

Supporting Information

Triple *ipso*-defluoroetherification of (trifluoromethyl)alkenes with fluoroalkylated alcohols: Access to fluoroalkylated orthoesters by C(sp³)-F bonds cleavage

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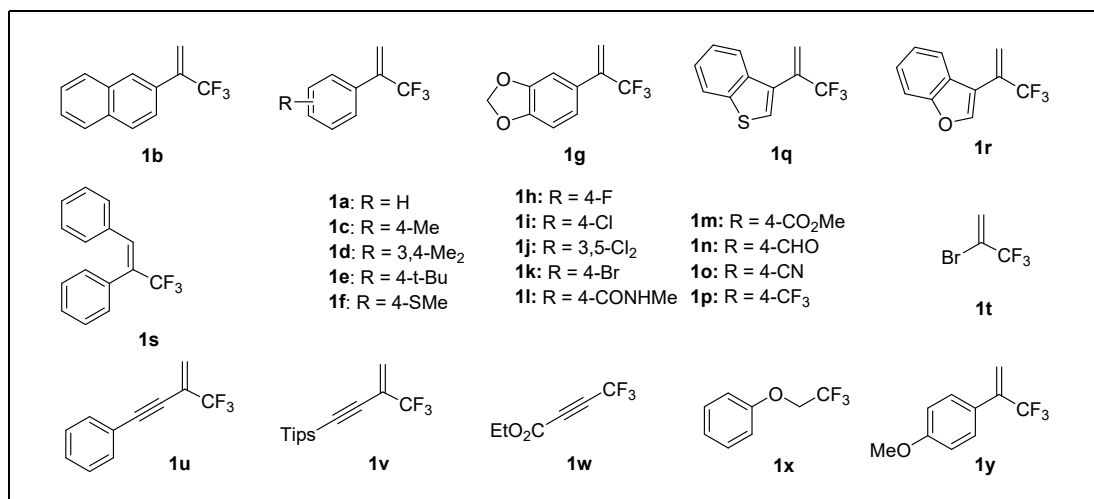
A. General Information

Melting points were measured using a melting point instrument and are uncorrected. Chemical shifts were reported in ppm from the solvent resonance as the internal standard (CDCl_3 $\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.16$ ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), td (triplet of doublets), m (multiplet), and *etc.* Coupling constants were reported in Hertz (Hz). ^1H , ^{13}C and ^{19}F NMR data are recorded with Bruker Advance III 400 MHz or 500 MHz. All ^{13}C and ^{19}F NMR spectra were performed under the conditions of ^1H -decoupled conditions, respectively. NMR spectra were recorded at room temperature unless otherwise stated. IR spectra were obtained with an infrared spectrometer on either potassium bromide pellets or liquid films between two potassium bromide pellets. HRMS was carried out on a high-resolution mass spectrometer (Thermo Q Exactive Plus ACPI/QE MS). TLC was performed using commercially available 100-400 mesh glass-backed silica-coated plates (GF₂₅₄). Visualization was typically performed using UV light and/or phosphomolybdic acid.

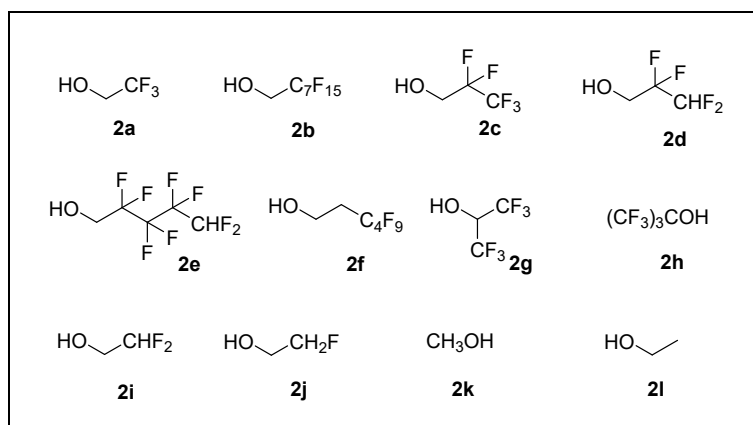
Materials. Commercially available reagents and solvents were purchased and used without further purification. The anhydrous THF was purchased from Energy Chemical (Energy Chemical, water ≤ 50 ppm). Analytical thin-layer chromatography was performed on 0.20 mm silica gel plates (GF₂₅₄) using UV light or phosphomolybdic acid as a visualizing agent. Flash column chromatography was carried out using silica gel (200-300 mesh) with the indicated solvent system. All reactions were conducted in oven-dried Schlenk tubes. All the reaction temperatures reported are oil bath temperatures.

B. Experiment Section

1) Substrates Preparation

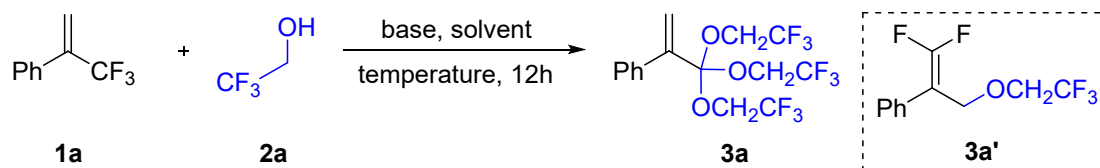


1t and 1w was known compound and commercial available (from Energy Chemical and Bidepharm). Compound 1a-1r,¹ 1s,² 1u-1v³, 1x⁴, 1y¹ were synthesized following the reported methods.



Alcohols 2 were known compounds. 2a-2l were purchased and used directly (from Energy Chemical, Bidepharm and Innochem).

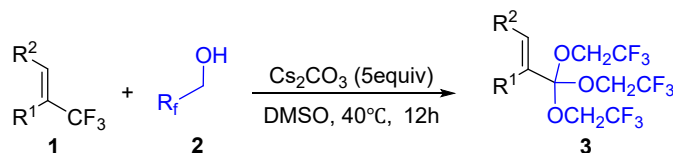
2) Optimization of the Reaction Conditions^a



Entry	Base	Solvent	Temperature (°C)	Yield of 3a (%) ^b
1	Cs ₂ CO ₃	toluene	60	0
2	Cs ₂ CO ₃	xylene	60	0
3	Cs ₂ CO ₃	THF	60	0
4	Cs ₂ CO ₃	MeCN	60	13
5	Cs ₂ CO ₃	DMSO	60	95
6	Cs ₂ CO ₃	DMF	60	82
7	Li ₂ CO ₃	DMSO	60	0
8	<i>t</i> -BuOLi	DMSO	60	80
9	<i>t</i> -BuONa	DMSO	60	72
10	<i>t</i> -BuOK	DMSO	60	68
11	KOH	DMSO	60	72
12	LiOH	DMSO	60	65
13	DBU	DMSO	60	0
14	DABCO	DMSO	60	0
15	Et ₃ N	DMSO	60	0
16	-	DMSO	30	0
17	Cs ₂ CO ₃	DMSO	50	97
18	Cs ₂ CO ₃	DMSO	40	99
19	Cs ₂ CO ₃	DMSO	30	88
20	Cs ₂ CO ₃	DMSO	80	88

^aUnless otherwise noted, the reactions were carried out with **1a** (0.2 mmol), **2a** (0.8 mmol), base (1.0 mmol), and solvent (2 mL) in a 25 mL Schlenk tube in an oil bath for 12 h. ^bIsolated yields.

3) General Procedure for the Reaction of Fluoroalkylated Alcohols with Alkenes

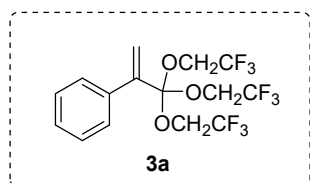


To a 25 mL Schlenk flask was charged with alkenes **1** (0.2 mmol, 1.0 equiv), fluoroalkylated alcohols (0.8 mmol, 4.0 equiv), Cs₂CO₃ (1.0 mmol, 5.0 equiv) and a solvent of DMSO (2.0 mL). The resulting solution was stirred at 40 °C for 12 h. Then the mixture was cooled to room temperature, quenched with H₂O (15 mL), extracted with EtOAc (15 mL × 3). The combined

organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated in vacuo. Further purification by flash column chromatography on silica gel provided the products **3**.

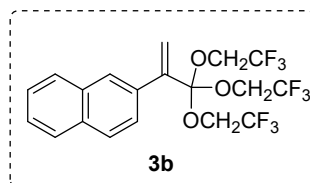
4) Characterization of Obtained Products

(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-en-2-yl)benzene (**3a**)



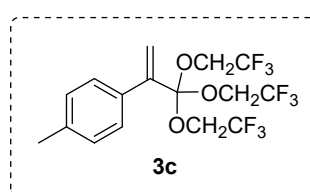
83.3 mg, 99% yield; yellow oil, eluting with EtOAc/PE = 1: 10; ^1H NMR (500 MHz, CDCl_3) δ 7.58 (dd, $J = 6.8, 3.0$ Hz, 2H), 7.42-7.31 (m, 3H), 5.97 (s, 1H), 5.90 (s, 1H), 3.88 (q, $J = 8.3$ Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 140.0, 134.6, 129.0, 128.7, 126.9, 123.3 (q, $^1J_{\text{F-C}} = 277.2$ Hz), 122.2, 113.8, 60.8 (q, $^2J_{\text{F-C}} = 36.5$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -73.7 (s, 9F); IR (KBr): 2950, 1421, 1287, 1172, 1094, 960, 854, 761, 700, 625, 549 cm^{-1} ; HRMS (APCI-QE, m/z): $[\text{M-H}]^-$ Calcd. for $\text{C}_{15}\text{H}_{13}\text{F}_9\text{O}_3\text{-H}$, 411.0648; found, 411.0649.

2-(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-en-2-yl)naphthalene (**3b**)



117.0 mg, 98% yield; white solid, mp: 70-71 $^\circ\text{C}$, eluting with EtOAc/PE = 1: 10; ^1H NMR (400 MHz, CDCl_3) δ 8.19 (d, $J = 1.9$ Hz, 1H), 7.97-7.84 (m, 3H), 7.73 (dd, $J = 8.7, 1.9$ Hz, 1H), 7.56 (dd, $J = 6.3, 3.2$ Hz, 2H), 6.17 (s, 1H), 6.06 (s, 1H), 3.99 (q, $J = 8.3$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 139.8, 133.3, 133.3, 131.7, 128.7, 128.3, 127.5, 126.9, 126.6, 126.5, 124.3, 123.3 (q, $^1J_{\text{F-C}} = 277.2$ Hz), 122.6, 114.0, 60.9 (q, $^2J_{\text{F-C}} = 36.4$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -73.7 (s, 9F); IR (KBr): 2977, 1421, 1286, 1167, 1102, 1021, 962, 857, 821, 748, 467 cm^{-1} ; HRMS (APCI-QE, m/z): $[\text{M}]^+$ Calcd. for $\text{C}_{19}\text{H}_{15}\text{F}_9\text{O}_3$, 462.0878; found, 462.0871.

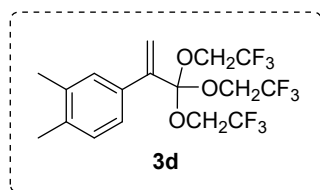
1-methyl-4-(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-en-2-yl)benzene (**3c**)



74.1 mg, 84% yield; yellow oil, eluting with PE; ^1H NMR (400 MHz, CDCl_3) δ 7.56-7.48 (m, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 5.98 (s, 1H), 5.90 (s, 1H), 3.90 (q, $J = 8.3$ Hz, 6H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 139.6, 139.1, 131.5, 129.4, 126.7, 123.3 (q, $^1J_{\text{F-C}} = 277.2$ Hz), 121.4, 113.9, 60.8 (q, $^2J_{\text{F-C}} = 36.5$ Hz), 21.1; ^{19}F NMR (471 MHz, CDCl_3) δ -73.7 (s, 9F); IR (KBr): 2895, 1513, 1419, 1284, 1164, 1096, 1017, 960, 823, 754, 686, 542, 473

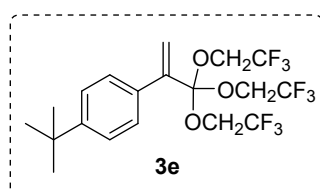
cm⁻¹; HRMS (APCI-QE, m/z): [M-H]⁻ Calcd. for C₁₆H₁₅F₉O₃-H, 425.0805; found, 425.0805.

1,2-dimethyl-4-(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-en-2-yl)benzene (3d)



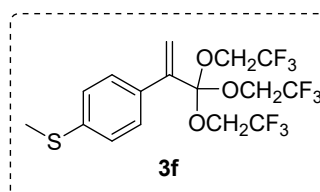
74.1 mg, 80% yield; yellow oil, eluting with PE; ¹H NMR (500 MHz, CDCl₃) δ 7.40-7.30 (m, 2H), 7.12 (d, *J* = 7.9 Hz, 1H), 5.94 (s, 1H), 5.85 (s, 1H), 3.87 (q, *J* = 8.3 Hz, 6H), 2.27 (s, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 139.7, 137.7, 136.9, 132.0, 129.9, 127.9, 124.2, 122.3 (q, ¹*J*_{F-C} = 277.2 Hz), 121.3, 114.0, 60.8 (q, ²*J*_{F-C} = 36.5 Hz), 19.8, 19.5; ¹⁹F NMR (471 MHz, CDCl₃) δ -73.7 (s, 9F); IR (KBr): 2963, 1607, 1513, 1461, 1422, 1287, 1168, 1097, 1023, 964, 841, 804, 746, 689, 605, 546 cm⁻¹; HRMS (APCI-QE, m/z): [M-H]⁻ Calcd. for C₁₇H₁₇F₉O₃-H, 439.0961; found, 439.0961.

1-(tert-butyl)-4-(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-en-2-yl)benzene (3e)



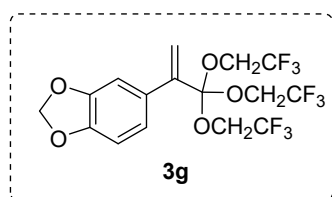
87.1 mg, 97% yield; yellow oil, eluting with PE; ¹H NMR (400 MHz, CDCl₃) δ 7.60-7.53 (m, 2H), 7.45-7.39 (m, 2H), 6.00 (s, 1H), 5.92 (s, 1H), 3.90 (q, *J* = 8.4 Hz, 6H), 1.36 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 152.2, 139.6, 131.4, 126.5, 125.6, 123.3 (q, ¹*J*_{F-C} = 277.8 Hz), 121.6, 113.9, 60.8 (q, ²*J*_{F-C} = 36.4 Hz), 34.6, 31.1; ¹⁹F NMR (471 MHz, CDCl₃) δ -73.7 (s, 9F); IR (KBr): 2963, 1741, 1411, 1283, 1168, 1108, 965, 840, 747, 556 cm⁻¹; HRMS (APCI-QE, m/z): [M+H]⁺ Calcd. for C₁₉H₂₁F₉O₃+H, 469.1420; found, 469.1412.

methyl(4-(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-en-2-yl)phenyl)sulfane (3f)



91.7 mg, 99% yield; yellow oil, eluting with PE; ¹H NMR (500 MHz, CDCl₃) δ 7.45 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.15 (dd, *J* = 8.4, 1.3 Hz, 2H), 5.89 (d, *J* = 1.2 Hz, 1H), 5.80 (d, *J* = 1.2 Hz, 1H), 3.79 (q, *J* = 8.3 Hz, 6H), 2.42 (d, *J* = 1.3 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 140.1, 139.1, 130.8, 127.1, 126.1, 123.3 (q, ¹*J*_{F-C} = 277.2 Hz), 121.4, 113.8, 60.8 (q, ²*J*_{F-C} = 36.5 Hz), 15.2; ¹⁹F NMR (471 MHz, CDCl₃) δ -73.7 (s, 9F); IR (KBr): 2962, 1598, 1495, 1422, 1285, 1168, 1095, 1019, 961, 834, 750, 689 cm⁻¹; HRMS (APCI-QE, m/z): [M]⁺ Calcd. for C₁₆H₁₅F₉O₃S, 458.0598; found, 458.0590.

5-(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-en-2-yl)benzo[d][1,3]dioxole (3g)

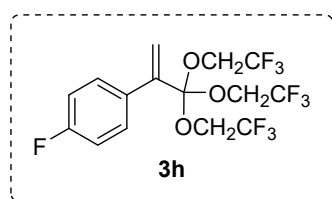


94.8 mg, 95% yield; yellow oil, eluting with EtOAc/PE = 1: 10;

^1H NMR (500 MHz, CDCl_3) δ 7.14-7.05 (m, 2H), 6.80 (d, $J = 8.2$ Hz, 1H), 5.99 (s, 2H), 5.88 (s, 1H), 5.83 (s, 1H), 3.87 (q, $J = 8.3$ Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 148.2, 148.0, 139.3,

128.4, 123.3 (q, $^1J_{F-C} = 277.2$ Hz), 121.1, 121.0, 113.8, 108.4, 107.2, 101.4, 60.8 (q, $^2J_{F-C} = 36.5$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -73.8 (s, 9F); IR (KBr): 3304, 1491, 1420, 1284, 1237, 1168, 1100, 960, 812, 751, 688 cm^{-1} ; HRMS (APCI-QE, m/z): $[\text{M}-\text{H}]^-$ Calcd. for $\text{C}_{16}\text{H}_{13}\text{F}_9\text{O}_5\text{-H}$, 455.0547; found, 455.0545.

1-fluoro-4-(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-en-2-yl)benzene (3h)

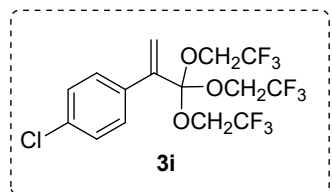


92.2 mg, 96% yield; yellow oil, eluting with PE; ^1H NMR (400

MHz, CDCl_3) δ 7.64-7.55 (m, 2H), 7.08 (t, $J = 8.7$ Hz, 2H), 5.96 (s, 1H), 5.90 (s, 1H), 3.90 (q, $J = 8.3$ Hz, 6H); ^{13}C NMR (101

MHz, CDCl_3) δ 163.1 (d, $^1J_{F-C} = 250.5$ Hz), 139.0, 130.6 (d, $^4J_{F-C} = 3.0$ Hz), 128.8 (d, $^3J_{F-C} = 8.1$ Hz), 123.2 (q, $^1J_{F-C} = 277.8$ Hz), 121.8, 115.6 (d, $^2J_{F-C} = 21.2$ Hz), 113.7, 60.8 (q, $^2J_{F-C} = 36.4$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -73.8 (s, 9F), δ -112.5 (s, 1F); IR (KBr): 2378, 1636, 1511, 1421, 1282, 1165, 1097, 962, 843, 751, 604, 536, 472 cm^{-1} ; HRMS (APCI-QE, m/z): $[\text{M}-\text{H}]^-$ Calcd. for $\text{C}_{15}\text{H}_{12}\text{F}_{10}\text{O}_3\text{-H}$, 429.0554; found, 429.0555.

1-chloro-4-(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-en-2-yl)benzene (3i)



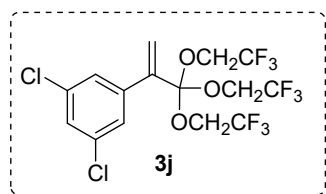
80.7 mg, 92% yield; white solid, mp: 64-65 $^\circ\text{C}$, eluting with PE;

^1H NMR (500 MHz, CDCl_3) δ 7.53 (d, $J = 8.7$ Hz, 2H), 7.34 (d, $J = 8.6$ Hz, 2H), 5.97 (s, 1H), 5.90 (s, 1H), 3.87 (q, $J = 8.3$ Hz, 6H);

^{13}C NMR (126 MHz, CDCl_3) δ 138.9, 135.1, 133.0, 128.9, 128.2,

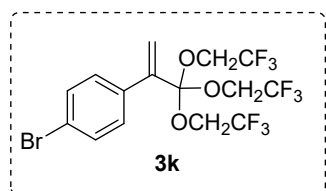
123.2 (q, $^1J_{F-C} = 277.2$ Hz), 122.4, 113.6, 60.8 (q, $^2J_{F-C} = 36.5$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -73.7 (s, 9F); IR (KBr): 2977, 2316, 1495, 1421, 1286, 1169, 1095, 1016, 961, 842, 749 cm^{-1} ; HRMS (APCI-QE, m/z): $[\text{M}-\text{H}]^-$ Calcd. for $\text{C}_{15}\text{H}_{12}\text{ClF}_9\text{O}_3\text{-H}$, 445.0259; found, 445.0262.

1,3-dichloro-5-(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-en-2-yl)benzene (3j)



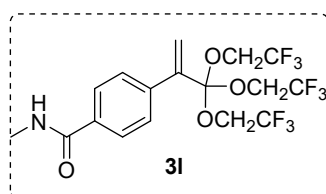
62.1 mg, 66% yield; white solid, mp: 68-69 °C, eluting with EtOAc/PE = 1: 10; ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 1.9 Hz, 2H), 7.39 (t, *J* = 1.9 Hz, 1H), 6.00 (s, 1H), 5.94 (s, 1H), 3.92 (q, *J* = 8.2 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 138.3, 137.7, 135.2, 128.9, 125.6, 123.1 (q, ¹*J*_{F-C} = 277.8 Hz), 123.6, 113.3, 61.0 (q, ²*J*_{F-C} = 36.4 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -73.7 (s, 9F); IR (KBr): 3055, 1559, 1420, 1269, 1169, 1100, 961, 857, 803, 743 cm⁻¹; HRMS (APCI-QE, *m/z*): [M+H]⁺ Calcd. for C₁₅H₁₁Cl₂F₉O₃+H, 481.0014; found, 481.0014.

1-bromo-4-(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-en-2-yl)benzene (3k)



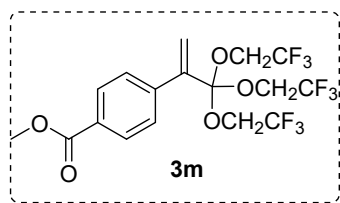
88.7 mg, 86% yield; yellow solid, mp: 72-73 °C, eluting with PE; ¹H NMR (400 MHz, CDCl₃) δ 7.57-7.44 (m, 4H), 6.00 (s, 1H), 5.93 (s, 1H), 3.90 (q, *J* = 8.3 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 139.0, 133.4, 131.8, 128.5, 123.4, 123.2 (q, ¹*J*_{F-C} = 277.8 Hz), 122.4, 113.6, 60.5 (q, ²*J*_{F-C} = 36.4 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -73.7 (s, 9F); IR (KBr): 2962, 1489, 1421, 1286, 1169, 1090, 961, 836, 752, 689, 548 cm⁻¹; HRMS (APCI-QE, *m/z*): [M]⁺ Calcd. for C₁₅H₁₂BrF₉O₃, 489.9826; found, 489.9830.

N-methyl-4-(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-en-2-yl)benzamide (3l)



88.0 mg, 94% yield; yellow solid, mp: 144-145 °C, eluting with EtOAc; ¹H NMR (500 MHz, CDCl₃) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 6.34-6.18 (m, 1H), 5.98 (s, 1H), 5.89 (s, 1H), 3.81 (q, *J* = 8.3 Hz, 6H), 2.95 (d, *J* = 4.9 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 167.5, 139.2, 137.4, 134.9, 127.2, 127.1, 123.3, 123.2 (q, ¹*J*_{F-C} = 277.2 Hz), 113.6, 60.8, 26.9 (q, ²*J*_{F-C} = 36.5 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -73.7 (s, 9F); IR (KBr): 3340, 2914, 1724, 1630, 1546, 1411, 1282, 1163, 1088, 955, 855, 766, 634, 467 cm⁻¹; HRMS (APCI-QE, *m/z*): [M+H]⁺ Calcd. for C₁₇H₁₆F₉NO₄+H, 470.1008; found, 470.1008.

methyl 4-(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-en-2-yl)benzoate (3m)



49.8 mg, 57% yield; yellow oil, eluting with EtOAc/PE = 1: 10;

^1H NMR (500 MHz, CDCl_3) δ 8.07-7.99 (m, 2H), 7.65 (d, $J = 8.1$ Hz, 2H), 6.06 (s, 1H), 5.98 (s, 1H), 3.98-3.82 (m, 9H); ^{13}C NMR

(126 MHz, CDCl_3) δ 166.6, 139.4, 139.0, 130.5, 129.9, 127.0,

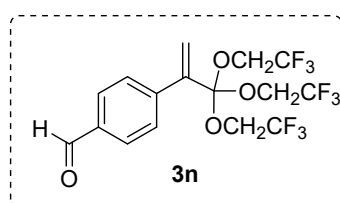
123.6, 123.2 (q, $^1J_{F-C} = 277.2$ Hz), 113.6, 60.9 (q, $^2J_{F-C} = 36.5$ Hz), 52.2; ^{19}F NMR (471 MHz,

CDCl_3) δ -73.7 (s, 9F); IR (KBr): 3152, 2974, 1752, 1641, 1426, 1288, 1173, 1097, 960, 856, 746,

688, 626 cm^{-1} ; HRMS (APCI-QE, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{17}\text{H}_{15}\text{F}_9\text{O}_5$, 471.0849; found,

471.0849.

4-(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-en-2-yl)benzaldehyde (3n)



93.3 mg, 76% yield; yellow solid, mp: 68-69 °C, eluting with

EtOAc/PE = 1: 10; ^1H NMR (500 MHz, CDCl_3) δ 10.03 (d, $J =$

1.8 Hz, 1H), 7.92-7.85 (m, 2H), 7.75 (d, $J = 8.1$ Hz, 2H), 6.09 (s,

1H), 6.01 (s, 1H), 3.91 (q, $J = 8.3$ Hz, 6H); ^{13}C NMR (126 MHz,

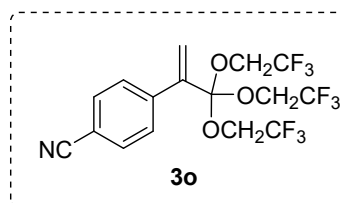
CDCl_3) δ 191.6, 140.6, 139.4, 136.3, 129.8, 127.6, 124.1, 123.1 (q, $^1J_{F-C} = 277.2$ Hz), 113.6, 60.9

(q, $^2J_{F-C} = 36.5$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -73.7 (s, 9F); IR (KBr): 2921, 1670, 1606,

1418, 1283, 1167, 1088, 959, 842, 754, 687 cm^{-1} ; HRMS (APCI-QE, m/z): $[\text{M}+\text{H}]^+$ Calcd. for

$\text{C}_{16}\text{H}_{13}\text{F}_9\text{O}_4+\text{H}$, 441.0743; found, 441.0744.

4-(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-en-2-yl)benzonitrile (3o)



70.2 mg, 80% yield; white solid, mp: 94-95 °C, eluting with

EtOAc/PE = 1: 10; ^1H NMR (500 MHz, CDCl_3) δ 7.67-7.54 (m,

4H), 5.98 (s, 1H), 5.92 (s, 1H), 3.82 (q, $J = 8.2$ Hz, 6H); ^{13}C

NMR (126 MHz, CDCl_3) δ 139.2, 138.9, 132.3, 127.7, 124.2,

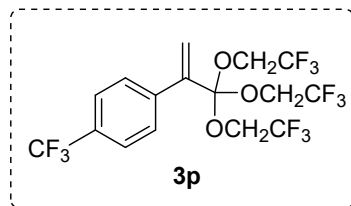
123.1 (q, $^1J_{F-C} = 277.2$ Hz), 118.4, 113.4, 112.6, 60.9 (q, $^2J_{F-C} = 36.5$ Hz); ^{19}F NMR (471 MHz,

CDCl_3) δ -73.7 (s, 9F); IR (KBr): 2967, 2229, 1608, 1421, 1281, 1169, 1092, 960, 848, 752, 688,

555 cm^{-1} ; HRMS (APCI-QE, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{16}\text{H}_{12}\text{F}_9\text{NO}_3+\text{H}$, 438.0746; found,

438.0745.

1-(trifluoromethyl)-4-(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-en-2-yl)benzene (3p)



95.2 mg, 99% yield; yellow oil, eluting with EtOAc/PE = 1: 10;

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.70 (d, $J = 8.3$ Hz, 2H), 7.63 (d,

$J = 8.3$ Hz, 2H), 6.04 (s, 1H), 5.98 (s, 1H), 3.90 (q, $J = 8.2$ Hz,

6H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 139.1, 138.2, 130.9 (q, $^2J_{F-C}$

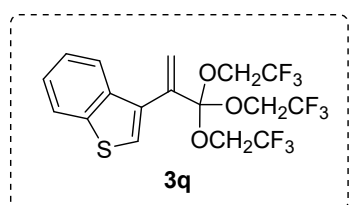
= 37.8 Hz), 127.3, 125.5 (q, $^3J_{F-C} = 3.8$ Hz), 123.9 (q, $^1J_{F-C} = 272.3$ Hz), 123.6, 123.1 (q, $^1J_{F-C} =$

277.2 Hz), 113.6, 60.9 (q, $^2J_{F-C} = 36.5$ Hz); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -63.0 (s, 3F), δ -73.8 (s,

9F); IR (KBr): 2977, 1421, 1329, 1286, 1169, 1078, 1019, 962, 850, 744, 696 cm^{-1} ; HRMS

(APCI-QE, m/z): $[\text{M}]^+$ Calcd. for $\text{C}_{16}\text{H}_{12}\text{F}_{12}\text{O}_3$, 480.0595; found, 480.0602.

3-(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-en-2-yl)benzo[b]thiophene (3q)



64.6 mg, 62% yield; white solid, mp: 63-64 °C, eluting with

EtOAc/PE = 1: 10; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.95 (ddt, $J =$

6.9, 2.8, 1.4 Hz, 2H), 7.75 (s, 1H), 7.53-7.39 (m, 2H), 6.25 (s,

1H), 6.12 (s, 1H), 3.95 (q, $J = 8.3$ Hz, 6H); $^{13}\text{C NMR}$ (101 MHz,

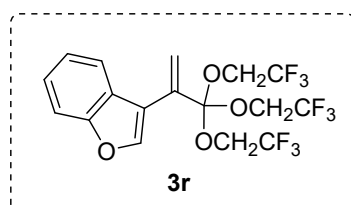
CDCl_3) δ 140.3, 137.5, 134.5, 129.0, 126.0, 124.8, 124.7, 123.4, 123.3 (q, $^1J_{F-C} = 277.8$ Hz), 123.2,

122.2, 113.7, 61.0 (q, $^2J_{F-C} = 36.4$ Hz); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -73.6 (s, 9F); IR (KBr):

2959, 1420, 1283, 1167, 1101, 1072, 961, 855, 741 cm^{-1} ; HRMS (APCI-QE, m/z): $[\text{M}]^+$ Calcd. for

$\text{C}_{17}\text{H}_{13}\text{F}_9\text{O}_3\text{S}$, 468.0442; found, 468.0437.

3-(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-en-2-yl)benzofuran (3r)



83.4 mg, 97% yield; yellow oil, eluting with EtOAc/PE = 1: 10;

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.60 (d, $J = 7.8$ Hz, 1H), 7.47 (d,

$J = 8.2$ Hz, 1H), 7.34 (t, $J = 7.8$ Hz, 1H), 7.24 (t, $J = 7.5$ Hz,

1H), 7.11 (s, 1H), 6.47 (s, 1H), 6.05 (s, 1H), 3.90 (q, $J = 8.2$ Hz,

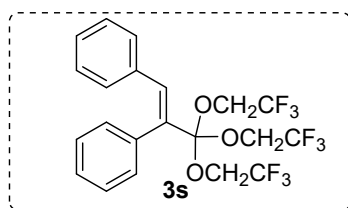
6H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 154.7, 149.3, 130.5, 128.7, 125.8, 123.3, 123.2 (q, $^1J_{F-C} =$

277.2 Hz), 122.1, 121.3, 112.7, 111.0, 106.8, 60.9 (q, $^2J_{F-C} = 36.5$ Hz); $^{19}\text{F NMR}$ (471 MHz,

CDCl_3) δ -73.7 (s, 9F); IR (KBr): 1627, 1421, 1285, 1169, 1100, 1019, 959, 851, 752, 689 cm^{-1} ;

HRMS (APCI-QE, m/z): $[\text{M}]^+$ Calcd. for $\text{C}_{17}\text{H}_{13}\text{F}_9\text{O}_4$, 452.0670; found, 452.0675.

(E)-(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-ene-1,2-diyl)dibenzene (3s)



73.9 mg, 76% yield; yellow oil, eluting with EtOAc/PE = 1: 10;

^1H NMR (500 MHz, CDCl_3) δ 7.33 (dd, $J = 5.1, 2.1$ Hz, 3H),

7.24-7.13 (m, 5H), 7.08 (s, 1H), 7.02-6.97 (m, 2H), 3.99 (q, $J =$

8.3 Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 134.4, 134.2, 134.0,

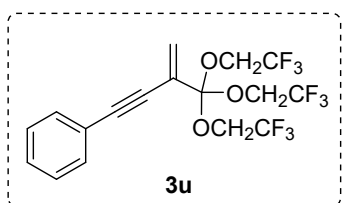
132.8, 130.0, 129.6, 128.8, 128.5, 128.4, 128.3, 123.3 (q, $^1J_{F-C} = 277.2$ Hz), 114.1, 61.0 (q, $^2J_{F-C} =$

36.5 Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -73.6 (s, 9F), IR (KBr): 2921, 1419, 1285, 1231, 1167,

964, 850, 755, 702 cm^{-1} ; HRMS (APCI-QE, m/z): $[\text{M}]^+$ Calcd. for $\text{C}_{21}\text{H}_{17}\text{F}_9\text{O}_3$, 488.1034; found,

488.1039.

(3-(tris(2,2,2-trifluoroethoxy)methyl)but-3-en-1-yn-1-yl)benzene (3u)



54.7 mg, 62% yield; yellow solid, mp: 46-47 °C, eluting with PE;

^1H NMR (500 MHz, CDCl_3) δ 7.50-7.42 (m, 2H), 7.36 (d, $J = 7.3$

Hz, 3H), 6.13 (s, 1H), 6.01 (s, 1H), 4.06 (q, $J = 8.3$ Hz, 6H); ^{13}C

NMR (126 MHz, CDCl_3) δ 131.7, 129.3, 128.8, 128.5, 125.4,

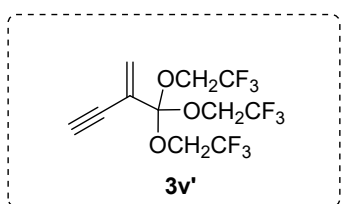
123.3 (q, $^1J_{F-C} = 277.2$ Hz), 121.8, 111.9, 92.9, 83.6, 61.3 (q, $^2J_{F-C} = 36.5$ Hz); ^{19}F NMR (471

MHz, CDCl_3) δ -73.9 (s, 9F), IR (KBr): 2919, 1649, 1421, 1287, 1172, 1113, 961, 851, 756, 690,

642 cm^{-1} ; HRMS (APCI-QE, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{17}\text{H}_{13}\text{F}_9\text{O}_3+\text{H}$, 437.0794; found,

437.0795.

2-(tris(2,2,2-trifluoroethoxy)methyl)but-1-en-3-yne (3v')



51.4 mg, 70% yield; yellow oil, eluting with EtOAc/PE = 1: 10;

^1H NMR (500 MHz, CDCl_3) δ 6.17 (s, 1H), 6.04 (s, 1H), 4.01 (q,

$J = 8.3$ Hz, 6H), 3.10 (s, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ

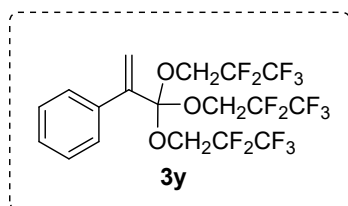
131.1, 124.7, 123.2 (q, $^1J_{F-C} = 277.2$ Hz), 111.6, 81.2, 78.1, 61.3

(q, $^2J_{F-C} = 36.5$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -74.0 (s, 9F), IR (KBr): 2979, 2890, 2318,

1763, 1425, 1289, 1184, 963, 755, 688, 755, 688, 443 cm^{-1} ; HRMS (APCI-QE, m/z): $[\text{M}-\text{H}]^-$

Calcd. for $\text{C}_{11}\text{H}_9\text{F}_9\text{O}_3-\text{H}$, 359.0335; found, 359.0335.

(3,3,3-tris(2,2,3,3,3-pentafluoropropoxy)prop-1-en-2-yl)benzene (3y)



103.6 mg, 71% yield; yellow oil, eluting with EtOAc/PE = 1: 10;

^1H NMR (500 MHz, CDCl_3) δ 7.53 (dd, $J = 6.4, 3.1$ Hz, 2H),

7.40-7.31 (m, 3H), 5.95 (s, 1H), 5.83 (s, 1H), 3.93 (t, $J = 12.8$

Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 139.8, 134.6, 128.9,

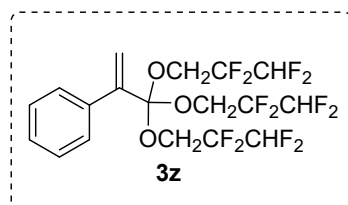
128.6, 126.9, 122.0, 118.4 (qt, $J = 286.0$ Hz, $J = 35.3$ Hz), 113.9, 112.4 (tq, $J = 254.5$ Hz, $J = 37.8$

Hz), 59.8 (t, $J = 27.7$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -83.8 (s, 3F), δ -123.4 (s, 2F); IR (KBr):

2962, 1363, 1206, 1110, 1057, 945, 755, 521 cm^{-1} ; HRMS (APCI-QE, m/z): $[\text{M}+\text{H}]^+$ Calcd. for

$\text{C}_{18}\text{H}_{13}\text{F}_{15}\text{O}_3+\text{H}$, 563.0698; found, 563.0695.

(3,3,3-tris(2,2,3,3-tetrafluoropropoxy)prop-1-en-2-yl)benzene (3z)



81.8 mg, 77% yield; colorless oil, eluting with EtOAc/PE = 1:

10; ^1H NMR (500 MHz, CDCl_3) δ 7.45-7.40 (m, 2H), 7.30-7.26

(m, 3H), 5.87-5.60 (m, 5H), 3.79 (t, $J = 12.5$ Hz, 6H); ^{13}C NMR

(126 MHz, CDCl_3) δ 140.0, 135.0, 128.9, 128.5, 126.9, 122.1,

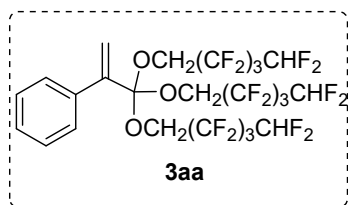
114.5 (tt, $J = 249.5$ Hz, $J = 27.7$ Hz), 113.8, 109.1 (tt, $J = 250.7$ Hz, $J = 35.3$ Hz), 60.0 (t, $J = 30.2$

Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -124.0 (t, $J = 3.7$ Hz, 2F), -138.4 --138.4 (m, 2F); IR (KBr):

2962, 1409, 1179, 1107, 943, 837, 779, 702, 546 cm^{-1} ; HRMS (APCI-QE, m/z): $[\text{M}-\text{H}]^-$ Calcd. for

$\text{C}_{18}\text{H}_{16}\text{F}_{12}\text{O}_3-\text{H}$, 507.0835; found, 507.0832.

