Supporting Information

Intermolecular Trifluoromethyl-Alkenylation of Alkenes Enabled by Metal-Free Photoredox Catalysis

Arun D. Kulthe,[a,b] Prathama S. Mainkar*[a,b] and Srirama Murthy Akondi*[a,b]

[a] Department of Organic Synthesis and Process Chemistry, CSIR-Indian Institute of Chemical Technology (CSIR- IICT), Hyderabad 500007, India; Email: sriramakondi@iict.res.in; sriramiict@gmail.com
[b] Academy of scientific and innovative research (AcSIR), Ghaziabad 201002, India

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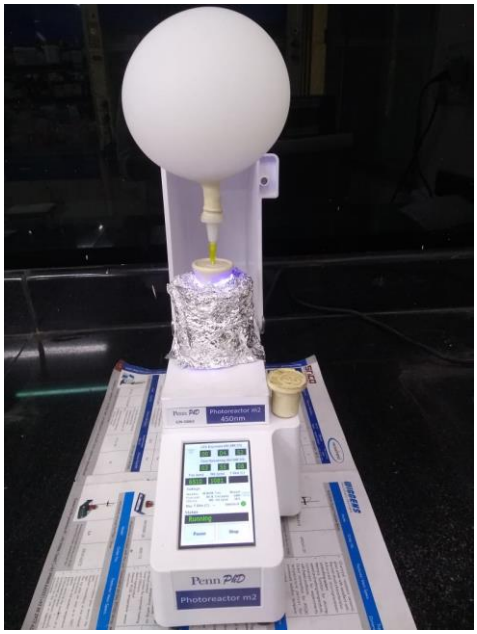
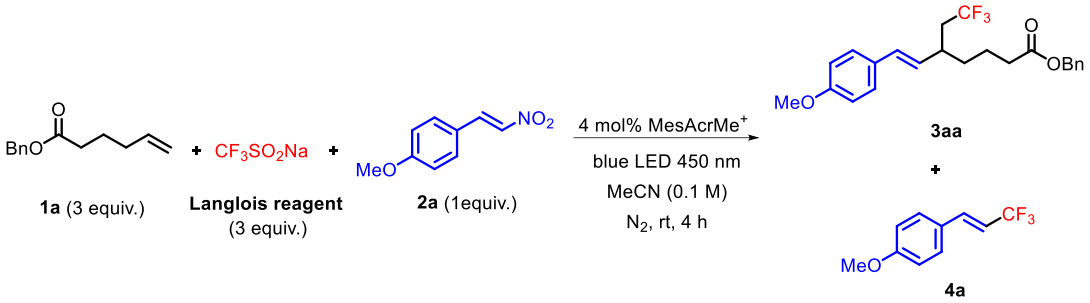
1. General information: Unless otherwise noted, all the solvents and chemicals from commercial suppliers were used without further purification. Silica gel thin-layer chromatography (TLC) was used to monitor the reactions. Silica gel (100-200 mesh) packed in glass column was used for the column chromatography. NMR spectra were recorded at 400, 500 MHz (H) and at 101, 126 MHz (C), respectively. ^{31}P and ^{19}F NMR spectra were recorded at 162 and 376 MHz respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (H: δ = 7.26 and C: δ = 77.0 ppm) as internal standard, and coupling constants (*J*) are measured in hertz (Hz). High-resolution mass spectra (HRMS) were recorded using ESI-TOF techniques. Melting points of solids were recorded using Electrothermal (IA9100) melting point apparatus. Irradiation was performed with Penn *PhD* photoreactor m2 (PR m2) (blue LED, 450 nm) purchased from Sigma- Aldrich.

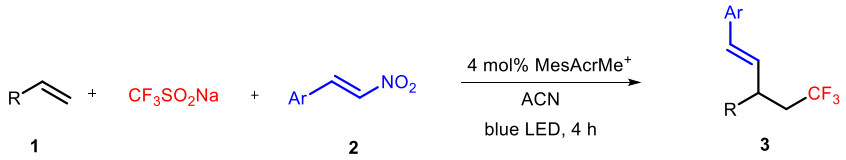


2. Optimization of the stoichiometry of the starting materials:



Entry	Deviation from the above condition	Isolated yields of 3aa and 4a
1	None	71% and trace
2	2 equiv. of alkene and 2 equiv. of Langlois reagent	53% and 12%
3	1 equiv. of alkene and 1 equiv. of Langlois reagent	39% and 21%

3. General procedure for the visible-light promoted trifluoromethyl-alkenylation of alkenes:



Alkene **1** (0.3 mmol), Langlois reagent (0.3 mmol) and nitroalkene **2** (0.1 mmol) were weighed in a round bottomed flask and MeCN (3.0 mL) was added to this mixture. The flask was introduced into Penn *PhD* photoreactor m2 (blue LED 450 nm) and allowed to stir under N_2 atmosphere. After completion of reaction (4 hours), the reaction mixture was concentrated using rotary evaporation and the crude reaction mixture was purified by column chromatography to get the desired compound **3**.

Alkenes **1b**-**1g** are commercially available. Alkenes **1a**, **1h**-**1o** were synthesized from the known procedures available in the literature.[1] Nitrostyrenes **2a**-**2i** are commercially available. Nitrostyrenes **2j**-**2o** were prepared by following the known procedures in the literature.[2]

(*E*)-1-methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (4a): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.7 Hz, 1H), 7.09 (dd, *J* = 16.1, 2.1 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.06 (dq, *J* = 16.1, 6.6 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.1, 137.1 (q, *J* = 6.7 Hz), 129.0, 126.1, 123.9 (q, *J* = 268.4Hz), 114.3, 113.4 (q, *J* = 33.7 Hz), 55.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9. This analytical data is in consistent with the one reported in the literature.[2c]

Benzyl (*E*)-7-(4-methoxyphenyl)-5-(2,2,2-trifluoroethyl)hept-6-enoate (3aa): Colorless oil (29.2 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 5H), 7.26 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.36 (d, *J* = 15.8 Hz, 1H), 5.77 (dd, *J* = 15.8, 9.0 Hz, 1H), 5.10 (s, 2H), 3.80 (s, 3H), 2.59 – 2.46 (m, 1H), 2.40 – 2.31 (m, 2H), 2.23 – 2.11 (m, 2H), 1.78 – 1.68 (m, 1H), 1.67 – 1.50 (m, 2H), 1.47 – 1.38 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 159.1, 136.0, 130.7, 129.8, 129.1, 128.6, 128.3, 127.4, 126.7 (q, *J* = 277.6 Hz), 114.0, 66.2, 55.3, 39.4 (q, *J* = 26.7 Hz), 37.4 (q, *J* = 2.3 Hz), 34.4, 34.0, 22.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1; HRMS (ESI) calcd for $C_{23}H_{26}O_3F_3$ $[M+H]^+$: 407.1829; found: 407.1830.

Benzyl (*E*)-7-(3-methoxyphenyl)-5-(2,2,2-trifluoroethyl)hept-6-enoate (3ab): Colorless oil (23.5 mg, 58%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 5H), 7.22 (t, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.89 – 6.85 (m, 1H), 6.78 (dd, *J* = 8.0, 2.3 Hz, 1H), 6.39 (d, *J* = 15.8 Hz, 1H), 5.92 (dd, *J* = 15.7, 9.1 Hz, 1H), 5.11 (s, 2H), 3.81 (s, 3H), 2.59 – 2.50 (m, 1H), 2.42 – 2.31 (m, 2H), 2.27 – 2.12 (m, 2H), 1.77 – 1.68 (m, 1H), 1.63 – 1.54 (m, 2H), 1.48 – 1.39 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 159.8, 138.4, 136.0, 131.6, 131.3, 129.5, 128.6, 128.3, 126.6 (q, *J* = 277.6 Hz), 118.9, 113.1, 111.6, 66.3, 55.2, 39.3 (q, *J* = 26.8 Hz), 37.4 (q,

J = 1.4 Hz), 34.3, 34.0, 22.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1; HRMS (ESI) calcd for $C_{23}H_{29}O_3NF_3$ $[M+NH_4]^+$: 424.2094; found: 424.2074.

Benzyl (*E*)-7-(2-methoxyphenyl)-5-(2,2,2-trifluoroethyl)hept-6-enoate (3ac): Colorless oil (29.2 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.36 – 7.29 (m, 5H), 7.21 (td, *J* = 8.2, 1.7 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.74 (d, *J* = 15.9 Hz, 1H), 5.93 (dd, *J* = 15.9, 9.0 Hz, 1H), 5.11 (s, 2H), 3.83 (s, 3H), 2.65 – 2.49 (m, 1H), 2.39 – 2.35 (m, 2H), 2.23 – 2.15 (m, 2H), 1.79 – 1.67 (m, 1H), 1.67 – 1.51 (m, 2H), 1.48 – 1.38 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 156.6, 136.0, 131.8, 128.6, 128.4, 128.2, 126.6, 126.7 (q, *J* = 277.8 Hz), 126.1, 126.0, 120.6, 111.0, 66.2, 55.5, 39.3 (q, *J* = 26.9 Hz), 37.7 (q, *J* = 1.7 Hz), 34.3, 34.0, 22.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0; HRMS (ESI) calcd for $C_{23}H_{26}O_3F_3$ $[M+H]^+$: 407.1829; found: 407.1830

Benzyl (*E*)-7-(2,5-dimethoxyphenyl)-5-(2,2,2-trifluoroethyl)hept-6-enoate (3ad): Colorless oil (24.4 mg, 56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 5H), 6.95 (d, *J* = 2.9 Hz, 1H), 6.81 – 6.69 (m, 3H), 5.93 (dd, *J* = 15.9, 9.0 Hz, 1H), 5.11 (s, 2H), 3.78 (s, 6H), 2.62 – 2. (m, 1H), 2.229 (m, 2H), 2.24 – 2.12 (m, 2H), 1.79 – 1.67 (m, 1H), 1.67 – 1.51 (m, 2H), 1.48 – 1.38 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 153.7, 151.1, 136.0, 132.1, 128.6, 128.2, 127.0, 125.9, 126.7 (q, *J* = 277.4 Hz), 113.3, 112.5, 112.1, 66.2, 56.3, 55.8, 39.3 (q, *J* = 26.8 Hz), 37.6 (q, *J* = 1.1 Hz), 34.3, 34.0, 22.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0; HRMS (ESI) calcd for $C_{24}H_{28}O_4F_3$ $[M+H]^+$: 437.1934; found: 437.1917.

Benzyl (*E*)-7-(3-chlorophenyl)-5-(2,2,2-trifluoroethyl)hept-6-enoate (3ae): Colorless oil (25.4 mg, 62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 6H), 7.24 – 7.15 (m, 3H), 6.36 (d, *J* = 15.7 Hz, 1H), 5.93 (dd, *J* = 15.7, 9.2 Hz, 1H), 5.11 (s, 2H), 2.63 – 2.49 (m, 1H), 2.43 – 2.30 (m, 2H), 2.28 – 2.10 (m, 2H), 1.78 – 1.67 (m, 1H), 1.66 – 1.51 (m, 2H), 1.49 – 1.34 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 138.8, 135.9, 134.5, 132.8, 130.2, 129.8, 128.6, 128.3, 127.9, 126.5 (q, *J* = 277.5 Hz), 126.1, 125.1, 66.3, 39.2 (q, *J* = 26.9 Hz), 37.5 (q, *J* = 1.2

Hz), 34.2, 33.9, 22.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1; HRMS (ESI) calcd for $C_{22}H_{21}O_2ClF_3$ $[M-H]^-$: 409.1177; found: 409.1152.

Benzyl (*E*)-7-(2,4-dichlorophenyl)-5-(2,2,2-trifluoroethyl)hept-6-enoate (3af): Colorless oil (29.7 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 7H), 7.18 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.72 (d, *J* = 15.8 Hz, 1H), 5.88 (dd, *J* = 15.8, 9.1 Hz, 1H), 5.11 (s, 2H), 2.65 – 2.58 (m, 1H), 2.43 – 2.33 (m, 2H), 2.29 – 2.12 (m, 2H), 1.77 – 1.68 (m, 1H), 1.67 – 1.54 (m, 2H), 1.48 – 1.40 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 135.9, 134.8, 133.9, 133.4, 133.3, 129.4, 128.6, 128.3, 127.7, 127.2, 126.9, 126.5 (q, *J* = 277.5 Hz), 66.3, 39.1 (q, *J* = 27.0 Hz), 37.6 (q, *J* = 1.4 Hz), 34.1, 33.9, 22.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0; HRMS (ESI) calcd for $C_{22}H_{25}O_2NCl_2F_3$ $[M+NH_4]^+$: 462.1209; found: 462.1183.

Benzyl (*E*)-7-(2,6-dichlorophenyl)-5-(2,2,2-trifluoroethyl)hept-6-enoate (3ag): Colorless oil (25.3 mg, 57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 5H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.08 (t, *J* = 8.1 Hz, 1H), 6.40 (d, *J* = 16.1 Hz, 1H), 5.90 (dd, *J* = 16.1, 9.2 Hz, 1H), 5.12 (s, 2H), 2.67 – 2.58 (m, 1H), 2.47 – 2.34 (m, 2H), 2.27 – 2.17 (m, 2H), 1.92 – 1.82 (m, 1H), 1.74 – 1.57 (m, 2H), 1.50 – 1.43 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 139.8, 136.0, 134.5, 134.4, 130.7, 128.6, 128.3, 128.2, 128.1, 126.5 (q, *J* = 277.5 Hz), 125.3, 66.3, 39.1 (q, *J* = 27.3 Hz), 37.9 (q, *J* = 1.8 Hz), 34.0, 33.9, 22.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1; HRMS (ESI) calcd for $C_{22}H_{25}O_2NCl_2F_3$ $[M+NH_4]^+$: 462.1209; found: 462.1183.

Benzyl (*E*)-7-(4-fluorophenyl)-5-(2,2,2-trifluoroethyl)hept-6-enoate (3ah): Colorless oil (25.5 mg, 64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 5H), 7.31 – 7.27 (m, 2H), 7.01 – 6.96 (m, 2H), 6.38 (d, *J* = 15.8 Hz, 1H), 5.83 (dd, *J* = 15.8, 9.1 Hz, 1H), 5.11 (s, 2H), 2.58 – 2.50 (m, 1H), 2.42 – 2.32 (m, 2H), 2.24 – 2.13 (m, 2H), 1.78 – 1.68 (m, 1H), 1.66 – 1.52 (m, 2H), 1.46 – 1.39 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 162.2 (d, *J* = 246.4 Hz), 138.1, 136.0, 133.1 (d, *J* = 3.1 Hz), 131.0, 130.3, 128.6, 128.3, 127.7 (d, *J* = 7.9 Hz), 126.6 (q, *J* = 277.6 Hz), 115.4 (d, *J* = 21.6 Hz), 66.3, 39.3 (q, *J* = 26.9 Hz), 37.4 (q, *J* = 1.6 Hz), 34.3, 34.0,

22.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1, -114.8; HRMS (ESI) calcd for $C_{22}H_{26}O_2NF_4$ $[M+NH_4]^+$: 412.1894; found: 412.1880.

Benzyl (*E*)-7-phenyl-5-(2,2,2-trifluoroethyl)hept-6-enoate (3ai): Colorless oil (22.9 mg, 61%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 9H), 7.24 – 7.21 (m, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 5.92 (dd, *J* = 15.8, 9.1 Hz, 1H), 5.11 (s, 2H), 2.59 – 2.52 (m, 1H), 2.42 – 2.32 (m, 2H), 2.25 – 2.14 (m, 2H), 1.77 – 1.69 (m, 1H), 1.67 – 1.53 (m, 2H), 1.47 – 1.40 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 137.0, 136.0, 131.4, 131.3, 128.6, 128.5, 128.3, 127.4, 126.6 (q, *J* = 277.6 Hz), 126.2, 66.3, 39.3 (q, *J* = 26.9 Hz), 37.4 (q, *J* = 1.6 Hz), 34.3, 34.0, 22.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1; HRMS (ESI) calcd for $C_{22}H_{27}O_2NF_3$ $[M+NH_4]^+$: 394.1988; found: 394.1968.

Benzyl (E)-7-(naphthalen-1-yl)-5-(2,2,2-trifluoroethyl)hept-6-enoate (3aj): Colorless oil (29.4 mg, 69%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.06 (m, 1H), 7.86 – 7.84 (m, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.47 (m, 3H), 7.45 – 7.42 (m, 1H), 7.36 – 7.31 (m, 5H), 7.17 (d, *J* = 15.5 Hz, 1H), 5.93 (dd, *J* = 15.5, 9.2 Hz, 1H), 5.13 (s, 2H), 2.75 – 2.68 (m, 1H), 2.46 – 2.38 (m, 2H), 2.30 – 2.22 (m, 2H), 1.87 – 1.79 (m, 1H), 1.76 – 1.70 (m, 1H), 1.66 – 1.59 (m, 1H), 1.55 – 1.47 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 136.0, 135.0, 134.7, 133.6, 131.2, 129.0, 128.6, 128.5, 128.3, 127.8, 126.7 (q, *J* = 277.6 Hz), 126.1, 125.8, 125.6, 124.0, 123.9, 66.3, 39.4 (q, *J* = 26.9 Hz), 37.8 (q, *J* = 1.5 Hz), 34.4, 34.0, 22.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9; HRMS (ESI) calcd for $C_{26}H_{26}O_2F_3$ $[M+H]^+$: 427.1879; found: 427.1864.

Benzyl (*E*)-7-(furan-2-yl)-5-(2,2,2-trifluoroethyl)hept-6-enoate (3ak): Colorless oil (18.7 mg, 51%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 6H), 6.28 (dd, *J* = 3.3, 1.8 Hz, 1H), , 6.16 (d, *J* = 15.8 Hz, 1H), 6.11 (d, *J* = 3.3 Hz, 1H), 5.81 (dd, *J* = 15.8, 9.2 Hz, 1H), 5.04 (s, 2H), 2.47 – 2.38 (m, 1H), 2.31 – 2.27 (m, 2H), 2.17 – 2.04 (m, 2H), 1.70 – 1.60 (m, 1H), 1.60 – 1.44 (m, 2H), 1.39 – 1.32 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 151.3, 140.7, 134.9,129.0, 127.6, 127.2, 125.5 (q, *J* = 277.6 Hz), 118.9, 110.2, 106.3, 65.2, 38.2 (q, *J* = 26.8

Hz), 36.2 (q, *J* = 1.2 Hz), 33.3, 32.9, 21.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2; HRMS (ESI) calcd for $C_{20}H_{20}O_3F_3$ $[M-H]^-$: 365.1359; found: 365.1359.

Benzyl (6*E*,8*E*)-9-phenyl-5-(2,2,2-trifluoroethyl)nona-6,8-dienoate (3al): Colorless oil (21.3 mg, 53%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 9H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.72 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.49 (d, *J* = 15.7 Hz, 1H), 6.23 (dd, *J* = 15.1, 10.4 Hz, 1H), 5.53 (dd, *J* = 15.1, 9.1 Hz, 1H), 5.11 (s, 2H), 2.53 – 2.43 (m, 1H), 2.43 – 2.29 (m, 2H), 2.23 – 2.07 (m, 2H), 1.77 – 1.65 (m, 1H), 1.65 – 1.48 (m, 2H), 1.43 – 1.33 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 137.3, 136.0, 135.5, 131.9, 131.8, 128.6, 128.5, 128.3, 127.5, 126.6 (q, *J* = 277.7 Hz), 126.3, 66.3, 39.2 (q, *J* = 26.8 Hz), 37.2 (q, *J* = 1.7 Hz), 34.3, 34.0, 22.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2; HRMS (EI) calcd for $C_{24}H_{25}O_2F_3$ $[M]^+$: 402.1807; found: 402.1826.

(*E*)-1-(3-Benzyl-5,5,5-trifluoropent-1-en-1-yl)-4-methoxybenzene (3ba): White solid, mp: 81- 83 ^{o}C (19.8 mg, 62%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.19 (m, 5H), 7.16 (d, *J* = 7.1 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.28 (d, *J* = 15.8 Hz, 1H), 5.89 (dd, *J* = 15.8, 8.7 Hz, 1H), 3.80 (s, 3H), 2.90 – 2.81 (m, 1H), 2.81 – 2.72 (m, 2H), 2.30 – 2.10 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 141.7, 131.0, 129.9, 129.4, 128.4, 128.4, 127.4, 126.7 (q, *J* = 277.7 Hz), 125.9, 114.0, 55.4, 39.5 (q, *J* = 26.8 Hz), 37.2 (q, *J* = 1.7 Hz), 36.7, 33.2 159.1, 138.7, 130.41, 130.0, 129.4, 129.1, 128.4, 127.4, 126.5, 126.8 (q, *J* = 277.6 Hz), 114.0, 55.3, 41.9, 39.1 (q, *J* = 1.3 Hz), 38.2 (q, *J* = 26.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9; HRMS (ESI) calcd for $C_{19}H_{19}OF_3$ $[M]^+$: 320.1388; found: 320.1375.

(*E*)-1-Methoxy-4-(5,5,5-trifluoro-3-phenethylpent-1-en-1-yl)benzene (3ca): Colorless oil (19.4 mg, 58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 4H), 7.21 – 7.13 (m, 3H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.38 (d, *J* = 15.8 Hz, 1H), 5.85 (dd, *J* = 15.8, 9.1 Hz, 1H), 3.81 (s, 3H), 2.77 – 2.66 (m, 1H), 2.62 – 2.51 (m, 2H), 2.33 – 2.18 (m, 2H), 1.94 – 1.82 (m, 1H), 1.78 – 1.66 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 141.7, 131.0, 129.9, 129.4, 128.5, 128.4, 127.4,

126.7 (q, *J* = 277.7 Hz), 125.9, 114.0, 55.4, 39.5 (q, *J* = 26.8 Hz), 37.2 (q, *J* = 1.7 Hz), 36.7, 33.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0; HRMS (ESI) calcd for $C_{20}H_{21}OF_3$ $[M]^+$: 334.1544; found: 334.1536.

(E)-1,2-Dimethoxy-4-(4-(4-methoxyphenyl)-2-(2,2,2-trifluoroethyl)but-3-en-1-yl)benzene (3da): Colorless oil (25.4 mg, 67%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.70 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.66 (d, *J* = 1.9 Hz, 1H), 6.28 (d, *J* = 15.8 Hz, 1H), 5.90 (dd, *J* = 15.8, 8.5 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.79 (s, 3H), 2.87 – 2.76 (m, 1H), 2.77 – 2.66 (m, 2H), 2.32 – 2.20 (m, 1H), 2.20 – 2.09 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 148.7, 147.6, 131.2, 130.4, 129.9, 129.2, 127.3, 126.7 (q, *J* = 277.7 Hz), 121.4, 114.0, 112.6, 111.1, 55.9, 55.8, 55.3, 41.4, 39.1, 38.5 (q, *J* = 26.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9; HRMS (ESI) calcd for $C_{21}H_{23}O_3F_3$ $[M+H]^+$: 380.1599; found: 380.1597.

(E)-(5,5,5-Trifluoro-1-(4-methoxyphenyl)pent-1-en-3-yl)cyclooctane (3ea): Colorless oil (14.6 mg, 43%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.27 (d, *J* = 15.7 Hz, 1H), 5.80 (dd, *J* = 15.7, 9.3 Hz, 1H), 3.73 (s, 3H), 2.39 – 2.32 (m, 1H), 2.24 – 2.07 (m, 2H), 1.65 – 1.58 (m, 2H), 1.56 – 1.45 (m, 8H), 1.42 – 1.25 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 131.0, 130.2, 128.1, 127.3, 127.2 (q, *J* = 277.1 Hz), 114.0, 55.4, 44.3, 41.6, 36.7 (q, *J* = 26.4 Hz), 31.6, 29.7, 29.4, 26.7, 26.6, 26.5, 26.4, 25.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1; HRMS (ESI) calcd for $C_{20}H_{27}F_3O$ $[M+H]^+$: 341.2092; found: 341.2072.

(E)-1-Methoxy-4-(3-(2,2,2-trifluoroethyl)henicos-1-en-1-yl)benzene (3fa): Colorless oil (30.9 mg, 64%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 5.81 (dd, *J* = 15.7, 9.0 Hz, 1H), 3.80 (s, 3H), 2.57 – 2.44 (m, 1H), 2.26 – 2.10 (m, 2H), 1.78 – 1.43 (m, 4H), 1.39 – 1.13 (m, 30H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 130.1, 130.0, 127.3, 126.8 (q, *J* = 277.7 Hz), 114.0,

55.3, 39.4 (q, *J* = 26.8 Hz), 37.5 (q, *J* = 1.2 Hz), 35.2, 32.0, 29.7, 29.6, 29.5, 29.4, 26.9, 22.7, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1; HRMS (ESI) calcd for $C_{30}H_{49}OF_3$ $[M]^+$: 482.3735; found: 482.3741.

±(E)-1-methoxy-4-(2-(2-(trifluoromethyl)cyclohexyl)vinyl)benzene (3ga): Colorless oil (16.8 mg, 59%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.33 (d, *J* = 15.7 Hz, 1H), 5.94 (dd, *J* = 15.7, 9.0 Hz, 1H), 3.80 (s, 3H), 2.31 – 2.22 (m, 1H), 2.06 – 1.93 (m, 2H), 1.85 – 1.83 (m, 1H), 1.79 – 1.77 (m, 2H), 1.39 – 1.25 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 131.2, 130.5, 128.5, 127.7 (q, *J* = 277.7 Hz), 127.2, 113.9, 55.3, 46.9 (q, *J* = 23.8 Hz), 41.9 (q, *J* = 1.1 Hz), 33.6, 25.3, 24.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.5; HRMS (ESI) calcd for $C_{16}H_{20}OF_3$ $[M+H]^+$: 285.1466; found: 285.1458.These NMR values are in accordance with the known *trans* compound in the literature.[3]

(E)-*tert*-Butyl((6-(4-methoxyphenyl)-4-(2,2,2-trifluoroethyl)hex-5-en-1-yl)oxy)dimethylsilane (3ha): Colorless oil (24.6 mg, 61%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.36 (d, *J* = 15.8 Hz, 1H), 5.81 (dd, *J* = 15.8, 9.0 Hz, 1H), 3.80 (s, 3H), 3.61 (t, *J* = 6.0 Hz, 2H), 2.59 – 2.50 (m, 1H), 2.29 – 2.12 (m, 2H), 1.67 – 1.54 (m, 2H), 1.53 – 1.39 (m, 2H), 0.89 (s, 9H), 0.04 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 130.4, 130.0, 129.7, 127.3, 126.8 (q, *J* = 277.7 Hz), 114.0, 62.9, 55.3, 39.5 (q, *J* = 26.8 Hz), 37.3 (q, *J* = 1.5 Hz), 31.4, 26.0, 18.9, -5.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1; HRMS (ESI) calcd for $C_{21}H_{34}O_2F_3Si$ $[M+H]^+$: 403.2275; found: 403.2276.

(E)-6-(4-Methoxyphenyl)-4-(2,2,2-trifluoroethyl)hex-5-en-1-yl 4-methylbenzenesulfonate (3ia): Colorless oil (27.8 mg, 63%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.30 (d, *J* = 15.8 Hz, 1H), 5.71 (dd, *J* = 15.8, 9.1 Hz, 1H), 4.03 (t, *J* = 6.2 Hz, 2H), 3.80 (s, 3H), 2.43 (s, 3H), 2.23 – 2.08 (m, 2H), 1.77 – 1.67 (m, 1H), 1.67 – 1.52 (m, 3H), 1.43 – 1.33 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 144.8, 133.1, 131.2, 129.9, 129.6, 128.5, 127.9, 127.4, 126.6 126.7

(q, *J* = 277.7 Hz), 114.0, 70.2, 55.3, 39.5 (q, *J* = 26.8 Hz), 37.2 (q, *J* = 1.6 Hz), 30.8, 26.5, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ -0.8; HRMS (ESI) calcd for $C_{22}H_{26}O_4F_3S$ $[M+H]^+$: 443.1498; found: 443.1496.

(E)-Diethyl (6-(4-methoxyphenyl)-4-(2,2,2-trifluoroethyl)hex-5-en-1-yl) phosphate (3ja): Colorless oil (27.6 mg, 65%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.37 (d, *J* = 15.8 Hz, 1H), 5.79 (dd, *J* = 15.8, 9.1 Hz, 1H), 4.13 – 4.01 (m, 6H), 3.81 (s, 3H), 2.59 – 2.50 (m, 1H), 2.26 – 2.16 (m, 2H), 1.73 – 1.59 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 131.0, 129.7, 129.0, 127.4, 126.7 (q, *J* = 277.7 Hz), 114.0, 67.2 (d, *J* = 6.0 Hz), 63.8 (d, *J* = 5.6 Hz), 55.3, 39.5 (q, *J* = 26.8 Hz), 37.3 (q, *J* = 1.4 Hz), 30.9, 27.8 (d, *J* = 6.8 Hz), 16.2 (d, *J* = 6.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ -0.8; HRMS (ESI) calcd for $C_{19}H_{28}O_5F_3P$ $[M]^+$: 424.1626; found: 424.1630.

