Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Frustrated Radical Pair-Initiated Atom Transfer Radical Addition of Perfluoroalkyl Halides to Alkenes

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1. General information

All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk–type glassware on a dual-manifold Schlenk line, a high-vacuum line, or an argon-filled glovebox. All solvents were stored over molecular sieves 4 Å. $CDCl_3$, CD_2Cl_2, C_6D_6, C_7D_8, $(CD_3)_2CO$, CD_3CN and $(CD_3)_2SO$ were purchased from Energy Chemical and Adamas-beta and were dried over molecular sieves 4 Å. NMR spectra were recorded on Bruker Avance II 500 (500 MHz, ^1H; 126 MHz, ^{13}C; 471 MHz, ^{19}F) instrument at room temperature. Chemical shifts for ^1H and ^{13}C spectra were referenced to internal solvent resonances and are reported as parts per million in relative to $SiMe_4$, whereas ^{19}F NMR spectra were referenced to external $CFCl_3$. In the $^{13}C\{^1H\}$ NMR spectra, the signal for carbons attached to fluorine did not appear in the collected spectra due to the splitting of ^{19}F. An example as $^{13}C\{^1H\}$ NMR spectroscopy spectrum of **3aa** in high concentration for 24 h measurement time were shown in "6. NMR spectra of products" part which was found that the signal attributed to -C_4F_9 were shown to be multi-peaks. Air sensitive NMR samples were conducted in Teflon-valve sealed J. Young-type NMR tubes. EPR experiments were conducted using Bruker E500 at the temperature of 20°C. UV-vis detections were conducted using PerkinElmer LAMBDA 1050+ UV/Vis/NIR Spectrometer. The light induced reactions with blue LED (brand: Xiang Zhao Zhi Guang, power: 50W; type: LED-100-XZZG) were equipped with a cooling fan to provide ambient temperature (about 23°C) and the reaction tubes were placed about 6 cm away from the light.

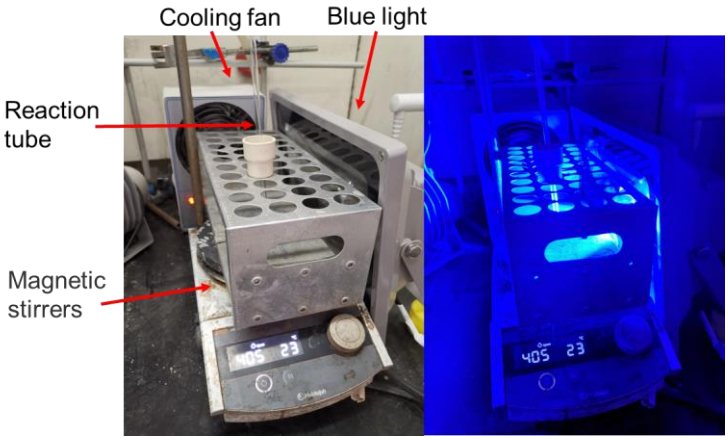


Figure S1. Reaction equipment setup (left) and during reaction (right).

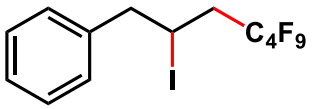
2. Typical procedure for synthesis of 3

In an argon-filled glovebox, a 2 mL NMR tube was added $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol), $CDCl_3$ (0.5 mL), $PhNMe_2$ (2.4 mg, 0.02 mol) or $PhNEt_2$ (3.0 mg, 0.02 mmol), halide reagents (0.12 mmol), alkenes (0.10 mmol) and mesitylene (12.0 mg, 0.10 mmol) as internal standard in sequence. Then the NMR tube was taken out of the glovebox and irradiated under blue LED at room temperature for certain time. After completion of the reaction and measurement of NMR, the reaction mixture was further purified by flash column chromatography on silica gel using hexane/ethyl acetate (20/1) as eluent to afford **3**.

3. Preparative scale synthesis of 3aa

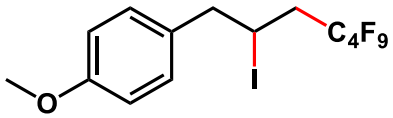
In an argon-filled glovebox, a 25 mL reaction tube was added with $B(C_6F_5)_3$ (307.2 mg, 0.6 mmol), $CHCl_3$ (8.0 mL), $PhNMe_2$ (72.6 mg, 0.6 mol), **1a** (0.35 g, 3.0 mmol) and **2a** (1.1 g, 3.2 mmol). The reaction tube was taken out of the glovebox and irradiated under blue LED at room temperature for 3 h. After completion of the reaction and measurement of NMR, the reaction mixture was further purified by flash column chromatography on silica gel (using hexane/ethyl acetate (20/1) as eluent) to afford 1.18 g of **3aa** as color less oil in 85% isolation yield.

4. Spectral data for products



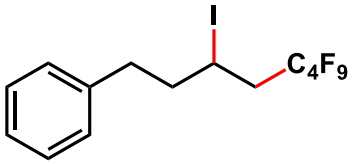
3aa

(4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)benzene (**3aa**).[1] This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 95%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (dq, *J* = 14.4, 7.1 Hz, 3H, H_{Ar}), 7.23 (d, *J* = 6.8 Hz, 2H, H_{Ar}), 4.49 (dq, *J* = 8.8, 6.3 Hz, 1H, C*H*I), 3.33 (dd, *J* = 14.6, 5.7 Hz, 1H, CH_2R_F), 3.23 (dd, *J* = 14.6, 8.9 Hz, 1H, CH_2R_F), 2.92 (tp, *J* = 24.4, 8.1 Hz, 2H, ArCH_2). ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.45 – -81.52 (m, 3F, CF_3), -112.21 (ddq, *J* = 269.9, 24.6, 11.9, 11.4 Hz, 1F, CH_2CF_2), -113.19 – -114.65 (m, 1F, CH_2CF_2), -124.56 (q, *J* = 9.0 Hz, 2F, CF_2), -125.89 (ddt, *J* = 19.9, 13.2, 6.6 Hz, 2F, CF_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.55, 128.95, 128.64, 127.35, 47.04, 40.73 (t, *J* = 20.8 Hz), 19.24. HRMS (ESI): Calculated for $C_{13}H_{10}F_9$ [M-I]: 377.0633, Found: 377.0648.



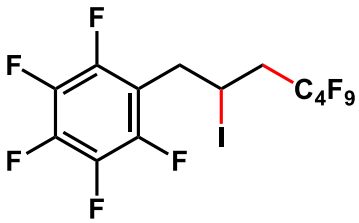
3ba

1-methoxy-4-(4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)benzene (**3ba**).[2] This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 90%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.7 Hz, 2H, H_{Ar}), 6.90 (d, *J* = 8.6 Hz, 2H, H_{Ar}), 4.45 (dq, *J* = 8.6, 6.4 Hz, 1H, C*H*I), 3.84 (s, 3H, OCH_3), 3.31 – 3.12 (m, 2H, CH_2R_F), 3.01 – 2.77 (m, 2H, ArCH_2). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.02 (t, *J* = 9.9 Hz, 3F, CF_3), -112.27 (ddq, *J* = 269.8, 25.7, 13.5, 12.6 Hz, 1F, CH_2CF_2), -113.94 (ddq, *J* = 270.9, 26.1, 13.4, 12.6 Hz, 1F, CH_2CF_2), -124.54 (q, *J* = 9.2 Hz, 2F, CF_2), -125.89 (tq, *J* = 11.3, 6.4, 5.8 Hz, 2F, CF_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.81, 130.64, 130.03, 113.98, 55.23, 46.23, 40.50, 20.12. HRMS (ESI): Calculated for $C_{14}H_{12}F_9O$ [M-I]: 367.0732, Found: 367.0739.



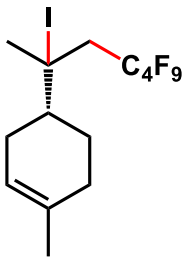
3ca

(5,5,6,6,7,7,8,8,8-nonafluoro-3-iodooctyl)benzene (**3ca**).[2] This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 92%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.6 Hz, 2H, H_{Ar}), 7.26 (d, *J* = 7.1 Hz, 3H, H_{Ar}), 4.37 – 4.23 (m, 1H, C*H*I), 3.11 – 2.68 (m, 4H, CH_2R_F and ArCH_2), 2.26 – 2.05 (m, 2H, CH_2). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.02 (t, *J* = 9.4 Hz, 3F, CF_3), -111.62 (ddt, *J* = 270.6, 44.0, 12.1 Hz, 1F, CH_2CF_2), -114.03 – -115.46 (m, 1F, CH_2CF_2), -124.12 – -124.97 (m, 2F, CF_2), -125.88 (dtd, *J* = 25.9, 13.2, 12.2, 4.6 Hz, 2F, CF_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.86, 128.61, 128.48, 126.39, 53.41, 41.79, 35.69, 19.99. HRMS (ESI): Calculated for $C_{14}H_{12}F_9$ [M-I]: 351.0790, Found: 351.0806.



3da

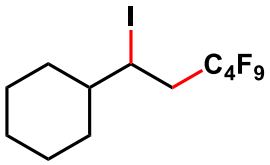
1,2,3,4,5-pentafluoro-6-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)benzene (**3da**).[2] This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 85%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.53 (ddt, *J* = 10.2, 8.1, 5.0 Hz, 1H, C*H*I), 3.52 – 3.26 (m, 2H, CH_2), 3.21 – 2.75 (m, 2H, CH_2R_F). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.01 (t, *J* = 9.7 Hz, 3F, CF_3), -110.05 – -112.20 (m, 1F, CH_2CF_2), -112.85 – -116.20 (m, 1F, CH_2CF_2), -124.43 (tt, *J* = 12.6, 6.7 Hz, 2F, CF_2), -125.88 (dtd, *J* = 18.2, 12.8, 12.4, 4.5 Hz, 2F, CF_2), -142.16 (dd, *J* = 22.0, 8.1 Hz, 2F, F_{Ar}), -154.40 (t, *J* = 20.8 Hz, 1F, F_{Ar}), -161.54 (td, *J* = 21.6, 7.8 Hz, 2F, F_{Ar}). ^{13}C NMR (126 MHz, $CDCl_3$) δ 41.81, 33.78, 14.42.



3ea

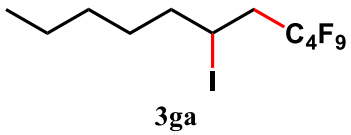
(4R)-1-methyl-4-(4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptan-2-yl)cyclohex-1-ene (**3ea**). This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 95%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.40 (s, 1H, C*H*I), 3.39 – 2.95 (m, 2H, CH_2R_F), 2.30 (s, 1H, C=C*H*), 2.22 (s, 3H, CH_3), 2.18 – 1.90

(m, 4H, CH_2), 1.71 (s, 3H, CH_3), 1.51 – 1.33 (m, 2H, CH_2), 0.67 (dt, J = 60.9, 10.7 Hz, 1H, CH). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.03 (t, J = 10.0 Hz, 3F, CF_3), -109.08 – -112.78 (m, 2F, CH_2CF_2), -124.30 (ddd, J = 40.6, 21.6, 8.8 Hz, 2F, CF_2), -125.67 (ddp, J = 20.1, 13.5, 6.3, 5.9 Hz, 2F, CF_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 46.46, 45.43, 45.14 – 44.75 (m), 34.64, 34.16, 31.15, 30.48, 30.04, 29.15, 23.18. HRMS (ESI): Calculated for $C_{14}H_{16}F_9$ [M-I]: 355.1103, Found: 355.1108.



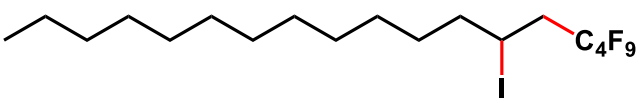
3fa

(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)cyclohexane (**3fa**).[1] This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 93%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.38 (td, J = 6.7, 3.0 Hz, 1H, CHI), 3.06 – 2.68 (m, 2H, CH_2R_F), 2.04 – 1.61 (m, 5H, CH_2), 1.51 – 1.06 (m, 5H, CH_2), 0.86 (tt, J = 11.1, 3.2 Hz, 1H, CH). ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.24 – -81.93 (m, 3F, CF_3), -112.88 (ddq, J = 270.0, 27.1, 14.1, 13.1 Hz, 1F, CH_2CF_2), -114.92 (ddq, J = 271.6, 28.4, 14.6, 12.9 Hz, 1F, CH_2CF_2), -124.51 (q, J = 11.2, 9.2 Hz, 2F, CF_2), -125.88 (dd, J = 14.6, 9.1 Hz, 2F, CF_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 44.18, 38.98 (t, J = 20.9 Hz), 33.70, 30.27, 29.72, 26.02, 25.75, 25.53.



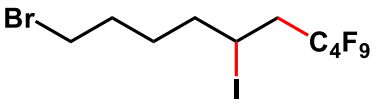
3ga

1,1,1,2,2,3,3,4,4-nonafluoro-6-iodoundecane (**3ga**).[4] This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 93%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.45 – 4.27 (m, 1H, CHI), 3.09 – 2.66 (m, 2H, CH_2R_F), 1.82 (dtt, J = 28.2, 9.7, 5.0 Hz, 2H, CH_2CHI), 1.67 – 1.15 (m, 6H, CH_2), 0.94 (t, J = 6.9 Hz, 3H, CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.68 – -81.37 (m, 3F, CF_3), -111.45 – -112.60 (m, 1F, CH_2CF_2), -114.17 – -115.49 (m, 1F, CH_2CF_2), -123.99 – -125.23 (m, 2F, CF_2), -125.90 (td, J = 20.0, 18.0, 12.5 Hz, 2F, CF_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 77.00, 41.80 – 41.37 (m), 40.31, 30.66, 29.21, 22.41, 20.80, 13.95. HRMS (ESI): Calculated for $C_{11}H_{14}F_9$ [M-I]: 317.0946, Found: 317.0941.



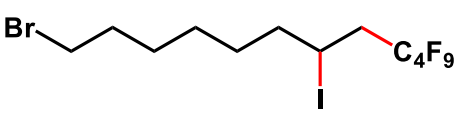
3ha

1,1,1,2,2,3,3,4,4-nonafluoro-6-iodooctadecane (**3ha**). This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 90%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.36 (tt, *J* = 8.9, 4.6 Hz, 1H, C*H*I), 3.03 – 2.68 (m, 2H, CH_2R_F), 1.82 (dqd, *J* = 28.1, 9.8, 4.7 Hz, 2H, CH_2CHI), 1.66 – 1.10 (m, 20H, CH_2), 0.91 (t, *J* = 6.8 Hz, 3H, CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.05 (t, *J* = 9.9 Hz, 3F, CF_3), -111.11 – -112.78 (m, 1F, CH_2CF_2), -114.03 – -116.02 (m, 1F, CH_2CF_2), -124.58 (p, *J* = 8.7 Hz, 2F, CF_2), -125.10 – -126.55 (m, 2F, CF_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 41.59 (t, *J* = 20.9 Hz), 40.36, 31.92, 29.63, 29.59, 29.54, 29.35, 28.50, 22.69, 20.80, 14.10.



3ia

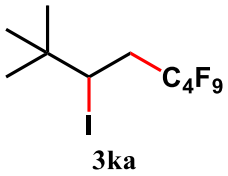
10-bromo-1,1,1,2,2,3,3,4,4-nonafluoro-6-iododecane (**3ia**).[5] This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 94%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.35 (tt, *J* = 8.8, 4.8 Hz, 1H, C*H*I), 3.45 (t, *J* = 6.7 Hz, 2H, CH_2Br), 2.88 (dddd, *J* = 76.1, 33.8, 15.9, 8.6 Hz, 2H, CH_2R_F), 2.04 – 1.58 (m, 6H, CH_2). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.00 (t, *J* = 9.6 Hz, 3F, CF_3), -111.15 – -112.63 (m, 1F, CH_2CF_2), -114.83 (d, *J* = 280.2 Hz, 1F, CH_2CF_2), -124.51 (d, *J* = 10.3 Hz, 2F, CF_2), -125.86 (dtd, *J* = 19.1, 13.0, 12.3, 4.3 Hz, 2F, CF_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 41.84 – 41.32 (m), 39.33, 32.97, 31.56, 28.31, 19.75. HRMS (ESI): Calculated for $C_{10}H_{11}BrF_9$ [M-I]: 380.9895, Found: 380.9902.



3ja

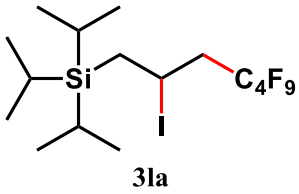
12-bromo-1,1,1,2,2,3,3,4,4-nonafluoro-6-iodododecane (**3ja**). This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 90%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.35 (tt, *J* = 8.9, 4.7 Hz, 1H, C*H*I), 3.44 (t, *J* = 6.8 Hz, 2H, CH_2Br), 2.87

(dddd, *J* = 66.7, 27.9, 15.9, 8.5 Hz, 2H, C*H*$_2$R$_F$), 2.04 – 1.14 (m, 11H, C*H*$_2$, C*H*$_3$). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.00 (t, *J* = 9.5 Hz, 3F, C*F*$_3$), -111.90 (dd, *J* = 271.7, 30.5 Hz, 1F, CH$_2$C*F*$_2$), -114.16 – -115.44 (m, 1F, CH$_2$C*F*$_2$), -124.14 – -124.94 (m, 2F, C*F*$_2$), -125.87 (dtd, *J* = 18.7, 12.8, 12.1, 5.0 Hz, 2F, C*F*$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 41.91 – 41.28 (m), 40.13, 33.72, 32.60, 29.41, 27.89, 27.66, 20.53. HRMS (ESI): Calculated for $C_{12}H_{15}BrF_9$ [M-I]: 409.0208, Found: 409.0196.



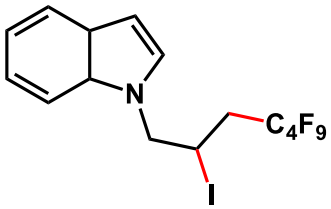
3ka

1,1,1,2,2,3,3,4,4-nonafluoro-6-iodo-7,7-dimethyloctane (**3ka**).[6] This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 91%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.20 (dd, *J* = 8.7, 1.9 Hz, 1H, C*H*I), 3.06 – 2.72 (m, 2H, C*H*$_2$R$_F$), 1.14 (s, 9H, C(C*H*$_3$)$_3$). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.03 (dd, *J* = 11.1, 7.7 Hz, 3F, C*F*$_3$), -113.82 – -115.27 (m, 1F, CH$_2$C*F*$_2$), -115.27 – -116.64 (m, 1F, CH$_2$C*F*$_2$), -124.61 (q, *J* = 10.0 Hz, 2F, C*F*$_2$), -125.04 – -126.48 (m, 2F, C*F*$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 38.19 (t, *J* = 20.6 Hz), 35.87, 34.39, 27.72.



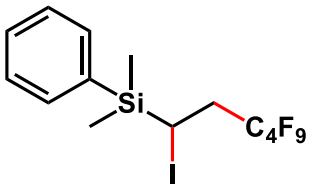
3la

triisopropyl(4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)silane (**3la**). This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 95%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.45 (tt, *J* = 7.9, 3.9 Hz, 1H, C*H*I), 2.47 – 2.20 (m, 2H, C*H*$_2$R$_F$), 1.81 (t, *J* = 3.6 Hz, 1H, C*H*$_2$R$_{Si}$), 1.08 (dd, *J* = 5.4, 3.0 Hz, 21H, C*H*$_3$C*H*R$_{Si}$), 0.95 (d, *J* = 4.4 Hz, 1H, C*H*$_2$R$_{Si}$). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.02 (t, *J* = 9.7 Hz, 3F, C*F*$_3$), -113.60 (ddq, *J* = 78.0, 26.1, 13.1 Hz, 2F, CH$_2$C*F*$_2$), -124.78 (q, *J* = 9.5 Hz, 2F, C*F*$_2$), -125.94 (h, *J* = 9.1, 7.7 Hz, 2F, C*F*$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 63.53, 41.50, 19.93, 18.80, 11.30. HRMS (ESI): Calculated for $C_{16}H_{26}F_9Si$ [M-I]: 417.1655, Found: 417.1650.



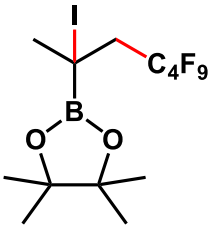
3ma

1-(3,3,4,4,5,5,6,6,6-nonafluoro-2-iodohexyl)-1H-indole (**3ma**). This product was obtained as white solid according to typical procedure for synthesis of **3**. Isolated yield was 53%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.8 Hz, 1H, H_{Ar}), 7.31 (t, *J* = 7.4 Hz, 1H, H_{Ar}), 7.28 – 7.26 (m, 1H, H_{Ar}), 7.22 – 7.11 (m, 2H, H_{Ar}), 6.57 (d, *J* = 3.2 Hz, 1H, H_{Ar}), 4.76 – 4.63 (m, 1H, C*H*I), 4.63 – 4.49 (m, 2H, CH_2R_N), 2.85 (dddd, *J* = 55.9, 35.7, 15.7, 7.6 Hz, 2H, CH_2R_F). ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.99 (t, *J* = 10.1 Hz, 3F, CF_3), -111.29 – -112.71 (m, 1F, CH_2CF_2), -112.91 – -114.49 (m, 1F, CH_2CF_2), -124.43 (q, *J* = 9.5 Hz, 2F, CF_2), -125.86 (td, *J* = 13.4, 4.6 Hz, 2F, CF_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 128.83, 127.74, 122.24, 121.42, 120.15, 108.81, 102.47, 77.01, 54.65, 14.87. HRMS (ESI): Calculated for $C_{15}H_{11}F_9N$ [M-I]: 376.0742, Found: 376.0739.



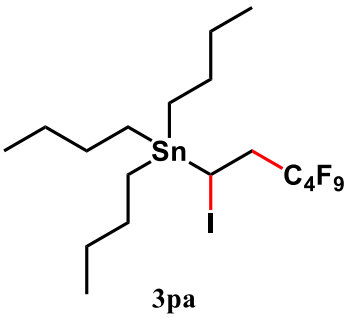
3na

dimethyl(2,2,3,3,4,4,5,5,5-nonafluoro-1-iodopentyl)(phenyl)silane (**3na**).[3] This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 95%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.51 (m, 2H, H_{Ar}), 7.51 – 7.37 (m, 3H, H_{Ar}), 3.40 (dd, *J* = 10.6, 2.5 Hz, 1H, C*H*I), 2.69 (dddd, *J* = 28.3, 16.4, 8.1, 1.7 Hz, 1H, CH_2R_F), 2.62 – 2.42 (m, 1H, CH_2R_F), 0.54 (d, *J* = 7.6 Hz, 6H, CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.09 (t, *J* = 10.0 Hz, 3F, CF_3), -114.00 (ddt, *J* = 268.7, 27.2, 12.5 Hz, 1F, CH_2CF), -115.98 (ddq, *J* = 267.7, 23.6, 11.2, 10.6 Hz, 1F, CH_2CF_2), -124.01 – -125.65 (m, 2F, CF_2), -125.99 (dt, *J* = 81.0, 13.3 Hz, 2F, CF_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.36, 133.96, 130.11, 128.18, 34.98 (t, *J* = 21.8 Hz), -0.78, -3.17, -4.54.



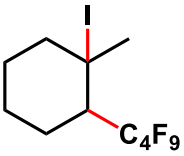
3oa

4,4,5,5-tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptan-2-yl)-1,3,2-dioxaborolane (**3oa**). This product was obtained according to typical procedure for synthesis of **3**. The isolation of **3oa** was failed due to its sensitivity to silica gel. The yields were determined by ^{1}H NMR spectroscopy (79%). HRMS (ESI): Calculated for $C_{13}H_{17}BF_9O_2$ [M-I]: 387.1172, Found: 387.1170.



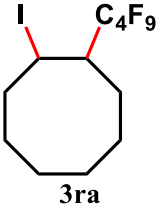
3pa

tributyl(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)stannane (**3pa**). This product was obtained according to typical produre for synthesis of **3**. The isolation of **3pa** was failed due to its sensitivity to silica gel. The yields were determined by ^{1}H NMR spectroscopy (90%). HRMS (ESI): Calculated for $C_{18}H_{30}F_9Sn$ [M-I]: 537.1220, Found: 537.1211.



3qa

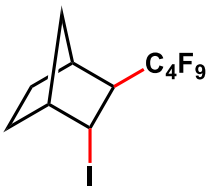
1-iodo-1-methyl-2-(perfluorobutyl)cyclohexane (**3qa**). This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 50%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.08 – 2.91 (m, 1H, C*H*$_2$CI), 2.49 (ddd, *J* = 13.8, 9.2, 4.0 Hz, 1H, C*H*$_2$CI), 2.24 (d, *J* = 4.0 Hz, 3H, C*H*$_3$), 2.20 (d, *J* = 3.6 Hz, 1H, C*H*R$_F$), 2.03 – 1.82 (m, 3H, C*H*$_2$), 1.59 – 1.44 (m, 3H, C*H*$_2$). ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.94 (dt, *J* = 33.6, 10.0 Hz, 3F, C*F*$_3$), -102.49 – -117.52 (m, 2F, CH$_2$C*F*$_2$), -120.38 – -128.05 (m, 4F, C*F*$_2$C*F*$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 50.95, 49.36, 32.51, 24.72, 24.60, 24.44, 23.22. HRMS (ESI): Calculated for $C_{11}H_{12}F_9$ [M-I]: 315.0790, Found: 315.0794.



3ra

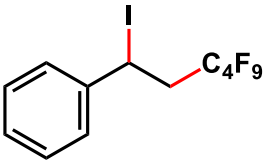
1-iodo-2-(perfluorobutyl)cyclooctane (**3ra**).[3] This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 79%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.71 – 4.50 (m, 1H, C*H*I), 2.55 – 2.22 (m, 3H, C*H*R$_F$ and C*H*$_2$), 2.24 – 1.80 (m, 5H, C*H*$_2$), 1.80 – 1.61 (m, 2H, C*H*$_2$), 1.55 – 1.34 (m, 2H, C*H*$_2$). ^{19}F NMR (471

MHz, $CDCl_3$) δ -80.88 (td, *J* = 9.8, 4.0 Hz, 3F, C*F*$_3$), -114.32 – -118.44 (m, 2F, C*F*$_2$), -118.87 – -122.35 (m, 2F, C*F*$_2$), -124.12 – -128.03 (m 2F, CH_2CF_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 39.50, 38.18, 35.94, 34.75 (d, *J* = 27.4 Hz), 27.13, 26.40, 25.37, 24.80, 23.90 – 23.22 (m). HRMS (ESI): Calculated for $C_{12}H_{14}F_9$ [M-I]: 329.0946, Found: 329.0940.



3sa

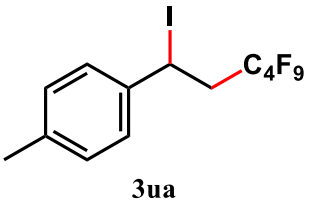
(1R,3S,4S)-2-iodo-3-(perfluorobutyl)bicyclo[2.2.1]heptane (**3sa**).[7] This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 96%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.33 (dt, *J* = 6.0, 2.7 Hz, 1H, C*H*I), 2.49 (dt, *J* = 26.2, 3.3 Hz, 2H, C*H*$_2$), 2.40 (ddd, *J* = 23.2, 9.9, 6.4 Hz, 1H, C*H*R_F), 1.92 (dddd, *J* = 11.2, 8.6, 4.6, 2.5 Hz, 1H, C*H*), 1.81 – 1.58 (m, 3H, C*H*$_2$ and C*H*), 1.46 – 1.20 (m, 2H, C*H*$_2$). ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.95 (td, *J* = 9.4, 4.2 Hz, 3F, C*F*$_3$), -115.16 – -116.55 (m, 1F, CH_2CF_2), -118.99 (dt, *J* = 278.1, 17.1 Hz, 1F, CH_2CF_2), -121.82 (ddt, *J* = 36.9, 15.5, 8.3 Hz, 2F, C*F*$_2$), -124.93 – -126.94 (m, 2F, C*F*$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.82 – 55.27 (m), 44.53, 37.84, 35.00, 29.69, 27.42, 25.89. HRMS (ESI): Calculated for $C_{11}H_{10}F_9$ [M-I]: 313.0633, Found: 313.0648.



3ta

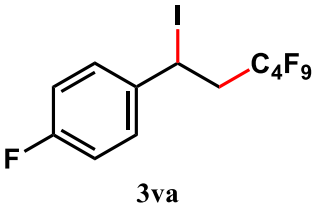
(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)benzene (**3ta**).[8] This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 82%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.4 Hz, 2H, *H*$_{Ar}$), 7.35 (t, *J* = 7.4 Hz, 2H, *H*$_{Ar}$), 7.32 – 7.27 (m, 1H, *H*$_{Ar}$), 5.47 (dd, *J* = 9.7, 5.1 Hz, 1H, C*H*I), 3.26 (dddd, *J* = 57.8, 28.8, 15.0, 7.8 Hz, 2H, C*H*$_2R_F$). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.05 (t, *J* = 9.9 Hz, 3F, C*F*$_3$), -111.84 – -113.28 (m, 1F, CH_2CF_2), -114.34 – -115.52 (m, 1F, CH_2CF_2), -124.48 (p, *J* = 9.5 Hz, 2F, C*F*$_2$), -125.94 (ddd, *J* = 19.5, 15.3, 8.9 Hz, 2F, C*F*$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.70,

128.90, 128.58, 126.71, 42.40 (t, *J* = 20.5 Hz), 16.47. HRMS (ESI): Calculated for $C_{12}H_8F_9$ [M-I]: 323.0477, Found: 323.0471.



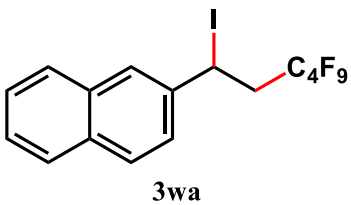
3ua

1-methyl-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)benzene (**3ua**).[9] This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 80%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.1 Hz, 2H, H_{Ar}), 7.22 (d, *J* = 7.9 Hz, 2H, H_{Ar}), 5.26 – 5.17 (m, 1H, C*H*I), 2.64 (ddd, *J* = 37.3, 16.6, 8.6 Hz, 2H, CH_2R_F), 2.38 (s, 3H, CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ -79.84 – -81.86 (m, 3F, CF_3), -112.66 (d, *J* = 273.4 Hz, 1F, CH_2CF_2), -113.38 – -114.94 (m, 1F, CH_2CF_2), -124.57 (d, *J* = 10.3 Hz, 2F, CF_2), -125.88 (qd, *J* = 12.7, 11.1, 6.1 Hz, 2F, CF_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.71, 138.29, 129.54, 125.57, 67.80, 39.77 (t, *J* = 20.4 Hz), 21.13. HRMS (ESI): Calculated for $C_{13}H_{10}F_9$ [M-I]: 337.0633, Found: 337.0634.



3va

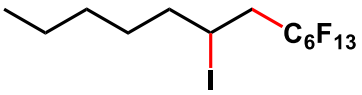
1-fluoro-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)benzene (**3va**). This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 53%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.37 (m, 2H, H_{Ar}), 7.11 – 6.92 (m, 2H, H_{Ar}), 5.46 (dd, *J* = 10.1, 4.9 Hz, 1H, C*H*I), 3.44 – 3.05 (m, 2H, CH_2R_F). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.03 (t, *J* = 9.6 Hz, 3F, CF_3), -111.58 – -113.01 (m, 1F, CH_2CF_2), -114.13 – -115.56 (m, 1F, CH_2CF_2), -124.47 (t, *J* = 10.3 Hz, 2F, CF_2), -125.93 (dtd, *J* = 25.6, 12.9, 12.1, 4.4 Hz, 2F, CF_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.60, 128.57, 115.83, 42.95 – 42.46 (m), 15.38. HRMS (ESI): Calculated for $C_{12}H_7F_{10}$ [M-I]: 341.0383, Found: 341.0368.



3wa

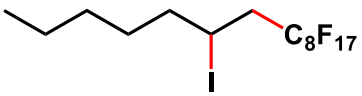
2-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)naphthalene (**3wa**). This product was obtained as white solid according to typical procedure for synthesis of **3**. Isolated yield was 50%. ^{1}H NMR (500 MHz, $CDCl_3$)

δ 8.02 – 7.73 (m, 4H, H_{Ar}), 7.64 – 7.42 (m, 4H, H_{Ar}), 5.43 (dd, *J* = 8.8, 3.2 Hz, 1H, C*H*I), 2.82 – 2.65 (m, 1H, CH_2R_F), 2.65 – 2.44 (m, 1H, CH_2R_F). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.00 (t, 3F, *J* = 9.7 Hz, CF_3), -112.60 (ddd, *J* = 274.1, 29.9, 13.3 Hz, 1F, CH_2CF_2), -113.94 (ddd, *J* = 272.4, 27.8, 12.9 Hz, 1F, CH_2CF_2), -124.52 (t, *J* = 9.6 Hz, 2F, CF_2), -125.90 (q, *J* = 12.9 Hz, 2F, CF_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.22, 128.93, 128.04, 127.77, 126.57, 126.41, 124.68, 123.28, 68.11, 39.79. HRMS (ESI): Calculated for $C_{16}H_{10}F_9$ [M-I]: 373.0633, Found: 373.0640.



3gb

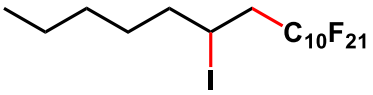
1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodotridecane (**3gb**). This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 90%. ^{1}H NMR (500 MHz, $CDCl_3$). δ 4.36 (dddd, *J* = 9.5, 8.3, 5.5, 4.2 Hz, 1H, C*H*I), 3.06 – 2.71 (m, 2H, CH_2R_F), 1.82 (dddd, *J* = 31.8, 19.5, 9.7, 4.8 Hz, 2H, CH_2CHI), 1.64 – 1.22 (m, 6H, CH_2), 0.94 (t, *J* = 7.0 Hz, 3H, CH_3). ^{19}F NMR (377 MHz, $CDCl_3$) δ -80.87 (t, *J* = 10.3 Hz, 3F, CF_3), -110.92 – -112.69 (m, 1F, CH_2CF_2), -113.82 – -115.44 (m, 1F, CH_2CF_2), -121.84 (dq, *J* = 22.6, 9.9, 6.4 Hz, 2F, CF_2), -122.43 – -123.12 (m, 2F, CF_2), -123.67 (d, *J* = 16.0 Hz, 2F, CF_2), -126.19 (td, *J* = 14.9, 12.6, 6.5 Hz, 2F, CF_2). ^{13}C NMR (126 MHz, $CDCl_3$). δ 41.68 (t, *J* = 21.0 Hz), 40.30, 30.66, 29.21, 22.40, 20.84, 13.92. HRMS (ESI): Calculated for $C_{13}H_{14}F_{13}$ [M-I]: 417.0882, Found: 417.0884.



3gc

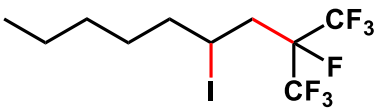
1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iodopentadecane (**3gc**). This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yields were 92%. ^{1}H NMR (500 MHz, $CDCl_3$). δ 4.36 (tt, *J* = 9.0, 4.8 Hz, 1H, C*H*I), 3.07 – 2.67 (m, 2H, CH_2R_F), 1.82 (dtt, *J* = 26.7, 9.7, 5.0 Hz, 2H, CH_2CHI), 1.66 – 1.24 (m, 6H, CH_2), 0.94 (t, *J* = 6.9 Hz, 3H, CH_3). ^{19}F NMR (471 MHz, $CDCl_3$). δ -80.90 (t, *J* = 10.2 Hz, 3F, CF_3), -110.82 – -112.90 (m, 1F, CH_2CF_2), -113.76 – -115.67 (m,

1F, CH_2CF_2), -121.36 – -121.79 (m, 2F, CF_2), -121.97 (dq, *J* = 27.1, 16.6, 12.5 Hz, 4F, CF_2), -122.80 (dt, *J* = 23.7, 10.2 Hz, 2F, CF_2), -123.68 (t, *J* = 14.7 Hz, 2F, CF_2), -126.21 (dd, *J* = 18.9, 11.2 Hz, 2F, CF_2). ^{13}C NMR (126 MHz, $CDCl_3$). δ 41.70 (t, *J* = 20.9 Hz), 40.30, 30.66, 29.21, 22.40, 20.84, 13.92. HRMS (ESI): Calculated for $C_{15}H_{14}F_{17}$ [M-I]: 517.0819, Found: 517.0808.



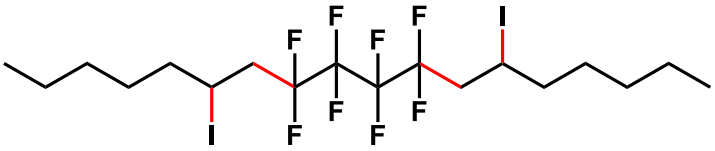
3gd

1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-henicosafluoro-12-iodoheptadecane (**3gd**). This product was obtained as white powder according to typical procedure for synthesis of **3**. Isolated yield was 93%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.34 (tt, *J* = 8.9, 4.8 Hz, 1H, C*H*I), 2.92 (ddt, *J* = 31.6, 15.5, 6.2 Hz, 1H, CH_2R_F), 2.78 (dq, *J* = 27.9, 7.9 Hz, 1H, CH_2R_F), 1.79 (dtt, *J* = 26.6, 9.8, 5.0 Hz, 2H, CH_2CHI), 1.62 – 1.22 (m, 6H, CH_2), 0.91 (t, *J* = 6.9 Hz, 3H, CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.75 (t, *J* = 10.0 Hz, 3F, CF_3), -110.75 – -112.21 (m, 1F, CH_2CF_2), -113.61 – -115.43 (m, 1F, CH_2CF_2), -121.17 – -122.20 (m, 12F, CF_2), -122.68, -123.52 (d, *J* = 14.9 Hz, 2F, CF_2), -126.09 (td, *J* = 14.6, 13.9, 6.3 Hz, 2F, CF_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 41.68 (t, *J* = 20.9 Hz), 39.32, 32.95, 31.56, 28.32, 19.82. HRMS (ESI): Calculated for $C_{17}H_{14}F_{21}$ [M-I]: 617.0755, Found: 617.0752.



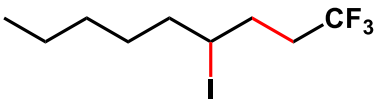
3ge

1,1,1,2-tetrafluoro-4-iodo-2(trifluoromethyl)nonane (**3ge**). This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 88%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.35 (tt, *J* = 8.8, 4.4 Hz, 1H, C*H*I), 2.91 (dddd, *J* = 47.1, 24.5, 16.1, 6.6 Hz, 2H, CH_2R_F), 1.80 (dtdd, *J* = 24.2, 14.7, 9.6, 4.8 Hz, 2H, CH_2), 1.64 – 1.22 (m, 6H, CH_2), 0.93 (t, *J* = 6.9 Hz, 3H, CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ -76.04 (p, *J* = 9.1 Hz, 3F, CF_3), -77.41 (p, *J* = 8.8 Hz, 3F, CF_3), -185.54 (ddh, *J* = 28.7, 14.0, 7.1 Hz, 1F, C*F*(CF_3)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.83, 39.77, 39.63, 30.61, 29.35, 22.89, 22.41, 13.94. HRMS (ESI): Calculated for $C_{10}H_{14}F_7$ [M-I]: 267.0978, Found: 267.0989.



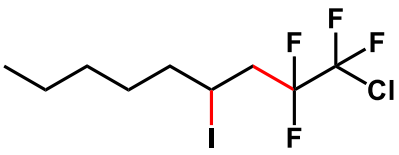
3gf

8,8,9,9,10,10,11,11-octafluoro-6,13-diiodooctadecane (**3gf**). This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 89%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.37 (tt, *J* = 8.8, 4.7 Hz, 1H, C*H*I), 2.85 (dddd, *J* = 72.5, 34.3, 15.7, 8.7 Hz, 2H, C*H*$_2$CH$_3$), 1.82 (ttd, *J* = 19.5, 9.8, 4.7 Hz, 2H, C*H*$_2$R$_F$), 1.65 – 1.19 (m, 6H, C*H*$_2$), 0.93 (t, *J* = 6.9 Hz, 3H, C*H*$_3$). ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.19 – -112.40 (m, 2F, CH$_2$C*F*$_2$), -114.03 – -115.44 (m, 2F, CH$_2$C*F*$_2$), -123.51 (p, *J* = 12.6, 12.1 Hz, 4F, CH$_2$C*F*$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 41.82 (t, *J* = 20.0 Hz), 40.33, 30.69, 29.23, 22.43, 21.46, 13.98. HRMS (ESI): Calculated for $C_{18}H_{28}F_8$ [M-2I]: 396.2063, Found: 396.2067.



3gg

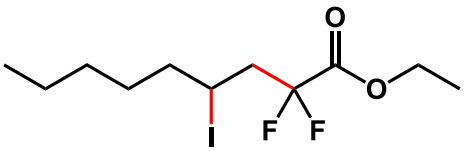
1,1,1-trifluoro-4-iodononane (**3gg**). This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 54%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.10 (tt, *J* = 8.9, 4.5 Hz, 1H, C*H*I), 2.53 – 2.34 (m, 1H, C*H*$_2$CHI), 2.33 – 2.14 (m, 1H, C*H*$_2$CHI), 2.14 – 1.97 (m, 2H, C*H*$_2$CHI), 1.93 (dddd, *J* = 14.8, 10.2, 8.7, 4.7 Hz, 1H, C*H*$_2$CF$_3$), 1.73 (ddt, *J* = 14.8, 10.3, 5.2 Hz, 1H, C*H*$_2$CF$_3$), 1.62 – 1.24 (m, 6H, C*H*$_2$), 0.93 (t, *J* = 7.0 Hz, 3H, C*H*$_3$). ^{19}F NMR (377 MHz, $CDCl_3$) δ -65.90 (t, *J* = 11.0 Hz, 3F, C*F*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.60, 35.98, 34.42 – 33.81 (m), 32.77, 30.90, 29.08, 22.46, 13.98.



3gh

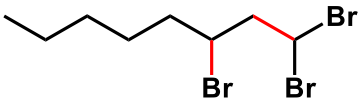
1-chloro-1,1,2,2-tetrafluoro-4-iodononane (**3gh**).[10] This product was obtained as colorless oil according to typical procedure for synthesis of **3** as a colorless oil. Isolated yield was 90%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.36 (tdd, *J* = 8.6, 5.5, 4.2 Hz, 1H, C*H*I), 3.03 – 2.71 (m, 2H, C*H*$_2$R$_F$), 1.83 (dqt, *J* = 23.6, 9.6, 4.7 Hz, 2H, C*H*$_2$CHI), 1.64 – 1.22 (m, 6H, C*H*$_2$), 0.94 (t, *J* = 7.0 Hz, 3H, C*H*$_3$). ^{19}F NMR

(377 MHz, $CDCl_3$) δ -71.65 (2F, CF_2Cl), -111.45 (ddd, *J* = 256.6, 30.5, 8.8 Hz, 1F, CF_2CH_2), -114.61 (ddd, *J* = 257.5, 27.4, 6.6 Hz, 1F, CF_2CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 41.73 – 41.25 (m), 40.20, 30.68, 29.21, 22.42, 21.62, 13.97. HRMS (ESI): Calculated for $C_9H_{14}ClF_4$ [M-I]: 233.0715, Found: 233.0725.



