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Supporting Information

Intermolecular Defluorinative 1,2-Diamination of Fluoroalkenyl Iodides with Sulfonamides: Synthesis of Acyclic and Cyclic Fluorinated 1,2-Enediamines

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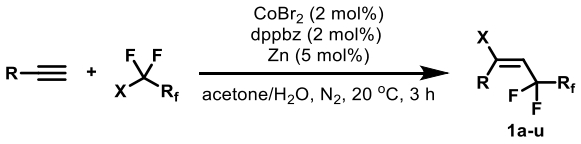
General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out under N_2 or air atmosphere using undistilled solvent. Melting points were recorded on an electrothermal digital melting point apparatus. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. ^1H, ^{19}F, and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Avance or Joel 400 MHz spectrometers. NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), doublet of doublets (dd), doublet of triplets (dt), doublet of quartets (dq), triplet of doublets (td), triplet of triplets (tt), and quartet of triplets (qt). The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. High resolution mass spectrometry (HRMS) data were obtained on a Waters LC-TOF mass spectrometer (Xevo G2-XS QTof) using electrospray ionization (ESI) in positive or negative mode. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions.

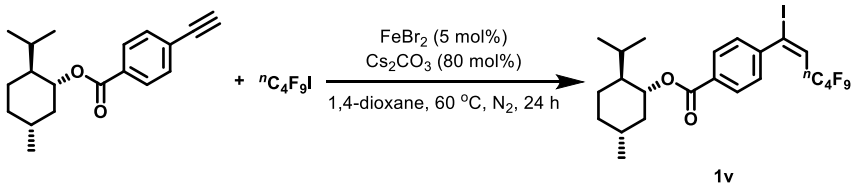
General procedure for the synthesis of fluoroalkenyl iodides 1[1-2]

General procedure A (GPA)[1]



To an oven-dried vial equipped with a stir bar was added alkyne (5 mmol, 1 equiv.), perfluoroalkyl iodide (7.5 mmol, 1.5 equiv.), $CoBr_2$ (21.9 mg, 0.1 mmol, 0.02 equiv.), 1,2-bis(diphenylphosphino)benzene (44.6 mg, 0.1 mmol, 0.02 equiv., dppbz), Zn (16.3 mg, 0.25 mmol, 0.05 equiv.), and acetone/H_2O (10 mL, 30/1) at room temperature. The vial was capped with a rubber septum, and the air in the vial was evacuated under reduced pressure and refilled with nitrogen (3 times). The reaction mixture was placed in an oil bath at 20 °C and stirred for 3 h. The reaction mixture was concentrated *in vacuo*. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (200/1~20/1) as eluent to afford the pure product **1**.

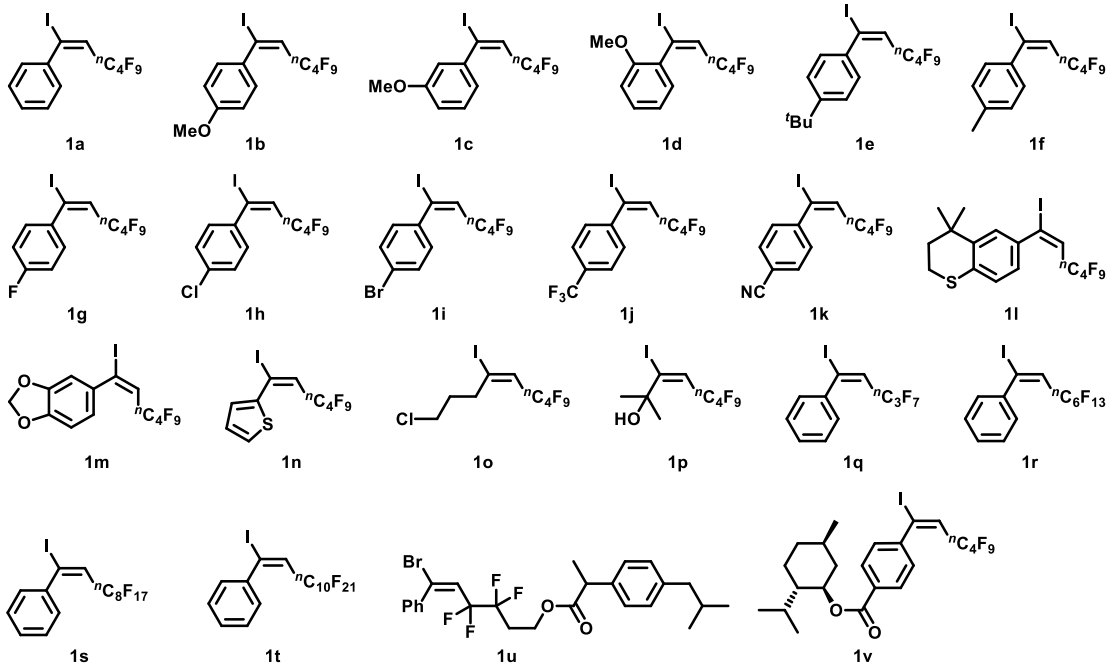
General procedure B (GPB)[2]



To an oven-dried vial equipped with a stir bar was added (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-ethynylbenzoate (1.71 g, 6 mmol, 1 equiv.), perfluorobutyl iodide (3.11 g, 9 mmol, 1.5 equiv.), $FeBr_2$ (0.06 g, 0.3 mmol, 0.05 equiv.), Cs_2CO_3 (1.56 g, 4.8 mmol, 0.8 equiv.), and anhydrous 1,4-dioxane (20 mL) at room temperature. The vial was capped with a rubber septum, and the air in the vial was evacuated under reduced pressure and refilled with nitrogen (3 times). The reaction mixture was placed in an oil bath at 60 °C and

stirred for 24 h. The reaction mixture was then cooled to room temperature and concentrated *in vacuo*. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (100/1) as eluent to afford the pure product **1v** (1.29 g, 34% yield).

Perfluoroalkenyl iodides 1 used in the reaction (*E*/*Z* ratio > 30/1):



Representative examples:

(*E*)-(3,3,4,4,5,5,6,6,6-Nonafluoro-1-iodohex-1-en-1-yl)benzene (1a)[1a]:

Following general procedure GPA.

Yield = 78% (6.99 g, 20 mmol scale). Colorless oil.

Purified by flash column chromatography through silica gel (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.27 (m, 5H), 6.59 (t, J = 13.6 Hz, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.86 – -81.04 (m, 3F), -105.37 (q, J = 10.6 Hz, 2F), -123.71 (t, J = 9.7 Hz, 2F), -125.78 (q, J = 110.0 Hz, 2F) ppm.

((*E*)-1-(*tert*-Butyl)-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (1e)[1b]:

Following general procedure GPA.

Yield = 76% (3.83 g, 10 mmol scale). Yellow oil.

Purified by flash column chromatography through silica gel (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.31 (m, 2H), 7.25–7.21 (m, 2H), 6.57 (t, J = 13.6 Hz, 1H), 1.32 (s, 9H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.89 (t, J = 9.9 Hz, 3F), -105.14 (q, J = 12.4 Hz, 2F), -123.70 – -123.80 (m, 2F), -125.67 – -125.79 (m, 2F) ppm.

***E*)-1-Methyl-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (1f)[1b]:**

Following general procedure GPA.

Yield = 78% (3.60 g, 10 mmol scale). Colorless oil.
Purified by flash column chromatography through silica gel (petroleum ether).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.12 (m, 4H), 6.57 (t, J = 13.5 Hz, 1H), 2.36 (s, 3H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.92 (t, J = 10.3 Hz, 3F), -105.20 (q, J = 13.0 Hz, 2F), -123.64 – -123.77 (m, 2F), -125.69 – -125.79 (m, 2F) ppm.

(*E*)-1-Fluoro-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (1g)[1b]:
Following general procedure GPA.
Yield = 82% (3.83 g, 10 mmol scale). Yellow oil.
Purified by flash column chromatography through silica gel (petroleum ether).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.26 (m, 2H), 7.06–6.99 (m, 2H), 6.59 (t, J = 13.5 Hz, 1H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.92 (t, J = 9.7 Hz, 3F), -105.37 (q, J = 12.3 Hz, 2F), -110.74 (dq, J = 12.0, 6.6 Hz, 1F), -123.73 (q, J = 9.8 Hz, 2F), -125.85 (tt, J = 11.2, 6.4 Hz, 2F) ppm.

(*E*)-1-Chloro-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (1h)[1b]:
Following general procedure GPA.
Yield = 80% (3.86 g, 10 mmol scale). Yellow oil.
Purified by flash column chromatography through silica gel (petroleum ether).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.30 (m, 2H), 7.26–7.20 (m, 2H), 6.60 (t, J = 13.5 Hz, 1H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.89 (t, J = 9.9 Hz, 3F), -105.41 (q, J = 13.0 Hz, 2F), -123.69 (q, J = 9.7 Hz, 2F), -125.72 – -125.93 (m, 2F) ppm.

(*E*)-1-(3,3,4,4,5,5,6,6,6-Nonafluoro-1-iodohex-1-en-1-yl)-4-(trifluoromethyl)benzene (1j)[1b]:
Following general procedure GPA.
Yield = 70% (903 mg, 2.5 mmol scale). Yellow oil.
Purified by flash column chromatography through silica gel (petroleum ether).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63–7.60 (m, 2H), 7.40 (d, J = 8.1 Hz, 2H), 6.65 (t, J = 13.4 Hz, 1H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.83 (s, 3F), -80.91 (t, J = 9.7 Hz, 3F), -105.54 (q, J = 12.7 Hz, 2F), -123.66 (q, J = 9.4 Hz, 2F), -125.74 (dt, J = 13.4, 6.1 Hz, 2F) ppm.

(*E*)-4,4-Dimethyl-6-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)thiochromane (1l)[1b]:
Following general procedure GPA.
Yield = 94% (1.65 g, 3.2 mmol scale). Yellow oil.
Purified by flash column chromatography through silica gel (petroleum ether).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (s, 1H), 7.06–6.97 (m, 2H), 6.53 (t, J = 13.6 Hz, 1H), 3.06–3.01 (m, 2H), 1.99–1.92 (m, 2H), 1.31 (s, 6H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.92 (s, 3F), -105.09 (d, J = 17.8 Hz, 2F), -123.58 (s, 2F), -125.74 (s, 2F) ppm.

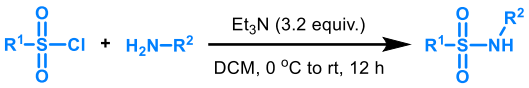
(*E*)-5-(3,3,4,4,5,5,6,6,6-Nonafluoro-1-iodohex-1-en-1-yl)benzo[*d*][1,3]dioxole (1m)[1b]:
Following general procedure GPA.

Yield = 39% (973 mg, 5 mmol scale). Yellow oil.
Purified by flash column chromatography through silica gel (petroleum ether).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.85–6.70 (m, 3H), 6.53 (t, J = 13.5 Hz, 1H), 6.00 (s, 2H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.86 (s, 3F), -105.21 (d, J = 28.2 Hz, 2F), -123.70 (s, 2F), -125.73 (s, 2F) ppm.

(*E*)-5,5,6,6,7,7,8,8,8-Nonafluoro-3-iodo-2-methyloct-3-en-2-ol (1p)[2]:
Following general procedure GPB.
Yield = 74% (6.36 g, 20 mmol scale). Colorless oil.
Purified by flash column chromatography through silica gel (petroleum ether).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.91–6.80 (m, 1H), 1.52 (s, 6H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -81.08 (t, J = 9.8 Hz, 3F), -108.64 (q, J = 13.0 Hz, 2F), -123.97 (q, J = 9.6 Hz, 2F), -125.82 (tt, J = 10.6, 5.3 Hz, 2F) ppm.

General procedure for the synthesis of sulfonamides 2[3-6]

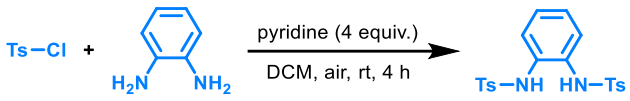
General procedure C (GPC)[3]



2b-n

To a stirred solution of amine (6 mmol, 1.2 equiv.) in dichloromethane (13 mL), triethylamine (2.2 mL, 16 mmol, 3.2 equiv.) was added, and subsequently, sulfonyl chloride (5 mmol, 1 equiv.) was added dropwise while maintaining the temperature at 0 °C. Then the mixture was stirred at room temperature overnight. The reaction mixture was concentrated *in vacuo*. The crude product was quenched by H_2O (50 mL) and extracted with EtOAc (50 mL x 3). The organic layer was washed with saturated brine (50 mL x 2), dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (4/1~1/1) as eluent to afford the pure product **2**.

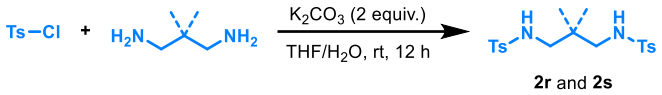
General procedure D (GPD)[4]



2p

The *o*-phenylenediamine (1.0814 g, 10 mmol, 1 equiv.) and pyridine (3.2 mL, 40 mmol, 4 equiv.) were dissolved in dichloromethane (20 mL), and then tosyl chloride (3.8130 g, 20 mmol, 2 equiv.) was added in batches. The mixture was stirred at room temperature for 4 h. The crude product was quenched by H_2O (50 mL) and extracted with EtOAc (50 mL x 3). The organic layer was washed with saturated brine (50 mL x 2), dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (4/1~1/4) as eluent to afford the pure product **2p** (3.04 g, 73% yield).

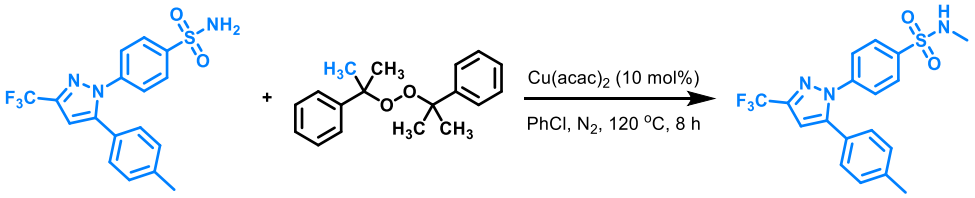
General procedure E (GPE)[5]



2r and **2s**

K_2CO_3 (2.7642 g, 20 mmol, 2 equiv.) was dissolved in water (10 mL), and diamine (10 mmol, 1 equiv.) was added to the solution. Tosyl chloride (3.8130 g, 20 mmol, 2 equiv.) dissolved in THF (20 mL) was then added to the mixture over a period of 10 mins. The reaction mixture was stirred at room temperature overnight. The crude product was quenched by H_2O (80 mL) and extracted with EtOAc (80 mL x 3). The organic layer was washed with saturated brine (50 mL x 2), dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (4/1~1/1) as eluent to afford the pure product **2**.

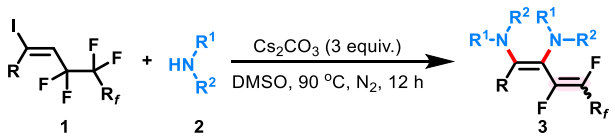
General procedure F (GPF)[6]



2t

To an oven-dried vial equipped with a stir bar was added (peroxybis(propane-2,2-diyl))dibenzene (2.7037 g, 10 mmol, 2 equiv.), 4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (1.9069 g, 5 mmol, 1 equiv.), $Cu(acac)_2$ (0.1309 g, 0.5 mmol, 0.1 equiv.), and chlorobenzene (25 mL) at room temperature. The vial was capped with a rubber septum, and the air in the vial was evacuated under reduced pressure and refilled with nitrogen (3 times). The reaction mixture was placed in an oil bath at 120 °C and stirred for 8 h. After cooling the reaction mixture to room temperature, it was filtered through a short pad of Celite and washed with methanol (50 mL x 3). The filtrate was concentrated under reduced pressure, and the crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (7/1) as eluent to afford the pure product **2t** (1.0478 g, 53% yield).

General procedure for the synthesis of fluorinated 1,2-enediamines 3

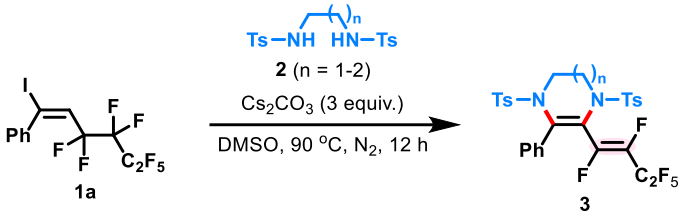


1 2 3

To an oven-dried vial equipped with a stir bar was added fluoroalkene (0.3 mmol, 1 equiv., **1**), *N*-nucleophile (0.9 mmol, 3 equiv., **2**), Cs_2CO_3 (293.2 mg, 0.9 mmol, 3 equiv.), and DMSO (2 mL) at room temperature. The vial was capped with a rubber septum, and the air in the vial was evacuated under reduced pressure and refilled with nitrogen (3 times). The reaction mixture was placed in an oil bath at 90 °C and stirred for 12 h. The reaction mixture was then cooled to room temperature, quenched by saturated NH_4Cl solution (20 mL), and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine (20 mL x 2), dried over $MgSO_4$, and concentrated

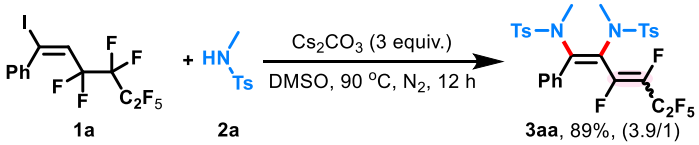
under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (20/1~4/1) as eluent to afford the pure product **3**.

Synthesis of tetrahydropyrazine and tetrahydrodiazepines 3



To an oven-dried vial equipped with a stir bar was added (3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (134.4 mg, 0.3 mmol, 1 equiv., **1a**), bi-sulfonamide (0.45 mmol, 1.5 equiv., **2**), Cs_2CO_3 (293.2 mg, 0.9 mmol, 3 equiv.), and DMSO (2 mL) at room temperature. The vial was capped with a rubber septum, and the air in the vial was evacuated under reduced pressure and refilled with nitrogen (3 times). The reaction mixture was placed in an oil bath at 90 °C and stirred for 12 h. The reaction mixture was then cooled to room temperature, quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine (20 mL x 2), dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (10/1~4/1) as eluent to afford the pure product **3**.

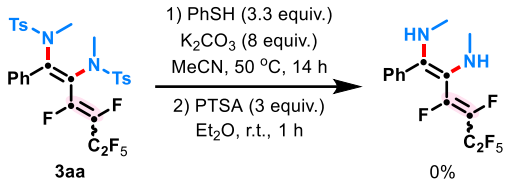
Scale-up synthesis of product 3aa



To an oven-dried vial equipped with a stir bar was added (3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (2.2404 g, 5 mmol, 1 equiv., **1a**), *N*-methyl-*p*-toluenesulfonamide (2.7786 g, 15 mmol, 3 equiv., **2a**), Cs_2CO_3 (4.8873 g, 15 mmol, 3 equiv.), and DMSO (33.4 mL) at room temperature. The vial was capped with a rubber septum, and the air in the vial was evacuated under reduced pressure and refilled with nitrogen (3 times). The reaction mixture was placed in an oil bath at 90 °C and stirred for 12 h. The reaction mixture was then cooled to room temperature, quenched by saturated NH_4Cl solution (50 mL), and extracted with EtOAc (50 mL x 3). The organic layer was washed with saturated brine (50 mL x 2), dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (20/1) as eluent to afford the pure product **3aa** (2.8973 g, 89% yield).

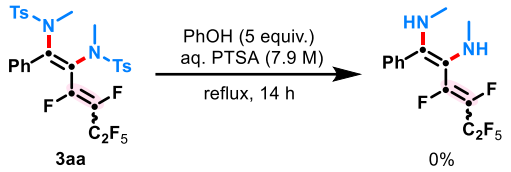
Desulfonylation of product 3aa

Method A[7]



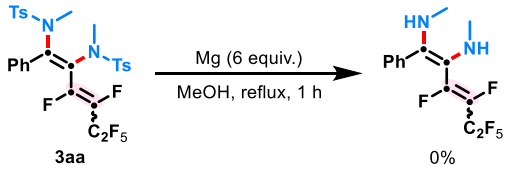
To an oven-dried vial equipped with a stir bar was added *N*,*N*'-((1*Z*)-3,4,5,5,6,6,6-heptafluoro-1-phenylhexa-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (130.1 mg, 0.2 mmol, 1 equiv., **3aa**), PhSH (72.7 mg, 0.66 mmol, 3.3 equiv.), K_2CO_3 (221.1 mg, 1.6 mmol, 8 equiv.), and MeCN (2 mL) at room temperature under air. The vial was capped with a rubber septum, placed in an oil bath at 50 °C, and stirred for 14 h. The vial was then cooled to room temperature, and the reaction solvent was removed. PTSA (103.3 mg, 0.6 mmol, 3 equiv.) and Et_2O (2 mL) were added to the reaction mixture, and the reaction was stirred for 1 h. No desulfonylated product was obtained, and only the starting material **3aa** was recovered.

Method B[7]



To an oven-dried vial equipped with a stir bar was added *N*,*N*'-((1*Z*)-3,4,5,5,6,6,6-heptafluoro-1-phenylhexa-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (130.1 mg, 0.2 mmol, 1 equiv., **3aa**), PhOH (94.1 mg, 1 mmol, 5 equiv.), PTSA (272.1 mg, 1.58 mmol, 7.9 equiv.), and H_2O (2 mL) at room temperature under air. The vial was capped with a rubber septum, placed in an oil bath at 100 °C, and stirred for 14 h. No desulfonylated product was obtained, and only the starting material **3aa** was recovered.

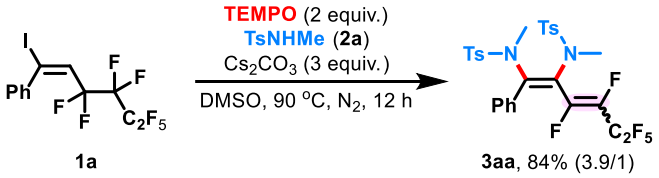
Method C[8]



To an oven-dried vial equipped with a stir bar was added *N*,*N*'-((1*Z*)-3,4,5,5,6,6,6-heptafluoro-1-phenylhexa-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (130.1 mg, 0.2 mmol, 1 equiv., **3aa**), Mg (29.2 mg, 1.2 mmol, 6 equiv.), and MeOH (2 mL) at room temperature under air. The vial was capped with a rubber septum, placed in an oil bath at 65 °C, and stirred for 1 h. No desulfonylated product was obtained, and only the starting material **3aa** was recovered.

Mechanistic studies

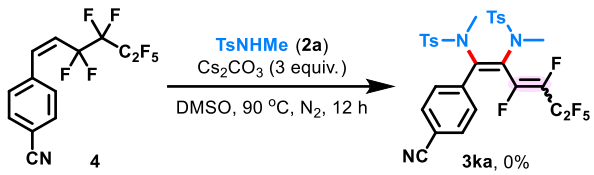
a) Radical trapping experiment



To an oven-dried vial equipped with a stir bar was added (3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (134.4 mg, 0.3 mmol, 1 equiv., **1a**), *N*-methyl-*p*-toluenesulfonamide (166.7 mg, 0.9 mmol, 3 equiv., **2a**), 2,2,6,6-tetramethyl-1-piperidyloxy (93.8 mg, 0.6 mmol, 2 equiv., TEMPO), Cs_2CO_3 (293.2 mg, 0.9 mmol, 3 equiv.), and DMSO (2 mL) at room temperature. The vial was capped with a rubber septum, and the air in the vial was evacuated under reduced pressure and refilled with nitrogen (3 times). The reaction mixture was placed in an oil bath at 90 °C and stirred for 12 h. The reaction mixture was then cooled to room temperature, quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine (20 mL x 2), dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (20/1) as eluent to afford the pure product **3aa** (163.7 mg, 84% yield).

<u>This result suggested that radical intermediates might not be involved in the reaction course.</u>

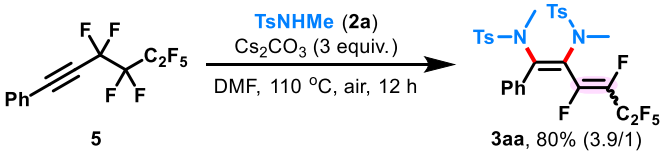
b) The reactivity of perfluoroalkylated alkene 4[9]



To an oven-dried vial equipped with a stir bar was added (*Z*)-4-(3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-yl)benzonitrile (69.4 mg, 0.2 mmol, 1 equiv., **4**), *N*-methyl-*p*-toluenesulfonamide (111.1 mg, 0.6 mmol, 3 equiv., **2a**), Cs_2CO_3 (195.5 mg, 0.6 mmol, 3 equiv.), and DMSO (2 mL) at room temperature. The vial was capped with a rubber septum, and the air in the vial was evacuated under reduced pressure and refilled with nitrogen (3 times). The reaction mixture was placed in an oil bath at 90 °C and stirred for 12 h. No desired product **3ka** was obtained. Almost all of the starting material **4** could be recovered.

<u>The necessity of an iodine atom at the α-position of the perfluoroalkyl alkene demonstrated that the initial reaction might go through a C-I bond displacement.</u>

c) Defluorinative 1,2-diamination of perfluoroalkyl alkyne 5[10]

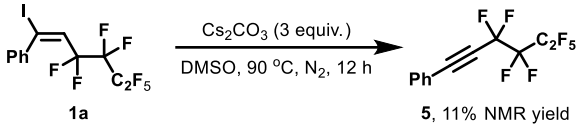


To an oven-dried vial equipped with a stir bar was added (perfluorohex-1-yn-1-yl)benzene (96 mg, 0.3 mmol, 1 equiv., **5**), *N*-methyl-*p*-toluenesulfonamide (166.7 mg, 0.9 mmol, 3 equiv., **2a**), Cs_2CO_3 (293.2 mg, 0.9 mmol, 3 equiv.), and DMF (2 mL) at room temperature under air. The vial was capped with a rubber septum, placed in an oil bath at 110 °C, and stirred for 12 h. The vial

was then cooled to room temperature, and the reaction mixture was quenched by saturated NH_4Cl solution (20 mL), followed by extraction with EtOAc (20 mL x 3). The organic layer was washed with saturated brine (20 mL x 2), dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (20/1) as eluent to afford the pure product **3aa** (156.2 mg, 80% yield).

Although the use of pre-synthesized fluoroalkyne 5 as substrate afforded the desired product 3aa in 80% yield, direct treatment of fluoroalkene 1a under standard reaction conditions only led to the formation of deiodized alkyne 5 in 11% NMR yield. This result underscores the necessity of an iodine atom on the C-C double bond and suggests that the previously reported sequence of dehydroiodination and hydroamination is not the primary pathway.

d) Deiodination of allylic fluoride 1a

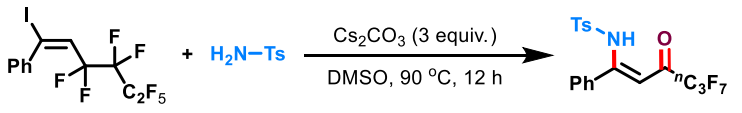


1a **5**, 11% NMR yield

To an oven-dried vial equipped with a stir bar was added (3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (134.4 mg, 0.3 mmol, 1 equiv., **1a**), Cs_2CO_3 (293.2 mg, 0.9 mmol, 3 equiv.), and DMSO (2 mL) at room temperature. The vial was capped with a rubber septum, and the air in the vial was evacuated under reduced pressure and refilled with nitrogen (3 times). The reaction mixture was placed in an oil bath at 90 °C and stirred for 12 h. The vial was then cooled to room temperature, and the reaction mixture was quenched by saturated NH_4Cl solution (20 mL), followed by extraction with EtOAc (20 mL x 3). The organic layer was washed with saturated brine (20 mL x 2), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was directly analyzed by NMR analysis. 11% NMR yield of (perfluorohex-1-yn-1-yl)benzene (**5**) and 80% NMR yield of unreacted starting material **1a** were determined by ^{19}F NMR analysis of the residue using 1-fluoro-4-methoxybenzene (0.1 mmol) as an internal standard.

This result suggests that perfluorobutyl alkyne 5 is the secondary reaction intermediate and the sequence of dehydroiodination and hydroamination is not the main pathway.

e) The use of $TsNH_2$ (6) as *N*-source



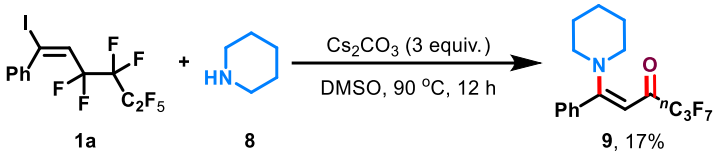
1a **6** **7**, 46% (*Z*/*E* = 2.4/1)

To an oven-dried vial equipped with a stir bar was added (3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (201.6 mg, 0.45 mmol, 1.5 equiv., **1a**), *p*-toluenesulfonamide (51.4 mg, 0.3 mmol, 1 equiv., **6**), Cs_2CO_3 (293.2 mg, 0.9 mmol, 3 equiv.), and DMSO (2 mL) at room temperature. The vial was capped with a rubber septum, placed in an oil bath at 90 °C, and stirred for 12 h. The vial was then cooled to room temperature, and the reaction mixture was quenched by saturated NH_4Cl solution (20 mL), followed by extraction with EtOAc (20 mL x 3). The organic layer was washed with saturated brine (20 mL x 2), dried over

$MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (20/1) as eluent to afford the pure product **7** (65 mg, 46% yield).

The observation of competitive 1,3-aminocarbonylation of fluoroalkenes demonstrates that: 1) deiodinative amination indeed occurs; 2) the structures and N-substituents present on the N-nucleophiles play a pivotal role in determining the chemoselectivity; 3) the involvement of a possible fluoroallene intermediate may help explain the occurrence of both 1,2-diamination and 1,3-aminocarbonylation.

f) The use of piperidine (8) as *N* source



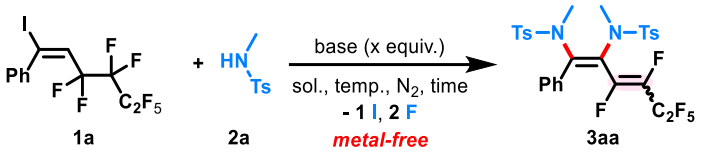
1a **8** **9**, 17%

To an oven-dried vial equipped with a stir bar was added (3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (134.4 mg, 0.3 mmol, 1 equiv., **1a**), Cs_2CO_3 (293.2 mg, 0.9 mmol, 3 equiv.), piperidine (76.6 mg, 0.9 mmol, 3 equiv., **8**), and DMSO (2 mL) at room temperature. The vial was capped with a rubber septum, placed in an oil bath at 90 °C, and stirred for 12 h. The vial was then cooled to room temperature, and the reaction mixture was quenched by saturated NH_4Cl solution (20 mL), followed by extraction with EtOAc (20 mL x 3). The organic layer was washed with saturated brine (20 mL x 2), dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (40/1) as eluent to afford the pure product **9** (19.9 mg, 17% yield).

The observation of competitive 1,3-aminocarbonylation of fluoroalkenes demonstrates that: 1) deiodinative amination indeed occurs; 2) the structures and N-substituents present on the N-nucleophiles play a pivotal role in determining the chemoselectivity; 3) the involvement of a possible fluoroallene intermediate may help explain the occurrence of both 1,2-diamination and 1,3-aminocarbonylation.

Optimization of the reaction conditions

Table S1. Optimization of the reaction conditions[a]

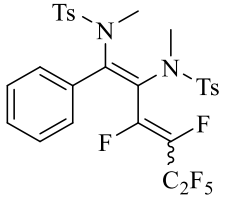


Entry	Base (x equiv)	Temp. (°C)	Solvent	Time (h)	Yield (%)[b] (*E*/*Z*)[c]
1	Cs_2CO_3 (4)	rt	DMSO	12	33[d] (5.3/1)
2	Cs_2CO_3 (4)	50	DMSO	12	67[d] (5.0/1)
3	Cs_2CO_3 (4)	70	DMSO	12	70[d] (4.3/1)
4	Cs_2CO_3 (4)	90	DMSO	6	82[d] (3.9/1)
5	Cs_2CO_3 (4)	110	DMSO	12	77[d] (3.5/1)
6	Cs_2CO_3 (4)	90	DCE	12	0
7	Cs_2CO_3 (4)	90	DMA	12	73[d] (4.1/1)
8	Cs_2CO_3 (4)	90	Pyridine	12	trace[d]
9	Cs_2CO_3 (4)	90	Hexane	12	18[d] (7.2/1)
10	Cs_2CO_3 (4)	90	DME	12	61[d] (3.6/1)
11	Cs_2CO_3 (4)	90	MeCN	12	63[d] (4.8/1)
12	Cs_2CO_3 (4)	90	1,4-dioxane	12	47[d] (4.2/1)
13	Cs_2CO_3 (4)	90	DMF	12	69[d] (4.2/1)
14	Cs_2CO_3 (4)	90	THF	12	43[d] (4.5/1)
15	Cs_2CO_3 (4)	90	Toluene	12	50[d] (5.3/1)
16	Cs_2CO_3 (4)	90	^{t}BuOH	12	8[d] (7.6/1)
17	Cs_2CO_3 (4)	90	^{i}PrOAc	12	44[d] (4.4/1)
18	Cs_2CO_3 (4)	90	DMSO	12	81 (3.7/1)
19	Cs_2CO_3 (4)	90	DMSO	24	76 (3.7/1)
20	Cs_2CO_3 (2)	90	DMSO	12	66 (4.5/1)
21	**Cs_2CO_3 (3)**	**90**	**DMSO**	**12**	**86 (4.5/1) (85)[e]**
22	Cs_2CO_3 (5)	90	DMSO	12	82 (3.7/1)
23	Et_3N (3)	90	DMSO	12	trace
24	K_3PO_4 (3)	90	DMSO	12	20 (4.9/1)
25	Na_2CO_3 (3)	90	DMSO	12	trace
26	LiOH (3)	90	DMSO	12	72 (4.8/1)

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.9 mmol), and base (0.6-1.5 mmol) in solvent (2 mL) at r.t.-110 °C under N_2 for 6-24 h. [b] Yields were determined by ^{19}F NMR analysis with 1-fluoro-4-methoxybenzene (0.1 mmol) as an internal standard. [c] *E*/*Z* ratio in parentheses. [d] H_2O (5 equiv.) was added. [e] Isolated yield.

Note: All the E/Z isomer ratios and NMR yields were calculated on the basis of the characteristic peaks of trifluoromethyl group observed within the range of -80 to -85 ppm in ^{19}F NMR spectra.

Characterization data for products



***N*,*N*'-((1*Z*)-3,4,5,5,6,6,6-Heptafluoro-1-phenylhexa-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (3aa):**

Yield = 85% (165.9 mg, *E*/*Z* = 3.9/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

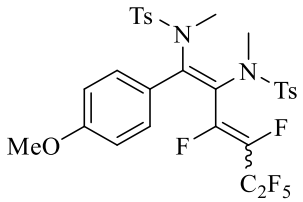
IR (KBr): ν = 3064, 1598, 1356, 1212, 1162, 783, 661, 569 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.77 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.36–7.32 (m, 2H), 7.25–7.18 (m, 5H), 7.11 (d, *J* = 8.1 Hz, 2H), 3.24 (s, 3H), 3.23 (s, 3H), 2.44 (s, 3H), 2.41 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -84.38 (s, 3F), -120.70 (dd, *J* = 24.7, 13.0 Hz, 2F), -135.60 (dt, *J* = 139.7, 24.8 Hz, 1F), -157.10 – -157.55 (m, 1F) ppm; ***Z*-isomer:** δ = -83.88 (s, 3F), -119.89 (s, 2F), -138.73 – -139.55 (m, 1F), -158.71 (d, *J* = 137.9 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 152.4–148.9 (m, 1C), 148.4 (dd, $J_{C\text{-}F}$ = 8.0, 2.0 Hz), 144.3, 144.1, 139.5–136.2 (m, 1C), 135.9, 135.1, 133.6, 130.3, 129.8, 129.6, 129.5, 128.4, 127.83, 127.75, 121.5 (dd, $J_{C\text{-}F}$ = 25.9, 5.9 Hz), 37.9, 36.3, 21.60, 21.57 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{28}H_{26}F_7N_2O_4S_2$ $[M+H]^+$ 651.1217, found: 651.1213.



***N*,*N*'-((1*Z*)-3,4,5,5,6,6,6-Heptafluoro-1-(4-methoxyphenyl)hexa-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (3ba):**

Yield = 93% (189.4 mg, *E*/*Z* = 3.1/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

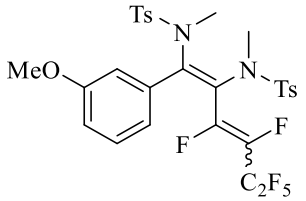
IR (KBr): ν = 2361, 1606, 1512, 1352, 1216, 1171, 841, 663, 542 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.77 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 3.20 (s, 3H), 3.17 (s, 3H), 2.45 (s, 3H), 2.43 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -84.35 (s, 3F), -120.34 – -120.52 (m, 2F), -135.53 (dt, *J* = 140.4, 25.1 Hz, 1F), -157.82 (d, *J* = 137.5 Hz, 1F) ppm; ***Z*-isomer:** δ = -83.90 (s, 3F), -119.89 (s, 2F), -138.36 – -139.97 (m, 1F), -159.35 (d, *J* = 136.9 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 161.5, 152.8–149.1 (m, 1C), 148.1 (d, $J_{C\text{-}F}$ = 8.9 Hz), 144.2, 144.1, 139.2–136.4 (m, 1C), 136.1, 135.1, 131.1, 129.7, 129.6, 127.8, 127.7, 125.8, 119.8 (dd, $J_{C\text{-}F}$ = 25.7, 6.4 Hz), 113.9, 55.4, 37.6, 35.9, 21.5 (2C) ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{29}H_{28}F_7N_2O_5S_2$ $[M+H]^+$ 681.1322, found: 681.1325.



***N*,*N*'-((1*Z*)-3,4,5,5,6,6,6-Heptafluoro-1-(3-methoxyphenyl)hexa-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (3ca):**

Yield = 93% (188.8 mg, *E*/*Z* = 4.2/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

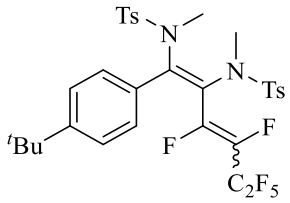
IR (KBr): ν = 2953, 1599, 1356, 1222, 1162, 1024, 660, 544 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.78 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.15 (dd, *J* = 9.0, 6.9 Hz, 1H), 6.89 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 6.50 (s, 1H), 3.58 (s, 3H), 3.24 (s, 3H), 3.23 (s, 3H), 2.43 (s, 3H), 2.40 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -84.30 – -84.63 (m, 3F), -120.86 (ddd, *J* = 24.5, 13.2, 3.2 Hz, 2F), -135.56 (dt, *J* = 138.7, 24.8 Hz, 1F), -157.21 – -157.86 (m, 1F) ppm; ***Z*-isomer:** δ = -83.98 (s, 3F), -120.04 (s, 2F), -139.43 (s, 1F), -158.88 (d, *J* = 135.9 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 159.4, 152.3–148.9 (m, 1C), 148.0 (d, $J_{C\text{-}F}$ = 7.1 Hz), 144.3, 144.1, 139.6–136.4 (m, 1C), 136.0, 135.1, 134.6, 129.7, 129.6, 129.5, 127.8, 127.7, 122.2, 121.3 (dd, $J_{C\text{-}F}$ = 26.0, 5.8 Hz), 116.7, 113.9, 55.0, 37.9, 36.2, 21.6, 21.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{29}H_{28}F_7N_2O_5S_2$ $[M+H]^+$ 681.1322, found: 681.1329.



***N*,*N*'-((1*Z*)-1-(4-(*tert*-Butyl)phenyl)-3,4,5,5,6,6,6-heptafluorohexa-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (3ea):**

Yield = 85% (179.9 mg, *E*/*Z* = 4.2/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

IR (KBr): ν = 2967, 1356, 1219, 1166, 1075, 837, 662, 544 cm^{-1}.

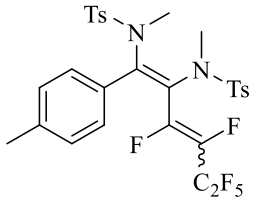
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.68 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.12–7.06 (m, 4H), 6.90 (d, *J* = 8.0 Hz, 2H), 3.17 (s, 3H), 3.16 (s, 3H), 2.34 (s, 3H), 2.31 (s, 3H), 1.18 (s, 9H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -84.47 (t, *J* = 3.9 Hz, 3F), -120.84 (ddd, *J* = 25.4, 13.3, 3.2 Hz, 2F), -135.92 (dt, *J* = 138.6, 25.2 Hz, 1F), -157.45 (dtt, *J* = 139.1, 13.3, 4.3 Hz, 1F) ppm; ***Z*-isomer:** δ = -83.98 (s, 3F), -120.00 (s, 2F), -139.10 (s, 1F), -159.12 (d, *J* = 136.1 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 153.8, 153.5–149.0 (m, 1C), 148.5 (d, $J_{C\text{-}F}$ = 8.8 Hz), 144.2, 143.8, 139.2–136.4 (m, 1C), 136.2, 135.1, 129.7, 129.53, 129.48, 129.3, 127.7 (2C), 125.3, 120.8 (dd, $J_{C\text{-}F}$ = 26.0, 6.1 Hz), 38.1, 36.3, 34.8, 31.1, 21.5 (2C) ppm, carbons

corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{32}H_{34}F_7N_2O_4S_2$ $[M+H]^+$ 707.1843, found: 707.1840.



***N*,*N*'-((1*Z*)-3,4,5,5,6,6,6-Heptafluoro-1-(*p*-tolyl)hexa-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (3fa):**

Yield = 87% (172.6 mg, *E*/*Z* = 2.8/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

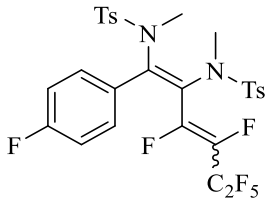
IR (KBr): ν = 3036, 1599, 1357, 1213, 1165, 824, 661, 543 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.77 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.04–7.00 (m, 2H), 7.01–6.97 (m, 2H), 3.21 (s, 3H), 3.18 (s, 3H), 2.44 (s, 3H), 2.42 (s, 3H), 2.32 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -84.12 – -84.81 (m, 3F), -120.75 (ddd, *J* = 24.6, 13.1, 3.2 Hz, 2F), -135.71 (dt, *J* = 138.6, 25.1 Hz, 1F), -156.81 – -158.35 (m, 1F) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 152.5–149.3 (m, 1C), 148.4 (d, $J_{C\text{-}F}$ = 8.8 Hz), 144.2, 144.1, 140.8, 139.4–136.1 (m, 1C), 136.0, 135.1, 130.0, 129.7, 129.5, 129.4, 129.1, 127.9, 127.8, 120.6 (dd, $J_{C\text{-}F}$ = 25.9, 5.8 Hz), 37.7, 36.0, 21.6 (2C), 21.3 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{29}H_{28}F_7N_2O_4S_2$ $[M+H]^+$ 665.1373, found: 665.1368.



***N*,*N*'-((1*Z*)-3,4,5,5,6,6,6-Heptafluoro-1-(4-fluorophenyl)hexa-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (3ga):**

Yield = 61% (122.5 mg, *E*/*Z* = 2.7/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

IR (KBr): ν = 1600, 1511, 1355, 1212, 1161, 842, 661, 543 cm^{-1}.

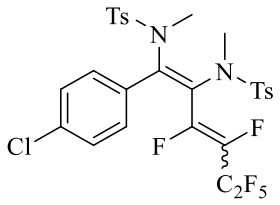
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.79–7.73 (m, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.10 (dd, *J* = 8.5, 5.3 Hz, 2H), 6.95–6.91 (m, 2H), 3.22 (s, 6H), 2.44 (s, 3H), 2.42 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -84.50 – -84.72 (m, 3F), -109.40 (s, 1F), -120.83 (ddd, *J* = 24.7, 13.1, 3.3 Hz, 2F), -135.84 (dt, *J* = 139.0, 24.9 Hz, 1F), -157.24 (dtd, *J* = 139.5, 13.5, 5.3 Hz, 1F) ppm; ***Z*-isomer:** δ = -84.02 (s, 3F), -109.48 (s, 1F), -120.06 (s, 2F), -138.93 – -140.03 (m, 1F), -158.61 (d, *J* = 136.3 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 164.0 (d, $J_{C\text{-}F}$ = 251.7 Hz), 152.4–148.7 (m, 1C), 147.2 (d, $J_{C\text{-}F}$ = 7.3 Hz), 144.4 (d, $J_{C\text{-}F}$ = 2.6 Hz), 135.9, 135.0, 131.7, 131.6, 130.1, 129.8, 129.68, 129.65, 128.1 (d, $J_{C\text{-}F}$ = 4.7 Hz), 127.8, 121.5 (dd, $J_{C\text{-}F}$ = 25.7, 5.9 Hz), 115.7 (d, $J_{C\text{-}F}$ = 22.1 Hz),

37.9, 36.3, 21.67, 21.65 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{28}H_{25}F_8N_2O_4S_2$ $[M+H]^+$ 669.1123, found: 669.1129.



***N*,*N*'-((1*Z*)-1-(4-Chlorophenyl)-3,4,5,5,6,6,6-heptafluorohexa-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (3ha):**

Yield = 78% (159.6 mg, *E*/*Z* = 2.4/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

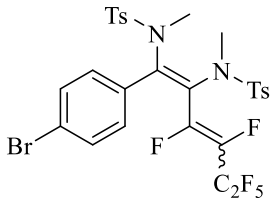
IR (KBr): ν = 1597, 1356, 1212, 1162, 1089, 835, 661, 568 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 3.22 (s, 3H), 3.22 (s, 3H), 2.43 (s, 3H), 2.42 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -84.28 – -84.57 (m, 3F), -120.73 (dd, *J* = 25.0, 13.1 Hz, 2F), -134.74 – -136.30 (m, 1F), -156.94 (dtd, *J* = 139.3, 13.2, 4.6 Hz, 1F) ppm; ***Z*-isomer:** δ = -83.89 (s, 3F), -119.93 (s, 2F), -138.9 – -139.61 (m, 1F), -158.21 (d, *J* = 136.4 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 152.7–148.2 (m, 1C), 147.0 (d, $J_{C\text{-}F}$ = 7.4 Hz), 144.42, 144.40, 139.7–136.8 (m, 1C), 136.6, 135.9, 135.0, 132.2, 130.8, 129.8, 129.7, 128.7, 127.8 (2C), 121.8 (dd, $J_{C\text{-}F}$ = 25.8, 5.6 Hz), 38.0, 36.3, 21.6 (2C) ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{28}H_{25}ClF_7N_2O_4S_2$ $[M+H]^+$ 685.0827, found: 685.0819.



***N*,*N*'-((1*Z*)-1-(4-Bromophenyl)-3,4,5,5,6,6,6-heptafluorohexa-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (3ia):**

Yield = 83% (181.4 mg, *E*/*Z* = 4.0/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

IR (KBr): ν = 1597, 1360, 1213, 1165, 1076, 838, 660, 568 cm^{-1}.

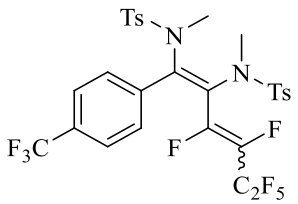
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.76 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 2.4 Hz, 2H), 7.34 (d, *J* = 2.5 Hz, 2H), 7.23 (d, *J* = 7.0 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 2H), 3.24 (s, 3H), 3.23 (s, 3H), 2.43 (s, 3H), 2.42 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -84.53 (t, *J* = 4.3 Hz, 3F), -120.88 (dd, *J* = 24.5, 12.9 Hz, 2F), -135.84 (dt, *J* = 138.3, 25.2 Hz, 1F), -156.67 – -157.49 (m, 1F) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 154.1–148.3 (m, 1C), 147.0 (d, $J_{C\text{-}F}$ = 8.1 Hz), 144.4, 144.3, 139.6–136.1 (m, 1C), 135.8, 134.9, 132.5, 131.6, 130.9, 129.7, 129.6, 127.64, 127.59, 124.8, 121.7 (dd, $J_{C\text{-}F}$ = 25.6, 6.0 Hz), 37.9, 36.2, 21.5 (2C) ppm, carbons corresponding

to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{28}H_{25}BrF_7N_2O_4S_2$ $[M+H]^+$ 729.0322, found: 729.0324.



***N*,*N*'-((1*Z*)-3,4,5,5,6,6,6-Heptafluoro-1-(4-(trifluoromethyl)phenyl)hexa-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (3ja):**

Yield = 80% (173.3 mg, *E*/*Z* = 1.1/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

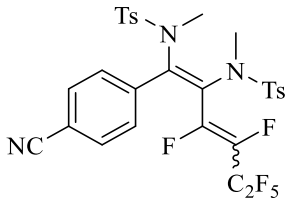
IR (KBr): ν = 2988, 1356, 1167, 1067, 847, 662, 547 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.73 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 1.8 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 2.6 Hz, 2H), 7.22 (d, *J* = 2.6 Hz, 2H), 3.24 (s, 3H), 3.21 (s, 3H), 2.44 (s, 3H), 2.42 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -63.18 (s, 3F), -84.63 (t, *J* = 4.3 Hz, 3F), -120.81 – -122.37 (m, 2F), -135.96 (dt, *J* = 139.7, 24.6 Hz, 1F), -156.30 – -156.84 (m, 1F) ppm; ***Z*-isomer:** δ = -62.88 (s, 3F), -84.02 (s, 3F), -120.13 (s, 2F), -138.91 – -139.88 (m, 1F), -157.69 (d, *J* = 136.4 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 152.7–147.8 (m, 1C), 146.6 (d, $J_{C\text{-}F}$ = 6.6 Hz), 144.6, 144.5, 135.9, 135.3, 134.9, 134.5, 133.0–131.1 (m, 1C), 130.2, 130.0, 129.9, 129.7, 127.7, 127.6, 125.7 (q, $J_{C\text{-}F}$ = 3.9 Hz), 123.0 (dd, $J_{C\text{-}F}$ = 26.2, 5.5 Hz), 38.4, 36.7, 21.7, 21.6 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{29}H_{25}F_{10}N_2O_4S_2$ $[M+H]^+$ 719.1091, found: 719.1093.



***N*,*N*'-((1*Z*)-1-(4-Cyanophenyl)-3,4,5,5,6,6,6-heptafluorohexa-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (3ka):**

Yield = 79% (159.7 mg, *E*/*Z* = 1.2/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

IR (KBr): ν = 2230, 1598, 1355, 1214, 1171, 840, 662, 543 cm^{-1}.