(3,3,3-tris((2,2,3,3,4,4,5,5-octafluoropentyl)oxy)prop-1-en-2-yl)benzene (3aa)



94.6 mg, 57% yield; yellow oil, eluting with EtOAc/PE = 1: 10;

^1H NMR (500 MHz, CDCl_3) δ 7.45 (dd, $J = 6.8, 3.0$ Hz, 2H),

7.31-7.24 (m, 3H), 6.06-5.72 (m, 5H), 3.91 (t, $J = 13.6$ Hz, 6H);

^{13}C NMR (126 MHz, CDCl_3) δ 139.0, 133.8, 127.9, 127.5, 126.0,

121.1, 113.1, 116.2-104.3 (complex signal, 4C), 59.0 (t, $J = 26.5$ Hz); ^{19}F NMR (471 MHz, CDCl_3)

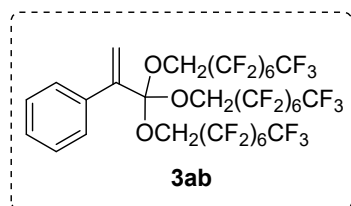
δ -119.7 (t, $J = 10.8$ Hz, 2F), -125.3 (d, $J = 8.8$ Hz, 2F), -130.2 (d, $J = 6.0$ Hz, 2F), -137.4 (d, $J =$

8.4 Hz, 2F); IR (KBr): 2967, 1405, 1266, 1174, 1126, 904, 756, 539 cm^{-1} ; HRMS (APCI-QE,

m/z): $[\text{M}-\text{H}]^-$ Calcd. for $\text{C}_{24}\text{H}_{16}\text{F}_{24}\text{O}_3-\text{H}$, 807.0643; found, 807.0648.

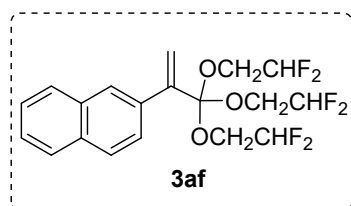
(3,3,3-tris((2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)oxy)prop-1-en-2-yl)benzene

(3ab)



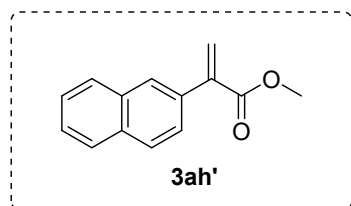
186.2 mg, 68% yield; colorless oil, eluting with EtOAc/PE = 1: 10; ¹H NMR (500 MHz, CDCl₃) δ 7.52 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.39-7.28 (m, 3H), 5.93 (s, 1H), 5.82 (s, 1H), 3.99 (t, *J* = 13.3 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 140.0, 134.7, 128.9, 128.5, 127.0, 121.8, 114.1, 118.3-108.2 (complex signal, 7C), 60.2 (t, *J* = 26.5 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -81.2 (t, *J* = 10.0 Hz, 3F), -119.6 (t, *J* = 13.2 Hz, 2F), -122.2--122.3 (m, 4F), -122.9--123.0 (m, 2F), -123.4--123.5 (m, 2F), -126.3--126.4 (m, 2F); IR (KBr): 2964, 2905, 2430, 1895, 1458, 1407, 1205, 1026, 953, 890, 784, 710, 650, 568, 529 cm⁻¹; HRMS (APCI-QE, *m/z*): [M+H]⁺ Calcd. for C₃₃H₁₃F₄₅O₃+H, 1313.0219; found, 1313.0214.

2-(3,3,3-tris(2,2-difluoroethoxy)prop-1-en-2-yl)naphthalene (3af)



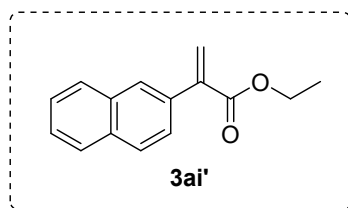
78.0 mg, 96% yield; yellow oil, yellow oil, eluting with EtOAc/PE = 1: 20; ¹H NMR (500 MHz, CDCl₃) δ 8.04 (d, *J* = 1.9 Hz, 1H), 7.82-7.67 (m, 3H), 7.59 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.41 (dt, *J* = 6.3, 3.5 Hz, 2H), 5.97 (s, 1H), 5.90 (s, 1H), 5.76 (tt, *J* = 55.1, 4.0 Hz, 3H), 3.65 (td, *J* = 13.8, 4.0 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 140.6, 133.2, 133.2, 132.7, 128.6, 128.2, 127.5, 126.7, 126.5, 126.4, 124.6, 122.4, 114.0, 113.6 (t, ¹*J*_{F-C} = 240.7 Hz), 62.2 (t, ²*J*_{F-C} = 29.0 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -125.0 (s, 6F); IR (KBr): 2986, 1629, 1419, 1267, 1085, 940, 900, 822, 755, 478 cm⁻¹; HRMS (APCI-QE, *m/z*): [M+H]⁺ Calcd. for C₁₉H₁₈F₆O₃+H, 409.1233; found, 409.1237.

methyl 2-(naphthalen-2-yl)acrylate (3ah')⁵



28.5 mg, 67% yield; yellow oil, eluting with EtOAc/PE = 1: 20; ¹H NMR (500 MHz, CDCl₃) δ 7.86-7.79 (m, 1H), 7.79-7.70 (m, 3H), 7.47-7.36 (m, 3H), 6.36 (d, *J* = 1.3 Hz, 1H), 5.93 (d, *J* = 1.2 Hz, 1H), 3.77 (s, 3H).

ethyl 2-(naphthalen-2-yl)acrylate (**3ai'**)⁶

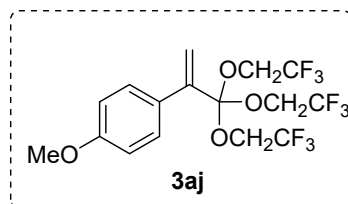


43.9 mg, 95% yield; yellow oil, eluting with EtOAc/PE = 1: 20;

¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, *J* = 1.9 Hz, 1H), 7.74 (td, *J* = 8.8, 4.7 Hz, 3H), 7.44 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.41-7.34 (m, 2H), 6.33 (d, *J* = 1.4 Hz, 1H), 5.91 (d, *J* = 1.4 Hz, 1H), 4.31-

4.17 (m, 2H), 1.25 (td, *J* = 7.1, 1.5 Hz, 3H).

1-methoxy-4-(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-en-2-yl)benzene (**3aj**)

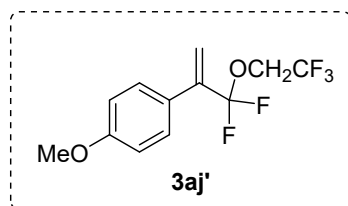


25.2 mg, 25% yield; yellow oil, eluting with PE; ¹H NMR (500

MHz, CDCl₃) δ 7.47 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 5.83 (s, 1H), 5.76 (s, 1H), 3.79 (m, 9H); ¹³C NMR (126

MHz, CDCl₃) δ 160.2, 139.0, 128.1, 126.7, 123.3 (q, ¹*J*_{F-C} = 277.2 Hz), 120.5, 114.0, 113.9, 60.8 (q, ²*J*_{F-C} = 36.5 Hz), 55.3; ¹⁹F NMR (376 MHz, CDCl₃) δ -73.7 (s, 9F); IR (KBr): 2920, 1642, 1389, 1271, 1170, 1095, 755 cm⁻¹; HRMS (APCI-QE, m/z): [M]⁺ Calcd. for C₁₆H₁₅F₉O₄, 442.0827; found, 442.0822.

1-(3,3-difluoro-3-(2,2,2-trifluoroethoxy)prop-1-en-2-yl)-4-methoxybenzene (**3aj'**)

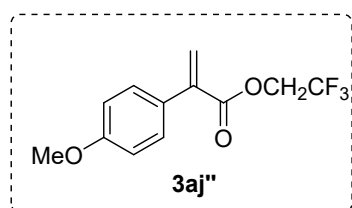


4.1 mg, 6% yield; yellow oil, eluting with PE; ¹H NMR (500

MHz, CDCl₃) δ 7.38-7.27 (m, 2H), 6.88-6.73 (m, 2H), 5.76 (d, *J* = 1.3 Hz, 1H), 5.54 (t, *J* = 1.6 Hz, 1H), 4.21 (q, *J* = 8.2 Hz, 2H), 3.74 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 159.9, 139.9 (t, ²*J*_{F-C}

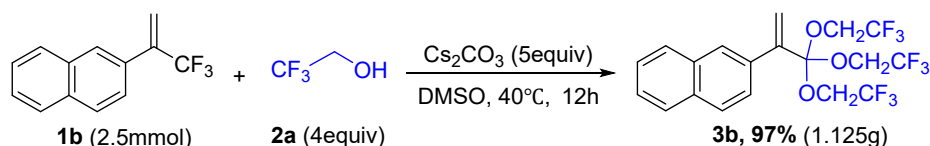
= 29.0 Hz), 128.8, 127.2, 122.8 (q, ¹*J*_{F-C} = 277.2 Hz), 121.9 (t, ¹*J*_{F-C} = 264.6 Hz), 118.5 (t, ³*J*_{F-C} = 6.3 Hz), 113.7, 60.8 (qt, *J* = 36.5 Hz, 6.3 Hz), 55.3; ¹⁹F NMR (471 MHz, CDCl₃) δ -72.5 (s, 2F), -74.2 (s, 3F); ¹IR (KBr): 2922, 2855, 1611, 1516, 1427, 1291, 1174, 1041, 952, 837, 752, 655, 534 cm⁻¹; HRMS (APCI-QE, m/z): [M+H]⁺ Calcd. for C₁₂H₁₂F₅O₂+H, 283.0752; found, 283.0746.

2,2,2-trifluoroethyl 2-(4-methoxyphenyl)acrylate (**3aj''**)



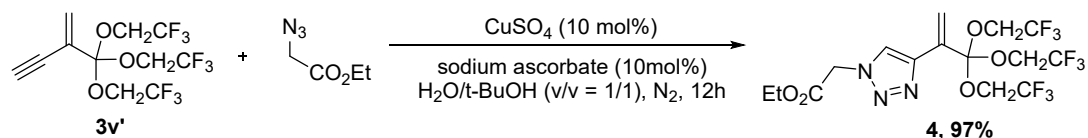
24.0 mg, 46% yield; yellow oil, eluting with PE; ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, $J = 8.9$ Hz, 2H), 6.93 (d, $J = 8.8$ Hz, 2H), 6.42 (d, $J = 0.9$ Hz, 1H), 6.01 (d, $J = 0.9$ Hz, 1H), 4.63 (q, $J = 8.4$ Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 165.2, 159.9, 139.1, 129.5, 128.3, 127.4, 123.0 (q, $^1J_{\text{F-C}} = 277.2$ Hz), 113.7, 60.8 (q, $^2J_{\text{F-C}} = 36.5$ Hz), 55.3; ^{19}F NMR (376 MHz, CDCl_3) δ -73.6 (s, 3F); IR (KBr): 1738, 1608, 1511, 1408, 1284, 1164, 1092, 1032, 966, 914, 833, 743, 659 cm^{-1} ; HRMS (APCI-QE, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{12}\text{H}_{11}\text{F}_3\text{O}_3+\text{H}$, 261.0733; found, 261.0729.

5) General Procedure for Gram-Scale Synthesis



To a 100 mL Schlenk flask was charged with alkenes **1b** (2.5 mmol, 1.0 equiv), fluoroalkylated alcohols (10 mmol, 4.0 equiv), Cs_2CO_3 (12.5 mmol, 5.0 equiv) and a solvent of DMSO (25 mL). The resulting solution was stirred at 40 °C for 12 h. Upon completion of the reaction, H_2O (50 mL) was added, and extracted with EtOAc (50 mL \times 3). The combined organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel to afford fluoroalkylated orthoester product **3b** (97% yield, 1.125 g).

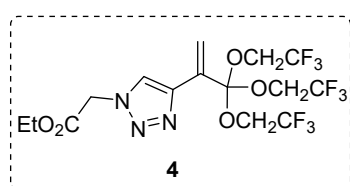
6) General Procedure for Further Derivatization of the Obtained Fluoroalkylated orthoesters



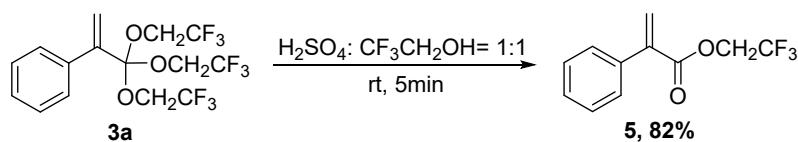
A 25 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, **3v'** (72.0 mg, 0.2 mmol) and azidoacetic acid ethyl ester (51.6 mg, 0.4 mmol) were dissolved in 2 mL of a 1:1 water/tert-butanol mixture. Sodium ascorbate (4.0 mg, 0.02 mmol, 200 μL of freshly prepared 0.1 M solution in water) and copper(II) sulfate pentahydrate (3.2 mg, 0.02 mmol, 200 μL of freshly

prepared 0.1 M solution in water) were added. The mixture was vigorously stirred at 60 °C for 12 h. Then the mixture was stopped stirring, added water (15 mL), extracted with EtOAc (15 mL × 3). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 1:5) provided product **4** in 97% isolated yield.

ethyl 2-(4-(3,3,3-tris(2,2,2-trifluoroethoxy)prop-1-en-2-yl)-1H-1,2,3-triazol-1-yl)acetate (4)

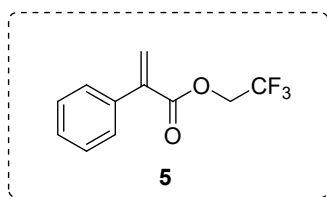


109.1 mg, 97% yield; colorless oil, eluting with PE; ¹H NMR (500 MHz, CDCl₃) δ 7.87 (s, 1H), 6.77 (s, 1H), 6.00 (s, 1H), 5.18 (s, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.87 (q, *J* = 8.3 Hz, 6H), 1.28 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 165.8, 141.0, 129.9, 123.6, 123.1 (q, ¹*J*_{F-C} = 277.2 Hz), 121.6, 113.1, 62.5, 60.8 (q, ²*J*_{F-C} = 36.5 Hz), 51.0, 13.9; ¹⁹F NMR (471 MHz, CDCl₃) δ -73.8 (s, 9F); IR (KBr): 2975, 1751, 1424, 1286, 1172, 1096, 960, 855, 749, 692, 620 cm⁻¹; HRMS (APCI-QE, *m/z*): [M+H]⁺ Calcd. for C₁₅H₁₆F₉N₃O₅+H, 490.1019; found, 490.1019.



3a (82.5 mg, 0.2 mmol) was added into a 10 mL Schlenk tube. Then 2.5 mL ethyl acetate and 2.5 ml 2,2,2-Trifluoroethanol were added. Then H₂SO₄ solution (2.5 ml) was added. The mixture was stirred for 5 min. The combined organic layers were washed with saturated NaHCO₃ and brine, dried over anhydrous Na₂SO₄, filtered and concentrated to give the **5**. The residue was purified by flash column chromatography over silica gel using petroleum ether/ethyl acetate (1:10), providing product **5** in 82% isolated yield.

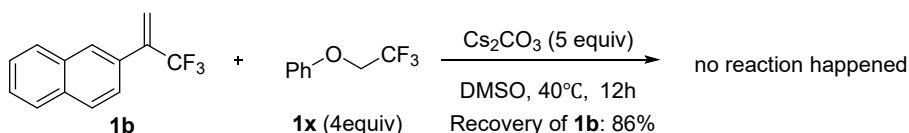
2,2,2-trifluoroethyl 2-phenylacrylate (5)⁷



37.5 mg, 82% yield; yellow oil, eluting with PE; ^1H NMR (500 MHz, CDCl_3) δ 7.49-7.33 (m, 5H), 6.48 (s, 1H), 6.04 (s, 1H), 4.61 (q, $J = 8.4$ Hz, 2H); ^{19}F NMR (471 MHz, CDCl_3) δ -73.6 (s, 9F).

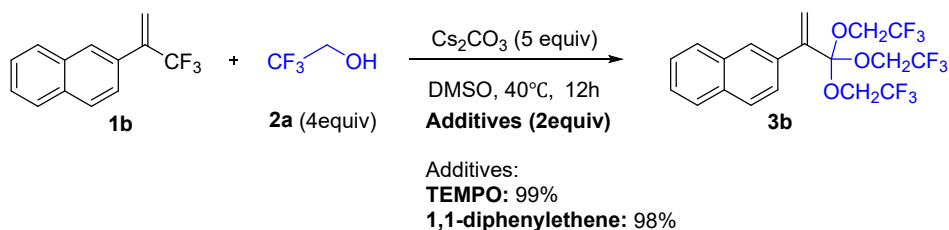
7) Control Experiments

To a 25 mL Schlenk flask was charged with alkenes **1b** (0.2 mmol, 1.0 equiv), **1x** (0.8 mmol, 4.0 equiv), Cs_2CO_3 (1.0 mmol, 5.0 equiv), and a solvent of DMSO (2.0 mL). The resulting solution was stirred at 40 °C for 12 h. Then the mixture was cooled to room temperature, quenched with H_2O (15 mL), extracted with EtOAc (15 mL \times 3). The combined organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated in vacuo. The yield was determined by ^{19}F NMR spectroscopy of the crude product.



Typical Procedure for Radical Trapping Experiment:

To a 25 mL Schlenk flask was charged with alkenes **1b** (0.2 mmol, 1.0 equiv), fluoroalkylated alcohols (0.8 mmol, 4.0 equiv), Cs_2CO_3 (1.0 mmol, 5.0 equiv), **additives** (0.4 mmol, 2.0 equiv) and a solvent of DMSO (2.0 mL). The resulting solution was stirred at 40 °C for 12 h. Then the mixture was cooled to room temperature, quenched with H_2O (15 mL), extracted with EtOAc (15 mL \times 3). The combined organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated in vacuo. Further purification by flash column chromatography on silica gel provided the products **3b**.



The reaction between **1a** and **2a** in $\text{DMSO}-d_6$ monitored by ^{19}F NMR:

To an oven-dried NMR tube was added **1a** (0.06 mmol, 1.0 equiv), **2a** (0.22 mmol, 4.0 equiv), Cs₂CO₃ (0.28 mmol, 5.0 equiv), and a solvent of DMSO-*d*₆ (0.55 mL). The resulting solution was stirred at room temperature. Then the reaction mixture was monitored by ¹⁹F NMR in different time. We tried different reaction concentrations, and this is the best set of spectra we have ever had. However, the peaks of **3a**⁷⁸ were not detected.

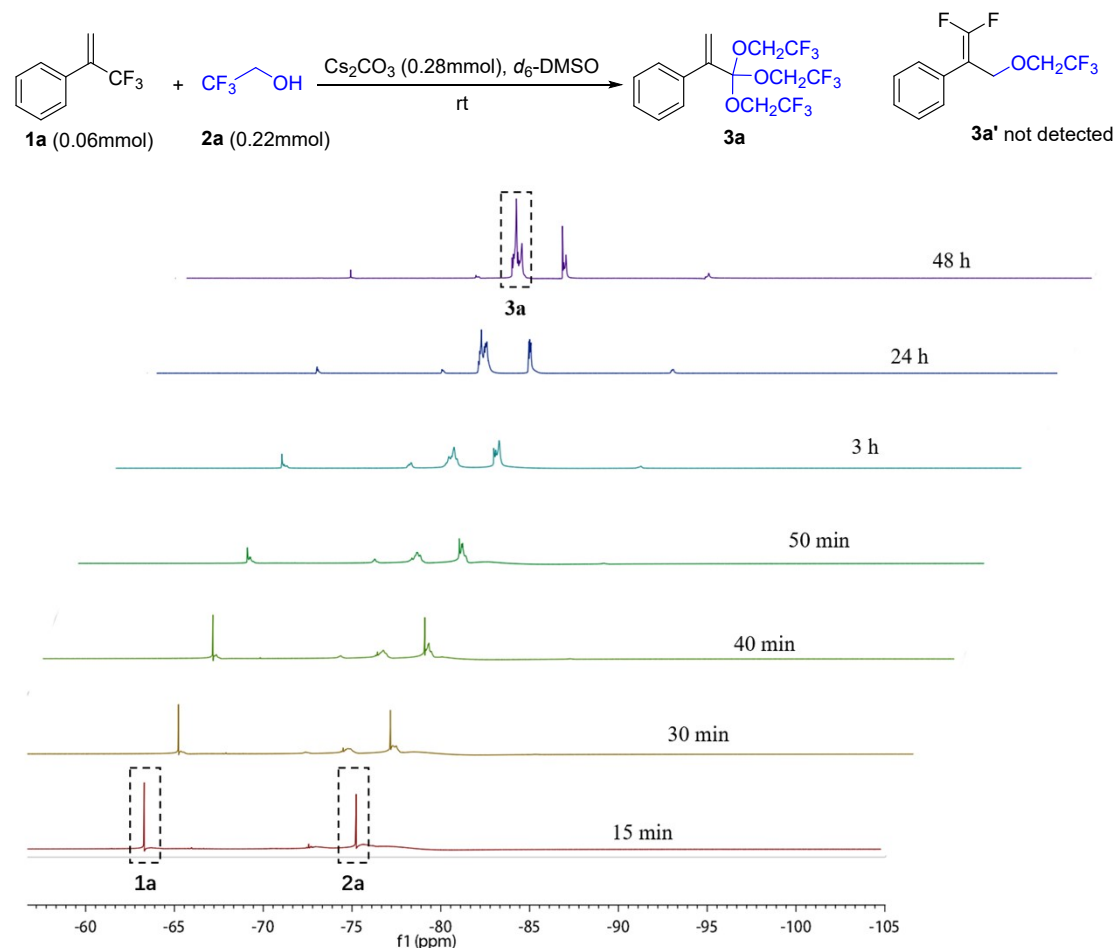


Figure 1

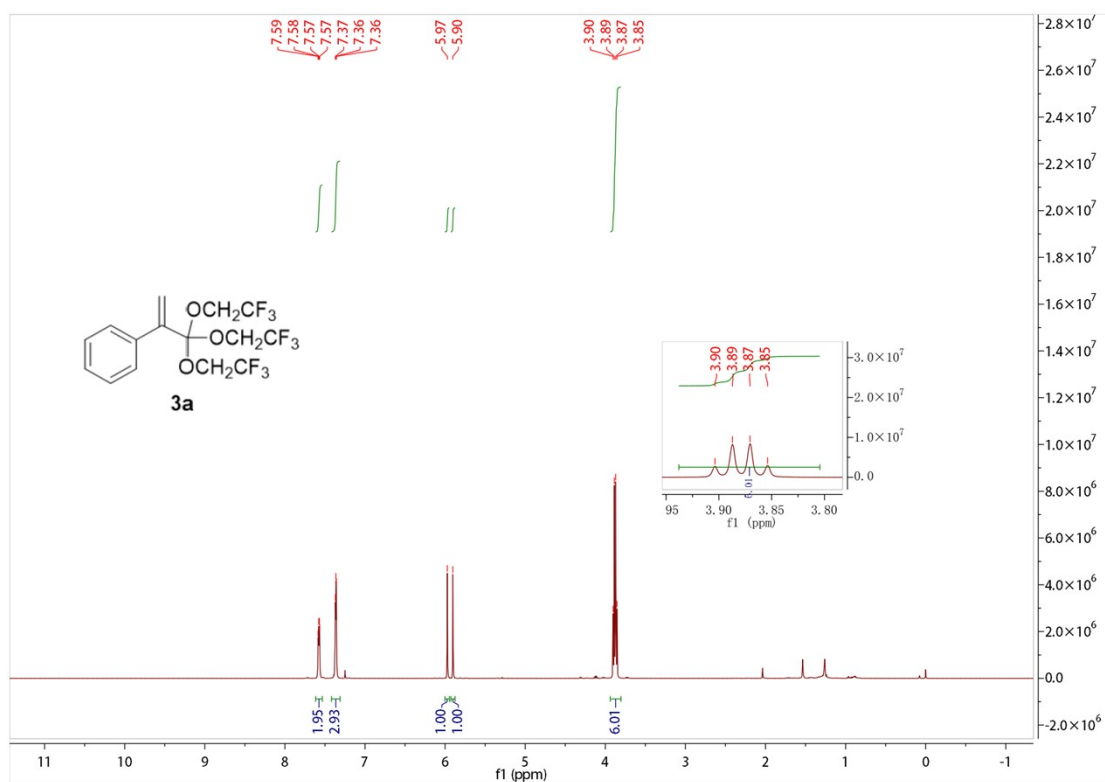
C. References

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- [2] Zhang, C. X.; Li, D.; Zhao, Y. L.; Zhao, J. F.; Qu, J. P.; and Zhou, Y. H. *ChemistrySelect.* 2020, **5**, 13099-13102.
- [3] Chen, S. J.; Zhang, J. H.; Yang, M. F.; Liu, F. G.; Xie, Z. P.; Liu, Y. L.; Lin, W. X.; Wang, D. R.; Li, X. R.; and Wang, J. H. *Chem. Commun.* 2019, **55**, 3879-3882.
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- [5] Kohsaka, Y.; Yamaguchi, E.; and Kitayama, T. *Polymer Chemistry.* 2014, **52**, 2806-2814.
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- [7] Dai, D. T.; Xu, J. L.; Chen, Z. Y.; Wang, Z. L.; Xu, Y. H. *Org. Lett.* 2021, **23**, 1898-1903.

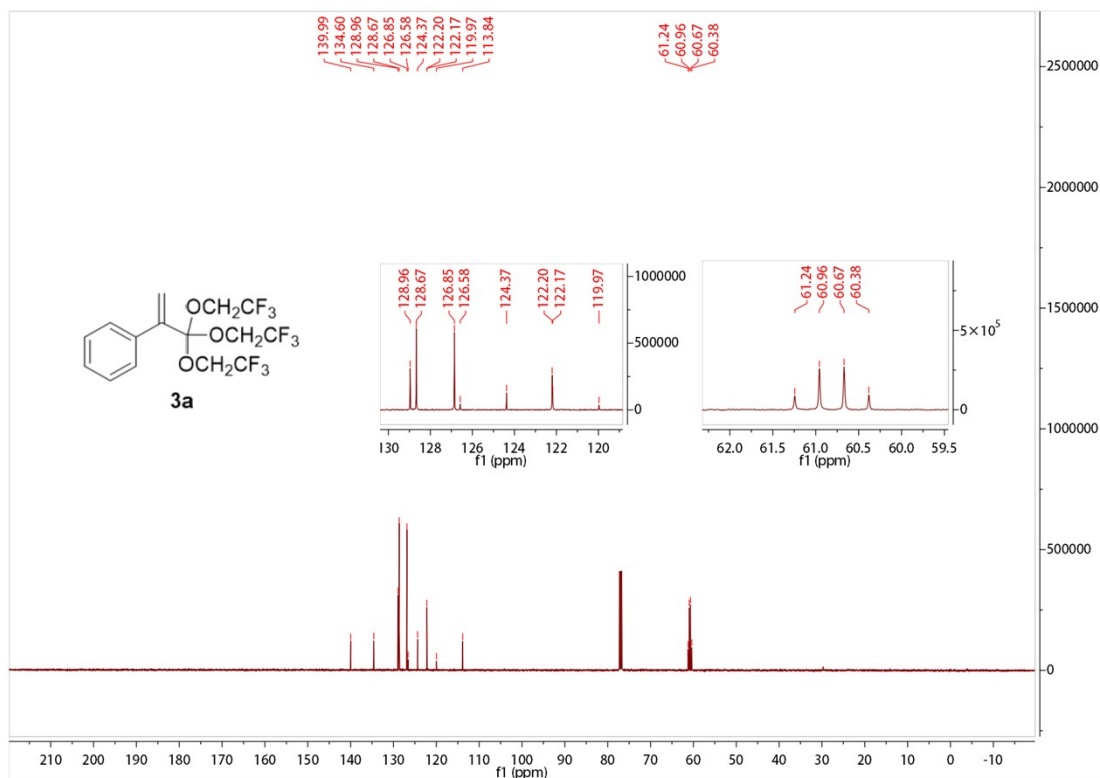
[8] Cai, Y. Y.; Zeng, H.; Zhu, C. L.; Liu, C.; Liu, G. Y.; and Jiang, H. F. *Org. Chem. Front.* 2020, 7, 1260-1265.

D. NMR Spectra of Compounds

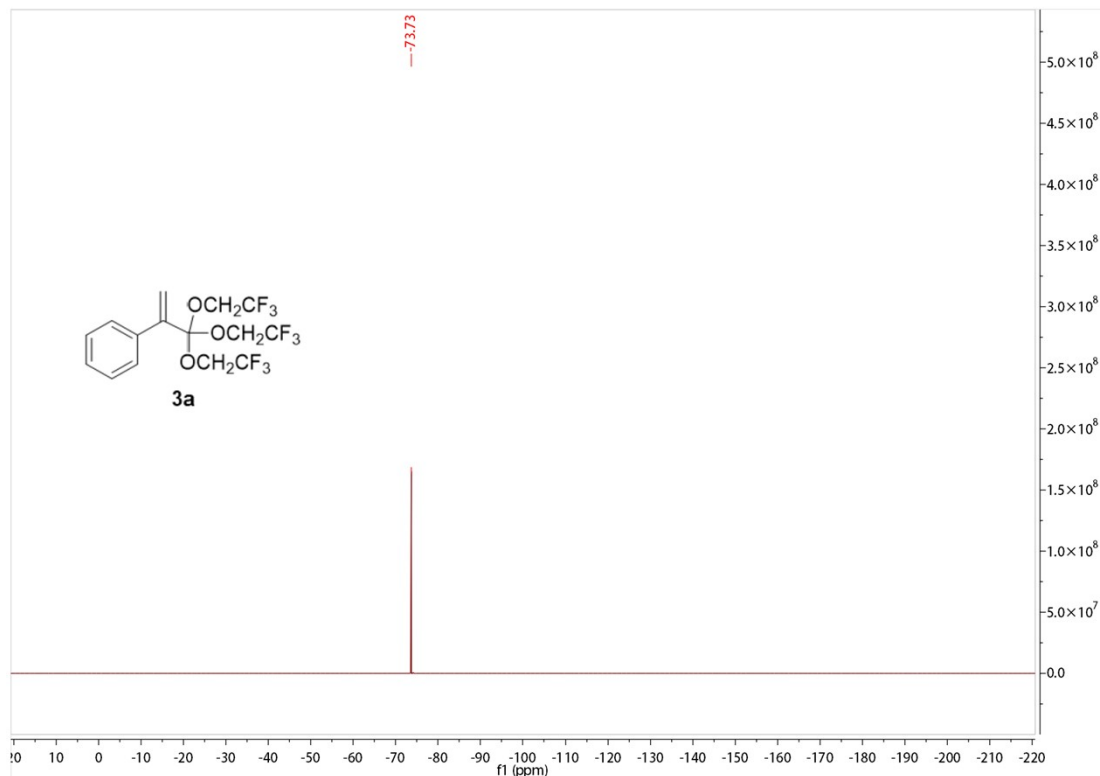
¹H NMR (500 MHz, CDCl₃) spectrum for 3a



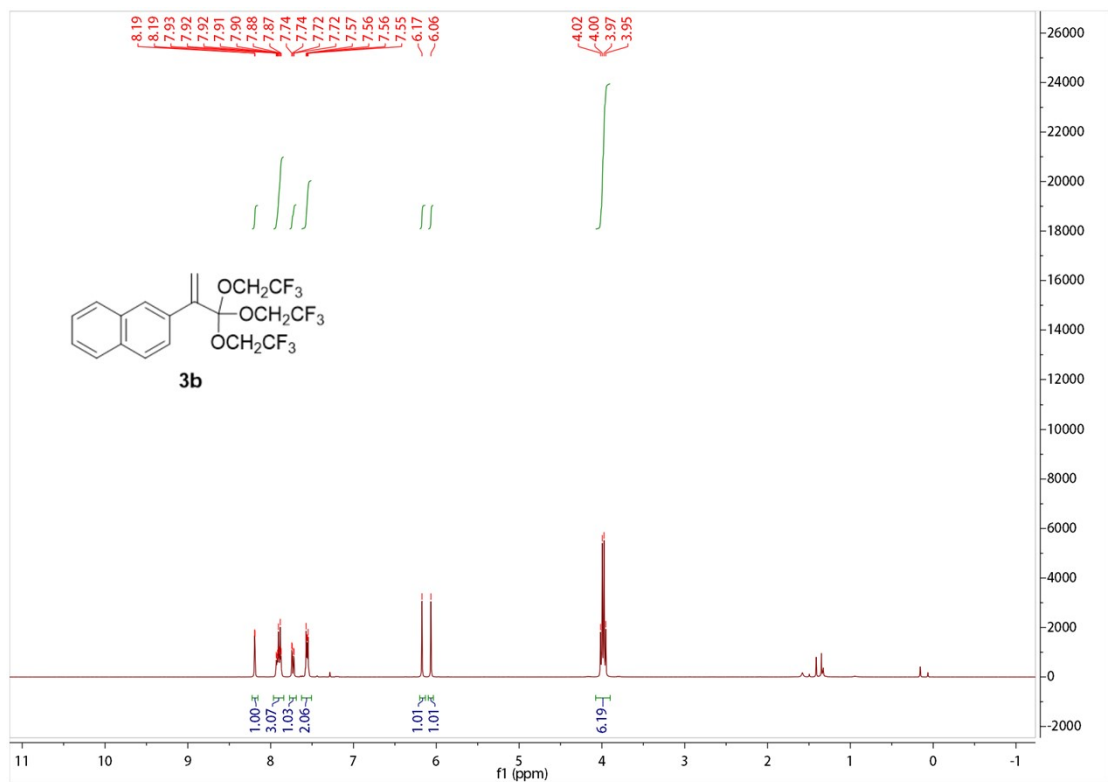
¹³C NMR (126 MHz, CDCl₃) spectrum for 3a



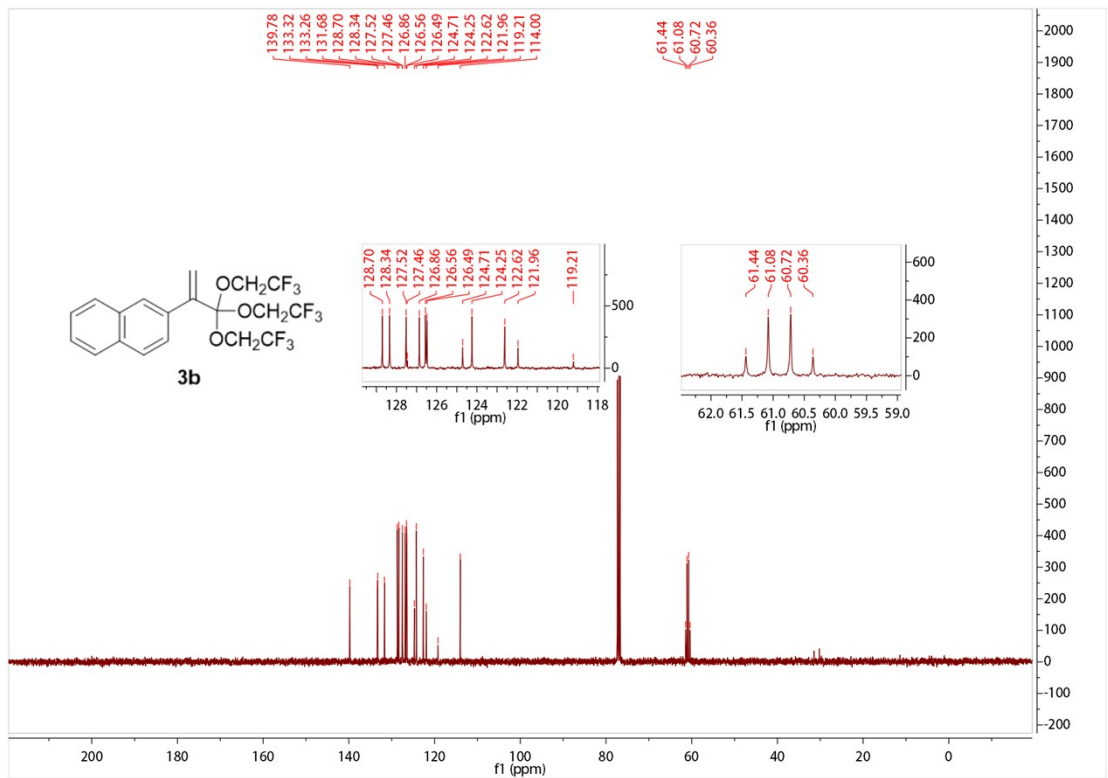
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3a



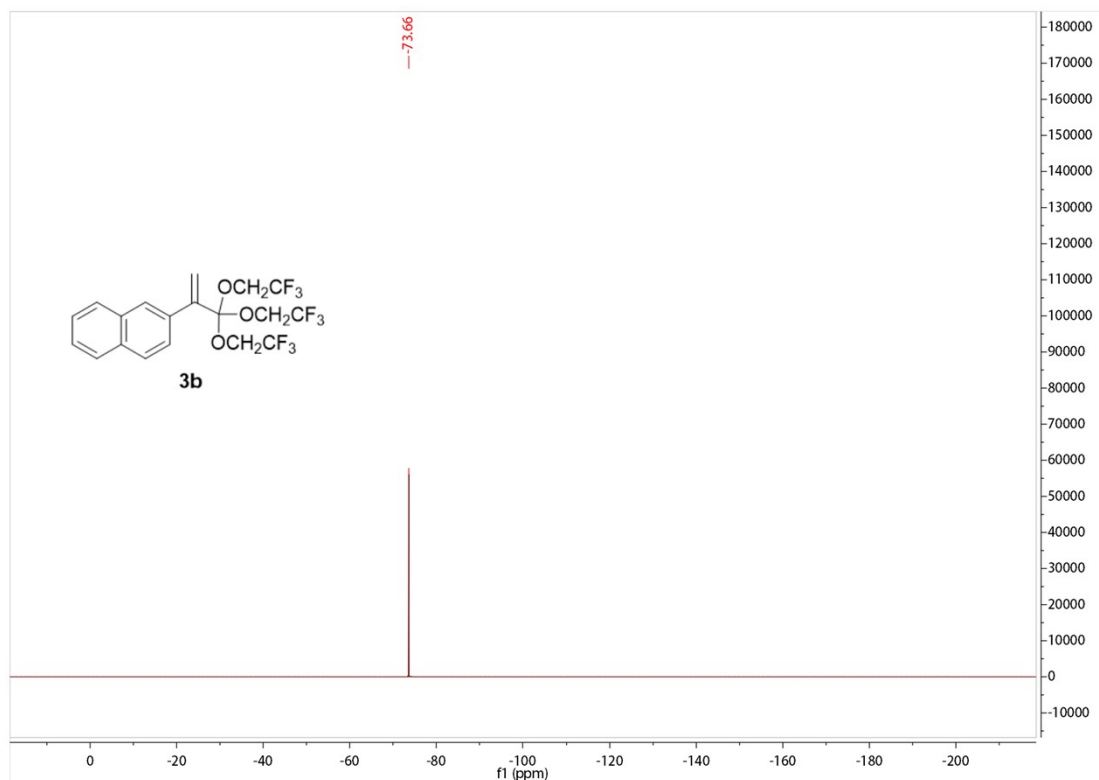
¹H NMR (400 MHz, CDCl₃) spectrum for 3b



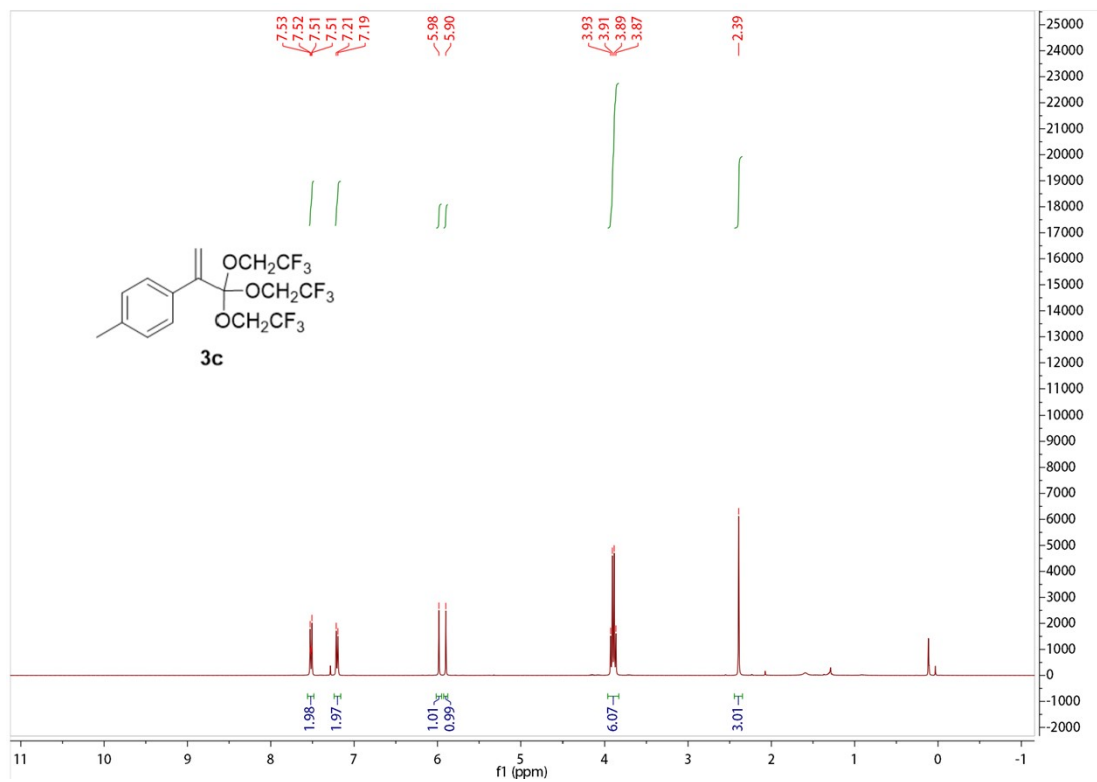
¹³C NMR (101 MHz, CDCl₃) spectrum for 3b