(E)-2-(6-(4-Methoxyphenyl)-4-(2,2,2-trifluoroethyl)hex-5-en-1-yl)isoindoline-1,3-dione (3ka): Colorless oil (30.5 mg, 73%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.36 (d, *J* = 15.7 Hz, 1H), 5.77 (dd, *J* = 15.7, 9.1 Hz, 1H), 3.79 (s, 3H), 3.69 (t, *J* = 7.2 Hz, 2H), 2.61 – 2.51 (m, 1H), 2.26 – 2.14 (m, 2H), 1.80 – 1.55 (m, 3H), 1.51 – 1.40 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 159.1, 134.0, 132.1, 130.9, 129.8, 128.9, 126.6 (q, *J* = 277.7 Hz), 127.4, 123.3, 114.0, 55.3, 39.5 (q, *J* = 26.7 Hz), 37.7, 37.4 (q, *J* = 1.4 Hz), 32.2, 26.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1; HRMS (ESI) calcd for $C_{23}H_{23}O_3NF_3$ $[M+H]^+$: 418.1624; found: 418.1621.

(E)-(6-(4-methoxyphenyl)-4-(2,2,2-trifluoroethyl)hex-5-en-1-yl)(phenyl)sulfane (3la): Colorless oil (21.3 mg, 56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.27 – 7.21 (m, 4H), 7.17 – 7.12 (m, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.33 (d, *J* = 15.8 Hz, 1H), 5.77 (dd, *J* = 15.8, 9.0 Hz, 1H), 3.81 (s, 3H), 2.99 – 2.85 (m, 2H), 2.59 – 2.47 (m, 1H), 2.25 – 2.11 (m, 2H),

1.77 – 1.49 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 136.5, 130.8, 129.8, 129.2, 129.2, 128.9, 127.4, 126.6 (q, *J* = 277.7 Hz), 125.9, 114.0, 55.35, 39.5 (q, *J* = 26.7 Hz), 37.2 (q, *J* = 1.2 Hz), 34.0, 33.6, 26.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1; HRMS (ESI) calcd for $C_{21}H_{23}OF_3S$ $[M]^+$: 380.1422; found: 380.1432.

(E)-1-Methoxy-4-(6-(phenylsulfinyl)-3-(2,2,2-trifluoroethyl)hex-1-en-1-yl)benzene (3ma): Colorless oil (23.0 mg, 58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H), 7.49 – 7.44 (m, 3H), 7.25 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.33 (d, *J* = 15.7 Hz, 1H), 5.73 (dd, *J* = 15.7, 9.1 Hz, 1H), 3.81 (s, 3H), 2.85 – 2.68 (m, 2H), 2.58 – 2.46 (m, 1H), 2.24 – 2.14 (m, 2H), 1.93 – 1.79 (m, 1H), 1.78 – 1.45 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 143.7, 131.2, 131.1, 129.6, 129.2, 128.6, 127.4, 126.5 (q, *J* = 277.7 Hz), 124.0, 114.0, 56.9, 55.4, 39.4 (q, *J* = 26.9 Hz), 37.5 (q, *J* = 1.8 Hz), 33.8, 20.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2; HRMS (ESI) calcd for $C_{21}H_{24}O_2F_3S$ $[M+H]^+$: 397.1444; found: 397.1434.

3-(((E)-4-(4-methoxyphenyl)-2-(2,2,2-trifluoroethyl)but-3-en-1-yl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (3na): (1:1 diastereomeric mixture) Colorless oil (31.2 mg, 61%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.72 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.66 (d, *J* = 2.4 Hz, 1H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.02 (dd, *J* = 15.9, 8.6 Hz, 1H), 4.06 – 3.99 (m, 1H), 3.95 – 3.86 (m, 1H), 3.81 (s, 3H), 3.07 – 2.97 (m, 1H), 2.93 – 2.86 (m, 2H), 2.71 – 2.56 (m, 1H), 2.50 (dd, *J* = 18.8, 8.5 Hz, 1H), 2.44 – 2.36 (m, 1H), 2.35 – 2.24 (m, 2H), 2.19 – 1.92 (m, 4H), 1.69 – 1.41 (m, 6H), 0.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.9, 159.3, 156.6, 137.9, 132.6, 132.0, 129.6, 127.5, 126.8 (q, *J* = 277.8 Hz), 126.4, 125.8, 114.7, 114.0, 112.2, 70.3, 55.3, 50.4, 48.0, 44.0, 38.4, 37.6, 36.0 (q, *J* = 17.0 Hz), 31.6, 29.7 (q, *J* = 6.9 Hz), 26.5, 25.9, 21.6, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1, -63.1 (1:1 ratio); HRMS (ESI) calcd for $C_{31}H_{36}O_3F_3$ $[M+H]^+$: 513.2617; found: 513.2593.

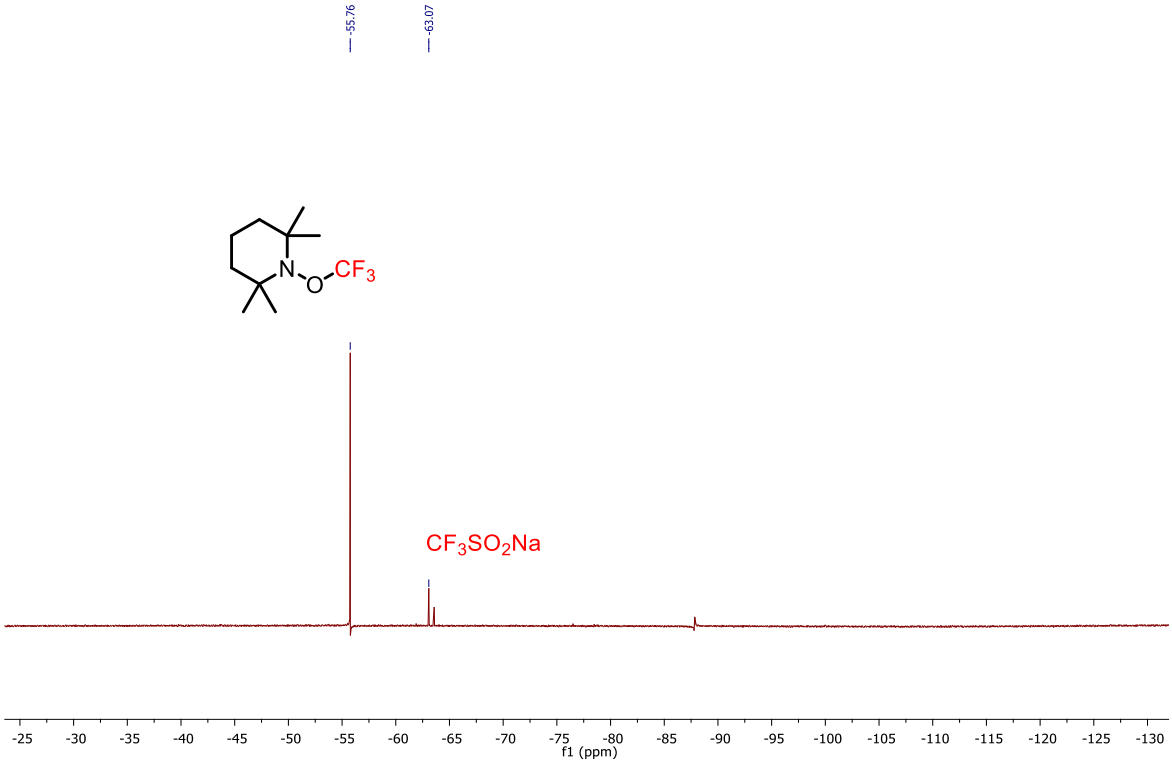
(E)-4-(4-Methoxyphenyl)-2-(2,2,2-trifluoroethyl)but-3-en-1-yl 2-((3-chloro-2-methylphenyl)amino)isonicotinate (3oa): Colorless oil (34.3 mg, 68%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.85 (s, 1H), 8.33 (dd, *J* = 4.7, 2.0 Hz, 1H), 8.21 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.84 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.28 (d, *J* = 8.7 Hz, 2H), 7.19 – 7.11 (m, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.72 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.53 (d, *J* = 15.8 Hz, 1H), 5.96 (dd, *J* = 15.8, 8.6 Hz, 1H), 4.39 (ddd, *J* = 28.4, 11.0, 6.4 Hz, 2H), 3.80 (s, 3H), 3.14 – 3.05 (m, 1H), 2.56 – 2.43 (m, 1H), 2.37 (s, 3H), 2.42 – 2.29 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 159.5, 156.6, 153.7, 140.0, 139.1, 134.9, 132.6, 129.2, 129.1, 127.5, 126.6, 126.5 (q, *J* = 277.7 Hz), 125.1, 124.8, 122.2, 114.1, 113.5, 106.7, 66.9, 55.3, 37.1 (q, *J* = 0.8 Hz), 36.1 (q, *J* = 27.9 Hz), 15.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2; HRMS (ESI) calcd for $C_{26}H_{25}O_3N_2ClF_3$ $[M+H]^+$: 505.1500; found: 505.1490.

4. Gram-scale experiment:

Alkene **1a** (12.0 mmol), Langlois reagent (12.0 mmol) and nitroalkene **2a** (4.0 mmol) were weighed in a round bottomed flask and MeCN (40 mL) was added to this mixture. The flask was back filled with N_2 and it was introduced into Penn *PhD* photoreactor m2 (blue LED 450 nm). After completion of reaction (8 hours), the reaction mixture was concentrated using rotary evaporation and the crude reaction mixture was purified by column chromatography to get the desired compound **3aa** (1.1 g, 68%).

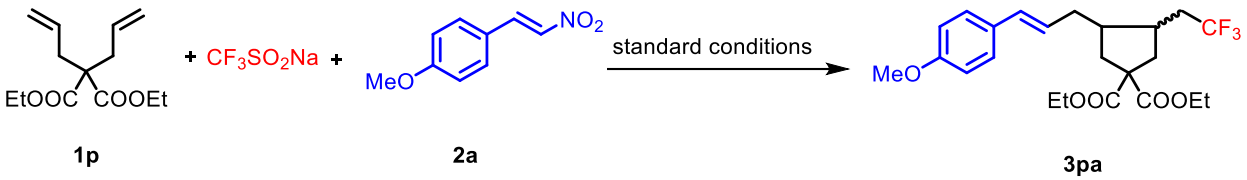
5. Radical inhibition and radical trapping experiment:

Alkene **1a** (0.3 mmol), Langlois reagent (0.3 mmol), nitroalkene **2a** (0.1 mmol) and TEMPO (0.3 mmol) were weighed in a screw capped vial and MeCN (3.0 mL) was added to this mixture. The vial was back filled with N_2 and it was introduced into Penn *PhD* photoreactor m2 (blue LED 450 nm). After completion of reaction (4 hours), the reaction mixture was concentrated using rotary evaporation and the crude reaction mixture was analyzed by ^{19}F nmr.



6. Radical clock cyclization experiment:

Diethyl (E)-3-(3-(4-methoxyphenyl)allyl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (3pa): (19:1 diastereomeric mixture)



1p **2a** **3pa**

Under the standard conditions, the dialkene **1p** was converted to the radical clock cyclized product **3pa** upon reaction with the Langlois reagent and **2a.** Colorless oil (18.1 mg, 41%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.34 (d, *J* = 15.7 Hz, 1H), 6.03 – 5.89 (m, 1H), 4.23 – 4.13 (m, 4H), 3.80 (s, 3H), 2.51 – 1.91 (m, 10H), 1.23 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 172.5, 158.9, 131.3, 131.2, 130.2, 127.1, 127.0 (q, *J* = 277.7 Hz), 125.8, 113.9, 61.6, 58.5, 55.3, 42.0, 38.4, 37.8, 36.2 (q, *J* = 1.2 Hz), 33.5 (q, *J* = 27.8 Hz), 32.3, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2; HRMS (ESI) calcd for $C_{23}H_{30}O_5F_3$ $[M+H]^+$: 443.2039; found: 443.2024.

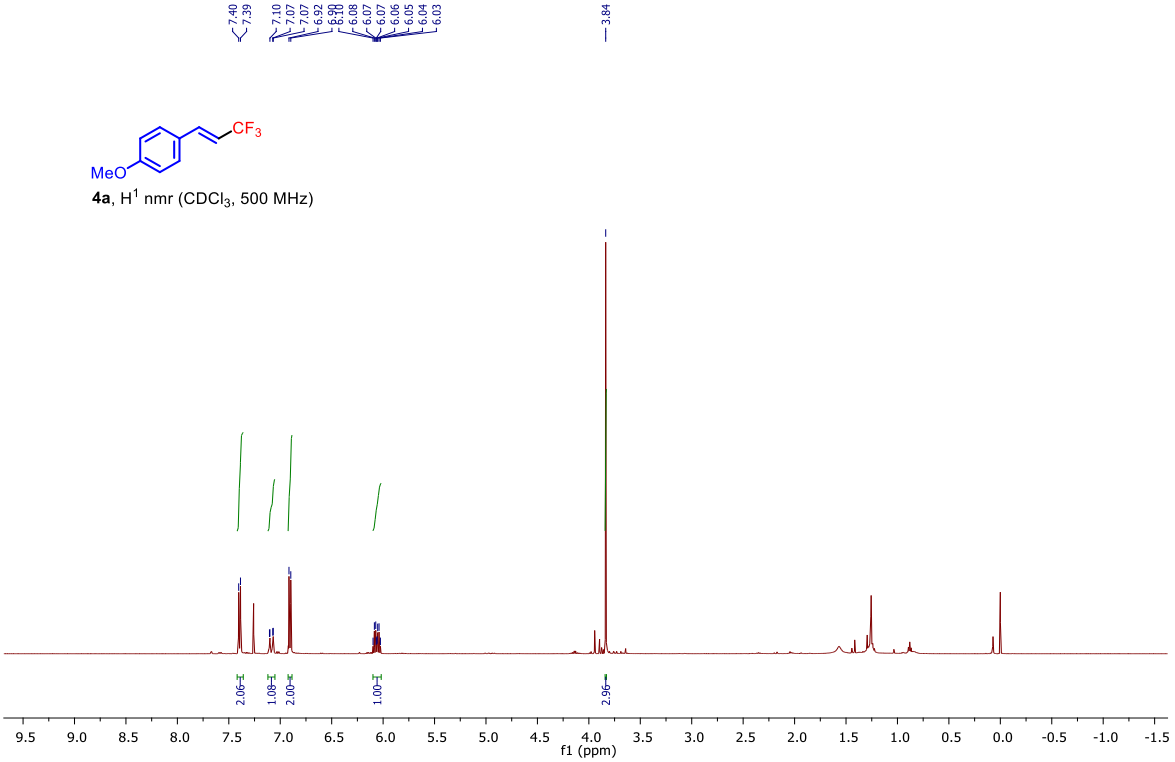
7. References:

1. a) M. R. Nadiveedhi, S. R. Cirandur and S. M. Akondi, *Green Chem.*, 2020, **22**, 5589–5593; b) B. R. Kusuma, L. B. Peterson, H. Zhao, G. Vielhauer, J. Holzbeierlein and B. S. J. Blagg, *J. Med. Chem.*, 2011, **54**, 6234–6253; c) G. Ma, W. Wan, J. Li, Q. Hu, H. Jiang, S. Zhu, J. Wang and J. Hao, *Chem. Commun.*, 2014, **50**, 9749–9752 d) T. Balalas, C. Peperidou, D. J. Hadjipavlou-Litina and K. E. Litinas, *Synthesis.*, 2016, **48**, 281–292; e) L. W. Lawrence Woo, B. Leblond, A. Purohit and B. V. L. Potter, *Bioorganic Med. Chem.*, 2012, **20**, 2506–2519.

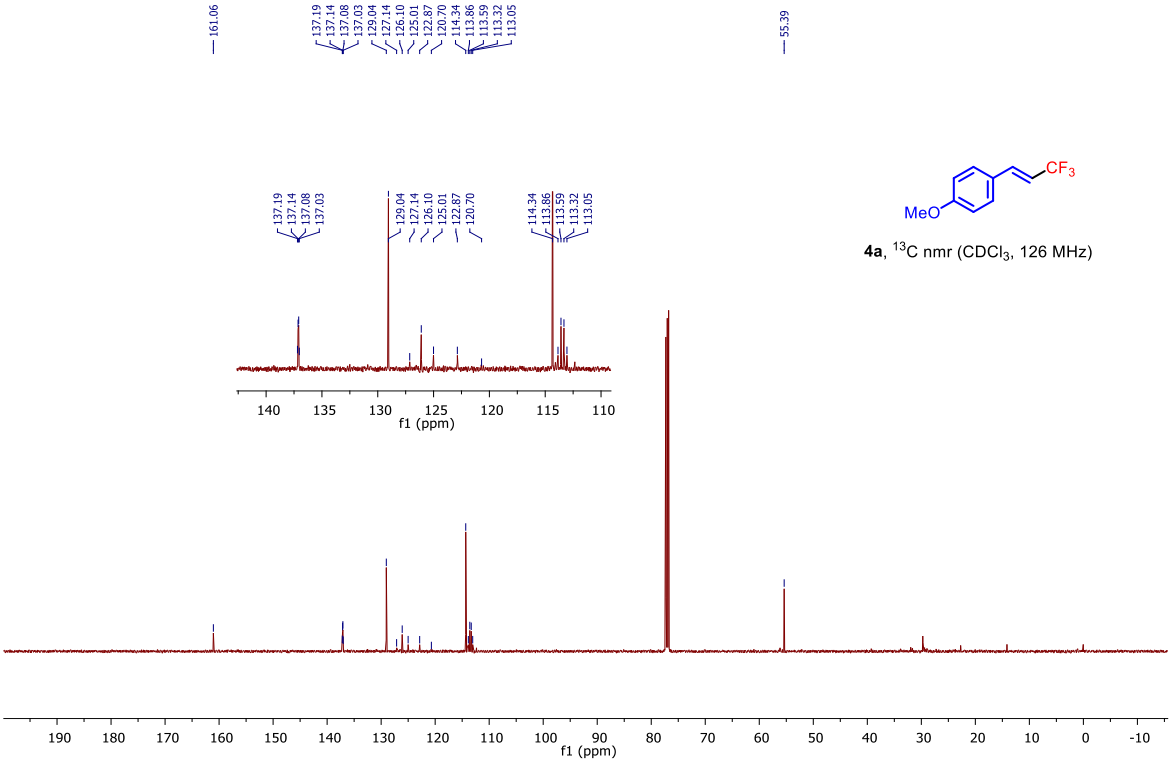
2. a) R. N. Mitra, K. Show, D. Barman, S. Sarkar and D. K. Maiti, *J. Org. Chem.*, 2019, **84**, 42–52; b) J. M. Rodríguez and M. Dolors Pujol, *Tetrahedron Lett.*, 2011, **52**, 2629–2632; c) S. P. Midya, J. Rana, T. Abraham, B. Aswin and E. Balaraman, *Chem. Commun.*, 2017, **53**, 6760–6763; d) N. Zhang, Z. J. Quan, Z. Zhang, Y. X. Da and X. C. Wang, *Chem. Commun.*, 2016, **52**, 14234–14237; e) T. P. Kogan and F. C. A. Gaeta, *Synth.*, 1988, **9**, 706–707.

3. J. Zhao, R. X. Liu, C. P. Luo and L. Yang, *Org. Lett.*, 2020, **22**, 6776–6779

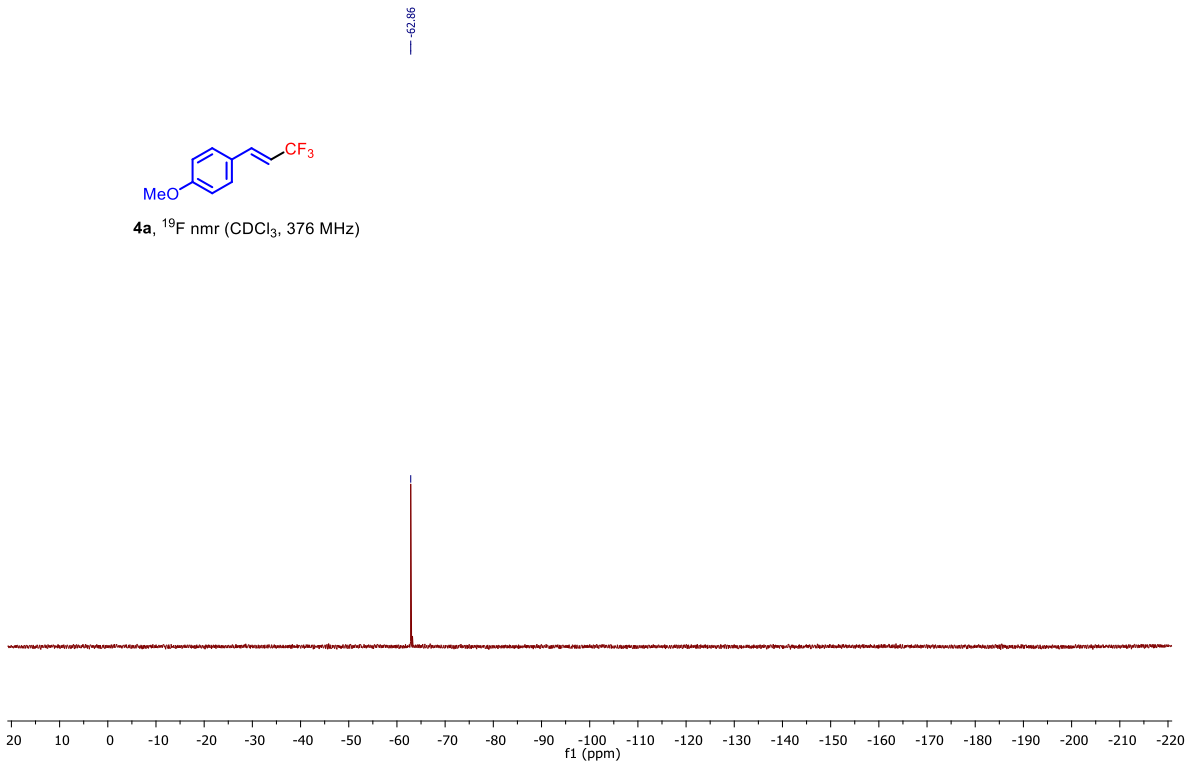
8. NMR Spectra:



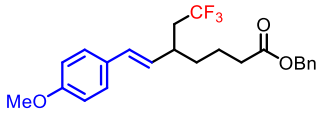
4a, H^1 nmr ($CDCl_3$, 500 MHz)



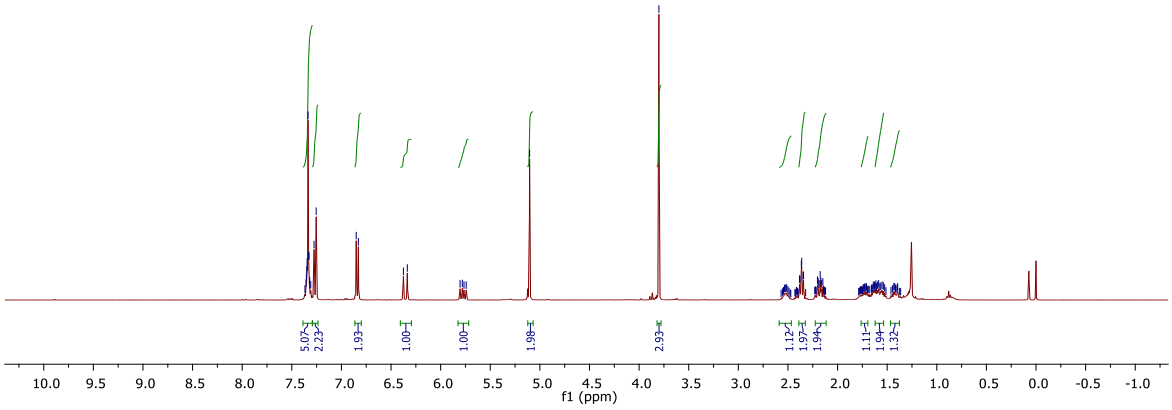
4a, ^{13}C nmr ($CDCl_3$, 126 MHz)

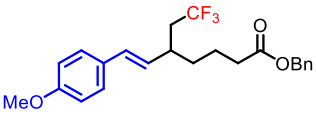


4a, ^{19}F nmr ($CDCl_3$, 376 MHz)

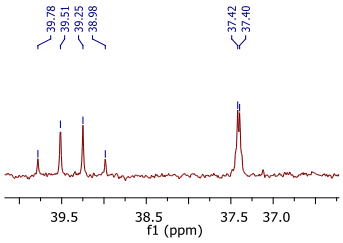


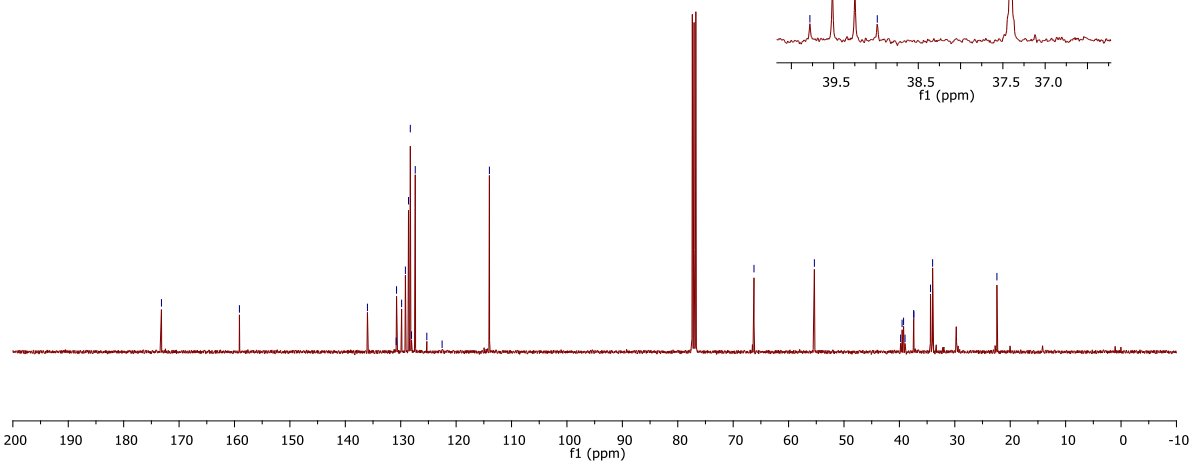
3aa, H^1 nmr ($CDCl_3$, 400 MHz)

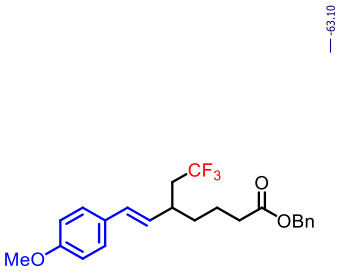




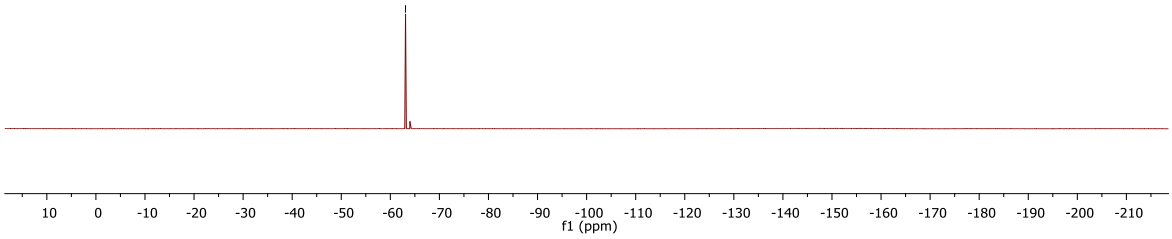
3aa, ^{13}C nmr ($CDCl_3$, 101 MHz)

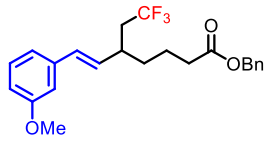




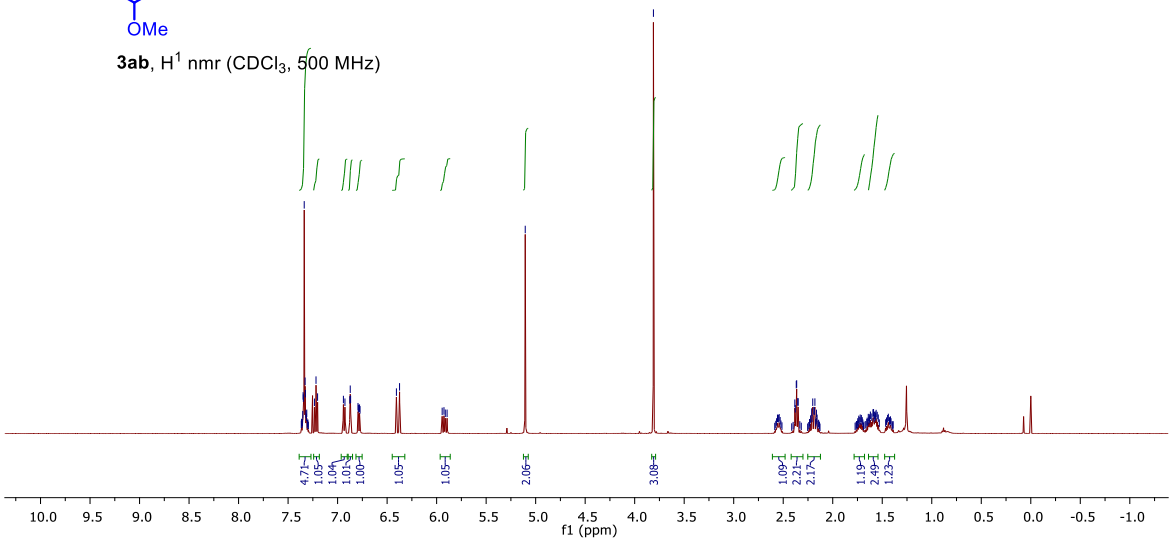


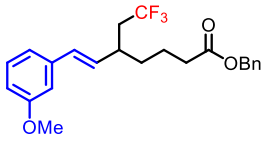
3aa, ^{19}F nmr ($CDCl_3$, 376 MHz)



