

Supporting Information

Divergent Pentafluoroethylation of Styrene Derivatives Using CuCF_2CF_3

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Experimental Procedures and Spectral Data

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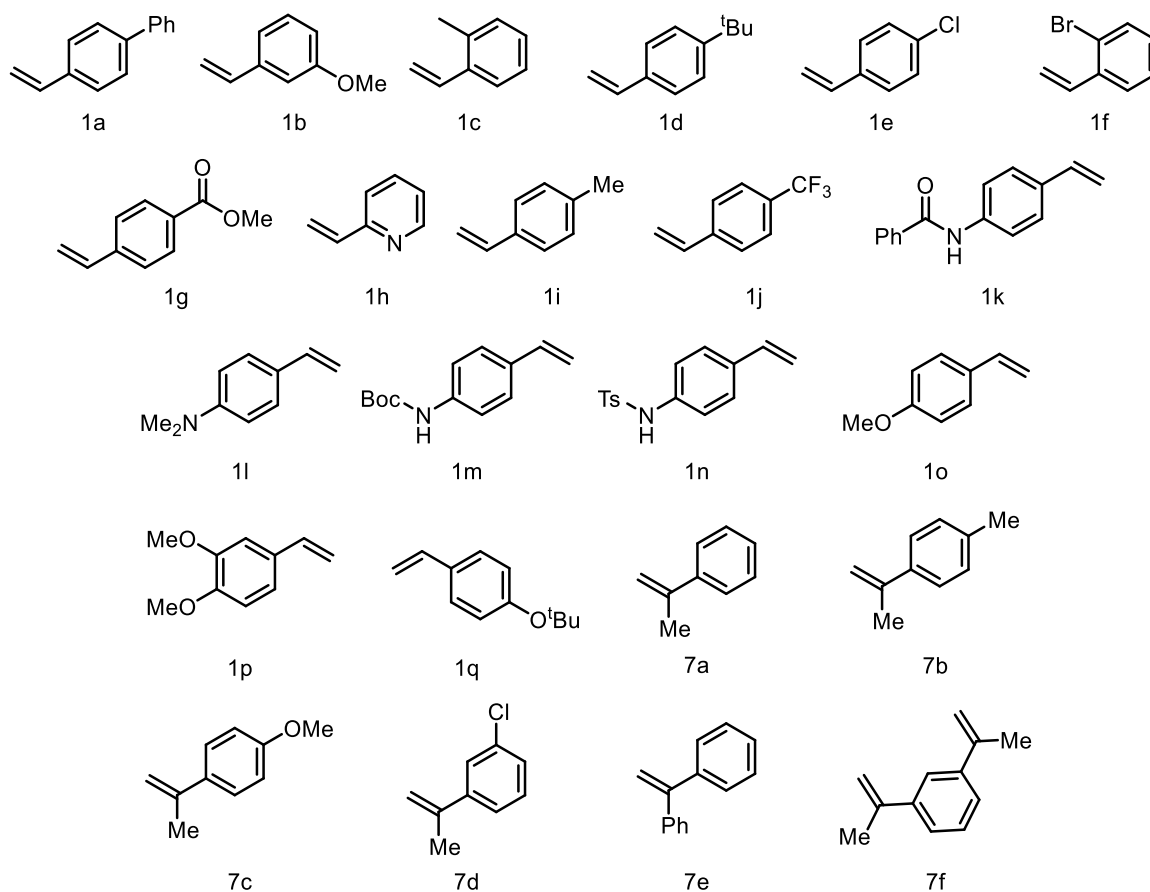
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General Experimental. Unless otherwise noted, reactions were carried out in a 10 mL glass tube with magnetic stirring. Analytical thin layer chromatography (TLC) was performed with EM Science silica gel 60 F254 aluminum plates. Visualization was done under a UV lamp (254 nm) and by immersion in potassium permanganate (KMnO₄), followed by heating using a heat gun. Organic solutions were concentrated by rotary evaporation at 23–35 °C. Purification of reaction products were generally done by flash column chromatography with Silicycle 60-230 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 and TREAT·HF was purchased from J&K Scientific and Macklin. Other chemicals for substrates preparation were purchased from Acros, J&K Scientific, Aldrich, Dikemann and Bide.

Instrumentation. Proton nuclear magnetic resonance spectra (¹H NMR) spectra, carbon nuclear magnetic resonance spectra (¹³C NMR) and fluorine nuclear magnetic resonance spectra (¹⁹F NMR) were recorded at 23 °C on a Bruker 400 spectrometer in CDCl₃ (400 MHz for ¹H, 101 MHz for ¹³C and 377 MHz for ¹⁹F) and Bruker 500 spectrometer in CDCl₃ (500 MHz for ¹H, 126 MHz for ¹³C and 471 MHz for ¹⁹F). Chemical shifts for protons were reported as parts per million in δ scale using solvent residual peak (CHCl₃: 7.26 ppm) or tetramethylsilane (0.00 ppm) as internal standards. Chemical shifts of ¹³C NMR spectra were reported in ppm from the central peak of CDCl₃ (77.16 ppm) on the δ scale. Chemical shifts of ¹⁹F 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) and integration. X-ray crystallography was conducted on a Bruker D8 Venture X-Ray Diffractometer. High resolution mass spectra (HRMS) were obtained on a Bruker SolariX 9.4T ICR Mass Spectrometer or a Thermo Q Exactive Focus Orbitrap Mass Spectrometer. The control experiment results were obtained on a Shimadzu GCMS-QP2010 SE GC MS Spectrometer.

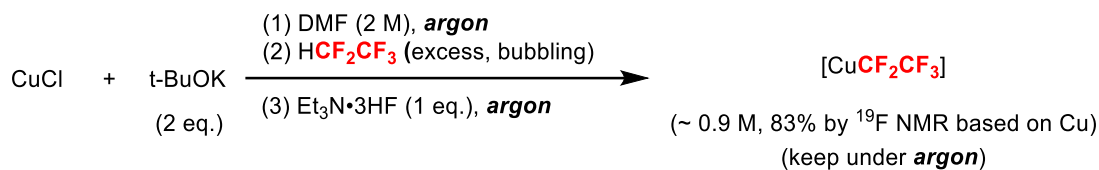
Substrate table



Styrene **1k**, **1m**, **1n**, **7c**, **7d** were synthesized according to literature procedure,^{2,3} and the spectral data were in full accordance with the literature report. Styrene **1a-1j**, **1l**, **1o-1q**, **7a**, **7b**, **7e**, **7f** was commercially available.

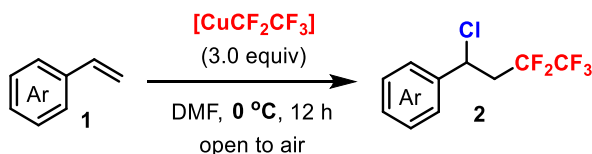
Experimental Procedures.

General procedure A for the preparation of pentafluoroethane-derived $[\text{CuCF}_2\text{CF}_3]$ reagent with 1.0 equiv. $\text{Et}_3\text{N}\cdot 3\text{HF}$:¹



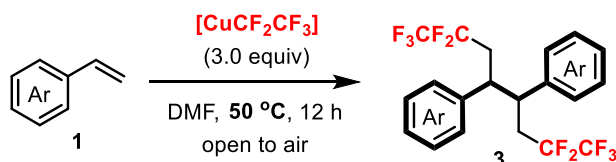
In a glove box, to a glass tube was charged CuCl (200 mg, 2.0 mmol), t-BuOK (464 mg, 4.0 mmol) and a stirrer bar. The flask was sealed with a septum, brought out of the glove box, and put under an argon atmosphere. Degassed DMF (1.0 mL) was added via syringe and the mixture was vigorously stirred at 0 °C 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 $\text{Et}_3\text{N}\cdot 3\text{HF}$ (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 $[\text{CuCF}_2\text{CF}_3]$ solution in DMF (~83%, ~0.9 M).

General procedure B for synthesis of 2:



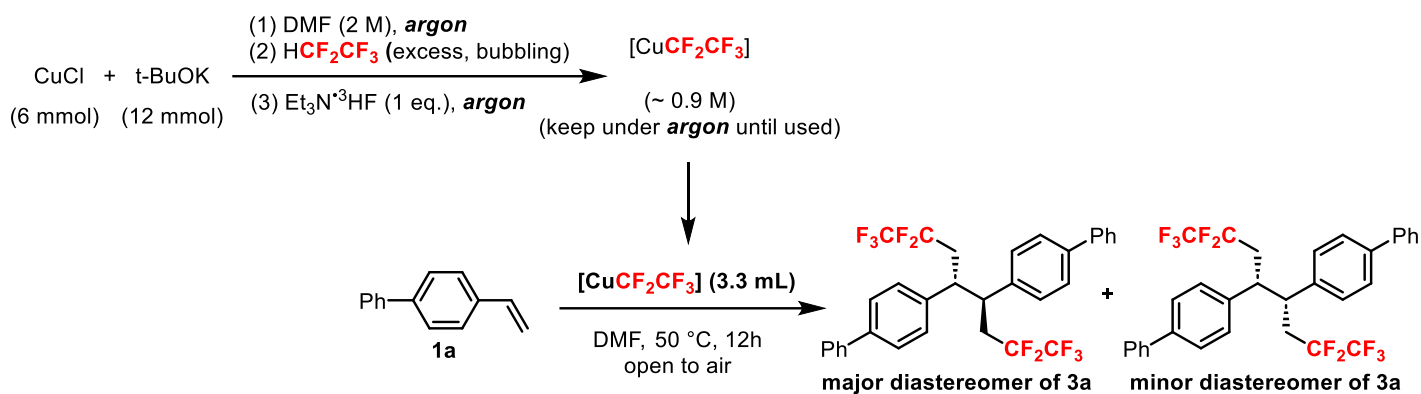
Under air, styrene **1** (0.3 mmol) and a magnetic stir bar were added to a glass tube. Then, freshly prepared $[\text{CuCF}_2\text{CF}_3]$ (from procedure A, 1.0 mL, 0.90 mmol in DMF, 3.0 equiv) was added at 0 °C. Then the tube was stirred at same temperature for 12 h. The color slowly changed from greyish yellow to pale grey to blue to dark red. The reaction mixture was quenched with aq. sat. EDTA·2Na and extracted with dichloromethane 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**.

General procedure C for synthesis of 3:



Under air, styrene **1** (0.3 mmol) and a magnetic stir bar were added to a glass tube. Then, freshly prepared $[\text{CuCF}_2\text{CF}_3]$ (from procedure A, 1.0 mL, 0.90 mmol in DMF, 3.0 equiv) was added at room temperature. Then the tube was stirred at 50 °C for 12 h. The color quickly 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 dichloromethane 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 **3**.

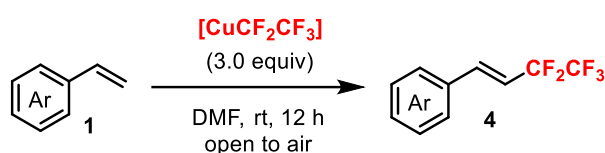
1 mmol scale reaction of 3a:



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 (HCF₂CF₃) was bubbled into the mixture by using a needle connected to the HCF₂CF₃ cylinder at room temperature for 10 min. After removing the HCF₂CF₃ inlet, the mixture was stirred for 5 min and Et₃N·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 [CuCF₂CF₃] solution in DMF (~0.9 M).

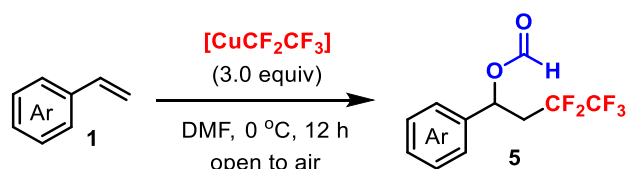
Under air, to a 25mL round-bottom flask equipped with a magnetic stir bar, styrene **1a** (180.0 mg, 1.0 mmol) and a magnetic stir bar were added to a glass tube. Then, freshly prepared [CuCF₂CF₃] (3.3 mL, 3.0 mmol in DMF) above was added at room temperature. Then the tube was stirred at 50 °C for 12 h. The color quickly 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 DCM three times. The organic layers were combined, washed with water then brine, dried over anhydrous Na₂SO₄, filtered, and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product major diastereomer of **3a** as a colorless solid (86.9 mg, 0.15 mmol, 29%). *R*_f = 0.48 (hexane: ethyl acetate = 10:1). Minor diastereomer of **3a** is obtained as a colorless solid (48.6 mg, 0.08 mmol, 16%). *R*_f = 0.51 (hexane: ethyl acetate = 10:1).

General procedure D for synthesis of 4:



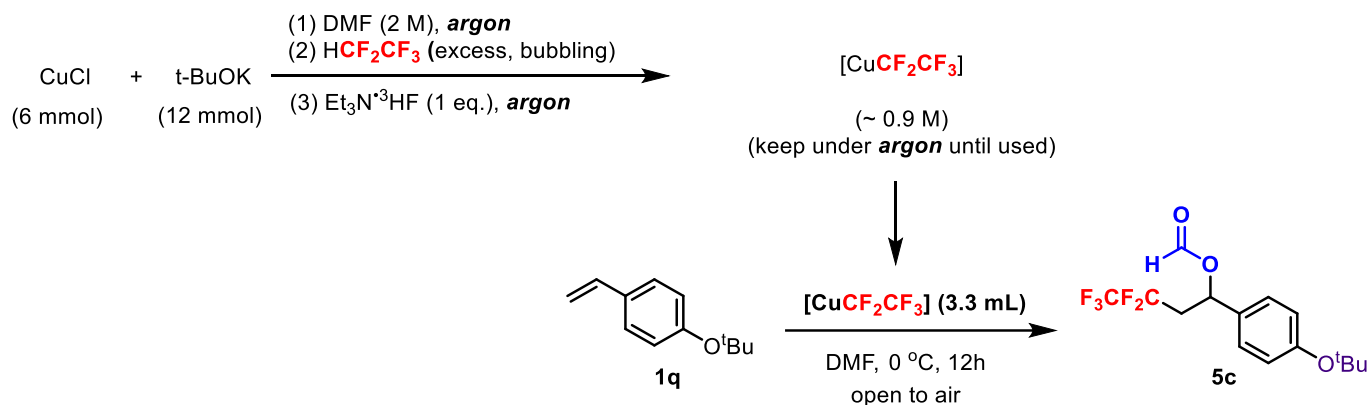
Under air, styrene **1** (0.3 mmol) and a magnetic stir bar were added to a glass tube. Then, freshly prepared [CuCF₂CF₃] (from procedure A, 1.0 mL, 0.90 mmol in DMF, 3.0 equiv) was added at room temperature. Then the tube was stirred at same temperature for 12 h. The color changed from greyish yellow to pale grey to blue to dark red. The reaction mixture was quenched with aq. sat. EDTA·2Na and extracted with dichloromethane three times. The organic layers were combined, washed with water then brine, dried over anhydrous Na₂SO₄, filtered, and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product **4**.

General procedure E for synthesis of 5:



Under air, styrene **1** (0.3 mmol) and a magnetic stir bar were added to a glass tube. Then, freshly prepared $[\text{CuCF}_2\text{CF}_3]$ (from procedure A, 1.0 mL, 0.90 mmol in DMF, 3.0 equiv) was added at 0 °C. Then the tube was stirred at same temperature for 12 h. The color 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 dichloromethane 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 **5**.

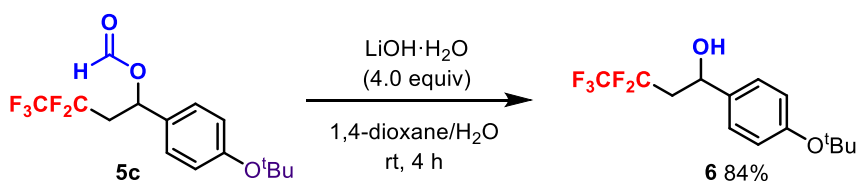
1 mmol scale reaction of **5c**:



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 $\text{Et}_3\text{N}\cdot\text{3HF}$ (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 $[\text{CuCF}_2\text{CF}_3]$ solution in DMF (~0.9 M).

Under air, to a 25mL round-bottom flask equipped with a magnetic stir bar, styrene **1q** (176.0 mg, 1.0 mmol) and a magnetic stir bar were added to a glass tube. Then, freshly prepared $[\text{CuCF}_2\text{CF}_3]$ (3.3 mL, 3.0 mmol in DMF) above was added at 0 °C. Then the flask was stirred at same temperature for 12 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 DCM 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 **3a** as a pale yellow solid (197.2 mg, 0.58 mmol, 58%). $R_f = 0.41$ (hexane: ethyl acetate = 10:1).

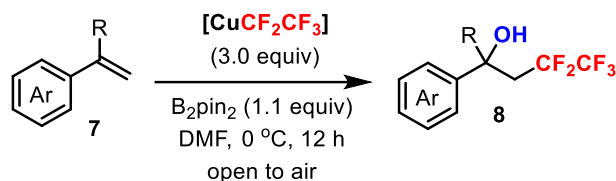
Synthesis of **6**:



Add $\text{LiOH}\cdot\text{H}_2\text{O}$ (50.4 mg, 1.2 mmol) to a solution of product **5c** (102.0 mg, 0.3 mmol) in dioxane and H_2O . Stir the reaction mixture at room temperature for 4h. The reaction mixture was neutralized with 2N HCl and extracted with ethyl acetate 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 product **6** was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 20) and obtained as a yellow oil (78.6 mg, 84% yield), $R_f = 0.25$ (ethyl acetate: hexane = 1: 10). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm) 7.19 (d, $J = 8.5$ Hz, 2H), 6.90 (d, $J = 8.5$ Hz, 2H), 5.07 (dd, $J = 8.9, 3.5$ Hz, 1H), 2.91 (s, 1H), 2.52 (ddt, $J = 24.4, 18.0, 9.1$ Hz, 1H), 2.31 (dddd, $J = 28.1, 15.3, 9.3, 3.5$ Hz, 1H), 1.31 (s, 9H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 155.1, 137.9, 126.4, 124.5,

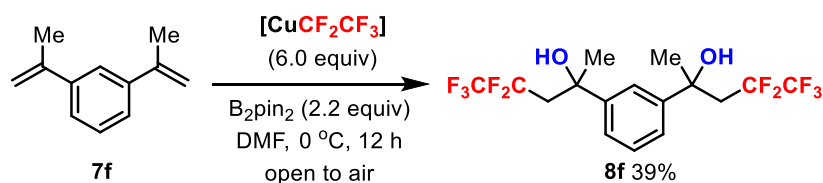
119.1 (qt, $J = 285.3, 35.9$ Hz), 115.2 (tq, $J = 253.0, 37.6$ Hz), 79.1, 67.5, 39.6 (t, $J = 20.4$ Hz), 28.8. ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -86.81 (t, $J = 3.7$ Hz, 3F), -117.40 (ddd, $J = 267.0, 27.7, 9.9$ Hz, 1F), -118.69 (ddd, $J = 267.4, 26.4, 9.9$ Hz, 1F). HRMS m/z (ESI): calcd. for $\text{C}_{14}\text{H}_{17}\text{F}_5\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 335.1041; found: 335.1041.

General procedure F for synthesis of **8**:



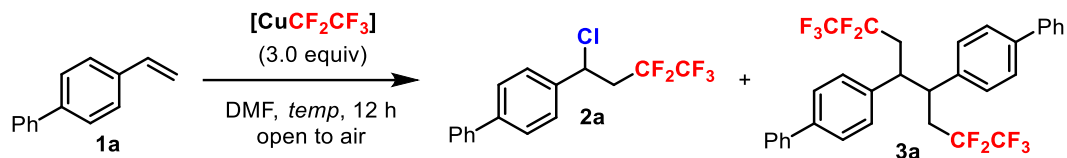
Under air, styrene **7** (0.3 mmol), B_2Pin_2 (0.33 mmol) and a magnetic stir bar were added to a glass tube. Then, freshly prepared $[\text{CuCF}_2\text{CF}_3]$ (from procedure A, 1.0 mL, 0.90 mmol in DMF, 3.0 equiv) was added at 0°C . Then the tube was stirred at same temperature for 12 h. The color 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 dichloromethane 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 **8**.

Synthesis of **8f**:



Under air, styrene **7f** (47.4 mg, 0.3 mmol), B_2Pin_2 (167.0 mg, 0.66 mmol) and a magnetic stir bar were added to a glass tube. Then, freshly prepared $[\text{CuCF}_2\text{CF}_3]$ (2.0 mL, 1.80 mmol in DMF) above was added at 0°C . The reaction reacted under 0°C for 12h. 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 dichloromethane 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 product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 20) and obtained as a pale yellow solid (50.3 mg, 39% yield), $R_f = 0.26$ (ethyl acetate: hexane = 1: 10). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.66 (d, $J = 5.3$ Hz, 1H), 7.38 (s, 3H), 2.71 – 2.47 (m, 4H), 2.36 (s, 2H), 1.77 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 146.9 (d, $J = 3.5$ Hz), 128.7, 123.6 (d, $J = 1.8$ Hz), 120.5 (d, $J = 3.2$ Hz), 118.8 (qt, $J = 285.9, 36.1$ Hz), 115.8 (tq, $J = 255.0, 37.4$ Hz), 72.9 (d, $J = 1.7$ Hz), 42.7 (t, $J = 19.3$ Hz), 30.4 (dd, $J = 5.8, 2.3$ Hz). ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -87.67 (d, $J = 6.9$ Hz, 6F), -115.67 (ddt, $J = 266.3, 32.3, 7.9$ Hz, 2F), -117.61 – -119.28 (m, 2F). HRMS m/z (ESI): calcd. for $\text{C}_{16}\text{H}_{15}\text{F}_{10}\text{O}_2$ $[\text{M}-\text{H}]^-$: 429.0918; found: 429.0920.

Optimization Table^a

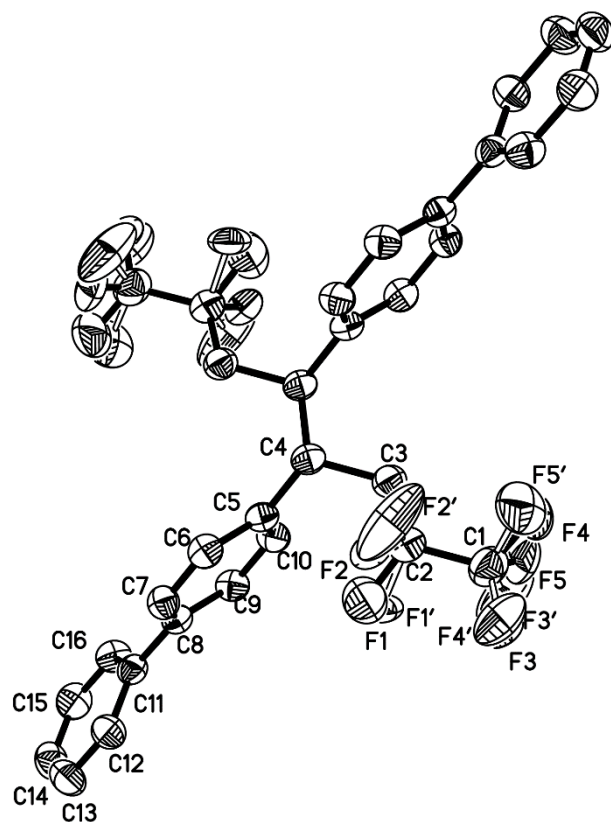


| entry | Temp (°C) | Additive (equiv.) | 2a (%) ^b | 3a (%) ^b |
|----------------|-----------|---------------------------|----------------------------|----------------------------|
| 1 | rt | None | 11 | 61 |
| 2 | 0 | None | 65 (70) ^c | 10 |
| 3 | 50 | None | 4 | 78 |
| 4 | 80 | None | 0 | 41 |
| 5 | -10 | None | 43 | 11 |
| 6 ^d | 0 | None | 36 | 5 |
| 7 ^e | 0 | None | 12 | 0 |
| 8 | 0 | NaCl (0.5) | 70 | 11 |
| 9 | 0 | NaCl (2.0) | 43 | 16 |
| 10 | 0 | NEt ₄ Cl (0.5) | 56 | 16 |
| 11 | 0 | LiCl (0.5) | 48 | 2 |

^aUnless specified otherwise, reactions were carried out using 0.1 mmol **1a** at 0.3 M concentration. $[\text{CuCF}_2\text{CF}_3]$ was added at 0 °C then the reaction mixture was stirred at the indicated temperature for 12 h. ^bDetermined by ¹⁹F NMR analysis of the crude mixture using benzotrifluoride as internal standard. ^cIsolated yield at 0.3 mmol scale. ^d0.1 M concentration. ^e0.53 equiv of stabilizer.

X-ray Structure of major diastereomer of **3a**

Crystals of major diastereomer of **3a** 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 major diastereomer of **3a** has been deposited with the Cambridge Crystallographic Data Centre (CCDC) under deposition number 2342656.



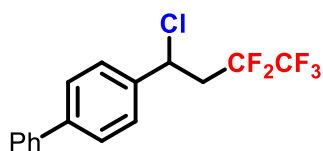
(Molecular structure of major diastereomer of **3a** with thermal ellipsoids at the 50% probability level)

Crystal data and structure refinement for major diastereomer of **3a**.

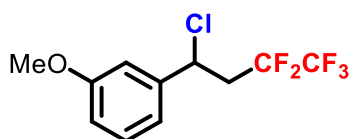
| | | |
|------------------------|--|--------------------------|
| Identification code | CCDC 2342656 | |
| Empirical formula | $\text{C}_{16}\text{H}_{12}\text{F}_5$ | |
| Formula weight | 299.26 | |
| Temperature | 296(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/c$ | |
| Unit cell dimensions | $a = 12.5210(10)$ Å | $a = 90^\circ$. |
| | $b = 6.0834(5)$ Å | $b = 102.427(2)^\circ$. |
| | $c = 18.8326(16)$ Å | $g = 90^\circ$. |
| Volume | $1400.9(2)$ Å ³ | |
| Z | 4 | |
| Density (calculated) | 1.419 Mg/m ³ | |
| Absorption coefficient | 0.128 mm ⁻¹ | |
| F(000) | 612 | |
| Crystal size | 0.500 x 0.400 x 0.300 mm ³ | |

| | |
|-----------------------------------|---|
| Theta range for data collection | 2.215 to 25.233°. |
| Index ranges | -15<=h<=15, -7<=k<=7, -19<=l<=22 |
| Reflections collected | 15238 |
| Independent reflections | 2534 [R(int) = 0.0652] |
| Completeness to theta = 25.233° | 99.9 % |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.7456 and 0.3580 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 2534 / 60 / 238 |
| Goodness-of-fit on F ² | 1.035 |
| Final R indices [I>2sigma(I)] | R1 = 0.0615, wR2 = 0.1532 |
| R indices (all data) | R1 = 0.0872, wR2 = 0.1747 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.329 and -0.165 e.Å ⁻³ |

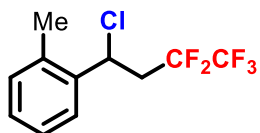
Characterization Data of Products:



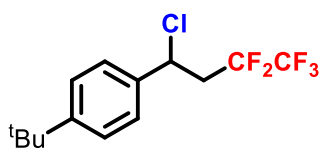
2a: 4-(1-chloro-3,3,4,4,4-pentafluorobutyl)-1,1'-biphenyl. Prepared according to general procedures B using styrene **7a** (54.0 mg, 0.3 mmol) and freshly prepared [CuCF₂CF₃] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 40) and obtained as a colorless solid (70.1 mg, 70% yield), *R*_f = 0.64 (ethyl acetate: hexane = 1: 10). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.68 – 7.56 (m, 4H), 7.54 – 7.44 (m, 4H), 7.42 – 7.34 (m, 1H), 5.29 (t, *J* = 6.9 Hz, 1H), 3.11 – 2.80 (m, 2H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 142.2, 140.3, 139.1, 129.0, 127.9, 127.8, 127.4, 127.3, 118.9 (qt, *J* = 285.9, 35.4 Hz), 114.2 (tq, *J* = 255.5, 38.3 Hz), 53.8, 40.5 (t, *J* = 20.5 Hz). ¹⁹F NMR (471 MHz, CDCl₃): δ (ppm) -86.96 (s, 3F), -118.62 (ddd, *J* = 19.2, 14.4, 8.1 Hz, 2F). HRMS *m/z* (ESI): calcd. for C₁₆H₁₂ClF₅ [M-Cl]⁺: 299.0854; found: 299.0856.



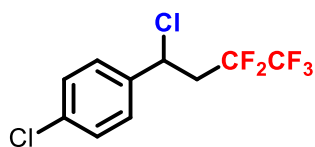
2b: 1-(1-chloro-3,3,4,4,4-pentafluorobutyl)-3-methoxybenzene. Prepared according to general procedures B using styrene **1b** (40.2 mg, 0.3 mmol) and freshly prepared [CuCF₂CF₃] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 40) and obtained as a colorless oil (25.9 mg, 30% yield), *R*_f = 0.45 (ethyl acetate: hexane = 1: 10). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.31 (t, *J* = 7.9 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.95 (t, *J* = 2.2 Hz, 1H), 6.89 (dd, *J* = 8.3, 2.6 Hz, 1H), 5.18 (t, *J* = 6.8 Hz, 1H), 3.83 (s, 3H), 3.05 – 2.66 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ (ppm) 160.1, 141.7, 130.2, 119.1, 118.9 (qt, *J* = 285.6, 35.4 Hz), 114.5, 114.2 (tq, *J* = 255.3, 37.9 Hz), 112.7, 55.5, 53.9 (t, *J* = 3.0 Hz), 40.6 (t, *J* = 20.5 Hz). ¹⁹F NMR (471 MHz, CDCl₃): δ (ppm) -86.99 (s, 3F), -118.78 (ddd, *J* = 19.6, 15.3, 4.9 Hz, 2F). HRMS *m/z* (ESI): calcd. for C₁₁H₁₀F₅O [M-Cl]⁺: 253.0646; found: 253.0648.



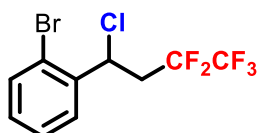
2c: 1-(1-chloro-3,3,4,4,4-pentafluorobutyl)-2-methylbenzene. Prepared according to general procedures B using styrene **1c** (35.4 mg, 0.3 mmol) and freshly prepared [CuCF₂CF₃] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 20) and obtained as a pale yellow oil (35.1 mg, 43% yield), *R*_f = 0.53 (DCM: hexane = 1: 10). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.47 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.35 – 7.14 (m, 3H), 5.52 (dd, *J* = 7.3, 6.1 Hz, 1H), 3.14 – 2.75 (m, 2H), 2.43 (s, 3H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 138.3, 135.0, 131.1, 129.0, 127.0, 126.6, 118.9 (qt, *J* = 285.7, 35.5 Hz), 114.3 (tq, *J* = 255.3, 38.0 Hz), 50.0, 39.7 (t, *J* = 20.5 Hz), 19.1. ¹⁹F NMR (471 MHz, CDCl₃): δ (ppm) -86.99 (s, 3F), -118.54 (ddd, *J* = 266.8, 25.2, 9.5 Hz, 1F), -119.44 (ddd, *J* = 266.3, 25.0, 9.3 Hz, 1F). HRMS *m/z* (APCI): calcd. for C₁₁H₁₀F₅ [M-Cl]⁺: 237.0697; found: 237.0701.



2d: 1-(tert-butyl)-4-(1-chloro-3,3,4,4,4-pentafluorobutyl)benzene. Prepared according to general procedures B using styrene **1d** (48.0 mg, 0.3 mmol) and freshly prepared [CuCF₂CF₃] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 40) and obtained as a colorless liquid (54.6 mg, 58% yield), *R*_f = 0.64 (ethyl acetate: hexane = 1: 8). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.50 – 7.31 (m, 4H), 5.23 (dd, *J* = 9.4, 4.4 Hz, 1H), 3.07 – 2.71 (m, 2H), 1.33 (d, *J* = 2.5 Hz, 9H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 152.4, 137.3, 126.6, 126.1, 118.9 (qt, *J* = 285.6, 35.5 Hz), 114.2 (tq, *J* = 255.2, 38.0 Hz), 53.9 (t, *J* = 3.1 Hz), 40.5 (t, *J* = 20.5 Hz), 34.8, 31.4. ¹⁹F NMR (471 MHz, CDCl₃): δ (ppm) -87.00 (s, 3F), -118.80 (td, *J* = 20.3, 13.3 Hz, 2F). HRMS *m/z* (ESI): calcd. for C₁₄H₁₅ClF₅ [M-H]⁺: 313.0788; found: 313.0780.

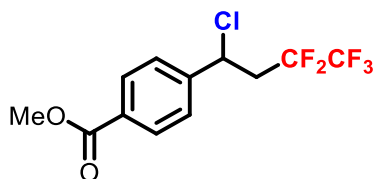


2e: 1-chloro-4-(1-chloro-3,3,4,4,4-pentafluorobutyl)benzene. Prepared according to general procedures B using styrene **1e** (41.8 mg, 0.3 mmol) and freshly prepared [CuCF₂CF₃] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 20) and obtained as a pale yellow liquid (49.8 mg, 57% yield), *R*_f = 0.69 (ethyl acetate: hexane = 1: 8). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.40 – 7.32 (m, 4H), 5.19 (t, *J* = 6.9 Hz, 1H), 3.02 – 2.72 (m, 2H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 138.7, 135.1, 129.4, 128.3, 118.8 (qt, *J* = 285.5, 35.2 Hz), 114.1 (tq, *J* = 255.4, 38.3 Hz), 53.2 (t, *J* = 3.1 Hz), 40.5 (t, *J* = 20.5 Hz). ¹⁹F NMR (471 MHz, CDCl₃): δ (ppm) -86.99 (s, 3F), -118.15 (ddd, *J* = 267.2, 23.9, 10.1 Hz, 1F), -118.93 (ddd, *J* = 267.2, 23.8, 10.6 Hz, 1F). HRMS *m/z* (APCI): calcd. for C₁₀H₇Cl₁F₅ [M-Cl]⁺: 257.0151; found: 257.0151.

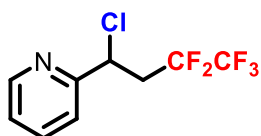


2f: 1-bromo-2-(1-chloro-3,3,4,4,4-pentafluorobutyl)benzene. Prepared according to general procedures B using styrene **1f** (54.9 mg, 0.3 mmol) and freshly prepared [CuCF₂CF₃] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 40) and obtained as a pale yellow liquid (40.3 mg, 40% yield), *R*_f = 0.44 (DCM: hexane = 1: 10). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.60 (dd, *J* = 14.9, 7.9 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J*

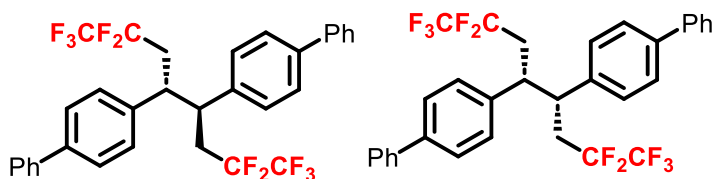
= 7.5 Hz, 1H), 5.77 (t, J = 6.7 Hz, 1H), 2.96 – 2.74 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 139.1, 133.4, 130.5, 128.8, 128.4, 122.5, 118.9 (qt, J = 285.7, 35.4 Hz), 114.1 (tq, J = 255.8, 37.9 Hz), 52.6, 39.7 (t, J = 20.7 Hz). ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -86.95 (s, 3F), -117.68 (ddd, J = 267.2, 23.4, 11.5 Hz, 1F), -119.59 (ddd, J = 267.3, 22.8, 10.9 Hz, 1F). HRMS m/z (APCI): calcd. for $\text{C}_{10}\text{H}_7\text{BrF}_5$ $[\text{M}-\text{Cl}]^+$: 300.9646; found: 300.9649.



2g: methyl 4-(1-chloro-3,3,4,4,4-pentafluorobutyl)benzoate. Prepared according to general procedures B using styrene **1g** (48.6 mg, 0.3 mmol) and freshly prepared $[\text{CuCF}_2\text{CF}_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 40) and obtained as a pale yellow liquid (46.6 mg, 49% yield), R_f = 0.55 (ethyl acetate: hexane = 1: 10). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 8.06 (d, J = 8.7 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 5.24 (t, J = 6.9 Hz, 1H), 3.93 (s, 3H), 3.07 – 2.75 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 166.5, 144.7, 131.0, 130.4, 127.1, 118.7 (qt, J = 285.6, 35.5 Hz), 114.1 (tq, J = 255.6, 38.0 Hz), 53.3 (t, J = 3.0 Hz), 52.5, 40.4 (t, J = 20.4 Hz). ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -87.01 (s, 3F), -118.53 (ddd, J = 70.4, 22.9, 10.7 Hz, 2F). HRMS m/z (APCI): calcd. for $\text{C}_{12}\text{H}_{11}\text{ClF}_5\text{O}_2$ $[\text{M}+\text{H}]^+$: 317.0362; found: 317.0361.



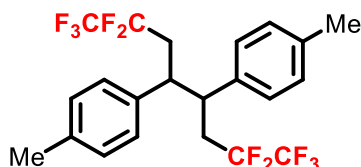
2h: 2-(1-chloro-3,3,4,4,4-pentafluorobutyl)pyridine. Prepared according to general procedures B using styrene **1h** (31.5 mg, 0.3 mmol) and freshly prepared $[\text{CuCF}_2\text{CF}_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 20) and obtained as a colorless liquid (39.2 mg, 50% yield), R_f = 0.68 (ethyl acetate: hexane = 1: 8). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 8.60 (s, 1H), 7.72 (t, J = 8.0 Hz, 1H), 7.42 (d, J = 7.7 Hz, 1H), 7.25 (d, J = 8.1 Hz, 1H), 5.27 (t, J = 6.8 Hz, 1H), 3.31 (ddt, J = 23.7, 15.3, 7.4 Hz, 1H), 2.92 (ddt, J = 24.3, 15.8, 7.9 Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 157.7, 149.9, 137.5, 123.9, 122.4, 118.9 (qt, J = 285.6, 35.5 Hz), 114.5 (tq, J = 254.8, 38.0 Hz), 53.9, 38.0 (t, J = 20.3 Hz). ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -86.95 (s, 3F), -117.92 (ddd, J = 266.7, 26.7, 9.2 Hz, 1F), -118.95 (ddd, J = 266.4, 26.3, 8.5 Hz, 1F). HRMS m/z (APCI): calcd. for $\text{C}_9\text{H}_8\text{ClF}_5\text{N}$ $[\text{M}+\text{H}]^+$: 260.0260; found: 260.0261.



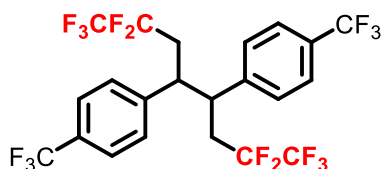
major diastereomer of **3a** minor diastereomer of **3a**

3a: 4,4''-1,1,1,2,2,7,7,8,8,8-decafluorooctane-4,5-diyl)di-1,1'-biphenyl. Prepared according to general procedures C using styrene **1a** (54.0 mg, 0.3 mmol) and freshly prepared $[\text{CuCF}_2\text{CF}_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 40) and obtained major diastereomer of **3a** as a colorless solid (35.4 mg, 39% yield), R_f = 0.48 (ethyl acetate: hexane = 1: 10). Also minor diastereomer is isolated as a colorless solid (17.5 mg, 19% yield), R_f = 0.51 (ethyl acetate: hexane = 1: 10) Major diastereomer of **3a** (**4,4''-((4R,5S)-1,1,1,2,2,7,7,8,8,8-decafluorooctane-4,5-diyl)di-1,1'-biphenyl**): ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.64 (d, J = 7.7 Hz, 8H), 7.47 (t, J = 7.5 Hz, 4H), 7.35 (dd, J = 23.7, 7.6 Hz, 6H), 3.31 (d, J = 8.6 Hz, 2H), 2.39 – 2.12 (m, 4H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 140.6, 140.5, 139.9, 129.0, 128.5, 127.8, 127.6, 127.2, 118.9 (qt, J = 285.7, 36.0 Hz), 115.5 (tq, J = 255.2, 37.6 Hz), 44.5, 34.6 (t, J = 20.3 Hz). ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -86.93 (s, 6F), -115.22 (ddd, J = 265.4, 28.6, 7.6 Hz, 2F), -119.32 (ddd, J =

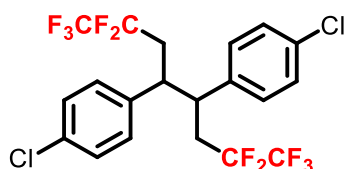
265.3, 26.8, 9.3 Hz, 2F). Minor diastereomer of **3a** (4,4''-((4R,5R)-1,1,1,2,2,7,7,8,8,8-decafluorooctane-4,5-diyl)di-1,1'-biphenyl): ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.62 (dd, *J* = 22.1, 7.7 Hz, 4H), 7.55 – 7.42 (m, 8H), 7.38 – 7.31 (m, 2H), 6.93 (d, *J* = 7.8 Hz, 4H), 3.62 (t, *J* = 5.3 Hz, 2H), 2.59 (dddd, *J* = 25.6, 15.7, 10.4, 5.2 Hz, 2H), 2.36 (dddd, *J* = 21.3, 15.8, 11.1, 6.1 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 140.5, 140.4, 137.2, 130.1, 129.0, 127.6, 127.1, 126.7, 119.1 (qt, *J* = 286.6, 36.0 Hz), 115.8 (tq, *J* = 253.6, 37.1 Hz), 42.1, 34.1 (t, *J* = 20.7 Hz). ¹⁹F NMR (471 MHz, CDCl₃): δ (ppm) -86.85 (s, 6F), -117.01 (ddd, *J* = 265.3, 25.4, 10.8 Hz, 2F), -117.79 (ddd, *J* = 265.6, 26.6, 10.8 Hz, 2F). HRMS *m/z* (APCI): calcd. for C₃₂H₂₄F₁₀Cl [M+Cl]⁻: 633.1412; found: 633.1413.



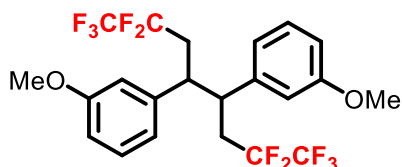
3b: 4,4'-((1,1,1,2,2,7,7,8,8,8-decafluorooctane-4,5-diyl)bis(methylbenzene)). Prepared according to general procedures C using styrene **1i** (35.4 mg, 0.3 mmol) and freshly prepared [CuCF₂CF₃] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 40) and obtained as a colorless solid (42.7 mg, 60% yield, dr = 2:1 by ¹⁹F NMR), *R*_f = 0.40 (ethyl acetate: hexane = 1: 10). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.23 – 7.08 (m, 17H), 7.05 (d, *J* = 7.9 Hz, 4H), 6.70 (d, *J* = 8.0 Hz, 3H), 3.47 (t, *J* = 5.3 Hz, 2H, minor diastereomer), 3.13 (d, *J* = 9.3 Hz, 4H, major diastereomer), 2.36 (s, 12H), 2.33 (s, 6H), 2.28 – 2.00 (m, 12H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 138.0, 137.4, 137.2, 135.2, 129.8, 129.5, 128.8, 127.9, 120.8 – 117.0 (m, 2C), 116.2 – 113.1 (m, 2C), 44.5, 42.0, 34.6 (dd, *J* = 21.2, 19.2 Hz), 34.0 (t, *J* = 20.6 Hz), 21.3, 21.2. ¹⁹F NMR (471 MHz, CDCl₃): δ (ppm) -86.94 (s, 6F, minor diastereomer), -87.00 (s, 12F, major diastereomer), -115.36 (ddd, *J* = 265.3, 28.8, 7.8 Hz, 4F, major diastereomer), -117.09 (ddd, *J* = 265.2, 26.5, 10.1 Hz, 2F, minor diastereomer), -117.97 (ddd, *J* = 265.3, 27.7, 9.9 Hz, 2F, minor diastereomer), -119.53 (ddd, *J* = 265.3, 26.8, 9.5 Hz, 4F, major diastereomer). HRMS *m/z* (ESI): calcd. for C₂₂H₂₀F₁₀Na [M+Na]⁺: 497.1298; found: 497.1304.



