Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Visible-light-mediated catalyst-free synthesis of trifluoromethyl (spiro)-epoxides bearing contiguous quaternary centers

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1. Materials and methods

Commercial reagents were used without purification and reactions were run under Ar atmosphere with exclusion of moisture from reagents using standard techniques for manipulating air-sensitive compounds. All reactions, unless noted, were performed in oven-dried glassware with magnetic stirring under an inert atmosphere of dry argon.

^{1}H NMR spectra (600 MHz/500 MHz/400 MHz), ^{13}C NMR spectra (151 MHz/126 MHz/101 MHz) and ^{19}F NMR spectra (282 MHz/376 MHz) were recorded using Bruker Avance 600/500/400 spectrometer with $CDCl_3$, CD_3OD or DMSO-d_6 as solvent. NMR spectra were calibrated using the solvent residual signals ($CDCl_3$: δ ^{1}H = 7.26, δ ^{13}C = 77.16; CD_3OD: δ ^{1}H = 3.34, δ ^{13}C = 49.86; DMSO-d_6: δ ^{1}H = 2.50, δ ^{13}C = 39.52). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, m = multiplet.

Thin layer chromatography (TLC) was performed using MilliporeSigma glass TLC plates (silica gel 60 coated with F_{254}, 250 μm) and spots were visualized using UV light (254 nm). SiliaFlash® P60 silica gel (particle size: 40-63 μm, pore size: 60 Å) was used for flash column chromatography. A hexane /EtOAc solvent system was used as mobile phase and commercial silica cartridges (12-80 g, Grace®) as stationary phase.

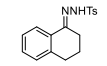
High-resolution mass spectra (HRMS) were recorded on an Agilent MSD-Trap-XCT or Q-Tof micro mass spectrometer.

Ultraviolet-visible absorption experiments were performed using a Agilent Cray 100 spectrophotometer.

Kessil lamps were purchased from Tansoole, with precise wavelengths (427 nm).

Trifluoroacetophenone (1b), a, a-Difluoroacetophenone, 1,8-Diazabicyclo [5.4.0] undecane-7-ene (DBU) were purchased from Bide Pharm, Tansoole, Fisher, TCI or Energy Chemical and used without further purification. Anhydrous DCM were purchased from Tansoole. *N*-tosylhydrazones 1a-35a were prepared using reported procedures.26a were purchased from Bide Pharm.

1.1 *N*-tosylhydrazones included in the manuscript



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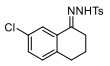

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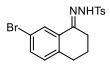

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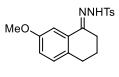
4a

5a



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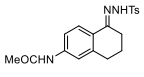

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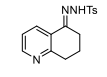

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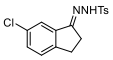

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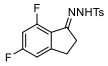

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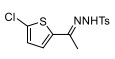

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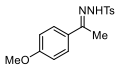

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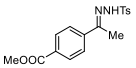

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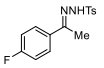

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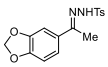

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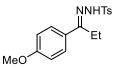

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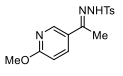

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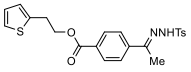

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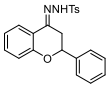

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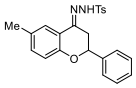

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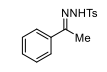

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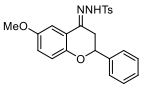

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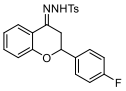

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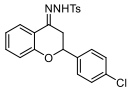

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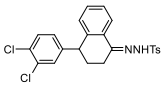

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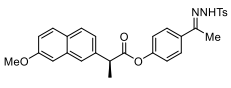

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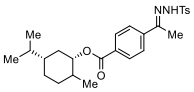

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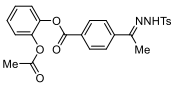

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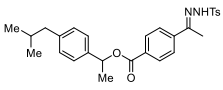

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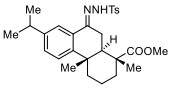
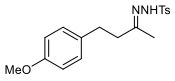
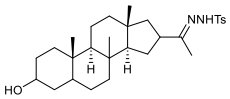


35a

1.2 unsuccessful substrates



N.D.



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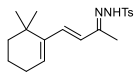

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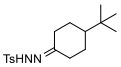

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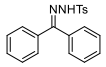


N.D.

2. Setup for photochemical reactions

The reaction setup is depicted in **Figure S1**. The reaction setup consists of commercially available Kessil lamp which was purchased from Tansoole, with precise wavelengths (427 nm), cooling of the setup was performed by two commercially available fans to keep the temperature around 30 ℃. Magnetic stirring was performed at 500 rpm. Low temperature reactions were passed through a low temperature reactor to keep the temperature around 5 ℃.

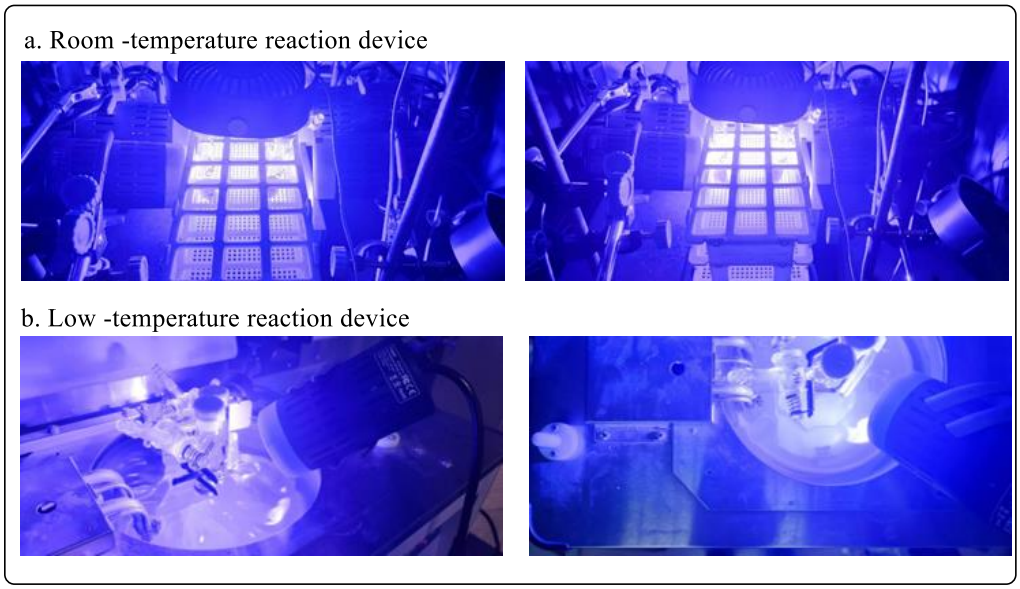
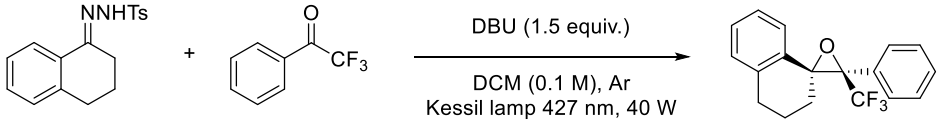


Figure S1: Kessil reaction setup. **a**. reaction was performed under room temperature controlled by fans; **b**. reaction was performed under lower temperature (5 ℃) controlled by low-temperature reactor.

3. Optimization of reaction conditions

3.1 Control experiments [a]

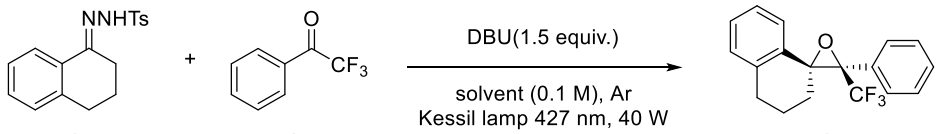


1a **1b** **1c**

Entry	Controlled parameter	Yield [%] [b]
1[a]	Standard conditions	92
2	456 nm	25
3	No light	0
4	No base	0
5[c]	K_2CO_3	0
6[c]	Cs_2CO_3	0

[a]Standard conditions: **1a** (0.1 mmol, 1.0 equiv.), **1b** (0.2 mmol, 2.0 equiv.), DBU (0.15 mmol, 1.5 equiv.), DCM (1 mL), irradiation with 40 W blue Kessil lamps (427 nm) at room temperature (around 30 °C) with cooling fan under argon atmosphere for 5 h. [b]Yields were determined by ^{1}H NMR using dibromomethane as the internal standard. [c]In darkness.

3.2 Screening of solvents [a]

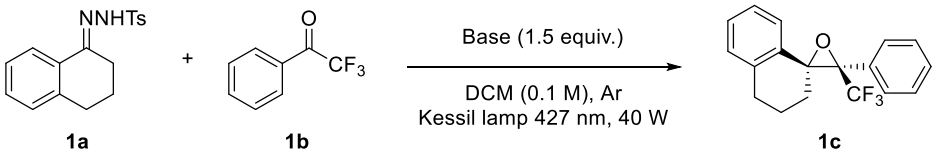


1a **1b** **1c**

Entry	Solvents	Yield [%] [b]
1	DCE	80
2	THF	67
3	EA	48
4	$CHCl_3$	57
5	2Me-THF	60

[a]Standard conditions: **1a** (0.1 mmol, 1.0 equiv.), **1b** (0.2 mmol, 2.0 equiv.), DBU (0.15 mmol, 1.5 equiv.), solvent (1 mL), irradiation with 40 W blue Kessil lamps (427 nm) at room temperature (around 30 °C) with cooling fan under argon atmosphere for 5 h. [b]Yields were determined by ^{1}H NMR using dibromomethane as the internal standard.

3.3 Screening of bases [a]



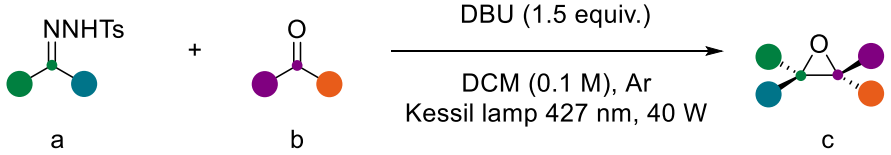
1a 1b 1c

Entry	Base	Yield [%] [b]
1	Na_2CO_3	trace
2	K_2CO_3	
3	Cs_2CO_3	78
4	K_3PO_4	71
5	DBN	75
6	Et_3N	42
7	CH_3ONa	60
8	NaOH	45
9	TMEDA	15

[a]Standard conditions: **1a** (0.1 mmol, 1.0 equiv.), **1b** (0.2 mmol, 2.0 equiv.), Base (0.15 mmol, 1.5 equiv.), DCM (1 mL), irradiation with 40 W blue Kessil lamps (427 nm) at room temperature (around 30 °C) with cooling fan under argon atmosphere for 5 h. [b]Yields were determined by ^{1}H NMR using dibromomethane as the internal standard.

4. General procedure for the synthesis of epoxides and starting materials

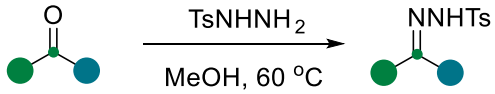
4.1 General procedures A for the (spiro)-epoxides



a b c

A dry 5 mL Schlenk tube containing a stirring bar was charged with 0.1 mmol of *N*-tosylhydrazone (1.0 equiv.), 0.2 mmol of trifluoroacetophenone (2.0 equiv.). After purging the flask for three times under vacuum and three times under argon, it was charged with 0.15 mmol of DBU (1.5 equiv.), DCM (1 mL), successively. The reaction was kept for 5 h under 40 W Kessil lamp reaction setup (the progress can be monitored *via* TLC). Then, the resulting mixture underwent an aqueous workup (using distilled water; or brine in case of slurry phase separation) and was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Products were purified *via* Flash chromatography chromatography with ethyl acetate and hexane as solvents.

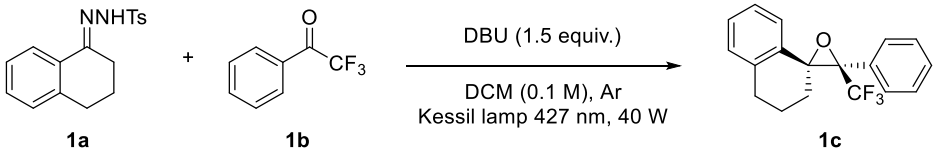
4.2 General procedures for the *N*-tosylhydrazones



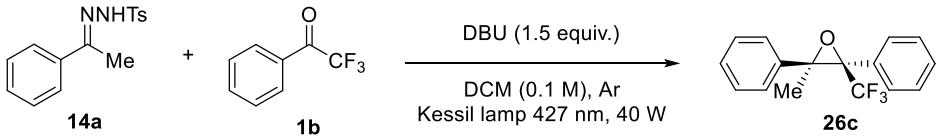
N-tosylhydrazones were prepared according a reported procedure.[1] To a stirred solution of tosylhydrazide (10 mmol) in MeOH (10 mL) at 60 °C, ketone (1 equiv.) was added dropwise (or portionwise if solid). The reaction was completed within 0.5-3 h. After that, the solvent was removed directly under reduced pressure, and further purified by recrystallization or via silica gel chromatography (hexane : EtOAc, 2:1).

5. Gram-scale synthesis and post functionalization

5.1 Synthesis of 1c and 26c in gram scale



Following the general procedure, the reaction with 1a (1.57 g, 5.0 mmol), DBU (1.17 g, 1.15 ml, 9.0 mmol, 3 equiv.), DCM (50 mL) and 1b (1.73 g, 1.40 ml, 10.0 mmol) under Ar for 5 h at 25 °C afforded **1c** as white solid (1.18 g, 82% yield).



Following the general procedure, the reaction with a (1.44 g, 5.0 mmol), DBU (1.17 g, 1.15 ml, 9.0 mmol, 3 equiv.), DCM (50 mL) and b (1.73 g, 1.40 mL, 10.0 mmol) under Ar for 5 h at 25 °C afforded **26c** as white solid (0.92 g, 67% yield).

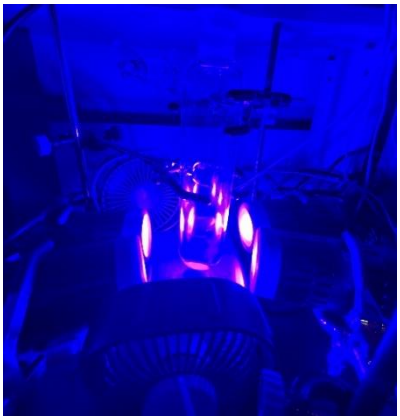
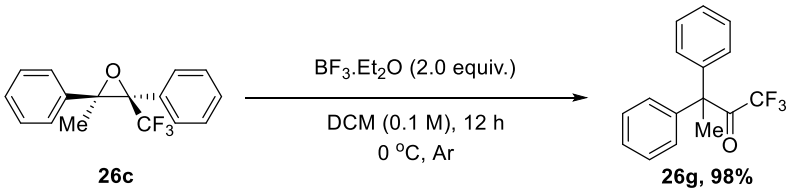


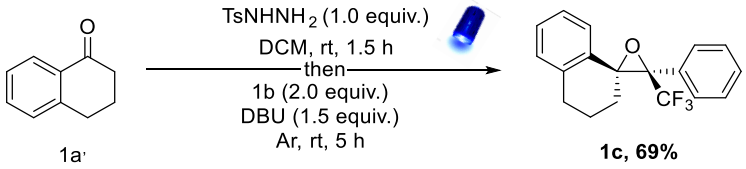
Figure S2: Kessil reaction setup with gram-scale reaction.

5.2 Later functionalization

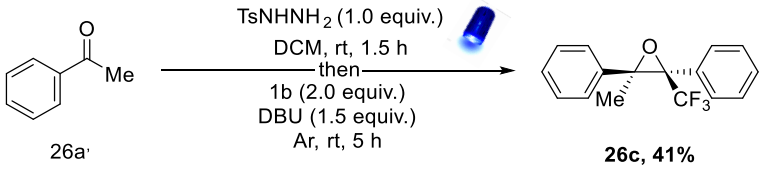


To a solution of 26c (55.6 mg, 0.2 mmol) in DCM (2 mL) was added $BF_3 \cdot Et_2O$ (56.8 mg, 0.4 mmol) at 0 °C under argon atmosphere. The mixture was stirred at the same temperature for 12 h. Then added distilled water (10 mL), and extracted with DCM (15 mL × 2). The combined organic layers were dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give the product **26g**.

5.3 One-pot method



To a solution of 1a' (29.2 mg, 0.2 mmol) in DCM (2 mL) was added 4-Methylbenzenesulfonhydrazide (36.8 mg, 0.2 mmol) at 25 °C under argon atmosphere. The mixture was stirred at the same temperature for 1.5 h. Then added Trifluoroacetophenone (56 μl, 0.4 mmol), and DBU (0.3 mmol, 1.5 equiv.). The reaction was kept for 5 h under 40 W Kessil lamp reaction setup (the progress can be monitored *via* TLC). and extracted with DCM (15 mL × 2). The combined organic layers were dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give the product **1c** (Yied:69%).

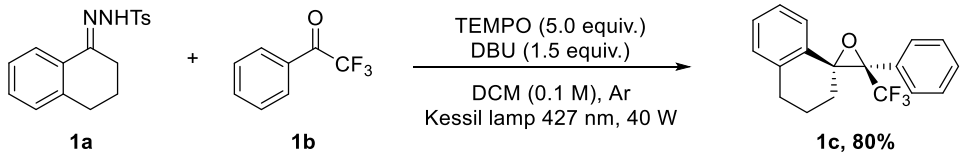


To a solution of 26a' (24 mg, 0.2 mmol) in DCM (2 mL) was added 4-Methylbenzenesulfonhydrazide (36.8 mg, 0.2 mmol) at 25 °C under argon atmosphere. The mixture was stirred at the same temperature for 1.5 h. Then added Trifluoroacetophenone (56 μl, 0.4 mmol, 2.0 equiv.), and DBU (46 μl, 0.3 mmol, 1.5 equiv.). The reaction was kept for 5 h under 40 W Kessil lamp reaction setup (the progress can be monitored *via* TLC). and extracted with DCM (15 mL × 2). The

combined organic layers were dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give the product **26c** (Yied:41%).

6. Mechanistic studies

6.1 Radical probing experiments



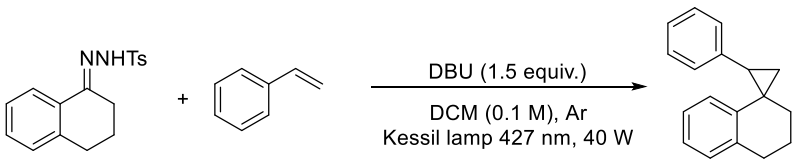
1a **1b** **1c, 80%**

A dry 5 mL reaction tube containing a stirring bar was charged with 0.1 mmol of **1a** (1.0 equiv.), 0.15 mmol of DBU (1.5 equiv.) and 0.5 mmol of **TEMPO** (5.0 equiv.), After purging the flask for three times under vacuum and three times under argon, it was charged with DCM (1 mL), 0.2 mmol of **1b** (2.0 equiv.). The reaction was kept for 5 h under 40 W Kessil lamp reaction setup.

1a **1b** **1c, 78%**

A dry 5 mL reaction tube containing a stirring bar was charged with 0.1 mmol of **1a** (1.0 equiv.), 0.15 mmol of DBU (1.5 equiv.) and 0.5 mmol of **BHT** (5.0 equiv.), After purging the flask for three times under vacuum and three times under argon, it was charged with DCM (1 mL), 0.2 mmol of **1b** (2.0 equiv.). The reaction was kept for 5 h under 40 W Kessil lamp reaction setup.

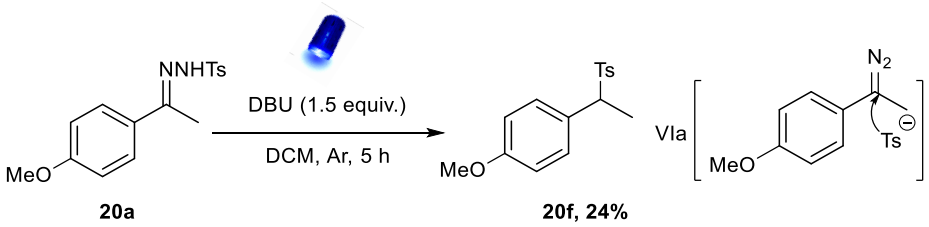
6.2 Carbene trapping experiment.



1a **1d** **1f, 0%**

A dry 5 mL reaction tube containing a stirring bar was charged with 0.1 mmol of **1a** (1.0 equiv.), 0.15 mmol of DBU (1.5 equiv.) and 0.5 mmol of **1d** (5.0 equiv.), After purging the flask for three times under vacuum and three times under argon, it was charged with DCM (1 mL). The reaction was kept for 5 h under 40 W Kessil lamp reaction setup.

6.3 Determination of sulfonyl anion experiment.



20a **20f, 24%**

A dry 5 mL reaction tube containing a stirring bar was charged with 0.1 mmol of **20a** (1.0 equiv.), 0.15 mmol of DBU (1.5 equiv.), After purging the flask for three times under vacuum and three times under argon, it was charged with DCM (1 mL). The reaction was kept for 5 h under 40 W Kessil lamp reaction setup.

1-methoxy-4-(1-tosylethyl)benzene(20f):

^{1}H NMR (500 MHz, CDCl3) δ 7.49 – 7.41 (m, 2H), 7.22 (dt, *J* = 7.9, 0.7 Hz, 2H), 7.12 – 7.05 (m, 2H), 6.84 – 6.77 (m, 2H), 4.19 (q, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 2.42 (s, 3H), 1.73 (d, *J* = 7.2 Hz, 3H).

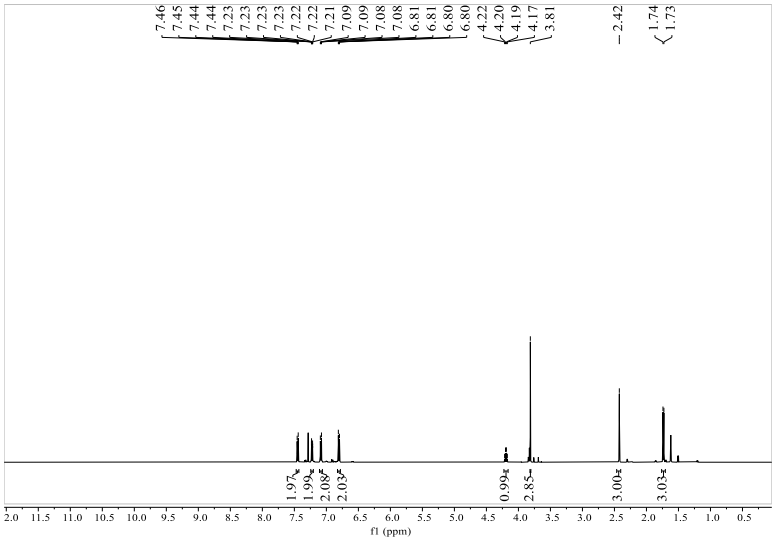


Figure S3:20f NMR spectra

6.4 Ultraviolet visible absorption experiments

Ultraviolet-visible absorption experiments were performed using an Agilent Cary 100 spectrophotometer. In each experiment, different samples were dissolved in DCM and placed in 1.0 cm quartz cuvettes. The concentration of each component was 2×10^{-4} M.

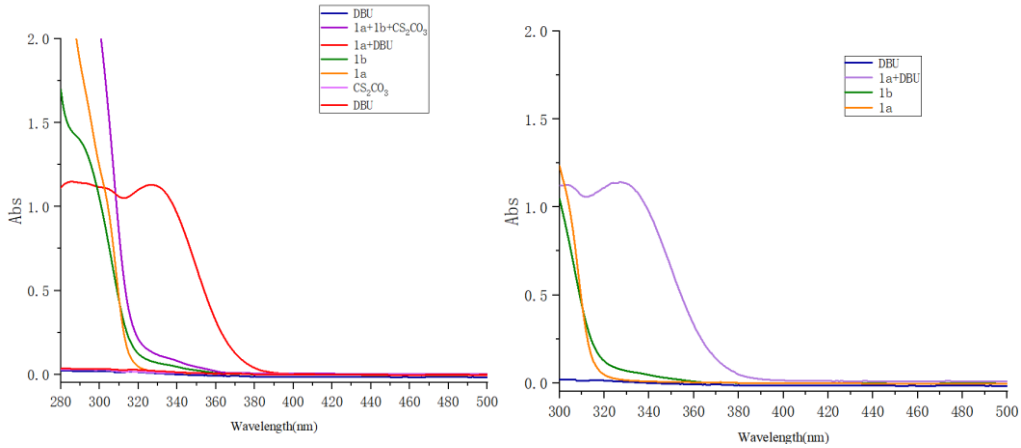
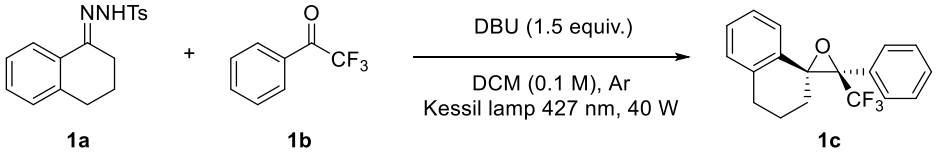


Figure S4: UV-vis absorption spectra.

6.5 On/off experiments and reaction profile



1a **1b** **1c**

Procedure: Tosylhydrazone 1a (0.3 mmol, 94.2 mg), DBU (0.45 mmol, 178.6 mg, 0.144 mL), 1b (0.6 mmol, 171.2 mg, 0.168 mL), and internal standard (1,3,5-Trimethoxybenzene, 16.8 mg) were added into a 10 mL snap vial equipped with a stirring bar. The vial was evacuated and back filled with Ar for three times, followed by the addition of DCM (3 mL) via syringe. Then the reaction mixture was irradiated by a 427 nm LED (40 W) at 25 °C. An aliquot of the reaction mixture was then taken at the indicated times and analyzed by H-NMR.

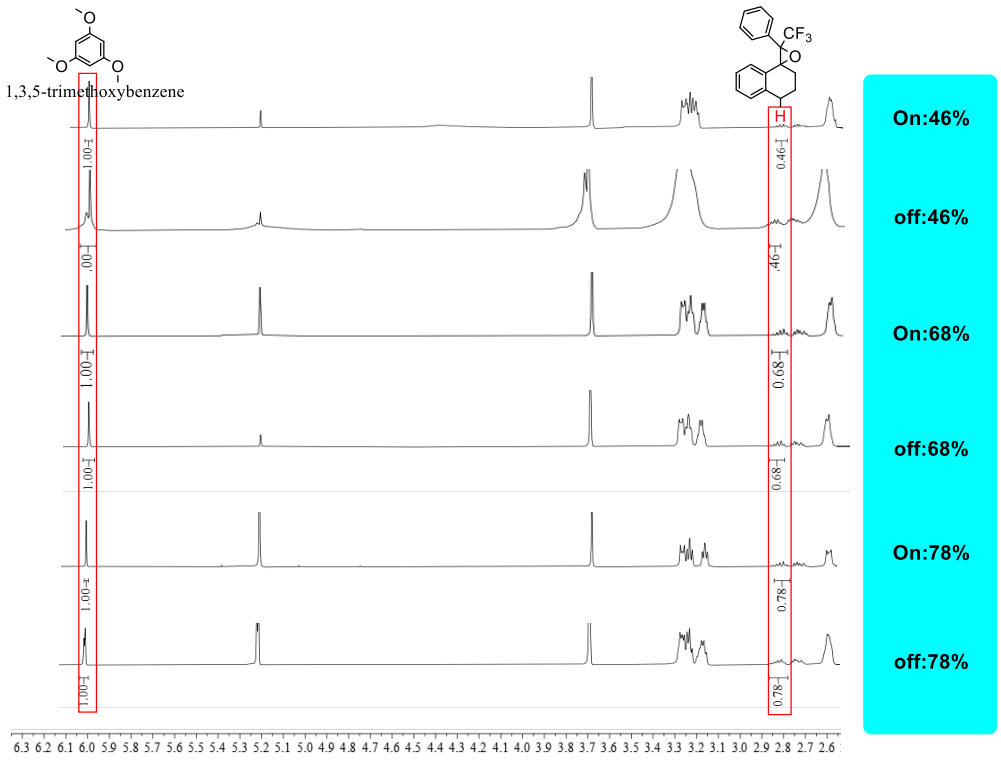


Figure S5: On/off experiments

6.6 HRMS data for 1k/1g intermediates

HRMS (ESI, *m/Z*) calcd. for **1k** $[M+H]^+$**:** 333.1209, found: 333.1210
HRMS (ESI, *m/Z*) calcd. for **1g** $[M+H]^+$**:** 333.1215, found: 333.1210

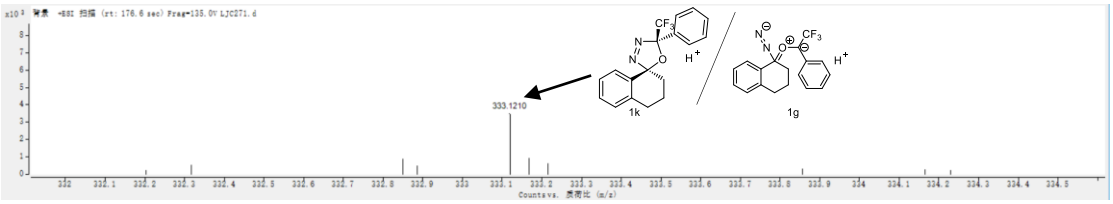
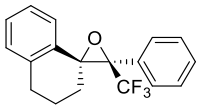


Figure S6: 1k/1g intermediate HRMS

7 Characterization data for products and synthesized substrates

7.1 Characterization data for the (spiro)-epoxides



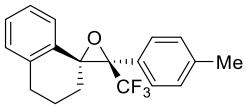
(1*R*,3'*R*)-3'-phenyl-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (1c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 92%). **1c** was known in the published literature.[2]

^{1}H NMR (500 MHz, CDCl3) δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.58 (dq, *J* = 7.4, 2.1 Hz, 2H), 7.48 (dq, *J* = 17.5, 5.0 Hz, 3H), 7.35 – 7.23 (m, 2H), 7.21 (d, *J* = 7.3 Hz, 1H), 2.93 (dt, *J* = 15.9, 8.0 Hz, 1H), 2.84 (ddd, *J* = 15.9, 7.2, 4.9 Hz, 1H), 1.89 – 1.81 (m, 1H), 1.79 – 1.63 (m, 2H), 1.28 (ddd, *J* = 11.5, 7.6, 2.6 Hz, 1H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 139.4, 133.7, 132.3, 129.1, 128.8, 128.2, 128.0, 127.3, 126.7, 125.1 (d,^{3} J_{F-C} = 3.8 Hz), 123.9 (d,^{1} J_{F-C} = 281.1 Hz), 69.3 (d, ^{2} J_{F-C}=62.9 Hz), 68.6 27.6, 27.2, 18.5.

^{19}F NMR (282 MHz, CDCl3) δ -64.4. (s,3F).

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{15}F_3O$ [M + Na] $^{+}$:327.0967, found:327.0954.



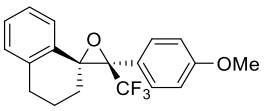
(1*R*,3'*R*)-3'-(p-tolyl)-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (2c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 76%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.59 (dq, *J* = 7.3, 2.1 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.33 (td, *J* = 7.4, 1.6 Hz, 2H), 7.28 (td, *J* = 7.0, 1.3 Hz, 2H), 7.22 (d, *J* = 7.3 Hz, 1H), 2.94 (dt, *J* = 15.5, 7.8 Hz, 1H), 2.84 (ddd, *J* = 15.3, 6.9, 4.8 Hz, 1H), 2.45 (s, 3H), 1.94 – 1.80 (m, 1H), 1.79 – 1.64 (m, 2H), 1.37 – 1.27 (m, 1H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 139.4, 139.0, 133.9, 129.4, 129.3, 128.9, 128.2, 127.9, 127.3, 126.6, 125.1 (d, $^{3}J_{F-C}$ = 18.4 Hz), 124.9, 121.6 (d, $^{1}J_{F-C}$ = 281.4 Hz), 69.2 (d, $^{2}J_{F-C}$ = 35.1 Hz), 68.6, 27.6 27.2, 21.3, 18.5.

^{19}F NMR (282 MHz, CDCl$_3$) δ -64.6, (s,3F).

HRMS (ESI+), *m/z*: calculated for $C_{19}H_{17}F_3O$ [M + Na] $^{+}$:341.1124, found:341.1146.



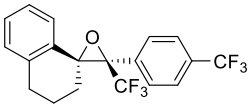
(1*R*,3'*R*)-3'-(4-methoxyphenyl)-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (3c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 71%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.54 – 7.48 (m, 2H), 7.47 (dt, *J* = 7.7, 2.0 Hz, 1H), 7.28 (td, *J* = 7.4, 1.4 Hz, 1H), 7.25 – 7.16 (m, 2H), 7.04 (d, *J* = 9.1 Hz, 2H), 3.85 (s, 3H), 2.96 – 2.86 (m, 1H), 2.82 (ddd, *J* = 15.8, 7.0, 4.8 Hz, 1H), 1.92 – 1.79 (m, 1H), 1.71 – 1.58 (m, 2H), 1.33 – 1.24 (m, 1H).

^{13}C NMR (126 MHz, CD_3OD) δ 160.4, 139.4, 133.8, 129.0, 127.8 (d, $^{3}J_{F\text{-}C}$ = 11.4 Hz), 126.9, 124.9, 124.5, 124.4, 124.0 (d, $^{1}J_{F\text{-}C}$ = 281.0 Hz), 123.9, 113.6, 68.8 (d, $^{2}J_{F\text{-}C}$ = 34.9 Hz), 68.5, 54.4, 27.0, 26.9, 18.1.

^{19}F NMR (282 MHz, CD_3OD) δ -66.3 (s,3F).

HRMS (ESI+), *m/z*: calculated for $C_{19}H_{17}F_3O_2$ [M + Na] $^{+}$:357.1073, found:357.1061.



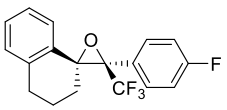
(1*R*,3'*R*)-3'-(trifluoromethyl)-3'-(4-(trifluoromethyl) phenyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (4c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 85%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (q, *J* = 8.4 Hz, 2H), 7.73 (q, *J* = 8.4 Hz, 2H), 7.59 (dp, *J* = 6.6, 2.3 Hz, 1H), 7.34 (td, *J* = 7.4, 1.5 Hz, 1H), 7.29 (td, *J* = 7.1, 2.5 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 2.94 (dt, *J* = 15.4, 7.4 Hz, 1H), 2.87 (ddd, *J* = 15.9, 8.4, 4.9 Hz, 1H), 1.90 – 1.67 (m, 3H), 1.26 – 1.17 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.4, 136.4, 133.1, 131.4 (d, $^{4}J_{F\text{-}C}$ = 32.8 Hz), 128.6, 128.5, 127.5, 127.2, 125.8, 125.3 (d, $^{4}J_{F\text{-}C}$ = 30.0 Hz), 125.2, 125.1, 123.9 (d, $^{3}J_{F\text{-}C}$ = 273.4 Hz), 123.5 (d, $^{1}J_{F\text{-}C}$ = 282.2 Hz), 69.1, 68.9 (d, $^{2}J_{F\text{-}C}$ = 35.4 Hz), 27.5, 27.3, 18.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (d, *J* = 2.6 Hz, 3 F), -64.08 (d, *J* = 2.6 Hz, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{19}H_{14}F_6O$ [M + Na] $^{+}$:395.0851, found:395.0862.



(1*R*,3'*R*)-3'-(4-fluorophenyl)-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (5c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the

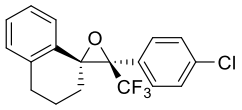
product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 80%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.69 – 7.60 (m, 2H), 7.48 (dp, *J* = 6.7, 2.2 Hz, 1H), 7.29 (td, *J* = 7.5, 1.5 Hz, 1H), 7.23 (tdd, *J* = 10.6, 7.2, 2.9 Hz, 4H), 2.92 (dt, *J* = 15.7, 7.7 Hz, 1H), 2.83 (ddd, *J* = 15.9, 7.1, 5.0 Hz, 1H), 1.91 – 1.79 (m, 1H), 1.72 – 1.60 (m, 2H), 1.26 – 1.18 (m, 1H).

^{13}C NMR (126 MHz, CD_3OD) δ 163.2 (d, $^{4}J_{F-C}$ = 248.2 Hz), 139.4, 133.4, 130.0 (d, $^{1}J_{F-C}$ = 18.0 Hz), 128.5 (d, $^{4}J_{F-C}$ = 195.0 Hz), 128.1, 127.0, 126.4 (d, $^{3}J_{F-C}$ = 107.1 Hz), 125.0, 124.5, 121.9 (d, $^{1}J_{F-C}$ = 203.3 Hz), 115.2 (dd, $^{1}J_{F-C}$ = 30.1, 22.1 Hz), 68.6 (q, $^{2}J_{F-C}$ = 35.2 Hz), 27.0, 26.9, 18.0.

^{19}F NMR (282 MHz, CD_3OD) δ -66.0 (s,3F), -78.3 (d, *J* = 6.7 Hz), -113.8 (s,1F).

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{14}F_4O$ [M + Na] $^{+}$:345.0873., found:345.0852.



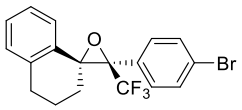
(1*R*,3'*R*)-3'-(4-chlorophenyl)-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (6c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 95%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2, 2.2 Hz, 1H), 7.57 (dt, *J* = 7.5, 2.1 Hz, 1H), 7.55 – 7.41 (m, 3H), 7.33 (td, *J* = 7.4, 1.5 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 2.92 (dt, *J* = 15.5, 7.7 Hz, 1H), 2.85 (ddd, *J* = 15.9, 7.1, 4.9 Hz, 1H), 1.89 – 1.67 (m, 3H), 1.27 (ddd, *J* = 10.5, 6.3, 2.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.3, 135.2, 133.3, 130.9, 129.6, 129.1, 128.6, 128.4, 128.0, 127.4, 125.4, 125.1 (d, $^{3}J_{F-C}$ = 3.9 Hz), 123.6 (d, $^{1}J_{F-C}$ = 281.0 Hz),68.86 (d, $^{2}J_{F-C}$ = 35.3 Hz), 27.5, 27.3, 18.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.4 (s, 3F)

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{14}ClF_3O$ [M + H] $^{+}$:339.0758, found:339.0772.



(1*R*,3'*R*)-3'-(4-bromophenyl)-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (7c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 95%).

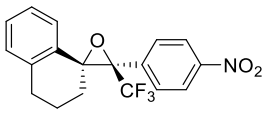
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.61 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.33 (td, *J* = 7.4, 1.5 Hz, 1H), 7.28 (td, *J* = 7.8, 1.3 Hz, 1H),

7.22 (d, *J* = 7.4 Hz, 1H), 2.92 (dt, *J* = 15.5, 7.7 Hz, 1H), 2.86 (ddd, *J* = 16.0, 7.2, 5.0 Hz, 1H), 1.89 – 1.68 (m, 3H), 1.31 – 1.24 (m, 1H).

^{13}C NMR **(126 MHz, $CDCl_3$)** δ 139.3, 133.3, 132.1, 129.9, 128.4, 128.3, 127.4, 125.4, 125.1 (d, $^3J_{F\text{-}C}$ = 3.9 Hz), 123.6(d, $^1J_{F\text{-}C}$ = 281.0 Hz), 123.5, 68.8 (d, $^2J_{F\text{-}C}$ = 35.4 Hz), 27.5, 27.3, 18.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.3 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{14}BrF_3O$ [M + Na] $^+$:405.0072, found:405.0055.



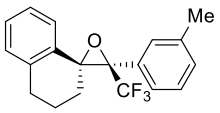
(1*R*,3'*R*)-3'-(4-nitrophenyl)-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (8c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane:EtOAc, 10:1) to give the title compound as a white solid (isolated yield: 62%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.39 (d, *J* = 8.3 Hz, 1H), 8.31 (d, *J* = 21.1 Hz, 1H), 8.09 (dd, *J* = 52.2, 7.7 Hz, 1H), 7.88 (q, *J* = 8.4 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.31 – 7.21 (m, 2H), 2.87 (dp, *J* = 16.9, 10.5, 9.8 Hz, 2H), 1.75 (dd, *J* = 14.1, 8.4 Hz, 2H), 1.65 (s, 1H), 1.09 (q, *J* = 9.2, 8.1 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 148.5 (d, $^3J_{F\text{-}C}$ = 38.7 Hz), 140.0, 134.6, 133.7, 133.6, 132.6, 131.4, 131.3, 129.2, 128.2, 125.8, 125.2 (d, $^1J_{F\text{-}}C$ = 15.7 Hz), 124.9, 122.6, 121.6, 69.6 (d, $^2J_{F\text{-}C}$ = 28.8 Hz), 27.5, 27.2, 18.2.

^{19}F NMR (376 MHz, DMSO-d_6) δ -58.5, -58.7 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{15}F_3NO_3$ [M + H] $^+$:350.0999, found:350.0986.



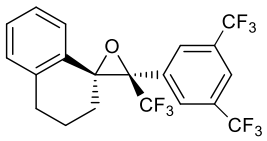
(1*R*,3'*R*)-3'-(m-tolyl)-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (9c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 90%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (dt, *J* = 7.5, 2.2 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.43 – 7.35 (m, 2H), 7.33 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.30 (td, *J* = 7.3, 1.5 Hz, 2H), 7.23 (d, *J* = 7.3 Hz, 1H), 2.96 (dq, *J* = 15.0, 7.4 Hz, 1H), 2.91 – 2.82 (m, 1H), 2.47 (s, 3H), 1.89 (dtd, *J* = 15.9, 8.7, 8.1, 5.1 Hz, 1H), 1.81 – 1.68 (m, 2H), 1.38 – 1.28 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.5, 138.6, 137.9, 133.8, 132.3 (d, $^3J_{F-C}$ = 23.1 Hz), 130.0, 129.8, 128.6, 128.2, 127.3, 127.2, 125.4, 125.1, 123.9 (d, $^1J_{F-C}$ = 281.0 Hz), 123.8, 69.3 (d, $^2J_{F-C}$ = 35.2 Hz), 68.6, 27.6, 27.3, 21.5, 18.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.4 (d, *J* = 63.9 Hz, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{19}H_{17}F_3O$ [M + Na] $^+$:341.1124, found:341.1133.



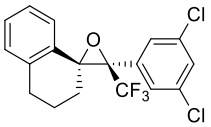
(1*R*,3'*R*)-3'-(3,5-bis(trifluoromethyl)phenyl)-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (10c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 90%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.02 (s, 2H), 7.58 (dp, *J* = 6.4, 2.2 Hz, 1H), 7.36 (td, *J* = 7.4, 1.4 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 3.02 – 2.86 (m, 2H), 1.91 – 1.83 (m, 1H), 1.82 – 1.73 (m, 2H), 1.16 – 1.07 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 139.2, 135.4,132.5 (d, $^2J_{F-C}$ = 34.7 Hz), 132.3, 132.0 (d, $^2J_{F-C}$ = 33.2 Hz), 128.8, 128.6, 127.6, 126.8, 125.8 (d, $^2J_{F-C}$ = 49.0 Hz), 125.5, 125.2 (d, $^4J_{F-C}$ = 3.8 Hz), 123.2 (d, $^1J_{F-C}$ = 280.9), 123.3 (dq, $^4J_{F-C}$ = 7.3, 3.6 Hz), 123.0 (d, $^1J_{F-C}$ = 271.8 Hz), 120.3 (d, $^2J_{F-C}$ = 24.5 Hz), 69.5, 68.5 (q, $^2J_{F-C}$ = 36.0 Hz), 27.5, 27.4, 18.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0 (s,3F), -63.0 (s,3F), -63.9 (s,3F).

HRMS (ESI+), *m/z*: calculated for $C_{20}H_{13}F_9O$ [M + H] $^+$:441.0895, found:441.0877.



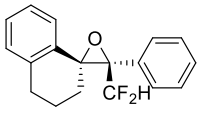
(1*R*,3'*R*)-3'-(3,5-dichlorophenyl)-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (11c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 87%).

^{1}H NMR (500 MHz, $CDCl_3$.) δ 7.58 (t, *J* = 1.7 Hz, 1H), 7.55 (dq, *J* = 6.5, 2.2 Hz, 1H), 7.48 (t, *J* = 1.9 Hz, 1H), 7.46 (t, *J* = 1.6 Hz, 1H), 7.34 (td, *J* = 7.4, 1.4 Hz, 1H), 7.27 (tt, *J* = 7.5, 1.2 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 2.97 – 2.82 (m, 2H), 1.92 – 1.72 (m, 3H), 1.33 – 1.24 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$.) δ 139.3, 135.8(d, $^3J_{F-C}$ = 5.4 Hz), 135.1, 132.7, 129.6, 128.6, 127.5, 126.7, 125.5, 125.2, 123.3 (d, $^1J_{F-C}$ = 281.1 Hz), 69.2, 68.4 (d, $^2J_{F-C}$= 35.8 Hz), 27.5, 27.3, 18.5.

^{19}F NMR (282 MHz, $CDCl_3$.) δ -64.0 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{14}Cl_2F_3O$ [M + H] $^+$:373.0368, found:373.0382.



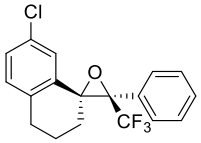
(1*R*,3'*R*)-3'-(difluoromethyl)-3'-phenyl-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (12c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 50%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (dt, *J* = 7.8, 1.5 Hz, 2H), 7.50 – 7.40 (m, 4H), 7.33 (td, *J* = 7.4, 1.6 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.26 – 7.23 (m, 1H), 5.82 (dd, *J* = 56.3, 53.2 Hz, 1H), 3.01 – 2.92 (m, 1H), 2.87 (dt, *J* = 16.3, 7.3 Hz, 1H), 2.00 – 1.88 (m, 1H), 1.87 – 1.73 (m, 2H), 1.40 – 1.34 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.0, 133.6, 131.6, 128.7 (d, $^3J_{F-C}$ = 4.0 Hz), 128.4, 128.2, 125.7, 124.3, 113.8 (d, $^1J_{F-C}$ = 241.4 Hz, d, $^1J_{F-C}$ = 243.4 Hz), 68.2 (d, $^2J_{F-C}$ = 33.0 Hz), 28.0, 26.9, 19.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -118.1 (d, *J* = 306.8 Hz, 1F), -124.5 (d, *J* = 307.2 Hz, 1F).

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{16}F_2O$ [M + Na] $^+$:309.1046, found:309.1033.



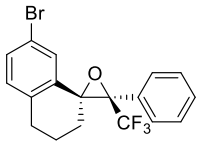
(1*R*,3'*R*)-7-chloro-3'-phenyl-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (13c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.31 (m, 6H), 7.30 – 7.21 (m, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 2.96 – 2.71 (m, 2H), 1.88 – 1.73 (m, 1H), 1.73 – 1.57 (m, 2H), 1.31 – 1.18 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.8, 135.6, 131.9, 131.4, 129.2, 128.8, 128.7, 128.3, 128.2, 128.0, 126.6, 125.3 (q, $^3J_{F-C}$ = 3.9 Hz), 123.6 (d, $^1J_{F-C}$ = 281.0 Hz), 69.3(d, $^2J_{F-C}$ = 35.4 Hz), 68.0, 27.0, 26.9, 18.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.4 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{14}ClF_3O$ [M + H] $^+$:339.0758, found:339.0761.



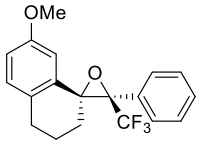
(1*R*,3'*R*)-7-bromo-3'-phenyl-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (14c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 89%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.69 (p, *J* = 2.3 Hz, 1H), 7.56 – 7.36 (m, 5H), 7.05 (d, *J* = 8.1 Hz, 1H), 2.90 – 2.69 (m, 2H), 1.82 (dddd, *J* = 12.2, 11.1, 8.6, 5.3 Hz, 1H), 1.73 – 1.59 (m, 2H), 1.37 – 1.10 (m, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 138.3, 135.9, 131.9, 131.3, 129.3, 129.0, 128.8, 128.3 (t, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 128.0, 126.5 (d, $^{3}J_{F\text{-}C}$ = 28.0 Hz), 123.6 (d, $^{1}J_{F\text{-}C}$ = 280.7 Hz), 119.2, 69.3 (d, $^{2}J_{F\text{-}C}$ = 35.4 Hz), 68.0, 27.1, 26.9, 18.3.

^{19}F NMR (376 MHz, CDCl$_3$) δ -64.4 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{14}BrF_3O$ [M + H] $^{+}$:383.0253, found:383.0238.



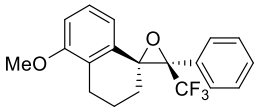
(1*R*,3'*S*)-7-methoxy-3'-phenyl-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (15c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 95%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.45 (dd, *J* = 6.6, 3.4 Hz, 1H), 7.41 – 7.30 (m, 3H), 7.03 (p, *J* = 2.4 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.76 (dd, *J* = 8.3, 2.7 Hz, 1H), 3.73 (s, 3H), 2.75 (dt, *J* = 15.7, 7.9 Hz, 1H), 2.67 (ddd, *J* = 15.6, 7.2, 5.0 Hz, 1H), 1.75 – 1.67 (m, 1H), 1.65 – 1.51 (m, 2H), 1.15 (ddd, *J* = 11.9, 7.5, 2.8 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 157.5, 134.8, 132.3, 131.5, 129.1, 128.8, 128.3, 128.2, 127.9, 126.7, 123.8 (d, $^{1}J_{F\text{-}C}$ = 280.9 Hz), 114.7, 110.1 (d, $^{3}J_{F\text{-}C}$ = 3.8 Hz), 69.4 (q, $^{2}J_{F\text{-}C}$ = 35.3 Hz), 68.8, 55.4, 27.3, 26.7, 18.7.

^{19}F NMR (376 MHz, CDCl$_3$) δ -64.2 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{19}H_{17}F_3O_2$ [M + Na] $^{+}$:357.1073, found:357.1077.



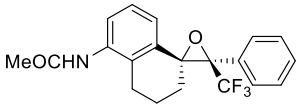
(1*R*,3'*R*)-5-methoxy-3'-phenyl-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (16c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.53 – 7.42 (m, 3H), 7.26 – 7.21 (m, 2H), 6.92 – 6.85 (m, 1H), 3.88 (s, 3H), 2.98 (dt, *J* = 17.3, 7.5 Hz, 1H), 2.77 – 2.67 (m, 1H), 1.95 – 1.80 (m, 1H), 1.79 – 1.66 (m, 2H), 1.24 (ddt, *J* = 12.1, 6.4, 3.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 134.6, 132.4, 129.0, 128.7, 128.1, 127.9 (d, $^{3}J_{F-C}$ = 4.3 Hz), 126.8, 125.5, 123.9 (d, $^{1}J_{F-C}$ = 282.2 Hz), 117.7 (d, $^{4}J_{F-C}$ = 4.3 Hz), 109.7, 69.4 (d, $^{2}J_{F-C}$ = 37.0 Hz),69.1, 55.4, 27.6, 21.0, 18.5.

^{19}F NMR (282 MHz, CDCl3) δ -63.5 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{19}H_{17}F_3O_2$ [M + Na] $^{+}$:357.1073, found:357.1061.



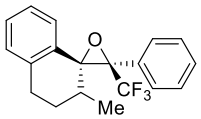
***N*-((1*R*,3'*R*)-3'-phenyl-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxiran]-5-yl) acetamide (17c):** Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane:EtOAc, 2:1) to give the title compound as a Light yellow solid (isolated yield: 70%, dr=9:1).

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.00 (s, 0.87H), 9.77 (s, 0.1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.58 – 7.42 (m, 5H), 7.40 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.36 – 7.27 (m, 1H), 2.85 (dt, *J* = 14.6, 7.2 Hz, 1H), 2.76 (dt, *J* = 15.8, 6.3 Hz, 0.82H), 2.60 (dq, *J* = 27.6, 7.9, 7.5 Hz, 0.13H), 2.21 (ddt, *J* = 24.3, 8.6, 4.4 Hz, 0.33H), 2.14 – 2.08 (m, 0.26H), 2.06 (s, 2.63H), 1.95 (s, 0.31H), 1.82 – 1.71 (m, 0.82H), 1.70 – 1.56 (m, 1.67H), 1.12 – 1.03 (m, 0.86H), 0.88 (dt, *J* = 29.5, 7.2 Hz, 0.09H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 168.8, 140.1(d, $^{3}J_{F-C}$ = 60.6 Hz), 132.0, 129.9, 129.4, 129.1, 127.9, 127.6, 127.1, 125.5, 124.2 (d, $^{1}J_{F-C}$ = 281.0 Hz)., 118.3, 116.4, 69.1 (d, $^{2}J_{F-C}$ = 34.6 Hz), 68.9, 27.6, 24.5, 18.6.

^{19}F NMR (376 MHz, DMSO-d_6) δ -63.3, 64.2 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{20}H_{18}F_3NO_2$ [M + Na] $^{+}$:384.1182, found:384.1196.



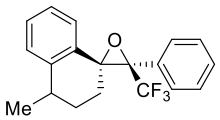
(1*R*,2*S*,3'*R*)-2-methyl-3'-phenyl-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (18c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 50%, dr=2:1).

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 7.61 (dt, *J* = 7.8, 1.5 Hz, 2H), 7.50 – 7.40 (m, 4H), 7.33 (td, *J* = 7.4, 1.6 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.26 – 7.23 (m, 1H), 5.82 (dd, *J* = 56.3, 53.2 Hz, 1H), 3.01 – 2.92 (m, 1H), 2.87 (dt, *J* = 16.3, 7.3 Hz, 1H), 2.00 – 1.88 (m, 1H), 1.87 – 1.73 (m, 2H), 1.40 – 1.34 (m, 1H).

^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 140.0, 131.9, 130.9, 130.0, 129.5, 129.2, 128.8, 128.0, 127.4, 127.0, 126.2 (d, $^3J_{F\text{-}C}$ = 3.8 Hz), 125.8, 124.0 (d, $^1J_{F\text{-}C}$ = 281.0 Hz), 71.7, 70.0 (d, $^2J_{F\text{-}C}$ = 34.2 Hz), 30.5, 27.0, 26.2, 17.5.

^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -63.6 (s, 3F)

HRMS (ESI+), *m/z*: calculated for $C_{19}H_{17}F_3O$ [M + Na] $^+$:319.1304, found:319.1319.



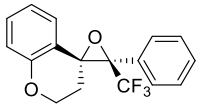
(1*R*,3'*R*)-4-methyl-3'-phenyl-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (19c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 65%, dr=1:1).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.71 – 7.61 (m, 2H), 7.59 (m,1H), 7.54 – 7.44 (m, 3H), 7.38 (m,1H), 7.34 – 7.29 (m, 1H), 7.29 – 7.23 (m, 1H), 3.11 – 2.93 (m, 1H), 2.03 – 1.86 (m, 1H), 1.82 – 1.72 (m, 1H), 1.44 (dd, *J* = 6.9, 2.6 Hz, 3H), 1.35 – 1.28 (m, 1H), 1.28 – 1.21 (m, 1H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 144.3, 143.2, 133.9, 132.4 (d, $^3J_{F\text{-}C}$ = 5.4 Hz), 132.1, 129.1, 129.0, 128.8, 128.7, 128.6, 128.3, 128.2, 128.0, 127.8, 126.7 (d, $^2J_{F\text{-}C}$ = 12.6 Hz), 126.0 (d, $^2J_{F\text{-}C}$ = 4.7 Hz), 125.4, 125.0, 124.5, 123.6, 122.7 (d, $^1J_{F\text{-}C}$ = 33.5 Hz), 68.8 (d, $^2J_{F\text{-}C}$ = 109.6 Hz), 32.7, 30.9, 29.0, 28.2, 27.6, 26.2, 24.7, 18.4.

^{19}F NMR (376 MHz, CDCl$_3$) δ -66.6, -75.0 (d, *J* = 3.0 Hz, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{19}H_{17}F_3O$ [M + Na] $^+$:319.1304, found:319.1321.



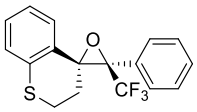
(3'*R*,4*R*)-3'-phenyl-3'-(trifluoromethyl) spiro[chromane-4,2'-oxirane] (20c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane:EtOAc, 30:1) to give the title compound as a white solid (isolated yield: 92%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 1H), 7.53 (dtd, *J* = 9.3, 4.5, 4.1, 2.5 Hz, 3H), 7.49 – 7.43 (m, 2H), 7.35 – 7.27 (m, 1H), 6.97 (td, *J* = 7.6, 1.2 Hz, 1H), 6.89 (dd, *J* = 8.3, 1.2 Hz, 1H), 4.33 (ddd, *J* = 11.3, 5.0, 2.1 Hz, 1H), 4.23 (ddd, *J* = 13.8, 11.3, 2.6 Hz, 1H), 2.15 (tdd, *J* = 13.5, 5.0, 1.1 Hz, 1H), 1.30 (dt, *J* = 13.3, 2.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4, 131.5, 130.4, 129.3, 129.1, 128.4, 127.7, 126.8 (q, $^{3}J_{F\text{-}C}$ = 5.1 Hz), 126.3, 123.8 (d, $^{1}J_{F\text{-}C}$ = 280.9 Hz), 119.6, 118.0, 116.3, 69.5 (d, $^{2}J_{F\text{-}C}$ = 35.8 Hz), 65.7, 64.5, 27.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.9 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{13}F_3O_2$ [M + H] $^{+}$:307.0940, found:307.0929.



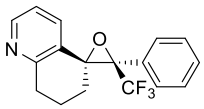
(2*R*,3*R*)-3-phenyl-3-(trifluoromethyl) spiro[oxirane-2,4'-thiochromane] (21c): Prepared according to the general procedure for the A. Following the workup, the product was purified by column chromatography (hexane:EtOAc, 20:1) to give the title compound as a white solid (isolated yield: 81%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 1H), 7.70 – 7.65 (m, 1H), 7.59 (ddd, *J* = 8.2, 2.3, 1.3 Hz, 1H), 7.56 – 7.42 (m, 3H), 7.33 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.26 – 7.17 (m, 1H), 2.99 – 2.77 (m, 2H), 2.12 – 1.91 (m, 1H), 1.79 – 1.61 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.3, 133.1, 131.2, 129.4, 128.8, 128.7, 128.3, 127.8, 127.7, 127.4, 126.0 (q, $^{3}J_{F\text{-}C}$ = 3.2 Hz), 124.7, 123.4 (d, $^{1}J_{F\text{-}C}$ = 282.8 Hz), 69.0 (q, $^{2}J_{F\text{-}C}$ = 35.5 Hz), 67.9, 28.9, 23.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{13}F_3OS$ [M + Na] $^{+}$:345.0531, found:345.0526



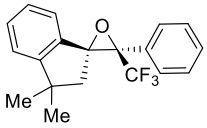
(2*R*,3*R*)-3-phenyl-3-(trifluoromethyl)-7',8'-dihydro-6'*H*-spiro[oxirane-2,5'-quinoline] (22c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane:EtOAc, 5:1) to give the title compound as a white solid (isolated yield: 78%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 – 8.50 (m, 1H), 7.86 (dq, *J* = 7.3, 2.4 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.56 (s, 1H), 7.53 – 7.40 (m, 3H), 7.19 (dd, *J* = 7.9, 4.8 Hz, 1H), 3.16 (ddd, *J* = 17.5, 8.0, 5.0 Hz, 1H), 3.08 – 2.95 (m, 1H), 1.97 – 1.71 (m, 3H), 1.29 (ddd, *J* = 12.8, 5.5, 3.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 149.2, 133.7 (d, $^3J_{F-C}$ = 4.7 Hz), 131.7, 129.7, 129.3, 128.9, 128.2, 127.8, 126.6, 123.7 (d, $^1J_{F-C}$ = 280.9 Hz), 120.5, 69.3 (d, $^2J_{F-C}$ = 35.4 Hz), 68.0, 30.6, 27.3, 17.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.6(s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{14}F_3O$ [M + Na] $^+$:328.0920, found:328.0933.



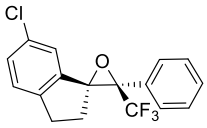
(1*R*,3'*R*)-3,3-dimethyl-3'-phenyl-3'-(trifluoromethyl)-2,3-dihydrospiro[indene-1,2'-oxirane] (23c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 60%).

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.55 – 7.52 (m, 2H), 7.52 – 7.46 (m, 3H), 7.44 – 7.41 (m, 1H), 7.40 – 7.37 (m, 1H), 7.36 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.31 (td, *J* = 7.5, 1.2 Hz, 1H), 1.88 (d, *J* = 13.3 Hz, 1H), 1.40 (d, *J* = 13.3 Hz, 1H), 1.24 (s, 3H), 1.16 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 155.2, 134.2, 132.9, 130.6, 129.8, 129.6, 129.2, 128.6 (d, $^3J_{F-C}$ = 131.7 Hz), 127.2, 126.6, 124.5 (q, *J* = 6.7 Hz), 124.4 (q, $^1J_{F-C}$ = 281.8 Hz), 122.8, 74.6, 68.2 (q, $^2J_{F-C}$ = 35.5 Hz), 47.2, 40.4, 30.1, 28.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -76.9 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{19}H_{17}F_3O$ [M + H] $^+$:319.1304, found:319.1311.



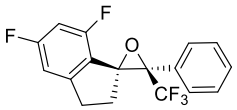
(1*R*,3'*R*)-6-chloro-3'-phenyl-3'-(trifluoromethyl)-2,3-dihydrospiro[indene-1,2'-oxirane] (24c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 89%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.53 (qt, *J* = 11.2, 3.6 Hz, 5H), 7.46 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.34 (q, *J* = 2.0 Hz, 1H), 2.96 – 2.87 (m, 1H), 2.78 (ddd, *J* = 16.1, 8.9, 1.8 Hz, 1H), 2.03 (dt, *J* = 13.7, 9.2 Hz, 1H), 1.57 (ddd, *J* = 13.7, 7.4, 1.8 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 145.7, 137.9, 132.5, 131.6, 130.2, 130.1, 129.6, 129.3, 127.5, 127.3, 126.9, 124.3 (d, $^3J_{F\text{-}C}$ = 7.2 Hz), 124.2 (d, $^1J_{F\text{-}C}$ = 279.7 Hz), 75.5, 68.6 (d, $^2J_{F\text{-}C}$ = 35.7 Hz), 32.8, 28.6, 27.3.

^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -63.5 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{12}ClF_3O$ [M + Na] $^+$:347.0421, found:347.0443.



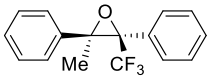
(1*R*,3'*R*)-5,7-difluoro-3'-phenyl-3'-(trifluoromethyl)-2,3-dihydrospiro[indene-1,2'-oxirane] (25c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 42%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.69 – 7.39 (m, 5H), 6.81 (dt, *J* = 7.7, 1.6 Hz, 1H), 6.73 – 6.67 (m, 1H), 3.00 – 2.89 (m, 1H), 2.76 (dd, *J* = 15.8, 8.3 Hz, 1H), 2.19 (td, *J* = 12.1, 8.3 Hz, 1H), 1.63 – 1.53 (m, 1H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 164.0 (dd, $^5J_{F\text{-}C}$ = 251.4, 11.8 Hz), 158.9 (d, $^4J_{F\text{-}C}$ = 245.8 Hz), 149.4 (dd, $^4J_{F\text{-}C}$ = 10.1, 4.7 Hz), 132.9, 129.3, 129.1, 128.4, 127.3, 127.1, 123.1 (d, $^3J_{F\text{-}C}$ = 279.6 Hz), 119.0 (dd, $^4J_{F\text{-}C}$ = 11.9, 3.3 Hz), 108.4 (dd, $^5J_{F\text{-}C}$ = 22.2, 3.9 Hz), 103.2 (t, $^1J_{F\text{-}C}$ = 26.2 Hz), 74.6, 67.3 (q, $^2J_{F\text{-}C}$ = 36.7 Hz), 33.7, 30.0 (d, $^2J_{F\text{-}C}$ = 76.6 Hz), 28.5.

^{19}F NMR (376 MHz, CDCl$_3$) δ -67.5 (s, 3F), -67.6 – -67.7 (m), -108.5 (d, *J* = 9.6 Hz, 1F), -108.7 (dd, *J* = 35.4, 9.6 Hz, 1F).

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{11}F_5O$ [M + Na] $^+$:347.0421, found:347.0448.



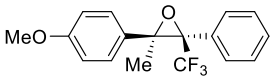
(2*R*,3*R*)-2-methyl-2,3-diphenyl-3-(trifluoromethyl) oxirane (26c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 84%).**26c** was known in the published literature.[2]

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.67 – 7.62 (m, 2H), 7.56 – 7.47 (m, 5H), 7.44 (td, *J* = 7.3, 1.1 Hz, 2H), 7.40 – 7.35 (m, 1H), 1.34 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 138.2, 131.8, 129.2, 128.3, 127.9, 125.9, 123.6 (d, $^1J_{F\text{-}C}$ = 280.2 Hz), 68.0, 67.6 (d, $^2J_{F\text{-}C}$ = 34.7 Hz), 23.7.

^{19}F NMR (376 MHz, CDCl$_3$) δ -67.2 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{13}F_3O$ [M + H] $^+$:279.0991, found:279.0986.



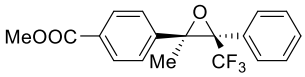
(2*R*,3*R*)-2-(4-methoxyphenyl)-2-methyl-3-phenyl-3-(trifluoromethyl) oxirane (27c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 90%).**27c** was known in the published literature.[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 2H), 7.53 – 7.45 (m, 3H), 7.41 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 1.30 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 131.9, 130.3, 129.1, 128.9, 127.5, 127.1, 123.6 (d, $^{1}J_{F-C}$ = 279.7 Hz), 113.6, 113.1, 67.7, 67.6 (q, $^{2}J_{F-C}$ = 34.0 Hz), 55.3, 23.8.

^{19}F NMR (282 MHz, $CDCl_3$) δ -66.9 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{15}F_3O_2$ [M + Na] $^{+}$:309.1097, found:309.1081.



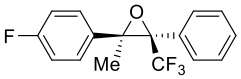
methyl 4-((2*R*,3*R*)-2-methyl-3-phenyl-3-(trifluoromethyl) oxiran-2-yl) benzoate (28c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 47%).**28c** was known in the published literature.[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 – 8.05 (m, 2H), 7.62 – 7.54 (m, 4H), 7.53 – 7.42 (m, 3H), 3.95 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 143.1, 131.3, 129.8, 129.6, 129.4, 129.1, 126.1, 123.3 (d, $^{1}J_{F-C}$ = 280.4 Hz), 67.7 (d, $^{2}J_{F-C}$ = 24.9 Hz), 67.6, 52.2, 23.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.2 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{15}F_3O_3$ [M + H] $^{+}$:337.1046, found:337.1061.



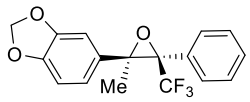
(2*R*,3*R*)-2-(4-fluorophenyl)-2-methyl-3-phenyl-3-(trifluoromethyl) oxirane (29c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 70%).**29c** was known in the published literature.[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 7.52 – 7.42 (m, 3H), 7.14 – 7.08 (m, 2H), 1.30 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2 (d, $^1J_{F\text{-}C}$ = 248.3 Hz), 134.1, 131.6, 130.0 (d, $^3J_{F\text{-}C}$ = 8.3 Hz), 129.3, 128.8, 127.7, 127.7(d, $^3J_{F\text{-}C}$ = 7.9 Hz), 123.4 (d, $^1J_{F\text{-}C}$ = 280.3 Hz), 115.4, 115.2, 67.7 (d, $^2J_{F\text{-}C}$ = 35.0 Hz), 67.4, 23.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.0 (s, 3 F), -114.0 (s, 1F).

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{12}F_4O$ [M + Na] $^+$:319.0716, found:319.0734.



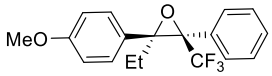
5-((2*R*,3*R*)-2-methyl-3-phenyl-3-(trifluoromethyl) oxiran-2-yl) benzo[*d*] [1,3] dioxole (30c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 67%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.51 – 7.42 (m, 3H), 6.99 – 6.92 (m, 2H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.01 (s, 2H), 1.28 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.5, 147.1, 132.1, 131.8, 129.2, 123.5 (d, $^1J_{F\text{-}C}$ = 280.3 Hz), 119.4, 108.2, 106.7, 101.2, 67.6 (d, $^2J_{F\text{-}C}$ = 35.1 Hz), 23.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.1 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{13}F_3O_3$ [M + Na] $^+$:345.0709, found:345.0726.



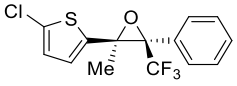
(2*R*,3*R*)-2-ethyl-2-(4-methoxyphenyl)-3-phenyl-3-(trifluoromethyl)oxirane (31c) Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 72%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.77 – 7.71 (m, 1H), 7.58 – 7.46 (m, 4H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.01 – 6.97 (m, 2H), 3.78 (s, 3H), 1.71 (dt, *J* = 14.9, 7.5 Hz, 1H), 1.03 (dq, *J* = 14.5, 7.4 Hz, 1H), 0.61 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 159.2, 131.5, 129.6, 129.4, 128.4, 128.2, 127.9, 127.6, 124.0 (d, *J* = 280.5 Hz), 113.9, 71.3, 68.0 (q, $^2J_{F\text{-}C}$ = 34.0 Hz), 55.5, 29.0, 8.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.8 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{13}F_3O_3$ [M + H] $^+$:323.1253, found:323.1244.



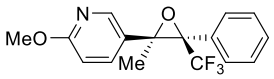
(2*R*,3*R*)-2-(5-chlorothiophen-2-yl)-2-methyl-3-phenyl-3-(trifluoromethyl) oxirane (32c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a white solid (isolated yield: 77%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 6.5 Hz, 2H), 7.48 (dt, *J* = 5.6, 2.9 Hz, 3H), 6.91 (d, *J* = 3.8 Hz, 1H), 6.84 (d, *J* = 3.8 Hz, 1H), 1.34 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1, 131.1, 129.7, 129.4, 128.9, 128.4, 127.9, 127.1, 125.7, 124.6, 123.3 (d, $^1J_{F\text{-}C}$ = 280.5 Hz), 68.4 (d, $^2J_{F\text{-}C}$ = 35.0 Hz), 64.3, 24.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.6 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{14}H_{10}ClF_3OS$ [M + Na] $^+$:340.9985, found:340.9963.



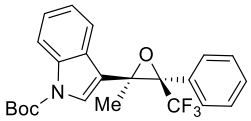
2-methoxy-5-((2*R*,3*R*)-2-methyl-3-phenyl-3-(trifluoromethyl) oxiran-2-yl) pyridine (33c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane : EtOAc, 30:1) to give the title compound as a white solid (isolated yield: 70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 2.5 Hz, 0.89H), 7.97 (d, *J* = 2.5 Hz, 0.7H), 7.68 (dd, *J* = 8.6, 2.5 Hz, 0.88H), 7.60 – 7.55 (m, 1.79H), 7.53 – 7.44 (m, 2.76H), 7.26 (dd, *J* = 8.6, 2.5 Hz, 0.07H), 7.22 – 7.14 (m, 0.22H), 6.79 (dd, *J* = 8.6, 2.5 Hz, 0.09H), 6.45 (d, *J* = 8.6 Hz, 0.07H), 3.99 (s, 2.77H), 3.82 (s, 0.22H), 2.01 (s,0.22H), 1.30 (s, 2.77H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8, 144.6, 136.6, 131.4, 129.3, 128.4 (d, $^3J_{F\text{-}C}$ = 97.2 Hz), 126.8, 123.4 (d, $^1J_{F\text{-}C}$ = 280.3 Hz), 110.5, 67.5 (d, $^2J_{F\text{-}C}$ = 34.8 Hz), 65.9, 53.6, 23.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.7, 65.2 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{14}F_3NO_2$ [M + H] $^+$:310.1049, found:310.1067.



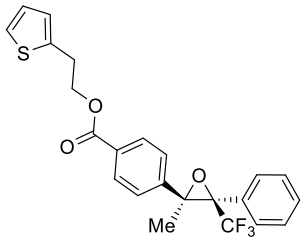
tert-butyl 3-((2*R*,3*R*)-2-methyl-3-phenyl-3-(trifluoromethyl)oxiran-2-yl)-1*H*-indole-1-carboxylate (34c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane : EtOAc, 10:1) to give the title compound as a white solid (isolated yield: 85%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.80 – 7.59 (m, 4H), 7.56 – 7.46 (m, 3H), 7.40 (ddd, *J* = 8.4, 7.2, 1.4 Hz, 1H), 7.37 – 7.32 (m, 1H), 1.72 (s, 9H), 1.41 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 135.3, 131.7, 129.3, 129.3, 128.9, 128.3, 127.3, 124.7, 123.3(d, $^1J_{F\text{-}C}$ = 104.3 Hz), 122.9, 119.5, 118.1, 115.5, 84.1, 67.3 (d, $^2J_{F\text{-}C}$ = 35.1 Hz), 65.9, 63.2, 28.2, 22.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.2 (s.3F).

HRMS (ESI+), *m/z*: calculated for $C_{23}H_{22}F_3NO_3$ [M + H] $^+$:418.1625, found:418.1633.



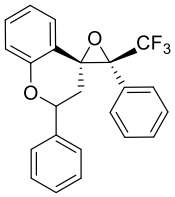
2-(thiophen-2-yl) ethyl 4-((2*R*,3*R*)-2-methyl-3-phenyl-3-(trifluoromethyl)oxiran-2-yl)benzoate (35c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane : EtOAc, 30:1) to give the title compound as a white solid (isolated yield: 69%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.7 Hz, 2H), 7.63 – 7.55 (m, 4H), 7.54 – 7.45 (m, 3H), 7.22 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.00 (dd, *J* = 5.2, 3.4 Hz, 1H), 6.96 (dd, *J* = 3.5, 1.1 Hz, 1H), 4.58 (t, *J* = 6.7 Hz, 2H), 3.34 (t, *J* = 6.6 Hz, 2H), 1.32 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 143.2, 140.0, 131.3, 129.7, 129.4, 127.0, 126.1, 125.7, 124.2(d, $^1J_{F\text{-}C}$ = 281.3 Hz), 67.8 (d, $^2J_{F\text{-}C}$ = 24.8 Hz), 65.3, 29.5, 23.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.2 (s,3F).

HRMS (ESI+), *m/z*: calculated for $C_{23}H_{19}F_3O_3$ [M + Na] $^+$:455.0899, found:455.0863.



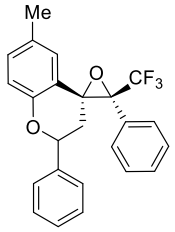
(3'*R*,4*R*)-2,3'-diphenyl-3'-(trifluoromethyl) spiro[chromane-4,2'-oxirane] (36c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane:EtOAc, 30:1) to give the title compound as a light yellow solid (isolated yield: 54%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (ddd, *J* = 7.8, 2.8, 1.7 Hz, 1H), 7.48 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.37 – 7.31 (m, 3H), 7.26 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.10 (dd, *J* = 7.3, 1.8 Hz, 2H), 7.09 – 7.03 (m, 2H), 6.91 (td, *J* = 7.7, 1.4 Hz, 1H), 5.96 (dq, *J* = 8.1, 1.7 Hz, 1H), 5.45 (dd, *J* = 6.4, 3.0 Hz, 1H), 2.44 (ddd, *J* = 13.9, 6.5, 0.9 Hz, 1H), 1.85 (dd, *J* = 13.8, 3.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 140.6, 131.3, 130.7, 128.7, 128.5, 128.1, 127.9, 127.8, 127.6 (d, $^3J_{F\text{-}C}$ = 5.9 Hz), 127.0, 125.86, 123.6 (d, $^1J_{F\text{-}C}$ = 281.4 Hz), 120.0., 116.5, 75.9, 70.7 (d, $^2J_{F\text{-}C}$ = 35.4 Hz), 64.0, 33.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.8 (s,3F).

HRMS (ESI+), *m/z*: calculated for $C_{23}H_{17}F_3O_2$ [M + H] $^+$:383.1253, found:383.1242.



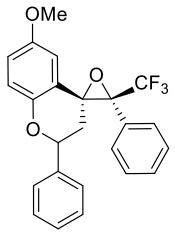
(3'*R*,4*R*)-6-methyl-2,3'-diphenyl-3'-(trifluoromethyl) spiro[chromane-4,2'-oxirane] (37c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane:EtOAc, 30:1) to give the title compound as a light yellow solid (isolated yield: 54%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dtd, *J* = 14.1, 6.4, 5.7, 3.0 Hz, 3H), 7.44 – 7.37 (m, 1H), 7.39 – 7.31 (m, 3H), 7.27 (ddd, *J* = 8.8, 6.8, 1.5 Hz, 1H), 7.22 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.12 (dd, *J* = 7.3, 1.8 Hz, 2H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.96 – 6.90 (m, 1H), 6.03 – 5.97 (m, 1H), 5.42 (dd, *J* = 6.5, 3.1 Hz, 1H), 2.47 – 2.40 (m, 1H), 2.41 (s, 3H), 1.88 – 1.81 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.4, 140.8, 131.5 (d, $^3J_{F\text{-}C}$ = 3.6 Hz), 129.2, 128.7, 128.5, 128.1, 127.9, 127.8, 127.6 (q, $^1J_{F\text{-}C}$ = 5.7 Hz), 127.1, 125.9, 123.7 (d, $^1J_{F\text{-}C}$ = 281.8 Hz), 118.1, 116.3, 75.9, 70.7 (q, $^2J_{F\text{-}C}$ = 35.6 Hz), 64.1, 33.3, 20.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.8 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{24}H_{19}F_3O_2$ [M + H] $^+$:397.1410, found:397.1413.



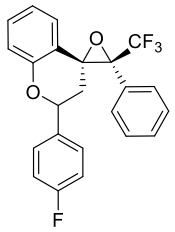
(3'*R*,4*R*)-6-methoxy-2,3'-diphenyl-3'-(trifluoromethyl)spiro[chromane-4,2'-oxirane] (38c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane:EtOAc, 30:1) to give the title compound as a light yellow solid (isolated yield: 56%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (dt, *J* = 7.8, 1.6 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.25 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.16 (tt, *J* = 2.6, 1.2 Hz, 1H), 7.09 (dd, *J* = 7.3, 1.7 Hz, 2H), 7.01 – 6.93 (m, 2H), 6.95 – 6.88 (m, 1H), 6.07 – 6.01 (m, 1H), 5.35 (dd, *J* = 6.5, 3.5 Hz, 1H), 3.84 (s, 3H), 2.40 (ddd, *J* = 13.8, 6.5, 0.9 Hz, 1H), 1.83 (dd, *J* = 13.8, 3.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.1, 151.6, 140.8, 131.3, 128.7, 128.6, 128.1, 127.8, 127.0, 126.9, 125.8, 123.5 (d, $^{1}J_{F\text{-}C}$ = 286.1 Hz), 119.1, 117.8, 117.4, 111.2 (d, $^{3}J_{F\text{-}C}$ = 6.2 Hz), 76.0, 64.2 (d, $^{2}J_{F\text{-}C}$ = 35.4 Hz), 55.8, 33.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.8 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{24}H_{19}F_3O_3$ [M + Na] $^{+}$:435.1179, found:435.1186.



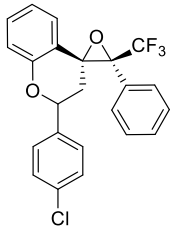
(3'*R*,4*R*)-2-(4-fluorophenyl)-3'-phenyl-3'-(trifluoromethyl)spiro[chromane-4,2'-oxirane] (39c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane:EtOAc, 30:1) to give the title compound as a light yellow solid (isolated yield: 58%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dtp, *J* = 7.1, 2.8, 1.4 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.45 – 7.33 (m, 2H), 7.29 (tt, *J* = 6.1, 1.3 Hz, 1H), 7.10 – 6.94 (m, 7H), 6.19 (d, *J* = 7.9 Hz, 1H), 5.43 (dd, *J* = 6.5, 3.1 Hz, 1H), 2.43 (dd, *J* = 13.8, 6.5 Hz, 1H), 1.86 (dd, *J* = 13.8, 3.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.5, 161.6, 157.2, 136.5 (d, $^{4}J_{F\text{-}C}$ = 3.2 Hz), 131.2, 130.8, 129.7 (d, $^{3}J_{F\text{-}C}$ = 107.1 Hz), 128.7, 128.0, 127.5, 127.4, 127.0, 126.8, 123.6 (d, $^{1}J_{F\text{-}C}$ = 281.8 Hz), 120.3, 118.5, 116.6, 115.6, 115.5, 75.4, 70.5 (d, $^{2}J_{F\text{-}C}$ = 35.4 Hz), 63.9, 33.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.7 (s. 3F), -114.5 (s. 1F).

HRMS (ESI+), *m/z*: calculated for $C_{23}H_{16}F_4O_2$ [M + H] $^{+}$:401.1159, found:401.1180.