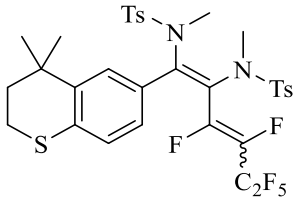
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 3.5 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.20–7.16 (m, 2H), 3.31 (s, 3H), 3.26 (s, 3H), 2.45 (s, 3H), 2.41 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -84.42 (t, *J* = 4.4 Hz, 3F), -121.00 (dd, *J* = 24.9, 12.7 Hz, 2F), -135.82 (dt, *J* = 139.2, 24.7 Hz, 1F), -156.18 – -156.76 (m, 1F) ppm; ***Z*-isomer:** δ = -84.04 (s, 3F), -120.19 (s, 2F), -139.02 – -139.87 (m, 1F), -157.29 (d, *J* = 136.6 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 152.6–147.7 (m, 1C), 146.0 (d, $J_{C\text{-}F}$ = 7.5 Hz), 144.8, 144.7, 143.3, 138.4, 137.6–136.7 (m, 1C), 135.5, 134.7, 132.1, 130.2, 129.8, 127.69,

127.66, 123.2 (dd, $J_{C\text{-}F}$ = 26.7, 5.7 Hz), 118.0, 113.7, 38.0, 36.5, 21.7 (2C) ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{29}H_{25}F_7N_3O_4S_2$ $[M+H]^+$ 676.1169, found: 676.1171.



***N*,*N*'-((1*Z*)-1-(4,4-Dimethylthiochroman-6-yl)-3,4,5,5,6,6,6-heptafluorohexa-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (3la):**

Yield = 86% (194.5 mg, *E*/*Z* = 4.2/1). Yellow solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

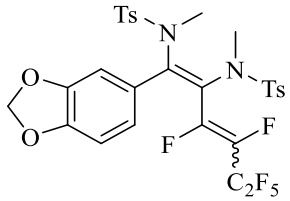
IR (KBr): ν = 2965, 1597, 1355, 1220, 1165, 815, 663, 545 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.82–7.75 (m, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 1.9 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.77 (dd, *J* = 8.2, 1.9 Hz, 1H), 3.21 (s, 3H), 3.16 (s, 3H), 3.03–2.99 (m, 2H), 2.44 (s, 3H), 2.41 (s, 3H), 1.90–1.85 (m, 2H), 1.11 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -84.32 (s, 3F), -120.07 – -120.60 (m, 2F), -135.19 (dt, *J* = 139.3, 27.0 Hz, 1F), -157.37 (d, *J* = 138.2 Hz, 1F) ppm; ***Z*-isomer:** δ = -83.84 (s, 3F), -119.80 (s, 2F), -138.24 – -140.10 (m, 1F), -159.21 (d, *J* = 138.0 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 152.8–148.9 (m, 1C), 148.1 (d, *J* = 9.0 Hz), 144.2, 144.0, 141.9, 139.9–136.6 (m, 1C), 136.1, 135.9, 135.1, 129.7 (2C), 129.0, 127.8, 127.7, 127.3, 127.0, 126.5, 120.3–119.5 (m, 1C), 37.6, 36.8, 35.8, 32.7, 29.3, 23.1, 21.6, 21.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{33}H_{34}F_7N_2O_4S_3$ $[M+H]^+$ 751.1563, found: 751.1566.



***N*,*N*'-((1*Z*)-1-(Benzo[*d*][1,3]dioxol-5-yl)-3,4,5,5,6,6,6-heptafluorohexa-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (3ma):**

Yield = 86% (179.3 mg, *E*/*Z* = 2.9/1). Yellow solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

IR (KBr): ν = 2929, 1352, 1214, 1170, 1169, 1024, 664, 544 cm^{-1}.

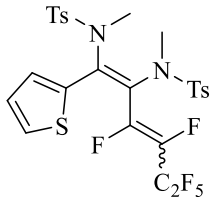
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.77 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 6.9 Hz, 2H), 6.69 (d, *J* = 1.6 Hz, 1H), 6.68 (s, 1H), 6.47 (d, *J* = 1.6 Hz, 1H), 5.93 (s, 2H), 3.19 (s, 3H), 3.18 (s, 3H), 2.43 (s, 3H), 2.42 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -84.41 (s, 3F), -120.35 – -120.97 (m, 2F), -134.62 – -136.24 (m, 1F), -157.67 (d, *J* = 137.9 Hz, 1F) ppm; ***Z*-isomer:** δ = -83.92 (s, 3F), -119.96 (s, 2F), -138.10 – -140.18 (m, 1F), -159.15 (d, *J* = 136.0 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 152.5–149.7 (m, 1C), 149.7, 147.8, 147.7 (d, $J_{C\text{-}F}$

= 3.6 Hz), 144.3, 144.2, 139.8–136.1 (m, 1C), 135.9, 135.0, 129.7, 129.6, 127.8, 127.7, 127.3, 124.7, 120.1 (dd, $J_{C\text{-}F}$ = 25.7, 6.1 Hz), 109.1, 108.2, 101.7, 37.6, 35.9, 21.5 (2C) ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{29}H_{26}F_7N_2O_6S_2$ $[M+H]^+$ 695.1115, found: 695.1123.



***N*,*N*'-((1*Z*)-3,4,5,5,6,6,6-Heptafluoro-1-(thiophen-2-yl)hexa-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (3na):**

Yield = 71% (139.4 mg, *E*/*Z* = 5.2/1). Yellow solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

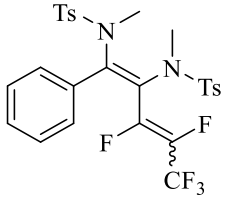
IR (KBr): ν = 1597, 1364, 1169, 1088, 894, 815, 661 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.80 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 1.3 Hz, 2H), 7.34–7.32 (m, 2H), 7.31 (s, 1H), 6.95 (dd, *J* = 3.7, 1.2 Hz, 1H), 6.92–6.90 (m, 1H), 3.10 (s, 3H), 3.05 (s, 3H), 2.44 (s, 3H), 2.43 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -84.25 (s, 3F), -120.55 (dd, *J* = 24.6, 12.8 Hz, 2F), -135.86 (dt, *J* = 139.3, 24.8 Hz, 1F), -157.31 (dtd, *J* = 139.3, 12.3, 6.1 Hz, 1F) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 152.7–148.7 (m, 1C), 144.3, 144.2, 140.2 (d, $J_{C\text{-}F}$ = 6.8 Hz), 139.5–136.8 (m, 1C), 135.9, 135.5, 135.0, 131.7, 130.7, 129.8, 129.7, 128.0 (2C), 127.6, 121.2 (dd, $J_{C\text{-}F}$ = 25.0, 6.2 Hz), 36.8, 35.0, 21.7, 21.6 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{26}H_{24}F_7N_2O_4S_3$ $[M+H]^+$ 657.0781, found: 657.0782.



***N*,*N*'-((1*Z*)-3,4,5,5,5-Pentafluoro-1-phenylpenta-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (3qa):**

Yield = 64% (115.6 mg, *E*/*Z* = 2.6/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 20/1).

IR (KBr): ν = 2360, 1599, 1346, 1158, 1046, 659, 547 cm^{-1}.

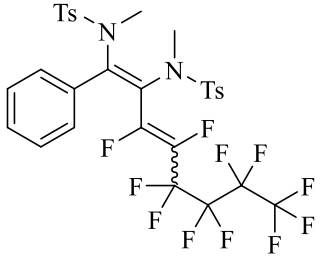
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.76 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.38–7.32 (m, 5H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 7.3 Hz, 2H), 3.25 (s, 3H), 3.25 (s, 3H), 2.44 (s, 3H), 2.40 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -68.14 (dd, *J* = 20.3, 11.0 Hz, 3F), -137.10 (dq, *J* = 137.8, 20.6 Hz, 1F), -159.65 (dq, *J* = 138.3, 11.1 Hz, 1F) ppm; ***Z*-isomer:** δ = -67.43 (dd, *J* = 21.1, 11.5 Hz, 3F), -140.29 – -141.26 (m, 1F), -160.59 (dd, *J* = 135.5, 11.5 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 148.3 (d, $J_{C\text{-}F}$ = 7.5 Hz), 147.8–145.1 (m, 1C), 144.3, 144.1, 140.8–136.8 (m, 1C), 135.9, 135.1, 133.6, 129.8, 129.63, 129.57, 129.5, 128.4,

127.8, 127.7, 121.4 (dd, $J_{C\text{-}F}$ = 25.8, 6.0 Hz), 37.9, 36.4, 21.61, 21.58 ppm, carbons corresponding to the CF_3 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{27}H_{26}F_5N_2O_4S_2$ $[M+H]^+$ 601.1249, found: 601.1251.



***N*,*N*'-((1*Z*)-3,4,5,5,6,6,7,7,8,8,8-Undecafluoro-1-phenylocta-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (3ra):**

Yield = 82% (184.8 mg, *E*/*Z* = 3.5/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 20/1).

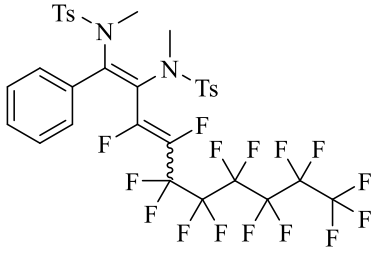
IR (KBr): ν = 1599, 1356, 1238, 1162, 996, 782, 546 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.79 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.25–7.18 (m, 5H), 7.13 (d, *J* = 7.3 Hz, 2H), 3.24 (s, 3H), 3.21 (s, 3H), 2.43 (s, 3H), 2.41 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -81.08 (t, *J* = 9.8 Hz, 3F), -117.46 (dq, *J* = 26.8, 13.5 Hz, 2F), -124.22 – -124.86 (m, 2F), -126.49 (t, *J* = 13.0 Hz, 2F), -135.04 (dt, *J* = 138.6, 25.9 Hz, 1F), -155.99 (dd, *J* = 138.7, 14.2 Hz, 1F) ppm; ***Z*-isomer:** δ = -80.90 (t, *J* = 9.9 Hz, 3F), -116.86 (s, 2F), -123.84 (s, 2F), -126.16 (s, 2F), -138.07 – -139.18 (m, 1F), -157.41 (d, *J* = 136.6 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 152.9–149.1 (m, 1C), 148.4 (d, $J_{C\text{-}F}$ = 8.9 Hz), 144.3, 144.1, 139.9–136.3 (m, 1C), 135.9, 135.2, 133.6, 129.74, 129.65, 129.60, 129.55, 128.4, 127.9, 127.8, 121.4 (dd, $J_{C\text{-}F}$ = 26.0, 5.9 Hz), 37.8, 36.1, 21.6, 21.5 ppm, carbons corresponding to the C_4F_9 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{30}H_{26}F_{11}N_2O_4S_2$ $[M+H]^+$ 751.1153, found: 751.1158.



***N*,*N*'-((1*Z*)-3,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluoro-1-phenyldeca-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (3sa):**

Yield = 94% (239.9 mg, *E*/*Z* = 3.0/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 20/1).

IR (KBr): ν = 1599, 1357, 1240, 1160, 1089, 781, 545 cm^{-1}.

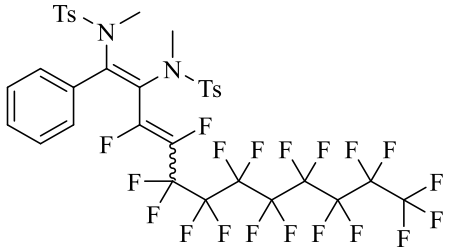
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.79 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.26–7.18 (m, 5H), 7.13 (d, *J* = 6.9 Hz, 2H), 3.24 (s, 3H), 3.21 (s, 3H),

2.43 (s, 3H), 2.41 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -80.89 (t, J = 9.9 Hz, 3F), -117.30 (dq, J = 27.1, 13.9 Hz, 2F), -122.24 – -122.55 (m, 2F), -122.93 (dt, J = 20.3, 10.1 Hz, 2F), -123.61 (qd, J = 14.0, 8.2 Hz, 2F), -126.23 (td, J = 14.6, 6.3 Hz, 2F), -135.03 (dt, J = 138.8, 26.0 Hz, 1F), -155.90 (d, J = 139.0 Hz, 1F) ppm; ***Z*-isomer:** δ = -80.84 (t, J = 6.7 Hz, 3F), -116.72 (s, 2F), -122.04 (t, J = 14.9 Hz, 2F), -122.59 – -122.82 (m, 4F), -126.05 – -126.17 (m, 2F), -137.92 – -139.14 (m, 1F), -157.34 (d, J = 136.5 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 153.2–149.1 (m, 1C), 148.4 (dd, $J_{C\text{-}F}$ = 8.0, 2.0 Hz), 144.3, 144.1, 140.0–136.4 (m, 1C), 136.0, 135.2, 133.6, 129.8, 129.7, 129.60, 129.56, 128.4, 127.9, 127.8, 121.5 (dd, $J_{C\text{-}F}$ = 25.6, 5.6 Hz), 37.8, 36.1, 21.5 (2C) ppm, carbons corresponding to the C_6F_{13} group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{32}H_{26}F_{15}N_2O_4S_2$ $[M+H]^+$ 851.1089, found: 851.1080.



***N*,*N*'-((1*Z*)-3,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Nonadecafluoro-1-phenyldodeca-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (3ta):**

Yield = 52% (147.7 mg, *E*/*Z* = 2.8/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 20/1).

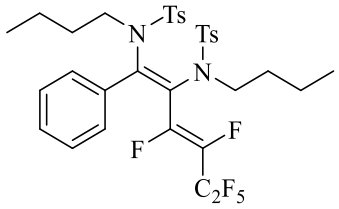
IR (KBr): ν = 3061, 1599, 1358, 1159, 940, 779, 661, 544 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.78 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.7 Hz, 2H), 7.27–7.18 (m, 5H), 7.12 (d, J = 6.9 Hz, 2H), 3.24 (s, 3H), 3.21 (s, 3H), 2.44 (s, 3H), 2.42 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -80.82 (d, J = 10.5 Hz, 3F), -117.01 – -117.53 (m, 2F), -121.88 – -122.05 (m, 4F), -122.18 (s, 2F), -122.75 (s, 2F), -123.54 (s, 2F), -126.13 (s, 2F), -135.07 (dt, J = 138.7, 25.5 Hz, 1F), -155.82 (d, J = 138.7 Hz, 1F) ppm; ***Z*-isomer:** δ = -80.77 (s, 3F), -116.69 (s, 2F), -121.74 (s, 4F), -121.85 (s, 2F), -122.88 (s, 4F), -126.18 (s, 2F), -137.98 – -139.12 (m, 1F), -157.25 (d, J = 136.8 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 153.1–148.9 (m, 1C), 148.4 (d, $J_{C\text{-}F}$ = 8.3 Hz), 144.3, 144.2, 137.6–136.3 (m, 1C), 136.0, 135.2, 133.7, 129.8, 129.7, 129.63, 129.59, 128.5, 127.9, 127.8, 121.5 (dd, $J_{C\text{-}F}$ = 25.8, 5.5 Hz), 37.9, 36.2, 21.6 (2C) ppm, carbons corresponding to the C_8F_{17} group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{34}H_{26}F_{19}N_2O_4S_2$ $[M+H]^+$ 951.1025, found: 951.1028.



***N*,*N*'-((1*Z*,3*E*)-3,4,5,5,6,6,6-Heptafluoro-1-phenylhexa-1,3-diene-1,2-diyl)bis(*N*-butyl-4-methylbenzenesulfonamide) (3ab):**

Yield = 59% (130.4 mg). White solid. M.p. 119.4-120.9 ºC.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 20/1).

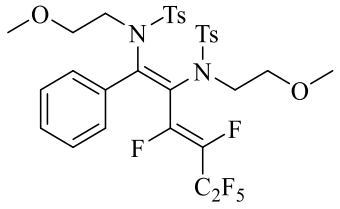
IR (KBr): ν = 2963, 1599, 1350, 1214, 1168, 813, 661, 543 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.2 Hz, 5H), 7.02 (d, J = 8.3 Hz, 3H), 6.96 (d, J = 8.1 Hz, 3H), 4.17–4.06 (m, 2H), 3.94–3.76 (m, 2H), 2.42 (s, 3H), 2.35 (s, 3H), 2.04–1.89 (m, 1H), 1.85–1.71 (m, 1H), 1.55–1.42 (m, 2H), 1.41–1.33 (m, 1H), 1.33–1.19 (m, 3H), 0.98 (t, J = 7.1 Hz, 3H), 0.88 (t, J = 7.1 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.36 (q, J = 3.9 Hz, 3F), -120.48 (dt, J = 33.5, 15.4 Hz, 2F), -134.09 (d, J = 138.0 Hz, 1F), -156.46 (d, J = 137.2 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.9–148.2 (m, 1C), 145.0, 144.2, 143.6, 137.9, 136.8, 136.6–136.0 (m, 1C), 134.2, 131.7, 129.8, 129.7, 129.2, 128.0, 127.3, 127.1, 119.0 (d, $J_{C\text{-}F}$ = 35.8 Hz), 49.3, 48.5, 30.8, 30.1, 21.6, 21.5, 20.1, 19.8, 13.9 (2C) ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{34}H_{38}F_7N_2O_4S_2$ $[M+H]^+$ 735.2156, found: 735.2158.



***N*,*N*'-((1*Z*,3*E*)-3,4,5,5,6,6,6-Heptafluoro-1-phenylhexa-1,3-diene-1,2-diyl)bis(*N*-(2-methoxyethyl)-4-methylbenzenesulfonamide) (3ac):**

Yield = 61% (135.6 mg). White solid. M.p. 130.6-131.9 ºC.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

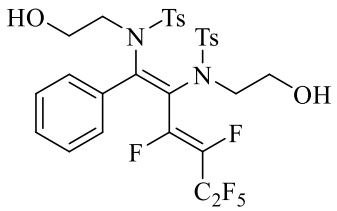
IR (KBr): ν = 2898, 1692, 1448, 1356, 1166, 956, 782, 657 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.3 Hz, 3H), 7.26–7.20 (m, 2H), 7.03 (d, J = 8.1 Hz, 3H), 6.95 (d, J = 8.1 Hz, 3H), 4.47 (ddd, J = 15.9, 9.9, 3.0 Hz, 1H), 4.39–4.28 (m, 1H), 4.20–4.10 (m, 1H), 4.06 (dt, J = 15.3, 4.5 Hz, 1H), 3.91–3.81 (m, 1H), 3.60 (dt, J = 11.6, 3.2 Hz, 1H), 3.56–3.49 (m, 2H), 3.30 (s, 3H), 3.20 (s, 3H), 2.42 (s, 3H), 2.33 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.33 (s, 3F), -120.65 (q, J = 19.1 Hz, 2F), -134.70 (d, J = 137.3 Hz, 1F), -156.76 (d, J = 137.5 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.9–148.9 (m, 1C), 144.7 (d $J_{C\text{-}F}$ = 6.0 Hz), 144.3, 143.4, 139.1–138.6 (m, 1C), 137.6, 136.4, 133.9, 131.2, 130.1, 129.8, 129.4, 128.6, 127.9, 127.7, 118.3 (d, $J_{C\text{-}F}$ = 25.8 Hz), 69.7, 69.1, 58.7, 58.1, 49.5, 48.3, 21.6, 21.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{32}H_{34}F_7N_2O_6S_2$ $[M+H]^+$ 739.1741, found: 739.1749.



***N*,*N*'-((1*Z*,3*E*)-3,4,5,5,6,6,6-Heptafluoro-1-phenylhexa-1,3-diene-1,2-diyl)bis(*N*-(2-hydroxyeth yl)-4-methylbenzenesulfonamide) (3ad):**

Yield = 35% (74.6 mg). Light yellow oil.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 15/1).

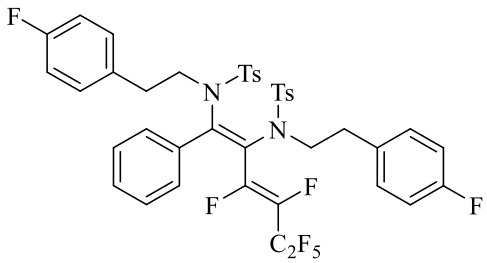
IR (KBr): ν = 3665, 1598, 1366, 1224, 1170, 802, 766 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.42 (m, 4H), 7.27 (d, J = 2.0 Hz, 1H), 7.26–7.22 (m, 8H), 3.92–3.85 (m, 8H), 2.42 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.55 – -84.67 (m, 3F), -121.02 – -121.19 (m, 2F), -135.32 – -135.90 (m, 1F), -158.49 (ddtd, J = 143.4, 17.6, 9.0, 4.5 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.6–148.6 (m, 1C), 144.7, 139.4–135.8 (m, 1C), 135.3, 133.4, 130.4 (dd, $J_{C\text{-}F}$ = 25.6, 5.3 Hz), 129.9 (2C), 129.4 (2C), 129.1, 127.9 (2C), 127.7 (2C), 124.8 (dd, $J_{C\text{-}F}$ = 7.2, 2.9 Hz), 65.0 (2C), 44.7 (2C), 21.7 (2C) ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{30}H_{30}F_7N_2O_6S_2$ $[M+H]^+$ 711.1428, found: 711.1425.



***N*,*N*'-((1*Z*,3*E*)-3,4,5,5,6,6,6-Heptafluoro-1-phenylhexa-1,3-diene-1,2-diyl)bis(*N*-(4-fluorophen ethyl)-4-methylbenzenesulfonamide) (3ae):**

Yield = 67% (173.6 mg). White solid. M.p. 173.8-174.5 °C.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 20/1).

IR (KBr): ν = 1599, 1512, 1349, 1222, 1165, 814, 736, 543 cm^{-1}.

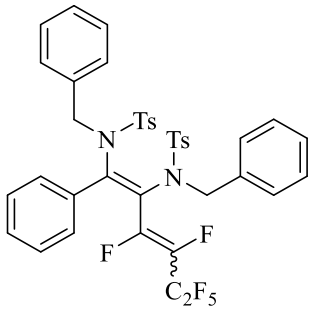
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, J = 8.0 Hz, 2H), 7.39 (dd, J = 8.8, 2.5 Hz, 3H), 7.37–7.30 (m, 3H), 7.25–7.16 (m, 3H), 7.10 (d, J = 8.3 Hz, 3H), 7.07–7.01 (m, 4H), 7.01–6.94 (m, 3H), 4.47–4.24 (m, 2H), 4.20–3.91 (m, 2H), 3.40–3.16 (m, 2H), 2.81 (td, J = 11.9, 5.0 Hz, 1H), 2.49 (s, 3H), 2.48–2.42 (m, 1H), 2.40 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.28 – -84.42 (m, 3F), -116.18 (s, 1F), -116.36 (s, 1F), -120.54 (dddd, J = 42.0, 20.1, 13.1, 3.3 Hz, 2F), -133.79 (d, J = 137.7 Hz, 1F), -156.02 (d, J = 137.6 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.1 (d, $J_{C\text{-}F}$ = 9.7 Hz), 160.7 (d, $J_{C\text{-}F}$ = 9.5 Hz), 152.5–148.7 (m, 1C), 145.4 (d, $J_{C\text{-}F}$ = 6.6 Hz), 144.5 (d, $J_{C\text{-}F}$ = 65.5 Hz), 137.4, 136.3, 133.8, 133.5 (d, $J_{C\text{-}F}$ = 3.3 Hz), 133.3 (d, $J_{C\text{-}F}$ = 3.2 Hz), 130.8 (d, $J_{C\text{-}F}$ = 7.9 Hz), 130.6 (d, $J_{C\text{-}F}$ = 7.9 Hz), 130.1, 130.0 (2C), 129.4 (2C), 128.1, 127.4 (2C), 127.2 (2C), 115.6 (d, $J_{C\text{-}F}$ = 3.4 Hz), 115.4 (d, $J_{C\text{-}F}$ = 3.4 Hz),

50.6, 50.2, 34.5, 34.0, 21.7, 21.6 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{42}H_{36}F_9N_2O_4S_2$ $[M+H]^+$ 867.1967, found: 867.1960.



***N*,*N*'-((1*Z*)-3,4,5,5,6,6,6-Heptafluoro-1-phenylhexa-1,3-diene-1,2-diyl)bis(*N*-benzyl-4-methylbenzenesulfonamide) (3af):**

Yield = 73% (174.5 mg, *E*/*Z* = 2.0/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 20/1).

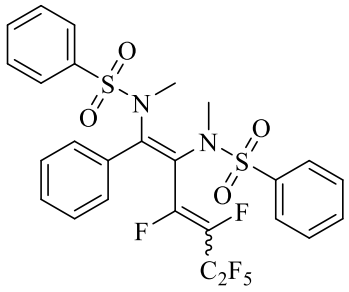
IR (KBr): ν = 3062, 1597, 1356, 1228, 1165, 699, 657, 542 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.46–7.33 (m, 8H), 7.33–7.21 (m, 10H), 6.85 (d, *J* = 8.0 Hz, 3H), 6.64 (s, 2H), 5.44 (s, 2H), 5.28 (s, 2H), 2.40 (s, 3H), 2.31 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -84.36 (t, *J* = 4.3 Hz, 3F), -120.33 – -120.85 (m, 2F), -134.06 (d, *J* = 134.6 Hz, 1F), -155.82 (d, *J* = 136.8 Hz, 1F) ppm; ***Z*-isomer:** δ = -83.57 (s, 3F), -118.74 – -119.89 (m, 2F), -136.70 (d, *J* = 136.5 Hz, 1F), -153.87 (d, *J* = 139.5 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 152.7–149.0 (m, 1C), 147.3, 144.2, 144.0, 143.5, 137.5, 136.84, 136.75, 136.2, 136.0, 135.4, 134.8, 134.2, 133.2, 130.8, 130.1, 129.9, 129.5, 128.73, 128.70, 128.3, 128.2, 127.8, 127.7, 54.8, 54.5, 21.5, 21.4 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{40}H_{34}F_7N_2O_4S_2$ $[M+H]^+$ 803.1843, found: 803.1844.



***N*,*N*'-((1*Z*)-3,4,5,5,6,6,6-Heptafluoro-1-phenylhexa-1,3-diene-1,2-diyl)bis(*N*-methylbenzenesulfonamide) (3ag):**

Yield = 87% (163.4 mg, *E*/*Z* = 4.2/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 20/1).

IR (KBr): ν = 3068, 1709, 1448, 1357, 1216, 1076, 790, 577 cm^{-1}.

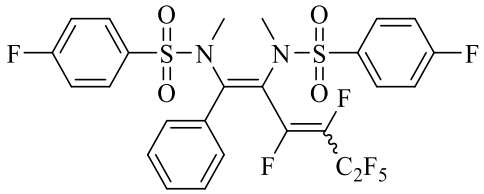
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.92–7.86 (m, 2H), 7.60–7.52 (m, 6H), 7.44–7.38 (m, 2H), 7.33–7.28 (m, 1H), 7.21–7.16 (m, 2H), 7.08 (d, *J* = 7.3 Hz, 2H), 3.26 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -84.27 – -84.65 (m, 3F), -120.75 (dd, *J* = 25.2,

13.2 Hz, 2F), -135.88 (dt, J = 139.4, 25.2 Hz, 1F), -157.17 (dtd, J = 138.2, 12.6, 5.4 Hz, 1F) ppm; ***Z*-isomer:** δ = -83.90 (s, 3F), -119.92 (s, 2F), -138.72 – -139.68 (m, 1F), -158.50 (d, J = 136.5 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 153.1–148.8 (m, 1C), 148.4 (dd, $J_{C\text{-}F}$ = 8.6, 3.0 Hz), 138.9, 138.0, 137.4–136.1 (m, 1C), 133.4, 133.3, 133.2, 130.4, 129.47, 129.45, 129.2, 129.0, 128.5, 127.7 (2C), 121.8–121.1 (m, 1C), 119.8–115.6 (m, 1C), 38.0, 36.4 ppm.

HRMS (m/z): calcd for $C_{26}H_{22}F_7N_2O_4S_2$ $[M+H]^+$ 623.0904, found: 623.0910.



***N*,*N*'-((1*Z*)-3,4,5,5,6,6,6-Heptafluoro-1-phenylhexa-1,3-diene-1,2-diyl)bis(4-fluoro-*N*-methylbenzenesulfonamide) (3ah):**

Yield = 43% (85.4 mg, *E*/*Z* = 3.7/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 20/1).

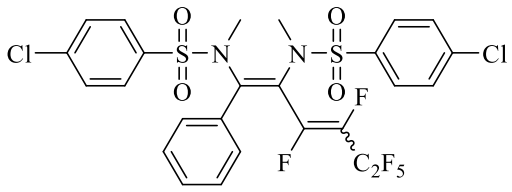
IR (KBr): ν = 3075, 1594, 1495, 1358, 1168, 945, 787, 540 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.93–7.87 (m, 2H), 7.67–7.54 (m, 2H), 7.39–7.35 (m, 1H), 7.29–7.24 (m, 4H), 7.14–7.08 (m, 4H), 3.24 (s, 3H), 3.23 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -84.43 – -84.58 (m, 3F), -104.01 (s, 1F), -104.14 (s, 1F), -120.69 – -121.09 (m, 2F), -136.36 (dt, J = 139.4, 24.7 Hz, 1F), -156.71 (dtt, J = 139.1, 13.1, 4.6 Hz, 1F) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 166.8 (d, $J_{C\text{-}F}$ = 16.4 Hz), 164.3 (d, $J_{C\text{-}F}$ = 16.3 Hz), 152.2–148.8 (m, 1C), 148.5 (d, $J_{C\text{-}F}$ = 9.2 Hz), 140.3–136.3 (m, 1C), 134.9 (d, $J_{C\text{-}F}$ = 3.3 Hz), 134.0 (d, $J_{C\text{-}F}$ = 3.4 Hz), 133.3, 130.7, 130.6 (t, $J_{C\text{-}F}$ = 8.0 Hz), 129.5, 128.7, 121.4 (dd, $J_{C\text{-}F}$ = 25.9, 6.2 Hz), 116.6, 116.4, 116.2, 38.0, 36.3 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{26}H_{20}F_9N_2O_4S_2$ $[M+H]^+$ 659.0715, found: 659.0717.



***N*,*N*'-((1*Z*)-3,4,5,5,6,6,6-Heptafluoro-1-phenylhexa-1,3-diene-1,2-diyl)bis(4-chloro-*N*-methylbenzenesulfonamide) (3ai):**

Yield = 79% (163.6 mg, *E*/*Z* = 3.4/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 20/1).

IR (KBr): ν = 2948, 1587, 1359, 1220, 1167, 1020, 788, 629 cm^{-1}.

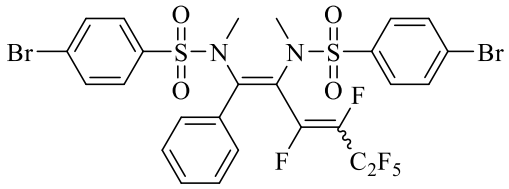
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.81–7.76 (m, 2H), 7.53–7.47 (m, 4H), 7.39–7.35 (m, 2H), 7.35–7.32 (m, 1H), 7.23–7.19 (m, 2H), 7.08 (d, J = 7.0 Hz, 2H), 3.20 (s, 3H), 3.19 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -84.35 (d, J = 3.8 Hz, 3F), -120.70 (dd, J = 24.8,

12.8 Hz, 2F), -136.22 (dt, *J* = 138.0, 25.0 Hz, 1F), -156.46 (ddt, *J* = 140.5, 15.9, 8.0 Hz, 1F) ppm; ***Z*-isomer:** δ = -83.92 (s, 3F), -119.97 (s, 2F), -138.73 – -139.92 (m, 1F), -157.83 (d, *J* = 136.9 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 152.1–148.7 (m, 1C), 148.7–148.3 (m, 1C), 146.0, 140.1, 139.9, 137.3, 136.4, 133.2, 130.7, 129.53, 129.46, 129.33, 129.29, 129.23, 129.18, 128.7, 121.6–121.1 (m, 1C), 119.8–115.7 (m, 1C), 38.0, 36.2 ppm.

HRMS (m/z): calcd for $C_{26}H_{20}Cl_2F_7N_2O_4S_2$ $[M+H]^+$ 691.0124, found: 691.0129.



***N*,*N*'-((1*Z*)-3,4,5,5,6,6,6-Heptafluoro-1-phenylhexa-1,3-diene-1,2-diyl)bis(4-bromo-*N*-methylbenzenesulfonamide) (3aj):**

Yield = 82% (190.7 mg, *E*/*Z* = 3.1/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 20/1).

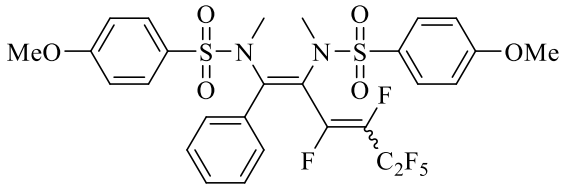
IR (KBr): ν = 2361, 1575, 1472, 1358, 1220, 1168, 787, 618 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.71–7.65 (m, 4H), 7.55–7.50 (m, 2H), 7.45–7.39 (m, 2H), 7.34–7.29 (m, 1H), 7.21 (d, *J* = 7.7 Hz, 2H), 7.07 (dd, *J* = 7.0, 1.5 Hz, 2H), 3.19 (s, 3H), 3.18 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -84.32 (t, *J* = 4.9 Hz, 3F), -120.68 (dd, *J* = 24.9, 13.0 Hz, 2F), -136.21 (dt, *J* = 139.0, 25.6 Hz, 1F), -156.07 – -156.75 (m, 1F) ppm; ***Z*-isomer:** δ = -83.89 (s, 3F), -119.95 (s, 2F), -138.72 – -139.93 (m, 1F), -157.79 (d, *J* = 136.7 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 152.0–148.6 (m, 1C), 148.5 (d, $J_{C\text{-}F}$ = 9.2 Hz), 146.0, 140.4–138.5 (m, 1C), 137.8, 136.9, 132.5, 132.33, 132.29, 130.7, 129.5, 129.30, 129.25, 128.9, 128.7, 128.4, 121.6–121.1 (m, 1C), 119.4–116.1 (m, 1C), 38.0, 36.2 ppm.

HRMS (m/z): calcd for $C_{26}H_{20}Br_2F_7N_2O_4S_2$ $[M+H]^+$ 778.9114, found: 778.9118.



***N*,*N*'-((1*Z*)-3,4,5,5,6,6,6-Heptafluoro-1-phenylhexa-1,3-diene-1,2-diyl)bis(4-methoxy-*N*-methylbenzenesulfonamide) (3ak):**

Yield = 57% (116.7 mg, *E*/*Z* = 3.8/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

IR (KBr): ν = 2947, 2359, 1597, 1355, 1262, 1159, 941, 837 cm^{-1}.

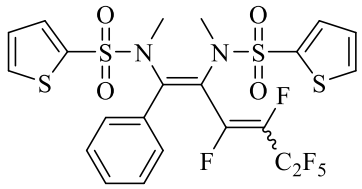
^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.86–7.79 (m, 2H), 7.57–7.47 (m, 2H), 7.29–7.20 (m, 3H), 7.16–7.11 (m, 2H), 7.03–6.99 (m, 2H), 6.91–6.85 (m, 2H), 3.88 (s, 3H), 3.85 (s, 3H), 3.23 (s, 3H), 3.21 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -84.37 (d, *J* = 6.0 Hz, 3F), -120.66 (dd, *J* = 24.9, 13.0 Hz, 2F), -135.53 (dt, *J* = 138.3, 24.3 Hz, 1F), -156.83 – -157.90 (m, 1F) ppm; ***Z*-isomer:** δ =

-83.91 (s, 3F), -119.86 (s, 2F), -138.60 – -139.58 (m, 1F), -158.77 (d, J = 136.3 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 163.4, 163.3, 152.7–149.1 (m, 1C), 148.8–147.7 (m, 1C), 145.9–135.7 (m, 1C), 133.6, 130.5, 130.4, 130.3, 130.0, 129.9, 129.5, 128.5, 121.7–121.2 (m, 1C), 114.3, 114.1, 55.7 (2C), 37.8, 36.2 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{28}H_{26}F_7N_2O_6S_2$ $[M+H]^+$ 683.1115, found: 683.1117.



_N_-((1_Z_)-3,4,5,5,6,6,6-Heptafluoro-1-(_N_-methylthiophene-2-sulfonamido)-1-phenylhexa-1,3-dien-2-yl)-_N_-methylthiophene-2-sulfonamide (3am):

Yield = 94% (178.9 mg, E/Z = 5.0/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

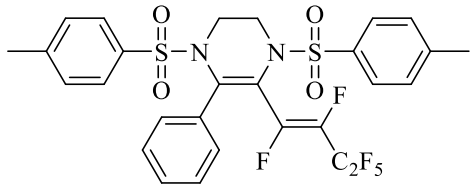
IR (KBr): ν = 3091, 1363, 1213, 1169, 1019, 788, 572 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.70–7.65 (m, 2H), 7.65–7.61 (m, 1H), 7.39–7.36 (m, 1H), 7.34 (dd, J = 3.8, 1.4 Hz, 1H), 7.30–7.27 (m, 2H), 7.20–7.14 (m, 3H), 7.04 (dd, J = 5.0, 3.8 Hz, 1H), 3.29 (s, 3H), 3.24 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -84.37 (t, J = 4.0 Hz, 3F), -120.73 (dd, J = 25.5, 12.0 Hz, 2F), -136.59 (dt, J = 139.3, 24.9 Hz, 1F), -156.01 – -156.72 (m, 1F) ppm; ***Z*-isomer:** δ = -83.83 (s, 3F), -119.99 (s, 2F), -139.74 – -140.62 (m, 1F), -158.16 (d, J = 136.3 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 151.9–148.7 (m, 1C), 148.6–148.3 (m, 1C), 146.0–139.5 (m, 1C), 139.2, 138.3, 133.4, 133.0, 132.92, 132.88, 132.85, 130.7, 129.4, 128.6, 127.7, 127.5, 121.5–120.7 (m, 1C), 37.8, 36.0 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{22}H_{18}F_7N_2O_4S_4$ $[M+H]^+$ 635.0032, found: 635.0038.



(_E_)-5-(Perfluorobut-1-en-1-yl)-6-phenyl-1,4-ditosyl-1,2,3,4-tetrahydropyrazine (3aq):

Yield = 73% (141.8 mg). White solid. M.p. 131.4-133.2 °C.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 7/1).

IR (KBr): ν = 3060, 1597, 1365, 1223, 1171, 1019, 772, 664 cm^{-1}.

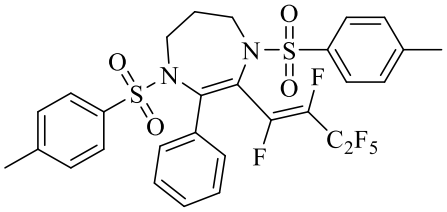
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.62 (m, 2H), 7.37–7.33 (m, 2H), 7.33–7.27 (m, 1H), 7.21–7.15 (m, 4H), 7.15–7.08 (m, 4H), 3.48–3.31 (m, 4H), 2.46 (s, 3H), 2.37 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.36 (q, J = 3.9 Hz, 3F), -120.97 – -121.22 (m, 2F), -124.41 – -125.02 (m, 1F), -158.90 (dddt, J = 141.1, 17.9, 13.7, 4.7 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.3–148.8 (m, 1C), 145.2, 144.7, 138.8–135.9 (m, 1C), 135.6, 133.8, 132.4, 130.3 (2C), 129.8, 129.4, 127.7, 127.5, 127.3, 119.9–116.0 (m, 1C), 110.3–

109.8 (m, 1C), 44.1, 43.5, 21.7, 21.6 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{28}H_{24}F_7N_2O_4S_2$ $[M+H]^+$ 649.1060, found: 649.1067.



(*E*)-2-(Perfluorobut-1-en-1-yl)-3-phenyl-1,4-ditosyl-4,5,6,7-tetrahydro-1*H*-1,4-diazepine (3ar):

Yield = 85% (168.3 mg). White solid. M.p. 184.1-185.8 ºC.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 4/1).

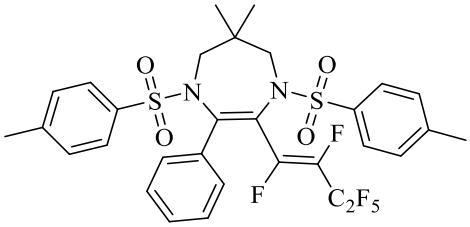
IR (KBr): ν = 2360, 1449, 1333, 1159, 1052, 964, 819 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.23–7.17 (m, 1H), 7.06–6.96 (m, 8H), 3.95 (s, 4H), 2.42 (s, 3H), 2.32 (s, 3H), 2.30–2.21 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.48 (s, 3F), -120.88 (dd, J = 24.6, 12.8 Hz, 2F), -127.23 (s, 1F), -157.40 (d, J = 140.9 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.0–148.1 (m, 1C), 144.5, 143.7, 139.1–137.8 (m, 1C), 137.7, 136.7, 136.3–135.4 (m, 1C), 132.3, 130.4, 129.9, 129.5, 129.3, 127.6, 127.4, 127.0, 120.0–115.8 (m, 1C), 50.7, 49.2, 28.8, 21.6, 21.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{29}H_{26}F_7N_2O_4S_2$ $[M+H]^+$ 663.1217, found: 663.1212.



(*E*)-6,6-Dimethyl-2-(perfluorobut-1-en-1-yl)-3-phenyl-1,4-ditosyl-4,5,6,7-tetrahydro-1*H*-1,4-diazepine (3as):

Yield = 70% (145.1 mg). White solid. M.p. 197.6-198.6 ºC.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

IR (KBr): ν = 3053, 1354, 1214, 1166, 1057, 811, 666, 545 cm^{-1}.

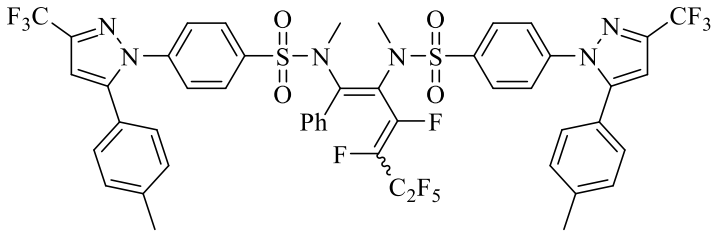
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.80 (m, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.29–7.23 (m, 1H), 7.10–6.99 (m, 4H), 6.97–6.89 (m, 4H), 4.00–2.64 (m, 4H), 2.41 (s, 3H), 2.29 (s, 3H), 1.06 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.96 – -85.10 (m, 3F), -116.99 (s, 1F), -121.30 (s, 2F), -156.99 (d, J = 144.3 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.7–148.5 (m, 1C), 148.4, 144.3, 143.3, 137.2, 137.0, 136.7–136.1 (m, 1C), 131.7, 129.8, 129.7, 129.6, 129.2, 127.7, 127.5, 127.0, 123.0–122.3 (m, 1C), 59.5, 57.9, 36.3, 24.0, 21.6, 21.5 ppm, carbons corresponding to the C_2F_5 group cannot be

identified due to C-F coupling.

HRMS (m/z): calcd for $C_{31}H_{30}F_7N_2O_4S_2$ $[M+H]^+$ 691.1530, found: 691.1538.



***N*-((1*Z*)-3,4,5,5,6,6,6-Heptafluoro-1-((*N*-methyl-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)sulfonamido)-1-phenylhexa-1,3-dien-2-yl)-*N*-methyl-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (3at):**

Yield = 90% (288.7 mg, *E*/*Z* = 3.6/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 7/1).

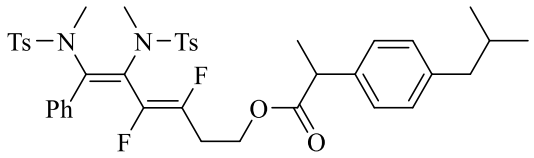
IR (KBr): ν = 3065, 1597, 1473, 1364, 1238, 1166, 976, 627 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.85 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.19–7.14 (m, 5H), 7.14–7.06 (m, 8H), 6.77–6.72 (m, 2H), 3.19 (s, 3H), 3.14 (s, 3H), 2.37 (s, 3H), 2.36 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -62.31 (s, 6F), -84.34 (t, *J* = 4.2 Hz, 3F), -120.64 (dd, *J* = 25.2, 12.9 Hz, 2F), -136.30 (d, *J* = 140.2 Hz, 1F), -156.11 (dd, *J* = 138.9, 14.2 Hz, 1F) ppm; ***Z*-isomer:** δ = -62.33 (s, 6F), -83.97 (s, 3F), -120.01 (s, 2F), -138.97 – -139.83 (m, 1F), -157.77 (d, *J* = 136.8 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 152.4–148.8 (m, 1C), 148.5 (d, *J* = 8.9 Hz), 145.44, 145.41, 144.5, 144.1, 143.1, 143.0, 140.0, 139.9, 138.1, 137.2, 133.3, 130.9, 129.9, 129.8, 129.5, 128.91, 128.86, 128.81, 128.77, 128.7, 125.78, 125.76, 125.6, 125.5, 122.5, 119.8, 106.6, 106.5, 37.7, 35.9, 21.4, 21.3 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{48}H_{36}F_{13}N_6O_4S_2$ $[M+H]^+$ 1071.2026, found: 1071.2023.



(5*Z*)-5,6-Bis((*N*,4-dimethylphenyl)sulfonamido)-3,4-difluoro-6-phenylhexa-3,5-dien-1-yl 2-(4-isobutylphenyl)propanoate (3ua):

Yield = 22% (49.4 mg, *E*/*Z* = 8.3/1). White solid.

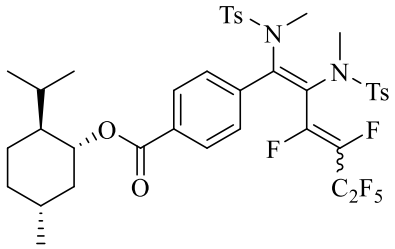
Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.79–7.71 (m, 3H), 7.69–7.64 (m, 2H), 7.39–7.29 (m, 7H), 7.24–7.19 (m, 2H), 7.13–7.08 (m, 2H), 7.06–6.94 (m, 1H), 5.34 (ddd, *J* = 24.7, 14.2, 3.4 Hz, 1H), 3.71 (q, *J* = 7.2 Hz, 1H), 3.02 (d, *J* = 2.3 Hz, 3H), 2.97 (s, 3H), 2.63 (d, *J* = 5.1 Hz, 1H), 2.45 (s, 3H), 2.44-2.42 (m, 7H), 1.83 (dq, *J* = 13.5, 6.8 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 3H), 0.90 (s, 3H), 0.89 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomer: δ = -131.21 (d, *J* = 113.4 Hz, 1F), -153.90 (dq, *J* = 119.2, 23.8 Hz, 1F) ppm; ***Z*-isomer:** δ = -122.50 (s, 1F), -143.05 (d, *J* = 22.6 Hz, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 180.3, 145.6 (m, 1C), 144.7, 144.6, 143.6, 140.9, 137.2, 135.8, 135.2, 134.5, 130.6 (m, 1C), 130.2, 130.0, 129.9, 129.8, 129.5, 128.1, 128.0, 127.4, 127.1, 96.0 (dd, *J* = 17.2, 5.1 Hz), 45.1, 45.0, 36.0, 32.1, 30.3, 29.4, 22.5, 21.8, 21.7, 21.6, 18.2 ppm.

HRMS (m/z): calcd for $C_{41}H_{47}F_2N_2O_6S_2$ $[M+H]^+$ 765.2838, found: 765.2836.



(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-((1*Z*)-1,2-bis((*N*,4-dimethylphenyl)sulfonamido)-3,4,5,5,6,6,6-heptafluorohexa-1,3-dien-1-yl)benzoate (3va):

Yield = 47% (117.6 mg, *E*/*Z* = 1.9/1). White solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

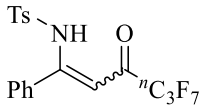
IR (KBr): ν = 2958, 1715, 1358, 1217, 1163, 785, 662, 543 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) of *E*-isomer: δ = 7.87 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.18 (dd, *J* = 16.4, 8.1 Hz, 4H), 4.93 (td, *J* = 10.8, 4.4 Hz, 1H), 3.24 (d, *J* = 2.5 Hz, 6H), 2.45 (s, 3H), 2.42 (s, 3H), 2.15–2.08 (m, 1H), 1.95–1.85 (m, 1H), 1.78–1.69 (m, 2H), 1.62–1.49 (m, 2H), 1.17–1.05 (m, 2H), 0.96–0.90 (m, 7H), 0.79 (d, *J* = 6.9 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.38 (t, *J* = 4.3 Hz, 3F), -120.78 (dd, *J* = 24.8, 12.9 Hz, 2F), -135.78 (dt, *J* = 138.5, 25.3 Hz, 1F), -156.36 – -156.97 (m, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*-isomer: δ = 165.3, 152.3–147.9 (m, 1C), 147.2 (d, *J* = 8.1 Hz), 144.5, 144.4, 137.9, 135.8, 135.0, 132.3, 129.9, 129.7, 129.6 (2C), 128.5–128.0 (m, 1C), 127.83, 127.81, 122.9–122.0 (m, 1C), 75.4, 47.4, 41.0, 38.0, 36.5, 34.4, 31.6, 26.8, 23.8, 22.2, 21.73, 21.71, 20.8, 16.7 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{39}H_{44}F_7N_2O_6S_2$ $[M+H]^+$ 833.2524, found: 833.2528.



***N*-(4,4,5,5,6,6,6-Heptafluoro-3-oxo-1-phenylhex-1-en-1-yl)-4-methylbenzenesulfonamide (7):**

Yield = 46% (65 mg, *Z*/*E* = 2.4/1). Yellow solid.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 7/1).

IR (KBr): ν = 3297, 1627, 1348, 1237, 1118, 945, 739 cm^{-1}.

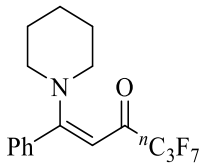
^{1}H NMR (400 MHz, $CDCl_3$) of *Z*-isomer: δ = 7.67–7.60 (m, 2H), 7.46–7.42 (m, 2H), 7.36–7.30 (m, 2H), 7.20–7.14 (m, 3H), 6.84 (brs, 1H), 5.34 (s, 1H), 2.36 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *Z*-isomer: δ = -80.09 (t, *J* = 9.7 Hz, 3F), -119.44 (q, *J* = 10.1 Hz, 2F), -126.44 (s, 2F) ppm; ***E*-isomer:** δ = -80.46 (t, *J* = 8.6 Hz, 3F), -121.49 (q, *J* = 8.9 Hz, 2F),

-126.62 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *Z*-isomer: δ = 177.3, 148.8–146.2 (m, 1C), 143.3, 139.4, 138.5, 130.6, 129.5, 128.2, 127.6, 127.0, 97.5–96.8 (m, 1C), 21.6 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{19}H_{15}F_7NO_3S$ $[M+H]^+$ 470.0655, found: 470.0660.



(*Z*)-4,4,5,5,6,6,6-Heptafluoro-1-phenyl-1-(piperidin-1-yl)hex-1-en-3-one (9):

Yield = 17% (19.9 mg). Yellow oil.

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 7/1).

IR (KBr): ν = 2942, 1652, 1449, 1343, 1223, 1113, 1012, 959 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (dd, J = 7.4, 2.0 Hz, 2H), 7.53 (dd, J = 8.4, 6.0 Hz, 1H), 7.50–7.42 (m, 2H), 6.32 (s, 1H), 3.16–3.06 (m, 4H), 1.67–1.58 (m, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.27 (s, 3F), -109.37 (s, 2F), -124.83 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.0, 148.8 (t, J = 21.9 Hz), 139.1, 132.6, 128.7, 128.4, 105.6, 53.3, 26.2, 23.7 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{17}H_{17}F_7NO$ $[M+H]^+$ 384.1193, found: 384.1195.