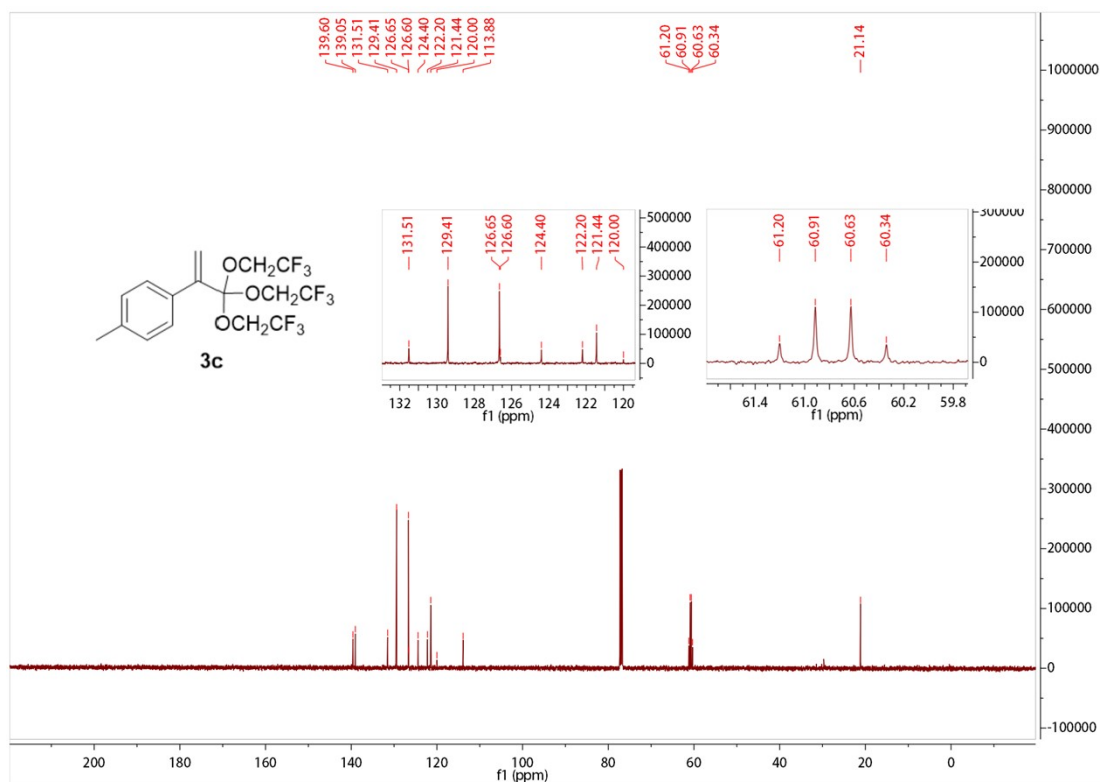
¹⁹F NMR (376 MHz, CDCl₃) spectrum for 3b



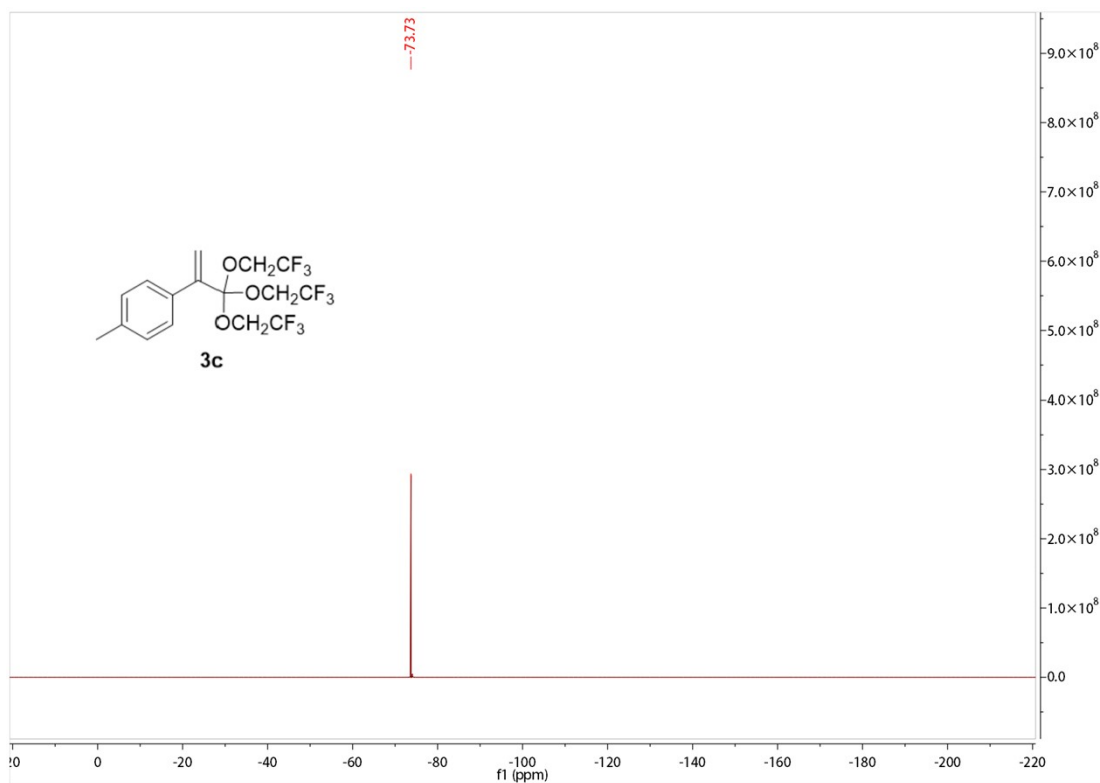
^1H NMR (400 MHz, CDCl_3) spectrum for **3c**



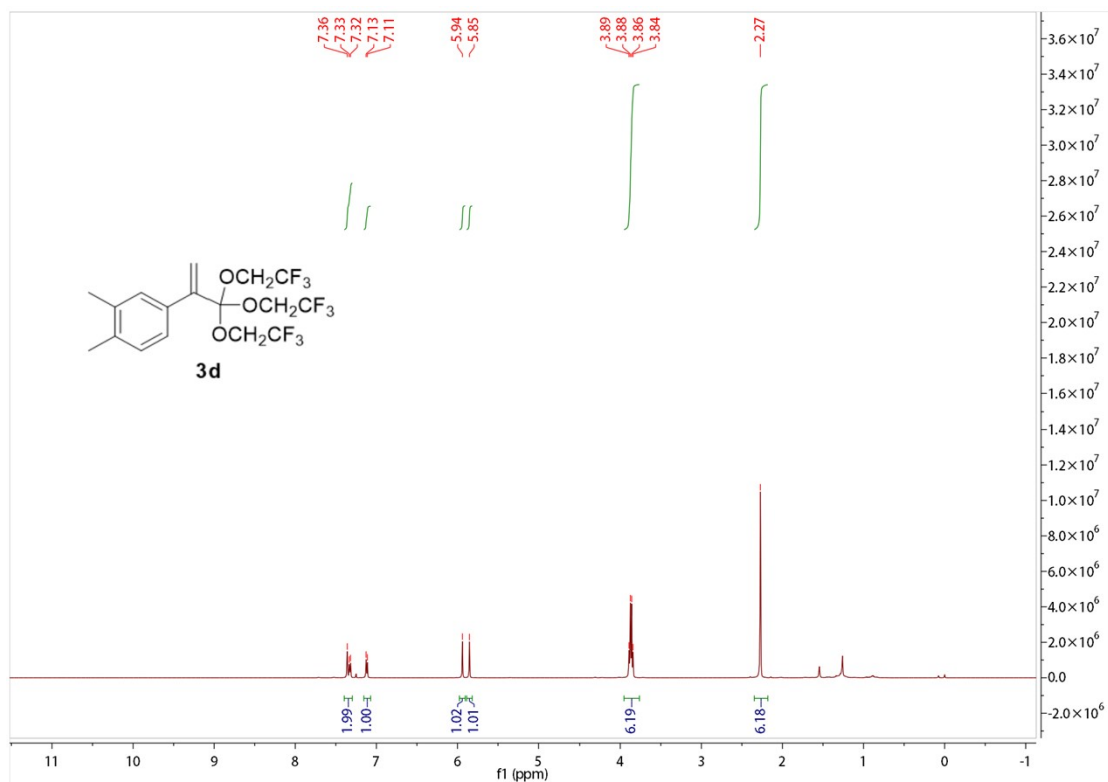
^{13}C NMR (126 MHz, CDCl_3) spectrum for **3c**



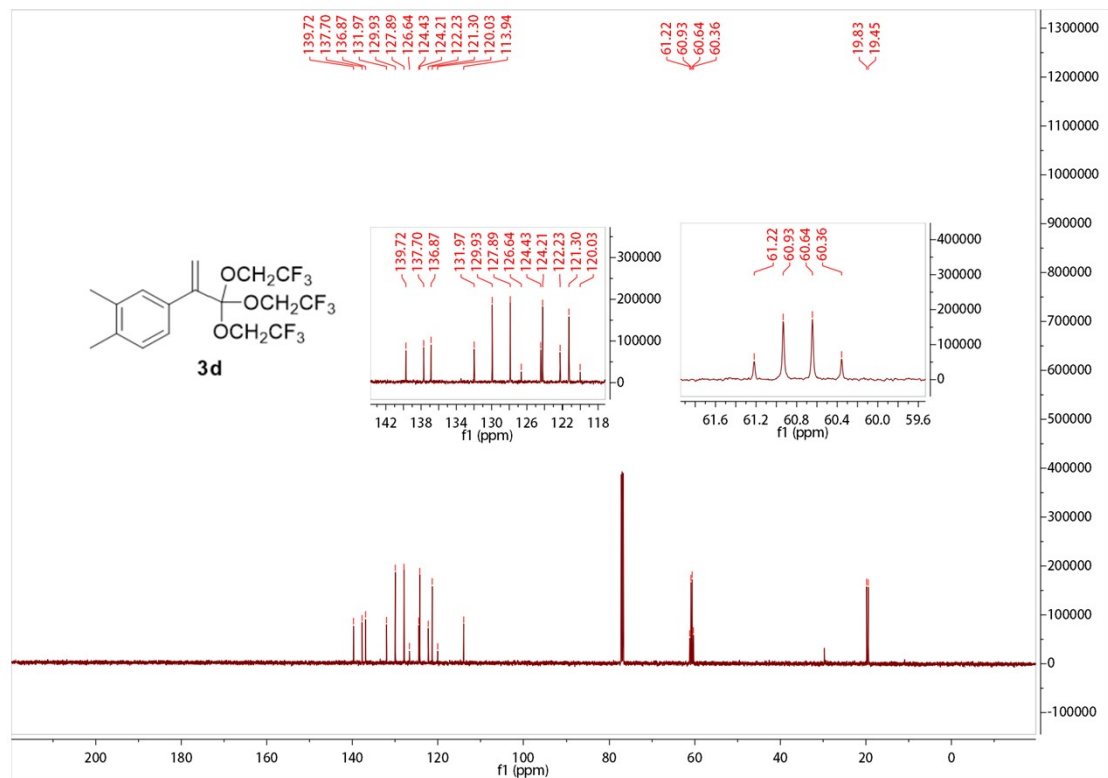
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3c



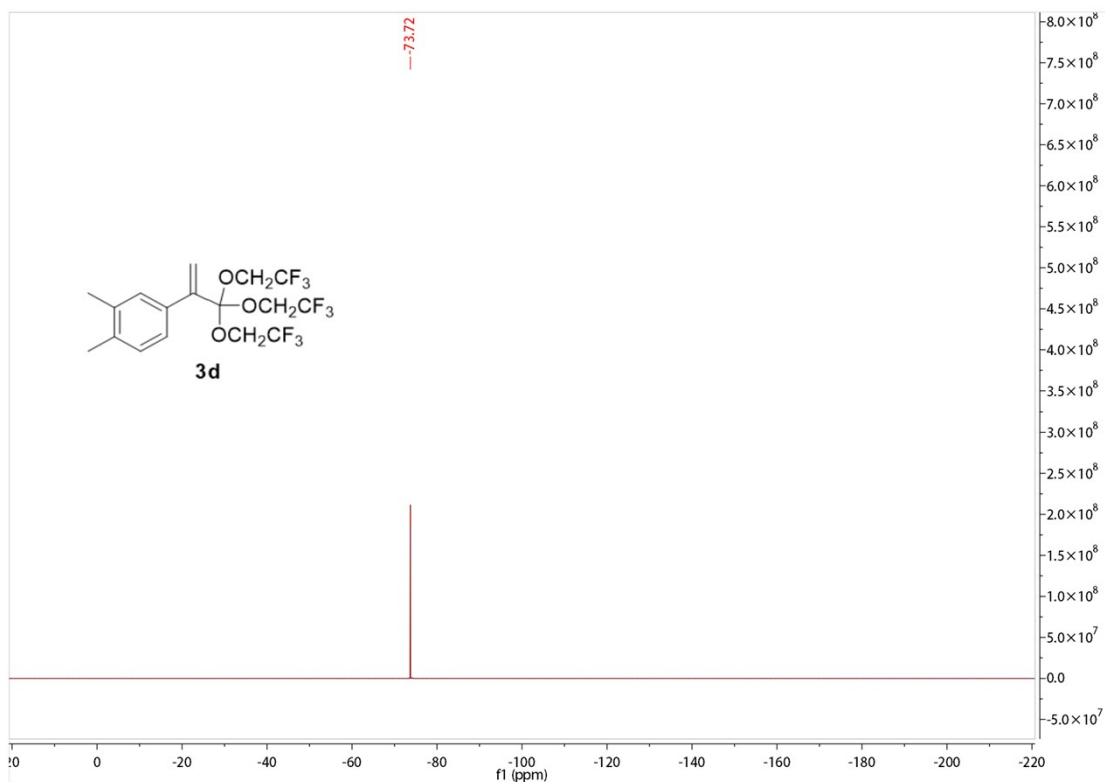
¹H NMR (500 MHz, CDCl₃) spectrum for 3d



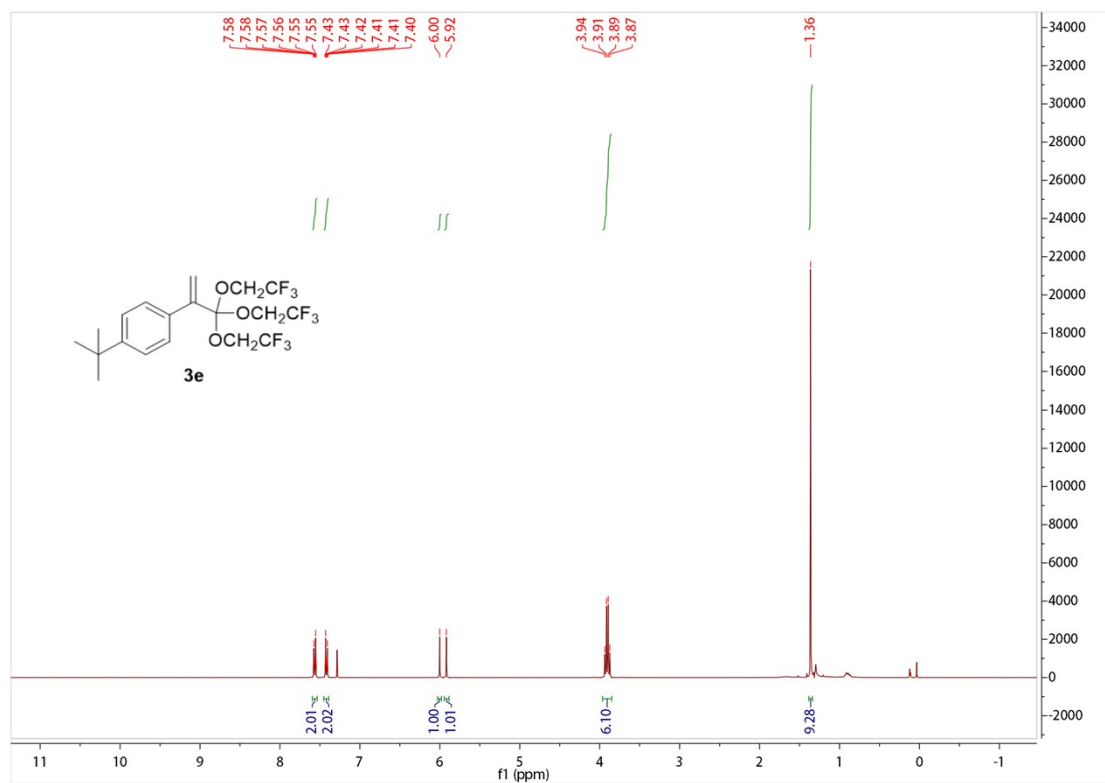
¹³C NMR (126 MHz, CDCl₃) spectrum for 3d



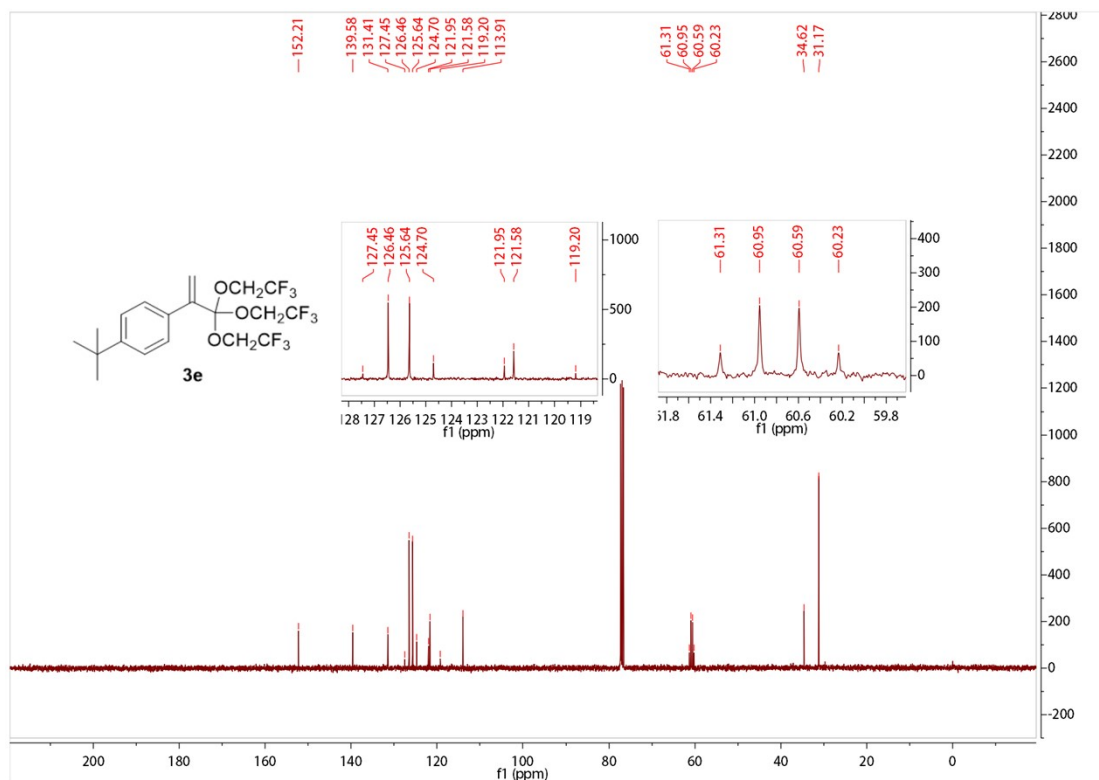
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3d



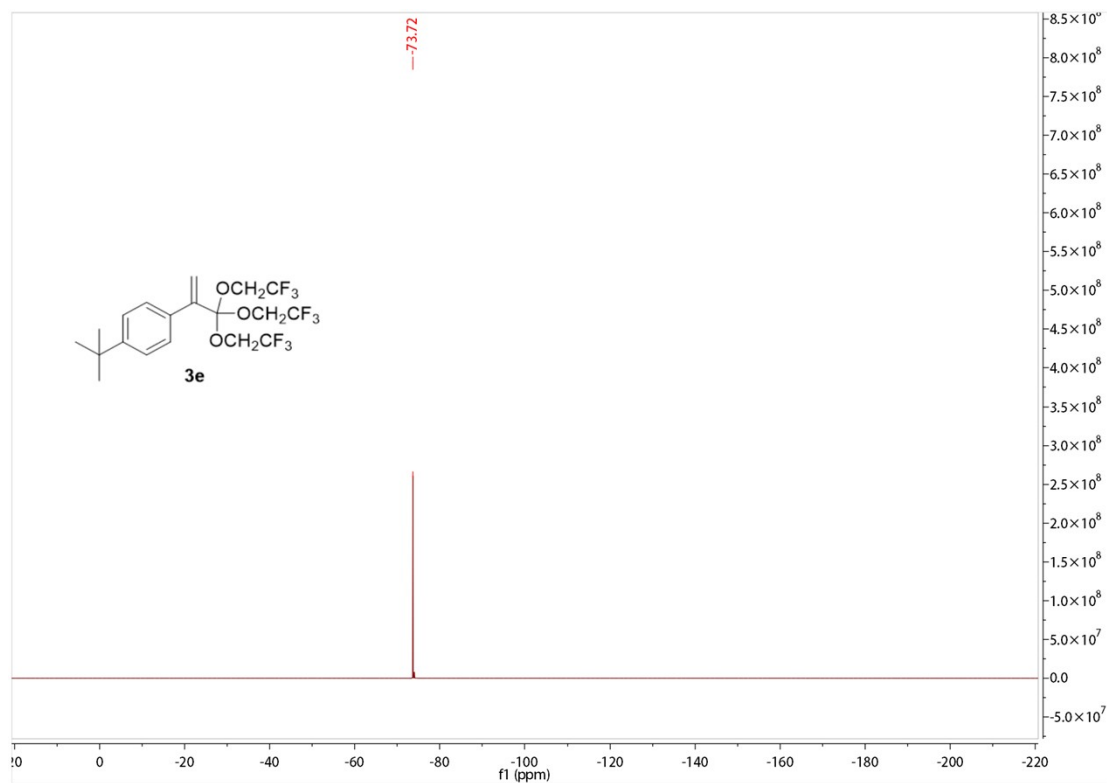
¹H NMR (400 MHz, CDCl₃) spectrum for 3e



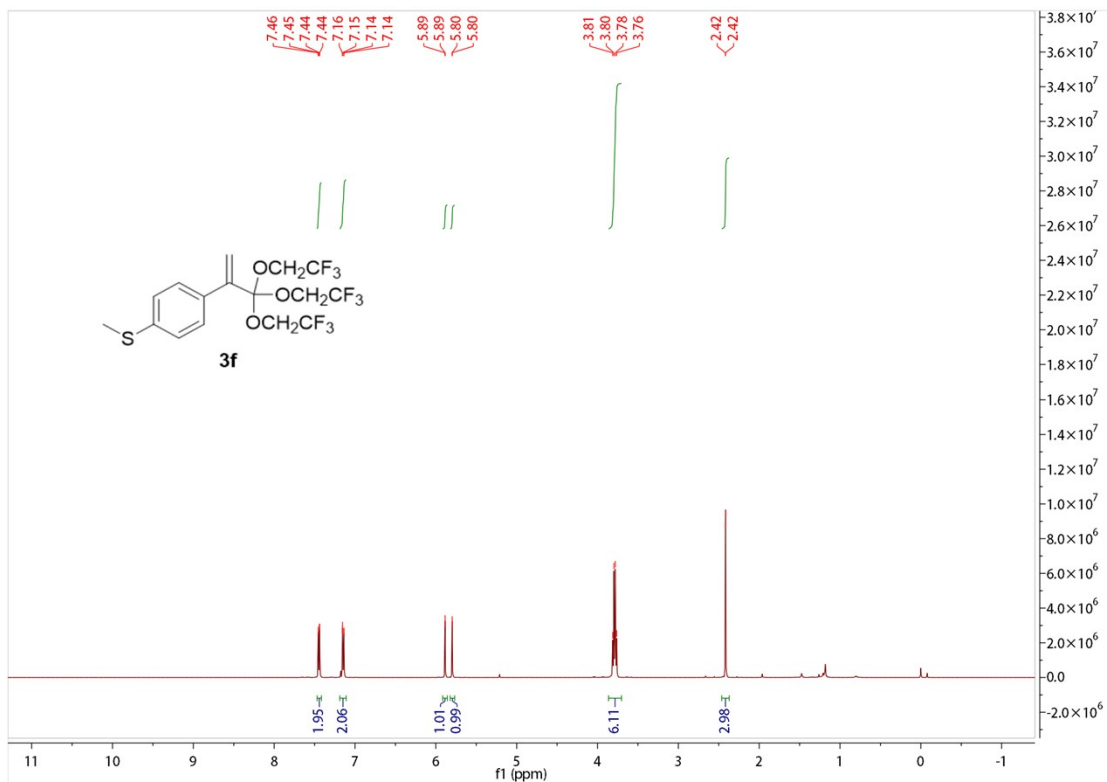
¹³C NMR (101 MHz, CDCl₃) spectrum for 3e



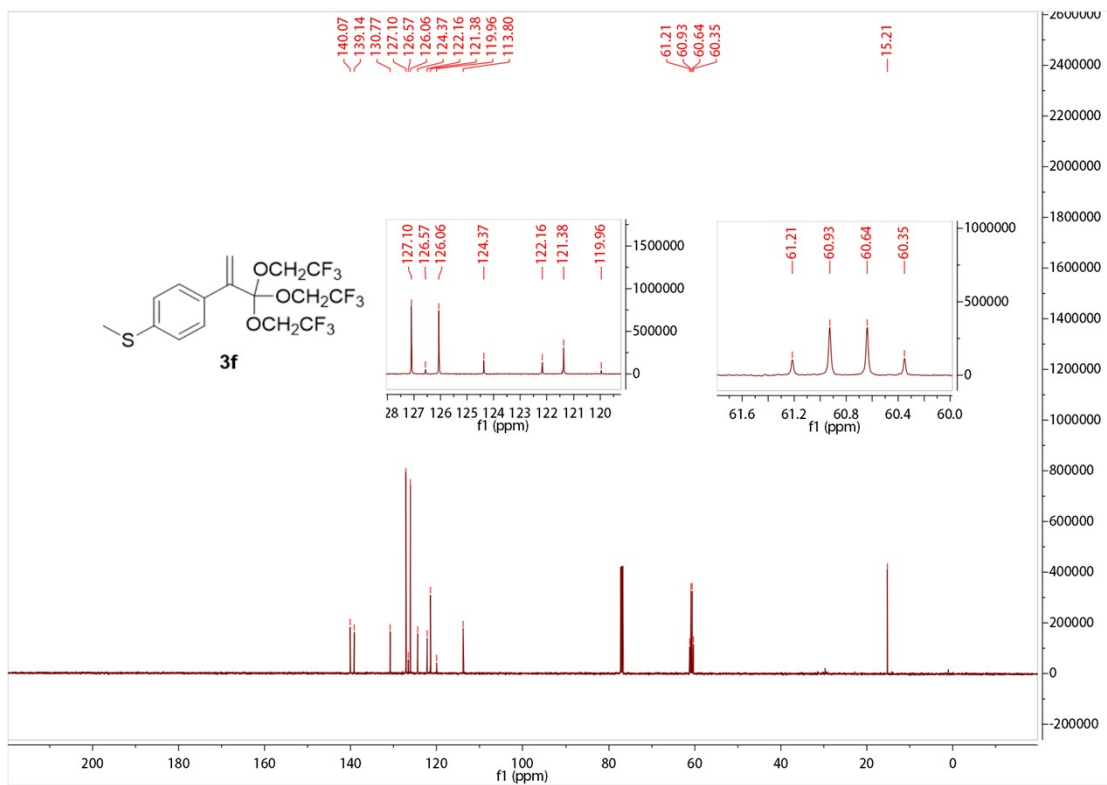
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3e



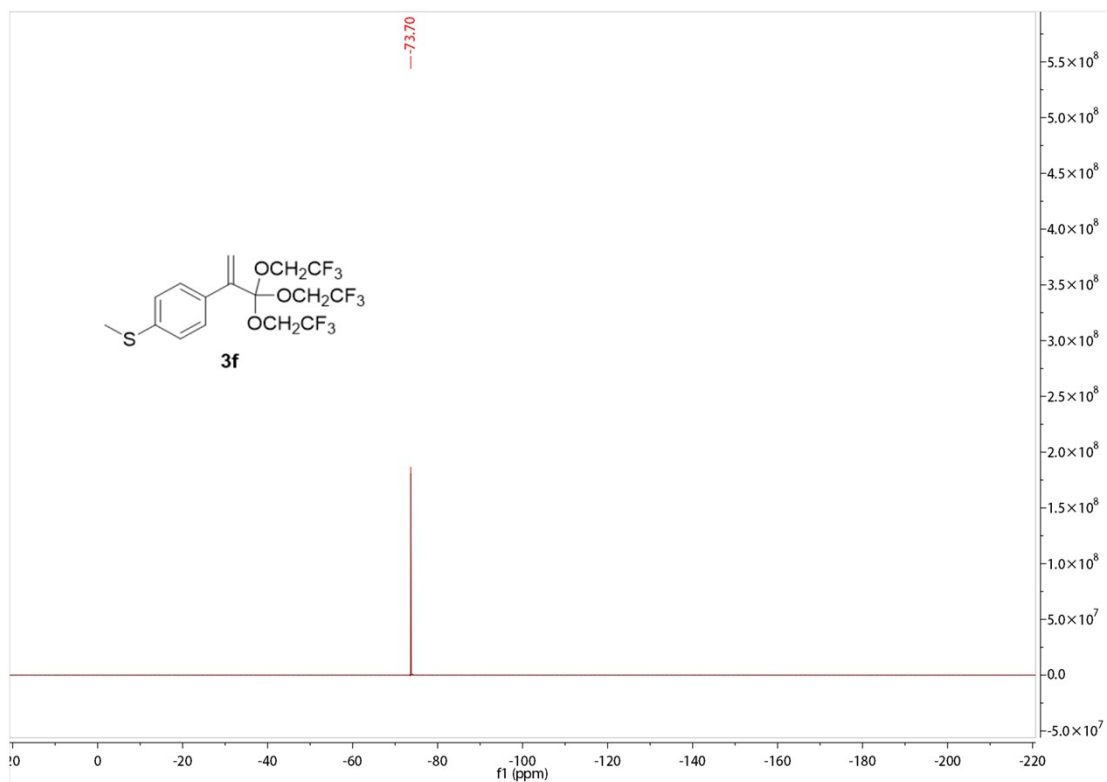
¹H NMR (500 MHz, CDCl₃) spectrum for 3f



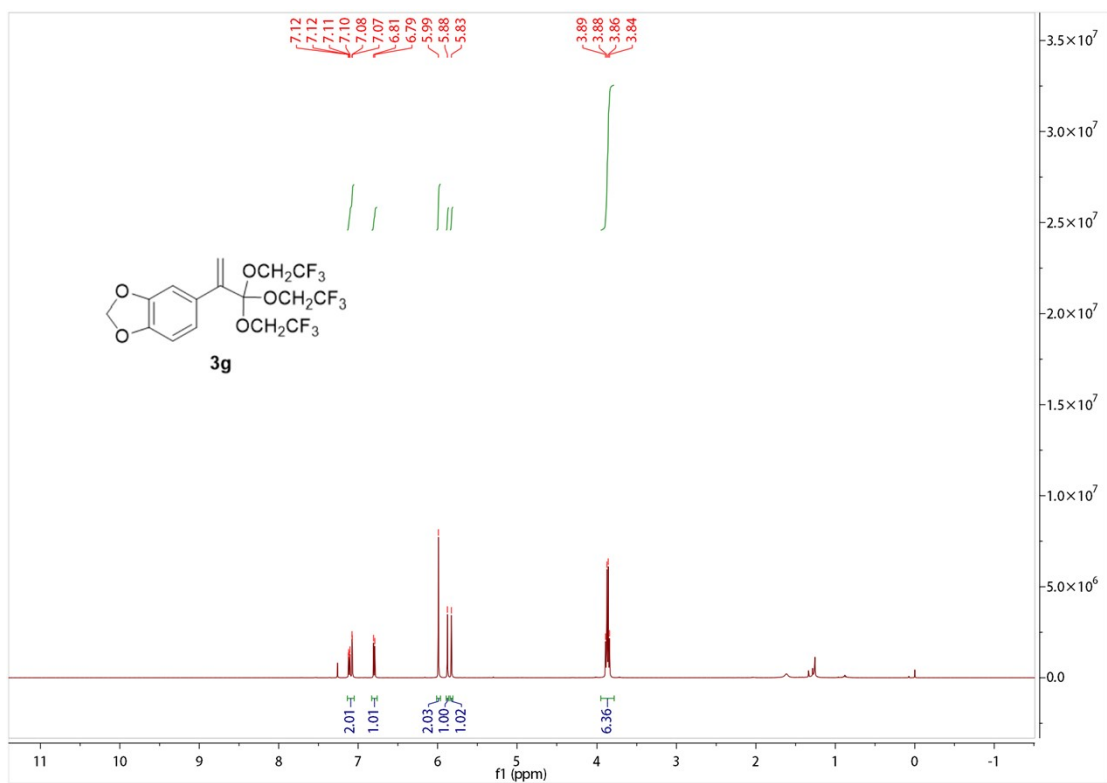
¹³C NMR (126 MHz, CDCl₃) spectrum for 3f



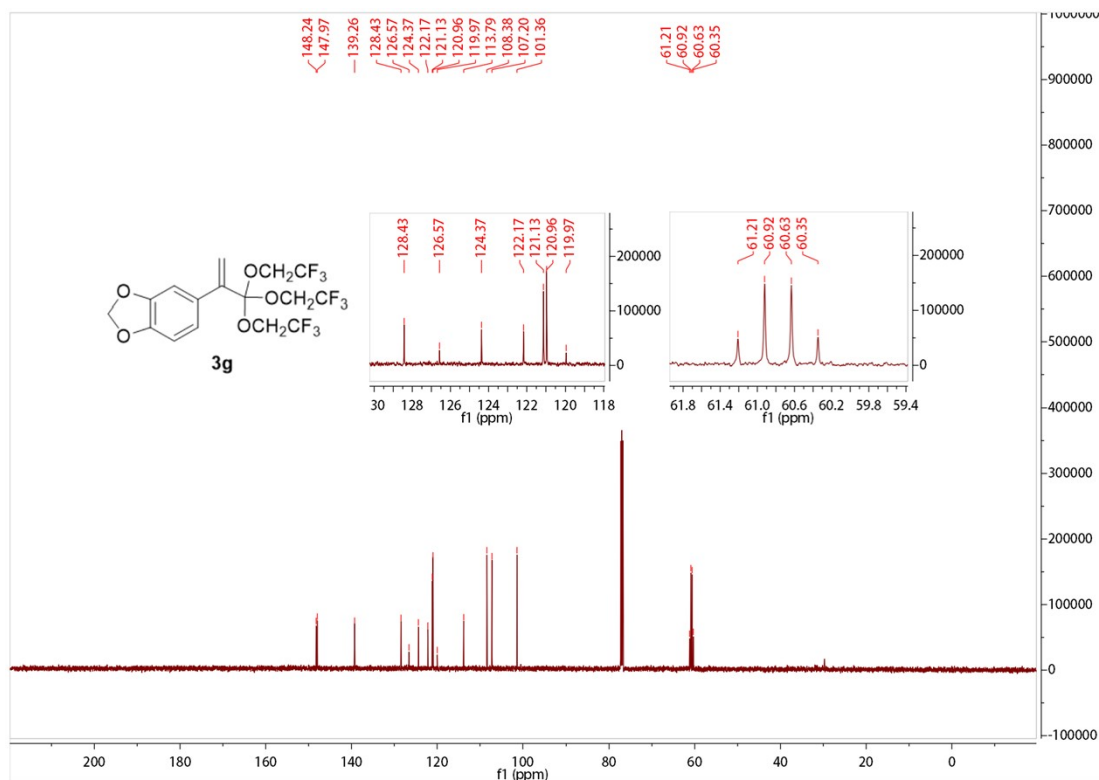
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3f



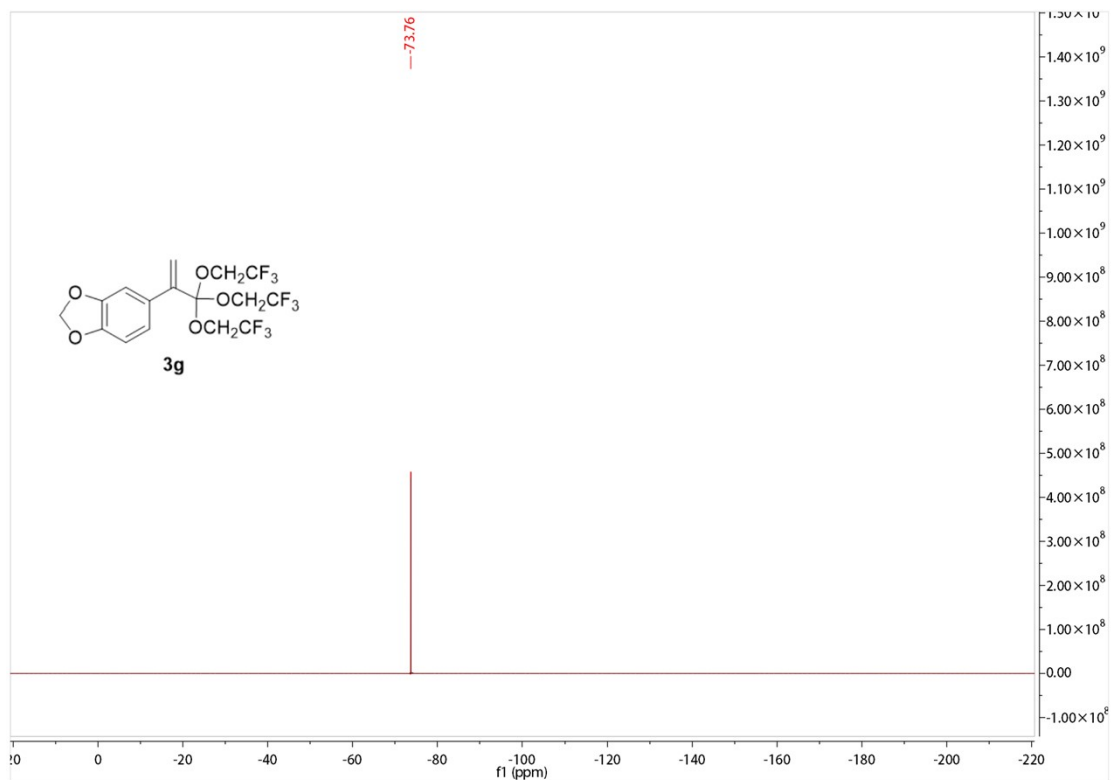
^1H NMR (500 MHz, CDCl_3) spectrum for **3g**



