_{R1} = 19.5 min (minor), t_{R2} = 23.6 min (major).



Signal 6: DAD1 F, Sig=273,4 Ref=360,100

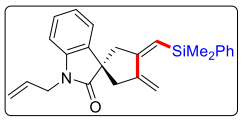
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.612	BB	0.3281	3778.66455	179.12192	50.8861
2	23.731	BB	0.4197	3647.06738	135.62816	49.1139
Totals :				7425.73193	314.75008	



Signal 6: DAD1 F, Sig=273,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.491	BB	0.3393	665.52673	30.41373	7.5255
2	23.574	BB	0.4229	8178.14795	301.06714	92.4745
Totals :				8843.67468	331.48087	

(*S*,*Z*)-1'-allyl-3-((dimethyl(phenyl)silyl)methylene)-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (4l)



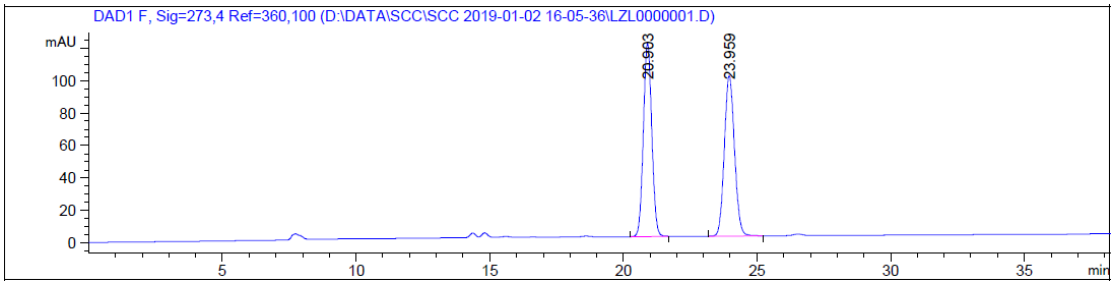
Prepared according to method **F**. The product **4l** was isolated in 80% yield (61.5 mg) and 88% ee.

The characterization data and spectrums of **4l** are same to **3m**.

$[\alpha]_D^{20}$ +14.2° (*c* 1.80, $CHCl_3$)

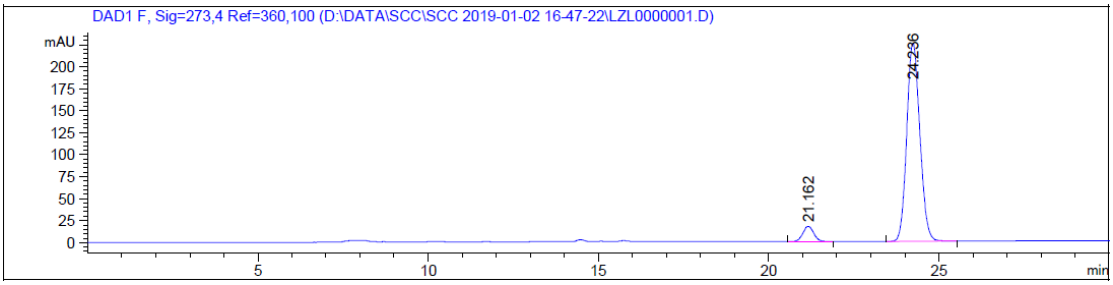
The enantiomeric excess of **4l** was determined by chiral HPLC analysis on IC-3 column.

Conditions: hexane/isopropanol = 90:10, flow rate = 0.4 mL/min, T = 25 °C, UV-Vis detection at λ = 273 nm, t_{R1} = 21.2 min (minor), t_{R2} = 24.2 min (major).



Signal 6: DAD1 F, Sig=273,4 Ref=360,100

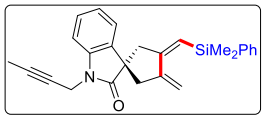
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.903	BB	0.3402	2597.11255	119.20599	49.8888
2	23.959	BB	0.4123	2608.69263	98.72852	50.1112
Totals :				5205.80518	217.93450	



Signal 6: DAD1 F, Sig=273,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.162	BB	0.3427	378.80591	17.21802	5.9214
2	24.236	BB	0.4154	6018.40771	225.45686	94.0786
Totals :				6397.21362	242.67488	

(*S*,*Z*)-1'-(but-2-yn-1-yl)-3-((dimethyl(phenyl)silyl)methylene)-4-methylenespiro[cyclopentane-1,3'-indolin]-2'-one (4m)

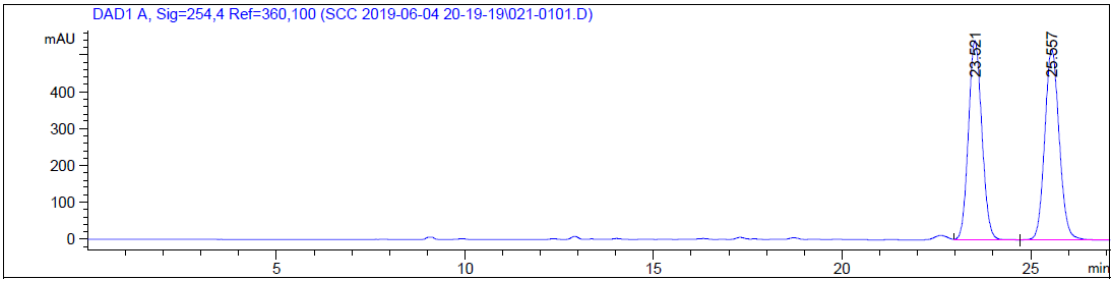


Prepared according to method **F**. The product **4m** was isolated in 67% yield (53.2 mg) and 91% ee.

The characterization data and spectrums of **4m** are same to **3n**.

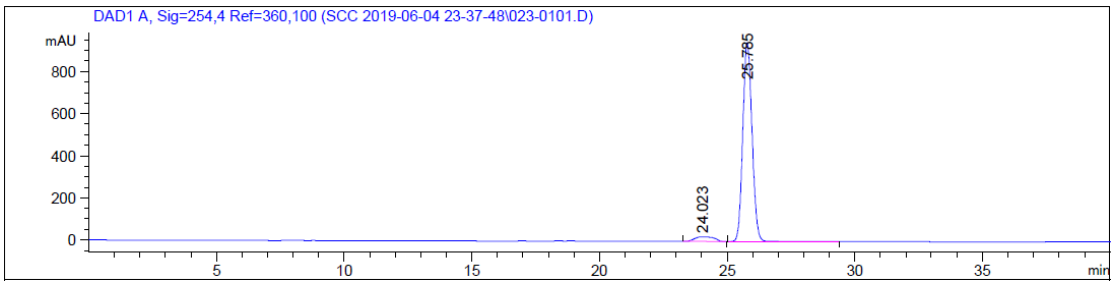
$[\alpha]_D^{20}$ +10.1° (*c* 1.51, $CHCl_3$)

The enantiomeric excess of **4m** was determined by chiral HPLC analysis on IC-3 column. Conditions: hexane/isopropanol = 90:10, flow rate = 0.4 mL/min, T = 25 °C, UV-Vis detection at λ = 254 nm, t_{R1} = 24.0 min (minor), t_{R2} = 25.8 min (major).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

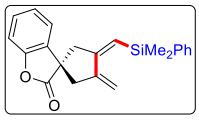
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.521	VB	0.3850	1.33895e4	540.59735	49.1962
2	25.557	BBA	0.4135	1.38270e4	517.91357	50.8038
Totals :				2.72165e4	1058.51093	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.023	BB	0.7418	1140.69580	21.61153	4.5832
2	25.785	BB	0.3912	2.37478e4	944.82587	95.4168
Totals :				2.48885e4	966.43740	

(*S*,*Z*)-3'-((dimethyl(phenyl)silyl)methylene)-4'-methylene-2*H*-spiro[benzofuran-3,1'-cyclopentan]-2-one (4n)