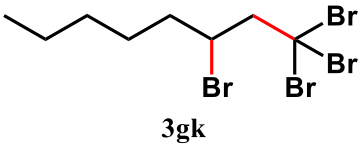
3gi

ethyl 2,2-difluoro-4-iodononanoate (**3gi**).[11] This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 63%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.37 (q, *J* = 7.2 Hz, 2H, CH_2CH_3), 4.25 (dtd, *J* = 8.8, 6.8, 4.3 Hz, 1H, C*H*I), 2.94 (dtd, *J* = 18.3, 16.0, 6.5 Hz, 1H, CH_2R_F), 2.76 (dddd, *J* = 17.8, 15.6, 12.6, 7.1 Hz, 1H, CH_2R_F), 1.79 (dddq, *J* = 34.2, 14.7, 9.8, 4.9 Hz, 2H, CH_2), 1.63 – 1.23 (m, 9H, $(CH_2)_3CH_3$), 0.93 (t, *J* = 7.0 Hz, 3H, CH_2CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ -102.14 (ddd, *J* = 262.9, 18.3, 12.6 Hz, 1F, CF_2), -106.77 (dt, *J* = 262.9, 17.2 Hz, 1F, CF_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 63.23, 45.37 (t, *J* = 23.2 Hz), 40.42, 30.71, 29.16, 23.34, 22.44, 13.98, 13.91. HRMS (ESI): Calculated for $C_{13}H_{19}F_2O_2$ [M-I]: 221.1348, Found: 221.1343.



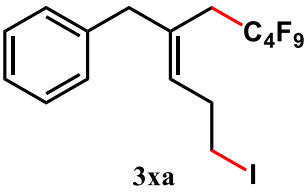
3gj

1,1,3-tribromooctane (**3gj**).[12] This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 63%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.93 (dd, *J* = 9.6, 4.0 Hz, 1H, C*H*Br_2), 4.15 (dddd, *J* = 11.8, 8.8, 5.1, 3.7 Hz, 1H, C*H*Br), 2.91 – 2.74 (m, 2H, CH_2CHBr_2), 1.98 – 1.81 (m, 2H, CH_2CHBr), 1.63 – 1.28 (m, 6H, CH_2), 0.98 – 0.89 (m, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 54.41, 53.50, 43.57, 38.46, 31.06, 26.89, 22.45, 13.97.



3gk

1,1,1,3-tetrabromooctane (**3gk**).[13] This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 59%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.23 (dq, *J* = 9.0, 4.5 Hz, 1H, C*H*Br), 3.86 (dd, *J* = 16.2, 4.5 Hz, 1H, C*H*$_2$R$_{Br}$), 3.57 (dd, *J* = 16.1, 4.9 Hz, 1H, C*H*$_2$R$_{Br}$), 2.10 (dddd, *J* = 14.2, 10.0, 6.0, 4.2 Hz, 1H, C*H*$_2$), 1.99 (dtd, *J* = 14.3, 9.4, 4.7 Hz, 1H, C*H*$_2$), 1.70 – 1.59 (m, 1H, C*H*$_2$), 1.59 – 1.48 (m, 1H, C*H*$_2$), 1.46 – 1.32 (m, 4H, C*H*$_2$), 1.01 – 0.86 (m, 3H, C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 66.93, 52.09, 39.72, 36.36, 30.92, 27.04, 22.50, 14.02. HRMS (ESI): Calculated for $C_8H_{14}Br_4$ [M]: 425.7829, Found: 425.7831.



3xa

(Z)-(4,4,5,5,6,6,7,7,7-nonafluoro-2-(3-iodopropylidene)heptyl)benzene (**3xa**). This product was obtained as colorless oil according to typical procedure for synthesis of **3**. Isolated yield was 76%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 2H, H$_{Ar}$), 7.31 – 7.22 (m, 2H, H$_{Ar}$), 7.22 – 7.13 (m, 1H, H$_{Ar}$), 5.64 (dt, *J* = 26.3, 7.2 Hz, 1H, C=C*H*), 3.55 (d, *J* = 25.3 Hz, 2H, C*H*$_2$I), 3.24 (dt, *J* = 11.4, 7.0 Hz, 2H, C*H*$_2$), 2.89 (q, *J* = 7.1 Hz, 1H, C*H*$_2$), 2.83 – 2.56 (m, 3H, C*H*$_2$). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.08 (q, *J* = 9.5 Hz, 3F, C*F*$_3$), -111.93 (p, *J* = 17.5 Hz, 1F, C*F*$_2$), -112.65 (p, *J* = 16.9 Hz, 1F, C*F*$_2$), -124.19 (ddd, *J* = 59.1, 13.3, 7.6 Hz, 2F, C*F*$_2$), -125.93 (ddt, *J* = 28.0, 15.4, 6.9 Hz, C*F*$_2$CH$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.18 (d, *J* = 35.1 Hz), 133.51 (d, *J* = 58.0 Hz), 129.68 (d, *J* = 49.1 Hz), 128.96 (d, *J* = 58.4 Hz), 128.62 (d, *J* = 7.2 Hz), 126.63 (d, *J* = 4.7 Hz), 44.83, 36.61 (d, *J* = 37.5 Hz), 32.30, 30.06, 4.39 (d, *J* = 69.7 Hz). HRMS (ESI): Calculated for $C_{16}H_{14}F_9$ [M-I]: 377.0946, Found: 377.0937.

5. Mechanistic study

5.1 Stoichiometric NMR Reaction performed in a 1:1 $B(C_6F_5)_3$/$PhNMe_2$ ratio

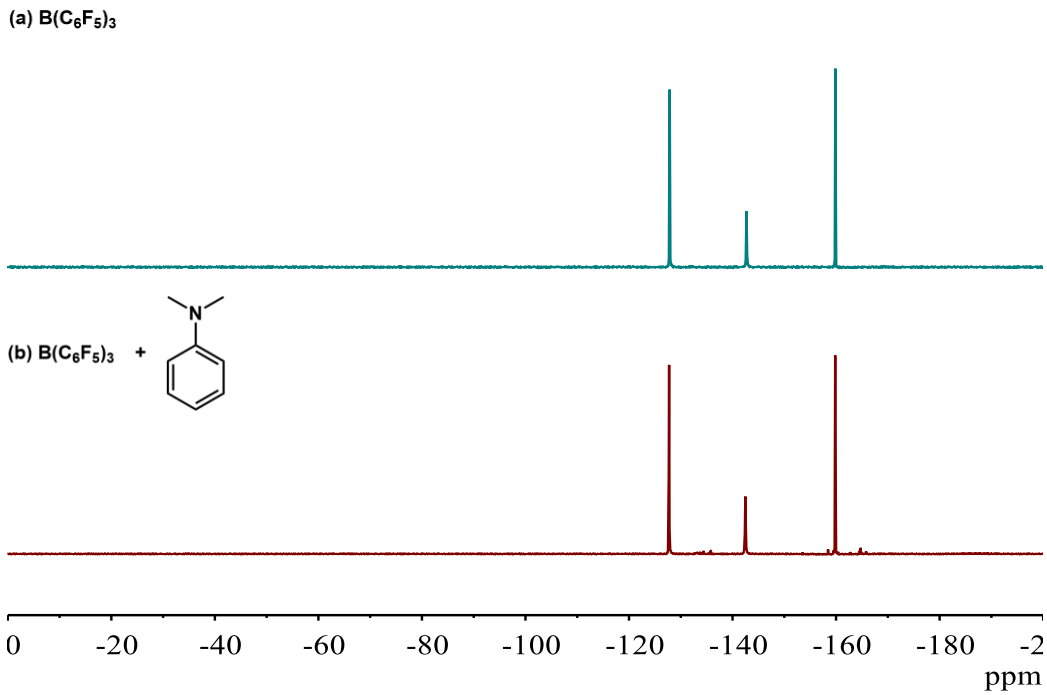


Figure S2. ^{19}F NMR spectrum obtained for (a) $B(C_6F_5)_3$, (b) mixture of $B(C_6F_5)_3$ and $PhNMe_2$ in a 1:1 ratio ($CDCl_3$, 471 MHz).

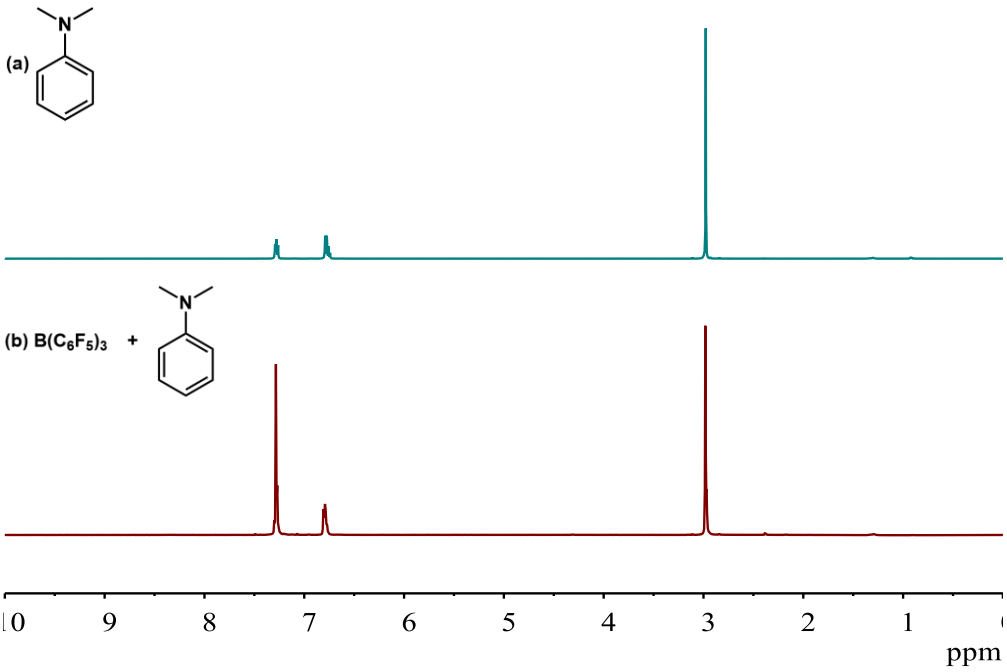


Figure S3. ^{1}H NMR spectrum obtained for (a) $PhNMe_2$, (b) mixture of $B(C_6F_5)_3$ and $PhNMe_2$ in a 1:1 ratio ($CDCl_3$, 500 MHz).

5.2 UV-Vis absorption experiment

In an argon-filled glovebox, seven 5 mL glass reaction tubes were added with different combination of $B(C_6F_5)_3$, $PhNMe_2$, **2a**, $B(C_6F_5)_3$ and $PhNMe_2$ in different ratios ($B(C_6F_5)_3$: $PhNMe_2$ = 1:1, $B(C_6F_5)_3$: **2a** =1:1 ratio, $PhNMe_2$: **2a** = 1:1, $B(C_6F_5)_3$: $PhNMe_2$: **2a** = 1:1:1) in the concentration of 0.2 mM in $CDCl_3$ (1 mL), respectively. These tubes were taken out of the glovebox and stirred at room temperature under the irradiation of blue LED for 3 h. The reaction mixtures were then diluted by $CHCl_3$ to 0.5 μM for measurement of UV-Vis absorption.

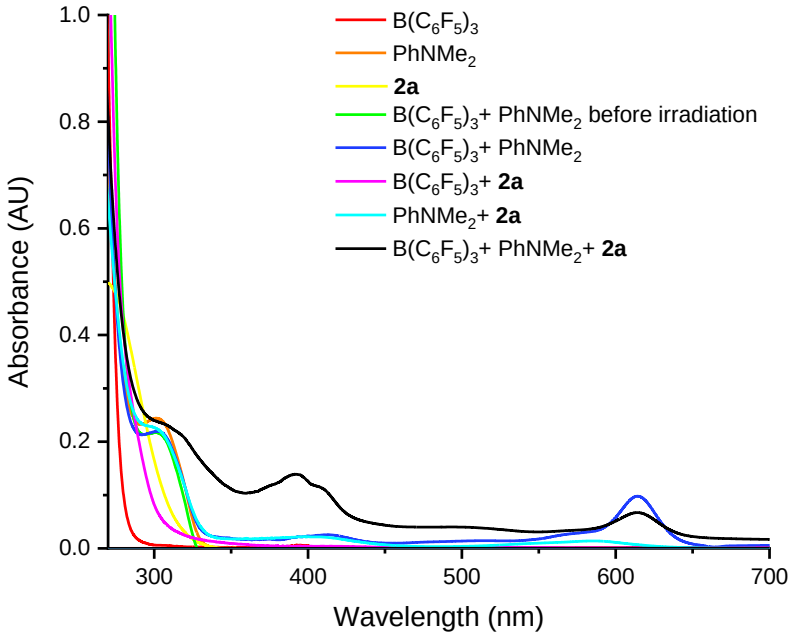


Figure S4. UV-vis absorption spectra measured in $CDCl_3$ (0.5 μM).

5.3 Stoichiometric NMR Reaction performed in a 1:1:1 $B(C_6F_5)_3$/$PhNMe_2$/2a ratio

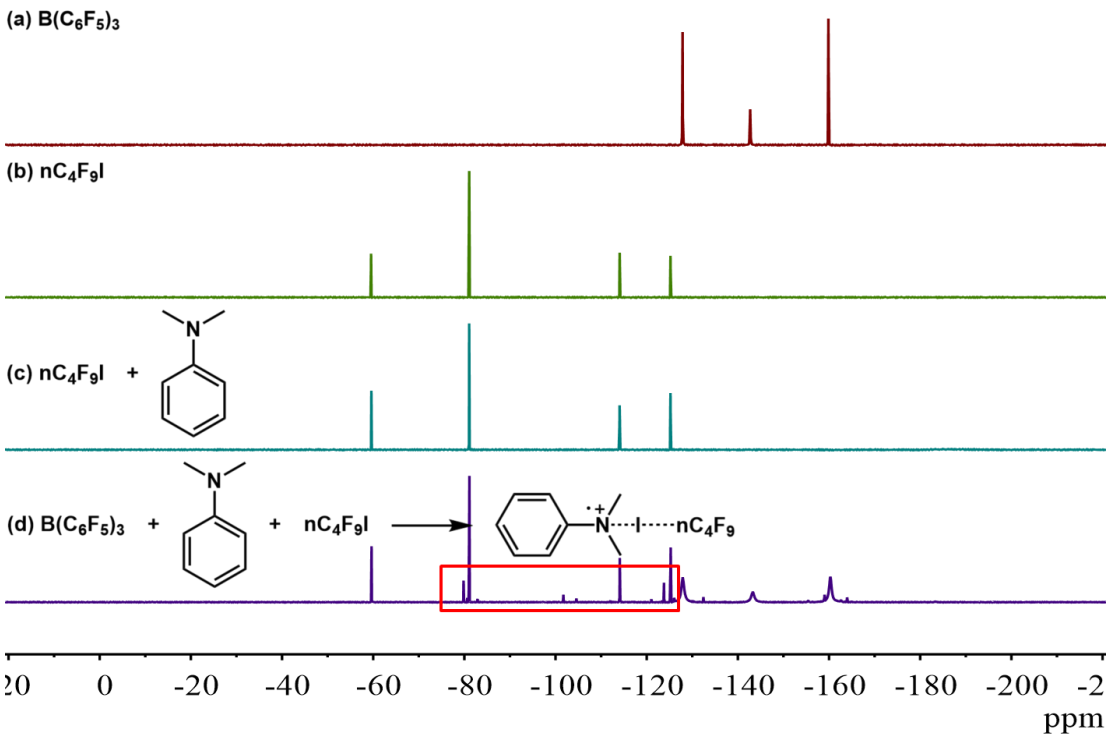
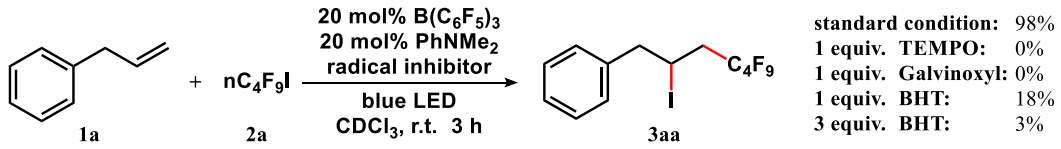


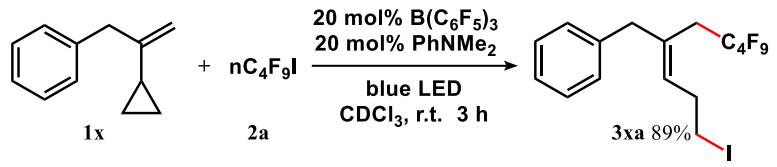
Figure S5. ^{19}F NMR spectrum obtained for (a) $B(C_6F_5)_3$, (b) **2a**, (c) mixture of $PhNMe_2$ and **2a** in a 1:1 ratio, (d) reaction of $B(C_6F_5)_3$, **2a** and $PhNMe_2$ in a 1:1:1 ratio ($CDCl_3$, 471 MHz).

5.4. Control experiments performed by using radical inhibitors



In an argon-filled glovebox, a 2 mL NMR tube were added with $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol), $CDCl_3$ (0.5 mL), $PhNMe_2$ (2.4 mg, 0.02 mol), **2a** (41.5 mg, 0.12 mmol), **1a** (11.8 mg, 0.10 mmol), mesitylene (12.0 mg, 0.10 mmol) as internal standard and with or without radical inhibitors (1-3 equiv.), respectively. The NMR tubes were then taken out of the glovebox and stirred at room temperature under the irradiation of blue LED for 3 h. The yields were determined by ^1H NMR spectroscopy.

5.5. Radical clock experiment



In an argon-filled glovebox, a 2 mL NMR tube was added $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol), $CDCl_3$ (0.5 mL), $PhNMe_2$ (2.4 mg, 0.02 mol), **2a** (41.5 mg, 0.12 mmol) **1x** (15.8 mg, 0.10 mmol) and mesitylene (12.0 mg, 0.10 mmol) as internal stand in sequence. Then the NMR tube was taken out of the glovebox and stirred at room temperature under blue LED irradiation for 3 h. The yields were determined by ^1H NMR spectroscopy.

5.6. EPR experiments

In an argon-filled glovebox, a 5 mL glass reaction tube was added $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol), $CDCl_3$ (0.5 mL) and $PhNMe_2$ (1.2 mg, 0.01 mol) in sequence. Then the tube was taken out of the glovebox and stirred at room temperature under blue LED irradiation for 1 h and the reaction mixture was transferred to an EPR tube for analysis.

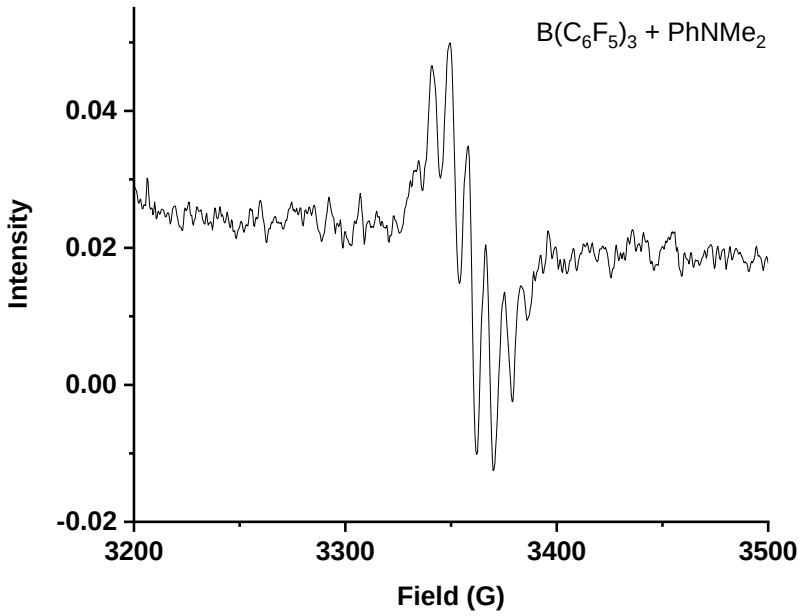


Figure S6. EPR spectrum of the mixture of 0.01 mmol $B(C_6F_5)_3$ and 0.01 mmol $PhNMe_2$ in $CDCl_3$ at room temperature after irradiation with blue LED.

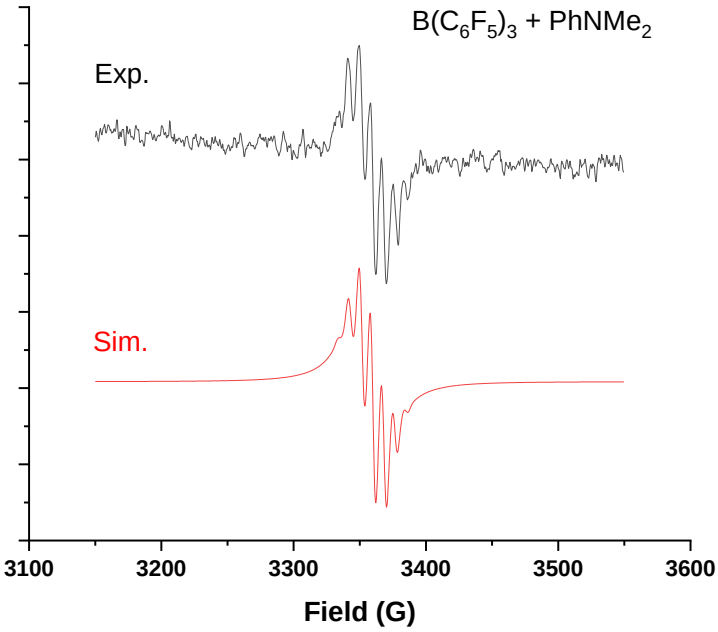


Figure S7. Experimental (above) and simulated (below) EPR spectrum of the mixture of $B(C_6F_5)_3$ and $PhNMe_2$. Red line: superposition of $B(C_6F_5)_3^{\cdot-}$ (g = 2.003) and $PhNMe_2^{\cdot+}$ (g = 2.00401).

In an argon-filled glovebox, a 5 mL glass reaction tube was added with $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol), $CDCl_3$ (0.5 mL), $PhNMe_2$ (2.4 mg, 0.02 mol), **2a** (34.9 mg, 0.10 mmol) and DMPO (11.0 mg, 0.10 mmol). The tube was taken out of the glovebox and stirred at room temperature under the irradiation of blue LED for 1 h, and then reaction mixture was transferred to an EPR tube for analysis.

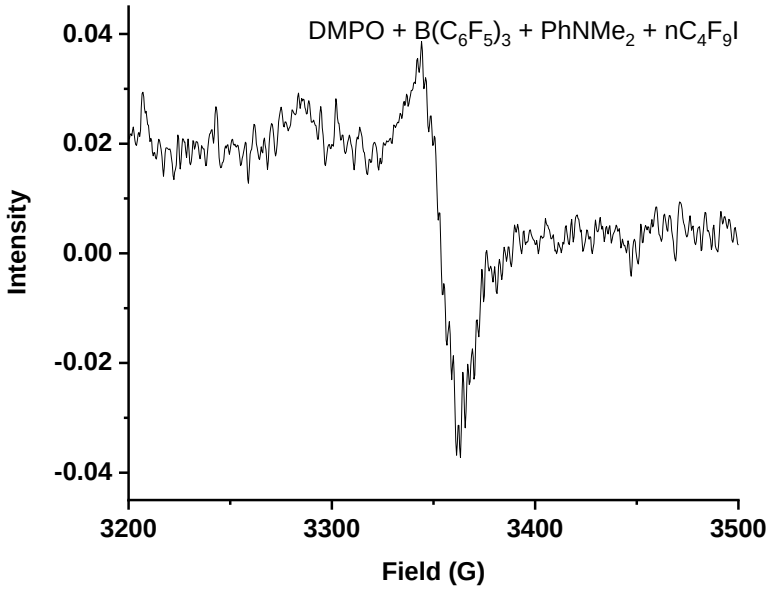


Figure S8. EPR spectrum obtained for the mixture of 0.02 mmol $B(C_6F_5)_3$, 0.02 mmol $PhNMe_2$, 0.10 mmol **2a** and 0.10 mmol DMPO in $CDCl_3$ at room temperature after irradiation of blue LED.

In an argon-filled glovebox, a 5 mL glass reaction tube was added with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol), $CDCl_3$ (0.5 mL) and $PhNEt_2$ (1.5 mg, 0.01 mol). The tube was taken out of the glovebox and stirred at room temperature under the irradiation of blue LED for 1 h, and then reaction mixture was transferred to an EPR tube for analysis.

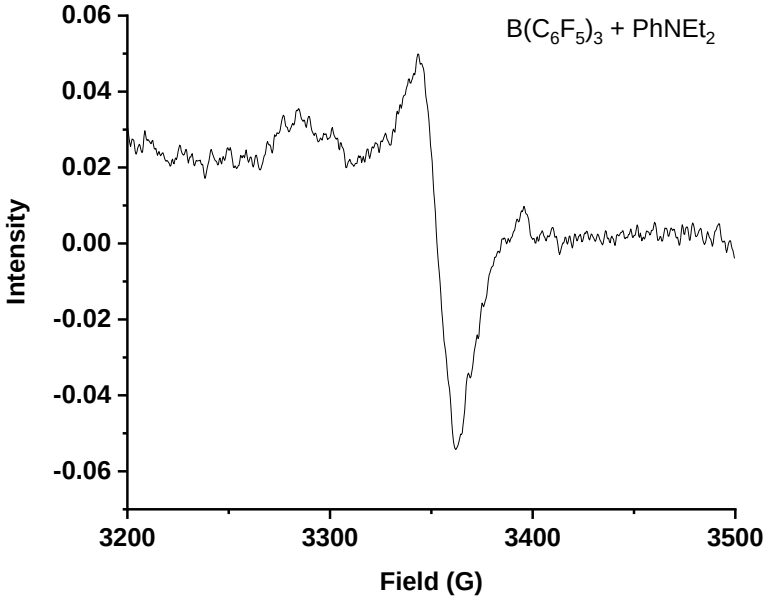


Figure S9. EPR spectrum obtained for the mixture of 0.01 mmol $B(C_6F_5)_3$ and 0.01 mmol $PhNEt_2$ in $CDCl_3$ at room temperature after the irradiation of blue LED.

5.7. ESI HRMS of standard reaction mixture

In an argon-filled glovebox, a 5 mL glass reaction tube was added $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol), $CDCl_3$ (0.5 mL) $PhNMe_2$ (2.4 mg, 0.02 mol), **2a** (34.9 mg, 0.10 mmol) and **1a** (11.8 mg, 0.10 mmol). The tube was taken out of the glovebox and stirred at room temperature under the irradiation of blue LED for 3 h. Then the reaction mixture was diluted by acetonitrile to an appropriate concentration for ESI HRMS measure.

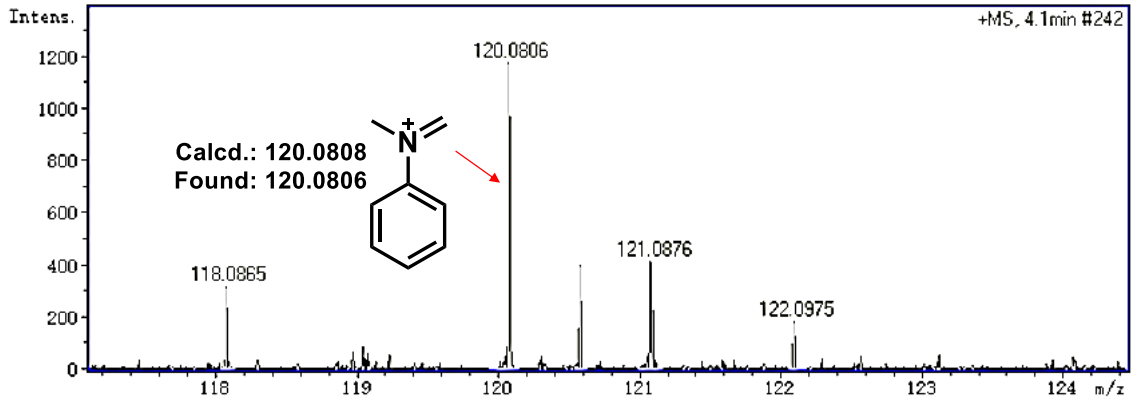


Figure S10. ESI HRMS of standard reaction mixture

5.8. In-situ NMR reaction of 1a and 2a

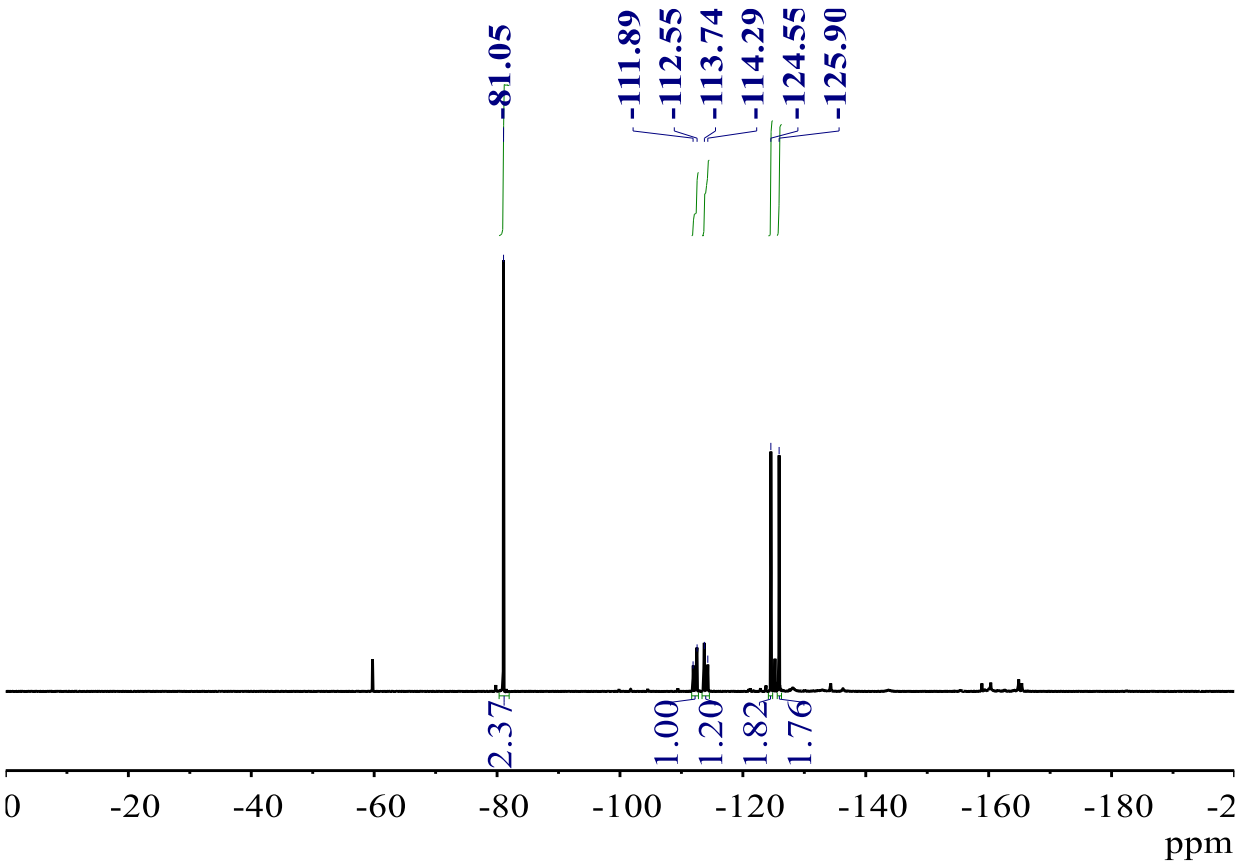
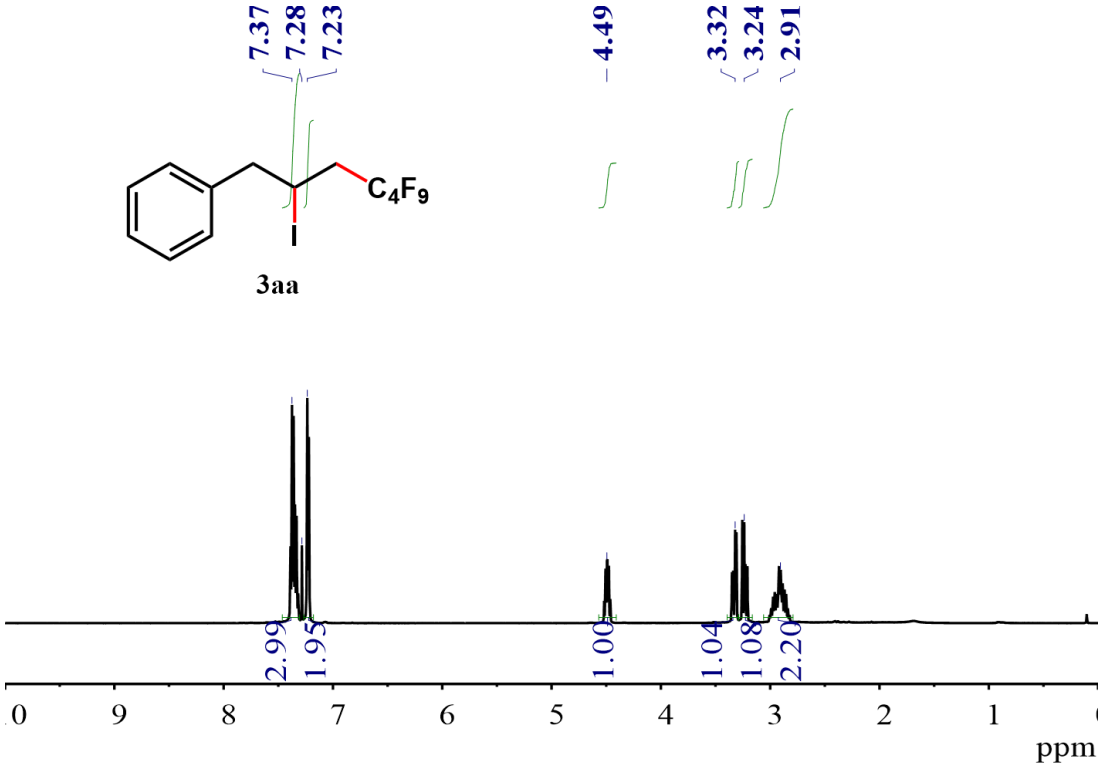
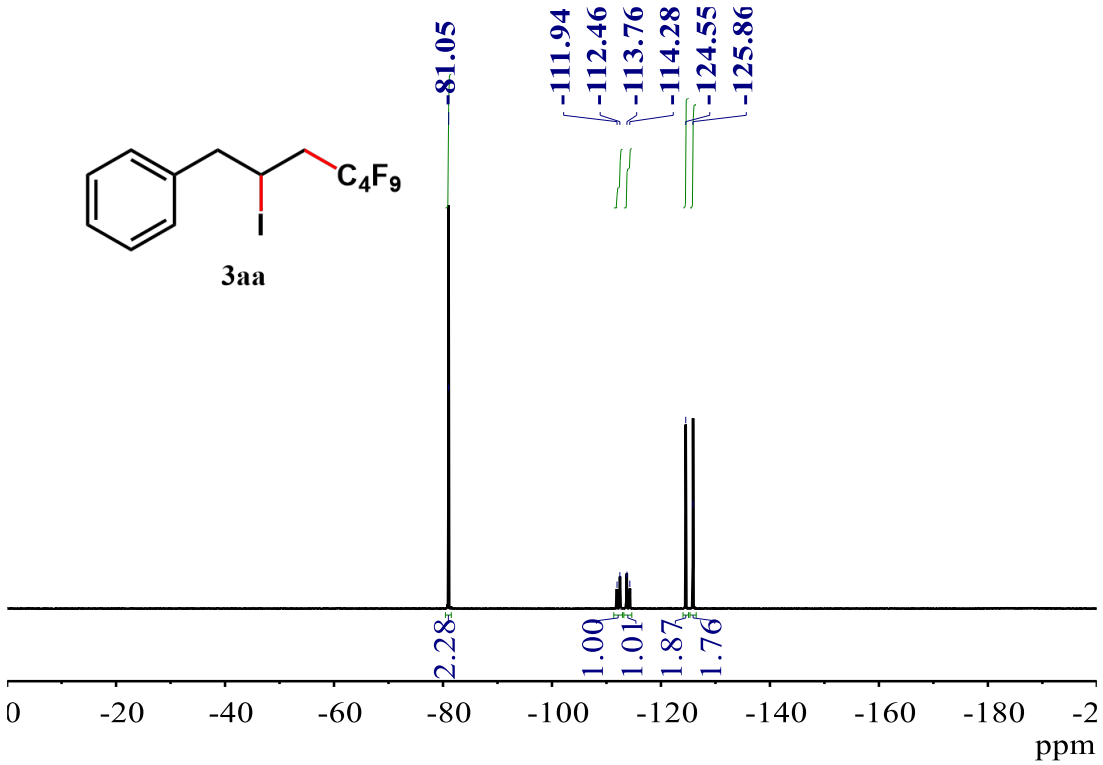


Figure S11. In-situ ^{19}F NMR spectrum obtained for reaction performed under standard condition ($B(C_6F_5)_3$ 0.02 mmol, $PhNMe_2$ 0.02 mol, **2a** 0.12 mmol, **1a** 0.10 mmol in 0.5 mL $CDCl_3$).

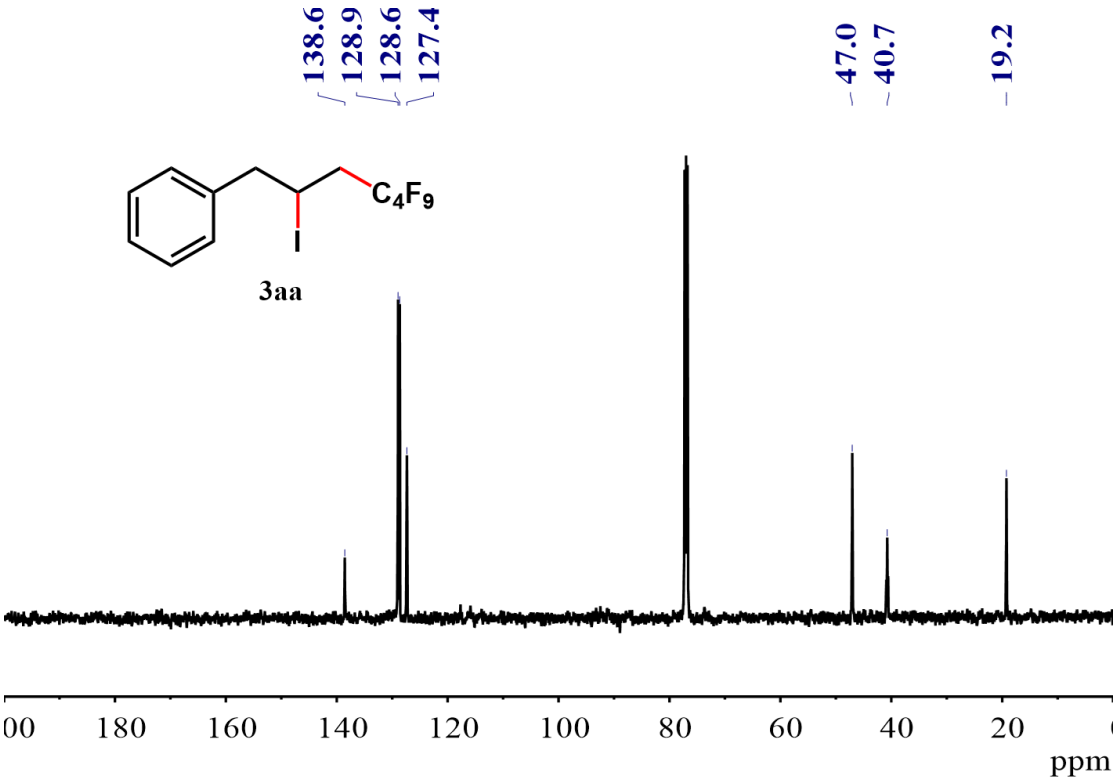
6. NMR spectra of products



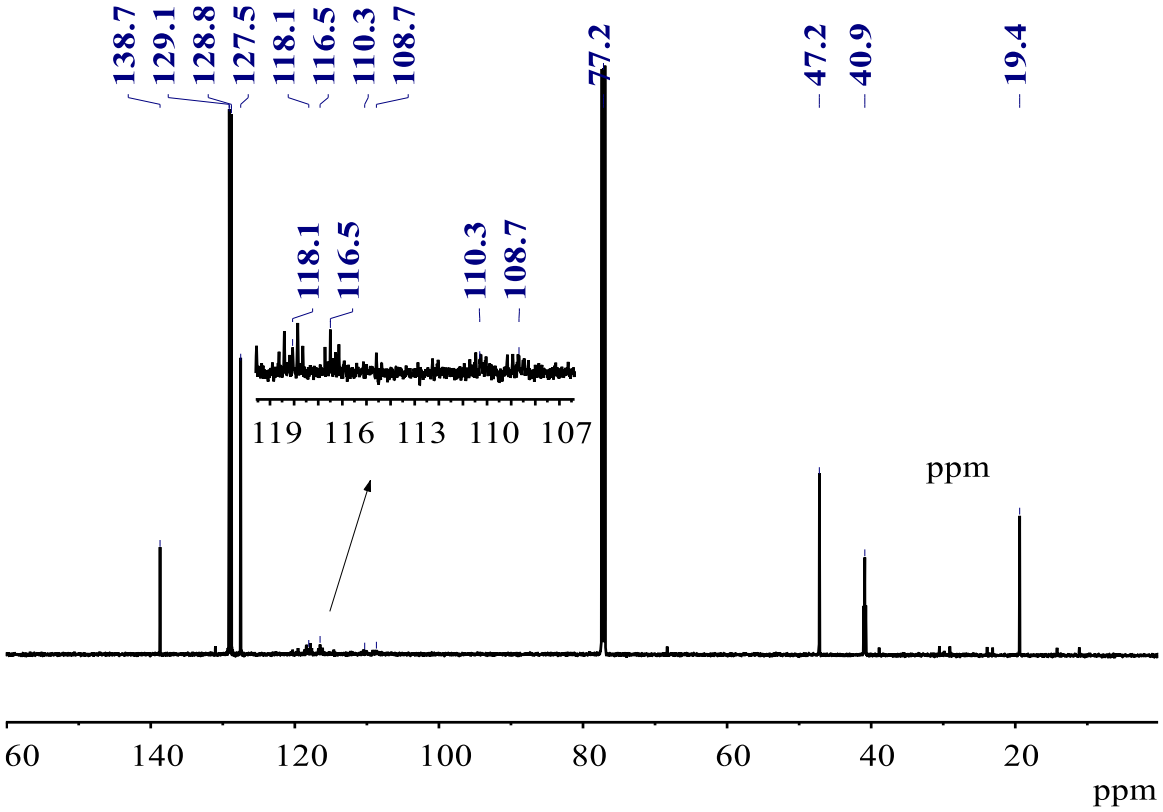
^{1}H NMR spectrum for (4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)benzene **3aa** ($CDCl_3$, 500 MHz).



^{19}F NMR spectrum for (4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)benzene **3aa** ($CDCl_3$, 471 MHz).