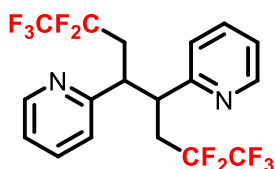
3c: 4,4'-((1,1,1,2,2,7,7,8,8,8-decafluorooctane-4,5-diyl)bis((trifluoromethyl)benzene)). Prepared according to general procedures C using styrene **1j** (51.6 mg, 0.3 mmol) and freshly prepared [CuCF₂CF₃] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 40) and obtained as a colorless solid (50.6 mg, 58% yield, dr = 2:1 by ¹⁹F NMR), *R*_f = 0.43 (ethyl acetate: hexane = 1: 10). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.75 – 7.45 (m, 14H), 7.37 (d, *J* = 7.9 Hz, 8H), 6.95 (d, *J* = 7.9 Hz, 2H), 3.59 (t, *J* = 5.1 Hz, 2H, minor diastereomer), 3.34 (d, *J* = 8.7 Hz, 4H, major diastereomer), 2.43 – 2.18 (m, 8H), 2.14 – 1.97 (m, 4H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 144.4, 142.2, 130.6 (q, *J* = 32.7 Hz), 130.3 (q, *J* = 32.9 Hz), 129.6, 128.5, 127.9, 127.8, 126.4 (q, *J* = 3.9 Hz), 125.4 (q, *J* = 3.7 Hz), 120.7 – 117.5 (m, 2C), 117.4 – 114.4 (m, 2C), 44.4, 42.6, 34.5 (t, *J* = 20.4 Hz), 34.1 (t, *J* = 21.1 Hz). ¹⁹F NMR (471 MHz, CDCl₃): δ (ppm) -63.80 (s, 18F), -86.85 (s, 6F, minor diastereomer), -86.98 (s, 12F, major diastereomer), -115.28 (ddd, *J* = 266.1, 28.4, 7.2 Hz, 4F, major diastereomer), -116.83 (ddd, *J* = 266.5, 26.9, 9.1 Hz, 2F, minor diastereomer), -117.93 (ddd, *J* = 266.1, 27.4, 8.8 Hz, 2F, minor diastereomer), -119.27 (ddd, *J* = 266.2, 26.7, 8.9 Hz, 4F, major diastereomer). HRMS *m/z* (ESI): calcd. for C₂₂H₁₄F₁₆Cl [M+Cl]⁻: 617.0527; found: 617.0534.



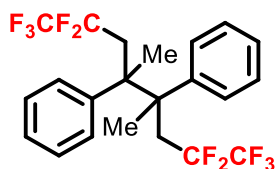
3d: 4,4'-(1,1,1,2,2,7,7,8,8,8-decafluorooctane-4,5-diyl)bis(chlorobenzene). Prepared according to general procedures C using styrene **1e** (41.4 mg, 0.3 mmol) and freshly prepared [CuCF₂CF₃] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 40) and obtained as a colorless solid (40.9 mg, 53% yield, dr = 2:1 by ¹⁹F NMR), *R*_f = 0.56 (ethyl acetate: hexane = 1: 10). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.44 – 7.31 (m, 7H), 7.28 – 7.20 (m, 7H), 7.18 – 7.05 (m, 7H), 6.75 (d, *J* = 7.9 Hz, 3H), 3.46 (t, *J* = 5.3 Hz, 2H, minor diastereomer), 3.18 (d, *J* = 8.4 Hz, 4H, major diastereomer), 2.55 – 2.35 (m, 4H), 2.30 – 1.98 (m, 8H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 139.0, 136.6, 133.9, 133.8, 130.6, 129.5, 129.3, 128.6, 120.9 – 116.7 (m, 2C), 116.2 – 112.3 (m, 2C), 44.1, 42.1, 34.5 (d, *J* = 20.4 Hz), 34.2 (d, *J* = 20.7 Hz). ¹⁹F NMR (471 MHz, CDCl₃): δ (ppm) -86.90 (s, 6F, minor diastereomer), -86.97 (s, 12F, major diastereomer), -115.41 (ddd, *J* = 265.9, 28.4, 7.3 Hz, 4F, major diastereomer), -116.94 (ddd, *J* = 265.7, 26.5, 9.3 Hz, 2F, minor diastereomer), -117.92 (ddd, *J* = 265.9, 27.3, 9.2 Hz, 2F, minor diastereomer), -119.35 (ddd, *J* = 265.4, 26.7, 9.0 Hz, 4F, major diastereomer). HRMS *m/z* (APCI): calcd. for C₂₀H₁₄Cl₃F₁₀ [M+Cl]⁻: 549.0007; found: 549.0010.



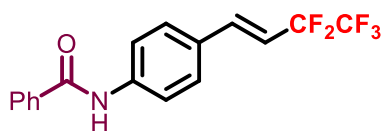
3e: 3,3'-(1,1,1,2,2,7,7,8,8,8-decafluorooctane-4,5-diyl)bis(methoxybenzene). Prepared according to general procedures C using styrene **1b** (40.2 mg, 0.3 mmol) and freshly prepared [CuCF₂CF₃] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 20) and obtained as a colorless solid (36.4 mg, 48% yield, dr = 1:1 by ¹⁹F NMR), *R*_f = 0.34 (ethyl acetate: hexane = 1: 10). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.30 (t, *J* = 7.9 Hz, 2H), 7.16 (t, *J* = 7.9 Hz, 2H), 6.93 – 6.70 (m, 8H), 6.47 (d, *J* = 7.8 Hz, 2H), 6.31 (t, *J* = 2.1 Hz, 2H), 3.83 (s, 6H), 3.70 (s, 6H), 3.49 (t, *J* = 4.9 Hz, 2H), 3.25 – 3.01 (m, 2H), 2.62 – 2.43 (m, 2H), 2.41 – 1.95 (m, 6H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 160.1, 159.2, 142.6, 140.0, 130.3, 129.1, 122.0, 120.3, 115.3, 118.5 – 110.9 (m, 4C), 114.3, 113.1, 112.7, 55.4, 55.2, 44.7, 42.4, 34.6 (dd, *J* = 21.1, 19.3 Hz), 33.9 (t, *J* = 20.6 Hz). ¹⁹F NMR (471 MHz, CDCl₃): δ (ppm) -86.9 (s, 6F), -87.0 (s, 6F), -115.5 (ddd, *J* = 265.3, 28.7, 7.6 Hz, 2F), -117.3 (ddd, *J* = 265.4, 25.2, 11.6 Hz, 2F), -118.0 (ddd, *J* = 265.4, 25.8, 11.4 Hz, 2F), -119.6 (ddd, *J* = 265.7, 26.8, 9.4 Hz, 2F). HRMS *m/z* (ESI): calcd. for C₂₂H₁₉F₁₀O₂ [M-H]⁻: 505.1231; found: 505.1225.



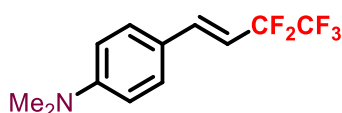
3f: 2,2'-(1,1,1,2,2,7,7,8,8,8-decafluorooctane-4,5-diyl)dipyridine. Prepared according to general procedures C using styrene **1h** (31.5 mg, 0.3 mmol) and freshly prepared [CuCF₂CF₃] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 40) and obtained as a pale yellow solid (32.8 mg, 49% yield, dr = 1:1 by ¹⁹F NMR), *R*_f = 0.31 (ethyl acetate: hexane = 1: 10). ¹H NMR (500 MHz, Acetone-*d*₆): δ (ppm) 8.65 (d, *J* = 4.6 Hz, 2H), 8.56 (d, *J* = 4.5 Hz, 2H), 7.79 (td, *J* = 7.7, 1.8 Hz, 2H), 7.66 (td, *J* = 7.7, 1.8 Hz, 2H), 7.44 (d, *J* = 7.7 Hz, 2H), 7.35 – 7.16 (m, 6H), 3.68 (d, *J* = 9.9 Hz, 2H), 3.63 (d, *J* = 9.4 Hz, 2H), 3.34 (ddt, *J* = 29.6, 16.7, 8.8 Hz, 2H), 2.90 – 2.82 (m, 2H), 1.96 (ddd, *J* = 29.9, 15.4, 9.9 Hz, 4H). ¹³C NMR (126 MHz, Acetone-*d*₆): δ (ppm) 161.0, 160.7, 150.7, 149.7, 137.6, 137.5, 125.7, 124.8, 123.3, 123.0, 119.9 (qt, *J* = 283.8, 35.9 Hz), 119.7 (qt, *J* = 285.0, 36.3 Hz), 117.0 (tq, *J* = 252.2, 39.6 Hz), 116.7 (tq, *J* = 252.4, 39.7 Hz), 45.5 (2C), 33.3 (t, *J* = 20.2 Hz), 29.2 (t, *J* = 20.5 Hz). ¹⁹F NMR (471 MHz, Acetone-*d*₆): δ (ppm) -86.90 (s, 6F), -87.16 (s, 6F), -116.01 (ddd, *J* = 264.6, 29.6, 7.1 Hz, 2F), -116.91 (ddd, *J* = 265.0, 29.3, 8.4 Hz, 2F), -117.82 – -119.41 (m, 4F). HRMS *m/z* (ESI): calcd. for C₁₈H₁₅F₁₀N₂ [M+H]⁺: 449.1070; found: 449.1069.



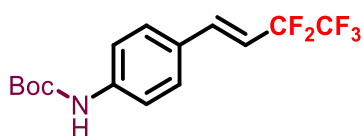
3g: (1,1,1,2,2,7,7,8,8,8-decafluoro-4,5-dimethyloctane-4,5-diyl)dibenzene. Prepared according to general procedures C using styrene **7a** (35.4 mg, 0.3 mmol) and freshly prepared $[\text{CuCF}_2\text{CF}_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 40) and obtained as a white solid (27.7 mg, 39% yield, dr = 1:1 by ^{19}F NMR), $R_f = 0.58$ (ethyl acetate: hexane = 1: 10). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.34 – 7.18 (m, 12H), 7.10 – 6.85 (m, 8H), 3.06 (dd, $J = 35.2, 15.4$ Hz, 2H), 2.56 (dd, $J = 36.0, 15.6$ Hz, 2H), 2.32 (dt, $J = 27.0, 14.6$ Hz, 2H), 2.13 (dt, $J = 26.6, 13.8$ Hz, 2H), 1.60 (d, $J = 3.1$ Hz, 6H), 1.56 (d, $J = 3.4$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 140.9, 140.7, 128.5, 128.2, 127.4, 127.4, 127.09, 127.07, 119.1 (qt, $J = 286.0, 36.3$ Hz), 119.0 (qt, $J = 286.1, 36.2$ Hz), 116.14 (tq, $J = 257.6, 36.4$ Hz), 116.10 (tq, $J = 257.9, 36.4$ Hz), 46.5, 46.3, 34.6 (dd, $J = 20.4, 17.7$ Hz), 34.3 (dd, $J = 19.8, 17.9$ Hz), 21.6 (d, $J = 4.3$ Hz), 21.1 (d, $J = 4.3$ Hz). ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -87.74 (s, 6F), -87.77 (s, 6F), -107.84 (ddd, $J = 71.8, 35.5, 12.6$ Hz, 2F), -108.40 (ddd, $J = 69.5, 35.5, 12.7$ Hz, 2F), -117.20 (ddd, $J = 264.0, 255.8, 25.2$ Hz, 4F). HRMS m/z (APCI): calcd. for $\text{C}_{22}\text{H}_{19}\text{F}_{10}$ $[\text{M}-\text{H}]^-$: 473.1333; found: 473.1341.



4a: (E)-N-(4-(3,3,4,4,4-pentafluorobut-1-en-1-yl)phenyl)benzamide. Prepared according to general procedures D using styrene **1k** (66.9 mg, 0.3 mmol) and freshly prepared $[\text{CuCF}_2\text{CF}_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 20) and obtained as a white solid (57.3 mg, 56% yield, dr > 20:1 by ^{19}F NMR), $R_f = 0.28$ (ethyl acetate: hexane = 1: 5). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.96 (s, 1H), 7.92 – 7.80 (m, 2H), 7.74 – 7.68 (m, 2H), 7.61 – 7.45 (m, 5H), 7.15 (dt, $J = 16.2, 2.4$ Hz, 1H), 6.13 (dt, $J = 16.2, 11.9$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) 165.9, 139.8, 138.9 (t, $J = 9.2$ Hz), 134.7, 132.3, 129.0, 128.7, 127.2 (2C), 120.3, 119.2 (qt, $J = 285.5, 38.7$ Hz), 113.2 (t, $J = 23.1$ Hz), 113.0 (tq, $J = 250.4, 38.6$ Hz). ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -86.22 (t, $J = 2.7$ Hz, 3F), -115.82 (dt, $J = 12.0, 2.3$ Hz, 2F). HRMS m/z (APCI): calcd. for $\text{C}_{17}\text{H}_{13}\text{F}_5\text{NO}$ $[\text{M}+\text{H}]^+$: 342.0912; found: 342.0912.

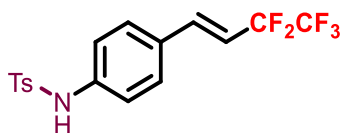


4b: (E)-N,N-dimethyl-4-(3,3,4,4,4-pentafluorobut-1-en-1-yl)aniline. Prepared according to general procedures using styrene **1l** (44.1 mg, 0.3 mmol) and freshly prepared $[\text{CuCF}_2\text{CF}_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 20) and obtained as a yellow liquid (38.9 mg, 49% yield, dr > 20:1 by ^{19}F NMR), $R_f = 0.63$ (ethyl acetate: hexane = 1: 10). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.39 – 7.33 (m, 2H), 7.07 (dt, $J = 16.0, 2.4$ Hz, 1H), 6.69 (d, $J = 8.4$ Hz, 2H), 5.93 (dt, $J = 16.2, 12.2$ Hz, 1H), 3.02 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 151.6, 139.5 (t, $J = 9.2$ Hz), 129.1, 121.6, 119.4 (qt, $J = 285.6, 39.4$ Hz), 113.5 (tq, $J = 288.0, 38.5$ Hz), 112.1, 108.6 (t, $J = 22.9$ Hz), 40.4. ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -86.34 (t, $J = 2.8$ Hz, 3F), -114.79 (d, $J = 12.1$ Hz, 2F). HRMS m/z (APCI): calcd. for $\text{C}_{12}\text{H}_{13}\text{F}_5\text{N}$ $[\text{M}+\text{H}]^+$: 266.0963; found: 266.0958.

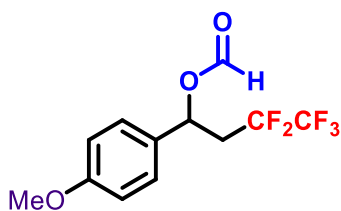


4c: tert-butyl (E)-4-(3,3,4,4,4-pentafluorobut-1-en-1-yl)carbamate. Prepared according to general procedures D

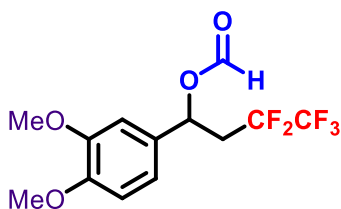
using styrene **1m** (65.7 mg, 0.3 mmol) and freshly prepared $[\text{CuCF}_2\text{CF}_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 20) and obtained as a white solid (64.80 mg, 64% yield, dr > 20:1 by ^{19}F NMR), $R_f = 0.50$ (ethyl acetate: hexane = 1: 5). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.40 (s, 4H), 7.10 (dt, $J = 16.1, 2.4$ Hz, 1H), 6.64 (s, 1H), 6.06 (dt, $J = 16.1, 12.0$ Hz, 1H), 1.53 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 152.5, 140.3, 139.1 (t, $J = 9.3$ Hz), 128.7, 128.2, 119.2 (dt, $J = 285.6, 38.8$ Hz), 118.5, 113.1 (tq, $J = 250.3, 38.3$ Hz), 112.3 (t, $J = 23.1$ Hz), 81.2, 28.4. ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -86.3 (s, 3F), -115.7 (d, $J = 12.1$ Hz, 2F). HRMS m/z (ESI): calcd. for $\text{C}_{15}\text{H}_{16}\text{F}_5\text{NO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 360.0993; found: 360.0990.



4d: (E)-4-methyl-N-(4-(3,3,4,4,4-pentafluorobut-1-en-1-yl)phenyl)benzenesulfonamide. Prepared according to general procedures D using styrene **1n** (81.9 mg, 0.3 mmol) and freshly prepared $[\text{CuCF}_2\text{CF}_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 10) and obtained as a pale yellow solid (73.7 mg, 63% yield, dr > 20:1 by ^{19}F NMR), $R_f = 0.20$ (ethyl acetate: hexane = 1: 5). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.71 (d, $J = 8.3$ Hz, 2H), 7.34 (d, $J = 8.7$ Hz, 2H), 7.29 – 7.22 (m, 2H), 7.18 (s, 1H), 7.12 (d, $J = 8.6$ Hz, 2H), 7.09 – 7.01 (m, 1H), 6.06 (dt, $J = 16.1, 11.9$ Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 144.5, 138.7 (t, $J = 9.2$ Hz), 138.4, 135.9, 130.00 (t, $J = 29.8$ Hz), 129.98, 128.9, 127.4, 120.8, 119.1 (qt, $J = 285.6, 38.4$ Hz), 113.7 (t, $J = 23.2$ Hz), 112.8 (dd, $J = 250.4, 38.6$ Hz), 21.7. ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -87.00 (s, 3F), -116.73 (d, $J = 11.9$ Hz, 2F). HRMS m/z (ESI): calcd. for $\text{C}_{17}\text{H}_{14}\text{F}_5\text{NO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 414.0558; found: 414.0556.

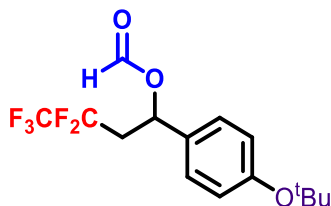


5a: 3,3,4,4,4-pentafluoro-1-(4-methoxyphenyl)butyl formate. Prepared according to general procedures E using styrene **1o** (40.2 mg, 0.3 mmol) and freshly prepared $[\text{CuCF}_2\text{CF}_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 20) and obtained as a pale yellow oil (65.3 mg, 73% yield), $R_f = 0.48$ (ethyl acetate: hexane = 1: 10). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 8.03 (s, 1H), 7.11 (dd, $J = 206.4, 8.5$ Hz, 4H), 6.26 (dd, $J = 9.2, 3.6$ Hz, 1H), 3.81 (s, 3H), 2.92 – 2.72 (m, 1H), 2.54 – 2.39 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 160.2, 159.6, 130.5, 128.1, 118.9 (qt, $J = 285.6, 35.6$ Hz), 114.41, 114.36 (tq, $J = 254.4, 38.1$ Hz), 68.2 (t, $J = 3.1$ Hz), 55.5, 37.1 (t, $J = 20.9$ Hz). ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -86.96 (s, 3F), -118.52 (ddd, $J = 47.6, 21.8, 11.9$ Hz, 2F). HRMS m/z (ESI): calcd. for $\text{C}_{12}\text{H}_{11}\text{F}_5\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 321.0521; found: 321.0521.

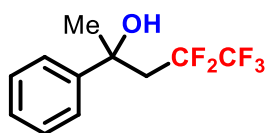


5b: 1-(3,4-dimethoxyphenyl)-3,3,4,4,4-pentafluorobutyl formate. Prepared according to general procedures E using styrene **1p** (49.2 mg, 0.3 mmol) and freshly prepared $[\text{CuCF}_2\text{CF}_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 20) and obtained as a pale yellow oil (64.6 mg, 66% yield), $R_f = 0.32$ (ethyl acetate: hexane = 1: 10). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 8.05 (s, 1H), 6.98 – 6.83 (m, 3H), 6.26 (dd, $J = 9.3, 3.5$

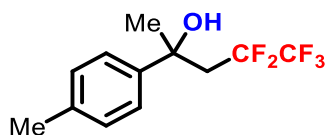
Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 2.82 (dddd, $J = 22.0, 15.3, 13.0, 9.3$ Hz, 1H), 2.63 – 2.38 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 159.5, 130.8, 119.2, 118.9 (qt, $J = 285.5, 35.6$ Hz), 118.0, 114.3 (tq, $J = 254.4, 38.1$ Hz), 111.3, 109.5, 108.7, 68.3 (t, $J = 3.1$ Hz), 56.11, 56.08, 37.2 (t, $J = 20.9$ Hz). ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -86.97 (s, 3F), -118.57 (ddd, $J = 39.8, 21.8, 12.6$ Hz, 2F). HRMS m/z (ESI): calcd. for $\text{C}_{13}\text{H}_{13}\text{F}_5\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 351.0626; found: 351.0628.



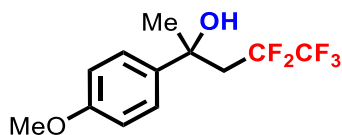
5c: 1-(4-(tert-butoxy)phenyl)-3,3,4,4,4-pentafluorobutyl formate. Prepared according to general procedures E using styrene **1q** (52.8 mg, 0.3 mmol) and freshly prepared $[\text{CuCF}_2\text{CF}_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 20) and obtained as a pale yellow oil (44.8 mg, 44% yield), $R_f = 0.41$ (ethyl acetate: hexane = 1: 10). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 8.04 (s, 1H), 7.30 – 7.25 (m, 2H), 7.02 – 6.96 (m, 2H), 6.29 (dd, $J = 9.4, 3.4$ Hz, 1H), 2.89 – 2.73 (m, 1H), 2.47 (dtd, $J = 22.5, 15.9, 14.8, 3.4$ Hz, 1H), 1.35 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 159.6, 156.3, 132.9, 127.3, 124.3, 118.9 (qt, $J = 285.5, 35.6$ Hz), 114.4 (tq, $J = 254.3, 38.2$ Hz), 79.1, 68.0 (t, $J = 3.1$ Hz), 37.2 (t, $J = 20.9$ Hz), 28.9. ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -86.98 (s, 3F), -118.61 (ddd, $J = 34.3, 21.5, 12.9$ Hz, 2F). HRMS m/z (ESI): calcd. for $\text{C}_{15}\text{H}_{17}\text{F}_5\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 363.0990; found: 363.0988.



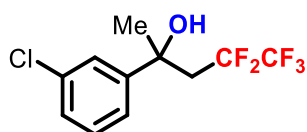
8a: 4,4,5,5,5-pentafluoro-2-phenylpentan-2-ol. Prepared according to general procedures F using styrene **7a** (35.4 mg, 0.3 mmol), B_2Pin_2 (83.5 mg, 0.33 mmol) and freshly prepared $[\text{CuCF}_2\text{CF}_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 40) and obtained as a colorless oil (55.6 mg, 73% yield), $R_f = 0.58$ (ethyl acetate: hexane = 1: 10). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.55 – 7.27 (m, 5H), 2.79 – 2.43 (m, 2H), 2.28 (s, 1H), 1.77 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 146.7, 128.6, 127.6, 124.5, 118.9 (qt, $J = 285.9, 35.7$ Hz), 115.9 (tq, $J = 255.1, 37.2$ Hz), 72.8, 42.7 (t, $J = 19.2$ Hz), 30.2. ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -87.56 (s, 3F), -115.64 (d, $J = 265.5$ Hz, 1F), -118.44 (d, $J = 266.2$ Hz, 1F). HRMS m/z (ESI): calcd. for $\text{C}_{11}\text{H}_{11}\text{F}_5\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 277.0622; found: 277.0624.



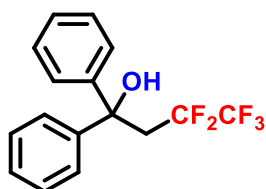
8b: 4,4,5,5,5-pentafluoro-2-(p-tolyl)pentan-2-ol. Prepared according to general procedures F using styrene **7b** (39.6 mg, 0.3 mmol), B_2Pin_2 (83.5 mg, 0.33 mmol) and freshly prepared $[\text{CuCF}_2\text{CF}_3]$ (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 20) and obtained as a colorless oil (53.6 mg, 67% yield), $R_f = 0.31$ (ethyl acetate: hexane = 1: 10). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.38 (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 7.9$ Hz, 2H), 2.71 – 2.46 (m, 2H), 2.37 (s, 3H), 2.33 (s, 1H), 1.76 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 143.8, 137.2, 129.2, 124.4, 118.9 (qt, $J = 285.7, 35.7$ Hz), 115.9 (tq, $J = 254.9, 37.3$ Hz), 72.7, 42.6 (t, $J = 19.2$ Hz), 30.1 (d, $J = 2.5$ Hz), 21.0. ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -87.69 (s, 3F), -115.85 (ddd, $J = 265.9, 31.6, 9.0$ Hz, 1F), -118.50 (ddd, $J = 265.6, 29.9, 7.8$ Hz, 1F). HRMS m/z (ESI): calcd. for $\text{C}_{12}\text{H}_{12}\text{F}_5$ $[\text{M}-\text{H}_2\text{O}+\text{H}]^+$: 251.0854; found: 251.0851.



8c: 4,4,5,5,5-pentafluoro-2-(4-methoxyphenyl)pentan-2-ol. Prepared according to general procedures F using styrene **7c** (44.4 mg, 0.3 mmol), B₂Pin₂ (83.5 mg, 0.33 mmol) and freshly prepared [CuCF₂CF₃] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 20) and obtained as a colorless oil (59.6 mg, 70% yield), *R_f* = 0.22 (ethyl acetate: hexane = 1: 10). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.40 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 2.75 – 2.41 (m, 2H), 2.24 (s, 1H), 1.75 (s, 3H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 158.9, 138.9, 125.8, 121.2 (qt, *J* = 285.8, 35.8 Hz), 116.8 (tq, *J* = 254.9, 37.4 Hz), 113.8, 72.5, 55.4, 42.7 (t, *J* = 19.2 Hz), 30.1. ¹⁹F NMR (471 MHz, CDCl₃): δ (ppm) -87.68 (s, 3F), -115.98 (ddd, *J* = 265.6, 31.8, 8.7 Hz, 1F), -118.64 (ddd, *J* = 266.0, 30.2, 7.4 Hz, 1F). HRMS *m/z* (ESI): calcd. for C₁₂H₁₂F₅O₂ [M-H]⁻: 283.0763; found: 283.0760.



8d: 2-(3-chlorophenyl)-4,4,5,5,5-pentafluoropentan-2-ol. Prepared according to general procedures F using styrene **7d** (45.6 mg, 0.3 mmol), B₂Pin₂ (83.5 mg, 0.33 mmol) and freshly prepared [CuCF₂CF₃] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 20) and obtained as a pale yellow oil (50.9 mg, 59% yield), *R_f* = 0.30 (ethyl acetate: hexane = 1: 8). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.51 (t, *J* = 1.9 Hz, 1H), 7.37 – 7.23 (m, 3H), 2.66 – 2.44 (m, 2H), 2.29 (s, 1H), 1.75 (s, 3H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 148.7, 134.6, 129.9, 127.7, 125.0, 122.8, 118.8 (qt, *J* = 285.7, 35.7 Hz), 115.8 (tq, *J* = 255.0, 37.5 Hz), 72.5, 42.5 (t, *J* = 19.3 Hz), 30.2. ¹⁹F NMR (471 MHz, CDCl₃): δ (ppm) -87.64 (s, 3F), -115.61 (ddd, *J* = 266.3, 31.6, 8.7 Hz, 1F), -118.47 (ddd, *J* = 266.2, 29.5, 7.4 Hz, 1F). HRMS *m/z* (ESI): calcd. for C₁₁H₉ClF₅O [M-H]⁻: 287.0268; found: 287.0273.

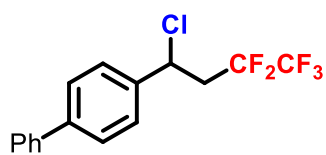


8e: 3,3,4,4,4-pentafluoro-1,1-diphenylbutan-1-ol. Prepared according to general procedures F using styrene **7e** (54.0 mg, 0.3 mmol), B₂Pin₂ (83.5 mg, 0.33 mmol) and freshly prepared [CuCF₂CF₃] (1.0 mL, 0.90 mmol in DMF). The product was purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 20) and obtained as a white solid (62.3 mg, 66% yield), *R_f* = 0.32 (ethyl acetate: hexane = 1: 10). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.44 (d, *J* = 7.4 Hz, 4H), 7.35 (t, *J* = 7.7 Hz, 4H), 7.28 (t, *J* = 7.5 Hz, 2H), 3.13 (t, *J* = 18.1 Hz, 2H), 2.75 (s, 1H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 145.5, 128.6, 127.7, 125.6, 119.0 (qt, *J* = 286.0, 35.8 Hz), 115.5 (tq, *J* = 256.2, 37.5 Hz), 76.5, 41.0 (t, *J* = 18.8 Hz). ¹⁹F NMR (471 MHz, CDCl₃): δ (ppm) -87.7 (s, 3F), -114.5 (t, *J* = 18.1 Hz, 2F). HRMS *m/z* (ESI): calcd. for C₁₆H₁₃F₅ONa [M+Na]⁺: 339.0779; found: 339.0783.

References.

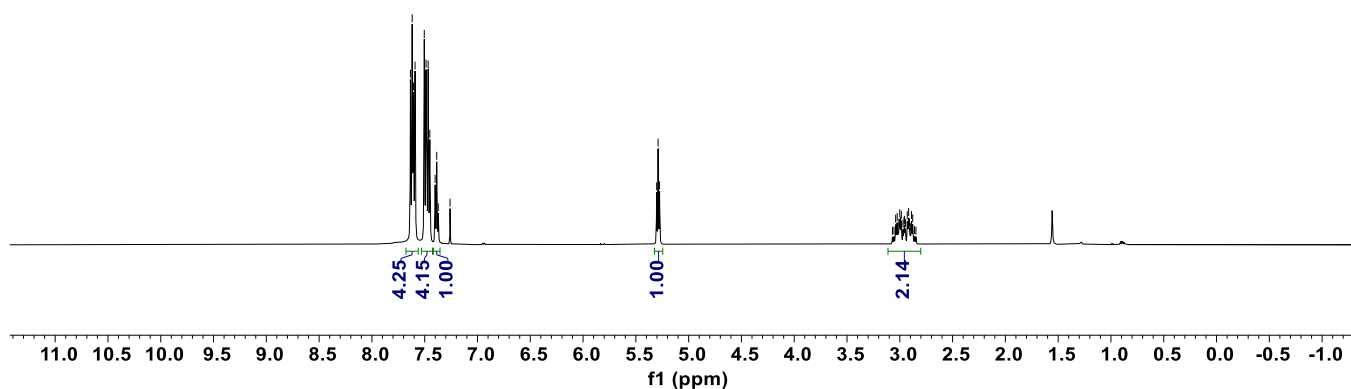
- (a) Yang, X.; Tsui, G. C. *Org. Lett.* **2020**, *22*, 4562. (b) Luo, Z.; Tsui, G. C. *Org. Chem. Front.* **2022**, *9*, 4969.
- (a) O'Broin, C. Q.; Guiry, P. J. *Org. Lett.* **2020**, *22*, 879. (b) Colomer, I.; Barcelos, R. C.; Christensen, K. E.; Donohoe, T. J. *Org. Lett.* **2016**, *18*, 5880. (c) Moon, S.-Y.; Nam, J.; Rathwell, K.; Kim, W.-S. *Org. Lett.* **2014**, *16*, 338.
- (a) Huang, J.; Hu, G.; An, S.; Chen, D.; Li, M.; Li, P. *J. Org. Chem.* **2019**, *84*, 9758. (b) Chandra, B.; Santanu, M. *Angew. Chem. Int. Ed.* **2013**, *125*, 8608.

Spectra.

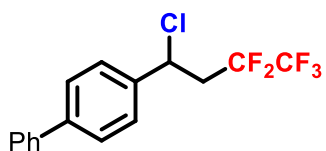


2a (^1H NMR, 500 MHz, CDCl_3)

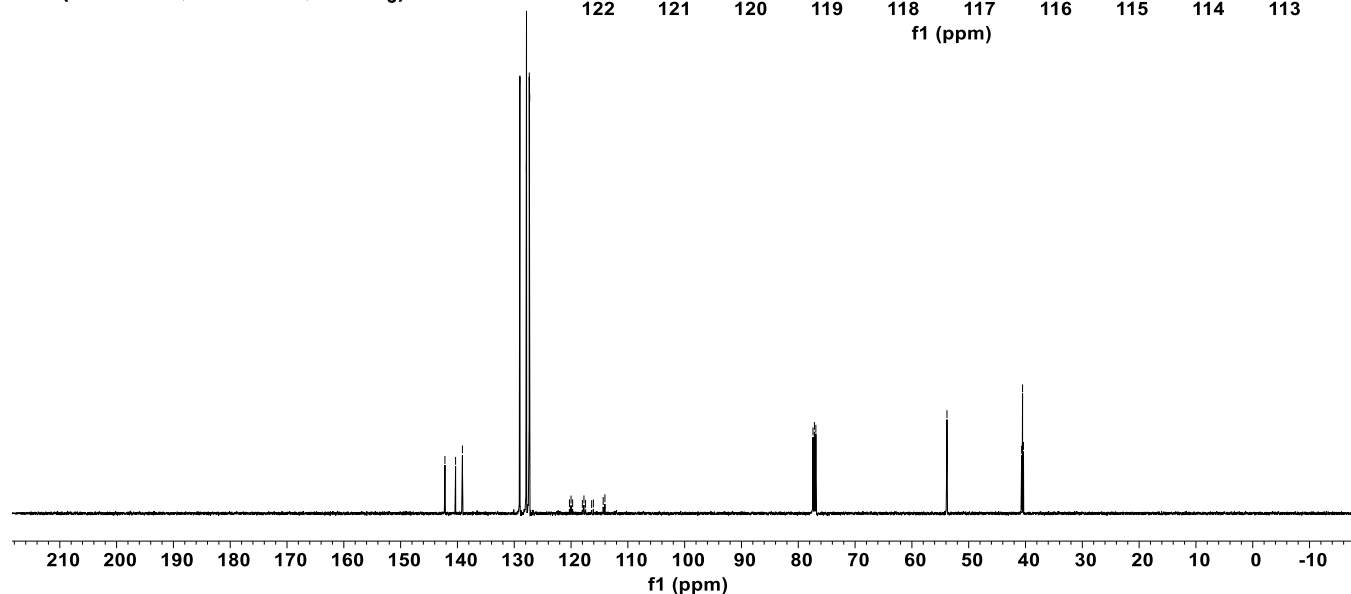
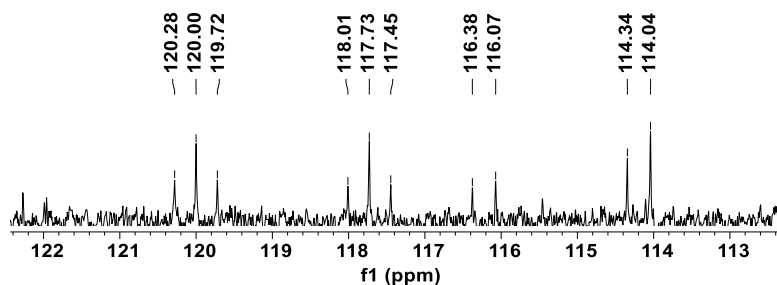
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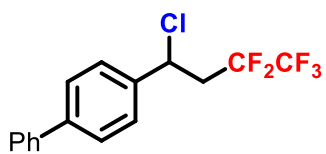


142.20 140.33 139.12 129.01 127.87 127.84 127.35 127.28 120.28 120.00 119.72 118.01 117.73 117.45 116.38 116.07 114.34 114.04 77.16 76.91 53.83 40.68 40.52 40.36

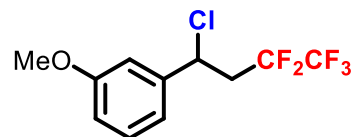
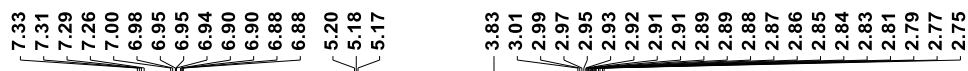
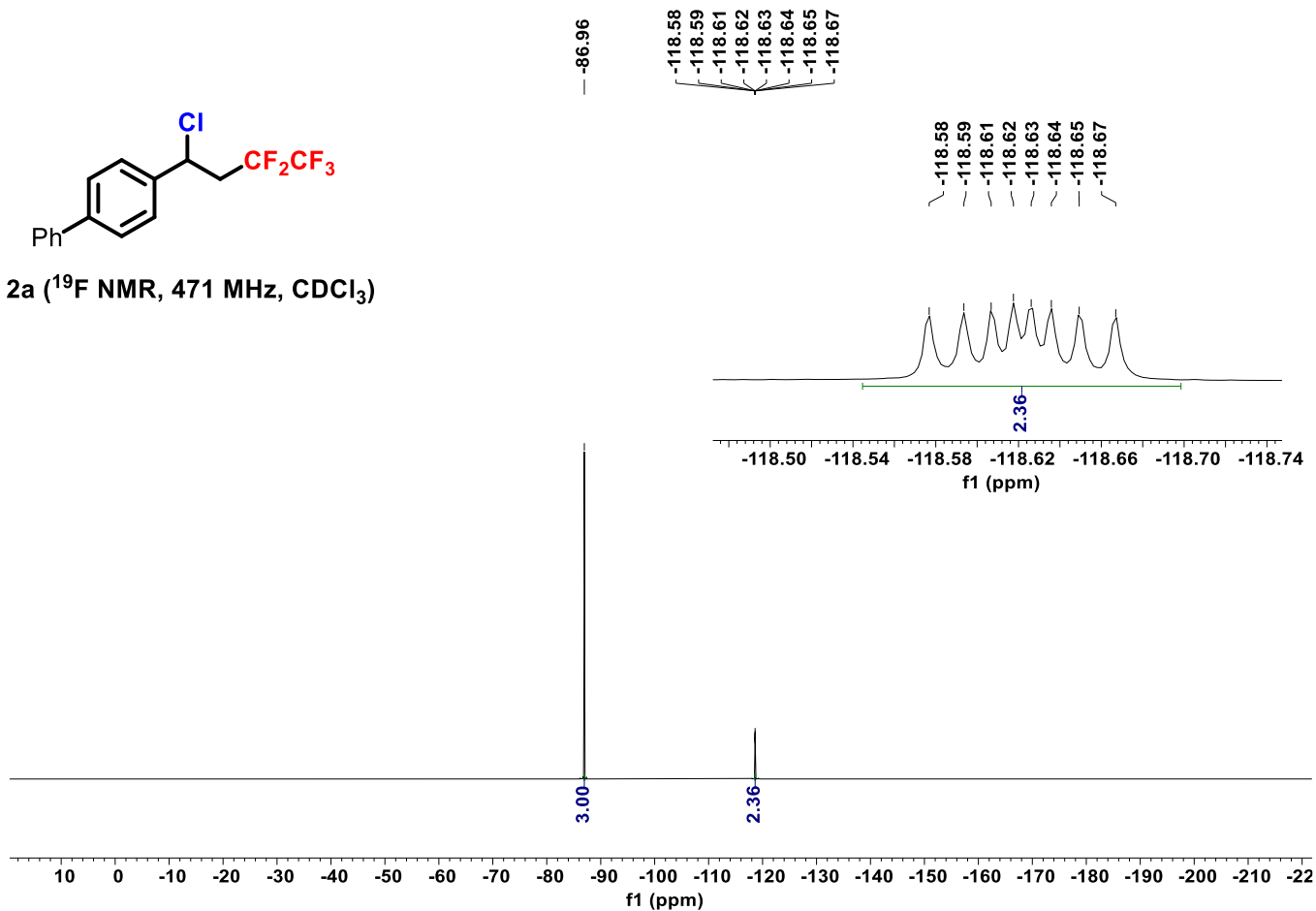


2a (^{13}C NMR, 126 MHz, CDCl_3)

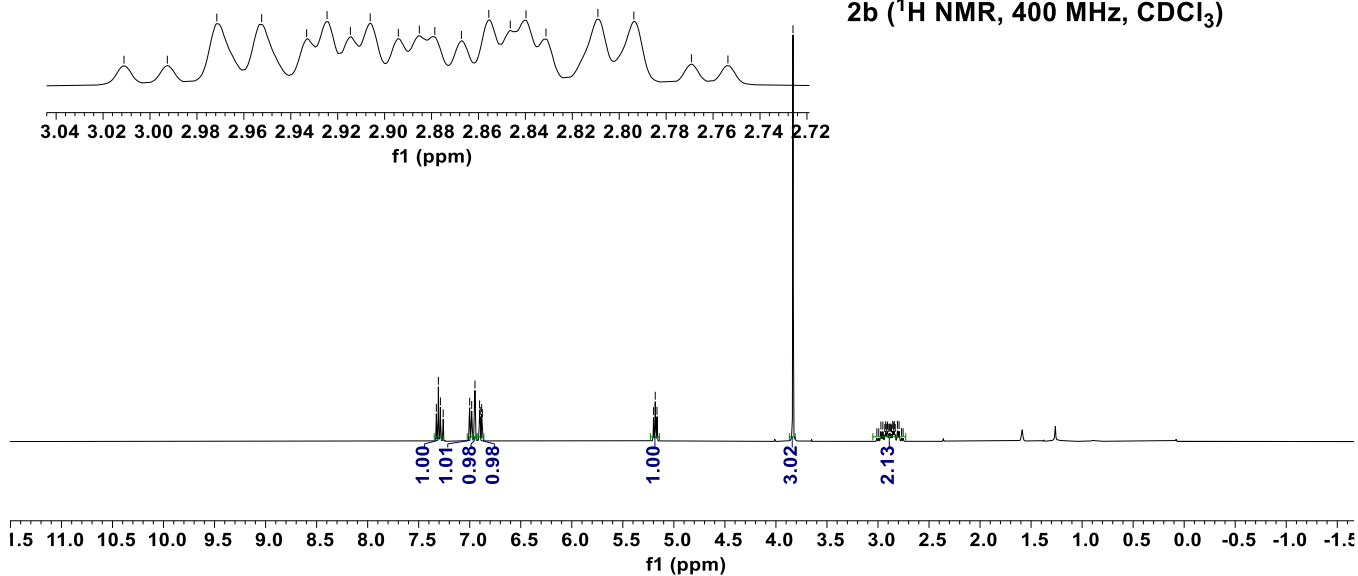


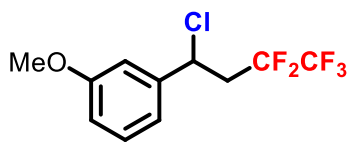


2a (^{19}F NMR, 471 MHz, CDCl_3)

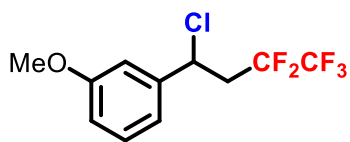
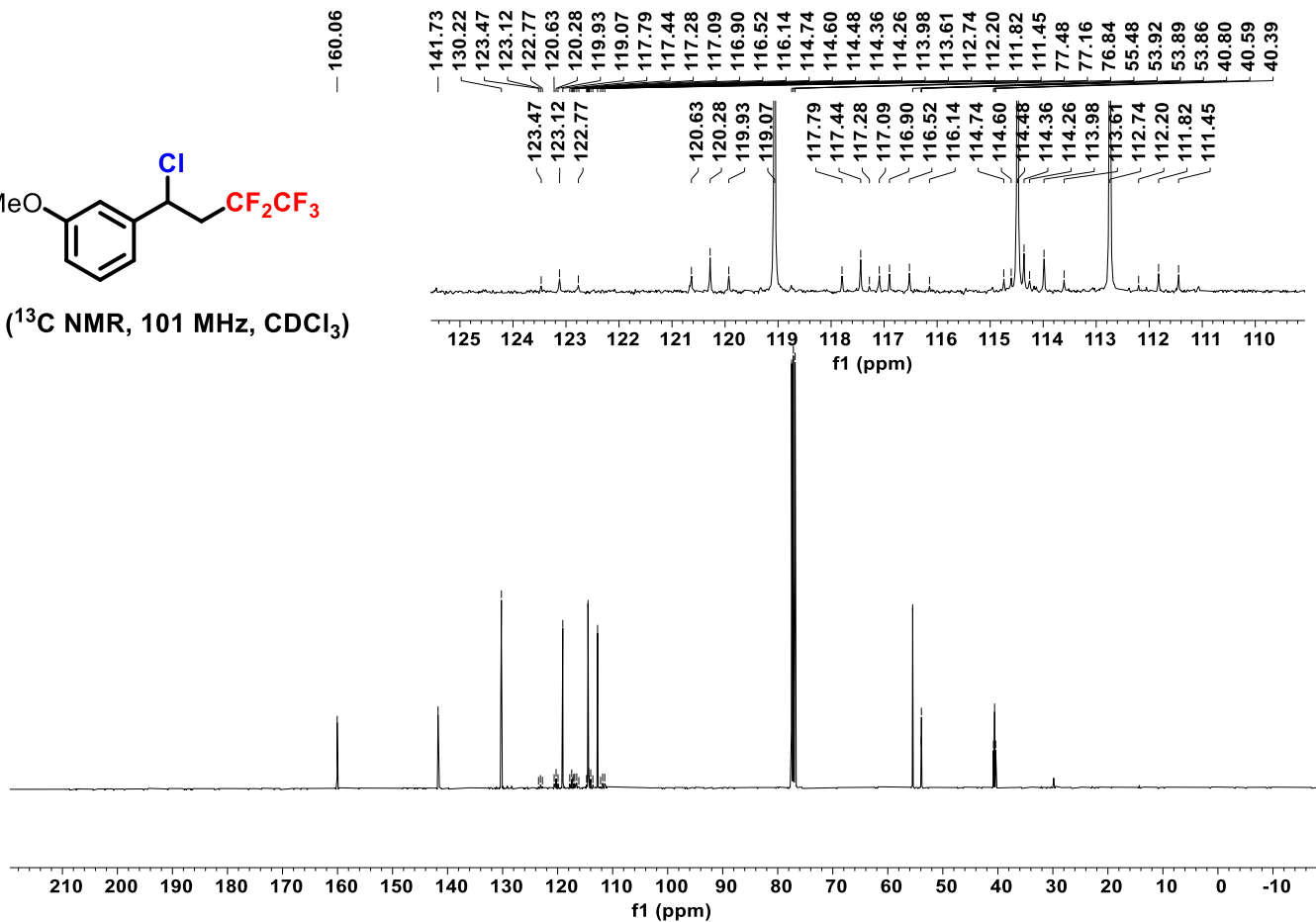


