

Supplementary Information

Four-Component Radical Cascade Trifluoromethylation Reaction of Alkenes Enabled by Electron-Donor-Acceptor Complex

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Table of Contents

1. General Information.....	S3
2. General Procedures.....	S4
3. Optimization Studies.....	S4
4. Characterization of Products.....	S5
5. A Three-Step Synthesis of CF ₃ -Naftidrofuryl.....	S24
6. Mechanistic studies.....	S27
7. Spectral Data.....	S35

1. General Information.

Commercial reagents were purchased from Aldrich, TCI, Energy Chemical and J&K chemical, and were used as received. All reactions were carried out in oven-dried glassware under an atmosphere of nitrogen unless otherwise noted. Chromatographic purification of products was accomplished by flash chromatography using silica gel. Thin-layer chromatography (TLC) was performed on Silicycle 250 mm silica gel F-254 plates. ^1H and ^{13}C NMR spectra were recorded on Bruker 400 (400 and 100 MHz) and Bruker 600 (600 and 150 MHz), and are internally referenced to residual solvent signals (for CDCl_3 , 7.26 and 77.0 ppm). Data for ^1H NMR and ^{19}F NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), integration, coupling constant (Hz). ^{13}C spectra were reported as chemical shifts in ppm and multiplicity where appropriate. High resolution mass spectra were obtained at Shanghai Institute of Organic Chemistry mass spectrometry facilities. UV–Vis measurements was performed with a Shimadzu UV-2550 UV/Vis spectrophotometer. All alkenes were used from commercial suppliers or prepared using standard literature procedures.

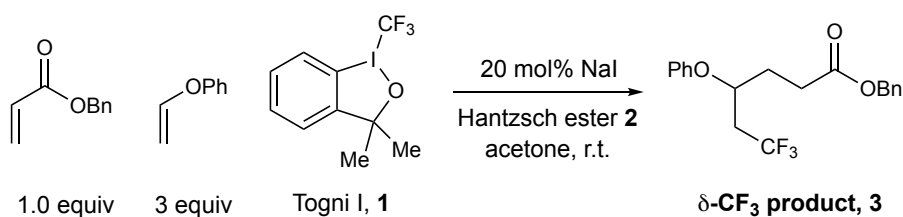
2. General procedures.

General procedure for the multicomponent radical cascade trifluoromethylation reaction: To a flame-dried 8 mL reaction vial was charged with Hantzsch ester (0.4 mmol, 2.0 equiv.), Togni's reagent (0.4 mmol, 2.0 equiv.). Subsequently, the vial was introduced into a nitrogen-filled glove box and charged with NaI (0.04 mmol, 0.2 equiv.). The vial was capped and taken out from the glovebox. Acetone [0.1 M] was added via syringe, followed by the addition of deficient alkene (0.2 mmol, 1.0 equiv.) and rich alkene (0.6 mmol, 3.0 equiv.). The reaction mixture was allowed to stir at 600 rpm for 24 h at r.t., or until complete consumption of the starting material as monitored by TLC analysis. After the reaction completed, the reaction mixture was poured into acetone (10 mL) and evaporated under vacuum. The crude material was purified by flash chromatography on silica to afford the product.

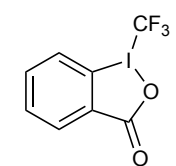
3. Optimization studies.

General procedure for the optimization studies: To a flame-dried 8 mL reaction vial was charged with Hantzsch ester (50.6 mg, 0.2 mmol, 2.0 equiv.), Togni's reagent (66 mg, 0.2 mmol, 2.0 equiv.). Subsequently, the vial was introduced into a nitrogen-filled glove box and charged with NaI (3 mg, 0.02 mmol, 0.2 equiv.). The vial was capped and taken out from the glovebox. Acetone [1 mL] was added via syringe, followed by the addition of benzyl acrylate (15.3 μ L, 0.1 mmol, 1.0 equiv.) and (vinylloxy)benzene (36.8 μ L, 0.3 mmol, 3.0 equiv.). The reaction mixture was allowed to stir at 600 rpm for 24 h at r.t. The reaction mixture was analyzed by GC with an internal standard.

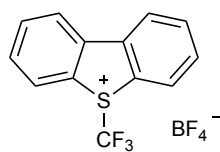
Table S1. Optimization of reaction conditions.^a



Entry	Variations from the standard conditions	Yield ^b
1	none	83%
2	w/o HE 2	0%
3	Me-HE, instead of HE 2	0%
4	Et ₃ N, instead of HE 2	0%
5	NMM, instead of HE 2	0%
6	<i>i</i> -Pr ₂ NH, instead of HE 2	0%
7	in the dark	74%
8	3W white light	78%
9	w/o NaI	73%
10	DME, instead of acetone	73%
11	CH ₃ CN, instead of acetone	57%
12	DCM, instead of acetone	67%
13	DMA, instead of acetone	57%
14	DMSO, instead of acetone	15%
15	Togni II reagent, instead of 1	61%
16	Umemoto reagent, instead of 1	42%



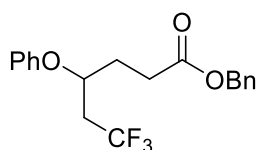
Togni II reagent



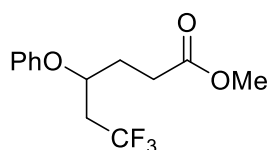
Umemoto reagent

^aReaction conditions: 20 mol% NaI, benzyl acrylate (1.0 equiv.), (vinylxy)benzene (3.0 equiv.), **1** (2.0 equiv.), HE **2** (2.0 equiv.), acetone [0.1M], 25 °C. ^bDetermined by GC using an internal standard. NMM = 4-methylmorpholine.

4. Characterization of Products

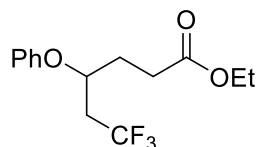


Benzyl 6,6,6-trifluoro-4-phenoxyhexanoate (3): According to the general procedure, benzyl acrylate (30.6 μ L, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (vinylloxy)benzene (73.7 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 30:1) as a pale-yellow oil liquid (57.2 mg, 81%). ^1H NMR (600 MHz, CDCl_3) δ 7.35 – 7.30 (m, 5H), 7.27 – 7.22 (m, 2H), 6.96 (t, J = 7.8 Hz, 1H), 6.87 (d, J = 7.8 Hz, 2H), 5.09 (s, 2H), 4.65 – 4.61 (m, 1H), 2.60 – 2.50 (m, 3H), 2.38 – 2.28 (m, 1H), 2.21 – 2.14 (m, 1H), 2.09 – 2.02 (m, 1H); ^{19}F NMR (565 MHz, CDCl_3) δ -63.13 (t, J = 10.8 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 172.6, 157.1, 135.7, 129.7, 128.5, 128.3, 125.7 (q, J = 277.0 Hz), 121.7, 115.9, 70.7, 66.4, 38.1 (q, J = 27.8 Hz), 29.6, 29.6; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{19}\text{H}_{22}\text{F}_3\text{O}_3$: 353.1359; found: 353.1352.

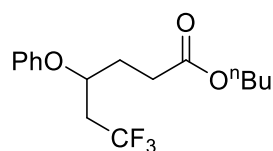


Methyl 6,6,6-trifluoro-4-phenoxyhexanoate (4): According to the general procedure, methyl acrylate (18.0 μ L, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (vinylloxy)benzene (73.7 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 30:1) as a pale-yellow oil liquid (46.9 mg, 85%). ^1H NMR (600 MHz, CDCl_3) δ 7.32 – 7.26 (m, 2H), 6.98 (t, J = 8.0 Hz, 1H), 6.90 (d, J = 8.0 Hz, 2H), 4.68 – 4.62 (m, 1H), 3.66 (s, 3H), 2.63 – 2.54 (m, 1H), 2.53 – 2.44 (m, 2H), 2.41

– 2.31 (m, 1H), 2.21 – 2.14 (m, 1H), 2.09 – 2.01 (m, 1H); ^{19}F NMR (565 MHz, CDCl_3) δ -63.22 (t, J = 10.8 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 173.2, 157.1, 129.7, 125.7 (q, J = 277.0 Hz), 121.7, 115.8, 70.7, 51.7, 38.1 (q, J = 27.8 Hz), 29.6, 29.3; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{13}\text{H}_{16}\text{F}_3\text{O}_3$: 277.1046; found: 277.1051.

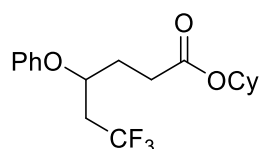


Ethyl 6,6,6-trifluoro-4-phenoxyhexanoate (5): According to the general procedure, ethyl acrylate (21.8 μL , 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (vinylloxy)benzene (73.7 μL , 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 30:1) as a pale-yellow oil liquid (46.4 mg, 80%). ^1H NMR (600 MHz, CDCl_3) δ 7.32 – 7.26 (m, 2H), 6.98 (t, J = 8.2 Hz, 1H), 6.91 (d, J = 8.2 Hz, 2H), 4.70 – 4.61 (m, 1H), 4.11 (q, J = 7.1 Hz, 2H), 2.63 – 2.53 (m, 1H), 2.51 – 2.43 (m, 2H), 2.41 – 2.31 (m, 1H), 2.20 – 2.13 (m, 1H), 2.09 – 2.01 (m, 1H), 1.22 (t, J = 7.1 Hz, 3H); ^{19}F NMR (565 MHz, CDCl_3) δ -63.23 (t, J = 10.8 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 172.8, 157.1, 129.7, 125.7 (q, J = 277.0 Hz), 121.7, 115.8, 70.8, 60.6, 38.2 (q, J = 27.8 Hz), 29.6, 29.6, 14.1; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. $\text{C}_{14}\text{H}_{18}\text{F}_3\text{O}_3$: 291.1203; found: 291.1200.

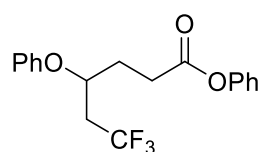


Butyl 6,6,6-trifluoro-4-phenoxyhexanoate (6): According to the general procedure, *n*-butyl acrylate (28.5 μL , 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (vinylloxy)benzene (73.7 μL , 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash

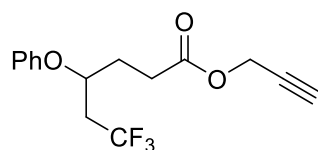
chromatography (PE: EA= 30:1) as a pale-yellow oil liquid (46.4 mg, 73%). ^1H NMR (600 MHz, CDCl_3) δ 7.32 – 7.26 (m, 2H), 6.98 (t, J = 7.4 Hz, 1H), 6.93 – 6.88 (m, 2H), 4.69 – 4.63 (m, 1H), 4.06 (t, J = 6.7 Hz, 2H), 2.64 – 2.53 (m, 1H), 2.52 – 2.44 (m, 2H), 2.41 – 2.30 (m, 1H), 2.20 – 2.13 (m, 1H), 2.09 – 2.00 (m, 1H), 1.60 – 1.53 (m, 2H), 1.38 – 1.30 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H); ^{19}F NMR (565 MHz, CDCl_3) δ -63.23 (t, J = 10.8 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 172.9, 157.1, 129.7, 125.7 (q, J = 277.0 Hz), 121.7, 115.9, 70.8, 64.5, 38.2 (q, J = 27.8 Hz), 30.6, 29.6, 29.6, 19.1, 13.6; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{16}\text{H}_{22}\text{F}_3\text{O}_3$: 319.1516; found: 319.1509.



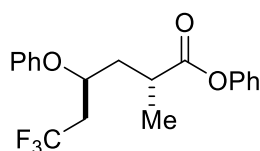
Cyclohexyl 6,6,6-trifluoro-4-phenoxyhexanoate (7): According to the general procedure, cyclohexyl acrylate (31.6 μL , 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (vinylloxy)benzene (73.7 μL , 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 30:1) as a pale-yellow oil liquid (50.4 mg, 73%). ^1H NMR (600 MHz, CDCl_3) δ 7.32 – 7.26 (m, 2H), 6.98 (t, J = 7.4 Hz, 1H), 6.91 (d, J = 7.4 Hz, 2H), 4.79 – 4.71 (m, 1H), 4.68 – 4.63 (m, 1H), 2.62 – 2.53 (m, 1H), 2.46 (t, J = 7.4 Hz, 2H), 2.41 – 2.31 (m, 1H), 2.19 – 2.11 (m, 1H), 2.09 – 2.00 (m, 1H), 1.85 – 1.78 (m, 2H), 1.74 – 1.66 (m, 2H), 1.56 – 1.50 (m, 1H), 1.40 – 1.32 (m, 4H), 1.26 – 1.22 (m, 1H); ^{19}F NMR (565 MHz, CDCl_3) δ -63.23 (t, J = 10.8 Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 172.2, 157.2, 129.7, 125.7 (q, J = 277.0 Hz), 121.7, 115.9, 72.9, 70.9, 38.2 (q, J = 27.8 Hz), 31.6, 30.0, 29.7, 25.3, 23.7; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{19}\text{H}_{22}\text{F}_3\text{O}_3$: 345.1672; found: 345.1671.



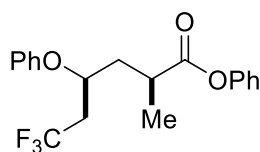
Phenyl 6,6,6-trifluoro-4-phenoxyhexanoate (8): According to the general procedure, phenyl acrylate (27.5 μ L, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (vinylloxy)benzene (73.7 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 30:1) as a pale-yellow oil liquid (57.5 mg, 85%). ^1H NMR (600 MHz, CDCl_3) δ 7.36 (t, J = 8.0 Hz, 2H), 7.30 (t, J = 8.0 Hz, 2H), 7.25 – 7.19 (m, 1H), 7.08 – 6.97 (m, 3H), 6.94 (d, J = 8.0 Hz, 2H), 4.82 – 4.66 (m, 1H), 2.75 (t, J = 7.3 Hz, 2H), 2.68 – 2.57 (m, 1H), 2.46 – 2.35 (m, 1H), 2.33 – 2.25 (m, 1H), 2.21 – 2.12 (m, 1H); ^{19}F NMR (565 MHz, CDCl_3) δ -63.13 (t, J = 10.8 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 171.4, 157.1, 150.5, 129.8, 129.4, 125.9, 125.7 (q, J = 277.0 Hz), 121.8, 121.4, 115.9, 70.7, 38.2 (q, J = 27.8 Hz), 29.7, 29.6; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{18}\text{H}_{18}\text{F}_3\text{O}_3$: 339.1203; found: 339.1205.



Prop-2-yn-1-yl 6,6,6-trifluoro-4-phenoxyhexanoate (9): According to the general procedure, prop-2-yn-1-yl acrylate (22.1 μ L, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (vinylloxy)benzene (73.7 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 30:1) as a pale-yellow oil liquid (40.8 mg, 68%). ^1H NMR (600 MHz, CDCl_3) δ 7.32 – 7.27 (m, 2H), 6.99 (t, J = 7.9 Hz, 1H), 6.90 (d, J = 7.9 Hz, 2H), 4.70 – 4.61 (m, 3H), 2.64 – 2.50 (m, 3H), 2.46 (t, J = 2.5 Hz, 1H), 2.41 – 2.32 (m, 1H), 2.23 – 2.16 (m, 1H), 2.11 – 2.03 (m, 1H); ^{19}F NMR (565 MHz, CDCl_3) δ -63.18 (t, J = 10.8 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 172.0, 157.0, 129.8, 125.7 (q, J = 277.0 Hz), 121.8, 115.9, 77.5, 74.9, 70.6, 52.1, 38.2 (q, J = 27.9 Hz), 29.5, 29.3; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{18}\text{H}_{24}\text{F}_3\text{O}_3$: 301.1046; found: 301.1049.

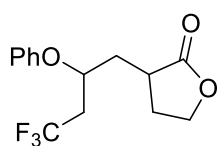


Phenyl-6,6,6-trifluoro-2-methyl-4-phenoxyhexanoate (*anti*-10): According to the general procedure, phenyl methacrylate (30.8 μ L, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (vinylxy)benzene (73.7 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 30:1) as a pale-yellow oil liquid (23.6 mg, 34%). ^1H NMR (600 MHz, CDCl_3) δ 7.34 (t, J = 7.8 Hz, 2H), 7.29 (t, J = 7.8 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 6.99 (t, J = 7.3 Hz, 1H), 6.97 – 6.87 (m, 4H), 4.83 – 4.74 (m, 1H), 3.07 – 2.97 (m, 1H), 2.68 – 2.56 (m, 1H), 2.45 – 2.35 (m, 1H), 2.35 – 2.28 (m, 1H), 2.03 – 1.93 (m, 1H), 1.39 (d, J = 7.1 Hz, 3H); ^{19}F NMR (377 MHz, CDCl_3) δ -62.86 (t, J = 10.8 Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 174.3, 157.2, 150.6, 129.8, 129.4, 125.8, 125.7 (q, J = 277.1 Hz), 121.9, 121.4, 116.0, 70.3, 39.0, 38.5 (q, J = 27.6 Hz), 35.8, 18.0; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{19}\text{H}_{20}\text{F}_3\text{O}_3$: 353.1359; found: 353.1358.

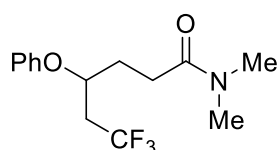


Phenyl-6,6,6-trifluoro-2-methyl-4-phenoxyhexanoate (*syn*-10): According to the general procedure, phenyl methacrylate (30.8 μ L, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (vinylxy)benzene (73.7 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 30:1) as a pale-yellow oil liquid (23.6 mg, 34%). ^1H NMR (600 MHz, CDCl_3) δ 7.36 (t, J = 8.0 Hz, 2H), 7.30 (t, J = 8.0 Hz, 2H), 7.22 (t, J = 8.0 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 6.99 (t, J = 8.0 Hz, 1H), 6.94 (d, J = 8.0 Hz, 2H),

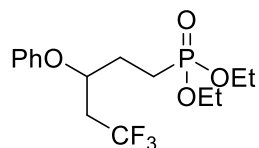
4.74 – 4.63 (m, 1H), 2.92 (h, $J = 7.0$ Hz, 1H), 2.68 – 2.57 (m, 1H), 2.47 – 2.38 (m, 2H), 1.98 – 1.91 (m, 1H), 1.36 (d, $J = 7.0$ Hz, 3H); ^{19}F NMR (377 MHz, CDCl_3) δ -63.01 (t, $J = 10.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 174.5, 156.9, 150.6, 129.8, 129.4, 125.8, 125.7 (q, $J = 277.1$ Hz), 121.8, 121.4, 115.9, 69.9, 38.6 (q, $J = 27.7$ Hz), 38.2, 36.4, 17.4; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{19}\text{H}_{20}\text{F}_3\text{O}_3$: 353.1359; found: 353.1358.



