Supporting Information

Four-Component Defluorinative Reaction of Allylic Fluorides, Amidines, and Cs_2CO_3 under Transition-Metal-Free Conditions

Yu-Lan Chen,[a] Li-Wen Sun,[a] Jia-Wei Chen,[a] Ming-Quan Zhu,[a] Mengtao Ma,[b] Zhi-Liang Shen,*[a] Xue-Qiang Chu*[a]

[a] *Technical Institute of Fluorochemistry (TIF), Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, China.*

[b] *Department of Chemistry and Materials Science, College of Science, Nanjing Forestry University, Nanjing 210037, China.*

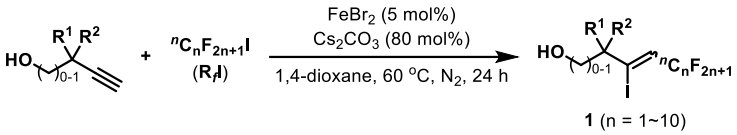
Table of Contents

General information	Page S2
General procedure for the synthesis of polyfluoroalkylated alkenes **1**	Page S2
General procedure for the four-component defluorinative cyclization	Page S2
General procedure for the scale-up synthesis of product **3a**	Page S3
Further transformation of products **3aa**	Page S3
Mechanistic studies	Page S4
Characterization data for products	Page S5
Reference	Page S19
The X-ray crystal structure of product **3ac**	Page S19
^{1}H, ^{19}F, and ^{13}C NMR spectra of products	Page S21

General information

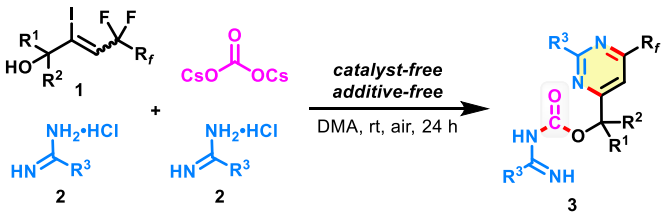
Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out under N_2 atmosphere using undistilled solvent. Melting points were recorded on an electrothermal digital melting point apparatus. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Avance or Joel 400 MHz spectrometers. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. High resolution mass spectra (HRMS) were obtained using a commercial apparatus (ESI source). 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 polyfluoroalkylated alkenes 1[1]



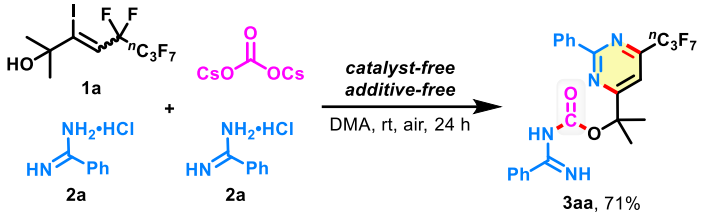
According to Hu's reported method, a solution of $FeBr_2$ (53.9 mg, 0.25 mmol), Cs_2CO_3 (1303 mg, 4 mmol), alkyne (5 mmol), and perfluoroalkyl iodide (7.5 mmol) in anhydrous 1,4-dioxane (20 mL) was stirred at 60 °C under N_2 for 24 h. The reaction was then quenched by saturated NH_4Cl solution (50 mL) and extracted with EtOAc (50 mL x 3). The organic layer was washed with saturated brine twice, 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 (100/1~80/1) as eluent to afford the pure product **1**.

General procedure for the four-component defluorinative cyclization



A solution of polyfluoroalkylated alkene **1** (0.3 mmol), amidine **2** (0.75 mmol), and Cs_2CO_3 (342.1 mg, 1.05 mmol) in DMA (2 mL) was stirred at room temperature under air for 24 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, 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 products **3**.

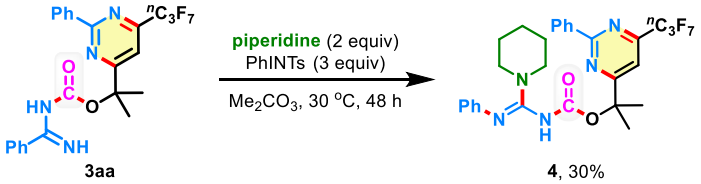
General procedure for the scale-up synthesis of product 3aa



A solution of 5,5,6,6,7,7,8,8,8-nonafluoro-3-iodo-2-methyloct-3-en-2-ol (2150 mg, 5 mmol, **1a**), benzamidine hydrochloride (1958 mg, 12.5 mmol, **2a**), and Cs_2CO_3 (5702 mg, 17.5 mmol) in DMA (34 mL) was stirred at room temperature under air for 24 h. The reaction was then quenched by saturated NH_4Cl solution (50 mL) and extracted with EtOAc (50 mL x 3). The organic layer was washed with saturated brine twice, 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) as eluent to afford the pure product **3aa** (1888 mg, 71% yield).

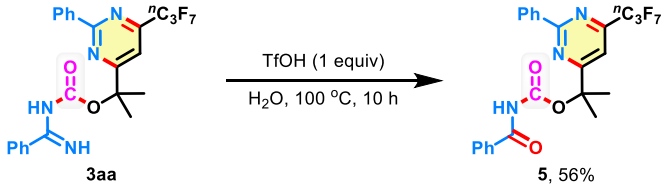
Further transformation of product 3aa

a) The reaction of product 3aa with piperidine[2]



A solution of 2-(6-(perfluoropropyl)-2-phenylpyrimidin-4-yl)propan-2-yl (imino(phenyl)methyl)carbamate (158.5 mg, 0.3 mmol, **3aa**), piperidine (51.1 mg, 0.6 mmol), and PhINTs (337.7 mg, 0.9 mmol) in Me_2CO_3 (2 mL) was stirred at 30 °C under air for 48 h. The reaction solvent was 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) as eluent to afford the pure product **4** (55.2 mg, 30% yield).

b) The reaction of product 3aa with TfOH



A solution of 2-(6-(perfluoropropyl)-2-phenylpyrimidin-4-yl)propan-2-yl (imino(phenyl)methyl)carbamate (158.5 mg, 0.3 mmol, **3aa**) and TfOH (45 mg, 0.3 mmol) in water (2 mL) was stirred at 100 °C under air for 10 h. The reaction solvent was 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) as eluent to afford the pure product **5** (89.1 mg, 56% yield).

Mechanistic studies

a) The reaction of 5,5,6,6,7,7,8,8,8-nonafluoro-3-iodooct-3-en-1-ol (1n) with amidine 2a

A solution of 5,5,6,6,7,7,8,8,8-nonafluoro-3-iodooct-3-en-1-ol (124.8 mg, 0.3 mmol, **1n**), benzamidine hydrochloride (117.5 mg, 0.75 mmol, **2a**), Cs_2CO_3 (342.1 mg, 1.05 mmol) in DMA (2 mL) was stirred at room temperature under air for 24 h. No desired product **3na** was obtained.

This result suggested that the length of the OH-containing chain in substrate has a dramatic effect on the transformation.

b) The reaction of 2-methylbut-3-yn-2-ol (1o) with amidine 2a

A solution of 2-methylbut-3-yn-2-ol (25.2 mg, 0.3 mmol, **1o**), benzamidine hydrochloride (117.5 mg, 0.75 mmol, **2a**), and Cs_2CO_3 (324.1 mg, 1.05 mmol) in DMA (2 mL) was stirred at room temperature under air for 24 h. No desired product **3oa** was obtained.

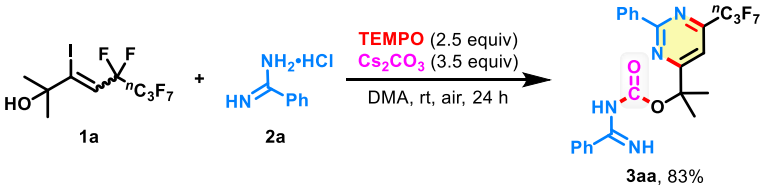
This result suggested the unique reactivity of the OH-containing polyfluoroalkylated alkenes for the success of the reaction.

c) The reaction of pre-formed pyrimidine 1p with amidine 2a

A solution of 2-(2-(4-bromophenyl)-6-(perfluoropropyl)pyrimidin-4-yl)propan-2-ol (46.1 mg, 0.1 mmol, **1p**), benzamidine hydrochloride (23.5 mg, 0.15 mmol, **2a**), and Cs_2CO_3 (114.0 mg, 0.35 mmol) in DMA (2 mL) was stirred at room temperature under air for 24 h. No desired product **3pa** was obtained.

This result suggested that the compound 1p might not be a possible intermediate.

d) Radical trapping experiment

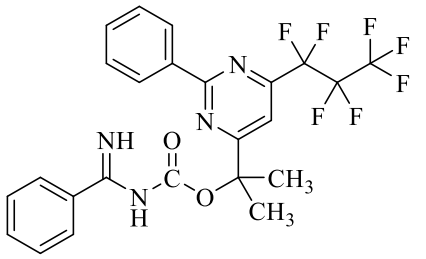


A solution of 5,5,6,6,7,7,8,8,8-nonafluoro-3-iodo-2-methyloct-3-en-2-ol (129 mg, 0.3 mmol, **1a**), benzamidine hydrochloride (117.5 mg, 0.75 mmol, **2a**), Cs_2CO_3 (342.1 mg, 1.05 mmol), and

2,2,6,6-tetramethylpiperidinooxy (TEMPO, 117.2 mg, 0.75 mmol) in DMA (2 mL) was stirred at room temperature under air for 24 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, 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) as eluent to afford the pure product **3aa** (132 mg, 83% yield).

This result suggested that four-component defluorinative cyclization might not proceed through a radical pathway.[3]

Characterization data for products



2-(6-(Perfluoropropyl)-2-phenylpyrimidin-4-yl)propan-2-yl (imino(phenyl)methyl)carbamate (3aa):

Yield = 89% (141.0 mg). White solid. M.p. 120.0–121.9 °C.

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

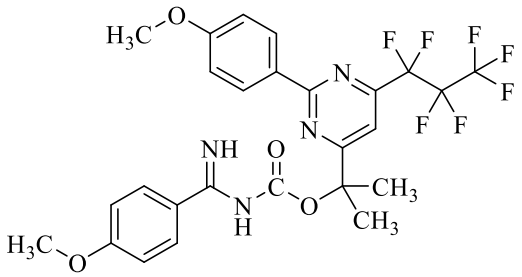
IR (KBr): ν = 3374, 1720, 1616, 1276, 1229, 1212, 1139, 1120, 739, 698 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.40 (brs, 1H), 8.57-8.53 (m, 2H), 7.85-7.82 (m, 2H), 7.66 (s, 1H), 7.56-7.48 (m, 4H), 7.46-7.40 (m, 2H), 6.44 (brs, 1H), 1.92 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.03 (s, 3F), -116.57 (s, 2F), -126.31 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.4, 168.7, 164.2, 163.3, 155.8 (t, $J_{C\text{-}F}$ = 26.3 Hz), 136.3, 134.1, 132.3, 131.4, 128.6, 128.6, 128.5, 127.1, 111.6 (t, $J_{C\text{-}F}$ = 4.7 Hz), 81.3, 27.1 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{24}H_{20}F_7N_4O_2$ $[M+H]^+$ 529.1469, found: 529.1470.



2-(2-(4-Methoxyphenyl)-6-(perfluoropropyl)pyrimidin-4-yl)propan-2-yl (imino(4-methoxyphenyl)methyl)carbamate (3ab):

Yield = 73% (129.4 mg). Yellow solid. M.p. 271–271.3 °C.

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

IR (KBr): ν = 3389, 1662, 1608, 1554, 1499, 1390, 1216, 1139, 848, 745 cm^{-1}.

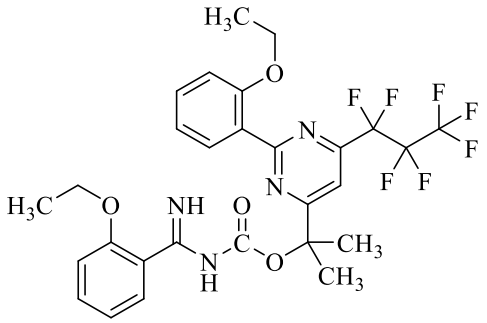
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.38 (brs, 1H), 8.49 (d, J = 8.9 Hz, 2H), 7.75 (d, J = 8.9 Hz, 2H), 7.56 (s, 1H), 6.97 (d, J = 8.9 Hz, 2H), 6.84-6.78 (m, 3H), 3.85 (s, 3H), 3.78 (s, 3H), 1.86 (s,

6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.06 (t, J = 8.9 Hz, 3F), -116.67 (q, J = 8.9 Hz, 2F), -126.39 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.3, 167.9, 163.9, 163.3, 162.9, 162.3, 155.6 (t, $J_{C\text{-}F}$ = 26.2 Hz), 130.4, 129.1, 129.1, 126.0, 113.8, 113.8, 110.7, 81.1, 55.3, 55.3, 27.1 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{26}H_{24}F_7N_4O_4$ $[M+H]^+$ 589.1680, found: 589.1674.



2-(2-(2-Ethoxyphenyl)-6-(perfluoropropyl)pyrimidin-4-yl)propan-2-yl ((2-ethoxyphenyl)(imino)methyl)carbamate (3ac):

Yield = 52% (95.5 mg). Yellow solid. M.p. 111.6–112.3 °C.

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

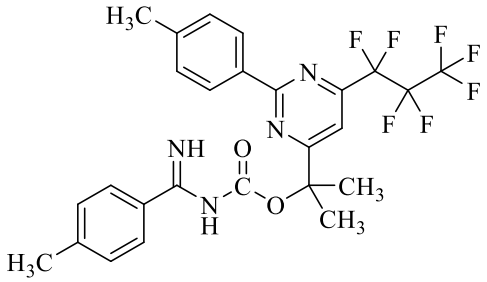
IR (KBr): ν = 3499, 1654, 1618, 1512, 1283, 1233, 1210, 1151, 1139, 965, 752 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.80 (brs, 1H), 8.54 (brs, 1H), 8.27 (d, J = 9.9 Hz, 1H), 7.91 (d, J = 9.6 Hz, 1H), 7.69 (s, 1H), 7.45-7.36 (m, 2H), 7.08-6.89 (m, 4H), 4.37-3.83 (m, 4H), 1.90 (s, 6H), 1.44 (t, J = 7.0 Hz, 3H), 1.36 (t, J = 6.9 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.12 (t, J = 8.9 Hz, 3F), -116.59 (q, J = 8.9 Hz, 2F), -126.21 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.3, 167.2, 165.2, 163.3, 158.2, 157.8, 155.0 (t, $J_{C\text{-}F}$ = 26.0 Hz), 133.7, 132.3, 131.9, 131.5, 127.2, 121.1, 120.4, 120.3, 113.4, 112.4, 111.3, 81.1, 64.8, 64.3, 27.3, 14.6, 14.5 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{28}H_{28}F_7N_4O_4$ $[M+H]^+$ 617.1993, found: 617.1995.



2-(6-(Perfluoropropyl)-2-(*p*-tolyl)pyrimidin-4-yl)propan-2-yl (imino(p-tolyl)methyl)carbamate (3ad):

Yield = 74% (122.8 mg). White solid. M.p. 147.0–147.9 °C.

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

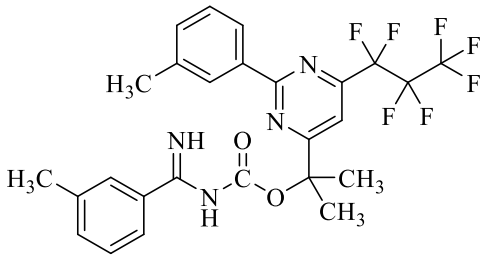
IR (KBr): ν = 3451, 3298, 1659, 1613, 1493, 1390, 1270, 1210, 1139, 1120, 742 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.39 (brs, 1H), 8.45-8.41 (m, 2H), 7.76-7.72 (m, 2H), 7.62 (s, 1H), 7.29 (d, J = 7.7 Hz, 2H), 7.23 (d, J = 7.8 Hz, 2H), 6.40 (brs, 1H), 2.43 (s, 3H), 2.40 (s, 3H), 1.90 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.04 (t, J = 8.9 Hz, 3F), -116.62 (q, J = 8.9 Hz, 2F), -126.36 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.3, 168.6, 164.3, 163.4, 155.7 (t, $J_{C\text{-}F}$ = 26.2 Hz), 142.9, 141.8, 133.7, 131.6, 129.3, 129.3, 128.6, 127.1, 111.2, 81.2, 27.1, 21.4, 21.3 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{26}H_{24}F_7N_4O_2$ $[M+H]^+$ 557.1782, found: 557.1785.



2-(6-(Perfluoropropyl)-2-(*m*-tolyl)pyrimidin-4-yl)propan-2-yl (imino(*m*-tolyl)methyl)carbamate (3ae):

Yield = 81% (134.8 mg). Yellow solid. M.p. 80.2–81.9 ºC.

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

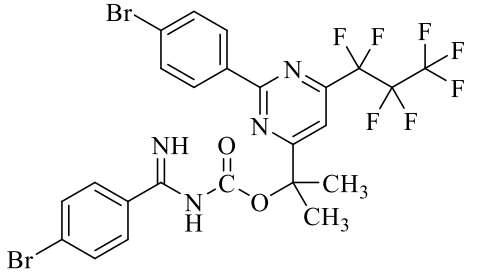
IR (KBr): ν = 3456, 3310, 1660, 1578, 1511, 1375, 1274, 1234, 1119, 789, 739 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.40 (brs, 1H), 8.37-8.33 (m, 2H), 7.70 (s, 1H), 7.64 (s, 1H), 7.60-7.56 (m, 1H), 7.41-7.35 (m, 1H), 7.35-7.29 (m, 3H), 6.42 (brs, 1H), 2.45 (s, 3H), 2.39 (s, 3H), 1.92 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.01 (s, 3F), -116.57 (s, 2F), -126.29 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.3, 168.9, 164.4, 163.5, 155.8 (t, $J_{C\text{-}F}$ = 26.0 Hz), 138.7, 138.2, 136.4, 134.2, 133.2, 132.2, 129.1, 128.6, 128.5, 128.0, 125.9, 124.0, 111.5, 81.3, 27.2, 21.5, 21.2 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{26}H_{24}F_7N_4O_2$ $[M+H]^+$ 557.1782, found: 557.1782.



2-(2-(4-Bromophenyl)-6-(perfluoropropyl)pyrimidin-4-yl)propan-2-yl ((4-bromophenyl)(imino)methyl)carbamate (3af):

Yield = 57% (118.4 mg). Yellow solid. M.p. 155.3–155.5 ºC.

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

IR (KBr): ν = 3469, 1669, 1612, 1554, 1508, 1387, 1265, 1140, 1011, 840, 743 cm^{-1}.

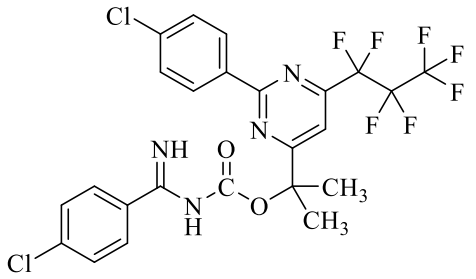
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.38 (brs, 1H), 8.40 (d, J = 8.6 Hz, 2H), 7.68 (d, J = 8.6 Hz,

2H), 7.63 (d, *J* = 5.5 Hz, 2H), 7.60 (s, 1H), 7.53 (d, *J* = 8.6 Hz, 2H), 6.61 (brs, 1H), 1.88 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -79.98 (t, *J* = 8.9 Hz, 3F), -116.63 (q, *J* = 8.9 Hz, 2F), -126.31 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.4, 167.7, 163.4, 163.3, 156.0 (t, $J_{C\text{-}F}$ = 26.1 Hz), 135.2, 133.0, 132.0, 131.8, 130.2, 128.7, 127.3, 126.4, 111.9, 81.3, 27.1 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{24}H_{18}Br_2F_7N_4O_2$ $[M+H]^+$ 684.9679, found: 684.9679.



2-(2-(4-Chlorophenyl)-6-(perfluoropropyl)pyrimidin-4-yl)propan-2-yl ((4-chlorophenyl)(imino)methyl)carbamate (3ag):

Yield = 65% (116.1 mg). White solid. M.p. >300 °C.

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

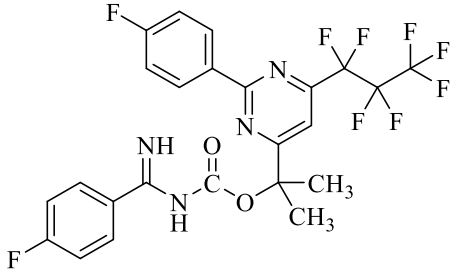
IR (KBr): ν = 3368, 1671, 1614, 1386, 1266, 1248, 1218, 1141, 1116, 843, 745 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.39 (brs, 1H), 8.47 (d, *J* = 8.6 Hz, 2H), 7.75 (d, *J* = 8.6 Hz, 2H), 7.63 (s, 1H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 6.64 (brs, 1H), 1.88 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.03 (t, *J* = 9.0 Hz, 3F), -116.65 (q, *J* = 9.2 Hz, 2F), -126.33 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.4, 167.6, 163.3, 163.3, 156.0 (t, $J_{C\text{-}F}$ = 26.4 Hz), 138.8, 137.8, 134.8, 132.5, 130.0, 129.0, 128.8, 128.6, 111.8, 81.3, 27.1 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{24}H_{18}Cl_2F_7N_4O_2$ $[M+H]^+$ 597.0690, found: 597.0695.



2-(2-(4-Fluorophenyl)-6-(perfluoropropyl)pyrimidin-4-yl)propan-2-yl ((4-fluorophenyl)(imino)methyl)carbamate (3ah):

Yield = 76% (127.9 mg). White solid. M.p. 156.5–157.9 °C.

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

IR (KBr): ν = 3318, 1907, 1489, 1273, 966, 850, 817, 744, 674, 649, 591, 525 cm^{-1}.

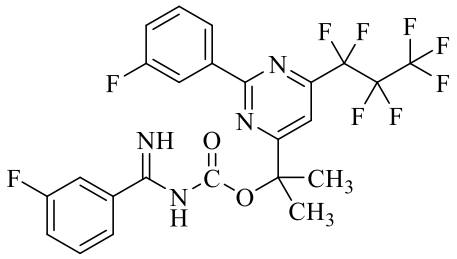
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.39 (brs, 1H), 8.58-8.50 (m, 2H), 7.86-7.77 (m, 2H), 7.61 (s,

1H), 7.19-7.10 (m, 2H), 7.08-7.00 (m, 2H), 6.75 (brs, 1H), 1.87 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.09 (t, J = 8.9 Hz, 3F), -106.36 ~ -106.43 (m, 1F), -108.61 ~ -108.68 (m, 1F), -116.67 (q, J = 9.3 Hz, 2F), -126.37 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.4, 167.6, 165.3 (d, $J_{C\text{-}F}$ = 252.1 Hz), 165.1 (d, $J_{C\text{-}F}$ = 252.1 Hz), 163.4, 156.0 (t, $J_{C\text{-}F}$ = 26.1 Hz), 132.6 (d, $J_{C\text{-}F}$ = 2.9 Hz), 130.9 (d, $J_{C\text{-}F}$ = 8.8 Hz), 130.3 (d, $J_{C\text{-}F}$ = 2.9 Hz), 129.6 (d, $J_{C\text{-}F}$ = 9.1 Hz), 116.0, 115.9 (d, $J_{C\text{-}F}$ = 21.7 Hz), 115.6 (d, $J_{C\text{-}F}$ = 21.6 Hz), 111.5 (t, $J_{C\text{-}F}$ = 4.0 Hz), 81.3, 27.1 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{24}H_{18}F_9N_4O_2$ $[M+H]^+$ 565.1281, found: 565.1279.



2-(2-(3-Fluorophenyl)-6-(perfluoropropyl)pyrimidin-4-yl)propan-2-yl ((3-fluorophenyl)(imino)methyl)carbamate (3ai):

Yield = 61% (103.3 mg). White solid. M.p. 119.7–120.0 ºC.

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

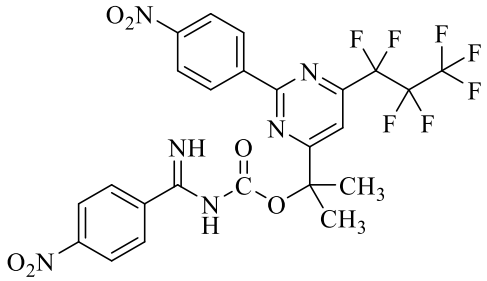
IR (KBr): ν = 3387, 3222, 1664, 1617, 1588, 1513, 1377, 1287, 968, 742 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.38 (brs, 1H), 8.34 (d, J = 7.8 Hz, 1H), 8.25-8.20 (m, 1H), 7.66 (s, 1H), 7.60-7.54 (m, 2H), 7.50-7.42 (m, 1H), 7.41-7.35 (m, 1H), 7.25-7.17 (m, 2H), 6.59 (brs, 1H), 1.90 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.06 (s, 3F), -111.27 (s, 1F), -112.77 (s, 1F), -116.60 (s, 2F), -126.32 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.5, 167.5, 163.3, 163.1 (d, $J_{C\text{-}F}$ = 243.9 Hz), 163.1 (d, $J_{C\text{-}F}$ = 2.6 Hz), 162.6 (d, $J_{C\text{-}F}$ = 246.7 Hz), 156.0 (t, $J_{C\text{-}F}$ = 26.2 Hz), 138.6 (d, $J_{C\text{-}F}$ = 8.1 Hz), 136.4 (d, $J_{C\text{-}F}$ = 7.5 Hz), 130.4 (d, $J_{C\text{-}F}$ = 7.8 Hz), 130.1 (d, $J_{C\text{-}F}$ = 8.0 Hz), 124.3 (d, $J_{C\text{-}F}$ = 2.7 Hz), 122.6 (d, $J_{C\text{-}F}$ = 3.2 Hz), 119.4 (d, $J_{C\text{-}F}$ = 21.1 Hz), 118.4 (d, $J_{C\text{-}F}$ = 21.4 Hz), 115.4 (d, $J_{C\text{-}F}$ = 23.4 Hz), 114.7 (d, $J_{C\text{-}F}$ = 23.6 Hz), 112.1, 81.4, 27.1 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{24}H_{18}F_9N_4O_2$ $[M+H]^+$ 565.1281, found: 565.1281.



2-(2-(4-Nitrophenyl)-6-(perfluoropropyl)pyrimidin-4-yl)propan-2-yl (imino(4-nitrophenyl)methyl)carbamate (3aj):

Yield = 59% (108.8 mg). Yellow solid. M.p. 147.3–148.4 °C.

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

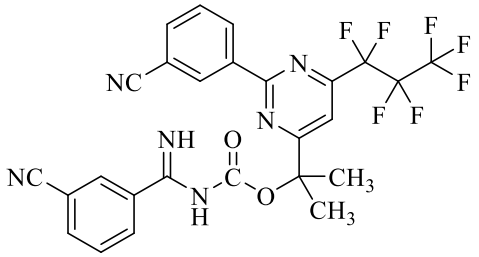
IR (KBr): ν = 3409, 1711, 1667, 1634, 1530, 1350, 1271, 1188, 872, 740 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.36 (brs, 1H), 9.20 (brs, 1H), 8.64 (d, J = 8.9 Hz, 2H), 8.43 (d, J = 8.9 Hz, 2H), 8.27 (d, J = 8.9 Hz, 2H), 8.17 (d, J = 8.9 Hz, 2H), 8.01 (s, 1H), 1.90 (s, 6H) ppm.

^{19}F NMR (376 MHz, DMSO-d_6): δ = -79.71 (t, J = 8.9 Hz, 3F), -115.88 (q, J = 8.8 Hz, 2F), -126.08 (s, 2F) ppm.

^{13}C NMR (100 MHz, DMSO-d_6): δ = 177.8, 165.2, 162.3, 161.6, 154.9 (t, $J_{C\text{-}F}$ = 26.1 Hz), 149.5, 149.4, 141.3, 140.0, 129.4, 129.3, 124.3, 123.4, 113.6, 80.1, 26.7 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{24}H_{18}F_7N_6O_6$ $[M+H]^+$ 619.1171, found: 619.1170.



2-(2-(3-Cyanophenyl)-6-(perfluoropropyl)pyrimidin-4-yl)propan-2-yl ((3-cyanophenyl)(imino)methyl)carbamate (3ak):

Yield = 30% (52.8 mg). White solid. M.p. 89.9–91.0 °C.

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

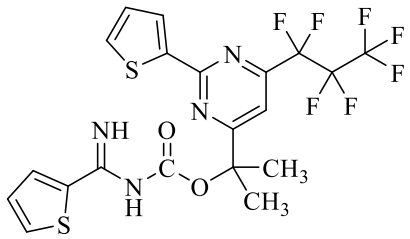
IR (KBr): ν = 3414, 2929, 2234, 1625, 1555, 1522, 1380, 1273, 1122, 741 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.38 (brs, 1H), 8.81-8.75 (m, 2H), 8.24-8.21 (m, 1H), 8.12-8.08 (m, 1H), 7.83-7.76 (m, 2H), 7.70 (s, 1H), 7.65-7.54 (m, 2H), 6.95 (brs, 1H), 1.91 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.00 (t, J = 9.1 Hz, 3F), -116.55 (t, J = 9.4 Hz, 2F), -126.22 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.7, 166.6, 163.1, 162.2, 156.2 (t, $J_{C\text{-}F}$ = 26.2 Hz), 137.4, 135.6, 135.4, 134.5, 132.8, 132.3, 131.5, 131.3, 129.7, 129.6, 118.6, 117.7, 113.0, 112.8, 112.7, 81.4, 27.1 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{26}H_{18}F_7N_6O_2$ $[M+H]^+$ 579.1374, found: 579.1371.



2-(6-(Perfluoropropyl)-2-(thiophen-2-yl)pyrimidin-4-yl)propan-2-yl (imino(thiophen-2-yl)methyl)carbamate (3al):

Yield = 43% (70.0 mg). White solid. M.p. 145.9–146.8 °C.

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

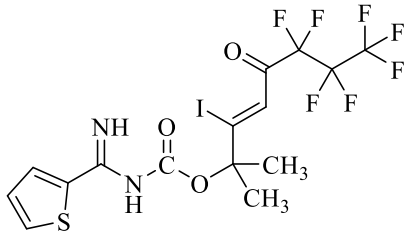
IR (KBr): ν = 3374, 1665, 1607, 1547, 1491, 1438, 1277, 1239, 1146, 1121, 741, 716 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.34 (brs, 1H), 8.09 (d, J = 3.8 Hz, 1H), 7.62 (d, J = 3.8 Hz, 1H), 7.54-7.48 (m, 3H), 7.13 (dd, J = 5.0, 3.7 Hz, 1H), 7.08 (dd, J = 5.0, 3.8 Hz, 1H), 6.71 (brs, 1H), 1.83 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.00 (t, J = 9.0 Hz, 3F), -116.70 (q, J = 9.0 Hz, 2F), -126.32 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.5, 163.1, 162.7, 161.0, 155.7 (t, $J_{C\text{-}F}$ = 26.2 Hz), 142.2, 138.3, 132.0, 131.0, 130.4, 128.8, 128.3, 128.0, 111.0, 81.3, 27.0 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{16}F_7N_4O_2S_2$ $[M+H]^+$ 541.0597, found: 541.0599.



(Z)-6,6,7,7,8,8,8-Heptafluoro-3-iodo-2-methyl-5-oxooct-3-en-2-yl (imino(thiophen-2-yl)methyl)carbamate (3al'):

Yield = 13% (22.4 mg). Yellow solid. M.p. 140.6–141.2 ºC.

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

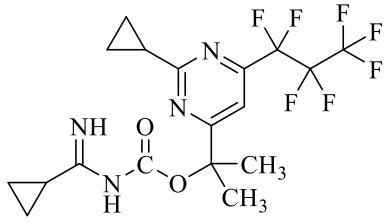
IR (KBr): ν = 3419, 3292, 2994, 1654, 1539, 1485, 1354, 1278, 1117, 962, 797 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.47 (brs, 1H), 7.64 (dd, J = 3.8, 1.1 Hz, 1H), 7.55 (d, J = 5.1 Hz, 1H), 7.11-7.09 (m, 1H), 6.56 (brs, 1H), 5.78 (s, 1H), 1.57 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.21 (t, J = 8.9 Hz, 3F), -120.12 (q, J = 9.5 Hz, 2F), -127.10 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.3, 163.4, 162.6, 147.1, 138.5, 131.9, 128.7, 128.0, 91.2, 82.9, 24.0 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{15}H_{13}F_7IN_2O_3S$ $[M+H]^+$ 560.9574, found: 560.9575.



2-(2-Cyclopropyl-6-(perfluoropropyl)pyrimidin-4-yl)propan-2-yl (cyclopropyl(imino)methyl)carbamate (3am):

Yield = 47% (64.7 mg). Yellow solid. M.p. 70.2–70.3 ºC.

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

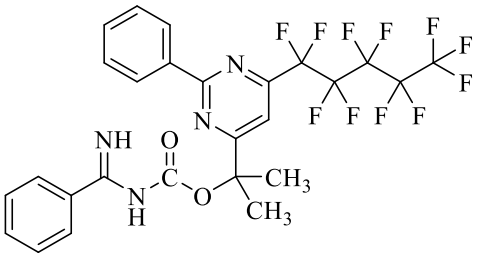
IR (KBr): ν = 3350, 3220, 1764, 1674, 1614, 1518, 1434, 1294, 1116, 942, 741 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.12 (brs, 1H), 7.37 (s, 1H), 6.37 (brs, 1H), 2.35-2.26 (m, 1H), 1.69 (s, 6H), 1.42-1.34 (m, 1H), 1.19-1.15 (m, 2H), 1.08 (dt, J = 8.2, 3.1 Hz, 2H), 1.01-0.95 (m, 2H), 0.90-0.84 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.12 (t, J = 9.1 Hz, 3F), -116.94 (q, J = 9.3 Hz, 2F), -126.46 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.1, 176.1, 172.4, 163.2, 154.9 (t, $J_{C\text{-}F}$ = 25.8 Hz), 110.5, 80.7, 27.2, 18.2, 16.6, 11.7, 9.1 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{18}H_{20}F_7N_4O_2$ $[M+H]^+$ 457.1469, found: 457.1466.



2-(6-(Perfluoropentyl)-2-phenylpyrimidin-4-yl)propan-2-yl (imino(phenyl)methyl)carbamate (3ba):

Yield = 64% (120.5 mg). Yellow solid. M.p. 100.2–100.6 °C.

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

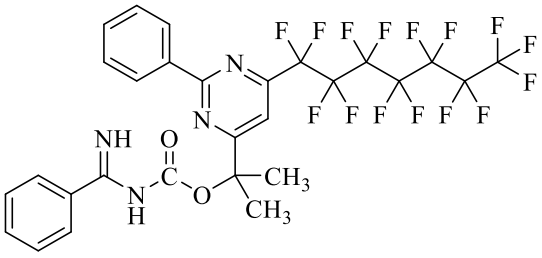
IR (KBr): ν = 3451, 3309, 1659, 1575, 1381, 1276, 1237, 1139, 865, 696 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.41 (brs, 1H), 8.59-8.53 (m, 2H), 7.78 (d, J = 7.1 Hz, 2H), 7.66 (s, 1H), 7.54-7.45 (m, 4H), 7.35 (t, J = 7.8 Hz, 2H), 6.83 (brs, 1H), 1.89 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.74 (t, J = 10.0 Hz, 3F), -115.58 (t, J = 13.3 Hz, 2F), -122.06 (dt, J = 60.3, 13.4 Hz, 4F), -126.12 (t, J = 14.4 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.4, 168.7, 164.2, 163.4, 156.0 (t, $J_{C\text{-}F}$ = 26.2 Hz), 136.4, 134.2, 132.3, 131.4, 128.6, 128.6, 128.5, 127.1, 111.7, 81.3, 27.1 ppm, carbons corresponding to the C_5F_{11} group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{26}H_{20}F_{11}N_4O_2$ $[M+H]^+$ 629.1405, found: 629.1408.



2-(6-(Perfluoroheptyl)-2-phenylpyrimidin-4-yl)propan-2-yl (imino(phenyl)methyl)carbamate (3ca):

Yield = 79% (172.8 mg). Yellow oil.