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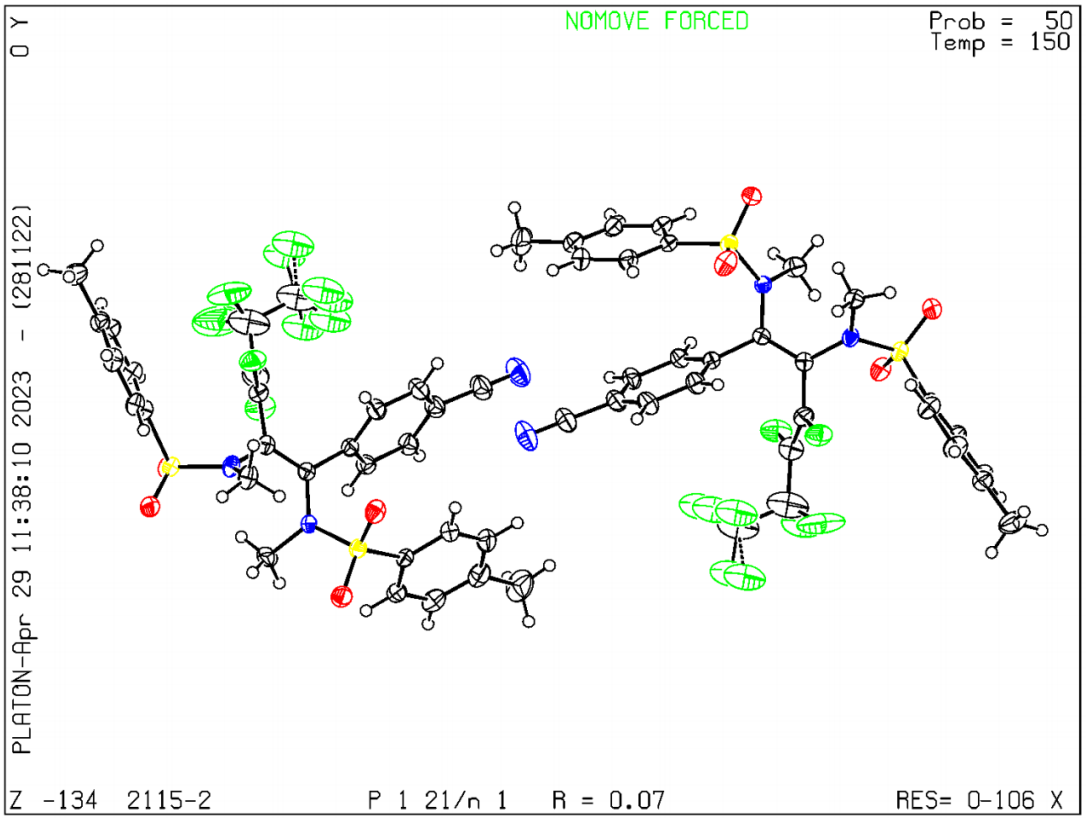
The X-ray crystal structure of product (*E*)-3ka

The single crystals were grown from the solution of MeCN by slowly evaporating the above solvents at room temperature.

(*E*)-*N*,*N*'-((1*Z*)-1-(4-Cyanophenyl)-3,4,5,5,6,6,6-heptafluorohexa-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) [(*E*)-3ka; displacement ellipsoids are drawn at the 50% probability levels**]:**



CCDC number: 2259863

Table 1 Crystal data and structure refinement for (*E*)**-3ka**

Identification code	(*E*)**-3ka**
Empirical formula	$C_{29}H_{24}F_7N_3O_4S_2$
Formula weight	675.63
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	29.6726(2)
b/Å	6.12887(5)
c/Å	35.8542(3)
α/°	90
β/°	99.3669(8)
γ/°	90
Volume/Å^3	6433.47(9)
Z	8
ρ_{calc}g/cm^3	1.395
μ/mm^{-1}	2.211
F(000)	2768.0

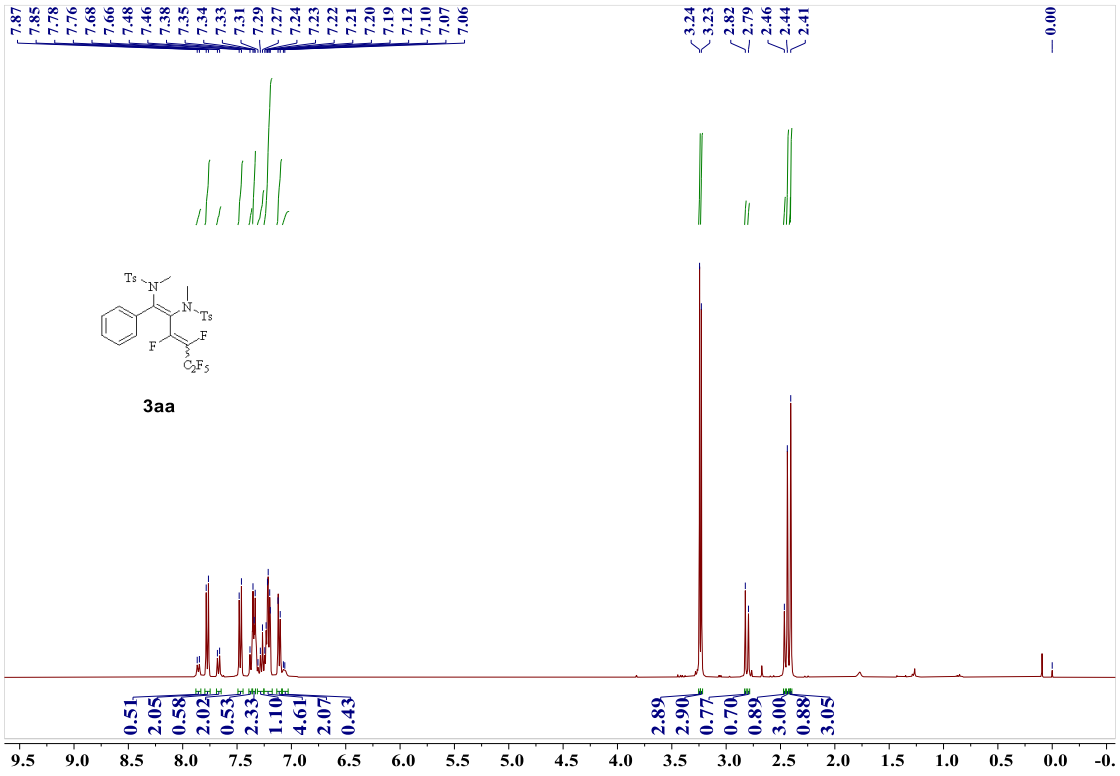
Crystal size/mm^3	0.14 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.038 to 143.048
Index ranges	-36 ≤ h ≤ 30, -7 ≤ k ≤ 7, -37 ≤ l ≤ 43
Reflections collected	27846
Independent reflections	12157 [R_{int} = 0.0231, R_{sigma} = 0.0305]
Data/restraints/parameters	12157/776/779
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0687, wR_2 = 0.1776
Final R indexes [all data]	R_1 = 0.0773, wR_2 = 0.1822
Largest diff. peak/hole / e Å^{-3}	1.26/-1.48

Crystal structure determination of [(*E*)-3ka]

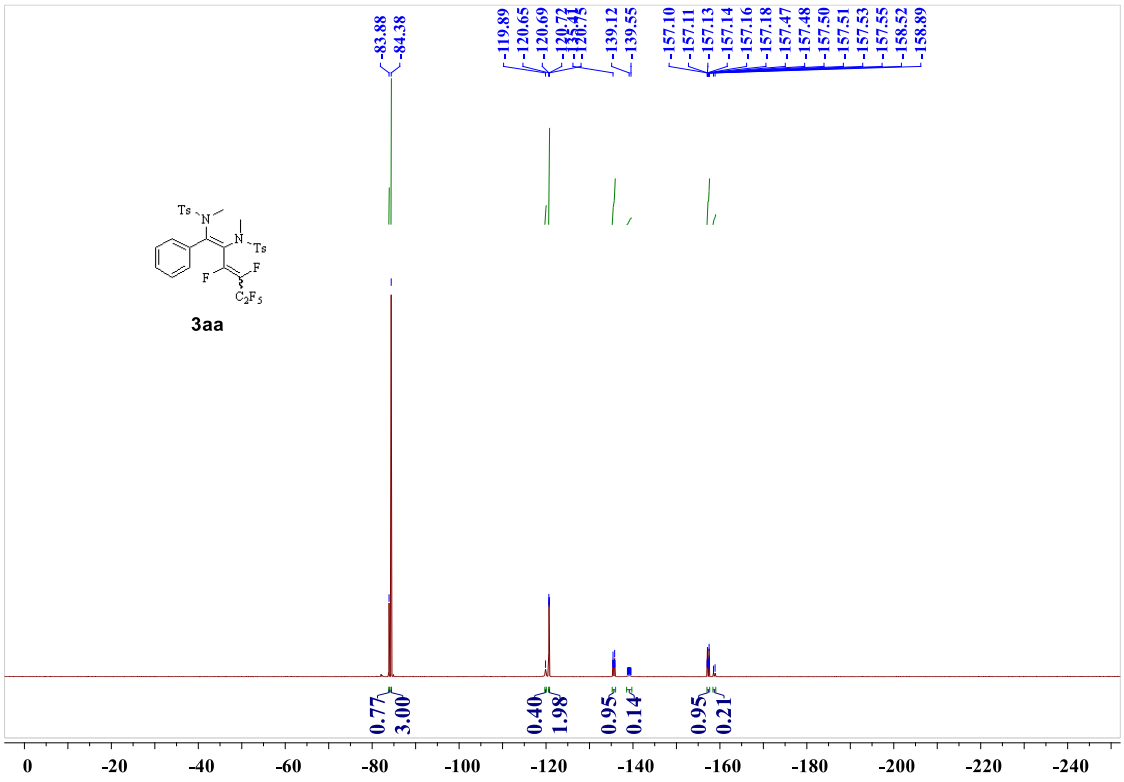
Crystal Data for $C_{29}H_{24}F_7N_3O_4S_2$ (*M* =675.63 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 29.6726(2) Å, *b* = 6.12887(5) Å, *c* = 35.8542(3) Å, *β* = 99.3669(8)°, *V* = 6433.47(9) Å^3, *Z* = 8, *T* = 150.00(10) K, μ(Cu Kα) = 2.211 mm^{-1}, *Dcalc* = 1.395 g/cm^3, 27846 reflections measured (6.038° ≤ 2Θ ≤ 143.048°), 12157 unique (R_{int} = 0.0231, R_{sigma} = 0.0305) which were used in all calculations. The final R_1 was 0.0687 (I > 2σ(I)) and wR_2 was 0.1822 (all data).

^{1}H, ^{19}F, and ^{13}C NMR spectra of products

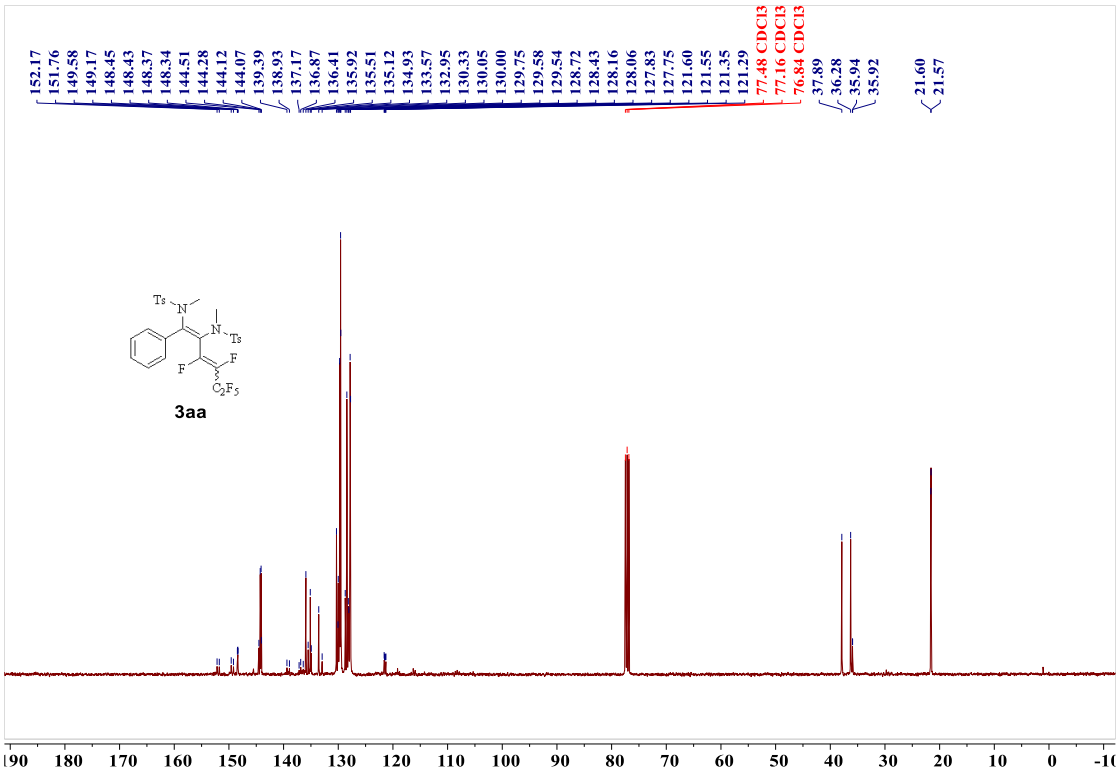
^{1}H NMR spectra of the product **3aa** (400 MHz, $CDCl_3$)



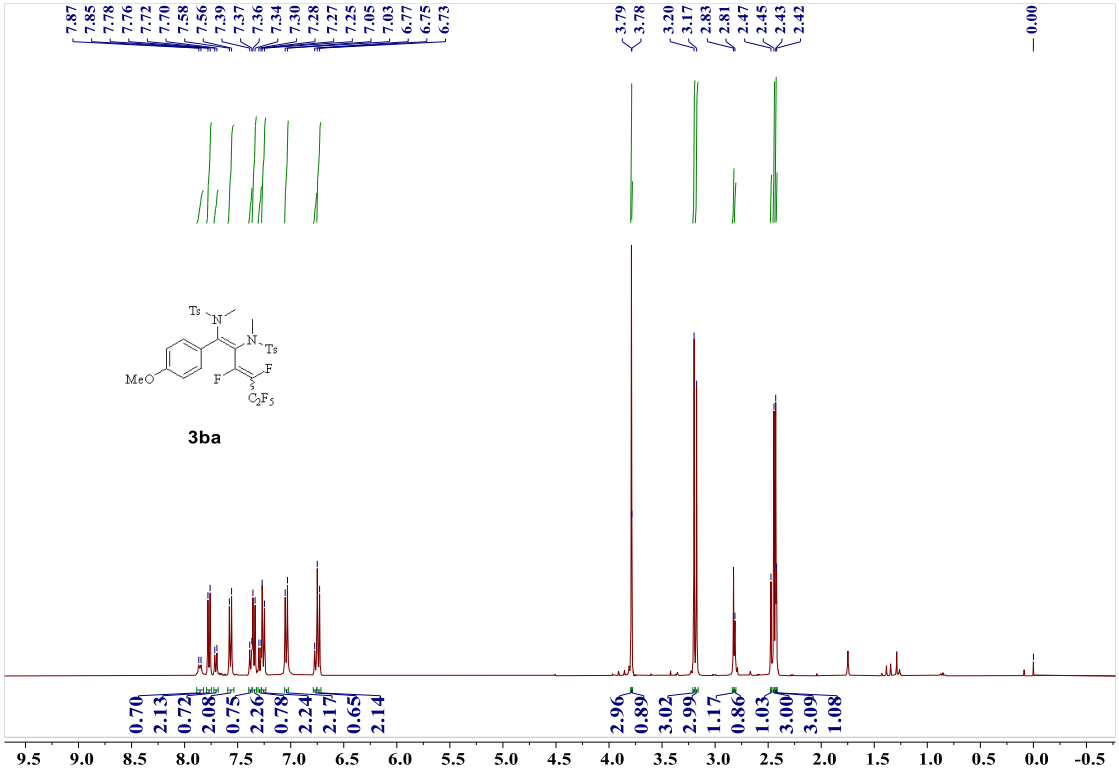
^{19}F NMR spectra of the product **3aa** (376 MHz, $CDCl_3$)



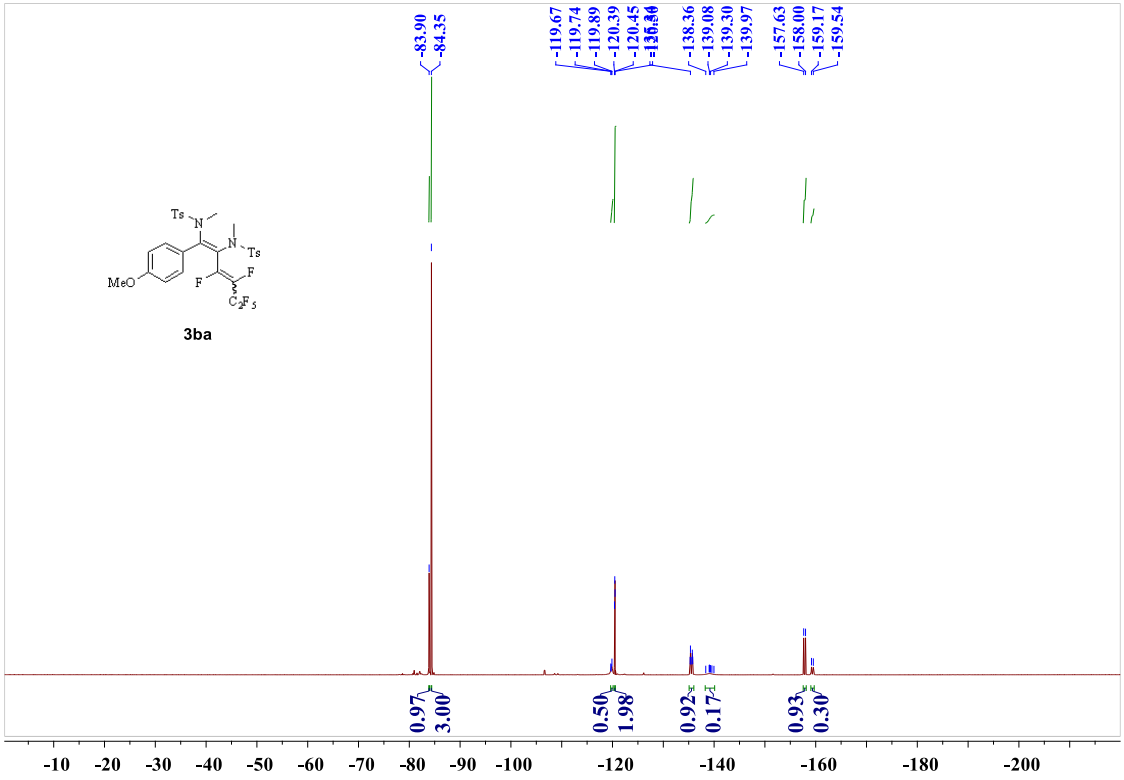
^{13}C NMR spectra of the product **3aa** (100 MHz, $CDCl_3$)



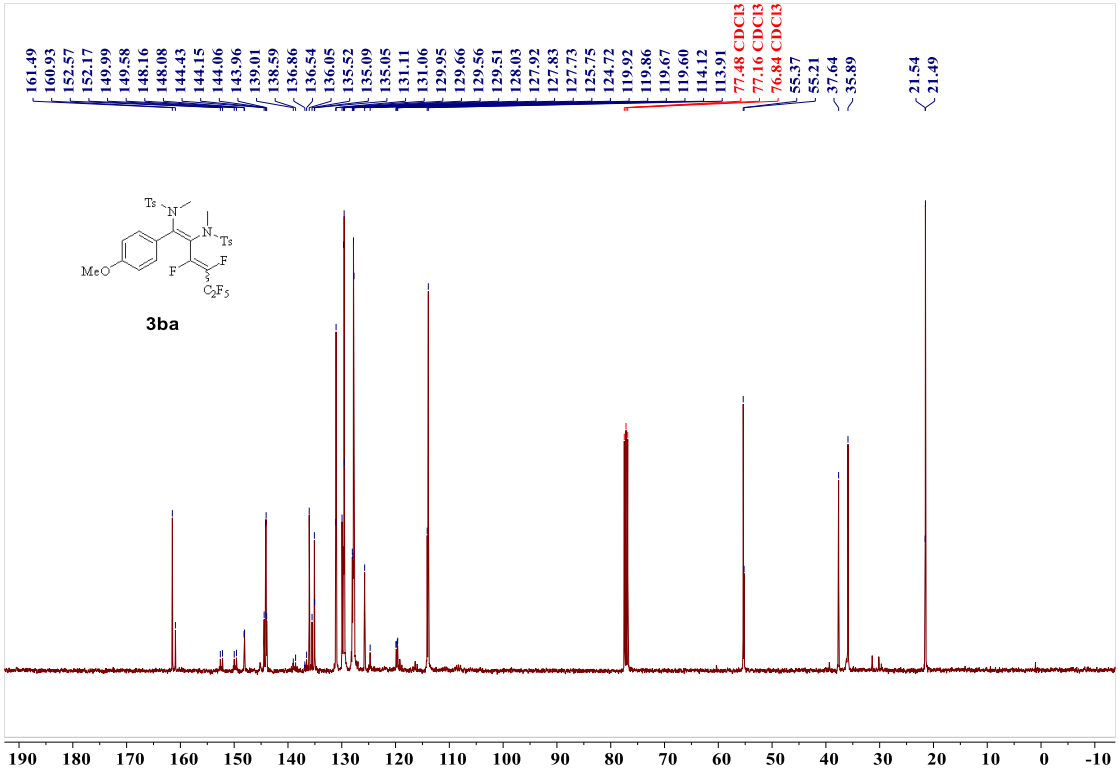
^{1}H NMR spectra of the product **3ba** (400 MHz, $CDCl_3$)



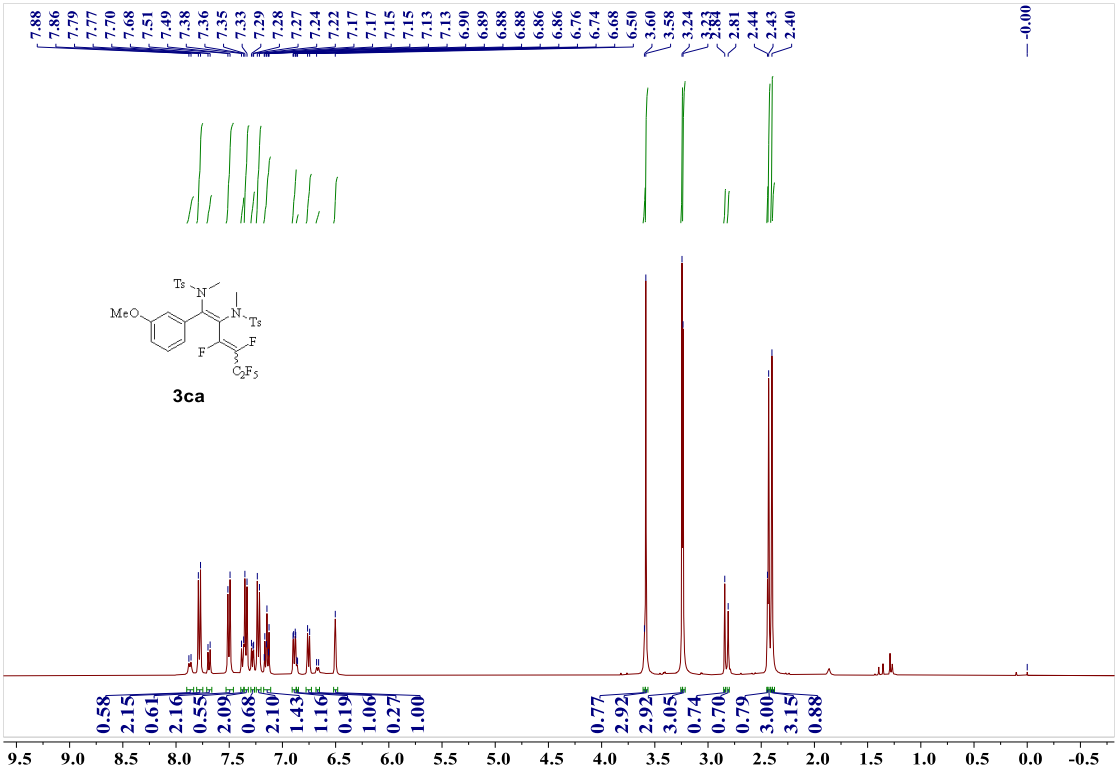
^{19}F NMR spectra of the product **3ba** (376 MHz, $CDCl_3$)



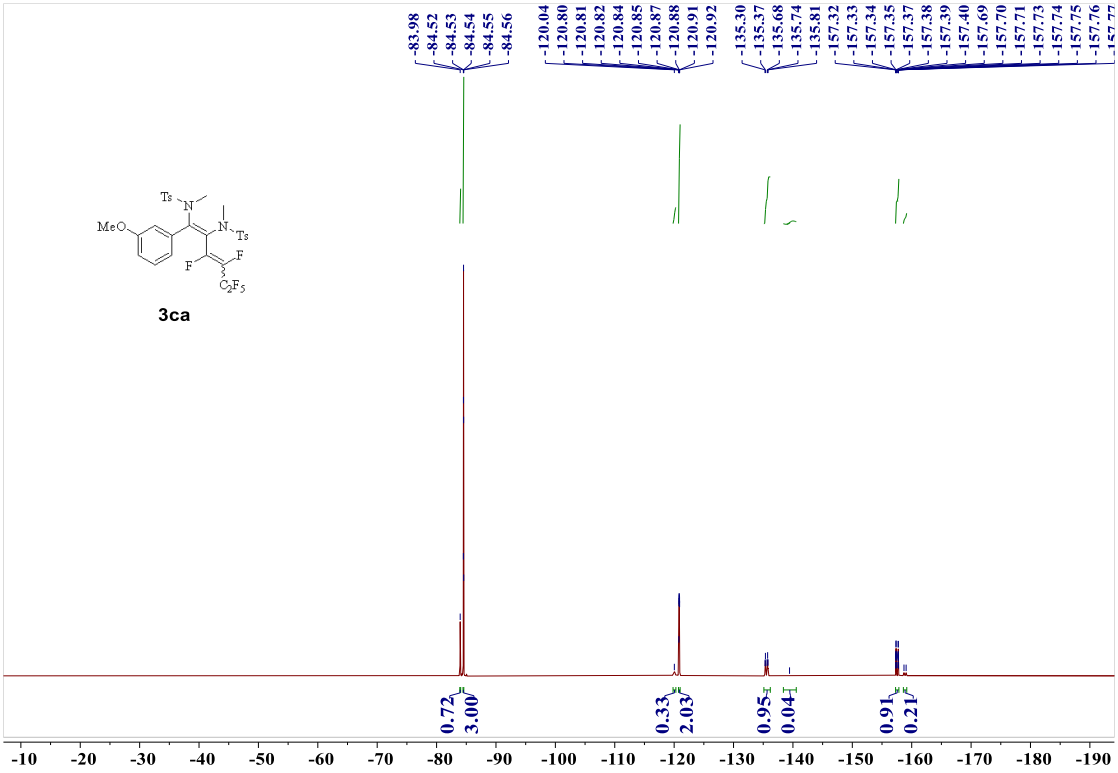
^{13}C NMR spectra of the product **3ba** (100 MHz, $CDCl_3$)



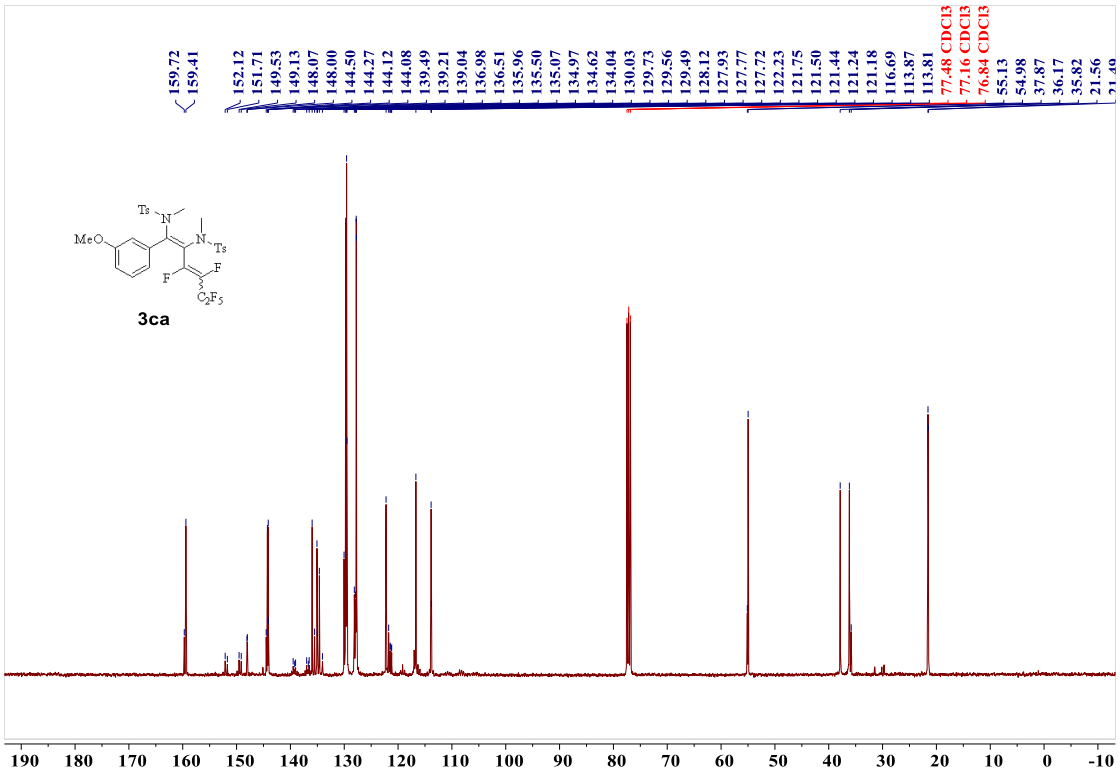
^{1}H NMR spectra of the product **3ca** (400 MHz, $CDCl_3$)



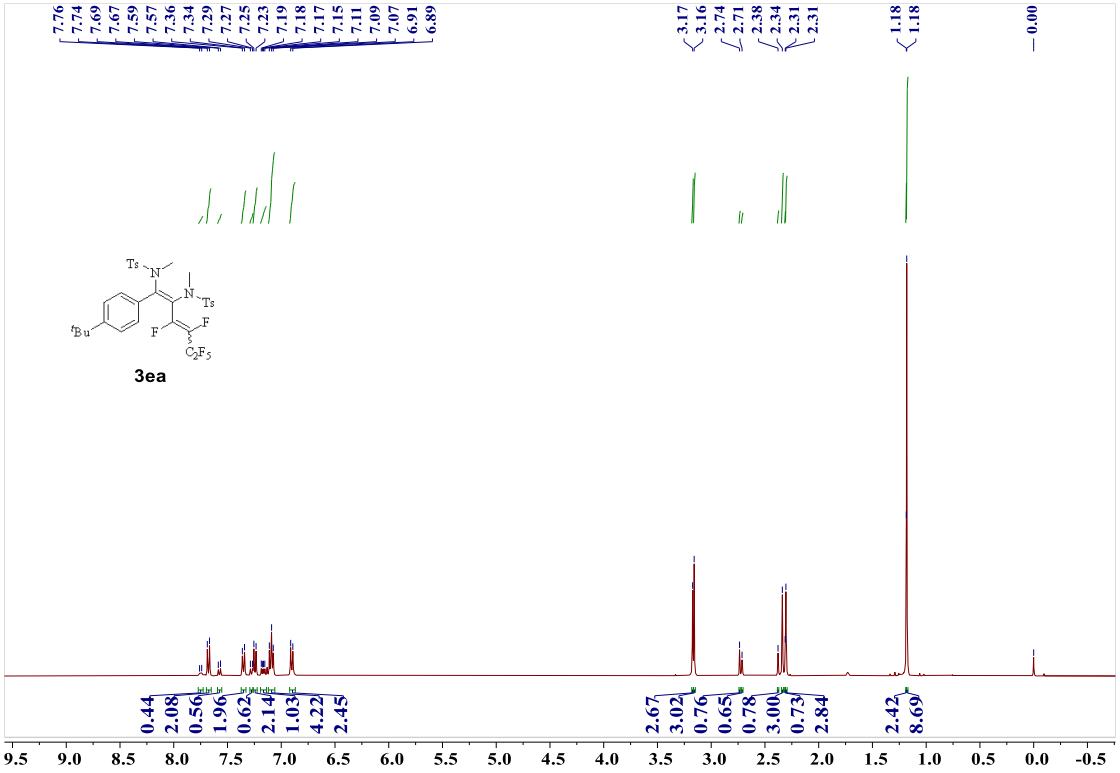
^{19}F NMR spectra of the product **3ca** (376 MHz, $CDCl_3$)



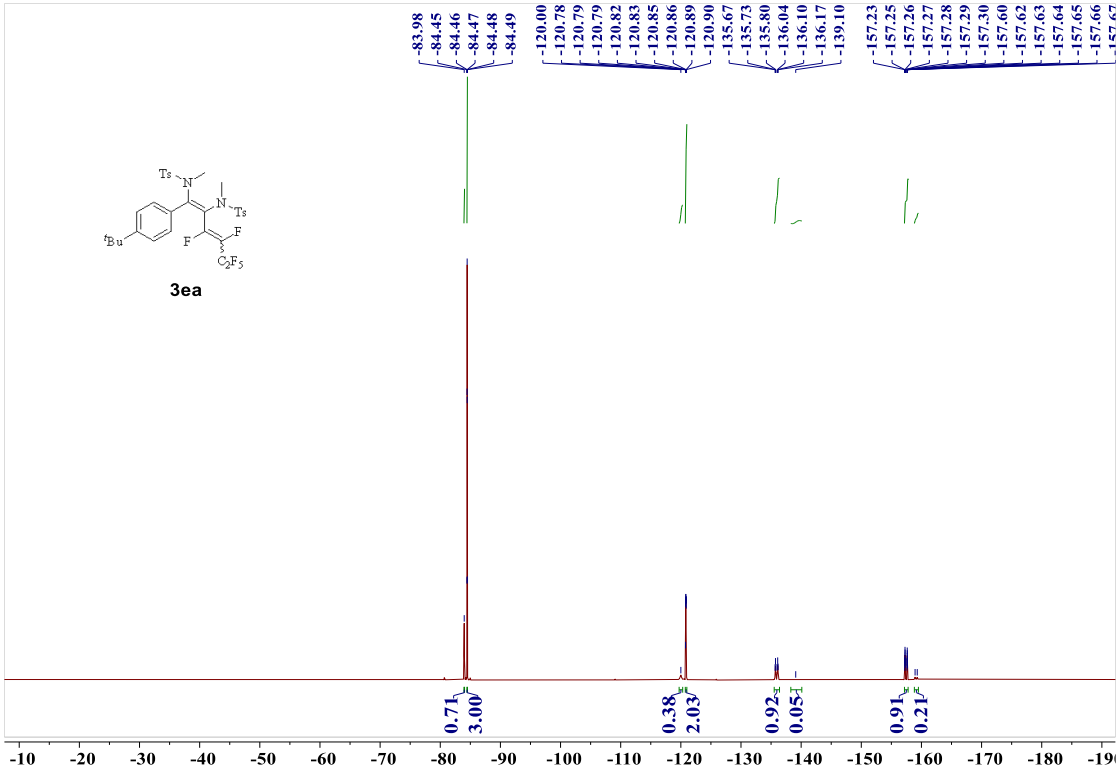
^{13}C NMR spectra of the product **3ca** (100 MHz, $CDCl_3$)



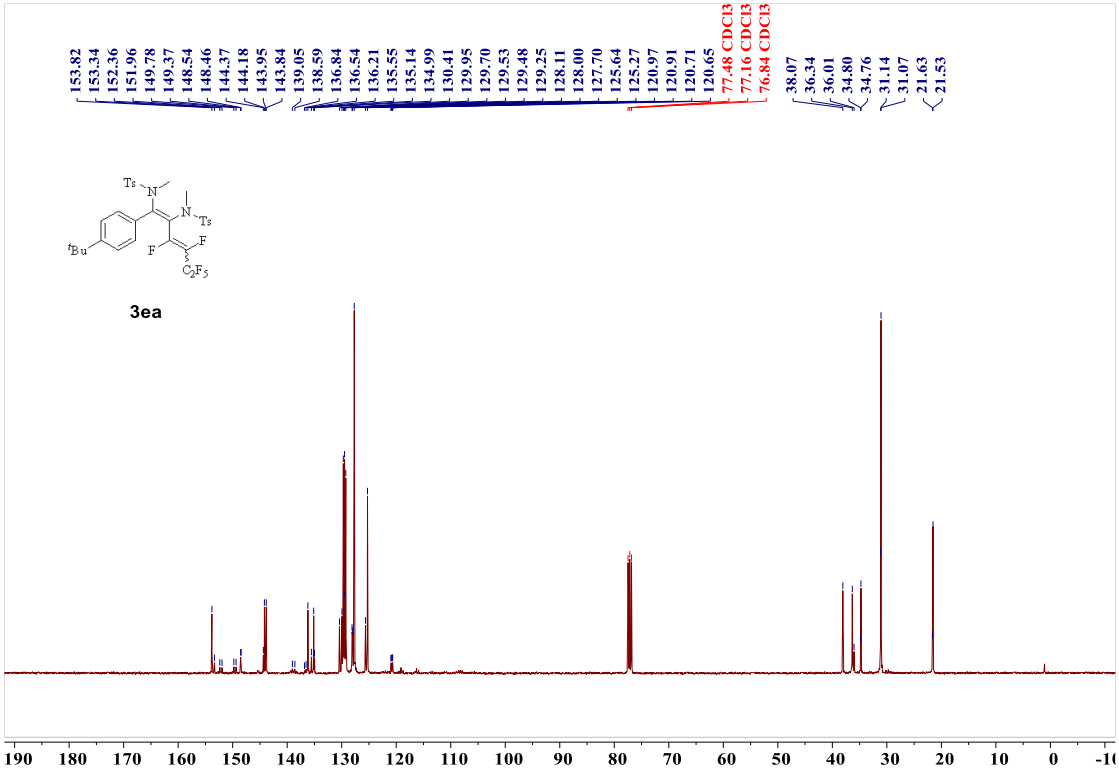
^{1}H NMR spectra of the product **3ea** (400 MHz, $CDCl_3$)



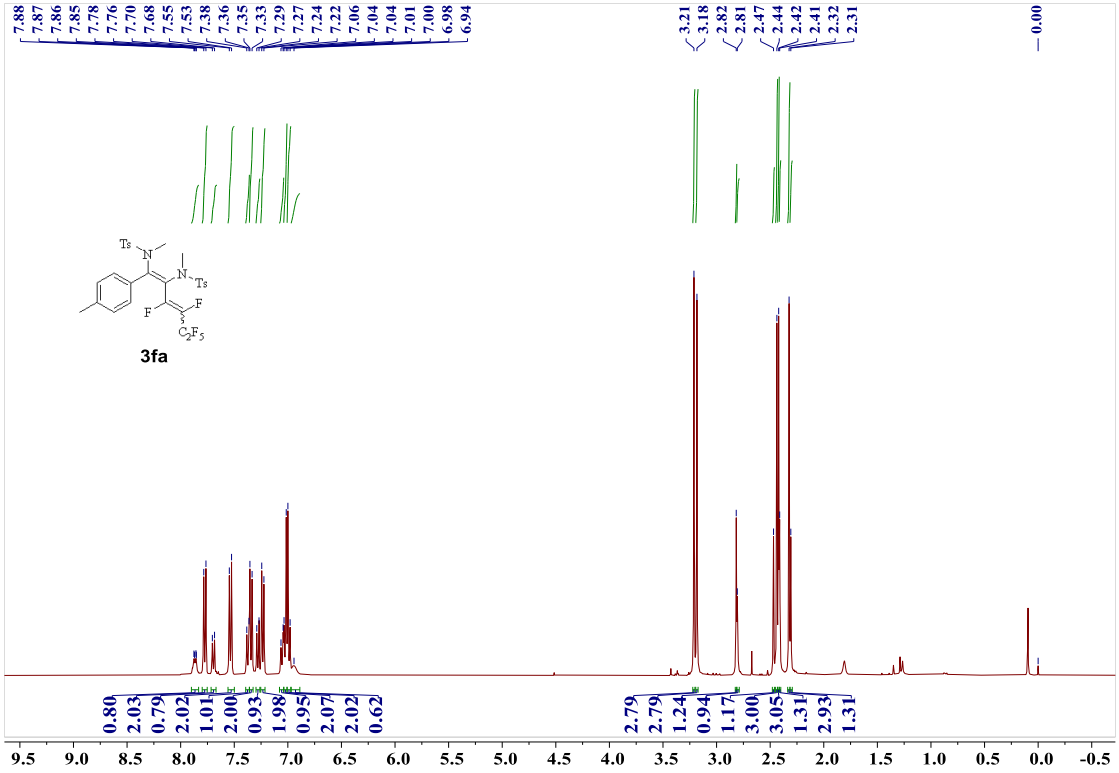
^{19}F NMR spectra of the product **3ea** (376 MHz, $CDCl_3$)



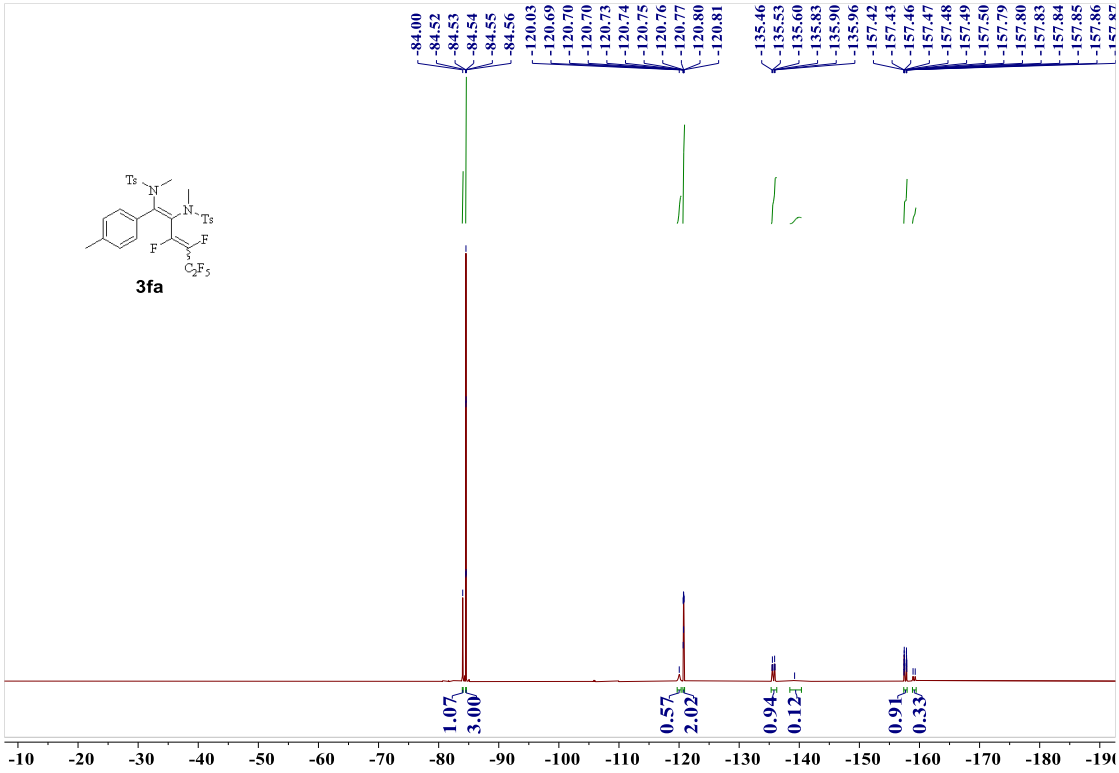
^{13}C NMR spectra of the product **3ea** (100 MHz, $CDCl_3$)



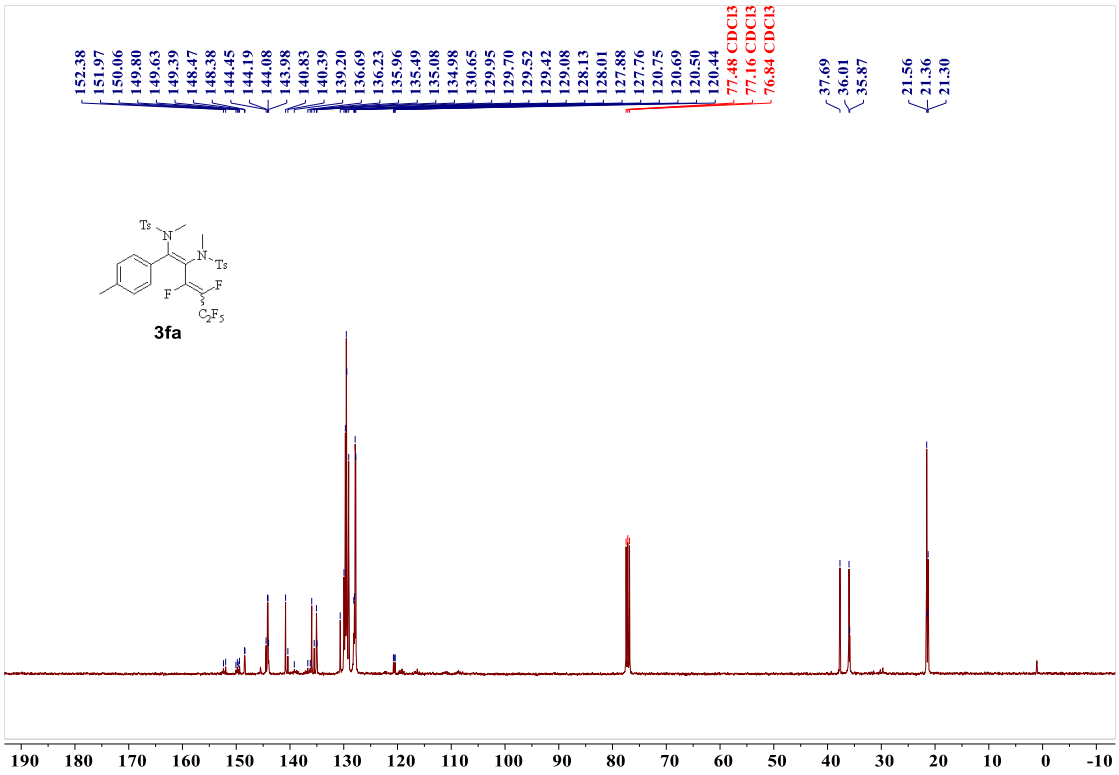
^{1}H NMR spectra of the product **3fa** (400 MHz, $CDCl_3$)



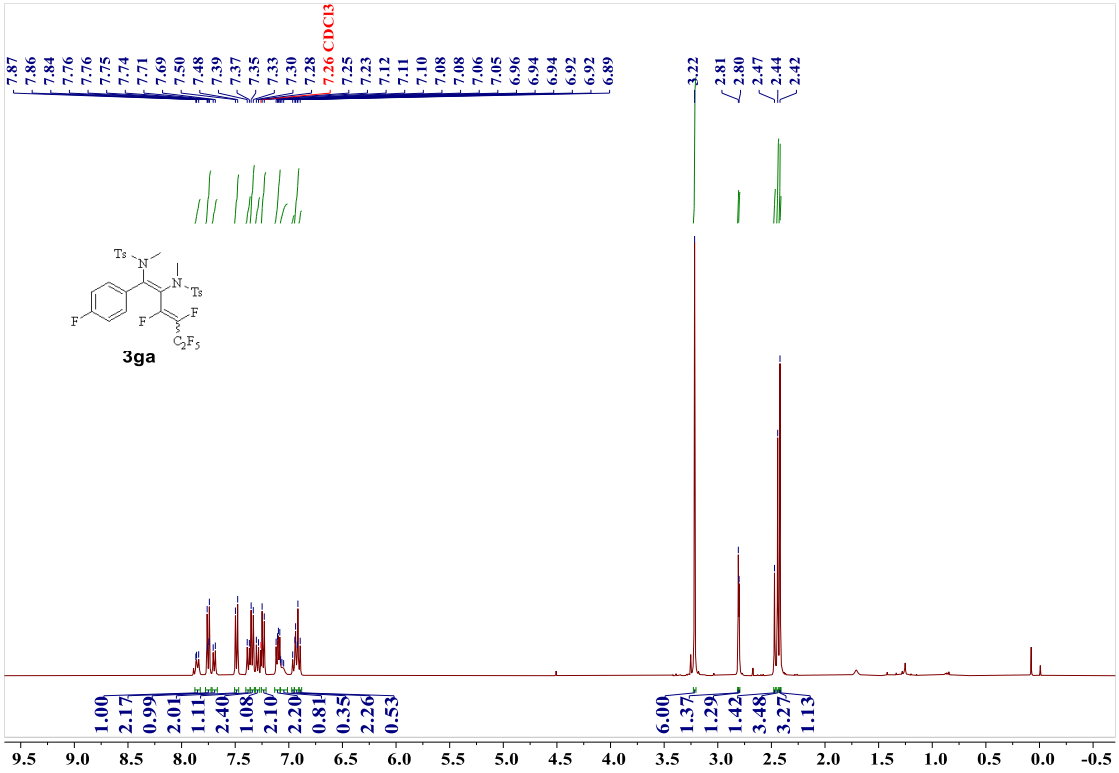
^{19}F NMR spectra of the product **3fa** (376 MHz, $CDCl_3$)



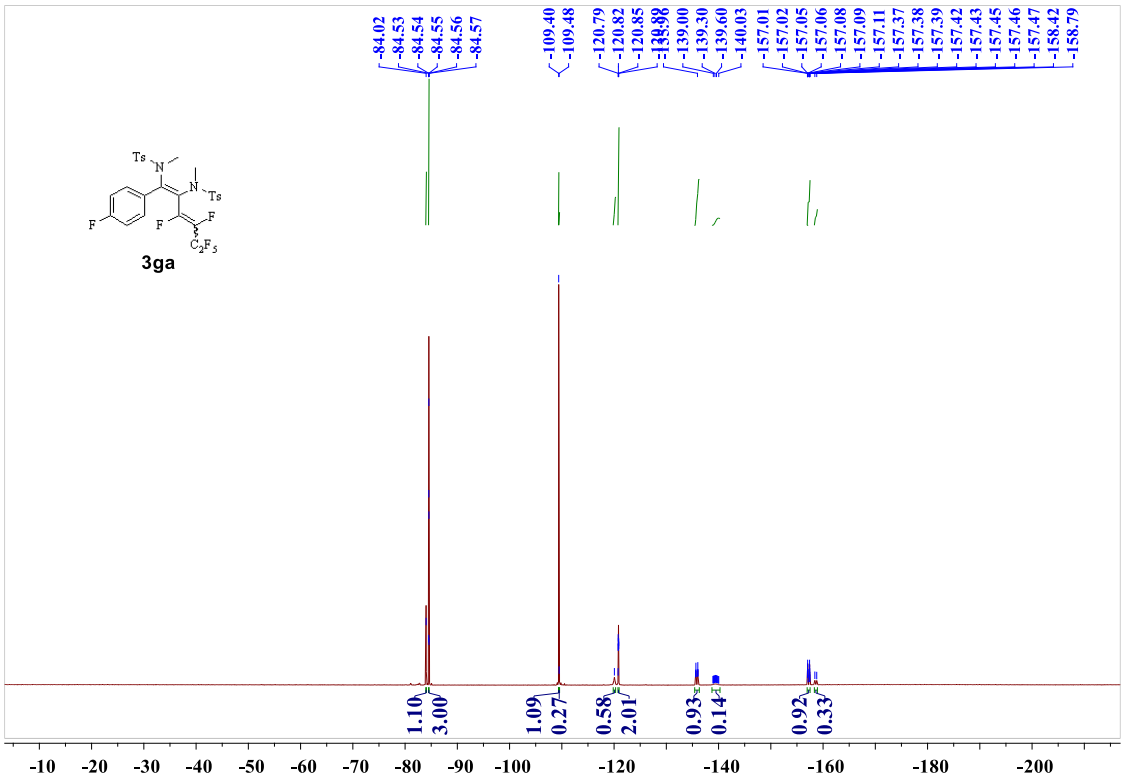
^{13}C NMR spectra of the product **3fa** (100 MHz, $CDCl_3$)



