Supporting Information for

Metal-free di- and tri-fluoromethylation of alkenes realized by visible-light-induced perylene photoredox catalysis

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Contents

Materials and methods

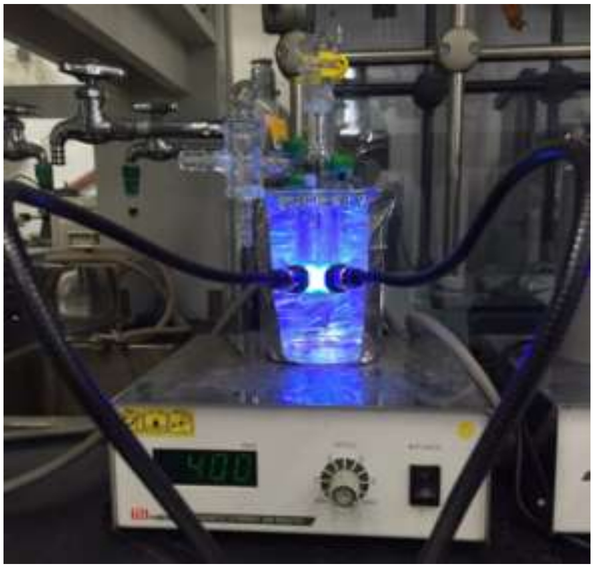
All the chemicals for synthesis of substrates were commercially available, and perylene was purchased from TCI. 2-(difluoromethylsulfonyl)benzo[d]thiazole (**D**), *N*-tosyl-*S*-difluoromethyl-*S*-phenylsulfoximine (**E**), and *S*-difluoromethyl-*S*-phenyl-2,3,4,5-tetramethylphenylsulfonium tetrafluoroborate (**G**) were prepared according to the procedures modified from the previously reported methods.[1] All the reactions were conducted using standard Schlenk techniques unless otherwise noted. Anhydrous CH_3CN was purchased from Kanto Chemical Co., Inc., and stored under N_2 atmosphere. Thin-layer chromatography was performed on TLC plate with 60 F_{254} Merck. Purification of substrates and products was performed by flush column chromatography on silica gel (Aldrich silica gel 60 Å). The crystallographic data were deposited at the Cambridge Crystallographic Data Centre: **1** (CCDC 1533276), **3c** (CCDC 1533274). Experiments and measurements were performed with following apparatuses.

Visible light irradiation: Relyon LED lamp (3 W × 2: λ = 425 nm ± 15 nm). NMR spectra: Bruker AVANCE-400 (400 MHz) and Bruker AVANCE-500 (500 MHz) (Reference of ^{1}H NMR spectra: Residual protio impurities in the deuterated solvents. Reference of ^{19}F NMR spectra: Trifluoroacetic acid (-76.55 ppm). Reference of ^{11}B NMR spectra: $BF_3 \cdot OEt_2$ (0.0 ppm). HRMS (ESI-TOF): Bruker micrOTOF II. GPC: Japan Analytical Industry Co., Ltd. (JAI) LC-9225. (Column: JAIGEL-1H-40 and JAIGEL-2H-40). UV-vis: JASCO V-670DS. Fluorescence: HITACHI F-7000. CV: Hokutodenkou HZ-5000. Excited-state lifetime: Hamamatsu Photonics C7700-ABS-N. Elemental analysis: J-SCIENCE JM10. Single-crystal X-ray measurement: Bruker SMART APEX II ULTRA.

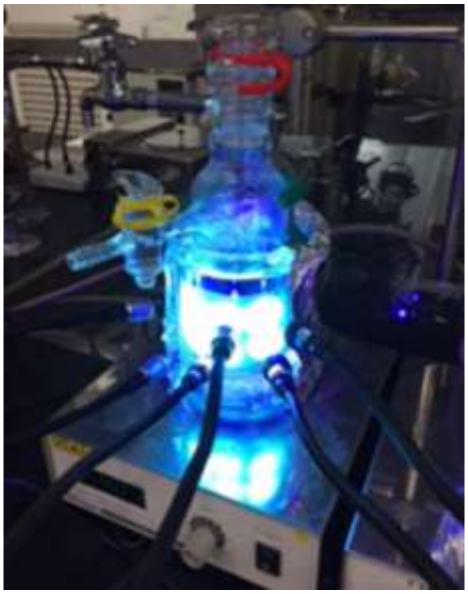
Reaction apparatus

Visible light irradiation was performed with Relyon LED lamps (3 W × 2: λ = 425 ± 15 nm) in a water bath.

(Normal preparative scale)

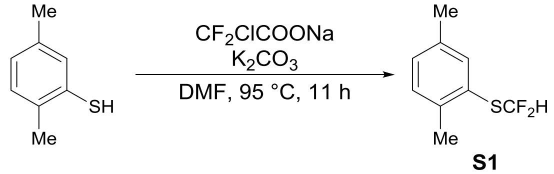


(Gram scale)



Procedures for synthesis of 1

(Difluoromethyl)(2,5-dimethylphenyl)sulfane (S1)



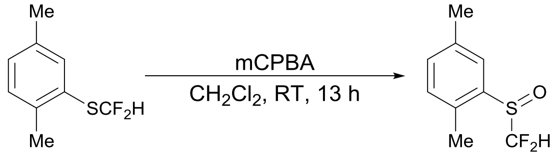
S1

S1 was prepared by the modified procedures according to the reported literature.[1c] Sodium chlorodifluoroacetate (9.20 g, 60.3 mmol) and K_2CO_3 (6.21 g, 44.9 mmol) were added to a 300 mL two-neck flask and dried *in vacuo*. Dry DMF (120 mL) and 2,5-dimethylbenzenthiol (4.31 g, 31.1 mmol) were added to the flask. After being stirred at 95 °C for 11 h, the mixture was cooled to room temperature. Water (100 mL) and pentane (100 mL) were added to the mixture and the organic phase was separated. The aqueous phase was extracted with pentane (50 mL × 3). The combined organic phase was dried over $MgSO_4$, filtered and concentrated. **S1** was obtained as a pale yellow oil (4.08 g, 21.7 mmol, 72%) after purification through flash column chromatography on silica-gel (pentane). The obtained product was used in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.40 (s, 1H; *Ar*), 7.18 (d, *J* = 7.6 Hz, 1H; *Ar*), 7.13 (d, *J* = 8.0 Hz, 1H; *Ar*), 6.77 (t, *J* = 57.2 Hz, 1H; CF_2*H*), 2.45 (s, 3H; *Me*), 2.32 (s, 3H; *Me*).

^{19}F NMR (376 MHz, $CDCl_3$, rt): δ -91.9 (d, *J* = 57.0 Hz, 2F).

2-(*S*-(Difluoromethyl)sulfinyl)-1,4-dimethylbenzene (S2)



S1 **S2**

S2 was prepared by the modified procedures according to the reported literature.[1e] To a CH_2Cl_2 (40 mL) solution of **S1** (4.08 g, 21.7 mmol) was added mCPBA (contains *ca.* 30% water, 5.61 g, 22.8 mmol) at 0 °C. After being stirred at room temperature for 13 h, the mixture was filtered with celite. The organic phase was washed with ice-cold NaOH aq (1 N, 30 mL), and the aqueous phase was extracted with CH_2Cl_2 (30 mL × 3). The combined organic phase was dried over Na_2SO_4, filtered and concentrated. **S2** was obtained as a pale yellow oil (4.13 g, 20.2 mmol, 92%) after purification through flash column chromatography on silica-gel (hexane/ethyl acetate = 5:1).

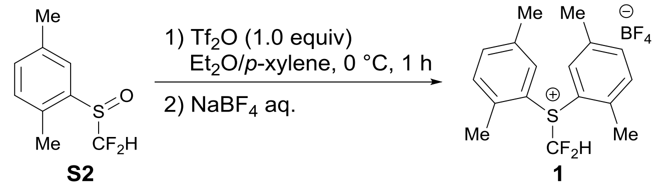
^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.72 (s, 1H; *Ar*), 7.29 (d, *J* = 7.6 Hz, 1H; *Ar*), 7.18 (d, *J* = 8.0 Hz, 1H; *Ar*), 6.05 (t, *J* = 55.6 Hz, 1H; CF_2*H*), 2.412 (s, 3H; *Me*), 2.405 (s, 3H; *Me*).

^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 137.6, 135.1, 134.7, 133.6, 131.4, 125.3, 122.4 (apparent t, *J* = 289.1 Hz), 21.1, 18.1.

^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ -118.3 (dd, *J* = 260.6 Hz, 55.6 Hz, 1F), -119.1 (dd, *J* = 260.2 Hz, 55.3 Hz, 1F).

HRMS (ESI-TOF) exact mass for $[C_9H_{10}F_2OS+Na]^+$ calcd m/z 227.0313, found 227.0316.

S-Difluoromethyl-*S*-di(*p*-xylyl)sulfonium tetrafluoroborate (1)



1 was prepared by the modified procedures according to the reported literature.[1e] To a solution of **S2** (2.55 g, 12.5 mmol) in *p*-xylene (15 mL) and Et_2O (25 mL) was slowly added Tf_2O (3.53 g, 12.5 mmol) at 0 °C. After stirring the mixture at the same temperature for 1 h, the beige precipitation was separated by filtration, and washed with Et_2O. The solid was dissolved in CH_2Cl_2 (20 mL) and washed with $NaBF_4$ aq. (1 M, 20 mL × 5). The organic phase was dried over $MgSO_4$, filtered and evaporated at 30 °C. Recrystallization with pentane and CH_2Cl_2 afforded **1** as white crystals (1.86 g, 39%).

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.37 (t, *J* = 52.8 Hz, 1H; CF_2H), 7.65 (s, 2H; *Ar*), 7.51, (d, *J* = 8.0 Hz, 2H; *Ar*), 7.40 (d, *J* = 7.6 Hz, 2H; *Ar*), 2.59 (s, 6H; *Me*), 2.48 (s, 6H; *Me*).

^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 140.9, 139.2, 136.9, 133.1, 131.5, 119.5 (t, *J* = 296.6 Hz), 117.3, 21.2, 19.7.

^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ -99.5 (d, *J* = 52.3 Hz, 2F; CF_2H), -152.7 (s, 4F; BF_4).

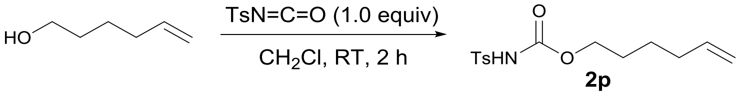
HRMS (ESI-TOF) calcd m/z for $[C_9H_{10}F_2OS+Na]^+$ 293.1170 found 293.1170.

EA: calculated for $C_{17}H_{19}BF_6S$: C, 53.71; H, 5.04, found: C, 53.44; H, 4.93.

Preparation of substrates

Styrene-type substrates except commercially available ones were prepared in the previous studies.[2] The aliphatic alkenes used for chlorotrifluoromethylation was prepared by the following method.

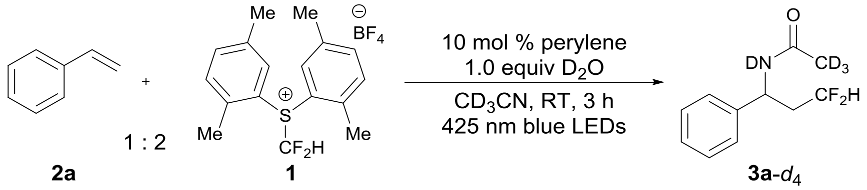
5-Hexen-1-yl tosylcarbamate (2p)



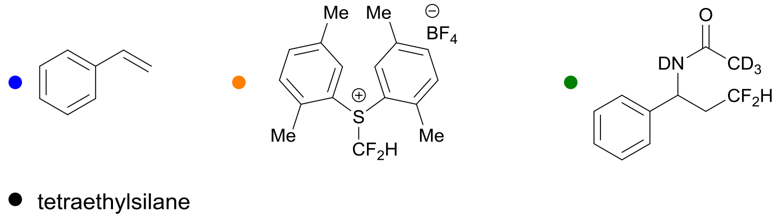
To a solution of 5-hexen-1-ol (0.502 g, 5.02 mmol) in CH_2Cl_2 (40 mL) was added dropwise TsN=C=O (0.986 g, 5.00 mmol) at 0 °C. After stirring the mixture for 2 h at room temperature, the solvent was evaporated. **2p** was obtained as a colorless oil (1.41 g, 4.73 mmol, 95%) after purification through flash column chromatography on silica-gel (hexane/AcOEt = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.92 (d, *J* = 8.4 Hz, 2H; *Ar*), 7.61 (brs, 1H; N*H*Ts), 7.34, (d, *J* = 8.0 Hz, 2H; *Ar*), 5.79-5.68 (m, 1H; CH_2=C*H*CH_2), 5.00-4.94 (2H; C*H*$_2$=CHCH_2), 4.08 (t, *J* = 6.4 Hz, 2H; OC*H*$_2$$CH_2$), 2.44 (s, 3H; *Me*), 2.04-1.99 (m, 2H; $CH_2=CHCH_2$), 1.62-1.54 (m, 2H; OCH_2CH_2), 1.39-1.31 (m, 2H; $CH_2CH_2CH_2$). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 150.6, 145.2, 138.2, 135.7, 129.7, 128.5, 115.1, 67.1, 33.2, 28.0, 24.9, 21.8. **HRMS** (ESI-TOF) calcd m/z for $[C_{14}H_{19}NO_4S+Na]^+$ 320.0927 found 320.0927

NMR experiments of the reaction of 2a with 1

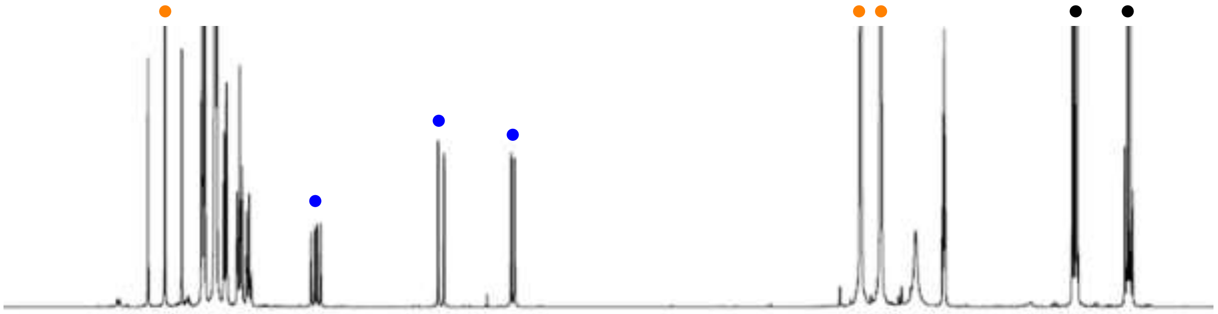


An NMR tube was charged with a CD_3CN (0.5 mL; containing 0.0250 mmol of D_2O) solution of styrene **2a** (2.6 mg, 0.0250 mmol), **1** (19.0 mg, 0.0500 mmol), perylene (0.6 mg, 2.50 μmol) and tetraethylsilane as an internal standard under N_2 atmosphere. The mixture was degassed by three freeze-pump-thaw cycles. The NMR tube was placed at 2−3 cm away from blue LED lamps (λ = 425 ± 15 nm) in a water bath. The reaction was carried out under visible light irradiation for 3 h at room temperature.



^{1}H NMR

Reaction time = 0 h



Reaction time = 3 h

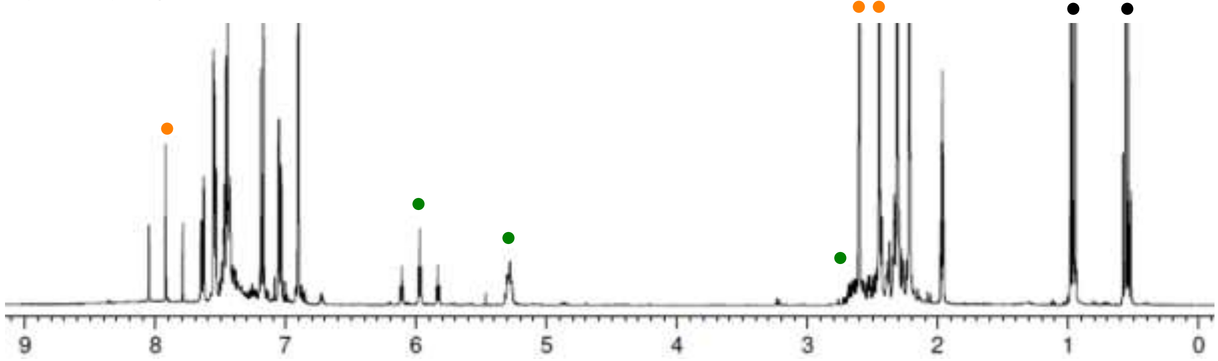


Figure S1. ^{1}H NMR spectra for the reaction of **2a** with **1**.

^{19}F NMR

Reaction time = 0 h

Reaction time = 3 h

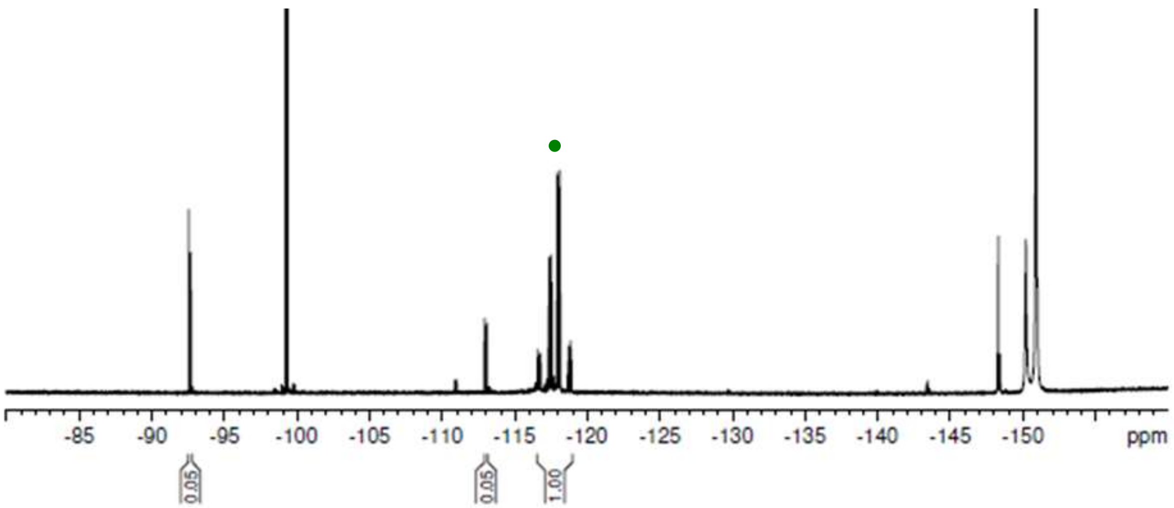
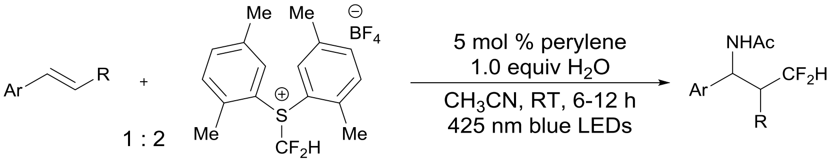


Figure S2. ^{19}F NMR spectra for the reaction of **2a** with **1**.

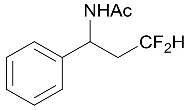
General procedures for aminodifluoromethylation of aromatic alkenes



2 **1** **3**

A 20 mL Schlenk tube was charged with a CH_3CN (5.00 mL) solution of an aromatic alkene **2** (0.250 mmol), **1** (190 mg, 0.500 mmol), perylene (3.2 mg, 0.0127 mmol) and H_2O (4.5 mg, 0.250 mmol) under N_2 atmosphere. The mixture was degassed by three freeze-pump-thaw cycles. The Schlenk tube was placed at 2−3 cm away from blue LED lamps (λ = 425 ± 15 nm) in a water bath. The mixture was stirred for 6−12 h at room temperature under visible light irradiation. After the reaction, H_2O (15 mL) was added and resulting suspension was extracted with CH_2Cl_2 (15 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The appropriate purification afforded the desired products.

***N*-(3,3-Difluoro-1-phenylpropyl)acetamide (3a)**



3a

According to the general procedures (reaction time = 6 h), styrene **2a** (26.2 mg, 0.252 mmol), **1** (190 mg, 0.500 mmol), perylene (3.2 mg, 0.0127 mmol), H_2O (4.5 mg, 0.250 mmol) and CH_3CN (5.00 mL) afforded **3a** as a white solid (40.7 mg, 76%) after purification through flash column chromatography on silica gel (hexane/ethyl acetate = 4 : 1 - 1 : 3) and GPC.

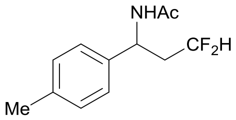
^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.40-7.29 (5H; *Ar*), 5.84 (brs, 1H; N*H*), 5.77 (apparent tt, *J* = 56.0 Hz, 4.8 Hz, 1H; CF_2*H*), 5.26 (apparent dt, *J* = 8.0 Hz, 6.0 Hz, 1H; C*H*CH_2CF_2H), 2.52-2.25 (m, 2H; CHC$H_2$$CF_2H$), 2.00 (s, 3H; NHCO*Me*).

^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 169.6, 140.3, 129.2, 128.2, 126.5, 115.9 (apparent t, *J* = 239.3 Hz), 48.9 (apparent t, *J* = 6.4 Hz), 40.5 (apparent t, *J* = 21.2 Hz), 23.4.

^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ -115.2 (dddd, *J* = 288.0 Hz, 56.0 Hz, 19.2 Hz, 13.2 Hz, 1F), -116.5 (dddd, *J* = 288.4 Hz, 56.0 Hz, 19.2 Hz, 12.8 Hz, 1F).

HRMS (ESI-TOF) calcd m/z for $[C_{11}H_{13}F_2NO+Na]^+$ 236.0857 found 236.0854.

N-(3,3-Difluoro-1-(*p*-tolyl)propyl)acetamide (3b)



3b

According to the general procedures (reaction time = 6 h), 4-methylstyrene **2b** (29.7 mg, 0.251 mmol), **1** (190 mg, 0.500 mmol), perylene (3.2 mg, 0.0127 mmol), H_2O (4.5 mg, 0.250 mmol) and CH_3CN (5.00 mL) afforded **3b** as a white solid (24.7 mg, 43%) after purification through flash column chromatography on silica gel (hexane/ethyl acetate = 4 : 1 - 1 : 3) and GPC.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.17 (4H; *Ar*), 5.94 (brd, *J* = 7.2 Hz, 1H; N*H*), 5.75 (apparent tt, *J* = 56.4 Hz, 4.8 Hz, 1H; CF_2H), 5.20 (apparent dt, *J* = 8.0 Hz, 6.4 Hz, 1H; $CHCH_2CF_2H$), 2.50-2.22 (m, 2H; $CHCH_2CF_2H$), 2.34 (s, 3H; *Me*), 1.98 (s, 3H; NHCO*Me*).

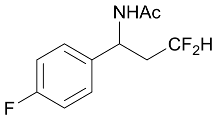
^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 169.5, 138.0, 137.4, 129.9, 126.4, 116.0 (apparent t, *J* = 239.3 Hz), 48.6 (apparent t, *J* = 6.5 Hz), 40.5 (apparent t, *J* = 21.1 Hz), 23.5, 21.2.

^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ -115.3 (dddd, *J* = 288.0 Hz, 56.4 Hz, 19.6 Hz, 13.2 Hz, 1F), -116.7 (dddd, *J* = 288.0 Hz, 56.4 Hz, 19.9 Hz, 13.2 Hz, 1F).

HRMS (ESI-TOF) calcd m/z for $[C_{12}H_{15}F_2NO+Na]^+$ 250.1014 found 250.1010.

EA: calculated for $C_{12}H_{15}F_2NO$: C, 63.42; H, 6.65; N, 6.16 found: C, 63.28; H, 6.88; N, 6.08.

N-(3,3-Difluoro-1-(4-fluorophenyl)propyl)acetamide (3c)



3c

According to the general procedures (reaction time = 12 h), 4-fluorostyrene **2c** (30.5 mg, 0.250 mmol), **1** (190 mg, 0.500 mmol), perylene (3.2 mg, 0.0127 mmol), H_2O (4.5 mg, 0.250 mmol) and CH_3CN (5.00 mL) afforded **3c** as a white solid (34.2 mg, 59%) after purification through flash column chromatography on silica gel (hexane/ethyl acetate = 4 : 1 - 1 : 3) and GPC.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.29-7.24 (2H; *Ar*), 7.07-7.02 (2H; *Ar*), 6.08 (brd, *J* = 6.0 Hz, 1H; N*H*), 5.76 (apparent tt, *J* = 56.0 Hz, 4.8 Hz, 1H; CF_2H), 5.22 (apparent dt, *J* = 8.0 Hz, 6.0 Hz, 1H; $CHCH_2CF_2H$), 2.48-2.22 (m, 2H; $CHCH_2CF_2H$), 1.99 (s, 3H; NHCO*Me*).

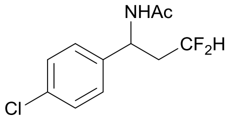
^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 169.8, 162.4 (d, *J* = 247 Hz), 136.4, 128.2 (d, *J* = 8.2 Hz), 116.0 (d, *J* = 21.5 Hz), 115.8 (apparent t, *J* = 239.6 Hz), 48.3 (apparent t, *J* = 6.3 Hz), 40.4 (apparent t, *J* = 21.4 Hz), 23.3.

^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ -114.9 (m, 1F; Ar*F*), -115.4 (dddd, *J* = 288.4 Hz, 56.0 Hz, 19.2 Hz, 13.5 Hz, 1F), -116.8 (dddd, *J* = 288.0 Hz, 56.4 Hz, 18.8 Hz, 13.2 Hz, 1F).

HRMS (ESI-TOF) calcd m/z for $[C_{11}H_{12}F_3NO+Na]^+$ 254.0763 found 254.0760.

EA: calculated for $C_{11}H_{12}F_3NO$: C, 57.14; H, 5.23; N, 6.06 found: C, 57.25; H, 5.22; N, 5.95.

***N*-(1-(4-Chlorophenyl)-3,3-difluoropropyl)acetamide (3d)**



3d

According to the general procedures (reaction time = 6 h), 4-chlorostyrene **2d** (34.6 mg, 0.250 mmol), **1** (190 mg, 0.500 mmol), perylene (3.2 mg, 0.0127 mmol), H_2O (4.5 mg, 0.250 mmol) and CH_3CN (5.00 mL) afforded **3d** as a pale yellow solid (37.9 mg, 61%) after purification through flash column chromatography on silica gel (hexane/ethyl acetate = 4 : 1 - 1 : 3) and reprecipitation (hexane and Et_2O).

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.34 (d, *J* = 8.4 Hz, 2H; *Ar*), 7.24 (d, *J* = 8.8 Hz, 2H; *Ar*), 5.83 (brs, 1H; N*H*), 5.78 (apparent tt, *J* = 56.0 Hz, 4.8 Hz, 1H; CF_2*H*), 5.23 (apparent dt, *J* = 8.0 Hz, 6.0 Hz, 1H; C*H*CH_2CF_2H), 2.48-2.23 (m, 2H; CH$\mathit{H}_2$$CF_2H$), 2.00 (s, 3H; NHCO*Me*).

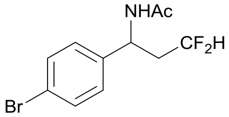
^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 169.7, 139.0, 134.0, 129.3, 127.9, 115.7 (apparent t, *J* = 239.7 Hz), 48.3 (apparent t, *J* = 6.2 Hz), 40.2 (apparent t, *J* = 21.5 Hz), 23.4.

^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ -115.1 (dddd, *J* = 288.8 Hz, 56.0 Hz, 19.2 Hz, 13.9 Hz, 1F), -116.6 (dddd, *J* = 288.8 Hz, 56.0 Hz, 18.0 Hz, 12.8 Hz, 1F).

HRMS (ESI-TOF) calcd m/z for $[C_{11}H_{12}ClF_2NO+Na]^+$ 270.0468 found 270.0465.

EA: calculated for $C_{11}H_{12}ClF_2NO$: C, 53.35; H, 4.88; N, 5.66 found: C, 53.32; H, 4.78; N, 5.58.

***N*-(1-(4-Bromophenyl)-3,3-difluoropropyl)acetamide (3e)**



3e

According to the general procedures (reaction time = 6 h), 4-bromostyrene **2e** (45.9 mg, 0.251 mmol), **1** (190 mg, 0.500 mmol), perylene (3.2 mg, 0.0127 mmol), H_2O (4.5 mg, 0.250 mmol) and CH_3CN (5.00 mL) afforded **3e** as a white solid (51.9 mg, 71%) after purification through flash column chromatography on silica gel (hexane/ethyl acetate = 4 : 1 - 1 : 3) and reprecipitation (hexane and Et_2O).

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.49 (d, *J* = 8.4 Hz, 2H; *Ar*), 7.17 (d, *J* = 8.4 Hz, 2H; *Ar*), 6.00 (brd, *J* = 7.2 Hz, 1H; N*H*), 5.77 (apparent tt, *J* = 56.0 Hz, 4.8 Hz, 1H; CF_2*H*), 5.21 (apparent dt, *J* = 8.0 Hz, 6.0 Hz, 1H; C*H*CH_2CF_2H), 2.47-2.22 (m, 2H; CH$\mathit{H}_2$$CF_2H$), 1.99 (s, 3H; NHCO*Me*).

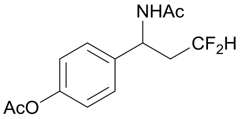
^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 169.6, 139.5, 132.3, 128.2, 122.1, 115.7 (apparent t, *J* = 239.5 Hz), 48.4 (apparent t, *J* = 6.3 Hz), 40.2 (apparent t, *J* = 21.4 Hz), 23.4.

^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ -115.2 (dddd, *J* = 288.8 Hz, 56.4 Hz, 19.6 Hz, 13.9 Hz, 1F), -116.7 (dddd, *J*

= 288.8 Hz, 55.6 Hz, 18.8 Hz, 13.5 Hz, 1F).

HRMS (ESI-TOF) calcd m/z for $[C_{11}H_{12}BrF_2NO+Na]^+$ 313.9963 found 313.9965.

4-(1-Acetamido-3,3-difluoropropyl)phenyl acetate (3f)



3f

According to the general procedures (reaction time = 6 h), 4-acetoxystyrene **2f** (40.7 mg, 0.251 mmol), **1** (190 mg, 0.500 mmol), perylene (3.2 mg, 0.0127 mmol), H_2O (4.5 mg, 0.250 mmol) and CH_3CN (5.00 mL) afforded **3f** as a pale yellow solid (40.7 mg, 60%) after purification through flash column chromatography on silica gel (hexane/ethyl acetate = 4 : 1 - 1 : 3) and reprecipitation (hexane and Et_2O).

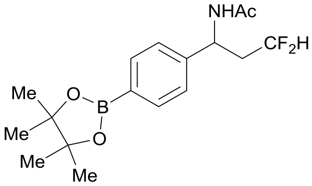
^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.30 (d, *J* = 8.4 Hz, 2H; *Ar*), 7.08 (d, *J* = 8.4 Hz, 2H; *Ar*), 6.04 (brs, 1H; N*H*), 5.78 (apparent tt, *J* = 56.0 Hz, 4.8 Hz, 1H; CF_2*H*), 5.25 (apparent dt, *J* = 8.0 Hz, 6.0 Hz, 1H; C*H*CH_2CF_2H), 2.49-2.23 (m, 2H; CHC*H*$_2CF_2H$), 2.30 (s, 3H; OCO*Me*), 1.98 (s, 3H; NHCO*Me*).

^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 169.8, 169.7, 150.3, 138.1, 127.7, 122.2, 115.8 (apparent t, *J* = 239.2 Hz), 48.2 (apparent t, *J* = 6.3 Hz), 40.3 (apparent t, *J* = 21.4 Hz), 23.2, 21.2.

^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ -115.3 (dddd, *J* = 288.4 Hz, 56.0 Hz, 19.2 Hz, 13.9 Hz, 1F), -116.8 (dddd, *J* = 288.0 Hz, 56.0 Hz, 18.4 Hz, 13.2 Hz, 1F).

HRMS (ESI-TOF) calcd m/z for $[C_{13}H_{15}F_2NO_3+Na]^+$ 294.0912 found 294.0915.

N-(3,3-Difluoro-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)acetamide (3g)



3g

According to the general procedures (reaction time = 6 h), 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane **2g** (57.5 mg, 0.250 mmol), **1** (190 mg, 0.500 mmol), perylene (3.2 mg, 0.0127 mmol), H_2O (4.5 mg, 0.250 mmol) and CH_3CN (5.00 mL) afforded **3g** as a pale yellow oil (25.3 mg, 30%) after purification through flash column chromatography on silica gel (hexane/ethyl acetate = 4 : 1 - 1 : 3) and GPC.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.81 (d, *J* = 8.0 Hz, 2H; *Ar*), 7.29 (d, *J* = 8.0 Hz, 2H; *Ar*), 6.06 (brd, *J* = 7.6 Hz, 1H; N*H*), 5.74 (apparent tt, *J* = 56.4 Hz, 4.8 Hz, 1H; CF_2*H*), 5.25 (apparent dt, *J* = 8.0 Hz, 6.0 Hz, 1H; C*H*CH_2CF_2H), 2.49-2.22 (m, 2H; CHC*H*$_2CF_2H$), 1.98 (s, 3H; NHCO*Me*), 1.33 (s, 12H; BOC*Me*$_2$).