(3'*R*,4*R*)-2-(4-chlorophenyl)-3'-phenyl-3'-(trifluoromethyl)spiro[chromane-4,2'-oxirane] (40c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the

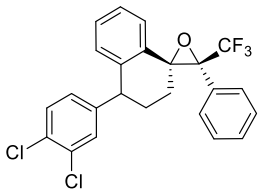
product was purified by column chromatography (hexane:EtOAc, 30:1) to give the title compound as a light yellow solid (isolated yield: 40%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.55 (m, 1H), 7.42 (dq, *J* = 4.0, 1.8 Hz, 1H), 7.38 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.34 (td, *J* = 7.6, 1.4 Hz, 1H), 7.30 – 7.24 (m, 3H), 7.04 (dtd, *J* = 8.3, 3.6, 1.2 Hz, 2H), 7.01 – 6.96 (m, 3H), 6.20 – 6.12 (m, 1H), 5.41 (dd, *J* = 6.6, 2.8 Hz, 1H), 2.49 – 2.35 (m, 1H), 1.84 (dd, *J* = 13.8, 2.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 139.3, 133.7, 131.0, 130.7, 128.8, 128.7, 128.1, 127.9, 127.4 (d, $^3J_{F\text{-}C}$ = 5.9 Hz), 127.1, 126.9, 126.7, 123.6 (d, $^1J_{F\text{-}C}$ = 281.8 Hz), 120.3, 118.5, 116.6, 75.2, 70.4 (d, $^2J_{F\text{-}C}$ = 35.6 Hz), 63.7, 33.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.7 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{23}H_{16}ClF_3O_2$ [M + Na] $^+$:439.0683, found:439.0691.



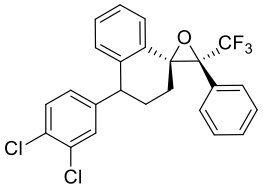
(1*R*,3'*R*)-4-(3,4-dichlorophenyl)-3'-phenyl-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] （41c）: Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane:EtOAc, 30:1) to give the title compound as a white solid (isolated yield: 80%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.59 – 7.56 (m, 1H), 7.52 – 7.41 (m, 4H), 7.32 (d, *J* = 2.1 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.24 (td, *J* = 7.5, 1.5 Hz, 1H), 7.05 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 1H), 4.10 (dd, *J* = 9.4, 7.0 Hz, 1H), 2.17 – 2.08 (m, 1H), 1.88 (dt, *J* = 13.3, 8.5 Hz, 1H), 1.82 – 1.73 (m, 1H), 1.42 – 1.30 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.5, 141.1, 133.5, 132.8, 132.2, 131.0, 130.9, 130.7, 129.4, 129.0, 128.4, 128.4 (d, $^3J_{F\text{-}C}$ = 8.0 Hz), 128.2, 126.6, 126.3, 126.2, 125.2, 123.8 (d, $^1J_{F\text{-}C}$ = 280.4 Hz), 69.5 (d, $^2J_{F\text{-}C}$ = 34.9 Hz), 68.2, 43.0, 27.4, 25.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.4 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{24}H_{17}Cl_2F_3O$ [M + Na] $^+$:471.0501, found:471.0515.



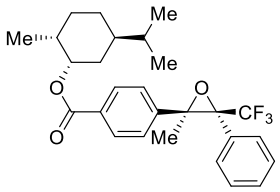
(1*S*,3'*S*)-4-(3,4-dichlorophenyl)-3'-phenyl-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (41c[a])

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (dp, *J* = 5.9, 3.1 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.45 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.30 – 7.25 (m, 4H), 7.00 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.96 – 6.93 (m, 1H), 4.16 (dd, *J* = 9.5, 7.3 Hz, 1H), 2.15 – 2.08 (m, 1H), 1.93 – 1.80 (m, 2H), 1.31 – 1.27 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.2, 140.7, 132.8, 130.9, 130.3, 129.7, 129.2, 129.0, 128.8, 128.2, 127.6 (d, $^{3}J_{F\text{-}C}$ = 9.5 Hz), 127.5, 126.5, 124.1 (d, *J* = 280.4 Hz), 126.1, 69.7 (d, *J* = 34.9 Hz), 68.9, 44.9, 30.9, 29.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.8 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{24}H_{17}Cl_2F_3O$ [M + Na] $^{+}$:471.0501, found:471.0518.



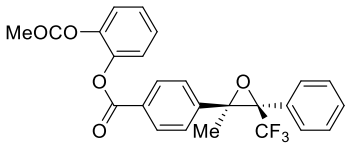
(1*S*,5*S*)-5-isopropyl-2-methylcyclohexyl 4-((2*R*,3*R*)-2-methyl-3-phenyl-3-(trifluoromethyl)oxiran-2-yl)benzoate (42c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane : EtOAc, 30:1) to give the title compound as a white solid (isolated yield: 35%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 – 8.05 (m, 2H), 7.60 (dd, *J* = 6.7, 2.2 Hz, 2H), 7.58 – 7.53 (m, 2H), 7.52 – 7.48 (m, 3H), 4.97 (td, *J* = 10.9, 4.4 Hz, 1H), 2.19 – 2.13 (m, 1H), 2.05 – 1.96 (m, 1H), 1.80 – 1.72 (m, 2H), 1.58 (dd, *J* = 10.8, 2.9 Hz, 2H), 1.31 (s, 3H), 1.23 – 1.07 (m, 2H), 0.96 (dd, *J* = 6.8, 1.5 Hz, 6H), 0.83 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 142.8, 130.9 (d, $^{3}J_{F\text{-}C}$ = 104.8 Hz), 129.6, 129.4, 126.0, 123.4 (d, $^{1}J_{F\text{-}C}$=277.2 Hz) 75.0, 67.7(d, $^{2}J_{F\text{-}C}$=35.1 Hz), 47.3, 41.0, 34.3, 31.5, 26.5, 23.6, 23.3, 22.1, 20.8, 16.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.2 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{27}H_3F_3O_3$ [M + H] $^{+}$:461.2298, found:461.2276.



2-acetoxyphenyl 4-((2*R*,3*R*)-2-methyl-3-phenyl-3-(trifluoromethyl)oxiran-2-yl)benzoate (43c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the

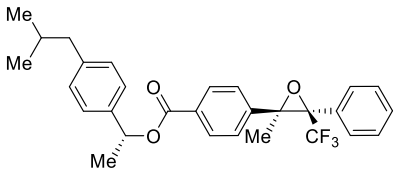
product was purified by column chromatography (hexane:EtOAc, 20:1) to give the title compound as a white solid (isolated yield: 70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.68 (ddd, *J* = 8.2, 7.5, 1.7 Hz, 1H), 7.63 – 7.59 (m, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.53 – 7.45 (m, 3H), 7.43 (td, *J* = 7.7, 1.2 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.23 – 7.12 (m, 2H), 2.35 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 162.8, 151.3, 150.1, 136.0, 134.7, 132.3, 131.6, 129.3, 127.3, 126.3, 124.1, 123.6 (d, $^1J_{F\text{-}C}$ = 280.0 Hz), 121.6, 67.6 (d, $^2J_{F\text{-}C}$ = 35.3 Hz), 23.5, 21.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.0 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{25}H_{19}F_3O_5$ [M + H] $^+$:457.1257, found:457.1246.



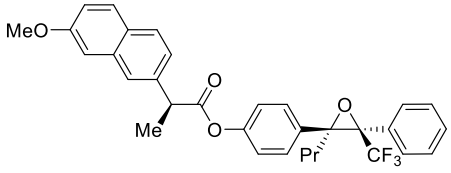
(*S*)-1-(4-isobutylphenyl)ethyl4-((2*R*,3*R*)-2-methyl-3-phenyl-3-(trifluoromethyl)oxiran-2-yl)benzoate (44c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane:EtOAc, 30:1) to give the title compound as a white solid (isolated yield: 50%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 2H), 7.50 – 7.42 (m, 4H), 7.37 – 7.32 (m, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.14 (dt, *J* = 7.3, 1.2 Hz, 1H), 7.09 – 7.04 (m, 2H), 3.97 (p, *J* = 6.6, 6.2 Hz, 1H), 2.51 (d, *J* = 7.1 Hz, 2H), 1.90 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.65 (d, *J* = 7.1 Hz, 3H), 1.28 (s, 3H), 0.95 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 150.4, 140.9, 137.1, 135.6, 131.6, 129.6, 129.2, 128.4 (d, $^3J_{F\text{-}C}$ = 94.8 Hz), 123.4 (d, $^1J_{F\text{-}C}$ = 279.9 Hz), 121.5, 121.3, 120.8, 67.5(d, $^2J_{F\text{-}C}$ = 35.4 Hz), 45.3, 45.1, 30.2, 23.5, 22.4, 18.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.1 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{29}H_{30}F_3O_3$ [M + H] $^+$:483.2142, found:483.2159.



4-((2*R*,3*R*)-3-phenyl-2-propyl-3-(trifluoromethyl)oxiran-2-yl)phenyl (*S*)-2-(7-methoxynaphthalen-2-yl)propanoate (45c): Prepared according to the general procedure for the (spiro)-epoxides.

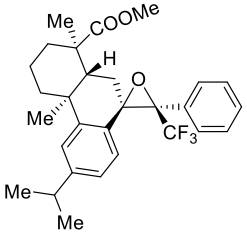
Following the workup, the product was purified by column chromatography (hexane : EtOAc, 30:1) to give the title compound as a white solid (isolated yield: 50%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.75 (m, 3H), 7.60 – 7.51 (m, 3H), 7.51 – 7.35 (m, 5H), 7.22 – 7.15 (m, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 1H), 3.96 (s, 3H), 1.73 (d, *J* = 7.1 Hz, 3H), 1.65 (ddd, *J* = 16.6, 9.2, 3.7 Hz, 2H), 1.27 – 1.17 (m, 1H), 1.17 – 1.09 (m, 1H), 1.07 (dd, *J* = 12.9, 5.2 Hz, 1H), 0.67 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 157.8, 150.3, 135.1, 133.8 (d, $^3J_{F\text{-}C}$ = 15.0 Hz), 131.6, 129.4, 129.2, 129.0, 128.8, 128.2, 127.8, 127.5, 127.1, 126.2 (d, $^1J_{F\text{-}C}$ = 8.1 Hz), 121.1, 119.2, 105.7, 70.3, 67.7(d, $^2J_{F\text{-}C}$ = 35.5 Hz), 55.4, 45.6, 37.5, 18.5, 17.6, 13.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.8 (d, *J* = 2.4 Hz, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{32}H_{30}F_3O_4$ [M + H] $^+$:535.2091, found:535.2067.



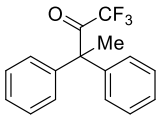
methyl (2*S*, 3*S*, 10*a*′*S*)-6'-isopropyl-1',4*a*'-dimethyl-3-phenyl-3-(trifluoromethyl)-2',3',4',4*a*',10',10*a*'-hexahydro-1'*H*-spiro[oxirane-2,9'-phenanthrene]-1'-carboxylate (46c): Prepared according to the general procedure for the (spiro)-epoxides. Following the workup, the product was purified by column chromatography (hexane:EtOAc, 60:1) to give the title compound as a white solid (isolated yield: 35%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.63 – 7.47 (m, 5H), 7.40 (p, *J* = 3.7, 3.0 Hz, 1H), 7.27 – 7.18 (m, 2H), 3.42 (s, 3H), 2.89 (dt, *J* = 13.7, 6.9 Hz, 1H), 2.22 – 2.12 (m, 1H), 1.86 (dd, *J* = 10.9, 9.1 Hz, 1H), 1.71 – 1.60 (m, 2H), 1.59 – 1.41 (m, 4H), 1.29 (dd, *J* = 10.2, 5.2 Hz, 1H), 1.23 – 1.17 (m, 9H), 0.75 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 177.1, 149.7, 145.3, 131.7, 130.1, 129.5, 129.4, 129.0, 128.2, 127.7, 127.2, 126.4, 125.2, 124.1(d, $^1J_{F\text{-}C}$ = 282.3 Hz), 124.0, 123.0, 122.2, 70.8 (d, $^2J_{F\text{-}C}$ = 34.0 Hz), 67.2, 52.3, 46.0, 44.4, 37.4, 36.9, 36.7, 33.5, 27.5, 24.4, 24.0, 22.0, 17.8, 16.1.

^{19}F NMR (376 MHz, DMSO-d_6) δ -60.7 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{29}H_{33}F_3O_3$ [M + Na] $^+$:509.2274, found:509.2255.



1,1,1-trifluoro-3,3-diphenylbutan-2-one (26g): Prepared according to the general procedure for the B. Following the workup, the product was purified by column chromatography (hexane) to give the title compound as a oil (isolated yield: 98%).[2]

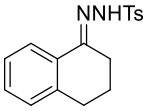
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44.– 7.35 (m, 6H), 7.21 – 7.16 (m, 4H), 2.10 (q, *J* = 1.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.1 (d, $^{2}J_{F\text{-}C}$ = 31.7 Hz), 140.5, 128.7, 128.2, 127.8, 116.3 (d, $^{1}J_{F\text{-}C}$ = 295.2 Hz), 59.7, 24.8.

^{19}F NMR (376 MHz, **$CDCl_3$**) δ -70.1 (s, 3F).

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{13}F_3O$ [M + H] $^{+}$:279.0991, found:279.0965.

Characterization data for the *N*-tosylhydrazones

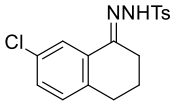


***N'*-(3,4-Dihydronaphthalen-1(2*H*)-ylidene)-4-methylbenzenesulfonohydrazide (1a)**: Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL), ketone (1.0 equiv.), *N*-tosylhydrazones **1a** was obtained as a white solid by recrystallization (isolated yield: 90%).**1a** was known in the published literature.[3]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 6.6 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.76 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.17 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 2.77 – 2.69 (m, 2H), 2.47 (t, *J* = 6.6 Hz, 2H), 2.41 (s, 3H), 1.89 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 139.3, 135.0, 131.0, 129.1, 129.1, 127.9, 127.7, 126.0, 124.6, 28.8, 24.9, 21.2, 20.9.

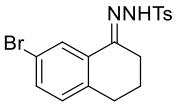
ESI HRMS: calculated for $C_{17}H_{18}N_2O_2S$ $[M + H]^+$: 315.1163, found: 315.1181.



***N'*-(7-Chloro-3,4-dihydronaphthalen-1(2*H*)-ylidene)-4-methylbenzenesulfonohydrazide (2a):**
Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL), ketone (1.0 equiv.), *N*-tosylhydrazones **2a**, it was obtained as a white solid by recrystallization (isolated yield: 76%). **2a** was known in the published literature.[4]

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.60 (s, 1H), 7.83 – 7.78 (m, 2H), 7.67 (d, *J* = 2.3 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.31 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 2.67 (t, *J* = 6.0 Hz, 2H), 2.53 (t, *J* = 6.6 Hz, 2H), 2.38 (s, 3H), 1.75 (p, *J* = 6.3 Hz, 2H).

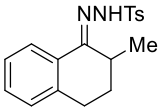
ESI HRMS: calcd. for $C_{17}H_{17}ClN_2O_2S$ $[M+H]^+$: 349.0772, found: 349.0786.



***N'*-(7-Bromo-3,4-dihydronaphthalen-1(2*H*)-ylidene)-4-methylbenzenesulfonohydrazide (3a):**
Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL), ketone (1.0 equiv.), *N*-tosylhydrazones **3a**, it was obtained as a white solid by recrystallization (isolated yield: 76%). **3a** was known in the published literature.[5]

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.59 (s, 1H), 7.81 – 7.79 (m, 3H), 7.44 – 7.39 (m, 3H), 7.13 (d, *J* = 8.2 Hz, 1H), 2.64 (t, *J* = 6.0 Hz, 2H), 2.54 – 2.49 (m, 2H), 2.36 (s, 3H), 1.73 (p, *J* = 6.4 Hz, 2H).

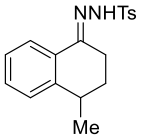
ESI HRMS: calcd. for $C_{17}H_{17}BrN_2O_2S$ $[M+H]^+$: 393.0267, found: 393.0259.



4-Methyl-*N*'-(2-methyl-3,4-dihydronaphthalen-1(2*H*)-ylidene)benzenesulfonohydrazide (4a): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv.), *N*-tosylhydrazones **4a** was obtained as a white solid by recrystallization (isolated yield: 85%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.86 (s, 1H), 7.37 – 7.28 (m, 2H), 7.26 – 7.06 (m, 3H), 3.09 – 2.86 (m, 2H), 2.73 – 2.60 (m, 1H), 2.41 (s, 3H), 2.01 – 1.88 (m, 1H), 1.84 – 1.74 (m, 1H), 1.08 (d, *J* = 7.2 Hz, 3H).

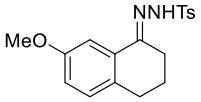
HRMS (ESI+), *m/z*: calculated for $C_{18}H_{20}N_2O_2S$ $[M + H]^+$: 329.1318, found: 329.1356.



4-Methyl-*N*'-(4-methyl-3,4-dihydronaphthalen-1(2*H*)-ylidene)benzenesulfonohydrazide (5a): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv.), *N*-tosylhydrazones **16a** was obtained as a white solid by recrystallization (isolated yield: 71%).**5a** was known in the published literature.[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.95 – 7.91 (m, 2H), 7.61 (s, 1H), 7.35 – 7.31 (m, 1H), 7.28 (td, *J* = 7.5, 1.5 Hz, 1H), 7.23 – 7.14 (m, 2H), 2.92 – 2.82 (m, 1H), 2.53 (ddd, *J* = 17.4, 8.6, 5.6 Hz, 1H), 2.48 – 2.35 (m, 4H), 1.97 (dddd, *J* = 12.9, 8.6, 5.8, 4.1 Hz, 1H), 1.75 – 1.65 (m, 1H), 1.24 (d, *J* = 7.0 Hz, 3H).

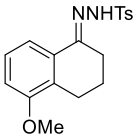
LC-MS: $[M+H]^+$ calculated for $[C_{18}H_{21}N_2O_2S]$ m/z 329.1, found m/z 329.1.



***N*'-(6-Methoxy-3,4-dihydronaphthalen-1(2*H*)-ylidene)-4-methylbenzenesulfonohydrazide (6a):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL), ketone (1.0 equiv.), *N*-tosylhydrazones **6a** was obtained as a white solid by recrystallization (isolated yield: 81%). 6**a** was known in the published literature.[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.5, 1.6 Hz, 3H), 7.60 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.75 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.58 (d, *J* = 2.6 Hz, 1H), 3.79 (s, 3H), 2.72 – 2.62 (m, 2H), 2.44 (t, *J* = 6.6 Hz, 2H), 2.41 (s, 3H), 1.93 – 1.79 (m, 2H).

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{20}N_2O_3S$ [M + H] $^+$: 345.1267, found: 345.1288.

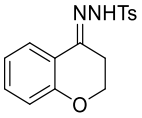


(*E*)-*N'*-(5-methoxy-3,4-dihydronaphthalen-1(2*H*)-ylidene)-4-methylbenzenesulfonohydrazide(7a): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL), ketone (1.0 equiv.), *N*-tosylhydrazones **7a** was obtained as a white solid by recrystallization (isolated yield: 89%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.63 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.50 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.15 (t, *J* = 8.1 Hz, 1H), 6.81 (dd, *J* = 8.2, 1.0 Hz, 1H), 3.81 (s, 3H), 2.69 (t, *J* = 6.1 Hz, 2H), 2.46 – 2.37 (m, 5H), 1.85 (p, *J* = 6.4 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7, 161.8, 157.0, 148.2, 144.4, 135.1, 135.0, 131.9, 129.7, 128.2, 128.0, 127.9, 124.9, 121.9, 119.3, 117.8, 115.8, 115.6, 114.6, 76.1, 32.2, 21.6.

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{20}N_2O_3S$ [M + H] $^+$: 345.1267, found: 345.1279.

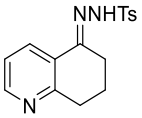


***N'*-(chroman-4-ylidene)-4-methylbenzenesulfonohydrazide (9a):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL), ketone (1.0 equiv.), *N*-tosylhydrazones (**9a)** was obtained as a white solid by recrystallization (isolated yield: 95%).**9a** was known in the published literature.[3]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 3H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.21 (m, 1H), 6.93 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1H), 6.84 (dd, *J* = 8.2, 1.2 Hz, 1H), 4.21 (t, *J* = 6.2 Hz, 2H), 2.68 (t, *J* = 6.2 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 147.5, 143.9, 134.7, 131.1, 129.2, 127.7, 124.5, 121.1, 119.2, 117.1, 64.0, 24.6, 21.2.

ESI HRMS: calculated for $C_{16}H_{16}N_2O_3S$ [M + H] $^+$: 317.0954, found: 317.0945.

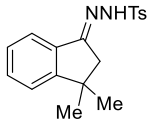


***N'*-(7,8-dihydroquinolin-5(6*H*)-ylidene)-4-methylbenzenesulfonohydrazide (11a):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL), ketone (1.0 equiv.), *N*-tosylhydrazones **11a** was obtained as a white solid by recrystallization (isolated yield: 90%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 4.9, 1.8 Hz, 1H), 8.29 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.93 – 7.88 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.20 (dd, *J* = 8.0, 4.8 Hz, 1H), 2.95 (t, *J* = 6.2 Hz, 2H), 2.49 (t, *J* = 6.6 Hz, 2H), 2.42 (s, 3H), 1.98 (p, *J* = 6.4 Hz, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 158.6, 151.6, 149.7, 143.4, 136.1, 131.7, 129.5, 127.6, 127.3, 122.1, 31.6, 25.4, 21.0, 20.4.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{17}N_3O_2S$ [M + H] $^+$: 316.1114, found: 316.1136.

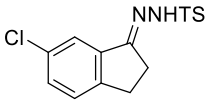


***N*'-(3,3-dimethyl-2,3-dihydro-1*H*-inden-1-ylidene)-4-methylbenzenesulfonohydrazide (12a):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL), ketone (1.0 equiv.), *N*-tosylhydrazones **12a** was obtained as a white solid by recrystallization (isolated yield: 94%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.33 (s, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.42 – 7.33 (m, 4H), 7.26 – 7.23 (m, 1H), 2.64 (s, 2H), 2.34 (s, 3H), 1.24 (s, 6H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 160.3, 157.0, 143.2, 136.3, 135.3, 131.1, 129.4, 127.6, 127.3, 123.2, 120.9, 43.8, 41.0, 29.9, 21.0.

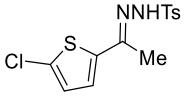
ESI HRMS: calcd. for $C_{18}H_{20}N_2O_2S$ [M+H]$^+$: 329.1318, found: 329.1331.



***N*'-(6-chloro-2,3-dihydro-1*H*-inden-1-ylidene)-4-methylbenzenesulfonohydrazide (13a):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL), ketone (1.0 equiv.), *N*-tosylhydrazones **13a** was obtained as a white solid by recrystallization (isolated yield: 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.39 – 7.32 (m, 3H), 7.29 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 1H), 3.07 – 3.00 (m, 2H), 2.69 – 2.62 (m, 2H), 2.43 (s, 3H).

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{15}ClN_2O_2S$ [M + H] $^+$: 335.0616, found: 335.0636.



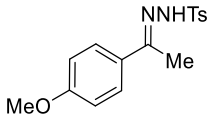
***N*'-(1-(5-chlorothiophen-2-yl)ethylidene)-4-methylbenzenesulfonohydrazide (15a):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from N-tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv.), *N*-tosylhydrazones **15a** was

obtained after column chromatography as a white solid (isolated yield: 78%).**15a** was known in the published literature.[7]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.82 (m, 3H), 7.39 – 7.30 (m, 2H), 6.94 (d, *J* = 4.0 Hz, 1H), 6.77 (d, *J* = 4.0 Hz, 1H), 2.43 (s, 3H), 2.10 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 143.9, 140.7, 134.5, 132.8, 129.2, 127.8, 125.8, 125.6, 21.2, 12.5.

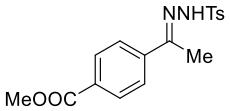
HRMS (ESI+), *m/z*: calculated for $C_{13}H_{13}ClN_2O_2S_2$ [M + H] $^+$: 329.0180, found: 329.0210.



***N'*-(1-(4-methoxyphenyl)ethylidene)-4-methylbenzenesulfonohydrazide (16a):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv.), *N*-tosylhydrazones **16a** was obtained as a white solid by recrystallization (isolated yield: 88%).**16a** was known in the published literature.[3]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.83 – 7.73 (m, 1H), 7.60 (d, *J* = 8.9 Hz, 2H), 7.35 – 7.28 (m, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.41 (s, 3H), 2.13 (s, 3H).

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{18}N_2O_3S$ [M + H] $^+$: 319.1111, found: 319.1134.

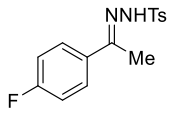


methyl 4-(1-(2-tosylhydrazono)ethyl)benzoate (17a): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv.), *N*-tosylhydrazones **17a** was obtained as a white solid by recrystallization (isolated yield: 99%).**17a** was known in the published literature.[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.99 (d, *J* = 8.6 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.30 (m, 2H), 3.91 (s, 3H), 2.41 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 150.6, 143.9, 140.8, 134.8, 130.3, 129.2, 129.1, 127.7, 125.7, 51.8, 21.2, 12.9.

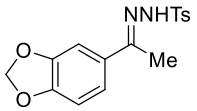
HRMS (ESI+), *m/z*: calculated for $C_{17}H_{18}N_2O_4S$ [M+Na]$^+$: 369.0885, found: 369.0897.



***N'*-(1-(4-fluorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (18a)**: Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv.), *N*-tosylhydrazones **18a** was obtained as a white solid by recrystallization (isolated yield: 78%). **18a** was known in the published literature.[8]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 8.3 Hz, 1H), 7.72 (s, 1H), 7.66 – 7.58 (m, 1H), 7.33 (d, J = 8.1 Hz, 1H), 7.05 – 6.98 (m, 1H), 2.42 (s, 1H), 2.14 (s, 1H).

ESI HRMS: calcd. for $C_{15}H_{15}FN_2O_2S$ [M+Na] $^+$: 329.0736, found: 329.0741.

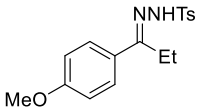


***N'*-(1-(benzo[d][1,3] dioxol-5-yl)ethylidene)-4-methylbenzenesulfonohydrazide (19a):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv.), *N*-tosylhydrazones **19a** was obtained as a white solid by recrystallization (isolated yield: 78%).**19a** was known in the published literature.[9]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.91 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.07 (dd, J = 8.2, 1.8 Hz, 1H), 6.74 (d, J = 8.2 Hz, 1H), 5.96 (s, 2H), 2.41 (s, 3H), 2.11 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 153.4, 148.9, 148.0, 143.8, 136.7, 132.1, 129.9, 128.1, 121.2, 108.3, 106.0, 101.8, 21.5, 14.8.

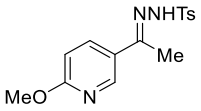
ESI HRMS: calculated for $C_{16}H_{16}N_2O_4S$ [M + H] $^+$: 333.0904, found: 333.0917.



***N'*-(1-(4-Methoxyphenyl)propylidene)-4-methylbenzenesulfonohydrazide (20a):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv.), *N*-tosylhydrazones **20a** was obtained as a white solid by recrystallization (isolated yield: 77%). **20a** was known in the published literature.[10]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91–7.87 (m, 2 H), 7.64 (s, 1 H), 7.62–7.56 (m, 2 H), 7.34–7.29 (m, 2 H), 6.89–6.83 (m, 2 H), 3.82 (s, 3 H), 2.55 (q, J=7.8 Hz, 2 H), 2.41 (s, 3 H), 1.08 (t, J=7.7 Hz, 3 H).

LC-MS: [M+H] $^+$ calculated for [$C_{17}H_{21}N_2O_3S$] m/z 333.1, found m/z 333.1.

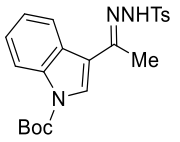


***N'*-(1-(6-methoxypyridin-3-yl)ethylidene)-4-methylbenzenesulfonohydrazide (21a)** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv.), *N*-tosylhydrazones **21a** was obtained after as a white solid (isolated yield: 73%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.77 (s, 1H), 8.57 (d, J = 2.5 Hz, 1H), 8.02 (dd, J = 8.5, 2.6 Hz, 1H), 7.82 – 7.77 (m, 2H), 7.51 (d, J = 8.4 Hz, 1H), 7.39 (d, J = 8.1 Hz, 2H), 2.35 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.9, 150.6, 145.2, 144.4, 136.7, 135.3, 129.8, 128.2, 126.7, 110.9, 53.9, 21.7, 13.3.

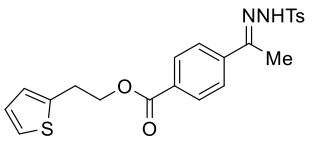
ESI HRMS: calcd. for $C_{15}H_{17}N_3O_3S$ [M + Na] $^+$: 342.0888, found: 342.0876.



***tert*-butyl 3-(1-(2-tosylhydrazono)ethyl)-1*H*-indole-1-carboxylate (22a):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv.), *N*-tosylhydrazones **22a** was obtained after column chromatography (hexane: EtOAc, 3:1) as a white solid (isolated yield: 78%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.56 (s, 1H), 8.10 – 8.02 (m, 2H), 8.01 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.35 (m, 1H), 7.25 (td, *J* = 7.6, 7.2, 1.0 Hz, 1H), 2.36 (s, 3H), 2.23 (s, 3H), 1.63 (s, 9H).

ESI HRMS: calculated for $C_{22}H_{25}N_3O_4S$ [M + H] $^+$: 428.1639, found: 428.1656.

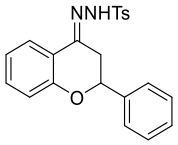


2-(thiophen-2-yl)ethyl 4-(1-(2-tosylhydrazono)ethyl)benzoate (23a): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv.), *N*-tosylhydrazones **23a** was obtained after column chromatography (hexane: EtOAc, 3:1) as a white solid (isolated yield: 89%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.72 (s, 1H), 7.95 (d, *J* = 8.6 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.38 – 7.34 (m, 1H), 6.97 (d, *J* = 4.9 Hz, 2H), 4.46 (t, *J* = 6.3 Hz, 2H), 3.27 (t, *J* = 6.3 Hz, 2H), 2.37 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 165.2, 151.7, 143.5, 141.8 140.0, 136.1, 130.0, 129.6, 129.5, 129.3, 127.64, 127.0, 126.3, 125.9, 124.6, 65.2, 28.7, 21.0, 14.3.

ESI HRMS: calcd. for $C_{22}H_{22}N_2O_4S$ [M + H] $^+$: 443.1099, found: 443.1091.

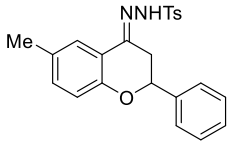


(Z)-4-methyl-N'-(2-phenylchroman-4-ylidene)benzenesulfonohydrazide(24a): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv.), *N*-tosylhydrazones **24a** was obtained after column

chromatography (hexane: EtOAc, 6:1) as a white solid (isolated yield: 85%).**24a** was known in the published literature.[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.1, 1.7 Hz, 1 H), 7.90 (d, *J* = 8.1 Hz, 2 H), 7.60 (s, 1 H), 7.40 (tt, *J* = 13.6, 6.4 Hz, 5 H), 7.34 – 7.24 (m, 3 H), 6.98 (t, *J* = 7.6 Hz, 1 H), 6.94 (d, *J* = 8.2 Hz, 1 H), 5.07 (dd, *J* = 12.4, 3.1 Hz, 1 H), 3.03 (dd, *J* = 16.5, 3.2 Hz, 1 H), 2.60 (dd, *J* = 16.5, 12.4 Hz, 1 H), 2.42 (s, 3 H).

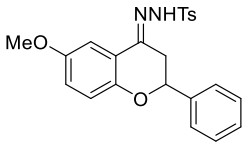
HRMS (ESI+), *m/z*: calculated for $C_{22}H_{21}N_2O_3S$ [M + H] $^+$:393.1273, found:393.1267.



(*Z*)-4-methyl-*N*'-(6-methyl-2-phenylchroman-4-ylidene)benzenesulfonohydrazide(25a): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv.), *N*-tosylhydrazones **25a** was obtained after column chromatography (hexane: EtOAc, 6:1) as a white solid (isolated yield: 65%)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.77 – 7.72 (m, 1H), 7.62 (s, 1H), 7.46 – 7.38 (m, 5H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.11 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 5.05 (dd, *J* = 12.4, 3.1 Hz, 1H), 3.01 (dd, *J* = 16.5, 3.2 Hz, 1H), 2.59 (dd, *J* = 16.5, 12.4 Hz, 1H), 2.45 (s, 3H), 2.33 (s, 3H).

HRMS (ESI+), *m/z*: calculated for $C_{23}H_{23}N_2O_3S$ [M + H] $^+$:407.1424, found:407.1411.

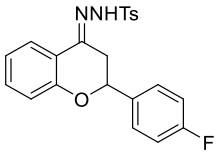


***N*'-(6-methoxy-2-phenylchroman-4-ylidene)-4-methylbenzenesulfonohydrazide (27a):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL), ketone (1.0 equiv.), *N*-tosylhydrazones **27a** was obtained after column chromatography (hexane: EtOAc, 5:1) as a yellow solid (isolated yield: 45%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.35 (m, 6H), 7.32 (d, *J* = 8.2 Hz, 3H), 6.92 – 6.84 (m, 2H), 5.06 – 4.97 (m, 1H), 3.82 (s, 3H), 2.96 (dd, *J* = 16.5, 3.1 Hz, 1H), 2.56 (dd, *J* = 16.5, 12.4 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (500 MHz, $CDCl_3$) δ 154.3, 151.7, 148.4, 144.4, 139.2, 135.2, 129.6, 128.8, 128.7, 128.2, 126.0, 119.9, 119.5, 118.9, 107.1, 76.9, 55.7, 32.3, 21.6.

HRMS (ESI+), *m/z*: calculated for $C_{23}H_{22}N_2O_4S$ [M + H] $^+$: 423.1379, found: 423.1393.

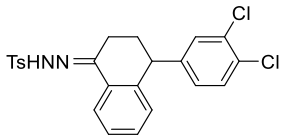


(*Z*)-*N*'-(2-(4-fluorophenyl)chroman-4-ylidene)-4-methylbenzenesulfonohydrazide(28a): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv.), *N*-tosylhydrazones **28a** was obtained after column chromatography (hexane: EtOAc, 5:1) as a yellow solid (isolated yield: 75%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 3H), 7.85 (d, *J* = 6.3 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.29 (m, 1H), 7.17 – 7.07 (m, 2H), 7.00 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1H), 6.94 (dd, *J* = 8.3, 1.1 Hz, 1H), 5.08 (dd, *J* = 12.4, 3.1 Hz, 1H), 3.06 (dd, *J* = 16.5, 3.1 Hz, 1H), 2.60 (dd, *J* = 16.5, 12.4 Hz, 1H), 2.44 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.7 (d, $^{2}J_{F\text{-}C}$ = 247.0 Hz), 157.0, 148.2, 144.4, 135.1 (d, $^{1}J_{F\text{-}C}$ = 6.7 Hz), 131.8, 129.7, 128.1, 128.0, 127.9, 124.9, 121.9, 119.3, 117.8, 115.8, 115.6, 76.1, 32.2, 21.6.

HRMS (ESI+), *m/z*: calculated for $C_{22}H_{20}FN_2O_4S$ [M + H] $^{+}$: 411.1173, found: 423.1156.

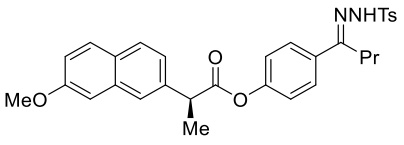


(*Z*)-*N*'-(4-(3,4-dichlorophenyl)-3,4-dihydronaphthalen-1(2*H*)-ylidene)-4-methylbenzenesulfonohydrazide(30a)： Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL), ketone (1.0 equiv.), *N*-tosylhydrazones **30a** was obtained after column chromatography (hexane: EtOAc, 5:1) as a yellow solid (isolated yield: 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (dd, *J*=7.3, 2.0 Hz, 1 H), 7.95–7.90 (m, 3 H), 7.32 (dd, *J* =13.6, 8.2 Hz, 3 H), 7.29–7.26 (m, 1 H). 7.24 (dd, *J*=7.3, 1.8 Hz, 1 H), 7.11 (d, *J*=2.1 Hz, 1 H), 6.82 (ddd, *J*=16.7, 7.7, 2.0 Hz, 2 H), 4.05 (dd, *J*=7.2, 4.3 Hz, 1 H), 2.51–2.44 (m, 1 H), 2.43 (s, 3 H), 2.41–2.34 (m, 1 H), 2.19 (ddt, *J*=13.3, 8.6, 5.0 Hz, 1 H), 2.05 (dtd, *J*=12.7, 7.2, 5.2 Hz, 1 H).

^{13}C NMR (126 MHz, DMSO-d_6) *δ* 145.0, 143.4, 140.6, 136.2, 131.8, 131.1, 130.6, 130.3, 129.7, 129.5, 129.1, 128.8, 128.6, 127.6, 127.0, 124.3, 42.7, 28.6, 23.3, 21.0.

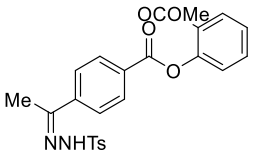
HRMS (ESI+), *m/z*: calculated for $C_{23}H_{21}Cl_2N_2O_2S$ [M + Na] $^{+}$: 481.0520, found :481.0502.



(*Z*)-4-(1-(2-tosylhydrazineylidene)ethyl)phenyl (*S*)-2-(7-methoxynaphthalen-2-yl)propanoate(31a): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv.), *N*-tosylhydrazones **31a** was obtained after column chromatography (hexane: EtOAc, 3:1) as a yellow solid (isolated yield: 88%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.79 – 7.72 (m, 4H), 7.61 – 7.55 (m, 2H), 7.49 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.21 – 7.12 (m, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 1H), 3.93 (s, 3H), 2.51 – 2.44 (m, 2H), 2.40 (s, 3H), 1.69 (d, *J* = 7.1 Hz, 3H), 1.51 – 1.41 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H).

HRMS (ESI+), *m/z*: calculated for $C_{29}H_{29}N_2O_5S$ [M + H] $^+$: 517.1792, found :517.1788.

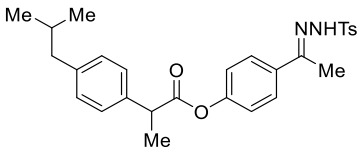


2-acetoxyphenyl (Z)-4-(1-(2-tosylhydrazineylidene)ethyl)benzoate (33a): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv.), *N*-tosylhydrazones **33a** was obtained after column chromatography (hexane: EtOAc, 2:1) as a yellow solid (isolated yield: 91%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.76 – 7.71 (m, 2H), 7.70 – 7.64 (m, 2H), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H), 7.37 – 7.34 (m, 2H), 7.20 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.19 – 7.16 (m, 2H), 2.45 (s, 3H), 2.33 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 162.8, 151.6, 151.5, 151.2, 144.3, 135.3, 135.2, 134.8, 132.3, 129.7, 128.1, 127.7, 126.3, 124.1, 122.3, 121.7, 21.6, 21.0, 13.4.

HRMS (ESI+), *m/z*: calculated for $C_{23}H_{21}Cl_2N_2O_2S$ [M + H] $^+$: 467.1271, found :467.1256.

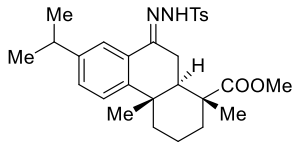


(*E*)-4-(1-(2-tosylhydrazineylidene)ethyl)phenyl 2-(4-isobutylphenyl)propanoate(34a): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv.), *N*-tosylhydrazones **34a** was obtained after column chromatography (hexane: EtOAc, 2:1) as a yellow solid (isolated yield: 75%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.82 (d, *J* = 1.8 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.35 – 7.29 (m, 4H), 7.21 – 7.13 (m, 2H), 7.01 – 6.94 (m, 2H), 3.95 (q, *J* = 7.1 Hz, 1H), 2.53 – 2.46 (m, 3H), 2.43 (s, 3H), 2.11 (s, 3H), 1.88 (dh, *J* = 13.4, 6.7 Hz, 1H), 1.62 (d, *J* = 7.1 Hz, 3H), 0.94 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 151.9, 151.7, 144.2, 140.9, 137.1, 135.4, 134.9, 130.0, 129.6, 129.6, 128.3, 128.1, 127.4, 127.2, 121.3, 45.3, 45.1, 30.2, 22.4, 21.6, 18.5, 13.4.

HRMS (ESI+), *m/z*: calculated for $C_{28}H_{33}N_2O_4S$ $[M+H]^+$:493.2161, found:493.2144.



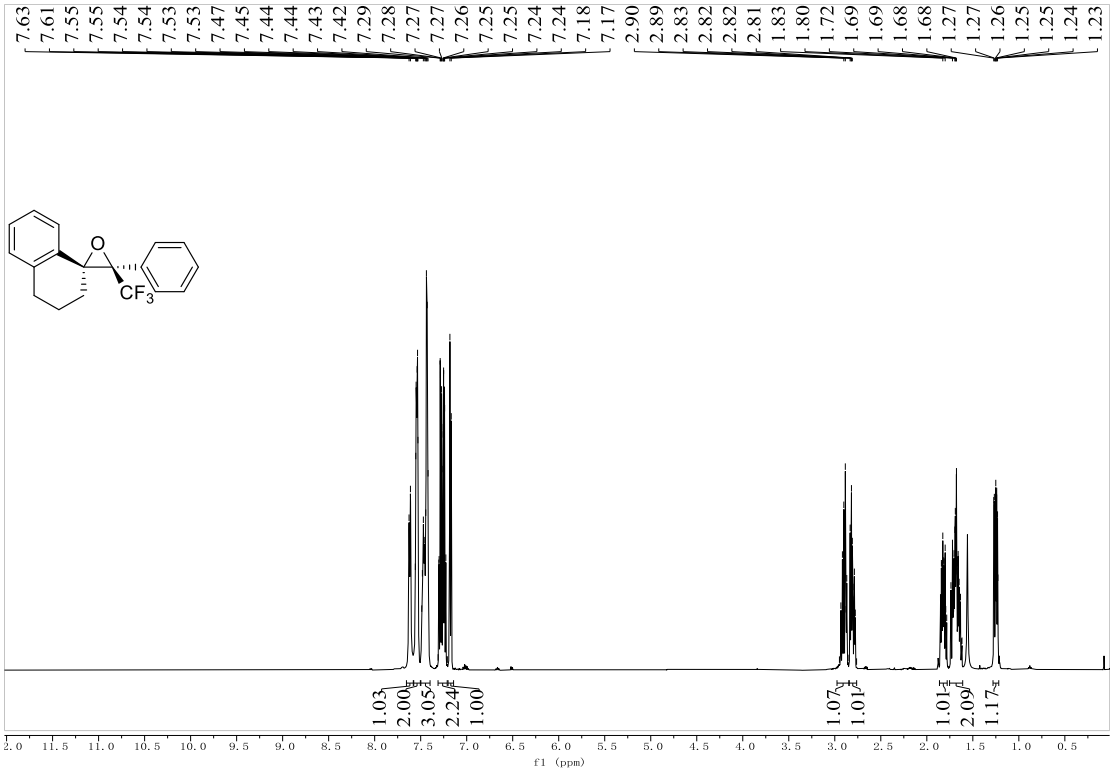
(1*R*,4a*S*,10a*R*)-Methyl 7-isopropyl-1,4a-dimethyl-9-(2-tosylhydrazono)-1,2,3,4,4a,9,10,10*a*-octahydrophenanthrene-1-carboxylate (35a): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv.), *N*-tosylhydrazones **35a** was obtained after column chromatography (hexane: EtOAc, 6:1) as a white solid (isolated yield: 65%).**35a** was known in the published literature[11].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.90 (m, 2H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 2.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.11 (m, 2H), 3.63 (s, 3H), 2.92 – 2.84 (m, 1H), 2.42 (s, 3H), 2.36 – 2.24 (m, 3H), 1.72 (dt, *J* = 8.6, 2.6 Hz, 4H), 1.33 (s, 3H), 1.24 (s, 6H), 1.03 (s, 3H), 0.93 – 0.90 (m, 2H).

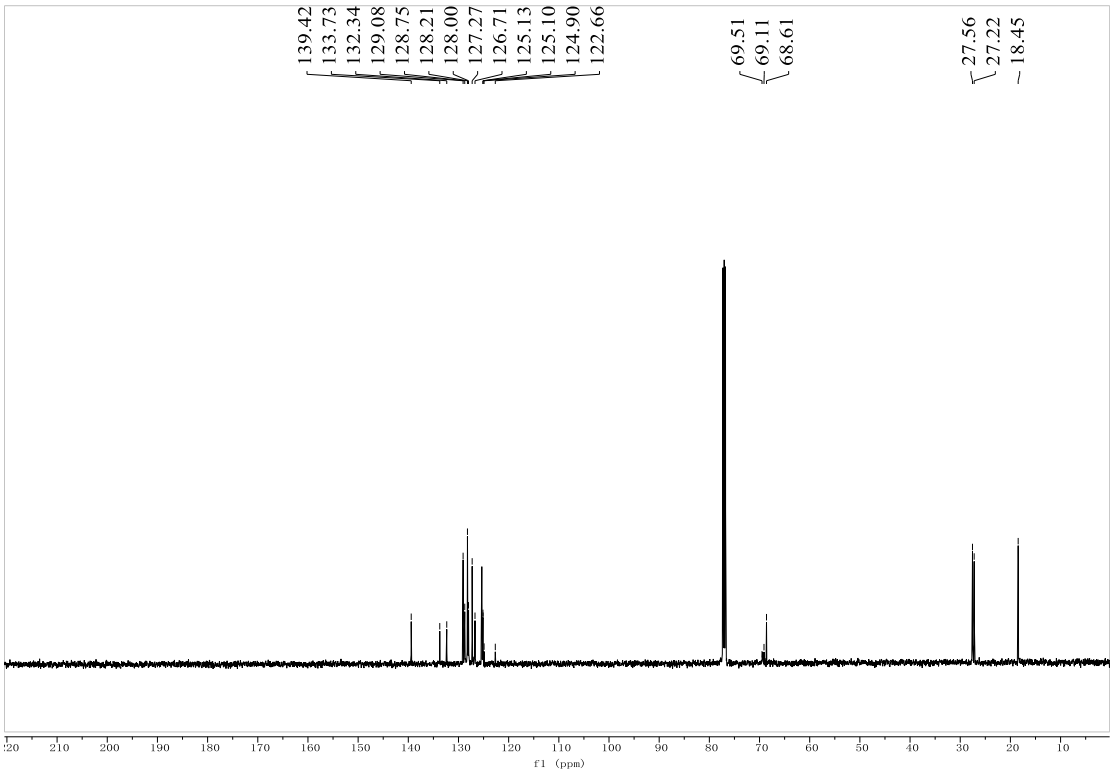
HRMS (ESI+), *m/z*: calculated for $C_{28}H_{36}N_2O_4S$ $[M + H]^+$: 497.2469, found: 497.2489.

8 NMR spectra of products and synthesized substrates

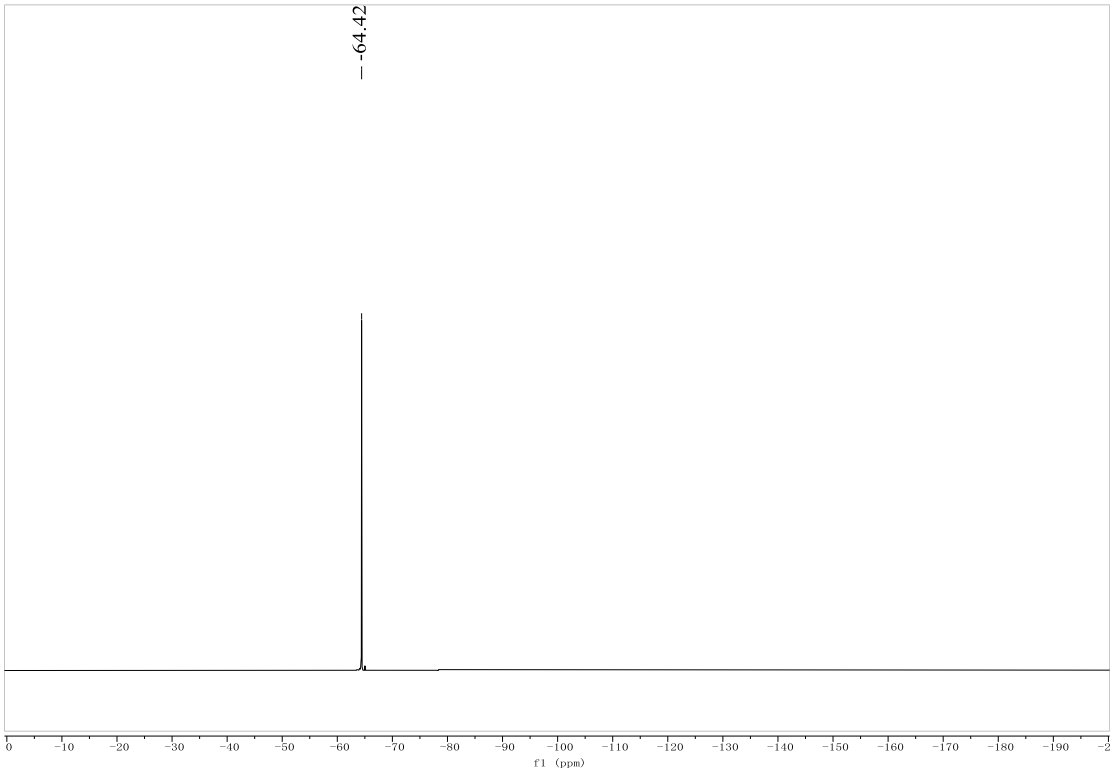
(1*R*,3'*R*)-3'-phenyl-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (1c)



^{1}H NMR spectrum in $CDCl_3$.

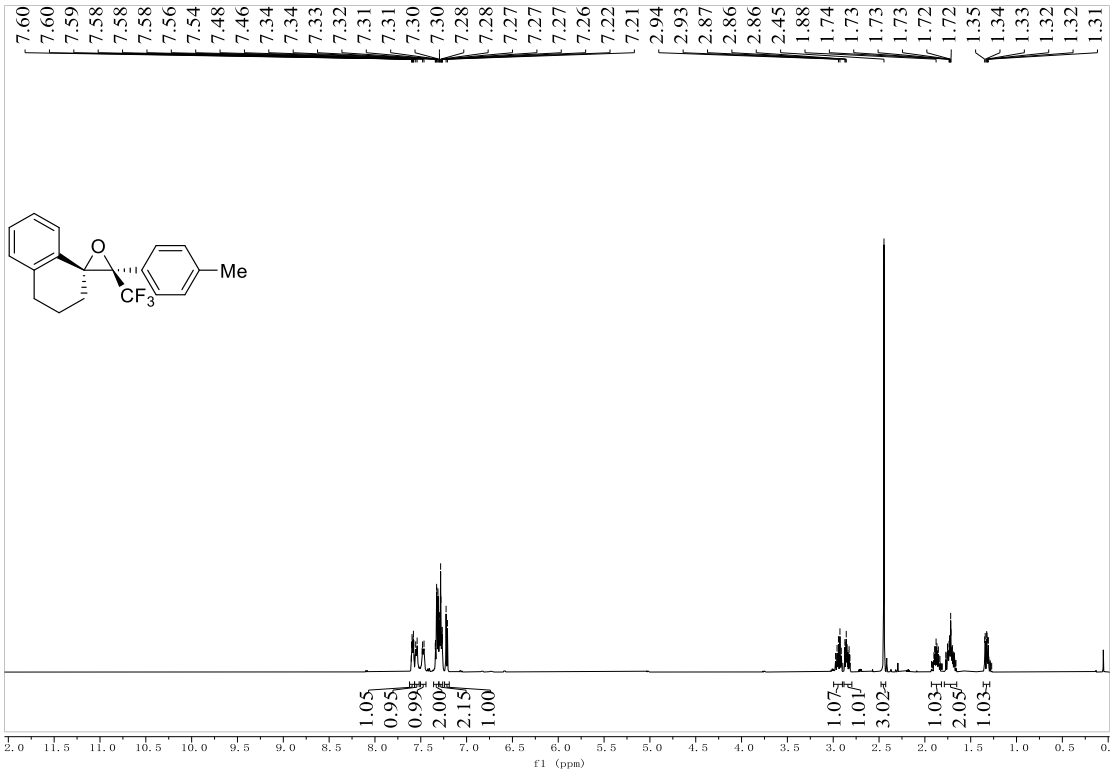


^{13}C NMR spectrum in $CDCl_3$.

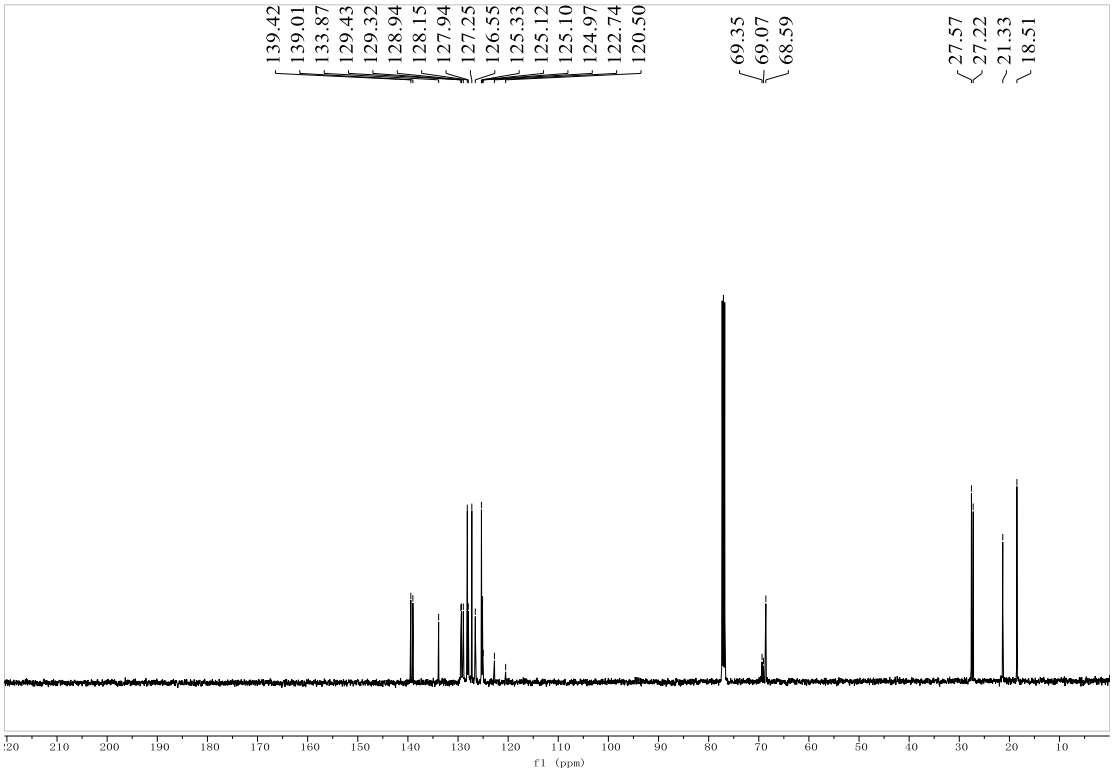


^{19}F NMR spectrum in $CDCl_3$.

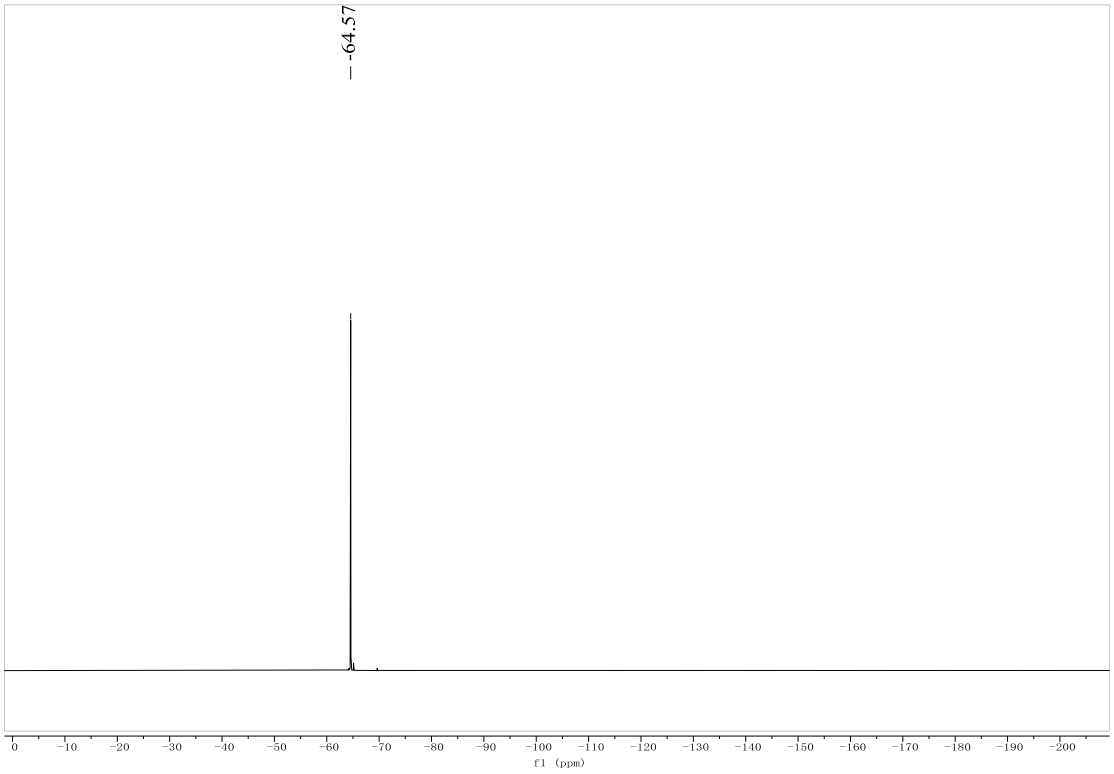
(1*R*,3'*R*)-3'-(p-tolyl)-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (2c)



^{1}H NMR spectrum in $CDCl_3$.

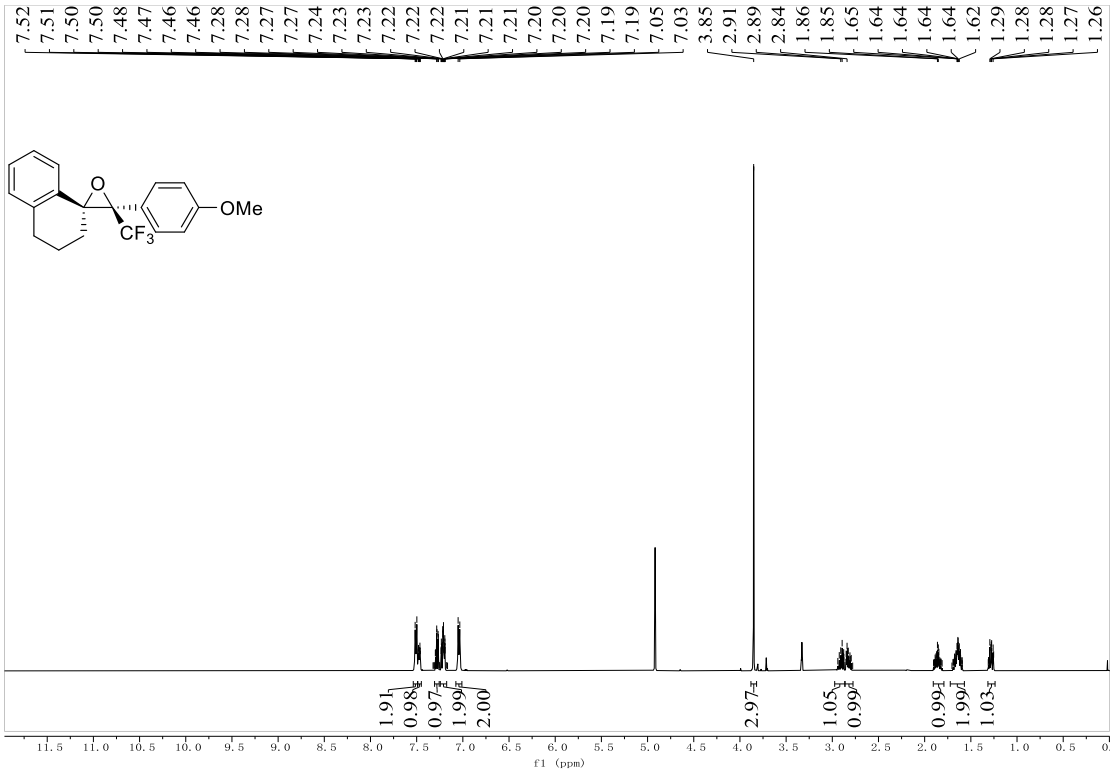


^{13}C NMR spectrum in $CDCl_3$.

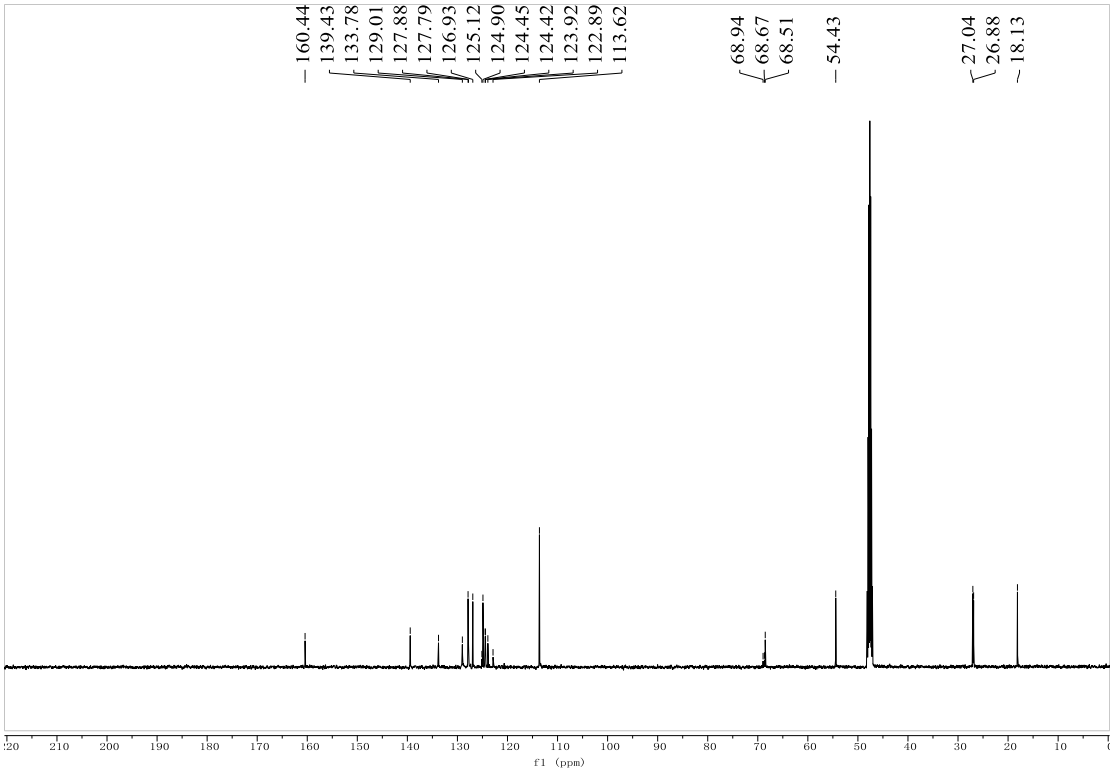


^{19}F NMR spectrum in $CDCl_3$.

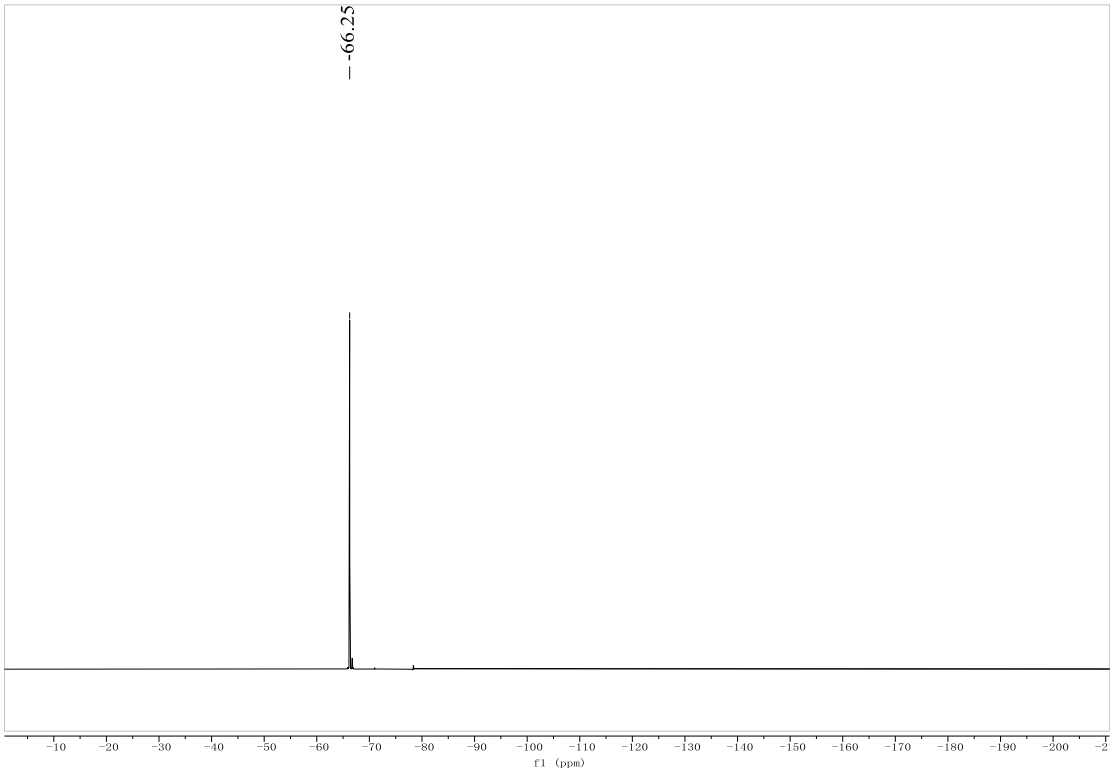
(1*R*,3'*R*)-3'-(4-methoxyphenyl)-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (3c)



^{1}H NMR spectrum in CD_3OD.

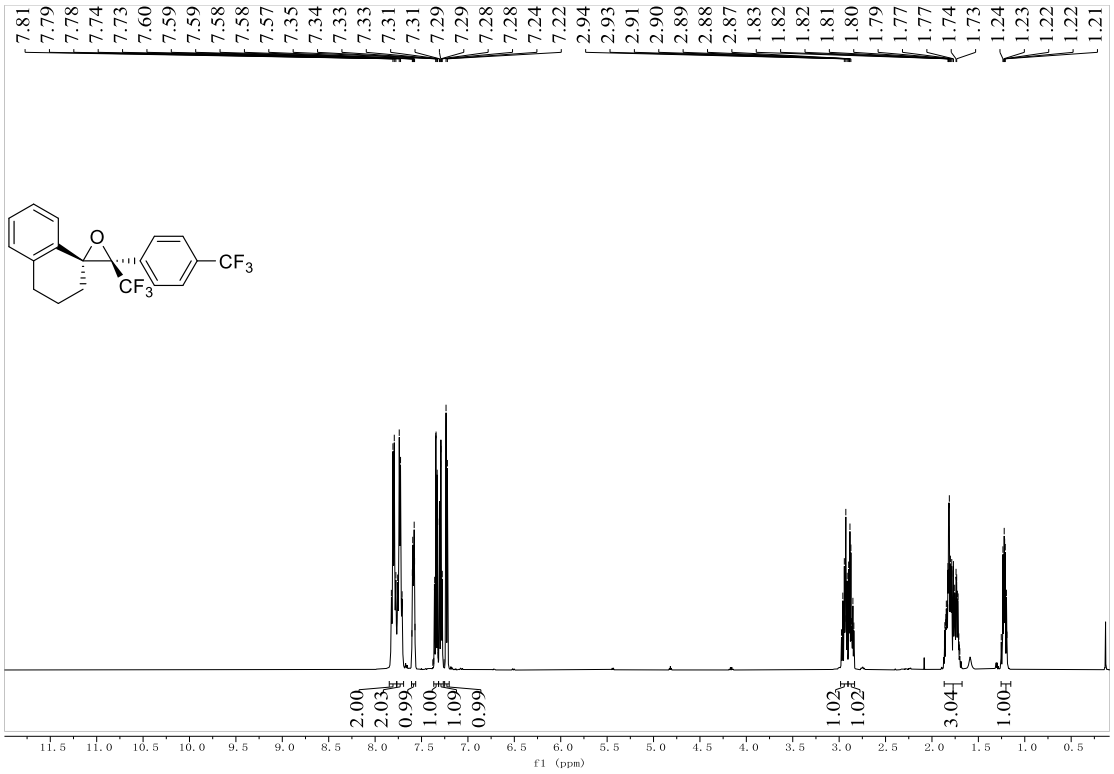


^{13}C NMR spectrum in CD_3OD.

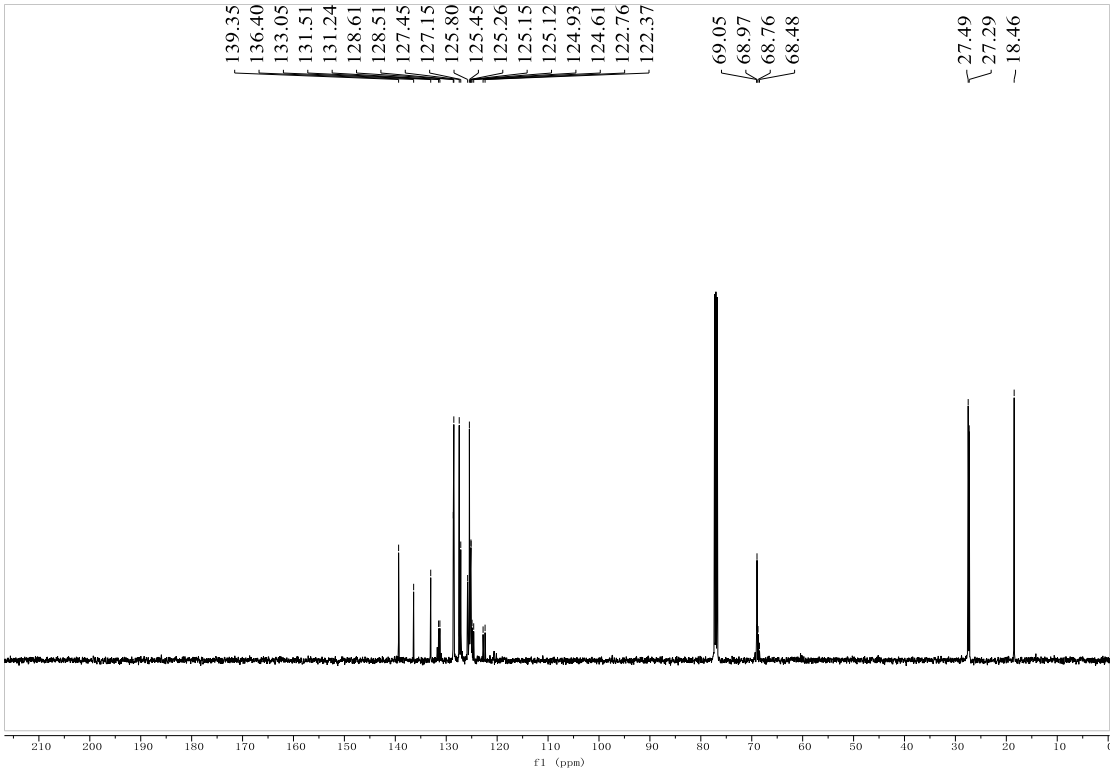


^{19}F NMR spectrum in CD_3OD.

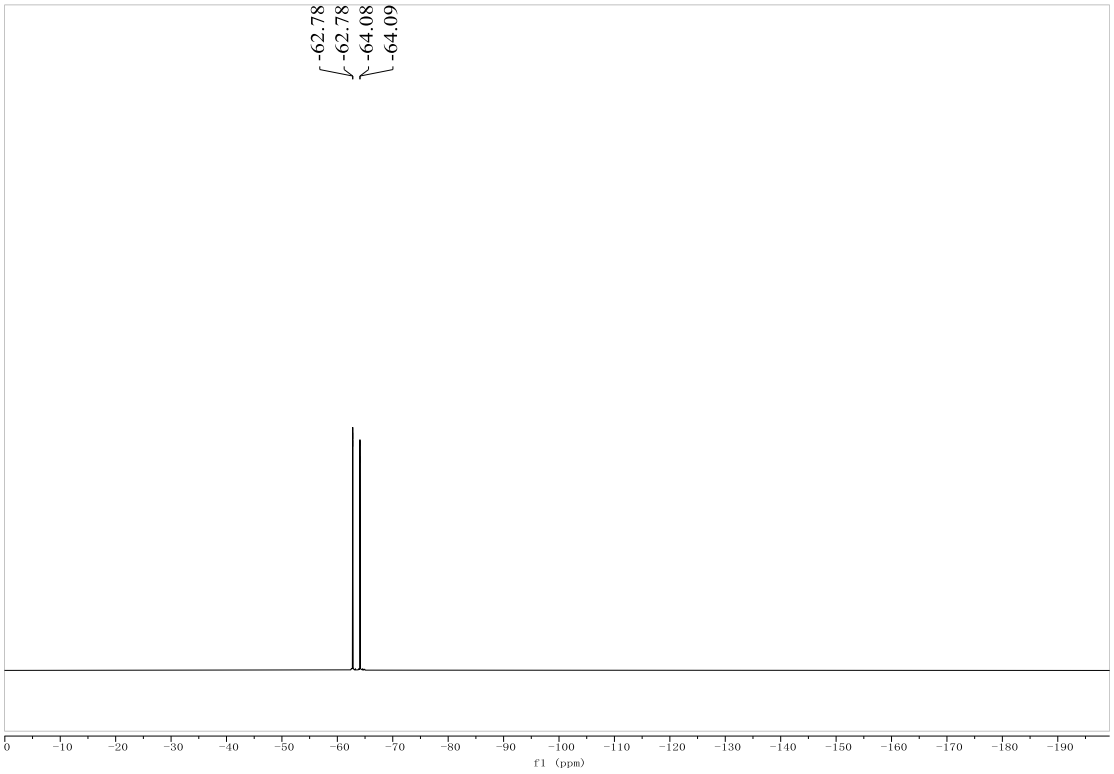
(1*R*,3'*R*)-3'-(trifluoromethyl)-3'-(4-(trifluoromethyl) phenyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (4c)



^{1}H NMR spectrum in $CDCl_3$.

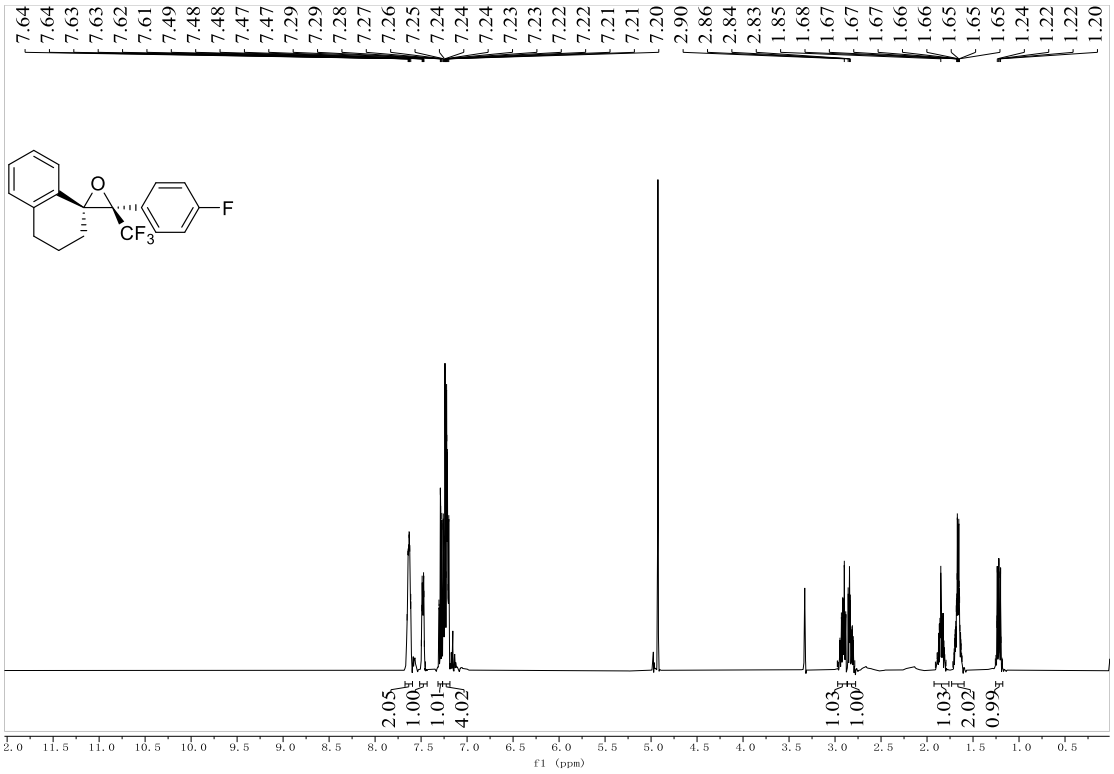


^{13}C NMR spectrum in $CDCl_3$.

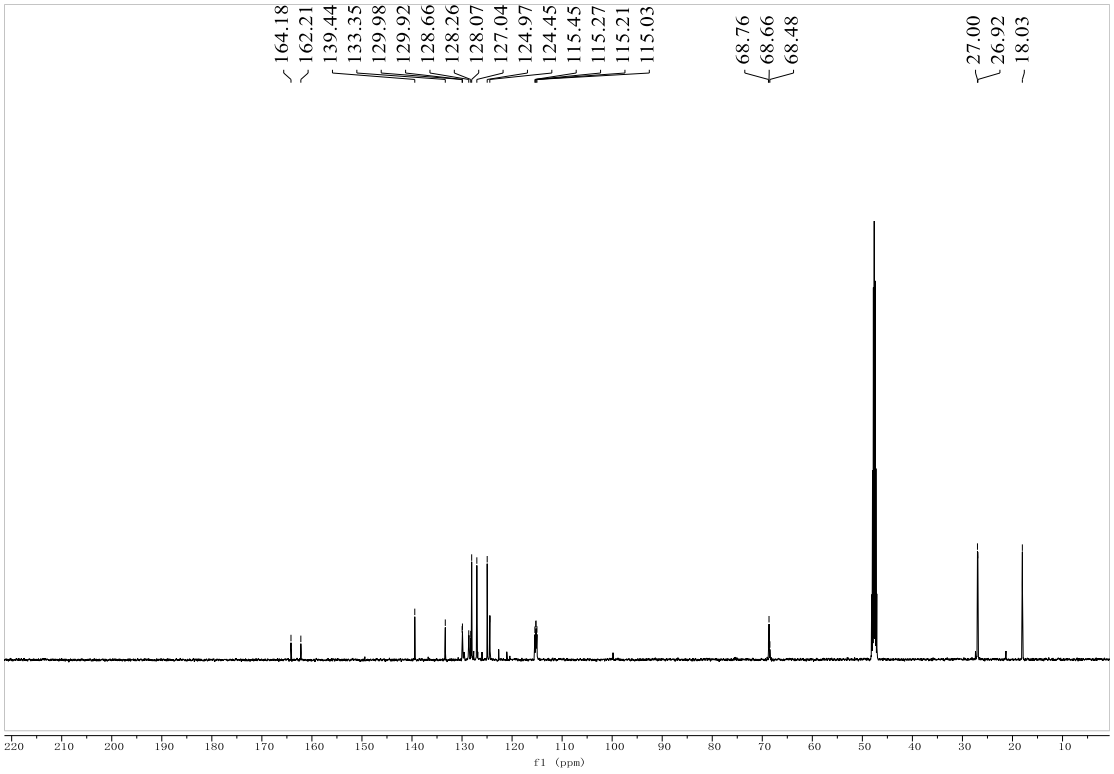


^{19}F NMR spectrum in $CDCl_3$.

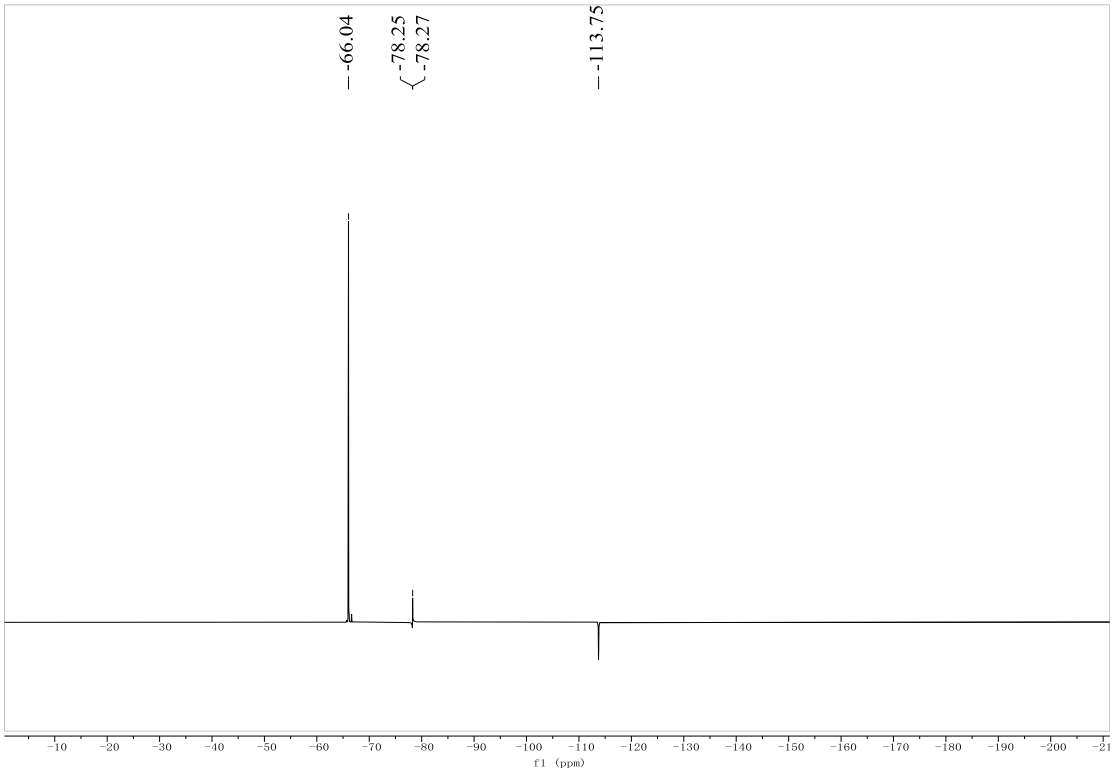
(1*R*,3'*R*)-3'-(4-fluorophenyl)-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (5c)



^{1}H NMR spectrum in CD_3OD.