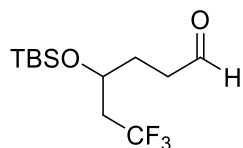
3-(4,4,4-Trifluoro-2-phenoxybutyl)dihydrofuran-2(3H)-one (11): According to the general procedure, 3-methylenedihydrofuran-2(3H)-one (17.5 μL , 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (vinylloxy)benzene (73.7 μL , 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 5:1) as a pale-yellow oil liquid (28.4 mg, 49%). ^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.27 (m, 2H), 7.03 – 6.97 (m, 1H), 6.97 – 6.88 (m, 2H), 5.04 – 4.96 (m, 0.56H), 4.73 – 4.65 (m, 0.44H), 4.38 – 4.29 (m, 1H), 4.19 – 4.10 (m, 1H), 2.88 – 2.53 (m, 2H), 2.49 – 2.27 (m, 3H), 2.10 – 1.87 (m, 2H); ^{19}F NMR (375 MHz, CDCl_3) δ -62.67 (t, $J = 10.8$ Hz, 1.68F), -63.07 (t, $J = 10.7$ Hz, 1.32F); ^{13}C NMR (101 MHz, CDCl_3) δ 178.8, 178.7, 156.9, 156.8, 129.89, 129.85, 125.61 (q, $J = 275.0$ Hz), 125.57 (q, $J = 275.0$ Hz), 121.89, 121.88, 115.8, 115.5, 70.0, 69.2, 66.5, 66.4, 38.4 (q, $J = 27.7$ Hz), 38.2 (q, $J = 27.7$ Hz), 36.1, 36.0, 35.7, 35.4, 29.7, 29.1; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{14}\text{H}_{16}\text{F}_3\text{O}_3$: 289.1046; found: 289.1046.



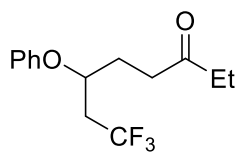
6,6,6-Trifluoro-*N,N*-dimethyl-4-phenoxyhexanamide (12): According to the general procedure, *N,N*-dimethylacrylamide (20.6 μ L, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (vinylxy)benzene (73.7 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 2:1) as a yellow oil liquid (43.9 mg, 76%). ^1H NMR (600 MHz, CDCl_3) δ 7.28 (t, J = 8.0 Hz, 2H), 6.96 (t, J = 8.0 Hz, 1H), 6.92 (d, J = 8.0 Hz, 2H), 4.76 – 4.72 (m, 1H), 2.92 (s, 3H), 2.89 (s, 3H), 2.62 – 2.51 (m, 1H), 2.45 (t, J = 7.2 Hz, 2H), 2.42 – 2.34 (m, 1H), 2.25 – 2.18 (m, 1H), 2.07 – 1.99 (m, 1H); ^{19}F NMR (565 MHz, CDCl_3) δ -63.14 (t, J = 10.8 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 171.7, 157.4, 129.7, 125.8 (q, J = 277.1 Hz), 121.4, 115.8, 70.9, 38.4 (q, J = 27.7 Hz), 37.0, 35.4, 30.0, 28.1; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{14}\text{H}_{19}\text{NF}_3\text{O}_2$: 290.1362; found: 290.1365.



Diethyl (5,5,5-trifluoro-3-phenoxypropyl)phosphonate (13): According to the general procedure, diethyl vinylphosphonate (30.7 μ L, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (vinylxy)benzene (73.7 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 3:2) as a yellow oil liquid (57.3 mg, 81%). ^1H NMR (600 MHz, CDCl_3) δ 7.30 (t, J = 8.0 Hz, 2H), 6.99 (t, J = 8.0 Hz, 1H), 6.92 (d, J = 8.0 Hz, 2H), 4.69 – 4.61 (m, 1H), 4.12 – 4.04 (m, 4H), 2.64 – 2.53 (m, 1H), 2.41 – 2.29 (m, 1H), 2.17 – 2.09 (m, 1H), 2.04 – 1.83 (m, 3H), 1.30 (q, J = 6.8 Hz, 6H); ^{19}F NMR (565 MHz, CDCl_3) δ -63.18 (t, J = 10.8 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 157.0, 129.7, 125.7 (q, J = 277.0 Hz), 121.8, 115.9, 71.2, 61.7, 37.9 (q, J = 27.8 Hz), 27.5, 21.7, 20.3, 16.3, 16.3; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{15}\text{H}_{23}\text{PF}_3\text{O}_4$: 355.1281; found: 355.1285.

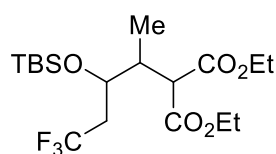


4-((*tert*-Butyldimethylsilyl)oxy)-6,6,6-trifluorohexanal (14): According to the general procedure, acrylaldehyde (13.4 μ L, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), *tert*-butyldimethyl(vinyloxy)silane (118.5 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 40:1) as a pale-yellow oil liquid (49.8 mg, 88%). ^1H NMR (600 MHz, CDCl_3) δ 9.80 (s, 1H), 4.15 – 4.05 (m, 1H), 2.61 – 2.44 (m, 2H), 2.32 – 2.16 (m, 2H), 2.04 – 1.91 (m, 1H), 1.85 – 1.74 (m, 1H), 0.88 (s, 9H), 0.07 (s, 6H); ^{19}F NMR (565 MHz, CDCl_3) δ -63.05 (t, J = 11.0 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 201.4, 125.9 (q, J = 277.0 Hz), 65.4 (q, J = 3.0 Hz), 40.9 (q, J = 26.8 Hz), 38.8, 29.3, 25.6, 17.8, -4.7, -5.1; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{12}\text{H}_{24}\text{SiF}_3\text{O}_2$: 285.1492; found: 285.1496.



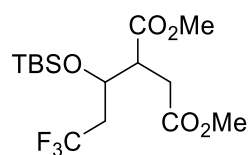
8,8,8-Trifluoro-6-phenoxyoctan-3-one (15): According to the general procedure, pent-1-en-3-one (19.8 μ L, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (vinyloxy)benzene (73.7 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 30:1) as a pale-yellow oil liquid (35.6 mg, 65%). ^1H NMR (600 MHz, CDCl_3) δ 7.33 – 7.26 (m, 2H), 6.97 (t, J = 7.4 Hz, 1H), 6.89 (d, J = 7.4 Hz, 2H), 4.66 – 4.61 (m, 1H), 2.61 – 2.50 (m, 3H), 2.44 – 2.29 (m, 3H), 2.16 – 2.10 (m,

1H), 2.02 – 1.94 (m, 1H), 1.03 (t, $J = 7.3$ Hz, 3H); ^{19}F NMR (565 MHz, CDCl_3) δ -63.24 (t, $J = 10.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 210.4, 157.2, 129.7, 125.7 (q, $J = 277.0$ Hz), 121.6, 115.8, 70.7, 38.3 (q, $J = 27.8$ Hz), 37.2, 36.0, 28.4, 7.7; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{14}\text{H}_{18}\text{F}_3\text{O}_2$: 275.1253; found: 275.1256.



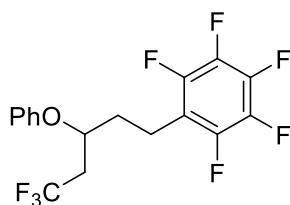
Diethyl 2-(3-((tert-butyldimethylsilyl)oxy)-5,5,5-trifluoropentan-2-yl)malonate (16):

According to the general procedure, diethyl 2-ethylidenemalonate (36.6 μL , 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), *tert*-butyldimethyl(vinyloxy)silane (118.5 μL , 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 40:1) as a pale-yellow oil liquid (65.8 mg, 79%). ^1H NMR (600 MHz, CDCl_3) δ 4.30 – 4.02 (m, 5H), 3.51 – 3.04 (m, 1H), 2.58 – 2.08 (m, 3H), 1.28 (t, $J = 7.1$ Hz, 6H), 1.00 – 0.93 (m, 3H), 0.89 (s, 9H), 0.15 – 0.01 (m, 6H); ^{19}F NMR (565 MHz, CDCl_3) δ -62.95 (t, $J = 10.7$ Hz, 2.48F), -63.19 (t, $J = 11.1$ Hz, 0.52F); ^{13}C NMR (101 MHz, CDCl_3) δ 168.7, 168.5, 168.1, 167.8, 126.6 (q, $J = 276.0$ Hz), 125.9 (q, $J = 275.0$ Hz), 67.4, 67.2, 61.6, 61.5, 61.41, 61.35, 54.8, 54.0, 39.0, 38.8 (q, $J = 26.8$ Hz), 38.2, 36.4 (q, $J = 26.9$ Hz), 25.7, 25.6, 18.0, 17.8, 14.0, 13.9, 10.9, 10.7, -4.6, -4.8, -5.0, -5.4; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{18}\text{H}_{34}\text{SiF}_3\text{O}_5$: 415.2122; found: 415.2126.



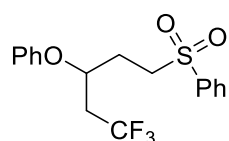
Dimethyl 2-(1-((tert-butyldimethylsilyl)oxy)-3,3,3-trifluoropropyl)succinate (17):

According to the general procedure, dimethyl fumarate (28.8 mg, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), *tert*-butyldimethyl(vinyloxy)silane (118.5 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 40:1) as a pale-yellow oil liquid (61.8 mg, 83%). ^1H NMR (600 MHz, CDCl_3) δ 4.52 – 4.33 (m, 1H), 3.75 – 3.63 (m, 6H), 3.27 – 3.04 (m, 1H), 2.91 – 2.67 (m, 1H), 2.66 – 2.41 (m, 1H), 2.40 – 2.12 (m, 2H), 0.86 (d, J = 9.9 Hz, 9H), 0.16 – 0.01 (m, 6H); ^{19}F NMR (565 MHz, CDCl_3) δ -63.26 (t, J = 10.9 Hz, 1.79F), -63.47 (t, J = 10.7 Hz, 1.21F); ^{13}C NMR (101 MHz, CDCl_3) δ 172.5, 172.4, 172.3, 171.8, 126.0 (q, J = 276.0) 125.7 (q, J = 275.0), 66.8, 66.2, 52.2, 52.1, 51.9, 47.7, 47.0, 39.2 (q, J = 27.1 Hz), 38.2 (q, J = 27.3 Hz), 30.32, 30.29, 29.8, 29.7, 25.5, 17.8, 17.7, -4.8, -5.0, -5.2, -5.3; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{15}\text{H}_{28}\text{SiF}_3\text{O}_5$: 373.1653; found: 373.1655.

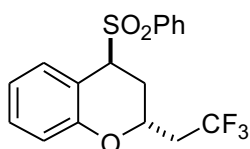


1,2,3,4,5-Pentafluoro-6-(5,5,5-trifluoro-3-phenoxypropyl)benzene (18): According to the general procedure, 1,2,3,4,5-pentafluoro-6-vinylbenzene (27.1 μ L, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (vinyloxy)benzene (73.7 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (hexane) as a pale-yellow oil liquid (60.1 mg, 78%). ^1H NMR (600 MHz, CDCl_3) δ 7.30 (t, J = 7.8 Hz, 2H), 7.00 (t, J = 7.8 Hz, 1H), 6.88 (d, J = 7.8 Hz, 2H), 4.64 – 4.57 (m, 1H), 2.94 – 2.79 (m, 2H), 2.69 – 2.58 (m, 1H), 2.46 – 2.35 (m, 1H), 2.14 – 2.06 (m, 1H), 2.05 – 1.99 (m, 1H); ^{19}F

NMR (565 MHz, CDCl₃) δ -63.21 (t, J = 10.7 Hz, 3F), -144.18 (dd, J = 21.8, 8.2 Hz, 2F), -157.26 (t, J = 21.8 Hz, 1F), -162.56 (td, J = 21.8, 8.2 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃) δ 156.8, 145.0 (dm, J = 245.7 Hz), 139.8 (dm, J = 246.9 Hz), 135.7 (dm, J = 252.2 Hz), 129.8, 125.7 (q, J = 277.0 Hz), 121.9, 115.8, 114.1 (m), 71.1, 37.9 (q, J = 27.8 Hz), 33.6, 18.1; HRMS (ESI) ([M+H]⁺) Calcd. for C₁₇H₁₃F₈O: 385.0833; found: 385.0836.

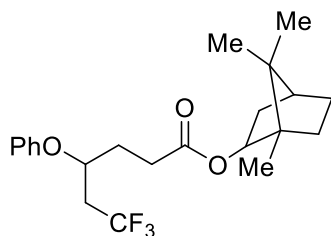


((5,5,5-Trifluoro-3-phenoxypropyl)sulfonyl)benzene (19): According to the general procedure, (vinylsulfonyl)benzene (33.6 mg, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (vinylloxy)benzene (73.7 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 5:1) as a pale-yellow oil liquid (52.3 mg, 73%). ¹H NMR (600 MHz, CDCl₃) δ 7.89 (d, J = 8.0 Hz, 2H), 7.67 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.5 Hz, 2H), 7.29 – 7.26 (m, 2H), 7.00 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 8.0 Hz, 2H), 4.71 – 4.64 (m, 1H), 3.34 – 3.20 (m, 2H), 2.63 – 2.50 (m, 1H), 2.36 – 2.24 (m, 2H), 2.18 – 2.08 (m, 1H); ¹⁹F NMR (565 MHz, CDCl₃) δ -63.04 (t, J = 10.7 Hz); ¹³C NMR (150 MHz, CDCl₃) δ 156.5, 138.8, 133.9, 129.9, 129.4, 128.0, 125.4 (q, J = 277.0 Hz), 122.3, 116.0, 69.9, 51.9, 38.0 (q, J = 27.9 Hz), 27.9; HRMS (ESI) ([M+H]⁺) Calcd. for C₁₇H₁₈F₃O₃S: 359.0923; found: 359.0921.



4-(Phenylsulfonyl)-2-(2,2,2-trifluoroethyl)chromane (19'): According to the general procedure, (vinylsulfonyl)benzene (33.6 mg, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (vinylloxy)benzene (73.7 μ L, 0.60 mmol, 3.0 equiv.),

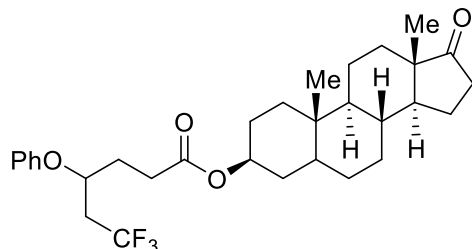
Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 5:1) as a pale-yellow oil liquid (16.3 mg, 23%). ^1H NMR (600 MHz, CDCl_3) δ 7.79 (d, J = 8.0 Hz, 2H), 7.72 (t, J = 7.4 Hz, 1H), 7.58 (t, J = 7.4 Hz, 2H), 7.30 - 7.27 (m, 1H), 7.16 (d, J = 8.0 Hz, 1H), 6.91 - 6.89 (m, 2H), 4.67 - 4.63 (m, 1H), 4.34 - 4.33 (m, 1H), 2.68 - 2.56 (m, 2H), 2.44 - 2.33 (m, 1H), 2.04 - 1.99 (m, 1H); ^{19}F NMR (565 MHz, CDCl_3) δ -62.89 (t, J = 10.7 Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 155.2, 136.9, 134.3, 131.8, 130.7, 129.32, 129.32, 125.4 (q, J = 277.1 Hz), 120.7, 117.6, 111.5, 65.5, 60.0, 39.8 (q, J = 28.7 Hz), 27.5; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{17}\text{H}_{16}\text{F}_3\text{O}_3\text{S}$: 357.0767; found: 357.0769.



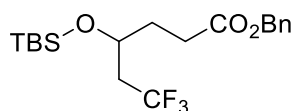
1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 6,6,6-trifluoro-4-phenoxyhexanoate (20):

According to the general procedure, 1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl acrylate (42.3 μL , 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (vinyloxy)benzene (73.7 μL , 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 30:1) as a pale-yellow oil liquid (62.1 mg, 78%). ^1H NMR (600 MHz, CDCl_3) δ 7.32 - 7.26 (m, 2H), 6.98 (t, J = 7.4 Hz, 1H), 6.94 - 6.88 (m, 2H), 4.70 - 4.60 (m, 2H), 2.62 - 2.53 (m, 1H), 2.50 - 2.42 (m, 2H), 2.39 - 2.30 (m, 1H), 2.19 - 2.11 (m, 1H), 2.08 - 2.00 (m, 1H), 1.81 - 1.76 (m, 1H), 1.73 - 1.65 (m, 3H), 1.57 - 1.50 (m, 1H), 1.17 - 1.11 (m, 1H), 1.10 - 1.04 (m, 1H), 0.93 (s, 3H), 0.82 (d, J = 2.8 Hz, 3H), 0.80 (d, J = 15.2 Hz, 3H); ^{19}F NMR (565 MHz, CDCl_3) δ -63.16 (t, J = 10.6 Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 172.2, 157.2, 129.7, 125.7 (q, J = 277.1 Hz), 121.7, 116.0, 81.2, 70.9,

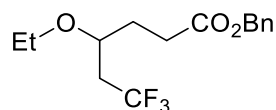
48.6, 46.9, 45.0, 38.7, 38.2 (q, $J = 27.7$ Hz), 33.7, 29.9, 29.7, 27.0, 20.0, 19.8, 11.4; HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{22}H_{30}F_3O_3$: 399.2142; found: 399.2141.



(3S,8R,9S,10S,13S,14S)-10,13-Dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 6,6,6-trifluoro-4-phenoxyhexanoate (21): According to the general procedure, (3S,8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl acrylate (68.9 mg, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (vinylxy)benzene (73.7 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 8:1) as a colorless solid (85.6 mg, 80%). 1H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 6.98 (t, $J = 7.9$ Hz, 1H), 6.91 (d, $J = 7.9$ Hz, 2H), 4.74 – 4.62 (m, 2H), 2.63 – 2.52 (m, 1H), 2.47 – 2.40 (m, 3H), 2.39 – 2.31 (m, 1H), 2.17 – 2.11 (m, 1H), 2.10 – 2.02 (m, 2H), 1.95 – 1.89 (m, 1H), 1.80 – 1.71 (m, 4H), 1.66 – 1.63 (m, 1H), 1.56 – 1.45 (m, 4H), 1.34 – 1.24 (m, 6H), 1.20 – 1.16 (m, 1H), 1.04 – 0.94 (m, 2H), 0.86 (s, 3H), 0.83 (s, 3H), 0.73 – 0.69 (m, 1H); ^{19}F NMR (565 MHz, $CDCl_3$) δ -63.20 (t, $J = 10.7$ Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 221.2, 172.3, 157.2, 129.7, 125.7 (q, $J = 277.0$ Hz), 121.6, 115.9, 73.8, 70.8, 54.3, 51.3, 47.7, 44.6, 38.2 (q, $J = 27.8$ Hz), 36.6, 35.8, 35.6, 35.0, 33.8, 31.5, 30.8, 30.0, 29.7, 28.2, 27.3, 21.7, 20.4, 13.8, 12.2; HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{31}H_{42}F_3O_4$: 535.3030; found: 535.3029.