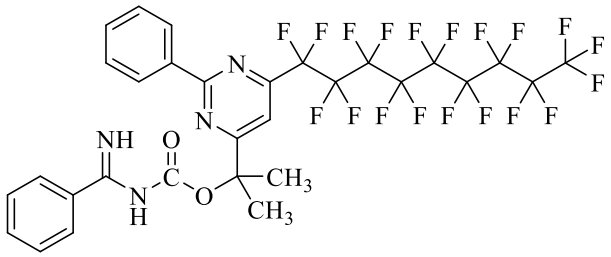
Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

IR (KBr): ν = 3352, 1776, 1617, 1578, 1519, 1387, 1278, 1143, 1011, 696 cm^{-1}.

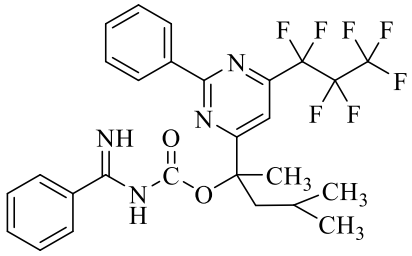
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.41 (brs, 1H), 8.59-8.53 (m, 2H), 7.77 (d, J = 7.1 Hz, 2H), 7.66 (s, 1H), 7.52-7.43 (m, 5H), 7.33 (t, J = 7.8 Hz, 2H), 1.89 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.83 (t, J = 9.6 Hz, 3F), -115.51 (t, J = 13.5 Hz, 2F), -121.18 (s, 2F), -121.69 (s, 2F), -121.97 (s, 2F), -122.74 (s, 2F), -126.17 (dq, J = 14.7, 7.3 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.2, 168.7, 164.3, 162.9, 156.1 (t, $J_{C\text{-}F}$ = 26.1 Hz), 136.3, 133.8, 132.4, 131.4, 128.6, 128.6, 128.5, 127.2, 111.6, 81.4, 27.0 ppm, carbons corresponding to the C_7F_{15} group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{28}H_{20}F_{15}N_4O_2$ $[M+H]^+$ 729.1341, found: 729.1342.

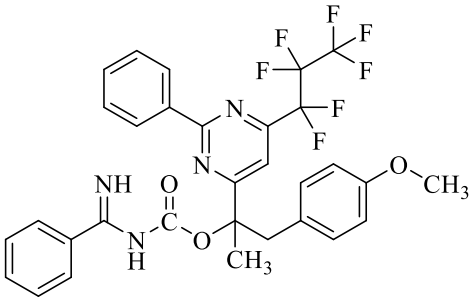


2-(6-(Perfluorononyl)-2-phenylpyrimidin-4-yl)propan-2-yl (imino(phenyl)methyl)carbamate (3da):
Yield = 69% (170.8 mg). White solid. M.p. 138.3–139.6 ºC.
Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).
IR (KBr): ν = 3349, 3181, 1676, 1614, 1552, 1519, 1385, 1216, 1151, 701 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.42 (brs, 1H), 8.56 (dd, J = 7.5, 2.3 Hz, 2H), 7.78 (d, J = 7.1 Hz, 2H), 7.66 (s, 1H), 7.48 (dd, J = 6.6, 4.9 Hz, 4H), 7.35 (t, J = 7.8 Hz, 2H), 6.80 (brs, 1H), 1.89 (s, 6H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.87 (t, J = 9.9 Hz, 3F), -115.55 (t, J = 13.5 Hz, 2F), -121.14 (s, 2F), -121.84 (d, J = 83.4 Hz, 8F), -122.77 (s, 2F), -126.20 (s, 2F) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.4, 168.7, 164.3, 163.4, 156.1 (t, $J_{C\text{-}F}$ = 26.5 Hz), 136.4, 134.2, 132.3, 131.4, 128.6, 128.6, 128.5, 127.2, 111.7, 81.3, 27.1 ppm, carbons corresponding to the C_9F_{19} group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{30}H_{20}F_{19}N_4O_2$ $[M+H]^+$ 829.1277, found: 829.1274.

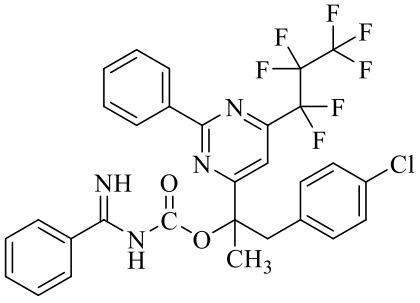


4-Methyl-2-(6-(perfluoropropyl)-2-phenylpyrimidin-4-yl)pentan-2-yl (imino(phenyl)methyl)carbamate (3fa):
Yield = 56% (95.7 mg). Yellow oil.
Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).
IR (KBr): ν = 3351, 2961, 1735, 1616, 1577, 1518, 1260, 1231, 962, 739, 696 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.42 (brs, 1H), 8.57 (dd, J = 7.4, 2.4 Hz, 2H), 7.79 (d, J = 8.5 Hz, 2H), 7.71 (s, 1H), 7.55-7.46 (m, 4H), 7.37 (t, J = 7.7 Hz, 2H), 6.83 (brs, 1H), 2.15 (d, J = 6.0 Hz, 2H), 2.01 (s, 3H), 1.85-1.75 (m, 1H), 0.90-0.84 (m, 6H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.01 (t, J = 9.0 Hz, 3F), -116.55 ~ -116.64 (m, 2F), -126.33 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.3, 168.6, 164.1, 163.4, 155.7 (t, $J_{C\text{-}F}$ = 26.2 Hz), 136.4, 134.3, 132.3, 131.4, 128.6, 128.6, 128.6, 127.2, 112.3, 84.0, 48.9, 24.3, 24.0, 24.0, 23.9 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{27}H_{26}F_7N_4O_2$ $[M+H]^+$ 571.1938, found: 571.1935.



1-(4-Methoxyphenyl)-2-(6-(perfluoropropyl)-2-phenylpyrimidin-4-yl)propan-2-yl (imino(phenyl)methyl)carbamate (3ga):
Yield = 57% (72.9 mg; using 0.2 mmol **1g**). Yellow solid. M.p. 137.4–138.1 °C.
Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).
IR (KBr): ν = 3329, 1659, 1617, 1514, 1384, 1279, 1232, 1121, 913, 791, 697 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.41 (brs, 1H), 8.56-8.51 (m, 2H), 7.85-7.81 (m, 2H), 7.57-7.48 (m, 4H), 7.46-7.20 (m, 2H), 7.32 (s, 1H), 6.92-6.88 (m, 2H), 6.74-6.69 (m, 2H), 6.50 (brs, 1H), 3.72 (s, 3H), 3.50 (d, J = 13.9 Hz, 1H), 3.38 (d, J = 13.9 Hz, 1H), 2.00 (s, 3H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.00 (t, J = 8.9 Hz, 3F), -116.55 (dt, J = 12.9, 6.3 Hz, 2F), -126.30 (s, 2F) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.1, 168.5, 164.0, 163.5, 158.5, 155.2 (t, $J_{C\text{-}F}$ = 26.5 Hz), 136.4, 134.2, 132.4, 131.5, 131.5, 128.7, 128.6, 128.6, 127.3, 127.2, 113.5, 112.9, 83.8, 55.1, 45.9, 23.4 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{31}H_{26}F_7N_4O_3$ $[M+H]^+$ 635.1888, found: 635.1888.

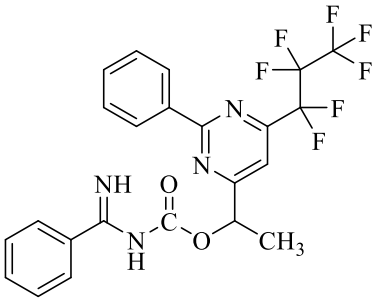


1-(4-Chlorophenyl)-2-(6-(perfluoropropyl)-2-phenylpyrimidin-4-yl)propan-2-yl (imino(phenyl)methyl)carbamate (3ha):
Yield = 66% (127.1 mg). Yellow solid. M.p. 80.3–81.2 °C.
Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).
IR (KBr): ν = 3629, 3310, 1735, 1654, 1492, 1382, 1273, 1231, 965, 697 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.43 (brs, 1H), 8.54 (dd, J = 7.8, 2.1 Hz, 2H), 7.80 (d, J = 7.8 Hz, 2H), 7.58-7.50 (m, 4H), 7.44-7.34 (m, 3H), 7.16 (d, J = 8.5 Hz, 2H), 6.96 (d, J = 8.3 Hz, 2H), 6.74 (brs, 1H), 3.49 (q, J = 13.9 Hz, 2H), 1.97 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.00 (t, J = 8.9 Hz, 3F), -116.58 (dd, J = 16.8, 8.9 Hz, 2F), -126.34 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.9, 168.7, 164.2, 163.3, 155.5 (t, $J_{C\text{-}F}$ = 26.2 Hz), 136.2, 134.1, 133.9, 132.8, 132.5, 131.8, 131.6, 128.8, 128.6, 128.6, 128.2, 127.2, 112.7, 83.4, 45.6, 23.8 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{30}H_{23}ClF_7N_4O_2$ $[M+H]^+$ 639.1392, found: 639.1389.



1-(6-(Perfluoropropyl)-2-phenylpyrimidin-4-yl)ethyl (imino(phenyl)methyl)carbamate (3ia):

Yield = 31% (48.5 mg). Yellow solid. M.p. 94.1–95.8 ºC.

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

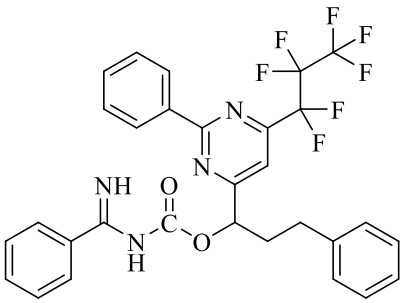
IR (KBr): ν = 3432, 3299, 1665, 1600, 1575, 1390, 1262, 1111, 739, 694 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.60 (brs, 1H), 8.55-8.51 (m, 2H), 7.92-7.88 (m, 2H), 7.73 (s, 1H), 7.60-7.55 (m, 1H), 7.52-7.45 (m, 5H), 6.56 (brs, 1H), 5.97 (dd, J = 6.9, 0.5 Hz, 1H), 1.76 (d, J = 6.9 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -79.98 (t, J = 9.0 Hz, 3F), -116.25 ~ -116.34 (m, 2F), -126.03 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.3, 168.9, 164.5, 163.8, 156.7 (t, $J_{C\text{-}F}$ = 26.2 Hz), 136.1, 134.2, 132.6, 131.6, 128.9, 128.7, 128.6, 127.2, 111.8, 73.5, 20.7 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{23}H_{18}F_7N_4O_2$ $[M+H]^+$ 515.1312, found: 515.1317.



1-(6-(Perfluoropropyl)-2-phenylpyrimidin-4-yl)-3-phenylpropyl (imino(phenyl)methyl)carbamate (3ja):

Yield = 20% (36.2 mg). Yellow solid. M.p. 106.9–107.1 ºC.

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

IR (KBr): ν = 3309, 1675, 1625, 1574, 1557, 1389, 1256, 1144, 963, 698 cm^{-1}.

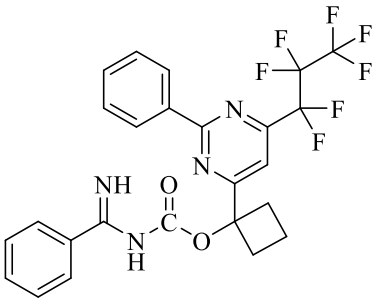
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.59 (brs, 1H), 8.56-8.51 (m, 2H), 7.92-7.86 (m, 2H), 7.70 (s, 1H), 7.60-7.43 (m, 7H), 7.30-7.22 (m, 4H), 7.20 (d, J = 7.0 Hz, 1H), 5.91 (t, J = 6.6 Hz, 1H),

2.94-2.86 (m, 2H), 2.41 (q, *J* = 7.2 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -79.97 (t, *J* = 9.0 Hz, 3F), -116.30 ~ -116.40 (m, 2F), -126.08 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.6, 169.1, 164.6, 164.0, 156.7 (t, $J_{C\text{-}F}$ = 26.2 Hz), 140.9, 136.1, 134.3, 132.5, 131.6, 128.9, 128.7, 128.6, 128.5, 128.5, 127.3, 126.1, 112.3, 76.5, 36.5, 31.6 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{30}H_{24}F_7N_4O_2$ $[M+H]^+$ 605.1782, found: 605.1780.



1-(6-(Perfluoropropyl)-2-phenylpyrimidin-4-yl)cyclobutyl (imino(phenyl)methyl)carbamate (3ka):

Yield = 32% (52.5 mg). Yellow solid. M.p. 108.1–109.9 °C.

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

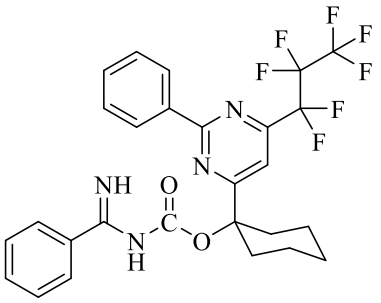
IR (KBr): ν = 3352, 1665, 1617, 1554, 1385, 1282, 1243, 1118, 736, 697 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.45 (brs, 1H), 8.64-8.57 (m, 2H), 7.86-7.78 (m, 2H), 7.60 (s, 1H), 7.54-7.49 (m, 4H), 7.40 (t, *J* = 7.8 Hz, 2H), 6.70 (brs, 1H), 2.96-2.87 (m, 2H), 2.79-2.68 (m, 2H), 2.29-2.05 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.02 (t, *J* = 8.9 Hz, 3F), -116.56 (q, *J* = 8.9 Hz, 2F), -126.30 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.5, 168.9, 164.5, 163.3, 156.1 (t, $J_{C\text{-}F}$ = 27.0 Hz), 136.4, 134.0, 132.5, 131.5, 128.7, 128.7, 128.6, 127.2, 110.9, 81.8, 34.2, 13.8 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{25}H_{20}F_7N_4O_2$ $[M+H]^+$ 541.1469, found: 541.1468.



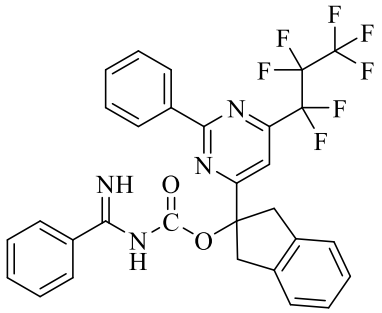
1-(6-(Perfluoropropyl)-2-phenylpyrimidin-4-yl)cyclohexyl (imino(phenyl)methyl)carbamate (3la):

Yield = 46% (78.6 mg). White solid. M.p. 115.1–115.7 °C.

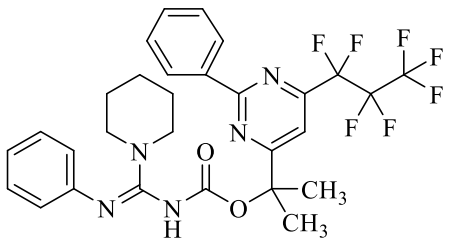
Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

IR (KBr): ν = 3349, 2940, 1614, 1577, 1382, 1240, 1119, 965, 736, 695 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.39 (brs, 1H), 8.58-8.53 (m, 2H), 7.83-7.79 (m, 2H), 7.63 (s, 1H), 7.55-7.48 (m, 4H), 7.44-7.38 (m, 2H), 6.40 (brs, 1H), 2.46 (d, *J* = 13.5 Hz, 2H), 2.13 (td, *J* = 13.2, 3.9 Hz, 2H), 1.95-1.83 (m, 2H), 1.82-1.71 (m, 3H), 1.48-1.37 (m, 1H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.04 (t, *J* = 8.9 Hz, 3F), -116.66 (q, *J* = 8.9 Hz, 2F), -126.42 (s, 2F) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.7, 168.7, 164.2, 163.4, 155.l (t, $J_{C\text{-}F}$ = 26.2 Hz), 136.5, 134.3, 132.2, 131.4, 128.6, 128.6, 128.5, 127.2, 112.0 (t, $J_{C\text{-}F}$ = 4.3 Hz), 82.6, 34.7, 25.1, 21.6 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{27}H_{24}F_7N_4O_2$ $[M+H]^+$ 569.1782, found: 569.1779.

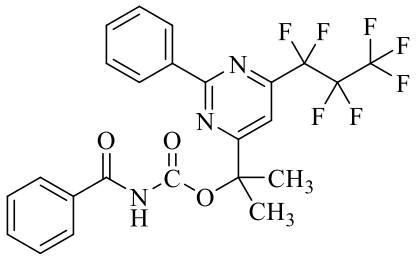


2-(6-(Perfluoropropyl)-2-phenylpyrimidin-4-yl)-2,3-dihydro-1*H*-inden-2-yl (imino(phenyl)methyl)carbamate (3ma):
Yield = 79% (143.1 mg). Yellow solid. M.p. 120.1–120.9 °C.
Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).
IR (KBr): ν = 3358, 1654, 1617, 1577, 1514, 1377, 1279, 1230, 740, 695 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.43 (brs, 1H), 8.48 (dd, *J* = 8.1, 1.7 Hz, 2H), 7.75 (d, *J* = 7.0 Hz, 2H), 7.72 (s, 1H), 7.52-7.43 (m, 4H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.30-7.22 (m, 4H), 6.80 (brs, 1H), 4.02 (d, *J* = 17.1 Hz, 2H), 3.76 (d, *J* = 17.0 Hz, 2H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -79.98 (t, *J* = 9.1 Hz, 3F), -116.57 (t, *J* = 8.9 Hz, 2F), -126.33 (s, 2H) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.5, 168.9, 164.2, 163.6, 156.2 (t, $J_{C\text{-}F}$ = 26.0 Hz), 139.7, 136.1, 133.9, 132.5, 131.5, 128.7, 128.6, 128.5, 127.1, 127.0, 124.3, 111.6, 90.5, 45.2 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{30}H_{22}F_7N_4O_2$ $[M+H]^+$ 603.1625, found: 603.1628.

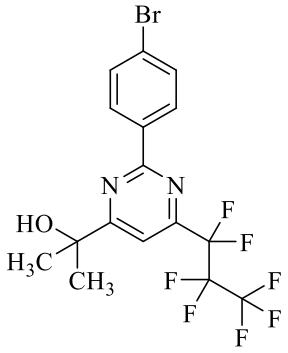


(Z)-3-Methyl-3-(6-(perfluoropropyl)-2-phenylpyrimidin-4-yl)-*N*-((phenylimino)(piperidin-1-yl)methyl)butanamide (4):
Yield = 30% (55.2 mg). White solid. M.p. 328.1–328.9 °C.
Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).
IR (KBr): ν = 3470, 3414, 1735, 1637, 1618, 1388, 1273, 1226, 1121, 614 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (dd, J = 7.6, 2.2 Hz, 2H), 7.65 (s, 1H), 7.49 (d, J = 7.7 Hz, 3H), 7.29-7.23 (m, 3H), 7.06 (t, J = 7.4 Hz, 1H), 6.92 (d, J = 7.4 Hz, 2H), 3.24 (t, J = 5.4 Hz, 4H), 1.87 (s, 6H), 1.50 (q, J = 6.2 Hz, 2H), 1.43-1.36 (m, 4H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.06 (t, J = 9.1 Hz, 3F), -116.65 (q, J = 9.2 Hz, 2F), -126.31 (s, 2F) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.3, 164.1, 162.3, 159.9, 155.5 (t, $J_{C\text{-}F}$ = 26.2 Hz), 139.9, 136.5, 131.3, 129.3, 128.6, 128.5, 124.3, 121.2, 111.9, 80.8, 47.8, 27.5, 25.2, 24.1 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{29}H_{29}F_7N_5O_2$ $[M+H]^+$ 612.2204, found: 612.2205.



2-(6-(Perfluoropropyl)-2-phenylpyrimidin-4-yl)propan-2-yl benzoylcarbamate (5):
Yield = 56% (89.1 mg). White solid. M.p. 141.3–142.7 ºC.
Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).
IR (KBr): ν = 3275, 3085, 1753, 1729, 1700, 1573, 1555, 1389, 1333, 1230, 739, 695 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (s, 1H), 8.53 (d, J = 8.6 Hz, 2H), 7.94-7.80 (m, 3H), 7.60-7.37 (m, 6H), 1.97 (s, 6H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -79.96 (t, J = 9.2 Hz, 3F), -116.23 (q, J = 9.3 Hz, 2F), -126.01 (s, 2F) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.5, 165.1, 164.5, 156.8 (t, $J_{C\text{-}F}$ = 26.2 Hz), 150.1, 136.1, 133.0, 132.8, 131.6, 128.7, 128.6, 128.6, 127.7, 111.6, 84.0, 26.6 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{24}H_{19}F_7N_3O_3$ $[M+H]^+$ 530.1309, found: 530.1305.



2-(2-(4-Bromophenyl)-6-(perfluoropropyl)pyrimidin-4-yl)propan-2-ol (1p):
Yield = 41% (57.3 mg). Yellow oil.
Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate, 50/1~20/1).
IR (KBr): ν = 3626, 3438, 1654, 1587, 1560, 1388, 1232, 1122, 1012, 743 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43-8.35 (m, 2H), 7.74 (s, 1H), 7.67-7.61 (m, 2H), 3.64 (brs, 1H), 1.65 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.00 (t, J = 9.5 Hz, 3F), -116.34 (q, J = 9.5 Hz, 2F), -126.03 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.9, 163.3, 156.9 (t, $J_{C\text{-}F}$ = 26.7 Hz), 134.8, 132.0, 130.1, 126.8, 111.5 (t, $J_{C\text{-}F}$ = 4.6 Hz), 73.1, 30.0 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{16}H_{13}BrF_7N_2O$ $[M+H]^+$ 461.0094, found: 461.0099.

Reference

[1] T. Xu, C. W. Cheung, X. Hu, Iron-Catalyzed 1,2-Addition of Perfluoroalkyl Iodides to Alkynes and Alkenes, *Angew. Chem. Int. Ed.* **2014**, *53*, 4910-4914.

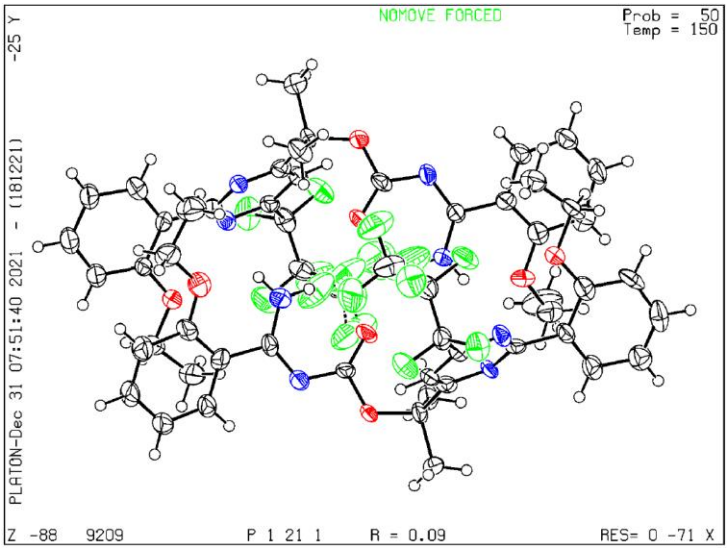
[2] M. Baetena, B. U. W. Maes, Guanidine Synthesis: Use of Amidines as Guanylating Agents, *Adv. Synth. Catal.* **2016**, *358*, 826-833.

[3] X.-Q. Chu, D. Ge, Z.-L. Shen, T.-P. Loh, Recent Advances in Radical-Initiated C(sp^3)-H Bond Oxidative Functionalization of Alkyl Nitriles, *ACS Catal.* **2018**, *8*, 258-271.

The X-ray crystal structure of product 3ac

The single crystals were grown from the mixed solution of DCM and EtOAc (v/v = 1:3) by slowly evaporating the above solvents at room temperature.

2-(2-(2-Ethoxyphenyl)-6-(perfluoropropyl)pyrimidin-4-yl)propan-2-yl ((2-ethoxyphenyl)(imino)methyl)carbamate (3ac):



CCDC number: 2131913

Table 1 Crystal data and structure refinement for 3ac.

Identification code	**3ac**
Empirical formula	$C_{28}H_{27}F_7N_4O_4$
Formula weight	616.53
Temperature/K	150.00(10)

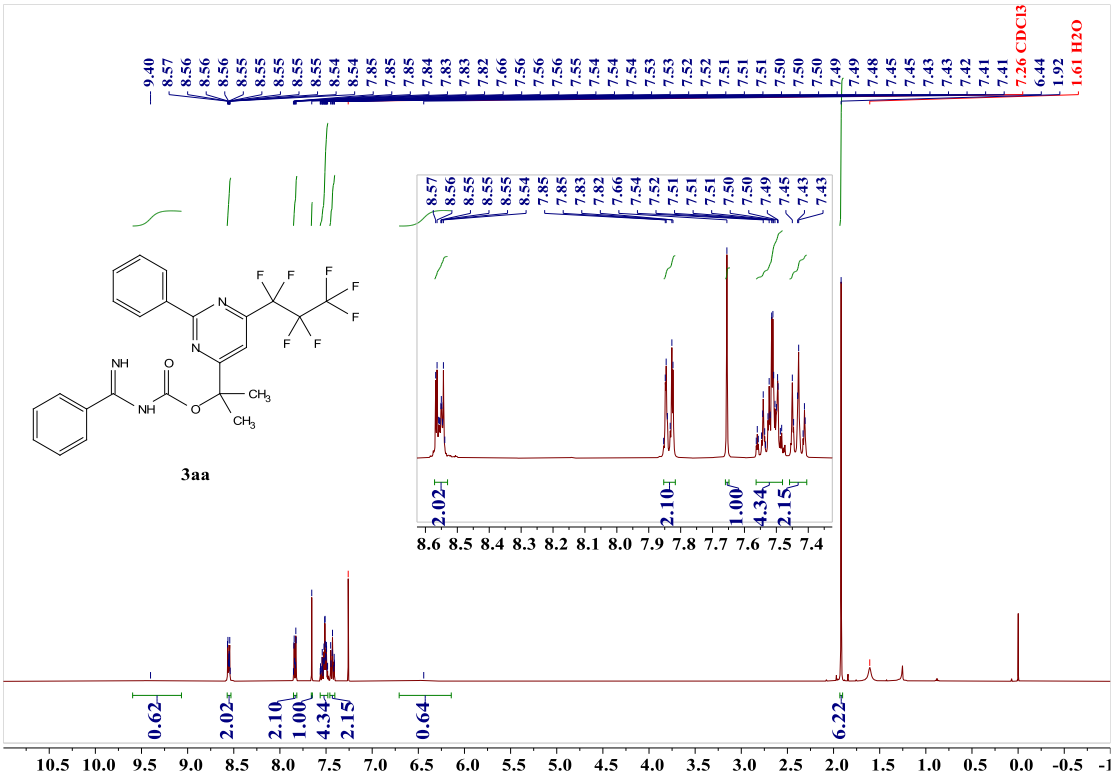
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.8007(8)
b/Å	19.4570(18)
c/Å	15.5025(12)
α/°	90
β/°	99.565(7)
γ/°	90
Volume/Å^3	2915.1(4)
Z	4
ρ_{calc}g/cm^3	1.405
μ/mm^{-1}	0.125
F(000)	1272.0
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.186 to 49.988
Index ranges	-11 ≤ h ≤ 11, -23 ≤ k ≤ 22, -18 ≤ l ≤ 15
Reflections collected	16749
Independent reflections	9243 [R_{int} = 0.1115, R_{sigma} = 0.1485]
Data/restraints/parameters	9243/61/812
Goodness-of-fit on F^2	1.005
Final R indexes [I>=2σ (I)]	R_1 = 0.0926, wR_2 = 0.2199
Final R indexes [all data]	R_1 = 0.1359, wR_2 = 0.2673
Largest diff. peak/hole / e Å^{-3}	0.41/-0.37
Flack parameter	-1.8(10)

Crystal structure determination of [3ac]

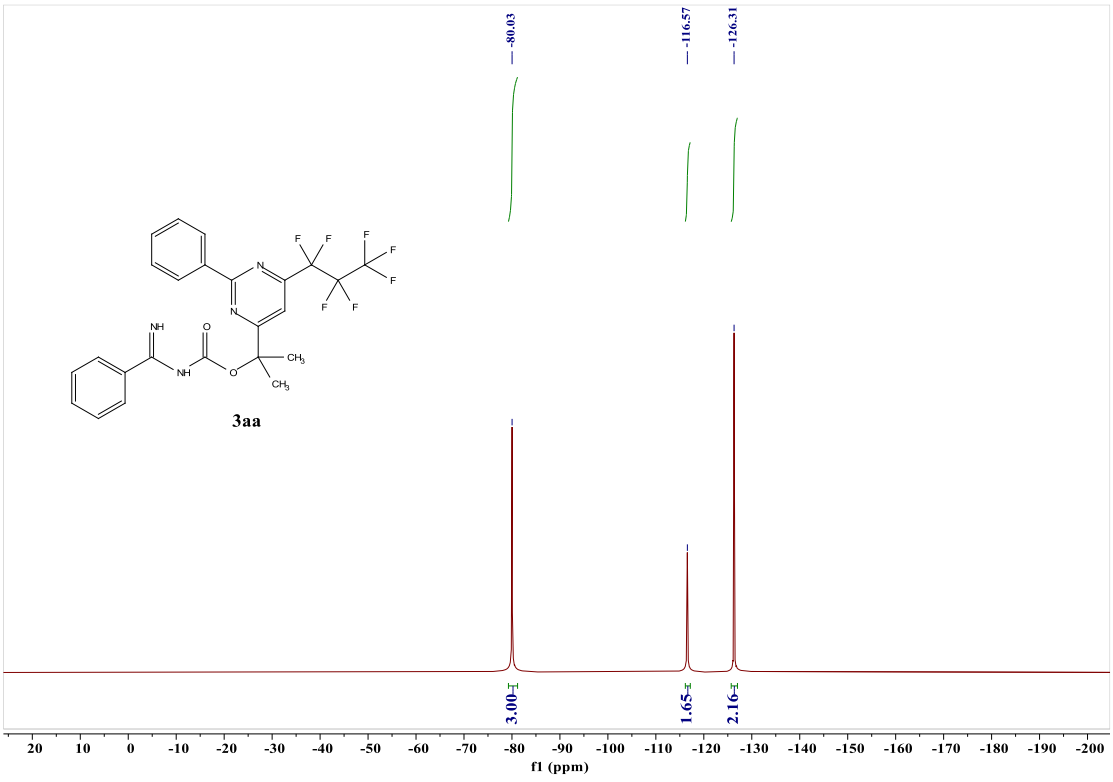
Crystal Data for $C_{28}H_{27}F_7N_4O_4$ (*M* =616.53 g/mol): monoclinic, space group $P2_1$ (no. 4), *a* = 9.8007(8) Å, *b* = 19.4570(18) Å, *c* = 15.5025(12) Å, *β* = 99.565(7) °, *V* = 2915.1(4) Å^3, *Z* = 4, *T* = 150.00(10) K, μ(Mo Kα) = 0.125 mm^{-1}, *Dcalc* = 1.405 g/cm^3, 16749 reflections measured (4.186 ° ≤ 2Θ ≤ 49.988°), 9243 unique (R_{int} = 0.1115, R_{sigma} = 0.1485) which were used in all calculations. The final R_1 was 0.0926 (I > 2σ(I)) and wR_2 was 0.2673 (all data).