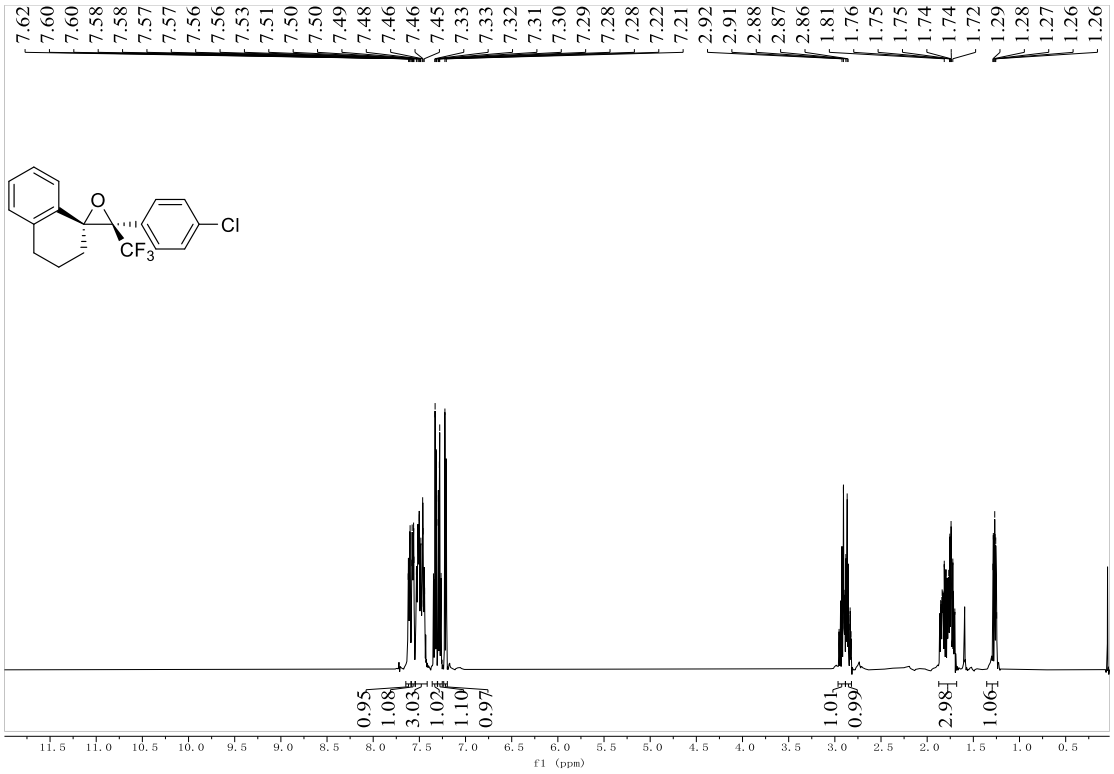


^{13}C NMR spectrum in CD_3OD.

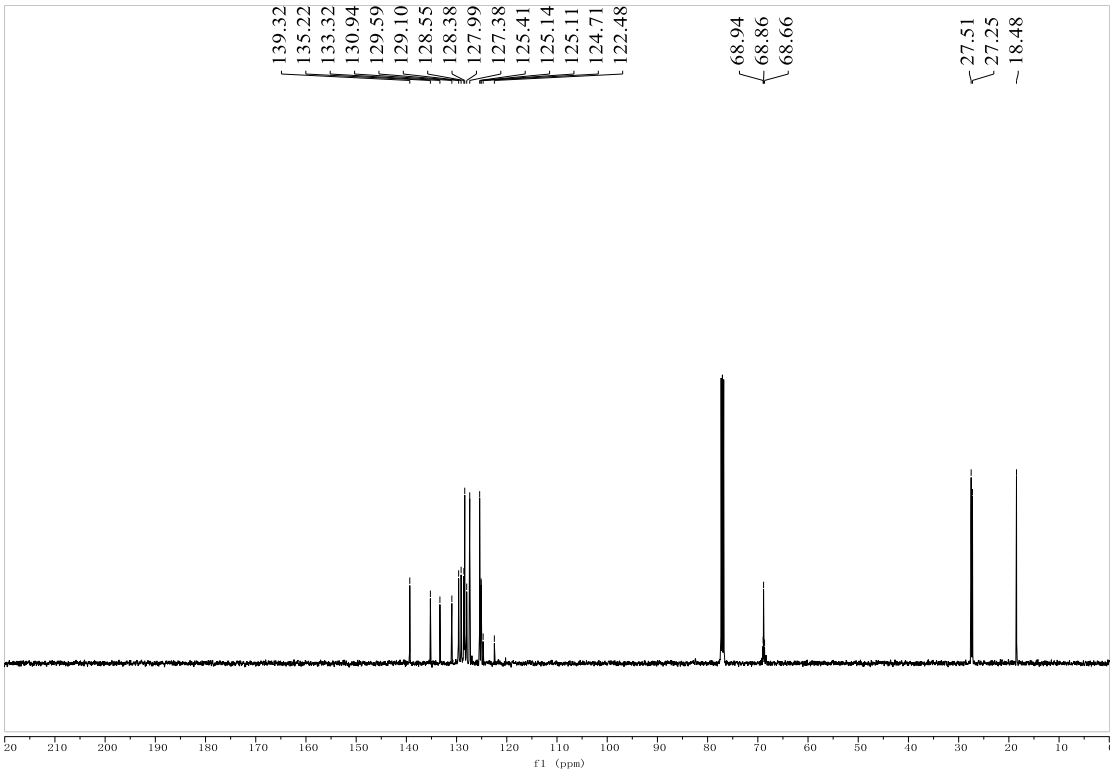


^{19}F NMR spectrum in CD_3OD.

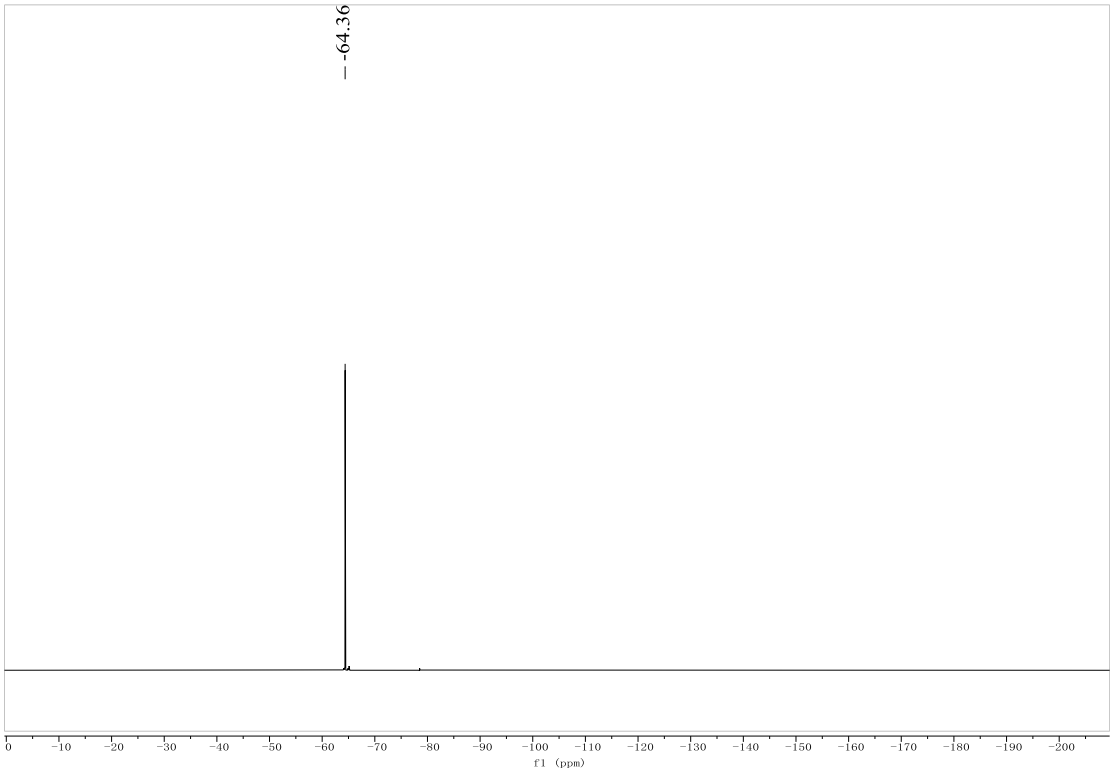
(1*R*,3'*R*)-3'-(4-chlorophenyl)-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (6c)



^{1}H NMR spectrum in $CDCl_3$.

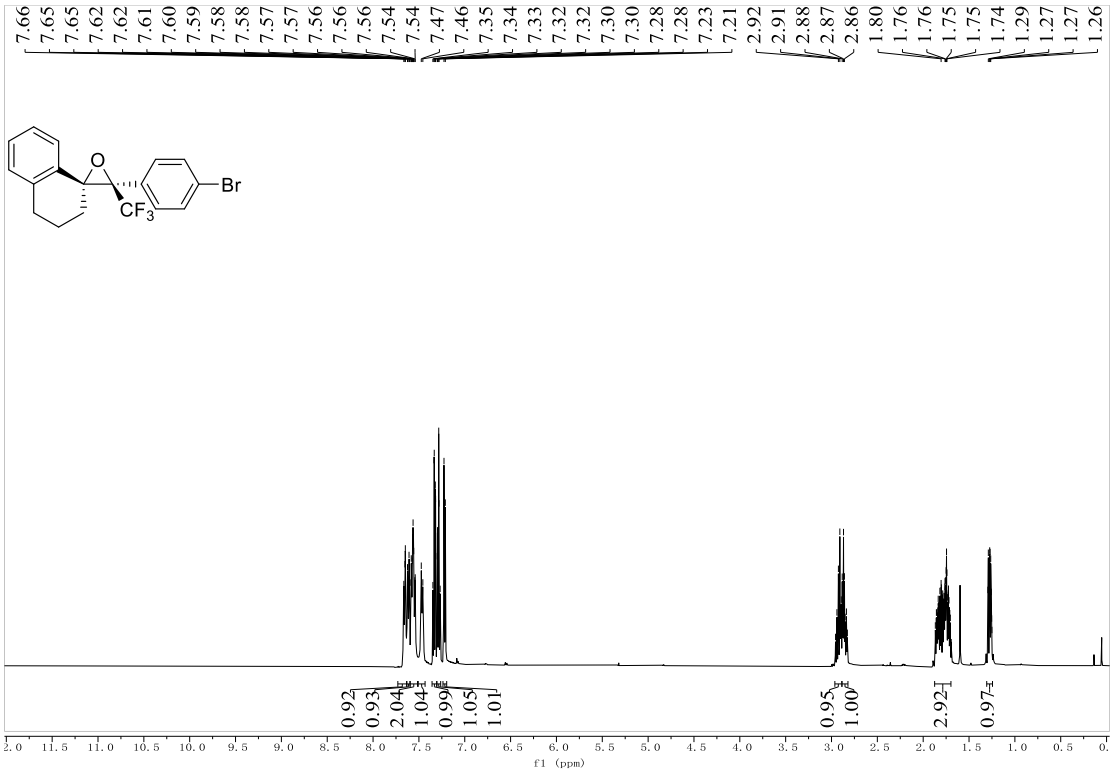


^{13}C NMR spectrum in $CDCl_3$.

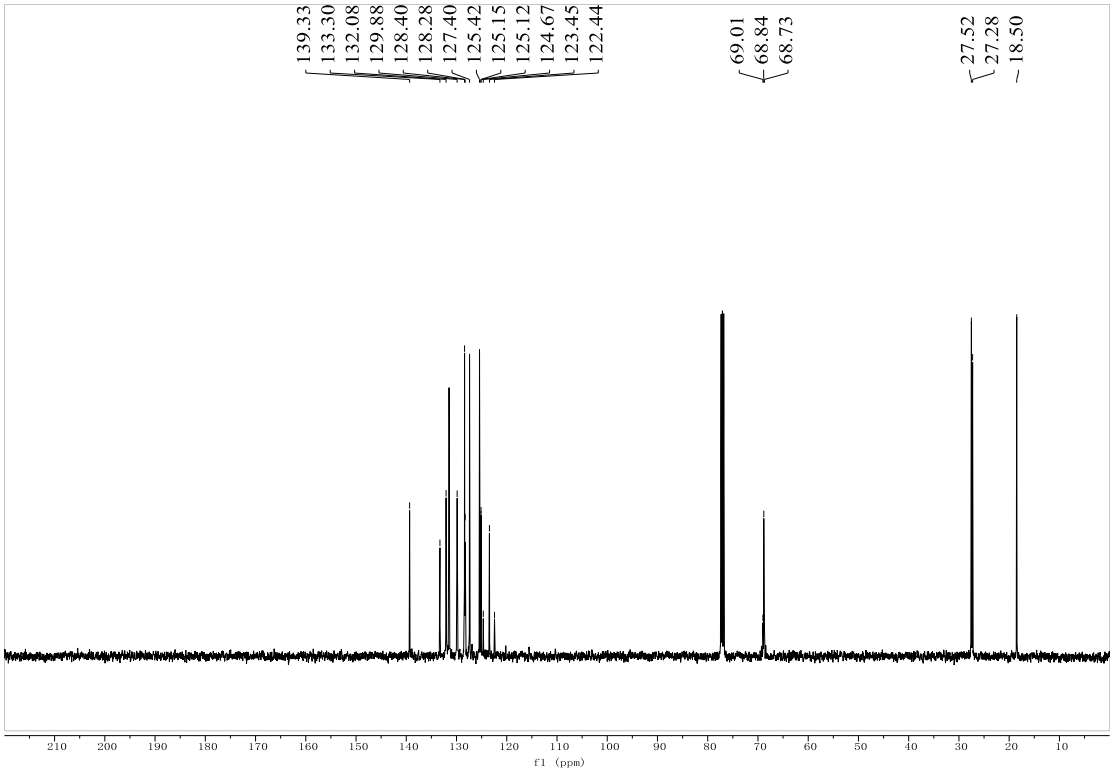


^{19}F NMR spectrum in $CDCl_3$.

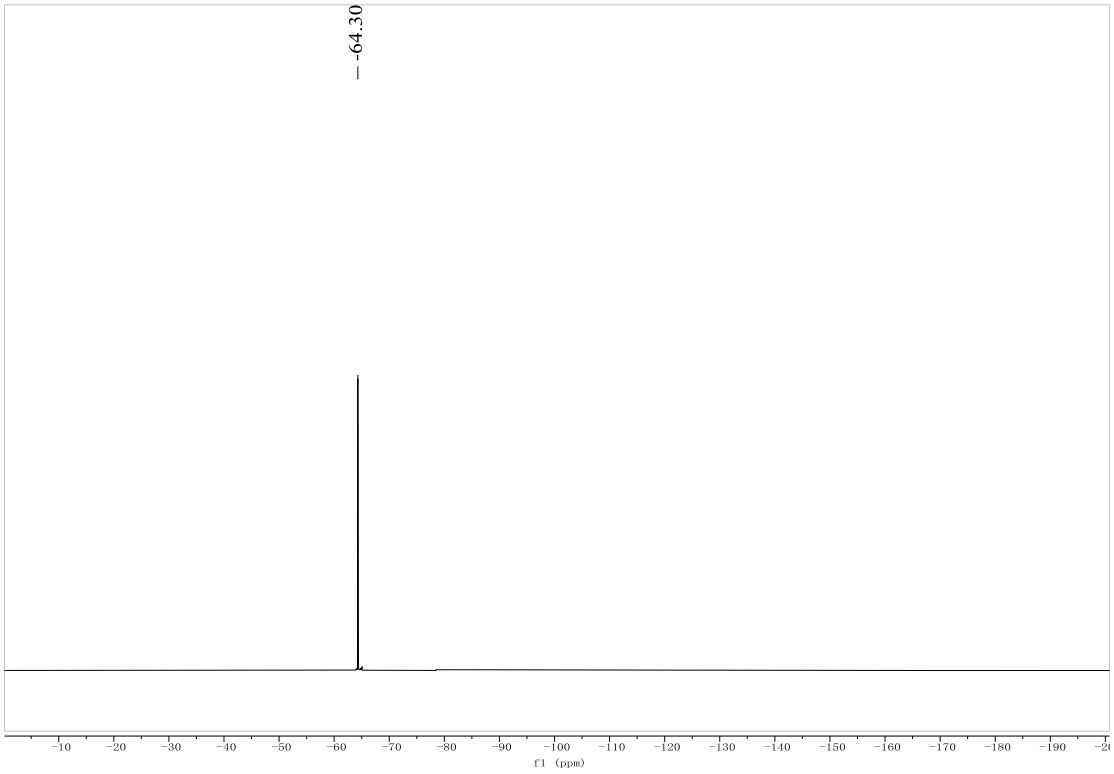
(1*R*,3'*R*)-3'-(4-bromophenyl)-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (7c)



^{1}H NMR spectrum in $CDCl_3$.

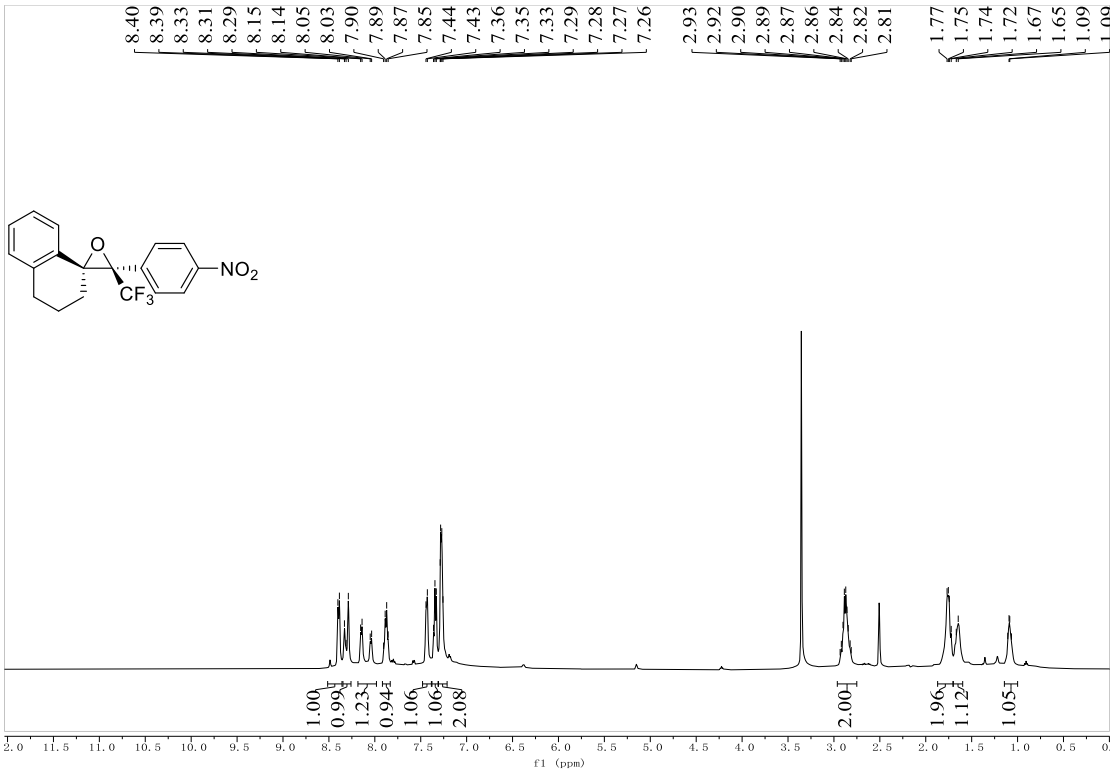


^{13}C NMR spectrum in $CDCl_3$.

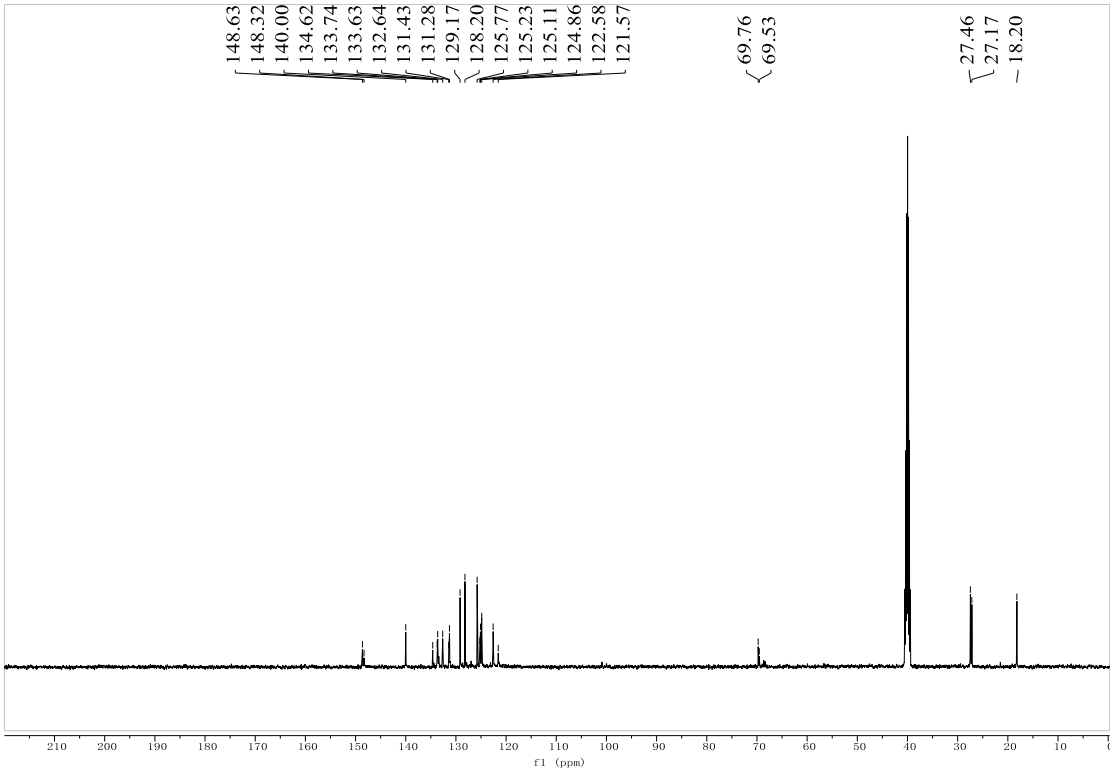


^{19}F NMR spectrum in $CDCl_3$.

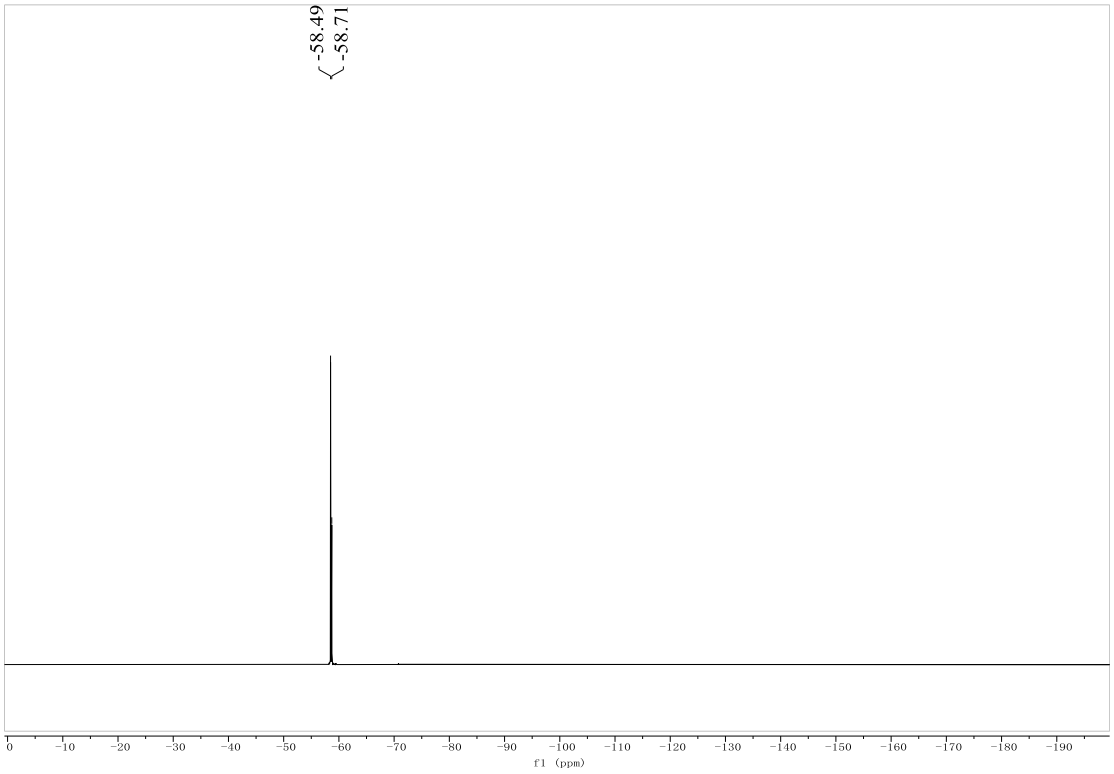
(1*R*,3'*R*)-3'-(4-nitrophenyl)-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (8c)



^{1}H NMR spectrum in DMSO-d_6.

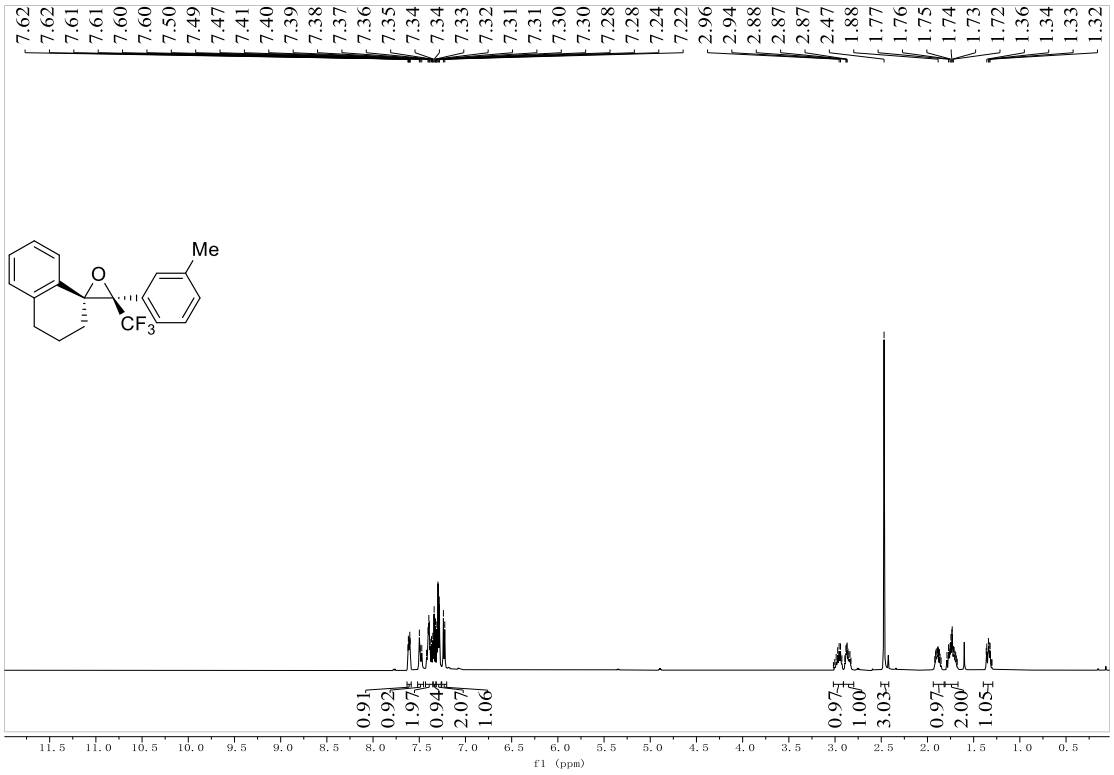


^{13}C NMR spectrum in DMSO-d_6.

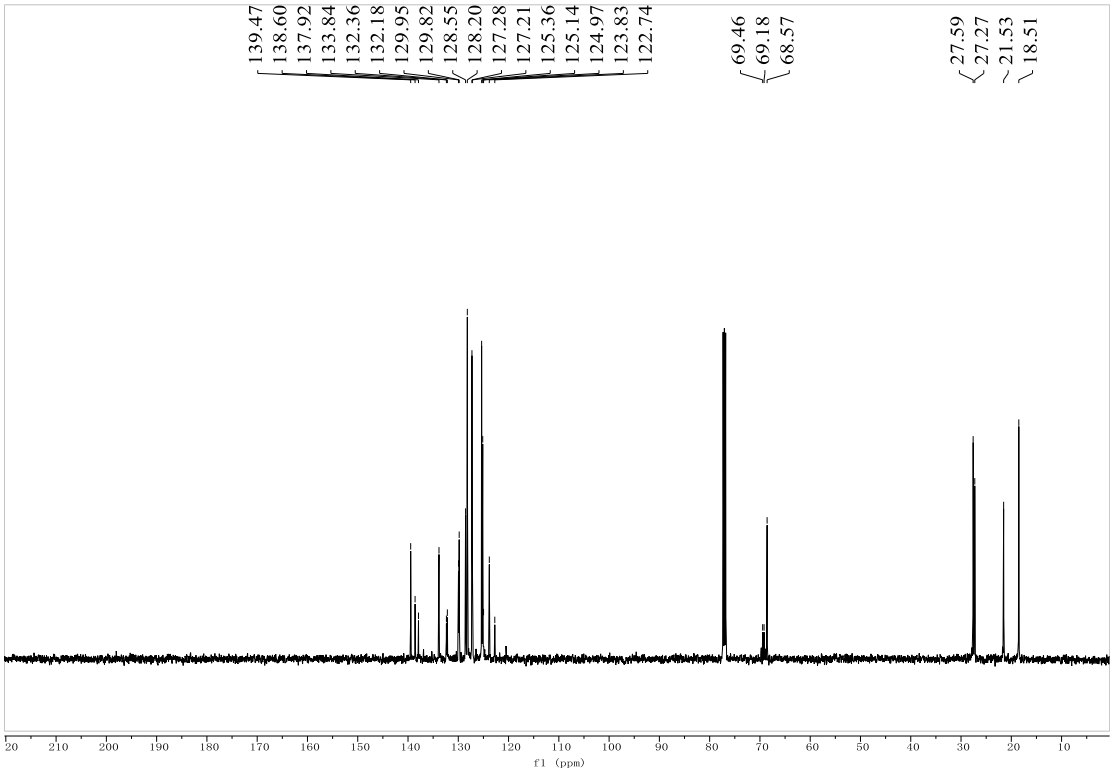


^{19}F NMR spectrum in DMSO-d_6.

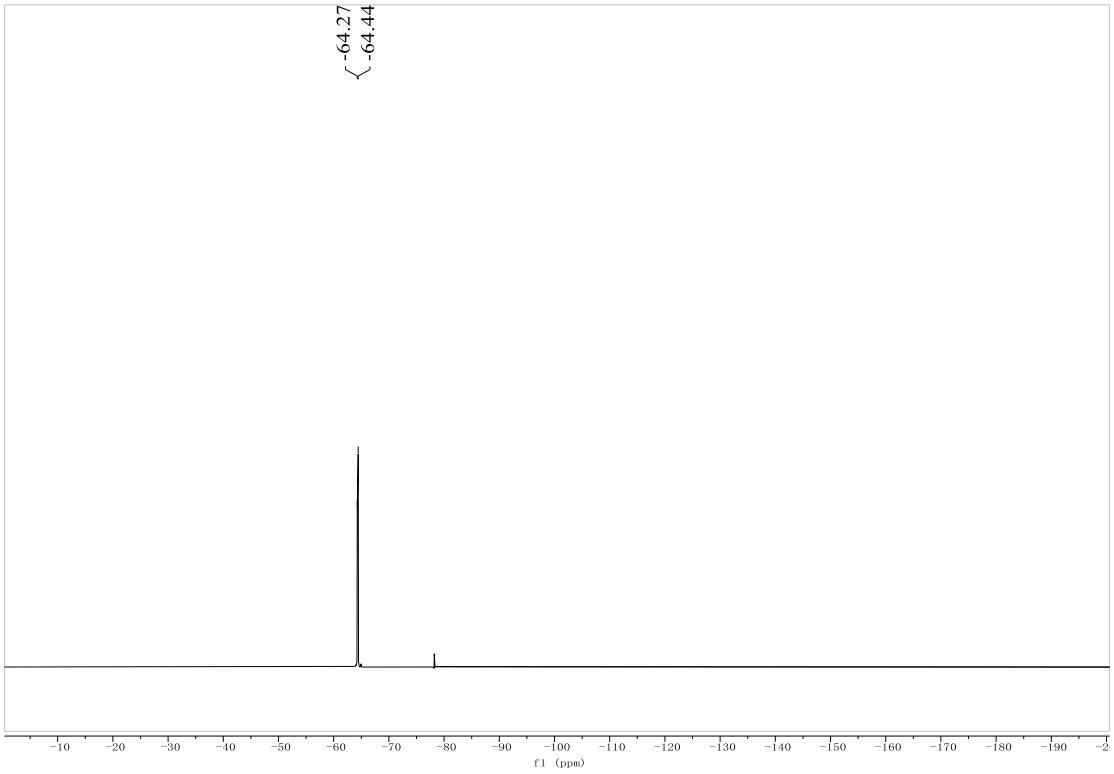
(1*R*,3'*R*)-3'-(m-tolyl)-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (9c)



^{1}H NMR spectrum in $CDCl_3$.

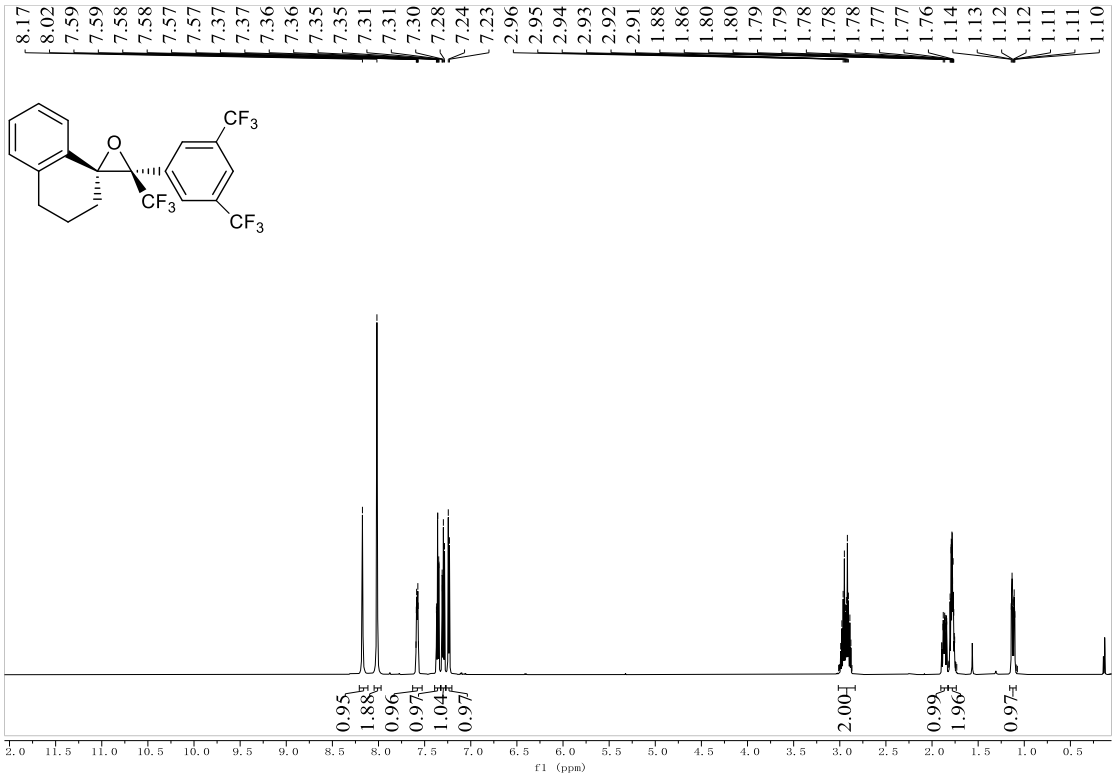


^{13}C NMR spectrum in $CDCl_3$.

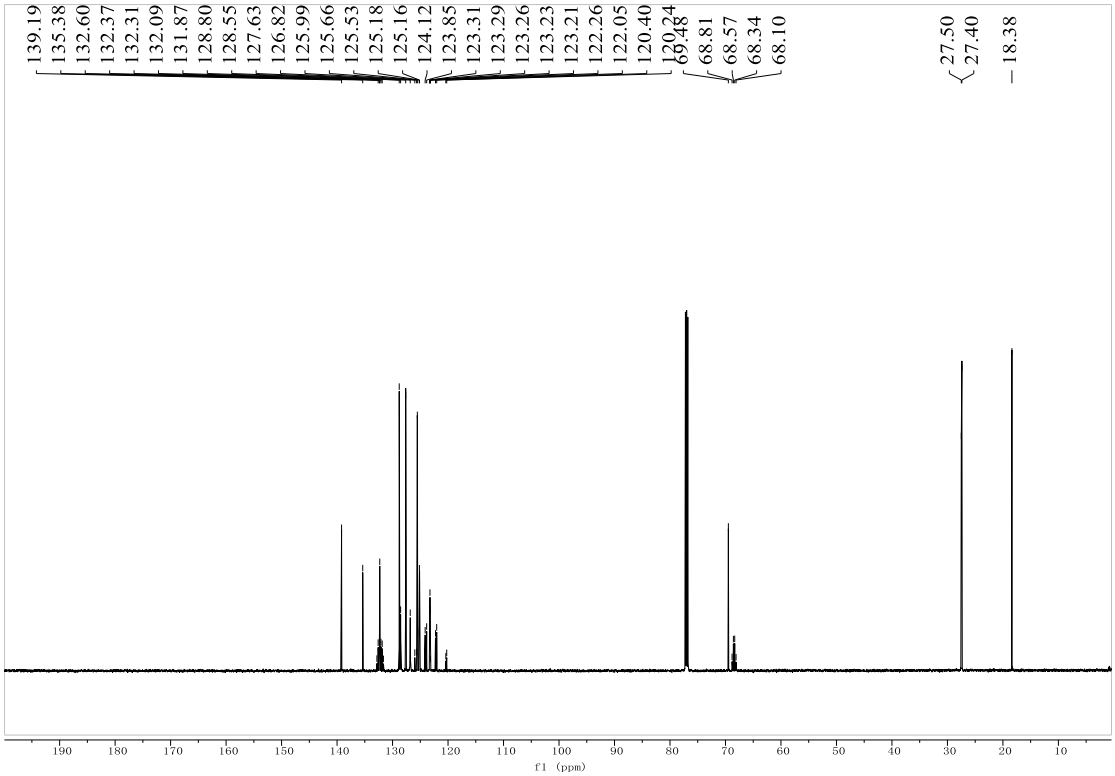


^{19}F NMR spectrum in $CDCl_3$.

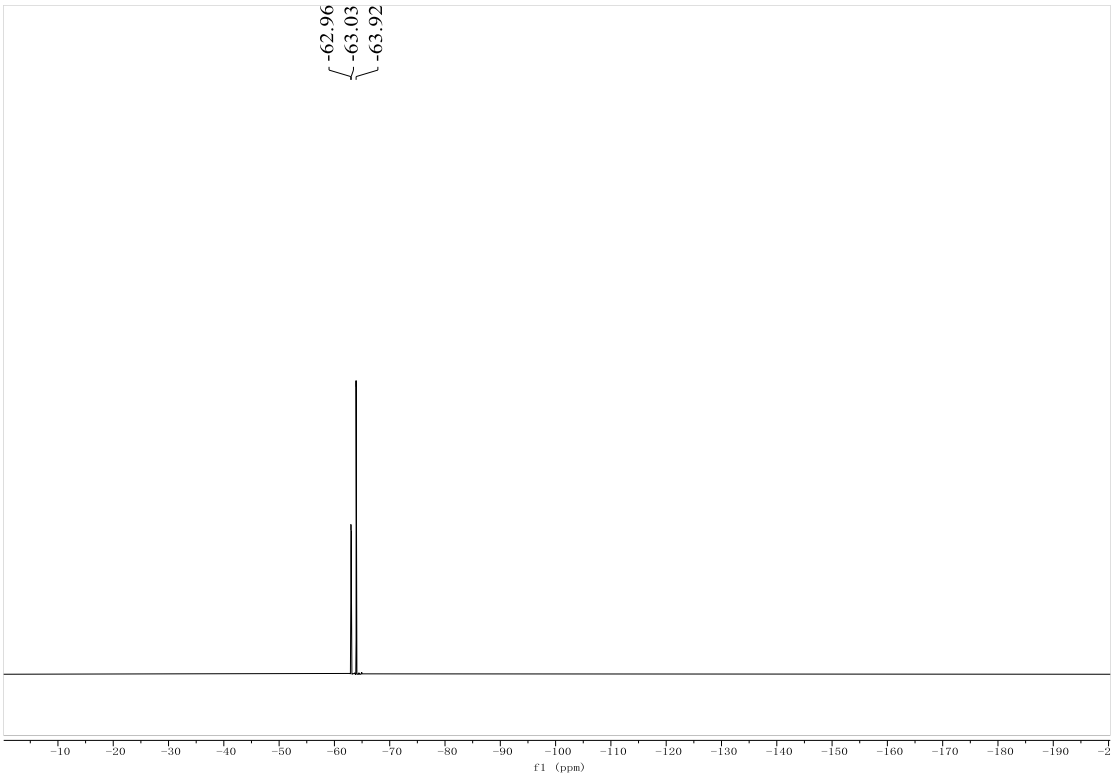
(1*R*,3'*R*)-3'-(3,5-bis(trifluoromethyl)phenyl)-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (10c)



^{1}H NMR spectrum in $CDCl_3$.

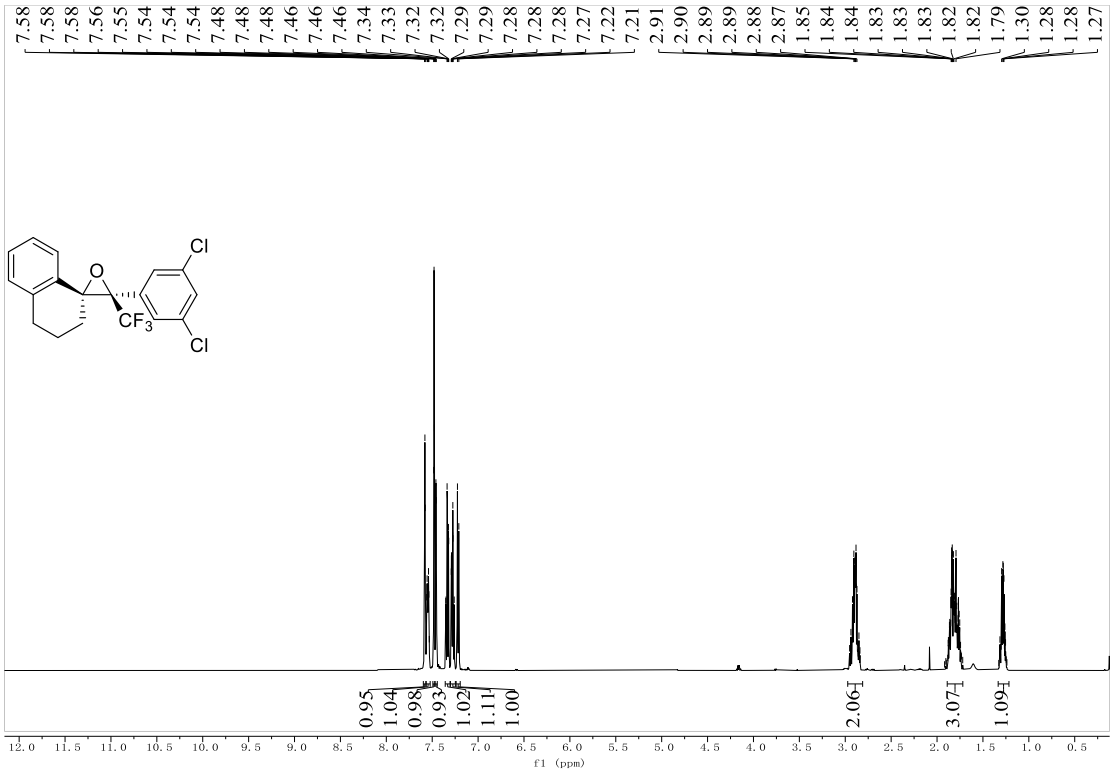


^{13}C NMR spectrum in $CDCl_3$.

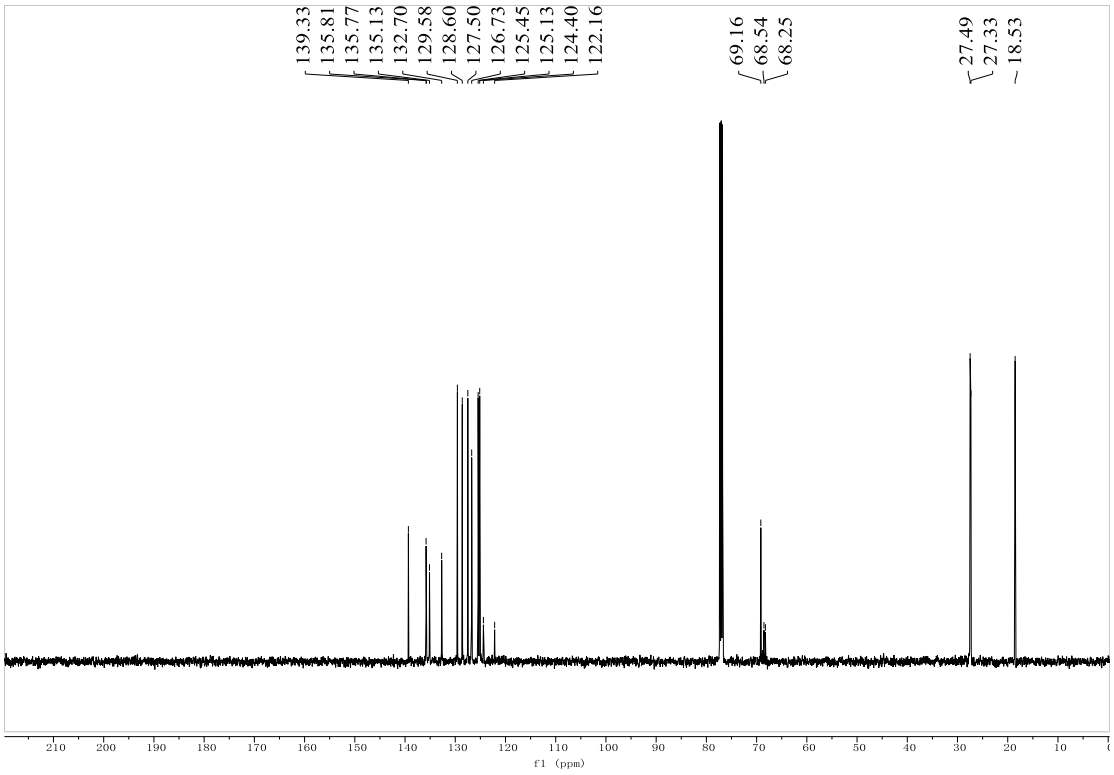


^{19}F NMR spectrum in $CDCl_3$.

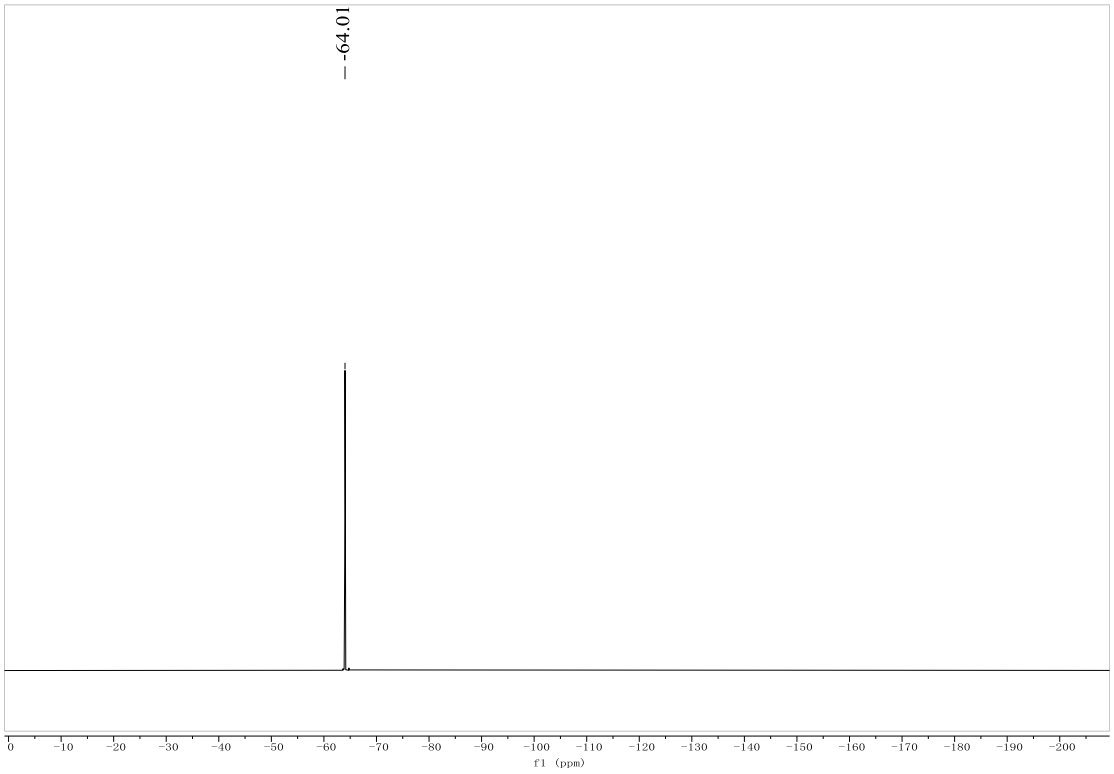
(1*R*,3'*R*)-3'-(3,5-dichlorophenyl)-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (11c)



^{1}H NMR spectrum in $CDCl_3$.

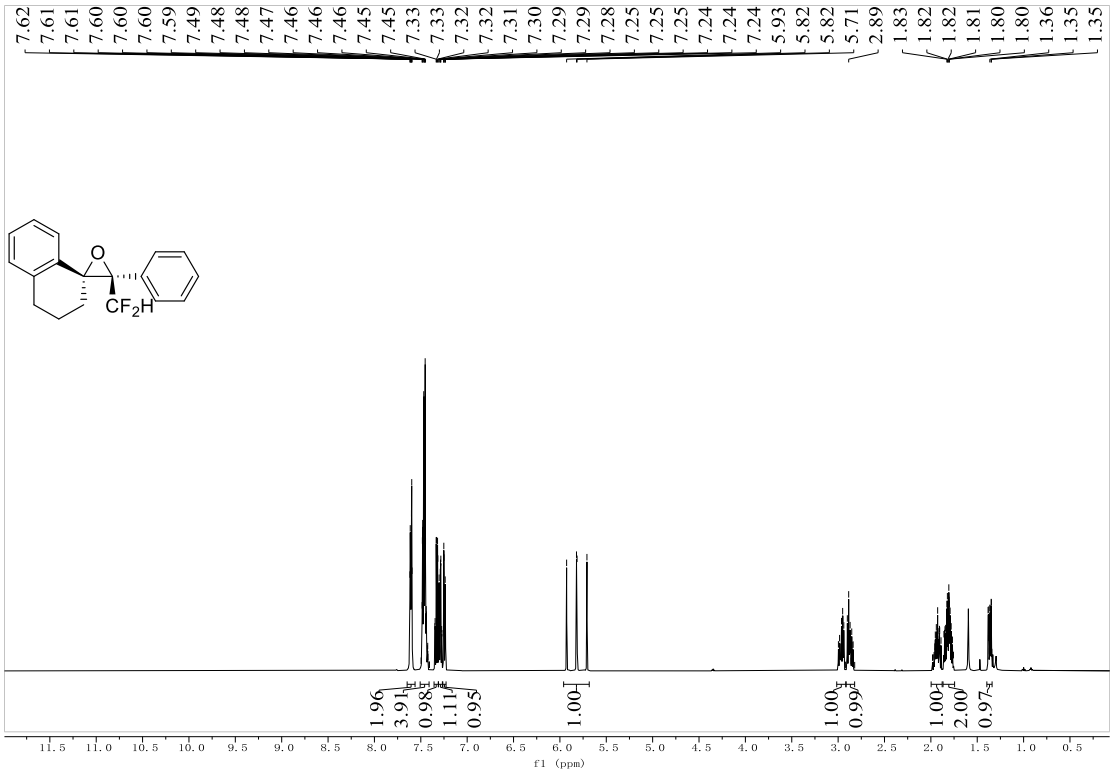


^{13}C NMR spectrum in $CDCl_3$.

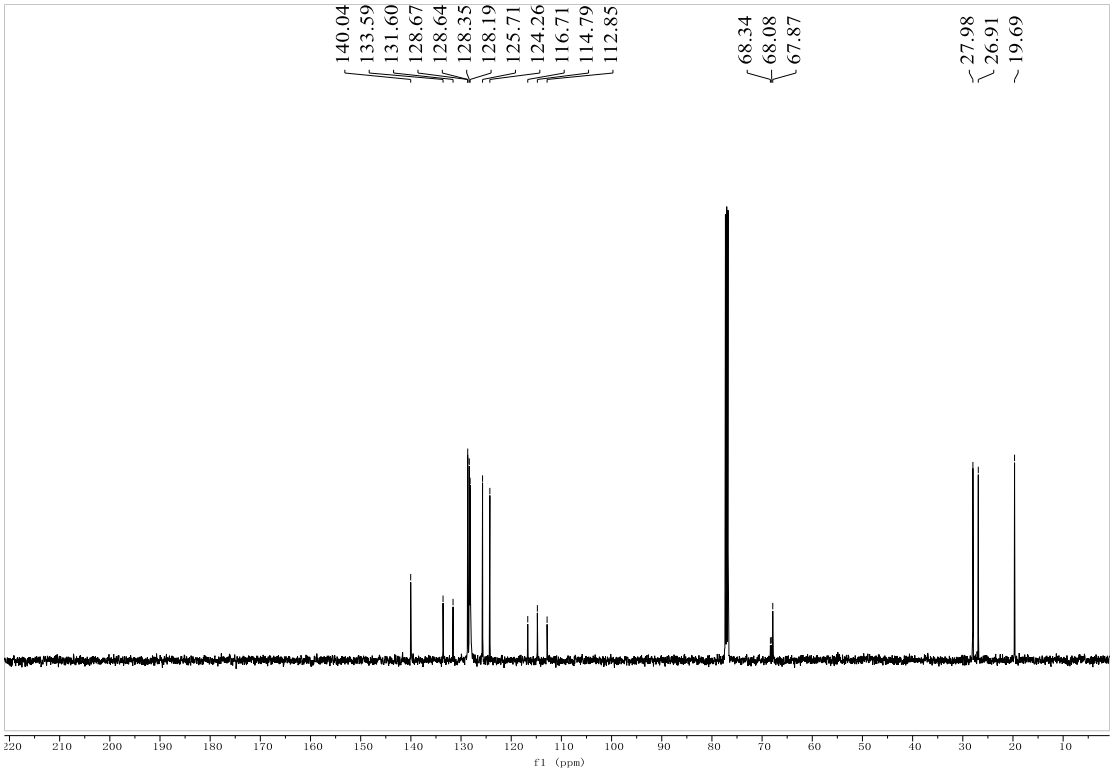


^{19}F NMR spectrum in $CDCl_3$.

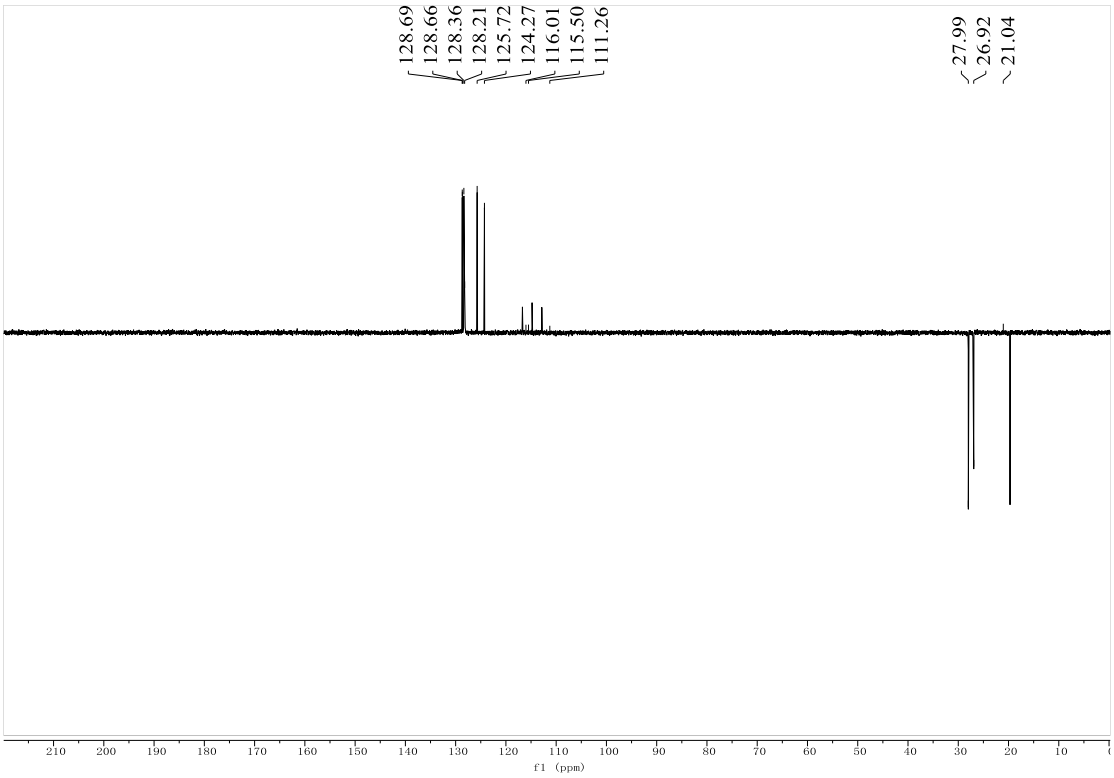
(1*R*,3'*S*)-3'-(difluoromethyl)-3'-phenyl-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (12c)



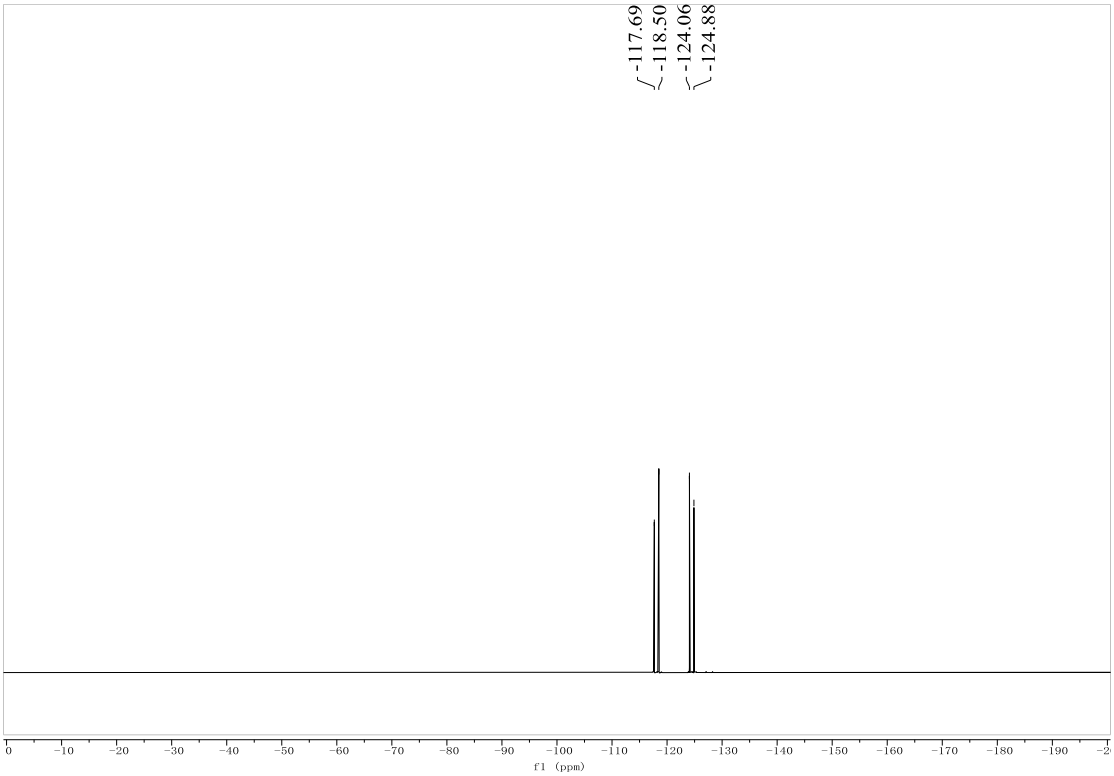
^{1}H NMR spectrum in $CDCl_3$.



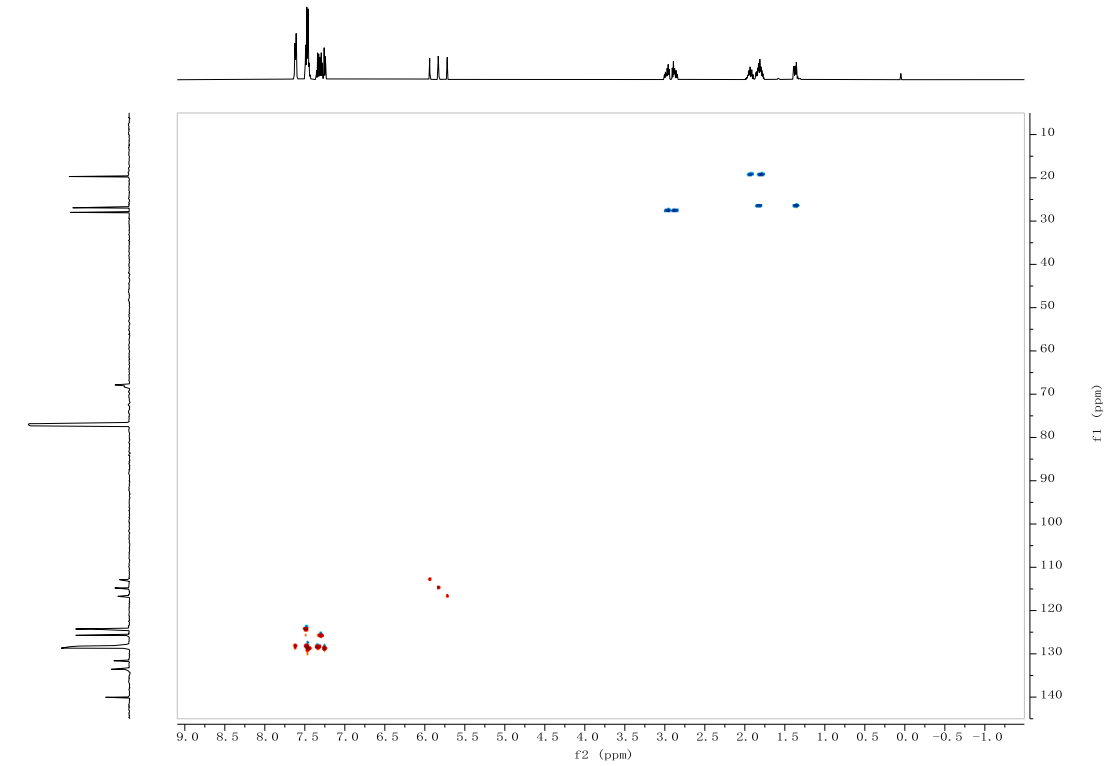
^{13}C NMR spectrum in $CDCl_3$.



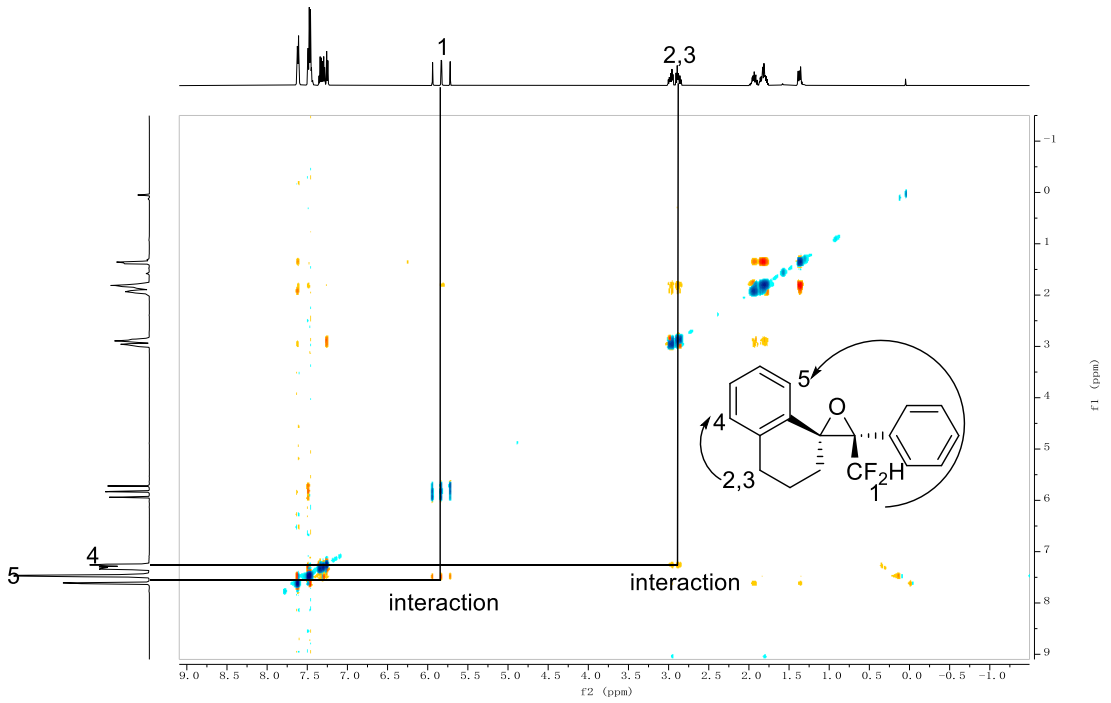
DEPT135 spectrum in $CDCl_3$.



^{19}F NMR spectrum in $CDCl_3$.

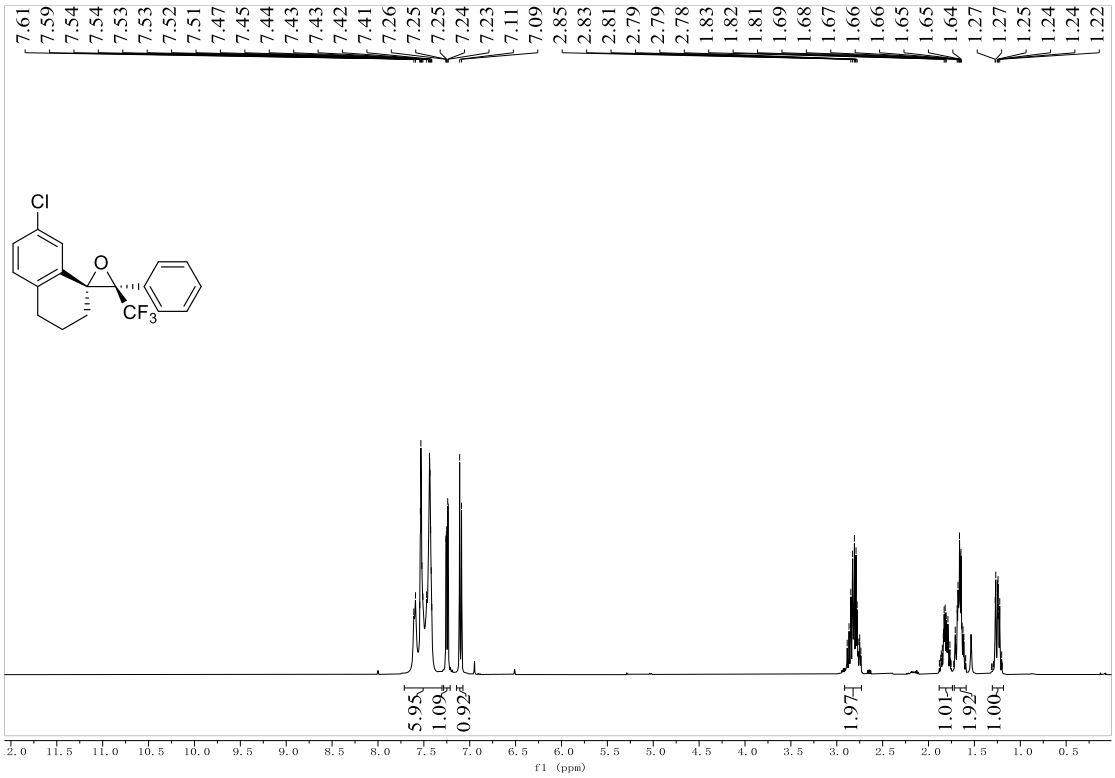


HSQC of 12c.

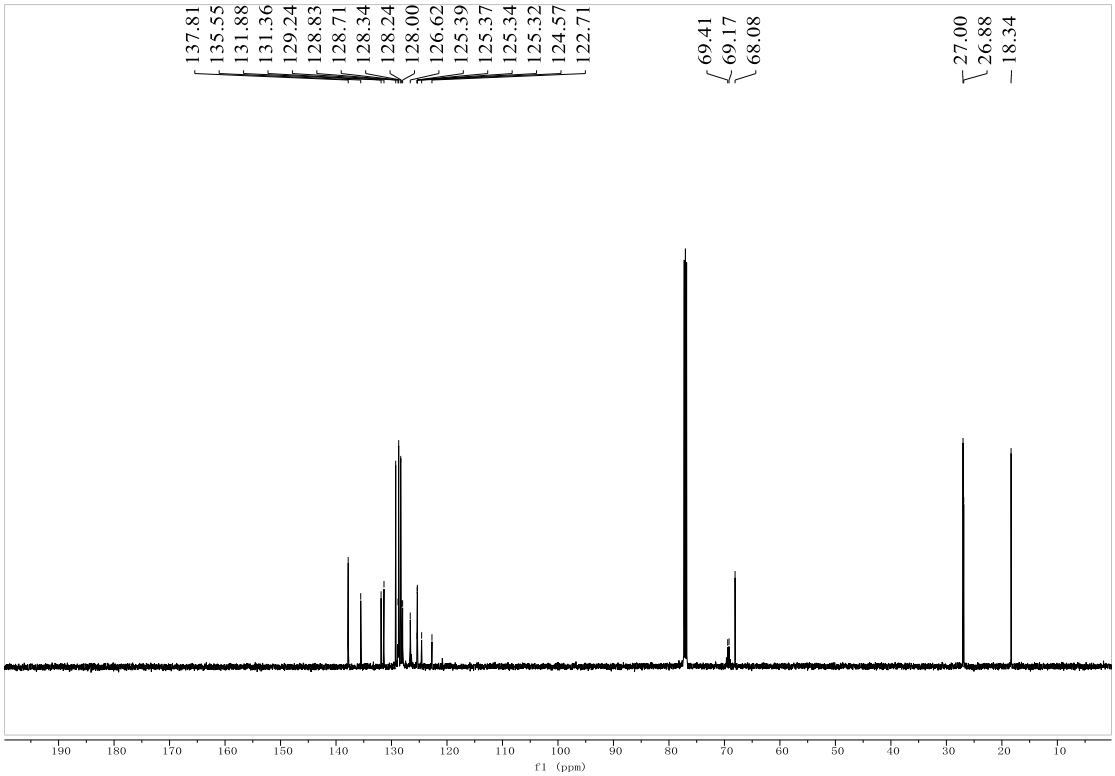


NOESY of 12c.

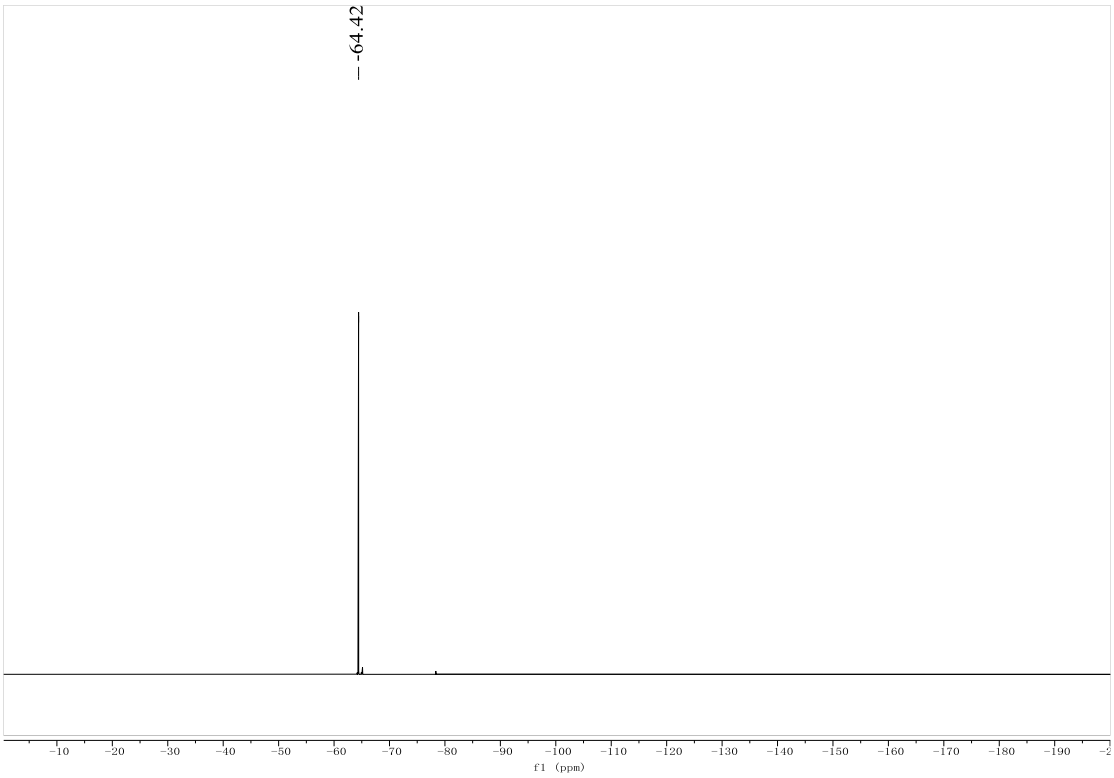
(1*R*,3'*R*)-7-chloro-3'-phenyl-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (13c)



^{1}H NMR spectrum in $CDCl_3$.



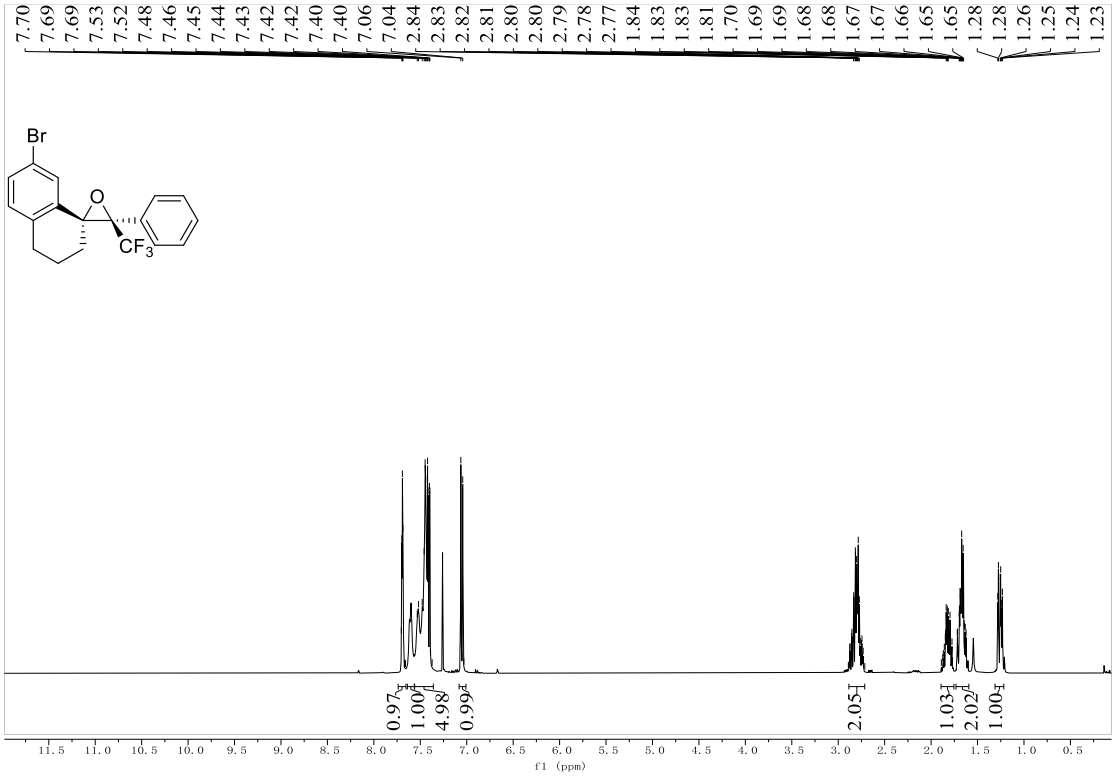
^{13}C NMR spectrum in $CDCl_3$.



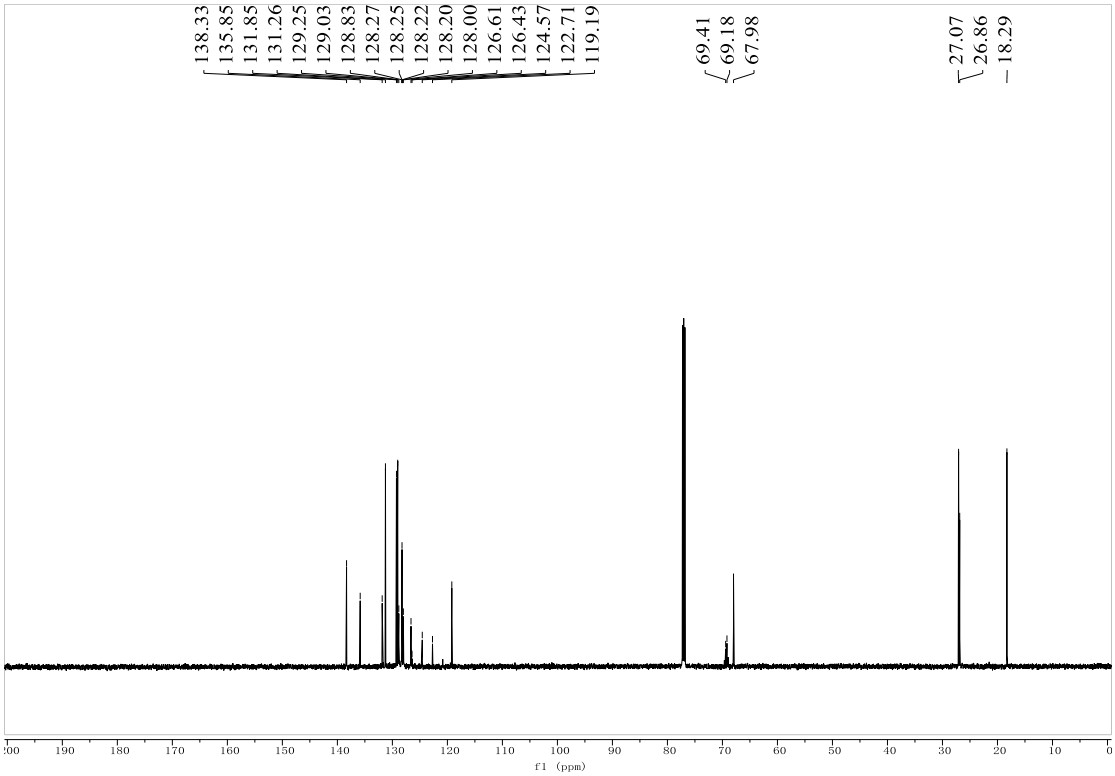
^{19}F NMR spectrum in $CDCl_3$.