^{11}B NMR (128 MHz, $CDCl_3$, rt): δ 30.4.

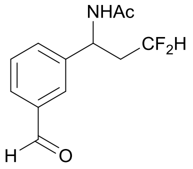
^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 169.6, 143.3, 135.7, 125.8, 115.9 (apparent t, *J* = 239.5 Hz), 84.1, 48.9

(apparent t, *J* = 6.4 Hz), 40.3 (apparent t, *J* = 21.3 Hz), 25.0, 23.4.

^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ -114.3 (dddd, *J* = 288.0 Hz, 56.0 Hz, 19.6 Hz, 13.2 Hz, 1F), -115.7 (dddd, *J* = 288.0 Hz, 55.6 Hz, 18.8 Hz, 12.4 Hz, 1F).

HRMS (ESI-TOF) calcd m/z for $[C_{17}H_{24}BF_2NO_3+Na]^+$ 362.1713 found 362.1709.

N-(3,3-Difluoro-1-(3-formylphenyl)propyl)acetamide (3h)



3h

According to the general procedures (reaction time = 12 h), 3-vinylbenzaldehyde **2h** (33.1 mg, 0.250 mmol), **1** (190 mg, 0.500 mmol), perylene (3.2 mg, 0.0127 mmol), H_2O (4.5 mg, 0.250 mmol) and CH_3CN (5.00 mL) afforded **3h** as a pale yellow oil (24.8 mg, 41%) after purification through flash column chromatography on silica gel (hexane/ethyl acetate = 4 : 1 - 1 : 3) and GPC.

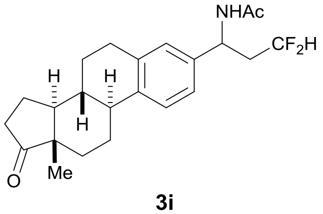
^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 9.99 (s, 1H; C*H*O), 7.83 (s, 1H; *Ar*), 7.78 (d, *J* = 7.6 Hz, 1H; *Ar*), 7.58 (d, *J* = 8.0 Hz, 1H; *Ar*), 7.52 (dd, *J* = 7.6 Hz, 7.6 Hz, *Ar*), 6.59 (brd, *J* = 7.2 Hz, 1H; N*H*), 5.80 (apparent tt, *J* = 56.0 Hz, 4.8 Hz, 1H; CF_2*H*), 5.32 (apparent dt, *J* = 8.0 Hz, 5.6 Hz, 1H; C*H*CH_2CF_2H), 2.45-2.25 (m, 2H; CHC*H*$_2CF_2$H), 2.00 (s, 3H; NHCO*Me*).

^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 192.2, 169.9, 142.2, 137.0, 133.0, 130.2, 129.9, 126.4, 115.6 (apparent t, *J* = 239.7 Hz), 48.5 (apparent t, *J* = 5.8 Hz), 40.3 (apparent t, *J* = 21.6 Hz), 23.3.

^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ -115.4 (dddd, *J* = 288.0 Hz, 56.0 Hz, 19.6 Hz, 14.7 Hz, 1F), -116.8 (dddd, *J* = 288.0 Hz, 55.6 Hz, 17.3 Hz, 13.2 Hz, 1F).

HRMS (ESI-TOF) calcd m/z for $[C_{12}H_{13}F_2NO_2+Na]^+$ 264.0807 found 264.0808.

N-(3,3-Difluoro-1-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)propyl)acetamide (3i)



3i

According to the general procedures (reaction time = 6 h), (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one **2i** (70.1 mg, 0.250 mmol), **1** (190 mg, 0.500 mmol), perylene (3.2 mg, 0.0127 mmol), H_2O (4.5 mg, 0.250 mmol) and CH_3CN (5.00 mL) afforded **3i** as a white solid (37.4 mg, 38%) after purification through flash column chromatography on silica gel (hexane/ethyl acetate = 4 : 1 - 1 : 3) and GPC.

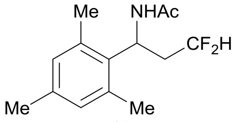
^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.29 (d, *J* = 8.0 Hz, 1H; *Ar*), 7.07 (d, *J* = 8.0 Hz, 1H; *Ar*), 7.02 (s, 1H; *Ar*), 5.88 (brs, 1H; N*H*CHCH$_2$), 5.77 (apparent tt, *J* = 56.0 Hz, 4.8 Hz, 1H; CF$_2$*H*), 5.19 (apparent dt, *J* = 8.0 Hz, 6.4 Hz, 1H; NHC*H*CH$_2$), 2.91 (dd, *J* = 8.8 Hz, 4.0 Hz, 2H; steroidal C*H*$_2$), 2.54-1.95 (9H; steroidal protons, CHC*H*$_2$CF$_2$H), 1.99 (s, 3H; NHCO*Me*), 1.68-1.39 (6H; steroidal protons), 0.91 (s, 3H; steroidal *Me*).

^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 220.9, 169.6, 139.8, 137.8, 137.4, 127.3 (apparent d, *J* = 7.5 Hz), 126.2, 123.7 (apparent d, *J* = 4.9 Hz), 116.0 (apparent t, *J* = 239.1 Hz), 50.6, 48.6 (apparent d, *J* = 5.0 Hz), 48.1, 44.4, 40.4 (apparent t, *J* = 18.7 Hz), 38.1, 35.9, 31.7, 29.5 (apparent d, *J* = 1.9 Hz), 26.5, 25.8, 23.4, 21.7, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ from -114.8 to -117.3 (m, 2F).

HRMS (ESI-TOF) calcd m/z for $[C_{23}H_{29}F_2NO_2+Na]^+$ 412.2059 found 412.2059.

N-(3,3-Difluoro-1-mesitylpropyl)acetamide (3j)



3j

According to the general procedures (reaction time = 6 h), 2,4,6-trimethylstyrene **2j** (36.6 mg, 0.250 mmol), **1** (190 mg, 0.500 mmol), perylene (3.2 mg, 0.0127 mmol), H_2O (4.5 mg, 0.250 mmol) and CH_3CN (5.00 mL) afforded **3j** as a white solid (33.0 mg, 52%) after purification through flash column chromatography on silica gel (hexane/ethyl acetate = 4 : 1 - 1 : 3) and GPC.

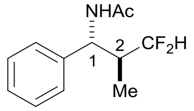
^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 6.85 (s, 2H; *Ar*), 6.07 (brs, 1H; N*H*), 5.85 (apparent tt, *J* = 56.4 Hz, 4.8 Hz, 1H; CF$_2$*H*), 5.62 (apparent dt, *J* = 7.2 Hz, 7.2 Hz, 1H; C*H*CH$_2$CF$_2$H), 2.63-2.21 (m, 2H; CHC*H*$_2$CF$_2$H), 2.41 (s, 6H; Ar*Me*), 2.25 (s, 3H; Ar*Me*), 1.96 (s, 3H; NHCO*Me*).

^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 169.7, 137.5, 135.9, 133.7, 130.6, 116.2 (apparent t, *J* = 239.6 Hz), 44.9 (apparent t, *J* = 6.5 Hz), 39.4 (apparent t, *J* = 20.9 Hz), 23.2, 21.0, 20.8.

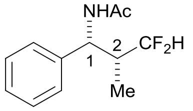
^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ -115.7 (dddd, *J* = 285.0 Hz, 56.0 Hz, 18.0 Hz, 15.0 Hz, 1F), -116.6 (dddd, *J* = 285.4 Hz, 56.4 Hz, 16.2 Hz, 16.2 Hz, 1F).

HRMS (ESI-TOF) calcd m/z for $[C_{14}H_{19}F_2NO+Na]^+$ 278.1327 found 278.1328.

N-(3,3-difluoro-2-methyl-1-phenylpropyl)acetamide (3l)



(1*R**,2*S**)-**3l**



(1*R**,2*R**)-**3l**

According to the general procedures (reaction time = 6 h), *trans*-β-methylstyrene **2l** (29.7 mg, 0.251 mmol), **1** (190 mg, 0.500 mmol), perylene (3.2 mg, 0.0127 mmol), H_2O (4.5 mg, 0.500 mmol) and CH_3CN (5.00 mL) gave crude products (dr 71:29; determined by ^{1}H NMR), and purification through flash column chromatography on silica gel (hexane/ethyl acetate = 4 : 1 - 1 : 3) and GPC afforded **3l** as a white solid (25.8 mg, 45%, a mixture of isomers, 74:26; determined by ^{1}H NMR).

Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.38-7.24 (5H; *Ar*), 6.07 (brs, 1H; N*H*CHCH$_2$), 5.71 (apparent td, *J* = 56.0 Hz, 3.2 Hz, 1H; CF$_2$*H*), 5.12 (dd, *J* = 4.2 Hz, 4.2 Hz, 1H; NHC*H*CH), 2.50-2.32 (m, 1H; CHC*H*CF$_2$H), 2.01 (s, 3H; NHCO*Me*), 0.98 (d, *J* = 6.8 Hz, 3H; CHCH*Me*).

^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 169.8, 139.7, 129.1, 128.0, 126.9, 117.5 (t, *J* = 239.5 Hz), 54.2 (dd, *J* = 6.9 Hz, 1.3 Hz), 42.1 (t, *J* = 19.4 Hz), 23.4, 8.8 (t, *J* = 4.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ -121.7 (ddd, *J* = 285.4 Hz, 55.3 Hz, 8.6 Hz, 1F), -126.5 (ddd, *J* = 285.8 Hz, 56.8 Hz, 22.9 Hz, 1F).

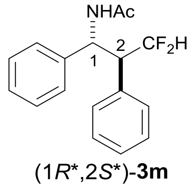
Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.38-7.24 (5H; *Ar*), 6.05 (brs, 1H; N*H*CHCH$_2$), 5.51 (apparent td, *J* = 56.0 Hz, 4.0 Hz, 1H; CF$_2$*H*), 5.17 (dd, *J* = 7.2 Hz, 4.8 Hz, 1H; NHC*H*CH), 2.50-2.32 (m, 1H; CHC*H*CF$_2$H), 2.02 (s, 3H; NHCO*Me*), 1.07 (d, *J* = 7.2 Hz, 3H; CHCH*Me*).

^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 169.7, 139.2, 129.0, 128.0, 126.9, 117.6 (t, *J* = 239.5 Hz), 53.6 (dd, *J* = 5.9 Hz, 4.0 Hz), 42.8 (t, *J* = 19.5 Hz), 23.4, 9.6 (t, *J* = 4.8 Hz).

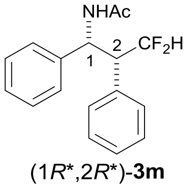
^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ -120.1 (ddd, *J* = 284.3 Hz, 56.0 Hz, 9.0 Hz, 1F), -128.5 (ddd, *J* = 284.3 Hz, 56.0 Hz, 19.2 Hz, 1F).

HRMS (ESI-TOF) calcd m/z for $[C_{12}H_{15}F_2NO+Na]^+$ 250.1014 found 250.1013.

N-(3,3-Difluoro-1,2-diphenylpropyl)acetamide (3m)



(1*R**,2*S**)-**3m**



(1*R**,2*R**)-**3m**

According to the general procedures (reaction time = 6 h), *trans*-stilbene **2m** (45.0 mg, 0.251 mmol), **1** (190 mg, 0.500 mmol), perylene (3.2 mg, 0.0127 mmol), H_2O (4.5 mg, 0.500 mmol) and CH_3CN (5.00 mL) gave crude products (dr 83:17; determined by ^{19}F NMR), and purification through flash column chromatography on silica gel (hexane/ethyl acetate = 4 : 1 - 1 : 3) and GPC afforded **3m** as a colorless oil (46.5 mg, 64%, a mixture of isomers, 85:15; determined by ^{19}F NMR).

Major isomer: ^{1}H NMR (400 MHz, CDCl$_3$, rt): δ 7.36-7.04 (10H; *Ar*), 6.09 (apparent td, *J* = 55.6 Hz, 4.8 Hz, 1H; CF$_2$*H*), 6.08 (brs, 1H; N*H*CHCH), 5.59 (t, *J* = 9.2 Hz, 1H; NHC*H*CH), 3.60-3.49 (m, 1H; CHC*H*CF$_2$H), 2.00 (s, 3H; NHCO*Me*).

^{13}C NMR (125 MHz, CDCl$_3$, rt): δ 169.6, 139.1, 133.8 (t, *J* = 3.3 Hz), 129.7, 128.6, 128.5, 127.9, 127.8, 127.5, 116.8 (t, *J* = 243.7 Hz), 54.5 (t, *J* = 19.6 Hz), 53.8 (t, *J* = 3.5 Hz), 23.5.

^{19}F NMR (376 MHz, CDCl$_3$, r.t.): δ -118.2 (ddd, *J* = 285.0 Hz, 56.0 Hz, 16.2 Hz, 1F), -120.3 (ddd, *J* = 284.6 Hz, 54.9 Hz, 12.4 Hz, 1F).

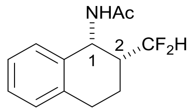
Minor isomer: ^{1}H NMR (400 MHz, CDCl$_3$, rt): δ 7.36-7.04 (10H; *Ar*), 5.84 (brd, *J* = 8.0 Hz, 1H; N*H*CHCH), 5.81 (apparent td, *J* = 55.6 Hz, 4.0 Hz, 1H; CF$_2$*H*), 5.56 (t, *J* = 8.8 Hz, 1H; NHC*H*CH), 3.47-3.39 (m, 1H; CHC*H*CF$_2$H), 1.81 (s, 3H; NHCO*Me*).

^{13}C NMR (125 MHz, CDCl$_3$, rt): δ 169.4, 139.8, 133.0, 129.9, 129.0, 128.7, 128.3, 128.2, 127.2, 115.8 (t, *J* = 243.4 Hz), 55.1 (t, *J* = 19.7 Hz), 52.8 (t, *J* = 2.8 Hz), 23.2.

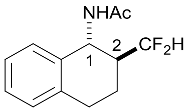
^{19}F NMR (376 MHz, CDCl$_3$, r.t.): δ -120.9 (ddd, *J* = 285.4 Hz, 55.6 Hz, 9.8 Hz, 1F), -124.6 (ddd, *J* = 285.0 Hz, 55.6 Hz, 20.7 Hz, 1F).

HRMS (ESI-TOF) calcd m/z for $[C_{17}H_{17}F_2NO+Na]^+$ 312.1170 found 312.1167.

N-(2-(Difluoromethyl)-1,2,3,4-tetrahydronaphthalen-1-yl)acetamide (3n)



(1*R**,2*R**)-**3n**



(1*R**,2*S**)-**3n**

According to the general procedures (reaction time = 6 h), 1,2-dihydronaphthalene **2n** (32.4 mg, 0.249 mmol), **1** (190 mg, 0.500 mmol), perylene (3.2 mg, 0.0127 mmol), H$_2$O (4.5 mg, 0.500 mmol) and CH$_3$CN (5.00 mL) gave crude products (dr 57:43; determined by ^{1}H NMR), and purification through flash column chromatography on silica gel (hexane/ethyl acetate = 4 : 1 - 1 : 3) and GPC afforded **3n** as a white solid (26.3 mg, 44%, a mixture of isomers, 53:47; determined by ^{1}H NMR).

Major isomer: ^{1}H NMR (400 MHz, CDCl$_3$, rt): δ 7.27-7.09 (4H; *Ar*), 5.87 (apparent td, *J* = 56.0 Hz, 3.2 Hz, 1H; CF$_2$*H*), 5.85 (brs, 1H; N*H*CHCH), 5.26 (t, *J* = 8.8 Hz, 8.8 Hz, 1H; NHC*H*CH), 2.98-2.78 (m, 2H; ArC*H*$_2$CH$_2$), 2.38-2.26 (m, 1H, CHC*H*CF$_2$H), 2.22-1.69 (m, 2H, ArC*H*$_2$CH$_2$), 2.05 (s, 3H; NHCO*Me*).

^{13}C NMR (125 MHz, CDCl$_3$, rt): δ 170.2, 117.0 (t, *J* = 242.0 Hz), 47.6 (dd, *J* = 6.2 Hz, 3.5 Hz), 45.2 (t, *J* = 20.1 Hz), 28.0, 23.4, 20.0 (t, *J* = 4.5 Hz).

Aromatic signals of major and minor diastereomers were overlapped around (136.9, 136.1, 135.6, 135.5, 129.9, 129.2, 129.0, 128.2, 128.1, 127.6, 126.9, 126.8).

^{19}F NMR (376 MHz, CDCl$_3$, r.t.): δ -123.5 (ddd, *J* = 283.5 Hz, 56.0 Hz, 10.2 Hz, 1F), -126.5 (ddd, *J* = 283.1 Hz, 56.4 Hz, 18.8 Hz, 1F).

Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.27-7.09 (4H; *Ar*), 5.96 (apparent td, *J* = 56.0 Hz, 3.6 Hz, 1H; CF_2*H*), 5.84 (brd, *J* = 8.4 Hz, 1H; N*H*CHCH), 5.47 (dd, *J* = 9.2 Hz, 4.0 Hz, 1H; NHC*H*CH), 2.87-2.83 (m, 2H; ArC$H_2$$CH_2$), 2.22-1.69 (m, 3H, ArC$H_2$$CH_2$, CHC*H*$CF_2$H), 1.97 (s, 3H; NHCO*Me*).

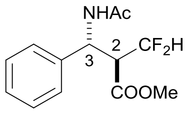
^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 169.6, 117.3 (t, *J* = 240.2 Hz), 46.0 (dd, *J* = 6.7 Hz, 3.5 Hz), 43.3 (t, *J* = 20.1 Hz), 27.7, 23.4, 17.1 (t, *J* = 4.7 Hz).

Aromatic signals of major and minor diastereomers were overlapped around (136.9, 136.1, 135.6, 135.5, 129.9, 129.2, 129.0, 128.2, 128.1, 127.6, 126.9, 126.8).

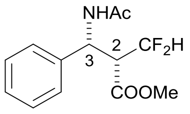
^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ -118.4 (ddd, *J* = 285.8 Hz, 55.6 Hz, 11.7 Hz, 1F), -127.0 (ddd, *J* = 285.8 Hz, 56.0 Hz, 17.3 Hz, 1F).

HRMS (ESI-TOF) calcd m/z for $[C_{13}H_{15}F_2NO+Na]^+$ 262.1014 found 262.1009.

Methyl 3-acetamido-2-(difluoromethyl)-3-phenylpropanoate (3o)



(2*R**,3*R**)-**3o**



(2*S**,3*R**)-**3o**

According to the general procedures (reaction time = 12 h), methyl cinnamate **2o** (40.6 mg, 0.250 mmol), **1** (190 mg, 0.500 mmol), perylene (3.2 mg, 0.0127 mmol), H_2O (4.5 mg, 0.500 mmol) and CH_3CN (5.00 mL) gave crude products (dr 73:27; determined by ^{1}H NMR), and purification through flash column chromatography on silica gel (hexane/ethyl acetate = 4 : 1 - 1 : 3) and GPC afforded **3o** as a pale yellow oil (40.9 mg, 60%, a mixture of isomers, 73:27; determined by ^{1}H NMR).

Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.36-7.21 (5H; *Ar*), 7.04 (brd, *J* = 9.2 Hz, 1H; N*H*), 6.03 (apparent td, *J* = 55.6 Hz, 6.4 Hz, 1H; CF_2*H*), 5.61 (dd, *J* = 9.6 Hz, 4.0 Hz, 1H; C*H*CHCF_2H), 3.63 (s, 3H; COO*Me*), 3.39-3.31 (m, 1H; CHC*H*CF_2H), 2.09 (s, 3H; NHCO*Me*).

^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 169.6, 169.5, 138.5, 129.0, 128.2, 126.1, 114.7 (t, *J* = 245.5 Hz), 54.7 (t, *J* = 22.4 Hz), 52.7, 50.0 (dd, *J* = 5.9 Hz, 3.4 Hz), 23.5.

^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ -120.5 (ddd, *J* = 289.5 Hz, 55.6 Hz, 10.9 Hz, 1F), -121.7 (ddd, *J* = 289.5 Hz, 55.3 Hz, 12.0 Hz, 1F).

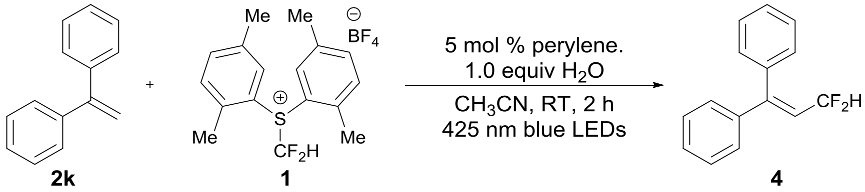
Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.36-7.21 (5H; *Ar*), 6.43 (brd, *J* = 8.4 Hz, 1H; N*H*), 5.92 (apparent td, *J* = 55.2 Hz, 6.4 Hz, 1H; CF_2*H*), 5.57 (dd, *J* = 8.0 Hz, 8.0 Hz, 1H; C*H*CHCF_2H), 3.61 (s, 3H; COO*Me*), 3.39-3.31 (m, 1H; CHC*H*CF_2H), 2.02 (s, 3H; NHCO*Me*).

^{13}C NMR (125 MHz, $CDCl_3$, rt): δ168.2, 168.1, 137.8, 129.0, 128.6, 127.0, 114.9 (t, *J* = 243.6 Hz), 55.0 (t, *J* = 21.3 Hz), 52.5, 51.2 (dd, *J* = 6.8 Hz, 2.5 Hz), 23.3.

^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ -119.1 (ddd, *J* = 291.0 Hz, 54.5 Hz, 12.0 Hz, 1F), -121.7 (ddd, *J* = 291.4 Hz, 55.3 Hz, 10.2 Hz, 1F).

HRMS (ESI-TOF) calcd m/z for $[C_{13}H_{15}F_2NO_3+Na]^+$ 294.0912 found 294.0916.

Procedures for synthesis of 3,3-difluoro-1,1-diphenylpropene (4)



20 mL Schlenk tube was charged with a CH_3CN (5.00 mL) solution of 1,1-diphenylethylene **2k** (0.250 mmol), **1** (190 mg, 0.500 mmol), perylene (3.2 mg, 0.0127 mmol) and H_2O (4.5 mg, 0.500 mmol) under N_2 atmosphere. The mixture was degassed by three freeze−pump−thaw cycles. The Schlenk tube was placed at 2−3 cm away from blue LED lamps (λ = 425 ± 15 nm) in the water bath. The mixture was stirred for 2 h at room temperature under visible light irradiation. After the reaction, H_2O (15 mL) was added and resulting mixture was extracted with Et_2O (15 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification through flash column chromatography on silica gel (pentane) and GPC afforded **4** as a colorless oil (31.3 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.42-7.22 (10H; *Ar*), 6.21-6.15 (m, 1H; $CF_2HCH{=}C$), 6.02 (td, *J* = 55.6 Hz, 7.6 Hz, 1H; CF_2H).

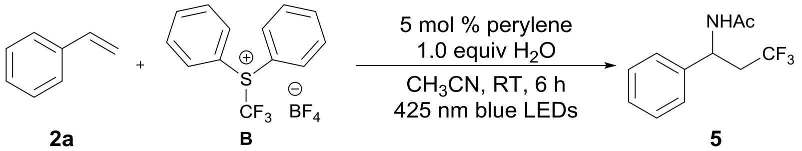
^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 150.8 (t, *J* = 13.1 Hz), 140.2, 137.4, 129.9, 129.2, 128.8, 128.60, 128.56, 128.2, 120.2 (t, *J* = 26.5 Hz), 113.9 (t, *J* = 229.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ -107.8 (dd, *J* = 54.6 Hz, 7.9 Hz, 2F).

HRMS (ESI-TOF) calcd m/z for $[C_{15}H_{12}F_2+Na]^+$ 253.0799 found 253.0804.

Trifluoromethylation of alkenes with various trifluoromethylating reagents

N-(3,3-Trifluoro-1-phenylpropyl)acetamide (5)



A 20 mL Schlenk tube was charged with a CH_3CN (5.00 mL) solution of **2a** (26.3 mg, 0.253 mmol), Yagupolskii reagent **B** (171.0 mg, 0.500 mmol), perylene (3.2 mg, 0.0127 mmol) and H_2O (4.5 mg, 0.250 mmol) under N_2 atmosphere. The mixture was degassed by three freeze−pump−thaw cycles. The Schlenk tube was placed at 2−3 cm away from blue LED lamps (λ = 425 ± 15 nm) in a water bath. The mixture was stirred for 6 h at room temperature under visible light irradiation. After the reaction, H_2O (15 mL) was added and resulting suspension was extracted with CH_2Cl_2 (15 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification through flash column chromatography on silica gel (hexane/ethyl acetate = 4 : 1 - 1 : 1) and GPC afforded **5** as a white solid (38.3 mg, 66%).

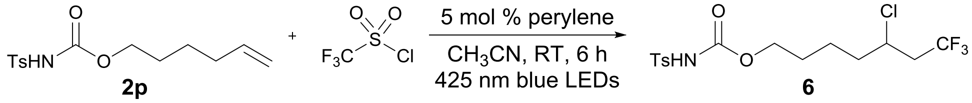
Spectral data is in agreement with the reported literature.[2a]

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.39-7.29 (5H; *Ar*), 5.74 (brs, 1H; N*H*CHCH$_2$), 5.35 (apparent dt, *J* = 8.0 Hz, 6.4 Hz, 1H; NHC*H*CH$_2$), 2.82-2.53 (m, CHC*H*$_2$CF$_3$), 2.00 (s, 3H; *Me*).

^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 169.6, 140.2, 129.1, 128.2, 126.5, 125.7 (q, *J* = 277.6 Hz), 48.4 (q, *J* = 3.1 Hz), 39.6 (q, *J* = 27.5 Hz), 23.2.

^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ -64.3 (t, *J* = 10.5 Hz, 3F).

5-Chloro-7,7,7-trifluoroheptyl tosylcarbamate (6)



A 20 mL Schlenk tube was charged with a CH_3CN (5.00 mL) solution of 5-hexen-1-yl tosylcarbamate **2p** (74.5 mg, 0.251 mmol), trifluoromethansulfonyl chloride (84.4 mg, 0.501 mmol) and perylene (3.2 mg, 0.0127 mmol) under N_2 atmosphere. The mixture was degassed by three freeze−pump−thaw cycles. The Schlenk tube was placed at 2−3 cm away from blue LED lamps (λ = 425 ± 15 nm) in a water bath. The mixture was stirred for 6 h at room temperature under visible light irradiation. After the reaction, the mixture was concentrated under reduced pressure. Purification through flash column chromatography on silica gel (hexane/ethyl acetate = 4 : 1) and GPC afforded **6** as a pale yellow oil (57.2 mg, 57%).

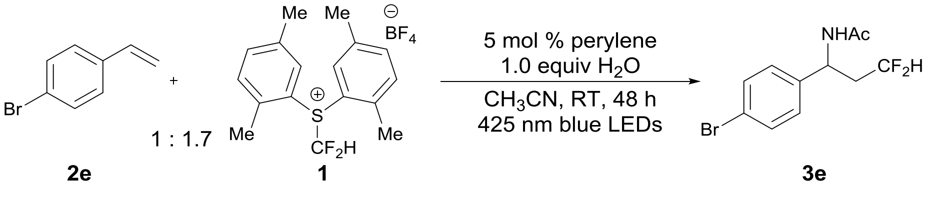
^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.98 (brs, 1H, N*H*Ts), 7.91 (d, *J* = 8.4 Hz, 2H; *Ar*), 7.34 (d, *J* = 8.4 Hz, 2H; *Ar*), 4.10 (t, *J* = 6.0 Hz, 2H; OC*H*$_2$CH$_2$), 4.06-4.01 (m, 1H; ClC*H*CH$_2$), 2.66-2.46 (m, 2H; CF$_3$C*H*$_2$CH), 2.44 (s, 3H; *Me*), 1.84-1.37 (6H; ClCHC*H*$_2$, OCH$_2$C*H*$_2$, CH$_2$C*H*$_2$CH$_2$).

^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 150.7, 145.3, 135.6, 129.8, 128.4, 125.3 (q, *J* = 277.6 Hz), 66.7, 53.9 (q, *J* = 3.0 Hz), 42.4 (q, *J* = 28.5 Hz), 37.5, 27.8, 22.3, 21.8.

^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ -64.8 (t, *J* = 10.5 Hz, 3F).

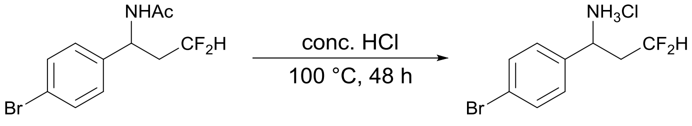
HRMS (ESI-TOF) calcd m/z for $[C_{15}H_{19}ClF_3NO_4S+Na]^+$ 424.0568 found 424.0568.

Gram-scale synthesis



A 200 mL Schlenk tube was charged with a CH_3CN (120 mL) solution of **2e** (1.10 g, 6.01 mmol), **1** (3.88 g, 10.2 mmol), perylene (75.7 mg, 0.300 mmol) and H_2O (0.109 g, 6.08 mmol) under N_2 atmosphere. The mixture was degassed by three freeze-pump-thaw cycles. The Schlenk tube was placed at 2−3 cm away from blue LED lamps (λ = 425 ± 15 nm) in a water bath. The mixture was stirred for 48 h at room temperature under visible light irradiation. After the reaction, the mixture was concentrated under reduced pressure. H_2O (50 mL) and CH_2Cl_2 (50 mL) were added and the organic layer was separated. The water phase was extracted with CH_2Cl_2 (50 mL × 2). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification through flash column chromatography on silica gel (hexane/ethyl acetate = 4 : 1 - 1 : 3) and reprecipitation afforded **3e** as a pale yellow sold (1.11 g, 64%)

Deprotection of 3e



3e

A 100 mL two-neck flask was charged with **3e** (0.296 g, 1.01 mmol) and conc. HCl (15 mL). The mixture was stirred for 48 h at 100 °C. Volatiles were evaporated by aspirator, and the residue was washed with Et_2O to afford the desired amine-salt as a beige solid (0.154 g, 53%).

^{1}H NMR (400 MHz, CD_3OD, rt): δ 7.67 (d, *J* = 8.4 Hz, 2H; *Ar*), 7.44, (d, *J* = 8.0 Hz, 2H; *Ar*), 5.92 (apparent tt, *J* = 55.2 Hz, 4.4 Hz, 1H; CF_2H), 4.60 (t, 1H; *J* = 7.6 Hz, $CHCH_2CF_2H$), 2.65-2.54 (m, 2H; $CHCH_2CF_2H$).

^{13}C NMR (125 MHz, CD_3OD, rt): δ 136.3, 133.8, 130.4, 124.8, 116.3 (apparent t, *J* = 238.8 Hz), 51.0 (apparent t, *J* = 7.7 Hz), 39.3 (apparent t, *J* = 22.3 Hz).

^{19}F NMR (376 MHz, CD_3OD, r.t.): δ-116.0 (dddd, *J* = 290.6 Hz, 54.9 Hz, 14.7 Hz, 14.7 Hz, 1F), -117.4 (dddd, *J* = 289.9 Hz, 55.6 Hz, 17.3 Hz, 17.3 Hz, 1F).

HRMS (ESI-TOF) calcd m/z for $[C_9H_{10}BrF_2N+H]^+$ 250.0037 found 250.0041.

Electro- and photo-chemical studies

Cyclic voltammograms of **1**, perylene and **G**

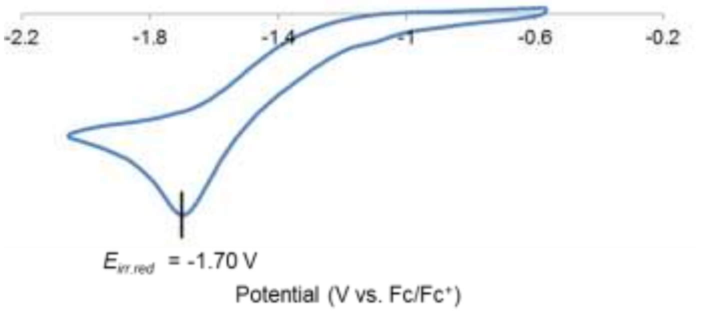


Figure S3. Cyclic voltammogram of **1**. The measurement was performed in CH_3CN ([**1**] = 1.00 mM, $[[NBu_4]PF_6]$ = 0.100 M, referenced by ferrocene).

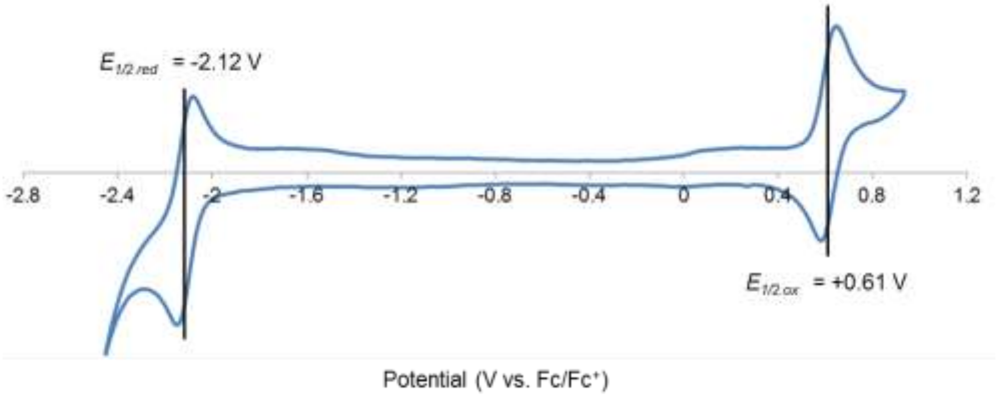


Figure S4. Cyclic voltammogram of perylene. The measurement was performed in CH_3CN ([perylene] = 1.00 mM, $[[NBu_4]PF_6]$ = 0.100 M, referenced by ferrocene).

