Radical Cyclization/Bis(pentafluoroethylation) of 1,6-Dienes Using HCF_2CF_3-Derived $CuCF_2CF_3$

Ziwei Luo and Gavin Chit Tsui*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR

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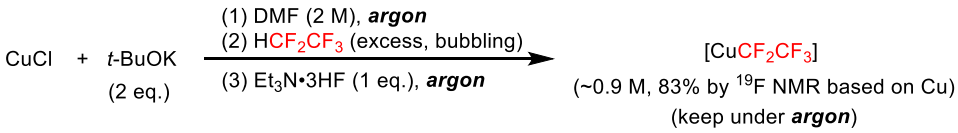
General Experimental. Analytical thin layer chromatography (TLC) was performed with EM Science silica gel 60 F254 aluminum plates. Visualization was done under a UV lamp (254 nm) and by immersion in ethanolic phosphomolybdic acid (PMA) or potassium permanganate ($KMnO_4$), followed by heating using a heat gun. Organic solutions were concentrated by rotary evaporation at 23–40 ℃. Purification of reaction products were generally done by flash column chromatography with Grace Materials Technologies 230−400 mesh silica gel.

Materials. Halocarbon 125-Pentafluoroethane (Purity: 99.0% min., 9.1kg in 16 L size cylinder) was purchased from SCIENTIFIC GAS ENGINEERING CO., LTD. Fluoroform (Research Grade, Purity: 99.999% min., 9.1kg in 16 L size cylinder) was purchased from SynQuest Laboratories, USA. Copper(I) chloride (extra pure, 99.99%) was purchased from Acros. Potassium tert-butoxide (97%) was purchased from Alfa Aesar. Anhydrous DMF was purchased from J&K Scientific. TREAT·HF was purchased from J&K Scientific and Macklin. Other chemicals for substrates preparation were purchased from Acros, J&K Scientific, Aldrich and Dikemann.

Instrumentation. Proton nuclear magnetic resonance spectra (^{1}H NMR) spectra, carbon nuclear magnetic resonance spectra (^{13}C NMR) and fluorine nuclear magnetic resonance spectra (^{19}F NMR) were recorded at 23 ℃ on a Bruker 400 spectrometer in $CDCl_3$ (400 MHz for ^{1}H, 101 MHz for ^{13}C and 377 MHz for ^{19}F) and Bruker 500 spectrometer in $CDCl_3$ (500 MHz for ^{1}H, 126 MHz for ^{13}C and 471 MHz for ^{19}F). Chemical shifts for protons were reported as parts per million in δ scale using solvent residual peak ($CHCl_3$: 7.26 ppm) or tetramethylsilane (0.00 ppm) as internal standards. Chemical shifts of ^{13}C NMR spectra were reported in ppm from the central peak of $CDCl_3$ (77.16 ppm) on the δ scale. Chemical shifts of ^{19}F NMR are reported as parts per million in δ scale using benzotrifluoride (-63.72 ppm) as internal standards. Data are represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintuplet, sx = sextet, sp = septuplet, m = multiplet, br = broad), and coupling constant (*J*, Hz). High resolution mass spectra (HRMS) were obtained on a Thermo Q Exactive Focus Orbitrap Mass Spectrometer or a Bruker 9.4T ICR Mass Spectrometer.

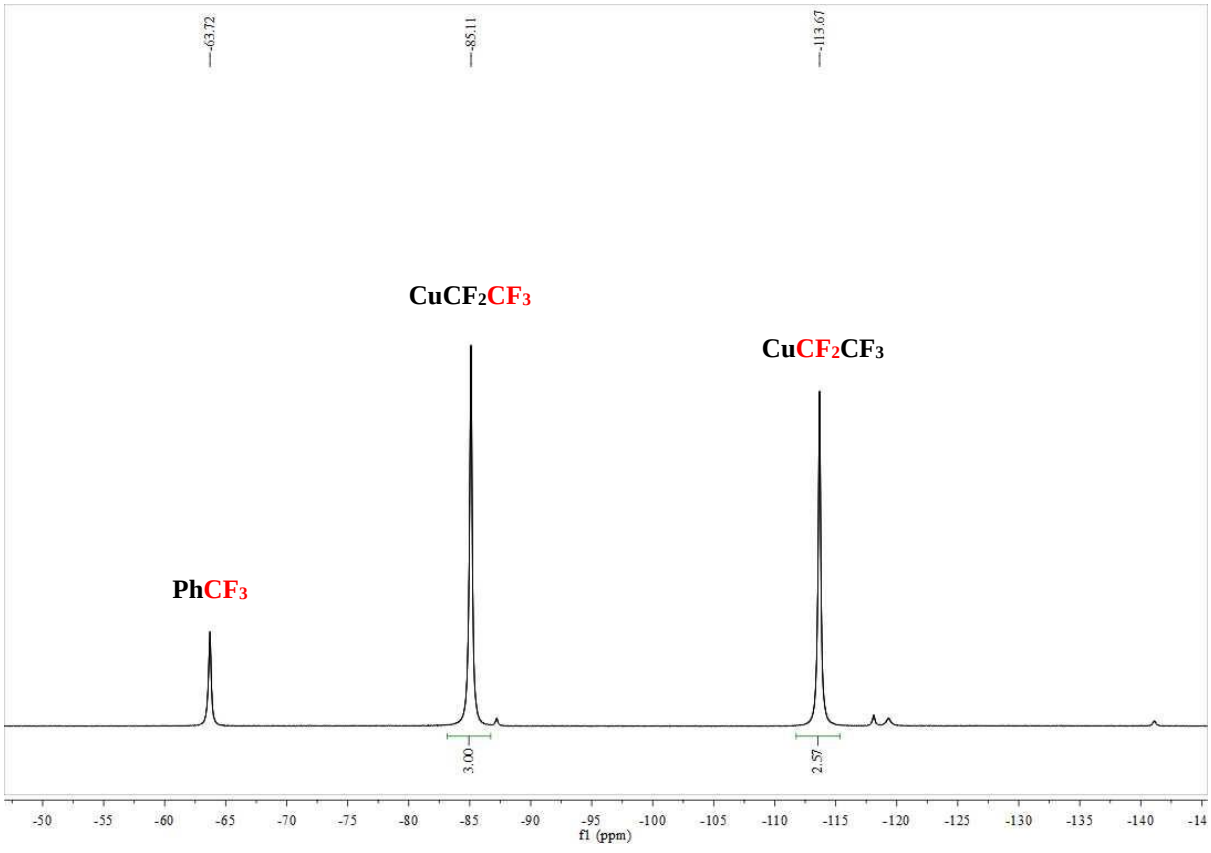
Experimental Procedures

Modified procedure for the preparation of pentafluoroethane-derived [$CuCF_2CF_3$] reagent[1]:

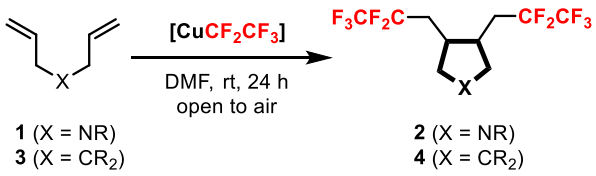


In a glove box, to a test tube was charged CuCl (200 mg, 2.0 mmol), *t*-BuOK (464 mg, 4.0 mmol) and a stirrer bar. The tube was sealed with a septum, brought out of the glove box and put under an argon atmosphere. Degassed DMF (1.0 mL) was added via syringe and the mixture was vigorously stirred at room temperature for 30 min. Then pentafluoroethane (HCF_2CF_3) was bubbled into the mixture by using a needle connected to the HCF_2CF_3 cylinder at room temperature for 5 min. After removing the HCF_2CF_3 inlet, the mixture was stirred for 5 min and $Et_3N{\cdot}3HF$ (326 μL, 2.0 mmol) was slowly added under argon and the mixture was stirred for another 5 min. A slightly greyish yellow solution with white precipitates was obtained as the [$CuCF_2CF_3$] solution in DMF (~83%, ~0.9 M).

^{19}F NMR of freshly prepared $CuCF_2CF_3$ reagent (in DMF, under argon, internal standard = $PhCF_3$):

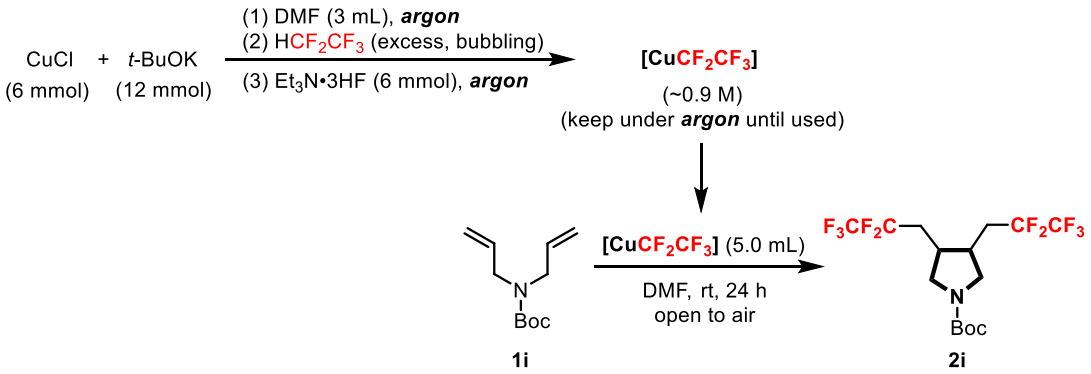


General procedure for cyclization/*bis*-pentafluoroethylation of 1,6-dienes:



Under air, to a test tube equipped with a magnetic stir bar and diene **1** or **3** (0.2 mmol) was added above freshly prepared [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF) at 0°C. Then the tube was warmed to room temperature and stirred for 24 h. The color slowly changed from greyish yellow to pale grey to blue to dark red. The reaction mixture was quenched with aq. sat. EDTA·2Na and extracted with diethyl ether three times. The organic layers were combined, washed with water then brine, dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product **2** or **4**.

1 mmol scale reaction:

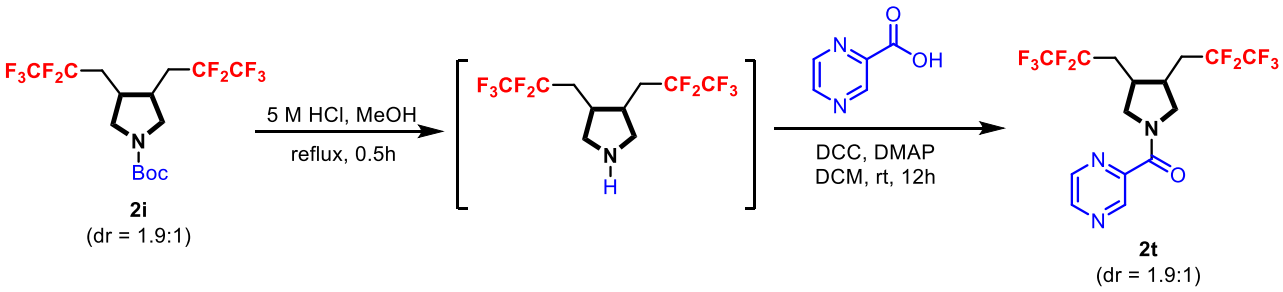


In a glove box, to a 25mL round-bottom flask was charged CuCl (600 mg, 6.0 mmol), *t*-BuOK (1.38 g, 12.0 mmol) and a stirrer bar. The flask was sealed with a septum, brought out of the glove box and put under an argon atmosphere. Degassed DMF (3.0 mL) was added via syringe in ambient water bath and the mixture was vigorously stirred at room temperature for 45 min. Then pentafluoroethane (HCF_2CF_3) was bubbled into the mixture by using a needle connected to the HCF_2CF_3 cylinder at room temperature for 10 min. After removing the HCF_2CF_3 inlet, the mixture was stirred for 5 min and $Et_3N{\cdot}3HF$ (0.98 mL, 6.0 mmol) was slowly added under argon and the mixture was stirred for another 5 min. A slightly greyish yellow solution with white precipitates was obtained as the [$CuCF_2CF_3$] solution in DMF (~0.9 M).

Under air, to a 25mL round-bottom flask equipped with a magnetic stir bar and **1i** (197.3 mg, 1.0 mmol) was added above freshly prepared [$CuCF_2CF_3$] (5.0 mL, 4.5 mmol in DMF) at 0°C. Then the flask was warmed to room temperature and stirred for 36 h. The color slowly changed from greyish yellow to pale grey to blue to dark red. The reaction mixture was quenched with aq. sat. EDTA·2Na and extracted with diethyl ether three times. The

organic layers were combined, washed with water then brine, dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product **2i** as a yellowish liquid (240.3 mg, 0.55 mmol, 55%, dr = 1.9:1 by GC-MS). R_f = 0.31 (hexane:EA = 10:1).

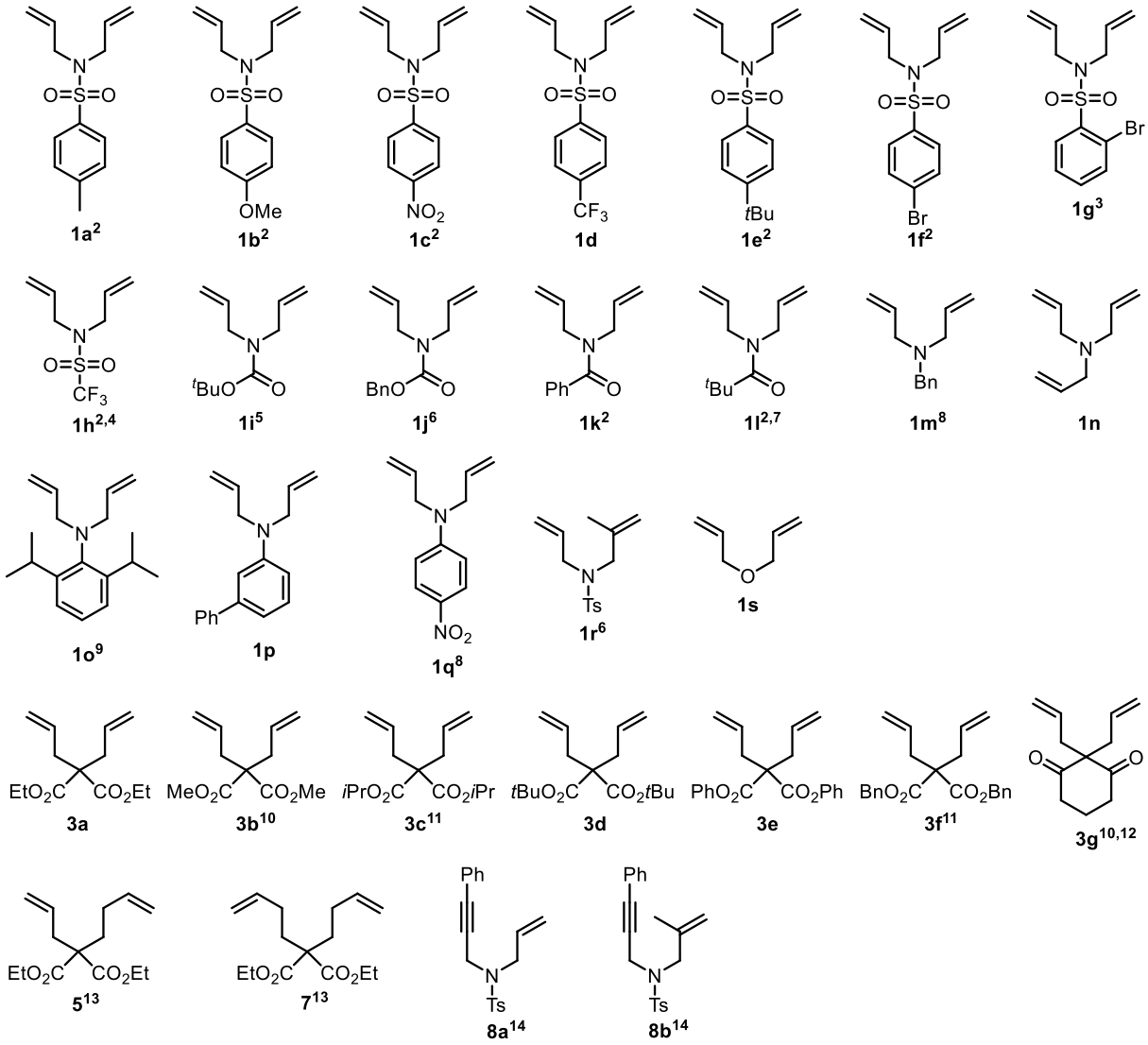
Derivatization of 2i:



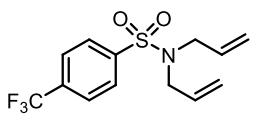
To a 10mL round-bottom flask equipped with a magnetic stir bar and **2i** (43.5mg, 0.1 mmol, dr = 1.9:1 by GC-MS) was added MeOH (2 mL) and 5M HCl (2 mL) at room temperature. Then the flask was heated to reflux (~80 ℃) and stirred for 0.5 h. Upon the starting material was detected to be fully converted by TLC, the reaction mixture was quenched with aq. sat. NaOH until pH = 11 and extracted with DCM three times. The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The crude product was directly used for the next step without further purification.

To a 10mL round-bottom flask equipped with a magnetic stir bar and the crude product above was added 2-pyrazinecarboxylic acid (18.6 mg, 0.15 mmol) and 4-(dimethylamino)pyridine (DMAP, 1.2 mg, 0.01 mmol). Then the solution of *N*,*N*′-dicyclohexylcarbodiimide (DCC, 41.3 mg, 0.2 mmol) in DCM (2 mL) was added to the mixture at room temperature. After being stirred for 12h, the reaction was diluted with DCM, washed with water three times then brine, dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product **2t** as a white solid (35.1 mg, 0.08 mmol, 80%, dr = 1.9:1 by GC-MS). R_f = 0.48 (hexane:EA = 1:1). **Major diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.20 (s, 1H), 8.60 (d, *J* = 60.2 Hz, 2H), 4.06 (dd, *J* = 12.0, 5.8 Hz, 1H), 3.97 – 3.86 (m, 2H), 3.69 (dd, *J* = 12.9, 5.3 Hz, 1H), 2.81 (s, 2H), 2.40 – 1.95 (m, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 164.4, 148.1, 146.3 (d, *J* = 36.4 Hz), 142.4, 118.9 (qtd, $J_{C\text{-}F}$ = 285.5, 35.7, 8.4 Hz), 115.5 (qt, $J_{C\text{-}F}$ = 253.4, 38.1 Hz), 52.1 (dd, *J* = 205.8, 3.1 Hz), 34.0 (d, *J* = 338.6 Hz), 28.6 (dt, *J* = 49.1, 21.6 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.74 (d, *J* = 34.2 Hz, 6F), -116.55 – -119.62 (m, 4F) ppm. **Minor diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.17 (s, 1H), 8.60 (d, *J* = 60.2 Hz, 2H), 4.25 (ddd, *J* = 18.0, 12.2, 4.6 Hz, 2H), 3.72 – 3.64 (m, 1H), 3.43 (dd, *J* = 12.8, 8.8 Hz, 1H), 2.40 – 1.95 (m, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 163.9, 148.3, 146.2 (d, *J* = 36.2 Hz), 142.4, 52.9 (dd, *J* = 213.2, 4.2 Hz), 36.8 (d, *J* = 334.3 Hz), 32.4 (dt, *J* = 40.6, 22.1 Hz) ppm (CF_2CF_3 peaks cannot be identified in detail). **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.66 (d, *J* = 18.3 Hz, 6F), -116.55 – -119.62 (m, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{15}H_{13}F_{10}N_3ONa$ $[M+Na]^+$: 464.0779; found: 464.0779.

Substrate table

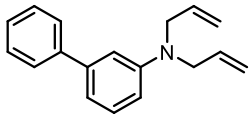


Amine derived 1,6-diene or enyne **1a**-**1c**, **1e**-**1m**, **1o**, **1q**-**1r**, **8a**-**8b**, malonate or dione derivative **3b**-**3c**, **3f**-**3g**, **5**, **7** were synthesized according to literature procedure, and the spectral data were in full accordance with the literature report. [2-14] **1n**, **1s** and **3a** were commercially available.

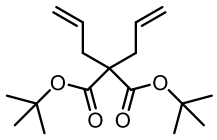


1d: *N,N*-diallyl-4-(trifluoromethyl)benzenesulfonamide. Prepared according to reported method.[2] Triethylamine (0.32 mL, 2.3 mmol) was added dropwise to a stirred solution of diallylamine (204.0 mg, 2.1 mmol) in DCM (10 mL) at 0 °C. Then 4-(trifluoromethyl)benzene sulfonyl chloride (489.2 mg, 2.0 mmol) was slowly added to the mixture. The reaction was allowed to warm up to room temperature and stirred overnight. Upon reaction completed, the reaction mixture was diluted with DCM, washed with water three times then brine, dried

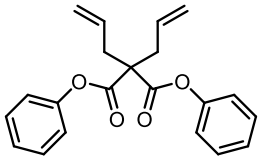
over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford **1d** as a white solid (2.0 mmol, 601.4 mg, 98 %), R_f = 0.36 (hexane:EA = 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 5.59 (tt, *J* = 16.7, 6.4 Hz, 2H), 5.21 – 5.09 (m, 4H), 3.84 (d, *J* = 6.3 Hz, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 144.2, 134.2 (q, J_{C-F} = 32.9 Hz), 132.1, 127.7, 126.3 (q, J_{C-F} = 3.6 Hz), 123.4 (q, J_{C-F} = 272.8 Hz), 119.6, 49.5 ppm. **HRMS** m/z (ESI): calcd. for $C_{13}H_{14}F_3NO_2SNa$ $[M+Na]^+$: 328.0590; found: 328.0583.



1p: *N,N*-diallyl-[1,1'-biphenyl]-3-amine. Prepared according to reported method.[8] To a round-bottom flask containing dry DMF (10 mL) and NaH (60% in mineral oil, 240.0 mg, 6.0 mmol) was added 3-phenyl aniline (507.6 mg 3.0 mmol) at 0 ℃ under argon. The reaction mixture was stirred for 30 minutes at room temperature. Then, allyl bromide (798.5 mg, 6.6 mmol) was added to the mixture dropwise at 0 ℃. The reaction was allowed to warm up to room temperature and stirred overnight. Upon reaction completed, the reaction mixture was quenched with aq. sat. $NaHCO_3$ and extracted with diethyl ether three times. The organic layers were combined, washed with water then brine, dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford **1p** as a yellowish oil (1.0 mmol, 249.6 mg, 33 %), R_f = 0.68 (hexane:EA = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.65 – 7.57 (m, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.30 (t, *J* = 8.1 Hz, 1H), 6.95 (d, *J* = 7.0 Hz, 2H), 6.78 – 6.69 (m, 1H), 5.93 (ddt, *J* = 17.0, 10.0, 4.8 Hz, 2H), 5.29 – 5.16 (m, 4H), 4.01 (dd, *J* = 2.8, 2.0 Hz, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 149.1, 142.3, 134.1, 129.5, 128.7, 127.4, 127.2, 116.2, 115.6, 111.5 (d, *J* = 5.6 Hz), 53.0 ppm. **HRMS** m/z (APCI): calcd. for $C_{18}H_{20}N$ $[M+H]^+$: 250.1590; found: 250.1587.

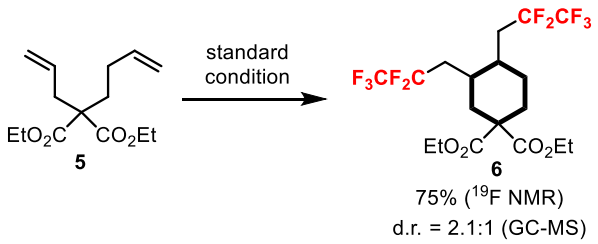


3d: Di-*tert*-butyl diallylmalonate. Prepared according to reported method.[13] To the solution of diisopropyl malonate (432.6 mg, 2.0 mmol) in dry THF (4 mL) and was added NaH (60% in mineral oil, 320.0 mg, 8.0 mmol) portionwise at 0 ℃ under argon. The reaction mixture was stirred for 30 minutes at room temperature. Then, allyl bromide (604.9 mg, 5.0 mmol) was added to the mixture dropwise. The reaction was heated to 60 ℃ and stirred overnight. Upon reaction completed, the reaction mixture was quenched with aq. sat. NH_4Cl and extracted with diethyl ether three times. The organic layers were combined, washed with water then brine, dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford **3d** as a white solid (1.9 mmol, 575.6 mg, 97 %), R_f = 0.47 (hexane:EA = 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.70 – 5.60 (m, 2H), 5.10 (dd, *J* = 13.6, 6.8 Hz, 4H), 2.55 (d, *J* = 7.4 Hz, 4H), 1.44 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 170.2, 132.8, 119.0, 81.4, 57.7, 36.6, 28.1 ppm. **HRMS** m/z (ESI): calcd. for $C_{17}H_{28}O_4Na$ $[M+Na]^+$: 319.1880; found: 319.1870.

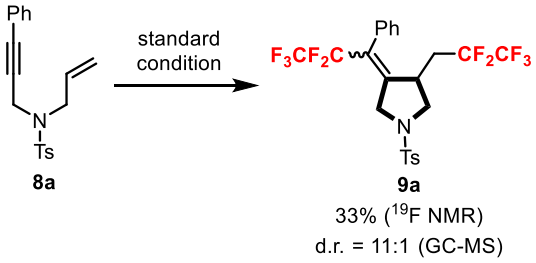


3e: Diphenyl diallylmalonate. Prepared according to reported method.[13] To the solution of diphenyl malonate (512.5 mg, 2.0 mmol) in dry THF (4 mL) and was added NaH (60% in mineral oil, 320.0 mg, 8.0 mmol) portionwise at 0 ℃ under argon. The reaction mixture was stirred for 30 minutes at room temperature. Then, allyl bromide (604.9 mg, 5.0 mmol) was added to the mixture dropwise. The reaction was heated to 60 ℃ and stirred overnight. Upon reaction completed, the reaction mixture was quenched with aq. sat. NH_4Cl and extracted with diethyl ether three times. The organic layers were combined, washed with water then brine, dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford **3e** as a yellowish oil (1.1 mmol, 368.0 mg, 55 %), R_f = 0.34 (hexane:EA = 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.44 (t, *J* = 7.9 Hz, 4H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.17 (d, *J* = 7.7 Hz, 4H), 5.96 (dq, *J* = 10.0, 7.5 Hz, 2H), 5.35 (dd, *J* = 26.1, 13.5 Hz, 4H), 2.99 (d, *J* = 7.5 Hz, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 169.1, 150.6, 131.8, 129.6, 126.3, 121.4, 120.2, 57.6, 37.2 ppm. **HRMS** m/z (ESI): calcd. for $C_{21}H_{20}O_4Na$ $[M+Na]^+$: 359.1254; found: 359.1244.

Control Experiment

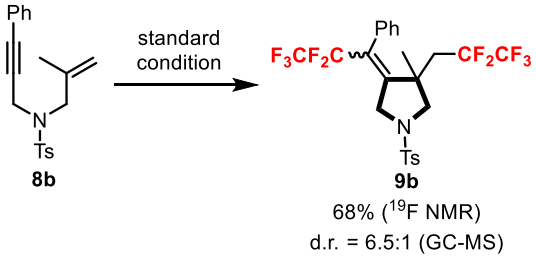


Under air, to a test tube equipped with a magnetic stir bar and 1,7-diene **5** (50.9 mg, 0.2 mmol) was added freshly prepared [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF) at 0°C. Then the tube was warmed to room temperature and stirred for 24 h. After the reaction mixture was diluted by DCM, the crude yields of products were analyzed by ^{19}F NMR (75 %) using $PhCF_3$ as the internal standard and GC-MS (dr = 2.1:1). The reaction mixture was quenched with aq. sat. EDTA·2Na and extracted with diethyl ether three times. The organic layers were combined, washed with water then brine, dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford a mixture of **6** and mono-pentafluoroethylated by-products as a yellowish liquid, R_f = 0.35 (hexane:EA = 10:1). **Compound 6**: **Major diastereomer**: **^{19}F NMR** (471 MHz, $CDCl_3$): δ -87.00 (dd, *J* = 38.0, 4.8 Hz, 6F), -116.75 – -119.43 (m, 4F) ppm. **Minor diastereomer**: **^{19}F NMR** (471 MHz, $CDCl_3$): δ -87.00 (dd, *J* = 91.4, 4.9 Hz, 6F), -116.75 – -119.43 (m, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{18}H_{22}F_{10}O_4Na$ $[M+Na]^+$: 515.1251; found: 515.1241.

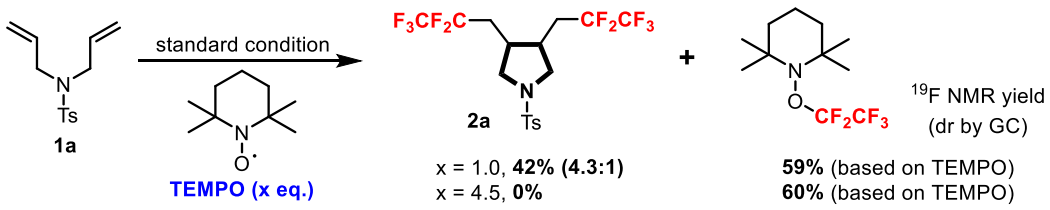


Under air, to a test tube equipped with a magnetic stir bar and enyne **8a** (65.1 mg, 0.2 mmol) was added freshly prepared [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF) at 0°C. Then the tube was warmed to room temperature and stirred for 24 h. After the reaction mixture was diluted by DCM, the crude yields of products were analyzed by ^{19}F NMR (33 %) using $PhCF_3$ as the internal standard and GC-MS (dr = 11:1). The reaction mixture was quenched with aq. sat. EDTA·2Na and extracted with diethyl ether three times. The organic layers were combined, washed with water then brine, dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product **9a** (with some impurity) as a yellowish liquid (34.7 mg, ~0.06 mmol, ~31 %, dr > 20:1 by GC-MS), R_f = 0.20 (hexane:EA = 10:1). **Major diastereomer (with impurity)**: **^1H NMR** (500 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.44 –

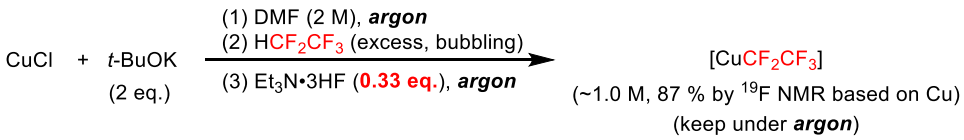
7.38 (m, 3H), 7.34 (d, J = 8.0 Hz, 2H), 7.04 (br, 2H), 3.75 (dd, J = 22.8, 13.4 Hz, 2H), 3.65 – 3.57 (m, 1H), 3.30 (dt, J = 16.7, 3.2 Hz, 1H), 3.03 (dd, J = 10.2, 5.3 Hz, 1H), 2.45 (s, 3H), 2.42 – 2.10 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 150.7, 144.6, 133.0 (t, J_{C-F} = 3.0 Hz), 132.0, 130.1, 129.4, 129.2, 128.9, 127.9, 125.6 (t, J_{C-F} = 22.1 Hz), 53.0, 51.7, 35.4, 34.2 (t, J_{C-F} = 21.9 Hz), 21.7 ppm (CF_2CF_3 peaks cannot be identified in detail). **^{19}F NMR** (471 MHz, $CDCl_3$): δ -83.46 (s, 3F), -87.12 (s, 3F), -111.65 (d, J = 25.9 Hz, 2F), -118.95 (dddd, J = 266.1, 33.9, 28.7, 6.6 Hz, 2F) ppm. **HRMS** m/z (ESI): calcd. for $C_{23}H_{19}F_{10}NO_2SNa$ $[M+Na]^+$: 586.0869; found: 586.0860.



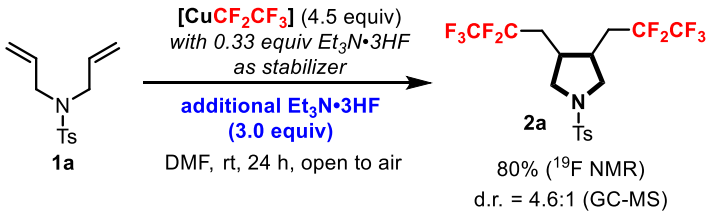
Under air, to a test tube equipped with a magnetic stir bar and enyne **8b** (67.9 mg, 0.2 mmol) was added freshly prepared $[CuCF_2CF_3]$ (1.0 mL, 0.90 mmol in DMF) at 0°C. Then the tube was warmed to room temperature and stirred for 24 h. After the reaction mixture was diluted by DCM, the crude yields of products were analyzed by ^{19}F NMR (68 %) using $PhCF_3$ as the internal standard and GC-MS (dr = 6.5:1). The reaction mixture was quenched with aq. sat. EDTA·2Na and extracted with diethyl ether three times. The organic layers were combined, washed with water then brine, dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product **9b** (with some impurity) as a yellowish liquid (64.3 mg, ~0.11 mmol, ~56 %, dr > 20:1 by GC-MS), R_f = 0.28 (hexane:EA = 10:1). **Major diastereomer (with impurity)**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.72 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 7.7 Hz, 5H), 7.12 (dd, J = 25.3, 7.3 Hz, 2H), 4.12 (ddt, J = 130.0, 16.2, 3.7 Hz, 2H), 3.12 (dd, J = 34.0, 9.6 Hz, 2H), 2.46 (s, 3H), 1.93 (ddd, J = 35.1, 15.5, 4.6 Hz, 1H), 1.61 (ddd, J = 34.3, 15.5, 6.8 Hz, 1H), 1.17 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 144.5, 131.6, 131.10 (t, J_{C-F} = 3.2 Hz), 130.97, 130.0, 129.5, 128.3, 128.2, 128.1, 125.1 (t, J_{C-F} = 22.9 Hz), 119.4 (qt, J_{C-F} = 287.1, 38.9 Hz), 118.5 (qt, J_{C-F} = 286.1, 35.7 Hz), 115.7 (qt, J_{C-F} = 256.3, 37.1 Hz), 113.3 (tq, J = 256.5, 38.4 Hz), 58.4 (d, J = 5.8 Hz), 51.4 (t, J_{C-F} = 9.1 Hz), 45.8, 36.3 (t, J_{C-F} = 19.3 Hz), 25.5 (d, J = 3.5 Hz), 21.7 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -82.86 (s, 3F), -87.86 (s, 3F), -111.38 (q, J = 267.9 Hz, 2F), -115.89 – -118.39 (m, 2F).ppm. **HRMS** m/z (ESI): calcd. for $C_{24}H_{21}F_{10}NO_2SNa$ $[M+Na]^+$: 600.1026; found: 600.1012.



Under air, to a test tube equipped with a magnetic stir bar was added diene **1a** (25.1 mg, 0.1 mmol), TEMPO (1.0 eq.: 15.6 mg; 4.5 eq.: 70.3 mg) and then freshly prepared [$CuCF_2CF_3$] (0.5 mL, 0.45 mmol in DMF) at 0°C. Then the tube was warmed to room temperature and stirred for 24 h. After the reaction mixture was diluted by DCM, the crude yields and dr ratio of **2a** and TEMPO-CF_2CF_3 were analyzed by ^{19}F NMR using $PhCF_3$ as the internal standard and GC-MS. **TEMPO-CF_2CF_3**: **^{19}F NMR** (471 MHz, $CDCl_3$): δ -84.90 (s, 2F), -85.87 (s, 3F) ppm. The spectral data are in full accordance with the literature report.[15]

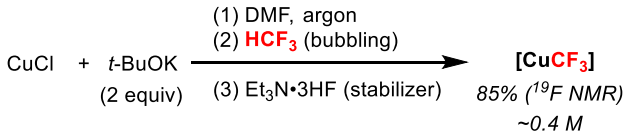


In a glove box, to a test tube was charged CuCl (200 mg, 2.0 mmol), *t*-BuOK (464 mg, 4.0 mmol) and a stirrer bar. The tube was sealed with a septum, brought out of the glove box and put under an argon atmosphere. Degassed DMF (1.0 mL) was added via syringe and the mixture was vigorously stirred at room temperature for 30 min. Then pentafluoroethane (HCF_2CF_3) was bubbled into the mixture by using a needle connected to the HCF_2CF_3 cylinder at room temperature for 5 min. After removing the HCF_2CF_3 inlet, the mixture was stirred for 5 min and $Et_3N{\cdot}3HF$ (107 μL, 0.67 mmol) was slowly added under argon and the mixture was stirred for another 5 min. A slightly greyish yellow solution with white precipitates was obtained as the [$CuCF_2CF_3$] solution in DMF (~87%, ~1.0 M).

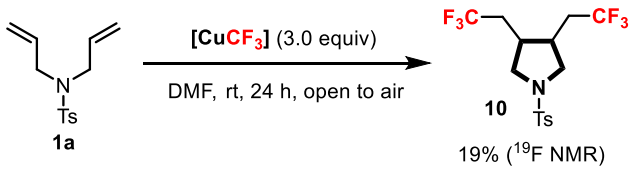


Under air, to a test tube equipped with a magnetic stir bar was added diene **1a** (25.1 mg, 0.1 mmol), $Et_3N{\cdot}3HF$ (48.9 μL, 0.3 mmol) and then above freshly prepared [$CuCF_2CF_3$] (0.45 mL, 0.45 mmol in DMF) at 0°C. Then the tube was warmed to room temperature and stirred for 24 h. After the reaction mixture was diluted by DCM, the crude yield and dr ratio of **2a** was analyzed by ^{19}F NMR (80 %) using $PhCF_3$ as the internal standard and GC-

MS (dr = 4.6:1).



According to literature procedure,[16] in a glove box, to a test tube was charged CuCl (100 mg, 1.0 mmol), *t*-BuOK (232 mg, 2.0 mmol) and a stirrer bar. The tube was sealed with a septum, brought out of the glove box and put under an argon atmosphere. Degassed DMF (2.0 mL) was added via syringe and the mixture was vigorously stirred at room temperature for 30 min. Then fluoroform (HCF_3) was bubbled into the mixture by using a needle connected to the HCF_3 cylinder at room temperature for 5 min. After removing the HCF_3 inlet, the mixture was stirred for 5 min and $Et_3N{\cdot}3HF$ (124 μL, 0.76 mmol) was slowly added under argon and the mixture was stirred for another 5 min. A slightly brown solution with white precipitates was obtained as the [$CuCF_3$] solution in DMF (~0.4 M).



Under air, to a test tube equipped with a magnetic stir bar and diene **1a** (25.1 mg, 0.1 mmol) was added above freshly prepared [$CuCF_3$] (0.75 mL, 0.3 mmol in DMF) at 0°C. Then the tube was warmed to room temperature and stirred for 24 h. After the reaction mixture was diluted by DCM, the crude yield of **10** was analyzed by ^{19}F NMR (19 %) using $PhCF_3$ as the internal standard and GC-MS. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -65.67 (t, *J* = 11.1 Hz, major diastereomer), -66.04 (t, *J* = 11.5 Hz, minor diastereomer) ppm. The spectral data are in full accordance with the literature report.[17]

X-ray Structure of 2c and 4g

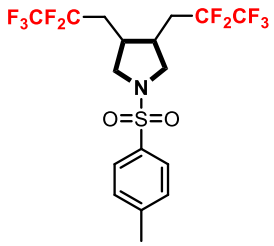
Crystals of **2c** were obtained by slow diffusion from the solution in $CHCl_3$ layered *n*-hexane. The crystal was kept at 296 K during data collection. Crystallographic data for **2c** has been deposited with the Cambridge Crystallographic Data Centre (CCDC) under deposition number 2151010.

Identification code	CCDC 2151010	
Empirical formula	$C_{16}H_{14}F_{10}N_2O_4S$	
Formula weight	520.35	
Temperature	297(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8.4047(8) Å	α= 90°.
	b = 21.134(2) Å	β= 101.665(3)°.
	c = 11.6700(11) Å	γ = 90°.
Volume	2030.1(3) $Å^3$	
Z	4	
Density (calculated)	1.702 Mg/m^3	
Absorption coefficient	0.278 mm^{-1}	
F(000)	1048	
Crystal size	0.500 x 0.400 x 0.300 mm^3	
Theta range for data collection	1.927 to 25.249°.	
Index ranges	-10<=h<=10, -25<=k<=25, -14<=l<=14	
Reflections collected	28311	
Independent reflections	3620 [R(int) = 0.0272]	
Completeness to theta = 25.242°	98.6 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.7456 and 0.6600	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3620 / 17 / 382	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0786, wR2 = 0.2206	
R indices (all data)	R1 = 0.0912, wR2 = 0.2399	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.376 and -0.400 $e.Å^{-3}$	

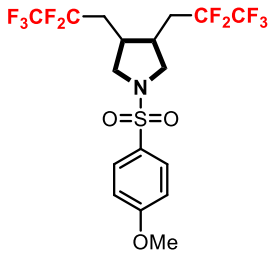
Crystals of **4g** were obtained by slow diffusion from the solution in $CHCl_3$ layered *n*-hexane. The crystal was kept at 296 K during data collection. Crystallographic data for **4g** has been deposited with the Cambridge Crystallographic Data Centre (CCDC) under deposition number 2151006.

Identification code	CCDC 2151006	
Empirical formula	$C_{16}H_{16}F_{10}O_2$	
Formula weight	430.29	
Temperature	296(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.9751(6) Å	α= 90°.
	b = 12.4668(7) Å	β= 99.824(3)°.
	c = 28.5860(18) Å	γ = 90°.
Volume	3502.8(4) $Å^3$	
Z	8	
Density (calculated)	1.632 Mg/m^3	
Absorption coefficient	1.607 mm^{-1}	
F(000)	1744	
Crystal size	0.400 x 0.300 x 0.200 mm^3	
Theta range for data collection	3.877 to 68.466°.	
Index ranges	-11<=h<=12, -14<=k<=15, -34<=l<=34	
Reflections collected	52073	
Independent reflections	6392 [R(int) = 0.0477]	
Completeness to theta = 67.679°	99.3 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.7531 and 0.5592	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6392 / 114 / 608	
Goodness-of-fit on F^2	1.076	
Final R indices [I>2sigma(I)]	R1 = 0.0887, wR2 = 0.2552	
R indices (all data)	R1 = 0.0939, wR2 = 0.2642	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.801 and -0.630 $e.Å^{-3}$	

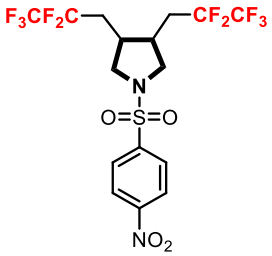
Characterization Data of Products



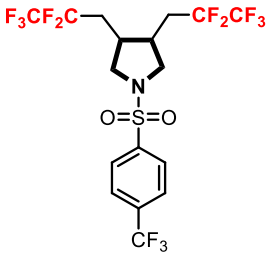
2a: 3,4-bis(2,2,3,3,3-pentafluoropropyl)-1-tosylpyrrolidine. Prepared according to the general procedure. Reaction was run using **1a** (50.3 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/EA) and obtained as a white solid (0.12 mmol, 58.4 mg, 60 %, dr = 4.3:1 by GC-MS), R_f = 0.19 (hexane:EA = 10:1). **Major diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 3.46 (dd, *J* = 10.4, 6.0 Hz, 2H), 3.22 (dd, *J* = 10.5, 5.4 Hz, 2H), 2.61 – 2.54 (m, 2H), 2.43 (s, 3H), 1.96 – 1.68 (m, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 144.3, 133.5, 130.1, 127.4, 118.8 (qt, J_{C-F} = 285.3, 36.0 Hz), 115.3 (tq, J_{C-F} = 253.6, 38.1 Hz), 51.5 (d, *J* = 3.3 Hz), 34.5, 28.4 (t, J_{C-F} = 21.7 Hz), 21.6 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.91 (s, 6F), -118.58 (dddd, *J* = 296.0, 268.1, 28.5, 7.9 Hz, 4F) ppm. **Minor diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 3.63 (dd, *J* = 10.4, 5.2 Hz, 2H), 2.97 (dd, *J* = 10.5, 7.4 Hz, 2H), 2.44 (s, 3H), 2.18 – 2.07 (m, 2H), 1.96 – 1.68 (m, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.3, 132.6, 130.1, 127.7, 52.4 (d, *J* = 4.0 Hz), 37.2, 32.9 (t, J_{C-F} = 21.9 Hz), 21.7 ppm (CF_2CF_3 peaks cannot be identified in detail). **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.83 (s, 6F), -118.35 (dddd, *J* = 266.3, 37.3, 29.8, 8.0 Hz, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{17}H_{17}F_{10}NO_2SNa$ $[M+Na]^+$: 512.0713; found: 512.0709.



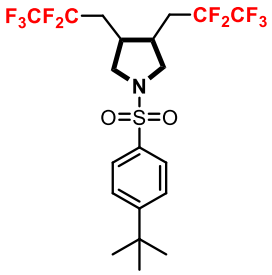
2b: 1-((4-methoxyphenyl)sulfonyl)-3,4-bis(2,2,3,3,3-pentafluoropropyl)pyrrolidine. Prepared according to the general procedure. Reaction was run using **1b** (53.5 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/EA) and obtained as a white solid (0.10 mmol, 52.9 mg, 52 %, dr > 20:1 by GC-MS), R_f = 0.21 (hexane:EA = 4:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.01 (d, *J* = 7.5 Hz, 2H), 3.87 (s, 3H), 3.45 (dd, *J* = 10.2, 5.8 Hz, 2H), 3.22 (dd, *J* = 10.4, 4.6 Hz, 2H), 2.00 – 1.72 (m, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 163.4, 129.5, 128.1, 118.8 (qt, J_{C-F} = 285.5, 35.8 Hz), 115.4 (tq, J_{C-F} = 253.4, 38.2 Hz), 114.6, 55.8, 51.6, 34.5, 28.4 (t, J_{C-F} = 21.7 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.89 (s, 6F), -117.43 – -119.66 (m, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{17}H_{17}F_{10}NO_3SNa$ $[M+Na]^+$: 528.0662; found: 528.0659.



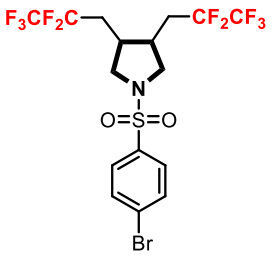
2c: 1-((4-nitrophenyl)sulfonyl)-3,4-bis(2,2,3,3,3-pentafluoropropyl)pyrrolidine. Prepared according to the general procedure. Reaction was run using **1c** (56.5 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/EA) and obtained as a white solid (0.10 mmol, 49.7 mg, 48 %, dr > 20:1 by GC-MS), R_f = 0.47 (hexane:EA = 4:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.40 (d, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 8.8 Hz, 2H), 3.48 (dd, *J* = 10.3, 6.0 Hz, 2H), 3.33 (dd, *J* = 10.4, 5.4 Hz, 2H), 2.68 – 2.61 (m, 2H), 2.08 – 1.95 (m, 2H), 1.91 – 1.78 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 150.5, 142.7, 128.6, 124.8, 118.8 (qt, $J_{C\text{-}F}$ = 285.3, 35.7 Hz), 115.3 (tq, $J_{C\text{-}F}$ = 253.8, 38.2 Hz), 51.5 (d, *J* = 3.6 Hz), 34.7, 28.4 (t, $J_{C\text{-}F}$ = 21.8 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.91 (s, 6F), -118.45 (dddd, *J* = 294.7, 267.0, 28.5, 7.6 Hz, 4F) ppm. **HRMS** m/z (APCI): calcd. for $C_{16}H_{15}F_{10}N_2O_4S$ $[M+H]^+$: 521.0587; found: 521.0589.



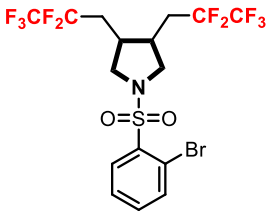
2d: 3,4-bis(2,2,3,3,3-pentafluoropropyl)-1-((4-(trifluoromethyl)phenyl)sulfonyl)pyrrolidine. Prepared according to the general procedure. Reaction was run using **1d** (61.1 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/EA) and obtained as a white solid (0.10 mmol, 54.9 mg, 51 %, dr > 20:1 by GC-MS), R_f = 0.27 (hexane:EA = 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 2H), 3.49 (dd, *J* = 10.2, 5.9 Hz, 2H), 3.29 (dd, *J* = 10.3, 5.1 Hz, 2H), 2.67 – 2.59 (m, 2H), 2.04 – 1.91 (m, 2H), 1.85 – 1.70 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 140.4, 135.0 (q, $J_{C\text{-}F}$ = 33.2 Hz), 127.8, 126.68 (q, $J_{C\text{-}F}$ = 3.4 Hz), 123.27 (q, $J_{C\text{-}F}$ = 272.9 Hz), 118.8 (qt, $J_{C\text{-}F}$ = 285.5, 35.9 Hz), 115.3 (tq, $J_{C\text{-}F}$ = 253.4, 38.2 Hz), 51.46 (d, *J* = 3.5 Hz), 34.6, 28.34 (t, $J_{C\text{-}F}$ = 21.7 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -64.45 (s, 3F), -86.92 (s, 6F), -118.50 (dddd, *J* = 266.8, 35.5, 28.5, 7.4 Hz, 4F) ppm. **HRMS** m/z (APCI): calcd. for $C_{17}H_{15}F_{13}NO_2S$ $[M+H]^+$: 544.0610; found: 544.0608.



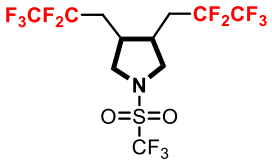
2e: 1-((4-(*tert*-butyl)phenyl)sulfonyl)-3,4-bis(2,2,3,3,3-pentafluoropropyl)pyrrolidine. Prepared according to the general procedure. Reaction was run using **1e** (58.7 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/EA) and obtained as a white solid (0.12 mmol, 62.0 mg, 58 %, dr = 4.8:1 by GC-MS), R_f = 0.26 (hexane:EA = 10:1). **Major diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 3.50 (dd, *J* = 10.2, 5.9 Hz, 2H), 3.23 (dd, *J* = 10.4, 5.2 Hz, 2H), 2.63 – 2.55 (m, 2H), 2.00 – 1.87 (m, 2H), 1.81 – 1.67 (m, 2H), 1.33 (s, 9H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 157.1, 133.5, 127.3, 126.5, 118.8 (qt, J_{C-F} = 285.5, 35.8 Hz), 115.4 (tq, J_{C-F} = 253.4, 38.1 Hz), 51.5 (d, *J* = 3.1 Hz), 35.3, 34.5, 31.1, 28.4 (t, J_{C-F} = 21.7 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.82 (s, 6F), -118.48 (dddd, *J* = 266.7, 35.5, 28.3, 7.7 Hz, 4F) ppm. **Minor diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 3.67 – 3.61 (m, 2H), 3.00 (dd, *J* = 10.1, 7.0 Hz, 2H), 2.17 – 2.11 (m, 2H), 2.19 – 2.06 (m, 2H), 2.00 – 1.87 (m, 2H), 1.34 (s, 9H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 157.2, 133.0, 127.6, 126.4, 52.4 (d, *J* = 3.9 Hz), 37.2, 35.3, 32.9 (t, J_{C-F} = 21.9 Hz), 31.1 ppm (CF_2CF_3 peaks cannot be identified in detail). **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.78 (s, 6F), -118.30 (dddd, *J* = 275.1, 266.2, 29.2, 7.8 Hz, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{20}H_{23}F_{10}NO_2SNa$ $[M+Na]^+$: 554.1182; found: 554.1177.



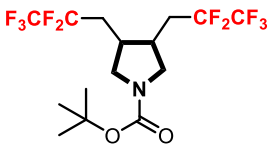
2f: 1-((4-bromophenyl)sulfonyl)-3,4-bis(2,2,3,3,3-pentafluoropropyl)pyrrolidine. Prepared according to the general procedure. Reaction was run using **1f** (63.2 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/EA) and obtained as a white solid (60.8 mg, 0.11 mmol, 55 %, dr > 20:1 by GC-MS), R_f = 0.21 (hexane:EA = 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.70 (s, 4H), 3.45 (dd, *J* = 10.3, 5.9 Hz, 2H), 3.25 (dd, *J* = 10.4, 5.2 Hz, 2H), 2.60 (dt, *J* = 15.6, 7.6 Hz, 2H), 2.05 – 1.90 (m, 2H), 1.89 – 1.74 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 135.7, 132.8, 128.9, 128.4, 118.8 (qt, J_{C-F} = 285.2, 35.5 Hz), 115.3 (tq, J_{C-F} = 253.6, 38.2 Hz), 51.5 (d, *J* = 3.4 Hz), 34.6, 28.4 (t, J_{C-F} = 21.7 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.91 (s, 6F), -118.54 (dddd, *J* = 266.8, 35.7, 28.4, 7.7 Hz, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{16}H_{14}F_{10}NO_2SBrNa$ $[M+Na]^+$: 577.9641; found: 577.9637.



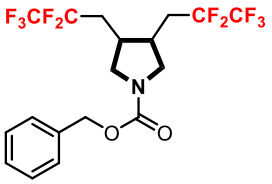
2g: 1-((2-bromophenyl)sulfonyl)-3,4-bis(2,2,3,3,3-pentafluoropropyl)pyrrolidine. Prepared according to the general procedure. Reaction was run using **1g** (63.2 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/EA) and obtained as a white solid (68.8 mg, 0.12 mmol, 62 %, dr = 4.3:1 by GC-MS), R_f = 0.21 (hexane:EA = 10:1). **Major diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.13 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.44 (dt, *J* = 24.7, 7.5 Hz, 2H), 3.65 (dd, *J* = 9.9, 5.9 Hz, 2H), 3.34 (dd, *J* = 10.1, 5.1 Hz, 2H), 2.82 – 2.71 (m, 2H), 2.13 – 2.00 (m, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 138.1, 135.8, 134.1, 132.5, 127.9, 120.5, 119.0 (qt, J_{C-F} = 285.5, 35.8 Hz), 115.4 (tq, J_{C-F} = 253.5, 38.0 Hz), 51.2 (d, *J* = 3.3 Hz), 34.9, 28.4 (t, J_{C-F} = 21.8 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.89 (s, 6F), -118.50 (dddd, *J* = 266.8, 38.2, 21.8, 14.2 Hz, 4F) ppm. **Minor diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.13 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.44 (dt, *J* = 24.7, 7.5 Hz, 2H), 3.89 – 3.83 (m, 2H), 3.20 – 3.13 (m, 2H), 2.34 – 2.26 (m, 2H), 2.33 – 2.16 (m, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 138.0, 135.8, 134.1, 132.5, 127.9, 120.5, 52.2 (d, *J* = 4.2 Hz), 37.5, 32.6 (t, J_{C-F} = 22.0 Hz) ppm (CF_2CF_3 peaks cannot be identified in detail). **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.79 (s, 6F), -116.93 – -119.55 (m, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{16}H_{14}F_{10}NO_2SBrNa$ $[M+Na]^+$: 577.9641; found: 577.9634.



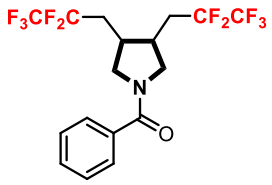
2h: 3,4-bis(2,2,3,3,3-pentafluoropropyl)-1-((trifluoromethyl)sulfonyl)pyrrolidine. Prepared according to the general procedure. Reaction was run using **1h** (91.7 mg, 0.4 mmol) and [$CuCF_2CF_3$] (2.0 mL, 1.8 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/EA) and obtained as a yellowish liquid (71.1 mg, 0.15 mmol, 38 %, dr = 4.0:1 by GC-MS), R_f = 0.09 (hexane:EA = 40:1). **Major diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.77 (dd, *J* = 10.1, 5.9 Hz, 2H), 3.50 (dd, *J* = 10.4, 5.3 Hz, 2H), 2.92 – 2.81 (m, 2H), 2.21 – 1.97 (m, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 120.3 (q, J_{C-F} = 323.0 Hz), 118.8 (qt, J_{C-F} = 285.2, 35.7 Hz), 115.3 (tq, J_{C-F} = 253.8, 38.2 Hz), 52.2 (d, J_{C-F} = 3.8 Hz), 34.9, 28.3 (t, J_{C-F} = 21.9 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -76.25 (s, 3F), -86.85 (s, 6F), -118.42 (dddd, *J* = 274.7, 268.1, 27.7, 7.9 Hz, 4F) ppm. **Minor diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.98 (t, *J* = 7.8 Hz, 2H), 3.30 (t, *J* = 9.2 Hz, 2H), 2.40 – 2.33 (m, 2H), 2.20 – 1.97 (m, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 52.9 (d, J_{C-F} = 4.8 Hz), 37.6, 32.3 (t, J_{C-F} = 22.1 Hz) ppm (CF_3, CF_2CF_3 peaks cannot be identified in detail). **^{19}F NMR** (471 MHz, $CDCl_3$): δ -76.18 (s, 3F), -86.73 (s, 6F) -116.70 – -119.63 (m, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{11}H_9F_{13}NO_2S$ $[M-H]^-$: 466.0152; found: 466.0153.



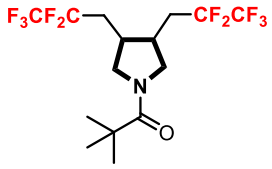
2i: *tert*-butyl 3,4-bis(2,2,3,3,3-pentafluoropropyl)pyrrolidine-1-carboxylate. Prepared according to the general procedure. Reaction was run using **1i** (39.5 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/EA) and obtained as a colorless liquid (67.2 mg, 0.15 mmol, 77 %, dr = 2.0:1 by GC-MS), R_f = 0.31 (hexane:EA = 10:1). **Major diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.54 (ddd, *J* = 35.8, 10.9, 5.8 Hz, 2H), 3.33 – 3.22 (m, 2H), 2.72 – 2.63 (m, 2H), 2.30 – 1.90 (m, 4H), 1.45 (s, 9H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 154.6, 118.98 (qt, $J_{C\text{-}F}$ = 285.4, 35.9 Hz), 115.6 (tqd , $J_{C\text{-}F}$ = 253.4, 37.9, 11.4 Hz), 80.2, 49.9 (d, *J* = 58.6 Hz), 34.17 (d, *J* = 82.5 Hz), 28.8 (t, $J_{C\text{-}F}$ = 21.6 Hz), 28.5 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.68 (d, *J* = 30.1 Hz, 6F), -116.61 – -119.56 (m, 4F) ppm. **Minor diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.82 (d, *J* = 51.9 Hz, 2H), 3.06 (d, *J* = 7.9 Hz, 2H), 2.30 – 1.90 (m, 6H), 1.45 (s, 9H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.0, 80.1, 50.8 (d, *J* = 33.5 Hz), 36.9 (d, *J* = 98.4 Hz), 32.6 (t, $J_{C\text{-}F}$ = 22.0 Hz), 28.6 ppm (CF_2CF_3 peaks cannot be identified in detail). **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.60 (d, *J* = 11.4 Hz, 6F), -116.61 – -119.56 (m, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{15}H_{19}F_{10}NO_2Na$ $[M+Na]^+$: 458.1148; found: 458.1146.



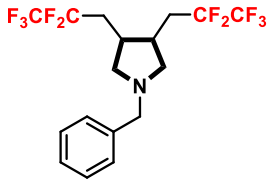
2j: benzyl 3,4-bis(2,2,3,3,3-pentafluoropropyl)pyrrolidine-1-carboxylate. Prepared according to the general procedure. Reaction was run using **1j** (46.3 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/EA) and obtained as a colorless liquid (74.5 mg, 0.16 mmol, 79 %, dr = 2.1:1 by GC-MS), R_f = 0.22 (hexane:EA = 10:1). **Major diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.43 – 7.29 (m, 5H), 5.15 (p, *J* = 12.3 Hz, 2H), 3.64 (ddd, *J* = 20.4, 11.2, 6.2 Hz, 2H), 3.38 (dd, *J* = 11.0, 4.8 Hz, 2H), 2.79 – 2.65 (m, 2H), 2.36 – 1.90 (m, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 154.9, 136.6, 128.6, 128.1, 118.9 (qt, $J_{C\text{-}F}$ = 286.2, 36.3 Hz), 115.5 (tqd, $J_{C\text{-}F}$ = 251.2, 36.2, 7.3 Hz), 67.2, 50.0 (d, *J* = 35.9 Hz), 34.2 (d, *J* = 91.4 Hz), 28.6 (td, $J_{C\text{-}F}$ = 21.7, 13.6 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.67 (d, *J* = 20.5 Hz, 6F), -116.55 – -119.52 (m, 4F) ppm. **Minor diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.43 – 7.29 (m, 5H), 5.22 – 5.08 (m, 2H), 3.99 – 3.86 (m, 2H), 3.15 (t, *J* = 9.9 Hz, 2H), 2.36 – 1.90 (m, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 154.4, 136.7, 128.2, 128.2, 67.2, 50.9 (d, *J* = 48.3 Hz), 36.9 (d, *J* = 102.8 Hz), 32.5 (t, $J_{C\text{-}F}$ = 22.1 Hz) ppm (CF_2CF_3 peaks cannot be identified in detail). **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.60 (d, *J* = 11.9 Hz, 6F), -116.55 – -119.52 (m, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{18}H_{17}F_{10}NO_2Na$ $[M+Na]^+$: 492.0992; found: 492.0982.



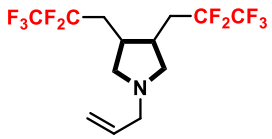
2k: 3,4-bis(2,2,3,3,3-pentafluoropropyl)pyrrolidin-1-yl)(phenyl)methanone. Prepared according to the general procedure. Reaction was run using **1k** (40.3 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/EA) and obtained as a yellowish liquid (59.8 mg, 0.14 mmol, 68 %, dr = 2.6:1 by GC-MS), R_f = 0.13 (hexane:EA = 5:1). **Major diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.52 – 7.38 (m, 5H), 3.86 (dd, *J* = 12.6, 7.2 Hz, 1H), 3.66 (dd, *J* = 11.2, 5.8 Hz, 1H), 3.57 (dd, *J* = 12.6, 7.4 Hz, 1H), 3.47 (dd, *J* = 11.2, 4.7 Hz, 1H), 2.88 – 2.79 (m, 1H), 2.75 – 2.67 (m, 1H), 2.37 – 1.84 (m, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 170.4, 135.9, 130.6, 128.6, 127.2, 118.9 (qtd, J_{C-F} = 285.2, 35.8, 15.2 Hz), 115.5 (tq, J_{C-F} = 253.4, 38.4 Hz), 51.7 (dd, *J* = 419.8, 2.5 Hz), 34.2 (d, *J* = 193.8 Hz), 28.5 (dt, J_{C-F} = 139.3, 21.6 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.83 (d, *J* = 59.6 Hz, 6F), -116.61 – -119.79 (m, 4F) ppm. **Minor diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.52 – 7.38 (m, 5H), 4.11 (td, *J* = 11.2, 4.2 Hz, 1H), 3.86 – 3.79 (m, 1H), 3.46 – 3.40 (m, 1H), 3.30 (t, *J* = 10.1 Hz, 1H), 2.37 – 1.84 (m, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 169.7, 135.9, 130.6, 128.6, 127.3, 52.7 (dd, *J* = 372.5, 2.0 Hz), 36.9 (d, *J* = 208.7 Hz), 32.4 (dt, J_{C-F} = 74.5, 22.0 Hz) ppm (CF_2CF_3 peaks cannot be identified in detail). **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.75 (d, *J* = 33.6 Hz, 6F), -116.61 – -119.79 (m, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{17}H_{15}F_{10}NONa$ $[M+Na]^+$: 462.0886; found: 462.0882.