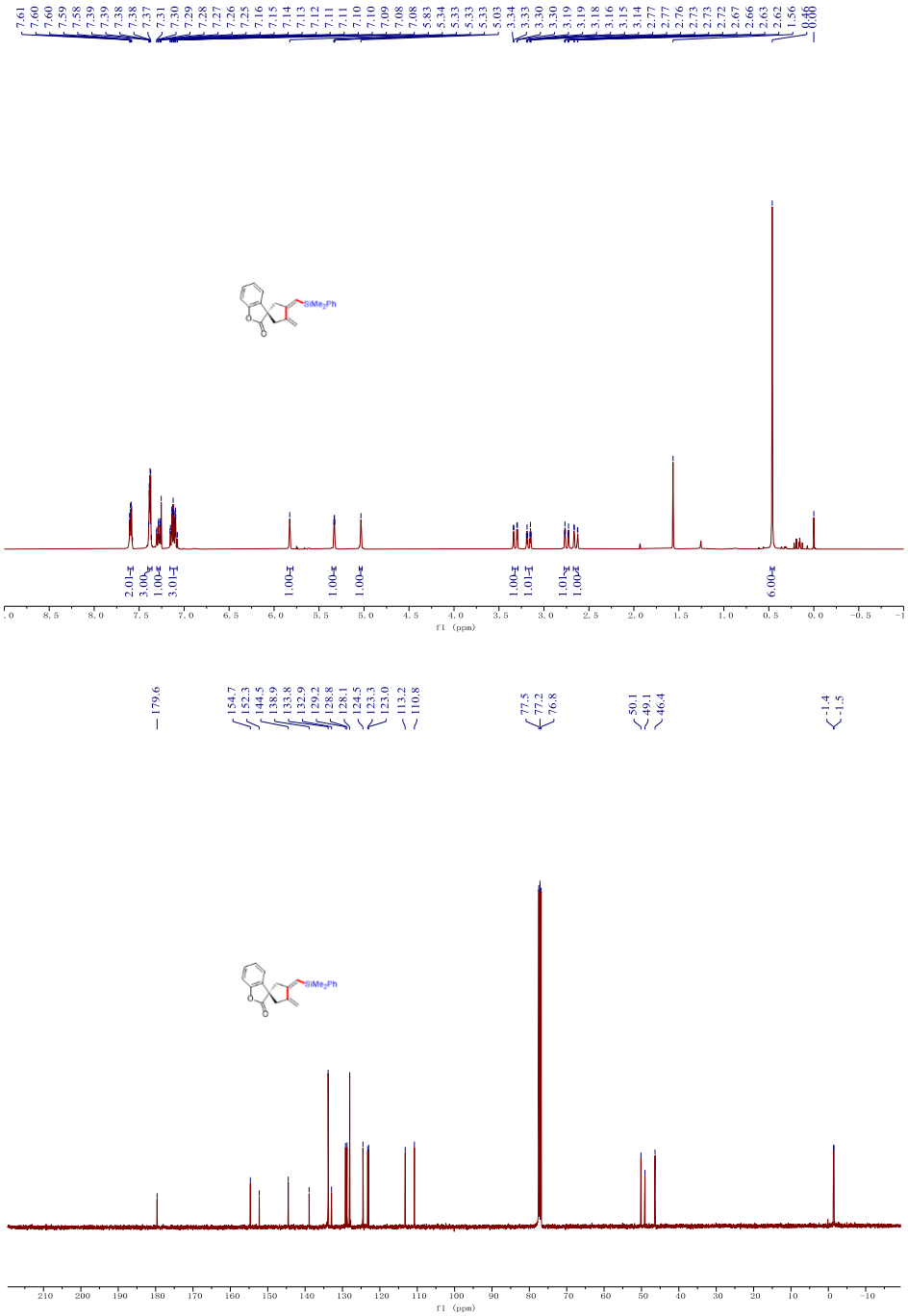


Prepared according to method **F**. The product **4n** was isolated in 51% yield (35.2 mg) and 81% ee.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 7.40 – 7.36 (m, 3H), 7.31 – 7.26 (m, 1H), 7.16 – 7.06 (m, 3H), 5.83 (s, 1H), 5.33 (dd, *J* = 2.8, 1.5 Hz, 1H), 5.03 (s, 1H), 3.32 (dd, *J* = 15.8, 2.5 Hz, 1H), 3.17 (dt, *J* = 15.4, 2.7 Hz, 1H), 2.78 – 2.71 (m, 1H), 2.69 – 2.61 (m, 1H), 0.46 (s, 6H).

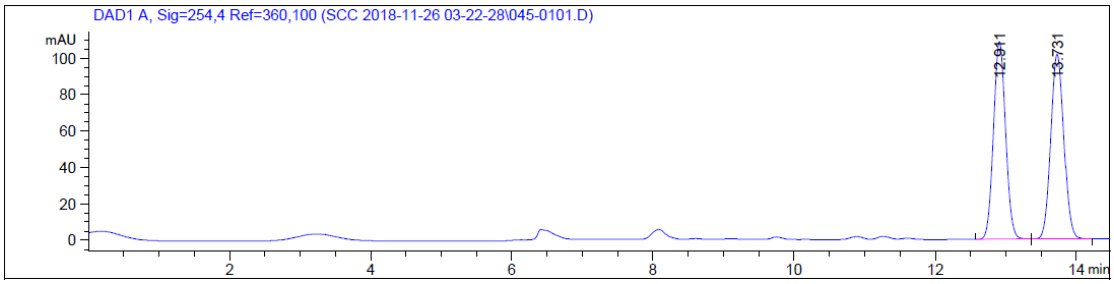
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 154.7, 152.3, 144.5, 138.9, 133.9, 132.9, 129.2, 128.8, 128.1, 124.5, 123.3, 123.0, 113.2, 110.8, 50.1, 49.1, 46.4, -1.4, -1.5.

HRMS (ESI): m/z Calcd. for $C_{22}H_{23}O_2Si$ $[M+H]^+$: 347.1467, found: 347.1468.



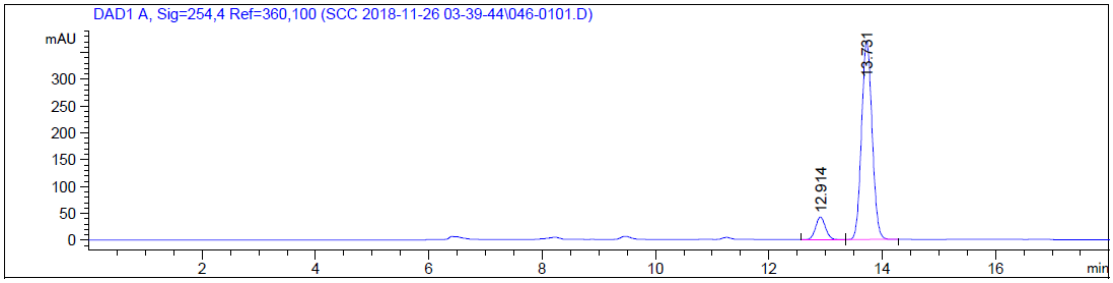
$[\alpha]_D^{20}$ +10.5° (*c* 1.45, $CHCl_3$)

The enantiomeric excess of **4n** was determined by chiral HPLC analysis on IC-3 column. Conditions: hexane/isopropanol = 95:5, flow rate = 0.5 mL/min, T = 25 °C, UV-Vis detection at λ = 254 nm, t_{R1} = 12.9 min (minor), t_{R2} = 13.7 min (major).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

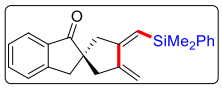
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.911	BB	0.1886	1306.95349	108.46664	49.9653
2	13.731	BB	0.2025	1308.77039	101.44193	50.0347
Totals :				2615.72388	209.90857	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.914	BB	0.1888	505.69666	41.91538	9.5325
2	13.731	BB	0.2010	4799.30029	370.70599	90.4675
Totals :				5304.99695	412.62138	

(*S*,*Z*)-3-((dimethyl(phenyl)silyl)methylene)-4-methylenespiro[cyclopentane-1,2'-inden]-1'(3'*H*)-one (4o)

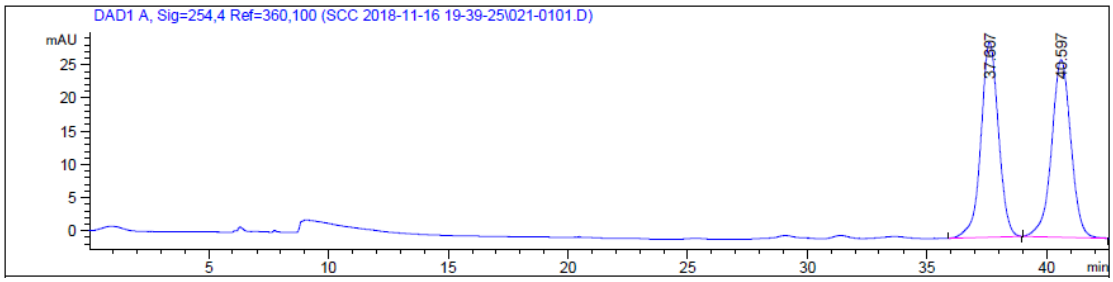


Prepared according to method **F**. The product **4o** was isolated in 57% yield (39.2 mg) and 56% ee.