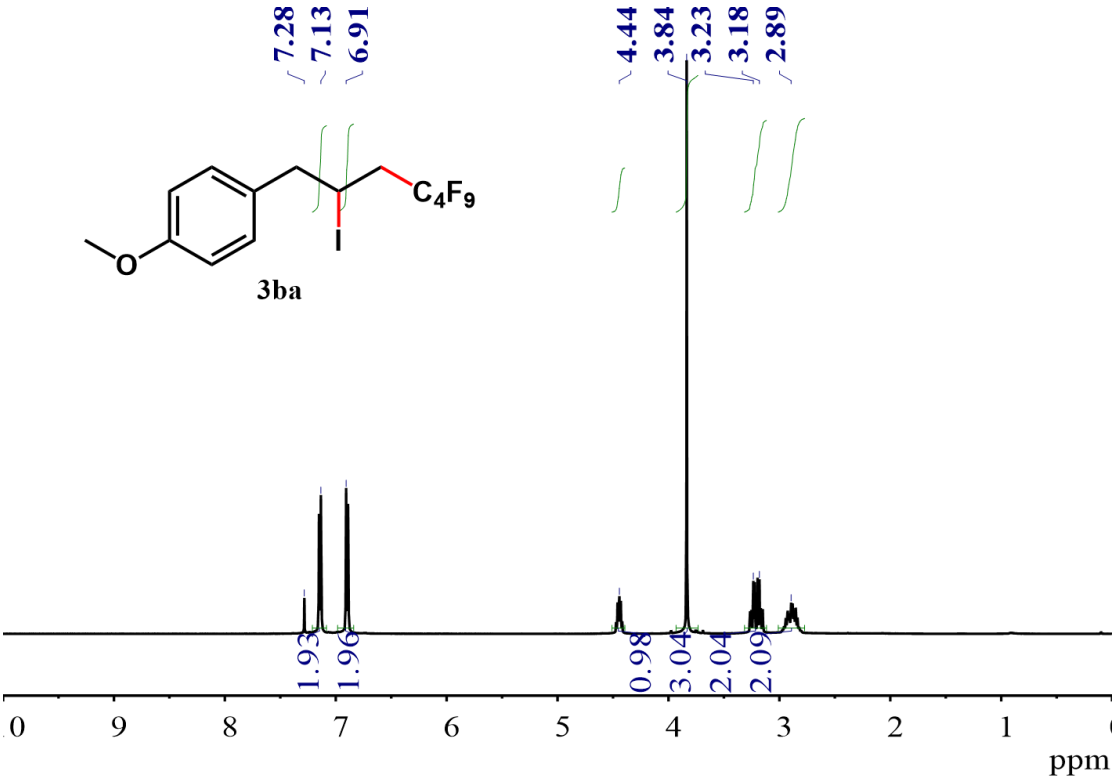


^{13}C NMR spectrum for (4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)benzene **3aa** ($CDCl_3$, 126 MHz).

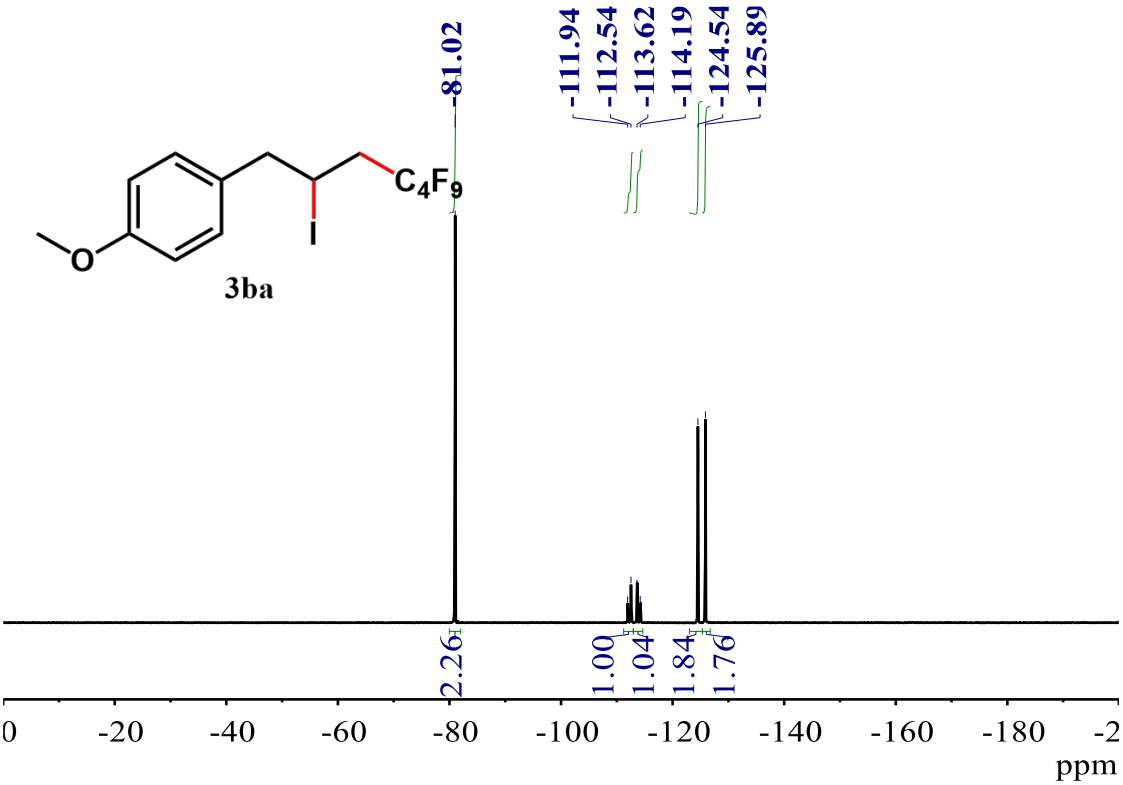


^{13}C NMR spectrum for (4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)benzene **3aa** ($CDCl_3$, 151 MHz

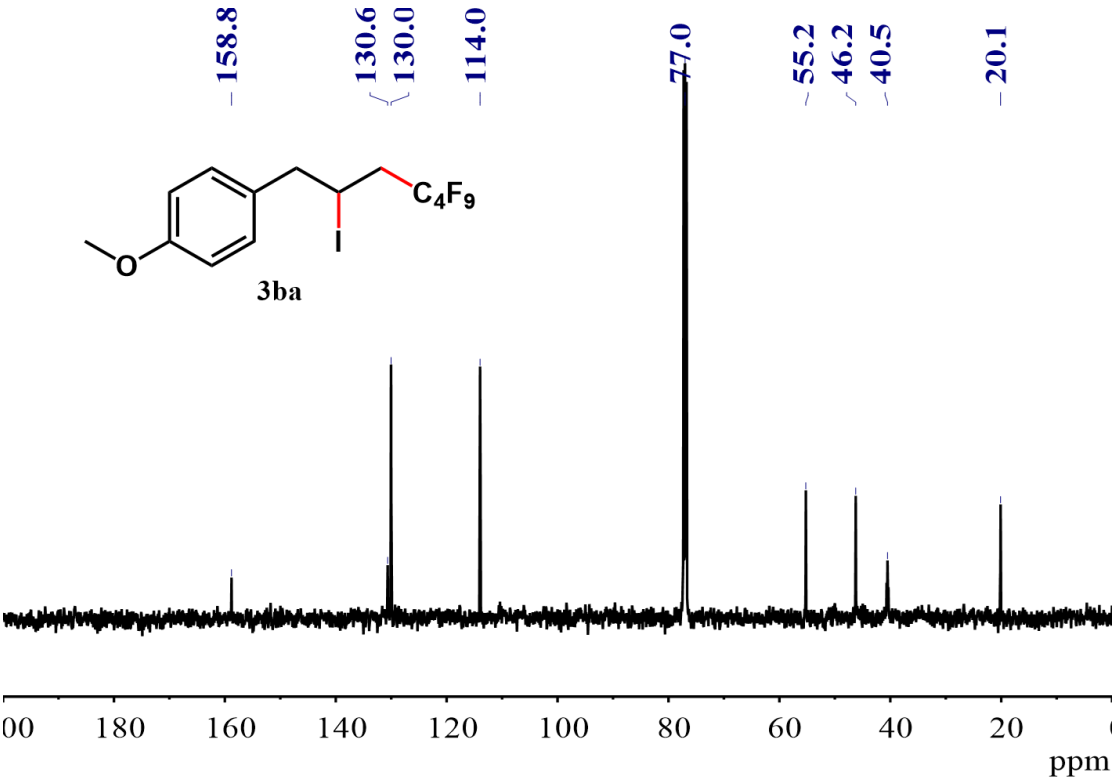
C_{Ph}: δ 138.71, 129.10, 128.80, 127.51, $CF_2CF_2C_2F_5$: 118.76 – 117.44 (m), CH_2CF_2: 116.85 – 116.22 (m), CF_2CF_3: 111.09 – 109.78 (m), $CF_2CF_2CF_3$: 109.37 – 108.16 (m), $PhCH_2$: 47.19 (d, J = 1.8 Hz), $CH_2C_4F_9$: 40.89 (t, J = 21.0 Hz), *C*HI: 19.39).



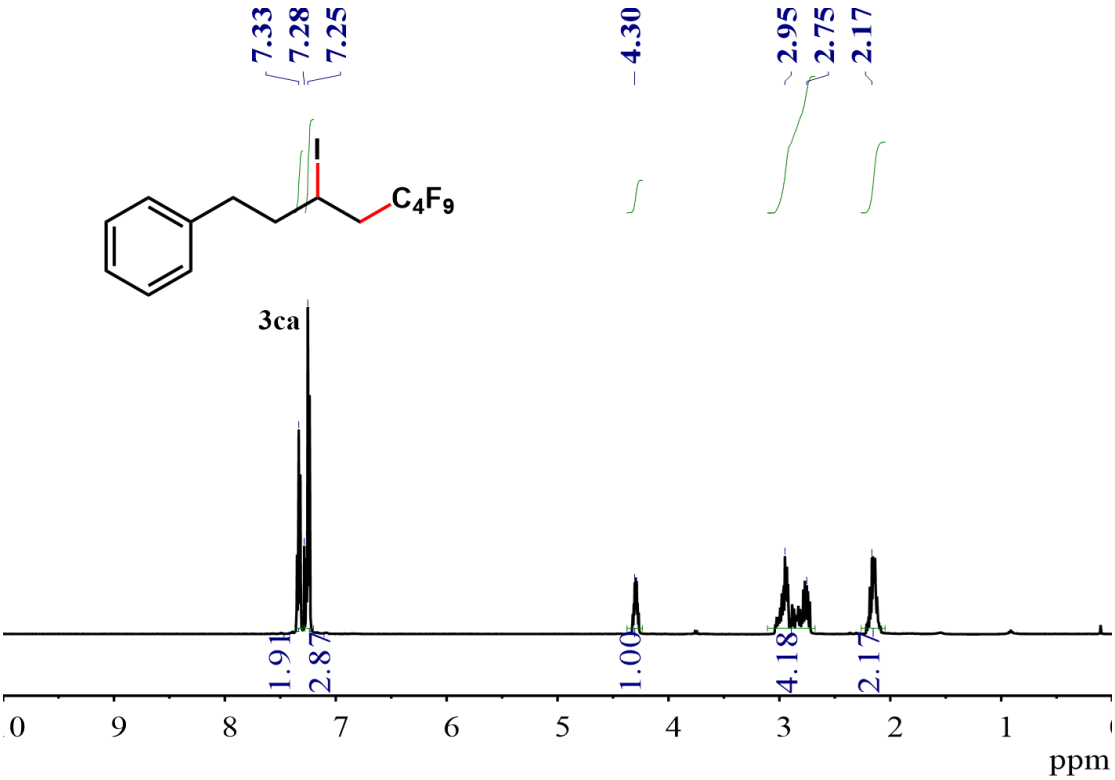
^{1}H NMR spectrum for 1-methoxy-4-(4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)benzene **3ba** ($CDCl_3$, 500 MHz).



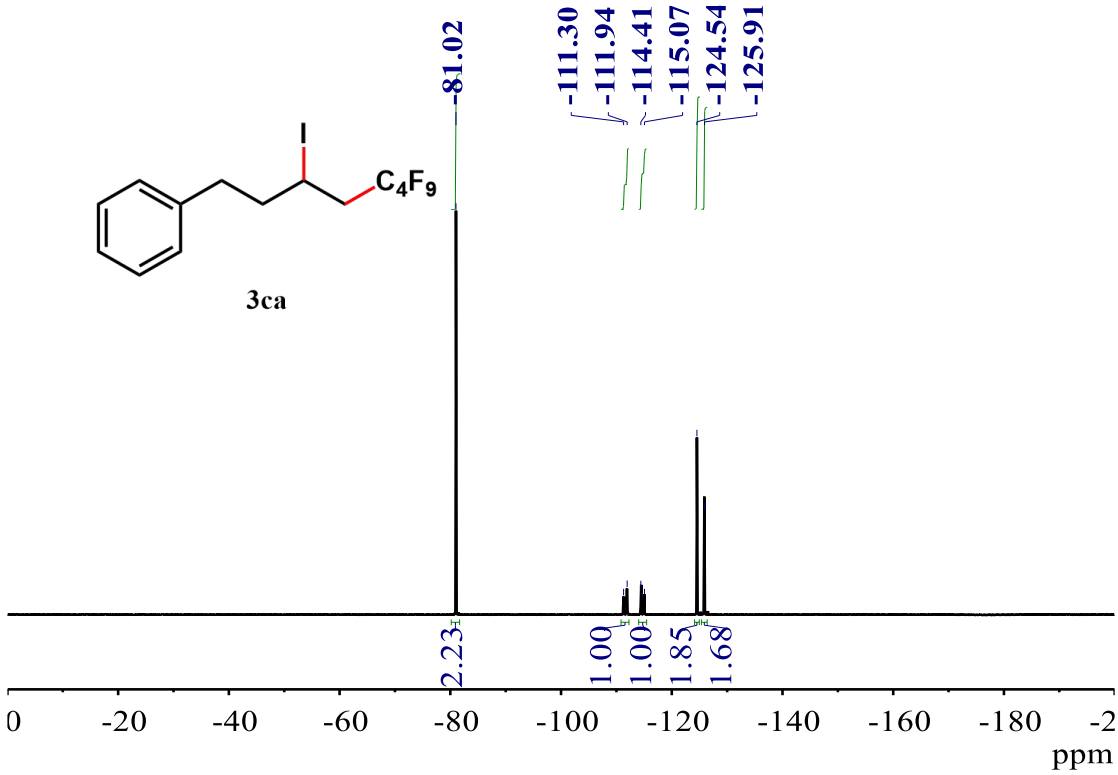
^{19}F NMR spectrum for 1-methoxy-4-(4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)benzene **3ba** ($CDCl_3$, 471 MHz).



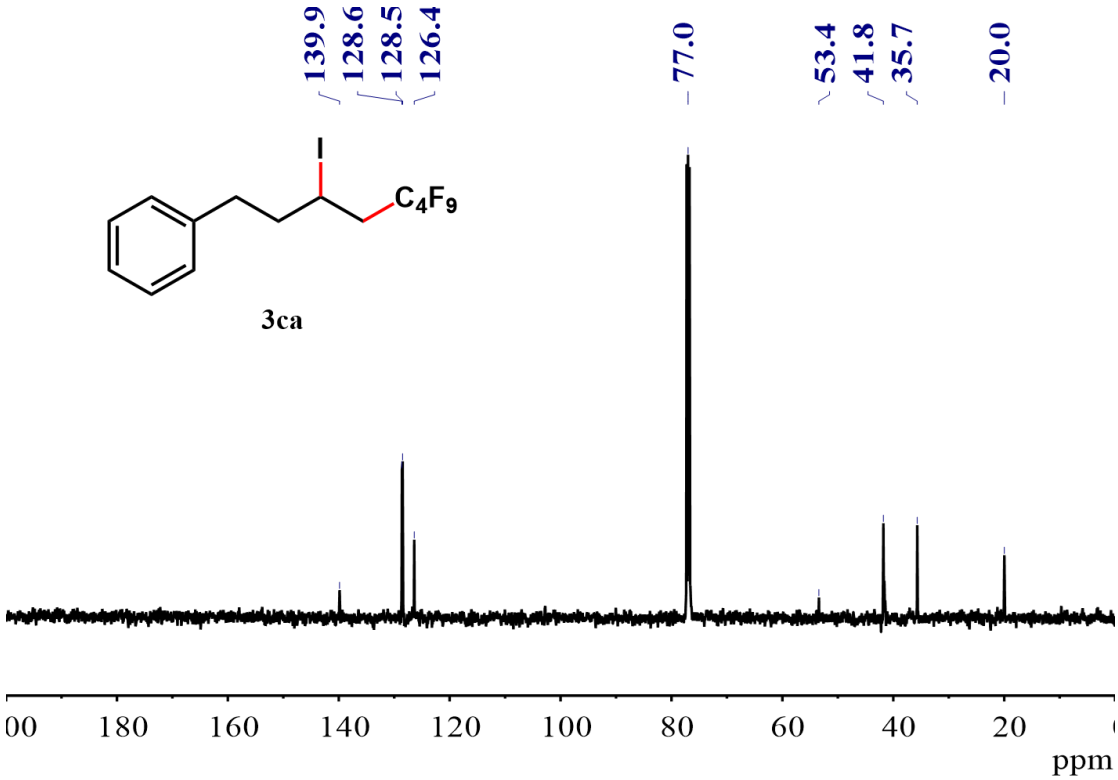
^{13}C NMR spectrum for 1-methoxy-4-(4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)benzene **3ba** ($CDCl_3$, 126 MHz).



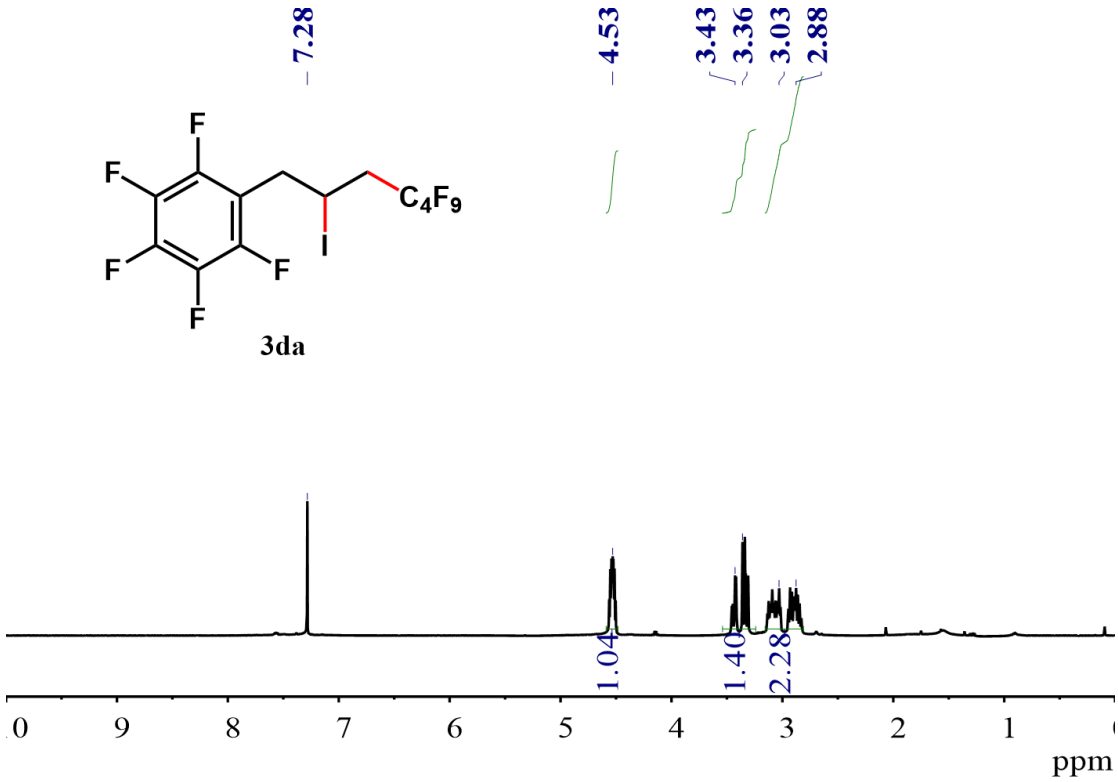
^{1}H NMR spectrum for (5,5,6,6,7,7,8,8,8-nonafluoro-3-iodooctyl)benzene **3ca** ($CDCl_3$, 500 MHz).



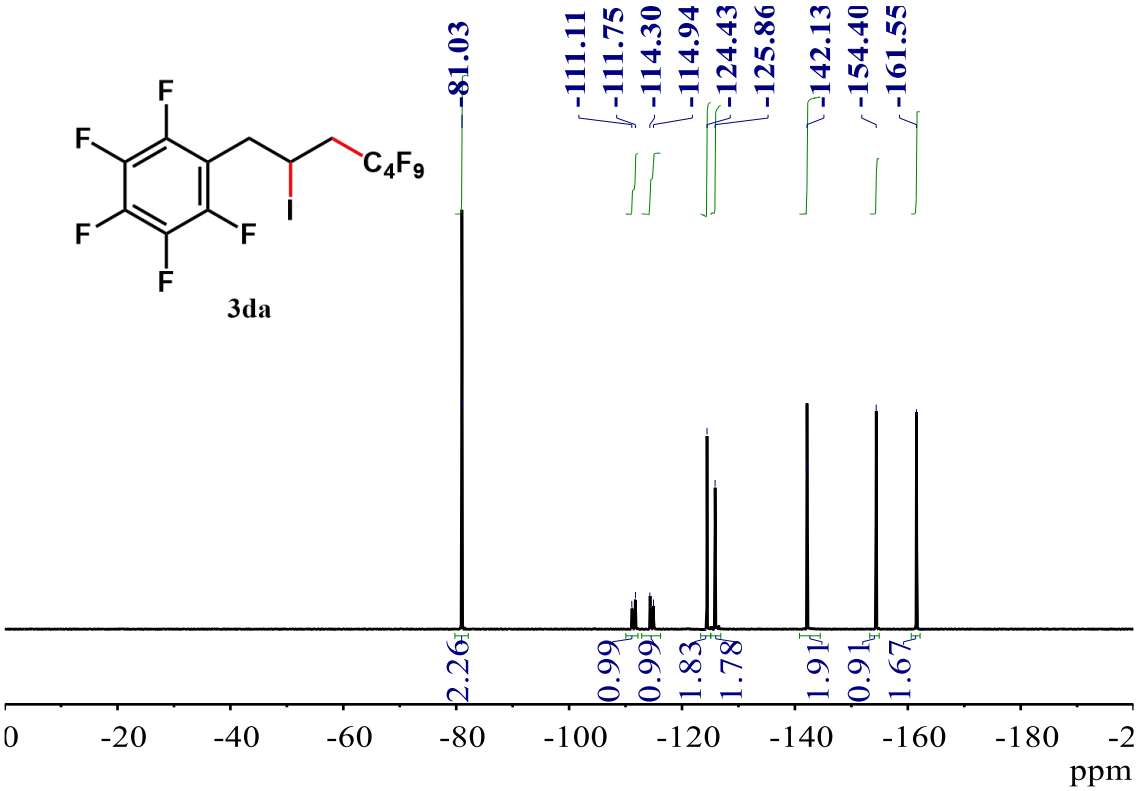
^{19}F NMR spectrum for (5,5,6,6,7,7,8,8,8-nonafluoro-3-iodooctyl)benzene **3ca** ($CDCl_3$, 471 MHz).



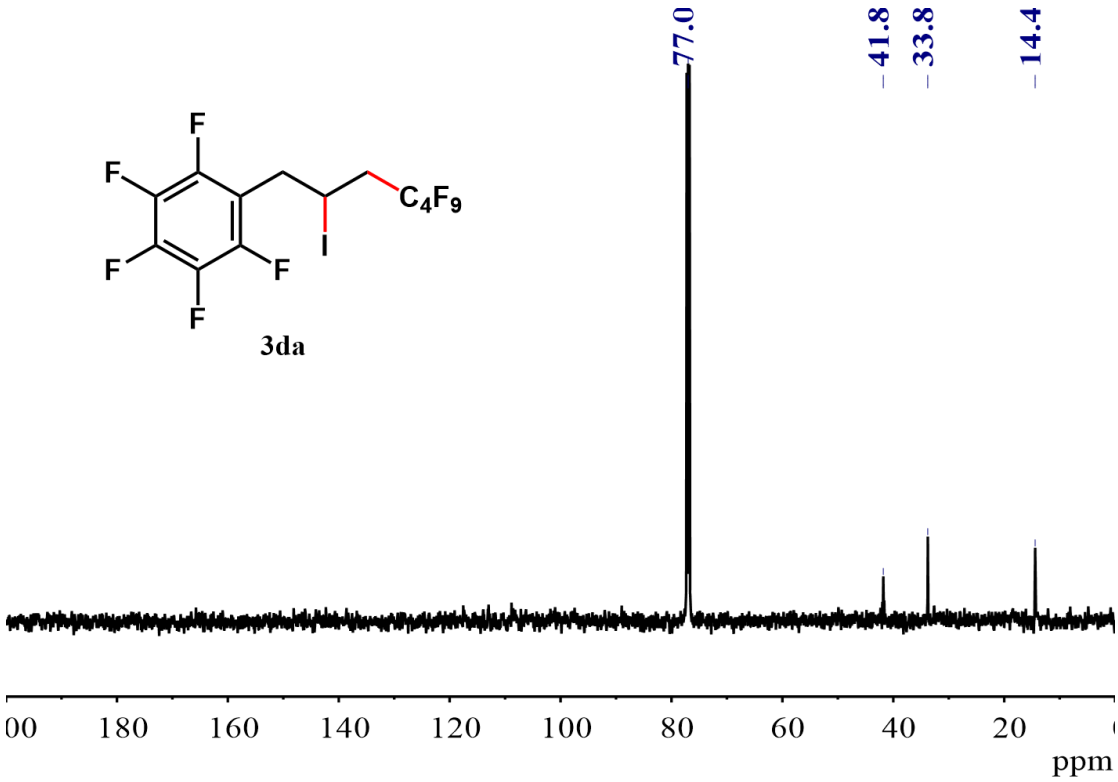
^{13}C NMR spectrum for (5,5,6,6,7,7,8,8,8-nonafluoro-3-iodooctyl)benzene **3ca** ($CDCl_3$, 126 MHz).



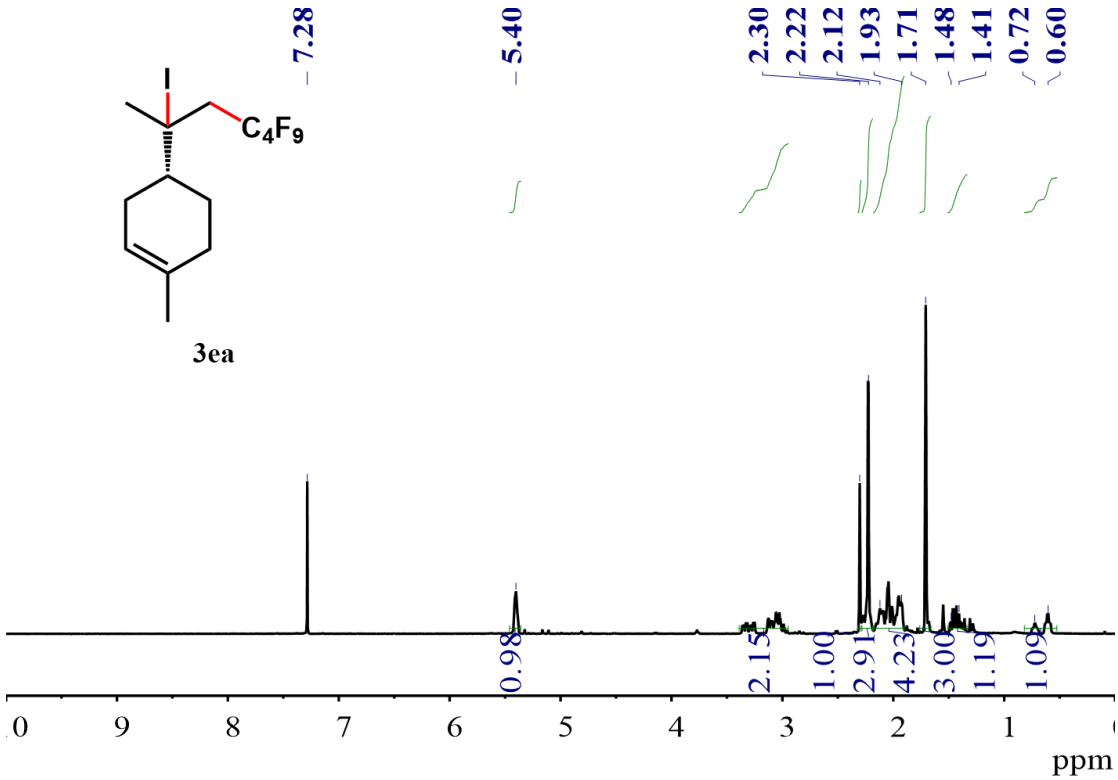
^{1}H NMR spectrum for 1,2,3,4,5-pentafluoro-6-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)benzene **3da** ($CDCl_3$, 500 MHz).



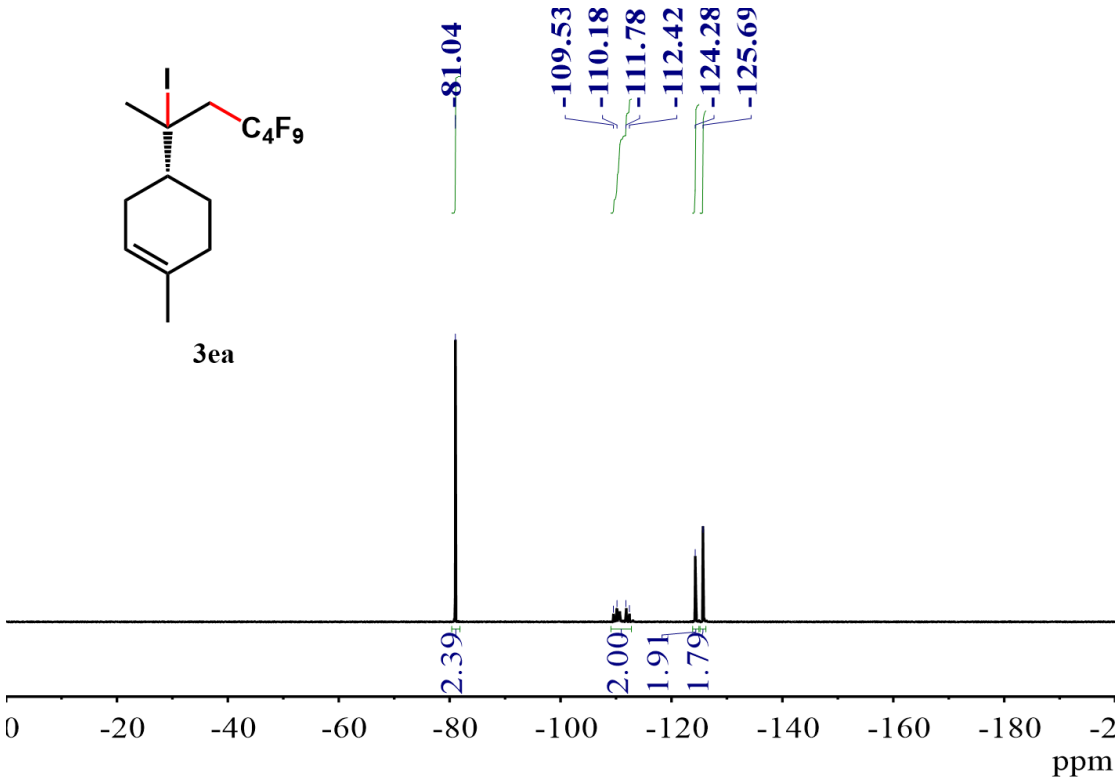
^{19}F NMR spectrum for 1,2,3,4,5-pentafluoro-6-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)benzene **3da** ($CDCl_3$, 471 MHz).



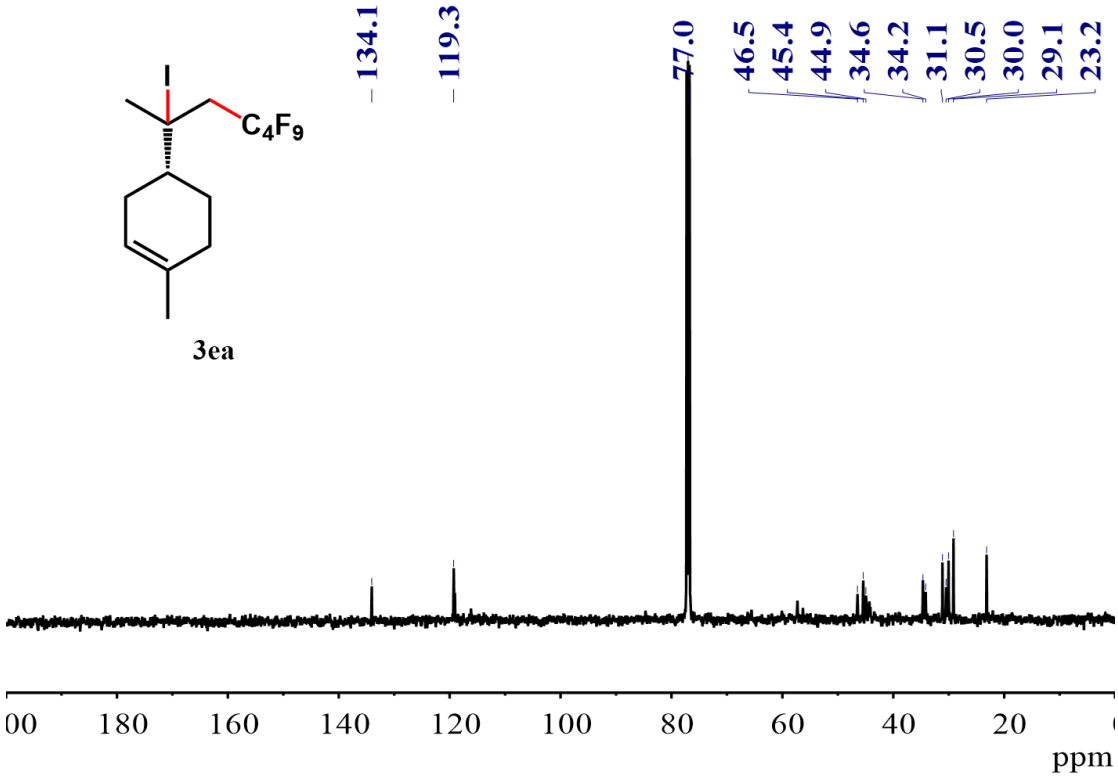
^{13}C NMR spectrum for 1,2,3,4,5-pentafluoro-6-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)benzene **3da** ($CDCl_3$, 126 MHz).



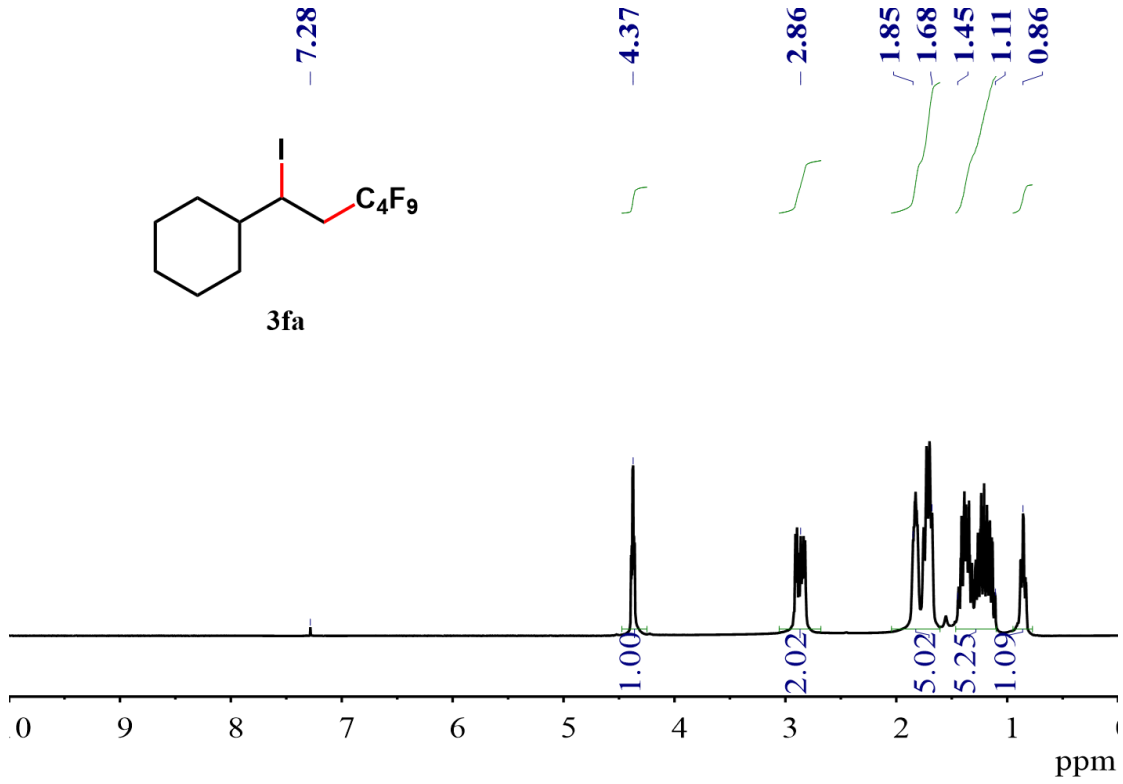
^{1}H NMR spectrum for (4R)-1-methyl-4-(4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptan-2-yl)cyclohex-1-ene **3ea** ($CDCl_3$, 500 MHz).



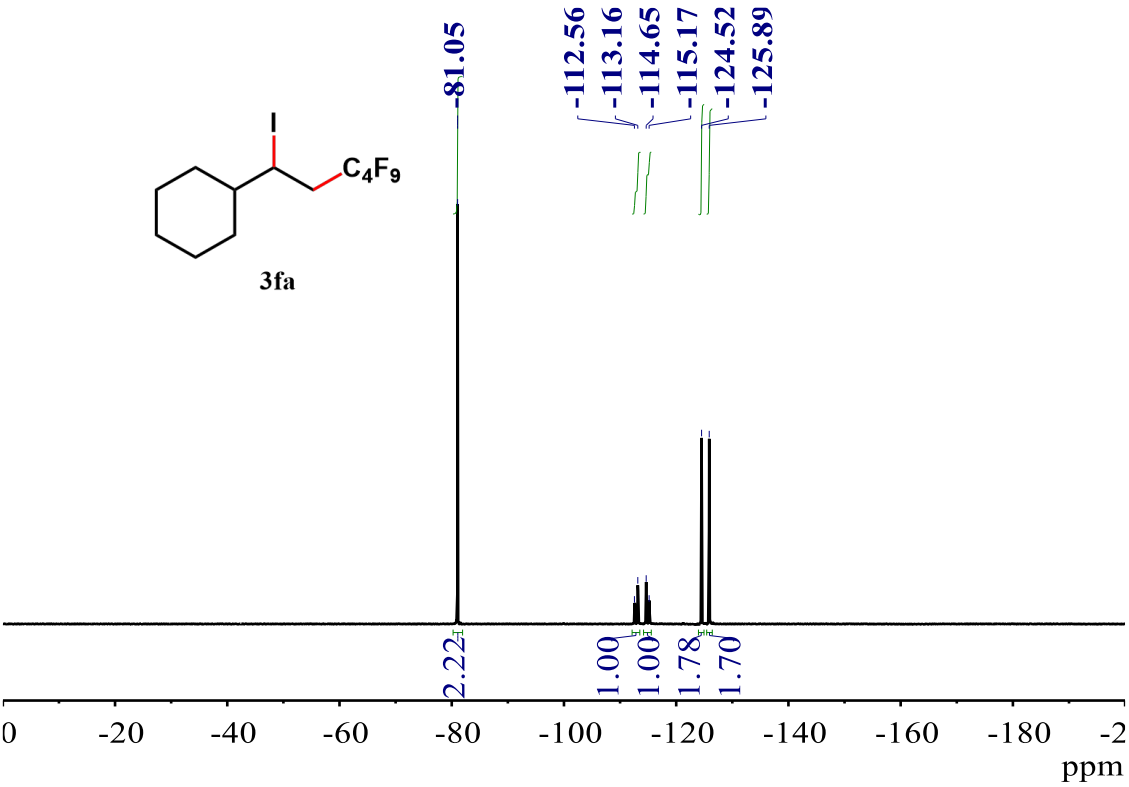
^{19}F NMR spectrum for (4R)-1-methyl-4-(4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptan-2-yl)cyclohex-1-ene **3ea** ($CDCl_3$, 471 MHz).



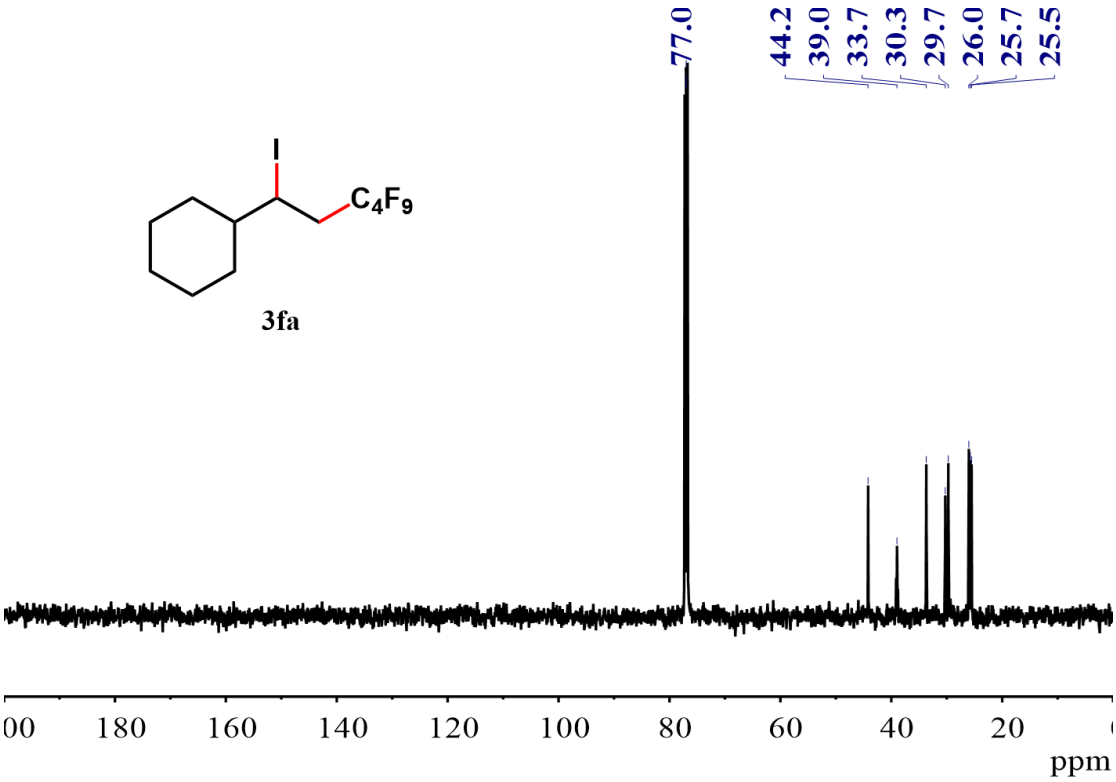
^{13}C NMR spectrum for (4R)-1-methyl-4-(4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptan-2-yl)cyclohex-1-ene **3ea** ($CDCl_3$, 126 MHz).