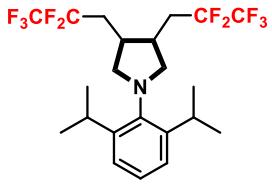
2l: 3,4-bis(2,2,3,3,3-pentafluoropropyl)pyrrolidin-1-yl)-2,2-dimethylpropan-1-one. Prepared according to the general procedure. Reaction was run using **1l** (36.3 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/EA) and obtained as a colorless liquid (38.4 mg, 0.09 mmol, 46 %, dr > 20:1 by GC-MS), R_f = 0.30 (hexane:EA = 4:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.72 (dd, *J* = 11.3, 6.4 Hz, 2H), 3.31 (br, 1H), 2.71 (s, 2H), 2.27 – 1.65 (m, 5H), 1.24 (s, 9H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 177.3, 118.9 (qt, J_{C-F} = 285.4, 35.8 Hz), 115.6 (tq, J_{C-F} = 289.8, 37.7 Hz), 51.7, 39.0, 33.9 (d, *J* = 398.4 Hz), 27.4 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -85.72 (s, 6F), -116.99 (dt, *J* = 507.2, 281.0 Hz, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{15}H_{19}F_{10}NONa$ $[M+Na]^+$: 442.1199; found: 442.1191.



2m: 1-benzyl-3,4-bis(2,2,3,3,3-pentafluoropropyl)pyrrolidine. Prepared according to the general procedure. Reaction was run using **1m** (37.5 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/EA) and obtained as a yellowish liquid (45.9 mg, 0.11 mmol, 54 %, dr = 2.1:1 by GC-MS), R_f = 0.37 (hexane:EA = 10:1). **Major diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.37 – 7.27 (m, 5H), 3.70 (s, 2H), 2.98 (t, *J* = 7.6 Hz, 2H), 2.78 – 2.68 (m, 2H), 2.52 – 2.45 (m, 2H), 2.30 – 1.97 (m, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 138.3, 128.8, 128.6, 127.4, 119.1 (qt, J_{C-F} = 288.3, 37.3 Hz), 115.8 (tq, J_{C-F} = 254.2, 38.4 Hz), 60.0, 58.6, 33.4, 30.3 (t, J_{C-F} = 21.3 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.92 (s, 6F), -118.60 (dddd, *J* = 266.1, 37.0, 23.0, 14.4 Hz, 4F) ppm. **Minor diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.37 – 7.27 (m, 5H), 3.63 (d, *J* = 3.6 Hz, 2H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.42 (dd, *J* = 8.9, 4.3 Hz, 2H), 2.30 – 1.97 (m, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 138.0, 129.0, 128.9, 127.5, 59.8, 59.5, 37.4, 34.8 (t, J_{C-F} = 21.7 Hz) ppm (CF_2CF_3 peaks cannot be identified in detail). **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.90 (s, 6F), -117.58 – -119.62 (m, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{17}H_{18}F_{10}N$ $[M+H]^+$: 426.1274; found: 426.1263.

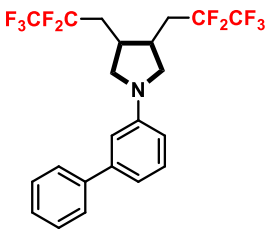


2n: 1-allyl-3,4-bis(2,2,3,3,3-pentafluoropropyl)pyrrolidine. Prepared according to the general procedure. Reaction was run using **1n** (54.9 mg, 0.4 mmol) and [$CuCF_2CF_3$] (2.0 mL, 1.8 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/EA) and obtained as a colorless liquid (25.9 mg, 0.07 mmol, 17 %, dr > 20:1 by GC-MS), R_f = 0.13 (hexane:EA = 10:1). **Major diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.86 (ddt, *J* = 16.8, 10.2, 6.4 Hz, 1H), 5.17 (dd, *J* = 37.0, 13.6 Hz, 2H), 3.14 (d, *J* = 6.4 Hz, 2H), 2.97 (dd, *J* = 8.4, 6.8 Hz, 2H), 2.77 – 2.63 (m, 2H), 2.41 (dd, *J* = 9.3, 5.8 Hz, 2H), 2.17 – 1.94 (m, 4H) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.93 (s, 6F), -118.65 (dddd, *J* = 266.0, 36.8, 27.2, 10.1 Hz, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{13}H_{16}F_{10}N$ $[M+H]^+$: 376.1118; found: 376.1107.

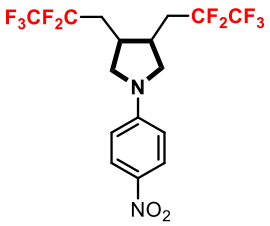


2o: 1-(2,6-diisopropylphenyl)-3,4-bis(2,2,3,3,3-pentafluoropropyl)pyrrolidine. Prepared according to the general procedure. Reaction was run using **1o** (51.5 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane) and obtained as a yellowish liquid (83.3 mg, 0.17 mmol, 84 %, dr = 3.4:1 by GC-MS), R_f = 0.52 (hexane). **Major diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.24 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 2H), 3.51 (dd, *J* = 8.5, 6.1 Hz, 2H), 3.44 – 3.33 (m, 1H), 3.28 – 3.13 (m, 3H), 2.98 – 2.87 (m, 2H), 2.42 – 2.13 (m, 4H), 1.26 (ddd, *J* = 20.1, 14.9, 6.0 Hz, 12H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 149.7, 140.9, 127.2, 123.7, 119.2 (qt, J_{C-F} = 285.2, 36.1 Hz), 116.0 (tq, J_{C-F} = 252.8, 37.7 Hz), 57.2 (d, *J* = 2.9 Hz), 35.7, 29.3 (t, J_{C-F} = 21.6 Hz), 28.4, 24.5 (d, *J* = 33.7 Hz) ppm. **^{19}F NMR**

(471 MHz, $CDCl_3$): δ -86.89 (s, 6F), -118.47 (dddd, *J* = 276.7, 266.3, 28.3, 9.0 Hz, 4F) ppm. **Minor diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.27 – 7.21 (m, 1H), 7.18 – 7.12 (m, 2H), 3.59 (d, *J* = 6.8 Hz, 2H), 3.29 – 3.15 (m, 1H), 3.09 – 2.99 (m, 3H), 2.54 – 2.44 (m, 2H), 2.42 – 2.13 (m, 4H), 1.43 – 1.17 (m, 12H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 150.2, 127.3, 125.0, 124.4, 58.7, 38.5, 33.6 (t, $J_{C\text{-}F}$ = 21.8 Hz), 28.3, 24.6 (d, *J* = 66.1 Hz) ppm (CF_2CF_3 peaks cannot be identified in detail). **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.73 (s, 6F), -117.09 – -119.45 (m, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{22}H_{28}F_{10}N$ $[M+H]^+$: 496.2057; found: 496.2050.

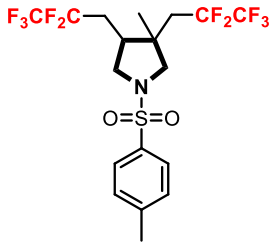


2p: 1-([1,1'-biphenyl]-3-yl)-3,4-bis(2,2,3,3,3-pentafluoropropyl)pyrrolidine. Prepared according to the general procedure. Reaction was run using **1p** (50.0 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/EA) and obtained as a yellowish solid (61.7 mg, 0.13 mmol, 63 %, dr = 2.1:1 by GC-MS), R_f = 0.17 (hexane). **Major diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.41 – 7.33 (m, 2H), 7.00 (d, *J* = 7.1 Hz, 1H), 6.78 (s, 1H), 6.64 – 6.58 (m, 1H), 3.59 (dd, *J* = 9.3, 6.0 Hz, 2H), 3.40 (dd, *J* = 9.5, 4.8 Hz, 2H), 2.94 – 2.82 (m, 2H), 2.49 – 2.08 (m, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 147.6, 142.8, 142.0, 129.8, 128.8, 127.5, 119.1 (qt, $J_{C\text{-}F}$ = 285.2, 35.9 Hz), 115.8 (tq, $J_{C\text{-}F}$ = 253.2, 37.8 Hz), 116.1, 110.9, 110.7, 52.1 (d, *J* = 2.7 Hz), 34.5, 29.2 (t, $J_{C\text{-}F}$ = 21.7 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.80 (s, 6F), -118.37 (dddd, *J* = 276.4, 267.0, 25.8, 11.4 Hz, 4F) ppm. **Minor diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.66 – 7.58 (m, 2H), 7.49 – 7.43 (m, 2H), 7.41 – 7.33 (m, 2H), 7.03 – 6.97 (m, 1H), 6.80 (s, 1H), 6.64 – 6.58 (m, 1H), 3.85 – 3.76 (m, 2H), 3.25 – 3.18 (m, 2H), 2.49 – 2.08 (m, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 147.2, 142.7, 142.0, 129.8, 128.8, 127.4, 116.3, 111.1, 110.9, 53.2, 37.2, 33.17 (t, $J_{C\text{-}F}$ = 21.9 Hz) ppm (CF_2CF_3 peaks cannot be identified in detail). **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.73 (s, 6F), -116.87 – -119.49 (m, 4F) ppm. **HRMS** m/z (APCI): calcd. for $C_{22}H_{20}F_{10}N$ $[M+H]^+$: 488.1431; found: 488.1430.

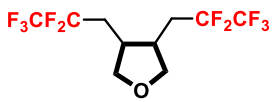


2q: 1-(4-nitrophenyl)-3,4-bis(2,2,3,3,3-pentafluoropropyl)pyrrolidine. Prepared according to the general procedure. Reaction was run using **1q** (43.7 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/EA) and obtained as two yellowish liquids (major diastereomer: 39.5 mg; minor diastereomer: 28.9 mg. total 68.4 mg, 0.15 mmol, 75 %, dr = 1.4:1 by isolation), R_f = 0.21, 0.24 (hexane:EA = 10:1). **Major diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.10 (d,

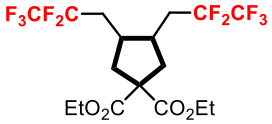
J = 9.1 Hz, 2H), 6.49 (d, J = 9.1 Hz, 2H), 3.64 (dd, J = 10.1, 5.9 Hz, 2H), 3.41 (dd, J = 10.3, 5.0 Hz, 2H), 2.98 – 2.89 (m, 2H), 2.27 – 2.02 (m, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 151.5, 137.9, 126.4, 118.9 (qt, $J_{C\text{-}F}$ = 285.4, 35.3 Hz), 115.6 (tq, $J_{C\text{-}F}$ = 253.2, 38.0 Hz), 110.8, 52.0 (d, J = 3.3 Hz), 34.4, 29.0 (t, $J_{C\text{-}F}$ = 21.7 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.81 (s, 6F), -118.32 (dddd, J = 266.9, 35.8, 28.0, 8.3 Hz, 4F) ppm. **Minor diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.11 (d, J = 9.2 Hz, 2H), 6.50 (d, J = 9.3 Hz, 2H), 3.88 – 3.81 (m, 2H), 3.26 – 3.20 (m, 2H), 2.49 – 2.31 (m, 4H), 2.22 – 2.08 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 150.9, 137.8, 126.4, 118.9 (qt, $J_{C\text{-}F}$ = 285.5, 35.7 Hz), 115.4 (tq, $J_{C\text{-}F}$ = 253.1, 38.2 Hz), 110.7, 52.9 (d, J = 4.2 Hz), 37.1, 32.7 (t, $J_{C\text{-}F}$ = 22.1 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.71 (s, 6F), -118.15 (dddd, J = 274.8, 266.1, 29.8, 7.1 Hz, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{16}H_{14}F_{10}N_2O_2Na$ $[M+Na]^+$: 479.0788; found: 479.0776.



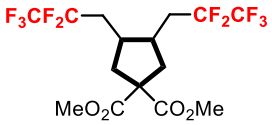
2r: 3-methyl-3,4-bis(2,2,3,3,3-pentafluoropropyl)-1-tosylpyrrolidine. Prepared according to the general procedure. Reaction was run using **1r** (53.1 mg, 0.2 mmol) and $[CuCF_2CF_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/EA) and obtained as a yellowish solid (83.0 mg, 0.16 mmol, 82 %, dr = 1.9:1 by GC-MS), R_f = 0.51 (hexane:EA = 4:1). **Major diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.70 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 7.9 Hz, 2H), 3.63 (d, J = 10.3 Hz, 2H), 3.02 (dd, J = 96.4, 9.8 Hz, 2H), 2.42 (s, 3H), 2.14 – 1.64 (m, 5H), 1.19 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 144.1, 133.7, 130.0, 127.4, 123.04 – 112.71 (m, CF_2CF_3 peaks), 57.3 (d, J = 5.9 Hz), 50.9 (d, J = 4.5 Hz), 42.7, 42.2, 31.1 (t, $J_{C\text{-}F}$ = 20.2 Hz), 28.8 (t, $J_{C\text{-}F}$ = 21.9 Hz), 21.9 (d, J = 3.5 Hz), 21.6 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.81 (s, 3F), -87.72 (s, 3F), -114.89 (ddd, J = 264.8, 34.2, 3.5 Hz, 1F), -117.07 (ddd, J = 265.6, 31.1, 5.5 Hz, 1F), -118.12 (ddd, J = 264.8, 32.2, 4.9 Hz, 1F), -120.01 (ddd, J = 265.3, 27.8, 8.2 Hz, 1F) ppm. **Minor diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.71 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 3.69 – 3.45 (m, 2H), 3.15 – 2.99 (m, 2H), 2.43 (s, 3H), 2.14 – 1.64 (m, 5H), 0.89 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 144.1, 133.7, 130.0, 127.5, 122.59 – 112.61 (m, CF_2CF_3 peaks), 58.9 (d, J = 6.4 Hz), 50.2 (d, J = 4.7 Hz), 41.7, 40.8, 37.4 (t, $J_{C\text{-}F}$ = 20.9 Hz), 29.0 (t, J = 22.0 Hz), 21.6, 18.1 (d, J = 3.9 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.77 (s, 3F), -87.56 (s, 3F), -114.62 (ddd, J = 264.9, 35.7, 6.0 Hz, 1F), -116.62 – -117.30 (m, 1F), -118.43 (dd, J = 264.8, 33.8 Hz, 1F), -119.90 (ddd, J = 265.4, 28.6, 8.3 Hz, 1F) ppm. **HRMS** m/z (ESI): calcd. for $C_{18}H_{19}F_{10}NO_2SNa$ $[M+Na]^+$: 526.0869; found: 526.0857.



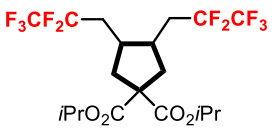
2s: 3,4-bis(2,2,3,3,3-pentafluoropropyl)tetrahydrofuran. Prepared according to the general procedure. Reaction was run using **1s** (19.6 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The crude product was analyzed by ^{19}F NMR (79 %) using $PhCF_3$ as the internal standard and GC-MS (dr = 4.2:1). **Major diastereomer**: **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.85 (s, 6F), -118.29 (dddd, *J* = 265.4, 37.1, 29.1, 8.5 Hz, 4F) ppm. **Minor diastereomer**: **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.82 (s, 6F), -118.19 (dddd, *J* = 274.9, 265.7, 30.0, 8.3 Hz, 4F) ppm.



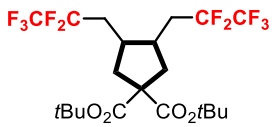
4a: diethyl 3,4-bis(2,2,3,3,3-pentafluoropropyl)cyclopentane-1,1-dicarboxylate. Prepared according to the general procedure. Reaction was run using **3a** (48.1 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/DCM) and obtained as a yellowish liquid (75.7 mg, 0.16 mmol, 79 %, dr = 11:1 by GC-MS), R_f = 0.65 (hexane:DCM = 1:1 twice). **Major diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.19 (qn, J = 10.1 Hz, 4H), 2.55 – 2.52 (m, 4H), 2.26 – 2.23 (m, 2H), 2.05 – 1.97 (m, 4H), 1.24 (td, *J* = 7.1, 3.7 Hz, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 172.3 (d, *J* = 68.6 Hz), 119.1 (qt, $J_{C\text{-}F}$ = 273.3, 36.2 Hz), 115.8 (tq, $J_{C\text{-}F}$ = 252.3, 37.7 Hz), 62.1 (d, *J* = 13.6 Hz), 58.2, 38.8 (d, *J* = 2.2 Hz), 35.4, 29.6 (t, $J_{C\text{-}F}$ = 21.6 Hz), 14.1(d, *J* = 7.8 Hz) ppm. **^{19}F NMR** (377 MHz, $CDCl_3$): δ -86.94 (s, 6F), -118.35 (dddd, *J* = 279.6, 266.6, 23.4, 14.4 Hz, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{17}H_{20}F_{10}O_4Na$ $[M+Na]^+$: 501.1094; found: 501.1091.



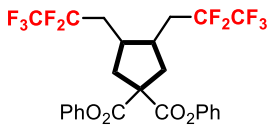
4b: dimethyl 3,4-bis(2,2,3,3,3-pentafluoropropyl)cyclopentane-1,1-dicarboxylate. Prepared according to the general procedure. Reaction was run using **3b** (42.5 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/DCM) and obtained as a yellowish liquid (72.0 mg, 0.16 mmol, 80 %, dr = 10:1 by GC-MS), R_f = 0.63 (hexane:DCM = 1:1 twice). **Major diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.74 (d, *J* = 6.2 Hz, 6H), 2.56 – 2.53 (m, 4H), 2.28 – 2.25 (m, 2H), 2.05 – 1.97 (m, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 172.7 (d, *J* = 68.2 Hz), 119.1 (qt, $J_{C\text{-}F}$ = 285.2, 35.8 Hz), 115.8 (tq, $J_{C\text{-}F}$ = 252.3, 37.7 Hz), 58.1, 53.2 (d, *J* = 1.4 Hz), 38.9 (d, *J* = 2.2 Hz), 35.4, 29.6 (t, $J_{C\text{-}F}$ = 21.6 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.97 (s, 6F), -117.13 – -119.64 (m, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{15}H_{16}F_{10}O_4Na$ $[M+Na]^+$: 473.0778; found: 473.0779.



4c: diisopropyl 3,4-bis(2,2,3,3,3-pentafluoropropyl)cyclopentane-1,1-dicarboxylate. Prepared according to the general procedure. Reaction was run using **3c** (53.7 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/DCM) and obtained as a yellowish liquid (64.9 mg, 0.13 mmol, 64 %, dr = 11:1 by GC-MS), R_f = 0.38 (hexane:DCM = 2:1). **Major diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.03 (dq, *J* = 12.3, 6.2 Hz, 2H), 2.59 – 2.46 (m, 4H), 2.22 (dd, *J* = 13.8, 6.0 Hz, 2H), 2.08 – 1.93 (m, 4H), 1.21 (dd, *J* = 6.3, 4.1 Hz, 12H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 171.9 (d, *J* = 69.1 Hz), 119.1 (qt, $J_{C\text{-}F}$ = 285.5, 36.2 Hz), 115.9 (tq, $J_{C\text{-}F}$ = 253.2, 37.6 Hz), 69.5 (d, *J* = 24.8 Hz), 58.3, 38.7 (d, *J* = 2.1 Hz), 35.4, 29.6 (t, $J_{C\text{-}F}$ = 21.5 Hz), 21.5 (d, *J* = 6.8 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.92 (s, 6F), -118.31 (dddd, *J* = 280.5, 266.4, 24.5, 13.2 Hz, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{19}H_{24}F_{10}O_4Na$ $[M+Na]^+$: 529.1407; found: 529.1401.

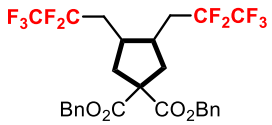


4d: di-*tert*-butyl 3,4-bis(2,2,3,3,3-pentafluoropropyl)cyclopentane-1,1-dicarboxylate. Prepared according to the general procedure. Reaction was run using **3d** (59.3 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/DCM) and obtained as a yellowish solid (67.0 mg, 0.13 mmol, 63 %, dr = 11:1 by GC-MS), R_f = 0.48 (hexane:DCM = 2:1). **Major diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.56 – 2.48 (m, 2H), 2.42 (dd, *J* = 14.1, 6.4 Hz, 2H), 2.16 (dd, *J* = 14.2, 6.3 Hz, 2H), 2.05 – 1.91 (m, 4H), 1.44 (d, *J* = 4.5 Hz, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 171.5 (d, *J* = 60.7 Hz), 119.1 (qt, $J_{C\text{-}F}$ = 285.4, 36.2 Hz), 115.9 (tq, $J_{C\text{-}F}$ = 253.1, 37.6 Hz), 81.9 (d, *J* = 19.0 Hz), 59.6, 38.6 (d, *J* = 2.1 Hz), 35.4, 29.6 (t, $J_{C\text{-}F}$ = 21.5 Hz), 27.9 (d, *J* = 12.4 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.94 (s, 6F), -118.32 (dddd, *J* = 279.4, 266.2, 23.6, 14.0 Hz, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{21}H_{28}F_{10}O_4Na$ $[M+Na]^+$: 557.1720; found: 557.1712.

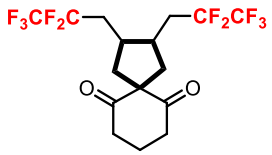


4e: diphenyl 3,4-bis(2,2,3,3,3-pentafluoropropyl)cyclopentane-1,1-dicarboxylate. Prepared according to the general procedure. Reaction was run using **3e** (67.3 mg, 0.2 mmol) and [$CuCF_2CF_3$] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/DCM) and obtained as a yellowish liquid (59.6 mg, 0.10 mmol, 52 %, dr = 11:1 by GC-MS), R_f = 0.61 (hexane:DCM = 1:1). **Major diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.42 (t, *J* = 7.7 Hz, 4H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.16 – 7.09 (m, 4H), 2.85 (dd, *J* = 14.2, 6.4 Hz, 2H), 2.79 – 2.70 (m, 2H), 2.57 (dd, *J* = 14.3, 6.4 Hz, 2H), 2.18 – 2.06 (m, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 170.7 (d, *J* = 86.8 Hz), 150.6 (d, *J* = 1.9 Hz), 129.9 (d, *J* = 3.8 Hz), 126.6 (d, *J* = 6.5 Hz), 121.1 (d, *J* = 2.8 Hz), 119.1 (qt, $J_{C\text{-}F}$ = 285.5, 35.8 Hz), 115.8 (tq, $J_{C\text{-}F}$ = 253.3, 37.7 Hz), 58.4, 38.9 (d, *J* = 2.1 Hz), 35.7, 29.6 (t, $J_{C\text{-}F}$ = 21.5 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.83 (s, 6F), -118.12

(dddd, J = 280.0, 266.7, 23.8, 13.8 Hz, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{25}H_{20}F_{10}O_4Na$ $[M+Na]^+$: 597.1094; found: 597.1092.



4f: dibenzyl 3,4-bis(2,2,3,3,3-pentafluoropropyl)cyclopentane-1,1-dicarboxylate. Prepared according to the general procedure. Reaction was run using **3f** (72.9 mg, 0.2 mmol) and $[CuCF_2CF_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/DCM) and obtained as a yellowish liquid (66.1 mg, 0.11 mmol, 55 %, dr = 12:1 by GC-MS), R_f = 0.53 (hexane:DCM = 1:1). **Major diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.31 – 7.27 (m, 6H), 7.23 – 7.18 (m, 4H), 5.09 (d, J = 6.0 Hz, 4H), 2.59 – 2.48 (m, 4H), 2.24 (dd, J = 16.3, 8.7 Hz, 2H), 2.03 – 1.88 (m, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 171.9 (d, J = 67.7 Hz), 135.2 (d, J = 14.7 Hz), 128.7 (d, J = 1.5 Hz), 128.6, 128.3 (d, J = 11.4 Hz), 119.1 (qt, $J_{C\text{-}F}$ = 285.2, 36.0 Hz), 115.8 (tq, $J_{C\text{-}F}$ = 253.3, 37.4 Hz), 67.8 (d, J = 14.9 Hz), 58.4, 38.9, 35.4, 29.6 (t, $J_{C\text{-}F}$ = 21.4 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.90 (s, 6F), -117.00 – -119.66 (m, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{27}H_{24}F_{10}O_4Na$ $[M+Na]^+$: 625.1407; found: 625.1403.



4g: 2,3-bis(2,2,3,3,3-pentafluoropropyl)spiro[4.5]decane-6,10-dione. Prepared according to the general procedure. Reaction was run using **3g** (38.5 mg, 0.2 mmol) and $[CuCF_2CF_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (hexane/EA) and obtained as a white solid (60.1 mg, 0.14 mmol, 70 %, dr > 20:1 by GC-MS), R_f = 0.60 (hexane:EA = 2:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.69 (dd, J = 14.1, 7.2 Hz, 4H), 2.60 – 2.52 (m, 2H), 2.29 (dd, J = 13.6, 6.1 Hz, 2H), 2.16 (dd, J = 13.7, 6.2 Hz, 2H), 2.10 – 1.92 (m, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ 207.9 (d, J = 131.3 Hz), 119.0 (qt, $J_{C\text{-}F}$ = 285.4, 36.1 Hz), 115.9 (tq, $J_{C\text{-}F}$ = 252.8, 37.7 Hz), 70.2, 37.9, 37.6, 36.8 (d, J = 2.2 Hz), 36.0, 29.3 (t, $J_{C\text{-}F}$ = 21.5 Hz), 17.5 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -86.93 (s, 6F), -118.21 (dddd, J = 276.6, 266.2, 28.5, 8.6 Hz, 4F) ppm. **HRMS** m/z (ESI): calcd. for $C_{16}H_{15}F_{10}O_2$ $[M-H]^-$: 429.0918; found: 429.0919.

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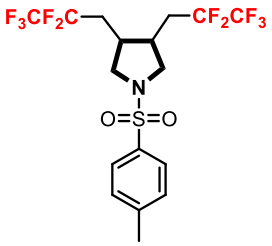
GC Spectra



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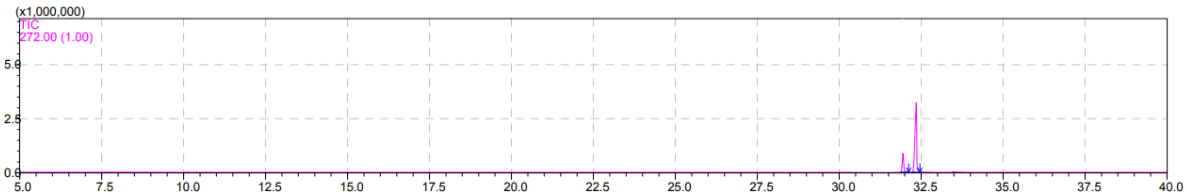

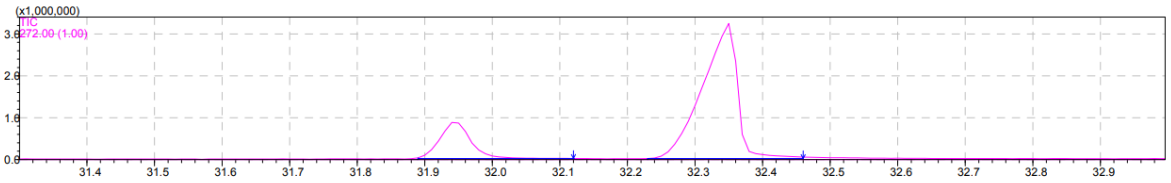

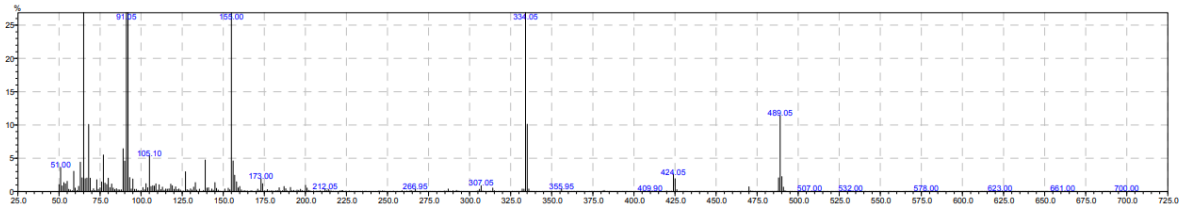

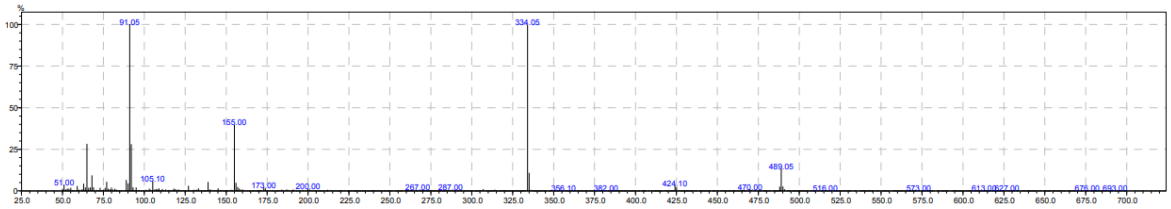

Peak Report TIC

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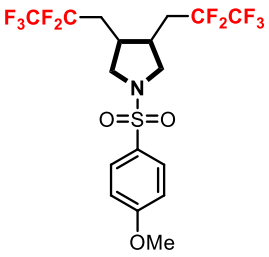

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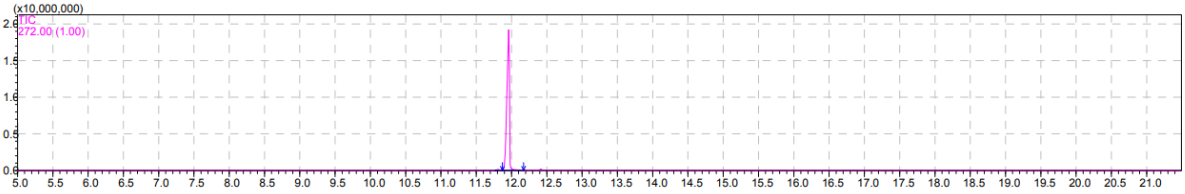

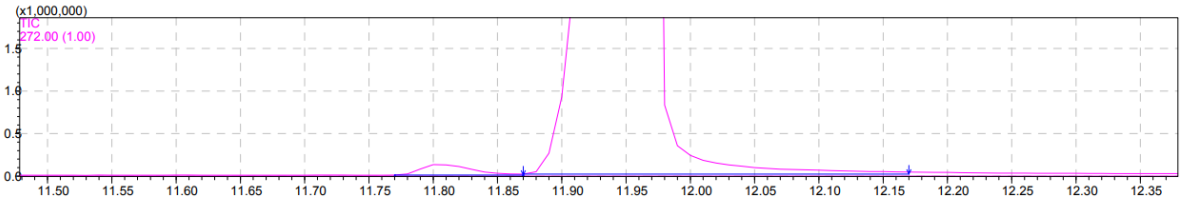

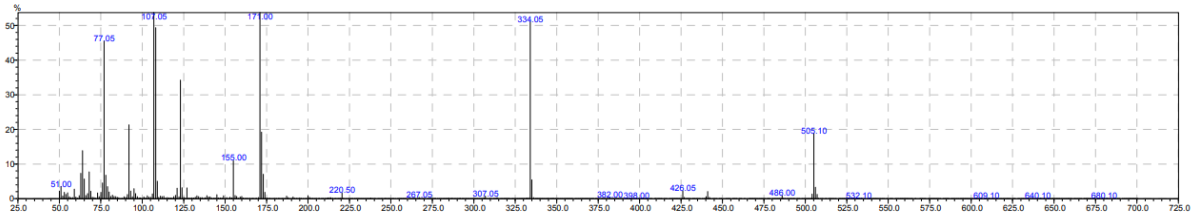

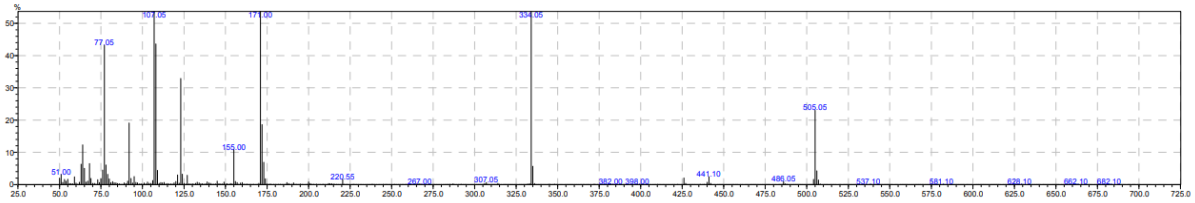

Peak Report TIC

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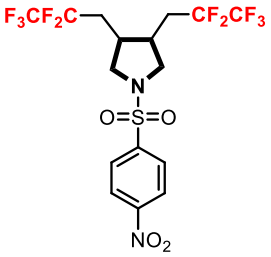

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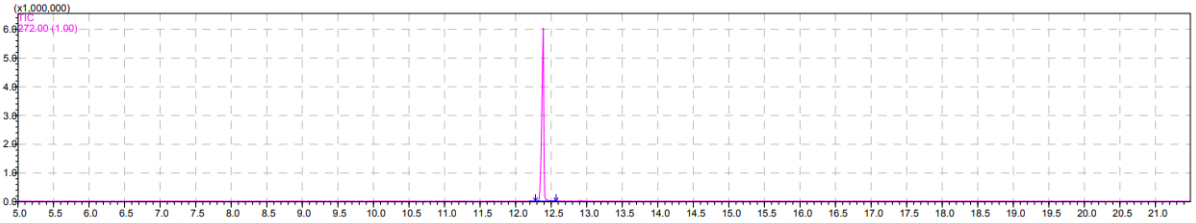

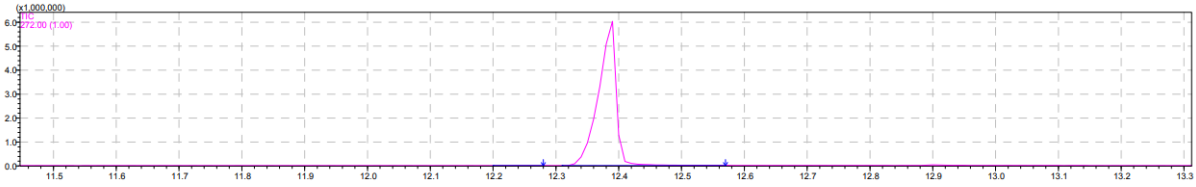

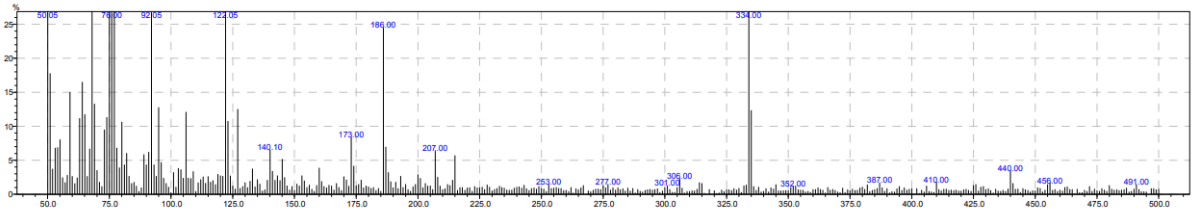

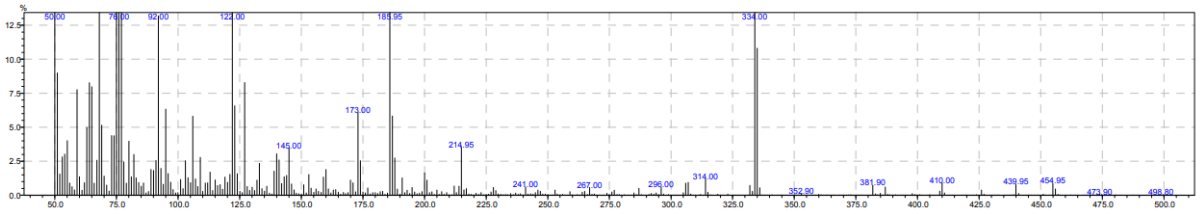

Peak Report TIC

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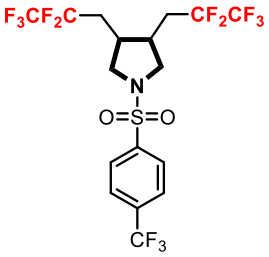
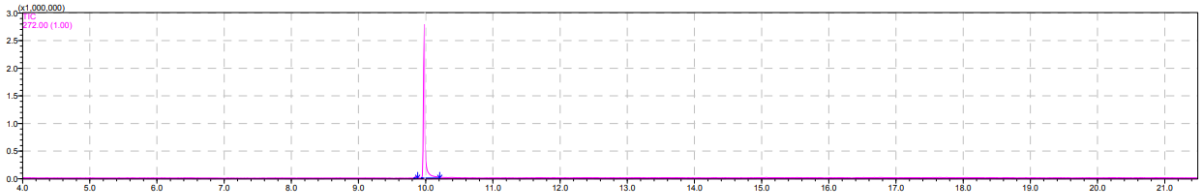
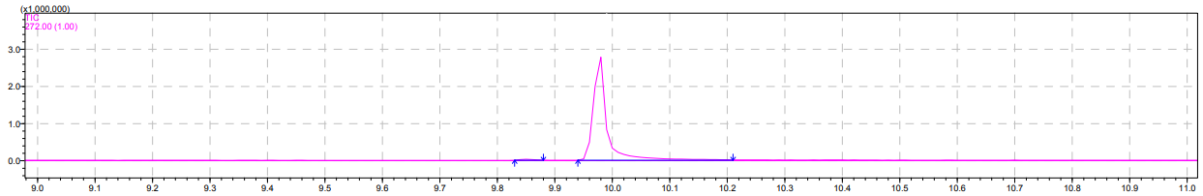
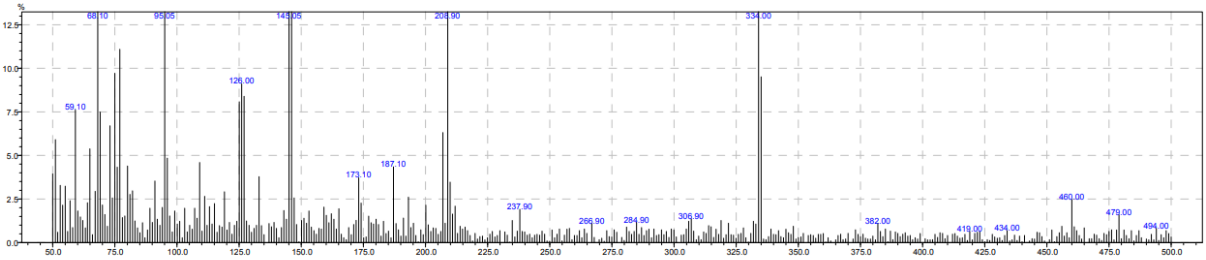
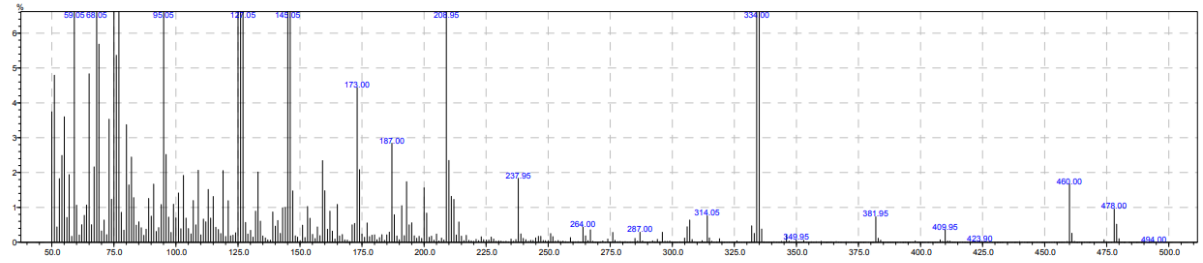


2d (dr = 97:1)









Peak Report TIC

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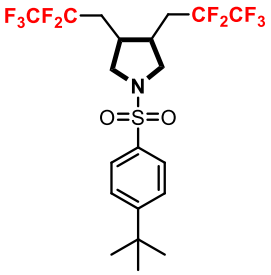
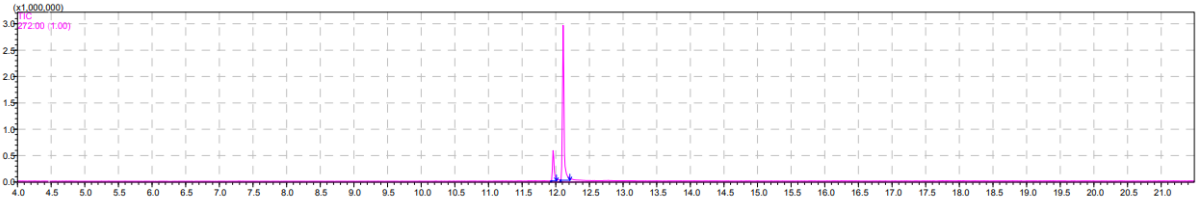
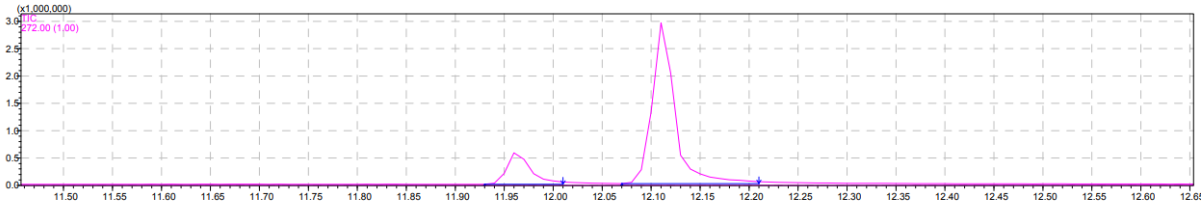
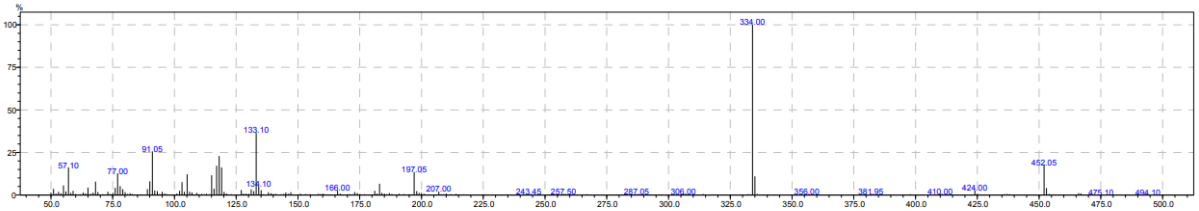
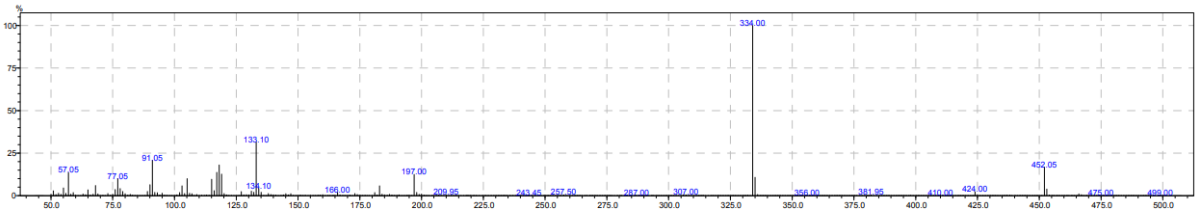


2e (dr = 4.8:1)



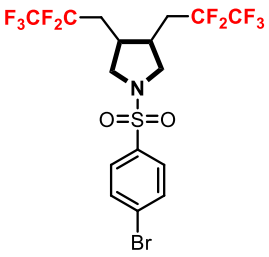




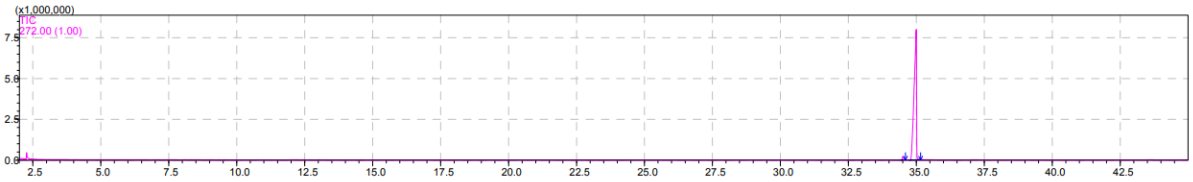


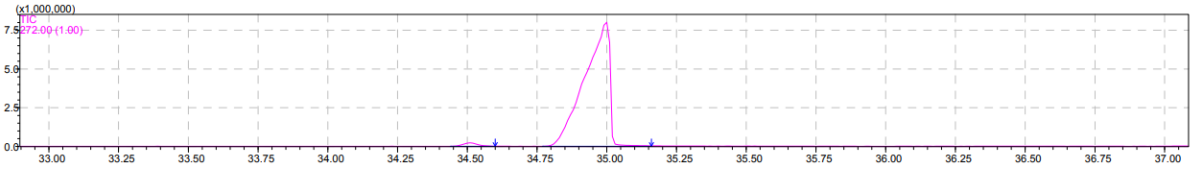
Peak Report TIC

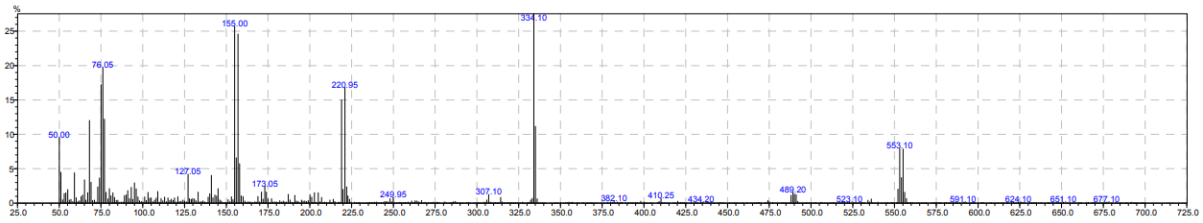
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	11.963	11.930	12.010	983544	17.14	574528	16.35	1.71	MI	
2	12.111	12.070	12.210	4753554	82.86	2938642	83.65	1.62	MI	
				5737098	100.00	3513170	100.00			

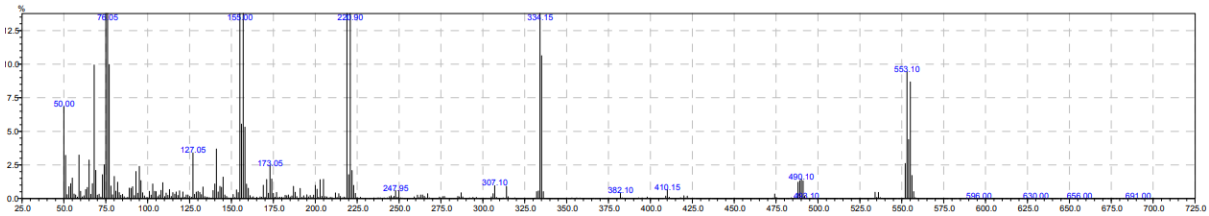


2f (dr = 63:1)



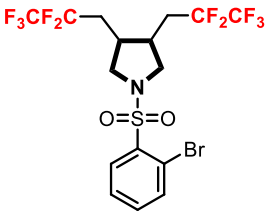




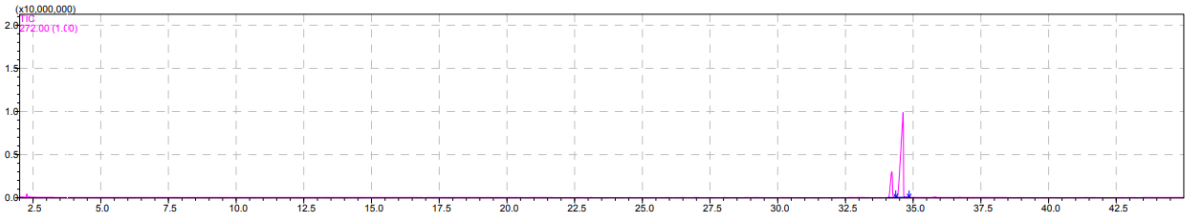


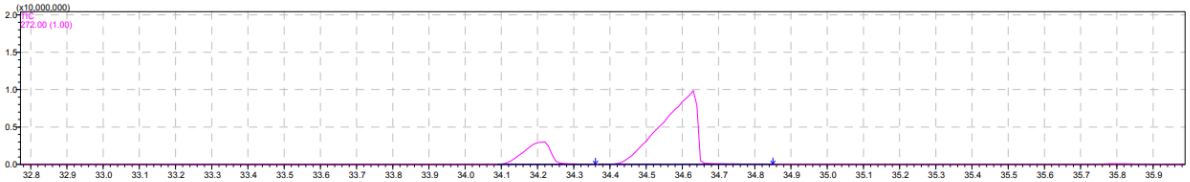
Peak Report TIC

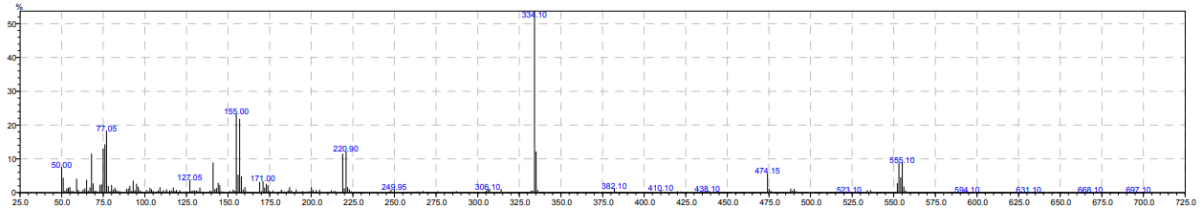
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	34.510	34.440	34.600	791391	1.56	220049	2.68	3.60	MI	
2	34.996	34.770	35.160	50095030	98.44	8004795	97.32	6.26	MI	
				50886421	100.00	8224844	100.00			

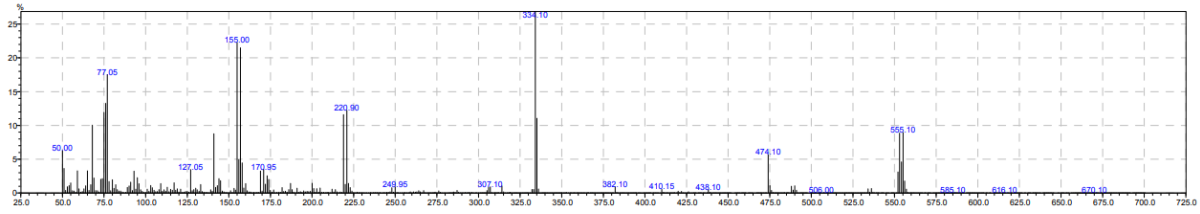


2g (dr = 4.3:1)



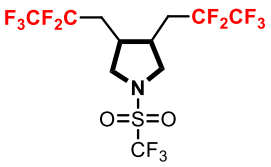




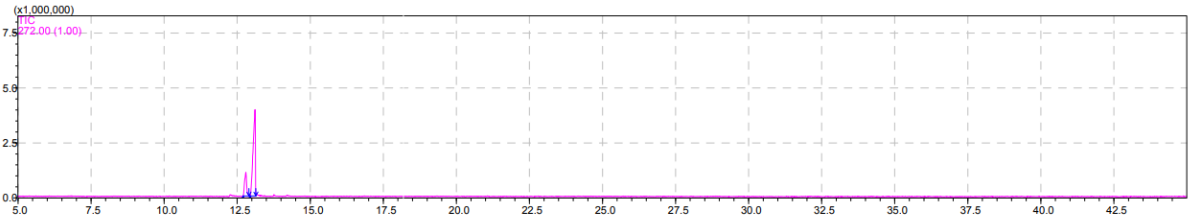


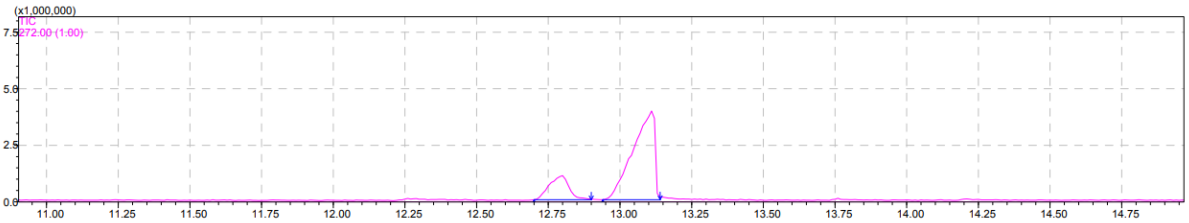
Peak Report TIC

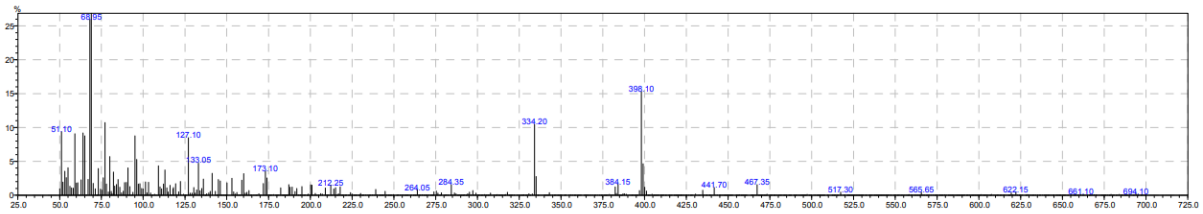
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	34.216	34.090	34.360	15060286	18.76	2973095	23.23	5.07	MI	
2	34.627	34.370	34.850	65209642	81.24	9825703	76.77	6.64	MI	
				80269928	100.00	12798798	100.00			

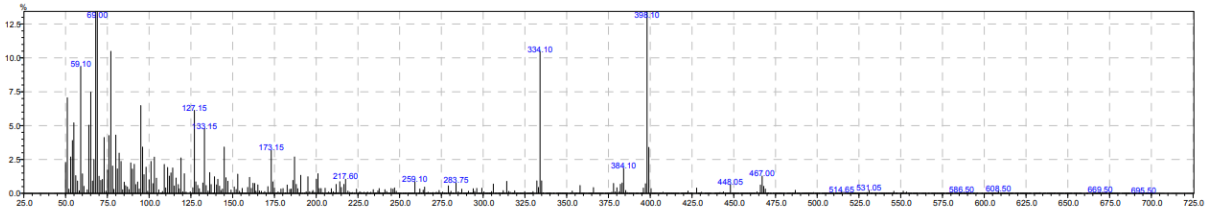


2h (dr = 4.0:1)



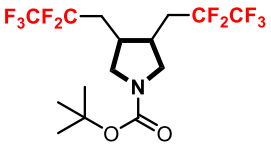




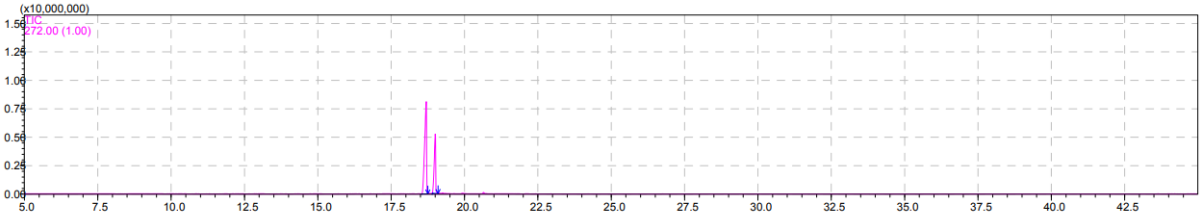


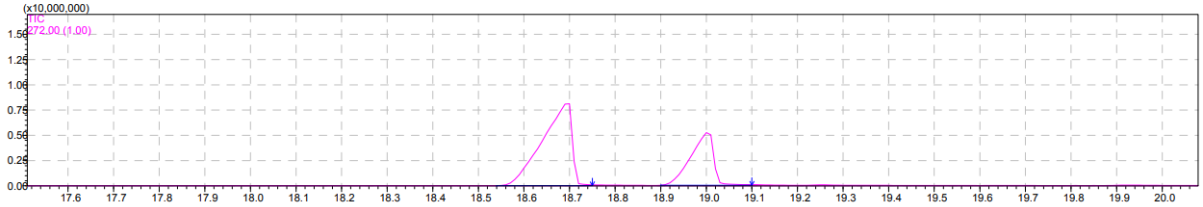
Peak Report TIC

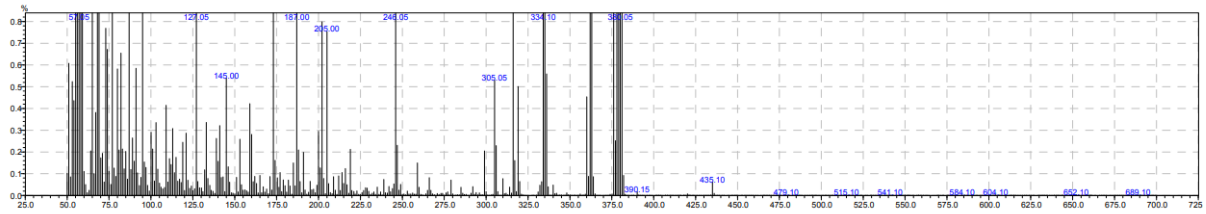
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	12.797	12.700	12.900	5177485	19.83	1070201	21.44	4.84	MI	
2	13.109	12.940	13.140	20926857	80.17	3921196	78.56	5.34	MI	
				26104342	100.00	4991397	100.00			

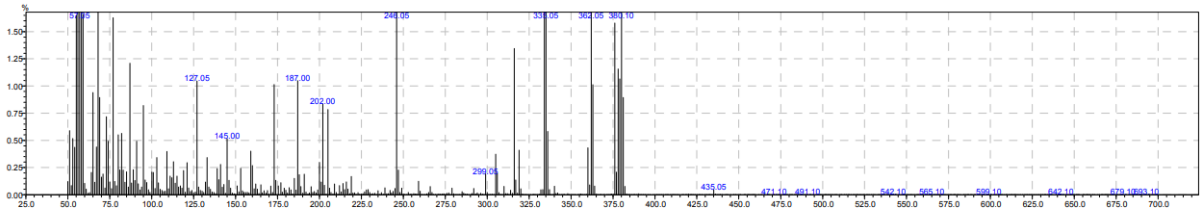


2i (dr = 2.0:1)



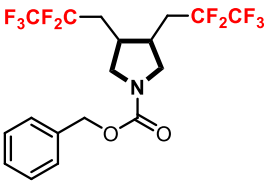




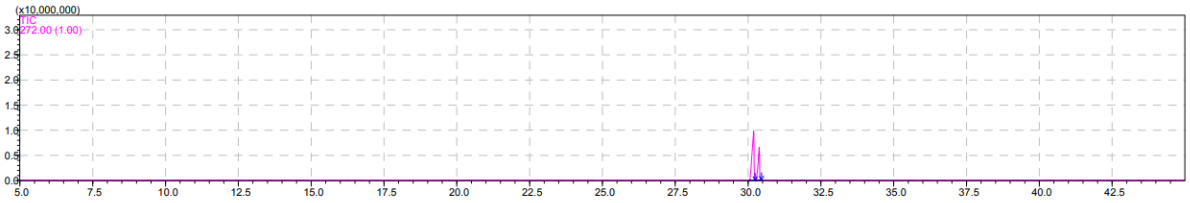


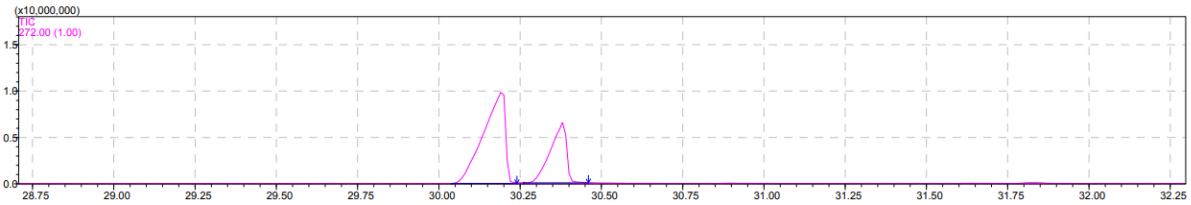
Peak Report TIC

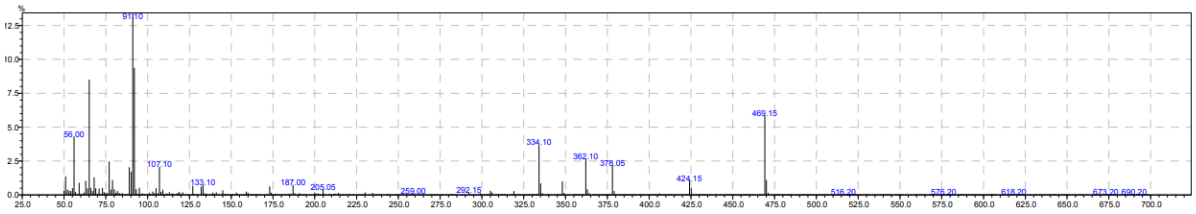
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	18.695	18.540	18.750	36759963	66.90	8104116	60.86	4.54	MI	
2	19.002	18.900	19.100	18189786	33.10	5212832	39.14	3.49	MI	
				54949749	100.00	13316948	100.00			

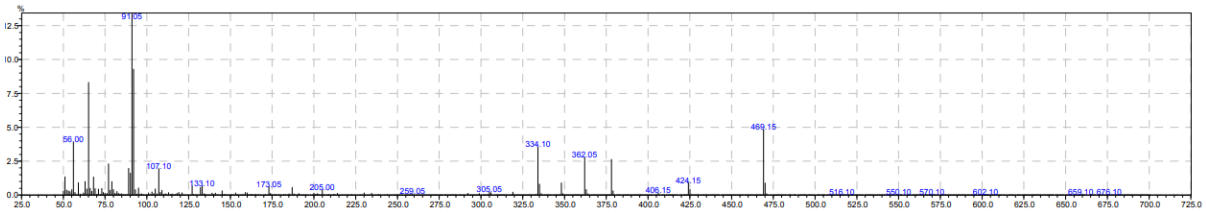


2j (dr = 2.1:1)