The characterization data and spectrums of **4o** are same to **3o**.

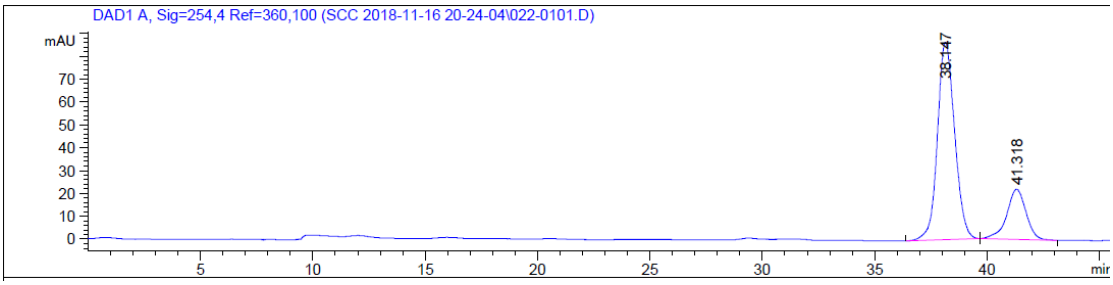
$[\alpha]_D^{20}$ -7.1° (*c* 1.43, $CHCl_3$)

The enantiomeric excess of **4o** was determined by chiral HPLC analysis on Chiralpak IC-3 column. Conditions: hexane/isopropanol = 99.6:0.4, flow rate = 0.5 mL/min, T = 25 °C, UV-Vis detection at λ = 254 nm, t_{R1} = 38.1 min (major), t_{R2} = 41.3 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

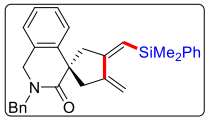
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.607	BB	0.7744	1490.62195	29.35661	49.9529
2	40.597	BBA	0.8569	1493.43420	26.68805	50.0471
Totals :				2984.05615	56.04466	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.147	BB	0.8139	4588.49170	86.35617	77.8924
2	41.318	BB	0.8952	1302.31616	21.85568	22.1076
Totals :				5890.80786	108.21185	

(*S*,*Z*)-2'-benzyl-3-((dimethyl(phenyl)silyl)methylene)-4-methylene-1',2'-dihydro-3'*H*-spiro[cyclopentane-1,4'-isoquinolin]-3'-one (4p)

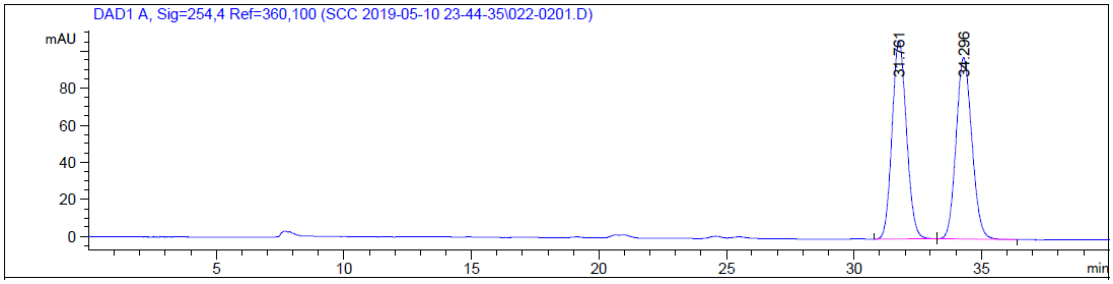


Prepared according to method **F**. The product **4p** was isolated in 65% yield (58.4 mg) and 95% ee.

The characterization data and spectrums of **4p** are same to **3w**.

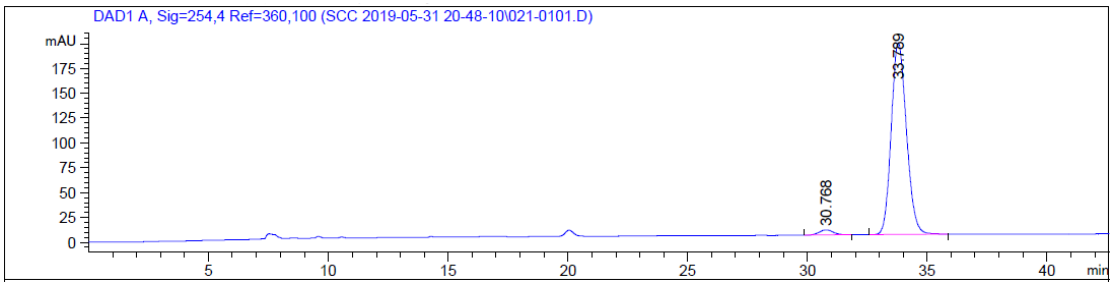
$[\alpha]_D^{20}$ +15.4° (*c* 1.46, $CHCl_3$)

The enantiomeric excess of **4p** was determined by chiral HPLC analysis on IC-3 column. Conditions: hexane/isopropanol = 80:20, flow rate = 0.4 mL/min, T = 25 °C, UV-Vis detection at λ = 254 nm, t_{R1} = 30.8 min (minor), t_{R2} = 33.8 min (major).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

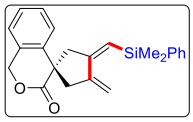
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.761	BB	0.6146	4199.35352	106.82281	49.9310
2	34.296	BB	0.6767	4210.95752	97.72299	50.0690
Totals :				8410.31104	204.54580	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.768	BB	0.5708	212.23781	5.19277	2.4351
2	33.789	BB	0.6846	8503.35938	192.77992	97.5649
Totals :				8715.59718	197.97270	

(*S*,*Z*)-3-((dimethyl(phenyl)silyl)methylene)-4-methylenespiro[cyclopentane-1,4'-isochroman]-3'-one (4q)

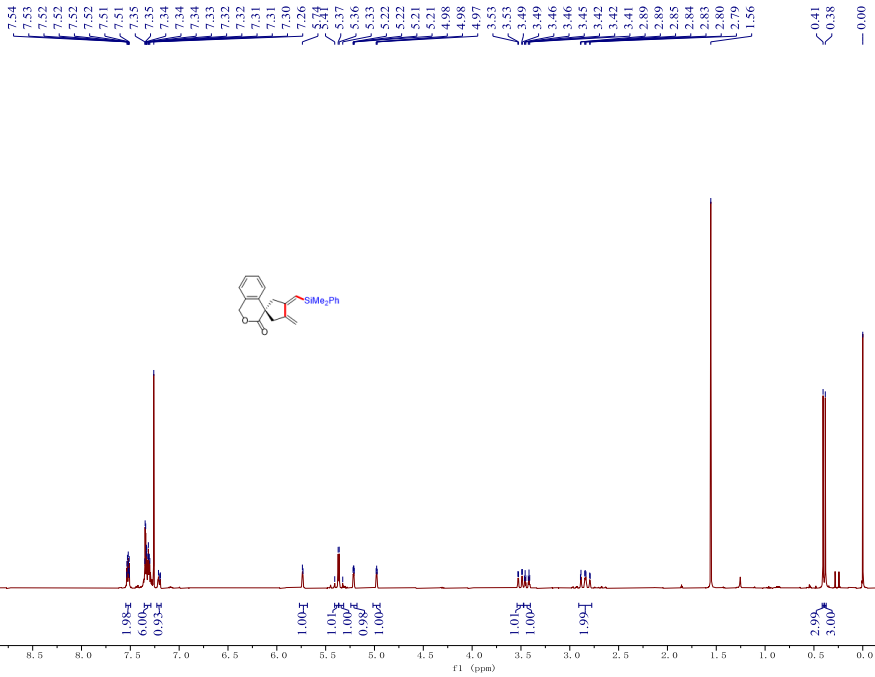


Prepared according to method **F**. The product **4q** was isolated in 65% yield (46.8 mg) and 87% ee.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.37 – 7.29 (m, 6H), 7.23 – 7.19 (m, 1H), 5.73 (d, *J* = 2.4 Hz, 1H), 5.39 (d, *J* = 14.2 Hz, 1H), 5.34 (d, *J* = 14.5 Hz, 1H), 5.21 (dd, *J* = 3.2, 1.5 Hz, 1H), 4.98 (t, *J* = 2.1 Hz, 1H), 3.51 (dd, *J* = 15.9, 2.6 Hz, 1H), 3.44 (dt, *J* = 15.9, 2.9 Hz, 1H), 2.90 – 2.78 (m, 2H), 0.41 (s, 3H), 0.38 (s, 3H).

