Supporting Information

Hydroperfluoroalkylation of electron-deficient olefins with perfluoroalkyl iodides promoted by Zinc / viologen

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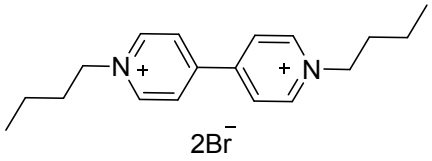
Contents

1. General information

Solvents and reagents were purchased from commercial sources and used as received unless otherwise noted. Acetonitrile and Chloroform were distilled from CaH_2. ^1H, ^{13}C and ^{19}F NMR spectra were detected on a 500 MHz, 400 MHz or 300 MHz NMR spectrometer. Data for ^1H, ^{13}C and ^{19}F NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, coupling constant (s) in Hz). Mass spectra were obtained on a GC-MS. High resolution mass data were recorded on a high resolution mass spectrometer in the EI or ESI mode.

2. The procedure for the synthesis of butyl viologen

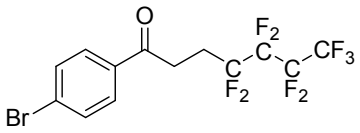
A mixture of 4,4'-dipyridyl (9.0g, 57.7mmol) and butyl bromide (31.6g, 231mmol) in CH_3CN (100ml) was refluxed for 24h. The resulting precipitate was filtered, washed with hot chloroform and then dried under vacuum to give the pure product.



1,1'-dibutyl-[4,4'-bipyridine]-1,1'-diium: ^1H NMR (400 MHz, D_2O) δ 9.10 (d, J = 6.6 Hz, 4 H, Ar-**H**), 8.52 (d, J = 6.1 Hz, 4 H, Ar-**H**), 4.71 (t, J = 7.4 Hz, 4 H, $\mathbf{CH_2}CH_2CH_2CH_3$), 2.12 – 1.97 (m, 4 H, $CH_2\mathbf{CH_2}CH_2CH_3$), 1.45 – 1.31 (m, 4 H, $CH_2CH_2\mathbf{CH_2}CH_3$), 0.94 (t, J = 7.4 Hz, 6 H, $CH_2CH_2CH_2\mathbf{CH_3}$).

3. The general procedure for the hydroperfluoroalkylation reaction

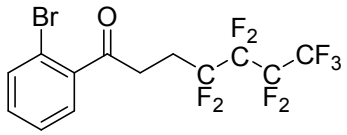
Into a mixture of olefin (0.2 mmol), zinc powder (78 mg, 1.2 mmol) (median 6-9 micron) and butyl viologen (172 mg, 0.4 mmol) in a sealed tube was added anhydrous chloroform (2 mL) and perfluoroalkyl iodide (0.6 mmol) under N_2 atmosphere. The tube was sealed and the resulting mixture was stirred at 110 °C for 4 h. After being cooled to room temperature, the solvent was removed by concentration, and the residue was subjected to flash column chromatography to afford the pure product.



3a

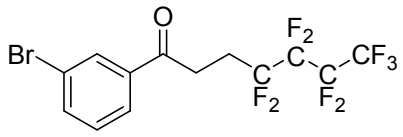
1-(4-bromophenyl)-4,4,5,5,6,6,7,7,7-nonafluoroheptan-1-one (**3a**): 62% yield, yellow solid.

^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.6 Hz, 2H, Ar-**H**), 7.63 (d, J = 8.6 Hz, 2H, Ar-**H**), 3.32 – 3.23 (m, 2H, CO$\mathbf{CH_2}$), 2.66 – 2.53 (m, 2H, $\mathbf{CH_2}CF_2$). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.17 (tt, J = 9.6, 3.2 Hz, 3F, $CF_2\mathbf{CF_3}$), -114.34 – -114.62 (m, 2F, $CH_2\mathbf{CF_2}$), -124.38 – -124.61 (m, 2F, $CF_2\mathbf{CF_2}CF_2$), -126.01 – -126.23 (m, 2F, $\mathbf{CF_2}CF_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.33 (s, **C**O), 134.83 (s, $\mathbf{C_{Ar}}$), 132.12 (s, $\mathbf{C_{Ar}}$), 129.48 (s, $\mathbf{C_{Ar}}$), 128.89 (s, $\mathbf{C_{Ar}}$), 29.47 (t, J = 2.9 Hz, CO$\mathbf{CH_2}$), 25.39 (t, J = 21.9 Hz, $\mathbf{CH_2}CF_2$). IR (neat) ν =1687, 1587, 1334, 1220, 1132, 982, 722, 529 cm-1. HRMS (EI) Calcd. for $C_{13}H_8BrF_9O$ [M+]: 429.9615, found 429.9610.



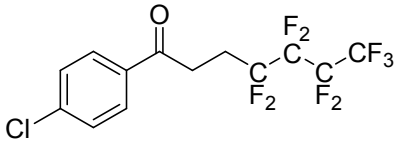
3b

1-(2-bromophenyl)-4,4,5,5,6,6,7,7,7-nonafluoroheptan-1-one (**3b**): 50% yield, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 8.1, 0.7 Hz, 1H, Ar-**H**), 7.45 – 7.31 (m, 3H, Ar-**H**), 3.30 – 3.23 (m, 2H, CO**CH$_2$**), 2.67 – 2.54 (m, 2H, **CH$_2$**CF_2). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.11 (tt, *J* = 9.6, 3.2 Hz, 3F, CF_2**CF$_3$**), -114.35 – -114.61 (m, 2F, CH_2**CF$_2$**), -124.45 – -124.47 (m, 2F, CF_2**CF$_2$**CF_2), -126.05 – -126.16 (m, 2F, **CF$_2$**CF_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.29 (s, **C**O), 140.69 (s, **C$_{Ar}$**), 133.90 (s, **C$_{Ar}$**), 132.10 (s, **C$_{Ar}$**), 128.58 (s, **C$_{Ar}$**), 127.59 (s, **C$_{Ar}$**), 118.77 (s, **C$_{Ar}$**), 33.48 (t, *J* = 2.9 Hz, CO**CH$_2$**), 25.52 (t, *J* = 22.1 Hz, **CH$_2$**CF_2). IR (neat) ν =1709, 1589, 1430, 1224, 1134, 975, 882, 753 cm^{-1} . HRMS (EI) Calcd. for $C_{13}H_8BrF_9O$ [M$^+$]: 429.9615, found 429.9618.



3c

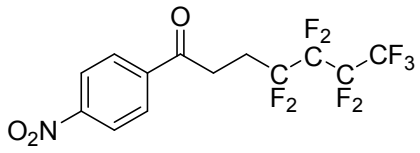
1-(3-bromophenyl)-4,4,5,5,6,6,7,7,7-nonafluoroheptan-1-one (**3c**): 54% yield, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H, Ar-**H**), 7.90 (d, *J* = 7.8 Hz, 1H, Ar-**H**), 7.73 (dd, *J* = 8.0, 0.9 Hz, 1H, Ar-**H**), 7.38 (t, *J* = 7.9 Hz, 1H, Ar-**H**), 3.32 – 3.23 (m, 2H, CO**CH$_2$**), 2.68 – 2.52 (m, 2H, **CH$_2$**CF_2). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.13 (tt, *J* = 9.6, 3.1 Hz, 3F, CF_2**CF$_3$**), -114.40 – -114.57 (m, 2F, CH_2**CF$_2$**), -124.46 – -124.51 (m, 2F, CF_2**CF$_2$**CF_2), -126.10 – -126.15 (m, 2F, **CF$_2$**CF_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.04 (s, **C**O), 137.79 (s, **C$_{Ar}$**), 136.50 (s, **C$_{Ar}$**), 131.09 (s, **C$_{Ar}$**), 130.37 (s, **C$_{Ar}$**), 126.53 (s, **C$_{Ar}$**), 123.18 (s, **C$_{Ar}$**), 29.61 (t, *J* = 2.9 Hz, CO**CH$_2$**), 25.34 (t, *J* = 21.9 Hz, **CH$_2$**CF_2). IR (neat) ν =1691, 1570, 1329, 1213, 1132, 1099, 979, 770, 676, 528 cm^{-1} . HRMS (EI) Calcd. for $C_{13}H_8BrF_9O$ [M$^+$]: 429.9615, found 429.9617.



3d

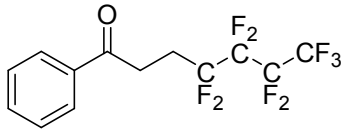
1-(4-chlorophenyl)-4,4,5,5,6,6,7,7,7-nonafluoroheptan-1-one (**3d**): 78% yield, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 2H, Ar-**H**), 7.47 (d, *J* = 8.6 Hz, 2H, Ar-**H**), 3.31 – 3.24 (m, 2H, CO**CH$_2$**), 2.67 – 2.53 (m, 2H, **CH$_2$**CF_2). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.15 (tt, *J* = 9.6, 3.1 Hz, 3F, CF_2**CF$_3$**), -112.48 – -117.92 (m, 2F, CH_2**CF$_2$**), -124.50 (m, 2F, CF_2**CF$_2$**CF_2), -125.94 – -126.29 (m, 2F, **CF$_2$**CF_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.15 (s, **C**O), 140.19 (s, **C$_{Ar}$**), 134.42 (s, **C$_{Ar}$**), 129.41 (s, **C$_{Ar}$**), 129.12 (s, **C$_{Ar}$**), 29.49 (t, *J* = 2.8 Hz, CO**CH$_2$**), 25.40 (t, *J* = 21.9 Hz, **CH$_2$**CF_2). IR (neat) ν =1686, 1592, 1330, 1218, 1133, 1098, 983, 729, 526, cm^{-1} . HRMS (EI) Calcd. for $C_{13}H_8ClF_9O$ [M$^+$]: 386.0120, found 382.0119. Elem. Anal. Calcd. for

$C_{13}H_8ClF_9O$: C, 40.38; H, 2.09; found C, 40.61; H, 2.19;



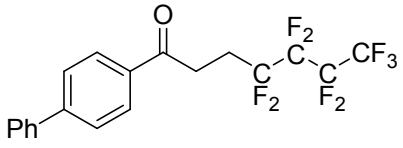
3e

4,4,5,5,6,6,7,7,7-nonafluoro-1-(4-nitrophenyl)heptan-1-one(**3e**): 38 % yield, pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.9 Hz, 2H, Ar-**H**), 8.15 (d, *J* = 8.9 Hz, 2H, Ar-**H**), 3.41 – 3.32 (m, 2H, CO**CH$_2$**), 2.72 – 2.55 (m, 2H, **CH$_2$**CF_2). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.08 (tt, *J* = 9.6, 3.1 Hz, 3F, CF_2**CF$_3$**), -114.21 – -114.48 (m, 2F, CH_2**CF$_2$**), -124.30 – -124.48 (m, 2F, CF_2**CF$_2$**CF_2), -125.92 – -126.12 (m, 2F, **CF$_2$**CF_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.92 (s, **C**O), 150.68 (s, **C$_{Ar}$**), 140.39 (s, **C$_{Ar}$**), 129.10 (s, **C$_{Ar}$**), 124.03 (s, **C$_{Ar}$**), 30.18 (t, *J* = 3.2 Hz, CO**CH$_2$**), 25.30 (t, *J* = 21.9 Hz, **CH$_2$**CF_2). IR (neat) ν =1697, 1604, 1530, 1350, 1269, 1224, 1133, 1100, 983, 857, 742 cm^{-1} . HRMS (EI) Calcd. for $C_{13}H_8F_9NO_3$ [M$^+$]: 397.0360, found 397.0353.



3f

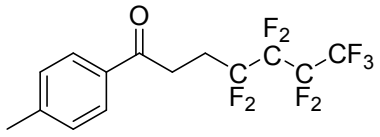
4,4,5,5,6,6,7,7,7-nonafluoro-1-phenylheptan-1-one (**3f**)[1]**:** 71% yield, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 2H, Ar-**H**), 7.60 (t, *J* = 7.4 Hz, 1H, Ar-**H**), 7.49 (t, *J* = 7.8 Hz, 2H, Ar-**H**), 3.35 – 3.25 (m, 2H, CO**CH$_2$**), 2.68 – 2.54 (m, 2H, **CH$_2$**CF_2). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.21 (tt, *J* = 9.6, 2.9 Hz, 3F, CF_2**CF$_3$**), -114.42 – -114.59 (m, 2F, CH_2**CF$_2$**), -124.50 – -124.57 (m, 2F, CF_2**CF$_2$**CF_2), -126.09 – -126.19 (m, 2F, **CF$_2$**CF_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.35 (s, **C**O), 136.16 (s, **C$_{Ar}$**), 133.58 (s, **C$_{Ar}$**), 128.75 (s, **C$_{Ar}$**), 127.99 (s, **C$_{Ar}$**), 29.45(t, *J* = 2.7 Hz, CO**CH$_2$**), 25.47 (t, *J* = 21.9 Hz, **CH$_2$**CF_2). IR (neat) ν =1686, 1599, 1450, 1330, 1220, 1133, 1098, 744, 689 cm^{-1} . HRMS (EI) Calcd. for $C_{13}H_9F_9O$ [M$^+$]: 352.0510, found 352.0515. Elem. Anal. Calcd. for $C_{13}H_9F_9O$: C, 44.33; H, 2.58; found C, 44.11; H, 2.61;



3g

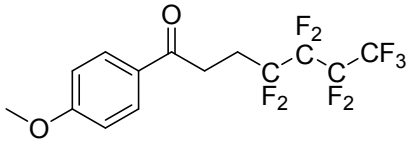
1-([1,1'-biphenyl]-4-yl)-4,4,5,5,6,6,7,7,7-nonafluoroheptan-1-one (**3g**): 71% yield, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.3 Hz, 2H, Ar-**H**), 7.72 (d, *J* = 8.3 Hz, 2H, Ar-**H**), 7.64 (d, *J* = 7.5 Hz, 2H, Ar-**H**), 7.49 (t, *J* = 7.5 Hz, 2H, Ar-**H**), 7.42 (t, *J* = 7.3 Hz, 1H, Ar-**H**), 3.40 – 3.30 (m, 2H, CO**CH$_2$**), 2.70 – 2.57 (m, 2H, **CH$_2$**CF_2). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.05 (t, *J* = 9.5 Hz, 3F, CF_2**CF$_3$**), -114.30 – -114.67 (m, 2F, CH_2**CF$_2$**), -124.46 (m, 2F, CF_2**CF$_2$**CF_2), -

125.93 – -126.22 (m, 2F, $\mathbf{CF_2}CF_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.95 (s, **C**O), 146.33 (s, $\mathbf{C_{Ar}}$), 139.64 (s, $\mathbf{C_{Ar}}$), 134.79 (s, $\mathbf{C_{Ar}}$), 128.99 (s, $\mathbf{C_{Ar}}$), 128.61 (s, $\mathbf{C_{Ar}}$), 128.38 (s, $\mathbf{C_{Ar}}$), 127.38 (s, $\mathbf{C_{Ar}}$), 127.26 (s, $\mathbf{C_{Ar}}$), 29.50 (t, *J* = 2.7 Hz, CO$\mathbf{CH_2}$), 25.50 (t, *J* = 21.8 Hz, $\mathbf{CH_2}CF_2$). IR (neat) ν = 1682, 1607, 1334, 1262, 1220, 1131, 1098, 1022, 984, 801, 757, 739, 703 cm^{-1} . HRMS (EI) Calcd. for $C_{19}H_{13}F_9O$ [M$^+$]: 428.0823, found 428.0815.



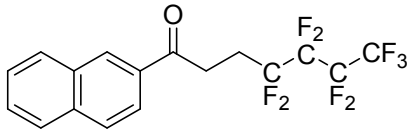
3h

4,4,5,5,6,6,7,7,7-nonafluoro-1-(p-tolyl)heptan-1-one (**3h**): 74% yield, yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 2H, Ar-**H**), 7.29 (d, *J* = 8.0 Hz, 2H, Ar-**H**), 3.30 – 3.26 (m, 2H, CO$\mathbf{CH_2}$), 2.66 – 2.53 (m, 2H, $\mathbf{CH_2}CF_2$), 2.42 (s, 3H, $\mathbf{CH_3}$). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.13 (tt, *J* = 9.6, 3.1 Hz, 3F, $CF_2\mathbf{CF_3}$), -113.17 – -116.32 (m, 2F, $CH_2\mathbf{CF_2}$), -123.65 – -125.46 (m, 2F, $CF_2\mathbf{CF_2}CF_2$), -125.67 – -127.28 (m, 2F, $\mathbf{CF_2}CF_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.00 (s, **C**O), 144.53 (s, $\mathbf{C_{Ar}}$), 133.71 (s, $\mathbf{C_{Ar}}$), 129.43 (s, $\mathbf{C_{Ar}}$), 128.12 (s, $\mathbf{C_{Ar}}$), 29.30 (t, *J* = 2.7 Hz, CO$\mathbf{CH_2}$), 25.52 (t, *J* = 21.8 Hz, $\mathbf{CH_2}CF_2$), 21.59 (s, $\mathbf{CH_3}$). IR (neat) ν =1681, 1607, 1216, 1189, 1135, 979, 741 cm^{-1} . HRMS (EI) Calcd. for $C_{14}H_{11}F_9O$ [M$^+$]: 366.0666, found 366.0661.



3i

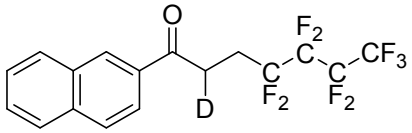
4,4,5,5,6,6,7,7,7-nonafluoro-1-(4-methoxyphenyl)heptan-1-one (**3i**)[2]: 64% yield, pale yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, 2H, Ar-**H**), 6.95 (d, *J* = 8.8 Hz, 2H, Ar-**H**), 3.88 (s, 3H, $\mathbf{CH_3}$O), 3.28 – 3.22 (m, 2H, CO$\mathbf{CH_2}$), 2.65 – 2.52 (m, 2H, $\mathbf{CH_2}CF_2$). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.13 (tt, *J* = 9.6, 3.1 Hz, 3F, $CF_2\mathbf{CF_3}$), -114.28 – -114.68 (m, 2F, $CH_2\mathbf{CF_2}$), -124.47 – -124.50 (m, 2F, $CF_2\mathbf{CF_2}CF_2$), -126.06 – -126.15 (m, 2F, $\mathbf{CF_2}CF_3$). ^{13}C NMR (101 MHz, CDCl3) δ 194.87 (s, **C**O), 163.91 (s, $\mathbf{C_{Ar}}$), 130.31 (s, $\mathbf{C_{Ar}}$), 129.24 (s, $\mathbf{C_{Ar}}$), 113.90 (s, $\mathbf{C_{Ar}}$), 55.46 (s, $\mathbf{CH_3}$O), 29.02 (t, J = 3.1 Hz, CO$\mathbf{CH_2}$), 25.57 (t, J = 22.0 Hz, $\mathbf{CH_2}CF_2$). HRMS (EI) Calcd. for $C_{14}H_{11}F_9O_2$ [M$^+$]: 382.0615, found 382.0613. Elem. Anal. Calcd. for $C_{14}H_{11}F_9O_2$: C, 43.99; H, 2.90; found C, 44.04; H, 3.03;



3j

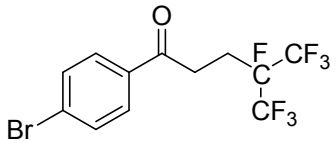
4,4,5,5,6,6,7,7,7-nonafluoro-1-(naphthalen-2-yl)heptan-1-one (**3j**): 64% yield, yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.04 (dd, *J* = 8.6, 1.7 Hz, 1H, Ar-**H**), 8.01 – 7.87 (m,

3H, Ar-**H**), 7.67 – 7.54 (m, 2H, Ar-**H**), 3.49 – 3.40 (m, 2H, CO**CH$_2$**), 2.73 – 2.60 (m, 2H, **CH$_2$**CF$_2$). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.04 (tt, *J* = 9.6, 3.1 Hz, 3F, CF$_2$**CF$_3$**), -114.20 – -114.51 (m, 2F, CH$_2$**CF$_2$**), -124.26 – -124.51 (m, 2F, CF$_2$**CF$_2$**CF$_2$), -125.95 – -126.09 (m, 2F, **CF$_2$**CF$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.31 (s, **C**O), 135.82 (s, **C$_{Ar}$**), 133.47 (s, **C$_{Ar}$**), 132.48 (s, **C$_{Ar}$**), 129.83 (s, **C$_{Ar}$**), 129.62 (s, **C$_{Ar}$**), 128.79 (s, **C$_{Ar}$**), 128.71 (s, **C$_{Ar}$**), 127.84 (s, **C$_{Ar}$**), 127.01 (s, **C$_{Ar}$**), 123.57 (s, **C$_{Ar}$**), 29.55 (t, *J* = 2.8 Hz, CO**CH$_2$**), 25.59 (t, *J* = 22.0 Hz, **CH$_2$**CF$_2$). IR (neat) ν =1684, 1627, 1354, 1266, 1219, 1135, 1096, 978, 741, 705 cm^{-1} . HRMS (EI) Calcd. for $C_{17}H_{11}F_9O$ [M$^+$]: 402.0666, found 402.0668.