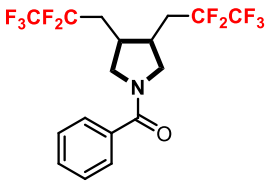




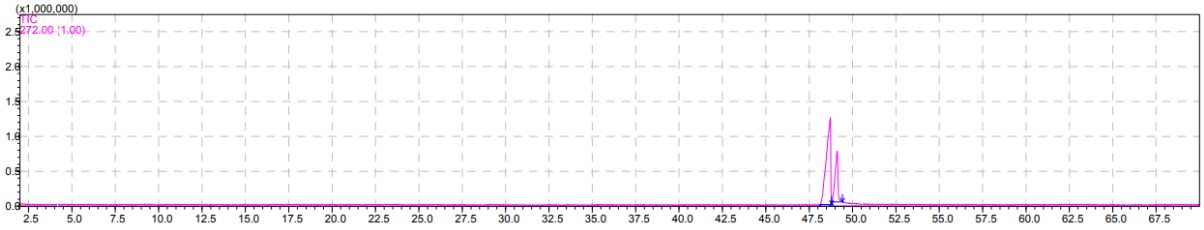


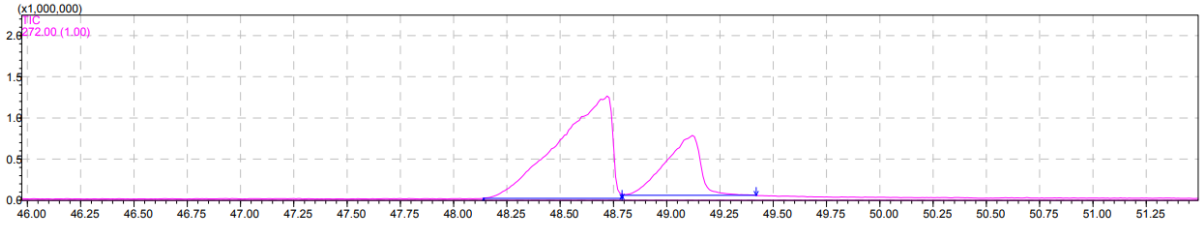
Peak Report TIC

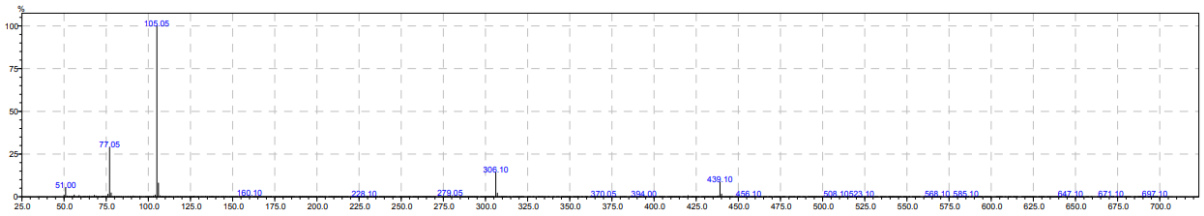
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	30.192	30.040	30.240	46126301	67.42	9819389	60.11	4.70	MI	
2	30.379	30.260	30.460	22289603	32.58	6517047	39.89	3.42	MI	
				68415904	100.00	16336436	100.00			

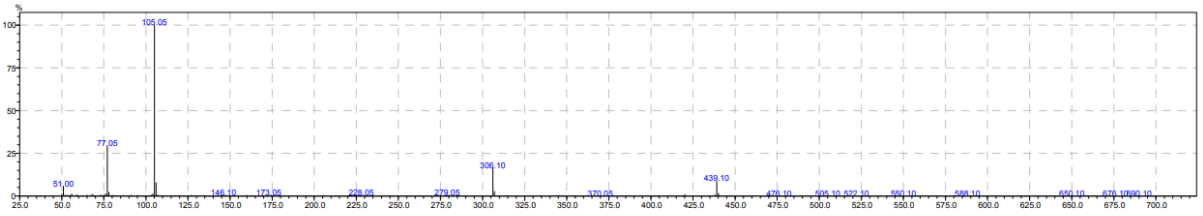


2k (dr = 2.6:1)



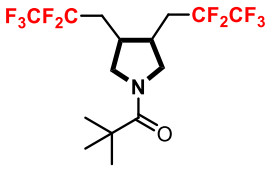




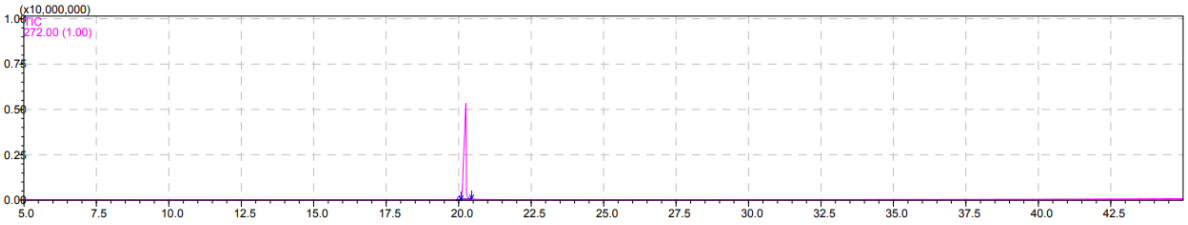


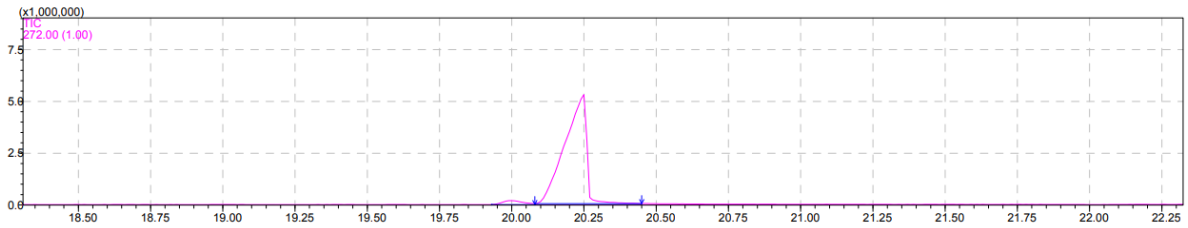
Peak Report TIC

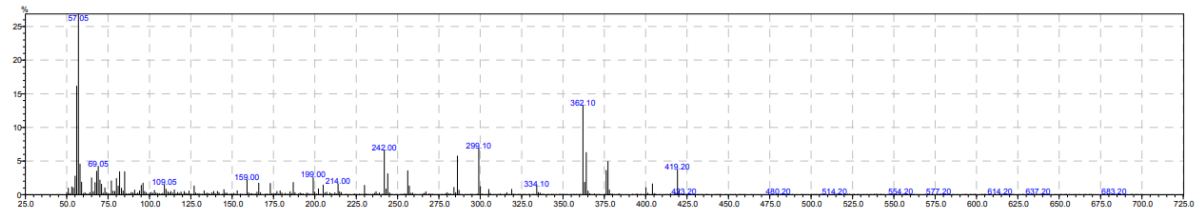
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	48.721	48.140	48.790	21664498	72.16	1242169	63.05	17.44	MI	
2	49.120	48.790	49.420	8356384	27.84	728114	36.95	11.48	MI	
				30020882	100.00	1970283	100.00			

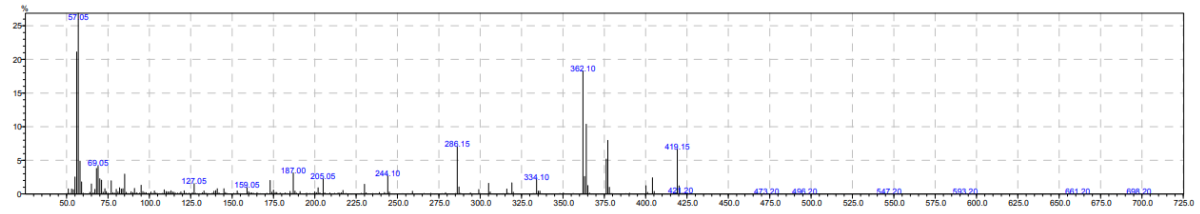


2l (dr = 29:1)



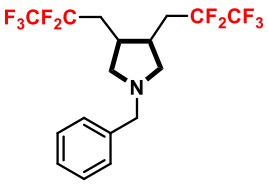




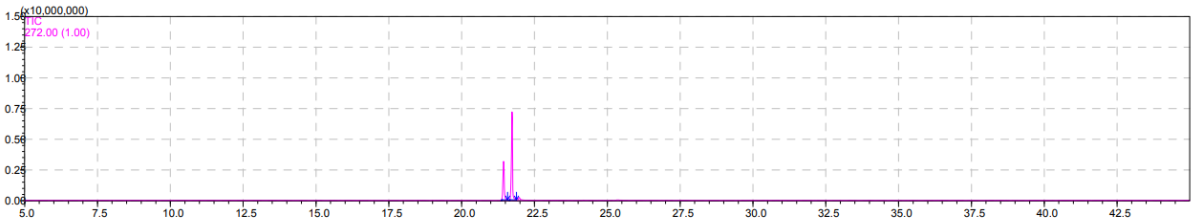


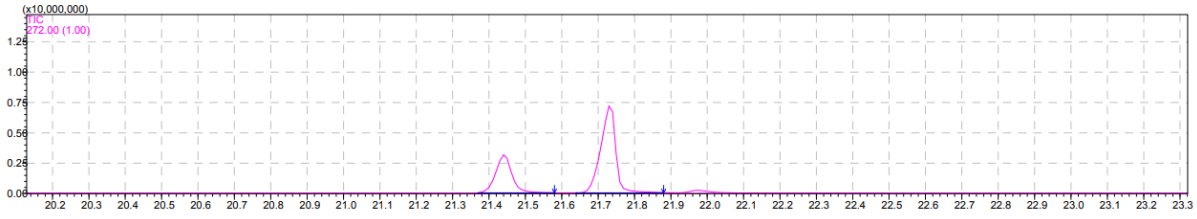
Peak Report TIC

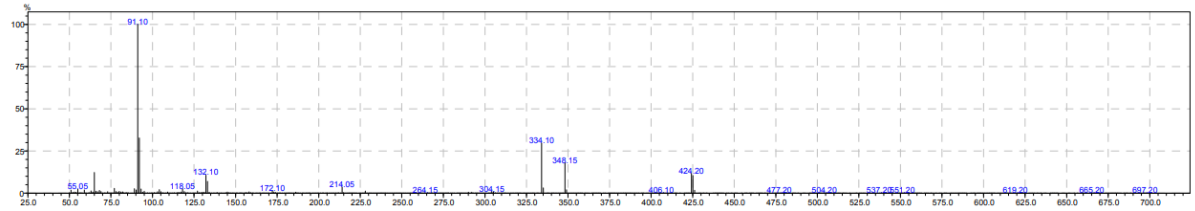
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	19.997	19.930	20.080	948678	3.35	186238	3.42	5.09	MI	
2	20.246	20.080	20.450	27394392	96.65	5265341	96.58	5.20	MI	
				28343070	100.00	5451579	100.00			

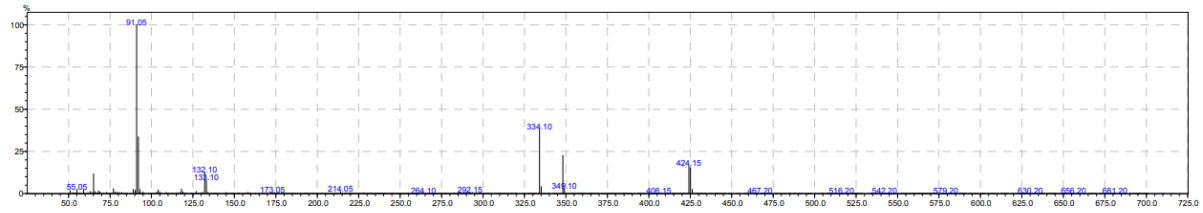


2m (dr = 2.1:1)



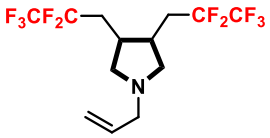




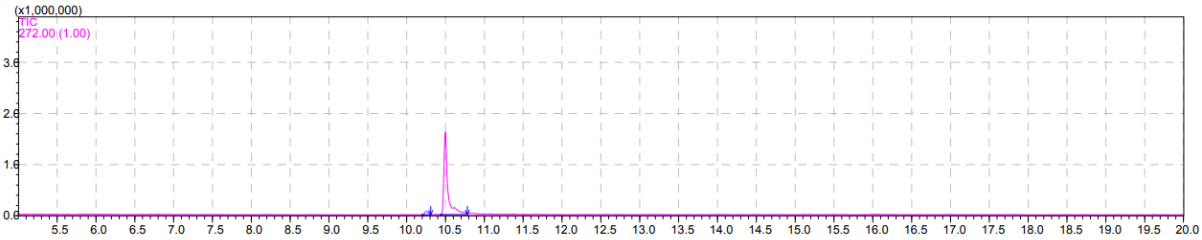


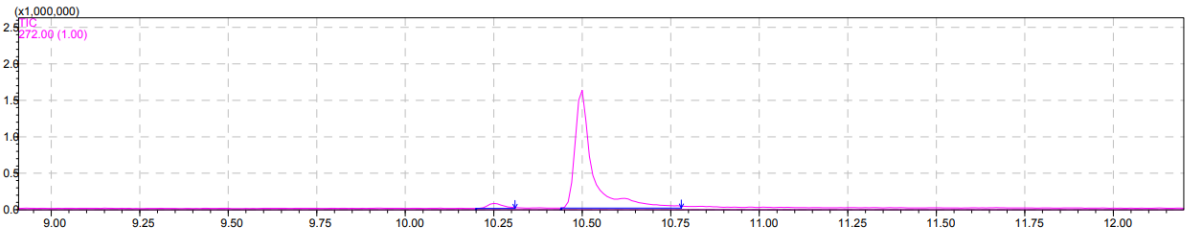
Peak Report TIC

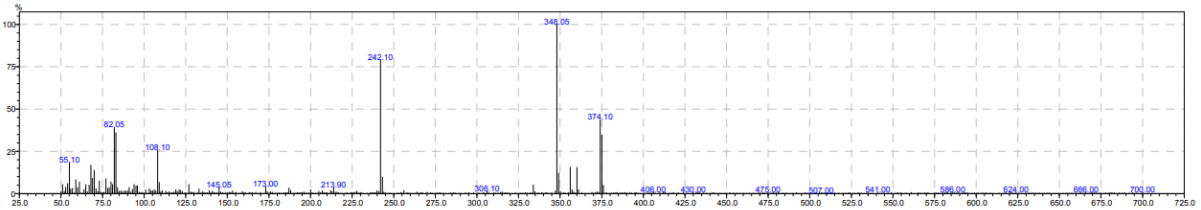
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	21.441	21.370	21.580	9661622	31.97	3134965	30.42	3.08	MI	
2	21.732	21.640	21.880	20554932	68.03	7169192	69.58	2.87	MI	
				30216554	100.00	10304157	100.00			

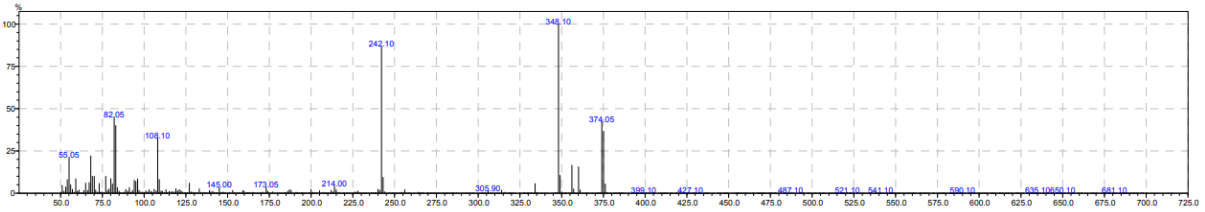


2n (dr = 26:1)



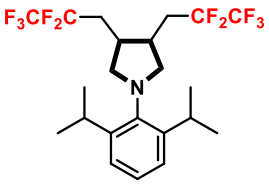




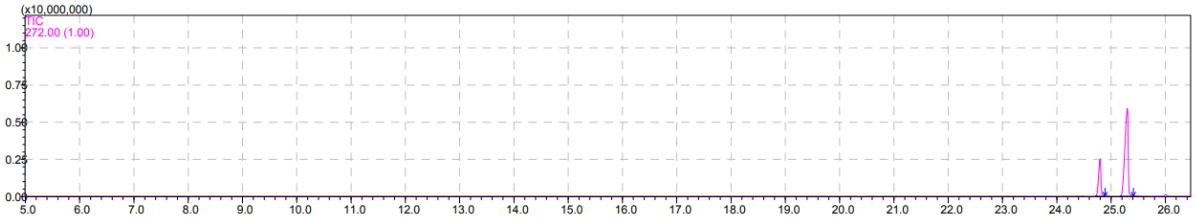


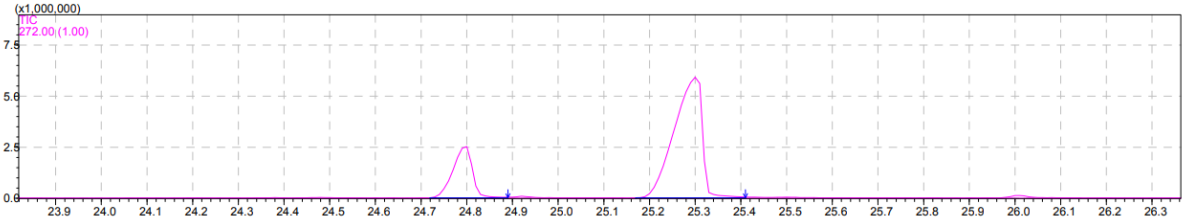
Peak Report TIC

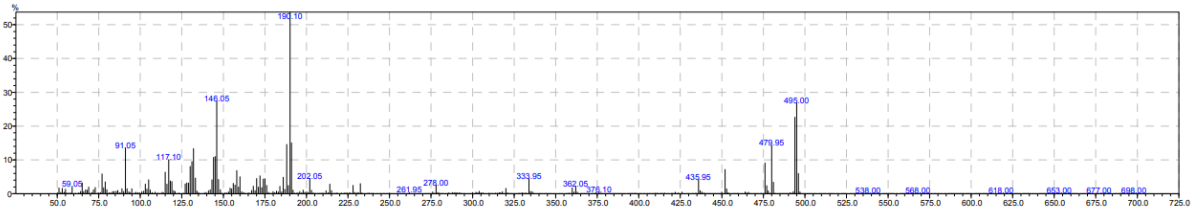
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	10.252	10.200	10.310	216239	3.75	68712	4.08	3.15	MI	
2	10.497	10.440	10.780	5553707	96.25	1614237	95.92	3.44	MI	
				5769946	100.00	1682949	100.00			

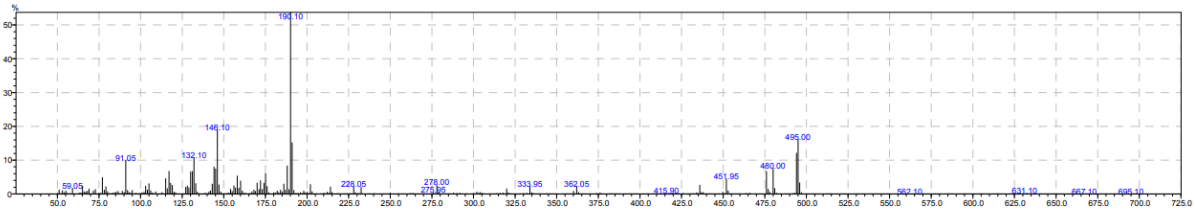


2o (dr = 3.4:1)



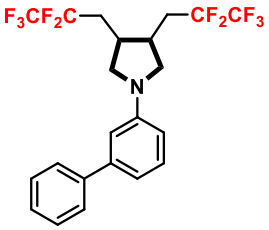




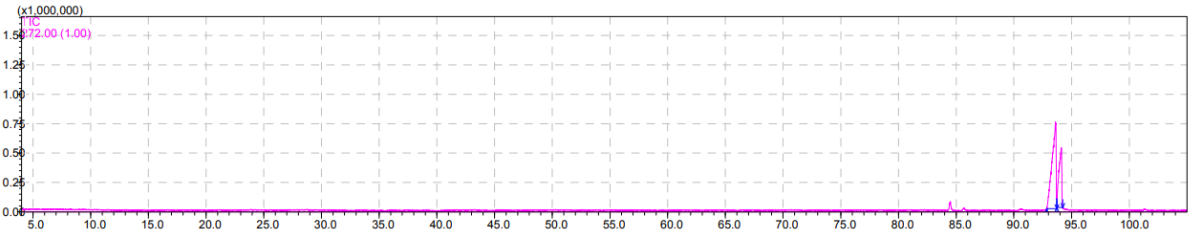


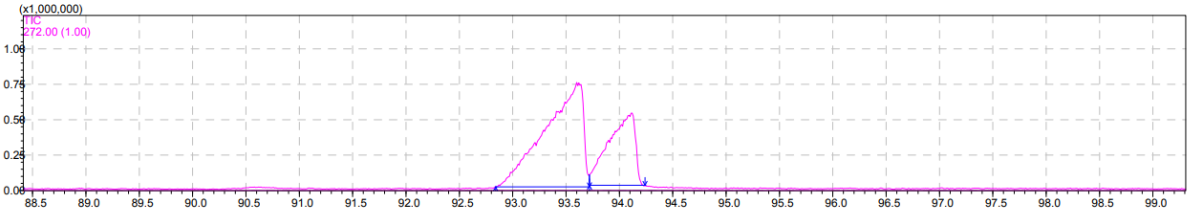
Peak Report TIC

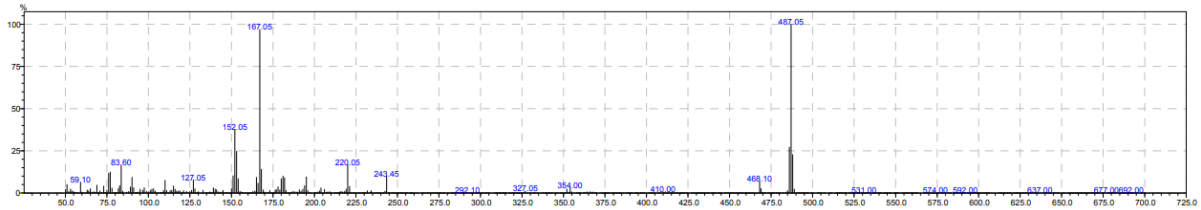
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	24.796	24.720	24.890	7482798	22.85	2514007	29.87	2.98	MI	
2	25.299	25.170	25.410	25259670	77.15	5903031	70.13	4.28	MI	
				32742468	100.00	8417038	100.00			

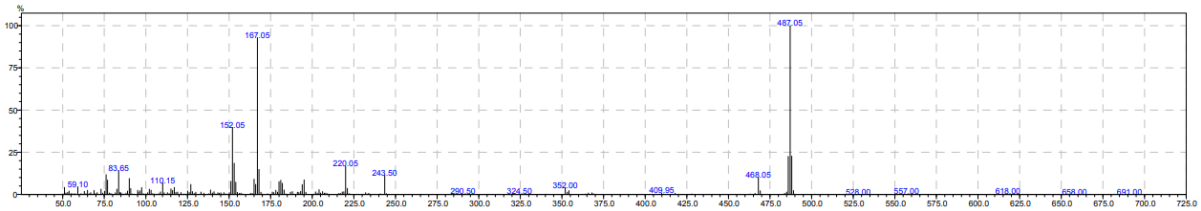


2p (dr = 2.1:1)



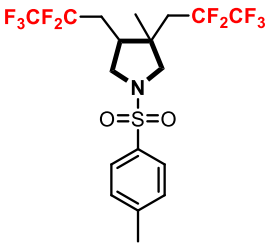




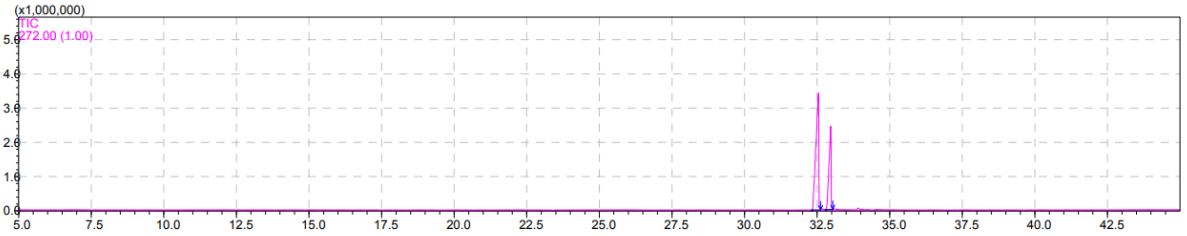


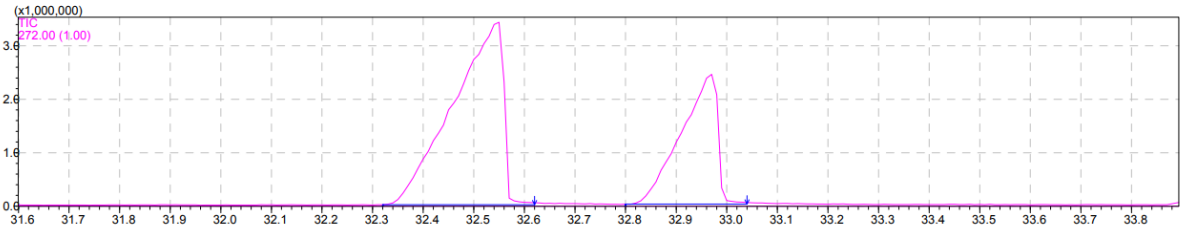
Peak Report TIC

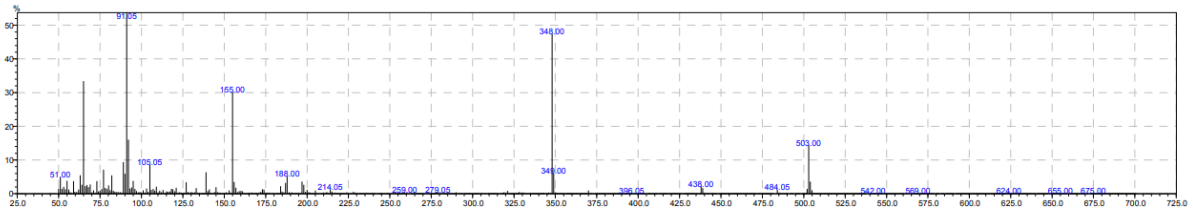
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	93.600	92.840	93.720	18172844	67.46	737236	59.10	24.65	MI	
2	94.116	93.720	94.240	8767486	32.54	510217	40.90	17.18	MI	
				26940330	100.00	1247453	100.00			

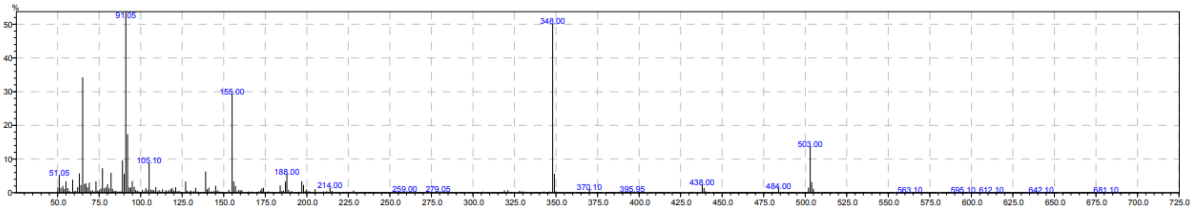


2r (dr = 1.9:1)



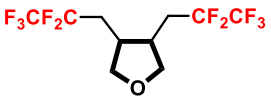




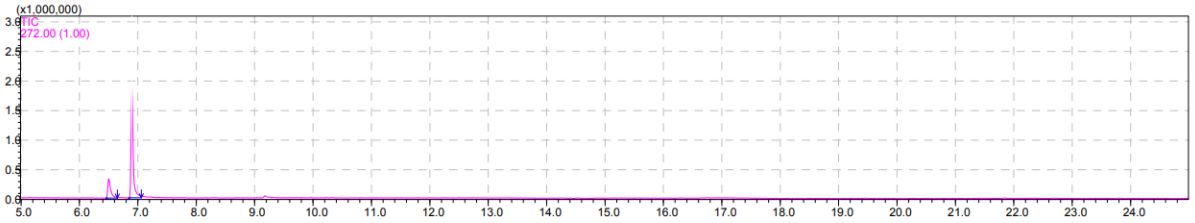


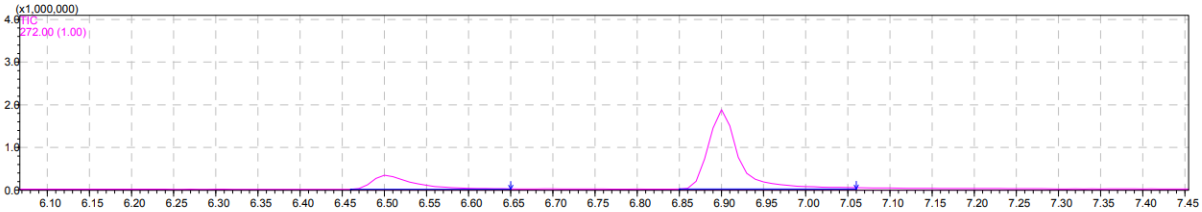
Peak Report TIC

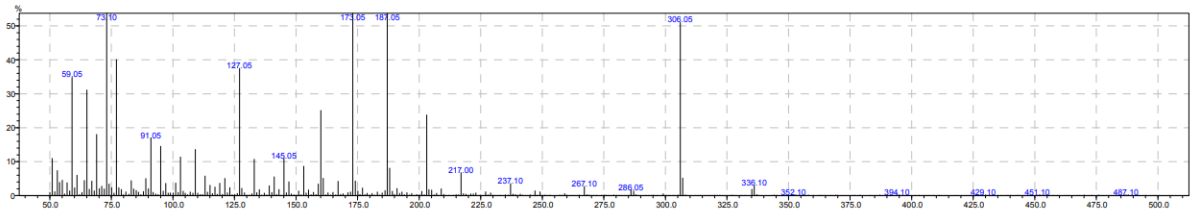
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	32.545	32.320	32.620	23681633	65.98	3416510	58.44	6.93	MI	
2	32.967	32.800	33.040	12210605	34.02	2429899	41.56	5.03	MI	
				35892238	100.00	5846409	100.00			

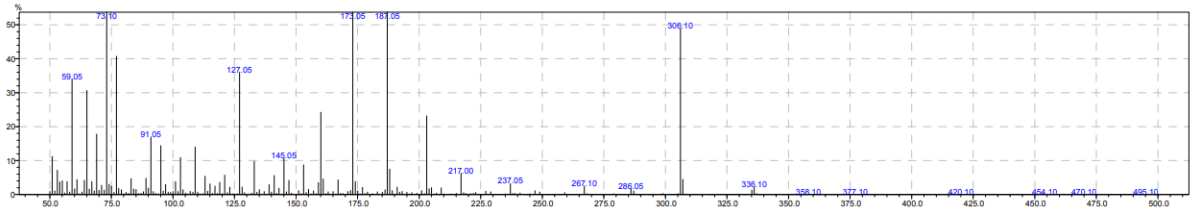


2s (crude dr = 4.2:1)



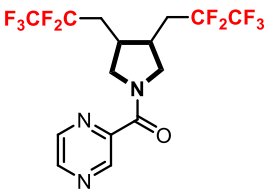




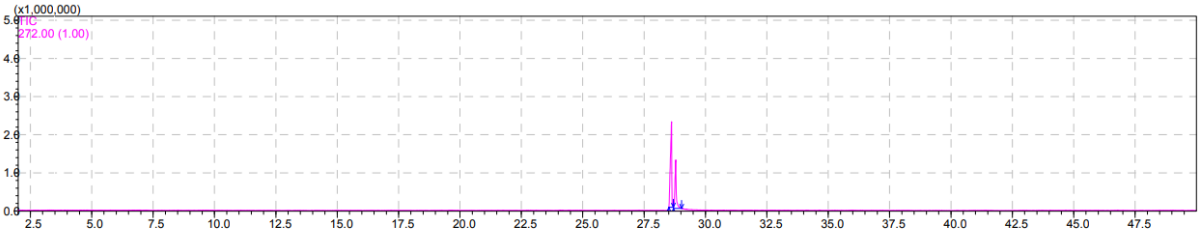


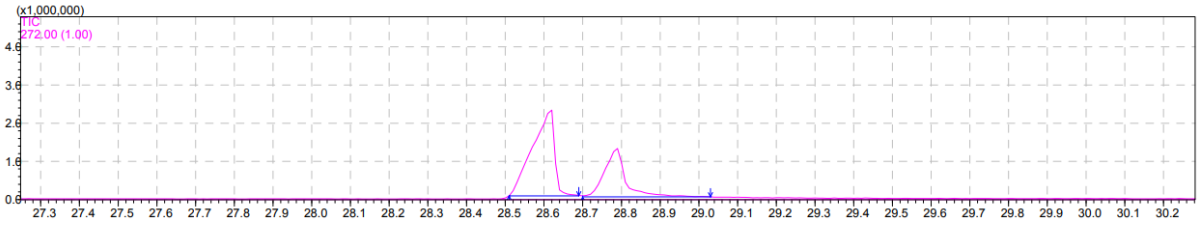
Peak Report TIC

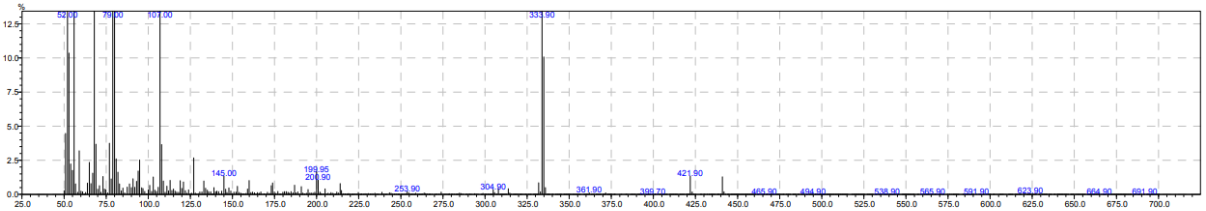
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	6.502	6.460	6.650	1131924	19.36	328528	15.01	3.45	MI	
2	6.900	6.850	7.060	4713694	80.64	1860403	84.99	2.53	MI	
				5845618	100.00	2188931	100.00			

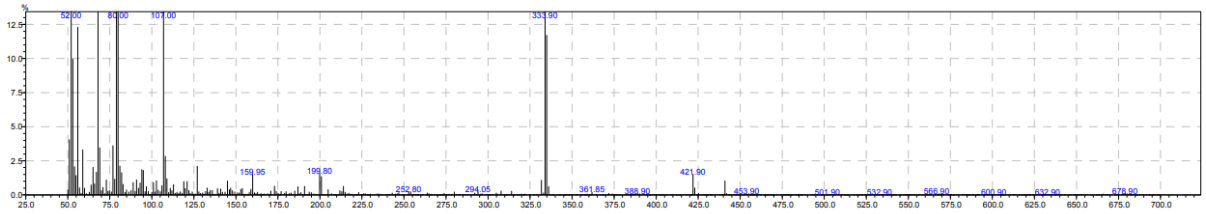


2t (dr = 1.9:1)



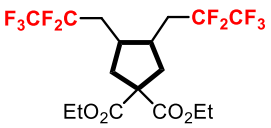




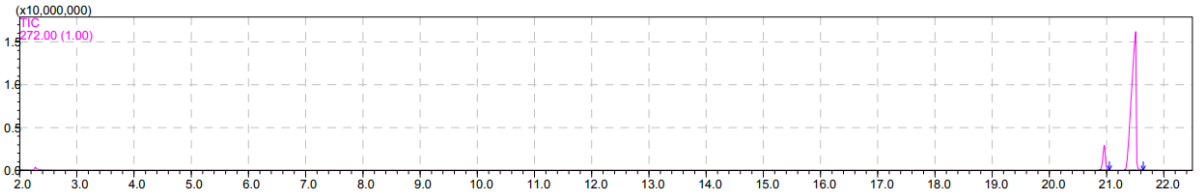


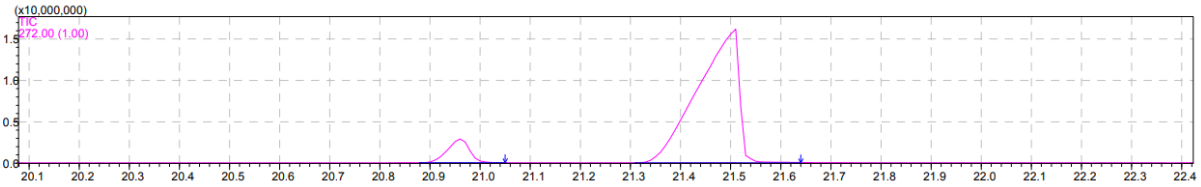
Peak Report TIC

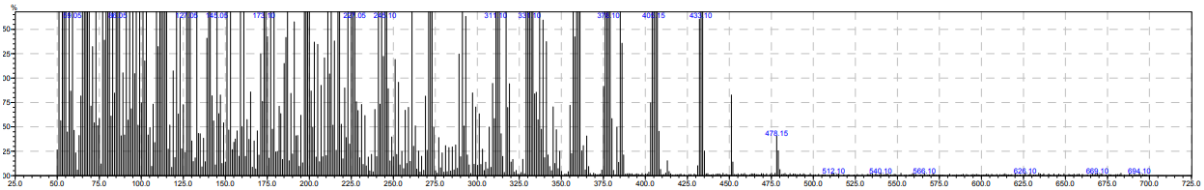
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	28.616	28.510	28.690	8908593	65.15	2245216	63.86	3.97	MI	
2	28.787	28.700	29.030	4765967	34.85	1270506	36.14	3.75	MI	
				13674560	100.00	3515722	100.00			

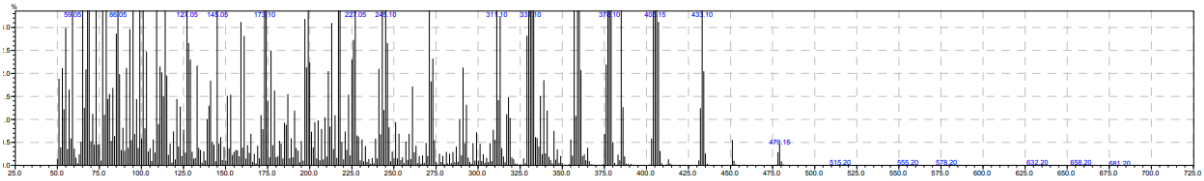


4a (dr = 11:1)



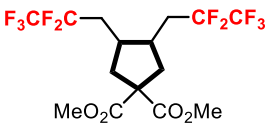




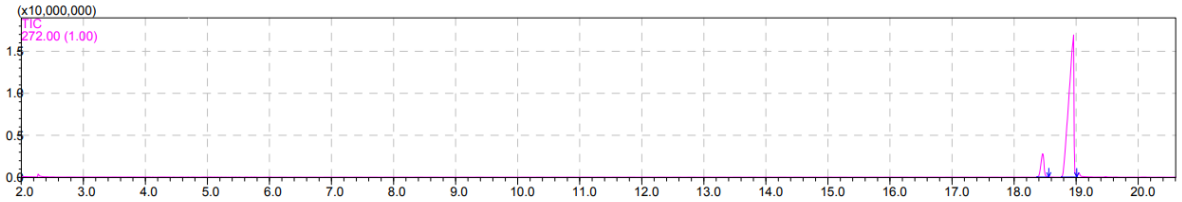


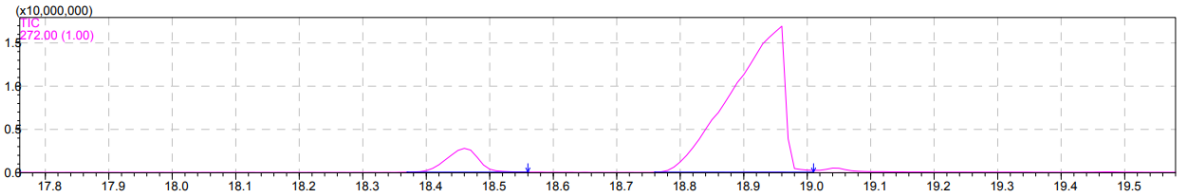
Peak Report TIC

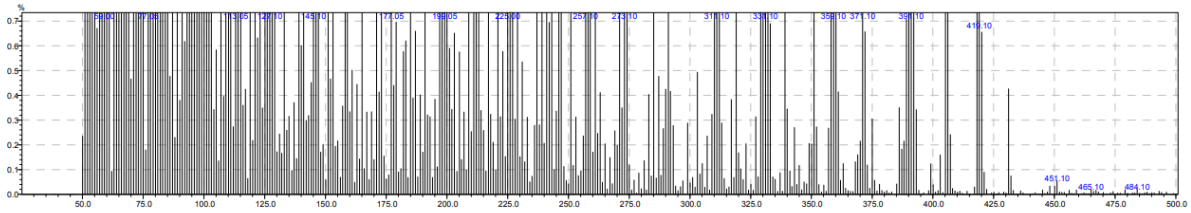
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	20.959	20.880	21.050	8759616	8.68	2877858	15.11	3.04	MI	
2	21.505	21.310	21.640	92181897	91.32	16170409	84.89	5.70	MI	
				100941513	100.00	19048267	100.00			

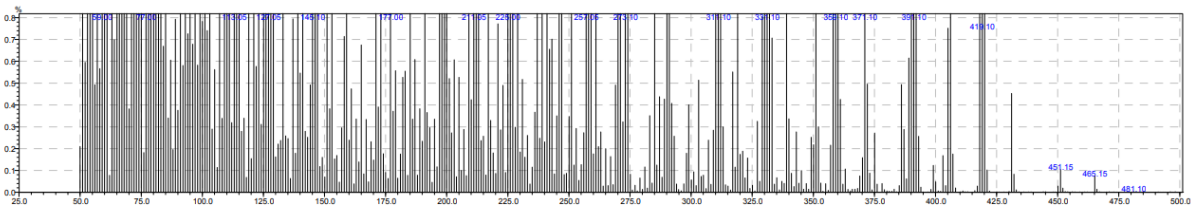


4b (dr = 10:1)



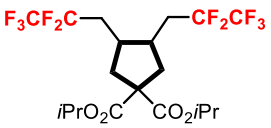




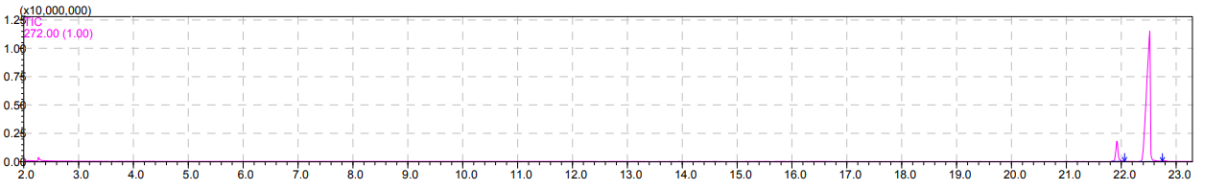


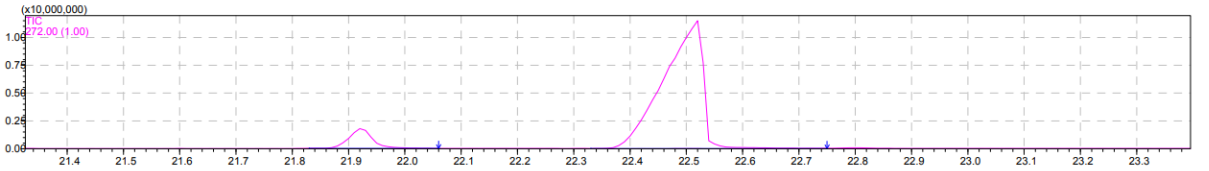
Peak Report TIC

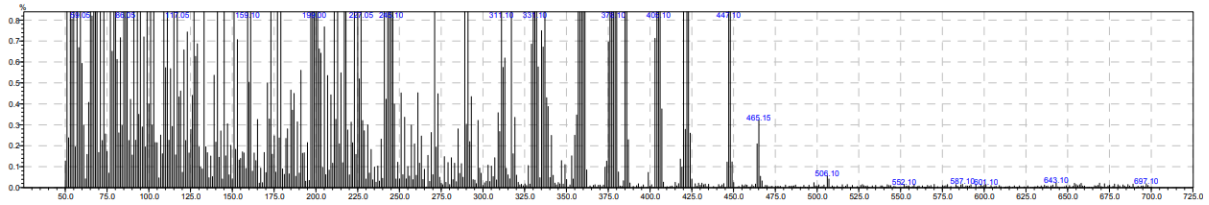
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	18.460	18.370	18.560	9681342	9.03	2770511	14.08	3.49	MI	
2	18.955	18.760	19.010	97474177	90.97	16904942	85.92	5.77	MI	
				107155519	100.00	19675453	100.00			

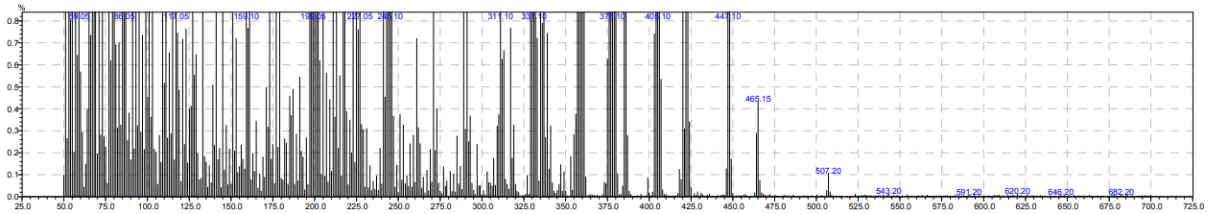


4c (dr = 11:1)



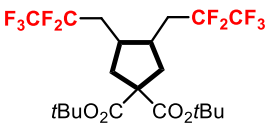




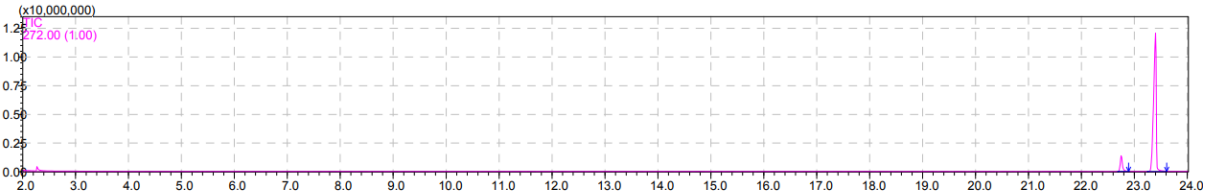


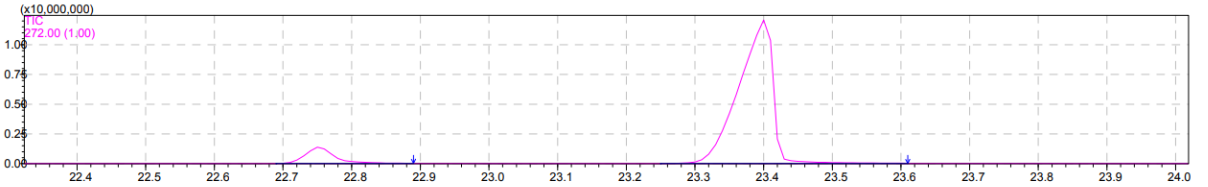
Peak Report TIC

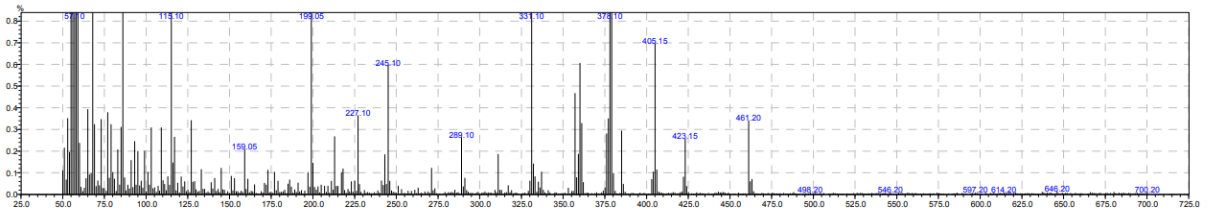
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	21.922	21.830	22.060	5231474	8.60	1774502	13.38	2.95	MI	
2	22.517	22.330	22.750	55599047	91.40	11484663	86.62	4.84	MI	
				60830521	100.00	13259165	100.00			

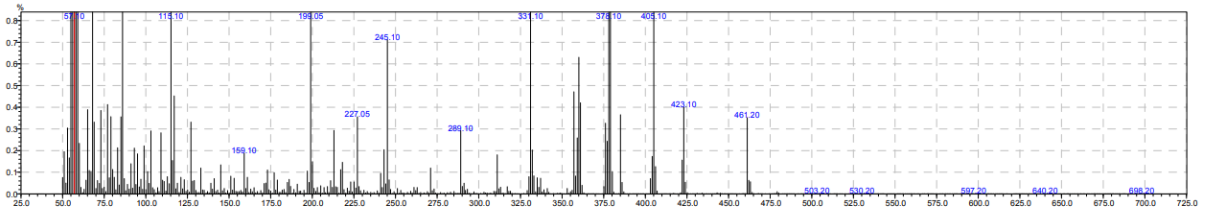


4d (dr = 11:1)



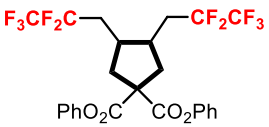




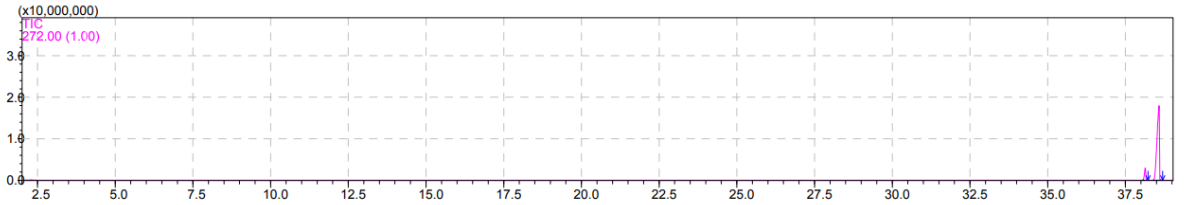


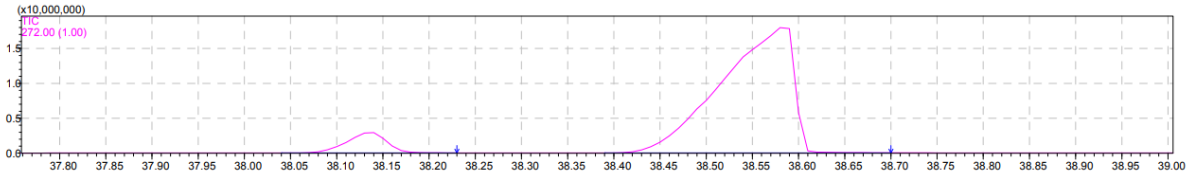
Peak Report TIC

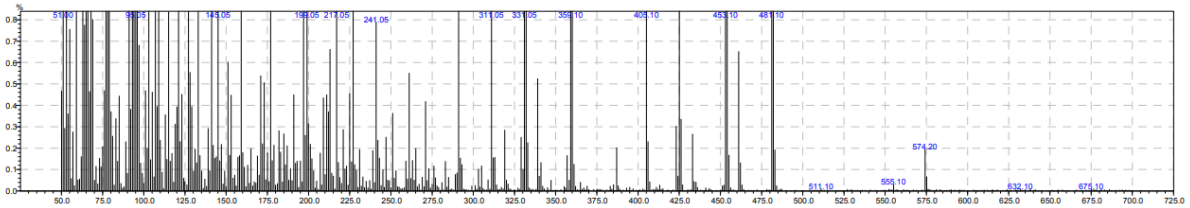
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	22.752	22.690	22.890	3960767	8.69	1362739	10.15	2.91	MI	
2	23.399	23.250	23.610	41614588	91.31	12059018	89.85	3.45	MI	
				45575355	100.00	13421757	100.00			

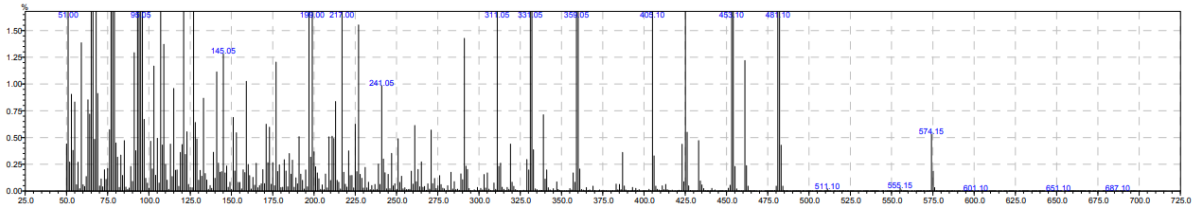


4e (dr = 11:1)



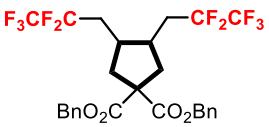




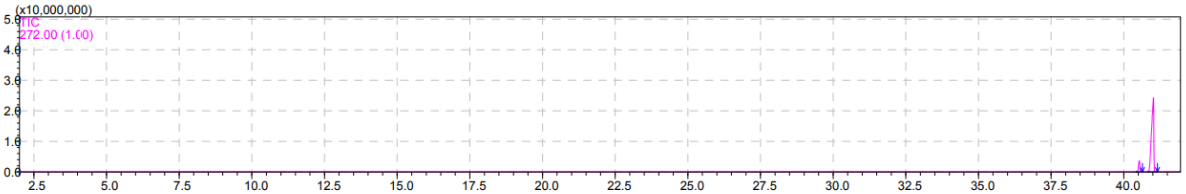


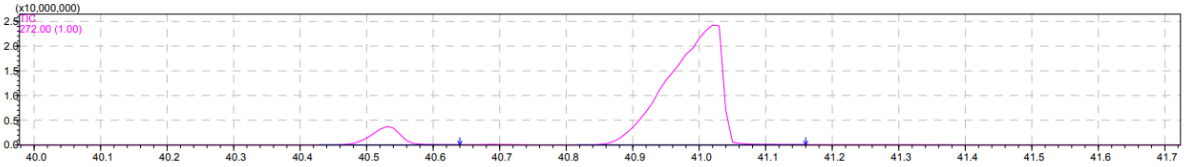
Peak Report TIC

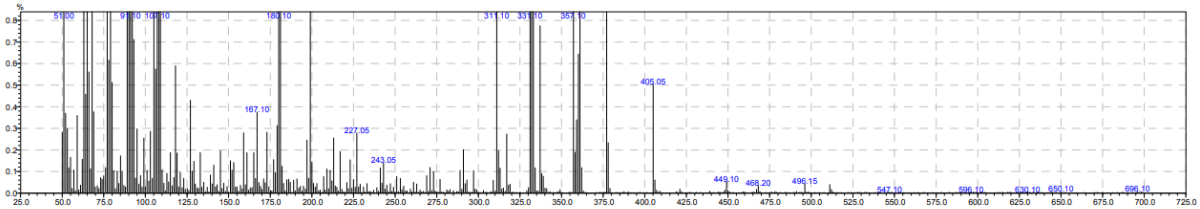
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	38.136	38.040	38.230	8971546	8.39	2935055	14.06	3.06	MI	
2	38.584	38.390	38.700	97919713	91.61	17943338	85.94	5.46	MI	
				106891259	100.00	20878393	100.00			

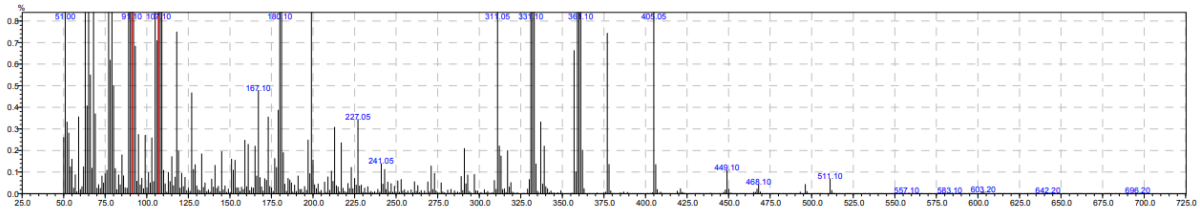


4f (dr = 12:1)



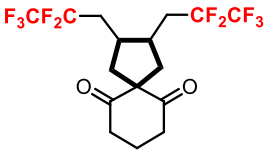




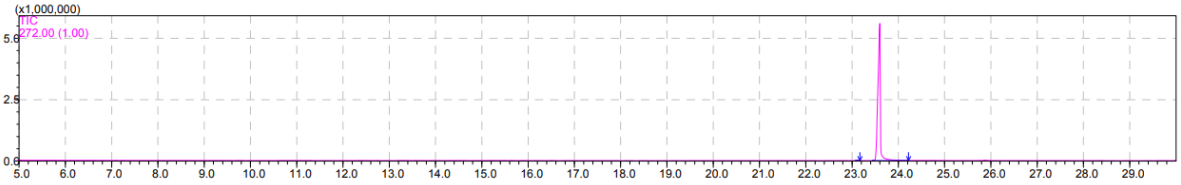


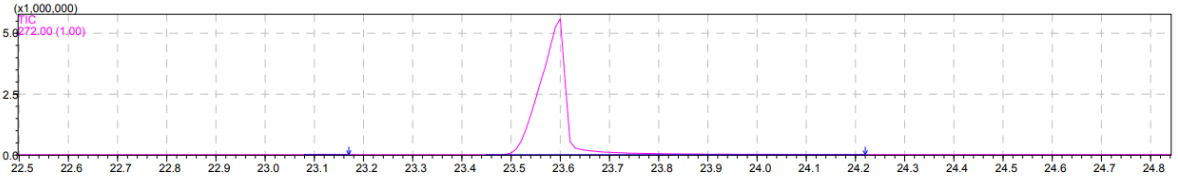
Peak Report TIC

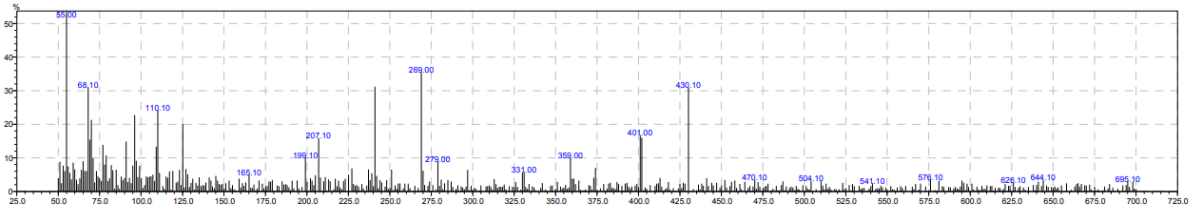
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	40.532	40.430	40.640	11087894	7.65	3692227	13.23	3.00	MI	
2	41.024	40.820	41.160	133784060	92.35	24220355	86.77	5.52	MI	
				144871954	100.00	27912582	100.00			

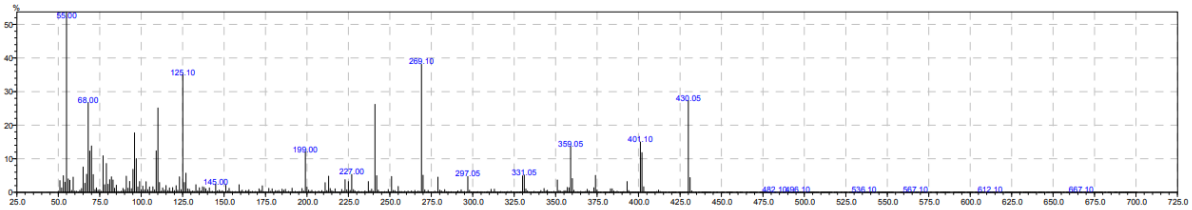


4g (dr = 416:1)



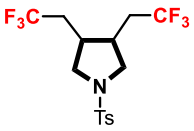




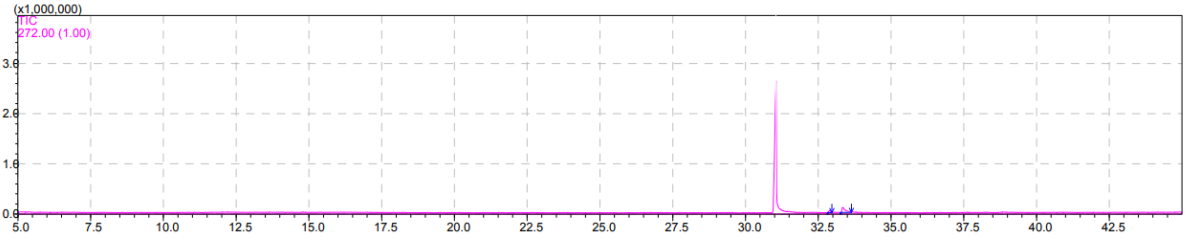


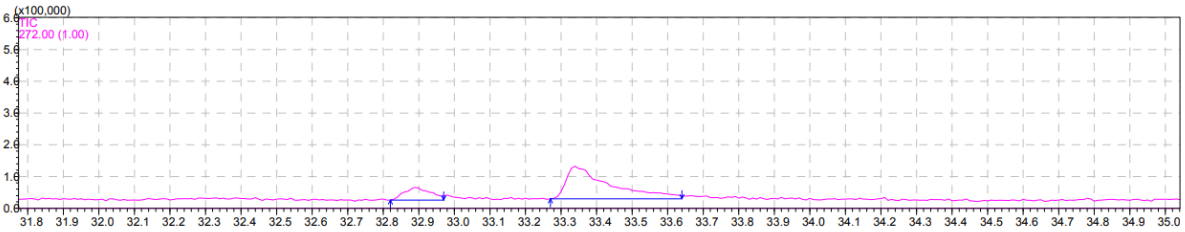
Peak Report TIC

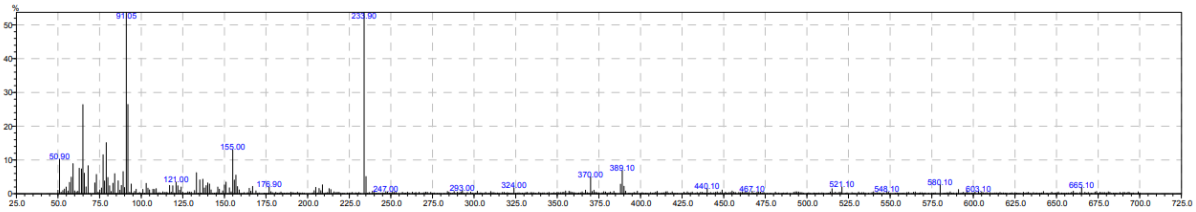
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	23.117	23.080	23.170	48053	0.24	17680	0.32	2.72	MI	
2	23.596	23.450	24.220	20377025	99.76	5587142	99.68	3.65	MI	
				20425078	100.00	5604822	100.00			

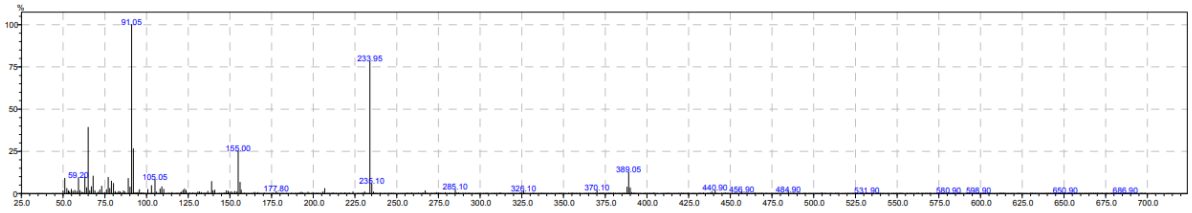


10 (crude)