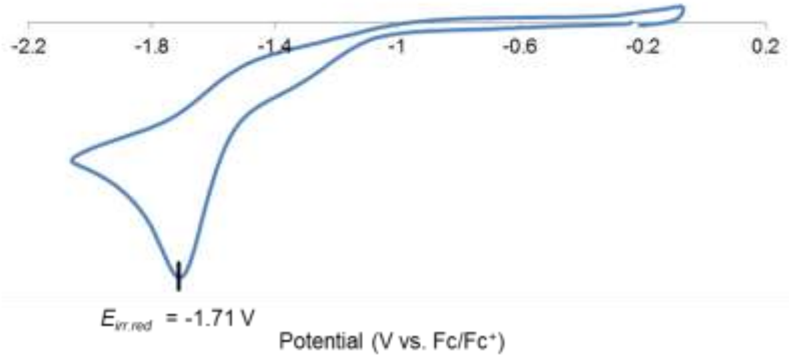


Figure S5. Cyclic voltammogram of **G**. The measurement was performed in CH_3CN ([CF_2H reagent] = 1.00 mM, $[[NBu_4]PF_6]$ = 0.100 M, referenced by ferrocene).

UV-vis spectra of perylene and **1**, and emission spectrum of perylene

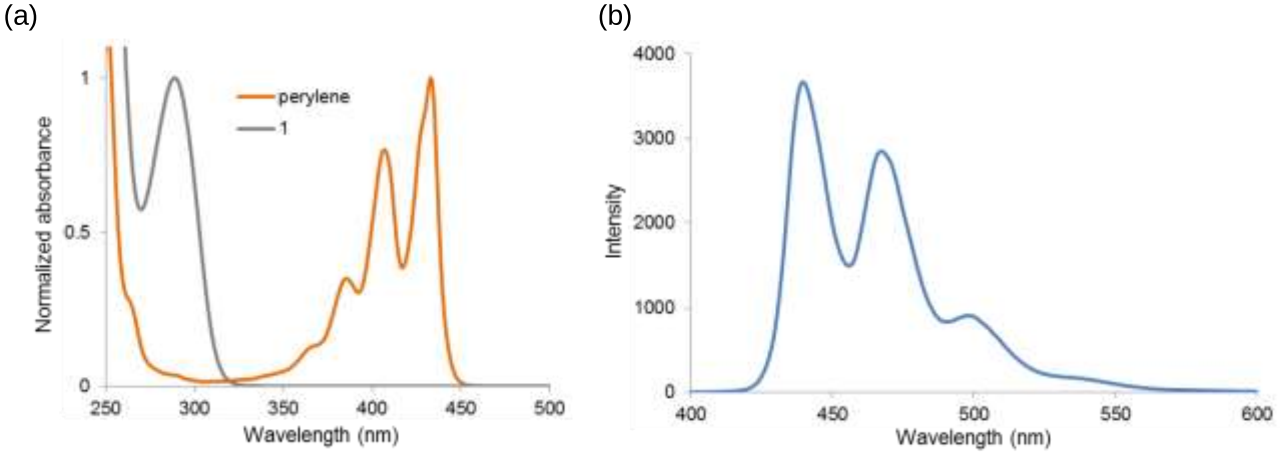


Figure S6. (a) UV-vis spectra of perylene and **1** and (b) emission spectrum of perylene. All the measurements were performed in CH_3CN at room temperature ((a): [perylene] = 0.040 mM, [**1**] = 0.132 mM, Normalized spectra are shown in the figure. (b): [perylene] = 0.004 mM, excitation light: λ = 380 nm).

UV-vis spectra of other PAHs

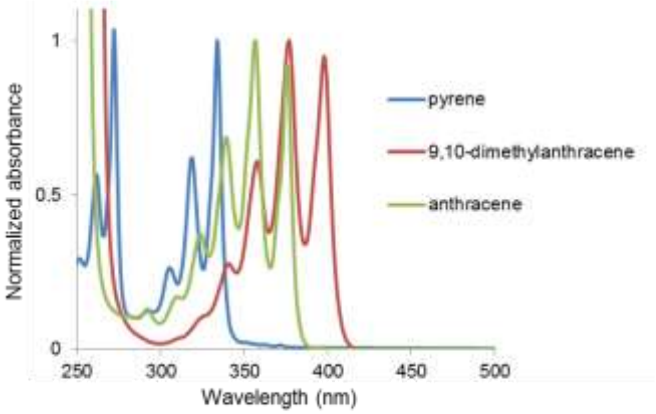


Figure S7. UV-vis spectra of other PAHs. All the measurements were performed in CH_3CN at room temperature ([pyrene] = 0.014 mM, [9,10-dimethylanthracene] = 0.040 mM, [anthracene] = 0.040 mM, Normalized spectra are shown in the figure).

Estimation of the excited state energy of perylene

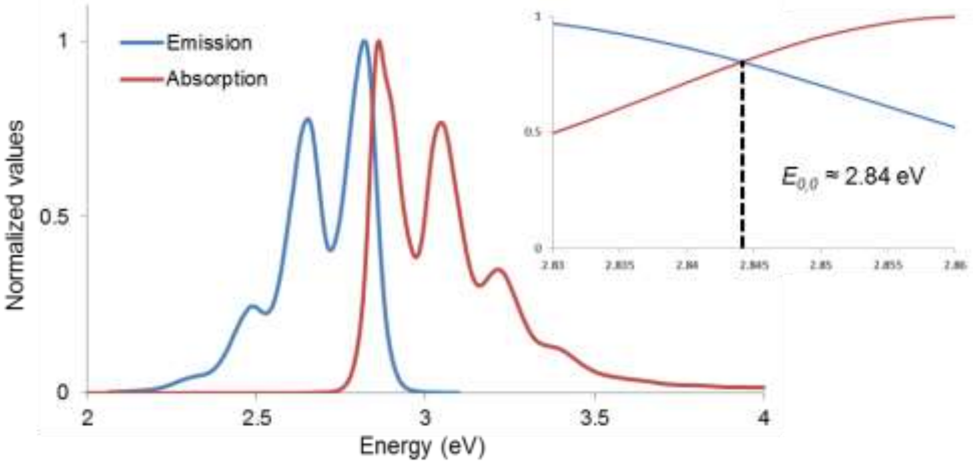


Figure S8. Normalized spectra for absorption and emission of perylene. All the measurements were performed in CH_3CN at room temperature. Excited state energy was estimated at the intersection between normalized absorption and emission spectra after converting the wavelength axis to energy scale.

Redox potentials at the excited state are estimated by the following formula. They were calculated by using redox potentials at the ground state and the excited state energy of perylene measured in the above experiments.[3]

$$E^*_{ox} = E_{1/2.ox} - E_{0,0} \qquad E^*_{ox} = \mathbf{-2.23\ V}$$

$$E^*_{red} = E_{1/2.red} + E_{0,0} \qquad E^*_{red} = \mathbf{+0.72\ V}$$

Excited-state lifetime of perylene

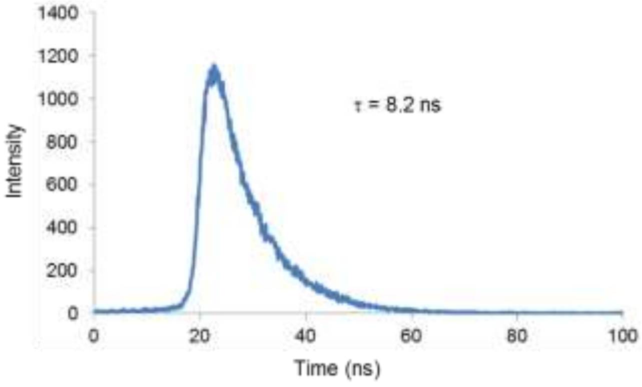


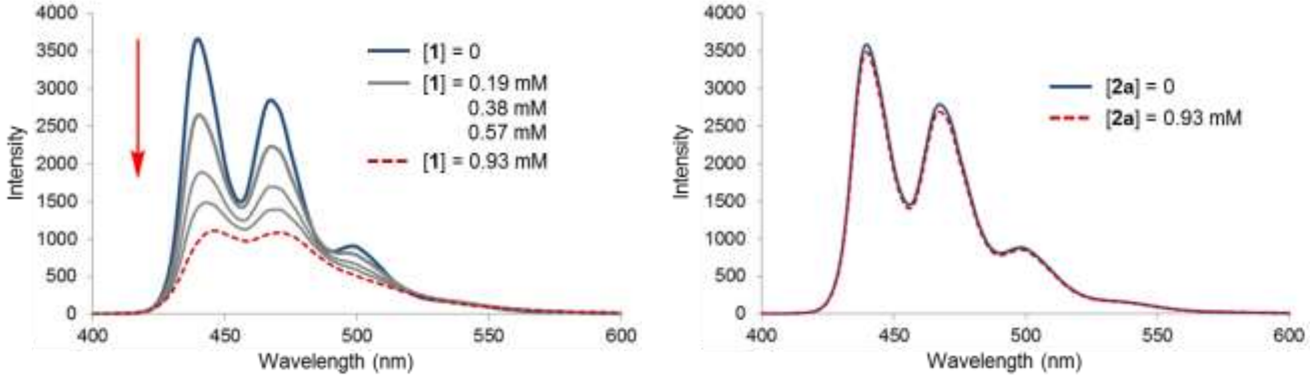
Figure S9. Luminescence decay of perylene. The measurement was performed in CH_3CN at room temperature.

Redox potentials and selected photophysical properties of perylene

Table S1 Redox potentials and selected photophysical properties of perylene.

$E_{1/2.ox}$ (V)	$E_{1/2.red}$ (V)	E^*_{ox} (V)	E^*_{red} (V)	excited-state lifetime τ (ns)	absorption λ (nm)	emission λ_{max} (nm)
+ 0.61	-2.12	-2.23	+0.72	8.2	434, 407	440

Luminescence quenching experiments

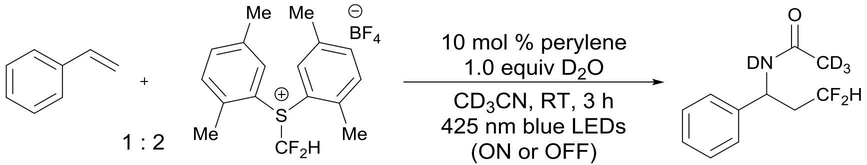


(a) Quencher: **1**

(b) Quencher: styrene (**2a**)

Figure S10. Luminescence quenching experiments of perylene. The measurement was performed in CH_3CN at room temperature and absorption of perylene was adjusted to 0.1 for measurements. The Solutions were degassed by three freeze-pump-thaw cycles before all the measurements. (a) **1** was used as a quencher, and (b) styrene (**2a**) was used as a quencher.

Time profile for the reaction of 2a with 1



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

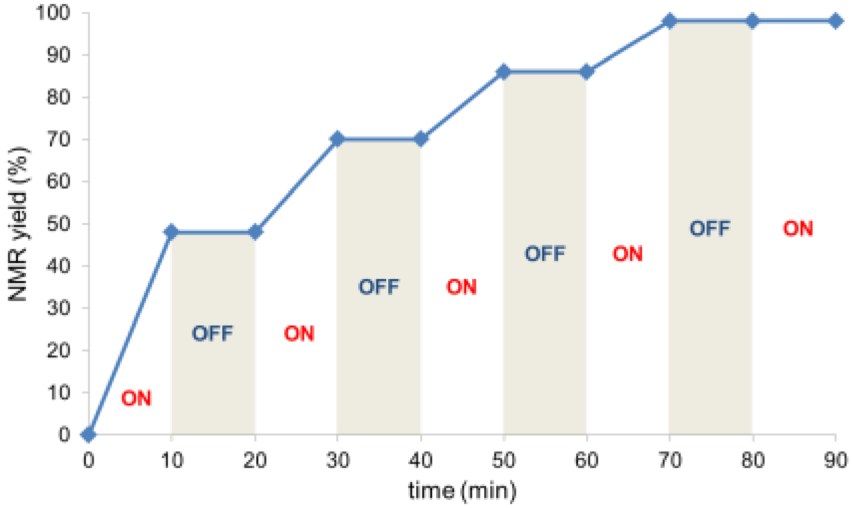
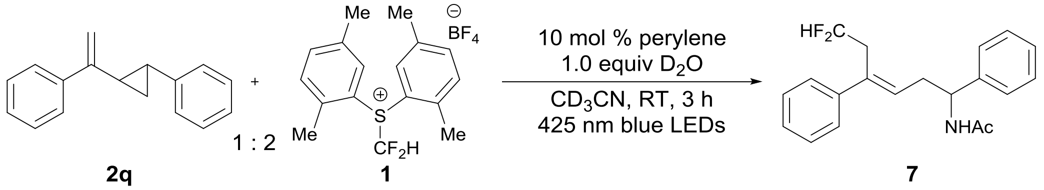


Figure S11. Time profile for the reaction of **2a** with **1**.

The above result suggested that perylene served as a redox catalyst, and radical chain reaction was not a main pathway in the present reaction.

Radical clock experiments

NMR experiment



An NMR tube was charged with a CD_3CN (0.5 mL; containing 0.0250 mmol of D_2O) solution of (1-(2-phenylcyclopropyl)vinyl)benzene **2q** (5.5 mg, 0.0250 mmol), **1** (19.0 mg, 0.0500 mmol), perylene (0.6 mg, 0.00250 mmol) and tetraethylsilane as an internal standard under N_2 atmosphere. The mixture was degassed by three freeze−pump−thaw cycles. The NMR tube was placed at 2−3 cm away from blue LED lamps (λ = 425 ± 15 nm). The reaction was carried out under visible light irradiation for 3 h at room temperature (49% NMR yield). As a result, the almost single product was formed in the reaction.

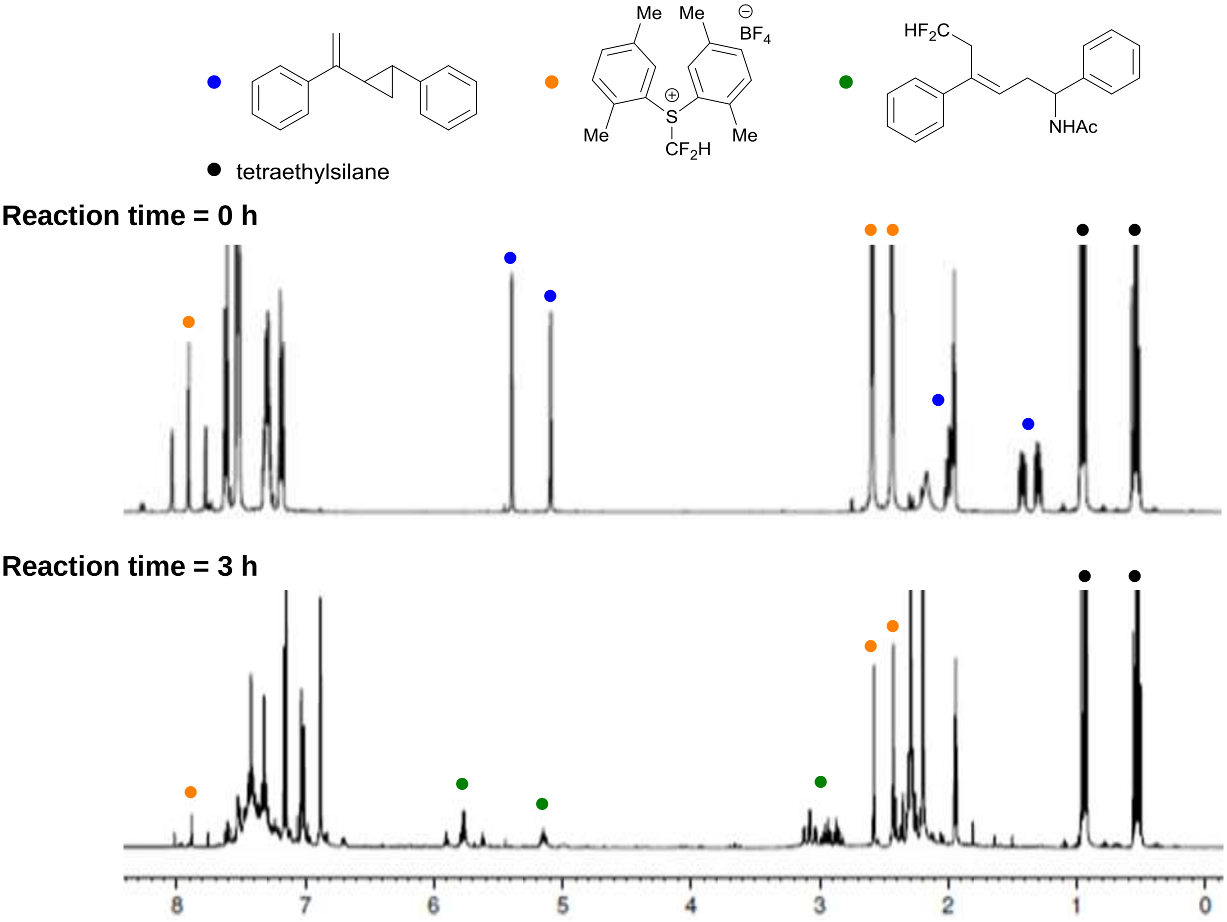
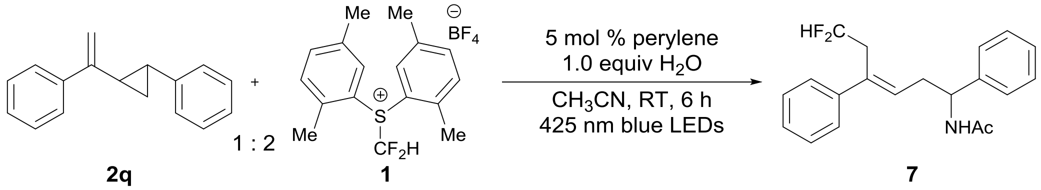


Figure S12. NMR experiment of the reaction of **2q** with **1**.

Preparative scale



A 20 mL Schlenk tube was charged with a CH_3CN (5.00 mL) solution of (1-(2-phenylcyclopropyl)vinyl) benzene **2q** (55.1 mg, 0.250 mmol), **1** (190 mg, 0.500 mmol), perylene (3.2 mg, 0.0127 mmol) and H_2O (4.5 mg, 0.250 mmol) under N_2 atmosphere. The mixture was degassed by three freeze−pump−thaw cycles. The Schlenk tube was placed at 2−3 cm away from blue LED lamps (λ = 425 ± 15 nm). The mixture was stirred for 6 h at room temperature under visible light irradiation. After the reaction, H_2O (15 mL) was added and resulting suspension was extracted with CH_2Cl_2 (15 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification through flash column chromatography on silica gel (hexane/ethyl acetate = 4 : 1 - 1 : 3) and GPC afforded a as a white solid (19.2 mg, 23%).

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.38-7.24 (10H; Ar), 5.94 (brd, *J* = 7.6 Hz, 1H; NH), 5.81 (t, *J* = 7.2 Hz, 1H; $C{=}CHCH_2$), 5.70 (tt, *J* = 56.8 Hz, 4.8 Hz, 1H; CF_2H), 5.17 (dd, *J* = 8.0 Hz, 6.0 Hz, 1H; $NHCHCH_2$), 3.10-3.00 (m, 2H; $CHCH_2CF_2H$), 2.85-2.70 (m, 2H; $C{=}CHCH_2$), 1.99 (s, 3H; NHCOMe).

^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 169.7, 141.52, 141.47, 134.1 (t, *J* = 5.9 Hz), 129.5, 128.9, 128.7, 127.7 (2C), 126.6, 126.5, 116.0 (t, *J* = 240.8 Hz), 53.3, 35.7, 35.5 (t, *J* = 22.4 Hz), 23.4.

^{19}F NMR (376 MHz, $CDCl_3$, r.t.): δ -114.8 (dddd, *J* = 278 Hz, 56.4 Hz, 15.4 Hz, 15.4 Hz, 1F), -115.8 (dddd, *J* = 277.9 Hz, 56.8 Hz, 19.2 Hz, 15.4 Hz, 1F).

HRMS (ESI-TOF) calcd m/z for $[C_{20}H_{21}F_2NO+Na]^+$ 352.1483 found 352.1480.

Crystallographic data of 1 and 3c

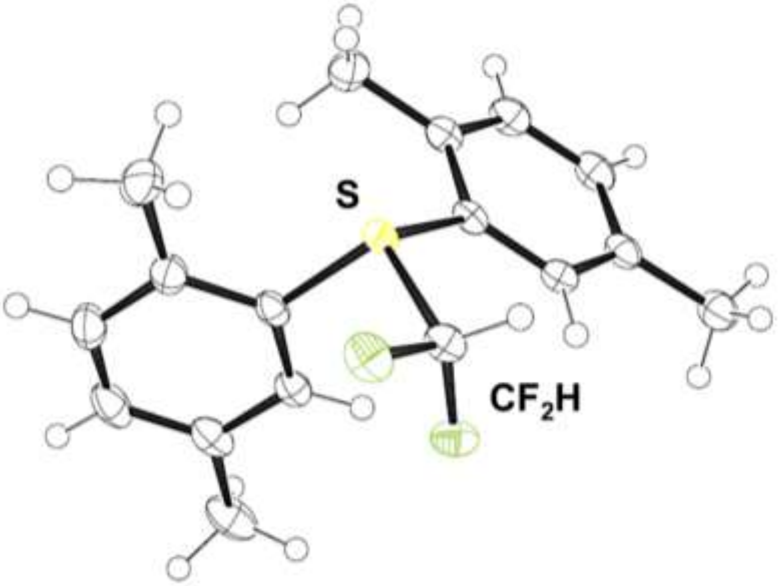


Figure S13. An ORTEP drawing of **1**. One BF_4 anion was omitted for clarity.

Table S2-1. Crystal data and structure refinement for **1**.

Chemical formula	$C_{17}H_{19}BF_6S$	
Formula weight	380.19	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal size	0.110 x 0.172 x 0.231 mm	
Crystal system	orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 13.8754(11) Å	α = 90°
	b = 14.2531(12) Å	β = 90°
	c = 17.5717(14) Å	γ = 90°
Volume	3475.1(5) $Å^3$	
Z	8	
Density (calculated)	1.453 g/cm^3	
Absorption coefficient	0.243 mm^{-1}	
F(000)	1568	
Theta range for data collection	2.32 to 25.03°	
Index ranges	-16<=h<=16, -16<=k<=15, -20<=l<=18	
Reflections collected	15395	

Independent reflections	3065 [R(int) = 0.0135]	
Coverage of independent reflections	100.00%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9740 and 0.9460	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	Σ w(Fo^2 - Fc^2)^2	
Data / restraints / parameters	3065 / 0 / 230	
Goodness-of-fit on F2	0.98	
Δ/σmax	0.001	
Final R indices	2832 data; I>2σ(I)	R1 = 0.0279, wR2 = 0.0694
	all data	R1 = 0.0306, wR2 = 0.0720
Weighting scheme	w=1/[σ^2(Fo^2)+(0.0302P)^2+2.8611P] where P=(Fo^2+2Fc^2)/3	
Largest diff. peak and hole	0.355 and -0.281 eÅ^{-3}	
R.M.S. deviation from mean	0.040 eÅ^{-3}	

Table S2-2. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for **1**.

	x/a	y/b	z/c	U(eq)
B1	0.34182(12)	0.58501(11)	0.00492(9)	0.0207(3)
C1	0.50262(10)	0.30523(9)	0.51920(8)	0.0188(3)
C2	0.42769(10)	0.29436(10)	0.46783(8)	0.0208(3)
C3	0.42665(10)	0.34824(10)	0.40151(8)	0.0233(3)
C4	0.50079(11)	0.41270(11)	0.39079(8)	0.0266(3)
C5	0.57443(11)	0.42295(10)	0.44305(9)	0.0269(3)
C6	0.57860(10)	0.36878(10)	0.50878(8)	0.0225(3)
C7	0.66011(11)	0.37884(11)	0.56465(9)	0.0299(3)
C8	0.34714(11)	0.33598(12)	0.34417(9)	0.0300(4)
C9	0.47304(10)	0.30370(10)	0.67918(8)	0.0205(3)
C10	0.39013(10)	0.35784(9)	0.67151(8)	0.0215(3)
C11	0.36018(12)	0.41377(10)	0.73206(9)	0.0274(3)
C12	0.41677(13)	0.41384(11)	0.79775(9)	0.0341(4)
C13	0.49885(12)	0.35956(12)	0.80404(9)	0.0340(4)
C14	0.52962(11)	0.30151(11)	0.74518(9)	0.0268(3)
C15	0.27044(13)	0.47223(11)	0.72645(10)	0.0381(4)
C16	0.61845(12)	0.24204(13)	0.75422(10)	0.0369(4)

C17	0.42029(10)	0.14099(10)	0.59529(8)	0.0220(3)
F1	0.43444(7)	0.09001(6)	0.65847(5)	0.0299(2)
F2	0.33200(6)	0.17793(6)	0.59883(5)	0.0270(2)
F3	0.33641(7)	0.56126(8)	0.92852(5)	0.0409(3)
F4	0.30186(7)	0.51428(7)	0.04835(6)	0.0417(3)
F5	0.43876(6)	0.59509(7)	0.02415(5)	0.0337(2)
F6	0.29424(8)	0.66792(7)	0.01728(7)	0.0476(3)
S1	0.51495(2)	0.23370(2)	0.60183(2)	0.01906(10)

Table S2-3. Bond lengths (Å) for **1**.

B1-F6	1.3710(19)	B1-F4	1.3807(18)
B1-F3	1.3866(19)	B1-F5	1.3942(18)
C1-C2	1.385(2)	C1-C6	1.402(2)
C1-S1	1.7824(14)	C2-C3	1.396(2)
C2-H2	0.95	C3-C4	1.392(2)
C3-C8	1.504(2)	C4-C5	1.382(2)
C4-H4	0.95	C5-C6	1.390(2)
C5-H5	0.95	C6-C7	1.504(2)
C7-H7A	0.98	C7-H7B	0.98
C7-H7C	0.98	C8-H8A	0.98
C8-H8B	0.98	C8-H8C	0.98
C9-C10	1.392(2)	C9-C14	1.401(2)
C9-S1	1.7835(14)	C10-C11	1.393(2)
C10-H10	0.95	C11-C12	1.396(2)
C11-C15	1.502(2)	C12-C13	1.381(3)
C12-H12	0.95	C13-C14	1.392(2)
C13-H13	0.95	C14-C16	1.504(2)
C15-H15A	0.98	C15-H15B	0.98
C15-H15C	0.98	C16-H16A	0.98
C16-H16B	0.98	C16-H16C	0.98
C17-F2	1.3348(17)	C17-F1	1.3413(16)
C17-S1	1.8666(14)	C17-H17	1

Table S2-4. Bond angles (°) for **1**.

C10-C9-C14	123.76(13)	C10-C9-S1	120.39(11)
C14-C9-S1	115.83(11)	C9-C10-C11	119.34(14)
C9-C10-H10	120.3	C11-C10-H10	120.3

C10-C11-C12	117.66(15)	C10-C11-C15	121.00(15)
C12-C11-C15	121.34(14)	C13-C12-C11	121.97(14)
C13-C12-H12	119	C11-C12-H12	119
C12-C13-C14	121.77(15)	C12-C13-H13	119.1
C14-C13-H13	119.1	C13-C14-C9	115.48(14)
C13-C14-C16	120.52(15)	C9-C14-C16	124.00(14)
C11-C15-H15A	109.5	C11-C15-H15B	109.5
H15A-C15-H15B	109.5	C11-C15-H15C	109.5
H15A-C15-H15C	109.5	H15B-C15-H15C	109.5
C14-C16-H16A	109.5	C14-C16-H16B	109.5
H16A-C16-H16B	109.5	C14-C16-H16C	109.5
H16A-C16-H16C	109.5	H16B-C16-H16C	109.5
F2-C17-F1	108.03(11)	F2-C17-S1	111.32(9)
F1-C17-S1	103.27(9)	F2-C17-H17	111.3
F1-C17-H17	111.3	S1-C17-H17	111.3
C1-S1-C9	105.64(7)	C1-S1-C17	106.69(7)
C9-S1-C17	102.33(6)		

Table S2-5. Anisotropic atomic displacement parameters (Å^2) for **1**.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[\, h^2 a^{*2} U_{11} + \ldots + 2\, h\, k\, a^* b^* U_{12}\,]$

	U11	U22	U33	U23	U13	U12
B1	0.0214(8)	0.0189(8)	0.0218(8)	0.0009(6)	-0.0001(6)	-0.0012(6)
C1	0.0234(7)	0.0160(7)	0.0169(7)	0.0018(5)	0.0052(6)	0.0031(5)
C2	0.0210(7)	0.0198(7)	0.0217(7)	0.0001(6)	0.0048(6)	0.0021(6)
C3	0.0249(7)	0.0242(7)	0.0207(7)	0.0000(6)	0.0041(6)	0.0075(6)
C4	0.0340(8)	0.0237(8)	0.0220(8)	0.0066(6)	0.0064(6)	0.0050(6)
C5	0.0309(8)	0.0217(7)	0.0280(8)	0.0028(6)	0.0068(6)	-0.0036(6)
C6	0.0247(7)	0.0198(7)	0.0229(7)	-0.0004(6)	0.0048(6)	-0.0006(6)
C7	0.0287(8)	0.0314(8)	0.0297(8)	0.0035(7)	0.0002(7)	-0.0100(7)
C8	0.0291(8)	0.0379(9)	0.0232(8)	0.0040(7)	0.0004(6)	0.0087(7)
C9	0.0247(7)	0.0191(7)	0.0177(7)	-0.0003(5)	0.0048(6)	-0.0049(6)
C10	0.0267(7)	0.0169(7)	0.0208(7)	0.0020(5)	0.0041(6)	-0.0035(6)
C11	0.0369(9)	0.0171(7)	0.0281(8)	-0.0007(6)	0.0116(7)	-0.0058(6)
C12	0.0470(10)	0.0297(8)	0.0257(8)	-0.0104(7)	0.0122(7)	-0.0143(7)
C13	0.0386(9)	0.0429(10)	0.0205(8)	-0.0023(7)	-0.0010(7)	-0.0171(8)
C14	0.0278(8)	0.0317(8)	0.0209(7)	0.0039(6)	0.0006(6)	-0.0101(6)

C15	0.0476(10)	0.0256(8)	0.0411(10)	-0.0036(7)	0.0192(8)	0.0052(7)
C16	0.0303(8)	0.0527(10)	0.0278(8)	0.0099(8)	-0.0052(7)	-0.0032(8)
C17	0.0254(7)	0.0170(7)	0.0235(7)	0.0027(5)	0.0045(6)	-0.0008(6)
F1	0.0389(5)	0.0231(4)	0.0276(5)	0.0091(4)	0.0043(4)	-0.0022(4)
F2	0.0228(4)	0.0223(4)	0.0359(5)	-0.0002(4)	0.0057(4)	-0.0014(3)
F3	0.0471(6)	0.0498(6)	0.0256(5)	-0.0090(4)	-0.0078(4)	0.0017(5)
F4	0.0379(5)	0.0402(6)	0.0469(6)	0.0200(5)	-0.0058(5)	-0.0145(4)
F5	0.0230(5)	0.0501(6)	0.0279(5)	-0.0014(4)	-0.0011(4)	-0.0078(4)
F6	0.0487(6)	0.0300(5)	0.0641(7)	-0.0083(5)	0.0059(5)	0.0135(5)
S1	0.02034(18)	0.01819(19)	0.01865(18)	0.00286(13)	0.00261(13)	0.00079(13)

Table S2-6. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for **1**.

	x/a	y/b	z/c	U(eq)
H2	0.3775	0.2507	0.4776	0.025
H4	0.5008	0.4507	0.3463	0.032
H5	0.6234	0.4681	0.4339	0.032
H7A	0.7076	0.4233	0.5446	0.045
H7B	0.6908	0.3177	0.5725	0.045
H7C	0.635	0.4021	0.6132	0.045
H8A	0.3387	0.2691	0.3331	0.045
H8B	0.3639	0.3694	0.2972	0.045
H8C	0.287	0.3615	0.3648	0.045
H10	0.3543	0.3567	0.6254	0.026
H12	0.3983	0.4524	0.8394	0.041
H13	0.5353	0.3619	0.8498	0.041
H15A	0.2876	0.5362	0.7112	0.057
H15B	0.2381	0.4737	0.776	0.057
H15C	0.227	0.4449	0.6885	0.057
H16A	0.6692	0.2654	0.7204	0.055
H16B	0.6033	0.1769	0.741	0.055
H16C	0.6407	0.245	0.8071	0.055
H17	0.4286	0.102	0.5484	0.026

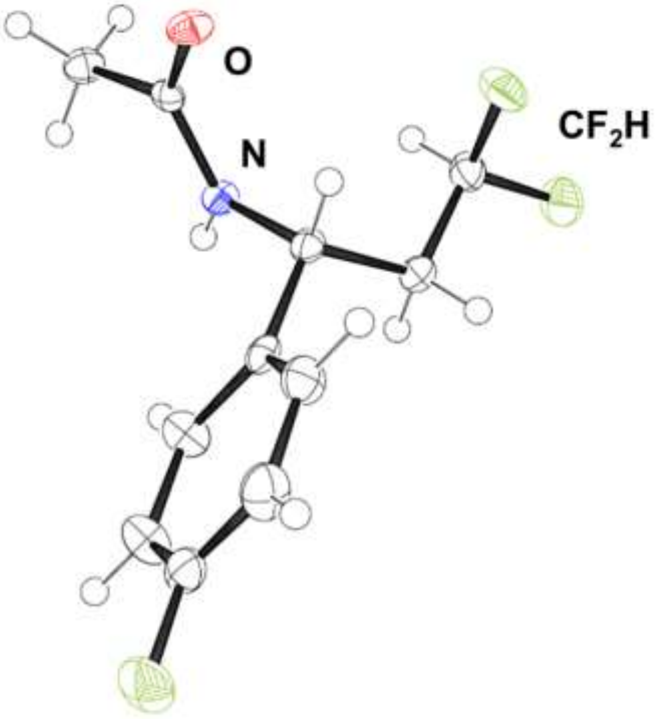


Figure S14. An ORTEP drawing of **3c**. The same structure was omitted for clarify

Table S3-1. Crystal data and structure refinement for **3c**.