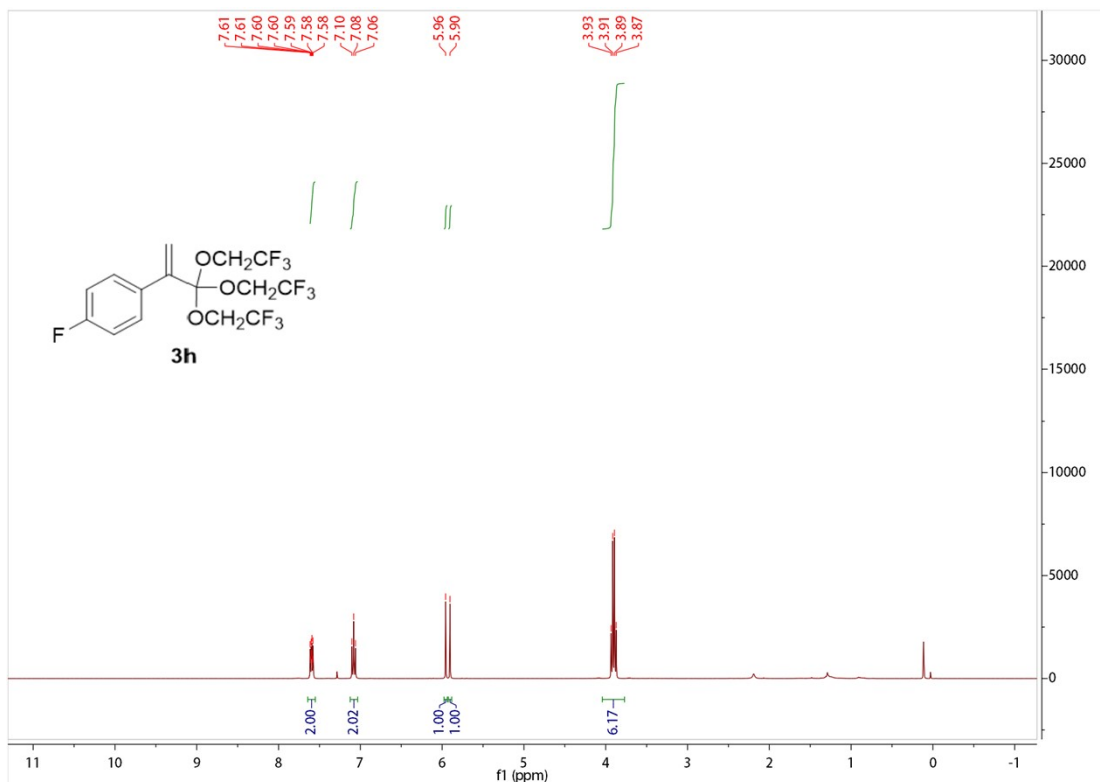
^{13}C NMR (126 MHz, CDCl_3) spectrum for **3g**



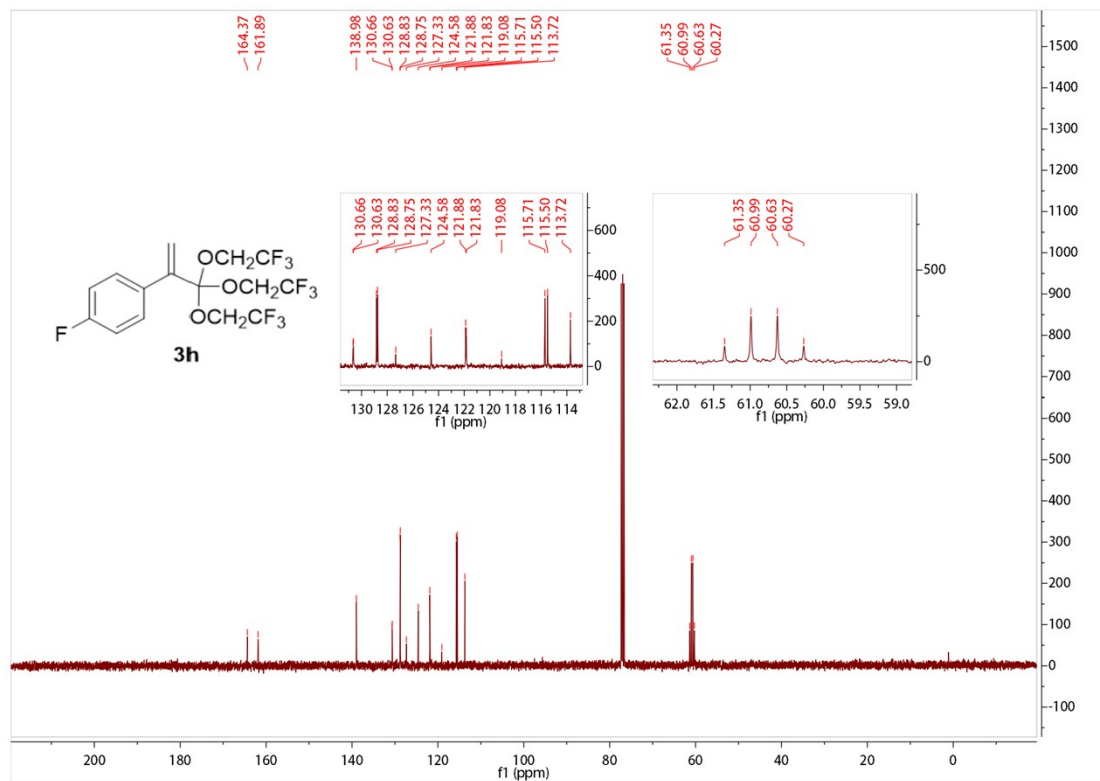
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3g



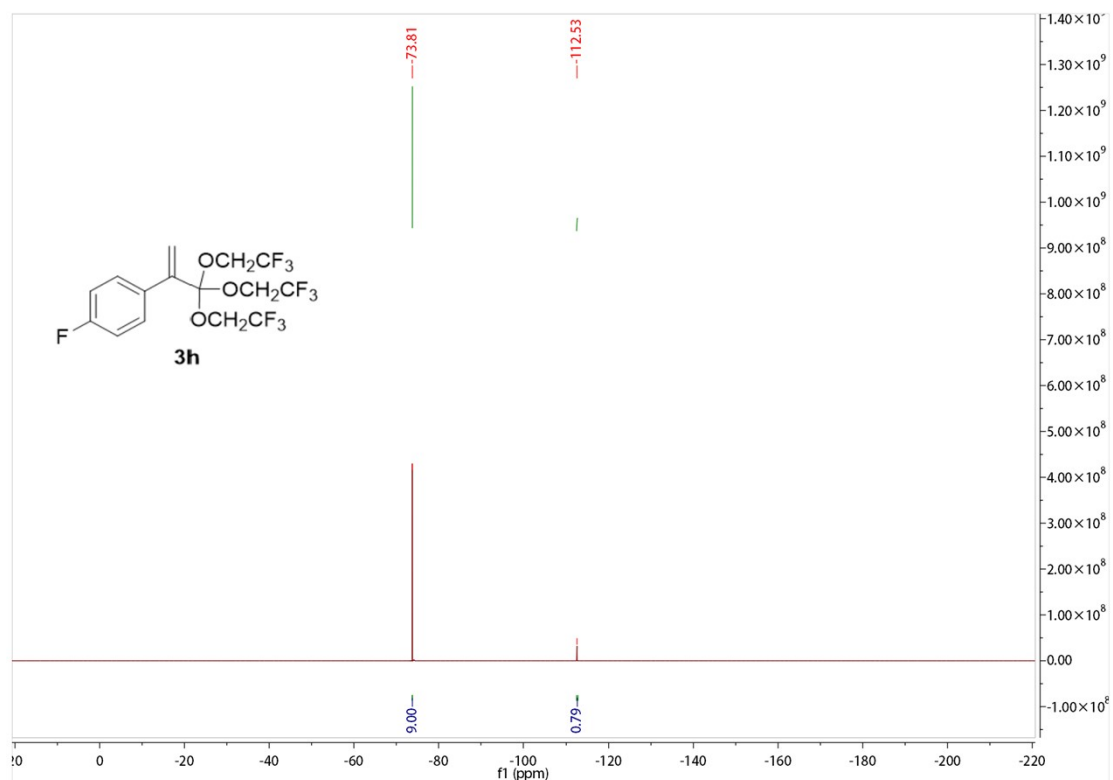
¹H NMR (400 MHz, CDCl₃) spectrum for 3h



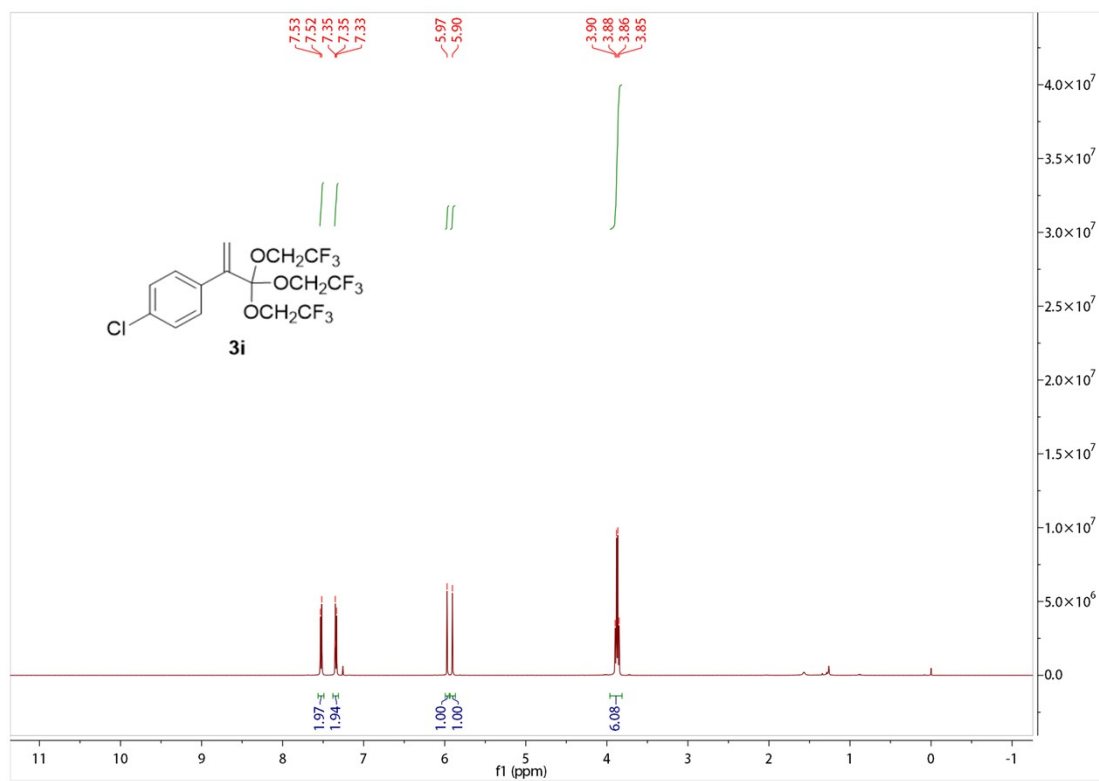
¹³C NMR (101 MHz, CDCl₃) spectrum for 3h



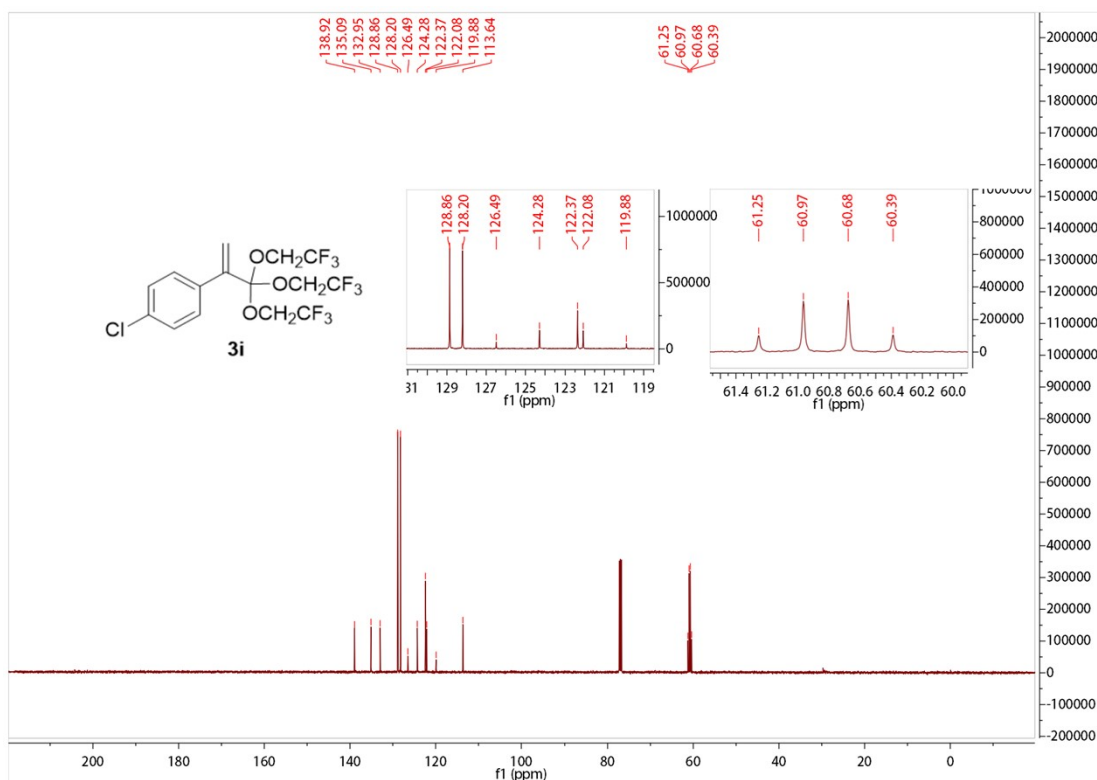
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3h



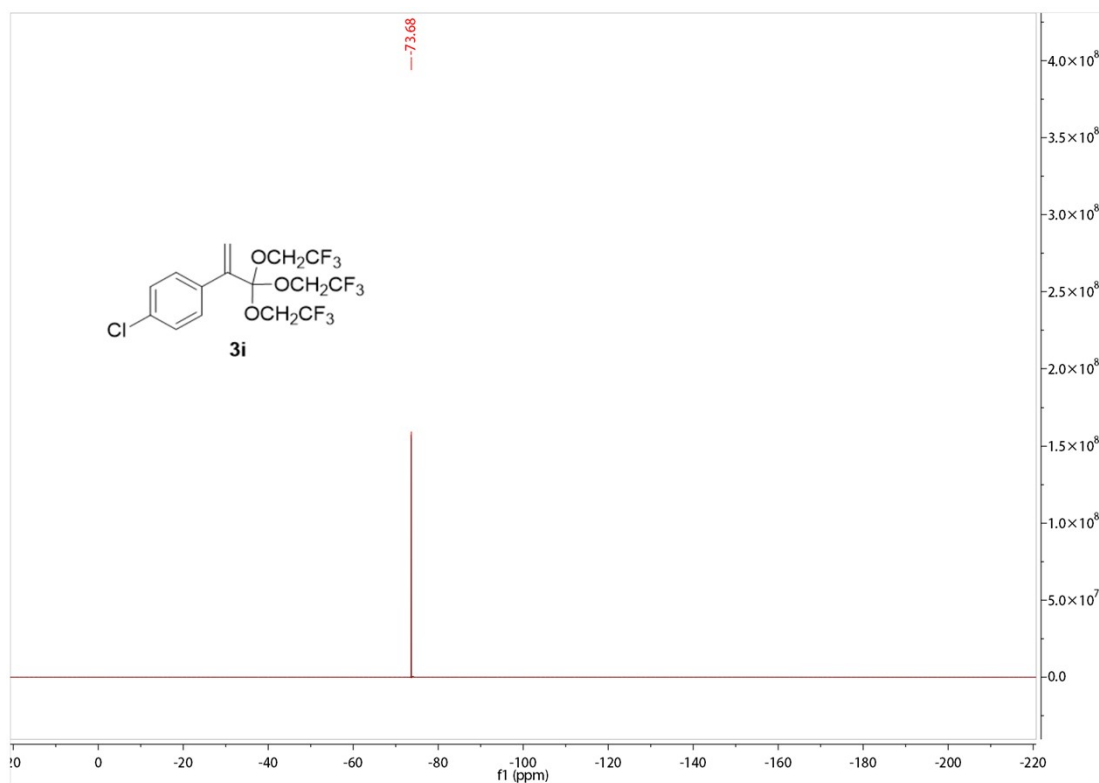
^1H NMR (500 MHz, CDCl_3) spectrum for **3i**



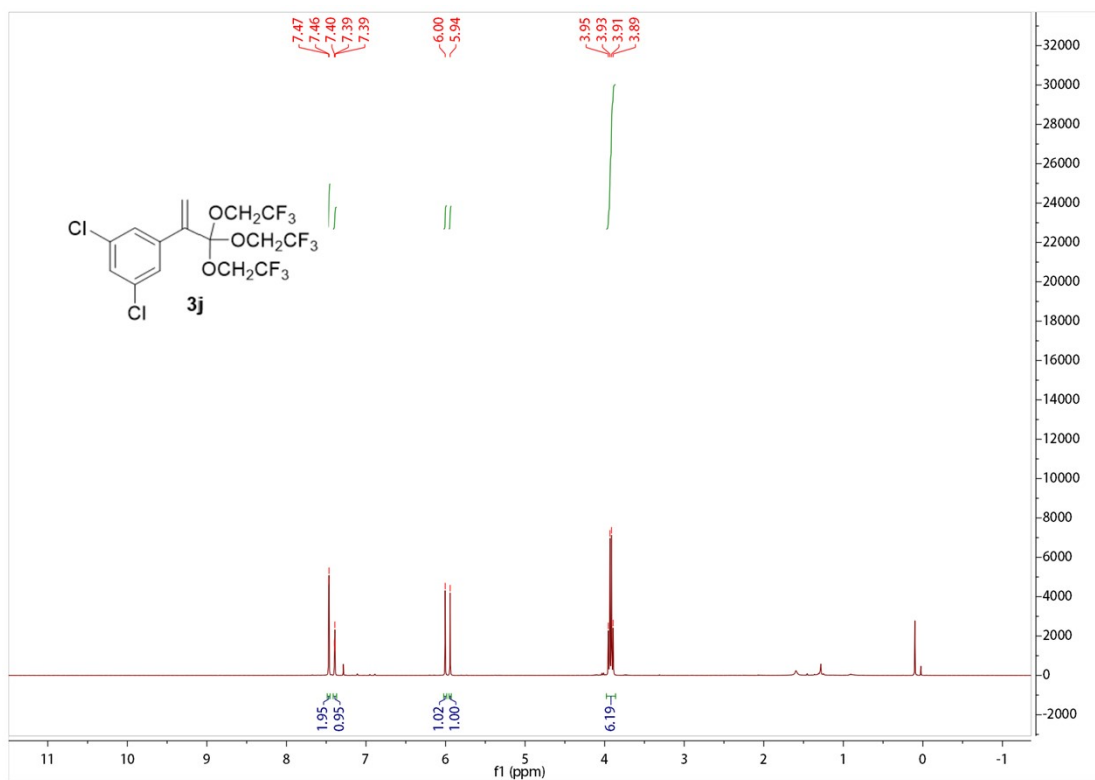
^{13}C NMR (126 MHz, CDCl_3) spectrum for **3i**



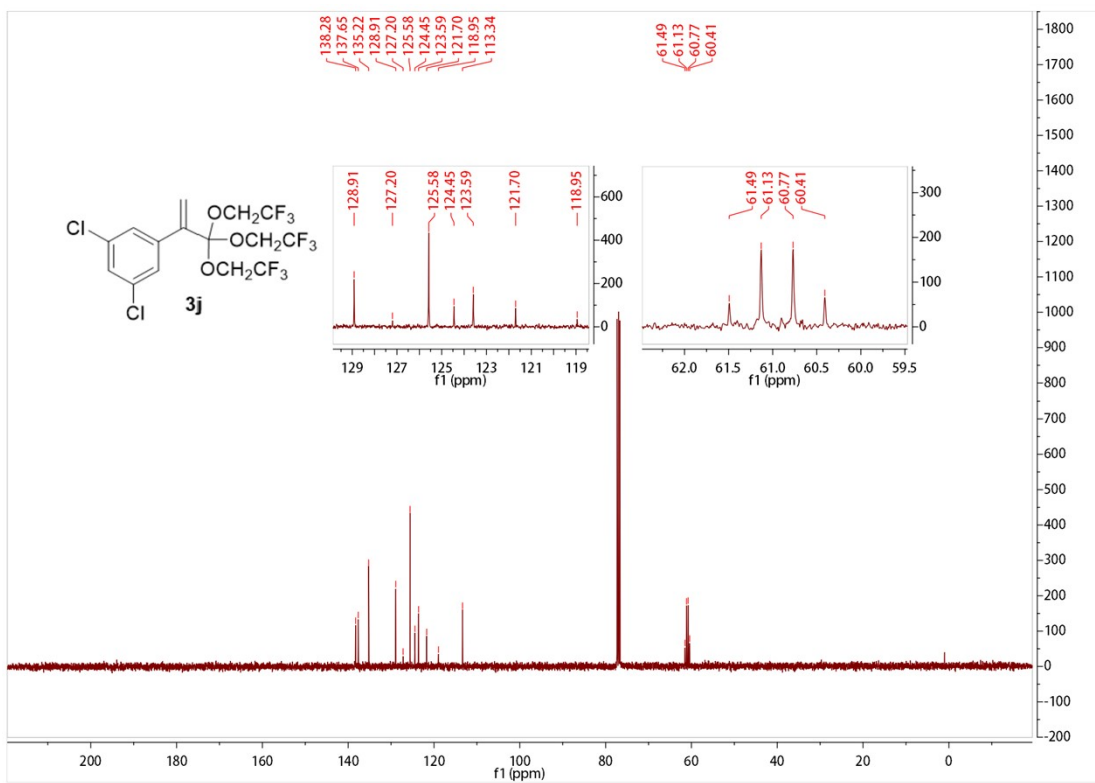
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3i



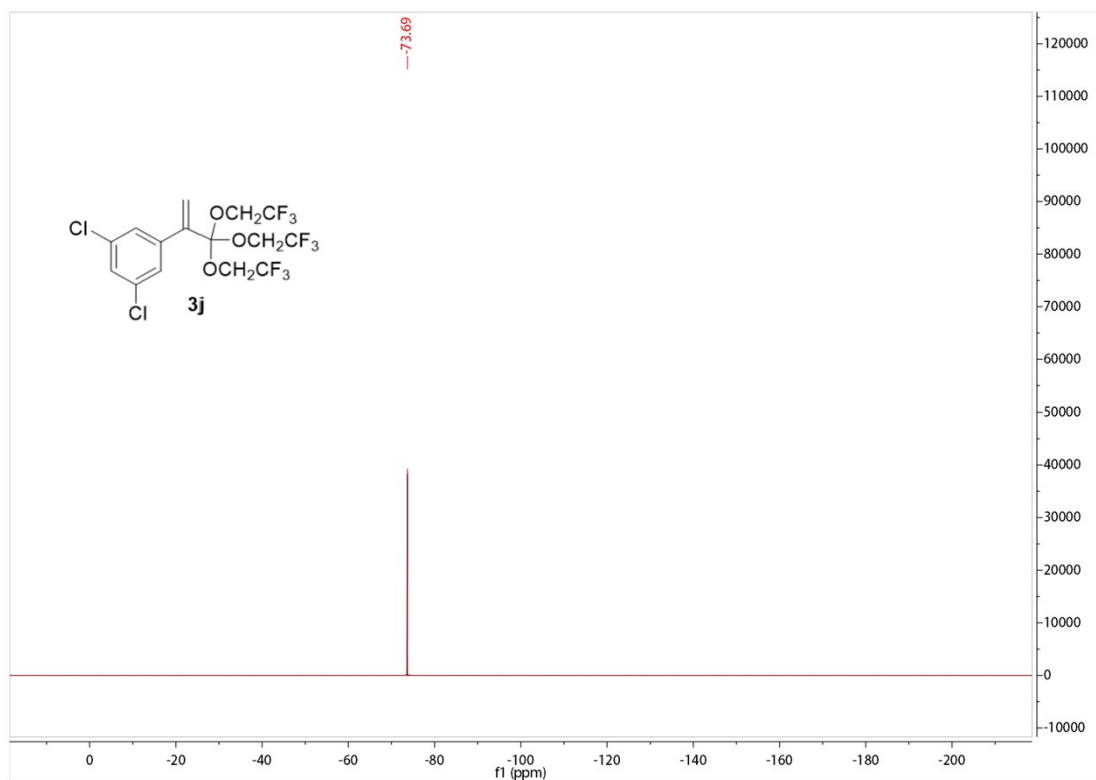
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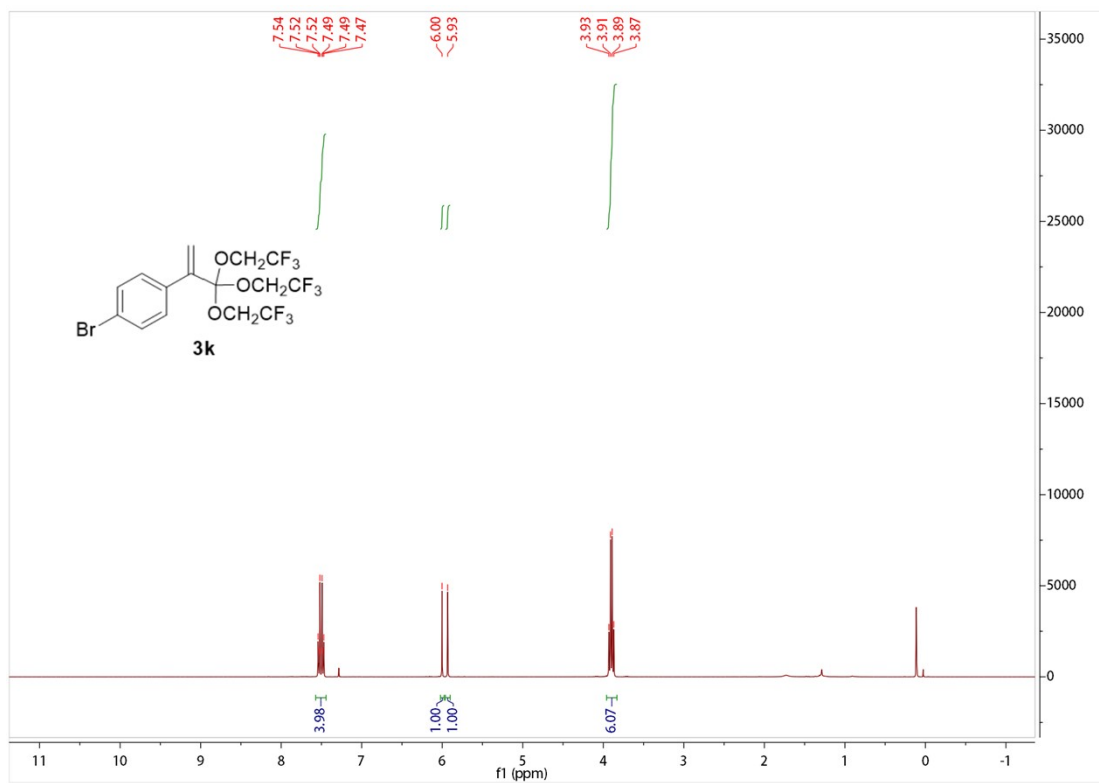
¹³C NMR (101 MHz, CDCl₃) spectrum for 3j



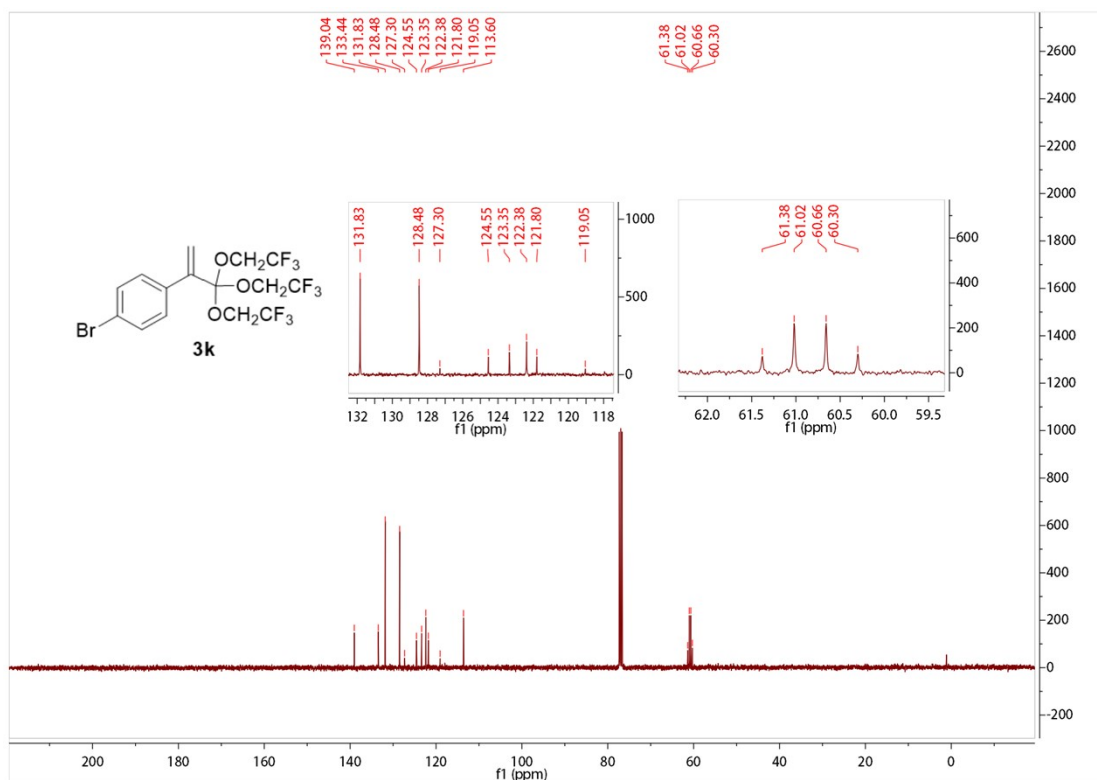
¹⁹F NMR (376 MHz, CDCl₃) spectrum for 3j



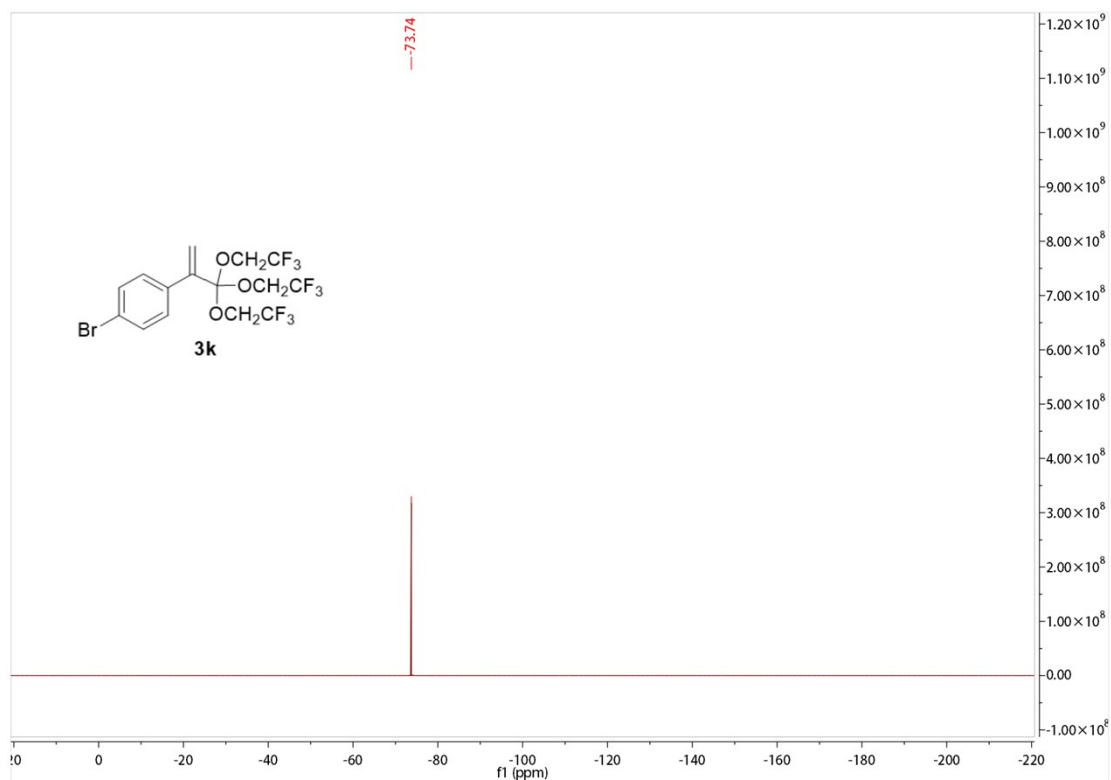
¹H NMR (400 MHz, CDCl₃) spectrum for 3k



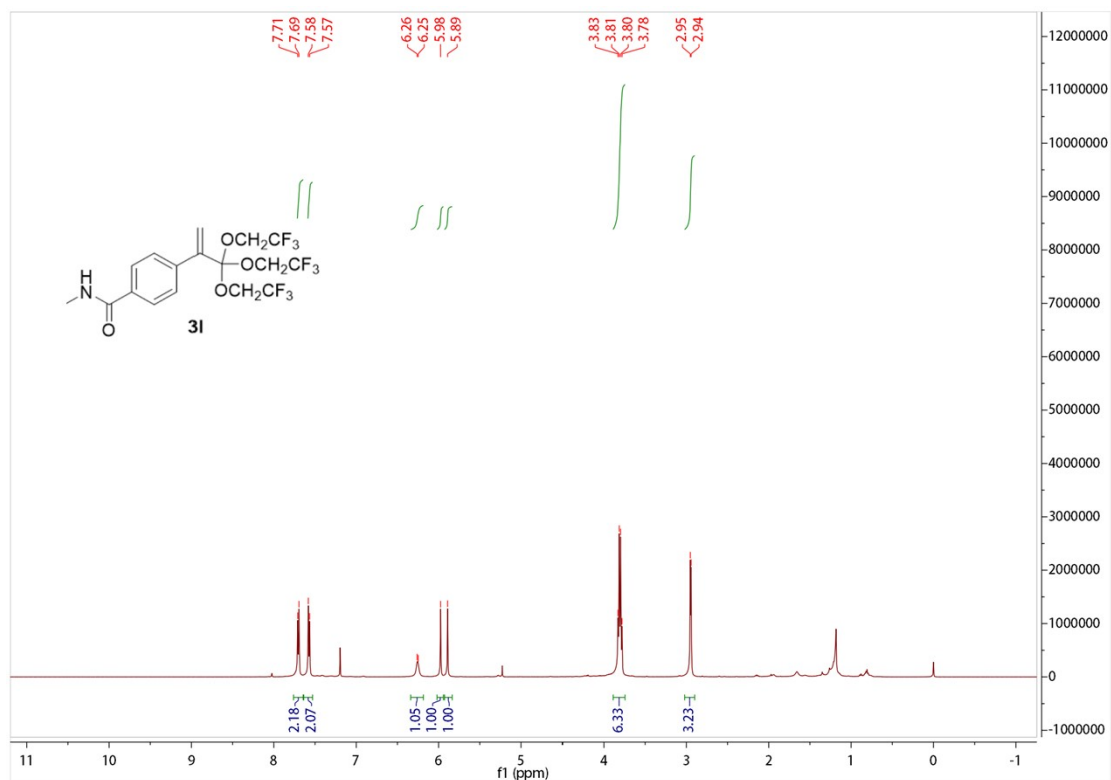
¹³C NMR (101 MHz, CDCl₃) spectrum for 3k



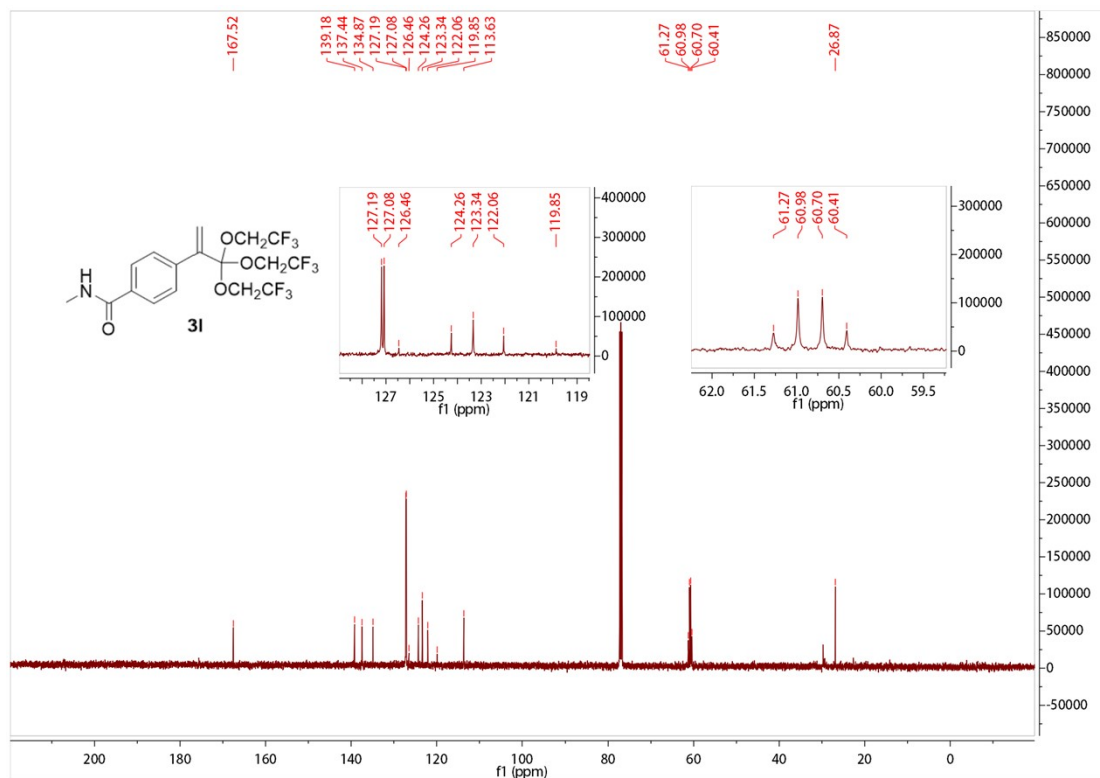
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3k