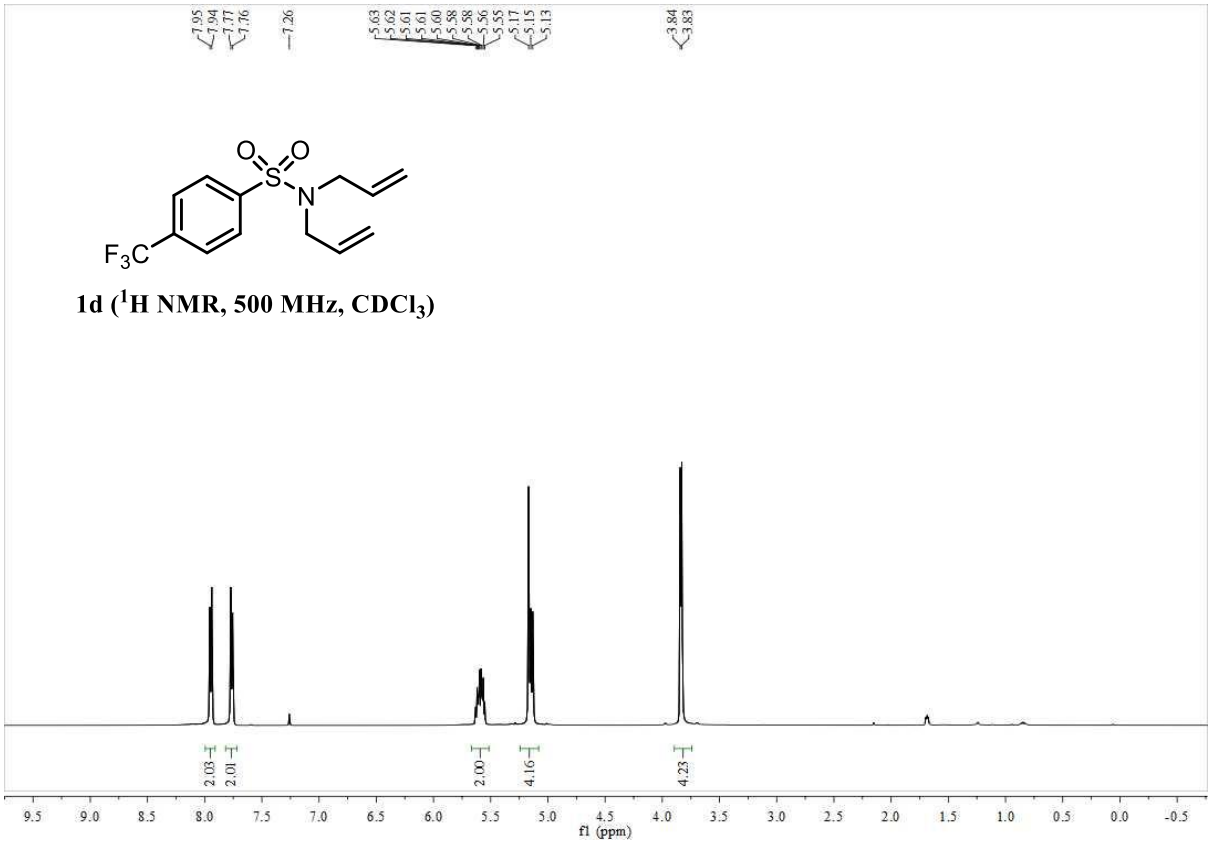




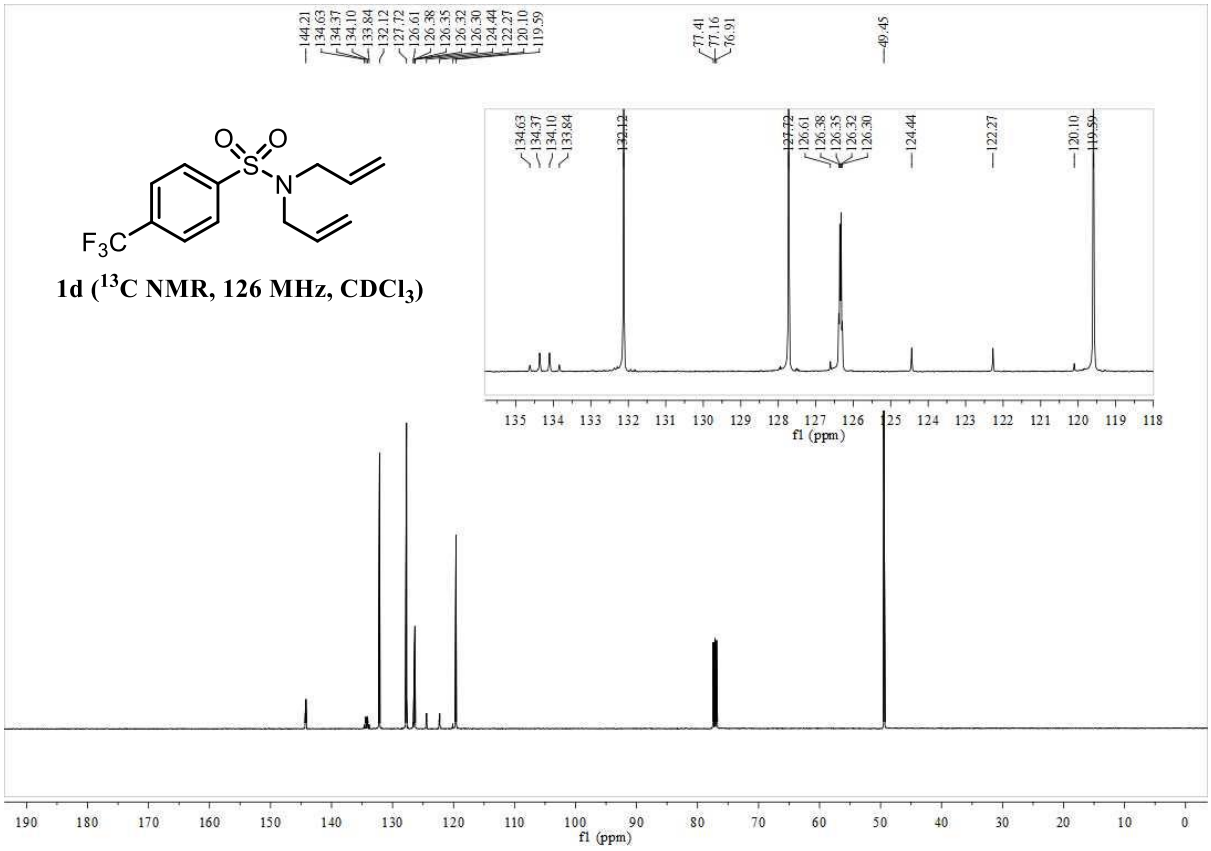
Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	32.891	32.820	32.970	208426	19.23	39865	28.01	5.23	MI	
2	33.339	33.270	33.640	875590	80.77	102457	71.99	8.55	MI	
				1084016	100.00	142322	100.00			

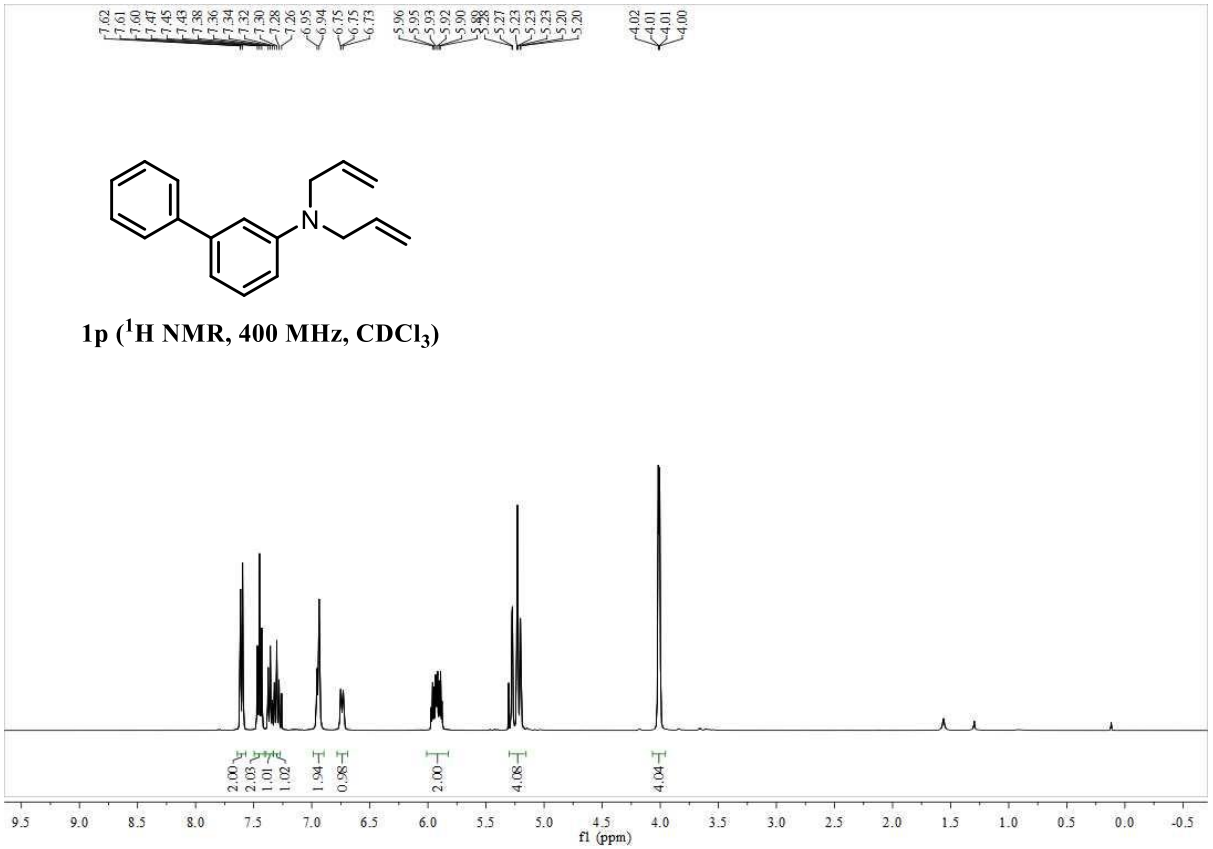
NMR Spectra



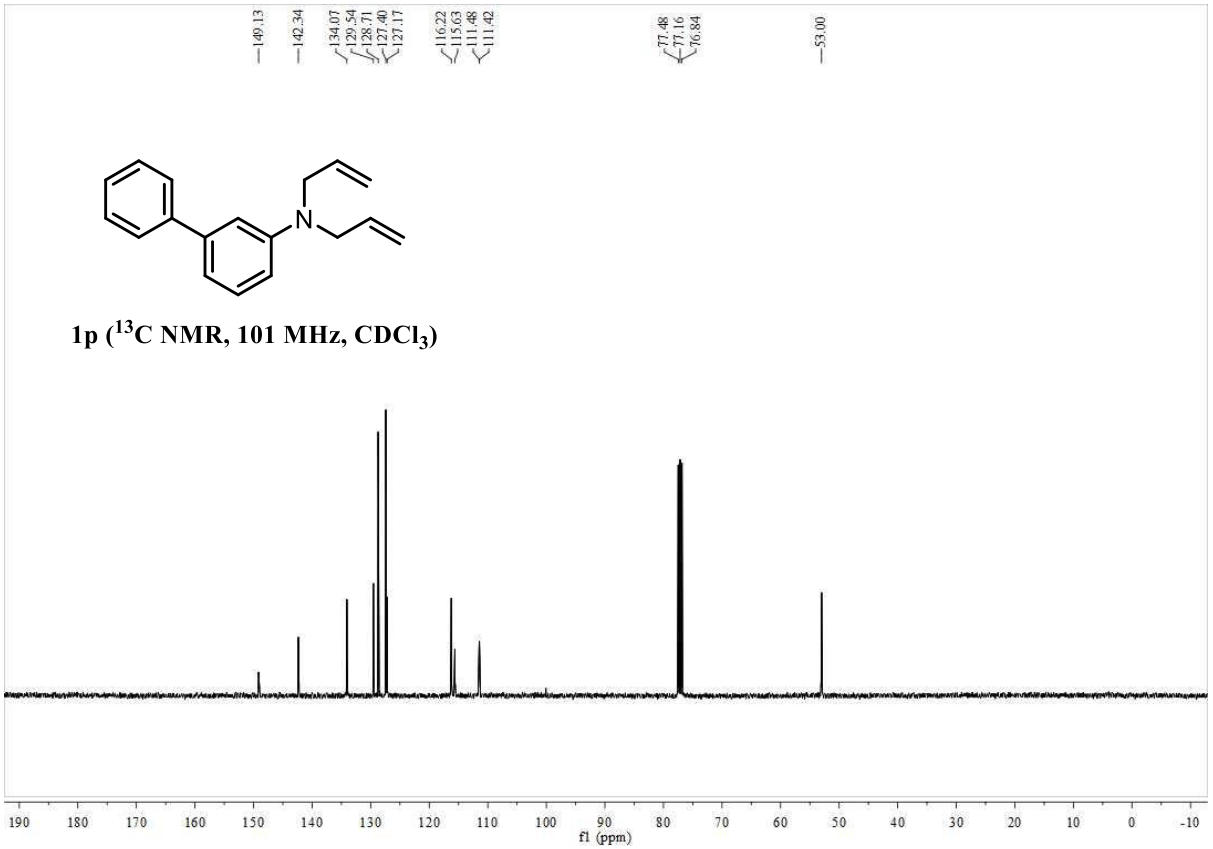
1d (^{1}H NMR, 500 MHz, $CDCl_3$)



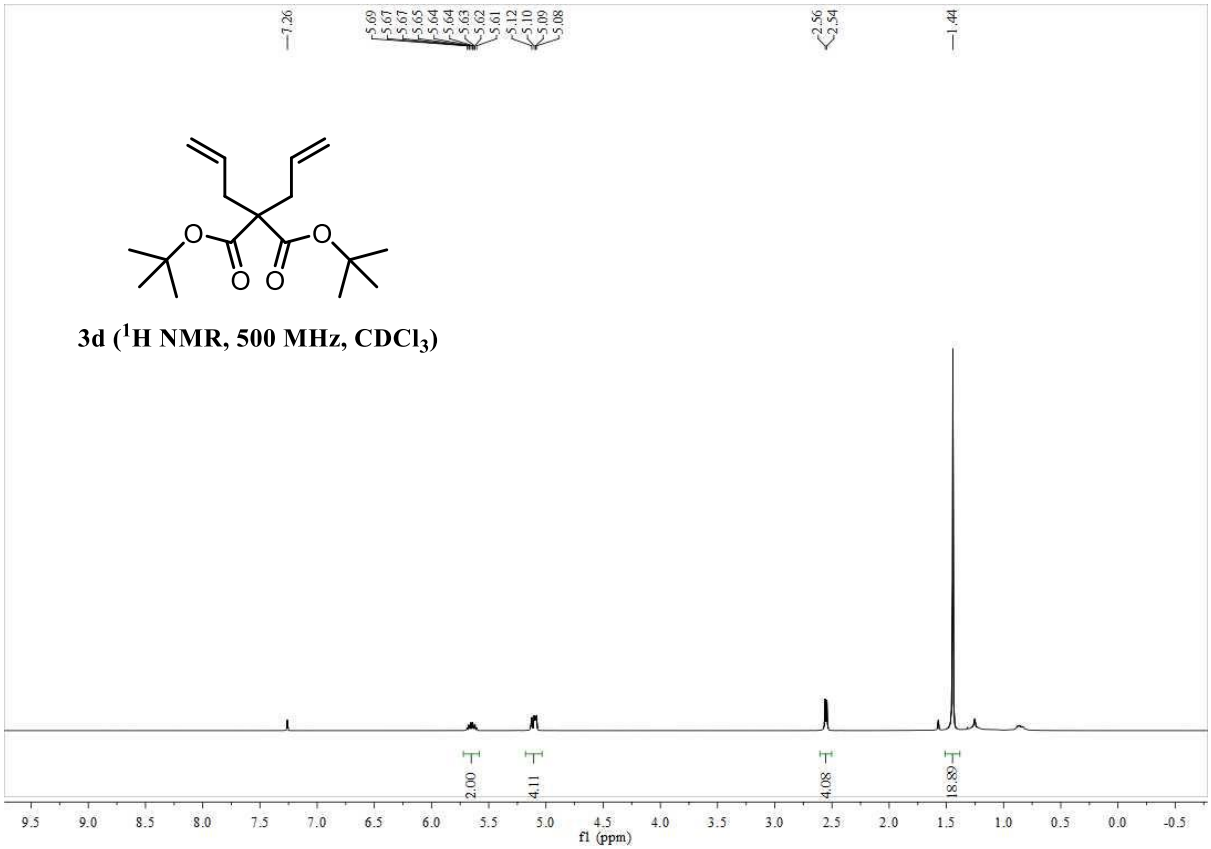
1d (^{13}C NMR, 126 MHz, $CDCl_3$)



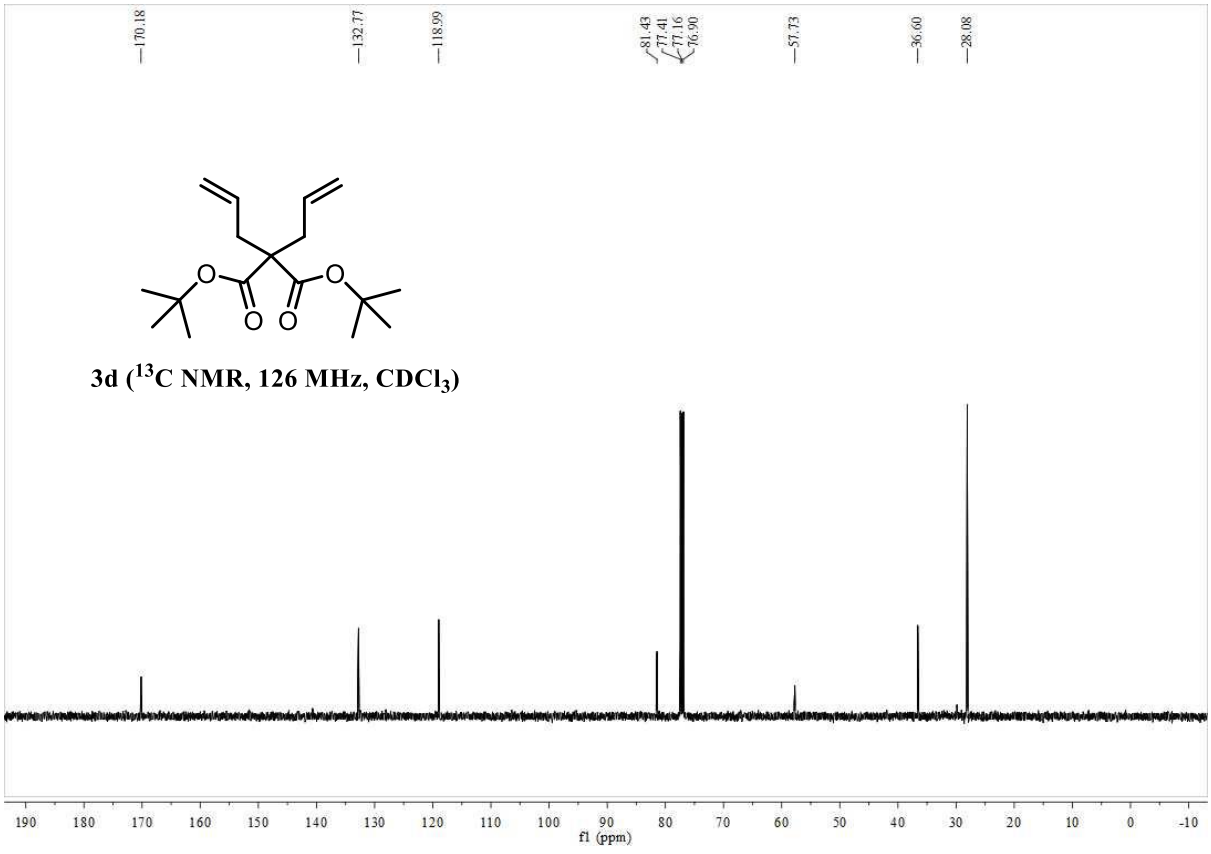
1p (^{1}H NMR, 400 MHz, $CDCl_3$)



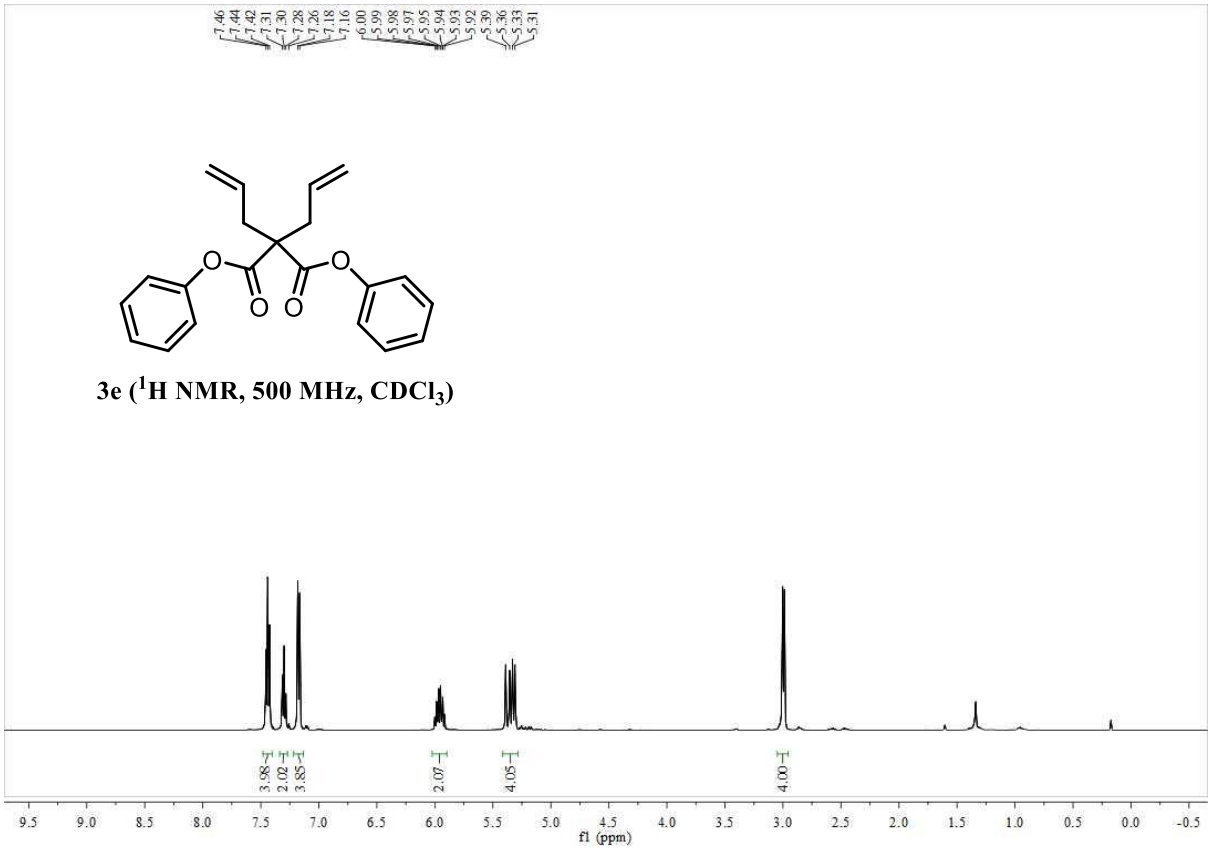
1p (^{13}C NMR, 101 MHz, $CDCl_3$)



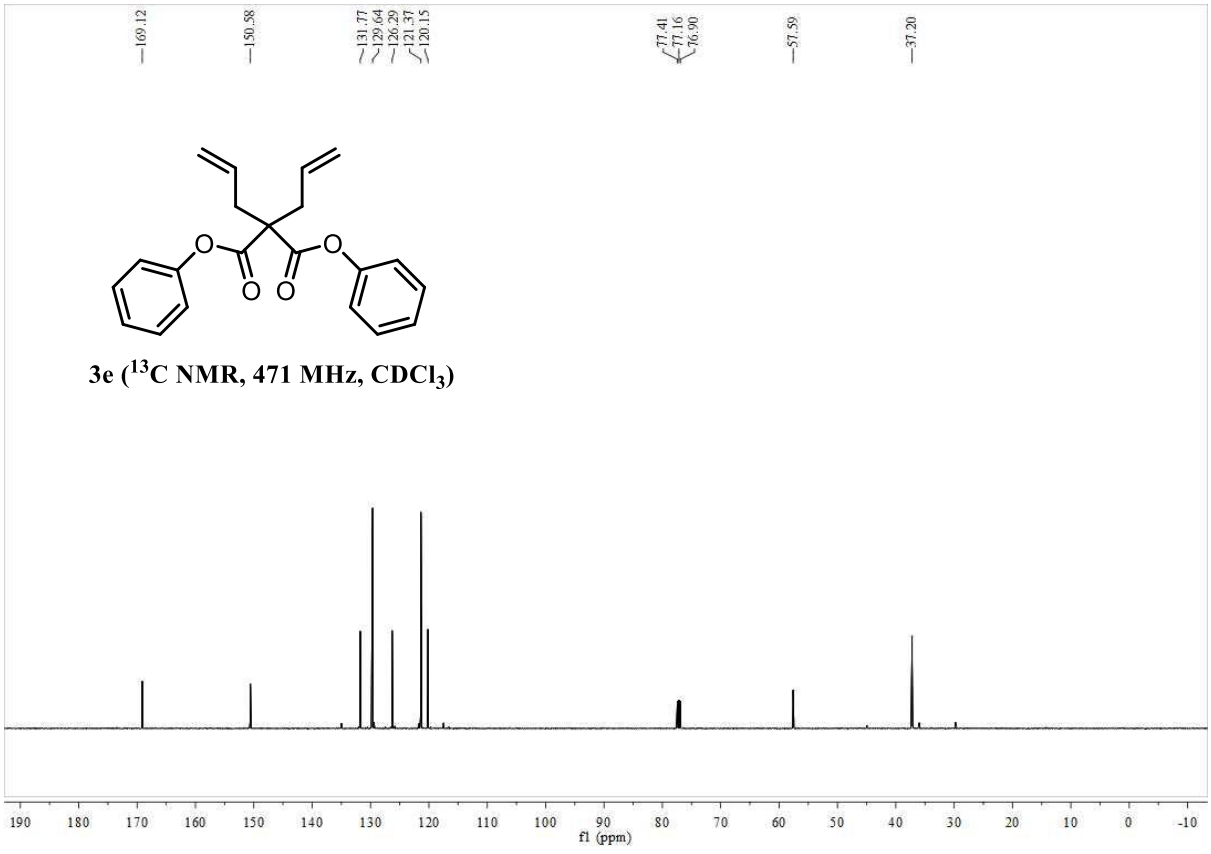
3d (^{1}H NMR, 500 MHz, $CDCl_3$)



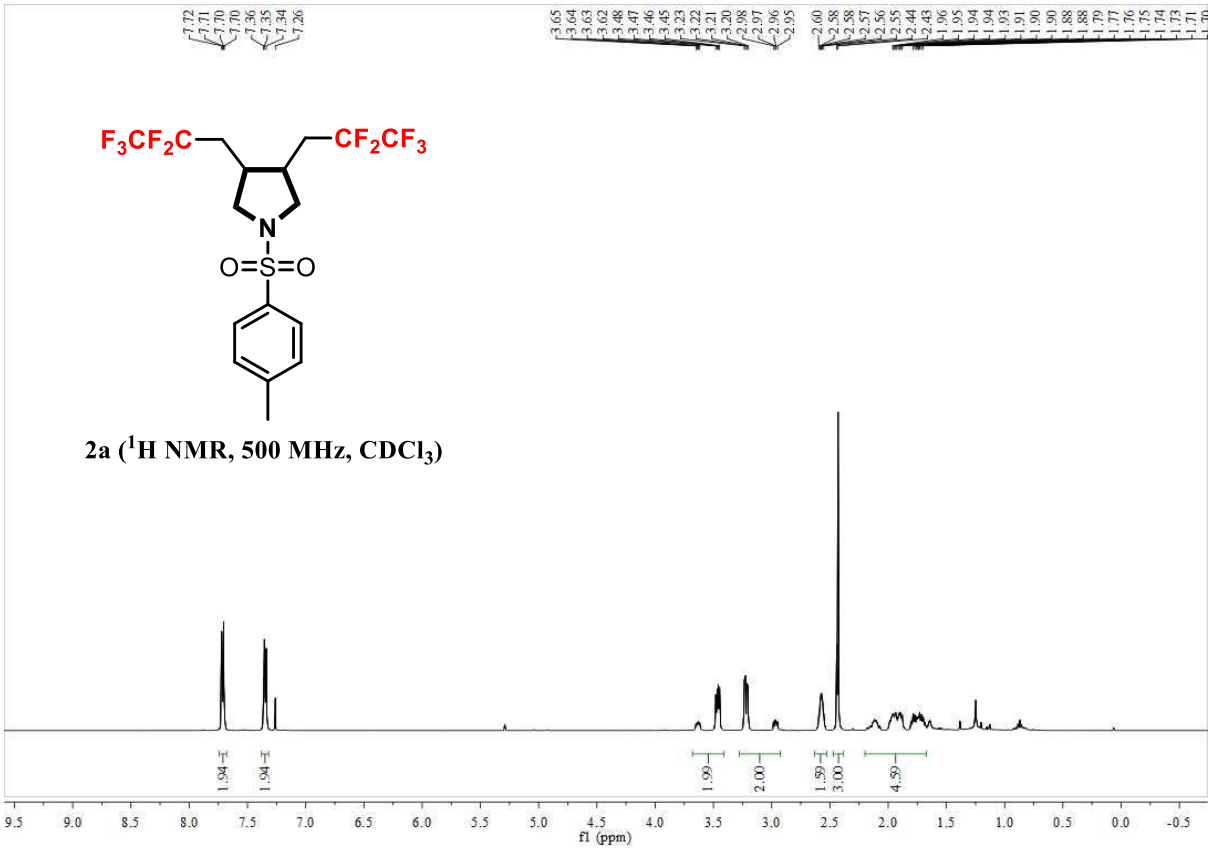
3d (^{13}C NMR, 126 MHz, $CDCl_3$)



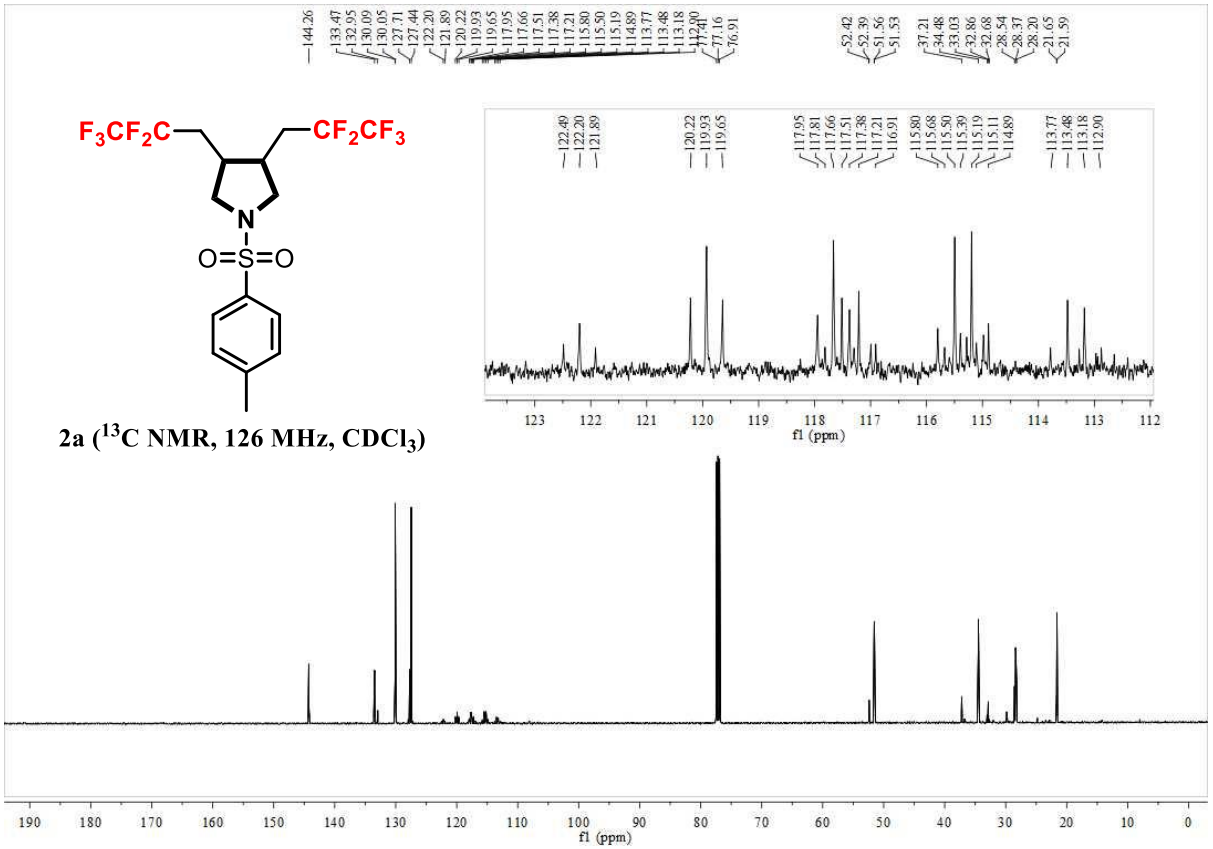
3e (^{1}H NMR, 500 MHz, $CDCl_3$)



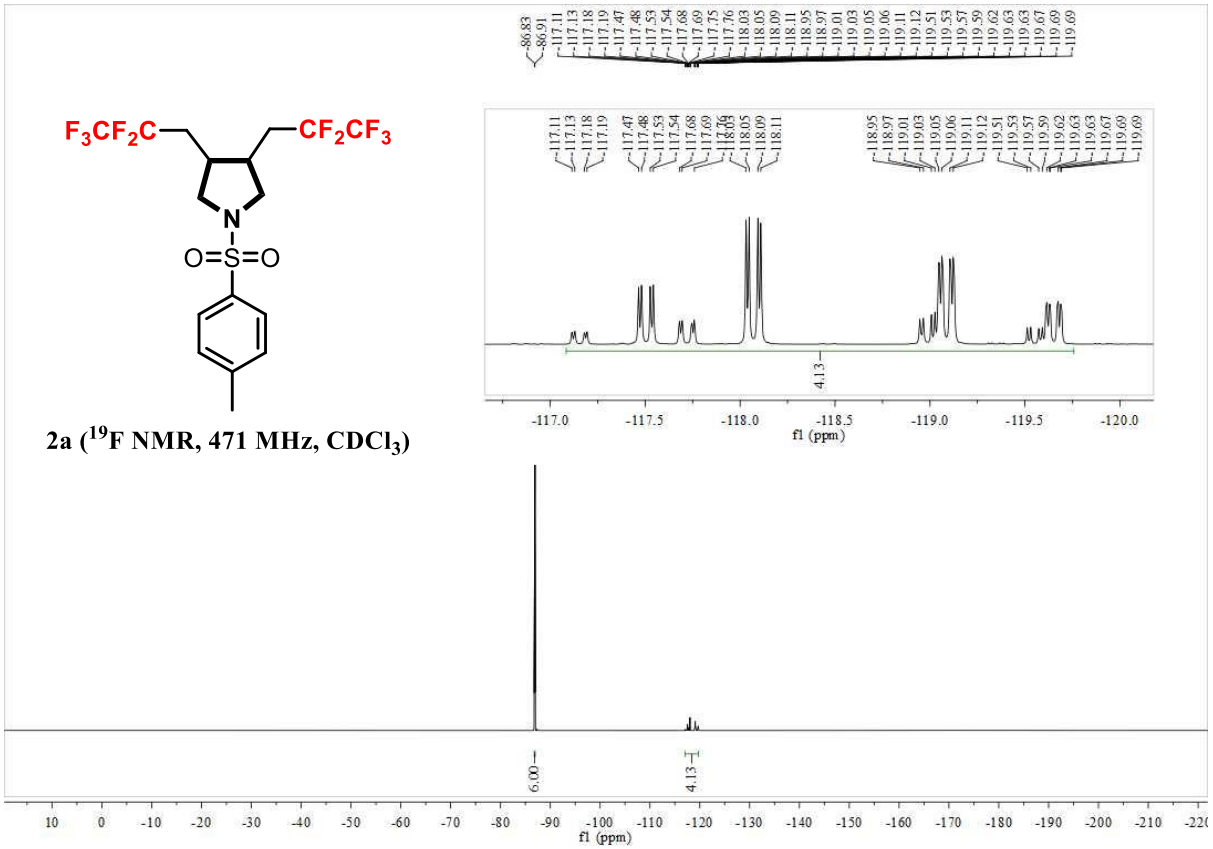
3e (^{13}C NMR, 471 MHz, $CDCl_3$)



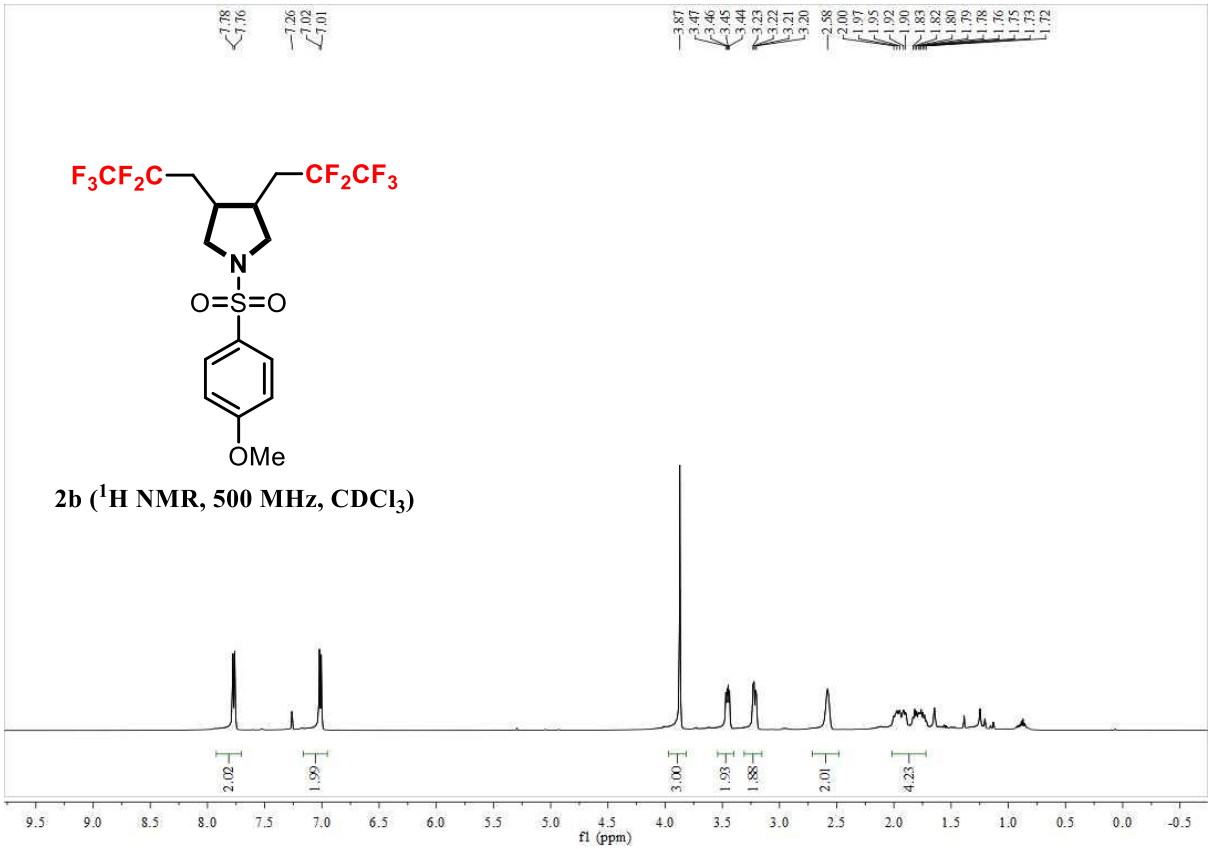
2a (^{1}H NMR, 500 MHz, $CDCl_3$)



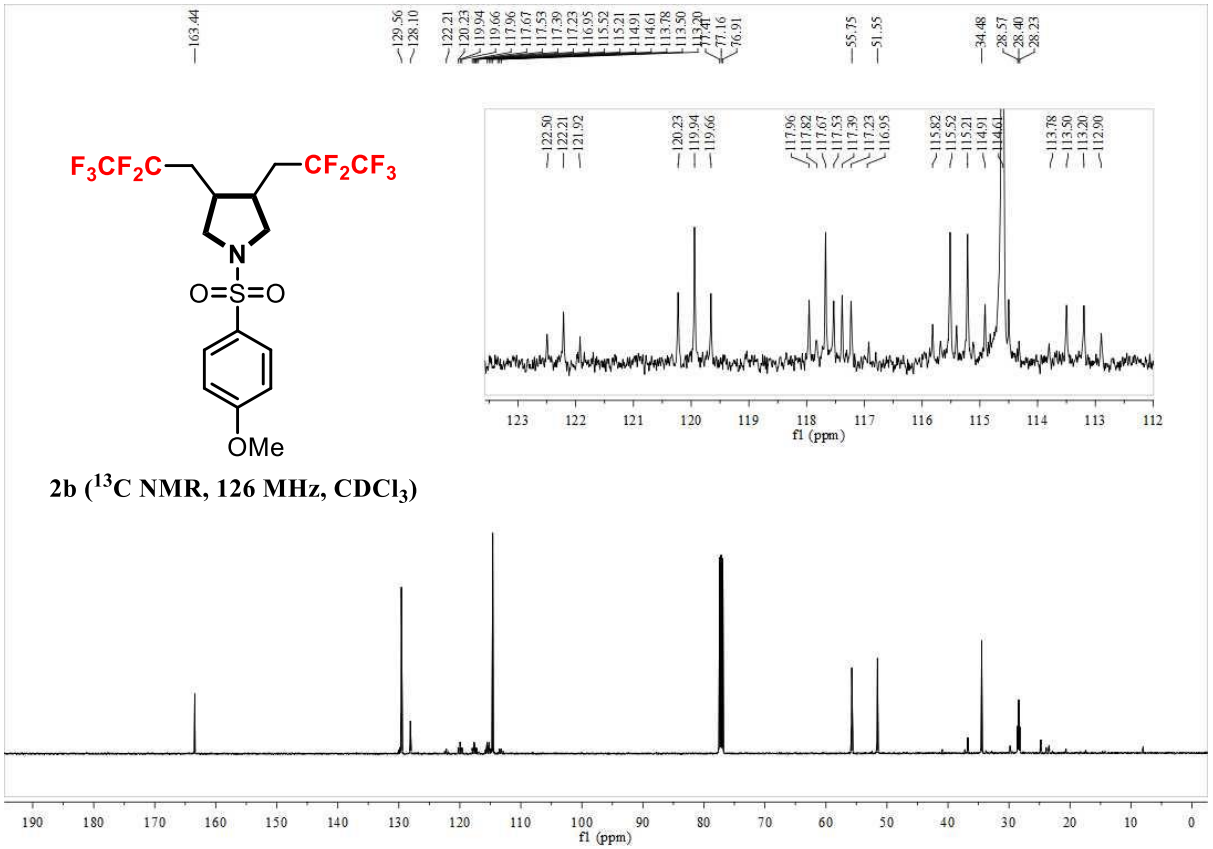
2a (^{13}C NMR, 126 MHz, $CDCl_3$)



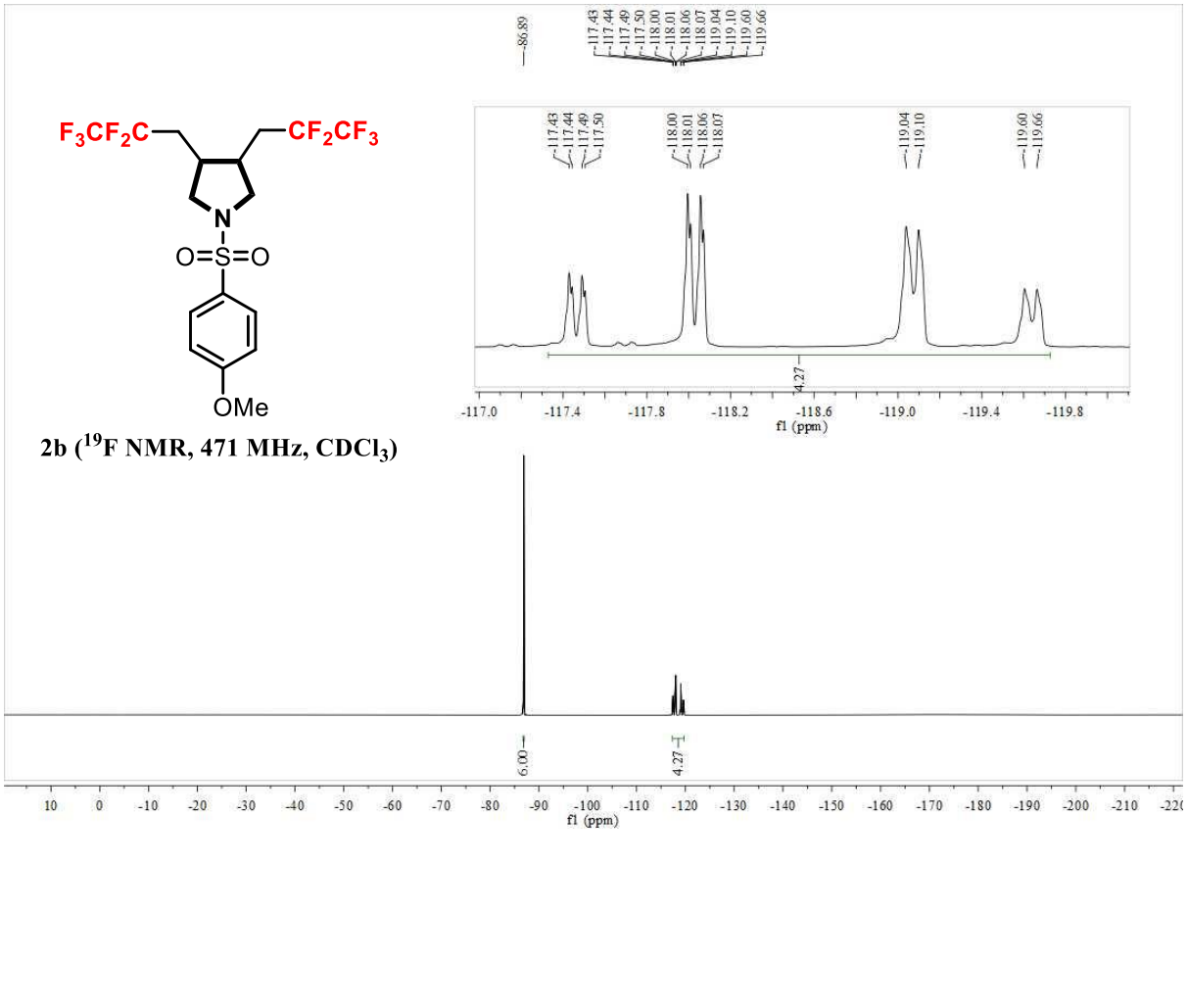
2a (^{19}F NMR, 471 MHz, $CDCl_3$)



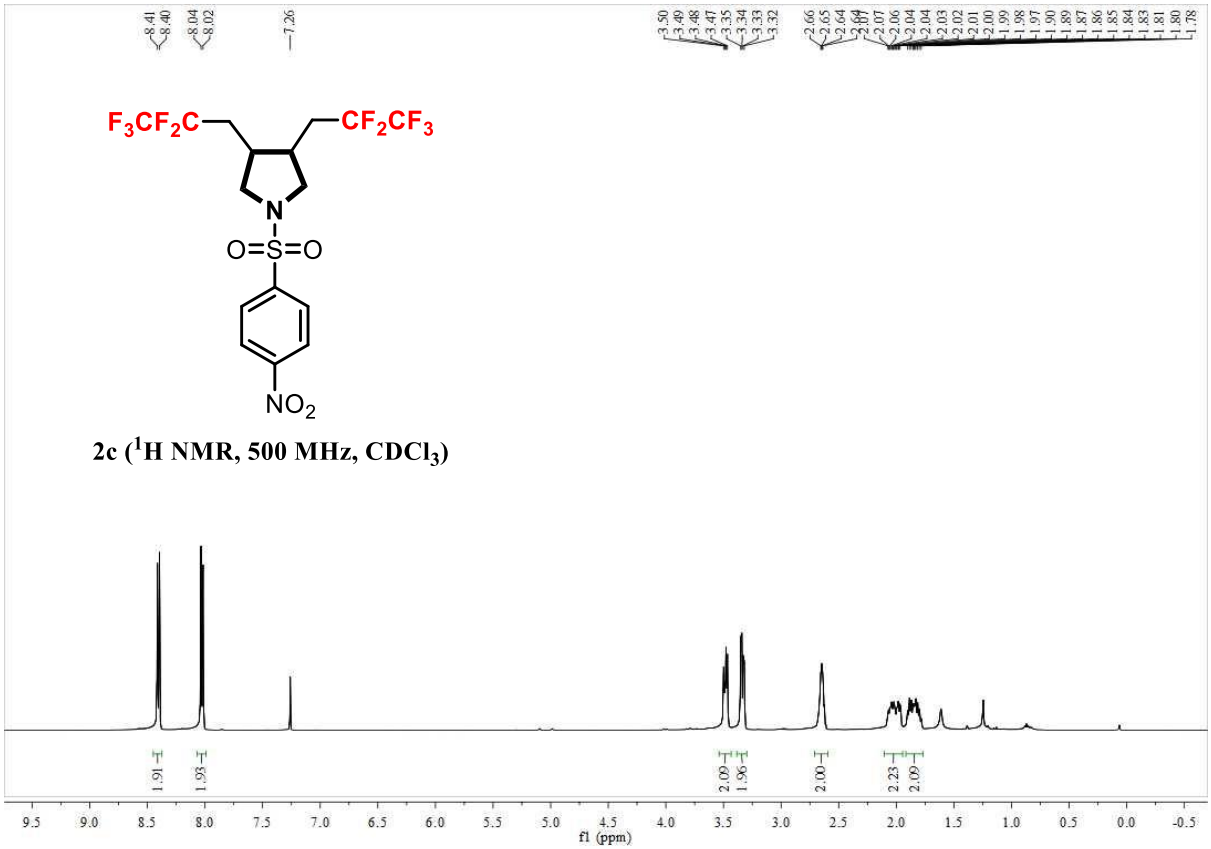
2b (^{1}H NMR, 500 MHz, $CDCl_3$)



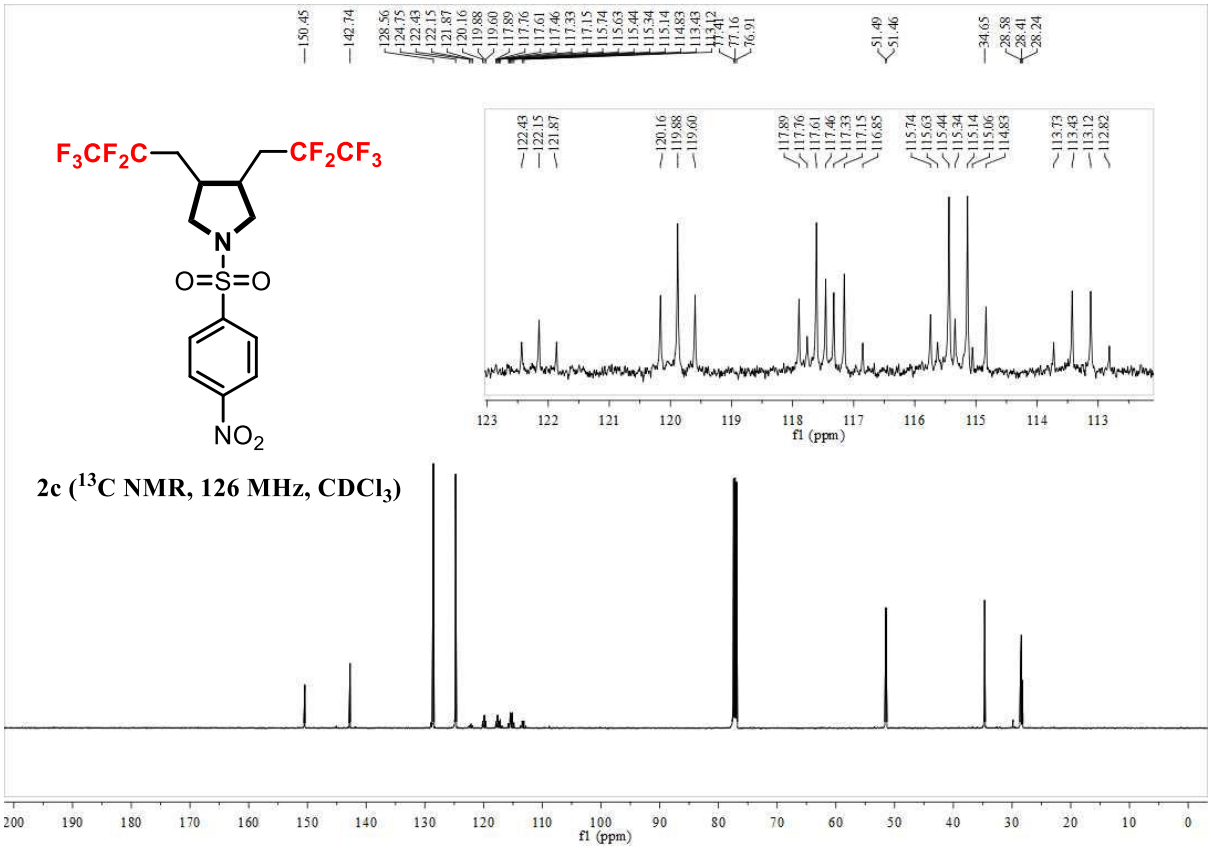
2b (^{13}C NMR, 126 MHz, $CDCl_3$)



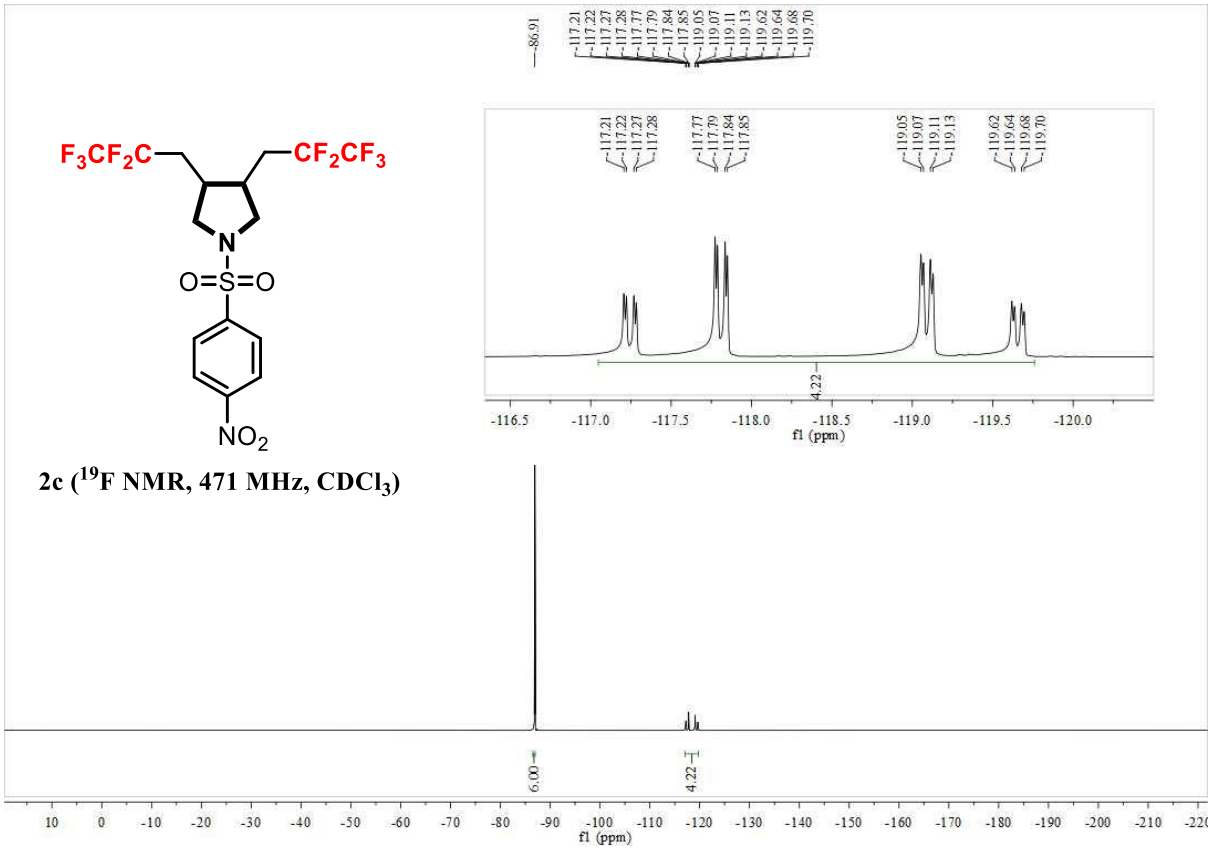
2b (^{19}F NMR, 471 MHz, $CDCl_3$)



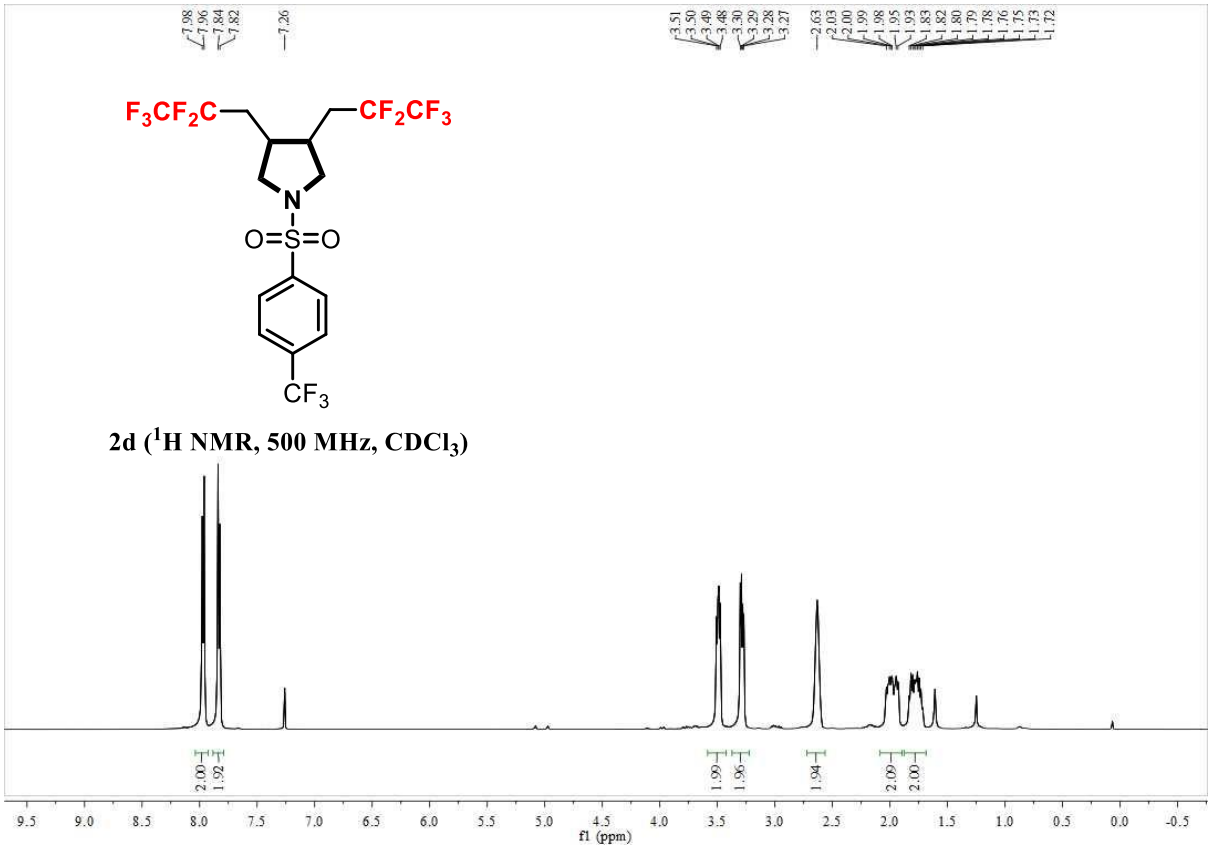
2c (^{1}H NMR, 500 MHz, $CDCl_3$)



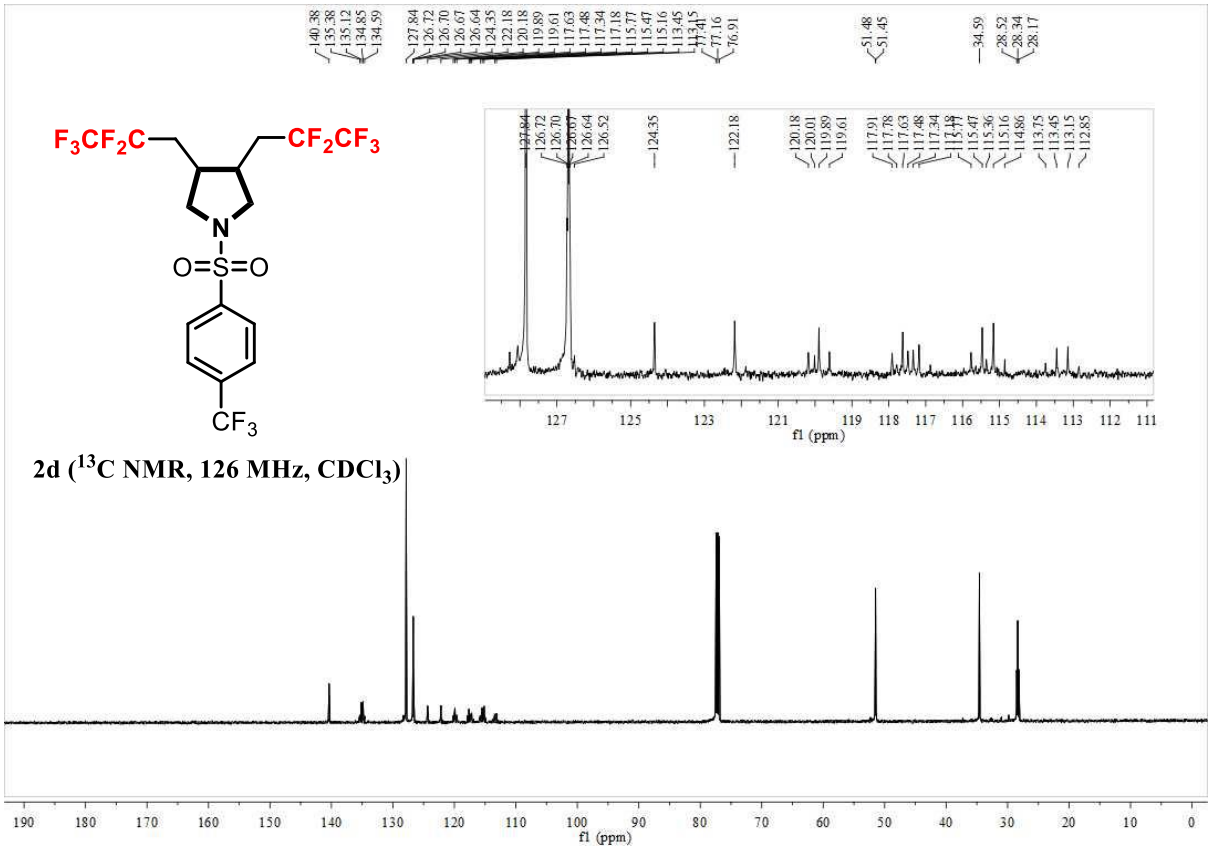
2c (^{13}C NMR, 126 MHz, $CDCl_3$)