Chemical formula	$C_{11}H_{12}F_3NO$	
Formula weight	231.22	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal size	0.060 x 0.095 x 0.127 mm	
Crystal system	triclinic	
Space group	P 1	
Unit cell dimensions	a = 5.0215(5) Å	α = 80.3440(10)°
	b = 8.6681(9) Å	β = 83.0720(10)°
	c = 12.6928(13) Å	γ = 88.4000(10)°
Volume	540.66(10) $Å^3$	
Z	2	
Density (calculated)	1.420 g/cm^3	
Absorption coefficient	0.126 mm^{-1}	
F(000)	240	
Theta range for data collection	1.64 to 25.01°	

Index ranges	-5<=h<=5, -9<=k<=10, -7<=l<=15	
Reflections collected	2564	
Independent reflections	2146 [R(int) = 0.0070]	
Coverage of independent reflections	97.20%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9920 and 0.9840	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	Σ w(Fo^2 - Fc^2)^2	
Data / restraints / parameters	2146 / 3 / 291	
Goodness-of-fit on F2	1.087	
Final R indices	2141 data; I>2σ(I)	R1 = 0.0210, wR2 = 0.0544
	all data	R1 = 0.0211, wR2 = 0.0545
Weighting scheme	w=1/[σ^2(Fo^2)+(0.0271P)^2+0.1434P] where P=(Fo^2+2Fc^2)/3	
Absolute structure parameter	0.2(2)	
Largest diff. peak and hole	0.118 and -0.129 eÅ^{-3}	
R.M.S. deviation from mean	0.029 eÅ^{-3}	

Table S3-2. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for **3c**.

	x/a	y/b	z/c	U(eq)
C1	0.4649(4)	0.0961(3)	0.48848(19)	0.0221(4)
C2	0.5260(4)	0.0442(2)	0.60134(18)	0.0206(4)
C3	0.3603(4)	0.9016(2)	0.65965(17)	0.0171(4)
C4	0.4029(4)	0.8645(2)	0.77738(17)	0.0180(4)
C5	0.6068(4)	0.7659(3)	0.81350(18)	0.0247(5)
C6	0.6475(4)	0.7376(3)	0.92131(19)	0.0284(5)
C7	0.4824(4)	0.8097(3)	0.99276(18)	0.0246(5)
C8	0.2763(5)	0.9069(3)	0.9611(2)	0.0306(5)
C9	0.2375(4)	0.9333(3)	0.85280(19)	0.0260(5)
C10	0.2283(4)	0.6888(2)	0.57084(15)	0.0147(4)
C11	0.3227(4)	0.5522(2)	0.51711(18)	0.0208(4)
C12	0.9981(4)	0.4447(3)	0.28402(18)	0.0199(4)
C13	0.8876(4)	0.4229(3)	0.18289(17)	0.0197(4)
C14	0.0444(4)	0.2984(2)	0.12763(16)	0.0160(4)
C15	0.9845(4)	0.3084(2)	0.01233(16)	0.0158(4)

C16	0.1331(4)	0.4110(2)	0.93181(18)	0.0225(5)
C17	0.0822(5)	0.4287(3)	0.82525(19)	0.0274(5)
C18	0.8788(4)	0.3418(3)	0.80130(17)	0.0239(5)
C19	0.7280(4)	0.2389(3)	0.87808(18)	0.0239(5)
C20	0.7808(4)	0.2231(3)	0.98428(17)	0.0210(4)
C21	0.1783(4)	0.0516(2)	0.23725(16)	0.0159(4)
C22	0.0811(4)	0.8975(2)	0.30181(18)	0.0226(5)
F1	0.6070(3)	0.22783(16)	0.44319(11)	0.0330(3)
F2	0.1991(2)	0.13892(16)	0.48808(11)	0.0304(3)
F3	0.5257(3)	0.78499(17)	0.09740(11)	0.0374(3)
F4	0.2493(2)	0.51009(16)	0.25776(11)	0.0281(3)
F5	0.8452(2)	0.55047(15)	0.33363(11)	0.0270(3)
F6	0.8257(3)	0.35736(18)	0.69743(11)	0.0369(3)
N1	0.4194(3)	0.76788(19)	0.60397(14)	0.0168(4)
N2	0.9900(3)	0.14310(19)	0.19128(14)	0.0161(3)
O1	0.9887(3)	0.72733(18)	0.58308(12)	0.0206(3)
O2	0.4156(3)	0.09073(17)	0.22830(13)	0.0222(3)

Table S3-3. Bond lengths (Å) for **3c**.

C1-F1	1.368(2)	C1-F2	1.376(2)
C1-C2	1.493(3)	C1-H1	1
C2-C3	1.540(3)	C2-H2A	0.99
C2-H2B	0.99	C3-N1	1.461(3)
C3-C4	1.515(3)	C3-H3	1
C4-C5	1.387(3)	C4-C9	1.391(3)
C5-C6	1.388(3)	C5-H5	0.95
C6-C7	1.371(3)	C6-H6	0.95
C7-F3	1.352(3)	C7-C8	1.371(3)
C8-C9	1.391(3)	C8-H8	0.95
C9-H9	0.95	C10-O1	1.238(2)
C10-N1	1.341(3)	C10-C11	1.501(3)
C11-H11A	0.98	C11-H11B	0.98
C11-H11C	0.98	C12-F5	1.365(3)
C12-F4	1.378(2)	C12-C13	1.500(3)
C12-H12	1	C13-C14	1.533(3)
C13-H13A	0.99	C13-H13B	0.99

C14-N2	1.463(3)	C14-C15	1.517(3)
C14-H14	1	C15-C20	1.392(3)
C15-C16	1.393(3)	C16-C17	1.389(3)
C16-H16	0.95	C17-C18	1.378(3)
C17-H17	0.95	C18-F6	1.360(3)
C18-C19	1.373(3)	C19-C20	1.389(3)
C19-H19	0.95	C20-H20	0.95
C21-O2	1.235(2)	C21-N2	1.342(3)
C21-C22	1.505(3)	C22-H22A	0.98
C22-H22B	0.98	C22-H22C	0.98
N1-H1A	0.88	N2-H2	0.88

Table S3-4. Bond angles (°) for **3c**.

F1-C1-F2	105.57(17)	F1-C1-C2	109.97(17)
F2-C1-C2	110.06(18)	F1-C1-H1	110.4
F2-C1-H1	110.4	C2-C1-H1	110.4
C1-C2-C3	112.81(17)	C1-C2-H2A	109
C3-C2-H2A	109	C1-C2-H2B	109
C3-C2-H2B	109	H2A-C2-H2B	107.8
N1-C3-C4	112.51(16)	N1-C3-C2	110.26(16)
C4-C3-C2	111.21(16)	N1-C3-H3	107.5
C4-C3-H3	107.5	C2-C3-H3	107.5
C5-C4-C9	118.0(2)	C5-C4-C3	122.29(18)
C9-C4-C3	119.74(18)	C4-C5-C6	121.3(2)
C4-C5-H5	119.4	C6-C5-H5	119.4
C7-C6-C5	118.9(2)	C7-C6-H6	120.6
C5-C6-H6	120.6	F3-C7-C8	119.1(2)
F3-C7-C6	118.9(2)	C8-C7-C6	122.0(2)
C7-C8-C9	118.4(2)	C7-C8-H8	120.8
C9-C8-H8	120.8	C4-C9-C8	121.5(2)
C4-C9-H9	119.2	C8-C9-H9	119.2
O1-C10-N1	121.87(18)	O1-C10-C11	122.14(18)
N1-C10-C11	115.99(16)	C10-C11-H11A	109.5
C10-C11-H11B	109.5	H11A-C11-H11B	109.5
C10-C11-H11C	109.5	H11A-C11-H11C	109.5
H11B-C11-H11C	109.5	F5-C12-F4	105.52(16)

F5-C12-C13	110.17(17)	F4-C12-C13	109.18(17)
F5-C12-H12	110.6	F4-C12-H12	110.6
C13-C12-H12	110.6	C12-C13-C14	111.95(16)
C12-C13-H13A	109.2	C14-C13-H13A	109.2
C12-C13-H13B	109.2	C14-C13-H13B	109.2
H13A-C13-H13B	107.9	N2-C14-C15	112.39(16)
N2-C14-C13	109.86(17)	C15-C14-C13	111.38(15)
N2-C14-H14	107.7	C15-C14-H14	107.7
C13-C14-H14	107.7	C20-C15-C16	118.67(19)
C20-C15-C14	122.58(17)	C16-C15-C14	118.71(17)
C17-C16-C15	121.34(19)	C17-C16-H16	119.3
C15-C16-H16	119.3	C18-C17-C16	117.9(2)
C18-C17-H17	121	C16-C17-H17	121
F6-C18-C19	118.5(2)	F6-C18-C17	118.9(2)
C19-C18-C17	122.6(2)	C18-C19-C20	118.7(2)
C18-C19-H19	120.7	C20-C19-H19	120.7
C19-C20-C15	120.73(19)	C19-C20-H20	119.6
C15-C20-H20	119.6	O2-C21-N2	122.62(18)
O2-C21-C22	121.82(18)	N2-C21-C22	115.56(17)
C21-C22-H22A	109.5	C21-C22-H22B	109.5
H22A-C22-H22B	109.5	C21-C22-H22C	109.5
H22A-C22-H22C	109.5	H22B-C22-H22C	109.5
C10-N1-C3	122.78(15)	C10-N1-H1A	118.6
C3-N1-H1A	118.6	C21-N2-C14	123.56(16)
C21-N2-H2	118.2	C14-N2-H2	118.2

Table S3-5. Anisotropic atomic displacement parameters (Å^2) for **3c**.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
C1	0.0186(10)	0.0194(10)	0.0270(12)	-0.0005(9)	-0.0027(8)	-0.0011(8)
C2	0.0192(10)	0.0185(10)	0.0243(11)	-0.0023(8)	-0.0046(9)	-0.0038(8)
C3	0.0127(9)	0.0160(10)	0.0232(11)	-0.0044(8)	-0.0030(8)	-0.0002(7)
C4	0.0148(10)	0.0153(10)	0.0241(11)	-0.0046(8)	-0.0008(8)	-0.0042(8)
C5	0.0201(10)	0.0308(12)	0.0211(12)	-0.0023(9)	0.0018(9)	0.0036(9)
C6	0.0267(11)	0.0325(13)	0.0231(12)	0.0016(10)	-0.0015(10)	0.0063(10)
C7	0.0333(12)	0.0218(11)	0.0177(11)	-0.0006(8)	-0.0013(9)	-0.0072(9)

C8	0.0388(13)	0.0263(12)	0.0265(12)	-0.0097(10)	0.0029(10)	0.0034(10)
C9	0.0287(11)	0.0227(11)	0.0277(12)	-0.0077(9)	-0.0035(10)	0.0055(9)
C10	0.0155(10)	0.0174(10)	0.0099(9)	0.0012(7)	-0.0010(7)	-0.0015(8)
C11	0.0196(10)	0.0239(11)	0.0202(11)	-0.0071(9)	-0.0026(8)	0.0000(8)
C12	0.0175(10)	0.0199(10)	0.0224(11)	-0.0060(8)	0.0015(8)	-0.0025(8)
C13	0.0184(10)	0.0207(10)	0.0208(11)	-0.0046(8)	-0.0049(8)	0.0033(8)
C14	0.0132(9)	0.0159(10)	0.0186(11)	-0.0009(8)	-0.0031(8)	-0.0005(7)
C15	0.0147(9)	0.0146(10)	0.0180(10)	-0.0031(8)	-0.0016(8)	0.0056(7)
C16	0.0260(11)	0.0189(11)	0.0223(12)	-0.0009(9)	-0.0040(9)	-0.0024(9)
C17	0.0336(12)	0.0236(11)	0.0230(13)	0.0009(9)	-0.0009(10)	-0.0019(9)
C18	0.0315(11)	0.0258(11)	0.0149(11)	-0.0048(9)	-0.0056(9)	0.0085(9)
C19	0.0202(10)	0.0298(12)	0.0231(11)	-0.0076(9)	-0.0045(9)	0.0023(9)
C20	0.0168(10)	0.0255(11)	0.0197(11)	-0.0026(9)	0.0002(8)	-0.0003(8)
C21	0.0173(10)	0.0171(10)	0.0139(10)	-0.0045(8)	-0.0013(8)	0.0006(8)
C22	0.0261(11)	0.0181(10)	0.0220(11)	0.0025(8)	-0.0043(9)	-0.0035(8)
F1	0.0356(7)	0.0284(7)	0.0312(8)	0.0067(6)	-0.0027(6)	-0.0085(6)
F2	0.0230(6)	0.0333(7)	0.0325(8)	0.0042(6)	-0.0082(6)	0.0044(5)
F3	0.0549(8)	0.0376(8)	0.0181(7)	-0.0009(6)	-0.0036(6)	0.0022(7)
F4	0.0192(6)	0.0352(8)	0.0325(7)	-0.0147(6)	0.0001(5)	-0.0072(5)
F5	0.0259(6)	0.0292(7)	0.0278(7)	-0.0146(5)	0.0031(5)	-0.0012(5)
F6	0.0489(8)	0.0451(9)	0.0174(7)	-0.0027(6)	-0.0095(6)	-0.0031(7)
N1	0.0095(7)	0.0186(9)	0.0228(9)	-0.0056(7)	-0.0014(7)	0.0016(6)
N2	0.0118(7)	0.0177(8)	0.0180(9)	0.0001(7)	-0.0022(7)	-0.0031(6)
O1	0.0107(7)	0.0271(8)	0.0258(8)	-0.0093(6)	-0.0020(6)	0.0005(6)
O2	0.0134(7)	0.0246(8)	0.0275(8)	0.0004(6)	-0.0041(6)	-0.0007(6)

Table S3-6. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for **3c**.

	x/a	y/b	z/c	U(eq)
H1	0.5085	1.0107	0.4449	0.026
H2A	0.4894	1.1319	0.6421	0.025
H2B	0.7192	1.0175	0.6004	0.025
H3	0.1665	0.9293	0.6561	0.021
H5	0.721	0.7167	0.7635	0.03
H6	0.7873	0.6694	0.9452	0.034
H8	0.1628	0.9551	1.0118	0.037
H9	0.0947	0.9999	0.8299	0.031

H11A	0.1922	0.4674	0.5381	0.031
H11B	0.497	0.5156	0.5393	0.031
H11C	0.3407	0.5846	0.4388	0.031
H12	0.0066	0.3425	0.3336	0.024
H13A	-0.1052	0.5237	0.1326	0.024
H13B	-0.3028	0.3916	0.2005	0.024
H14	0.2398	0.3194	0.1257	0.019
H16	0.2722	0.47	-0.0499	0.027
H17	0.1844	0.4986	-0.2294	0.033
H19	-0.4096	0.1797	-0.1411	0.029
H20	-0.3232	0.1532	0.0384	0.025
H22A	0.209	-0.1855	0.2862	0.034
H22B	-0.0948	-0.1259	0.2825	0.034
H22C	0.0659	-0.0963	0.3787	0.034
H1A	0.5876	0.738	0.5916	0.02
H2	-0.1752	0.1078	0.1999	0.019

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2 (*a*) Y. Yasu, T. Koike and M. Akita, *Org. Lett.*, 2013, **15**, 2136–2139. (*b*) K. Miyazawa, T. Koike and M. Akita, *Chem. Eur.J.*, 2015, **21**, 11677–11680.

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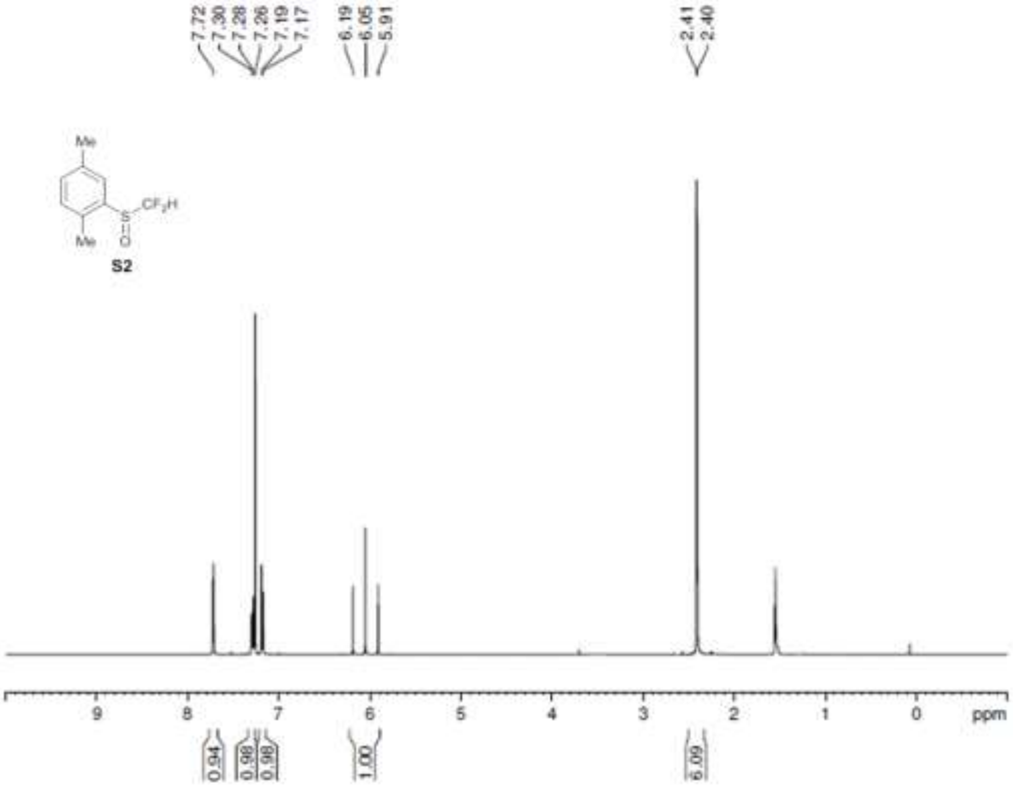
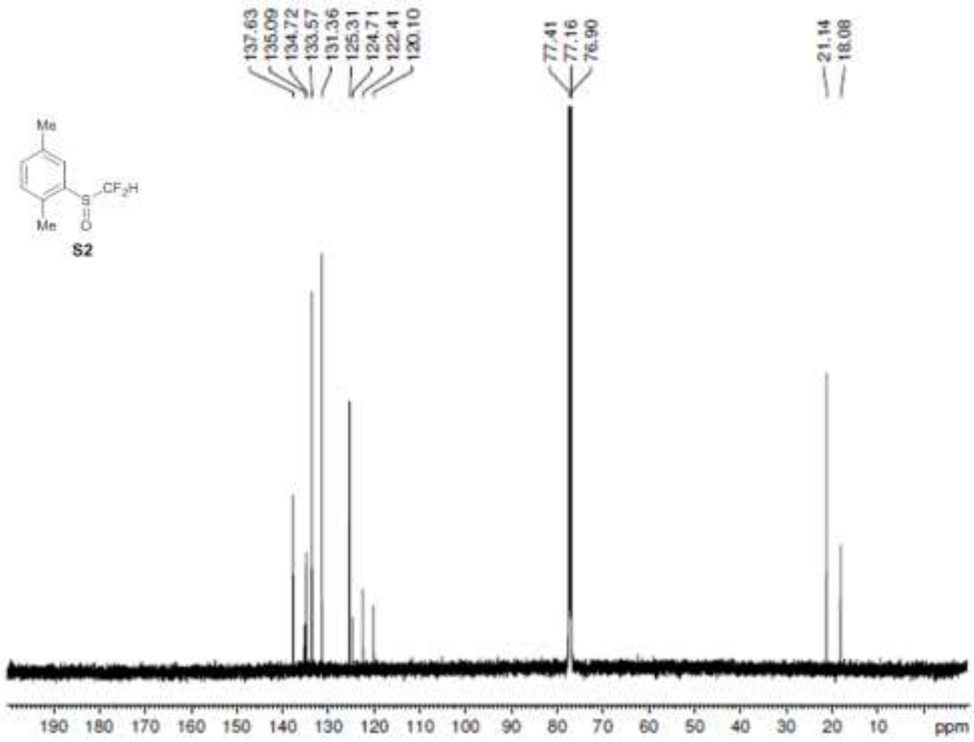
NMR spectra

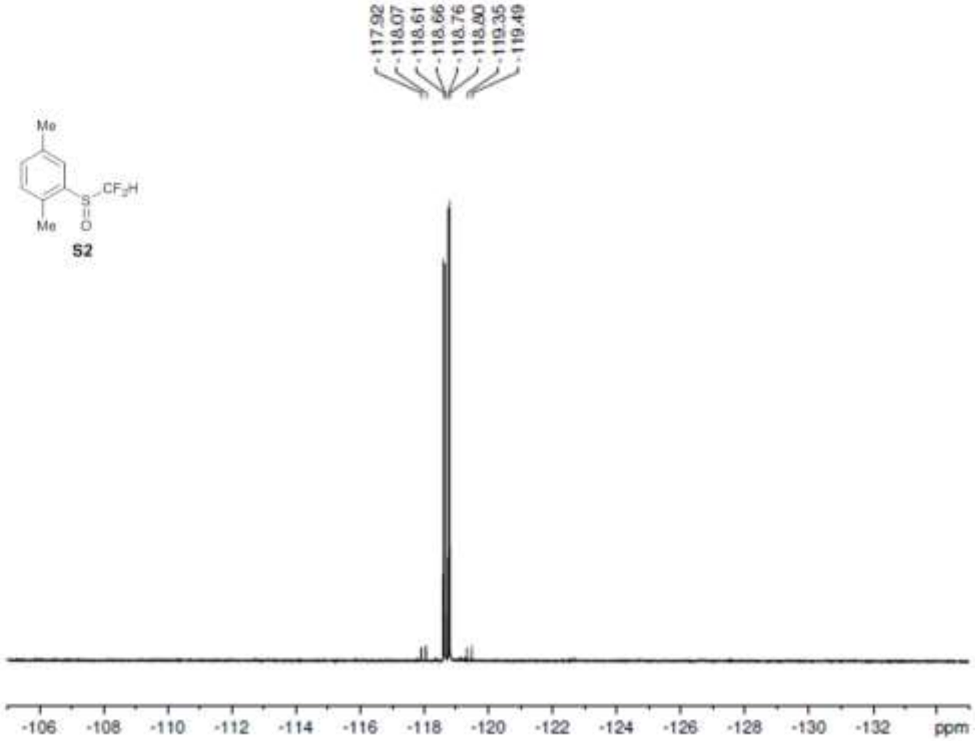
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)



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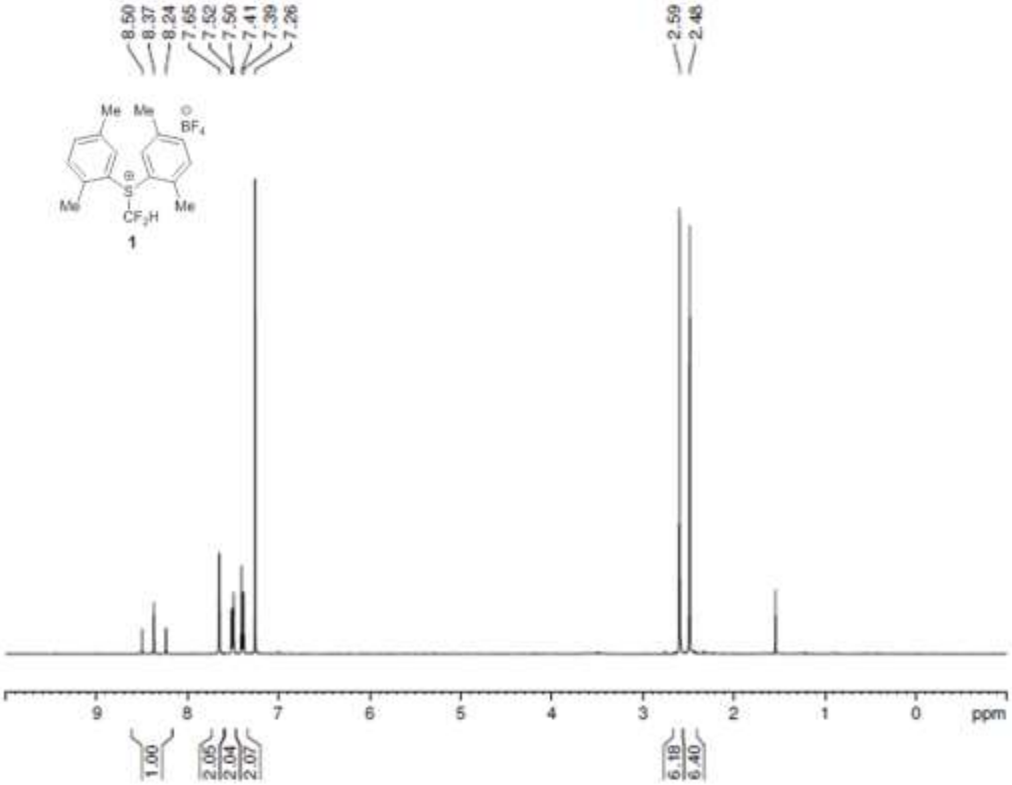

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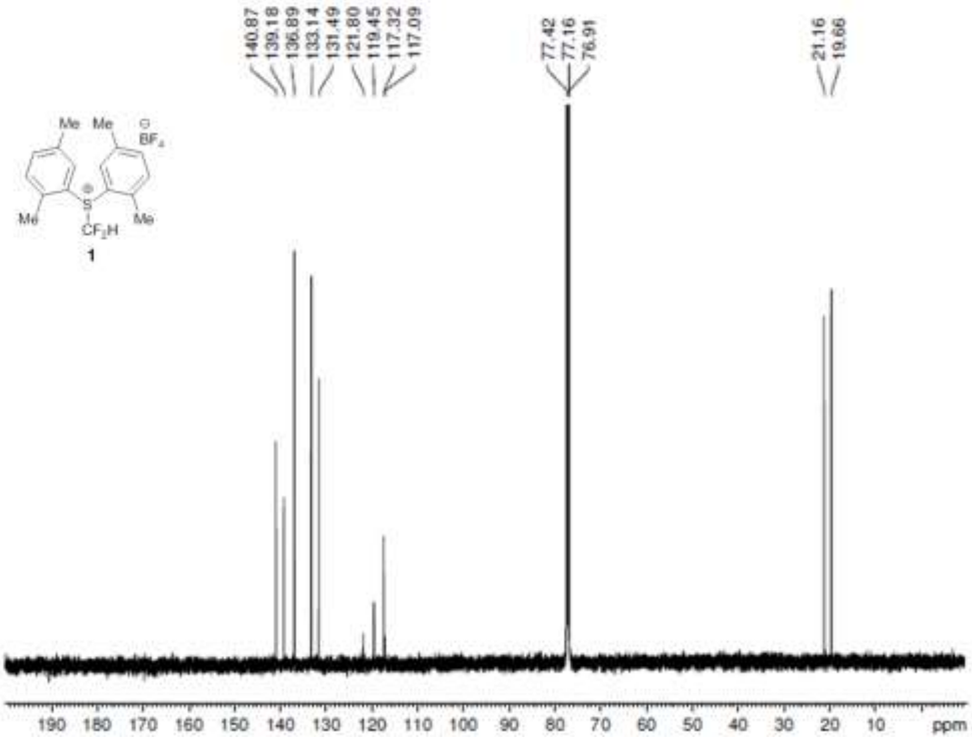

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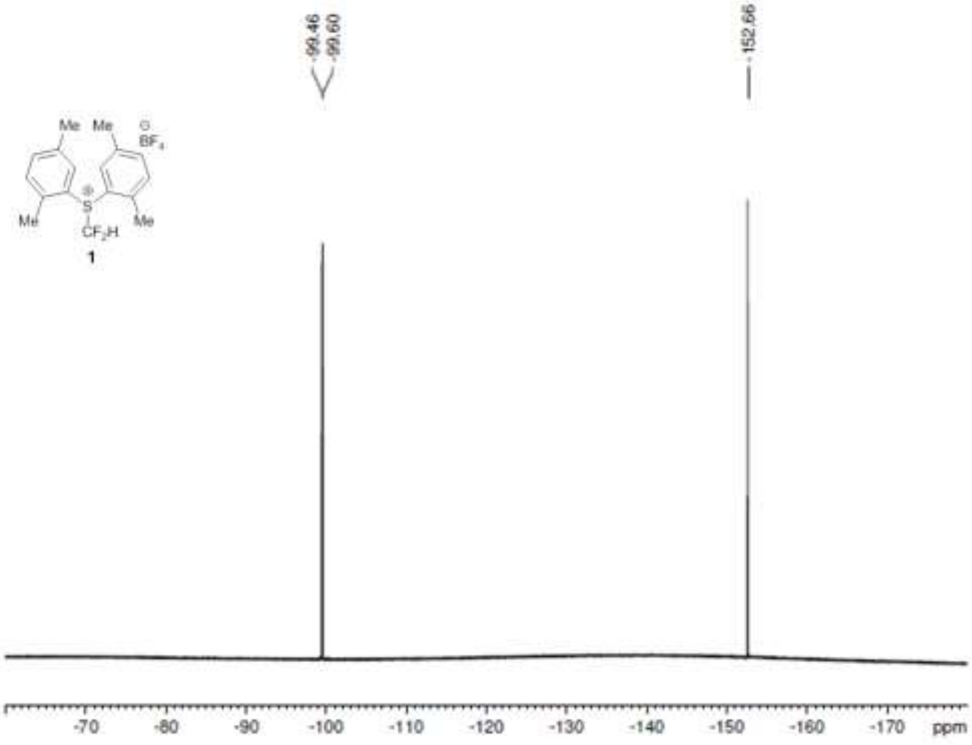

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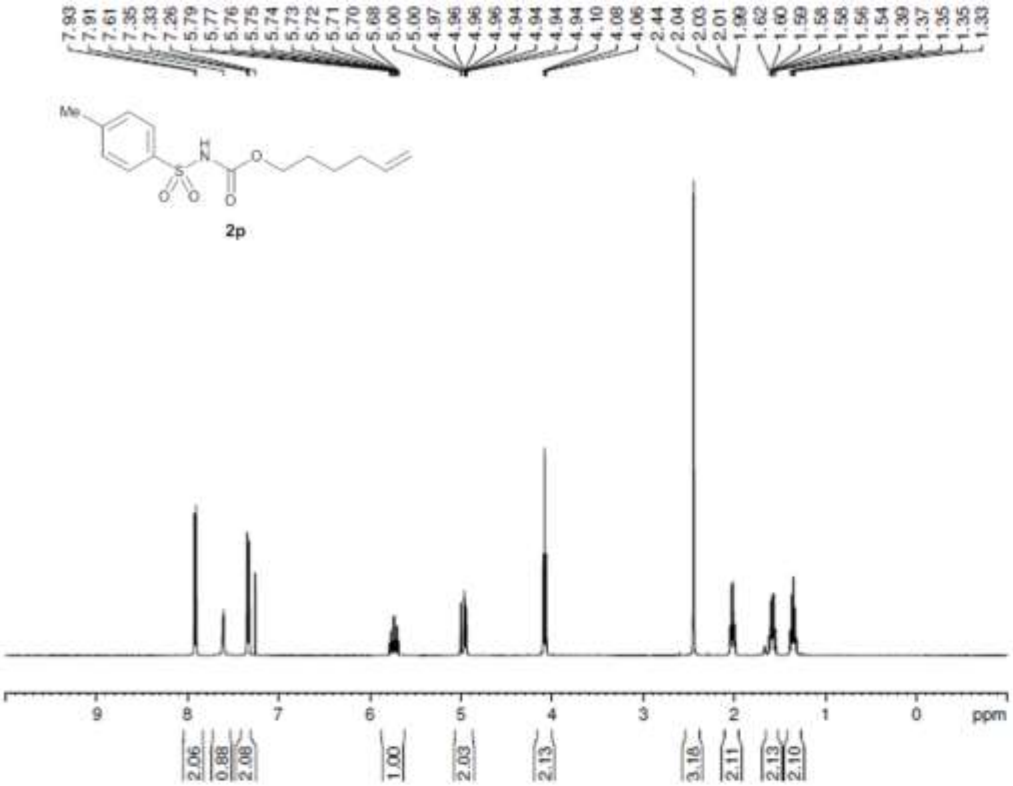