D-3j

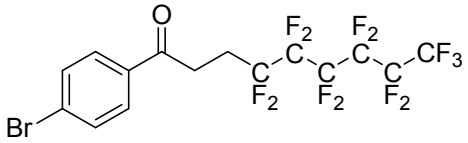
4,4,5,5,6,6,7,7,7-nonafluoro-1-(naphthalen-2-yl)heptan-1-one-2-d (**D-3j**): 53% yield, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H, Ar-**H**), 8.04 (dd, *J* = 8.6, 1.7 Hz, 1H, Ar-**H**), 8.01 – 7.86 (m, 3H, Ar-**H**), 7.65 – 7.56 (m, 2H, Ar-**H**), 3.46 – 3.40 (m, 1.39H, CO**CH**D), 2.74 – 2.59 (m, 2H, **CH$_2$**CF$_2$). ^{2}H NMR (61 MHz, $CHCl_3$) δ 3.61 (s, 1D, COCH**D**). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.09 (tt, *J* = 9.5, 3.2 Hz, 3F, CF$_2$**CF$_3$**), -114.18 – -114.56 (m, 2F, CH$_2$**CF$_2$**), -124.31 – -124.54 (m, 2F, CF$_2$**CF$_2$**CF$_2$), -125.95 – -126.17 (m, 2F, **CF$_2$**CF$_3$). HRMS (EI) Calcd. for $C_{17}H_{10}DF_9O$ [M$^+$]: 403.0729, found 403.0728.



3k

1-(4-bromophenyl)-4,5,5,5-tetrafluoro-4-(trifluoromethyl)pentan-1-one (**3k**): 42% yield, brown liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.6 Hz, 2H, Ar-**H**), 7.63 (d, *J* = 8.6 Hz, 2H, Ar-**H**), 3.28 – 3.19 (m, 2H, CO**CH$_2$**), 2.68 – 2.54 (m, 2H, **CH$_2$**CF$_2$). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.59 (d, *J* = 6.8 Hz, 6F, **CF$_3$**), -184.84 – -185.05 (m, 1F, **CF**). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.34 (s, **C**O), 134.79 (s, **C$_{Ar}$**), 132.14 (s, **C$_{Ar}$**), 129.46 (s, **C$_{Ar}$**), 128.92 (s, **C$_{Ar}$**), 30.53 (s, CO**CH$_2$**), 22.79 (d, *J* = 20.3 Hz, **CH$_2$**CF). IR (neat) ν =1694, 1587, 1400, 1351, 1286, 1224, 1158, 1072, 1004, 721 cm^{-1} . HRMS (EI) Calcd. for $C_{12}H_8BrF_7O$ [M$^+$]: 379.9647, found 379.9641.

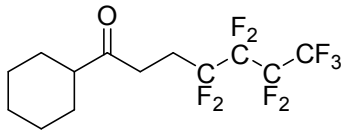


3l

1-(4-bromophenyl)-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononan-1-one (**3l**): 54% yield, pale yellow

solid.

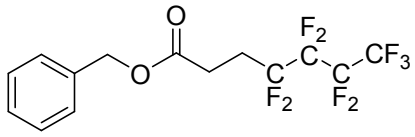
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 2H, Ar-**H**), 7.64 (d, *J* = 8.4 Hz, 2H, Ar-**H**), 3.32 – 3.22 (m, 2H, CO**CH$_2$**), 2.67 – 2.53 (m, 2H, **CH$_2$**CF_2). ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.86 – -80.92 (m, 3F, CF_2**CF$_3$**), -114.14 – -114.28 (m, 2F, **CF$_2$**$CF_2CF_2CF_2CF_3$), -121.92 – -121.95 (m, 2F, CF_2**CF$_2$CF$_2$CF$_2$**CF_2CF_3), -122.95 (s, 2F, CF_2**CF$_2$CF$_2$CF$_2$**CF_2CF_3), -123.50 – -123.53 (m, 2F, CF_2**CF$_2$CF$_2$CF$_2$**CF_2CF_3), -126.13 – -126.35 (m, 2F, $CF_2CF_2CF_2CF_2$**CF$_2$**CF_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.37 (s, **C**O), 134.83 (s, **C$_{Ar}$**), 132.13 (s, **C$_{Ar}$**), 129.50 (s, **C$_{Ar}$**), 128.91 (s, **C$_{Ar}$**), 29.50 (t, *J* = 2.9 Hz, CO**CH$_2$**), 25.48 (t, *J* = 21.9 Hz, CH_2**CF$_2$**). IR (neat) ν =1685, 1589, 1334, 1239, 1140, 1096, 1120, 1013, 701 cm^{-1}. HRMS (EI) Calcd. for $C_{15}H_8BrF_{13}O$ [M^+]: 529.9551, found 529.9546.



3m

1-cyclohexyl-4,4,5,5,6,6,7,7,7-nonafluoroheptan-1-one (**3m**): 76% yield, brown liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 – 2.68 (m, 2H, CO**CH$_2$**), 2.47 – 2.30 (m, 3H, **CH$_2$**CF_2 and **CH**CO), 1.92 – 1.60 (m, 5H, **C$_6$H$_{11}$**), 1.43 – 1.13 (m, 5H, **C$_6$H$_{11}$**). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.21 – -81.27 (m, 3F, CF_2**CF$_3$**), -114.62 – -115.79 (m, 2F, CH_2**CF$_2$**), -124.61 – -124.63 (m, 2F, CF_2**CF$_2$**CF_2), -126.19– -126.25 (m, 2F, **CF$_2$**CF_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.18 (s, **C**O), 50.86 (s, **CH**CO), 31.03 (t, *J* = 2.6 Hz, CO**CH$_2$**), 28.45 (s, **CH$_2$**$CH_2CH_2CH_2$**CH$_2$**), 25.69 (s, CH_2CH_2**CH$_2$**CH_2CH_2), 25.51 (s, CH_2**CH$_2$**CH_2**CH$_2$**CH_2), 25.01 (t, *J* = 22.0 Hz, **CH$_2$**CF_2). IR (neat) ν =2935, 2859, 1716, 1453, 1355, 1235, 1134, 880 cm^{-1} . HRMS (EI) Calcd. for $C_{13}H_{15}F_9O$ [M^+]: 358.0979, found 358.0976. Elem. Anal. Calcd. for $C_{13}H_{15}F_9O$: C, 43.58; H, 4.22; found C, 43.66; H, 4.07;



3n

benzyl 4,4,5,5,6,6,7,7,7-nonafluoroheptanoate (**3n**): 80% yield, yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 5H, Ar-**H**), 5.18 (s, 2H, Ph**CH$_2$**O), 2.74 – 2.66 (m, 2H, CO**CH$_2$**CH_2), 2.57 – 2.44 (m, 2H, **CH$_2$**CF_2). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.24 (tt, *J* = 9.6, 3.1 Hz, 3F, CF_2**CF$_3$**), -115.04 – -115.27 (m, 2F, CH_2**CF$_2$**), -124.50 – -124.71 (m, 2F, CF_2**CF$_2$**CF_2), -126.11 – -126.32 (m, 2F, **CF$_2$**CF_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.91 (s, **C**O), 135.43 (s, **C$_{Ar}$**), 128.63 (s, **C$_{Ar}$**), 128.48 (s, **C$_{Ar}$**), 128.35 (s, **C$_{Ar}$**), 67.00 (s, Ph**CH$_2$**O), 26.44 (t, *J* = 22.2 Hz, **CH$_2$**CF_2), 25.49 (t, *J* = 4.1 Hz, CO**CH$_2$**CH_2). IR (neat) ν = 3034, 2950, 1742, 1457, 1351, 1235, 1135, 881, 745, 698 cm^{-1} . HRMS (EI) Calcd. for $C_{14}H_{11}F_9O_2$ [M^+]: 382.0615, found 382.0613.

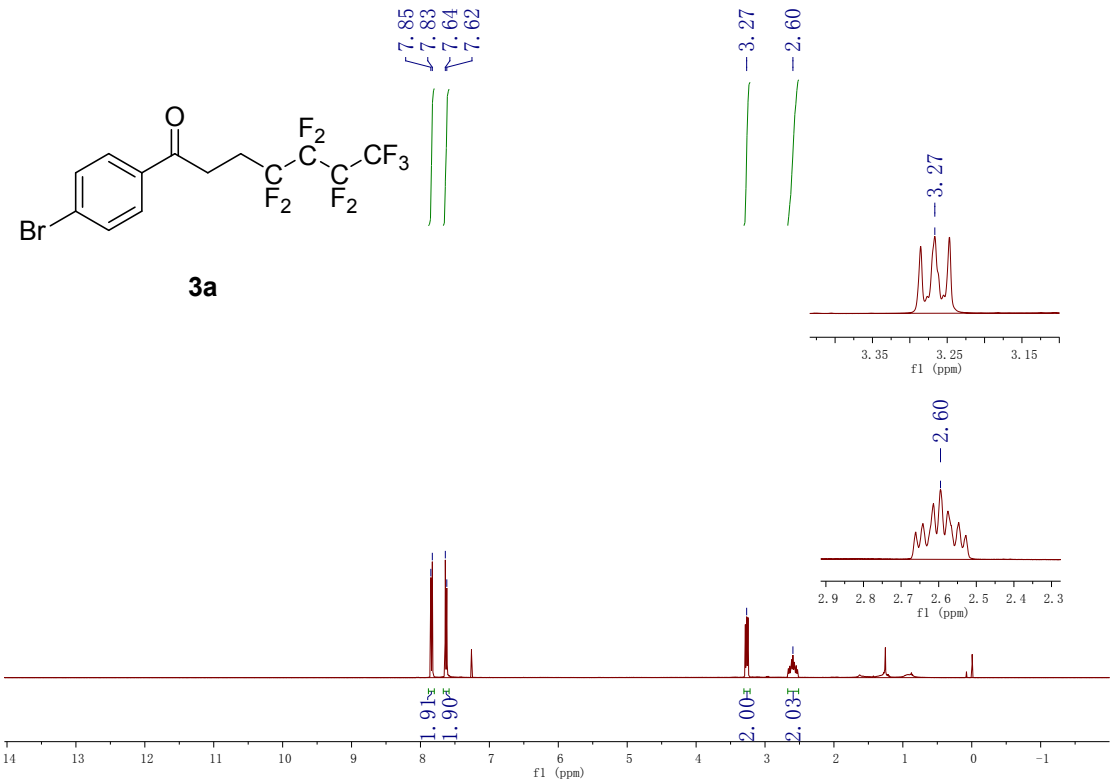
4. References:

1. Y. Nakamura, S. Takeuchi, K. Okumura, Y. Ohgo, H. Matsuzawa and K. Mikami, *Tetrahedron*

Lett., 2003, **44**, 6221-6225.
2. Z. Ye, K. E. Gettys, X. Shen and M. Dai, *Org. Lett.*, 2015, **17**, 6074-6077.

5. Copies of ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra

^{1}H NMR:



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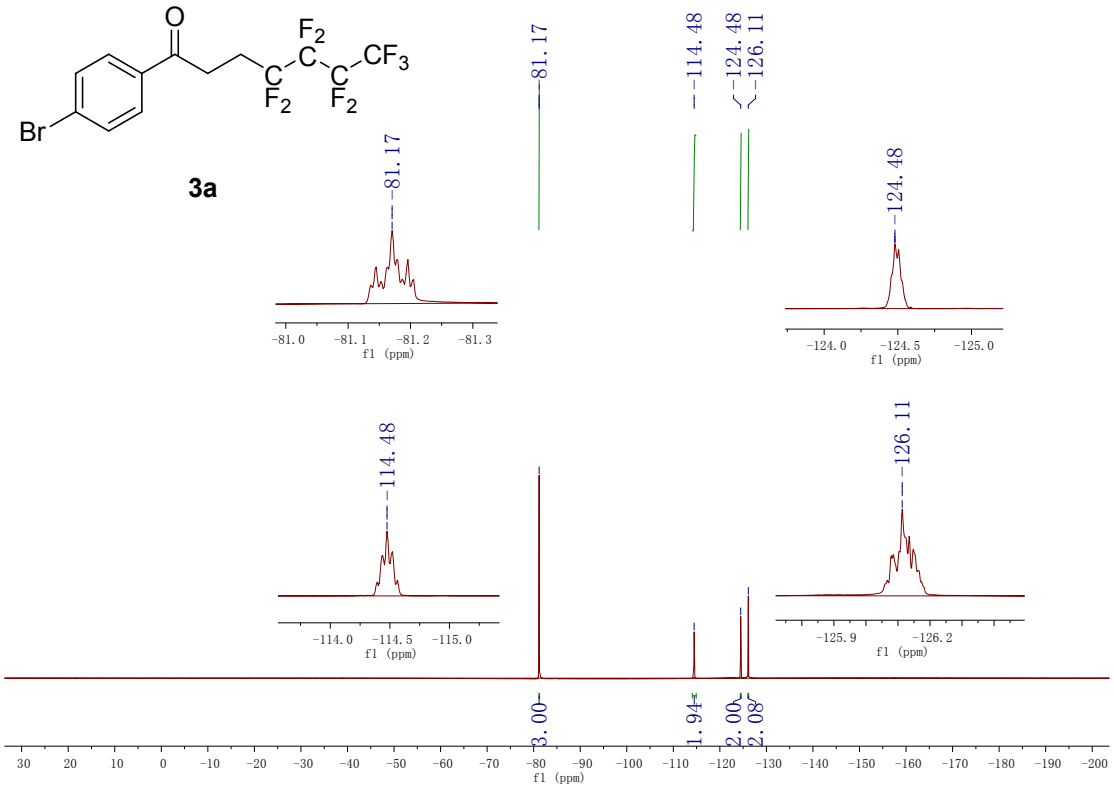
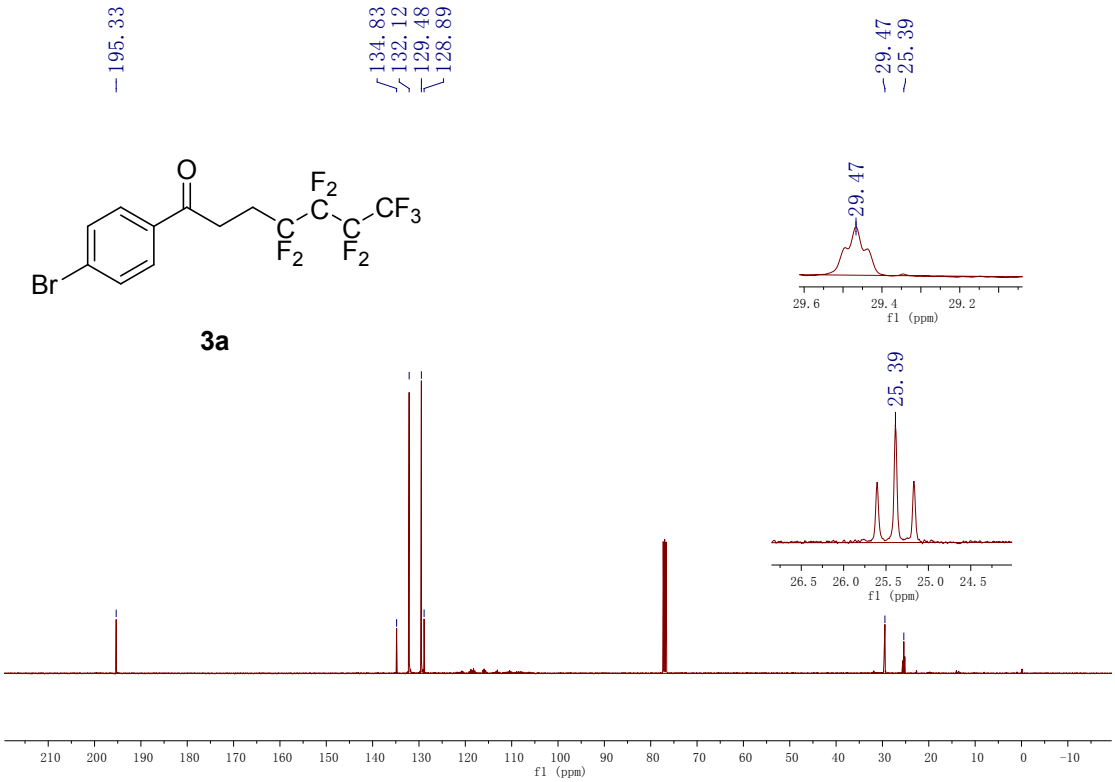
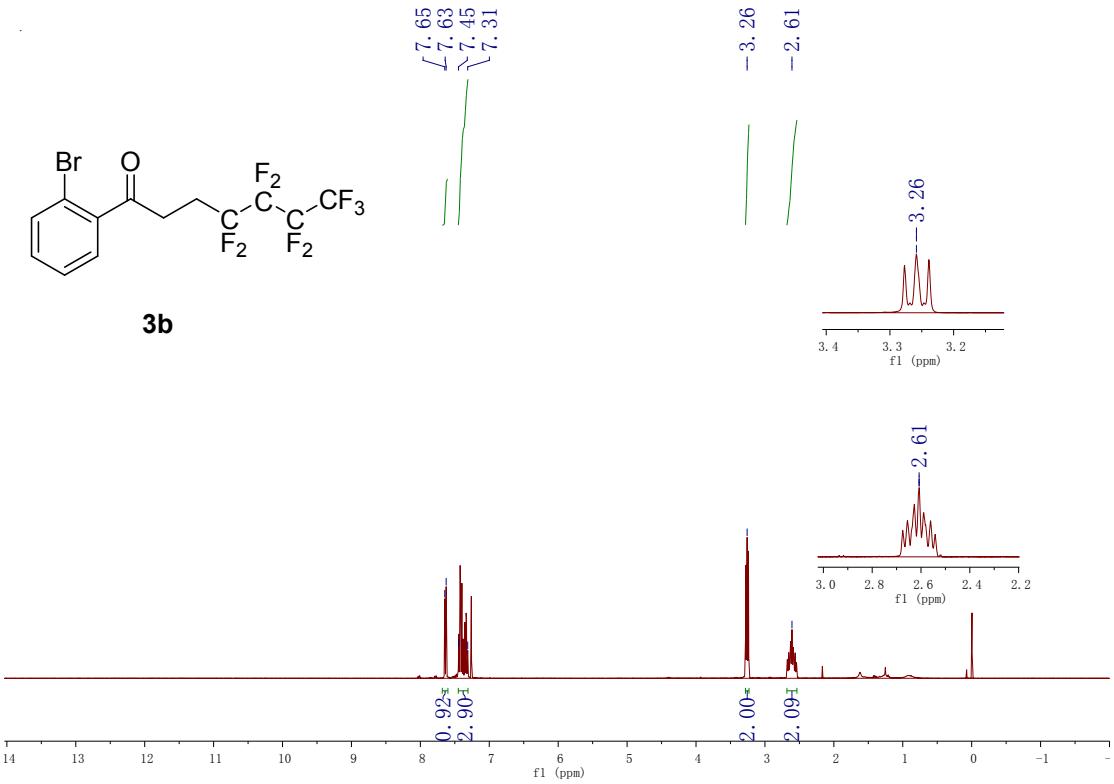