(1*R*,3'*R*)-7-bromo-3'-phenyl-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane]

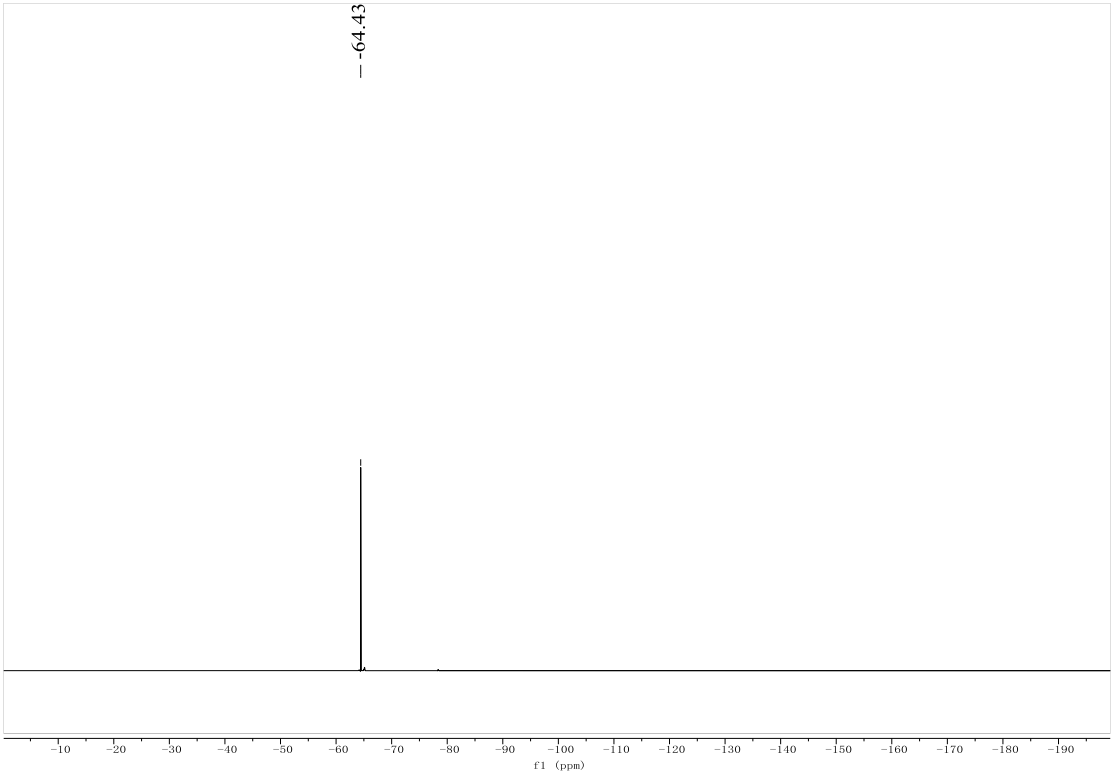
(14c)



^{1}H NMR spectrum in $CDCl_3$.

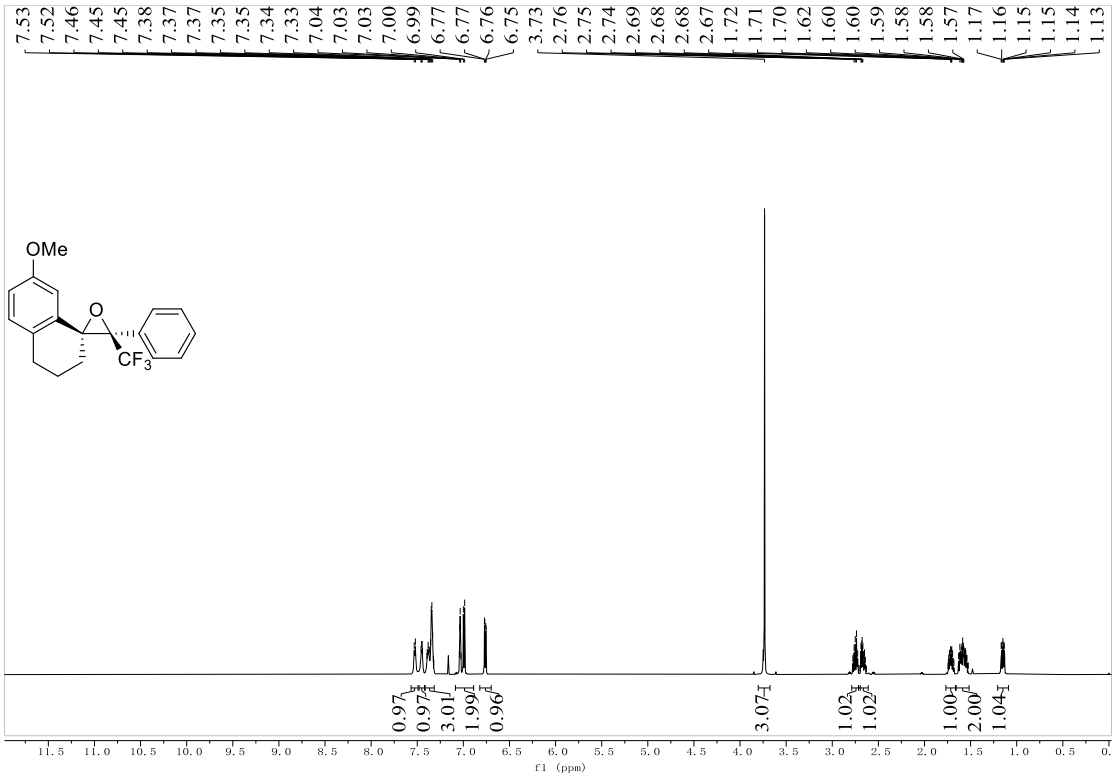


^{13}C NMR spectrum in $CDCl_3$.

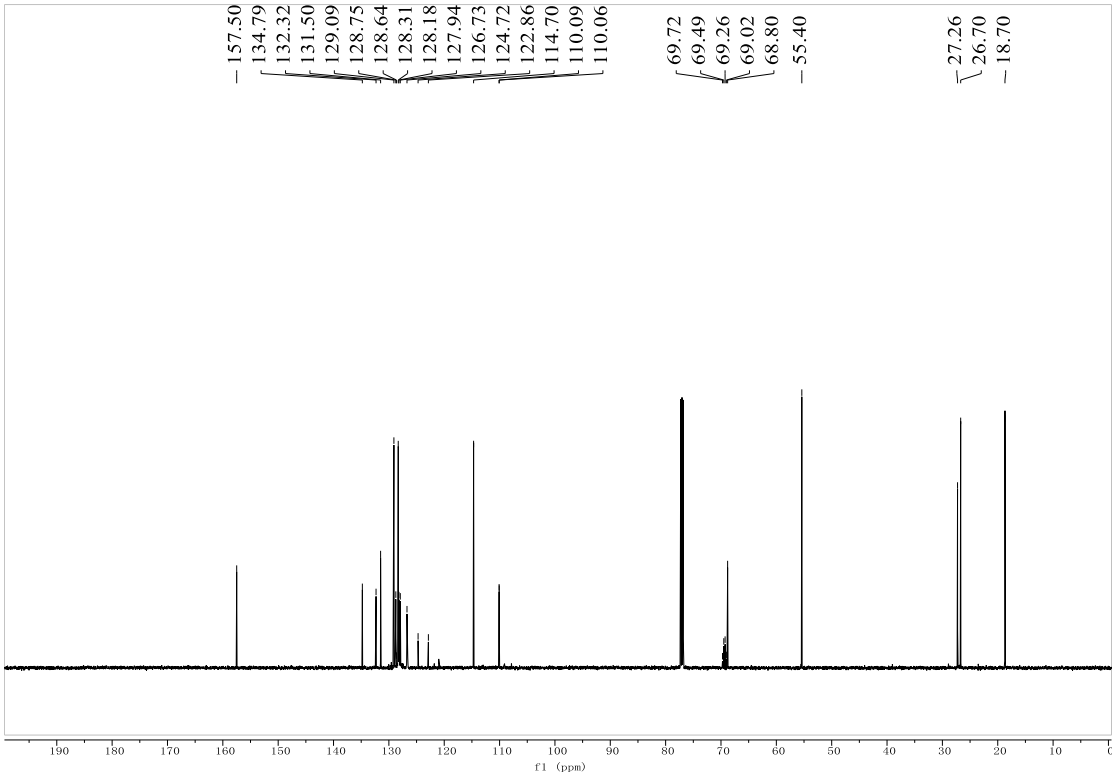


^{19}F NMR spectrum in $CDCl_3$.

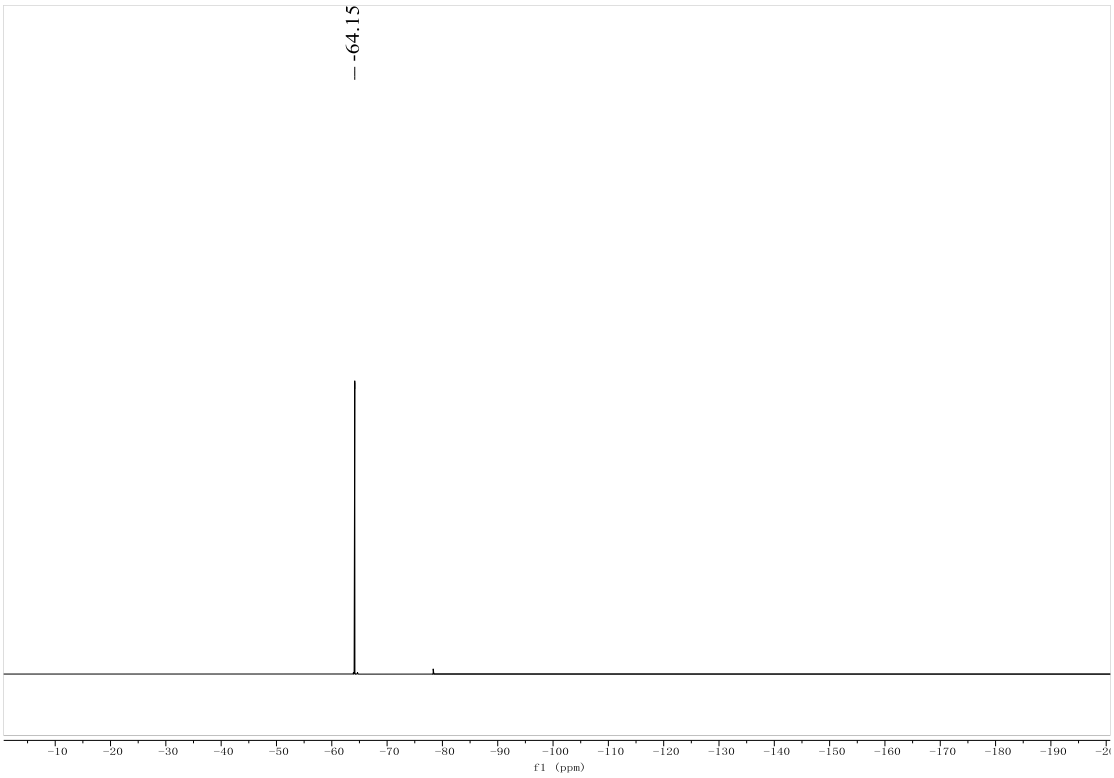
(1*R*,3'*S*)-7-methoxy-3'-phenyl-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (15c)



^{1}H NMR spectrum in $CDCl_3$.

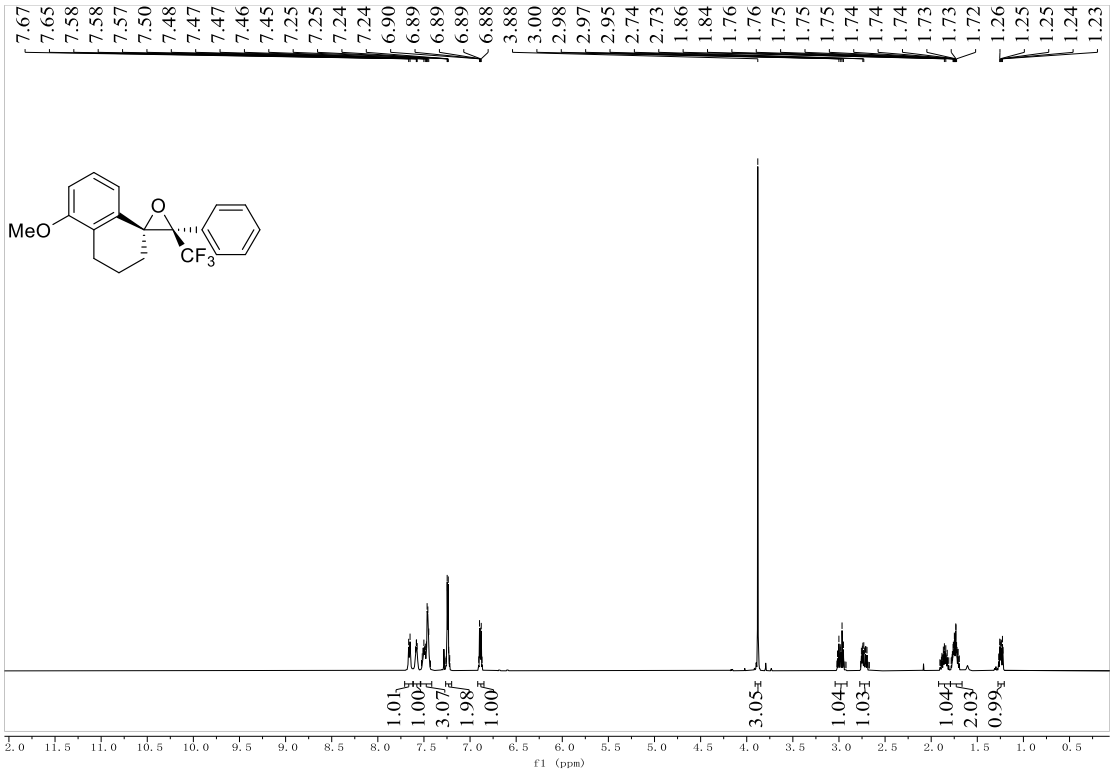


^{13}C NMR spectrum in $CDCl_3$.

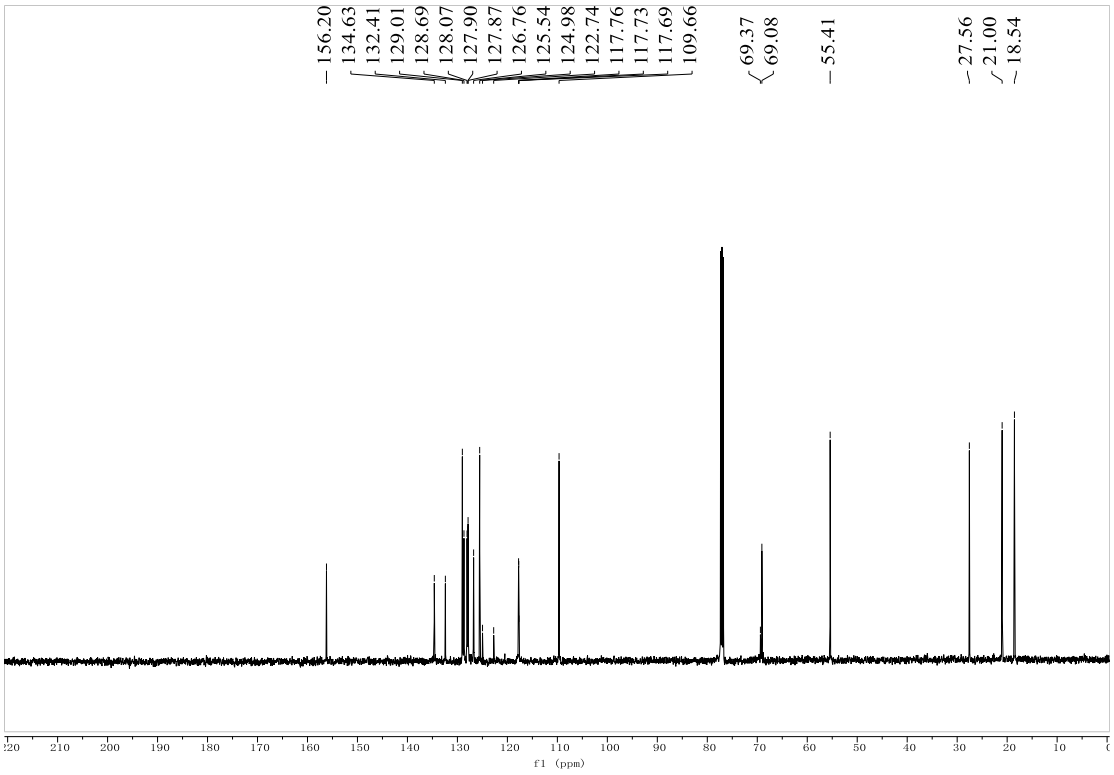


^{19}F NMR spectrum in $CDCl_3$.

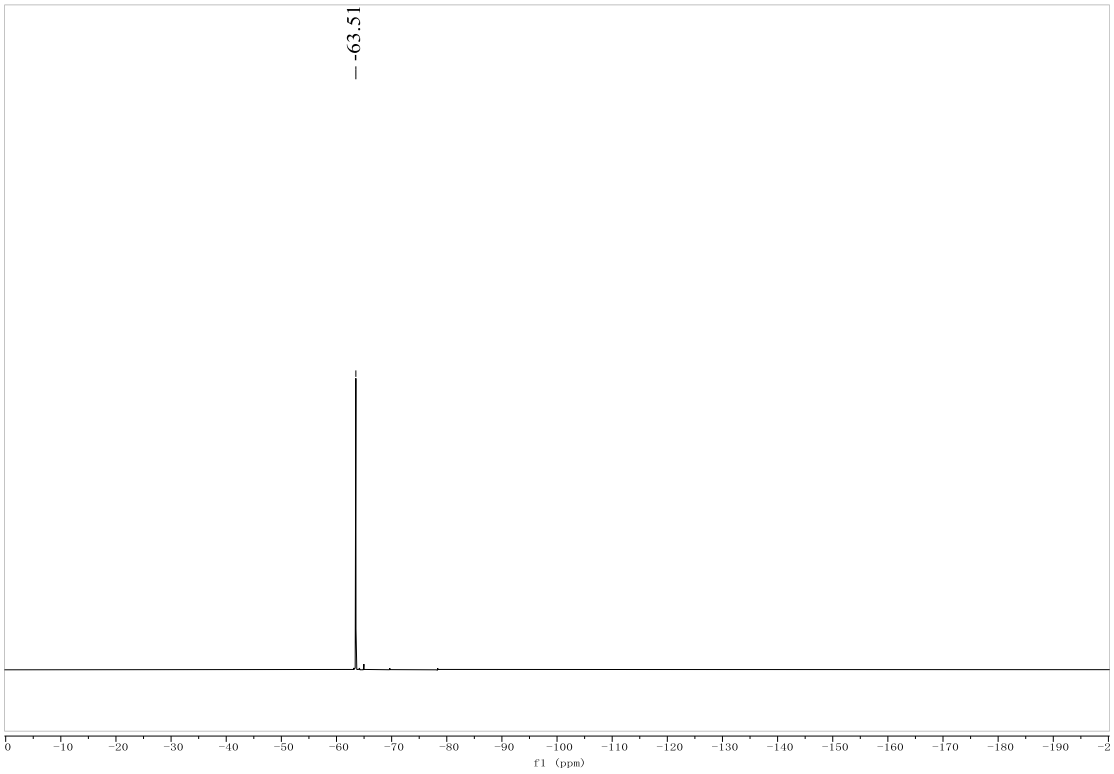
(1*R*,3'*S*)-7-methoxy-3'-phenyl-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (16c)



^{1}H NMR spectrum in $CDCl_3$.

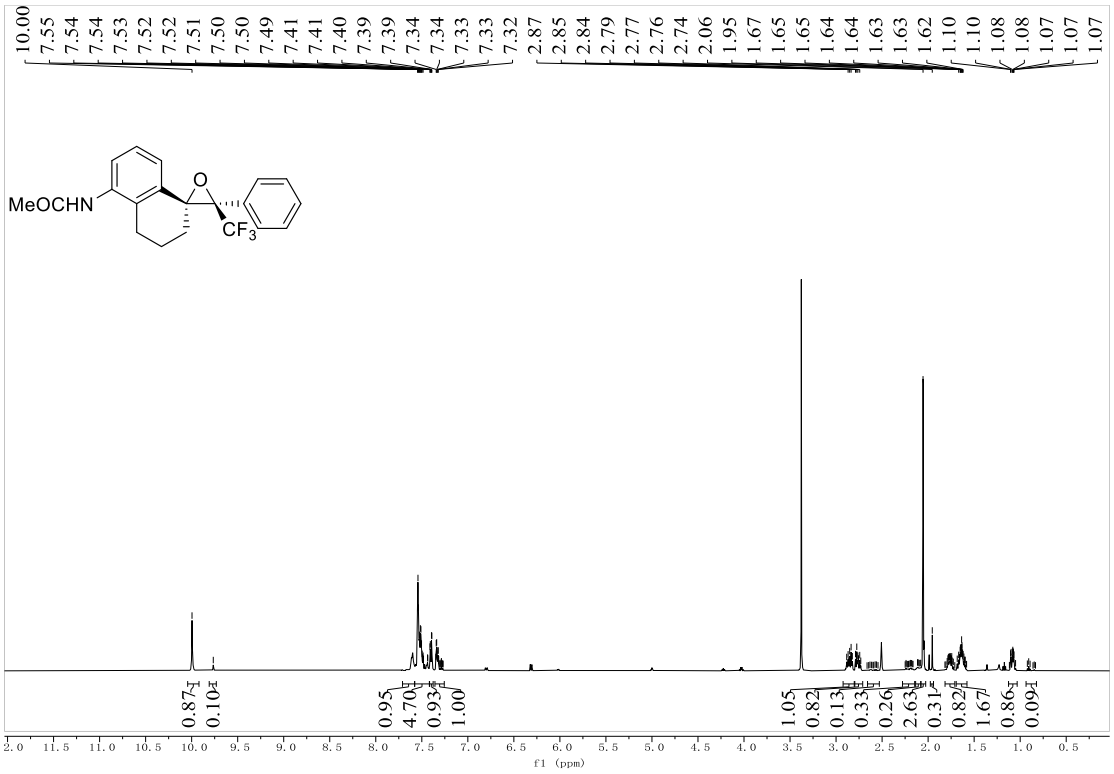


^{13}C NMR spectrum in $CDCl_3$.

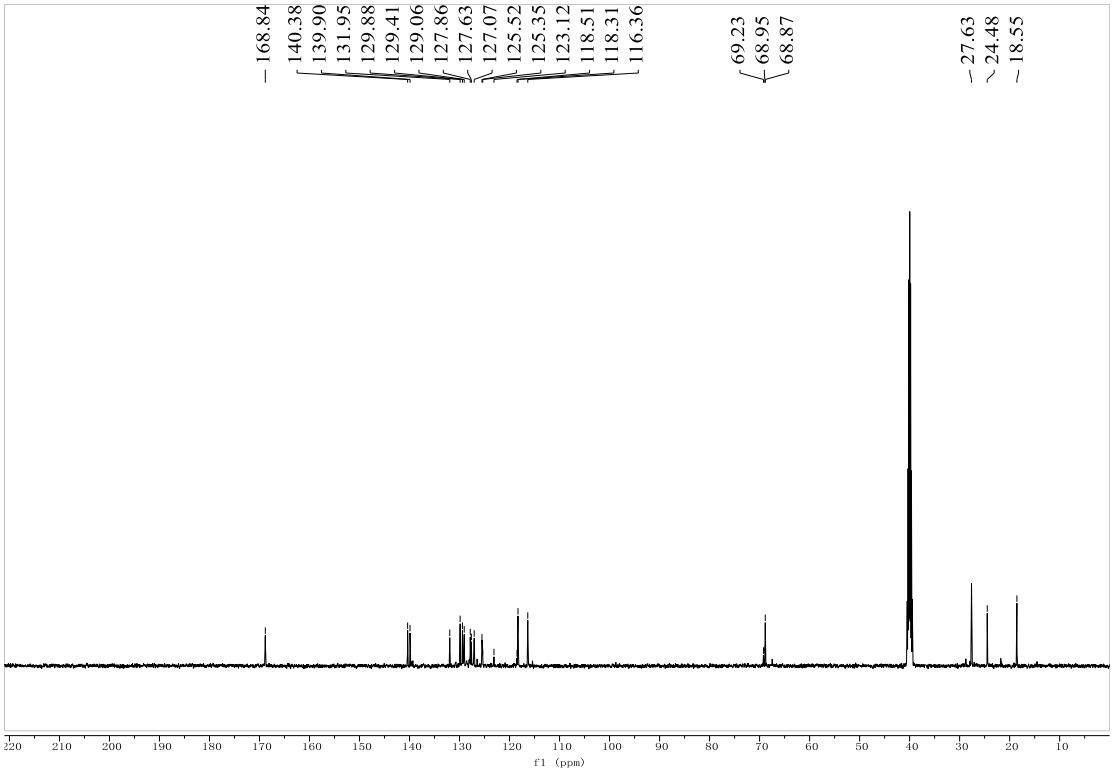


^{19}F NMR spectrum in $CDCl_3$.

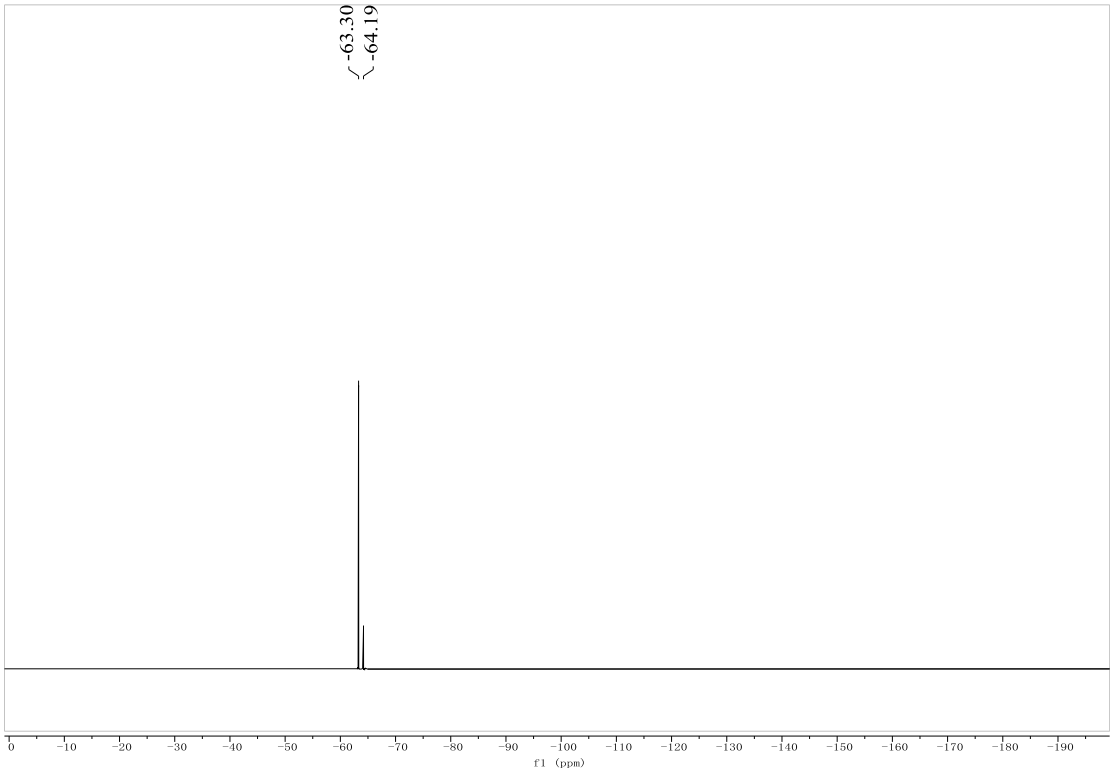
***N*-((1*R*,3'*R*)-3'-phenyl-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxiran]-5-yl) acetamide (17c)**



^{1}H NMR spectrum in DMSO-d_6.

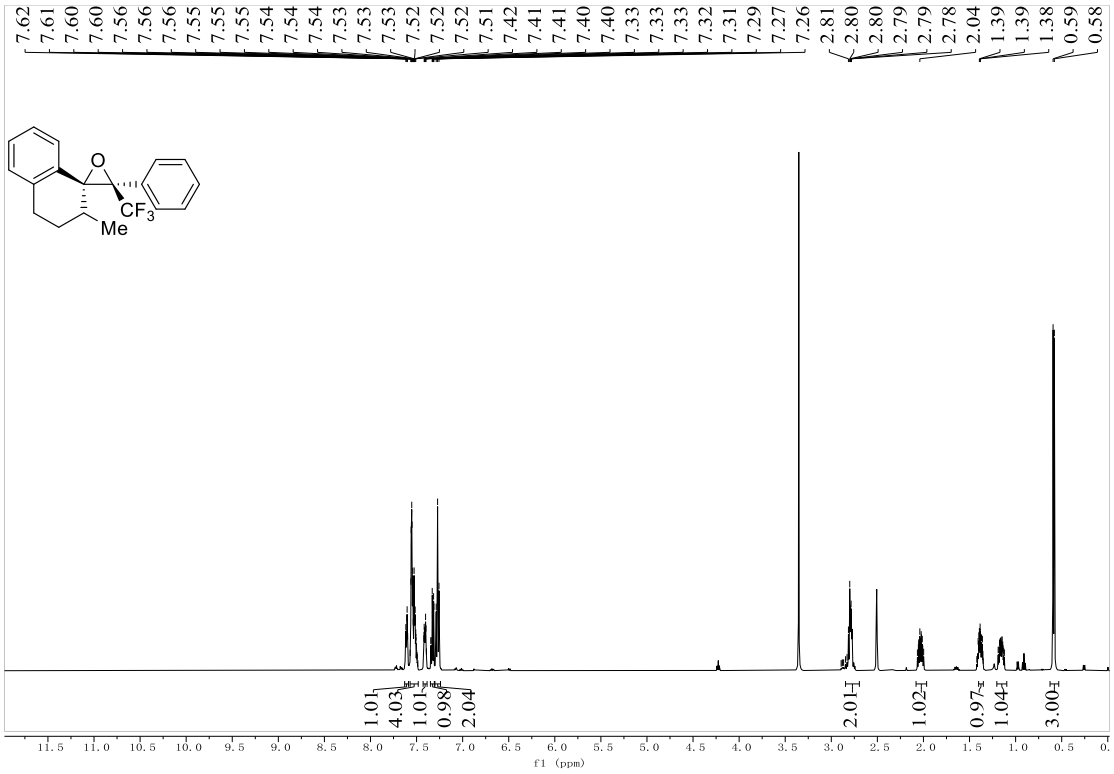


^{13}C NMR spectrum in DMSO-d_6.

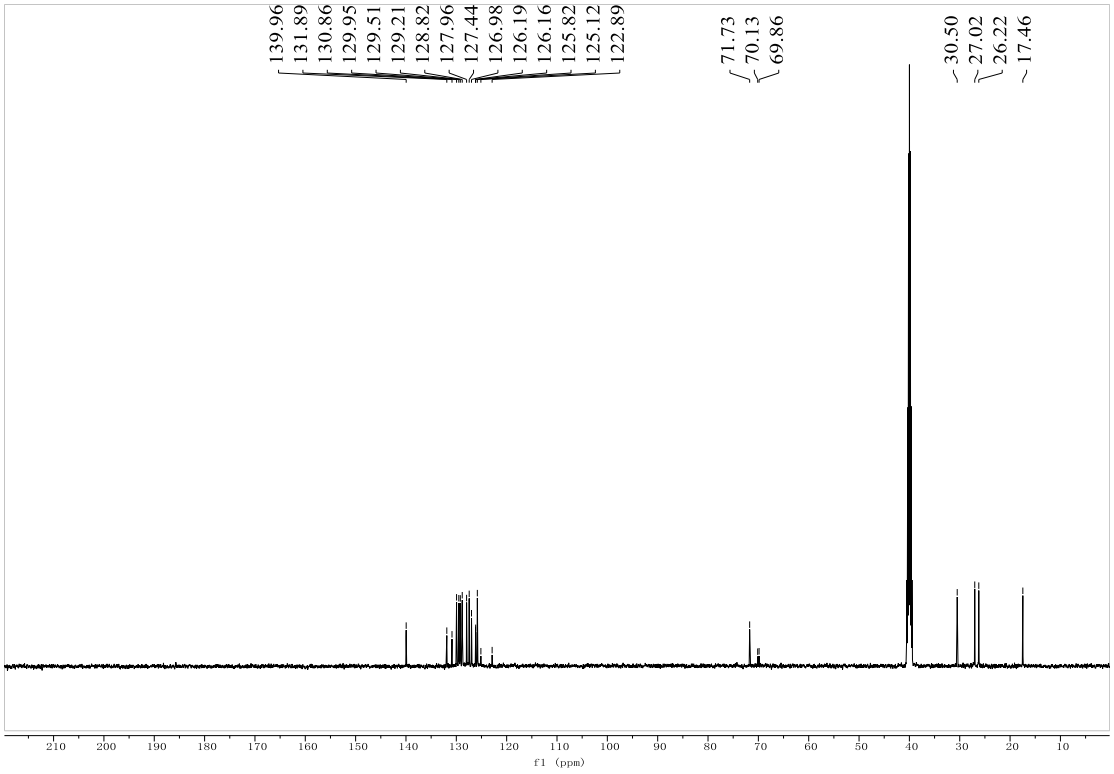


^{19}F NMR spectrum in DMSO-d_6.

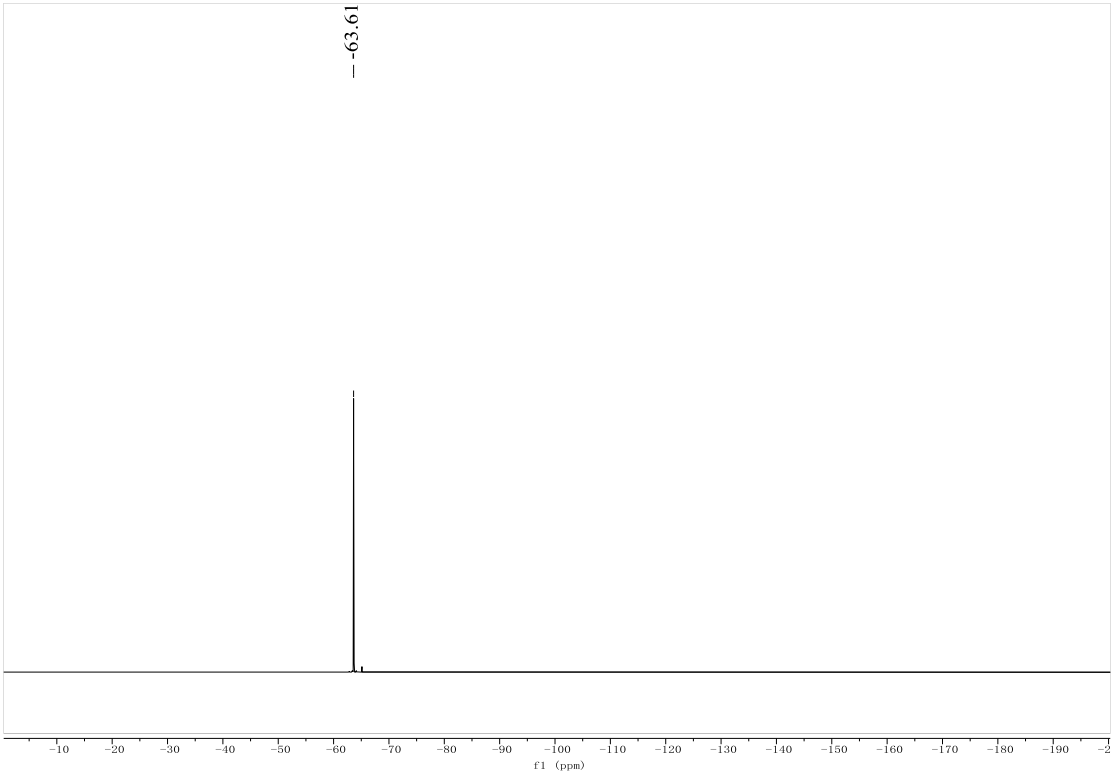
(1*R*,2*S*,3'*R*)-2-methyl-3'-phenyl-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (18c)



^{1}H NMR spectrum in DMSO-d_6.

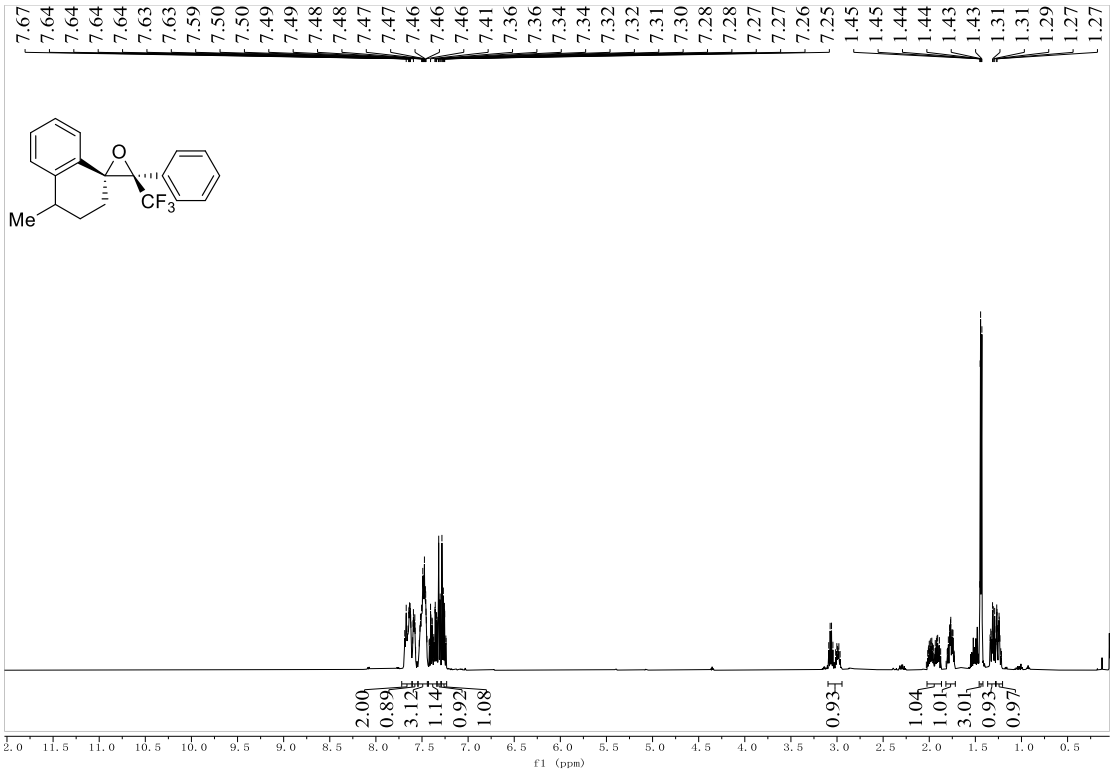


^{13}C NMR spectrum in DMSO-d_6.

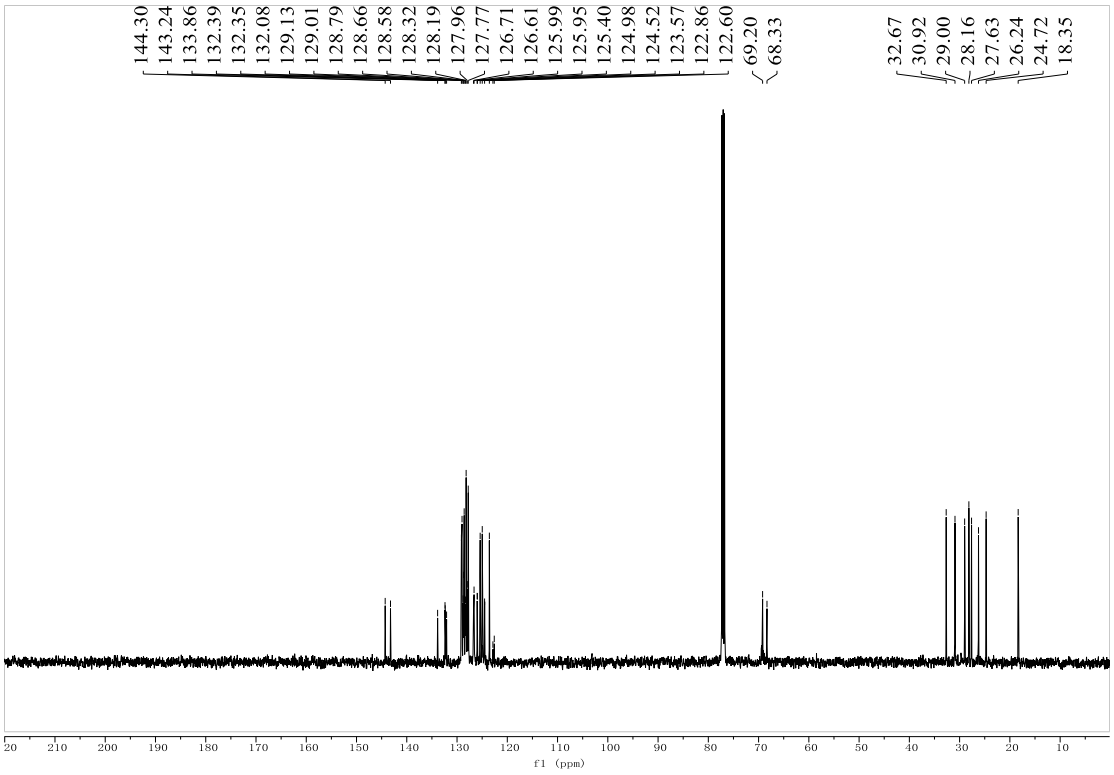


^{19}F NMR spectrum in DMSO-d_6.

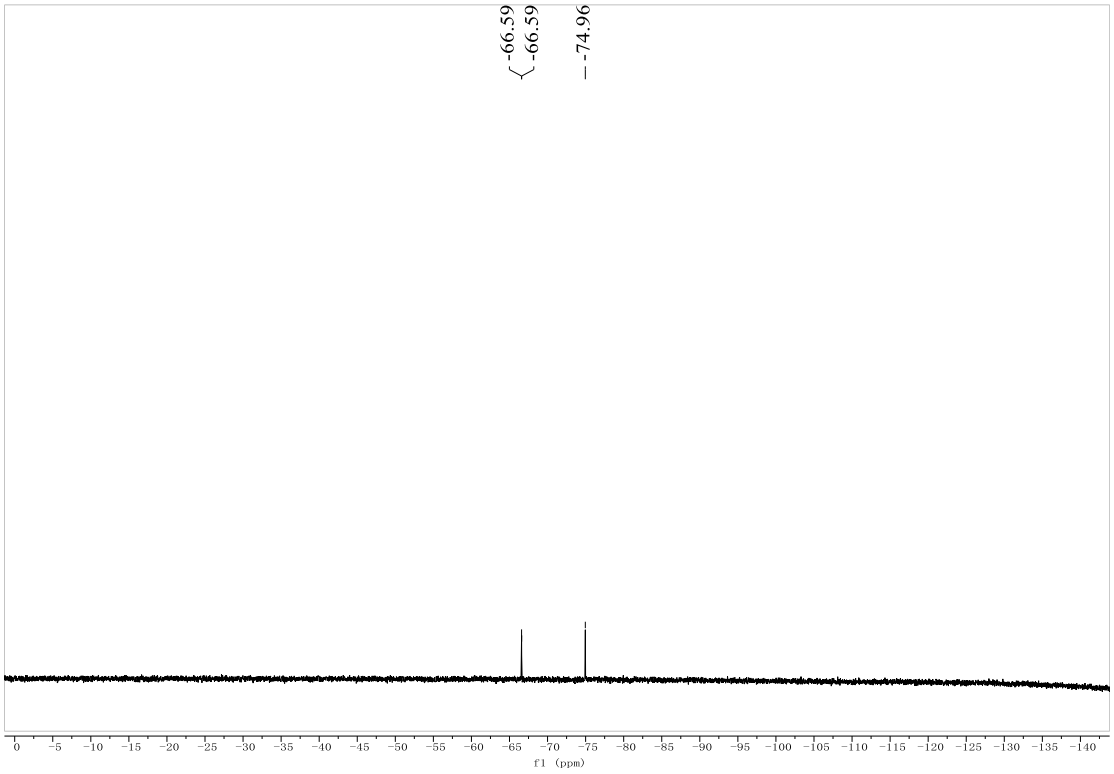
(1*R*,3'*R*)-4-methyl-3'-phenyl-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (19c)



^{1}H NMR spectrum in $CDCl_3$.

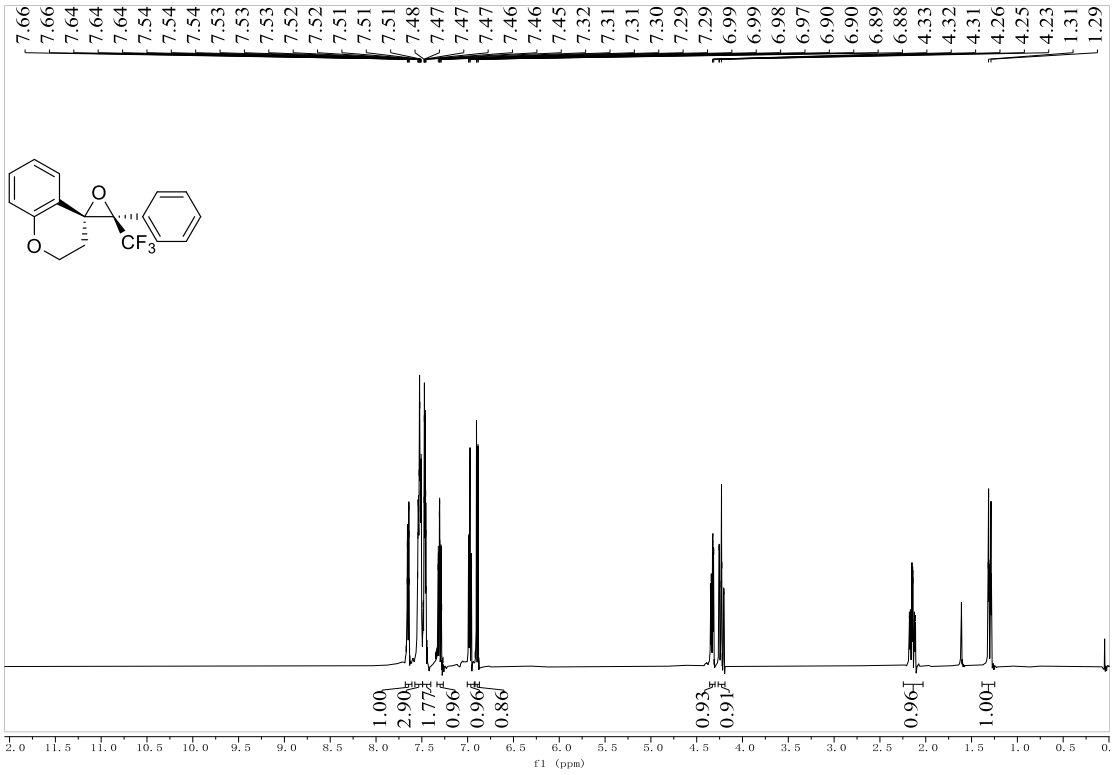


^{13}C NMR spectrum in $CDCl_3$.

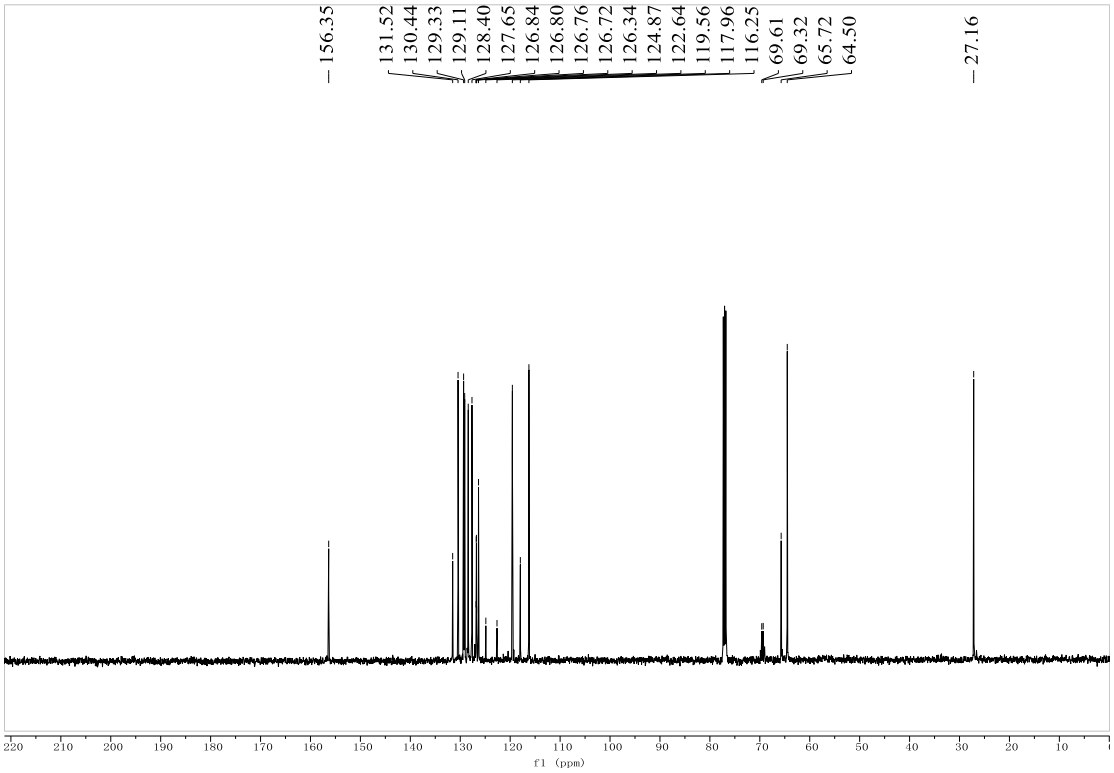


^{19}F NMR spectrum in $CDCl_3$.

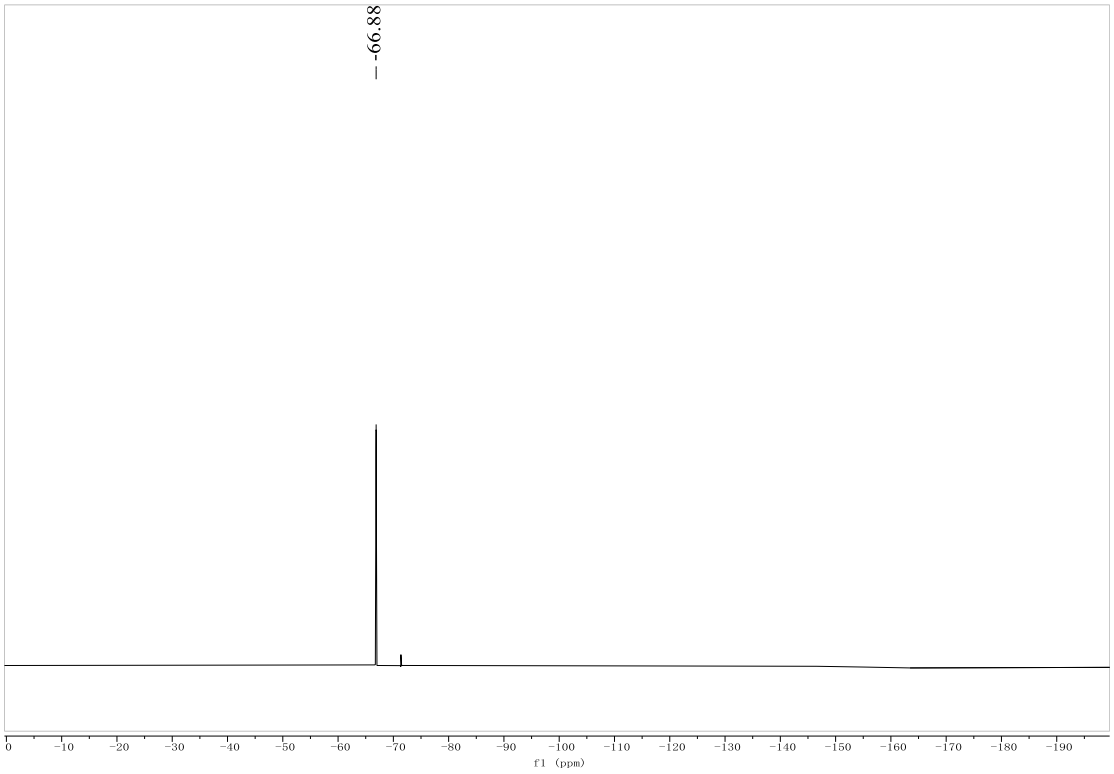
(3'*R*,4*R*)-3'-phenyl-3'-(trifluoromethyl) spiro[chromane-4,2'-oxirane] (20c)



^{1}H NMR spectrum in $CDCl_3$.

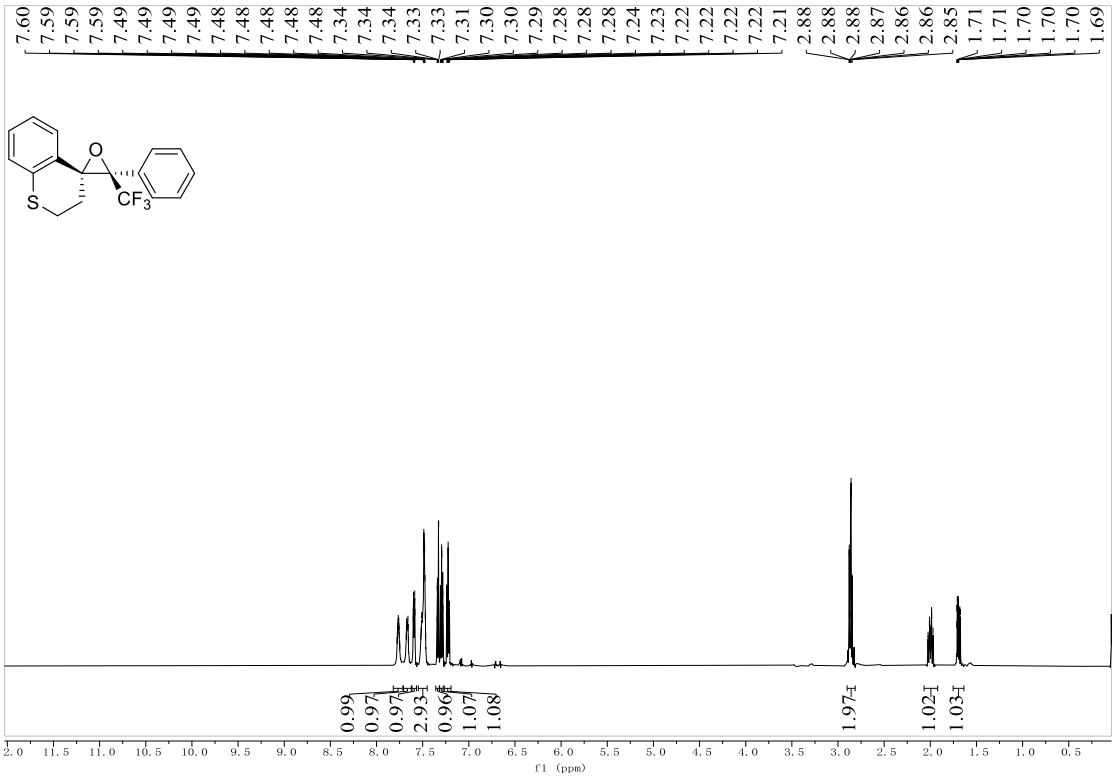


^{13}C NMR spectrum in $CDCl_3$.

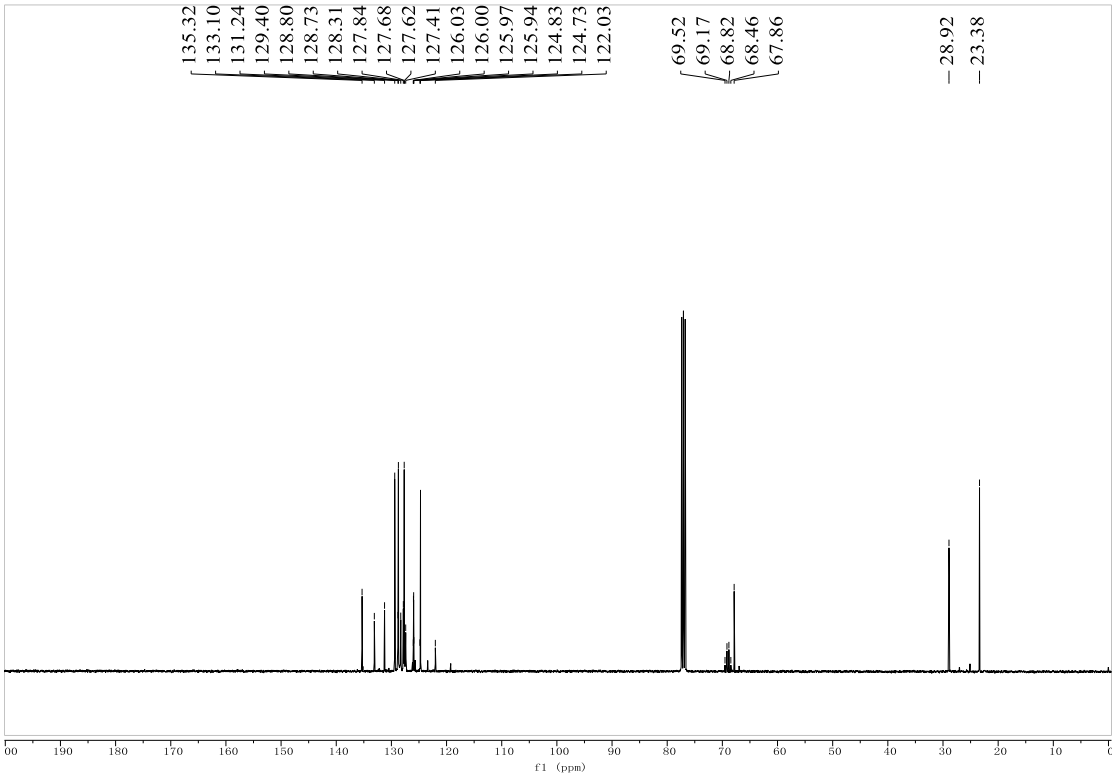


^{19}F NMR spectrum in $CDCl_3$.

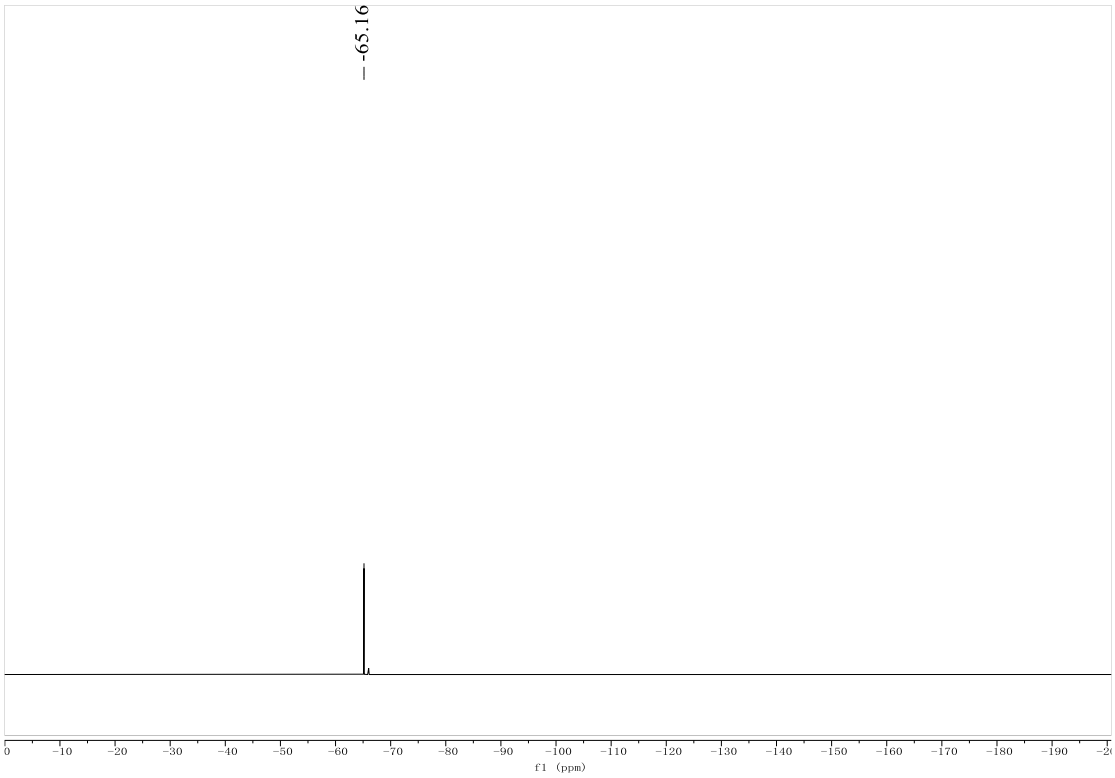
(2*R*,3*R*)-3-phenyl-3-(trifluoromethyl)spiro[oxirane-2,4'-thiochromane](21c)



^{1}H NMR spectrum in $CDCl_3$.

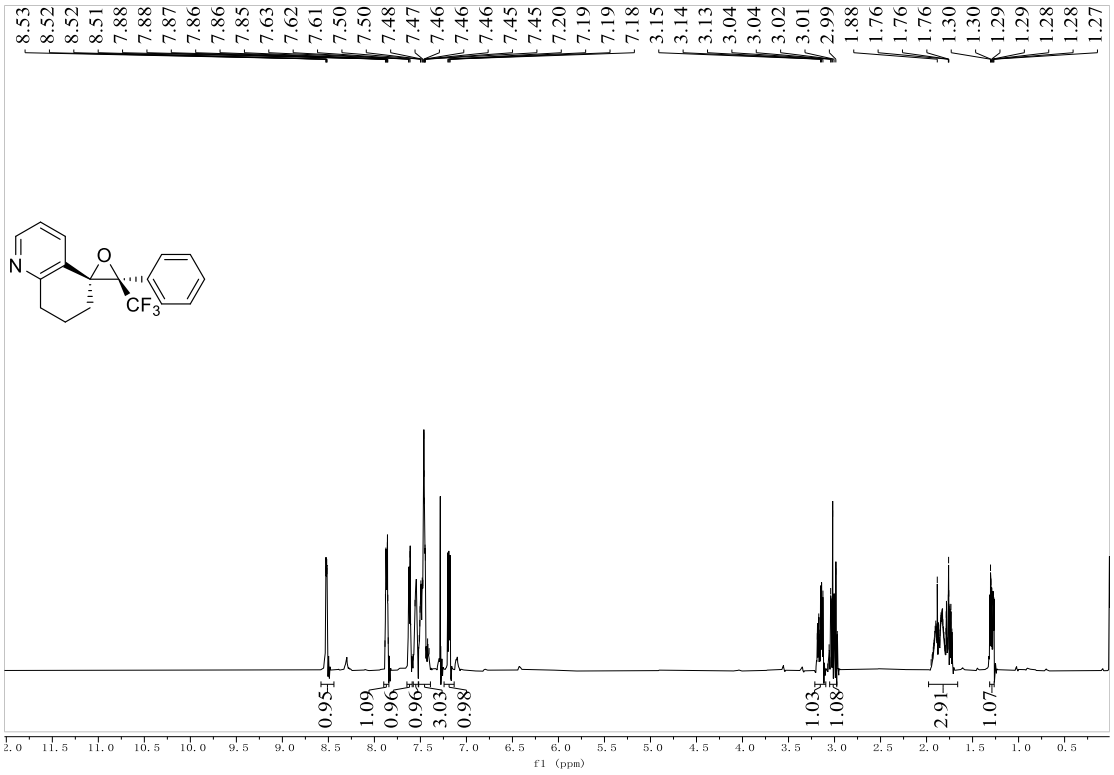


^{13}C NMR spectrum in $CDCl_3$.

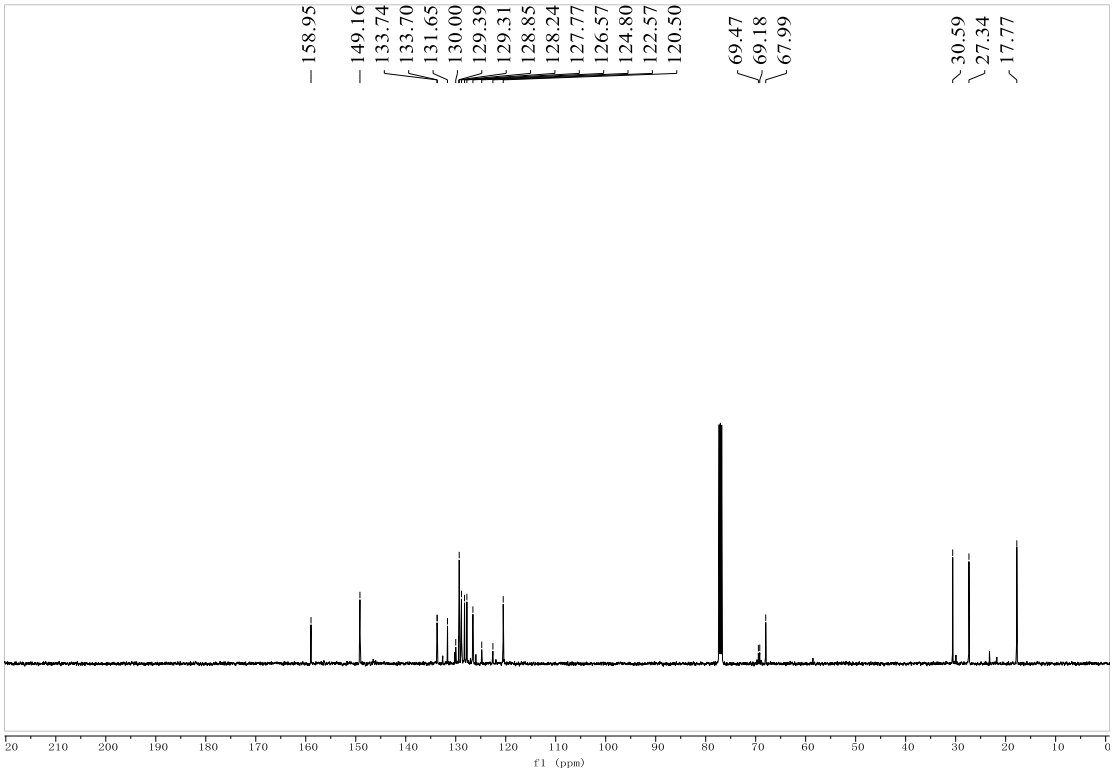


^{19}F NMR spectrum in $CDCl_3$.

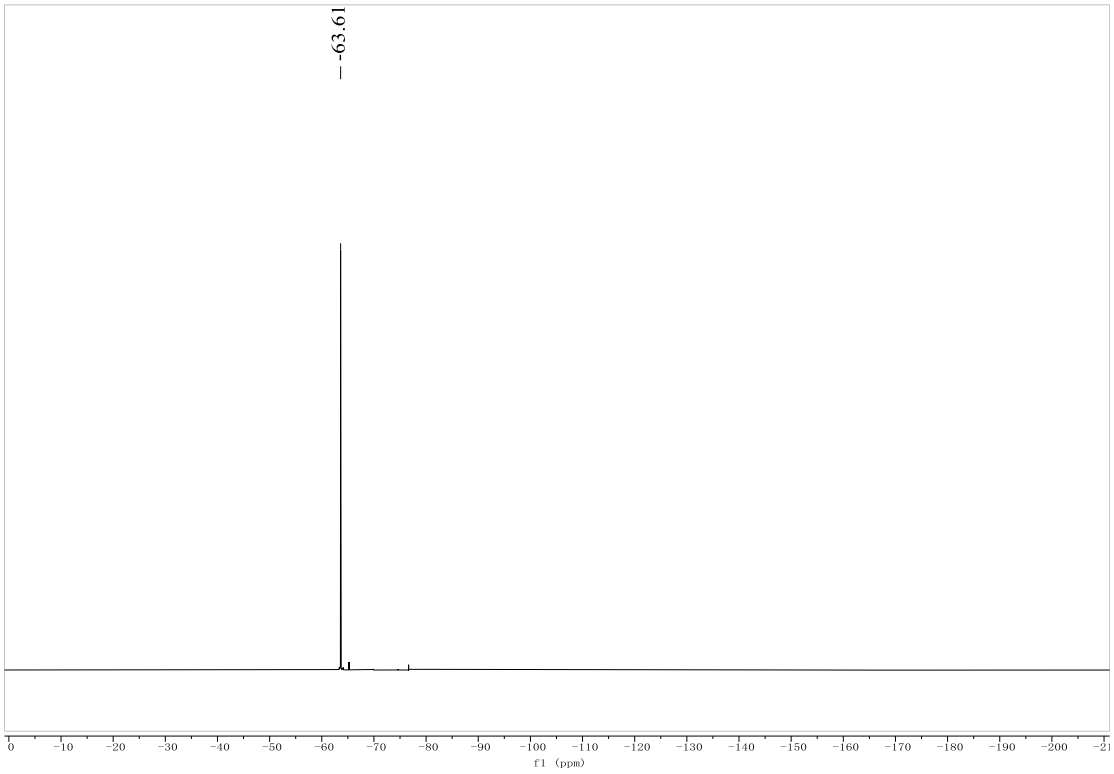
(2*R*,3*R*)-3-phenyl-3-(trifluoromethyl)-7',8'-dihydro-6'*H*-spiro[oxirane-2,5'-quinoline] (22c)



^{1}H NMR spectrum in $CDCl_3$.

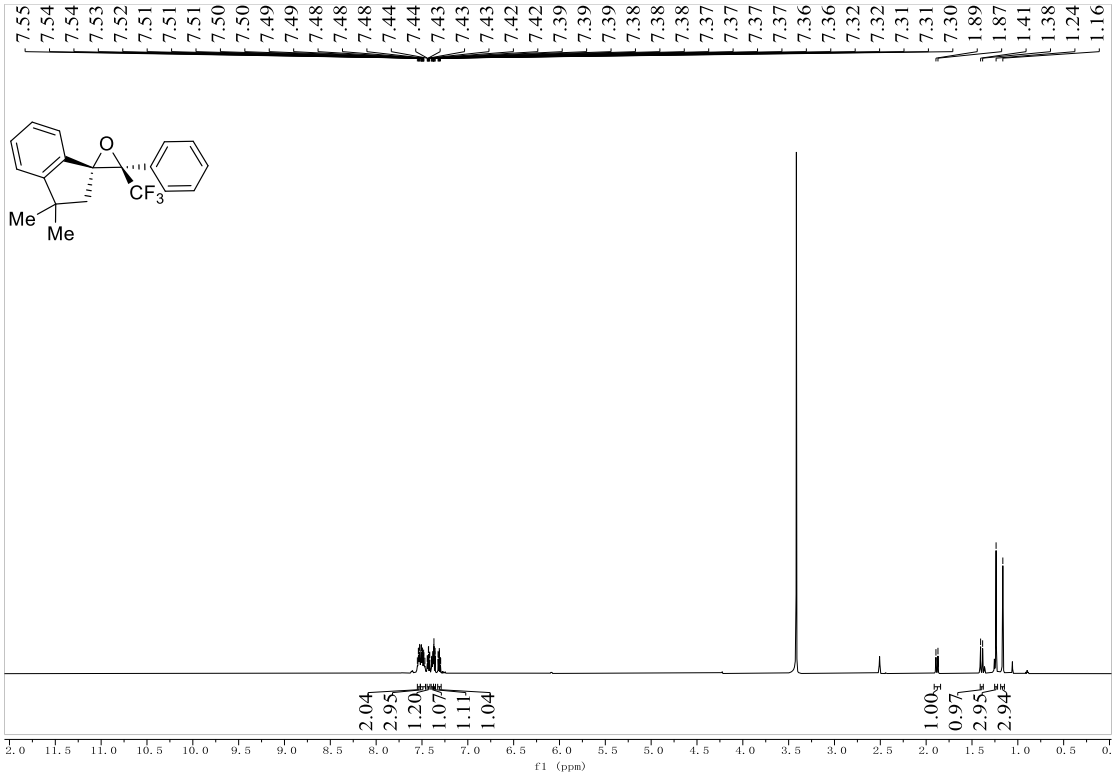


^{13}C NMR spectrum in $CDCl_3$.

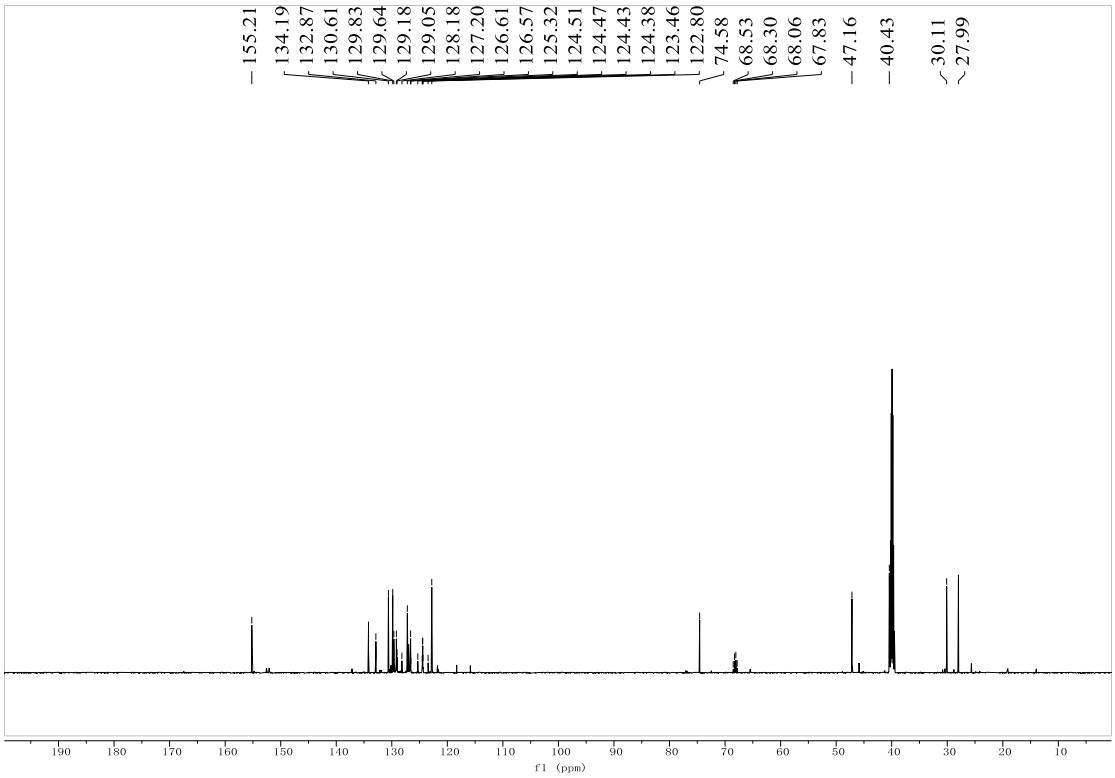


^{19}F NMR spectrum in $CDCl_3$.

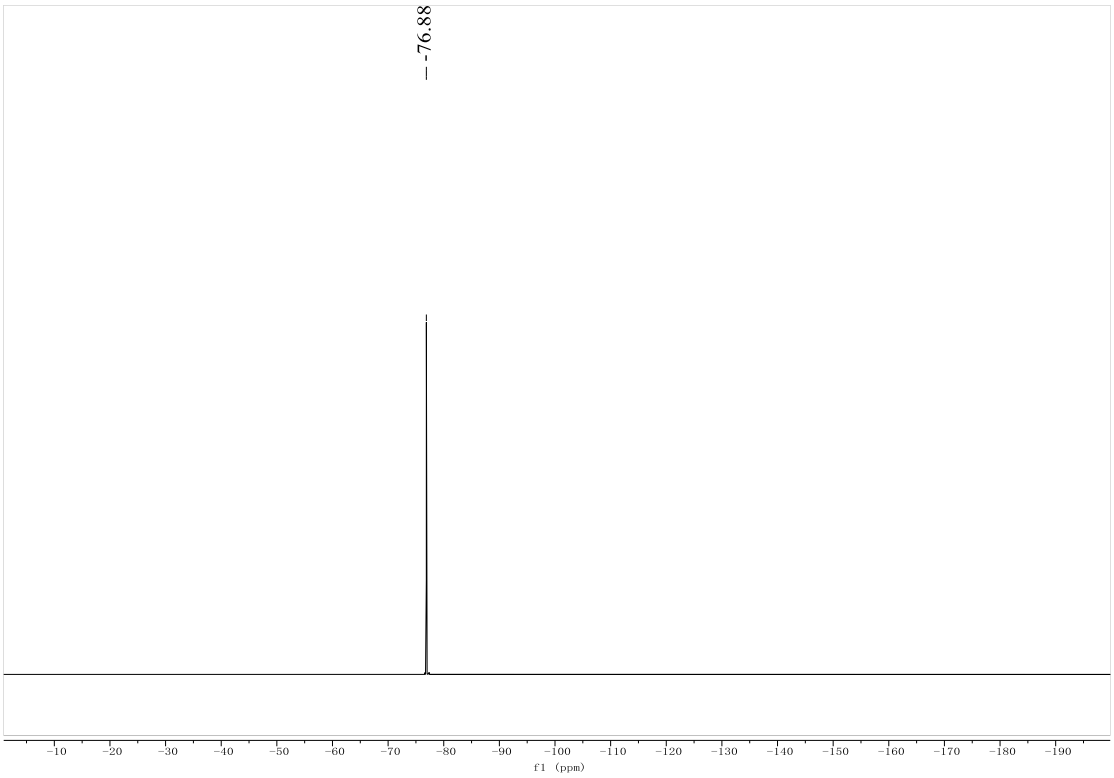
(1*R*,3'*R*)-3,3-dimethyl-3'-phenyl-3'-(trifluoromethyl)-2,3-dihydrospiro[indene-1,2'-oxirane] (23c)



^{1}H NMR spectrum in DMSO-d_6.

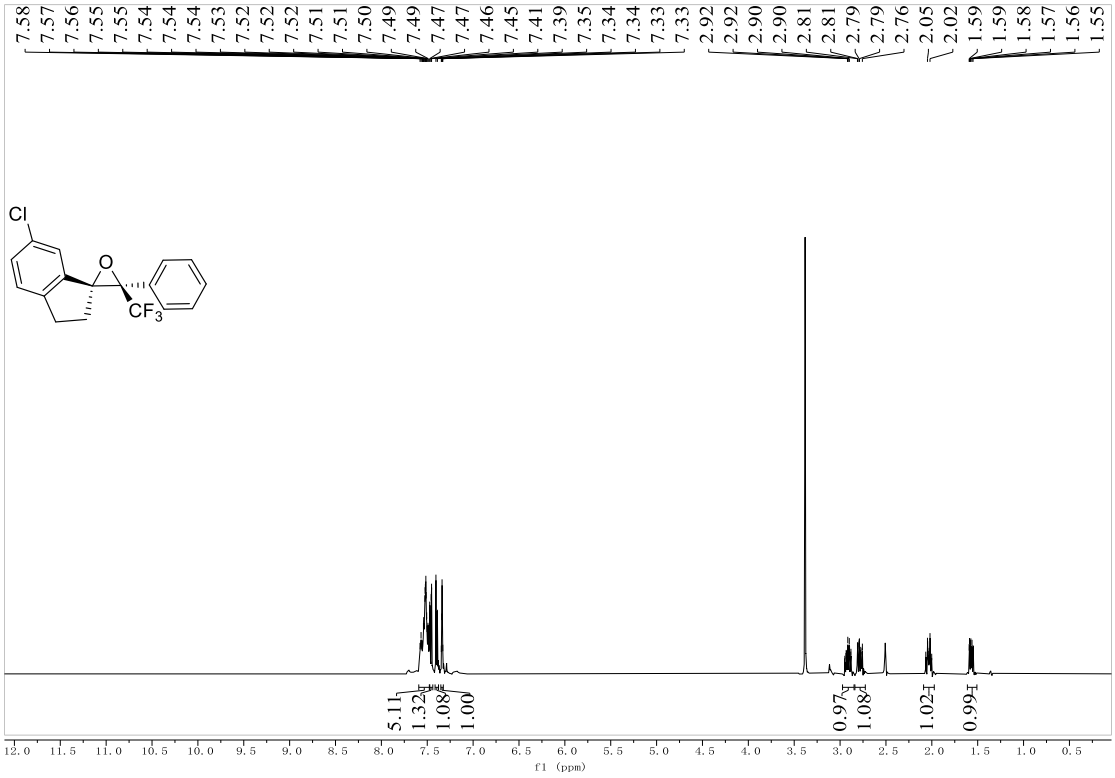


^{13}C NMR spectrum in DMSO-d_6.