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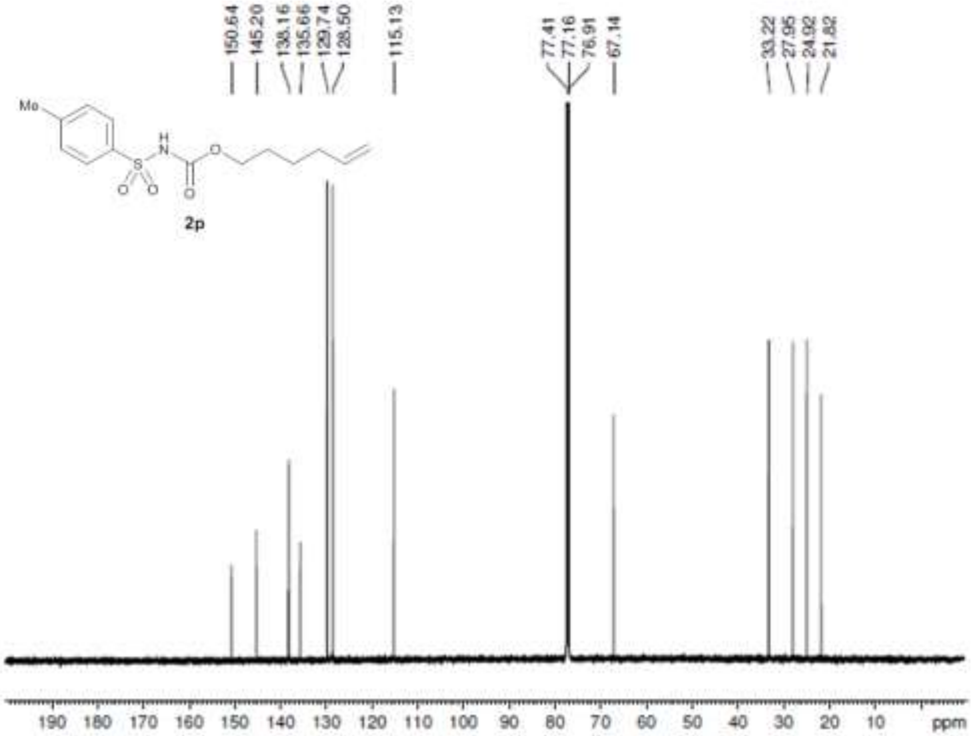

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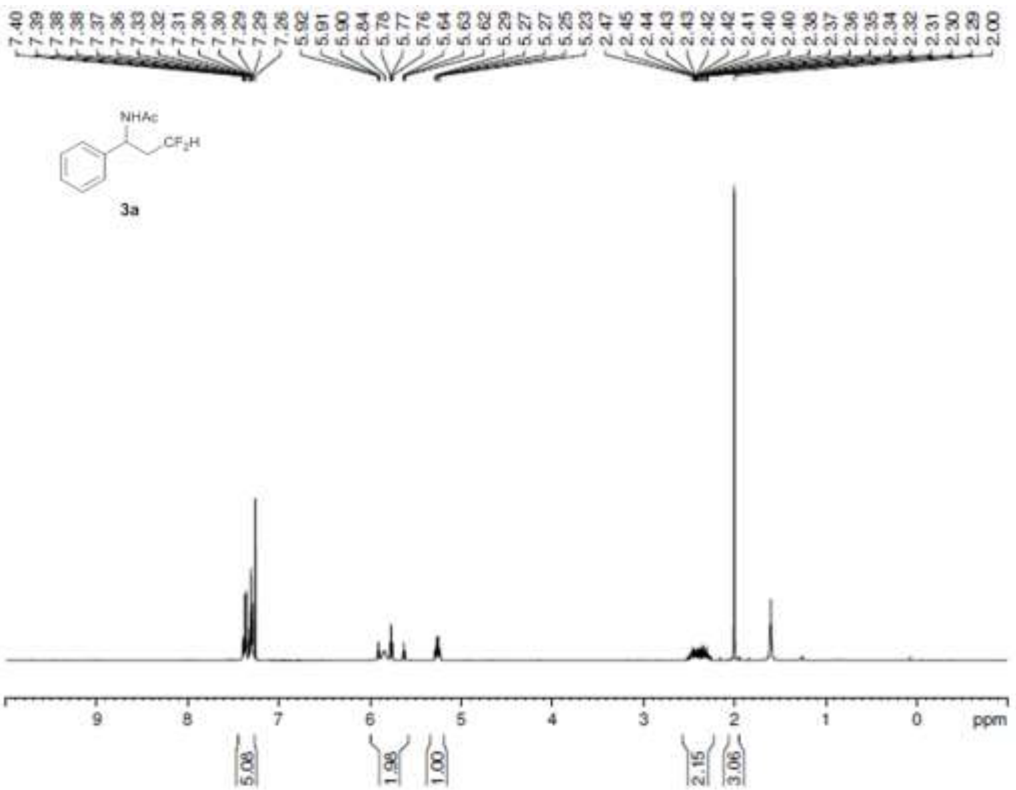

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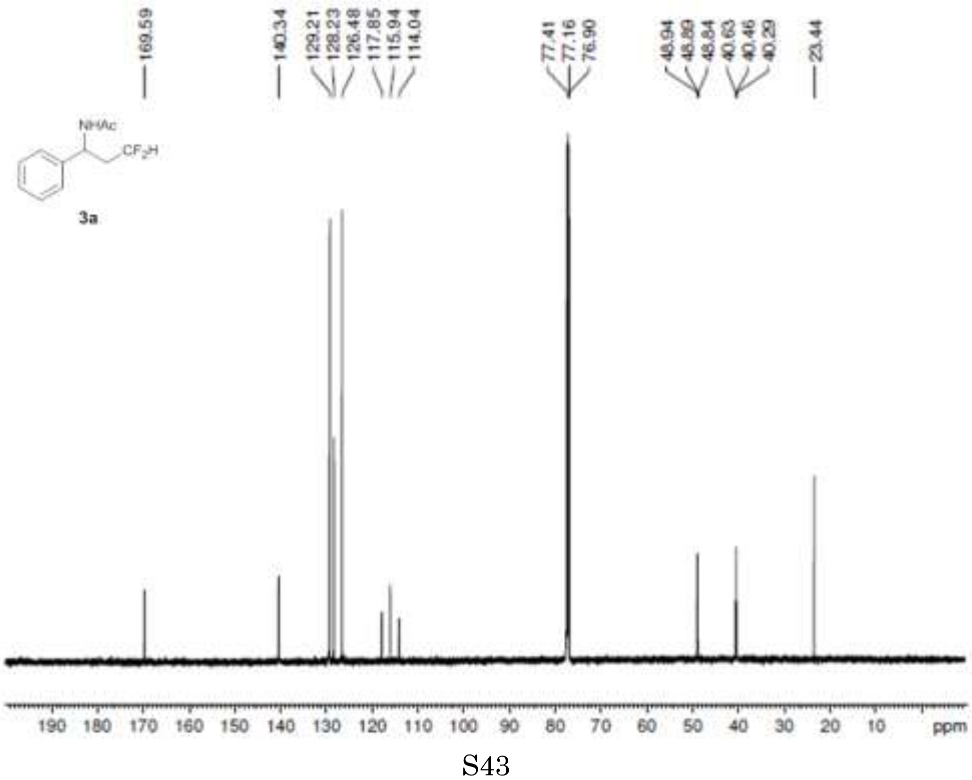

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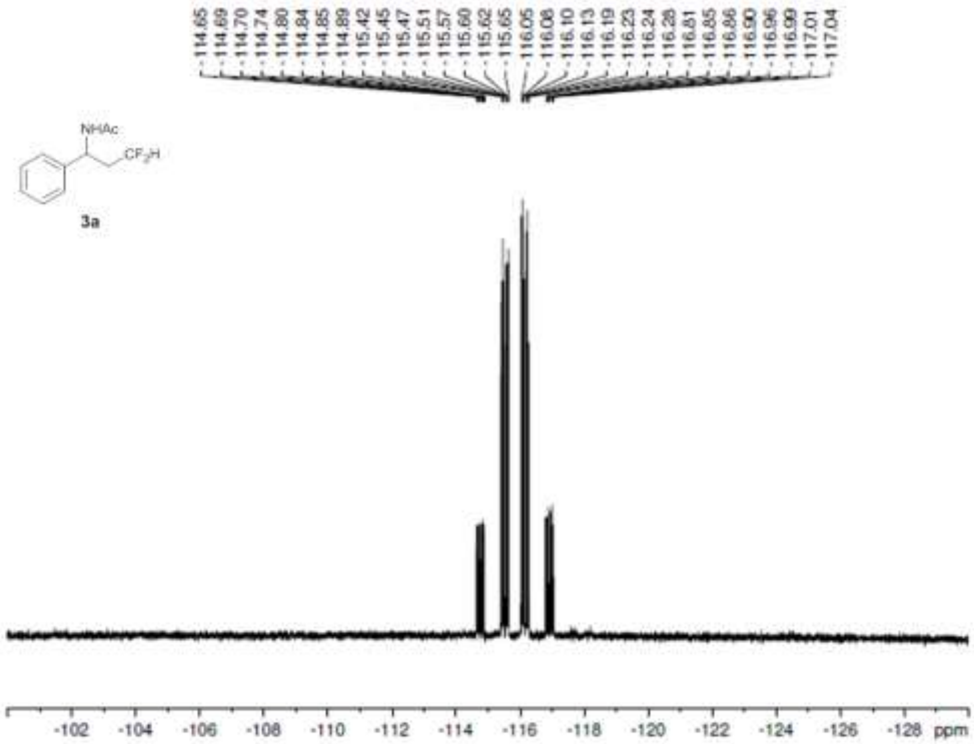

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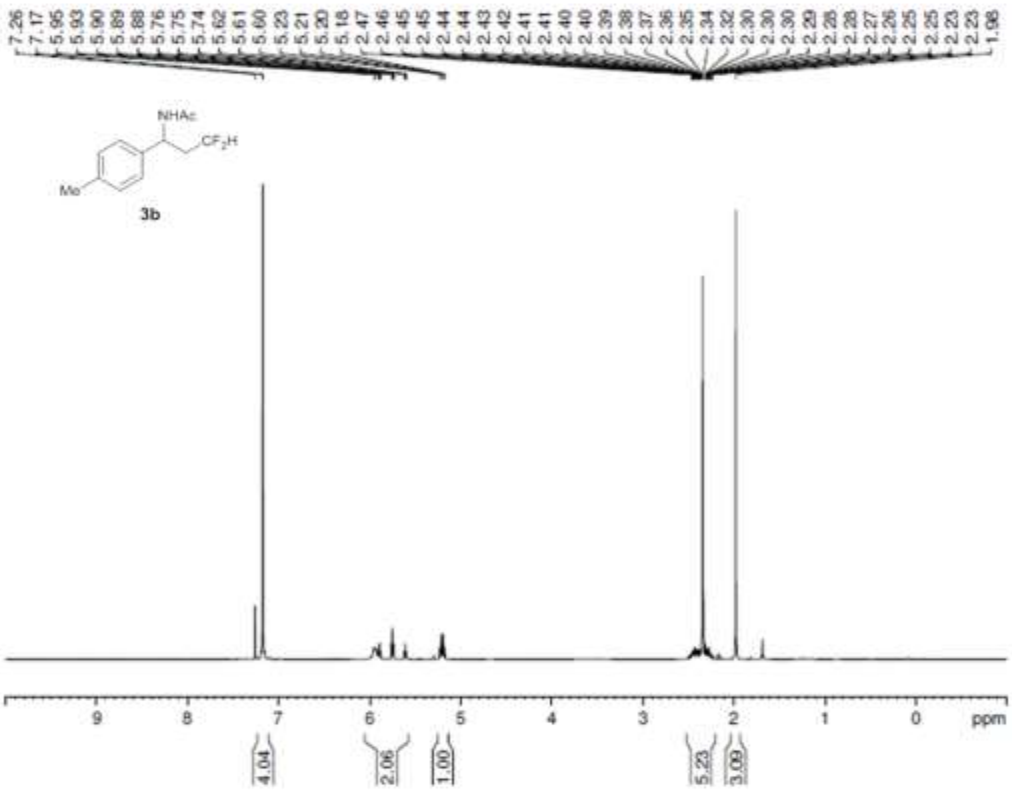

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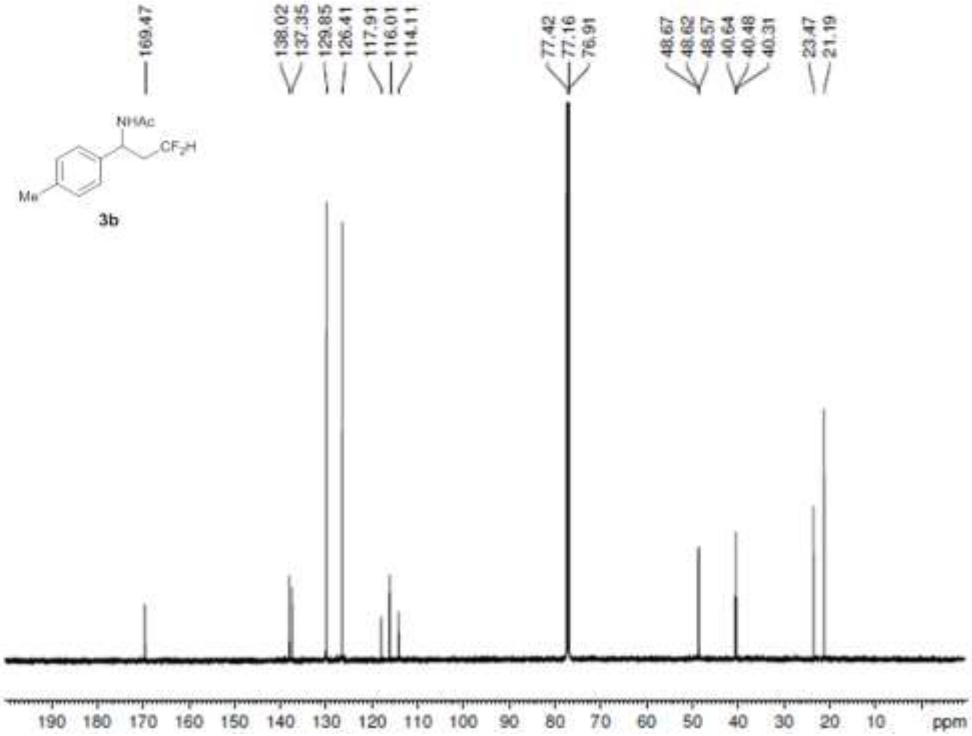

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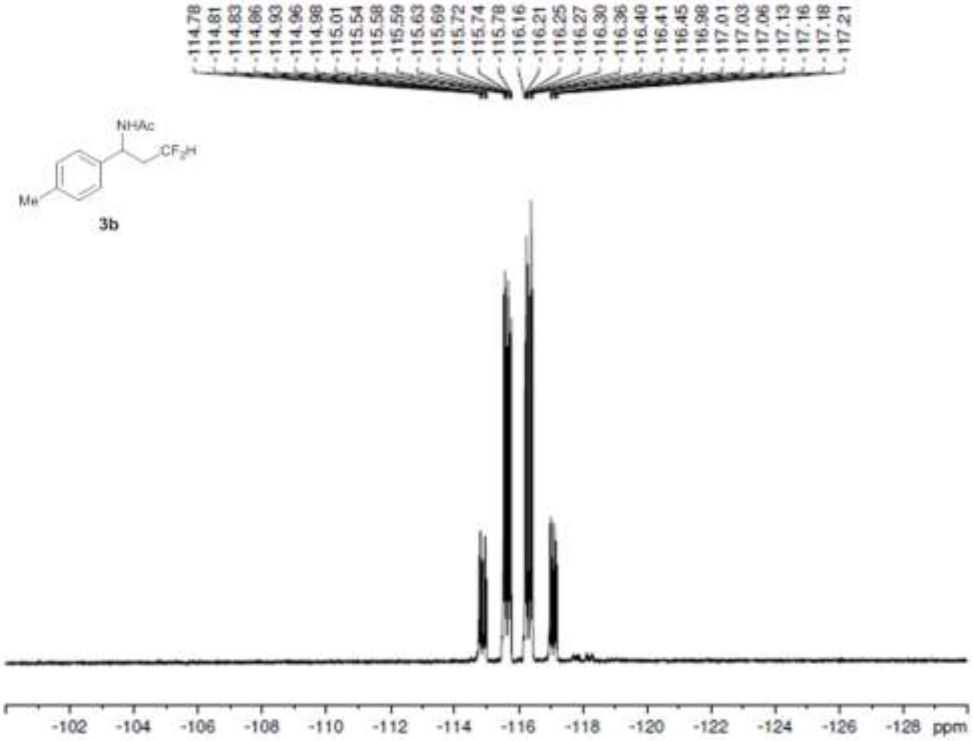

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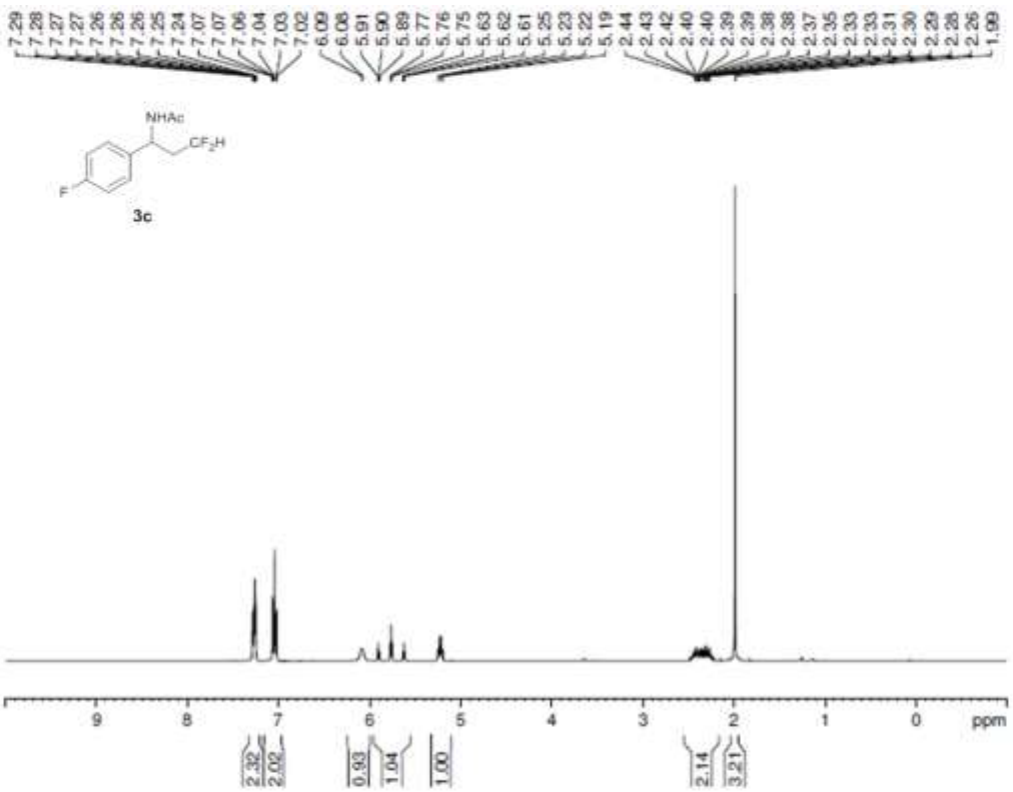

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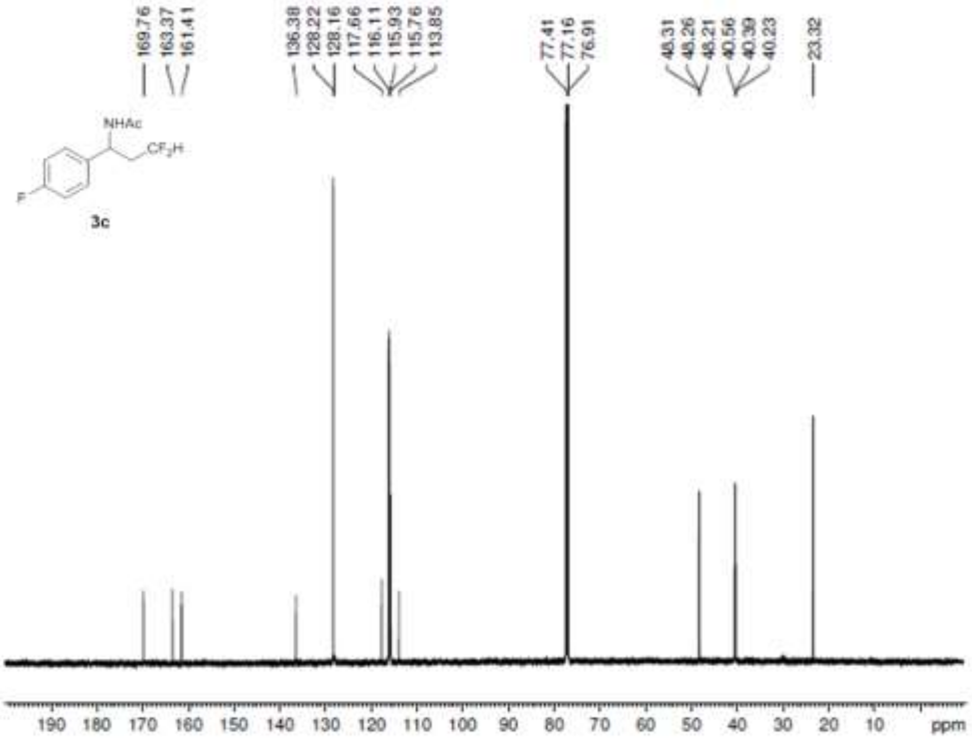

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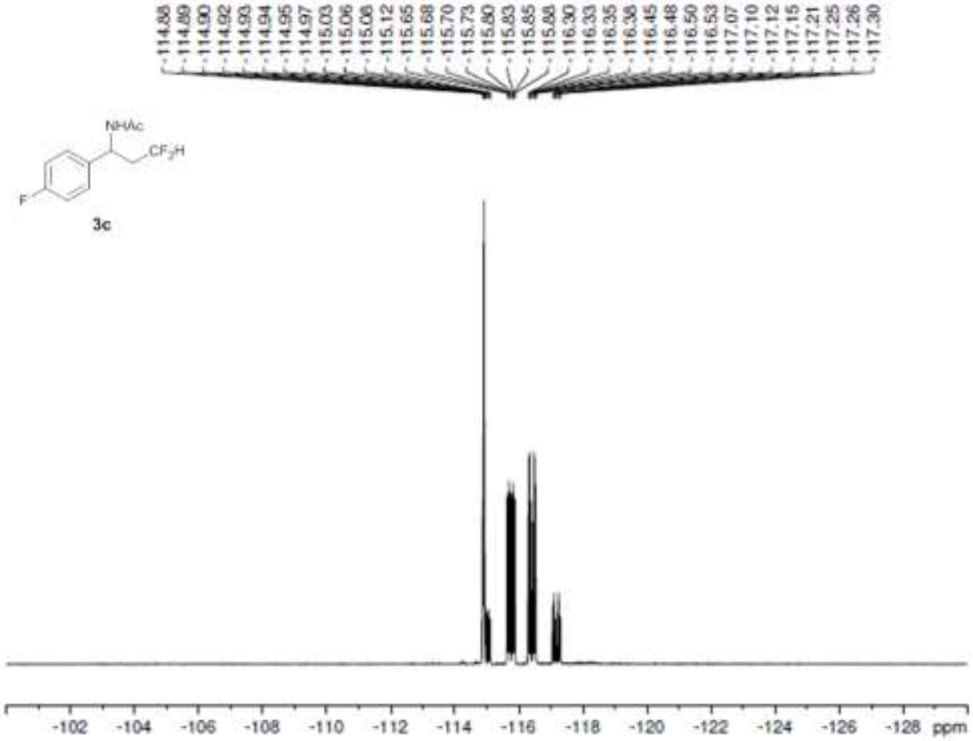

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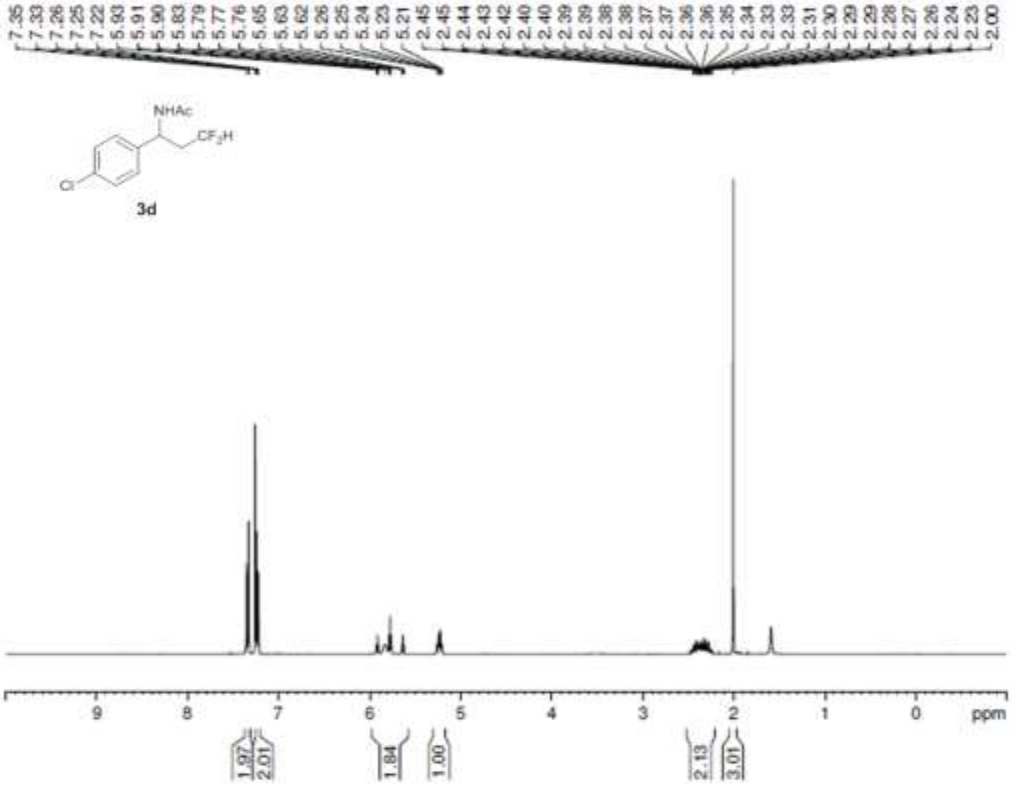

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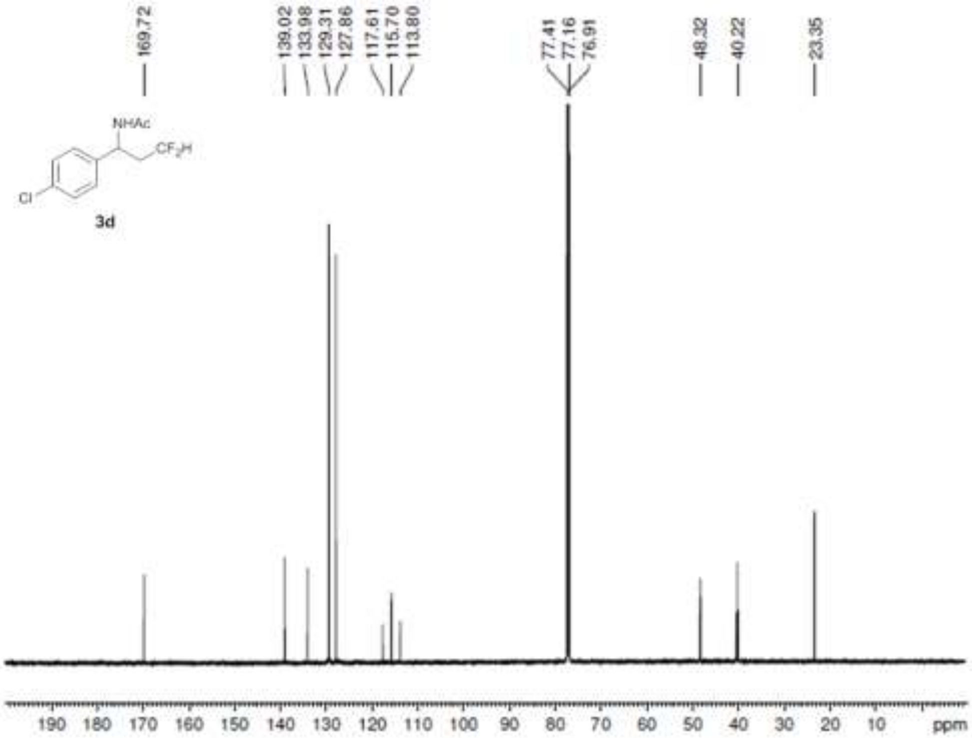
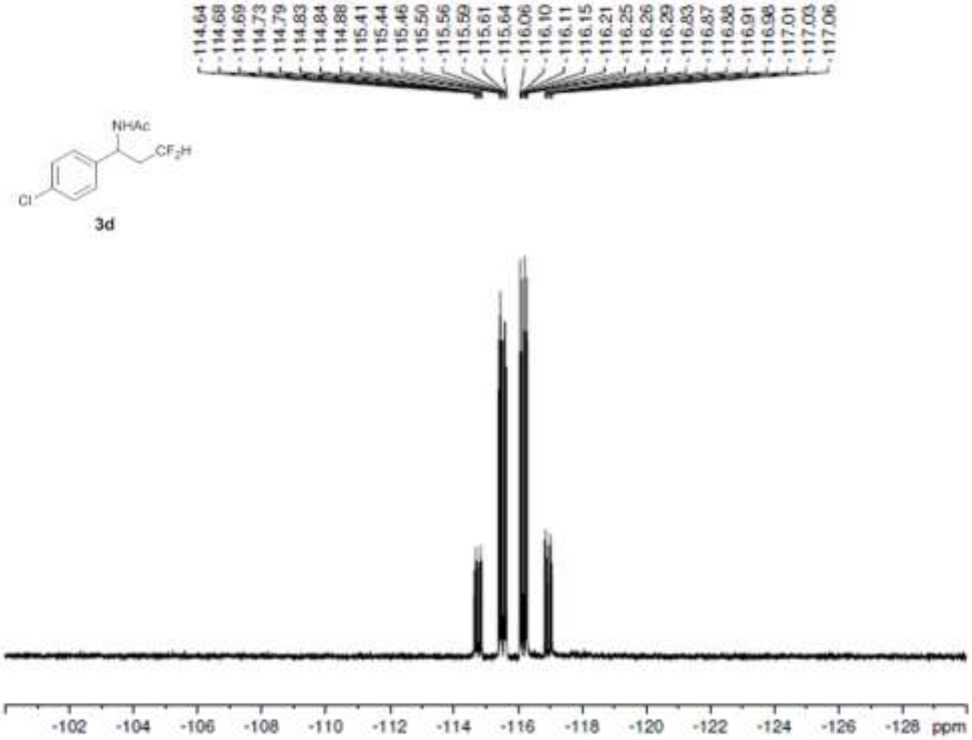


3d

^{19}F NMR (376 MHz, CDCl$_3$)



3d

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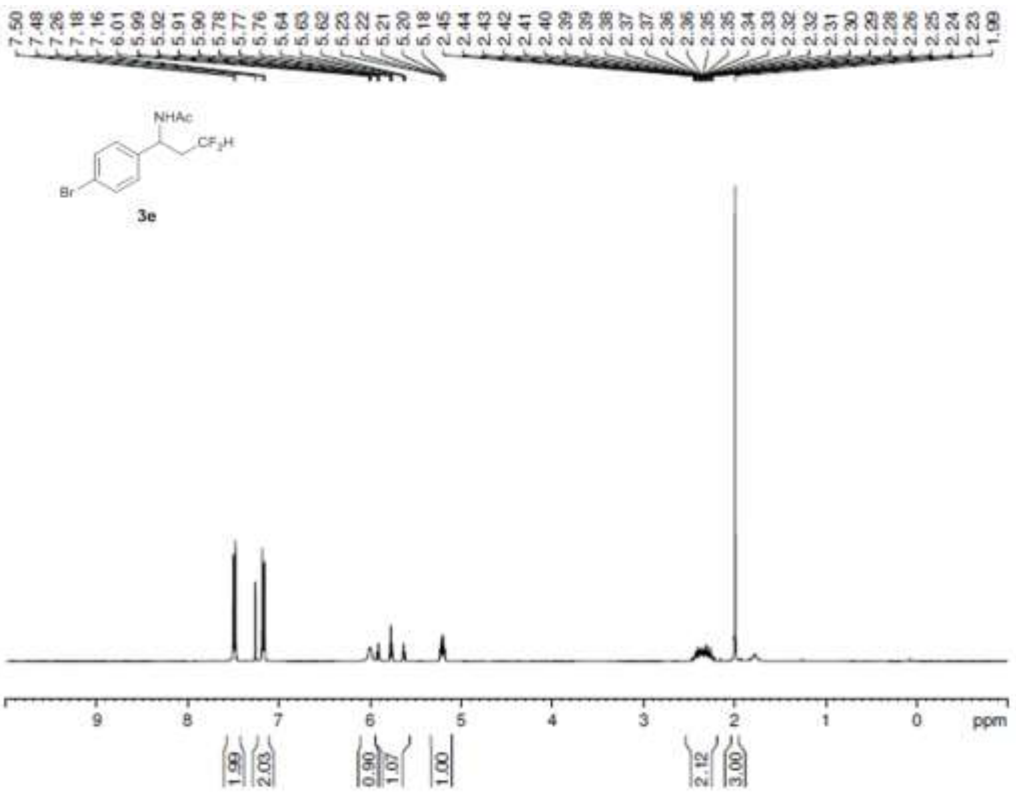