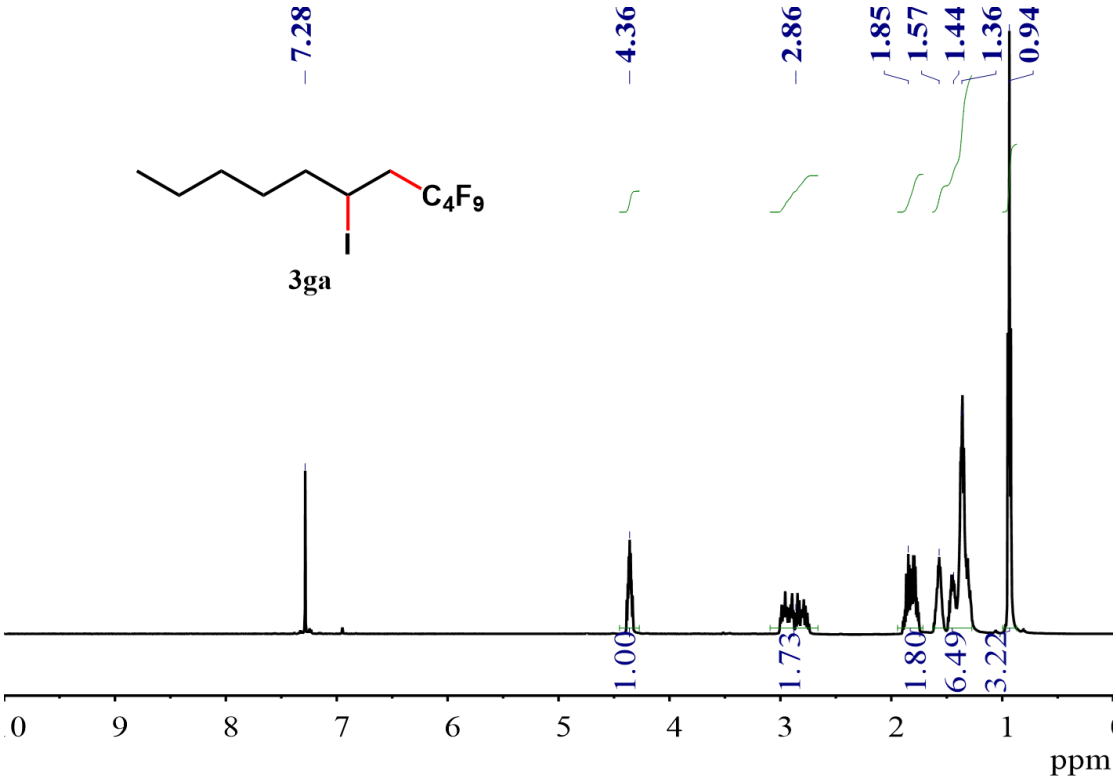
^{1}H NMR spectrum for (3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)cyclohexane **3fa** ($CDCl_3$, 500 MHz).



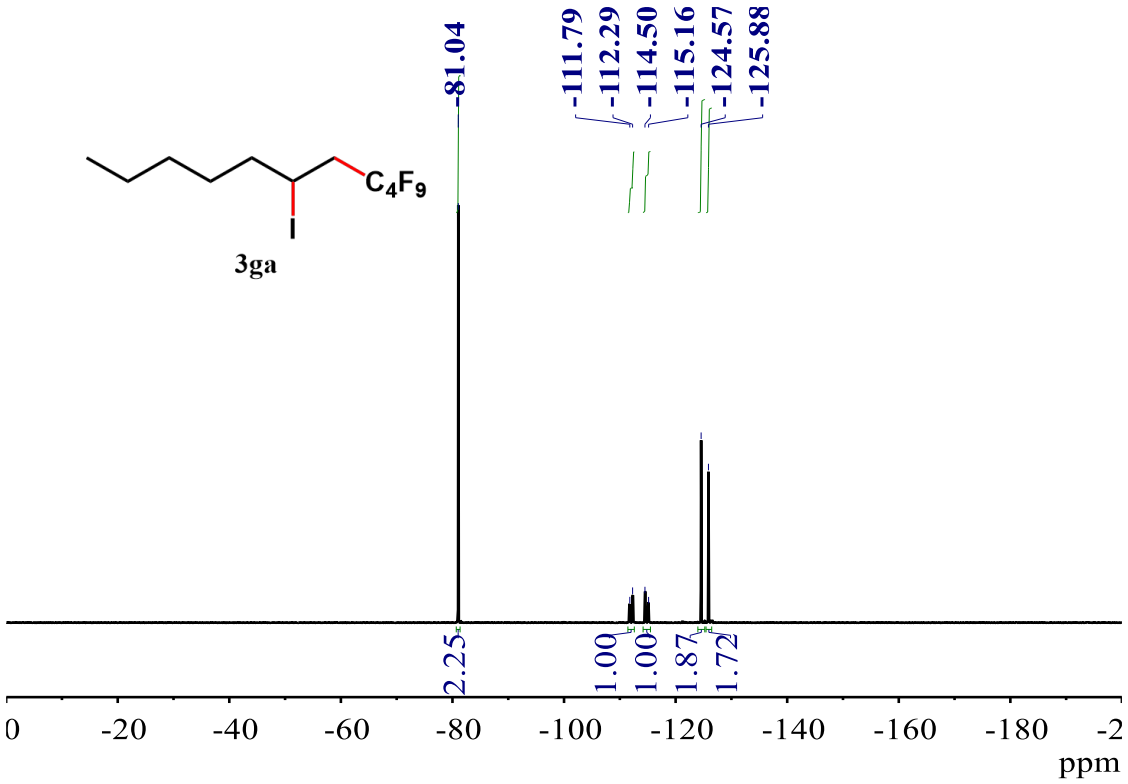
^{19}F NMR spectrum for (3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)cyclohexane **3fa** ($CDCl_3$, 471 MHz).



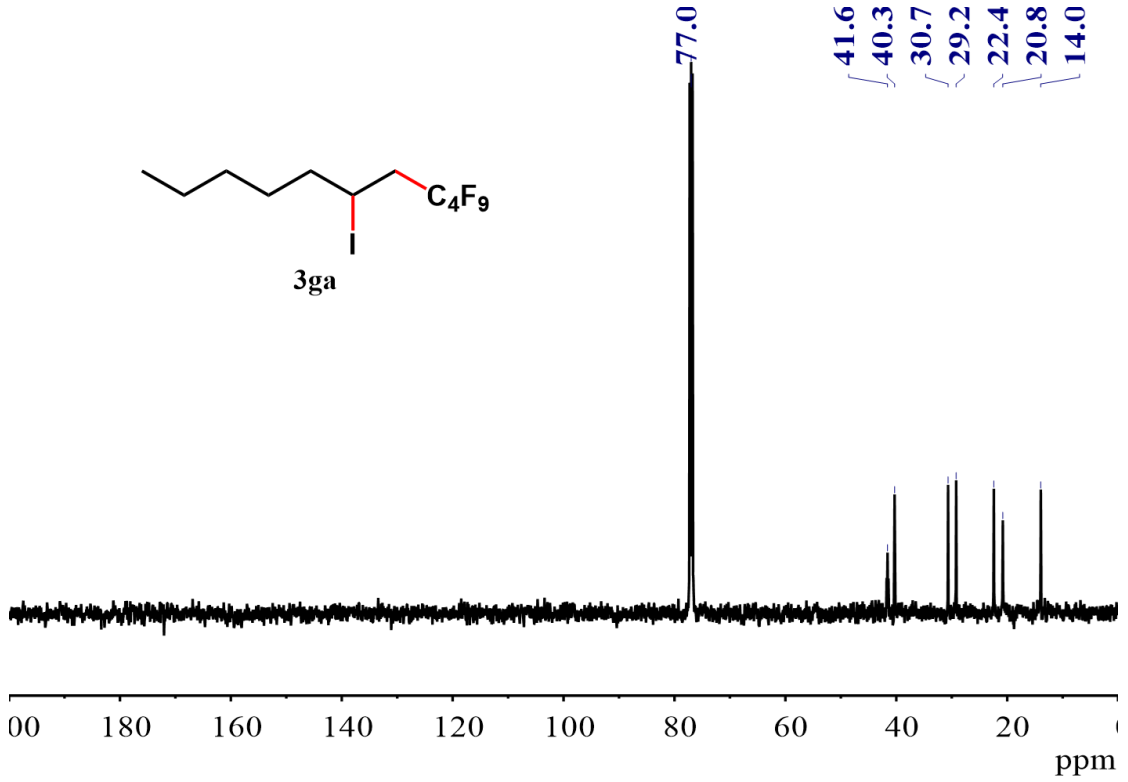
^{13}C NMR spectrum for (3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)cyclohexane **3fa** ($CDCl_3$, 126 MHz).



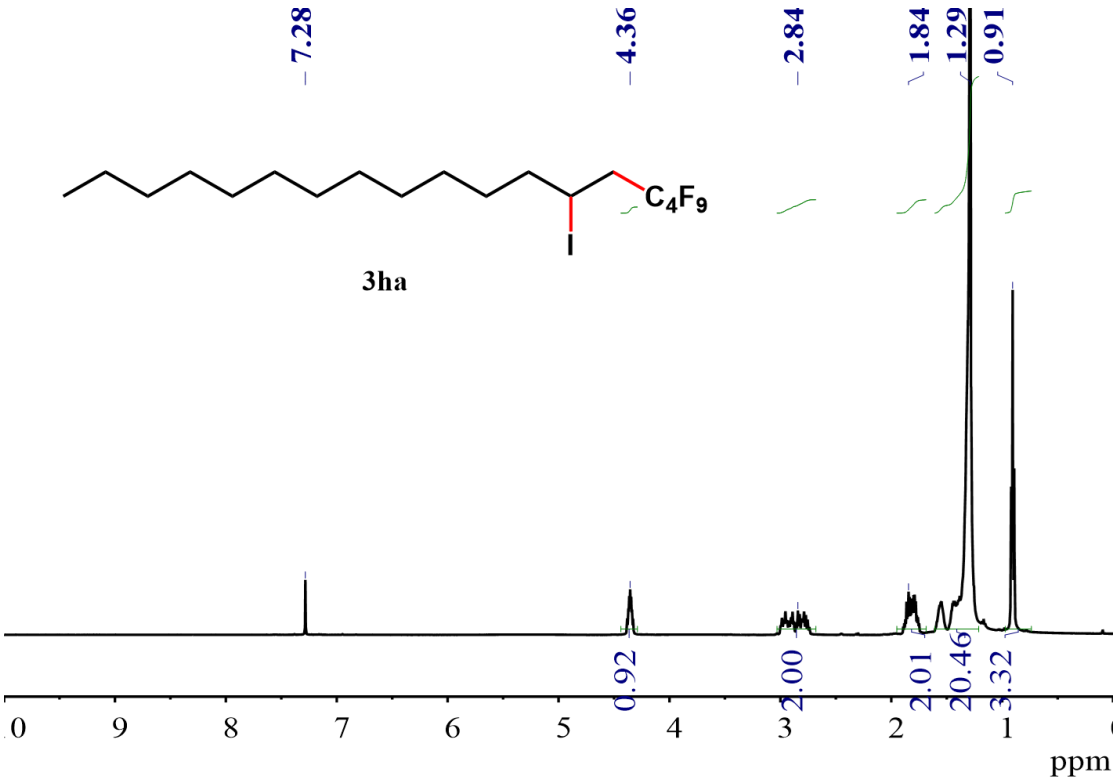
^{1}H NMR spectrum for 1,1,1,2,2,3,3,4,4,5,5-undecafluoro-7-iodododecane **3ga** ($CDCl_3$, 500 MHz).



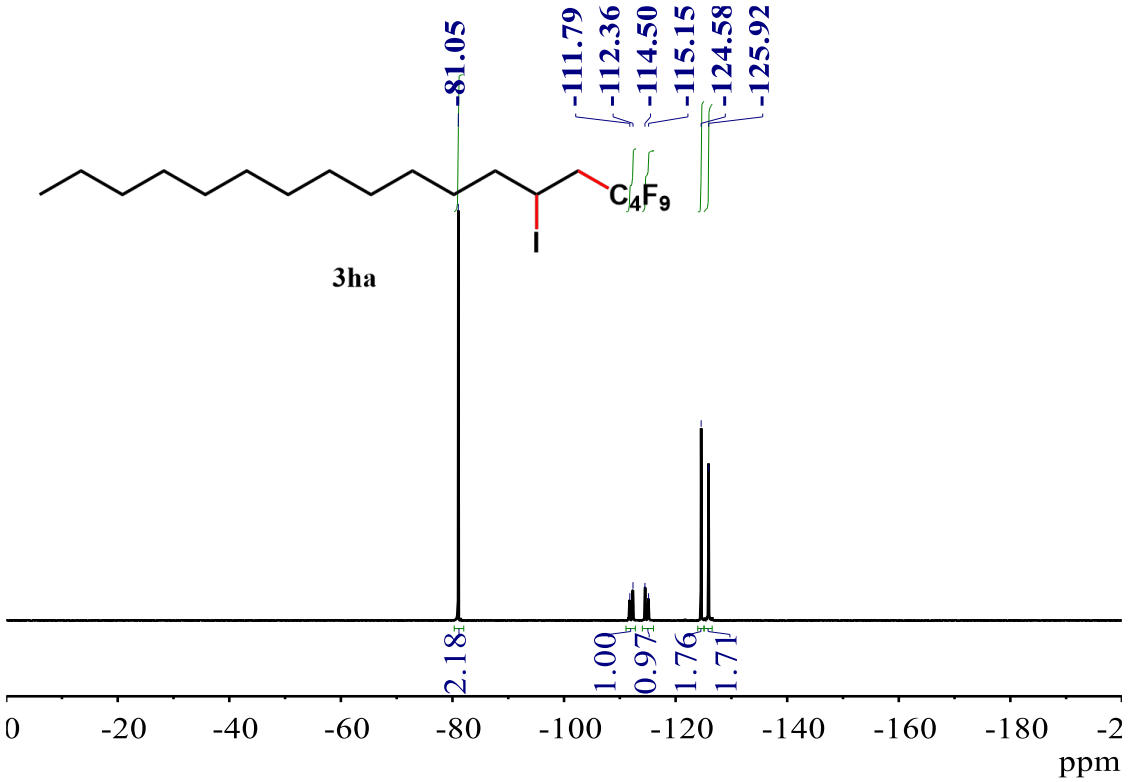
^{19}F NMR spectrum for 1,1,1,2,2,3,3,4,4,5,5-undecafluoro-7-iodododecane **3ga** ($CDCl_3$, 471 MHz).



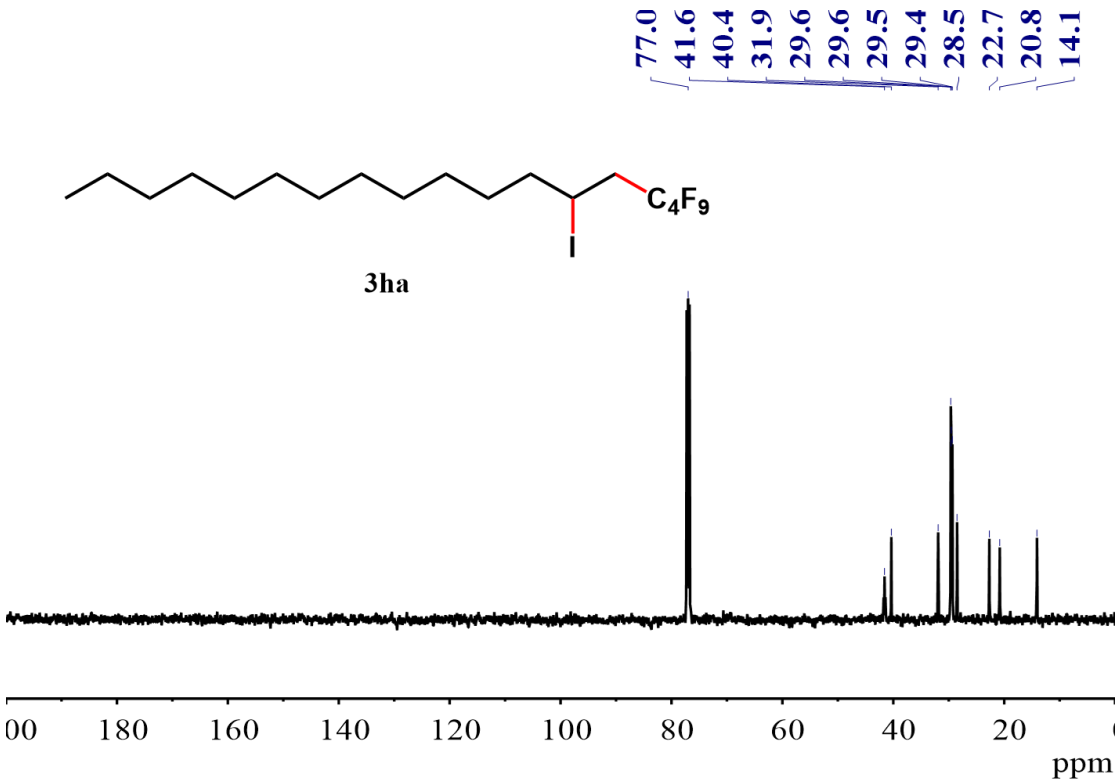
^{13}C NMR spectrum for 1,1,1,2,2,3,3,4,4,5,5-undecafluoro-7-iodododecane **3ga** ($CDCl_3$, 126 MHz).



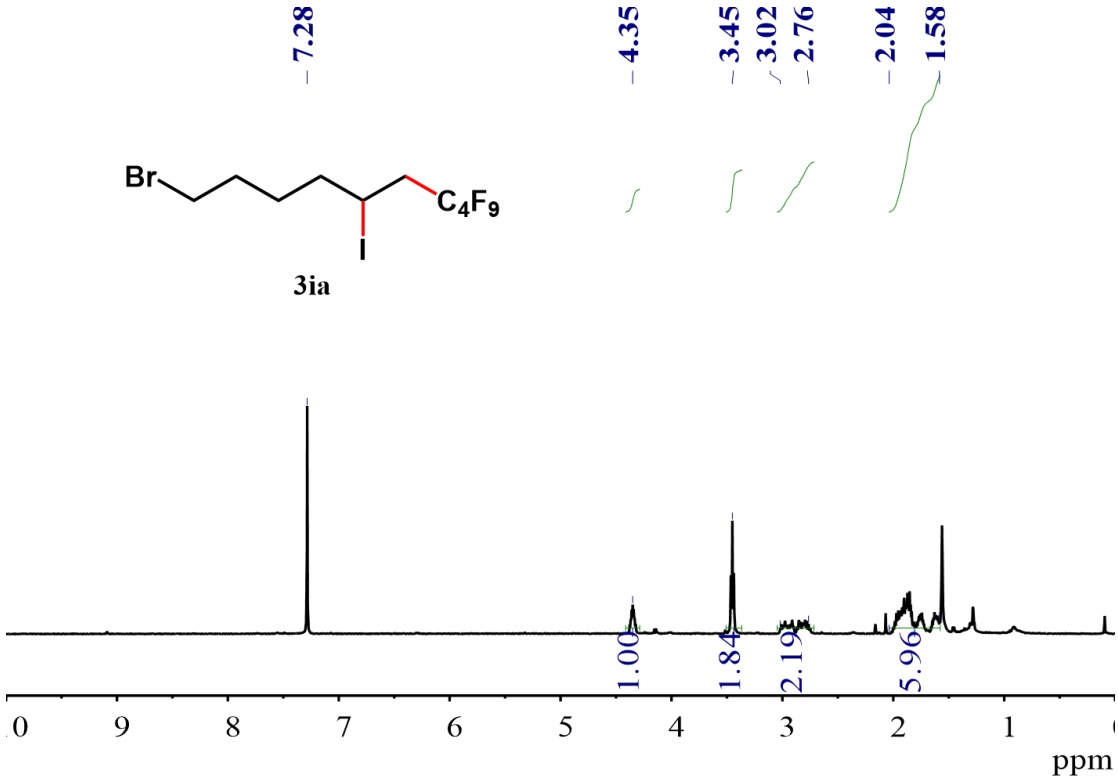
^{1}H NMR spectrum for 1,1,1,2,2,3,3,4,4,5,5-undecafluoro-7-iodononadecane **3ha** ($CDCl_3$, 500 MHz).



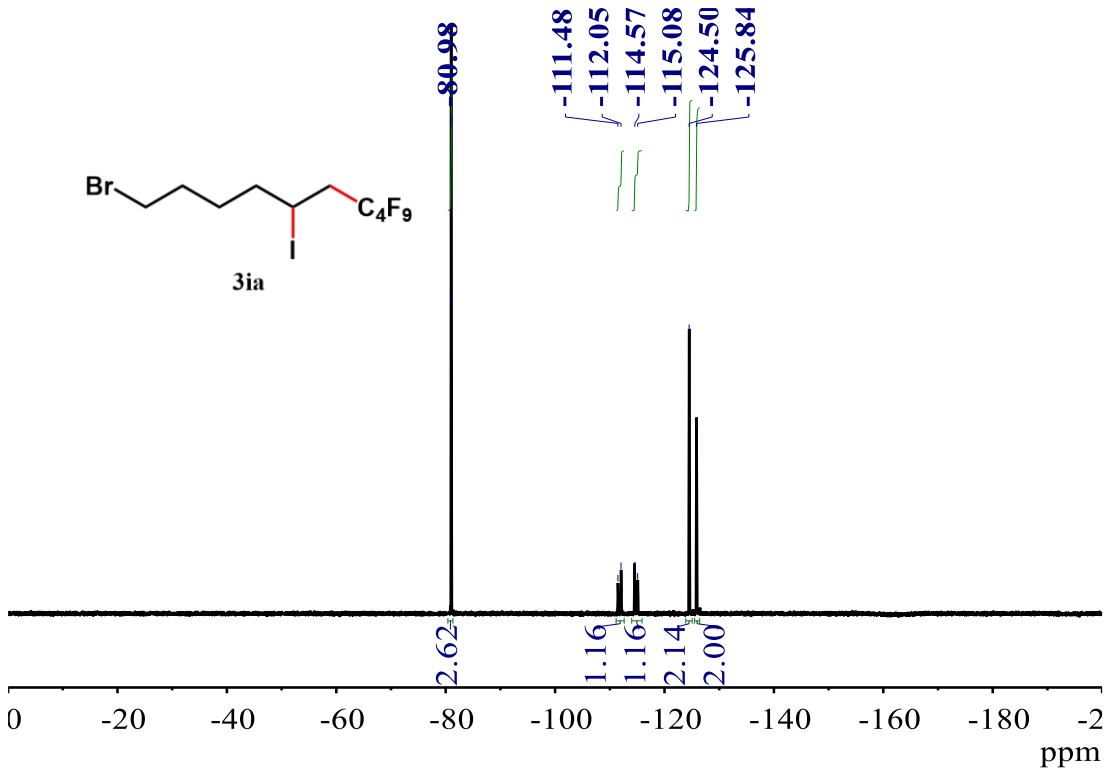
^{19}F NMR spectrum for 1,1,1,2,2,3,3,4,4,5,5-undecafluoro-7-iodononadecane **3ha** ($CDCl_3$, 471 MHz).



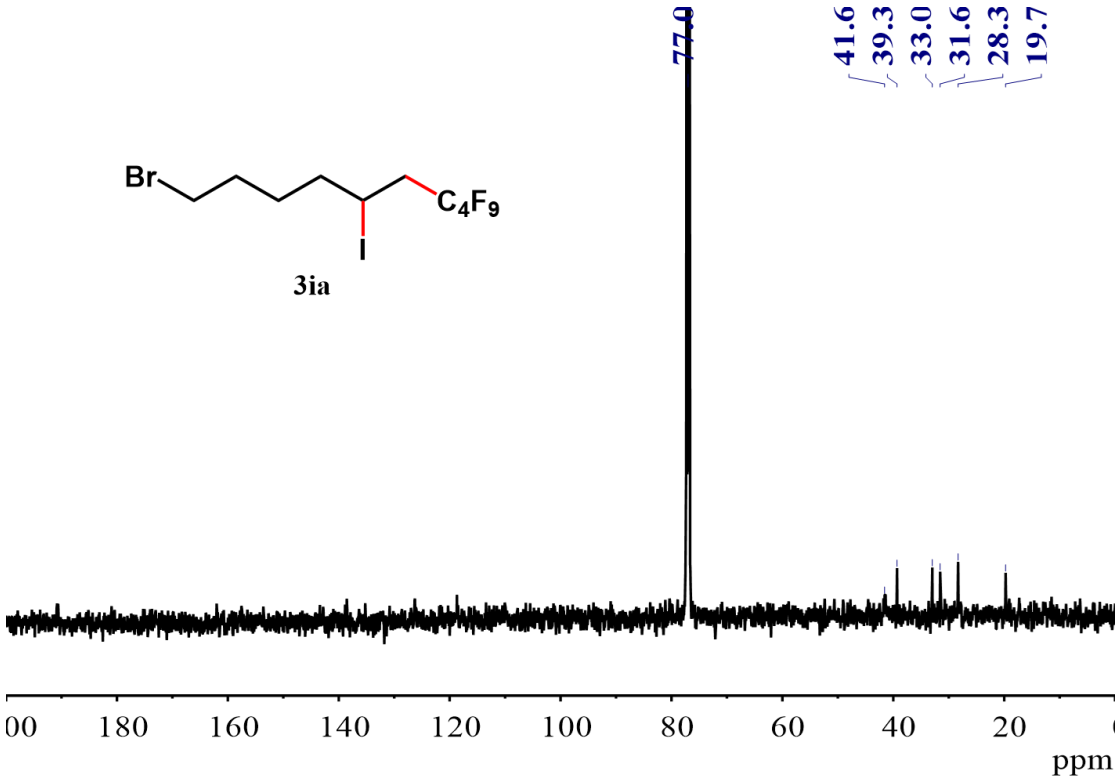
^{13}C NMR spectrum for 1,1,1,2,2,3,3,4,4,5,5-undecafluoro-7-iodononadecane **3ha** ($CDCl_3$, 126 MHz).



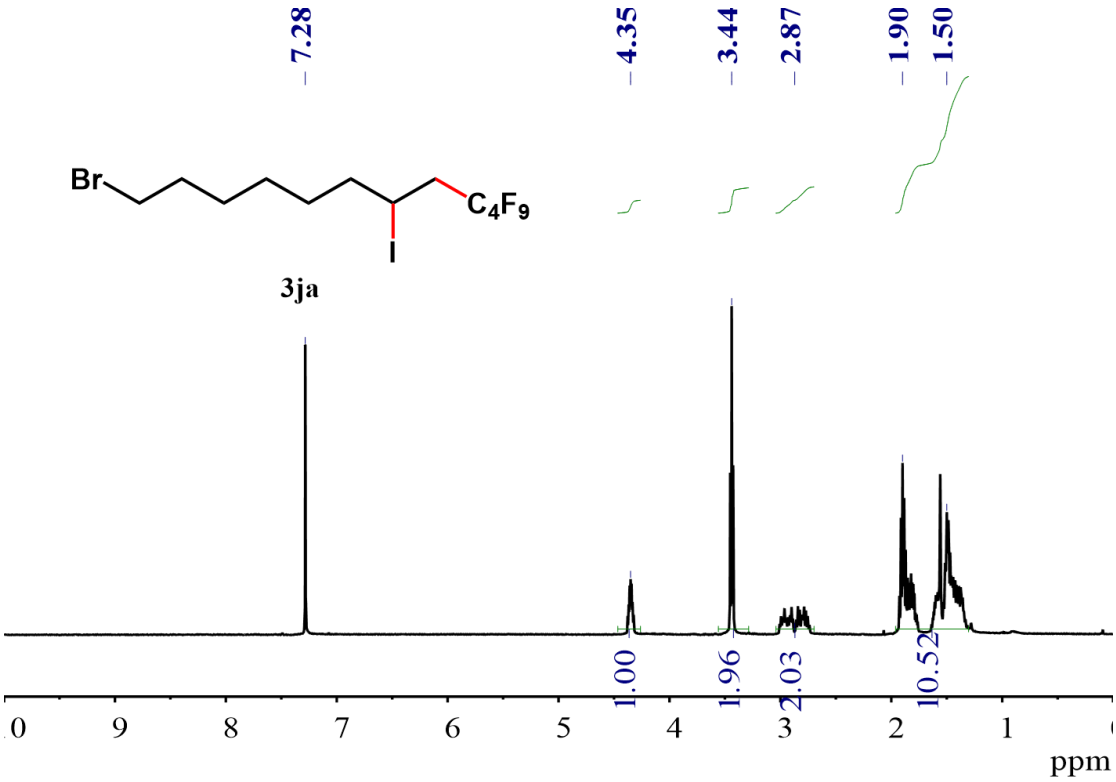
^{1}H NMR spectrum for 10-bromo-1,1,1,2,2,3,3,4,4-nonafluoro-6-iododecane **3ia** ($CDCl_3$, 500 MHz).



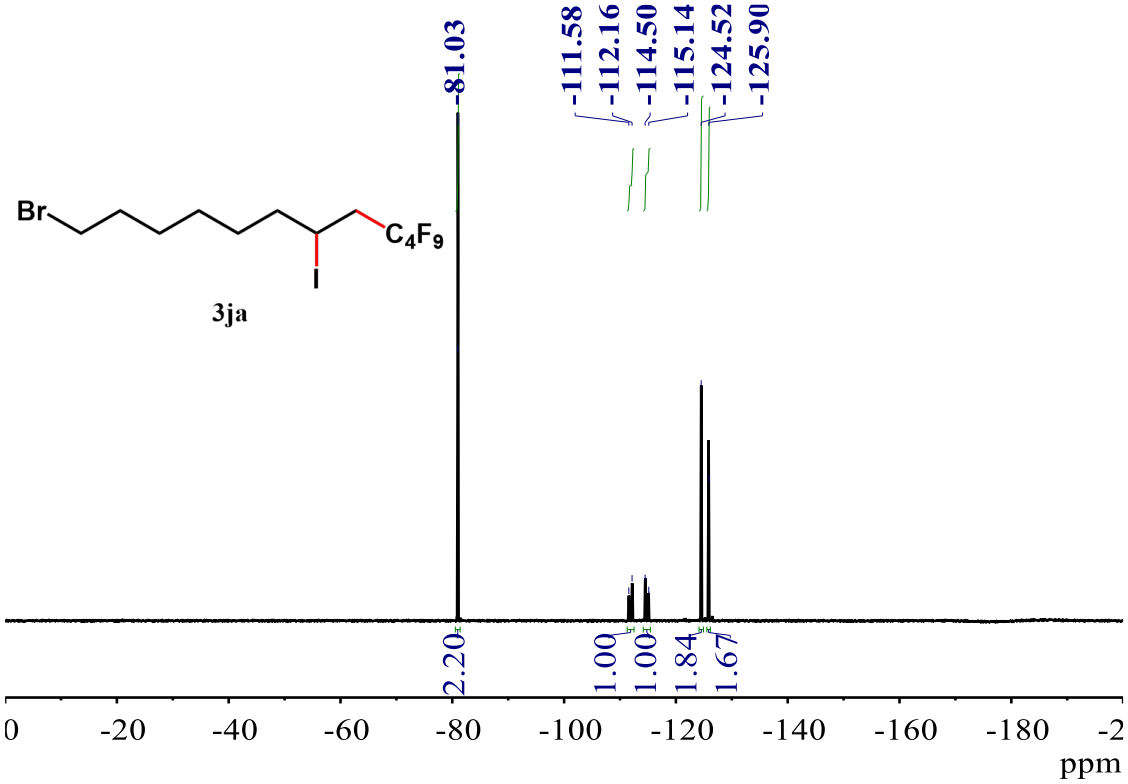
^{19}F NMR spectrum for 10-bromo-1,1,1,2,2,3,3,4,4-nonafluoro-6-iododecane **3ia** ($CDCl_3$, 471 MHz).



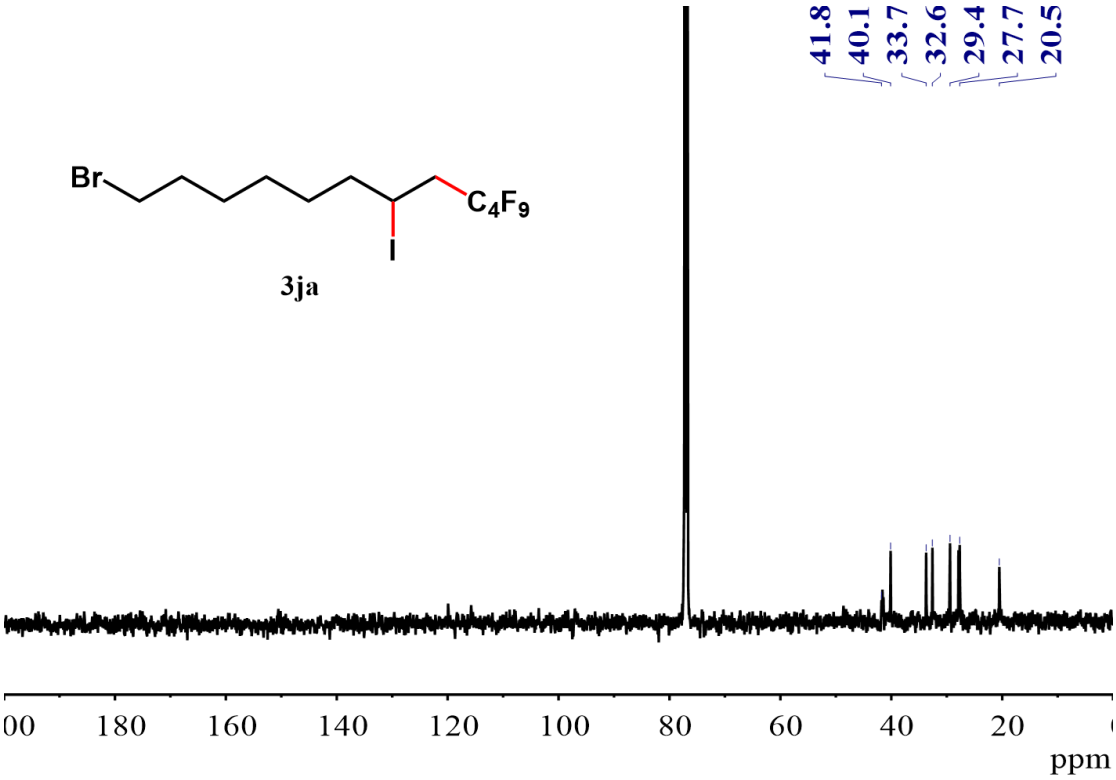
^{13}C NMR spectrum for 10-bromo-1,1,1,2,2,3,3,4,4-nonafluoro-6-iododecane **3ia** ($CDCl_3$, 126 MHz).



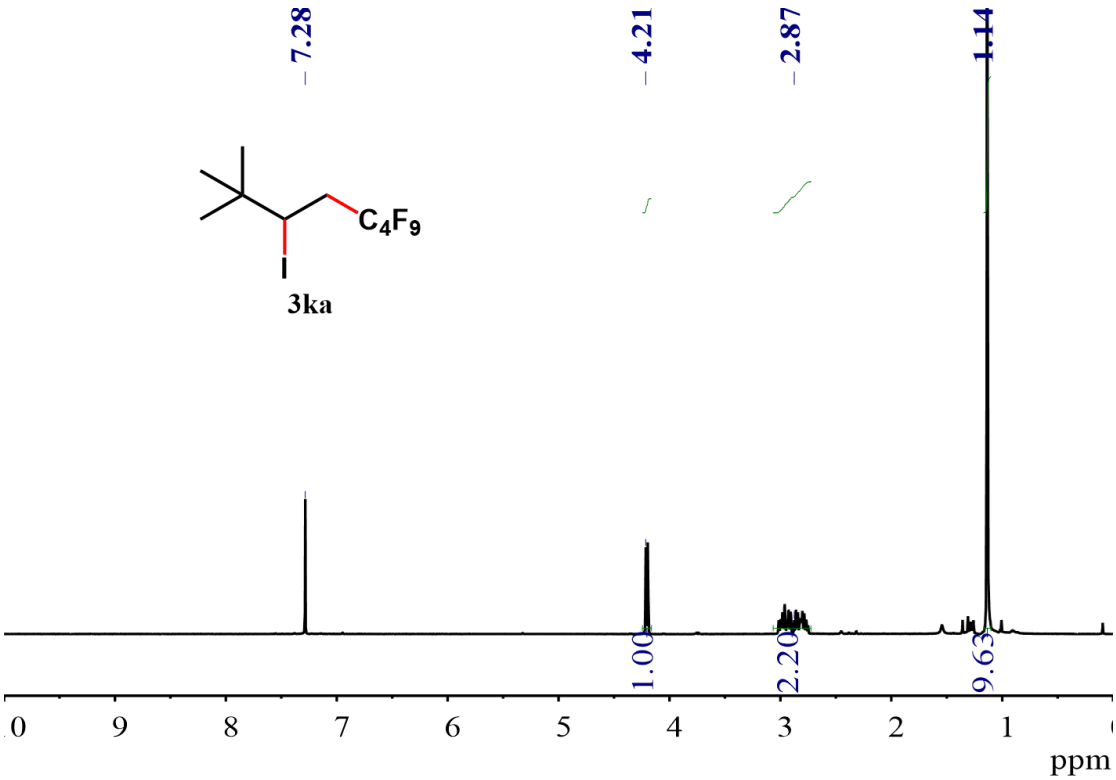
^{1}H NMR spectrum for 12-bromo-1,1,1,2,2,3,3,4,4-nonafluoro-6-iododododecane **3ja** ($CDCl_3$, 500 MHz).



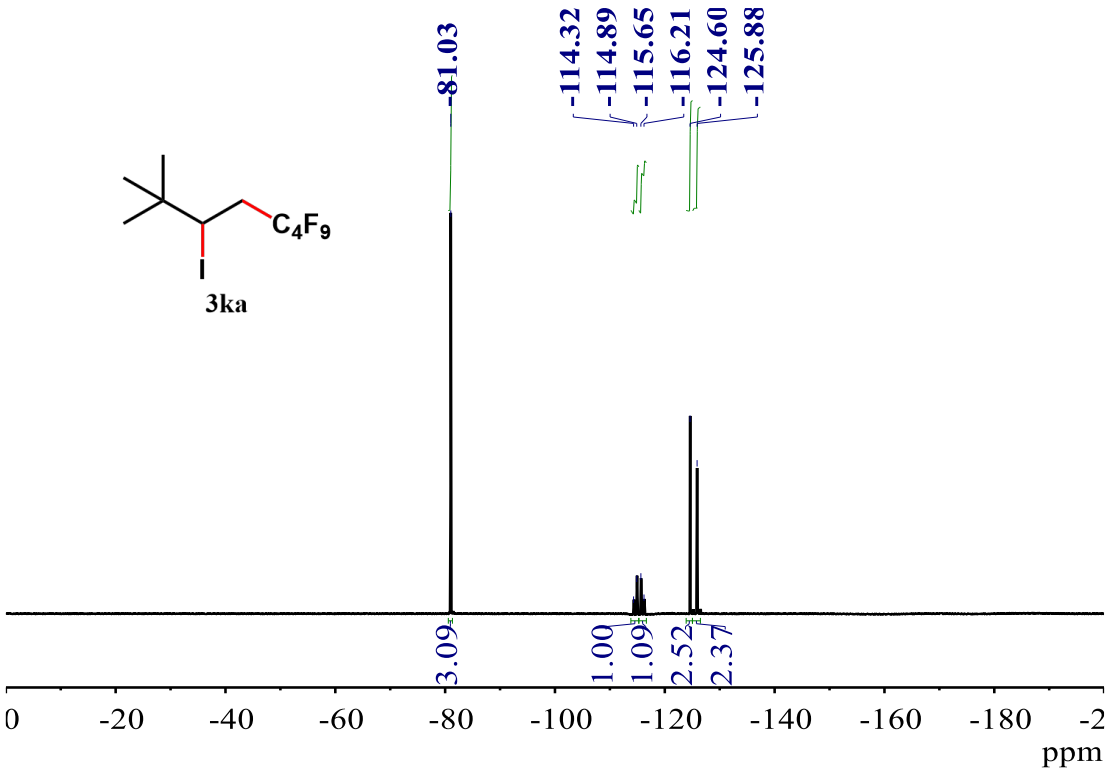
^{19}F NMR spectrum for 12-bromo-1,1,1,2,2,3,3,4,4-nonafluoro-6-iododododecane **3ja** ($CDCl_3$, 471 MHz).



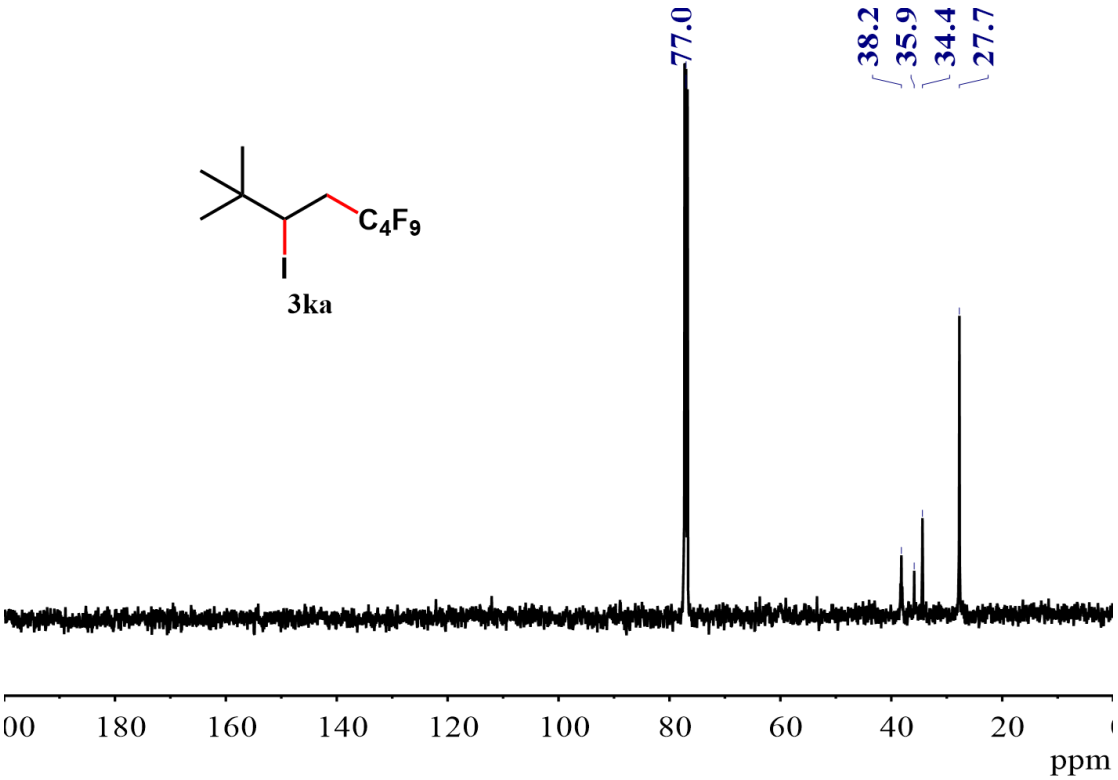
^{13}C NMR spectrum for 12-bromo-1,1,1,2,2,3,3,4,4-nonafluoro-6-iodododecane **3ja** ($CDCl_3$, 126 MHz).



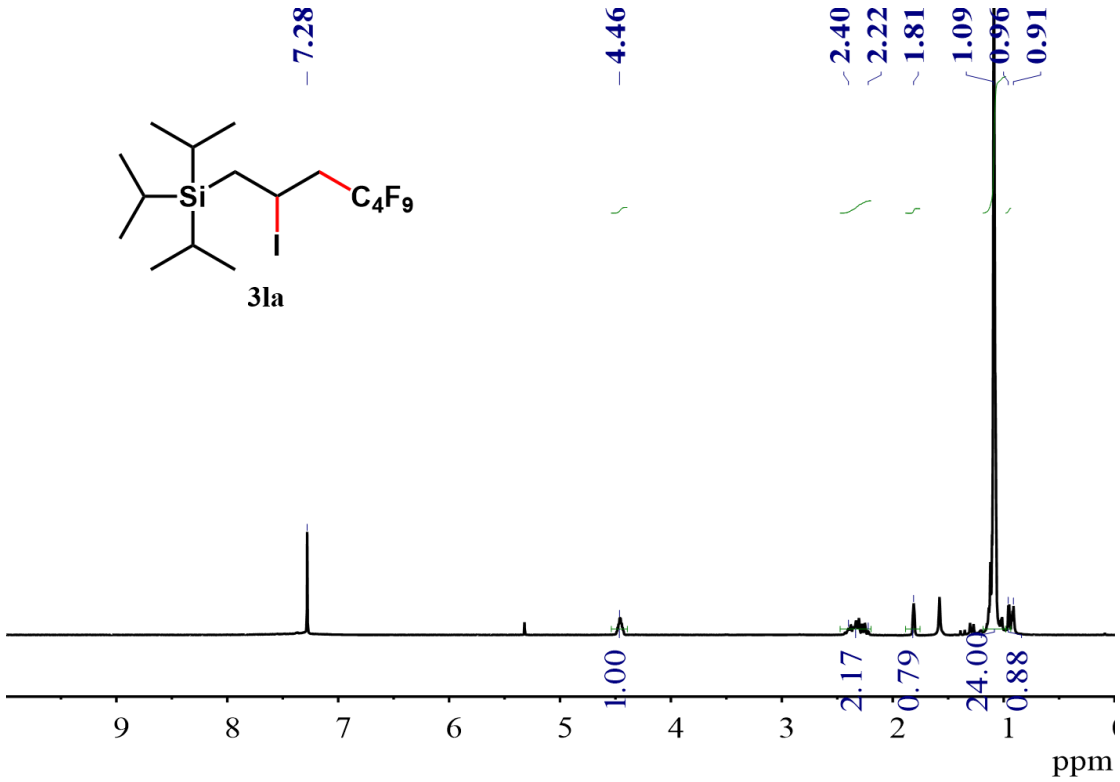
^{1}H NMR spectrum for 1,1,1,2,2,3,3,4,4-nonafluoro-6-iodo-7,7-dimethyloctane **3ka** ($CDCl_3$, 500 MHz).