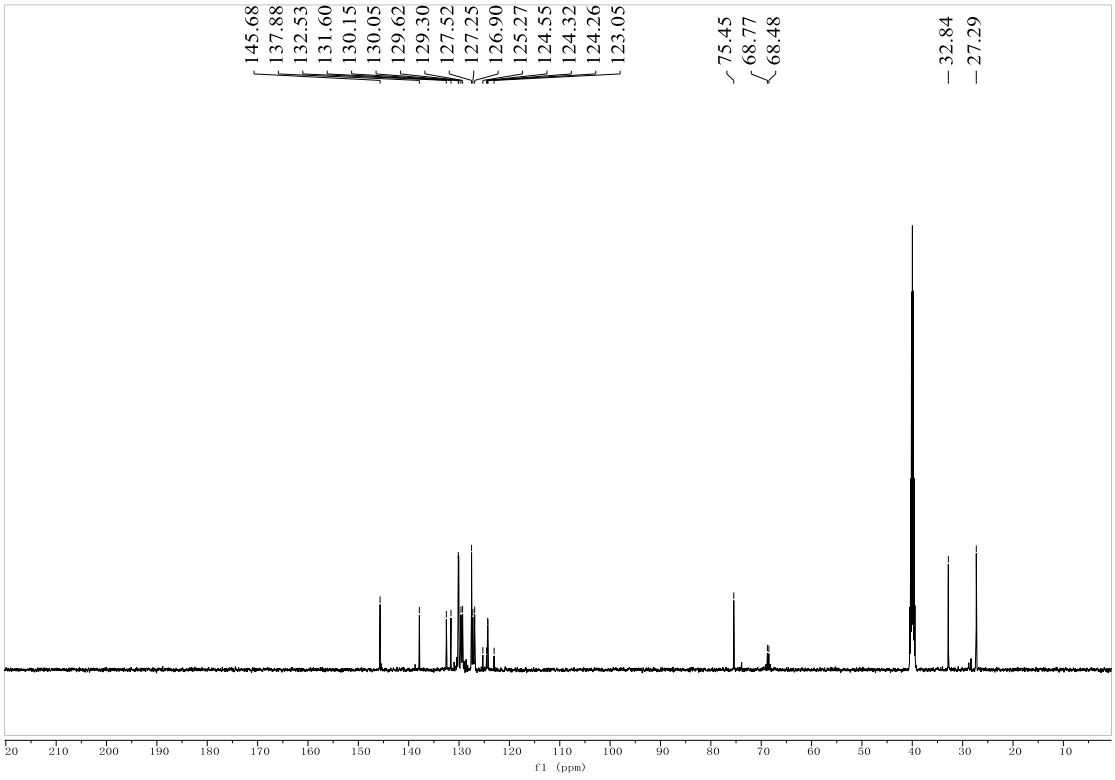


^{19}F NMR spectrum in $CDCl_3$.

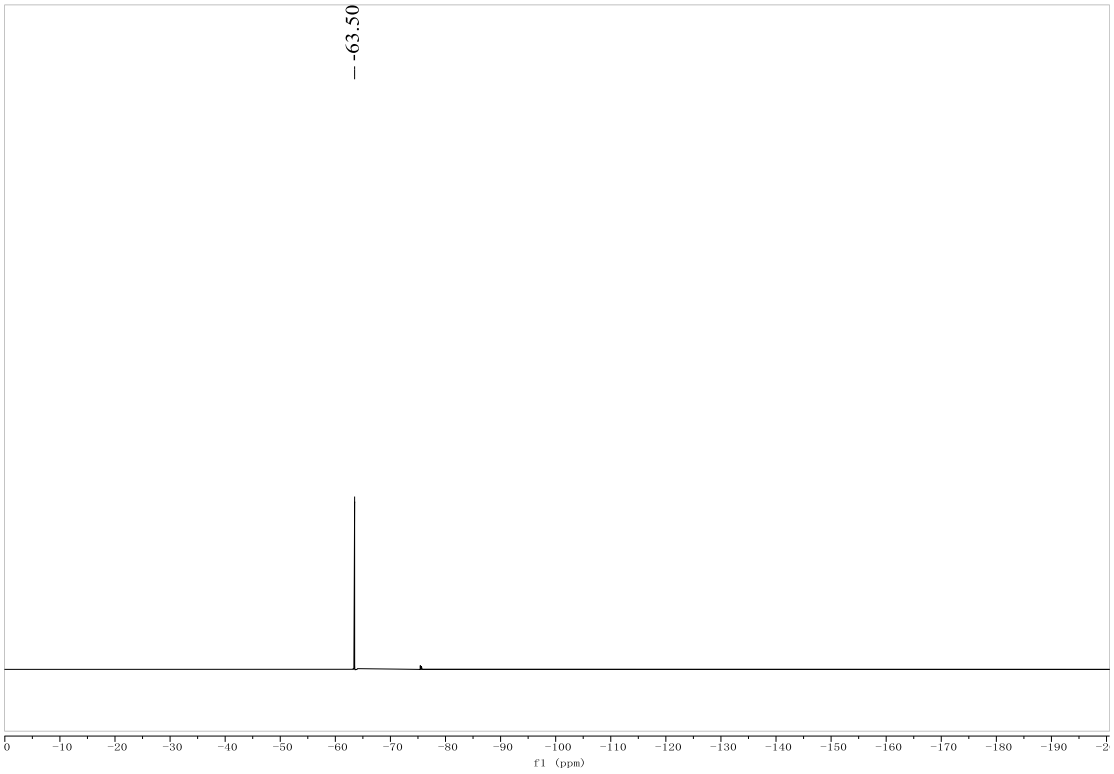
(1*R*,3'*R*)-6-chloro-3'-phenyl-3'-(trifluoromethyl)-2,3-dihydrospiro[indene-1,2'-oxirane] (24c)



^{1}H NMR spectrum in DMSO-d_6.

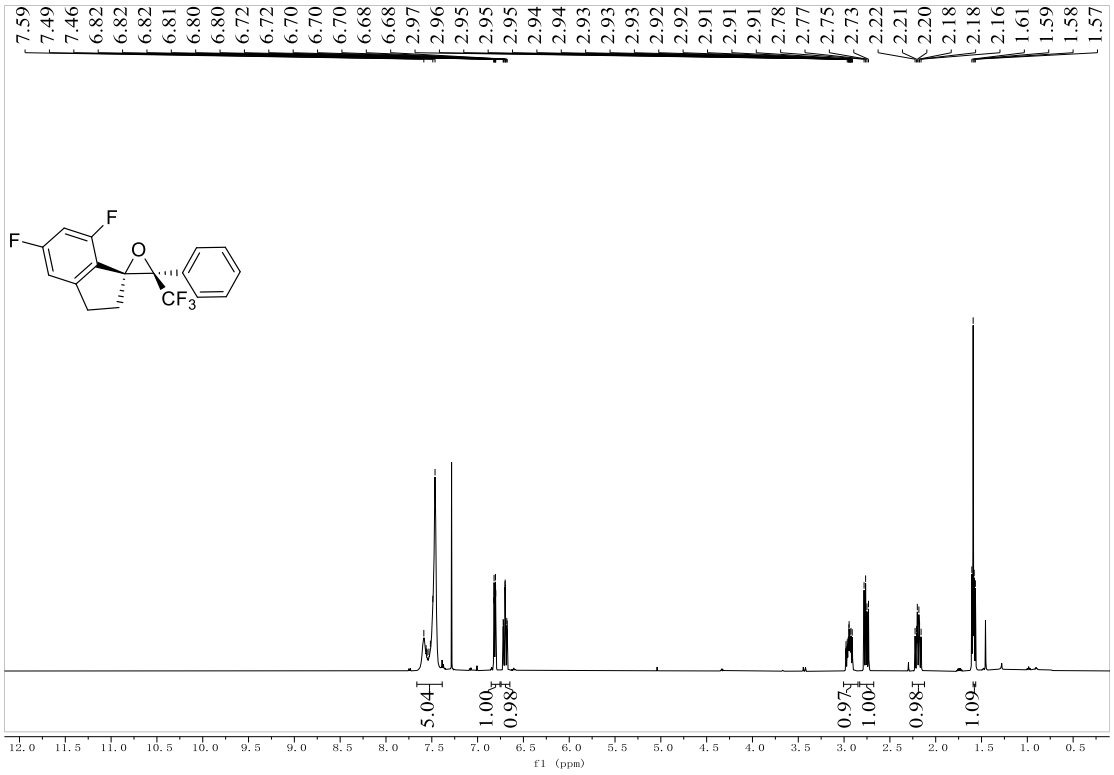


^{13}C NMR spectrum in DMSO-d_6.

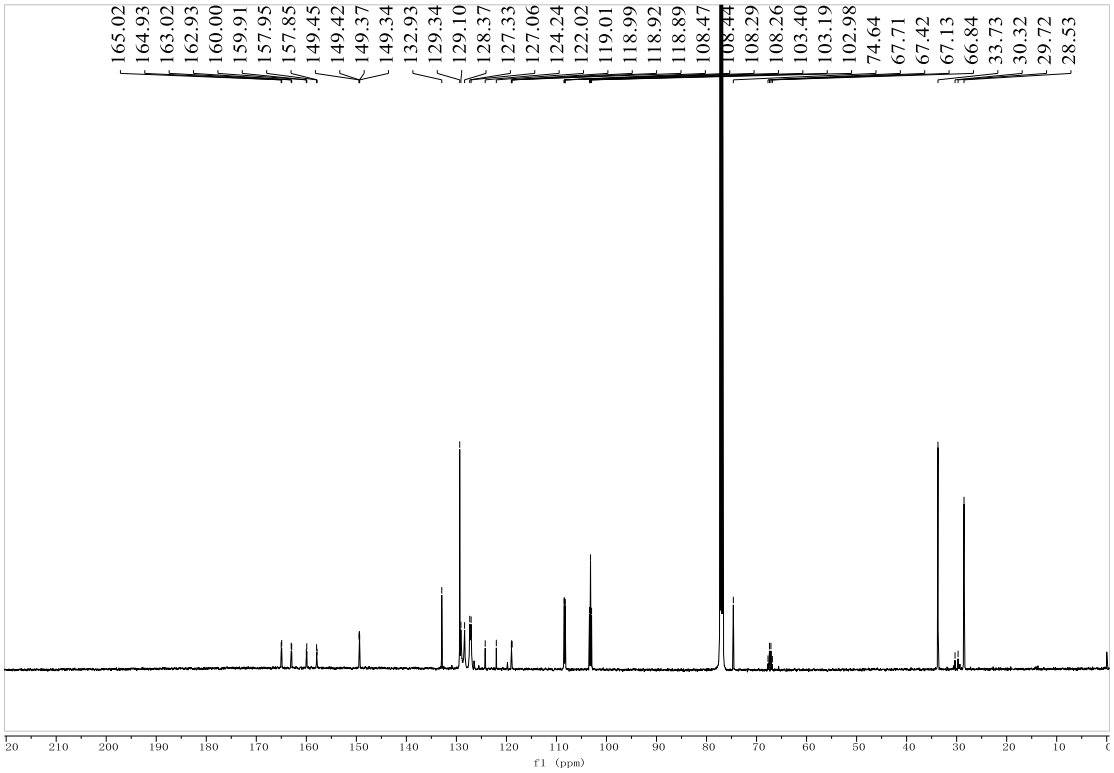


^{19}F NMR spectrum in DMSO-d_6.

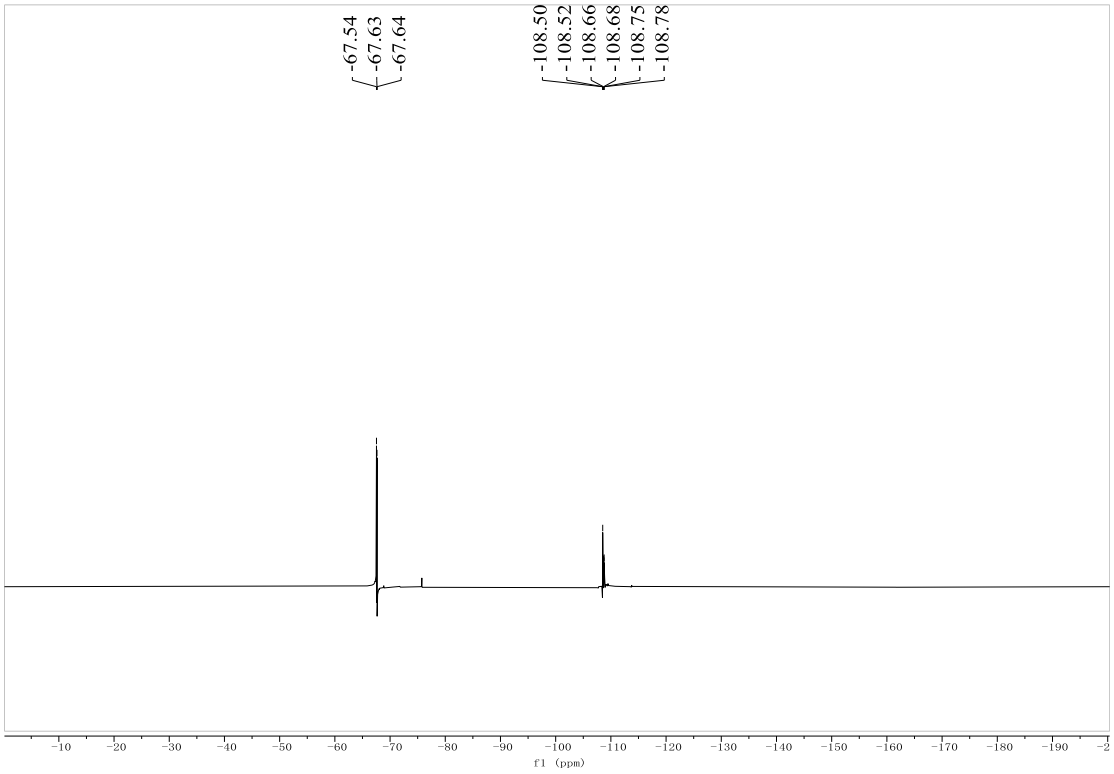
(1*R*,3'*R*)-5,7-difluoro-3'-phenyl-3'-(trifluoromethyl)-2,3-dihydrospiro[indene-1,2'-oxirane] (25c)



^{1}H NMR spectrum in $CDCl_3$.

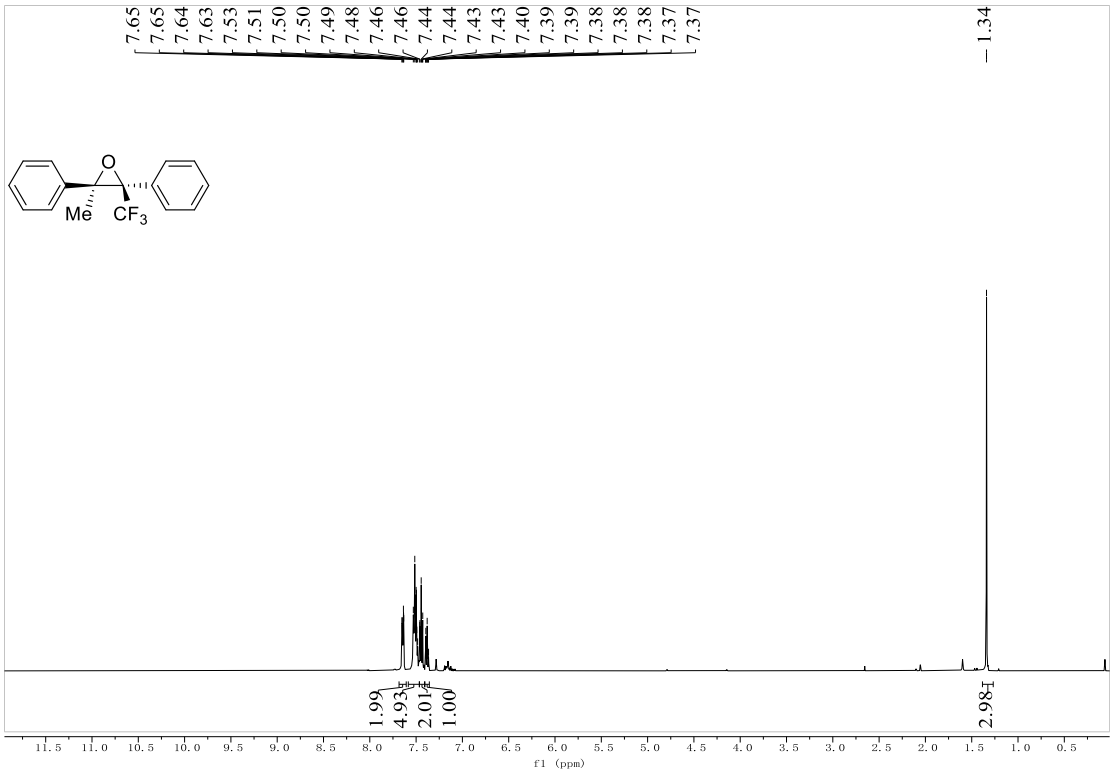


^{13}C NMR spectrum in $CDCl_3$.

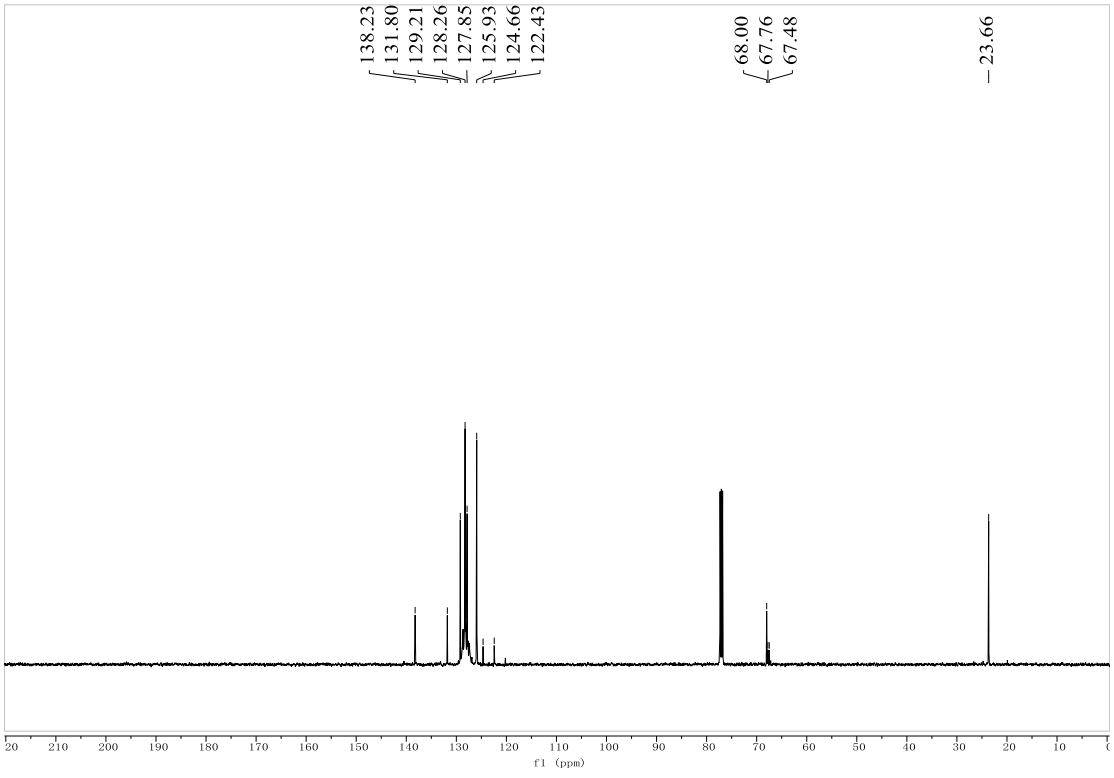


^{19}F NMR spectrum in $CDCl_3$.

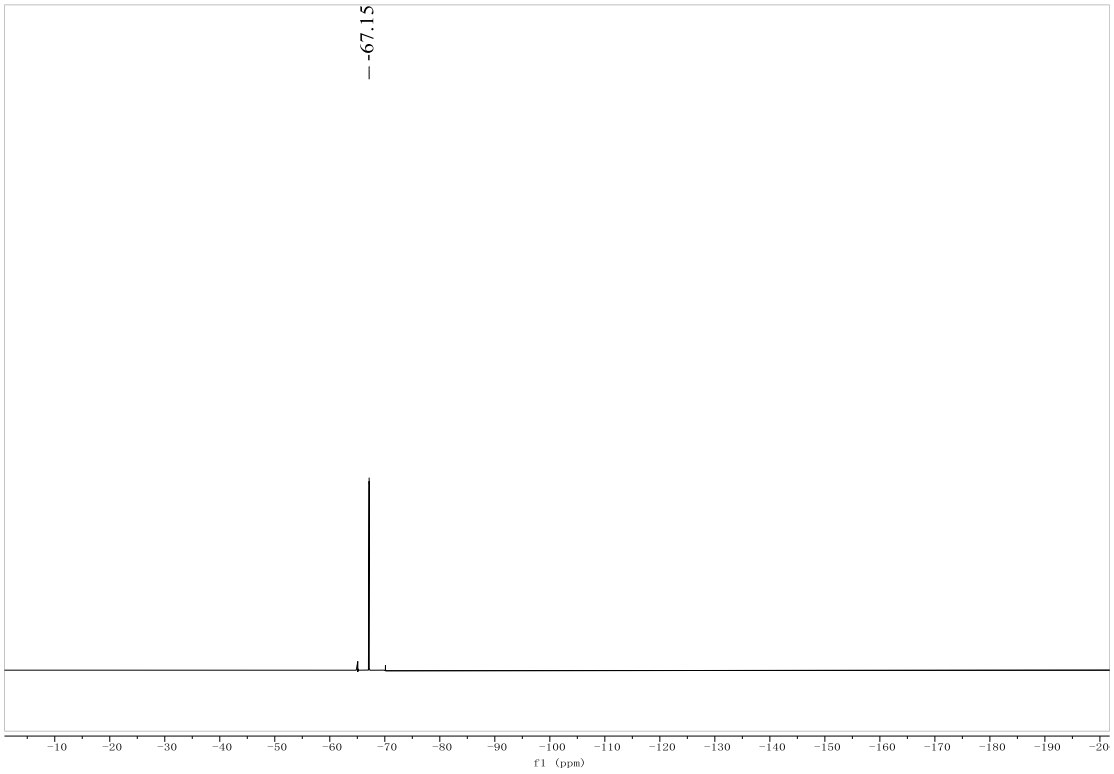
(2*R*,3*R*)-2-methyl-2,3-diphenyl-3-(trifluoromethyl)oxirane (26c)



^{1}H NMR spectrum in $CDCl_3$.

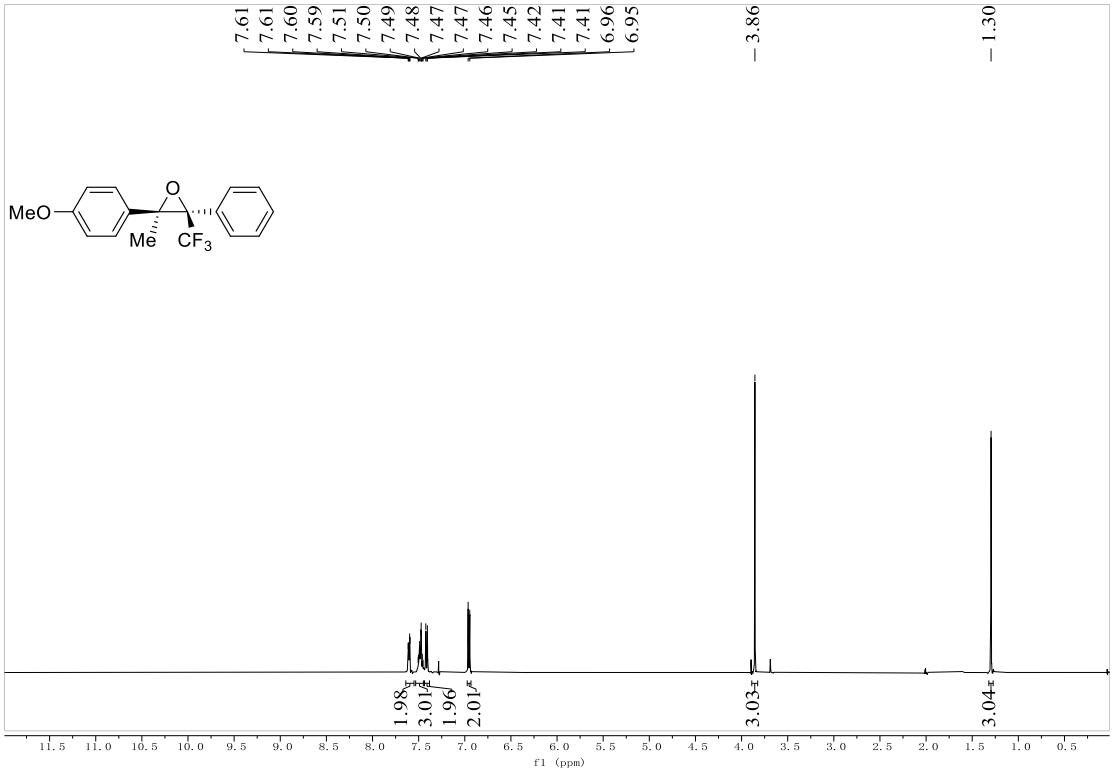


^{13}C NMR spectrum in $CDCl_3$.

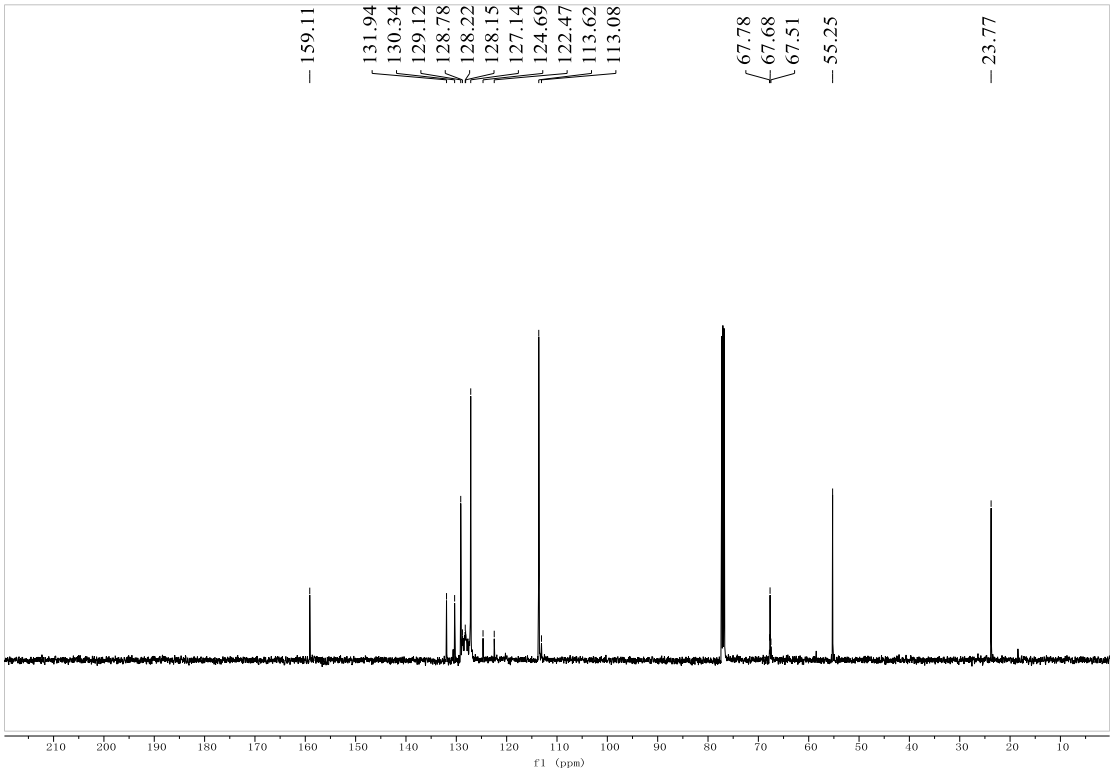


^{19}F NMR spectrum in $CDCl_3$.

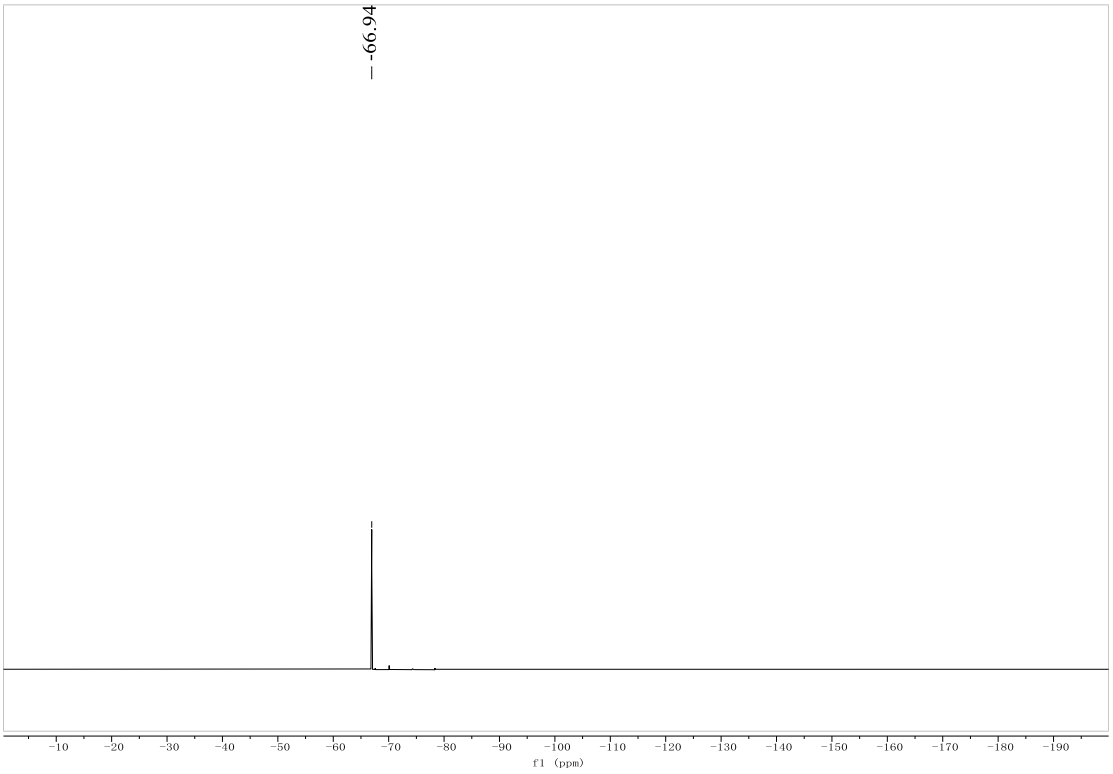
(2*R*,3*R*)-2-(4-methoxyphenyl)-2-methyl-3-phenyl-3-(trifluoromethyl) oxirane (27c)



^{1}H NMR spectrum in $CDCl_3$.

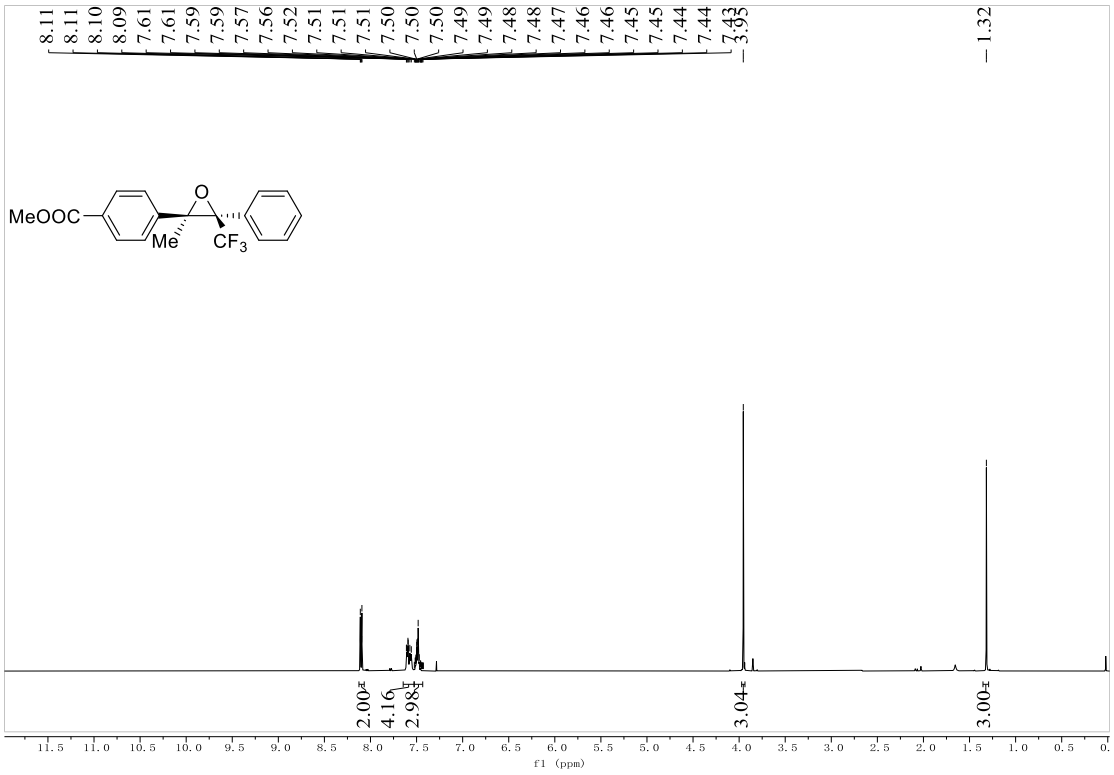


^{13}C NMR spectrum in $CDCl_3$.

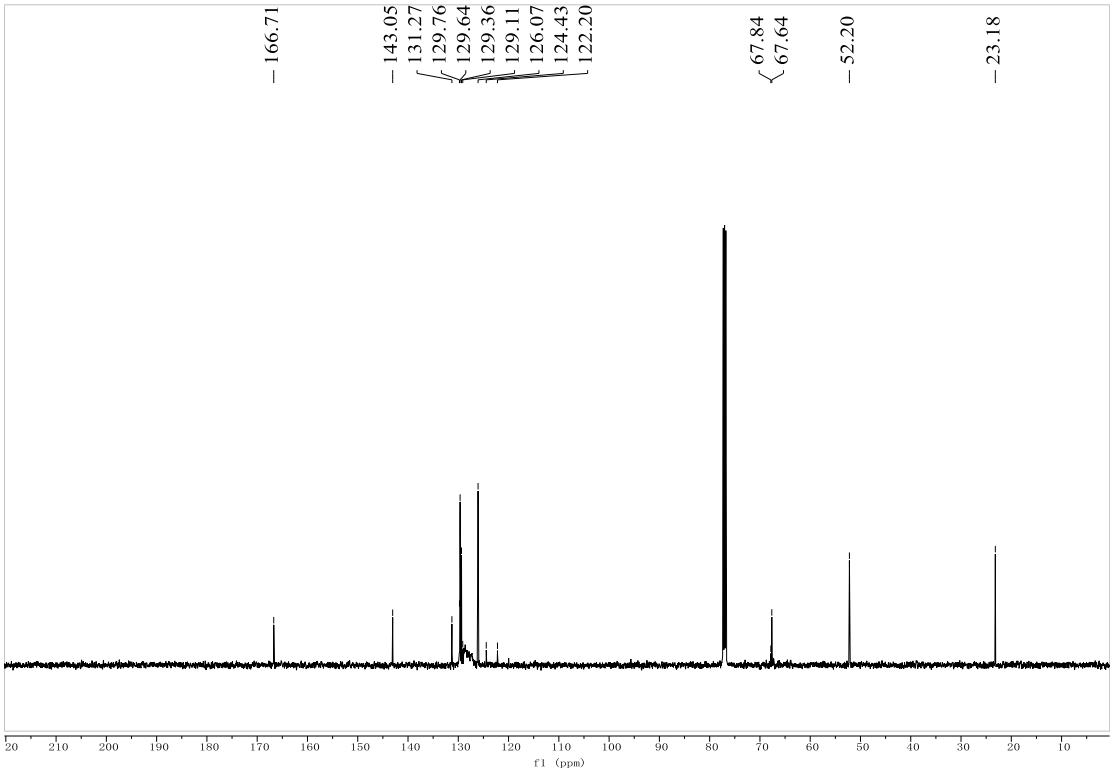


^{19}F NMR spectrum in $CDCl_3$.

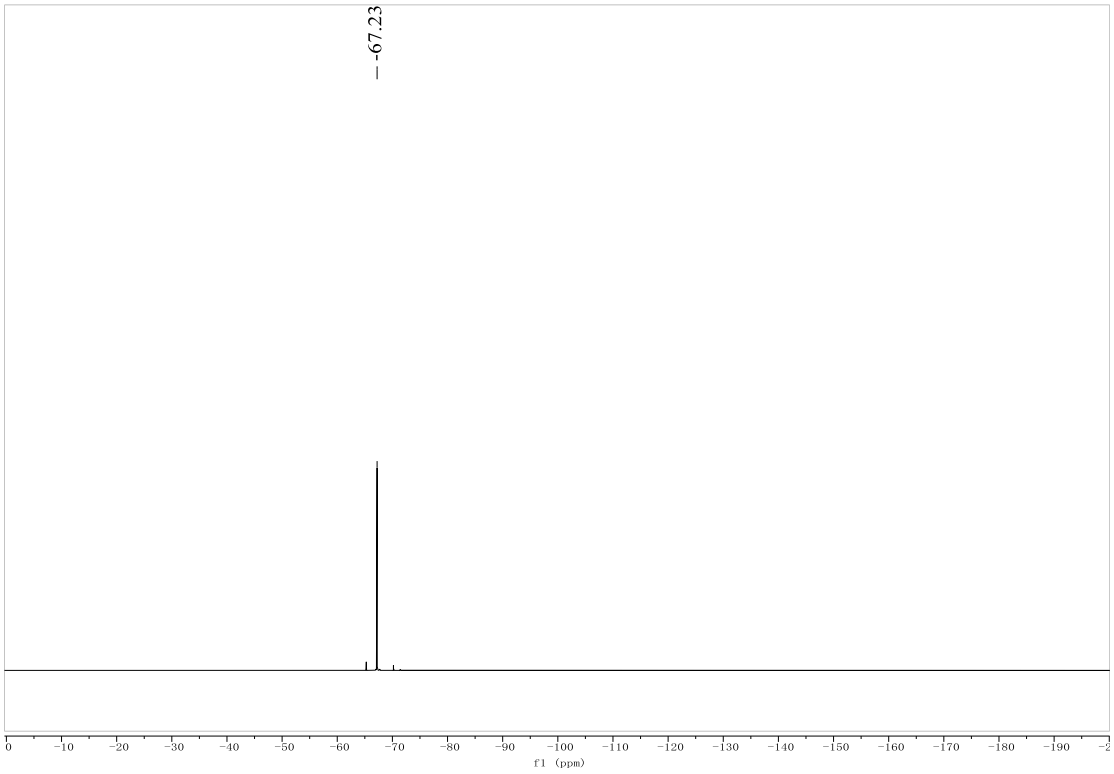
methyl 4-((2*R*,3*R*)-2-methyl-3-phenyl-3-(trifluoromethyl) oxiran-2-yl) benzoate (28c)



^{1}H NMR spectrum in $CDCl_3$.

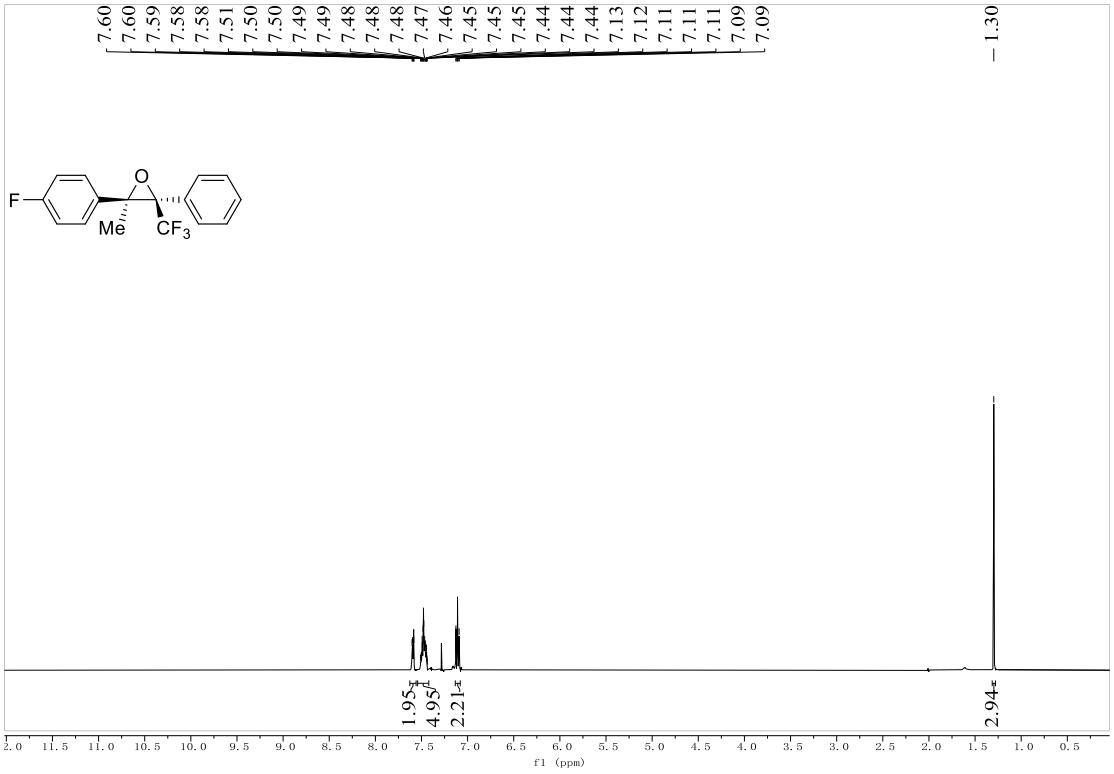


^{13}C NMR spectrum in $CDCl_3$.

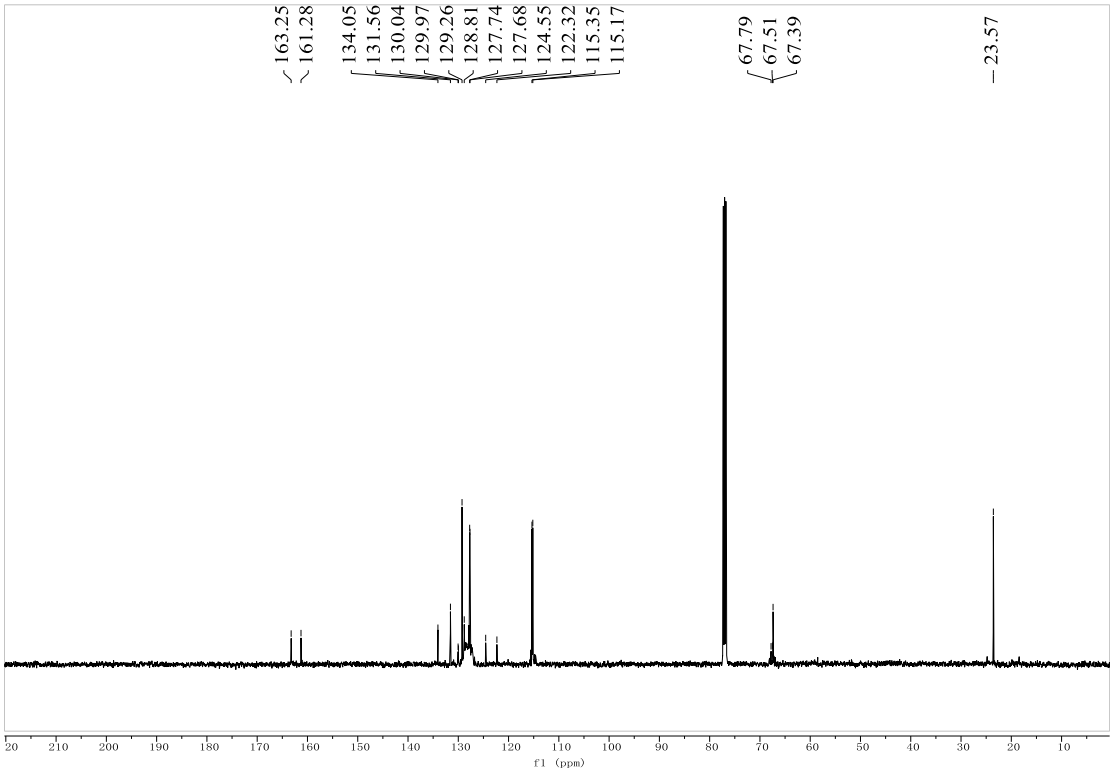


^{19}F NMR spectrum in $CDCl_3$.

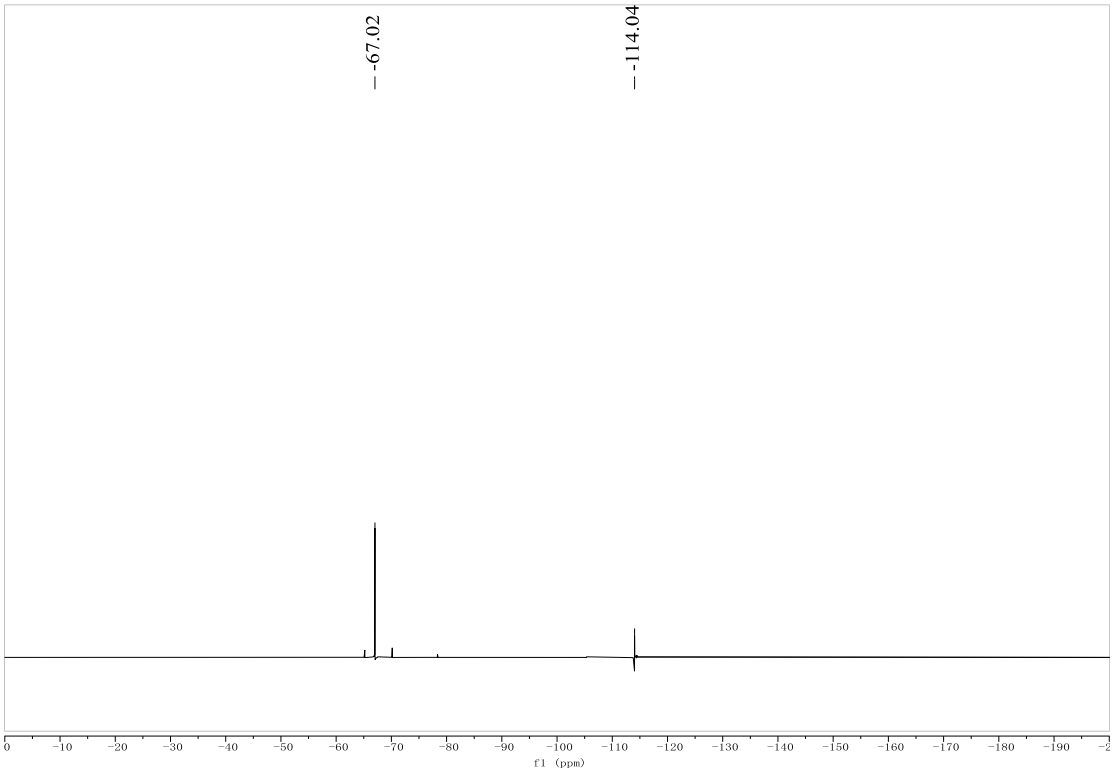
(2*R*,3*R*)-2-(4-fluorophenyl)-2-methyl-3-phenyl-3-(trifluoromethyl) oxirane (29c)



^{1}H NMR spectrum in $CDCl_3$.

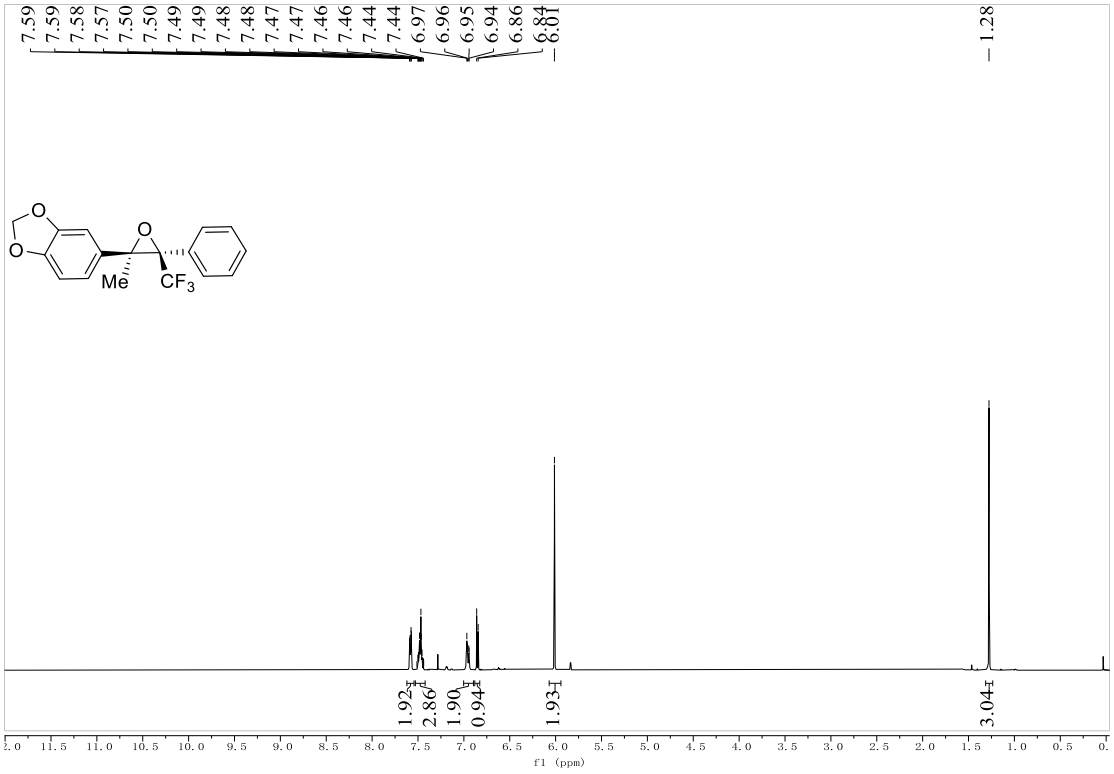


^{13}C NMR spectrum in $CDCl_3$.

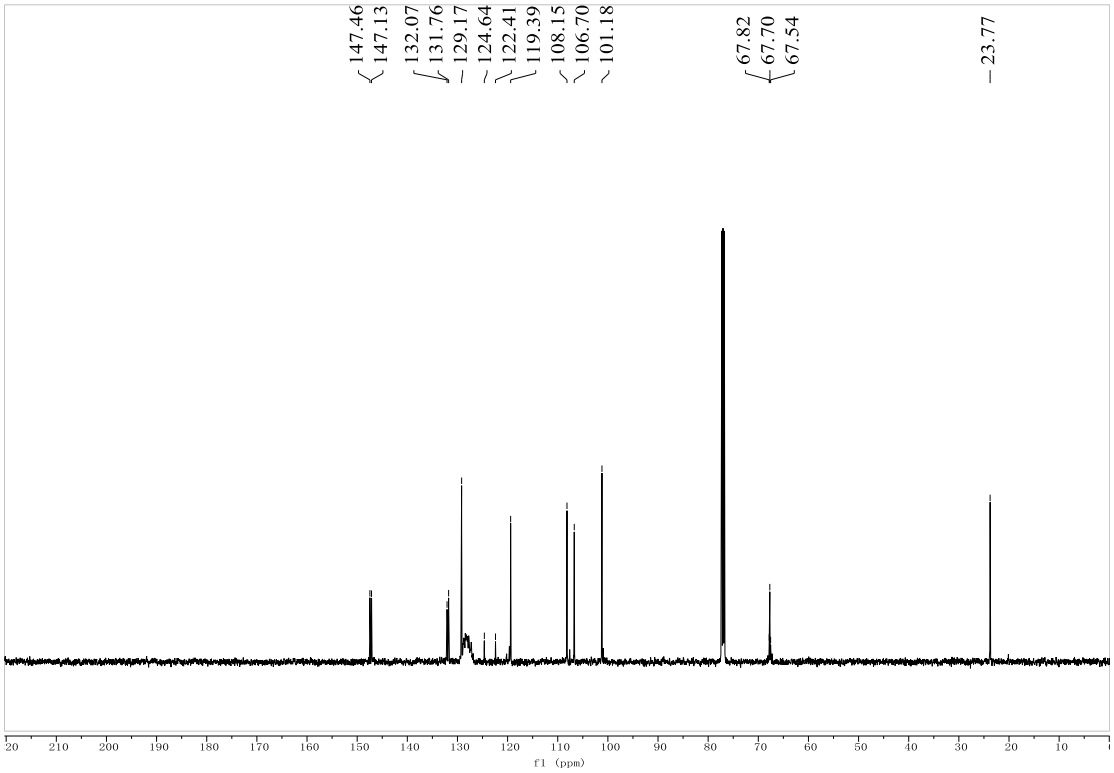


^{19}F NMR spectrum in $CDCl_3$.

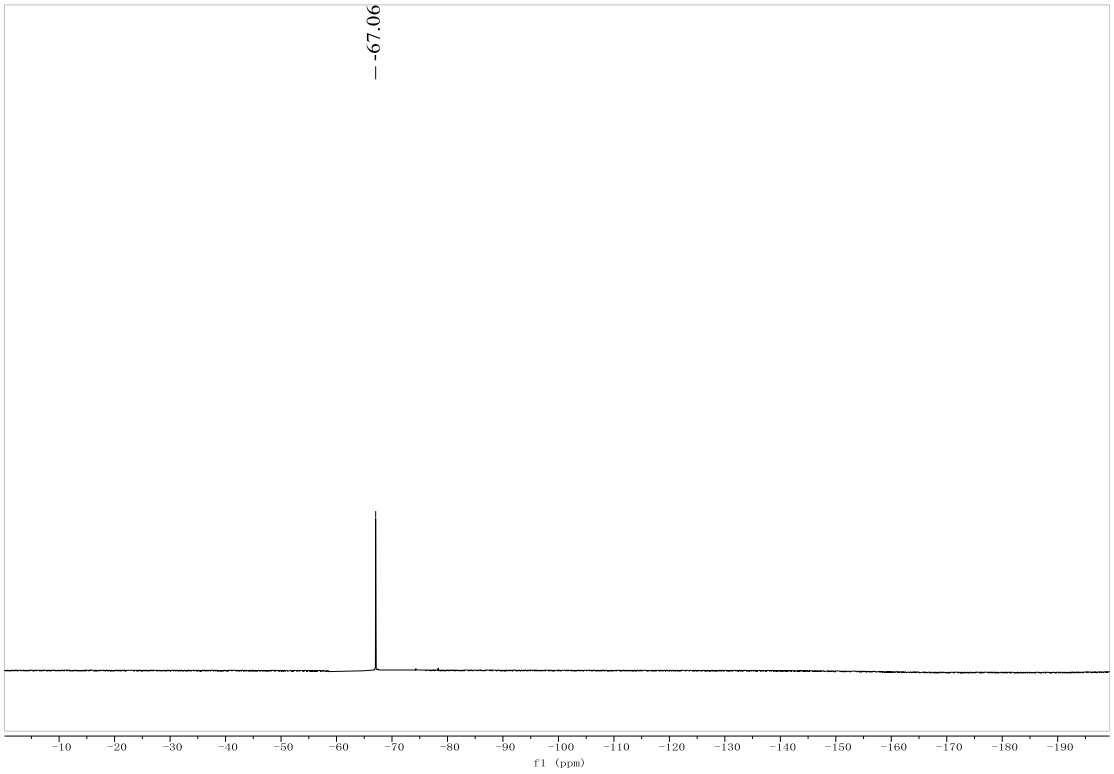
5-((2*R*,3*R*)-2-methyl-3-phenyl-3-(trifluoromethyl) oxiran-2-yl) benzo[*d*] [1,3] dioxole (30c)



^{1}H NMR spectrum in $CDCl_3$.

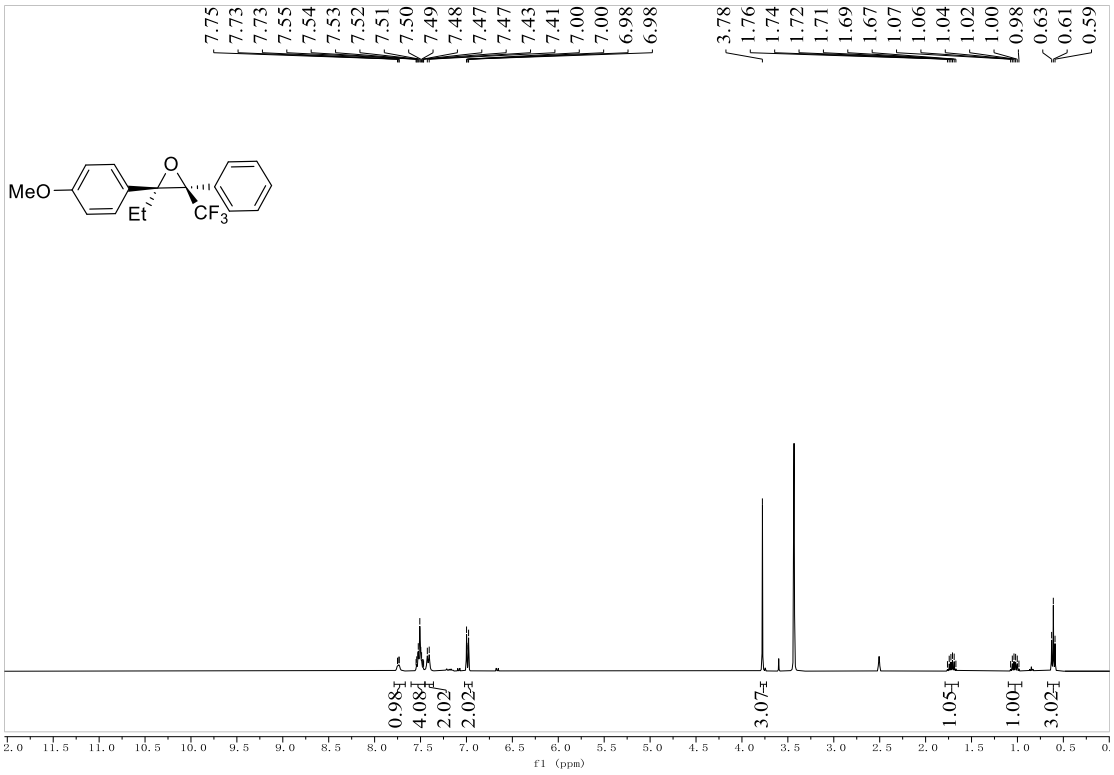


^{13}C NMR spectrum in $CDCl_3$.

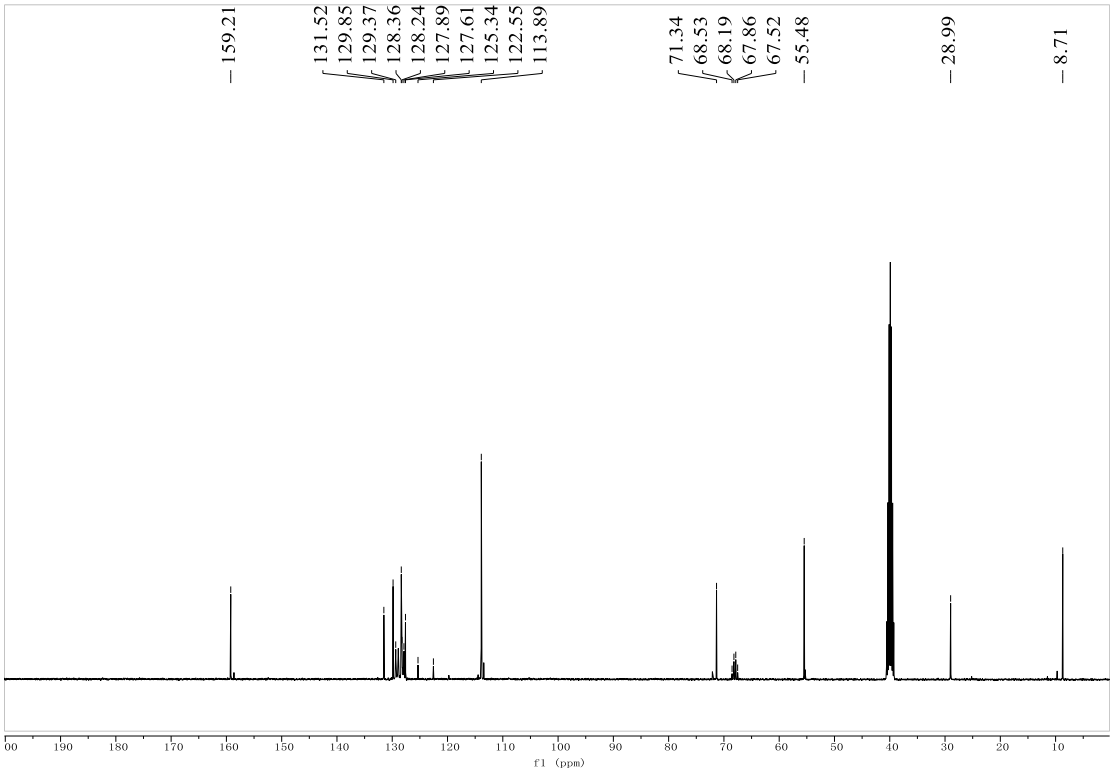


^{19}F NMR spectrum in $CDCl_3$.

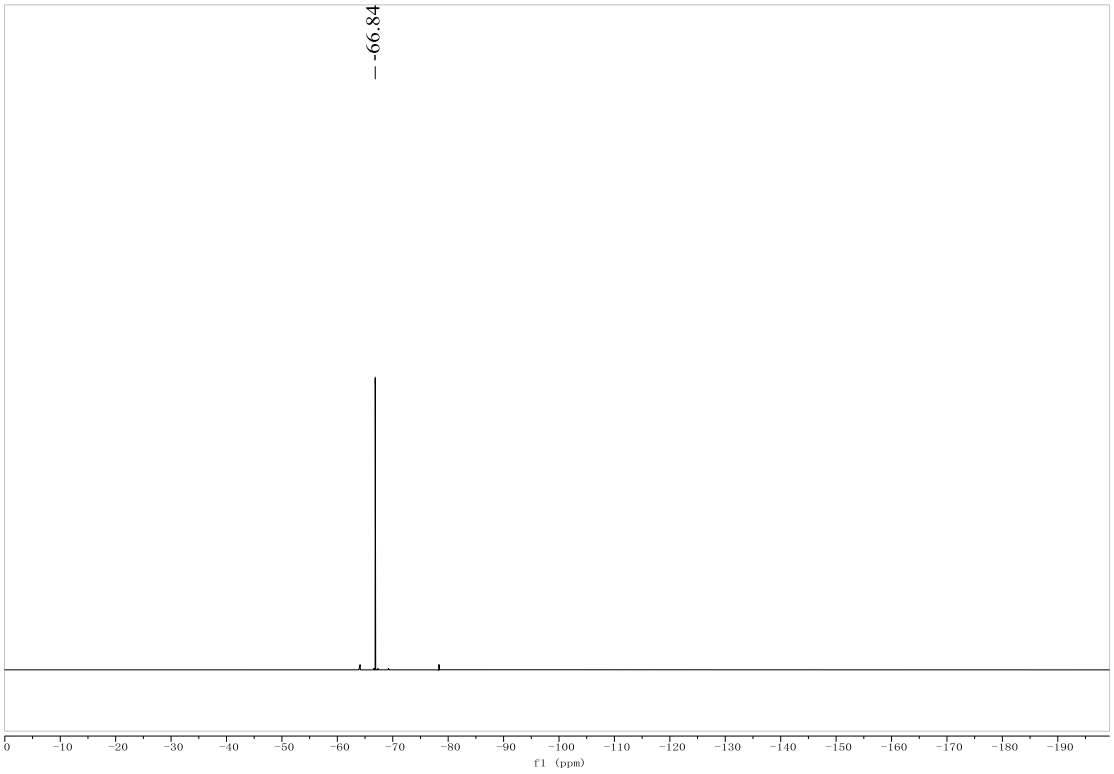
(2*R*,3*R*)-2-ethyl-2-(4-methoxyphenyl)-3-phenyl-3-(trifluoromethyl)oxirane (31c)



^{1}H NMR spectrum in DMSO-d_6.

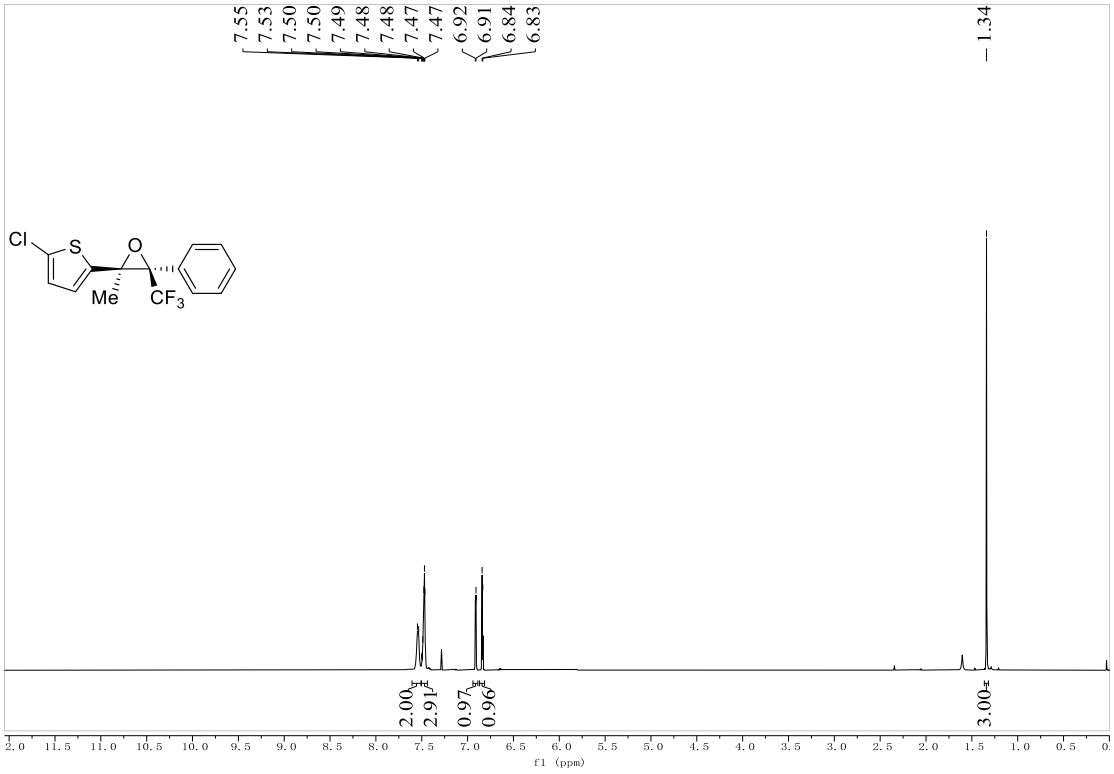


^{13}C NMR spectrum in DMSO-d_6.

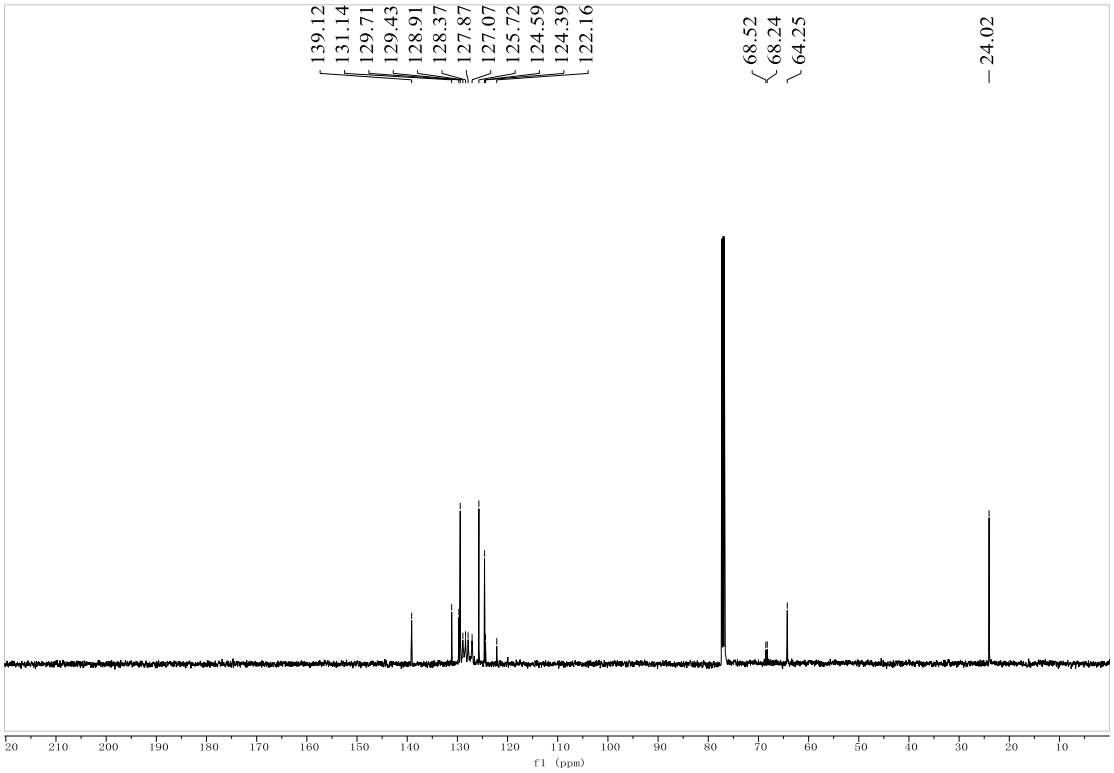


^{19}F NMR spectrum in $CDCl_3$.

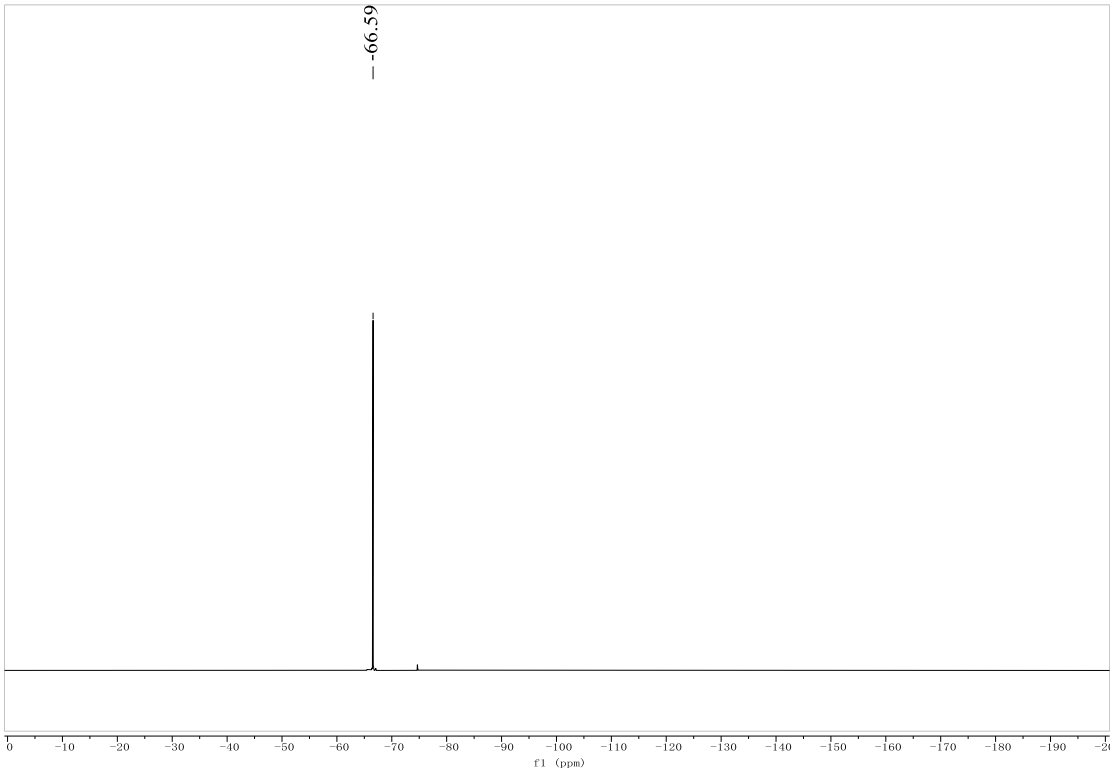
(2*R*,3*R*)-2-(5-chlorothiophen-2-yl)-2-methyl-3-phenyl-3-(trifluoromethyl) oxirane (32c)



^{1}H NMR spectrum in $CDCl_3$.

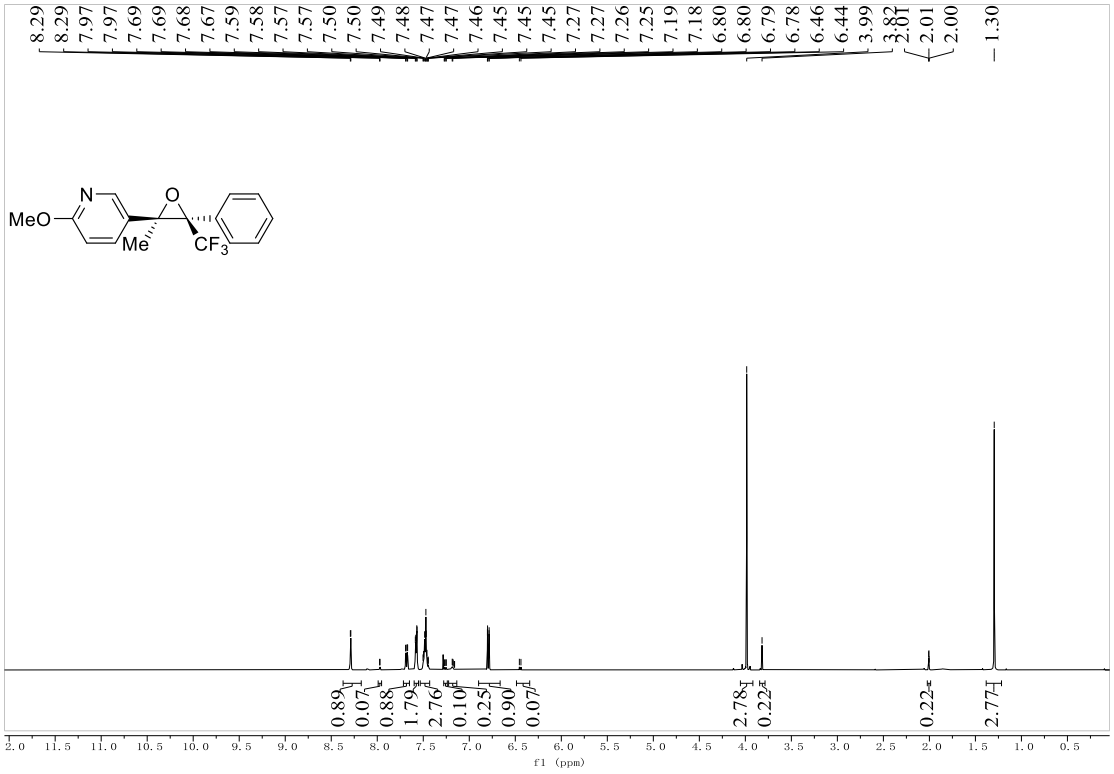


^{13}C NMR spectrum in $CDCl_3$.

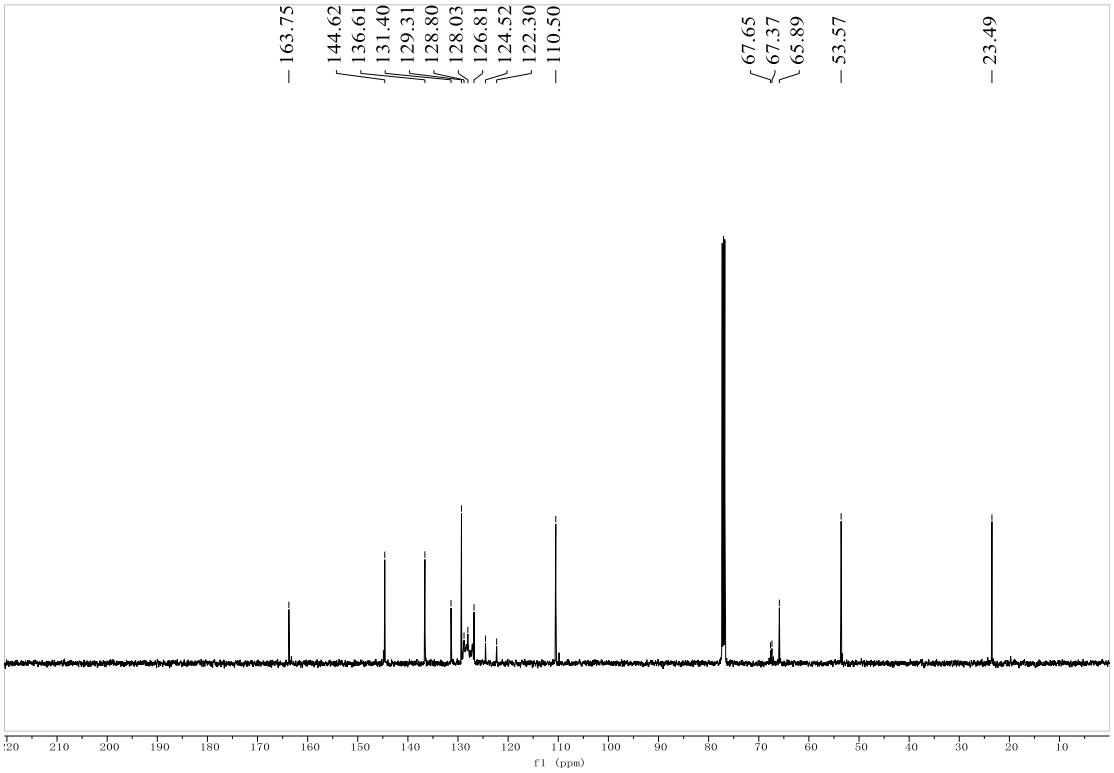


^{19}F NMR spectrum in $CDCl_3$.

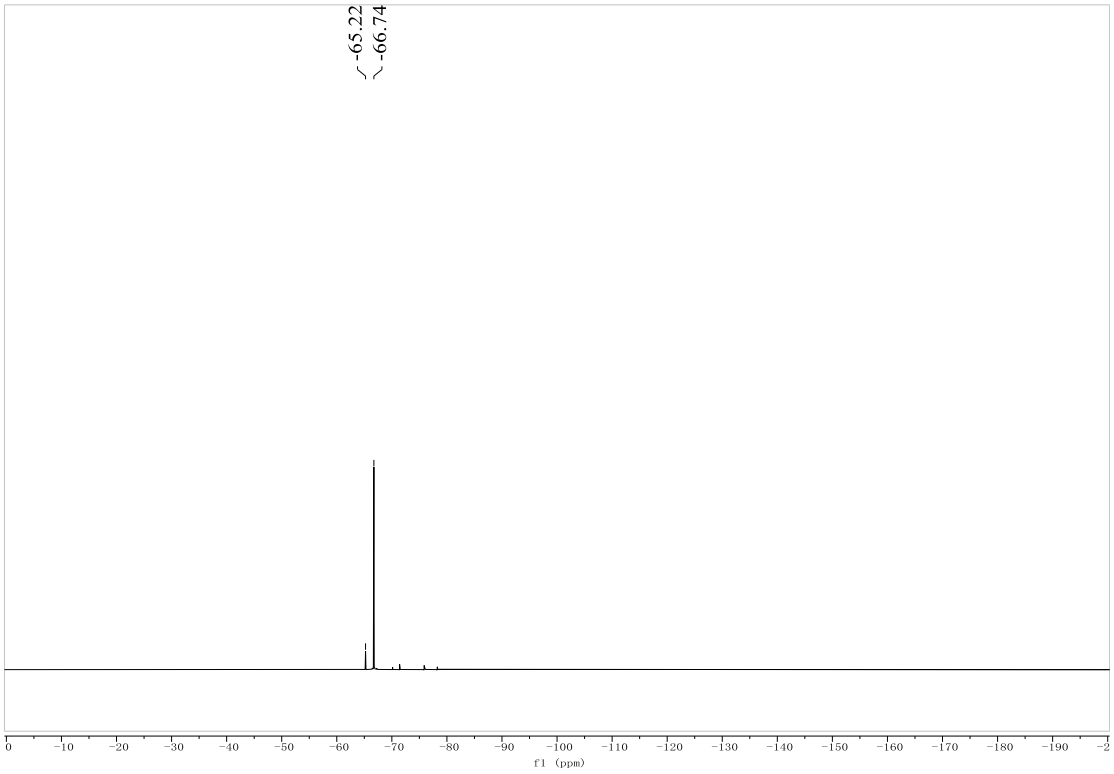
2-methoxy-5-((2*R*,3*R*)-2-methyl-3-phenyl-3-(trifluoromethyl) oxiran-2-yl) pyridine (33c)



^{1}H NMR spectrum in $CDCl_3$.

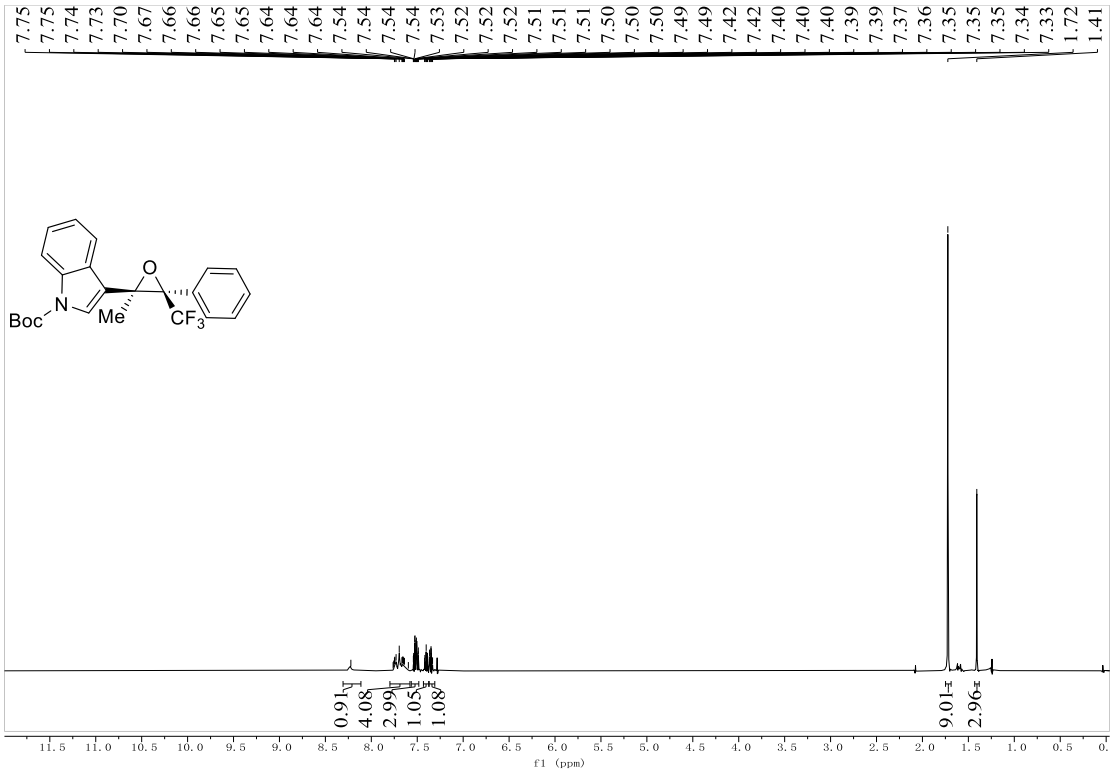


^{13}C NMR spectrum in $CDCl_3$.