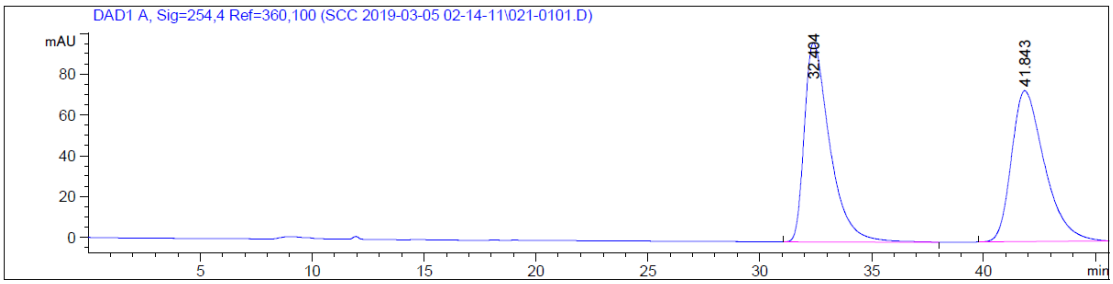
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 155.4, 144.9, 138.9, 138.3, 133.9, 131.2, 129.1, 128.8, 128.0, 127.4, 125.5, 125.0, 122.3, 112.6, 69.2, 49.3, 48.0, 43.7, -1.2, -1.6.

HRMS (ESI): m/z Calcd. for $C_{23}H_{25}O_2Si$ $[M+H]^+$: 361.1624, found: 361.1623.



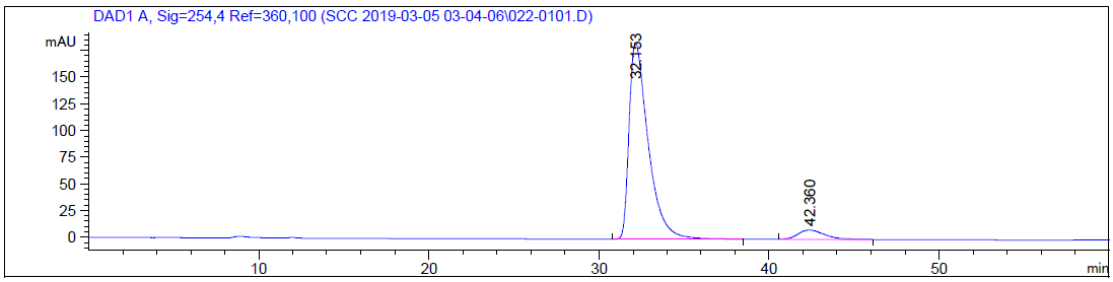
$[\alpha]_D^{20}$ -2.3° (*c* 2.33, $CHCl_3$)

The enantiomeric excess of **4q** was determined by chiral HPLC analysis on OJ-3 column. Conditions: hexane/isopropanol = 80:20, flow rate = 0.35 mL/min, T = 25 °C, UV-Vis detection at λ = 254 nm, t_{R1} = 32.2 min (major), t_{R2} = 42.4 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

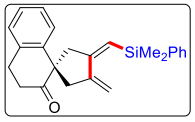
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.404	BB	1.1816	7726.62402	97.60458	50.4137
2	41.843	BBA	1.5223	7599.79834	73.99151	49.5863
Totals :				1.53264e4	171.59608	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.153	BB	1.1682	1.43874e4	184.01392	93.7338
2	42.360	BB	1.2960	961.81494	8.82151	6.2662
Totals :				1.53492e4	192.83542	

(*S*,*Z*)-3-((dimethyl(phenyl)silyl)methylene)-4-methylene-3',4'-dihydro-2'*H*-spiro[cyclopentane-1,1'-naphthalen]-2'-one (4r)

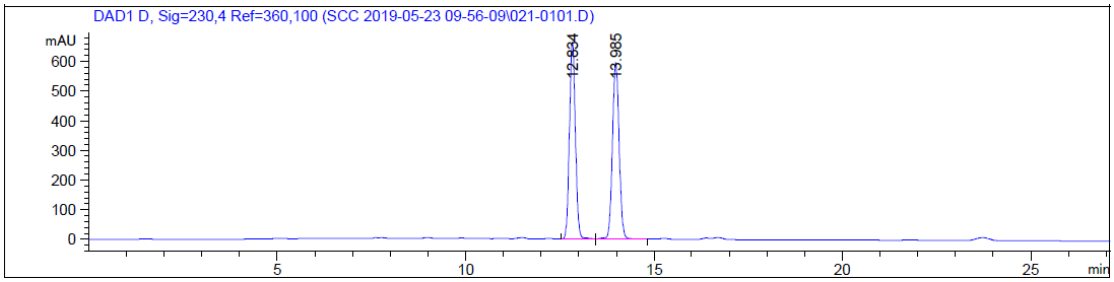


Prepared according to method **F**. The product **4r** was isolated in 78% yield (55.8 mg) and 85% ee.

The characterization data and spectrums of **4r** are same to **3s**.

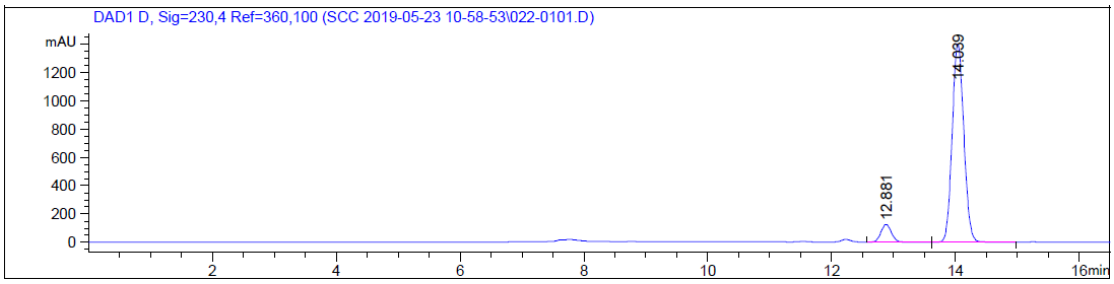
$[\alpha]_D^{20}$ +19.9° (*c* 1.72, $CHCl_3$)

The enantiomeric excess of **4r** was determined by chiral HPLC analysis on IC-3 column. Conditions: hexane/isopropanol = 90:10, flow rate = 0.4 mL/min, T = 25 °C, UV-Vis detection at λ = 230 nm, t_{R1} = 12.9 min (minor), t_{R2} = 14.0 min (major).



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

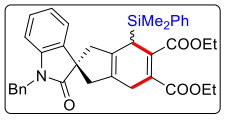
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.834	BB	0.1726	7299.65820	662.39099	49.8869
2	13.985	BB	0.1941	7332.76074	593.86212	50.1131
Totals :				1.46324e4	1256.25311	



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.881	BB	0.1827	1472.31384	125.61085	7.4383
2	14.039	BB	0.2043	1.83213e4	1403.66333	92.5617
Totals :				1.97936e4	1529.27418	

(*S*)-Diethyl 1'-benzyl-4-(dimethyl(phenyl)silyl)-2'-oxo-1,3,4,7-tetrahydrospiro[indene-2,3'-indo-line]-5,6-dicarboxylate (5a)