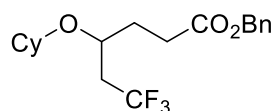


Benzyl 4-((*tert*-butyldimethylsilyl)oxy)-6,6,6-trifluorohexanoate (22): According to the general procedure, benzyl acrylate (30.6 μ L, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), *tert*-butyldimethyl(vinyloxy)silane (118.5 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 50:1) as a pale-yellow oil liquid (67.9 mg, 87%). ^1H NMR (600 MHz, CDCl_3) δ 7.38 – 7.31 (m, 5H), 5.12 (s, 2H), 4.13 – 4.05 (m, 1H), 2.50 – 2.39 (m, 2H), 2.29 – 2.15 (m, 2H), 2.01 – 1.94 (m, 1H), 1.86 – 1.79 (m, 1H), 0.87 (s, 9H), 0.05 (d, J = 2.1 Hz, 6H); ^{19}F NMR (565 MHz, CDCl_3) δ -62.98 (t, J = 11.0 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 173.0, 135.9, 128.6, 128.26, 128.25, 126.0 (q, J = 277.1 Hz), 66.4, 65.4, 40.9 (q, J = 26.7 Hz), 32.2, 29.1, 25.7, 17.8, -4.7, -5.1; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{19}\text{H}_{30}\text{SiF}_3\text{O}_3$: 391.1911; found: 391.1913.

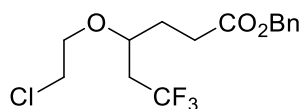


Benzyl 4-ethoxy-6,6,6-trifluorohexanoate (23): According to the general procedure, benzyl acrylate (30.6 μ L, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), ethoxyethene (57.5 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 30:1) as a pale-yellow oil liquid (44.2 mg, 73%). ^1H NMR (600 MHz, CDCl_3) δ 7.41 – 7.28 (m, 5H), 5.12 (s, 2H), 3.66 – 3.58 (m, 1H), 3.55 – 3.47 (m, 1H), 3.47 – 3.40 (m, 1H), 2.47 (t, J = 7.4 Hz, 2H), 2.41 – 2.31 (m, 1H), 2.22 – 2.12 (m, 1H), 2.02 – 1.95 (m, 1H), 1.87 – 1.78 (m, 1H), 1.15 (t, J = 7.0 Hz, 3H); ^{19}F NMR (565 MHz, CDCl_3) δ -63.46 (t, J = 11.0 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 172.9, 135.9, 128.6, 128.3, 128.3, 126.0 (q, J = 276.9 Hz), 72.5, 66.3, 65.1, 38.7 (q, J = 27.3 Hz), 29.8,

29.7, 15.2; HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{15}H_{20}F_3O_3$: 305.1359; found: 305.1361.

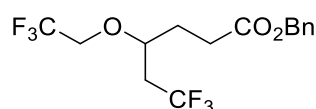


Benzyl 4-(cyclohexyloxy)-6,6,6-trifluorohexanoate (24): According to the general procedure, benzyl acrylate (30.6 μ L, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (vinylloxy)cyclohexane (85.0 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 30:1) as a pale-yellow oil liquid (56.3 mg, 79%). 1H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 5H), 5.12 (s, 2H), 3.80 – 3.70 (m, 1H), 3.30 – 3.19 (m, 1H), 2.47 (t, J = 7.5 Hz, 2H), 2.40 – 2.29 (m, 1H), 2.23 – 2.14 (m, 1H), 2.03 – 1.95 (m, 1H), 1.85 – 1.77 (m, 3H), 1.74 – 1.66 (m, 2H), 1.55 – 1.49 (m, 1H), 1.29 – 1.17 (m, 5H); ^{19}F NMR (565 MHz, $CDCl_3$) δ -63.11 (t, J = 11.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 135.8, 128.5, 128.28, 128.26, 126.0 (q, J = 277.0 Hz), 76.4, 69.4, 66.3, 39.3 (q, J = 27.0 Hz), 32.7, 30.2, 29.7, 25.6, 24.2; HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{19}H_{26}F_3O_3$: 359.1829; found: 359.1831.

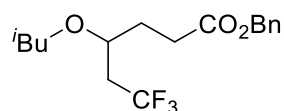


Benzyl 4-(2-chloroethoxy)-6,6,6-trifluorohexanoate (25): According to the general procedure, benzyl acrylate (30.6 μ L, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (2-chloroethoxy)ethene (61.0 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash

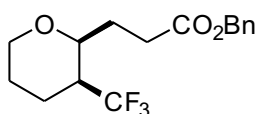
chromatography (PE: EA= 30:1) as a pale-yellow oil liquid (52.9 mg, 78%). ^1H NMR (600 MHz, CDCl_3) δ 7.42 – 7.28 (m, 5H), 5.13 (s, 2H), 3.75 – 3.68 (m, 2H), 3.66 – 3.61 (m, 1H), 3.54 (t, J = 5.7 Hz, 2H), 2.57 – 2.46 (m, 2H), 2.44 – 2.34 (m, 1H), 2.25 – 2.15 (m, 1H), 2.04 – 1.97 (m, 1H), 1.91 – 1.83 (m, 1H); ^{19}F NMR (565 MHz, CDCl_3) δ -63.42 (t, J = 10.9 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 172.8, 135.8, 128.6, 128.29, 128.28, 125.9 (q, J = 276.9 Hz), 73.3, 69.9, 66.4, 42.8, 38.6 (q, J = 27.6 Hz), 29.8, 29.5; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{15}\text{H}_{19}\text{ClF}_3\text{O}_3$: 339.0969; found: 339.0974.



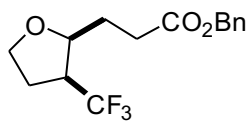
Benzyl 6,6,6-trifluoro-4-(2,2,2-trifluoroethoxy)hexanoate (26): According to the general procedure, benzyl acrylate (30.6 μL , 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (2,2,2-trifluoroethoxy)ethene (66.7 μL , 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 30:1) as a pale-yellow oil liquid (52.3 mg, 73%). ^1H NMR (600 MHz, CDCl_3) δ 7.42 – 7.29 (m, 5H), 5.12 (s, 2H), 3.88 – 3.72 (m, 3H), 2.54 – 2.44 (m, 2H), 2.43 – 2.35 (m, 1H), 2.29 – 2.19 (m, 1H), 2.05 – 1.98 (m, 1H), 1.93 – 1.86 (m, 1H); ^{19}F NMR (565 MHz, CDCl_3) δ -63.61 (t, J = 10.8 Hz), -74.65 (t, J = 8.5 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 172.5, 135.7, 128.6, 128.4, 128.3, 125.6 (q, J = 276.8 Hz), 123.5 (q, J = 278.7 Hz), 75.0, 67.3 (q, J = 34.5 Hz), 66.5, 38.7 (q, J = 28.1 Hz), 29.6, 29.1; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{15}\text{H}_{17}\text{F}_6\text{O}_3$: 359.1076; found: 359.1079.



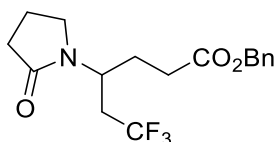
Benzyl 6,6,6-trifluoro-4-isobutoxyhexanoate (27): According to the general procedure, benzyl acrylate (30.6 μ L, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), 2-methyl-1-(vinylloxy)propane (78.1 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 30:1) as a pale-yellow oil liquid (55.2 mg, 64%). ^1H NMR (600 MHz, CDCl_3) δ 7.39 – 7.30 (m, 5H), 5.12 (s, 2H), 3.66 – 3.55 (m, 1H), 3.22 – 3.11 (m, 2H), 2.47 (t, J = 7.5 Hz, 2H), 2.41 – 2.32 (m, 1H), 2.22 – 2.11 (m, 1H), 2.04 – 1.96 (m, 1H), 1.88 – 1.75 (m, 2H), 0.88 (s, 3H), 0.87 (s, 3H); ^{19}F NMR (565 MHz, CDCl_3) δ -63.31 (t, J = 11.1 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 172.9, 135.9, 128.6, 128.3, 126.1 (q, J = 276.9 Hz), 76.5, 72.7, 66.3, 38.5 (q, J = 27.3 Hz), 29.6, 29.6, 28.7, 19.3; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{17}\text{H}_{24}\text{F}_3\text{O}_3$: 333.1672; found: 333.1675.



Benzyl 3-(3-(trifluoromethyl)tetrahydro-2H-pyran-2-yl)propanoate (syn-28): According to the general procedure, benzyl acrylate (30.6 μ L, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), 3,4-dihydro-2H-pyran (54.7 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 30:1) as a pale-yellow oil liquid (26.8 mg, 42%). ^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.28 (m, 5H), 5.12 (s, 2H), 3.95 – 3.87 (m, 1H), 3.40 – 3.25 (m, 2H), 2.59 – 2.43 (m, 2H), 2.22 – 2.02 (m, 3H), 1.88 – 1.77 (m, 1H), 1.69 – 1.58 (m, 2H), 1.55 – 1.46 (m, 1H); ^{19}F NMR (377 MHz, CDCl_3) δ -67.92 (d, J = 8.5 Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 173.3, 136.1, 128.5, 128.2, 128.1, 126.5 (q, J = 279.8 Hz), 75.5, 67.8, 66.1, 44.6 (q, J = 24.7 Hz), 29.9, 28.8, 24.6, 23.3; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{16}\text{H}_{20}\text{F}_3\text{O}_3$: 317.1359; found: 317.1358.

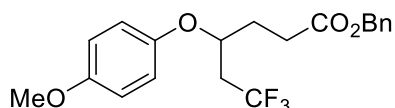


Benzyl 3-(3-(trifluoromethyl)tetrahydrofuran-2-yl)propanoate (syn-29): According to the general procedure, benzyl acrylate (30.6 μ L, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), 2,3-dihydrofuran (45.4 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 30:1) as a pale-yellow oil liquid (43.5 mg, 72%). ^1H NMR (600 MHz, CDCl_3) δ 7.41 – 7.28 (m, 5H), 5.12 (s, 2H), 4.00 – 3.93 (m, 1H), 3.91 – 3.86 (m, 1H), 3.75 (dd, J = 15.9, 7.7 Hz, 1H), 2.59 – 2.45 (m, 3H), 2.17 – 2.09 (m, 1H), 2.08 – 2.00 (m, 2H), 1.91 – 1.83 (m, 1H); ^{19}F NMR (565 MHz, CDCl_3) δ -69.75 (d, J = 9.4 Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 172.8, 135.9, 128.5, 128.2, 128.2, 127.1 (q, J = 277.4 Hz), 77.7, 67.1, 66.3, 48.2 (q, J = 26.7 Hz), 30.7, 30.1, 27.0; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{O}_3$: 303.1203; found: 303.1202.



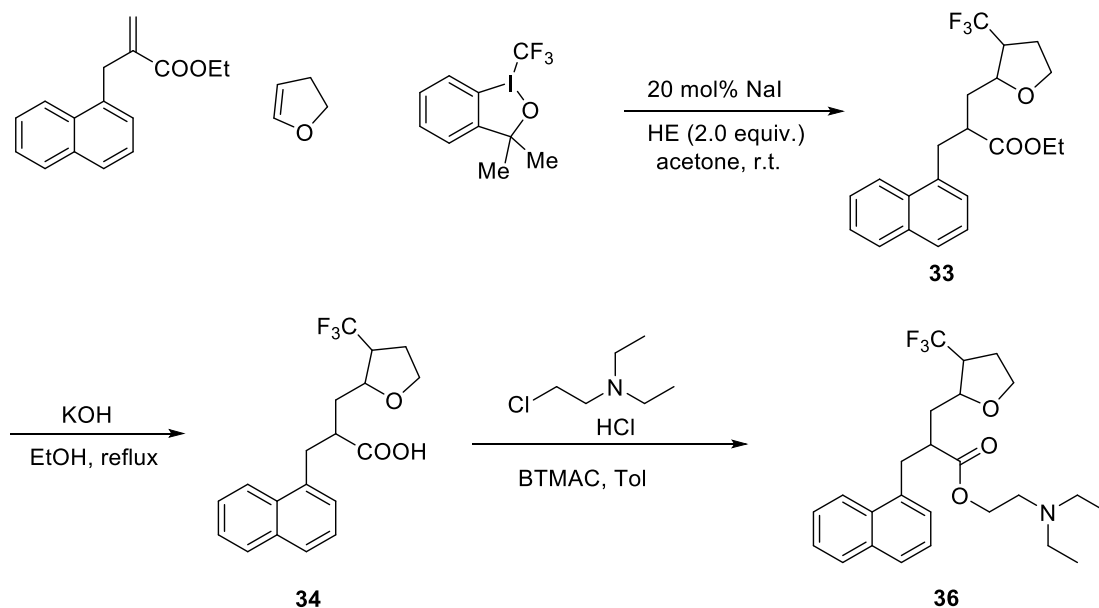
Benzyl 6,6,6-trifluoro-4-(2-oxopyrrolidin-1-yl)hexanoate (30): According to the general procedure, benzyl acrylate (30.6 μ L, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), 1-vinylpyrrolidin-2-one (64.1 μ L, 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 3:1) as a pale-yellow oil liquid (46.7 mg, 68%). ^1H NMR (600 MHz, CDCl_3) δ 7.39 – 7.31 (m, 5H), 5.12 (s, 2H), 4.37 – 4.28 (m, 1H), 3.29 – 3.24 (m, 2H), 2.59 – 2.51 (m, 1H), 2.40 – 2.28 (m, 4H), 2.24 – 2.17 (m, 1H), 2.05 –

1.95 (m, 3H), 1.93 – 1.86 (m, 1H); ^{19}F NMR (565 MHz, CDCl_3) δ -64.49 (t, J = 10.5 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 175.3, 172.3, 135.6, 128.6, 128.31, 128.28, 125.6 (q, J = 277.1 Hz), 66.5, 46.1, 43.4, 35.5 (q, J = 28.1 Hz), 31.2, 30.6, 27.1, 18.3; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{17}\text{H}_{21}\text{NF}_3\text{O}_3$: 344.1468; found: 344.1470.



Benzyl 6,6,6-trifluoro-4-(4-methoxyphenoxy)hexanoate (31): According to the general procedure, benzyl acrylate (30.6 μL , 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), 1-methoxy-4-(vinylloxy)benzene (89.6 μL , 0.60 mmol, 3.0 equiv.), Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv.) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 3:1) as a pale-yellow oil liquid (56.6 mg, 74%). ^1H NMR (600 MHz, CDCl_3) δ 7.39 – 7.28 (m, 5H), 6.84 – 6.78 (m, 4H), 5.10 (s, 2H), 4.52 – 4.46 (m, 1H), 3.76 (s, 3H), 2.58 – 2.50 (m, 3H), 2.36 – 2.28 (m, 1H), 2.20 – 2.13 (m, 1H), 2.07 – 2.00 (m, 1H); ^{19}F NMR (565 MHz, CDCl_3) δ -63.11 (t, J = 10.8 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 172.7, 154.6, 151.1, 135.7, 128.6, 128.3, 125.8 (q, J = 277.0 Hz), 117.5, 114.8, 72.1 (q, J = 2.6 Hz), 66.5, 55.6, 38.1 (q, J = 27.8 Hz), 29.7, 29.6; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{20}\text{H}_{22}\text{F}_3\text{O}_4$: 383.1465; found: 383.1470.

5. A three-step Synthesis of CF₃-Naftidrofuryl ¹



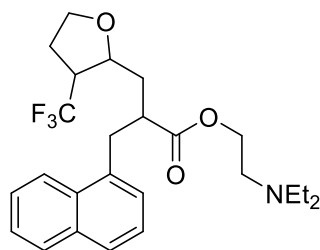
To a flame-dried 8 mL reaction vial was charged with Togni's reagent (199 mg, 0.60 mmol, 3.0 equiv.) and Hantzsch ester (101.2 mg, 0.4 mmol, 2.0 equiv.). Subsequently, the vial was introduced into a nitrogen-filled glove box and charged with NaI (6 mg, 0.04 mmol, 0.2 equiv.). The vial was capped and taken out from the glovebox. Acetone [2 mL] was added via syringe, followed by addition of ethyl 2-(naphthalen-1-ylmethyl)acrylate ² (45.8 μ L, 0.20 mmol, 1.0 equiv.) and 2,3-dihydrofuran (75.6 μ L, 1.00 mmol, 5.0 equiv.) was added via syringe. The reaction mixture was allowed to stir at 600 rpm for 24 h at 25 °C. After 24 h, the resulting mixture was filtered and the solvent was removed under reduced pressure to give crude product **33** which was used for next reaction without further purification.

[1] J. Hao, B. Chen, Y. Yao, M. Hossain, T. Nagatomo, H. Yao, L. Kong, H. Sun, *Bioorganic & Medicinal Chemistry Letters* **2012**, 22, 3441.

[2] O. Tamura, T. Shiro, M. Ogasawara, A. Toyao, and H. Ishibashi, *J. Org. Chem.* **2005**, 70, 4569.

The crude product **33** was dissolved in ethanol (4 mL), 0.2 mL of 80% KOH solution was added dropwise, the reaction mixture was stirred under reflux overnight. After cooling to room temperature, the organic solvents were removed under reduced pressure. To the residue was added ethyl acetate, and the pH was adjusted to 1.0 by adding 36% HCl slowly at 0 °C, the resulting mixture was extracted with ethyl acetate. The organic layers were combined and washed with brine, dried over anhydrous sodium sulfate, filtered, and the solvent was removed under reduced pressure, the product **34** was isolated by flash chromatography (PE: EA: HOAc= 3:1:0.04) as a brown oil liquid (55.6 mg, 79%).

Compound **34** (35.2 mg, 0.1 mmol, 1.0 equiv.) was dissolved in toluene (2.0 mL), and potassium carbonate (34.5 mg, 0.25 mmol, 2.5 equiv.) was dissolved in water (2.0 mL), and 2-diethylaminoethylchloride hydrochloride (17.2 mg, 0.1 mmol, 1.0 equiv.) was added, the mixture was stirred at room temperature for 1 h. Then benzyltrimethylammonium chloride (BTMAC) (1.9 mg, 0.01 mmol, 0.1 equiv.) was added after the combination of these two solutions. The reaction mixture was stirred at 90 °C overnight. After cooling to room temperature, the mixture was extracted with ethyl acetate. The organic layers were combined and washed with brine, dried over anhydrous sodium sulfate, filtered, and the solvent was removed under reduced pressure, the product **36** was isolated by column chromatography (PE: EA: NEt₃= 3:1:0.01) as a brown oil liquid (35.3 mg, 78%).