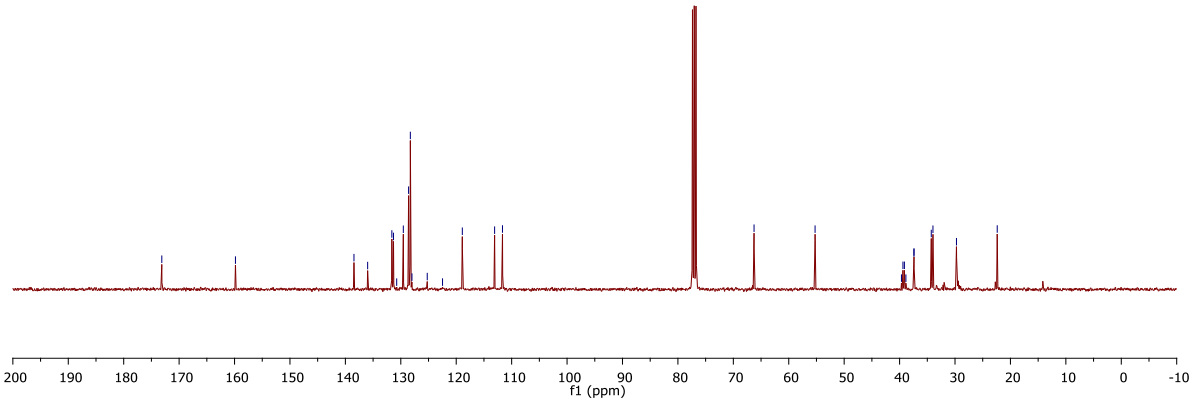


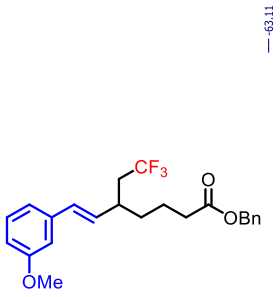
3ab, H^1 nmr ($CDCl_3$, 500 MHz)



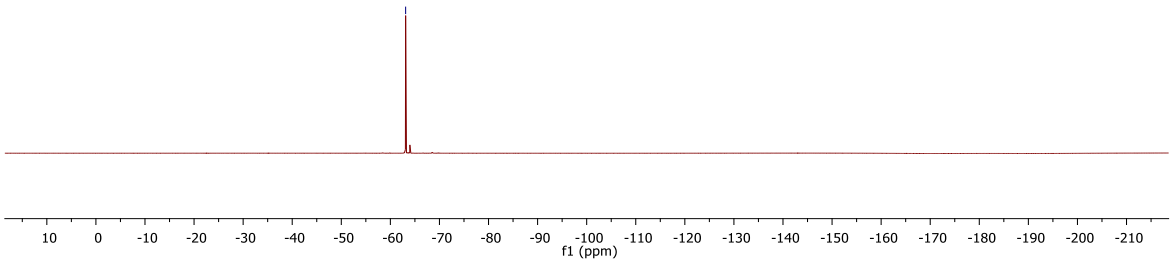


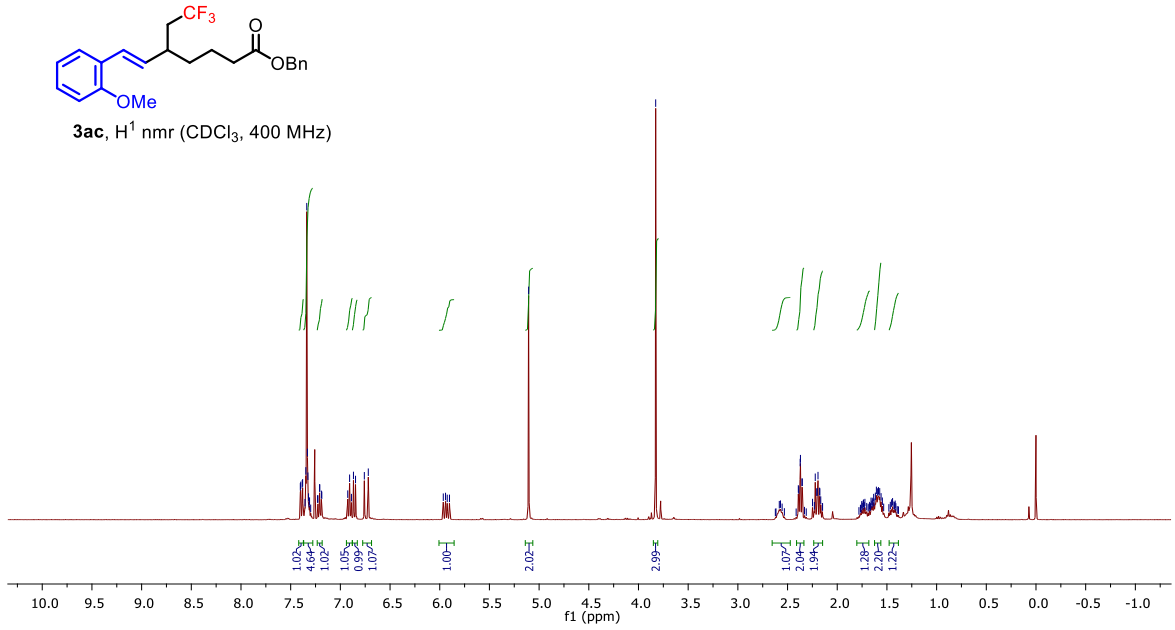
3ab, ^{13}C nmr ($CDCl_3$, 101 MHz)



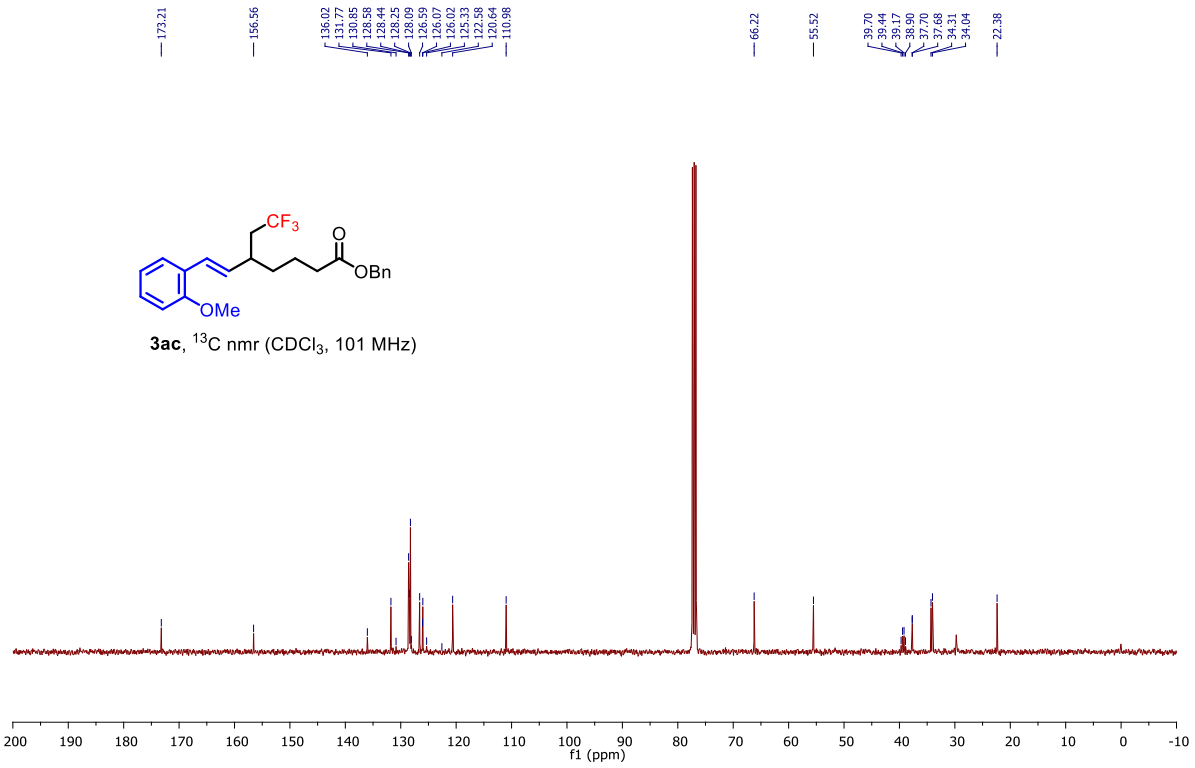


3ab, ^{19}F nmr ($CDCl_3$, 376 MHz)

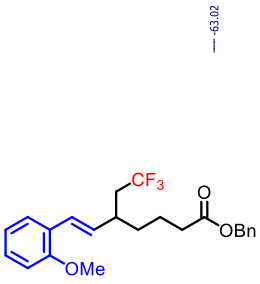




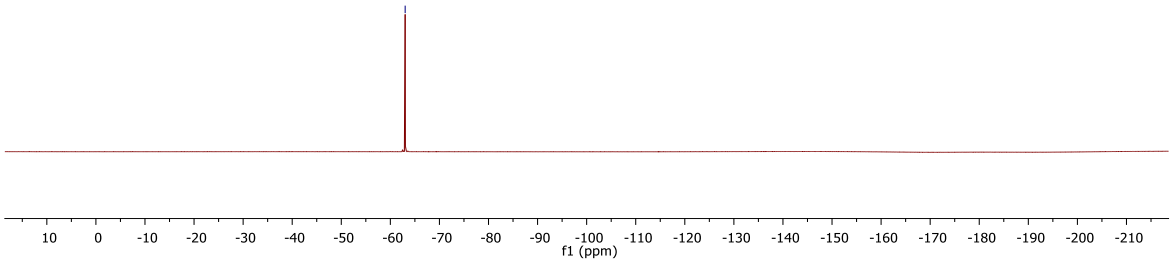
3ac, H^1 nmr ($CDCl_3$, 400 MHz)

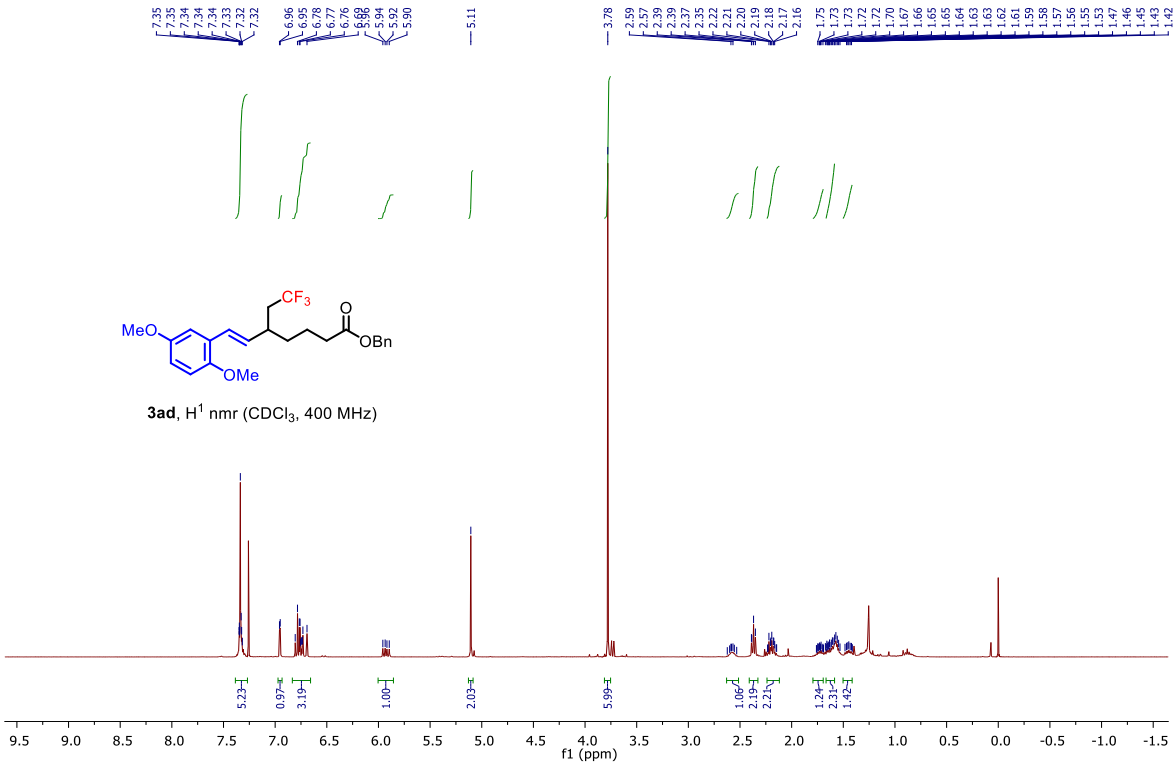


3ac, ^{13}C nmr ($CDCl_3$, 101 MHz)

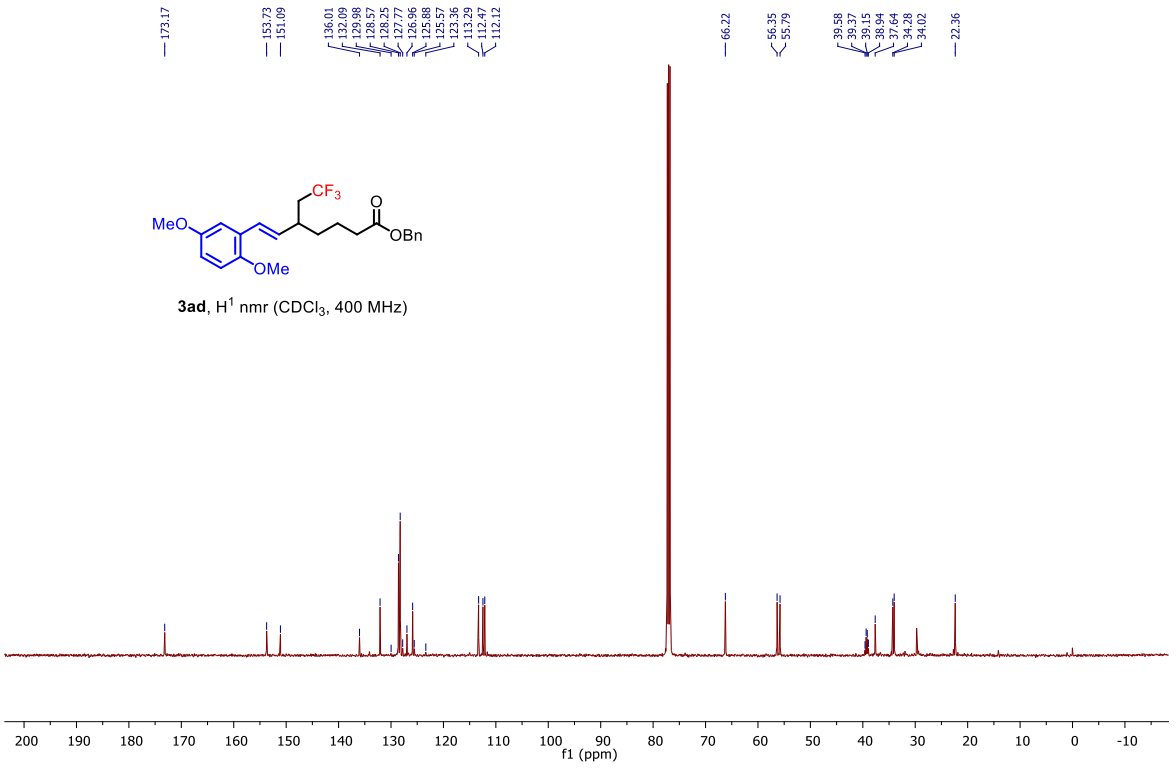


3ac, ^{19}F nmr ($CDCl_3$, 376 MHz)

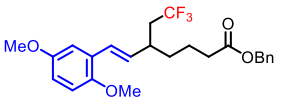




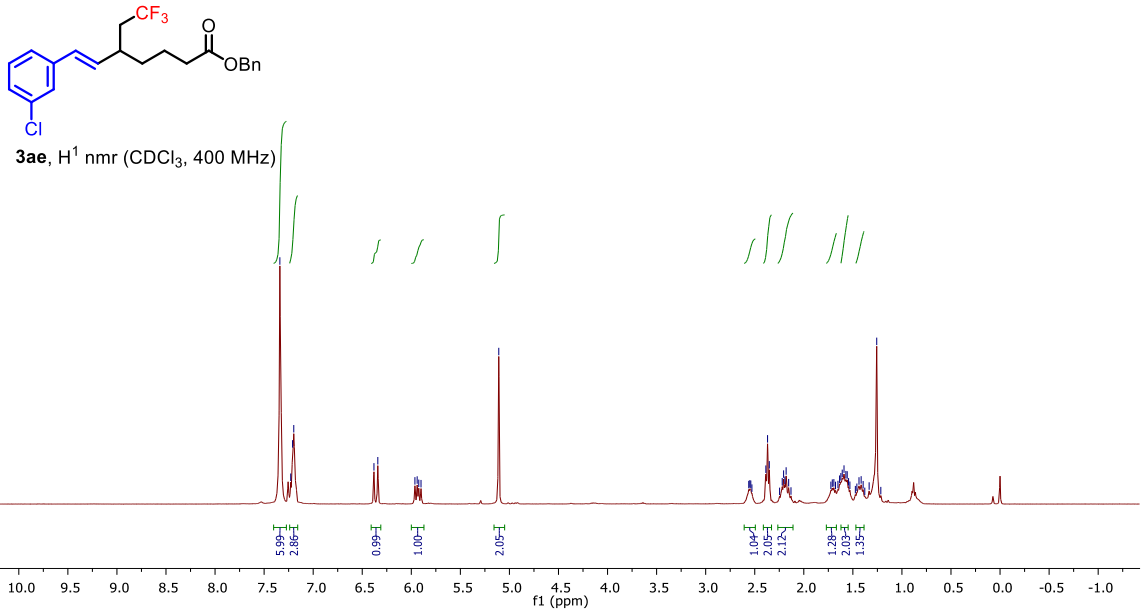
3ad, H^1 nmr ($CDCl_3$, 400 MHz)



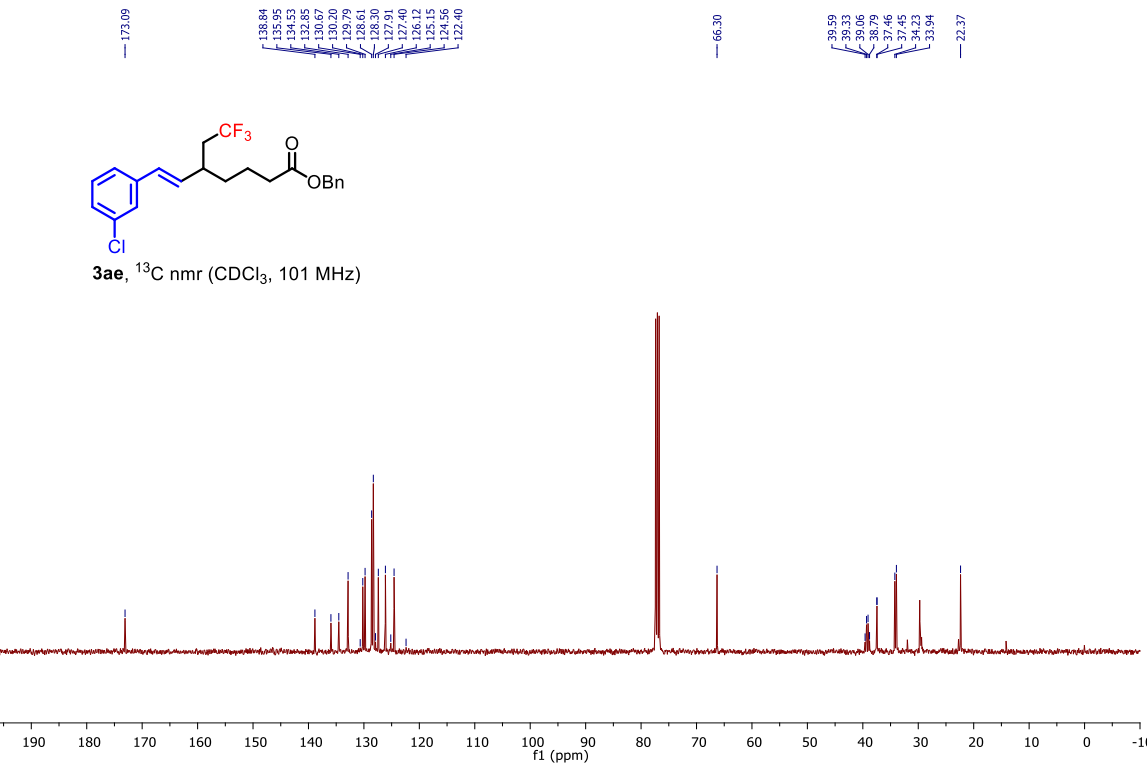
3ad, H^1 nmr ($CDCl_3$, 400 MHz)



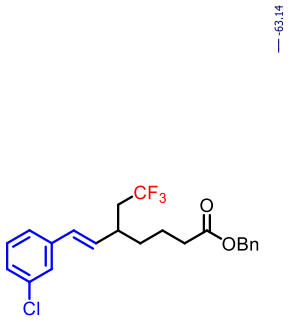
3ad, ^{19}F nmr ($CDCl_3$, 376 MHz)



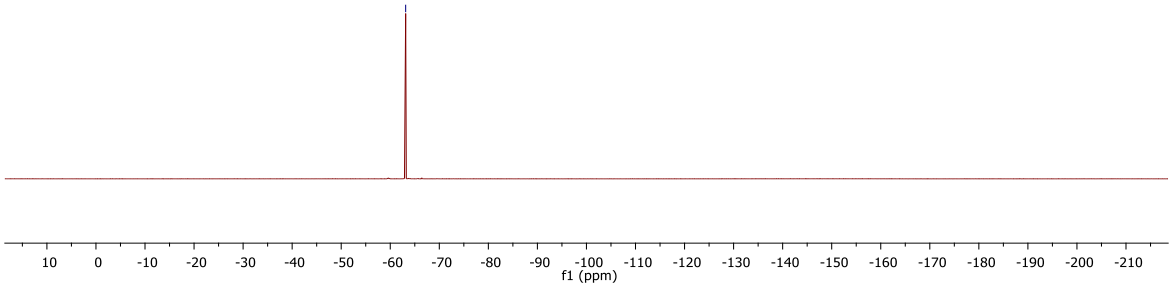
3ae, H^1 nmr ($CDCl_3$, 400 MHz)

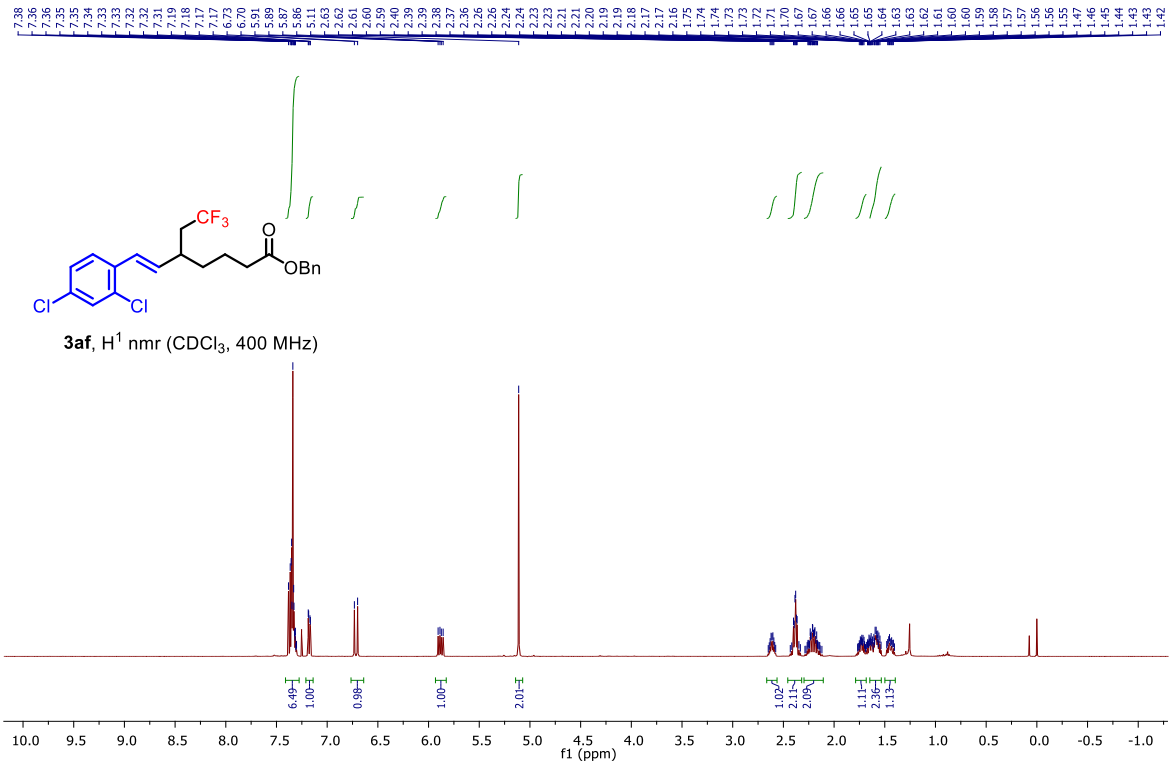


3ae, ^{13}C nmr ($CDCl_3$, 101 MHz)

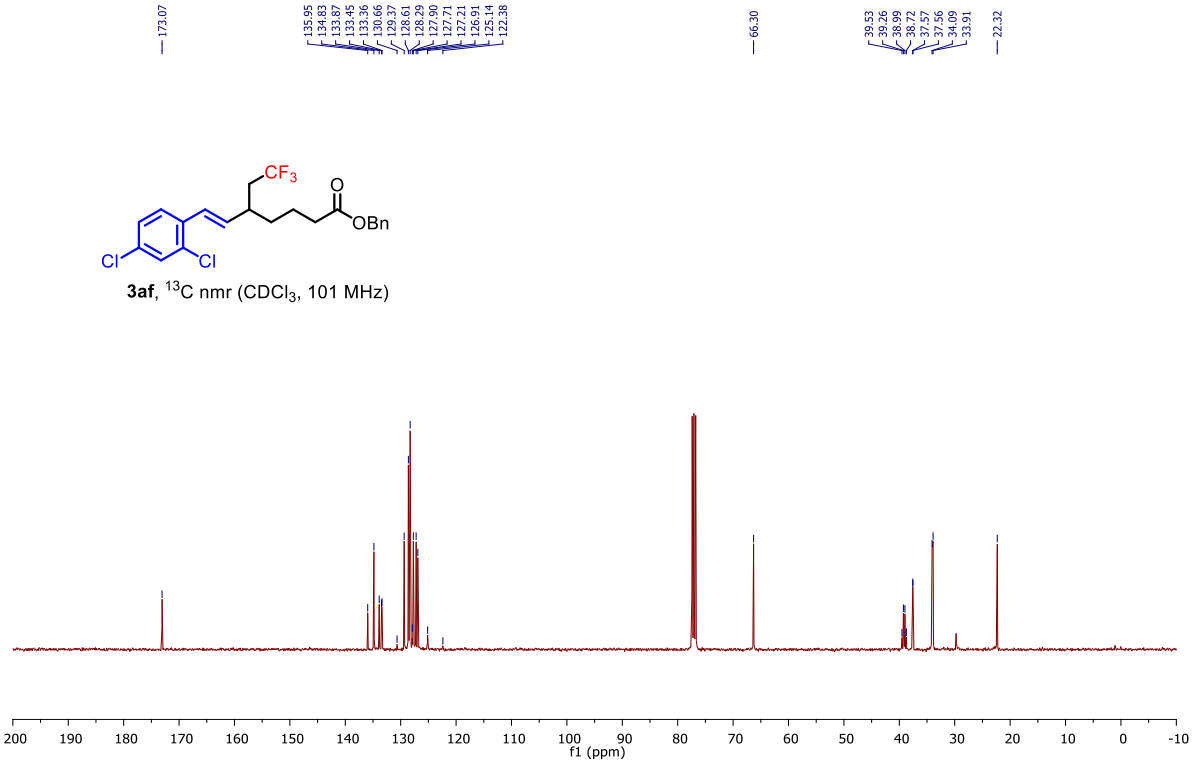


3ae, ^{19}F nmr ($CDCl_3$, 376 MHz)