2b (^1H NMR, 400 MHz, CDCl_3)

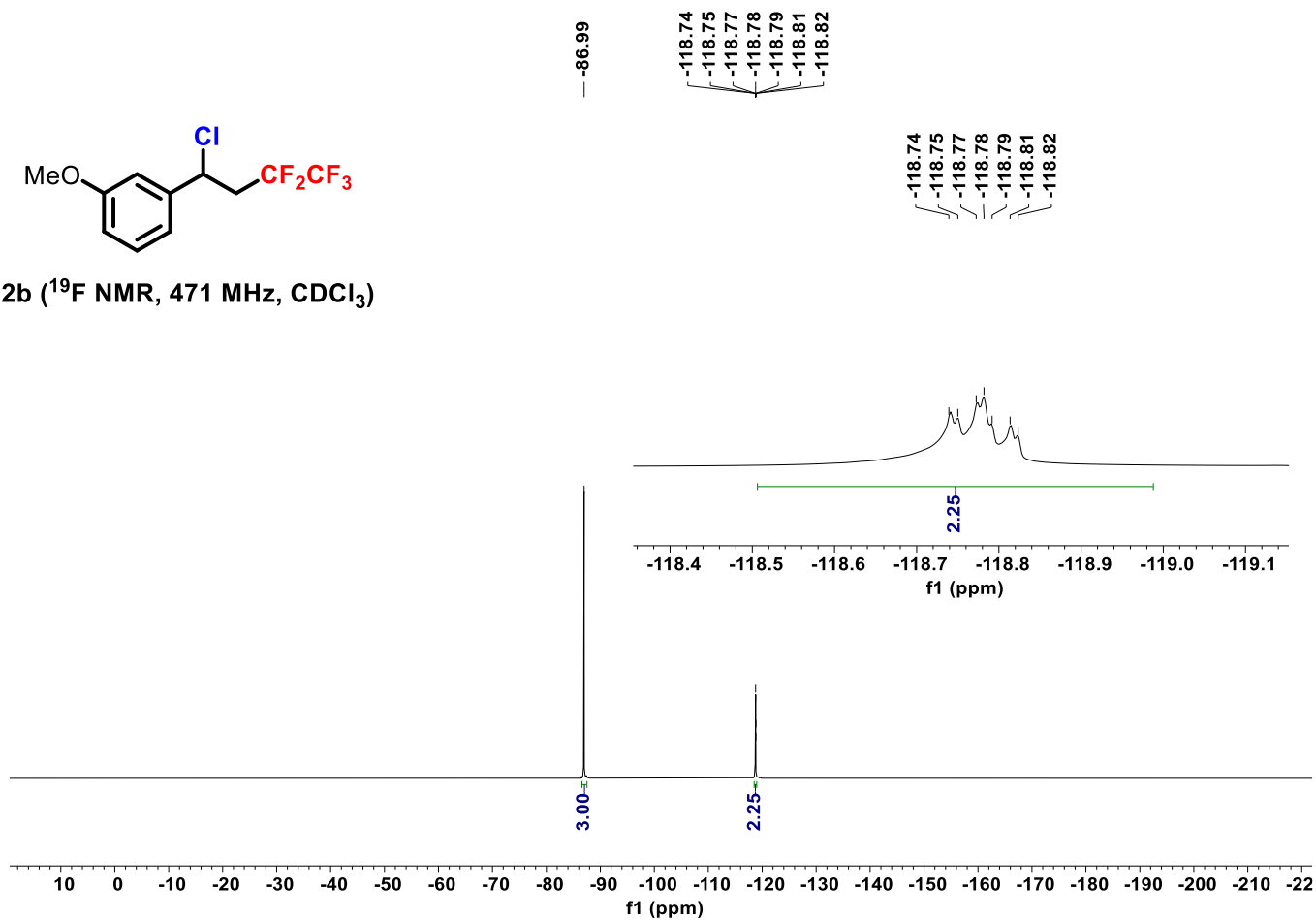


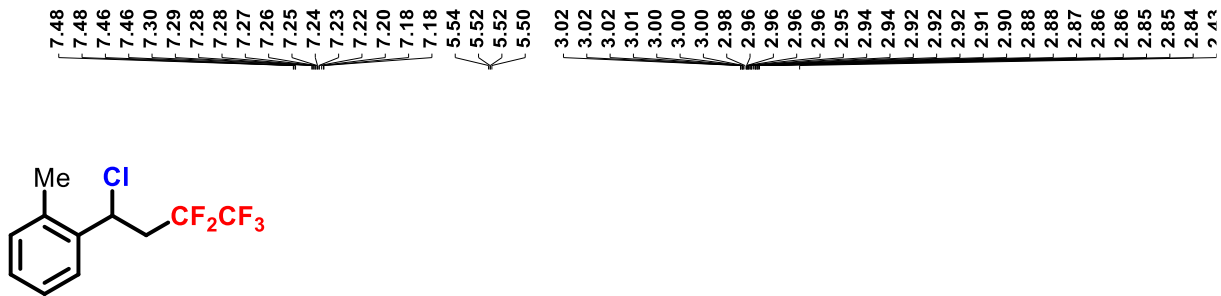


2b (¹³C NMR, 101 MHz, CDCl₃)

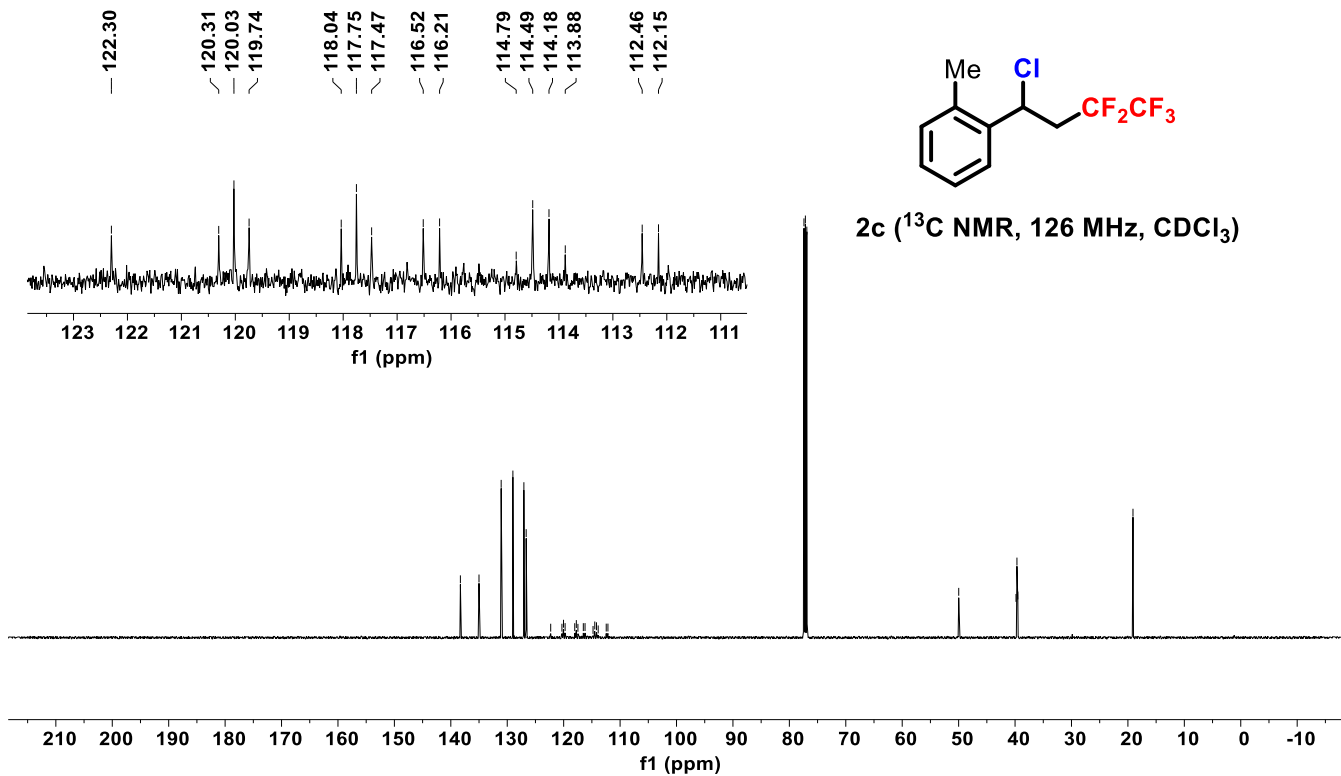
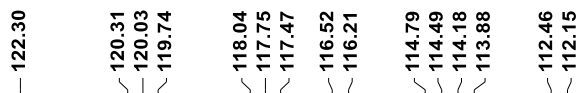
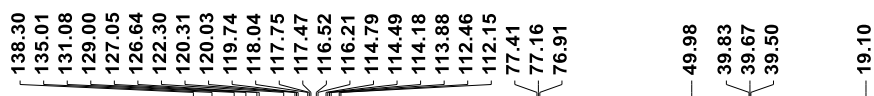
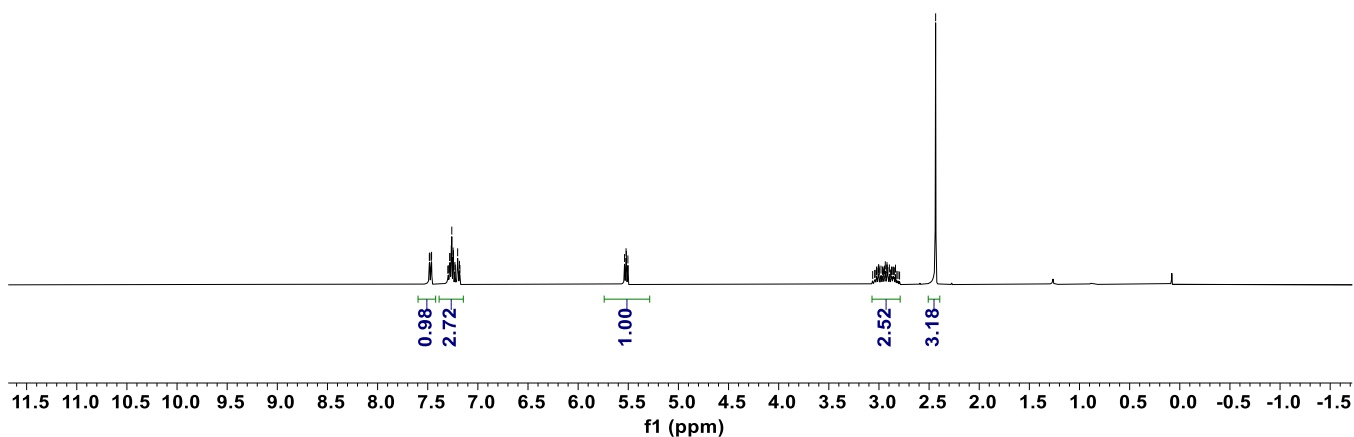


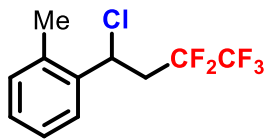
2b (¹⁹F NMR, 471 MHz, CDCl₃)



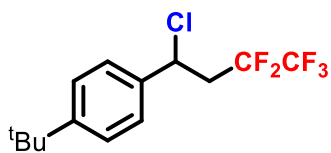
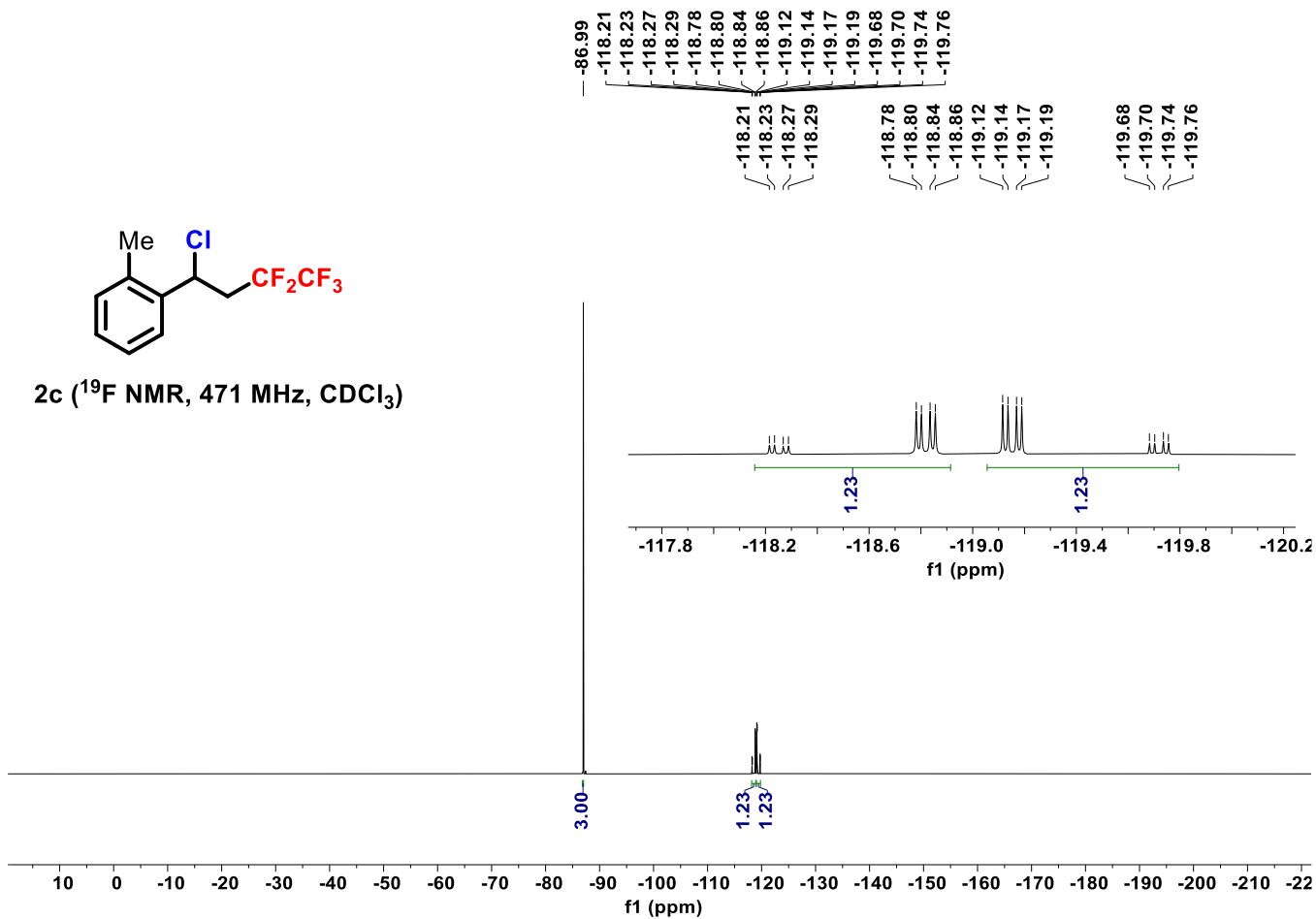


2c (¹H NMR, 400 MHz, CDCl₃)

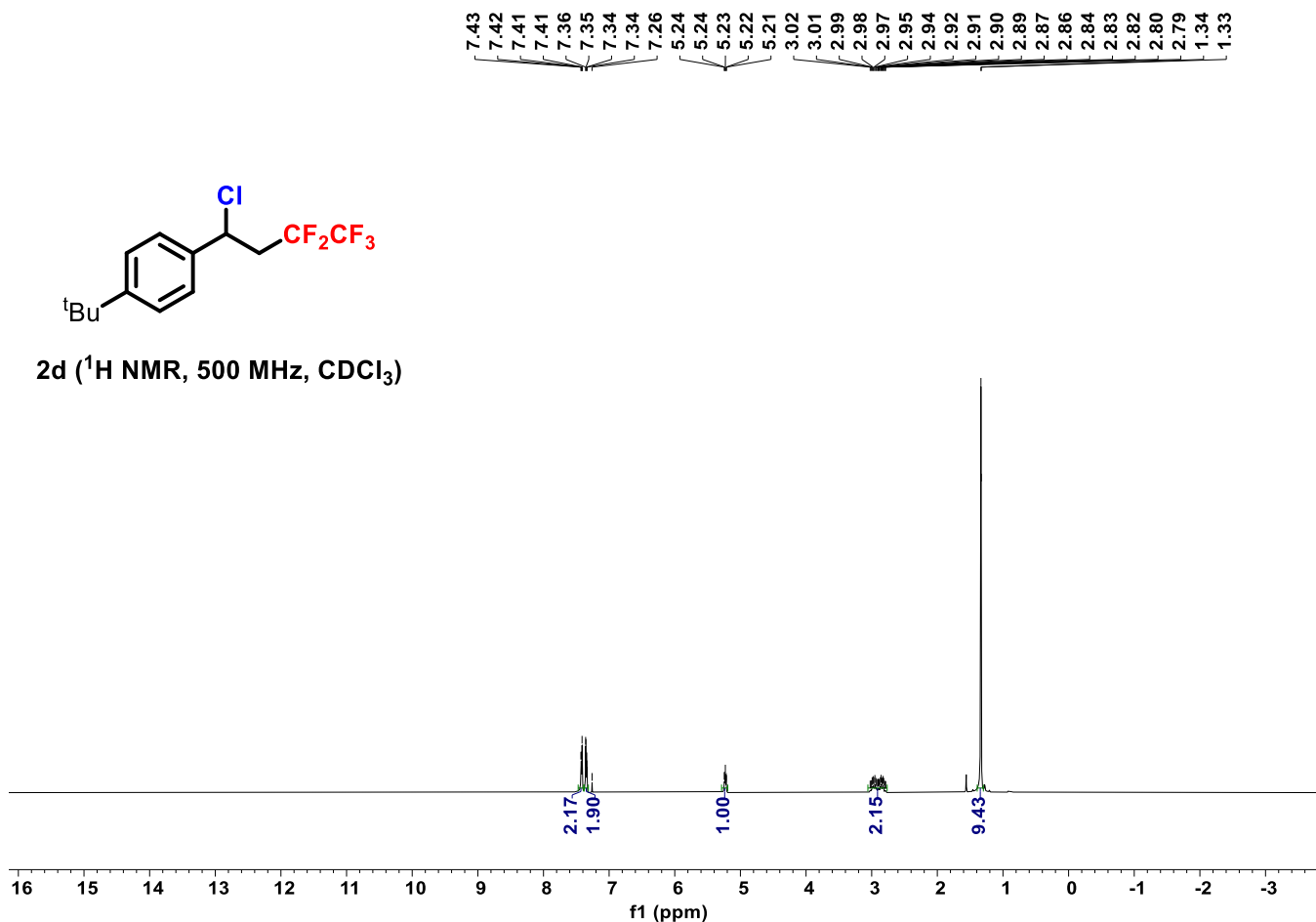


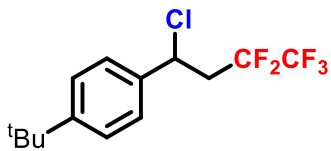


2c (^{19}F NMR, 471 MHz, CDCl_3)

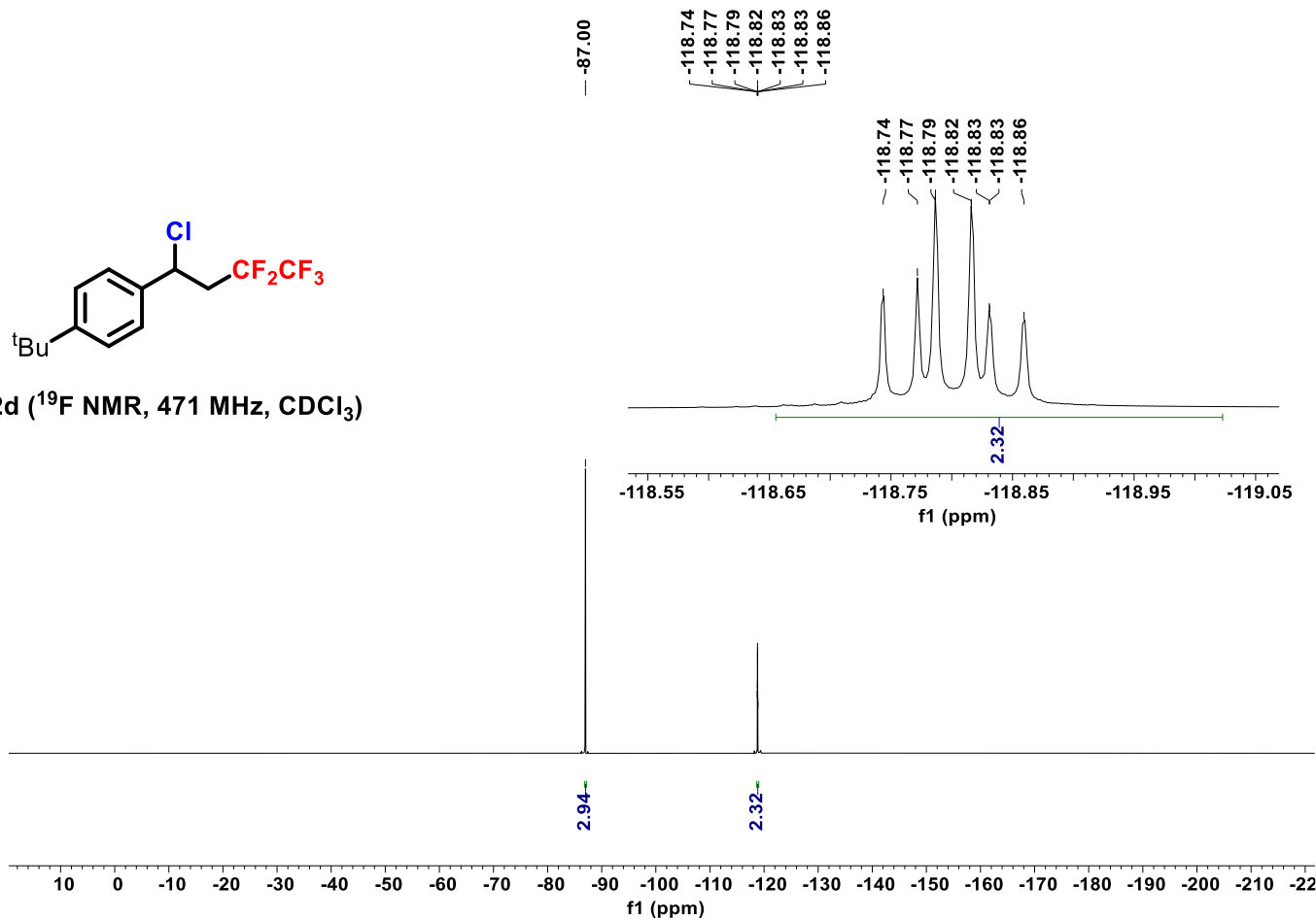
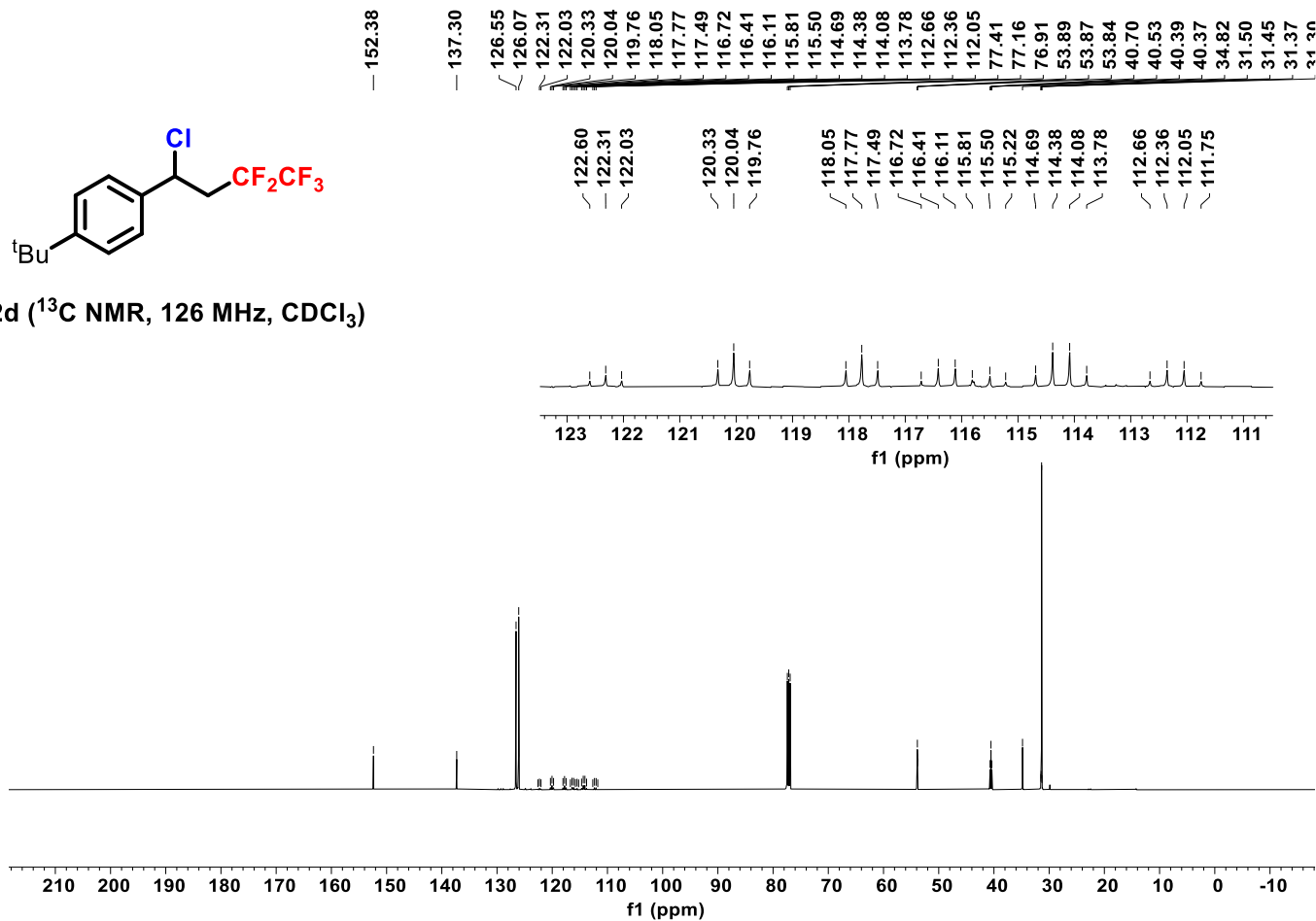


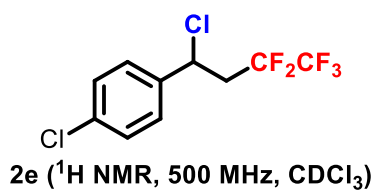
2d (^1H NMR, 500 MHz, CDCl_3)



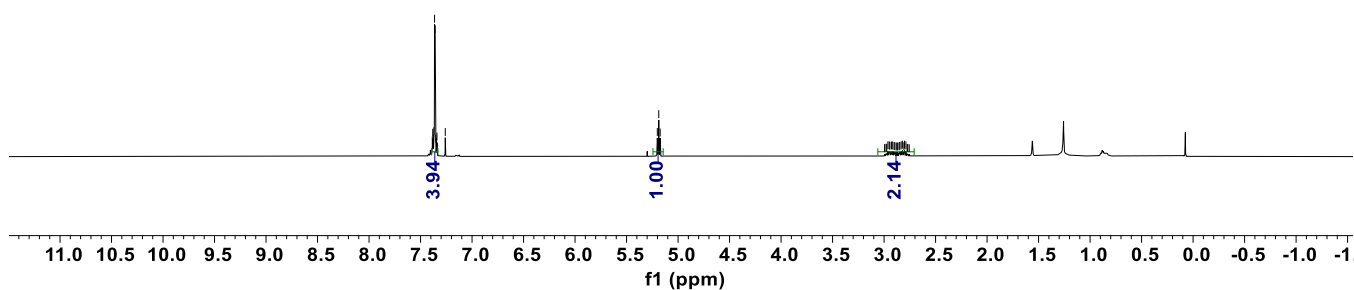


2d (^{13}C NMR, 126 MHz, CDCl_3)

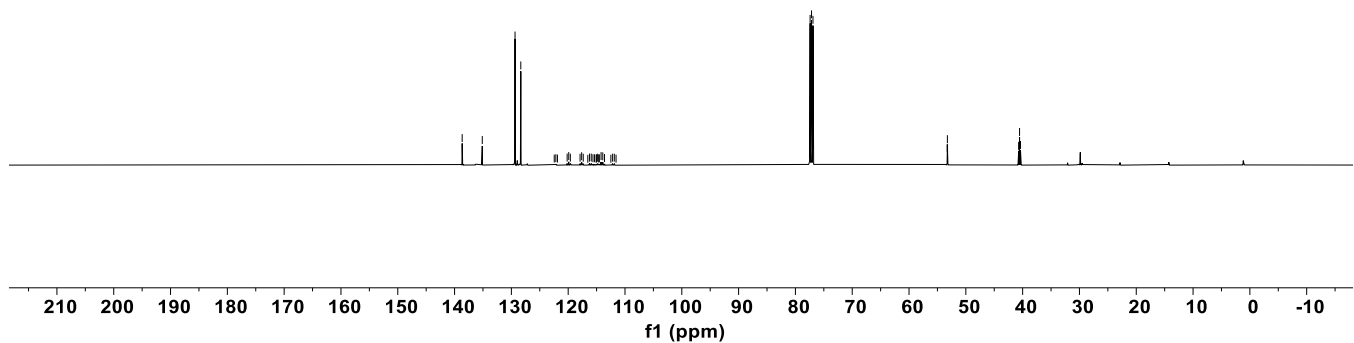
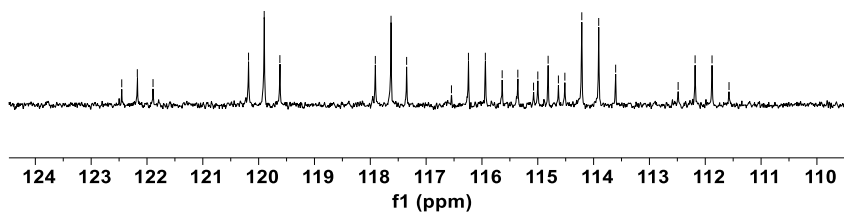
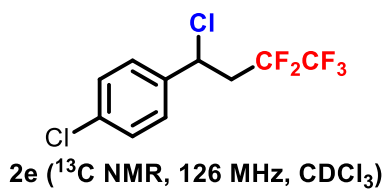


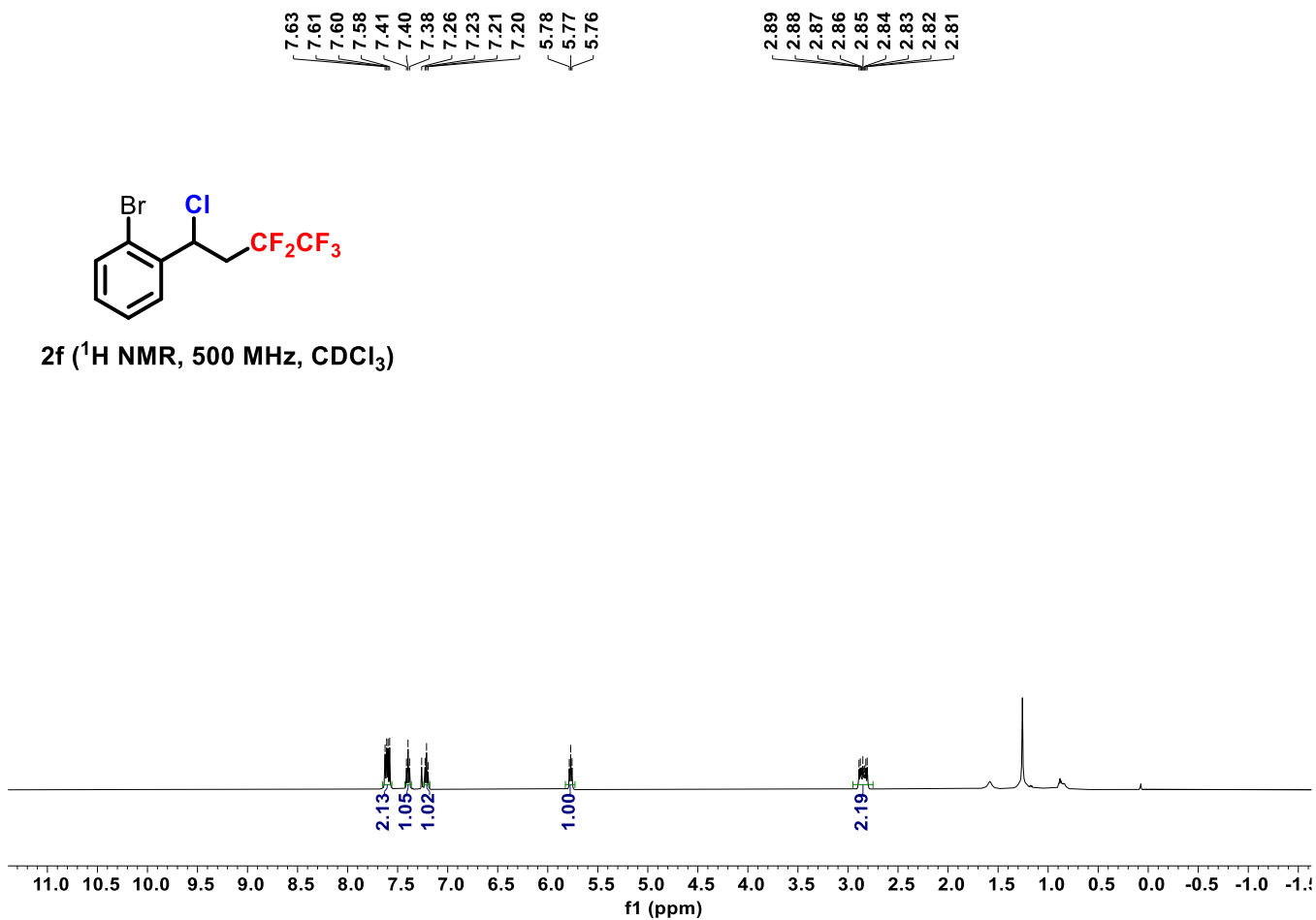
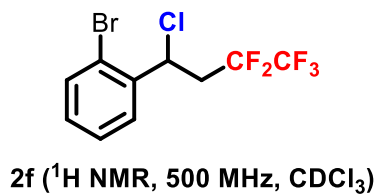
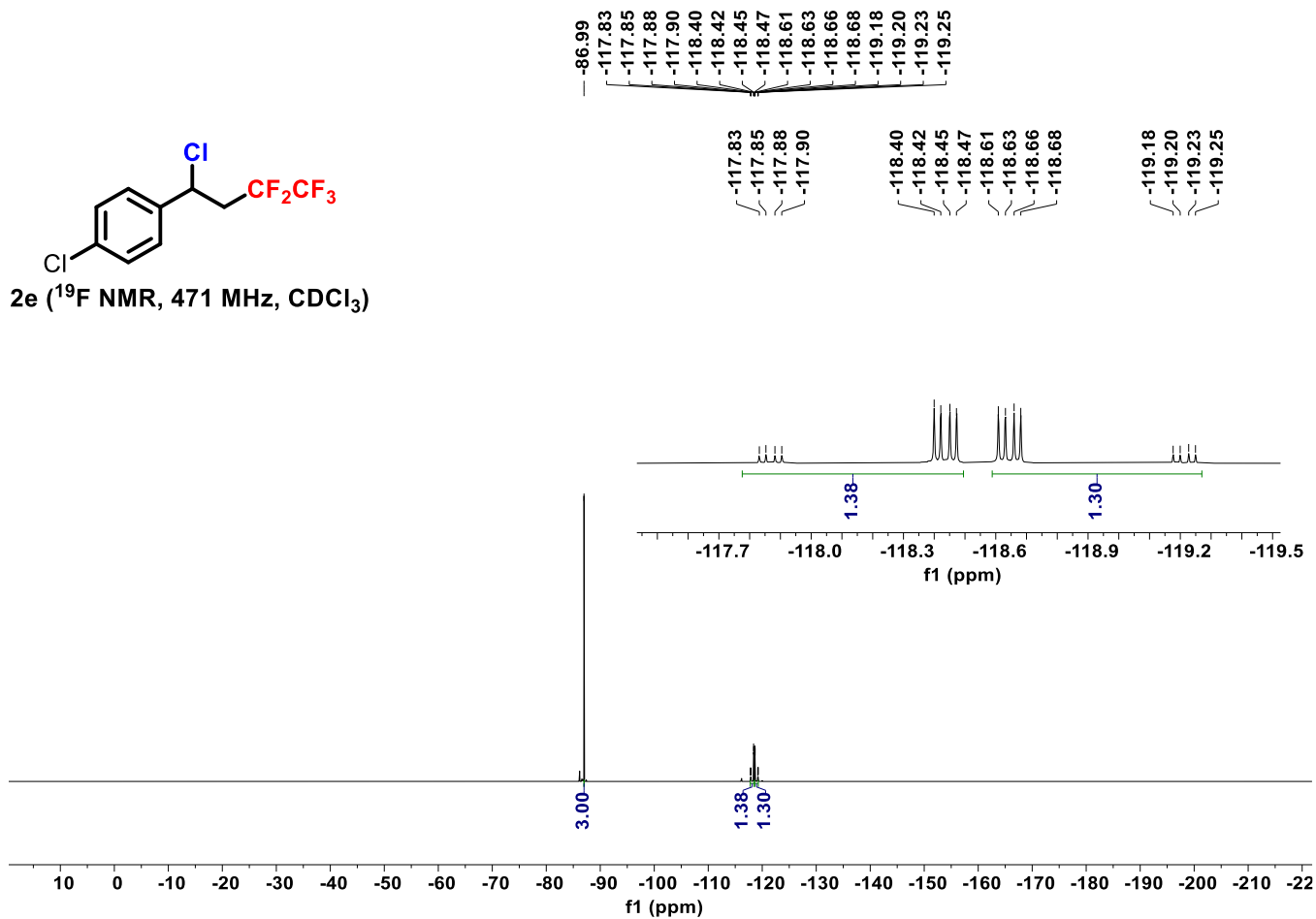
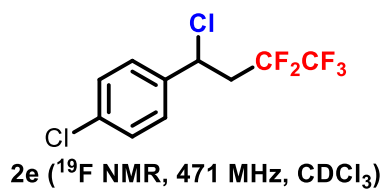


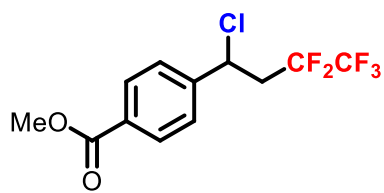
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138.66, 135.12, 129.36, 128.34, 122.45, 122.17, 121.89, 120.18, 119.90, 119.62, 117.91, 117.63, 117.35, 116.55, 116.24, 115.94, 115.64, 115.36, 115.08, 115.00, 114.81, 114.63, 114.51, 114.21, 114.21, 113.91, 113.61, 112.49, 112.18, 111.88, 111.57, 77.41, 77.16, 76.91, 53.27, 53.25, 53.22, 40.70, 40.54, 40.38
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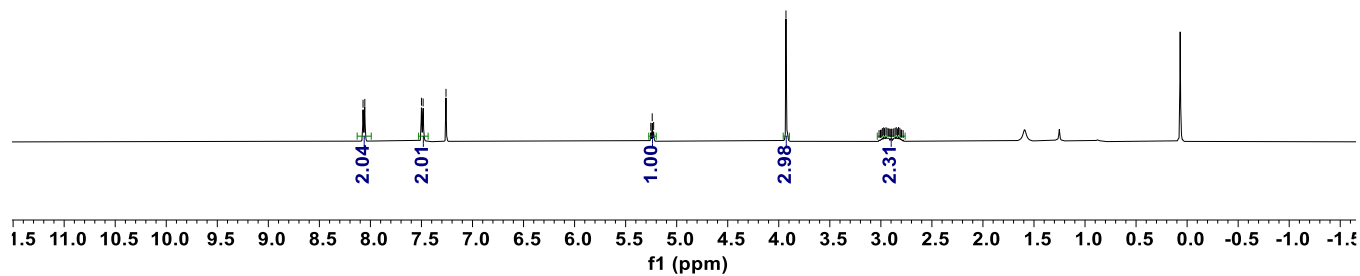




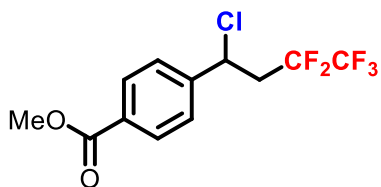


2g (¹H NMR, 500 MHz, CDCl₃)

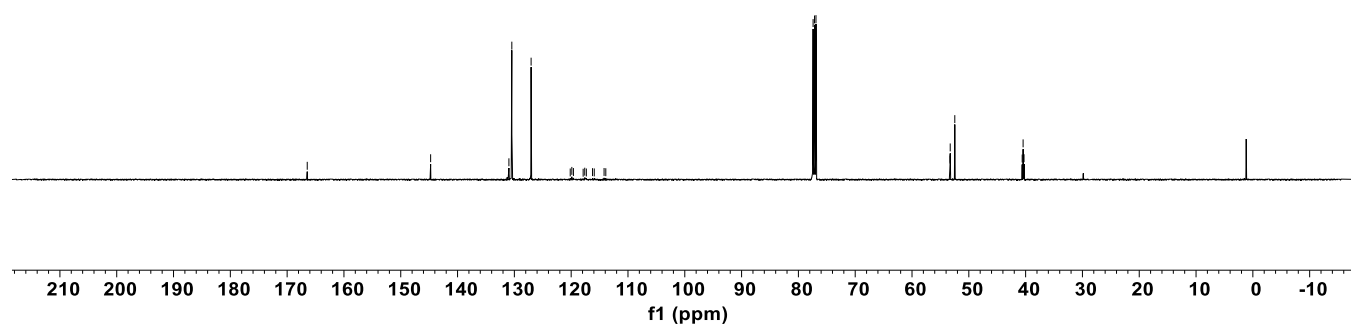
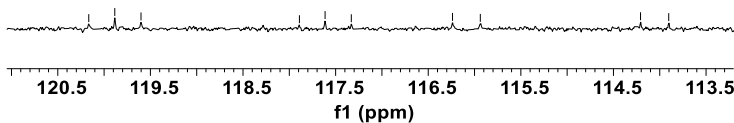
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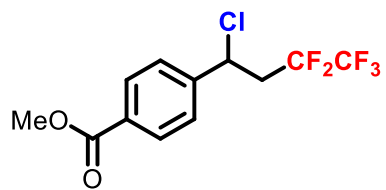