2-(Diethylamino)ethyl

3-(naphthalen-1-yl)-2-((3-(trifluoromethyl)tetrahydrofuran-2-yl)methyl)propanoate

(36): ^1H NMR (600 MHz, CDCl_3) δ 8.04 (d, $J = 8.2$ Hz, 1H), 7.84 (d, $J = 8.2$ Hz, 1H), 7.73 (d, $J = 8.2$ Hz, 1H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.4$ Hz, 1H), 7.38 – 7.35 (m, 1H), 7.33 – 7.28 (m, 1H), 4.10 – 3.92 (m, 3H), 3.92 – 3.77 (m, 1H), 3.77 – 3.65 (m, 1H), 3.50 – 3.34 (m, 1H), 3.34 – 3.21 (m, 1H), 3.17 – 3.03 (m, 1H), 2.49 – 2.37 (m, 7H), 2.19 – 1.98 (m, 3H), 1.90 – 1.68 (m, 1H), 0.97 – 0.88 (m, 6H); ^{19}F NMR (565 MHz, CDCl_3) δ -69.63 (d, $J = 9.3$ Hz, 2.1F), -69.81 (d, $J = 9.3$ Hz, 0.9F); ^{13}C NMR (100 MHz, CDCl_3) δ 175.3, 174.9, 134.80, 134.77, 133.9, 131.9, 131.8, 128.8, 127.6 (q, $J = 278.6$ Hz), 127.40, 127.36, 127.2, 127.13, 127.07 (q, $J = 275.6$ Hz), 126.09, 126.06, 125.6, 125.3, 123.6, 67.1, 67.0, 62.6, 62.5, 50.7, 50.6, 48.7 (q, $J = 26.4$ Hz), 48.4 (q, $J = 26.5$ Hz), 47.7, 47.41, 47.38, 44.2, 43.4, 37.3, 37.1, 36.2, 35.7, 26.83, 26.81, 11.83, 11.80; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{25}\text{H}_{33}\text{NF}_3\text{O}_3$: 452.2407; found: 452.2405.

6. Mechanistic studies:

6.1. UV/vis absorption spectrometry between Togni's reagent 1 and HE 2.

UV/vis absorption spectra between Hantzsch ester (0.05 M) and Togni's reagent (0.05 M) in 3 mL DCM were recorded in 1 cm path quartz cuvettes using a Shimadzu UV-2550 UV/Vis spectrometer.

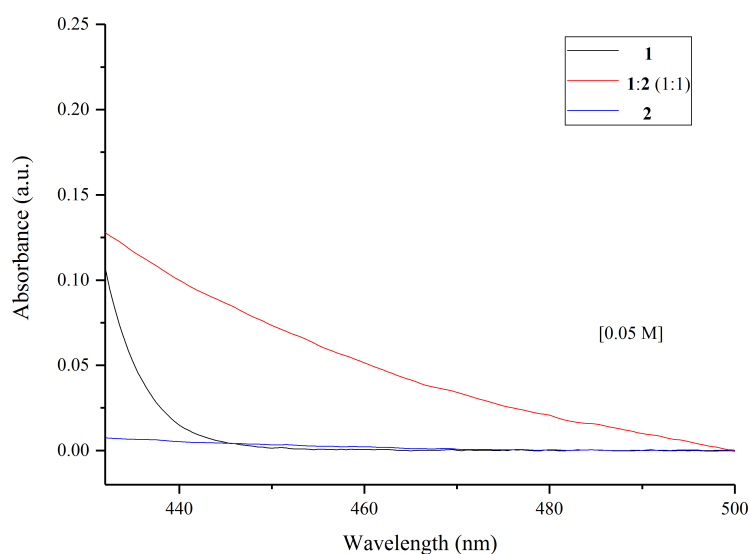


Figure S1: UV/vis absorption spectrometry between 1 and 2.

6.2. Stoichiometry of the EDA complex.

The stoichiometry of the EDA complexes was calculated using the Job's plot method³. The Job's plot of the EDA complex between HE and Togni's reagent was calculated measuring the absorption of DCM solutions at 450 nm with different donor/acceptor ratios with constant concentration (0.05 M) of the two components. The absorbance values were plotted against the molar fraction (%) of HE. The Job's plot analysis of the EDA complex between HE and Togni's reagent showed a maximal absorbance at 50% molar fraction of HE indicated the 1:1 stoichiometry of the EDA complex in solution.

[3] P. Job, *Ann. Chim.* **1928**, 9, 113.

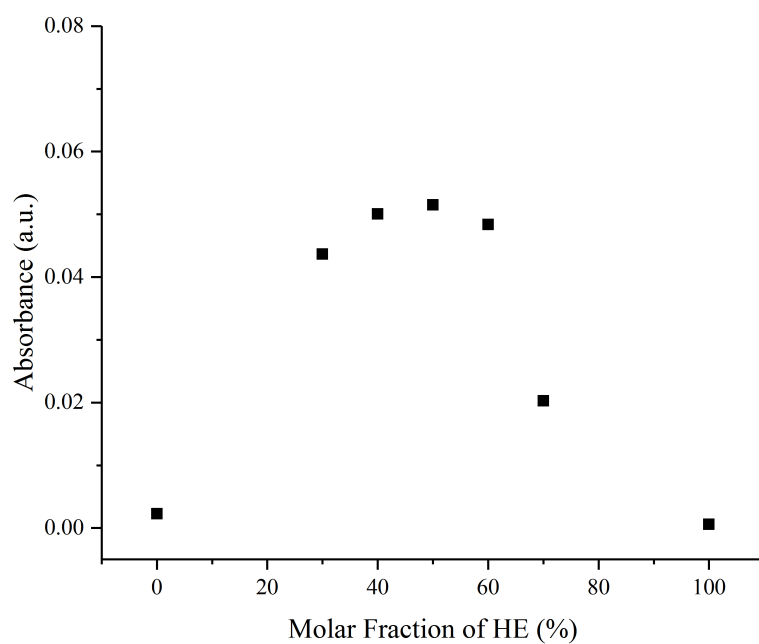


Figure S2. Job's plots of the EDA complexes between HE and Togni's reagent.

6.3. NMR titration experiments:

Solutions containing equal molar concentrations of the donor (HE, 0.1 M in CDCl_3) and the acceptor (Togni's reagent, 0.1 M in CDCl_3) were prepared and mixed to cover acceptor/donor ratio from 0:10, 1:10, 2:10 to 10:10 (from 1 to 11 in Figure S3).

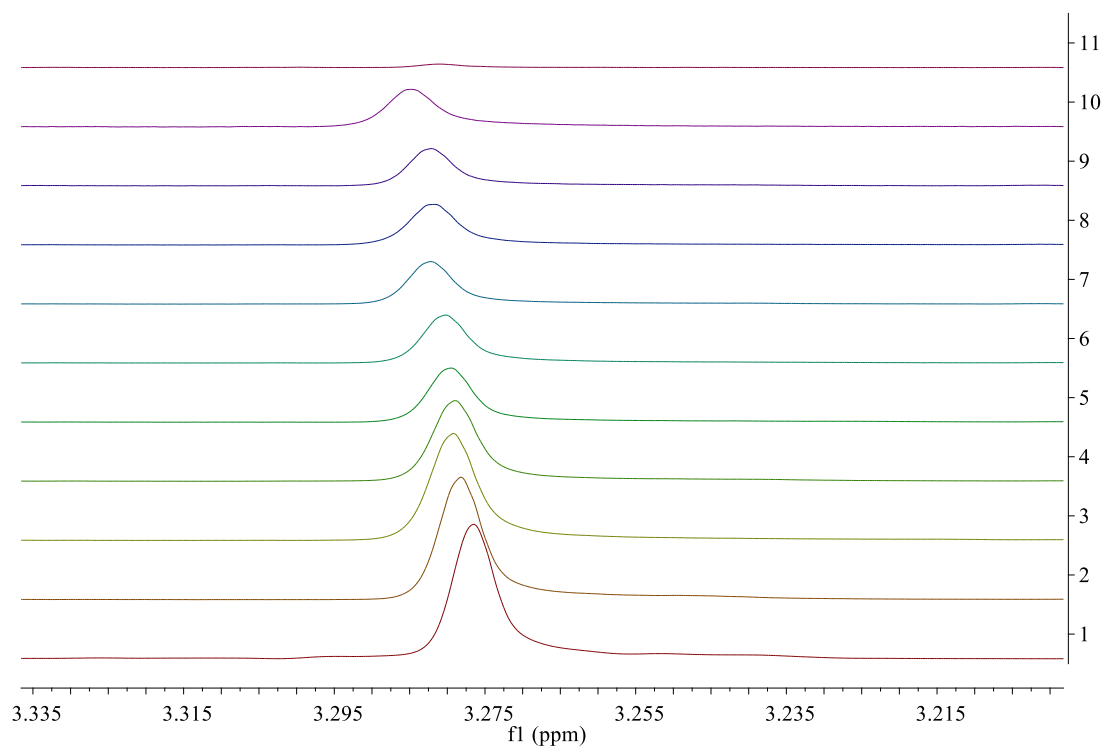
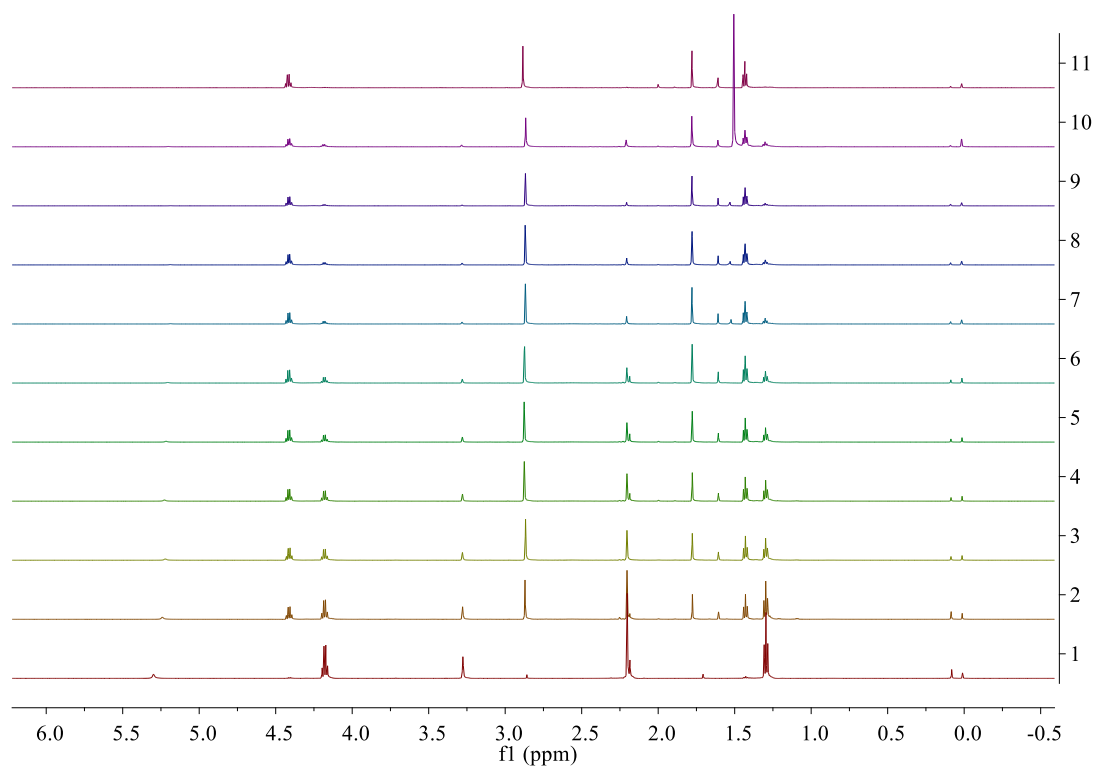
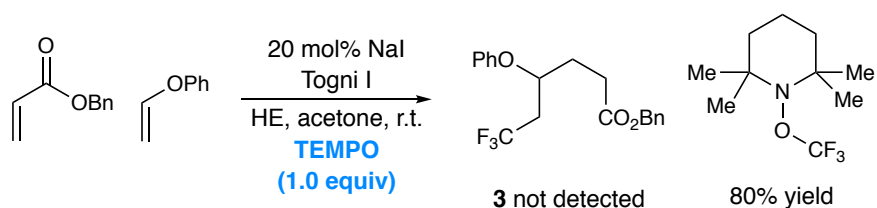


Figure S3. ^1H NMR titration between HE and Togni's reagent.

6.4. Radical inhibition experiments:



^{19}F NMR analysis of this reaction mixture showed that TEMPO- CF_3 was formed in 80% yield, the desired compound **3** could not be detected and 1.06 equiv. of Togni's reagent was remained.

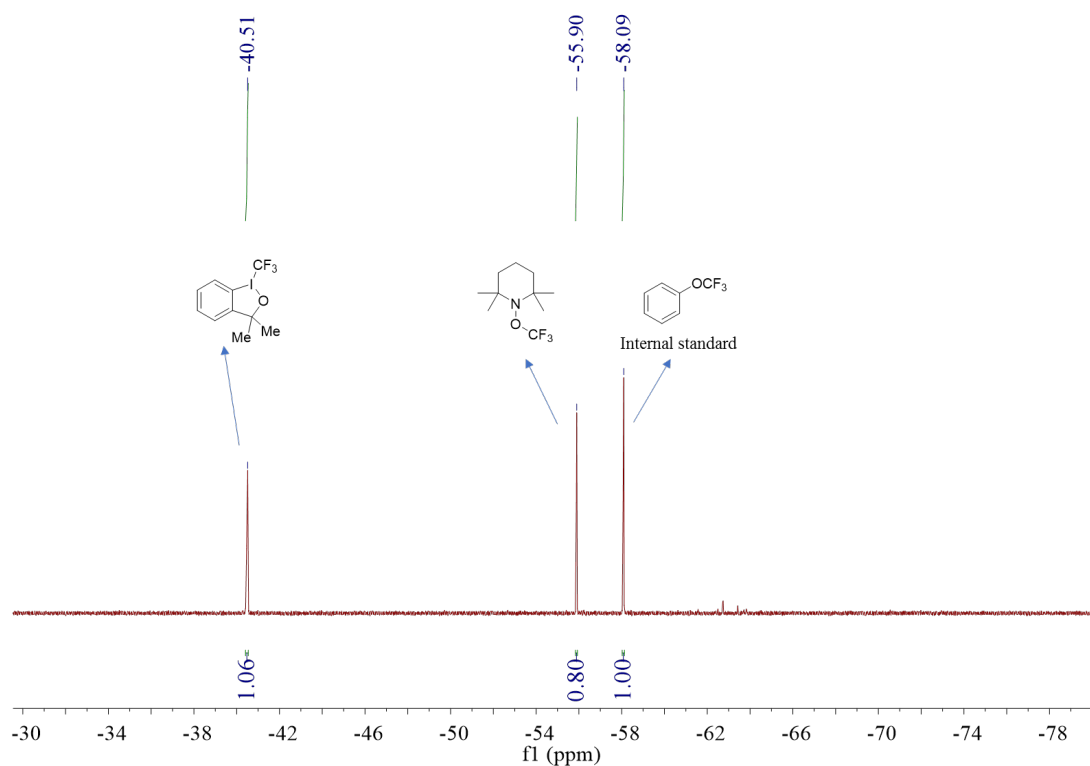
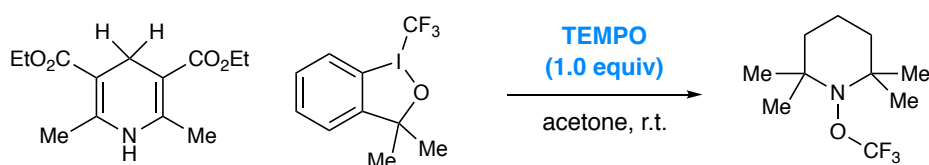


Figure S4: ^{19}F NMR spectrum of the crude mixture.



The mixture of HE (25.3 mg, 0.1 mmol, 1.0 equiv.), Togni's reagent (33.0 mg, 0.1 mmol, 1.0 equiv.) and TEMPO (15.6 mg, 0.1 mmol, 1.0 equiv.) in acetone [0.1M] at

600 rpm for 24 h at r.t. ^{19}F NMR analysis of this reaction mixture showed that TEMPO- CF_3 was formed in 31% yield, and 0.48 equiv. of Togni's reagent was remained.

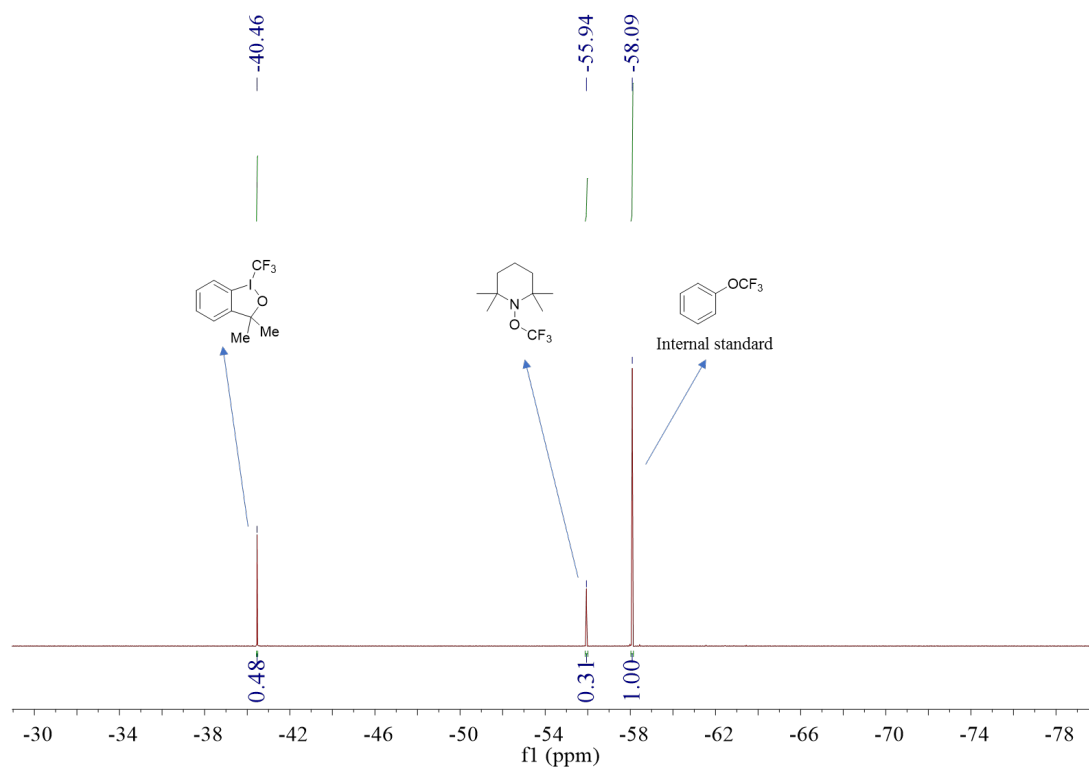
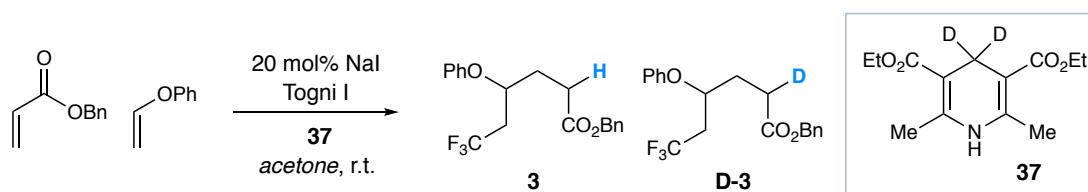
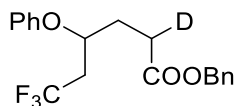


Figure S5: ^{19}F NMR spectrum of the crude mixture.