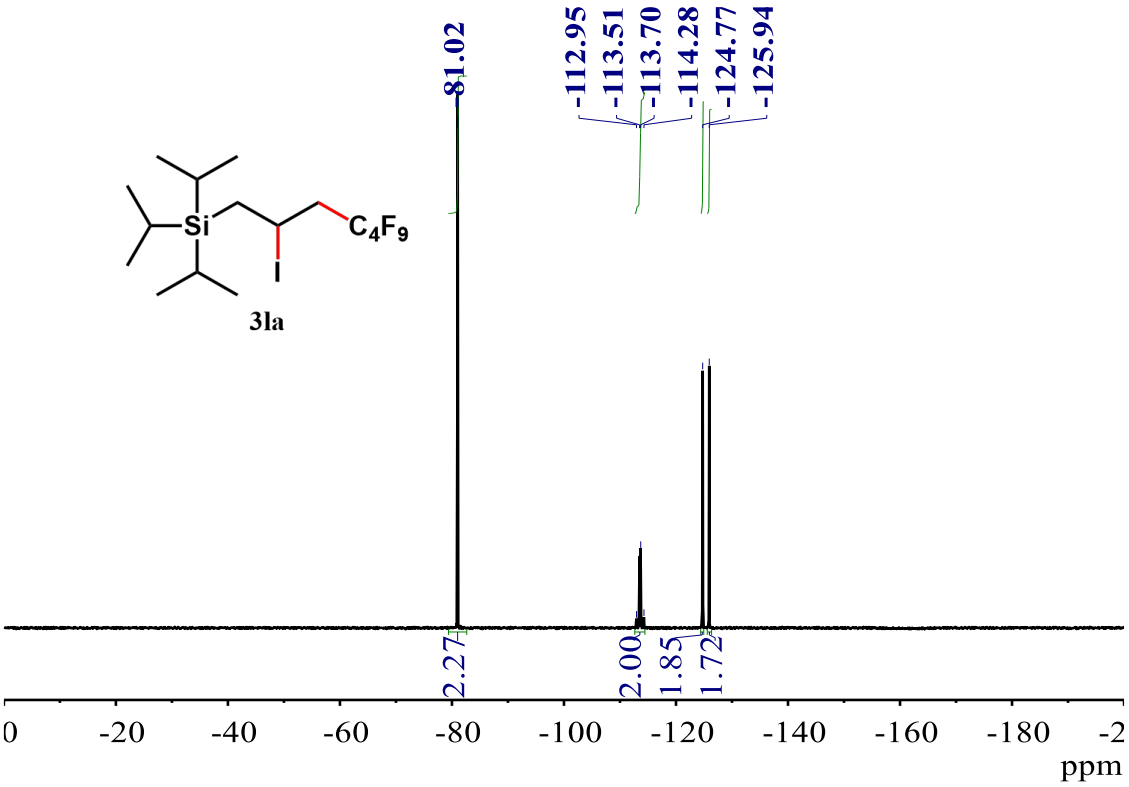
^{19}F NMR spectrum for 1,1,1,2,2,3,3,4,4-nonafluoro-6-iodo-7,7-dimethyloctane **3ka** ($CDCl_3$, 471 MHz).



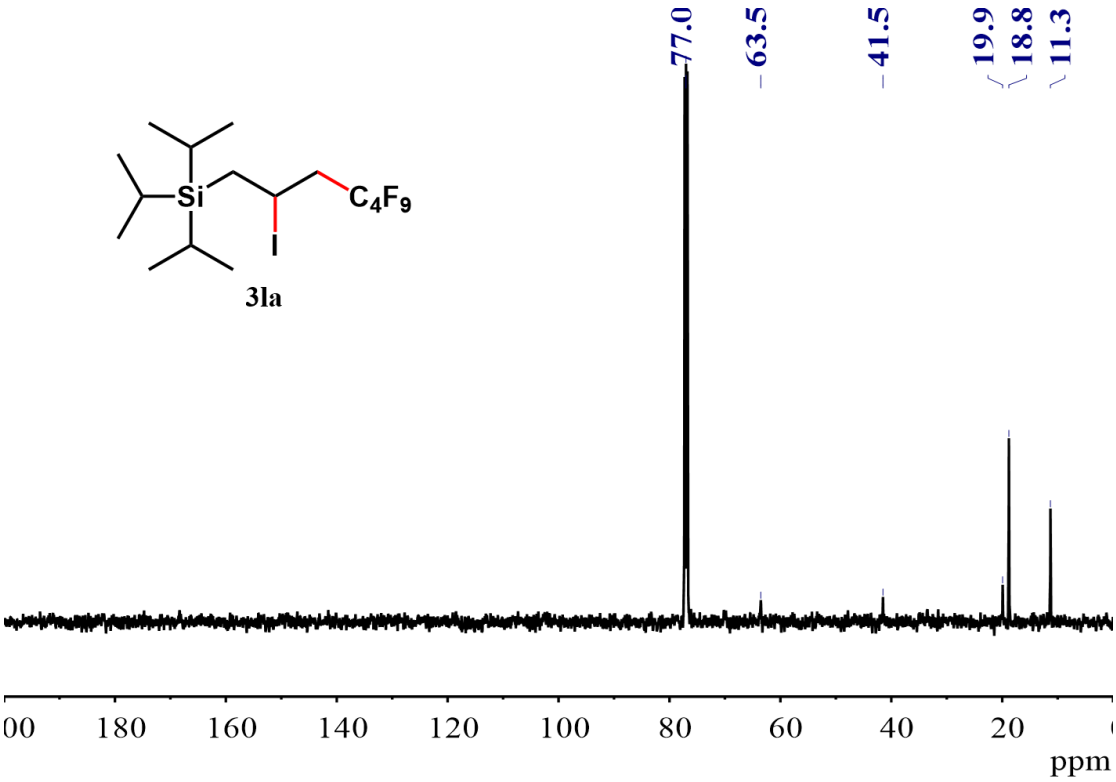
^{13}C NMR spectrum for 1,1,1,2,2,3,3,4,4-nonafluoro-6-iodo-7,7-dimethyloctane **3ka** ($CDCl_3$, 126 MHz).



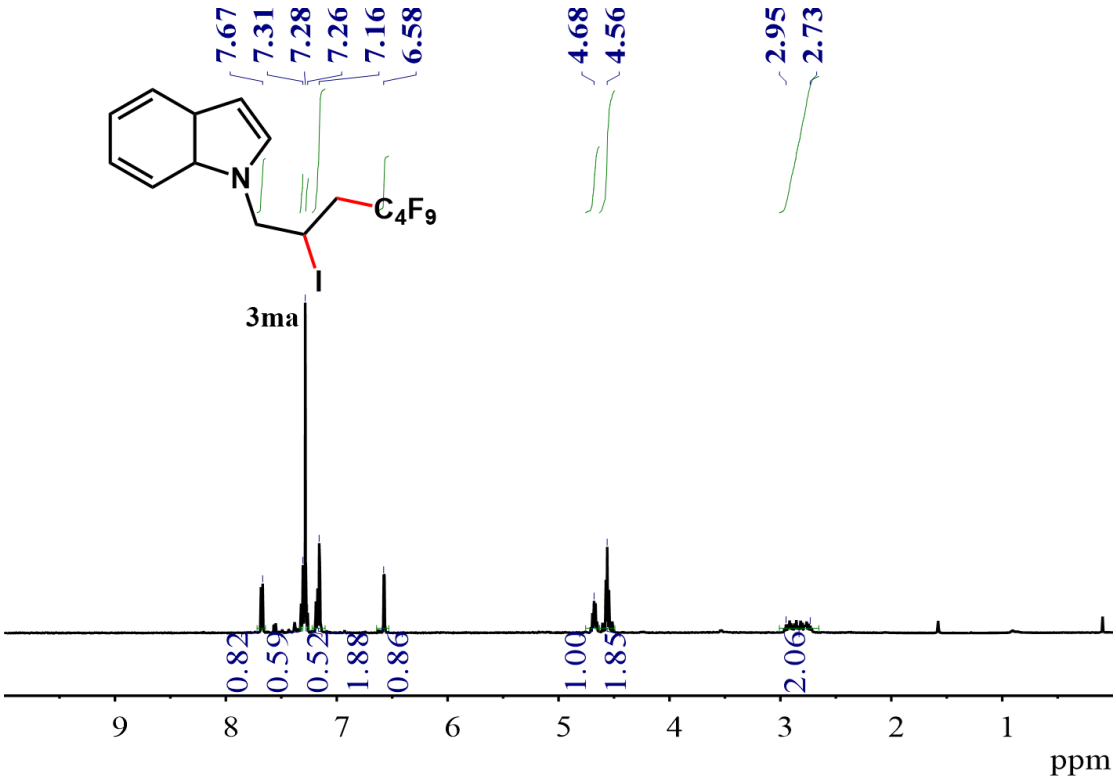
^{1}H NMR spectrum for triisopropyl(4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)silane **3la** ($CDCl_3$, 500 MHz).



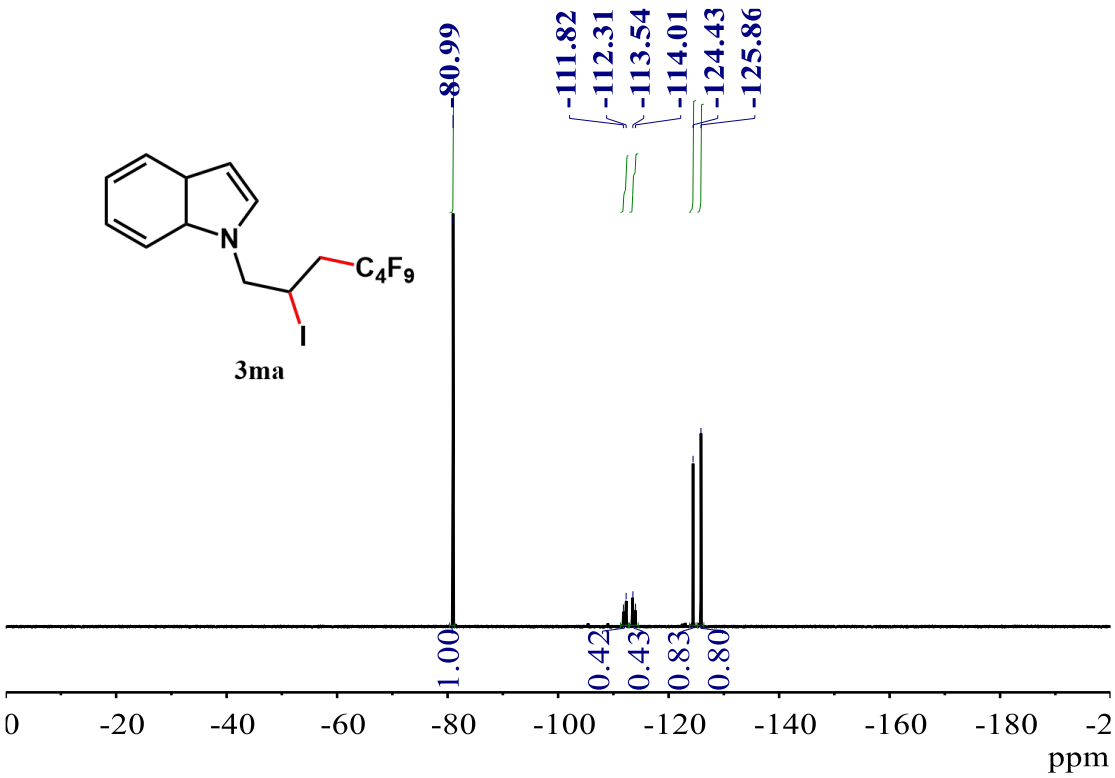
^{19}F NMR spectrum for triisopropyl(4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)silane **3la** ($CDCl_3$, 471 MHz).



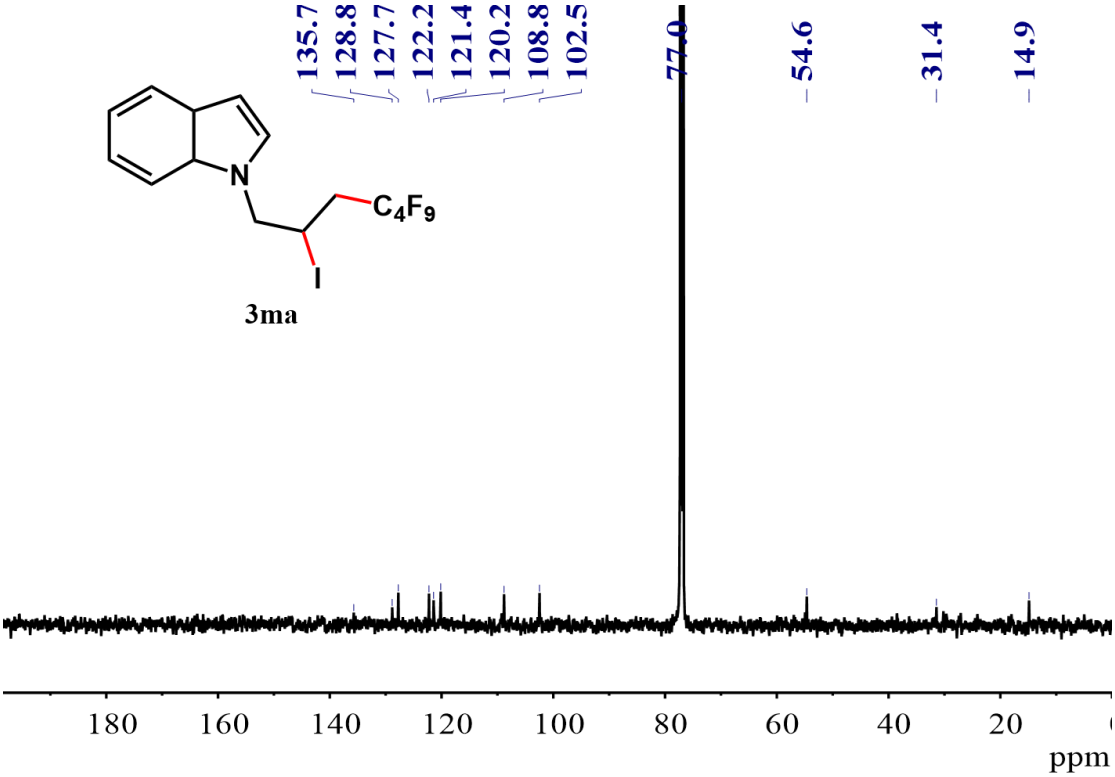
^{13}C NMR spectrum for triisopropyl(4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)silane **3la** ($CDCl_3$, 126 MHz).



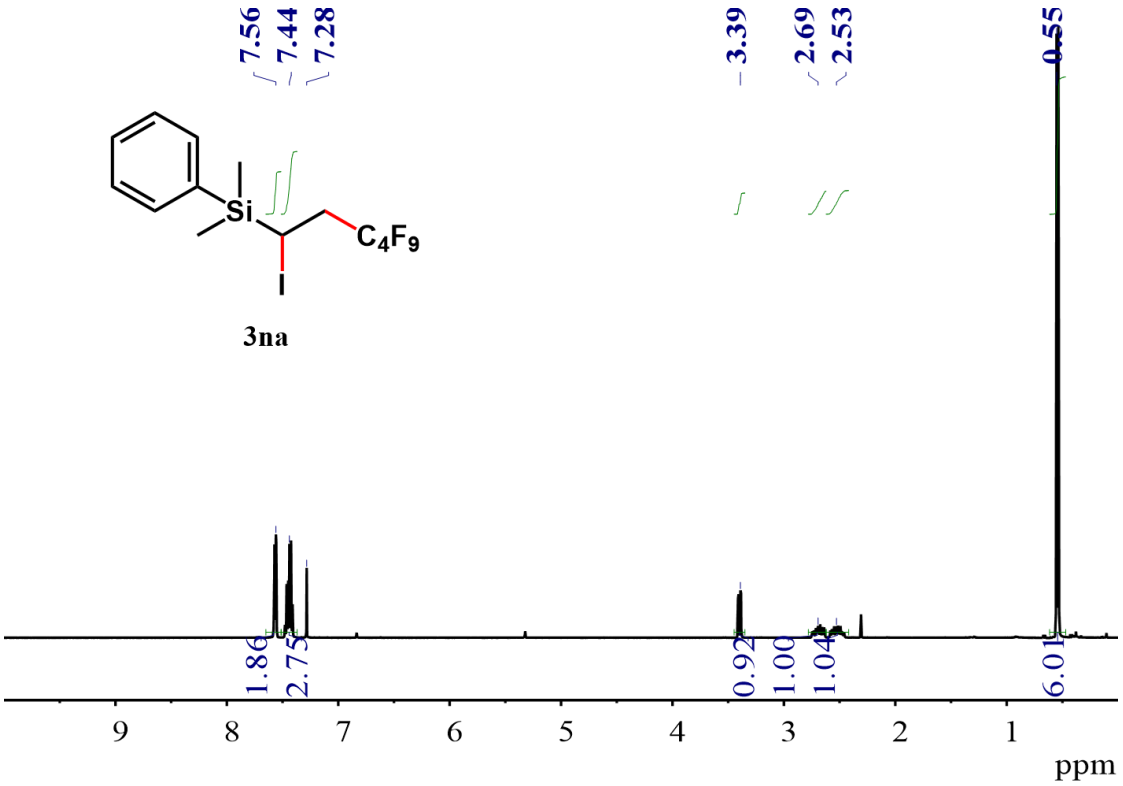
^{1}H NMR spectrum for 1-(3,3,4,4,5,5,6,6,6-nonafluoro-2-iodohexyl)-1H-indole **3ma** ($CDCl_3$, 500 MHz).



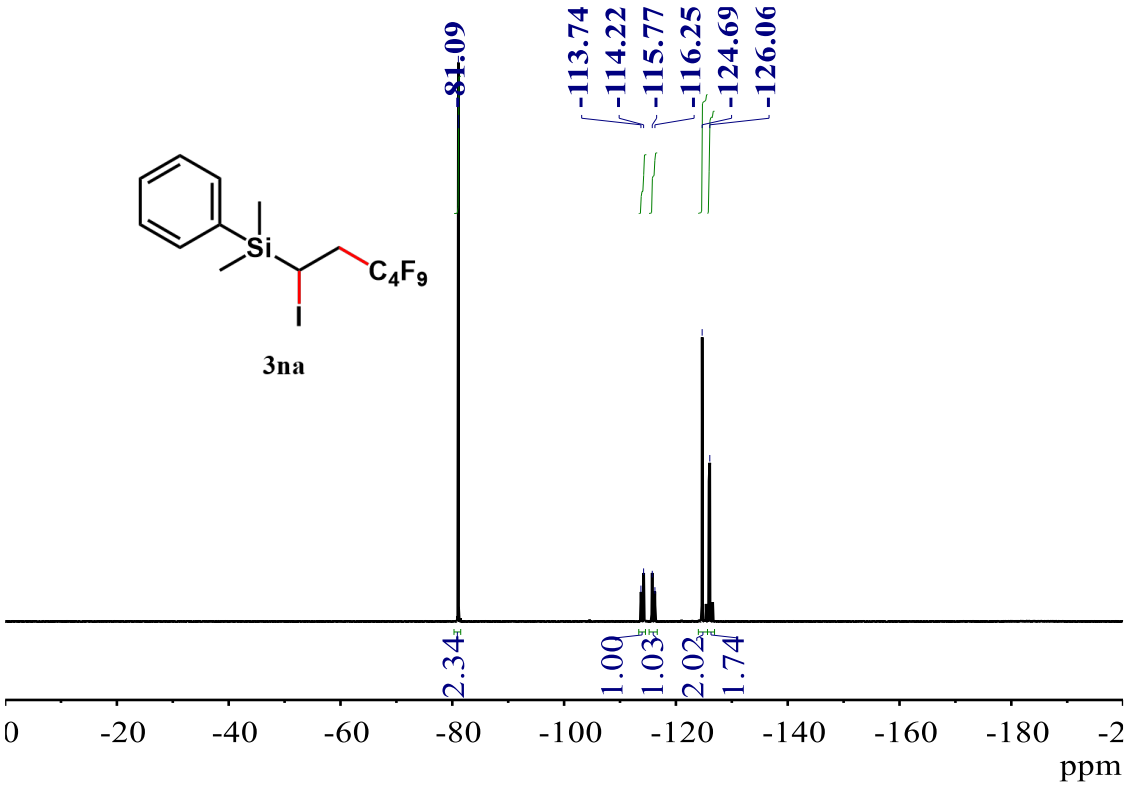
^{19}F NMR spectrum for 1-(3,3,4,4,5,5,6,6,6-nonafluoro-2-iodohexyl)-1H-indole **3ma** ($CDCl_3$, 471 MHz).



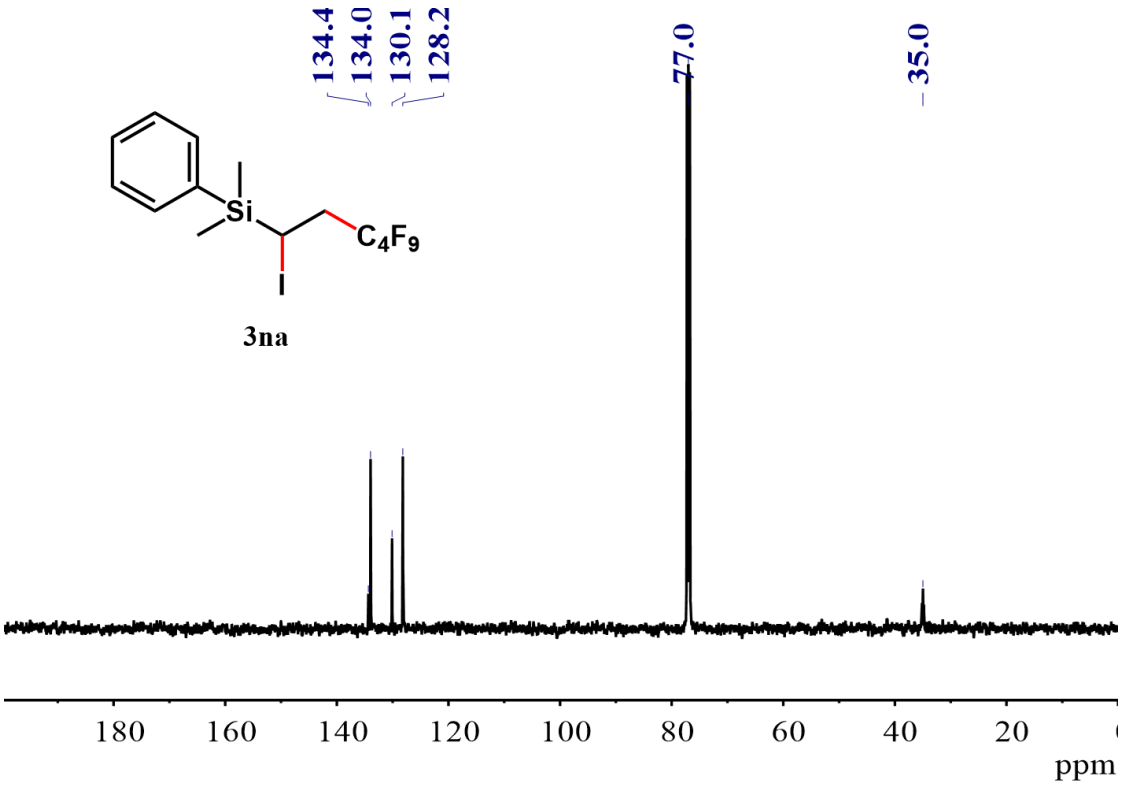
^{13}C NMR spectrum for 1-(3,3,4,4,5,5,6,6,6-nonafluoro-2-iodohexyl)-1H-indole **3ma** ($CDCl_3$, 126 MHz).



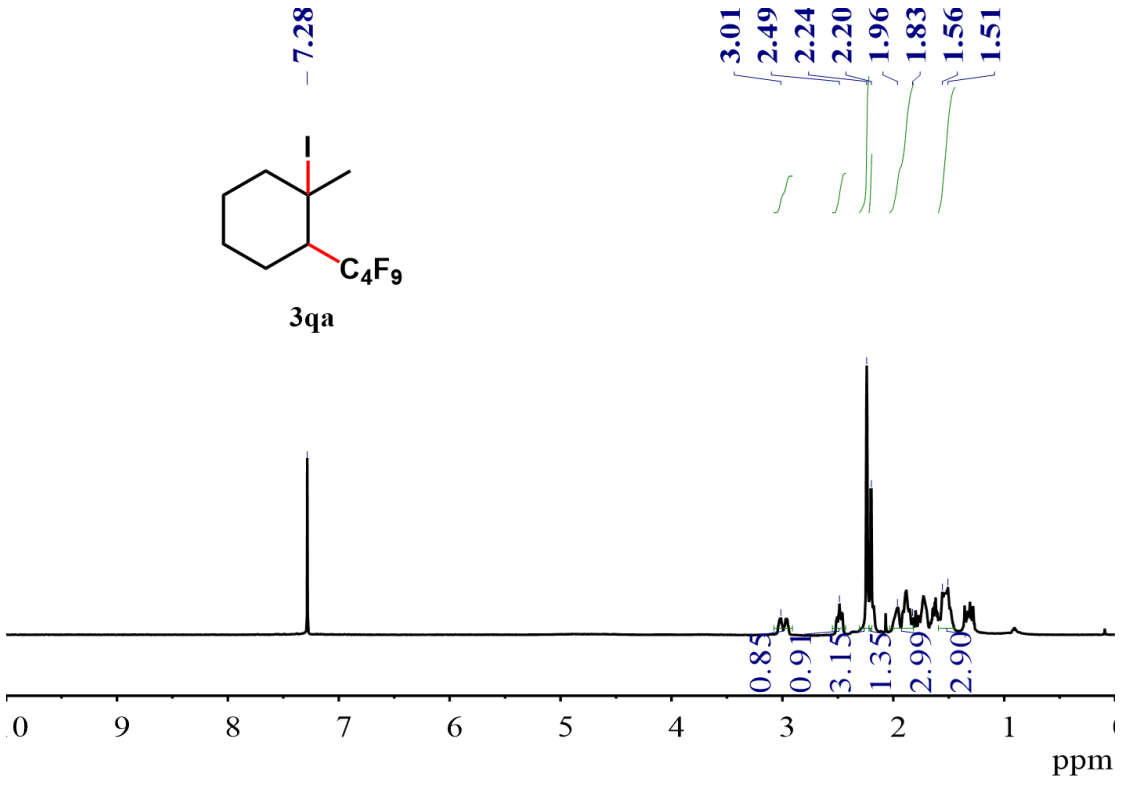
^{1}H NMR spectrum for dimethyl(2,2,3,3,4,4,5,5,5-nonafluoro-1-iodopentyl)(phenyl)silane **3na** ($CDCl_3$, 500 MHz).



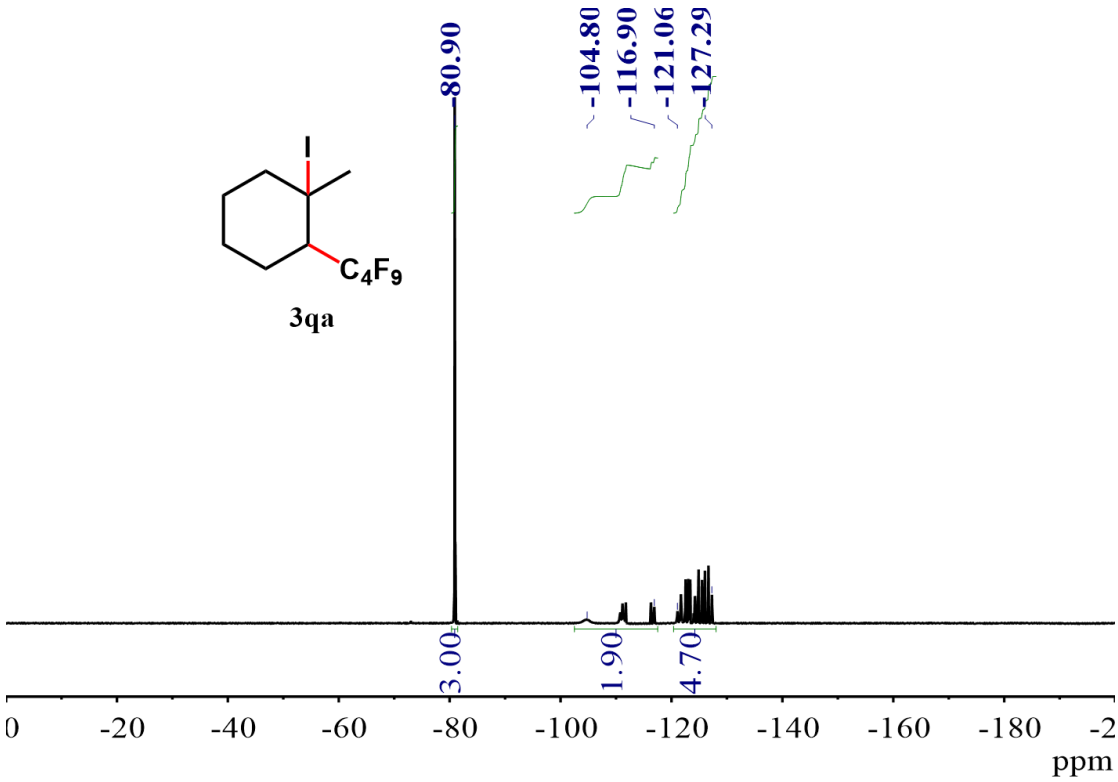
^{19}F NMR spectrum for dimethyl(2,2,3,3,4,4,5,5,5-nonafluoro-1-iodopentyl)(phenyl)silane **3na** ($CDCl_3$, 471 MHz).



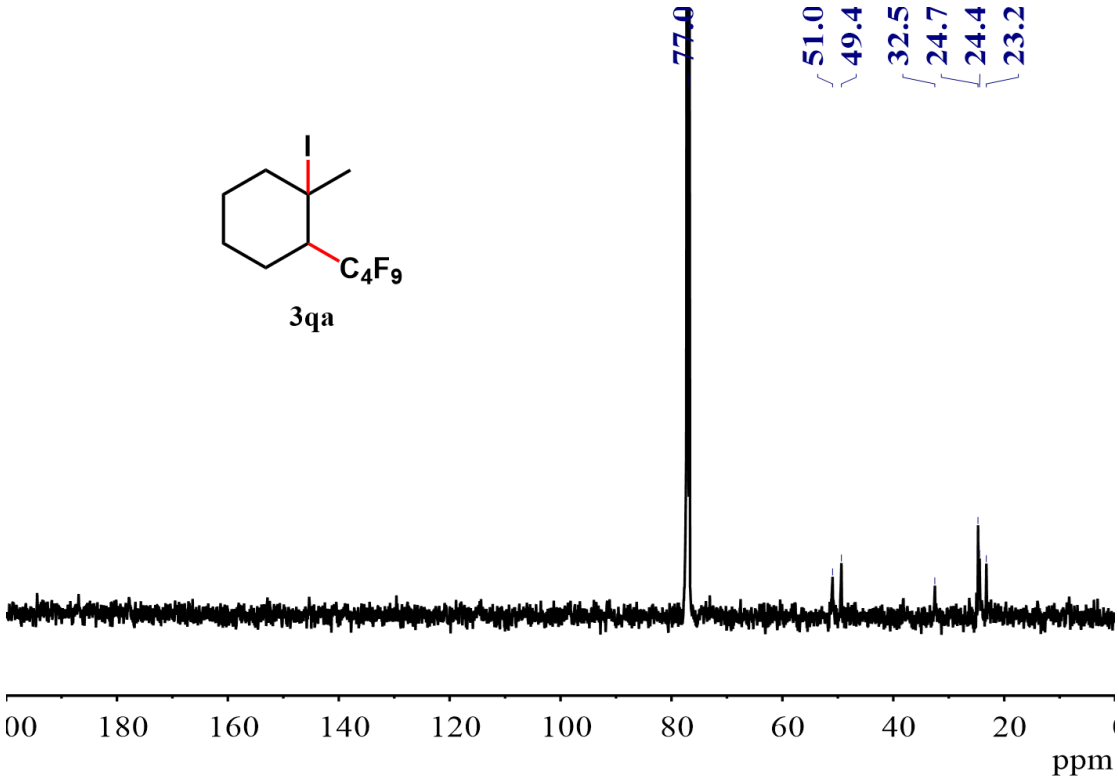
^{13}C NMR spectrum for dimethyl(2,2,3,3,4,4,5,5,5-nonafluoro-1-iodopentyl)(phenyl)silane **3na** ($CDCl_3$, 126 MHz).



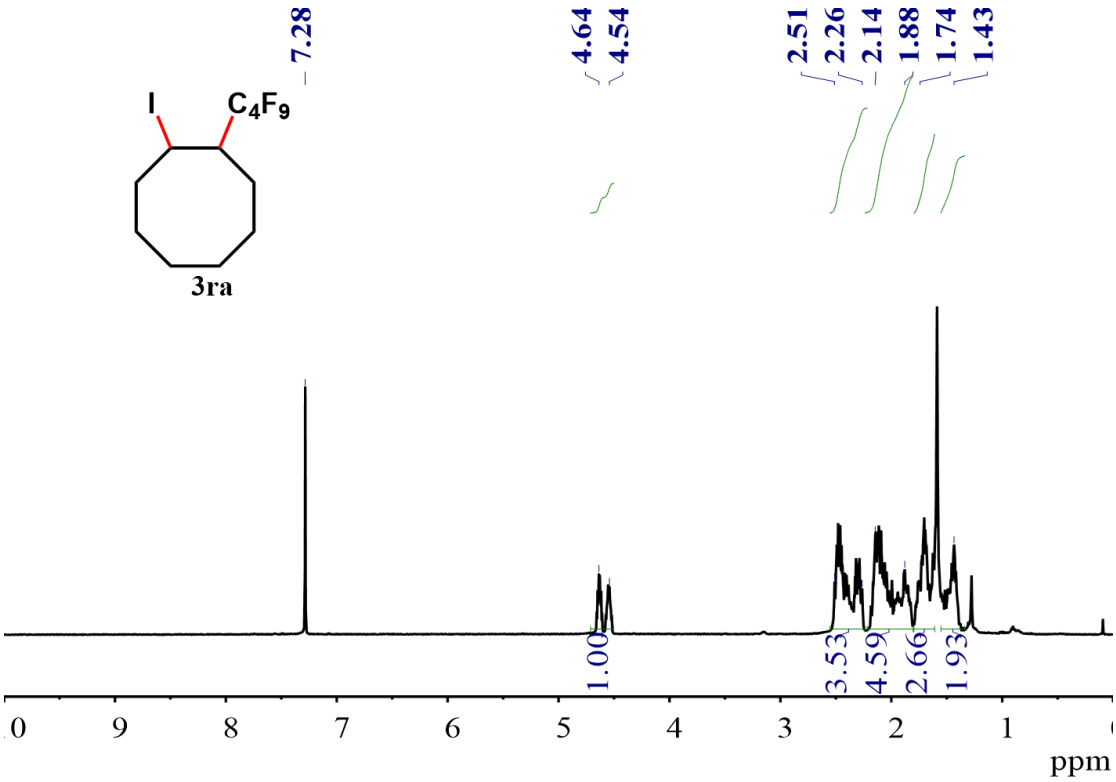
^{1}H NMR spectrum for 1-iodo-1-methyl-2-(perfluorobutyl)cyclohexane **3qa** ($CDCl_3$, 500 MHz).



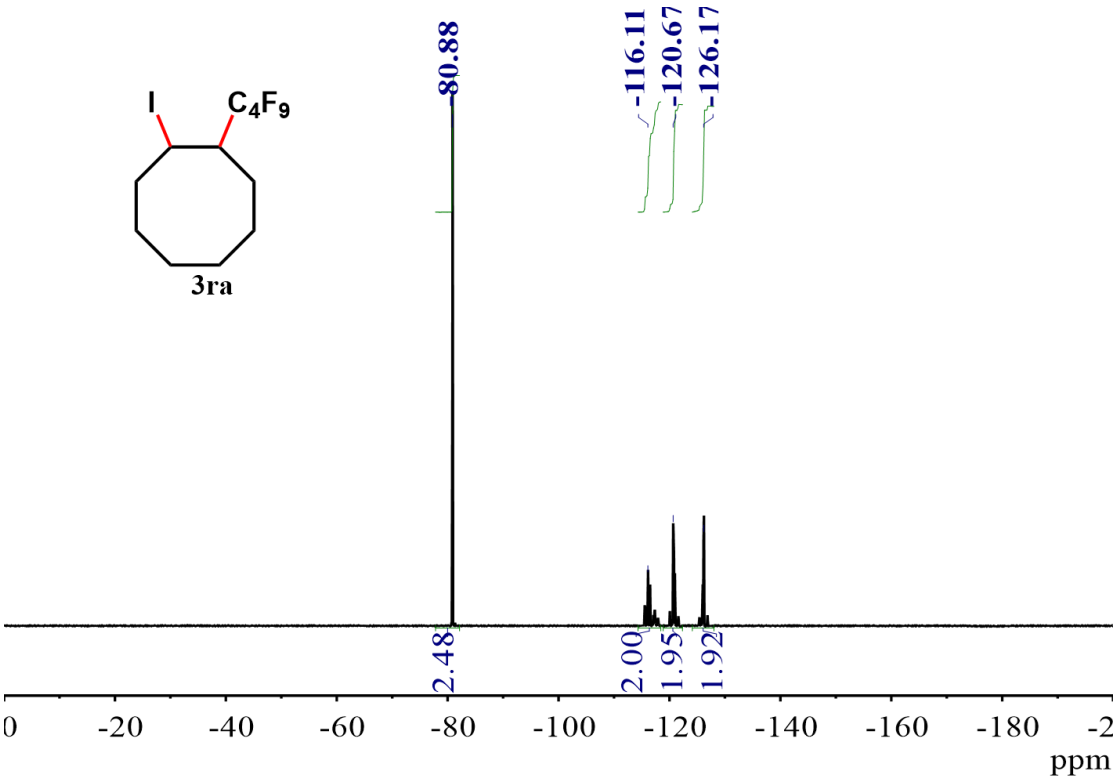
^{19}F NMR spectrum for 1-iodo-1-methyl-2-(perfluorobutyl)cyclohexane **3qa** ($CDCl_3$, 471 MHz).



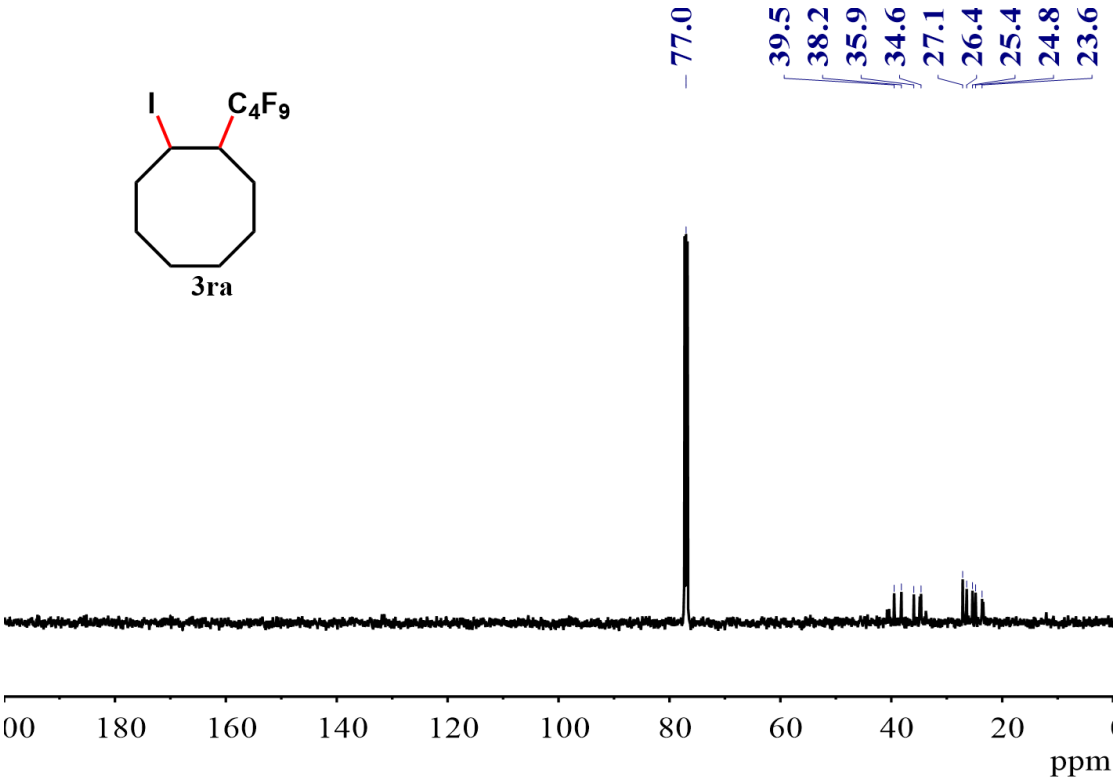
^{13}C NMR spectrum for 1-iodo-1-methyl-2-(perfluorobutyl)cyclohexane **3qa** ($CDCl_3$, 126 MHz).