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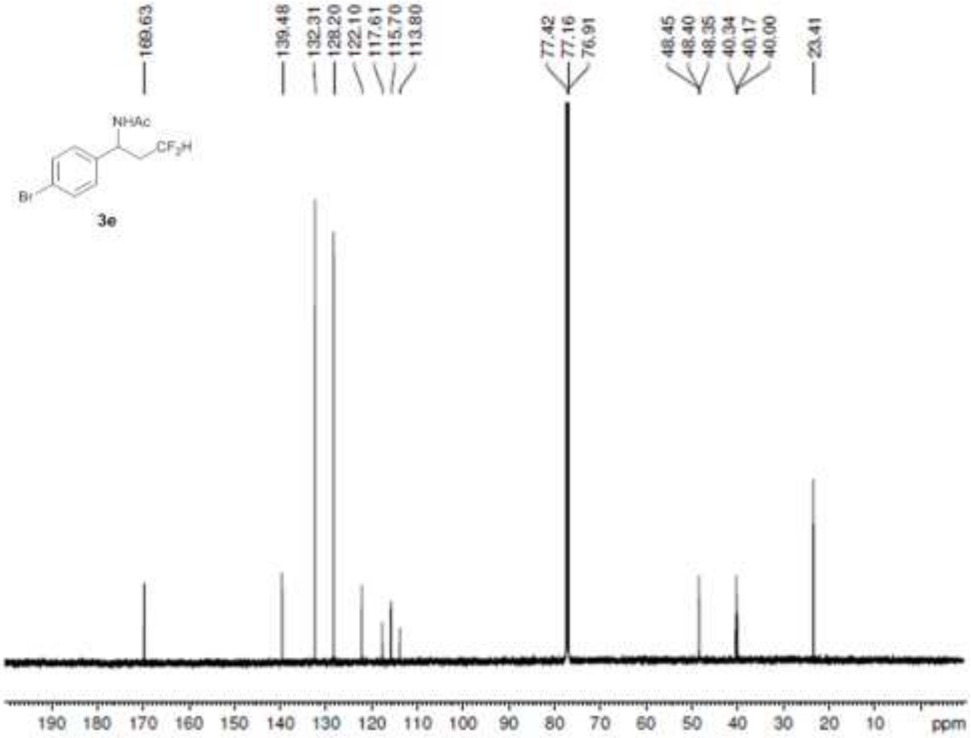

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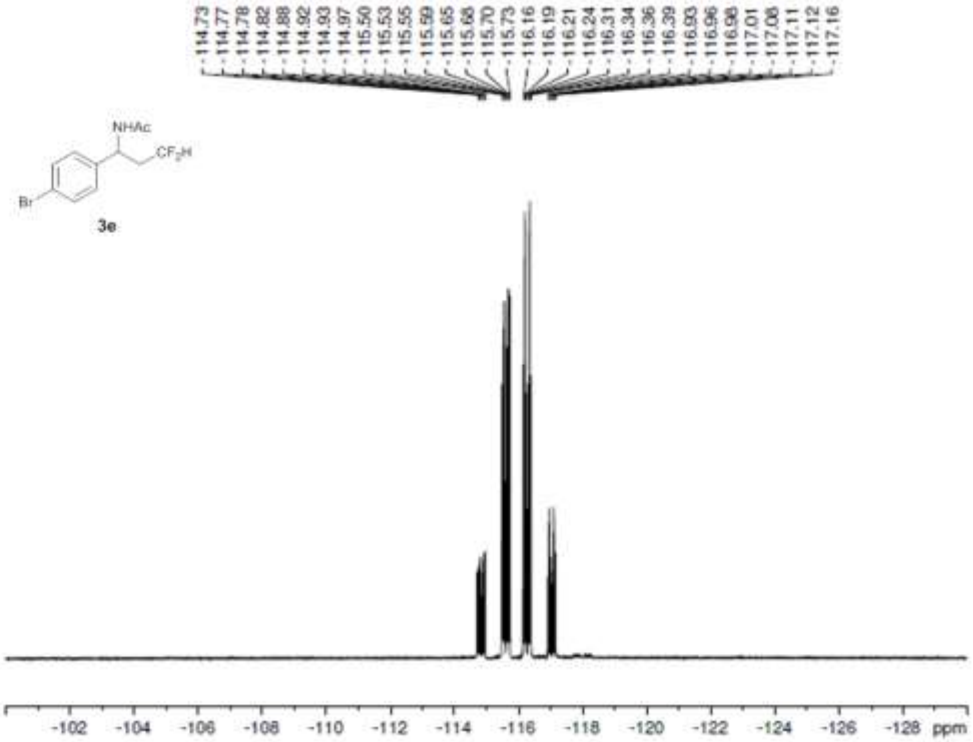

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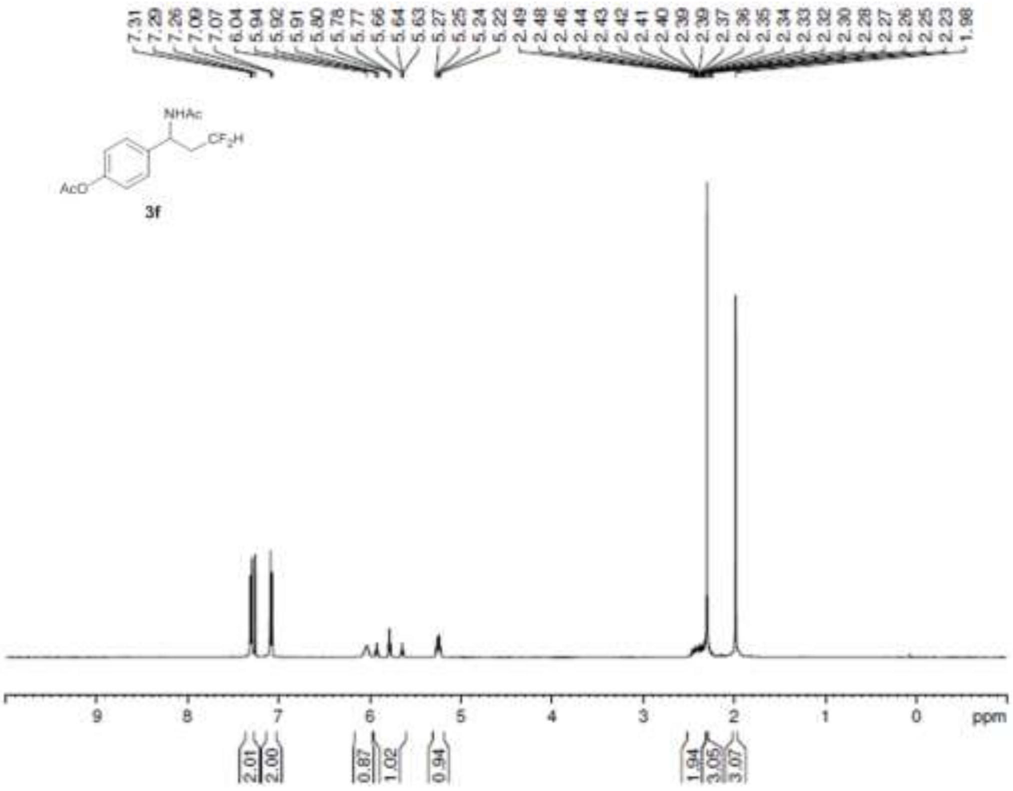

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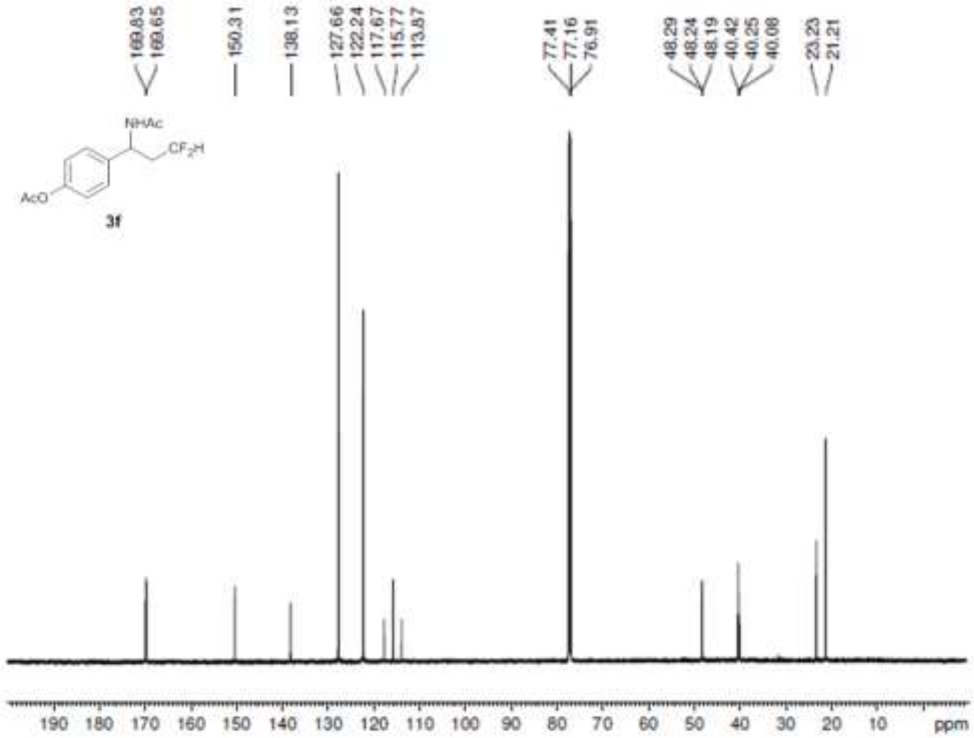

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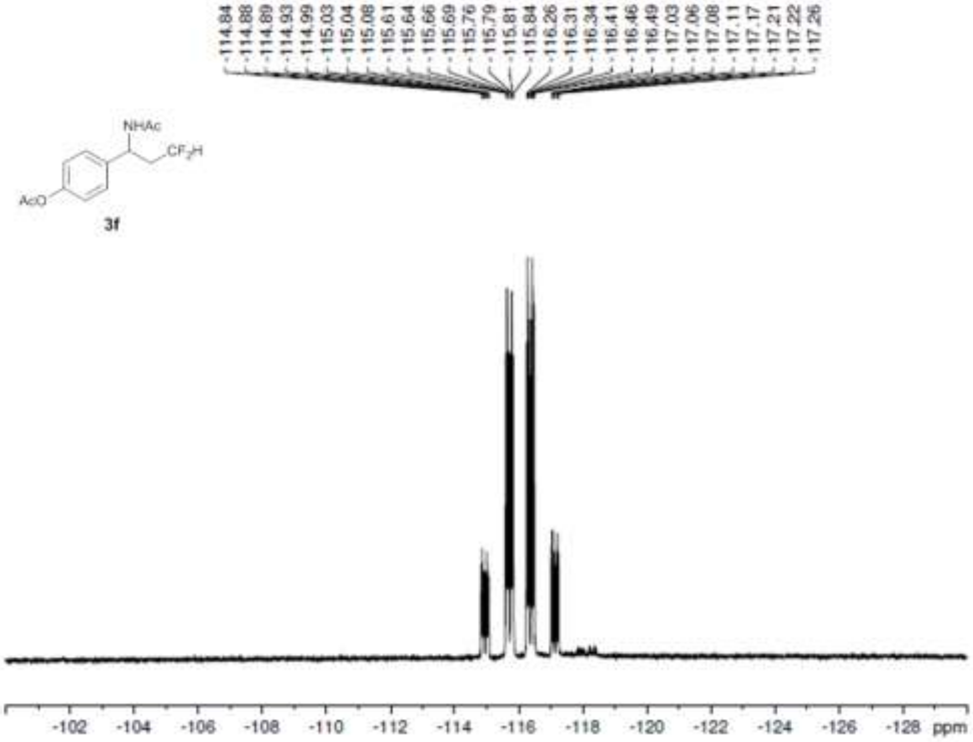

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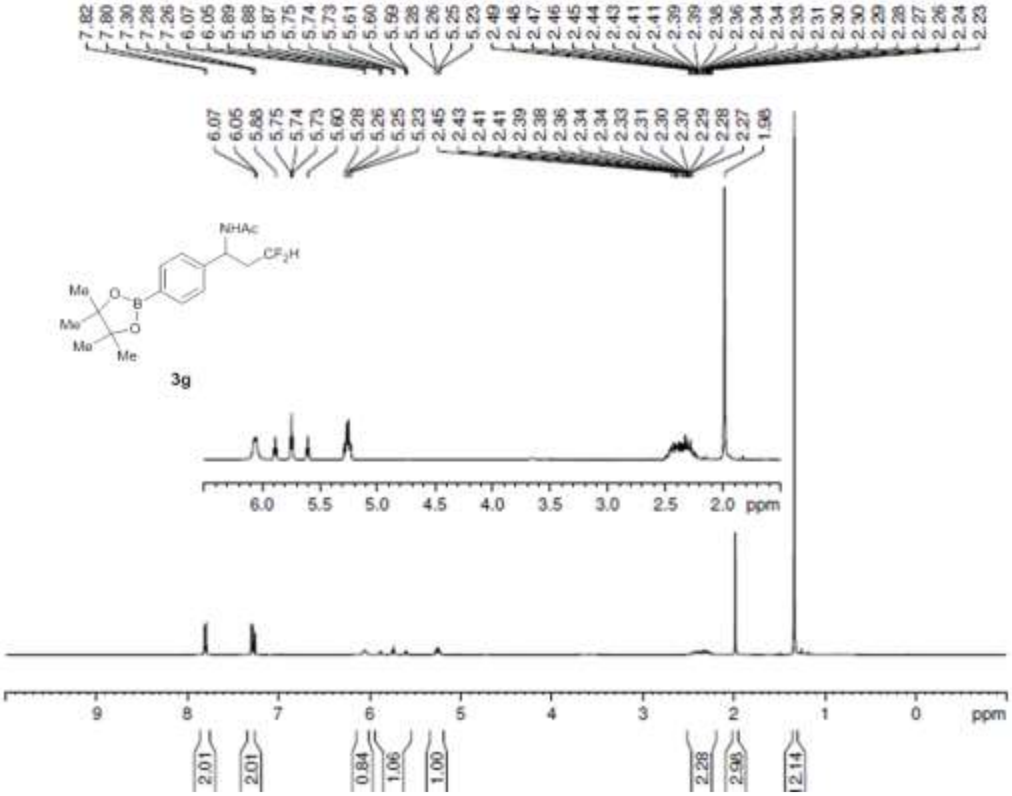
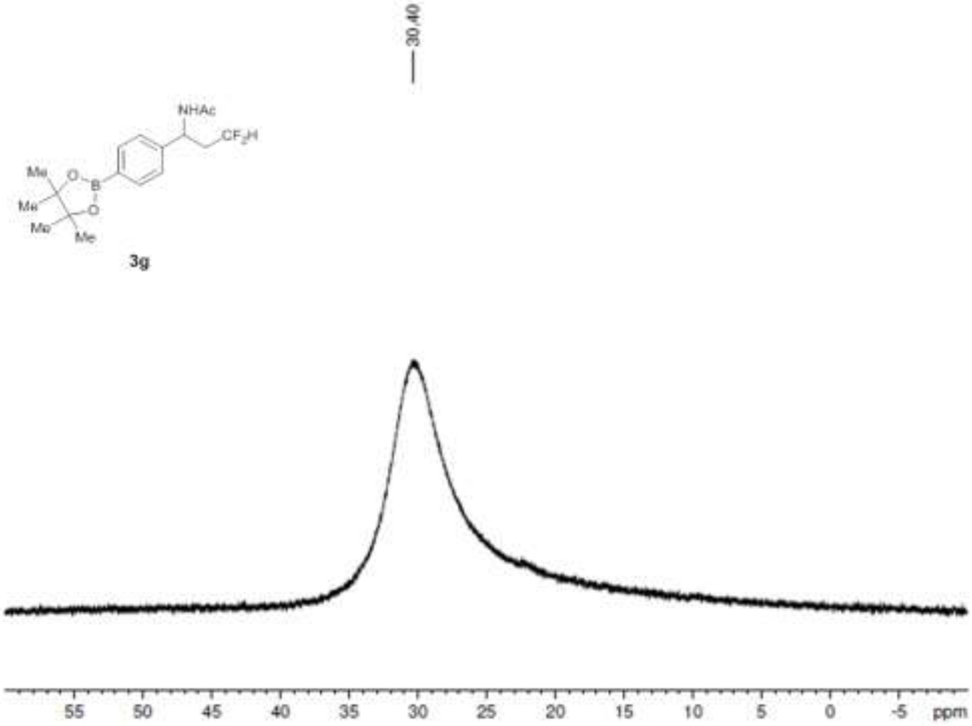


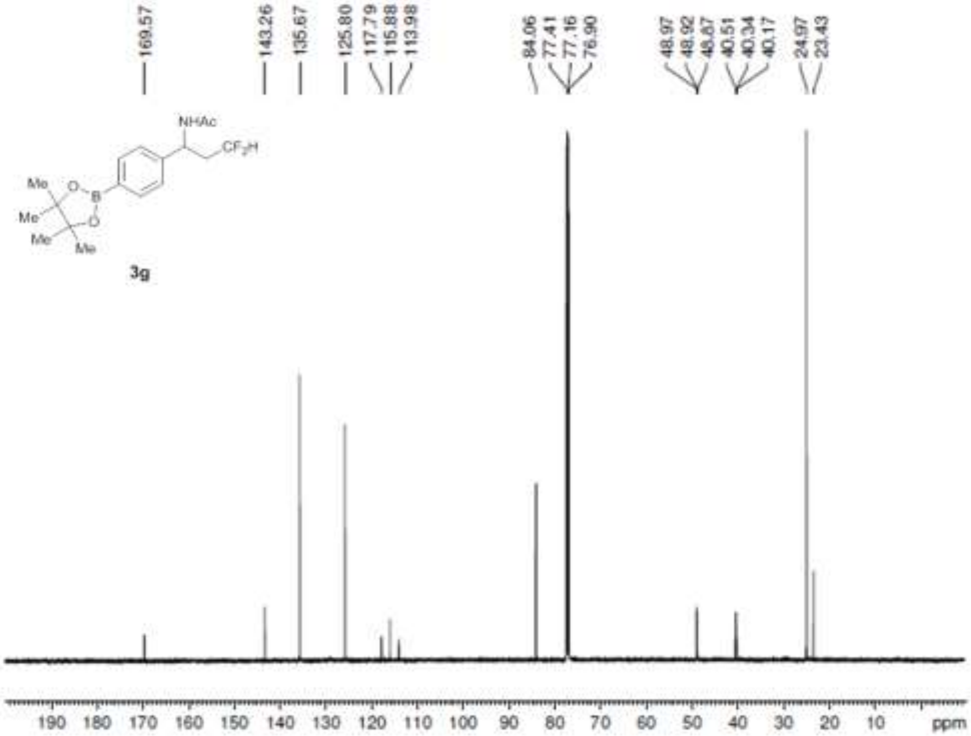
3g

^{11}B NMR (128 MHz, CDCl$_3$)



3g

^{13}C NMR (125 MHz, CDCl$_3$)



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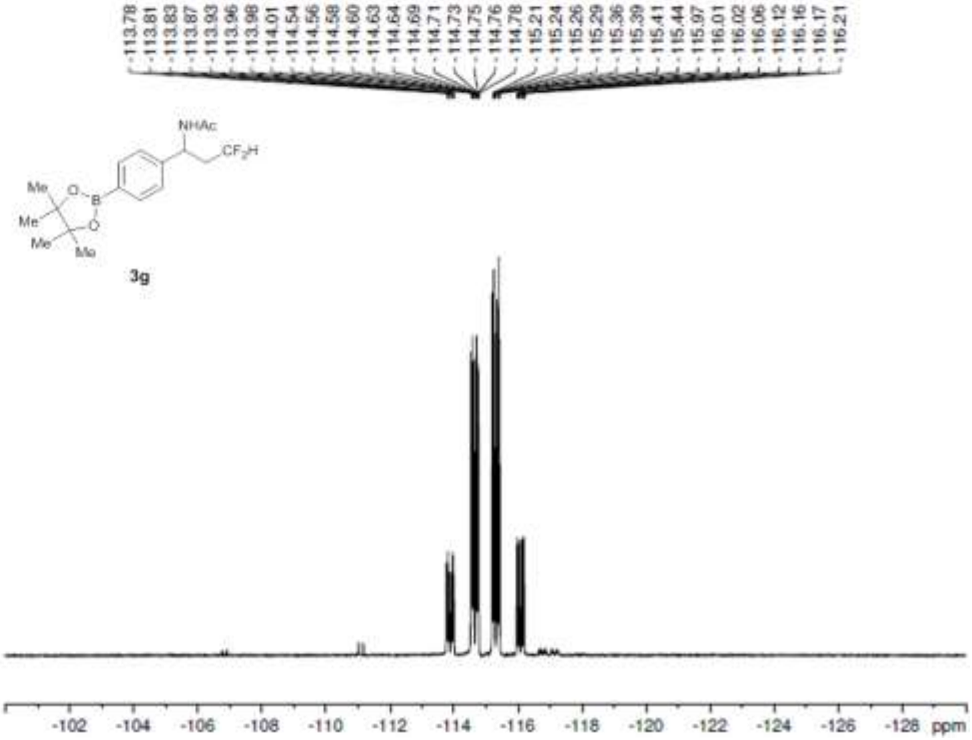

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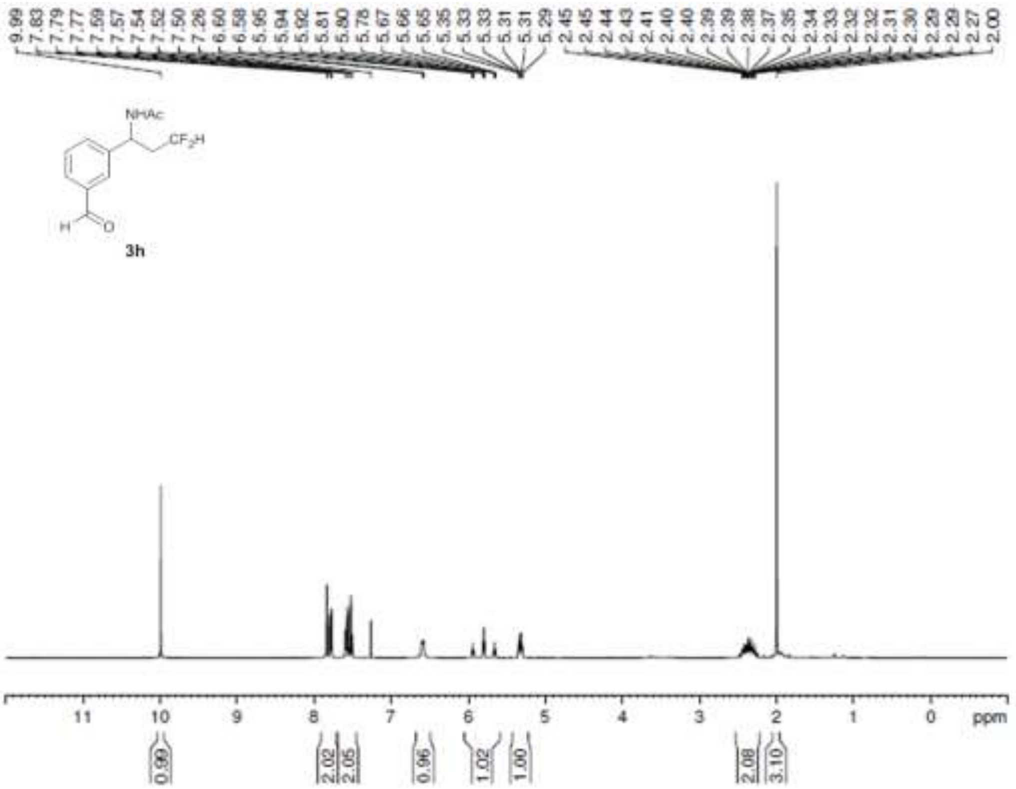

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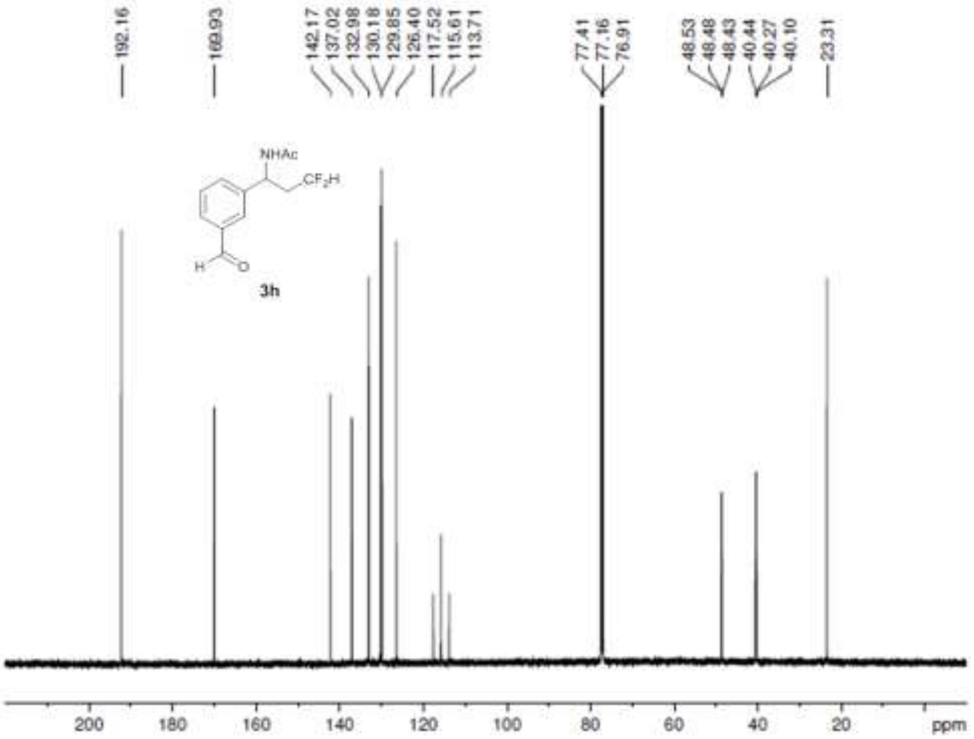

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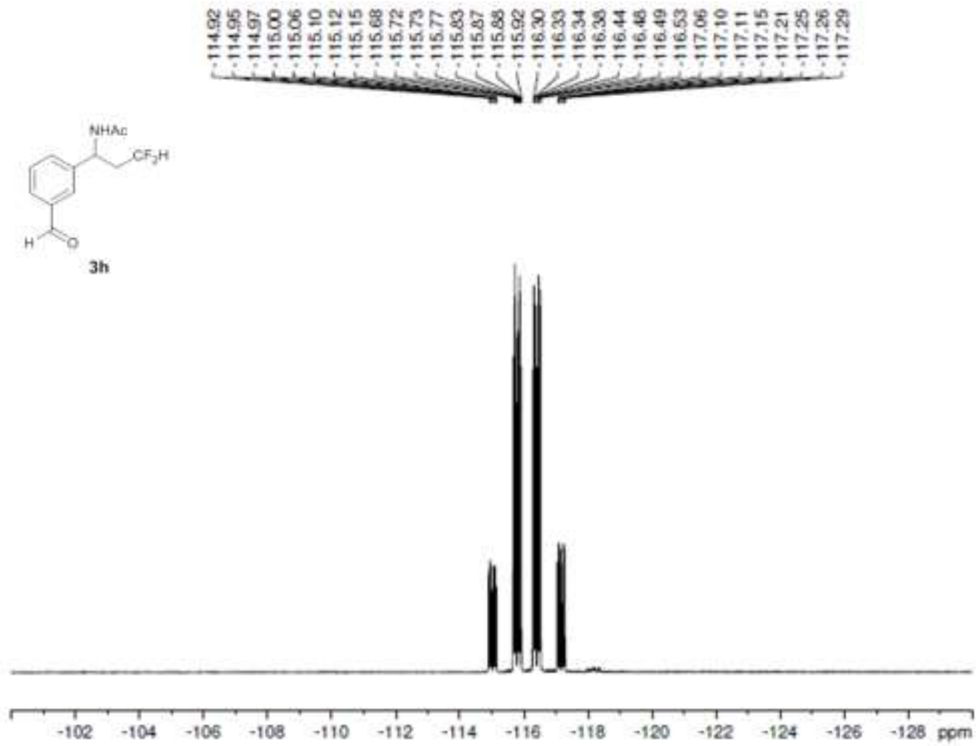

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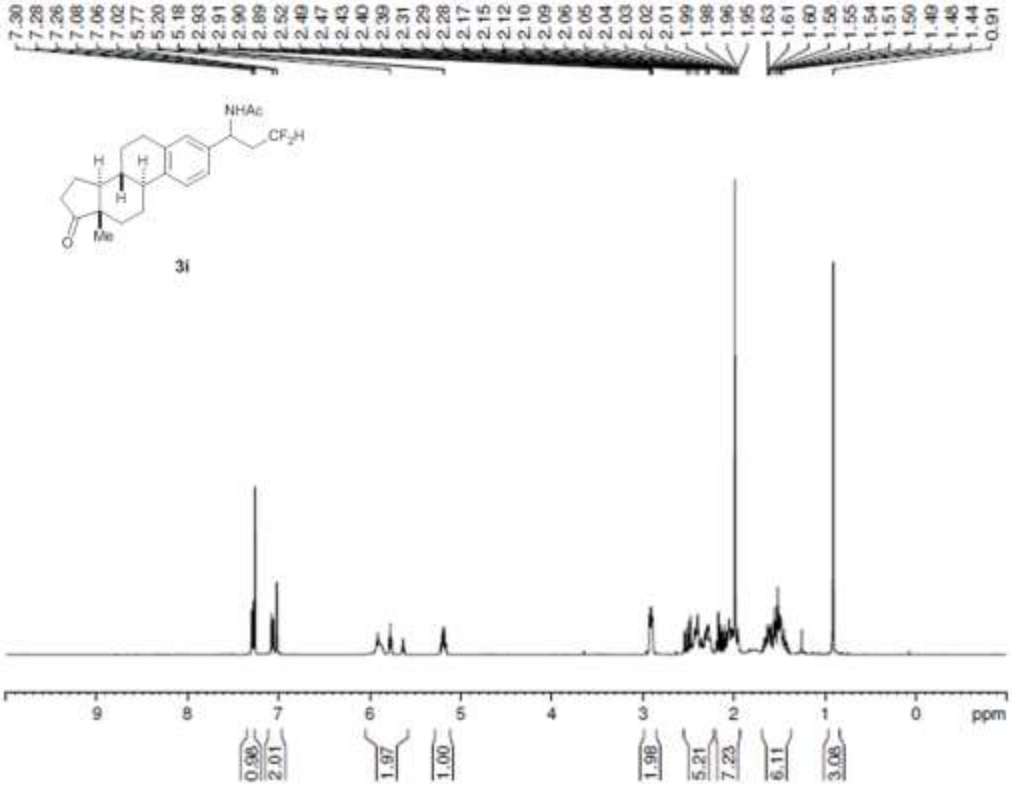

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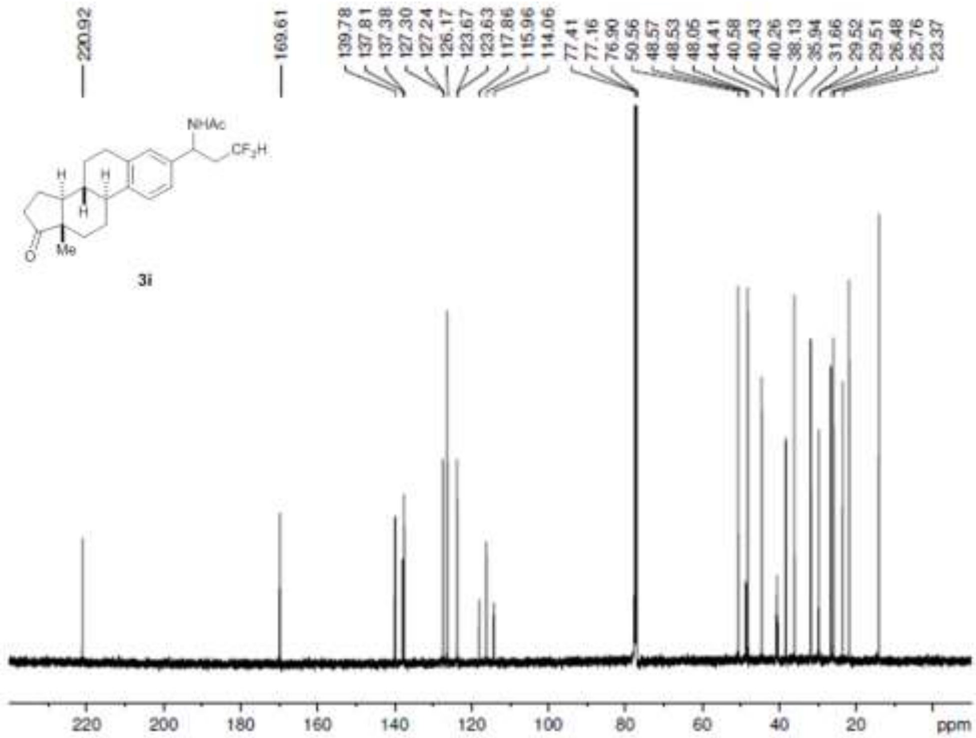