6.5. Deuteration experiments:

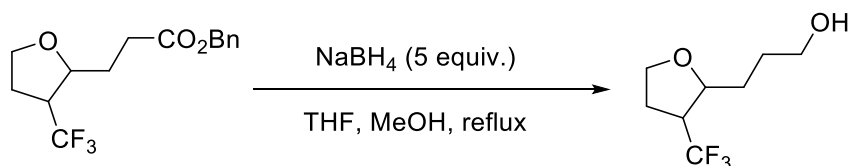


Deuterated HE was used for this reaction system under the standard reaction conditions instead of HE, the desired compound **3** could not be obtained, instead, deuterated product **D-3** was isolated exclusively in 49% yield.



Benzyl 6,6,6-trifluoro-4-phenoxyhexanoate-2-d (D-3): According to the general procedure, benzyl acrylate (30.6 μ L, 0.20 mmol, 1.0 equiv.), Togni's reagent (132 mg, 0.40 mmol, 2.0 equiv.), (vinylloxy)benzene (73.7 μ L, 0.60 mmol, 3.0 equiv.), *d*-Hantzsch ester (102 mg, 0.4 mmol, 2.0 equiv), and NaI (6.0 mg, 0.04 mmol, 0.2 equiv) in acetone (2 mL) were used. After 24 h, the product was isolated by flash chromatography (PE: EA= 30:1) as a pale-yellow oil liquid (34.6 mg, 49%). ^1H NMR (600 MHz, CDCl_3) δ 7.38 – 7.19 (m, 7H), 6.97 (t, J = 7.3 Hz, 1H), 6.87 (d, J = 8.0 Hz, 2H), 5.10 (s, 2H), 4.69 – 4.58 (m, 1H), 2.62 – 2.49 (m, 2H), 2.40 – 2.29 (m, 1H), 2.22 – 2.15 (m, 1H), 2.09 – 2.02 (m, 1H); ^{19}F NMR (565 MHz, CDCl_3) δ -63.18 (t, J = 10.8 Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 172.6, 157.1, 135.7, 129.7, 128.6, 128.3, 125.7 (q, J = 277.1 Hz), 121.7, 115.9, 70.7, 66.5, 38.2 (q, J = 27.8 Hz), 29.6; HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{19}\text{H}_{19}\text{DF}_3\text{O}_3$: 354.1422; found: 354.1420.

6.6. Reduction of ester to alcohol:



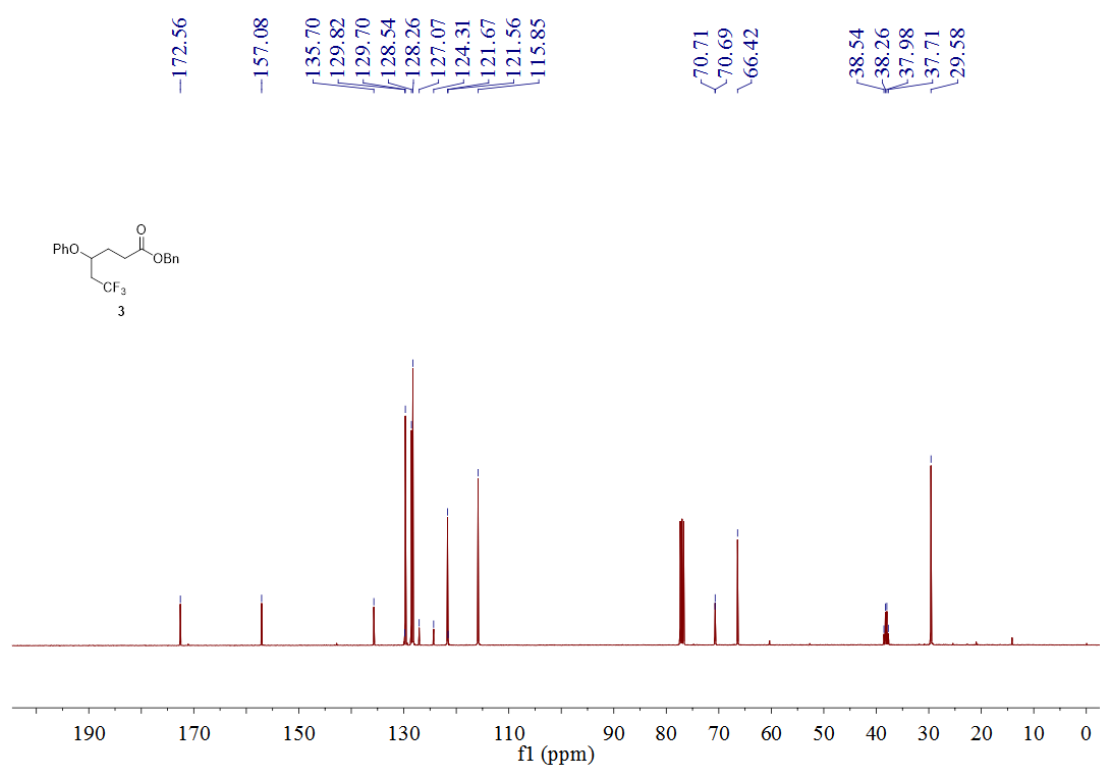
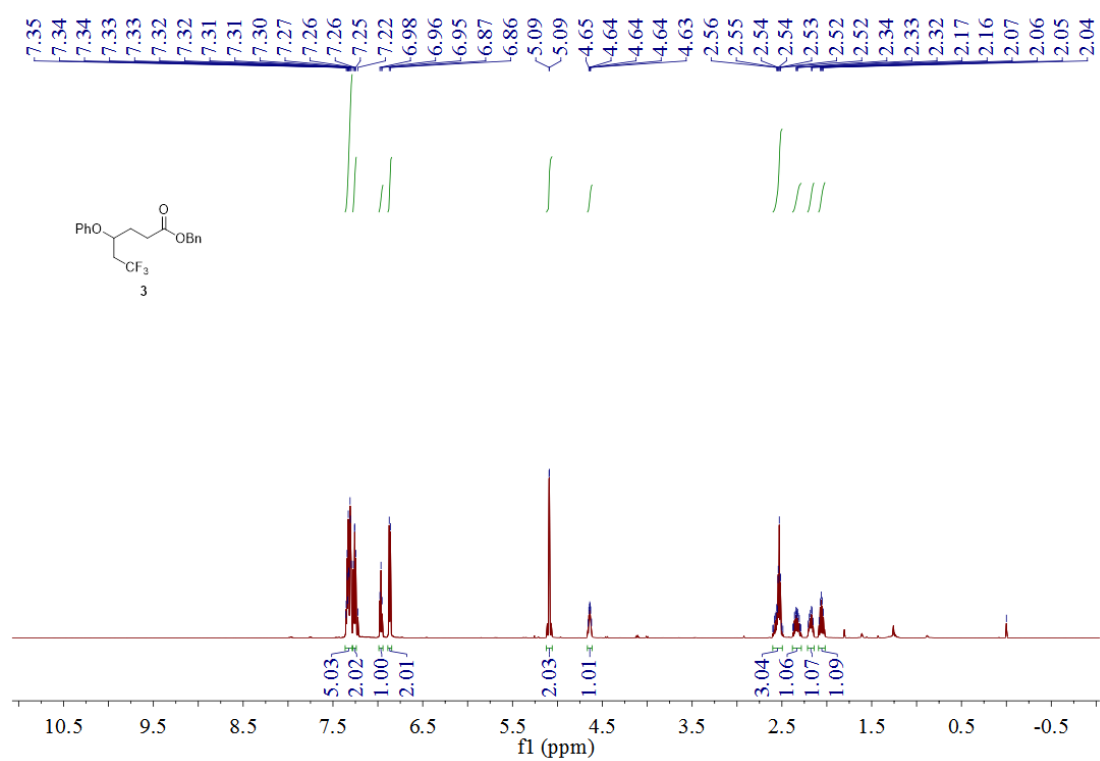
To a solution of the benzyl 3-(3-(trifluoromethyl)tetrahydrofuran-2-yl)propanoate (60.4 mg, 0.2 mmol, 1.0 equiv.) in THF (2 mL) was added NaBH_4 (37.8 mg, 1.0 mmol, 5.0 equiv.). When the mixture was heated to gently reflux, MeOH (0.2 mL) was added dropwise from a syringe. After refluxing for another 12 h, the mixture was cooled to room temperature and poured into 10 mL ice water, and extracted with EtOAc (10 mL \times 3). The combined organic phase was washed with brine, dried over anhydrous MgSO_4 , and concentrated. The product was isolated by flash chromatography (PE: Acetone= 4:1) as a pale-yellow oil liquid (29.4 mg, 74%). ^1H NMR (600 MHz, CDCl_3) δ 3.99 – 3.94 (m,

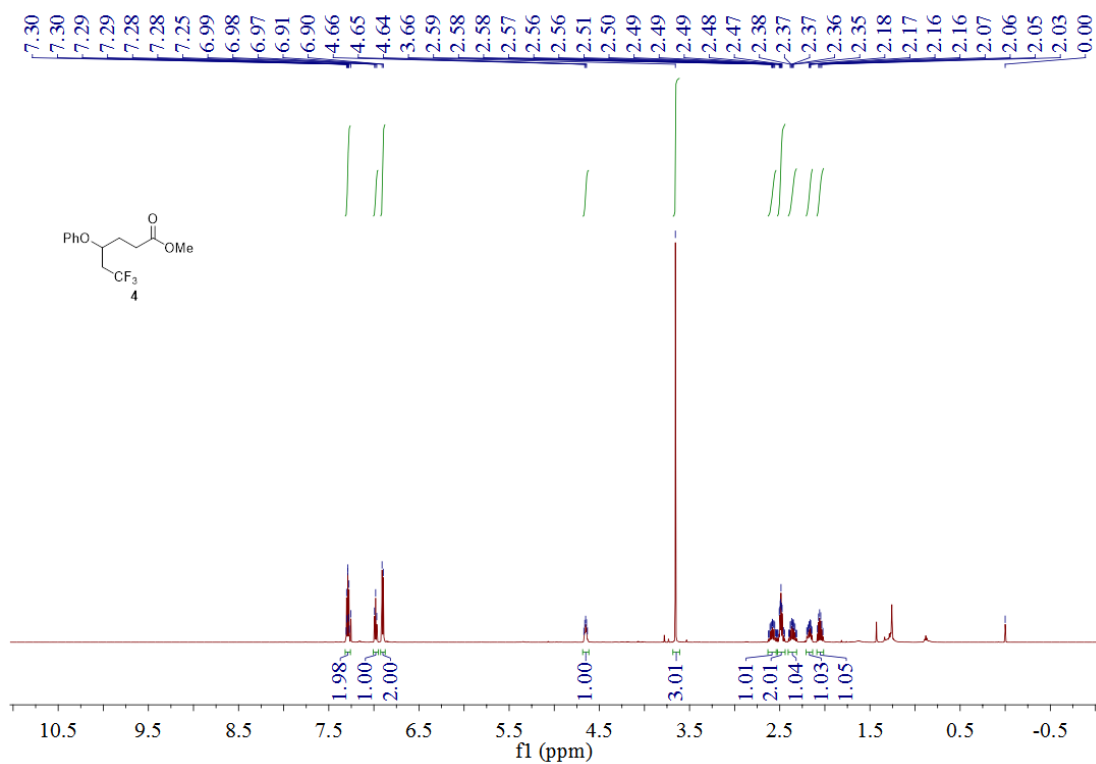
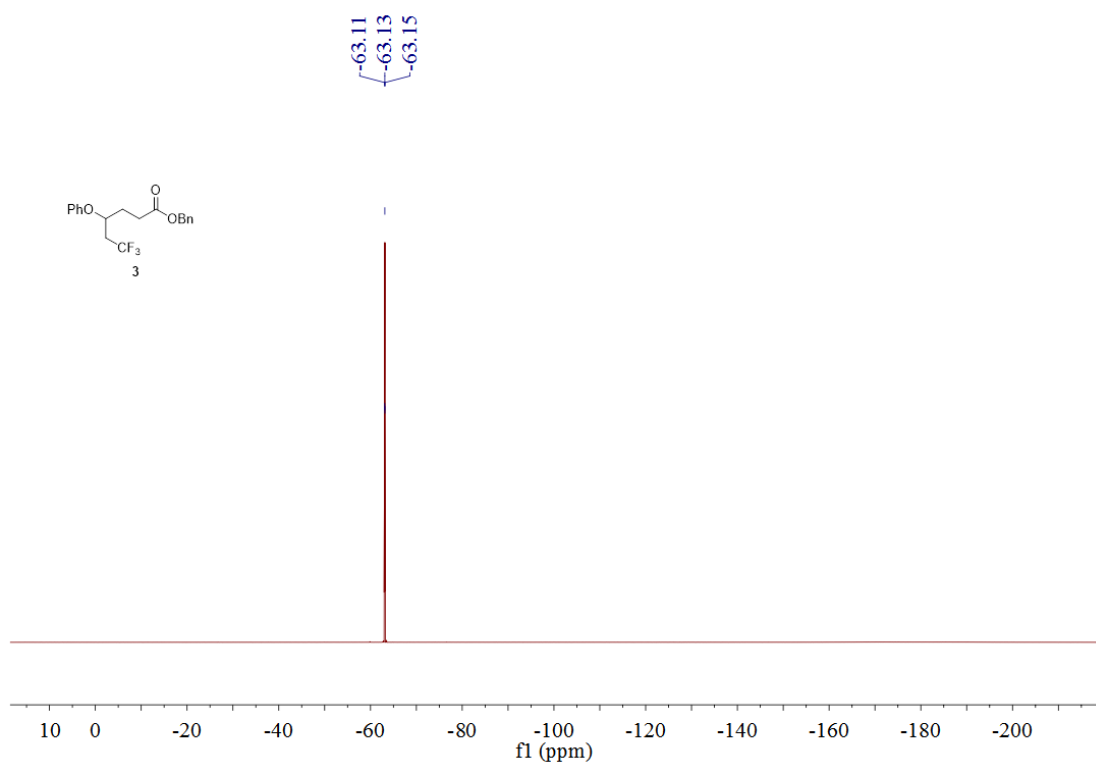
2H), 3.80 – 3.76 (m, 1H), 3.71 – 3.63 (m, 2H), 2.57 – 2.50 (m, 1H), 2.46 (s, 1H), 2.19 – 2.12 (m, 1H), 2.11 – 2.04 (m, 1H), 1.86 – 1.79 (m, 1H), 1.76 – 1.69 (m, 2H), 1.68 – 1.60 (m, 1H); ^{19}F NMR (377 MHz, CDCl_3) δ -69.74 (d, $J = 9.4$ Hz).

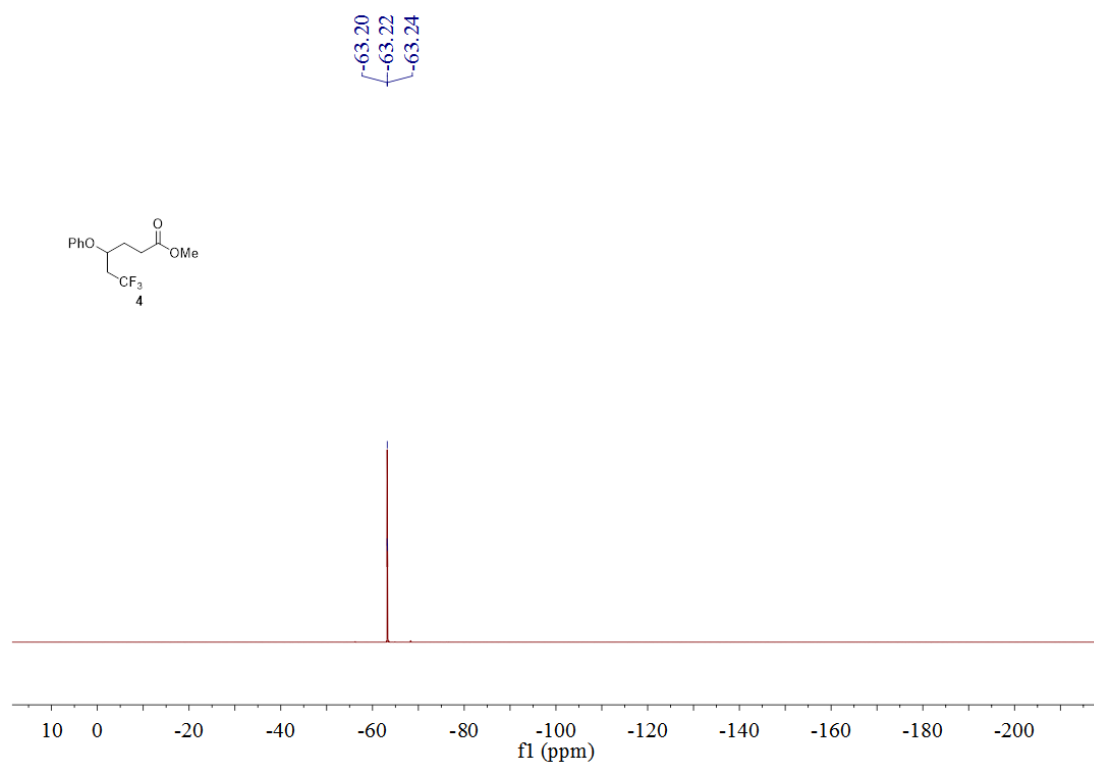
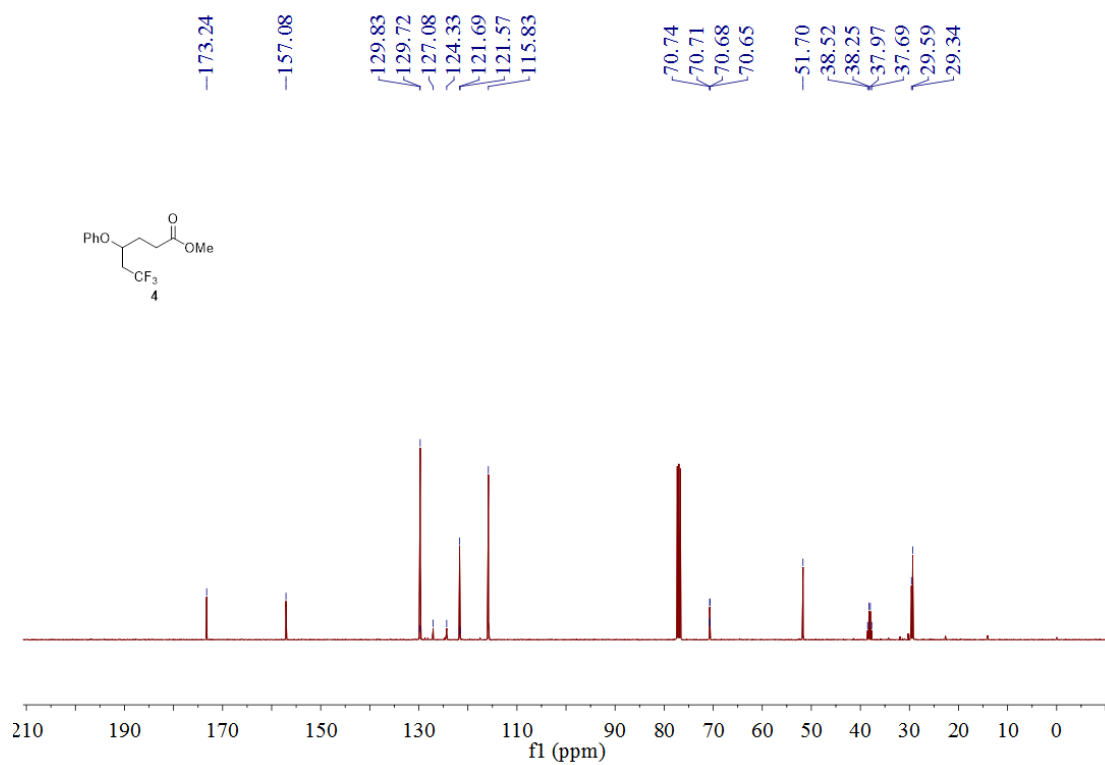
Note: The structure of this alcohol is very similar to a known compound, the structure of which has been ambiguously defined.¹