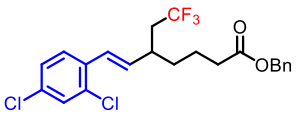




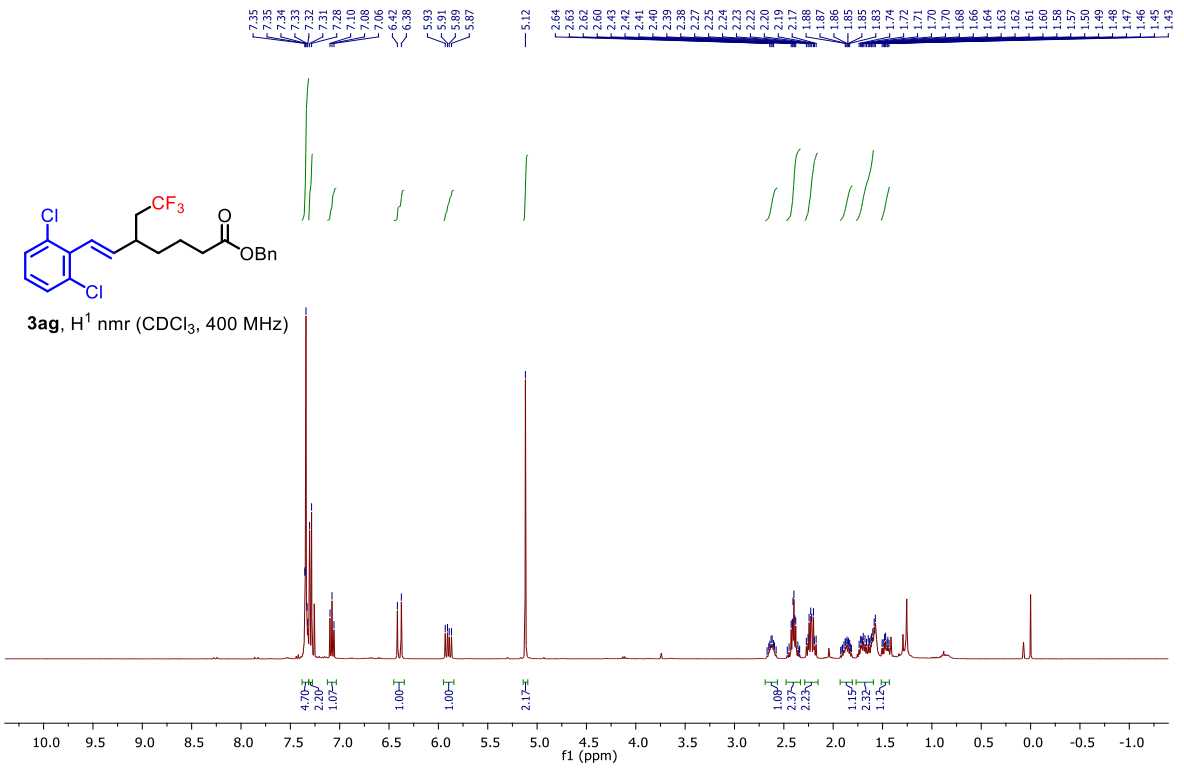
3af, H^1 nmr ($CDCl_3$, 400 MHz)



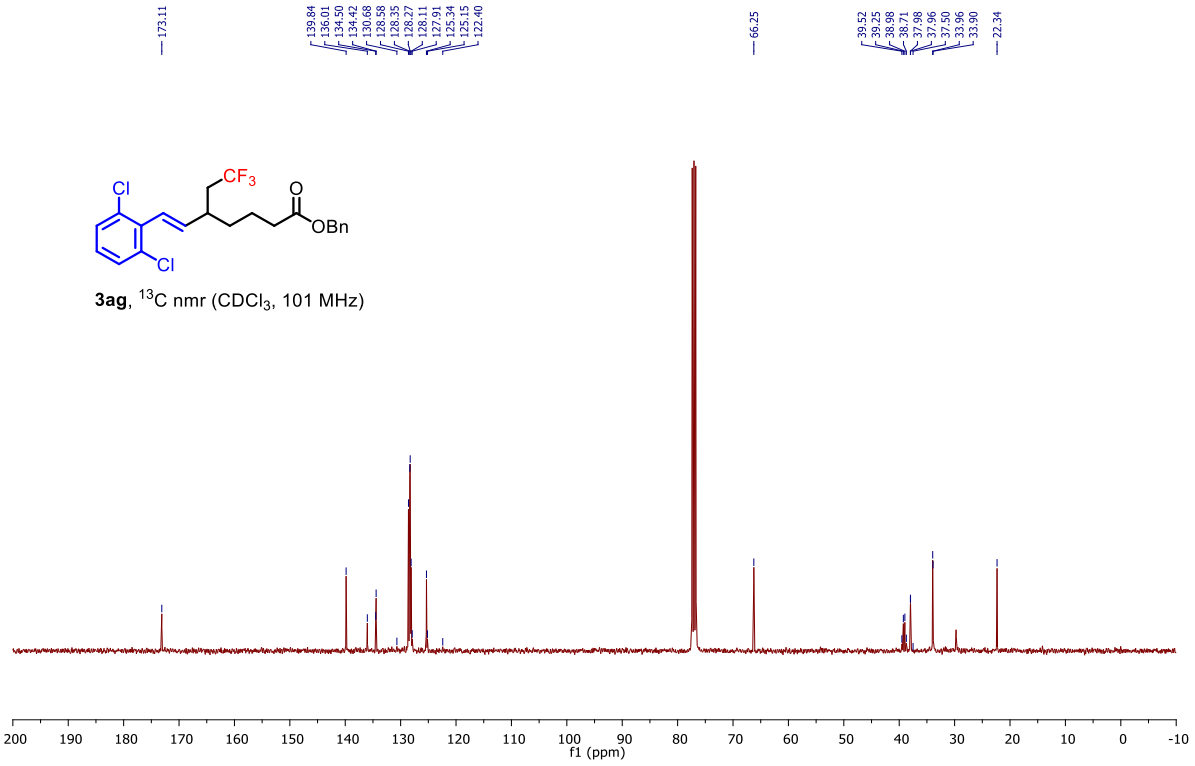
3af, ^{13}C nmr ($CDCl_3$, 101 MHz)



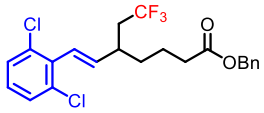
3af, ^{19}F nmr ($CDCl_3$, 376 MHz)



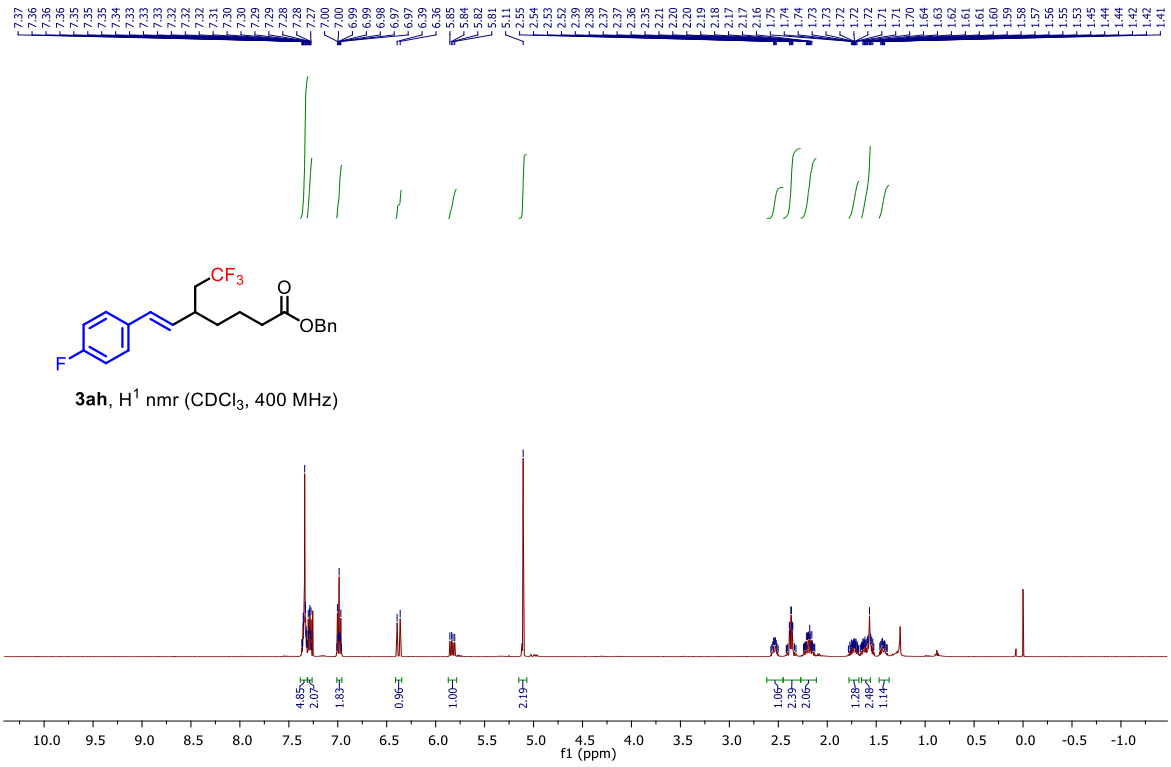
3ag, H^1 nmr ($CDCl_3$, 400 MHz)



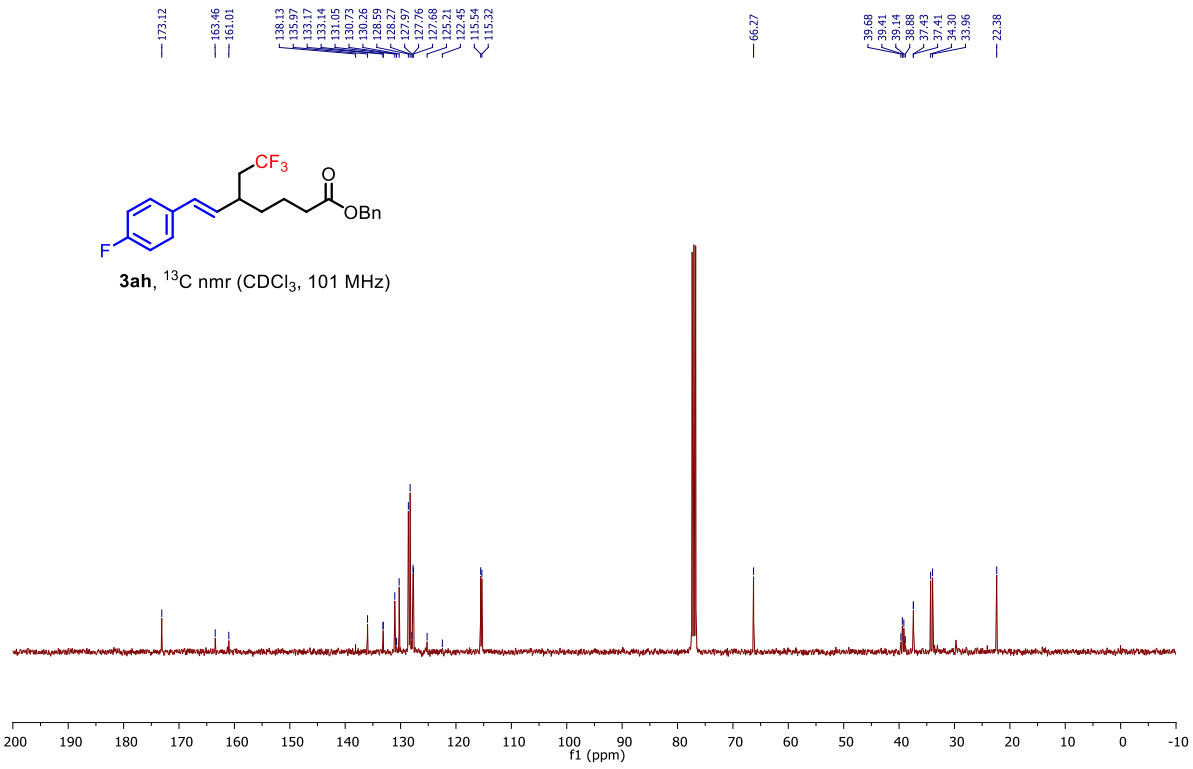
3ag, ^{13}C nmr ($CDCl_3$, 101 MHz)



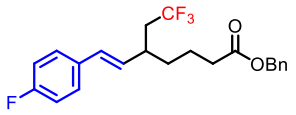
3ag, ^{19}F nmr ($CDCl_3$, 376 MHz)



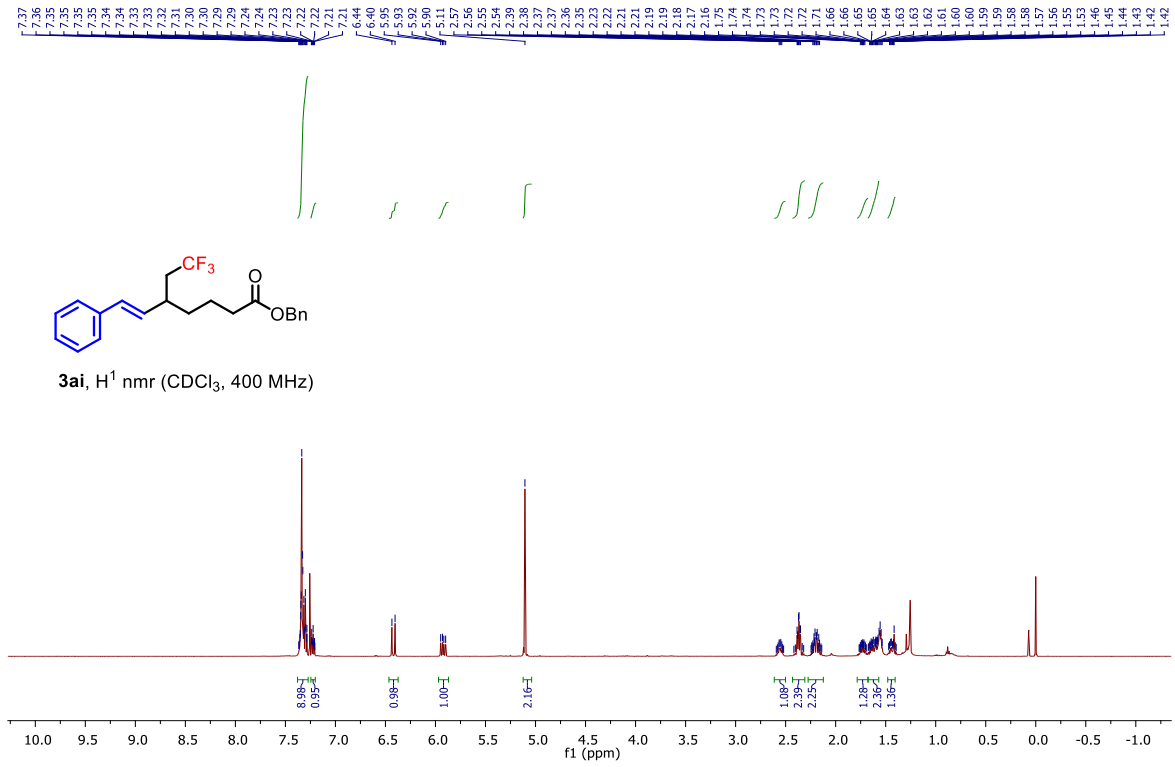
3ah, H^1 nmr ($CDCl_3$, 400 MHz)



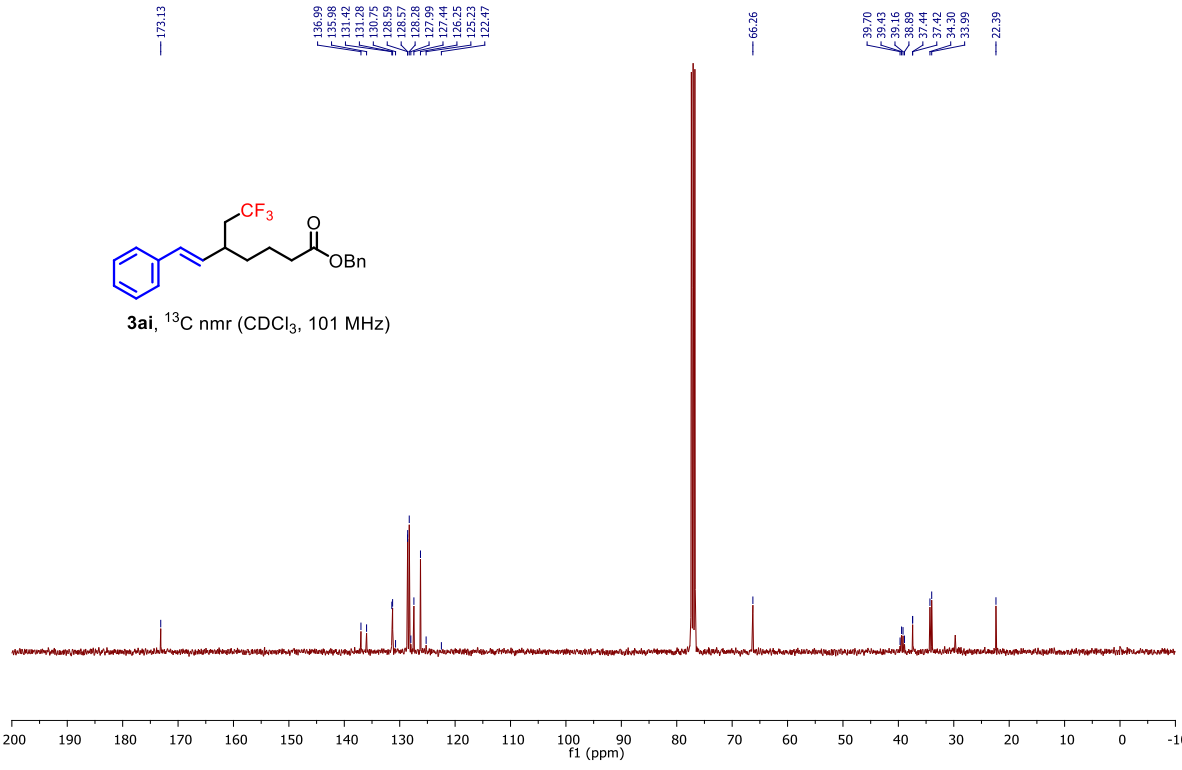
3ah, ^{13}C nmr ($CDCl_3$, 101 MHz)



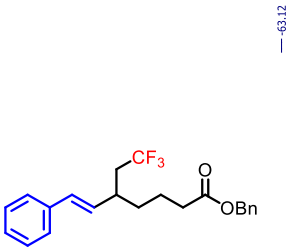
3ah, ^{19}F nmr ($CDCl_3$, 376 MHz)



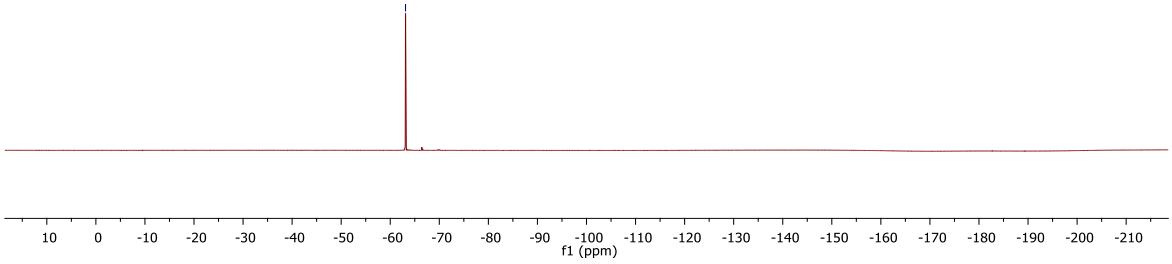
3ai, H^1 nmr ($CDCl_3$, 400 MHz)

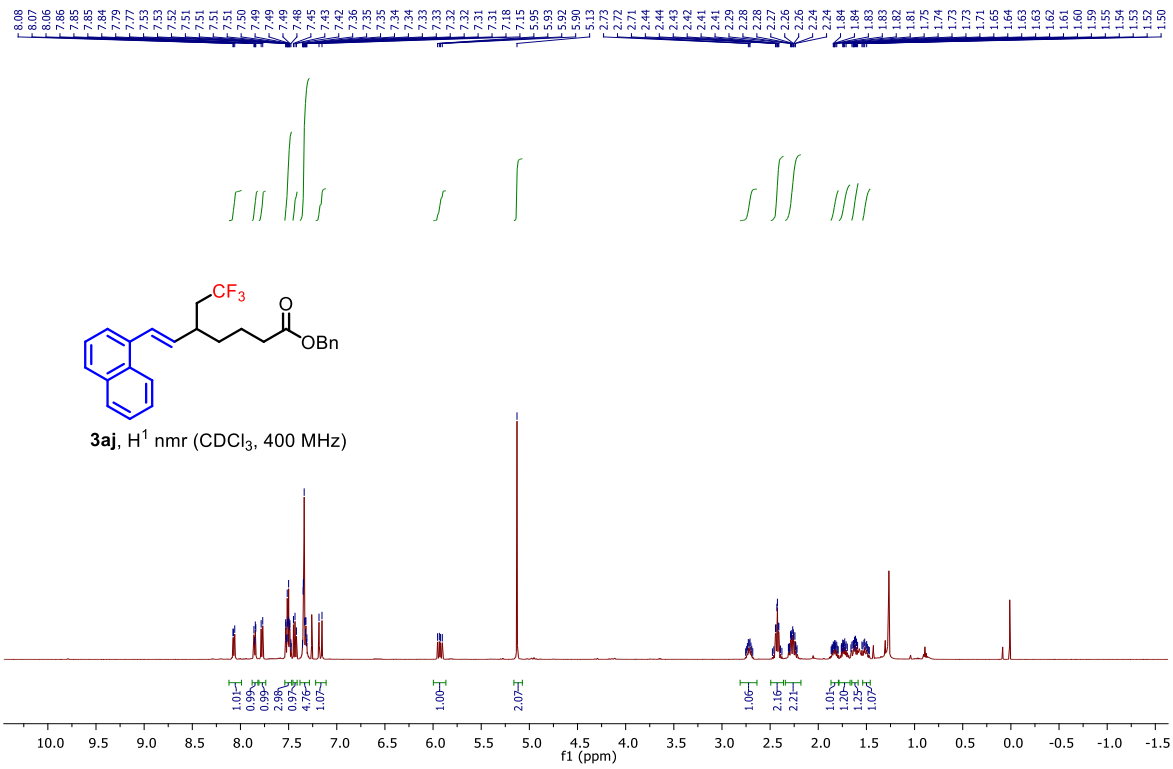


3ai, ^{13}C nmr ($CDCl_3$, 101 MHz)

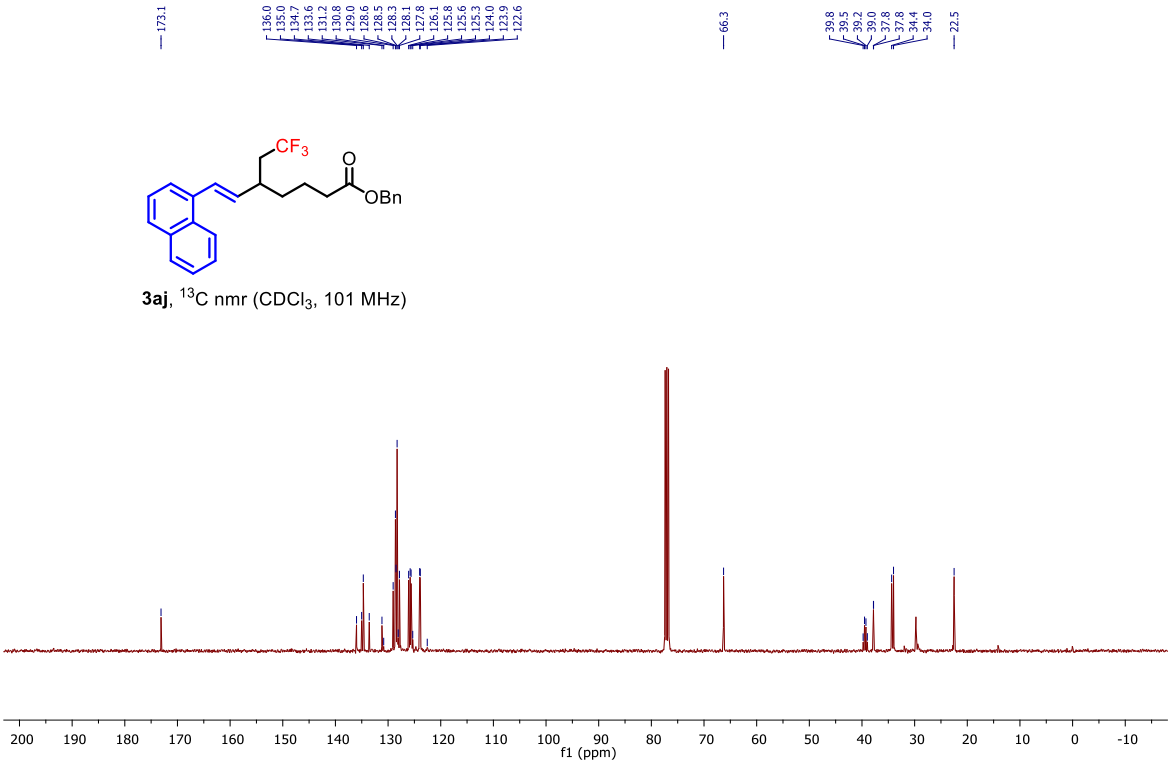


3ai, ^{19}F nmr ($CDCl_3$, 376 MHz)

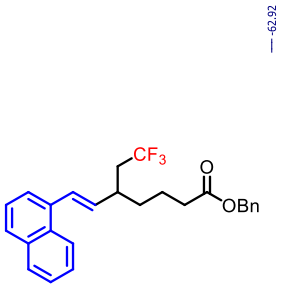




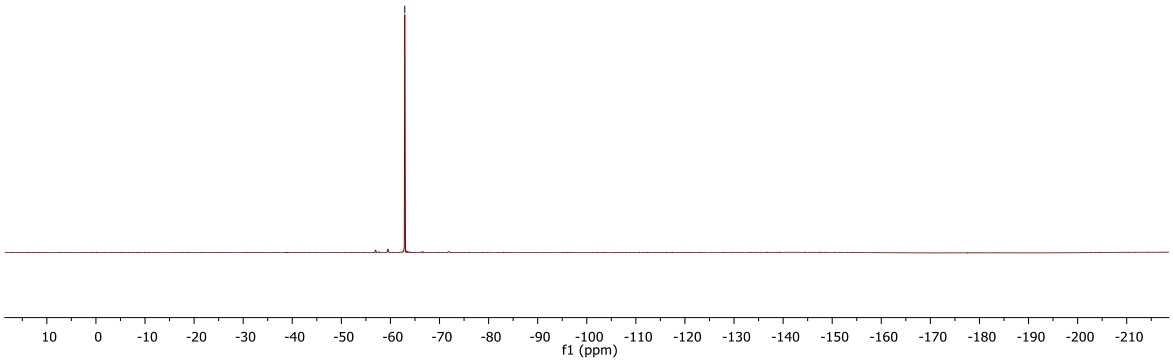
3aj, H^1 nmr ($CDCl_3$, 400 MHz)

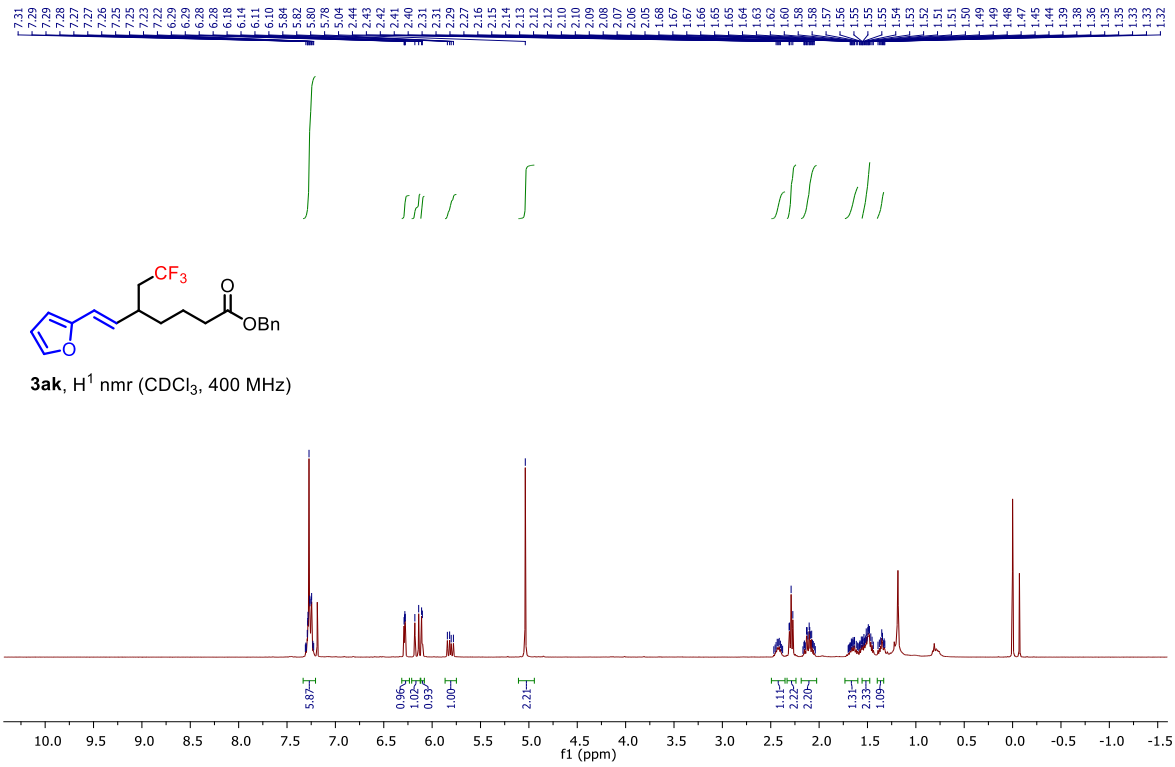


3aj, ^{13}C nmr ($CDCl_3$, 101 MHz)