^{13}C NMR:



^{1}H NMR：



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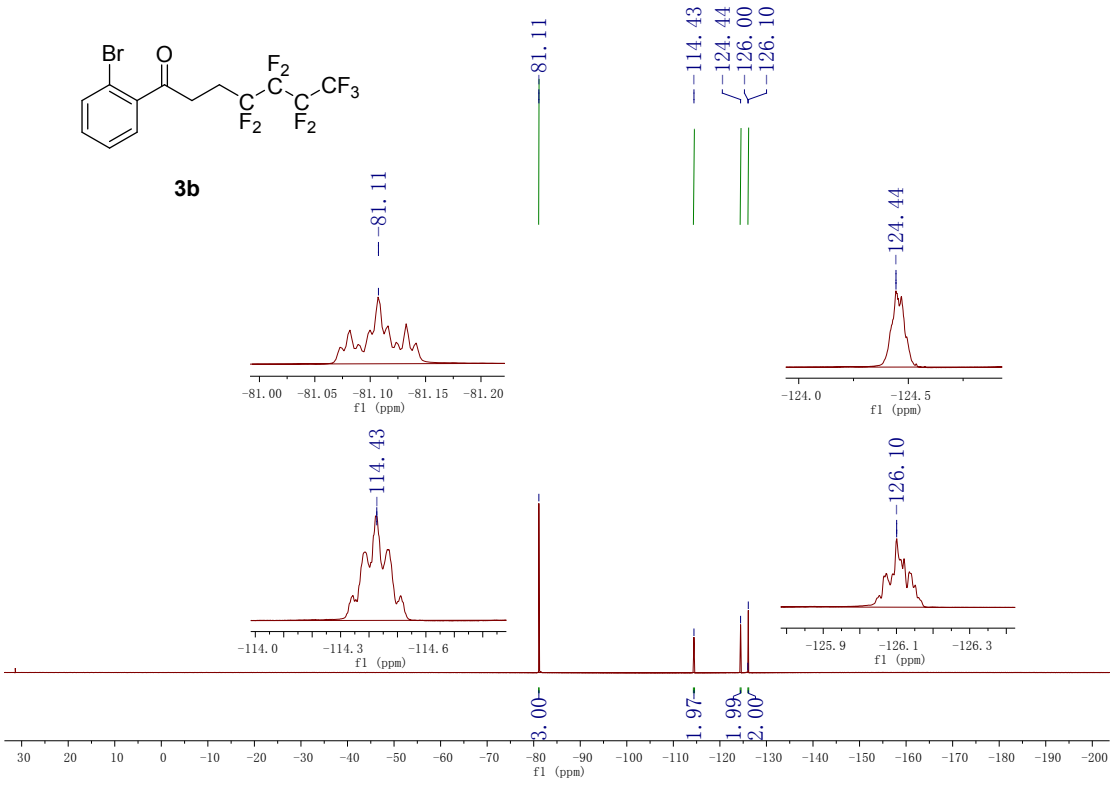

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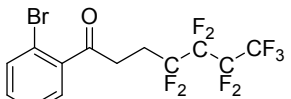

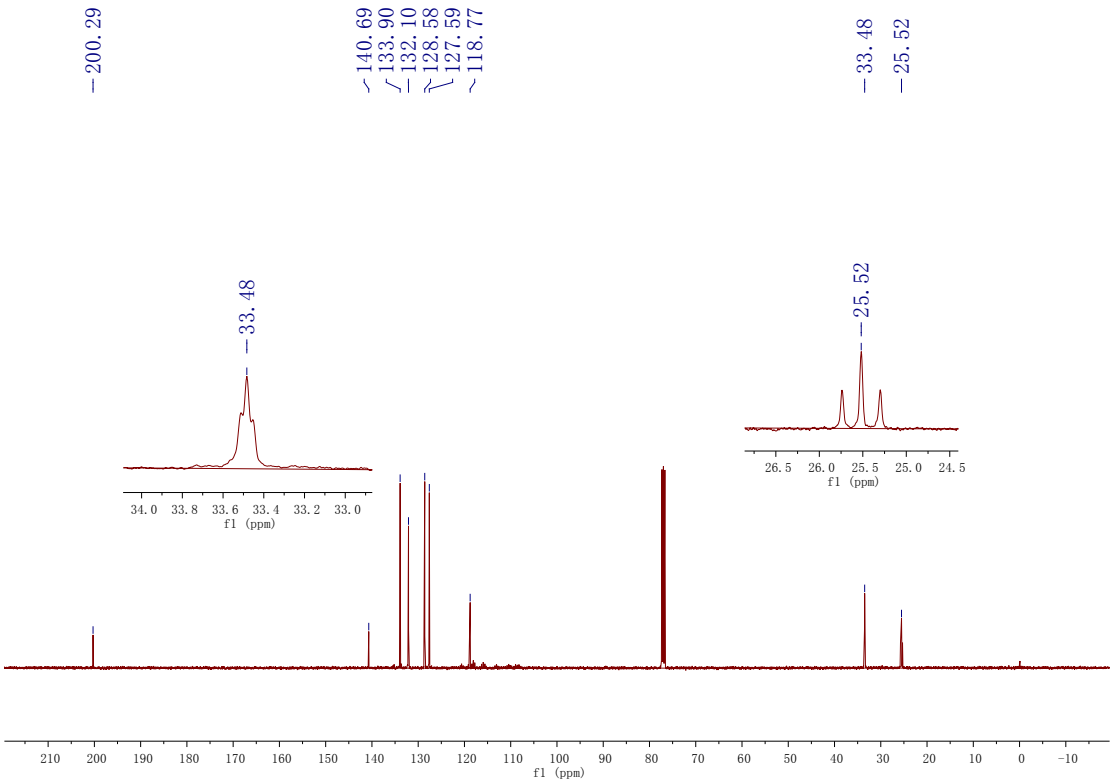

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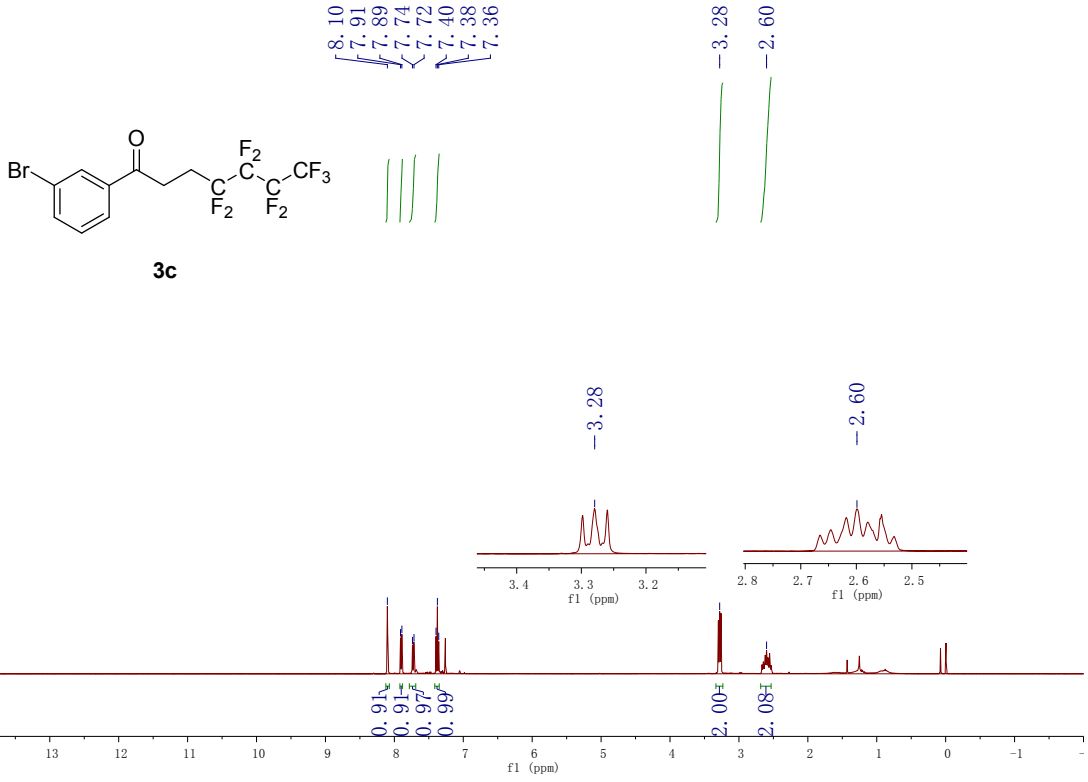

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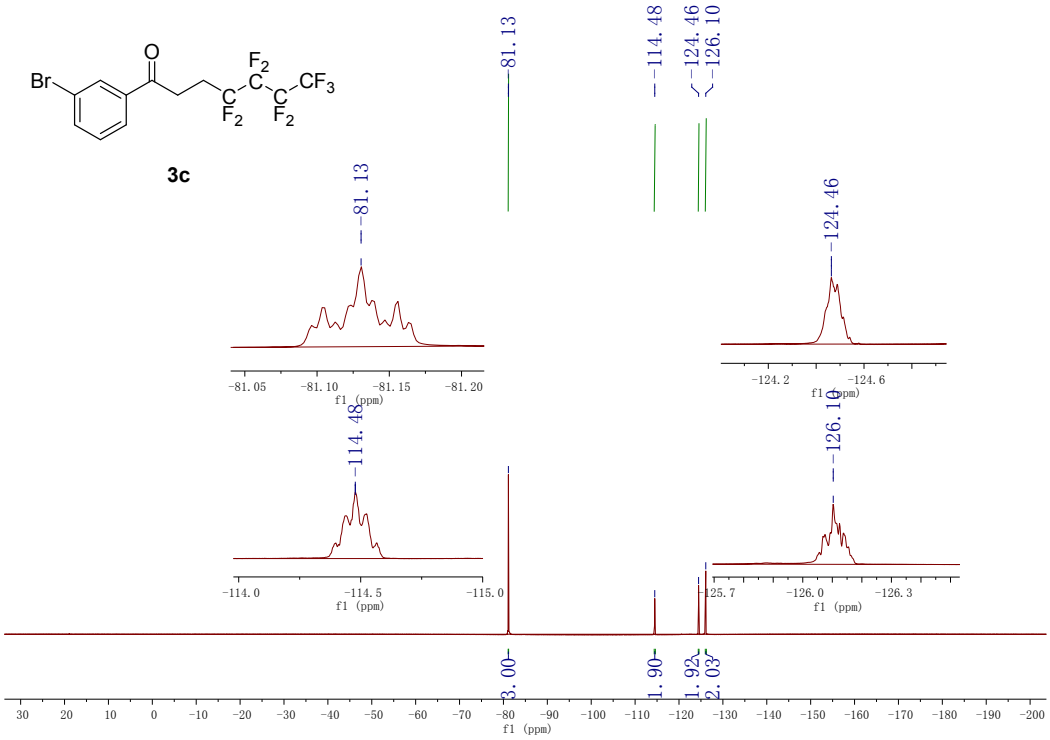

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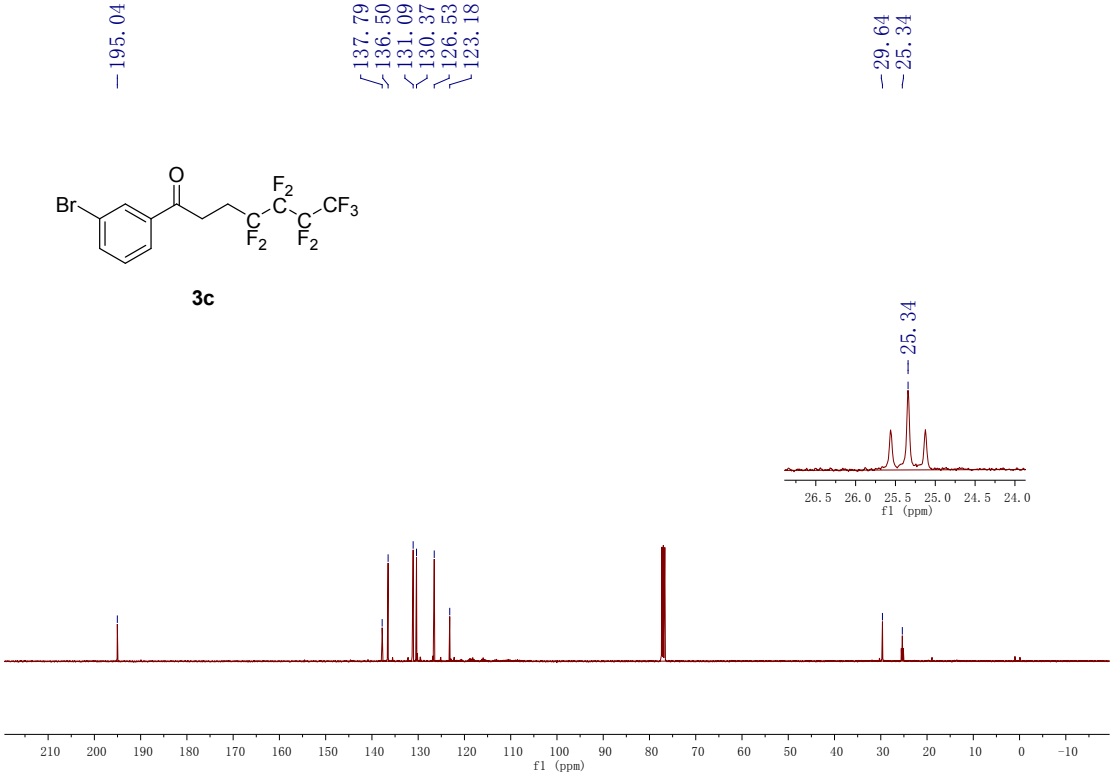

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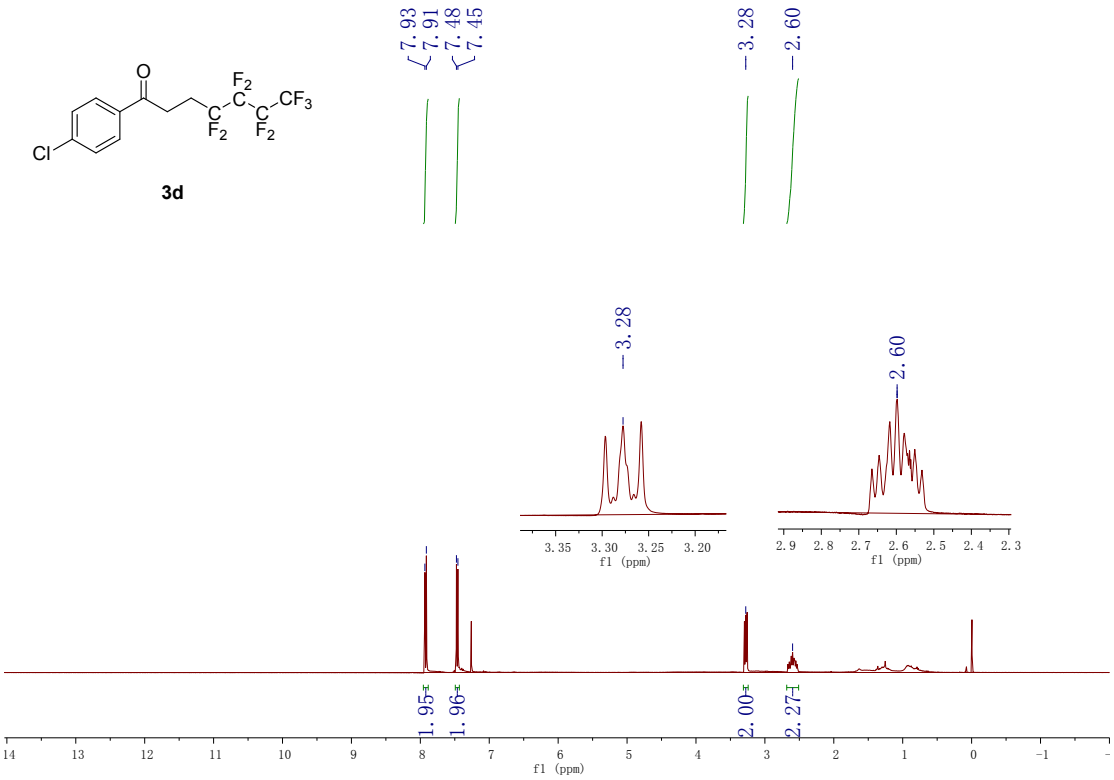