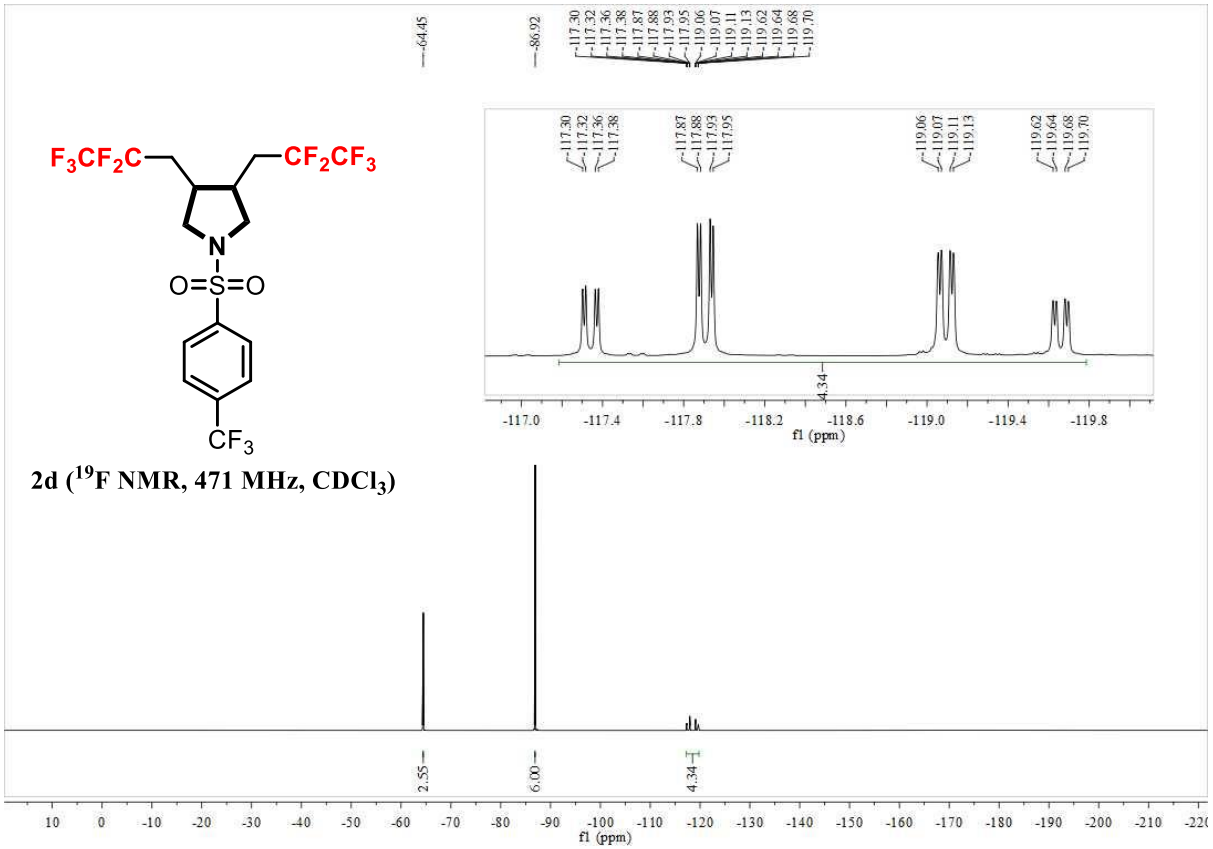


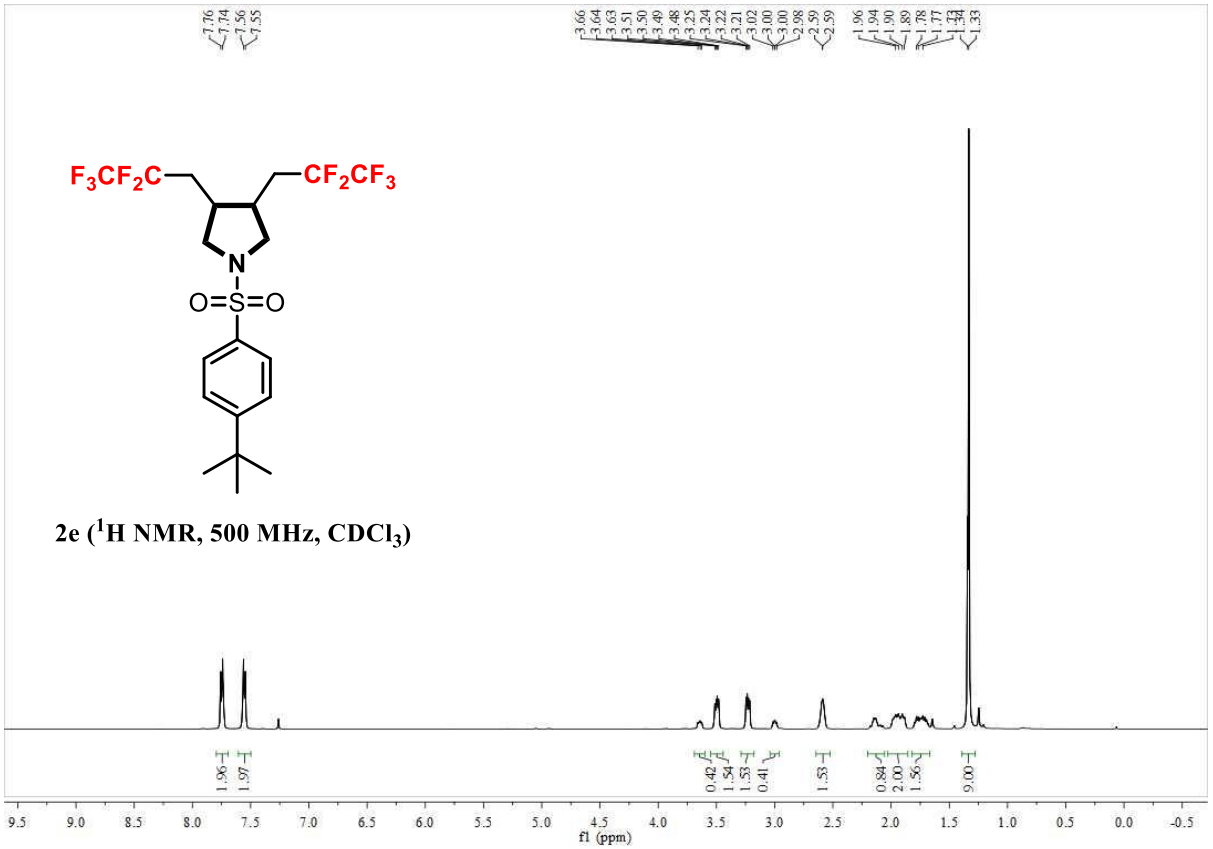
2c (^{19}F NMR, 471 MHz, $CDCl_3$)



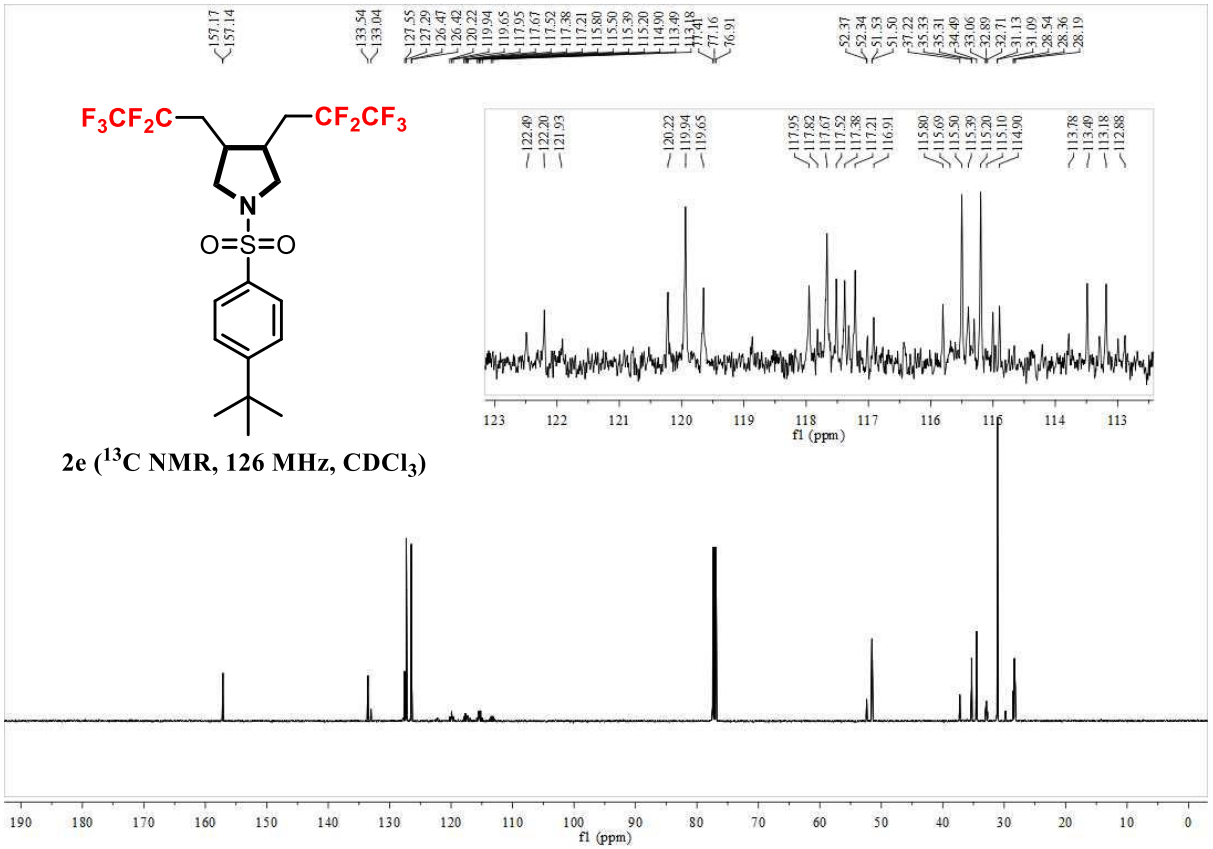
2d (^{1}H NMR, 500 MHz, $CDCl_3$)


F3CF2C
CF2CF3
N
O=S=O
CF3
2d (13C NMR, 126 MHz, CDCl3)
f1 (ppm)

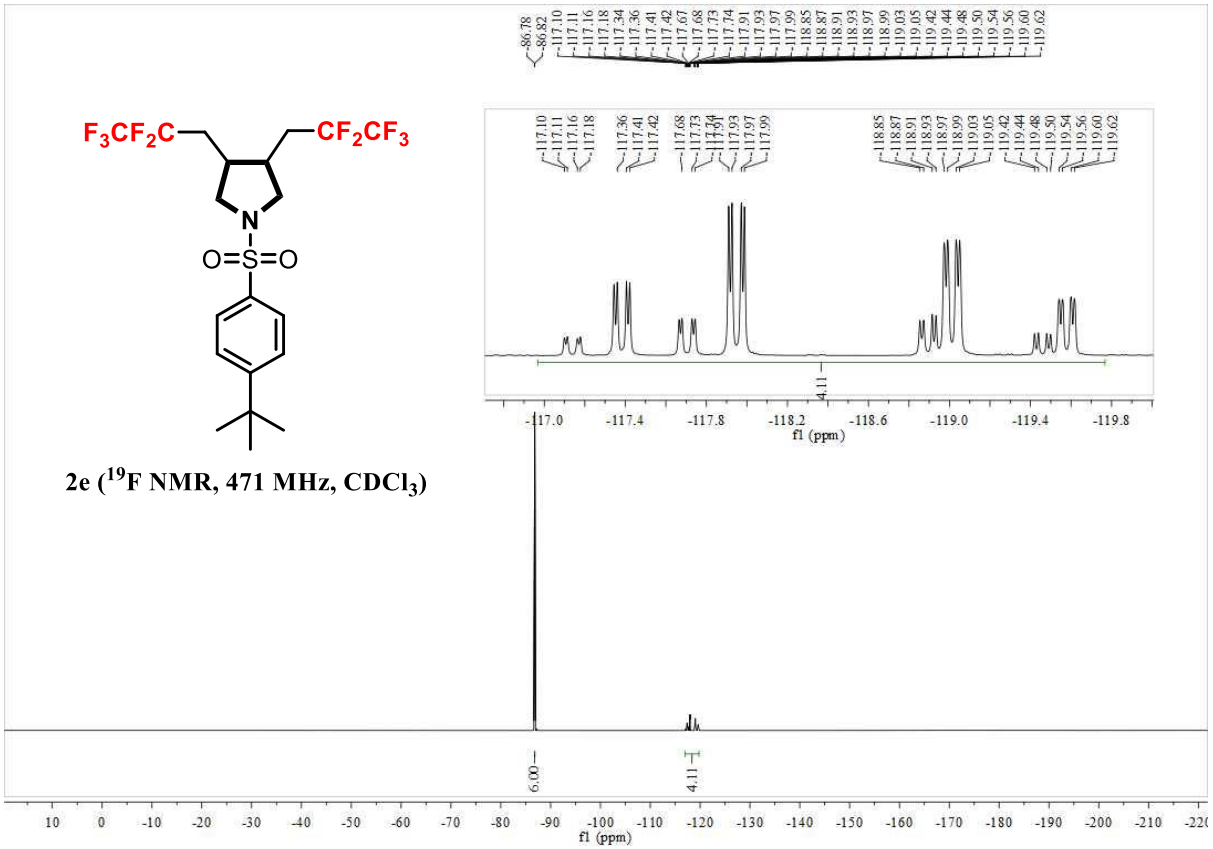

F3CF2C
CF2CF3
N
O=S=O
CF3
2d (19F NMR, 471 MHz, CDCl3)
f1 (ppm)



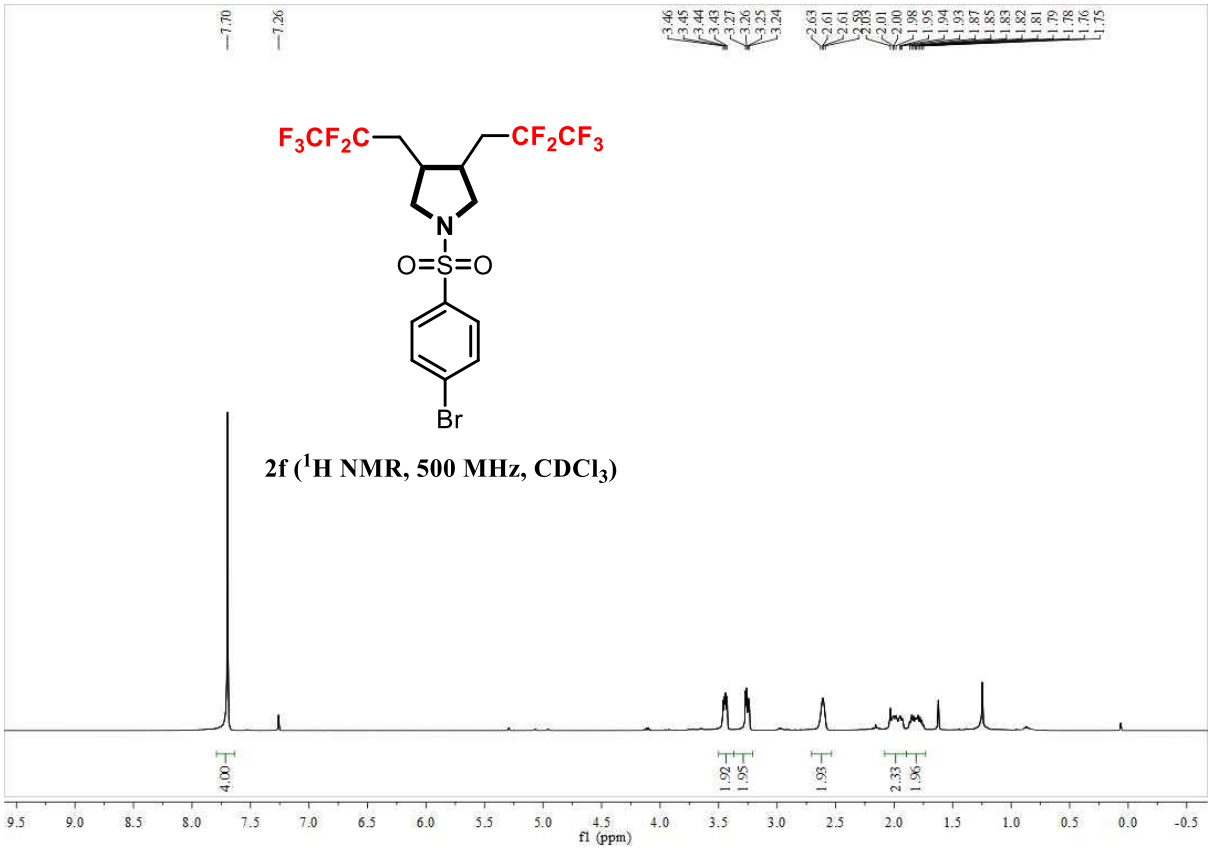
2e (^{1}H NMR, 500 MHz, $CDCl_3$)



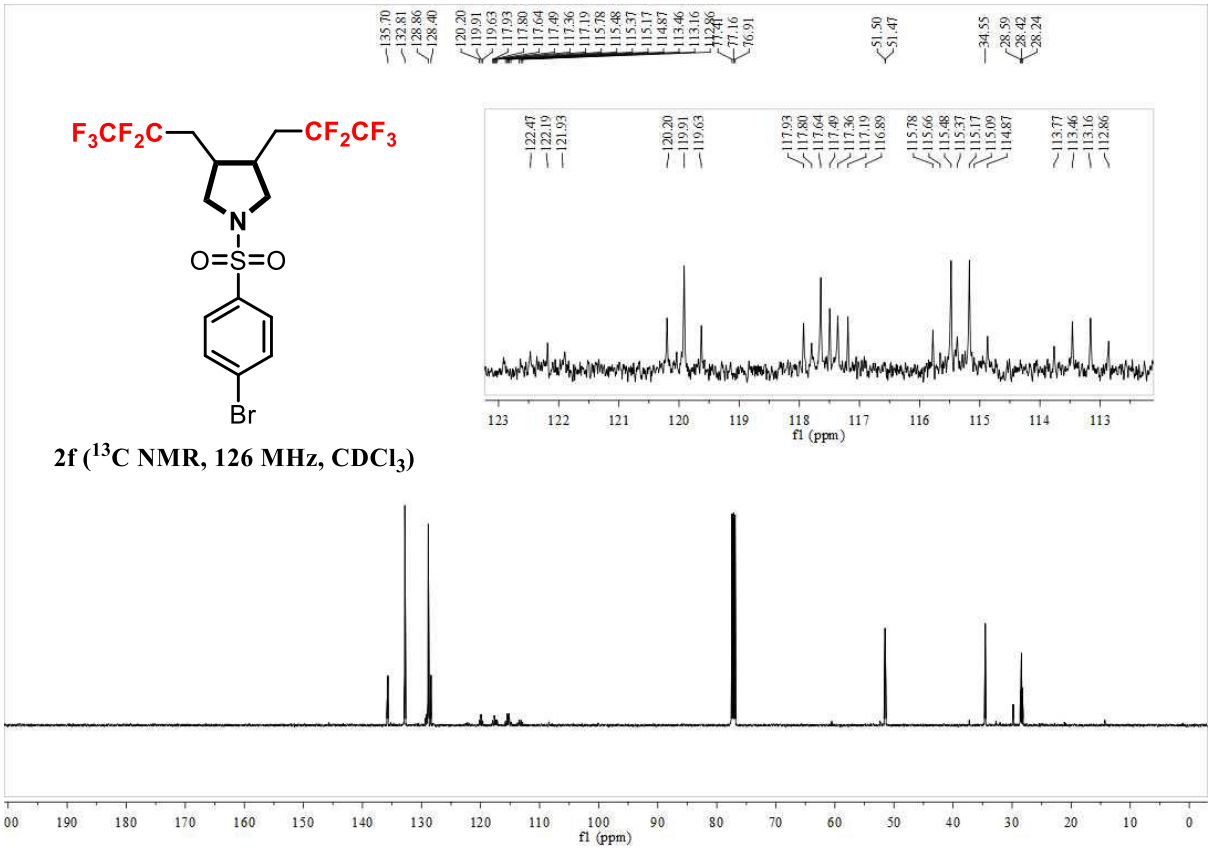
2e (^{13}C NMR, 126 MHz, $CDCl_3$)



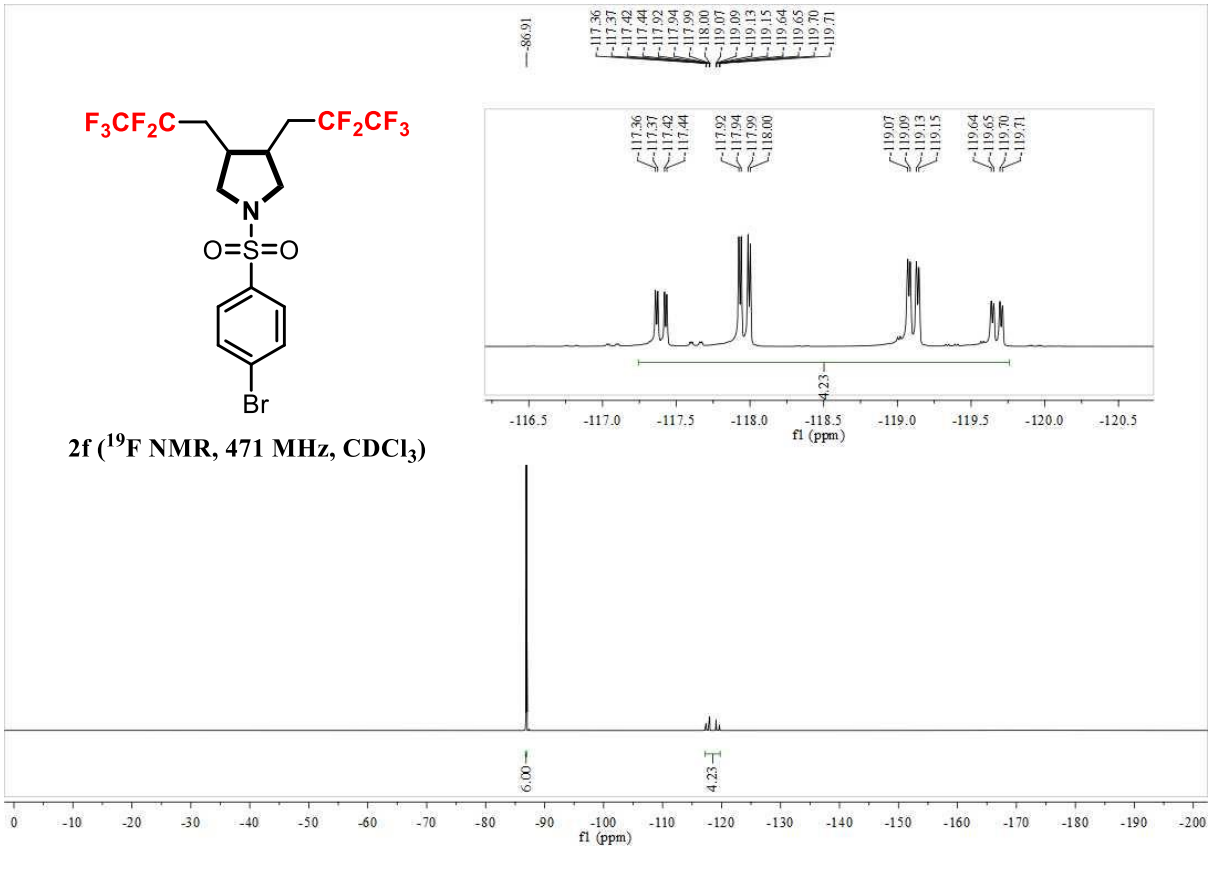
2e (^{19}F NMR, 471 MHz, $CDCl_3$)



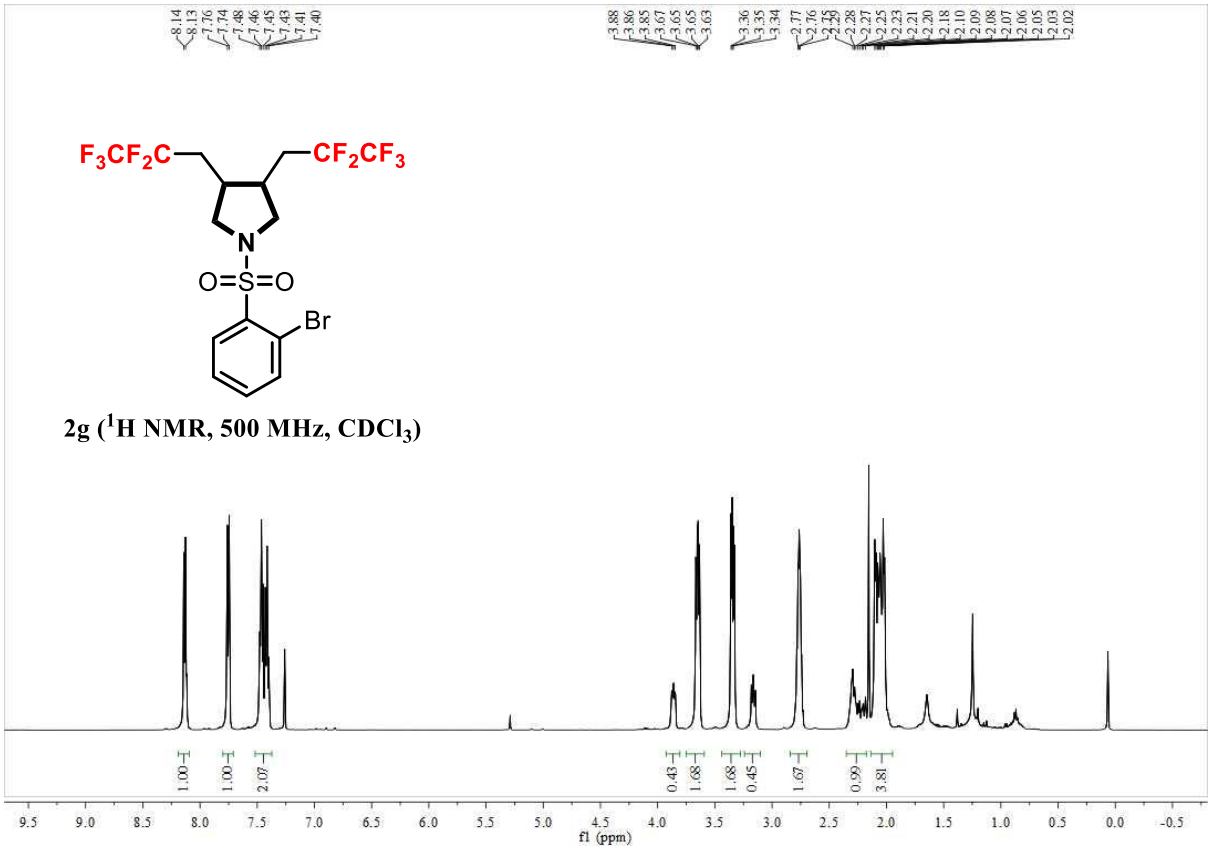
2f (^{1}H NMR, 500 MHz, $CDCl_3$)



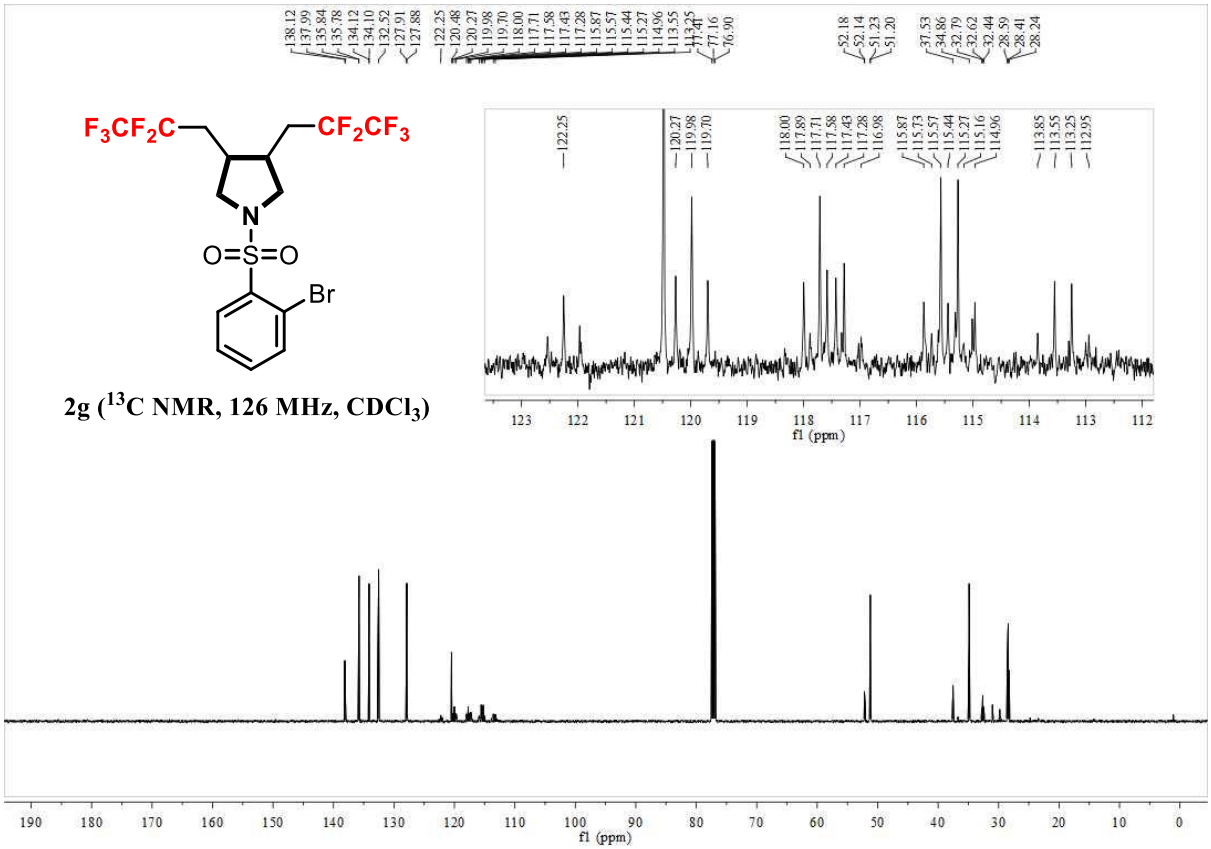
2f (^{13}C NMR, 126 MHz, $CDCl_3$)



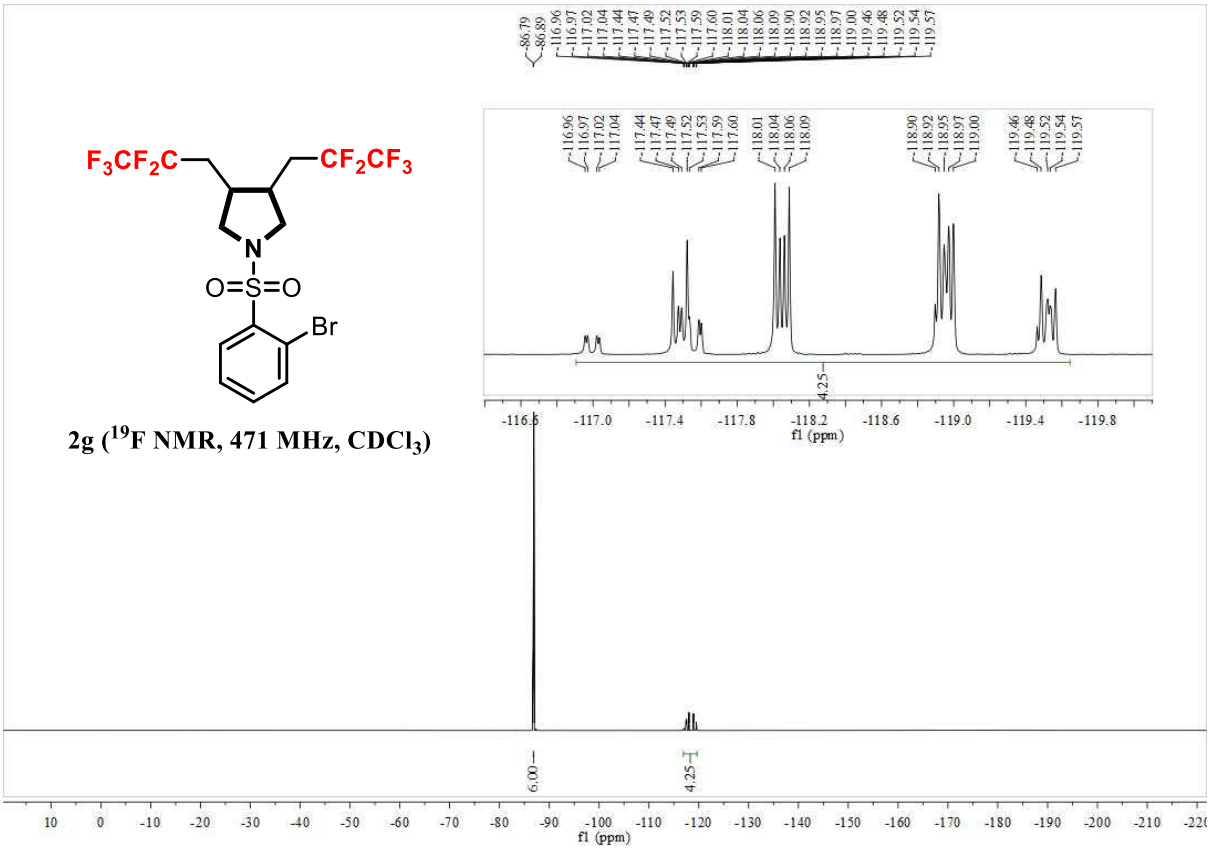
2f (^{19}F NMR, 471 MHz, $CDCl_3$)



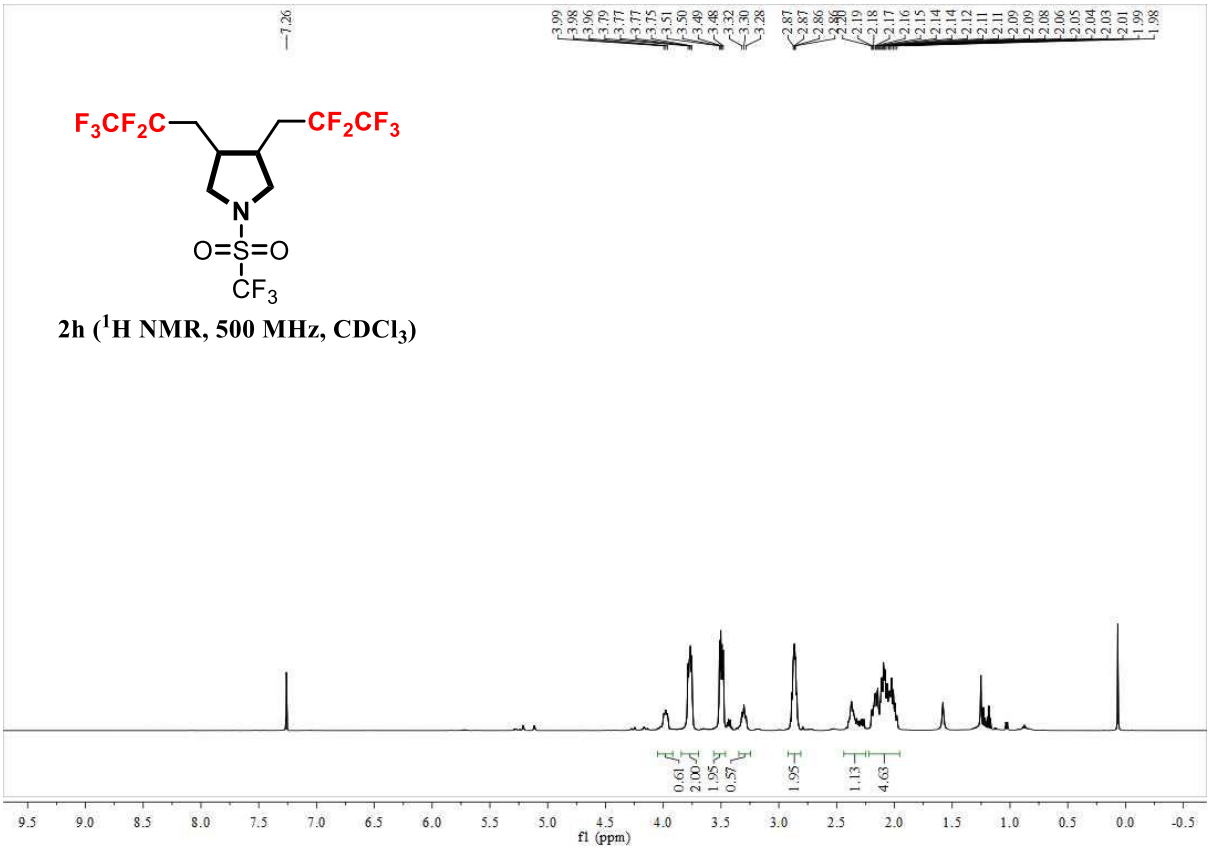
2g (^{1}H NMR, 500 MHz, $CDCl_3$)



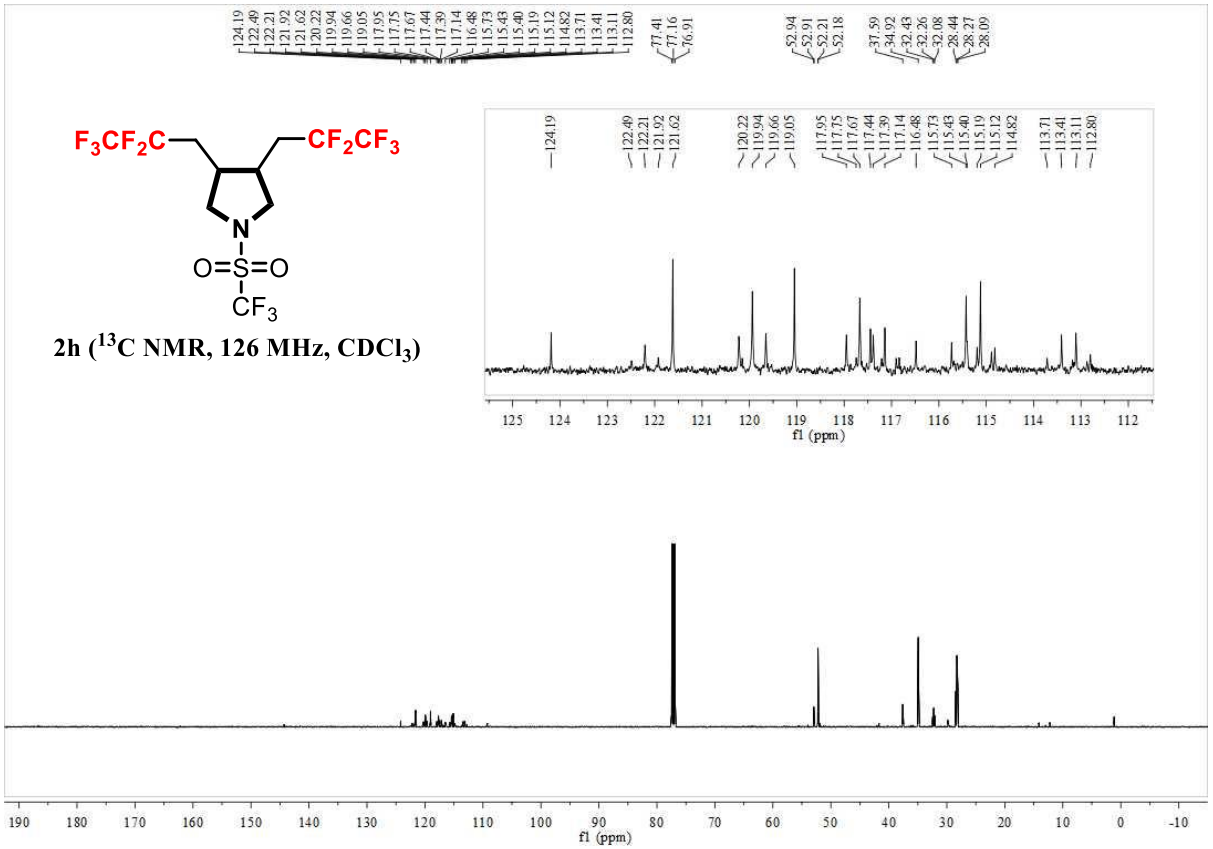
2g (^{13}C NMR, 126 MHz, $CDCl_3$)



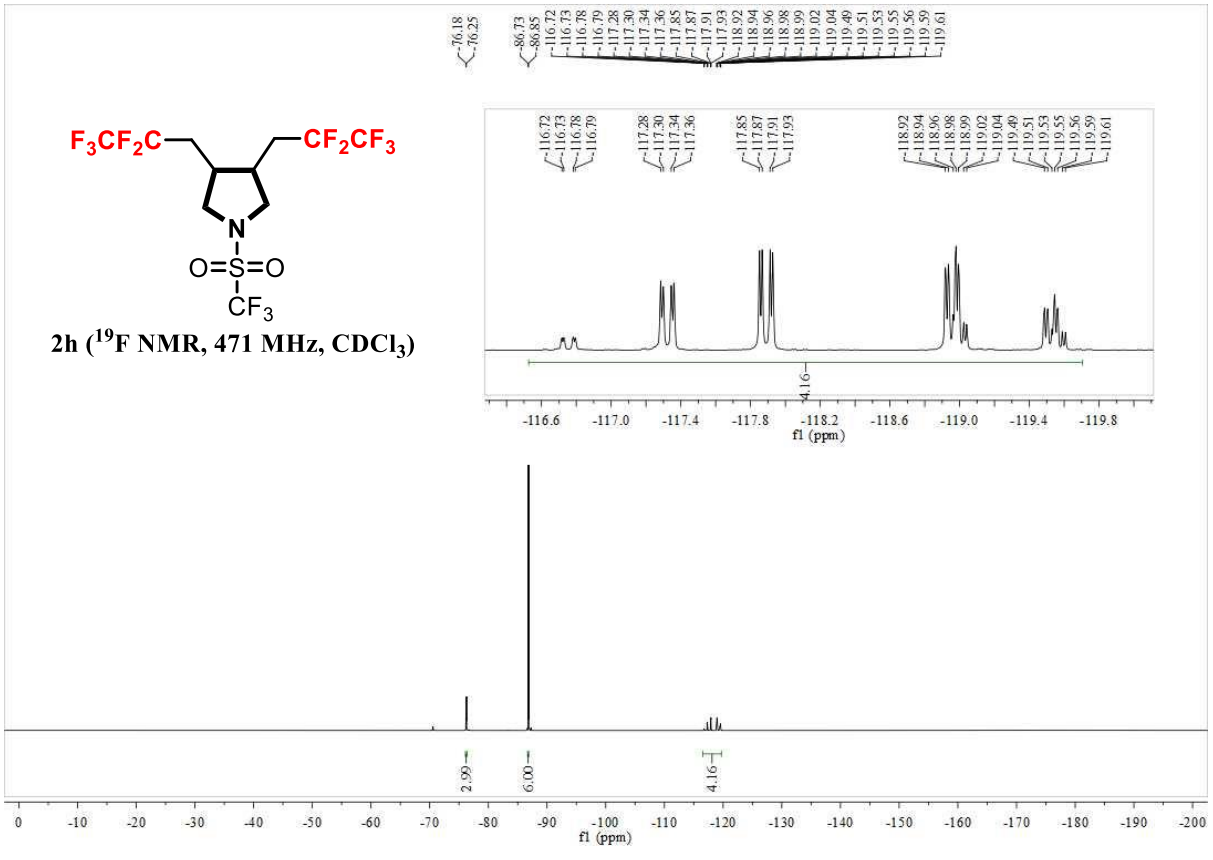
2g (^{19}F NMR, 471 MHz, $CDCl_3$)



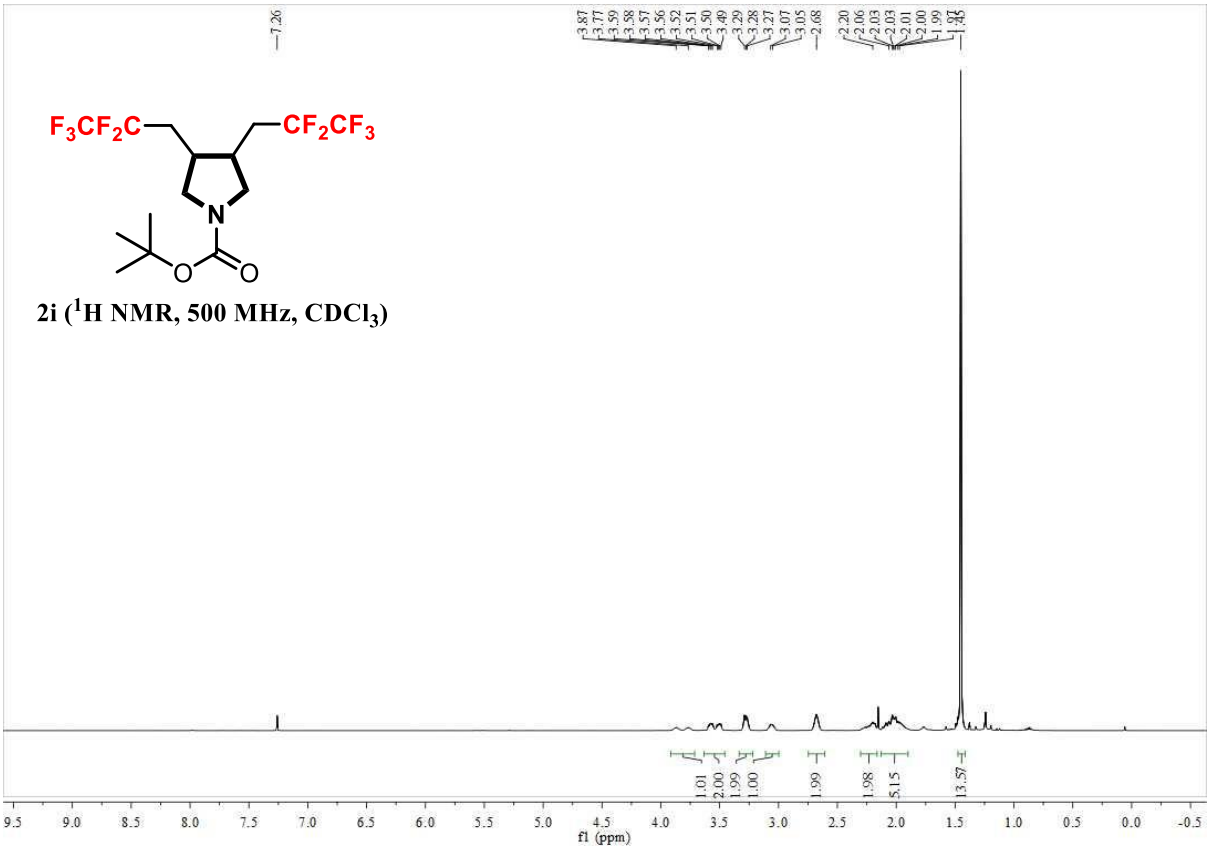
2h (^{1}H NMR, 500 MHz, $CDCl_3$)



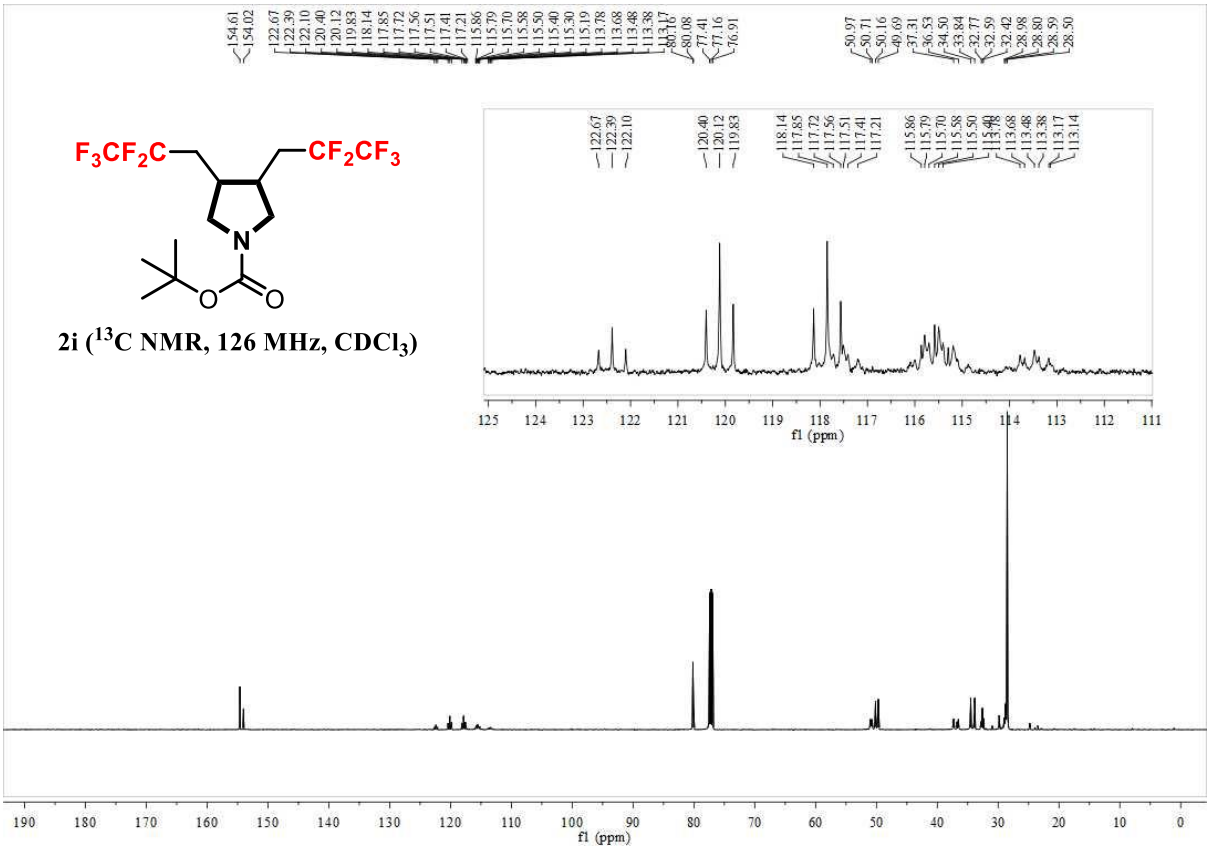
2h (^{13}C NMR, 126 MHz, $CDCl_3$)



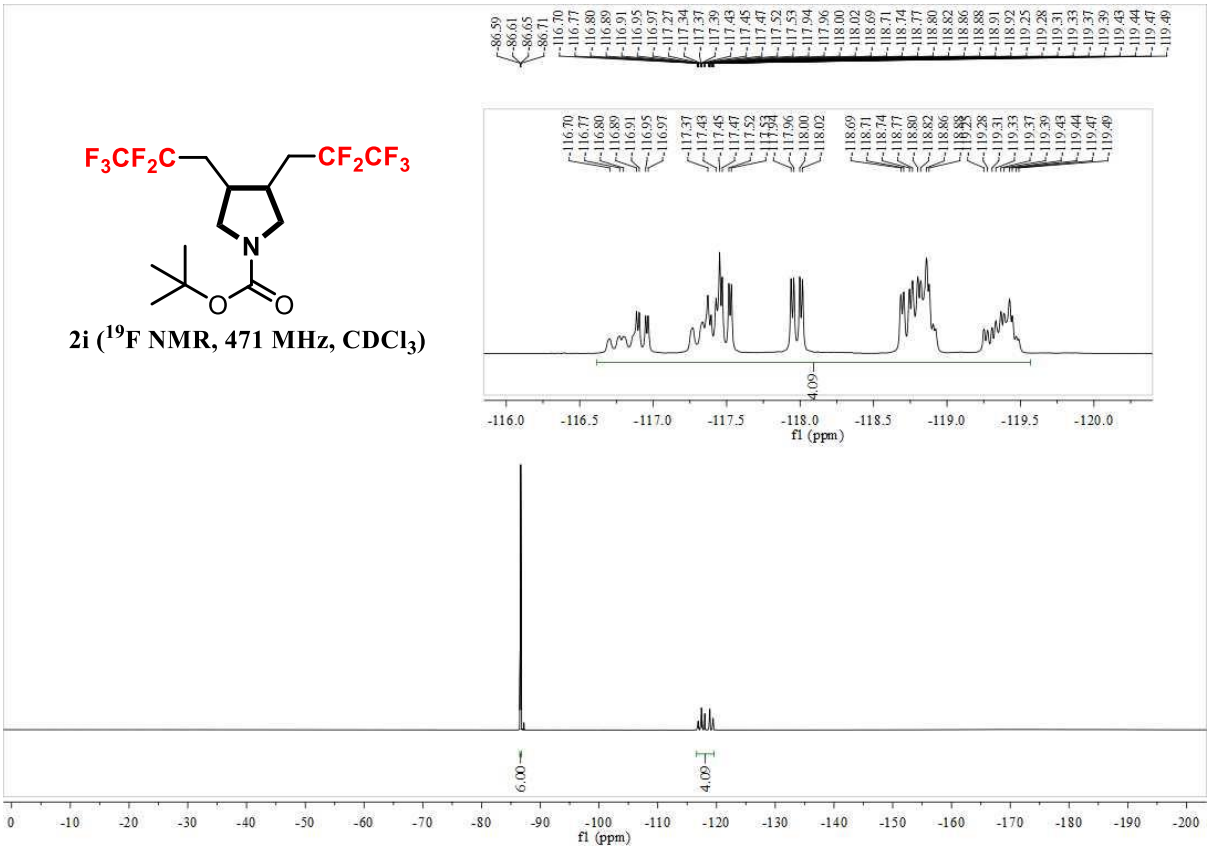
2h (^{19}F NMR, 471 MHz, $CDCl_3$)



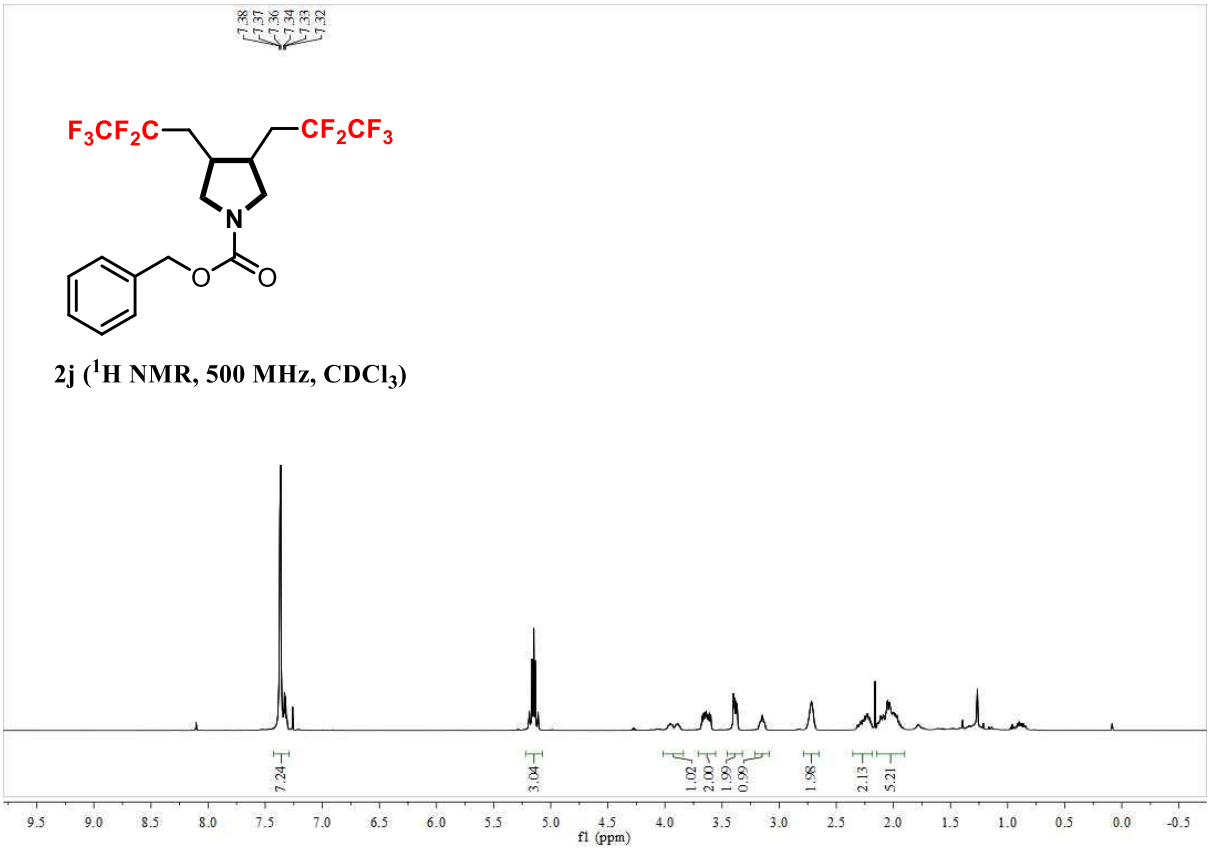
2i (^{1}H NMR, 500 MHz, $CDCl_3$)



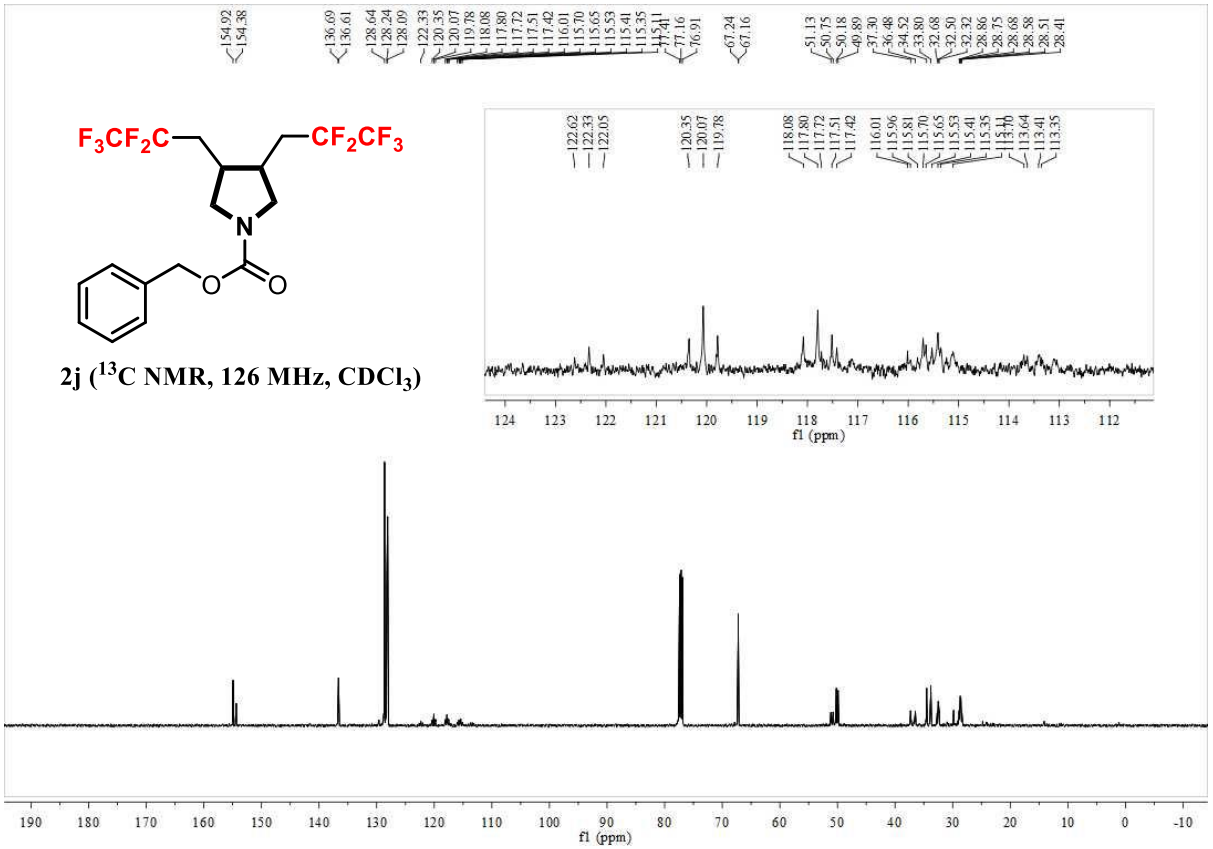
2i (^{13}C NMR, 126 MHz, $CDCl_3$)



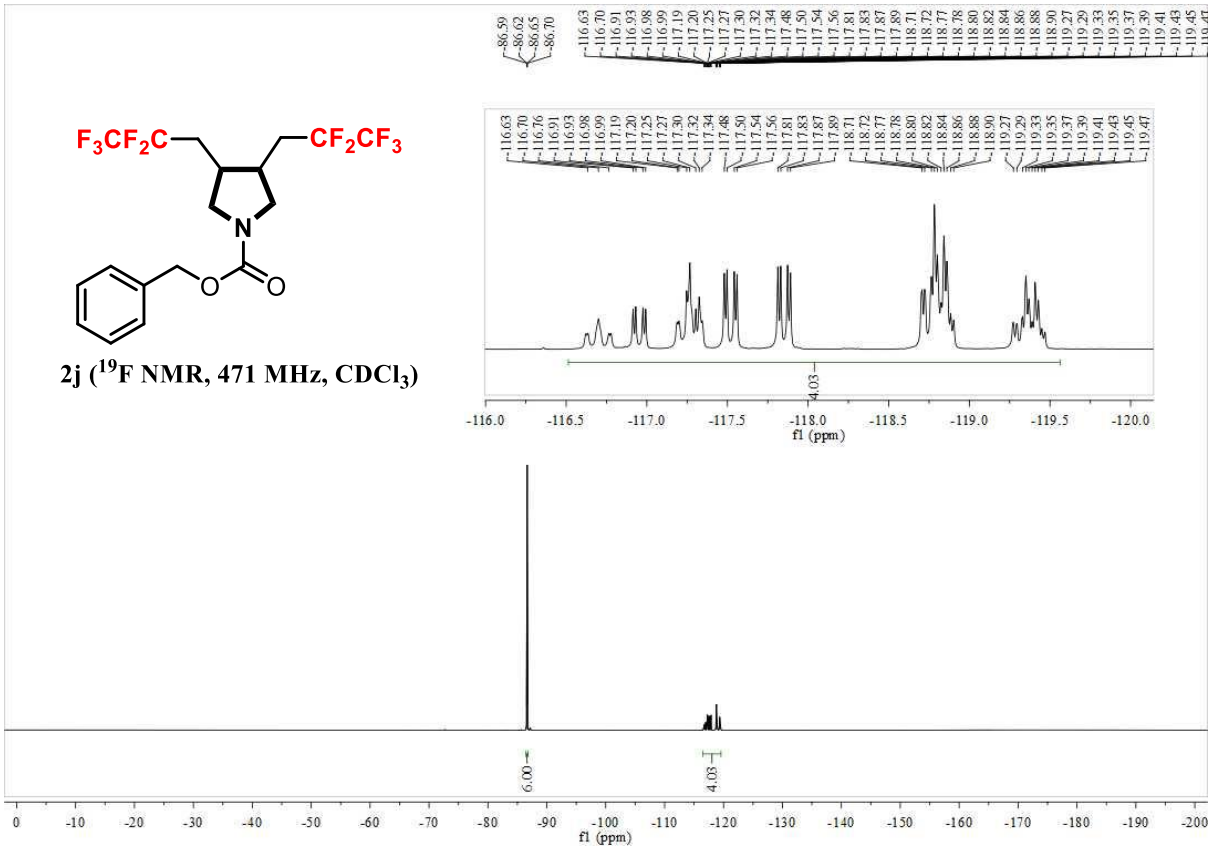
2i (^{19}F NMR, 471 MHz, $CDCl_3$)