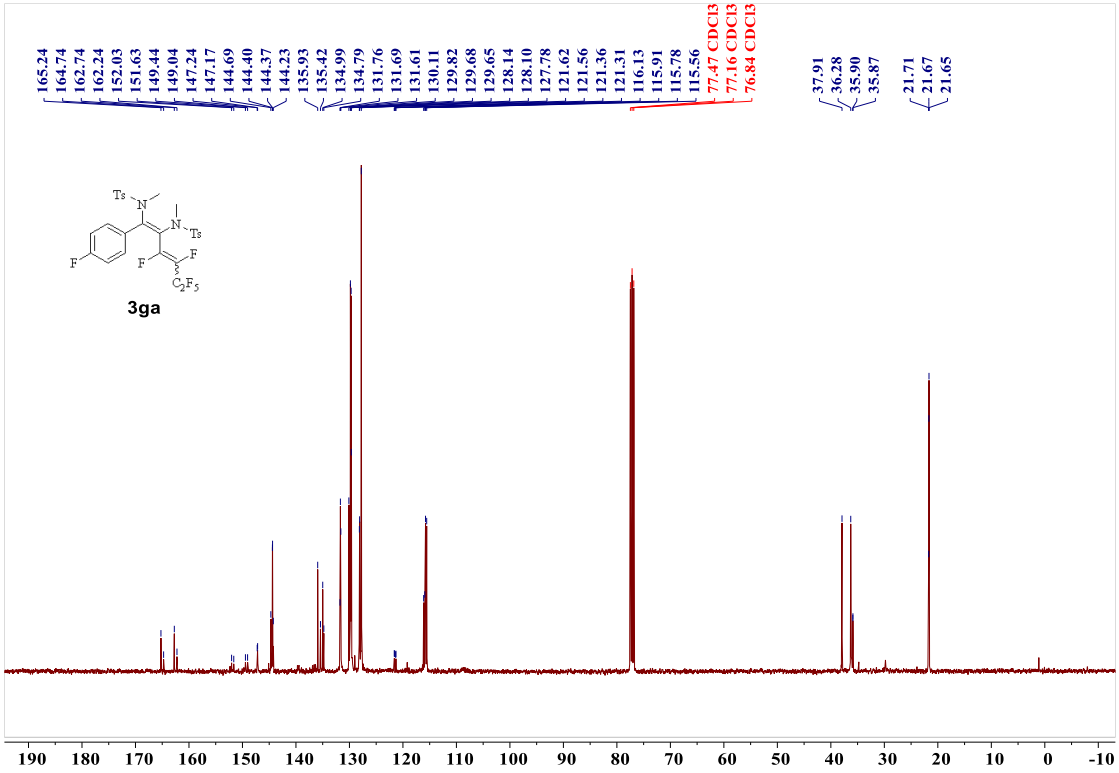
^{1}H NMR spectra of the product **3ga** (400 MHz, $CDCl_3$)



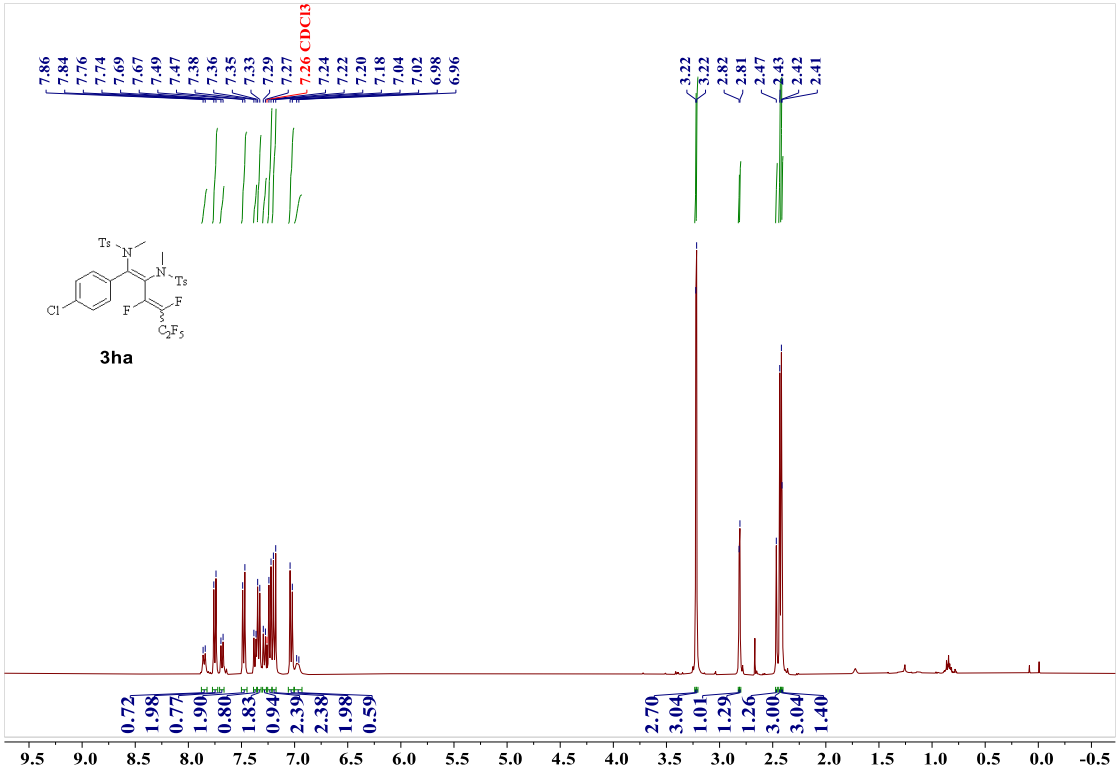
^{19}F NMR spectra of the product **3ga** (376 MHz, $CDCl_3$)



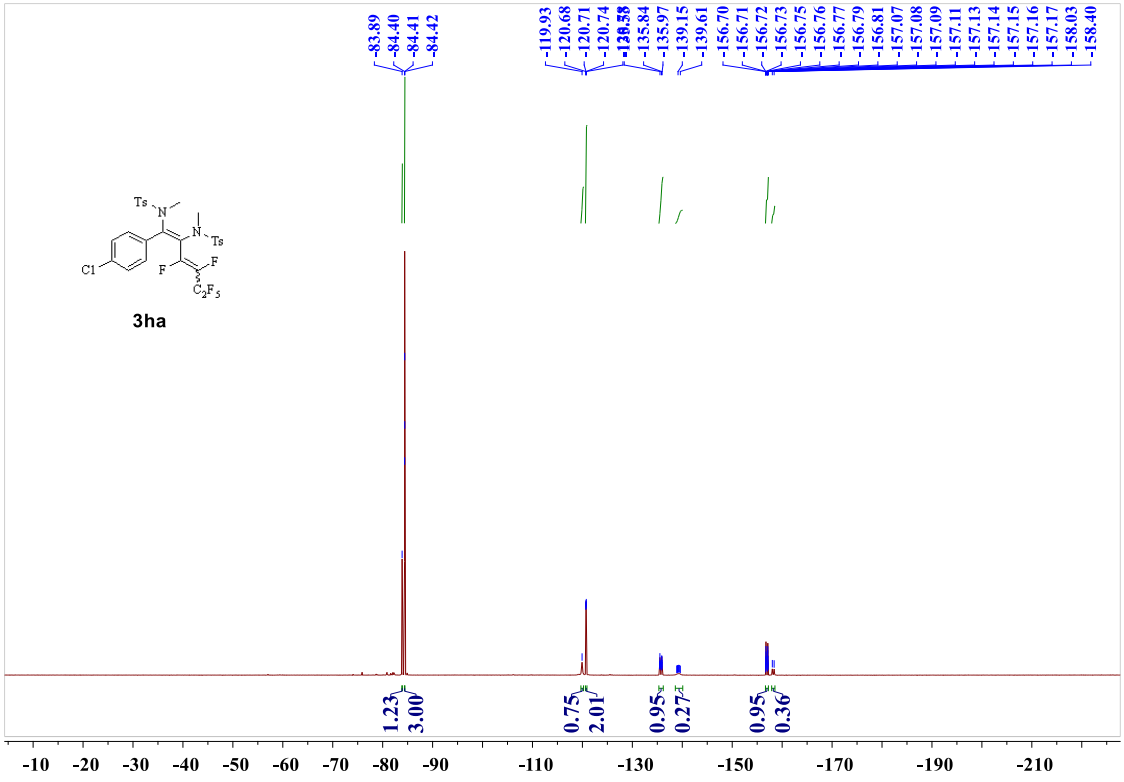
^{13}C NMR spectra of the product **3ga** (100 MHz, $CDCl_3$)



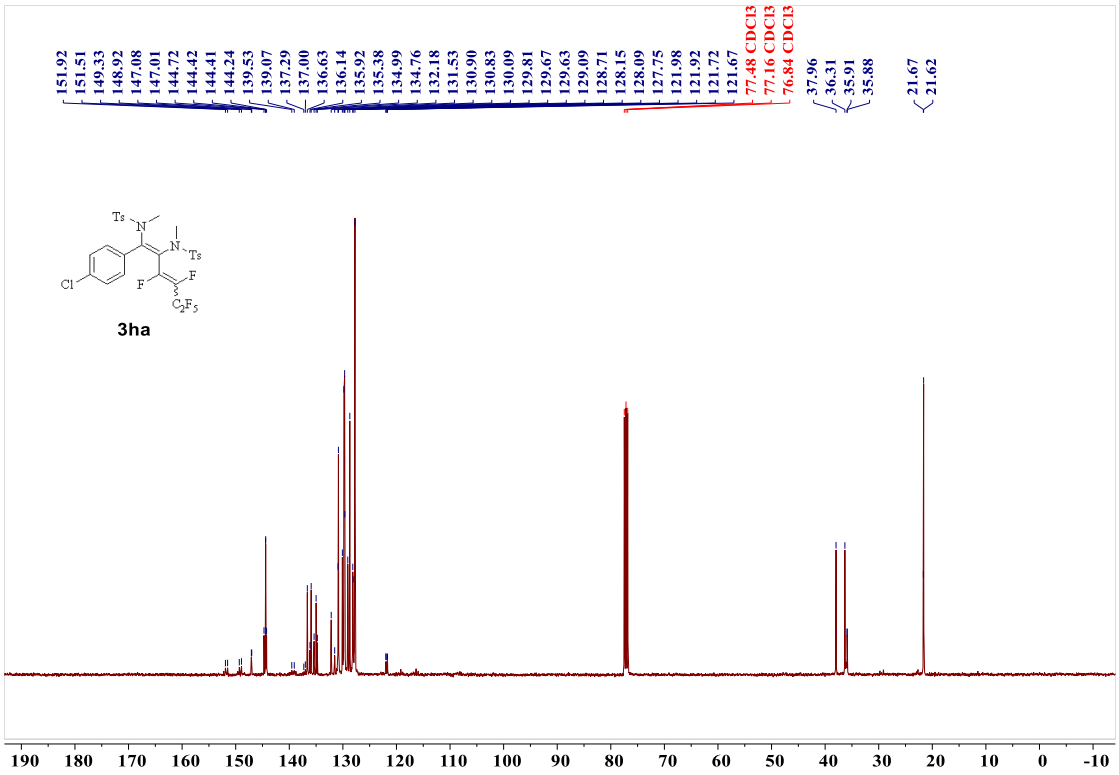
^{1}H NMR spectra of the product **3ha** (400 MHz, $CDCl_3$)



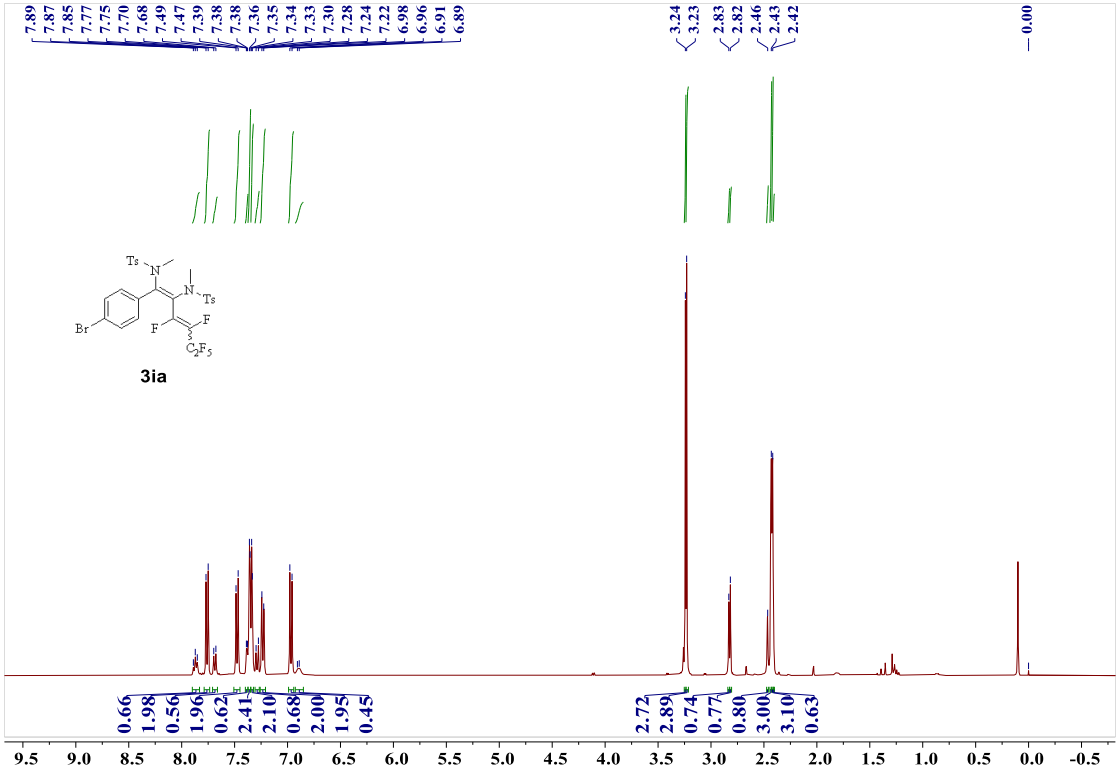
^{19}F NMR spectra of the product **3ha** (376 MHz, $CDCl_3$)



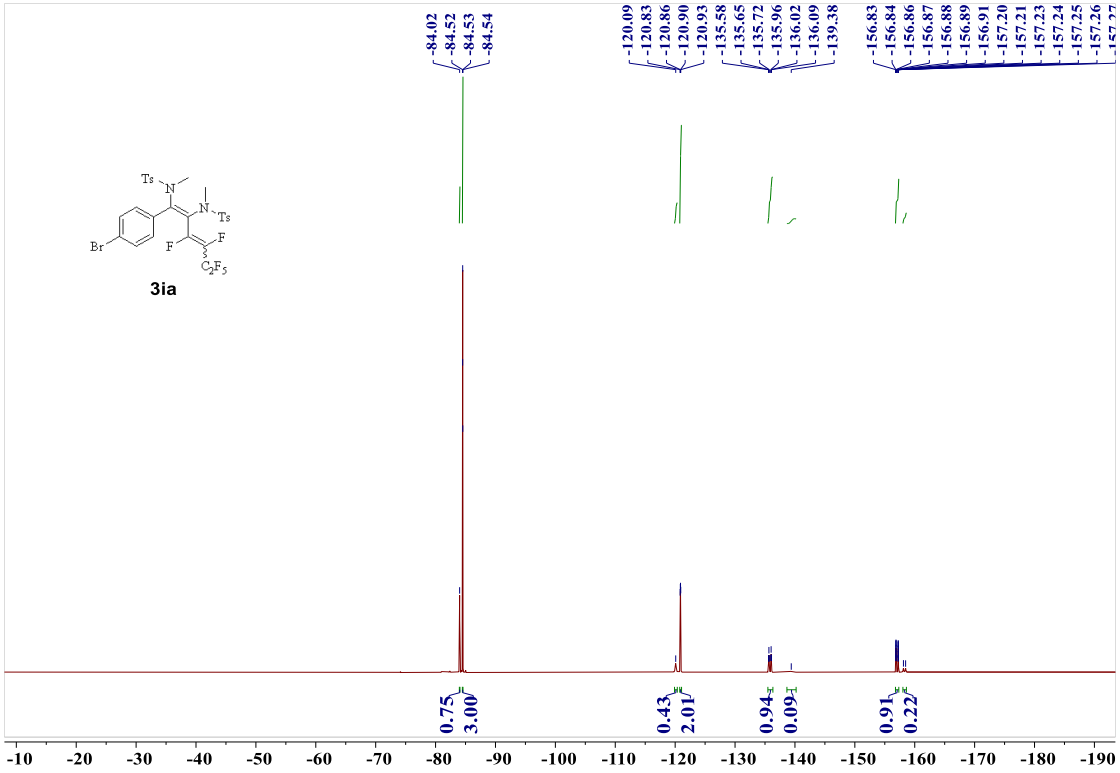
^{13}C NMR spectra of the product **3ha** (100 MHz, $CDCl_3$)



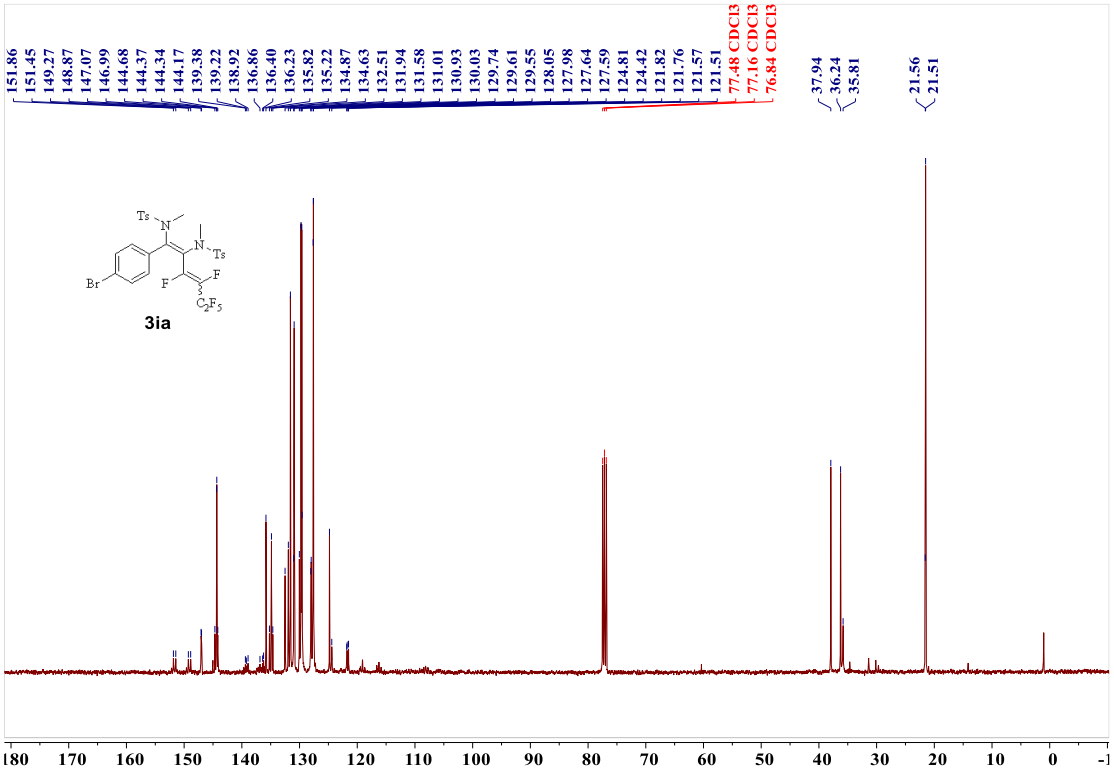
^{1}H NMR spectra of the product **3ia** (400 MHz, $CDCl_3$)



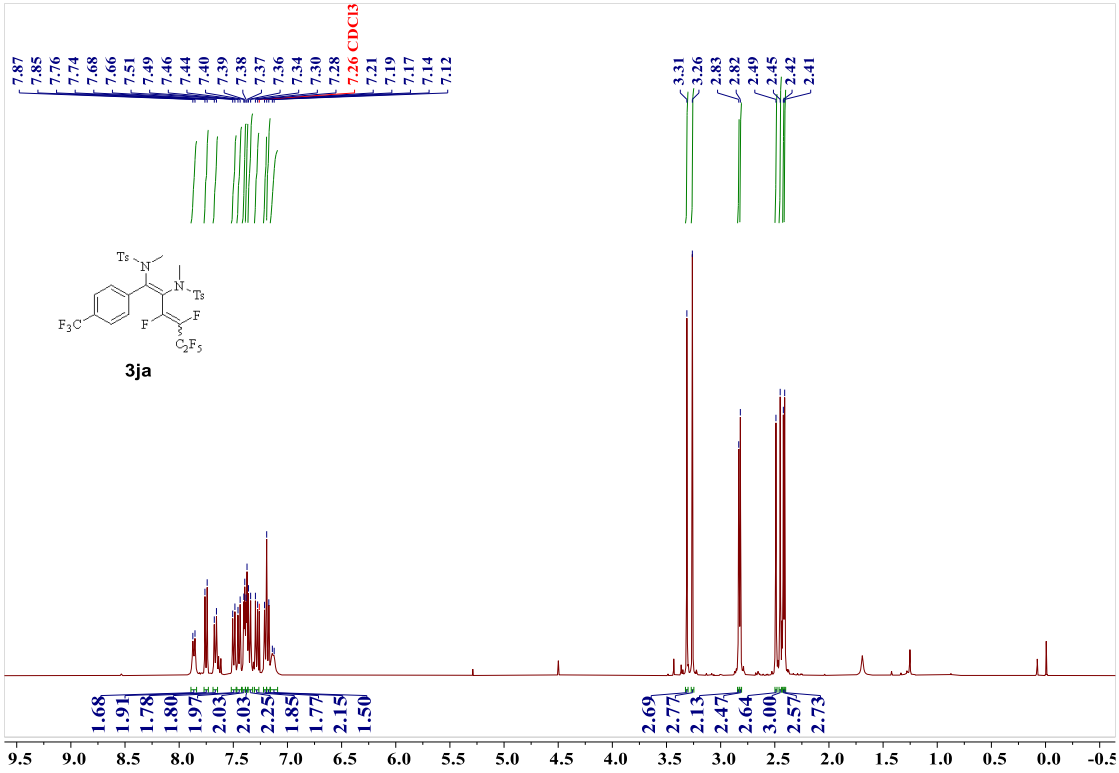
^{19}F NMR spectra of the product **3ia** (376 MHz, $CDCl_3$)



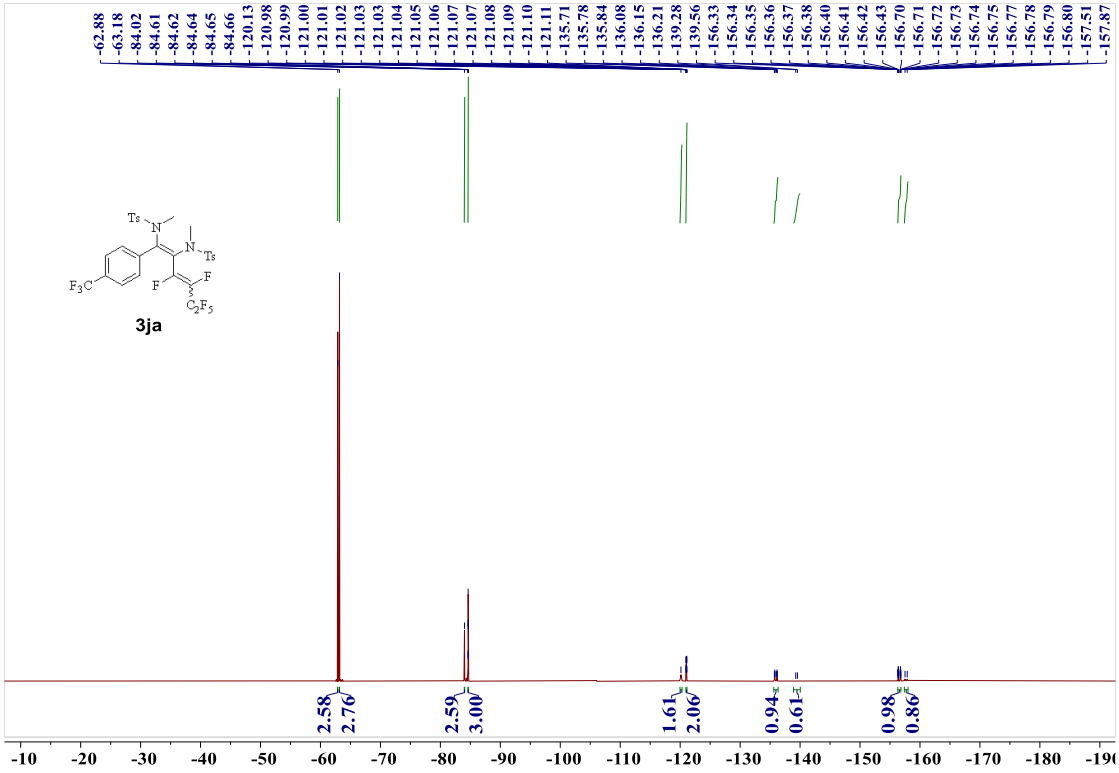
^{13}C NMR spectra of the product **3ia** (100 MHz, $CDCl_3$)



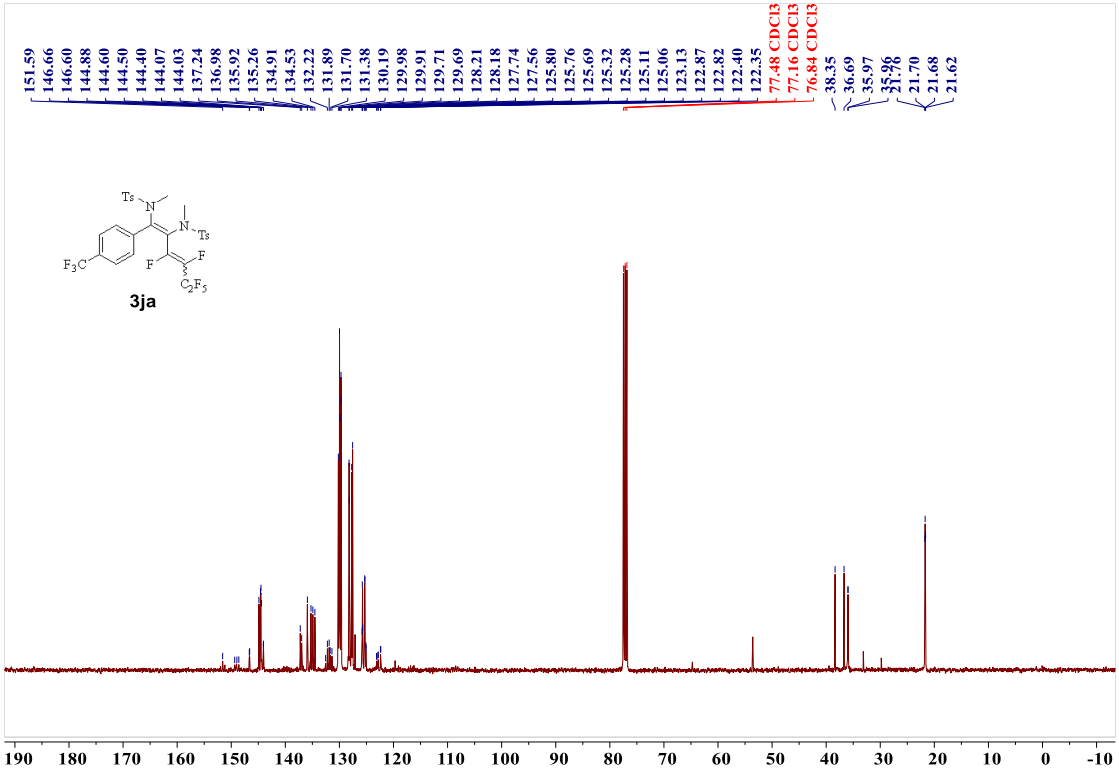
^{1}H NMR spectra of the product **3ja** (400 MHz, $CDCl_3$)



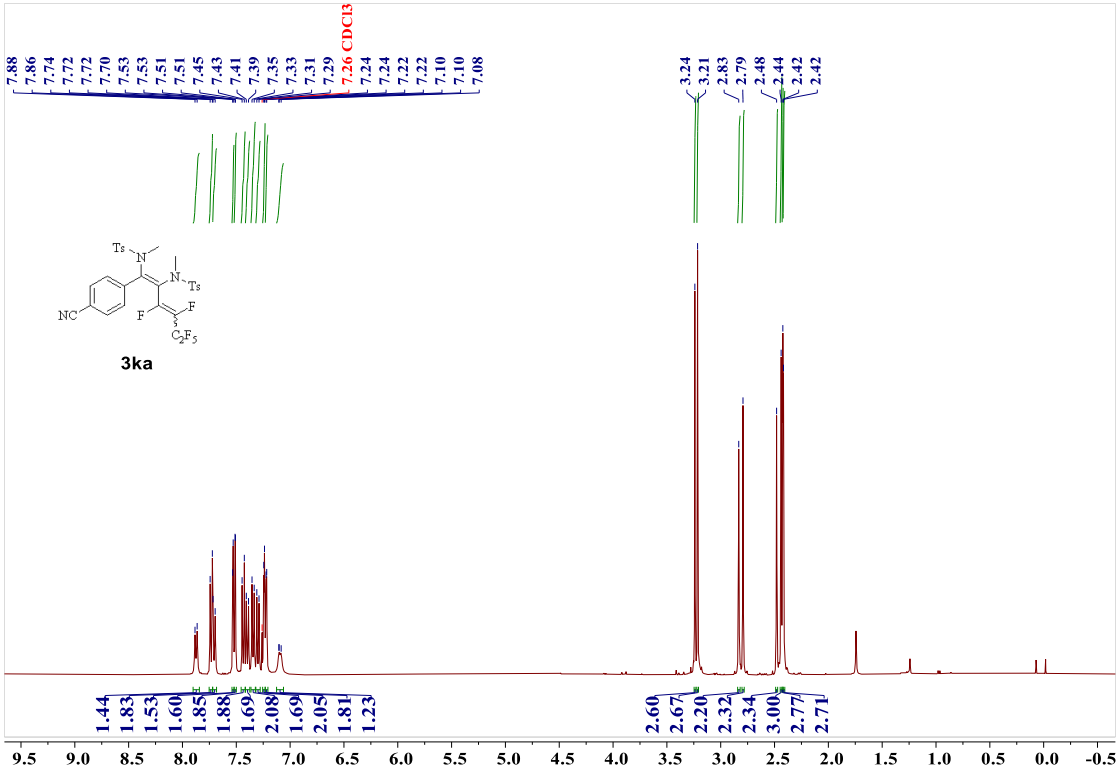
^{19}F NMR spectra of the product **3ja** (376 MHz, $CDCl_3$)



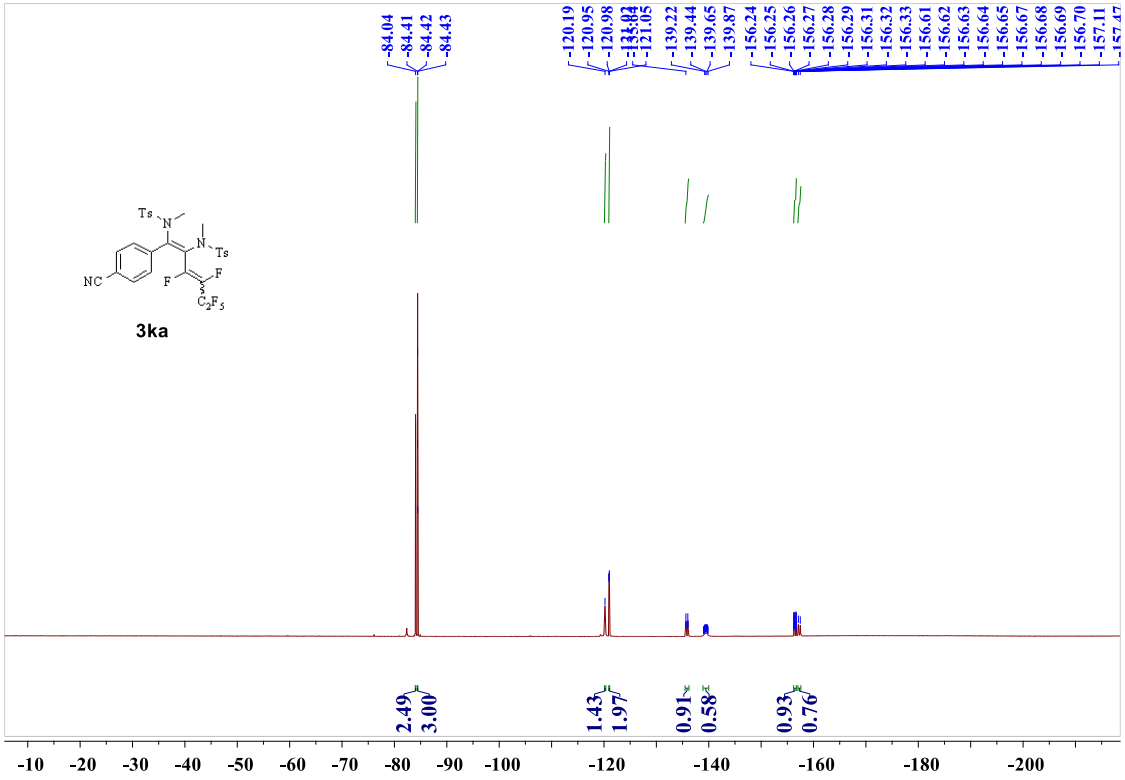
^{13}C NMR spectra of the product **3ja** (100 MHz, $CDCl_3$)



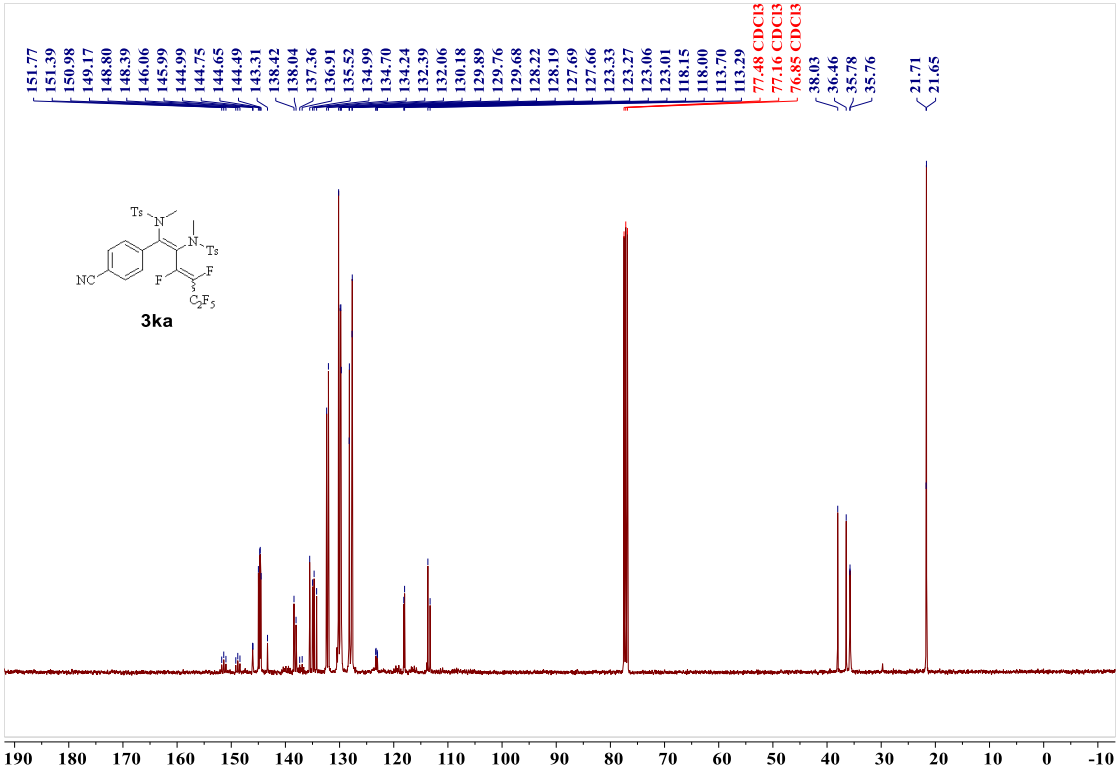
^{1}H NMR spectra of the product **3ka** (400 MHz, $CDCl_3$)



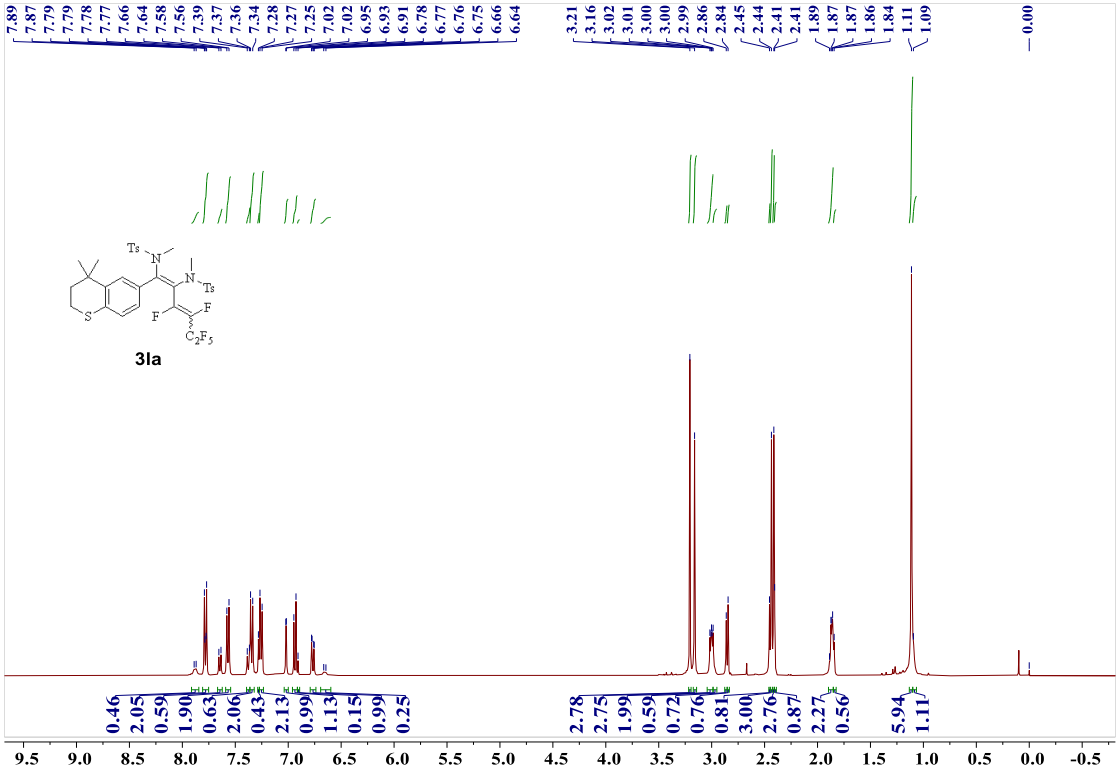
^{19}F NMR spectra of the product **3ka** (376 MHz, $CDCl_3$)



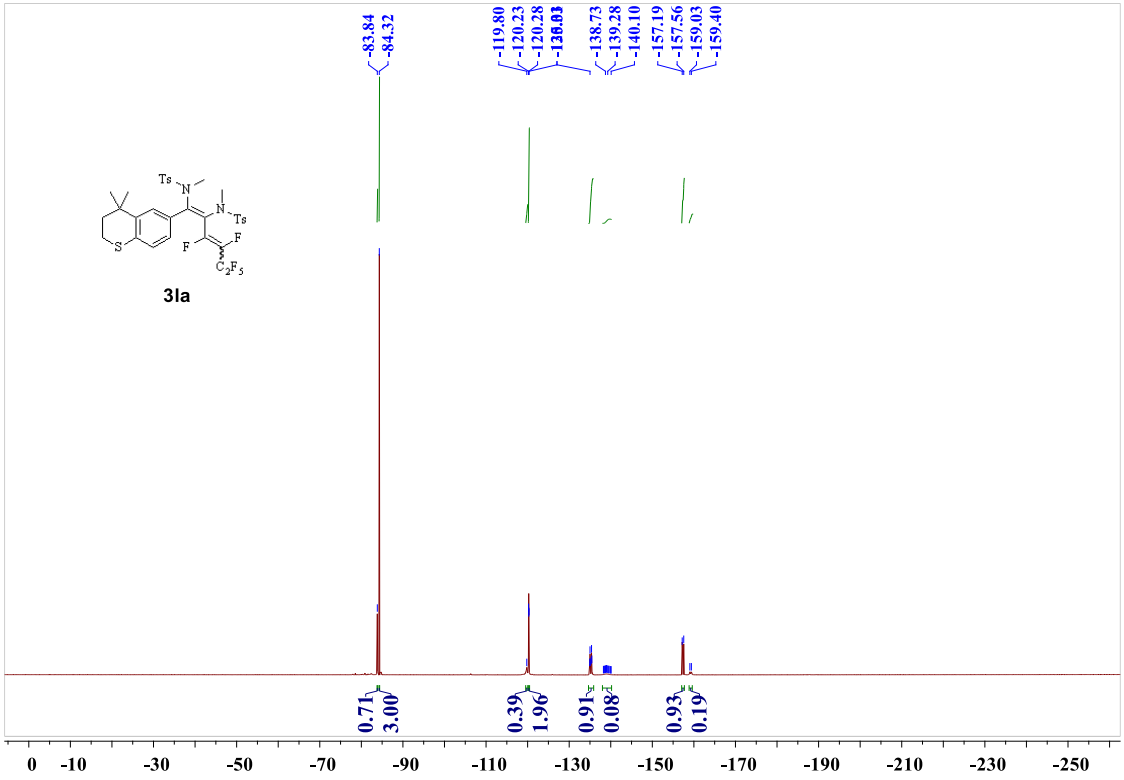
^{13}C NMR spectra of the product **3ka** (100 MHz, $CDCl_3$)



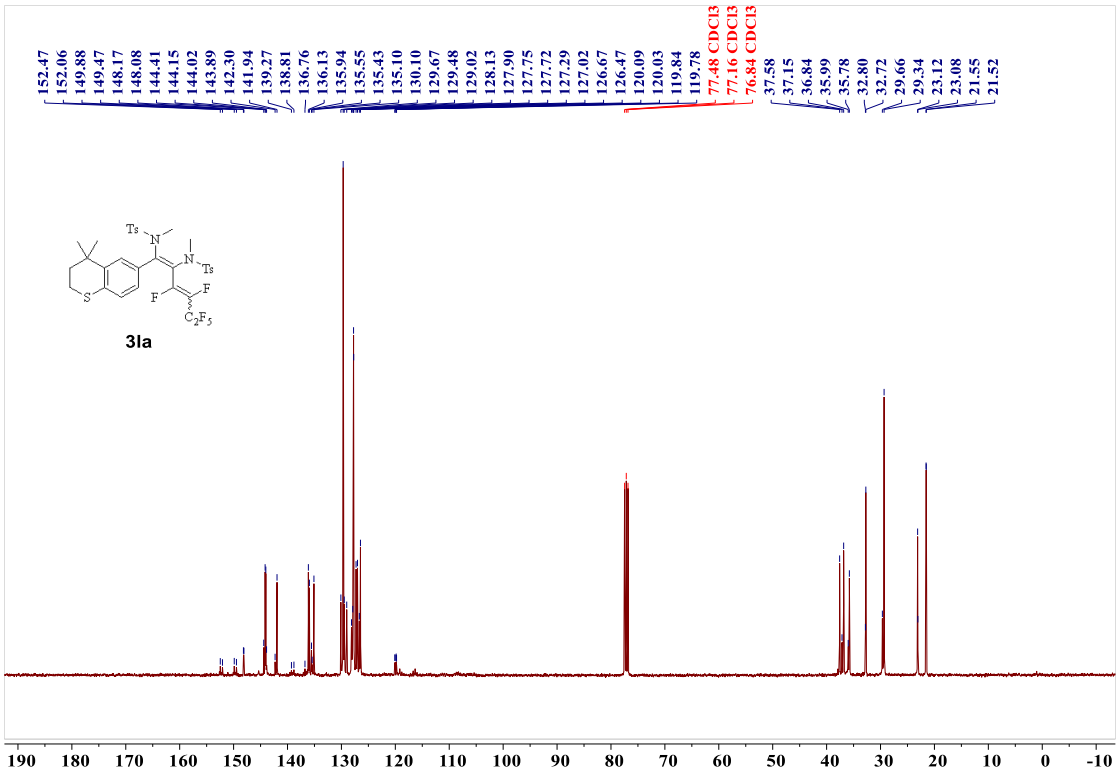
^{1}H NMR spectra of the product **3la** (400 MHz, $CDCl_3$)



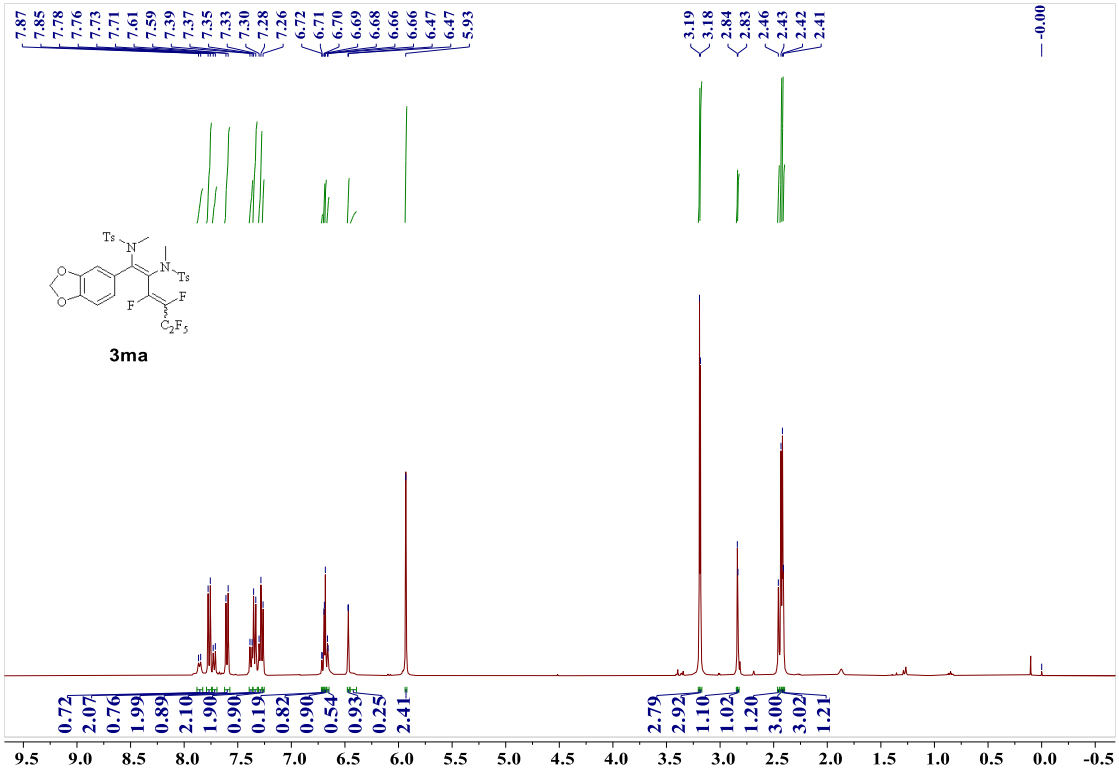
^{19}F NMR spectra of the product **3la** (376 MHz, $CDCl_3$)



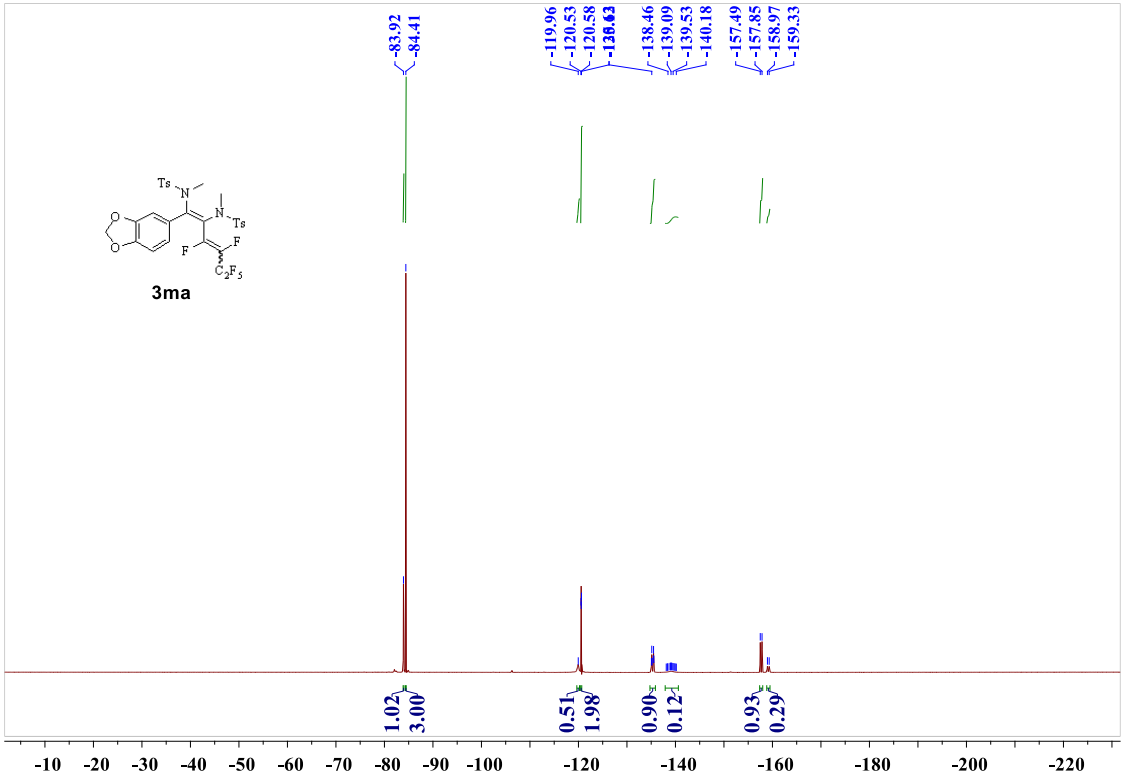
^{13}C NMR spectra of the product **3la** (100 MHz, $CDCl_3$)