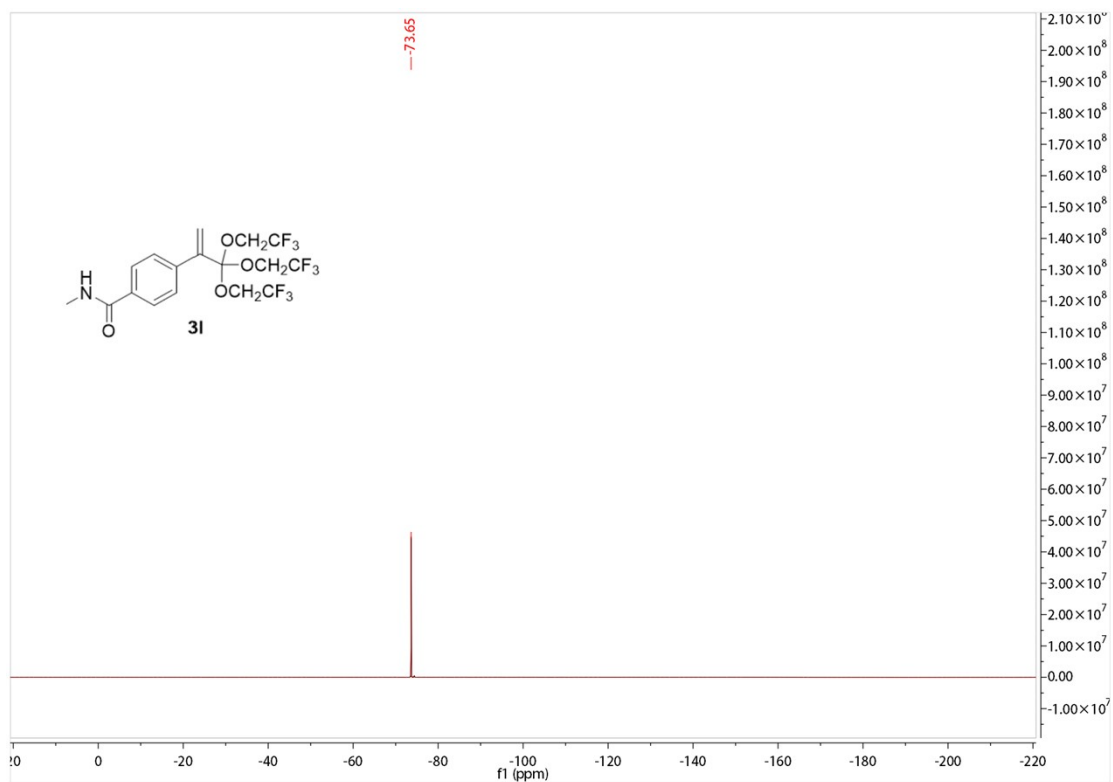
¹H NMR (500 MHz, CDCl₃) spectrum for 3l



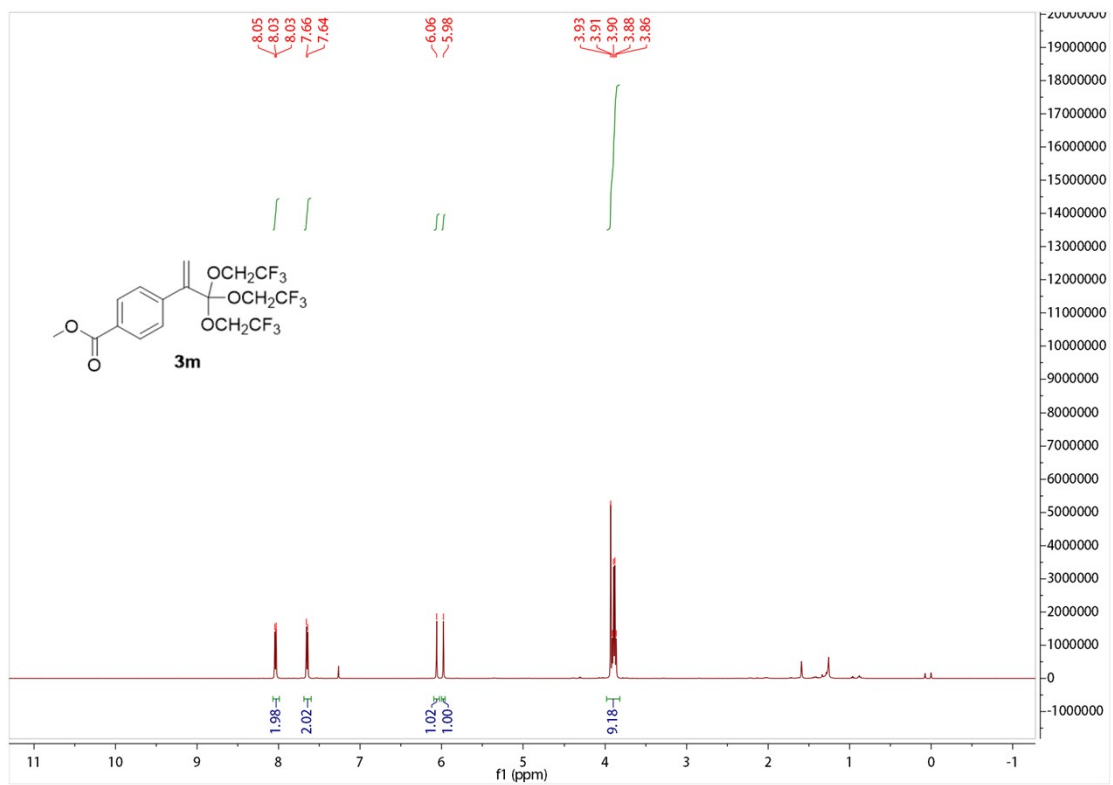
¹³C NMR (126 MHz, CDCl₃) spectrum for 31



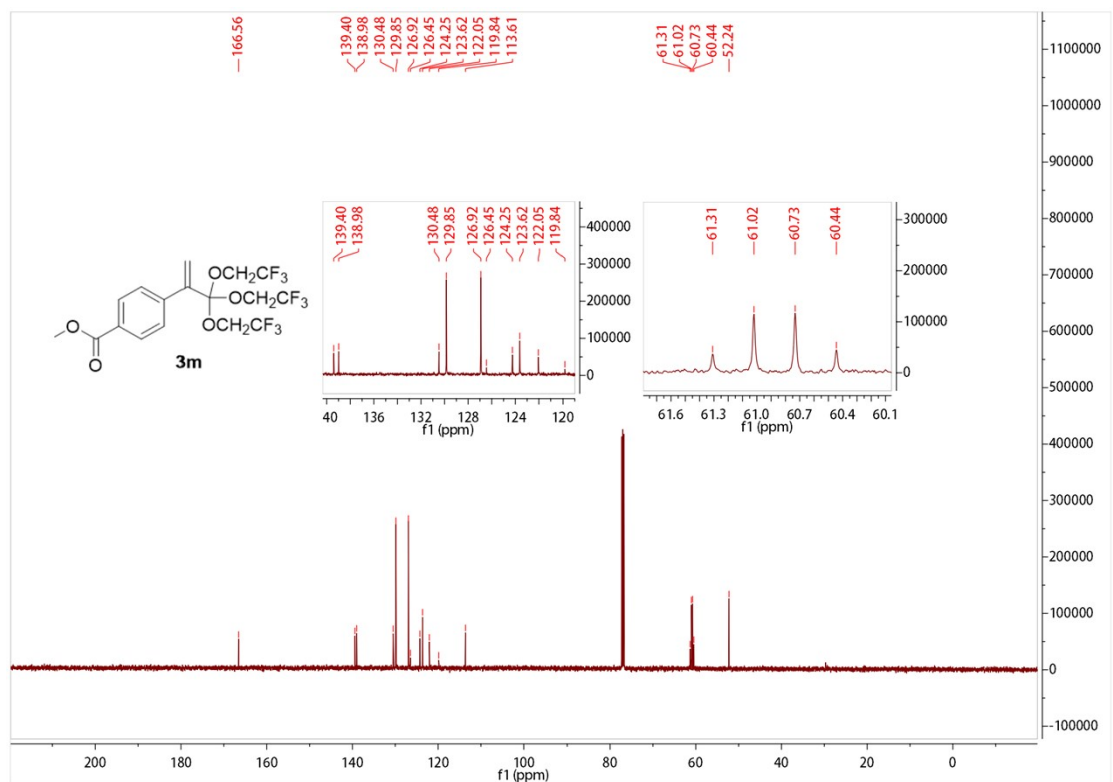
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 31



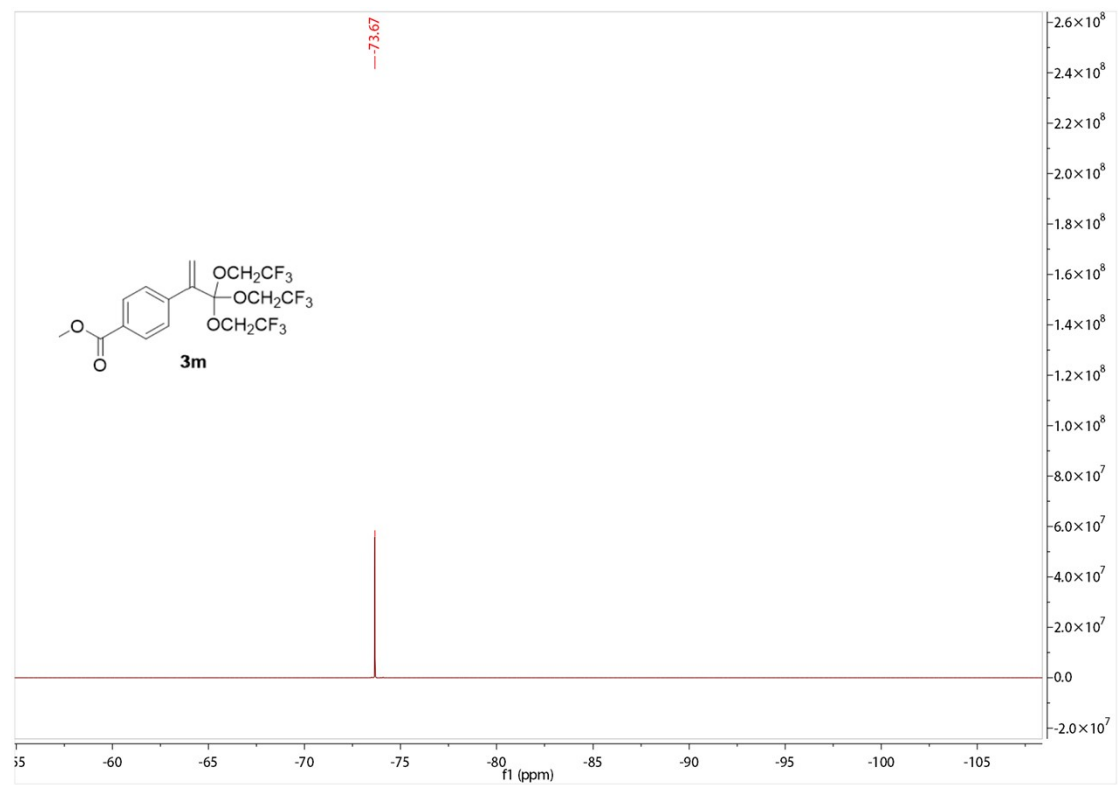
¹H NMR (500 MHz, CDCl₃) spectrum for 3m



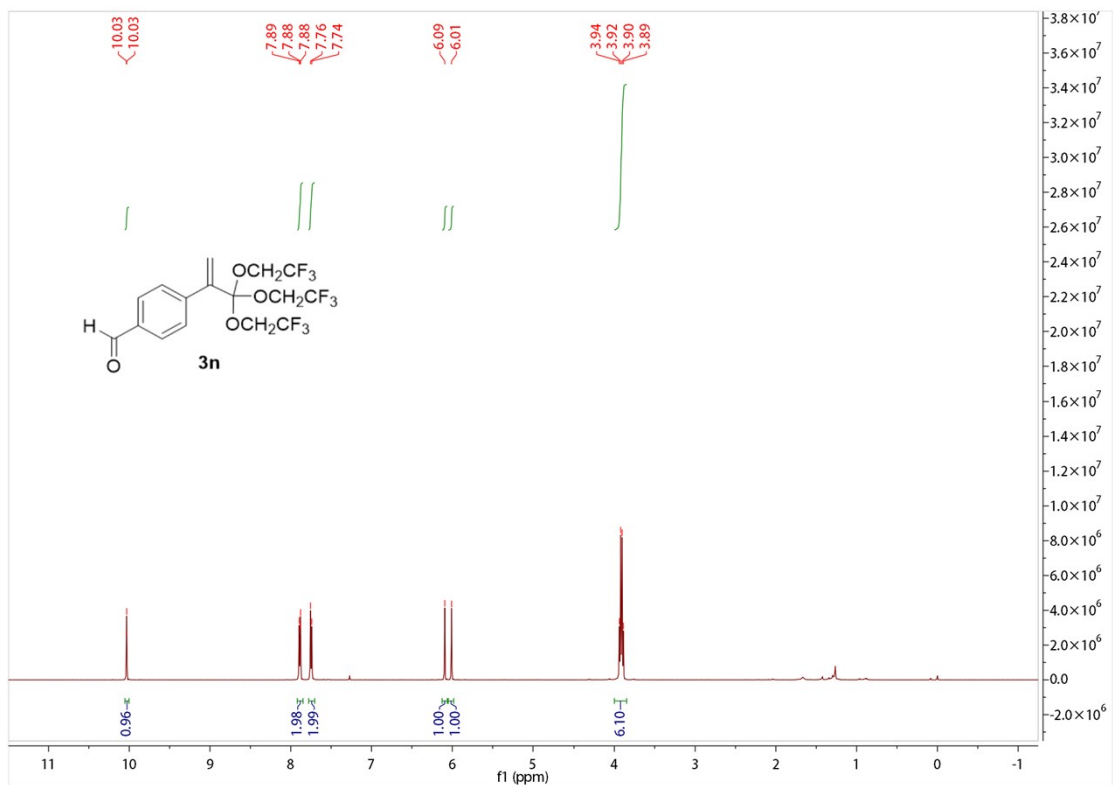
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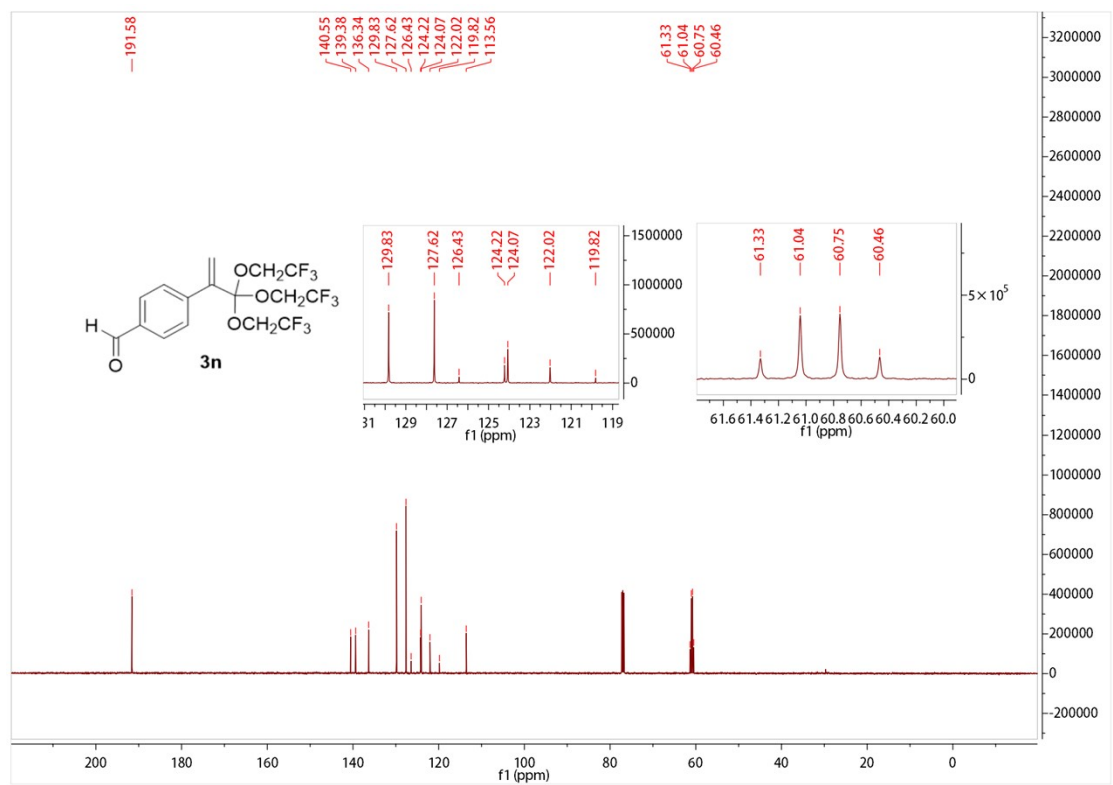
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3m



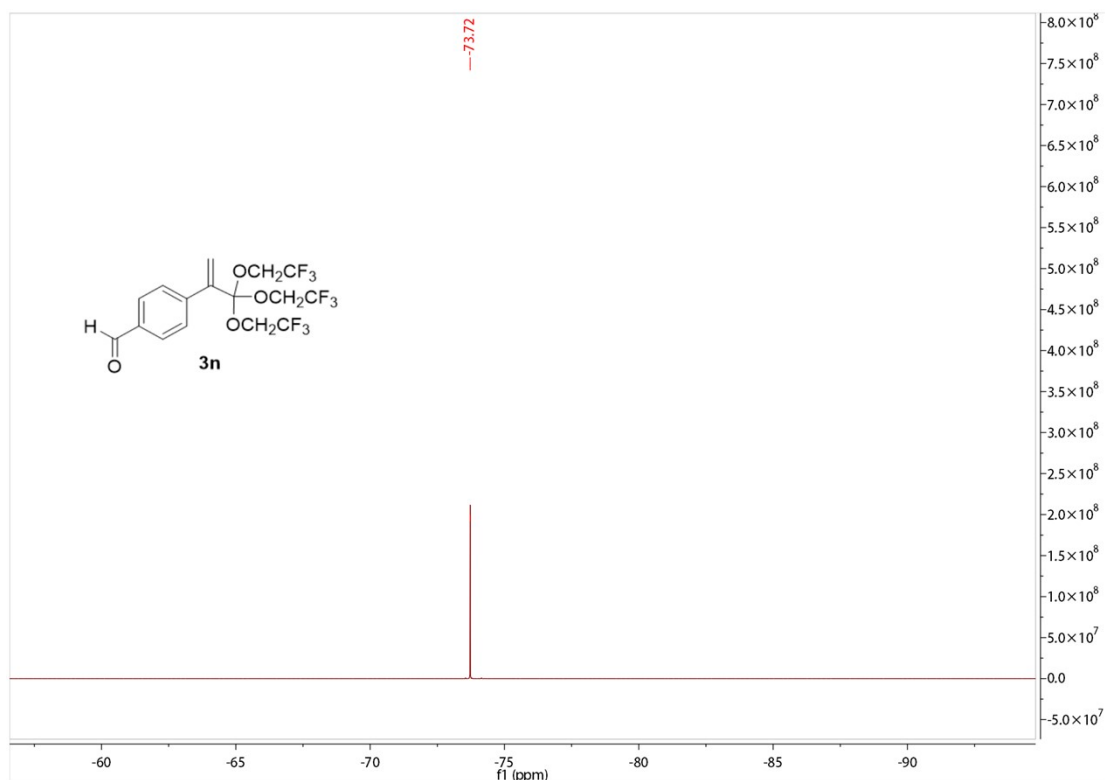
¹H NMR (500 MHz, CDCl₃) spectrum for 3n



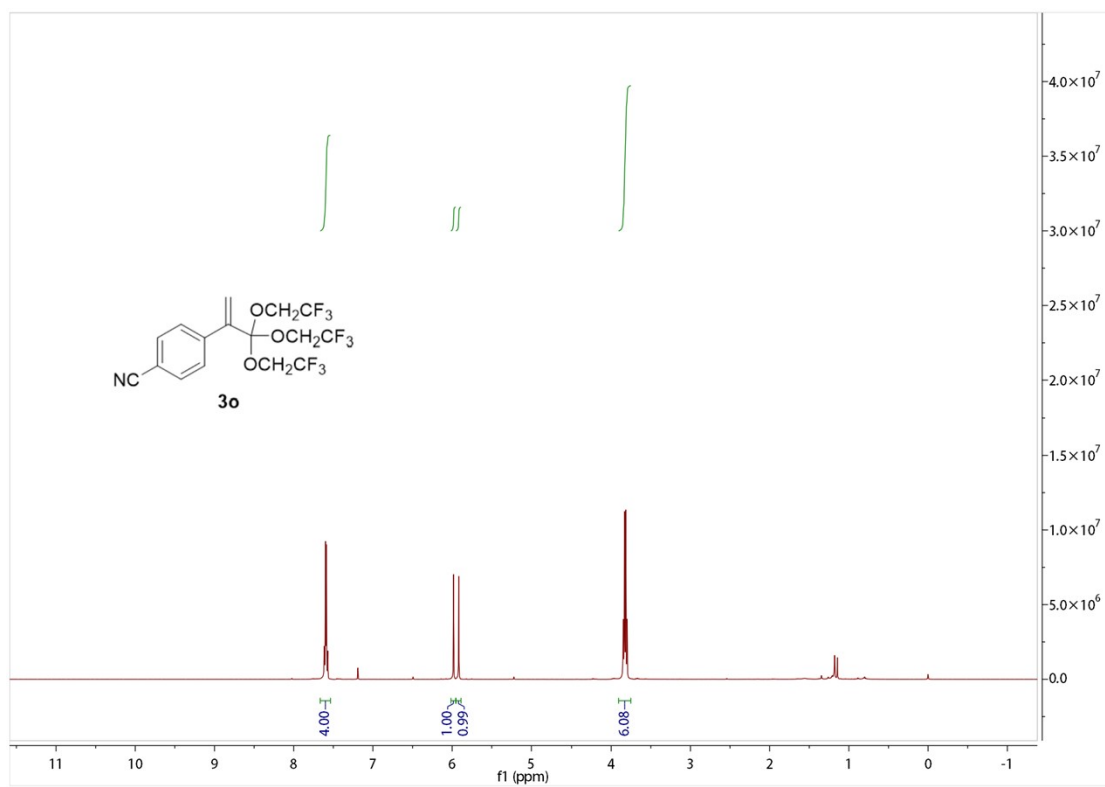
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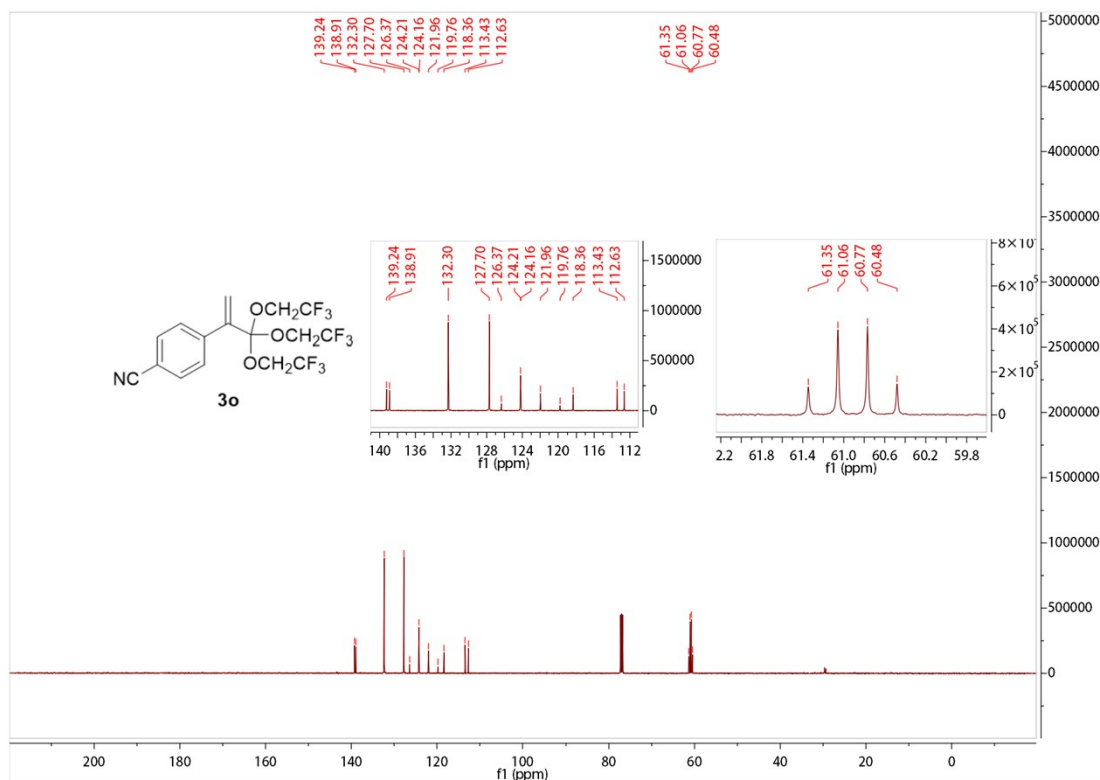
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3n



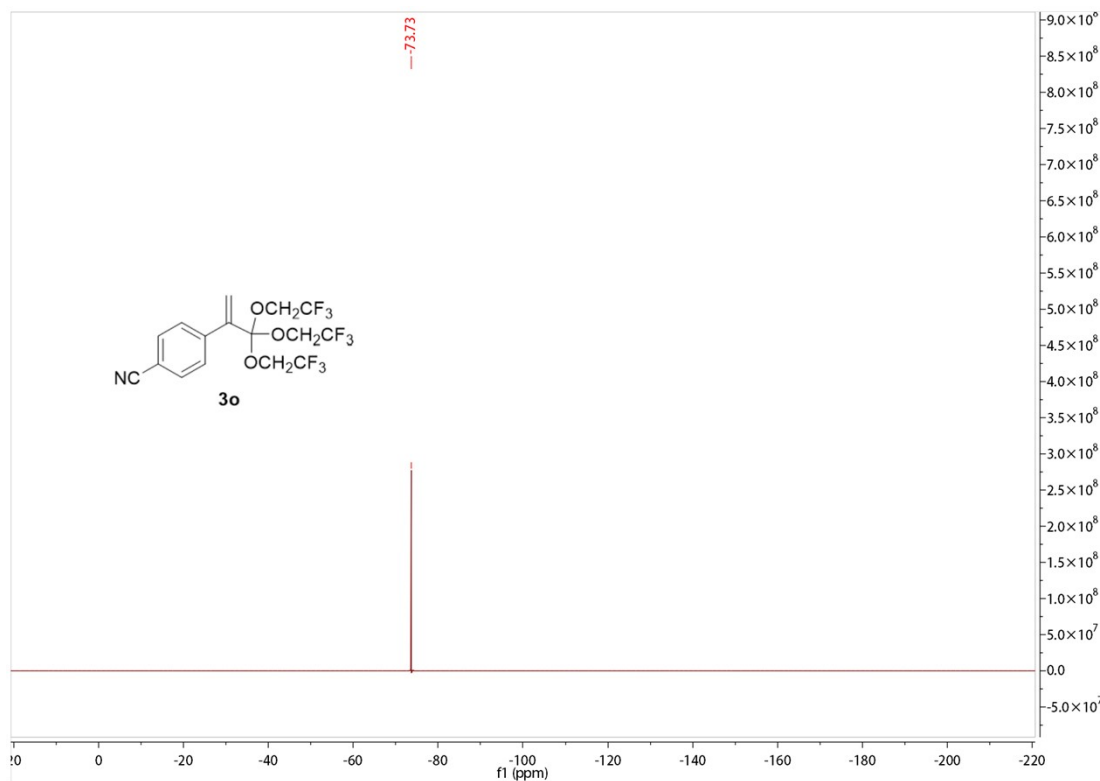
^1H NMR (500 MHz, CDCl_3) spectrum for **3o**



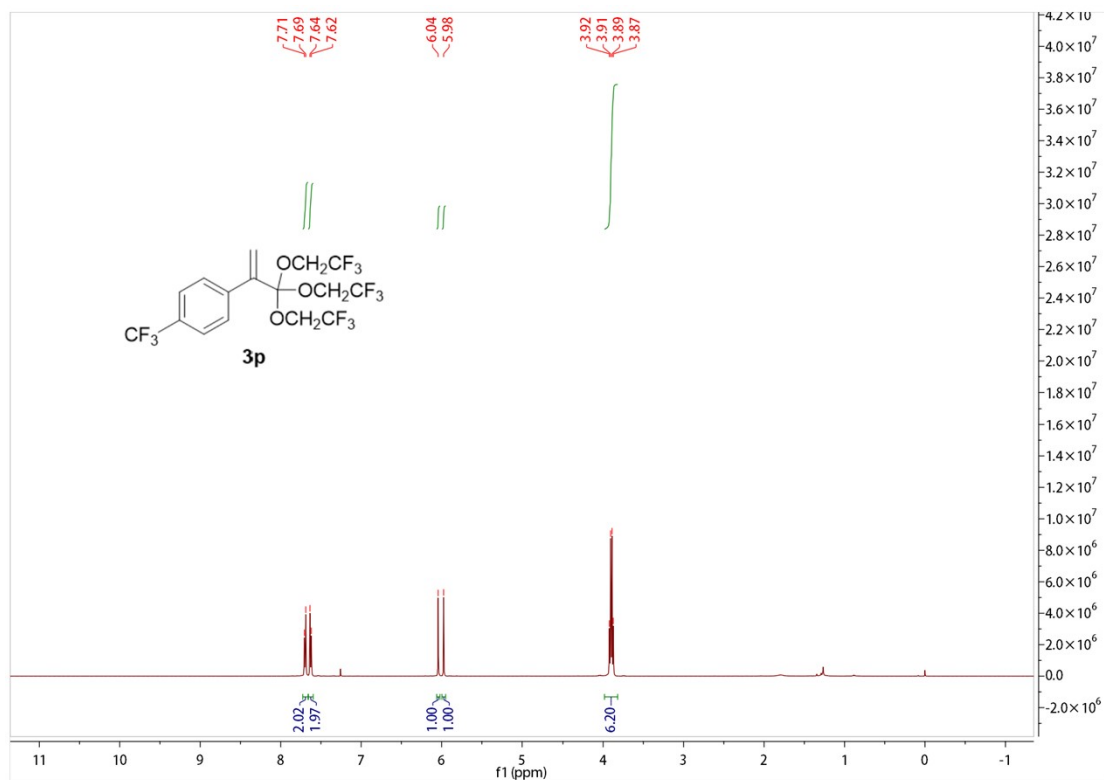
^{13}C NMR (126 MHz, CDCl_3) spectrum for **3o**



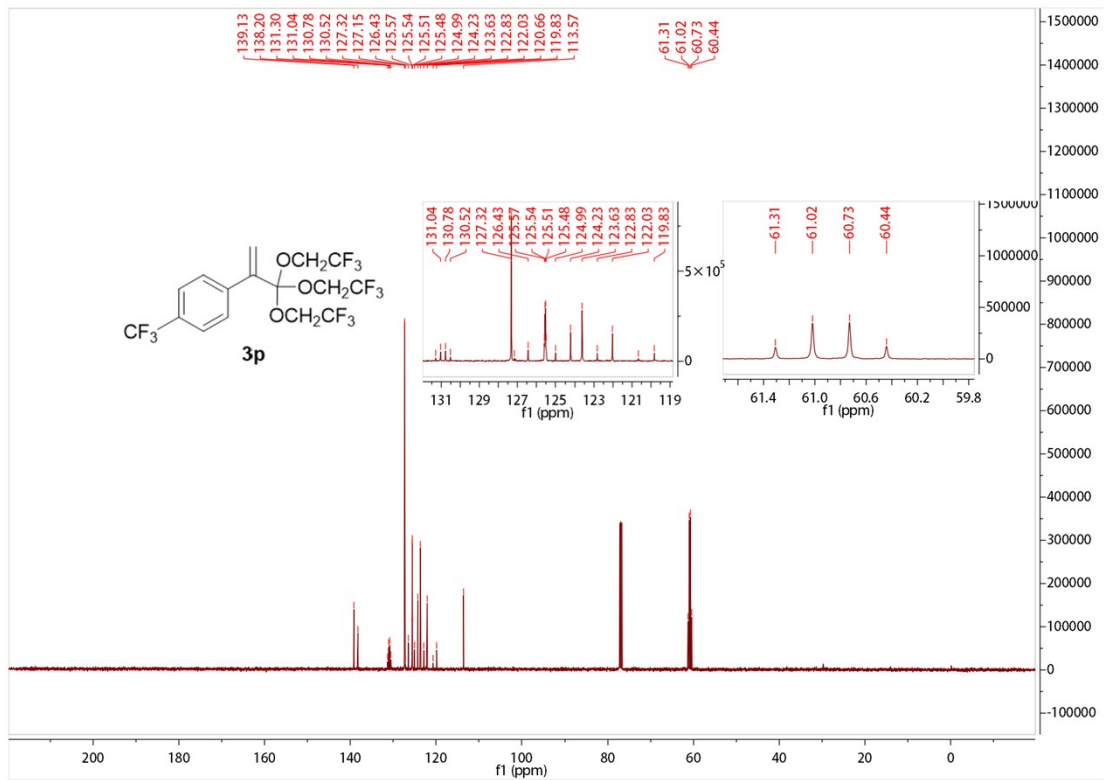
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3o



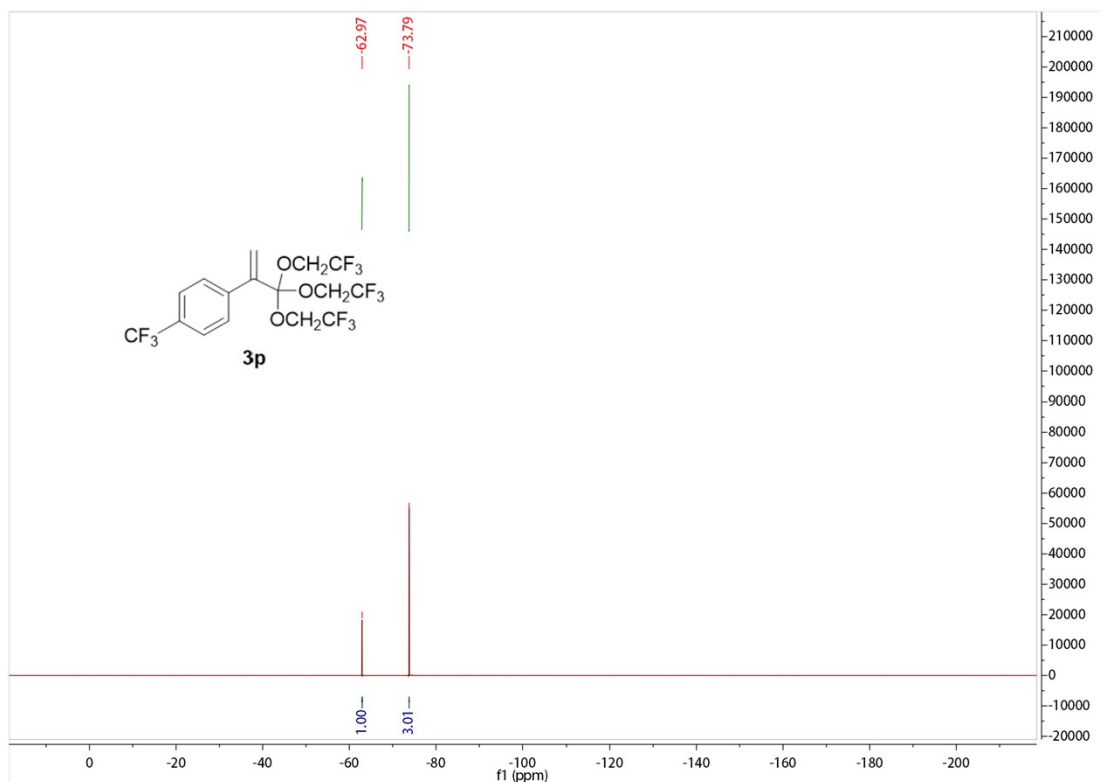
¹H NMR (500 MHz, CDCl₃) spectrum for 3p



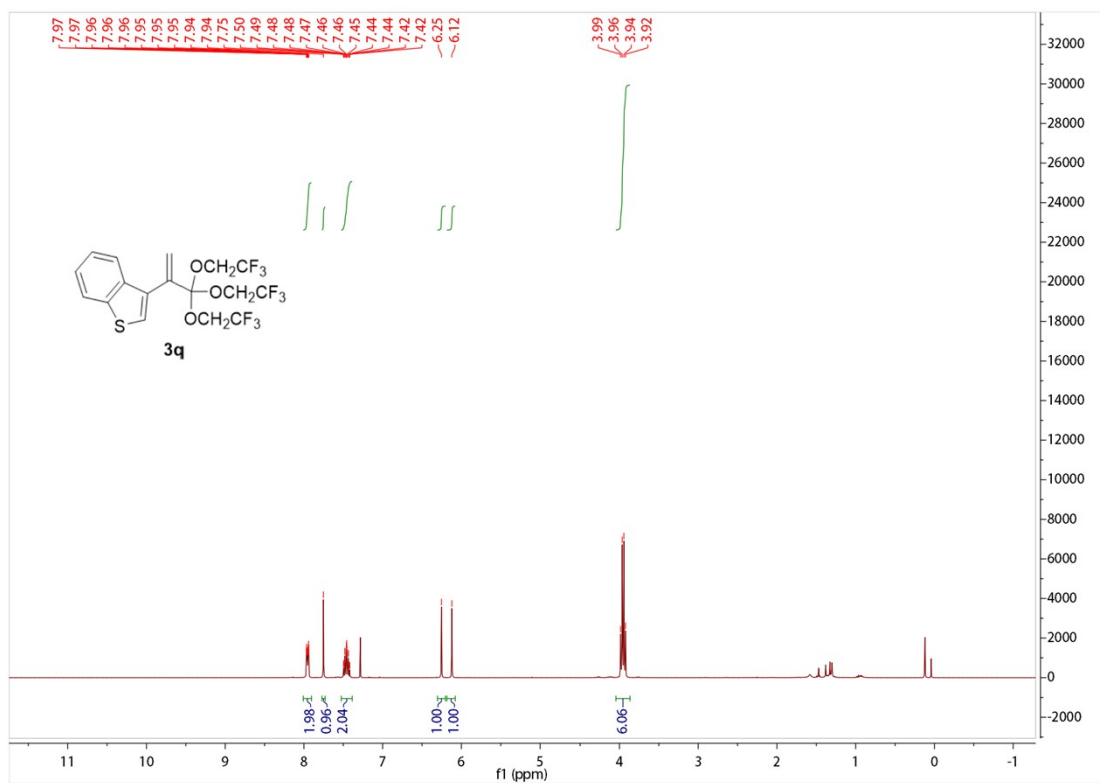
¹³C NMR (126 MHz, CDCl₃) spectrum for 3p



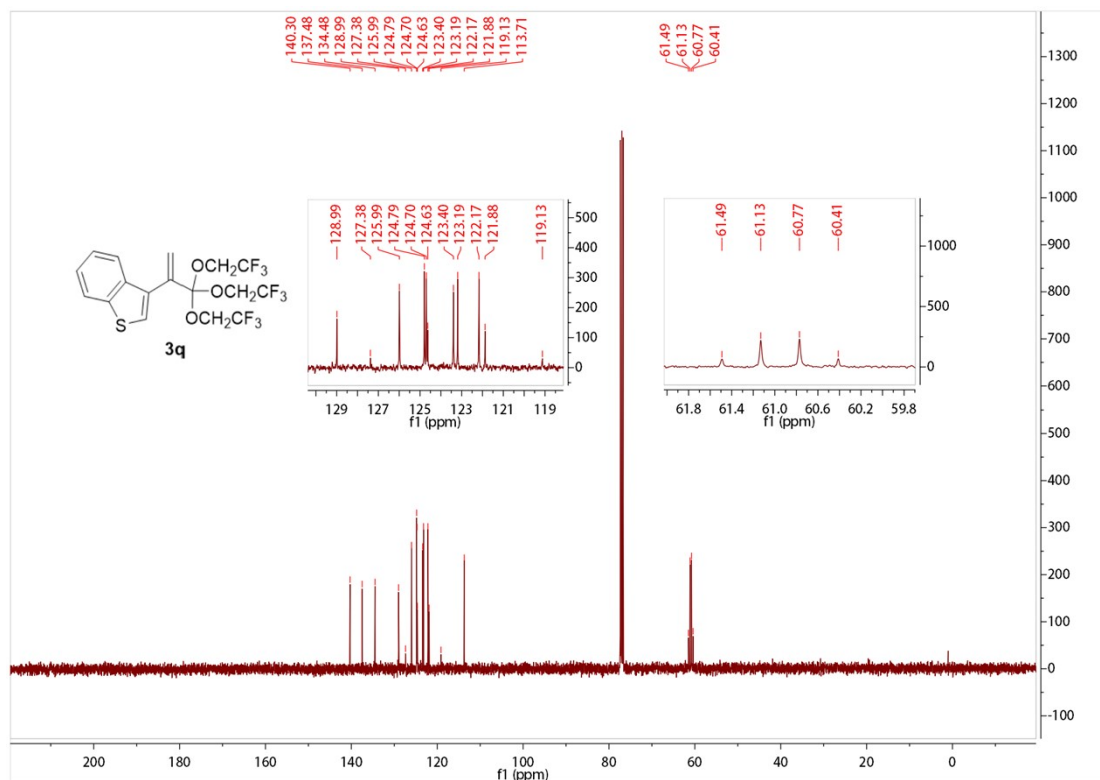
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3p