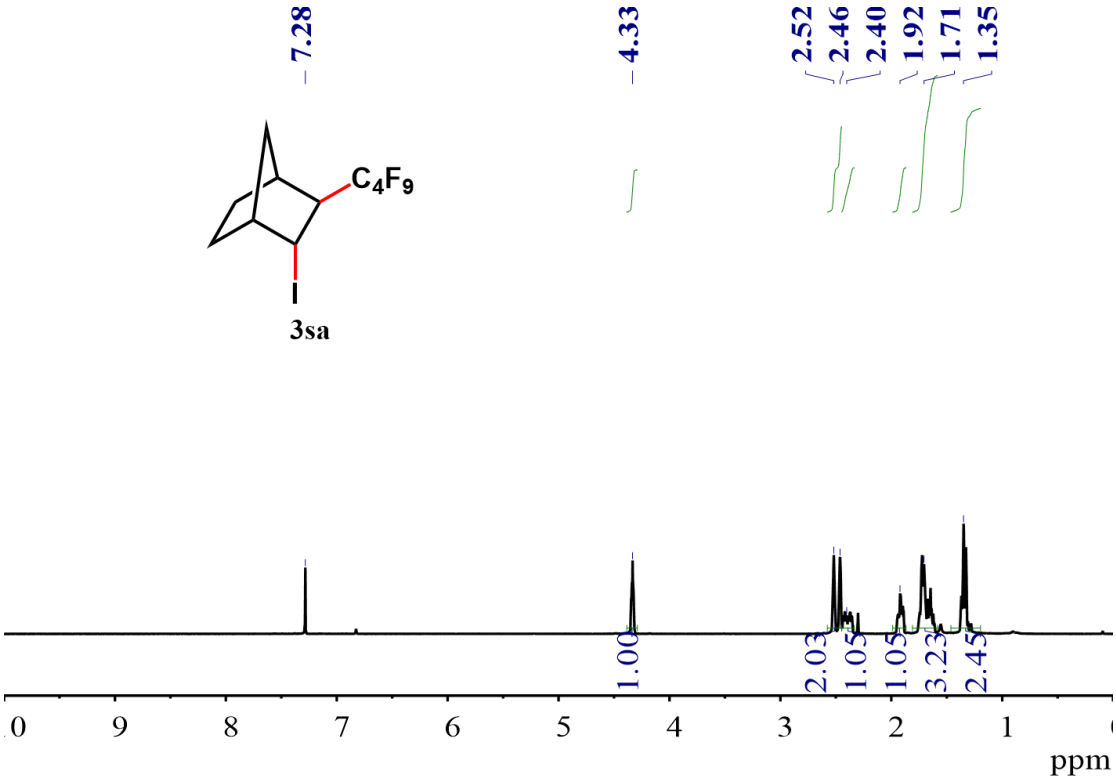
^{1}H NMR spectrum for 1-iodo-2-(perfluorobutyl)cyclooctane **3ra** ($CDCl_3$, 500 MHz).



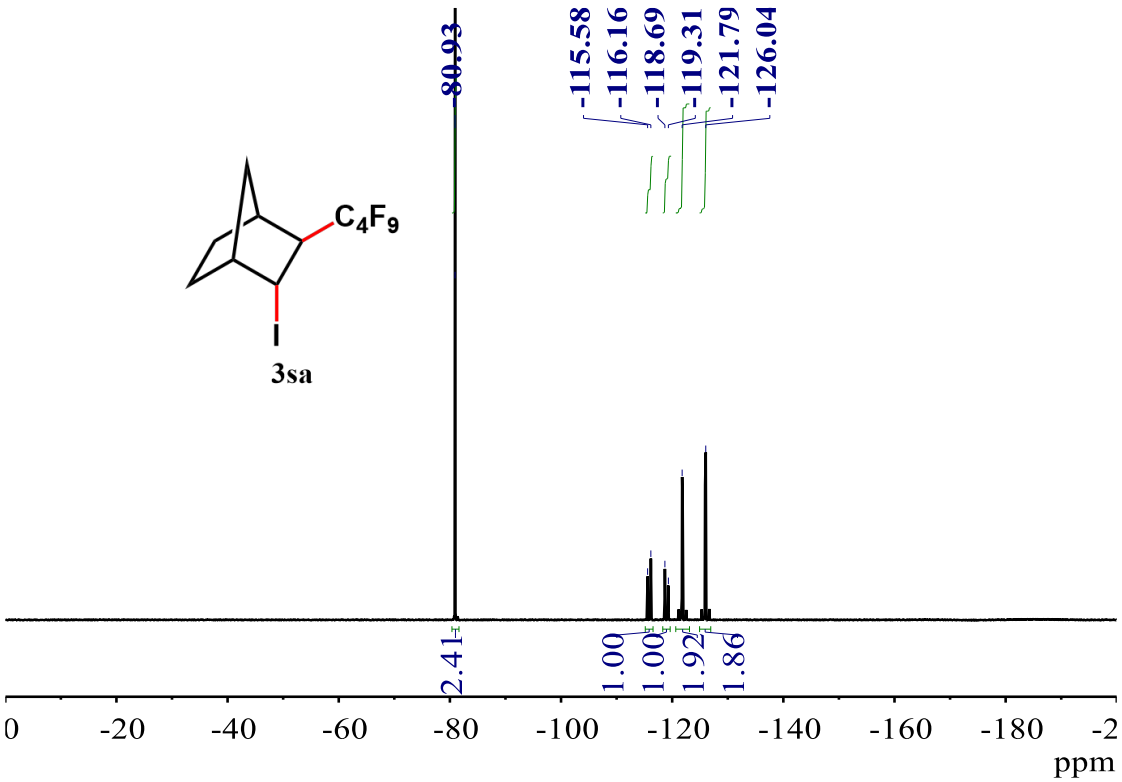
^{19}F NMR spectrum for 1-iodo-2-(perfluorobutyl)cyclooctane **3ra** ($CDCl_3$, 471 MHz).



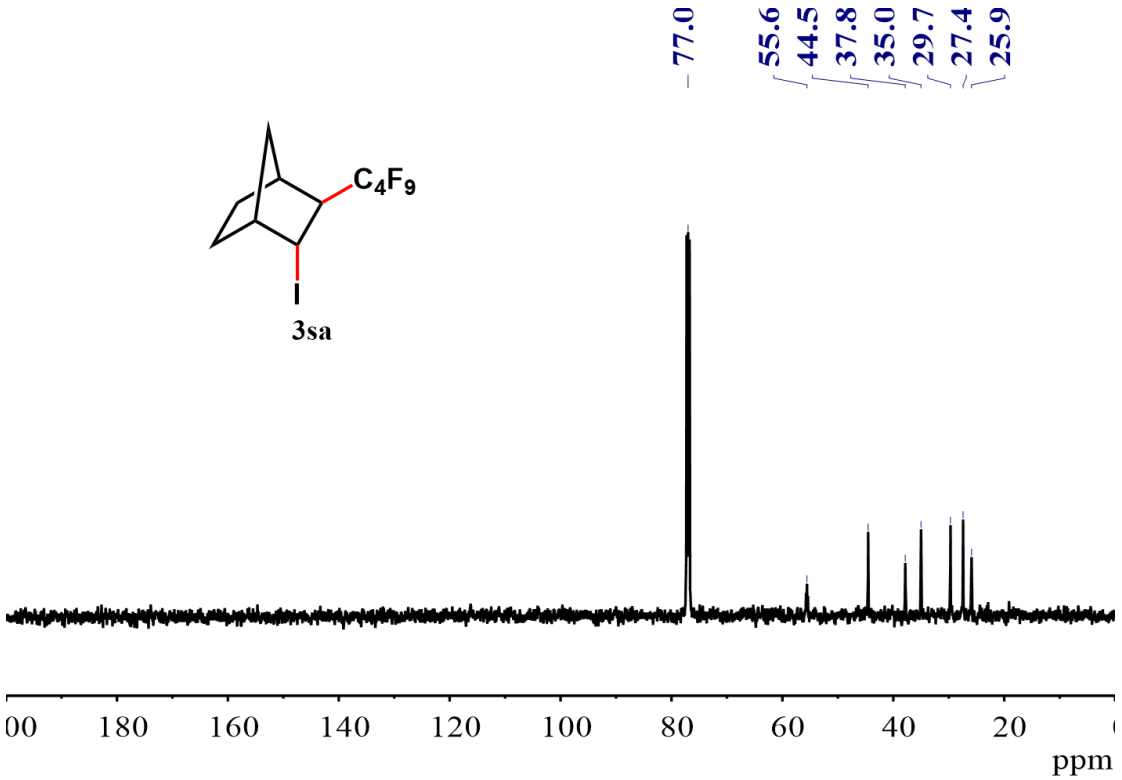
^{13}C NMR spectrum for 1-iodo-2-(perfluorobutyl)cyclooctane **3ra** ($CDCl_3$, 126 MHz).



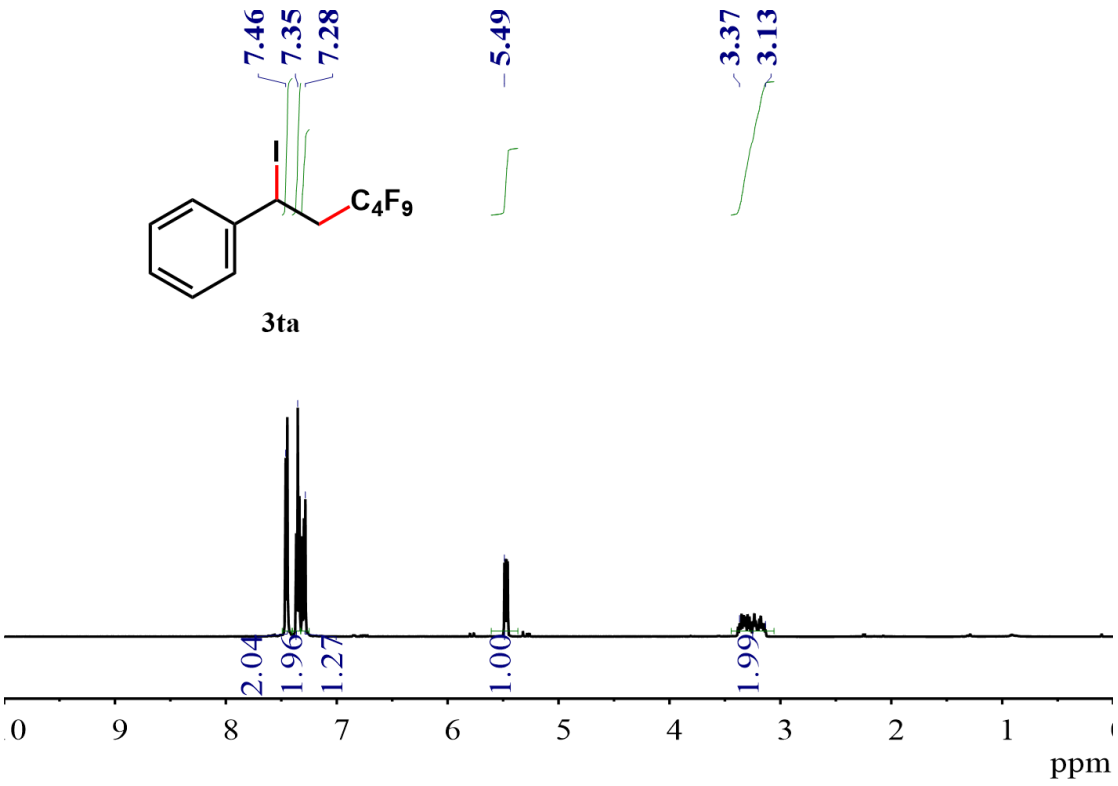
^{1}H NMR spectrum for (1R,3S,4S)-2-iodo-3-(perfluorobutyl)bicyclo[2.2.1]heptane **3sa** ($CDCl_3$, 500 MHz).



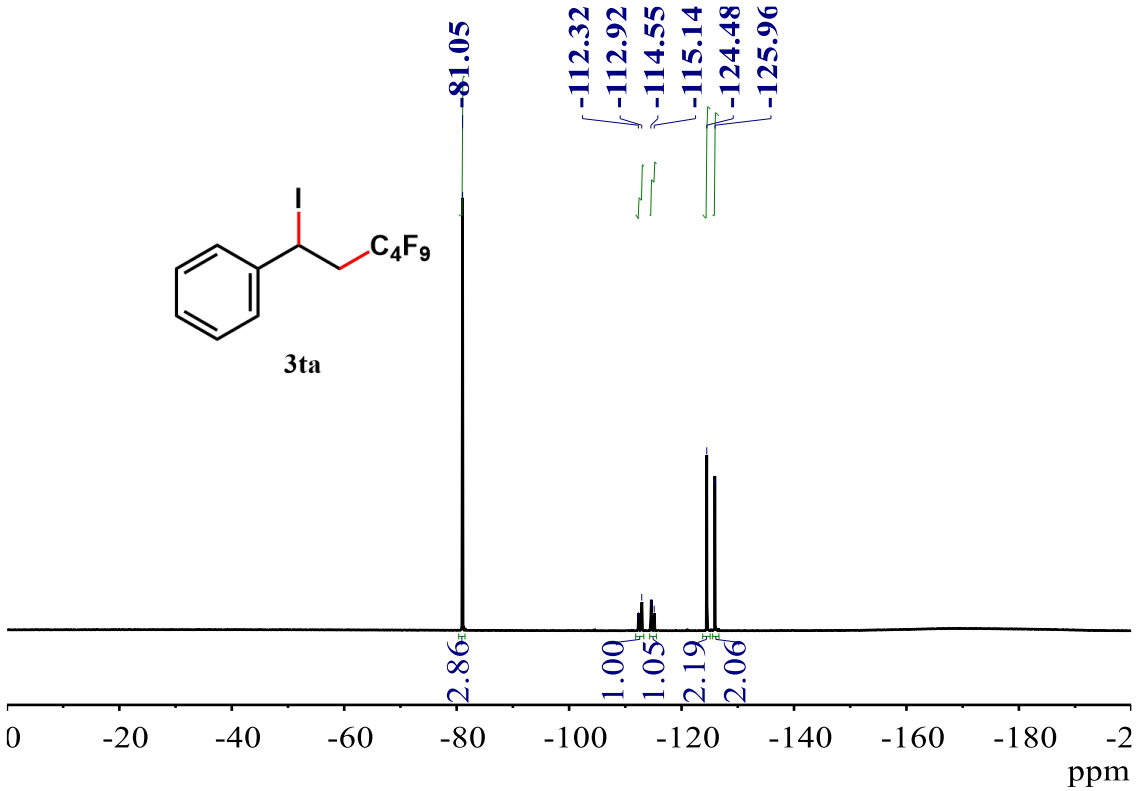
^{19}F NMR spectrum for (1R,3S,4S)-2-iodo-3-(perfluorobutyl)bicyclo[2.2.1]heptane **3sa** ($CDCl_3$, 471 MHz).



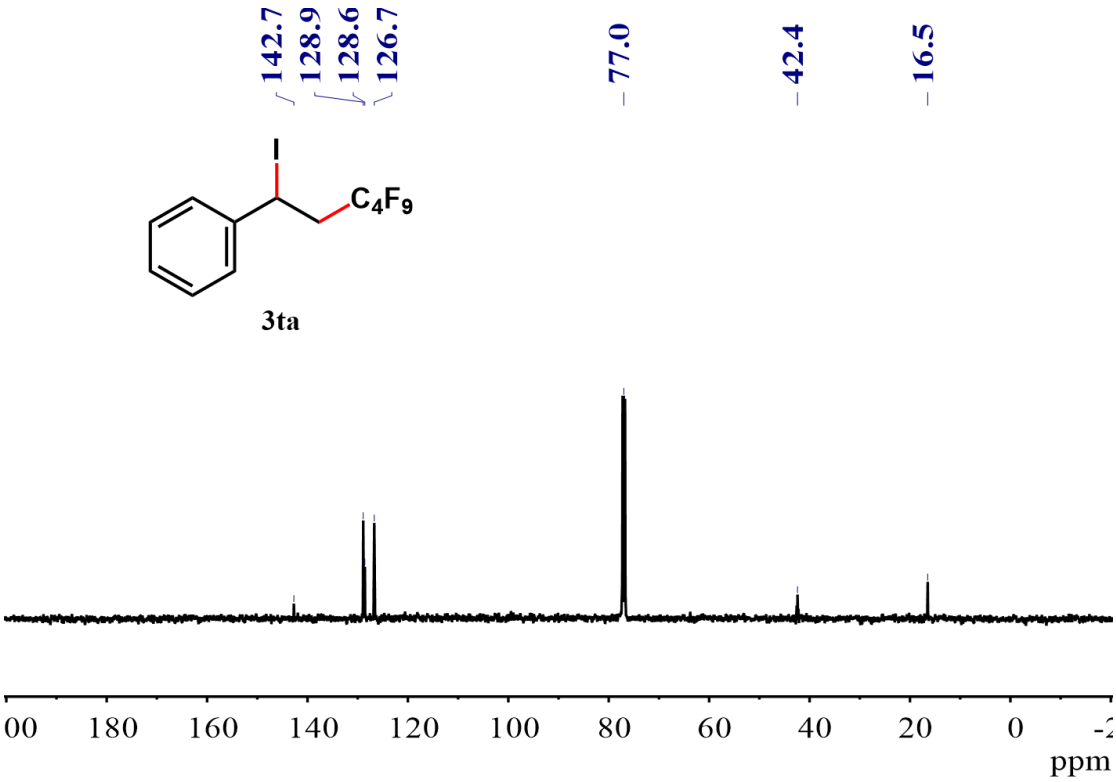
^{13}C NMR spectrum for (1R,3S,4S)-2-iodo-3-(perfluorobutyl)bicyclo[2.2.1]heptane **3sa** ($CDCl_3$, 126 MHz).



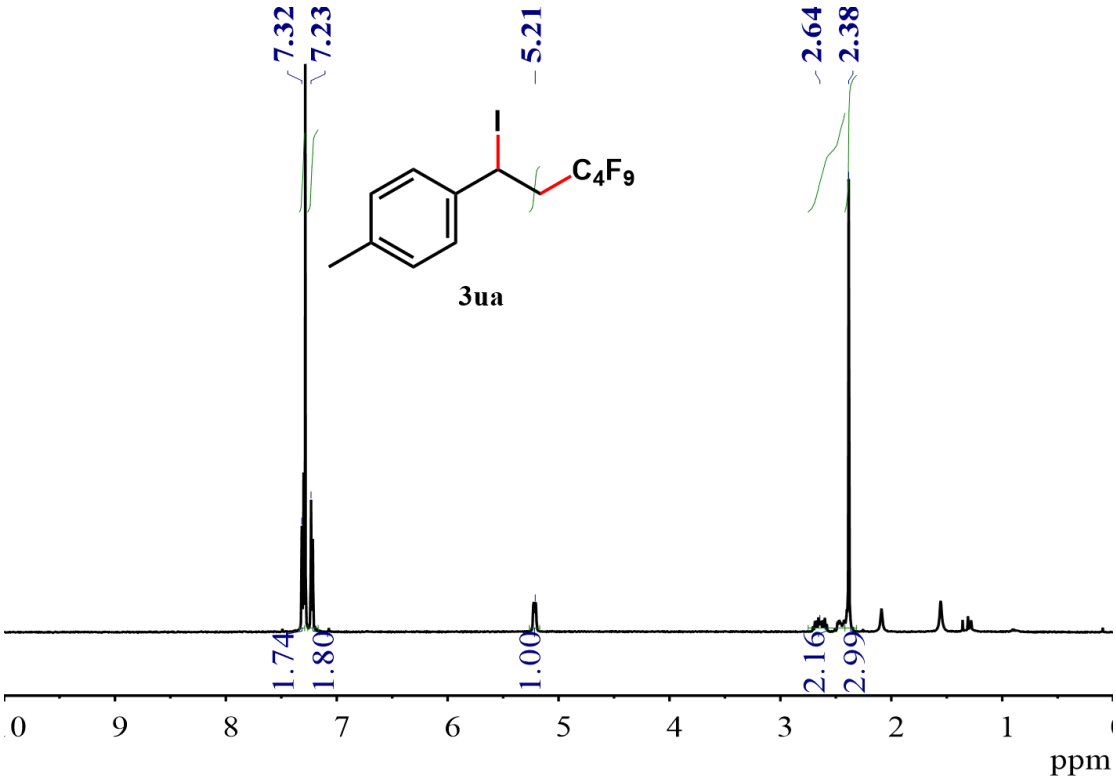
^{1}H NMR spectrum for (3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)benzene **3ta** ($CDCl_3$, 500 MHz).



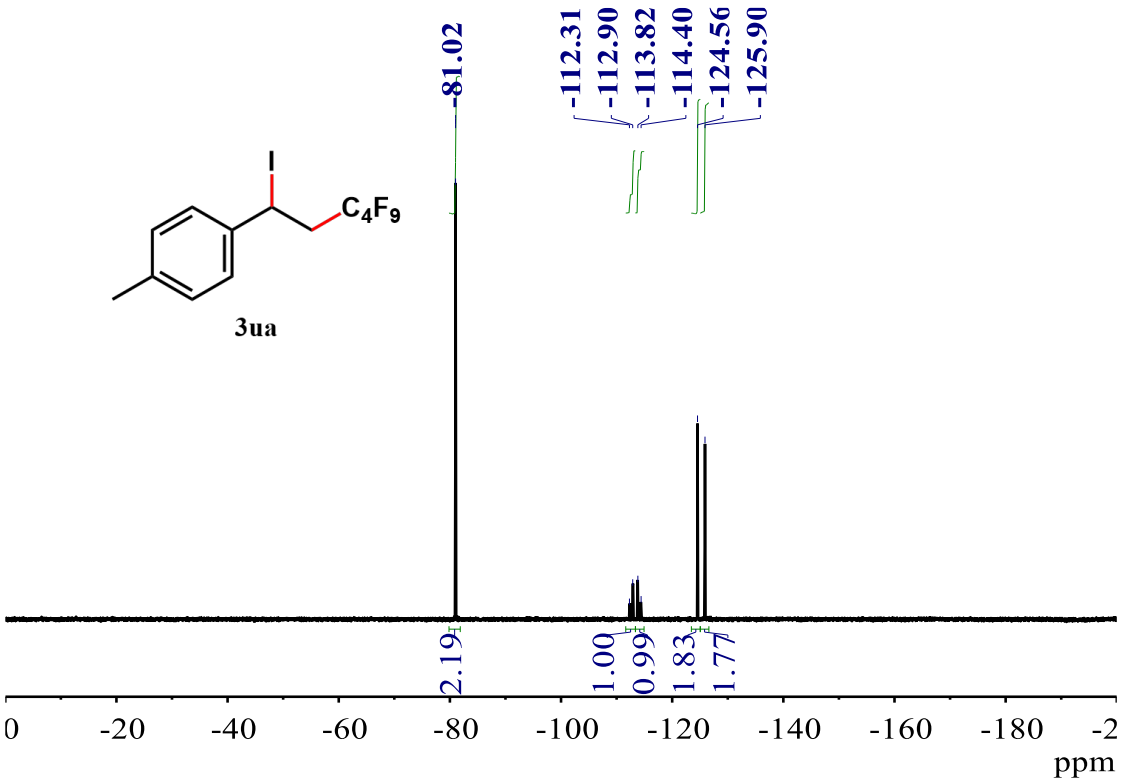
^{19}F NMR spectrum for (3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)benzene **3ta** ($CDCl_3$, 471 MHz).



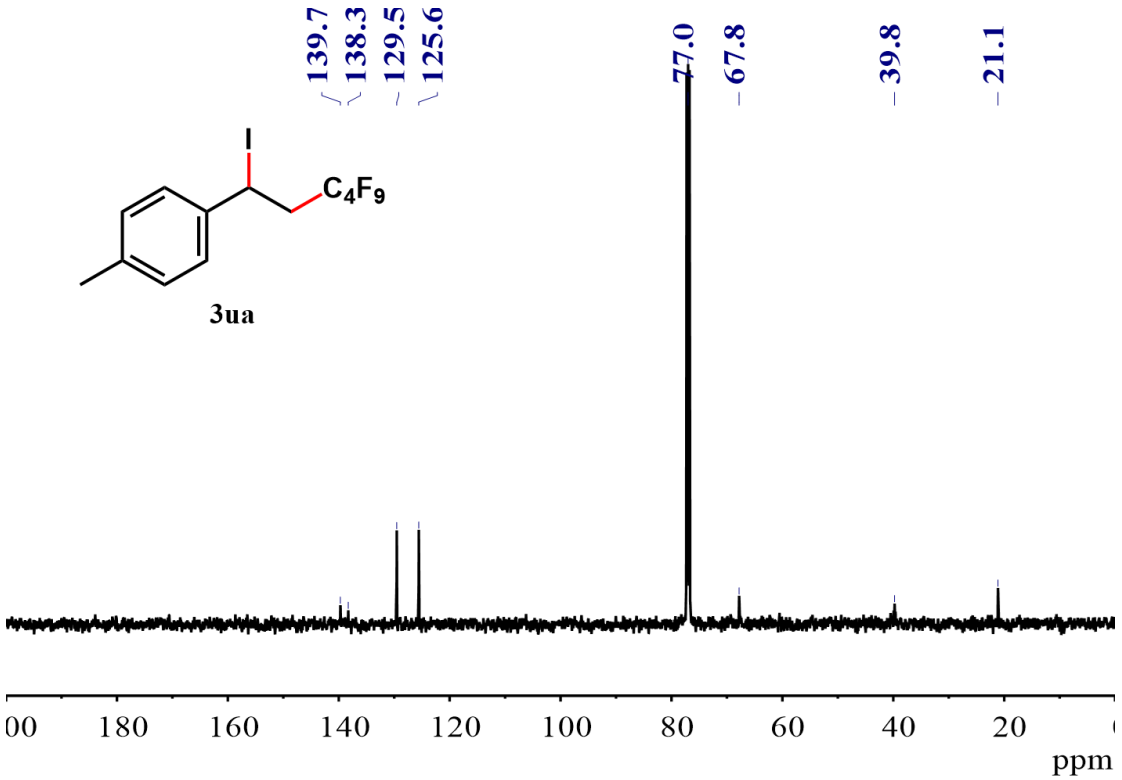
^{13}C NMR spectrum for (3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)benzene **3ta** ($CDCl_3$, 126 MHz).



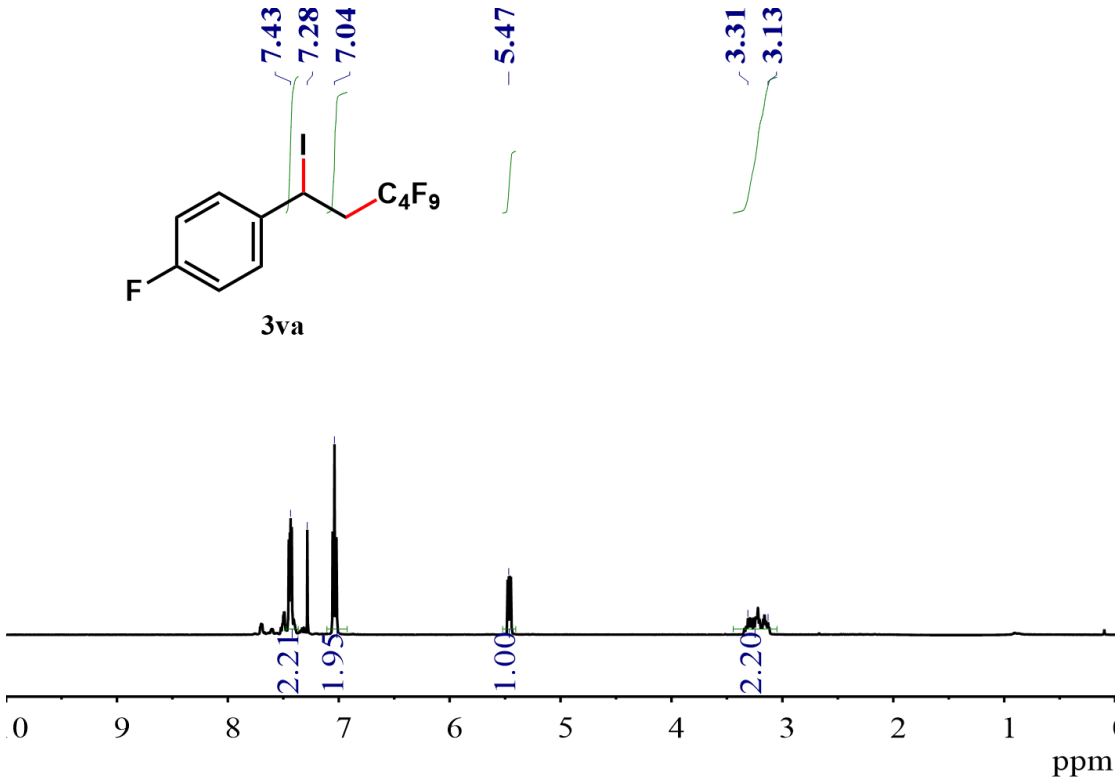
^{1}H NMR spectrum for 1-methyl-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)benzene **3ua** ($CDCl_3$, 500 MHz).



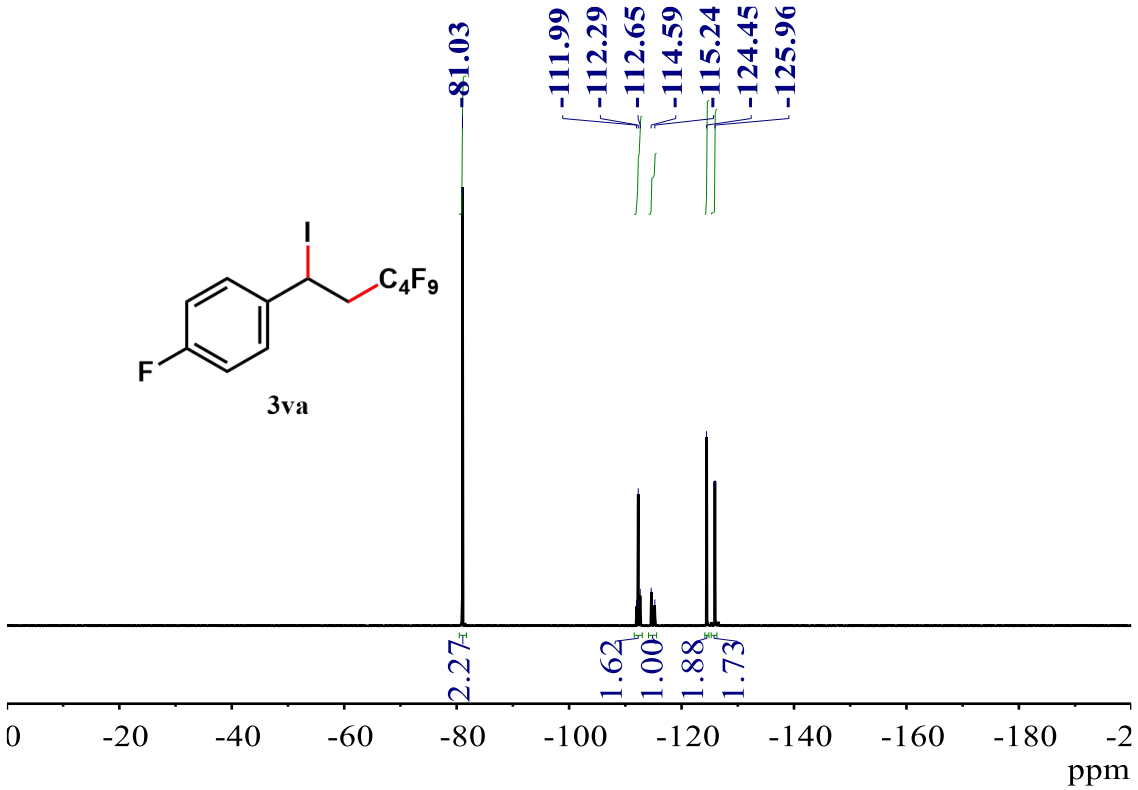
^{19}F NMR spectrum for 1-methyl-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)benzene **3ua** ($CDCl_3$, 471 MHz).



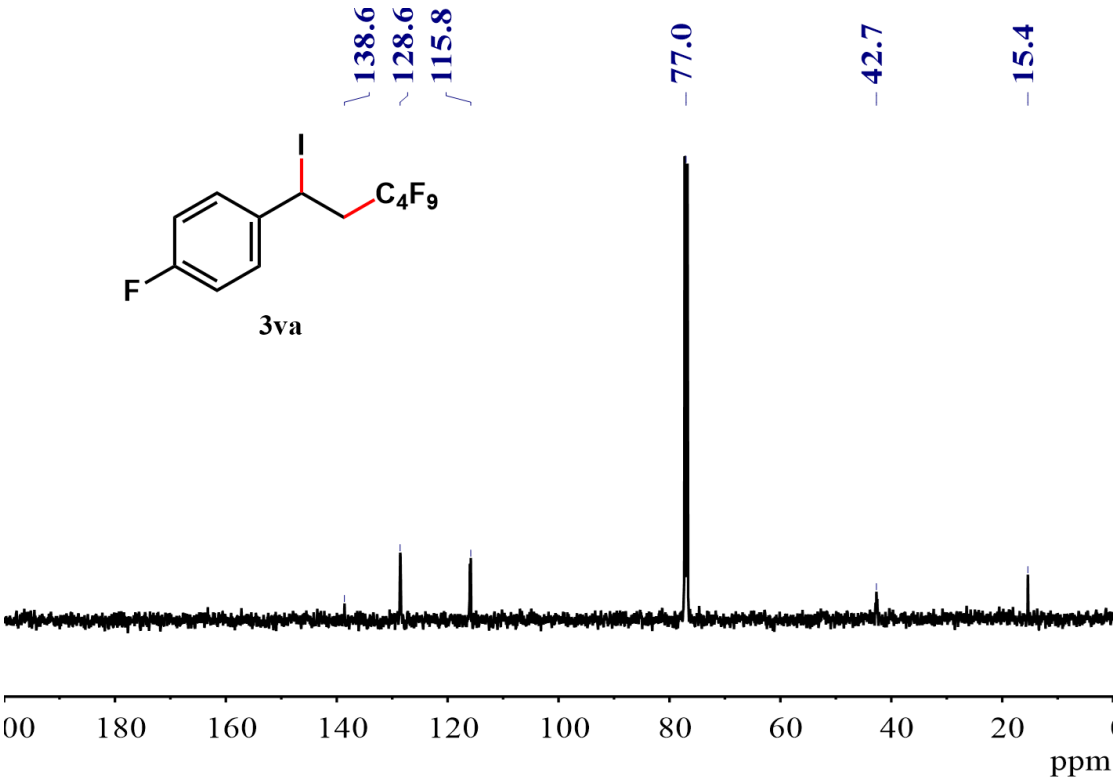
^{13}C NMR spectrum for 1-methyl-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)benzene **3ua** ($CDCl_3$, 126 MHz).



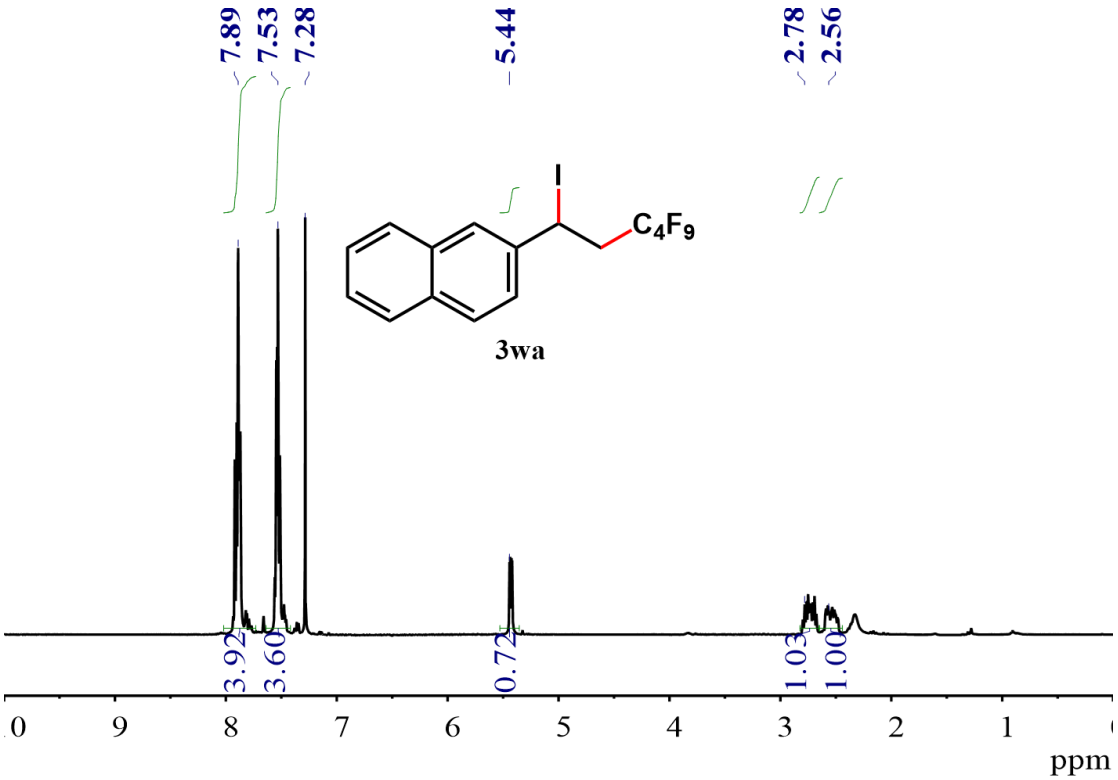
^{1}H NMR spectrum for 1-fluoro-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)benzene **3va** ($CDCl_3$, 500 MHz).



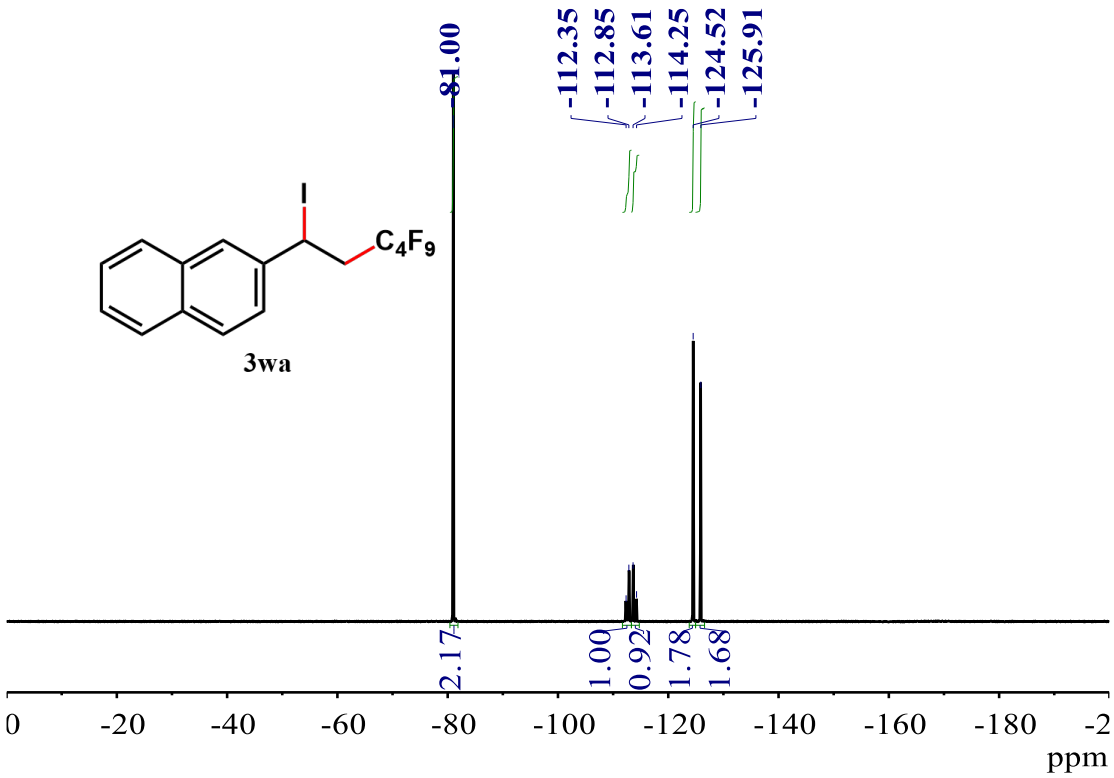
^{19}F NMR spectrum for 1-fluoro-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)benzene **3va** ($CDCl_3$, 471 MHz).



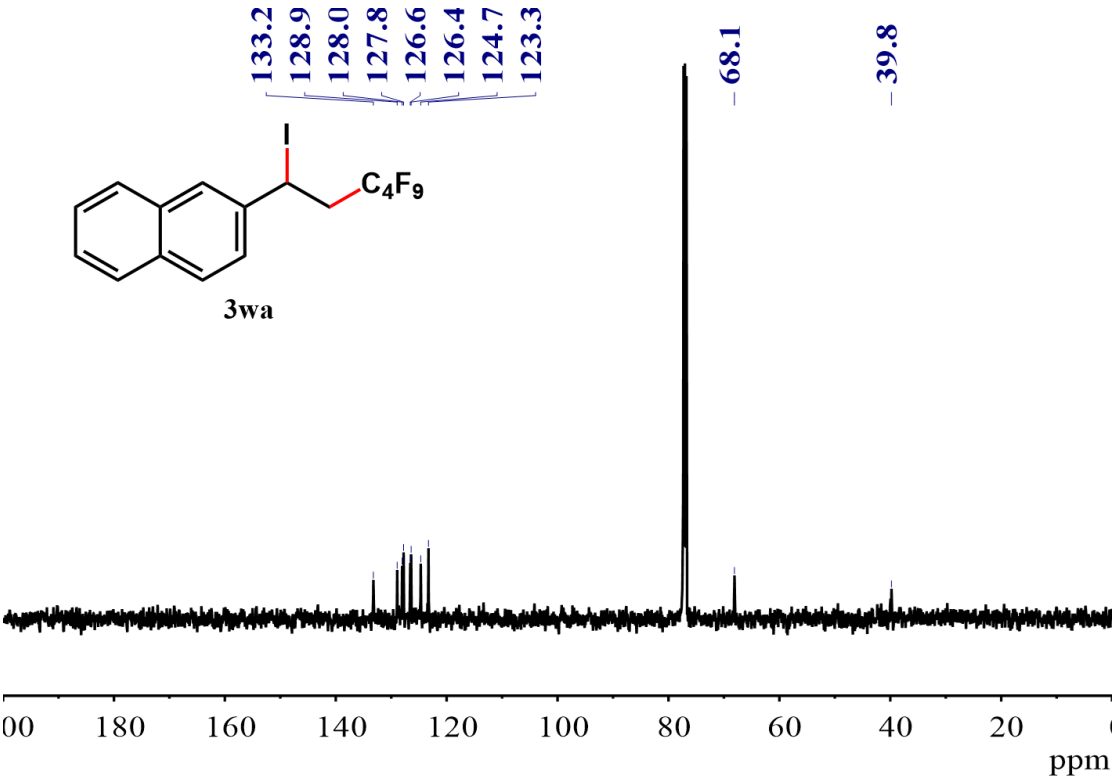
^{13}C NMR spectrum for 1-fluoro-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)benzene **3va** ($CDCl_3$, 126 MHz).



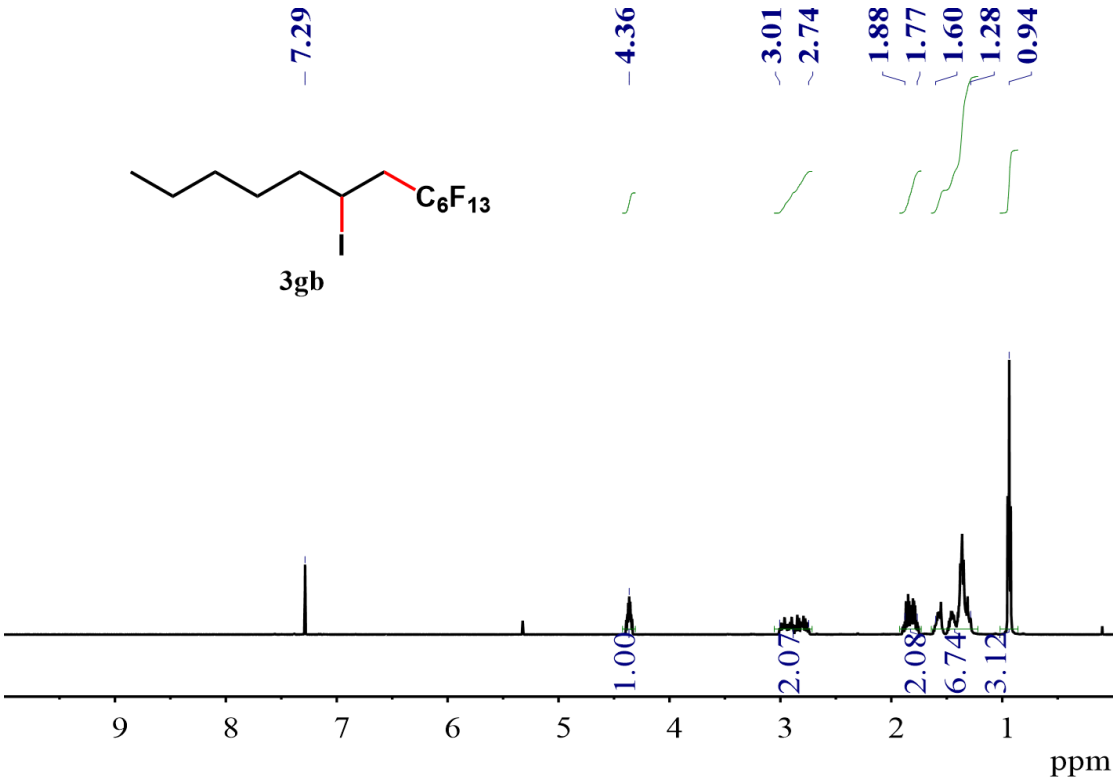
^{1}H NMR spectrum for 2-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)naphthalene **3wa** ($CDCl_3$, 500 MHz).