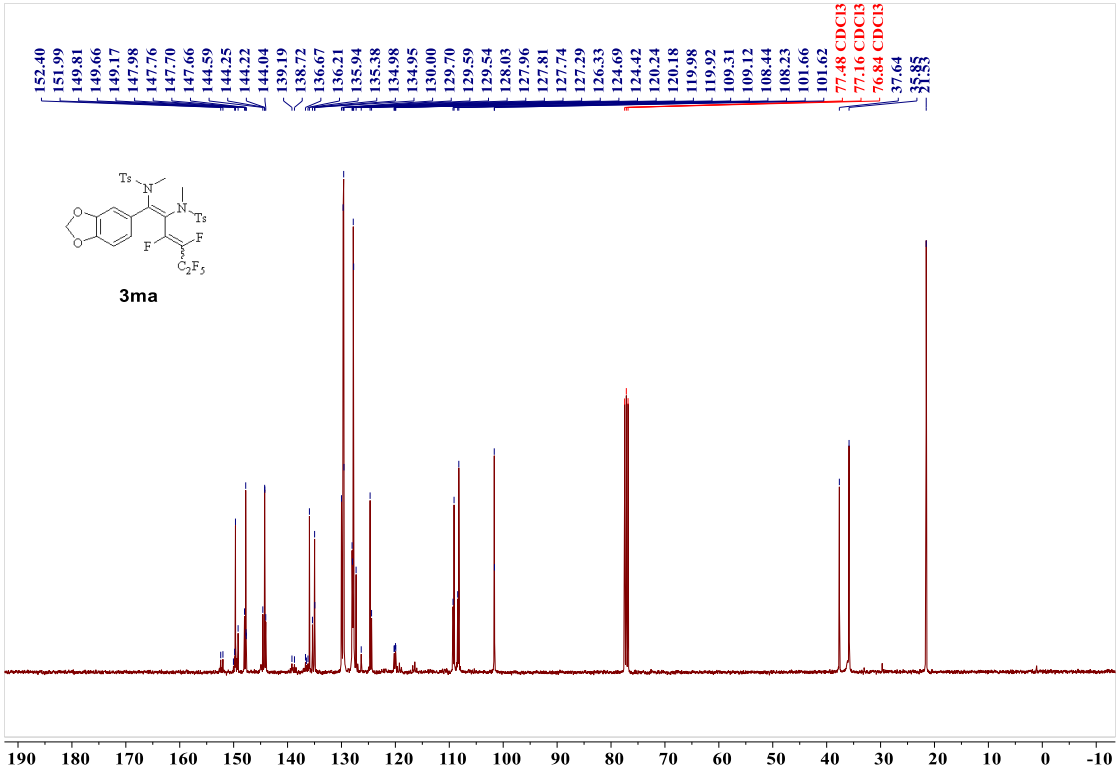
^{1}H NMR spectra of the product **3ma** (400 MHz, $CDCl_3$)



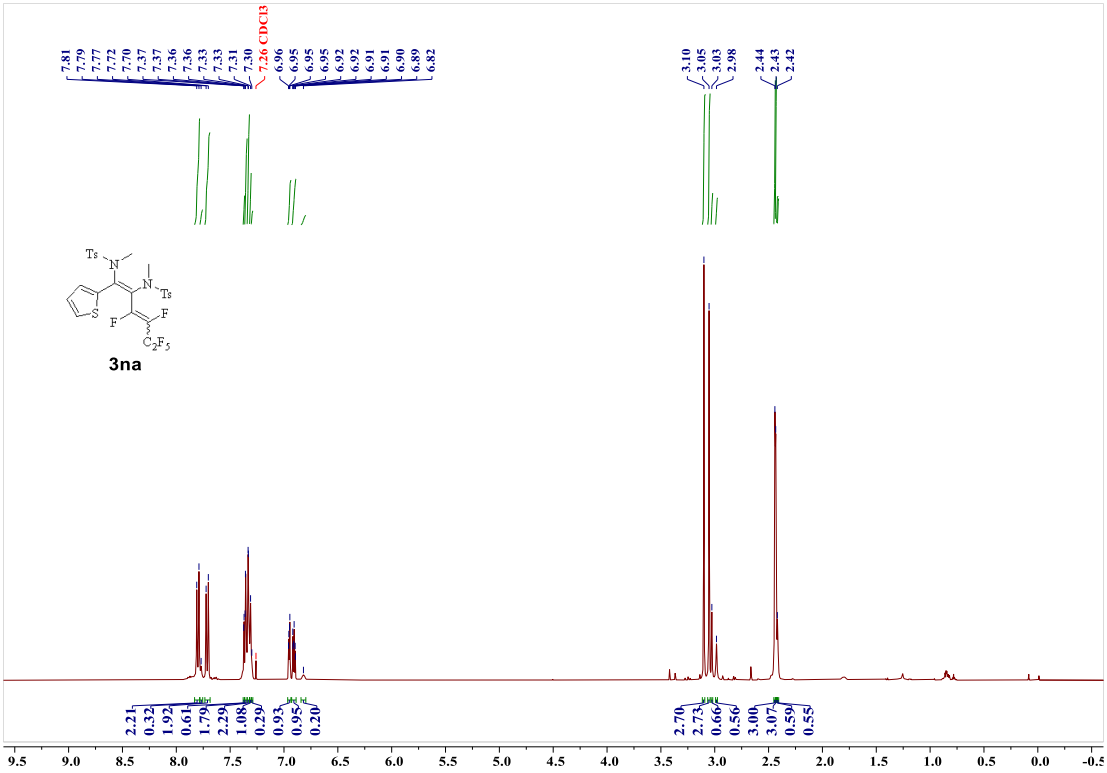
^{19}F NMR spectra of the product **3ma** (376 MHz, $CDCl_3$)



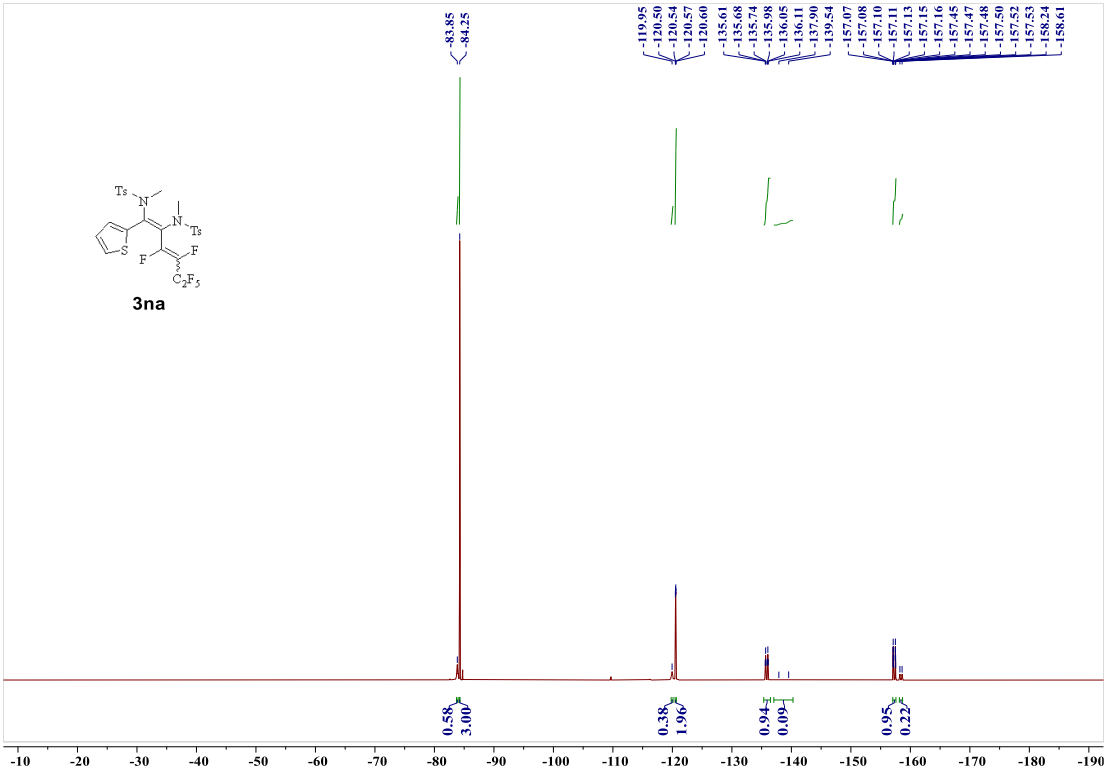
^{13}C NMR spectra of the product **3ma** (100 MHz, $CDCl_3$)



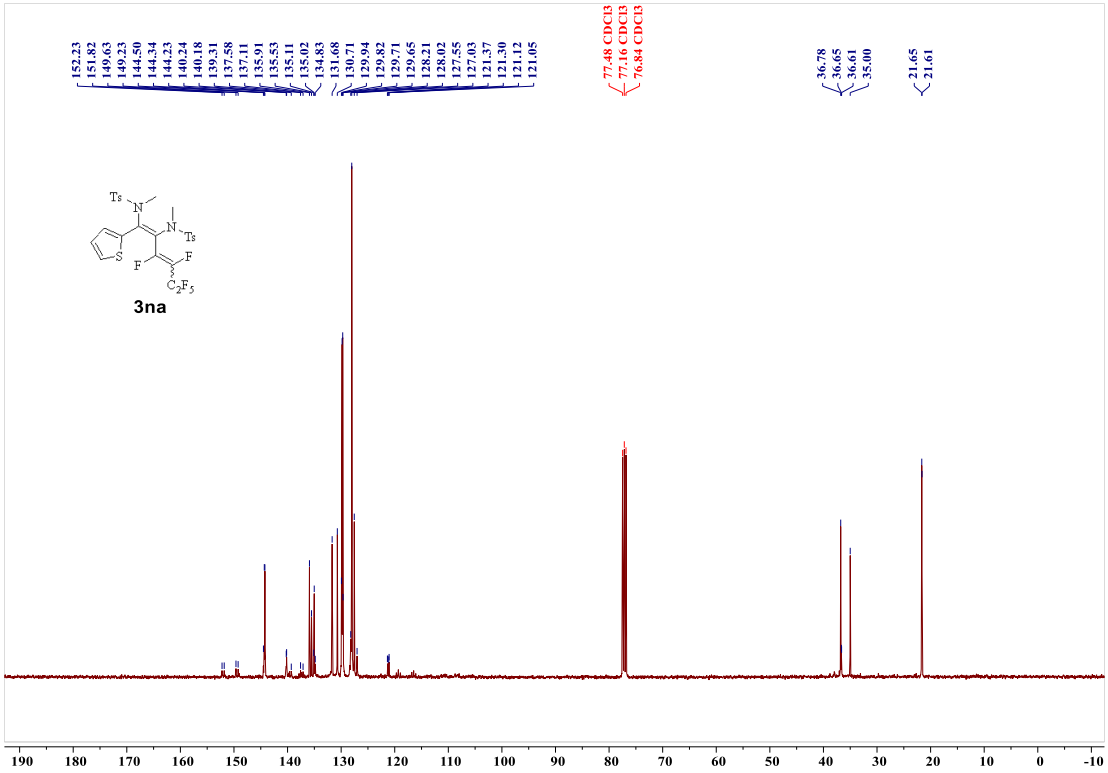
^{1}H NMR spectra of the product **3na** (400 MHz, $CDCl_3$)



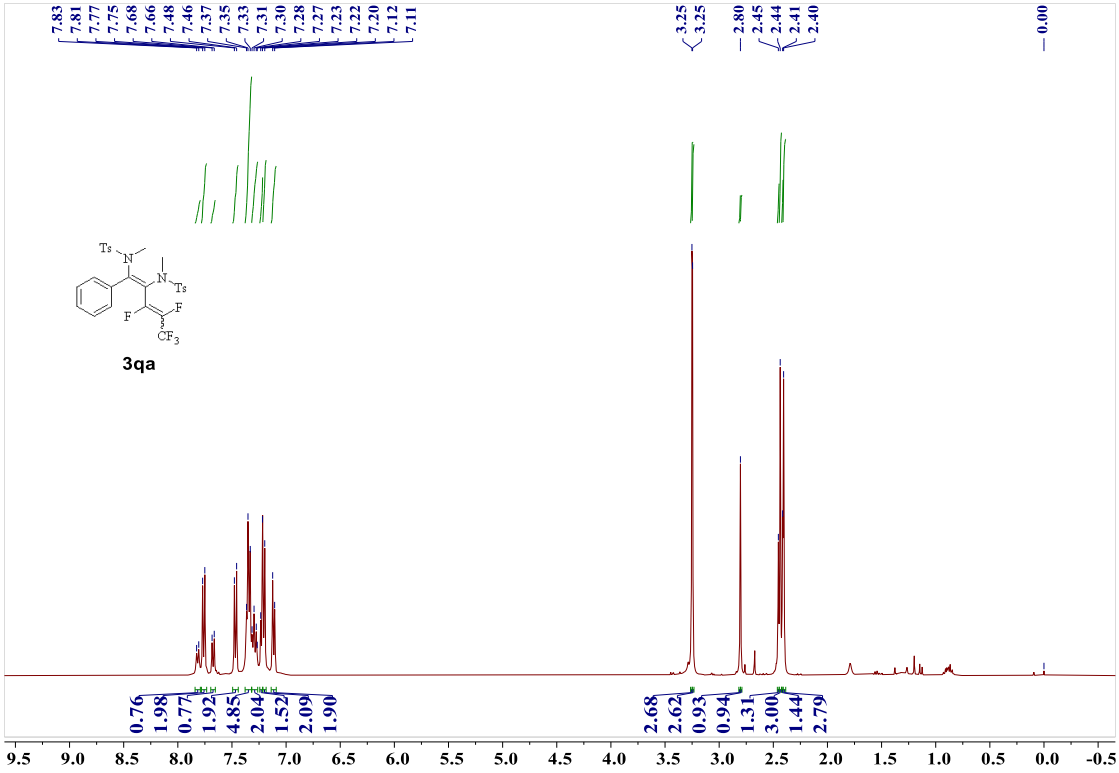
^{19}F NMR spectra of the product **3na** (376 MHz, $CDCl_3$)



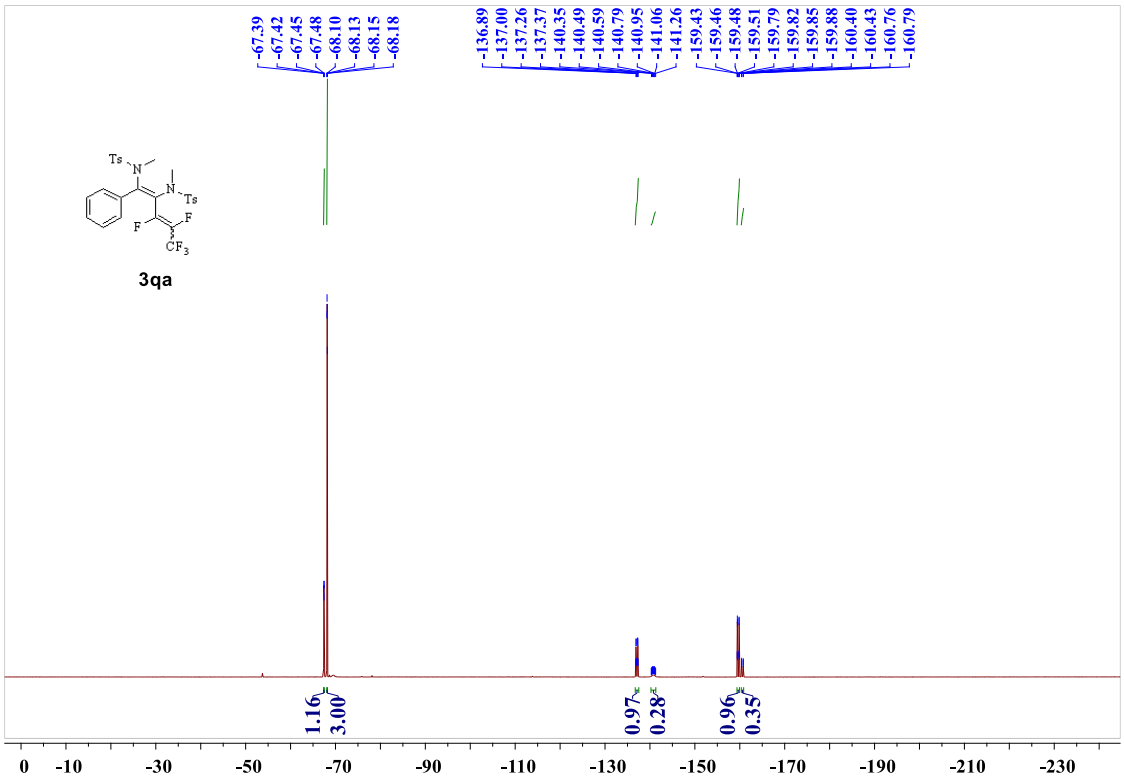
^{13}C NMR spectra of the product **3na** (100 MHz, $CDCl_3$)



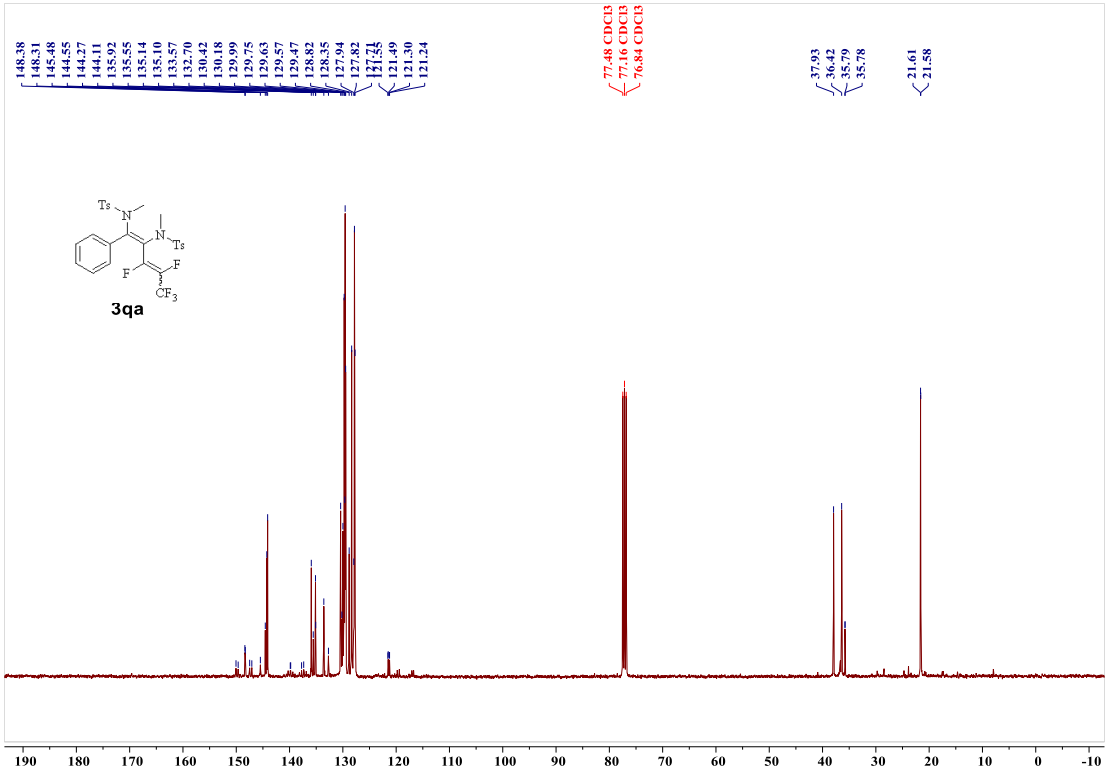
^{1}H NMR spectra of the product **3qa** (400 MHz, $CDCl_3$)



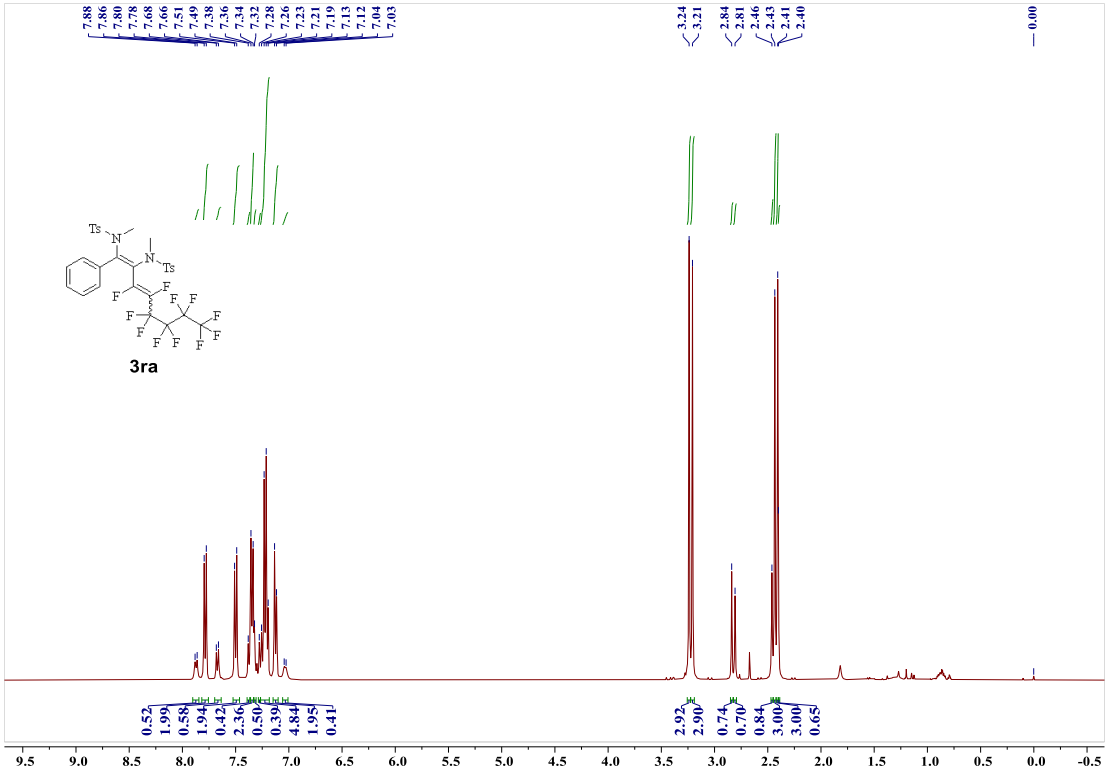
^{19}F NMR spectra of the product **3qa** (376 MHz, $CDCl_3$)



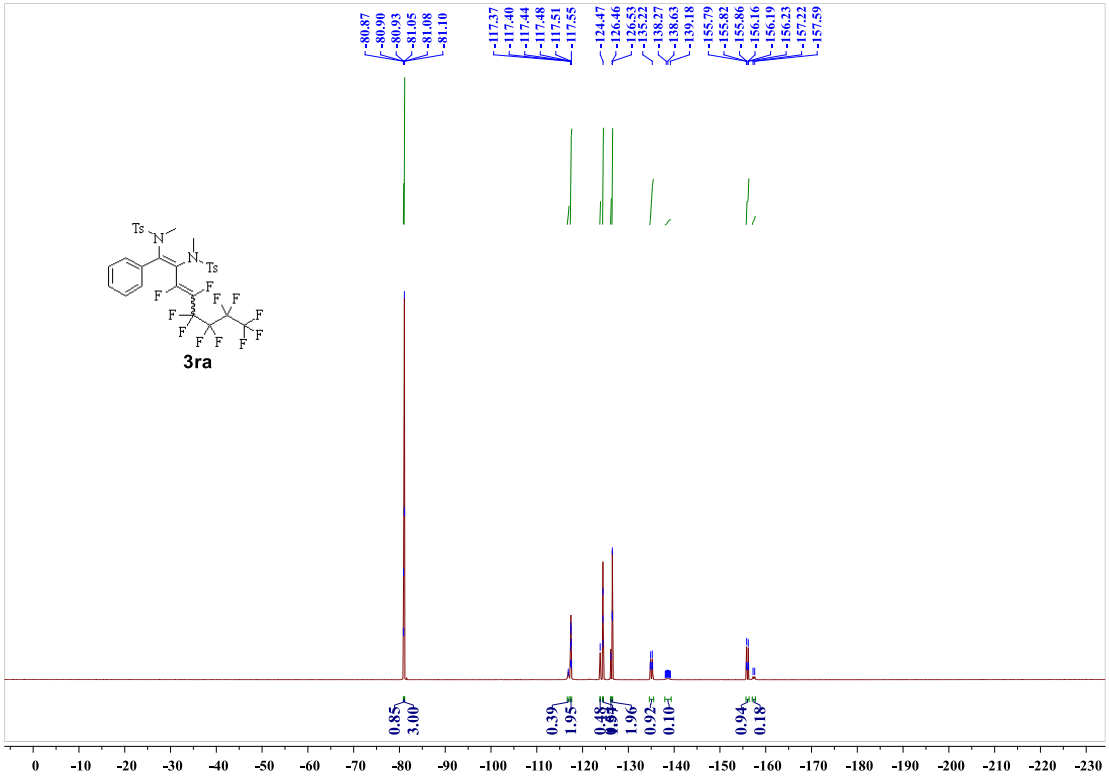
^{13}C NMR spectra of the product **3qa** (100 MHz, $CDCl_3$)



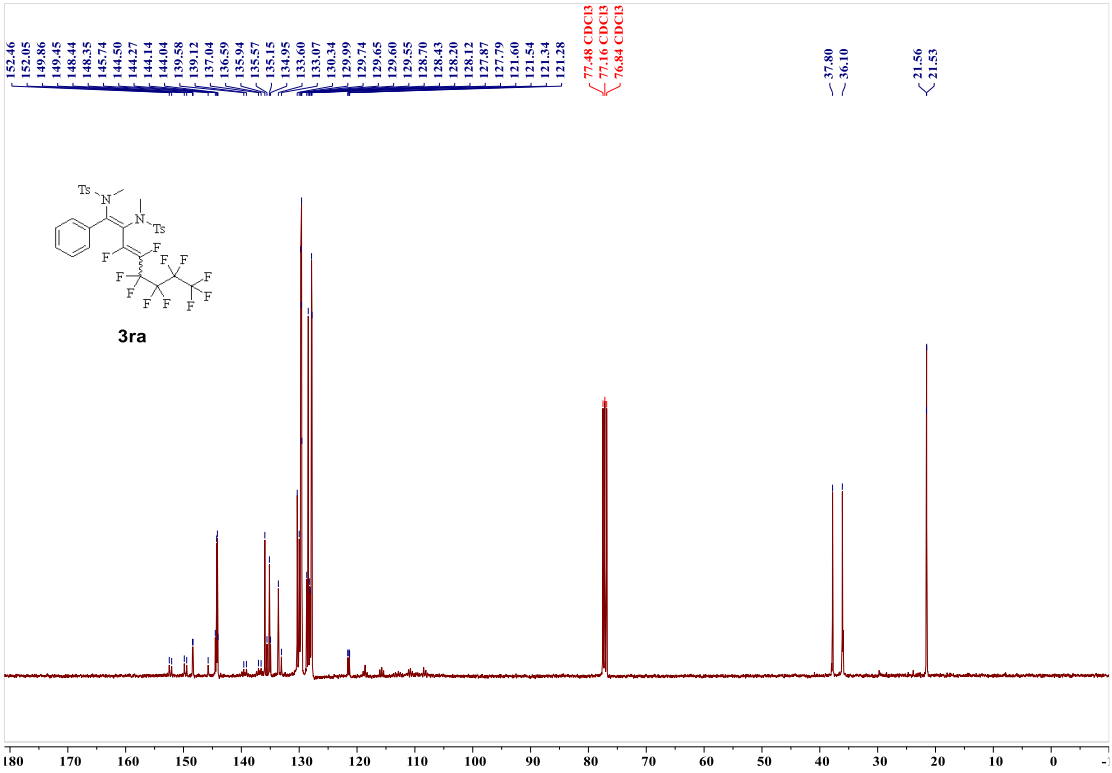
^{1}H NMR spectra of the product **3ra** (400 MHz, $CDCl_3$)



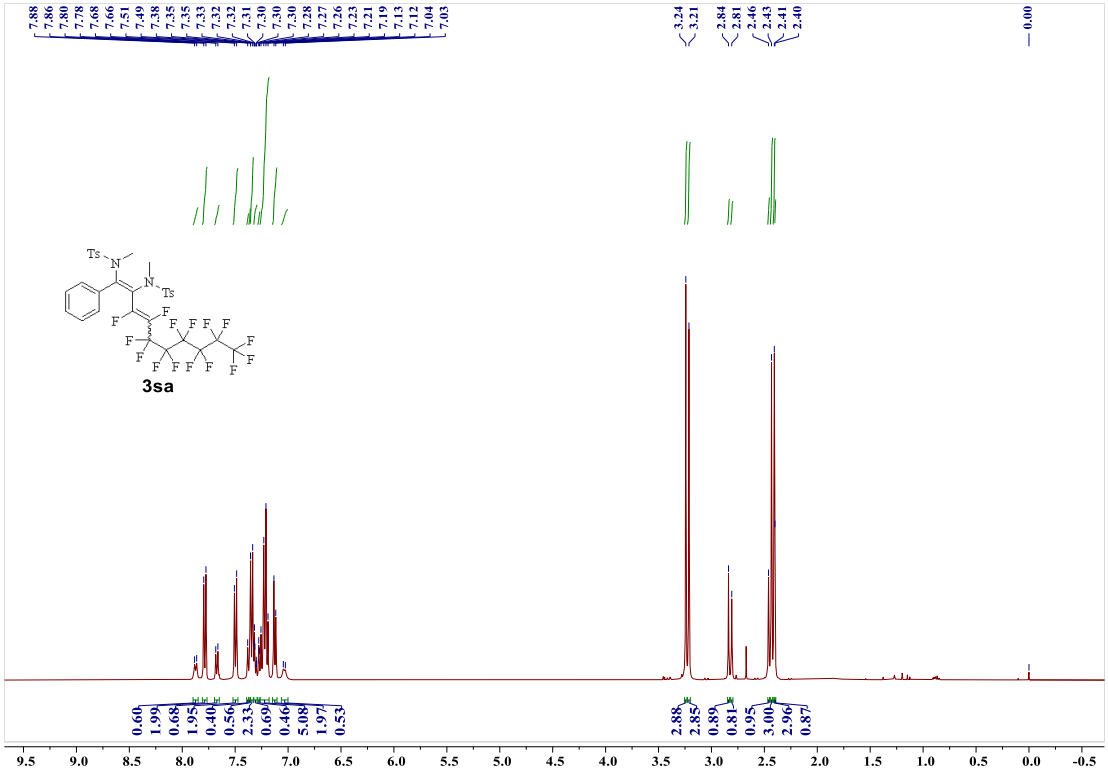
^{19}F NMR spectra of the product **3ra** (376 MHz, $CDCl_3$)



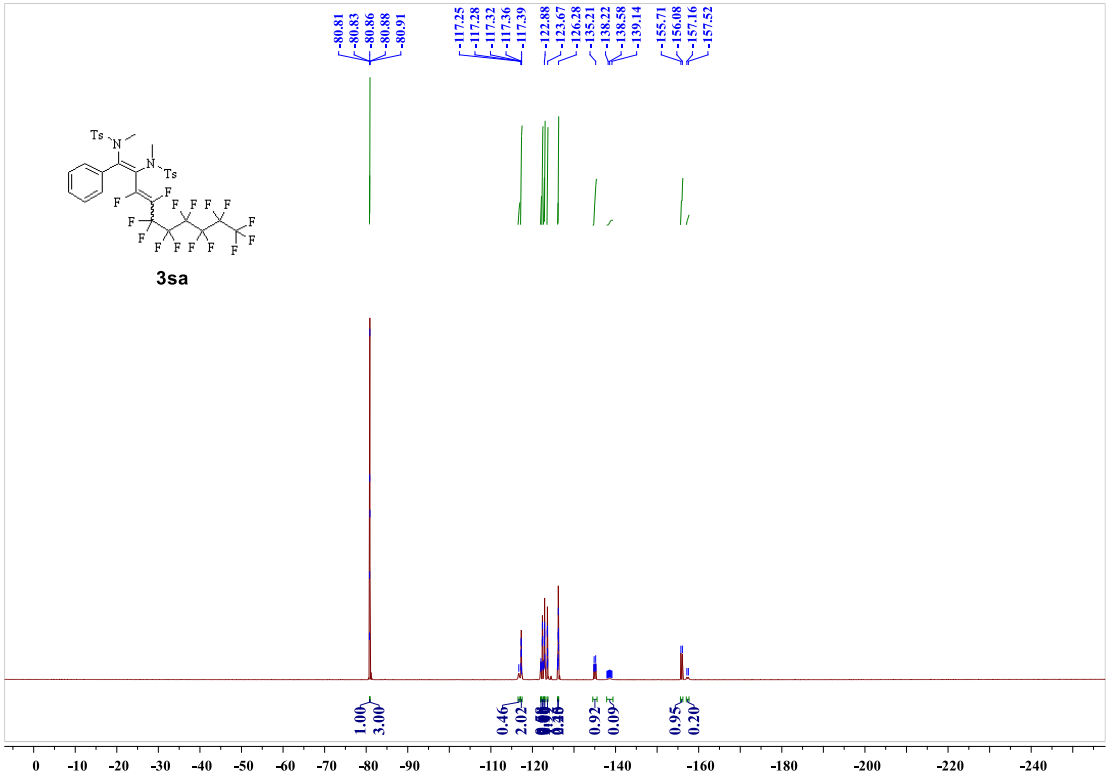
^{13}C NMR spectra of the product **3ra** (100 MHz, $CDCl_3$)



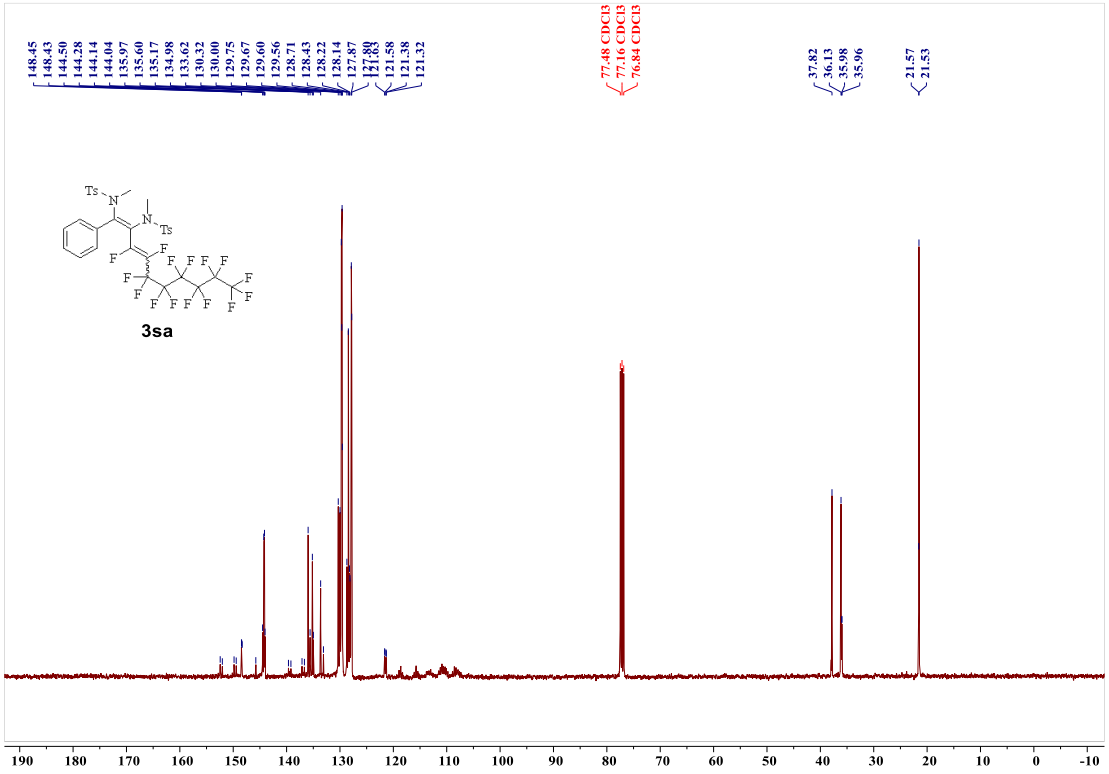
^{1}H NMR spectra of the product **3sa** (400 MHz, $CDCl_3$)



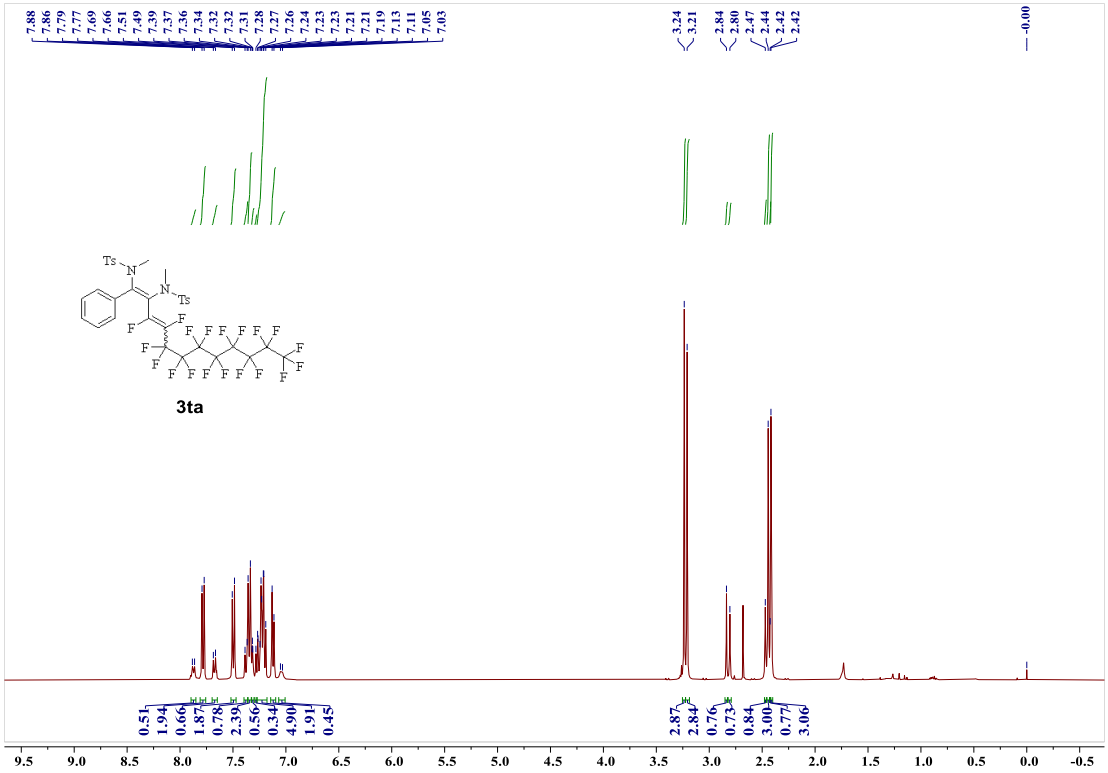
^{19}F NMR spectra of the product **3sa** (376 MHz, $CDCl_3$)



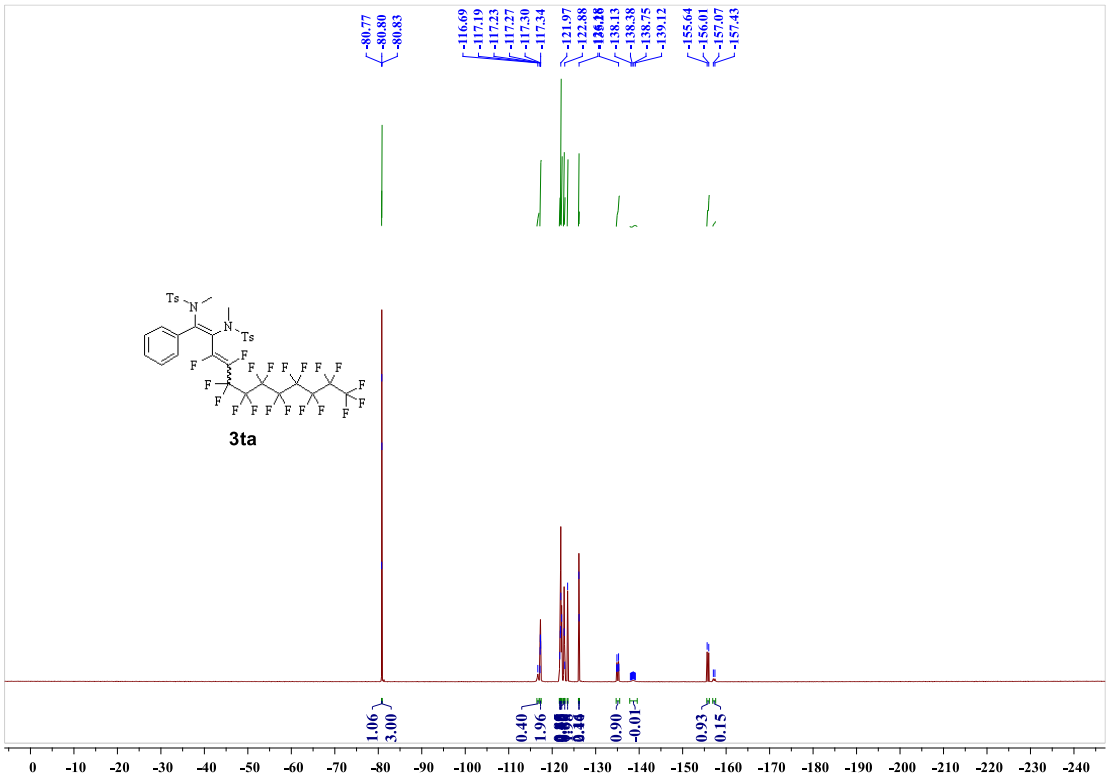
^{13}C NMR spectra of the product **3sa** (100 MHz, $CDCl_3$)



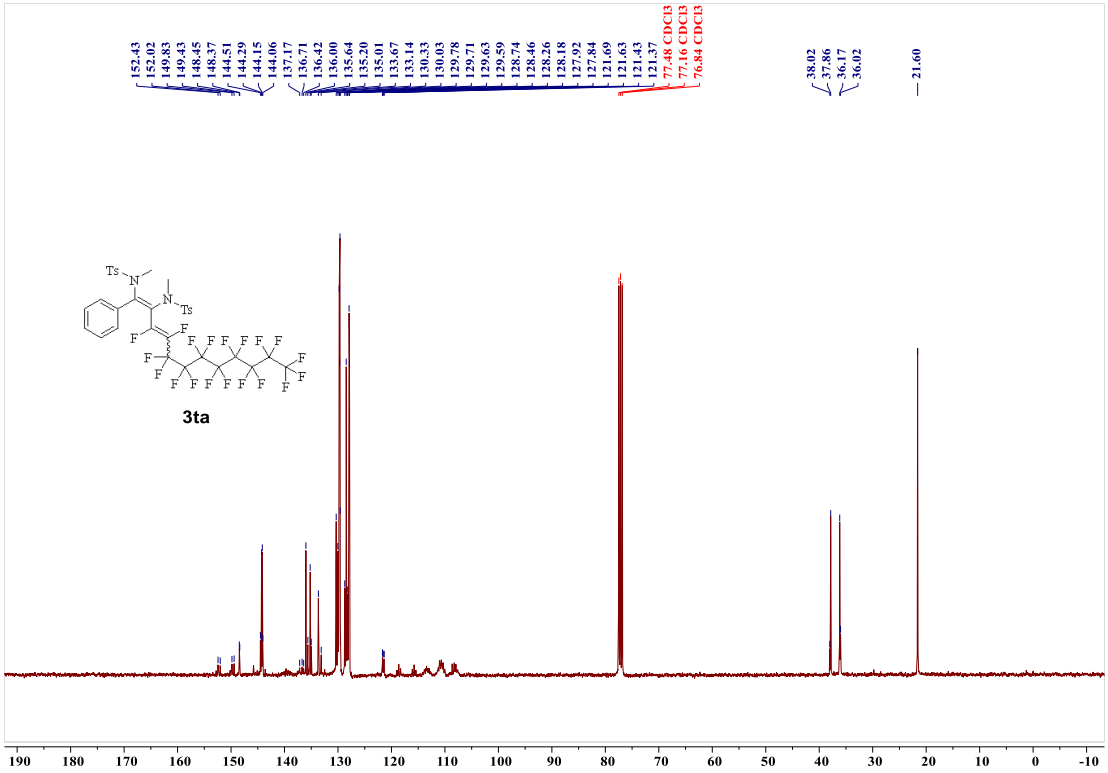
^{1}H NMR spectra of the product **3ta** (400 MHz, $CDCl_3$)



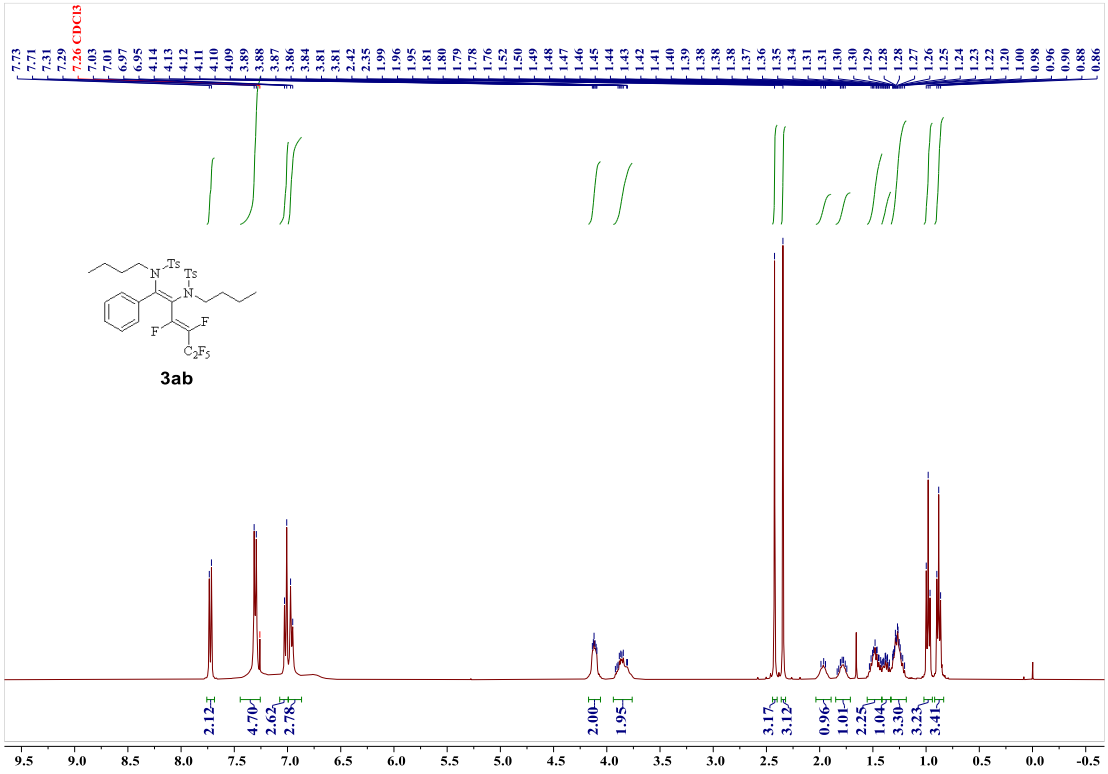
^{19}F NMR spectra of the product **3ta** (376 MHz, $CDCl_3$)



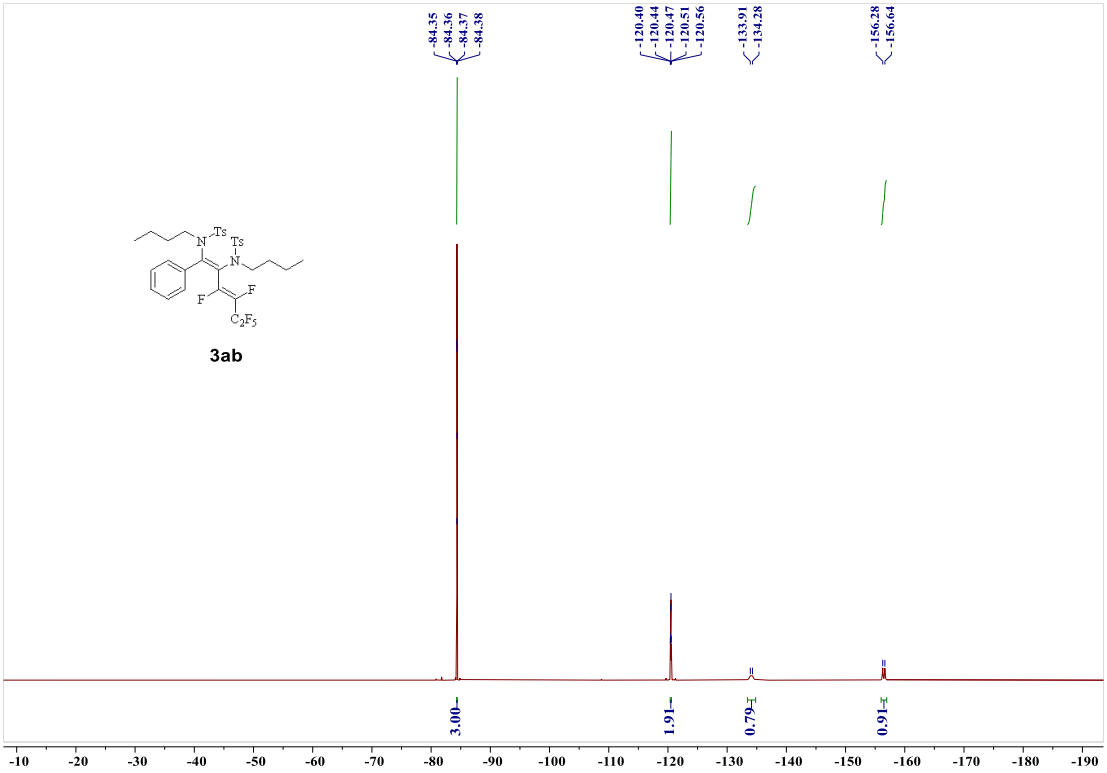
^{13}C NMR spectra of the product **3ta** (100 MHz, $CDCl_3$)