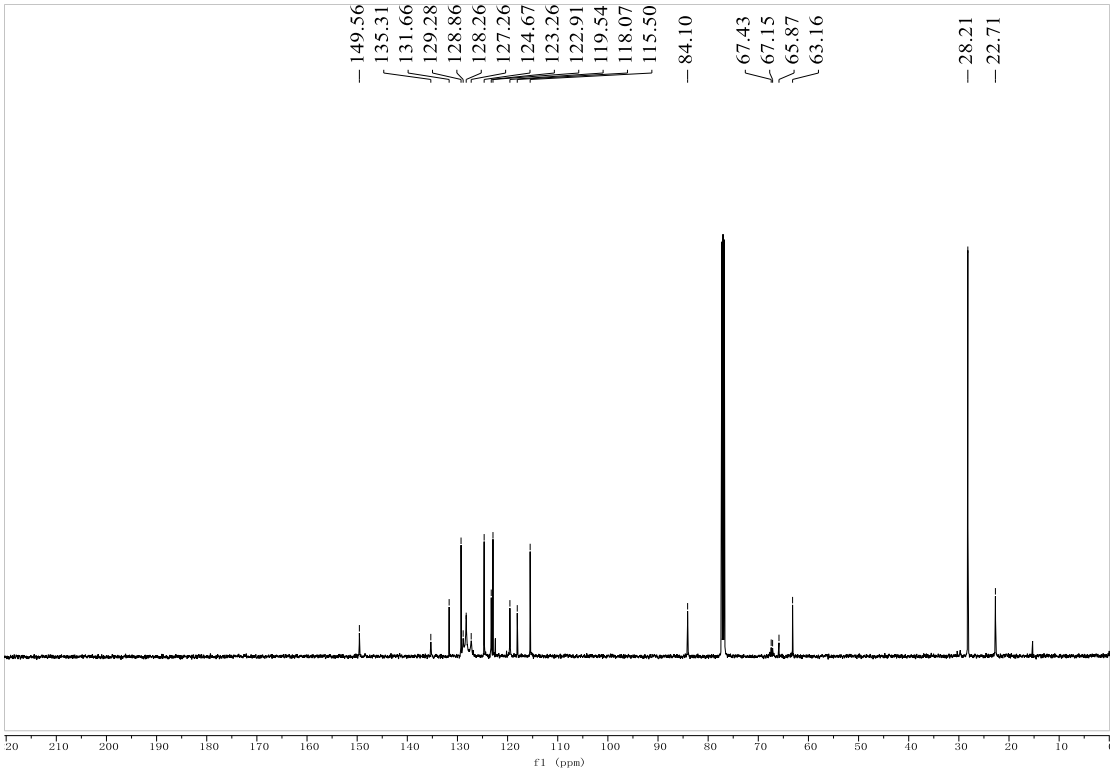


^{19}F NMR spectrum in $CDCl_3$.

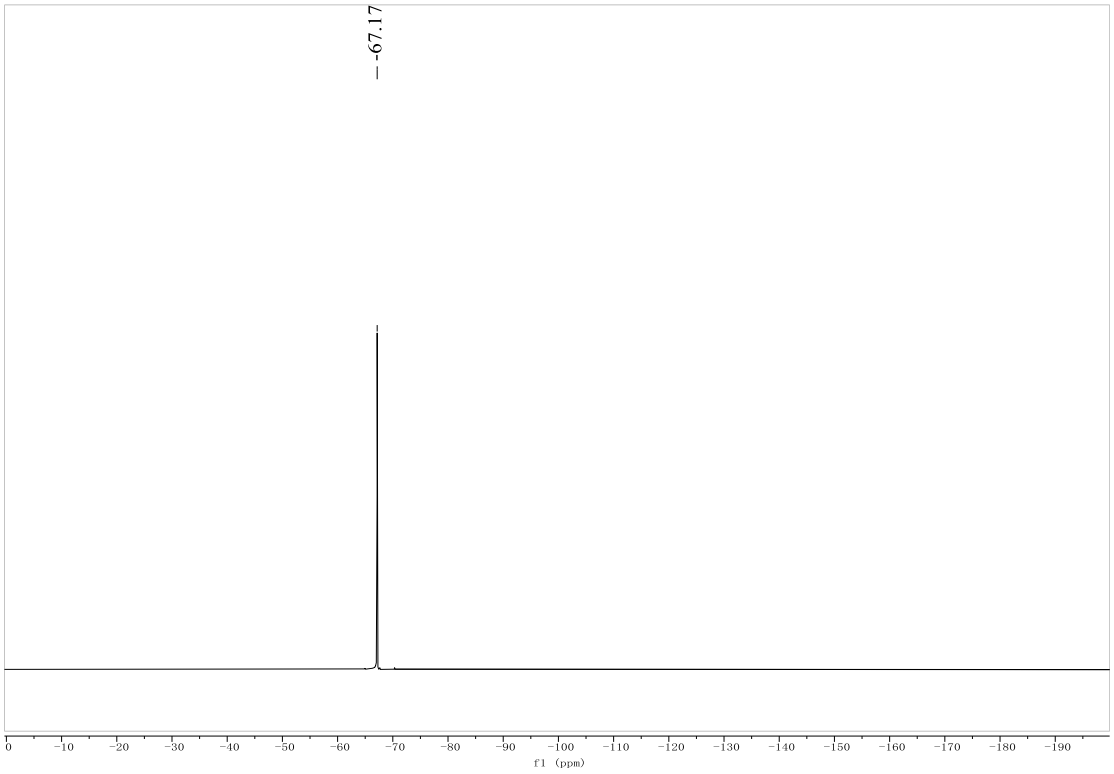
tert-butyl 3-((2*R*,3*R*)-2-methyl-3-phenyl-3-(trifluoromethyl)oxiran-2-yl)-1*H*-indole-1-carboxylate (34c)



^{1}H NMR spectrum in $CDCl_3$.

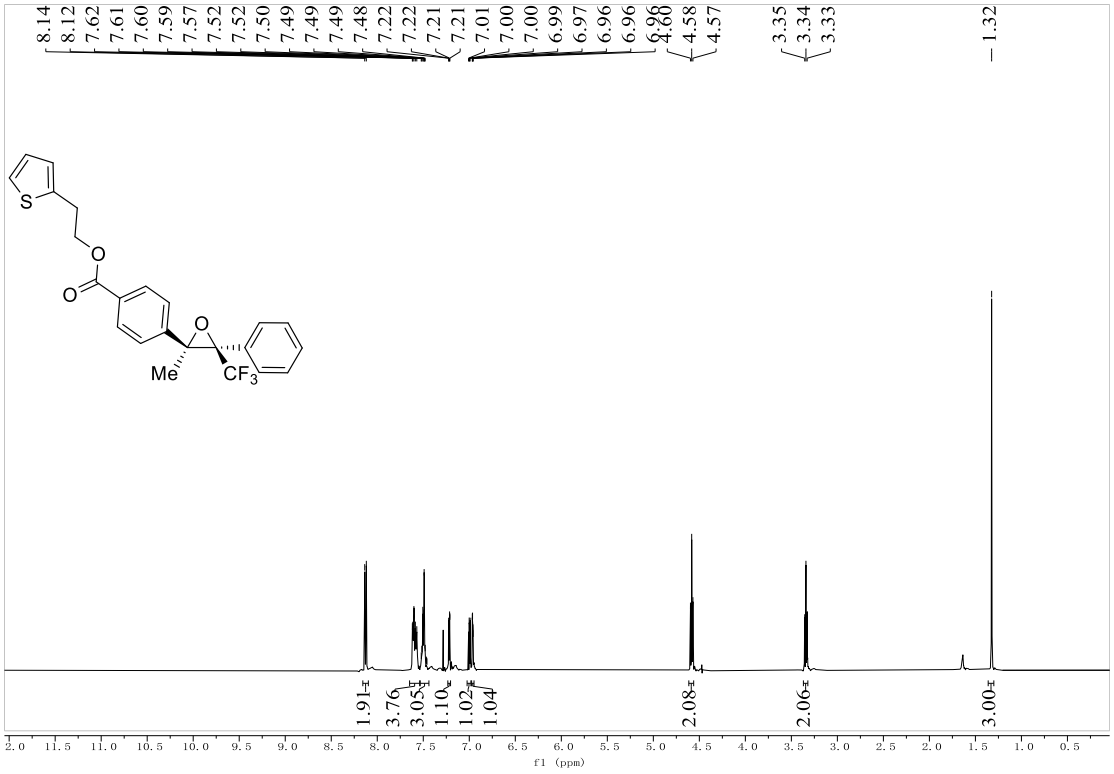


^{13}C NMR spectrum in $CDCl_3$.

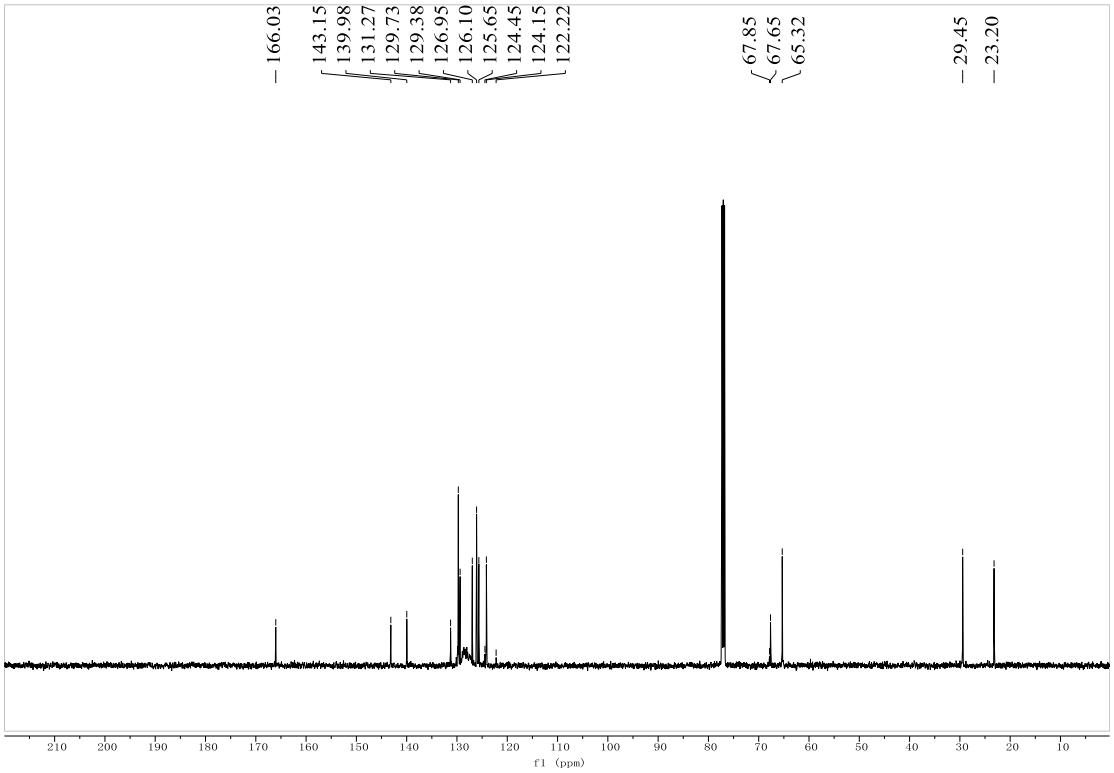


^{19}F NMR spectrum in $CDCl_3$.

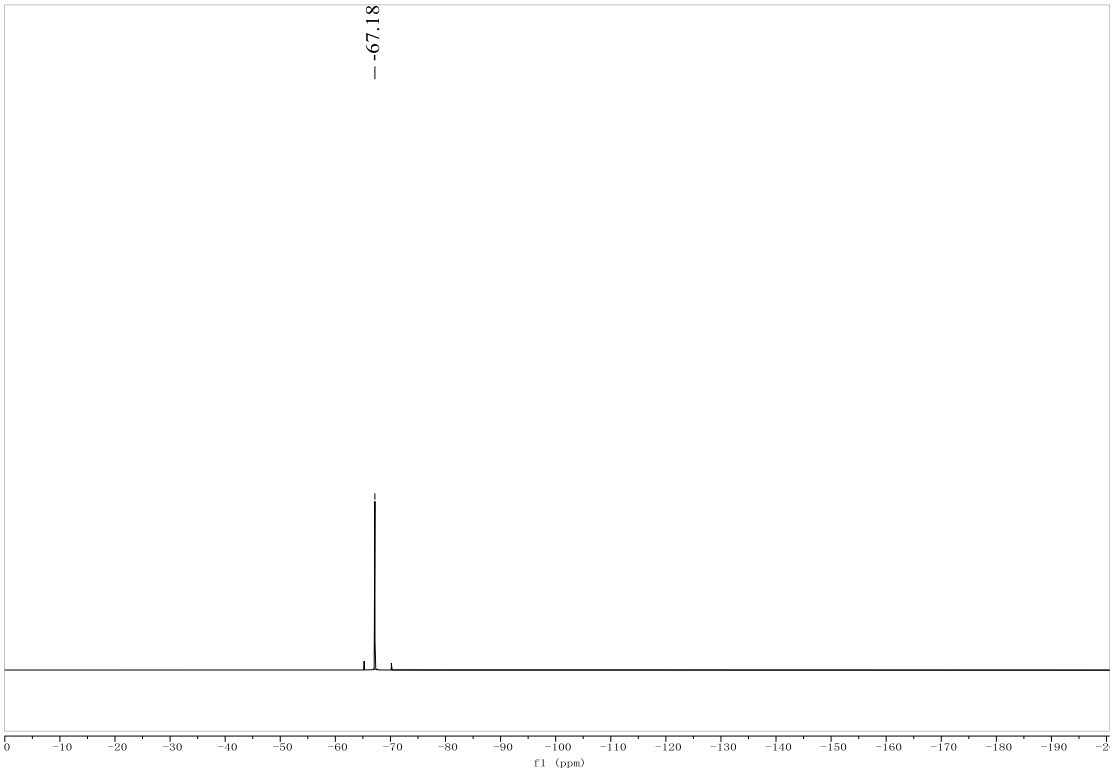
2-(thiophen-2-yl)ethyl 4-((2*R*,3*R*)-2-methyl-3-phenyl-3-(trifluoromethyl)oxiran-2-yl)benzoate (35c)



^{1}H NMR spectrum in $CDCl_3$.

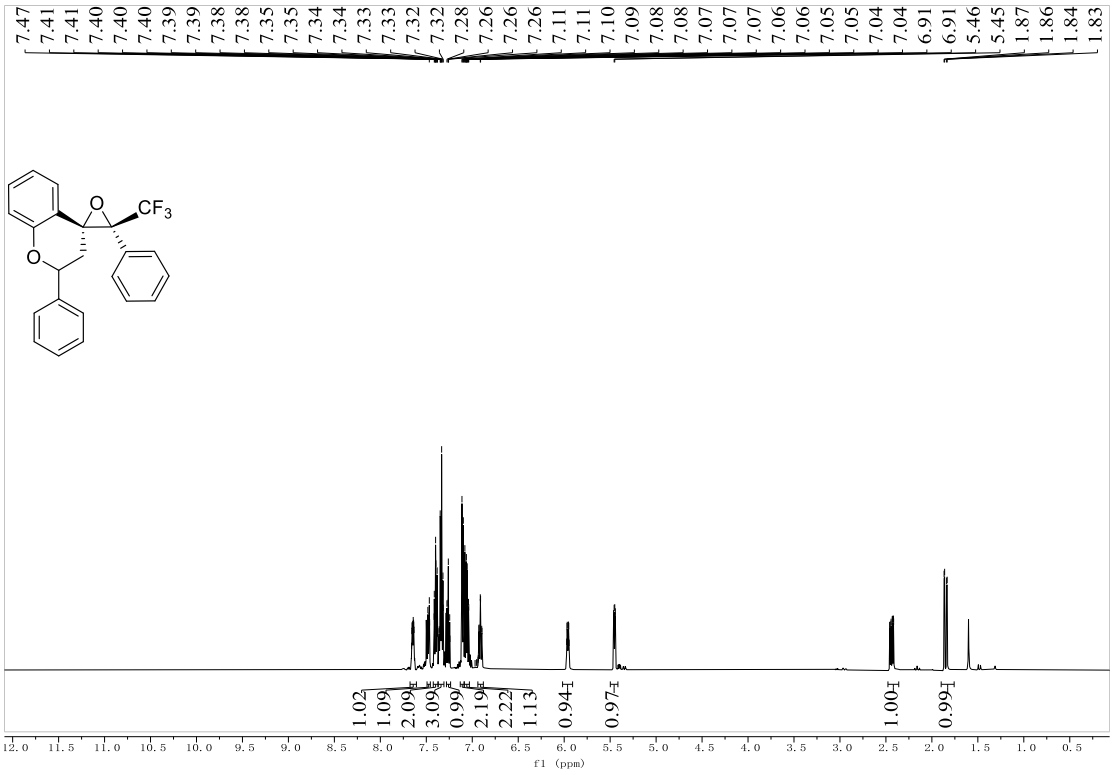


^{13}C NMR spectrum in $CDCl_3$.

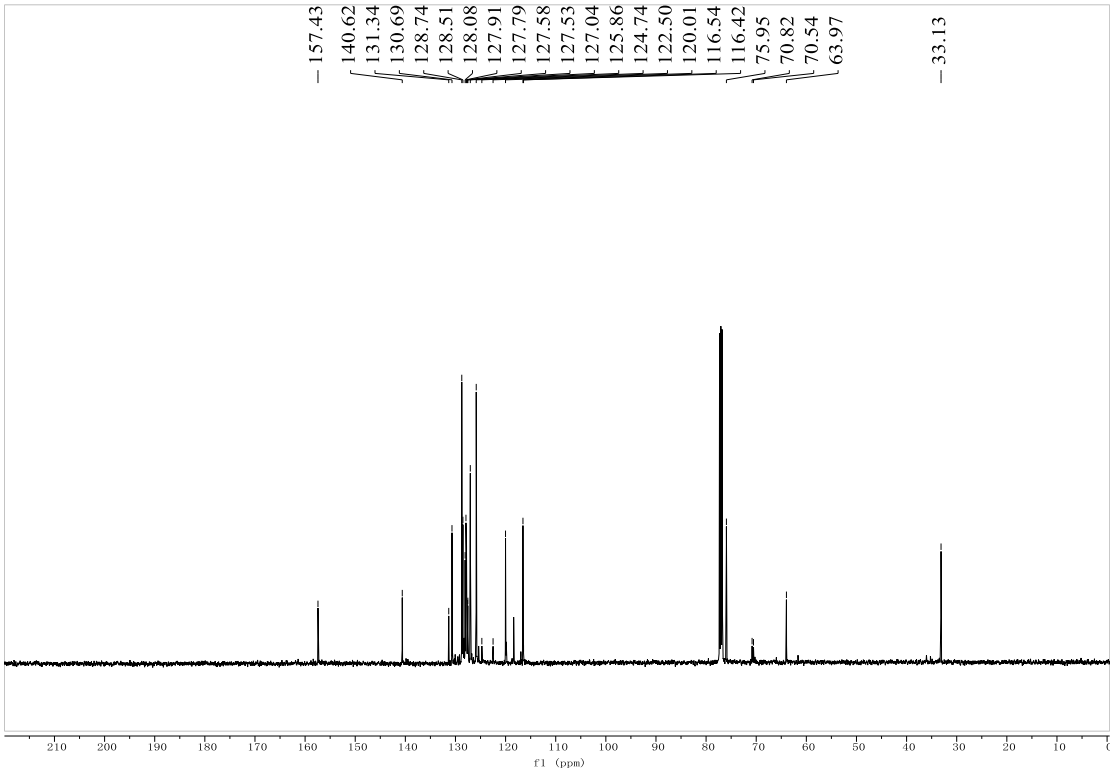


^{19}F NMR spectrum in $CDCl_3$.

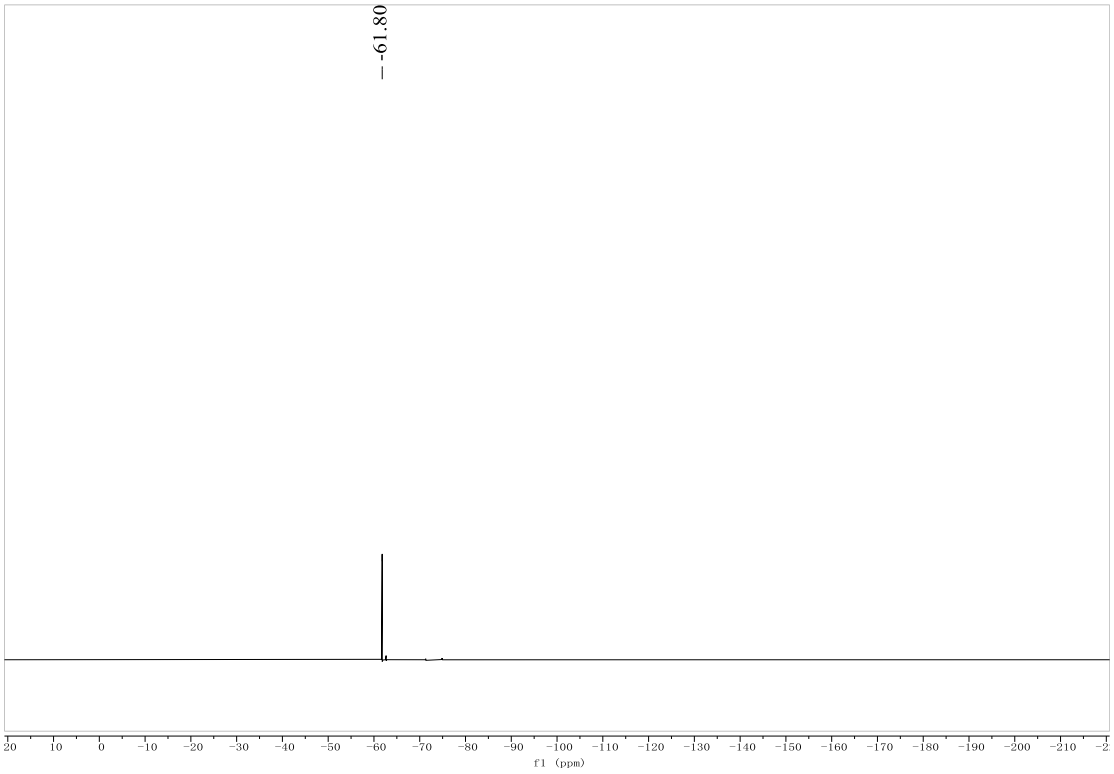
(3'*R*,4*R*)-2,3'-diphenyl-3'-(trifluoromethyl) spiro[chromane-4,2'-oxirane] (36c)



^{1}H NMR spectrum in $CDCl_3$.

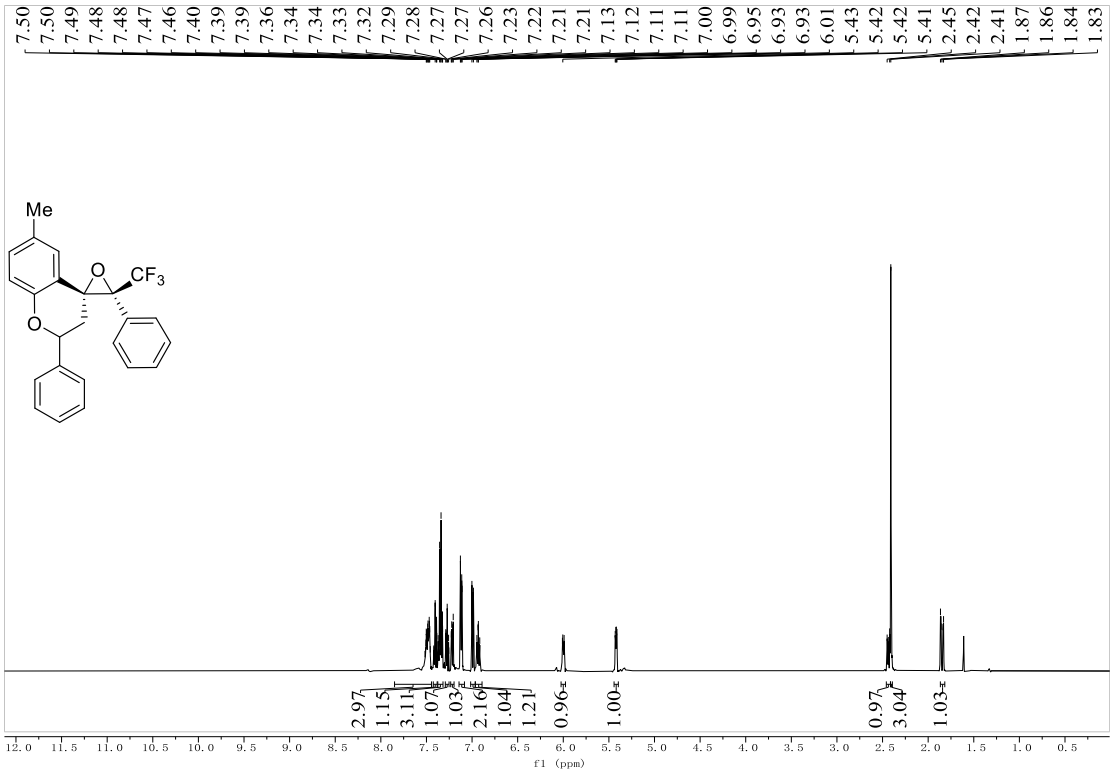


^{13}C NMR spectrum in $CDCl_3$.

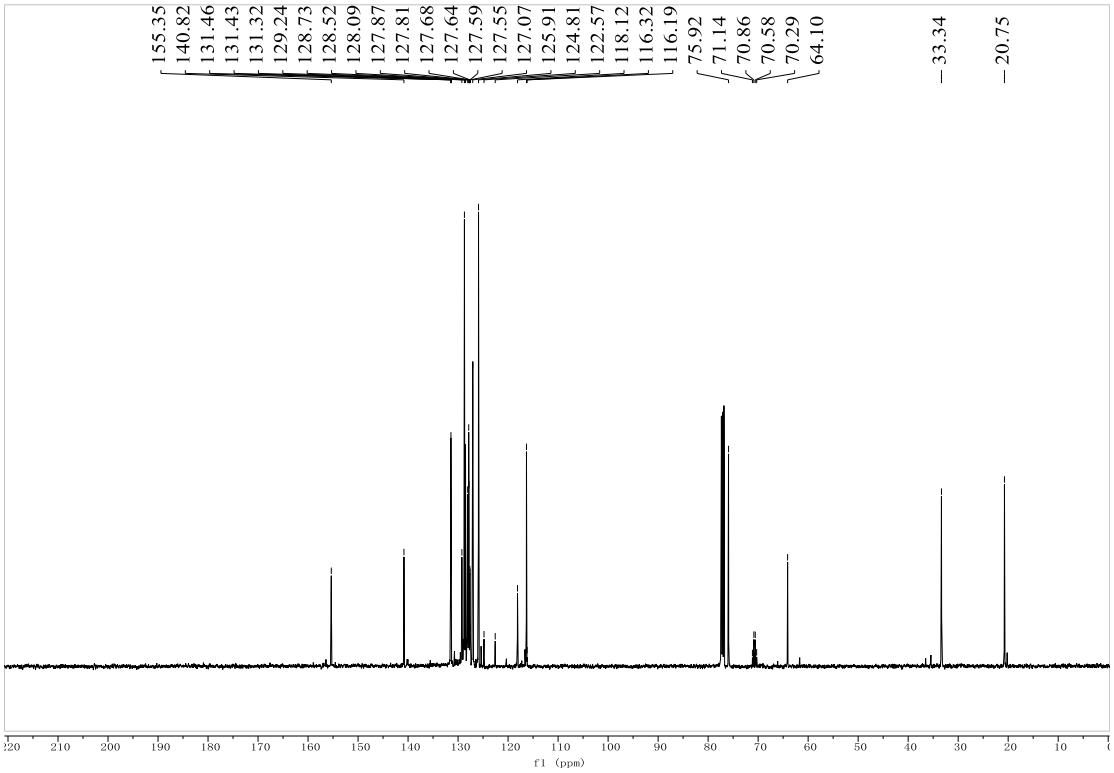


^{19}F NMR spectrum in $CDCl_3$.

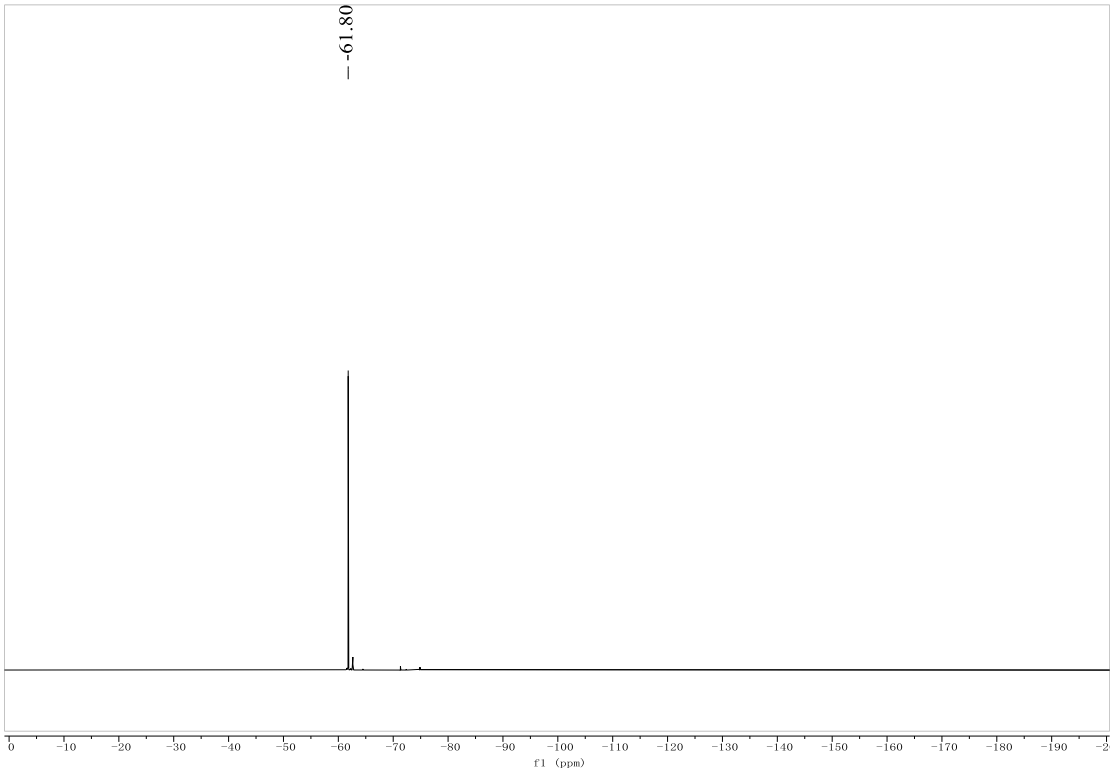
(3'*R*,4*R*)-6-methyl-2,3'-diphenyl-3'-(trifluoromethyl) spiro[chromane-4,2'-oxirane] (37c)



^{1}H NMR spectrum in $CDCl_3$.

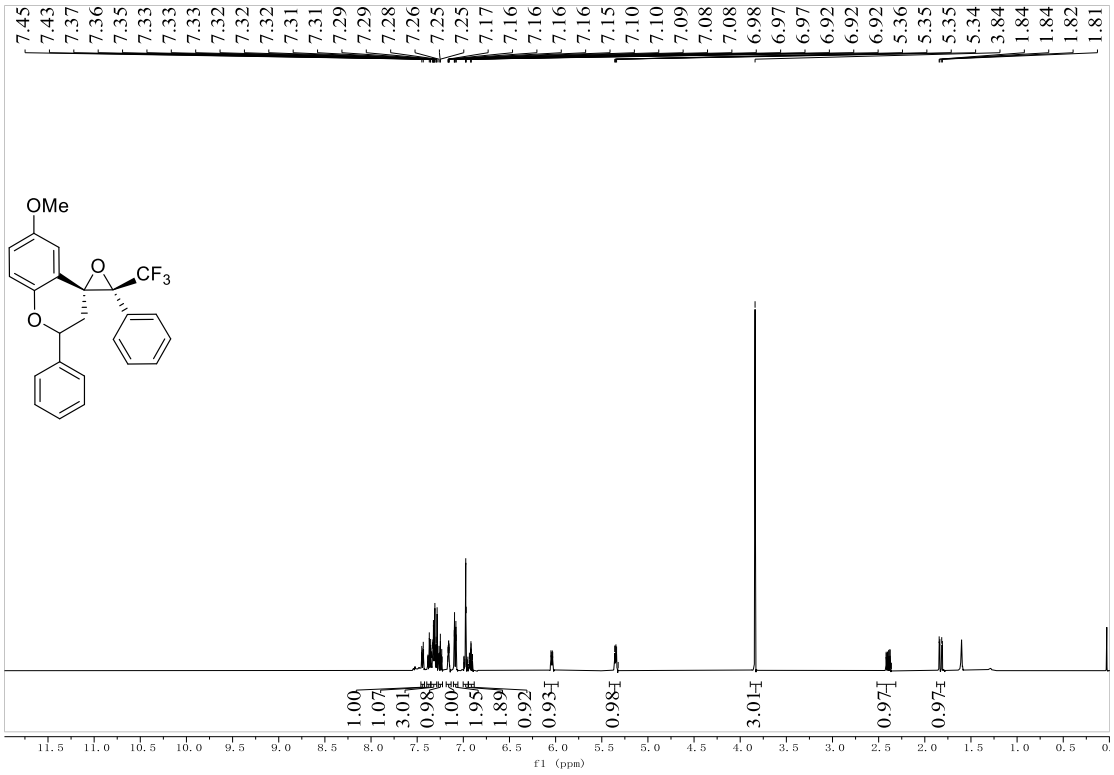


^{13}C NMR spectrum in $CDCl_3$.

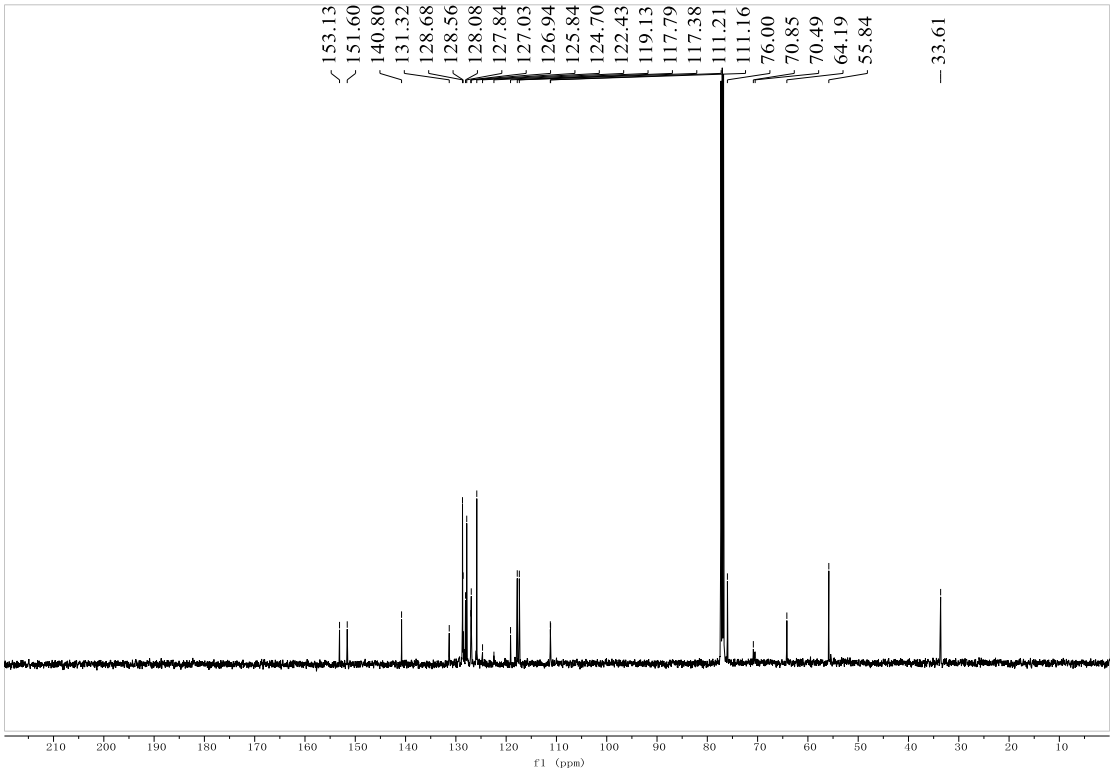


^{19}F NMR spectrum in $CDCl_3$.

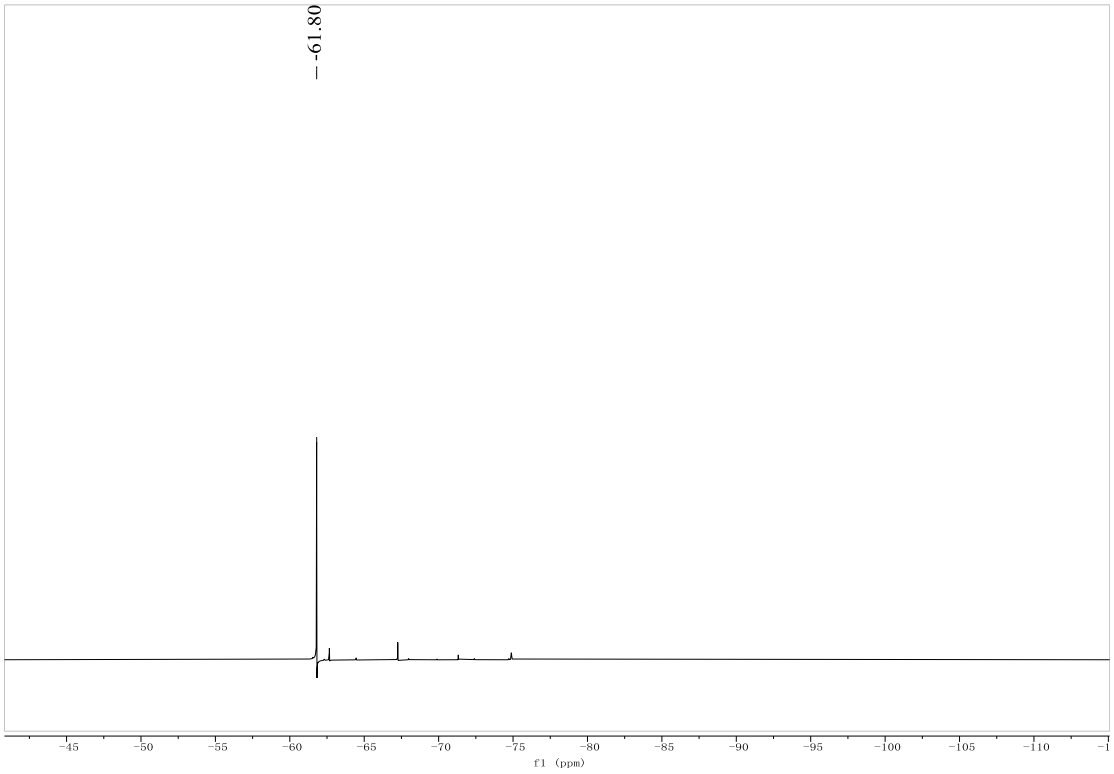
(3'*R*,4*R*)-6-methoxy-2,3'-diphenyl-3'-(trifluoromethyl)spiro[chromane-4,2'-oxirane] (38c)



^{1}H NMR spectrum in $CDCl_3$.

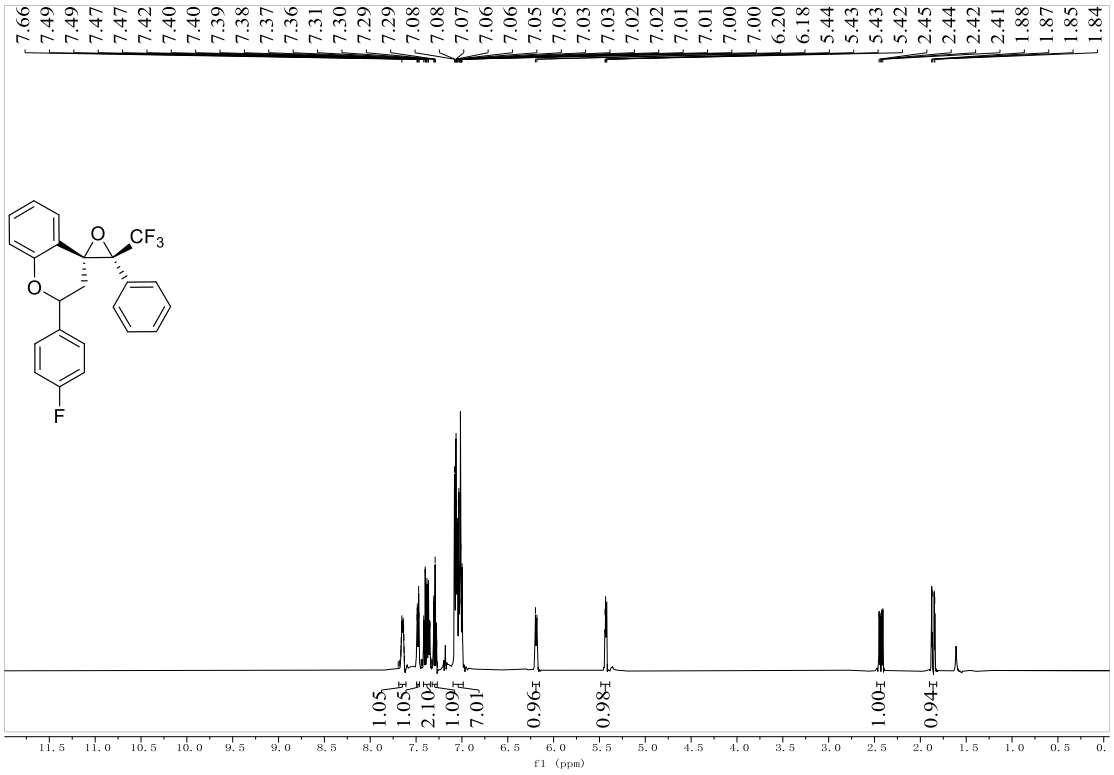


^{13}C NMR spectrum in $CDCl_3$.

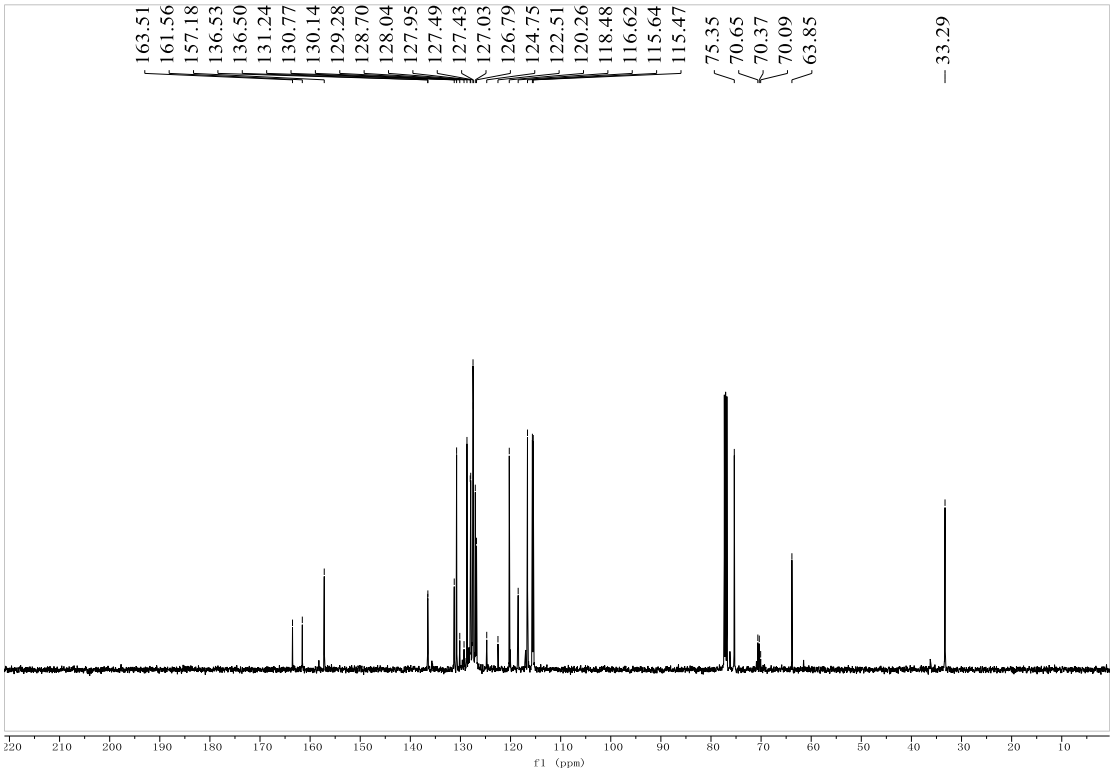


^{19}F NMR spectrum in $CDCl_3$.

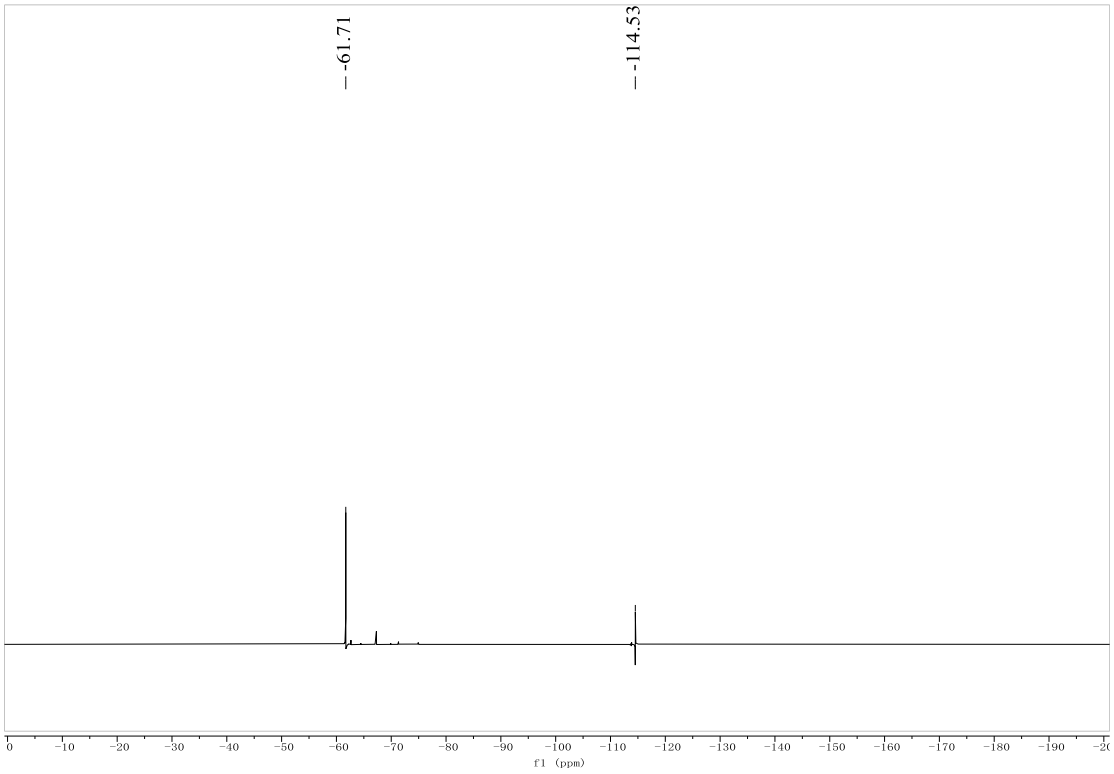
(3'*R*,4*R*)-2-(4-fluorophenyl)-3'-phenyl-3'-(trifluoromethyl)spiro[chromane-4,2'-oxirane] (39c)



^{1}H NMR spectrum in $CDCl_3$.

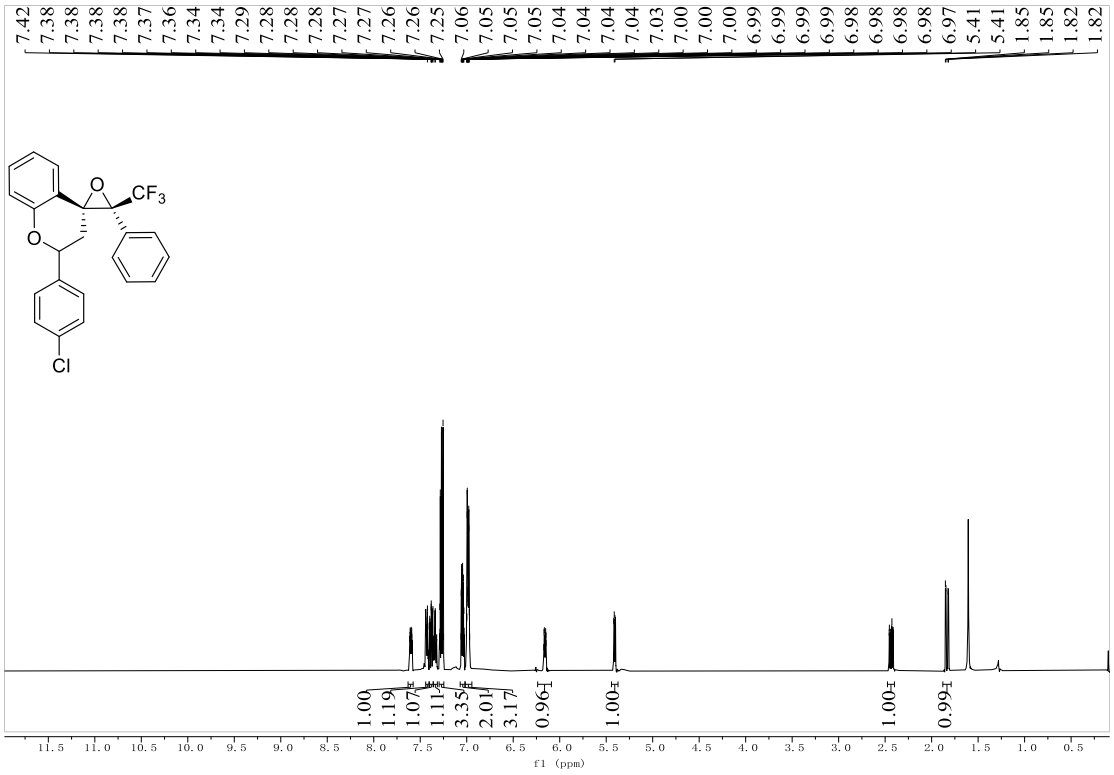


^{13}C NMR spectrum in $CDCl_3$.

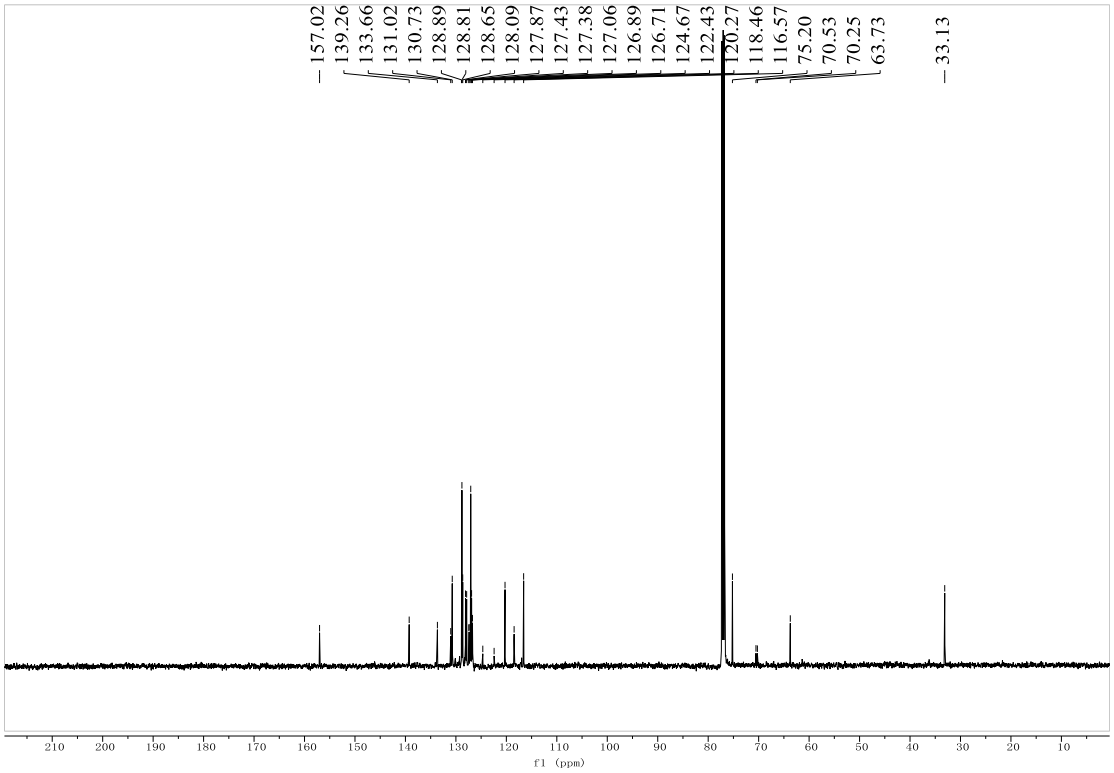


^{19}F NMR spectrum in $CDCl_3$.

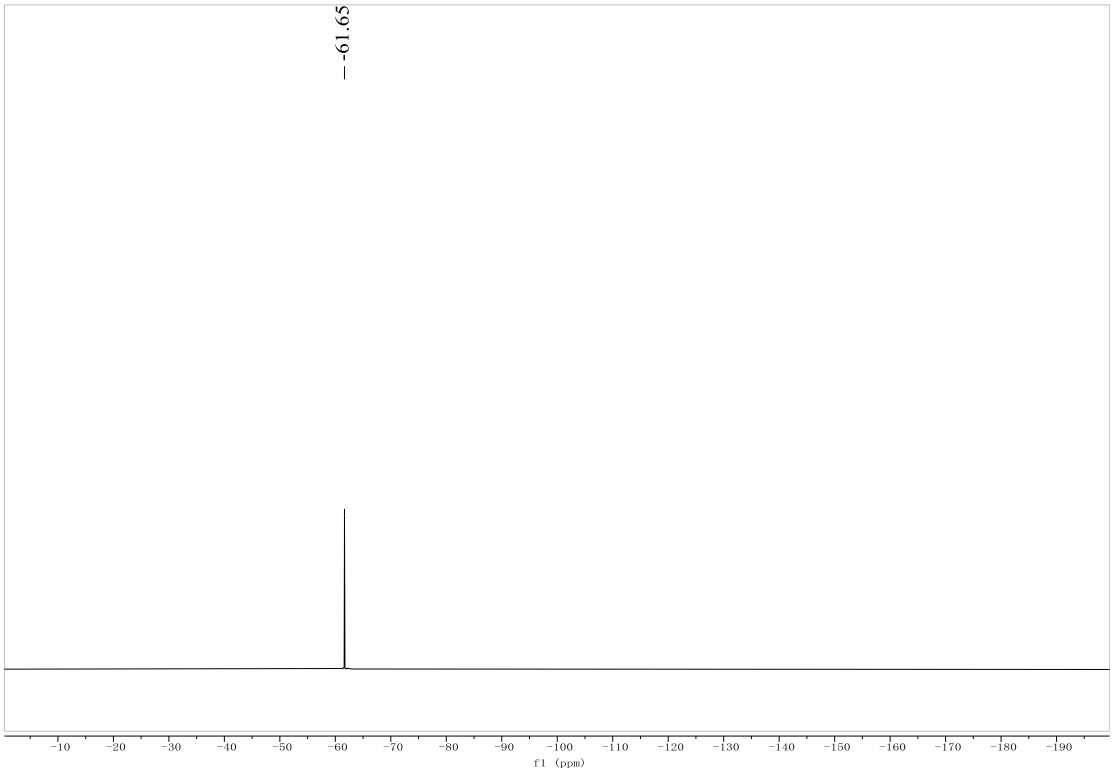
(3'*R*,4*R*)-2-(4-chlorophenyl)-3'-phenyl-3'-(trifluoromethyl)spiro[chromane-4,2'-oxirane] (40c)



^{1}H NMR spectrum in $CDCl_3$.

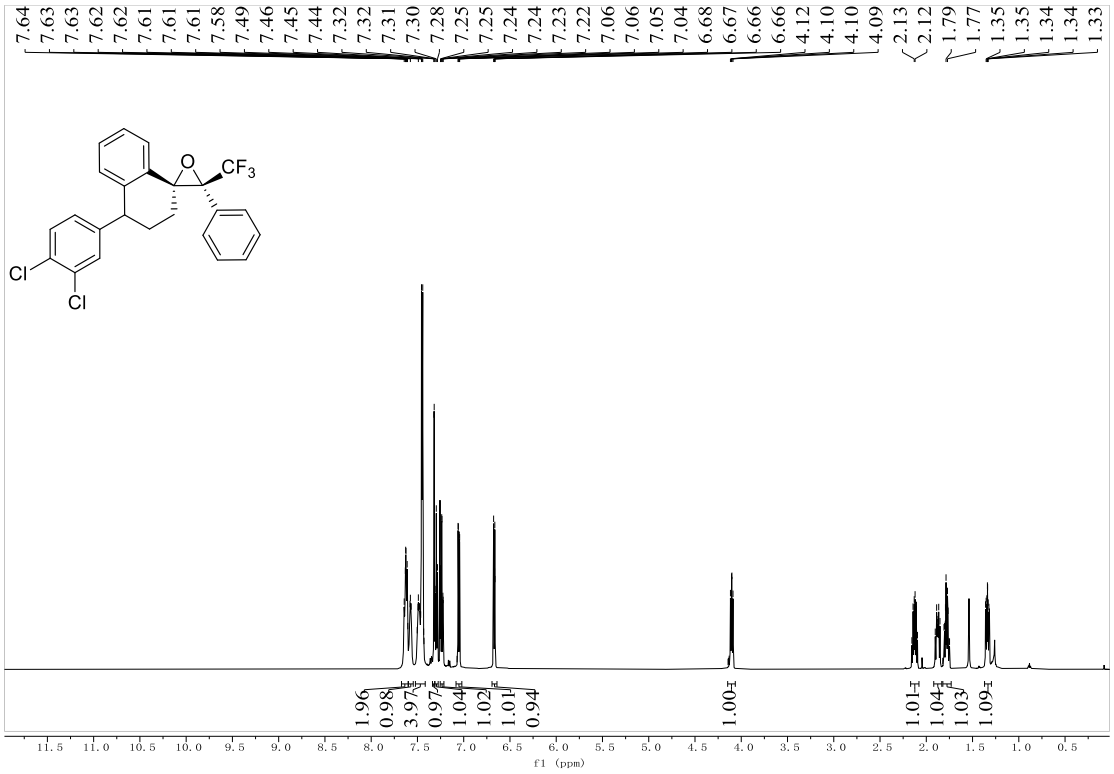


^{13}C NMR spectrum in $CDCl_3$.

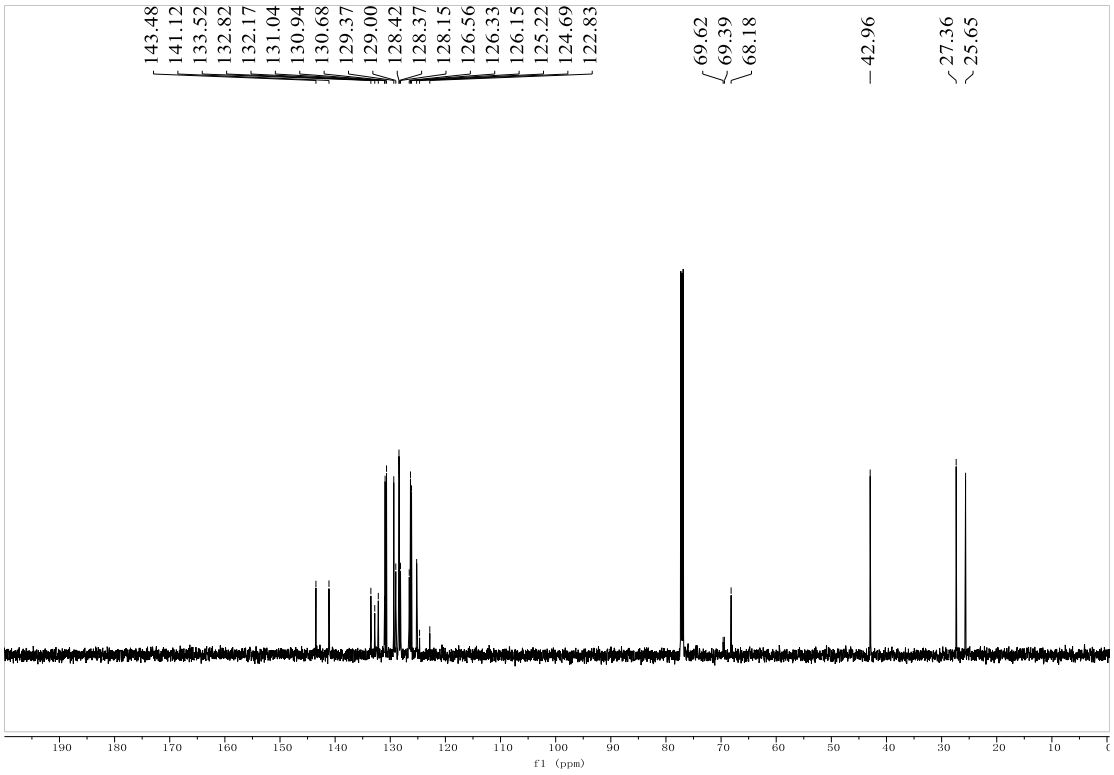


^{19}F NMR spectrum in $CDCl_3$.

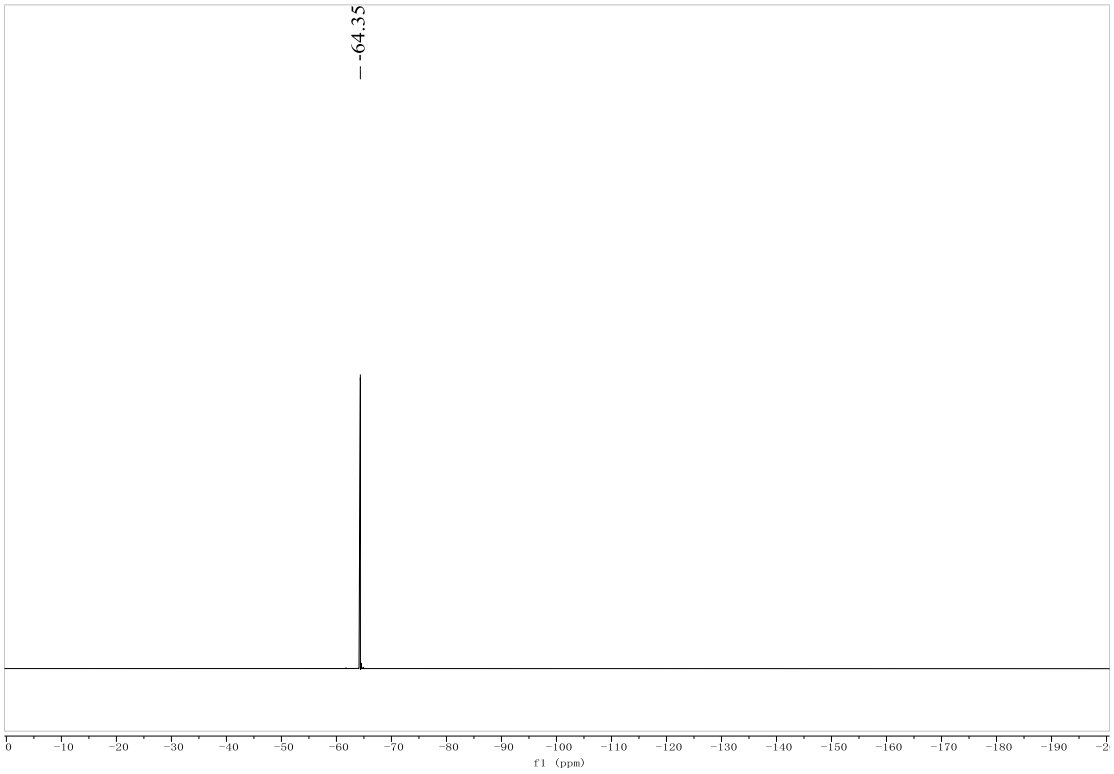
(1*R*,3'*R*)-4-(3,4-dichlorophenyl)-3'-phenyl-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] （41c）



^{1}H NMR spectrum in $CDCl_3$.

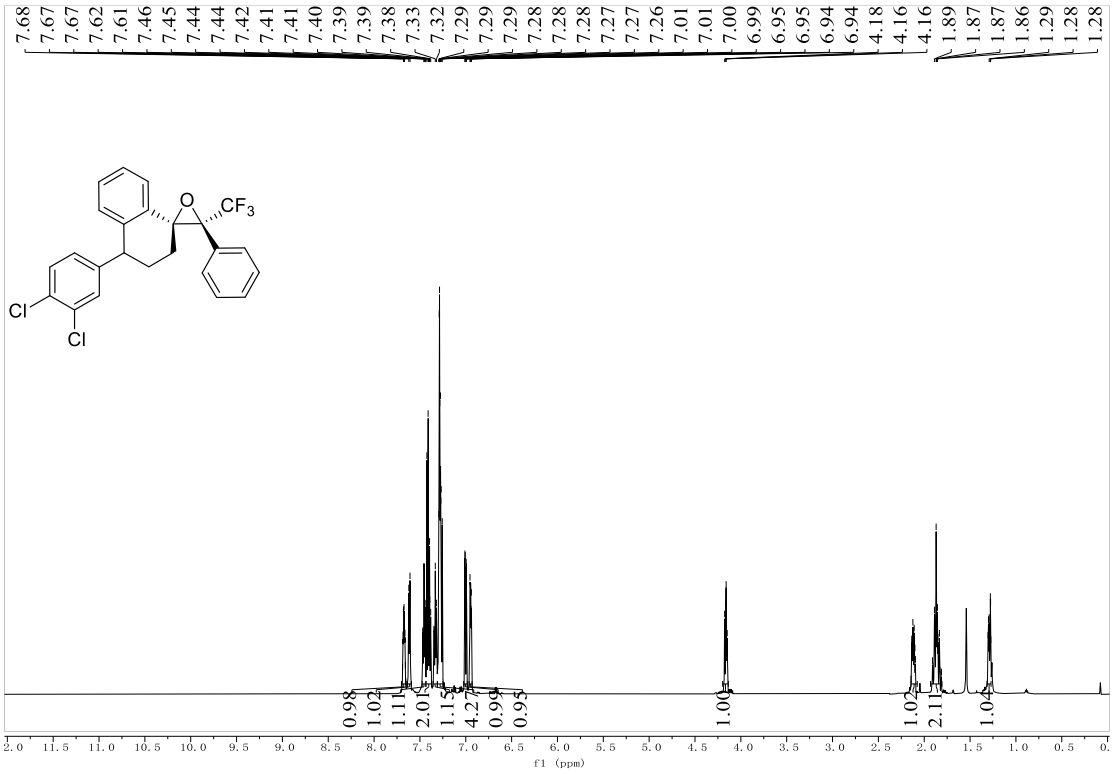


^{13}C NMR spectrum in $CDCl_3$.

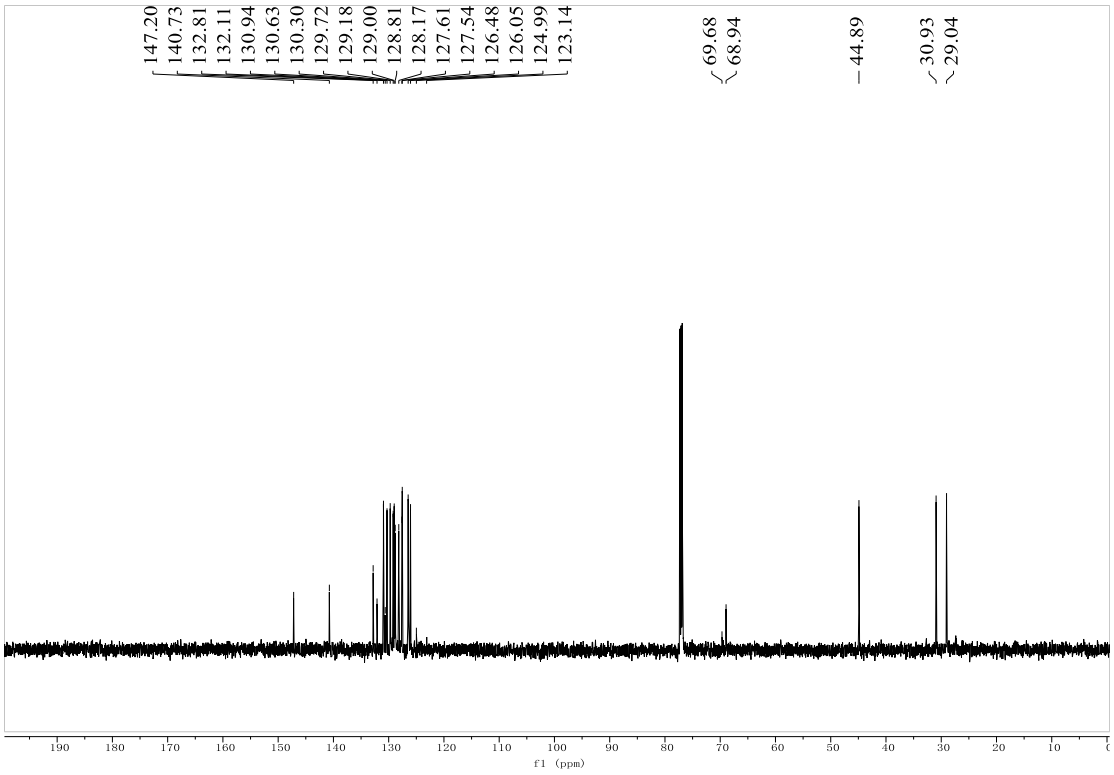


^{19}F NMR spectrum in $CDCl_3$.

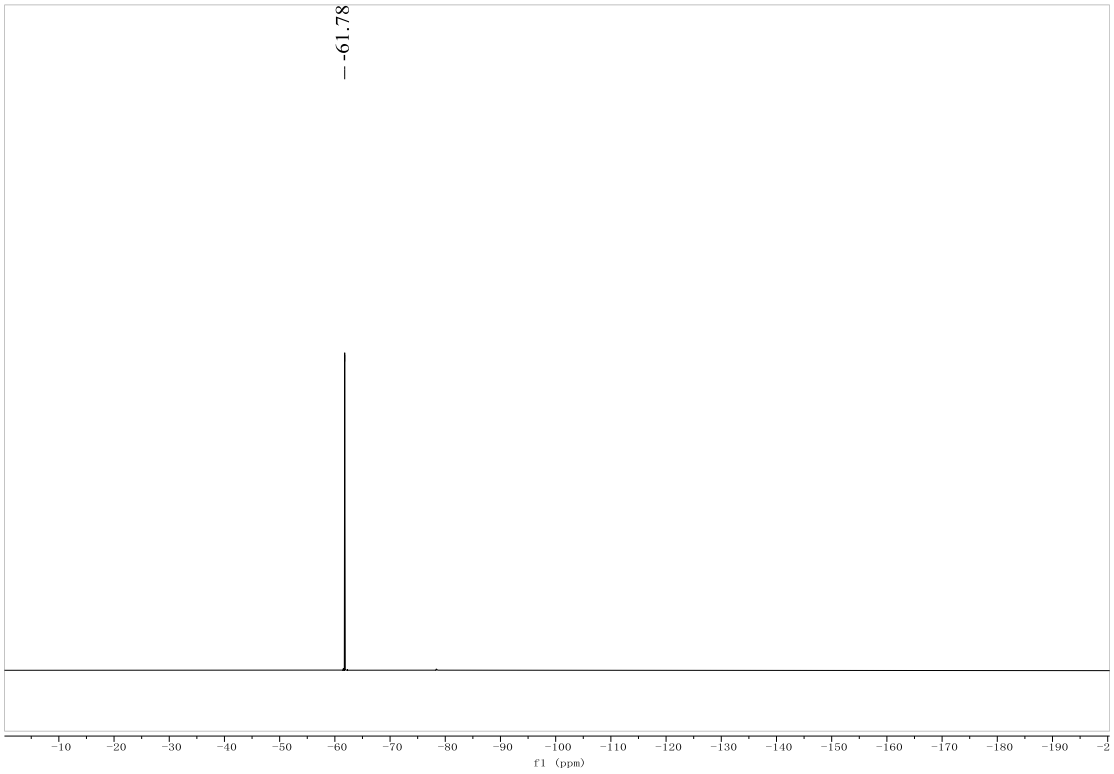
(1*S*,3'*S*)-4-(3,4-dichlorophenyl)-3'-phenyl-3'-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane] (41c[a])



^{1}H NMR spectrum in $CDCl_3$.

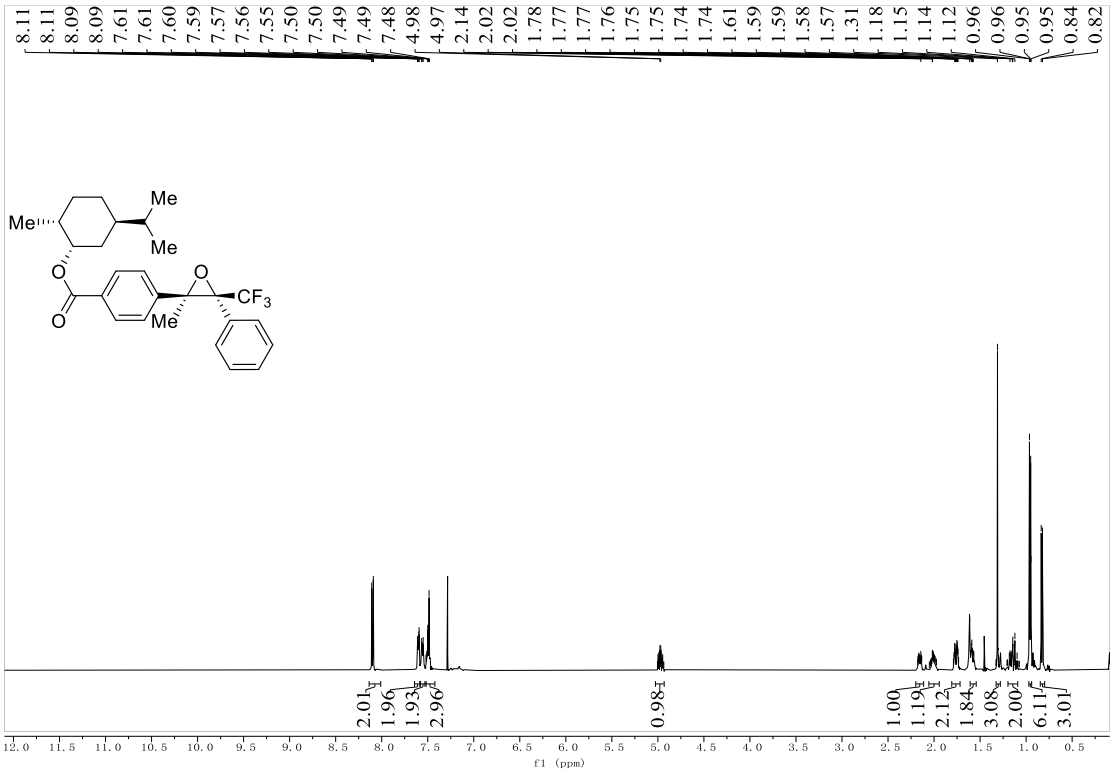


^{13}C NMR spectrum in $CDCl_3$.

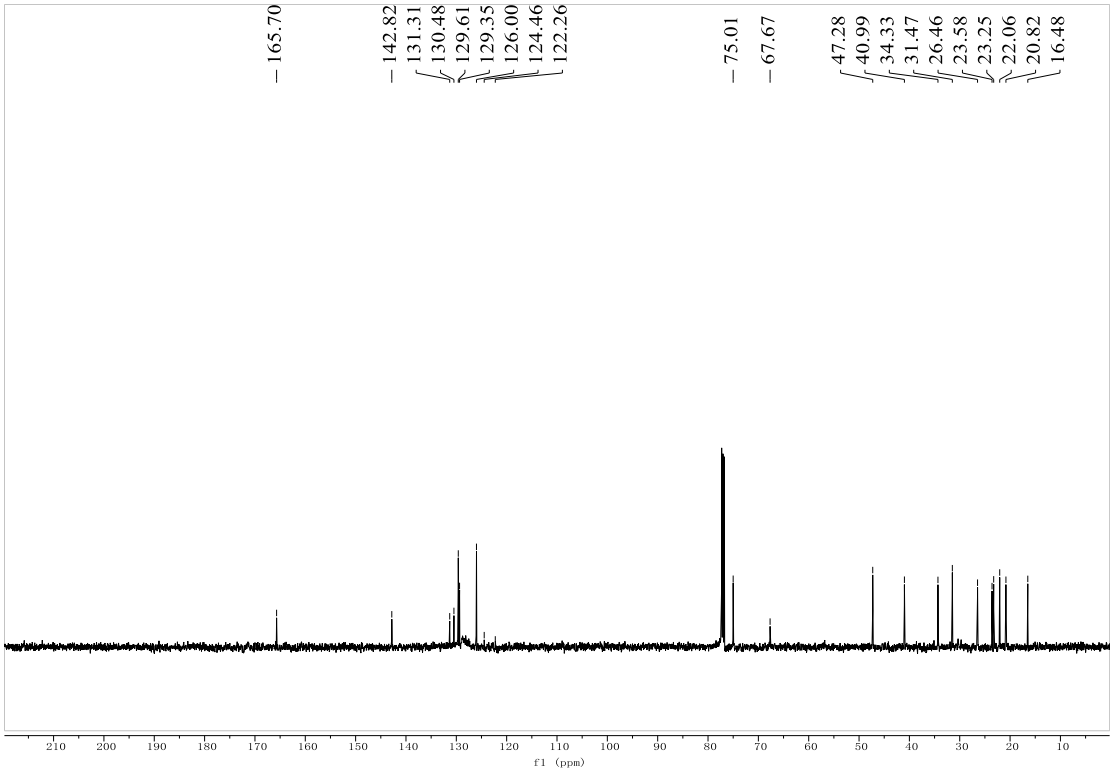


^{19}F NMR spectrum in $CDCl_3$.

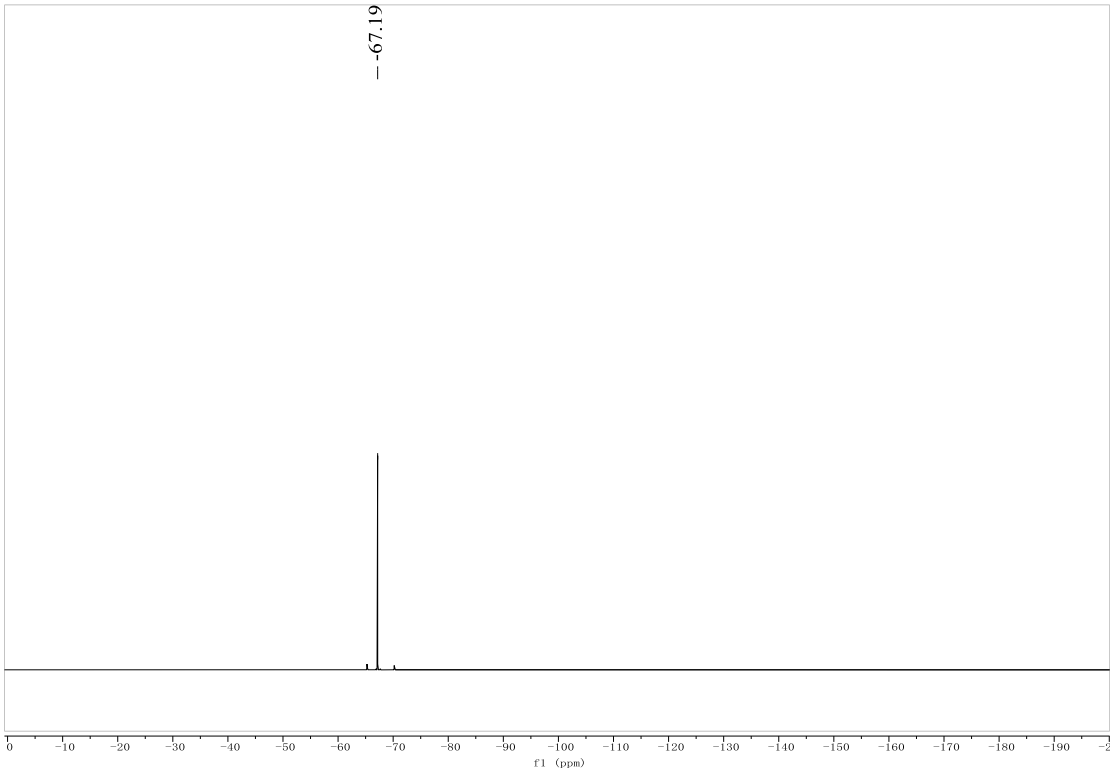
(1*S*,5*S*)-5-isopropyl-2-methylcyclohexyl 4-((2*R*,3*R*)-2-methyl-3-phenyl-3-(trifluoromethyl)oxiran-2-yl)benzoate (42c)



^{1}H NMR spectrum in $CDCl_3$.