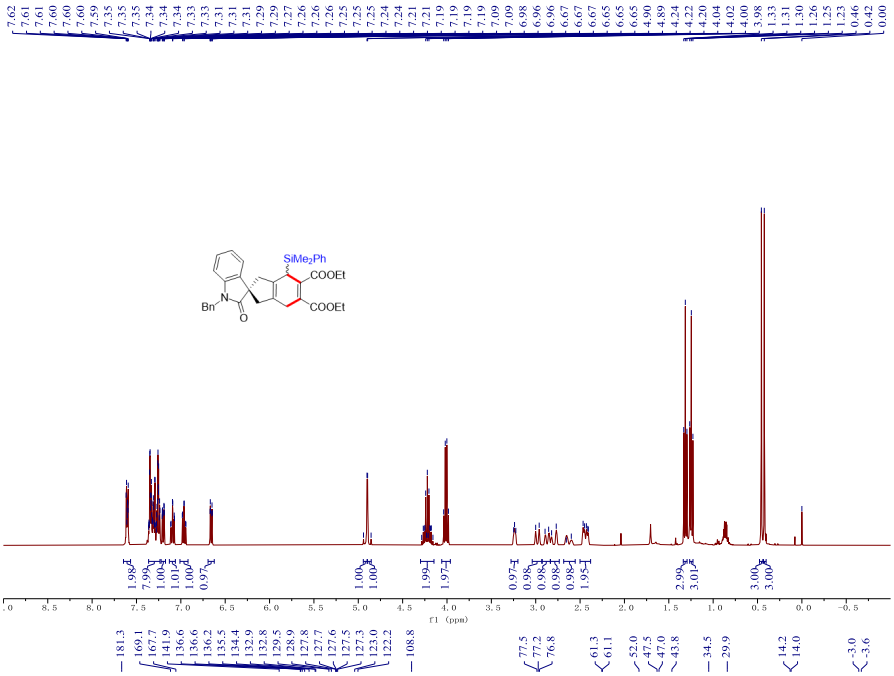


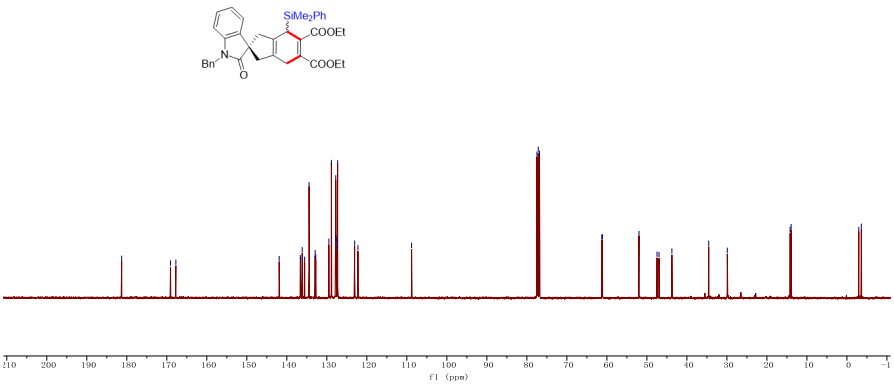
Prepared according to method **G** The product **5a** was obtained as white solid in 76% yield (91.9 mg, dr = 61:39).

(5a major) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.38 – 7.22 (m, 8H), 7.20 (ddd, *J* = 7.4, 1.4, 0.5 Hz, 1H), 7.09 (td, *J* = 7.7, 1.3 Hz, 1H), 6.96 (td, *J* = 7.5, 1.0 Hz, 1H), 6.66 (dt, *J* = 7.7, 0.8 Hz, 1H), 4.92 (d, *J* = 15.7 Hz, 1H), 4.88 (d, *J* = 15.7 Hz, 1H), 4.30 – 4.15 (m, 2H), 4.01 (q, *J* = 7.1 Hz, 2H), 3.27 – 3.19 (m, 1H), 2.98 (d, *J* = 15.9 Hz, 1H), 2.87 (d, *J* = 16.2 Hz, 1H), 2.85 – 2.74 (m, 1H), 2.69 – 2.56 (m, 1H), 2.50 – 2.38 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.46 (s, 3H), 0.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 181.3, 169.1, 167.7, 141.9, 136.6, 136.6, 136.2, 135.6, 134.4, 132.9, 132.8, 129.5, 128.9, 127.8, 127.7, 127.6, 127.5, 127.3, 123.1, 122.2, 108.8, 61.3, 61.1, 52.0, 47.5, 47.0, 43.8, 34.5, 29.9, 14.2, 14.0, -3.0, -3.6.

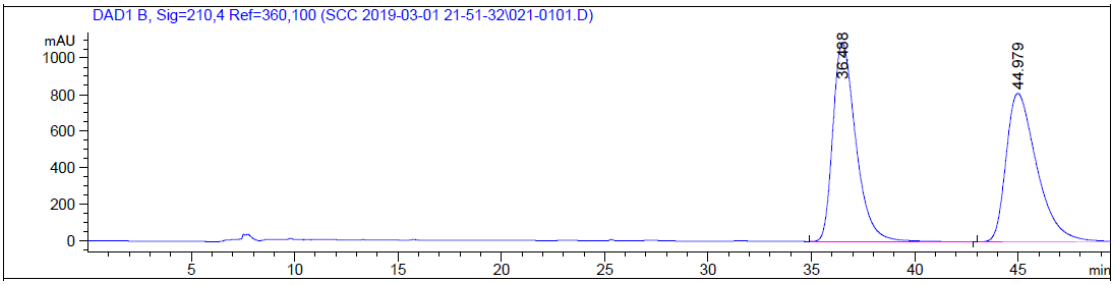
HRMS (ESI): m/z Calcd. for $C_{37}H_{40}NO_5Si$ $[M+H]^+$: 606.2676, found: 606.2673.





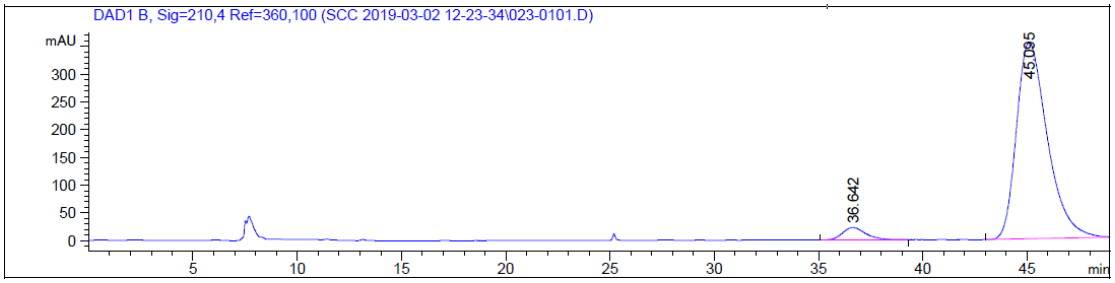
5a (major): (91% ee) $[\alpha]_D^{20}$ -12.5° (*c* 1.83, $CHCl_3$)

The enantiomeric excess of **5a (major)** was determined by chiral HPLC analysis on IC-3 column. Conditions: hexane/isopropanol = 90:10, flow rate = 0.4 mL/min, T = 25 °C, UV-Vis detection at λ = 210 nm, t_{R1} = 36.6 min (minor), t_{R2} = 45.1 min (major).