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

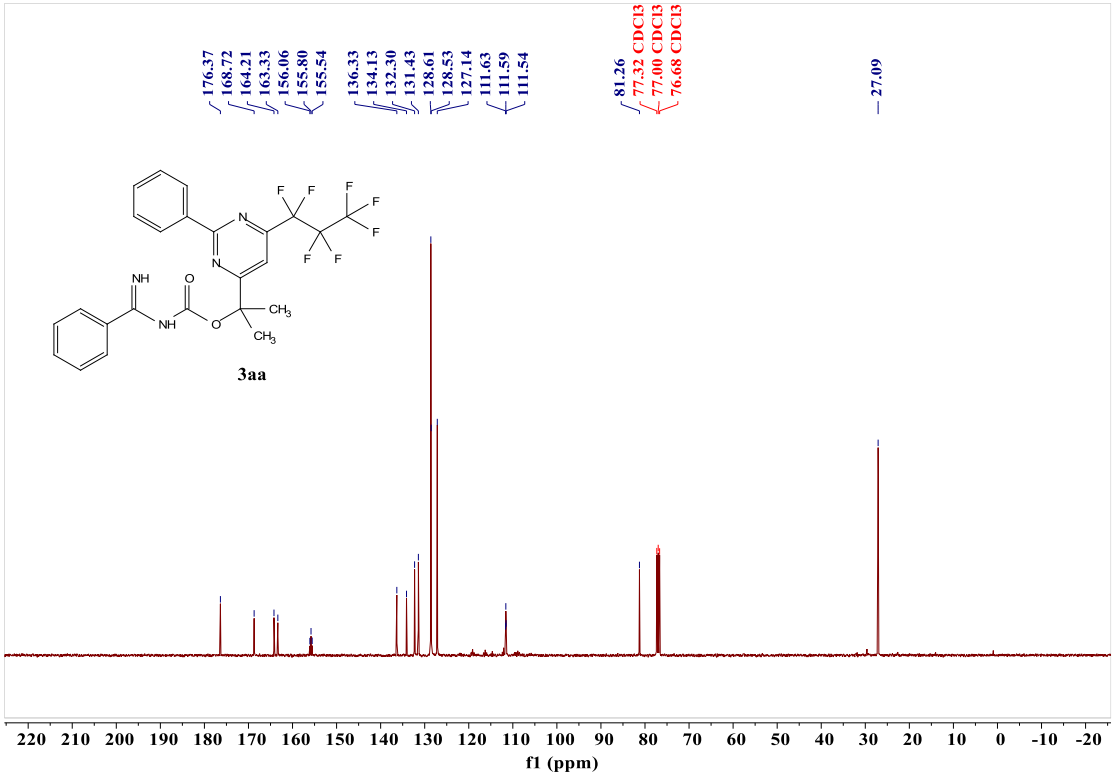
^{1}H NMR spectra of the product **3aa**



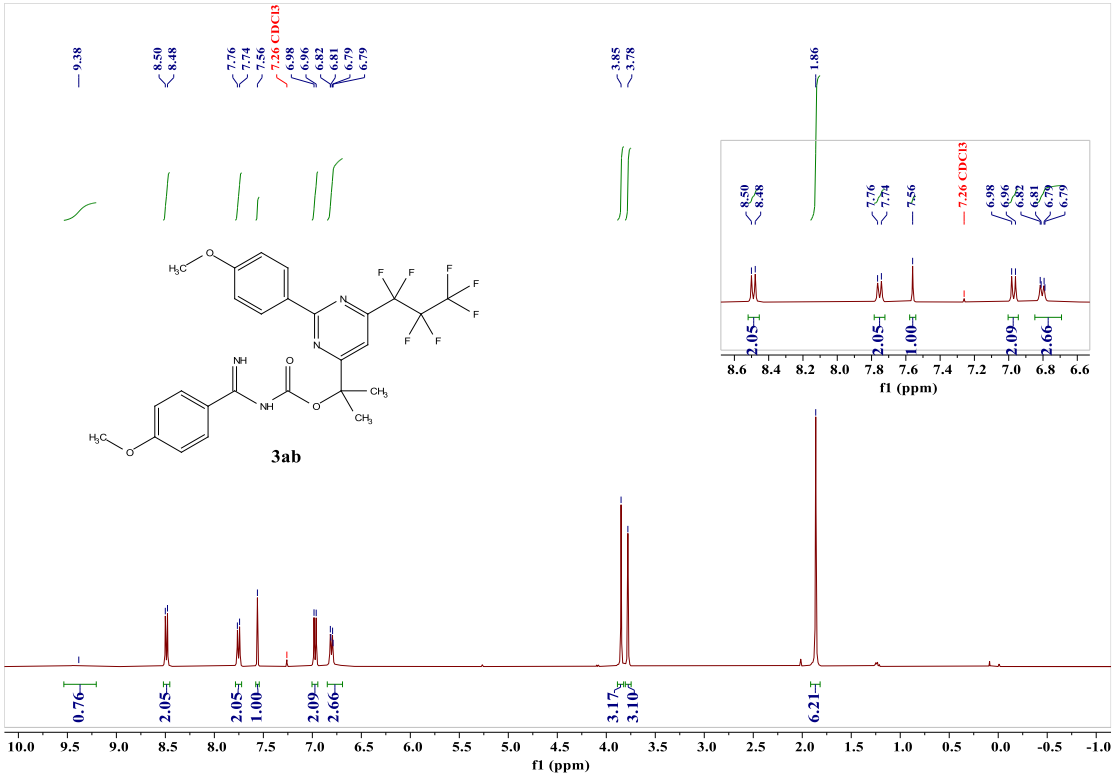
^{19}F NMR spectra of the product **3aa**



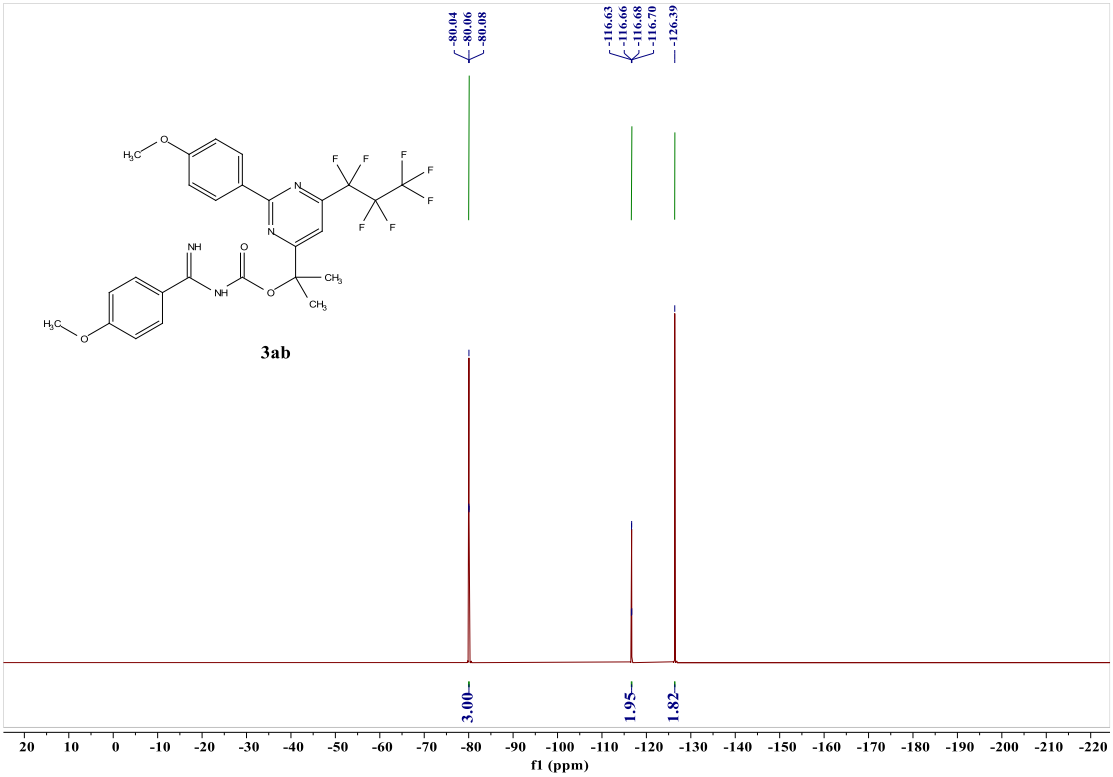
^{13}C NMR spectra of the product **3aa**



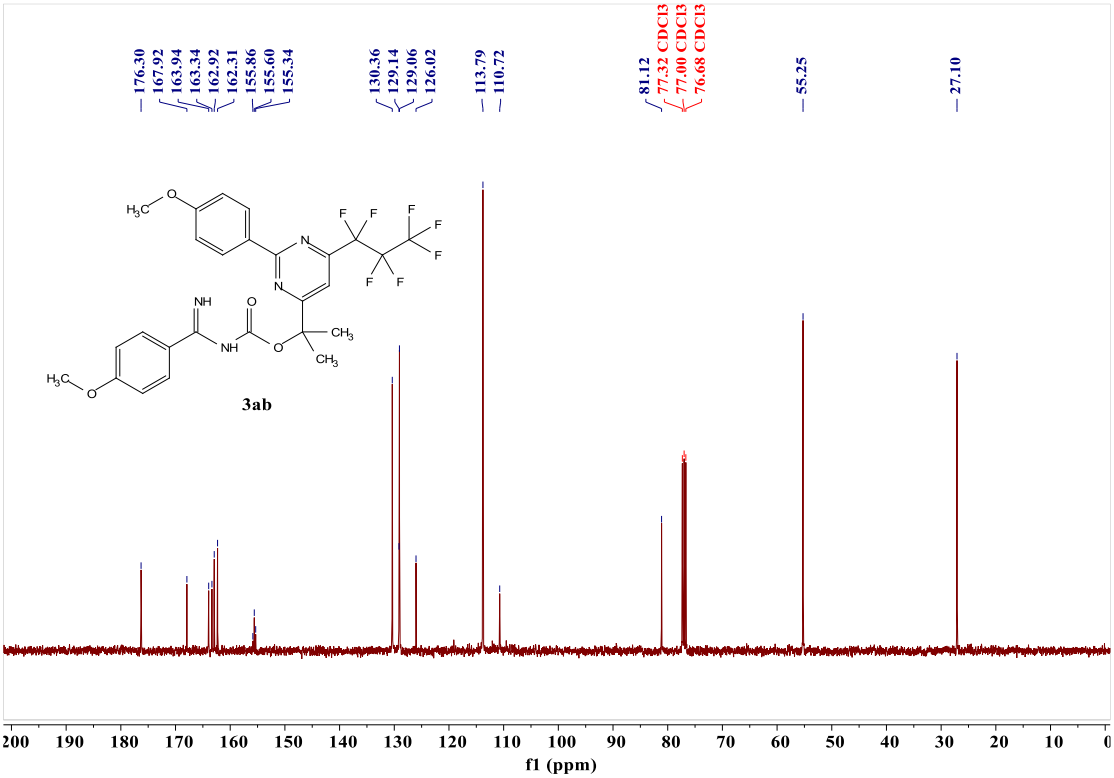
^{1}H NMR spectra of the product **3ab**



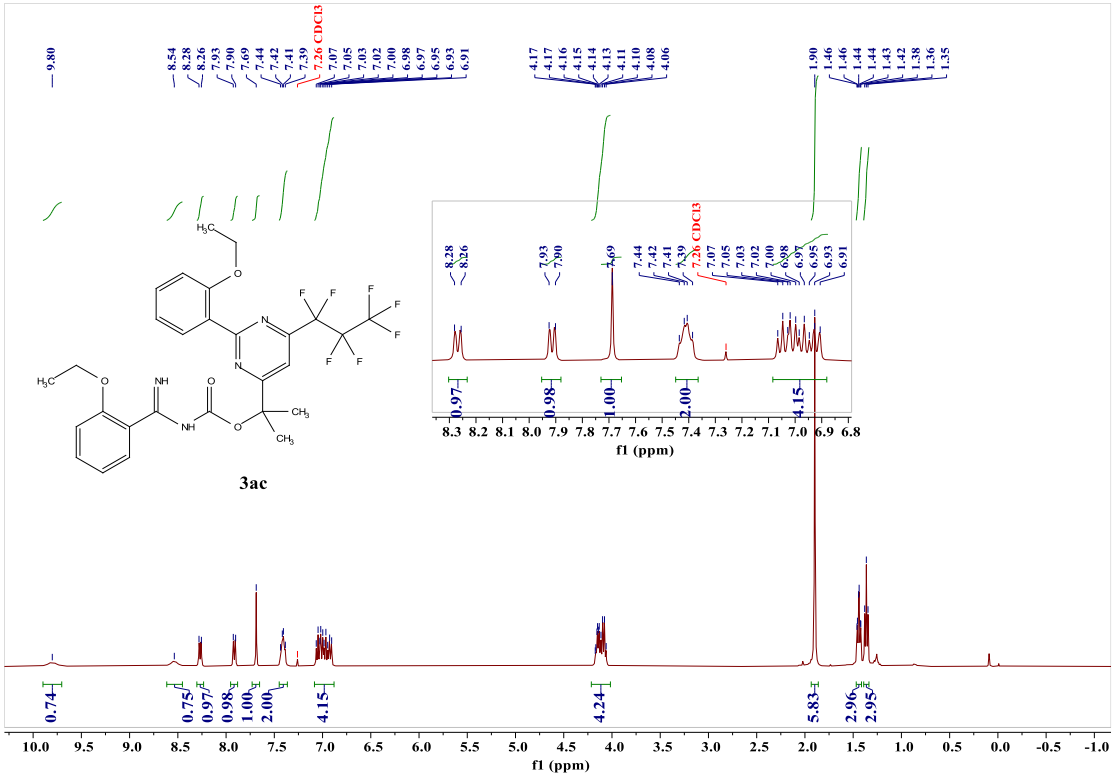
^{19}F NMR spectra of the product **3ab**



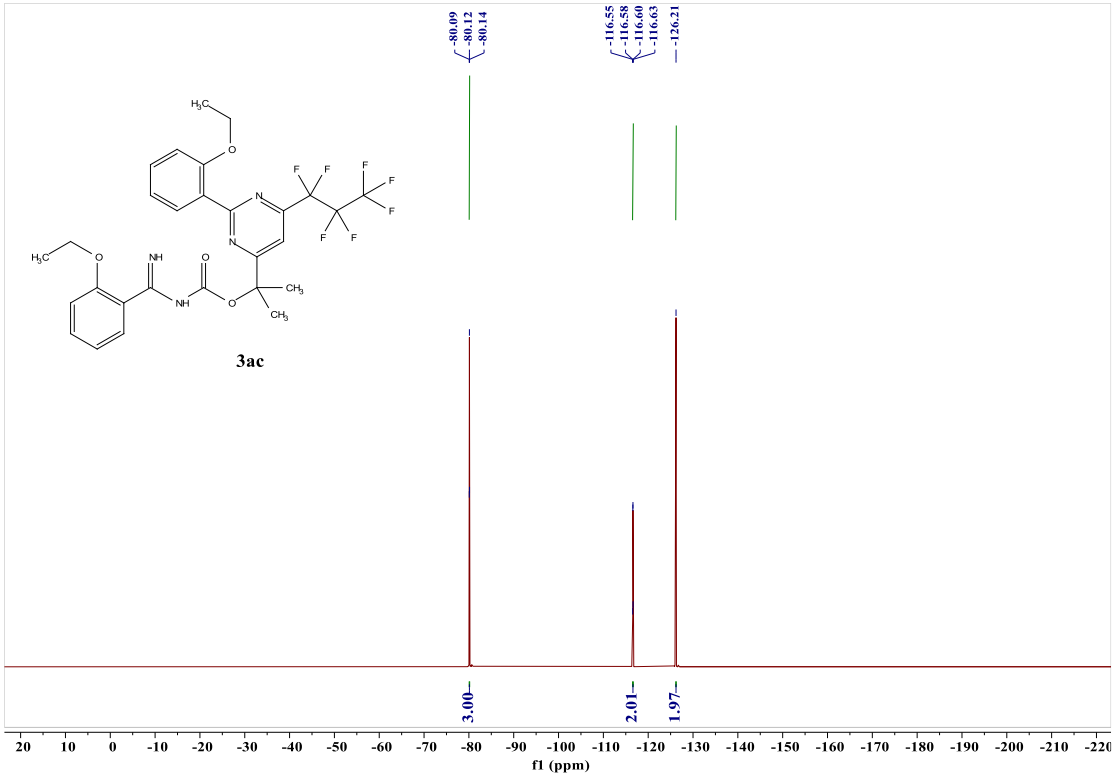
^{13}C NMR spectra of the product **3ab**



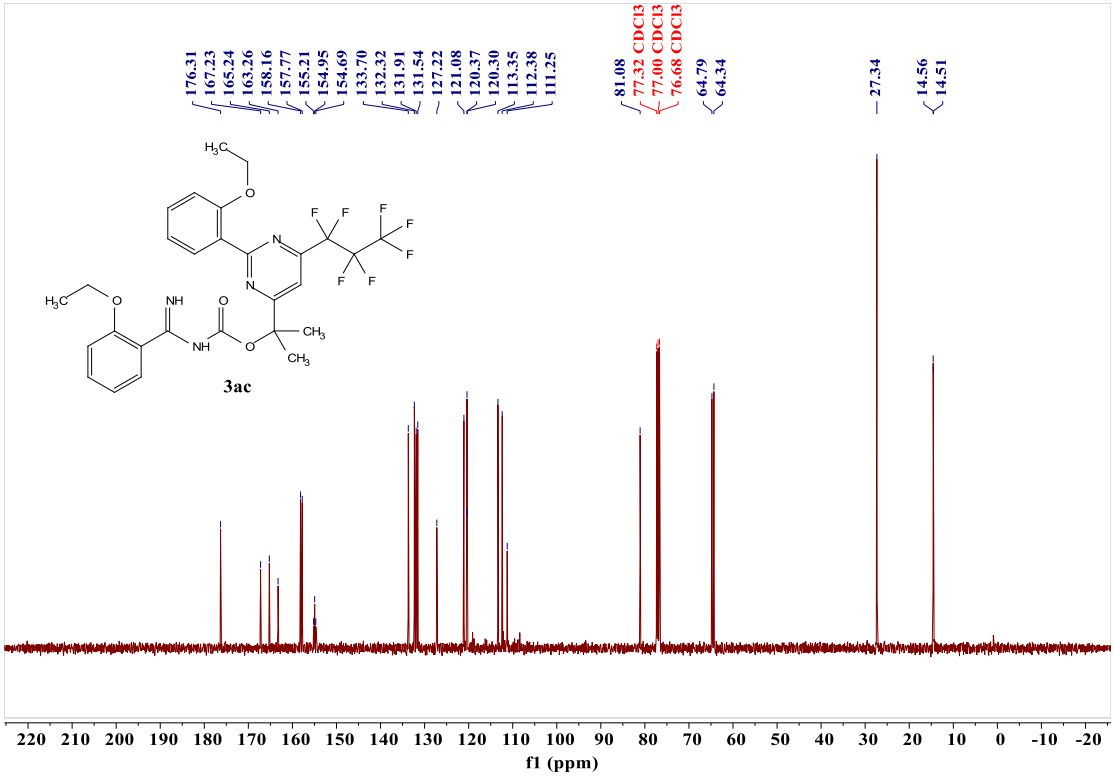
^{1}H NMR spectra of the product **3ac**



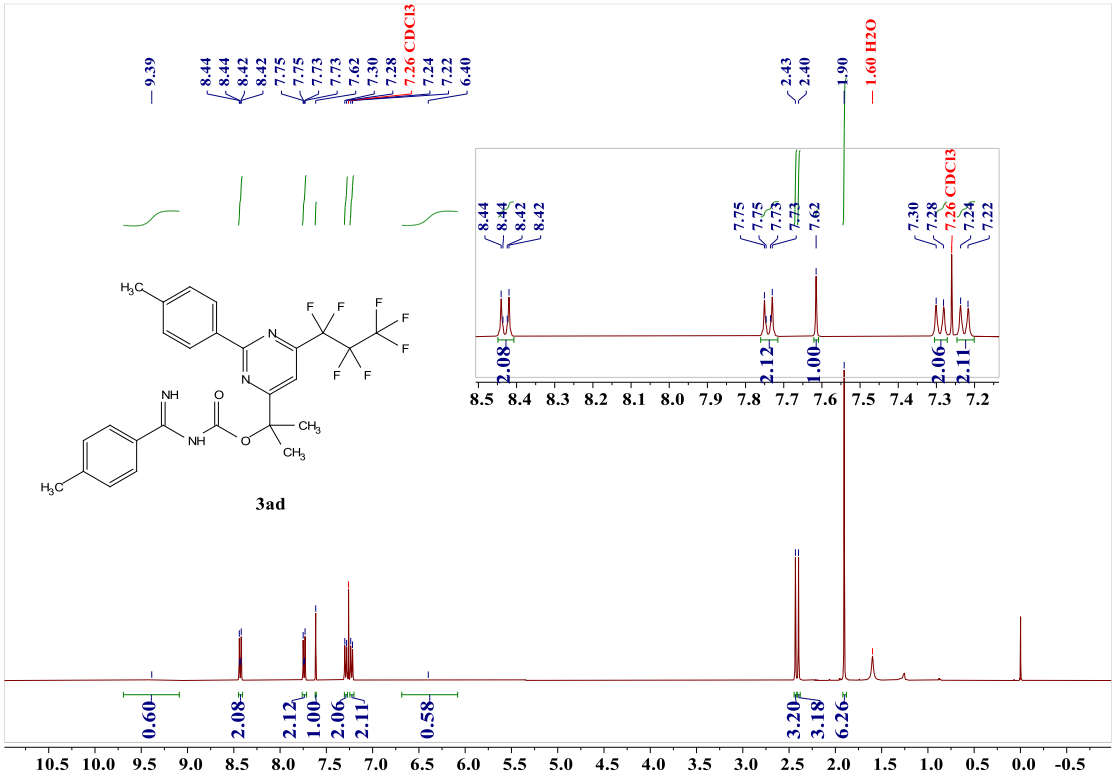
^{19}F NMR spectra of the product **3ac**



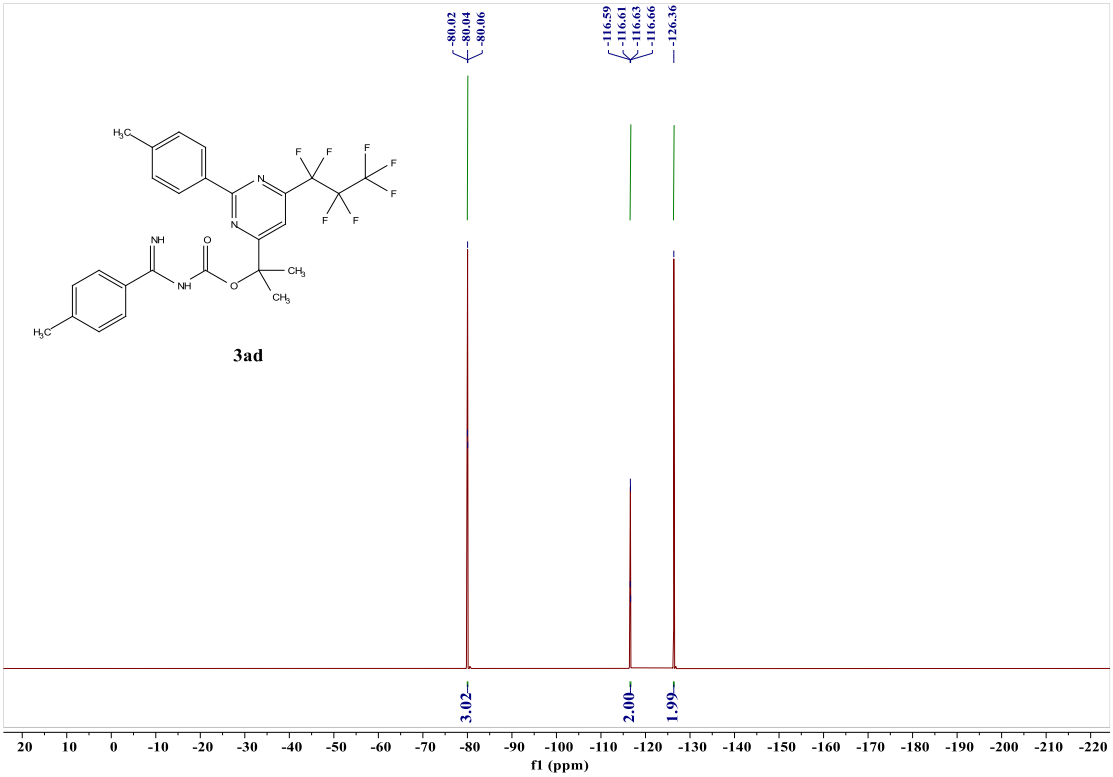
^{13}C NMR spectra of the product **3ac**



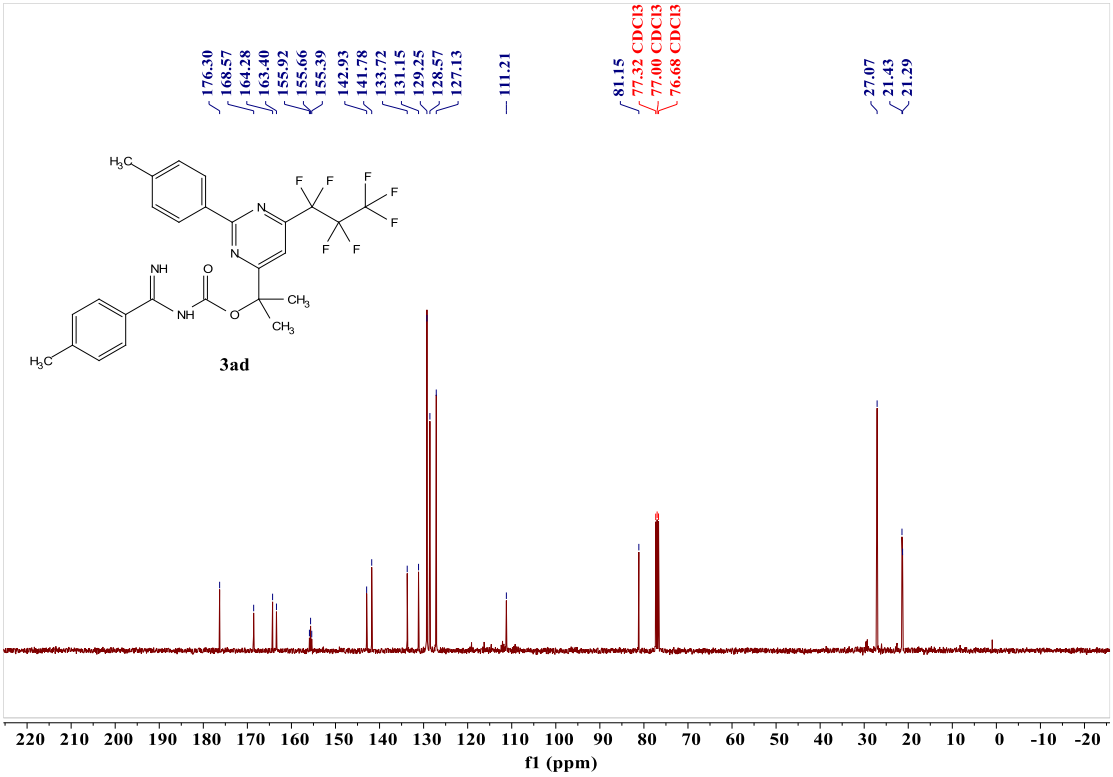
^{1}H NMR spectra of the product **3ad**



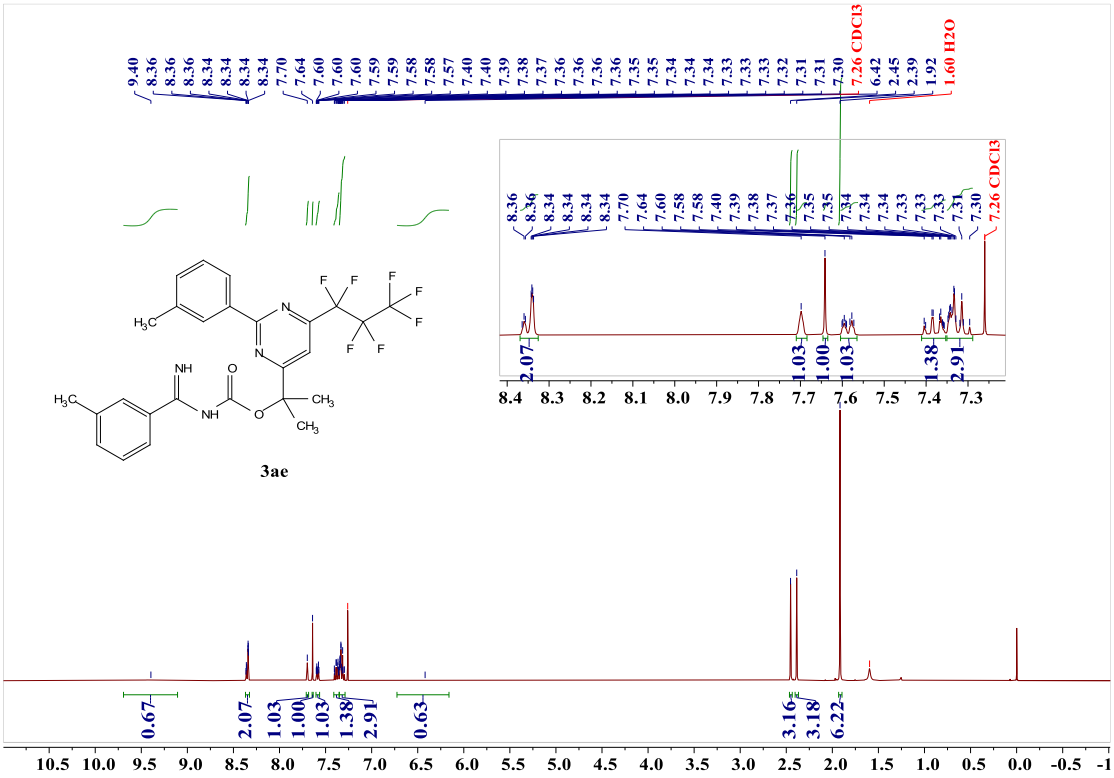
^{19}F NMR spectra of the product **3ad**



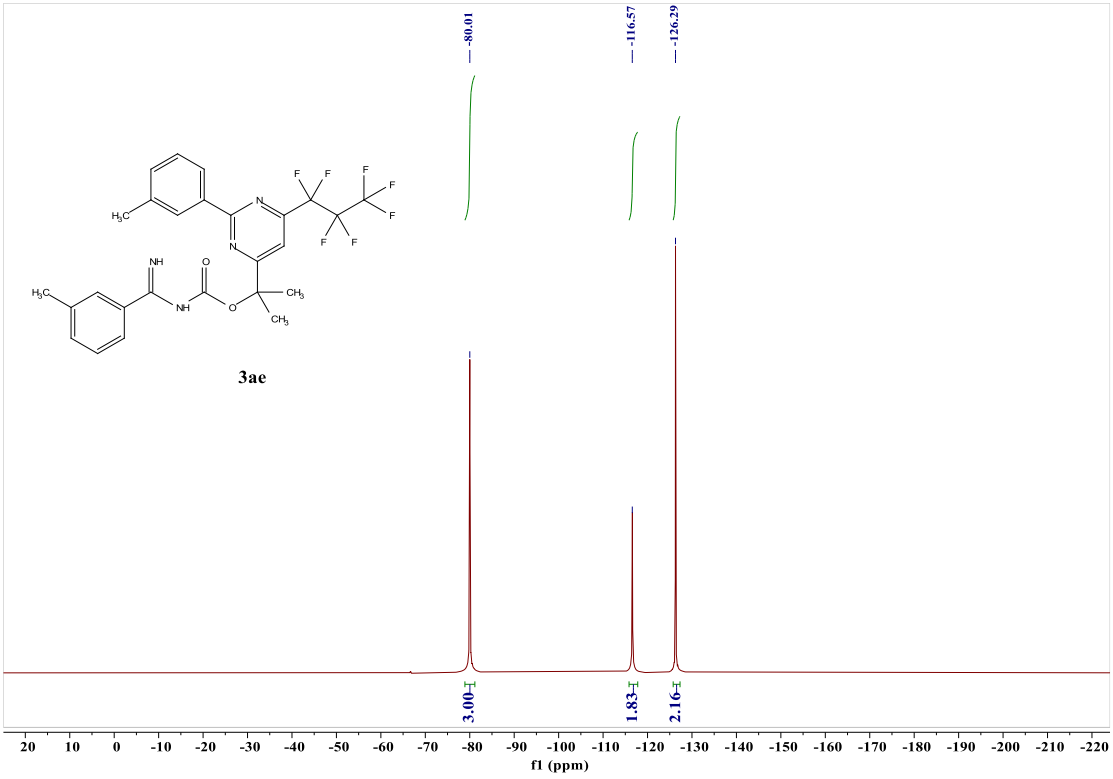
^{13}C NMR spectra of the product **3ad**



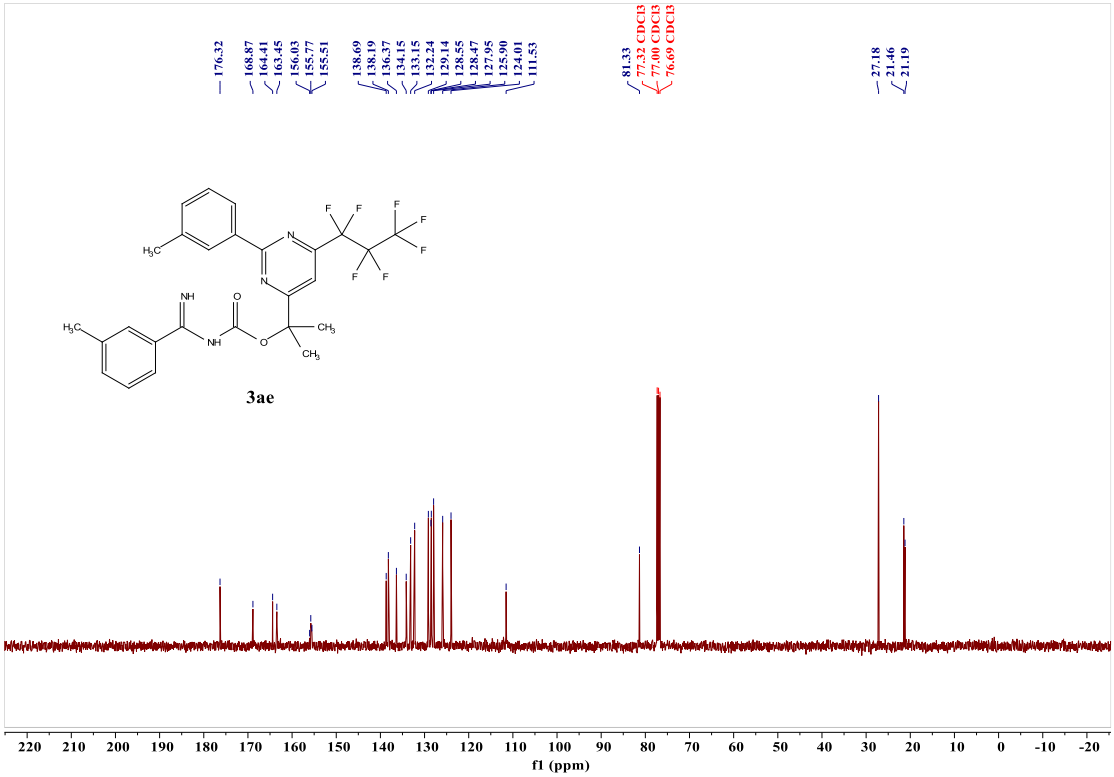
^{1}H NMR spectra of the product **3ae**



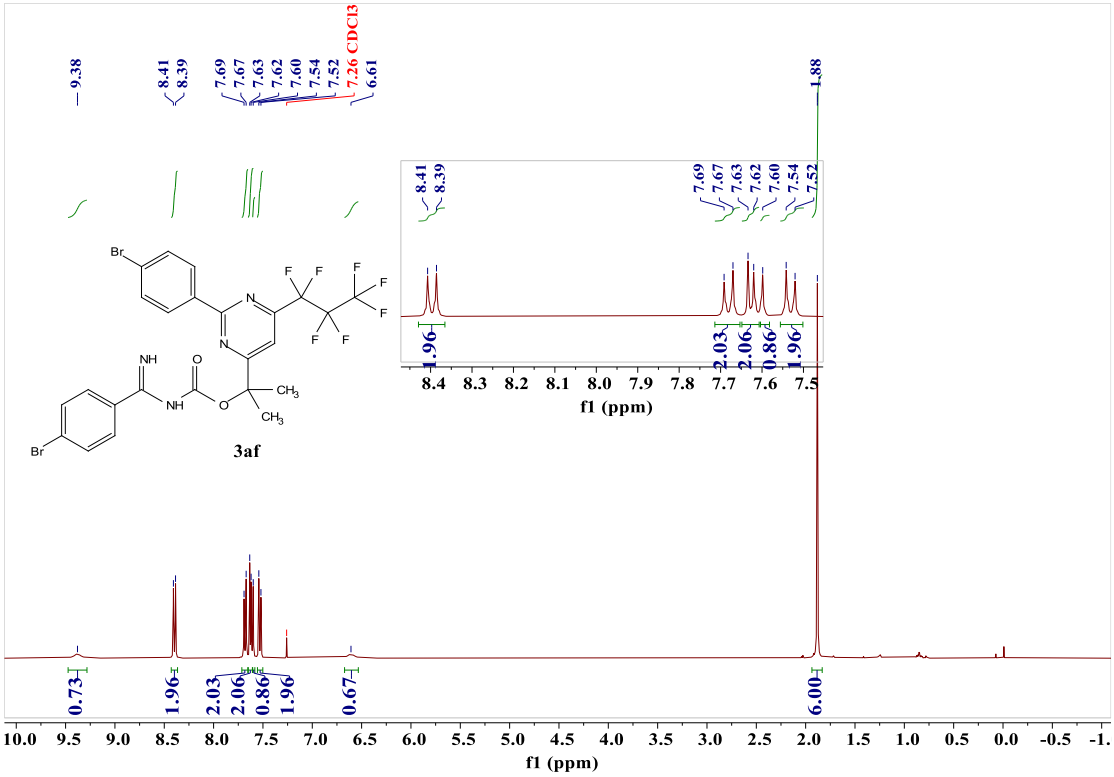
^{19}F NMR spectra of the product **3ae**



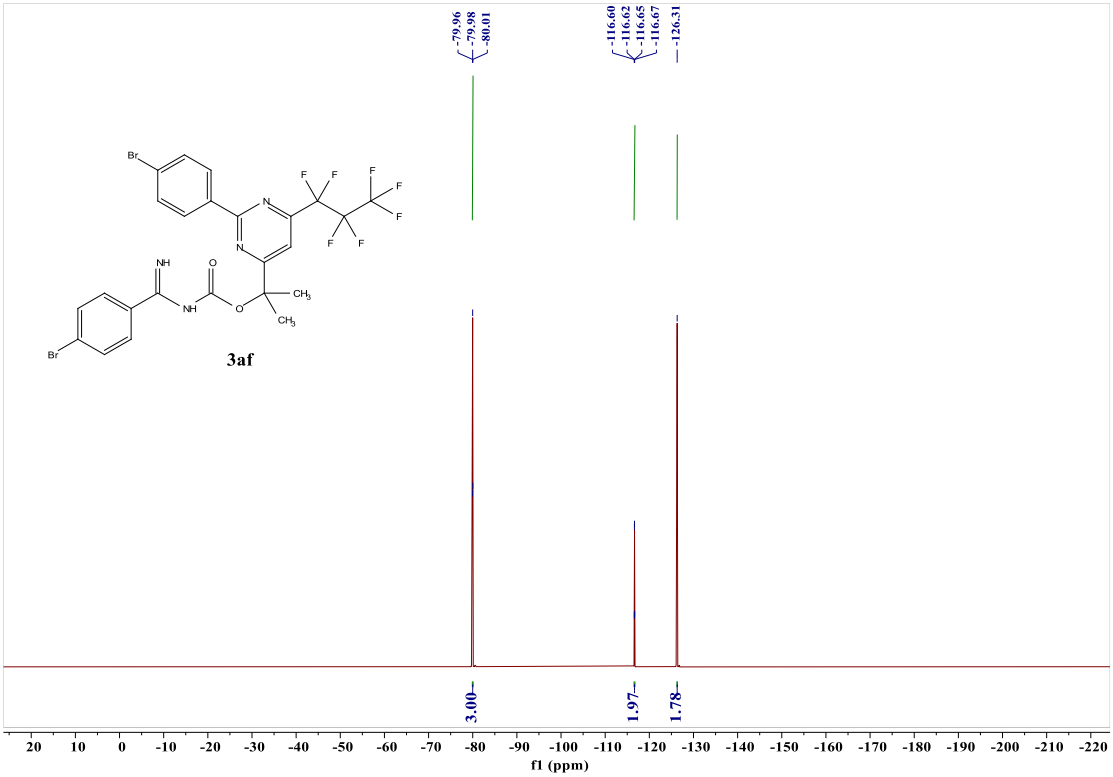
^{13}C NMR spectra of the product **3ae**