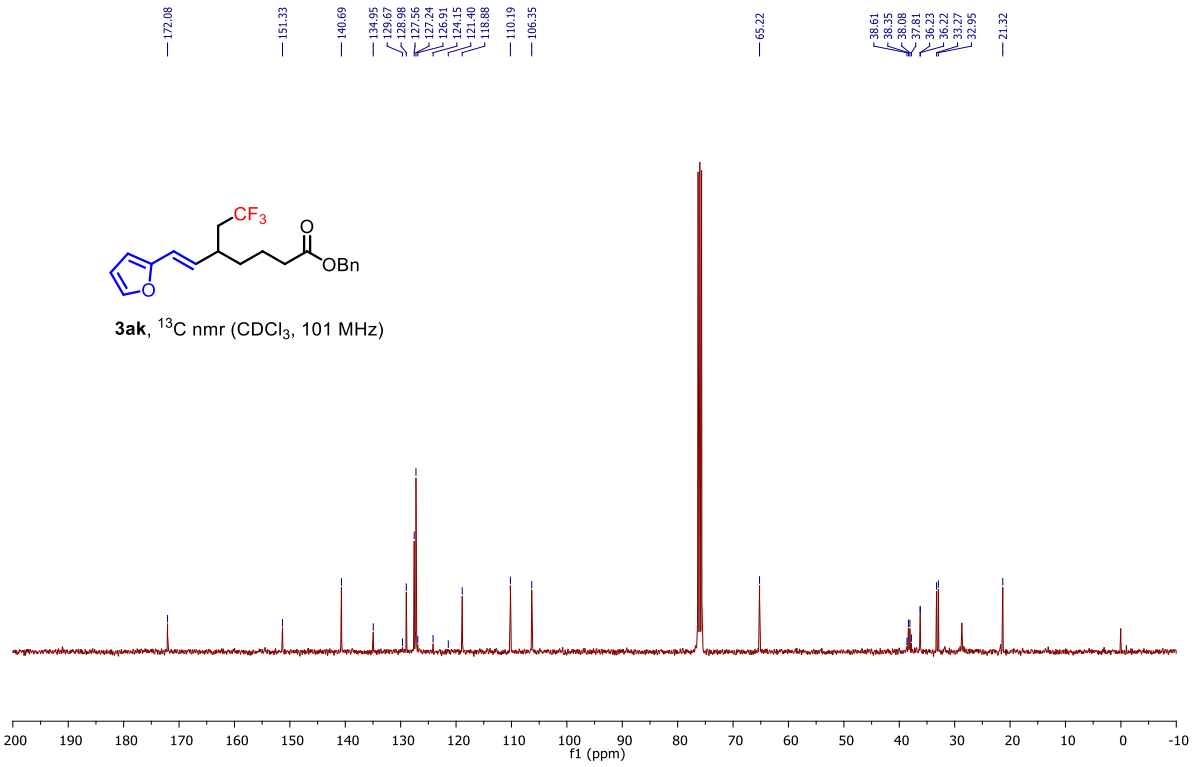


3aj, ^{19}F nmr ($CDCl_3$, 376 MHz)

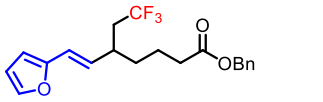




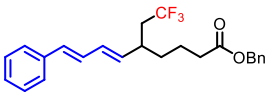
3ak, H^1 nmr ($CDCl_3$, 400 MHz)



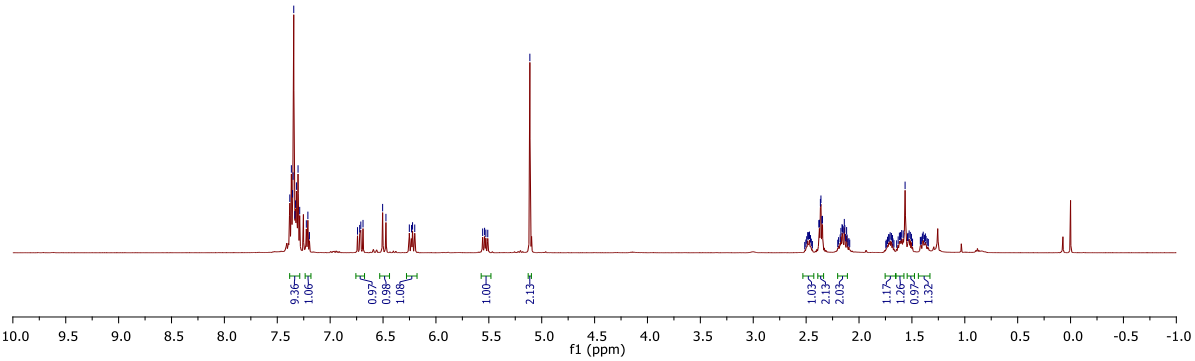
3ak, ^{13}C nmr ($CDCl_3$, 101 MHz)

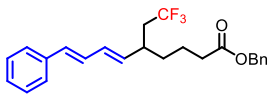


3ak, ^{19}F nmr ($CDCl_3$, 376 MHz)

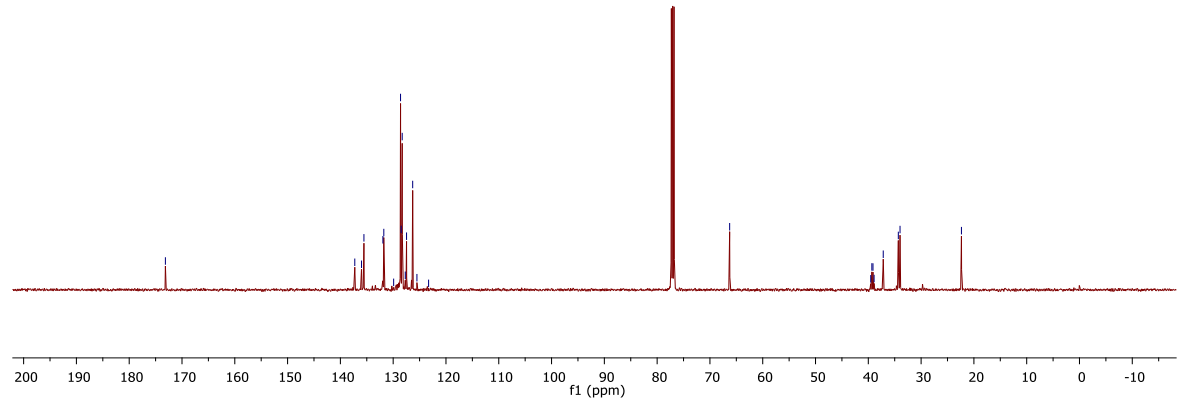


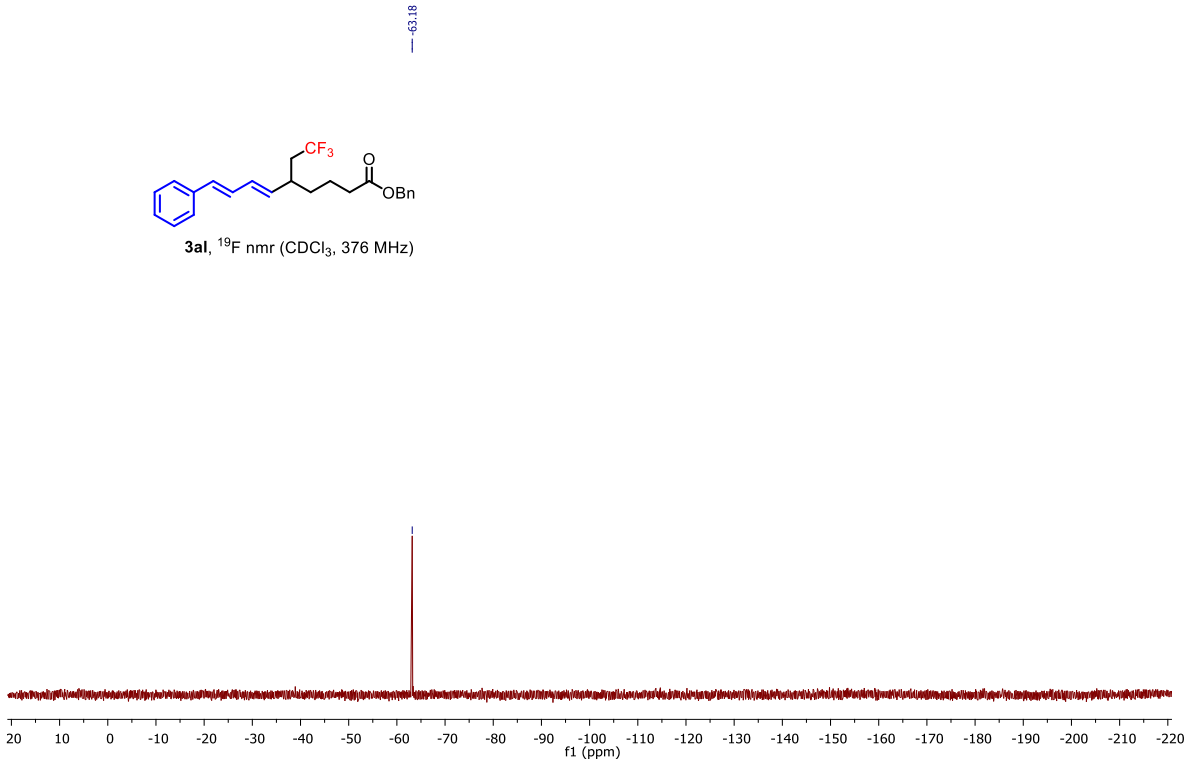
3al, H^1 nmr ($CDCl_3$, 500 MHz)



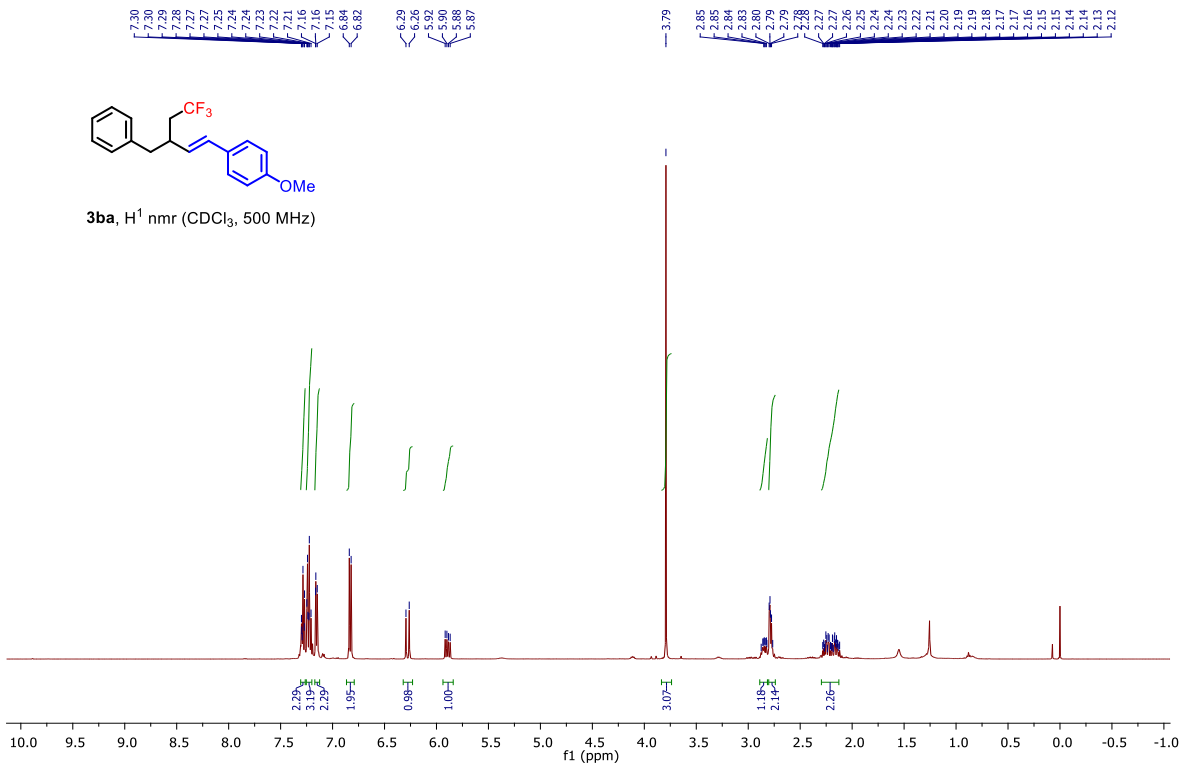


3al, ^{13}C nmr ($CDCl_3$, 126 MHz)

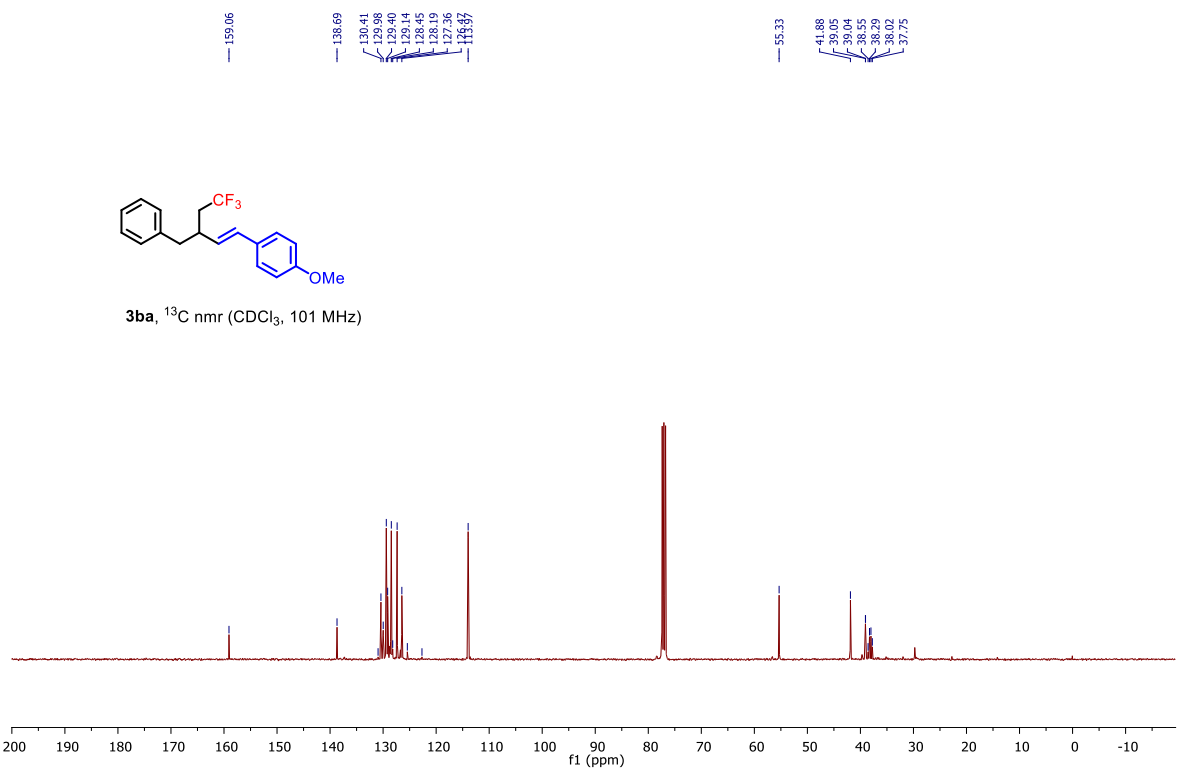




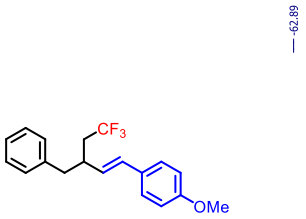
3al, ^{19}F nmr ($CDCl_3$, 376 MHz)



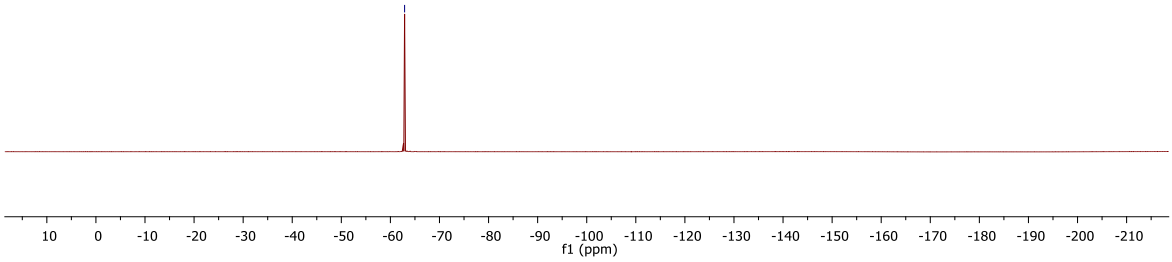
3ba, H^1 nmr ($CDCl_3$, 500 MHz)

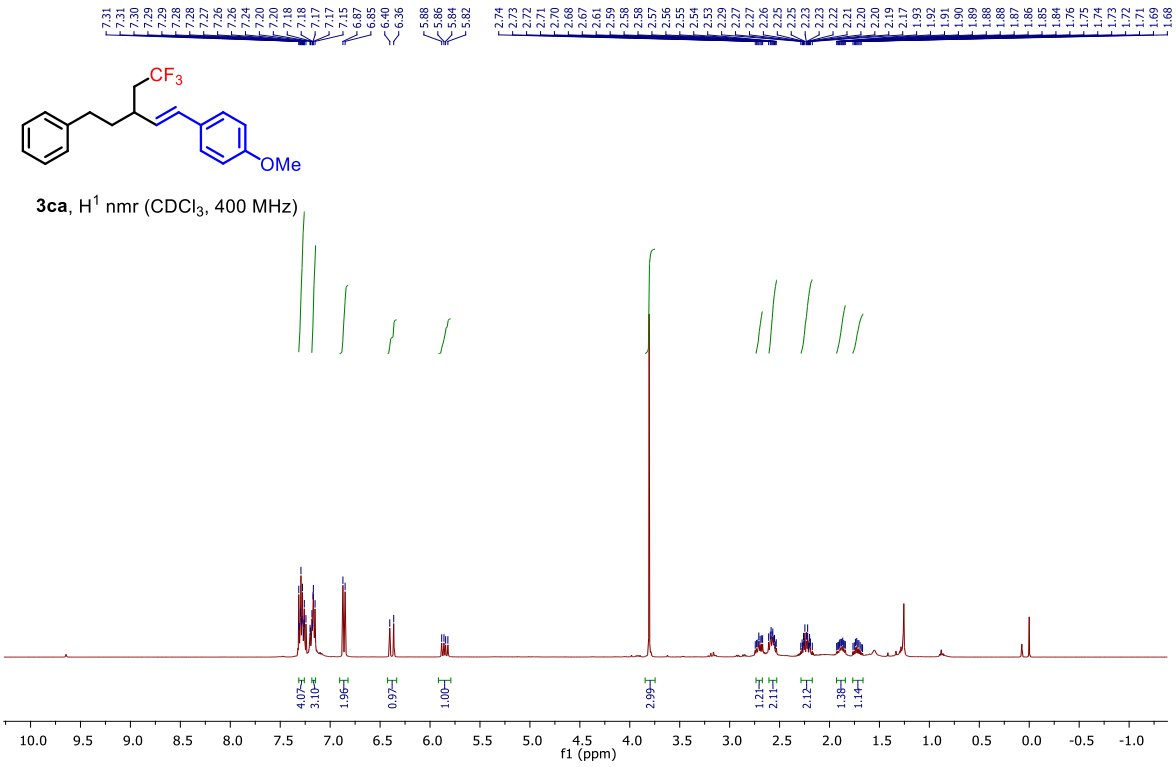


3ba, ^{13}C nmr ($CDCl_3$, 101 MHz)

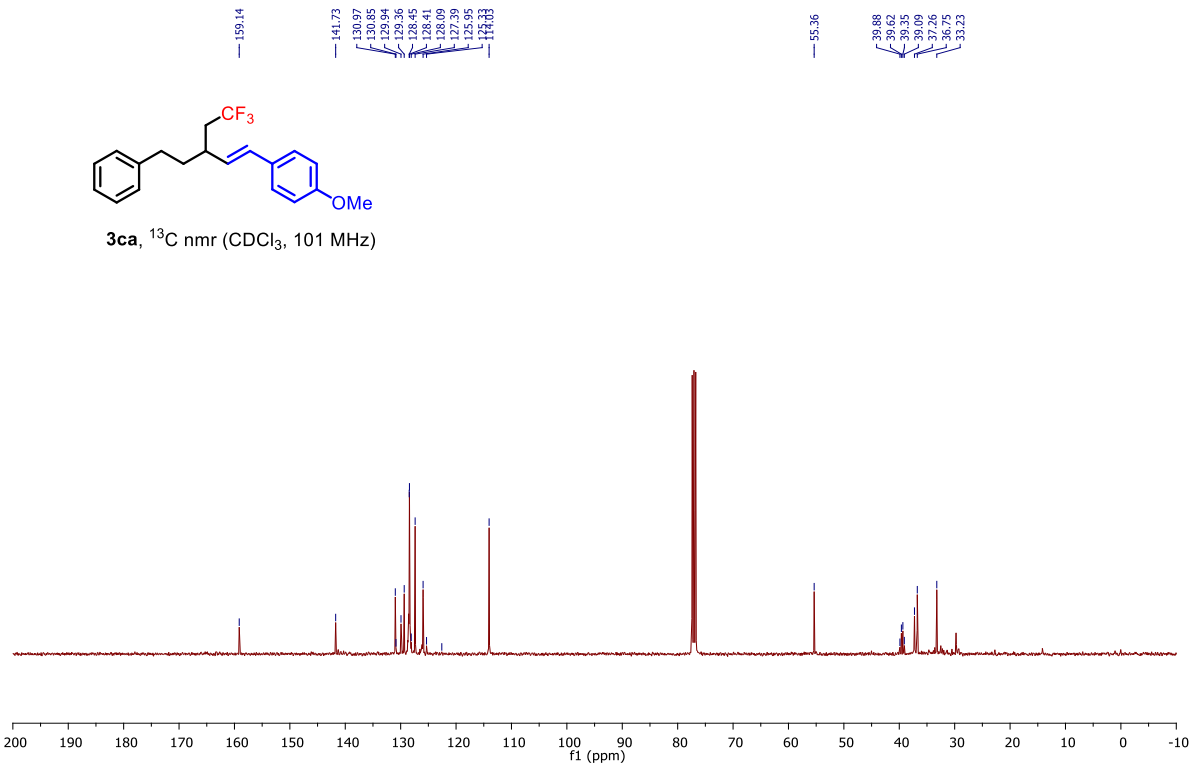


3ba, ^{19}F nmr ($CDCl_3$, 376 MHz)

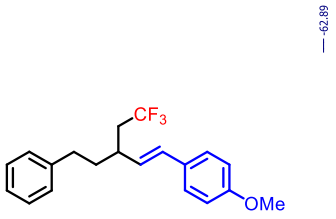




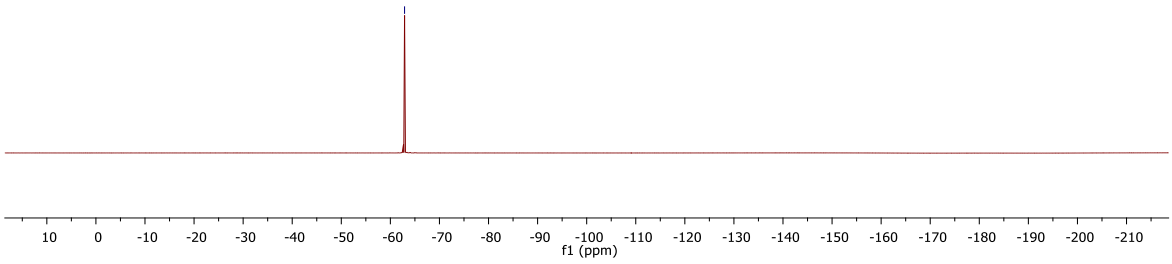
3ca, H^1 nmr ($CDCl_3$, 400 MHz)

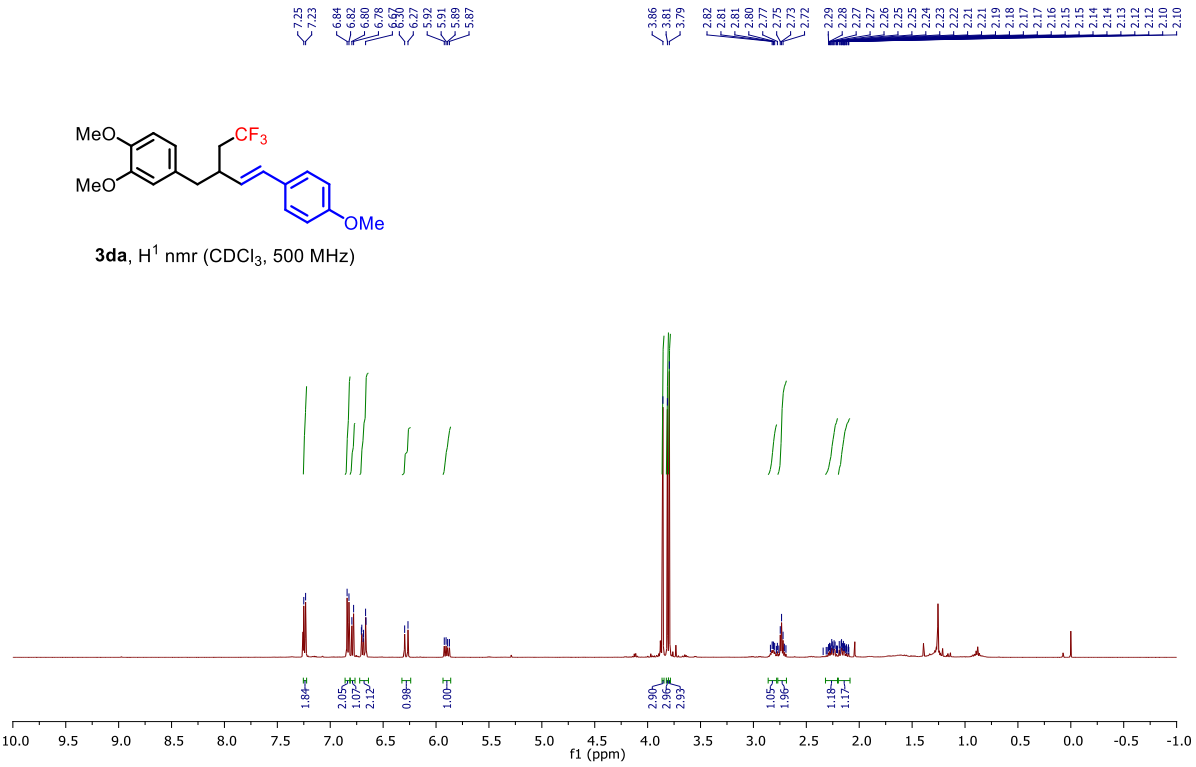


3ca, ^{13}C nmr ($CDCl_3$, 101 MHz)

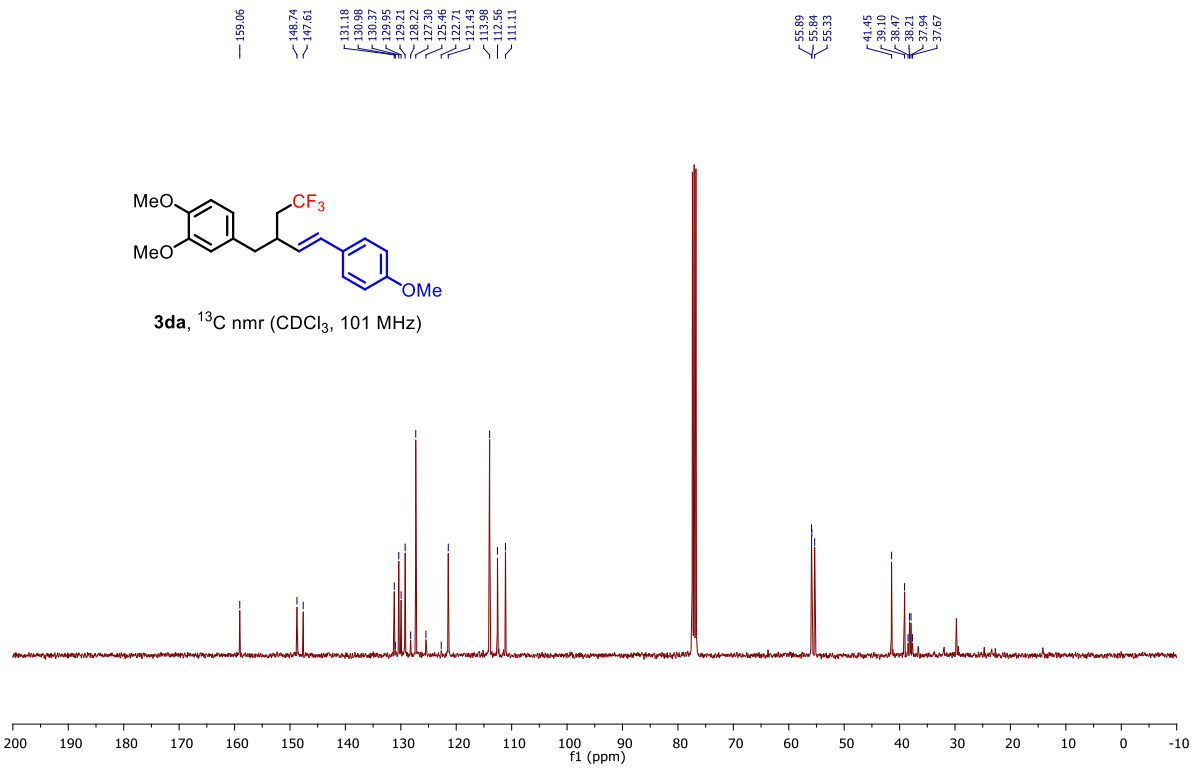


3ca, ^{19}F nmr ($CDCl_3$, 376 MHz)