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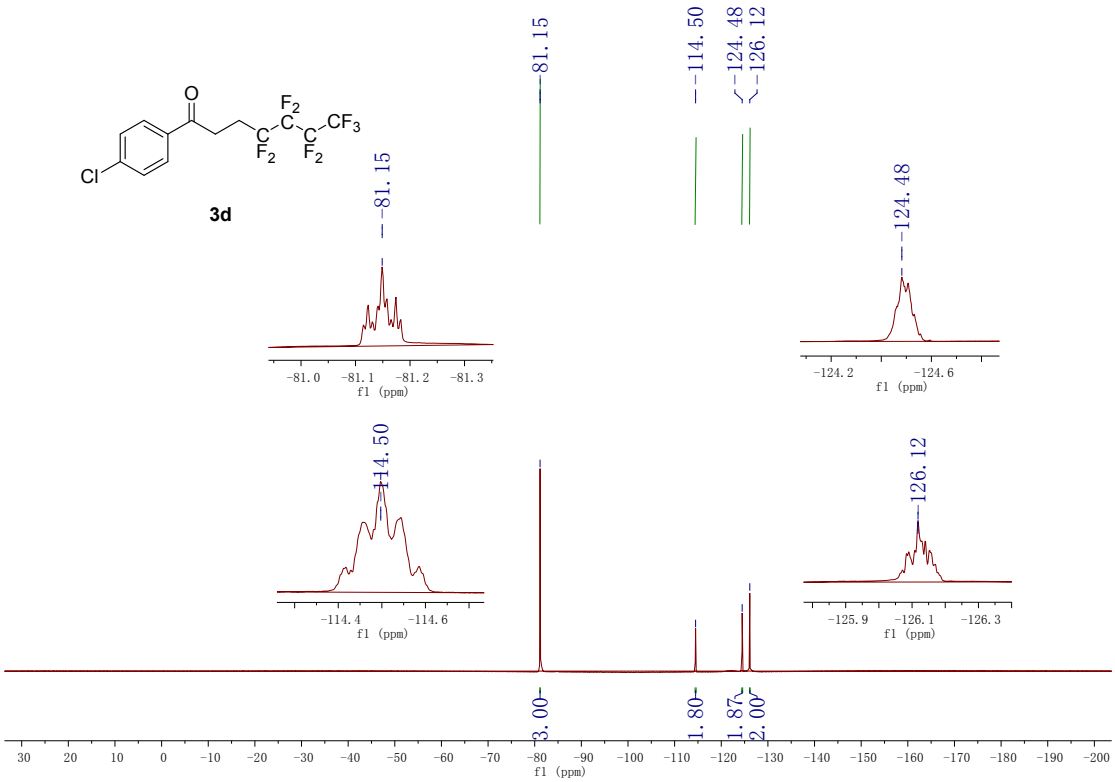

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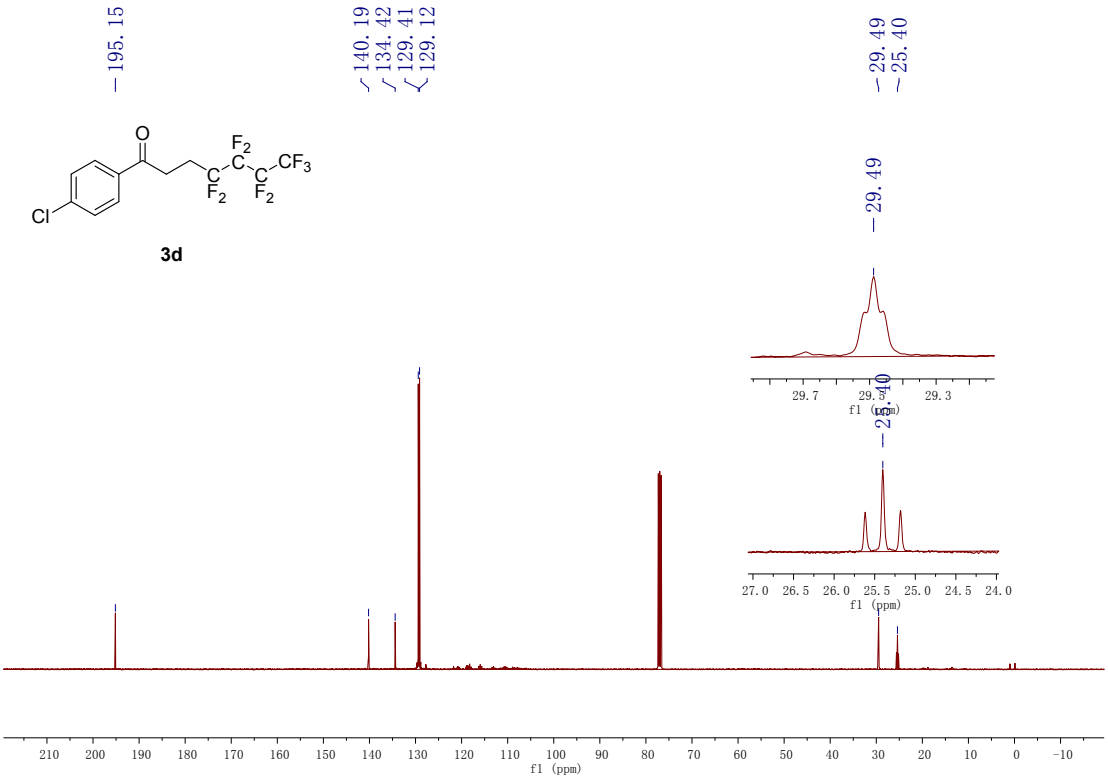

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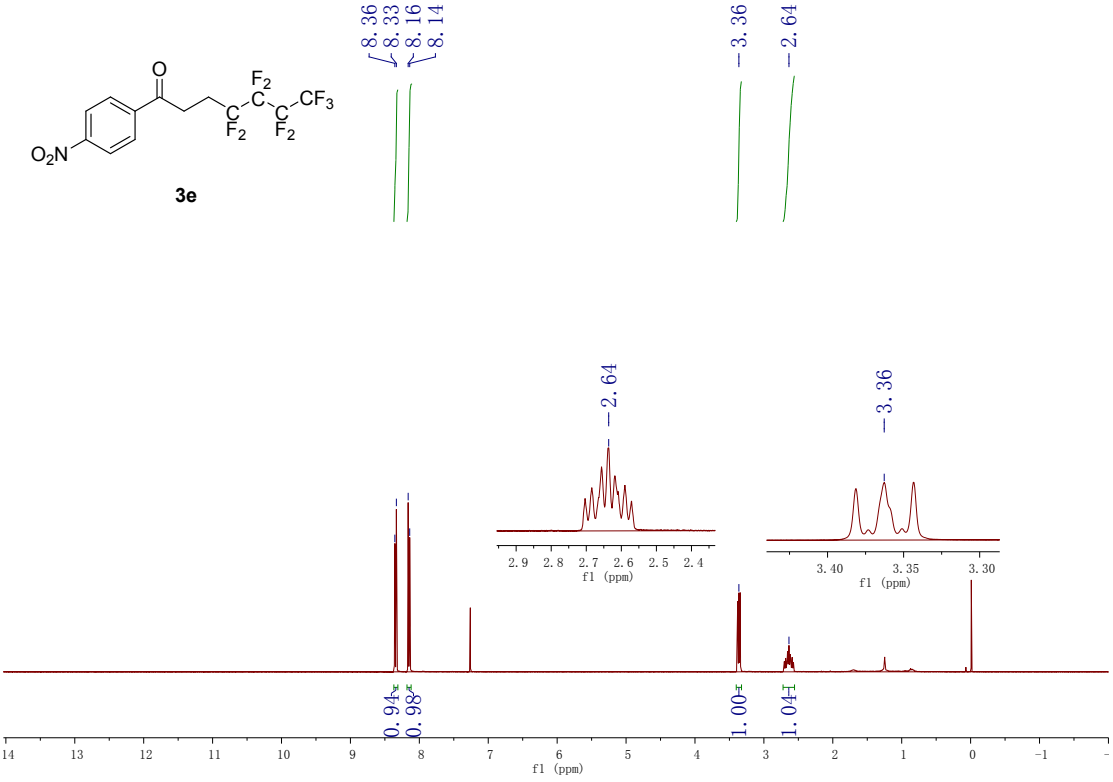

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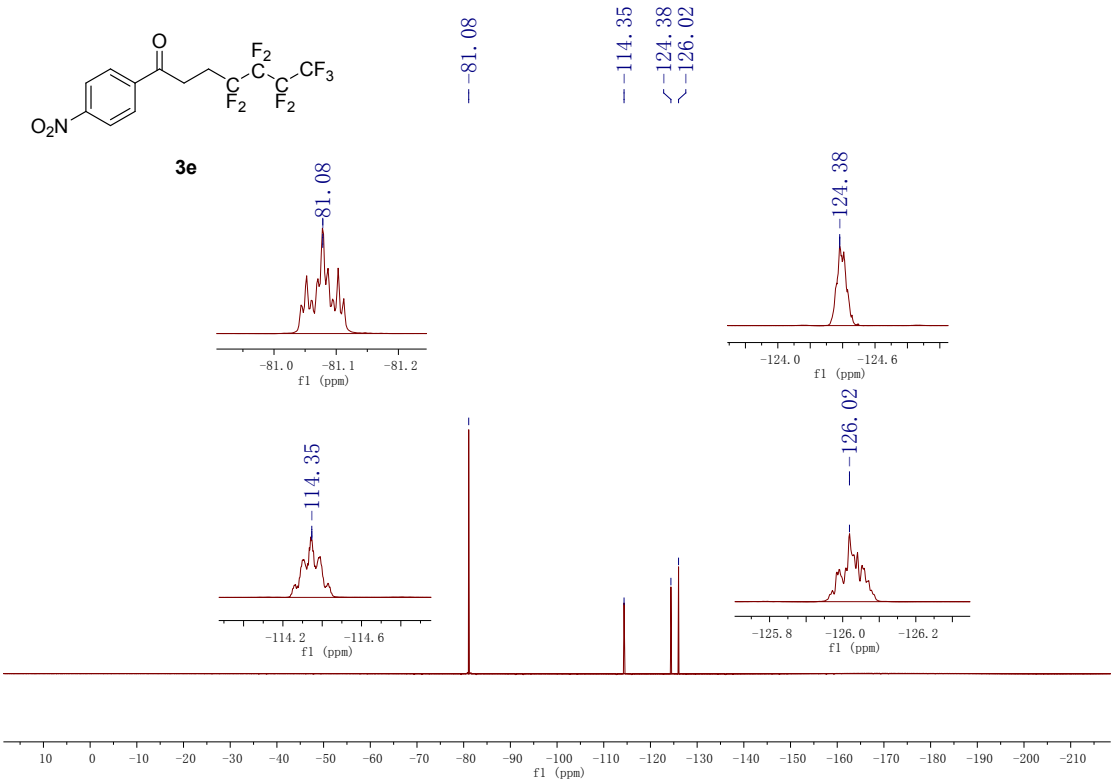

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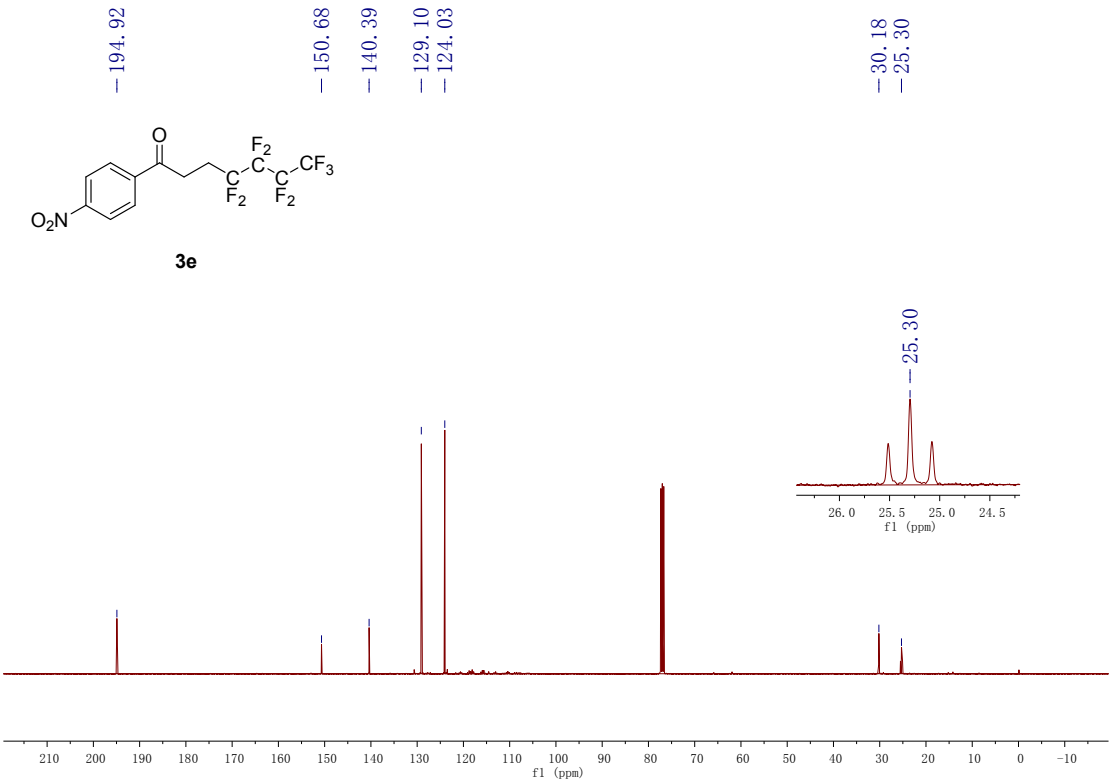

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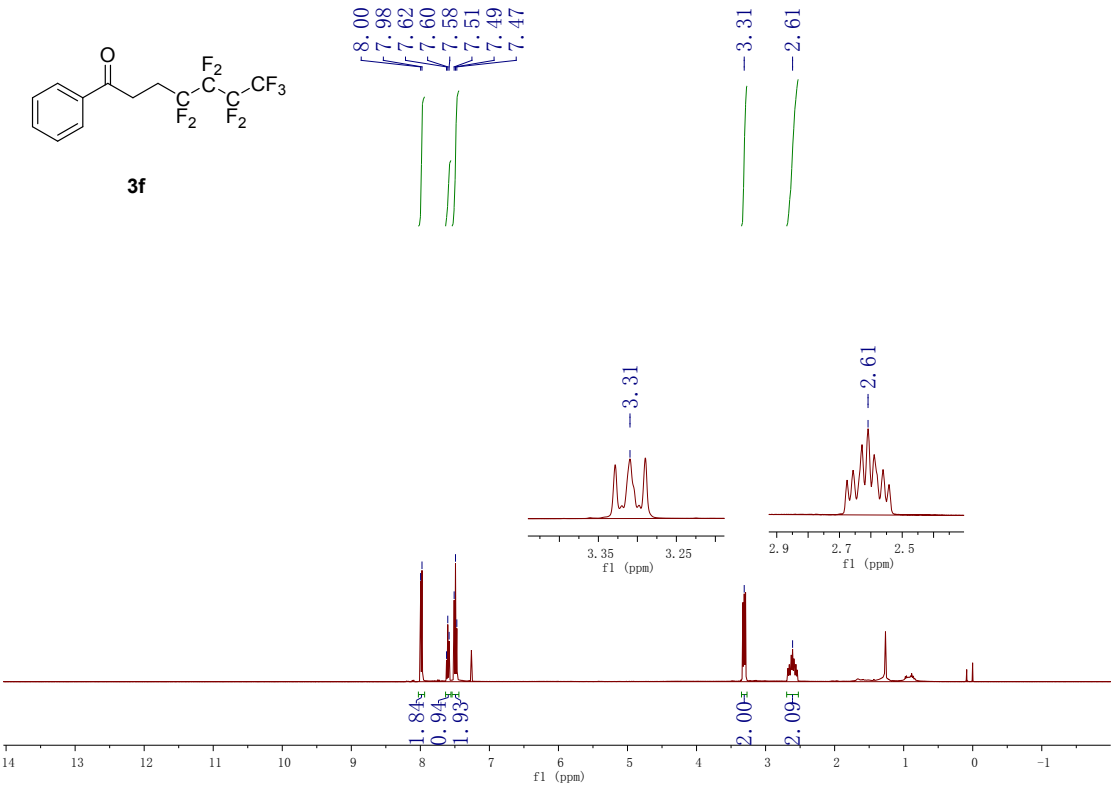

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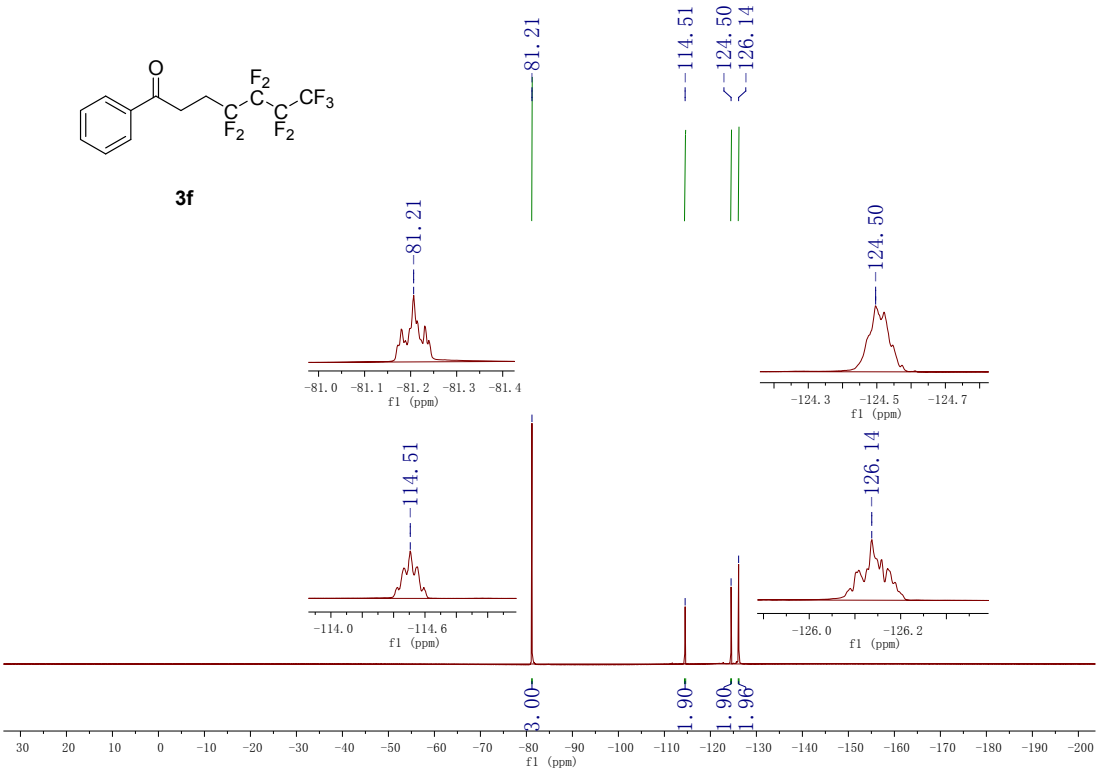