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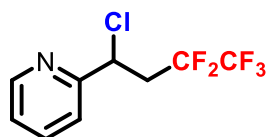
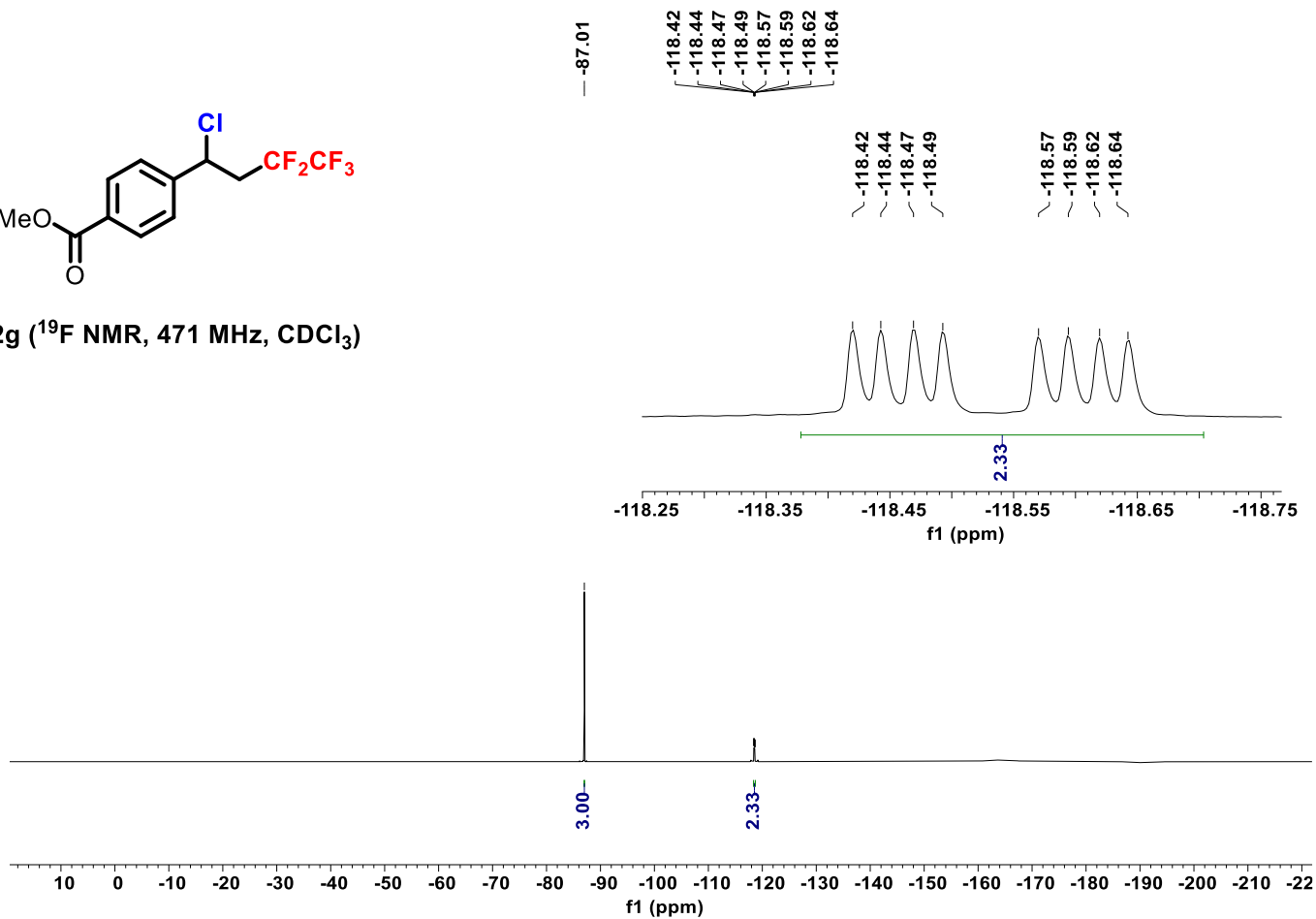


2g (¹³C NMR, 126 MHz, CDCl₃)

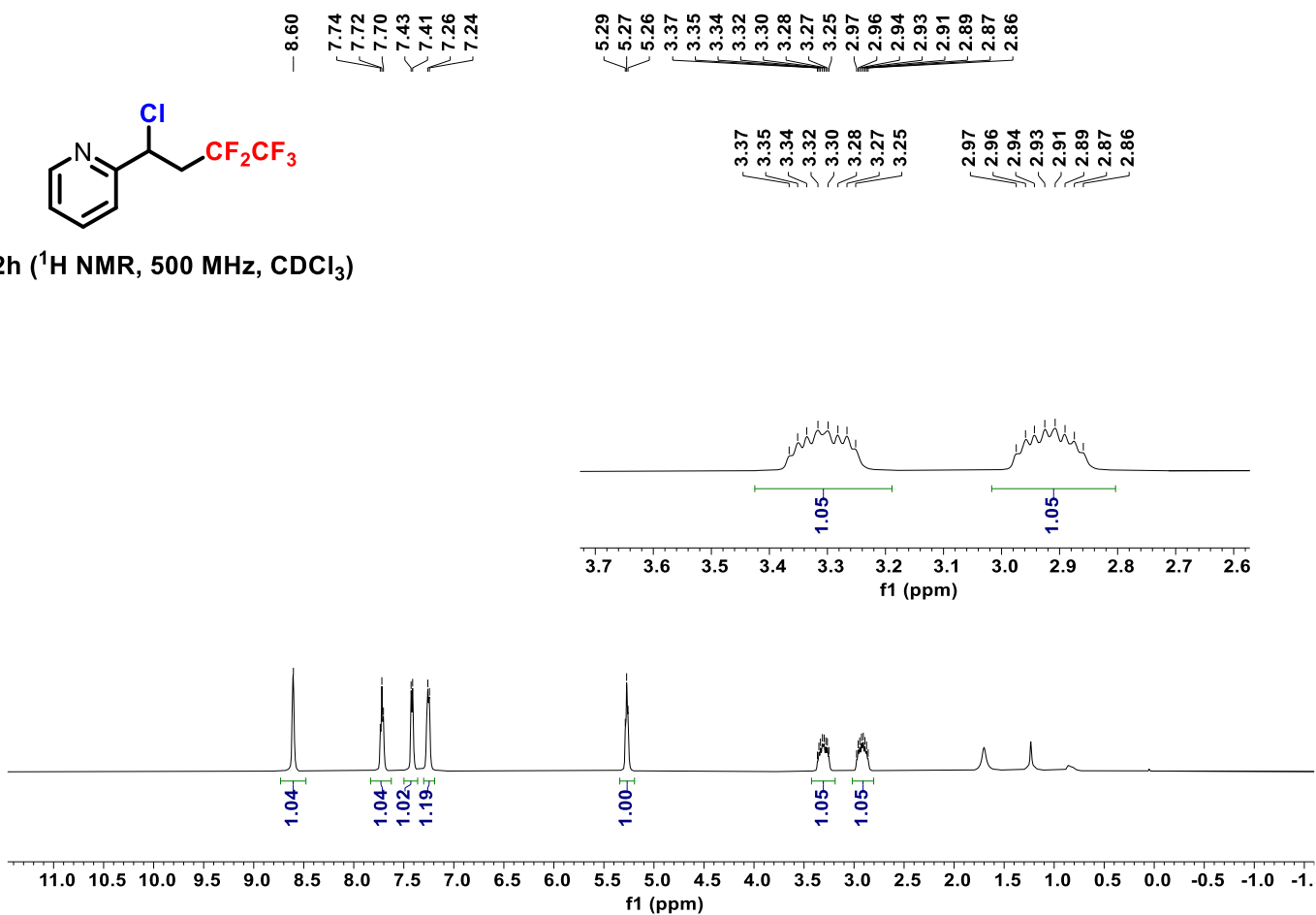


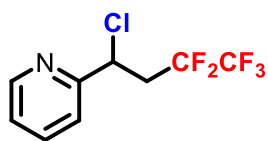


2g (^{19}F NMR, 471 MHz, CDCl_3)

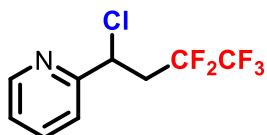
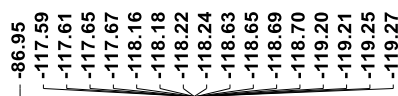
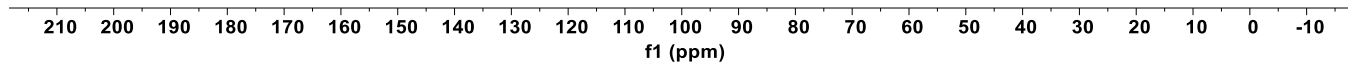
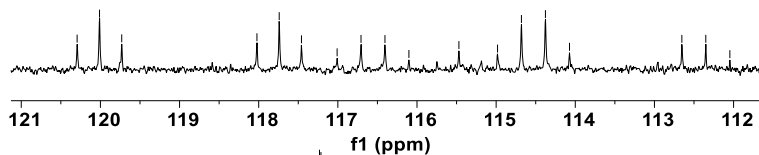
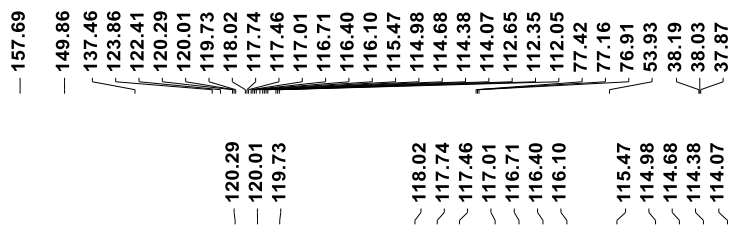


2h (^1H NMR, 500 MHz, CDCl_3)

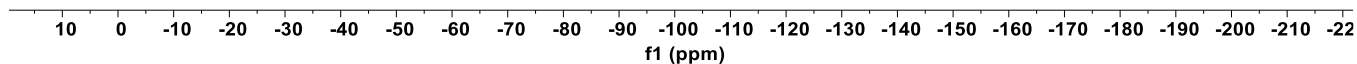
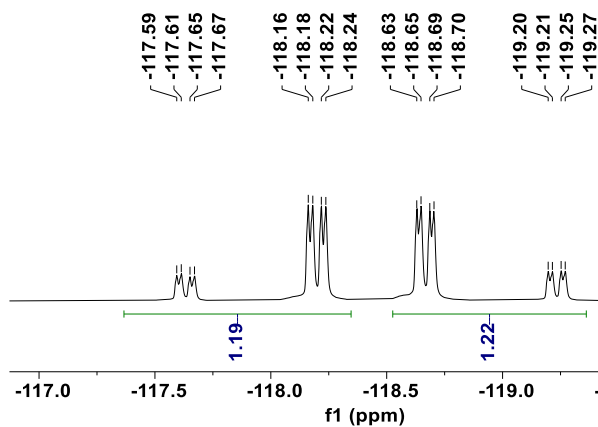


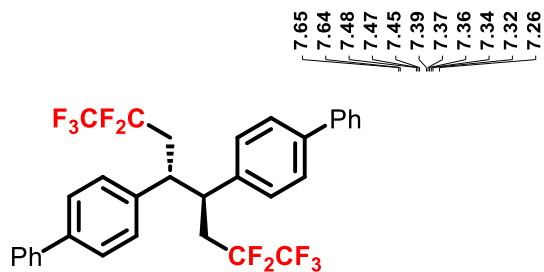


2h (¹³C NMR, 126 MHz, CDCl₃)

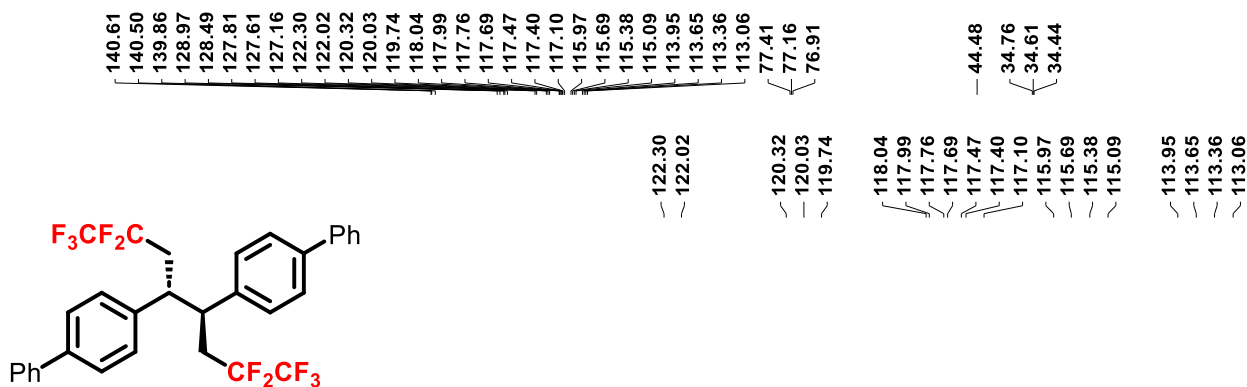
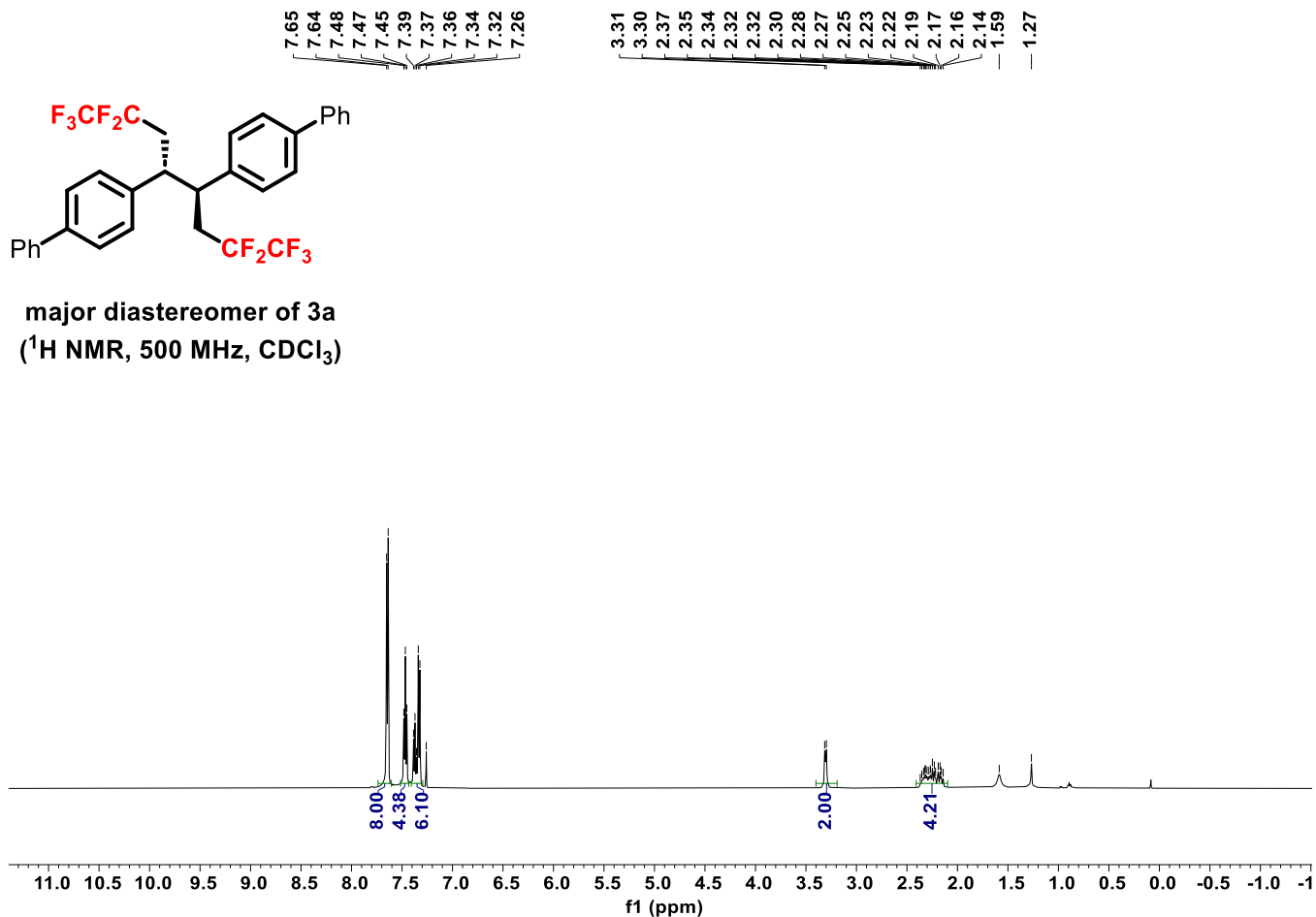


2h (¹⁹F NMR, 471 MHz, CDCl₃)

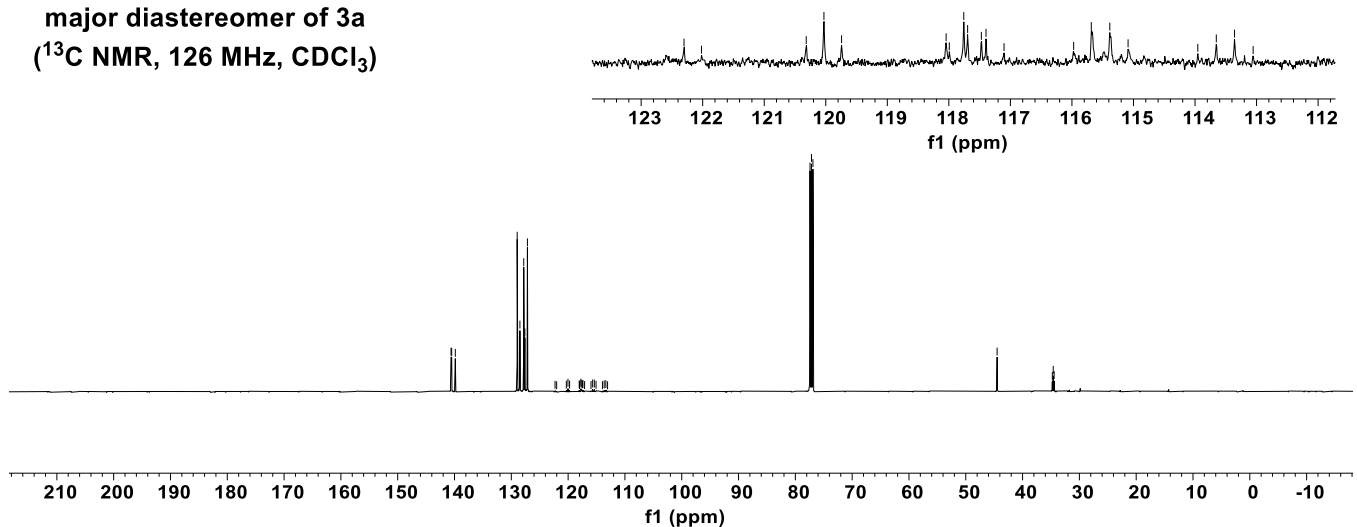


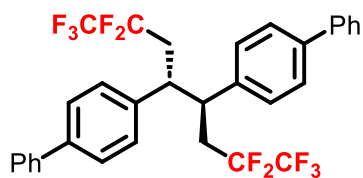


major diastereomer of 3a
 $(^1H$ NMR, 500 MHz, $CDCl_3$)

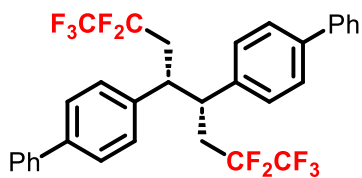
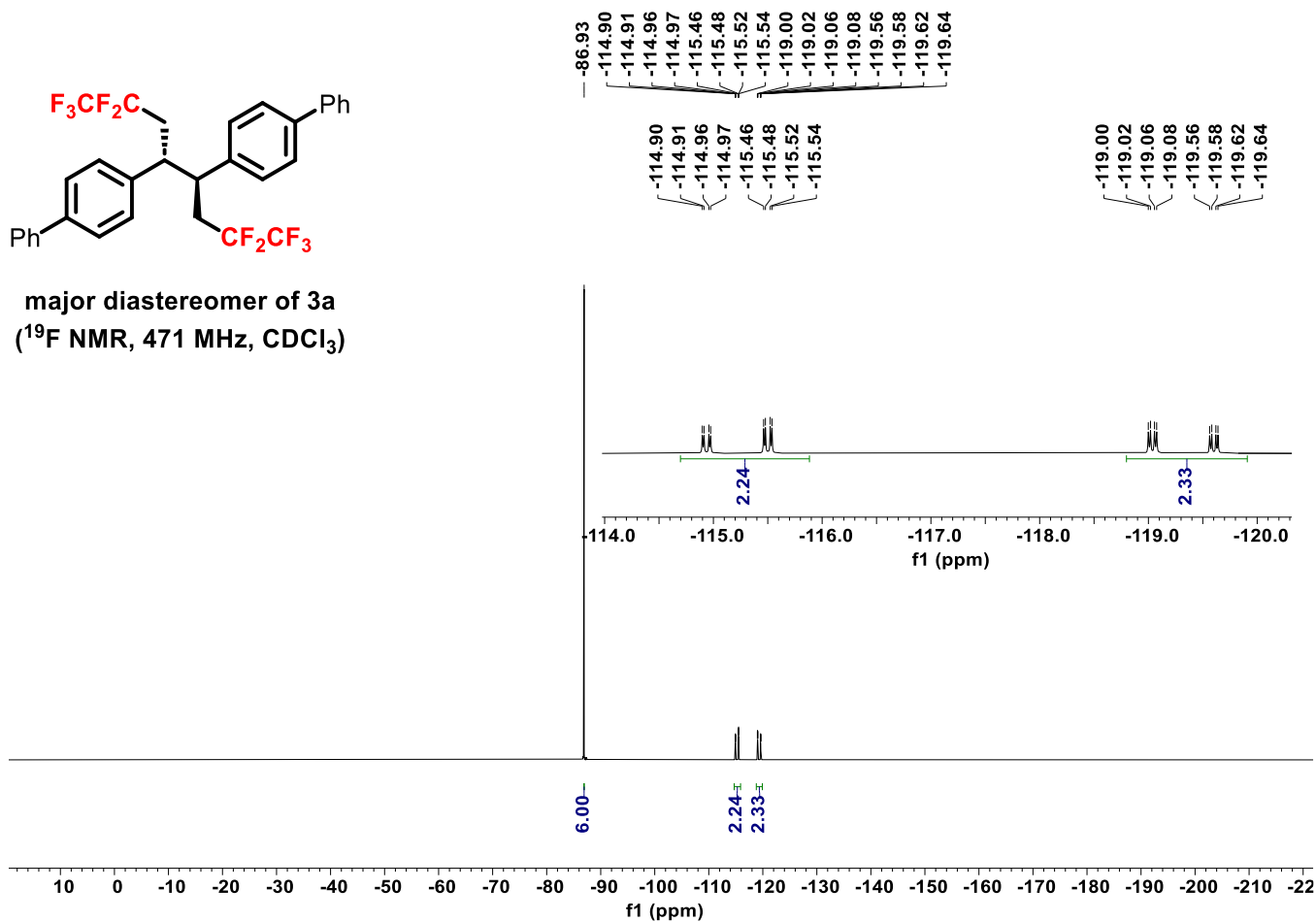


major diastereomer of 3a
 $(^{13}C$ NMR, 126 MHz, $CDCl_3$)

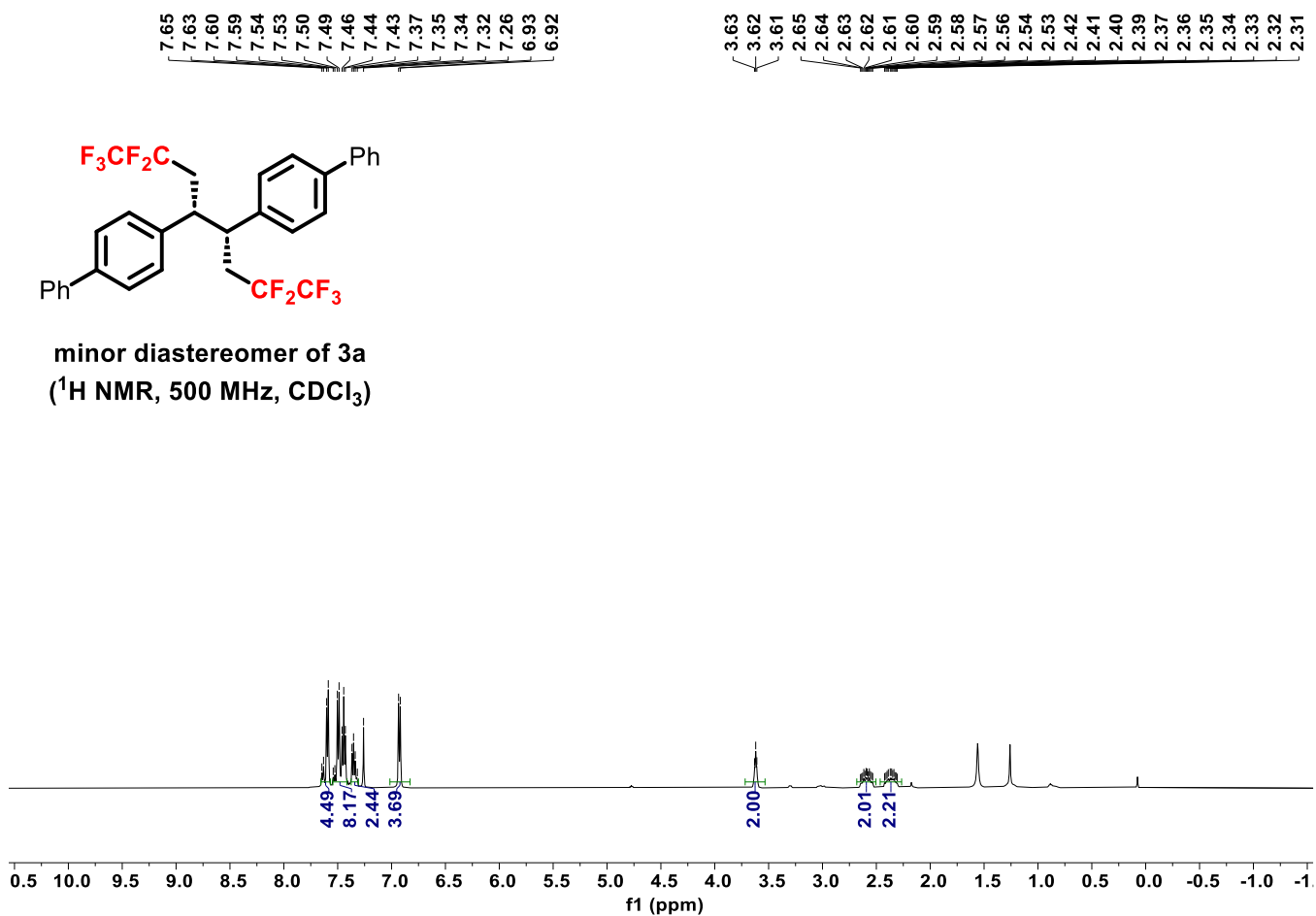


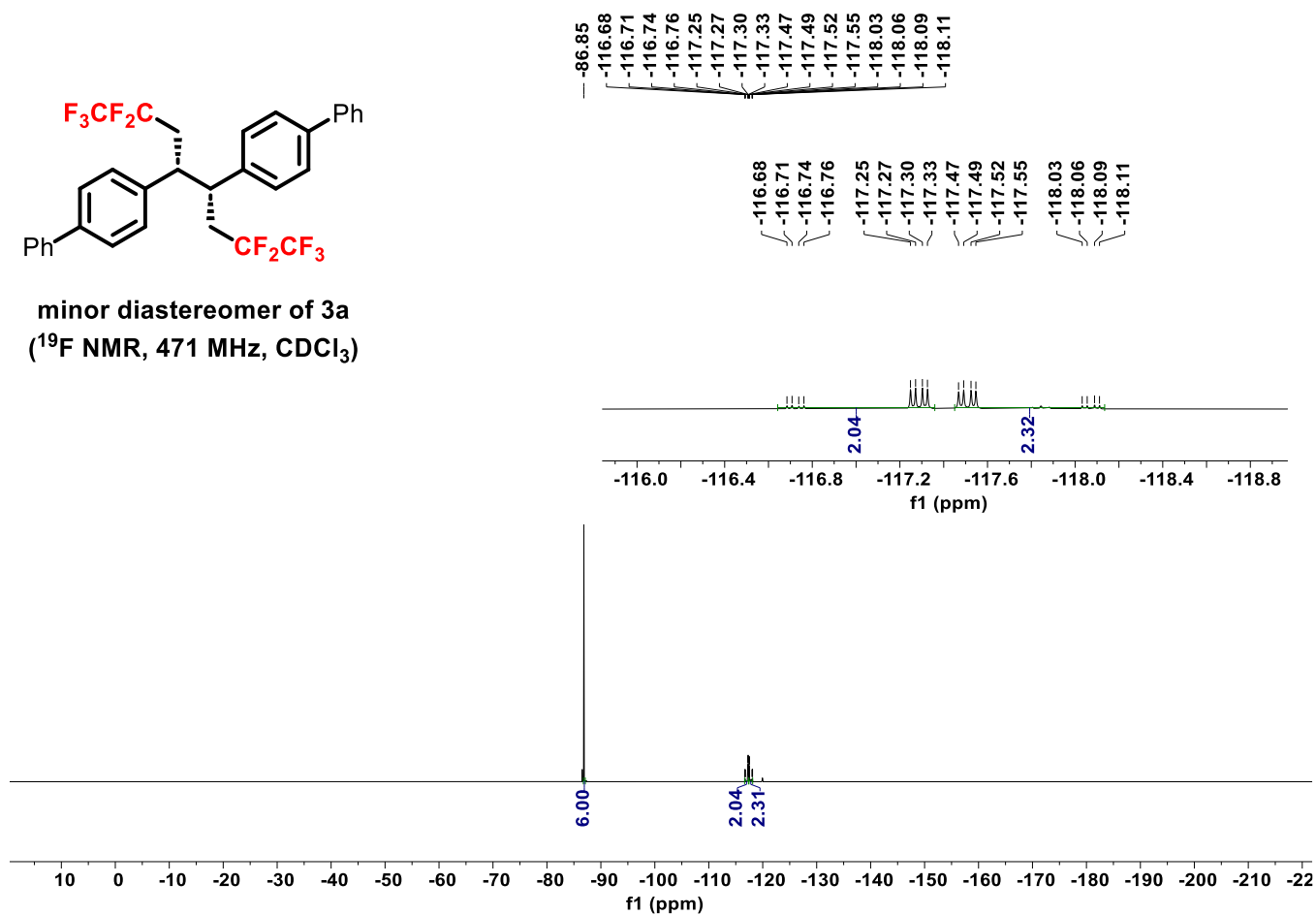
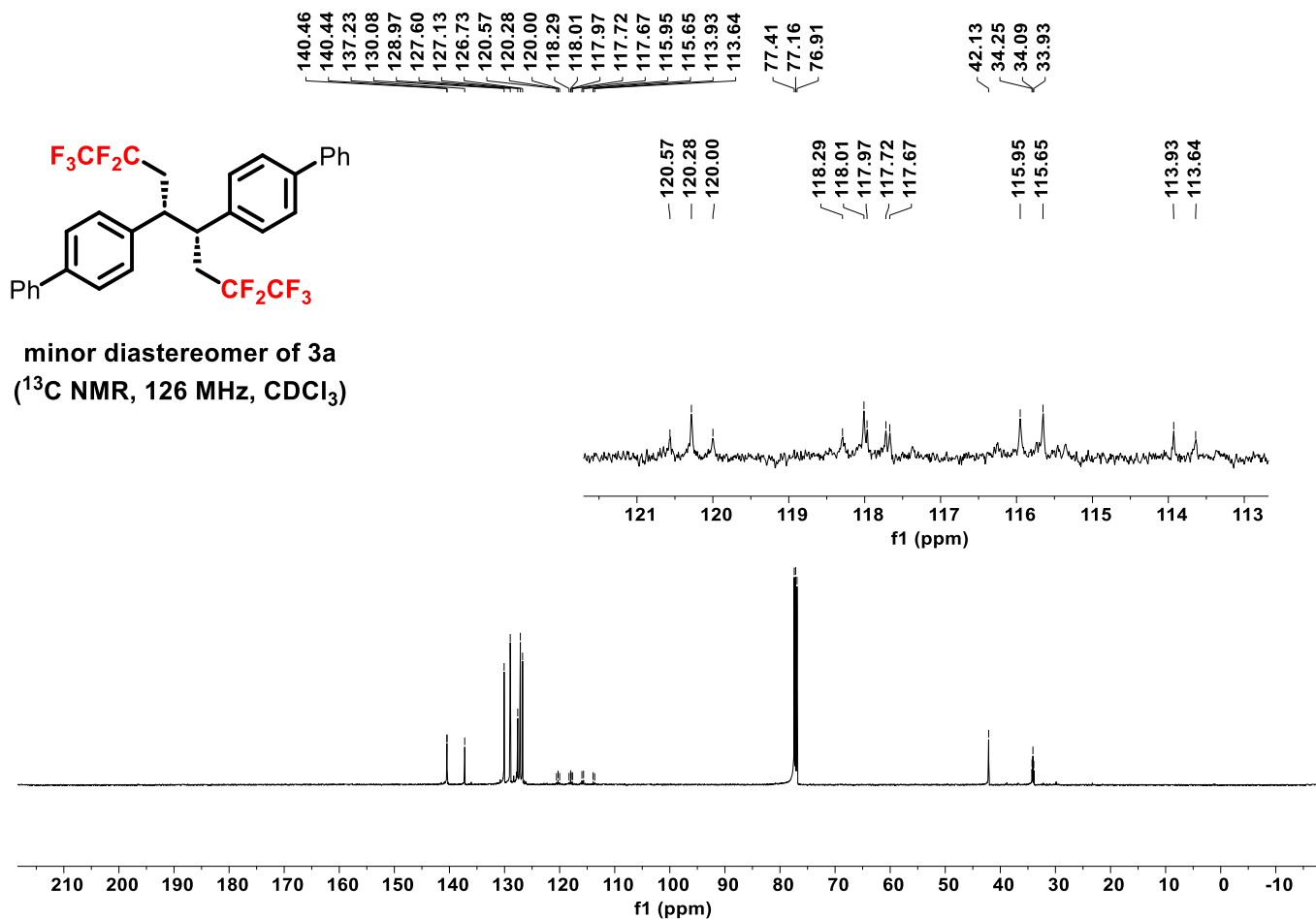


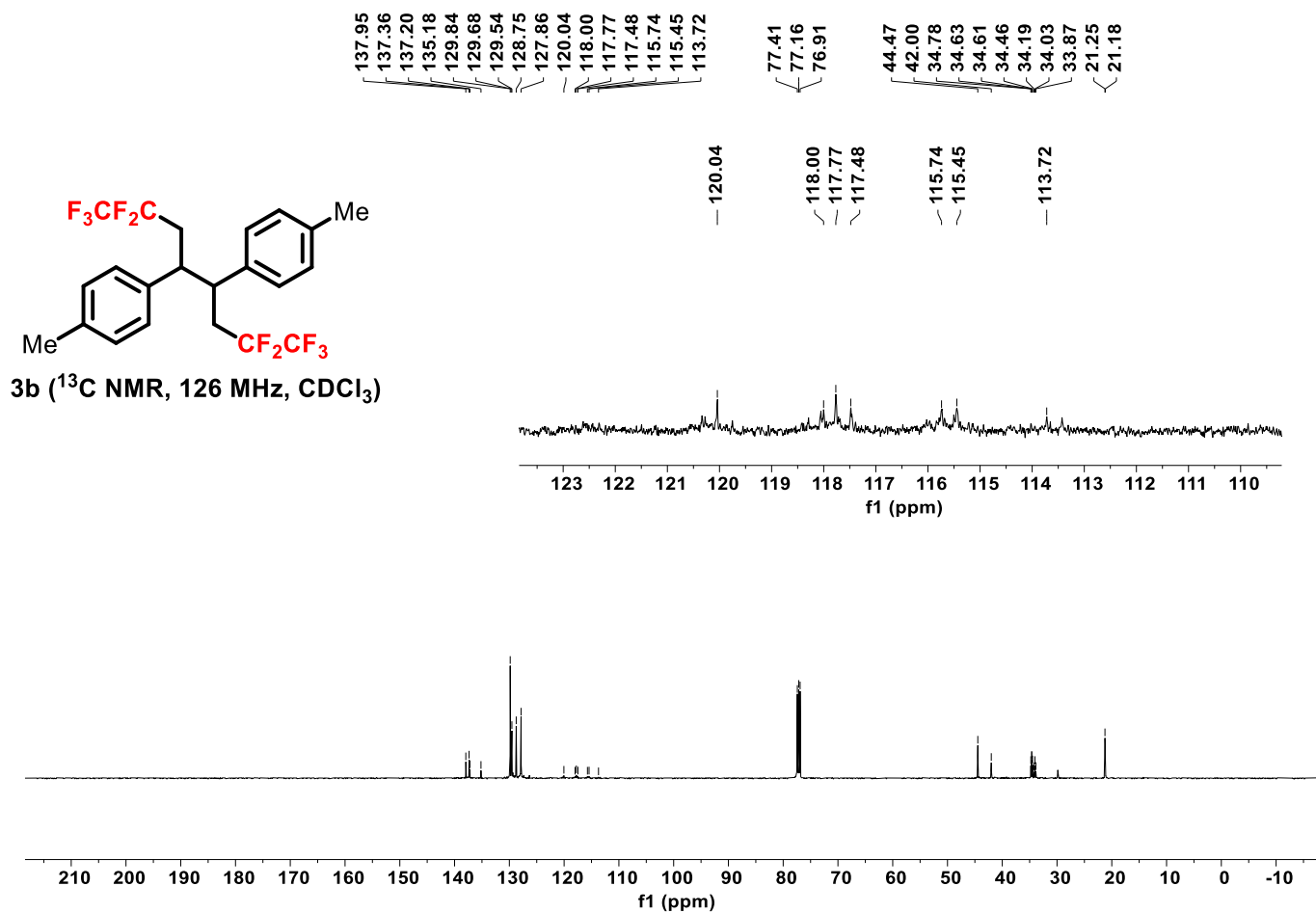
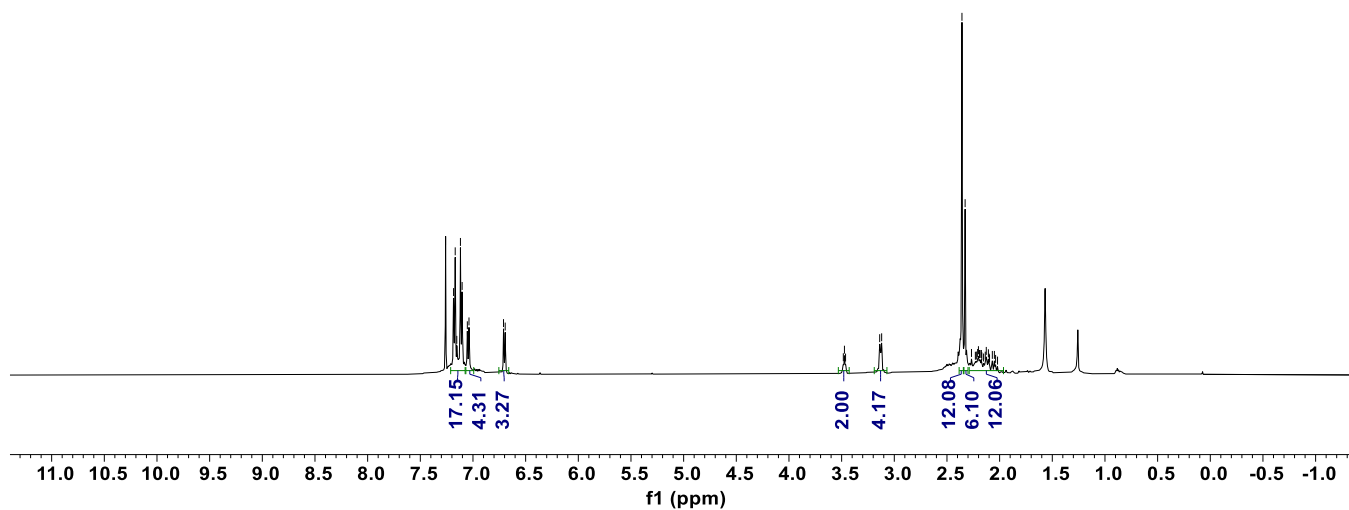
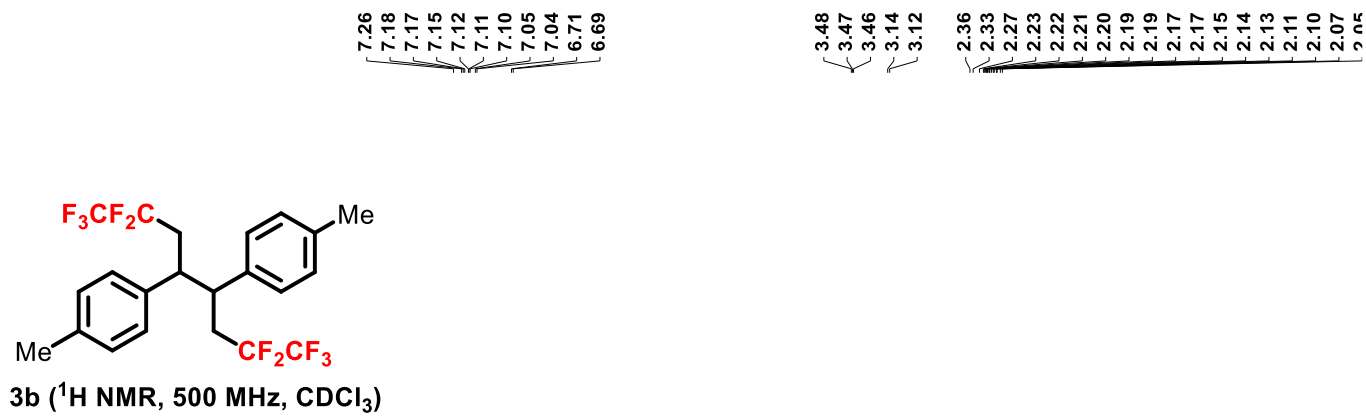
major diastereomer of 3a
(^{19}F NMR, 471 MHz, CDCl_3)

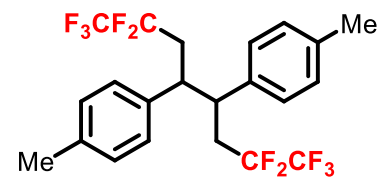


minor diastereomer of 3a
(^1H NMR, 500 MHz, CDCl_3)

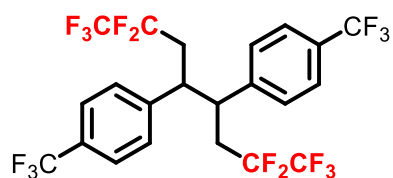
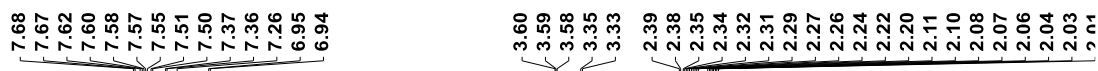
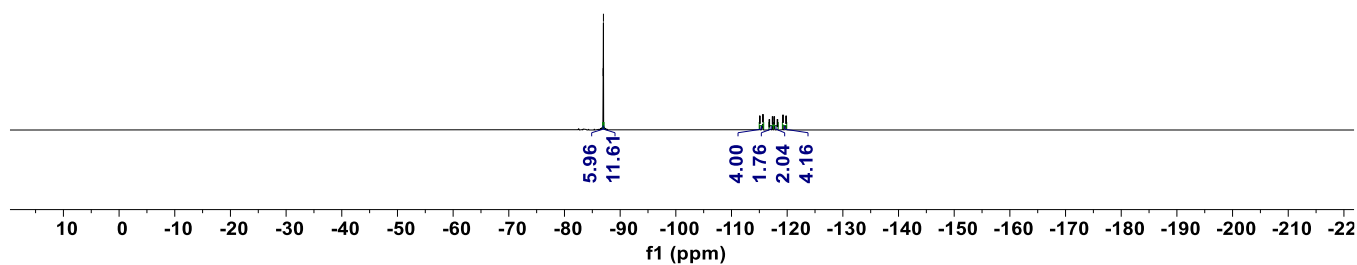
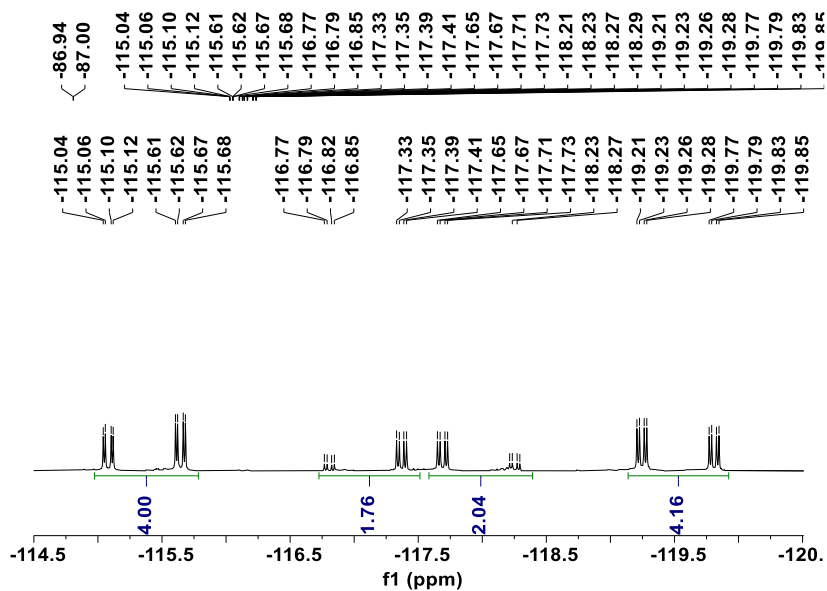