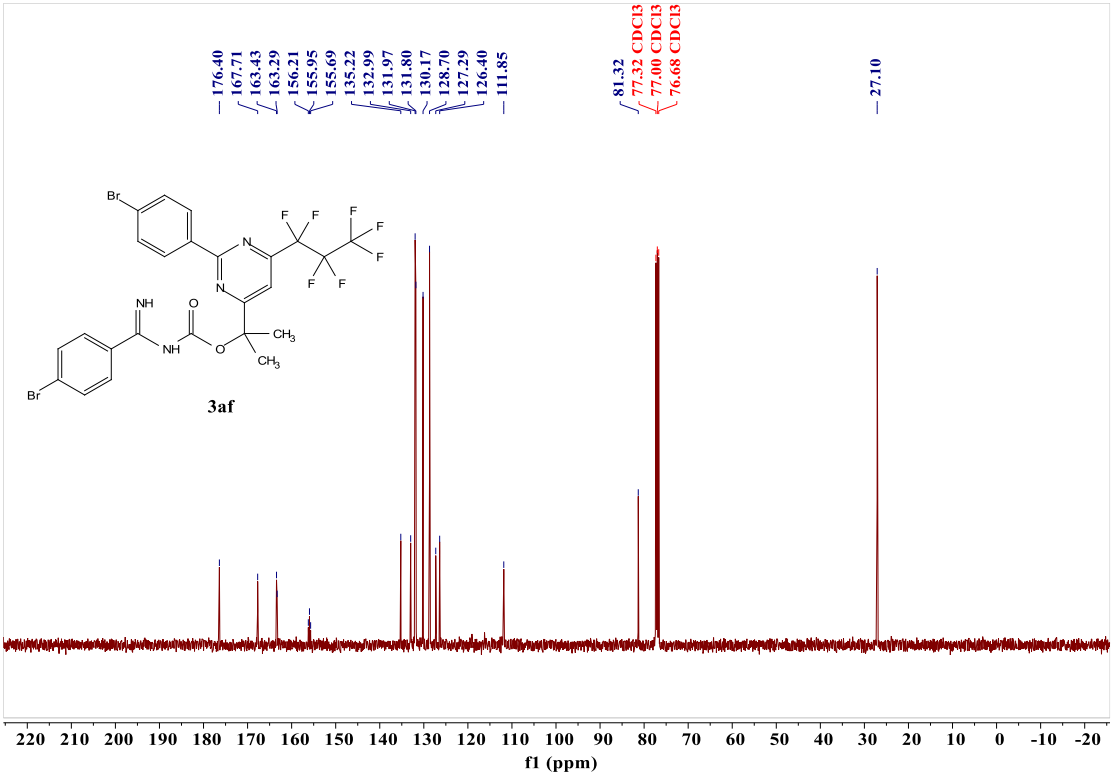
^{1}H NMR spectra of the product **3af**



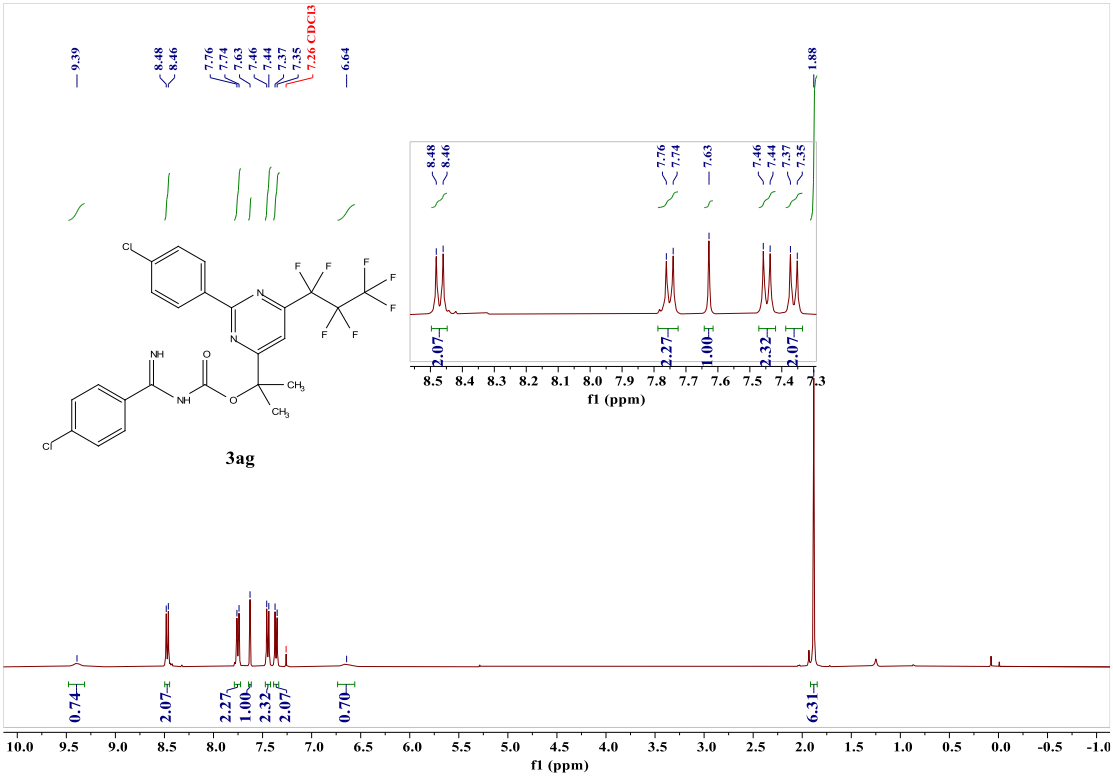
^{19}F NMR spectra of the product **3af**



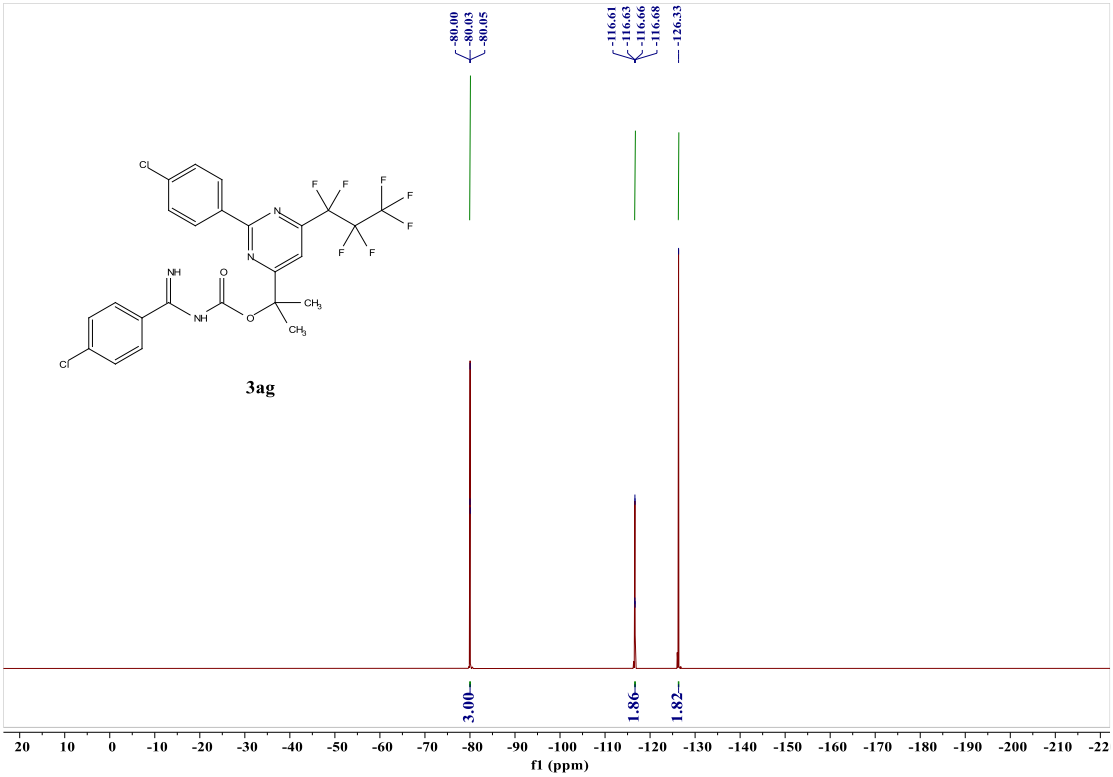
^{13}C NMR spectra of the product **3af**



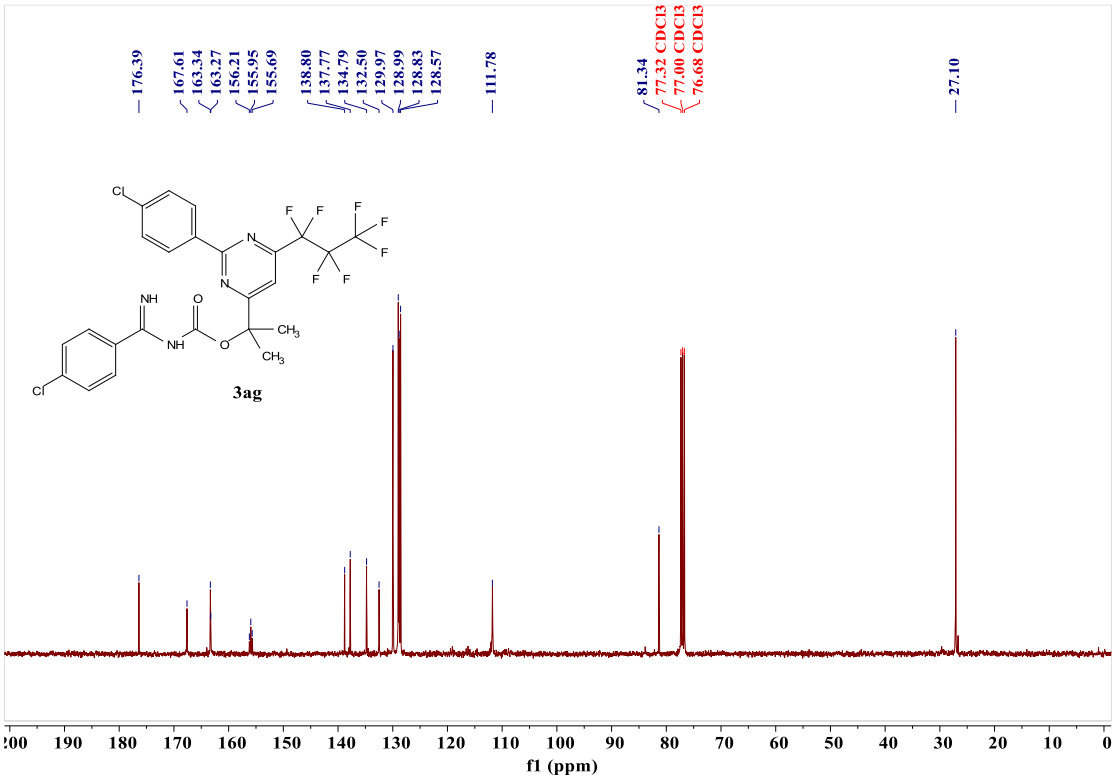
^{1}H NMR spectra of the product **3ag**



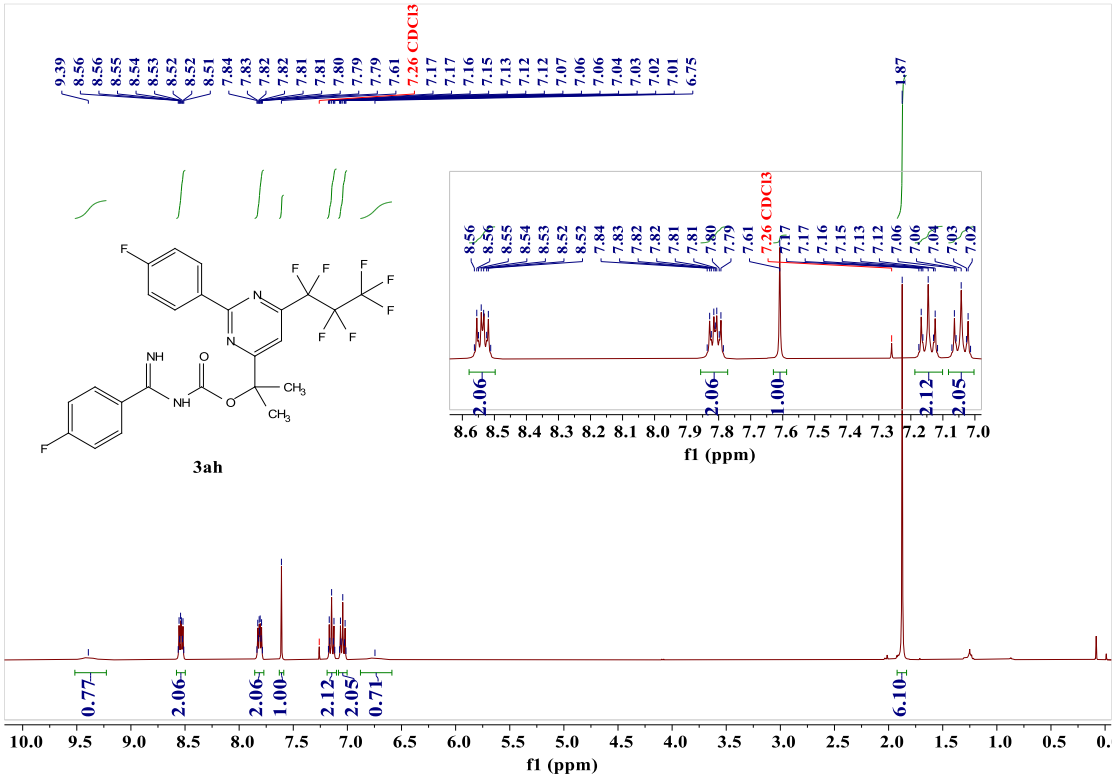
^{19}F NMR spectra of the product **3ag**



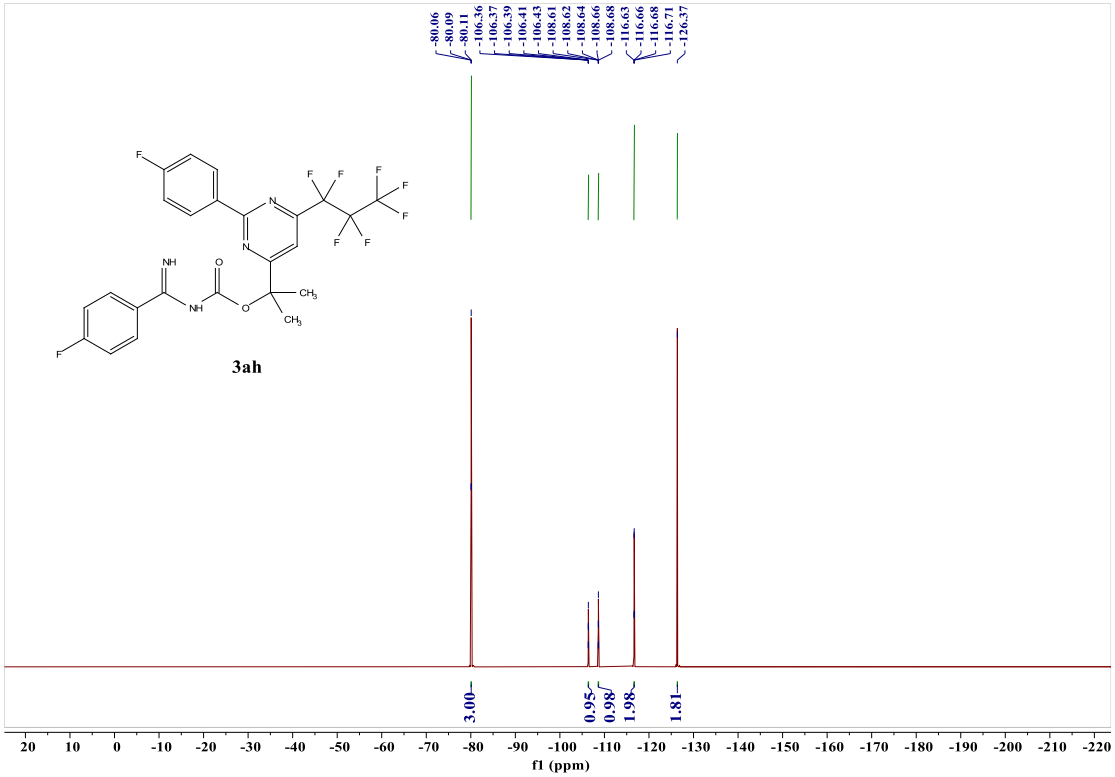
^{13}C NMR spectra of the product **3ag**



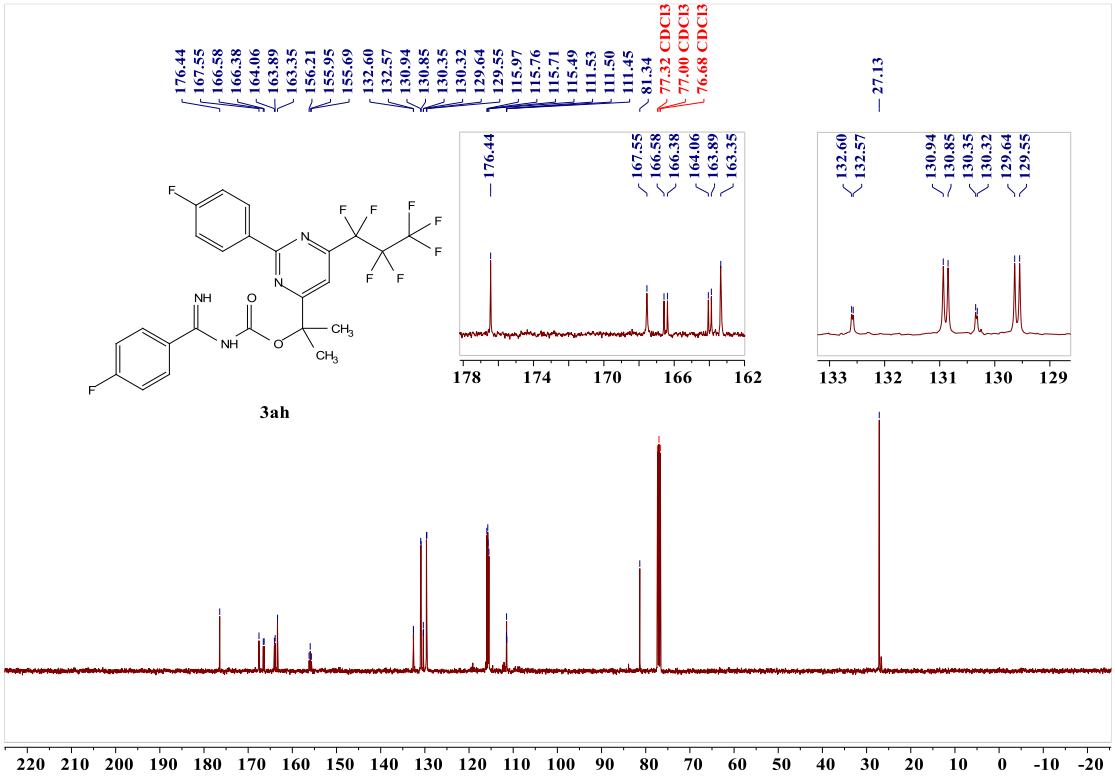
^{1}H NMR spectra of the product **3ah**



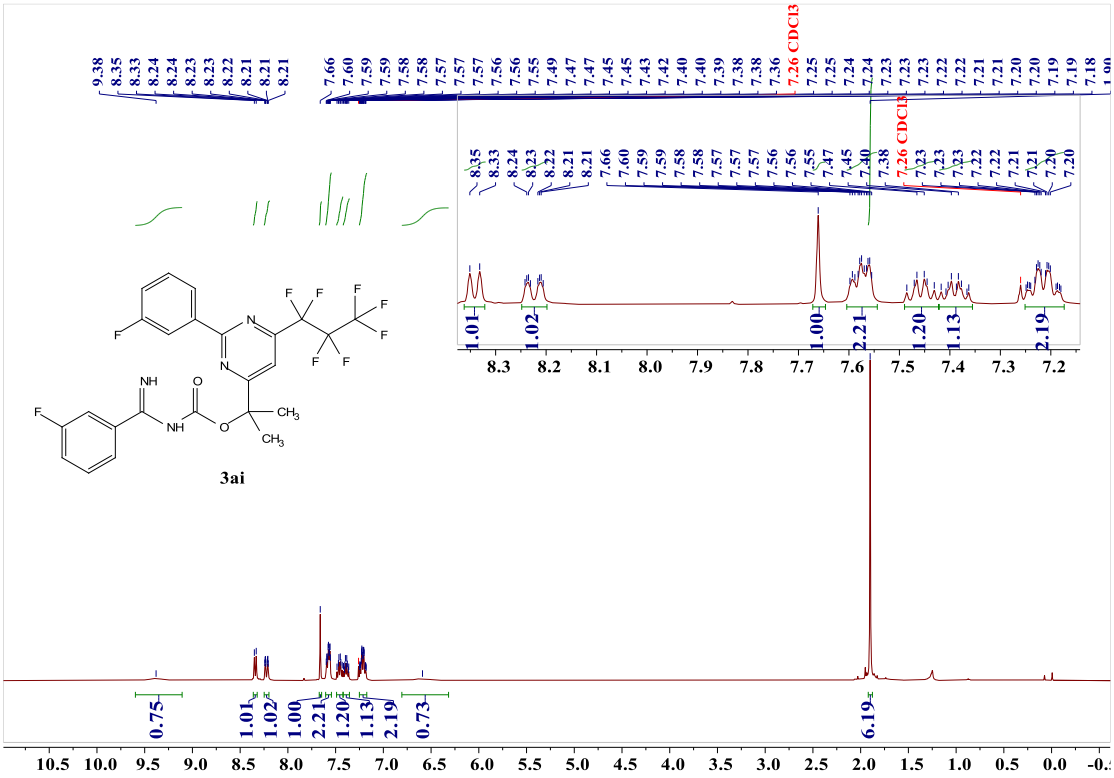
^{19}F NMR spectra of the product **3ah**



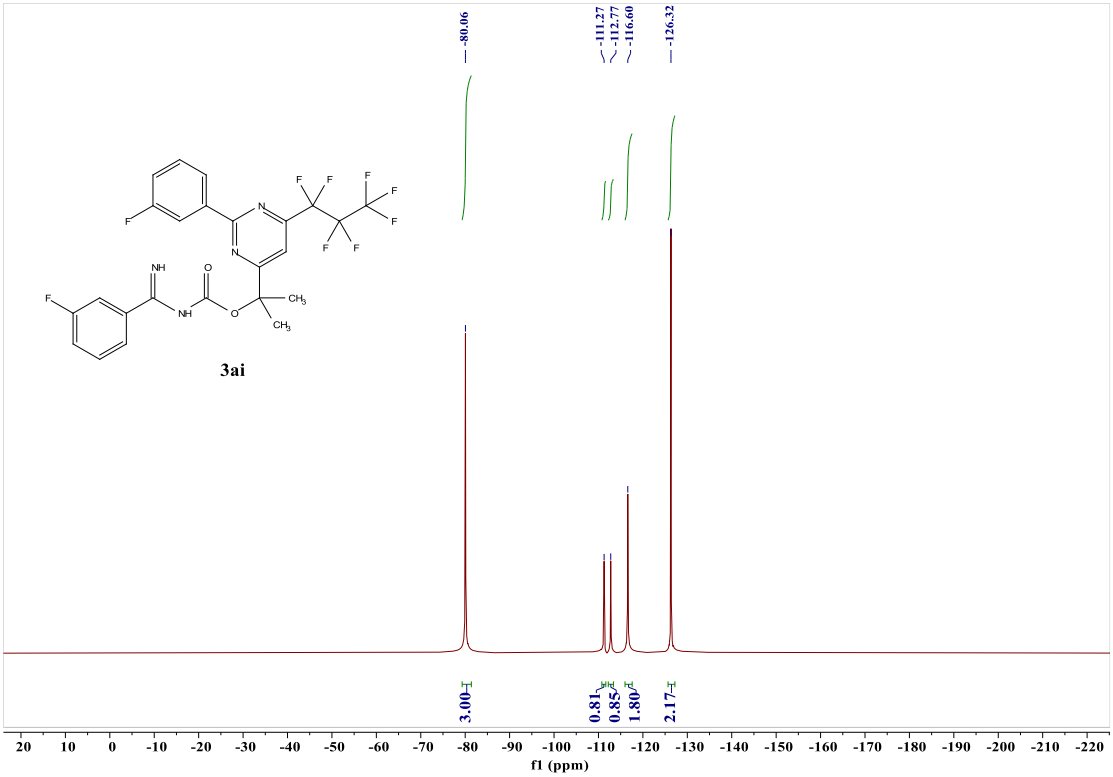
^{13}C NMR spectra of the product **3ah**



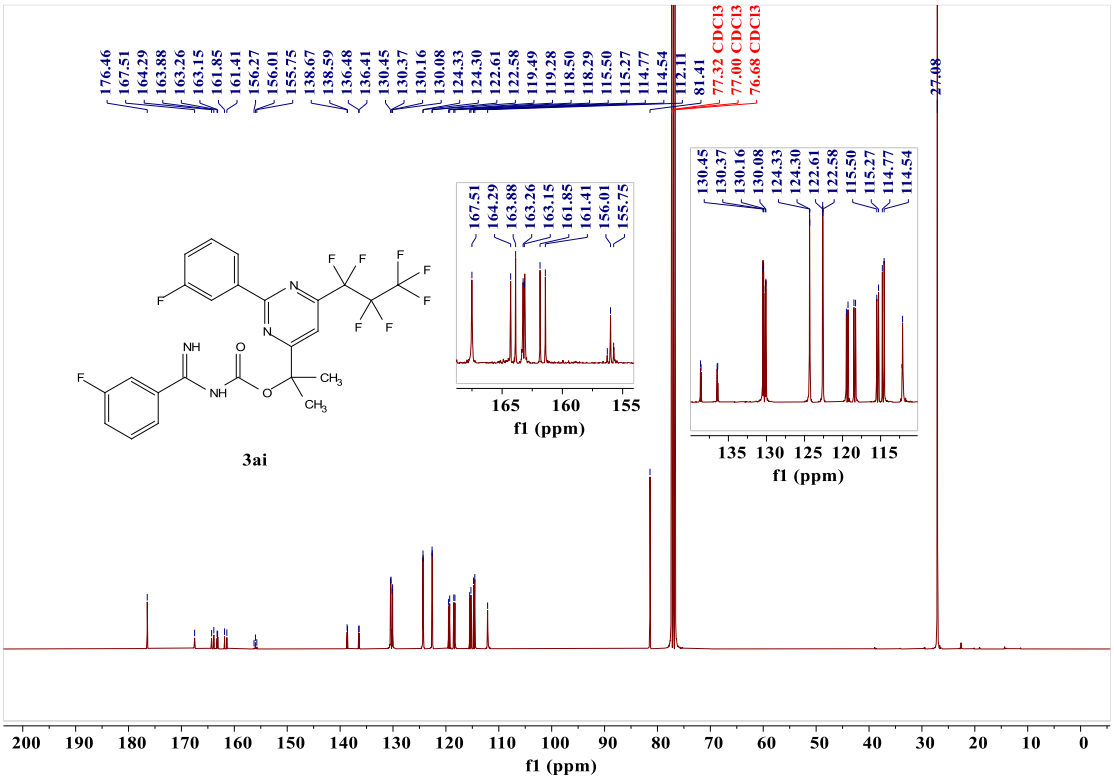
^{1}H NMR spectra of the product **3ai**



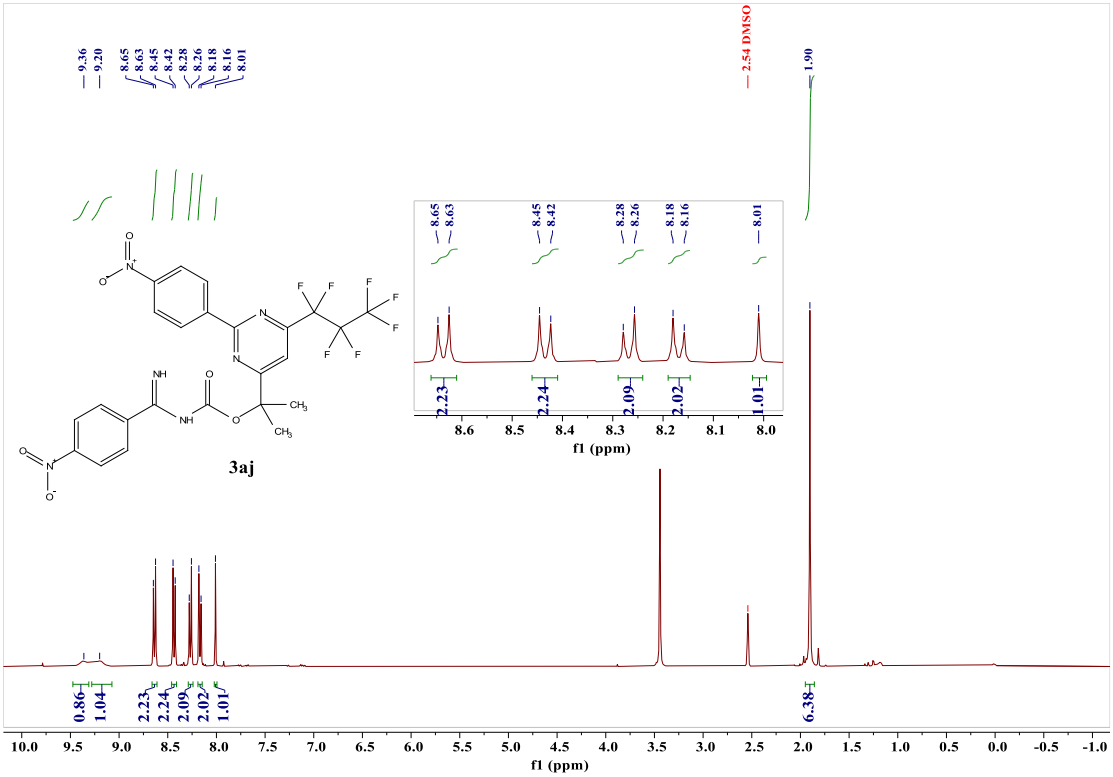
^{19}F NMR spectra of the product **3ai**



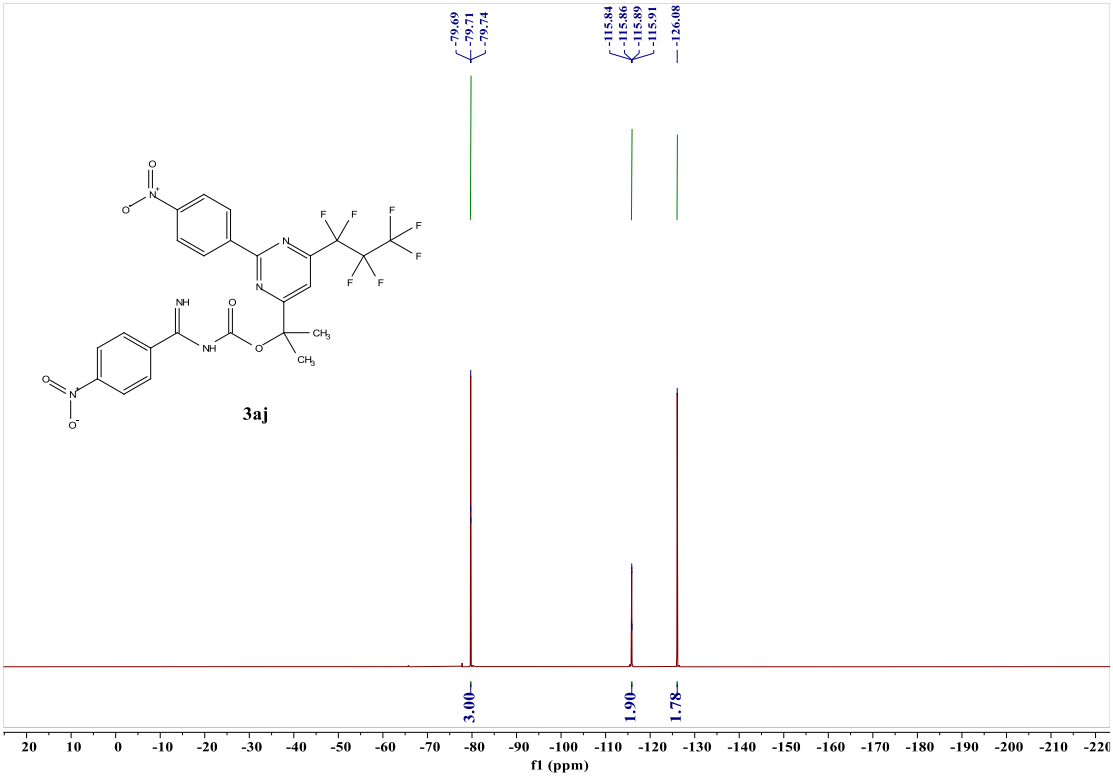
^{13}C NMR spectra of the product **3ai**



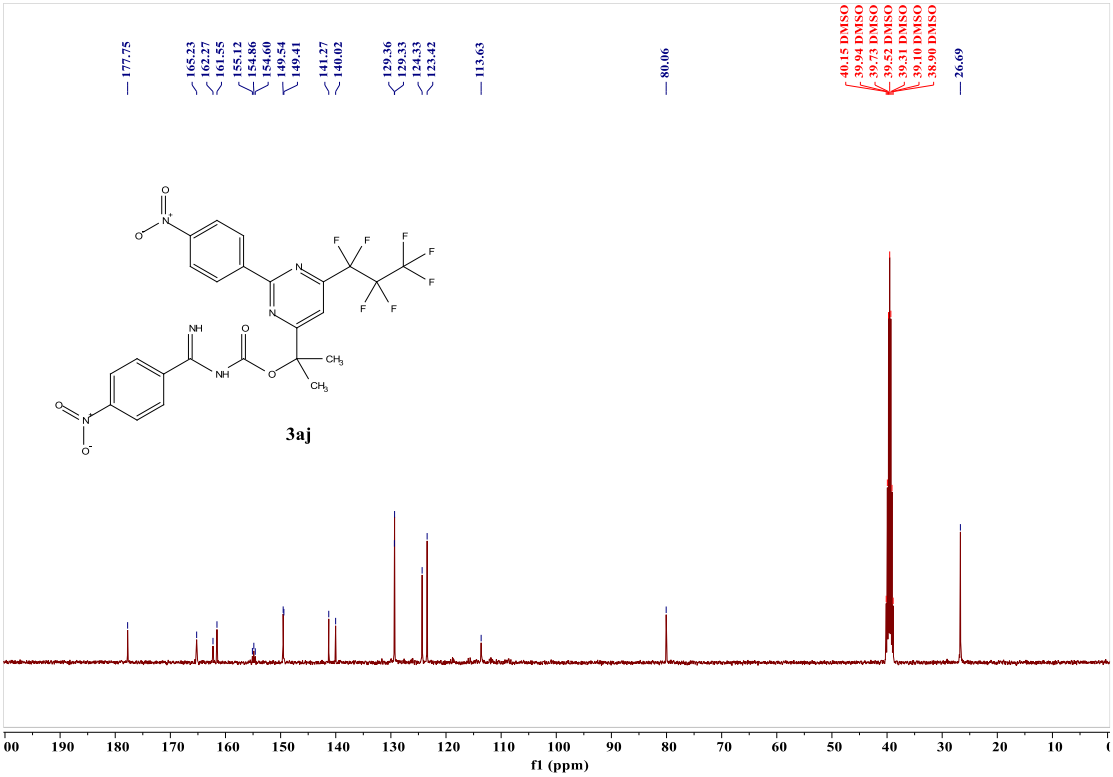
^{1}H NMR spectra of the product **3aj**