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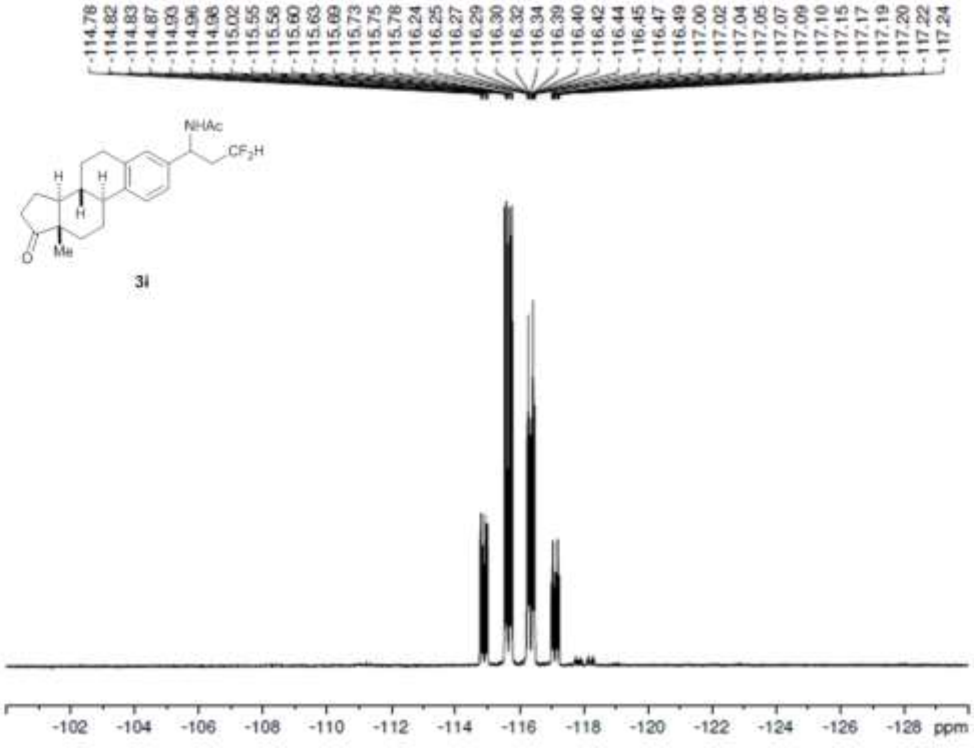

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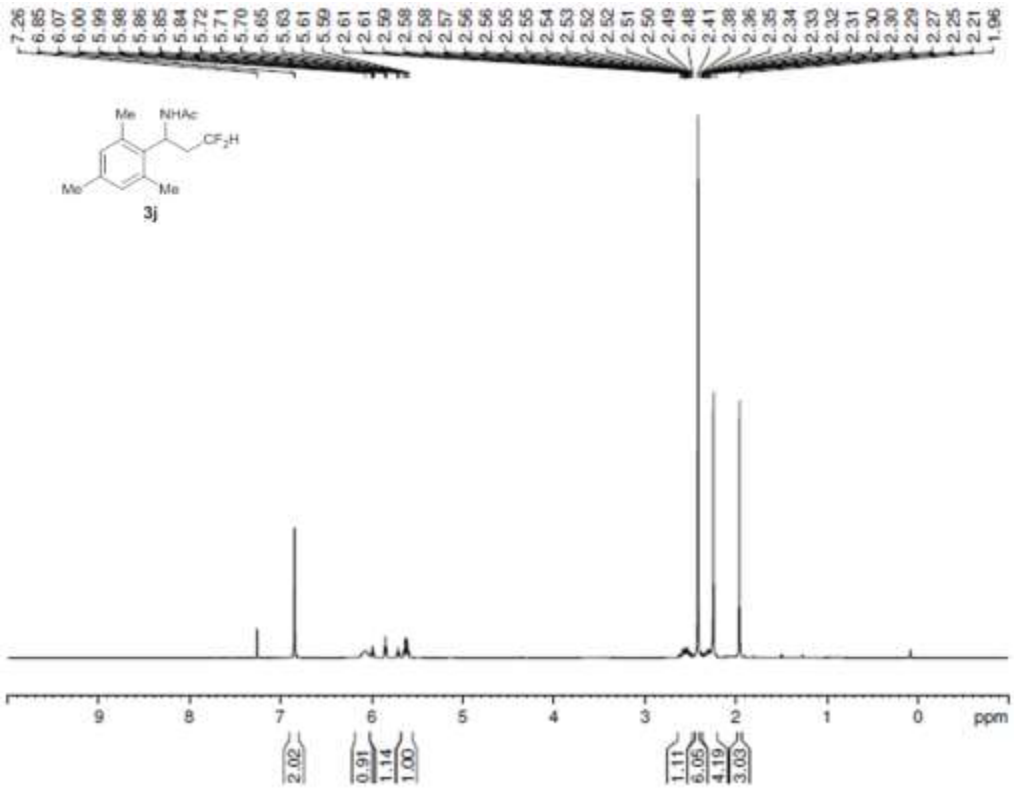

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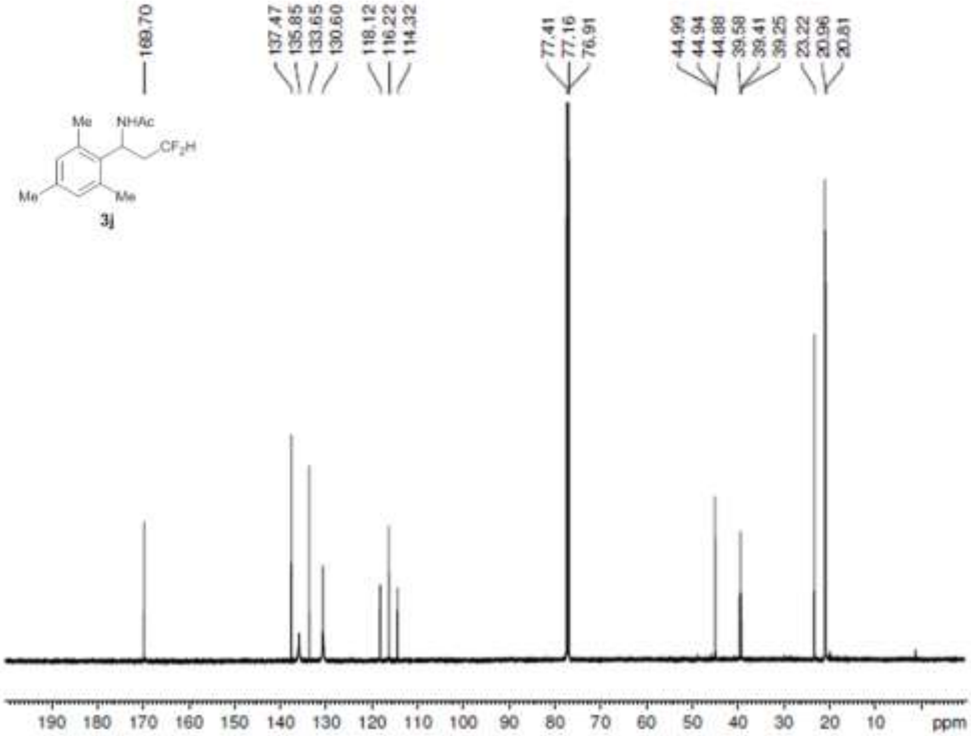

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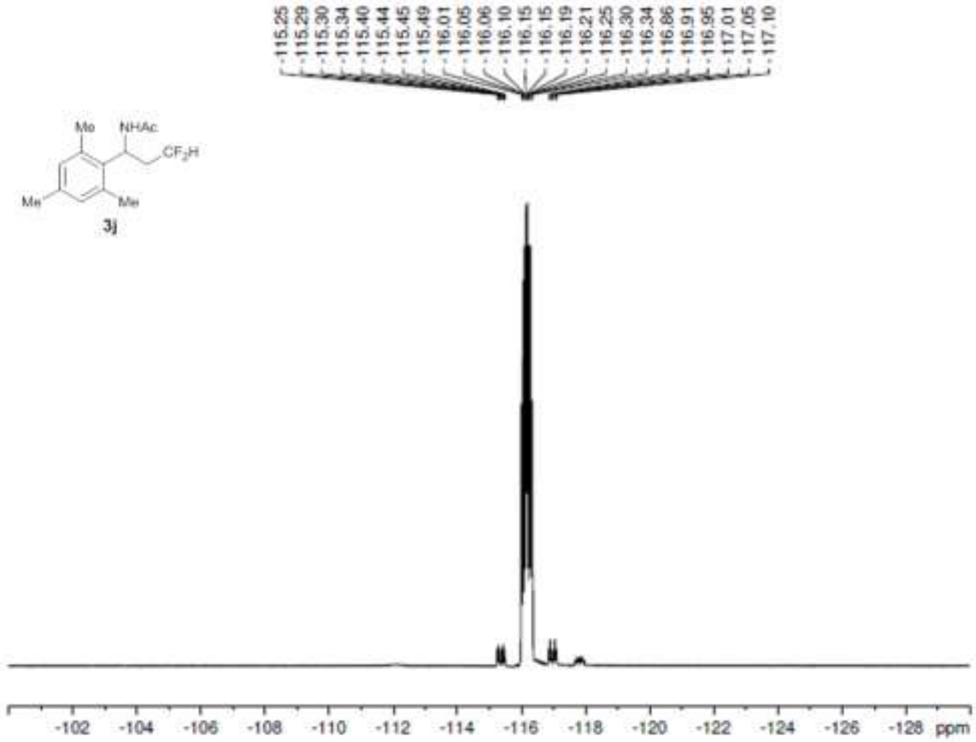

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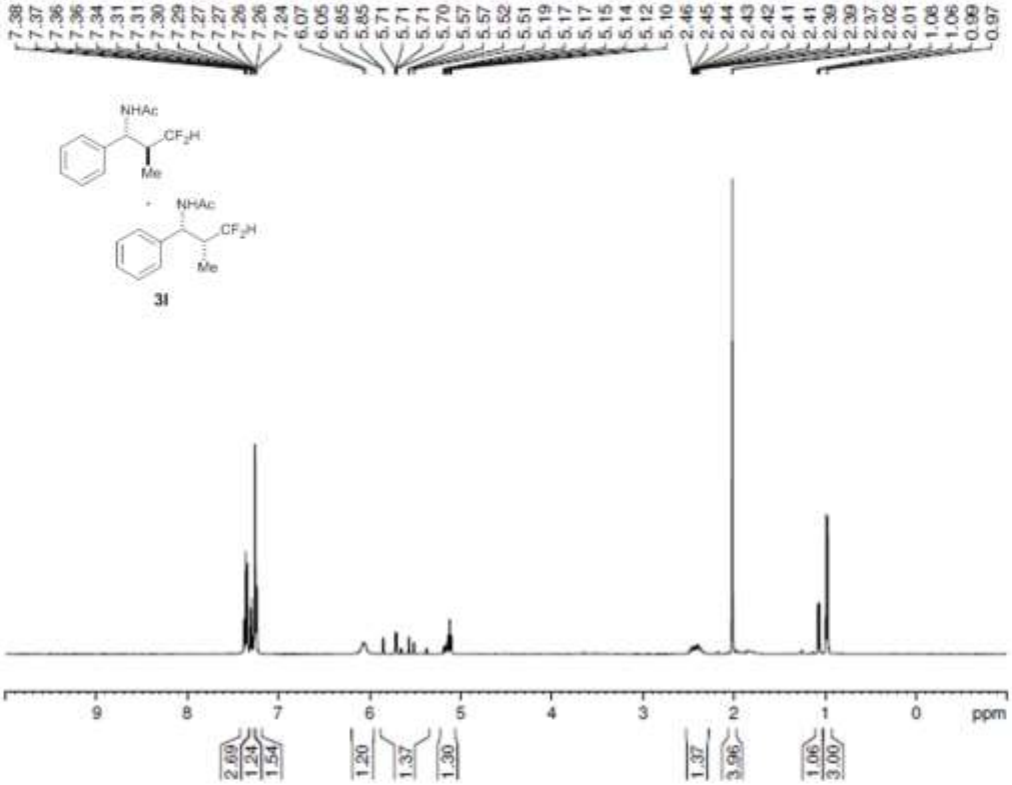

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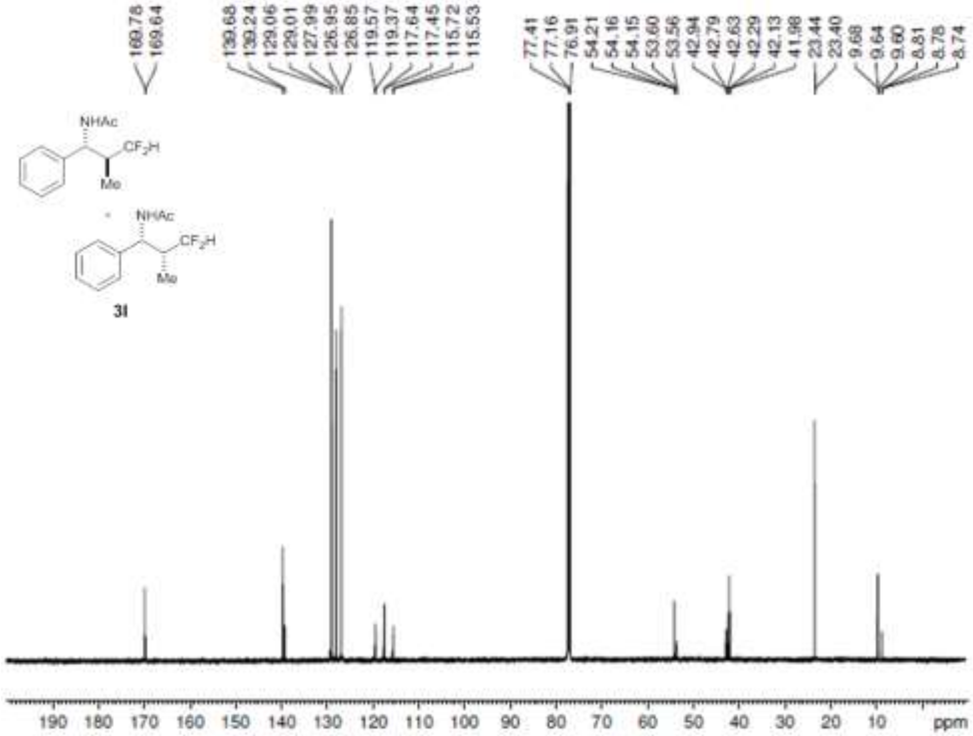

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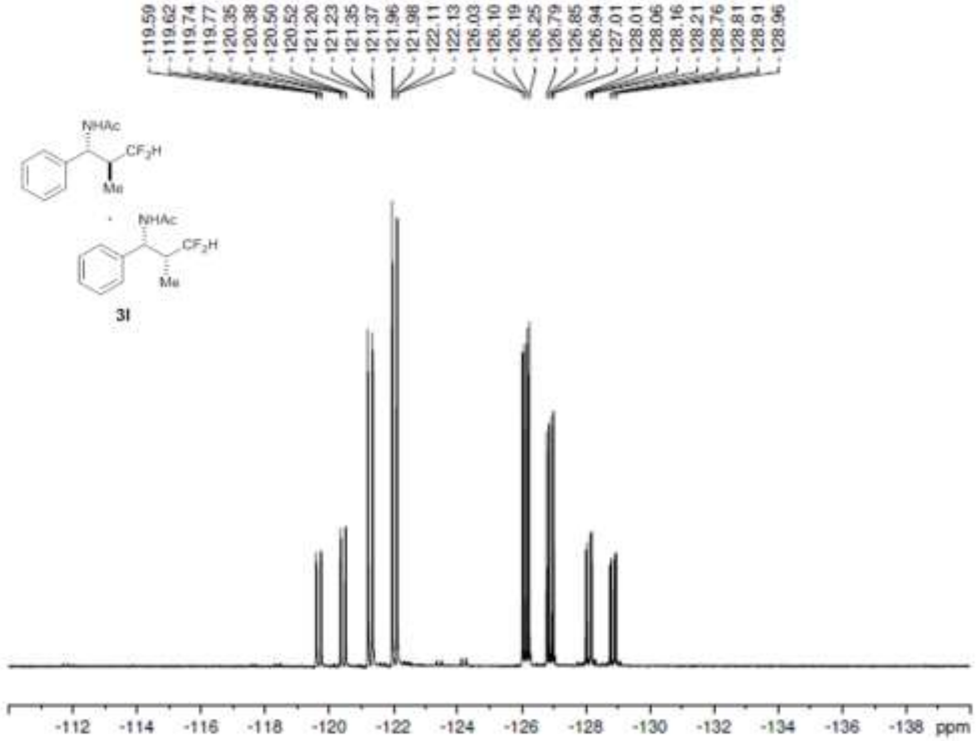

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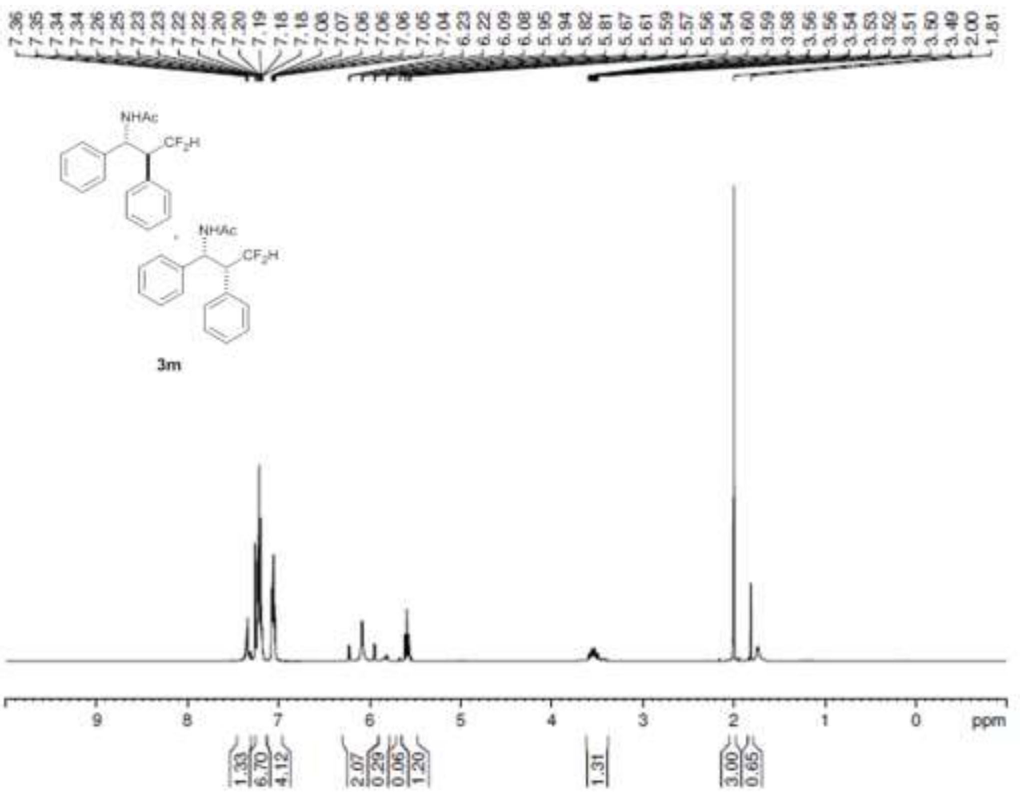

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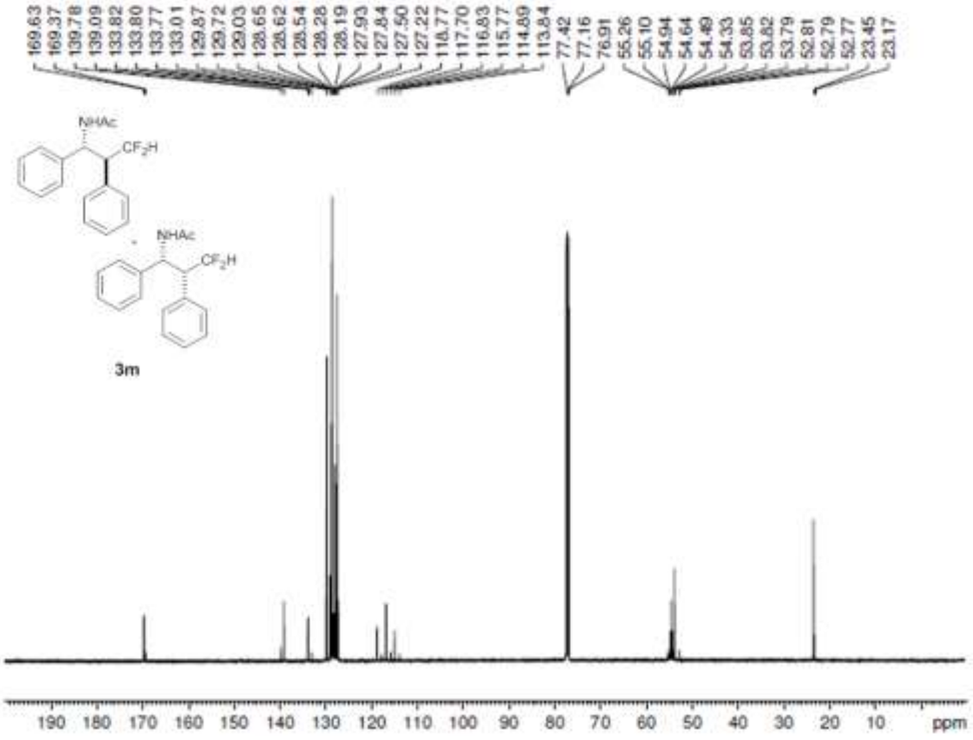

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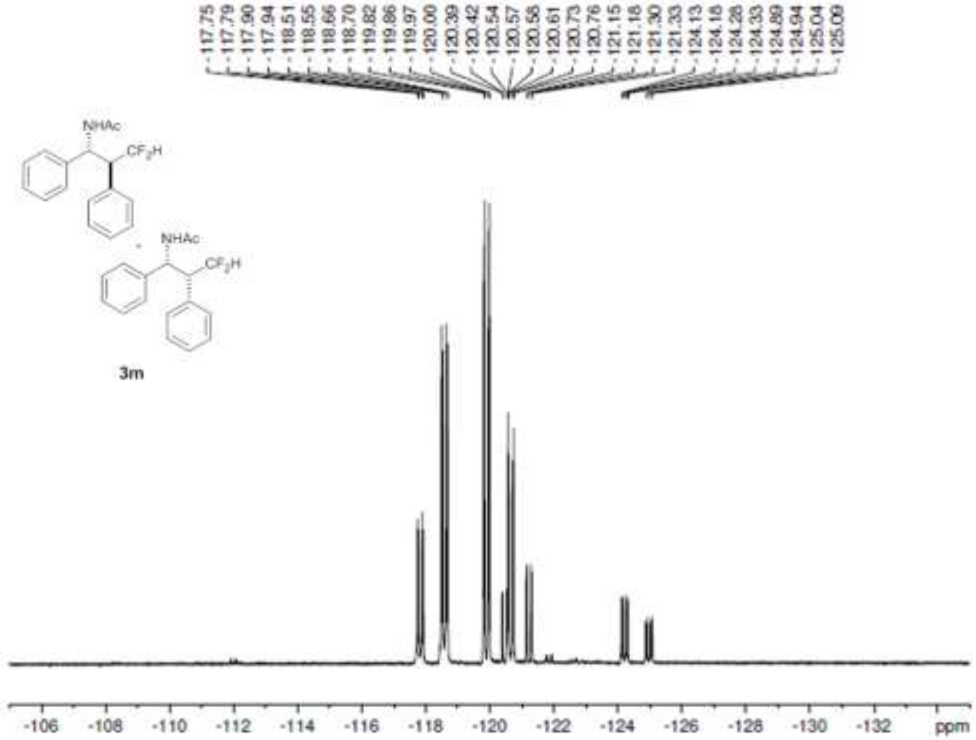
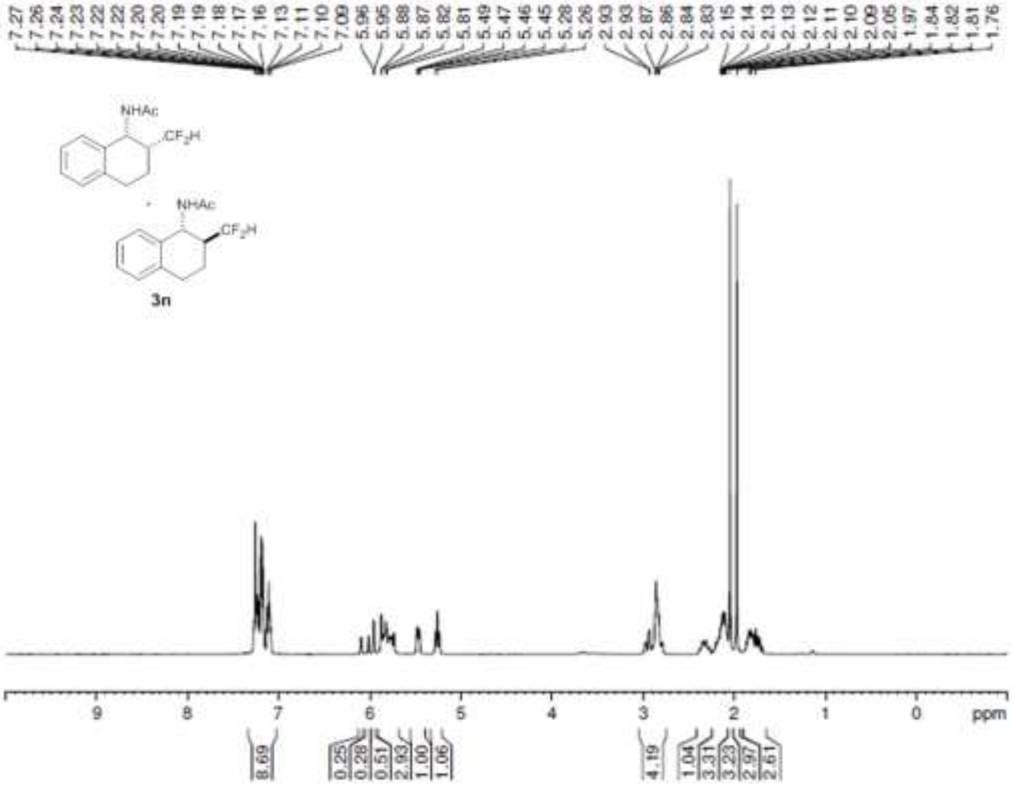
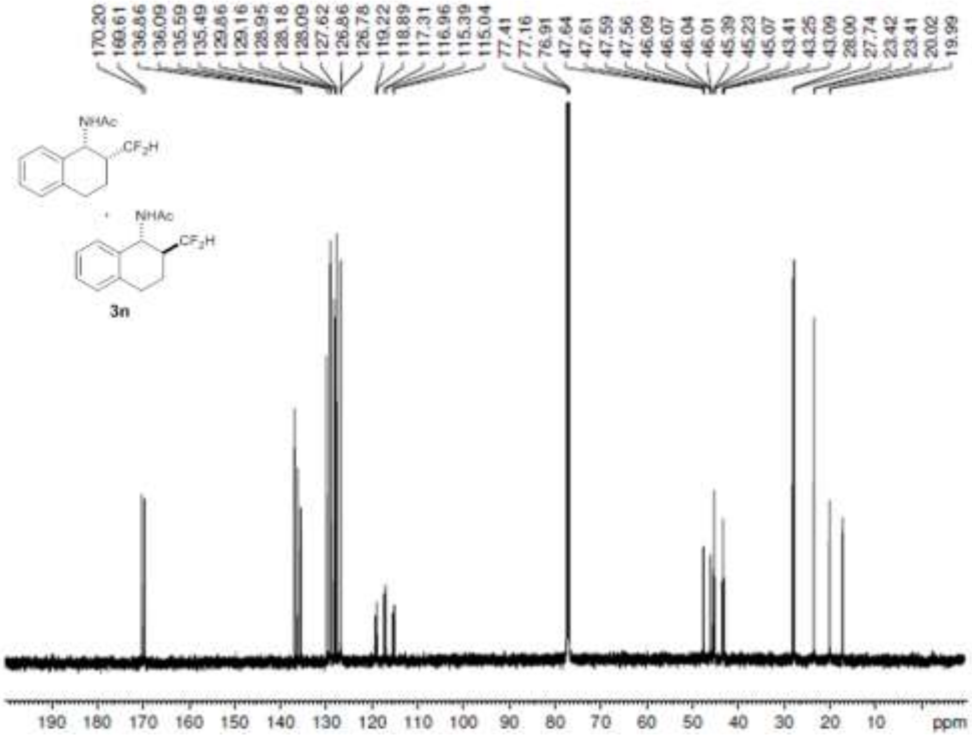


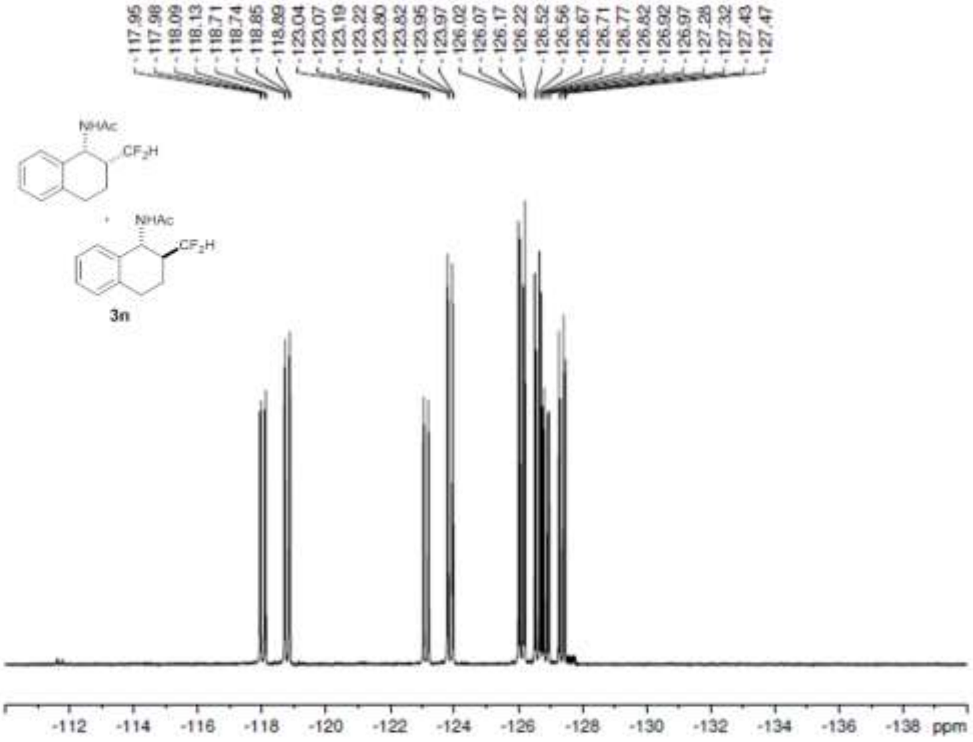
^{1}H NMR (400 MHz, $CDCl_3$)



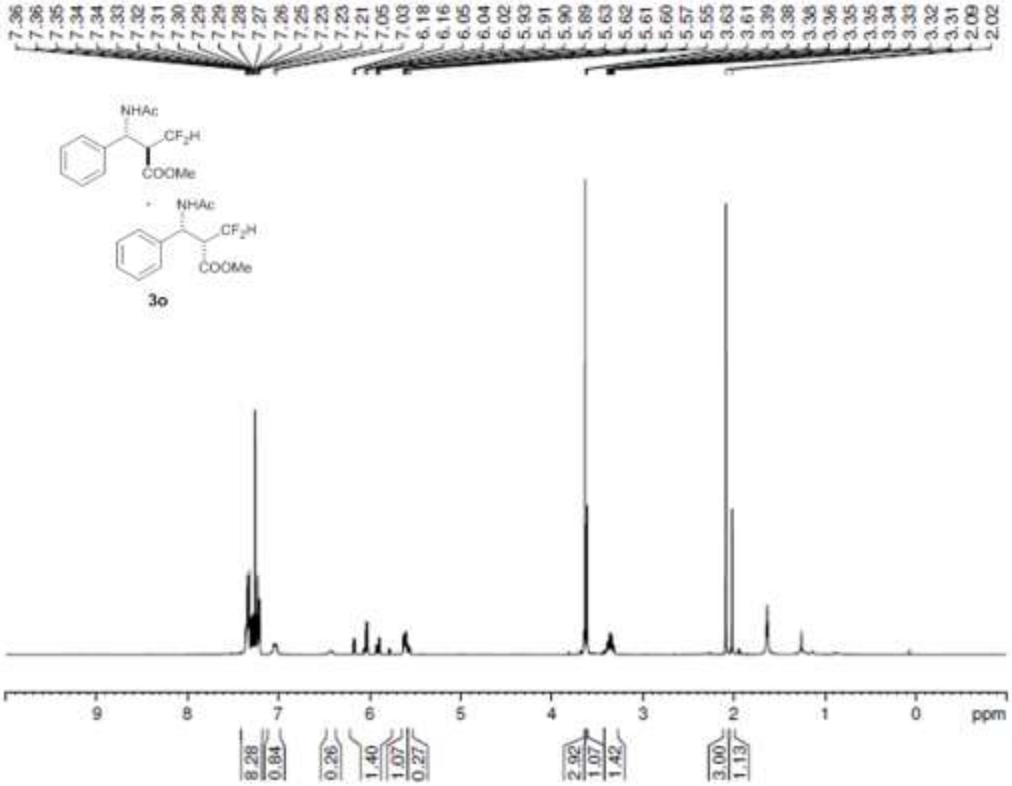
^{13}C NMR (125 MHz, $CDCl_3$)