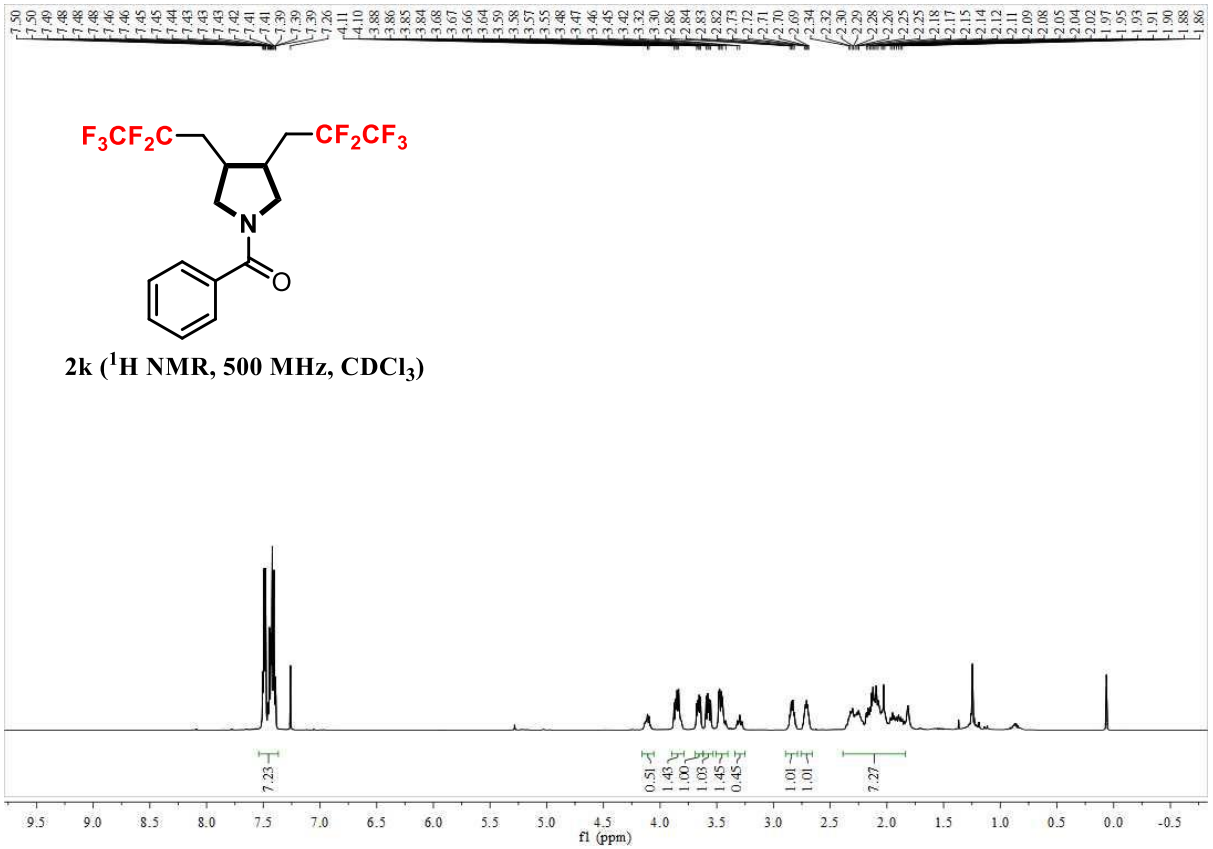
2j (^{1}H NMR, 500 MHz, $CDCl_3$)



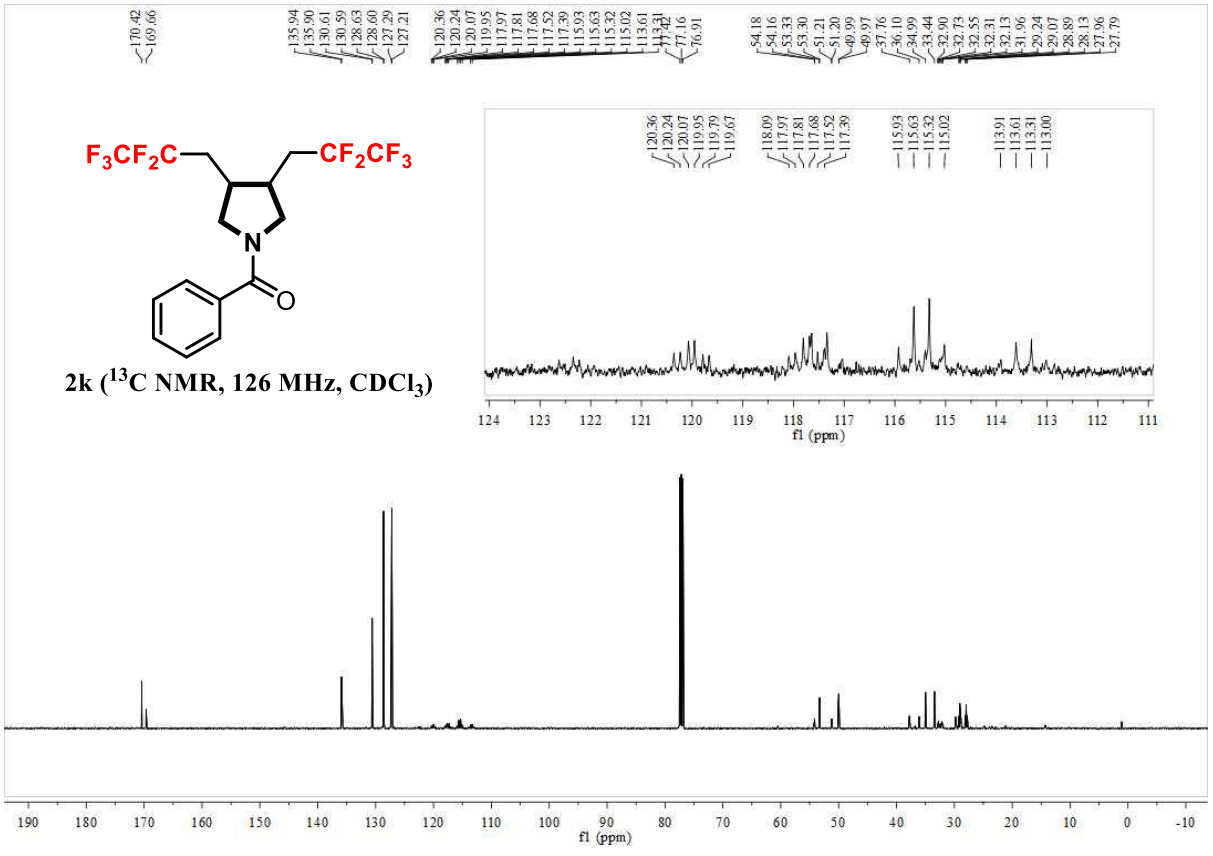
2j (^{13}C NMR, 126 MHz, $CDCl_3$)



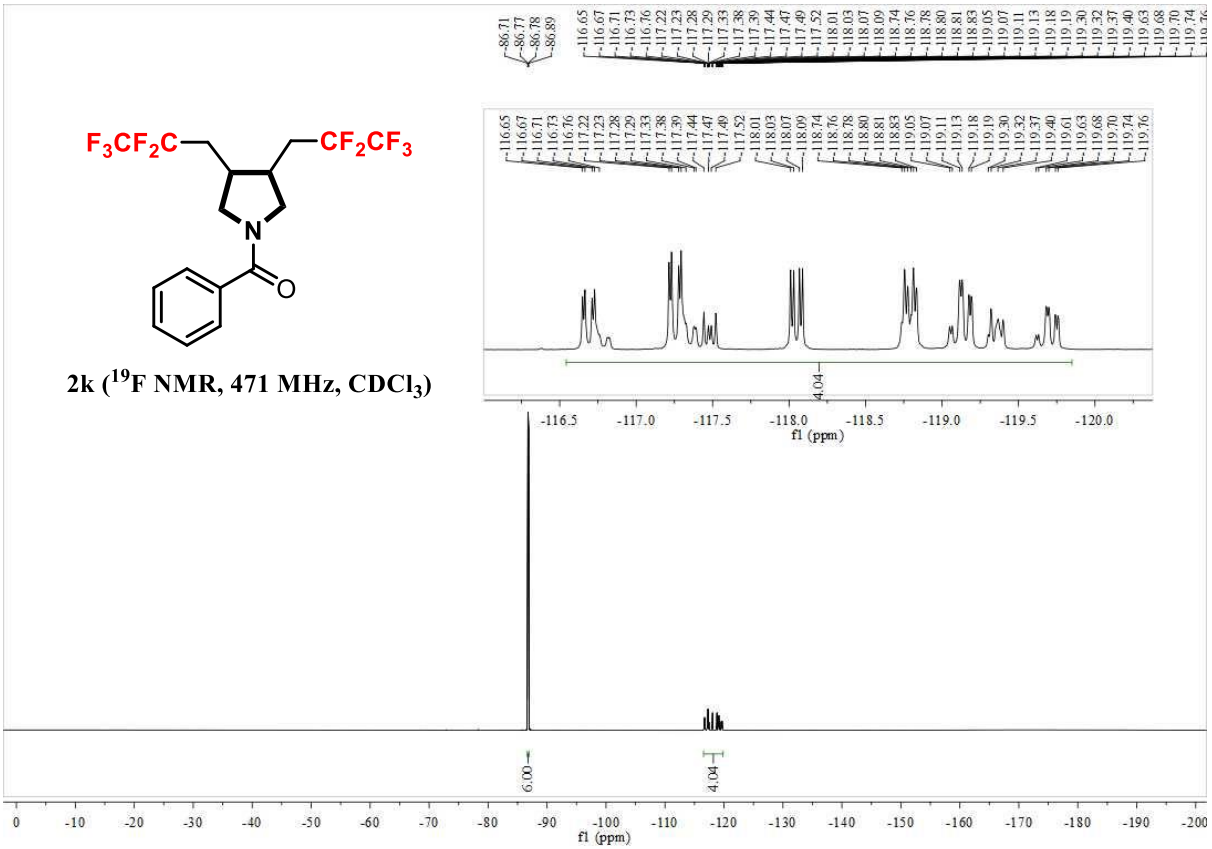
2j (^{19}F NMR, 471 MHz, $CDCl_3$)



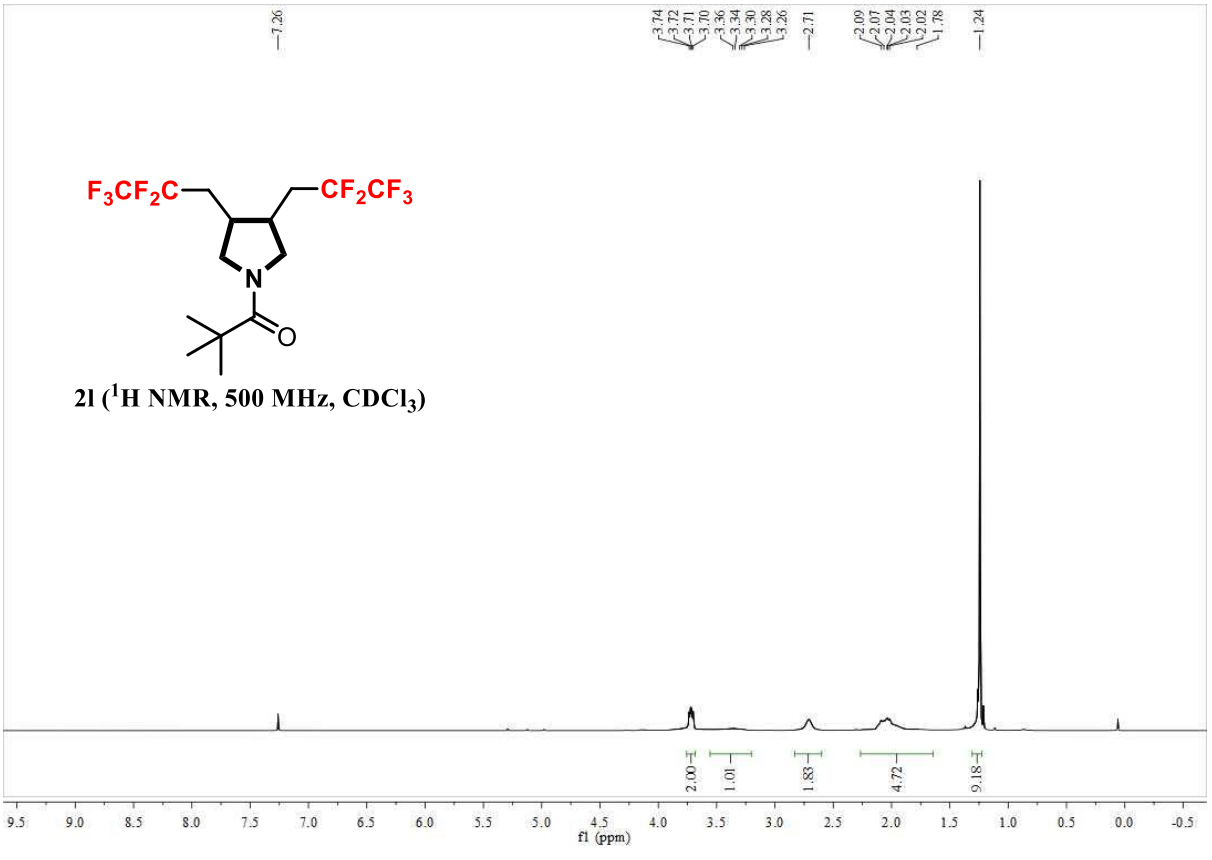
2k (^{1}H NMR, 500 MHz, $CDCl_3$)



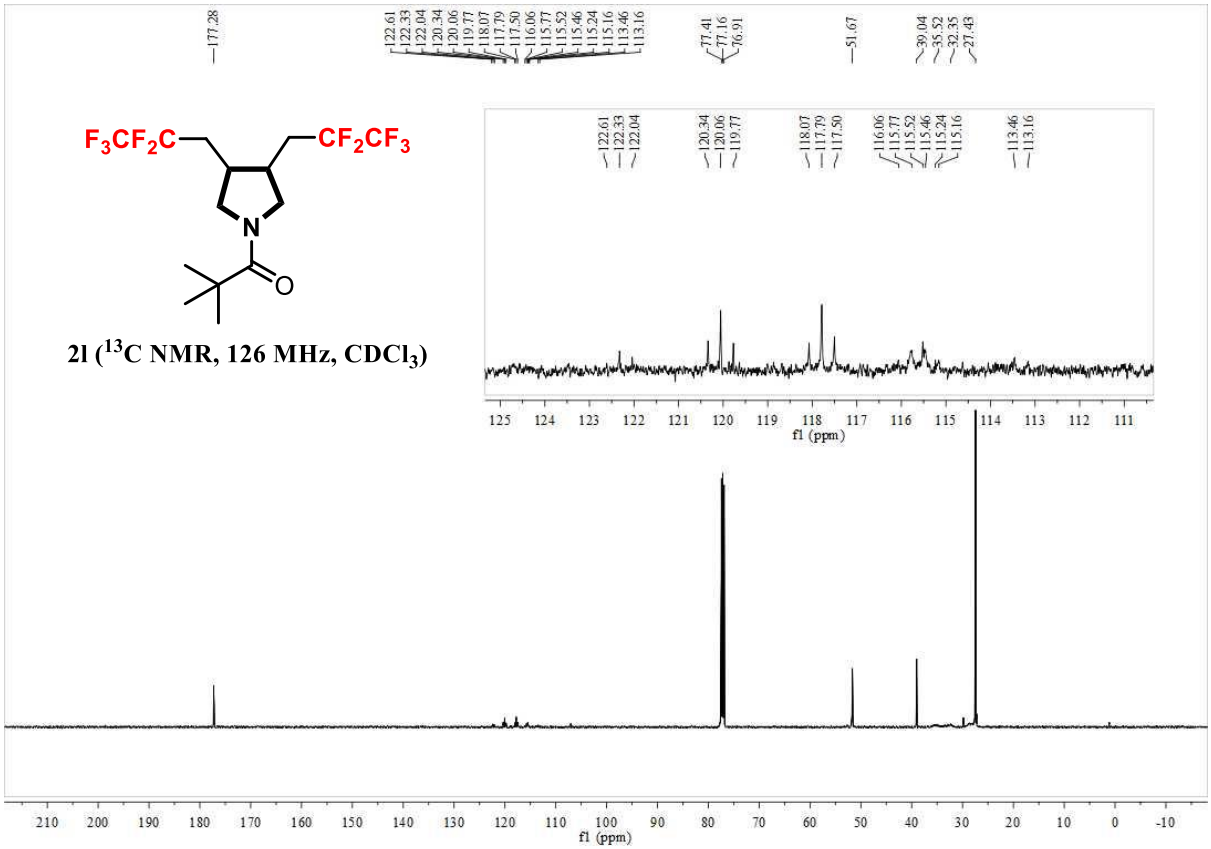
2k (^{13}C NMR, 126 MHz, $CDCl_3$)



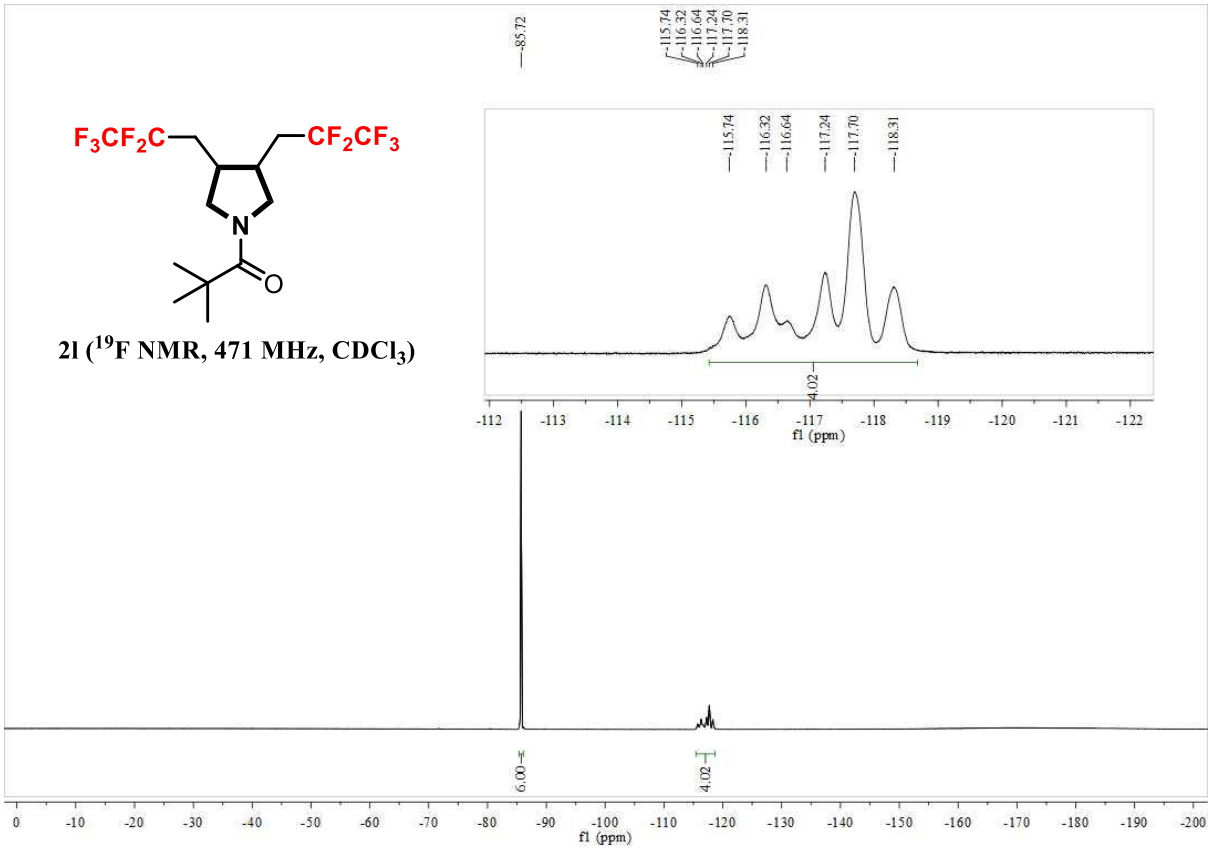
2k (^{19}F NMR, 471 MHz, $CDCl_3$)



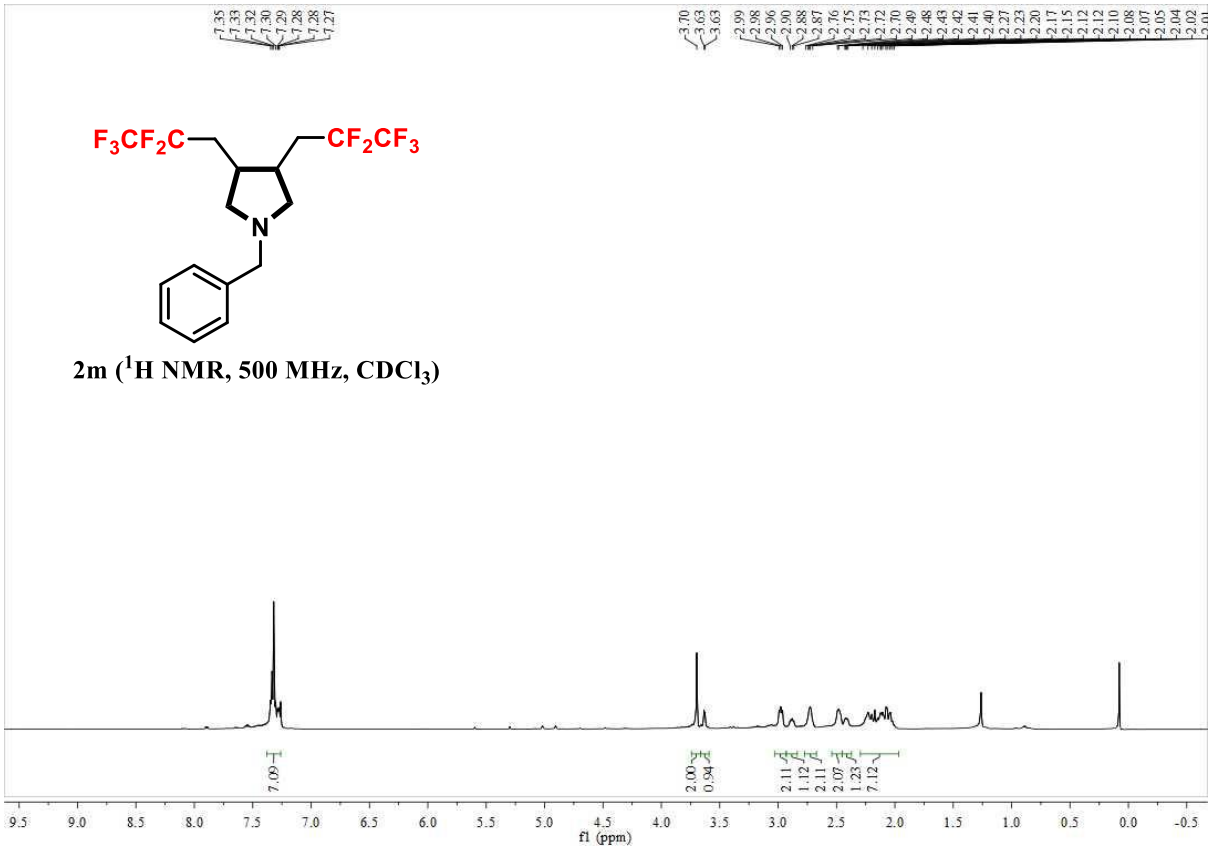
2l (^{1}H NMR, 500 MHz, $CDCl_3$)

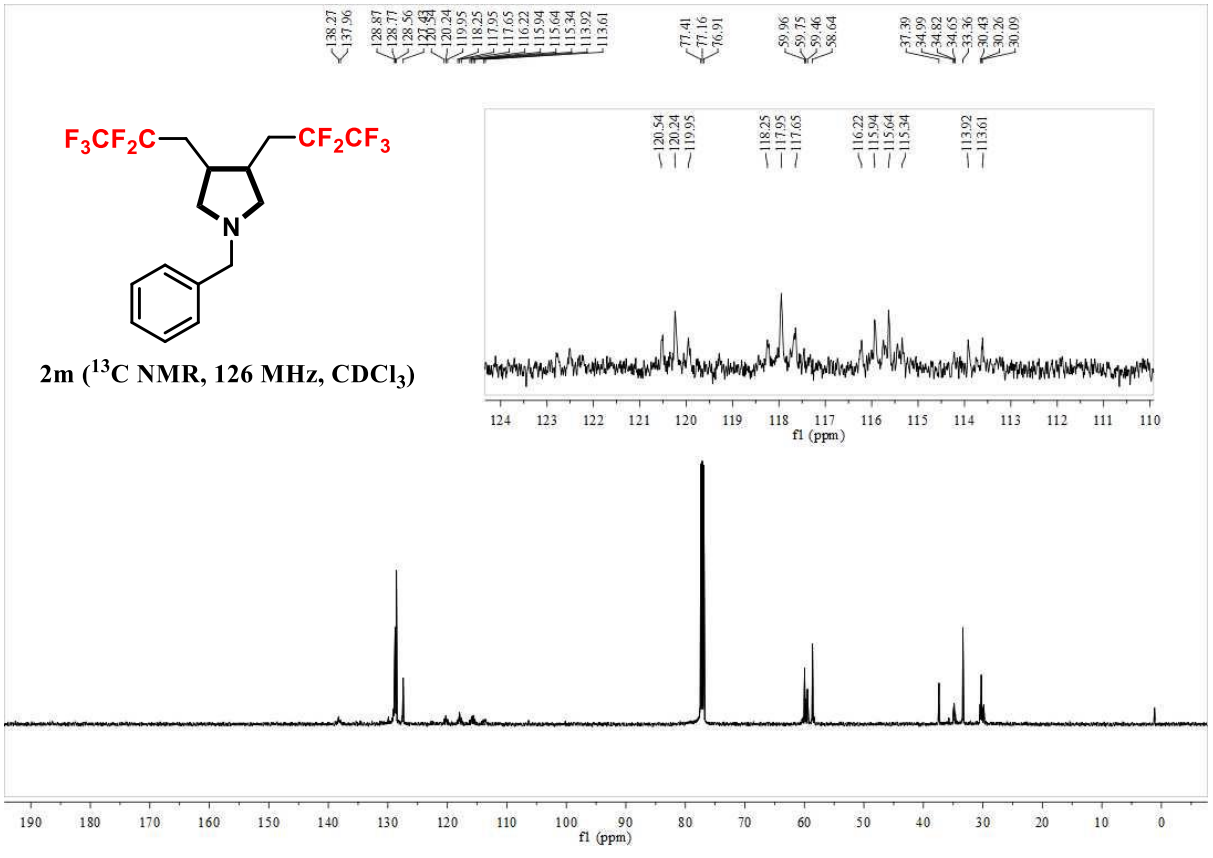


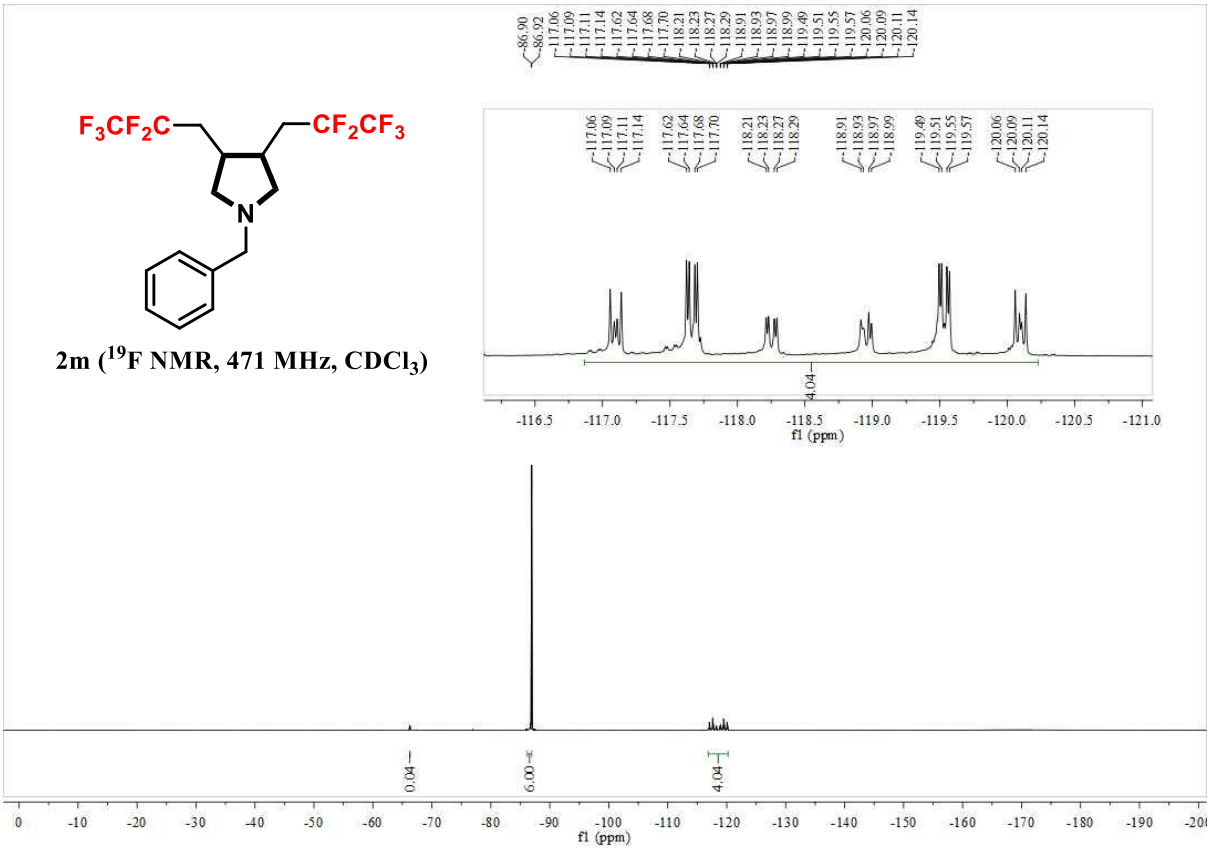
2l (^{13}C NMR, 126 MHz, $CDCl_3$)



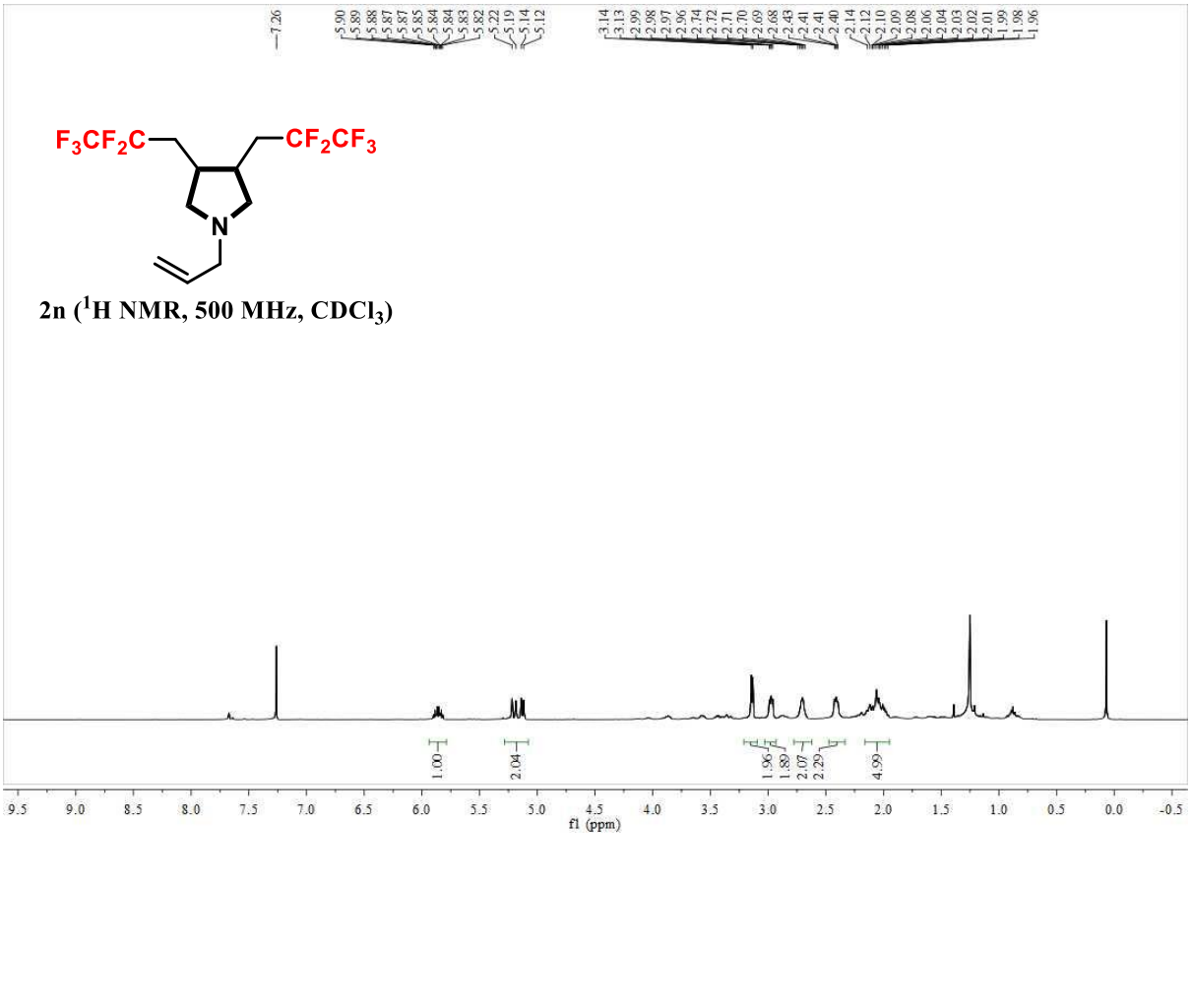
2l (^{19}F NMR, 471 MHz, $CDCl_3$)


F3CF2C
CF2CF3
N
2m (1H NMR, 500 MHz, CDCl3)
f1 (ppm)

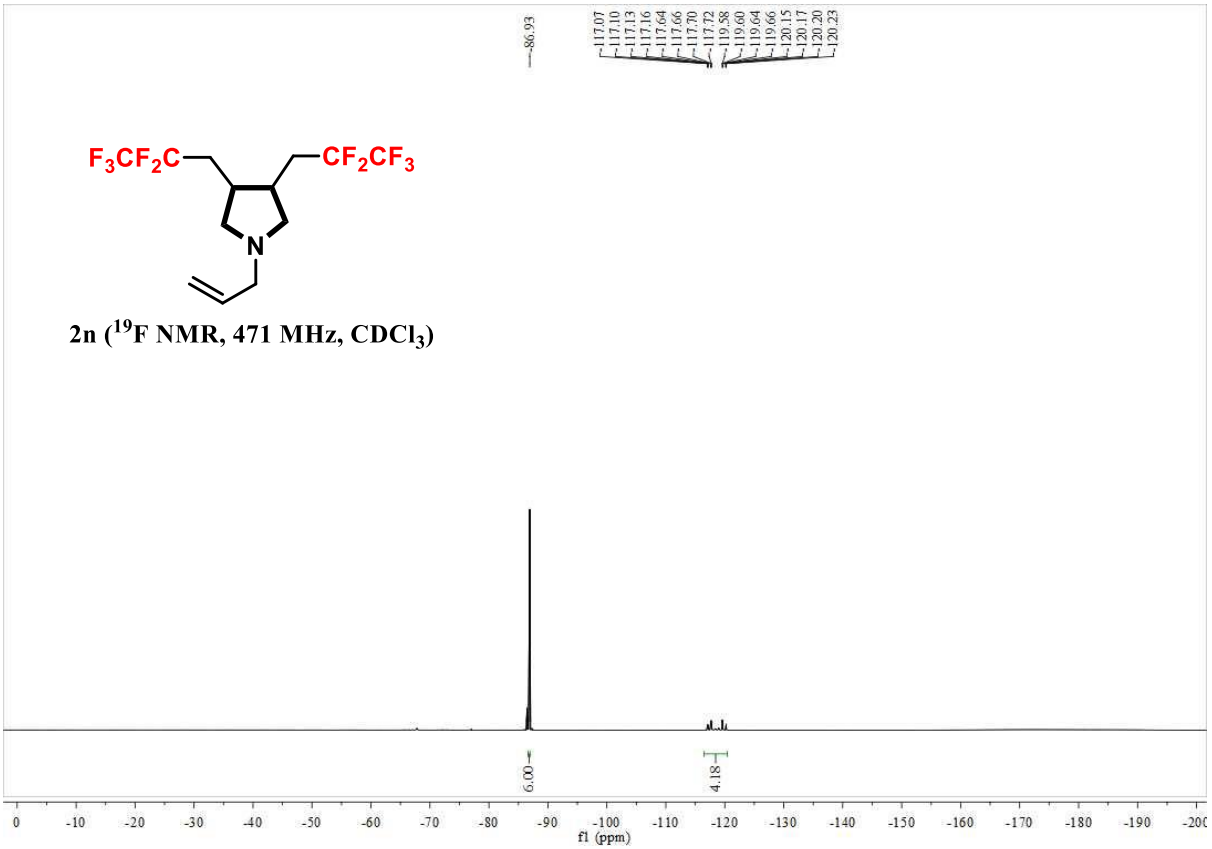

F3CF2C
CF2CF3
N
2m (13C NMR, 126 MHz, CDCl3)
f1 (ppm)



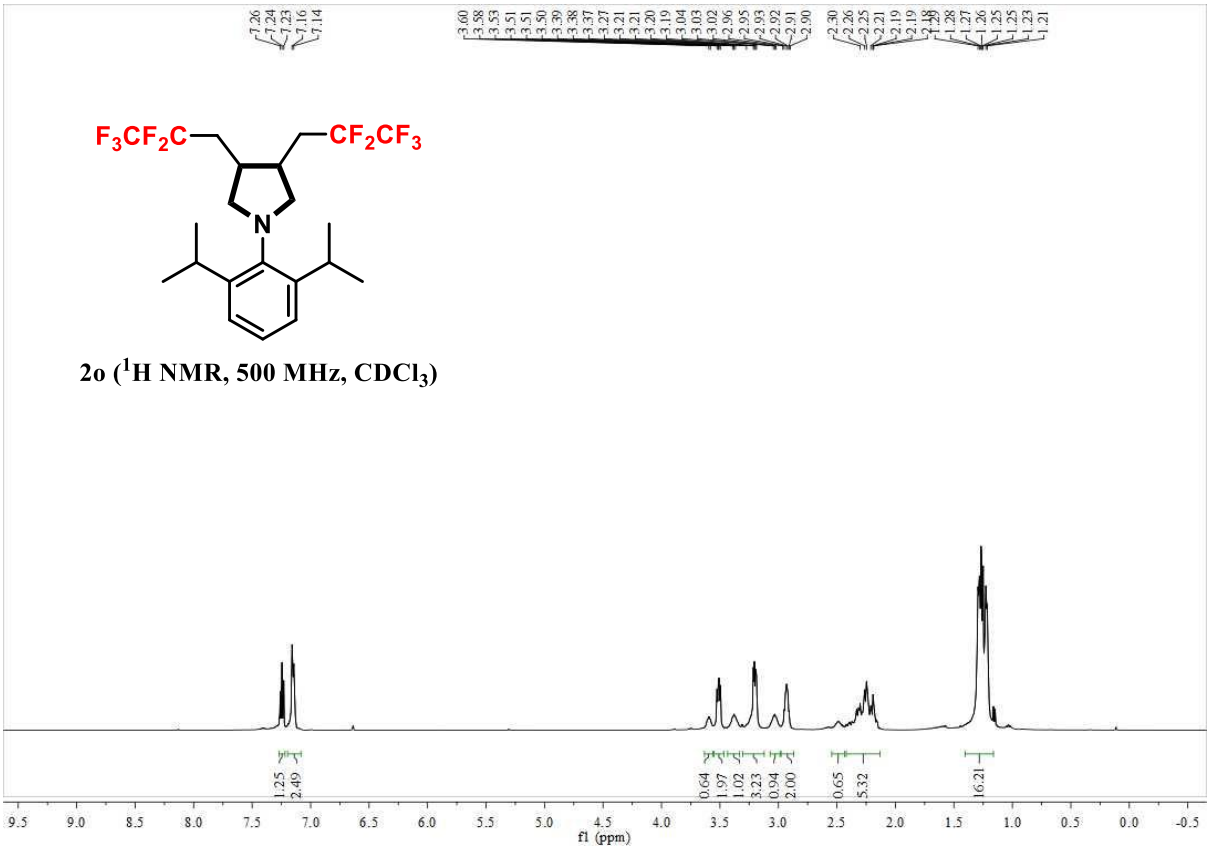
2m (^{19}F NMR, 471 MHz, $CDCl_3$)



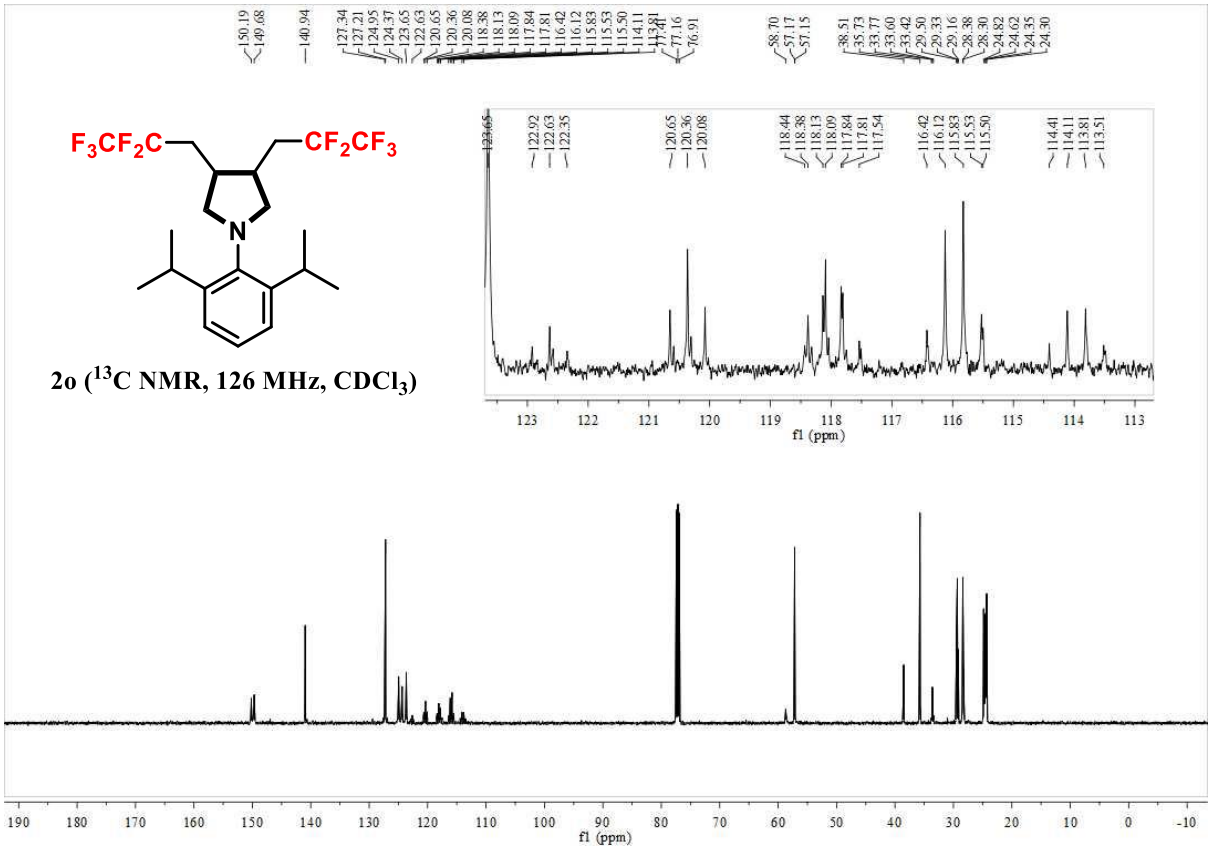
2n (^{1}H NMR, 500 MHz, $CDCl_3$)



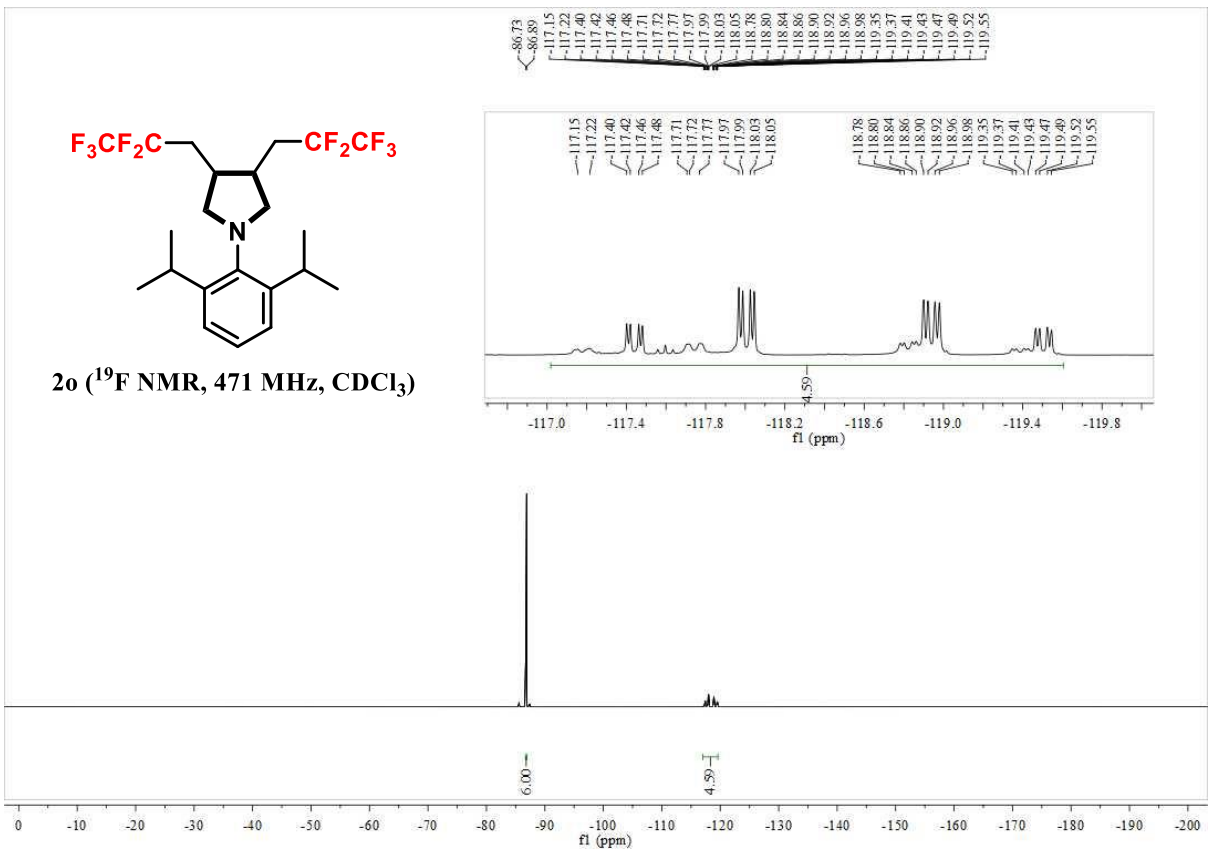
2n (^{19}F NMR, 471 MHz, $CDCl_3$)



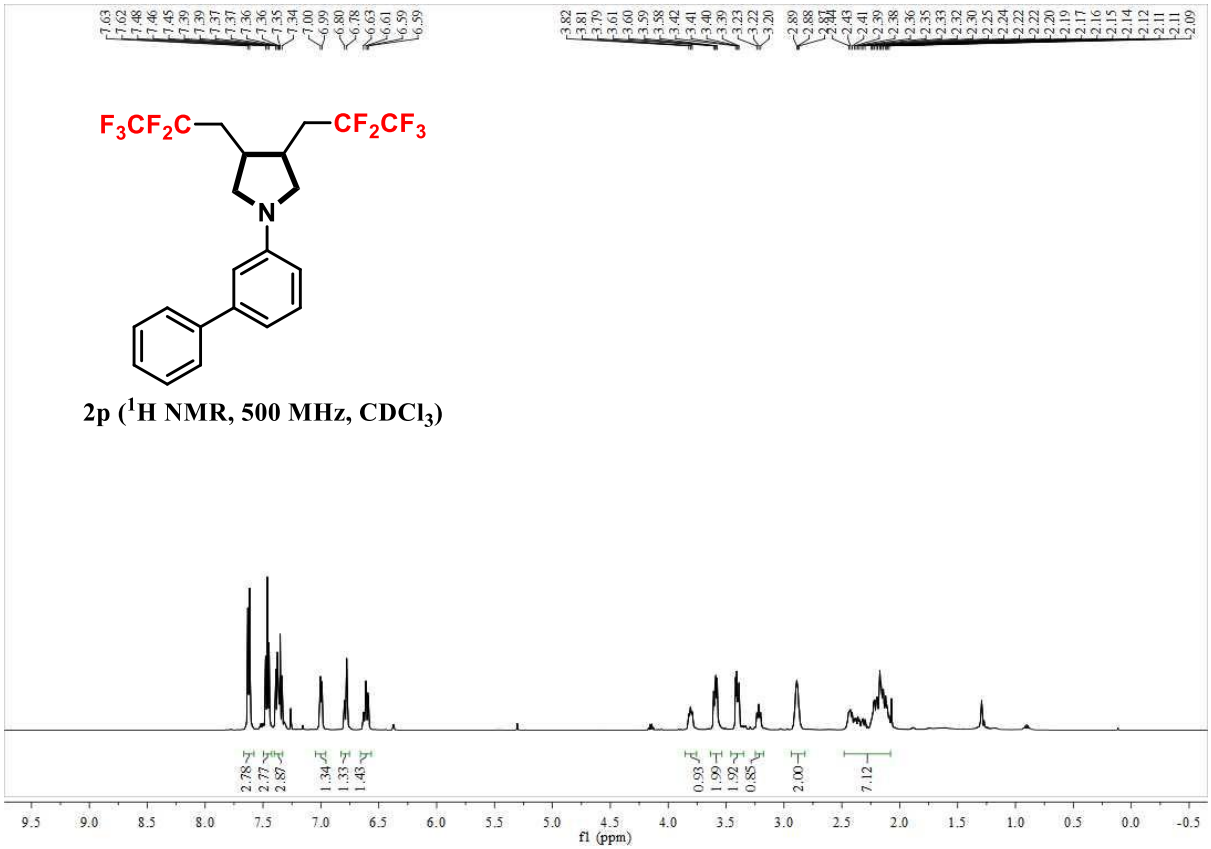
2o (^{1}H NMR, 500 MHz, $CDCl_3$)



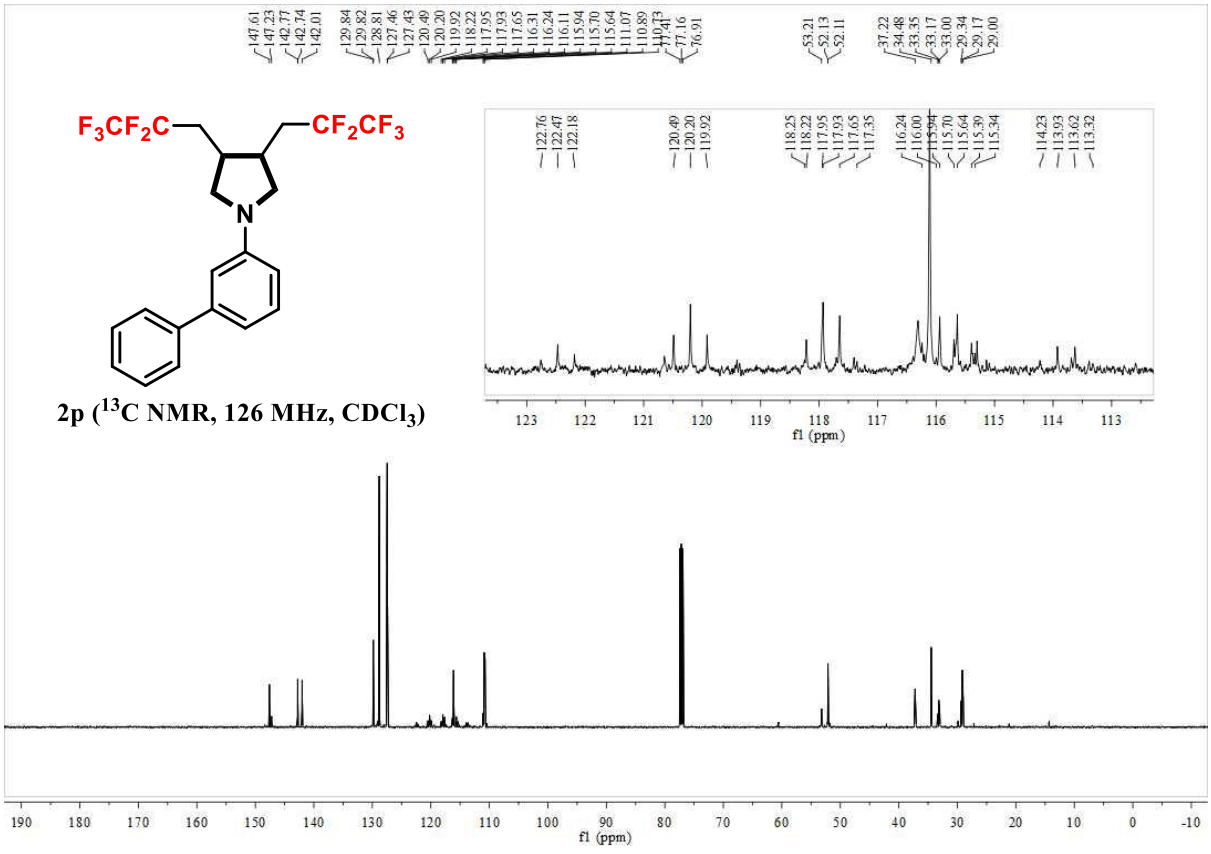
2o (^{13}C NMR, 126 MHz, $CDCl_3$)



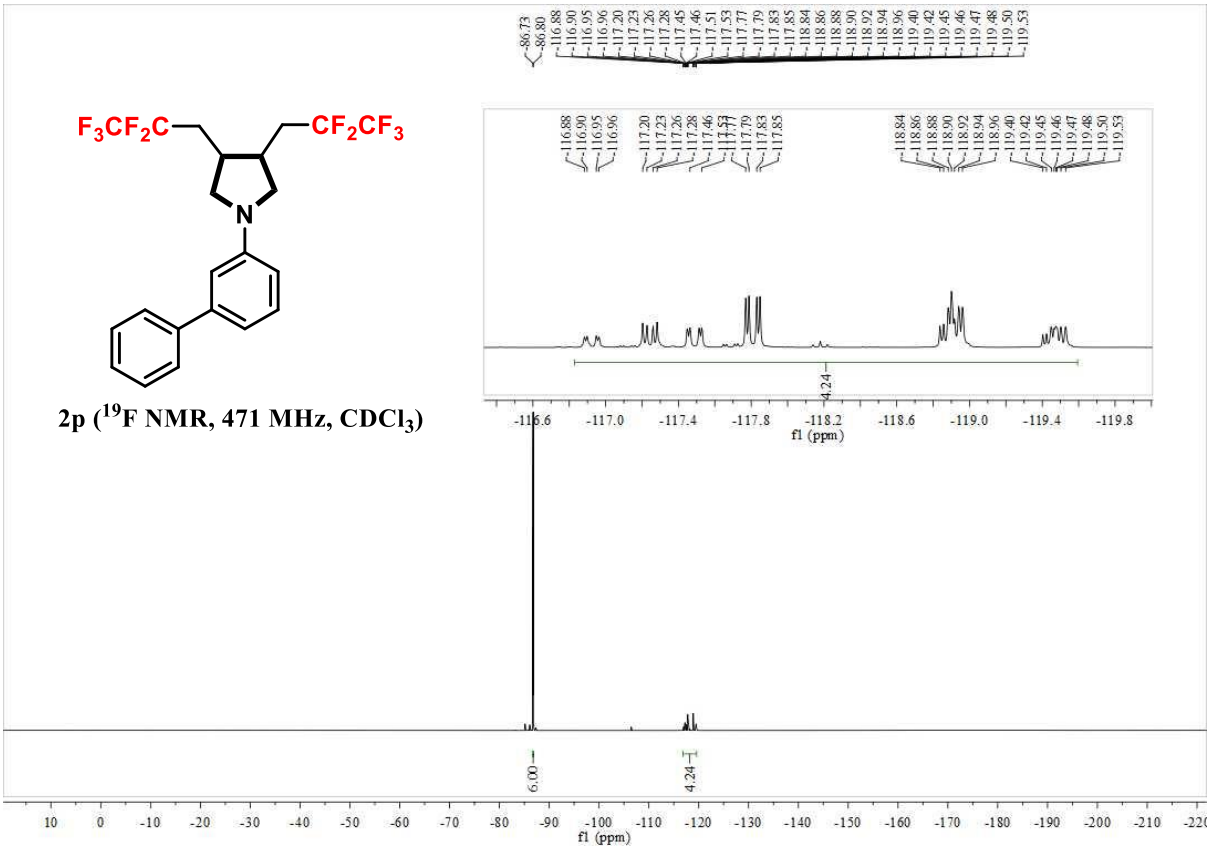
2o (^{19}F NMR, 471 MHz, $CDCl_3$)



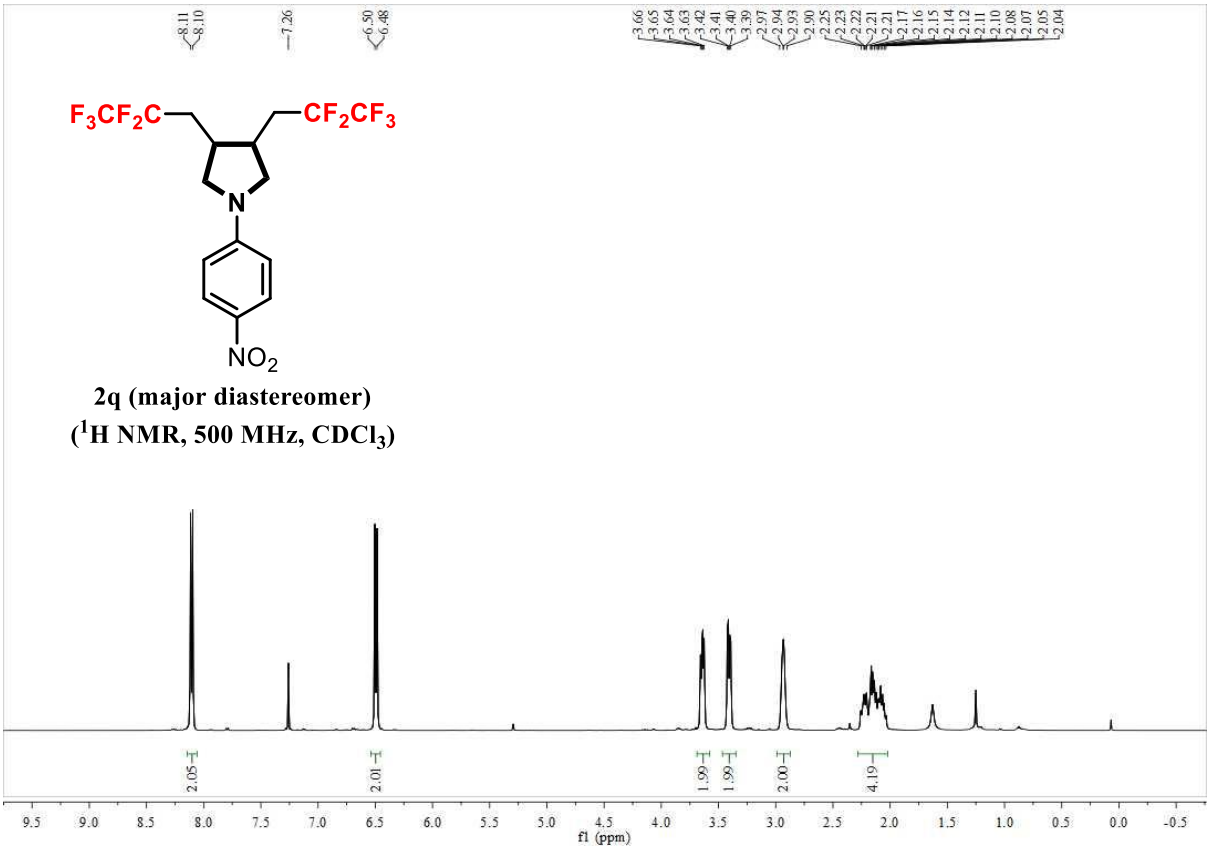
2p (^{1}H NMR, 500 MHz, $CDCl_3$)