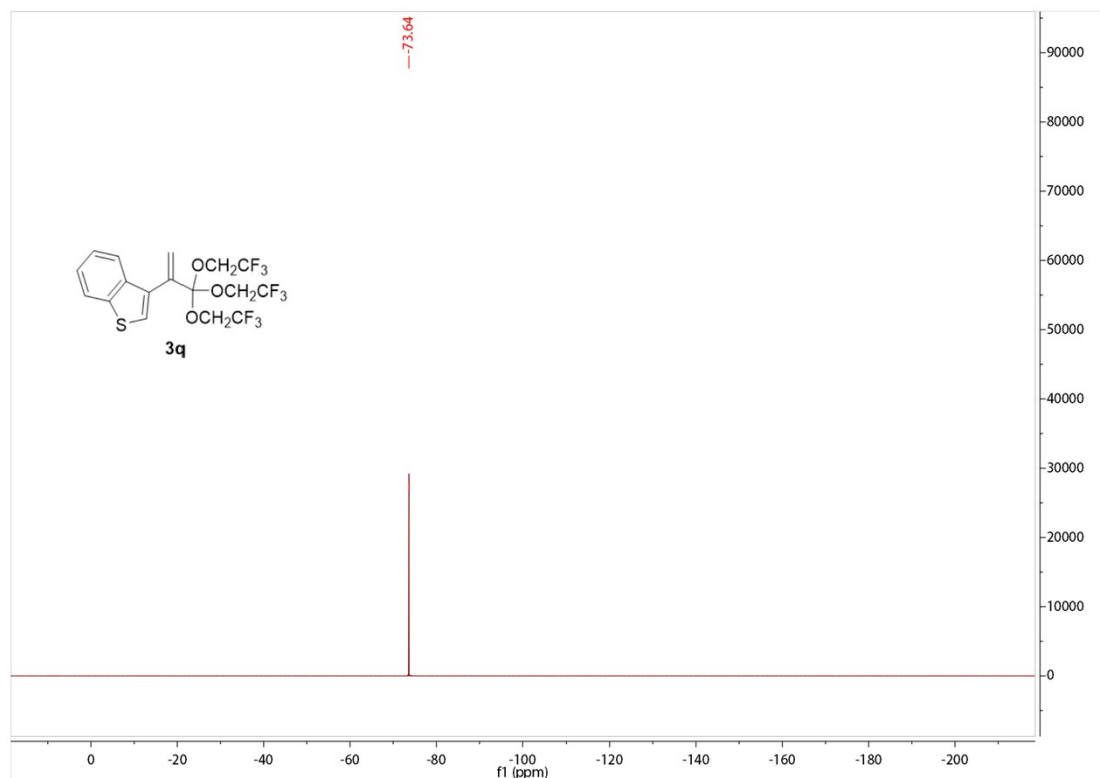
¹H NMR (400 MHz, CDCl₃) spectrum for 3q



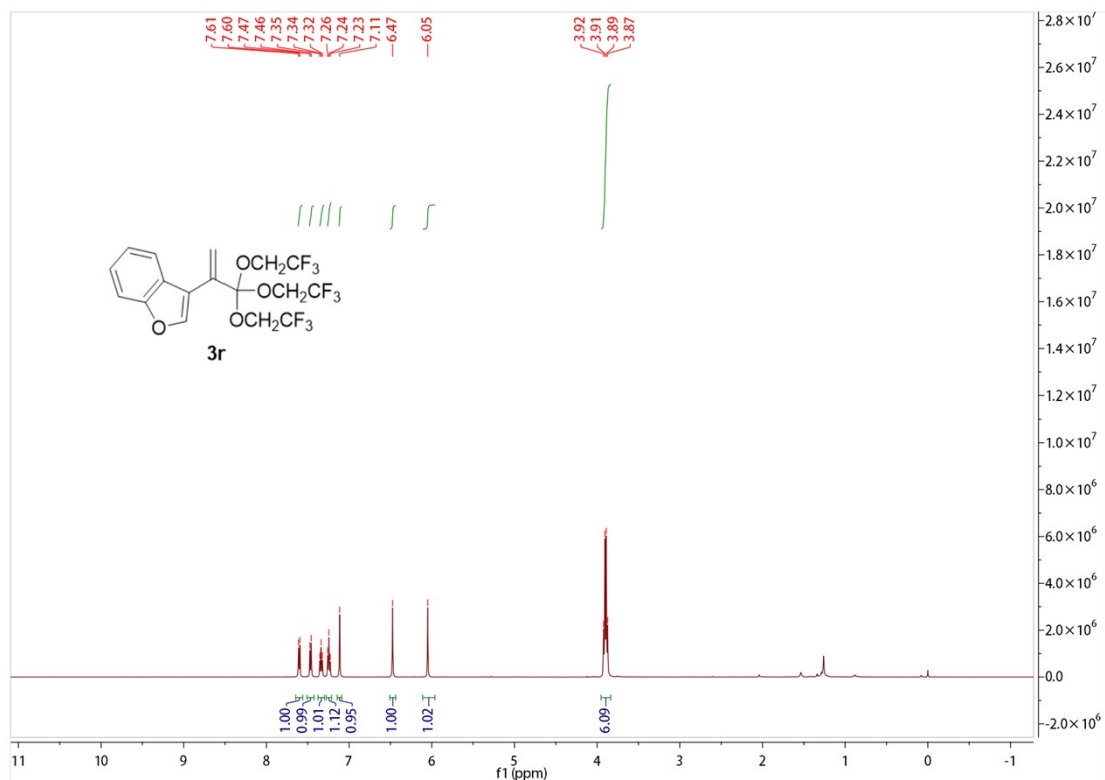
¹³C NMR (101 MHz, CDCl₃) spectrum for 3q



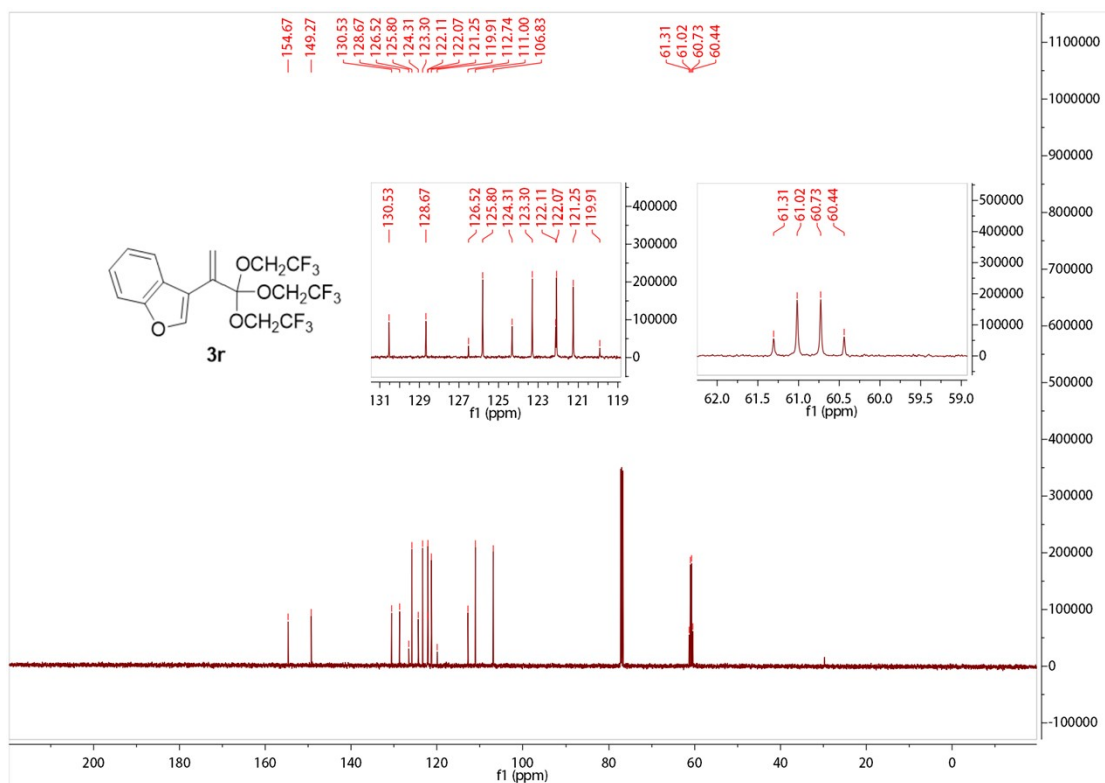
¹⁹F NMR (376 MHz, CDCl₃) spectrum for 3q



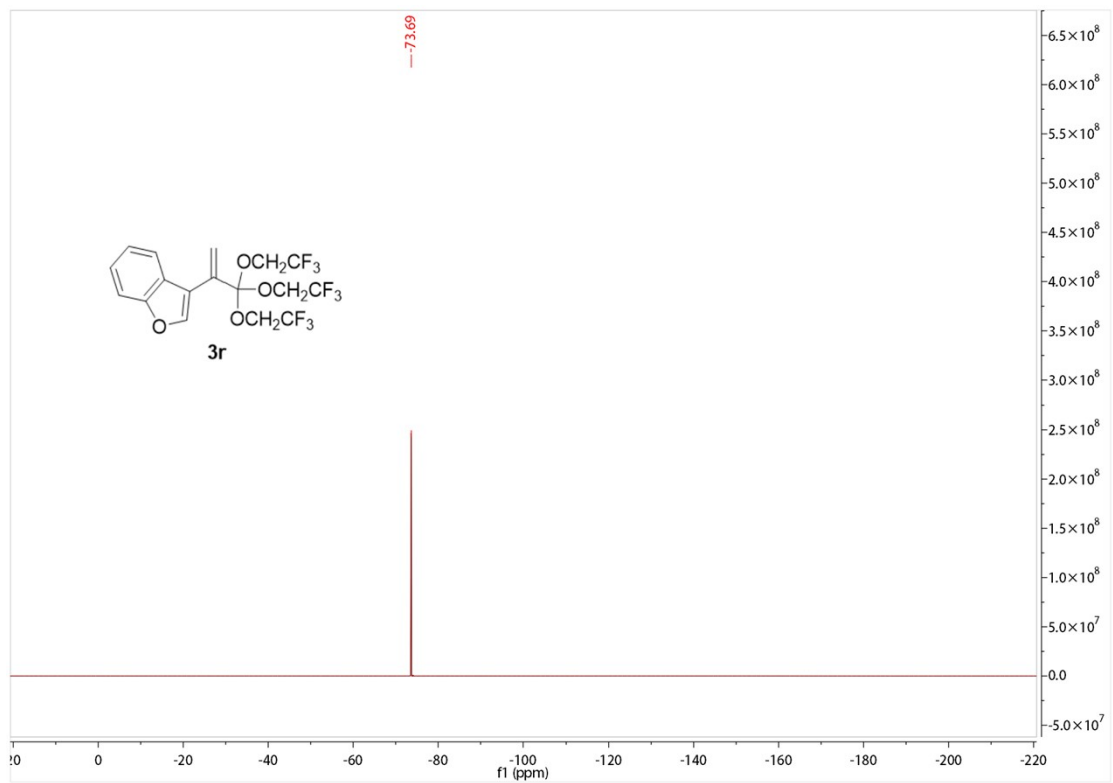
¹H NMR (500 MHz, CDCl₃) spectrum for 3r



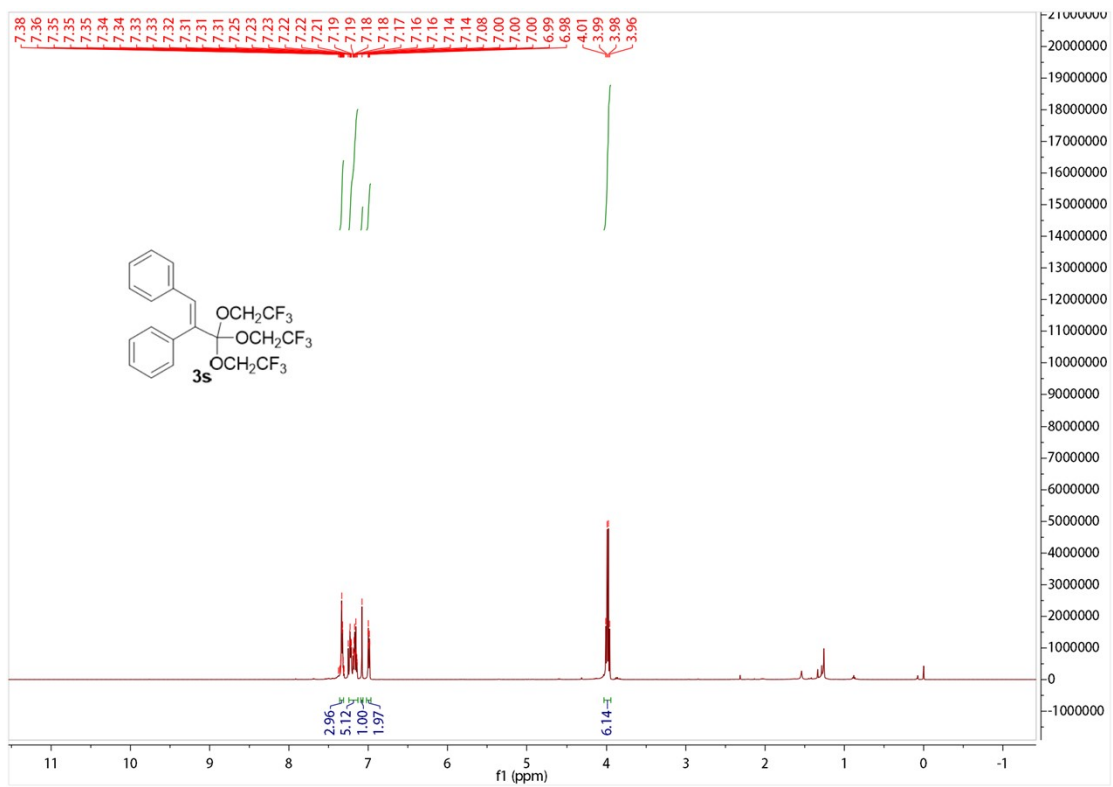
¹³C NMR (126 MHz, CDCl₃) spectrum for 3r



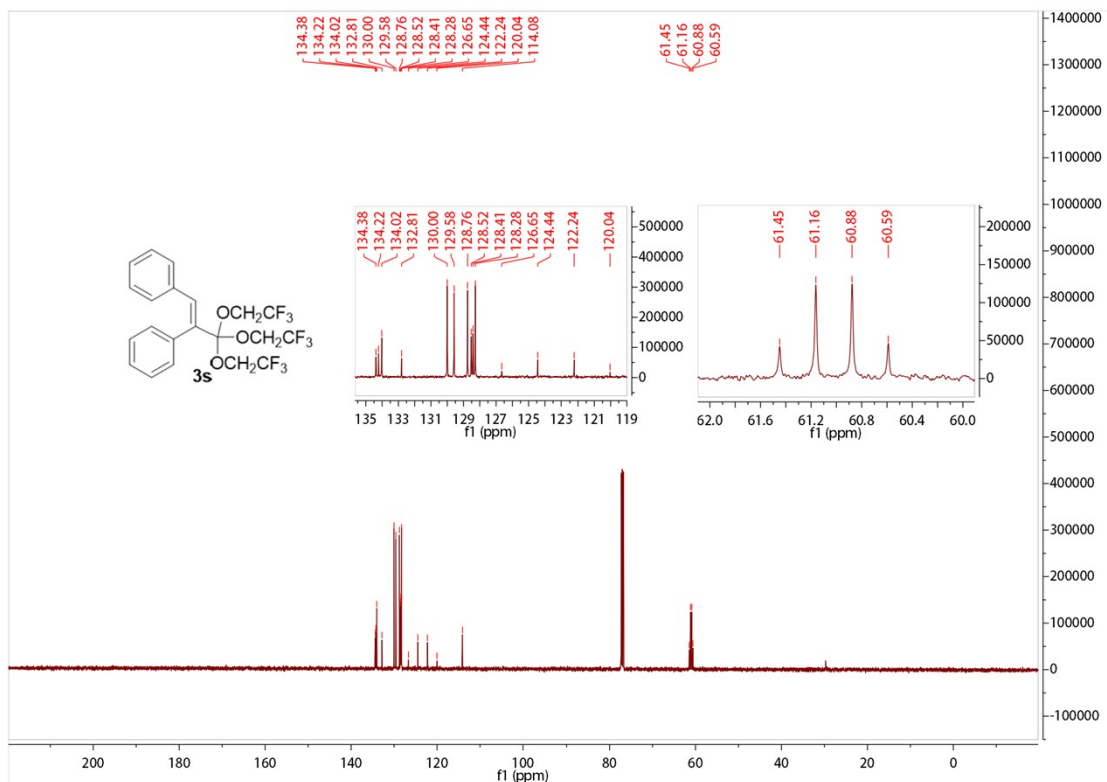
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3r



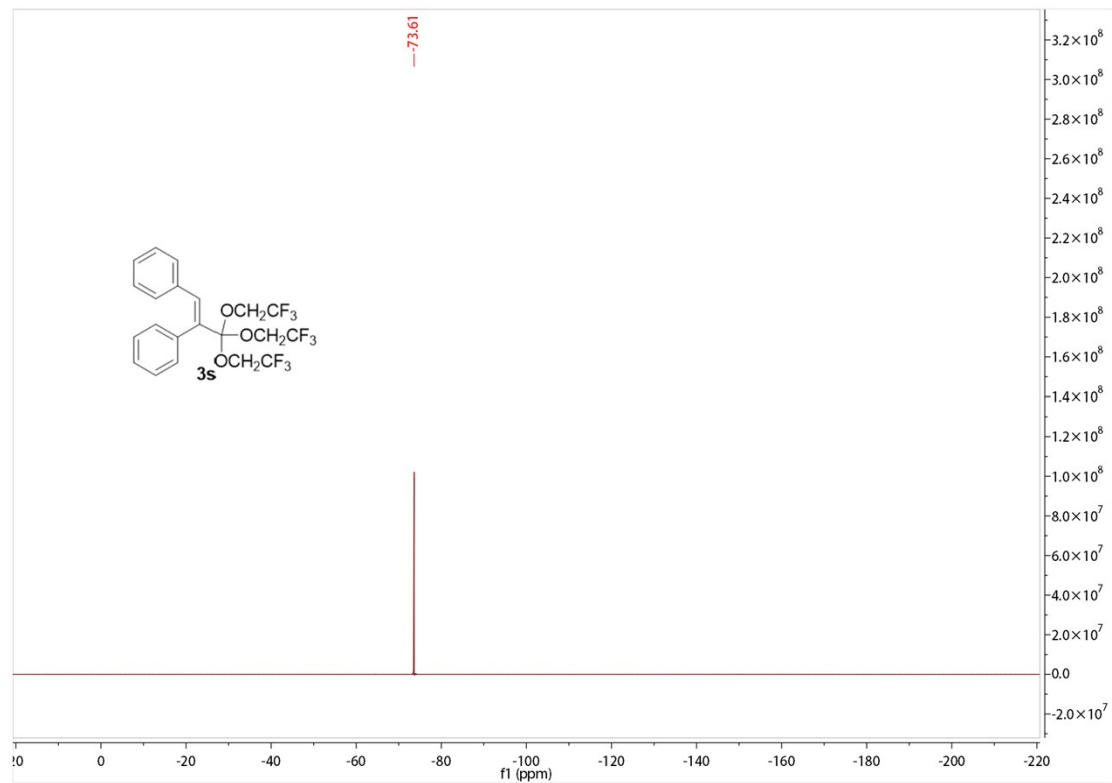
¹H NMR (500 MHz, CDCl₃) spectrum for 3s



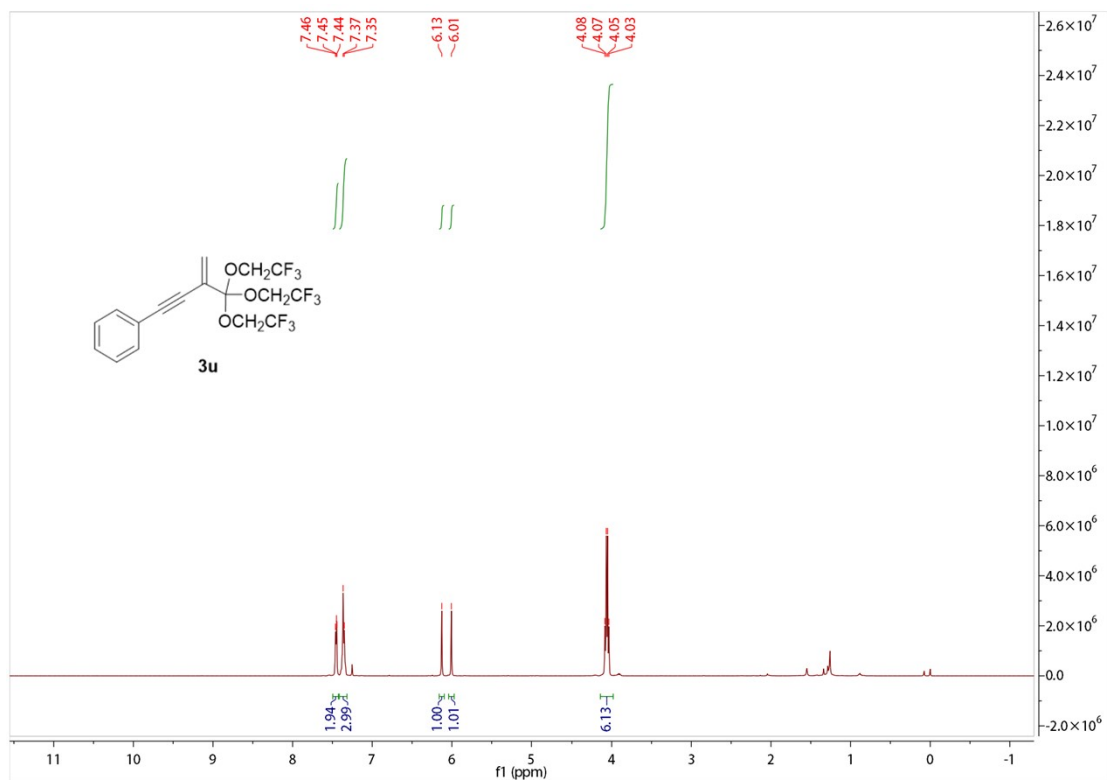
¹³C NMR (126 MHz, CDCl₃) spectrum for 3s



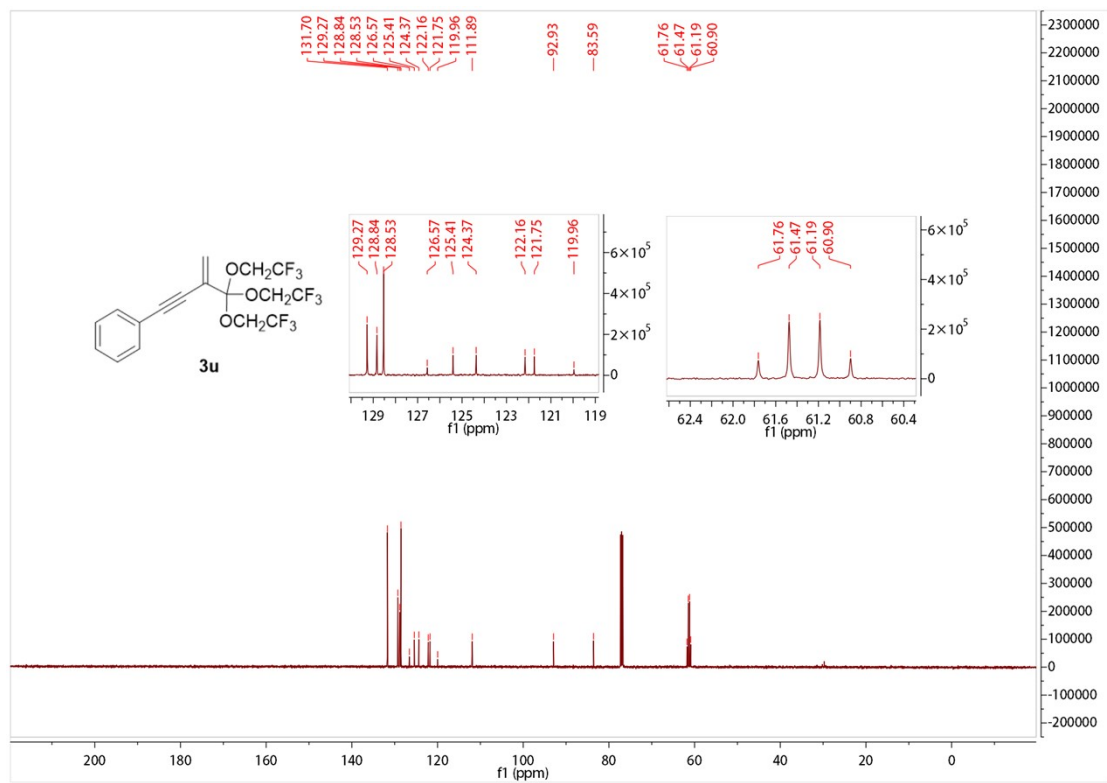
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3s



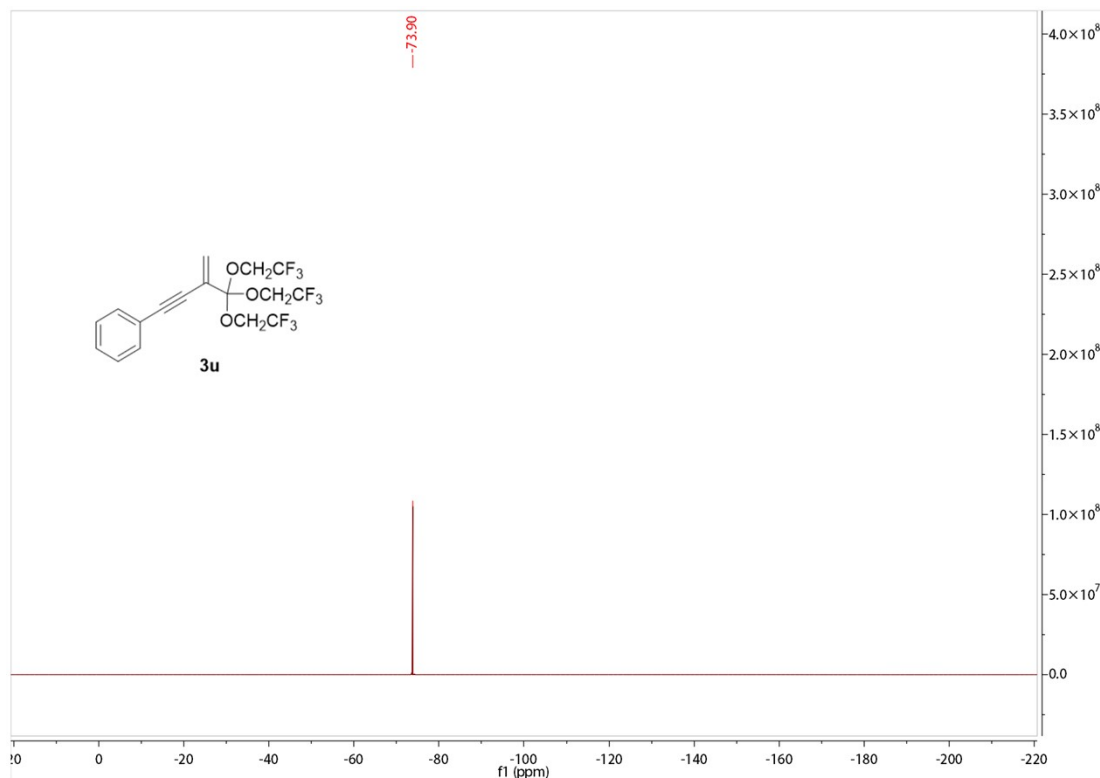
¹H NMR (500 MHz, CDCl₃) spectrum for 3u



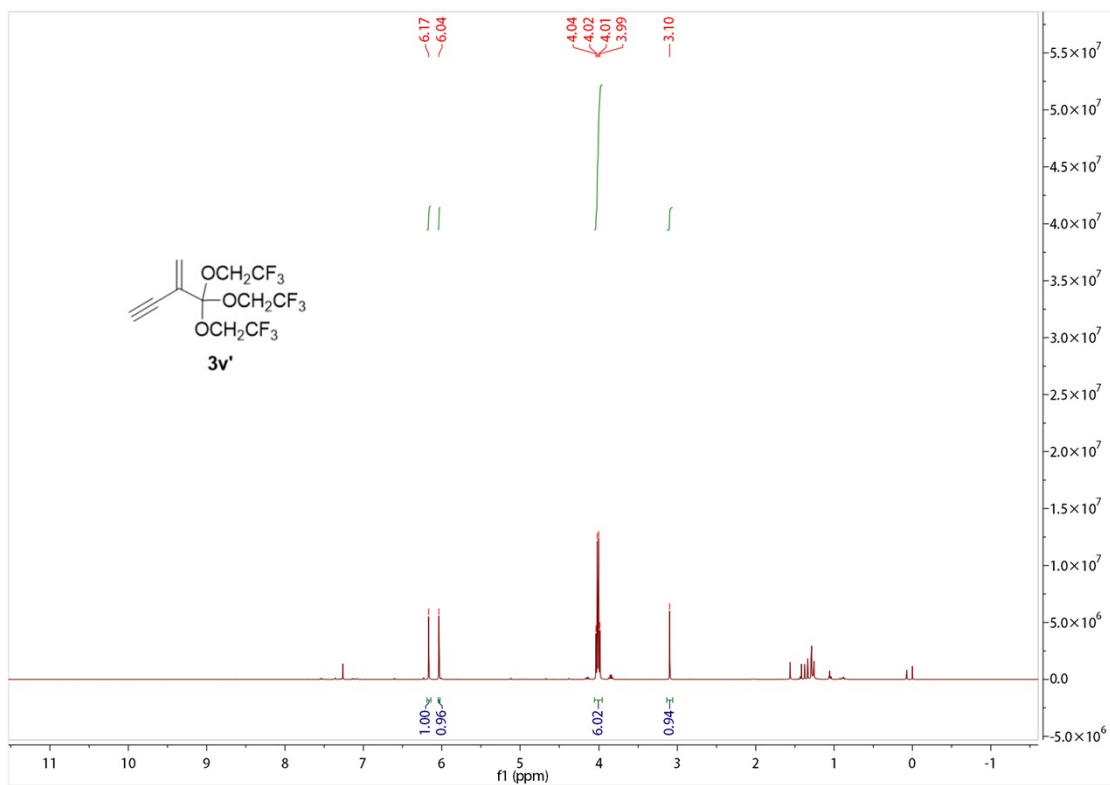
¹³C NMR (126 MHz, CDCl₃) spectrum for 3u



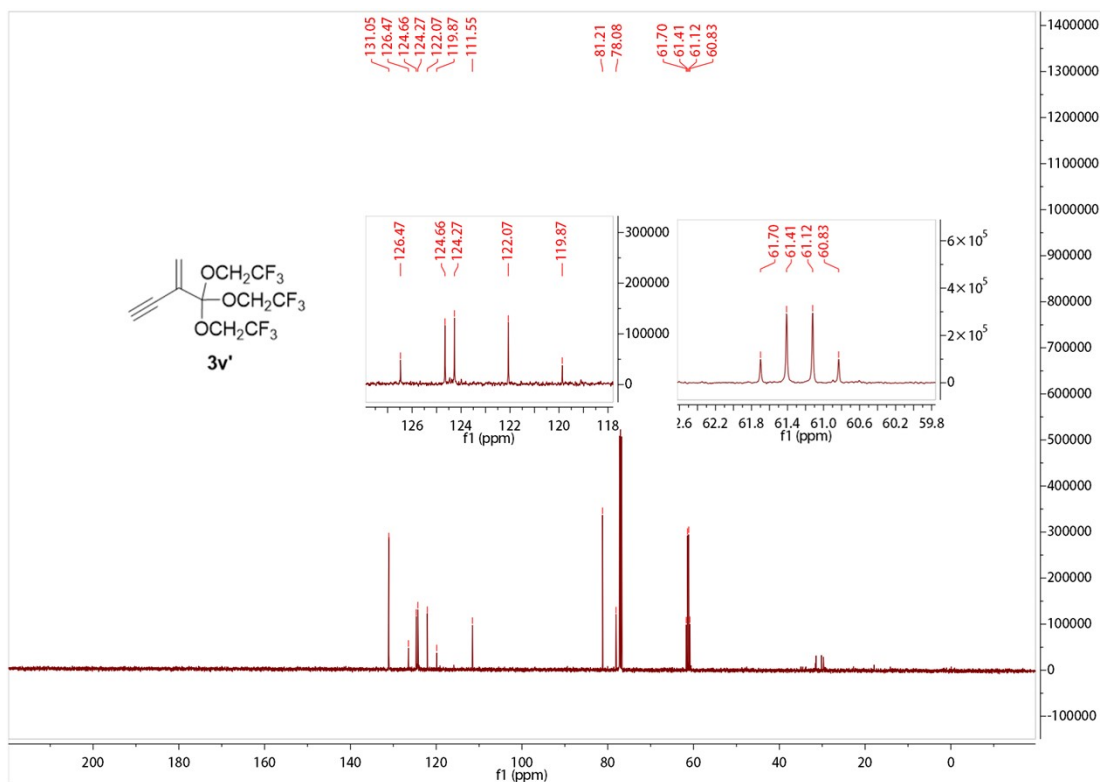
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3u



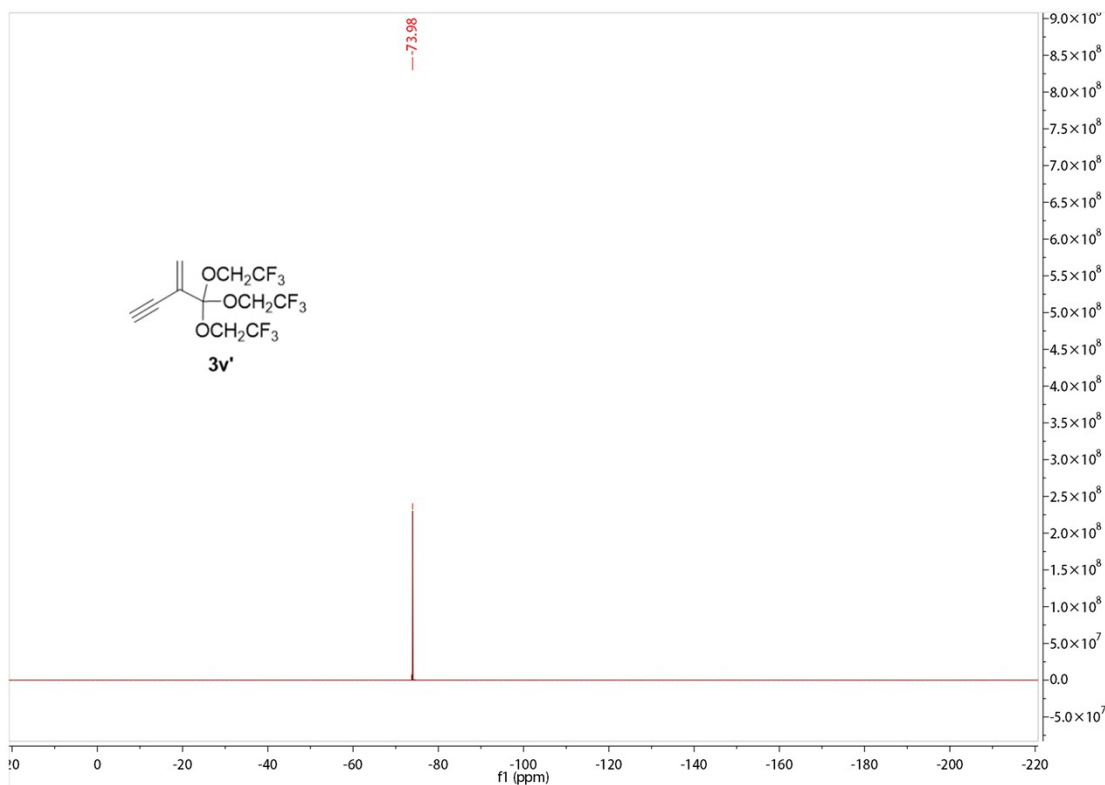
^1H NMR (500 MHz, CDCl_3) spectrum for **3v'**



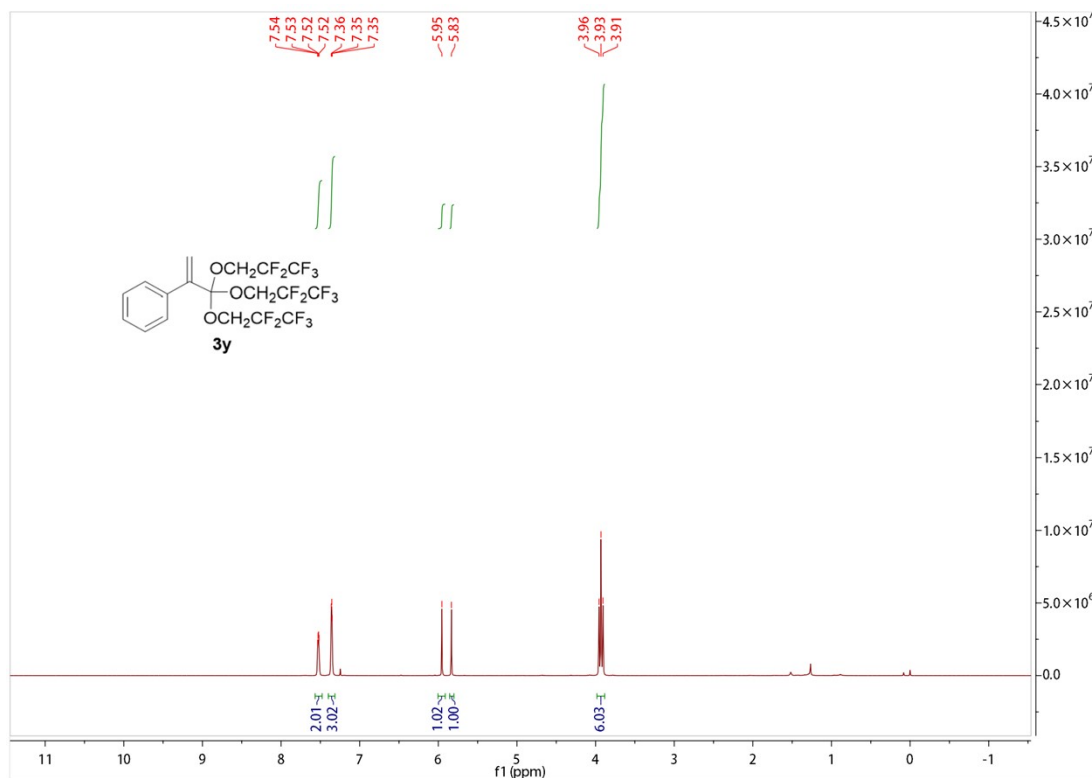
^{13}C NMR (126 MHz, CDCl_3) spectrum for **3v'**