Signal 2: DAD1 B, Sig=210,4 Ref=360,100

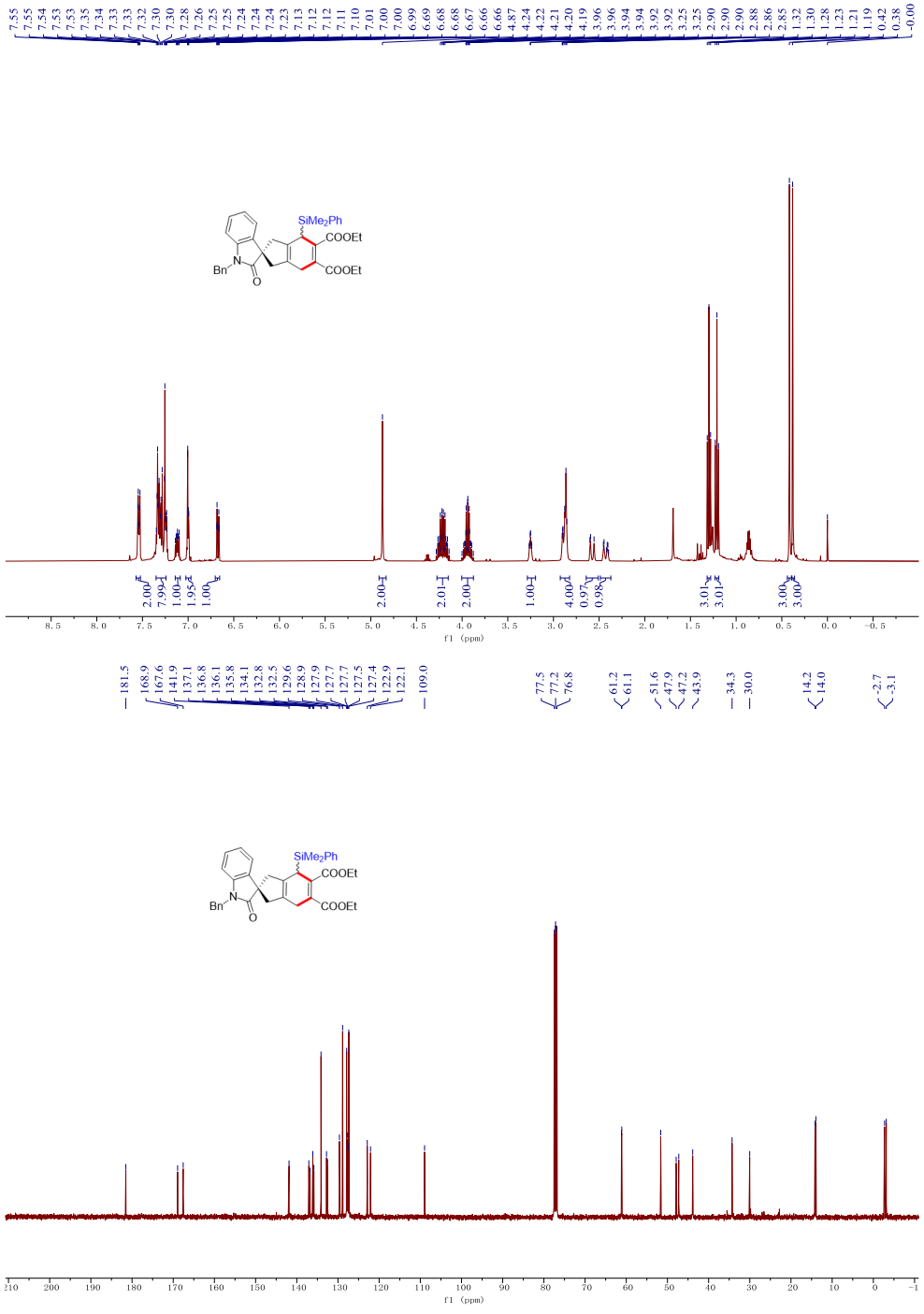
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.488	BB	1.1844	8.41248e4	1090.01758	50.1956
2	44.979	BBA	1.5403	8.34692e4	811.30933	49.8044
Totals :				1.67594e5	1901.32690	



Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.642	BB	1.0039	1749.68176	22.33530	4.5781
2	45.095	BBA	1.5377	3.64691e4	354.07010	95.4219
Totals :				3.82188e4	376.40540	

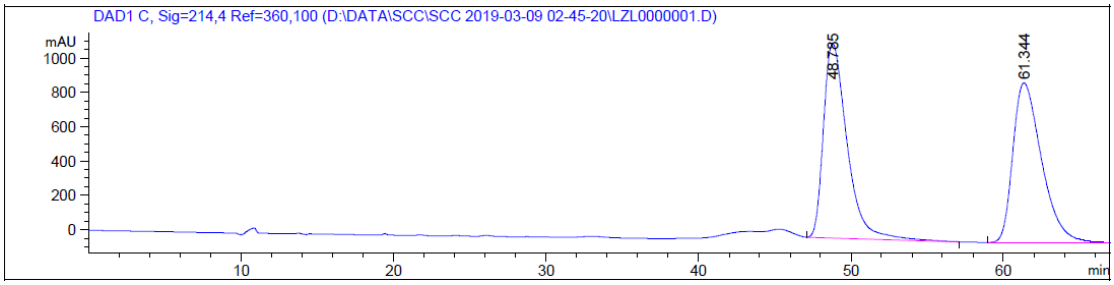
(5a (minor)) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.4, 2.0 Hz, 2H), 7.37 – 7.21 (m, 8H), 7.12 (ddd, *J* = 7.8, 5.5, 3.5 Hz, 1H), 7.00 (dd, *J* = 4.1, 1.4 Hz, 2H), 6.67 (dt, *J* = 7.8, 0.9 Hz, 1H), 4.87 (s, 2H), 4.29 – 4.13 (m, 2H), 4.01 – 3.87 (m, 2H), 3.25 (dt, *J* = 5.2, 2.7 Hz, 1H), 2.93 – 2.83 (m, 4H), 2.63 – 2.53 (m, 1H), 2.48 – 2.39 (m, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.42 (s, 3H), 0.38 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 181.5, 168.9, 167.6, 141.9, 137.1, 136.8, 136.1, 135.9, 134.1, 132.8, 132.5, 129.6, 128.9, 127.9, 127.7, 127.7, 127.5, 127.4, 122.9, 122.1, 109.0, 61.2, 61.1, 51.6, 47.9, 47.3, 43.9, 34.3, 30.0, 14.2, 14.0, -2.7, -3.1.
HRMS (ESI): m/z Calcd. for $C_{37}H_{40}NO_5Si$ $[M+H]^+$: 606.2676, found: 606.2672.



5a (minor): (90% ee) $[\alpha]_D^{20}$ -9.9° (*c* 1.02, $CHCl_3$)

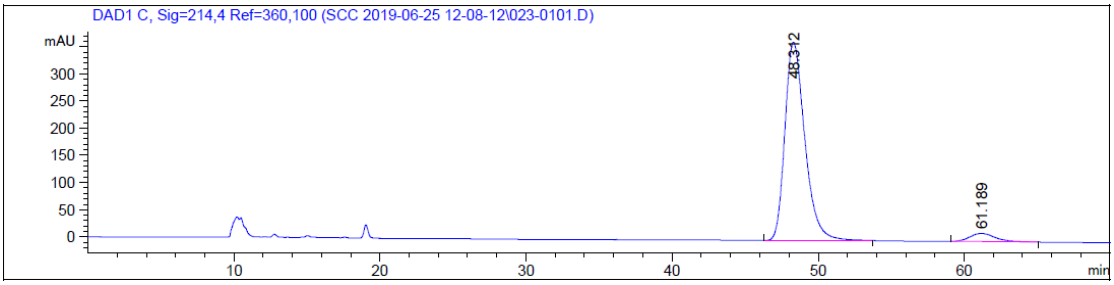
The enantiomeric excess of **5a (minor)** was determined by chiral HPLC analysis on Chiralpak IC-3 column.

Conditions: hexane/isopropanol = 65:35, flow rate = 0.3 mL/min, T = 25 °C, UV-Vis detection at λ = 214 nm, t_{R1} = 48.3 min (major), t_{R2} = 61.2 min (minor).



Signal 3: DAD1 C, Sig=214,4 Ref=360,100

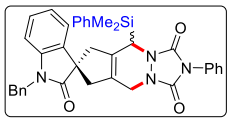
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	48.785	BB	1.6246	1.21734e5	1133.78870	50.1471
2	61.344	BBA	1.9520	1.21020e5	927.66992	49.8529
Totals :				2.42754e5	2061.45862	



Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	48.312	BB	1.4332	3.47244e4	365.22043	95.0099
2	61.189	BB	1.4242	1823.80042	15.21760	4.9901
Totals :				3.65482e4	380.43803	

(*S*)-1'-benzyl-5-(dimethyl(phenyl)silyl)-2-phenyl-6,9-dihydro-1*H*,5*H*,8*H*-spiro[cyclopenta[*d*][1,2,4]triazolo[1,2-*a*]pyridazine-7,3'-indoline]-1,2',3(2*H*)-trione (6a (major))