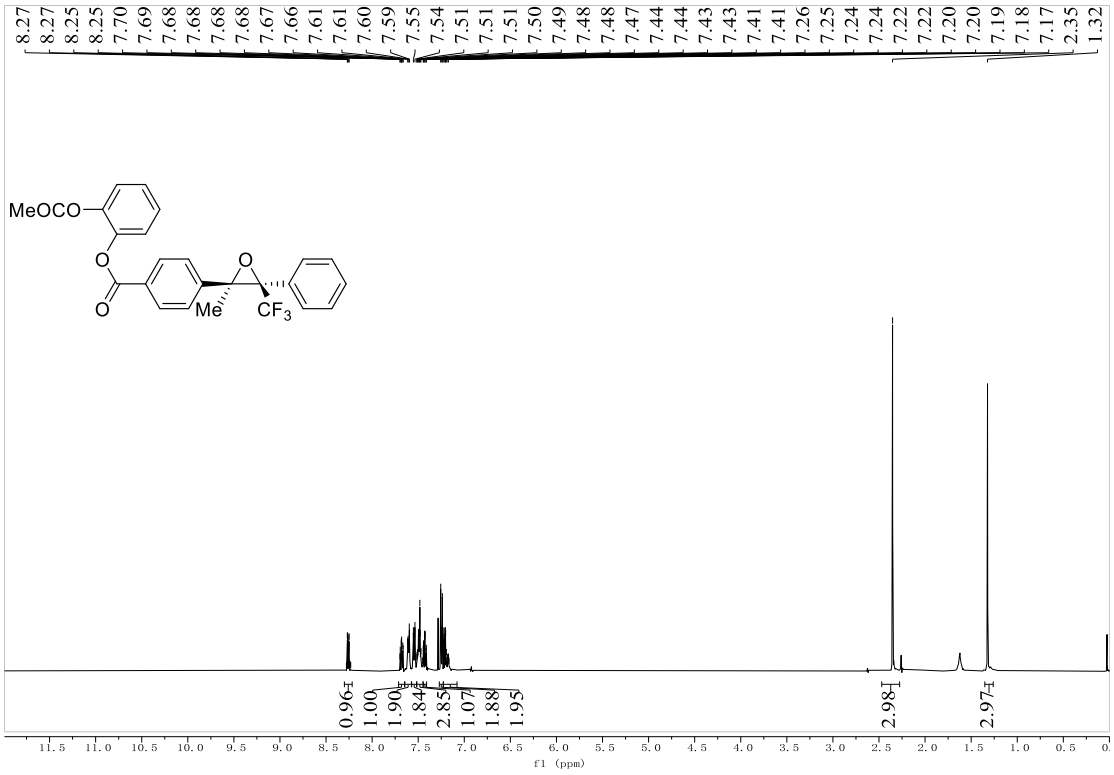


^{13}C NMR spectrum in $CDCl_3$.

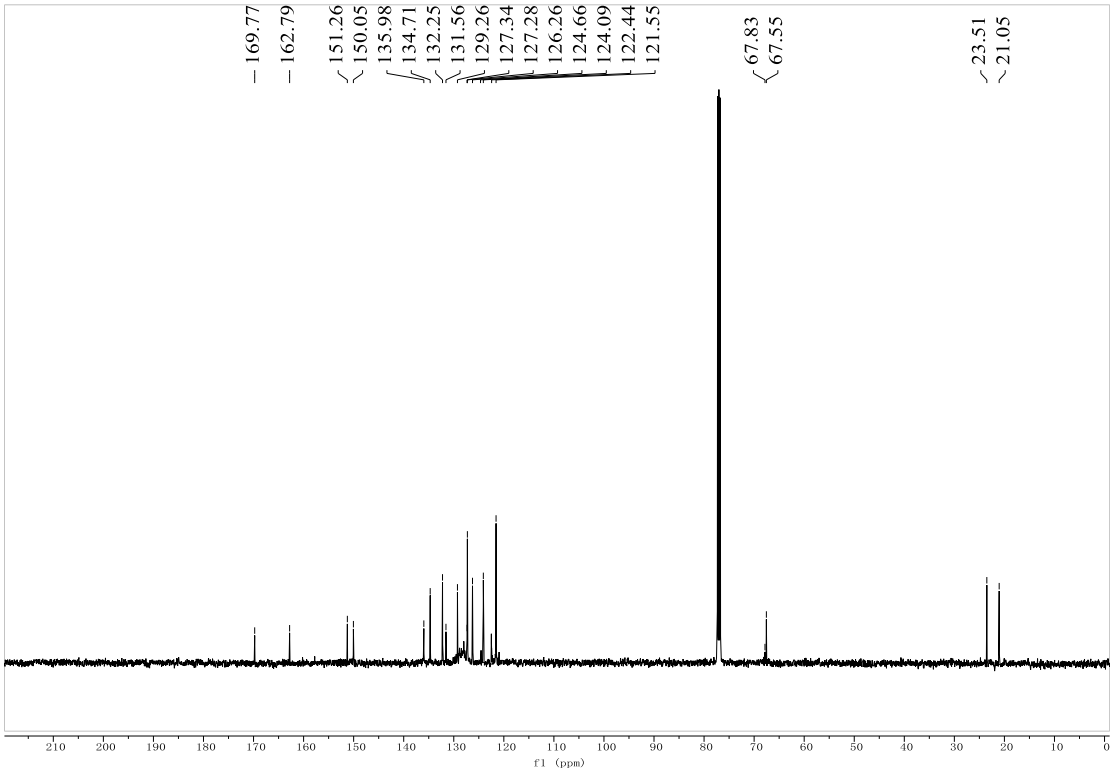


^{19}F NMR spectrum in $CDCl_3$.

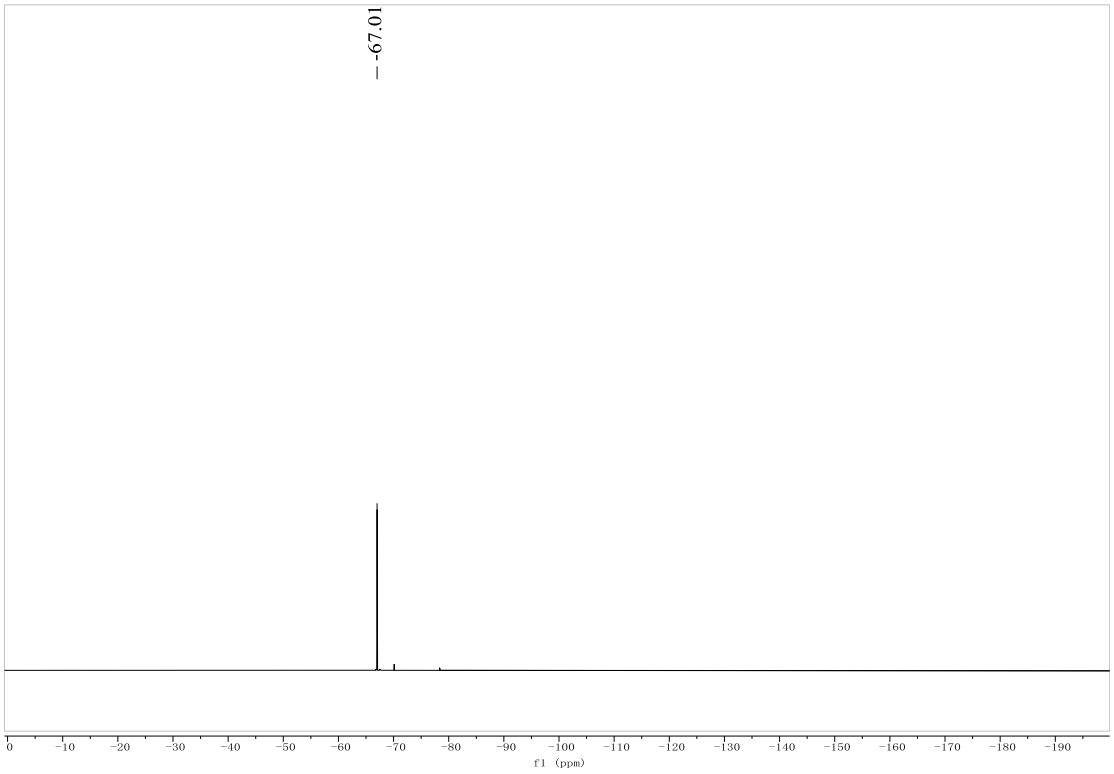
2-acetoxyphenyl 4-((2*R*,3*R*)-2-methyl-3-phenyl-3-(trifluoromethyl)oxiran-2-yl)benzoate (43c)



^{1}H NMR spectrum in $CDCl_3$.

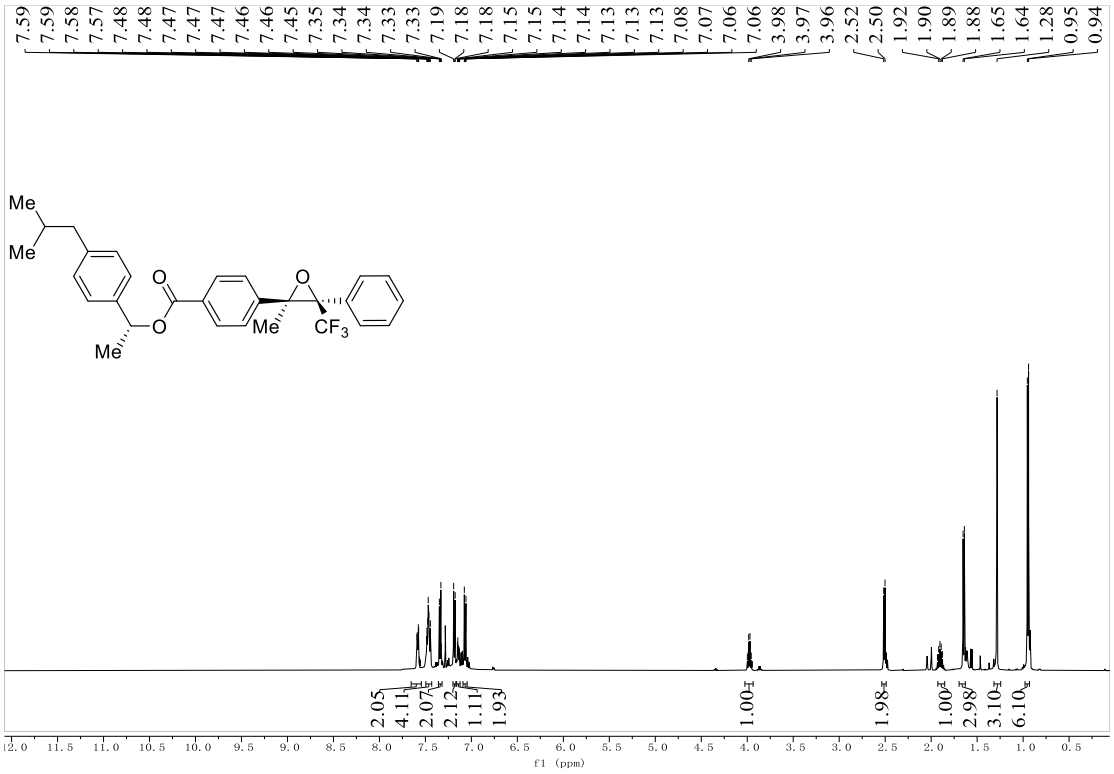


^{13}C NMR spectrum in $CDCl_3$.

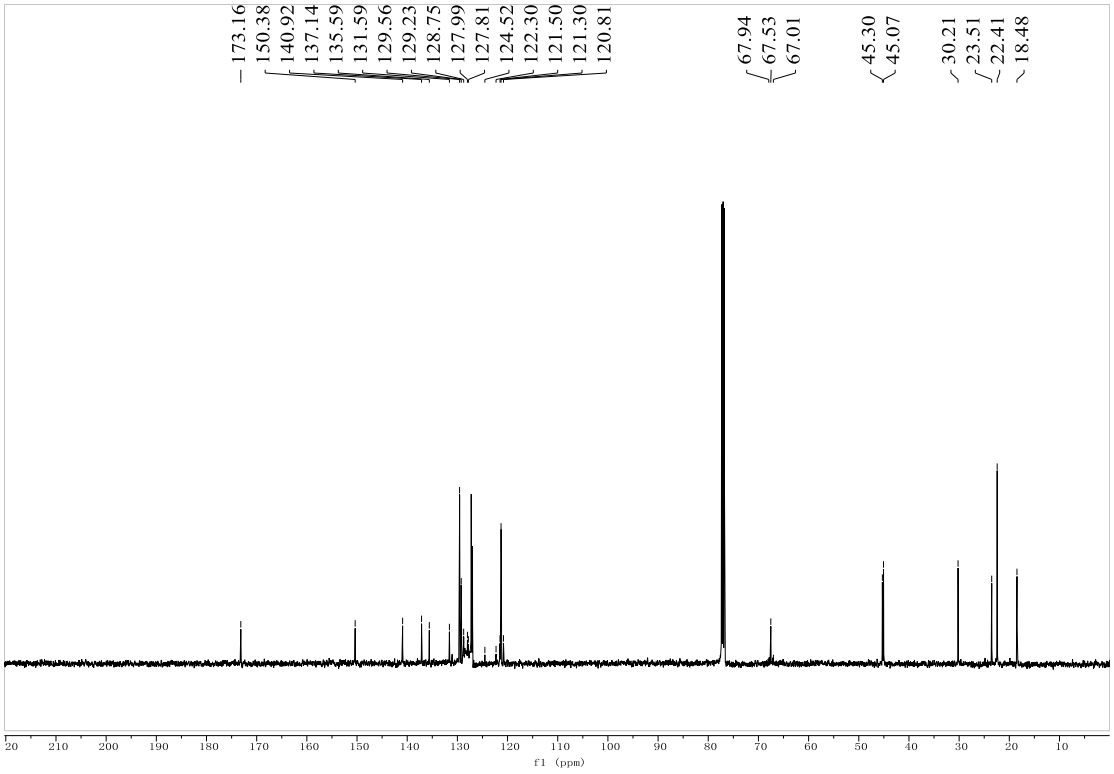


^{19}F NMR spectrum in $CDCl_3$.

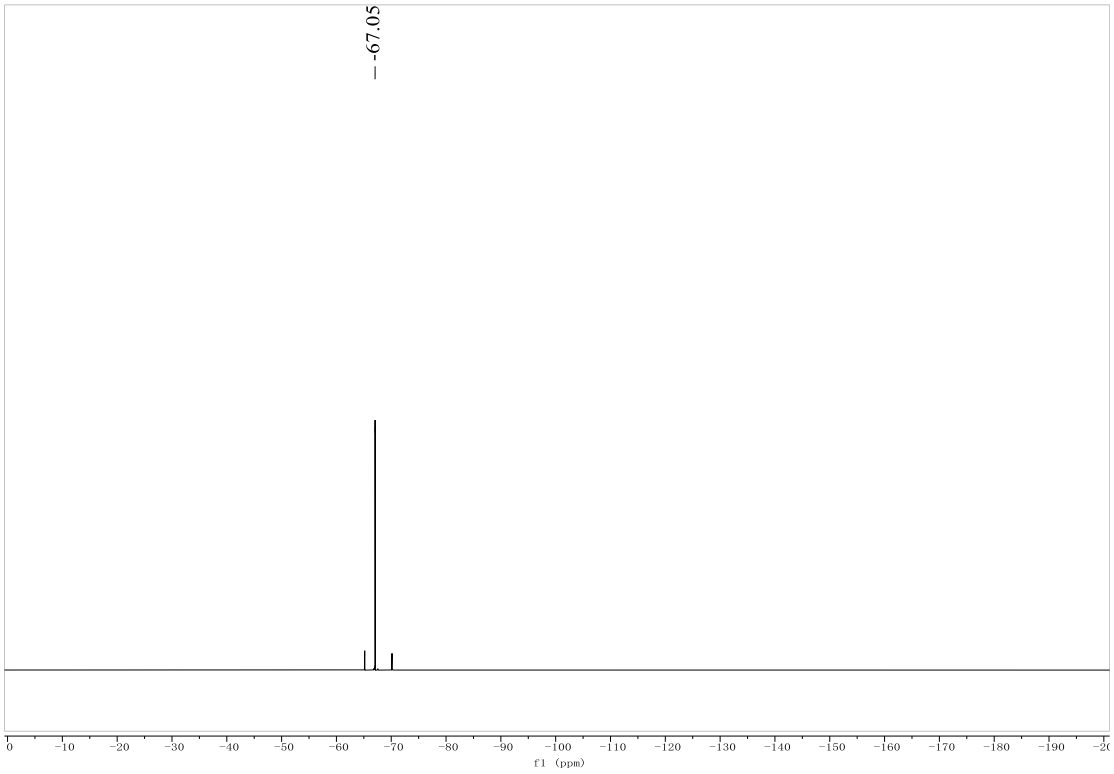
1-(4-isobutylphenyl)ethyl 4-((2*R*,3*R*)-2-methyl-3-phenyl-3-(trifluoromethyl)oxiran-2-yl)benzoate (44c)



^{1}H NMR spectrum in $CDCl_3$.

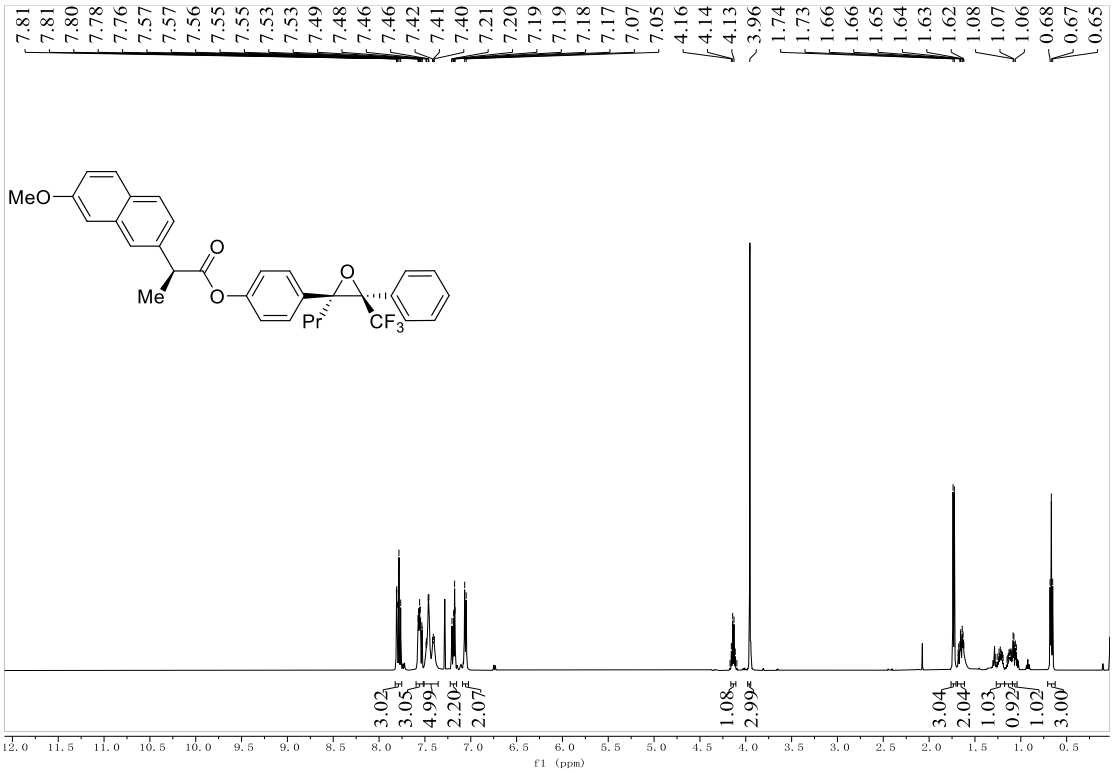


^{13}C NMR spectrum in $CDCl_3$.

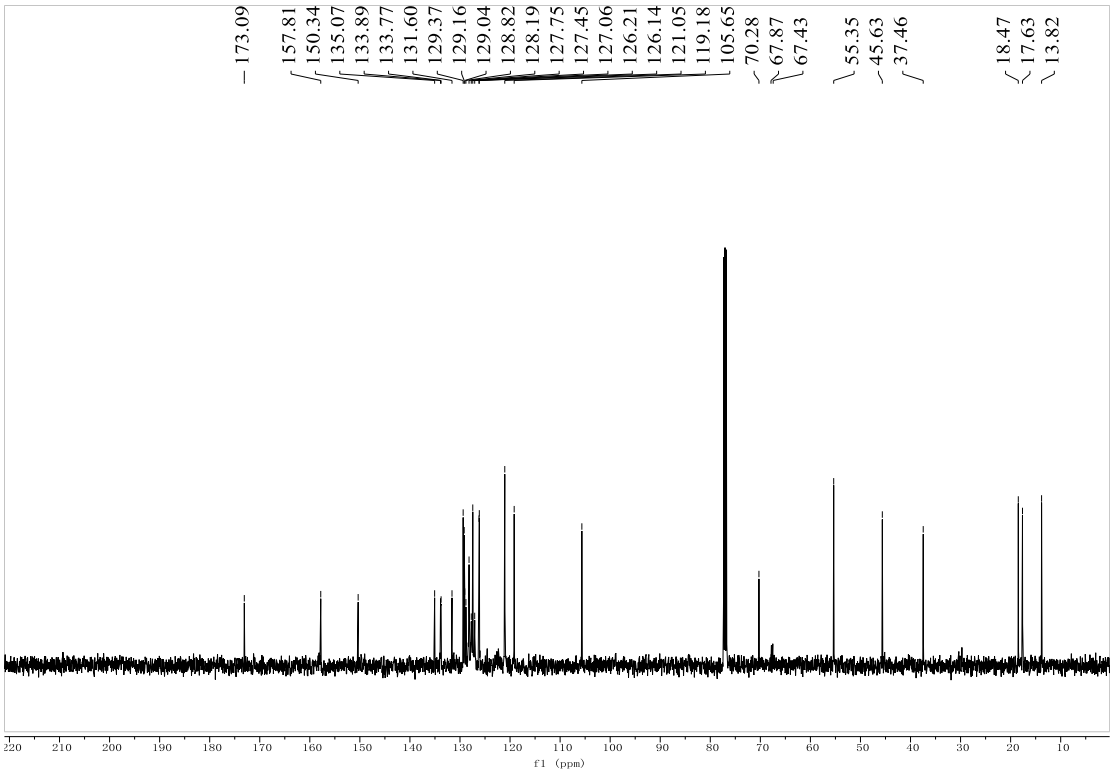


^{19}F NMR spectrum in $CDCl_3$.

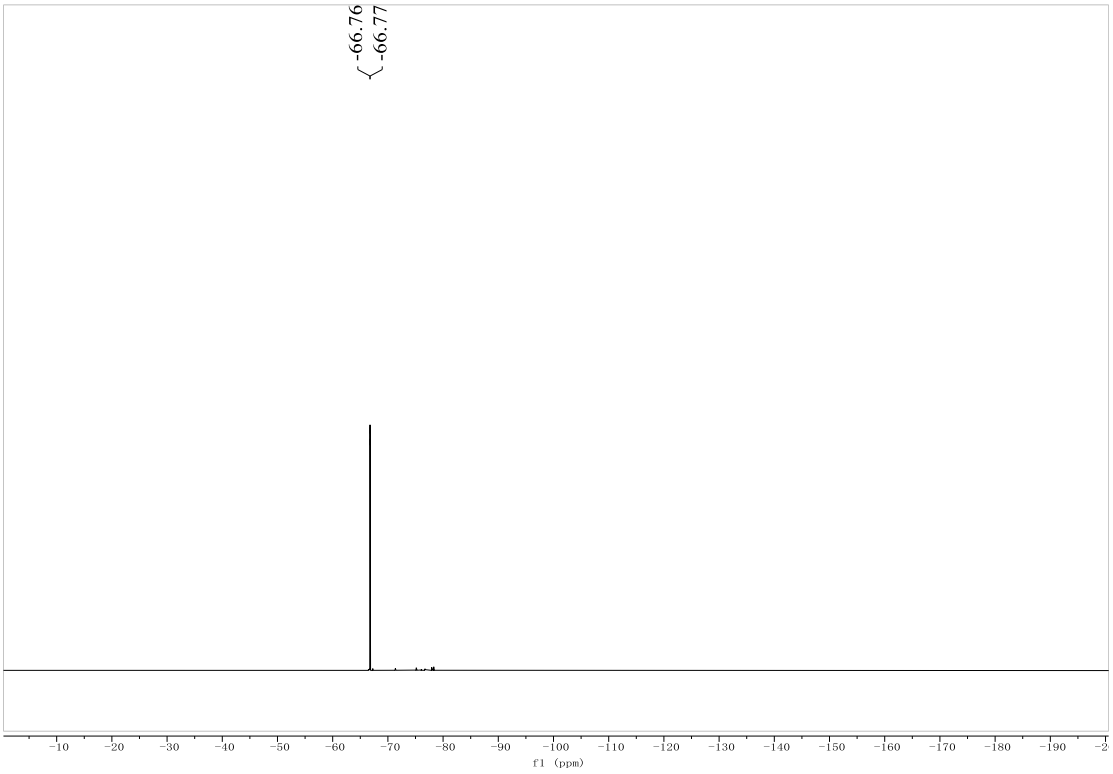
4-((2*R*,3*R*)-3-phenyl-2-propyl-3-(trifluoromethyl)oxiran-2-yl)phenyl (*S*)-2-(7-methoxynaphthalen-2-yl)propanoate (45c)



^{1}H NMR spectrum in $CDCl_3$.

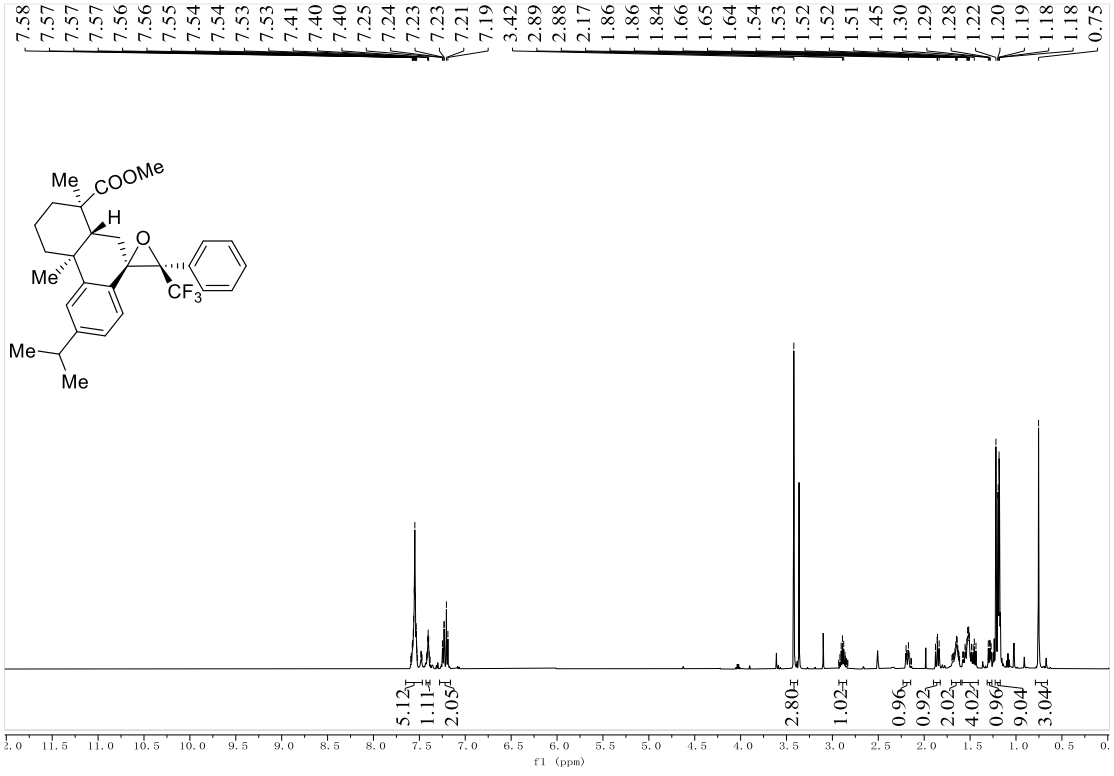


^{13}C NMR spectrum in $CDCl_3$.

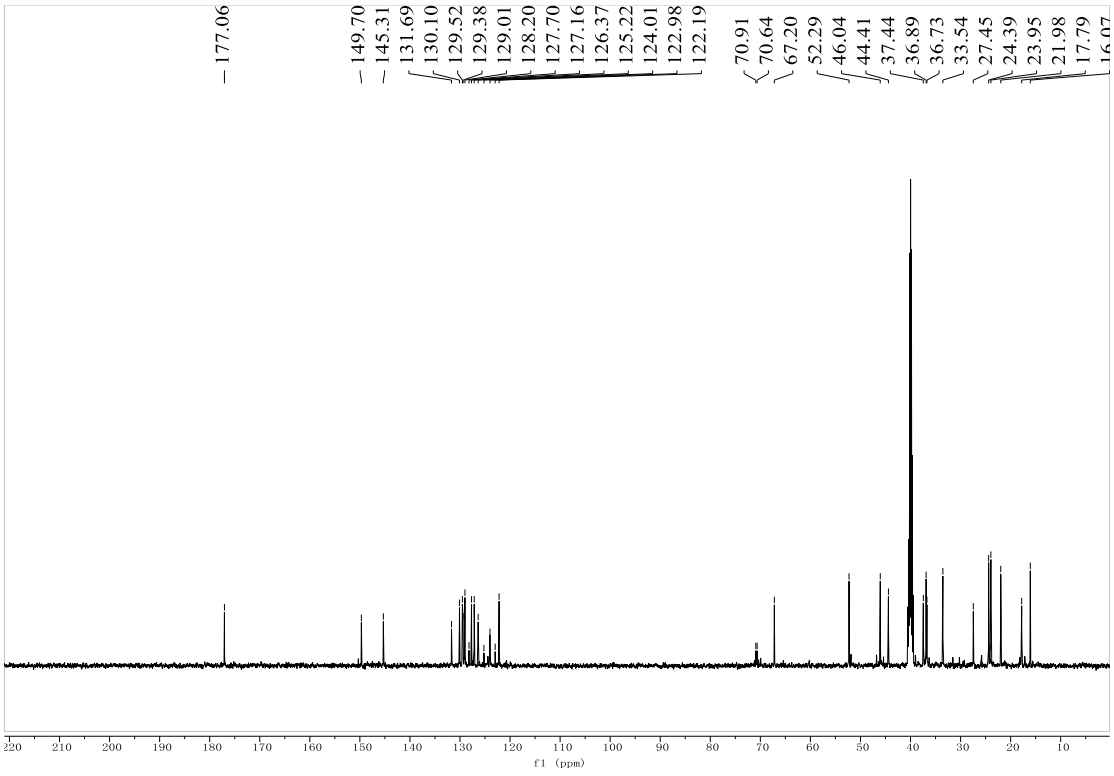


^{19}F NMR spectrum in $CDCl_3$.

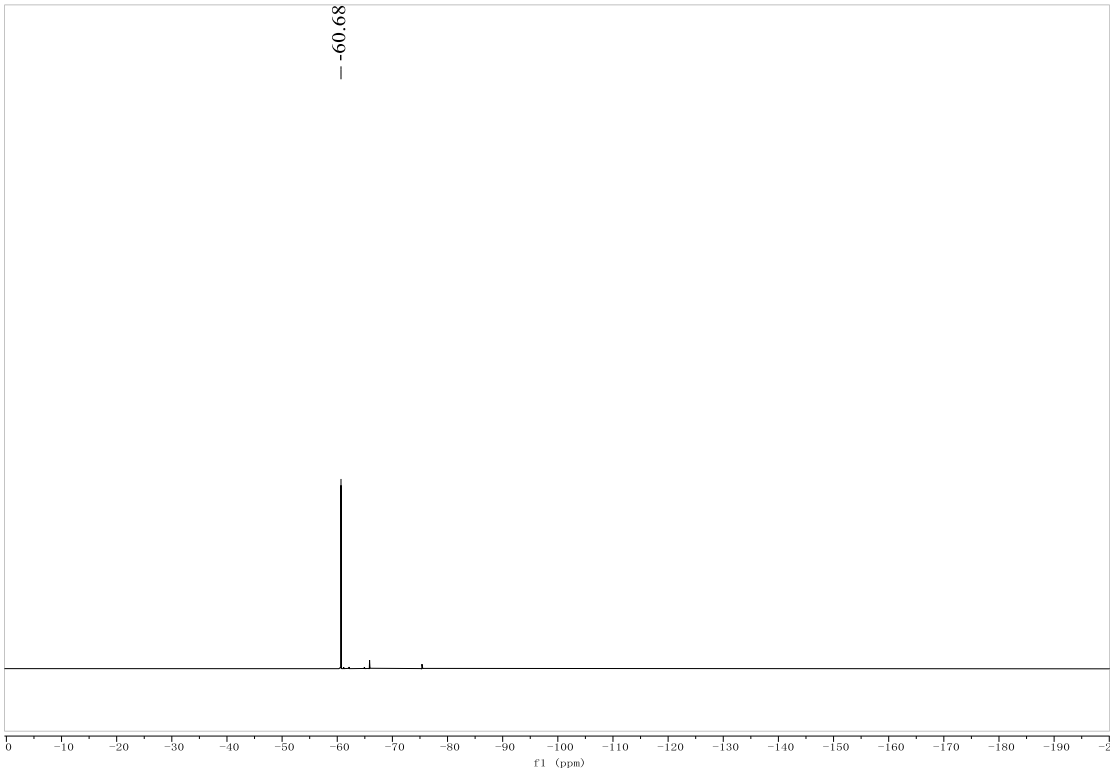
methyl (2*S*,3*S*,10*a*'*S*)-6'-isopropyl-1',4*a*'-dimethyl-3-phenyl-3-(trifluoromethyl)-2',3',4',4*a*',10',10*a*'-hexahydro-1'*H*-spiro[oxirane-2,9'-phenanthrene]-1'-carboxylate (46c)



^{1}H NMR spectrum in DMSO-d_6.

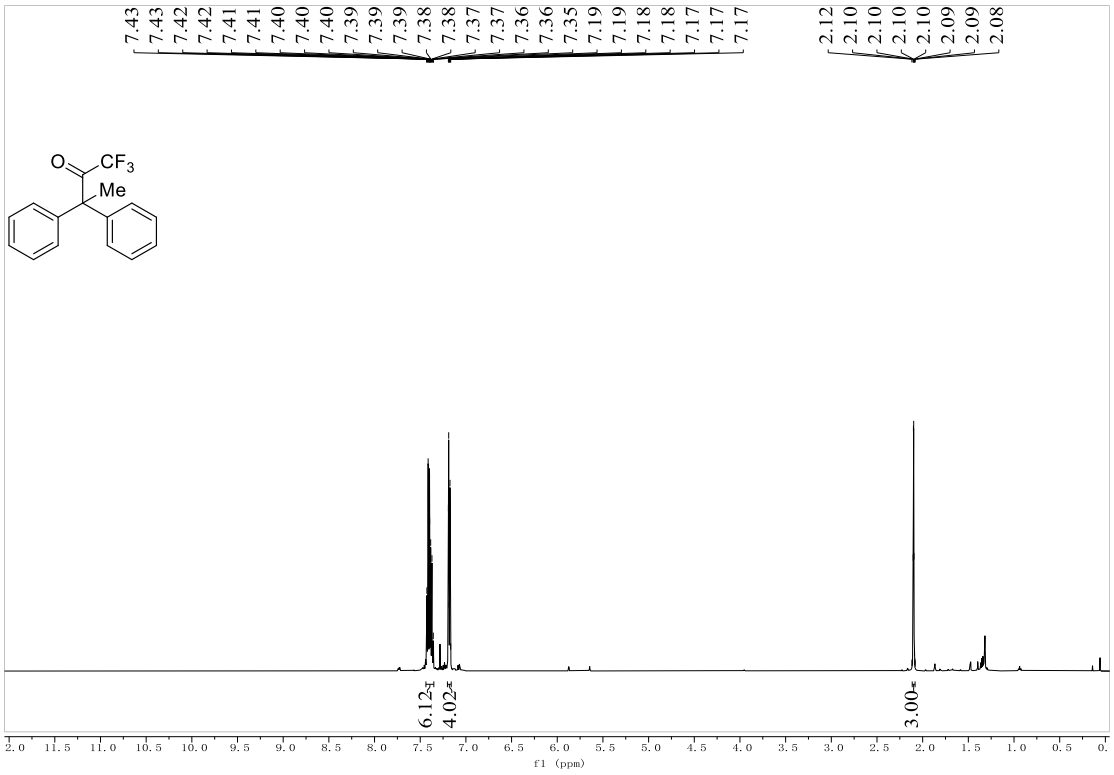


^{13}C NMR spectrum in DMSO-d_6.

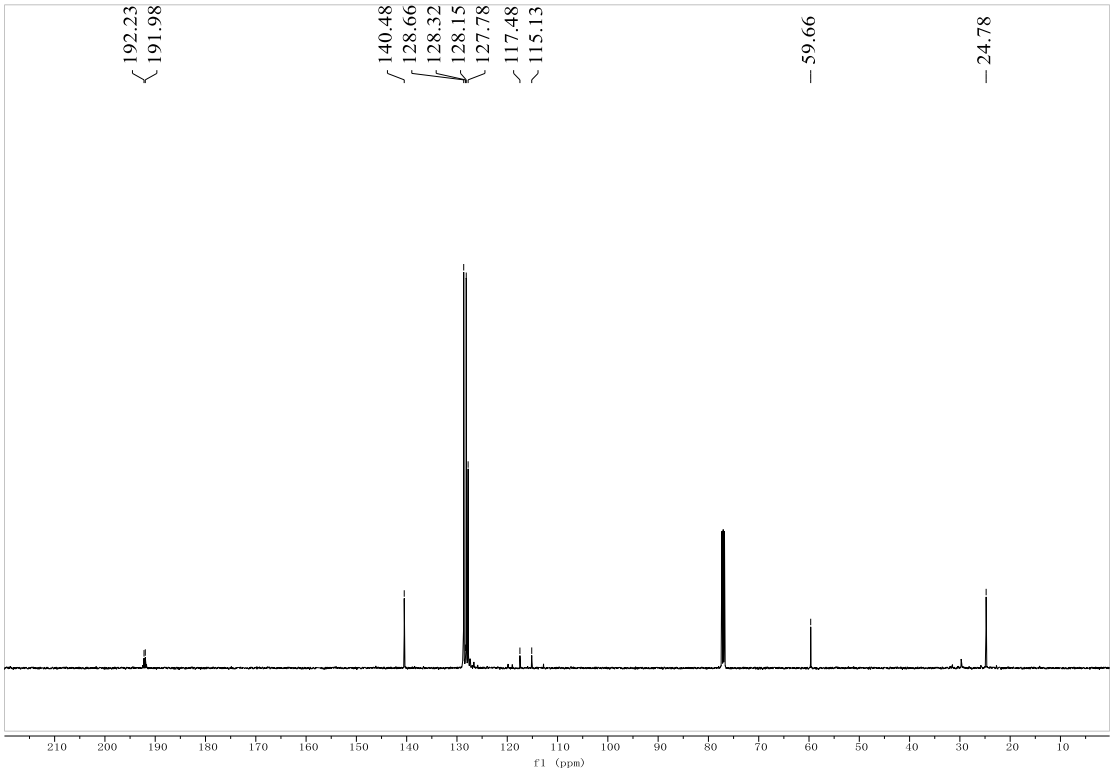


^{19}F NMR spectrum in DMSO-d_6.

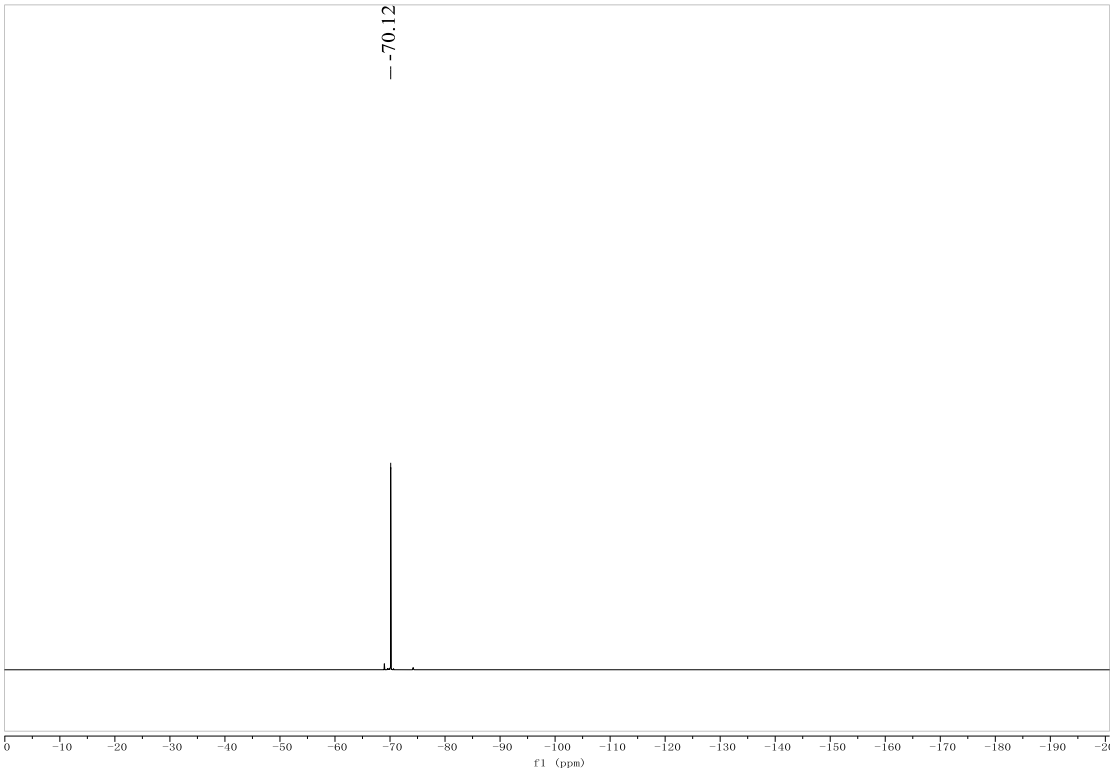
1,1,1-trifluoro-3,3-diphenylbutan-2-one (26g)



^{1}H NMR spectrum in $CDCl_3$.

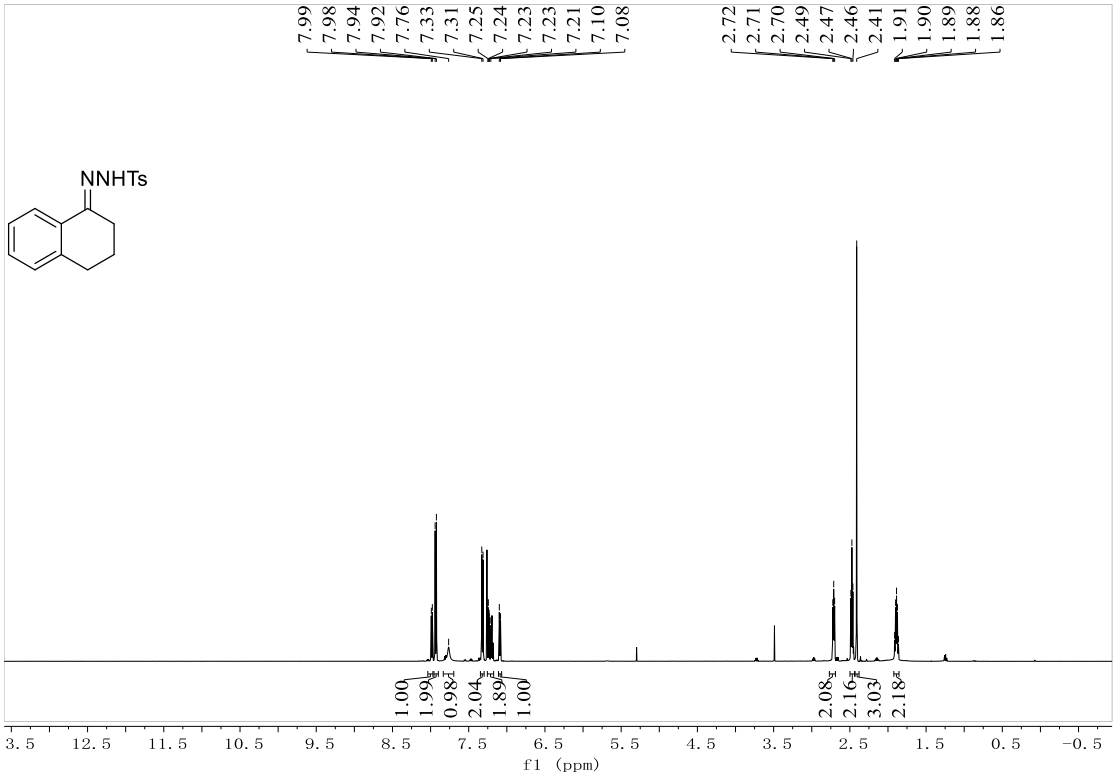


^{13}C NMR spectrum in $CDCl_3$.

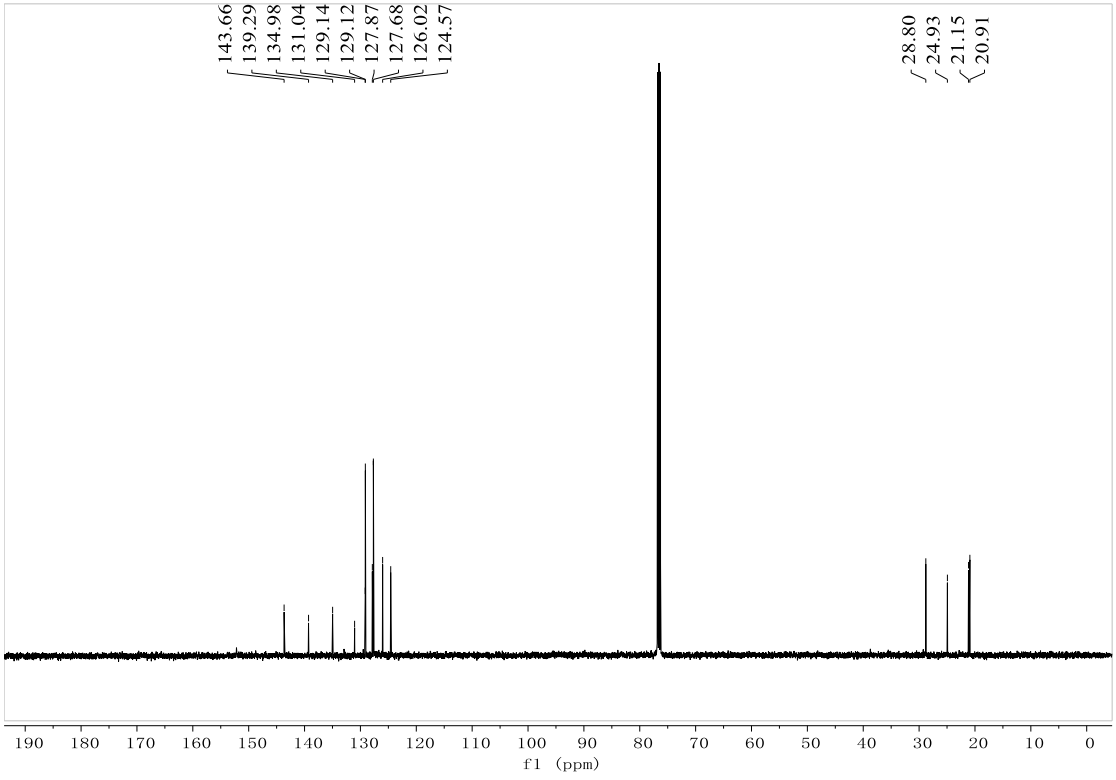


^{19}F NMR spectrum in $CDCl_3$.

***N'*-(3,4-Dihydronaphthalen-1(2*H*)-ylidene)-4-methylbenzenesulfonohydrazide (1a):**

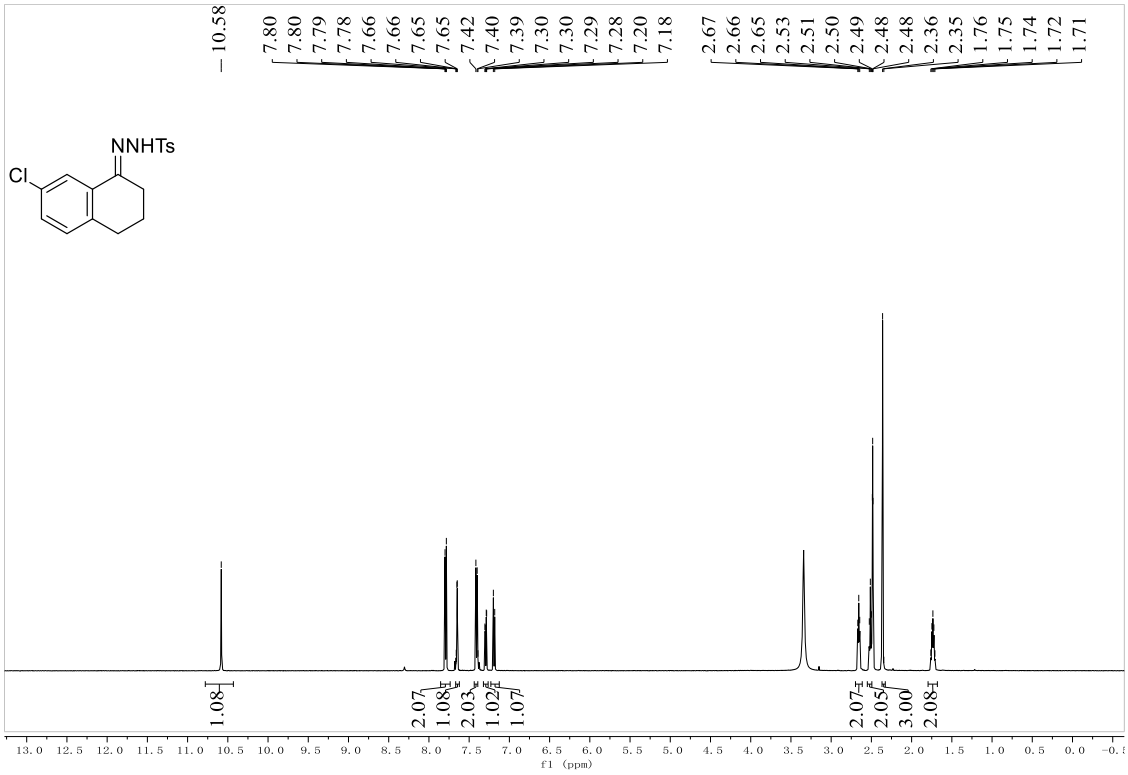


^{1}H NMR spectrum in $CDCl_3$.



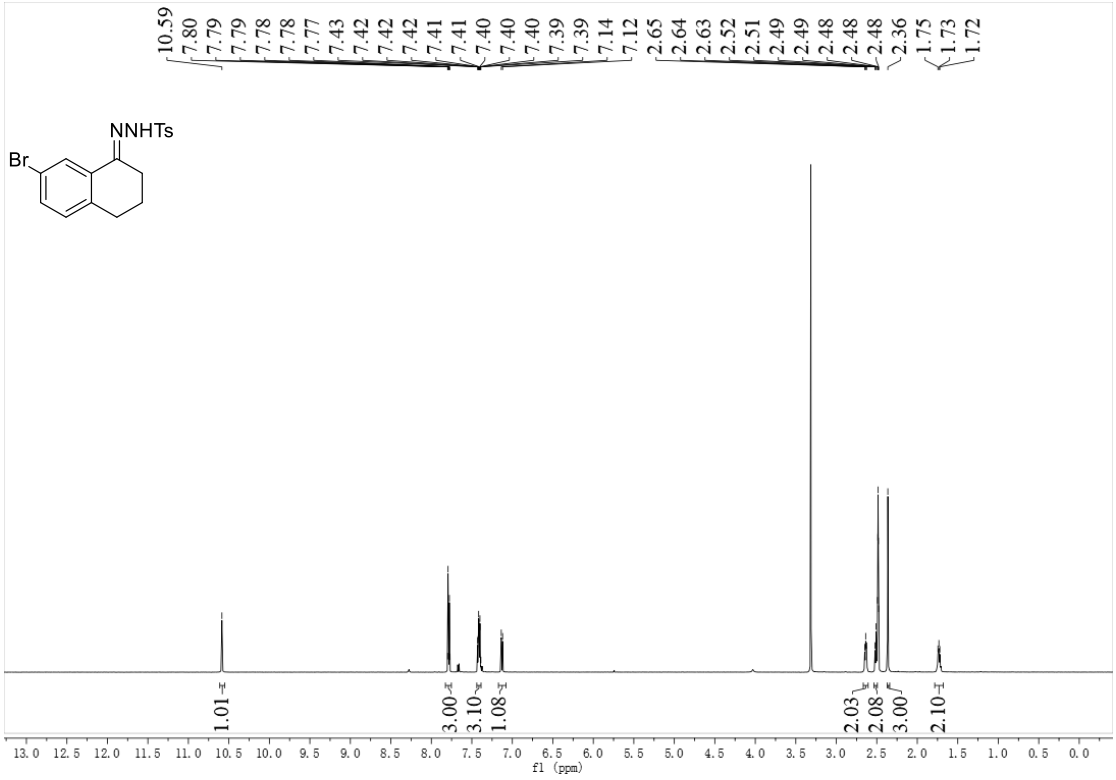
^{13}C NMR spectrum in $CDCl_3$.

***N'*-(7-Chloro-3,4-dihydronaphthalen-1(2*H*)-ylidene)-4-methylbenzenesulfonohydrazide (2a)**



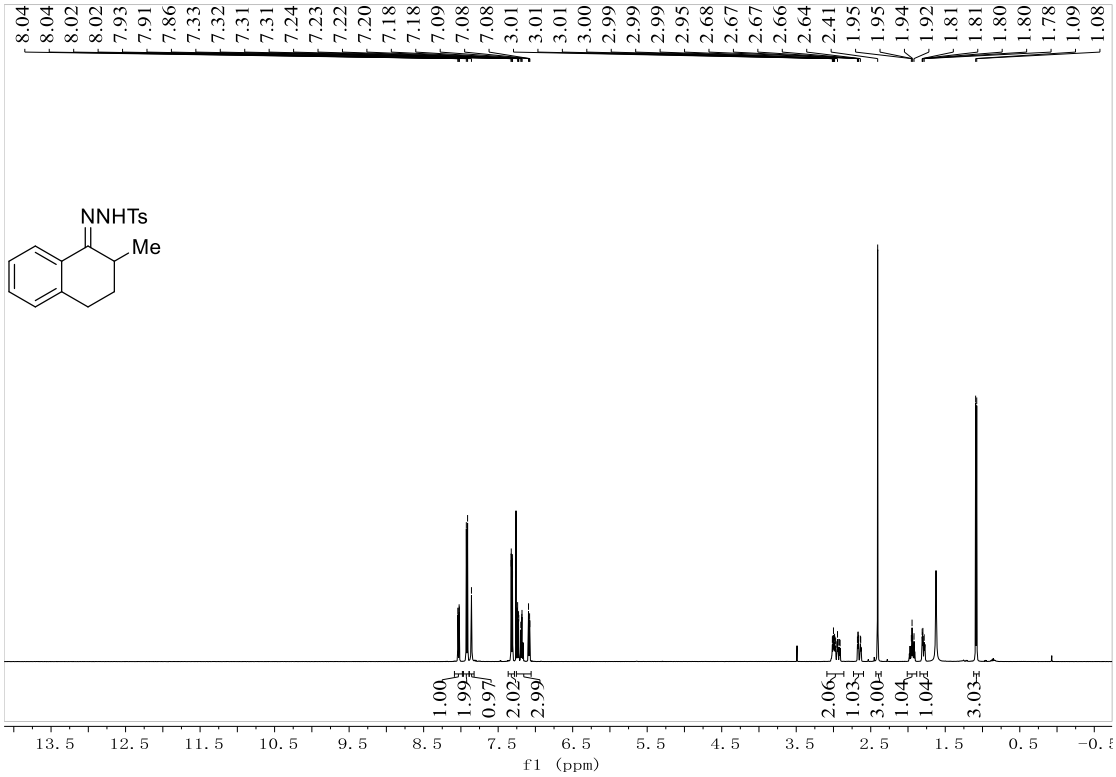
^{1}H NMR spectrum in $CDCl_3$.

***N'*-(7-Bromo-3,4-dihydronaphthalen-1(2*H*)-ylidene)-4-methylbenzenesulfonohydrazide (3a)**



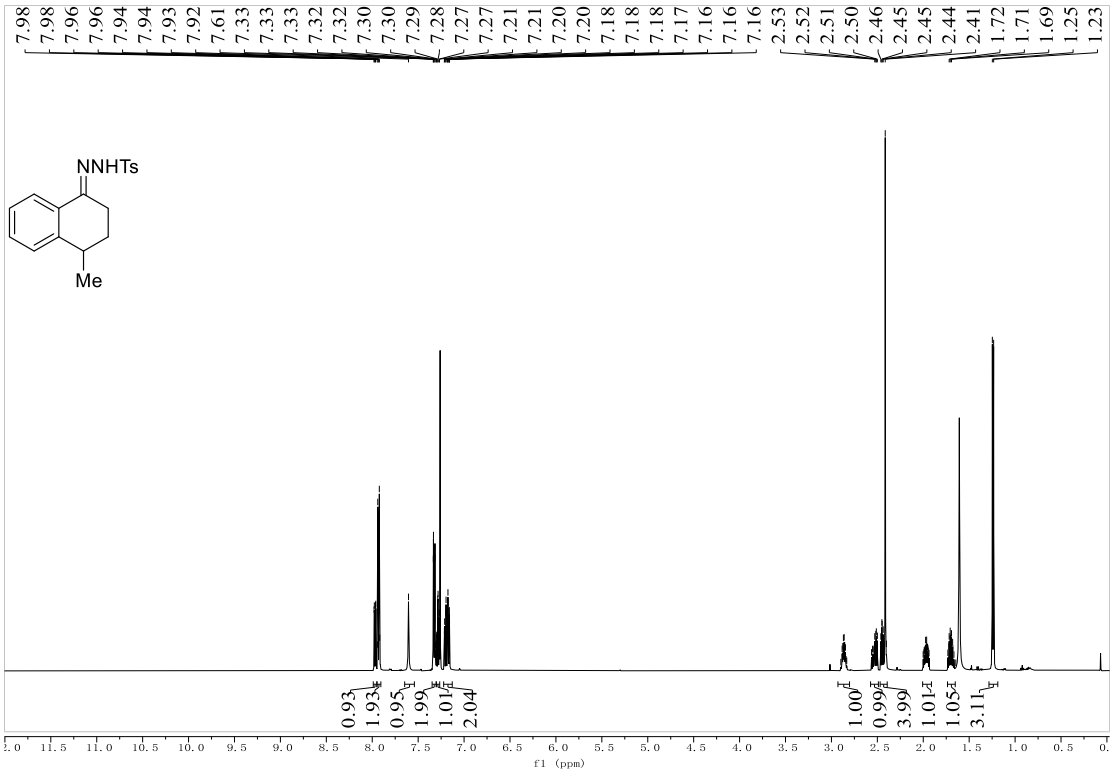
^{1}H NMR spectrum in $CDCl_3$.

(*Z*)-4-methyl-N'-(2-methyl-3,4-dihydronaphthalen-1(2*H*)-ylidene)benzenesulfonohydrazide(4a)



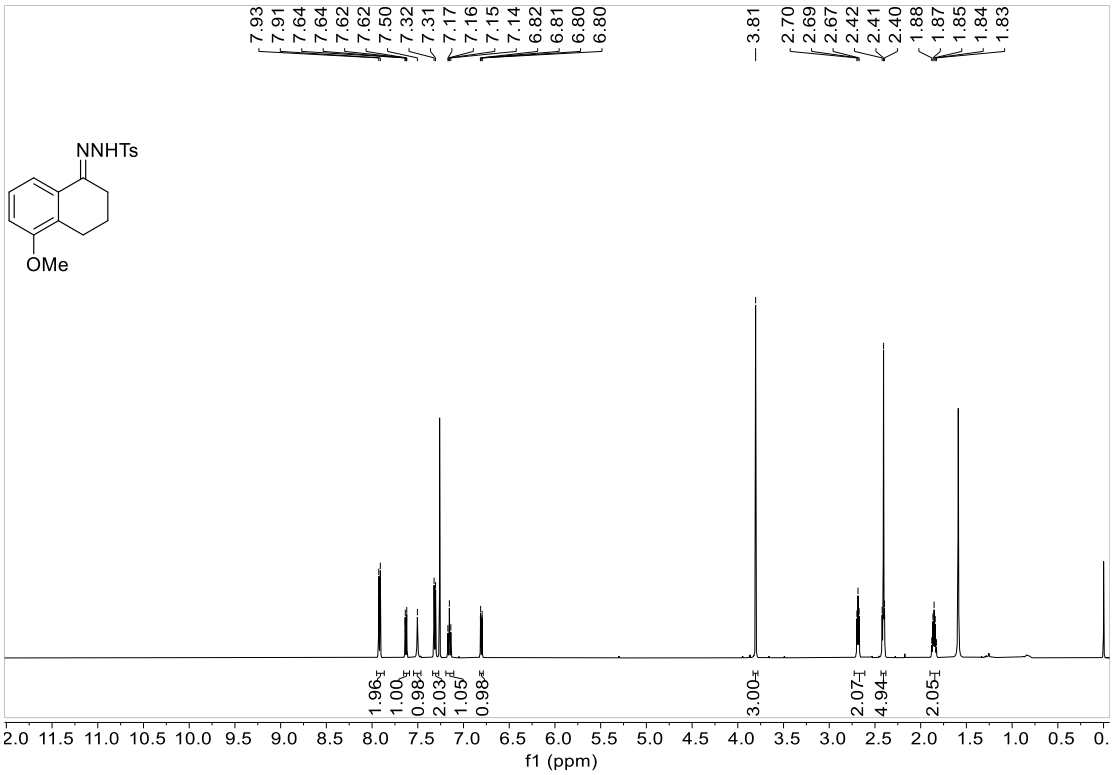
^{1}H NMR spectrum in $CDCl_3$.

4-Methyl-*N'*-(4-methyl-3,4-dihydronaphthalen-1(2*H*)-ylidene)benzenesulfonohydrazide (5a)

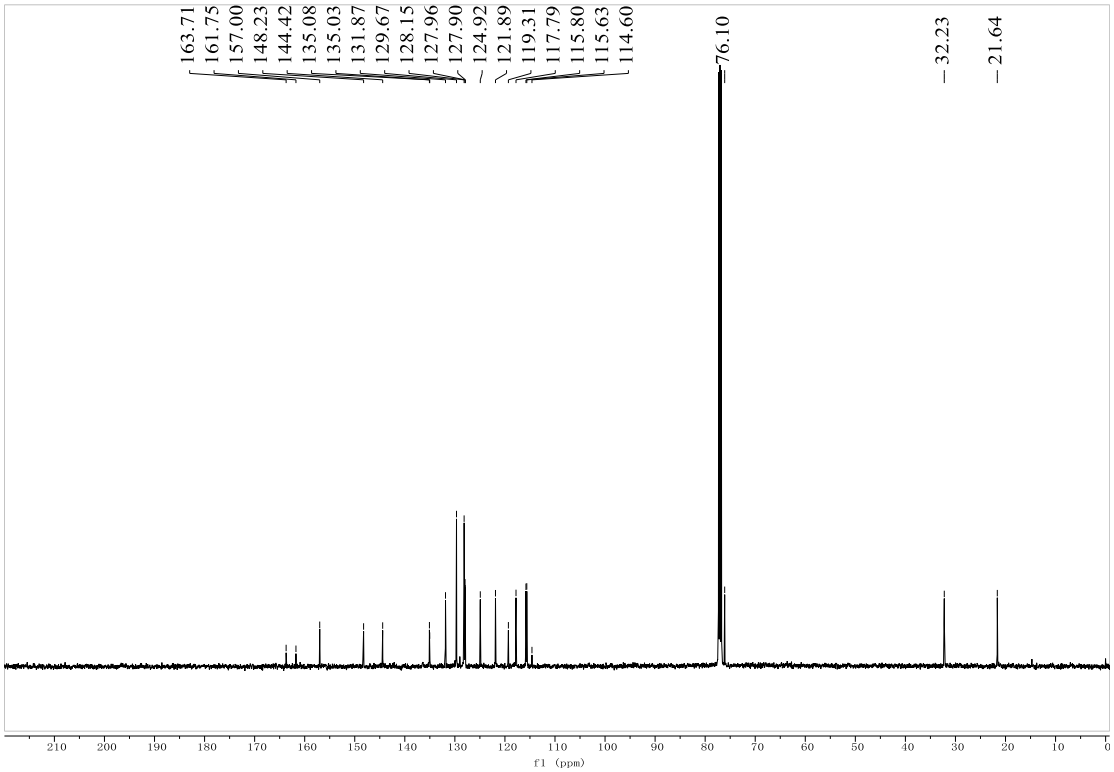


^{1}H NMR spectrum in $CDCl_3$.

(*E*)-*N'*-(5-methoxy-3,4-dihydronaphthalen-1(2*H*)-ylidene)-4-methylbenzenesulfonohydrazide(7a)

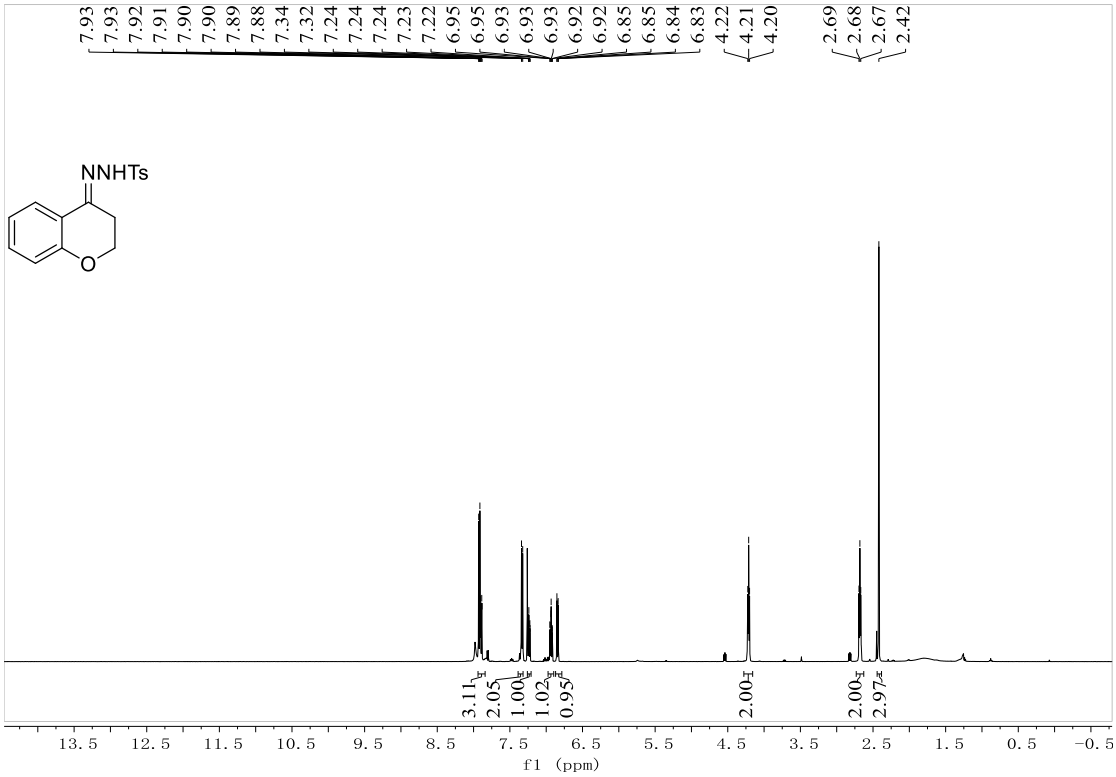


^{1}H NMR spectrum in $CDCl_3$.

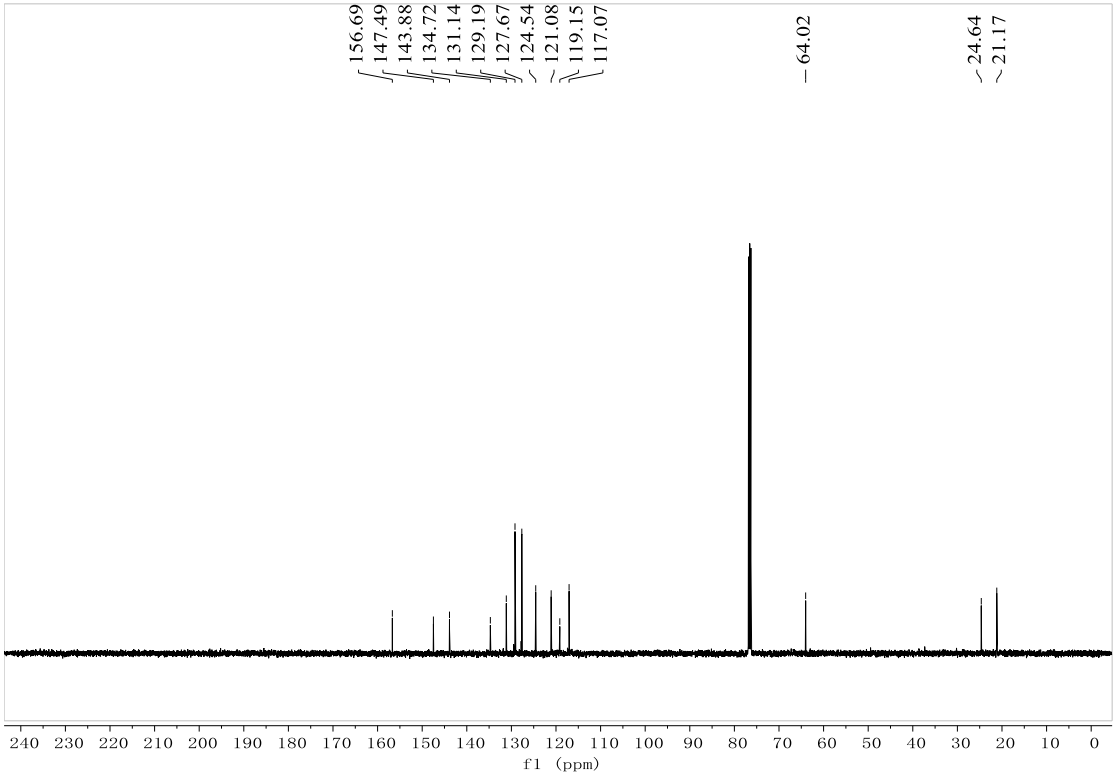


^{13}C NMR spectrum in $CDCl_3$.

***N'*-(chroman-4-ylidene)-4-methylbenzenesulfonohydrazide (9a)**

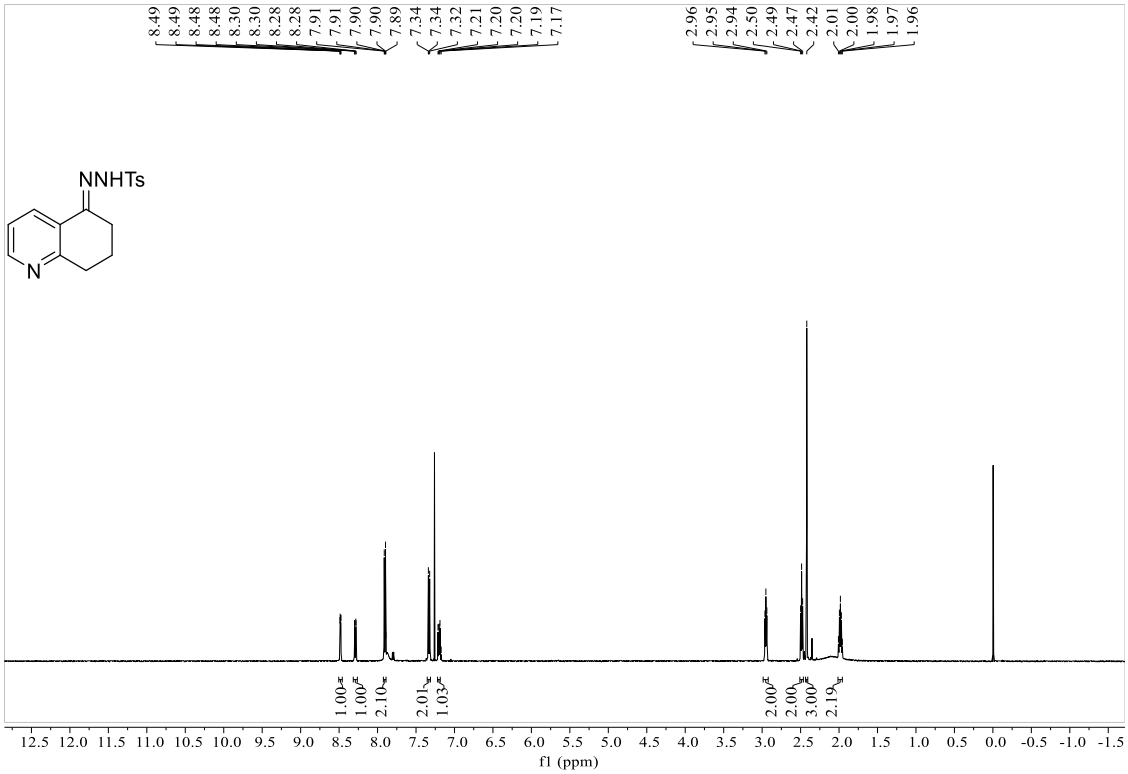


^{1}H NMR spectrum in $CDCl_3$.

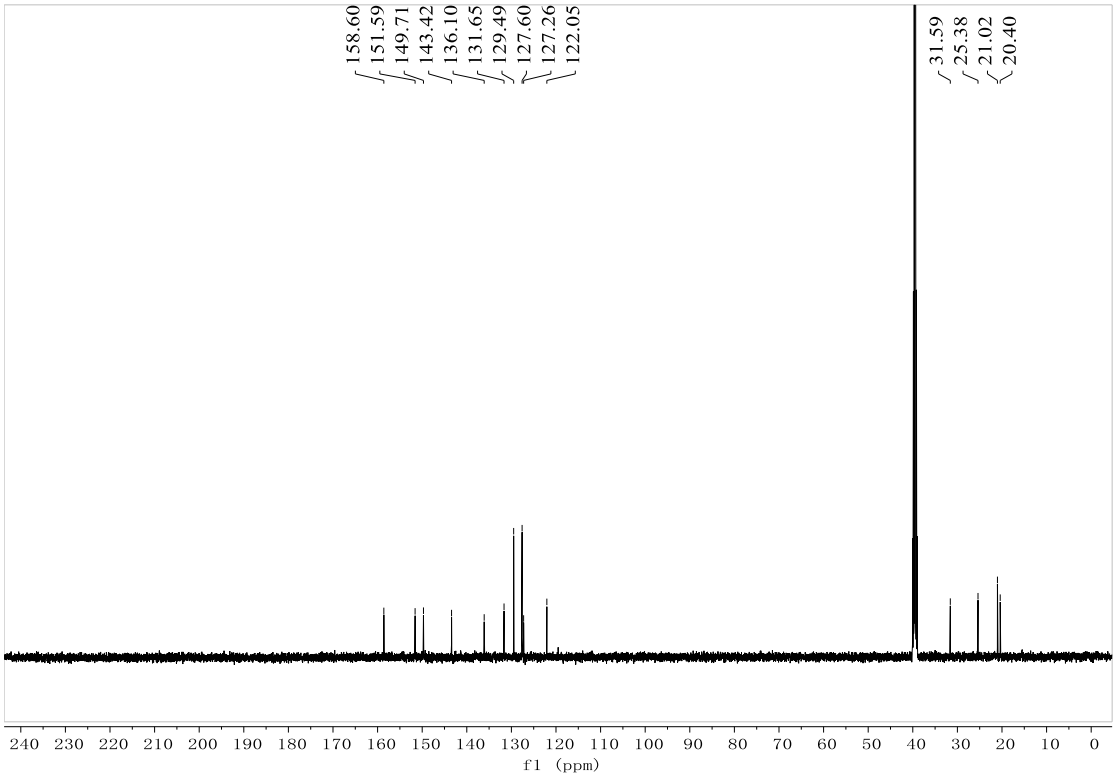


^{13}C NMR spectrum in $CDCl_3$.

(*Z*)-*N*'-(7,8-dihydroquinolin-5(6*H*)-ylidene)-4-methylbenzenesulfonohydrazide(11a)

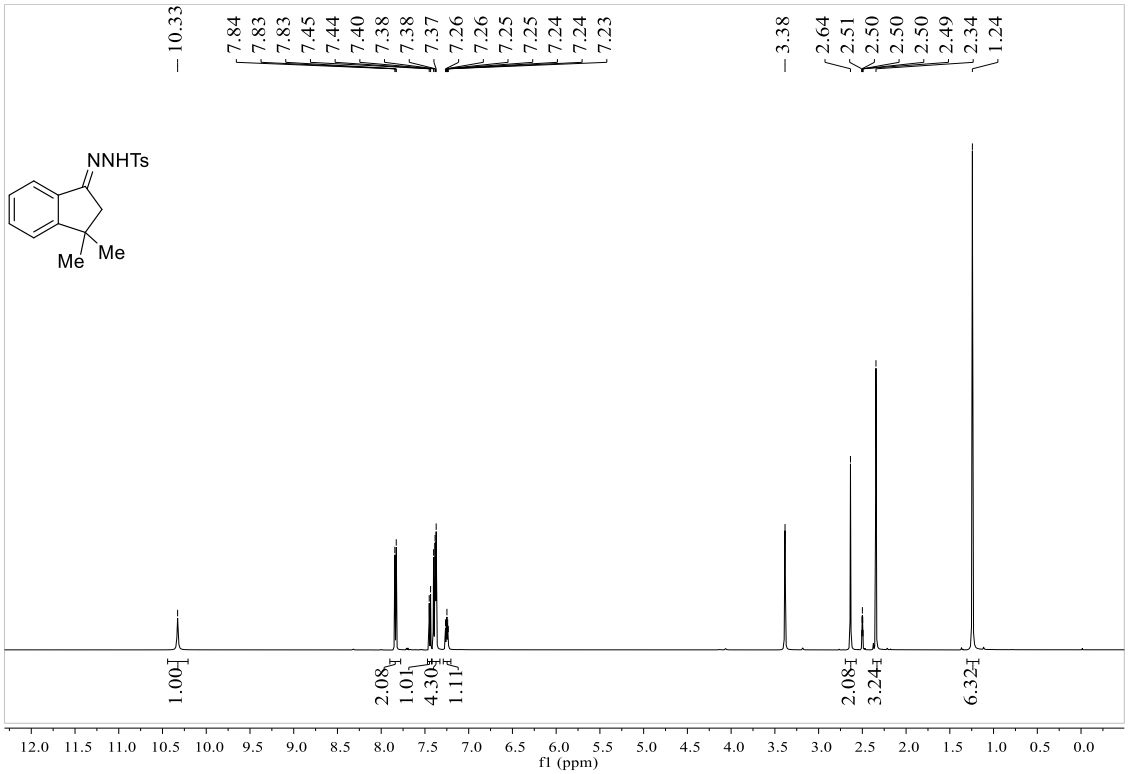


^{1}H NMR spectrum in $CDCl_3$.