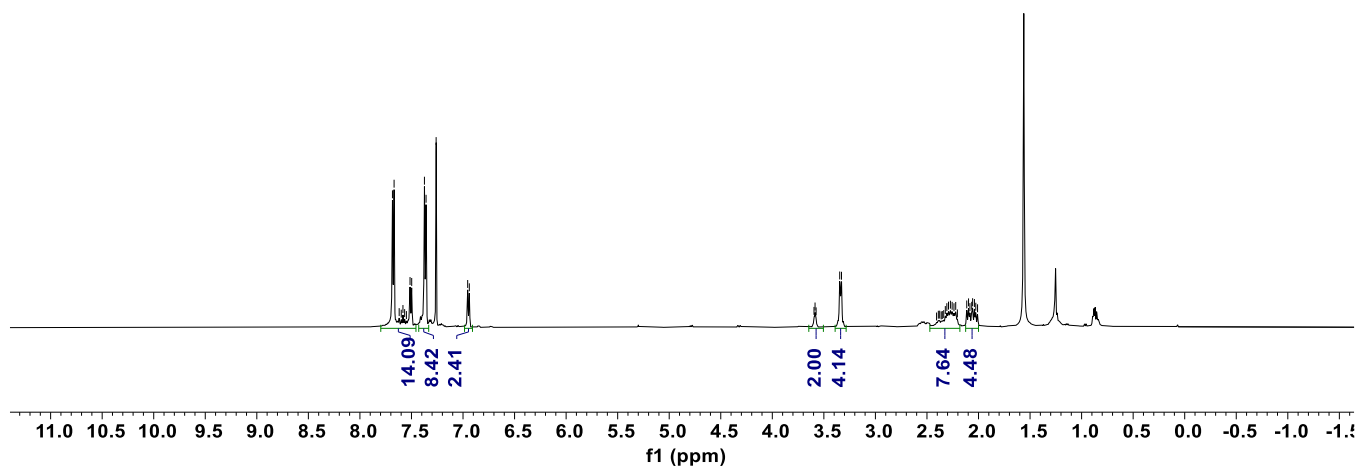


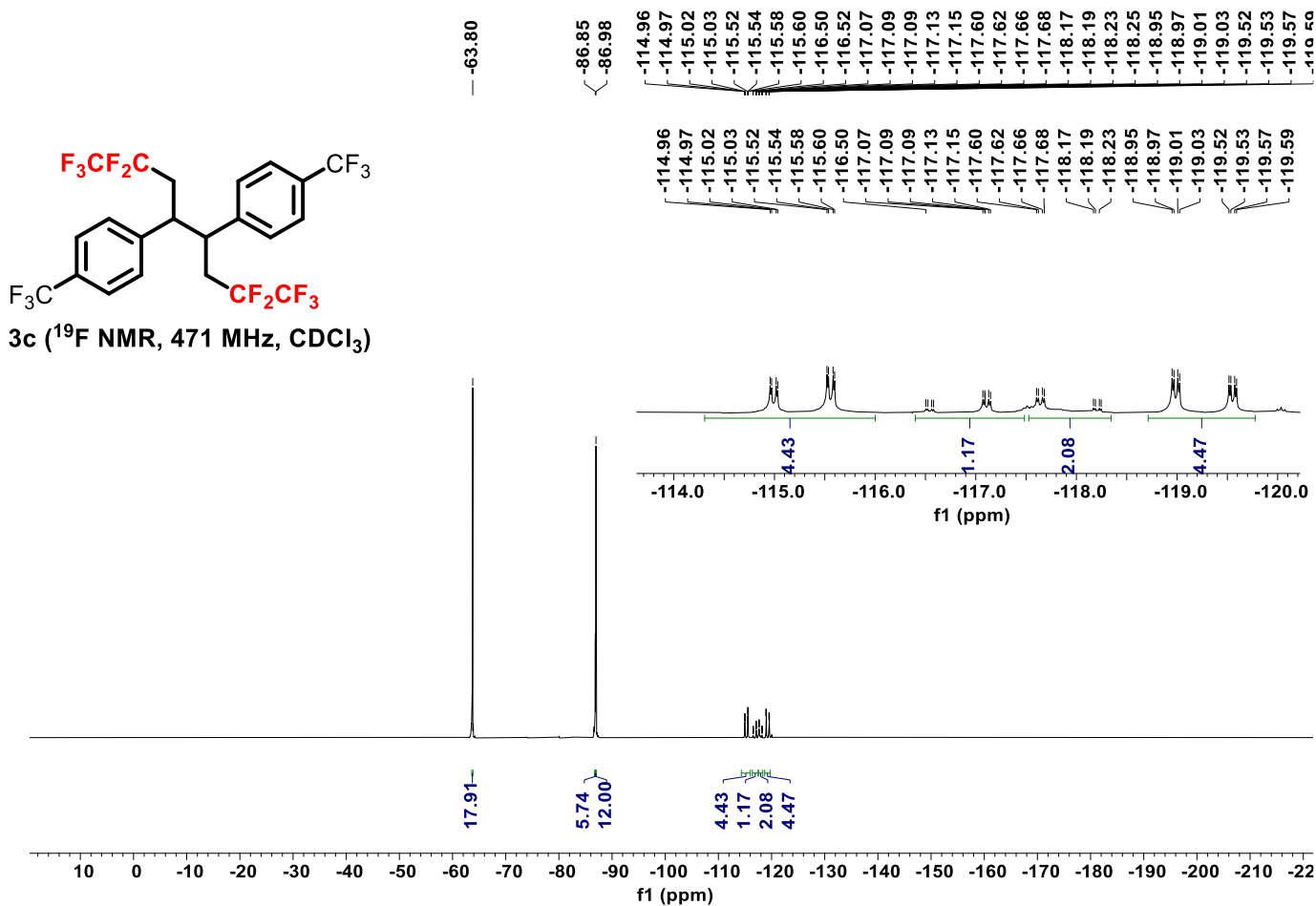
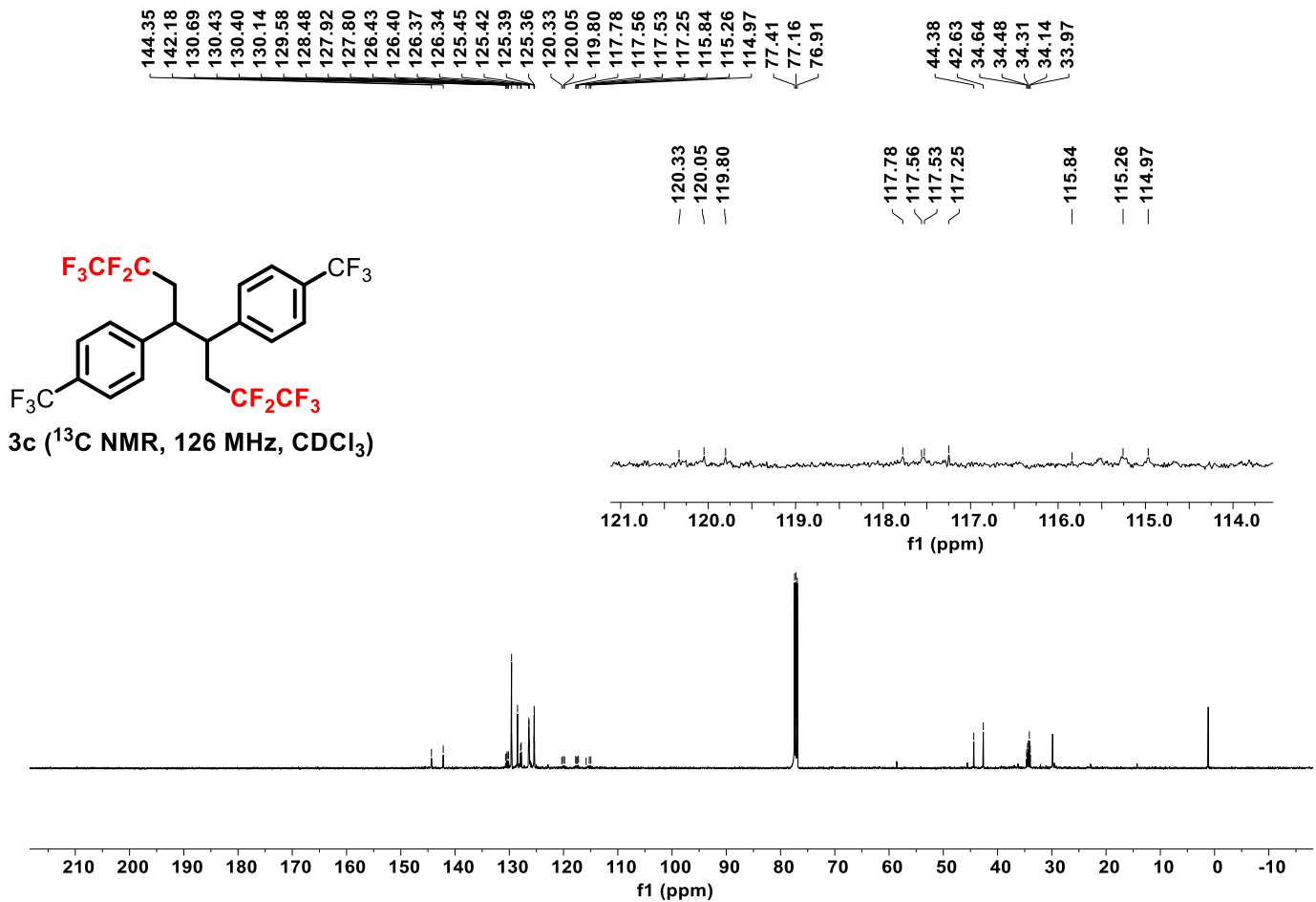


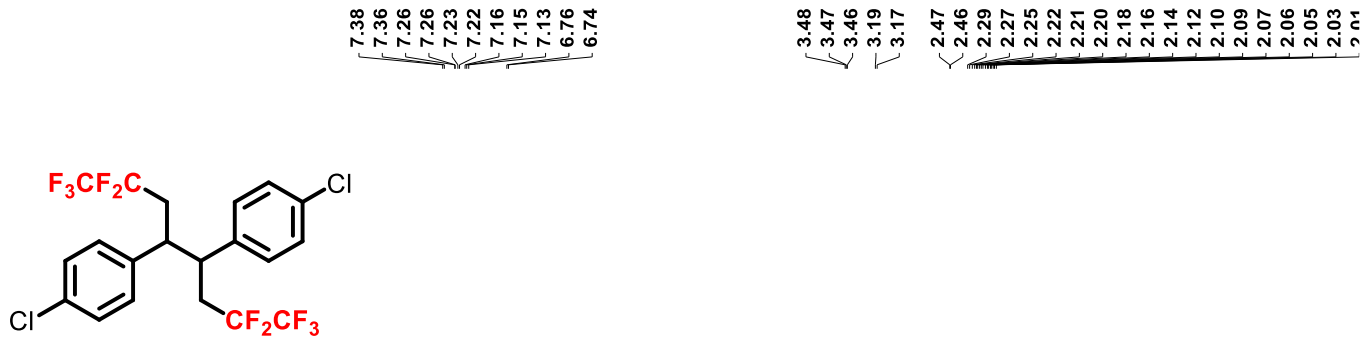
3b (^{19}F NMR, 471 MHz, CDCl_3)



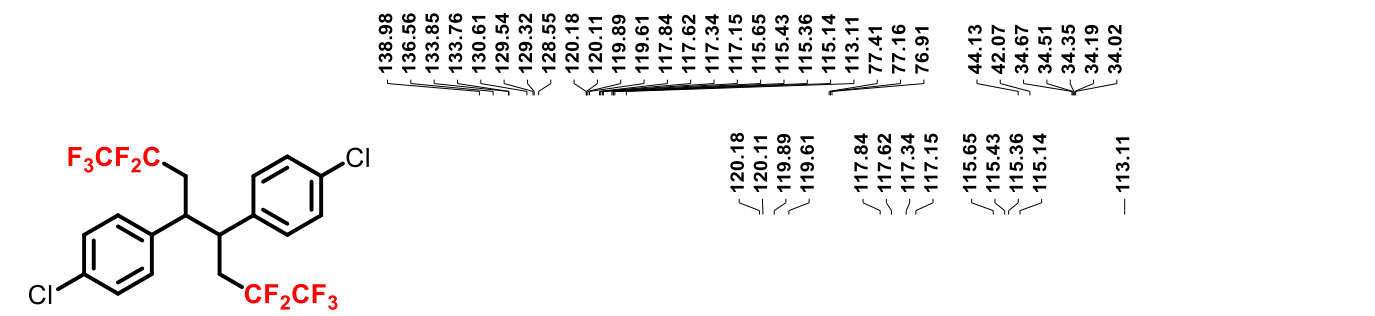
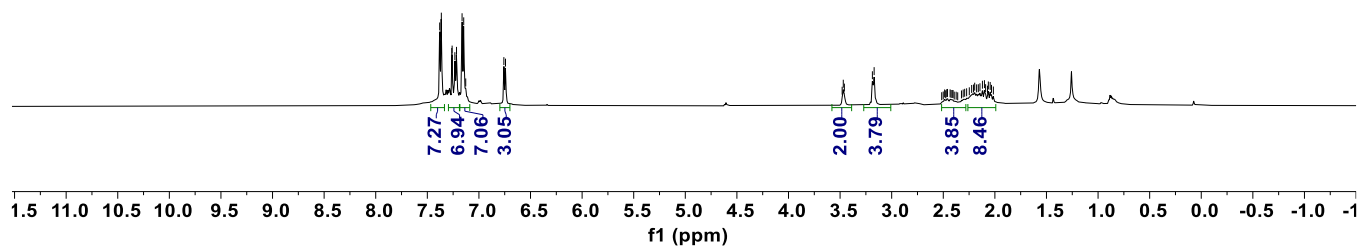
3c (^1H NMR, 500 MHz, CDCl_3)



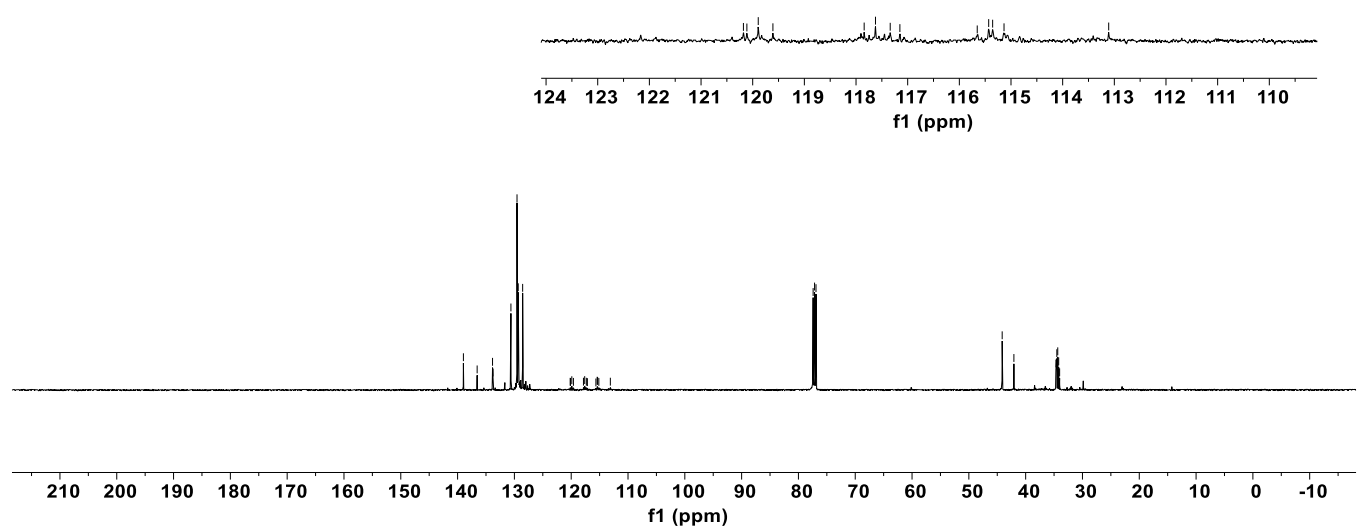


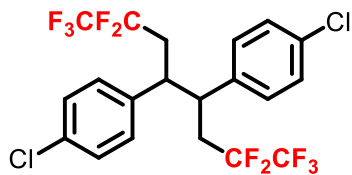


3d ($^1\text{H NMR}$, 500 MHz, CDCl_3)

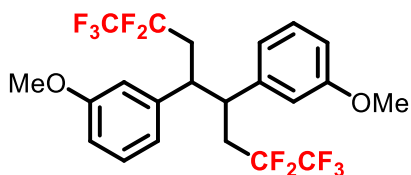
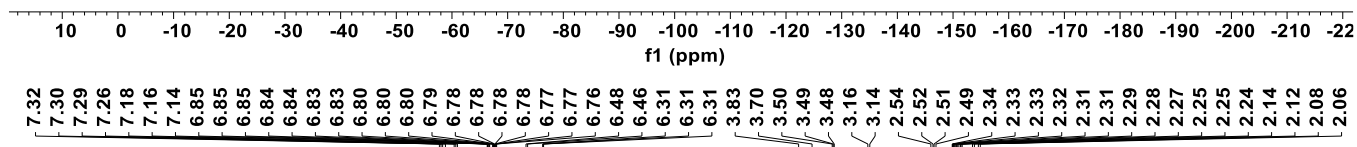
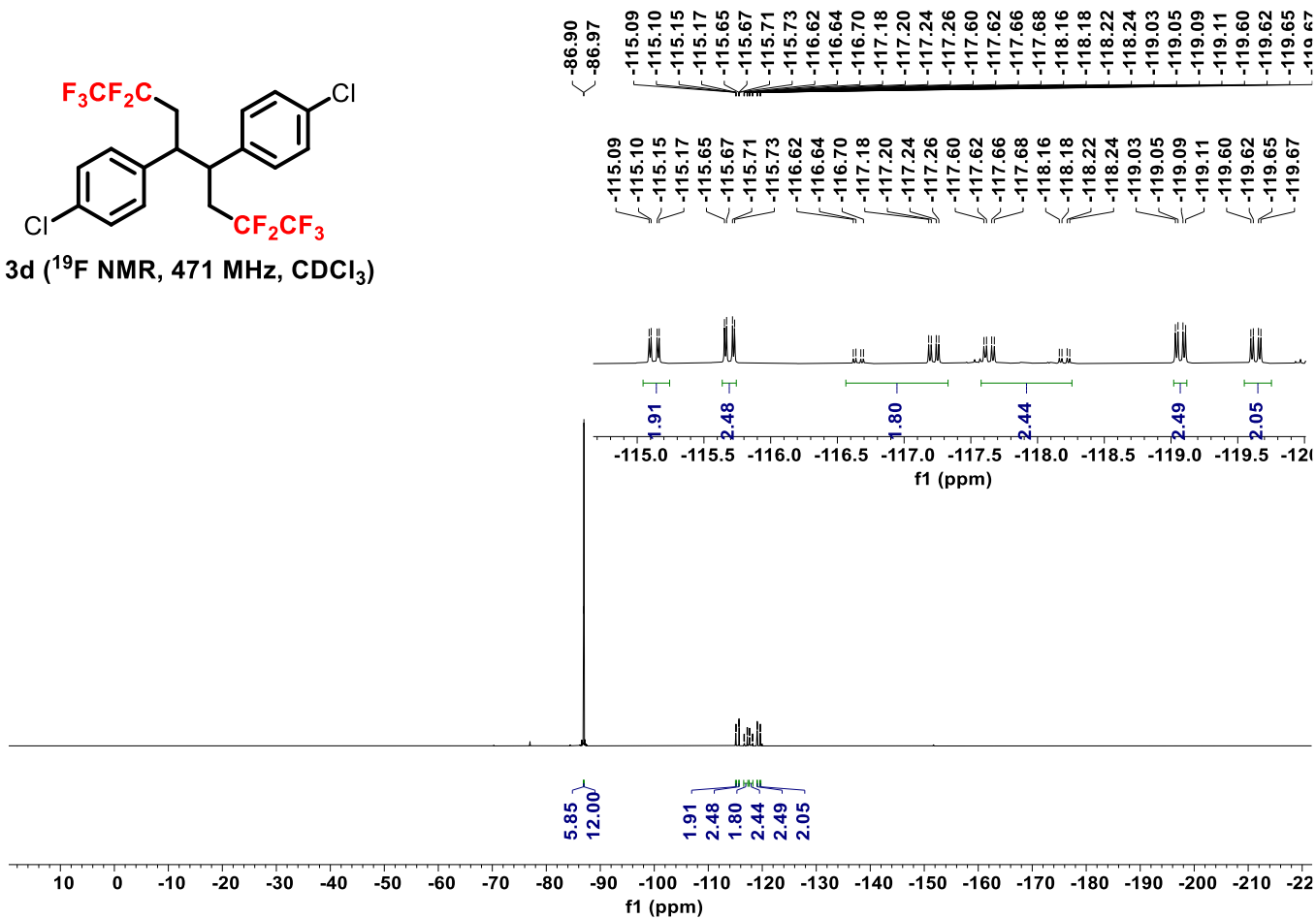


3d ($^{13}\text{C NMR}$, 126 MHz, CDCl_3)

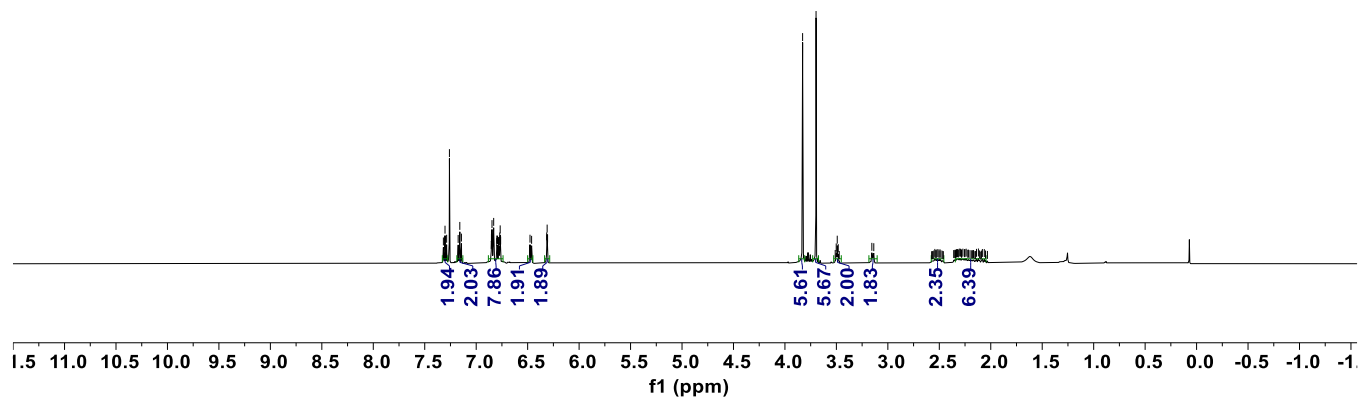




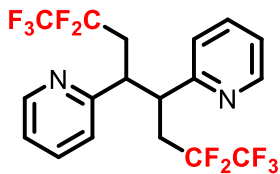
3d (^{19}F NMR, 471 MHz, CDCl_3)



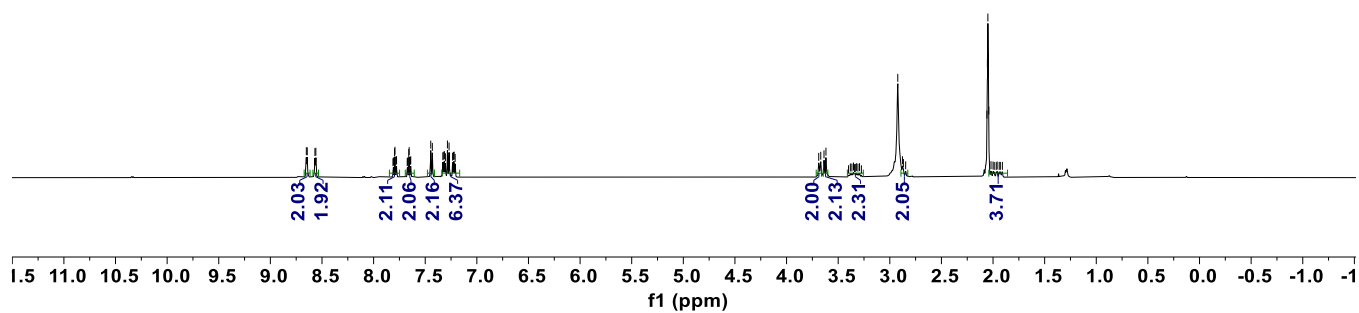
3e (^1H NMR, 500 MHz, CDCl_3)



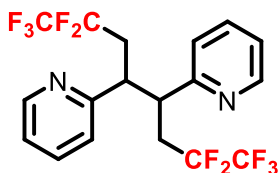
8.65 8.64 8.57 8.56 7.81 7.81 7.80 7.79 7.78 7.78 7.67 7.67 7.66 7.66 7.64 7.64 7.45 7.45 7.43 7.43 7.33 7.32 7.31 7.31 7.30 7.28 7.27 7.27 7.23 7.23 7.22 7.21 3.69 3.67 3.64 3.62 3.38 3.37 3.37 3.35 3.34 3.34 3.33 3.32 3.31 3.29 2.92 2.88 2.87 2.85 2.06 2.05 2.05 2.04 2.02 2.00 1.99 1.97 1.96 1.94 1.93 1.91



3f (1H NMR, 500 MHz, Acetone- d_6)

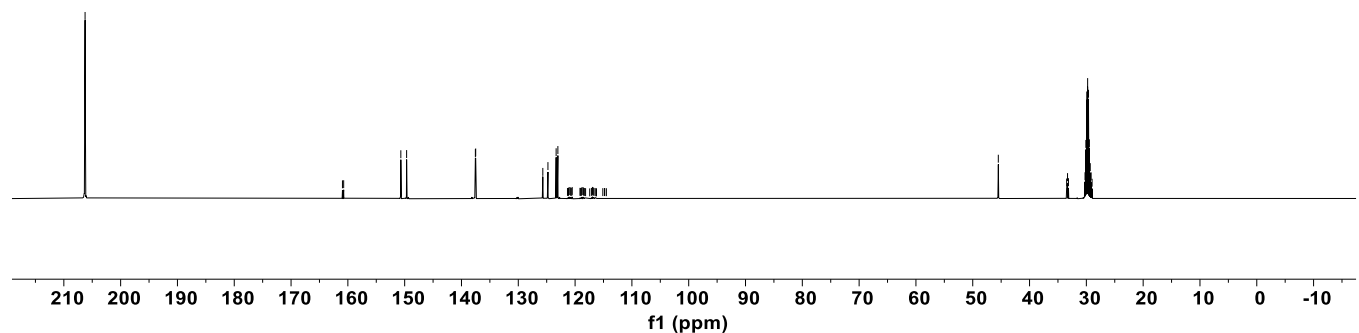
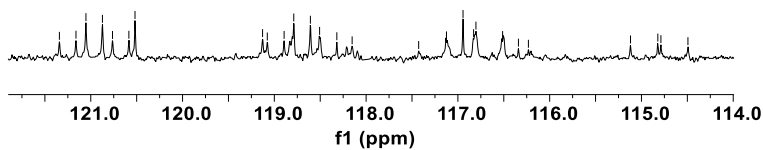


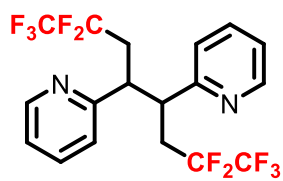
206.26 160.95 160.74 150.68 149.66 137.56 137.50 125.68 124.78 123.34 123.03 121.34 121.16 121.05 120.87 120.76 120.58 120.52 119.13 119.08 118.89 118.79 118.61 118.51 118.32 118.15 117.12 116.94 116.83 116.80 116.51 45.50 33.47 33.31 33.15 30.24 30.08 29.93 29.77 29.62 29.47 29.31 29.15 29.00



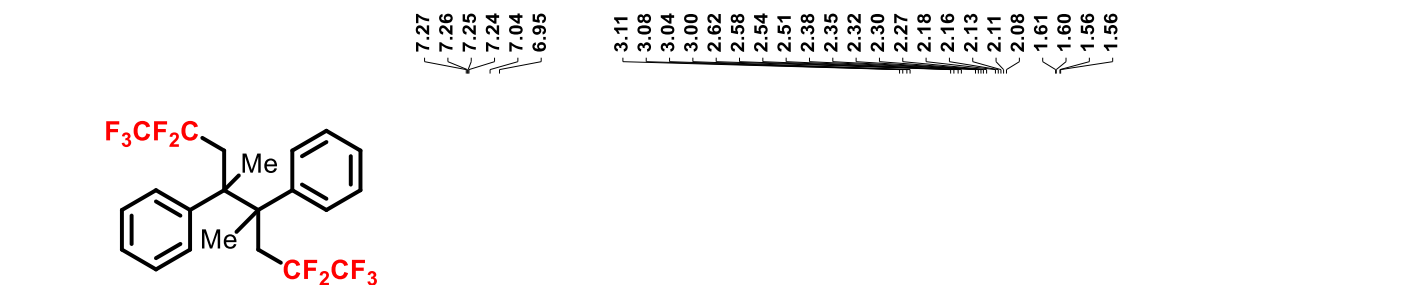
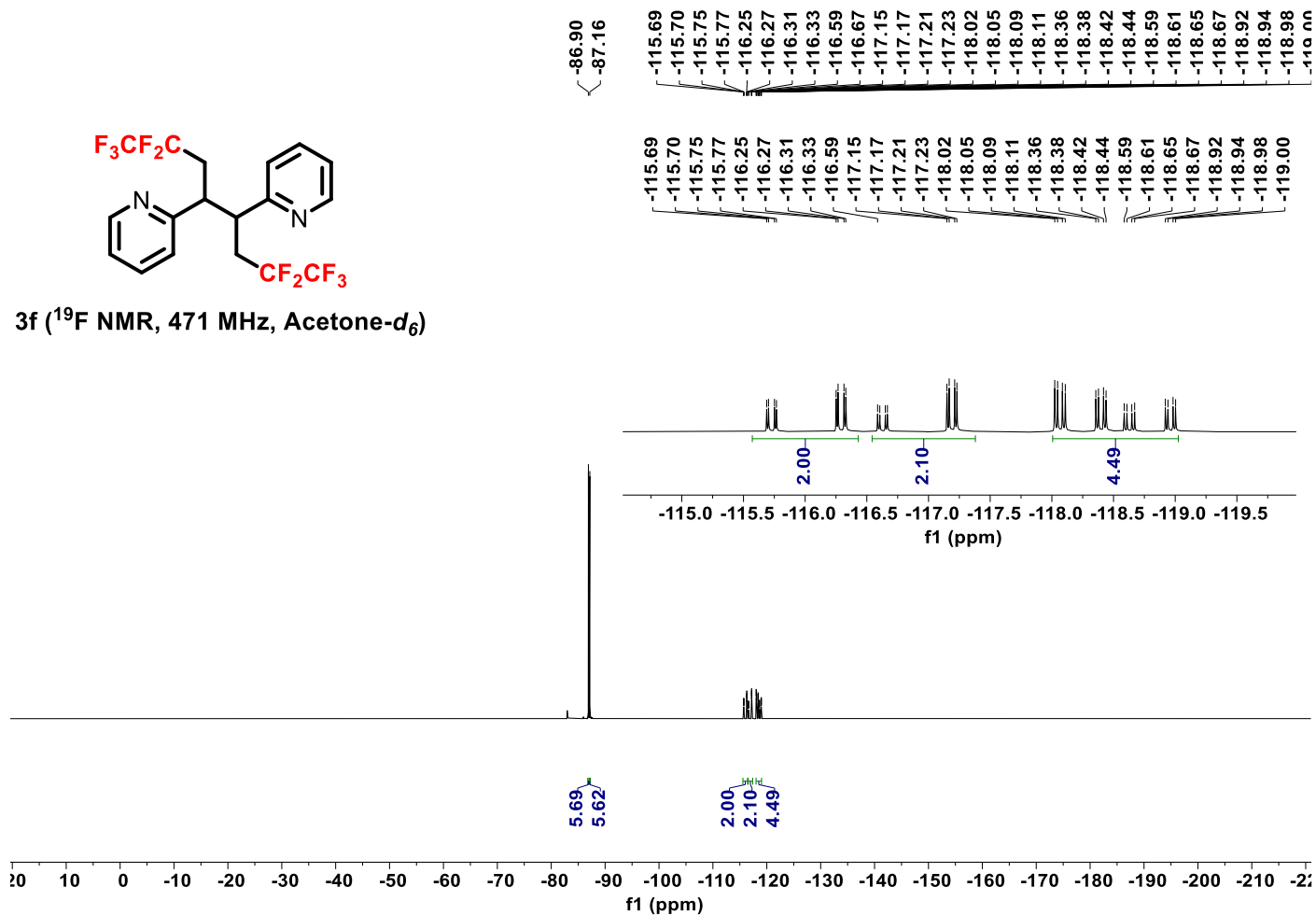
3f (^{13}C NMR, 126 MHz, Acetone- d_6)

121.34 121.16 121.05 120.87 120.76 120.58 120.52 119.13 119.08 118.89 118.79 118.61 118.51 118.32 118.15 117.12 116.94 116.83 116.80 116.51 116.34 116.23 115.12 114.82 114.79 114.49

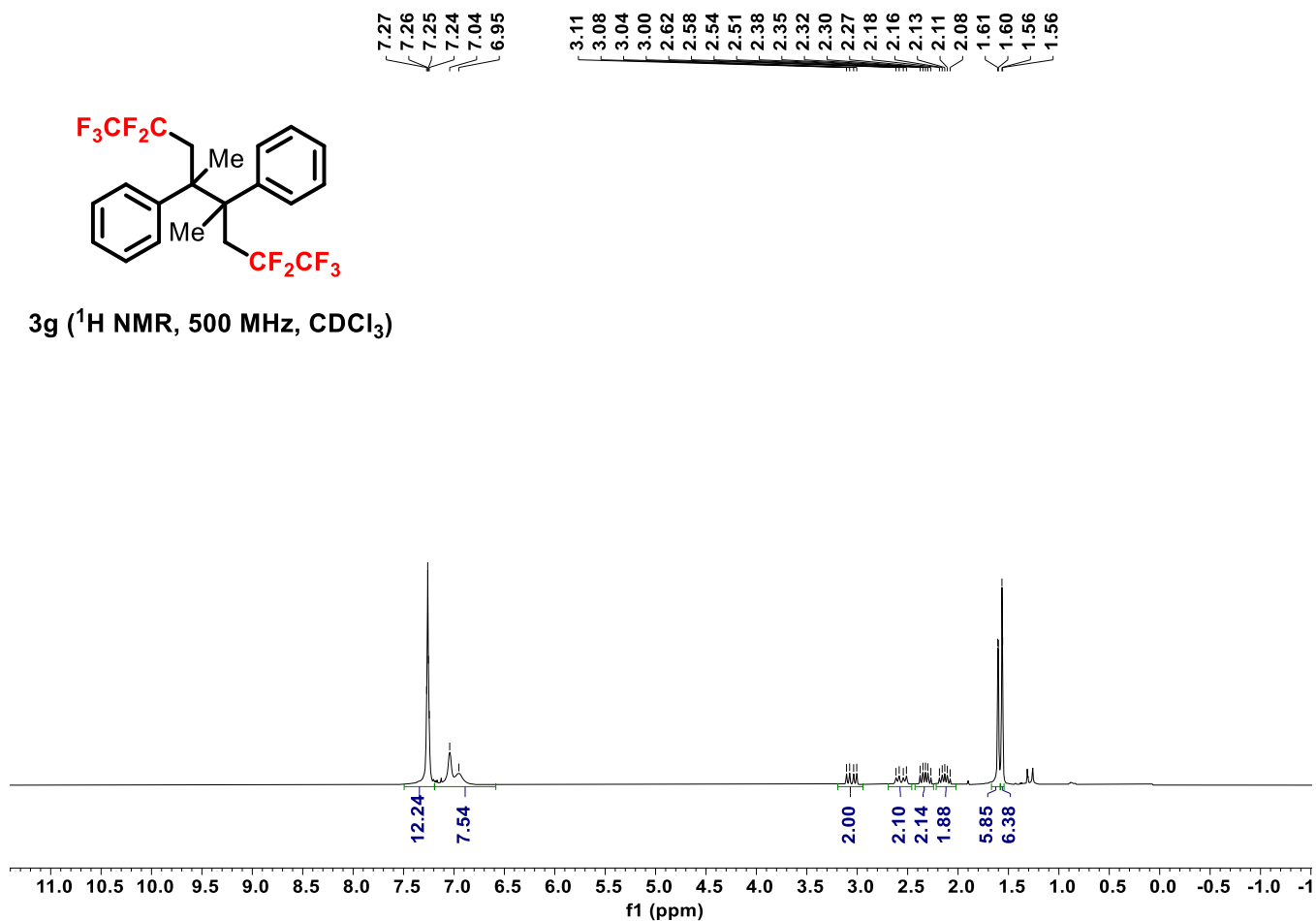




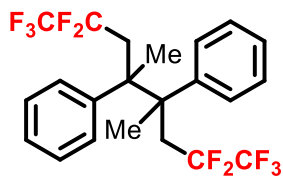
3f (^{19}F NMR, 471 MHz, Acetone- d_6)



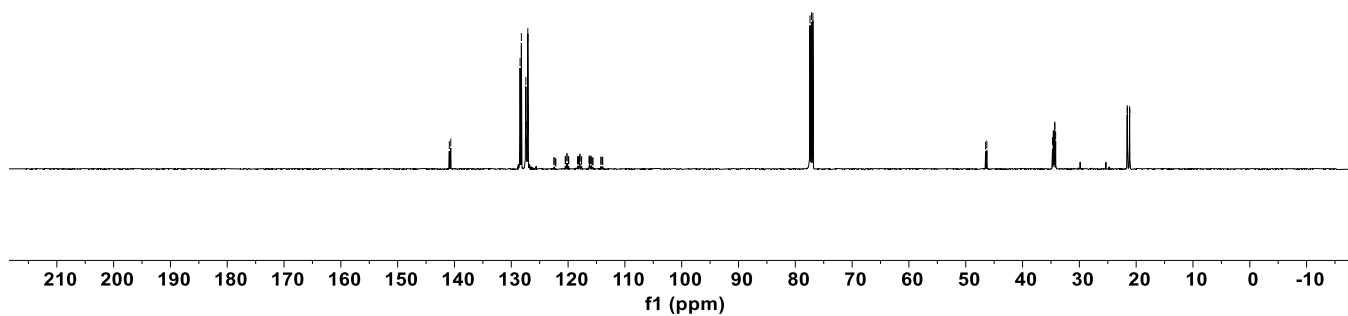
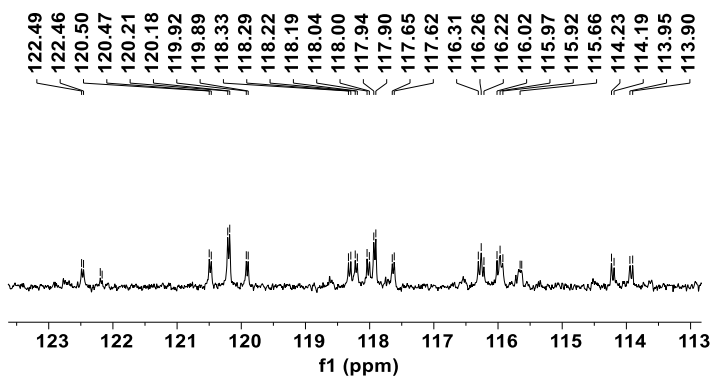
3g (^1H NMR, 500 MHz, CDCl_3)



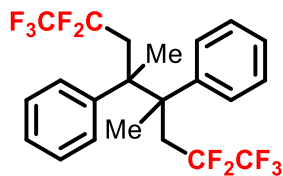
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127.37
127.09
127.07
122.49
122.46
122.20
122.17
120.50
120.47
120.21
120.18
119.92
119.89
118.33
118.29
118.22
118.19
118.04
118.00
117.94
117.90
117.65
117.62
116.31
116.26
116.22
116.02
115.97
115.92
115.66
115.63
114.23
114.19
113.95
113.90
77.41
77.16
76.91
46.50
46.28
34.73
34.59
34.57
34.47
34.43
34.33
34.31
34.17
21.58
21.54
21.15
21.12