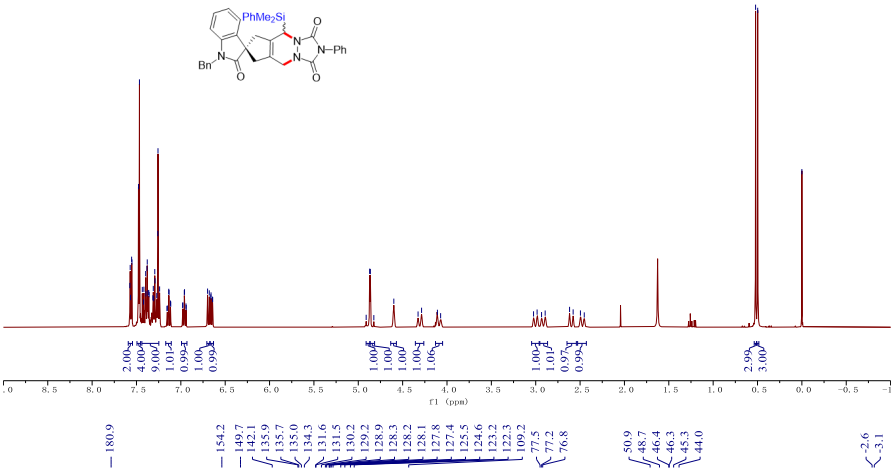


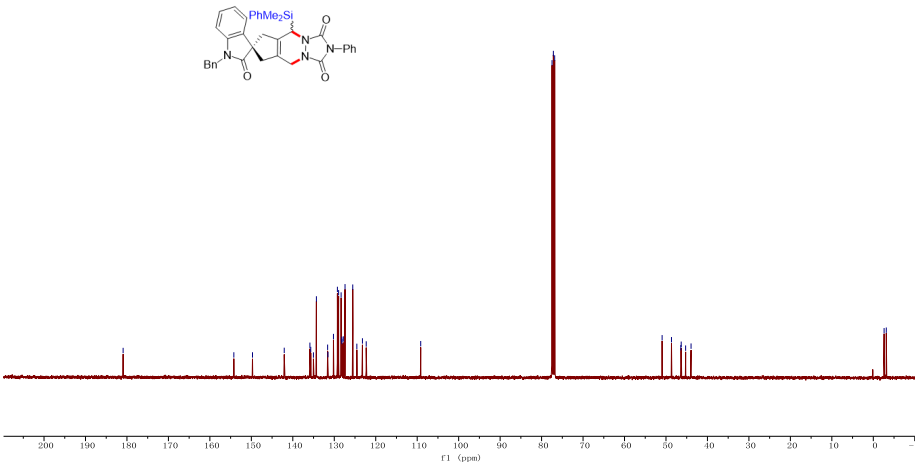
Prepared according to the above general method **G**. The product **6a (major)** was obtained as white solid.

(6a (major)) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.47 (d, *J* = 4.1 Hz, 4H), 7.46 – 7.21 (m, 9H), 7.13 (td, *J* = 7.7, 1.2 Hz, 1H), 6.96 (td, *J* = 7.6, 1.0 Hz, 1H), 6.69 (dt, *J* = 7.8, 0.8 Hz, 1H), 6.69 – 6.62 (m, 1H), 4.89 (d, *J* = 15.6 Hz, 1H), 4.84 (d, *J* = 15.7 Hz, 1H), 4.60 (s, 1H), 4.31 (d, *J* = 15.8 Hz, 1H), 4.09 (d, *J* = 14.5 Hz, 1H), 3.00 (d, *J* = 16.0 Hz, 1H), 2.91 (d, *J* = 16.4 Hz, 1H), 2.60 (d, *J* = 16.0 Hz, 1H), 2.47 (d, *J* = 17.3 Hz, 1H), 0.52 (s, 3H), 0.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.9, 154.2, 149.7, 142.1, 135.9, 135.7, 135.0, 134.3, 131.6, 131.5, 130.2, 129.2, 129.0, 128.4, 128.2, 128.2, 127.8, 127.4, 125.5, 124.6, 123.2, 122.3, 109.2, 50.9, 48.7, 46.4, 46.3, 45.3, 44.0, -2.6, -3.1.

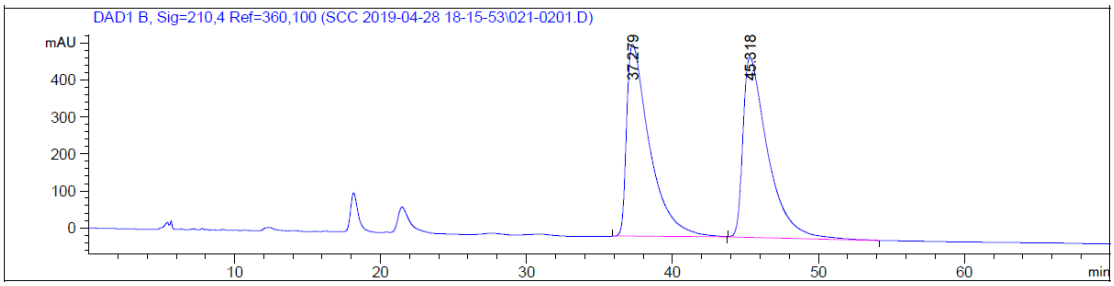
HRMS (ESI): m/z Calcd. for $C_{37}H_{35}N_4O_3Si$ $[M+H]^+$: 611.2478, found: 611.2480.





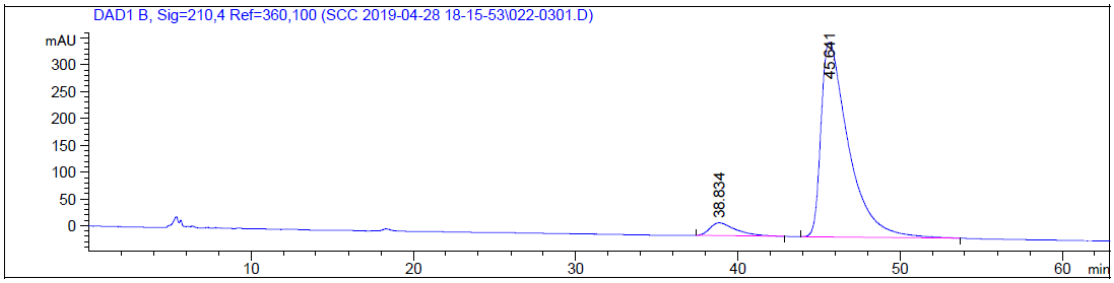
6a (major): (88% ee), $[\alpha]_D^{20}$ -141.4° (*c* 1.16, $CHCl_3$)

The enantiomeric excess of **6a (major)** was determined by chiral HPLC analysis on IB column. Conditions: hexane/isopropanol = 70:30, flow rate = 0.6 mL/min, T = 25 °C, UV-Vis detection at λ = 210 nm, t_{R1} = 38.8 min (minor), t_{R2} = 45.6 min (major).



Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.279	BB	1.5180	5.64965e4	518.98224	49.6820
2	45.318	BB	1.6198	5.72198e4	486.63623	50.3180
Totals :				1.13716e5	1005.61847	