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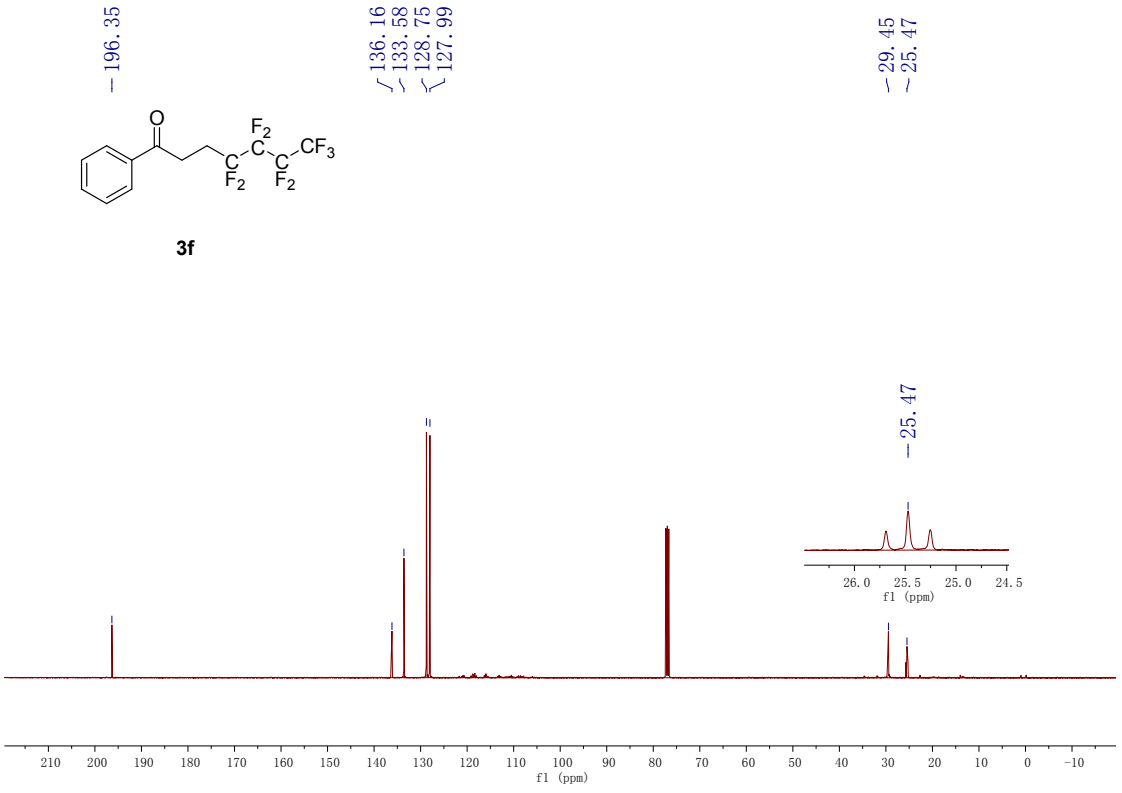

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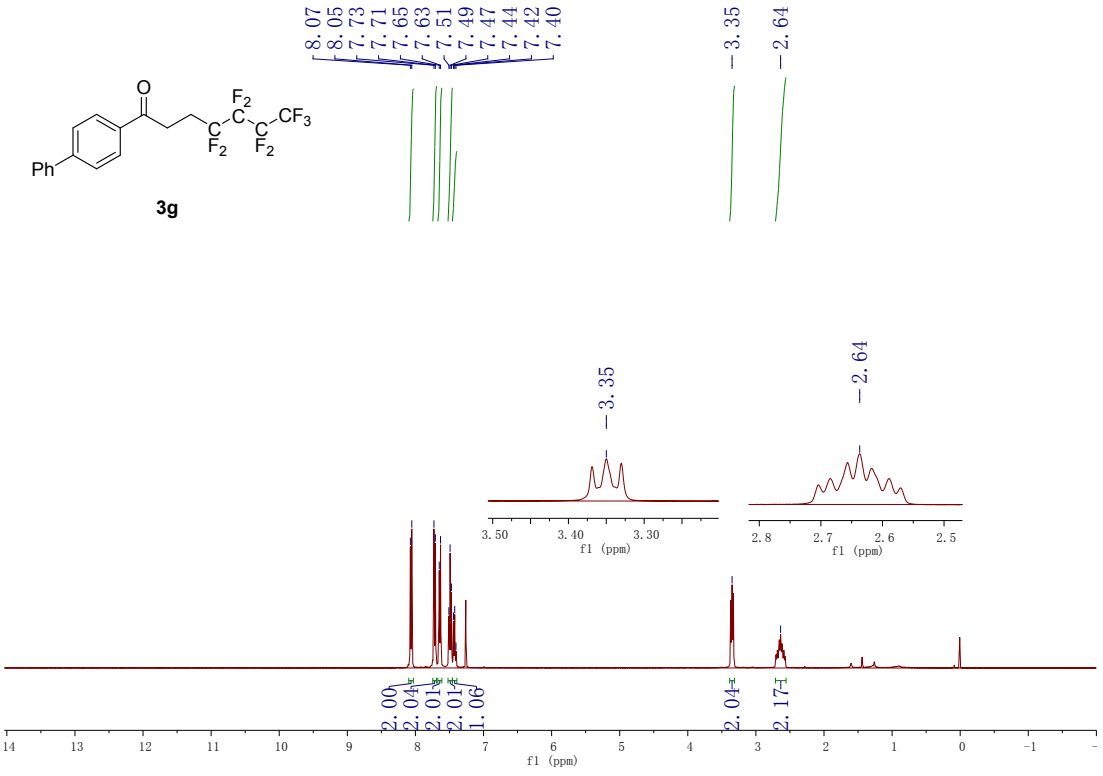

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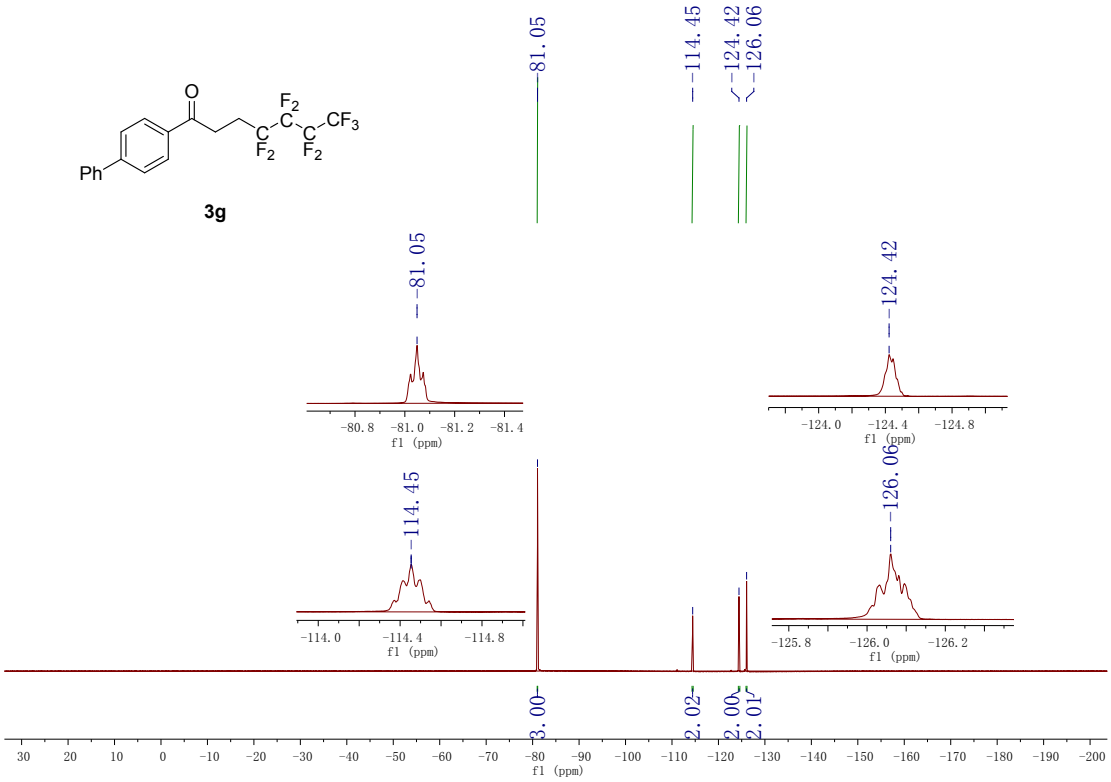

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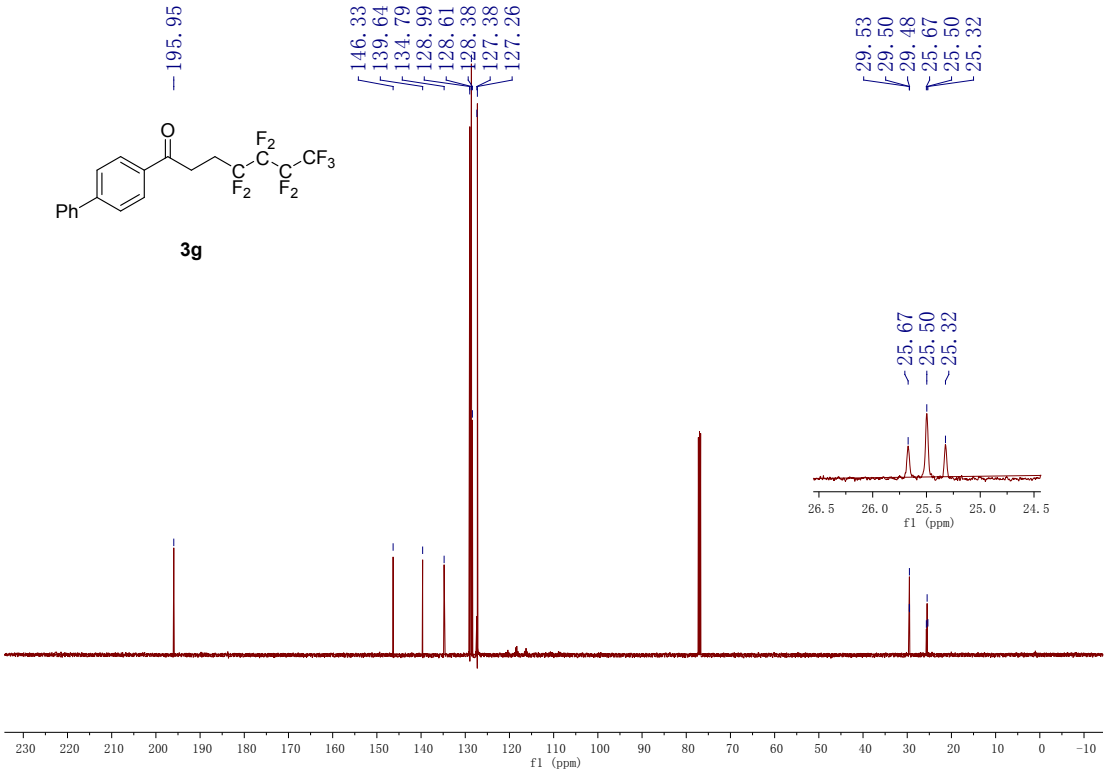

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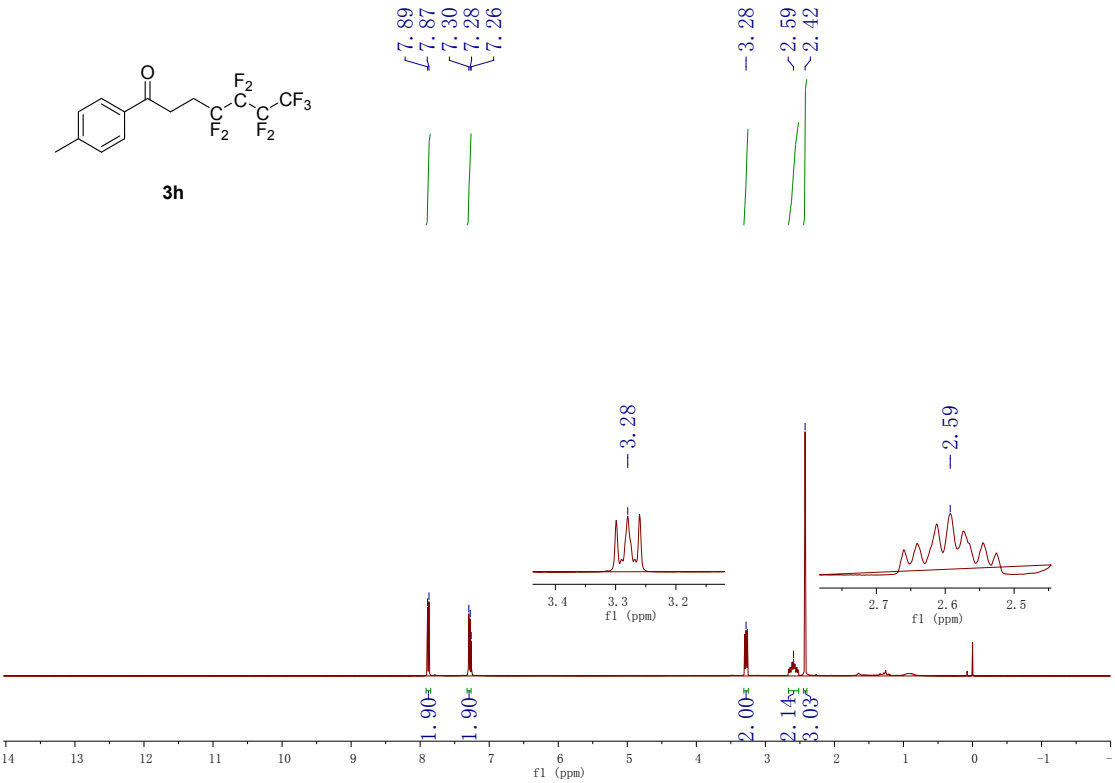

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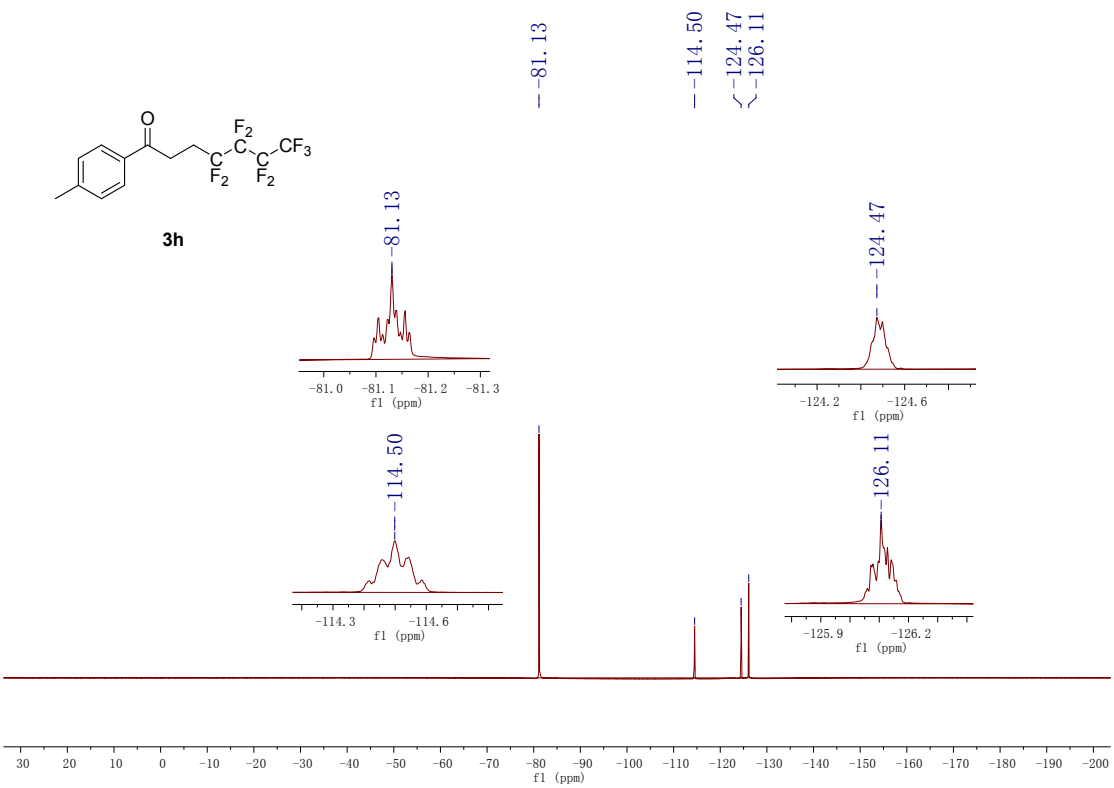

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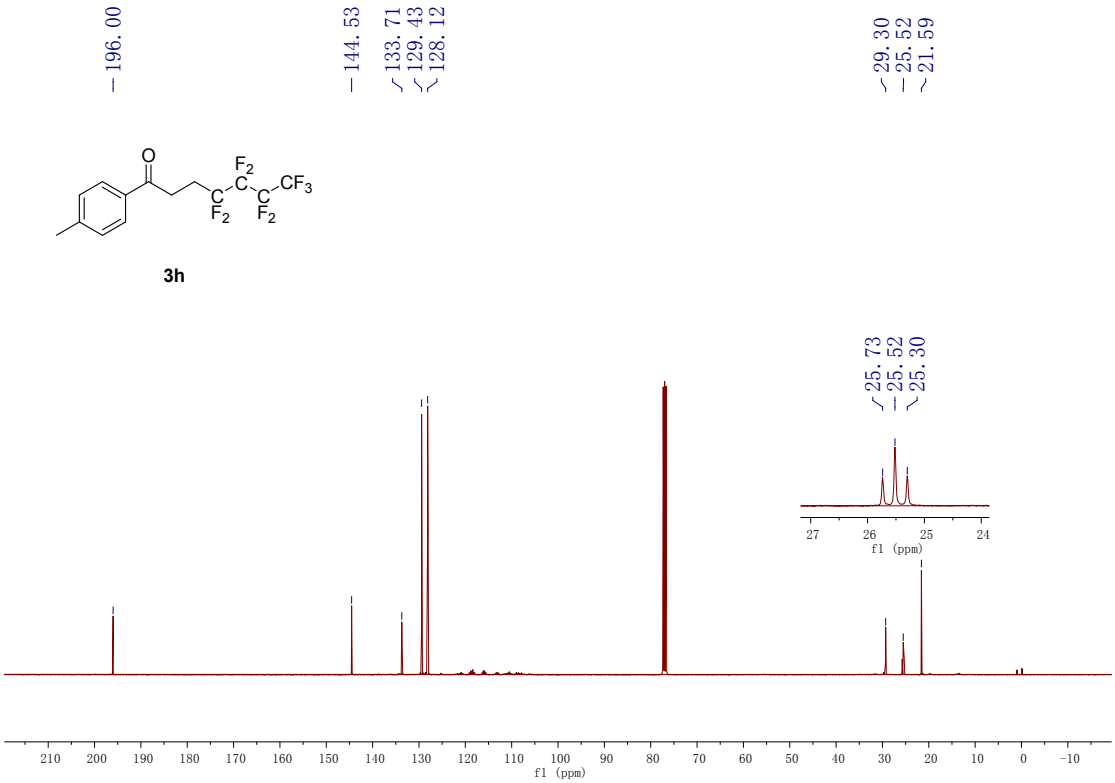