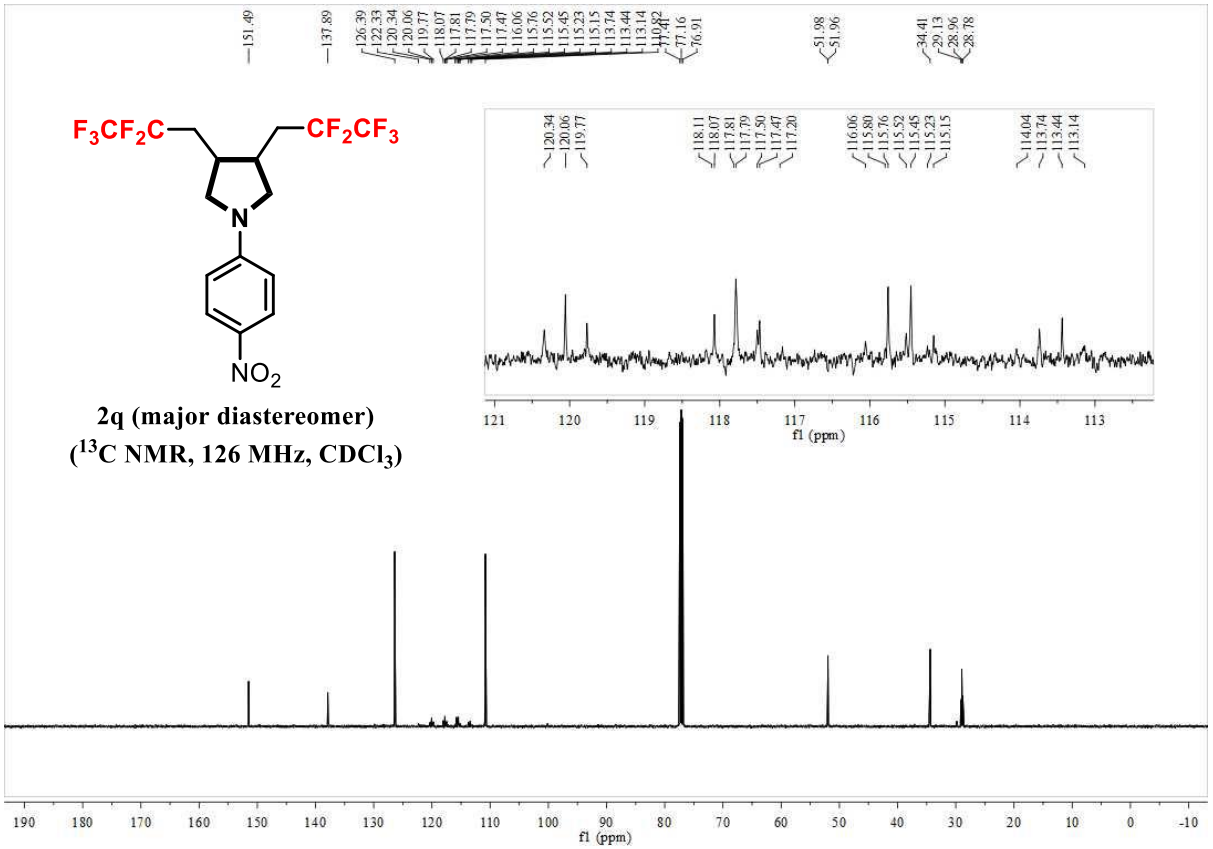
2p (^{13}C NMR, 126 MHz, $CDCl_3$)

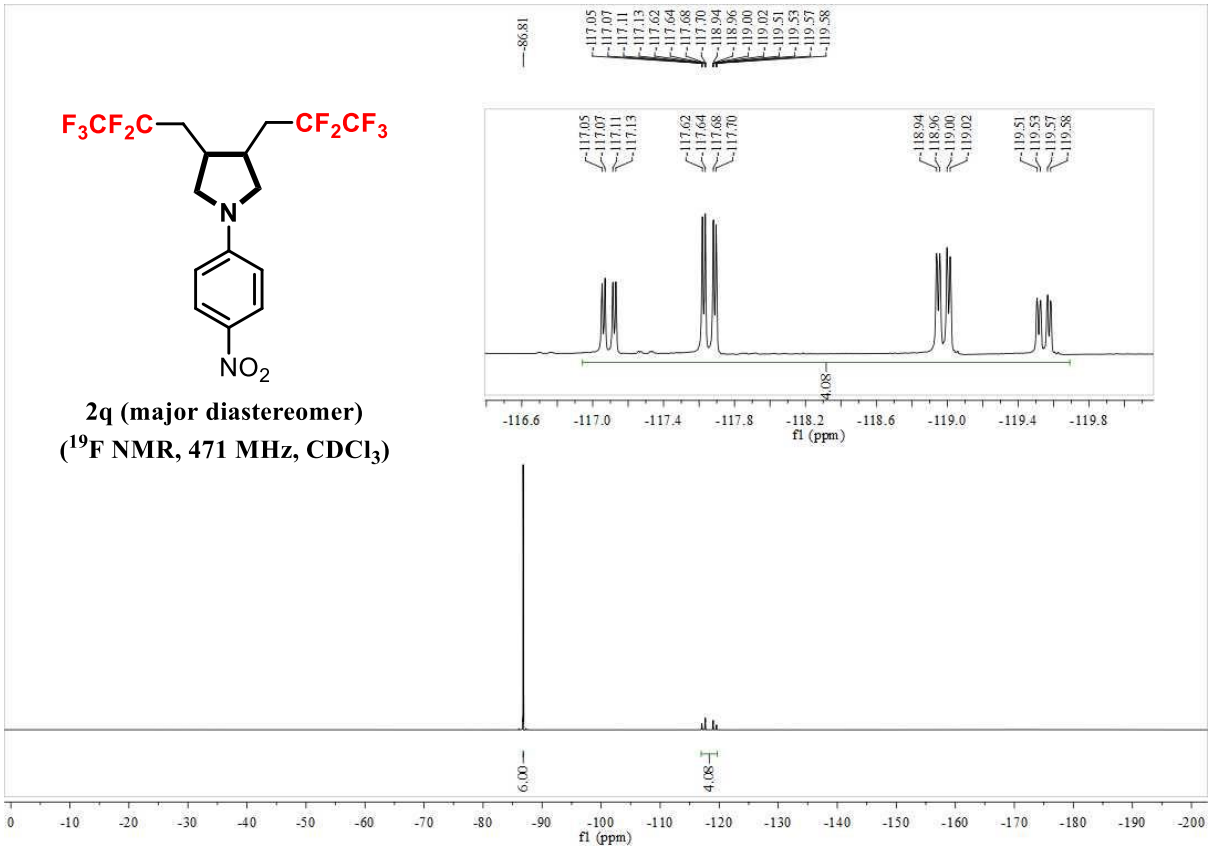


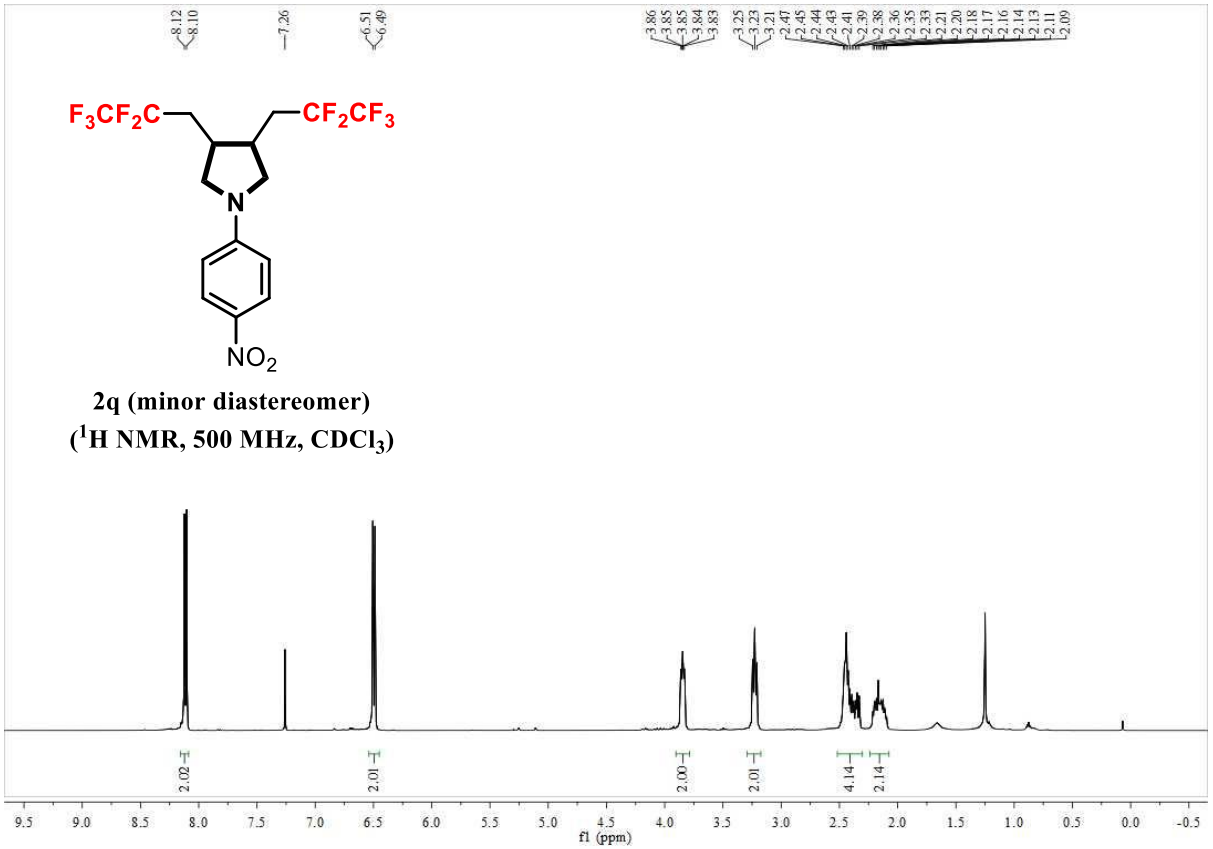
2p (^{19}F NMR, 471 MHz, $CDCl_3$)

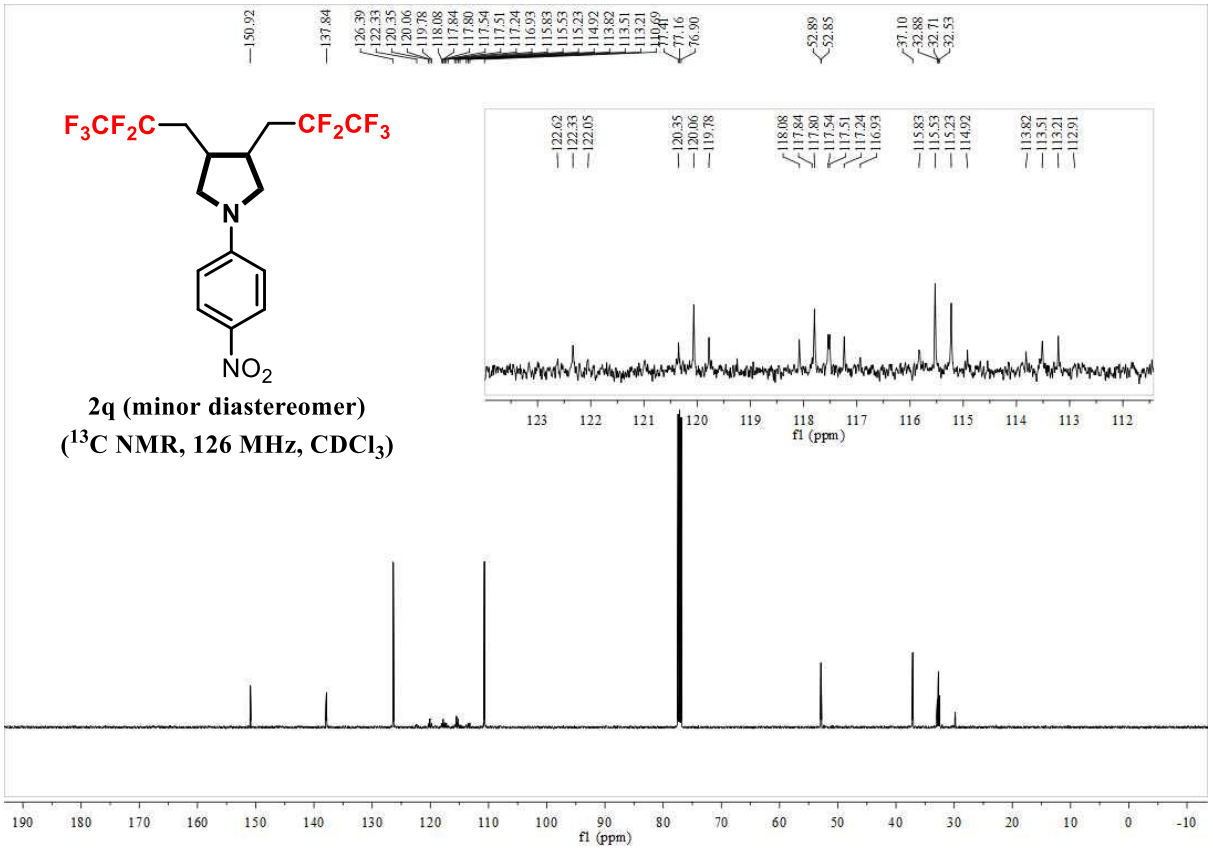


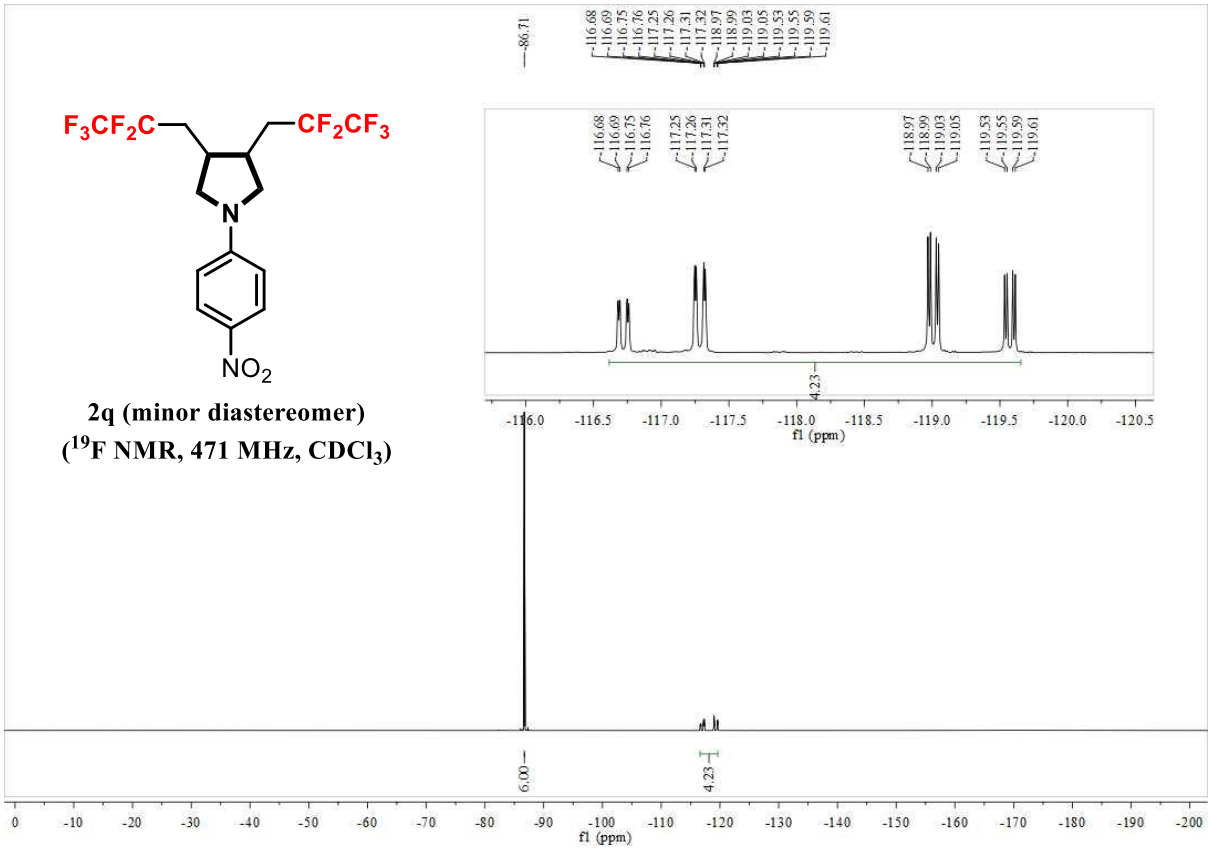
2q (major diastereomer)
(^{1}H NMR, 500 MHz, $CDCl_3$)


F3CF2C
CF2CF3
N
NO2
2q (major diastereomer)
(13C NMR, 126 MHz, CDCl3)
f1 (ppm)

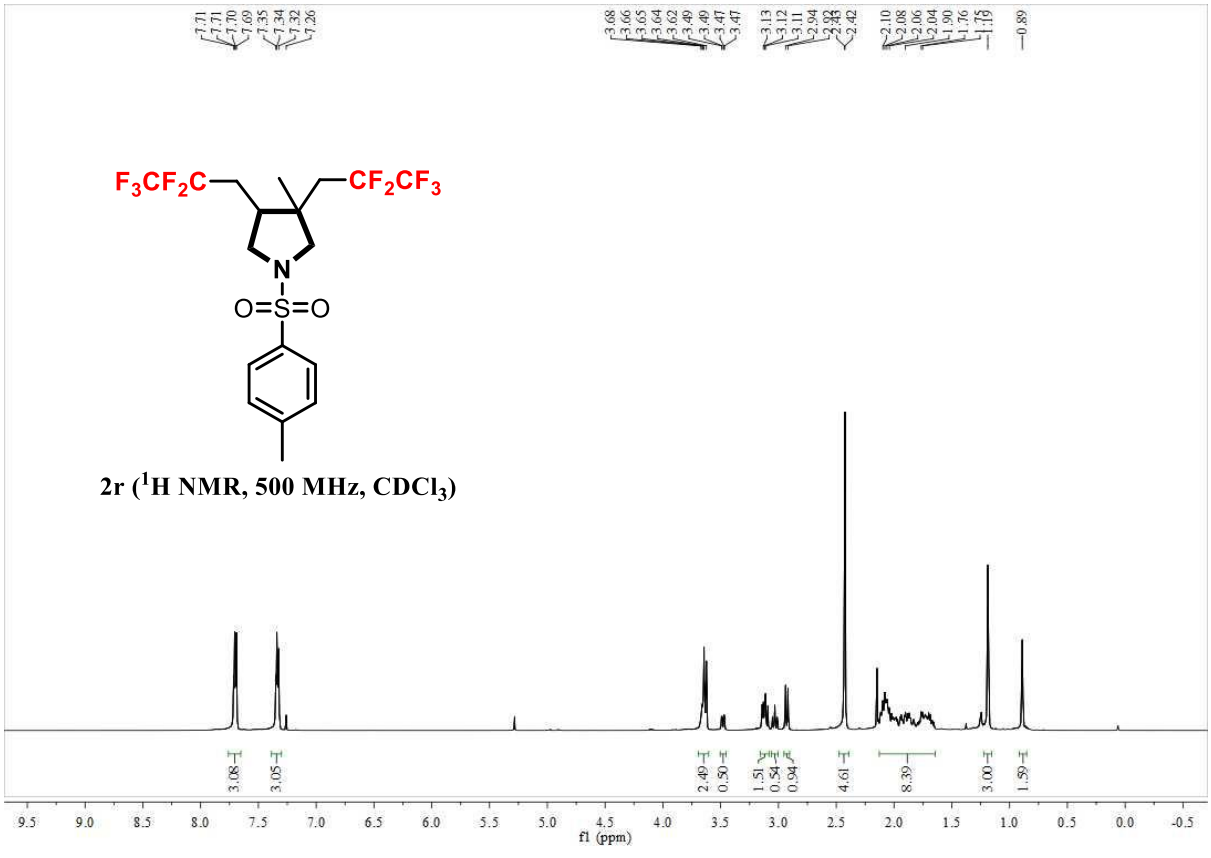

F3CF2C
CF2CF3
N
NO2
2q (major diastereomer)
(19F NMR, 471 MHz, CDCl3)
4.08
6.00
4.08
f1 (ppm)


F3CF2C
CF2CF3
N
NO2
2q (minor diastereomer)
(1H NMR, 500 MHz, CDCl3)
f1 (ppm)

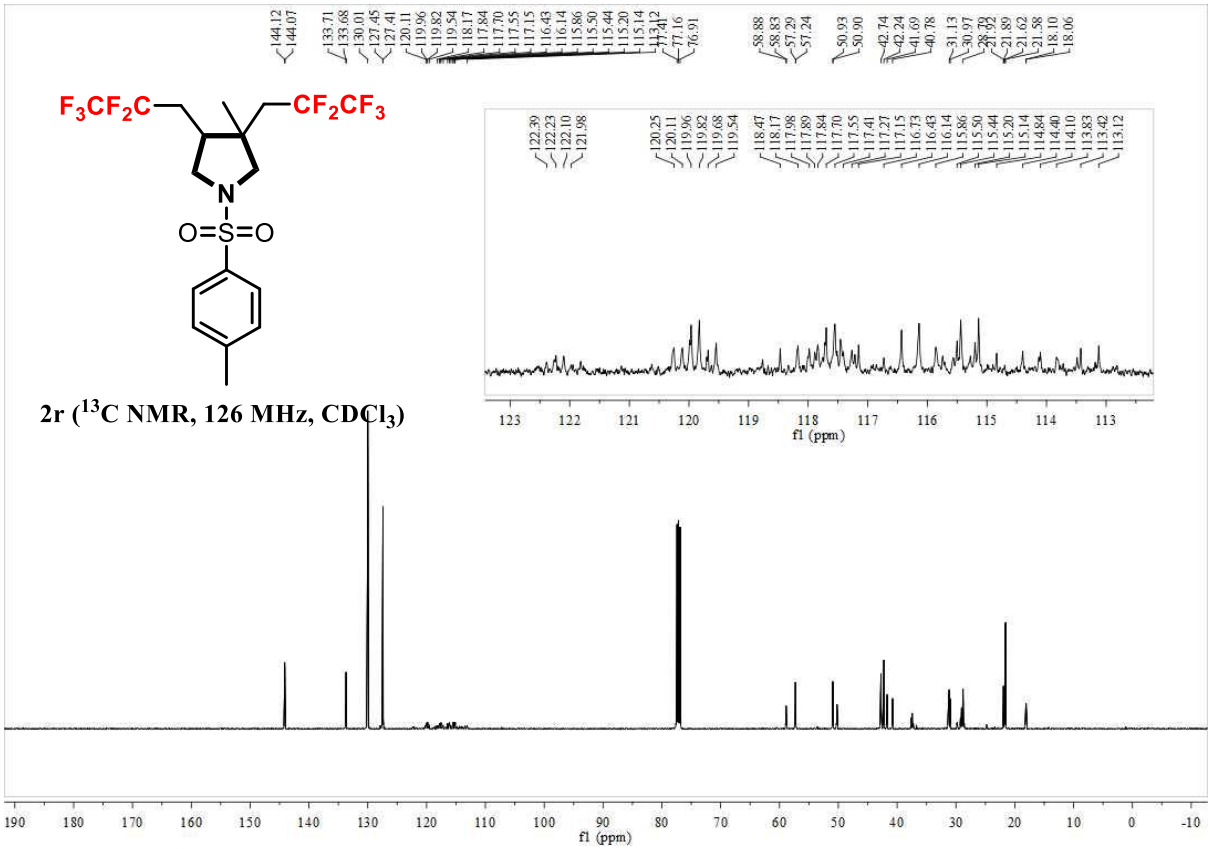

F3CF2C
CF2CF3
N
NO2
2q (minor diastereomer)
(13C NMR, 126 MHz, CDCl3)
f1 (ppm)



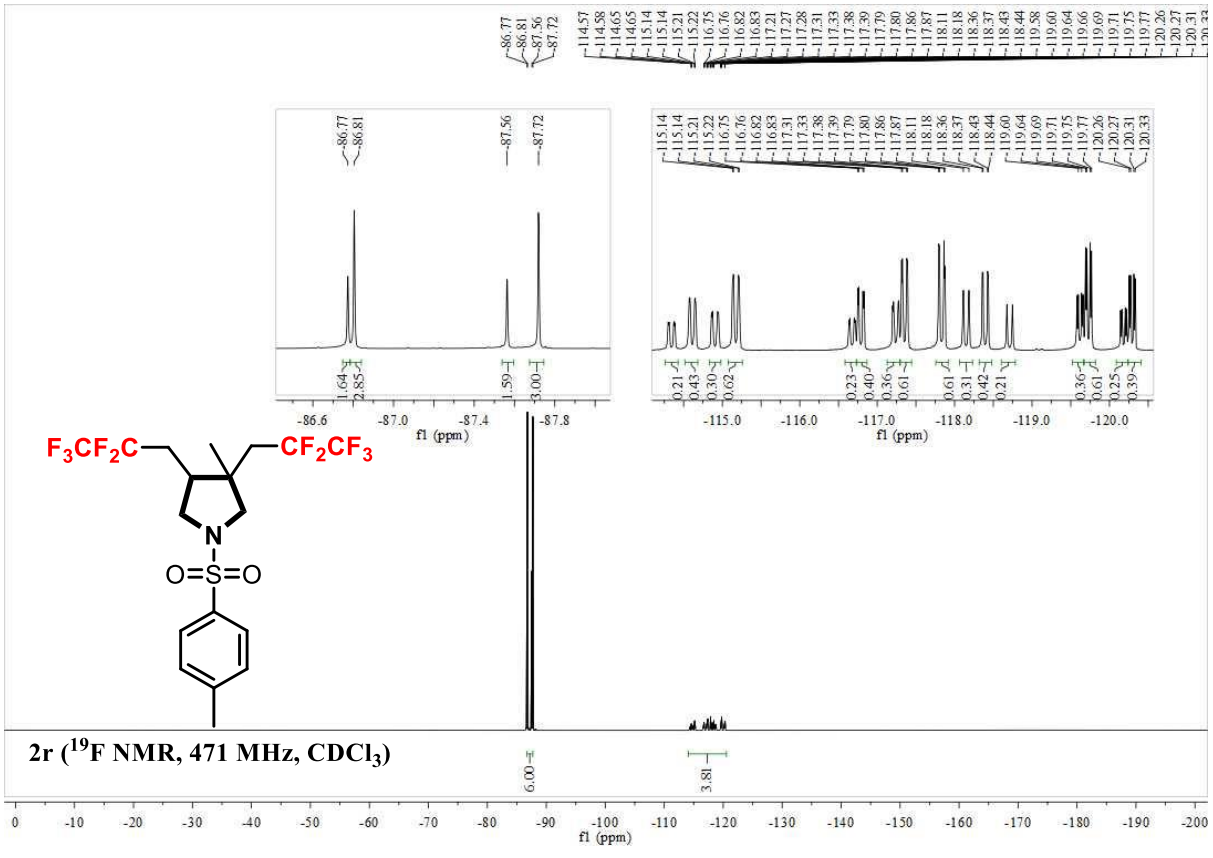
2q (minor diastereomer)
(^{19}F NMR, 471 MHz, $CDCl_3$)



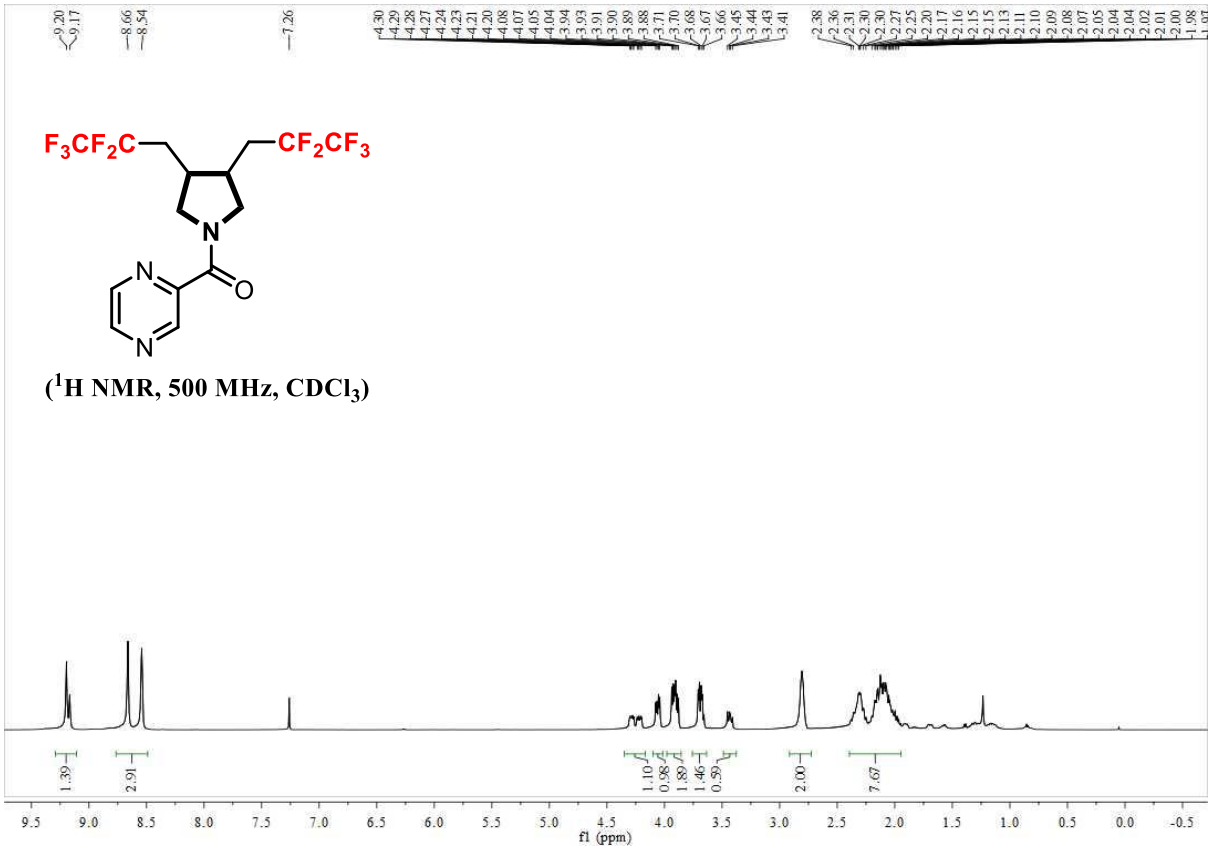
2r (^{1}H NMR, 500 MHz, $CDCl_3$)



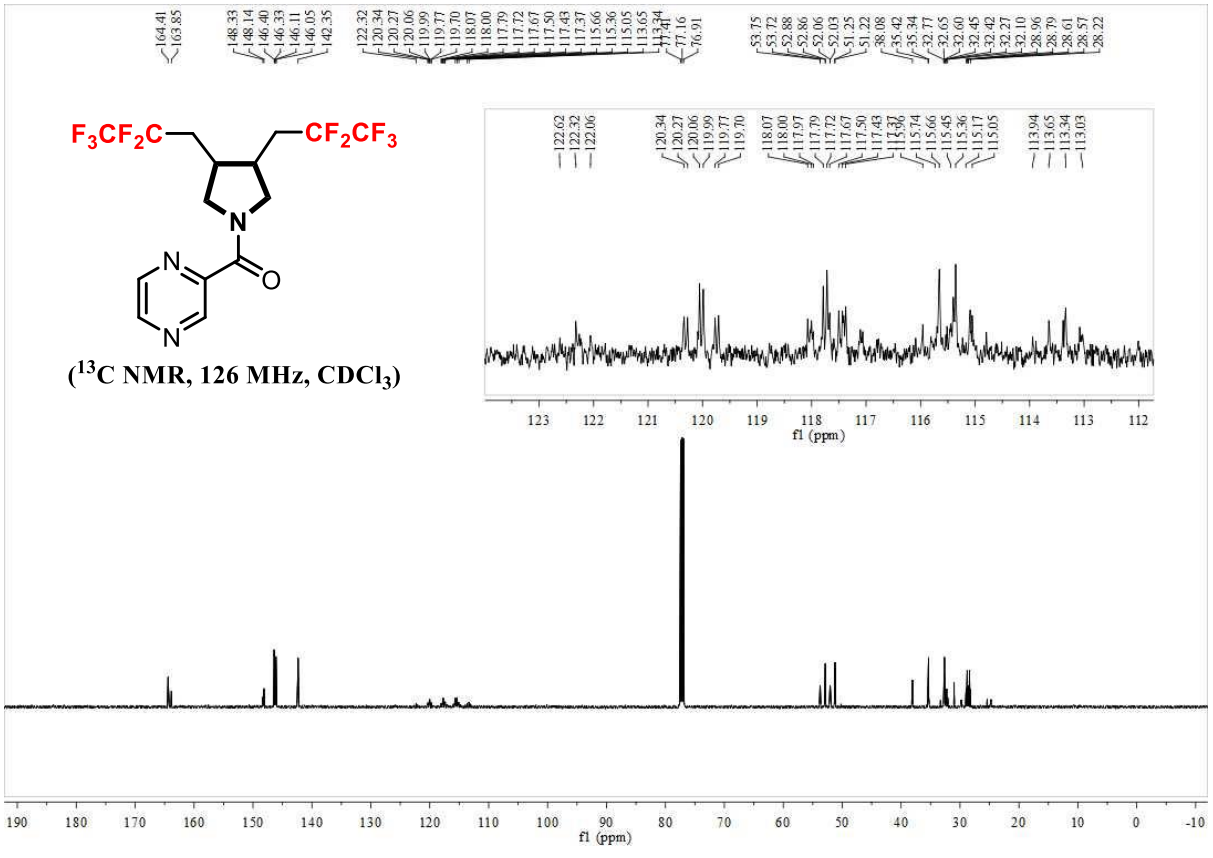
2r (^{13}C NMR, 126 MHz, $CDCl_3$)



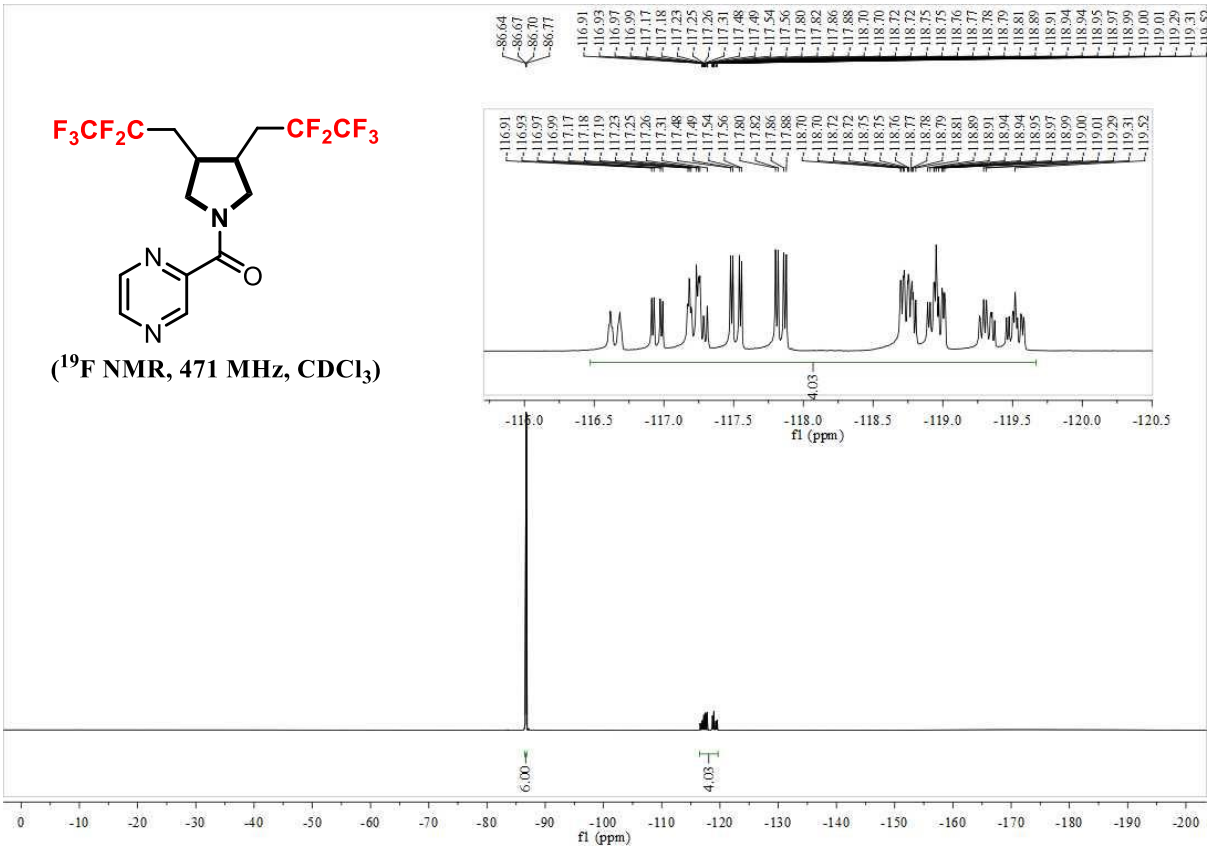
2r (^{19}F NMR, 471 MHz, $CDCl_3$)

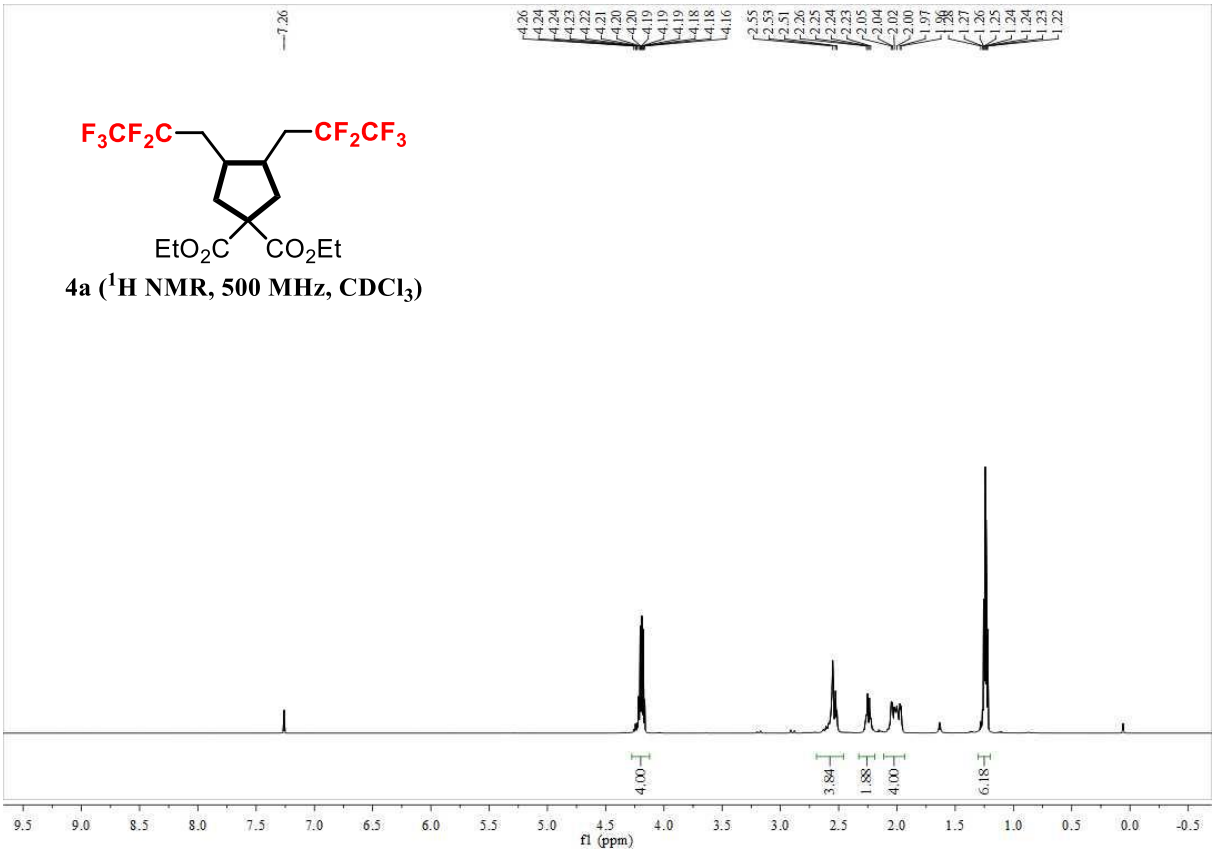


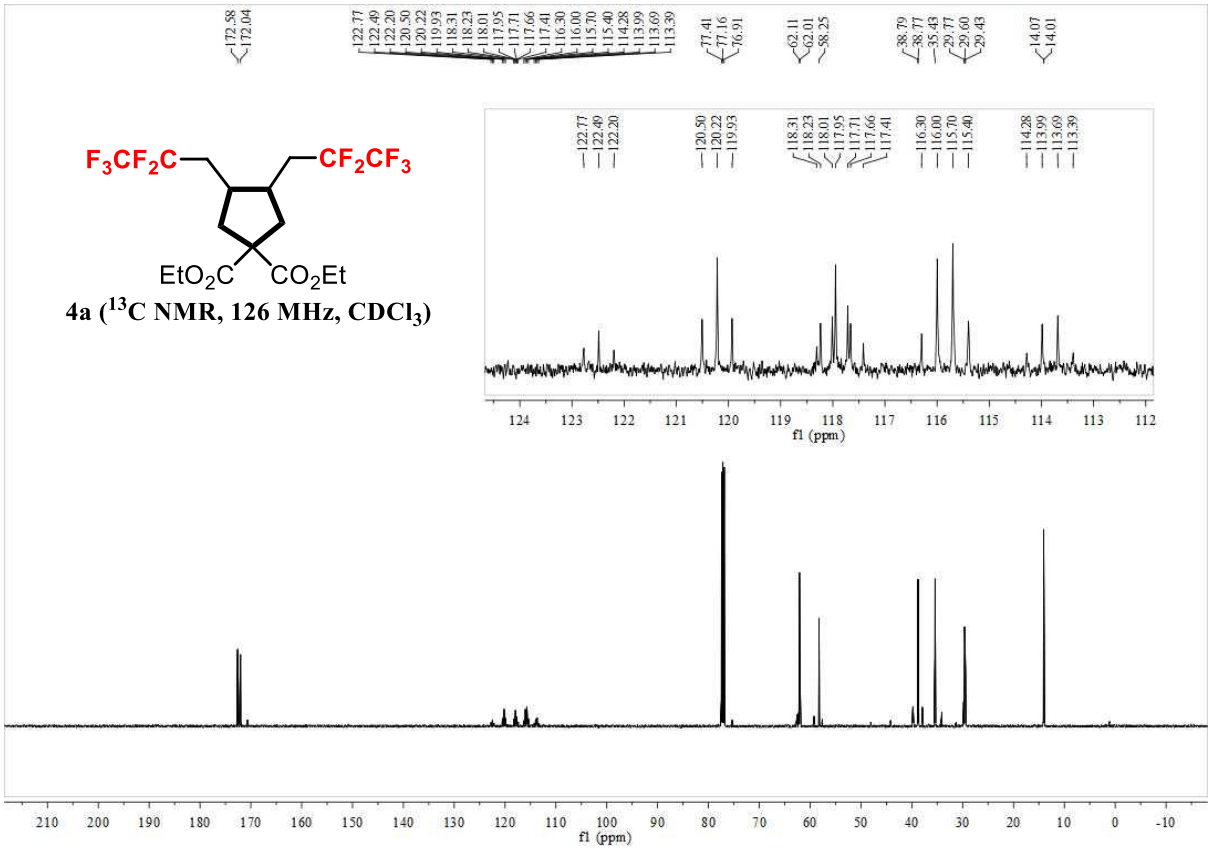
(¹H NMR, 500 MHz, $CDCl_3$)



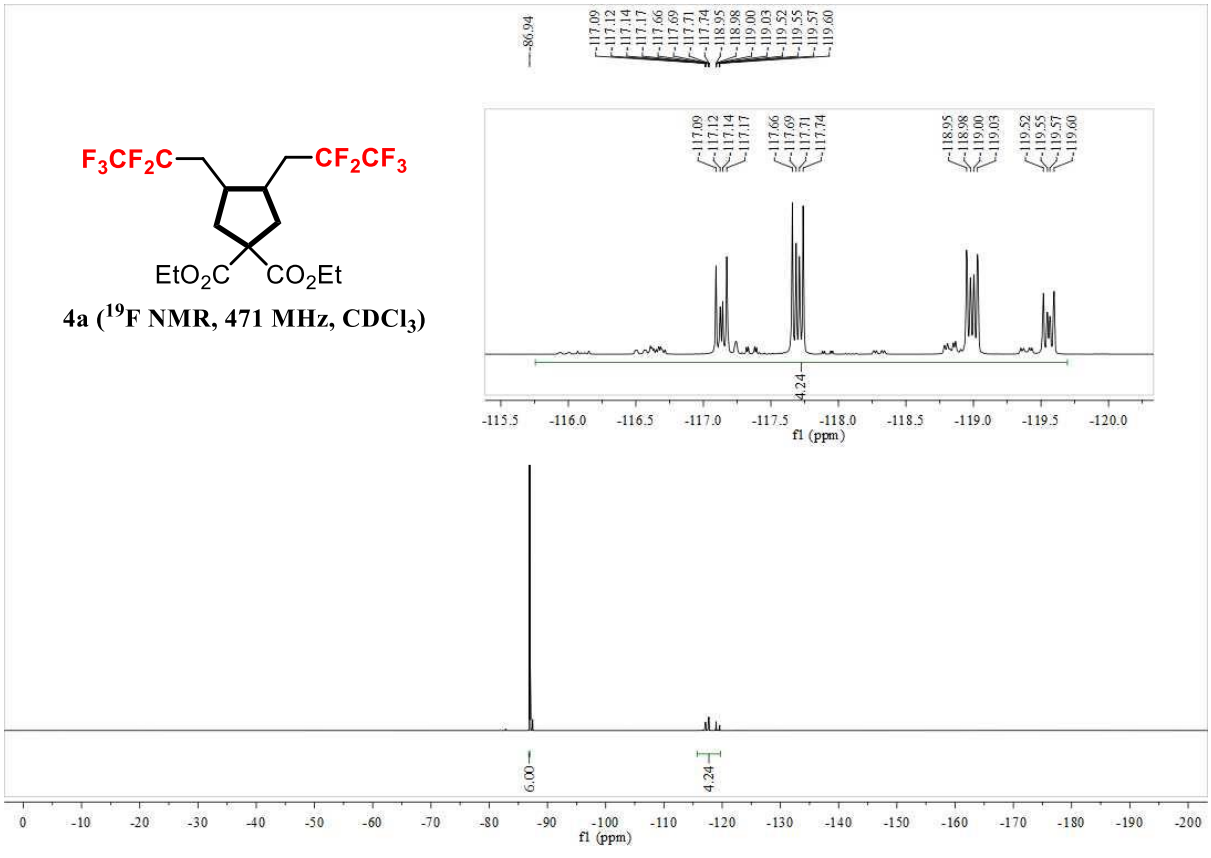
(¹³C NMR, 126 MHz, $CDCl_3$)


F3CF2C
CF2CF3
N
N
N
O
(19F NMR, 471 MHz, CDCl3)
4.03
f1 (ppm)
6.00
4.03
f1 (ppm)

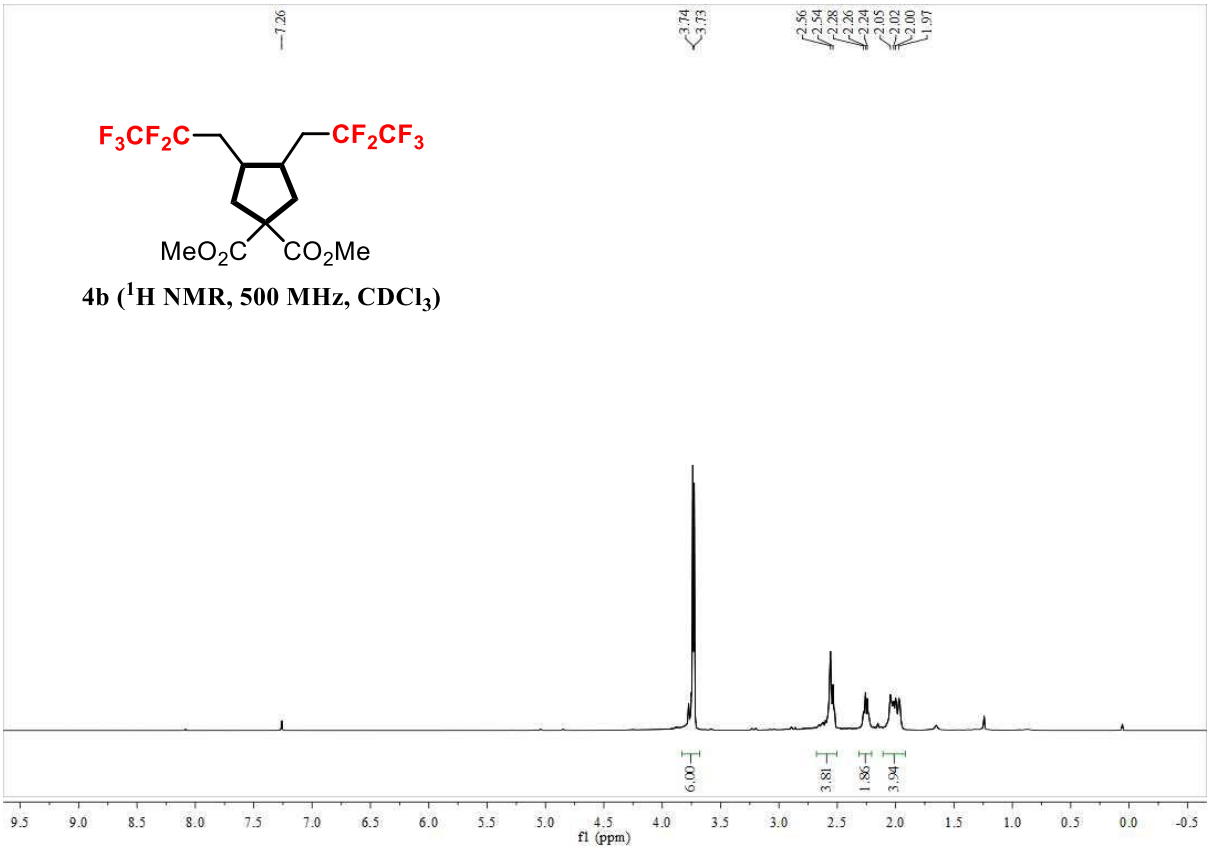

F3CF2C
CF2CF3
EtO2C
CO2Et
4a (1H NMR, 500 MHz, CDCl3)
4.00
3.84
1.88
4.00
6.18
f1 (ppm)



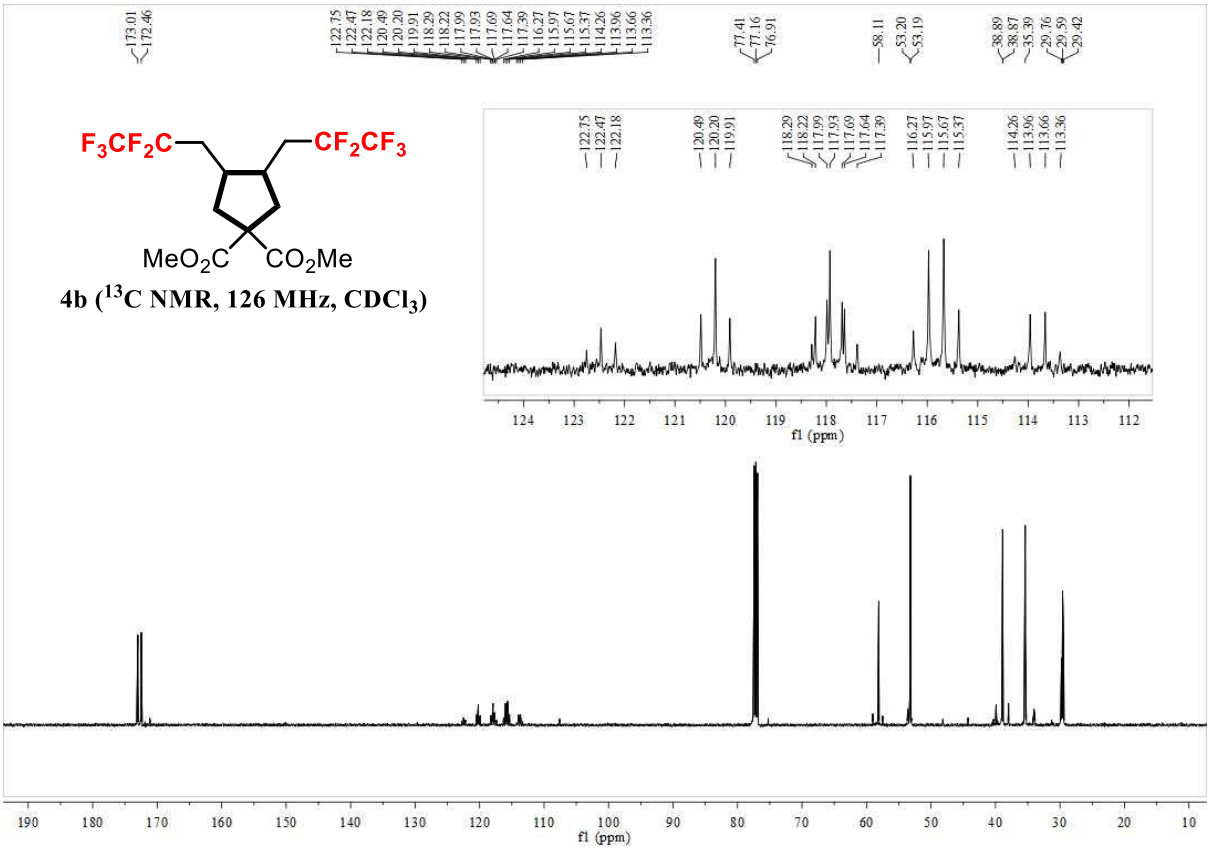
4a (^{13}C NMR, 126 MHz, $CDCl_3$)



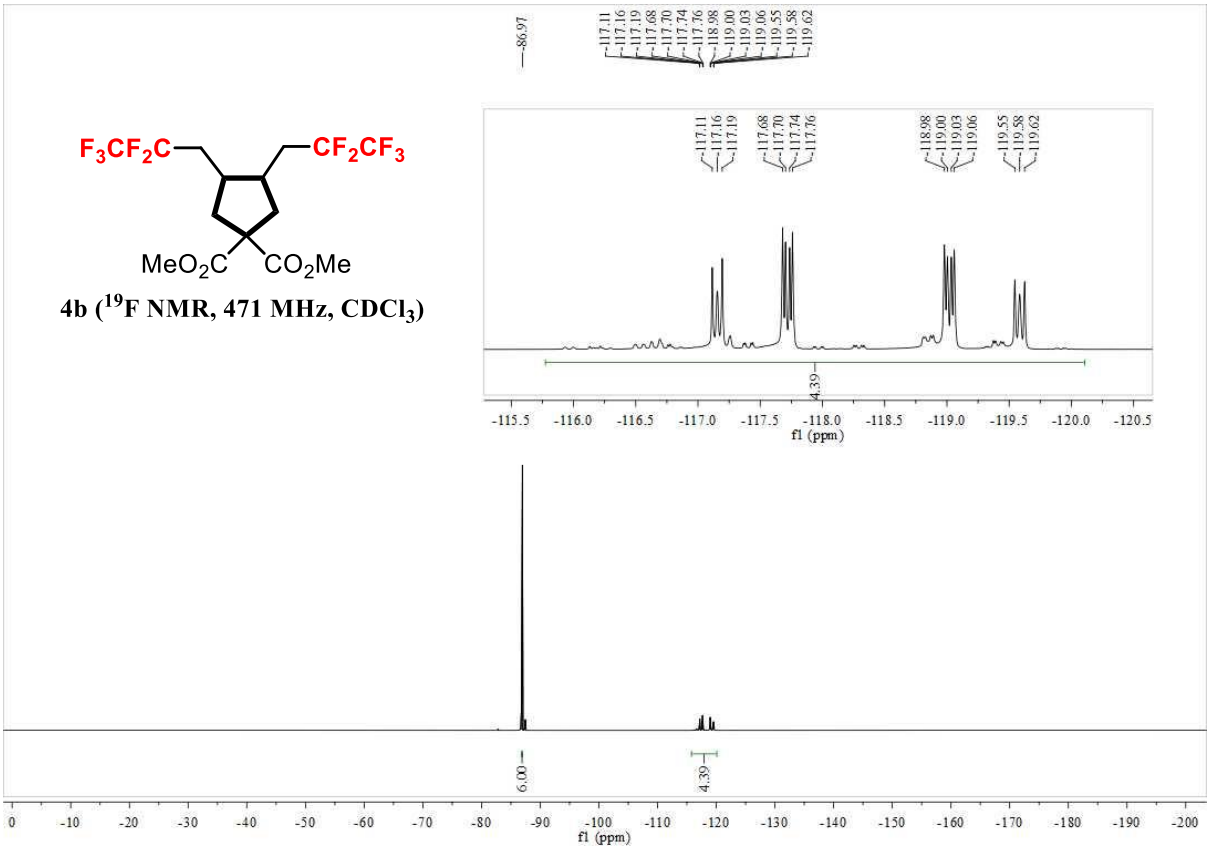
4a (^{19}F NMR, 471 MHz, $CDCl_3$)



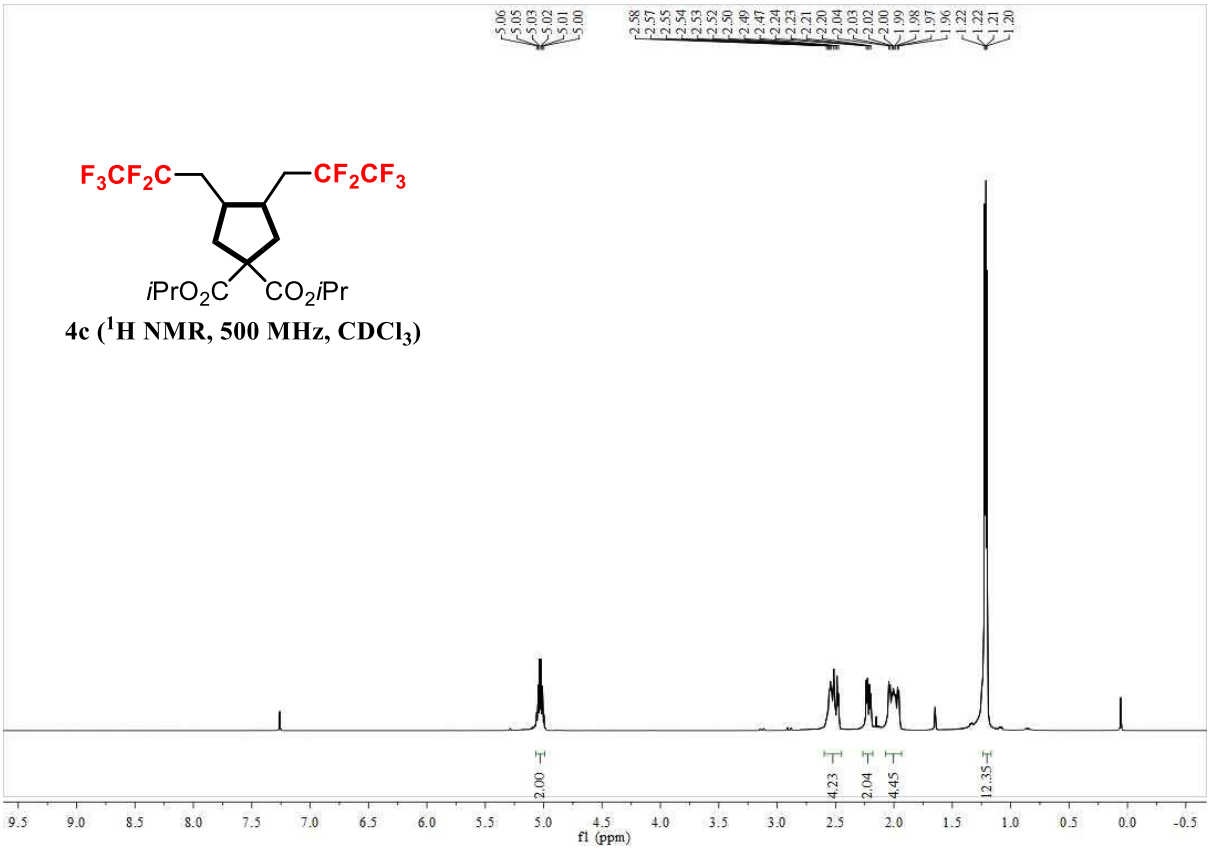
4b (^{1}H NMR, 500 MHz, $CDCl_3$)



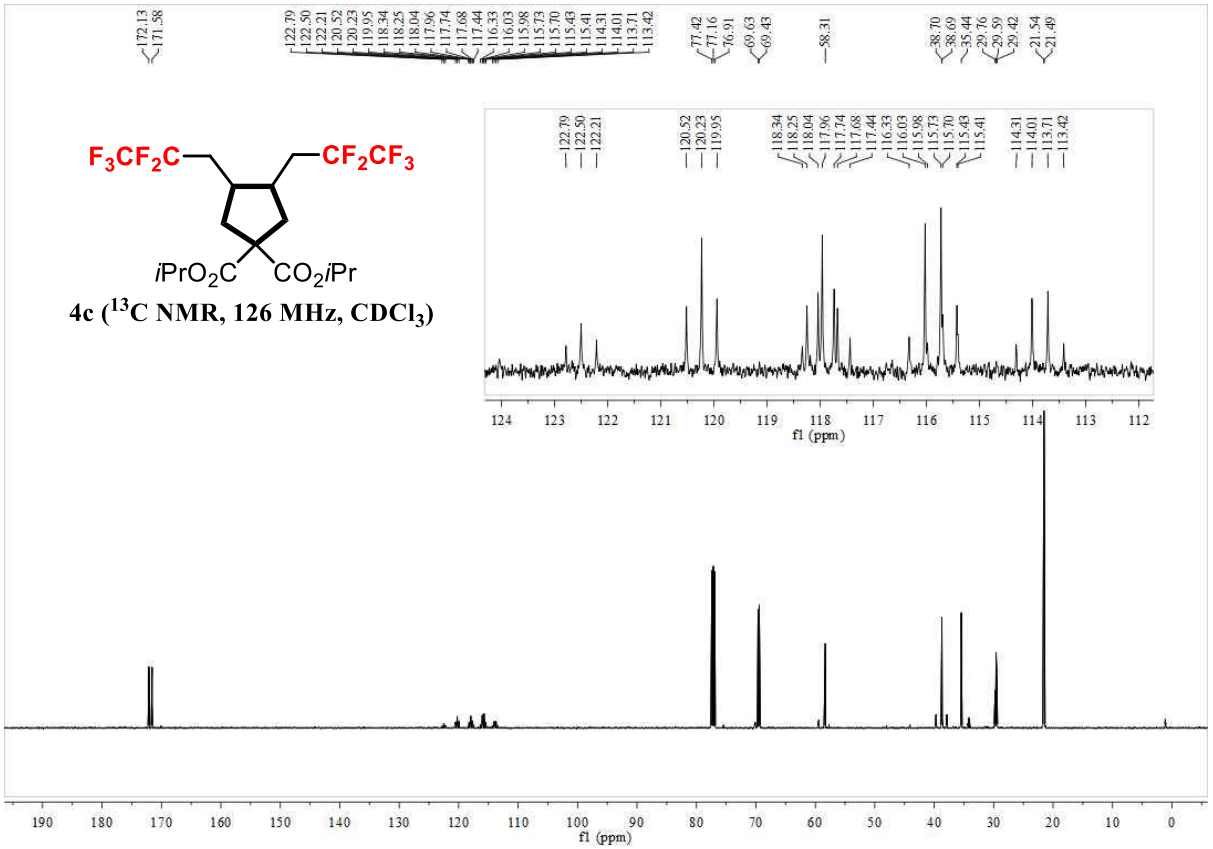
4b (^{13}C NMR, 126 MHz, $CDCl_3$)