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

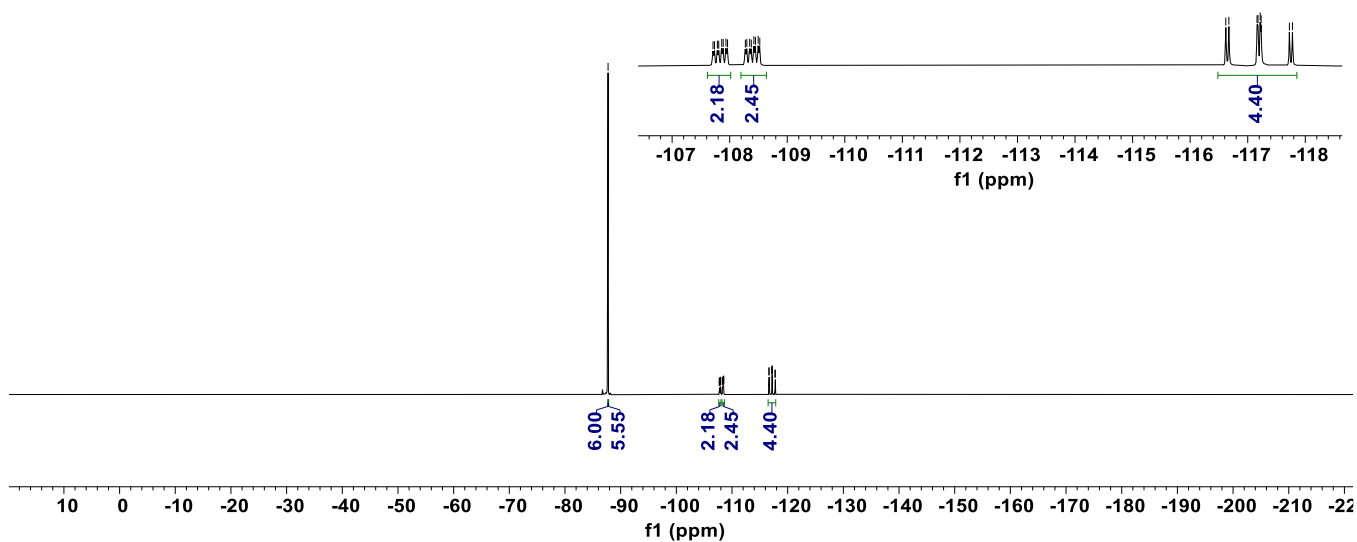


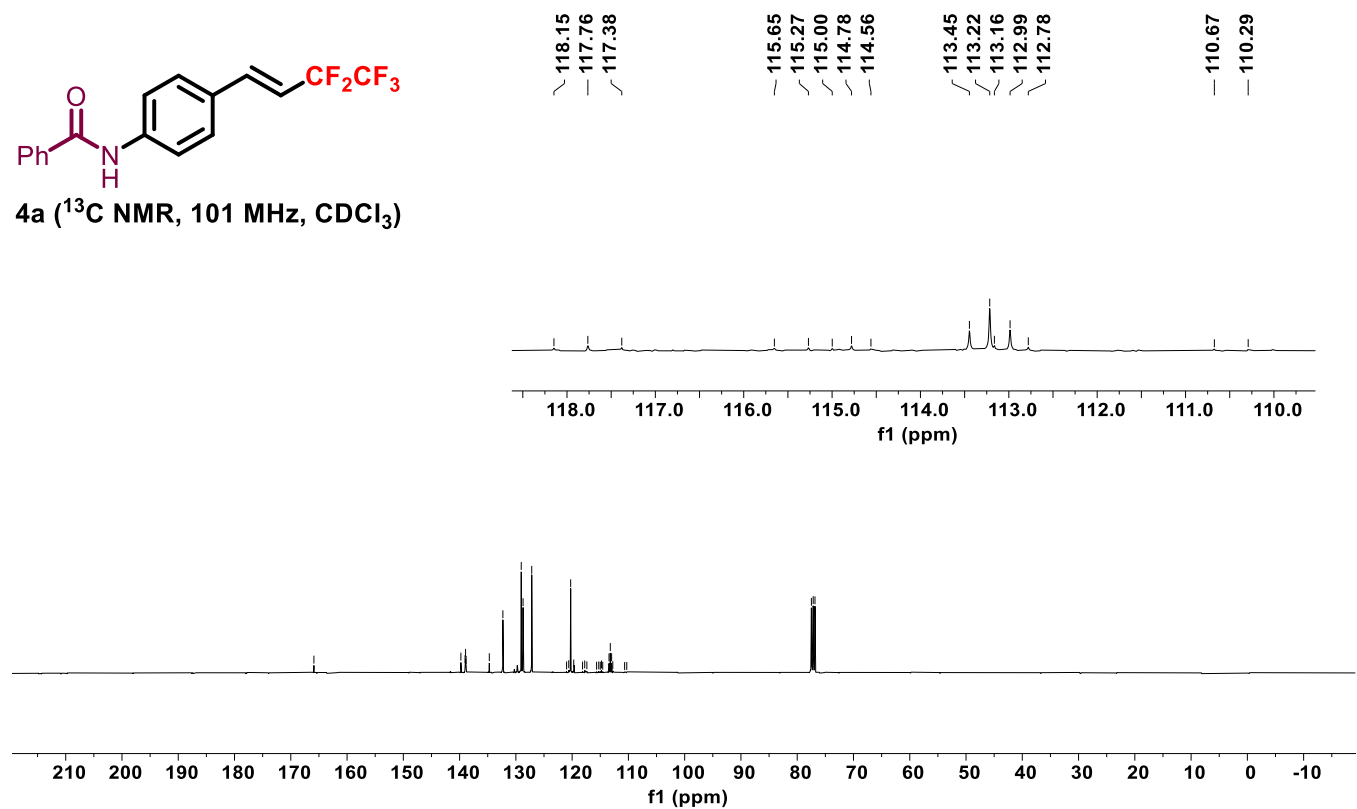
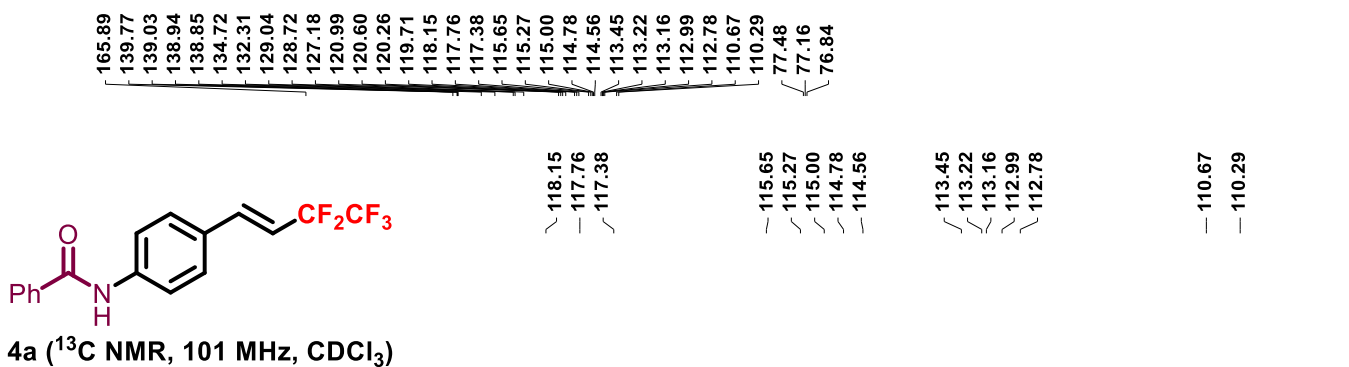
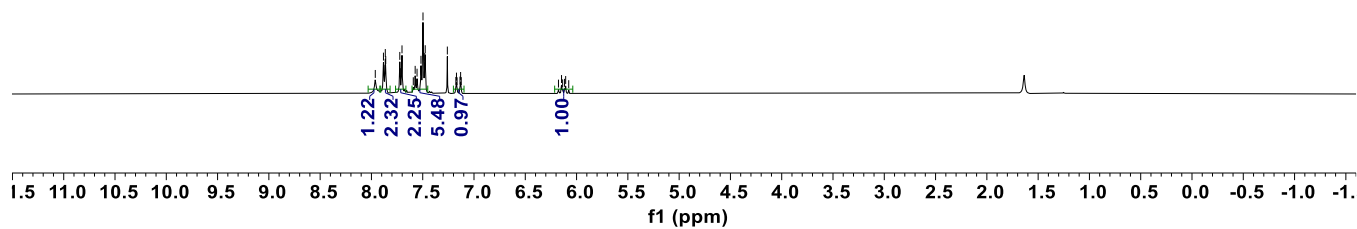
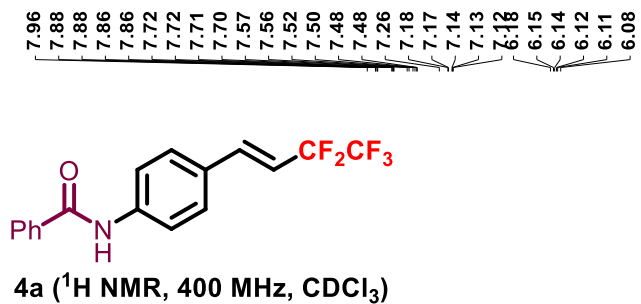
-87.74
-87.77
-107.71
-107.74
-107.79
-107.81
-107.86
-107.89
-107.94
-107.96
-108.27
-108.30
-108.35
-108.38
-108.42
-108.45
-108.49
-108.52
-116.62
-116.67
-117.16
-117.18
-117.22
-117.23
-117.72
-117.78

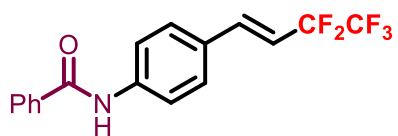


3g (^{19}F NMR, 471 MHz, CDCl_3)

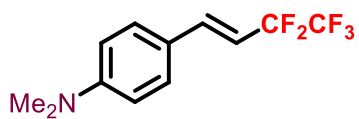
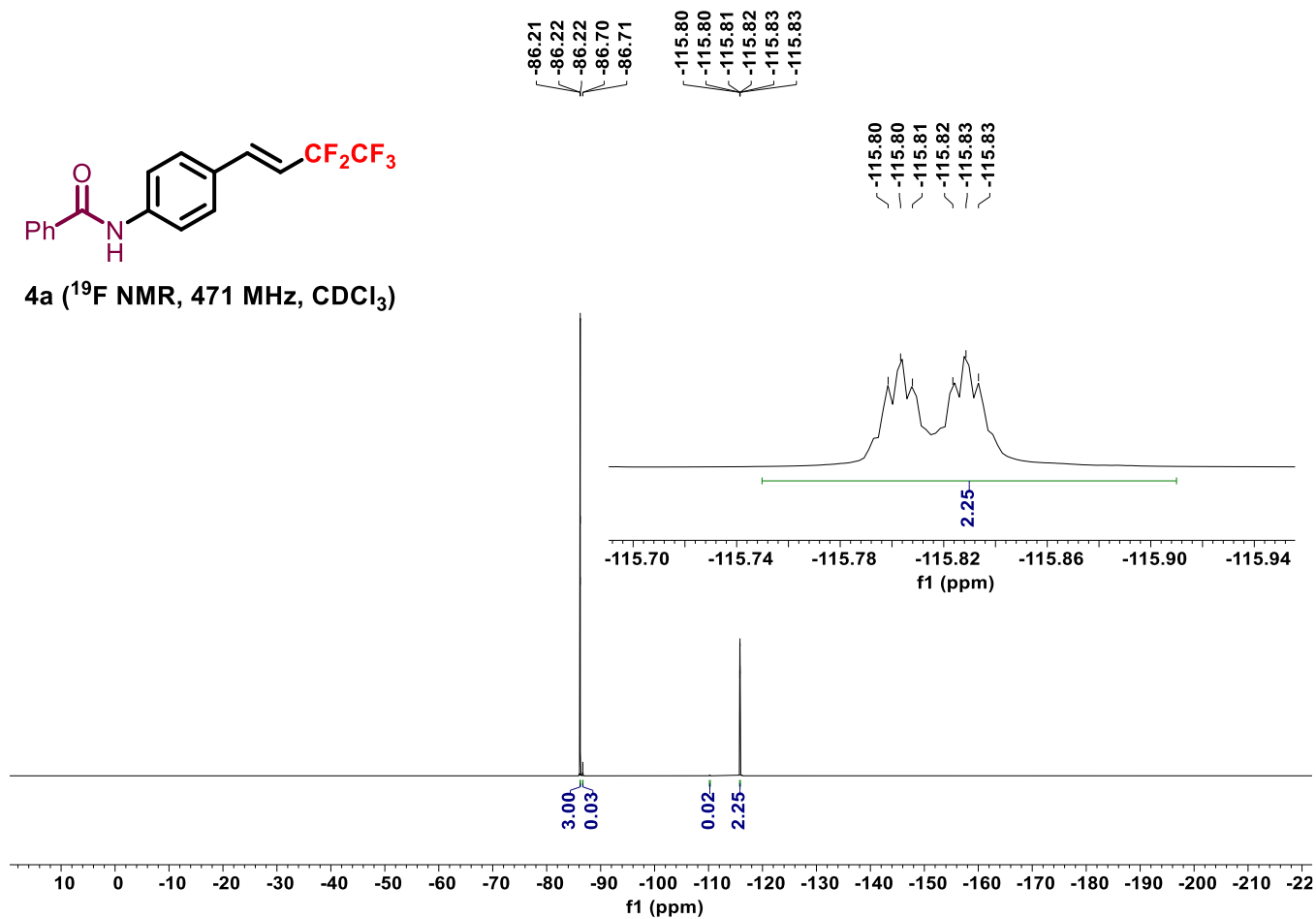
-107.71
-107.74
-107.79
-107.81
-107.86
-107.89
-107.94
-107.96
-108.27
-108.30
-108.35
-108.38
-108.42
-108.45
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-117.16
-117.18
-117.22
-117.23
-117.72
-117.78



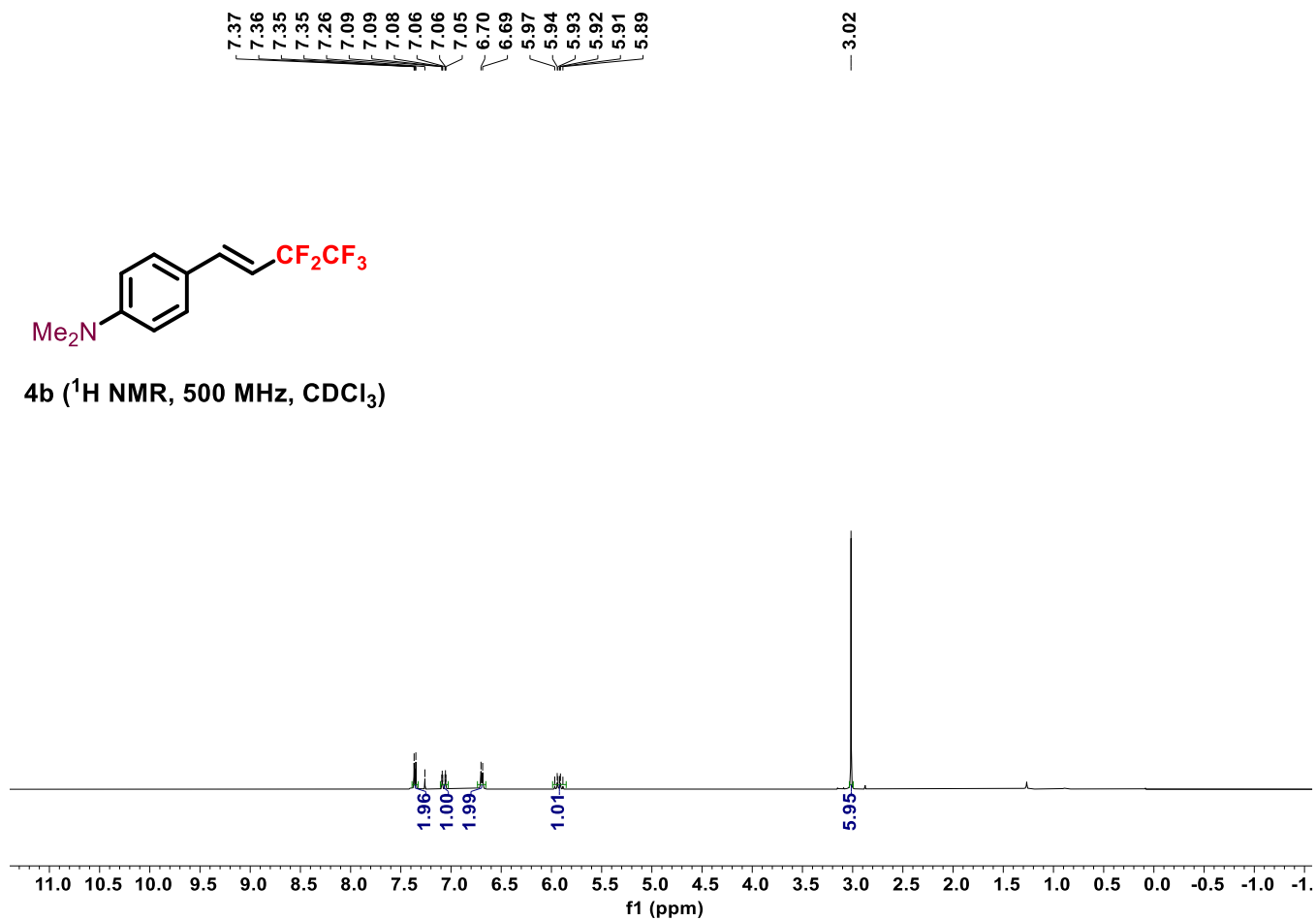


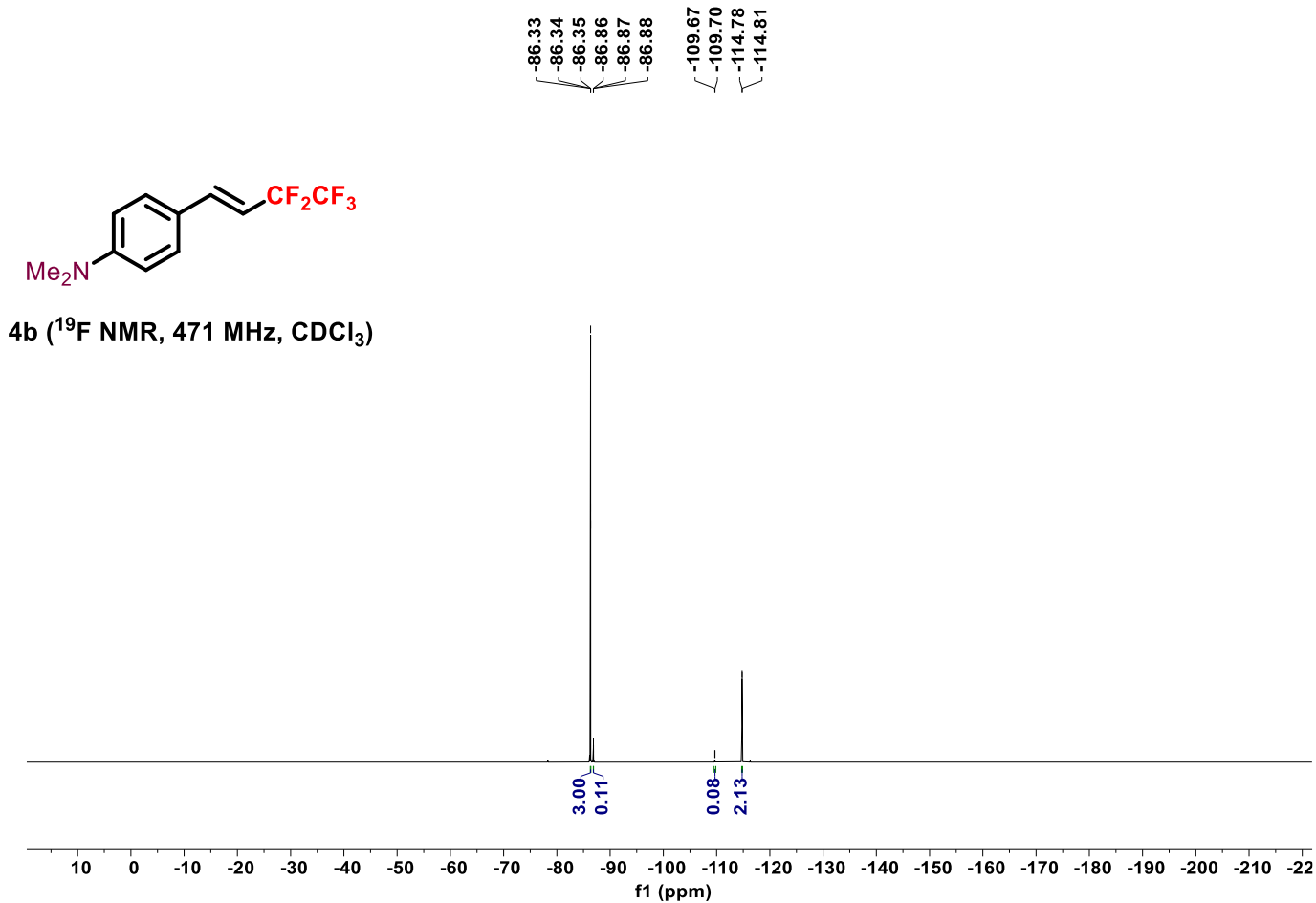
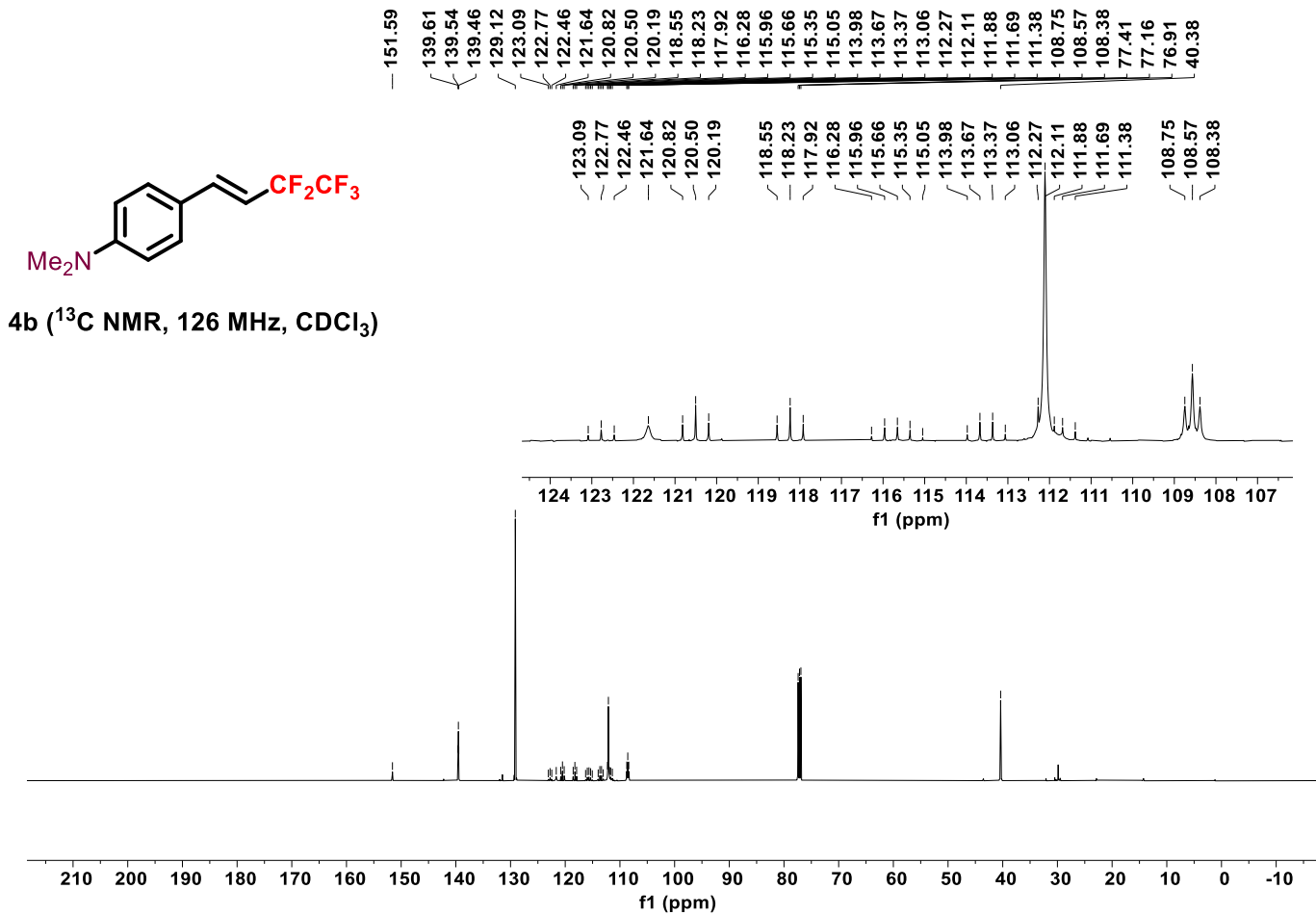


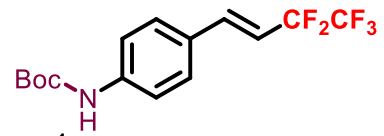
4a (^{19}F NMR, 471 MHz, CDCl_3)



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



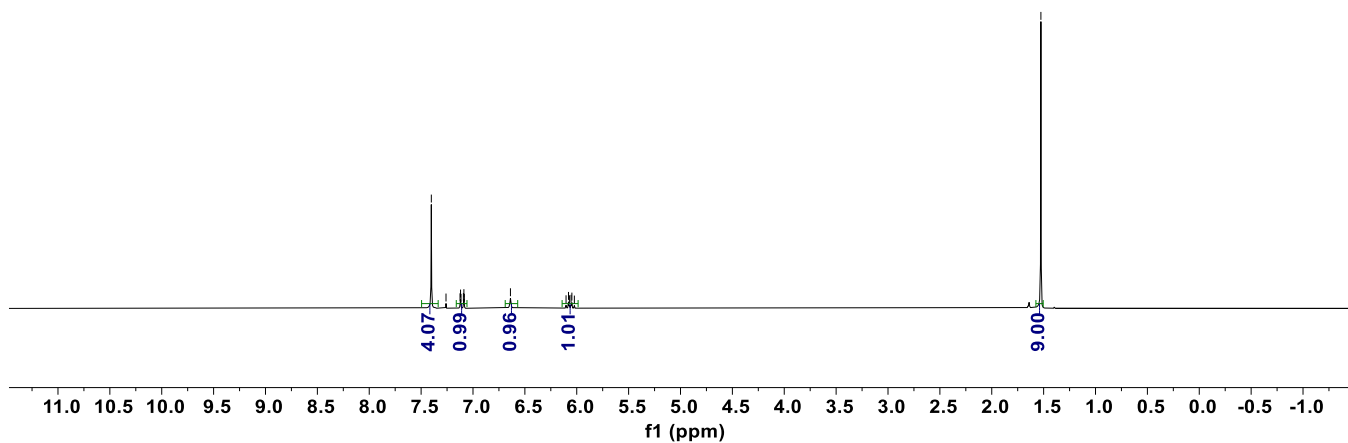
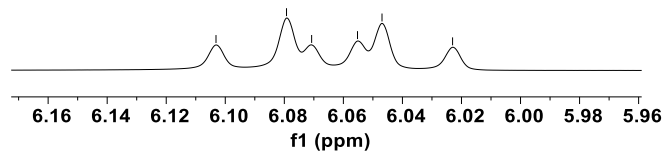




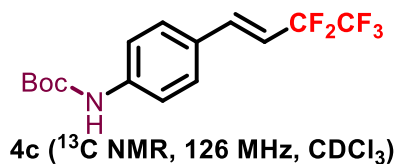
7.40
7.26
7.12
7.12
7.09
7.09
7.08
6.64
6.10
6.08
6.07
6.06
6.05
6.02

6.10
6.08
6.07
6.06
6.05
6.02

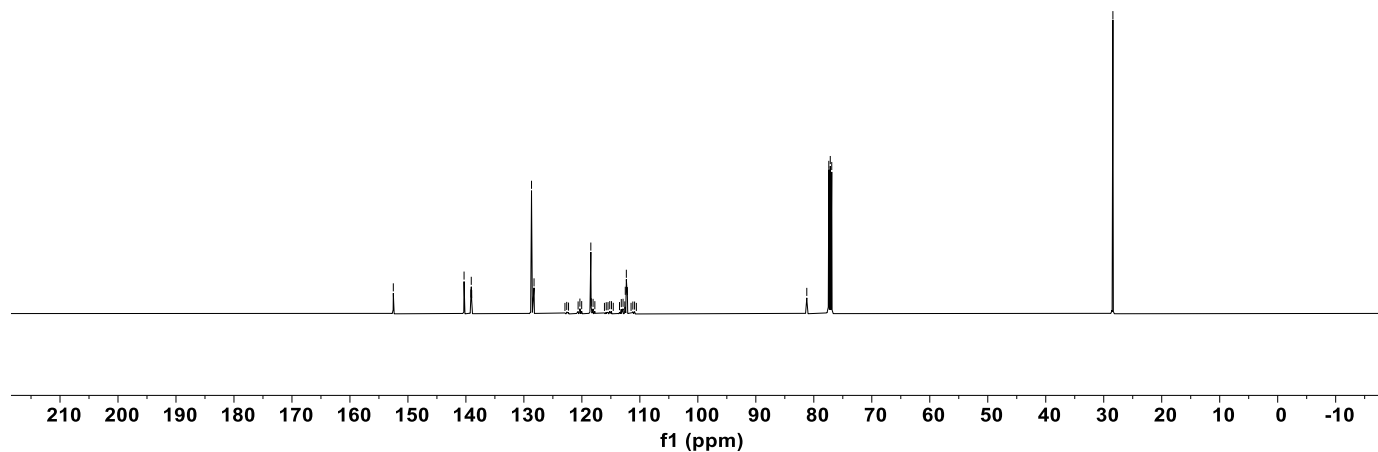
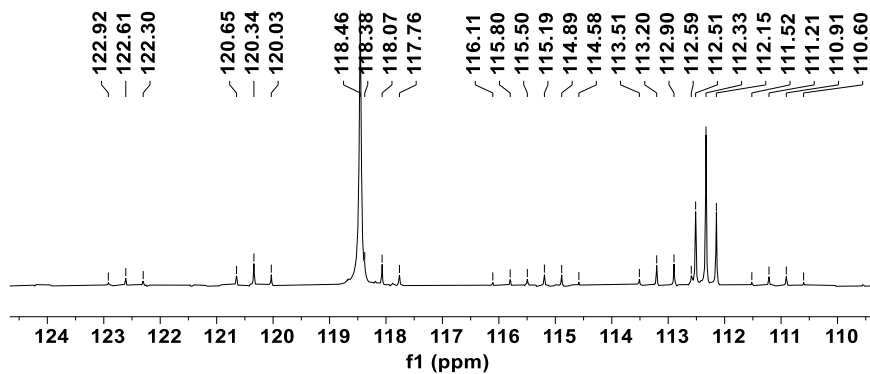
1.53

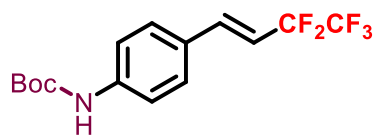


152.52
140.32
139.15
139.08
139.00
128.68
128.25
122.92
122.61
122.30
120.65
120.34
120.03
118.46
118.38
118.07
117.76
116.11
115.80
115.50
115.19
114.89
114.58
113.51
113.20
112.90
112.59
112.51
112.33
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111.52
111.21
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76.91
28.42

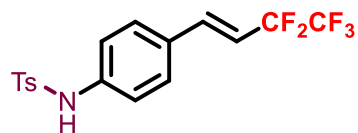
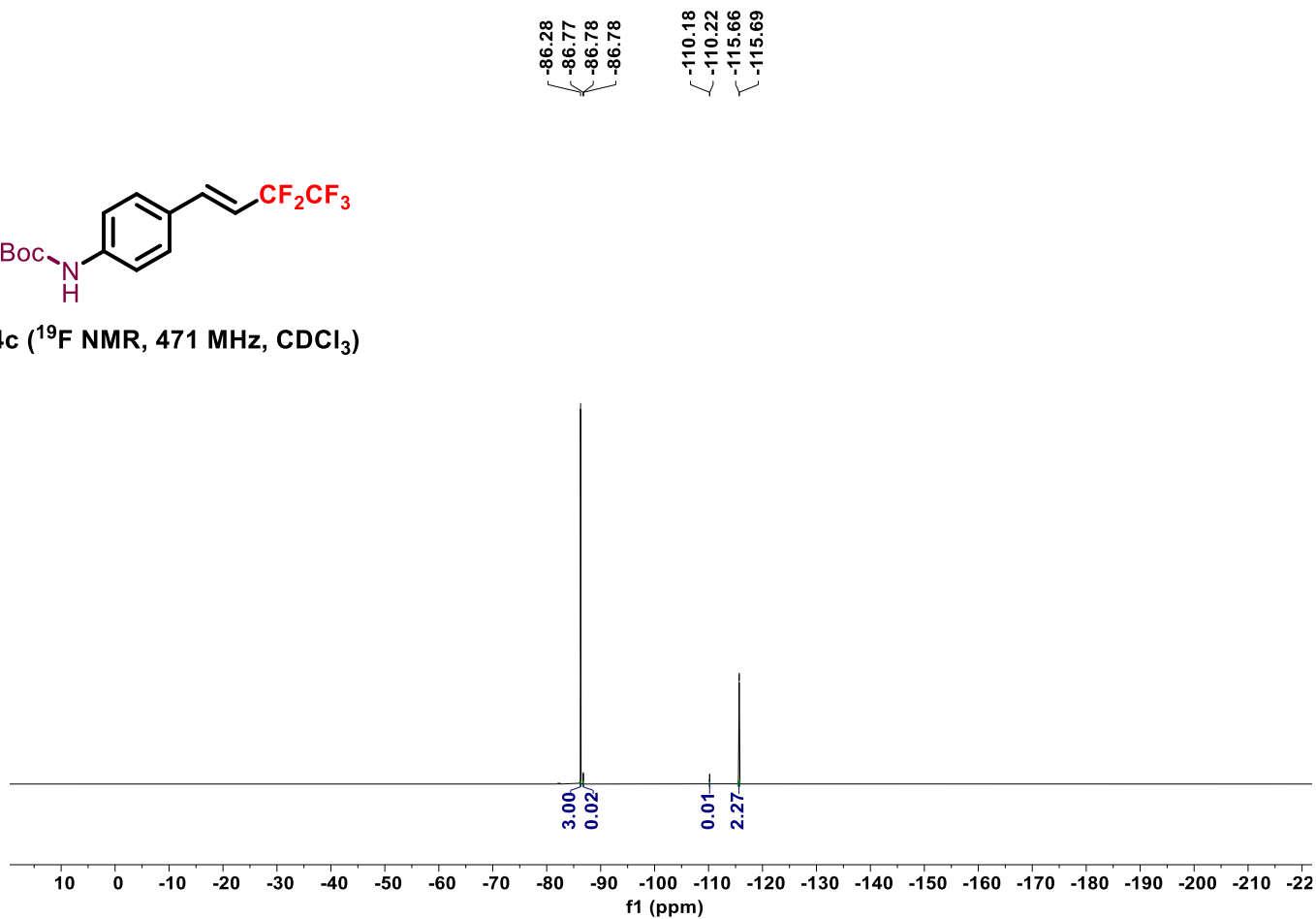


122.92
122.61
122.30
120.65
120.34
120.03
118.46
118.38
118.07
117.76
116.11
115.80
115.50
115.19
114.89
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110.91
110.60

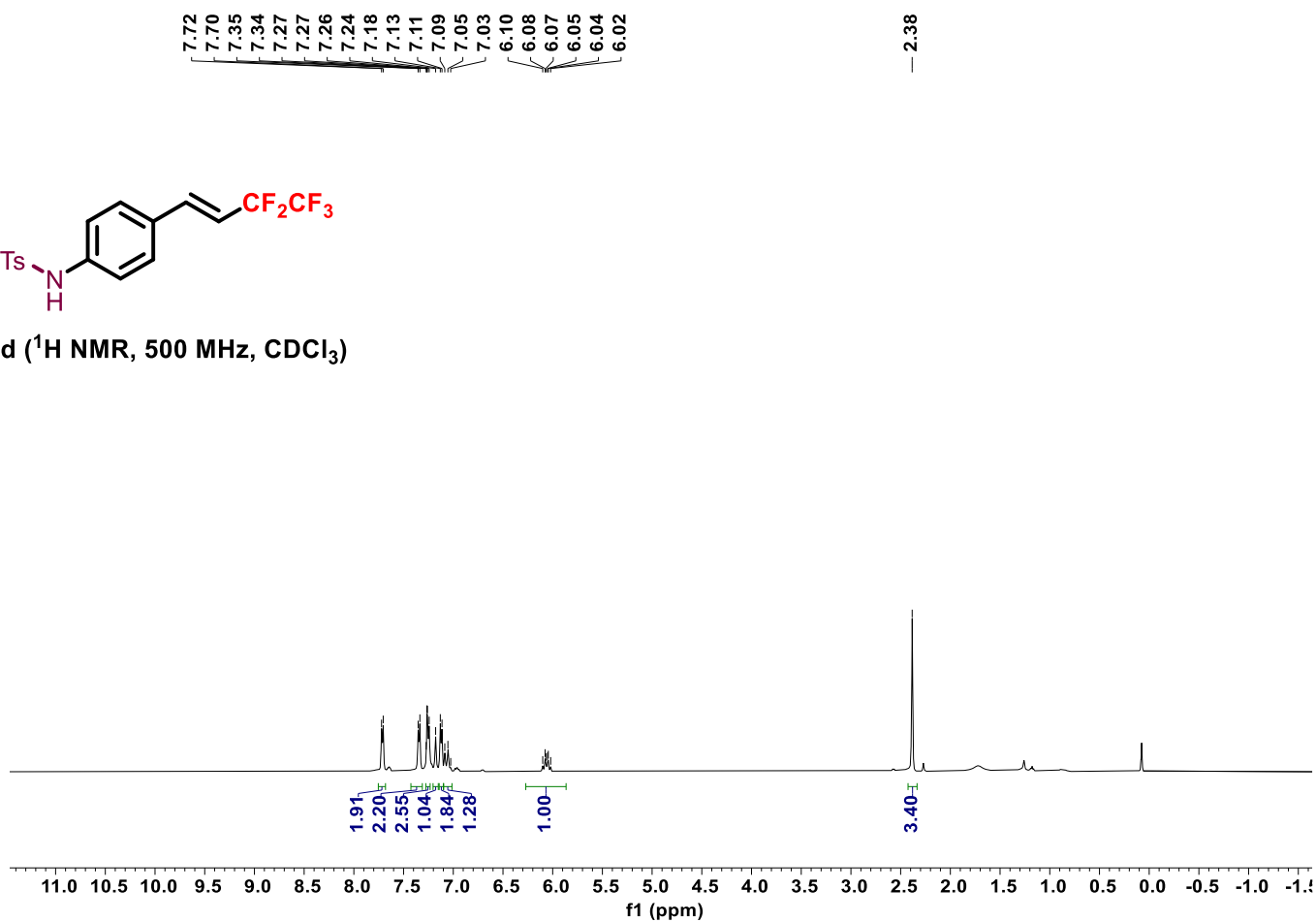


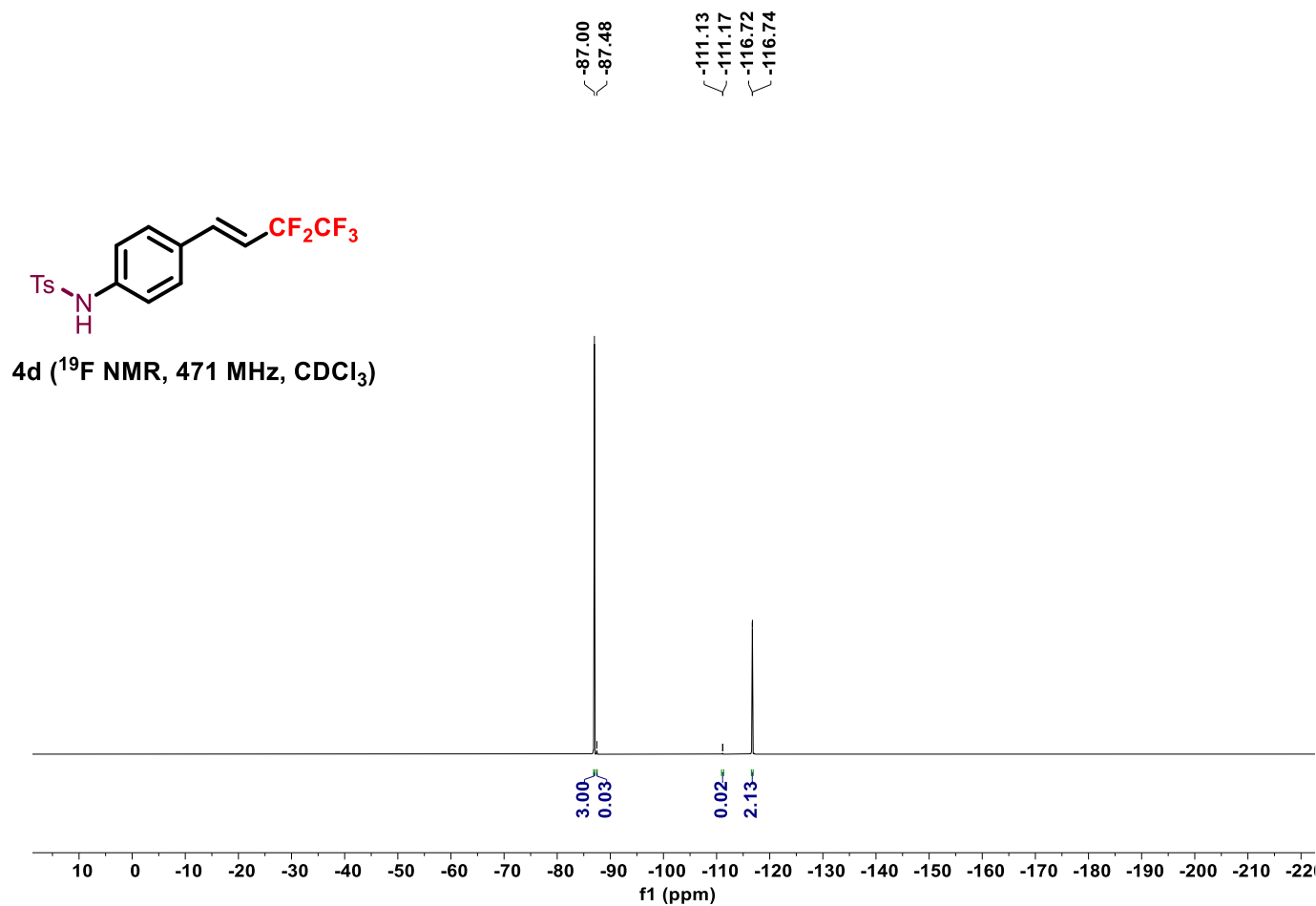
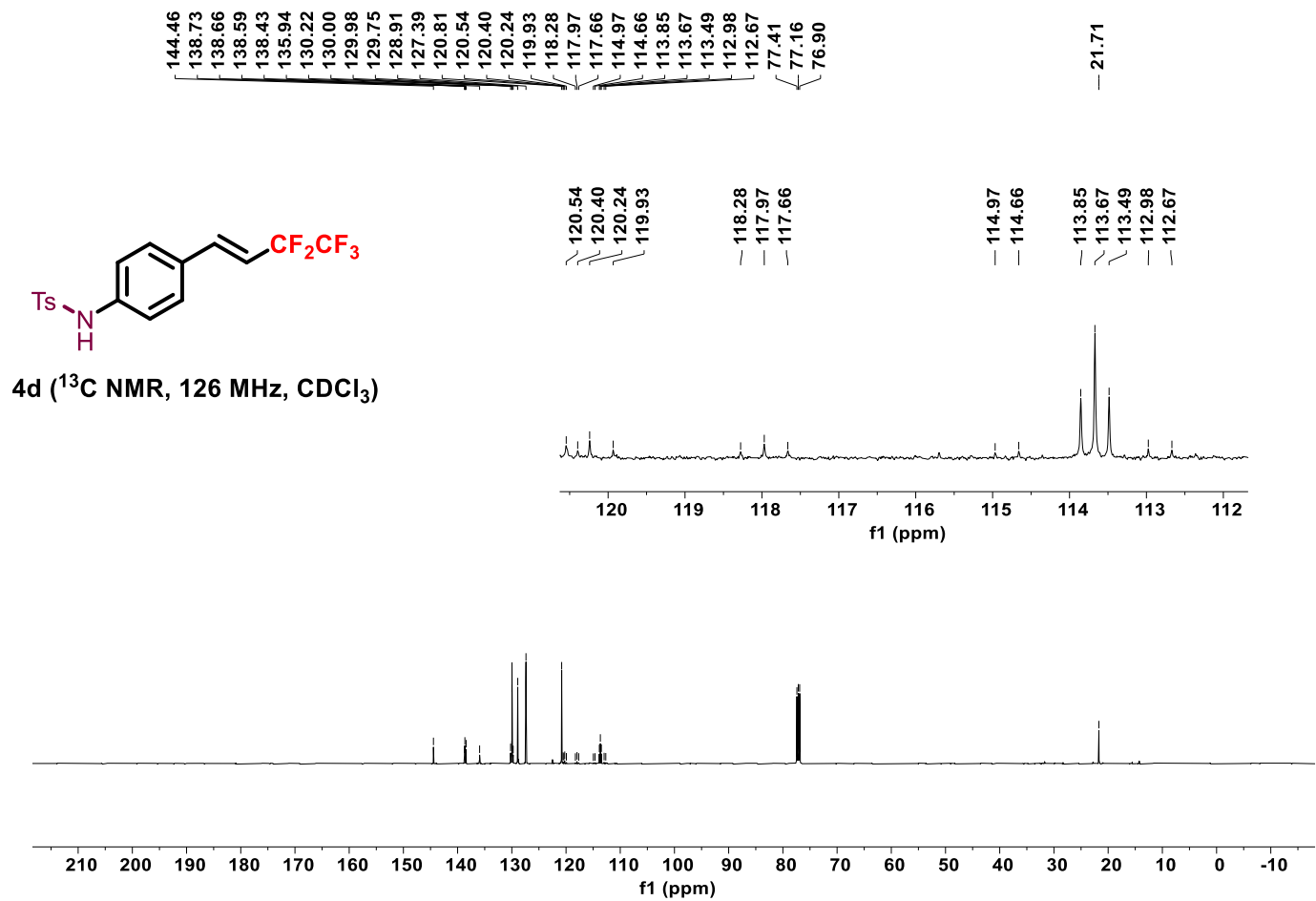


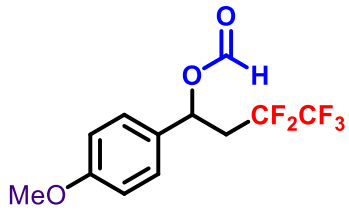
4c (^{19}F NMR, 471 MHz, CDCl_3)