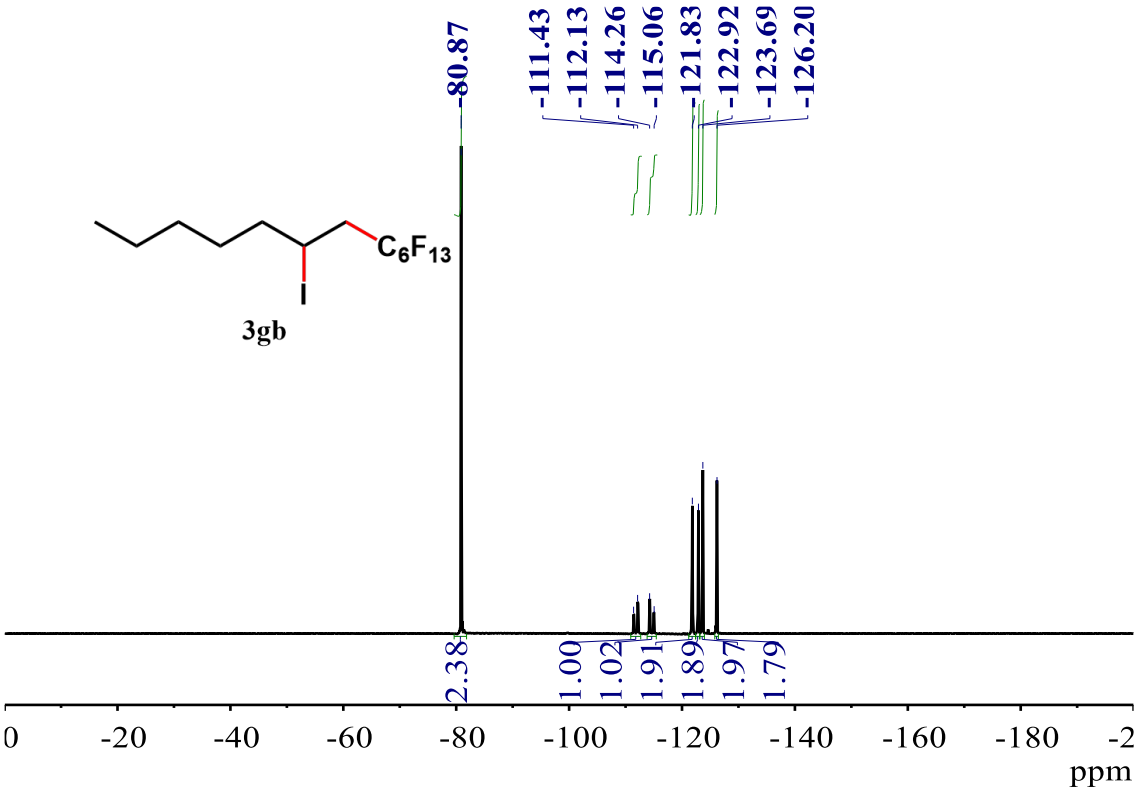
^{19}F NMR spectrum for 2-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)naphthalene **3wa** ($CDCl_3$, 471 MHz).



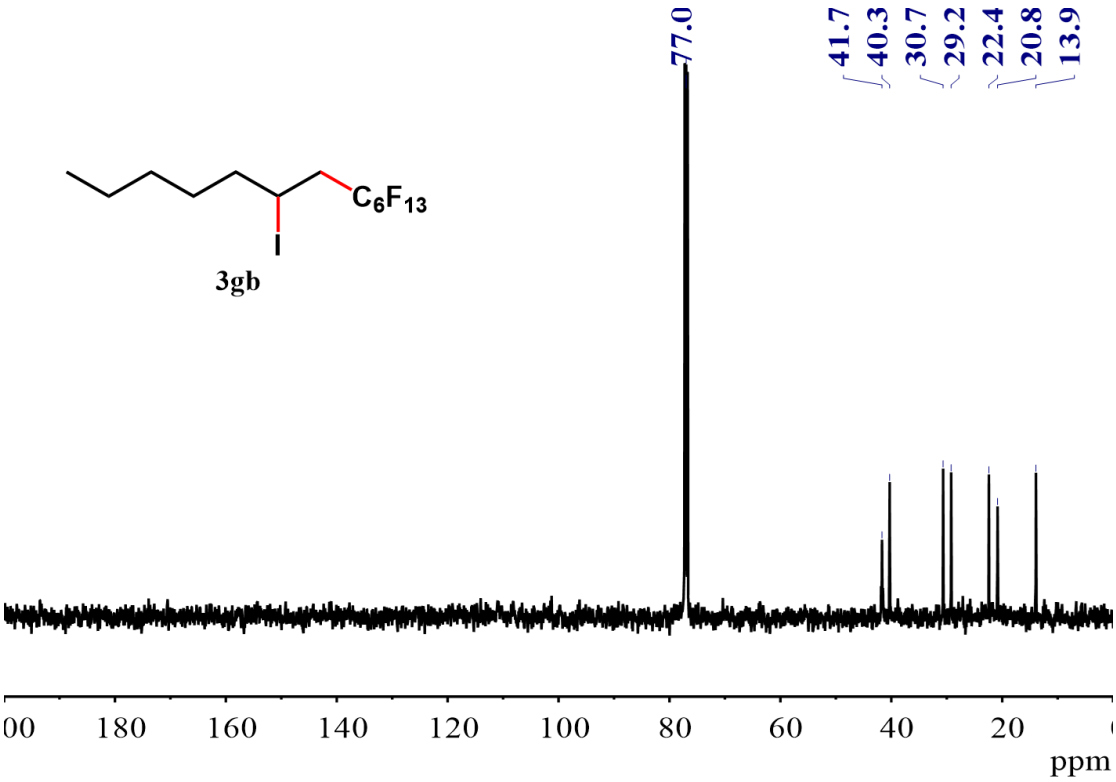
^{13}C NMR spectrum for 2-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)naphthalene **3wa** ($CDCl_3$, 126 MHz).



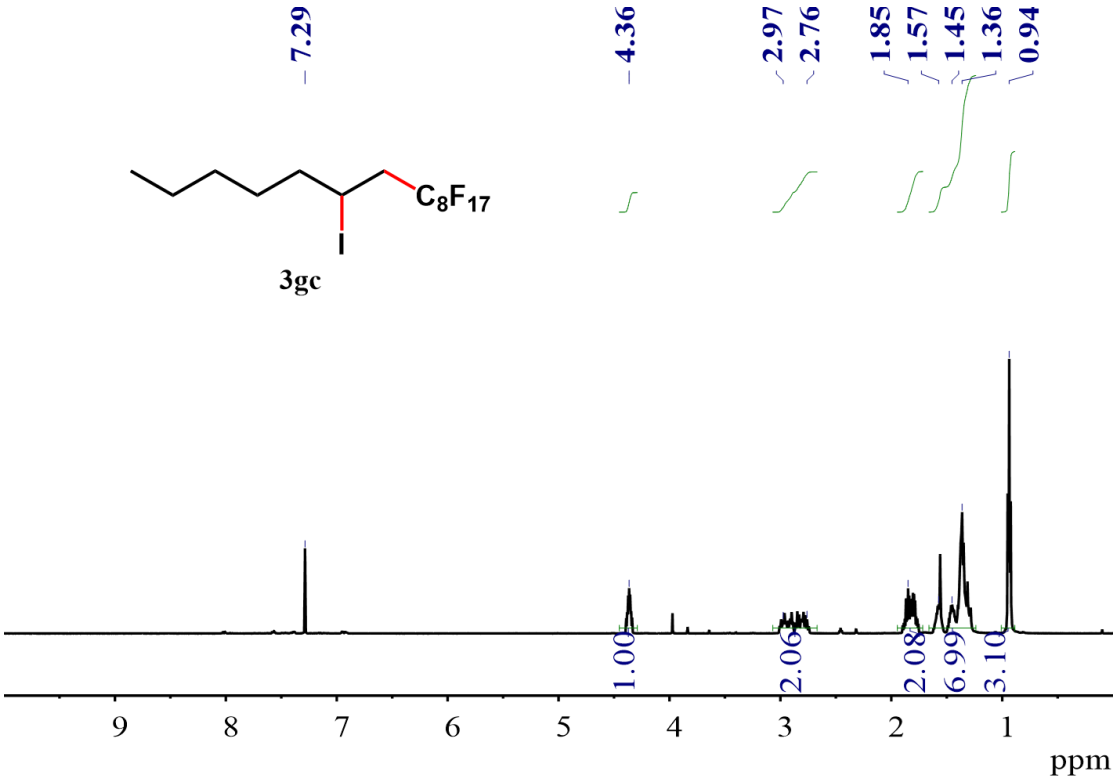
^{1}H NMR spectrum for 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodotridecane **3gb** ($CDCl_3$, 500 MHz).



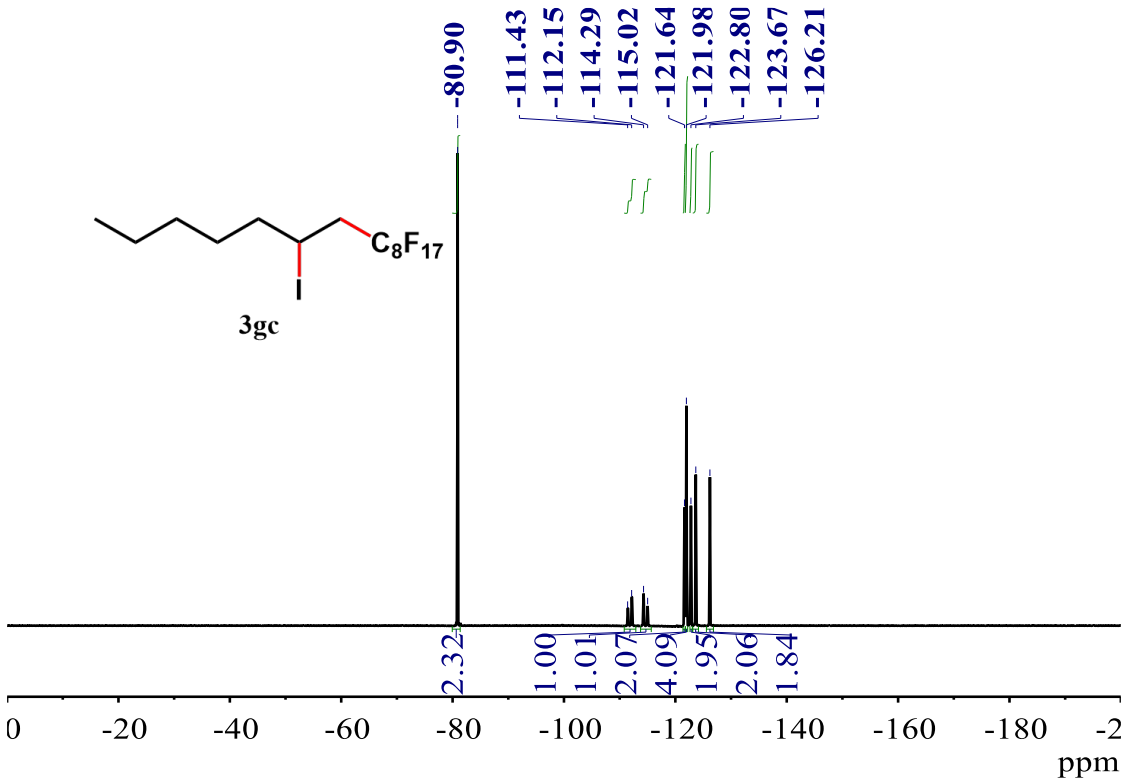
^{19}F NMR spectrum for 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodotridecane **3gb** ($CDCl_3$, 471 MHz).



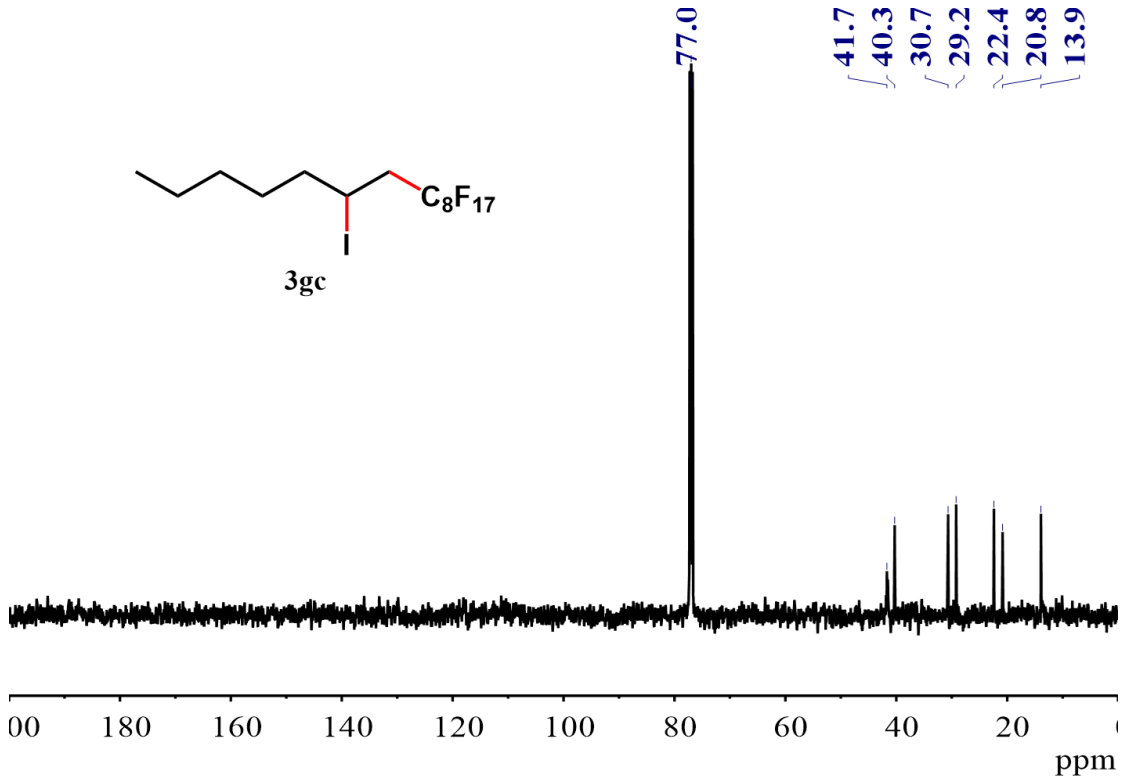
^{13}C NMR spectrum for 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodotridecane **3gb** ($CDCl_3$, 126 MHz).



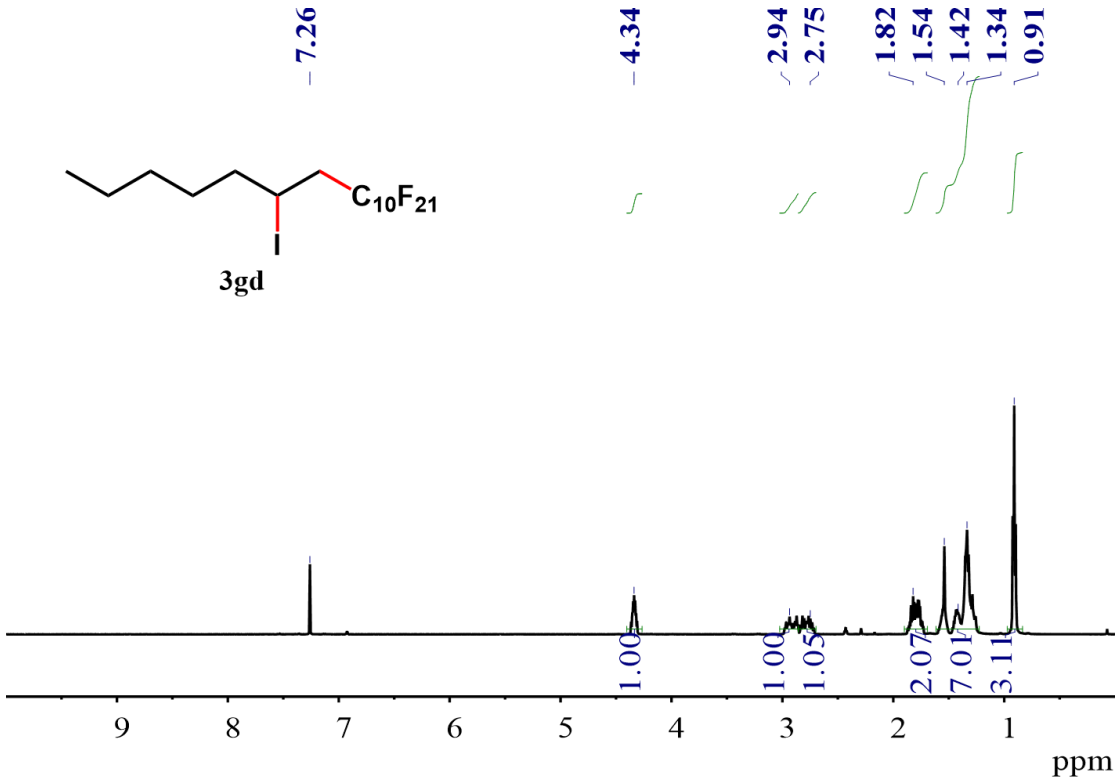
^{1}H NMR spectrum for 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iodopentadecane **3gc** ($CDCl_3$, 500 MHz).



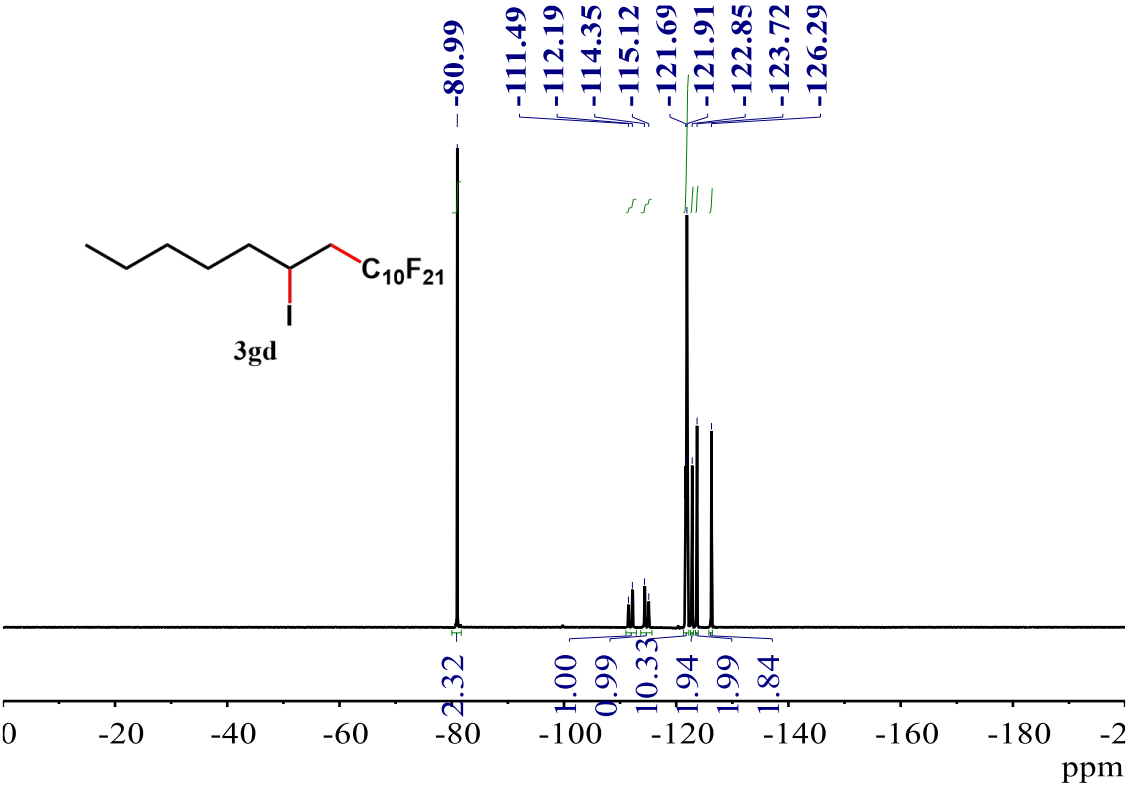
^{19}F NMR spectrum for 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iodopentadecane **3gc** ($CDCl_3$, 471 MHz).



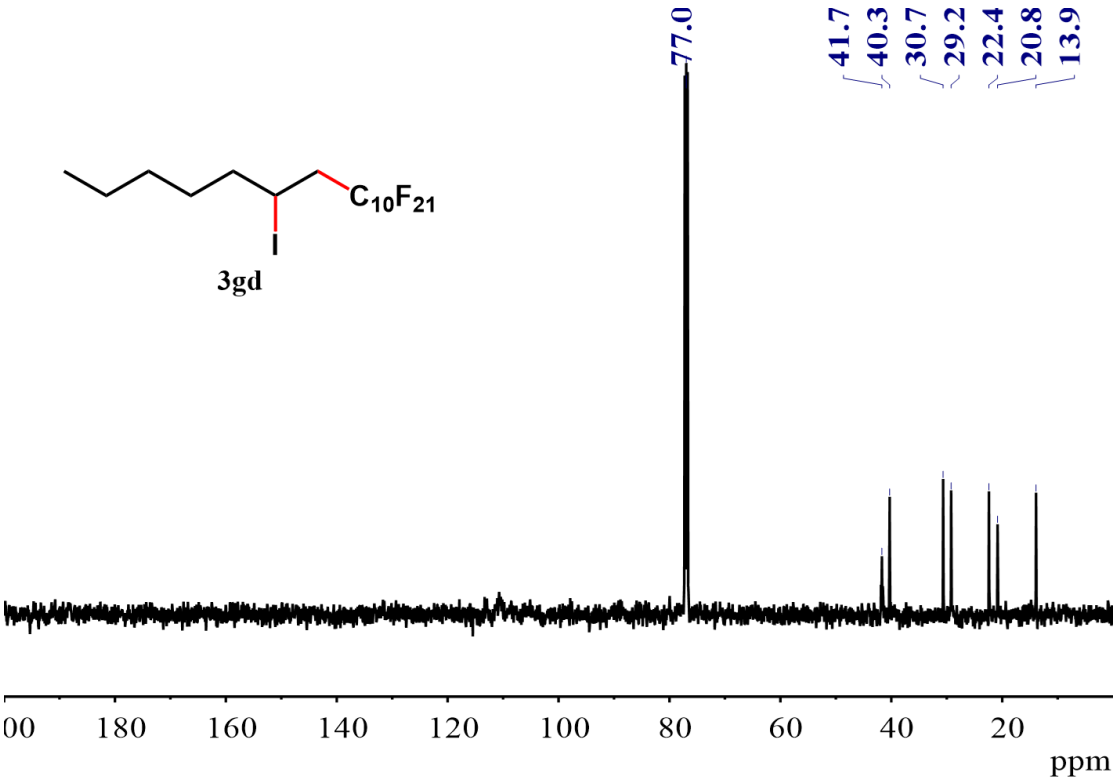
^{13}C NMR spectrum for 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iodopentadecane **3gc** ($CDCl_3$, 126 MHz).



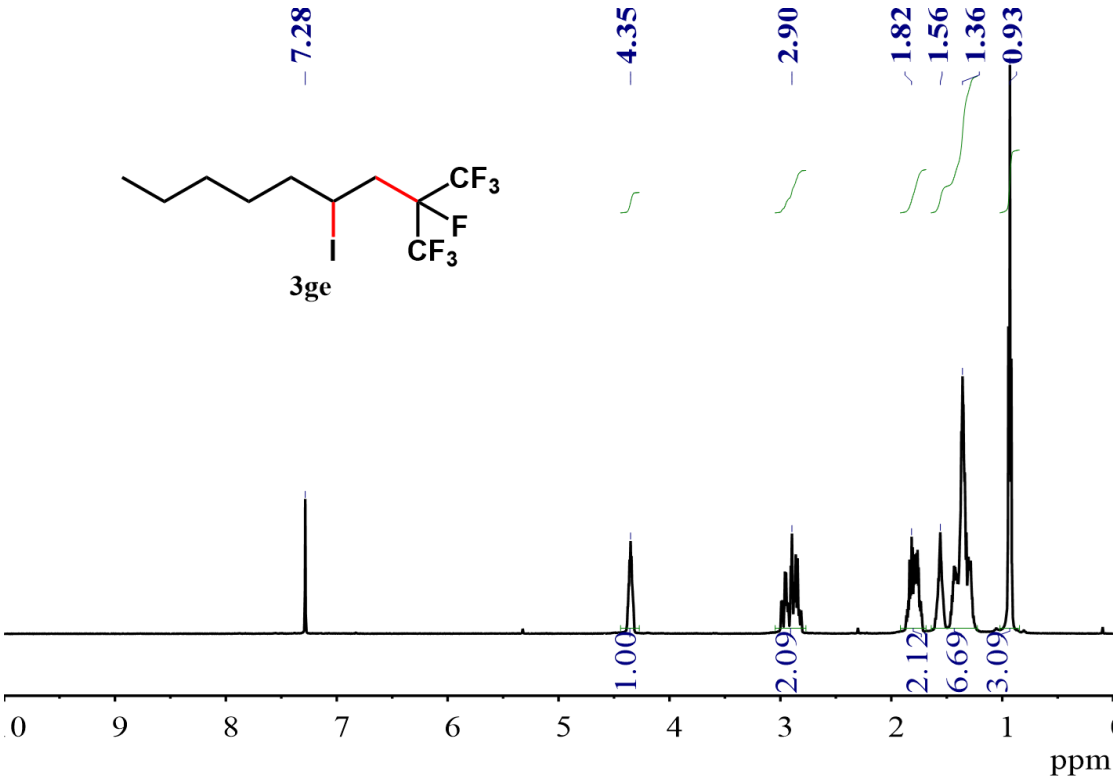
^{1}H NMR spectrum for 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-henicosafluoro-12-iodoheptadecane **3gd** ($CDCl_3$, 500 MHz).



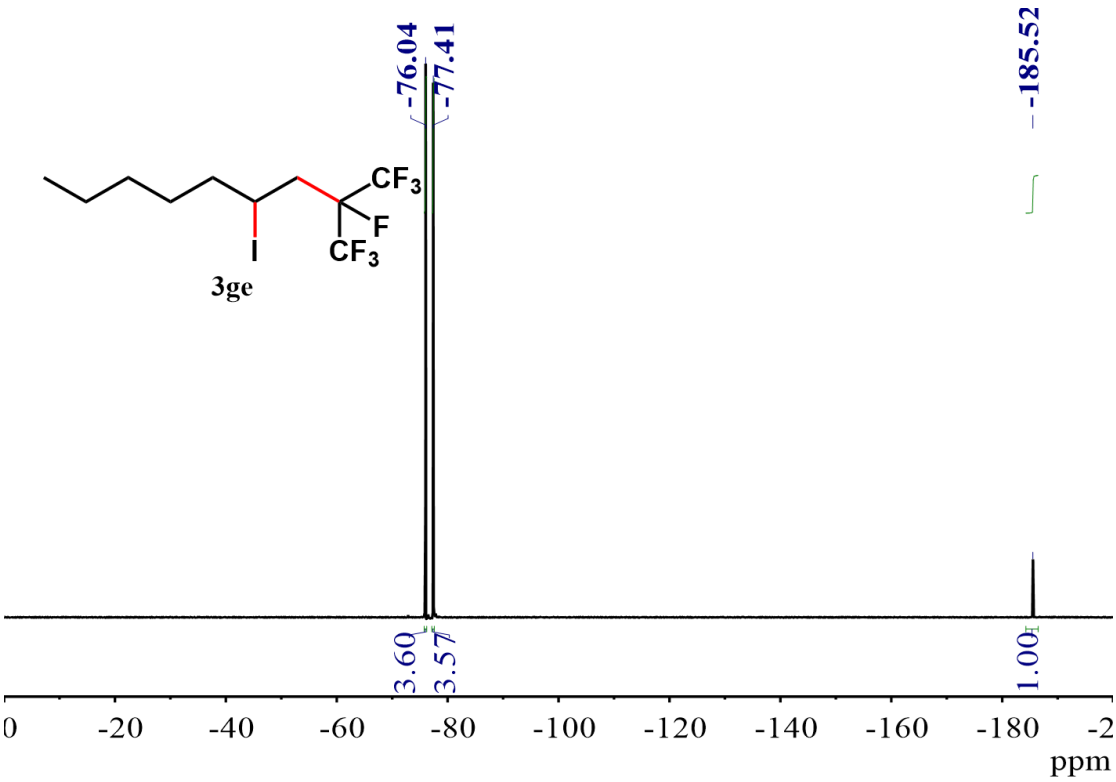
^{19}F NMR spectrum for 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-henicosafluoro-12-iodoheptadecane **3gd** ($CDCl_3$, 471 MHz).



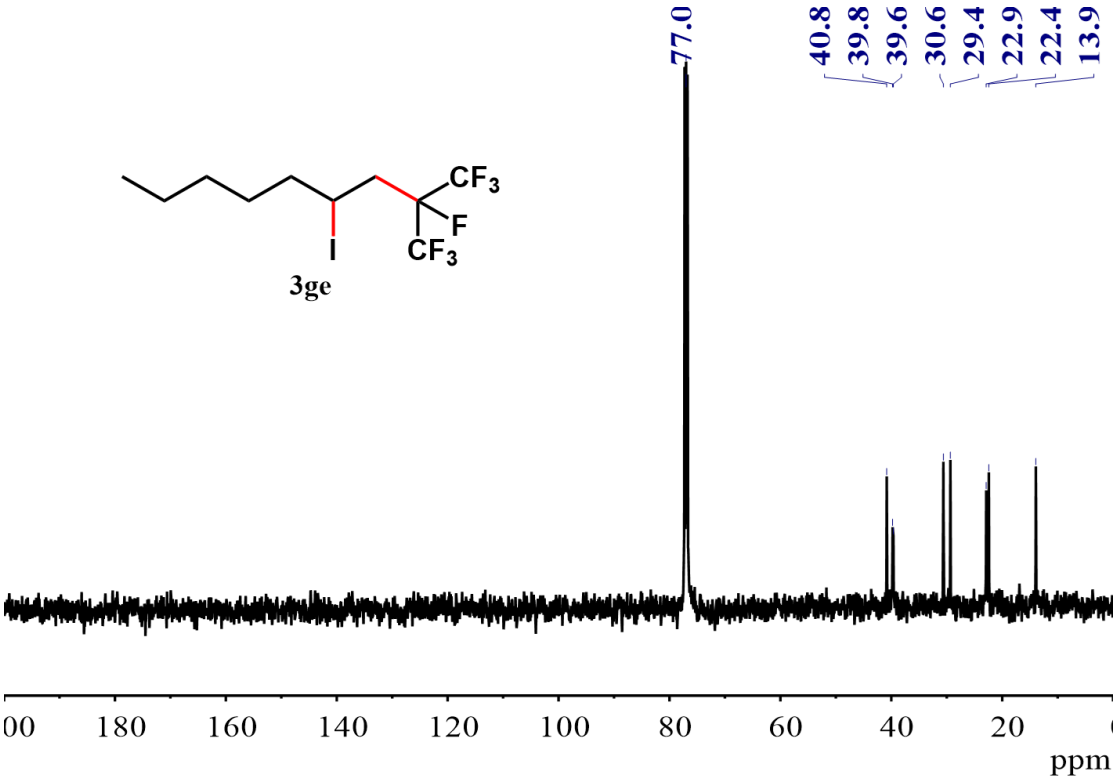
^{13}C NMR spectrum for 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-henicosafluoro-12-iodoheptadecane **3gd** ($CDCl_3$, 126 MHz).



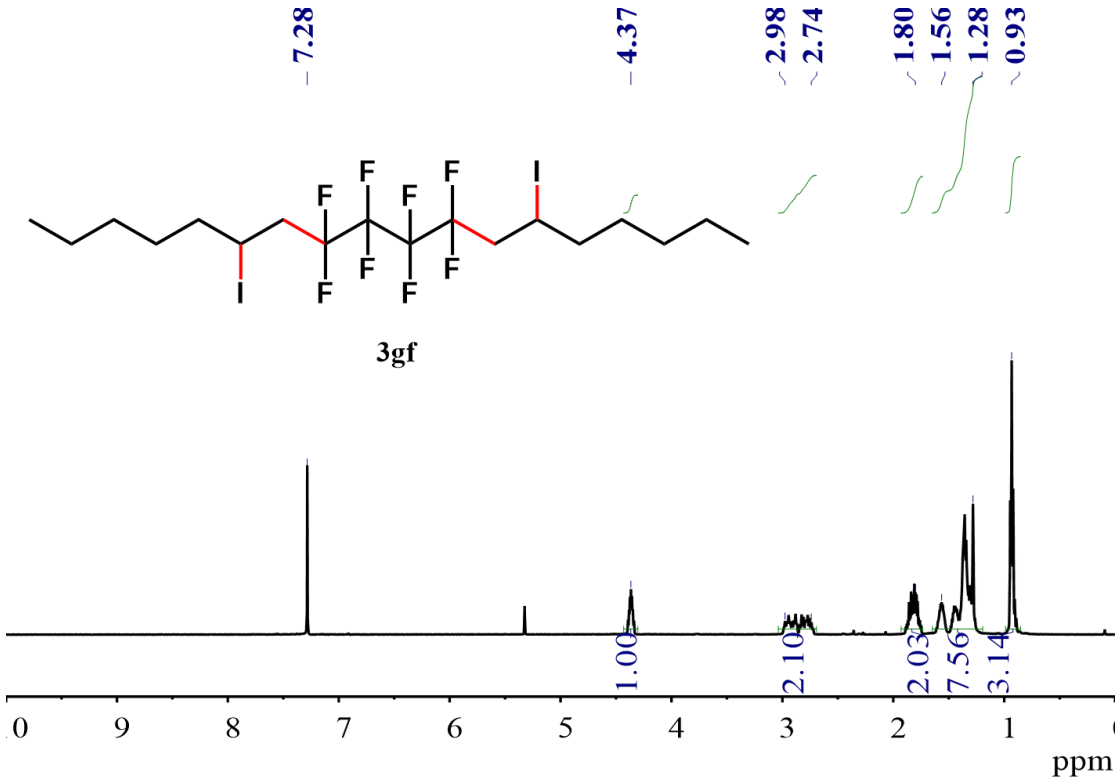
^{1}H NMR spectrum for 1,1,1,2-tetrafluoro-4-iodo-2-(trifluoromethyl)nonane **3ge** ($CDCl_3$, 500 MHz).



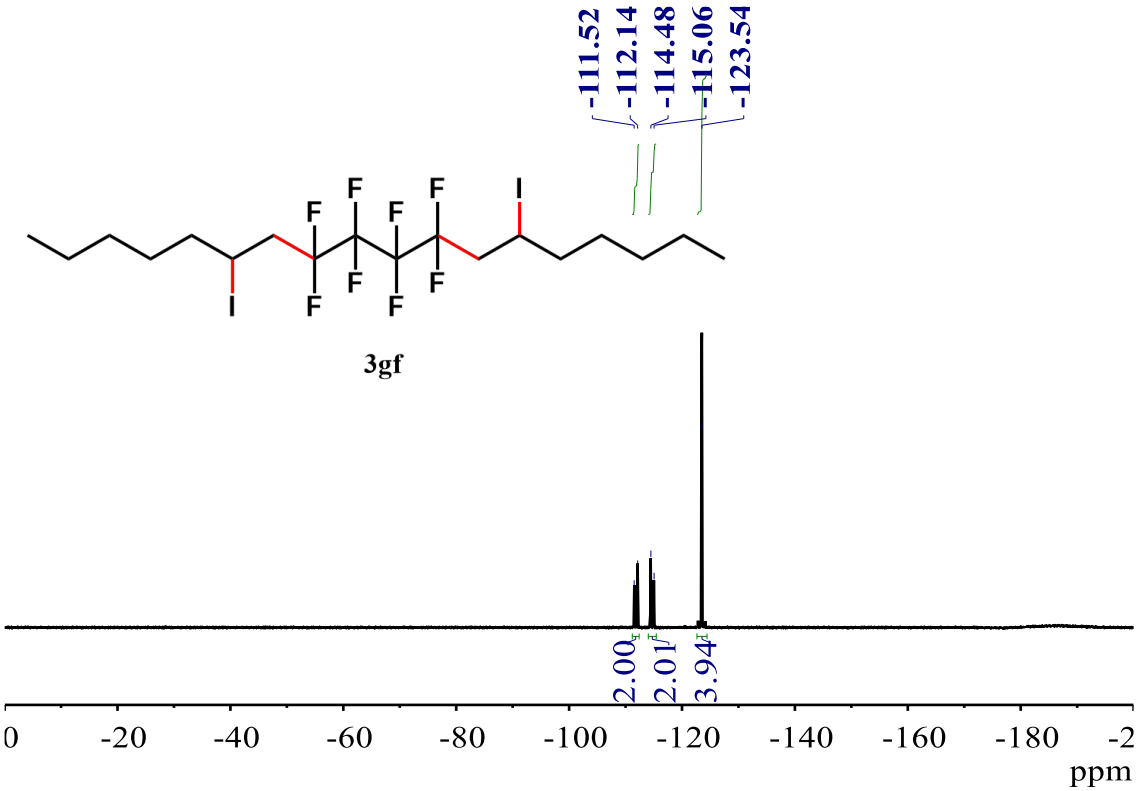
^{19}F NMR spectrum for 1,1,1,2-tetrafluoro-4-iodo-2-(trifluoromethyl)nonane **3ge** ($CDCl_3$, 471 MHz).



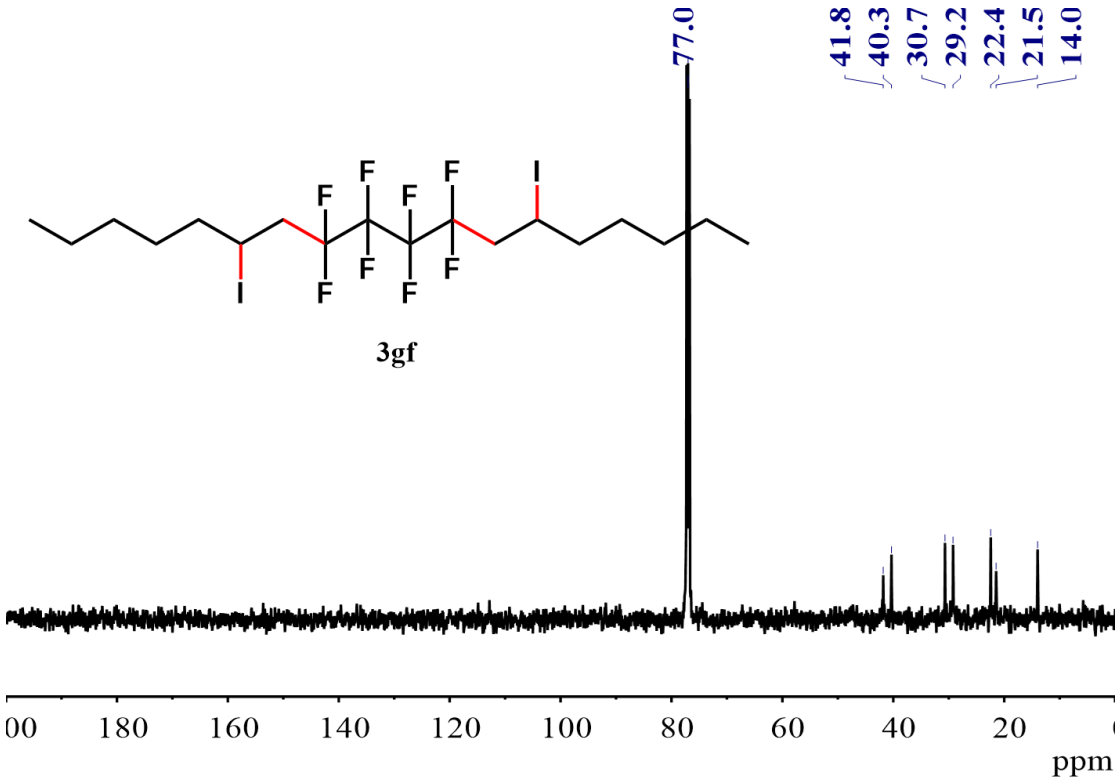
^{13}C NMR spectrum for 1,1,1,2-tetrafluoro-4-iodo-2-(trifluoromethyl)nonane **3ge** ($CDCl_3$, 126 MHz).



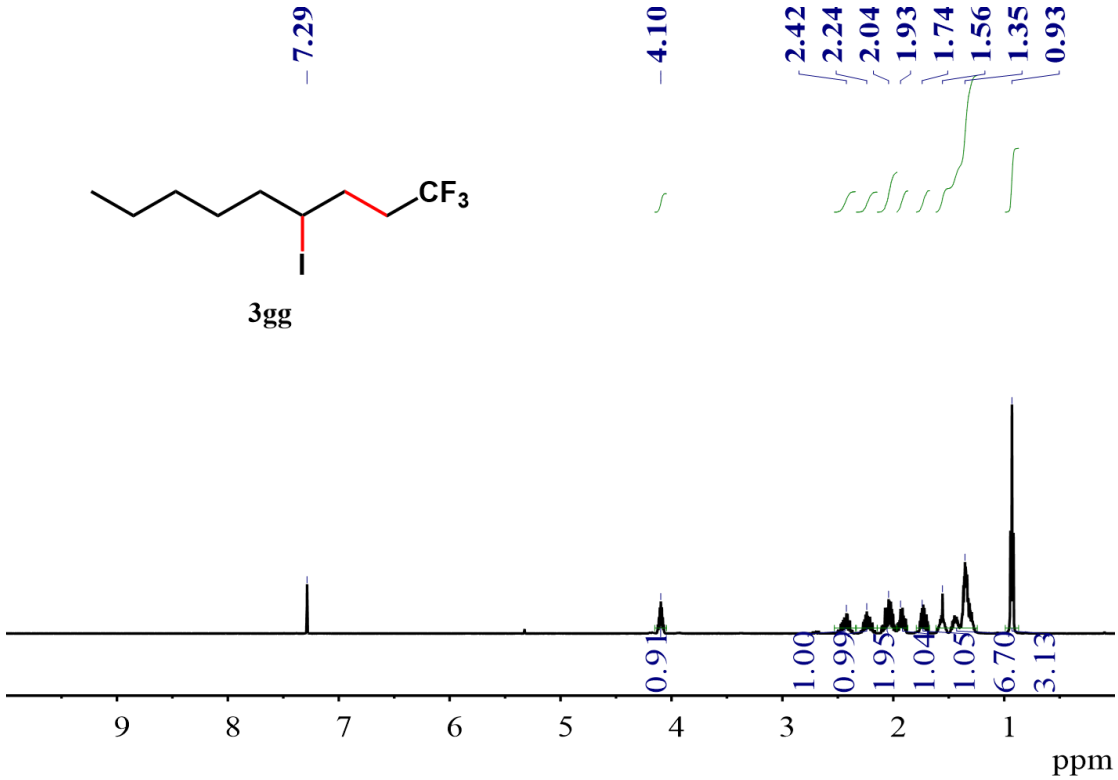
^{1}H NMR spectrum for 8,8,9,9,10,10,11,11-octafluoro-6,13-diiodooctadecane **3gf** ($CDCl_3$, 500 MHz).