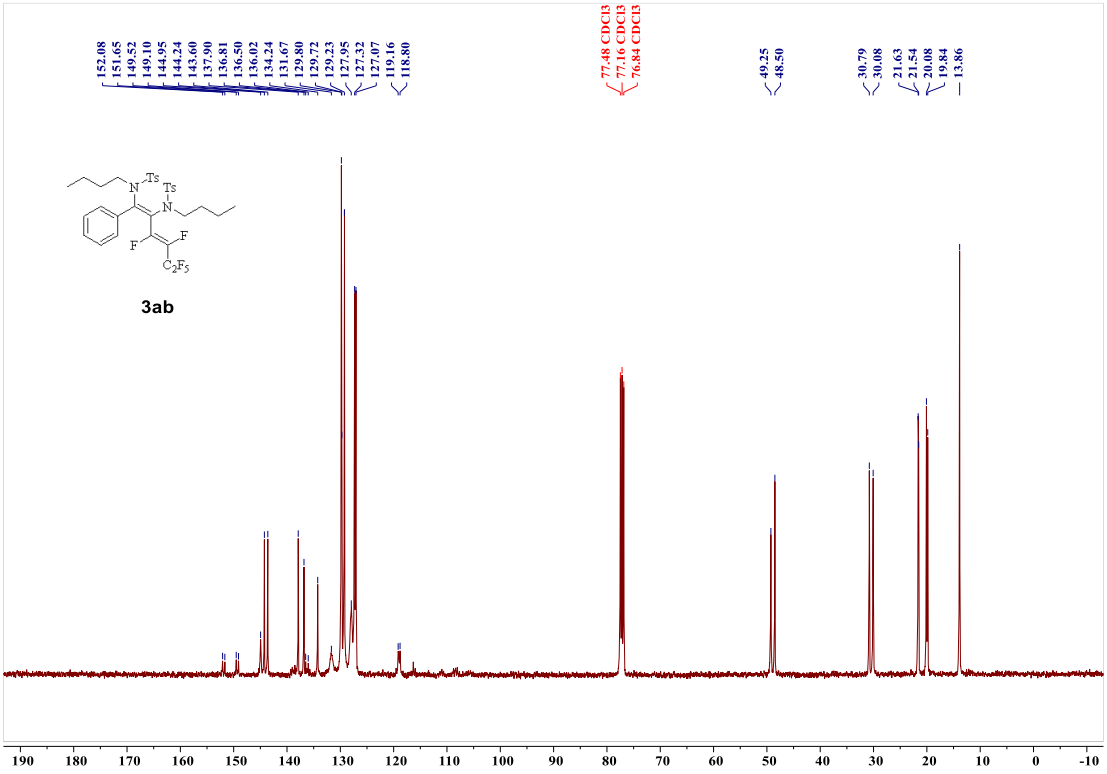
^{1}H NMR spectra of the product **3ab** (400 MHz, $CDCl_3$)



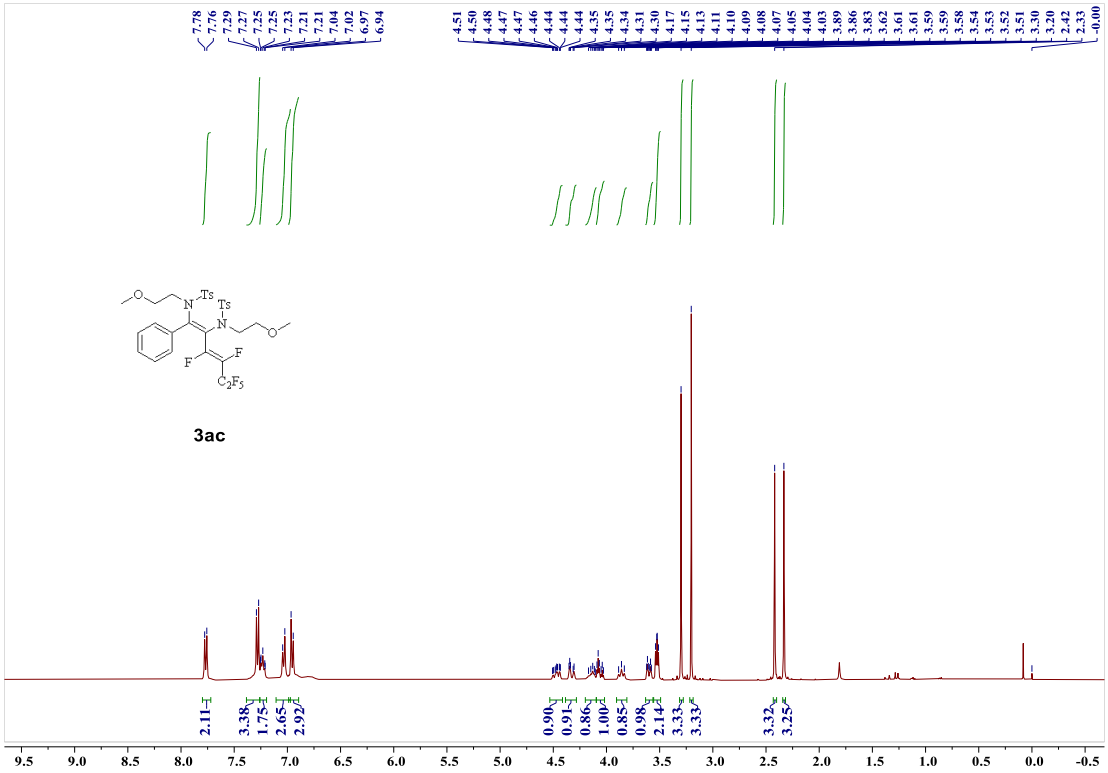
^{19}F NMR spectra of the product **3ab** (376 MHz, $CDCl_3$)



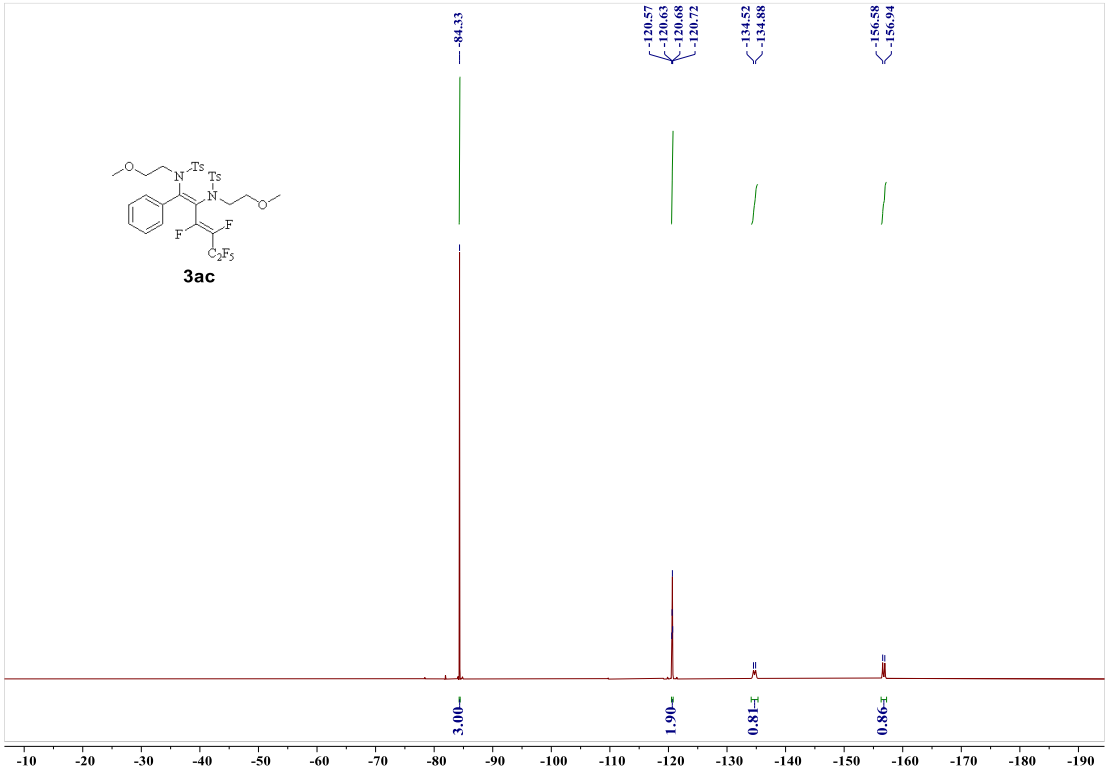
^{13}C NMR spectra of the product **3ab** (100 MHz, $CDCl_3$)



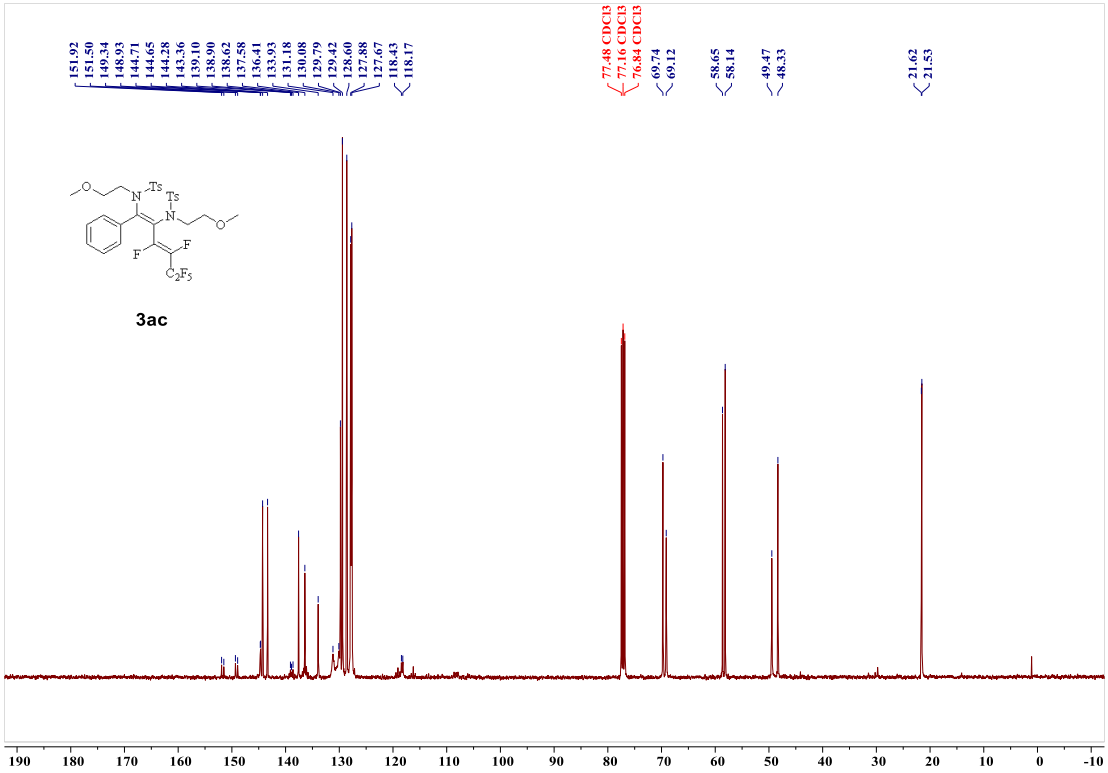
^{1}H NMR spectra of the product **3ac** (400 MHz, $CDCl_3$)



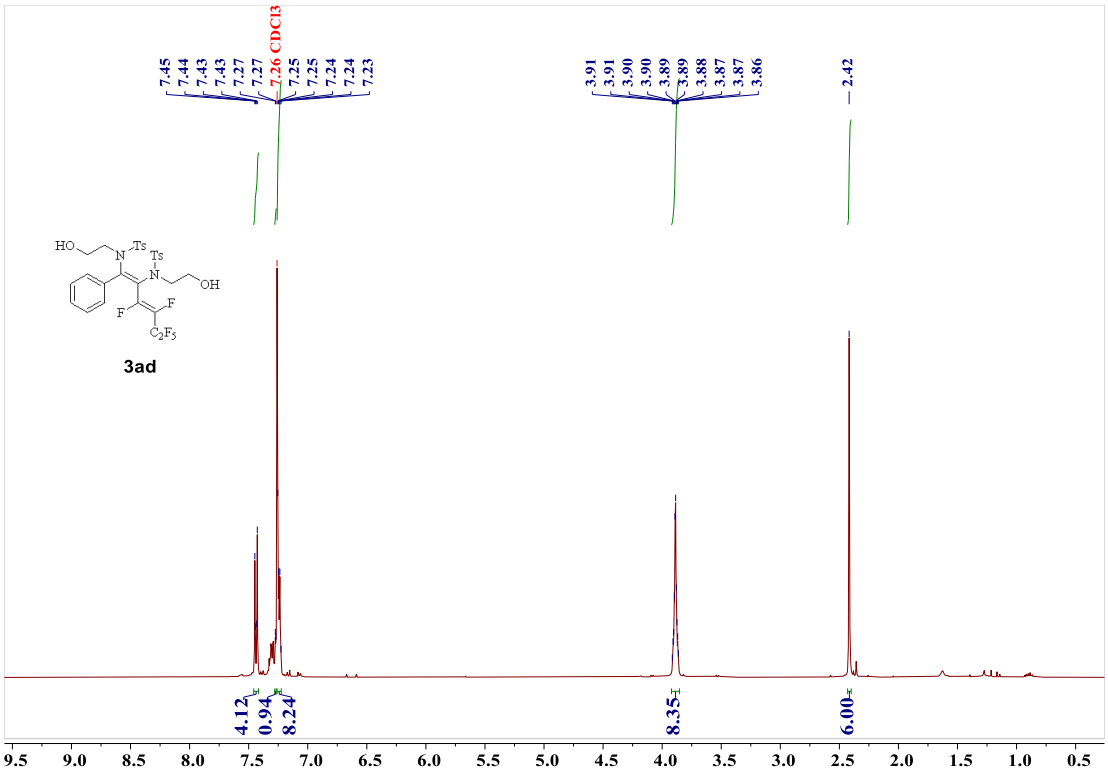
^{19}F NMR spectra of the product **3ac** (376 MHz, $CDCl_3$)



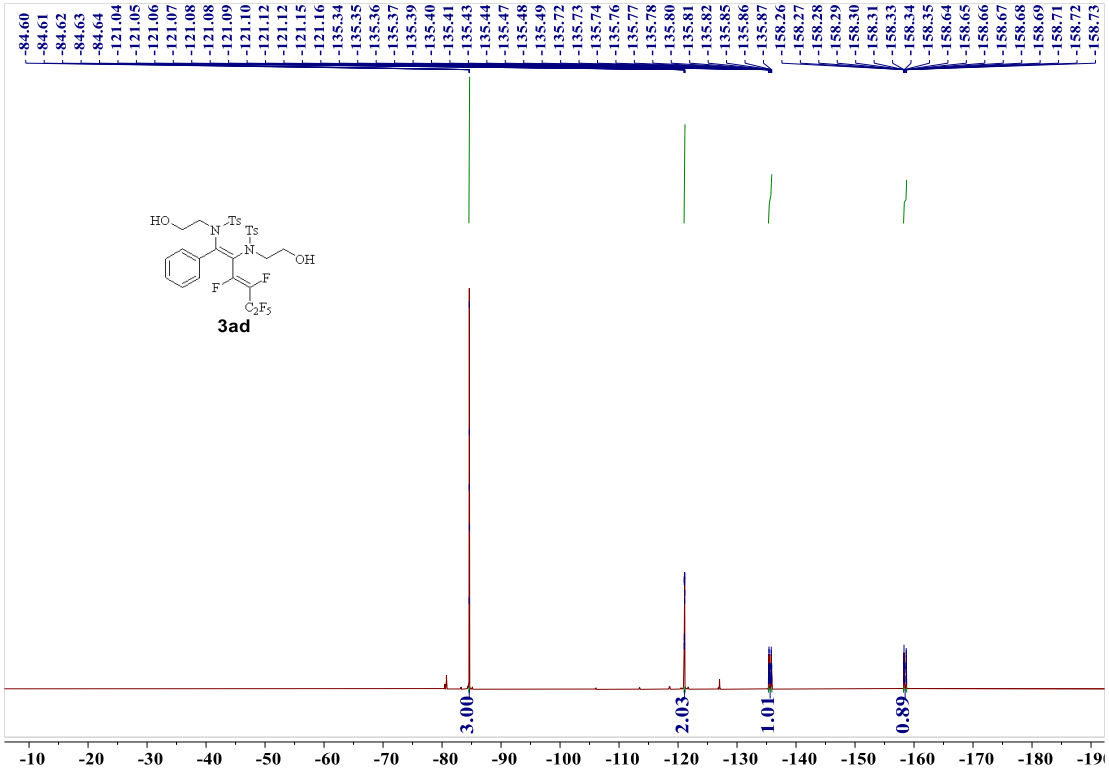
^{13}C NMR spectra of the product **3ac** (100 MHz, $CDCl_3$)



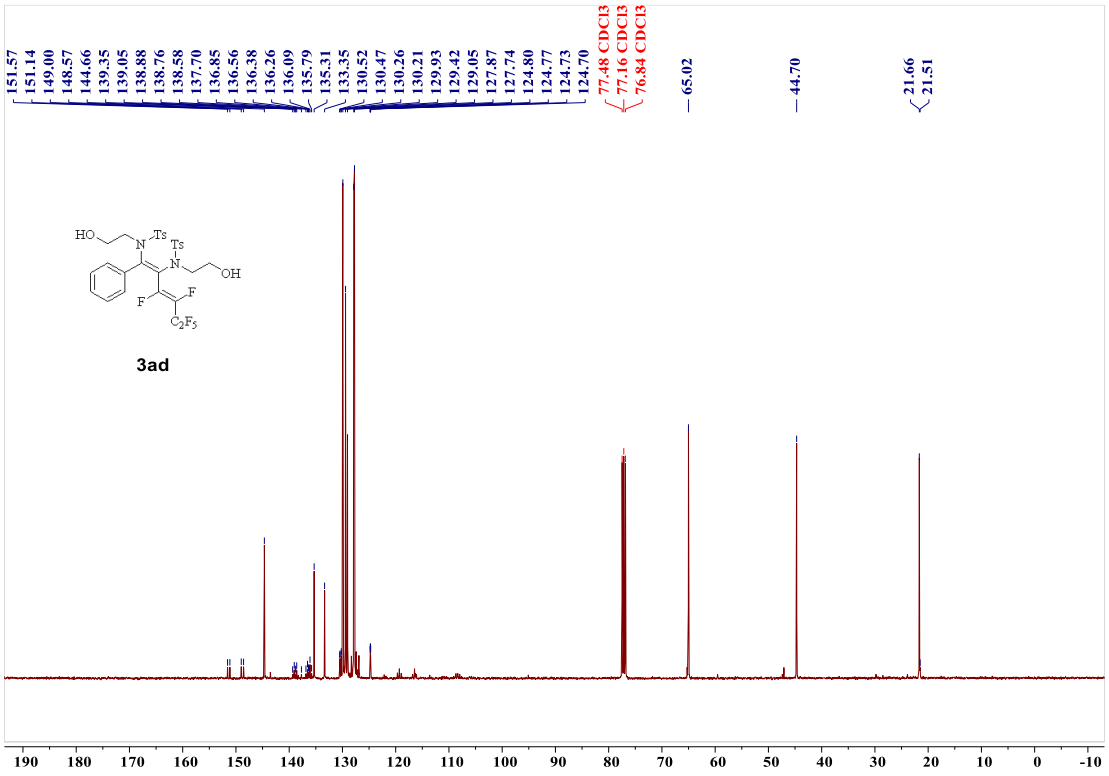
^{1}H NMR spectra of the product **3ad** (400 MHz, $CDCl_3$)



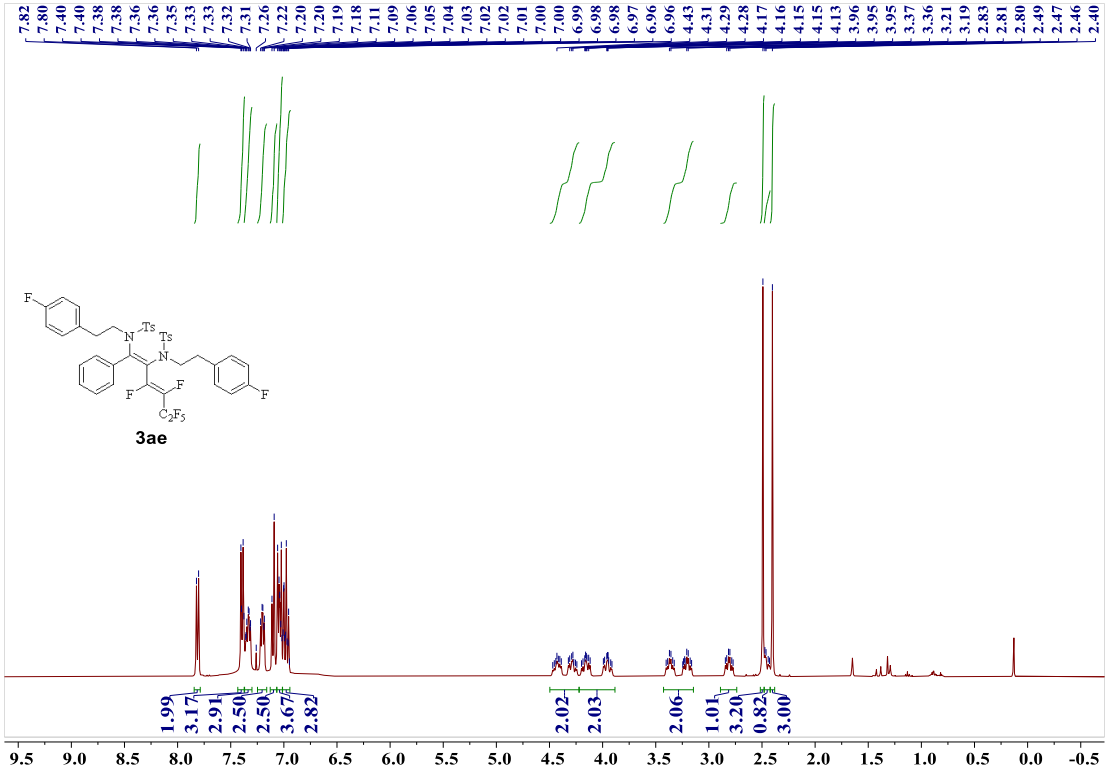
^{19}F NMR spectra of the product **3ad** (376 MHz, $CDCl_3$)



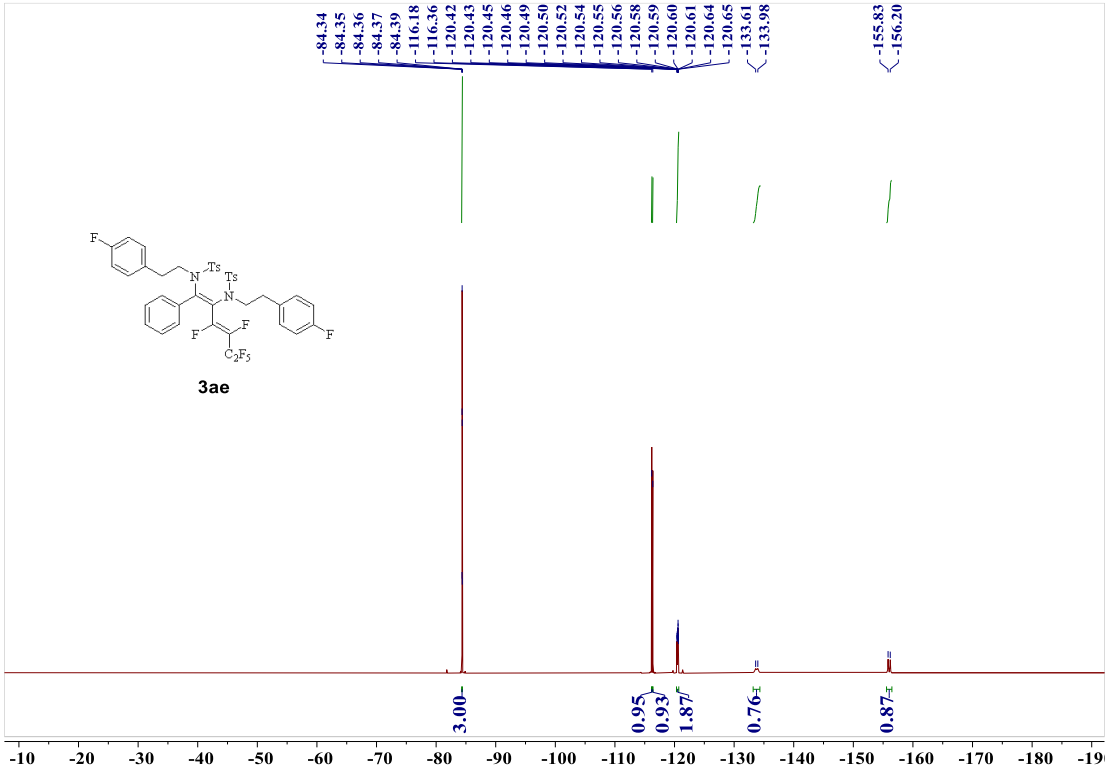
^{13}C NMR spectra of the product **3ad** (100 MHz, $CDCl_3$)



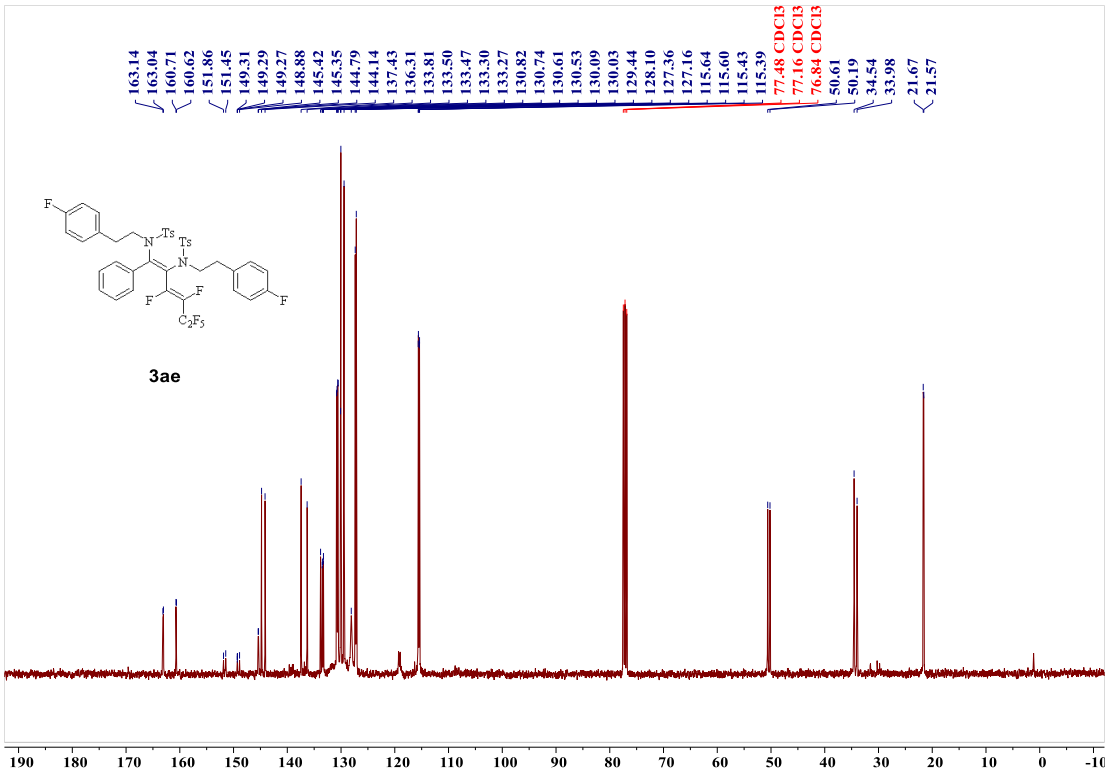
^{1}H NMR spectra of the product **3ae** (400 MHz, $CDCl_3$)



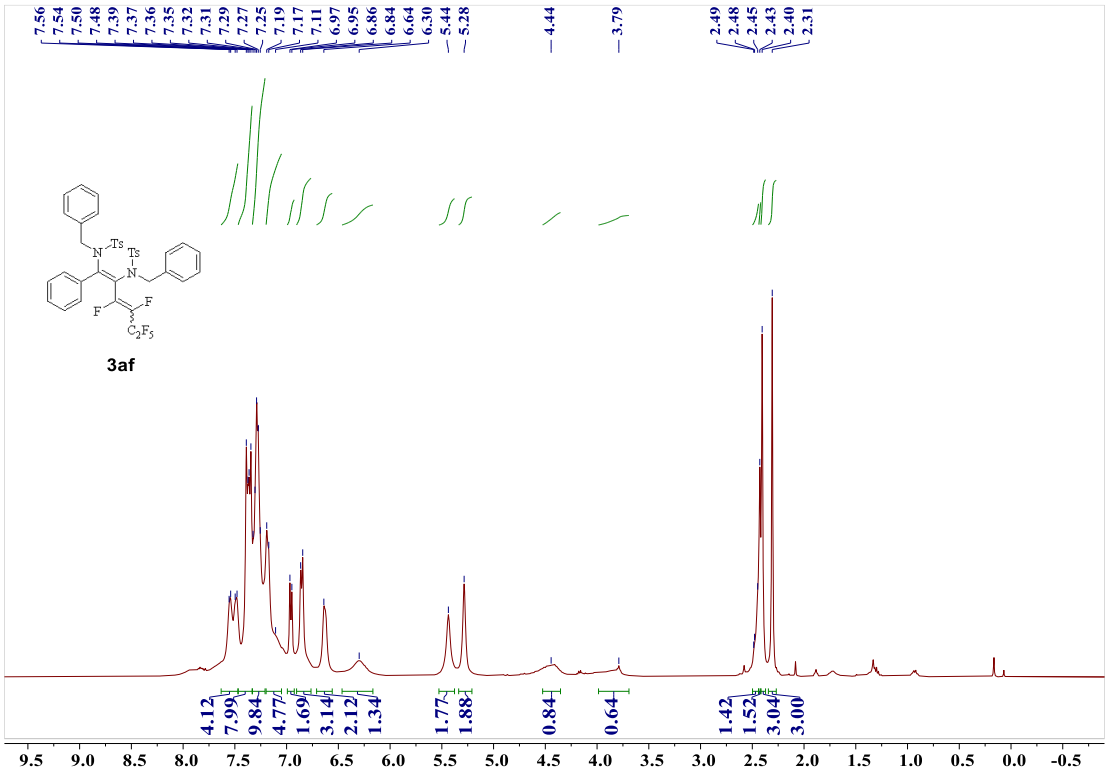
^{19}F NMR spectra of the product **3ae** (376 MHz, $CDCl_3$)



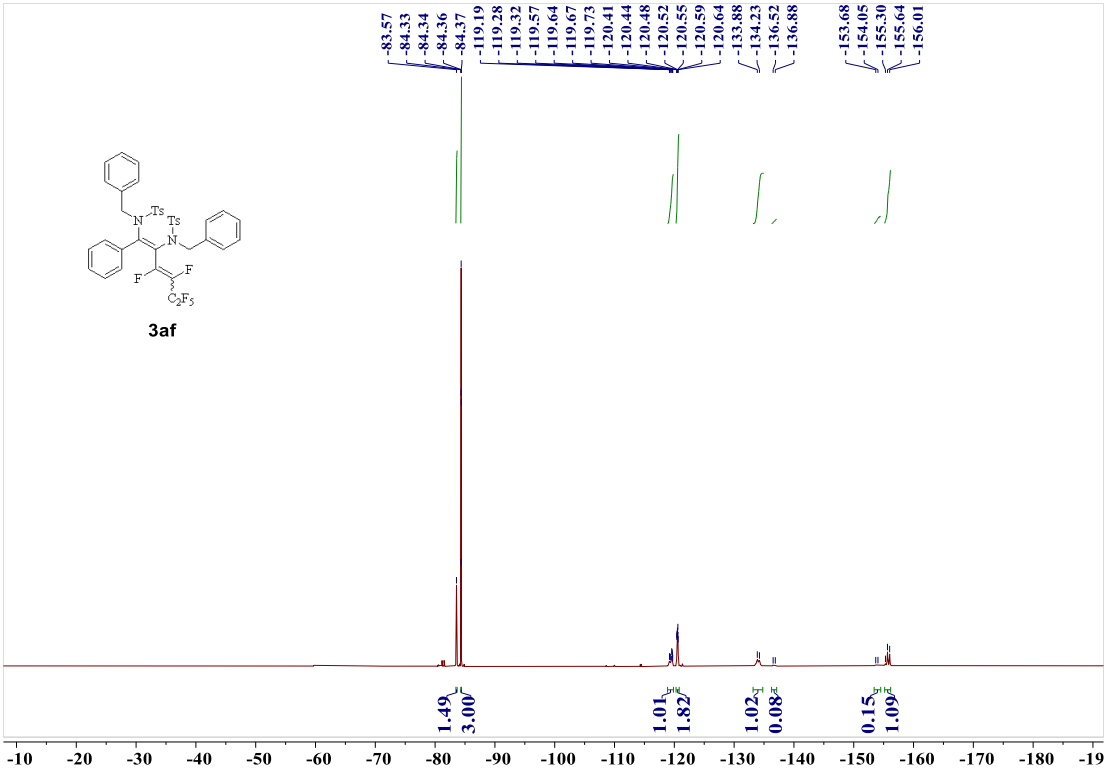
^{13}C NMR spectra of the product **3ae** (100 MHz, $CDCl_3$)



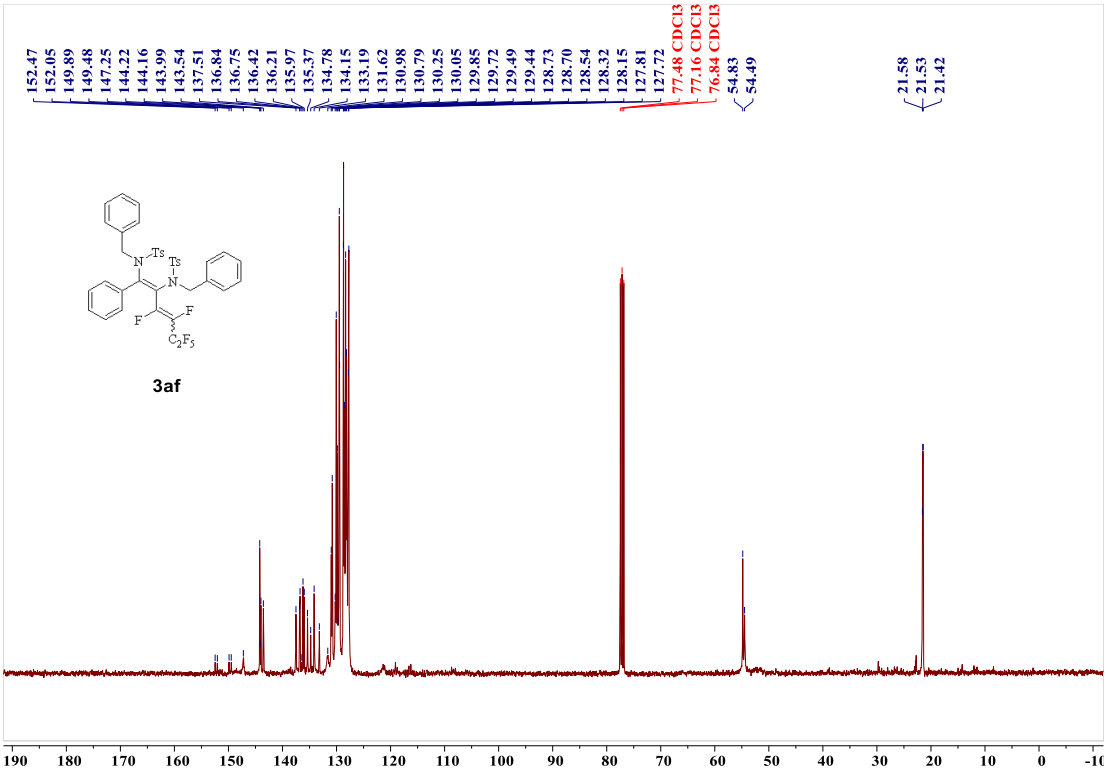
^{1}H NMR spectra of the product **3af** (400 MHz, $CDCl_3$)



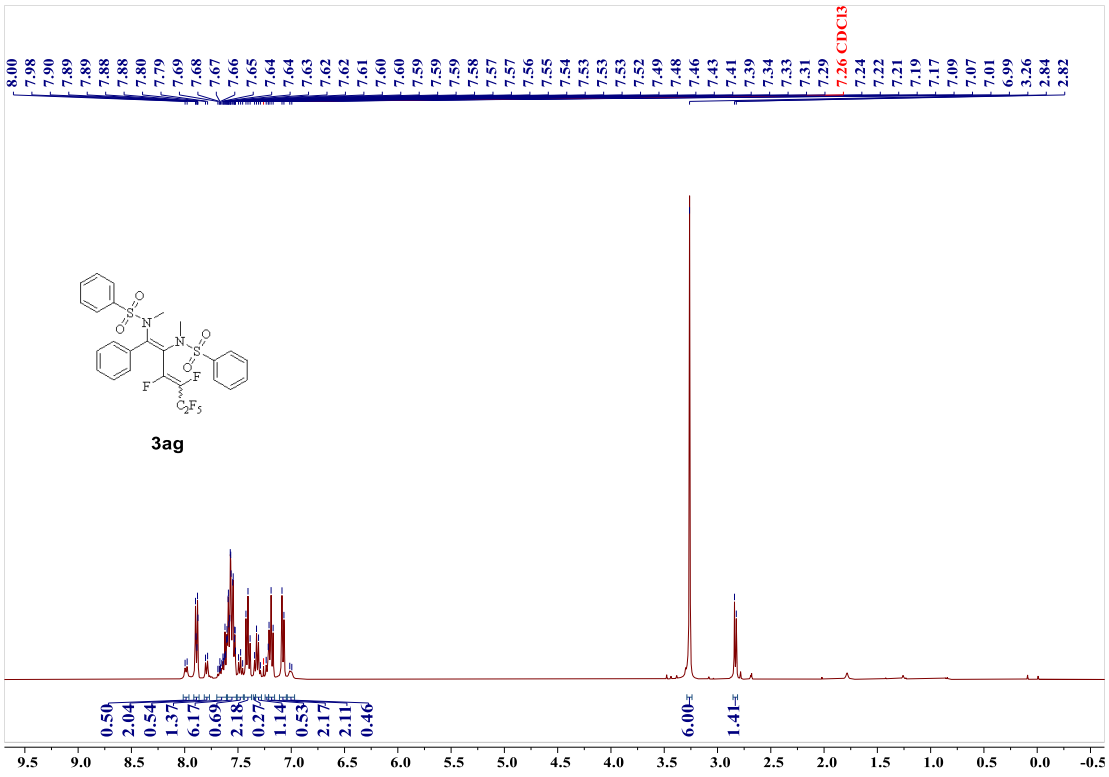
^{19}F NMR spectra of the product **3af** (376 MHz, $CDCl_3$)



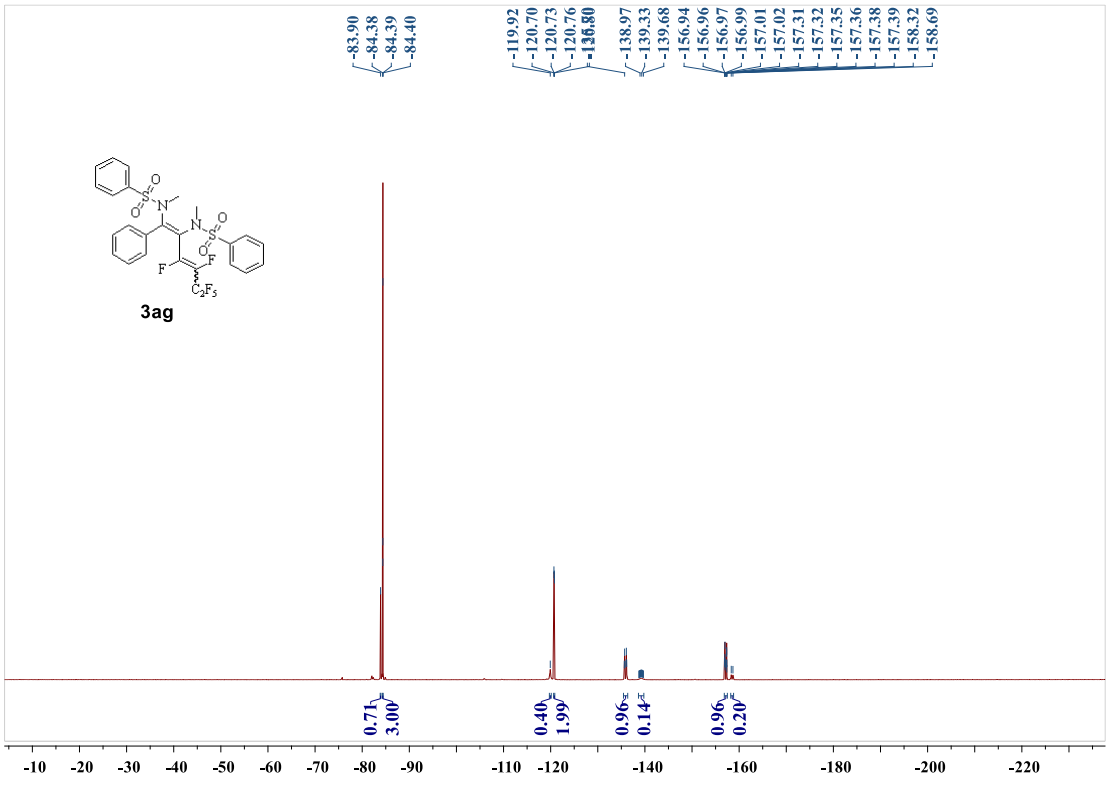
^{13}C NMR spectra of the product **3af** (100 MHz, $CDCl_3$)



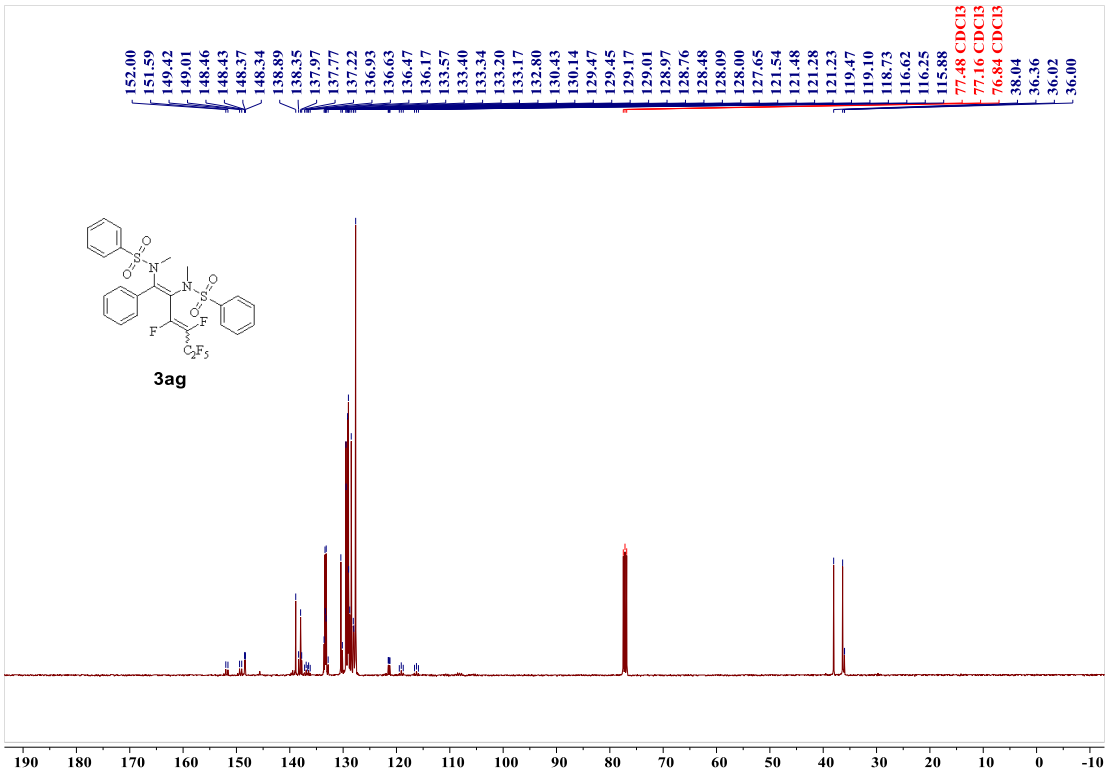
^{1}H NMR spectra of the product **3ag** (400 MHz, $CDCl_3$)



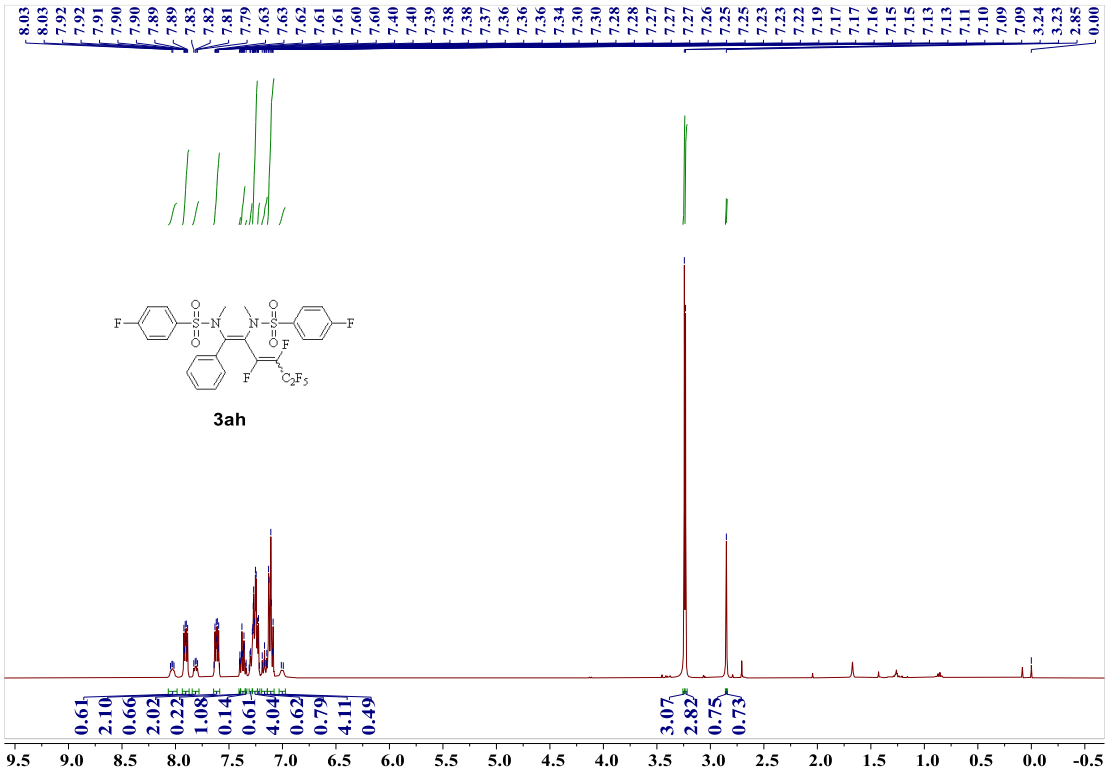
^{19}F NMR spectra of the product **3ag** (376 MHz, $CDCl_3$)



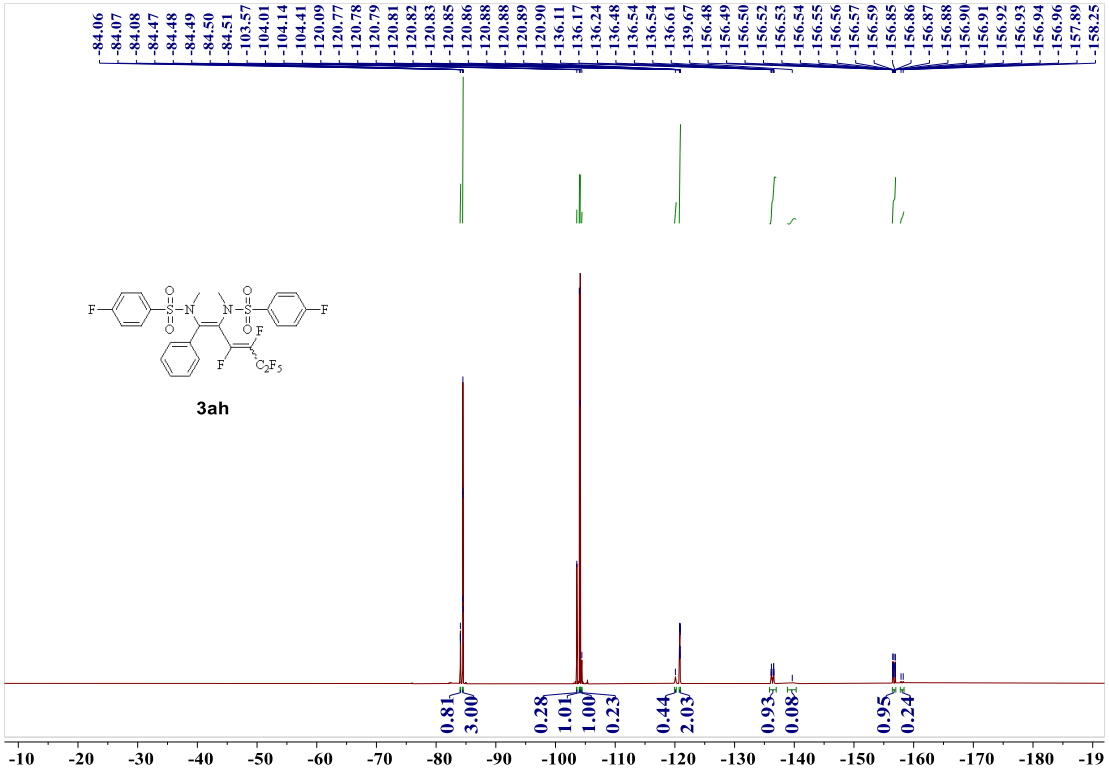
^{13}C NMR spectra of the product **3ag** (100 MHz, $CDCl_3$)