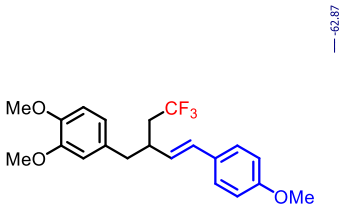




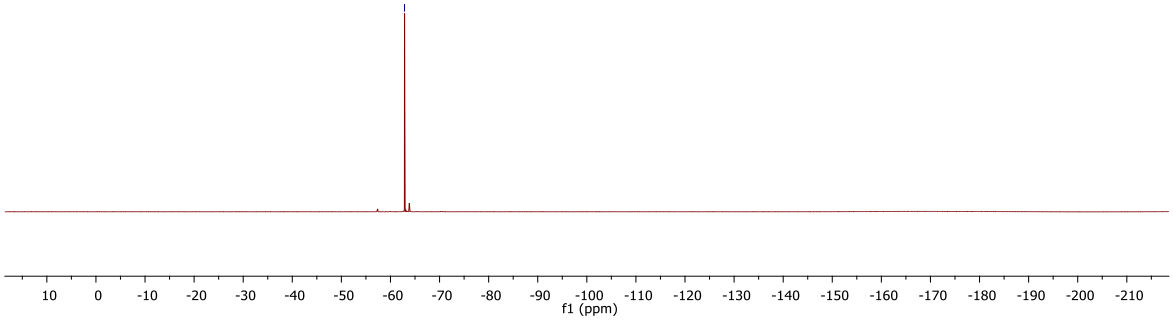
3da, H^1 nmr ($CDCl_3$, 500 MHz)

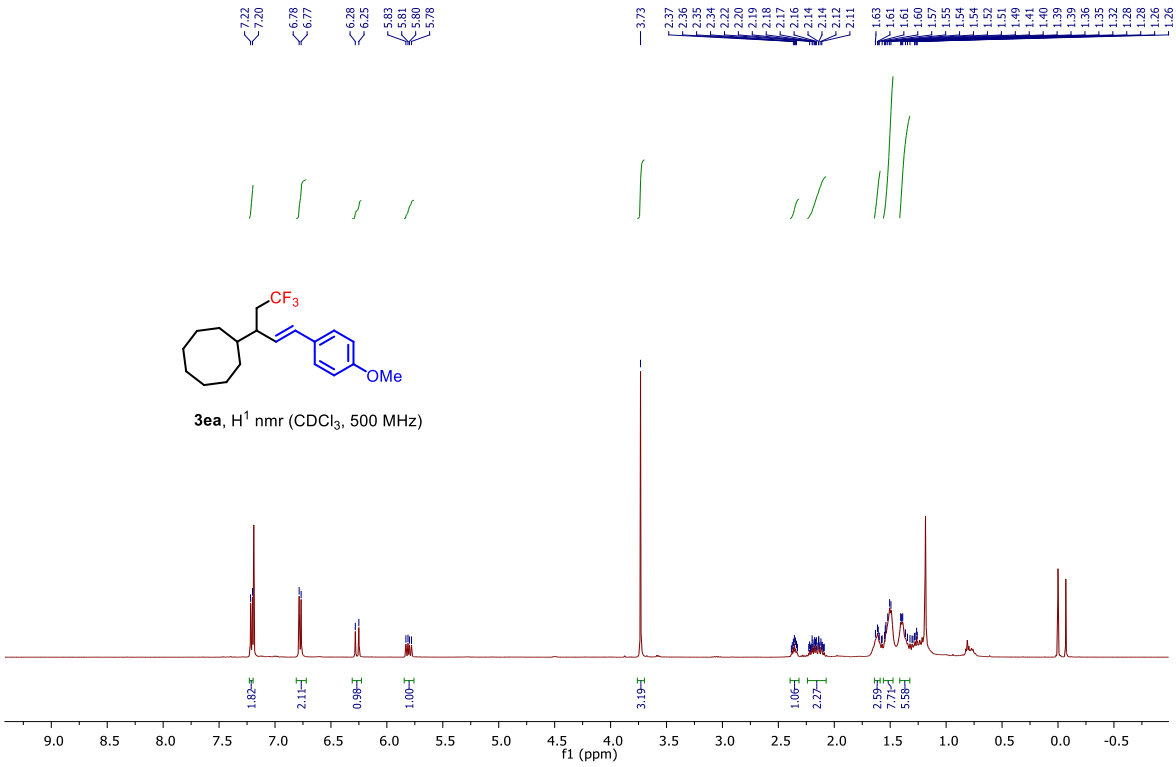


3da, ^{13}C nmr ($CDCl_3$, 101 MHz)

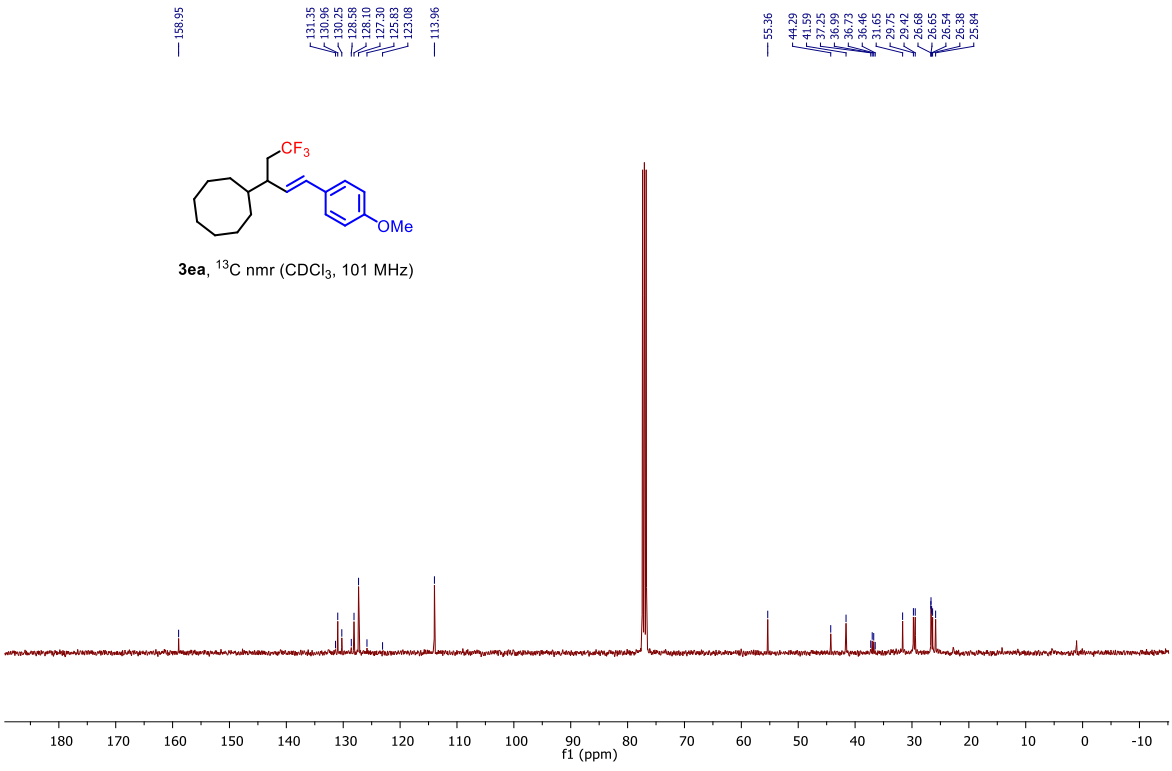


3da, ^{19}F nmr ($CDCl_3$, 376 MHz)

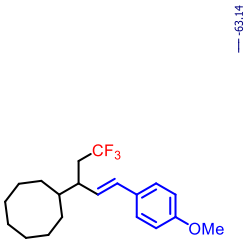




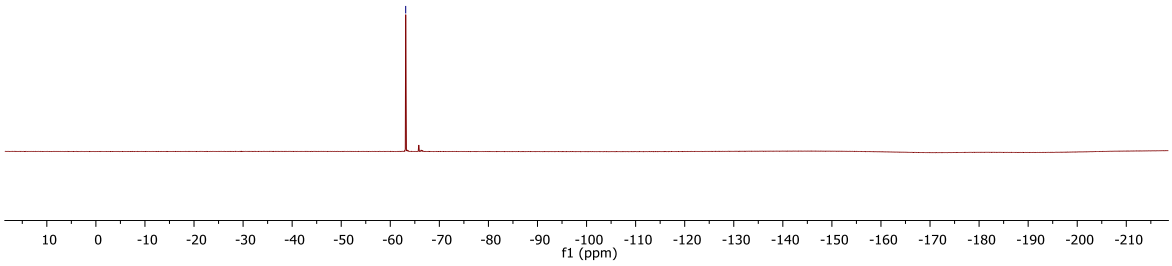
3ea, H^1 nmr ($CDCl_3$, 500 MHz)

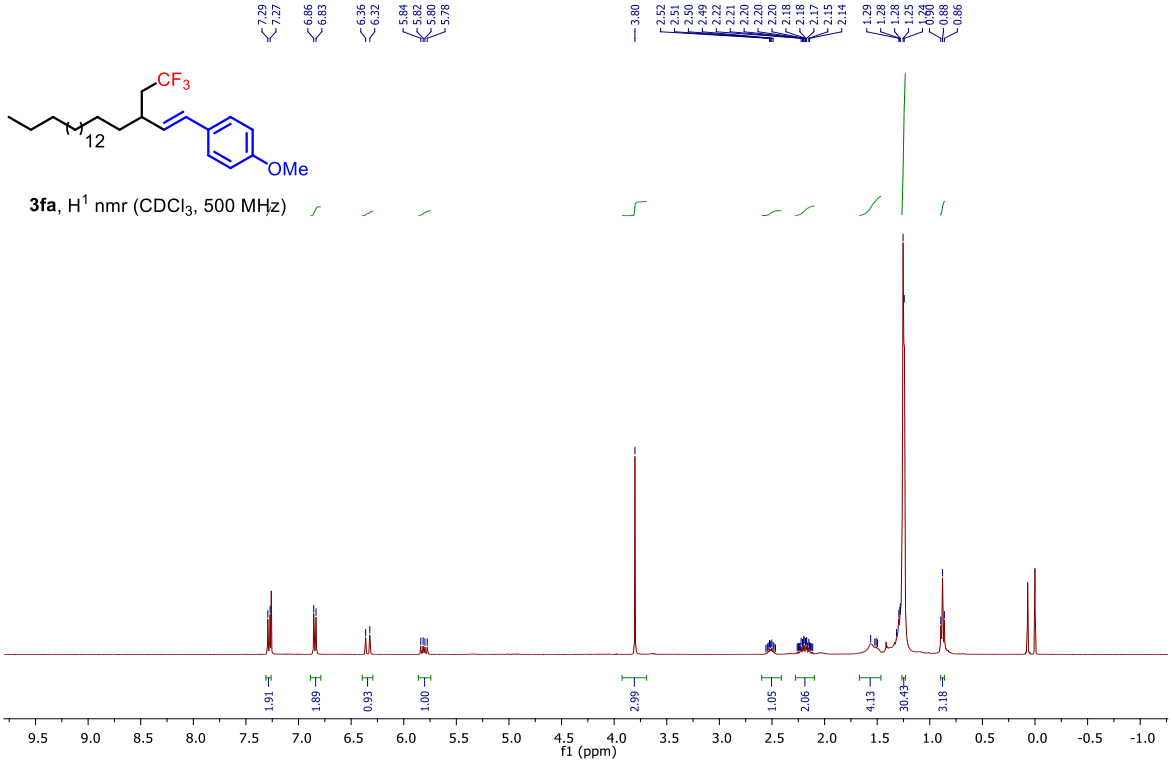


3ea, ^{13}C nmr ($CDCl_3$, 101 MHz)

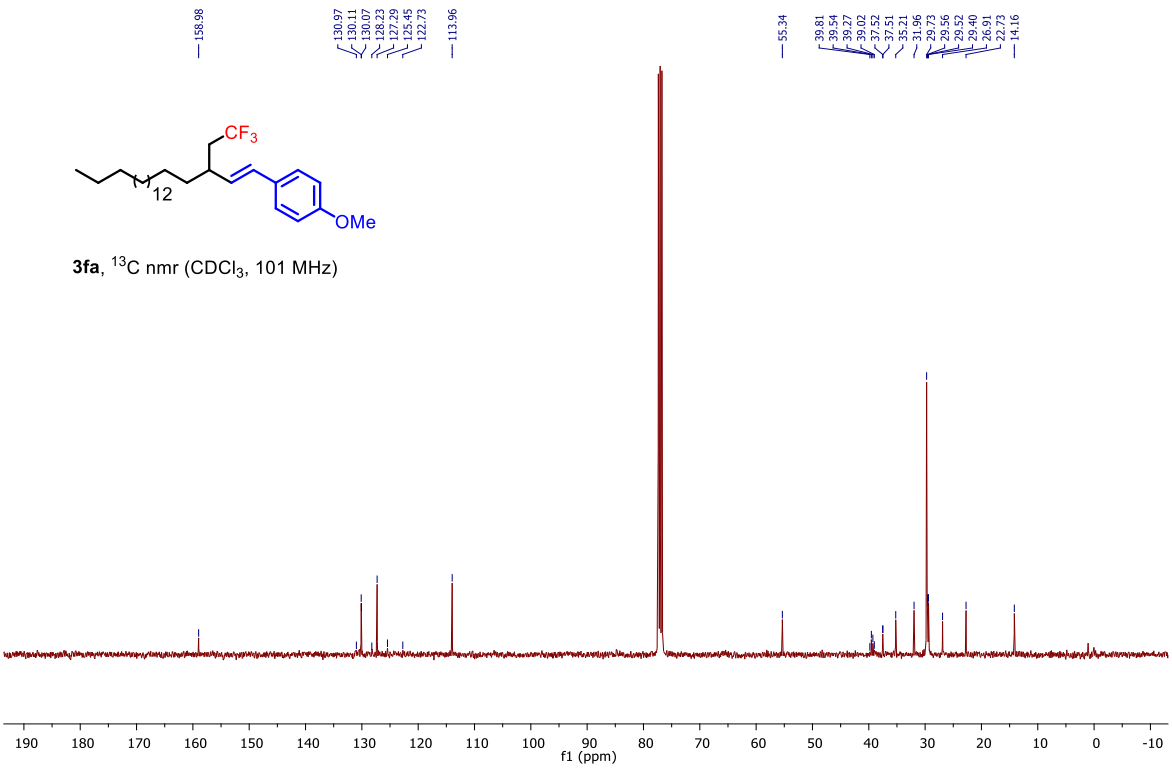


3ea, ^{19}F nmr ($CDCl_3$, 376 MHz)

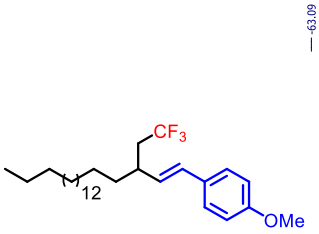




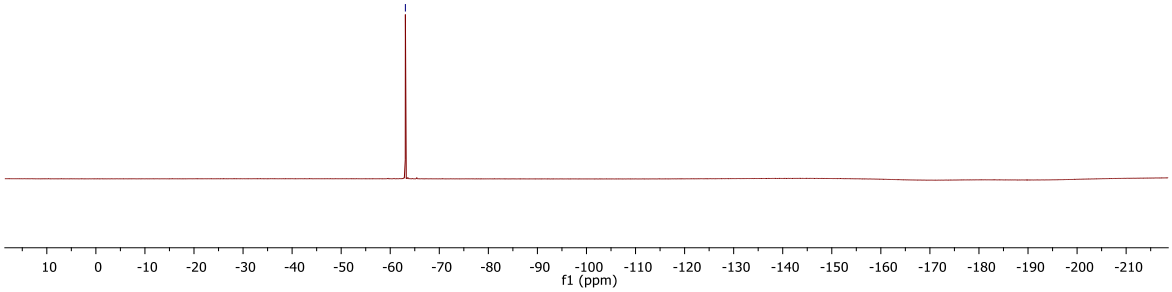
3fa, H^1 nmr ($CDCl_3$, 500 MHz)

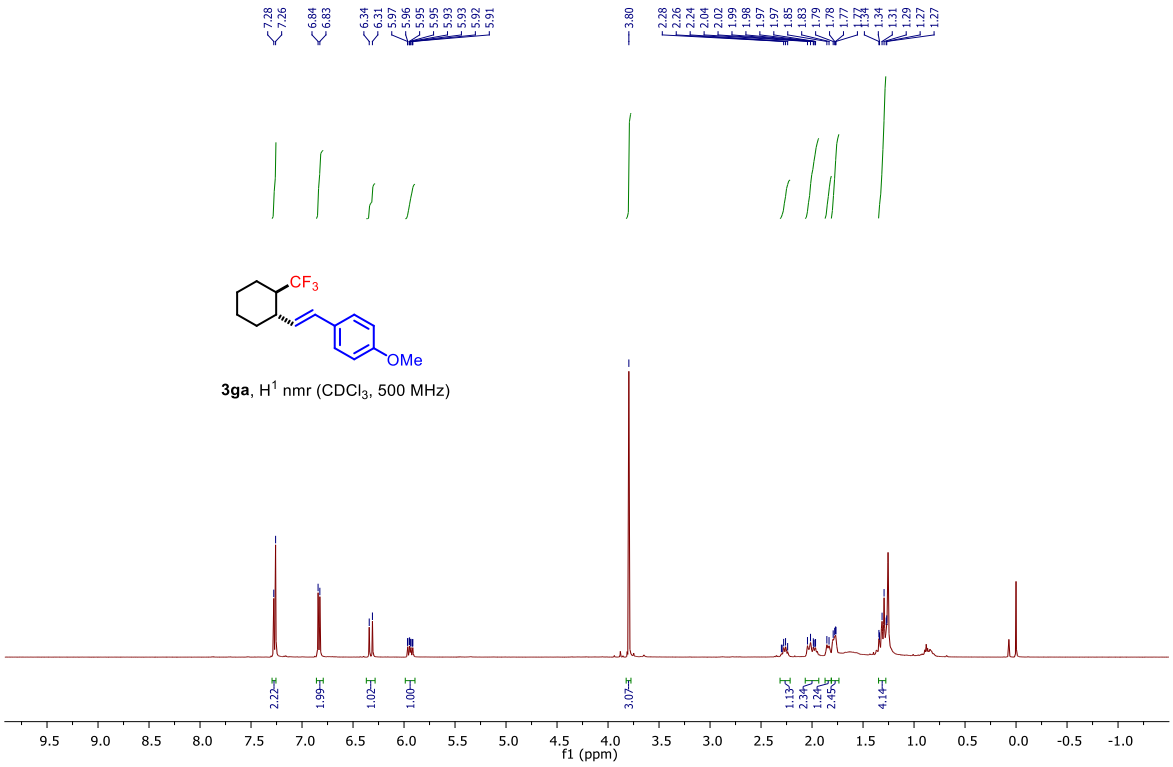


3fa, ^{13}C nmr ($CDCl_3$, 101 MHz)

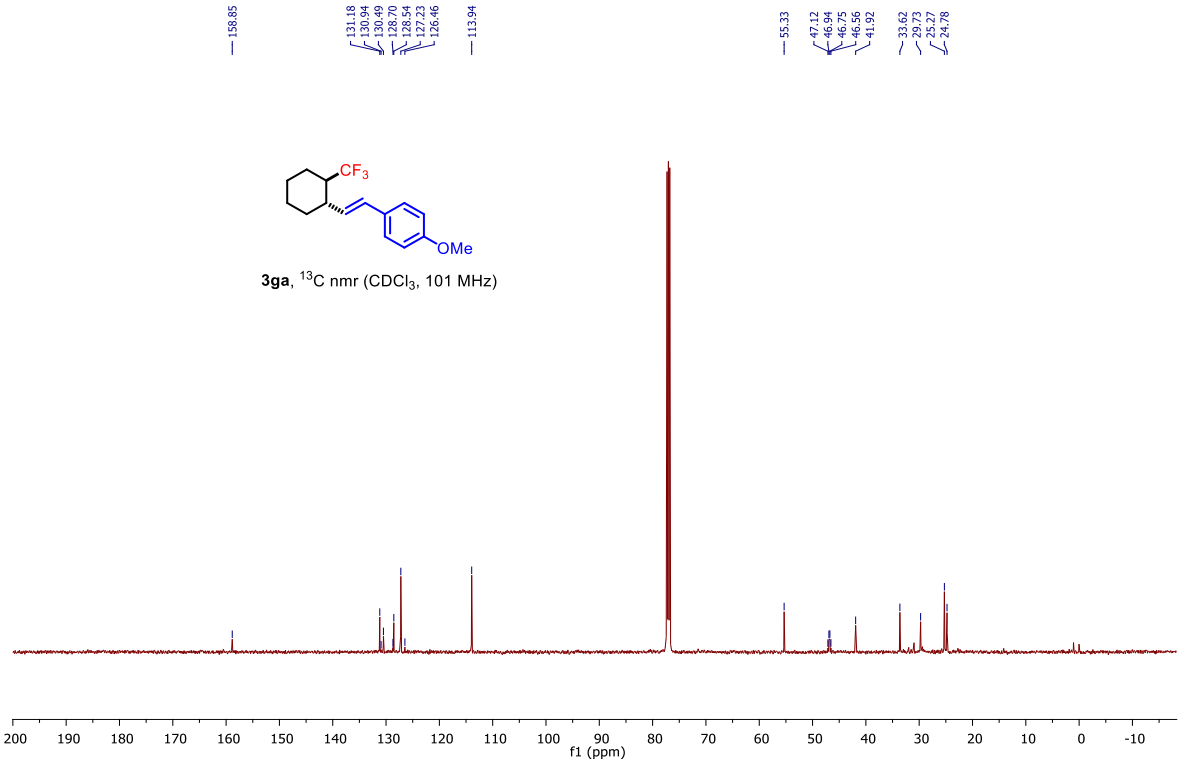


3fa, ^{19}F nmr ($CDCl_3$, 376 MHz)

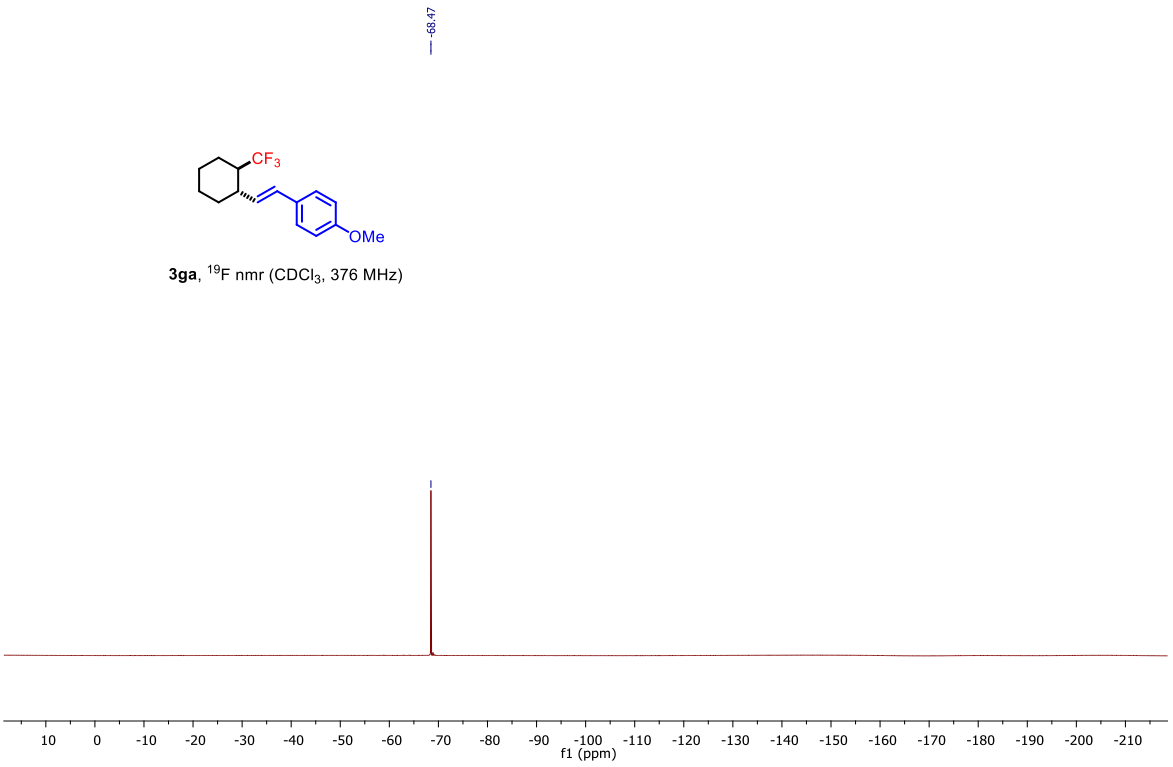




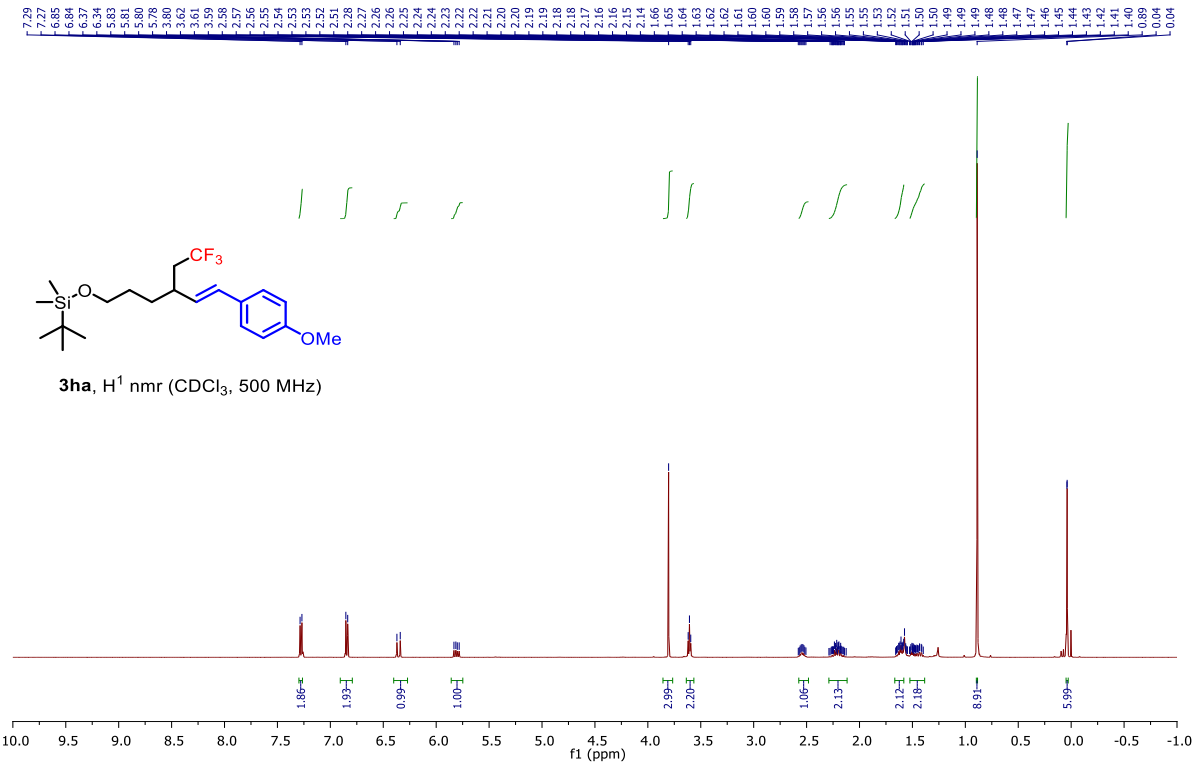
3ga, H^1 nmr ($CDCl_3$, 500 MHz)