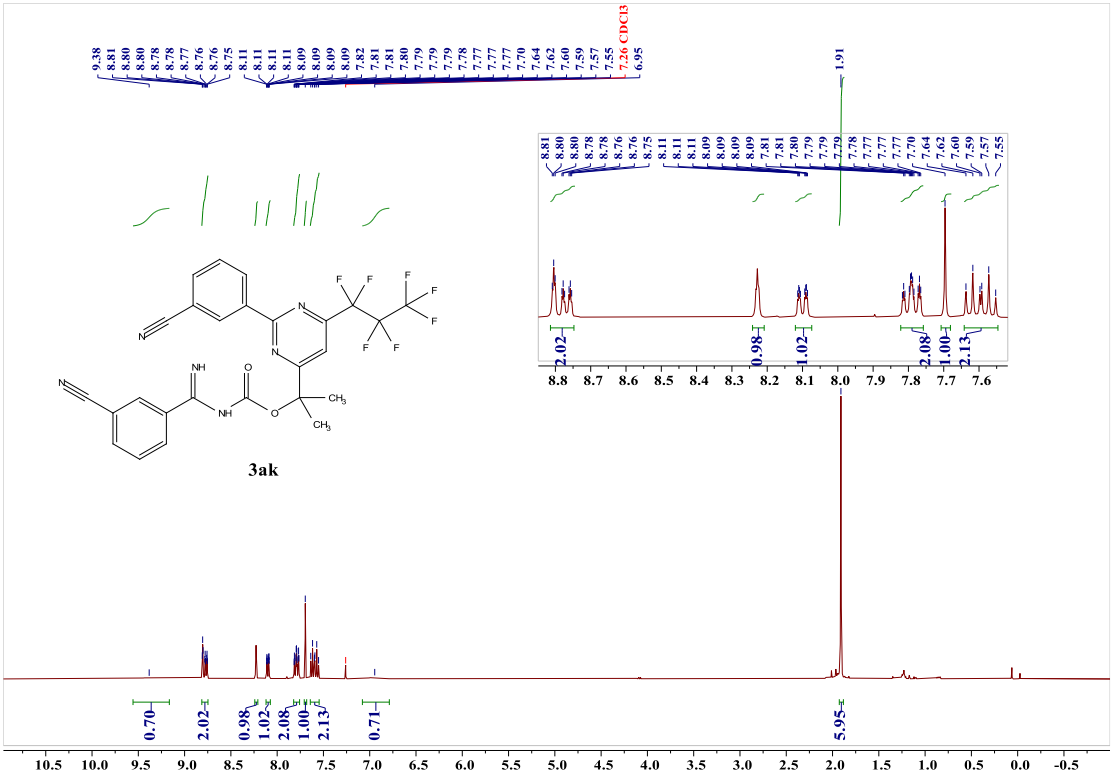
^{19}F NMR spectra of the product **3aj**



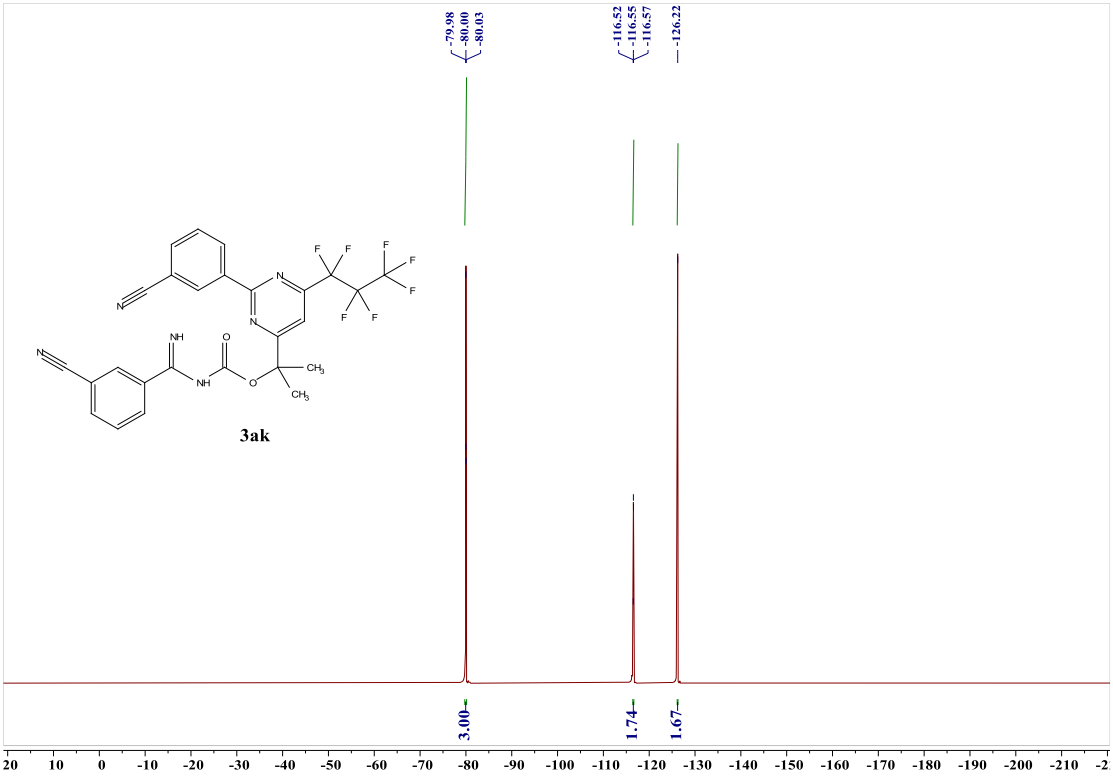
^{13}C NMR spectra of the product **3aj**



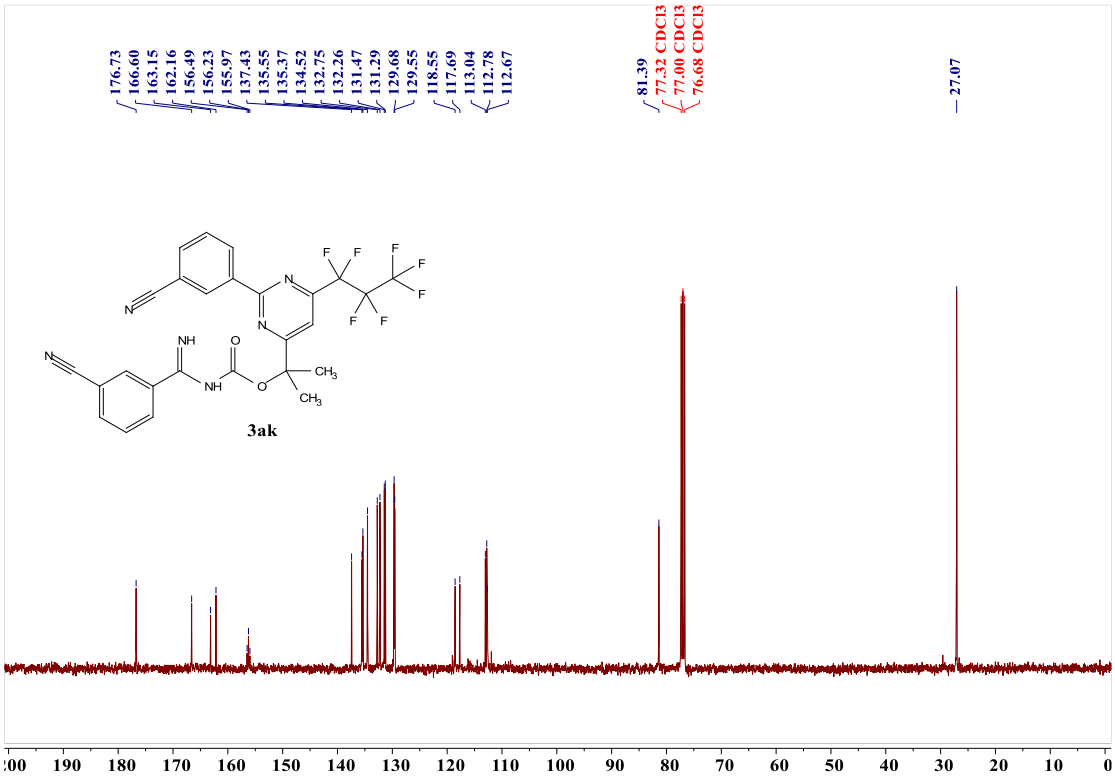
^{1}H NMR spectra of the product **3ak**



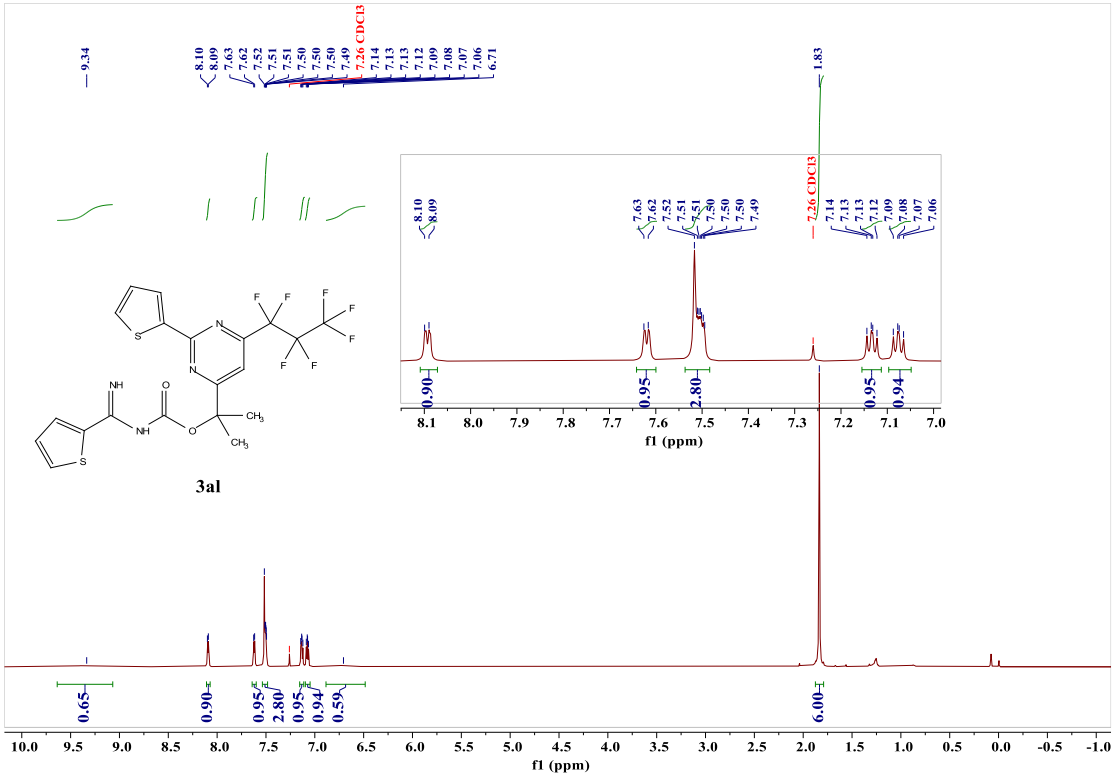
^{19}F NMR spectra of the product **3ak**



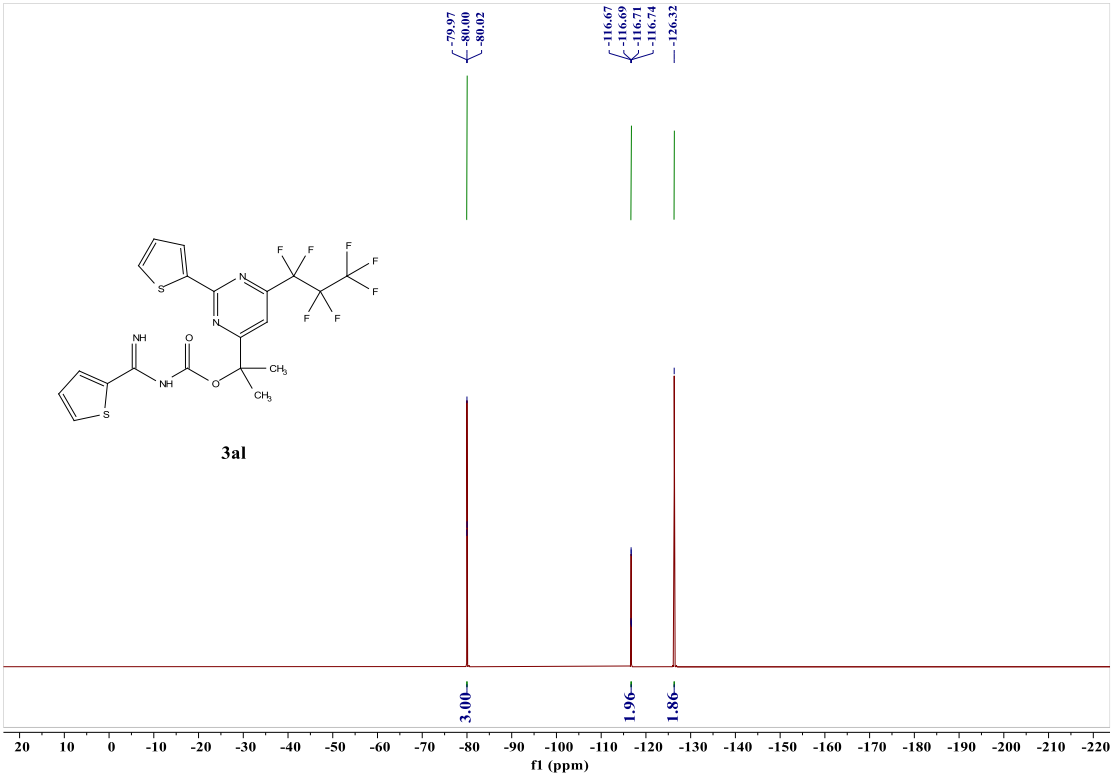
^{13}C NMR spectra of the product **3ak**



^{1}H NMR spectra of the product **3al**

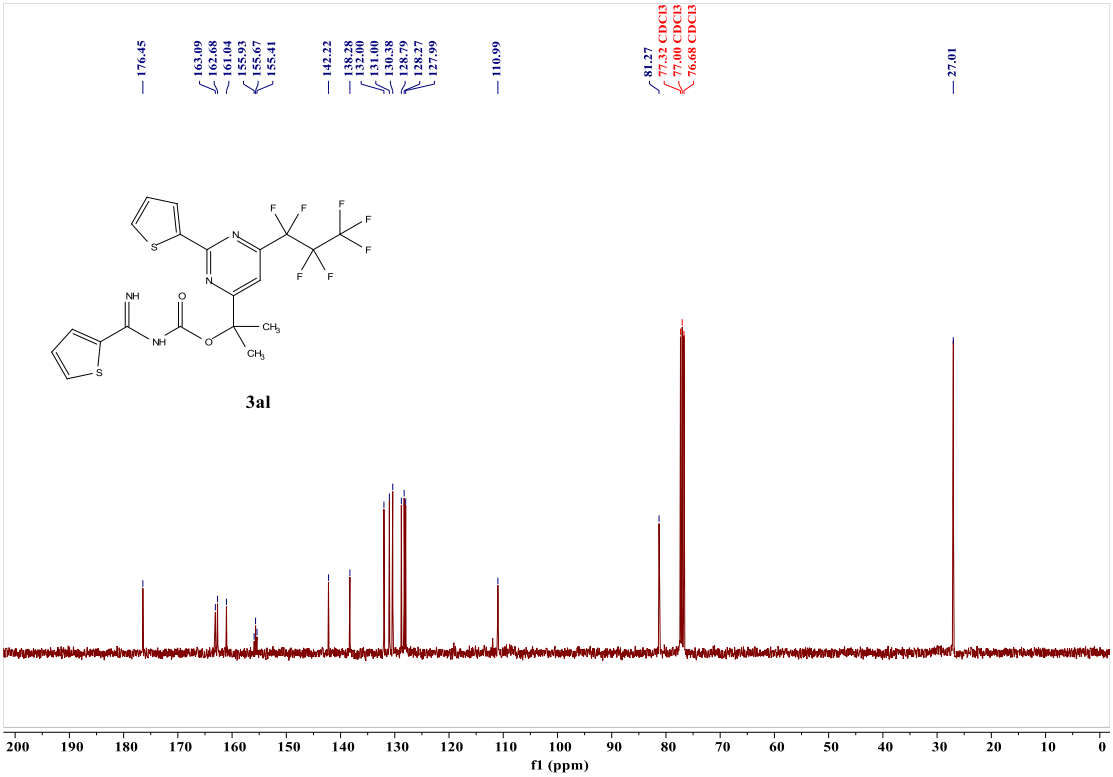


^{19}F NMR spectra of the product **3al**



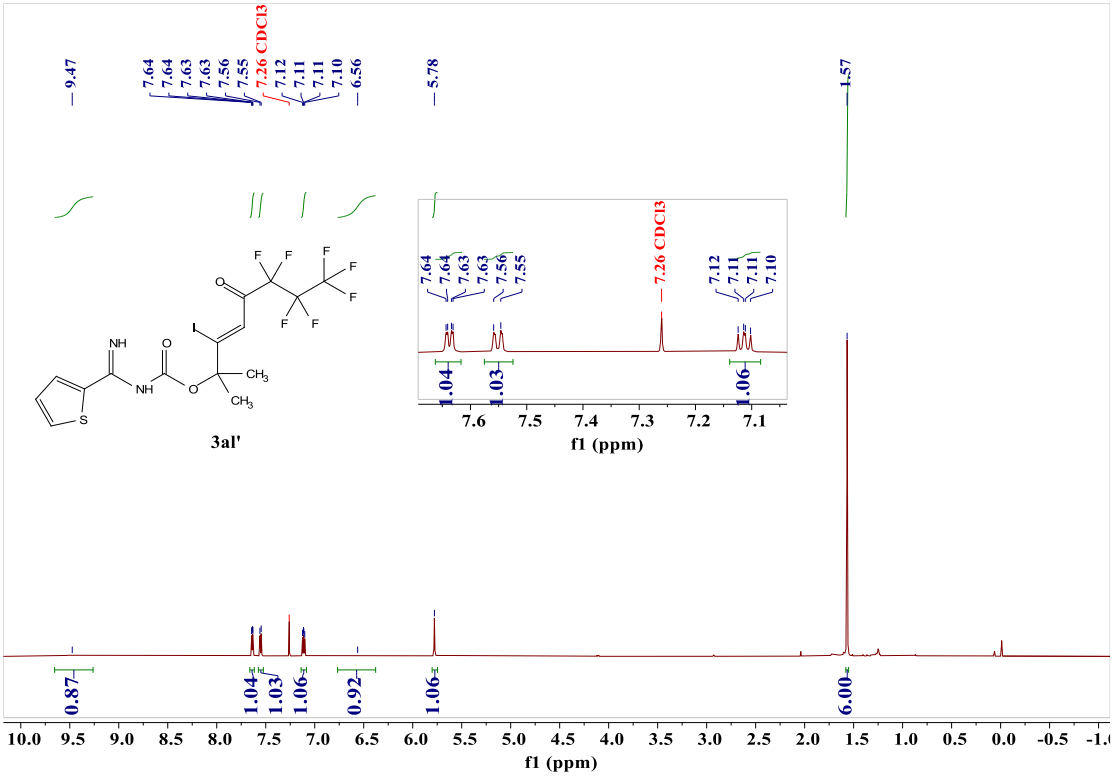
3al

^{13}C NMR spectra of the product **3al**

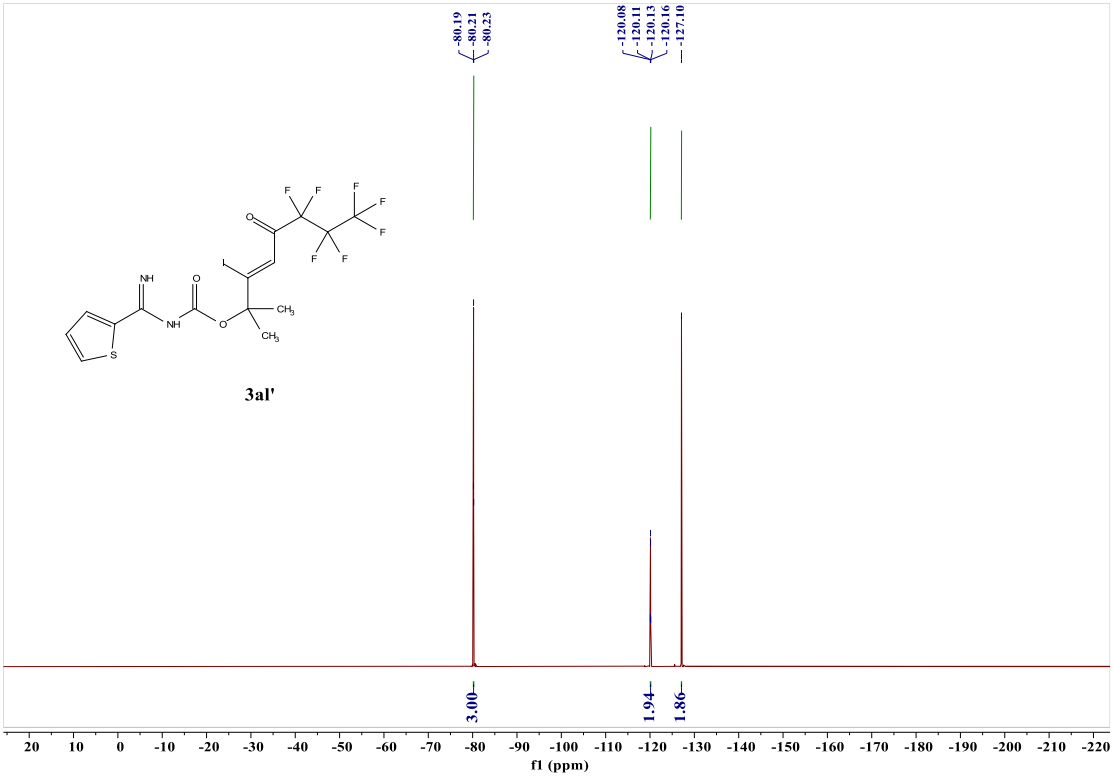


3al

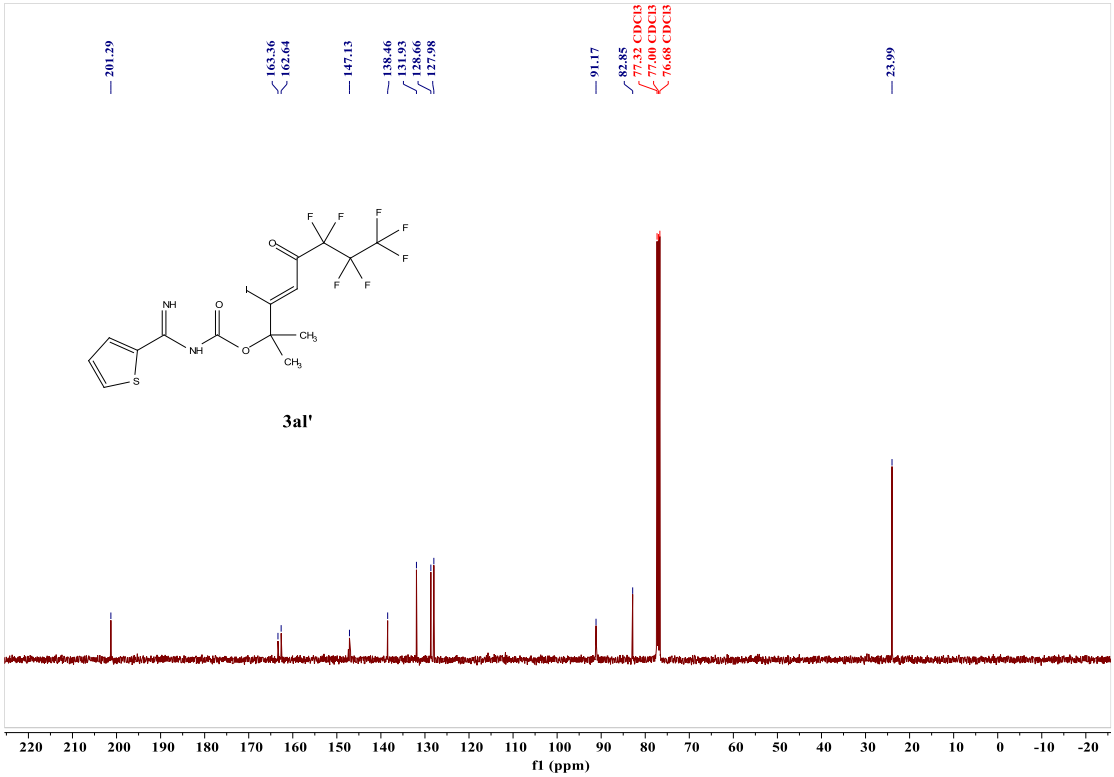
^{1}H NMR spectra of the product **3al'**



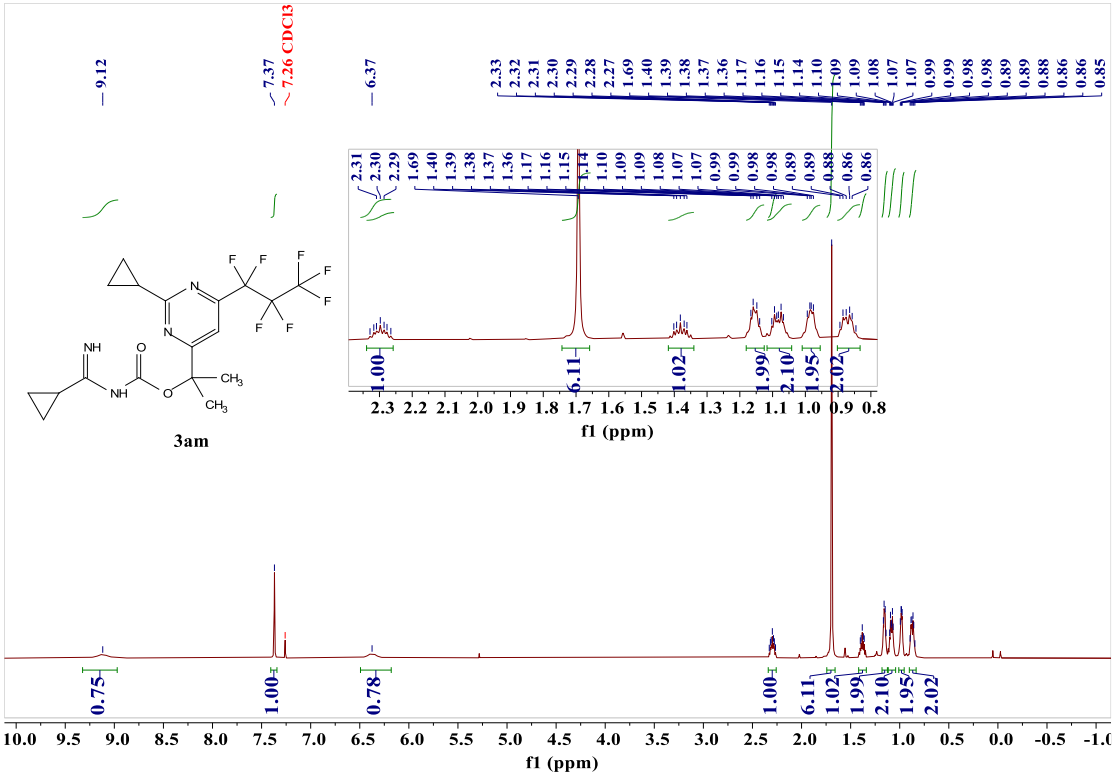
^{19}F NMR spectra of the product **3al'**



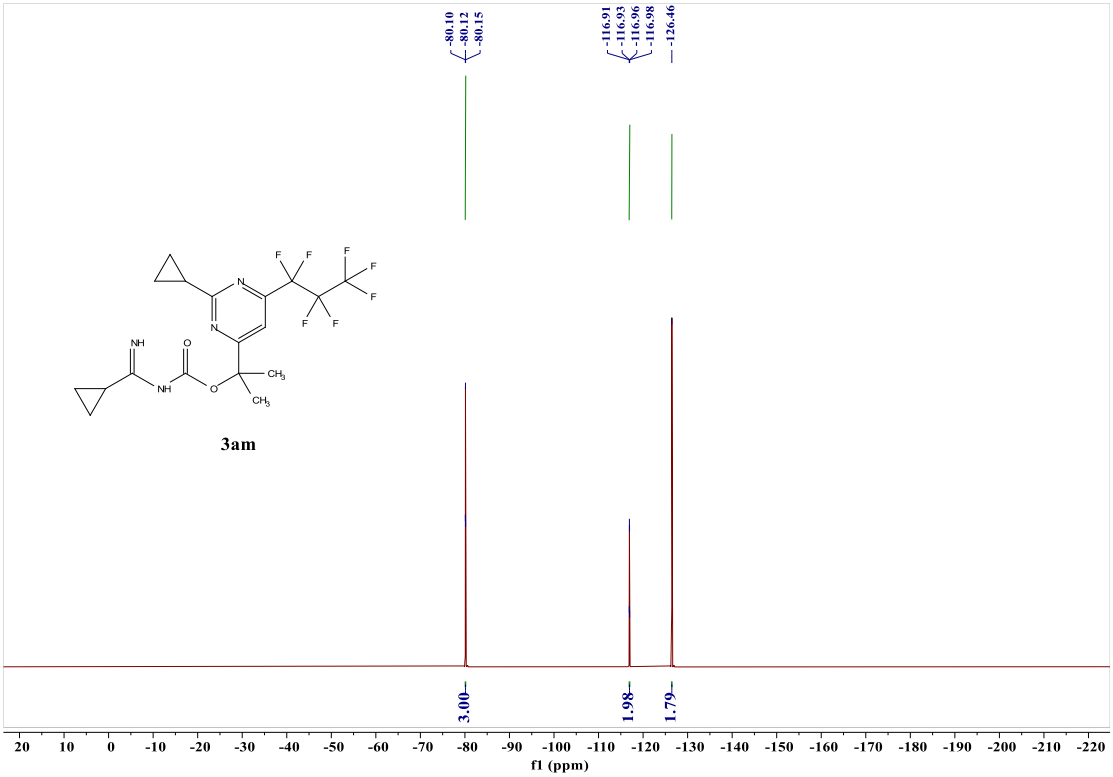
^{13}C NMR spectra of the product **3al'**



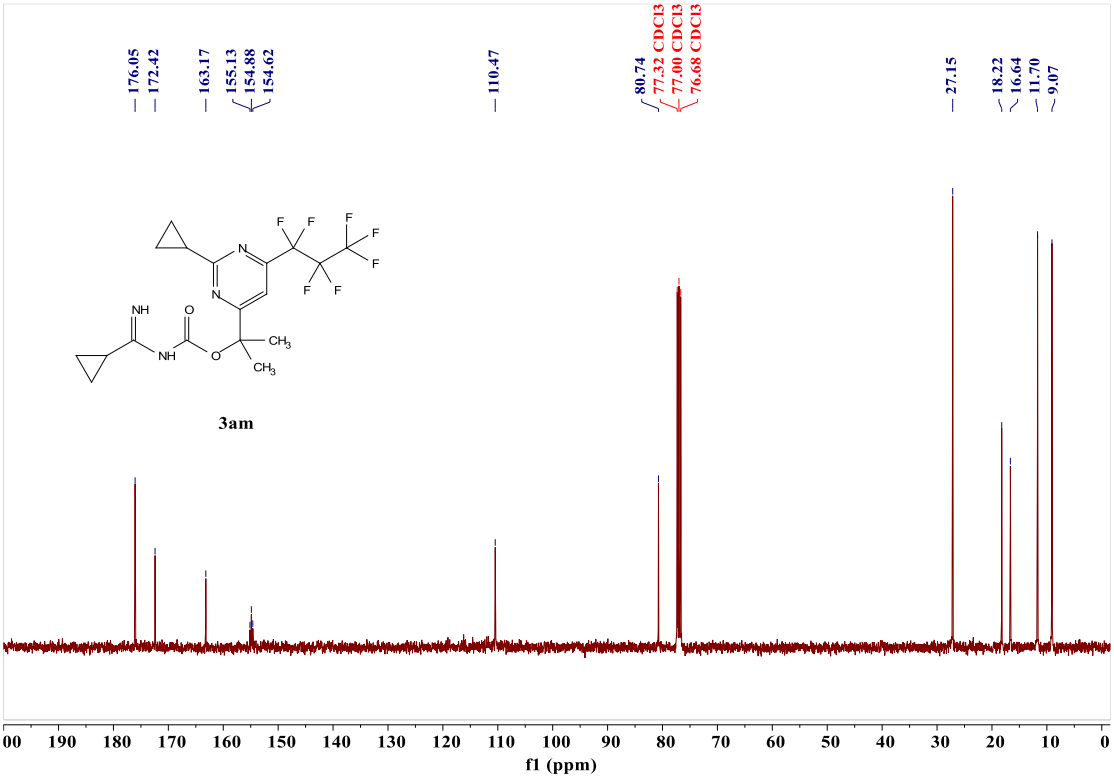
^{1}H NMR spectra of the product **3am**



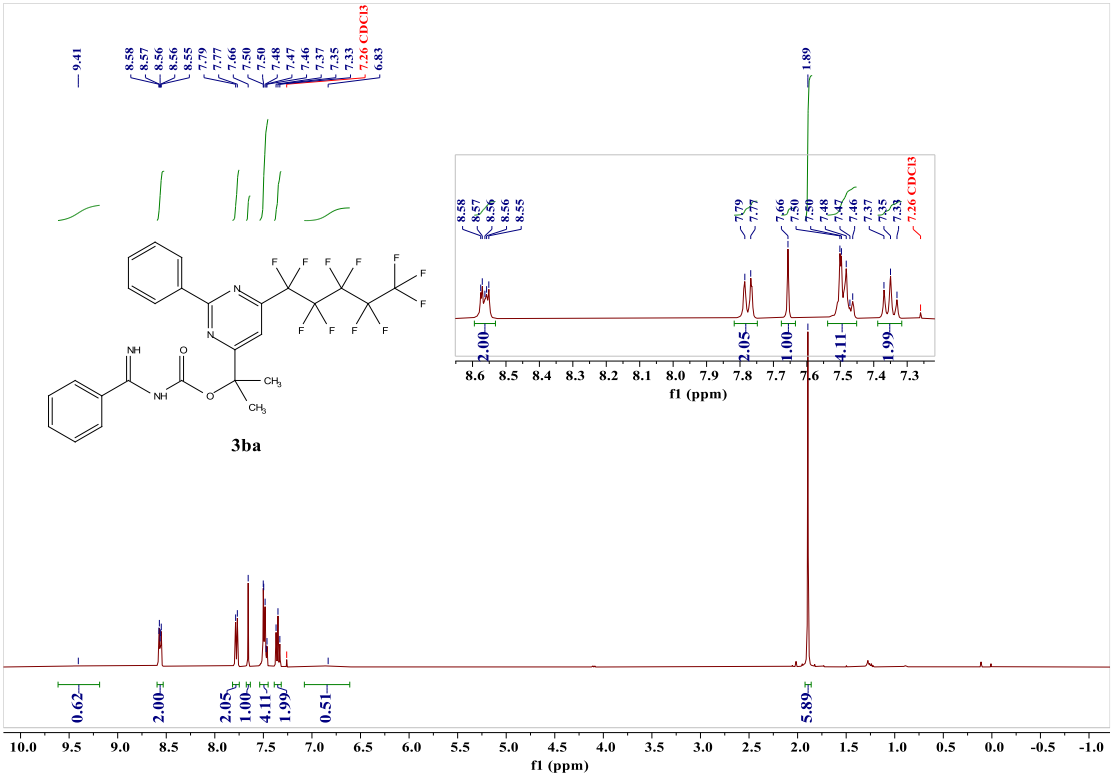
^{19}F NMR spectra of the product **3am**