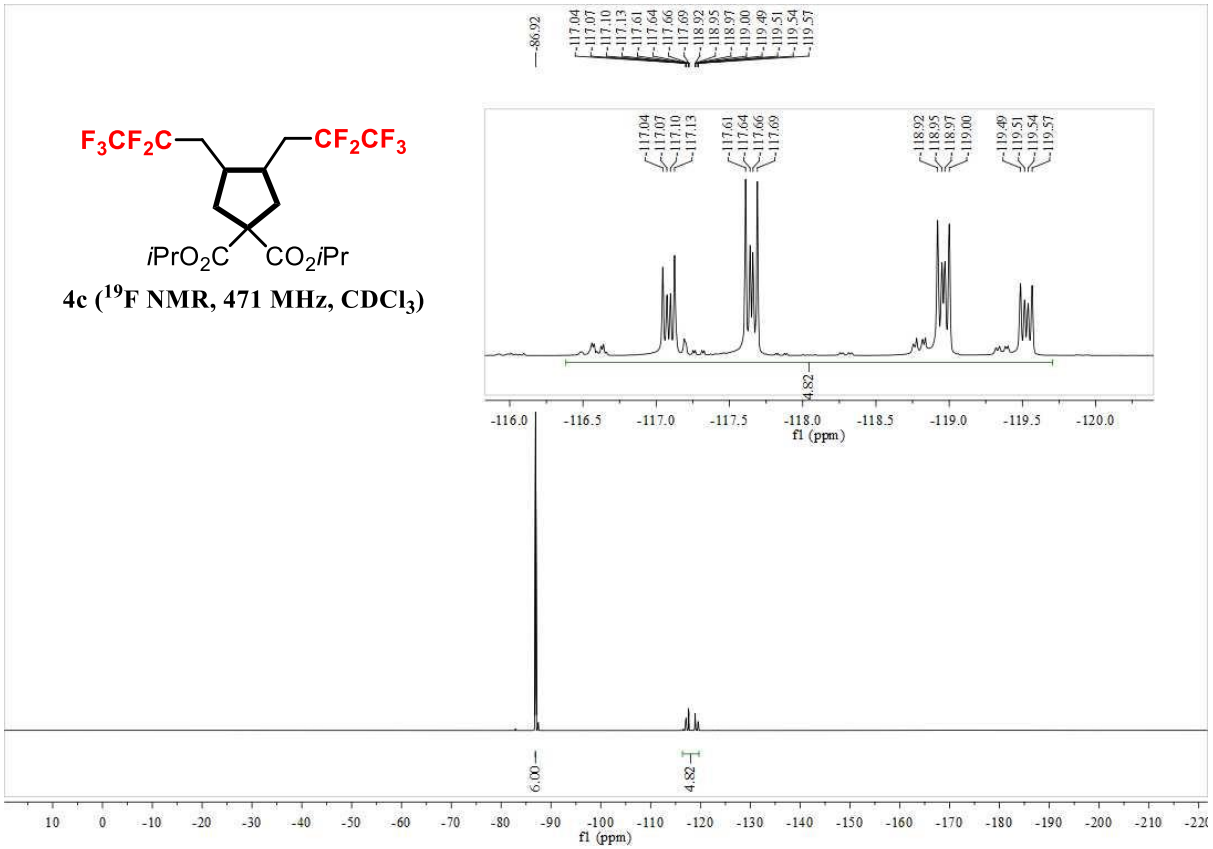
4b (^{19}F NMR, 471 MHz, $CDCl_3$)



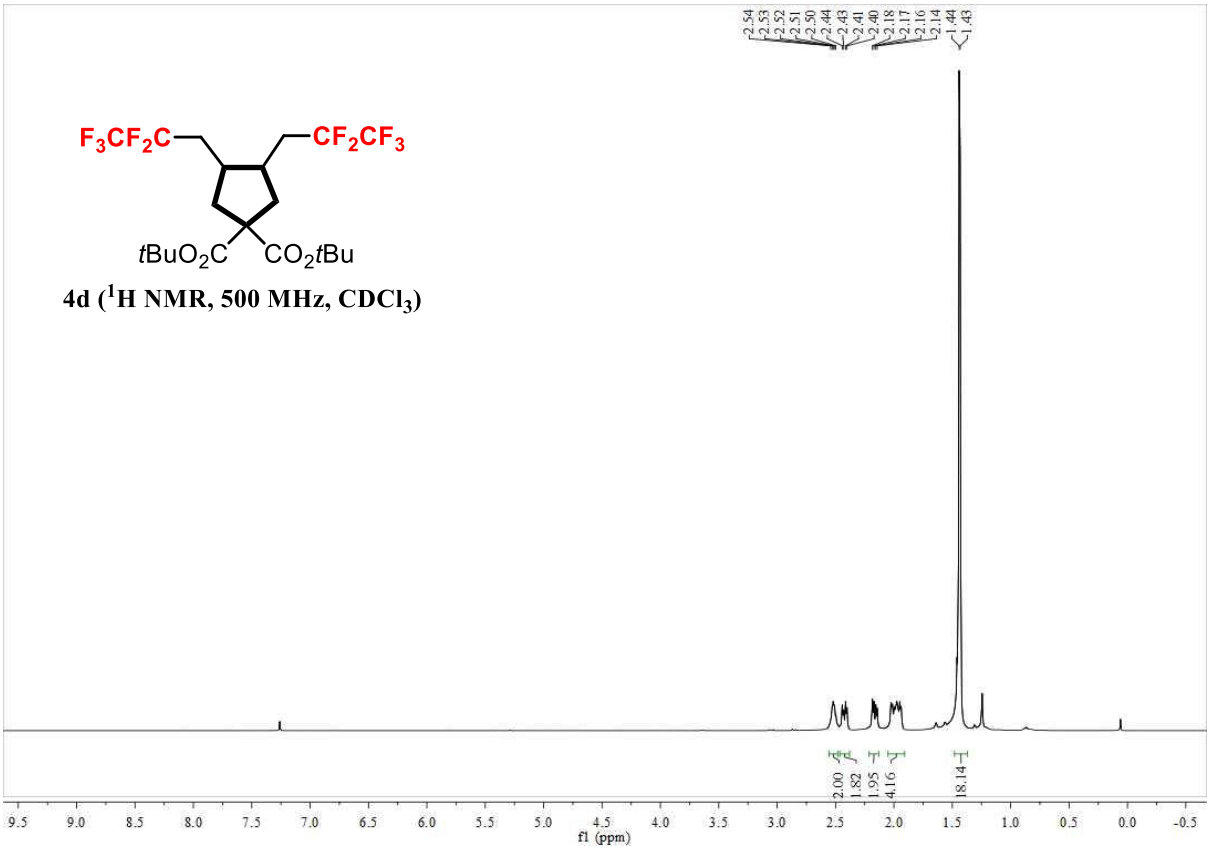
4c (^{1}H NMR, 500 MHz, $CDCl_3$)



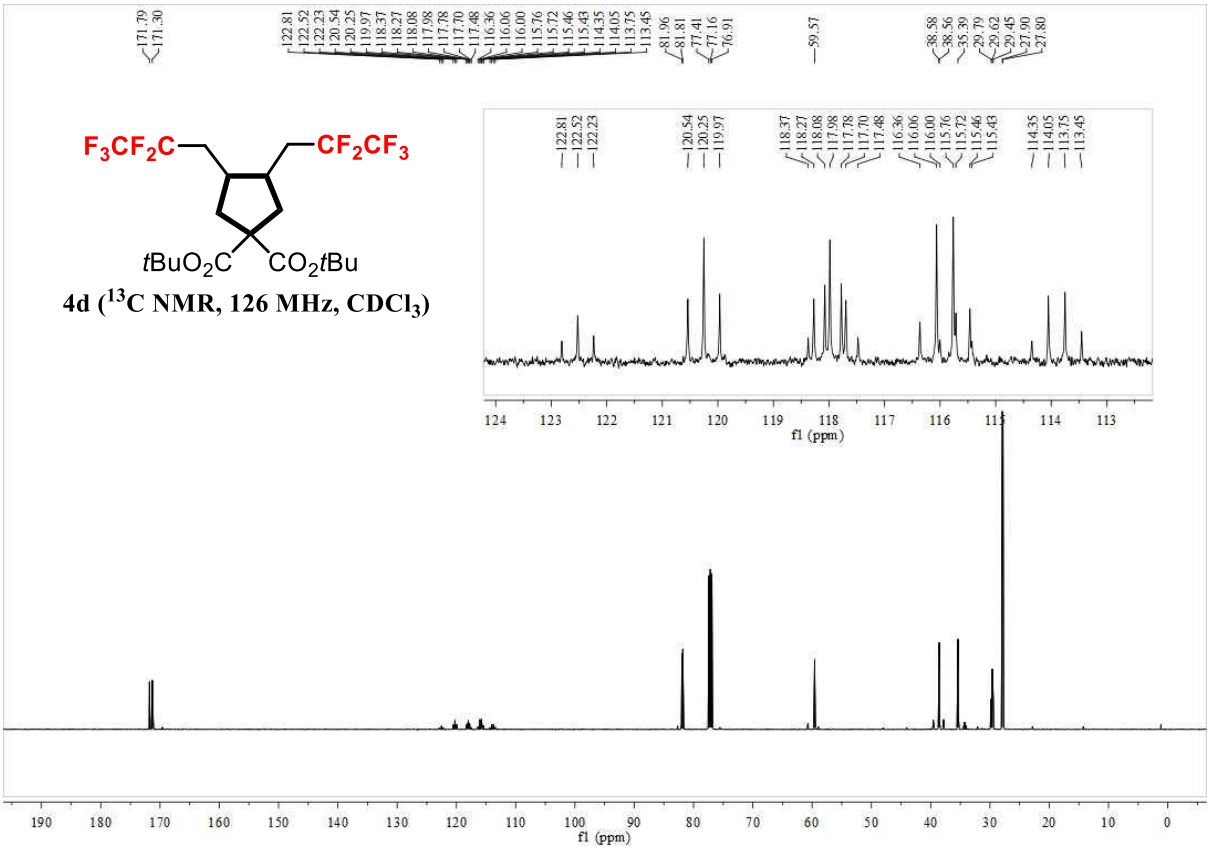
4c (^{13}C NMR, 126 MHz, $CDCl_3$)



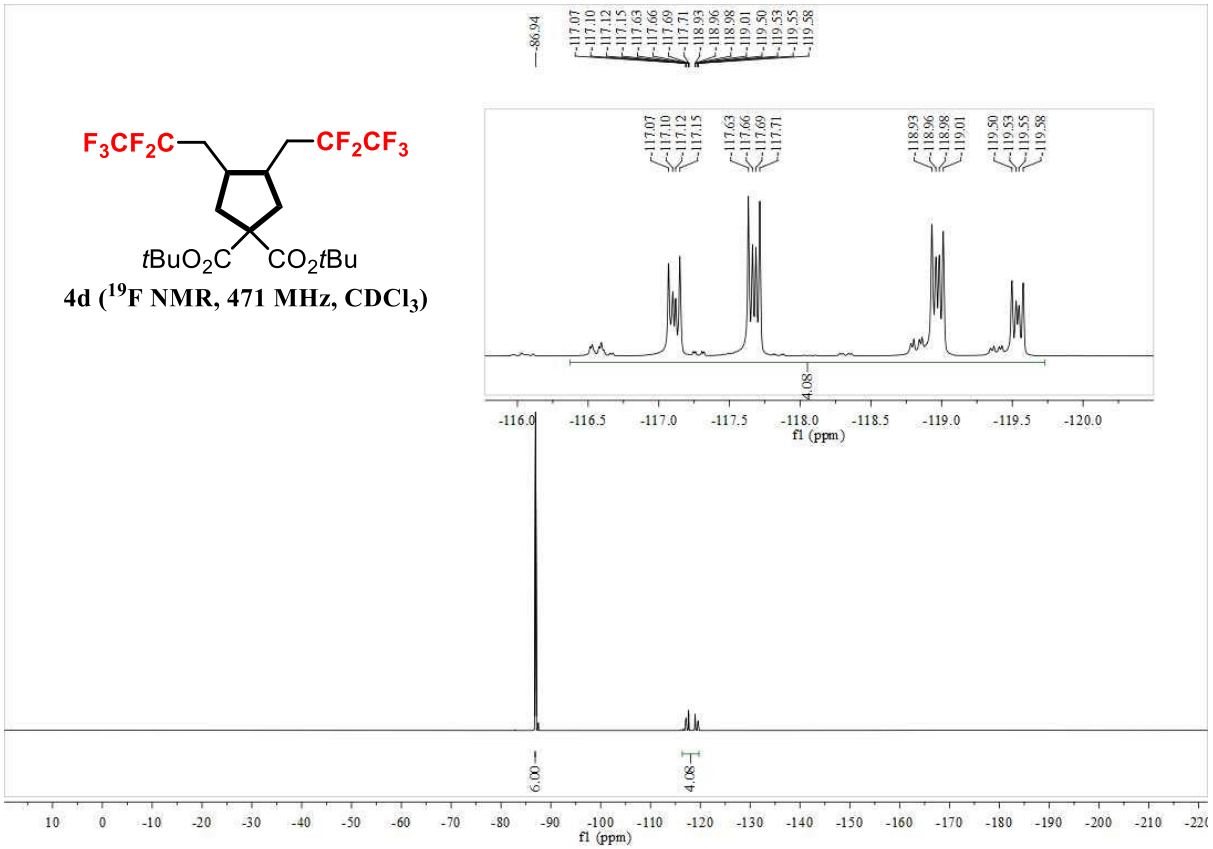
4c (^{19}F NMR, 471 MHz, $CDCl_3$)



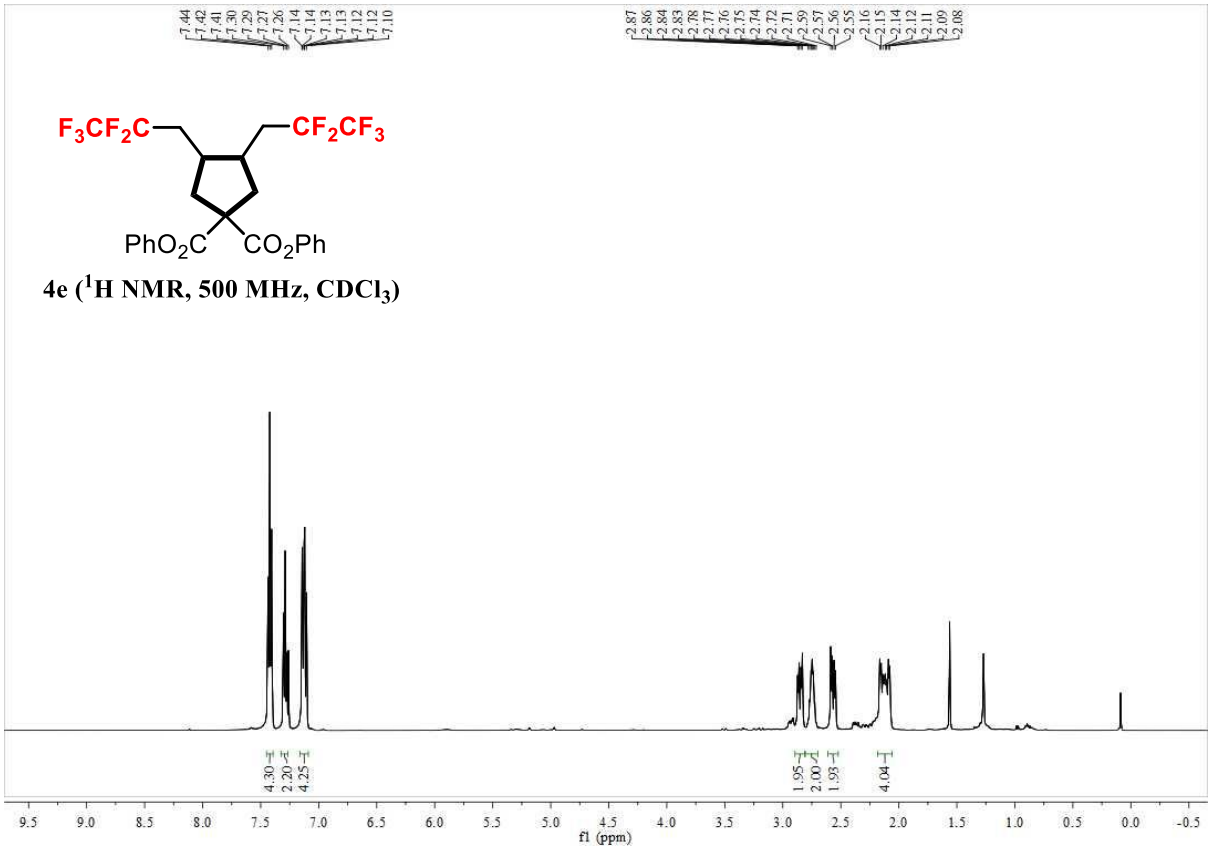
4d (^{1}H NMR, 500 MHz, $CDCl_3$)



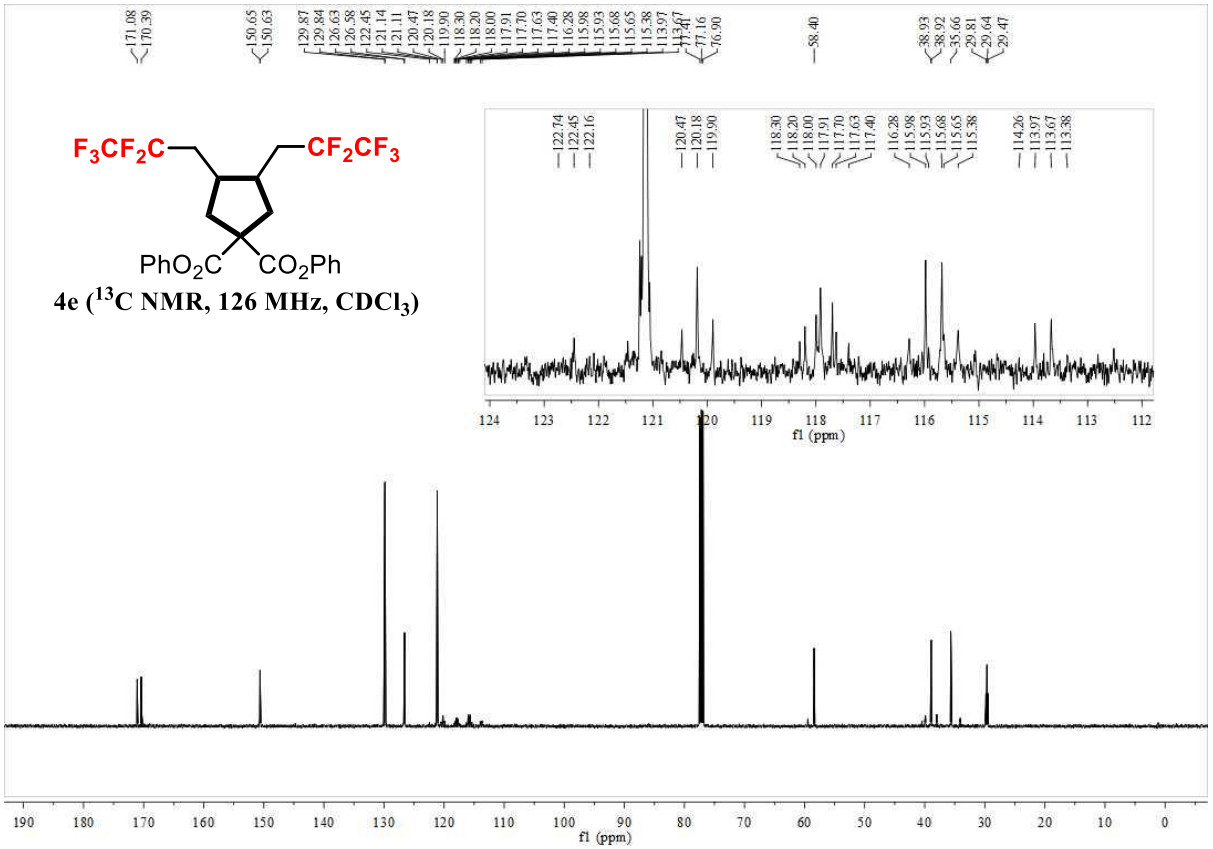
4d (^{13}C NMR, 126 MHz, $CDCl_3$)



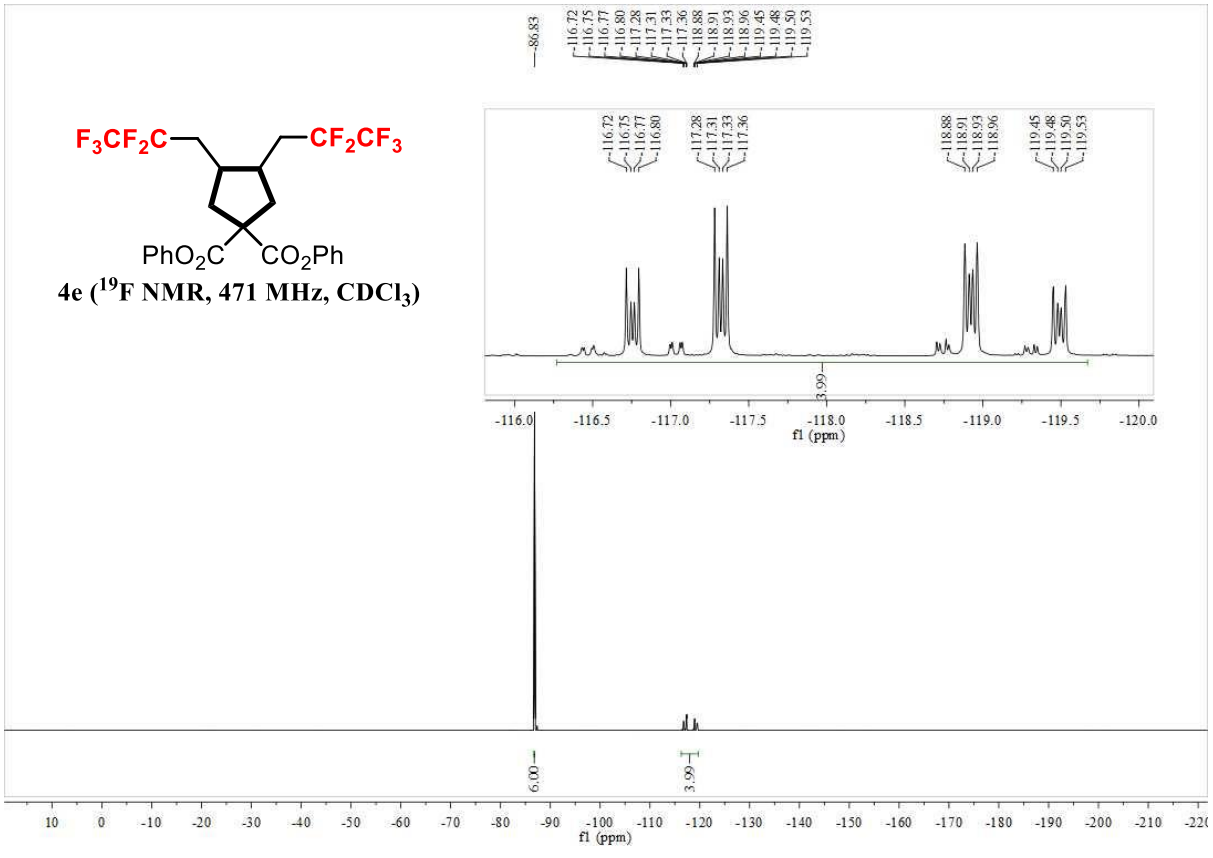
4d (^{19}F NMR, 471 MHz, $CDCl_3$)



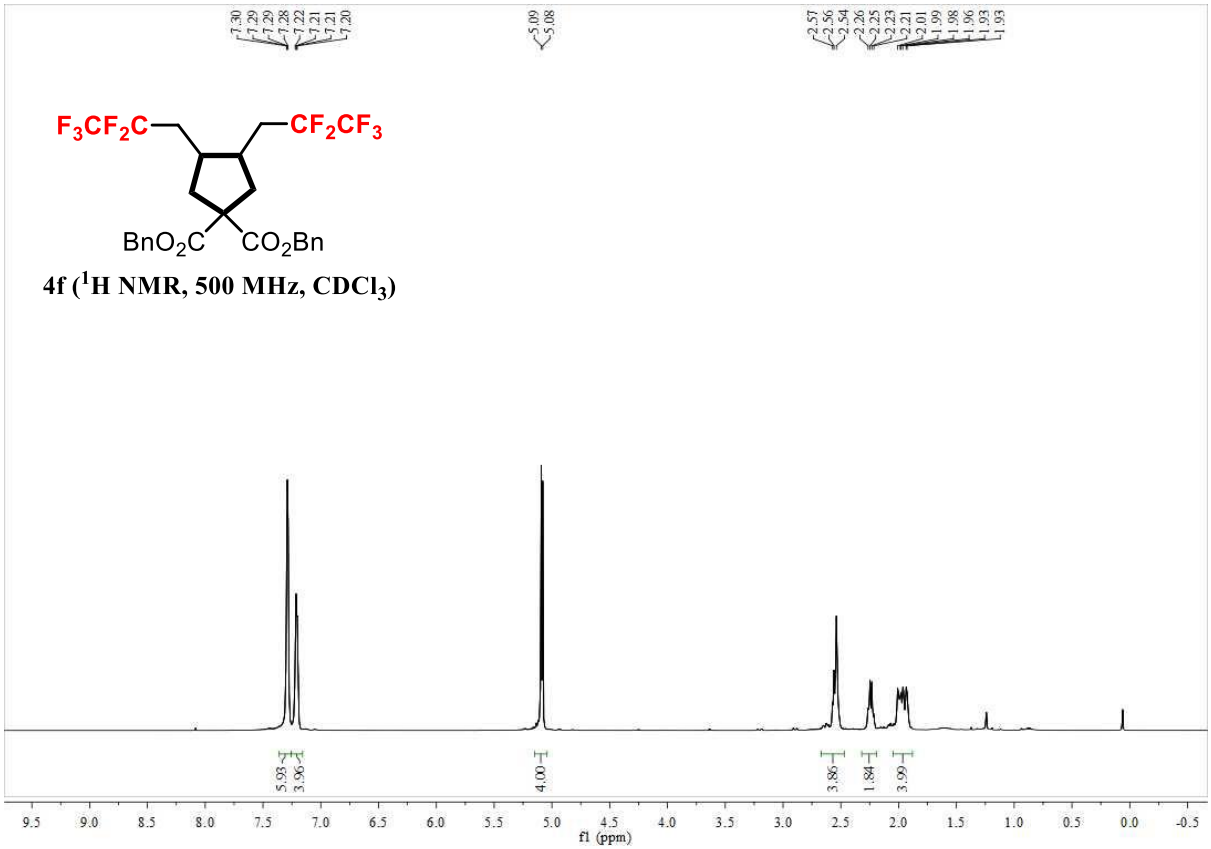
4e (^{1}H NMR, 500 MHz, $CDCl_3$)



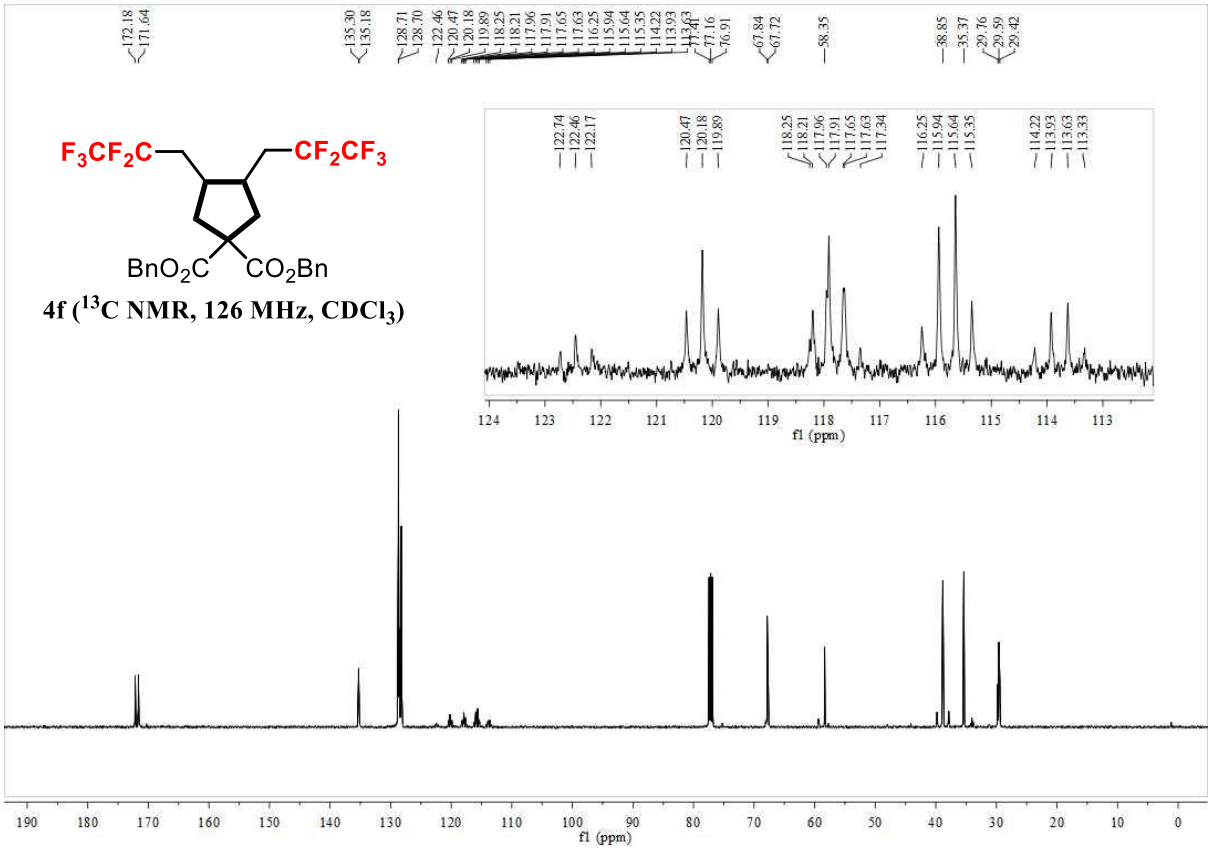
4e (^{13}C NMR, 126 MHz, $CDCl_3$)



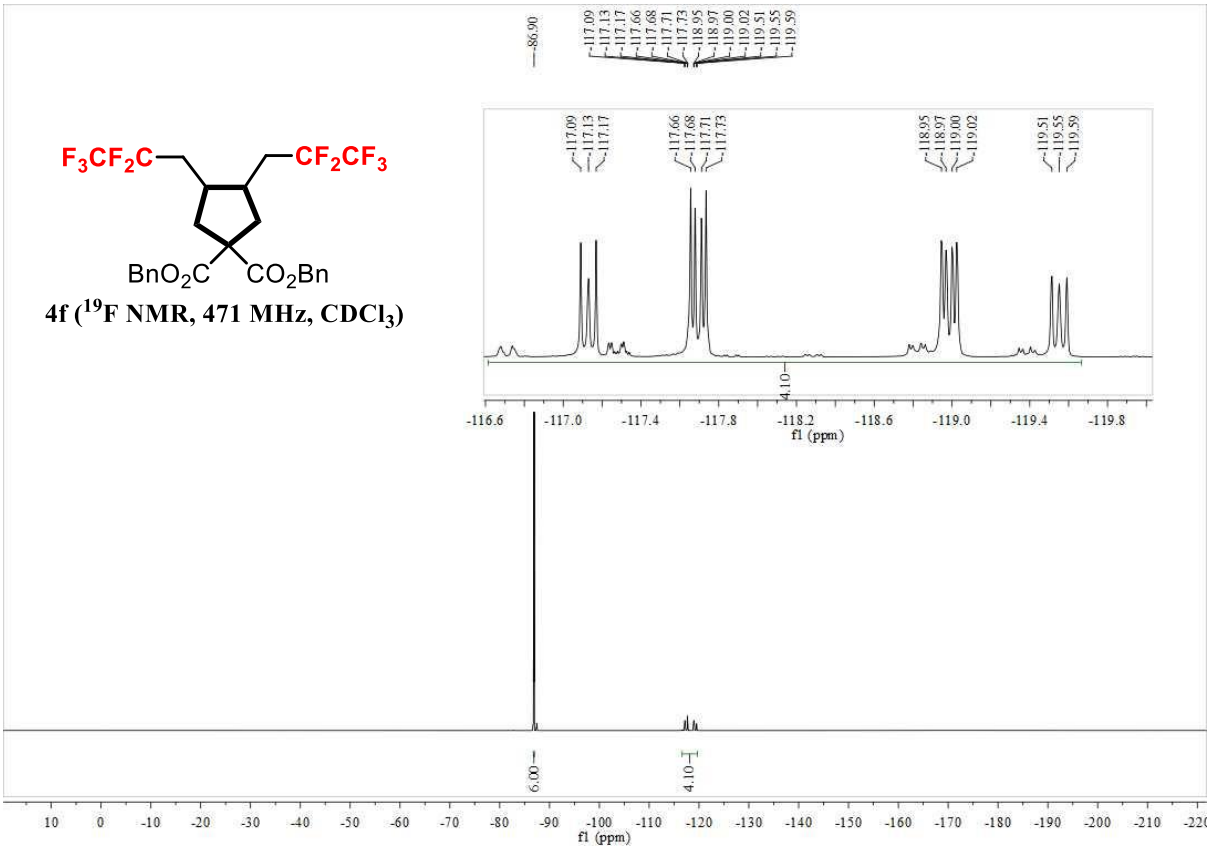
4e (^{19}F NMR, 471 MHz, $CDCl_3$)



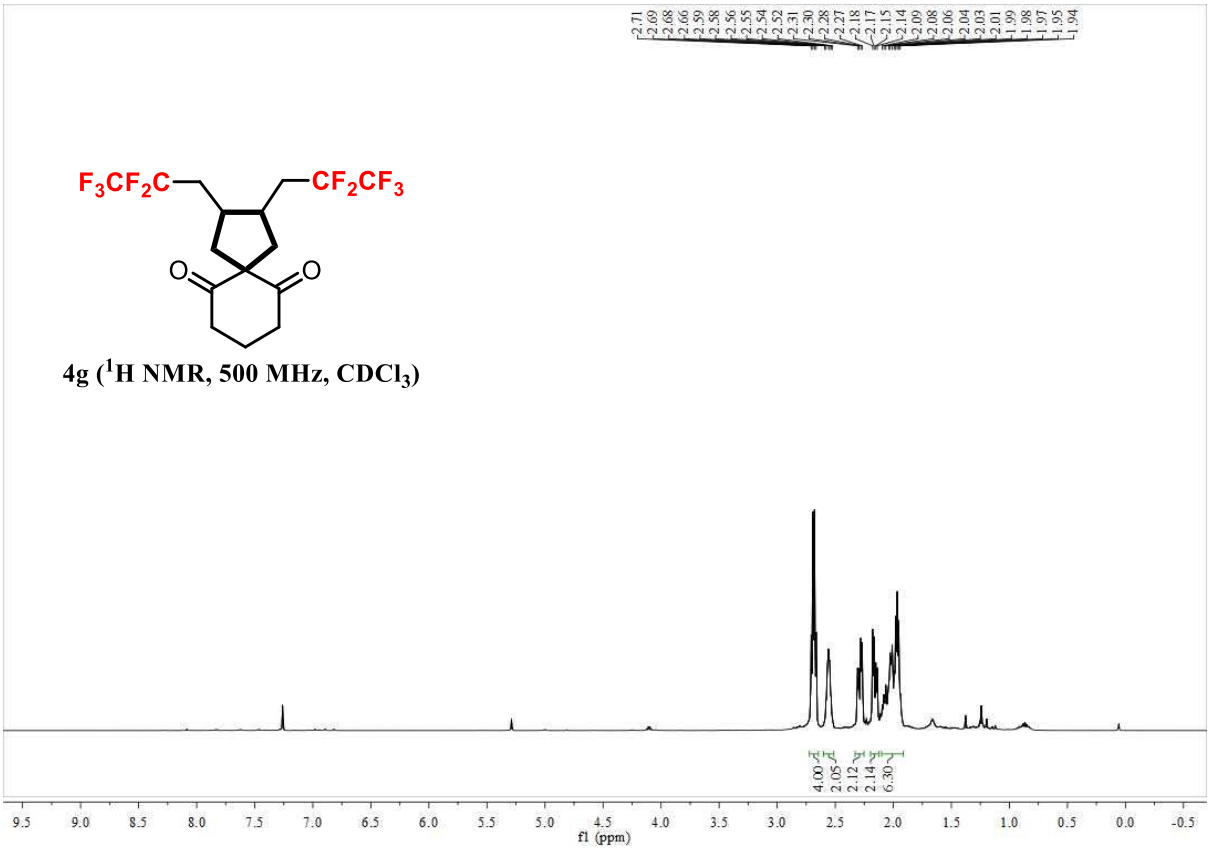
4f (^{1}H NMR, 500 MHz, $CDCl_3$)



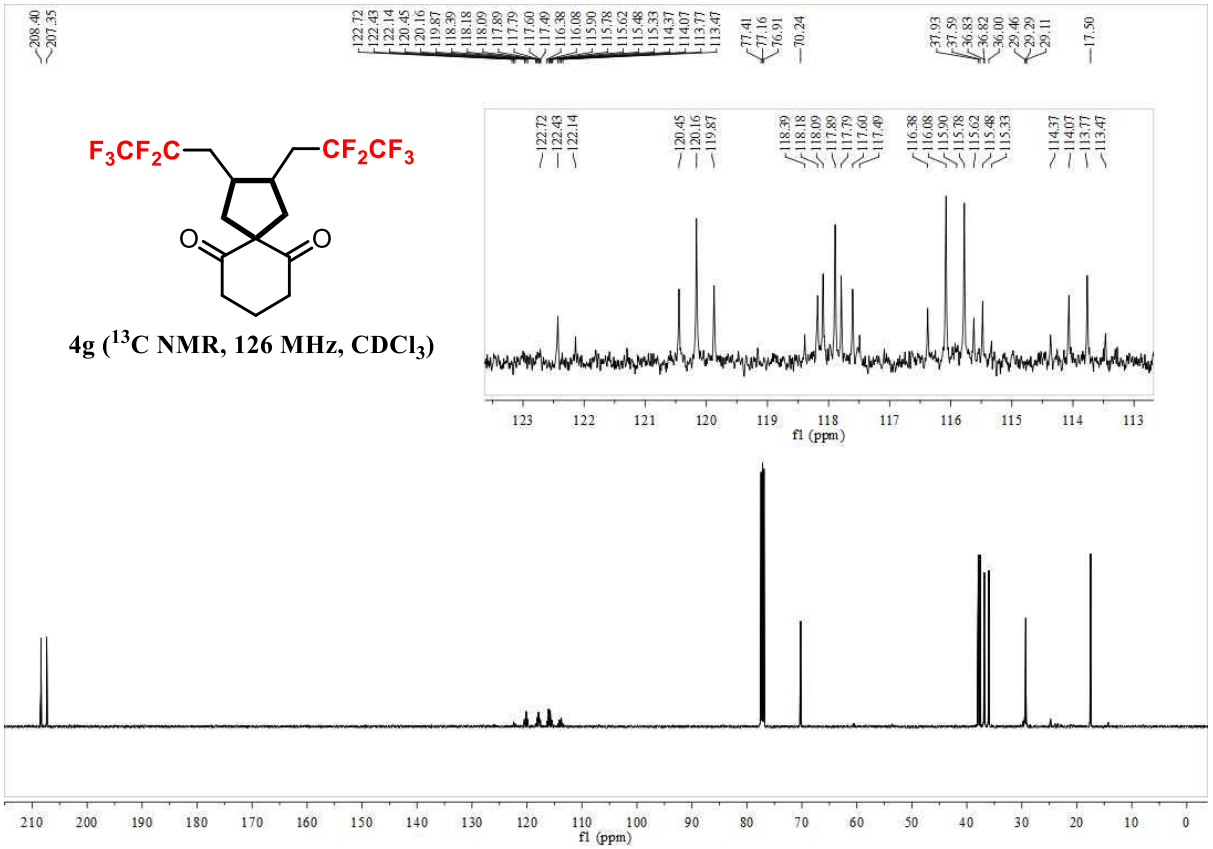
4f (^{13}C NMR, 126 MHz, $CDCl_3$)



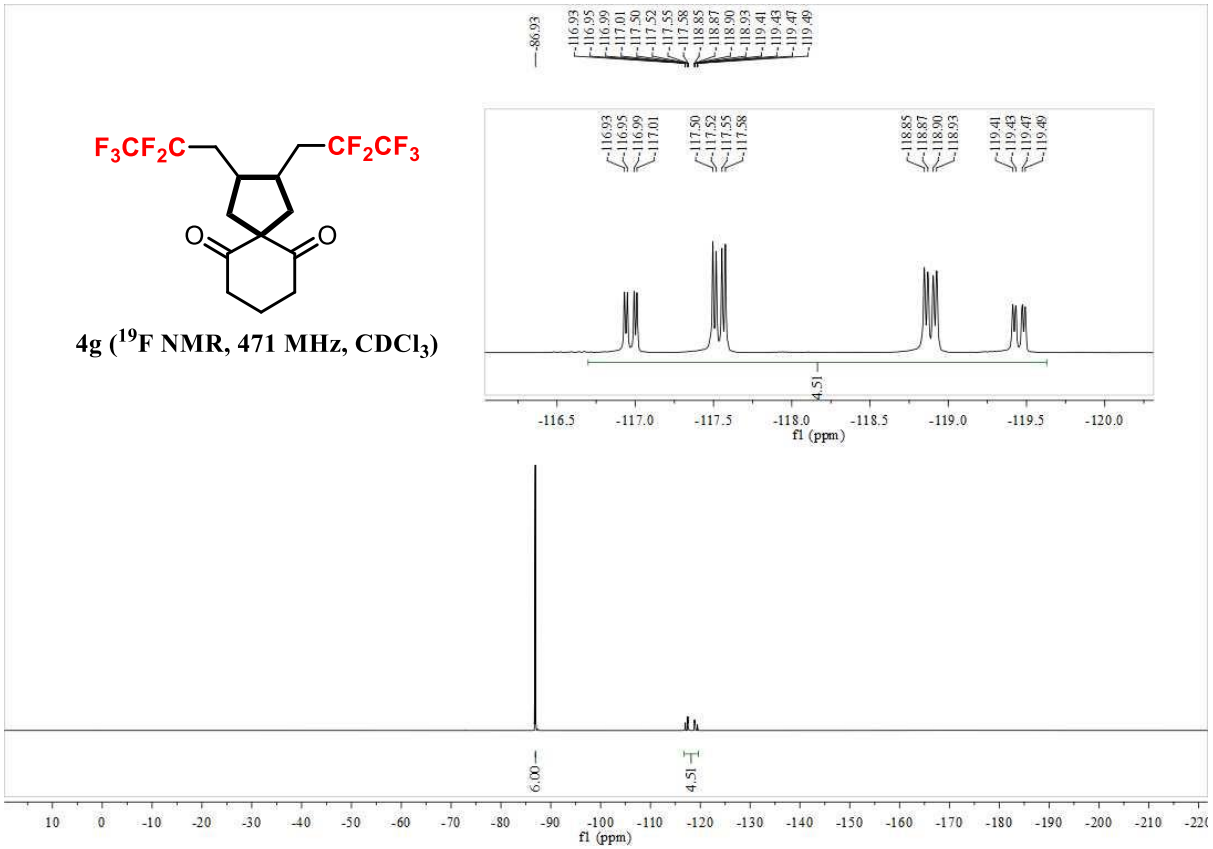
4f (^{19}F NMR, 471 MHz, $CDCl_3$)



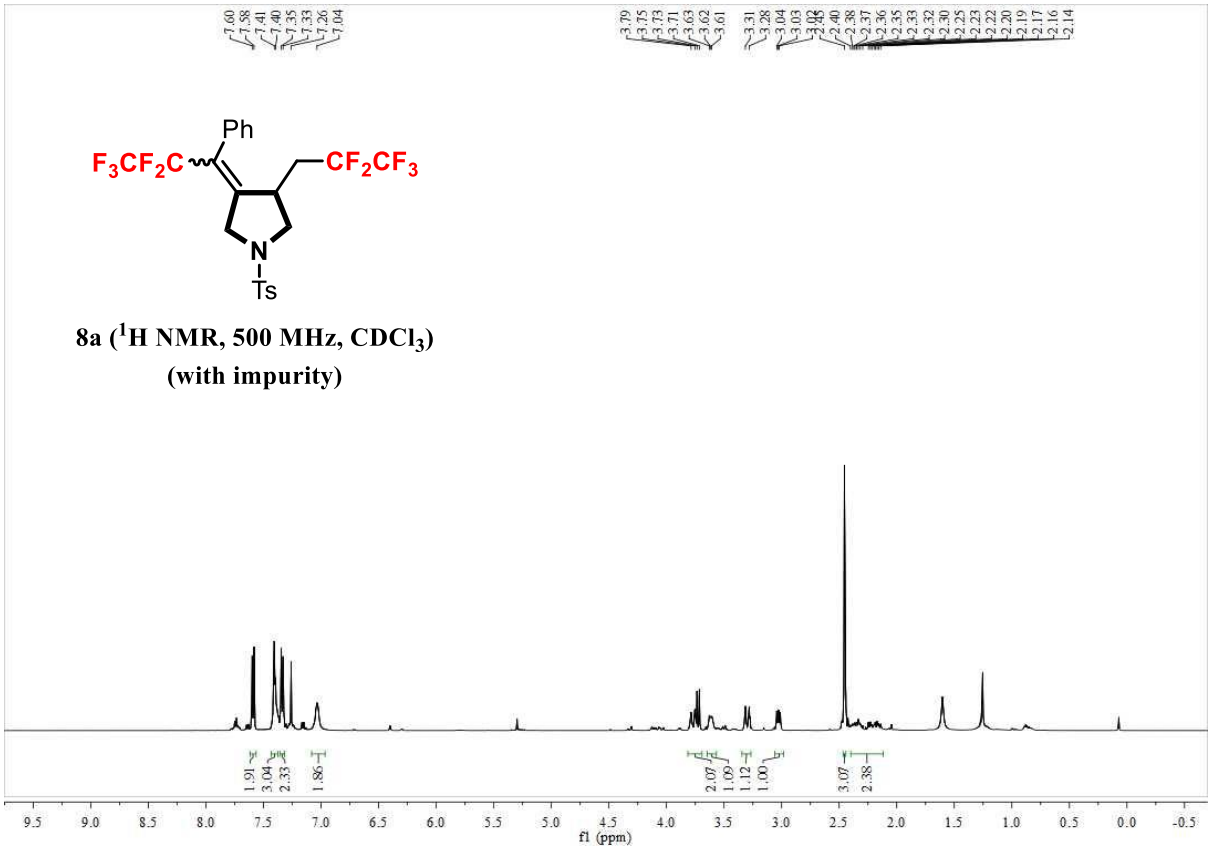
4g (^{1}H NMR, 500 MHz, $CDCl_3$)



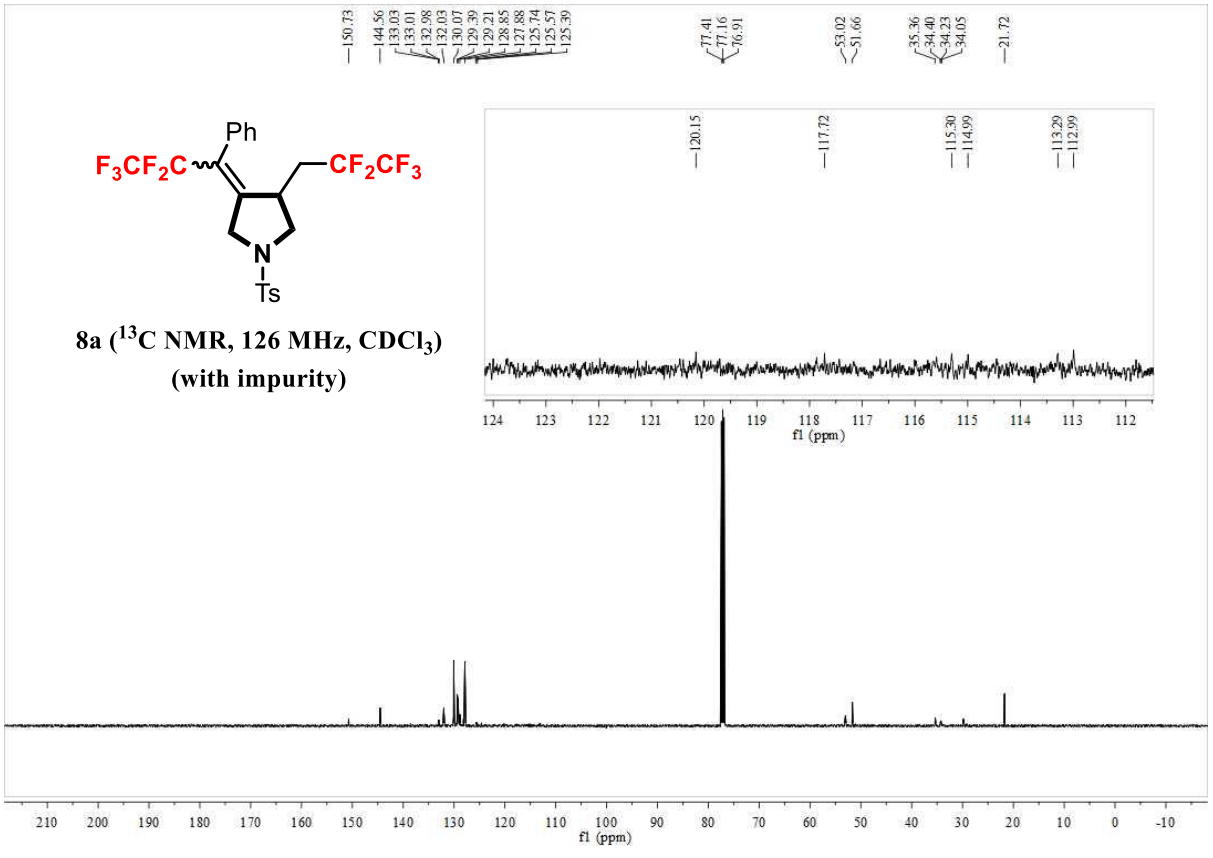
4g (^{13}C NMR, 126 MHz, $CDCl_3$)



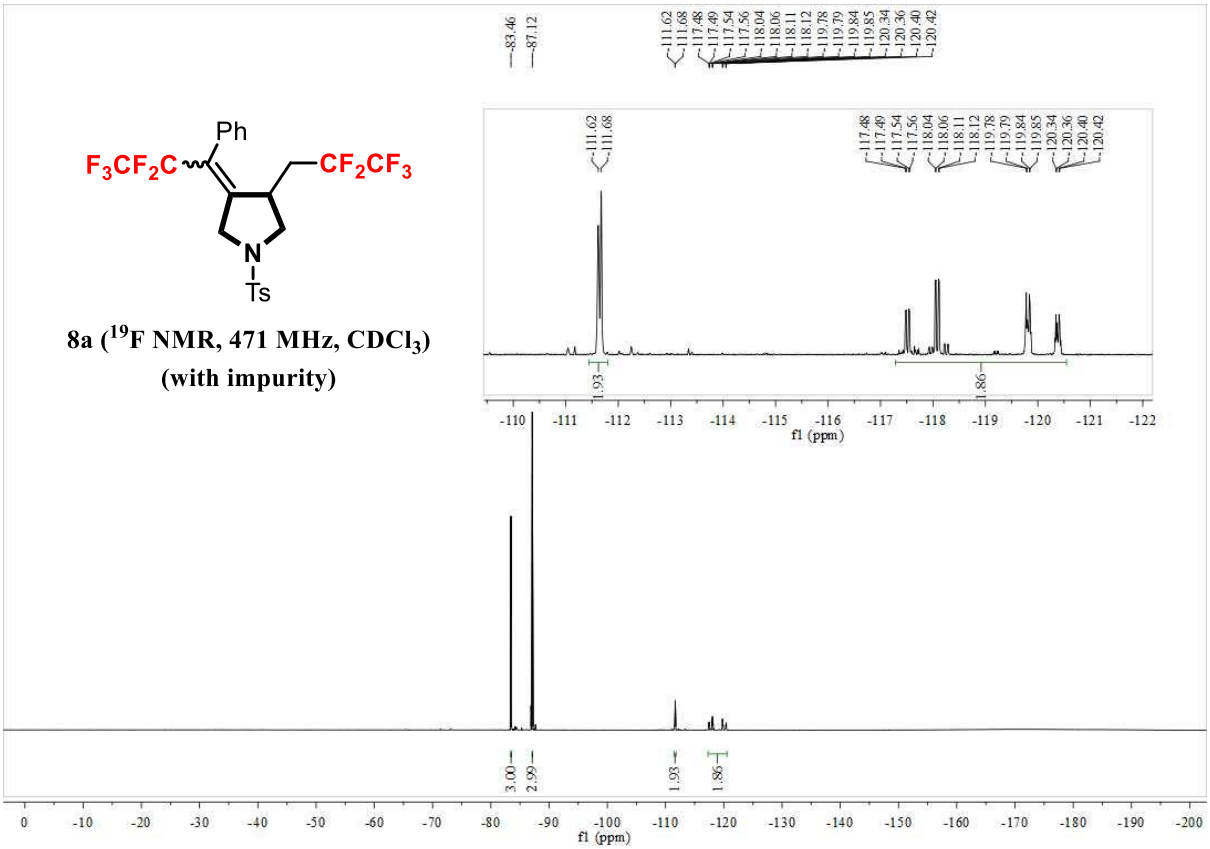
4g (^{19}F NMR, 471 MHz, $CDCl_3$)



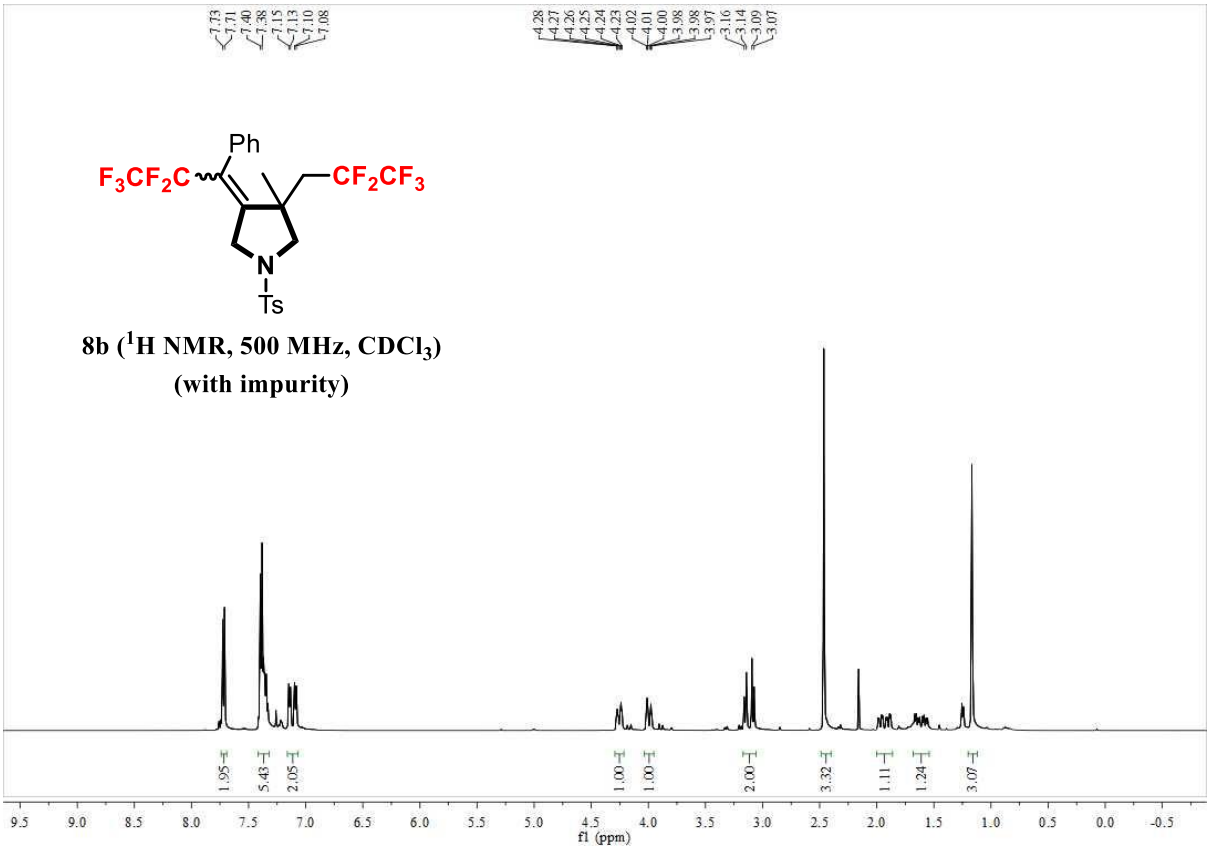
8a (^{1}H NMR, 500 MHz, $CDCl_3$)
(with impurity)



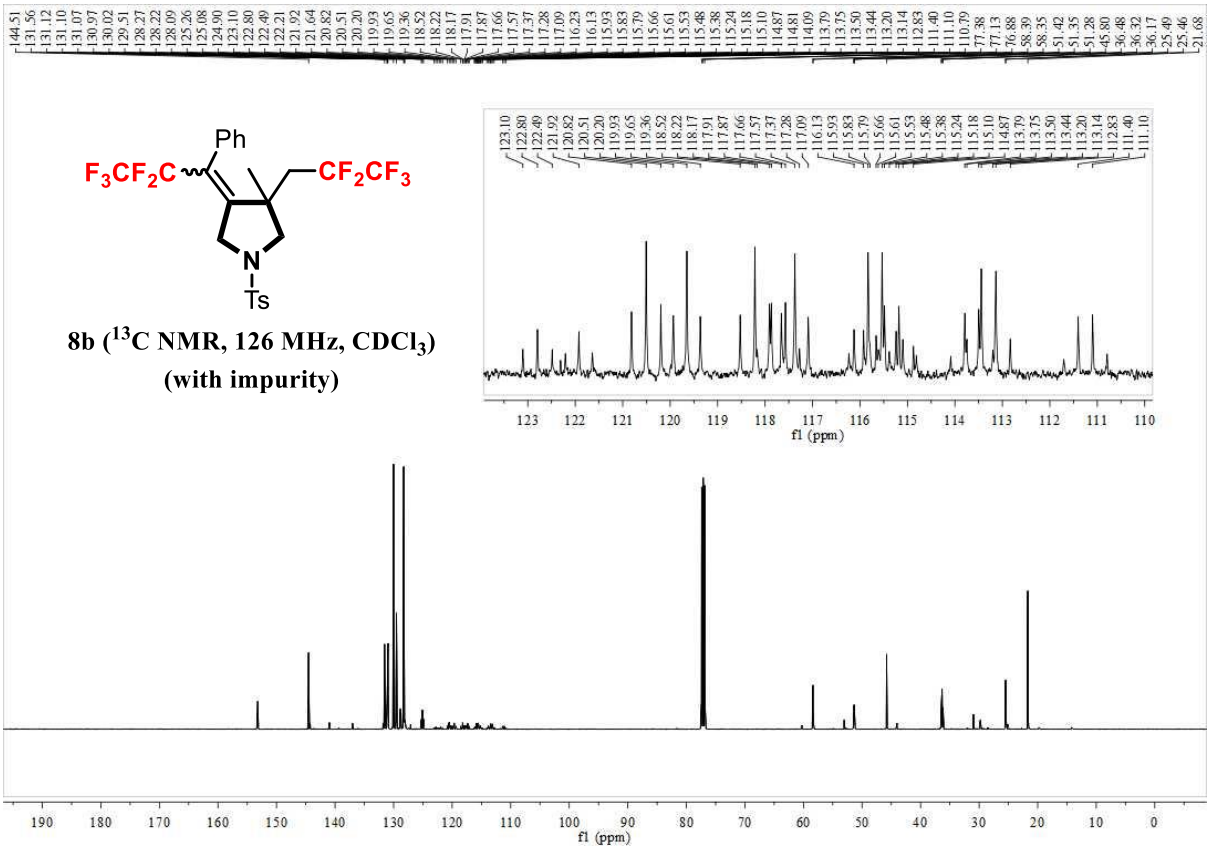
8a (^{13}C NMR, 126 MHz, $CDCl_3$)
(with impurity)



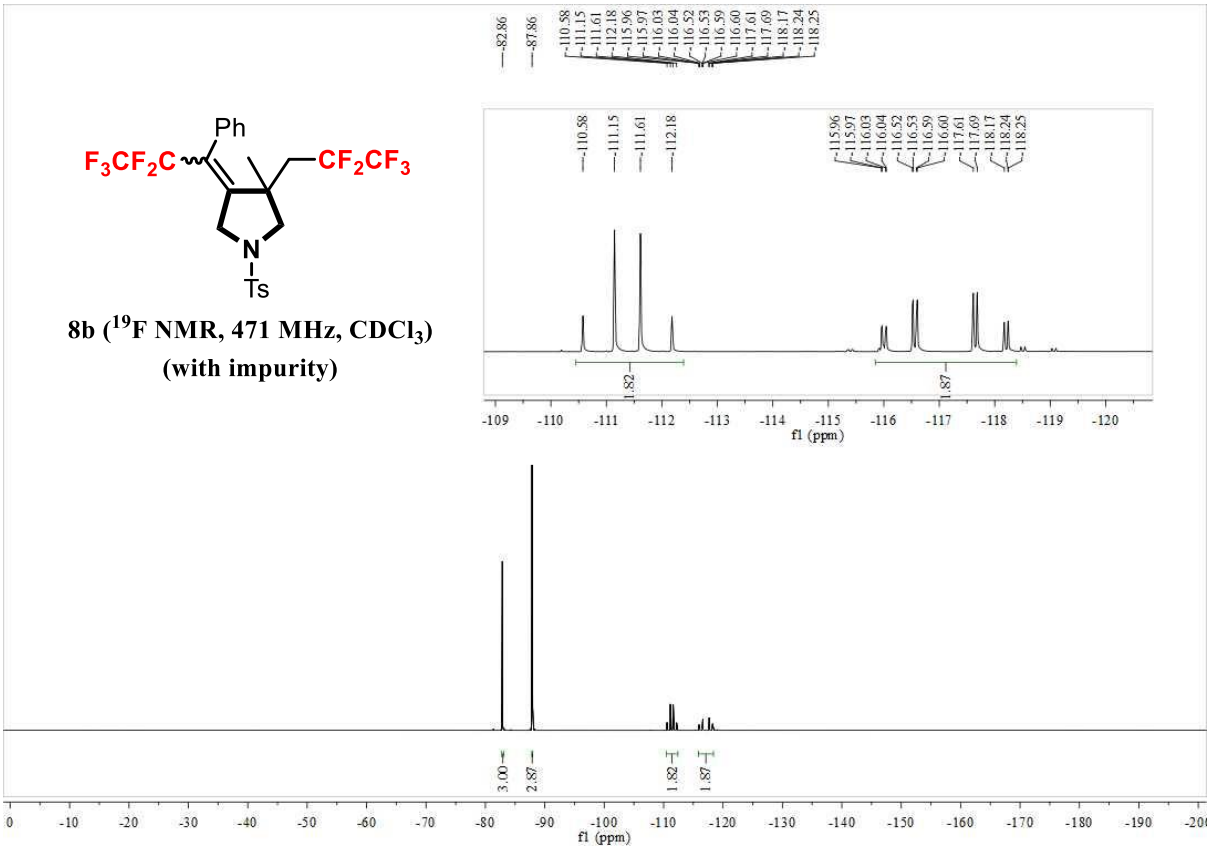
8a (^{19}F NMR, 471 MHz, $CDCl_3$)
(with impurity)



8b (^{1}H NMR, 500 MHz, $CDCl_3$)
(with impurity)



8b (^{13}C NMR, 126 MHz, $CDCl_3$)
(with impurity)



8b (^{19}F NMR, 471 MHz, $CDCl_3$)
(with impurity)