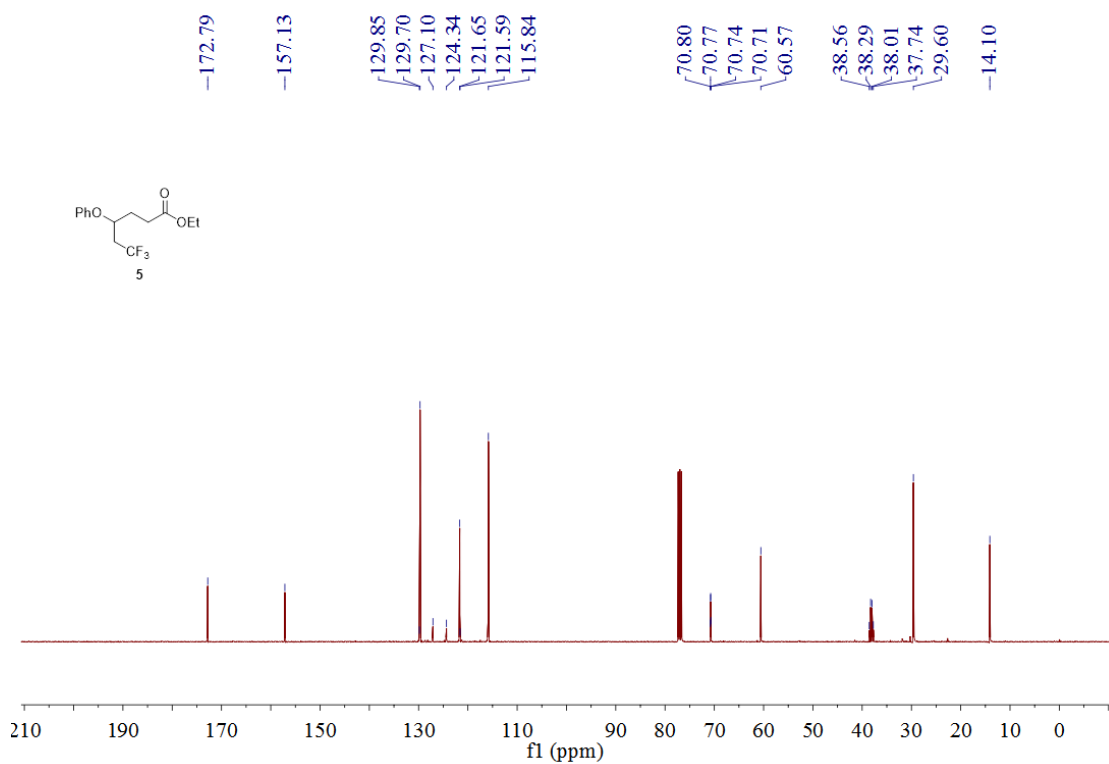
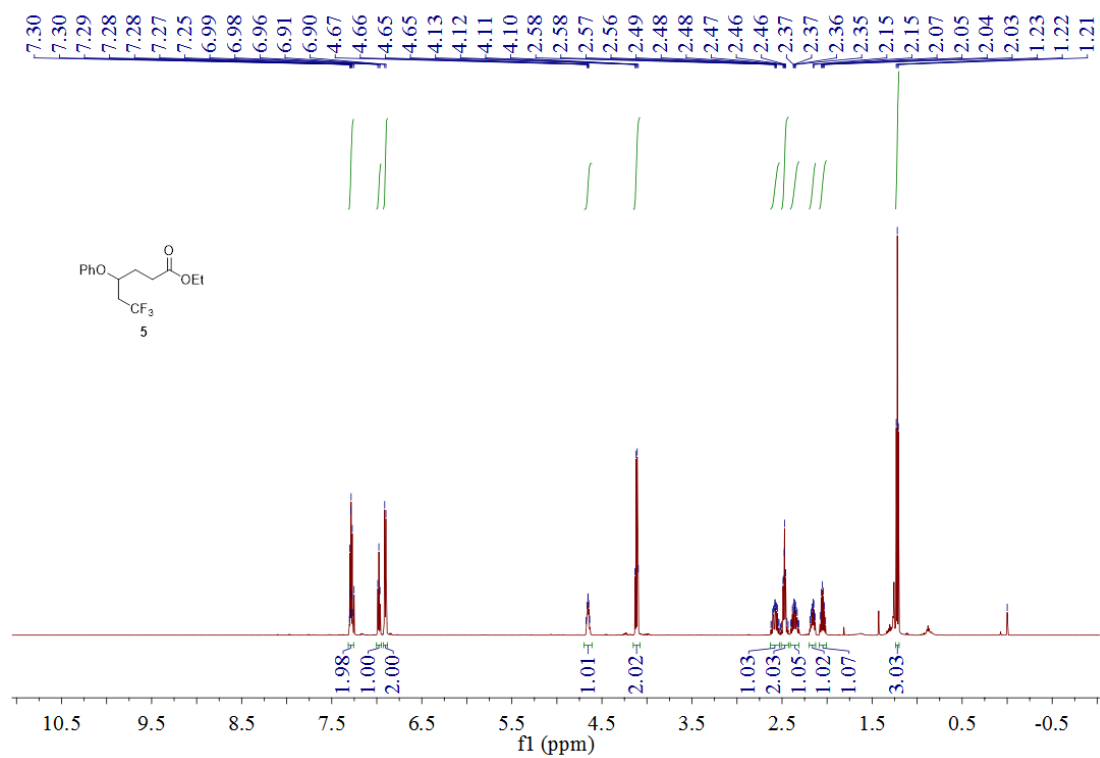
¹ Y. Wang, M. Jiang, J.-T. Liu, *Adv. Synth. Catal.* **2016**, 358, 1322 – 1327.

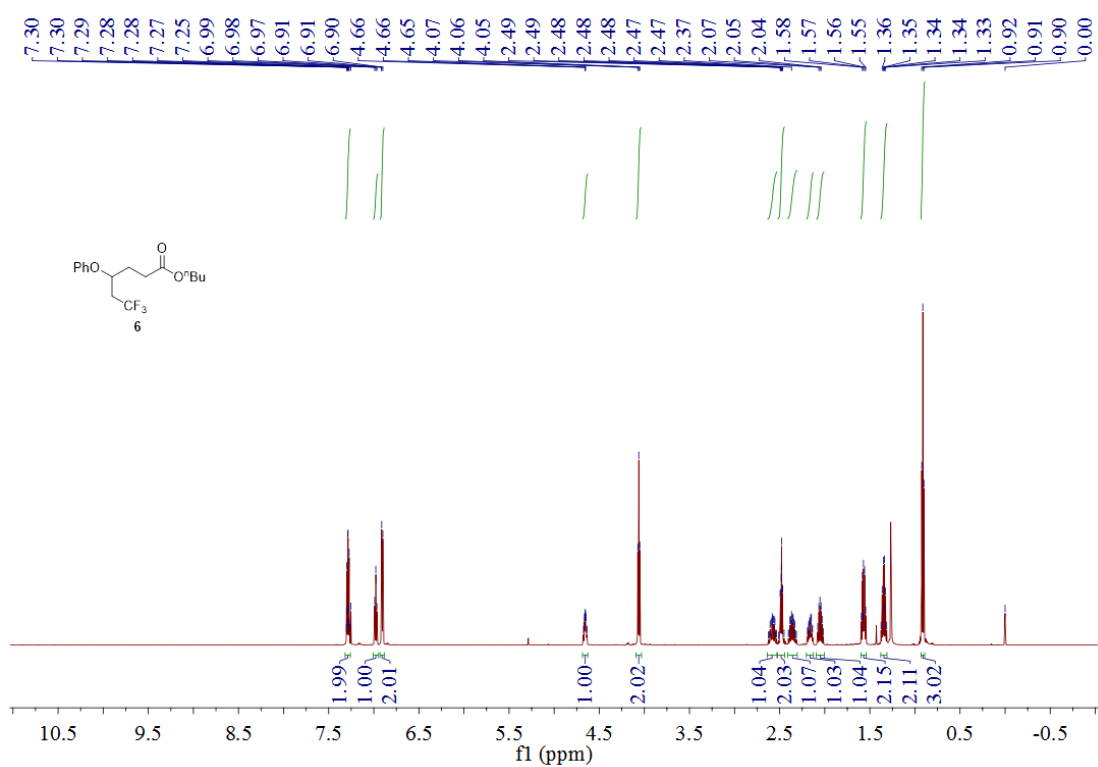
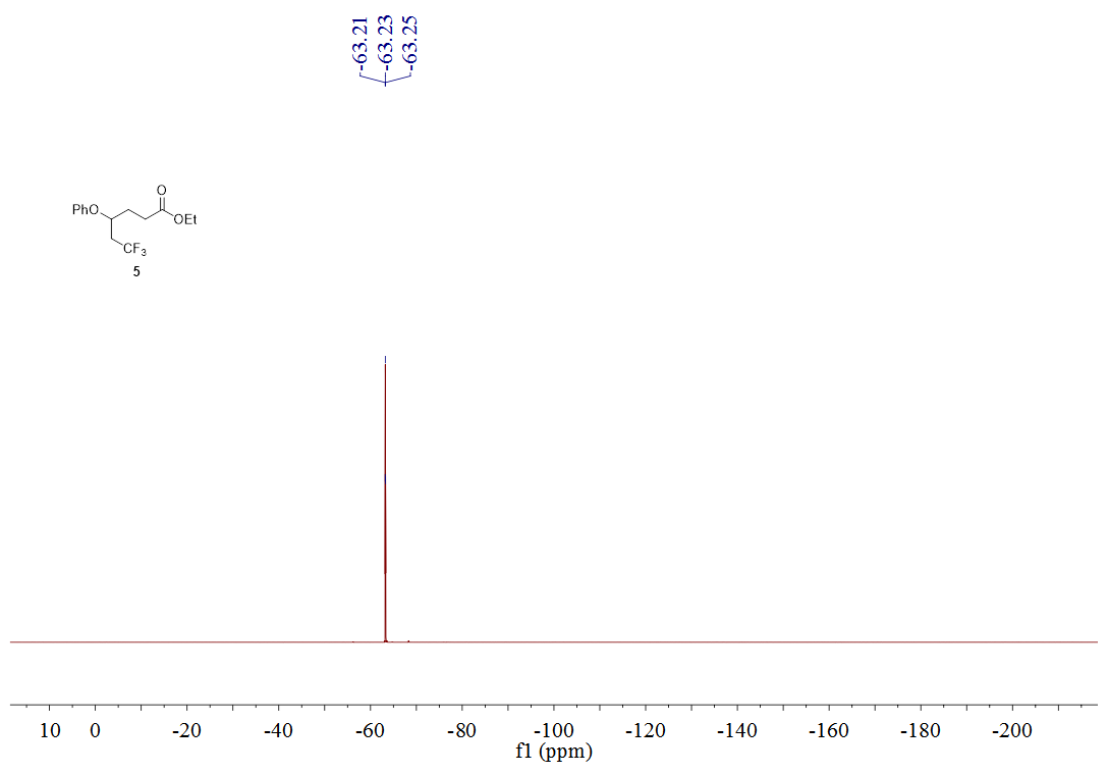
7. Spectral data

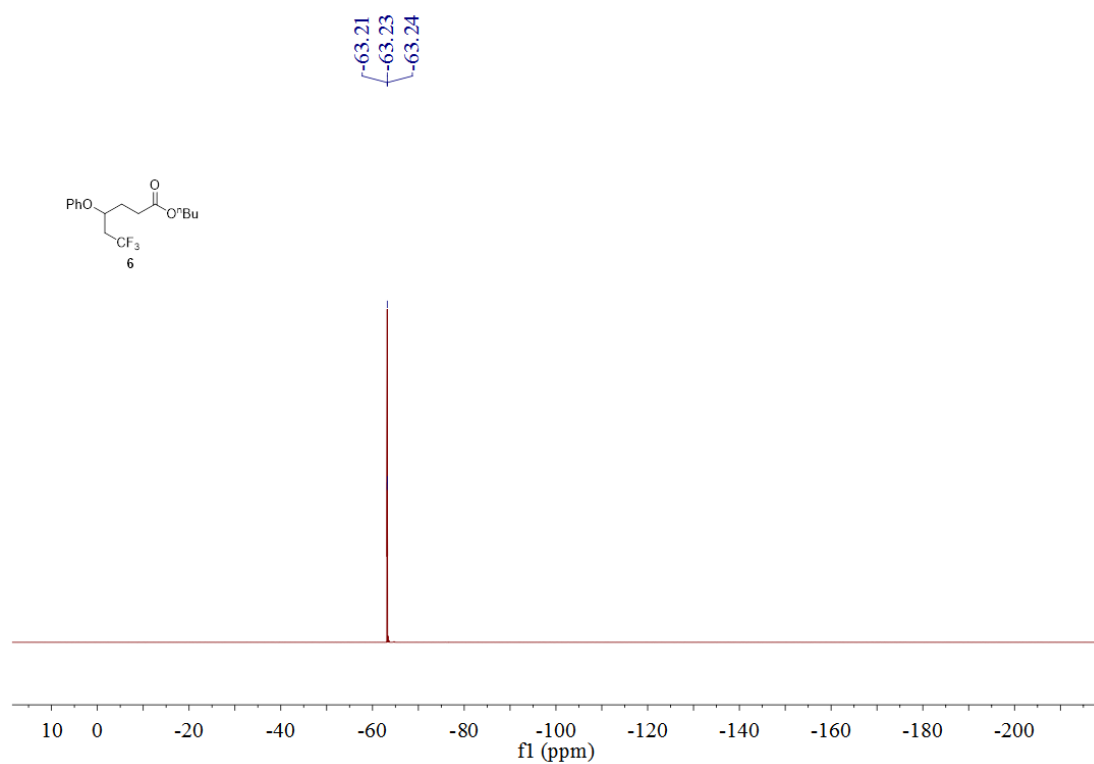
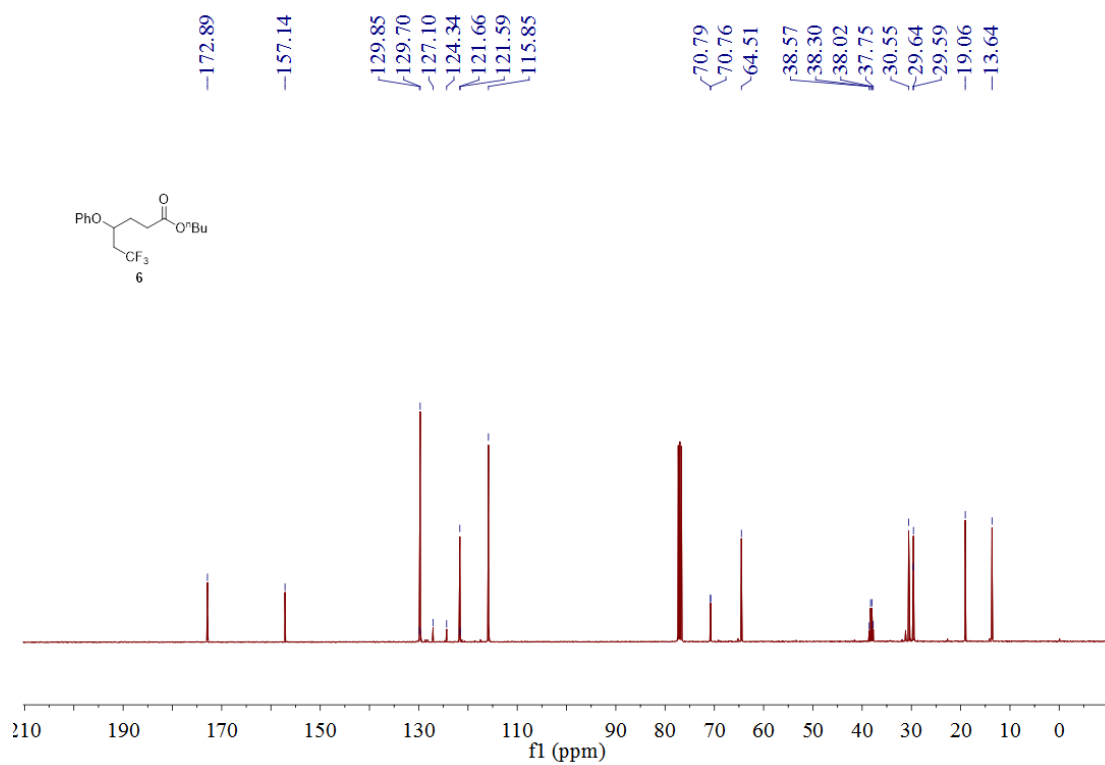