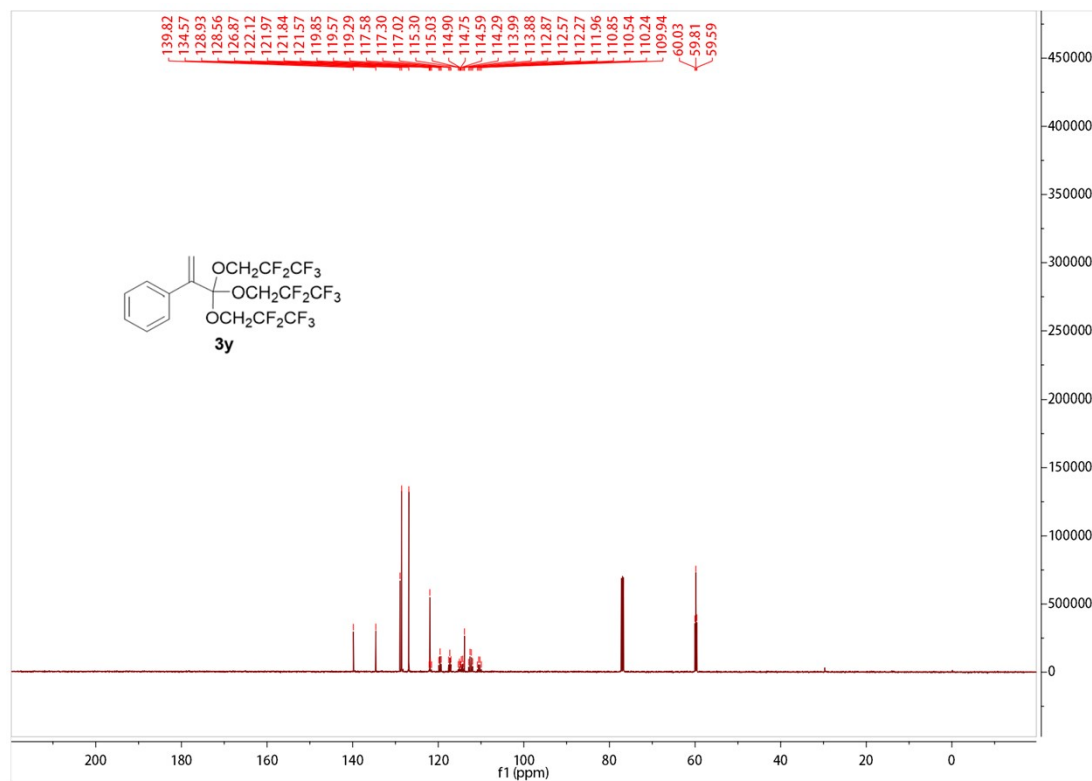
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3v'



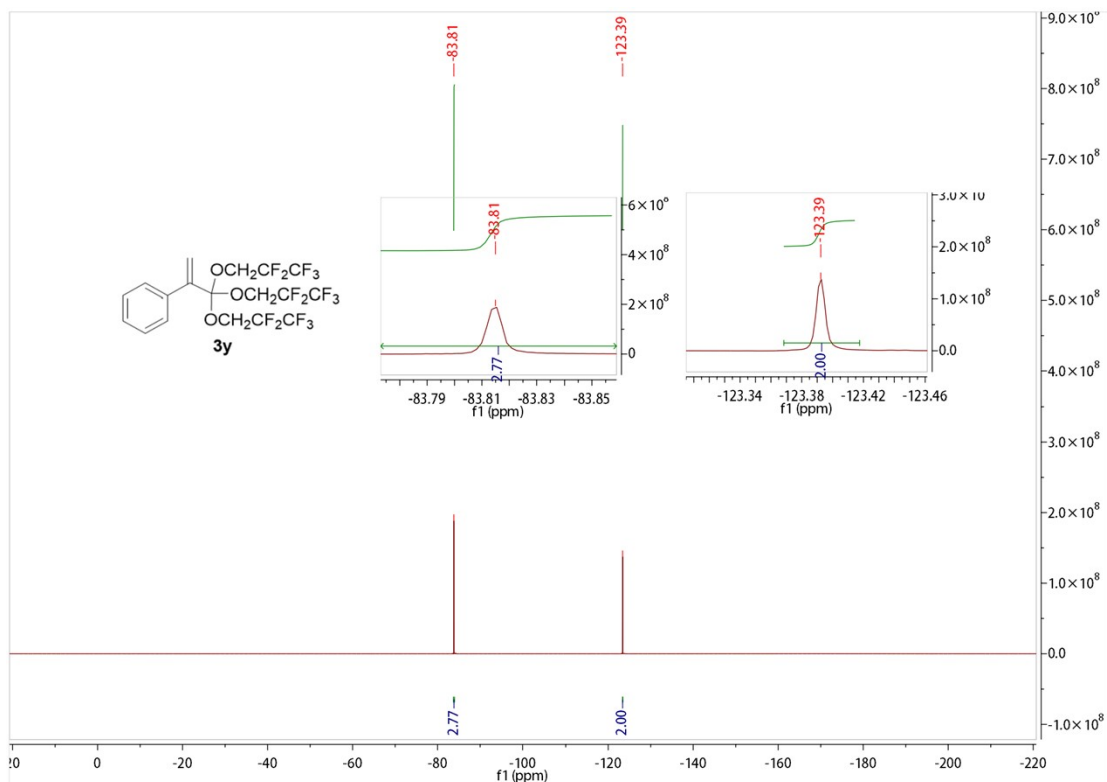
¹H NMR (500 MHz, CDCl₃) spectrum for 3y



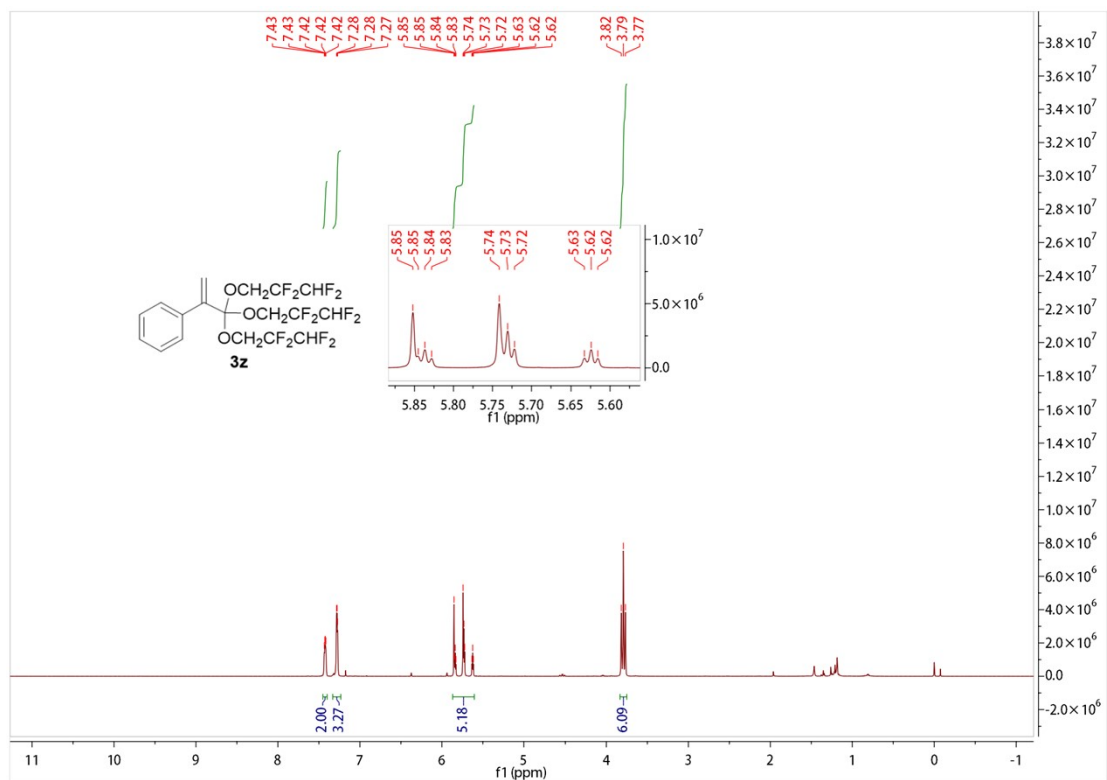
¹³C NMR (126 MHz, CDCl₃) spectrum for 3y



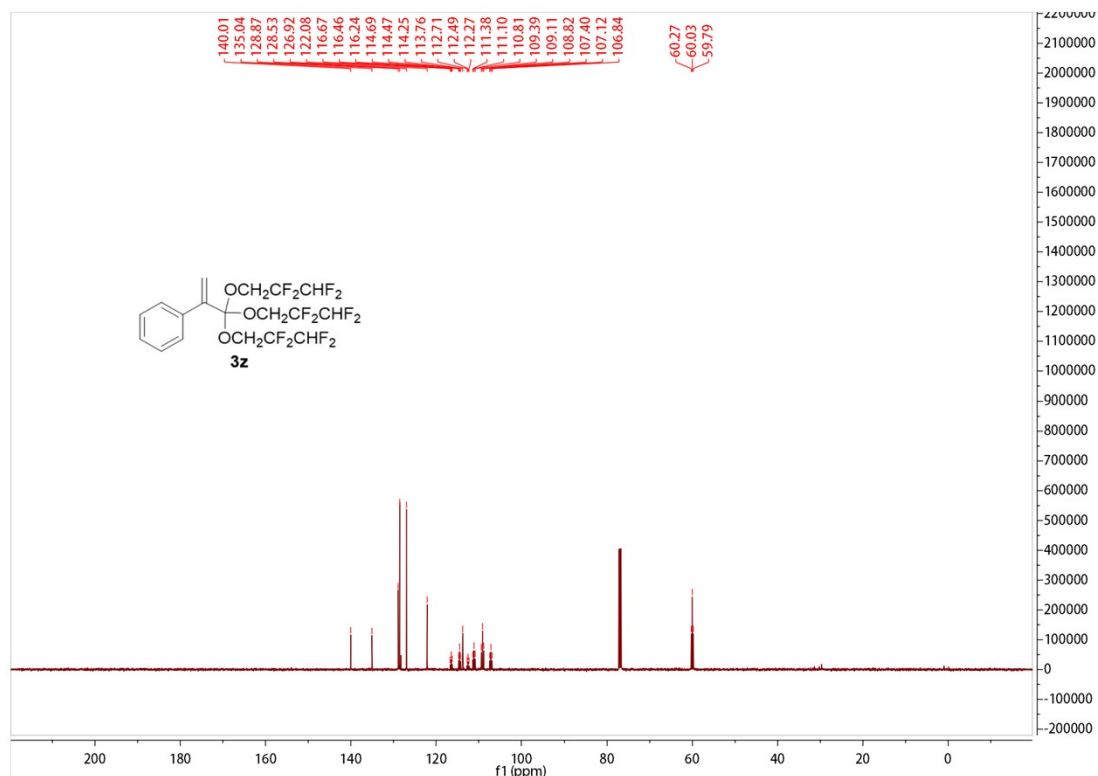
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3y



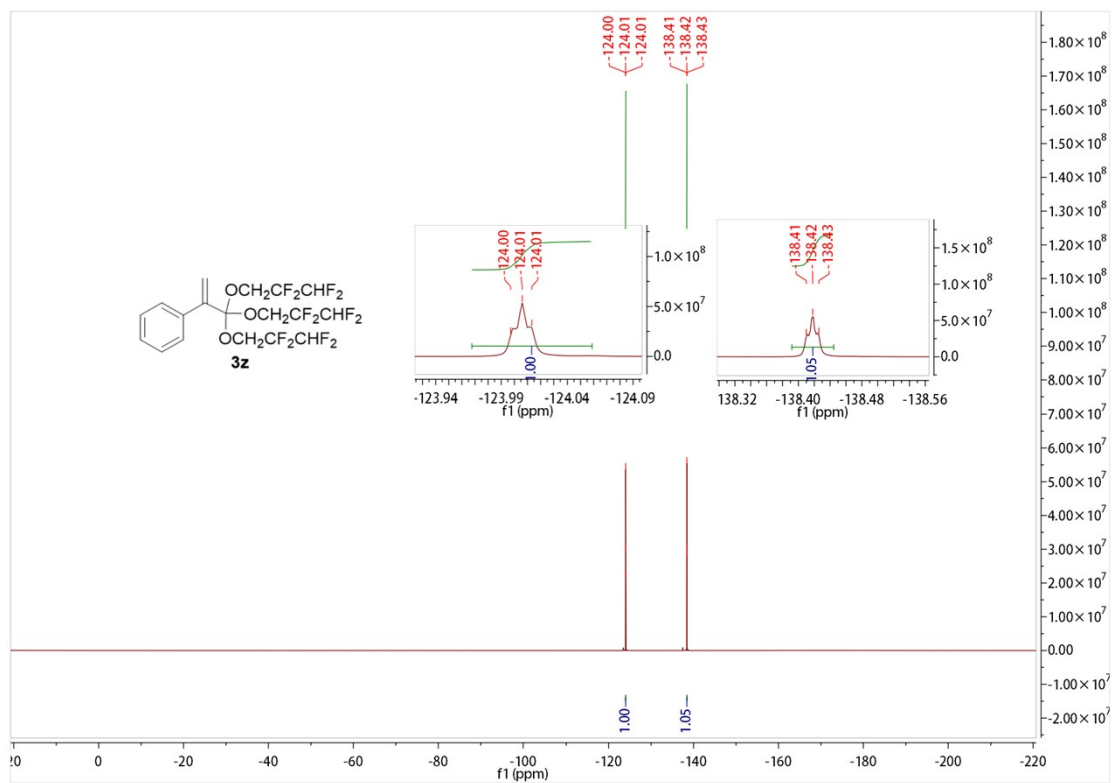
¹H NMR (500 MHz, CDCl₃) spectrum for 3z



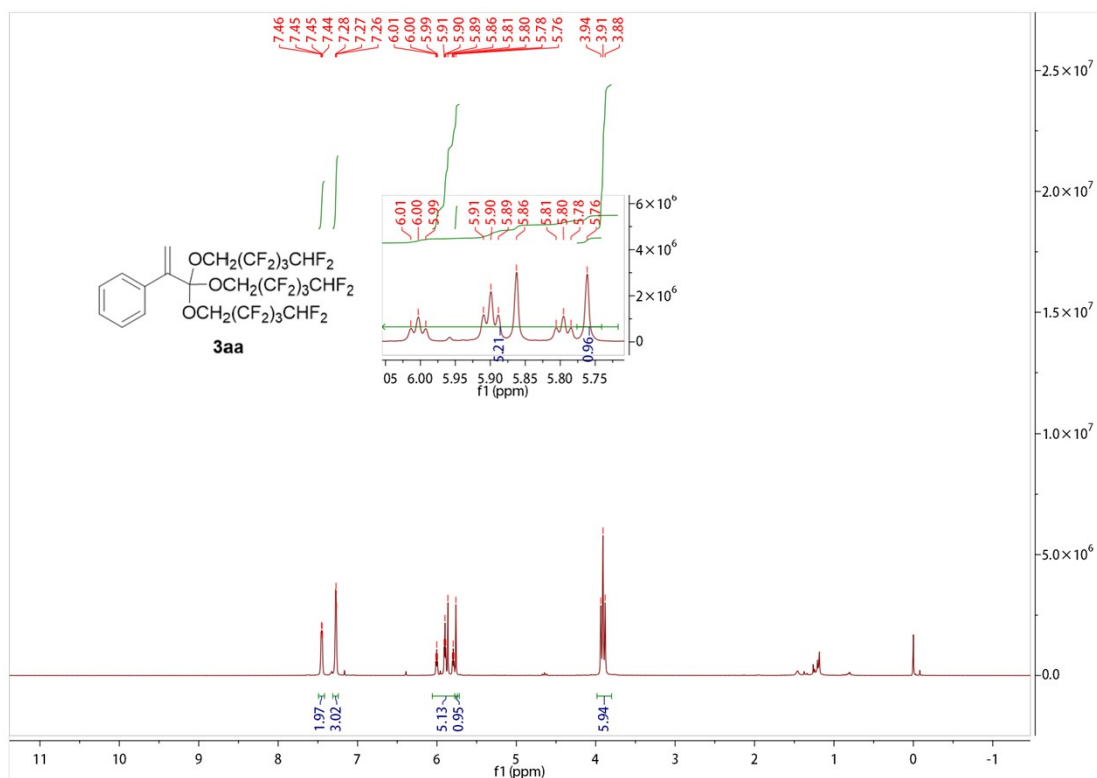
¹³C NMR (126 MHz, CDCl₃) spectrum for 3z



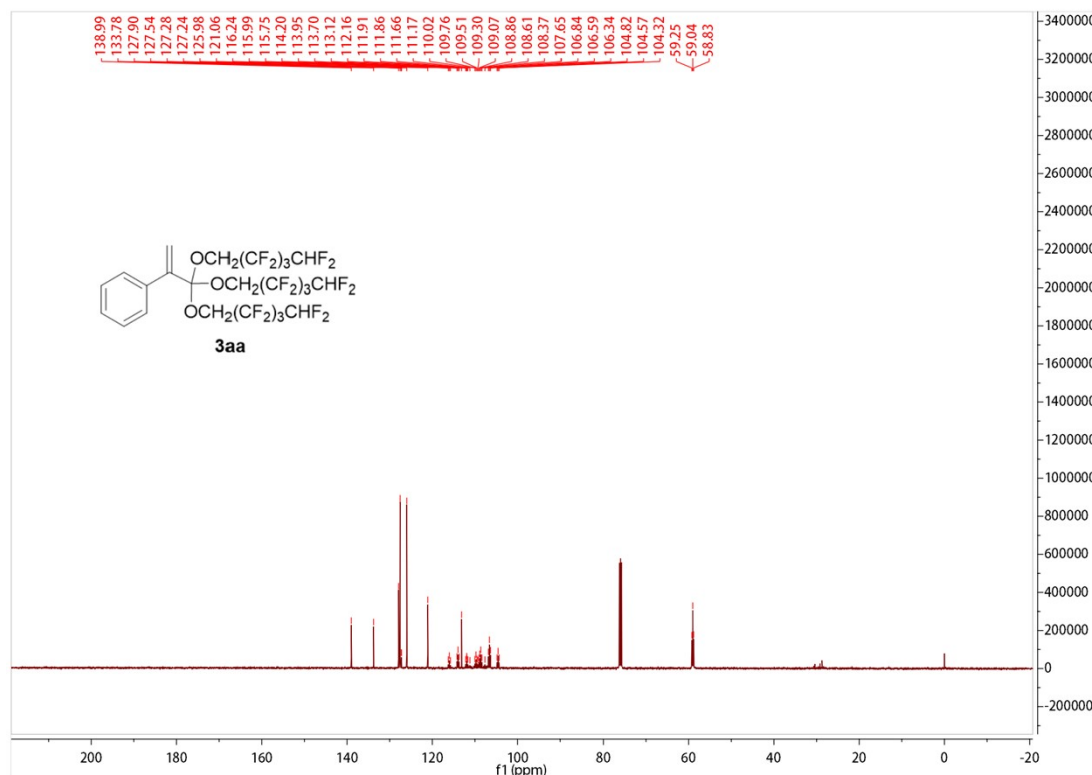
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3z



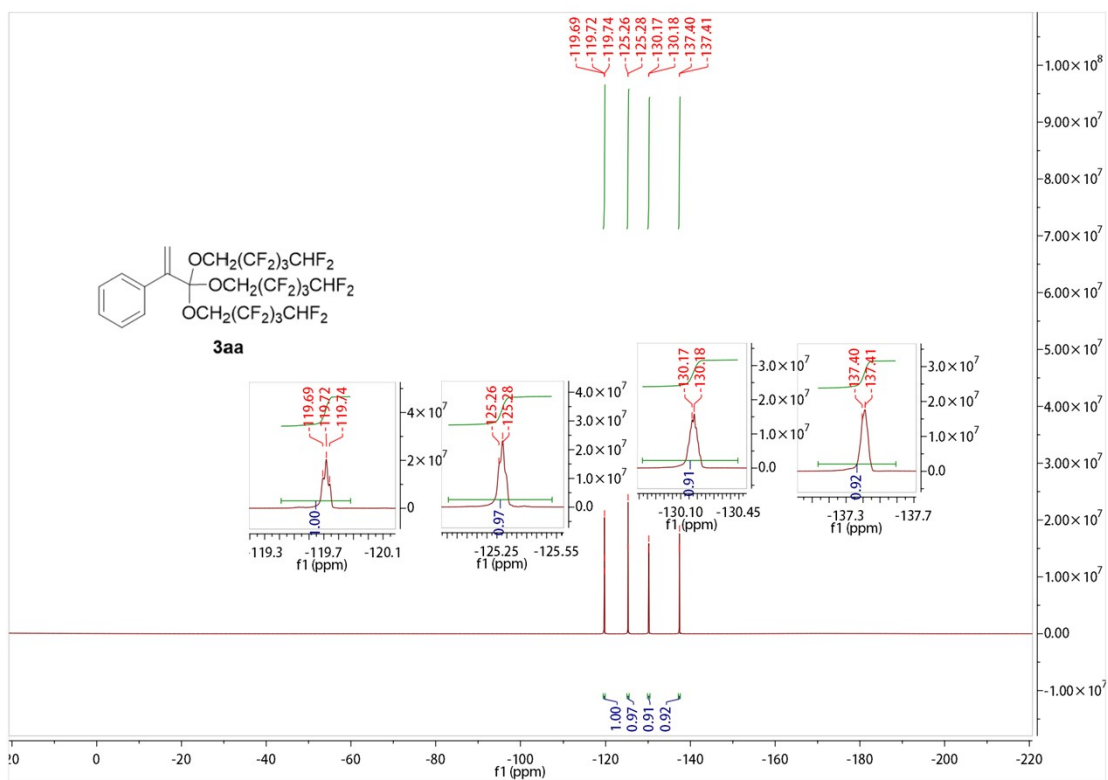
¹H NMR (500 MHz, CDCl₃) spectrum for 3aa



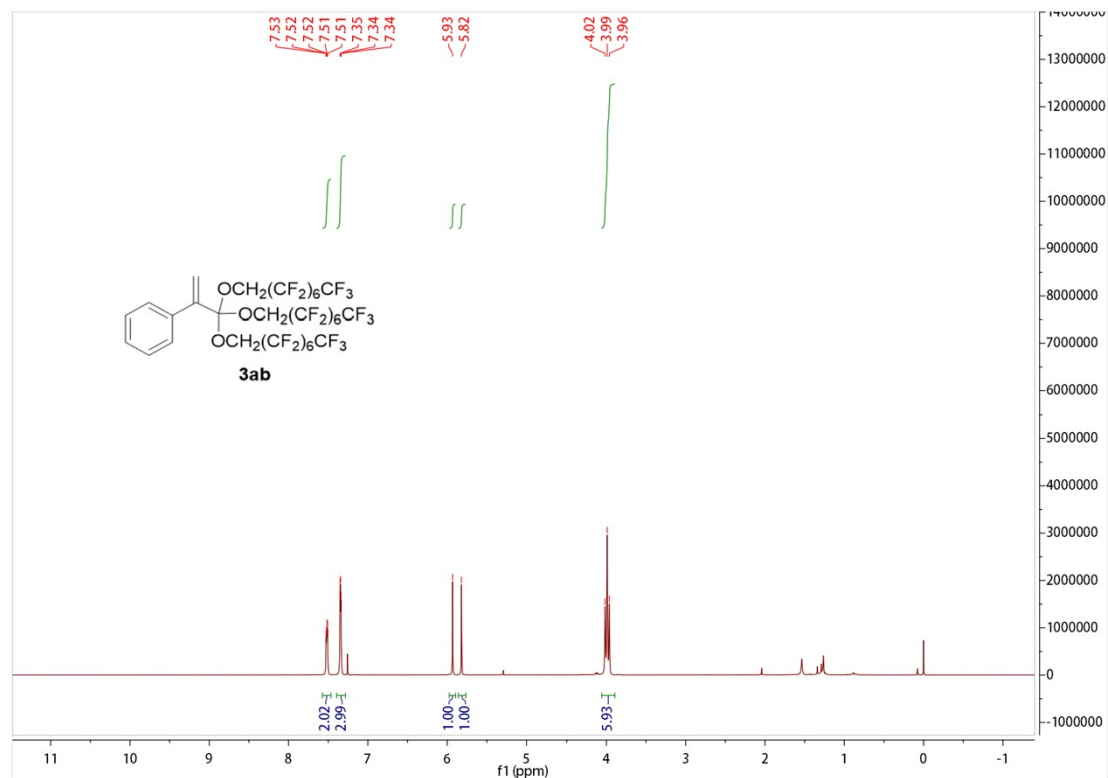
¹³C NMR (126 MHz, CDCl₃) spectrum for 3aa



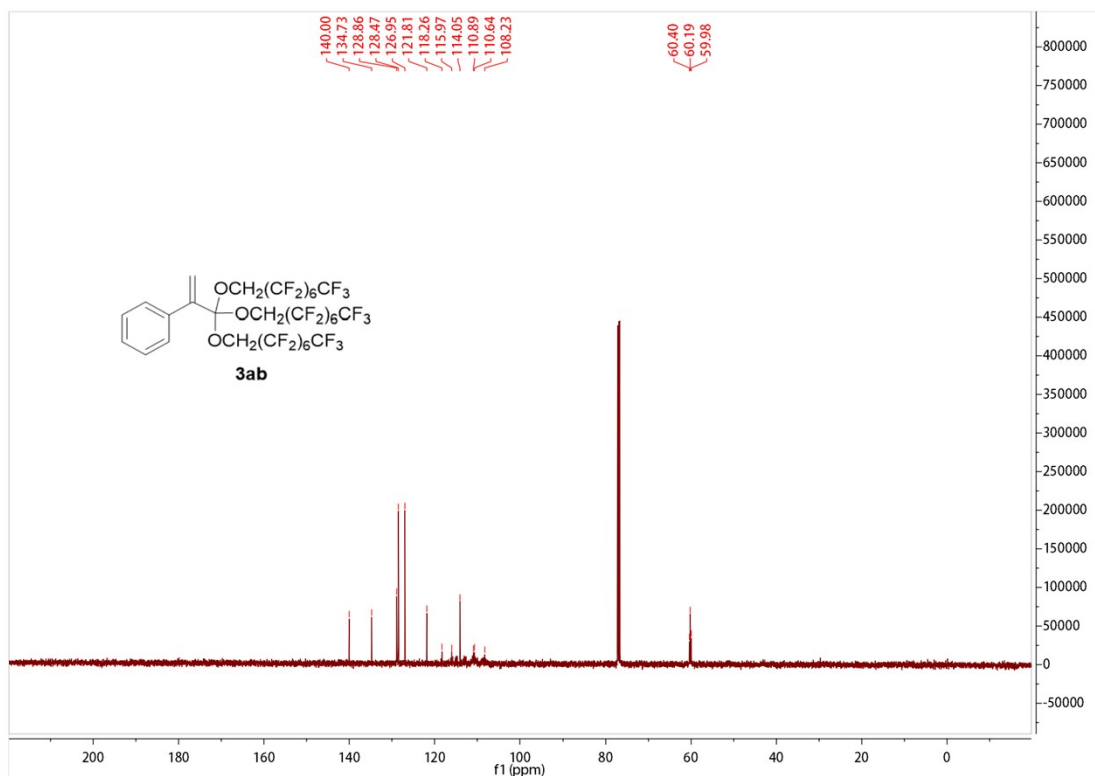
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3aa



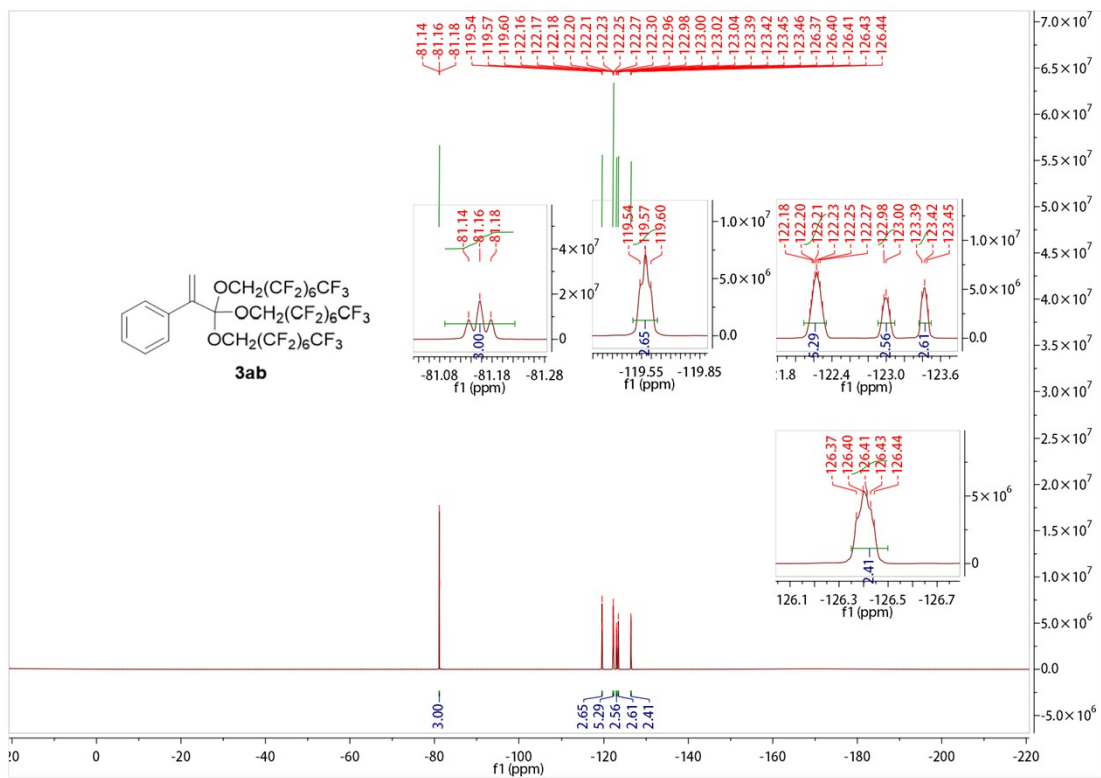
^1H NMR (500 MHz, CDCl_3) spectrum for **3ab**



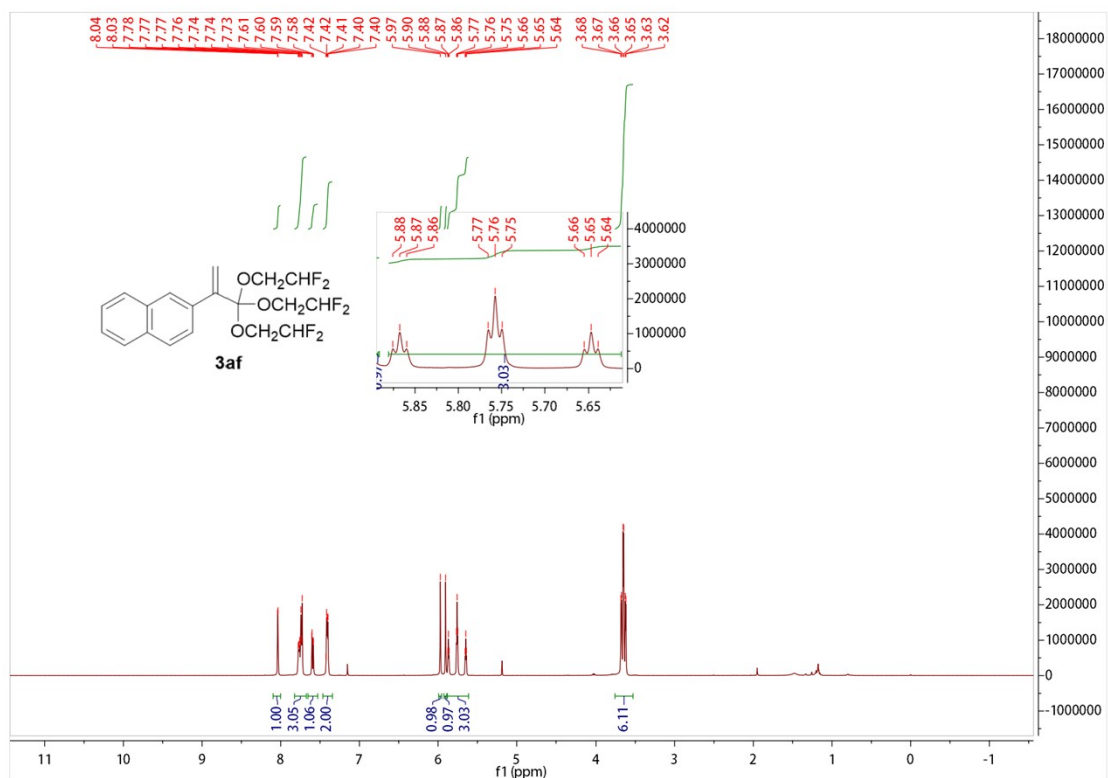
^{13}C NMR (126 MHz, CDCl_3) spectrum for **3ab**



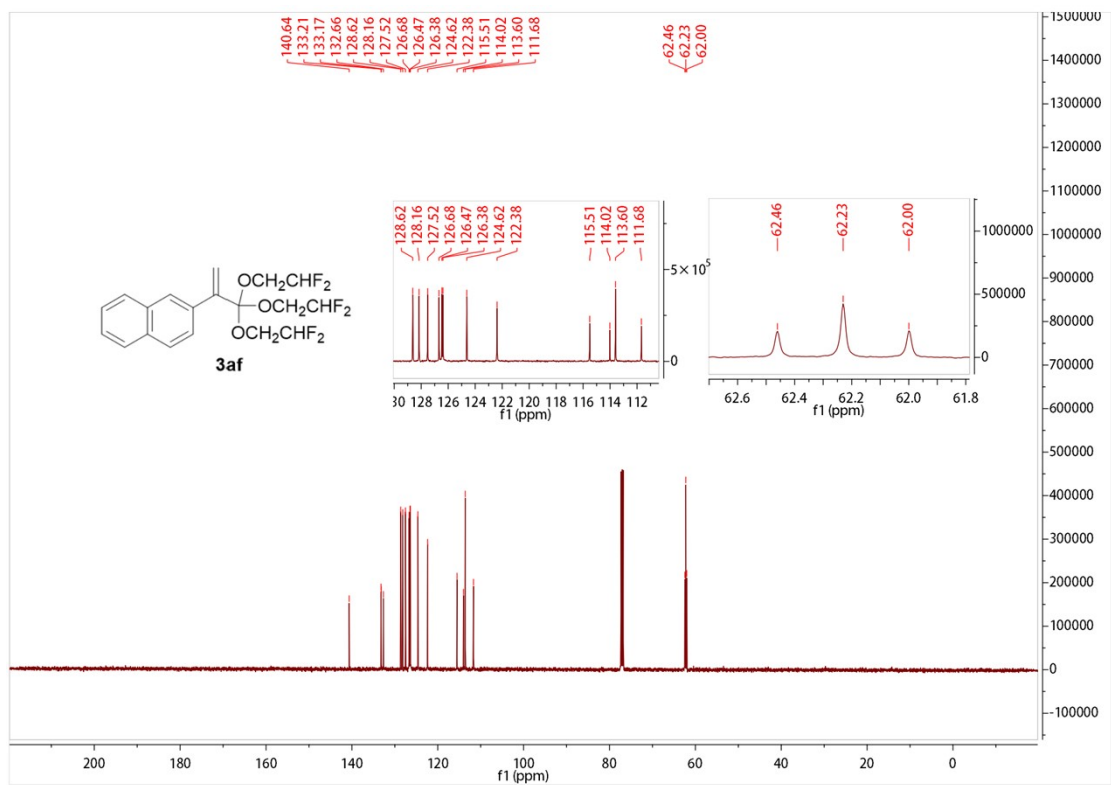
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3ab



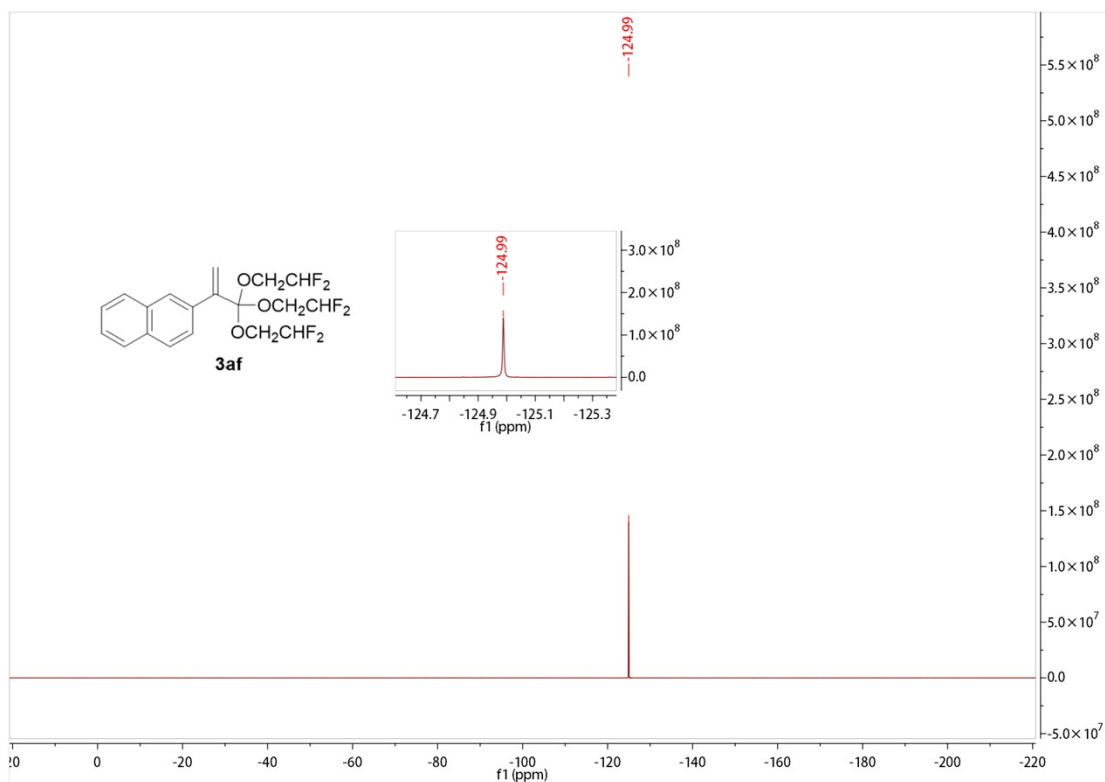
¹H NMR (500 MHz, CDCl₃) spectrum for 3af



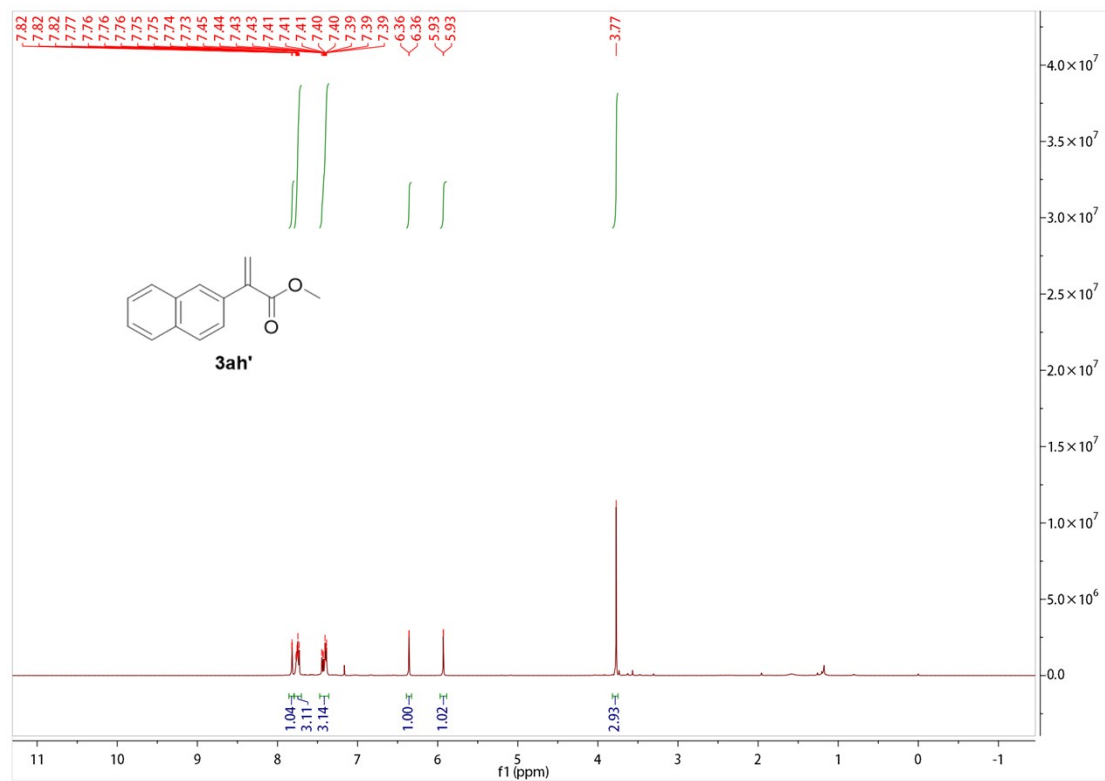
¹³C NMR (126 MHz, CDCl₃) spectrum for 3af