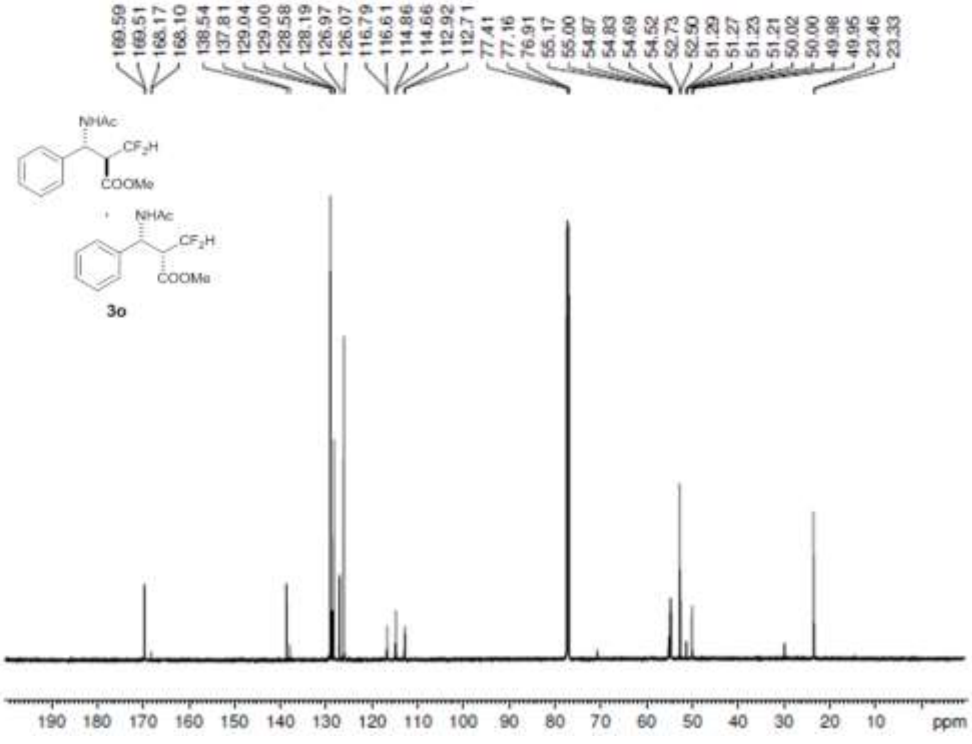
^{19}F NMR (376 MHz, $CDCl_3$)



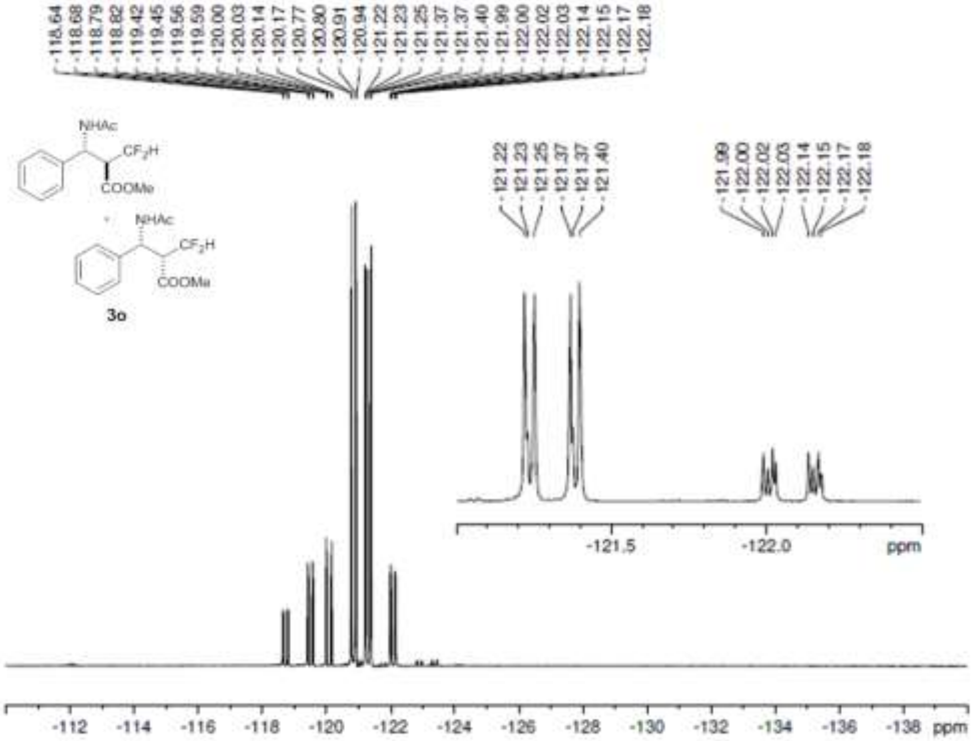
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

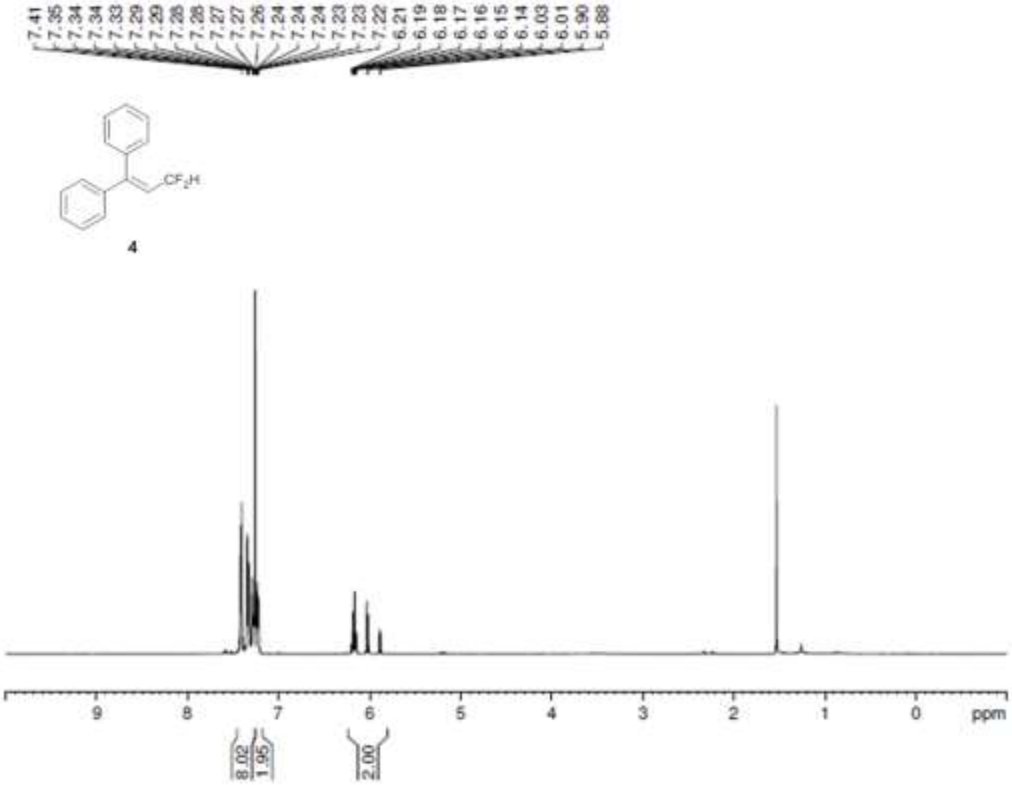


^{19}F NMR (376 MHz, $CDCl_3$)



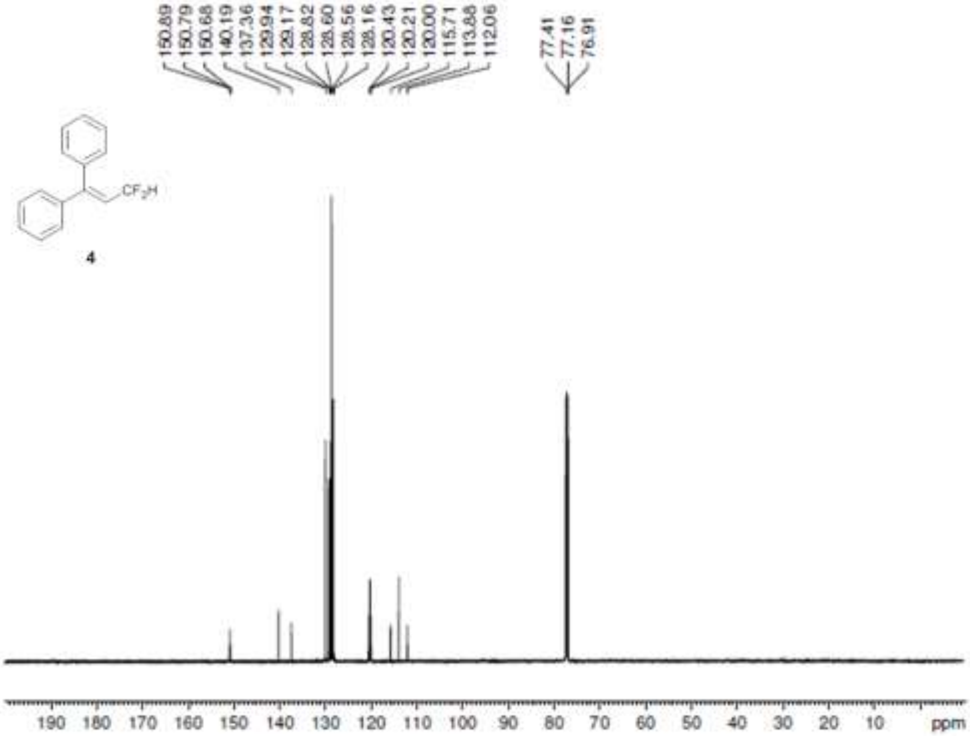
3o

^{1}H NMR (400 MHz, $CDCl_3$)

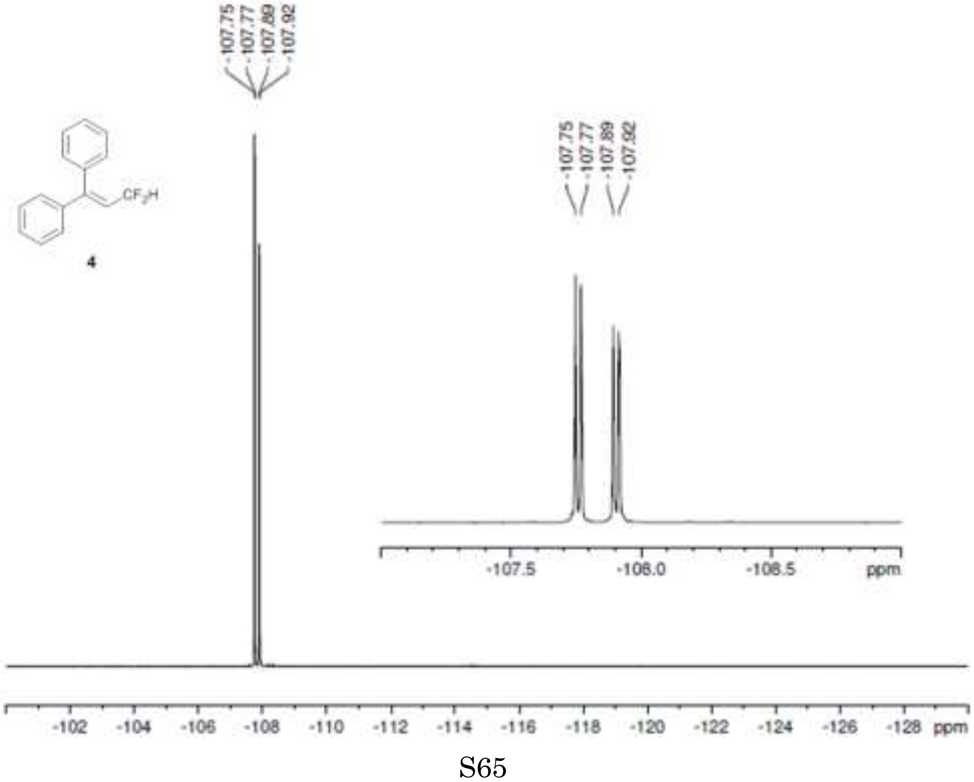


4

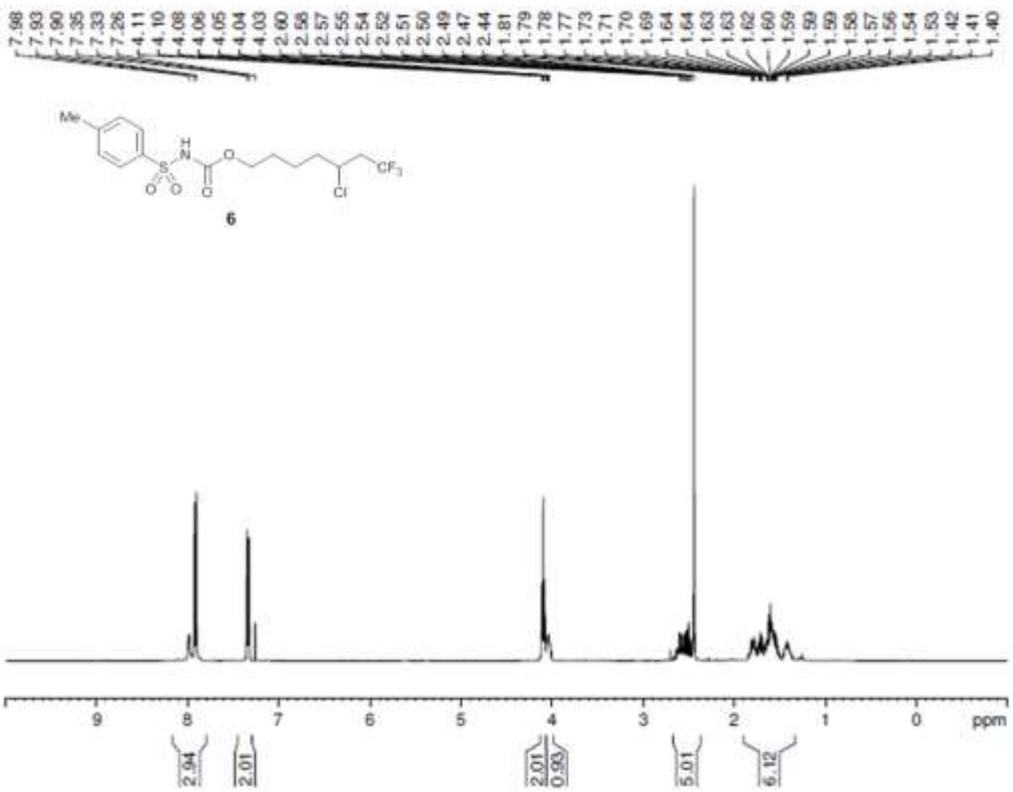
^{13}C NMR (125 MHz, $CDCl_3$)



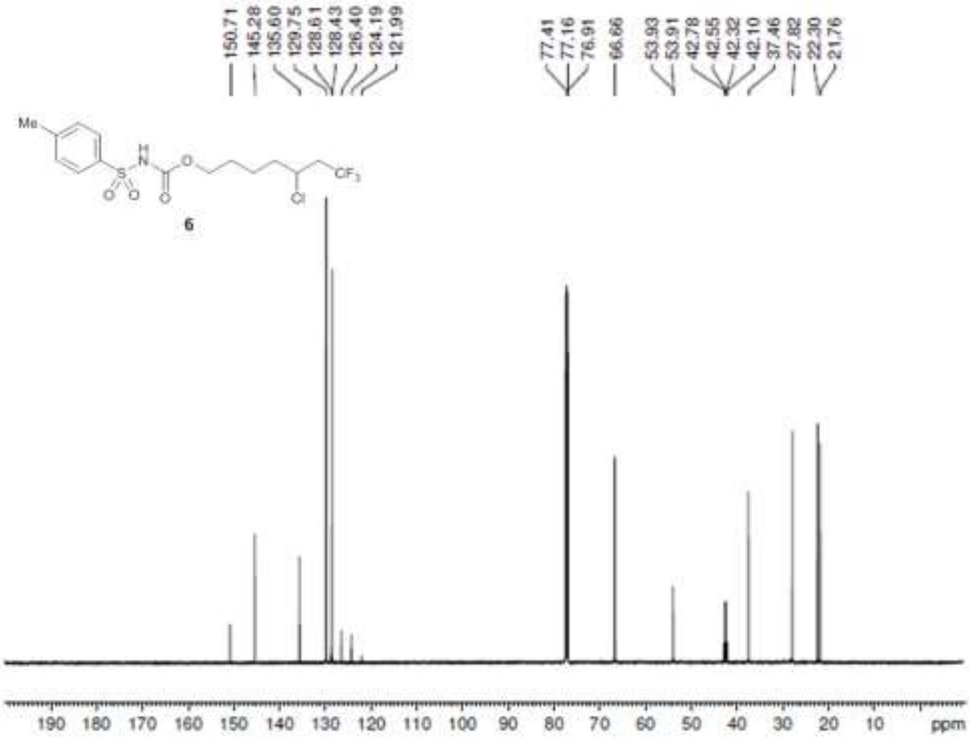
^{19}F NMR (376 MHz, $CDCl_3$)



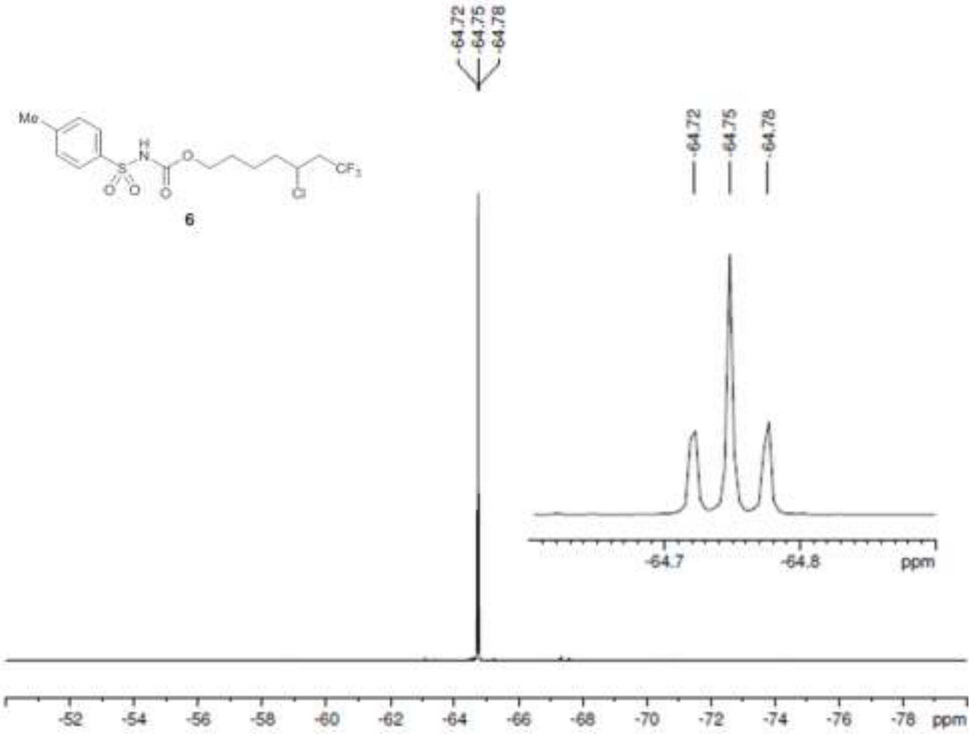
^{1}H NMR (400 MHz, CDCl$_3$)



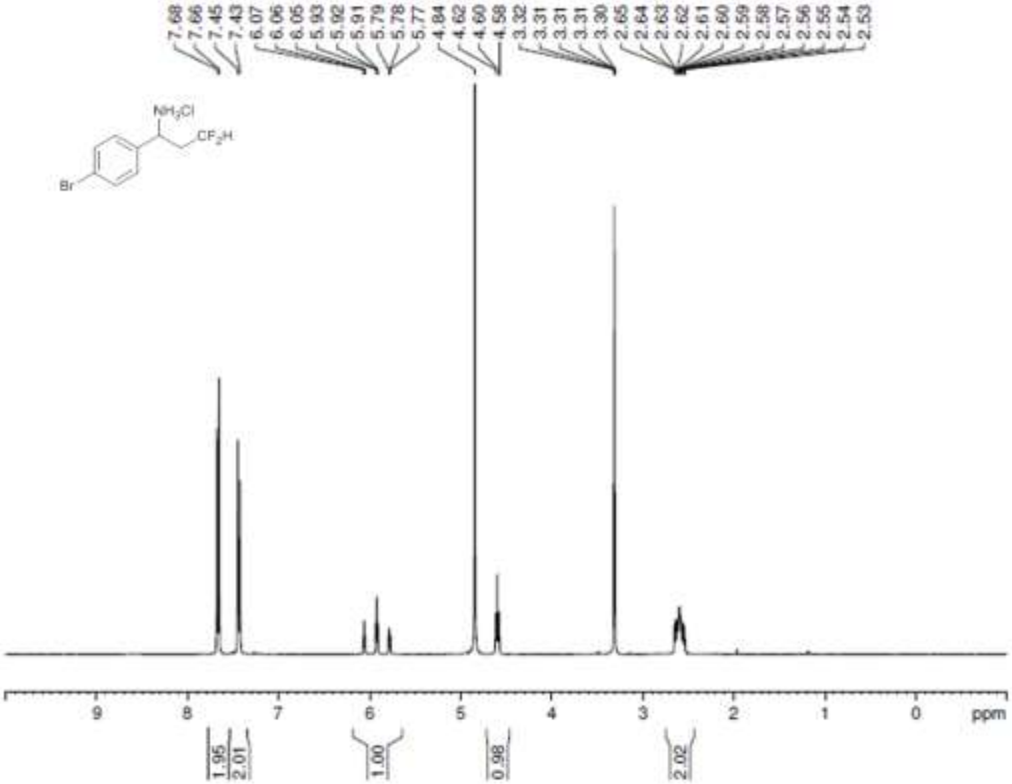
^{13}C NMR (125 MHz, CDCl$_3$)



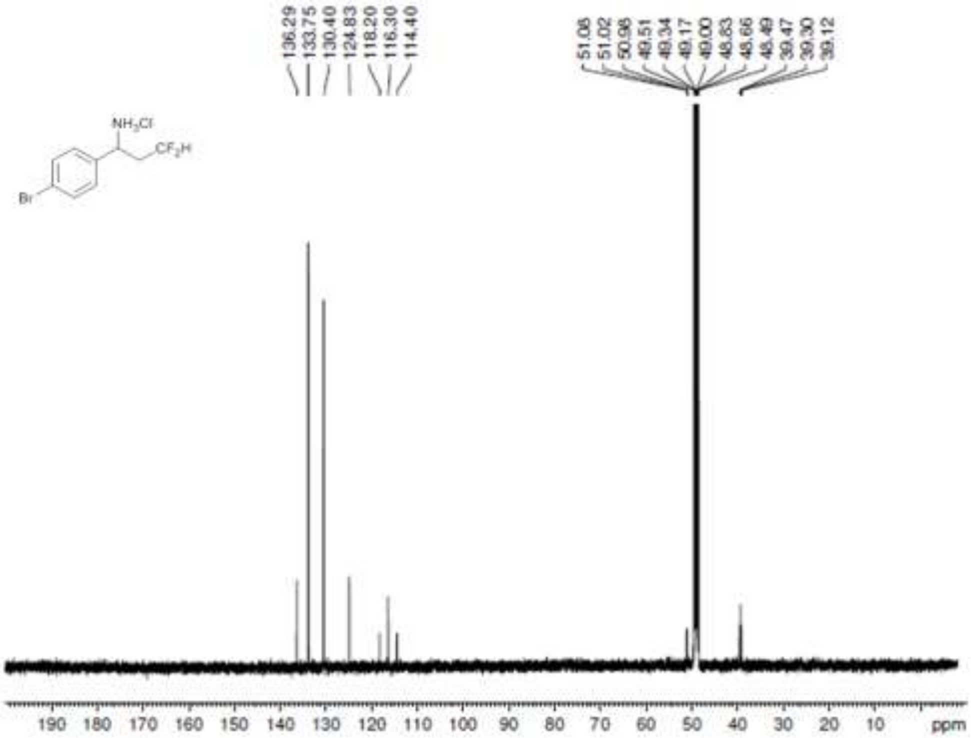
^{19}**F NMR** (376 MHz, $CDCl_3$)


6

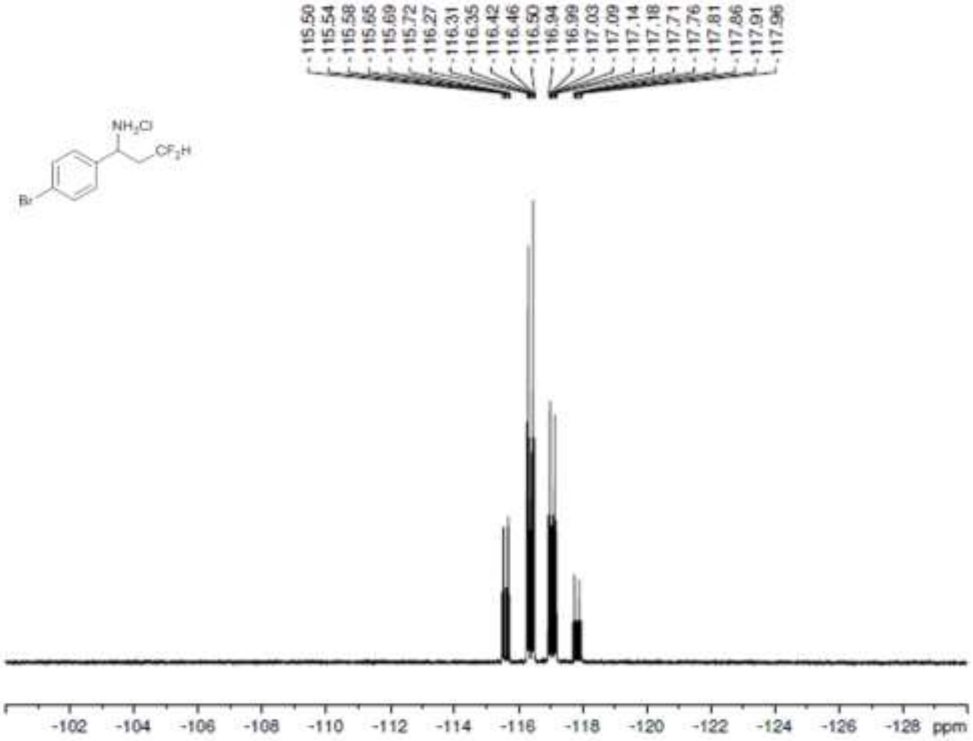
^{1}**H NMR** (400 MHz, CD_3OD)



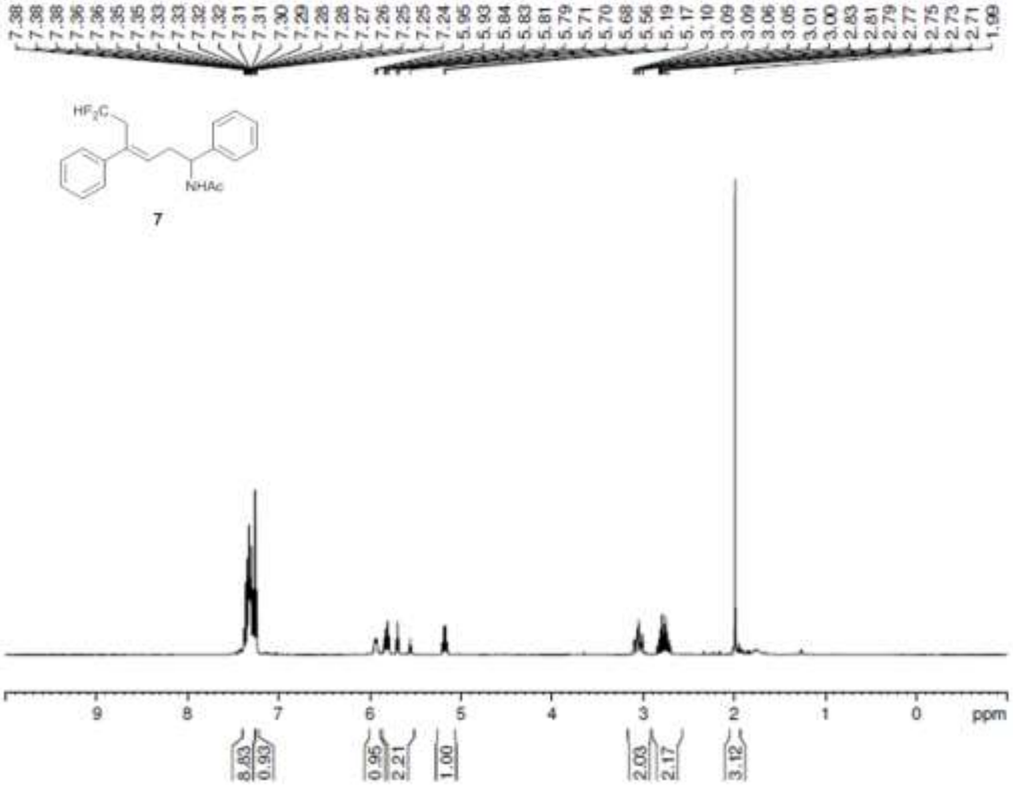
^{13}C NMR (125 MHz, CD_3OD)



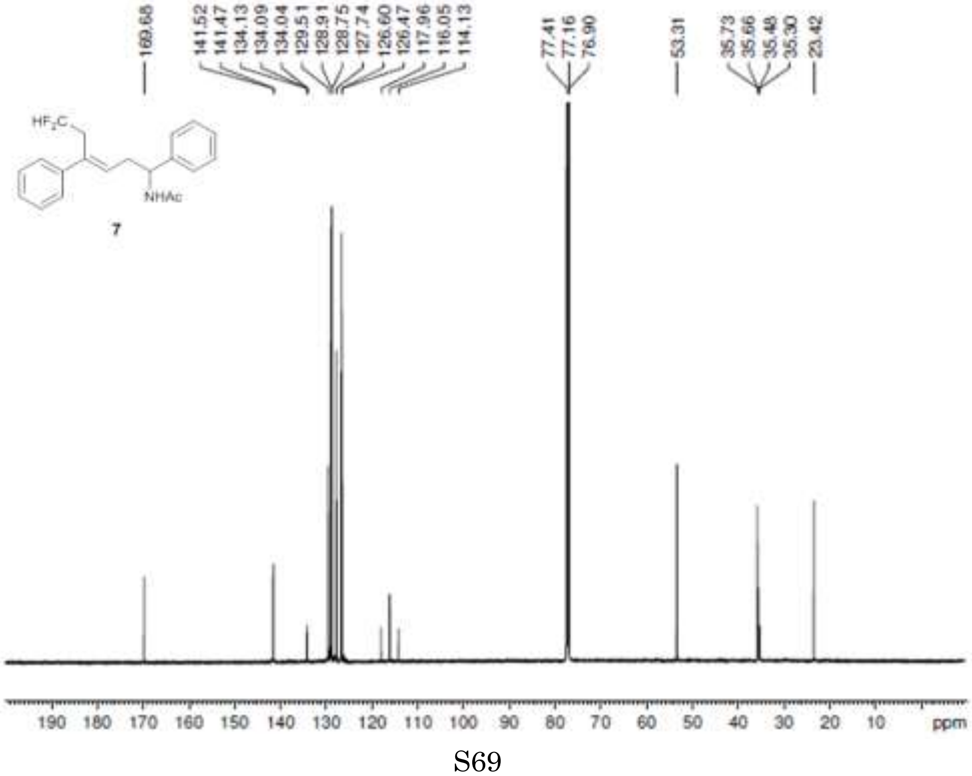
^{19}F NMR (376 MHz, CD_3OD)



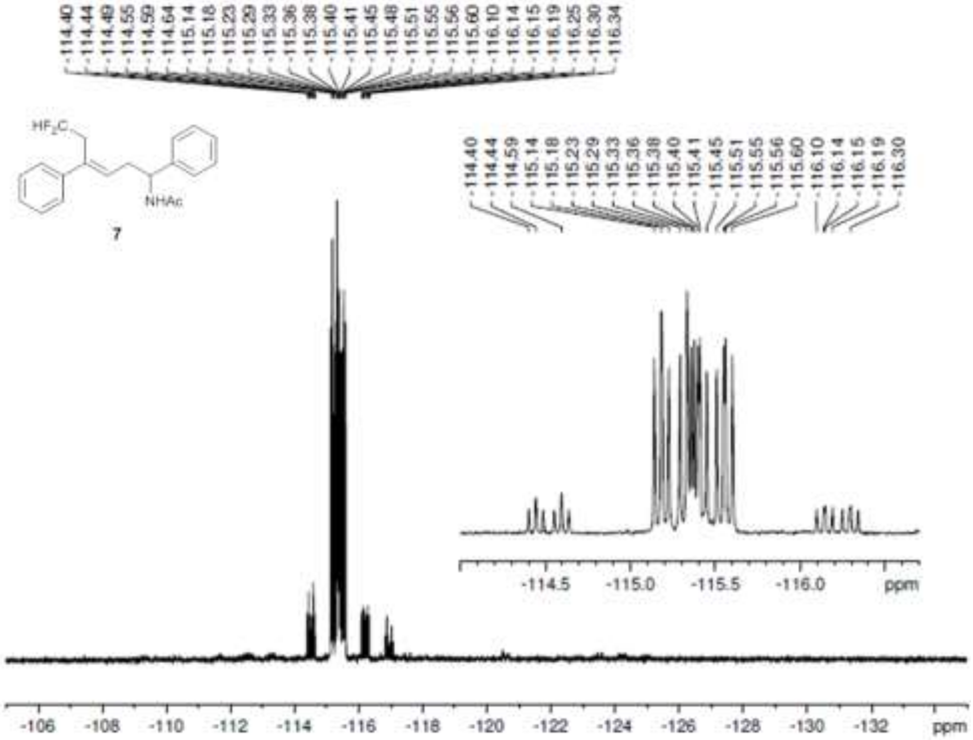
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, CDCl$_3$)



^{1}H-^{1}H NOESY (400 MHz, CDCl$_3$)