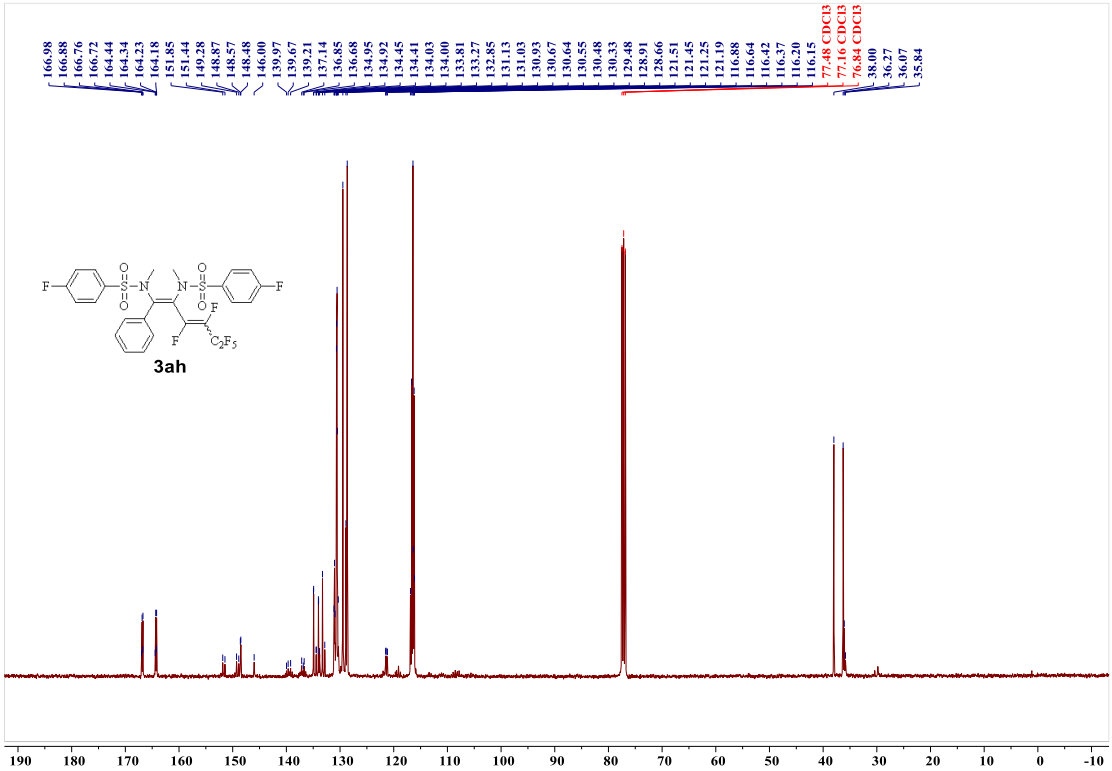
^{1}H NMR spectra of the product **3ah** (400 MHz, $CDCl_3$)



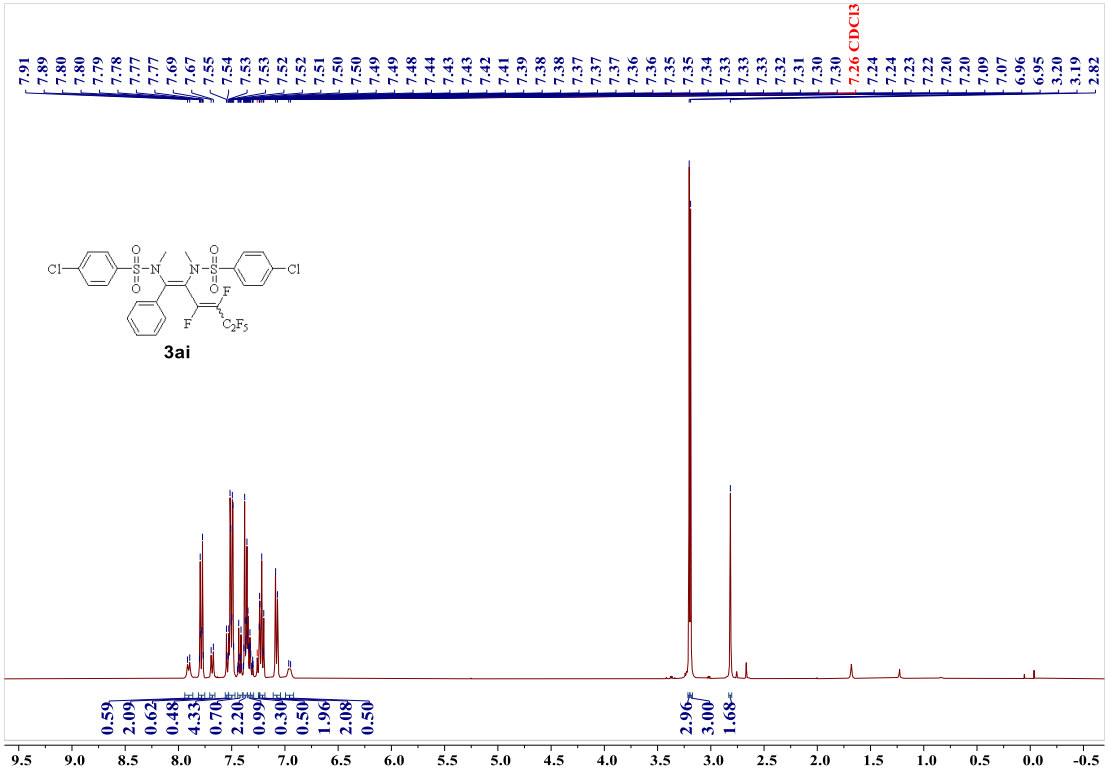
^{19}F NMR spectra of the product **3ah** (376 MHz, $CDCl_3$)



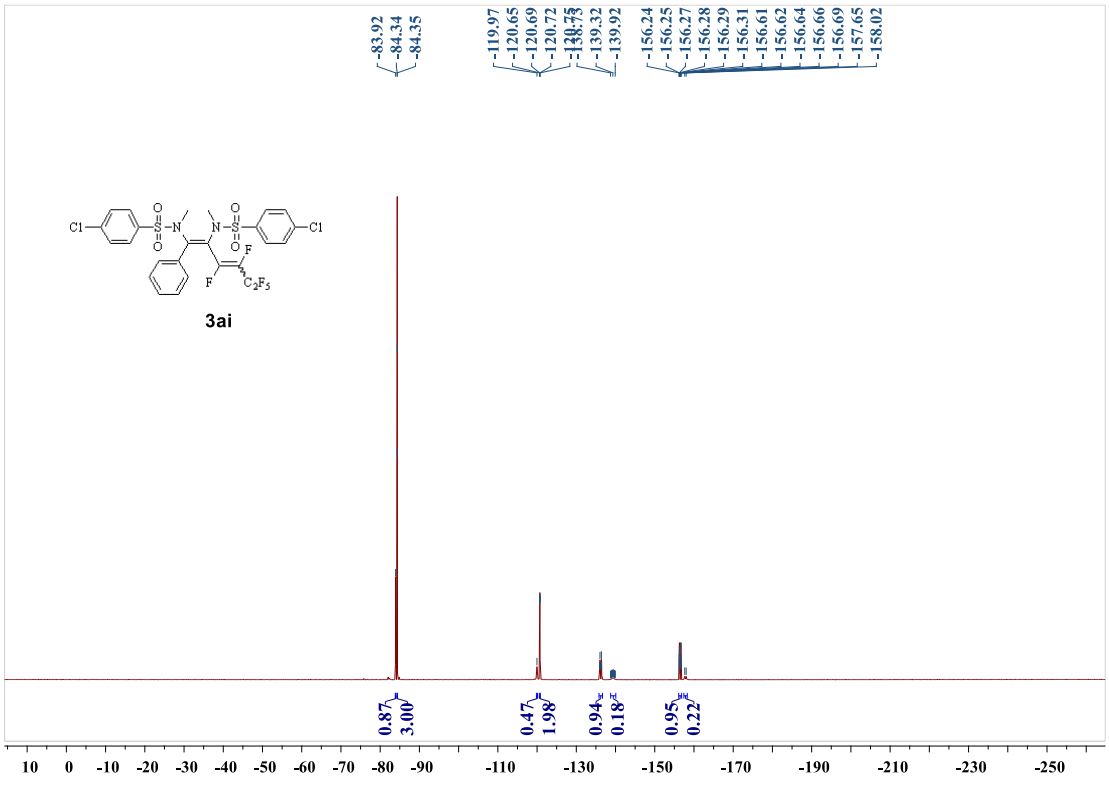
^{13}C NMR spectra of the product **3ah** (100 MHz, $CDCl_3$)



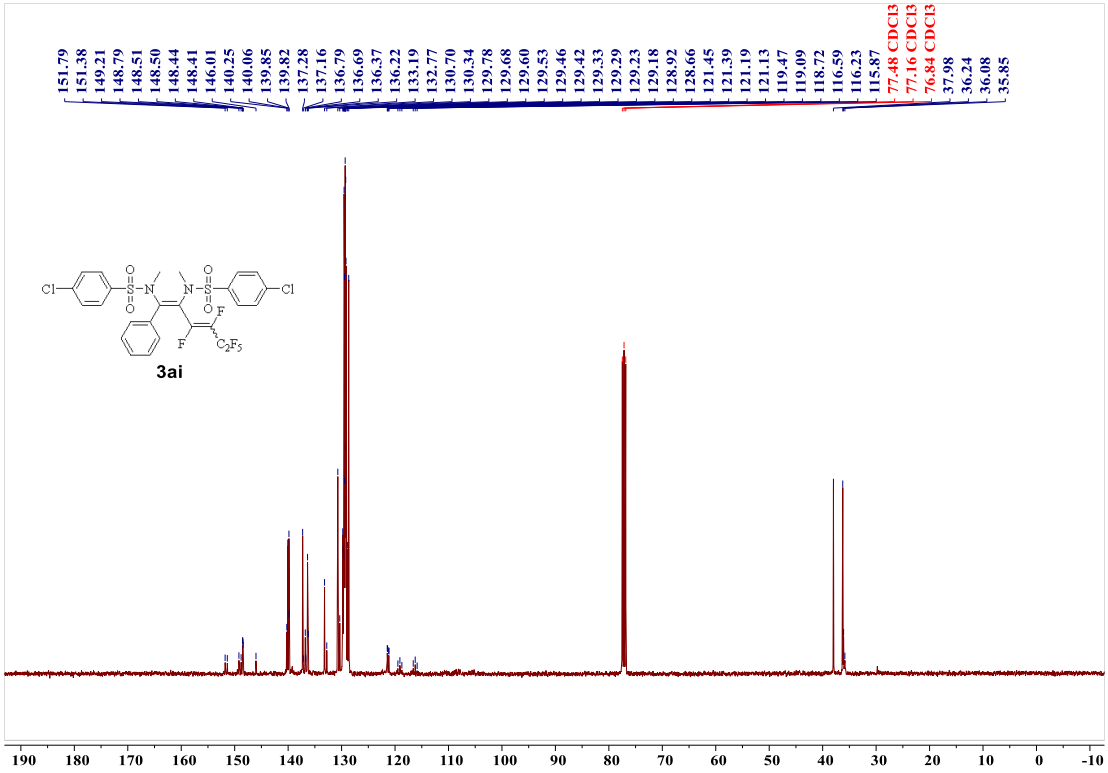
^{1}H NMR spectra of the product **3ai** (400 MHz, $CDCl_3$)



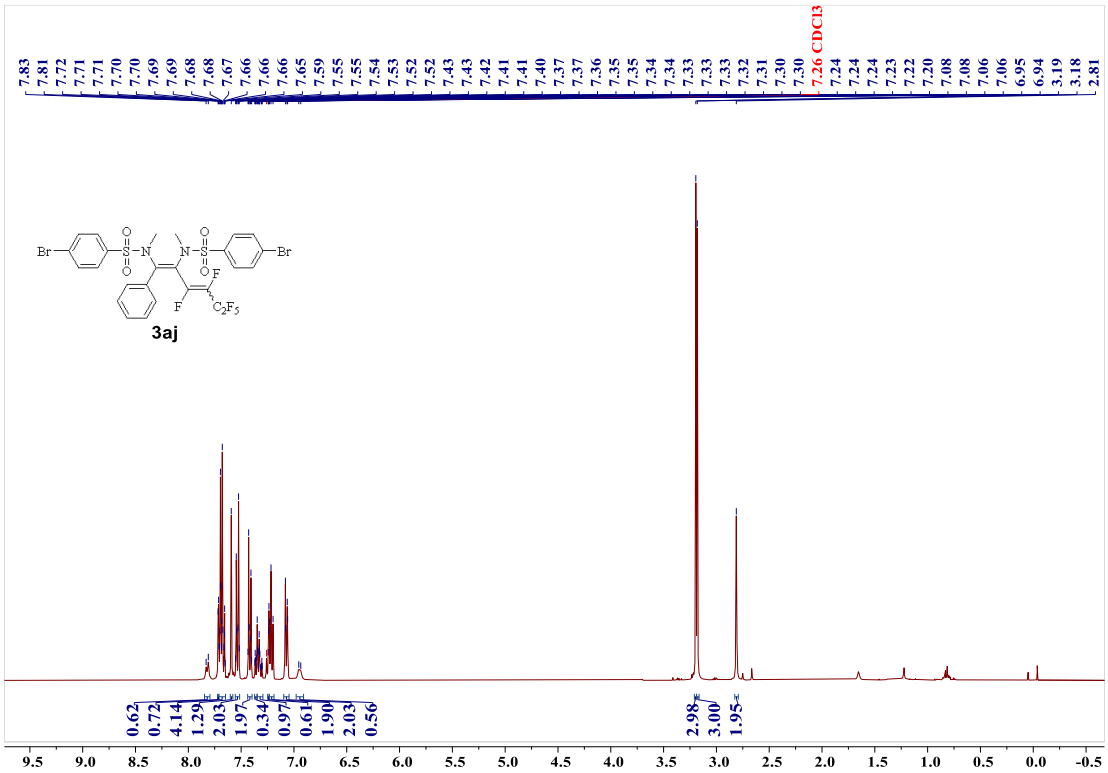
^{19}F NMR spectra of the product **3ai** (376 MHz, $CDCl_3$)



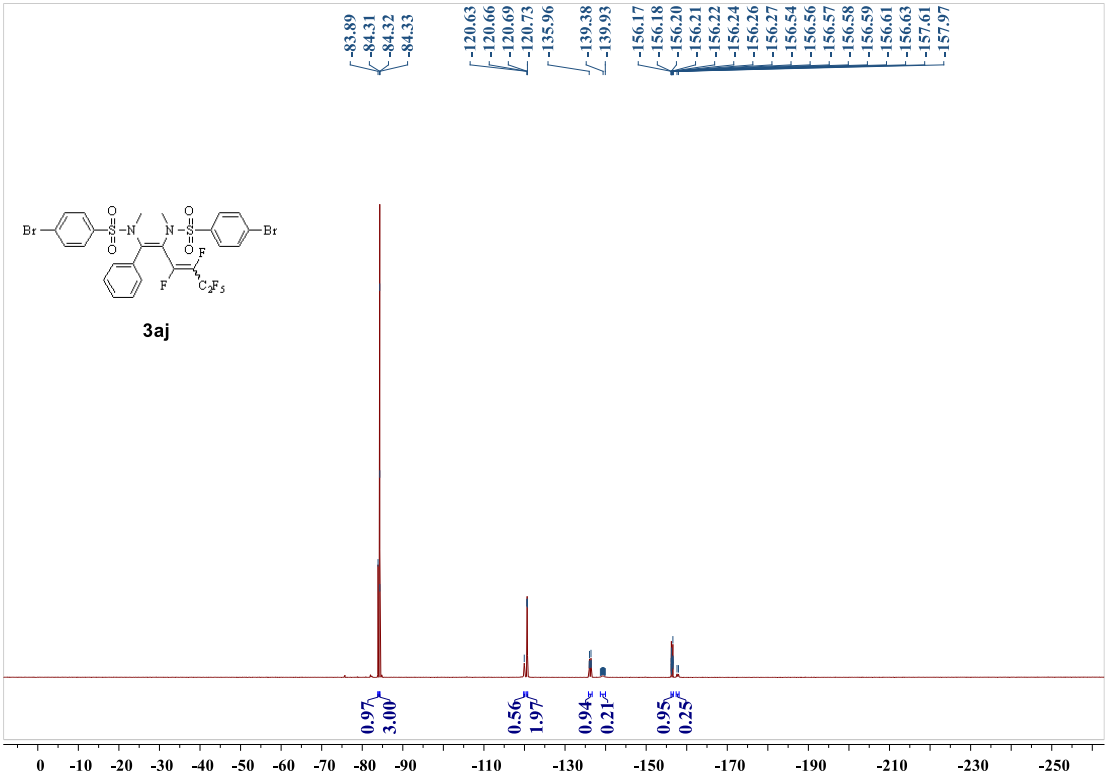
^{13}C NMR spectra of the product **3ai** (100 MHz, $CDCl_3$)



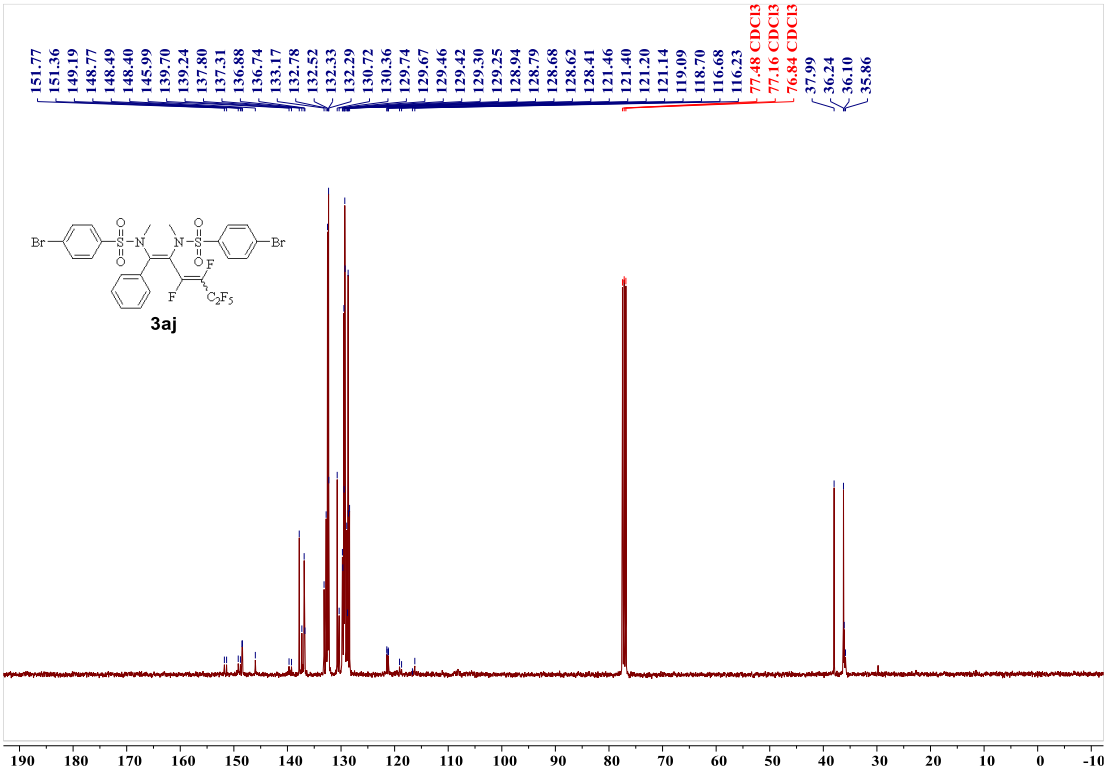
^{1}H NMR spectra of the product **3aj** (400 MHz, $CDCl_3$)



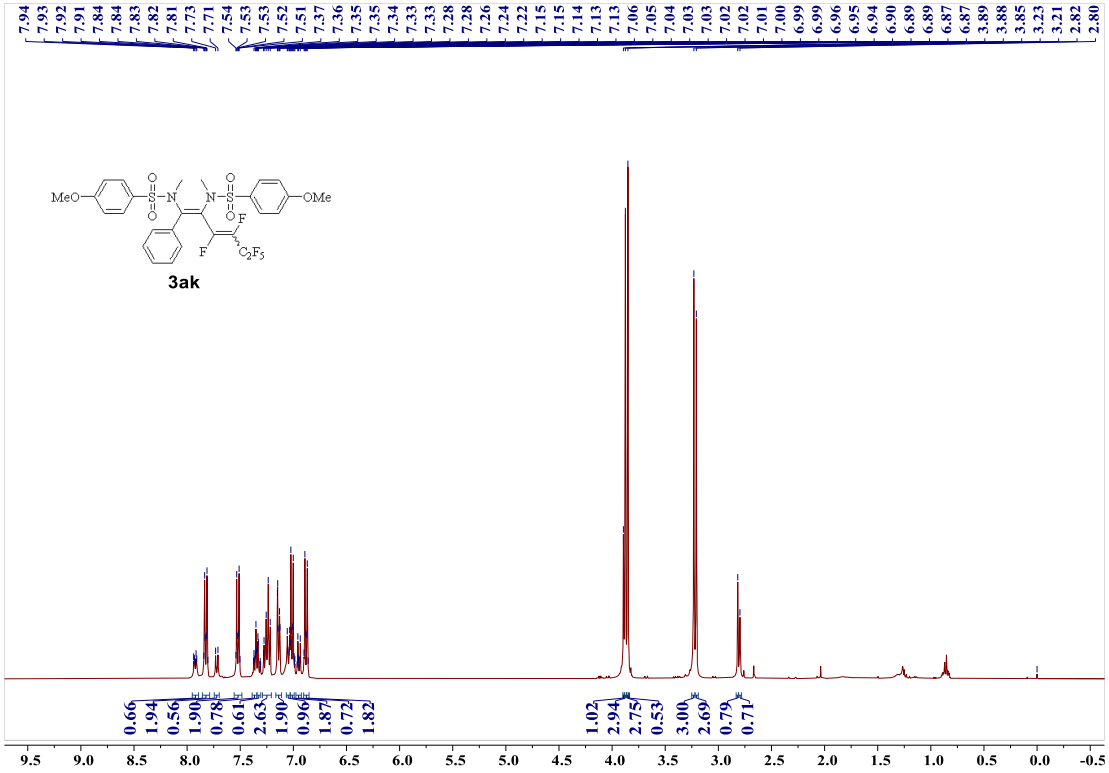
^{19}F NMR spectra of the product **3aj** (376 MHz, $CDCl_3$)



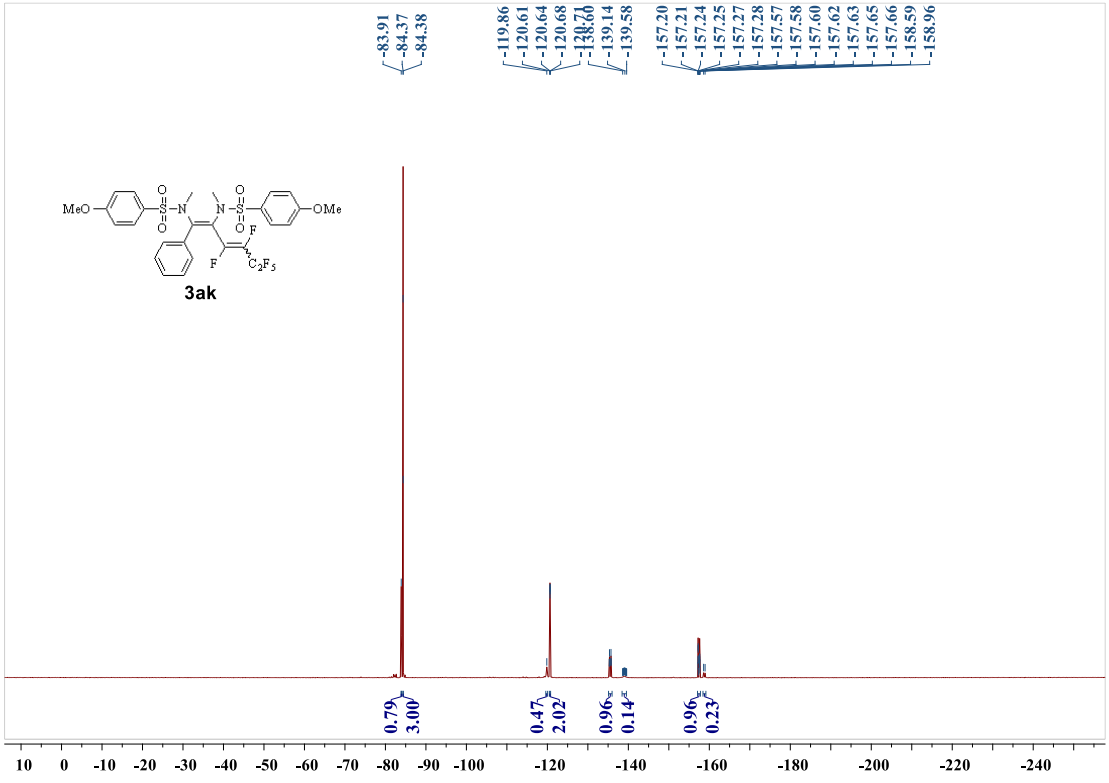
^{13}C NMR spectra of the product **3aj** (100 MHz, $CDCl_3$)



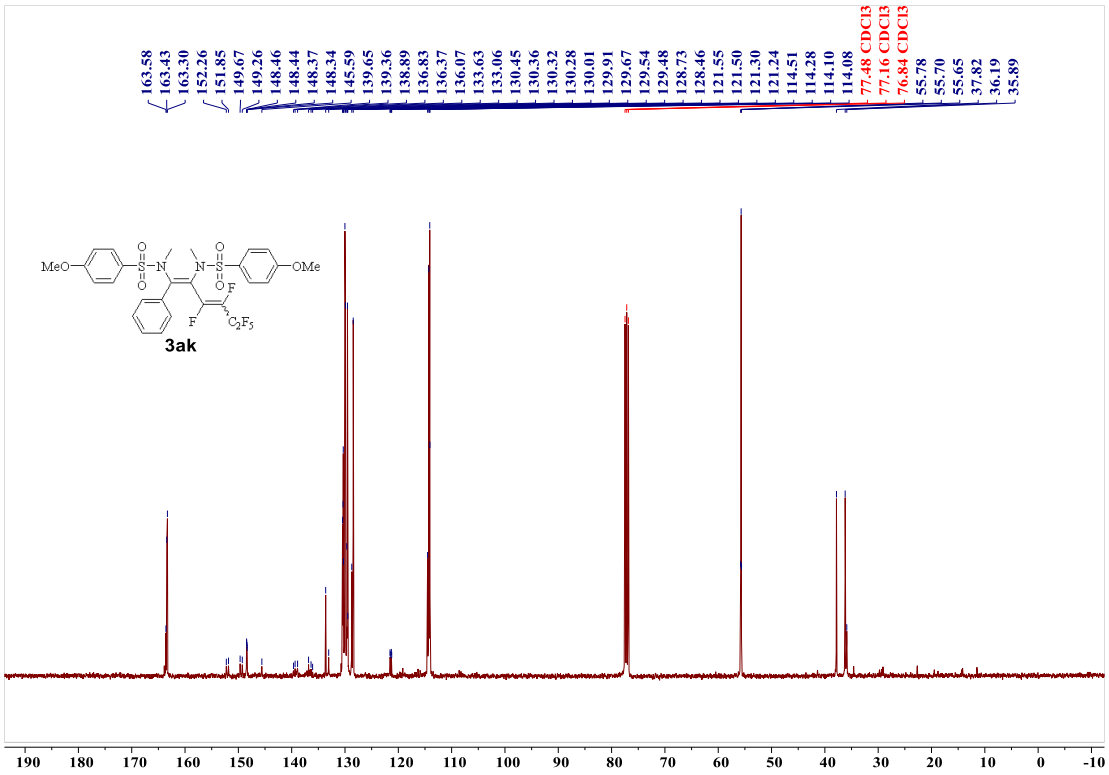
^{1}H NMR spectra of the product **3ak** (400 MHz, $CDCl_3$)



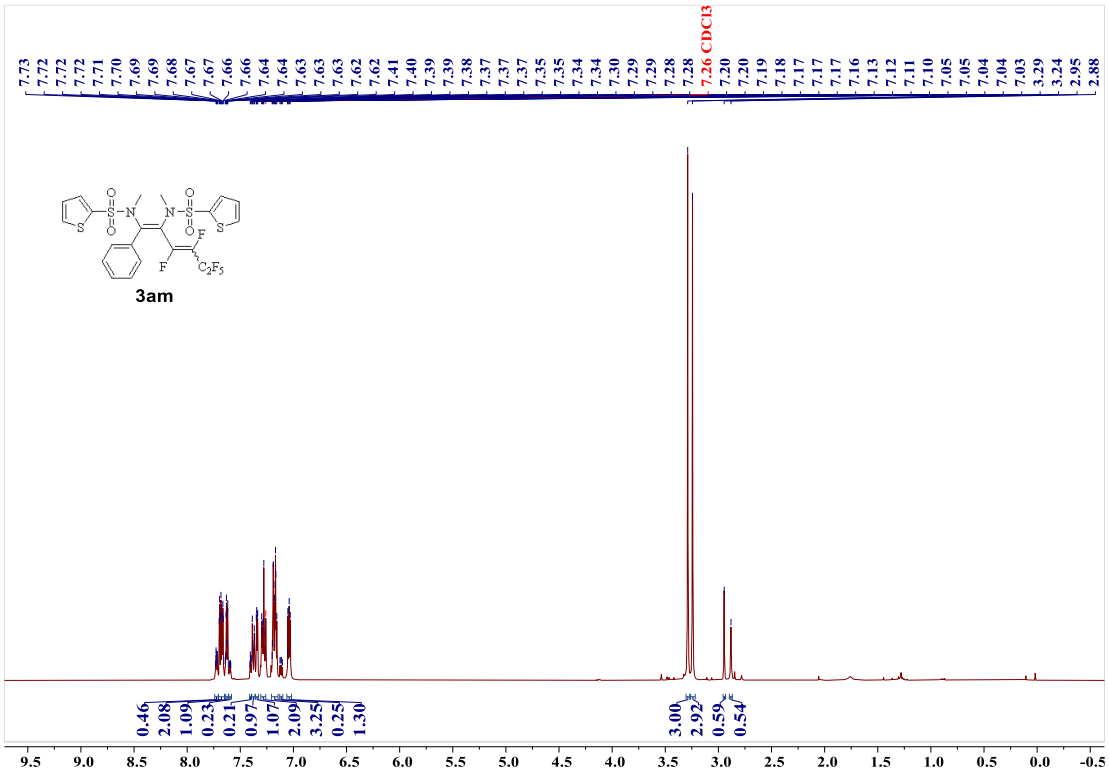
^{19}F NMR spectra of the product **3ak** (376 MHz, $CDCl_3$)



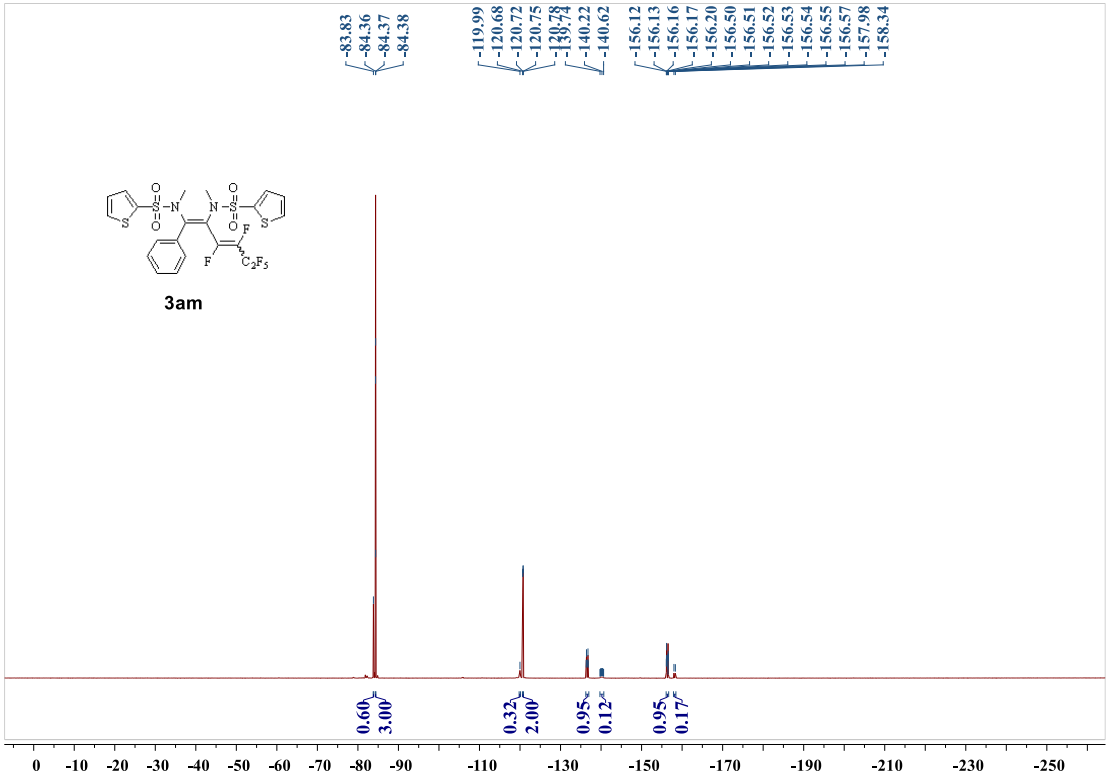
^{13}C NMR spectra of the product **3ak** (100 MHz, $CDCl_3$)



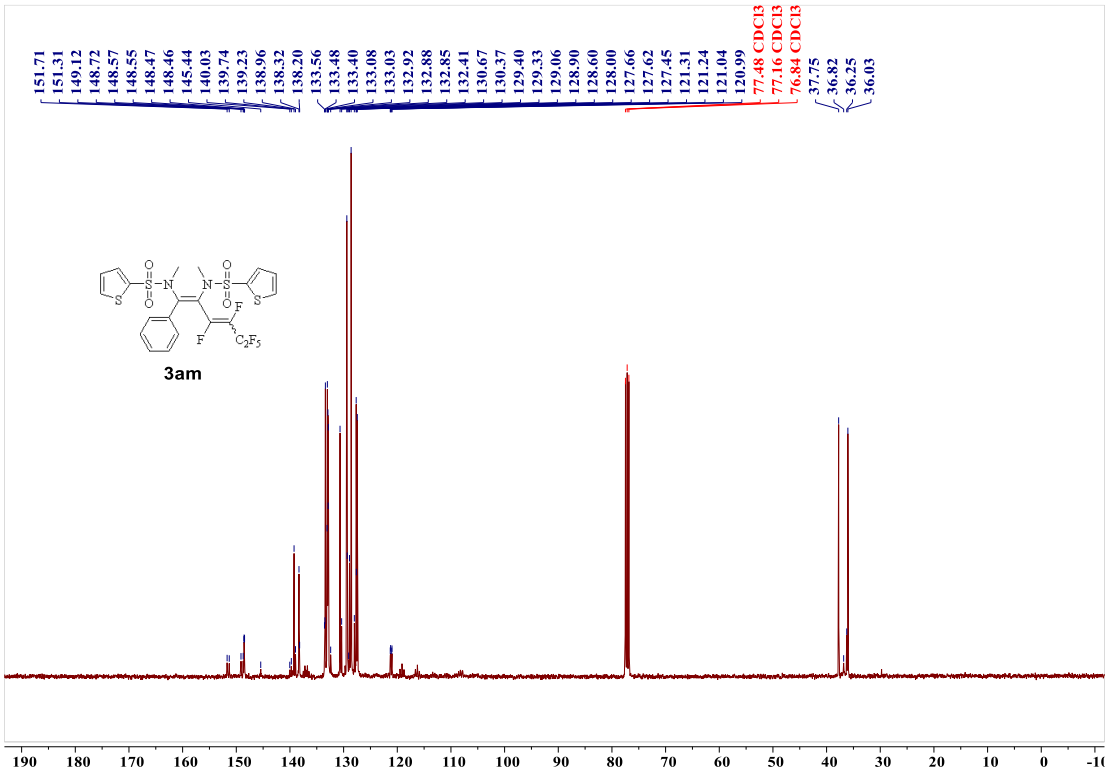
^{1}H NMR spectra of the product **3am** (400 MHz, $CDCl_3$)



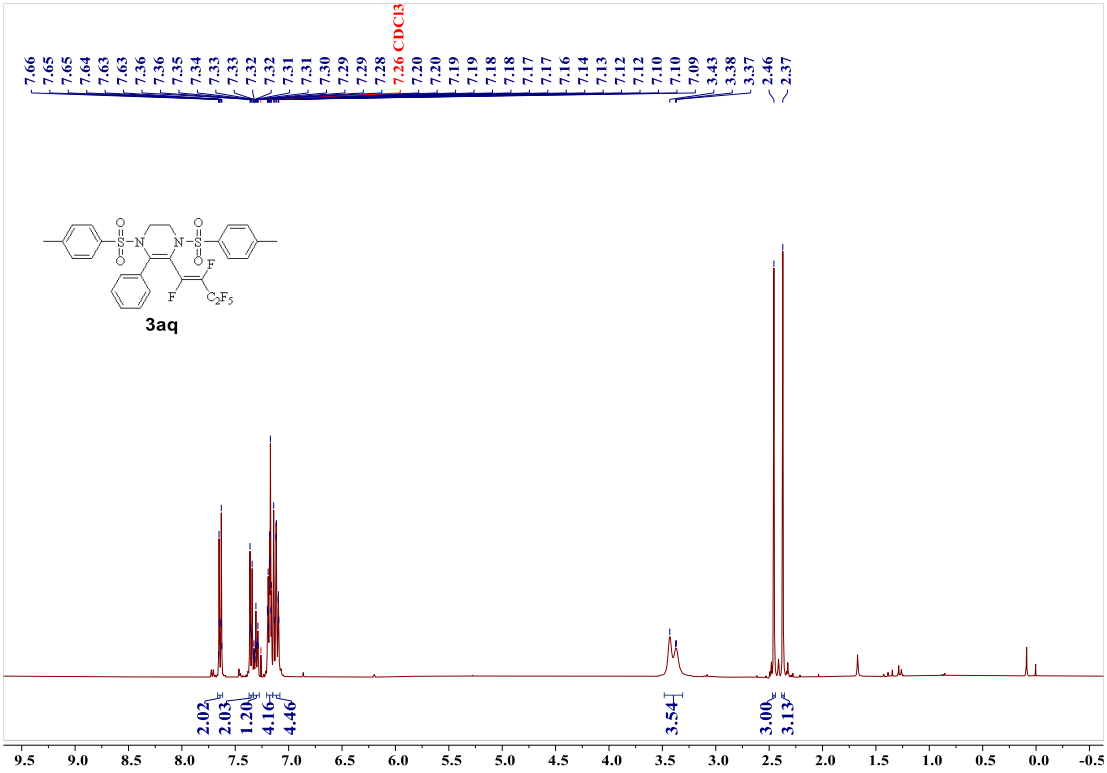
^{19}F NMR spectra of the product **3am** (376 MHz, $CDCl_3$)



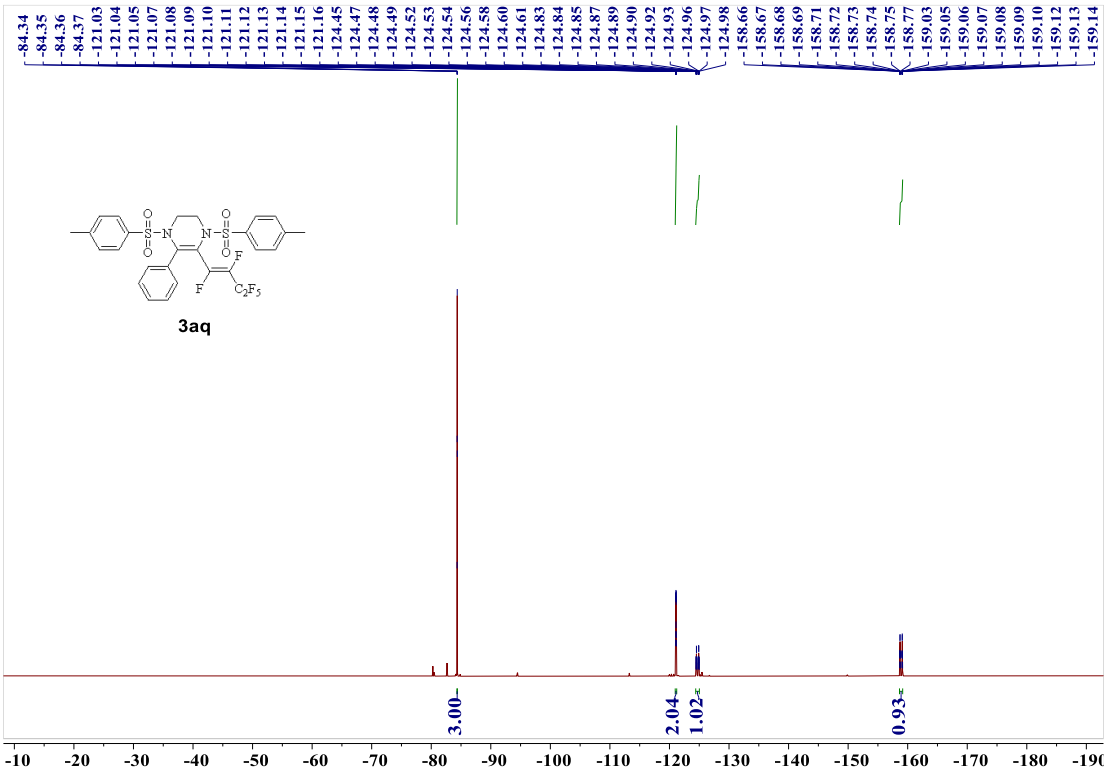
^{13}C NMR spectra of the product **3am** (100 MHz, $CDCl_3$)



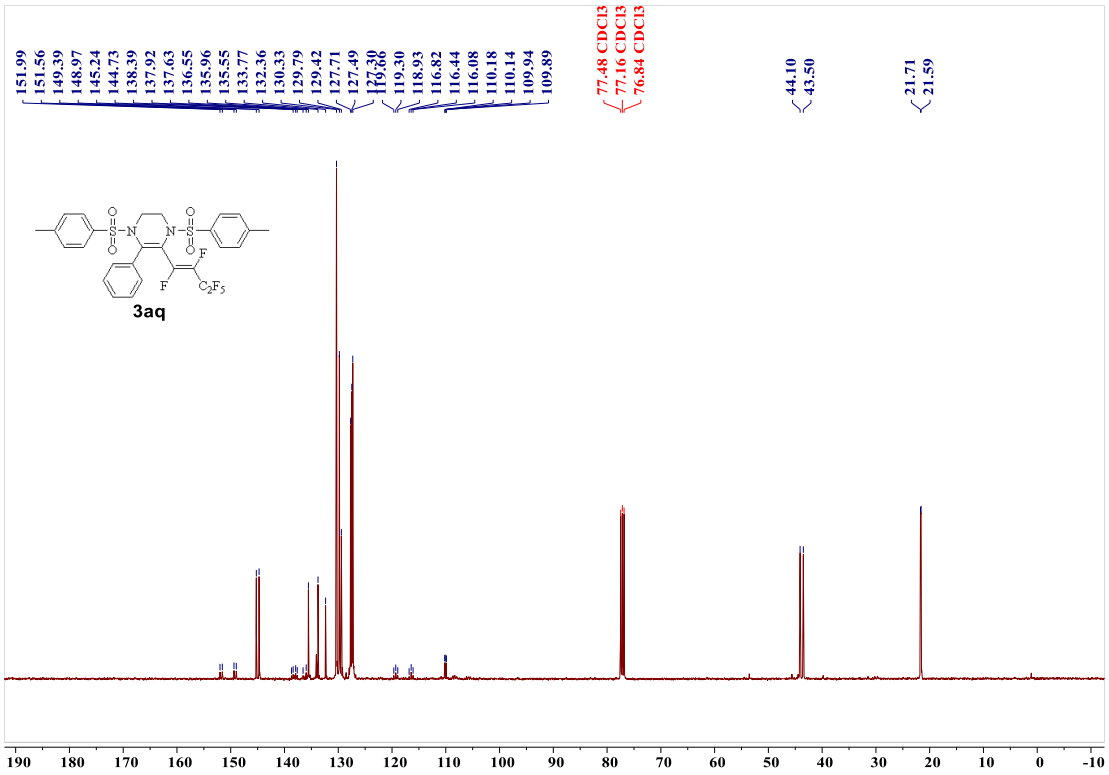
^{1}H NMR spectra of the product **3aq** (400 MHz, $CDCl_3$)



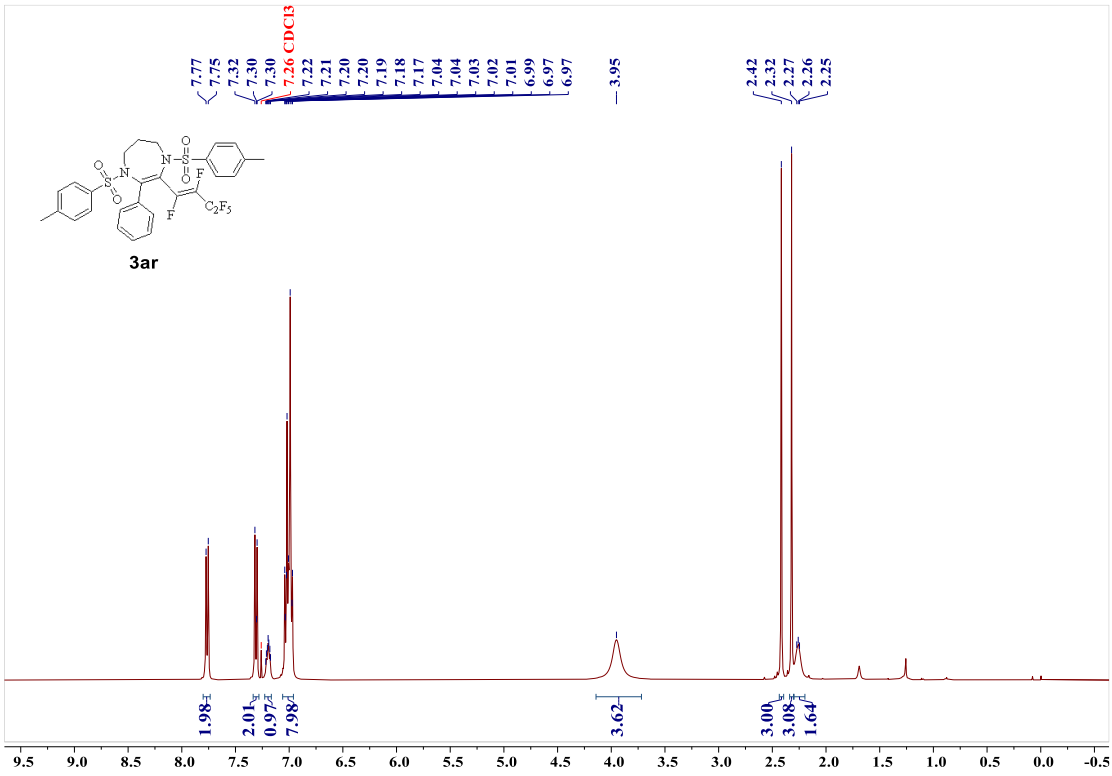
^{19}F NMR spectra of the product **3aq** (376 MHz, $CDCl_3$)



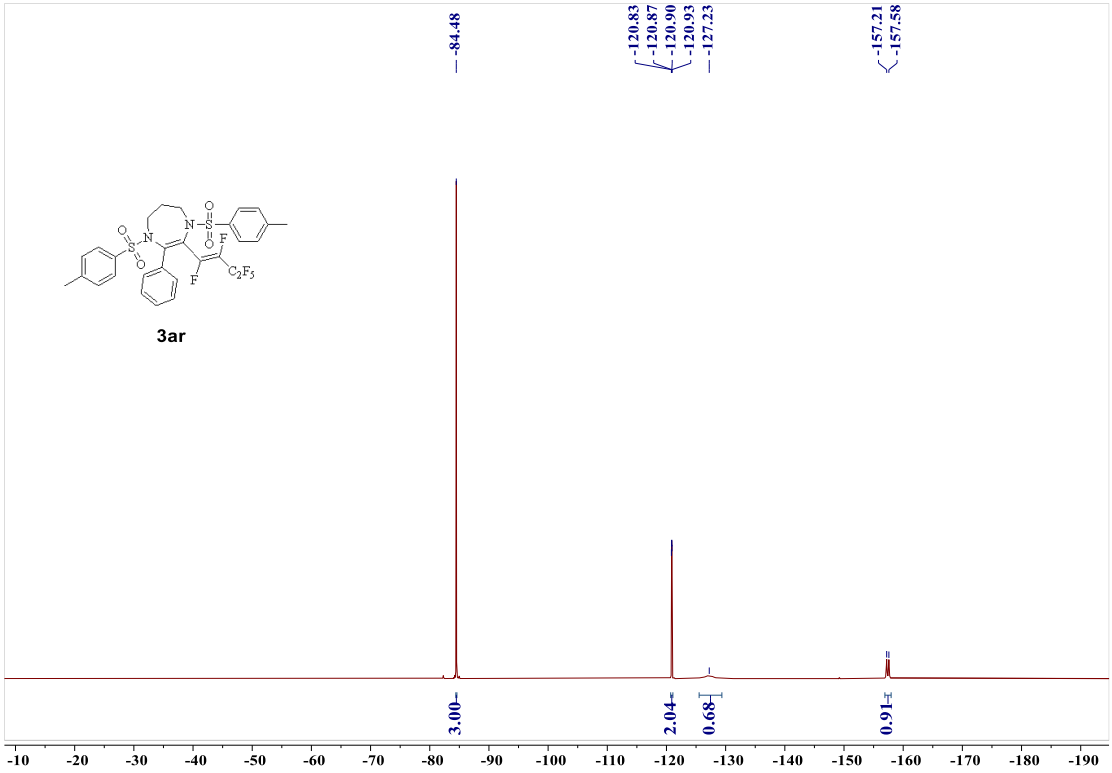
^{13}C NMR spectra of the product **3aq** (100 MHz, $CDCl_3$)



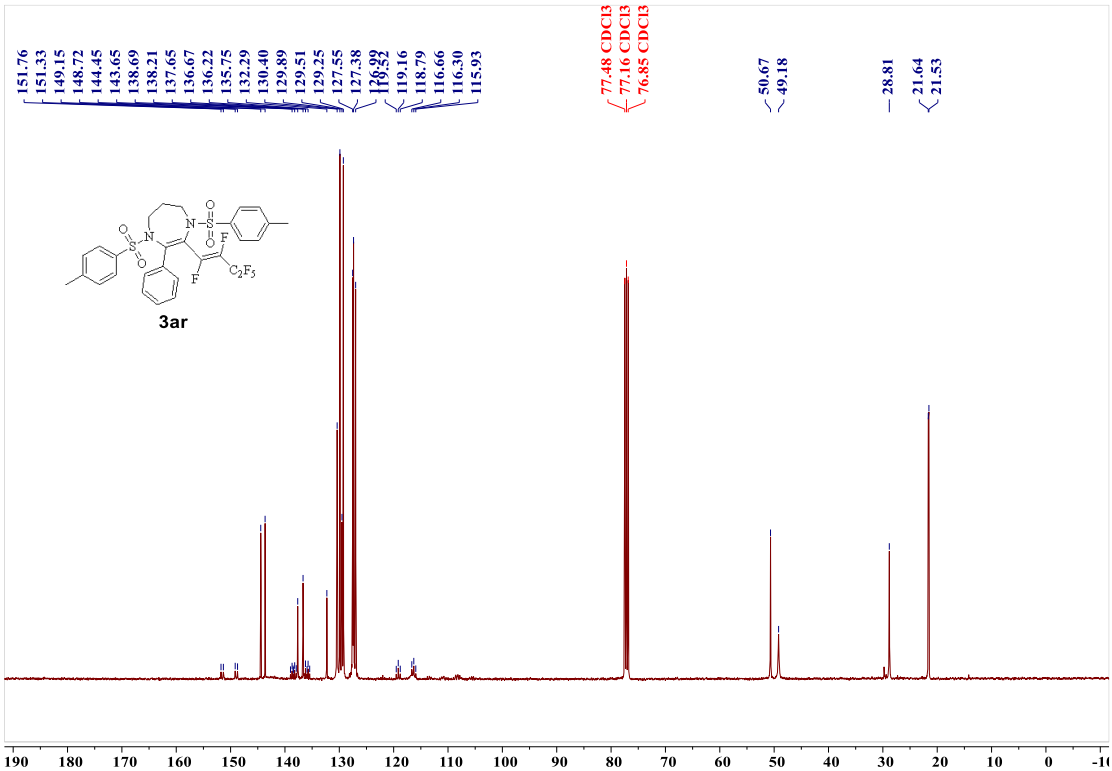
^{1}H NMR spectra of the product **3ar** (400 MHz, $CDCl_3$)