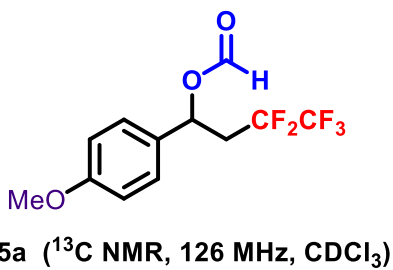
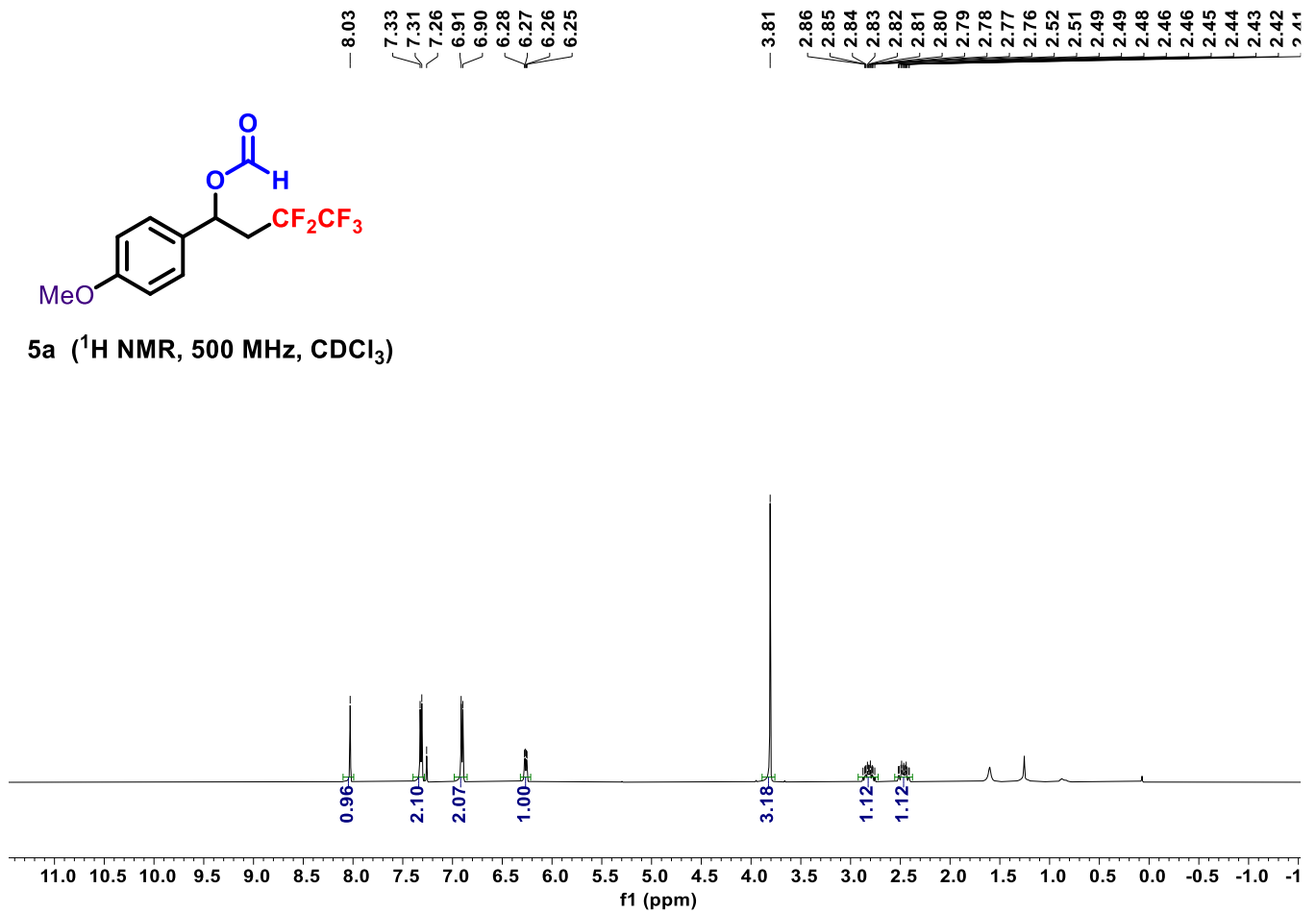
4d (^1H NMR, 500 MHz, CDCl_3)



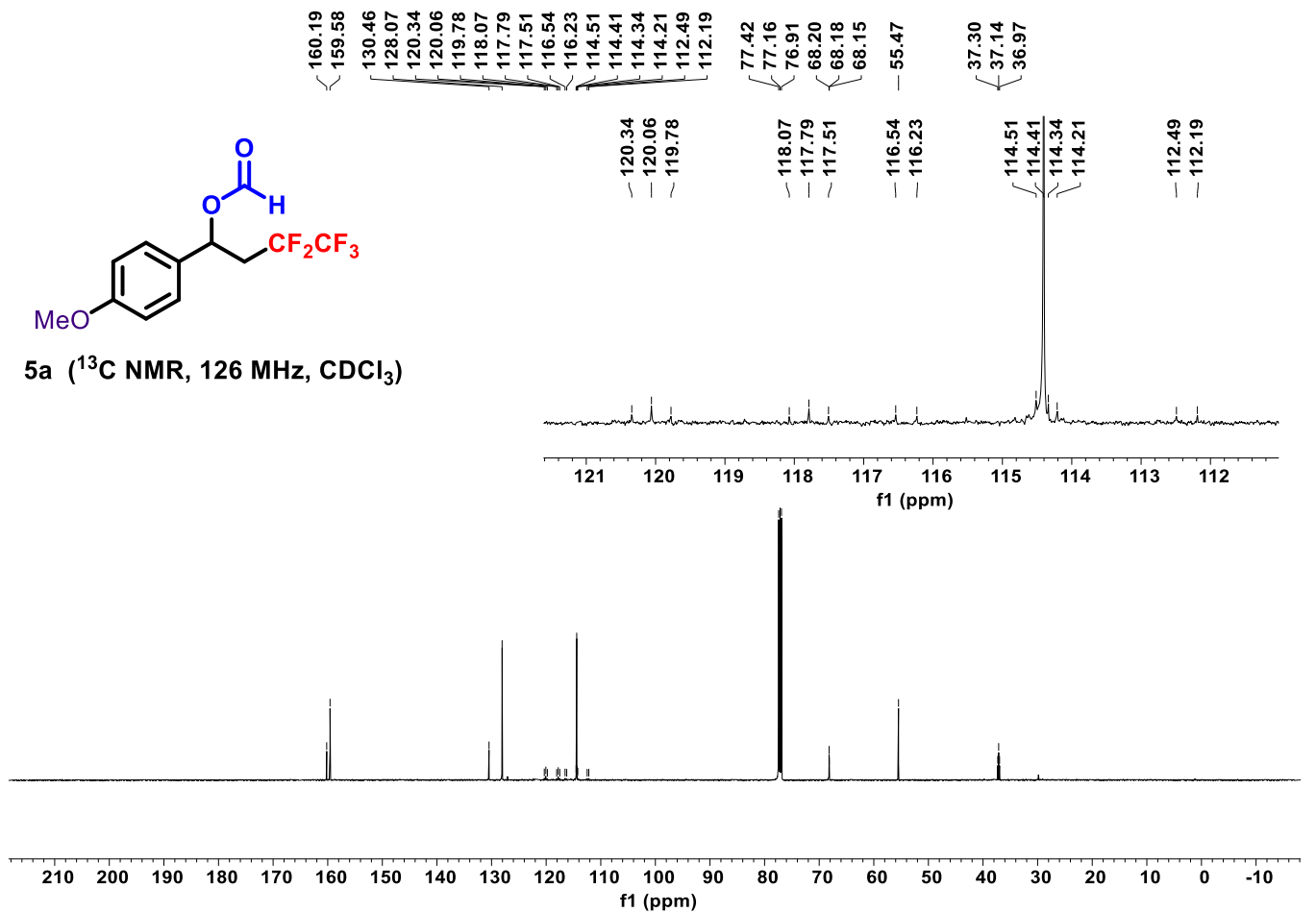


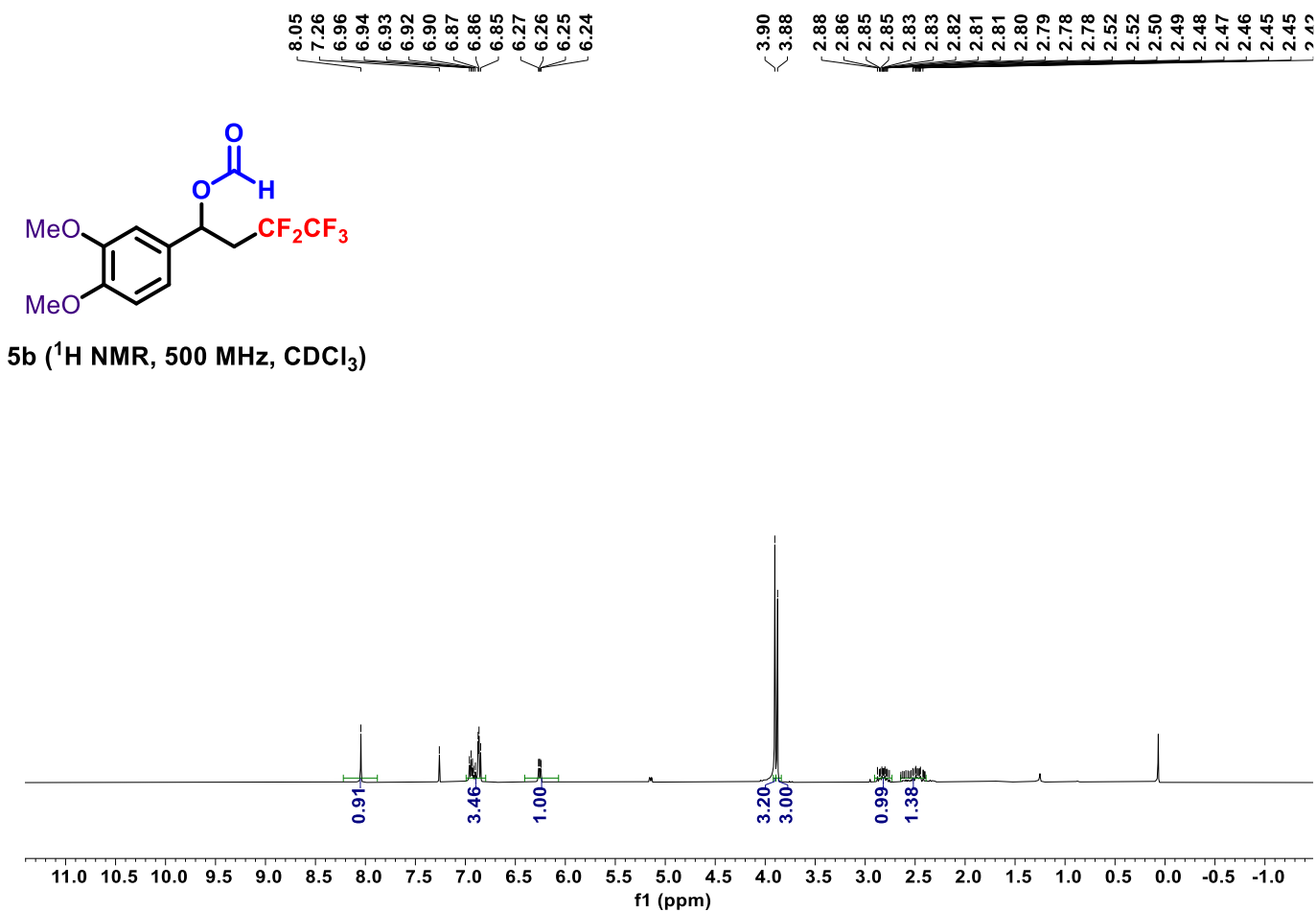
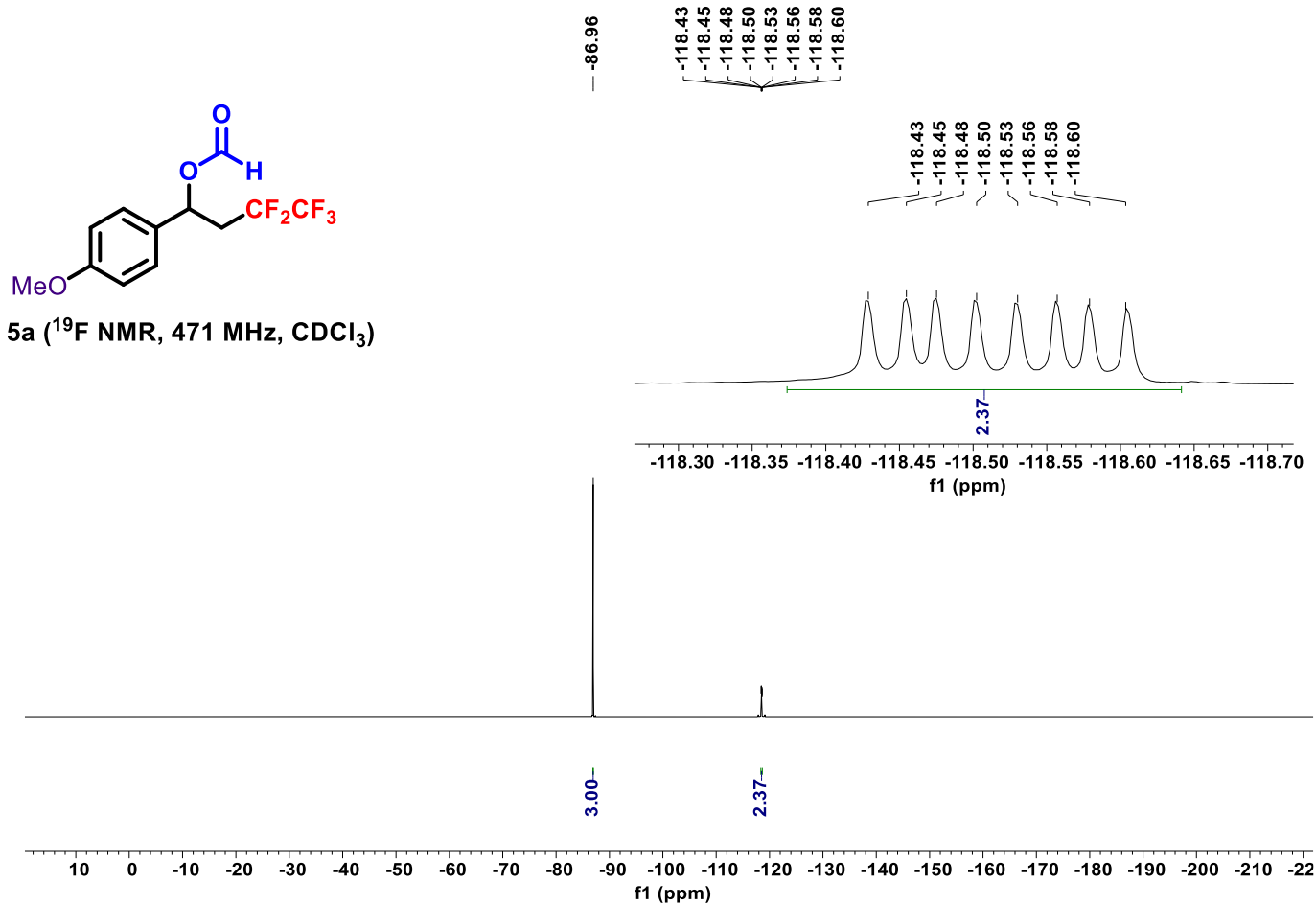


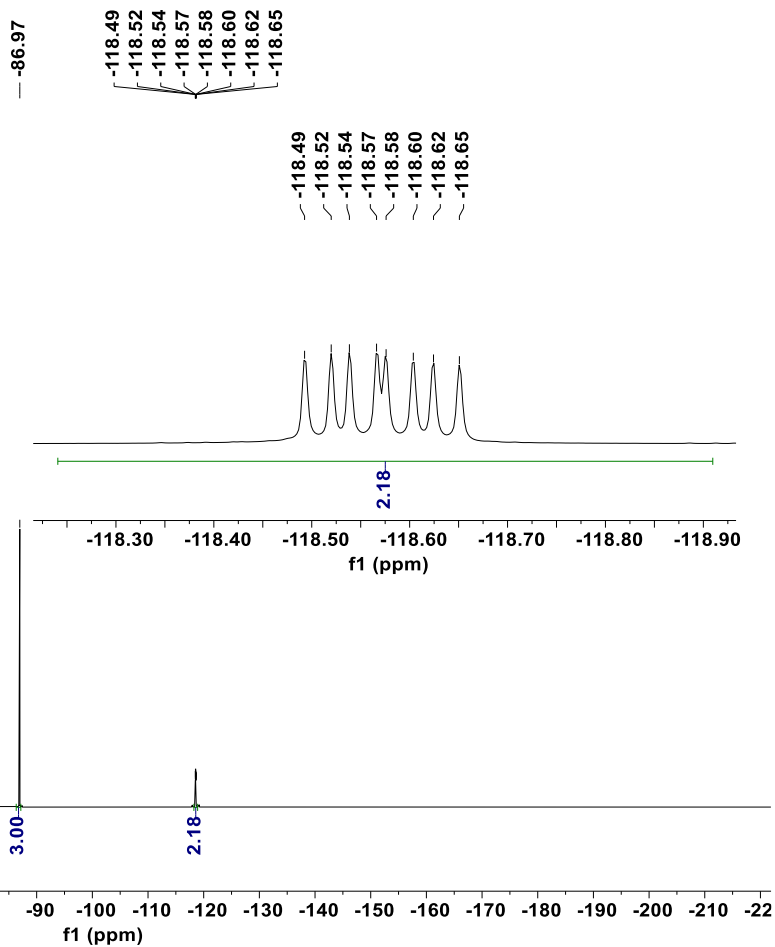
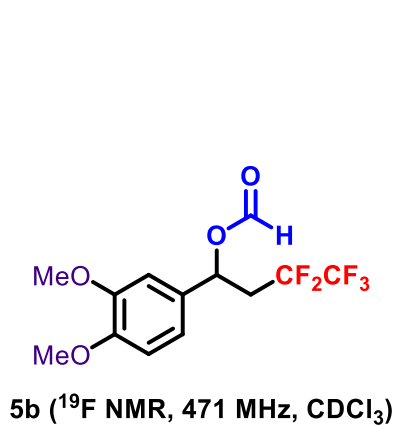
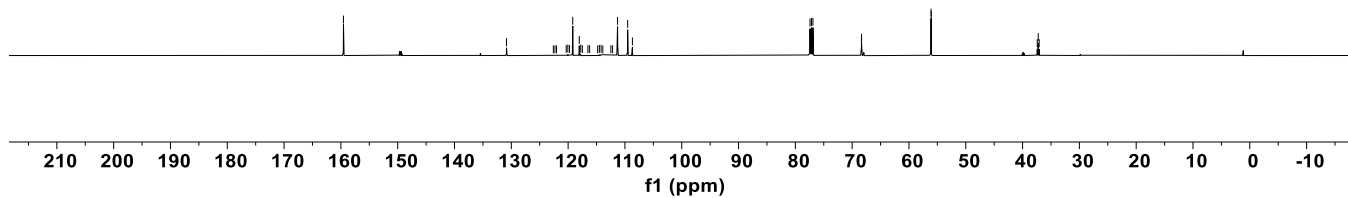
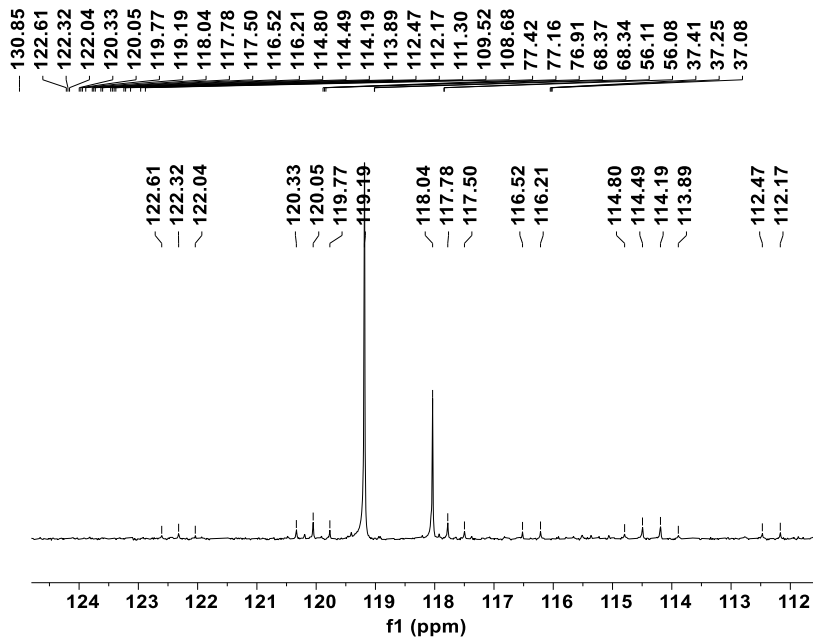
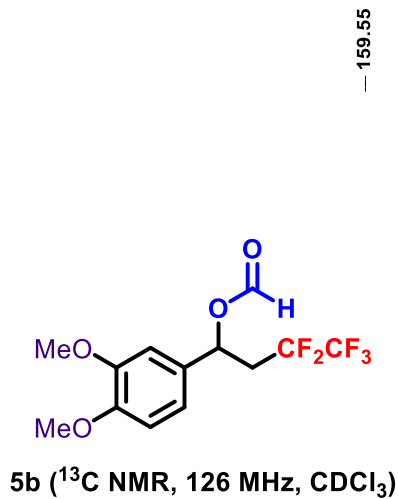
5a (^1H NMR, 500 MHz, CDCl_3)

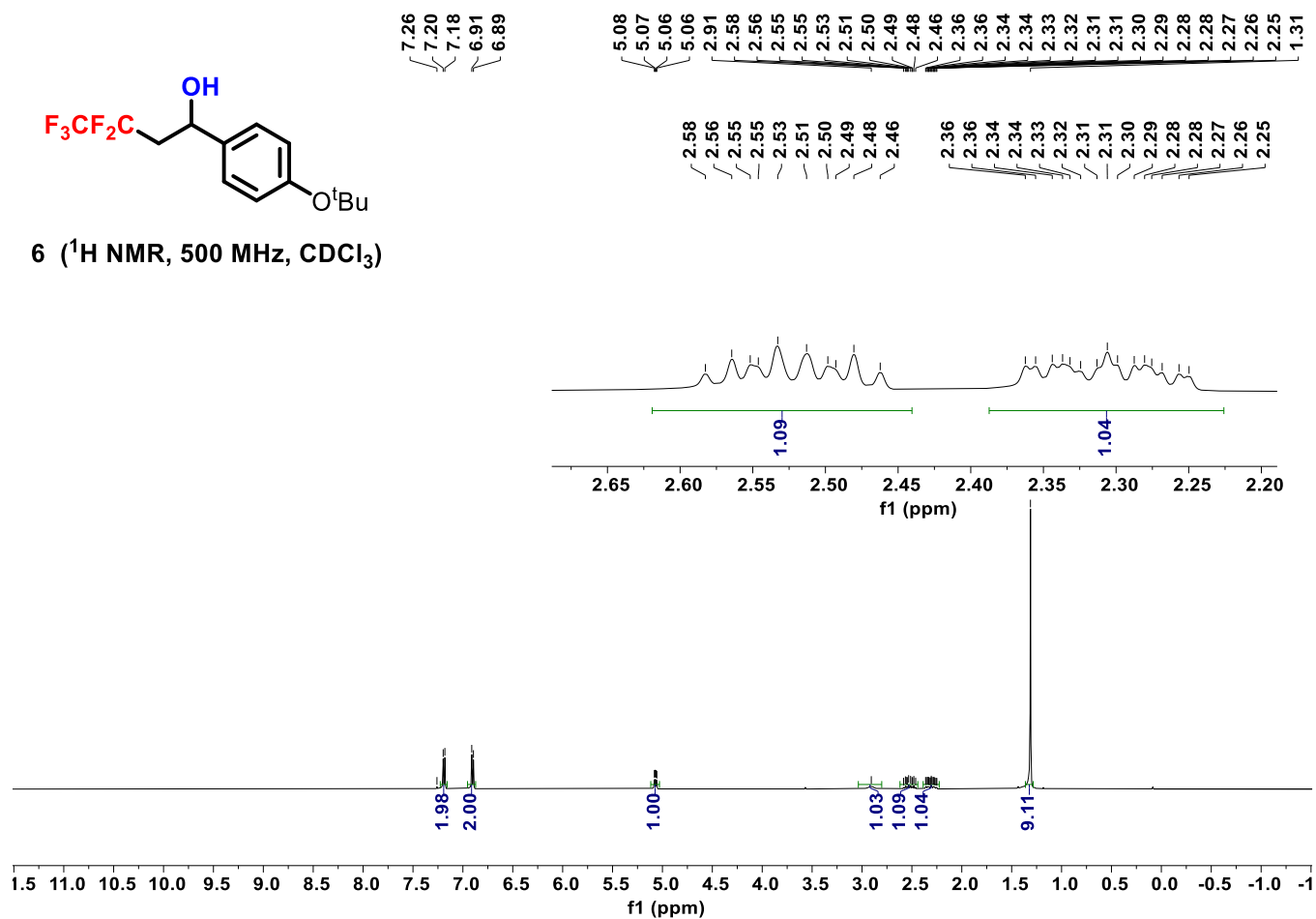
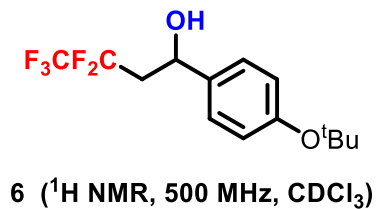
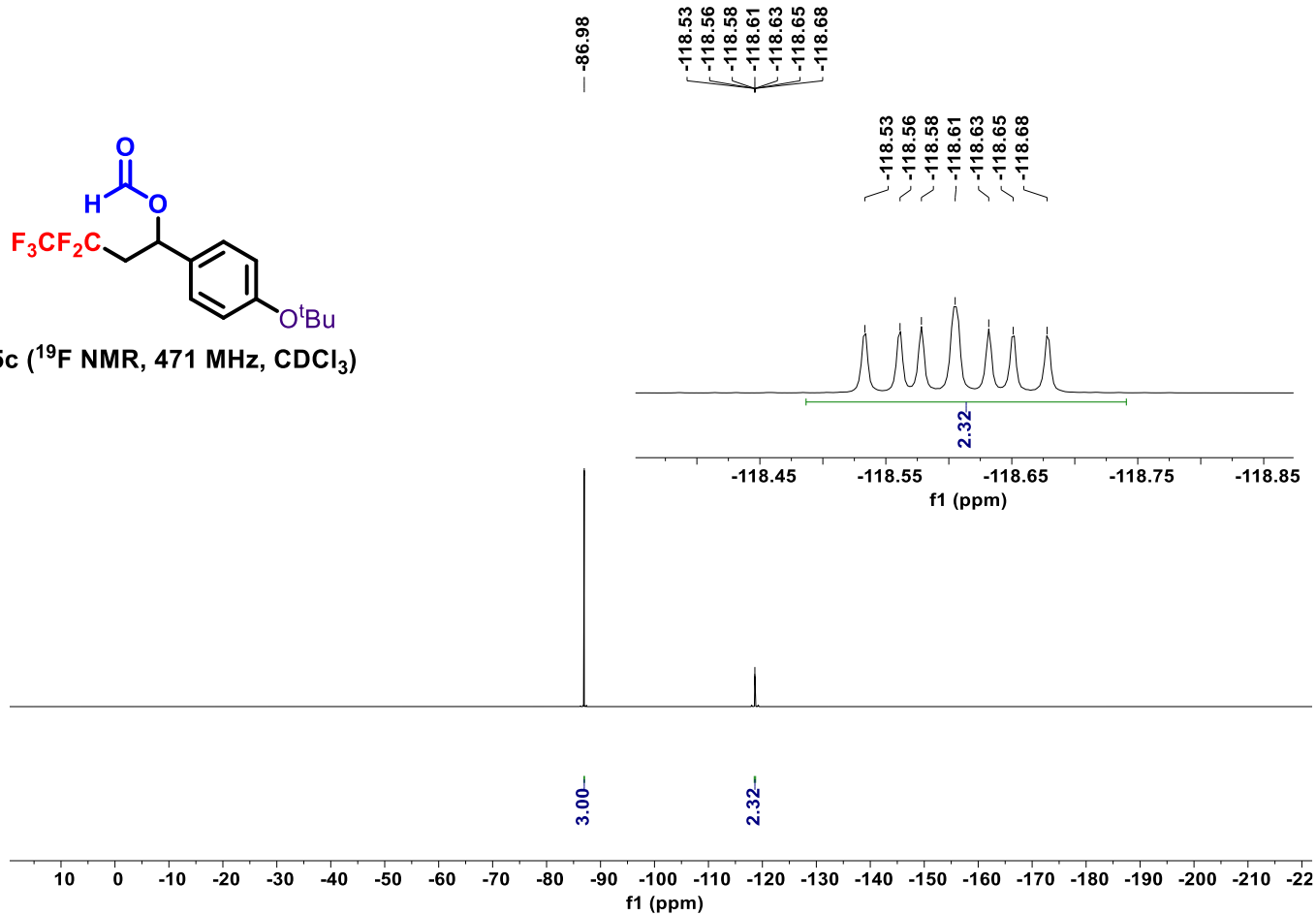
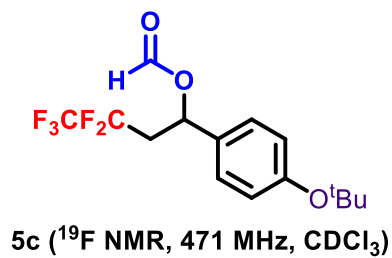


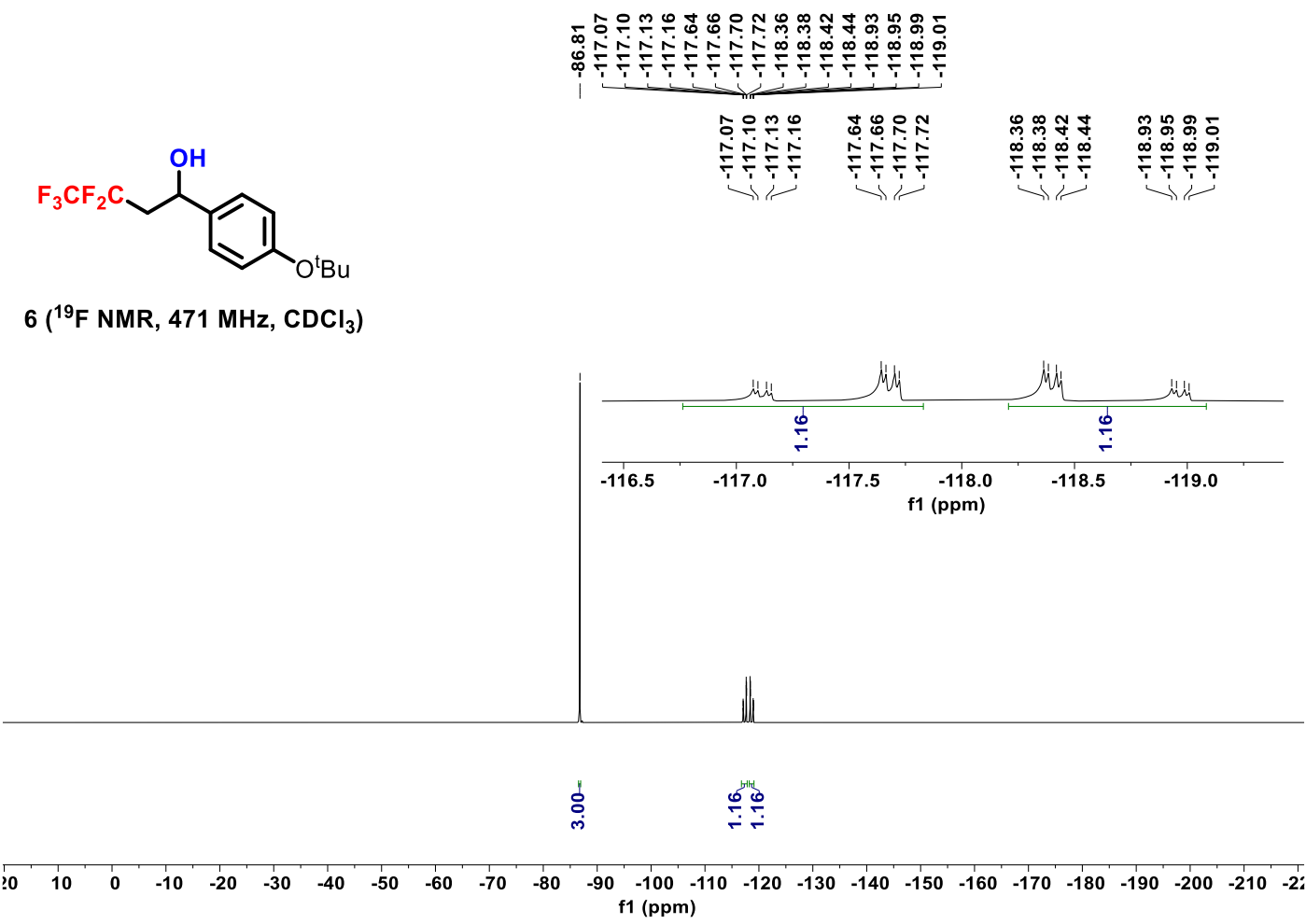
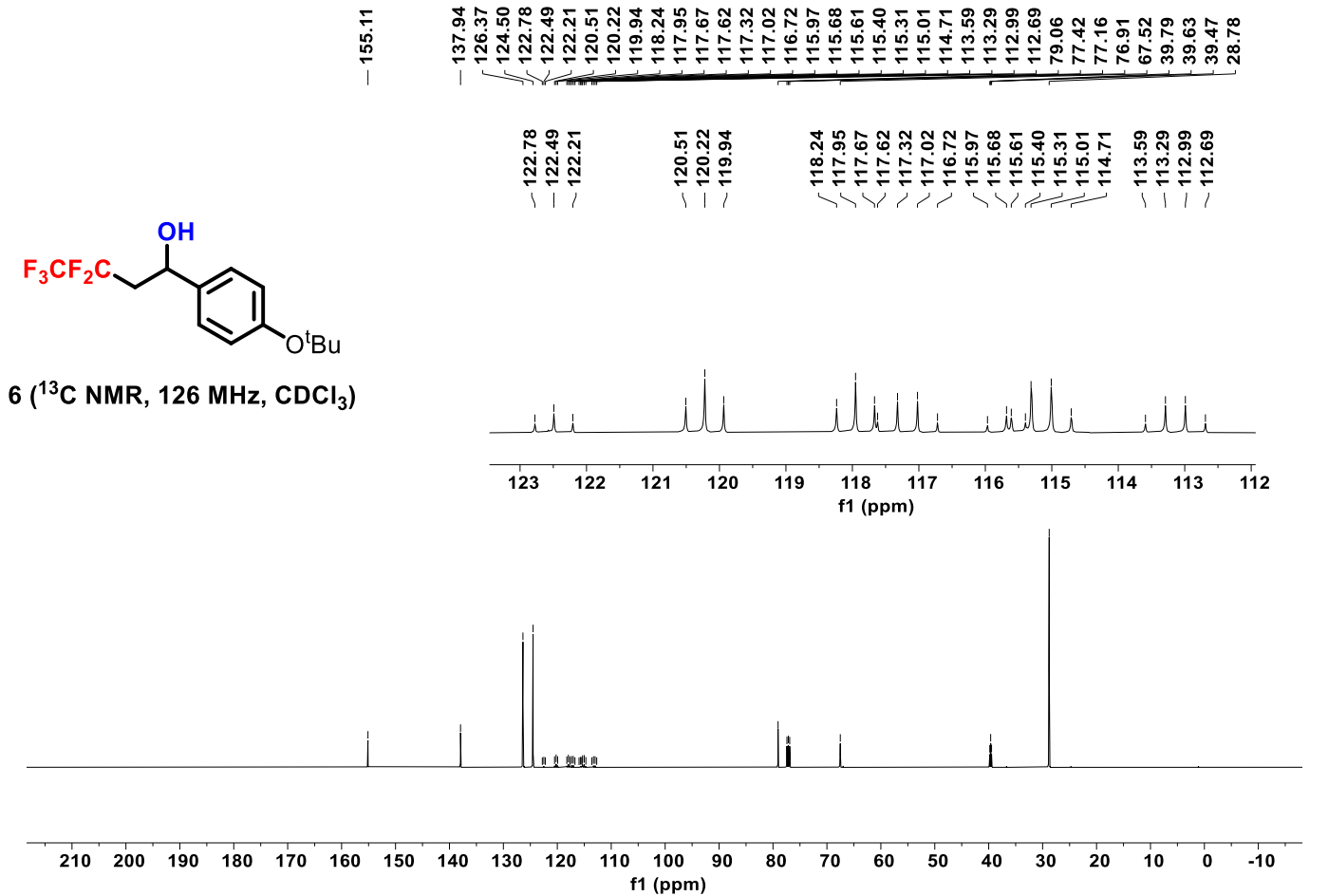
5a (^{13}C NMR, 126 MHz, CDCl_3)

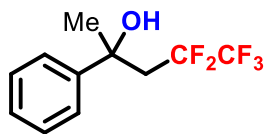




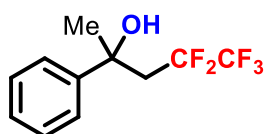
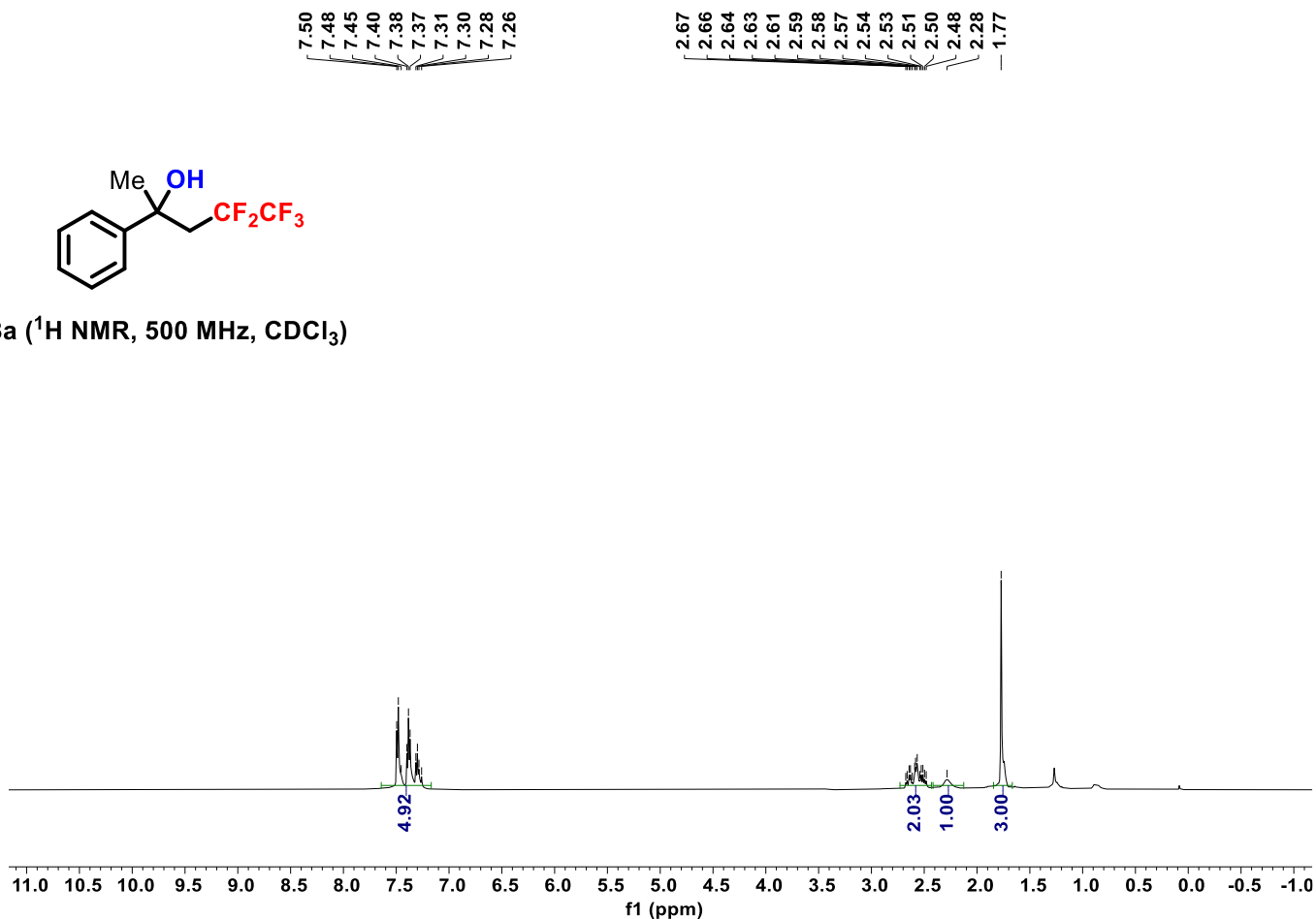




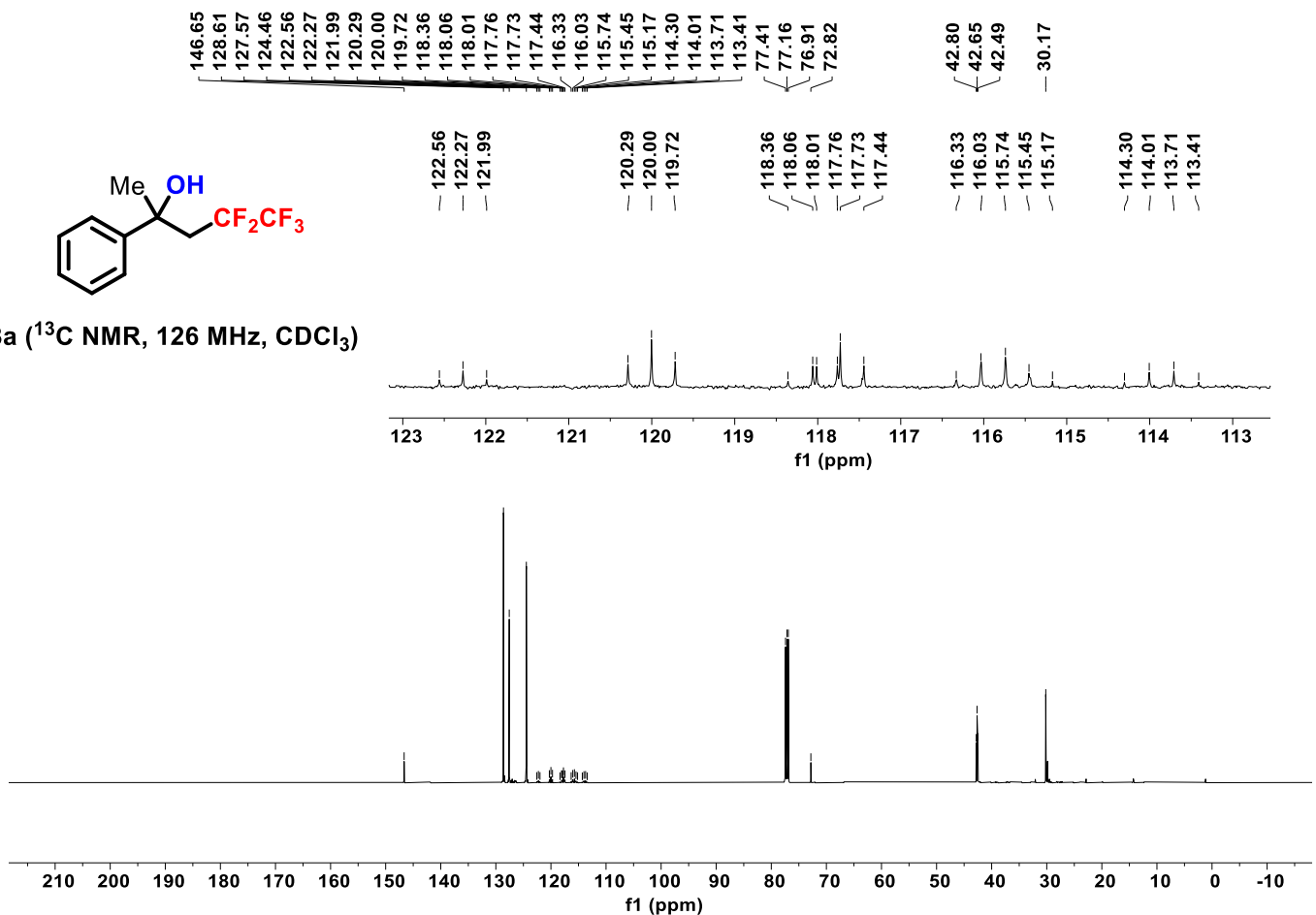


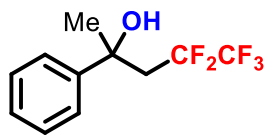


8a (¹H NMR, 500 MHz, CDCl₃)