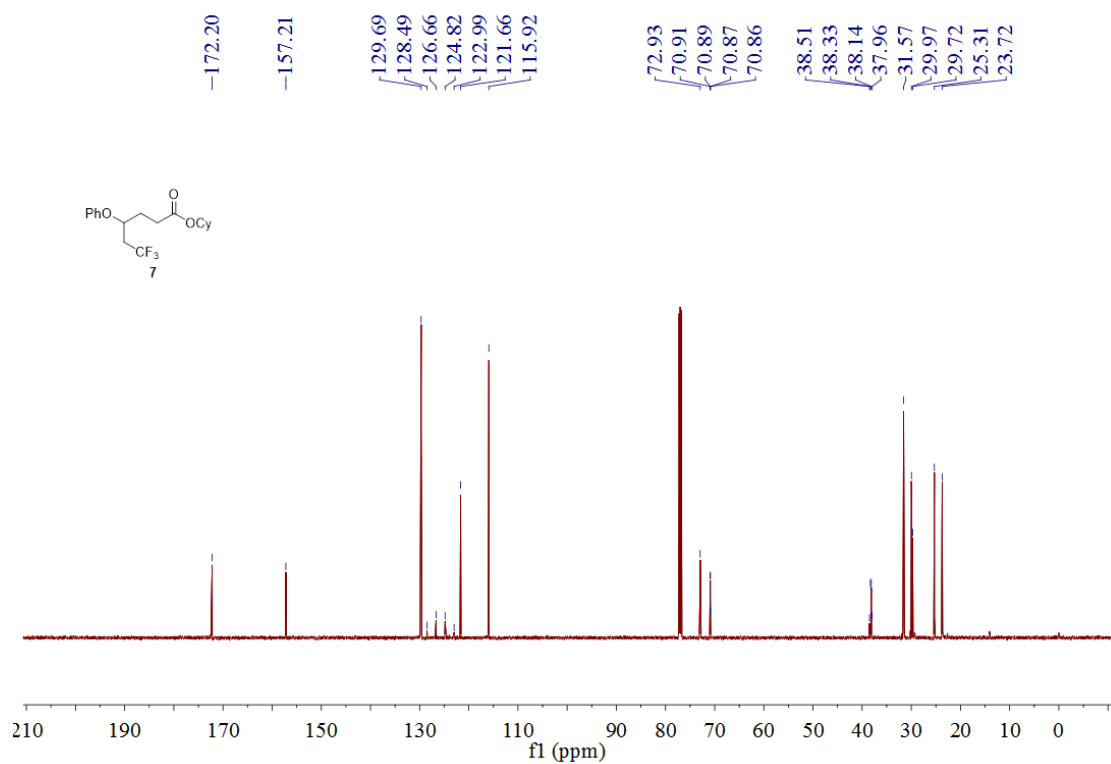
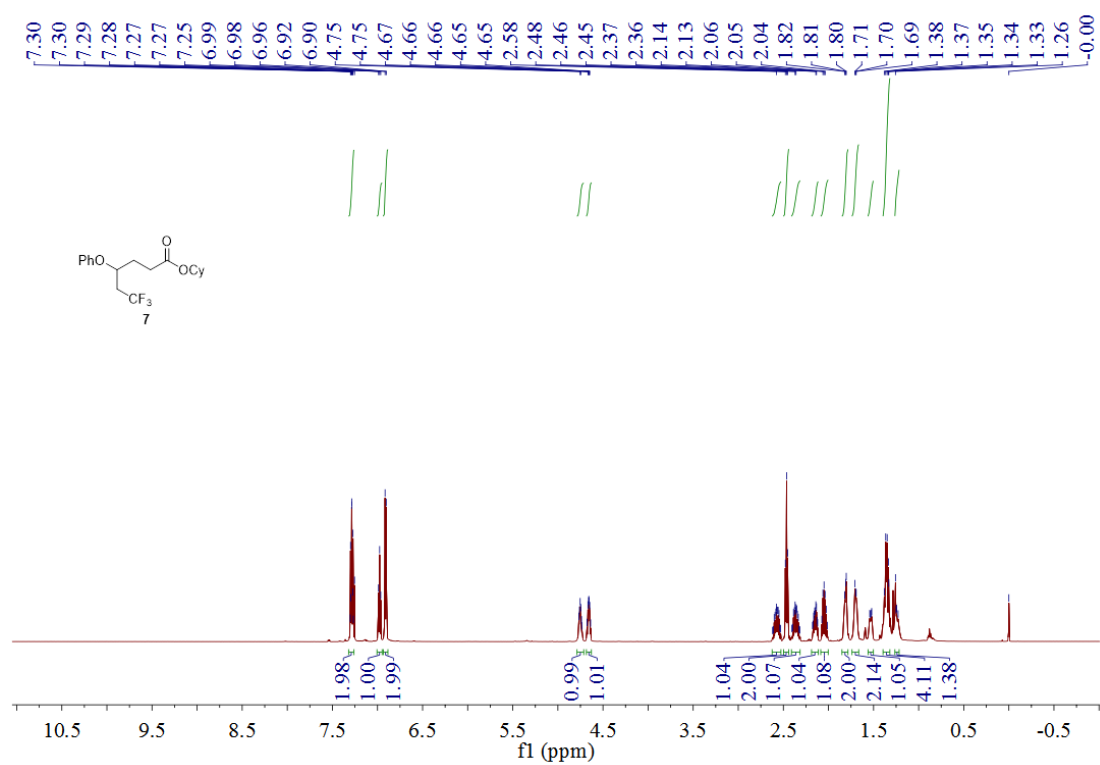


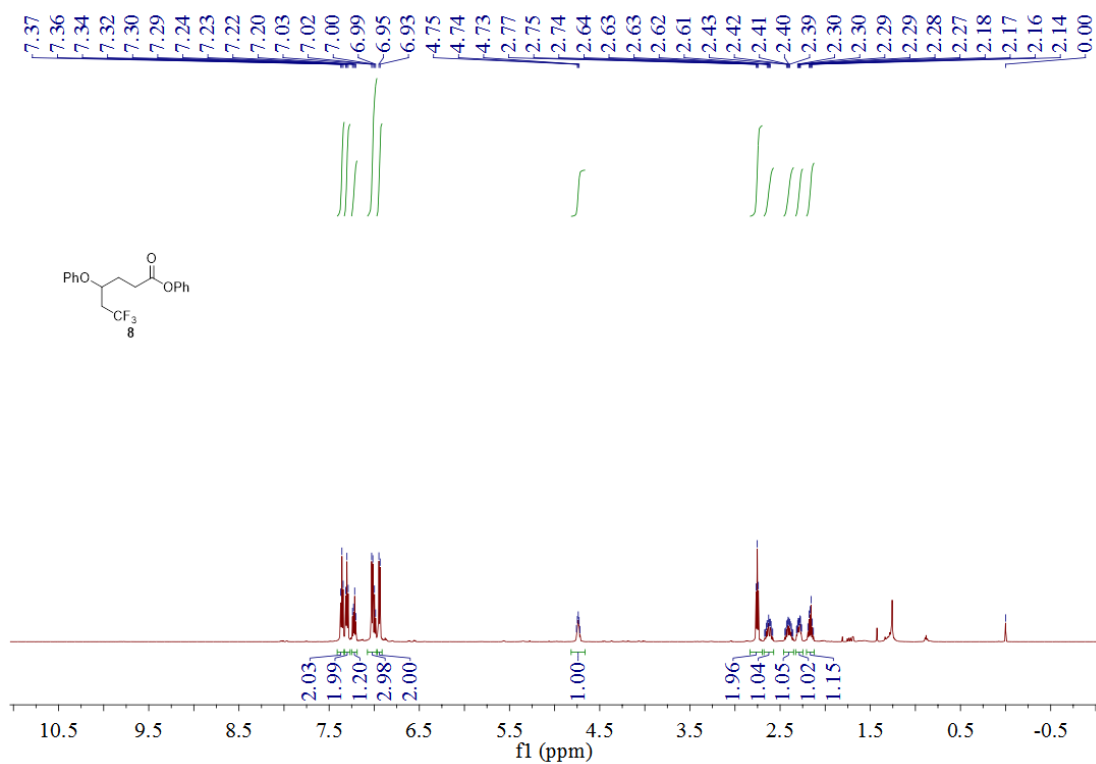
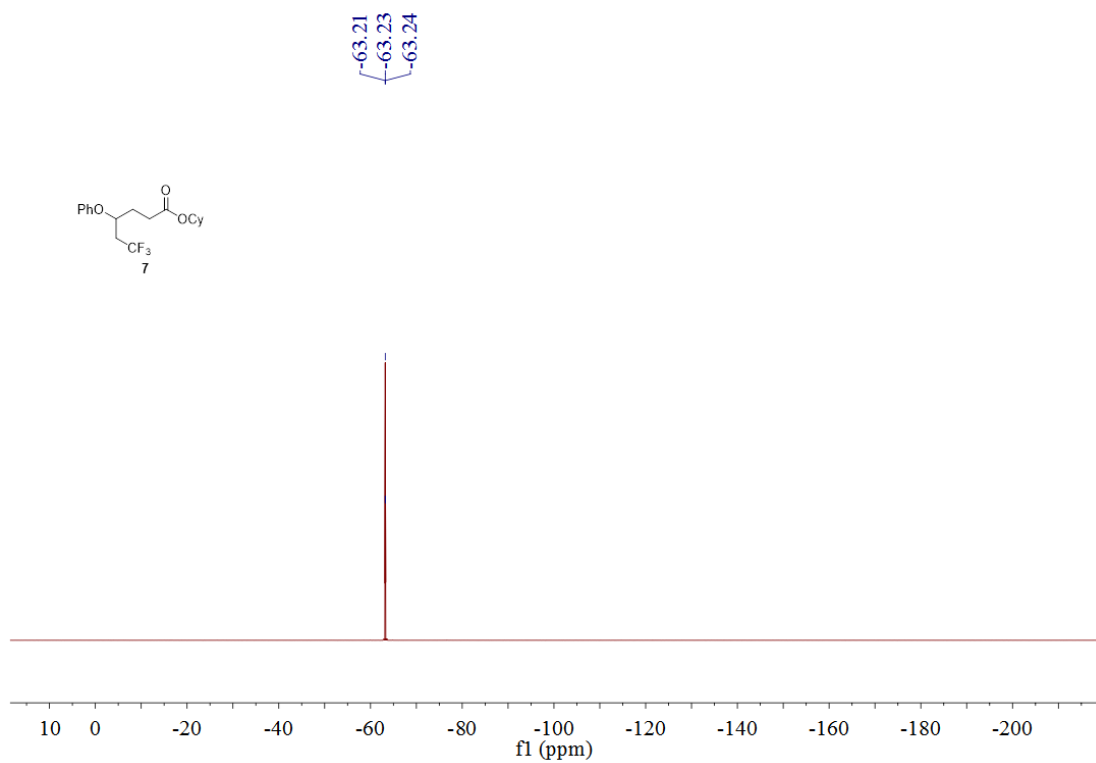


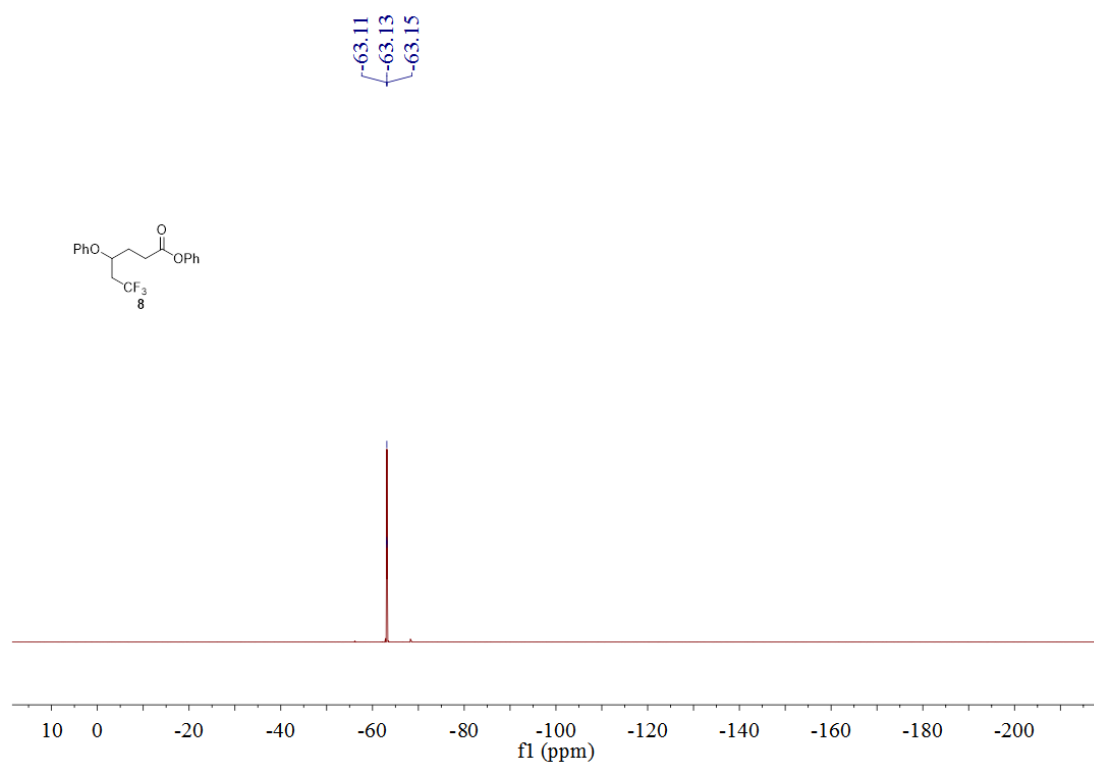
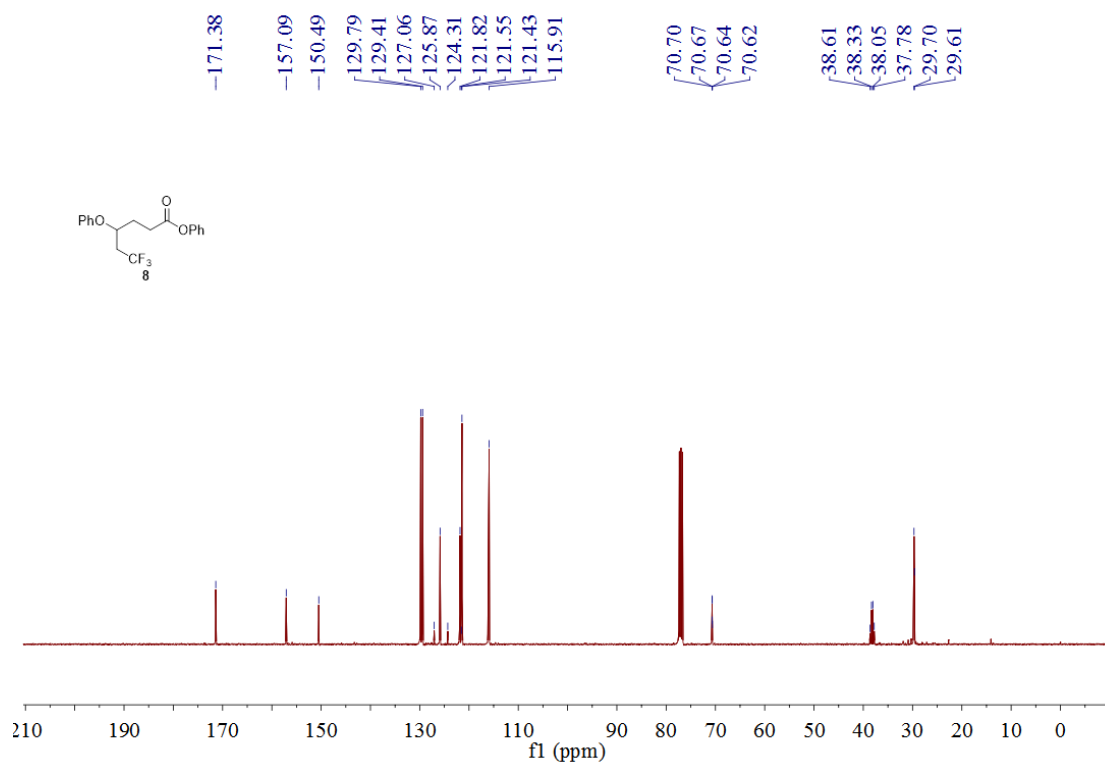


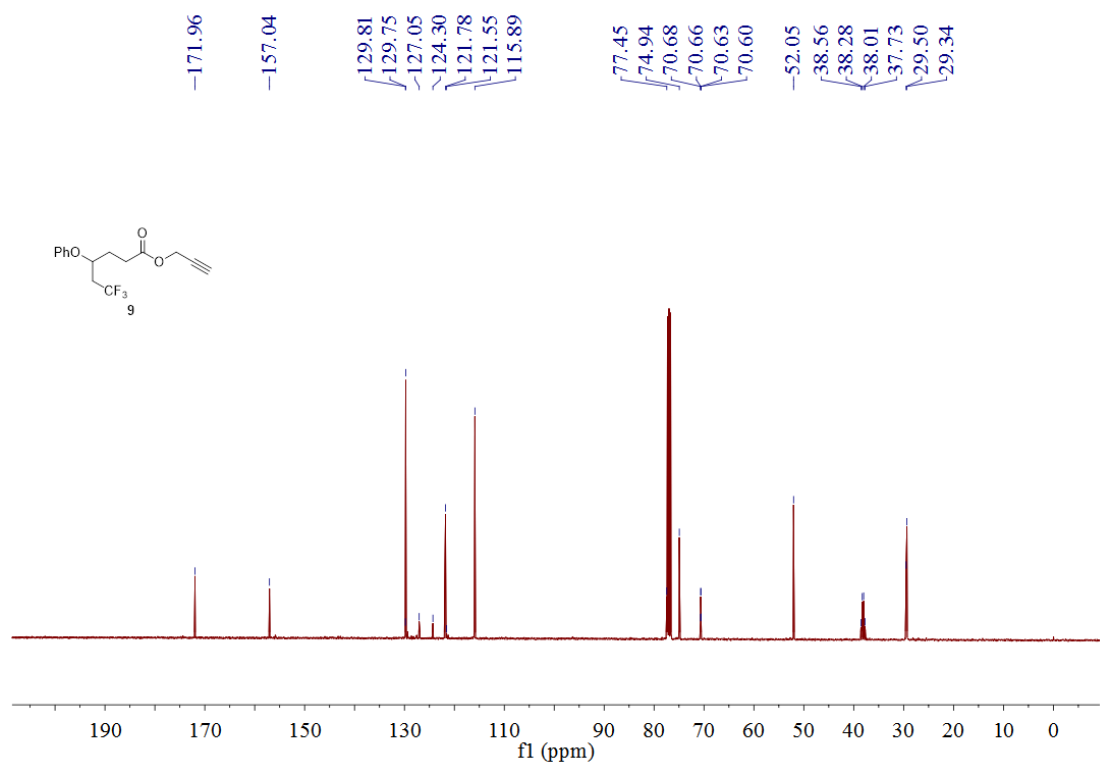
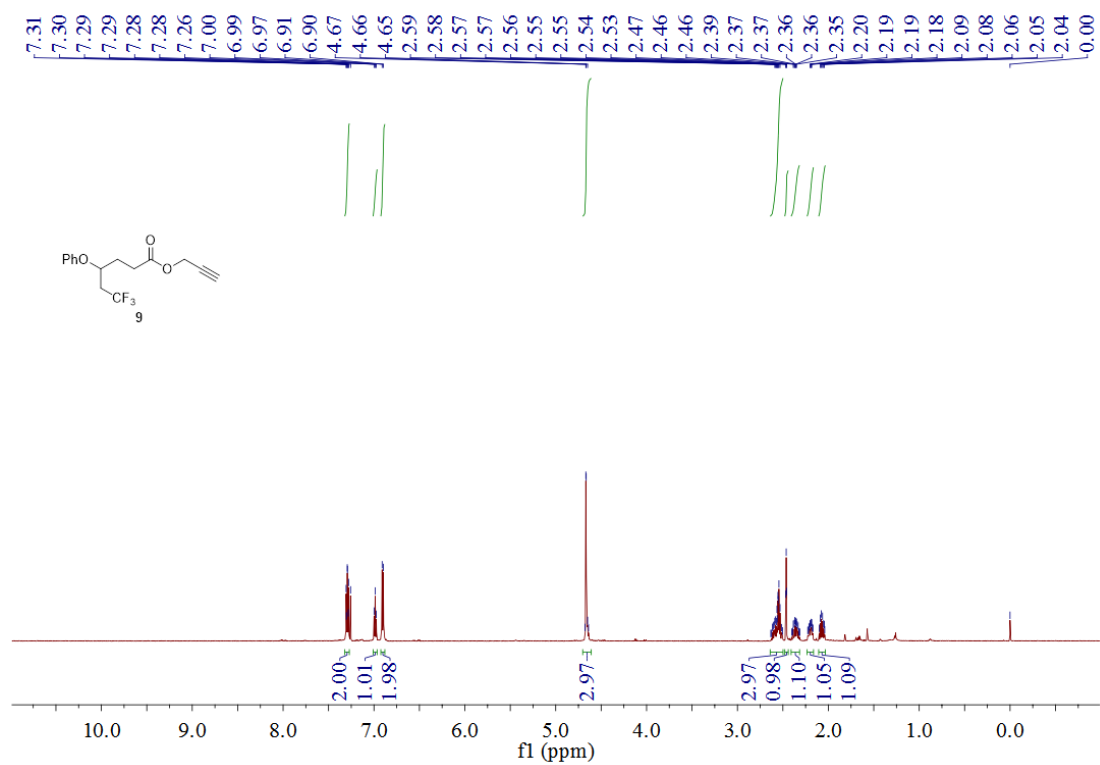