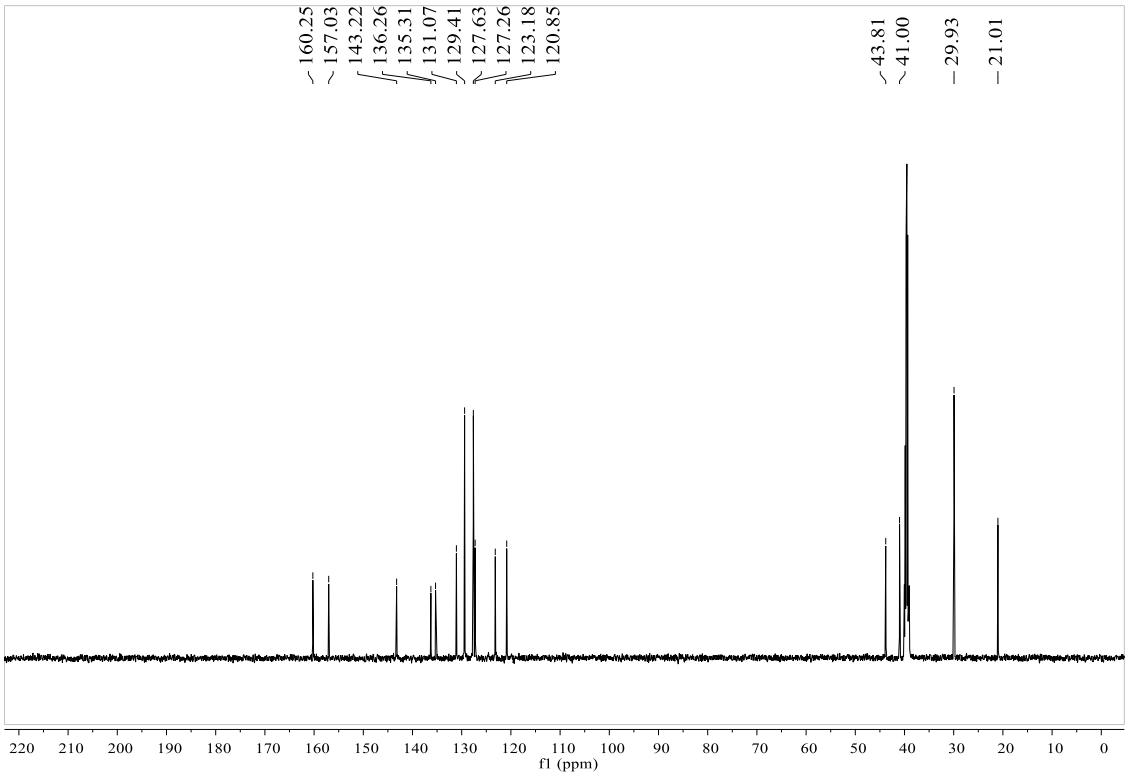


^{13}C NMR spectrum in DMSO-d_6.

***N*'-(3,3-dimethyl-2,3-dihydro-1*H*-inden-1-ylidene)-4-methylbenzenesulfonohydrazide (12a)**

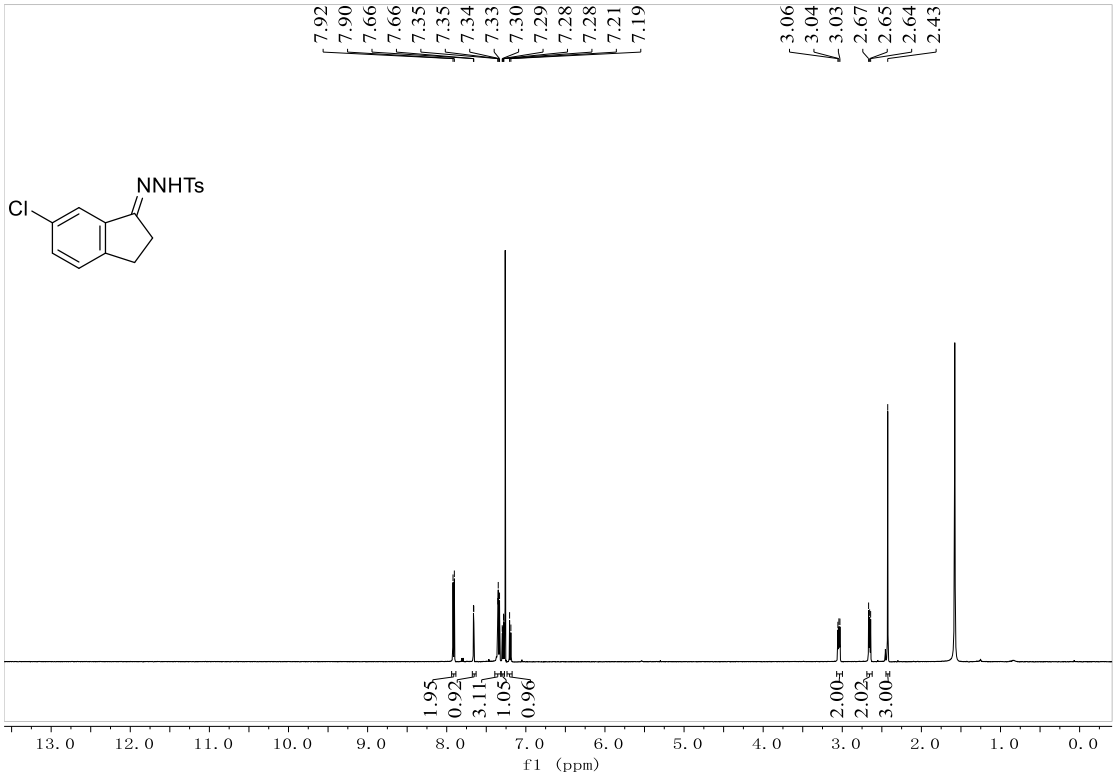


^{1}H NMR spectrum in DMSO-d$_6$.



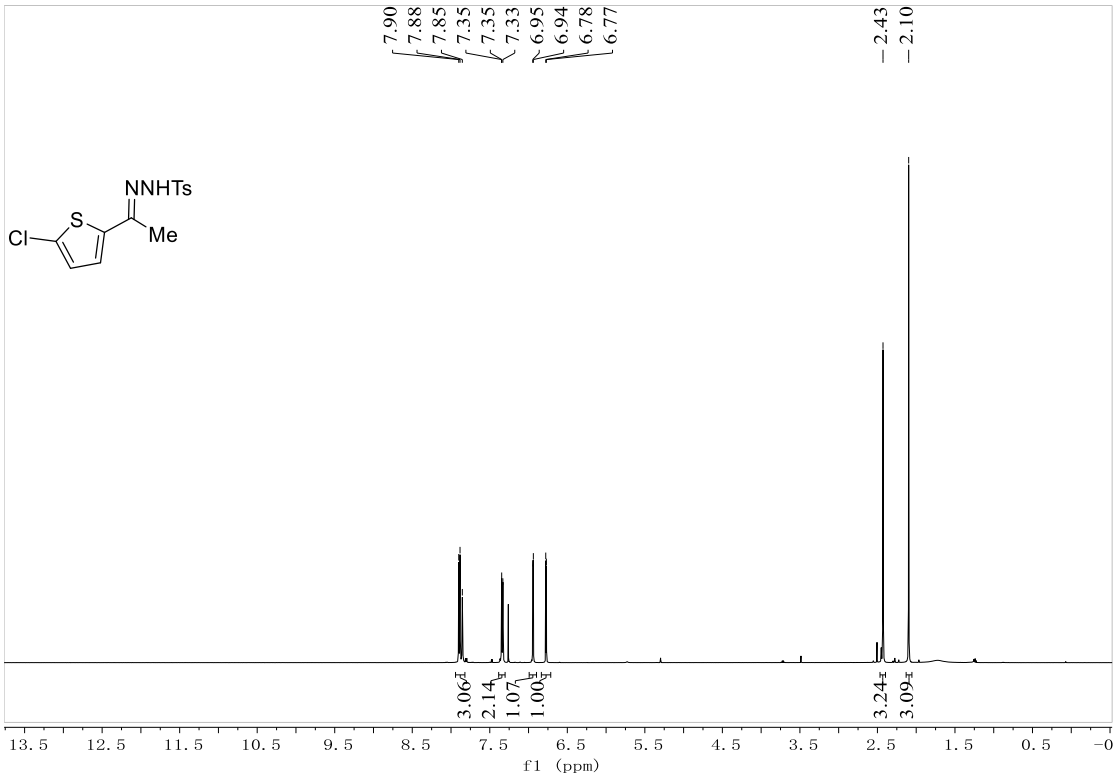
^{13}C NMR spectrum in DMSO-d$_6$.

(*Z*)-*N*'-(6-chloro-2,3-dihydro-1H-inden-1-ylidene)-4-methylbenzenesulfonohydrazide(13a)

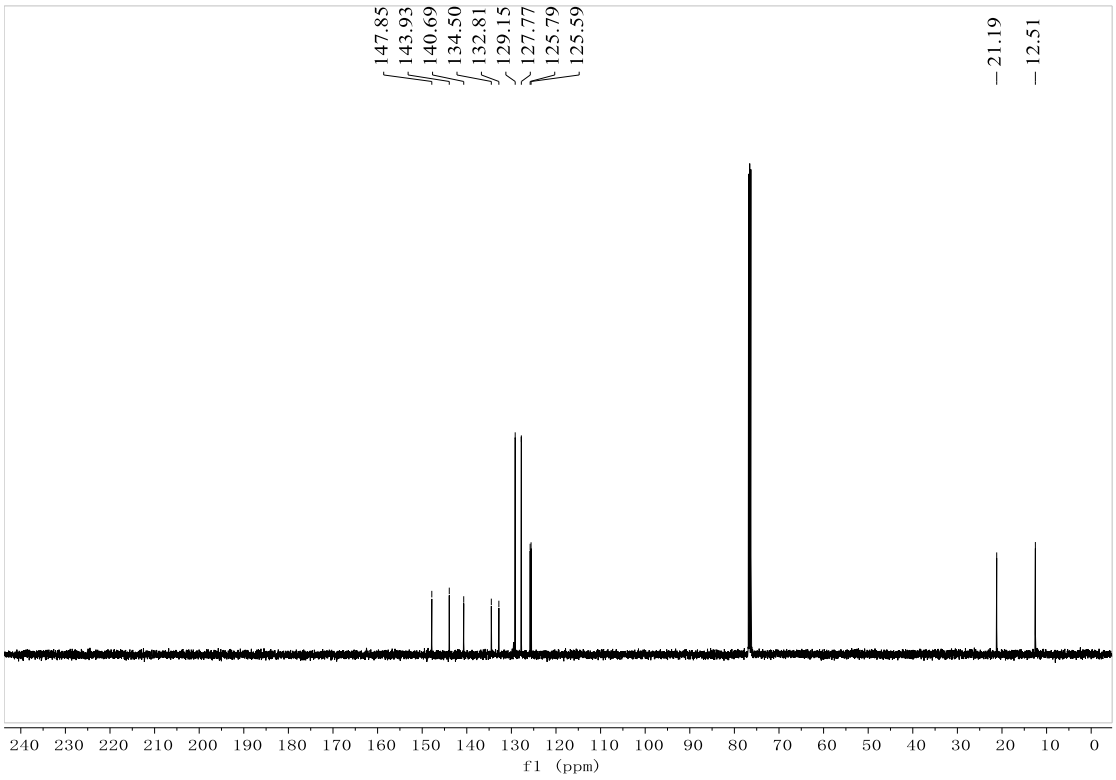


^{1}H NMR spectrum in $CDCl_3$.

(*E*)-*N*'-(1-(5-chlorothiophen-2-yl)ethylidene)-4-methylbenzenesulfonohydrazide(15a)

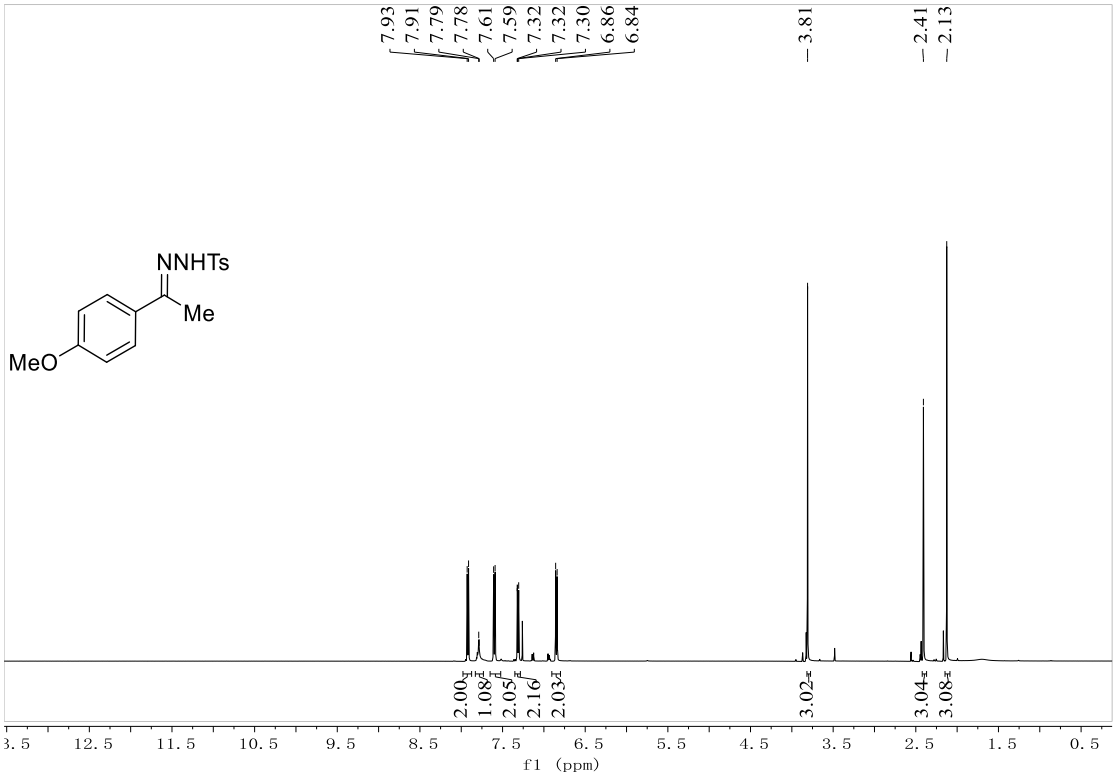


^{1}H NMR spectrum in $CDCl_3$.



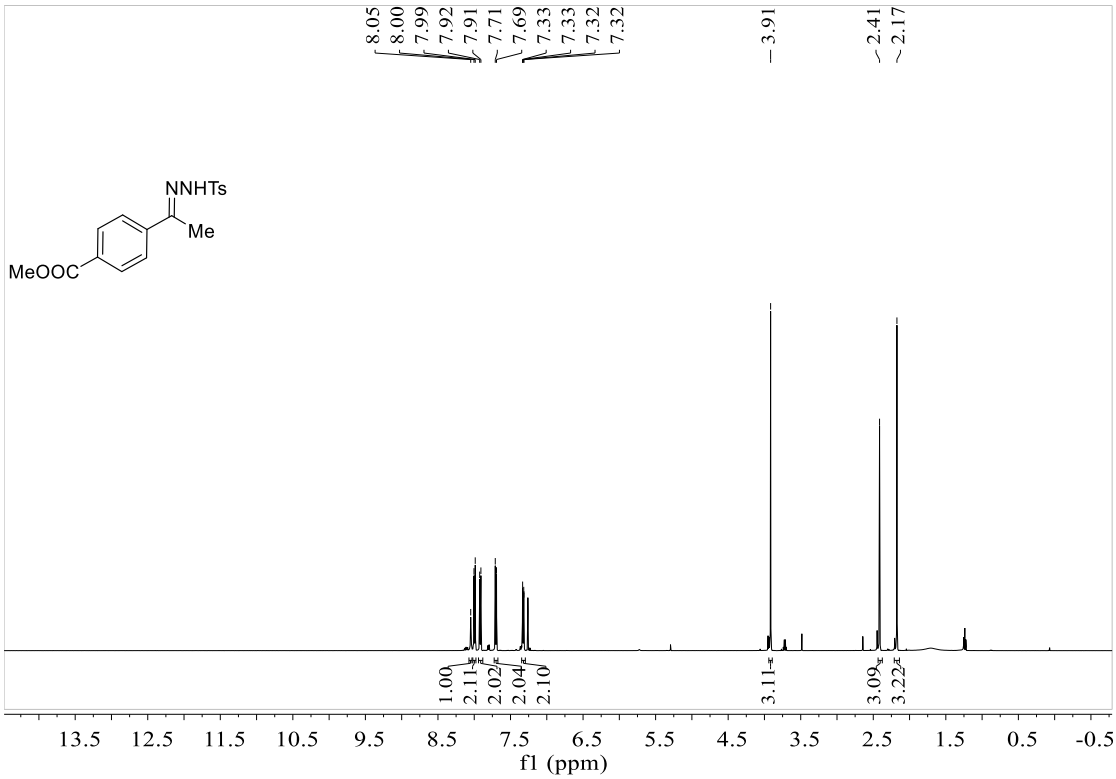
^{13}C NMR spectrum in $CDCl_3$.

(*Z*)-*N*'-(1-(4-methoxyphenyl)ethylidene)-4-methylbenzenesulfonohydrazide(16a)

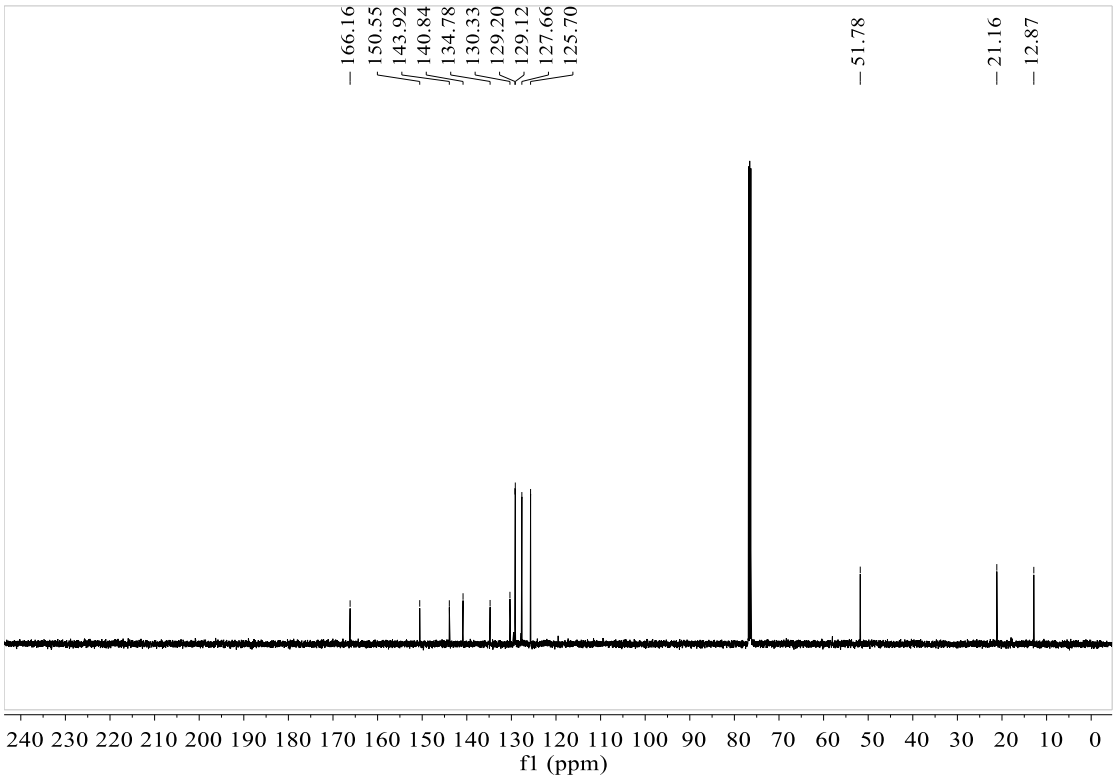


^{1}H NMR spectrum in $CDCl_3$.

methyl (*Z*)-4-(1-(2-tosylhydrazineylidene)ethyl)benzoate(17a)

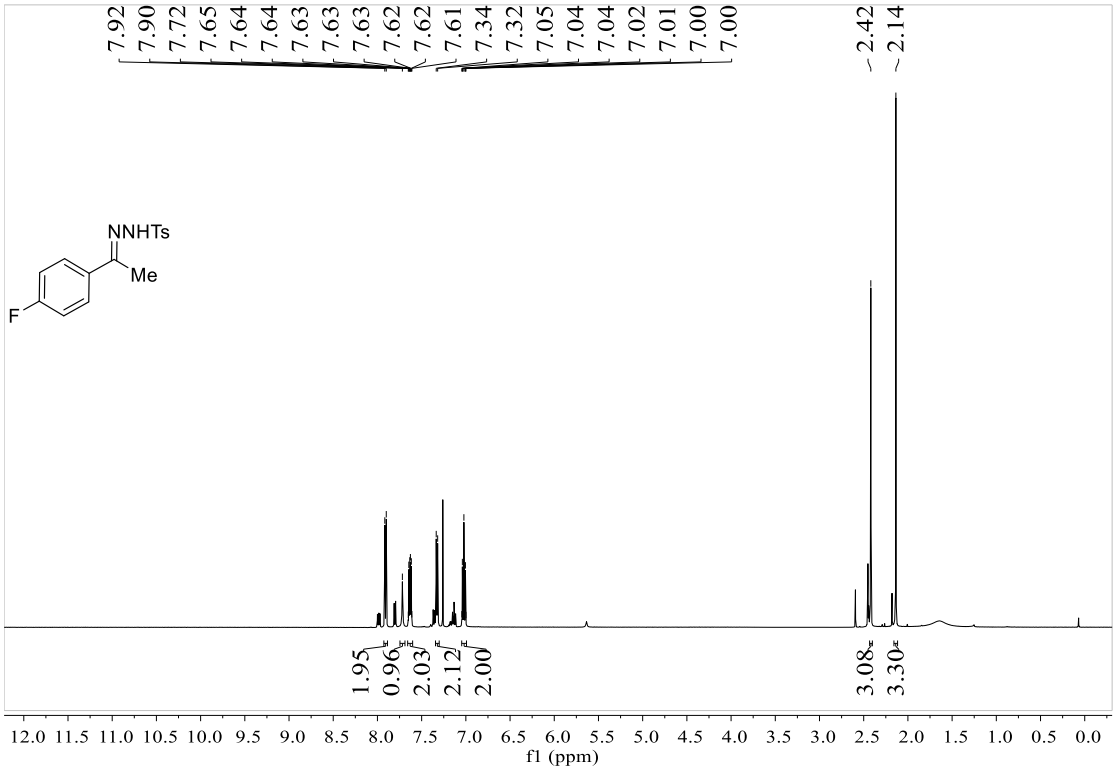


^{1}H NMR spectrum in $CDCl_3$.



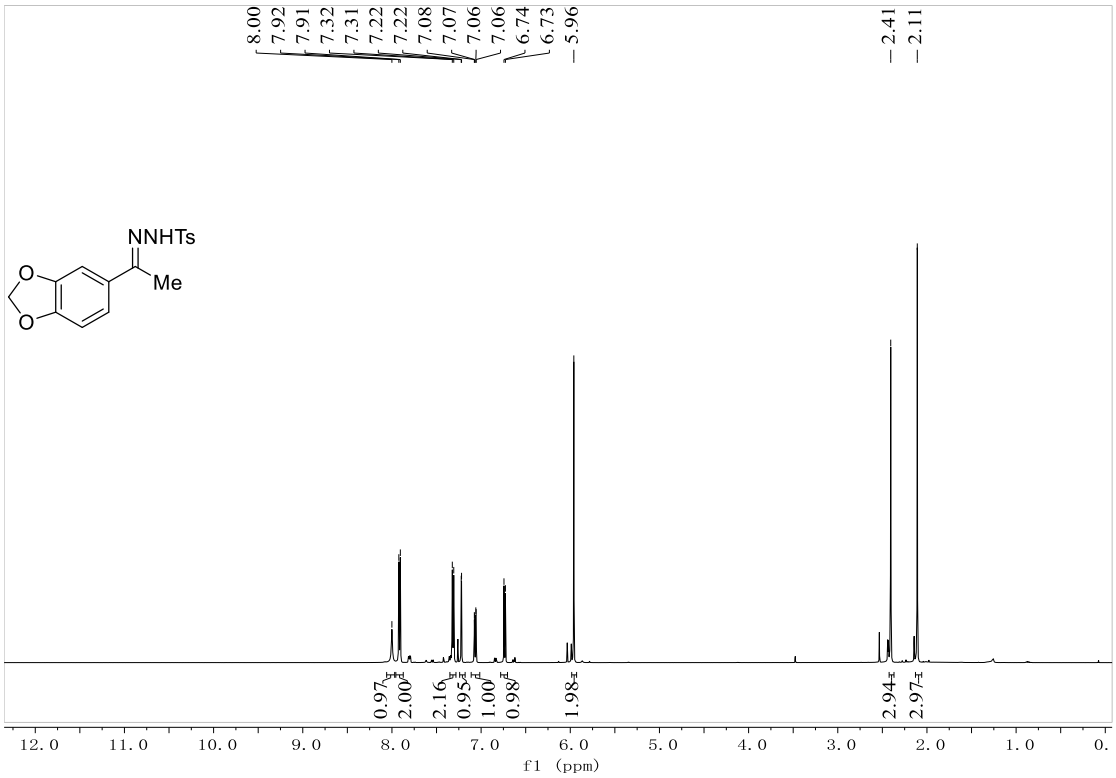
^{13}C NMR spectrum in $CDCl_3$.

***N'*-(1-(4-fluorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide(18a)**



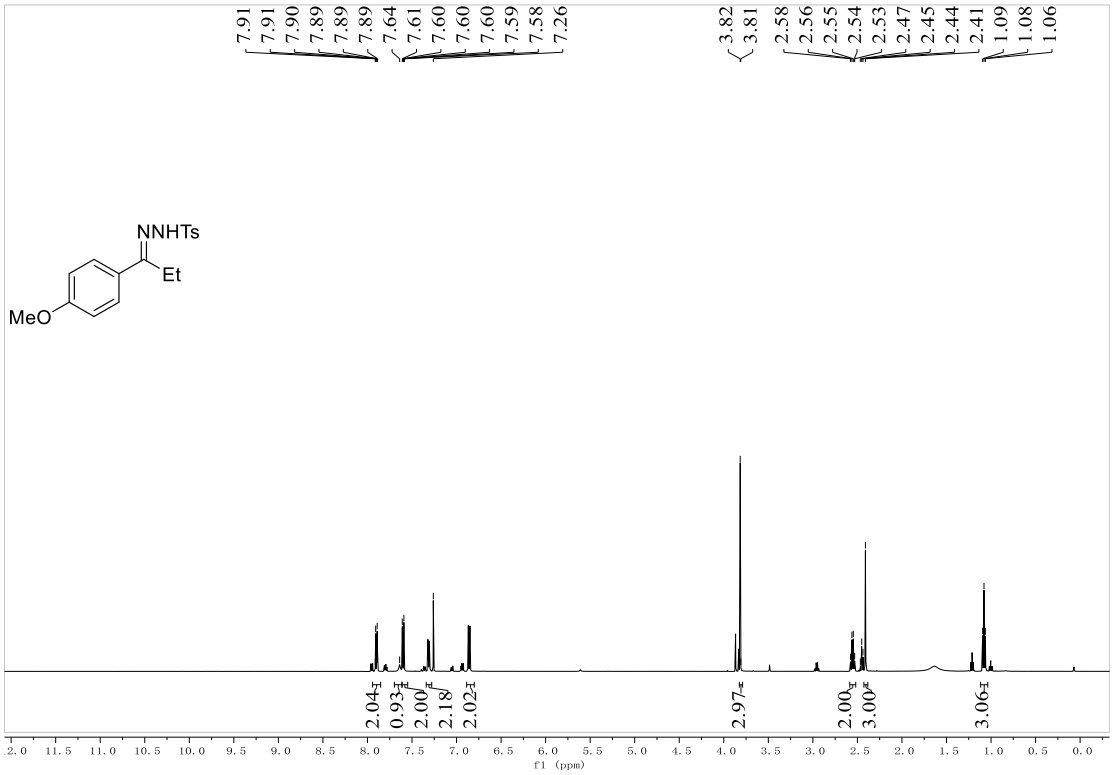
^{1}H NMR spectrum in $CDCl_3$.

(*Z*)-*N*'-(1-(benzo[d][1,3]dioxol-5-yl)ethylidene)-4-methylbenzenesulfonohydrazide (19a)



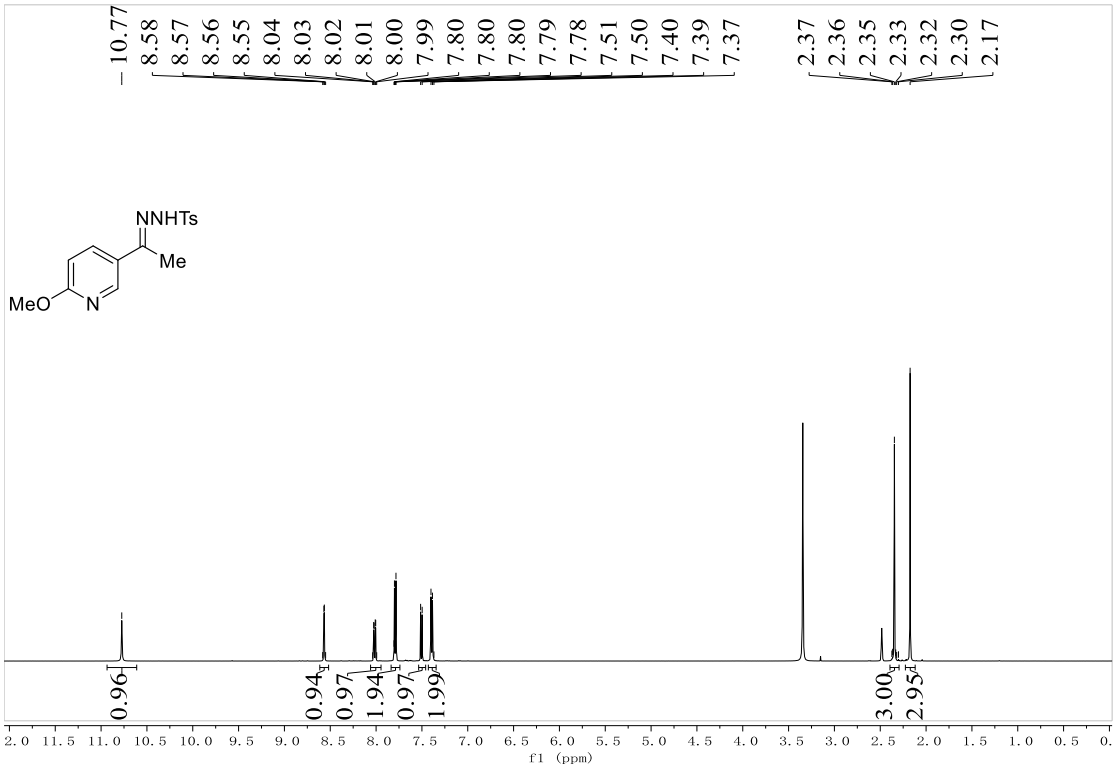
^{1}H NMR spectrum in $CDCl_3$.

(Z)-*N*'-(1-(4-methoxyphenyl)propylidene)-4-methylbenzenesulfonohydrazide (20a)

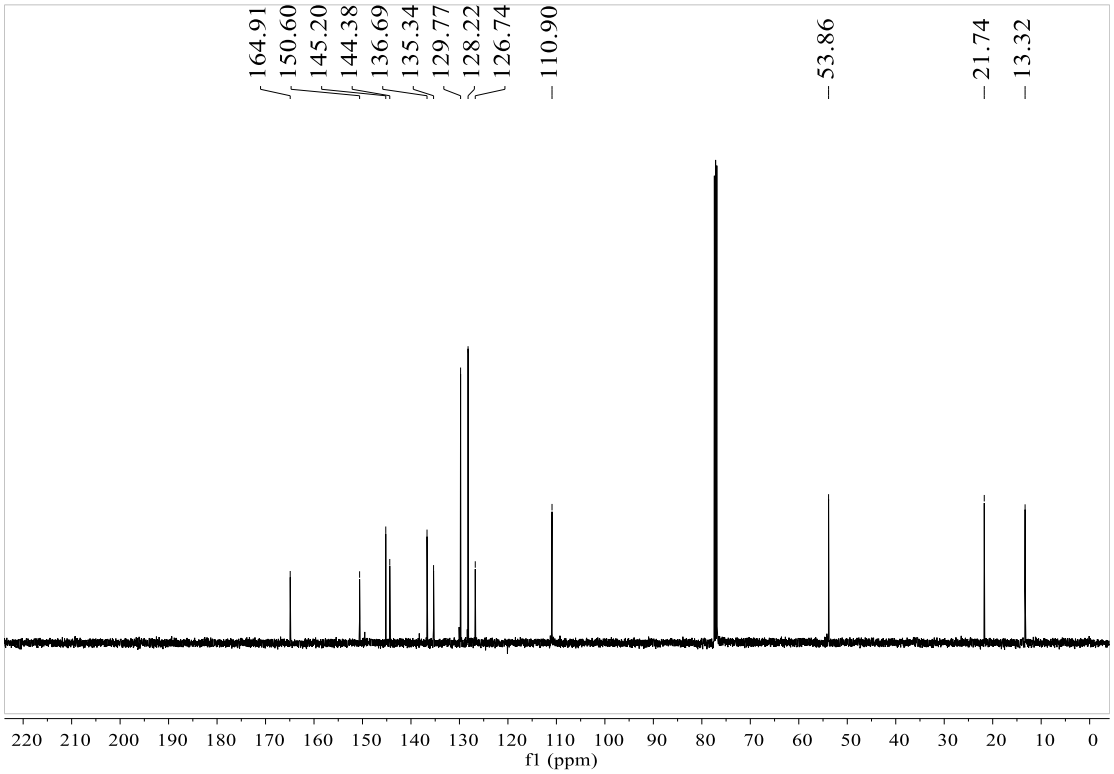


^{1}H NMR spectrum in $CDCl_3$.

***N*'-(1-(6-methoxypyridin-3-yl)ethylidene)-4-methylbenzenesulfonohydrazide(21a)**

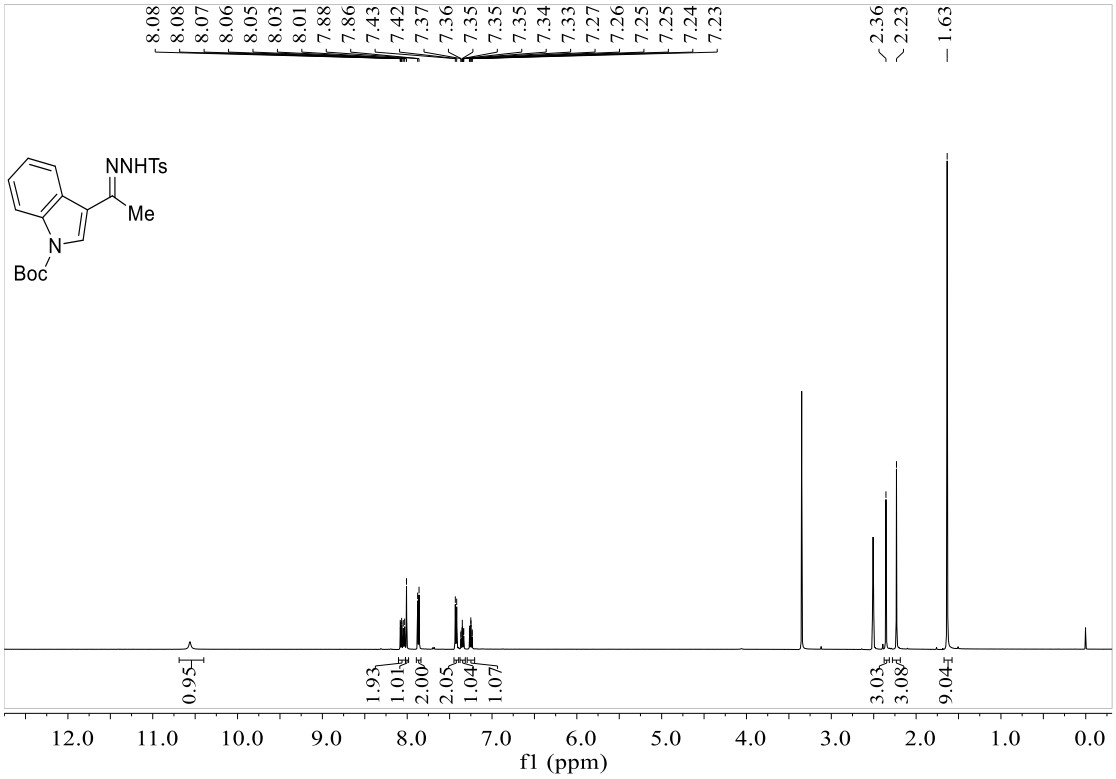


^{1}H NMR spectrum in DMSO-d_6.



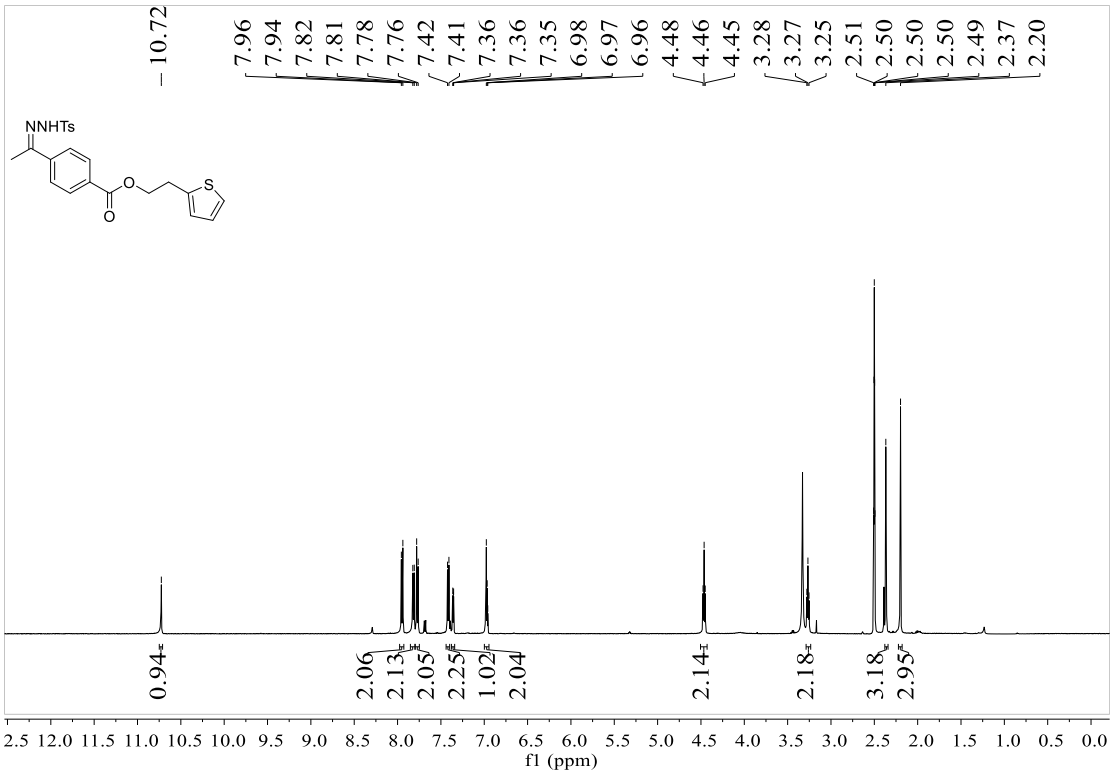
^{13}C NMR spectrum in $CDCl_3$.

***tert*-butyl 3-(1-(2-tosylhydrazono)ethyl)-1*H*-indole-1-carboxylate (22a)**

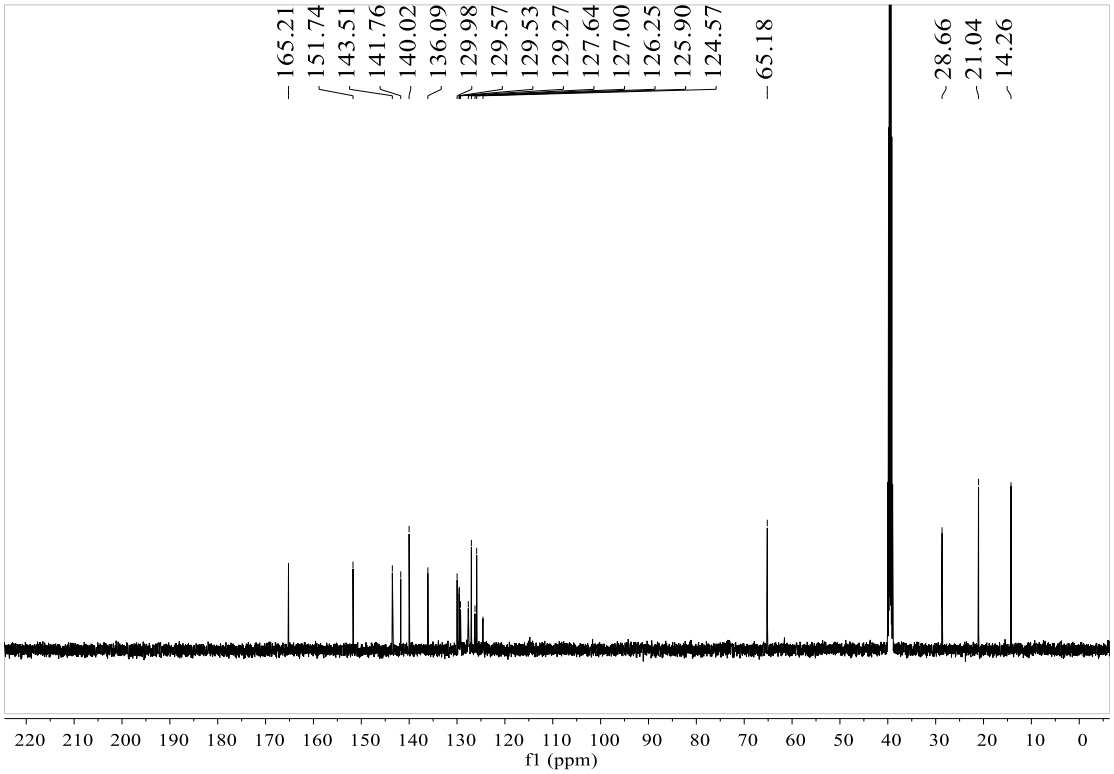


^{1}H NMR spectrum in DMSO-d$_6$.

2-(thiophen-2-yl)ethyl 4-(1-(2-tosylhydrazono)ethyl)benzoate(23a)

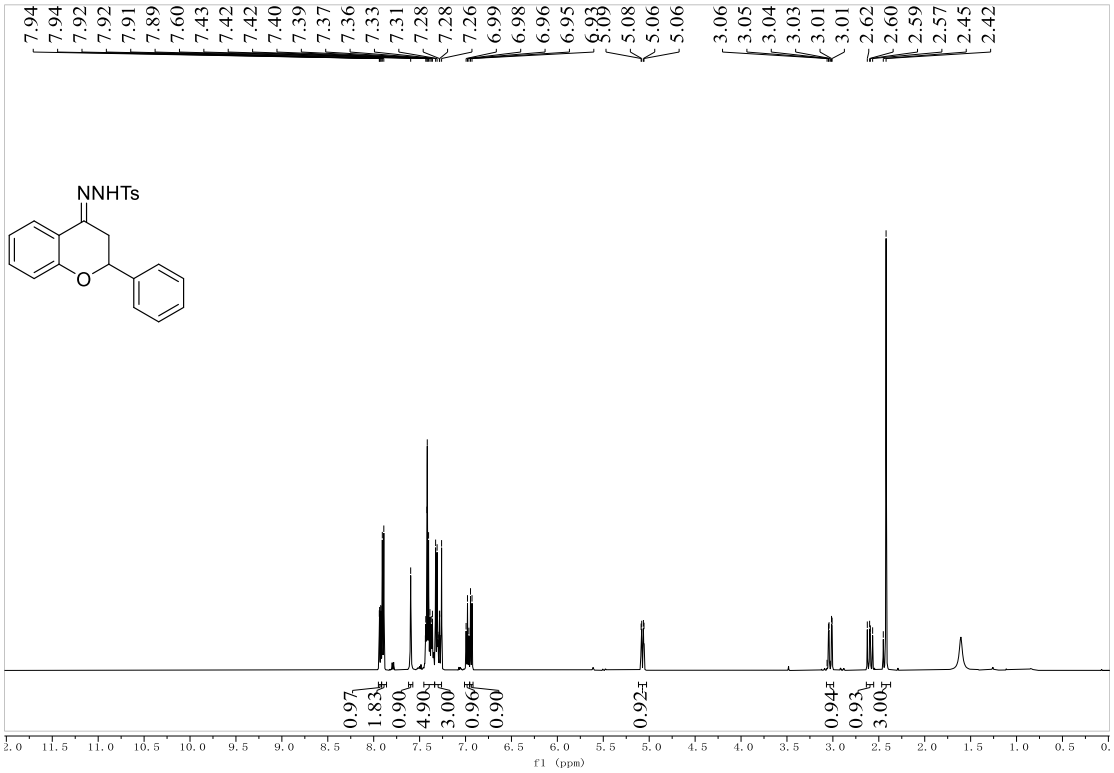


^{1}H NMR spectrum in DMSO-*d*$_6$.



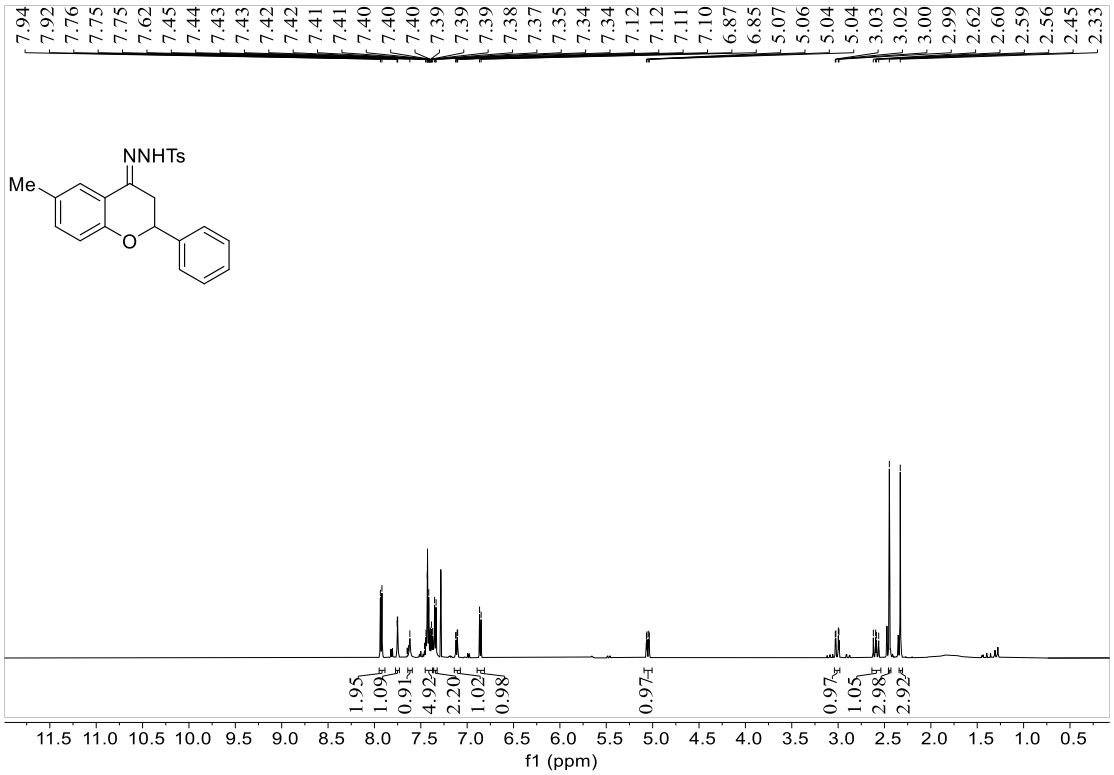
^{13}C NMR spectrum in DMSO-d_6.

(*E*)-4-methyl-*N'*-(2-phenylchroman-4-ylidene)benzenesulfonohydrazide(24a)



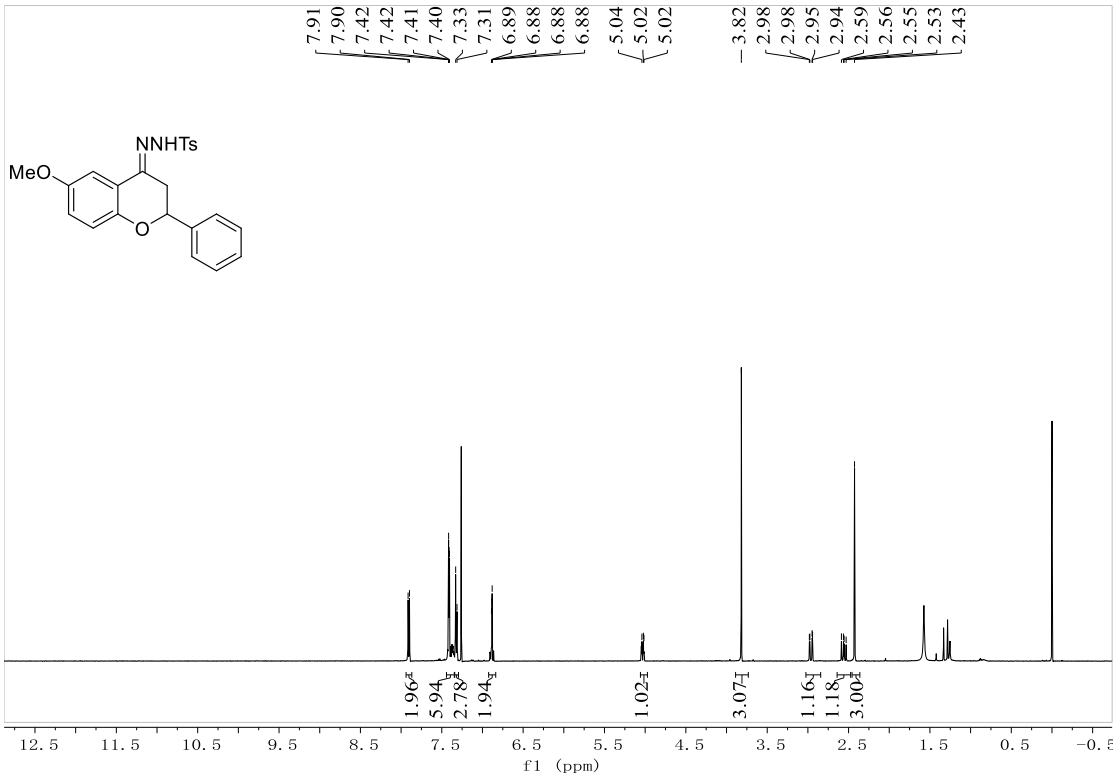
^{1}H NMR spectrum in $CDCl_3$.

(*Z*)-4-methyl-*N*'-(6-methyl-2-phenylchroman-4-ylidene)benzenesulfonohydrazide(27a)

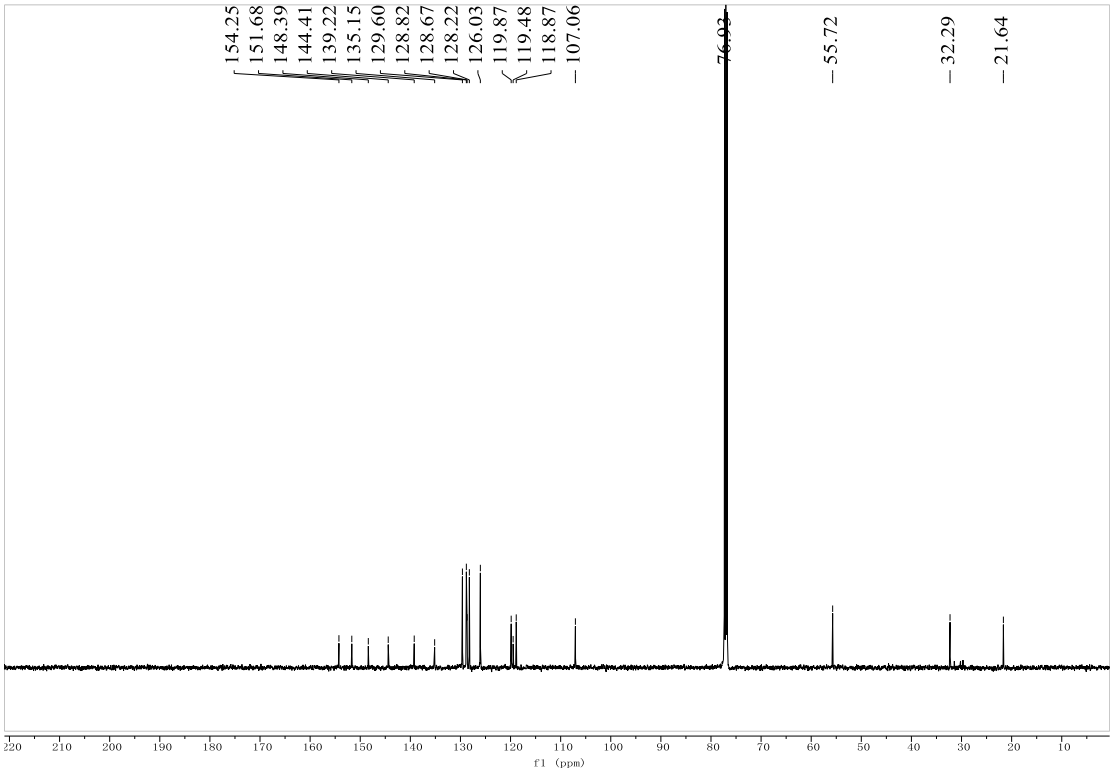


^{1}H NMR spectrum in $CDCl_3$.

(*Z*)-*N*'-(6-methoxy-2-phenylchroman-4-ylidene)-4-methylbenzenesulfonohydrazide(28a)

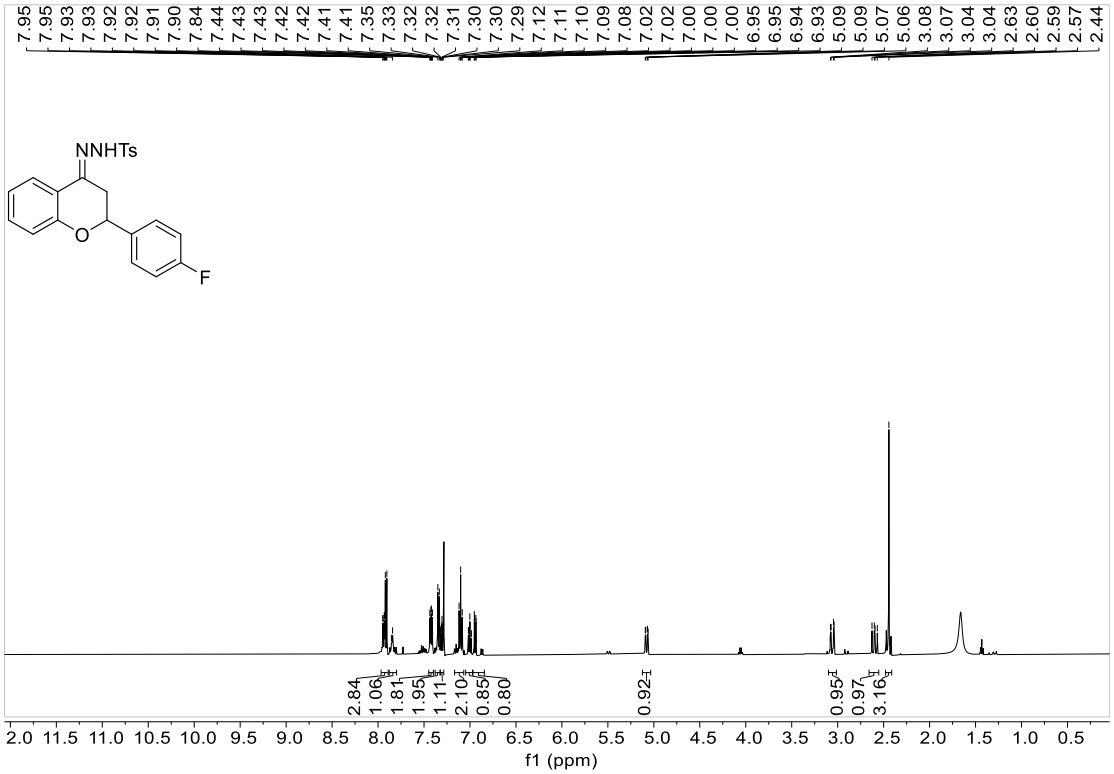


^{1}H NMR spectrum in $CDCl_3$.

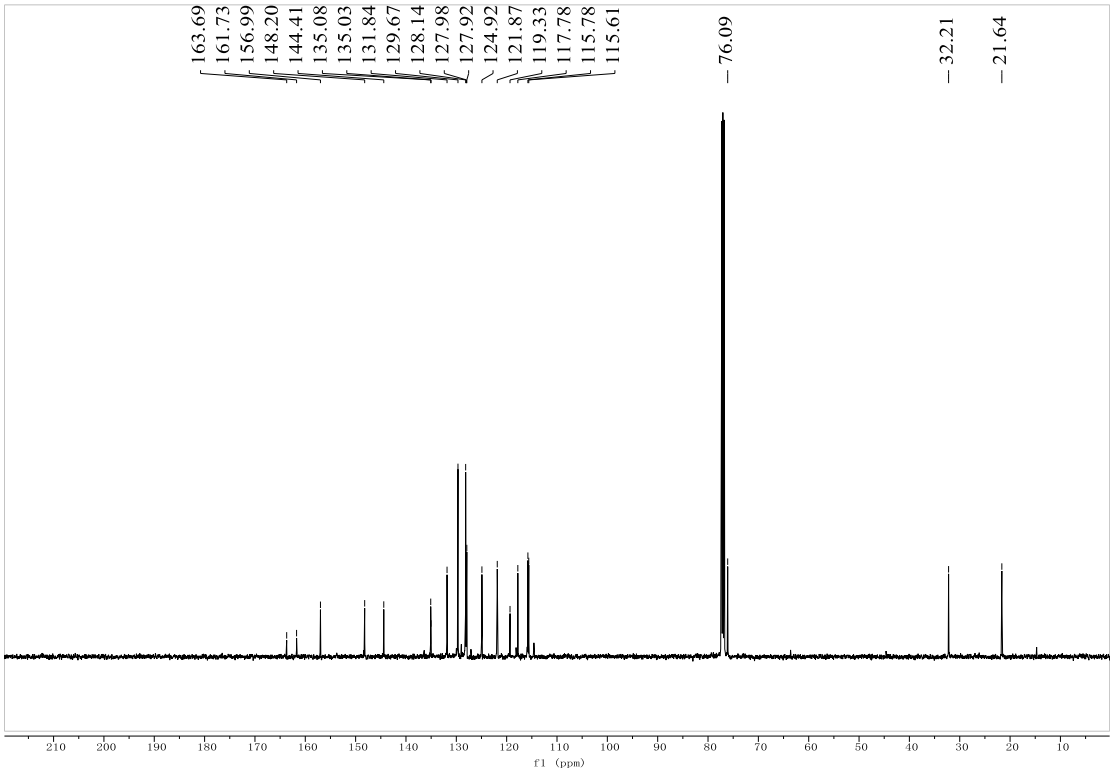


^{13}C NMR spectrum in $CDCl_3$.

(*Z*)-*N*'-(2-(4-fluorophenyl)chroman-4-ylidene)-4-methylbenzenesulfonohydrazide(29a)

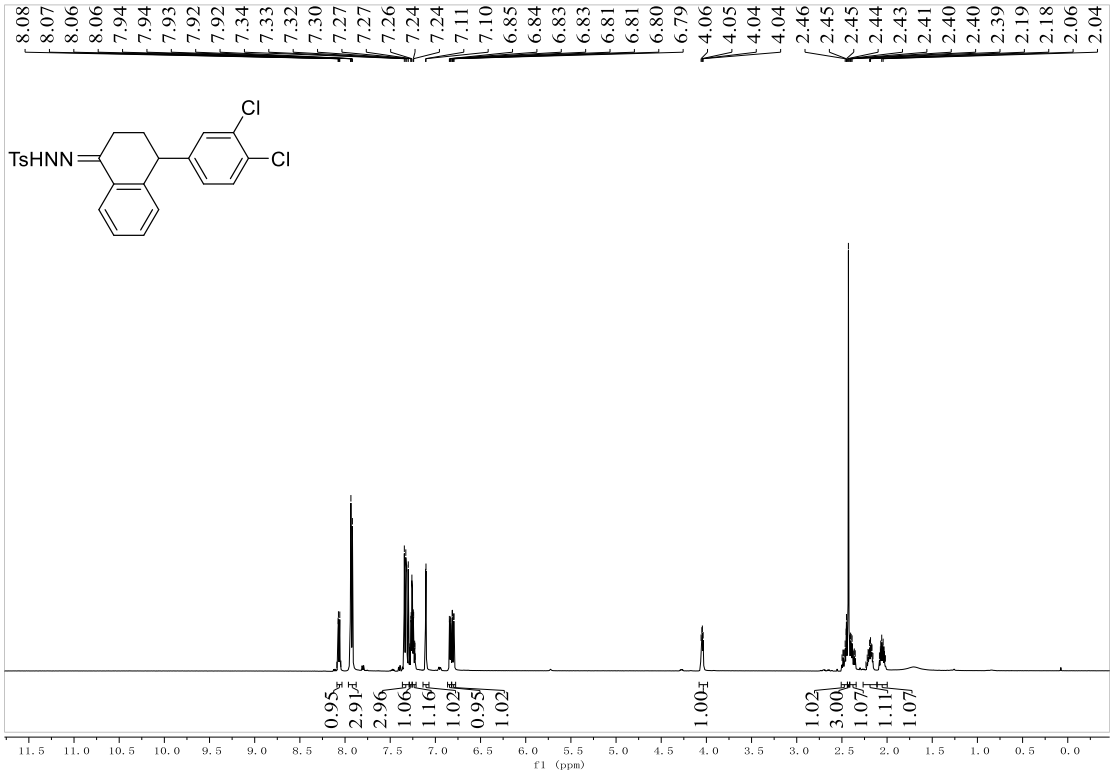


^{1}H NMR spectrum in $CDCl_3$.

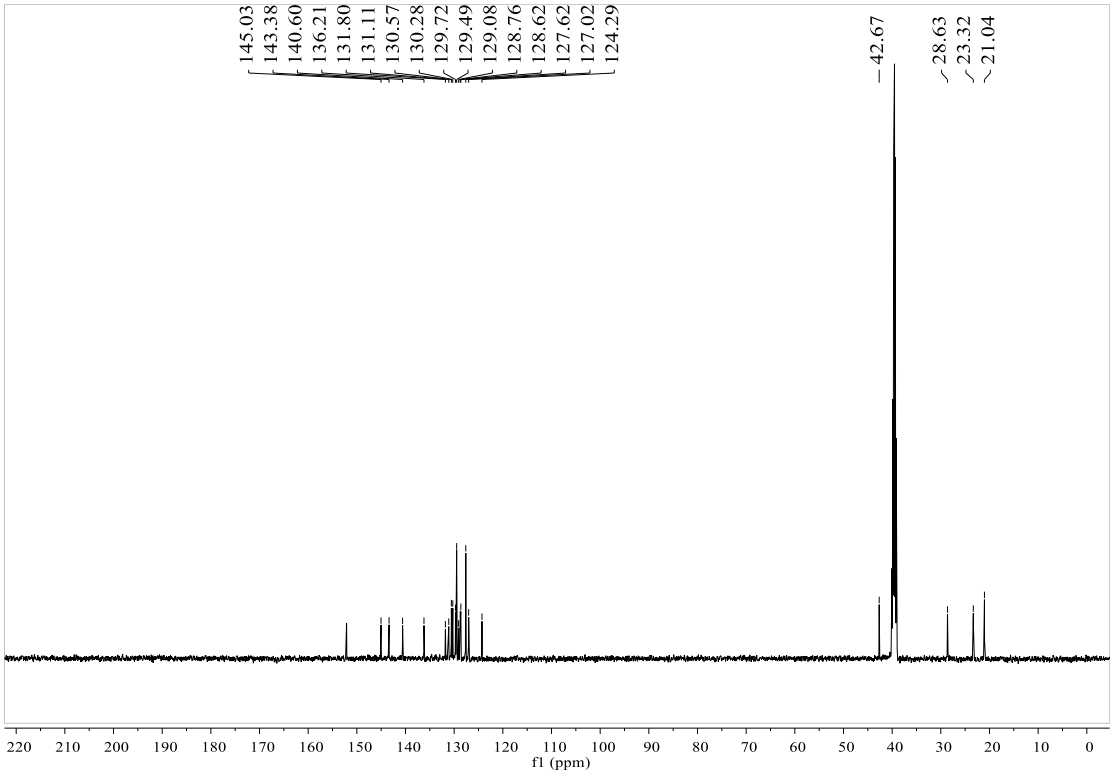


^{13}C NMR spectrum in $CDCl_3$.

***N*'-(4-(3,4-dichlorophenyl)-3,4-dihydronaphthalen-1(2*H*)-ylidene)-4-methylbenzenesulfonohydrazide (30a)**

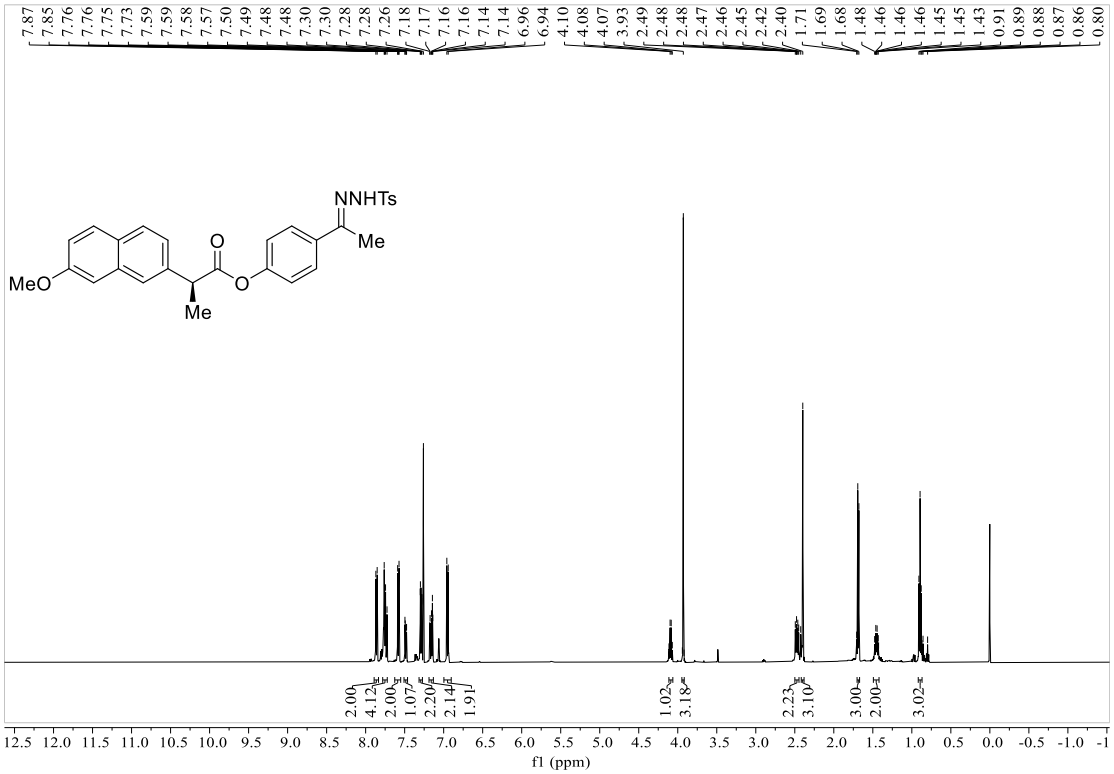


^{1}H NMR spectrum in $CDCl_3$.



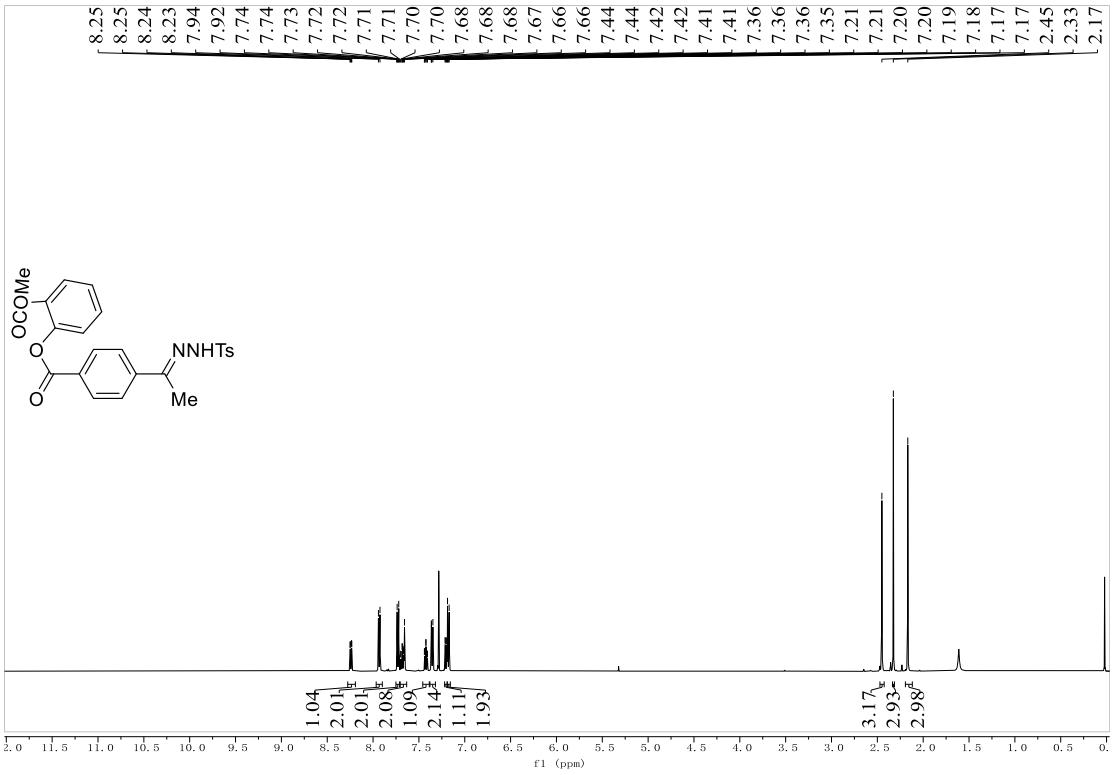
^{13}C NMR spectrum in DMSO-d_6.

(*Z*)-4-(1-(2-tosylhydrazineylidene)ethyl)phenyl (*S*)-2-(7-methoxynaphthalen-2-yl)propanoate(31a)

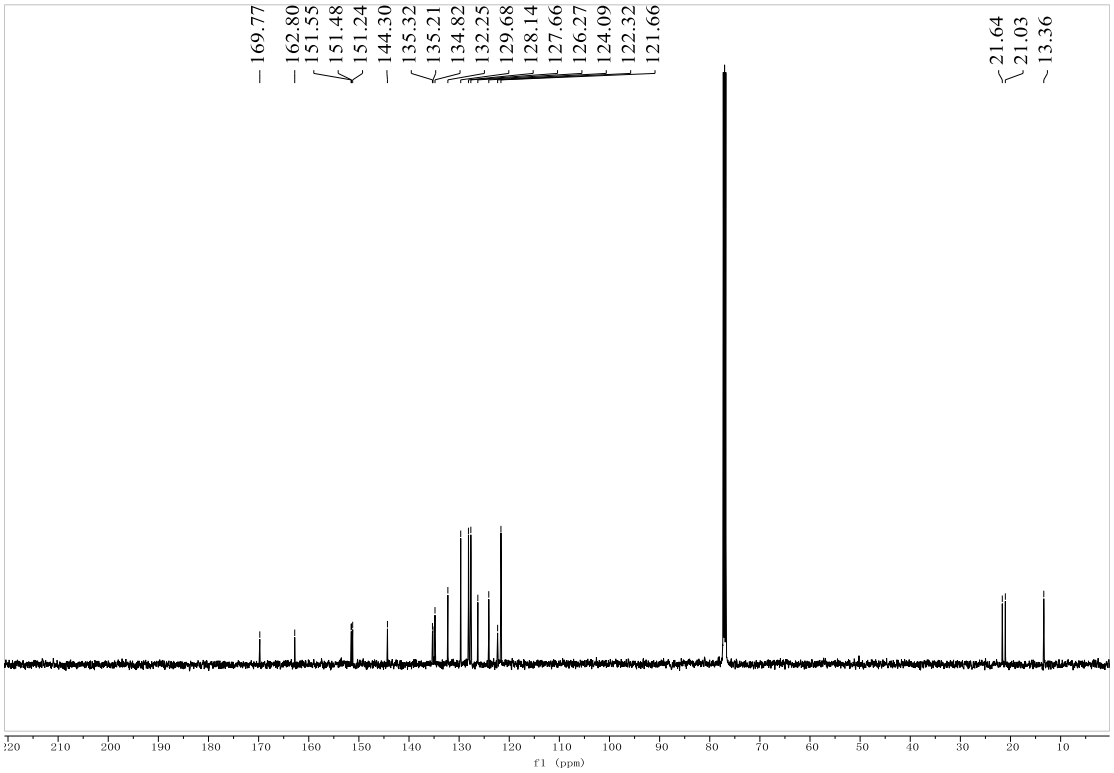


^{1}H NMR spectrum in $CDCl_3$.

2-acetoxyphenyl (*Z*)-4-(1-(2-tosylhydrazineylidene)ethyl)benzoate (33a)

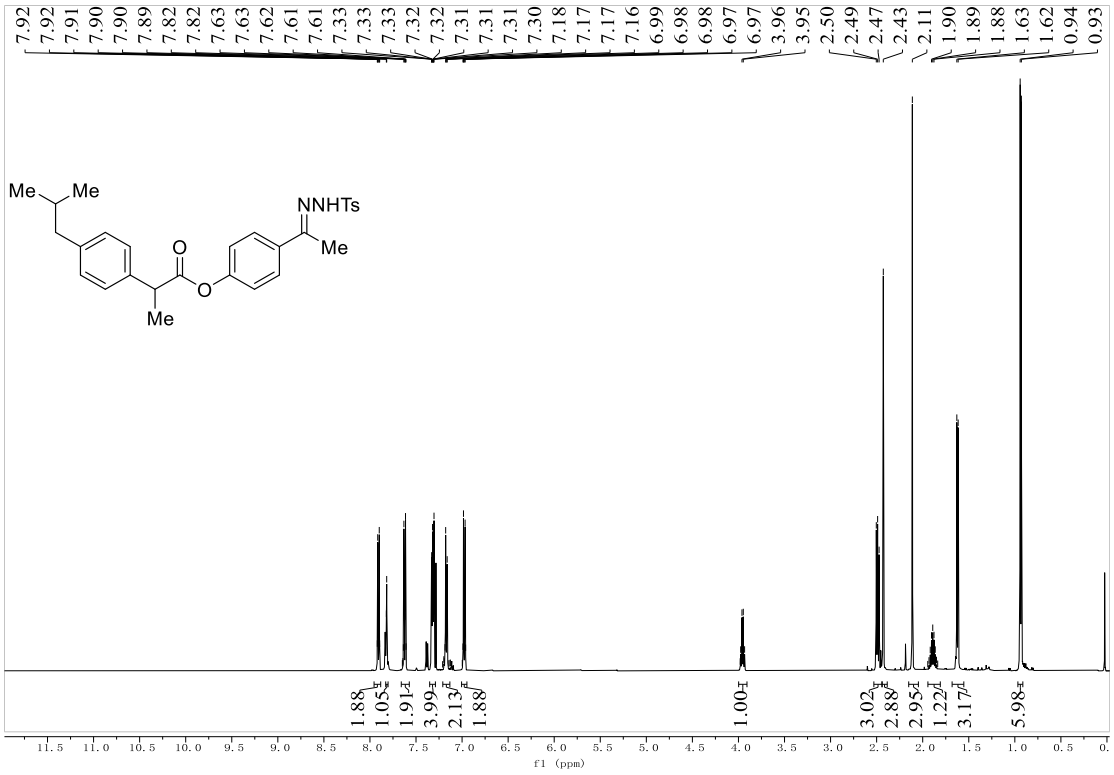


^{1}H NMR spectrum in $CDCl_3$.

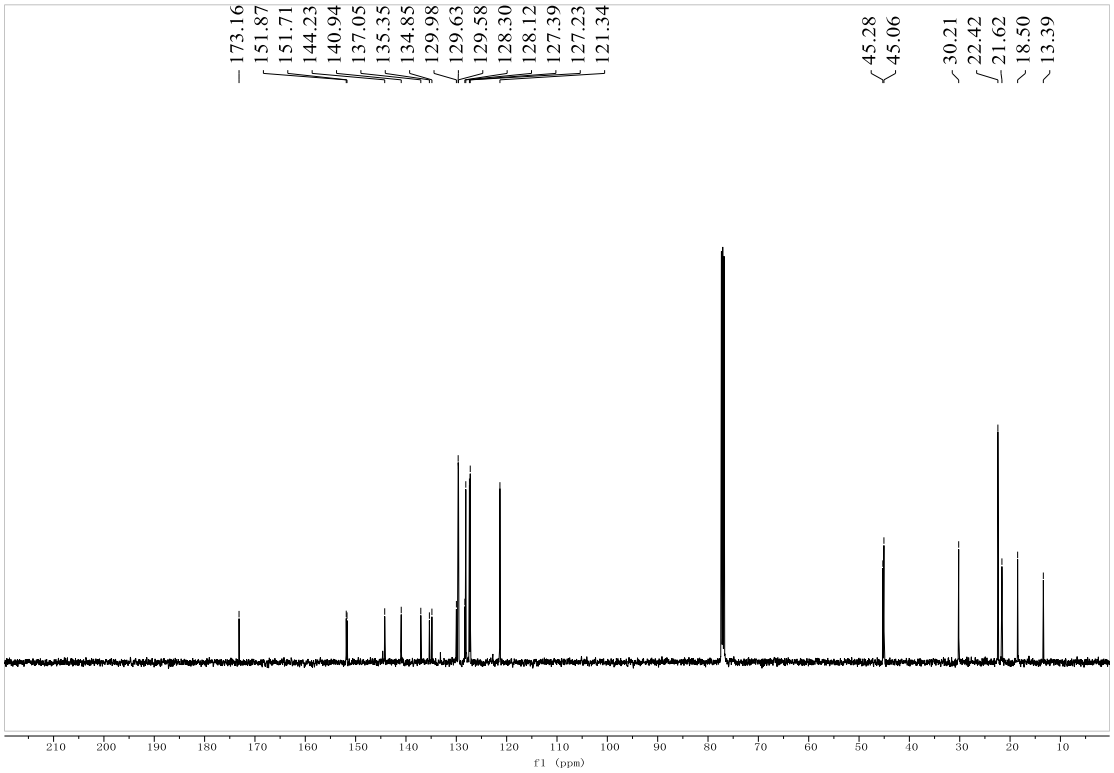


^{13}C NMR spectrum in $CDCl_3$.

(*E*)-4-(1-(2-tosylhydrazineylidene)ethyl)phenyl 2-(4-isobutylphenyl)propanoate(34a)

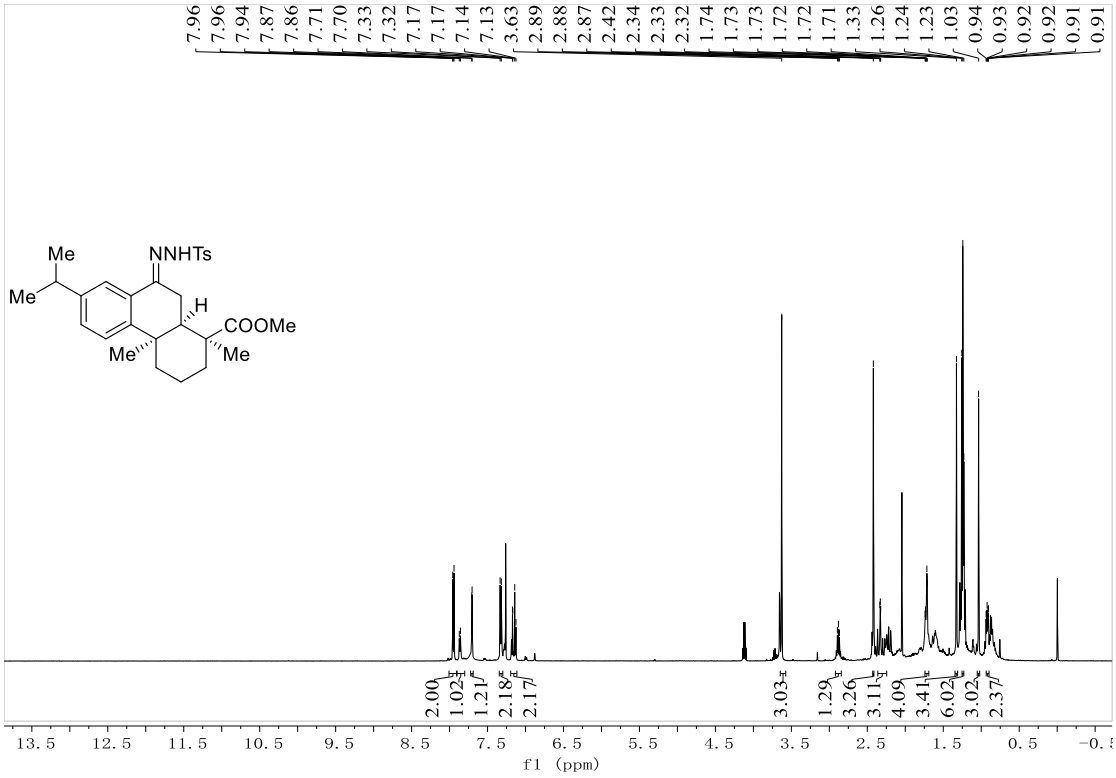


^{1}H NMR spectrum in $CDCl_3$.



^{13}C NMR spectrum in $CDCl_3$.

methyl (1*R*, 4*aS*, 10*aR*, *Z*)-7-isopropyl-1, 4a-dimethyl-9-(2-tosylhydrazineylidene)-1, 2, 3, 4, 4a, 9, 10, 10a-octahydrophenanthrene-1-carboxylate(35a)



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