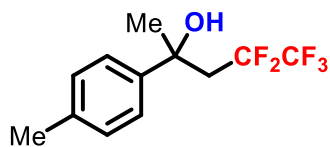
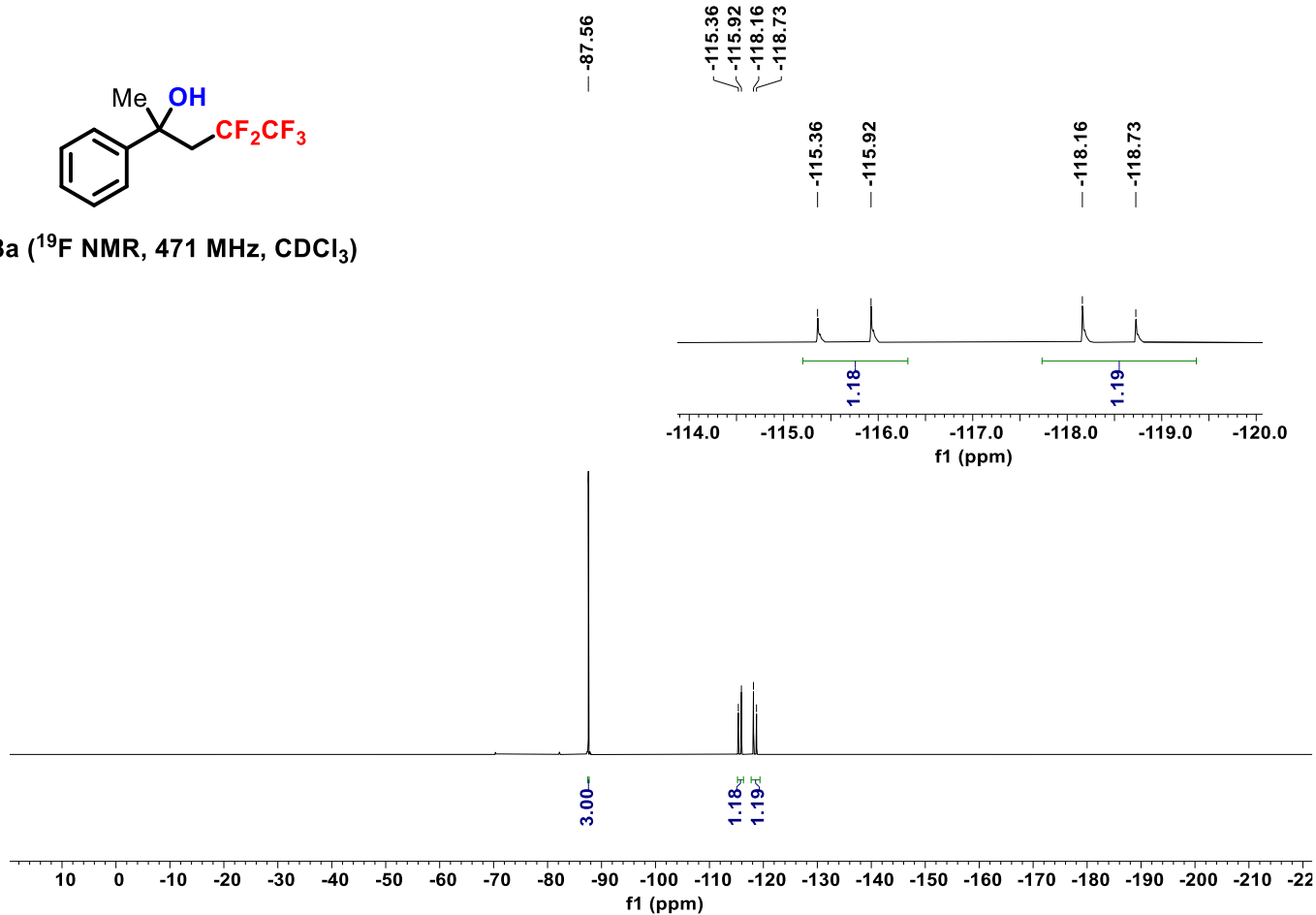


8a (¹³C NMR, 126 MHz, CDCl₃)

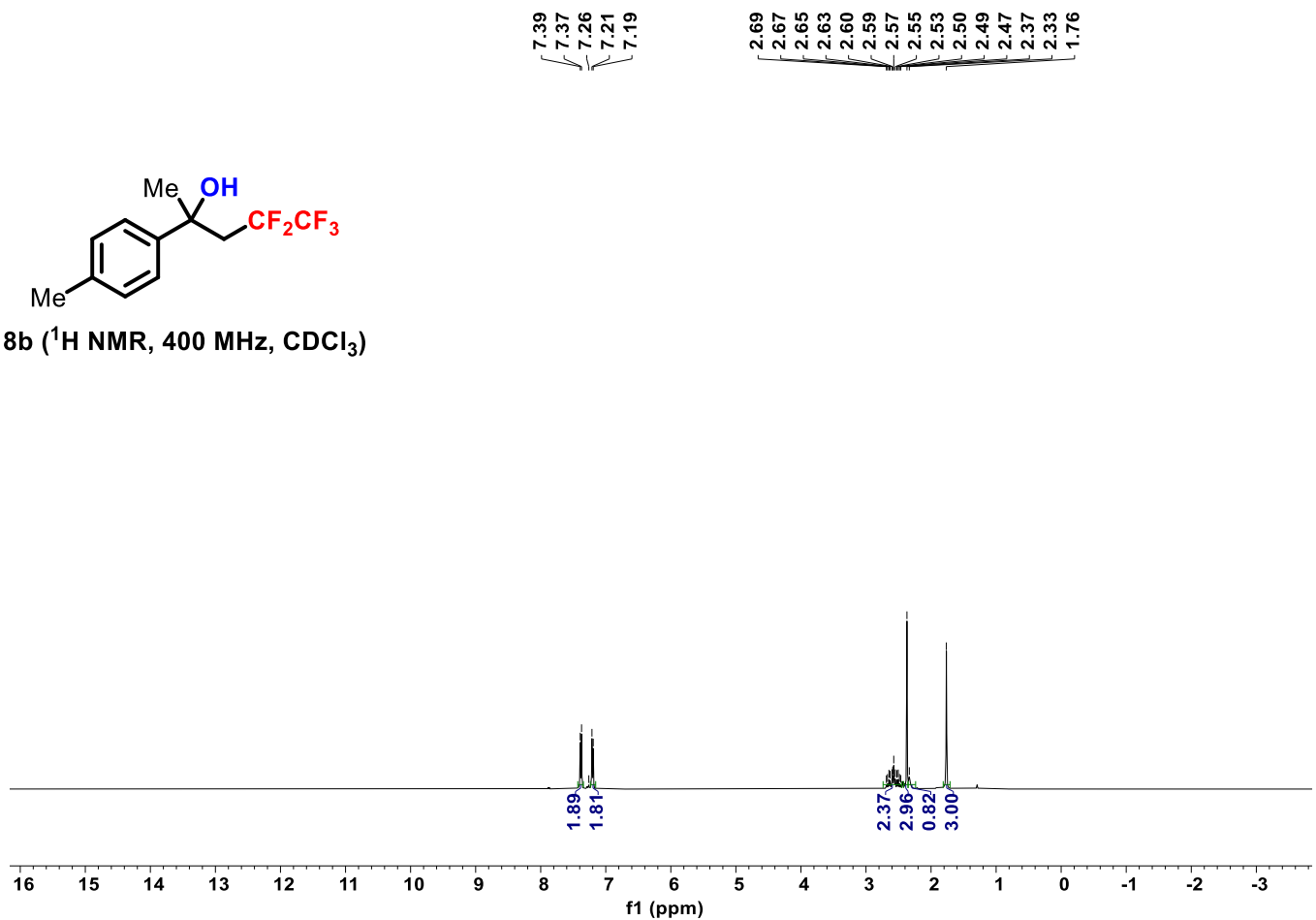


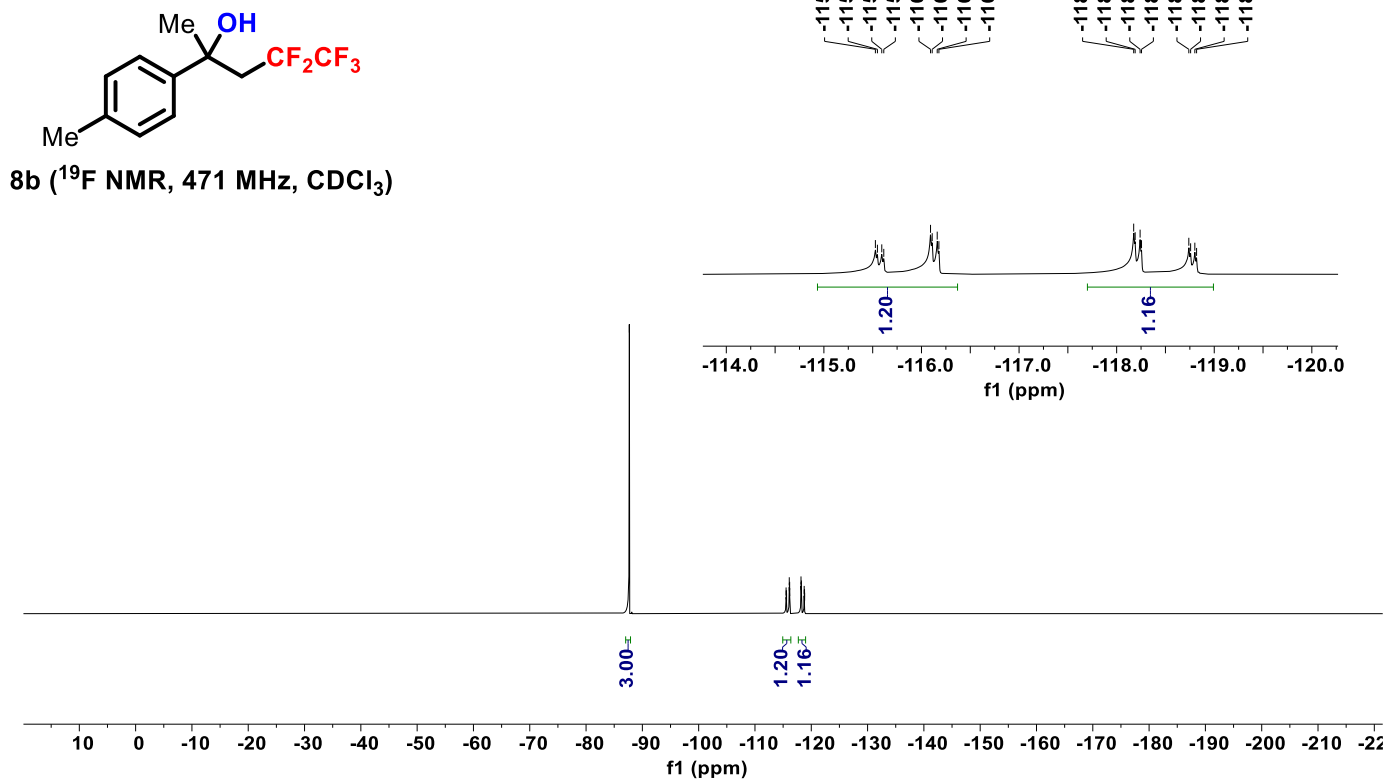
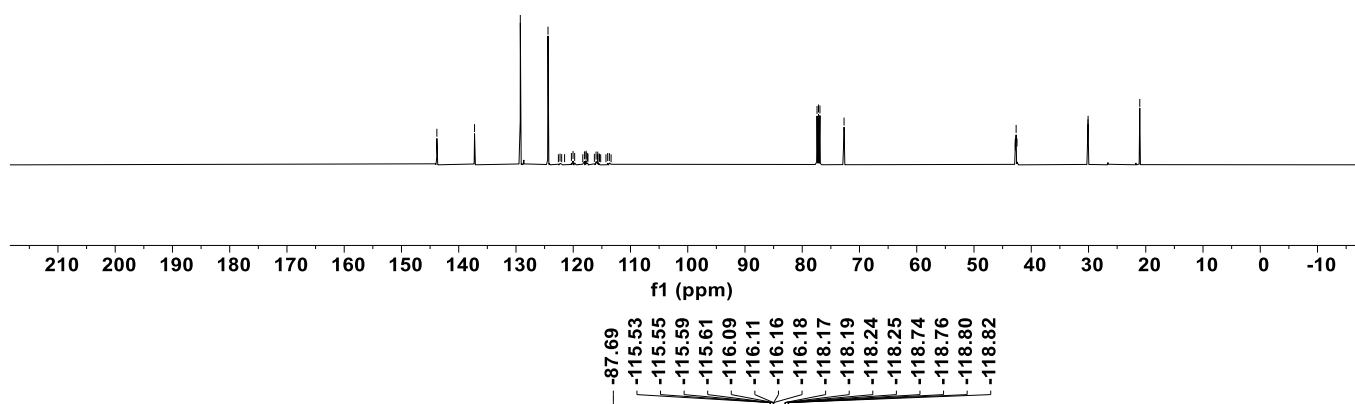
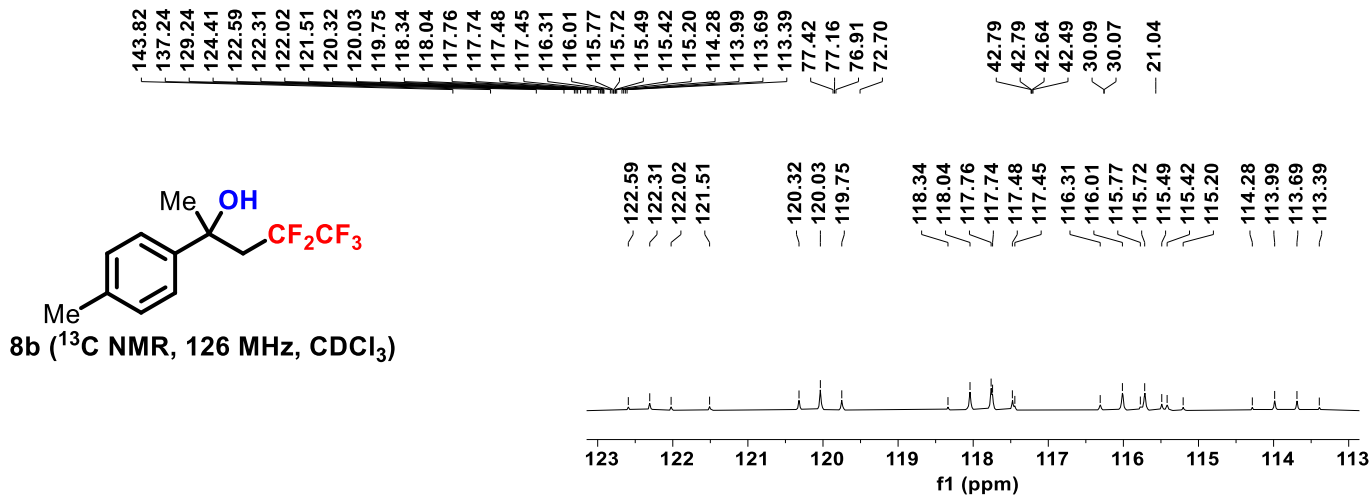


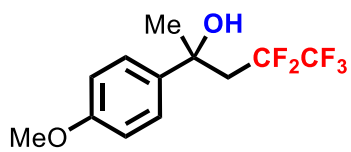
8a (¹⁹F NMR, 471 MHz, CDCl₃)



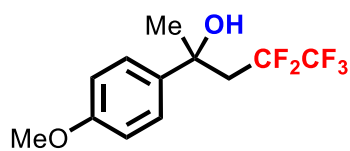
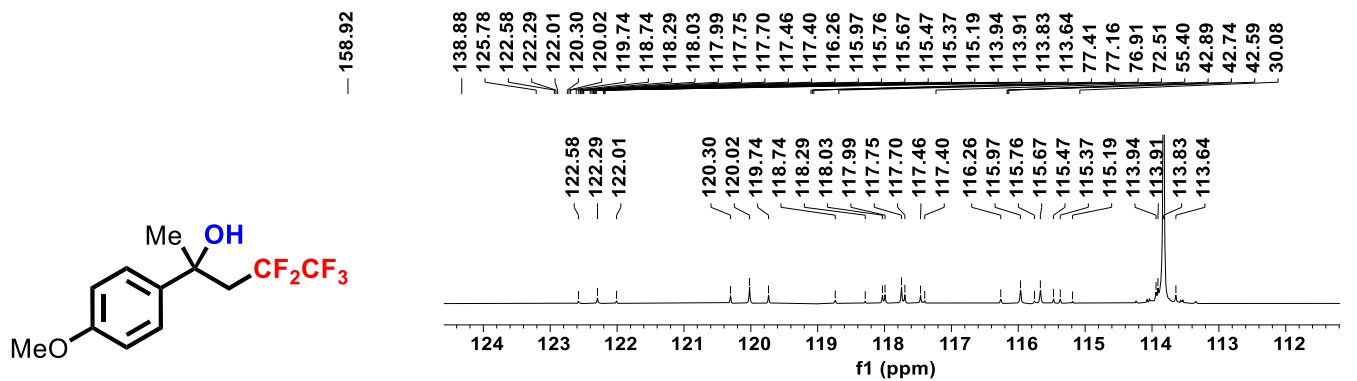
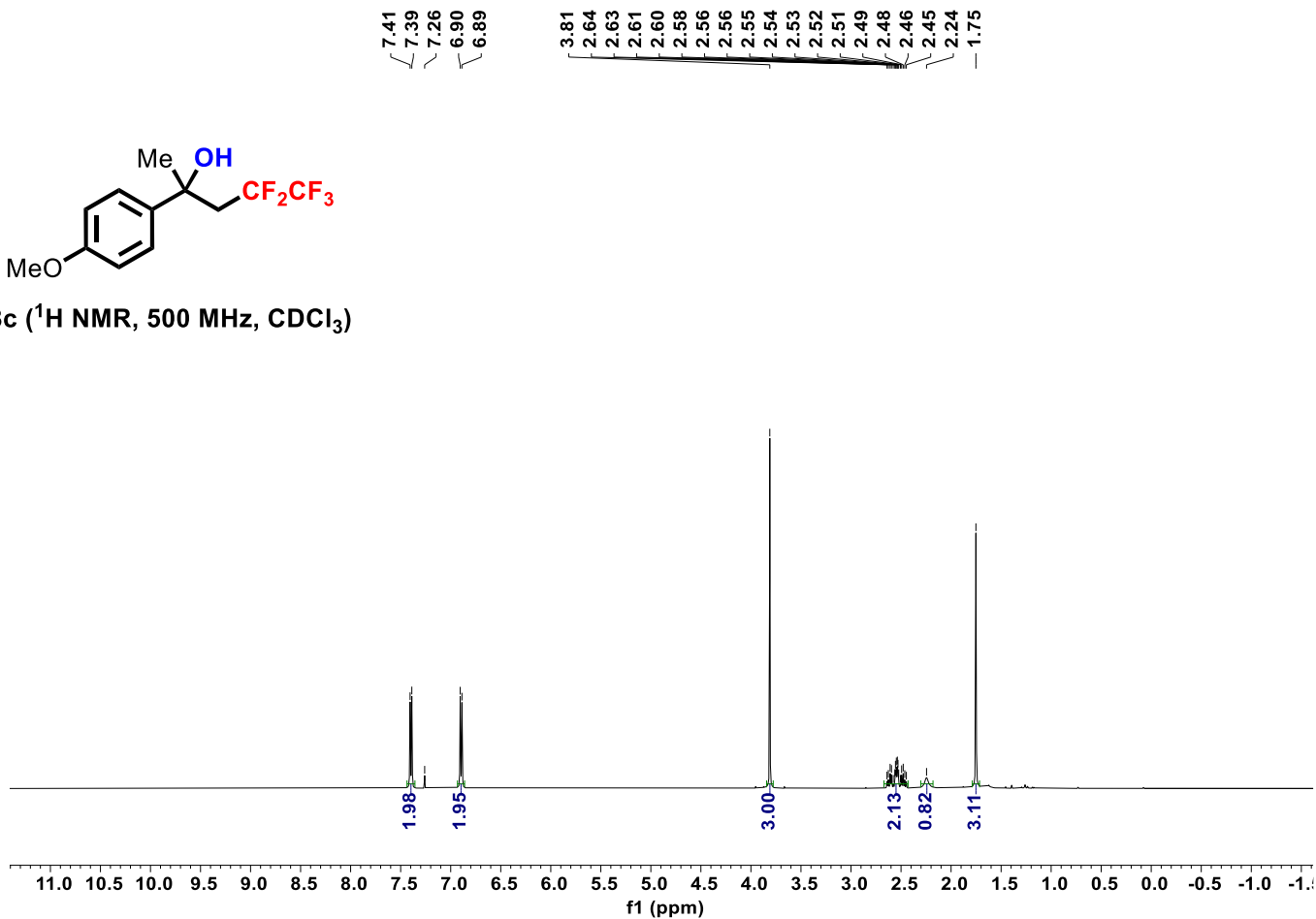
8b (¹H NMR, 400 MHz, CDCl₃)



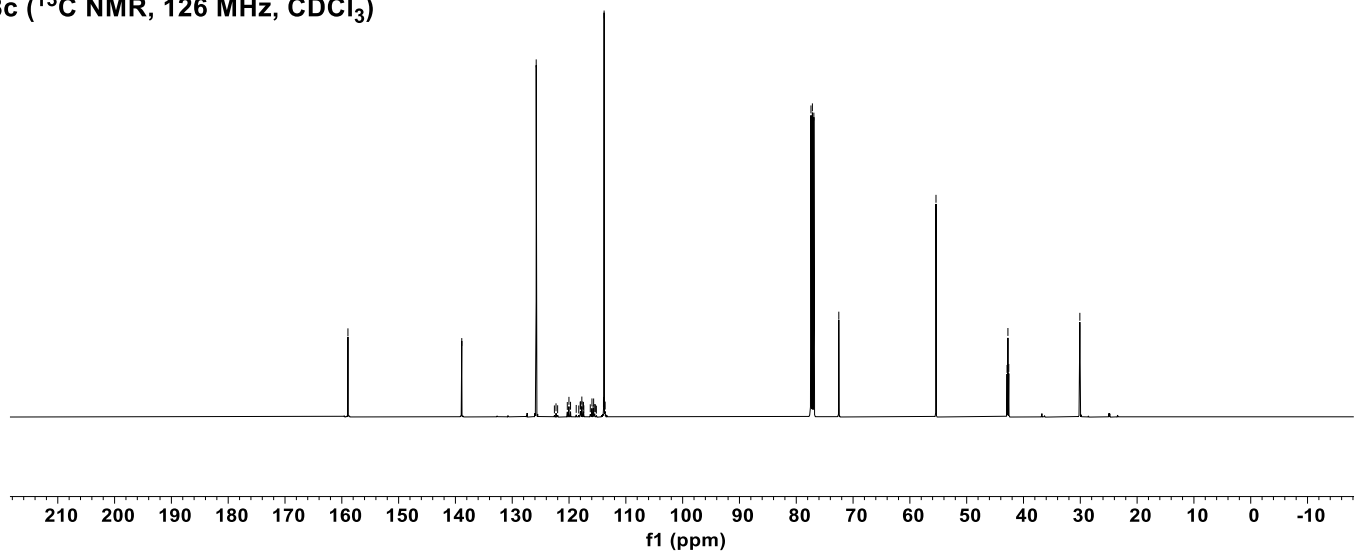


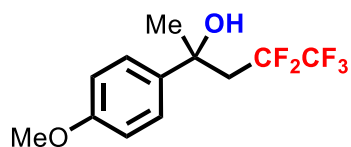


8c (¹H NMR, 500 MHz, CDCl₃)

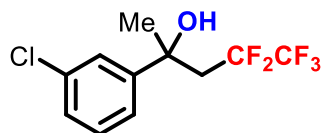
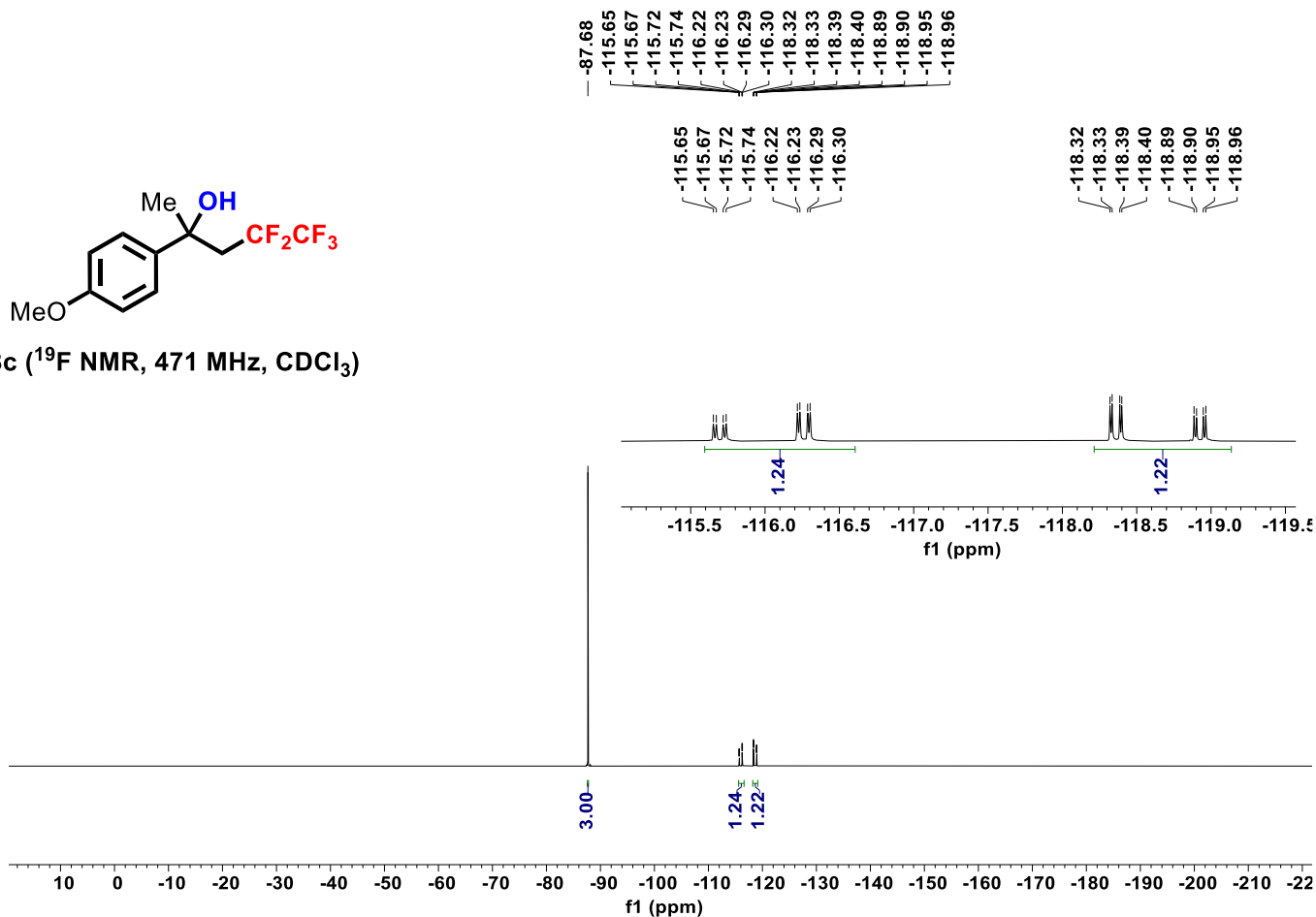


8c (¹³C NMR, 126 MHz, CDCl₃)

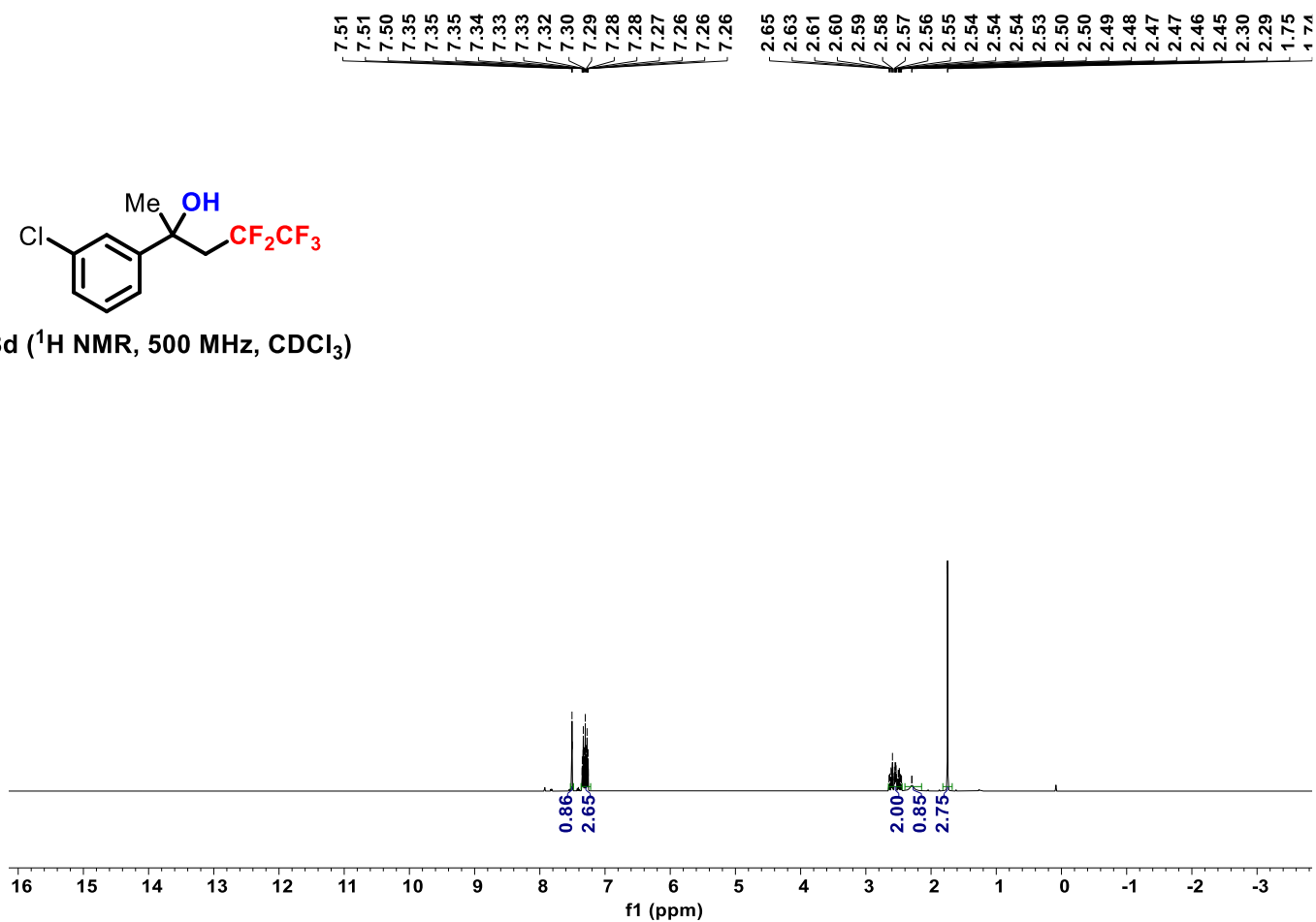


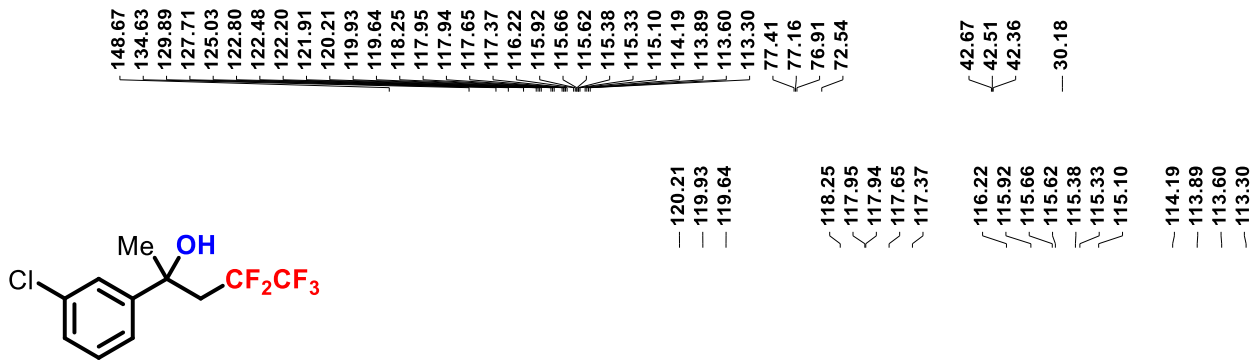


8c (¹⁹F NMR, 471 MHz, CDCl₃)

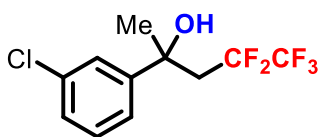
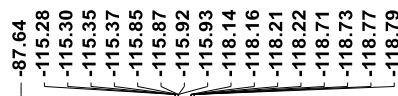
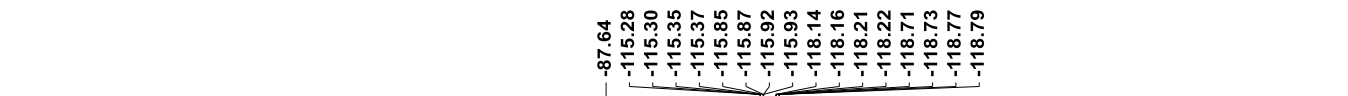
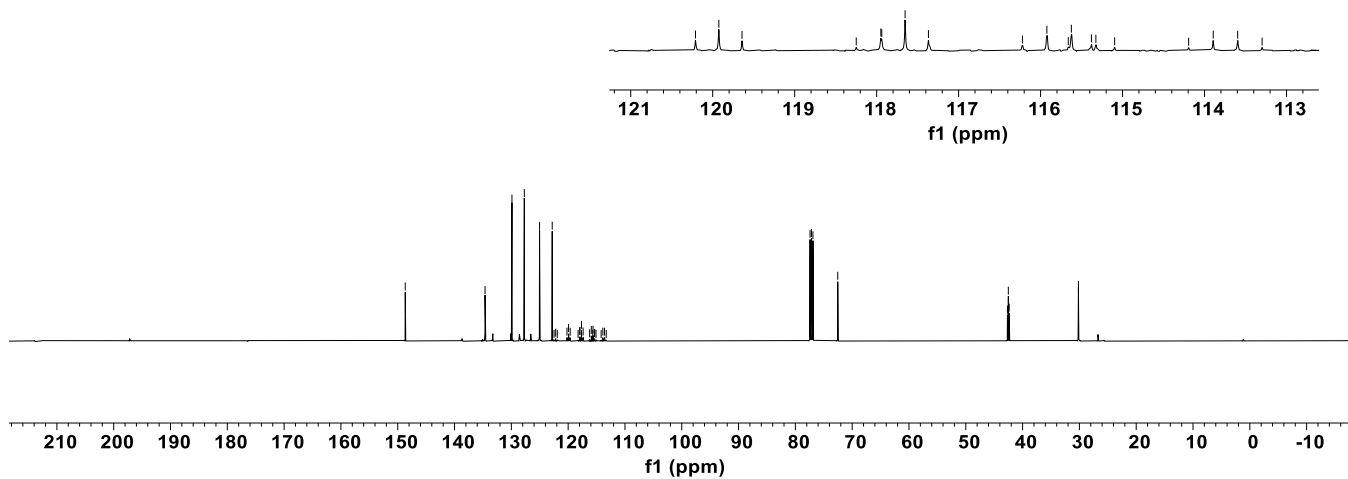


8d (¹H NMR, 500 MHz, CDCl₃)

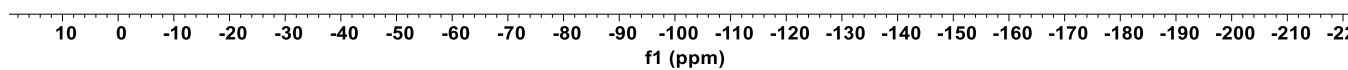
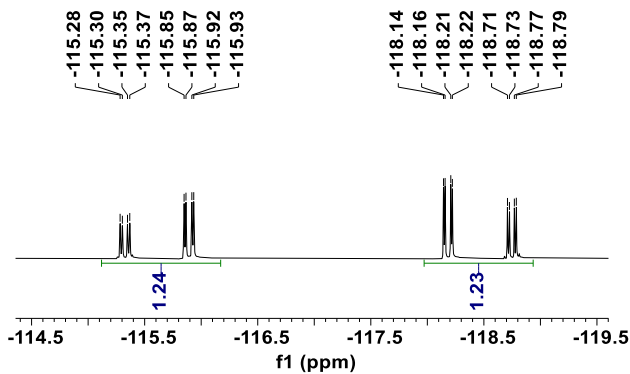


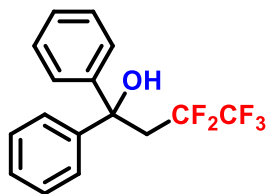


8d (^{13}C NMR, 126 MHz, CDCl_3)



8d (^{19}F NMR, 471 MHz, CDCl_3)

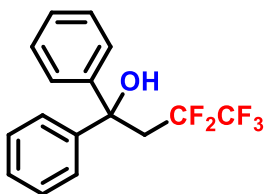
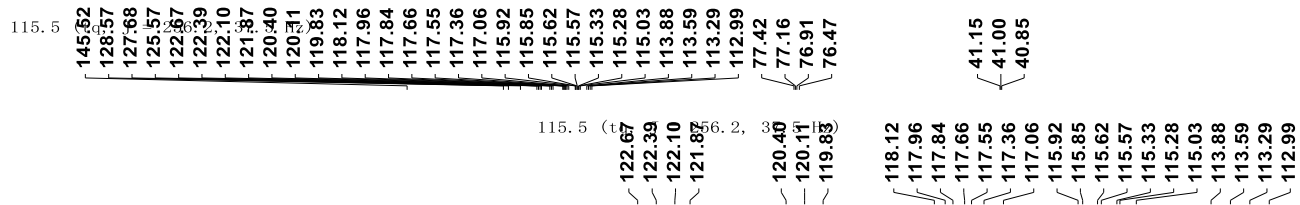
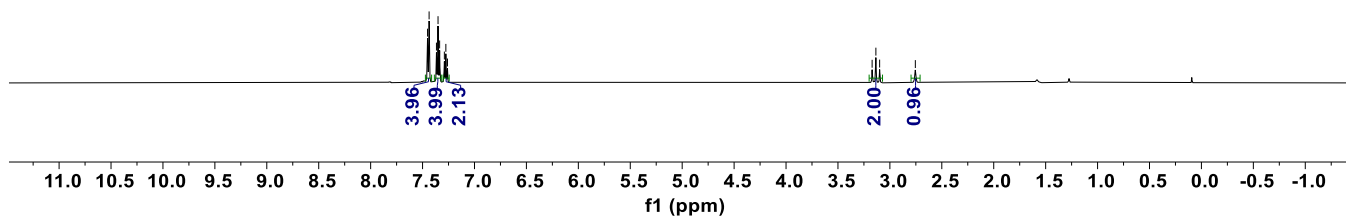




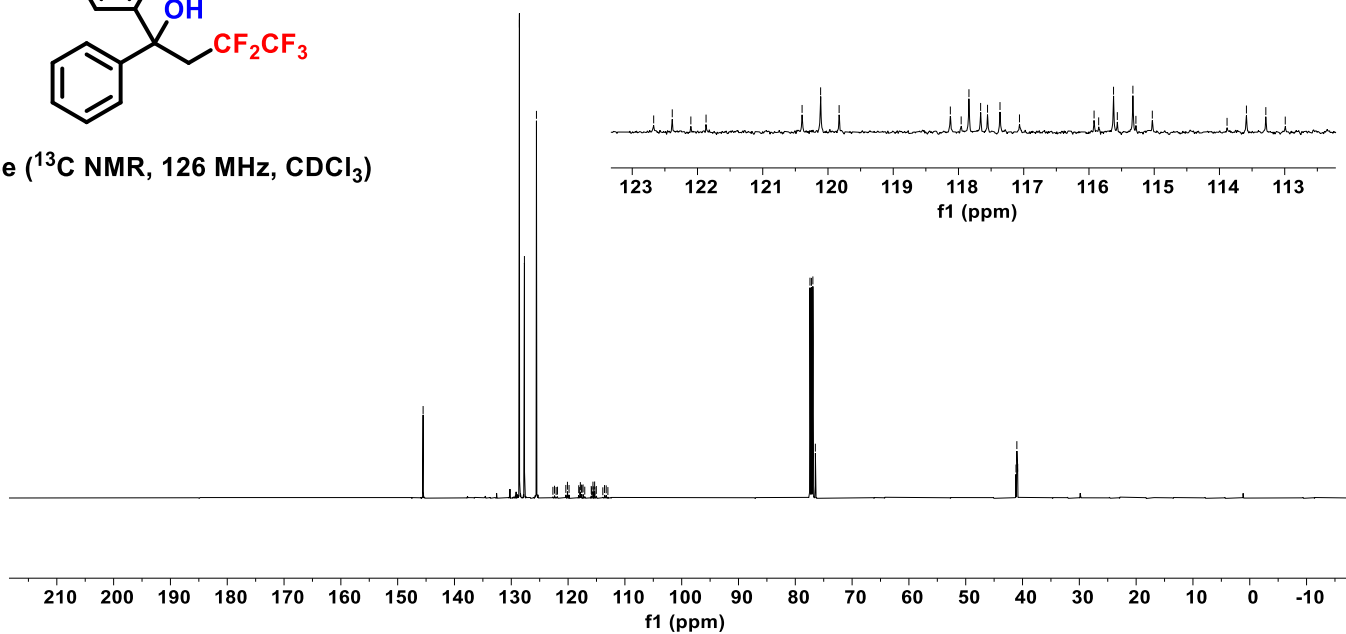
8e (¹H NMR, 500 MHz, CDCl₃)

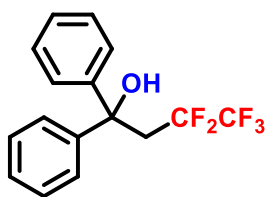
7.45
7.44
7.37
7.35
7.34
7.29
7.28
7.26

3.17
3.13
3.10
2.75

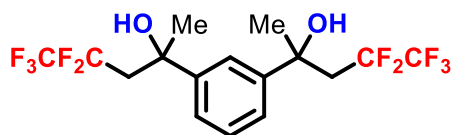
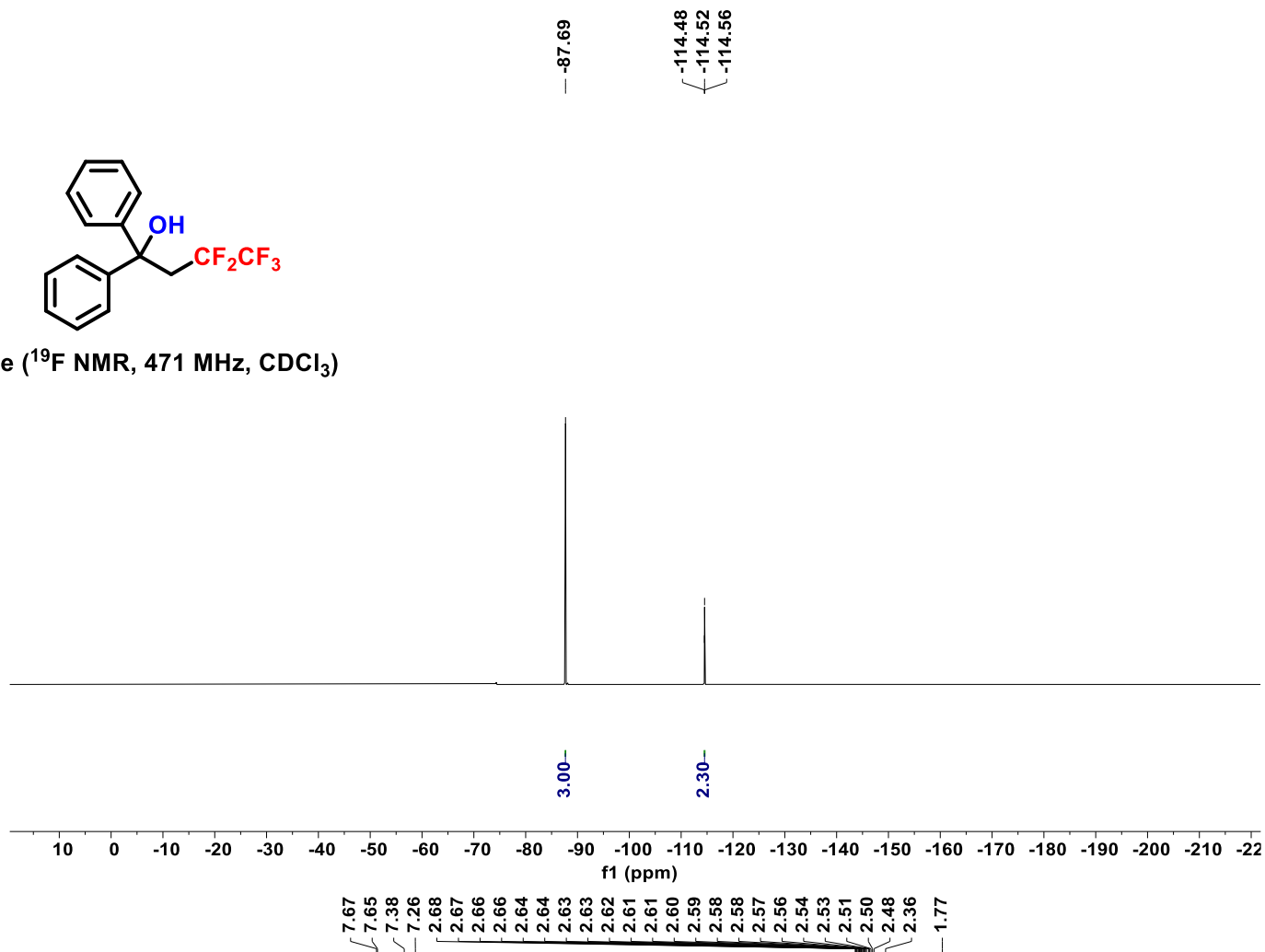


8e (¹³C NMR, 126 MHz, CDCl₃)





8e (^{19}F NMR, 471 MHz, CDCl_3)



8f (^1H NMR, 500 MHz, CDCl_3)