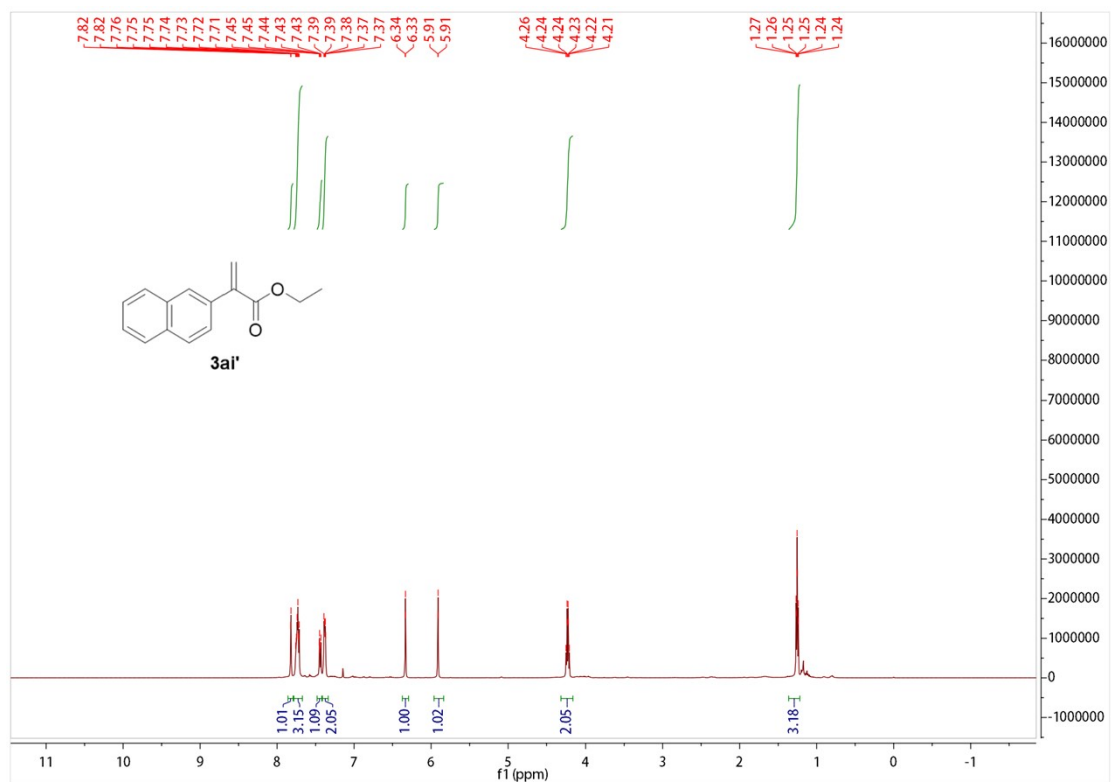
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3af



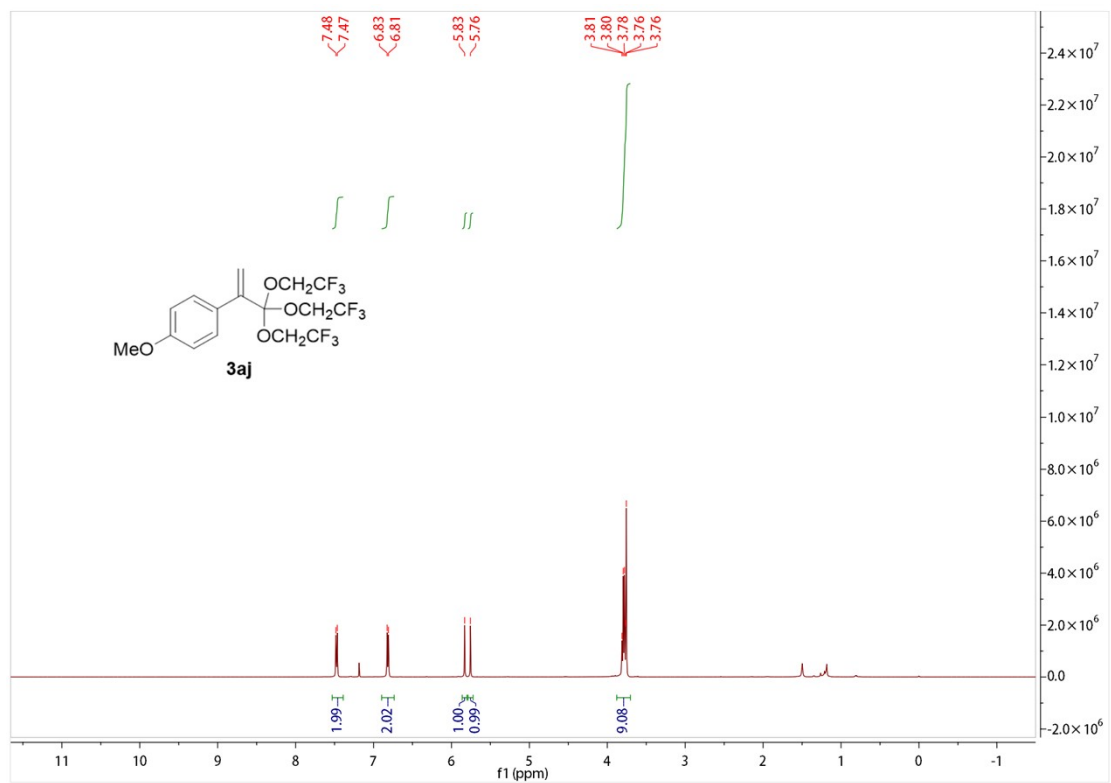
^1H NMR (500 MHz, CDCl_3) spectrum for **3ah'**



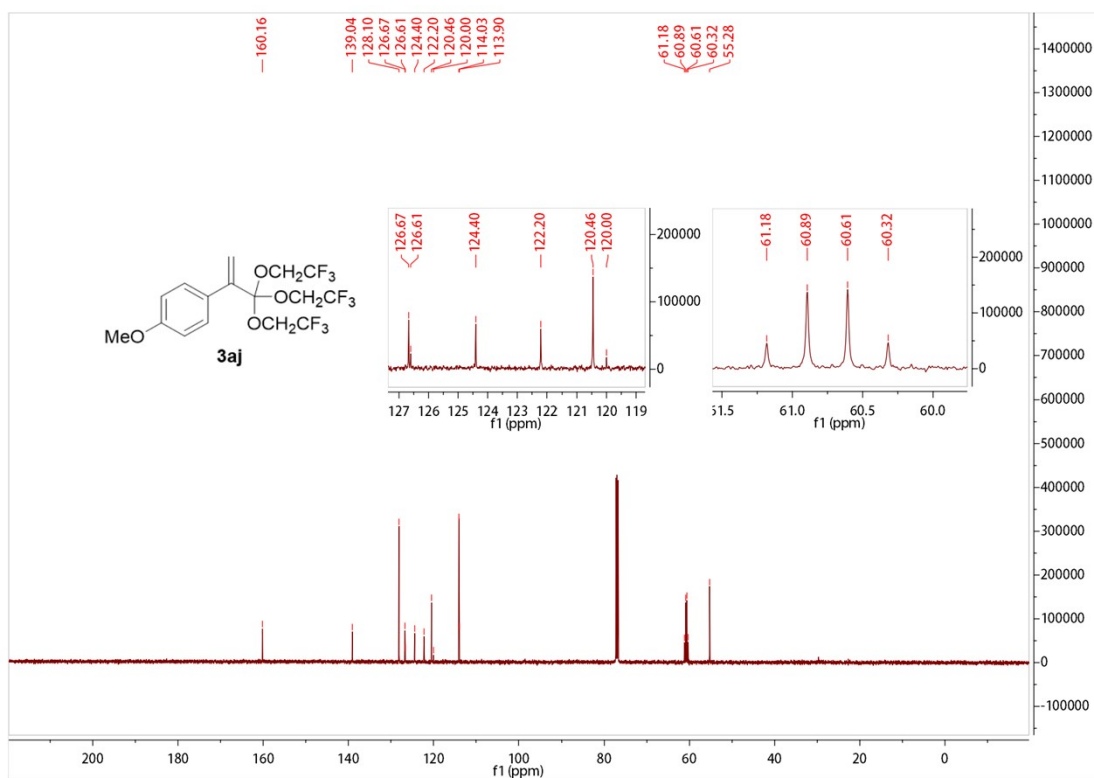
^1H NMR (500 MHz, CDCl_3) spectrum for **3ai'**



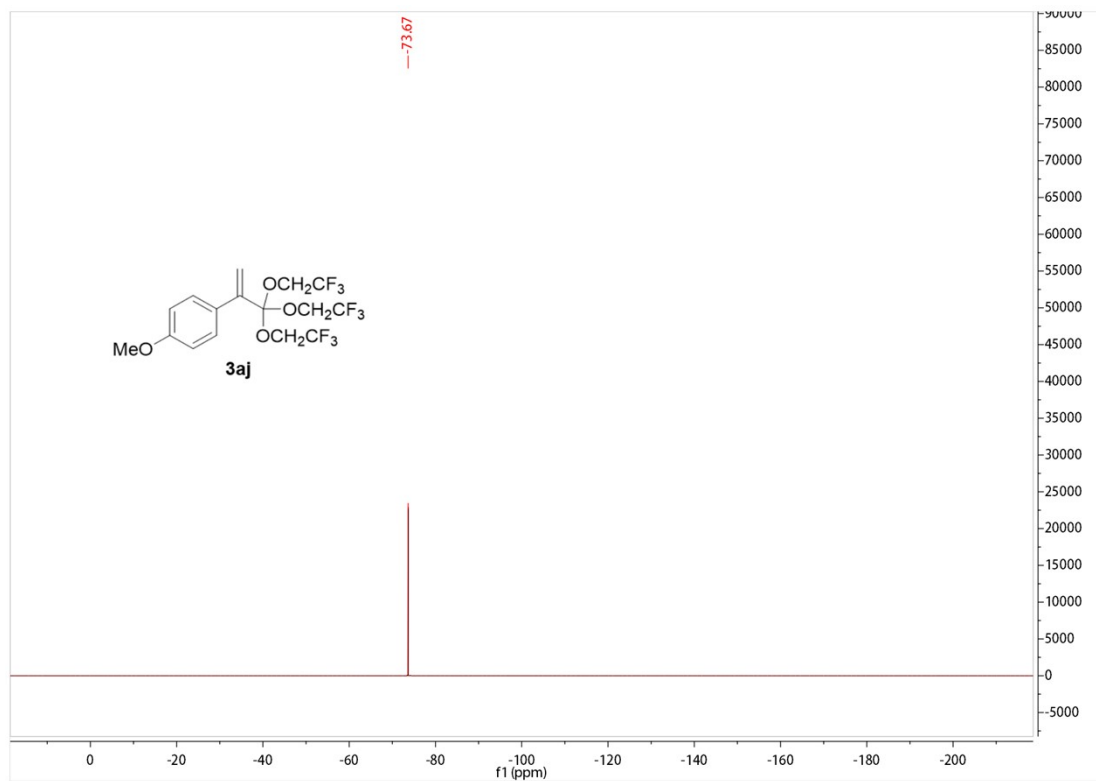
¹H NMR (500 MHz, CDCl₃) spectrum for 3aj



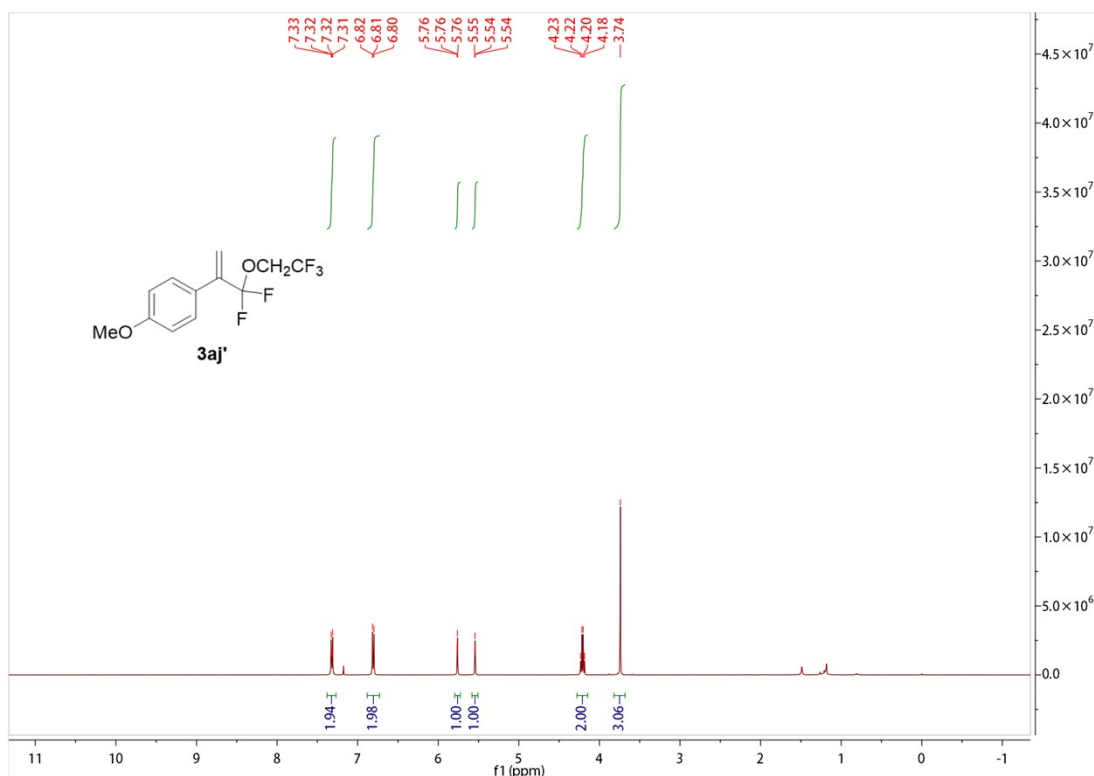
¹³C NMR (126 MHz, CDCl₃) spectrum for 3aj



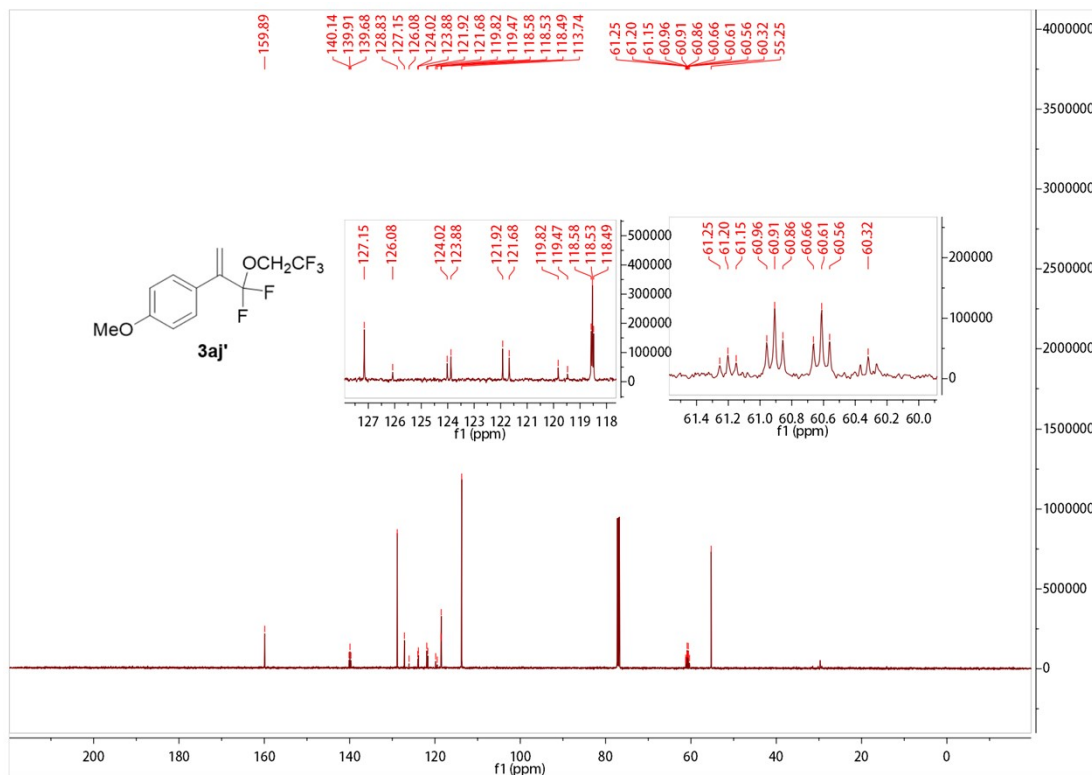
¹⁹F NMR (376 MHz, CDCl₃) spectrum for 3aj



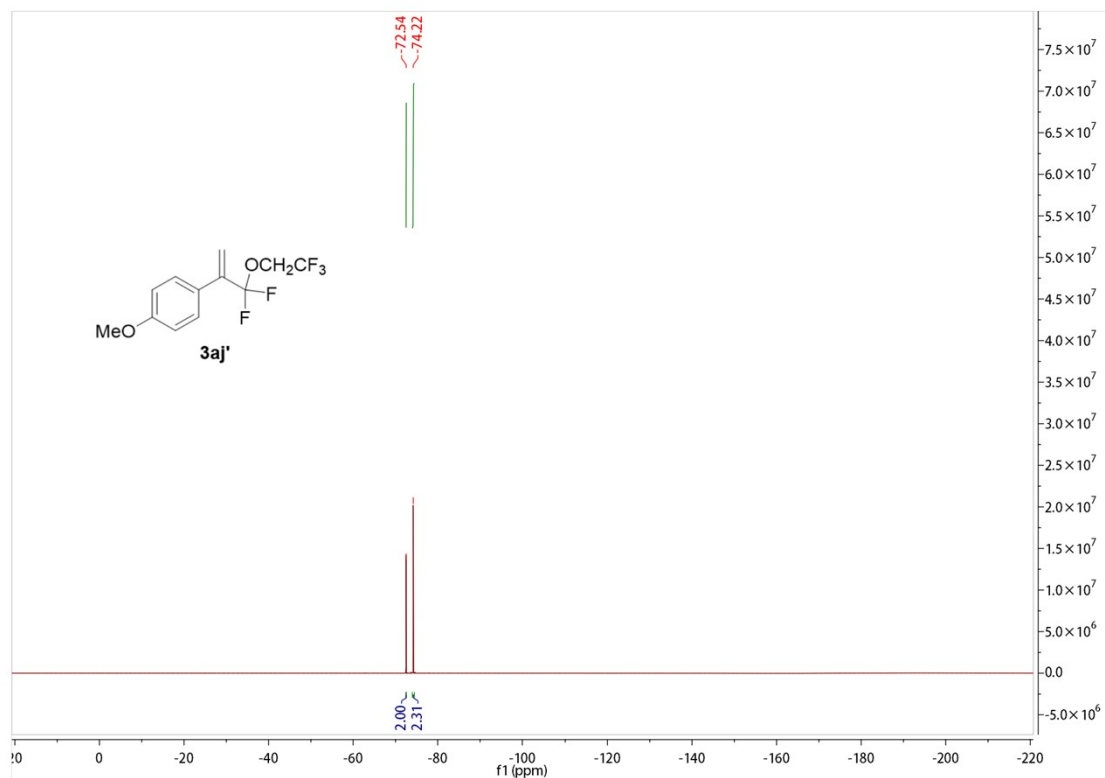
¹H NMR (500 MHz, CDCl₃) spectrum for 3aj'



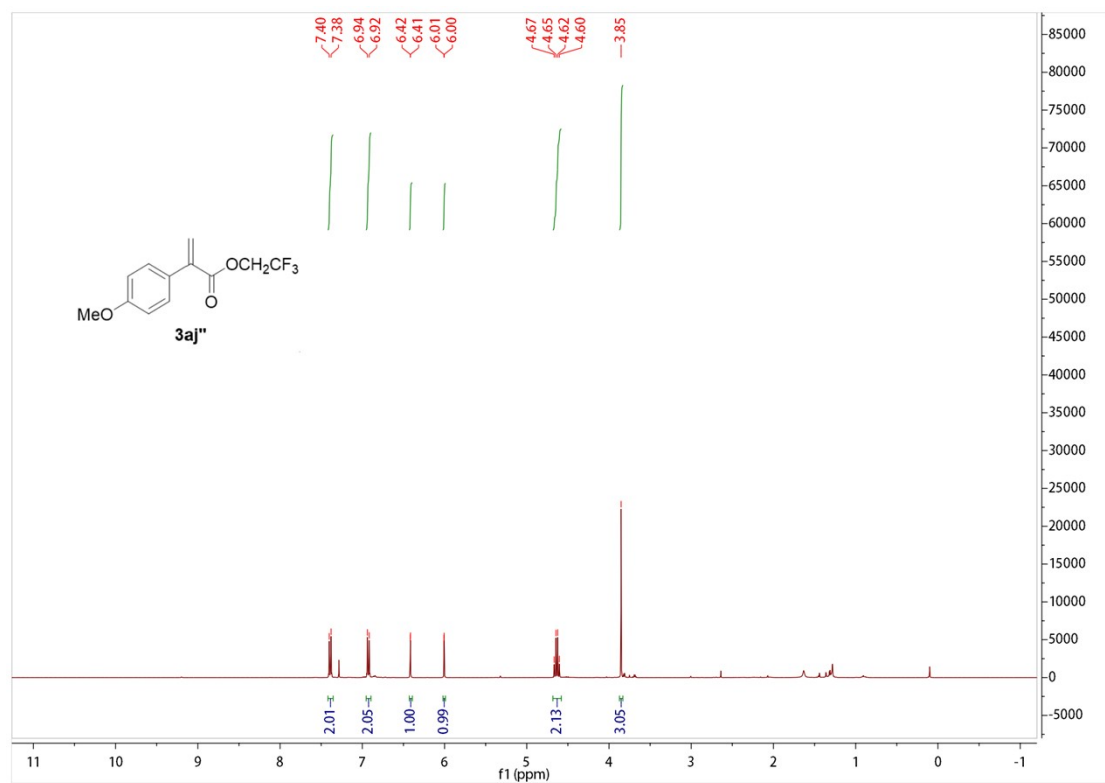
¹³C NMR (126 MHz, CDCl₃) spectrum for 3aj'



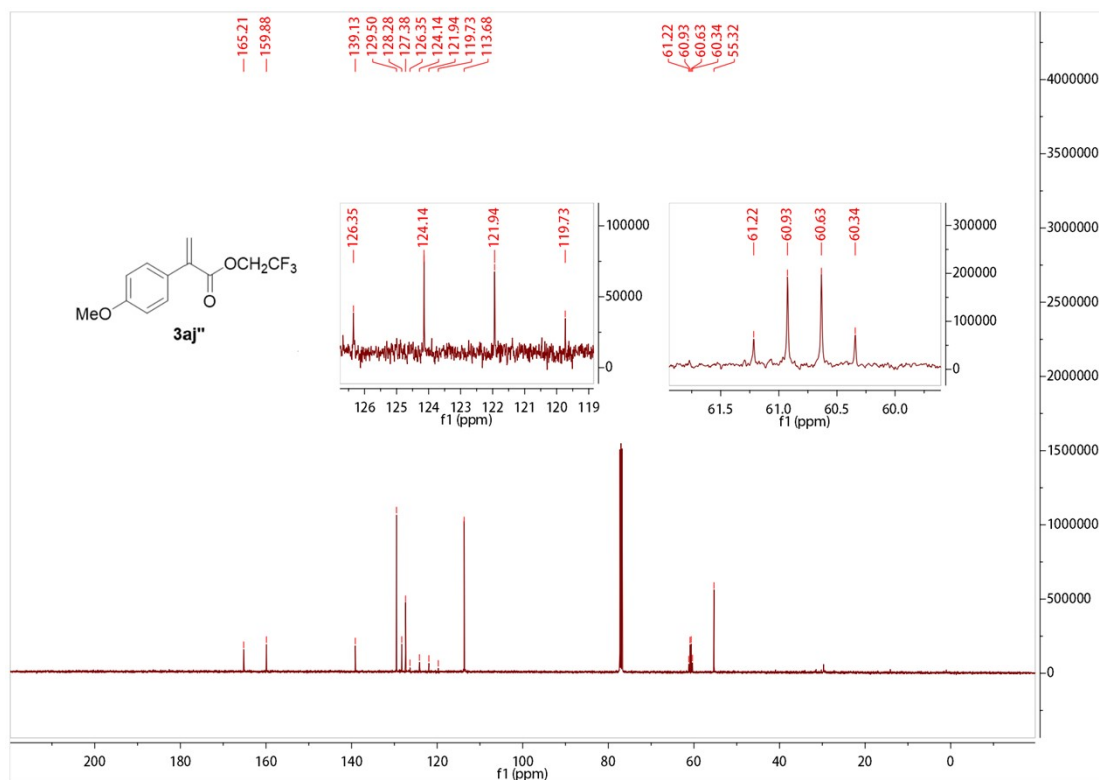
¹⁹F NMR (471 MHz, CDCl₃) spectrum for 3aj'



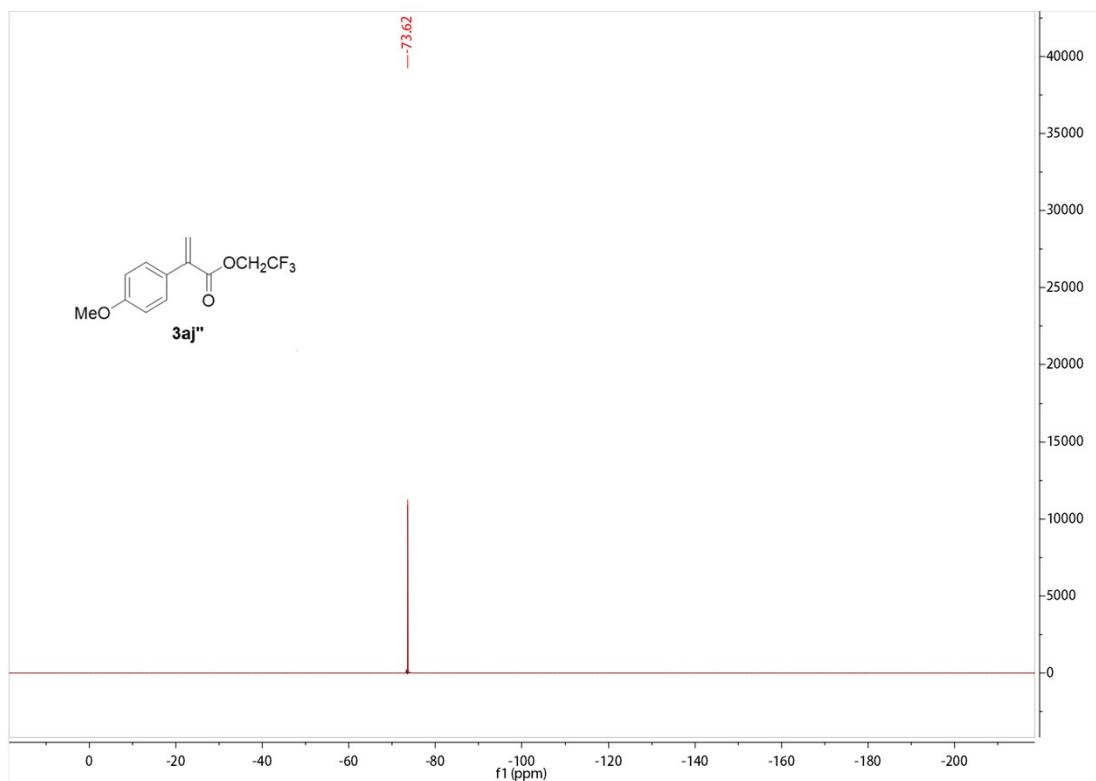
¹H NMR (400 MHz, CDCl₃) spectrum for 3aj''



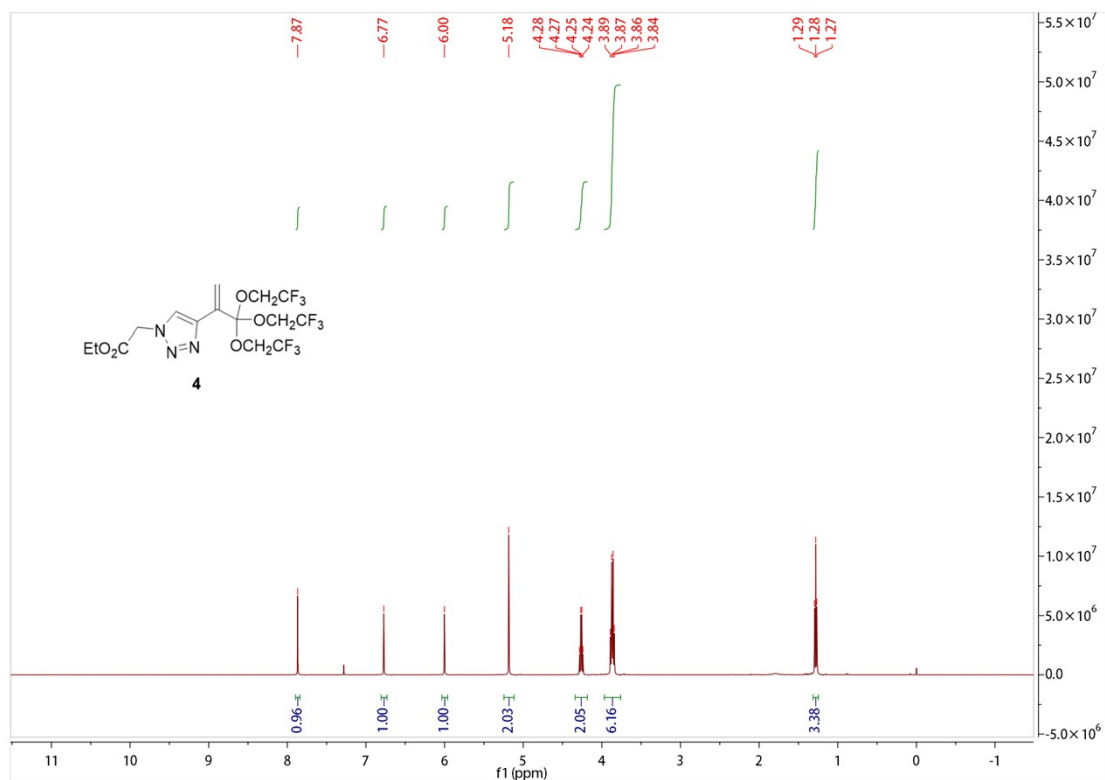
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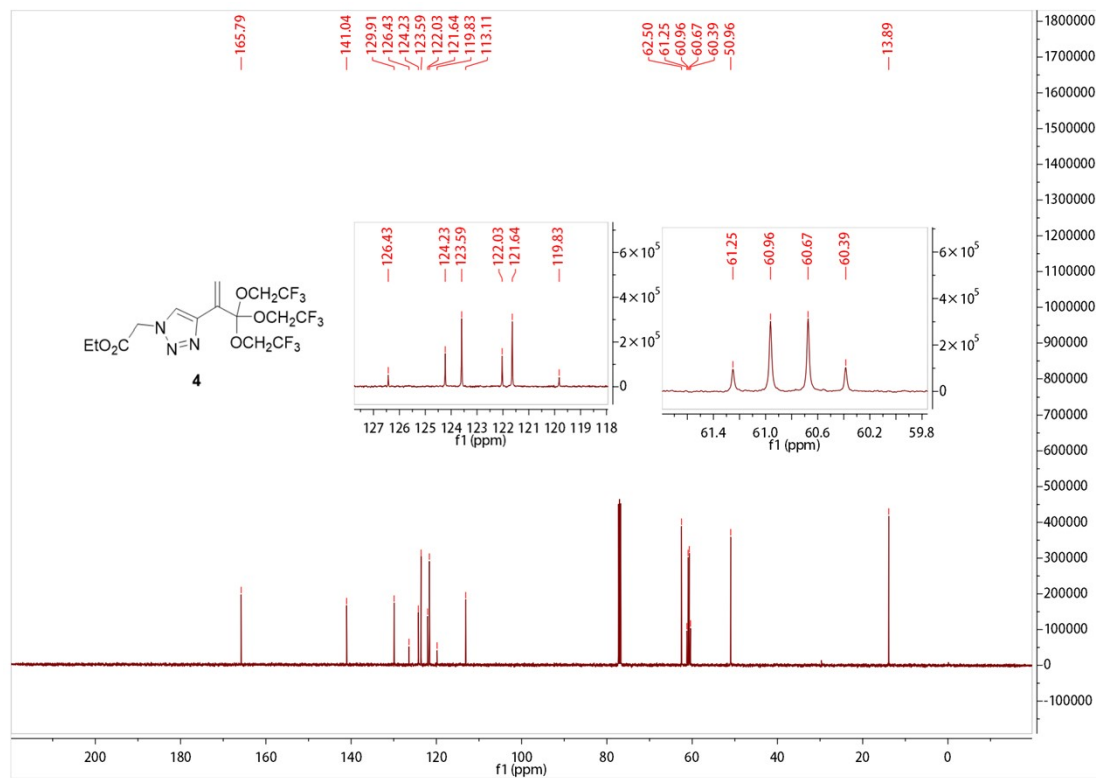
¹⁹F NMR (376 MHz, CDCl₃) spectrum for 3aj''



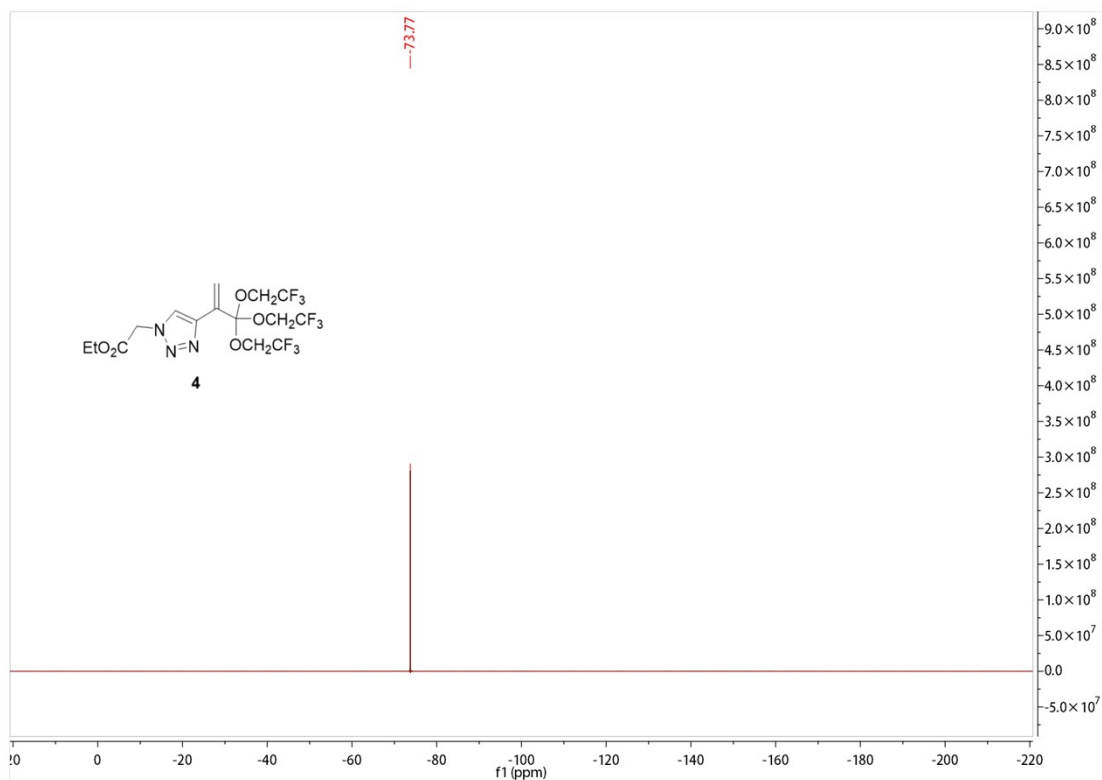
¹H NMR (500 MHz, CDCl₃) spectrum for 4



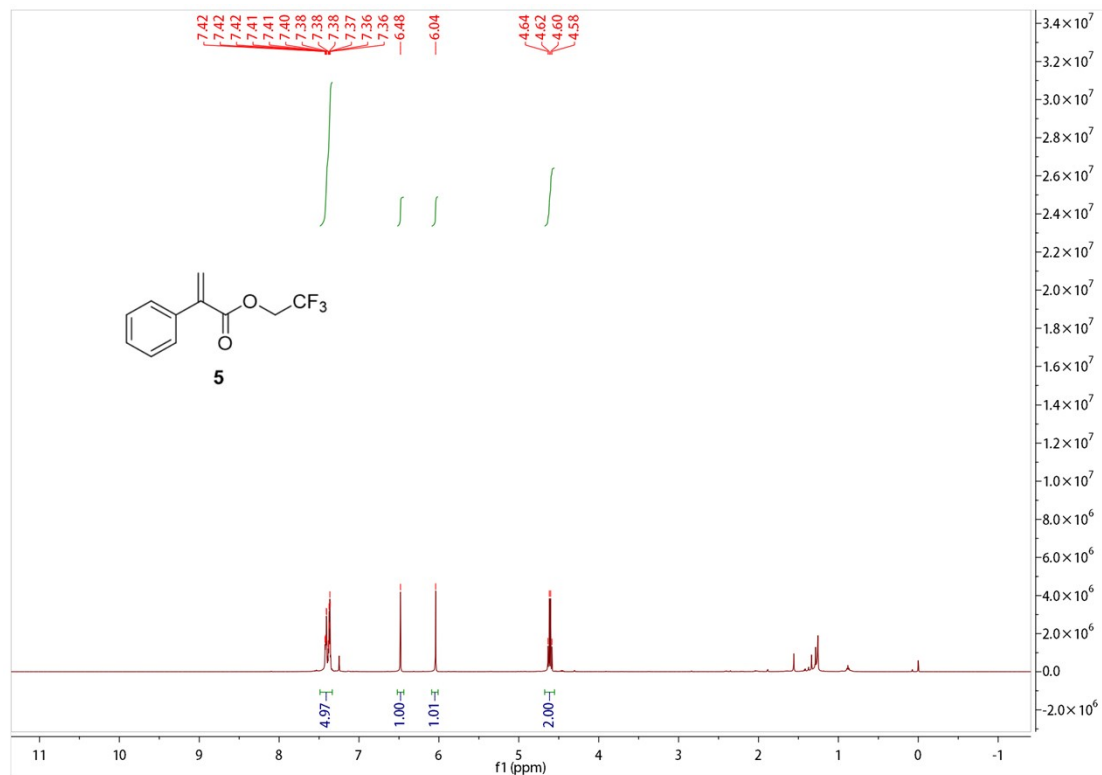
¹³C NMR (126 MHz, CDCl₃) spectrum for 4



¹⁹F NMR (471 MHz, CDCl₃) spectrum for 4



¹H NMR (500 MHz, CDCl₃) spectrum for 5



¹⁹F NMR (471 MHz, CDCl₃) spectrum for 5