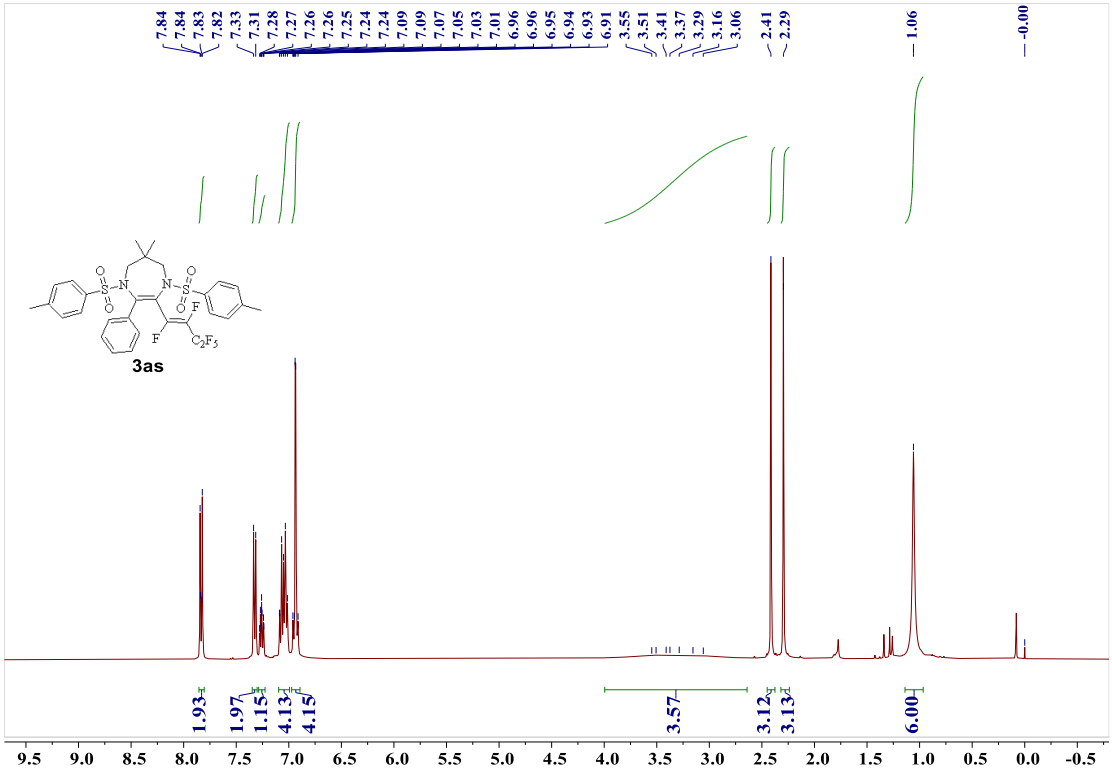
^{19}F NMR spectra of the product **3ar** (376 MHz, $CDCl_3$)



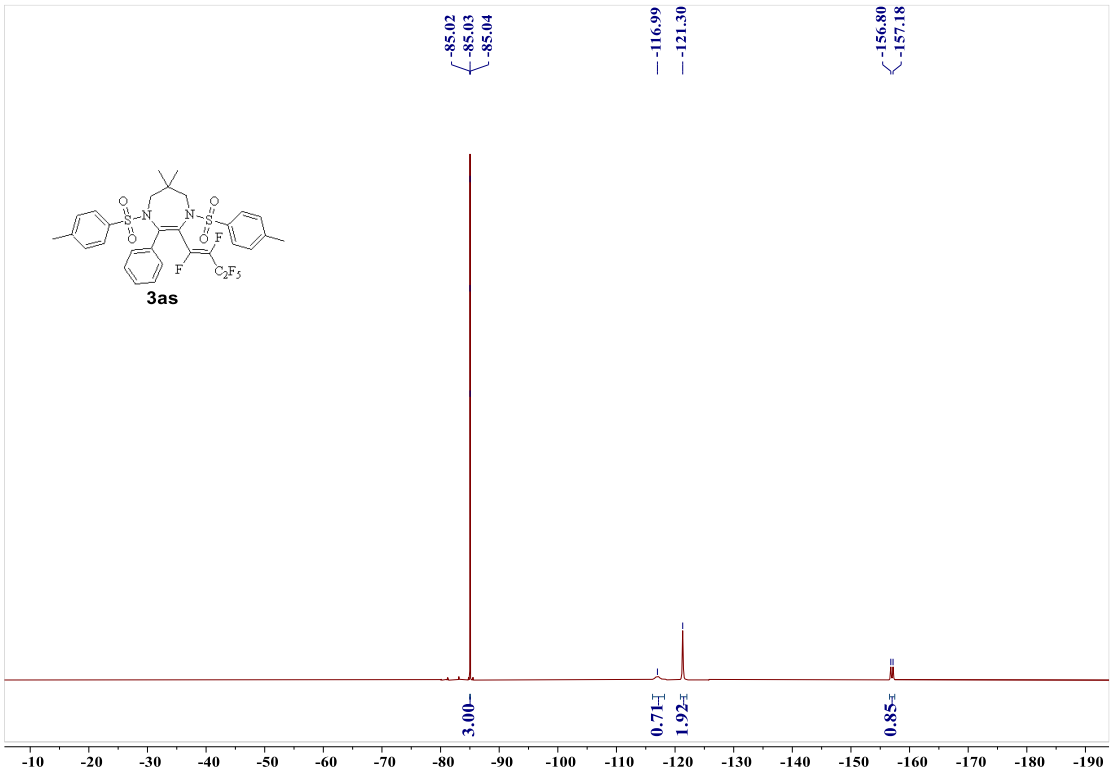
^{13}C NMR spectra of the product **3ar** (100 MHz, $CDCl_3$)



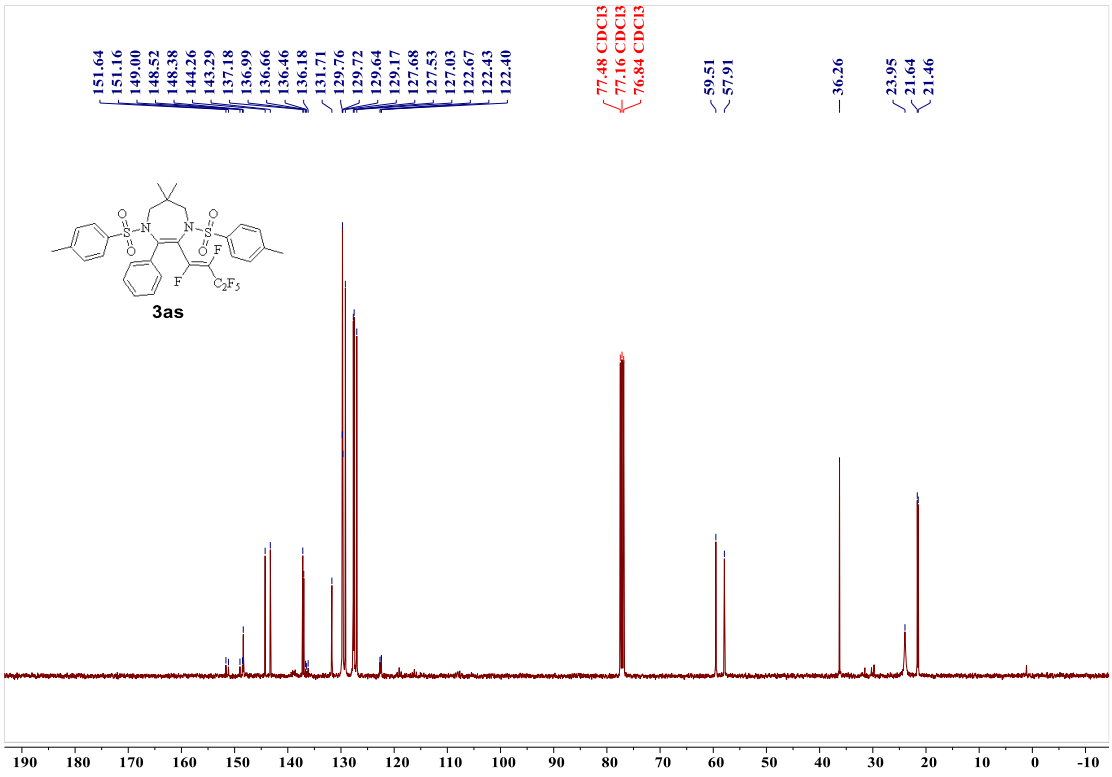
^{1}H NMR spectra of the product **3as** (400 MHz, $CDCl_3$)



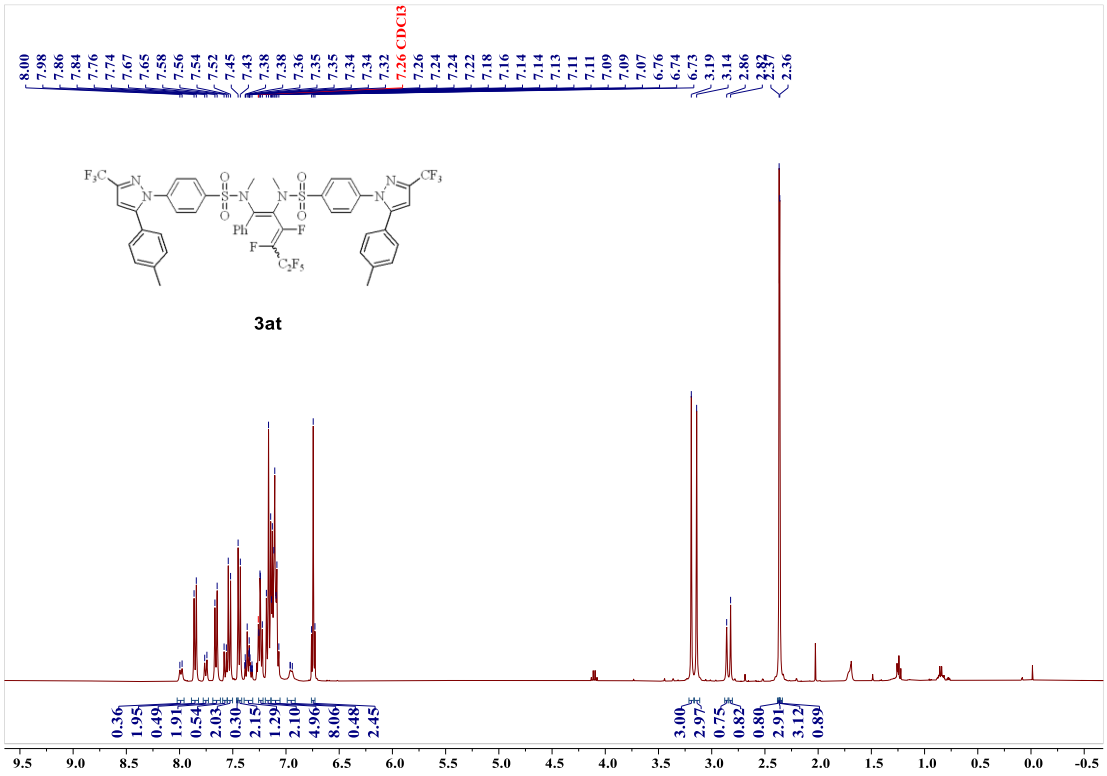
^{19}F NMR spectra of the product **3as** (376 MHz, $CDCl_3$)



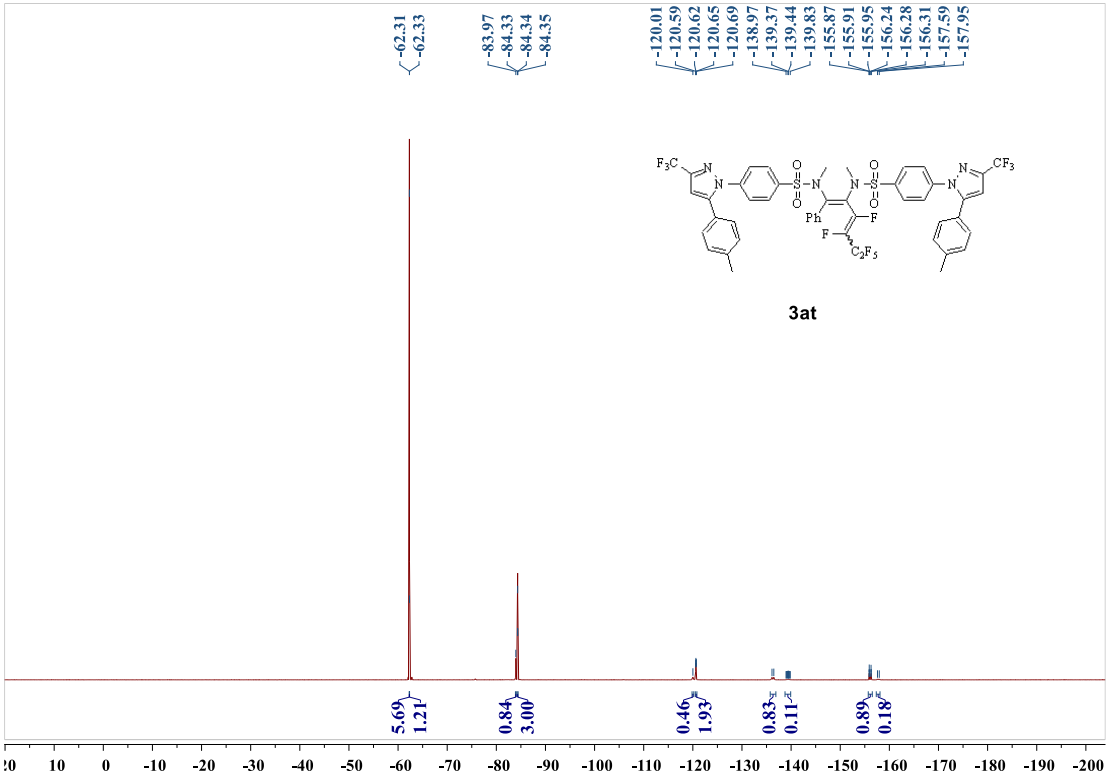
^{13}C NMR spectra of the product **3as** (100 MHz, $CDCl_3$)



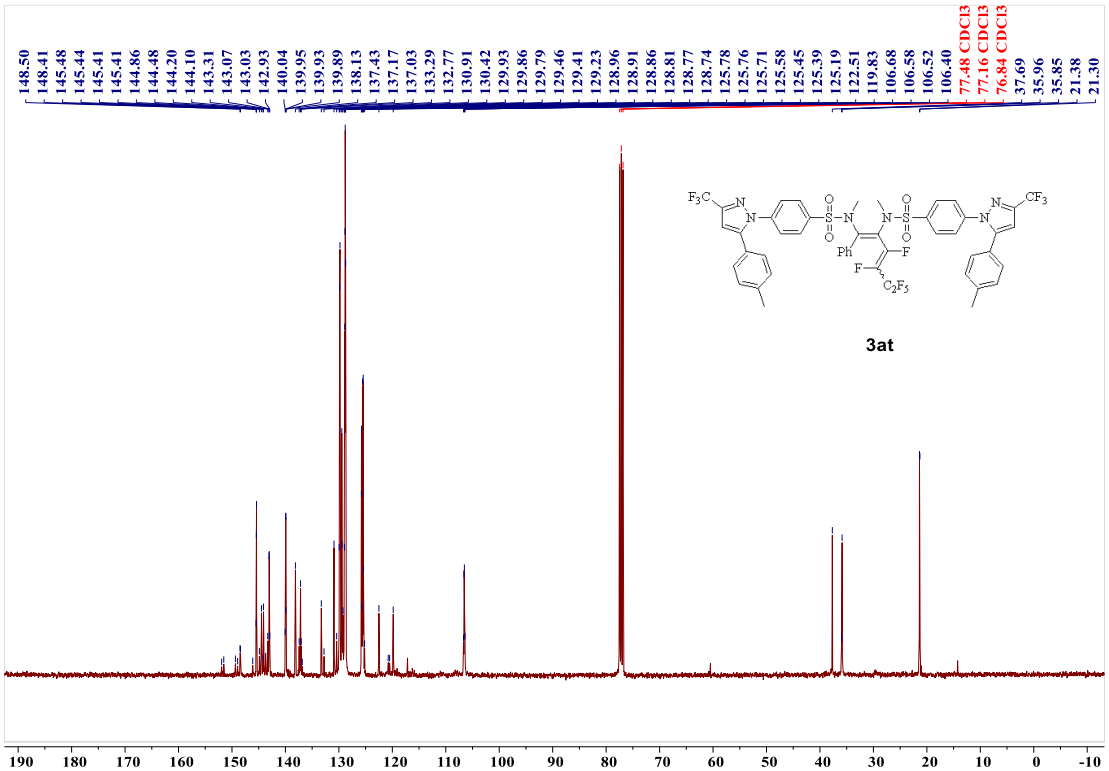
^{1}H NMR spectra of the product **3at** (400 MHz, $CDCl_3$)



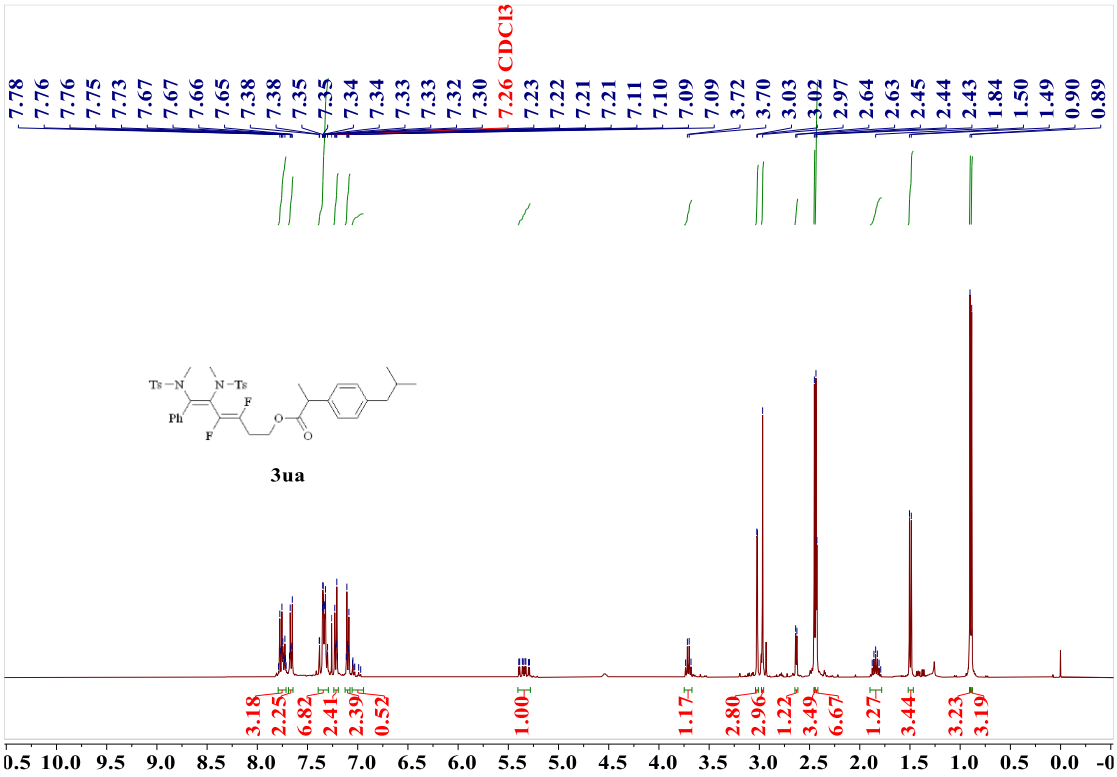
^{19}F NMR spectra of the product **3at** (376 MHz, $CDCl_3$)



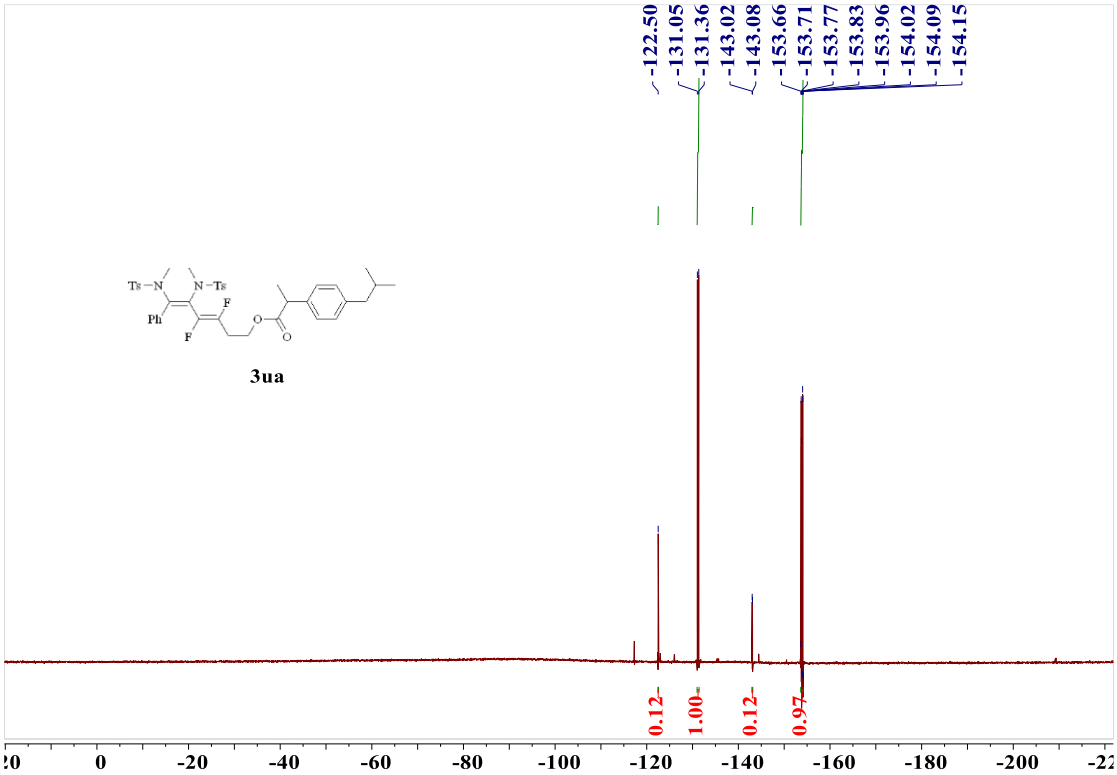
^{13}C NMR spectra of the product **3at** (100 MHz, $CDCl_3$)



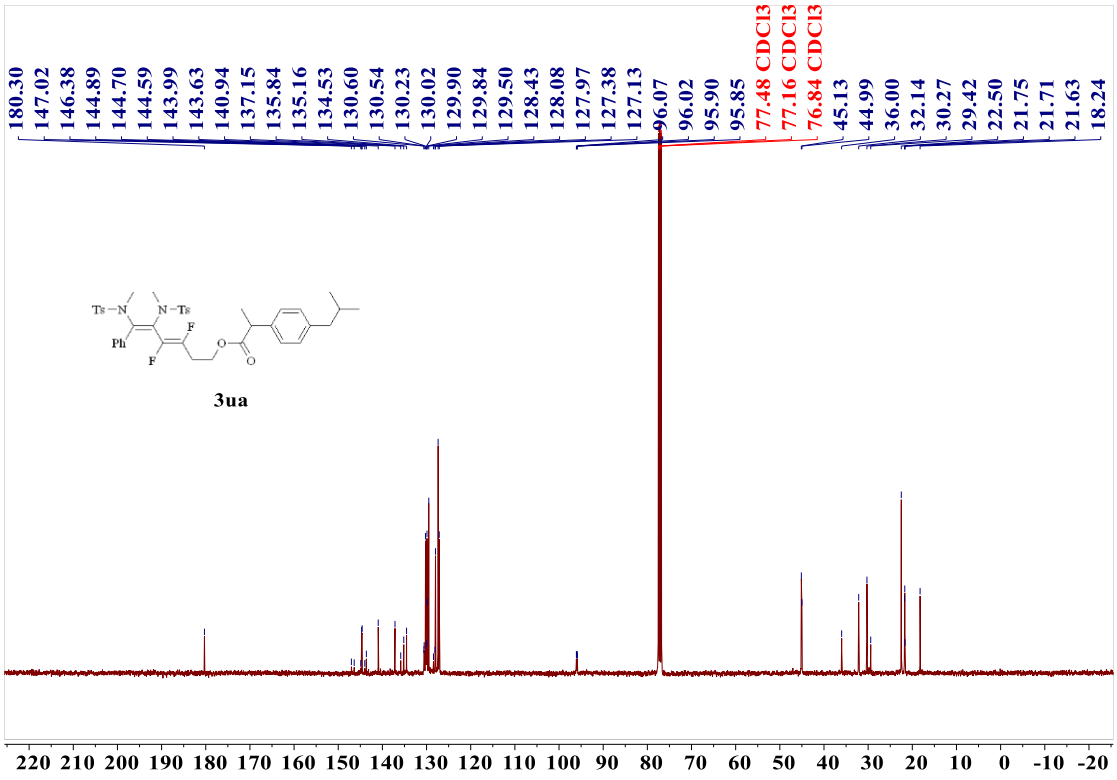
^{1}H NMR spectra of the product **3ua** (400 MHz, $CDCl_3$)



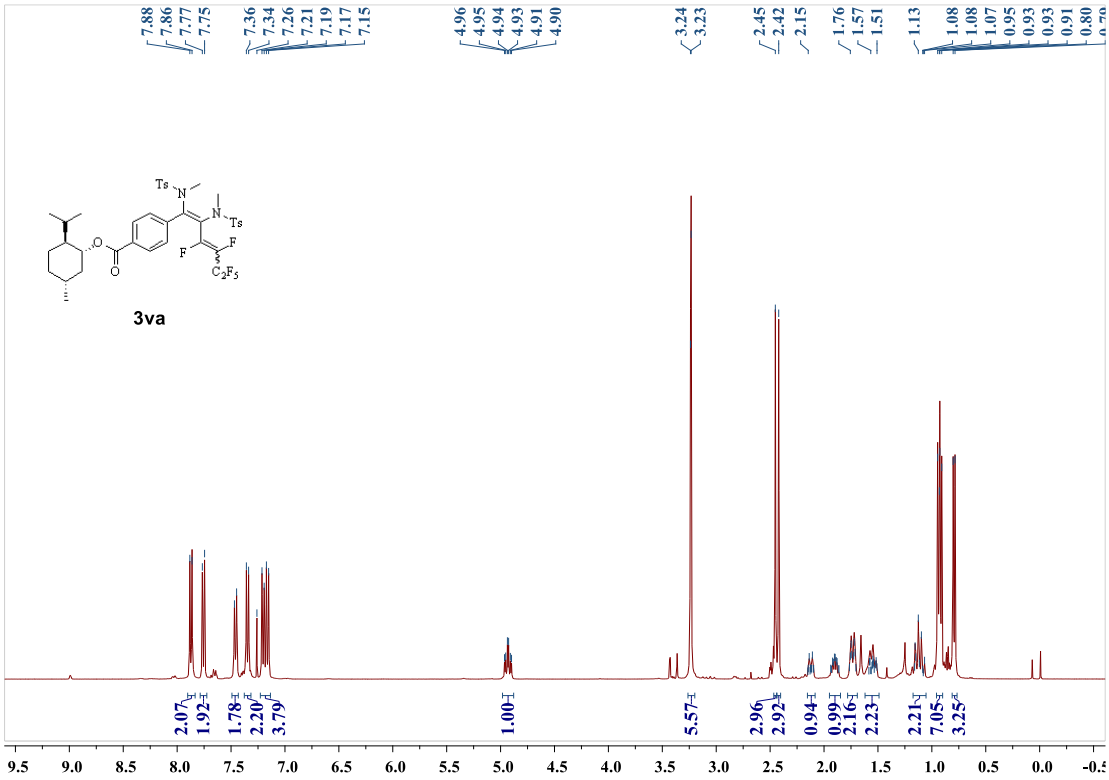
^{19}F NMR spectra of the product **3ua** (376 MHz, $CDCl_3$)



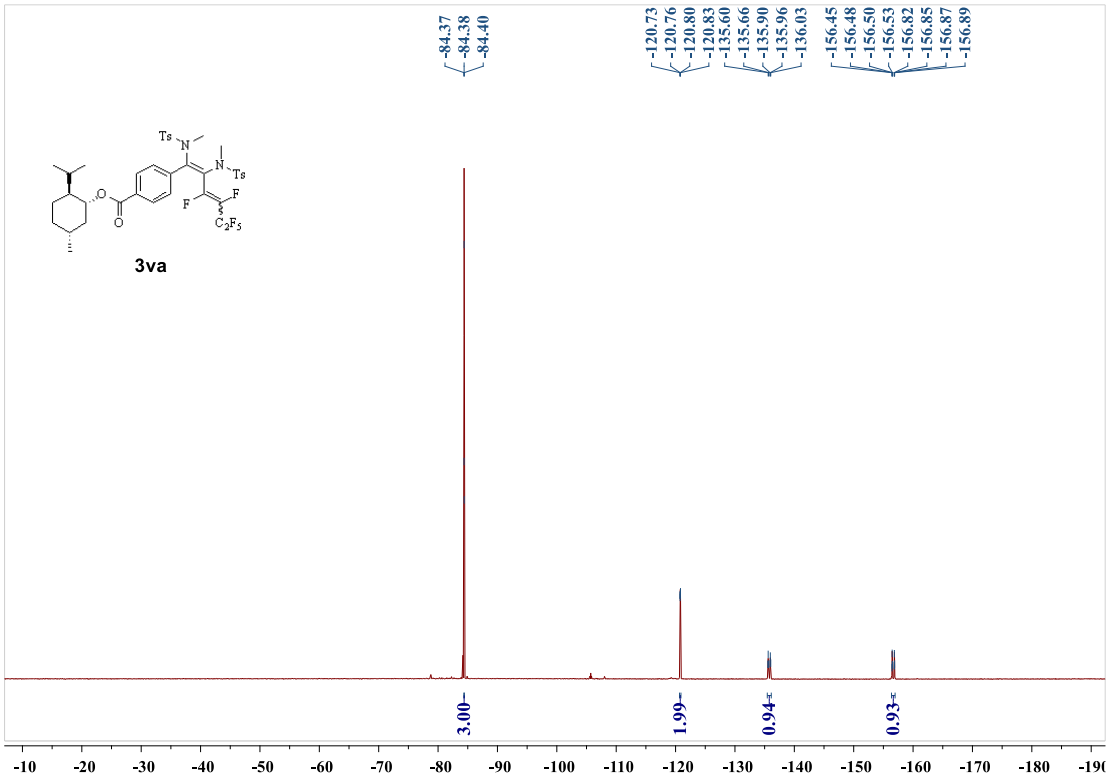
^{13}C NMR spectra of the product **3ua** (100 MHz, $CDCl_3$)



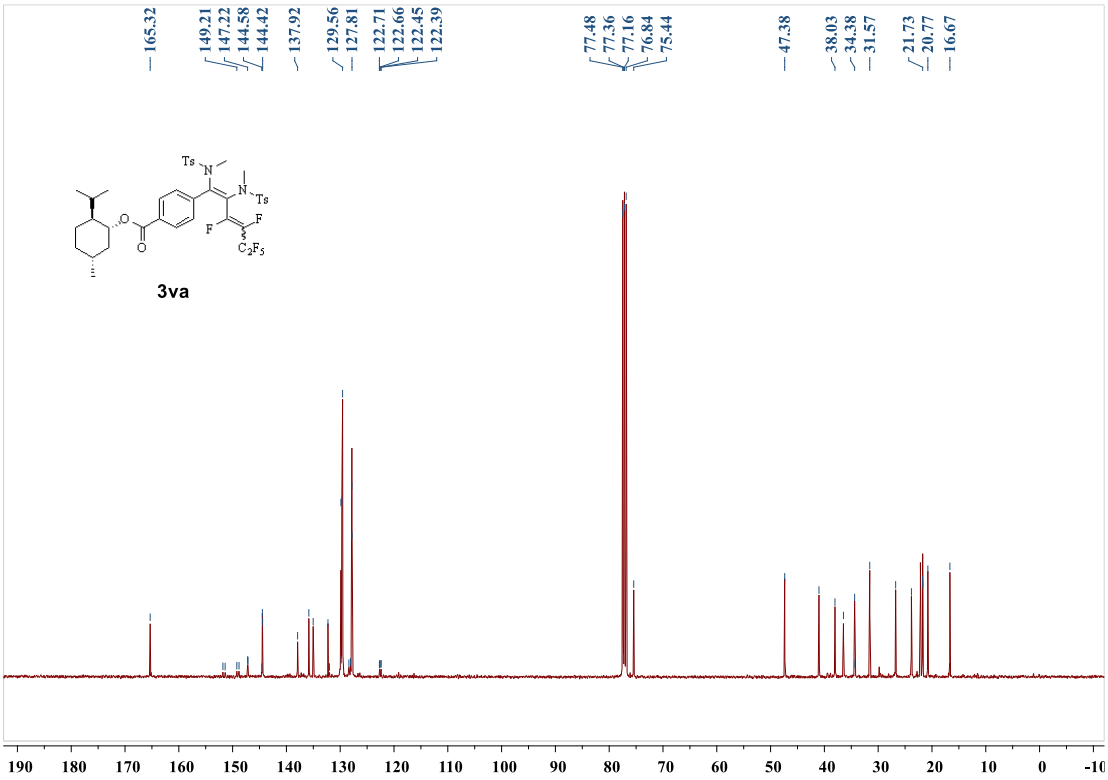
^{1}H NMR spectra of the product **3va** (400 MHz, $CDCl_3$)



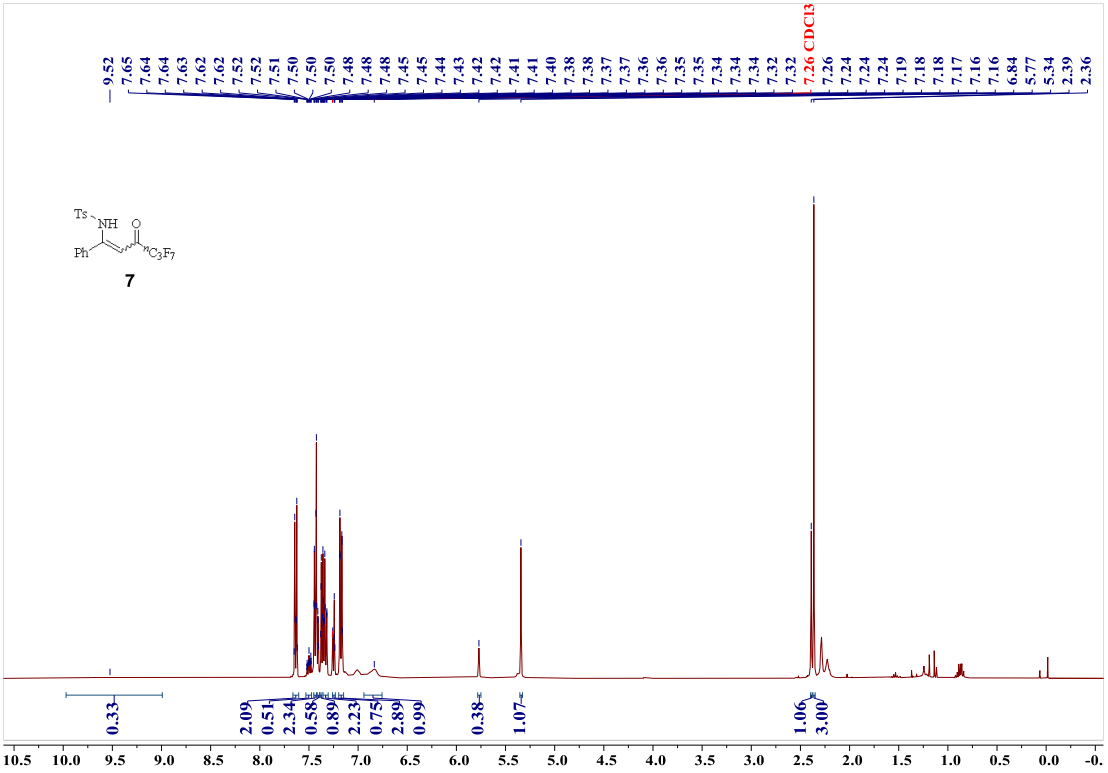
^{19}F NMR spectra of the product **3va** (376 MHz, $CDCl_3$)



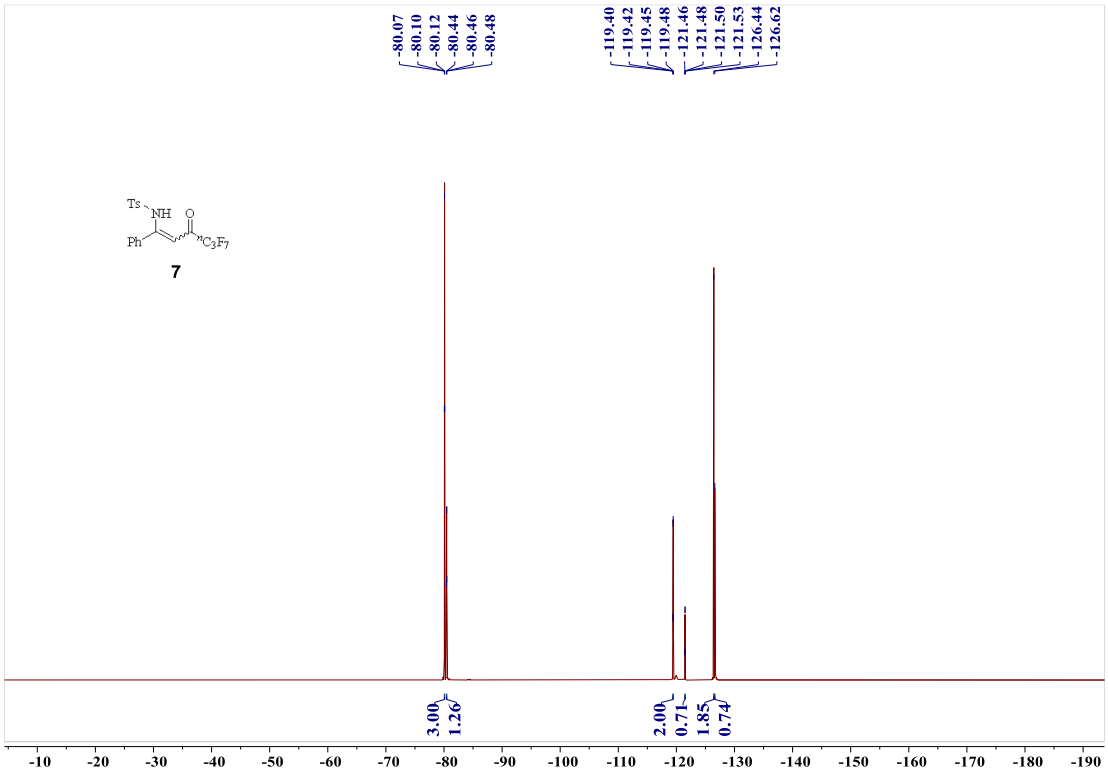
^{13}C NMR spectra of the product **3va** (100 MHz, $CDCl_3$)



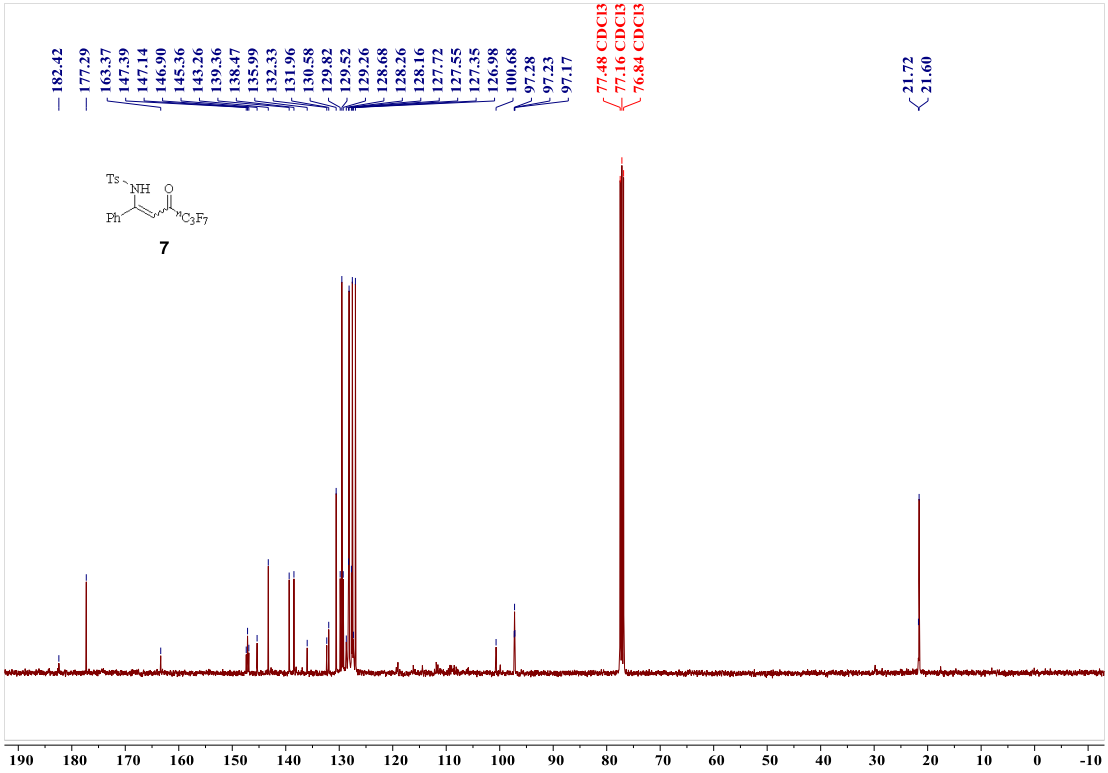
^{1}H NMR spectra of the product **7** (400 MHz, $CDCl_3$)



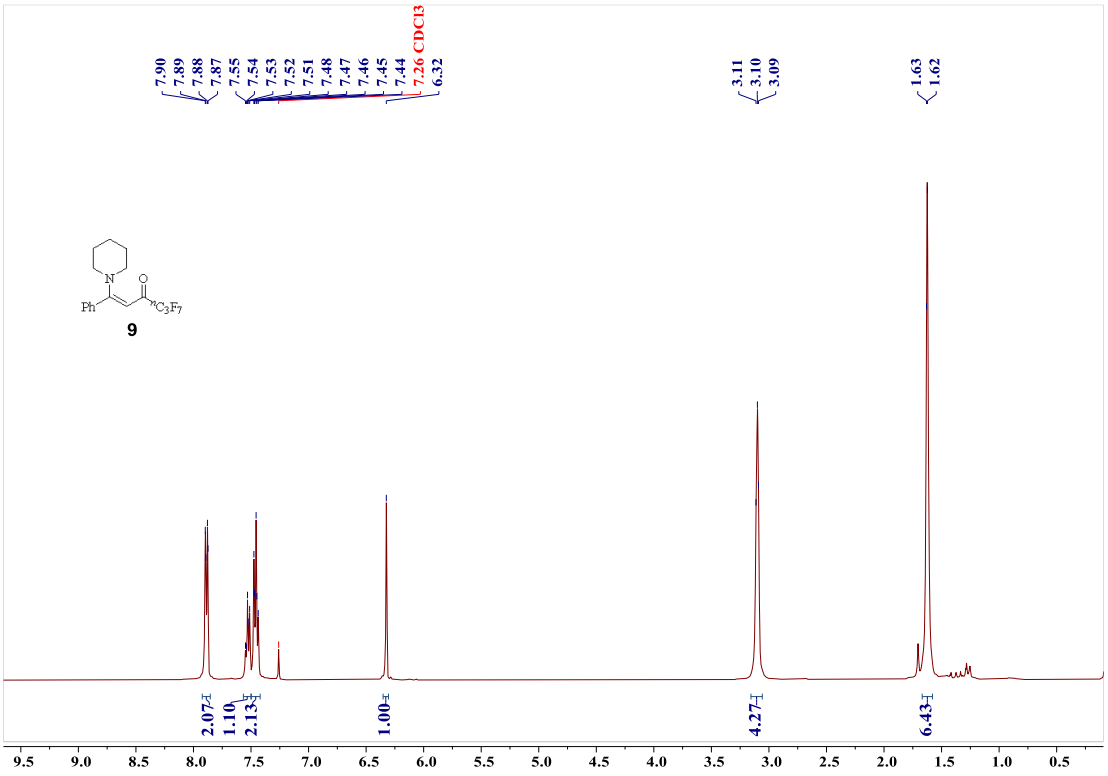
^{19}F NMR spectra of the product **7** (376 MHz, $CDCl_3$)



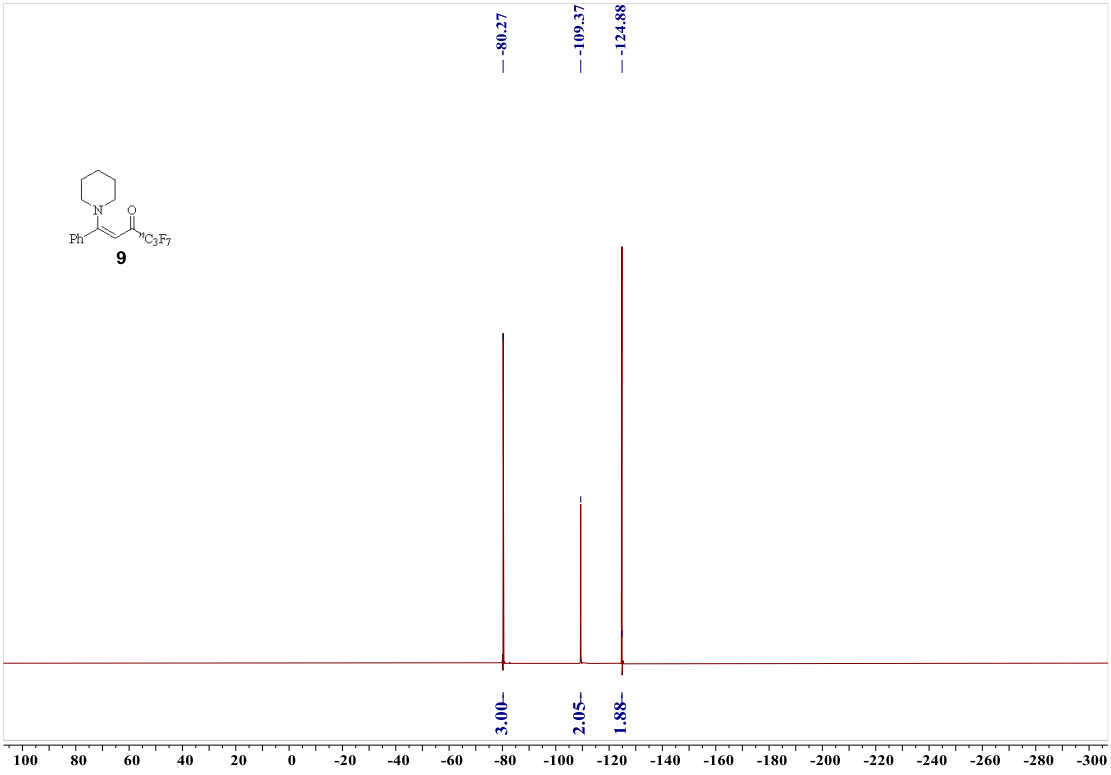
^{13}C NMR spectra of the product **7** (100 MHz, $CDCl_3$)



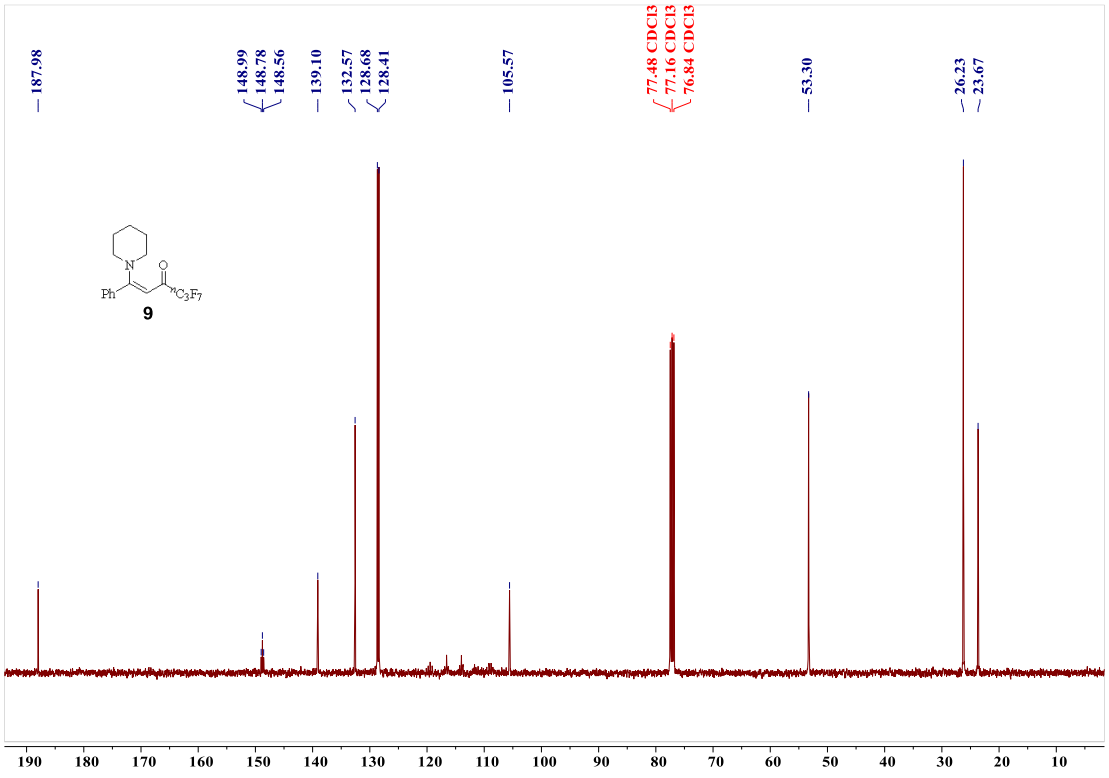
^{1}H NMR spectra of the product **9** (400 MHz, $CDCl_3$)



^{19}F NMR spectra of the product **9** (376 MHz, $CDCl_3$)



^{13}C NMR spectra of the product **9** (100 MHz, $CDCl_3$)


187.98
148.99
148.78
148.56
139.10
132.57
128.68
128.41
105.57
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
53.30
26.23
23.67
Ph
$^nC_3F_7$
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