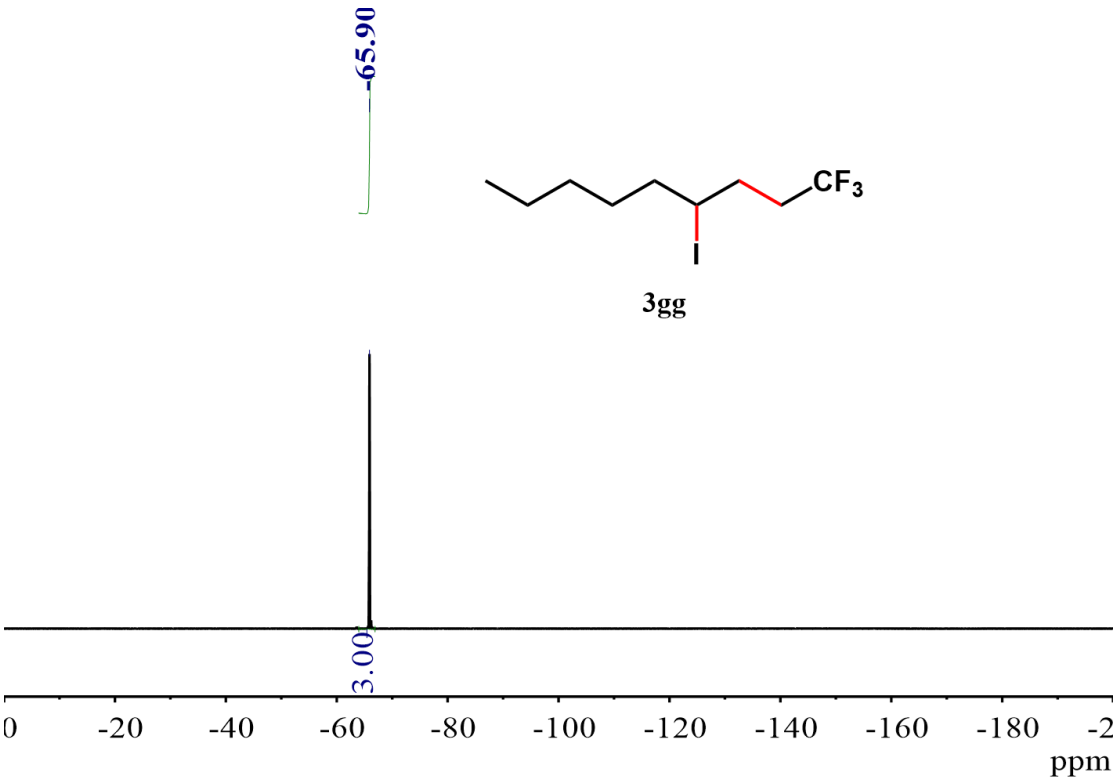
^{19}F NMR spectrum for 8,8,9,9,10,10,11,11-octafluoro-6,13-diiodooctadecane **3gf** ($CDCl_3$, 471 MHz).



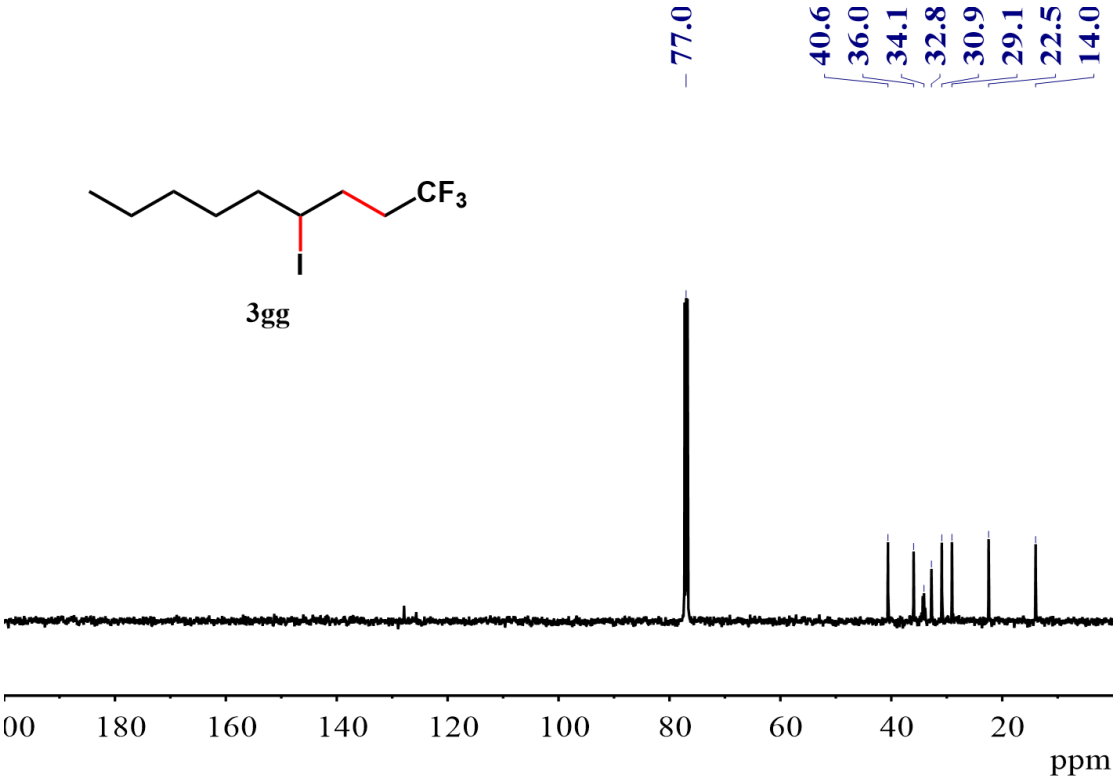
^{13}C NMR spectrum for 8,8,9,9,10,10,11,11-octafluoro-6,13-diiodooctadecane **3gf** ($CDCl_3$, 126 MHz).



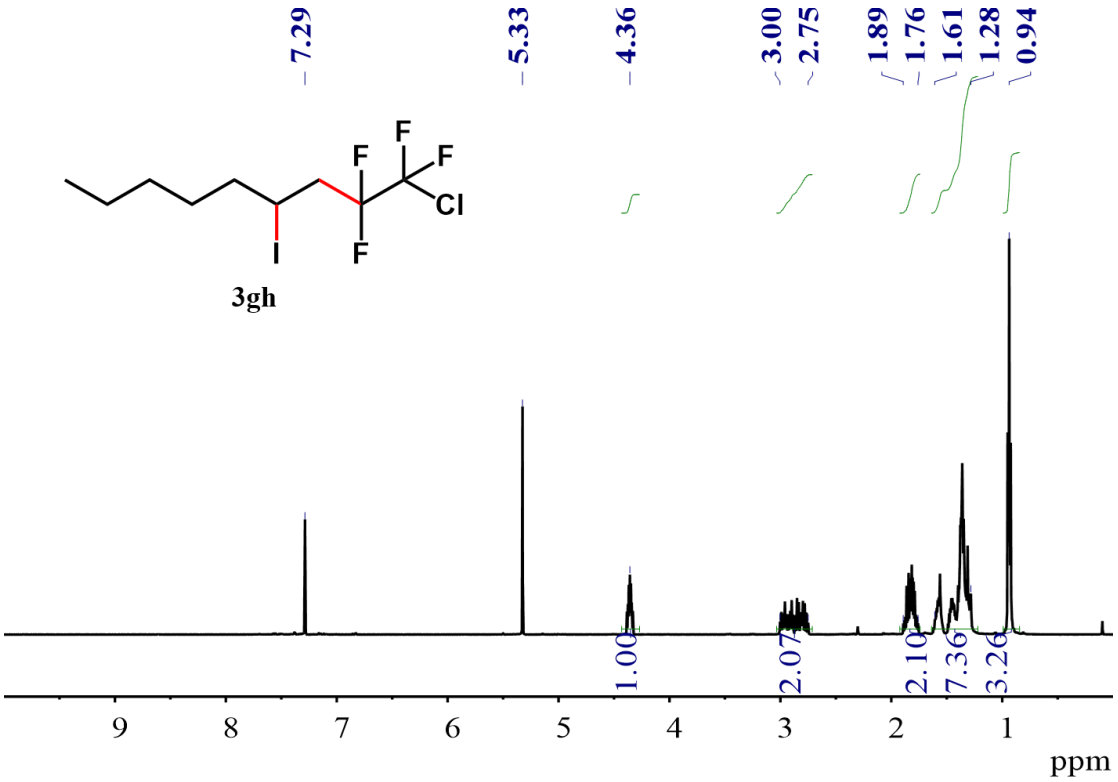
^{1}H NMR spectrum for 1,1,1-trifluoro-4-iodononane **3gg** ($CDCl_3$, 500 MHz).



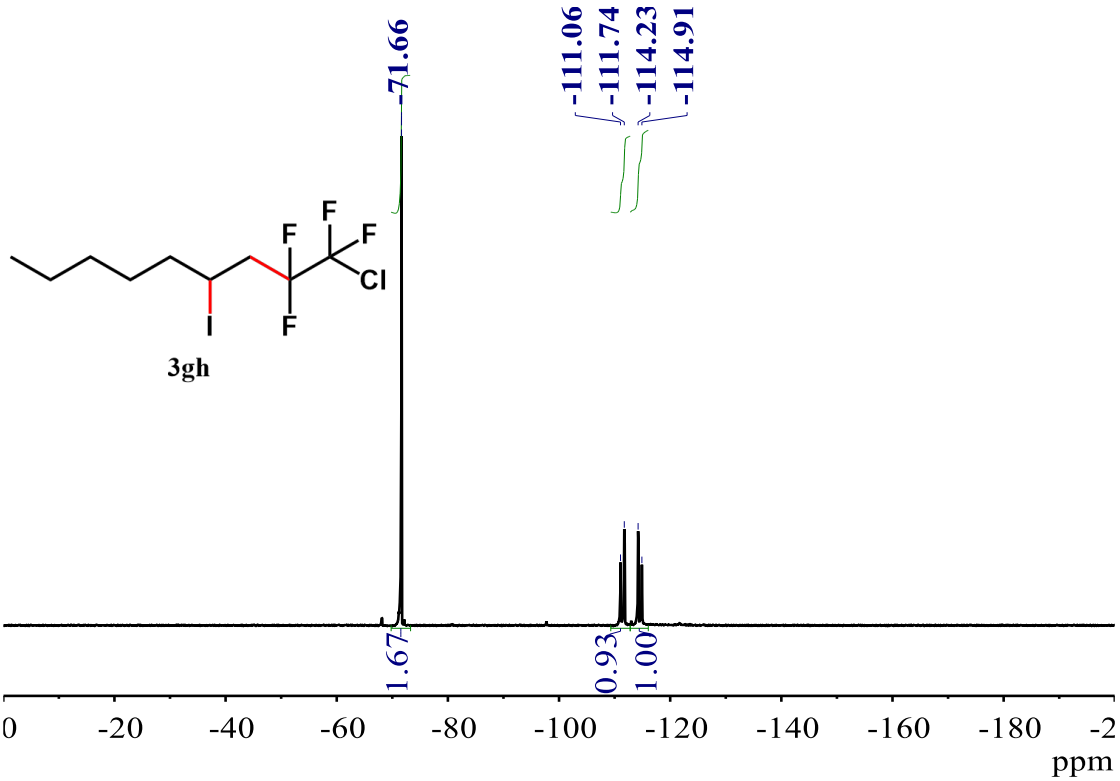
^{19}F NMR spectrum for 1,1,1-trifluoro-4-iodononane **3gg** ($CDCl_3$, 471 MHz).



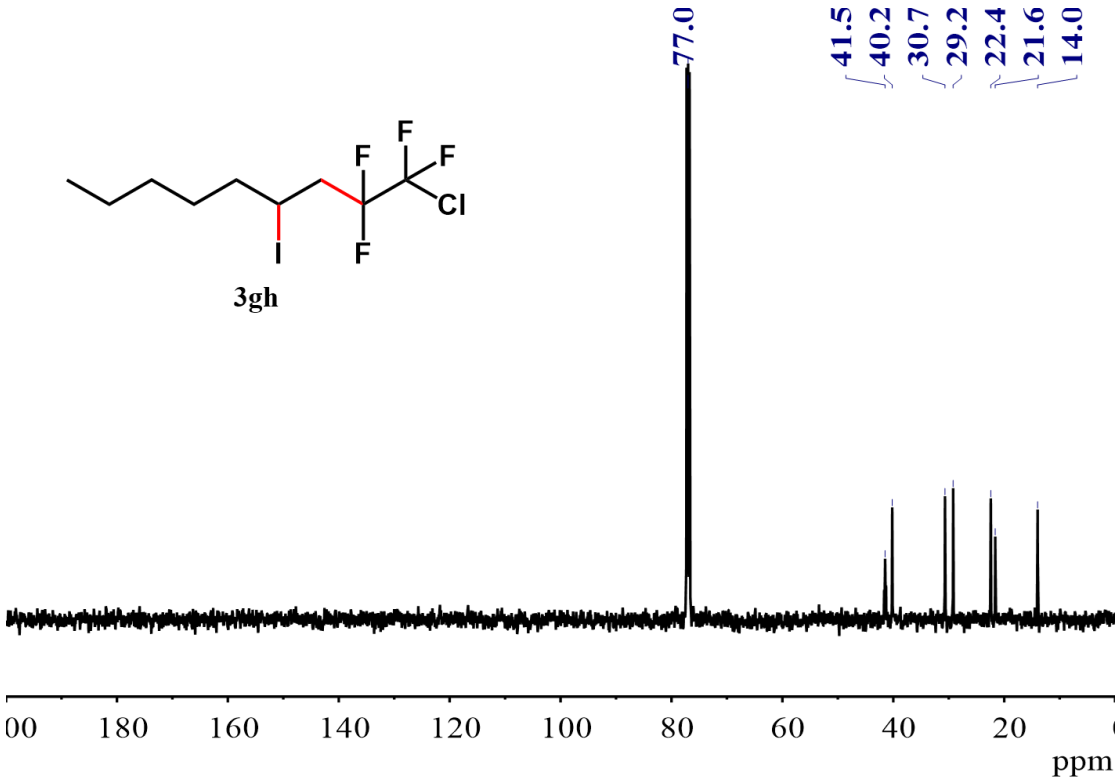
^{13}C NMR spectrum for 1,1,1-trifluoro-4-iodononane **3gg** ($CDCl_3$, 126 MHz).



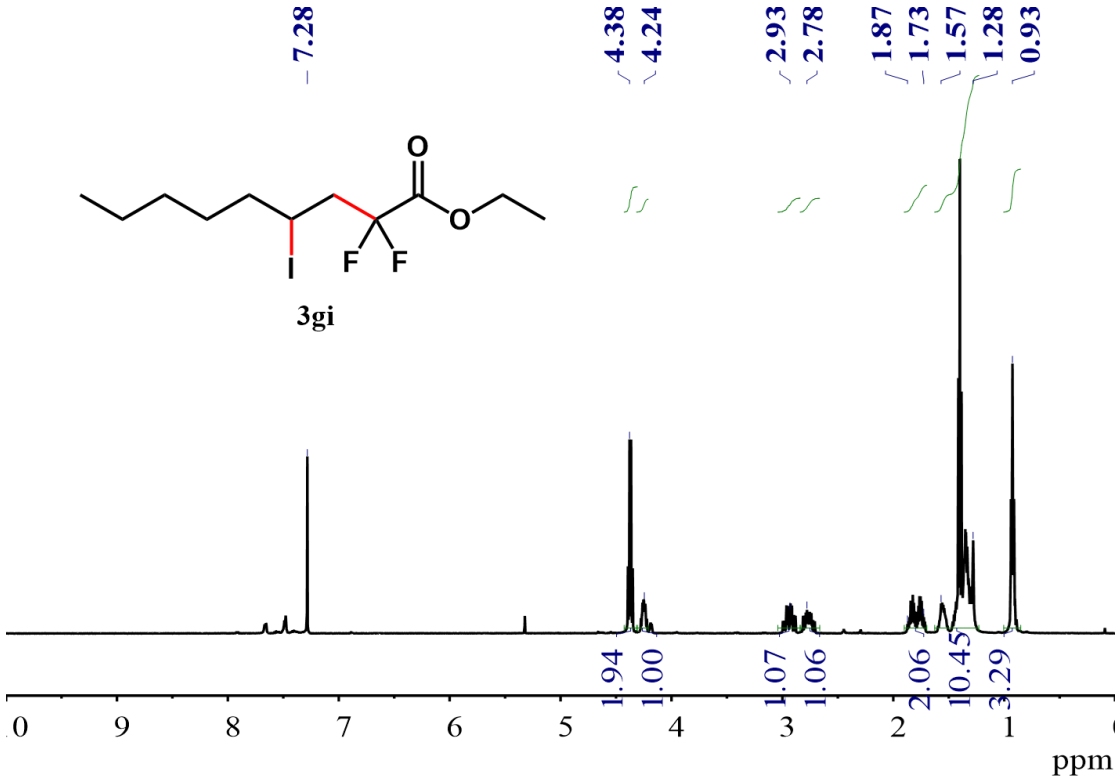
^{1}H NMR spectrum for 1-chloro-1,1,2,2-tetrafluoro-4-iodononane **3gh** ($CDCl_3$, 500 MHz).



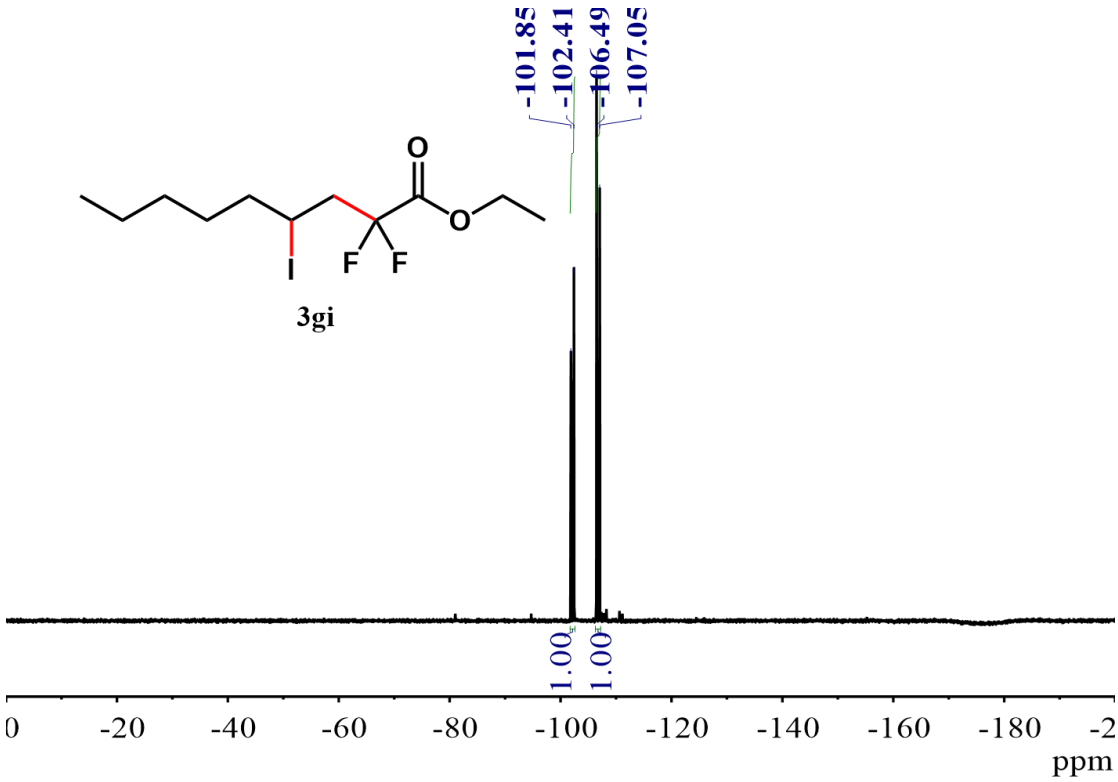
^{19}F NMR spectrum for 1-chloro-1,1,2,2-tetrafluoro-4-iodononane **3gh** ($CDCl_3$, 471 MHz).



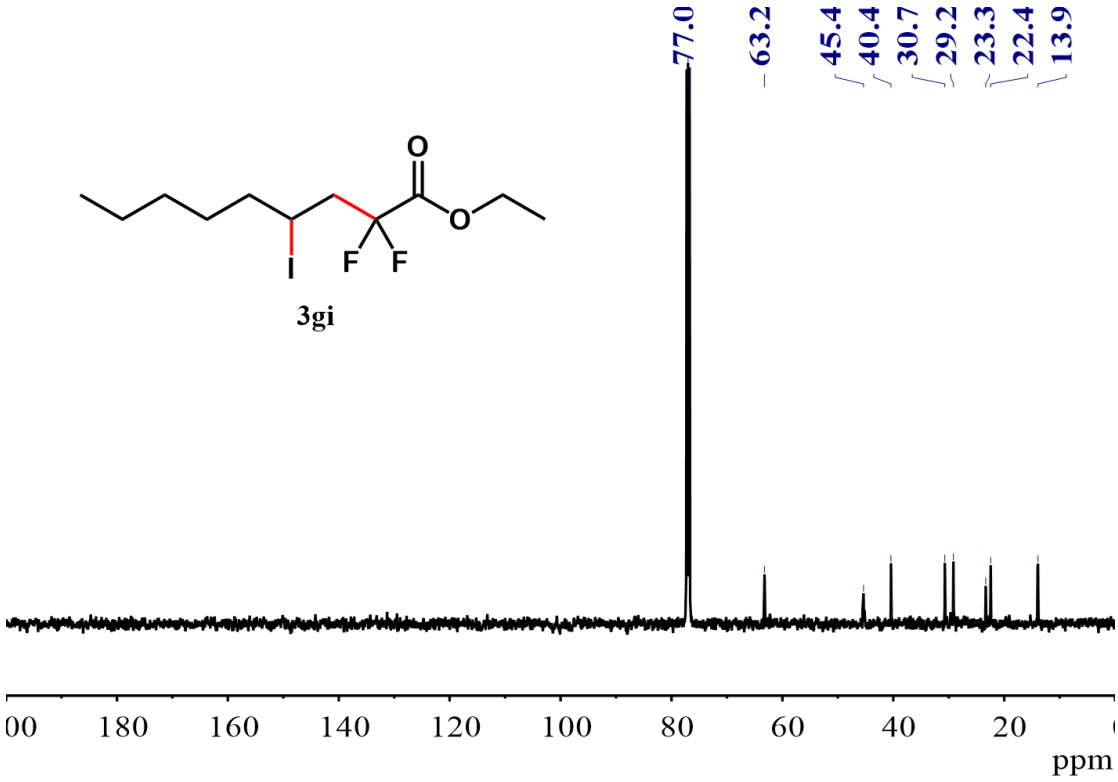
^{13}C NMR spectrum for 1-chloro-1,1,2,2-tetrafluoro-4-iodononane **3gh** ($CDCl_3$, 126 MHz).



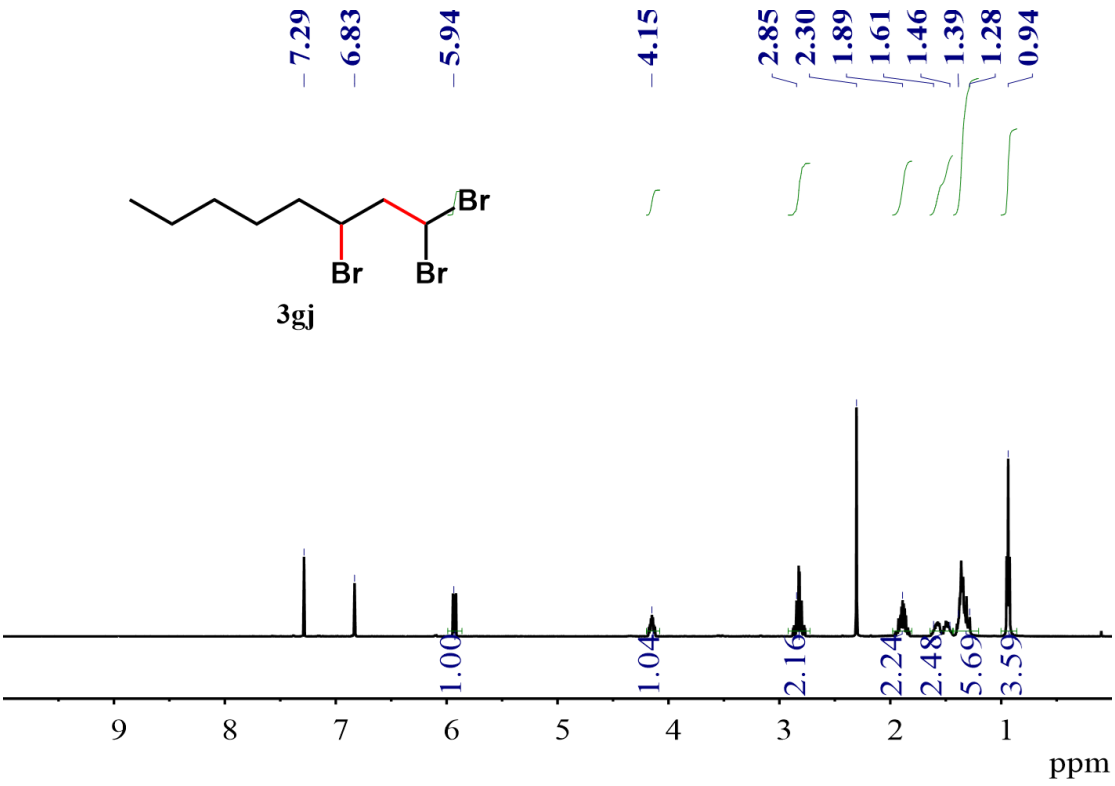
^{1}H NMR spectrum for ethyl 2,2-difluoro-4-iodononanoate **3gi** ($CDCl_3$, 500 MHz).



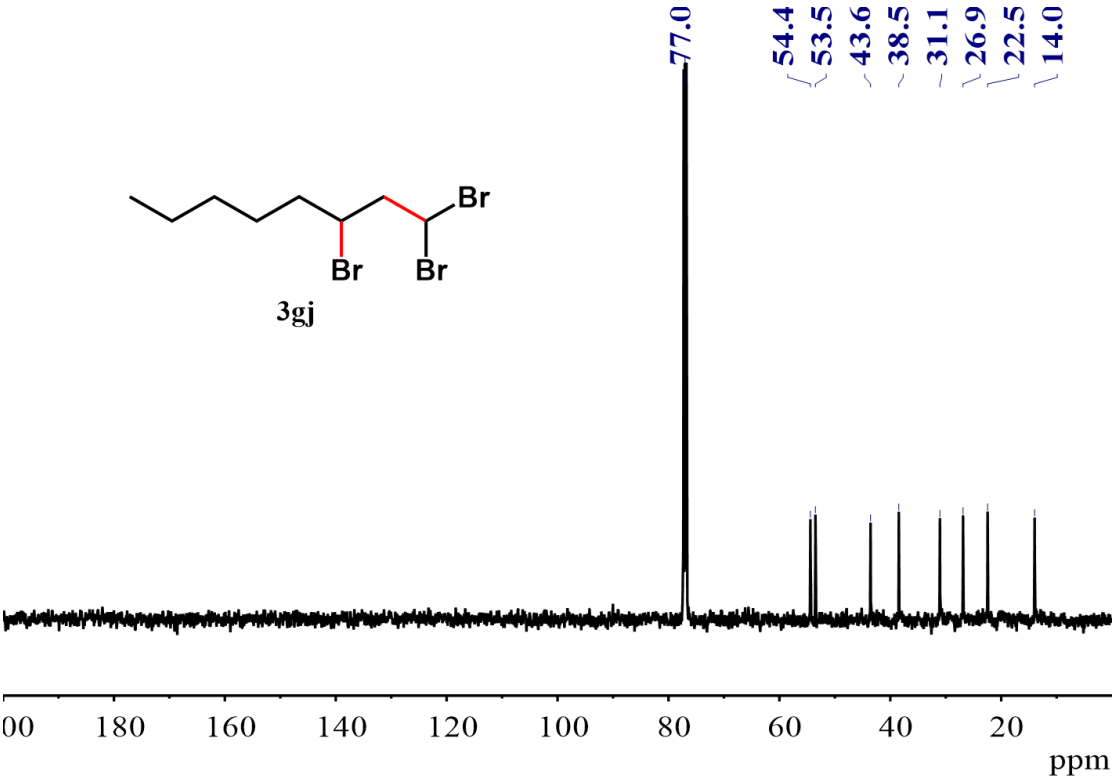
^{19}F NMR spectrum for ethyl 2,2-difluoro-4-iodononanoate **3gi** ($CDCl_3$, 471 MHz).



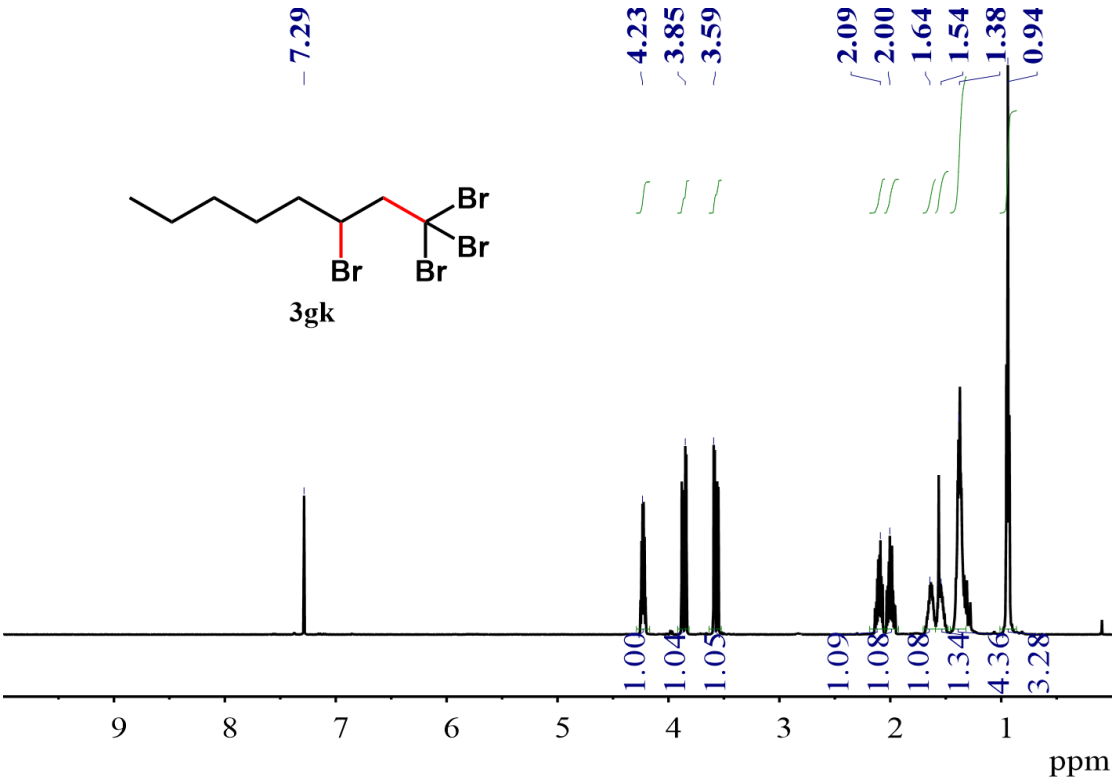
^{13}C NMR spectrum for ethyl 2,2-difluoro-4-iodononanoate **3gi** ($CDCl_3$, 126 MHz).



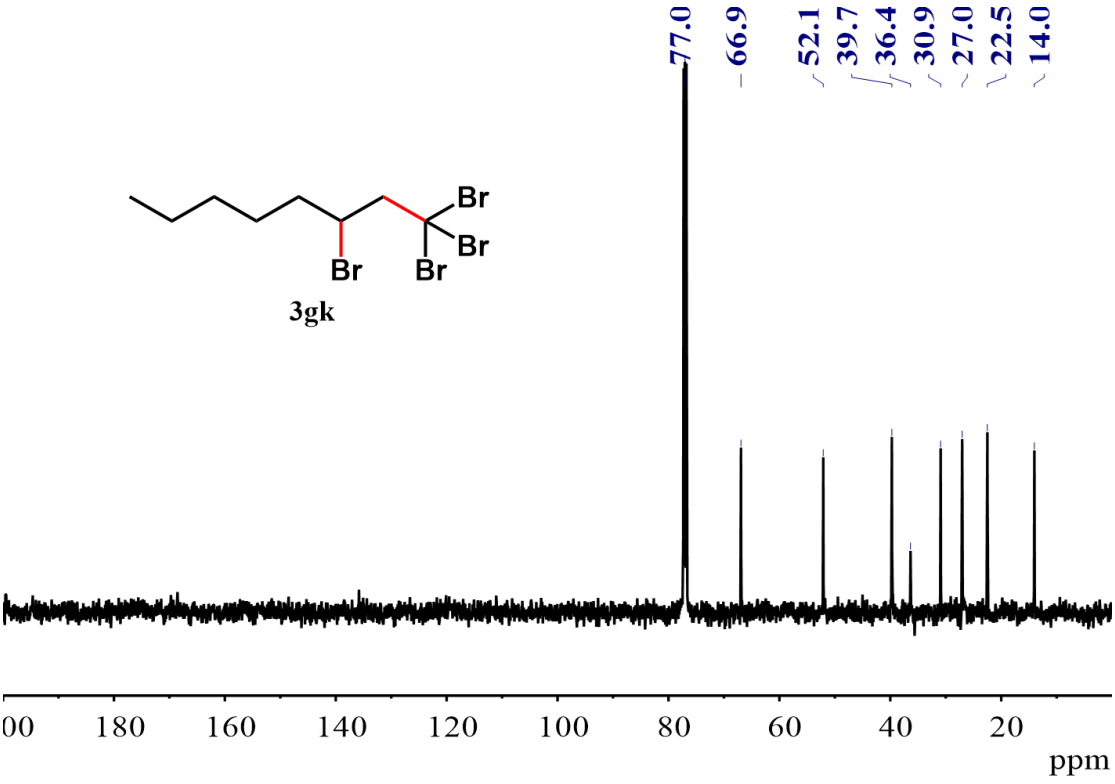
^{1}H NMR spectrum for 1,1,3-tribromooctane **3gj** ($CDCl_3$, 500 MHz).



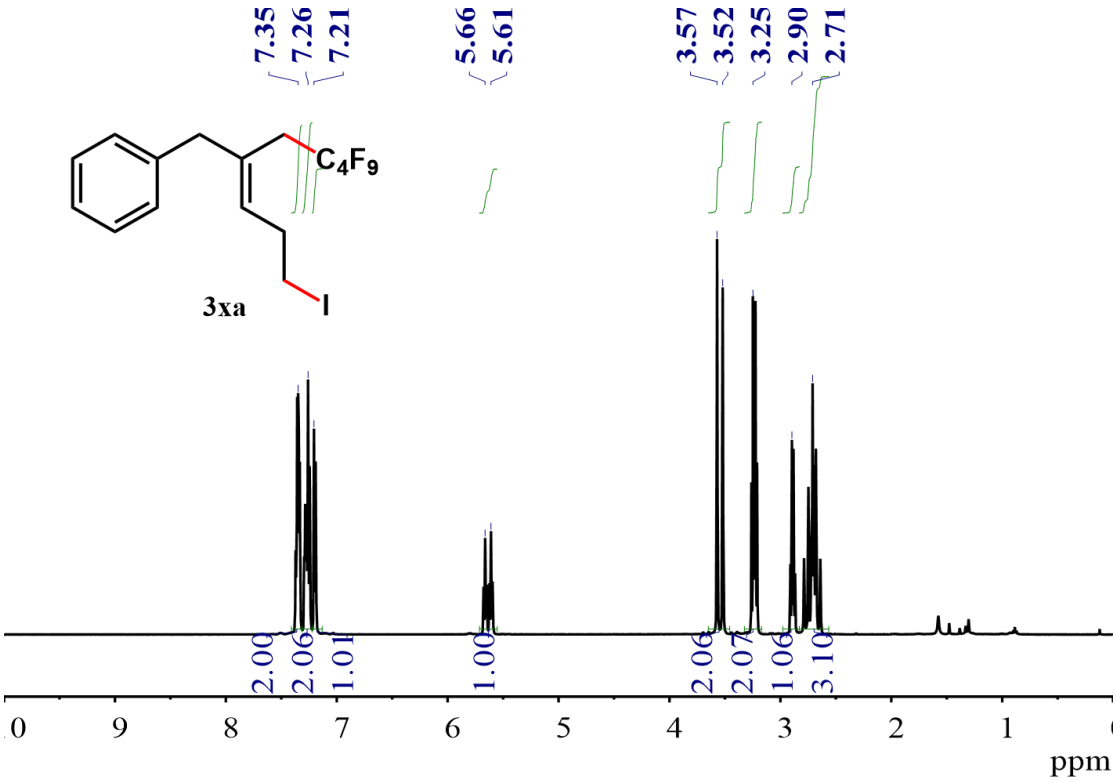
^{13}C NMR spectrum for 1,1,1,3-tetrabromooctane **3gj** ($CDCl_3$, 126 MHz).



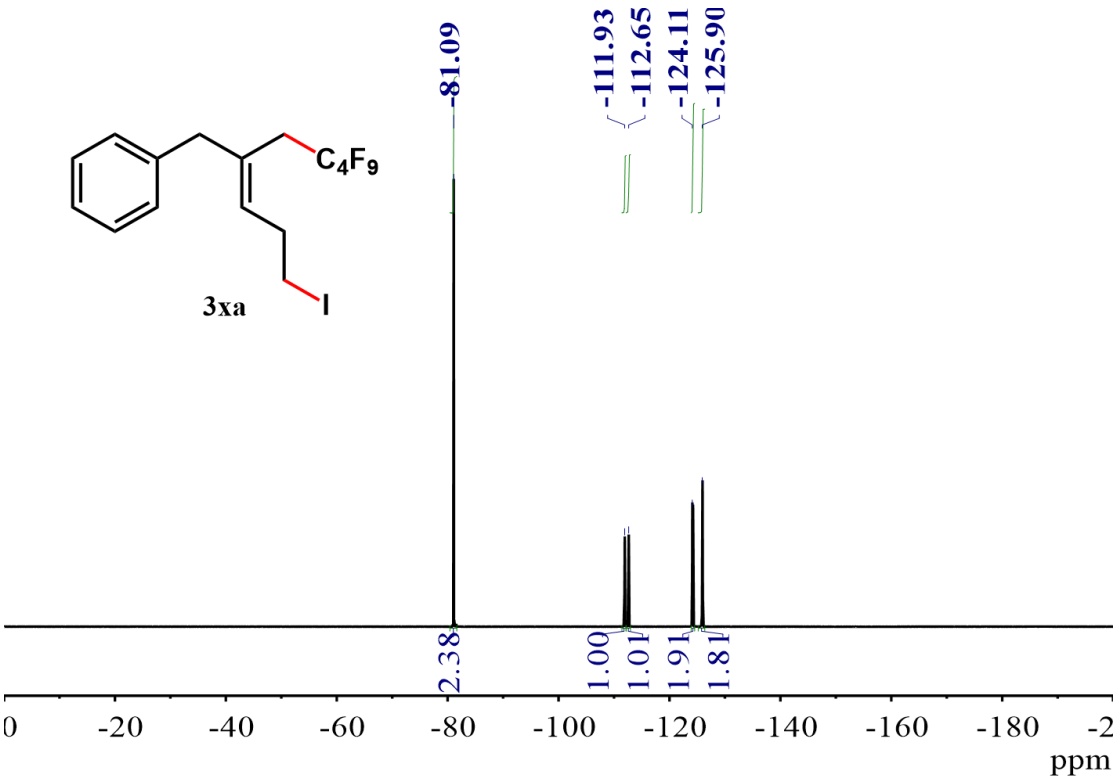
^{1}H NMR spectrum for 1,1,1,3-tetrabromooctane **3gk** ($CDCl_3$, 500 MHz).



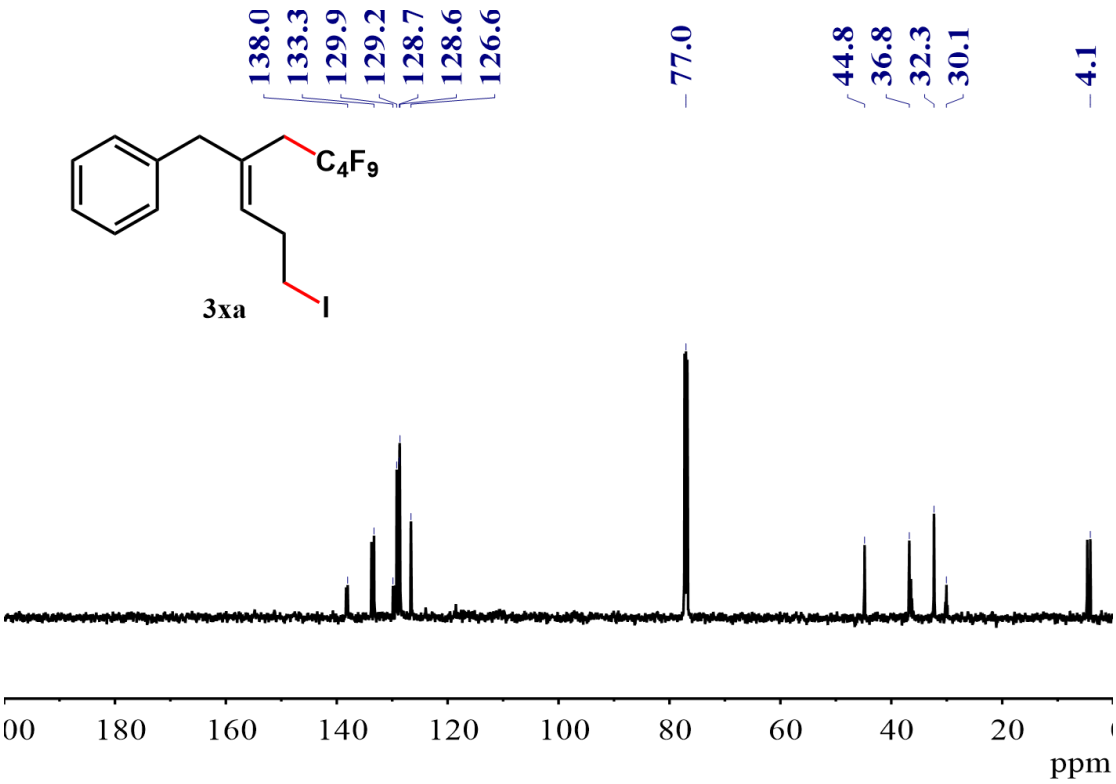
^{13}C NMR spectrum for 1,1,3,7-tetrabromoheptane **3gk** ($CDCl_3$, 126 MHz).



^{1}H NMR spectrum for (Z)-(4,4,5,5,6,6,7,7,7-nonafluoro-2-(3-iodopropylidene)heptyl)benzene **3xa** ($CDCl_3$, 500 MHz).



^{19}F NMR spectrum for (Z)-(4,4,5,5,6,6,7,7,7-nonafluoro-2-(3-iodopropylidene)heptyl)benzene **3xa** ($CDCl_3$, 471 MHz).



^{13}C NMR spectrum for (Z)-(4,4,5,5,6,6,7,7,7-nonafluoro-2-(3-iodopropylidene)heptyl)benzene **3xa** ($CDCl_3$, 126 MHz).

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