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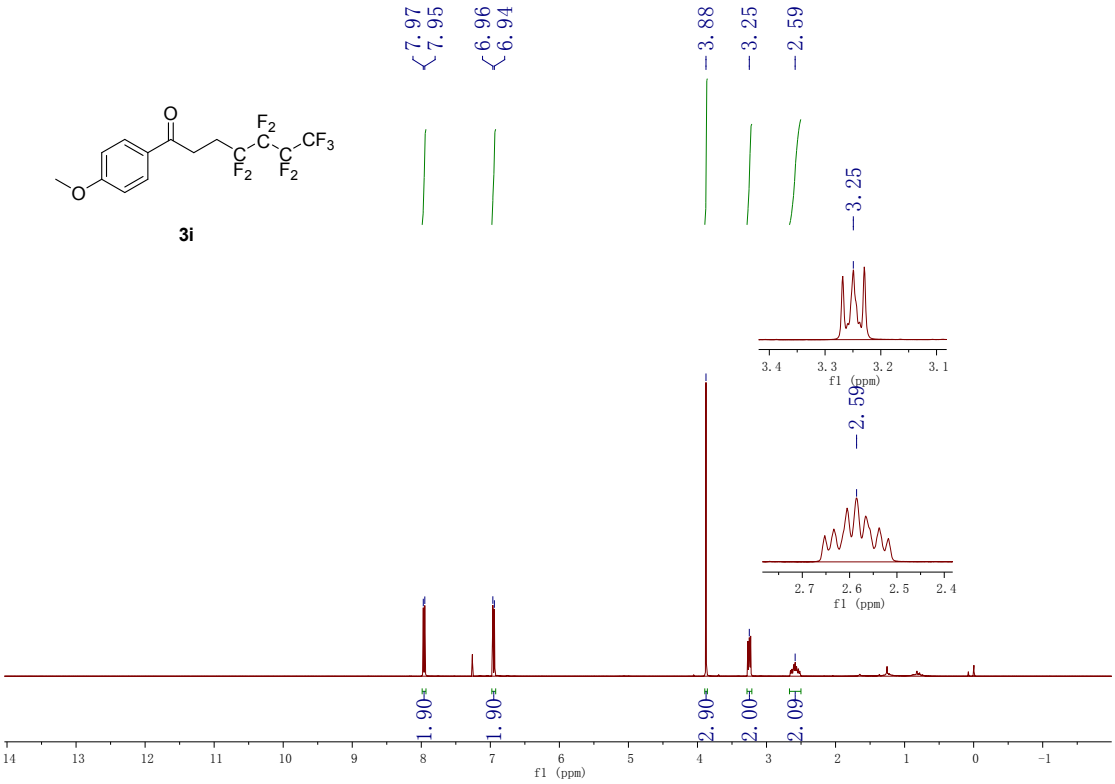

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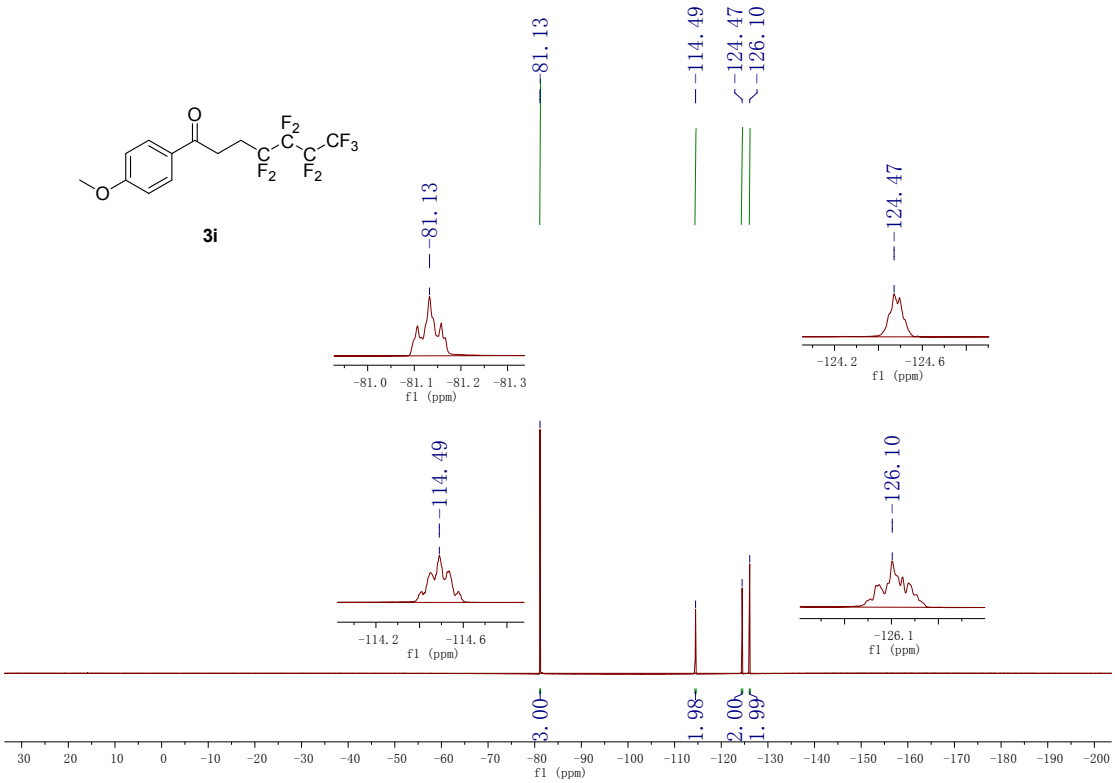

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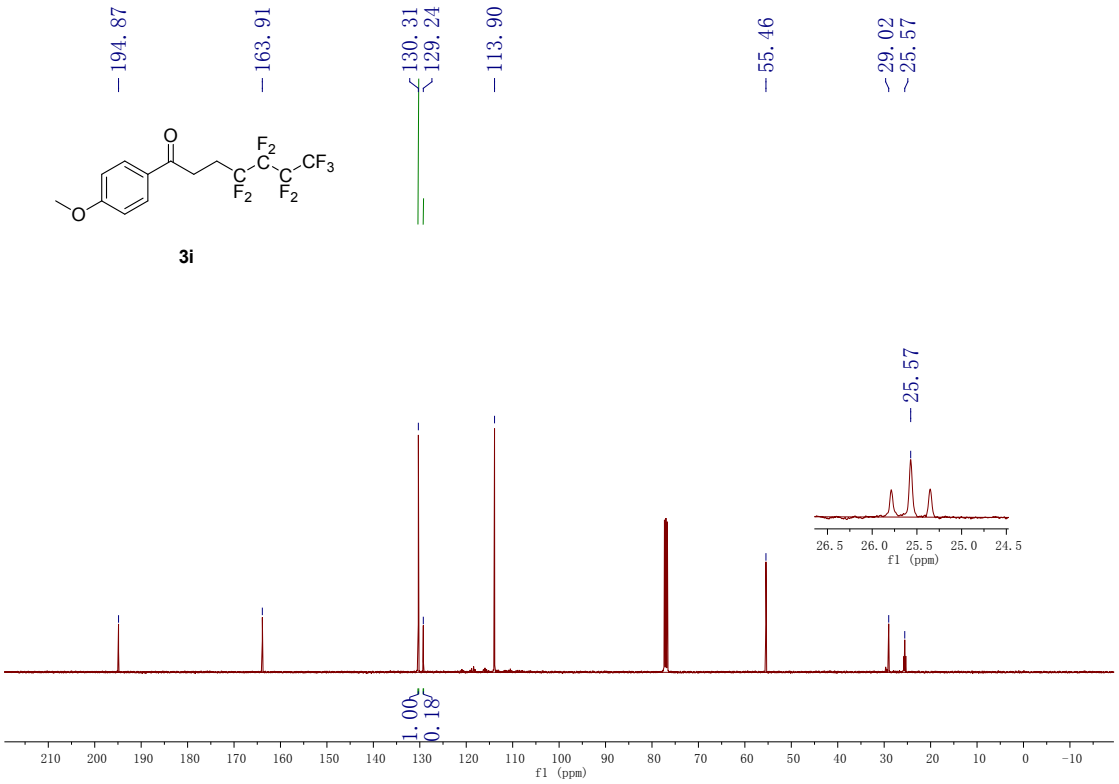

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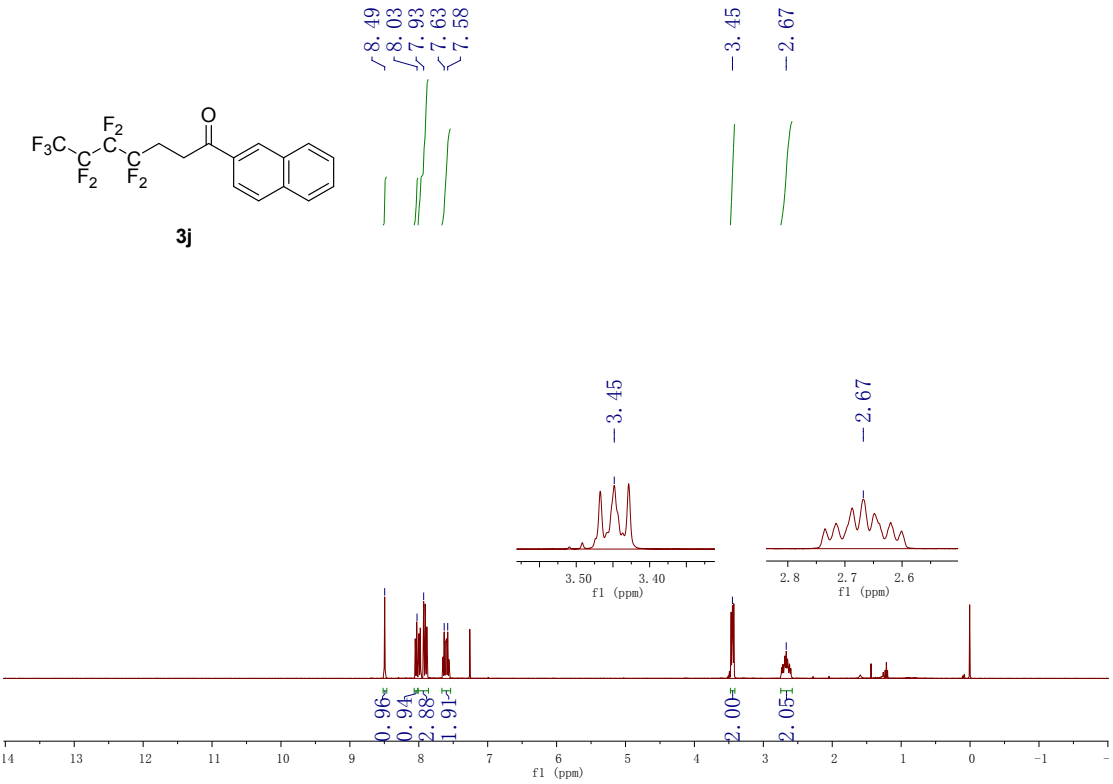

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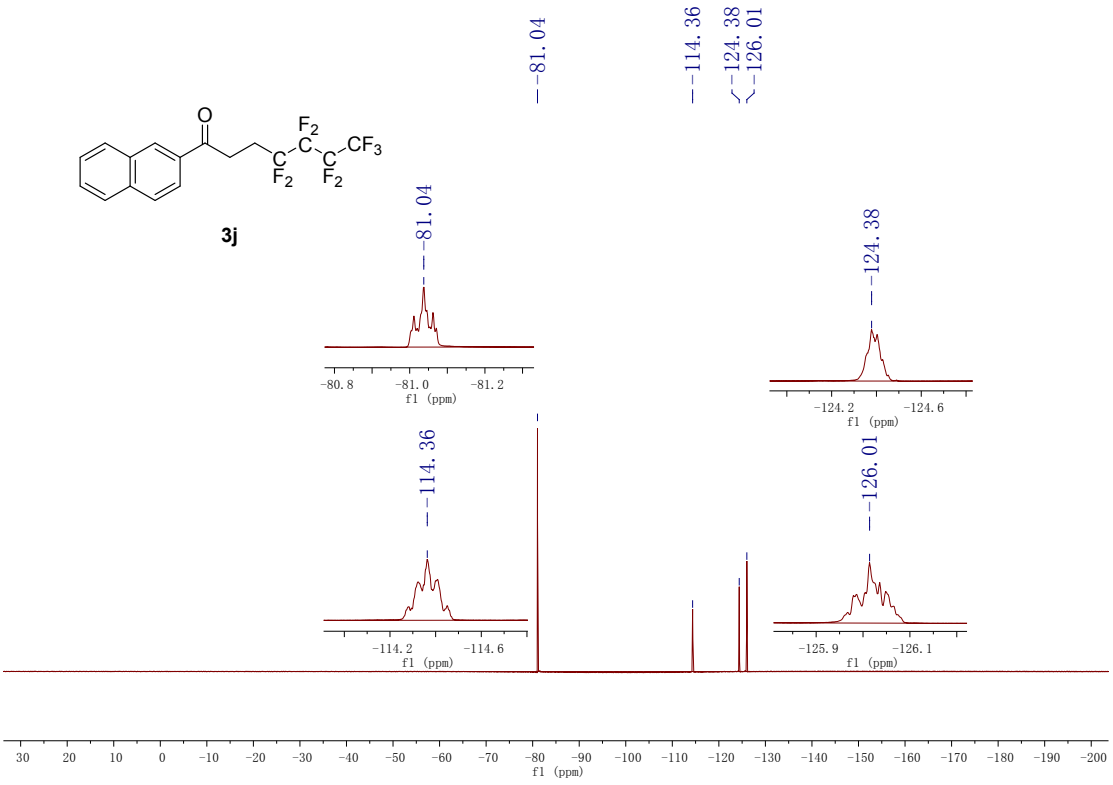

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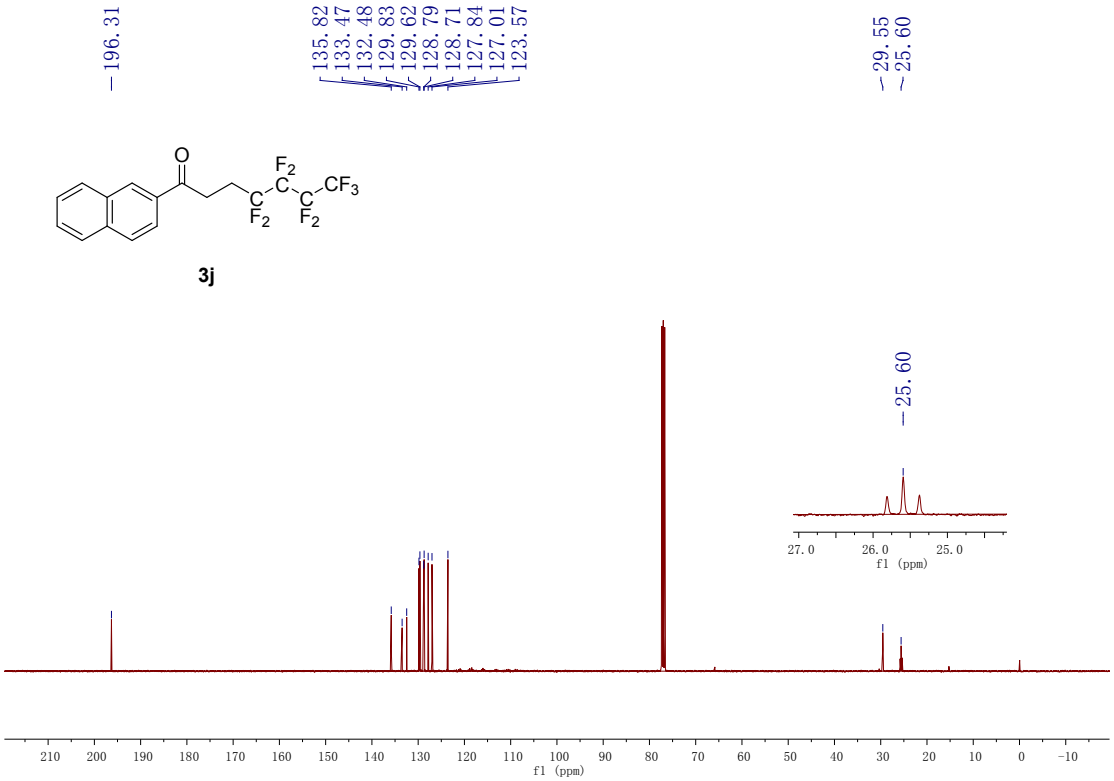
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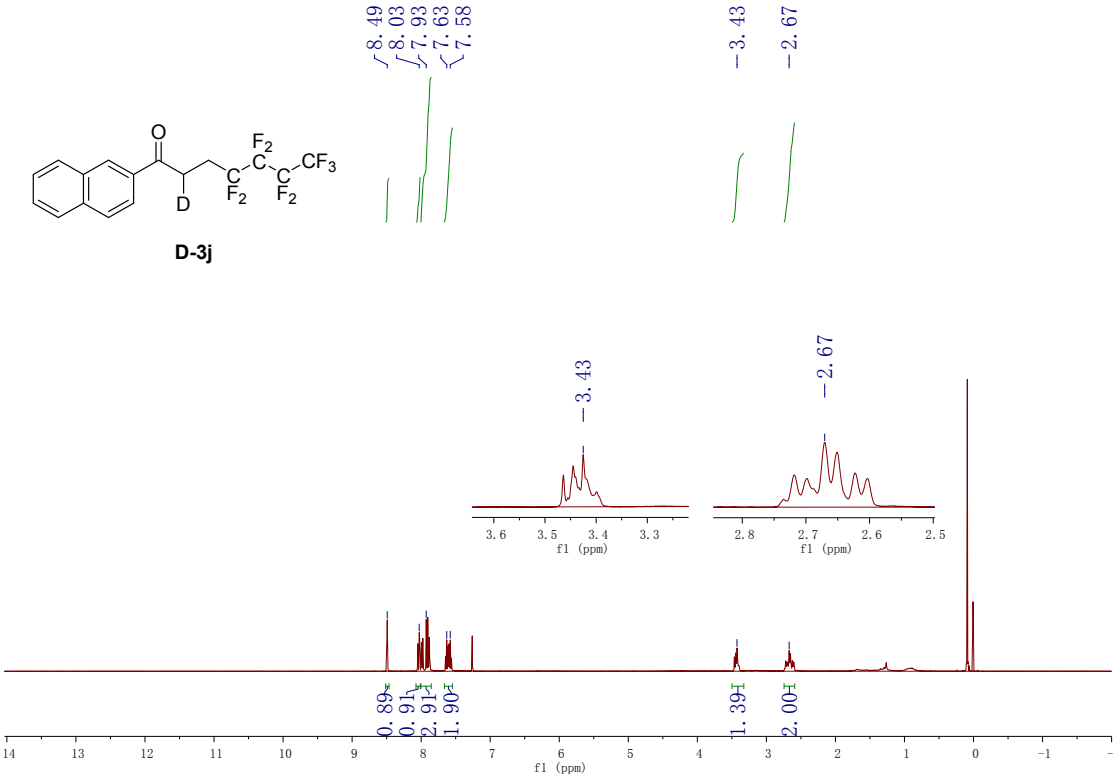
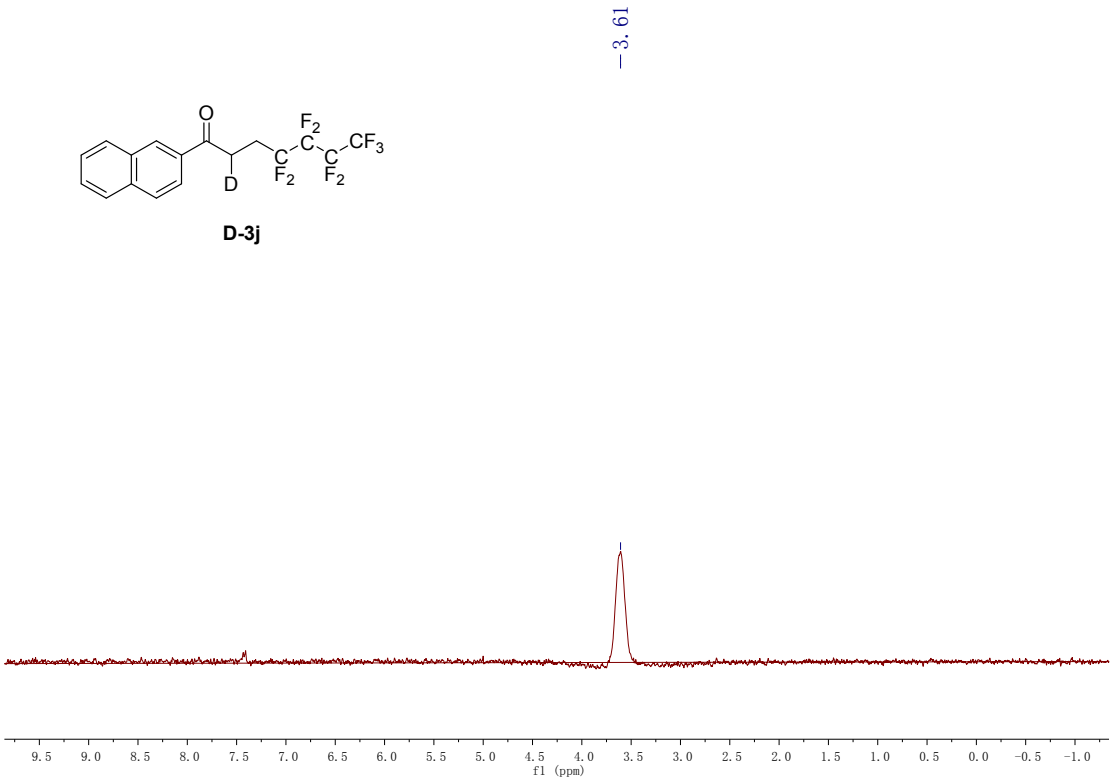
135.82
133.47
132.48
129.83
129.62
128.79
128.71
127.84
127.01
123.57
29.55
25.60
O
F2
C
CF3
C
F2
C
F2
3j
25.60
27.0
26.0
25.0
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{1}H NMR：