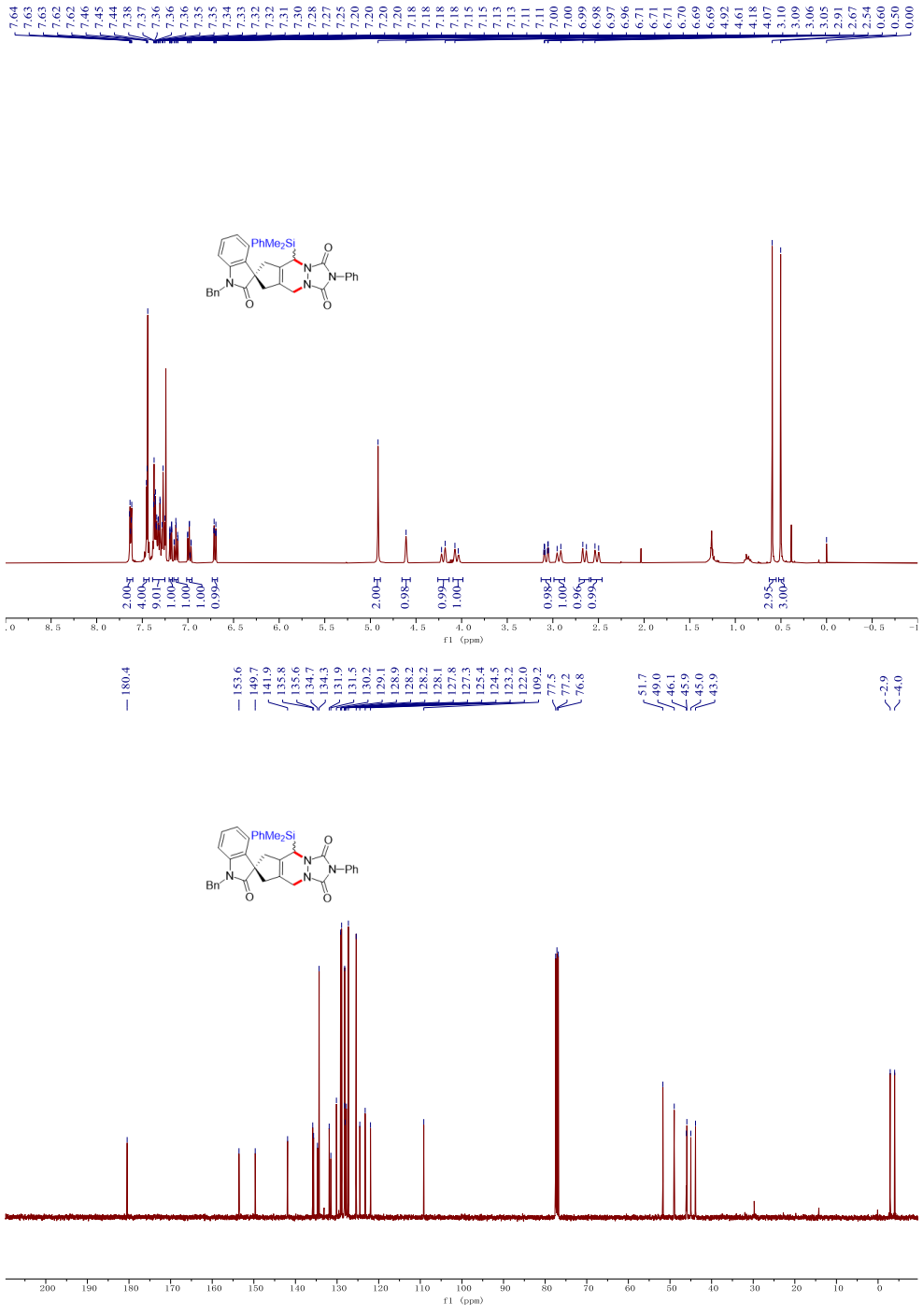
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.834	BB	1.3157	2668.97363	23.88519	5.8790
2	45.641	BB	1.6314	4.27298e4	362.96719	94.1210
Totals :				4.53988e4	386.85238	

(6a (minor)) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.48 – 7.42 (m, 4H), 7.40 – 7.23 (m, 9H), 7.19 (ddd, *J* = 7.4, 1.4, 0.6 Hz, 1H), 7.13 (td, *J* = 7.7, 1.3 Hz, 1H), 6.98 (td, *J* = 7.5, 1.0 Hz, 1H), 6.70 (dt, *J* = 7.8, 0.8 Hz, 1H), 4.92 (s, 2H), 4.61 (s, 1H), 4.20 (d, *J* = 16.0 Hz, 1H), 4.06 (d, *J* = 14.4 Hz, 1H), 3.07 (dq, *J* = 15.7, 2.0 Hz, 1H), 2.93 (d, *J* = 16.2 Hz, 1H), 2.65 (d, *J* = 15.8 Hz, 1H), 2.52 (d, *J* = 16.1 Hz, 1H), 0.60 (s, 3H), 0.50 (s, 3H).

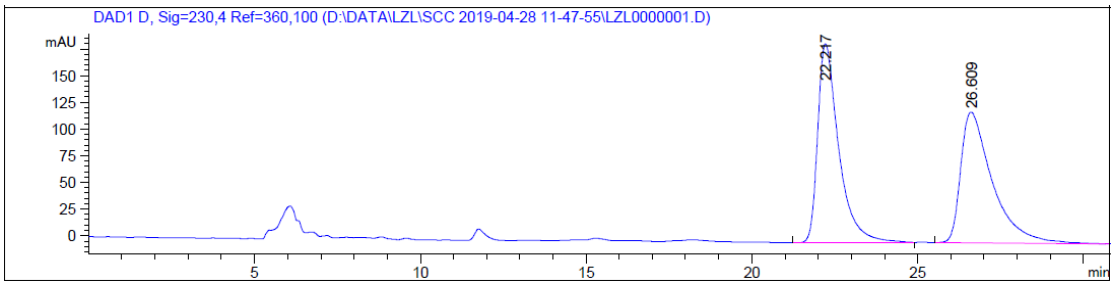
^{13}C NMR (101 MHz, $CDCl_3$) δ 180.4, 153.6, 149.7, 141.9, 135.9, 135.7, 134.7, 134.3, 131.9, 131.5, 130.2, 129.1, 128.9, 128.2, 128.2, 128.1, 127.8, 127.3, 125.4, 124.5, 123.3, 122.0, 109.2, 51.7, 49.0, 46.1, 46.0, 45.0, 43.9, -2.9, -4.0.

HRMS (ESI): m/z Calcd. for $C_{37}H_{35}N_4O_3Si$ $[M+H]^+$: 611.2478, found: 611.2488.



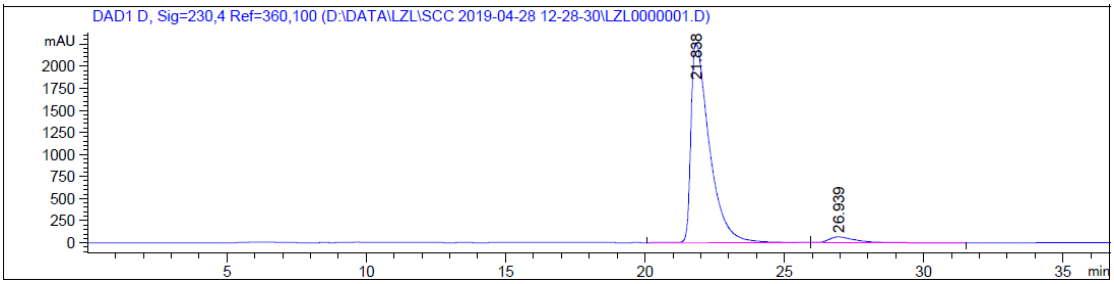
6a (minor): (92% ee), $[\alpha]_D^{20}$ +58.1° (*c* 2.56, $CHCl_3$)

The enantiomeric excess of **6a (minor)** was determined by chiral HPLC analysis on IB column. Conditions: hexane/isopropanol = 75:25, flow rate = 0.6 mL/min, T = 25 °C, UV-Vis detection at λ = 230 nm, t_{R1} = 21.8 min (major), t_{R2} = 26.9 min (minor).



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

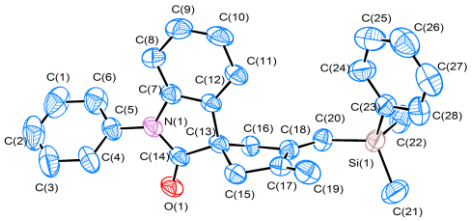
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.217	BB	0.6568	8219.46484	186.26212	50.2408
2	26.609	BBA	0.9756	8140.66406	122.44772	49.7592
Totals :				1.63601e4	308.70983	



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.838	BB	0.6780	1.03869e5	2260.74707	95.9719
2	26.939	BB	0.9997	4359.59229	64.57137	4.0281
Totals :				1.08229e5	2325.31844	

V. Crystal Data for Compound 4i



Empirical formula	C28H27NOSi
Formula weight	421.59
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	P212121
a/Å	9.08856(12)
b/Å	12.68486(17)
c/Å	21.2932(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2454.84(6)
Z	4
ρcalcg/cm^3	1.141
μ/mm^{-1}	0.975
F(000)	896.0
Crystal size/mm3	0.12 × 0.09 × 0.08
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.114 to 147.77
Index ranges	-11 ⩽ h ⩽ 7, -15 ⩽ k ⩽ 15, -26 ⩽ l ⩽ 26
Reflections collected	13241
Independent reflections	4734 [Rint = 0.0213, Rsigma = 0.0177]
Data/restraints/parameters	4734/13/294
Goodness-of-fit on F2	1.040
Final R indexes [I>=2σ (I)]	R1 = 0.0409, wR2 = 0.1168
Final R indexes [all data]	R1 = 0.0434, wR2 = 0.1205
Largest diff. peak/hole / e Å^{-3}	0.32/-0.28
Flack parameter	0.017(12)

VI. References

1. Zhang, Q.; Liang, Q.-J.; Xu, J.-L.; Xu, Y.-H.; Loh, T.-P. Palladium-Catalyzed Silaborative Carbocyclizations of 1,6-Diynes. *Chem. Commun.* **2018**, *54*, 2357–2360.
2. Matsumoto, US Patent No. US6525081 (2003).