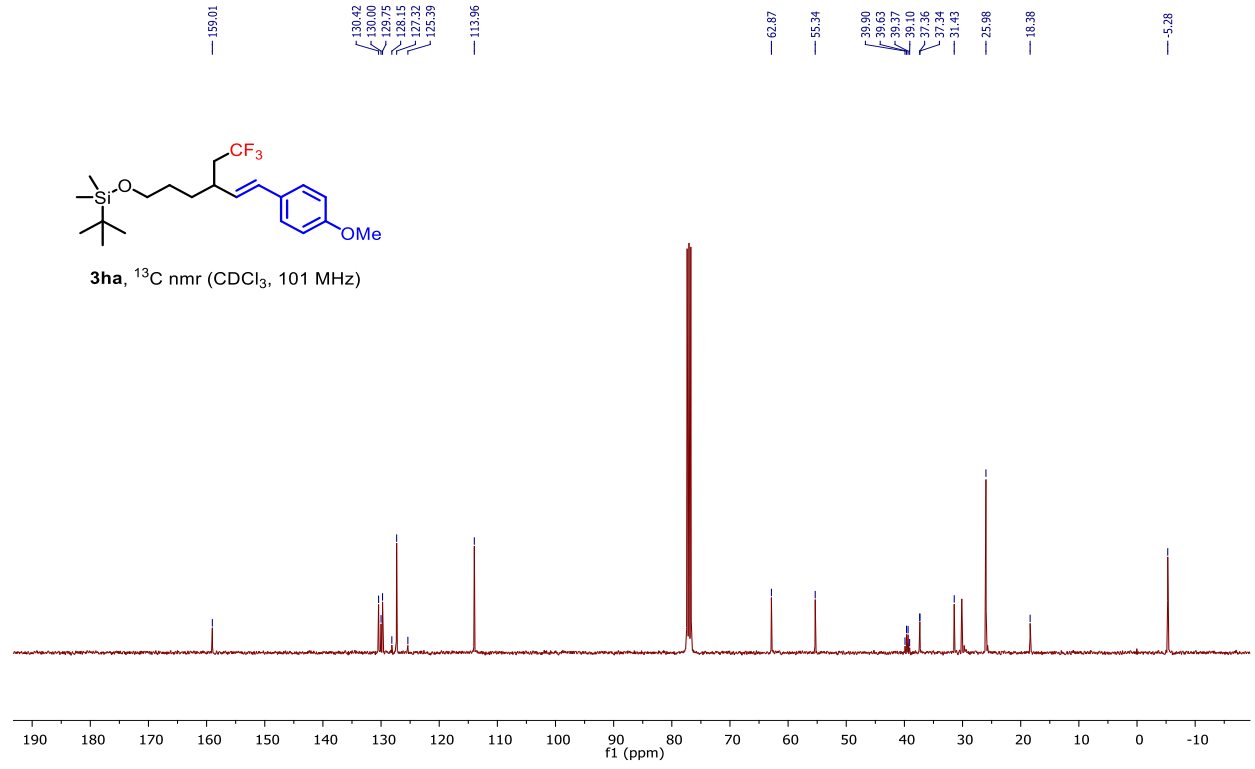
3ga, ^{13}C nmr ($CDCl_3$, 101 MHz)



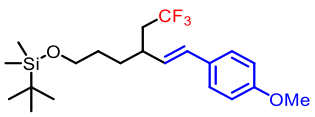
3ga, ^{19}F nmr ($CDCl_3$, 376 MHz)



3ha, H^1 nmr ($CDCl_3$, 500 MHz)

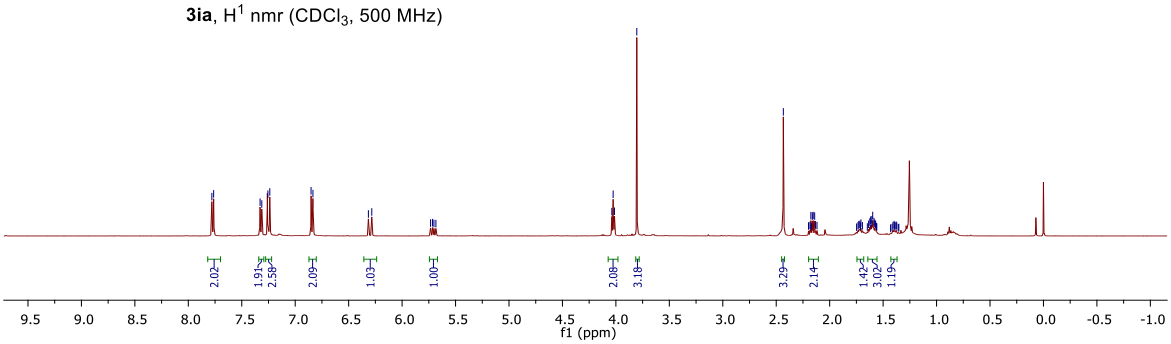


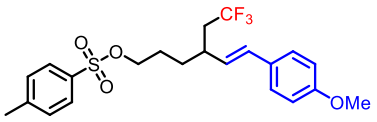
3ha, ^{13}C nmr ($CDCl_3$, 101 MHz)



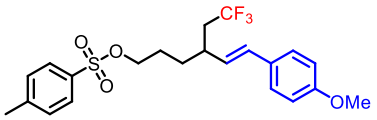
3ha, ^{19}F nmr ($CDCl_3$, 376 MHz)

3ia, H^1 nmr ($CDCl_3$, 500 MHz)

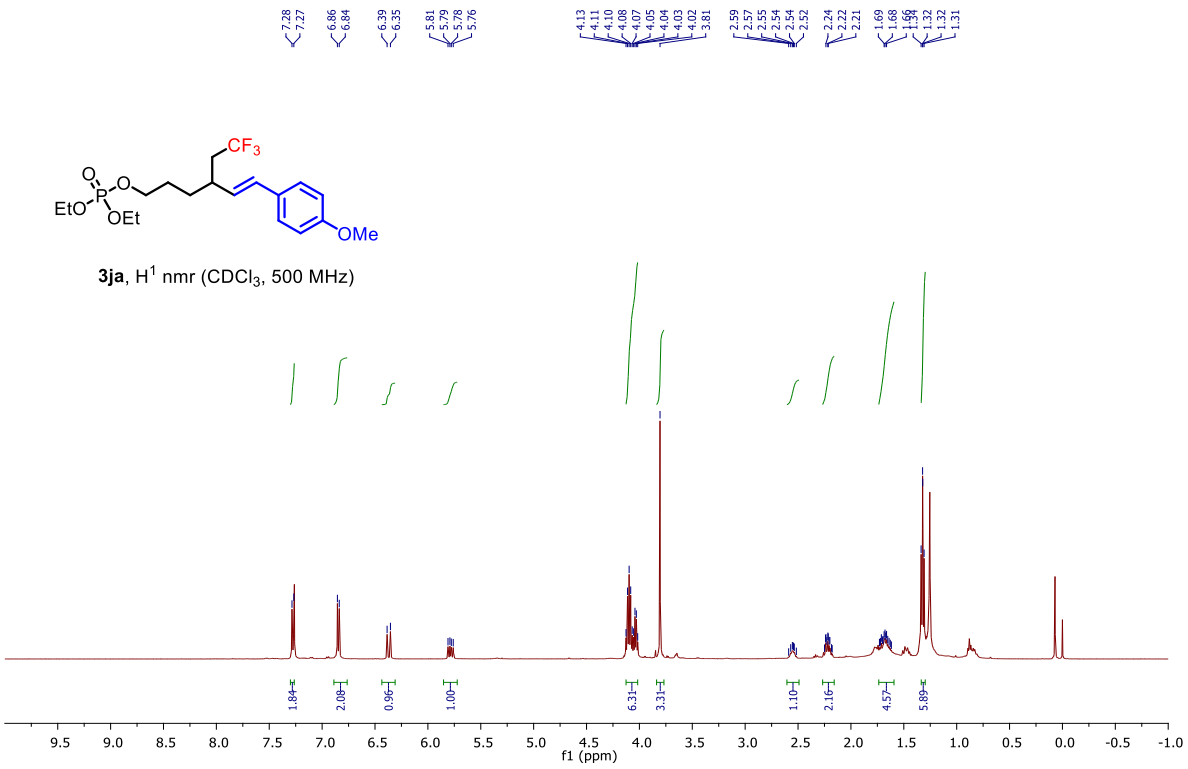




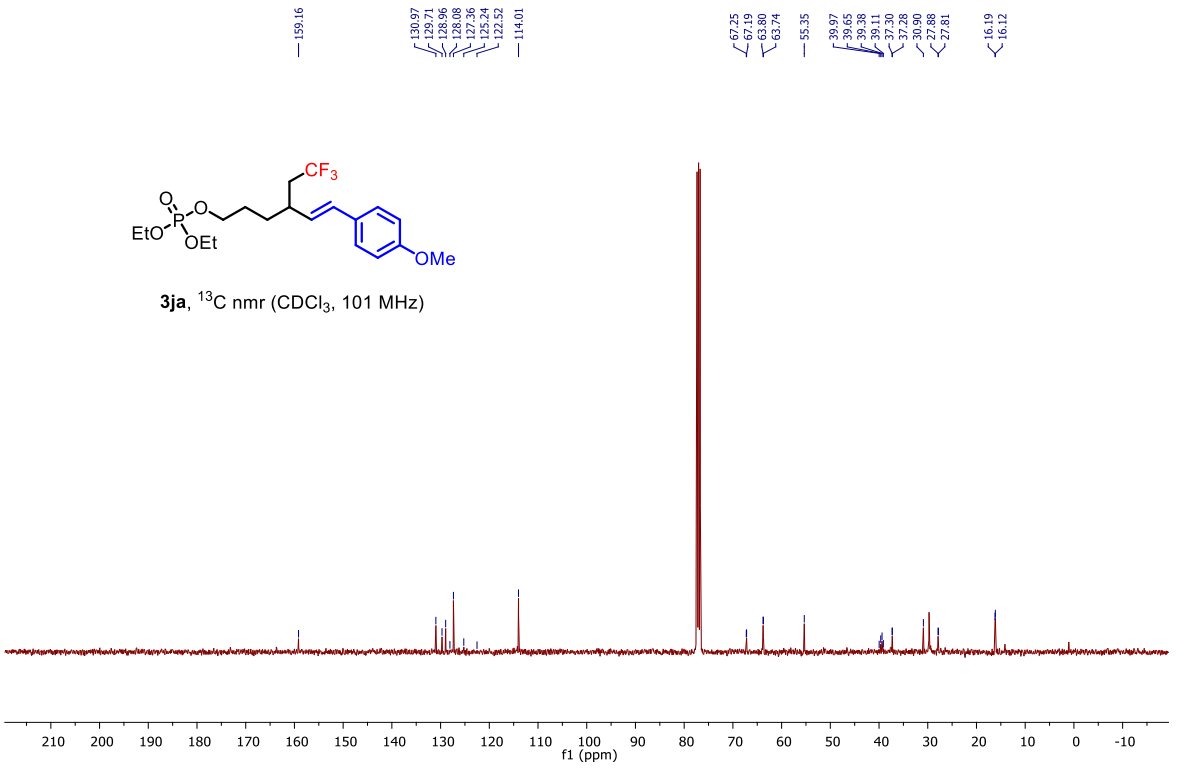
3ia, ^{13}C nmr ($CDCl_3$, 101 MHz)



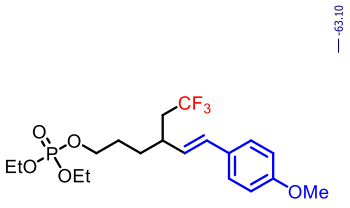
3ia, ^{19}F nmr ($CDCl_3$, 376 MHz)



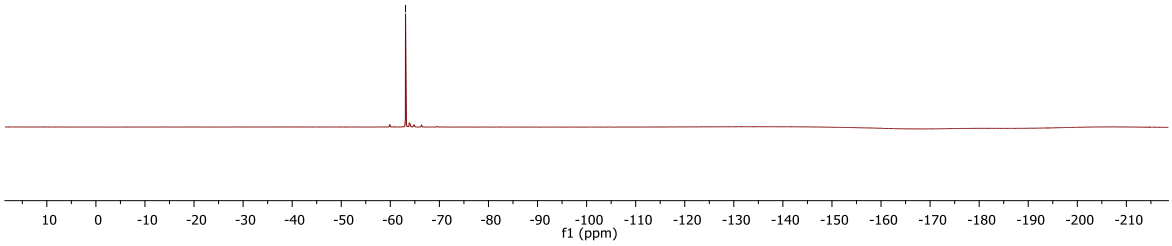
3ja, H^1 nmr ($CDCl_3$, 500 MHz)

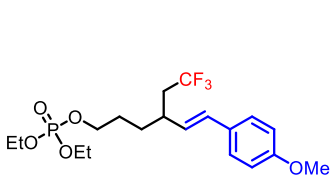


3ja, ^{13}C nmr ($CDCl_3$, 101 MHz)

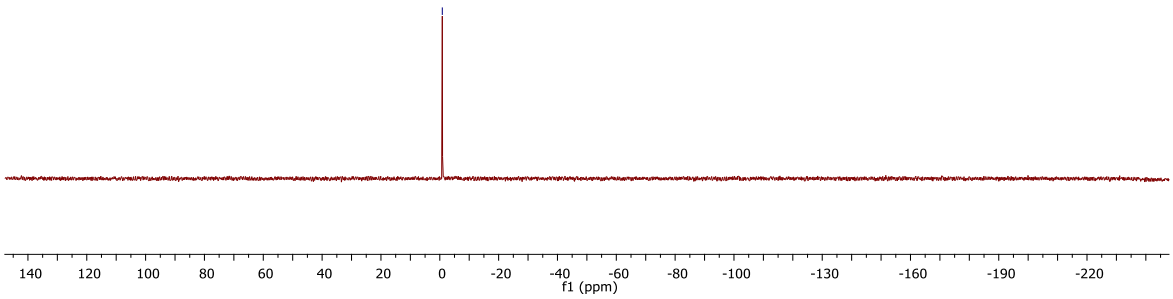


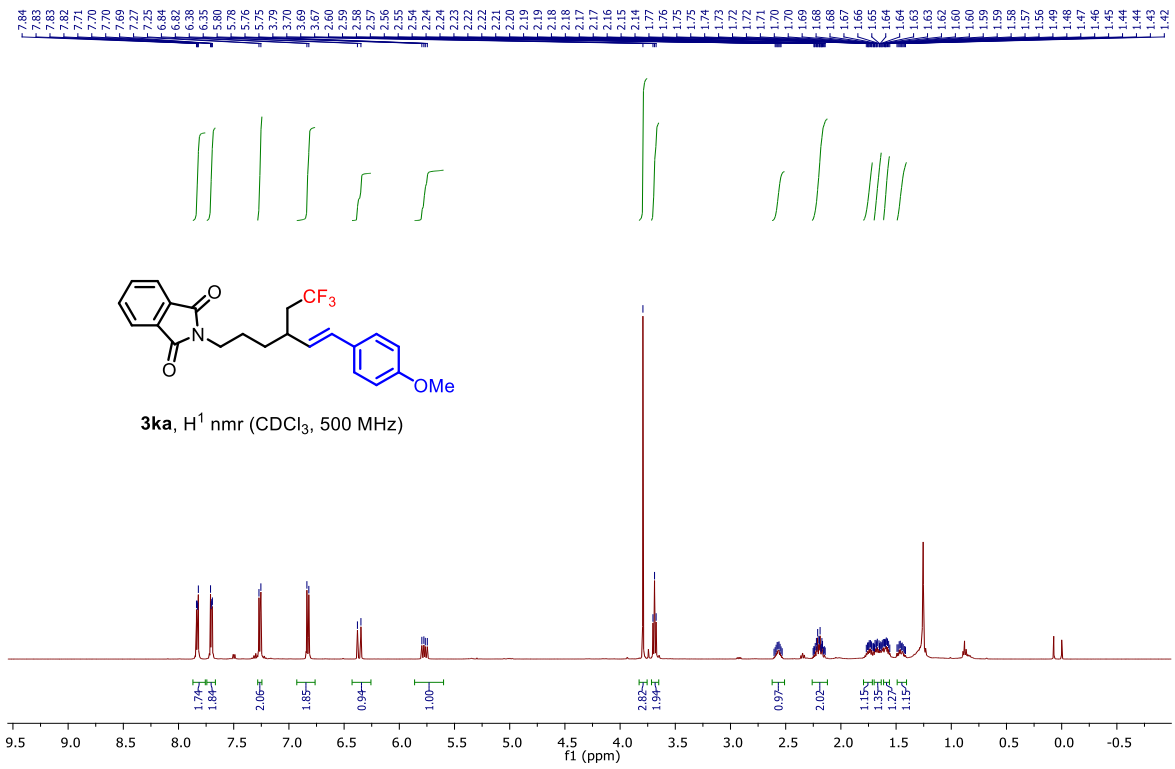
3ja, ^{19}F nmr ($CDCl_3$, 376 MHz)



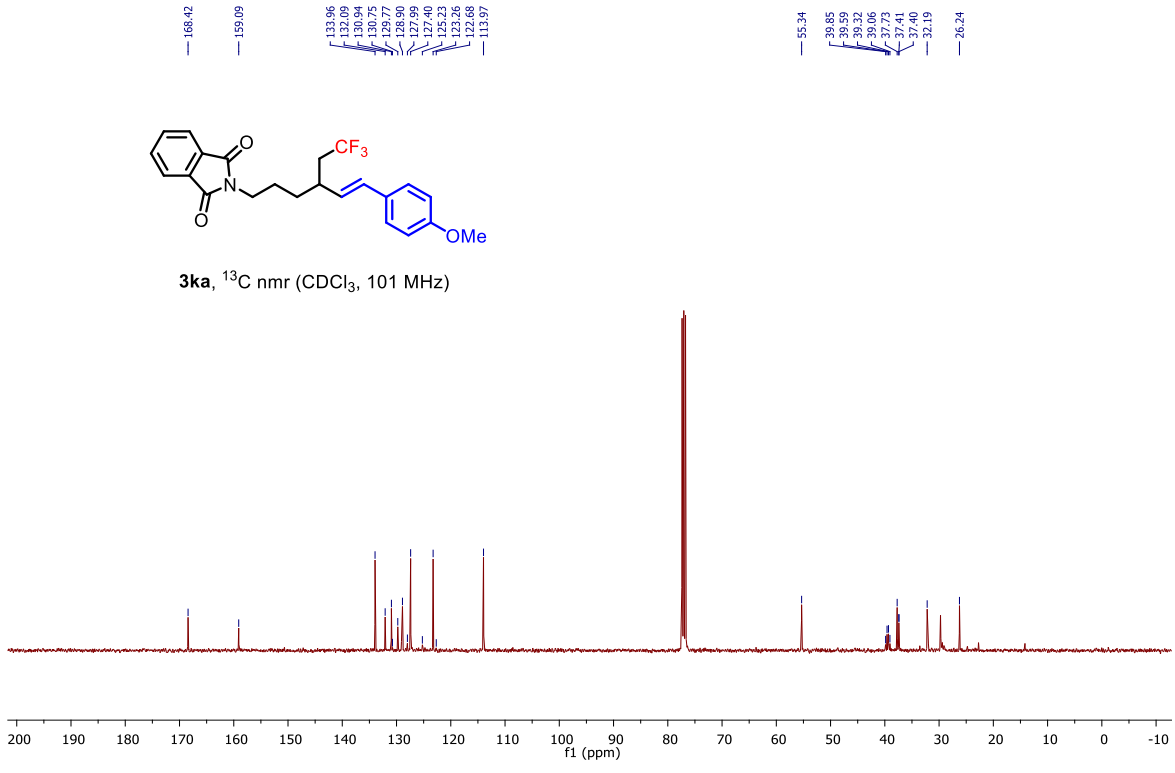


3ja, ^{31}P nmr ($CDCl_3$, 162 MHz)

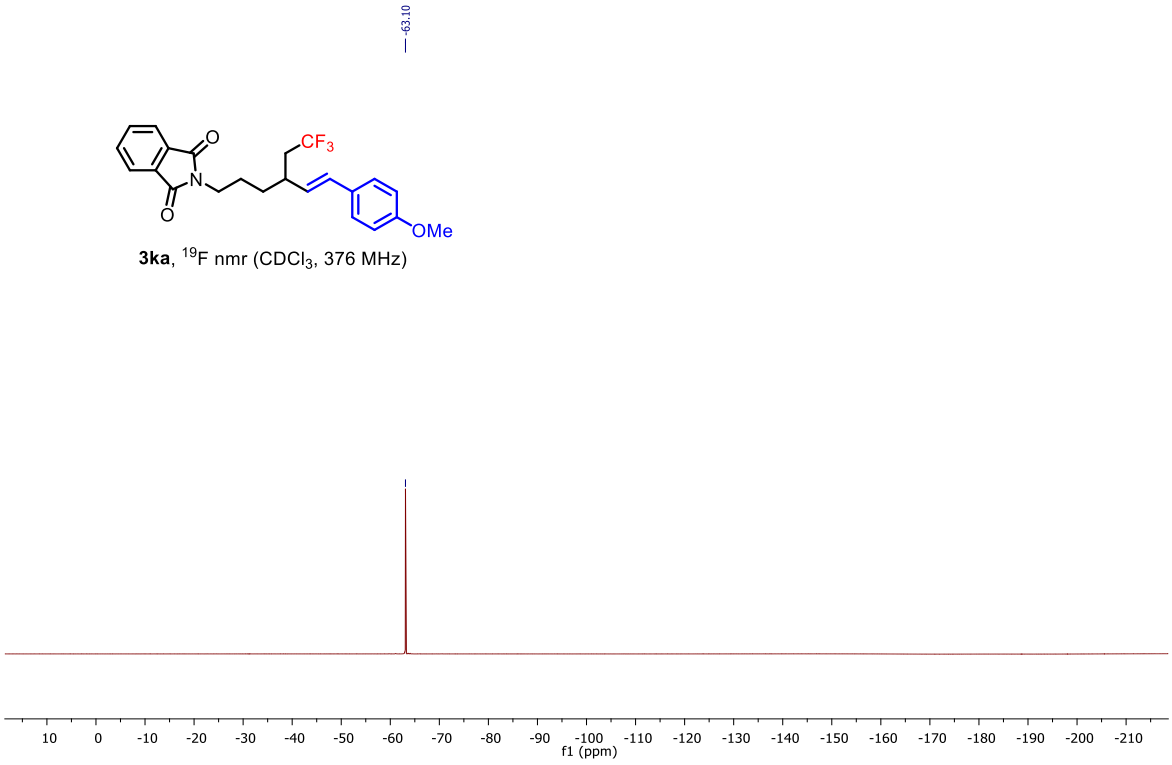




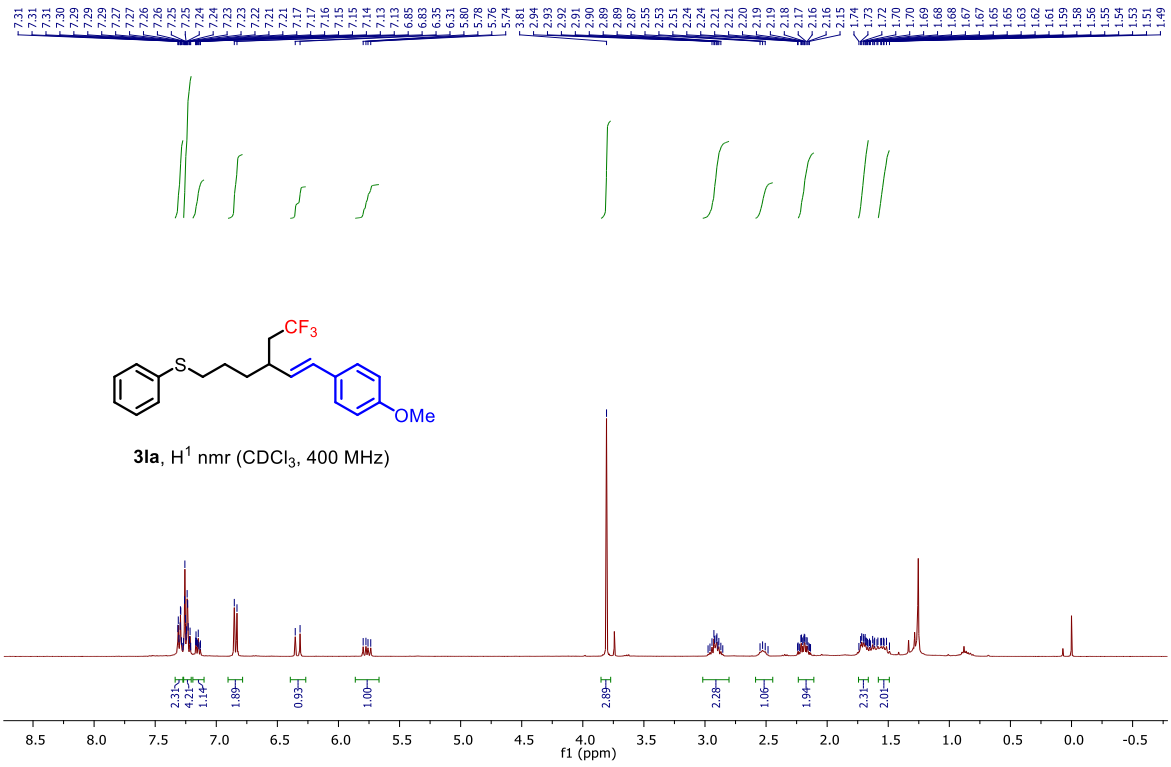
3ka, H^1 nmr ($CDCl_3$, 500 MHz)



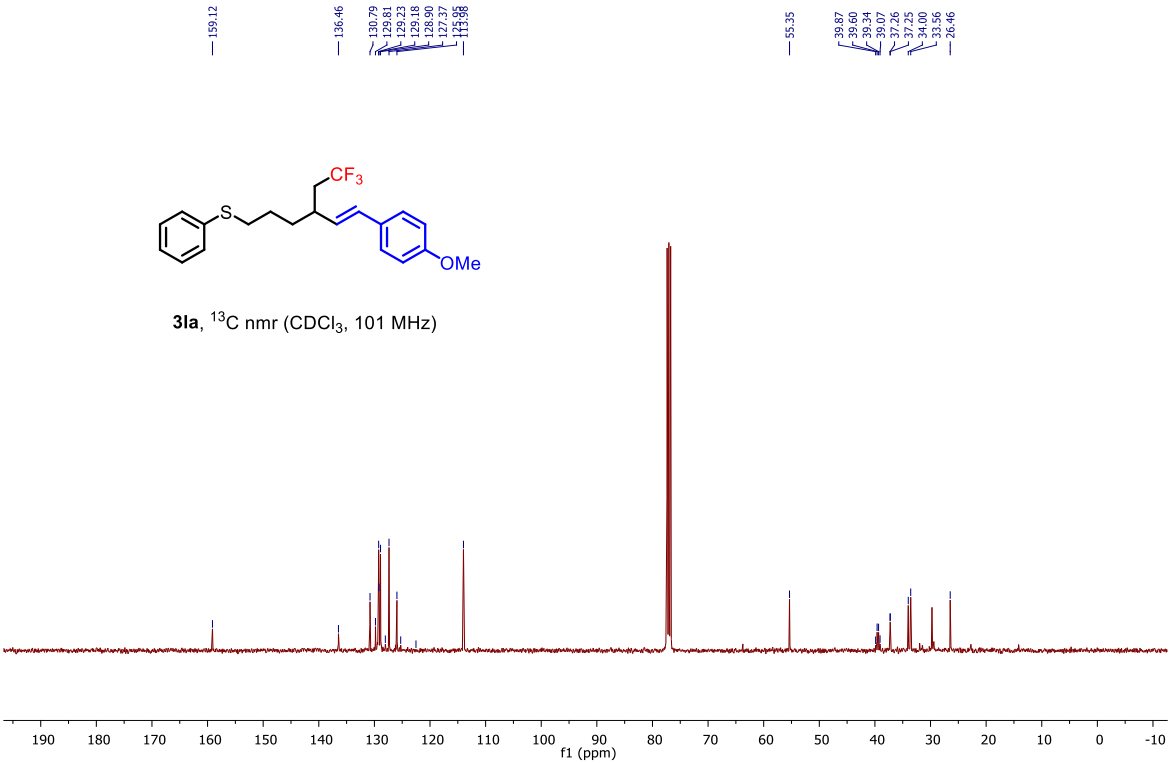
3ka, ^{13}C nmr ($CDCl_3$, 101 MHz)



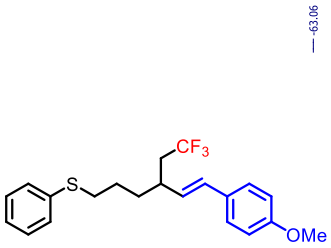
3ka, ^{19}F nmr ($CDCl_3$, 376 MHz)



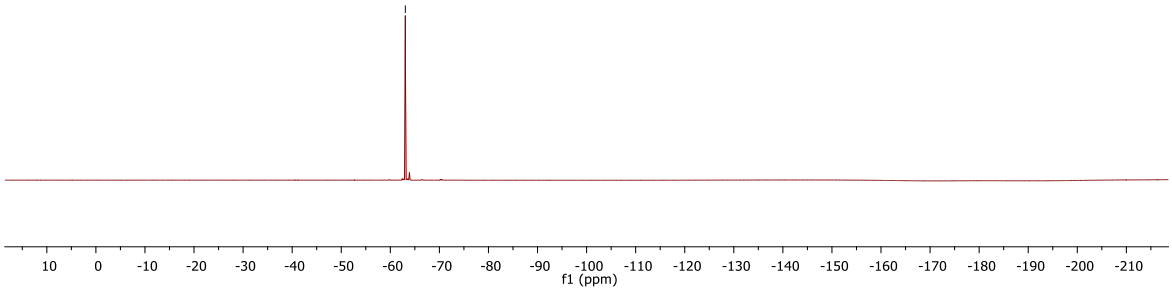
3la, H^1 nmr ($CDCl_3$, 400 MHz)