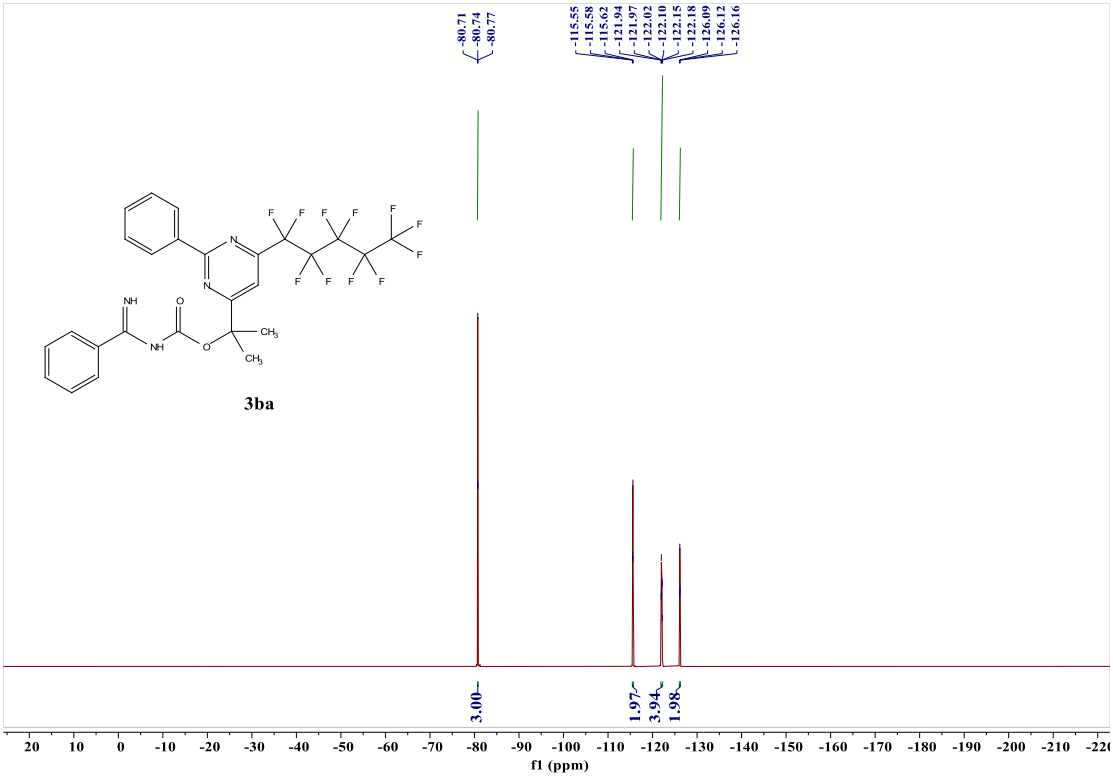
^{13}C NMR spectra of the product **3am**



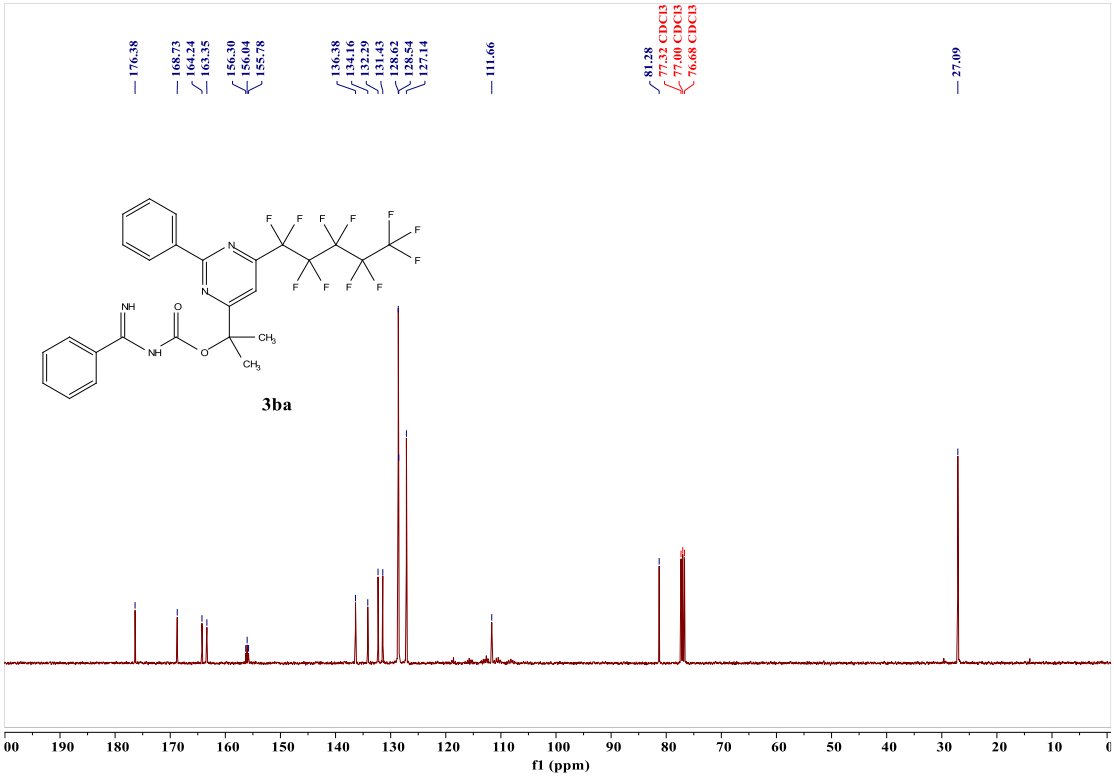
^{1}H NMR spectra of the product **3ba**



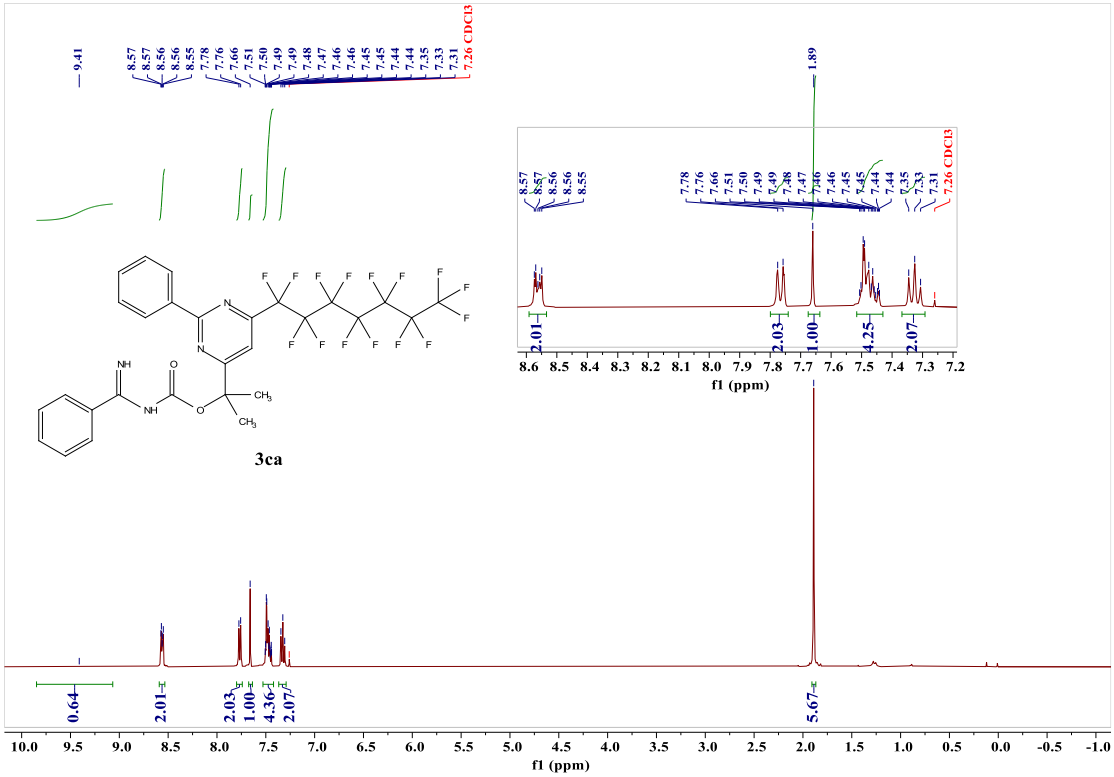
^{19}F NMR spectra of the product **3ba**



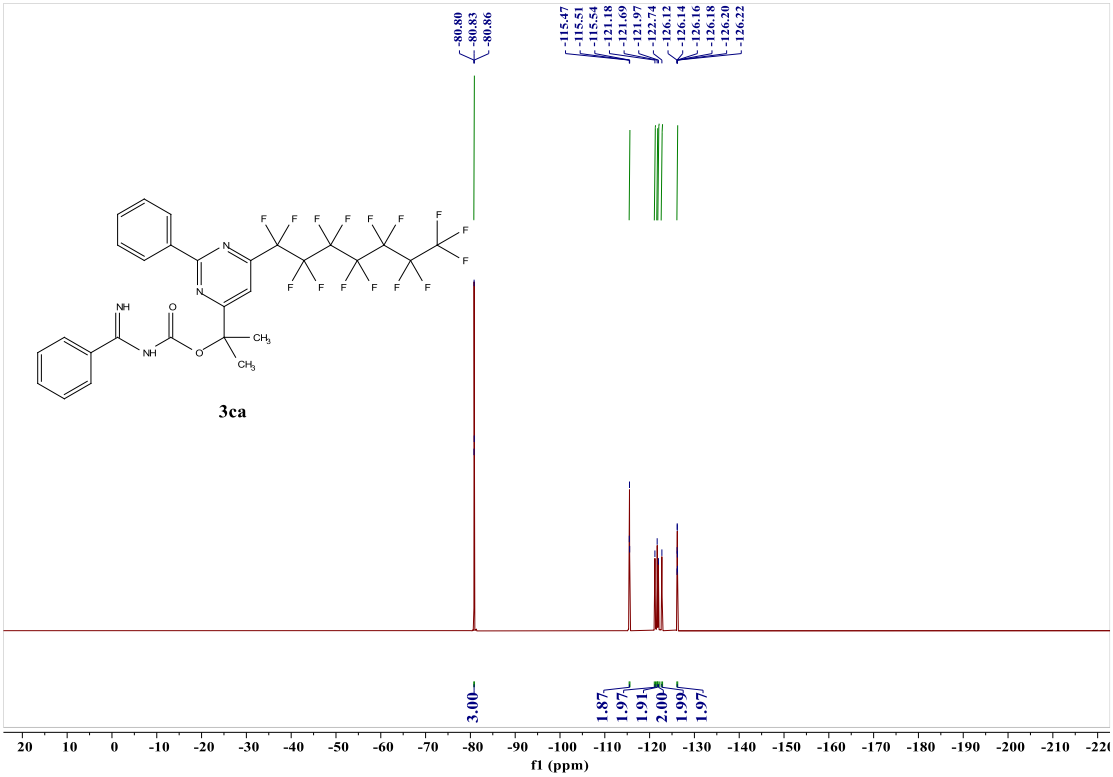
^{13}C NMR spectra of the product **3ba**



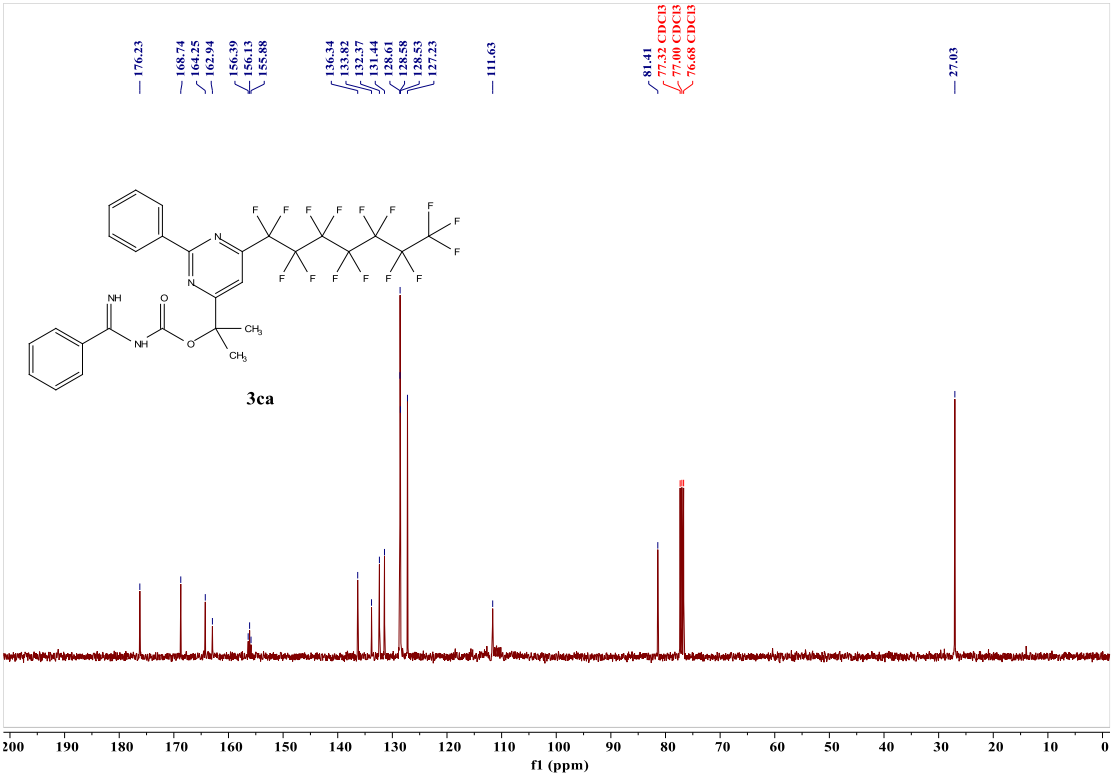
^{1}H NMR spectra of the product **3ca**



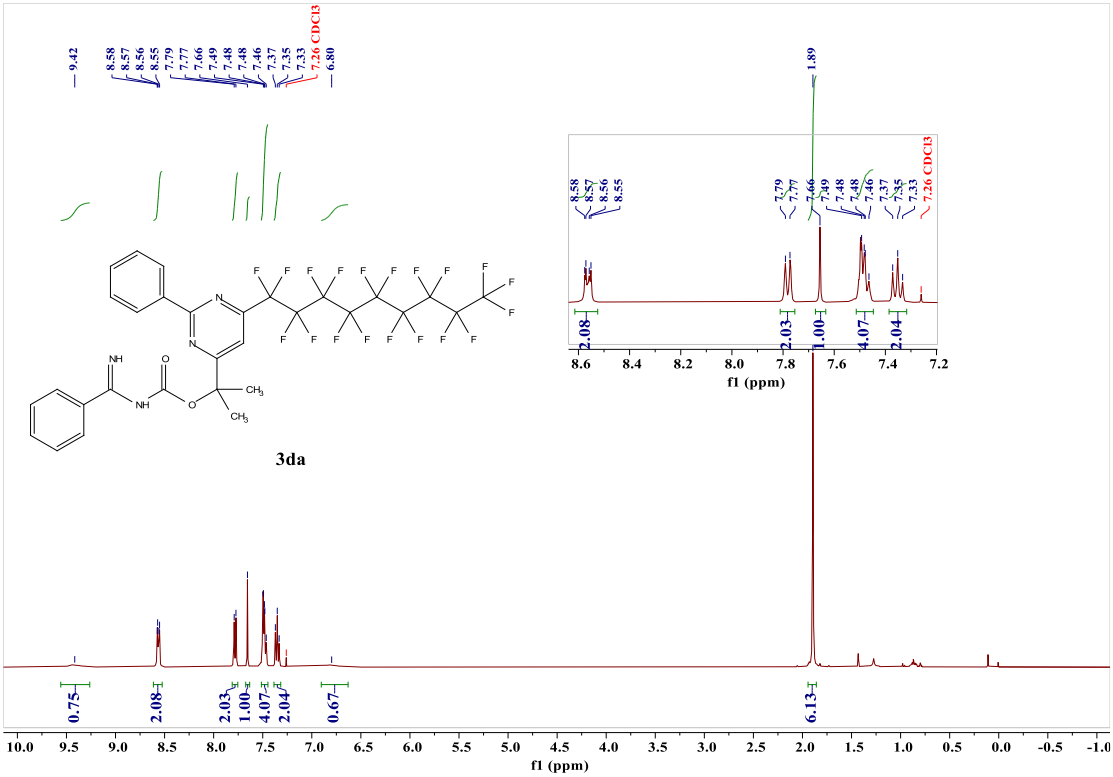
^{19}F NMR spectra of the product **3ca**



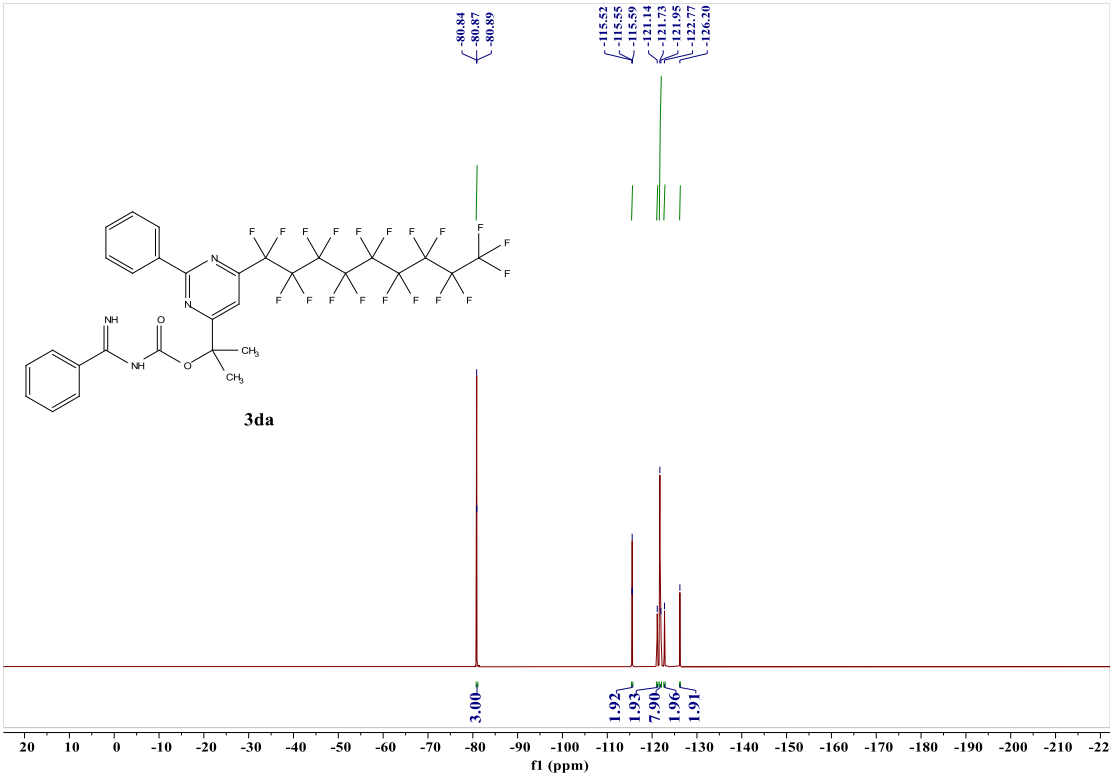
^{13}C NMR spectra of the product **3ca**



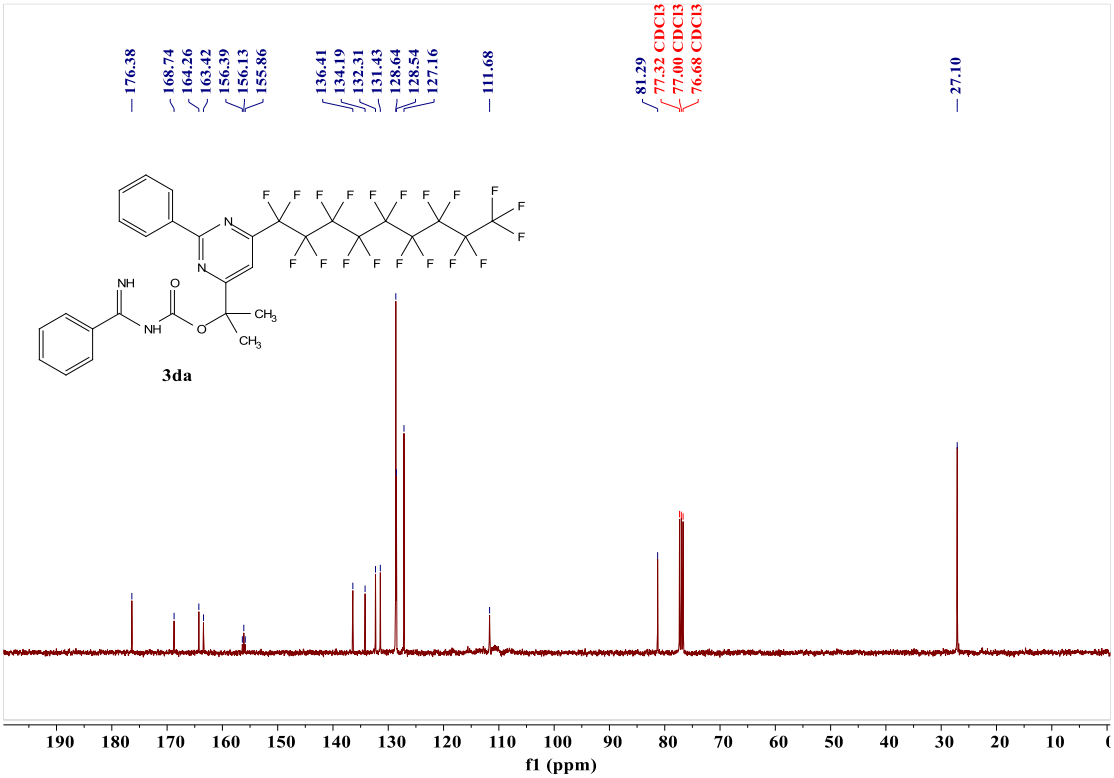
^{1}H NMR spectra of the product **3da**



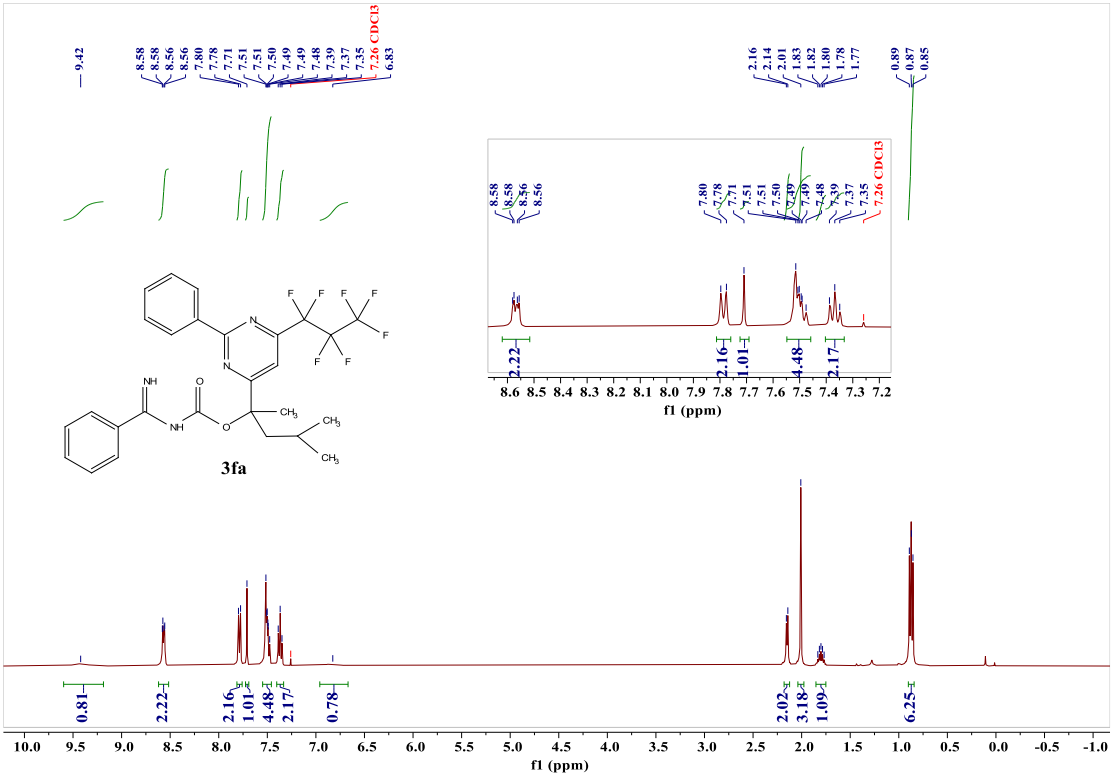
^{19}F NMR spectra of the product **3da**



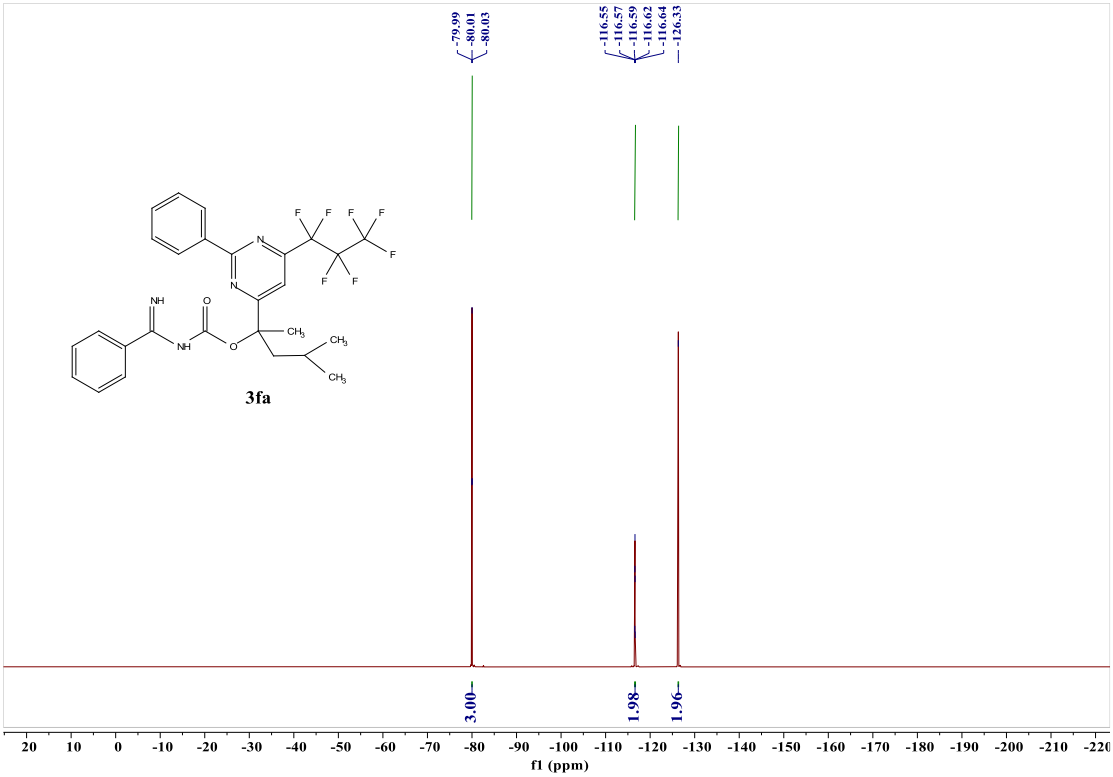
^{13}C NMR spectra of the product **3da**



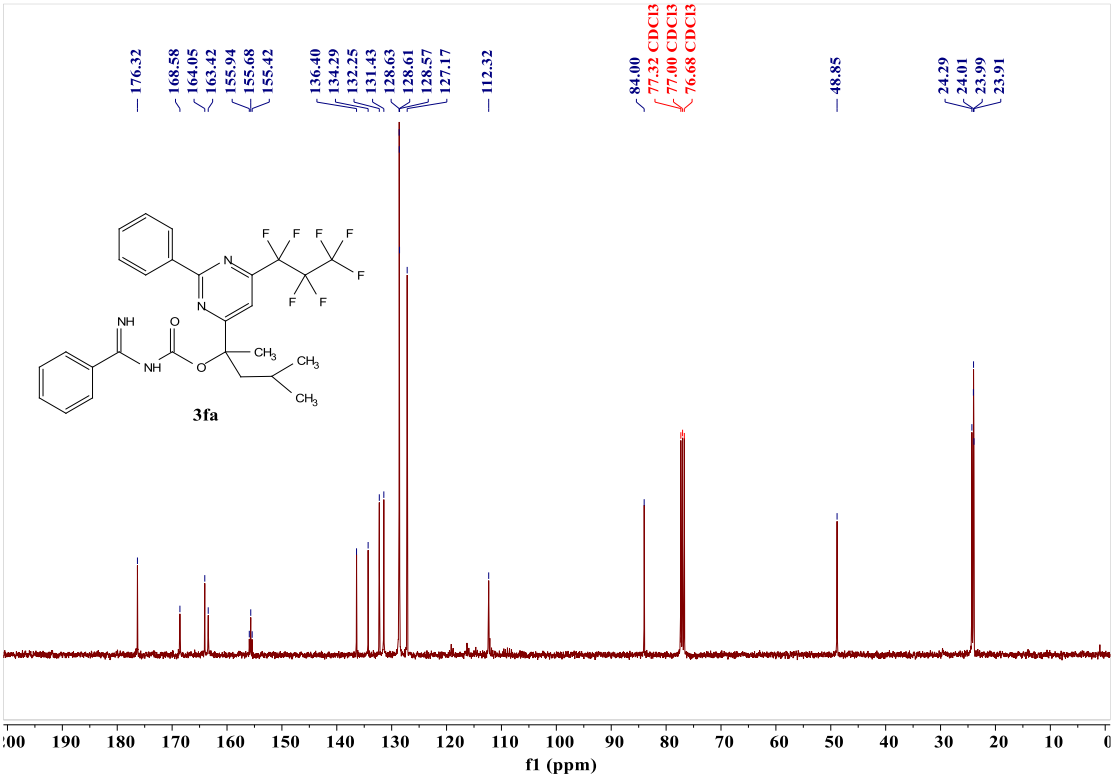
^{1}H NMR spectra of the product **3fa**



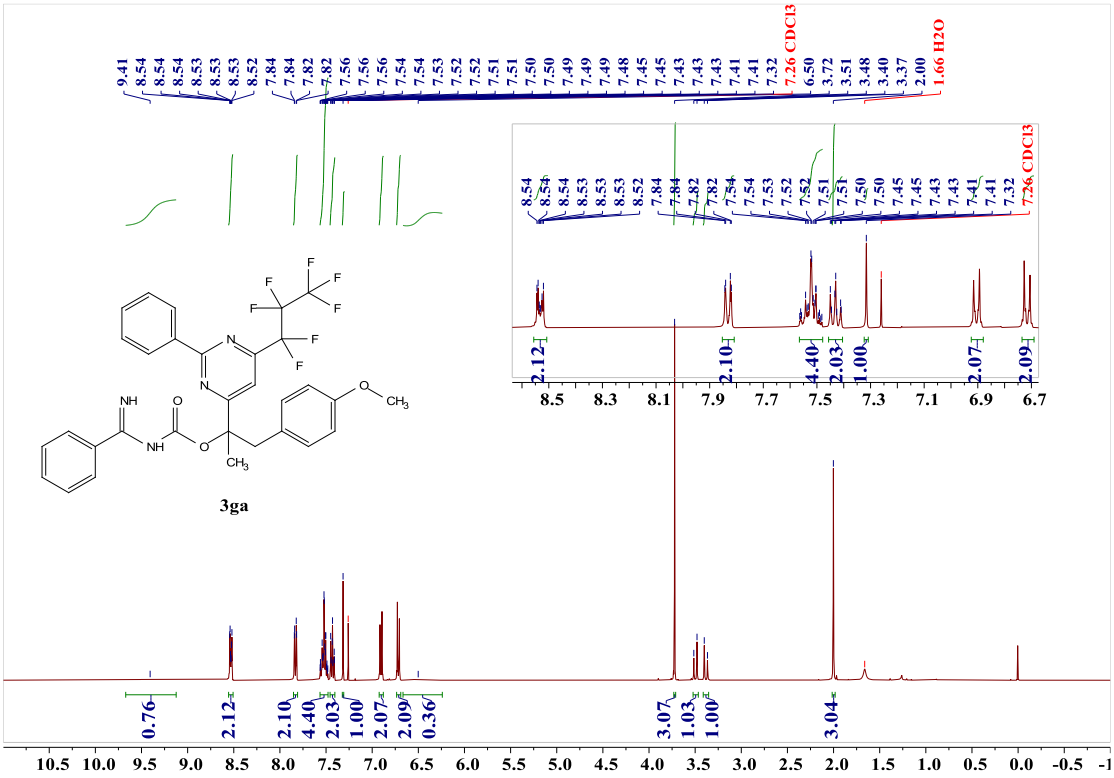
^{19}F NMR spectra of the product **3fa**



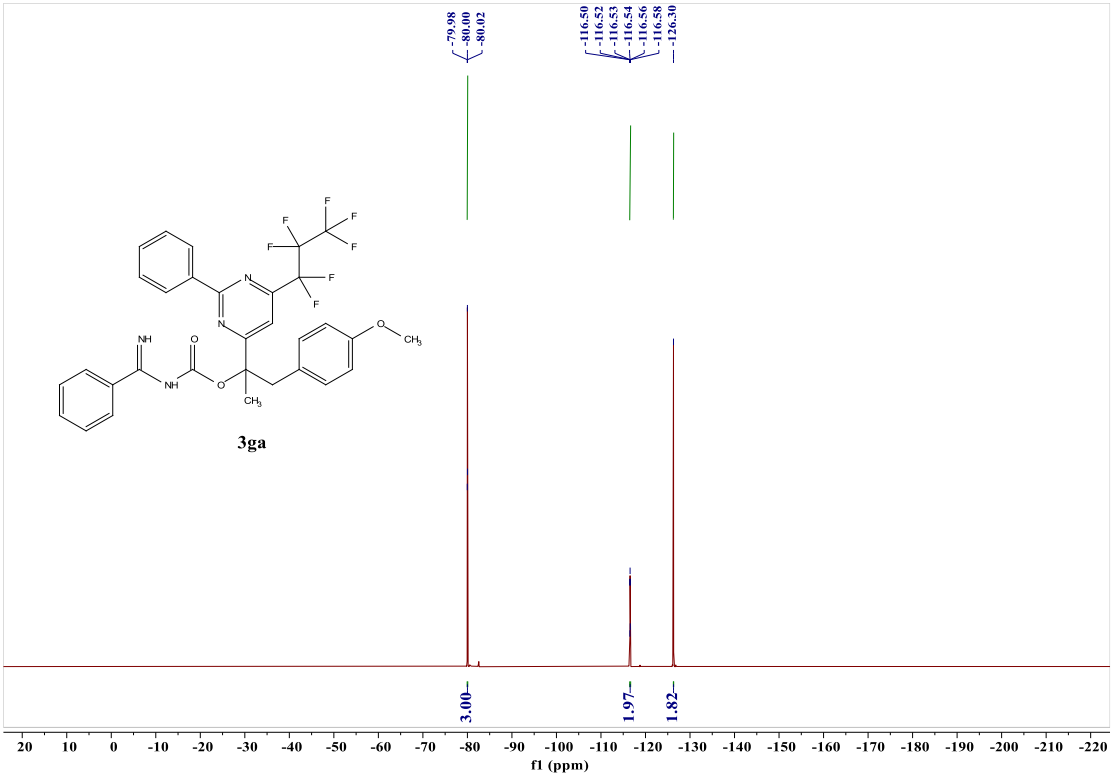
^{13}C NMR spectra of the product **3fa**



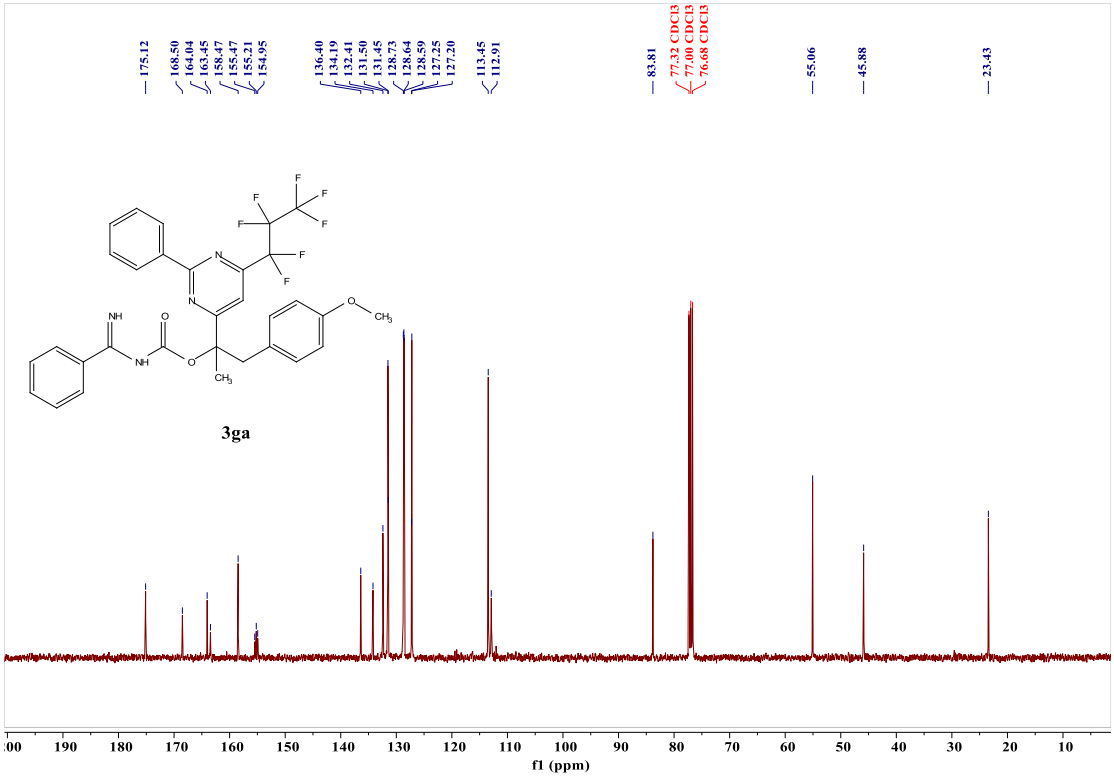
^{1}H NMR spectra of the product **3ga**