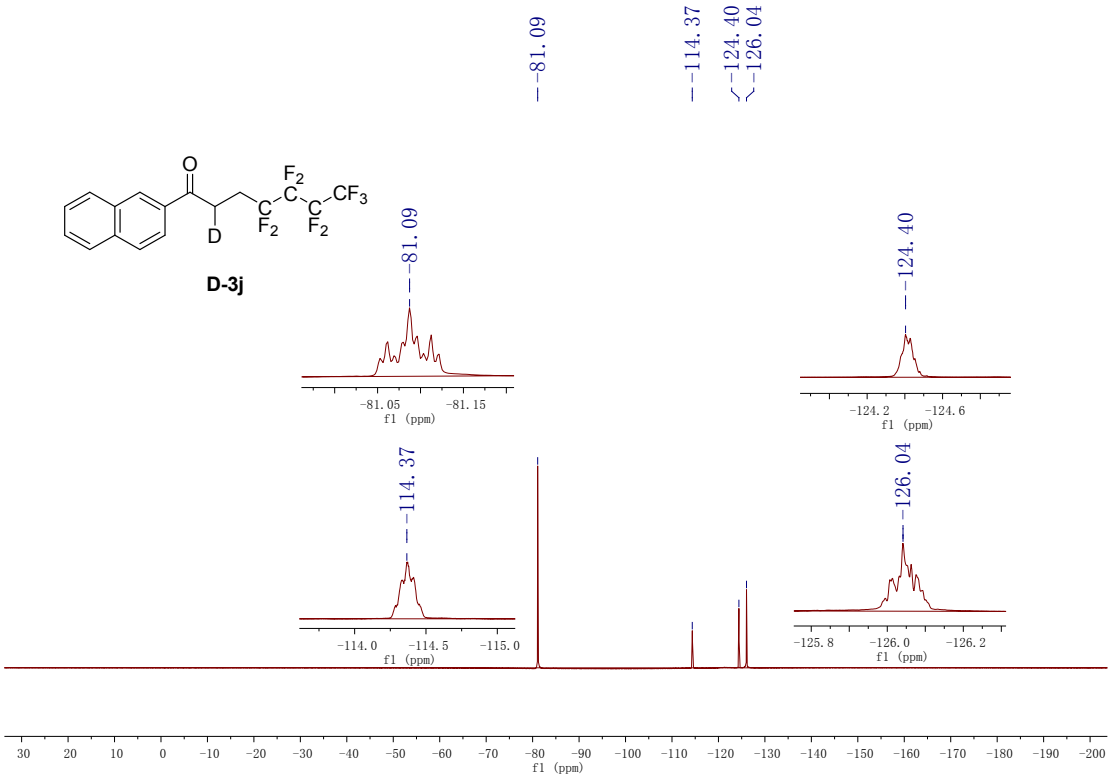

8.49
8.03
7.93
7.63
7.58
3.43
2.67
O
F2
C
CF3
C
F2
C
F2
D
D-3j
3.43
2.67
3.6
3.5
3.4
3.3
2.8
2.7
2.6
2.5
f1 (ppm)
0.89
0.91
2.91
1.90
1.39
2.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

^{2}H NMR：



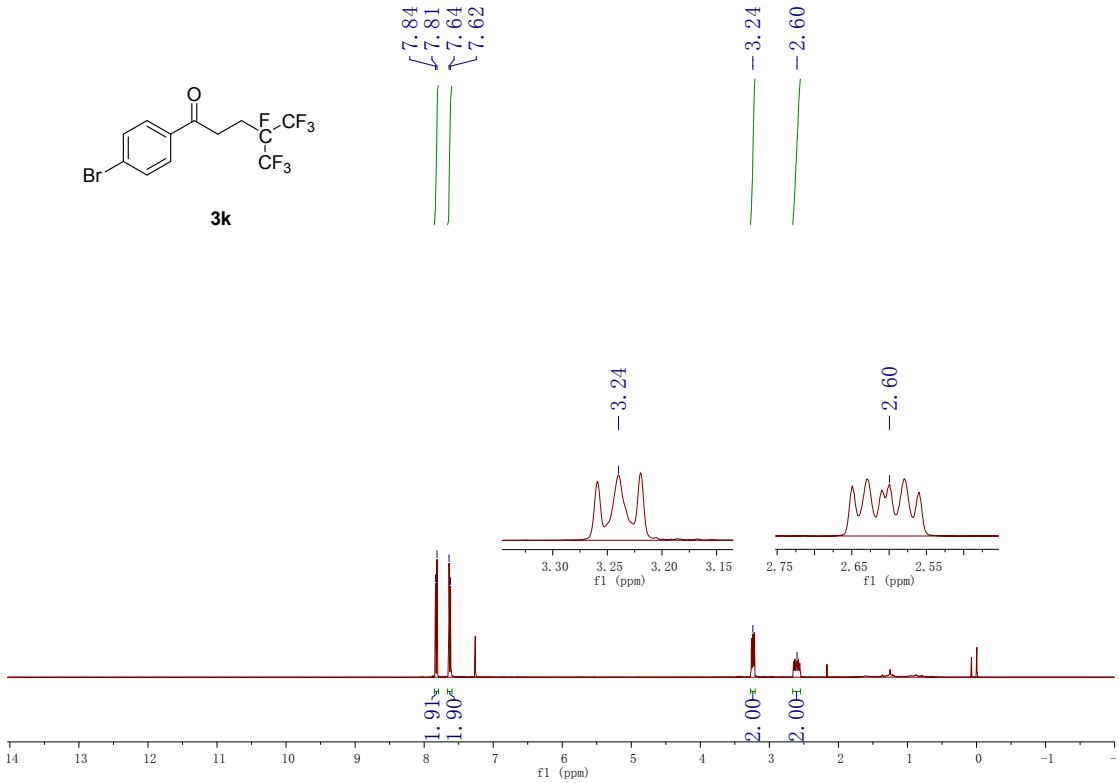
D-3j

^{19}F NMR:

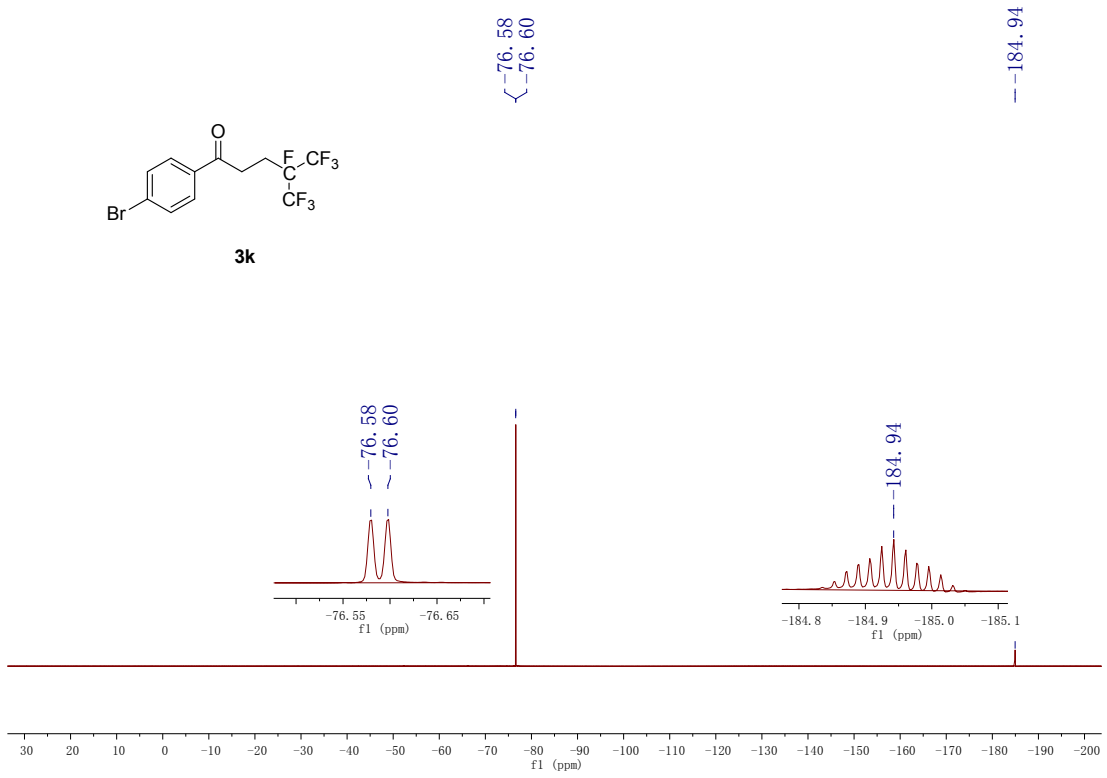


D-3j

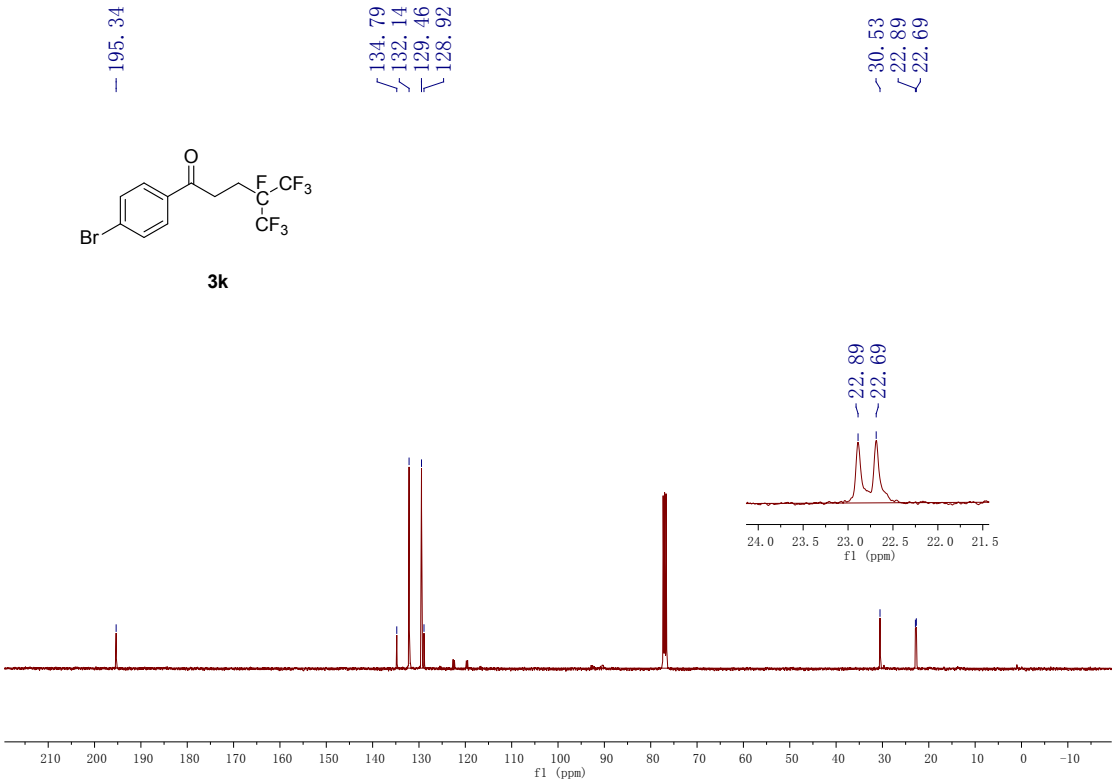
^{1}H NMR：



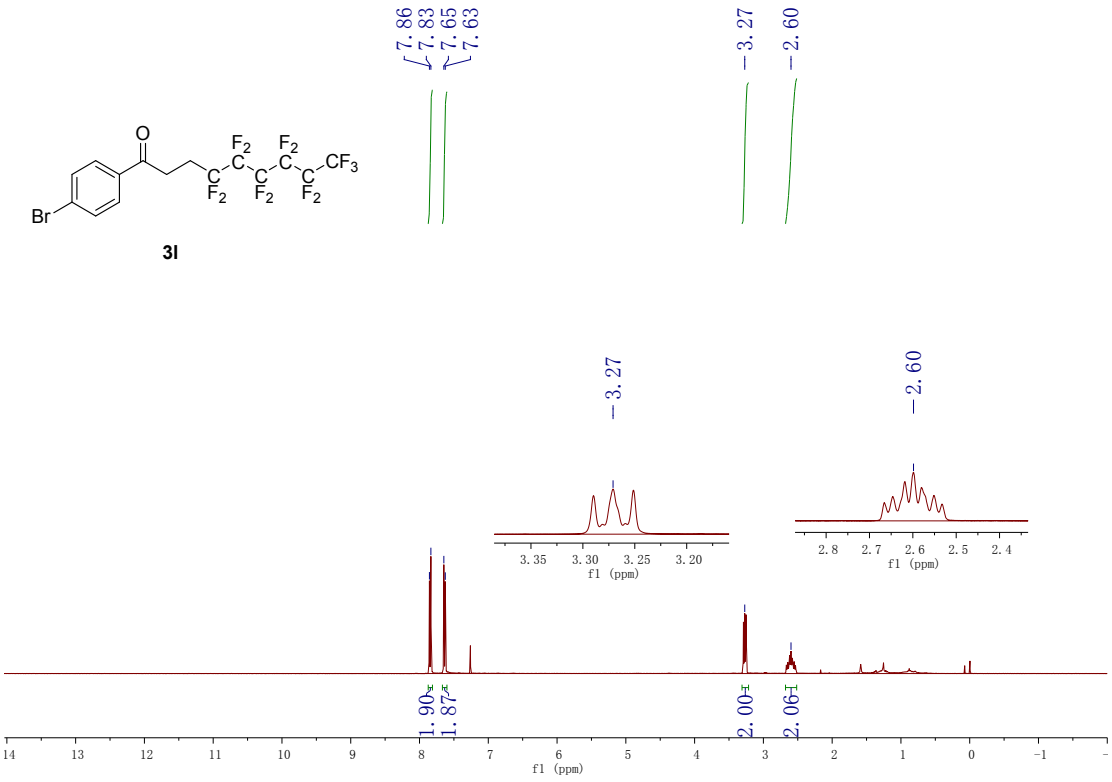
^{19}F NMR:



^{13}C NMR:



^{1}H NMR:



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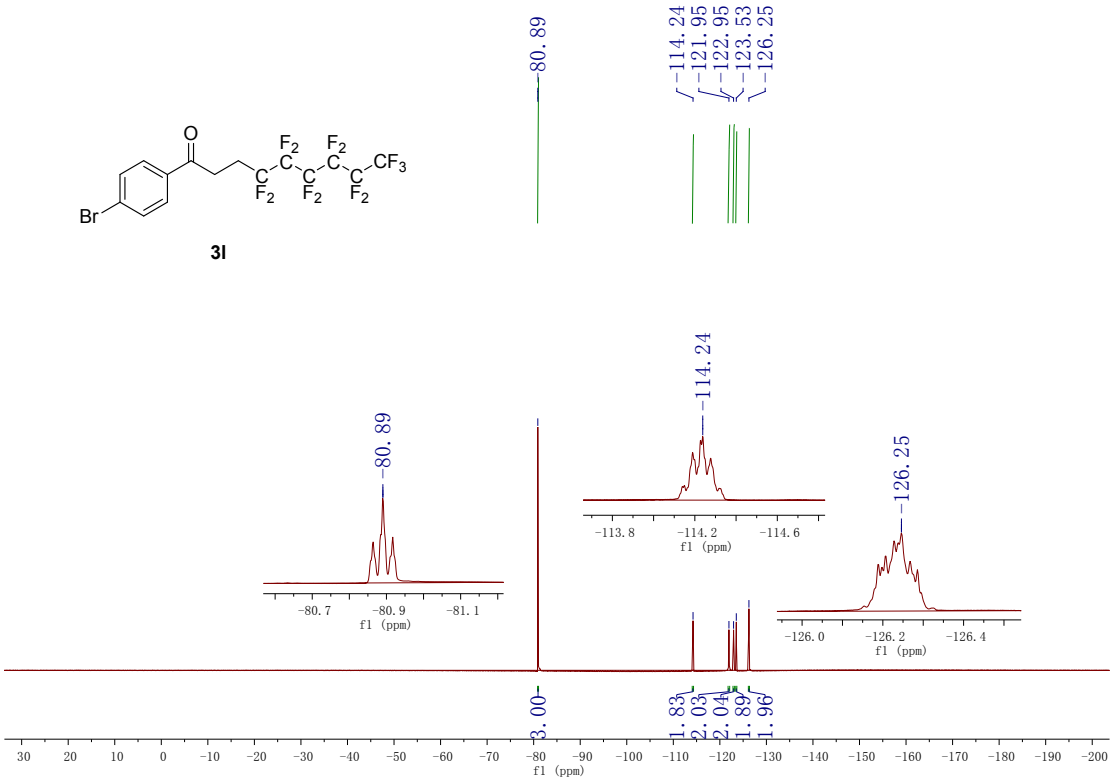