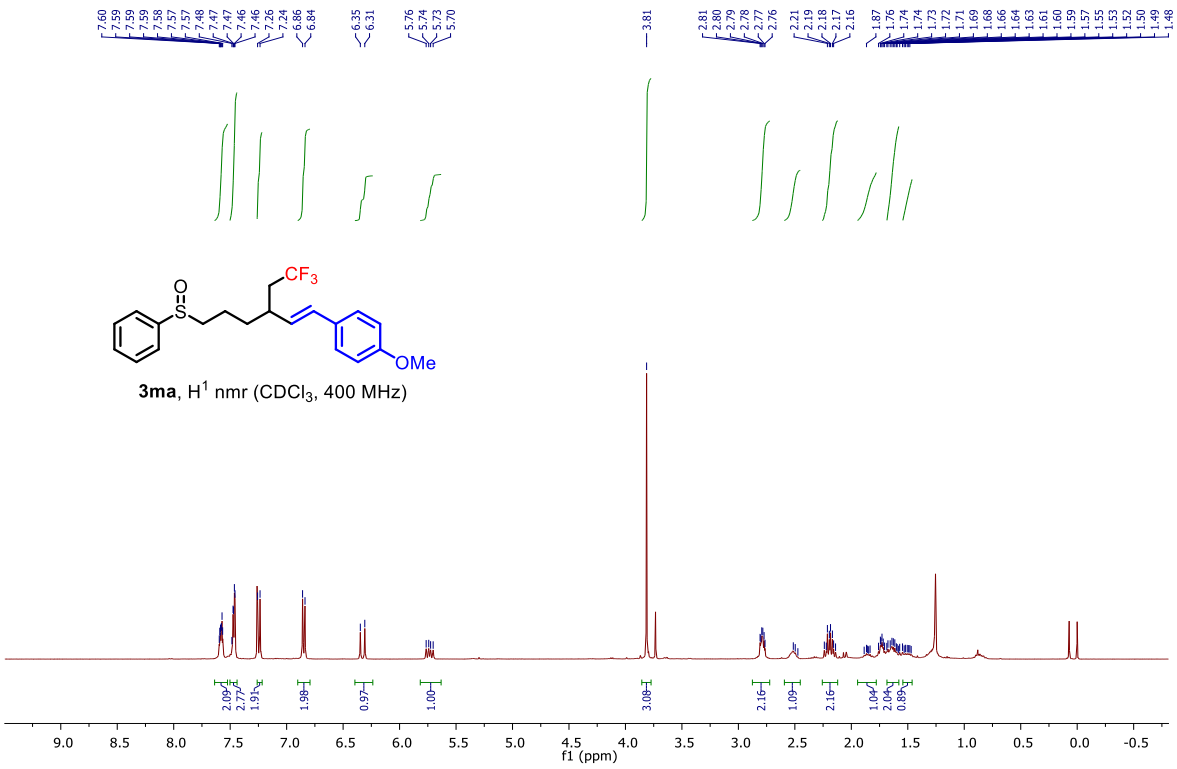


3la, ^{13}C nmr ($CDCl_3$, 101 MHz)

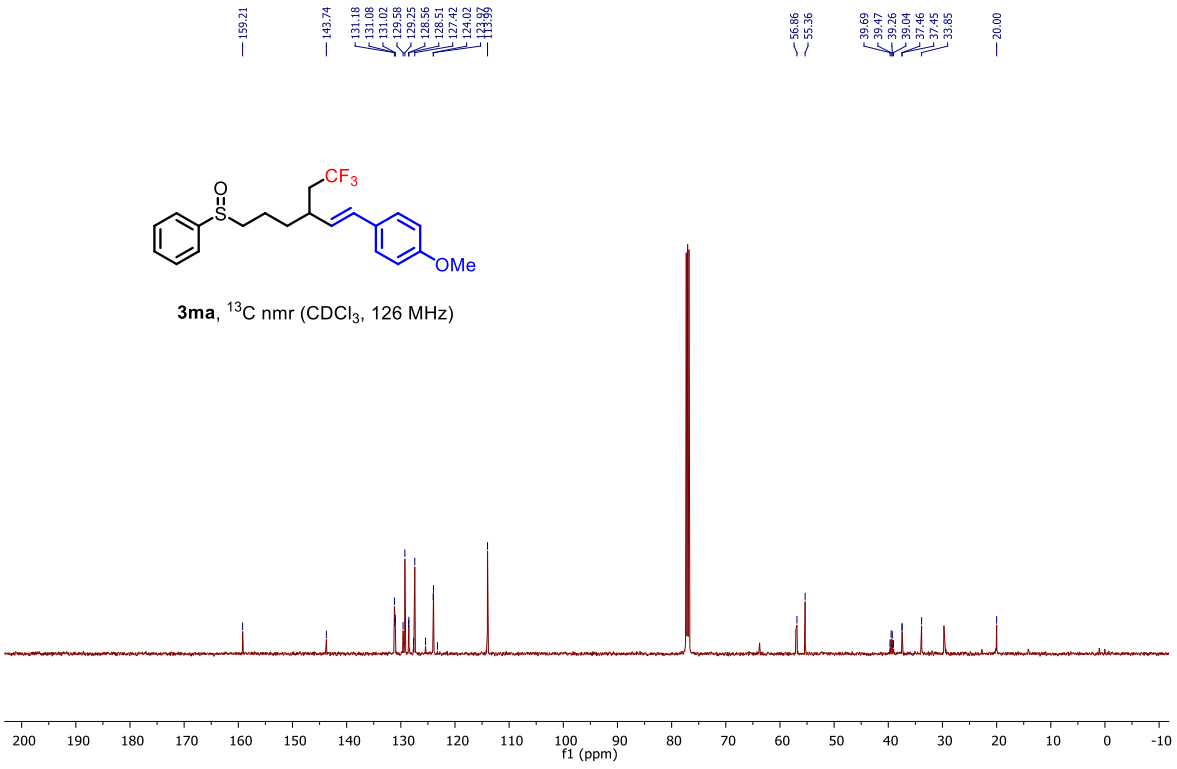


3la, ^{19}F nmr ($CDCl_3$, 376 MHz)

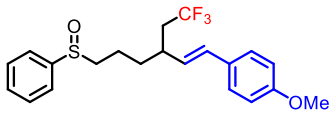




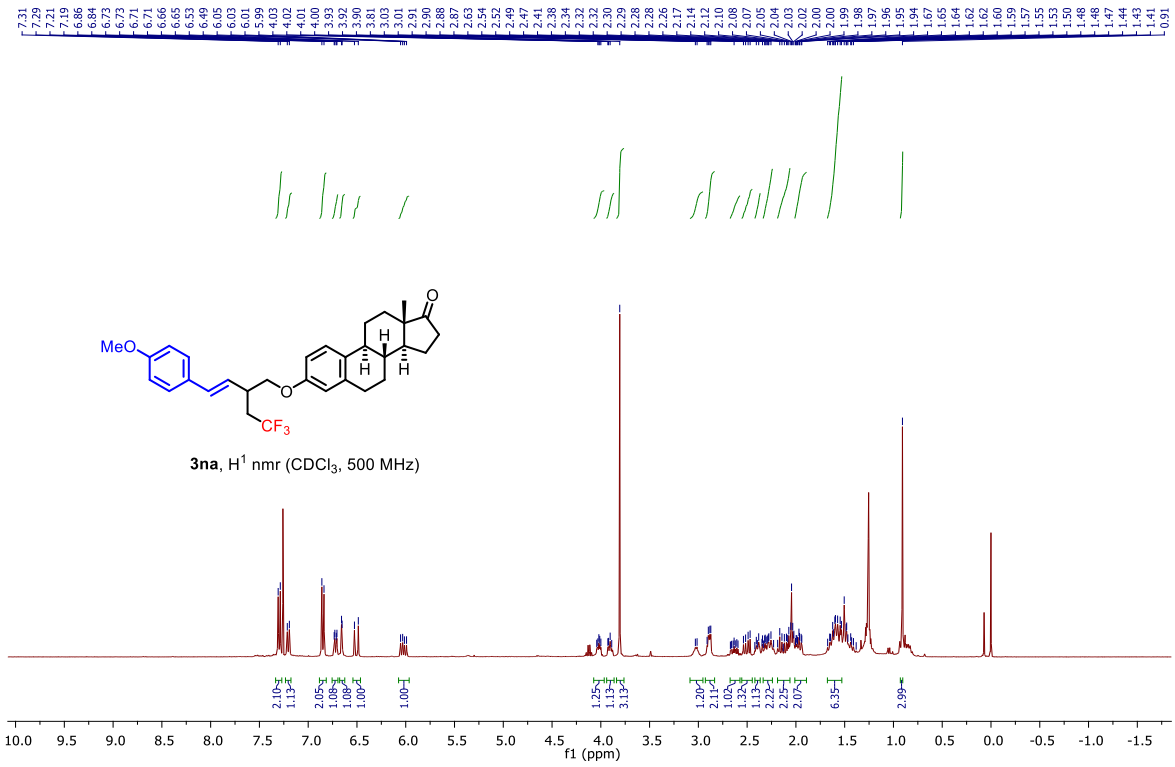
3ma, H^1 nmr ($CDCl_3$, 400 MHz)



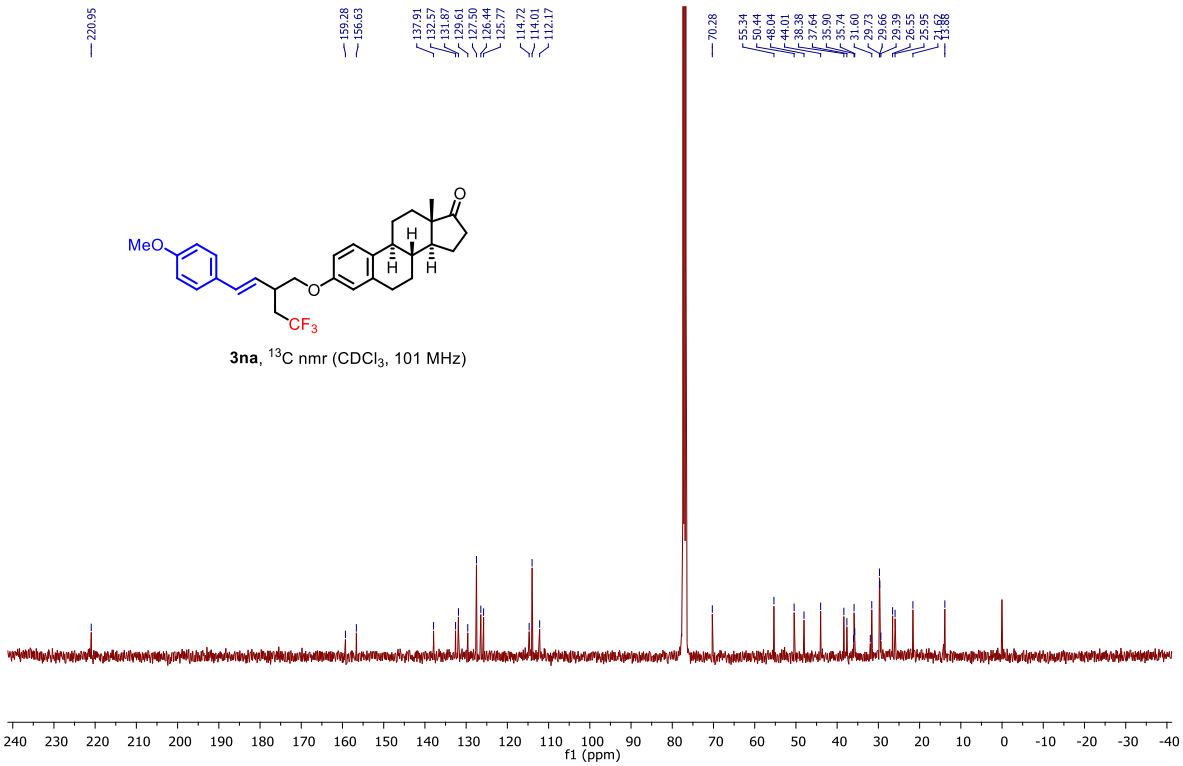
3ma, ^{13}C nmr ($CDCl_3$, 126 MHz)



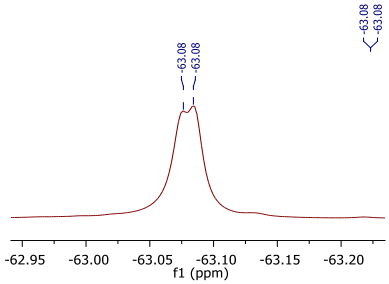
3ma, ^{19}F nmr ($CDCl_3$, 376 MHz)

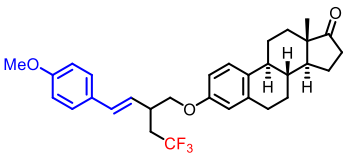


3na, H^1 nmr ($CDCl_3$, 500 MHz)

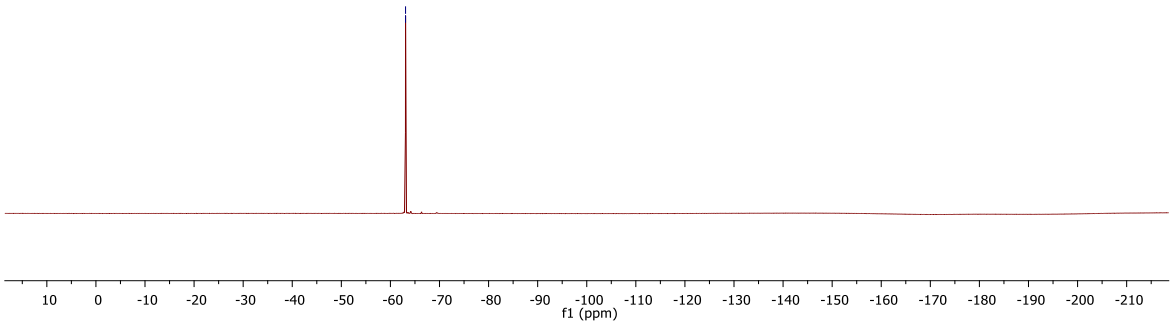


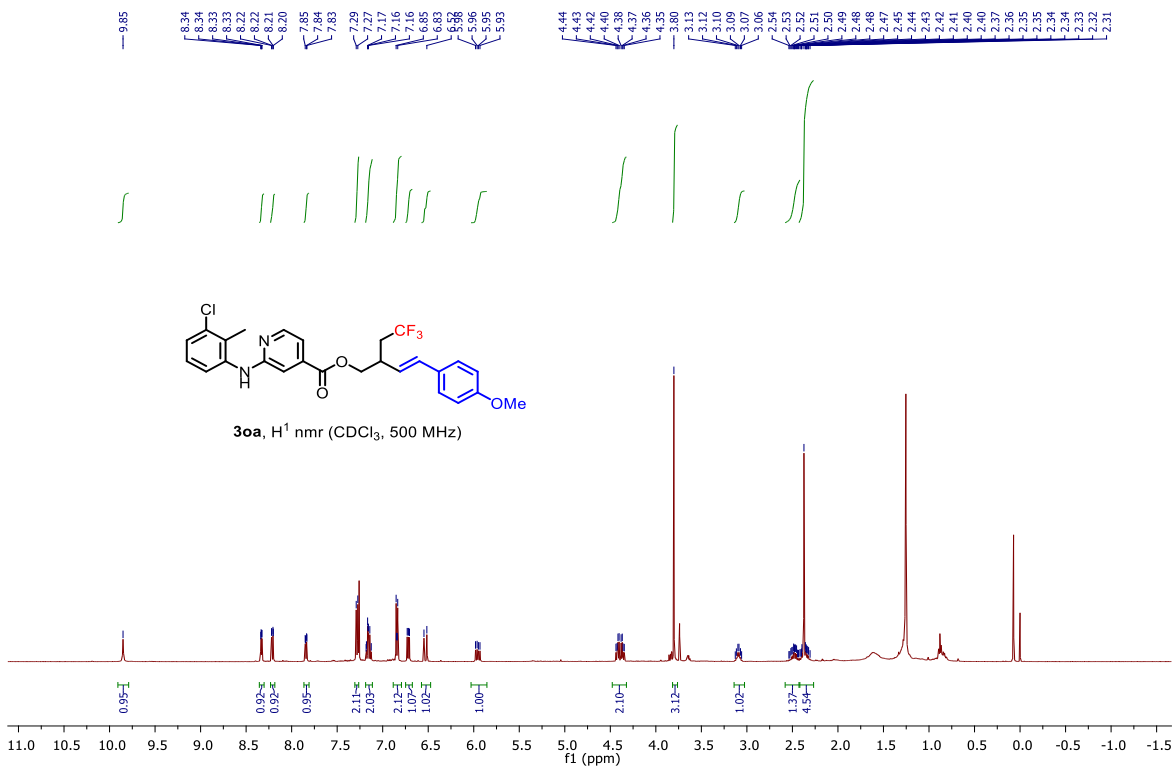
3na, ^{13}C nmr ($CDCl_3$, 101 MHz)



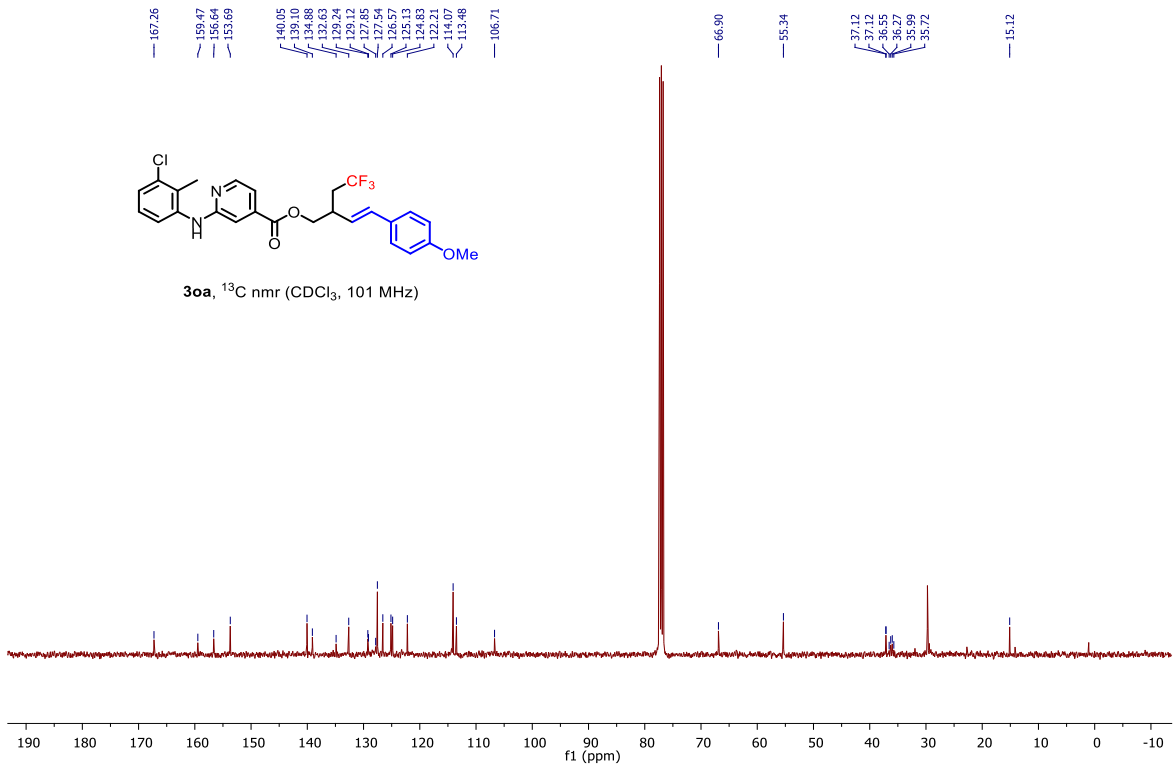


3na, ^{19}F nmr ($CDCl_3$, 376 MHz)

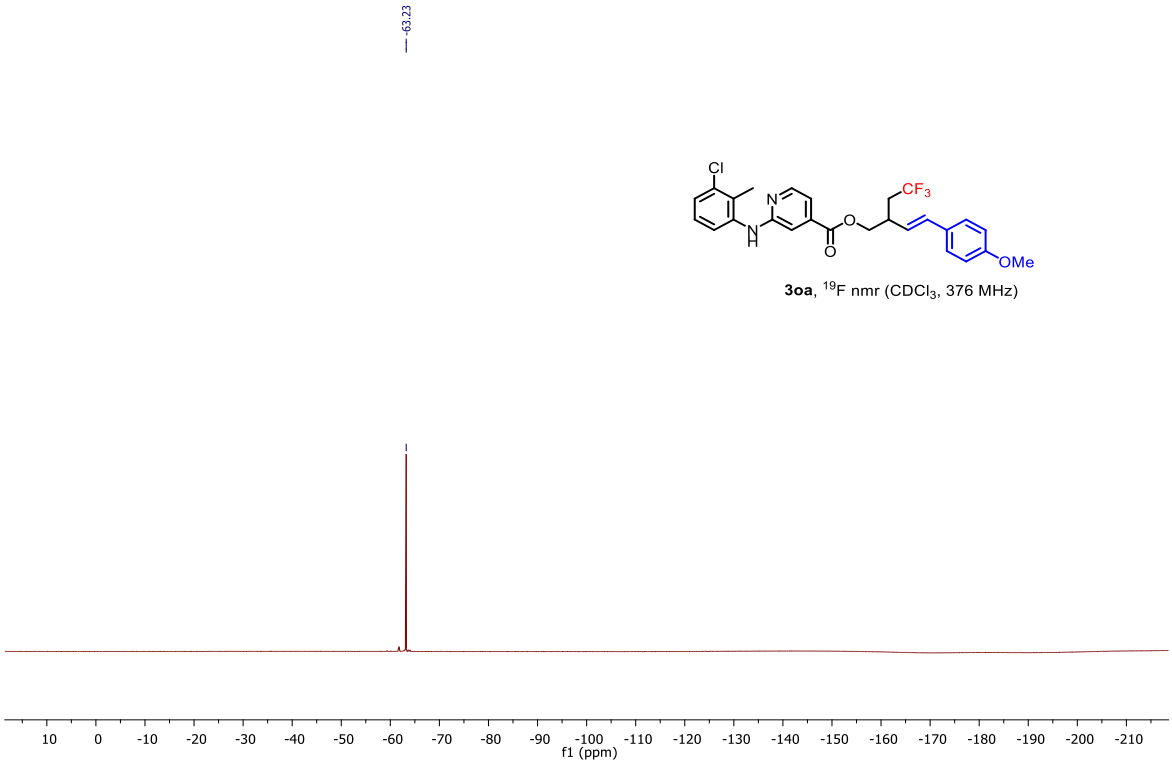




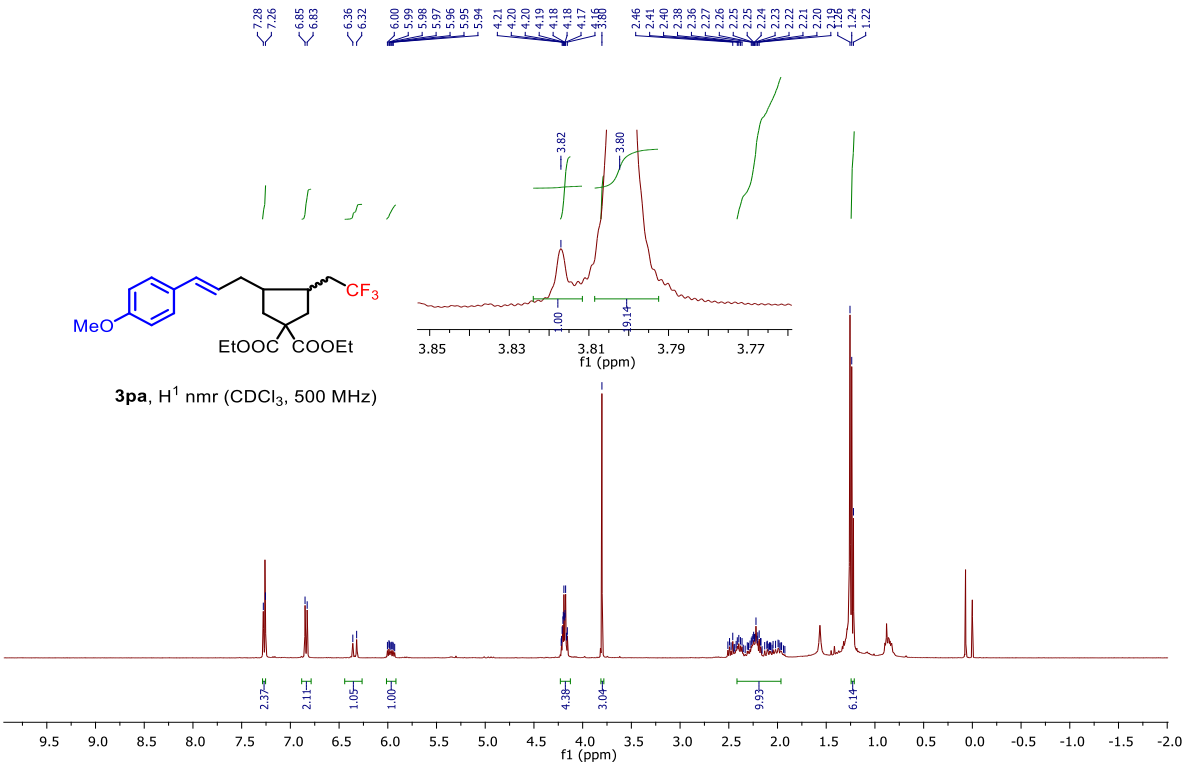
3oa, H^1 nmr ($CDCl_3$, 500 MHz)



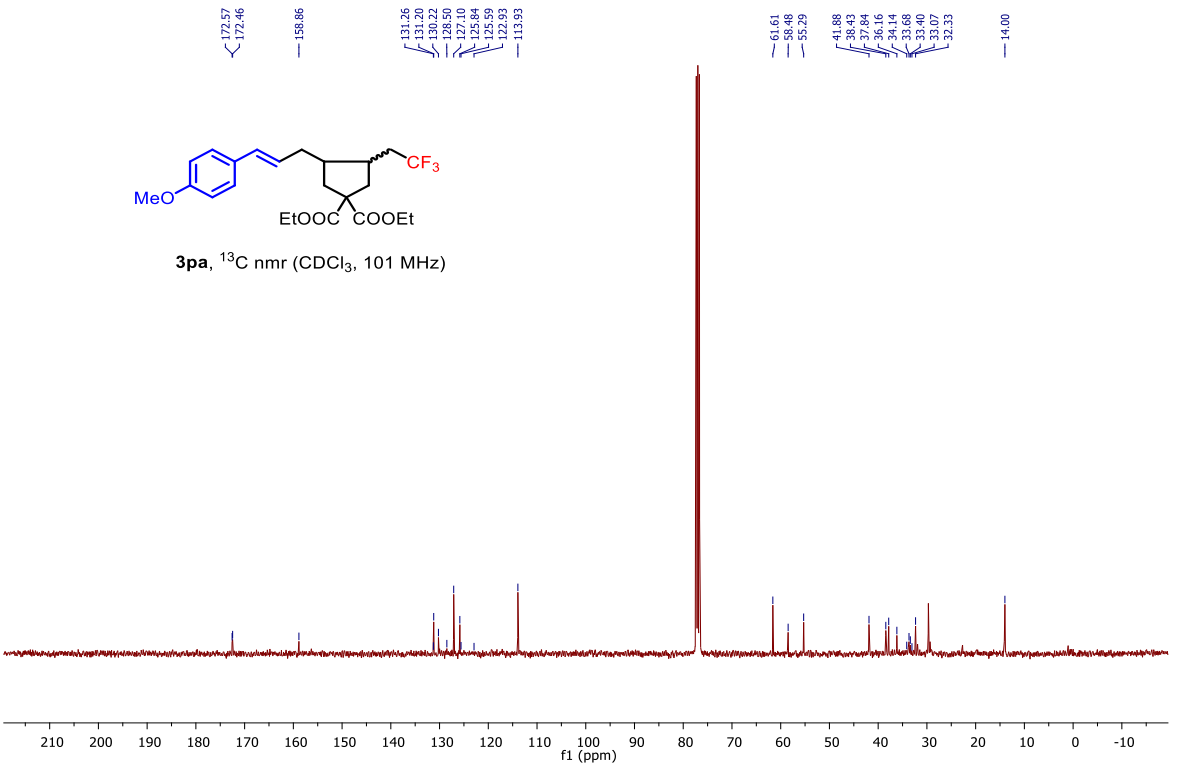
3oa, ^{13}C nmr ($CDCl_3$, 101 MHz)



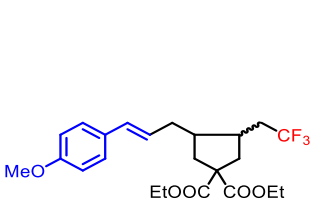
3oa, ^{19}F nmr ($CDCl_3$, 376 MHz)



3pa, H^1 nmr ($CDCl_3$, 500 MHz)



3pa, ^{13}C nmr ($CDCl_3$, 101 MHz)



3pa, ^{19}F nmr ($CDCl_3$, 376 MHz)