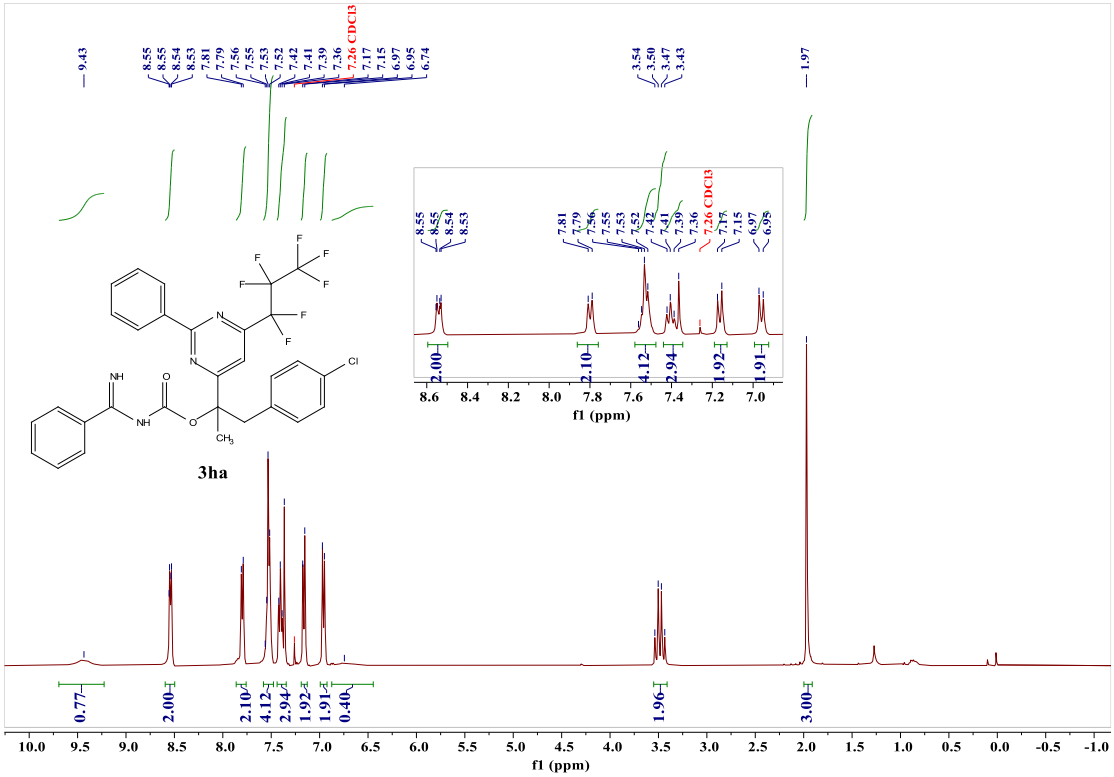
^{19}F NMR spectra of the product **3ga**



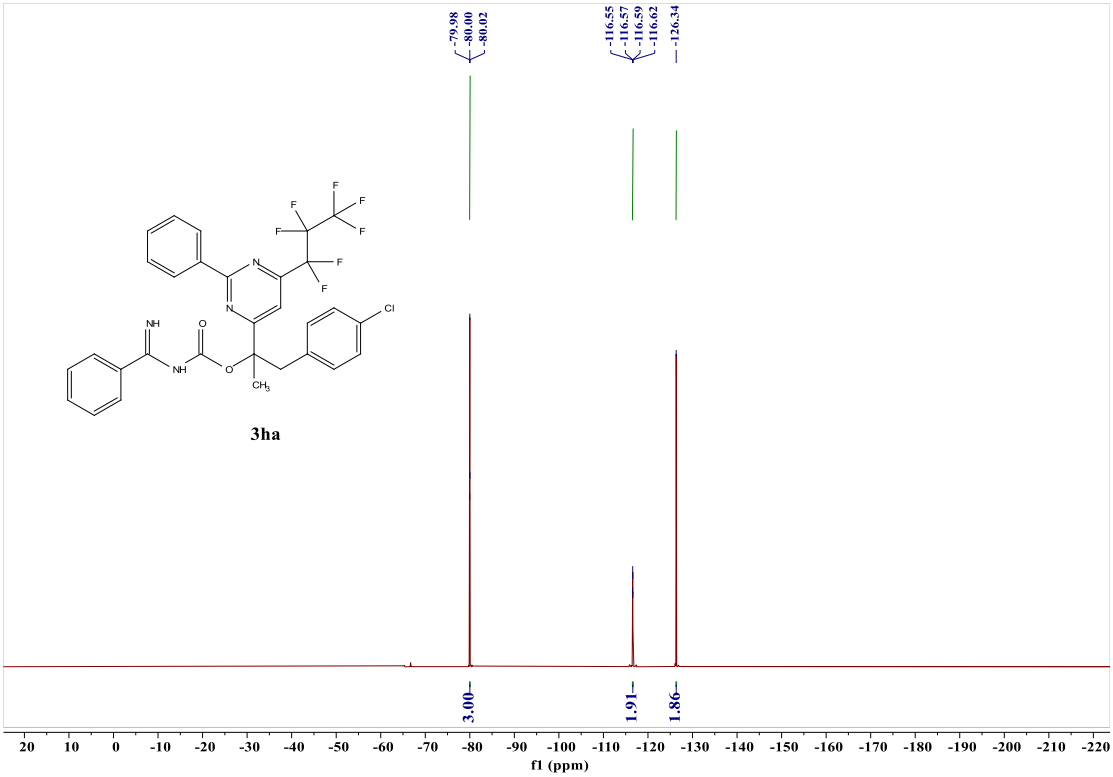
^{13}C NMR spectra of the product **3ga**



^{1}H NMR spectra of the product **3ha**

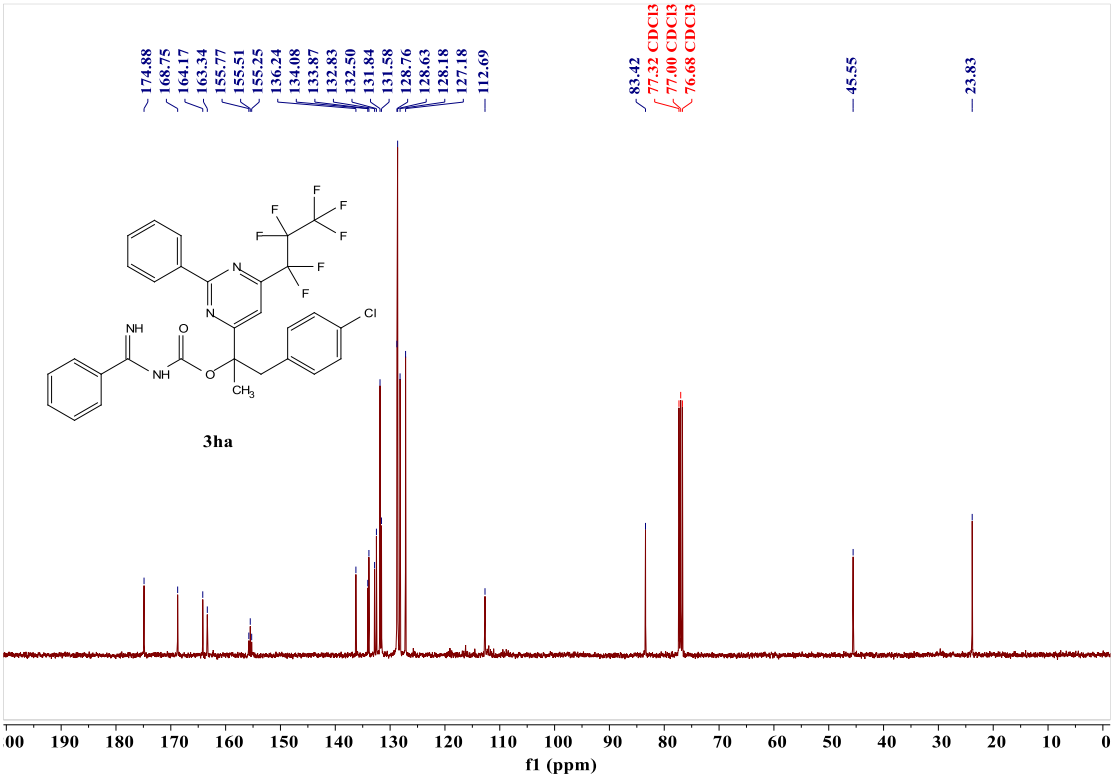


^{19}F NMR spectra of the product **3ha**



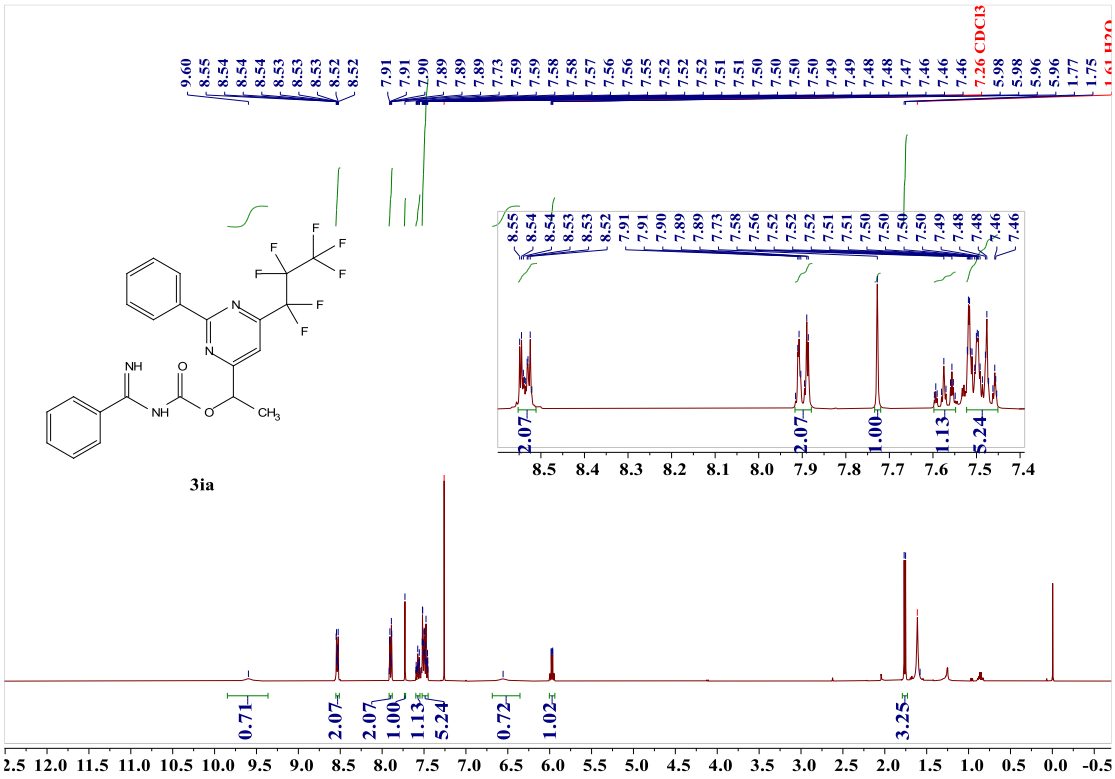
3ha

^{13}C NMR spectra of the product **3ha**

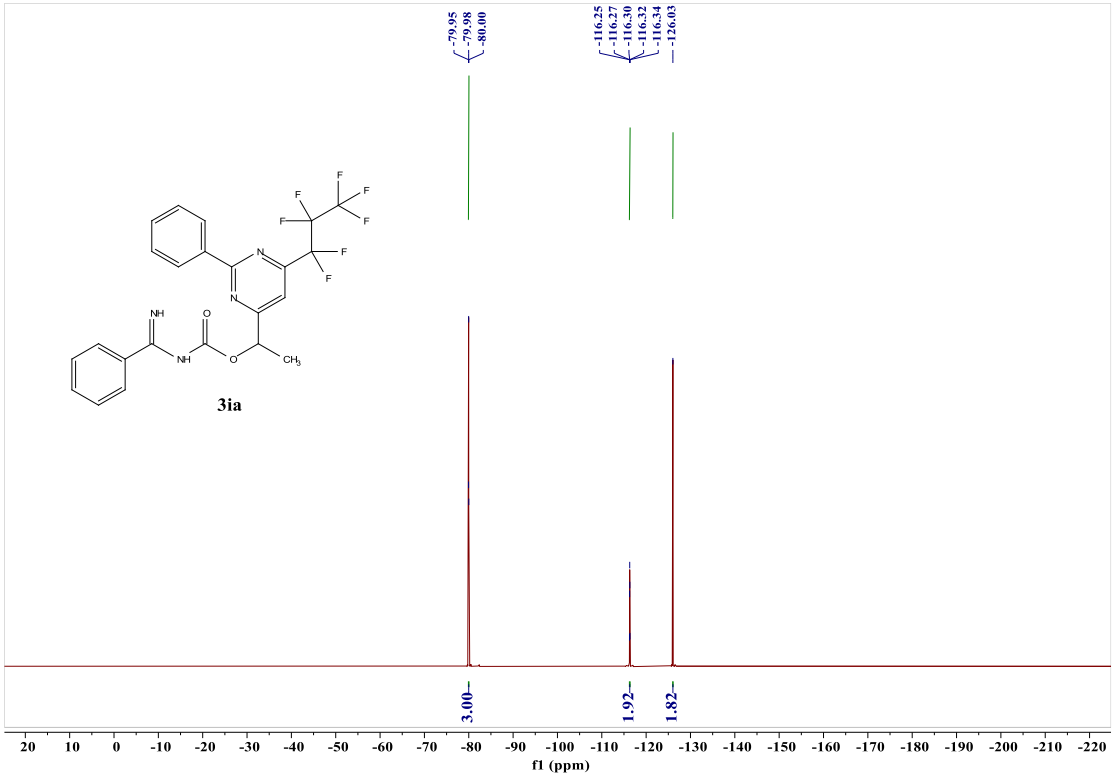


3ha

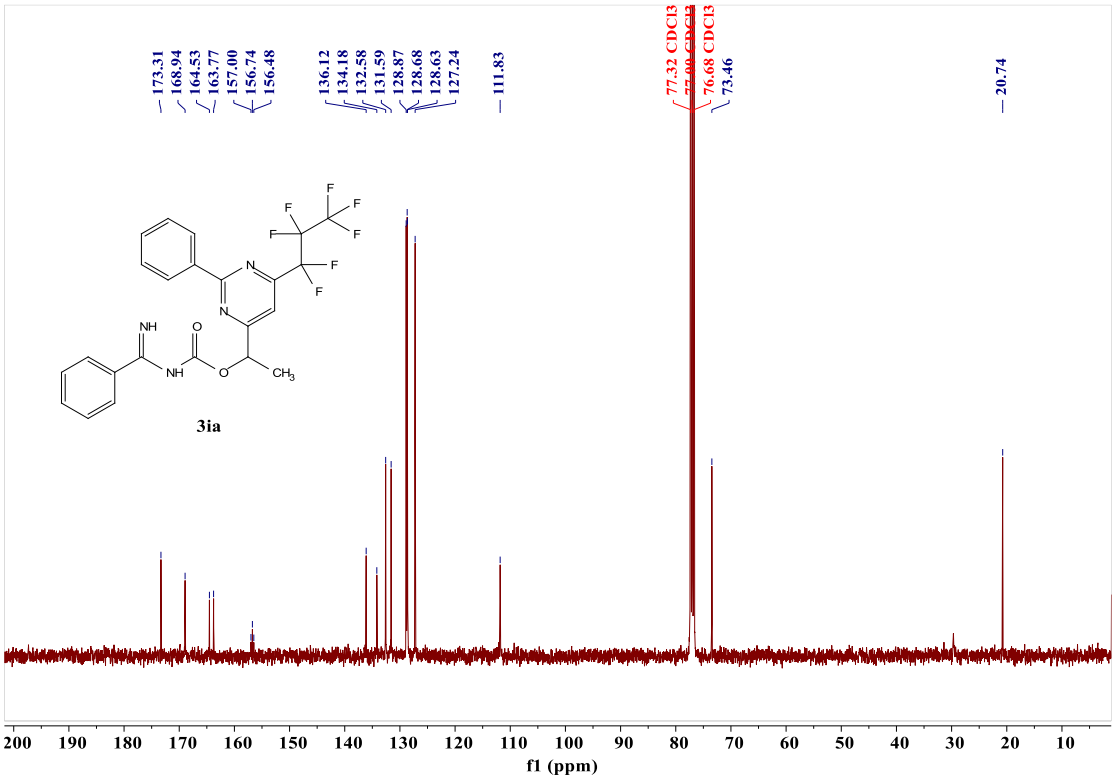
^{1}H NMR spectra of the product **3ia**



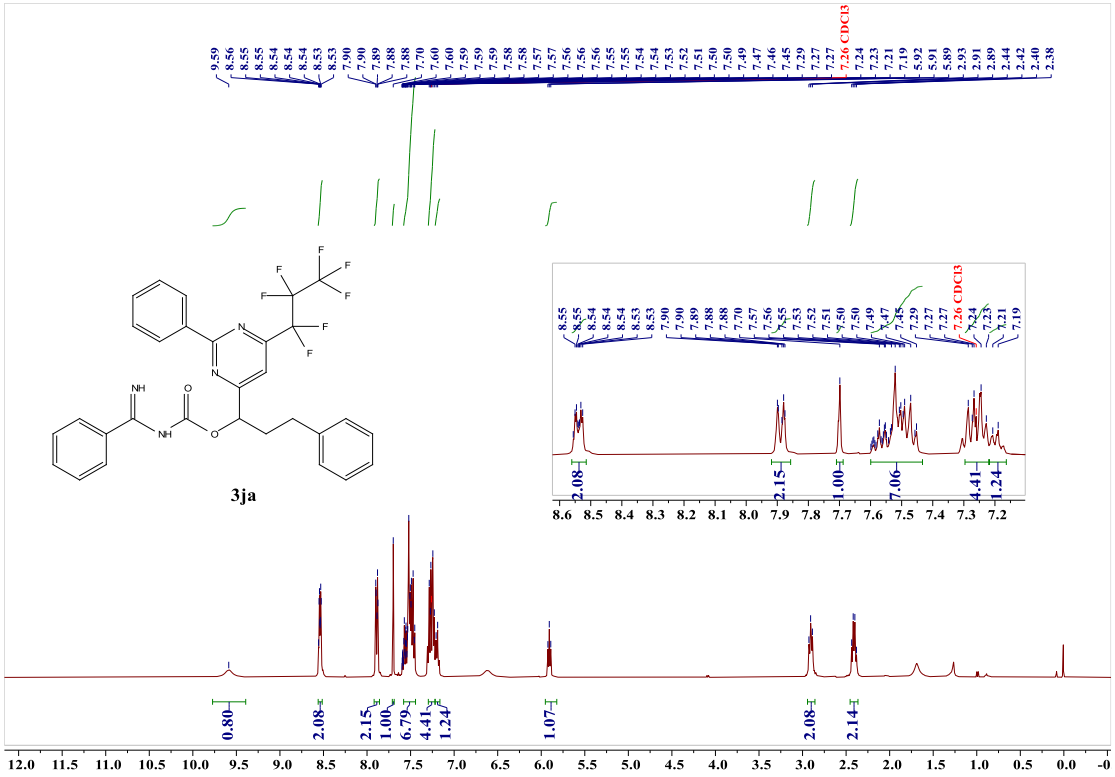
^{19}F NMR spectra of the product **3ia**



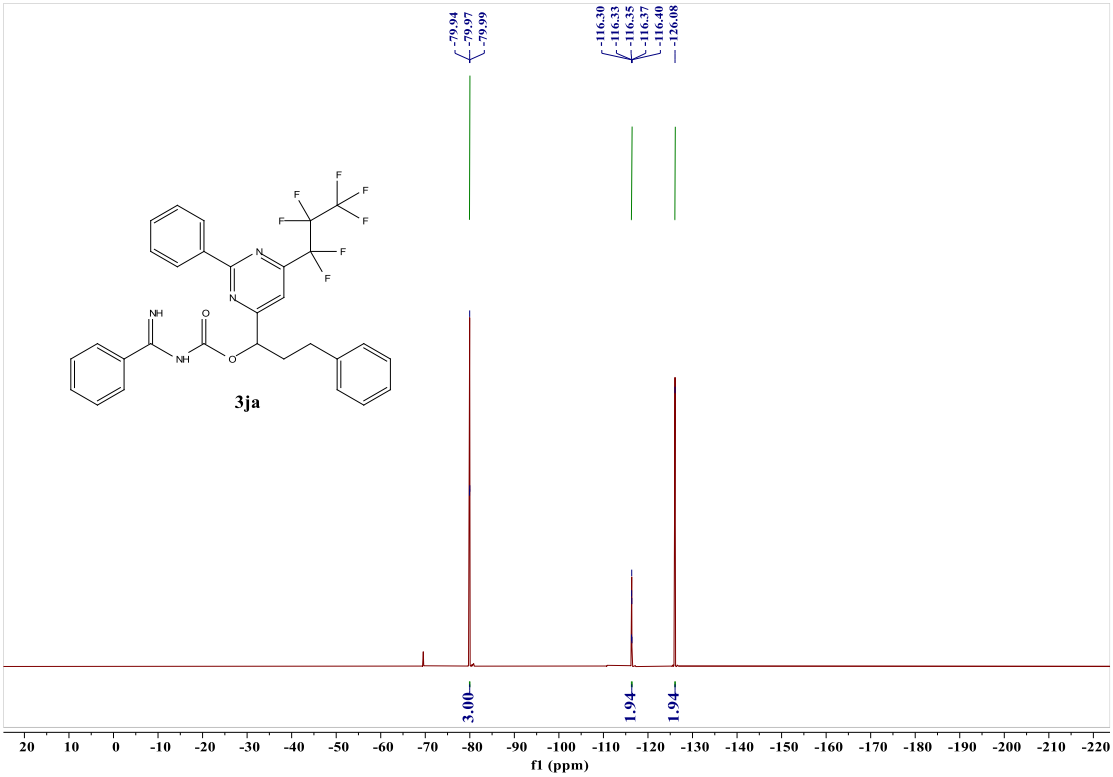
^{13}C NMR spectra of the product **3ia**



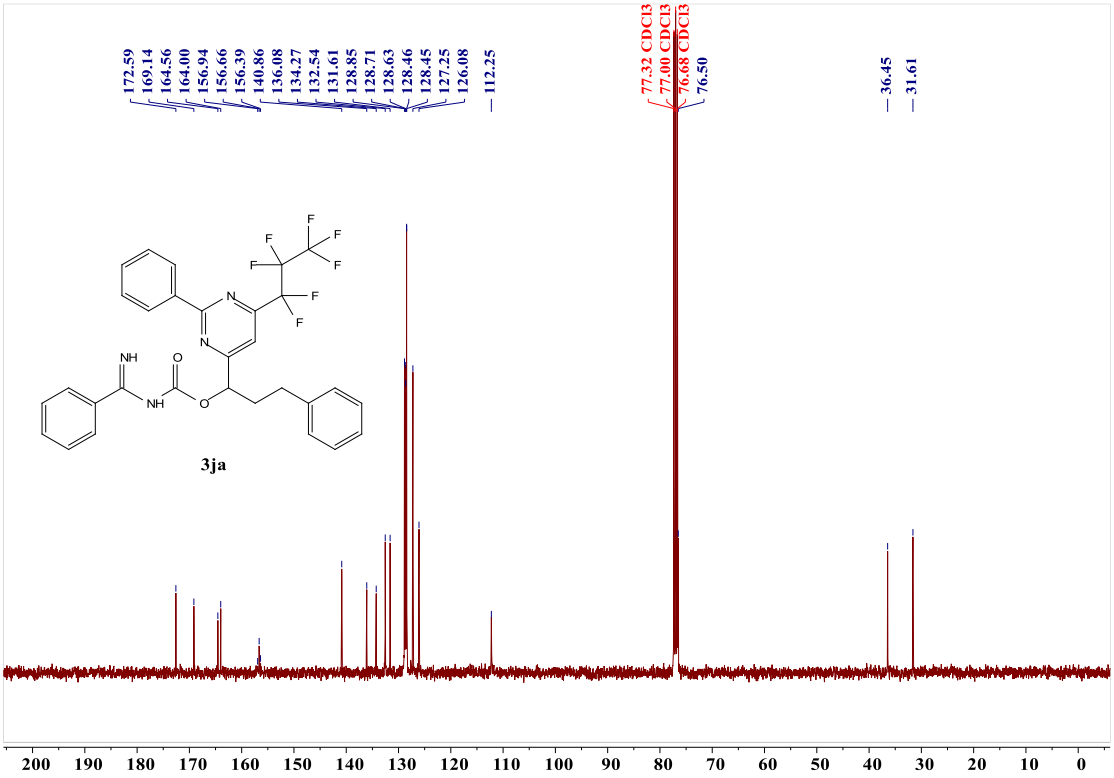
^{1}H NMR spectra of the product **3ja**



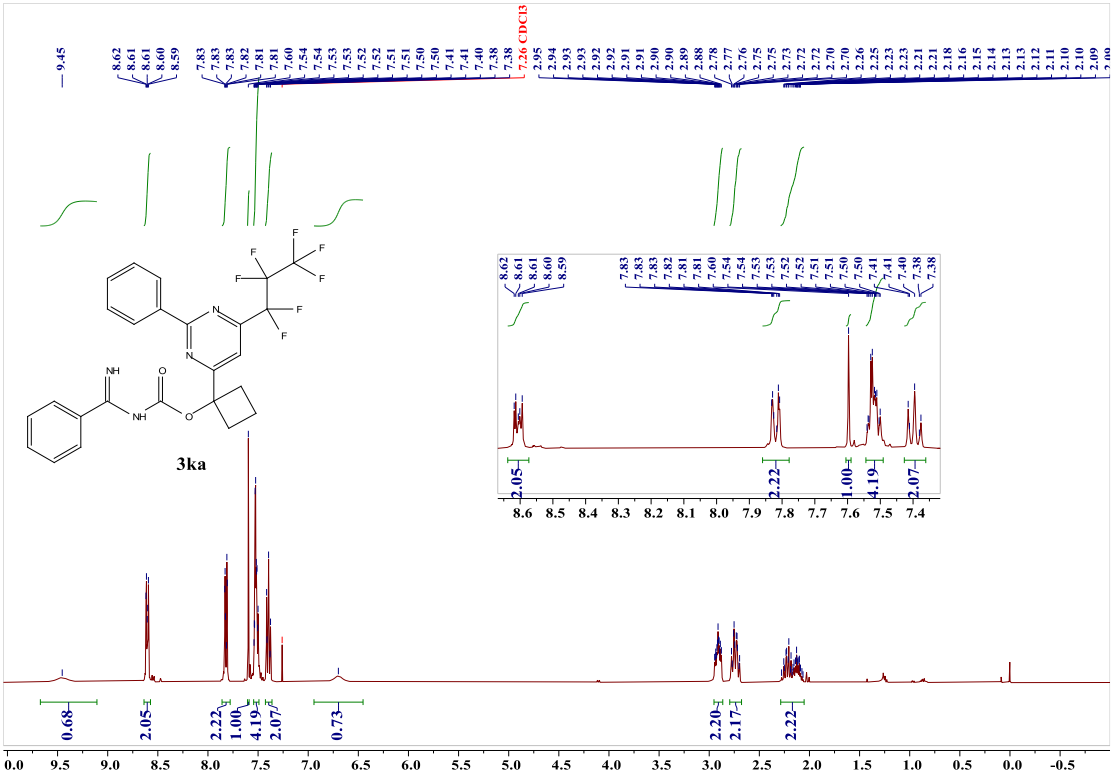
^{19}F NMR spectra of the product **3ja**



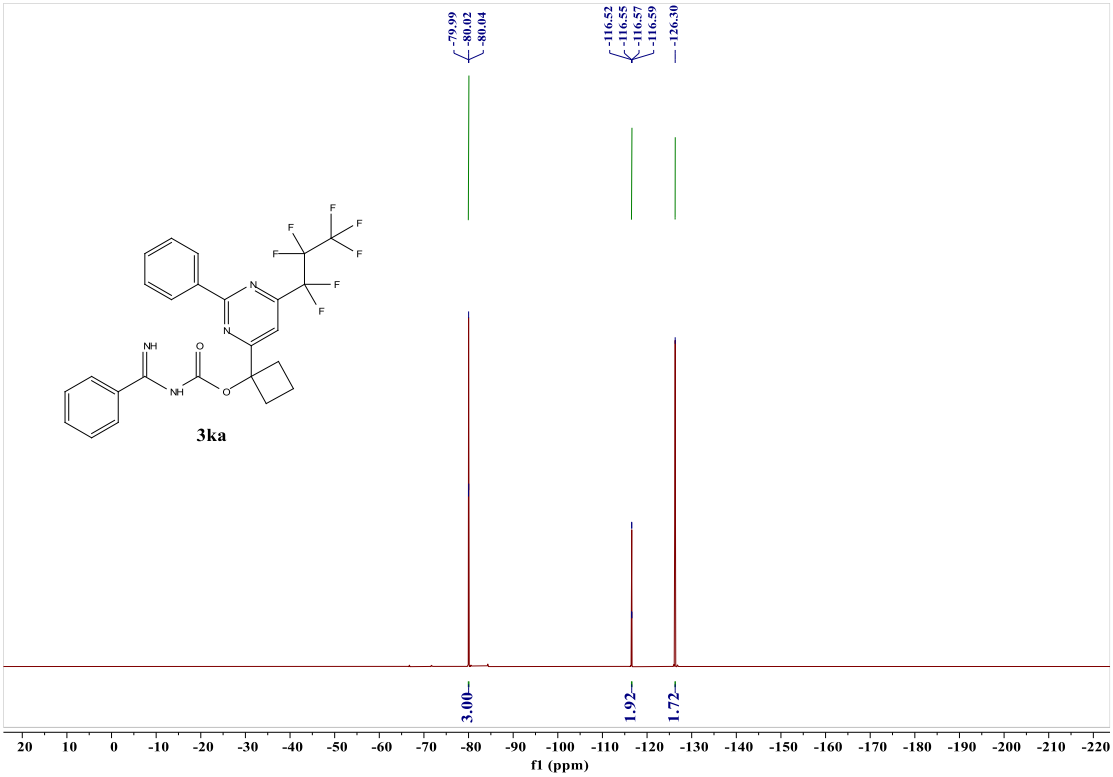
^{13}C NMR spectra of the product **3ja**



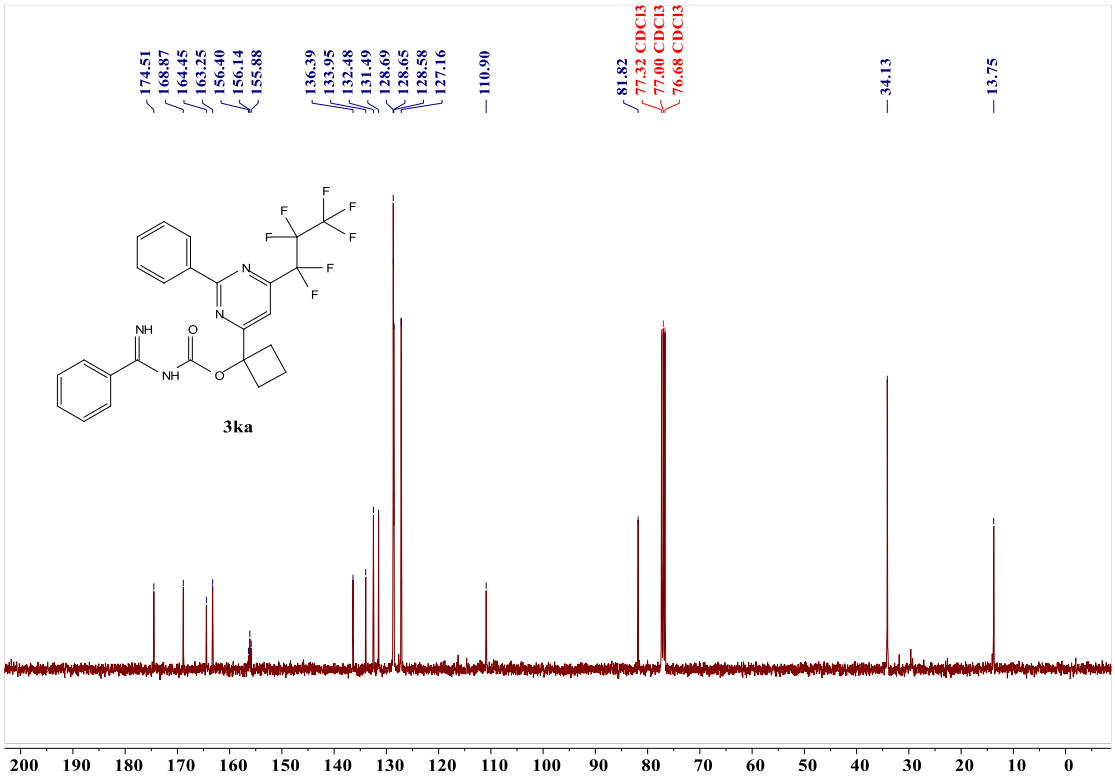
^{1}H NMR spectra of the product **3ka**



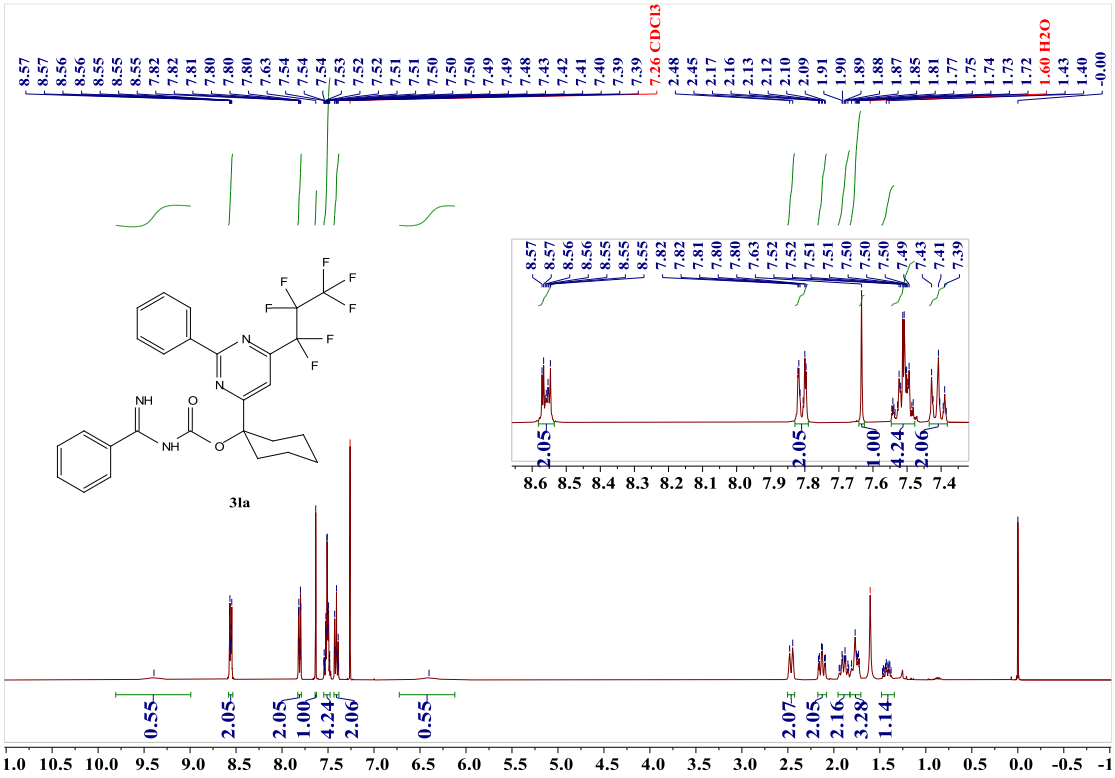
^{19}F NMR spectra of the product **3ka**