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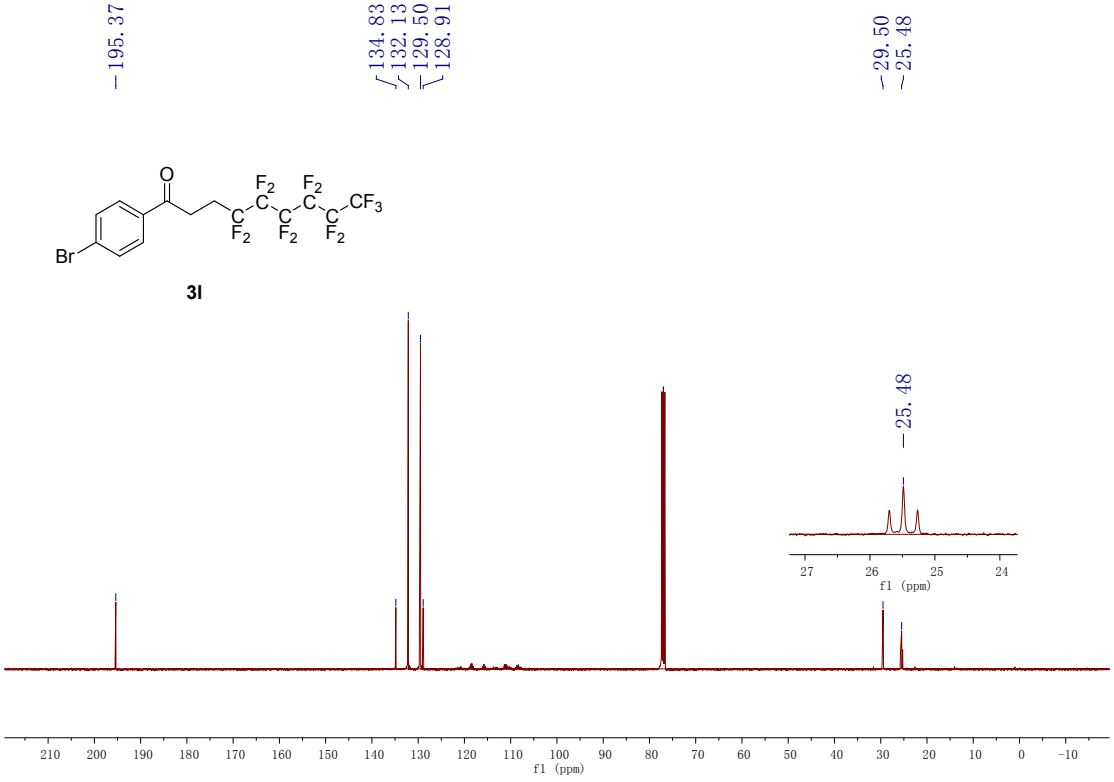

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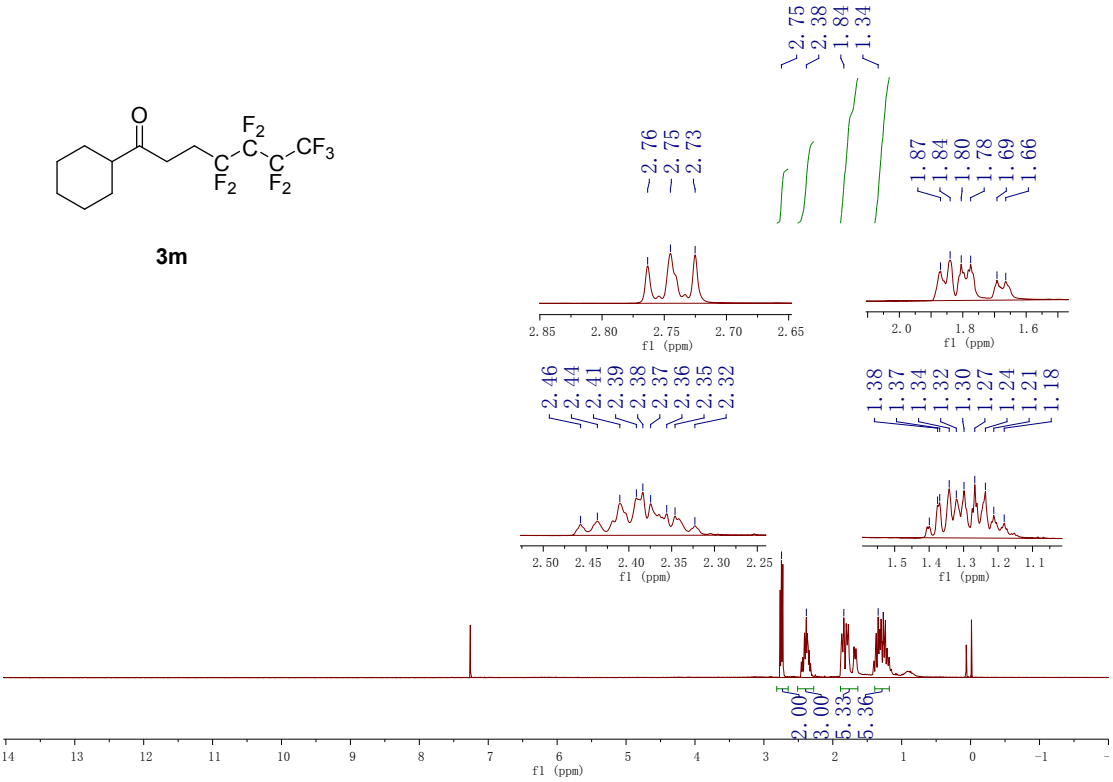

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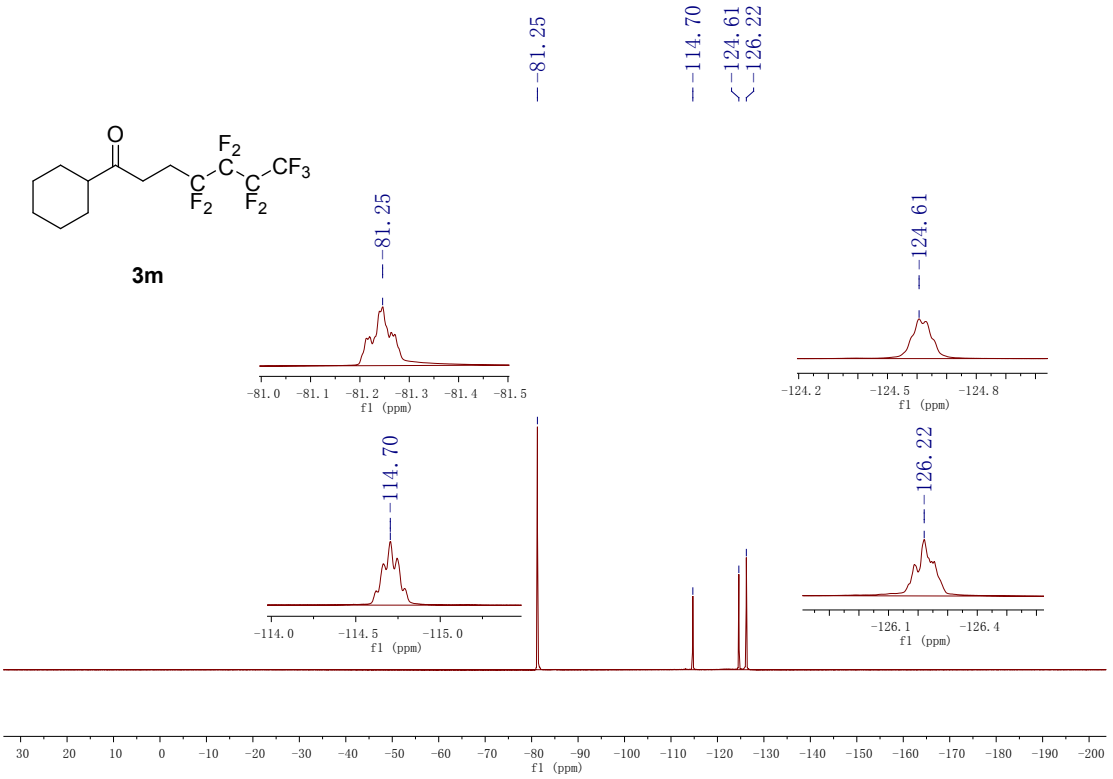
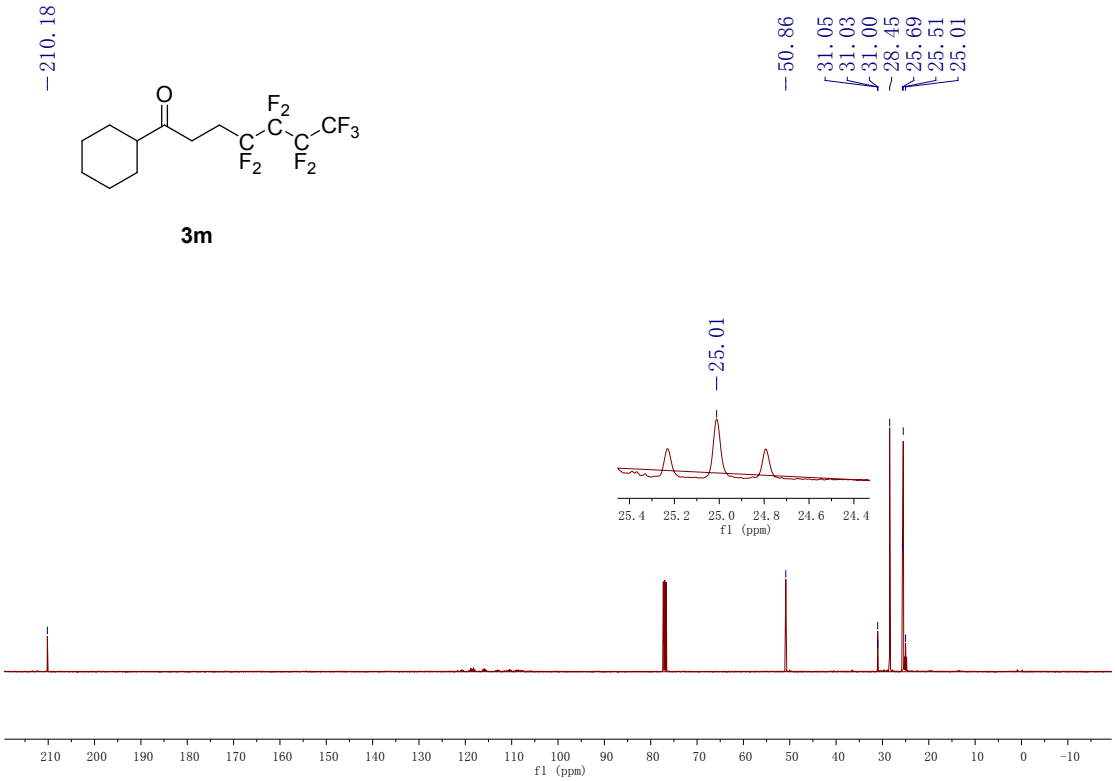


^{13}C NMR:



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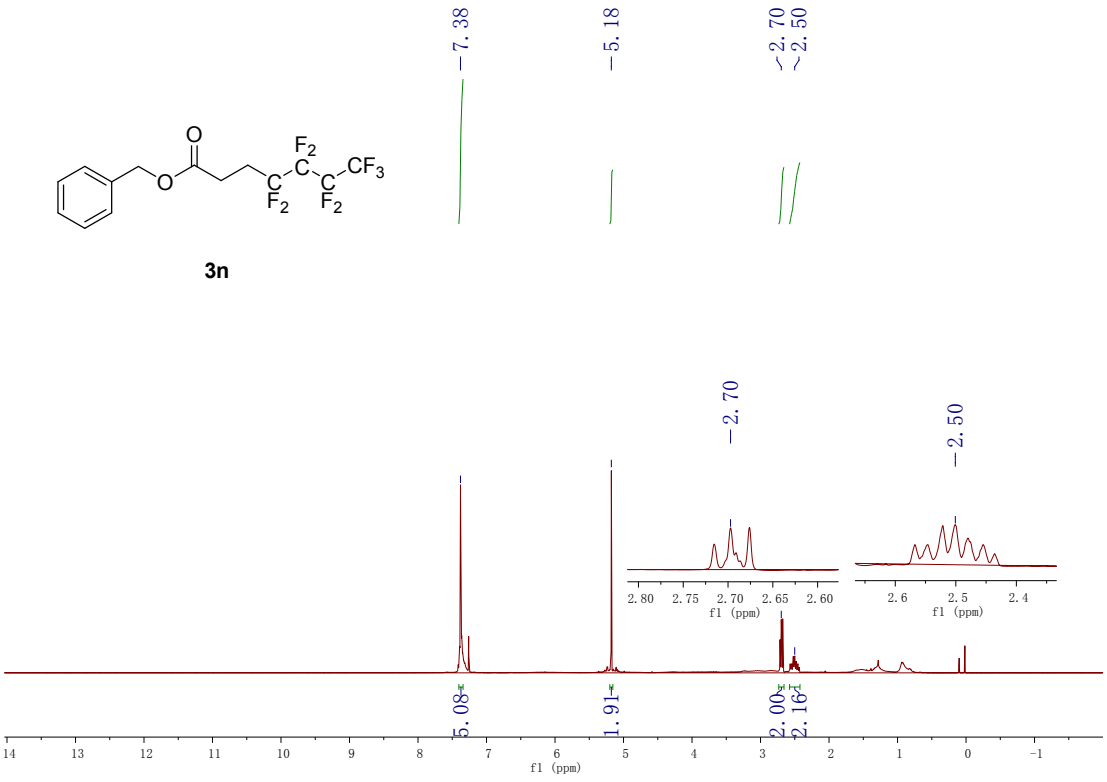

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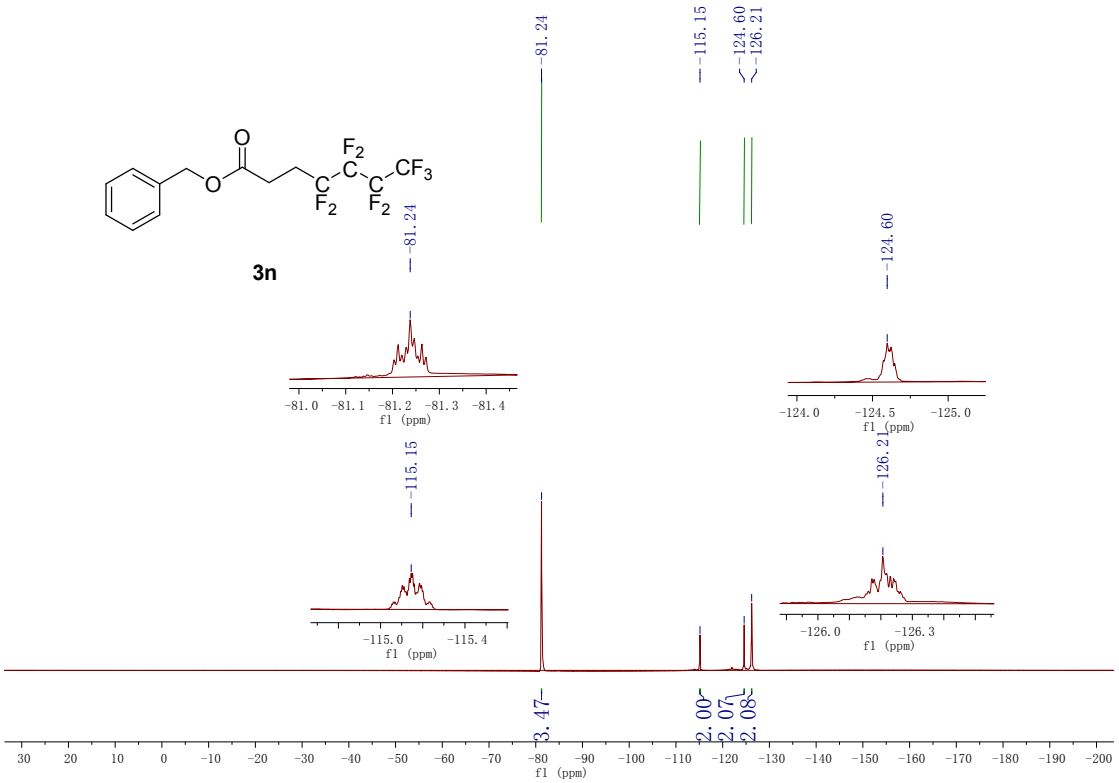
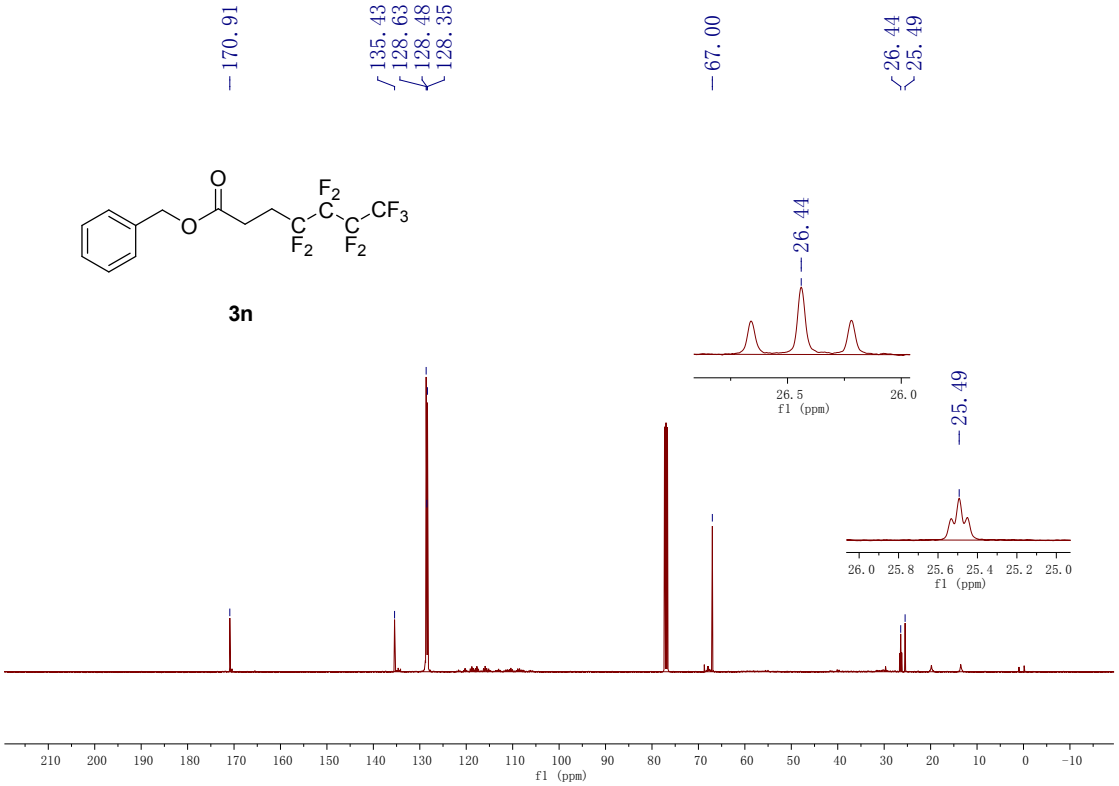

-81.24
-115.15
-124.60
-126.21
3n
-81.24
-124.60
-115.15
-126.21
f1 (ppm)
3.47
2.00
2.07
2.08

^{13}C NMR:


-170.91
135.43
128.63
128.48
128.35
-67.00
26.44
25.49
3n
26.44
25.49
f1 (ppm)