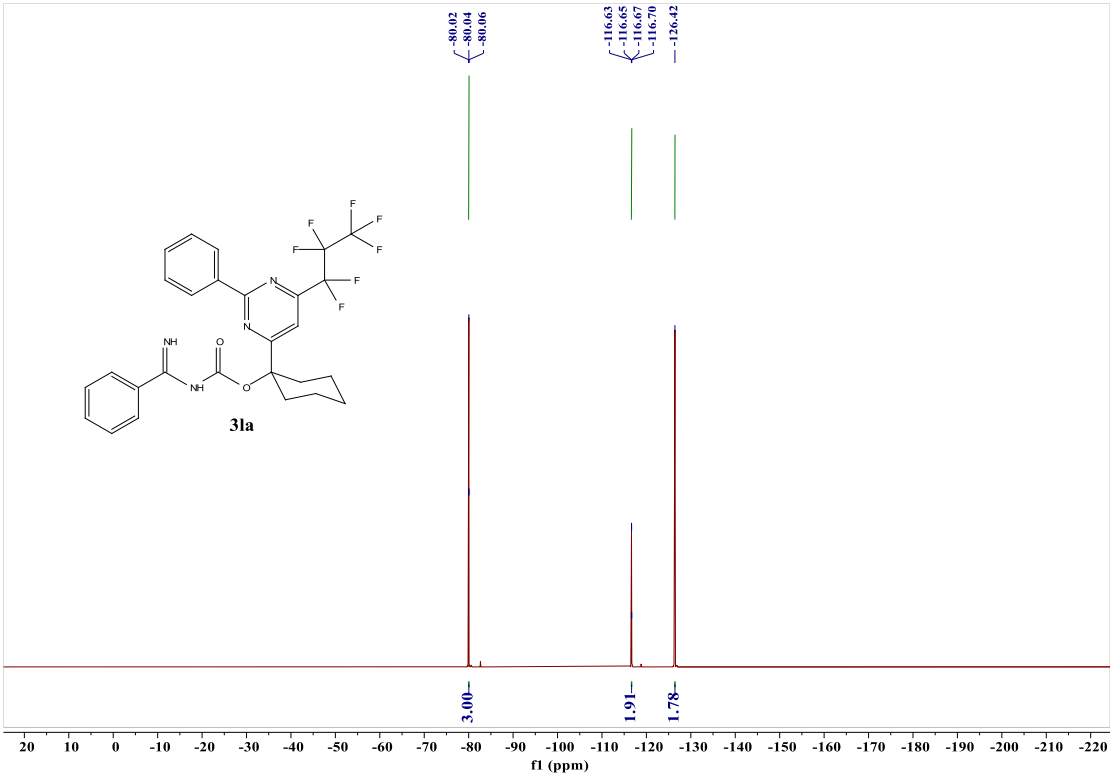
^{13}C NMR spectra of the product **3ka**



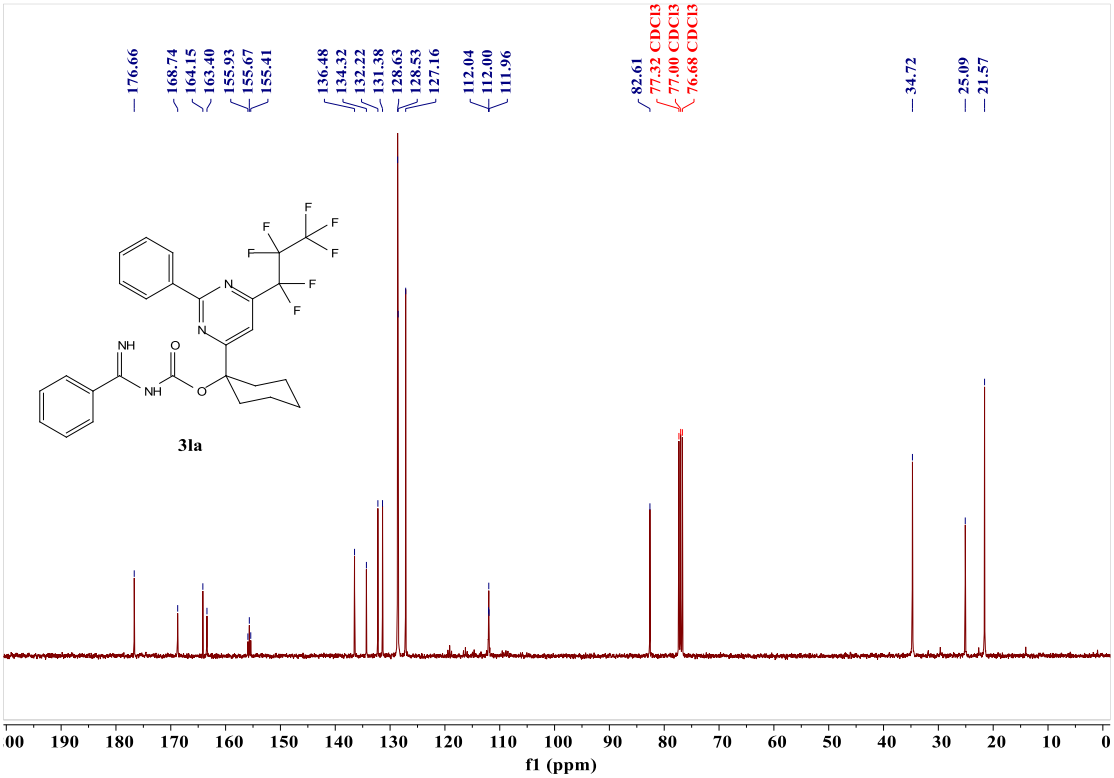
^{1}H NMR spectra of the product **3la**



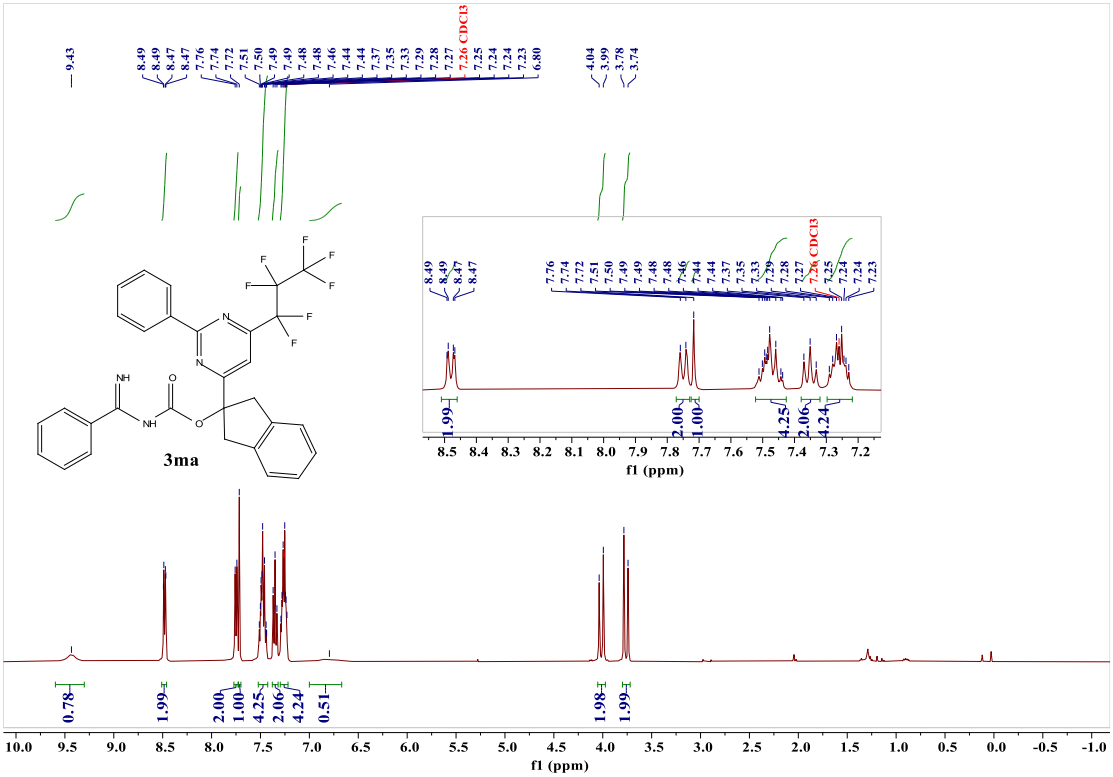
^{19}F NMR spectra of the product **3la**



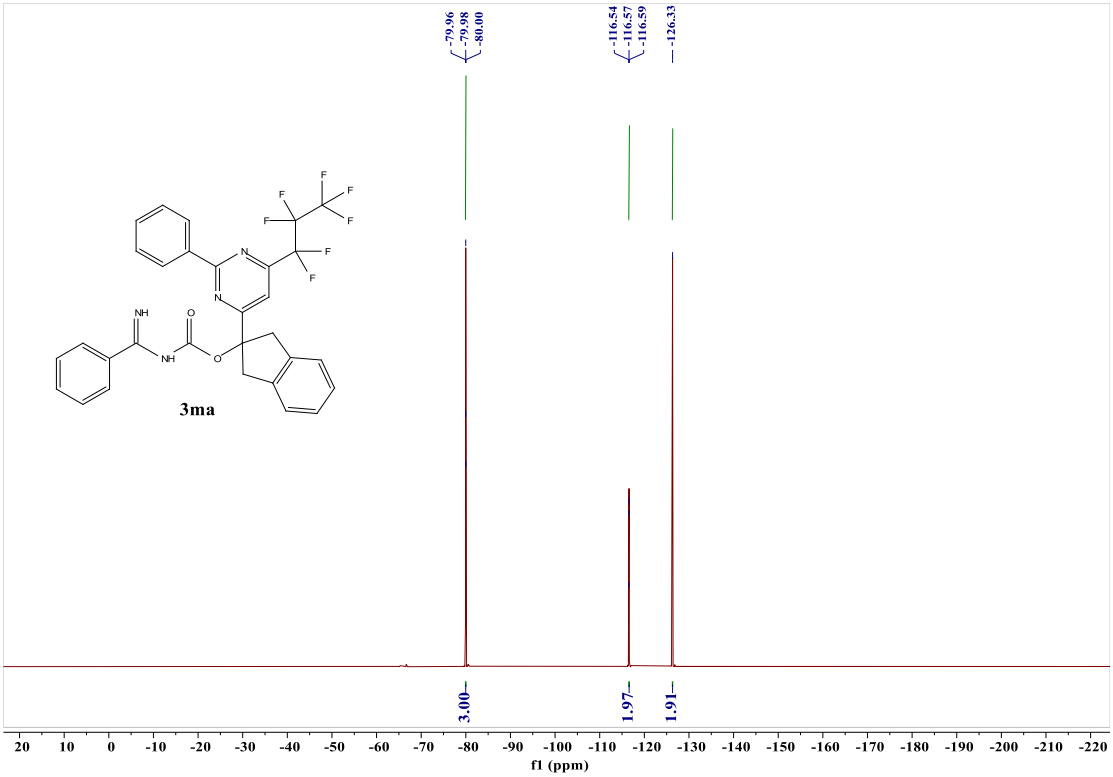
^{13}C NMR spectra of the product **3la**



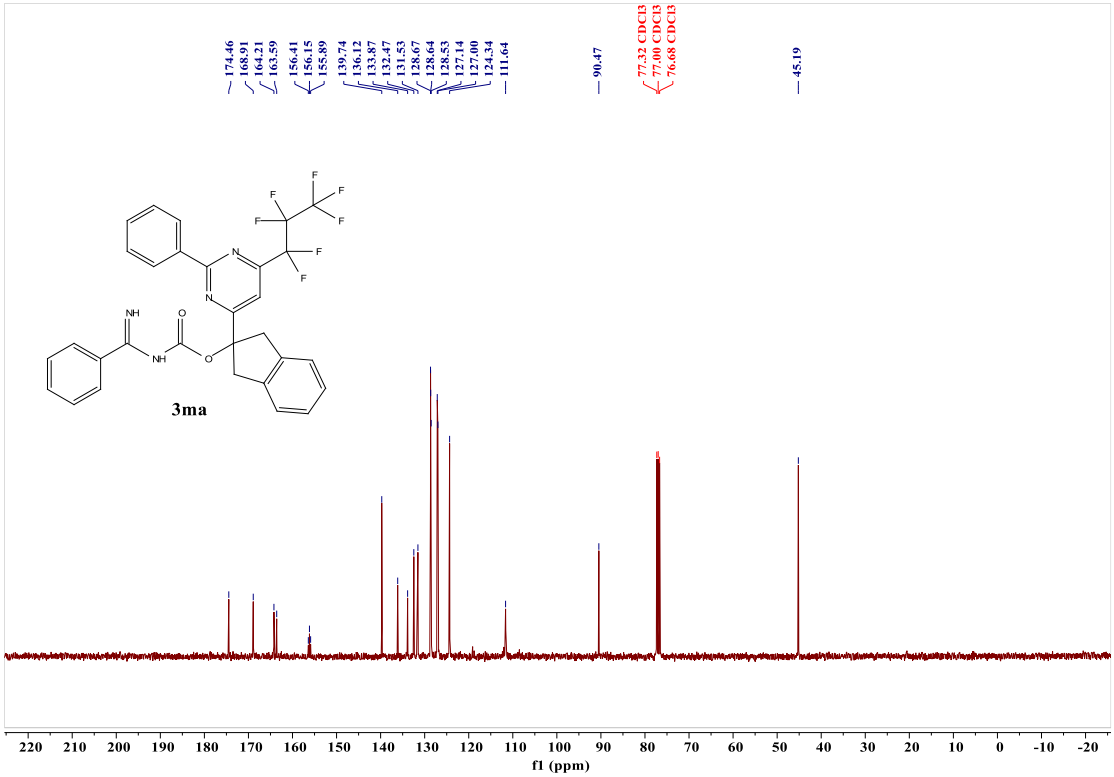
^{1}H NMR spectra of the product **3ma**



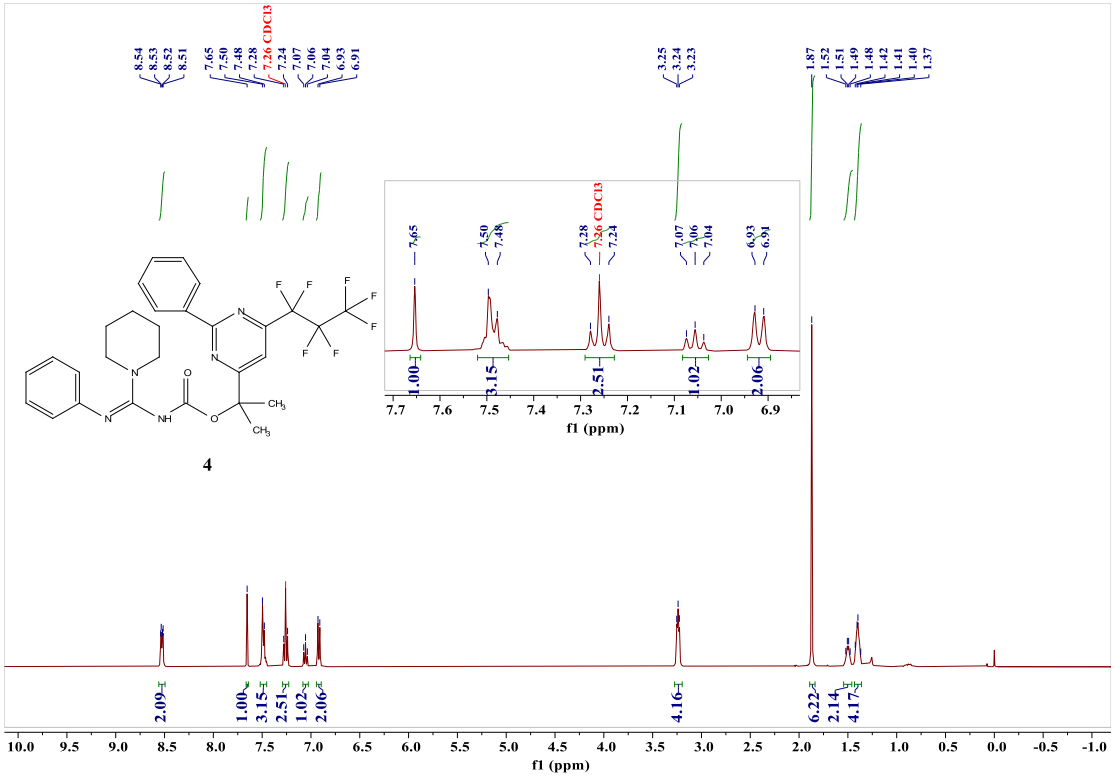
^{19}F NMR spectra of the product **3ma**



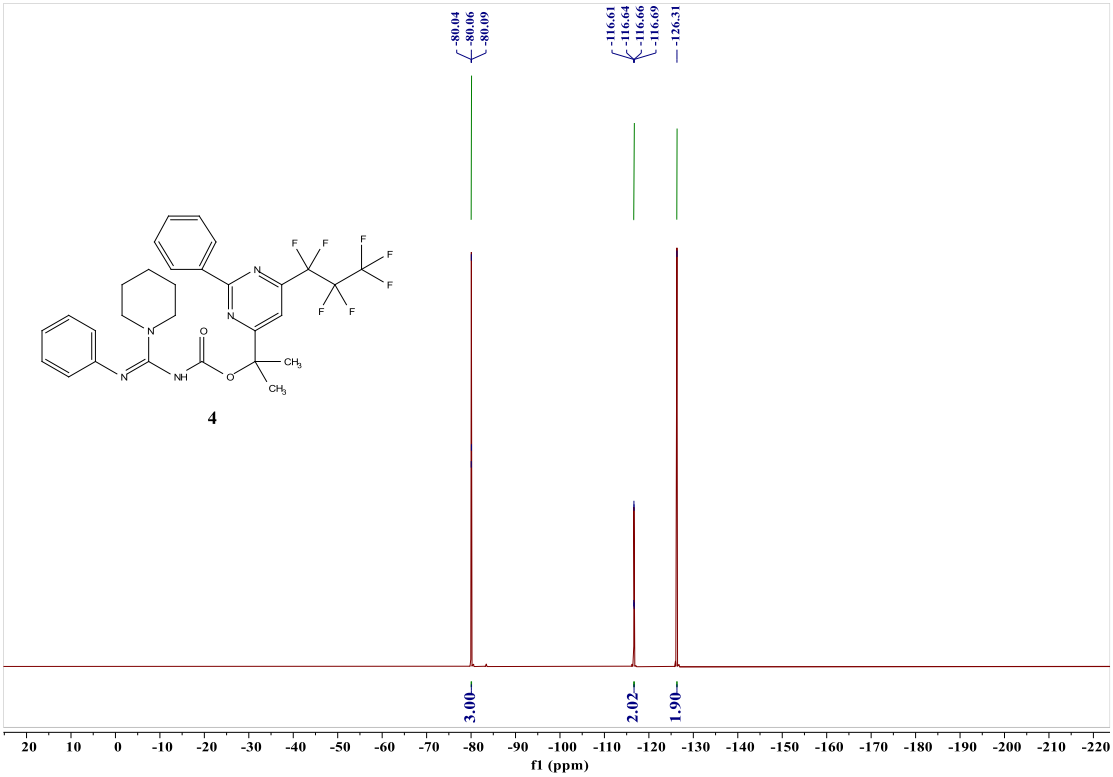
^{13}C NMR spectra of the product **3ma**



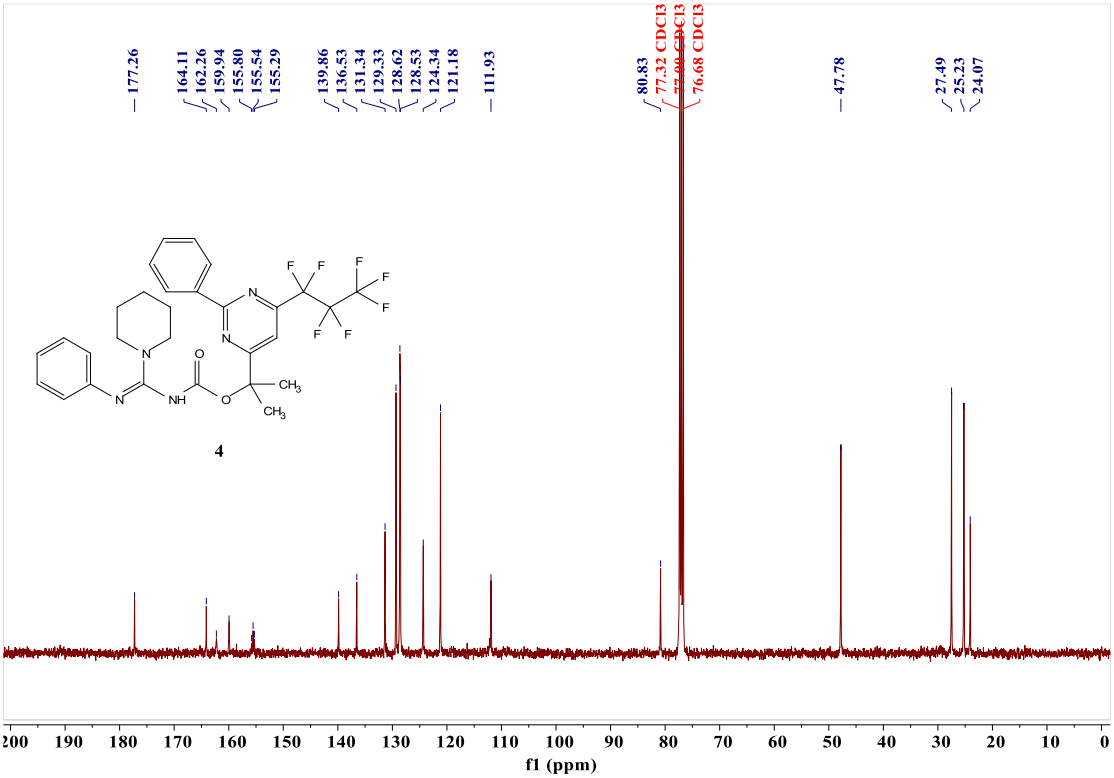
^{1}H NMR spectra of the product **4**



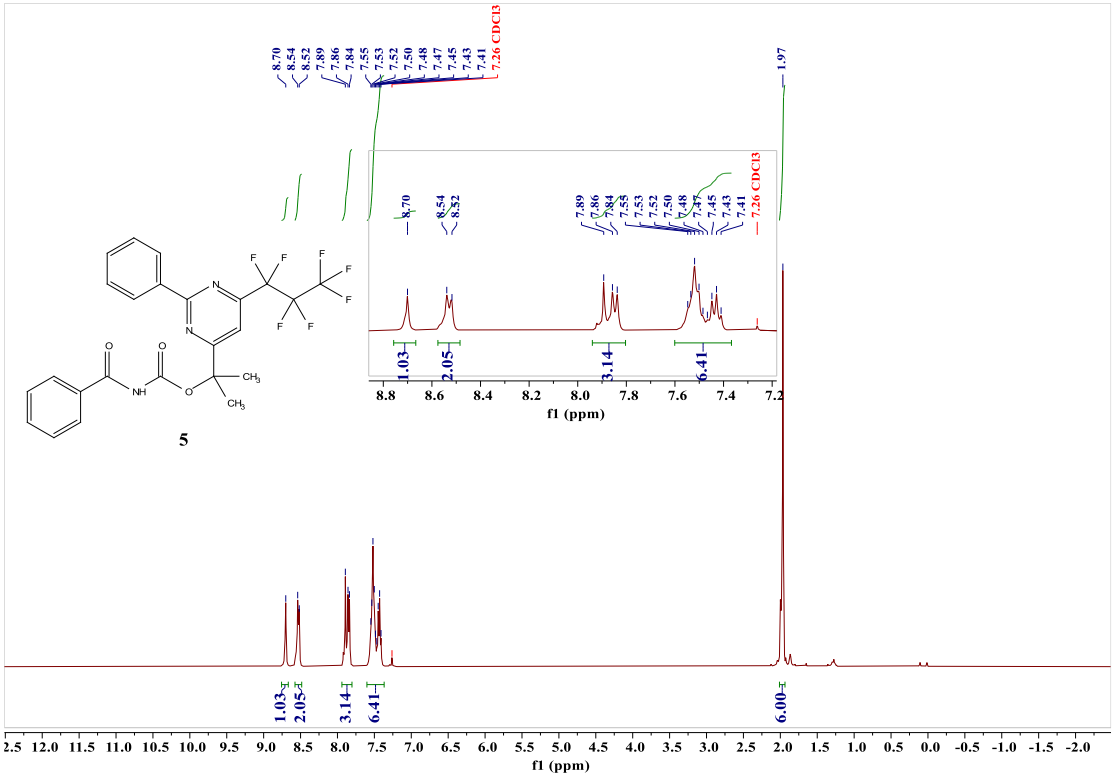
^{19}F NMR spectra of the product **4**



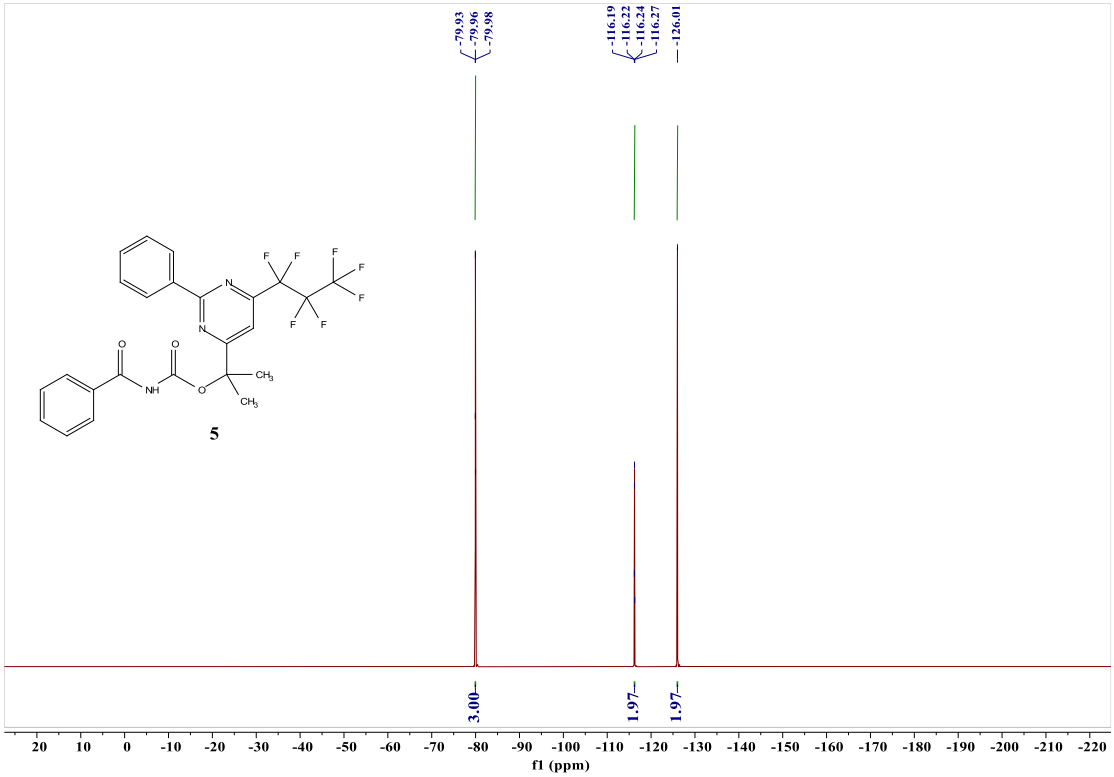
^{13}C NMR spectra of the product **4**



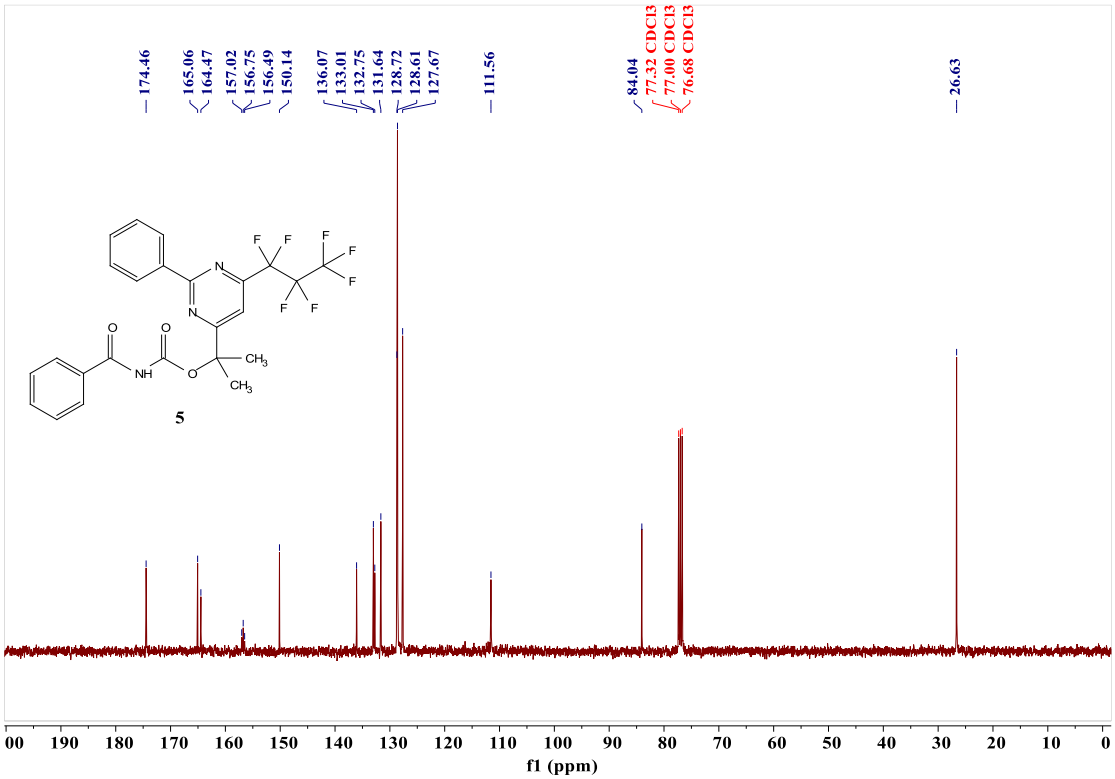
^{1}H NMR spectra of the product **5**



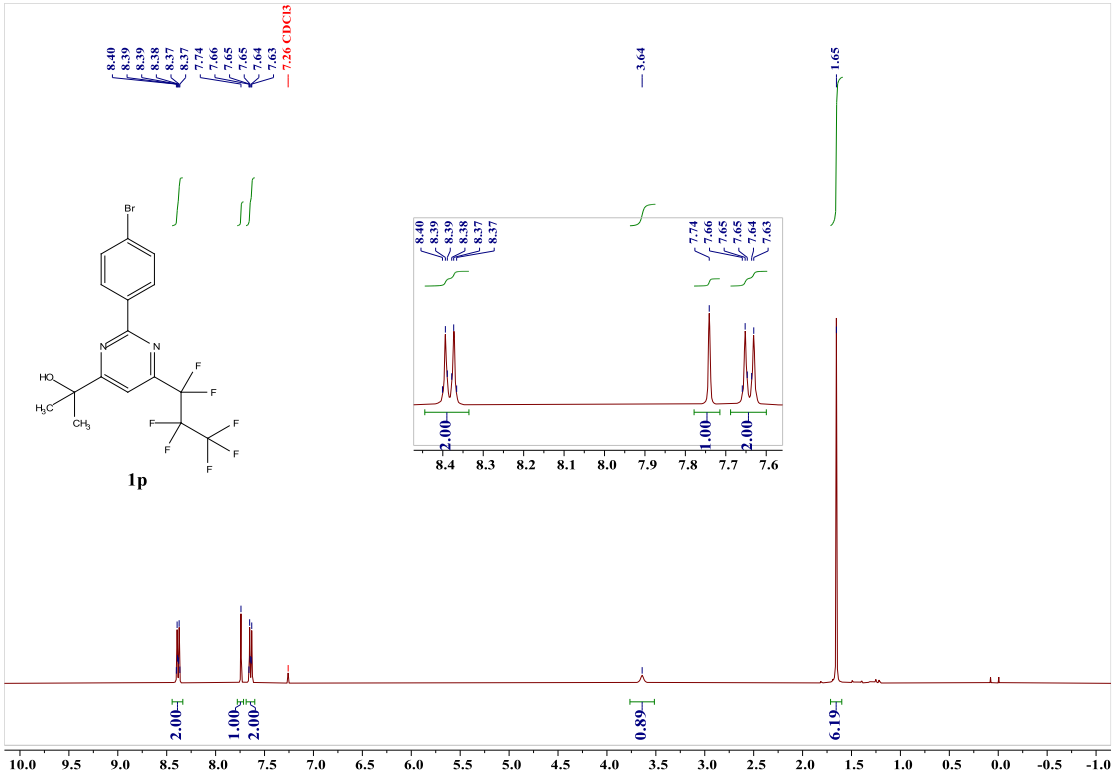
^{19}F NMR spectra of the product **5**



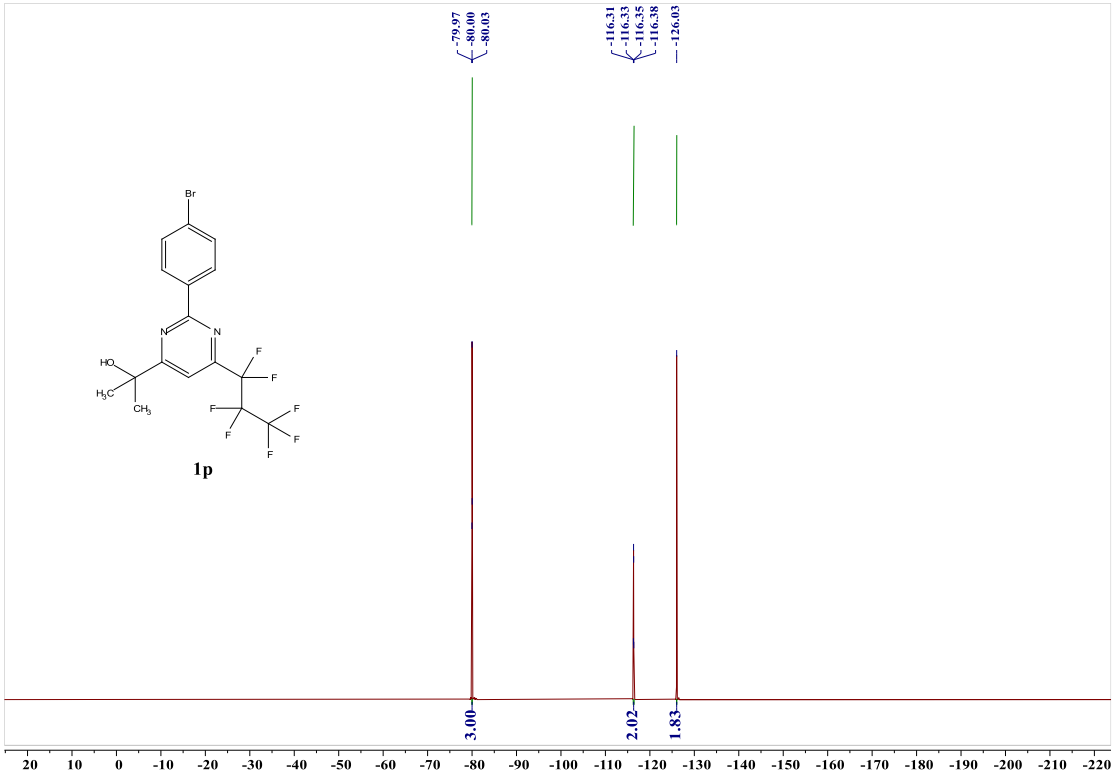
^{13}C NMR spectra of the product **5**



^{1}H NMR spectra of the product **1p**



^{19}F NMR spectra of the product **1p**



^{13}C NMR spectra of the product **1p**