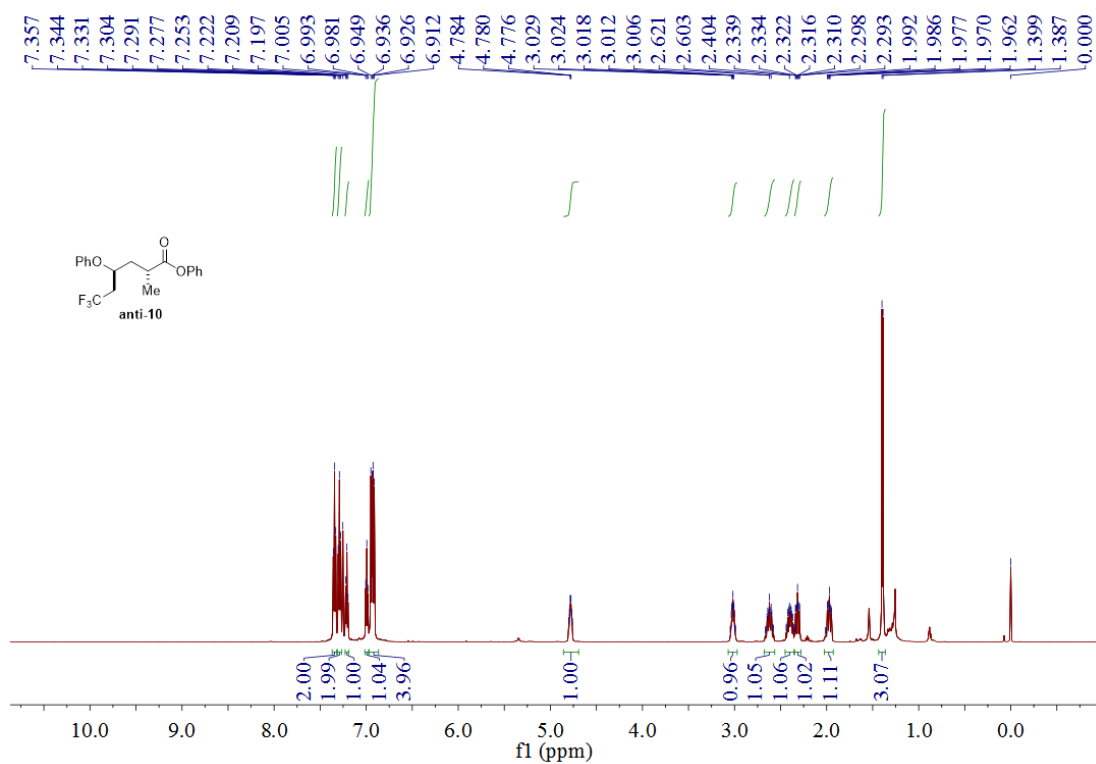
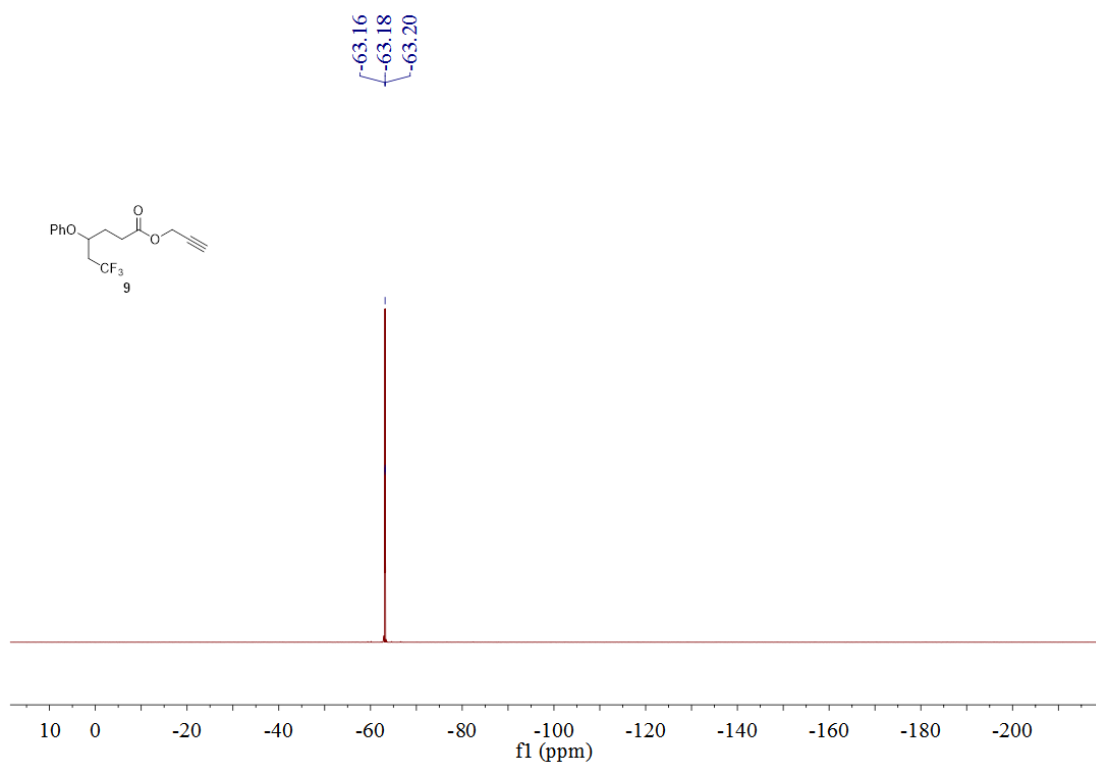


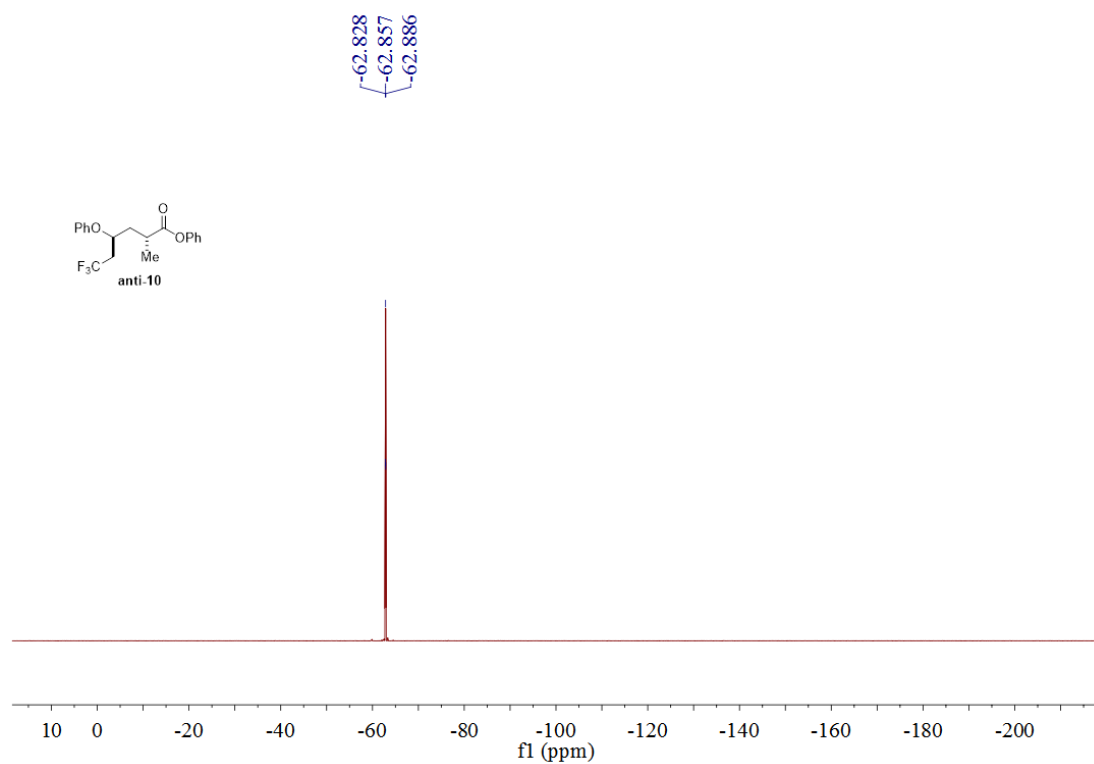
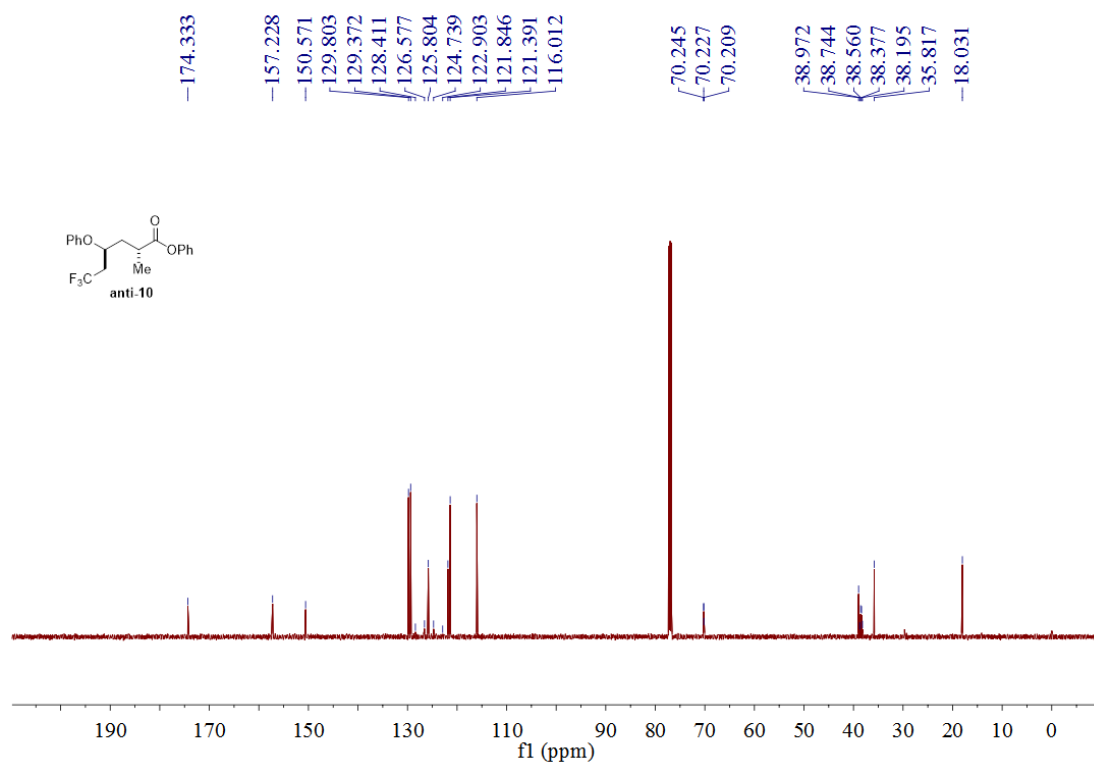


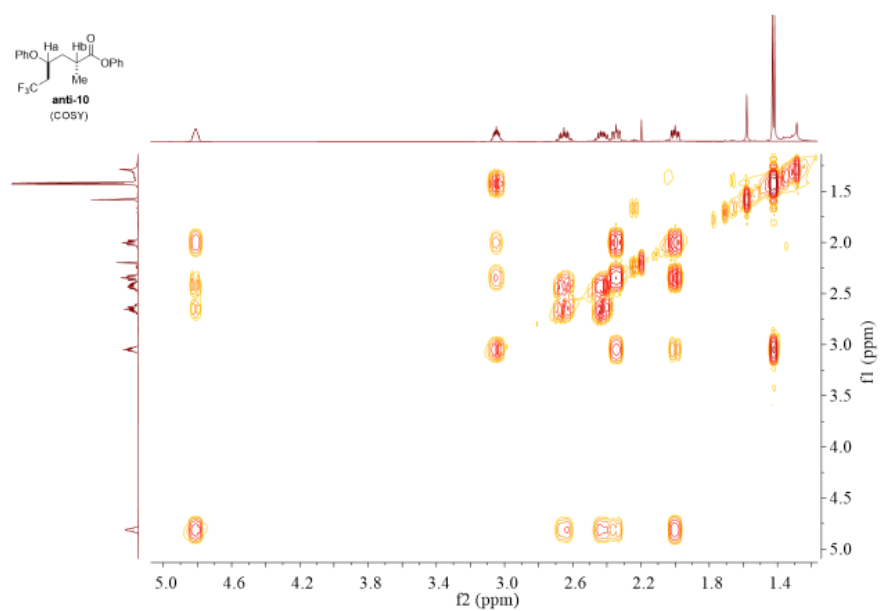
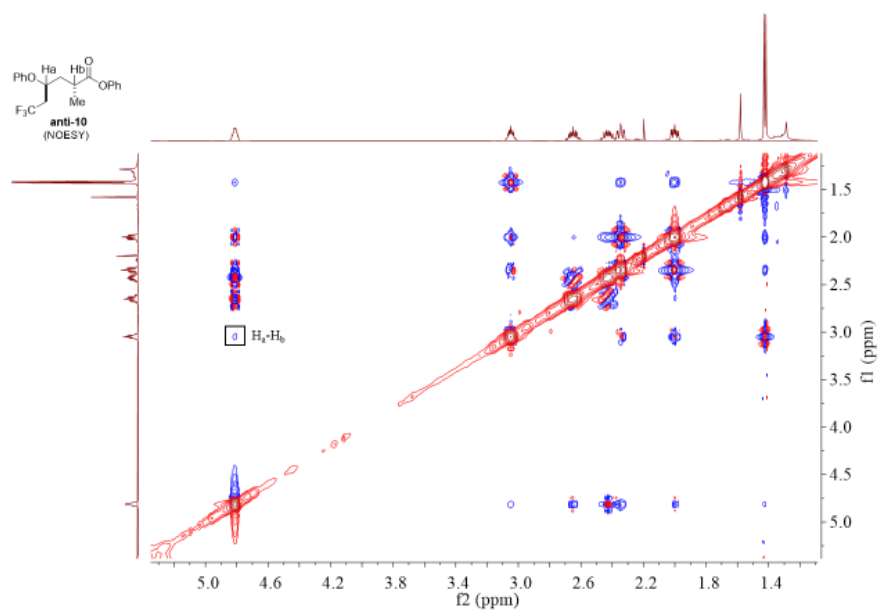


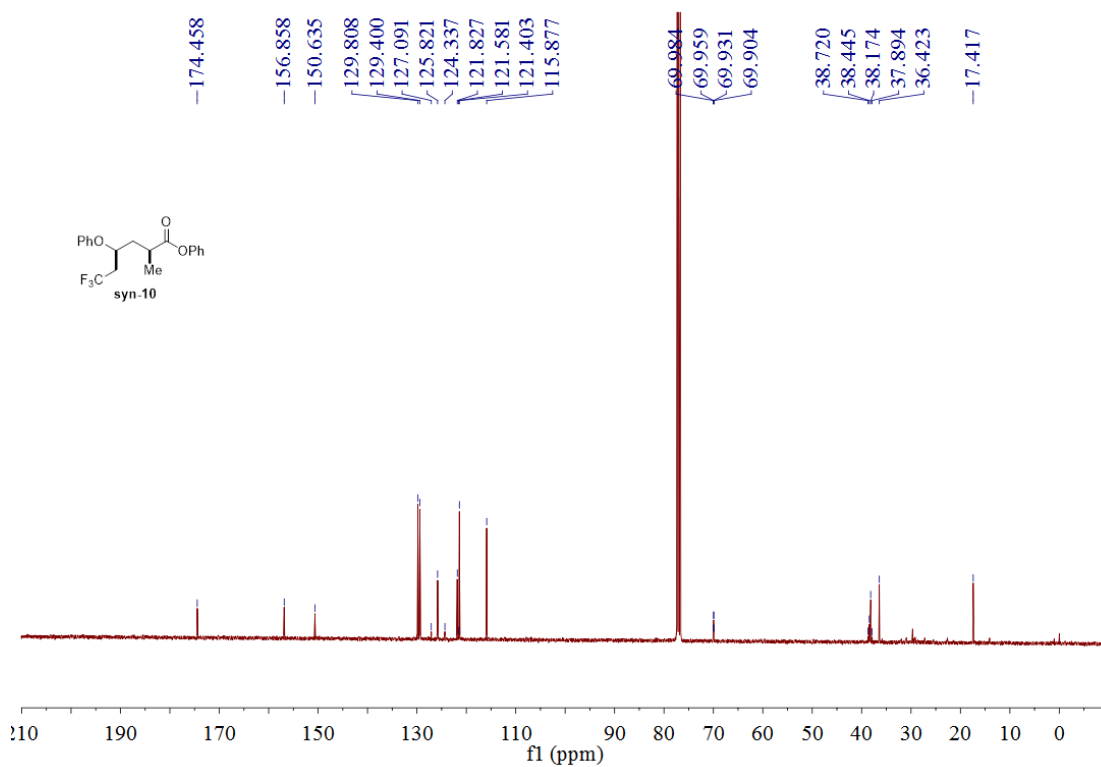
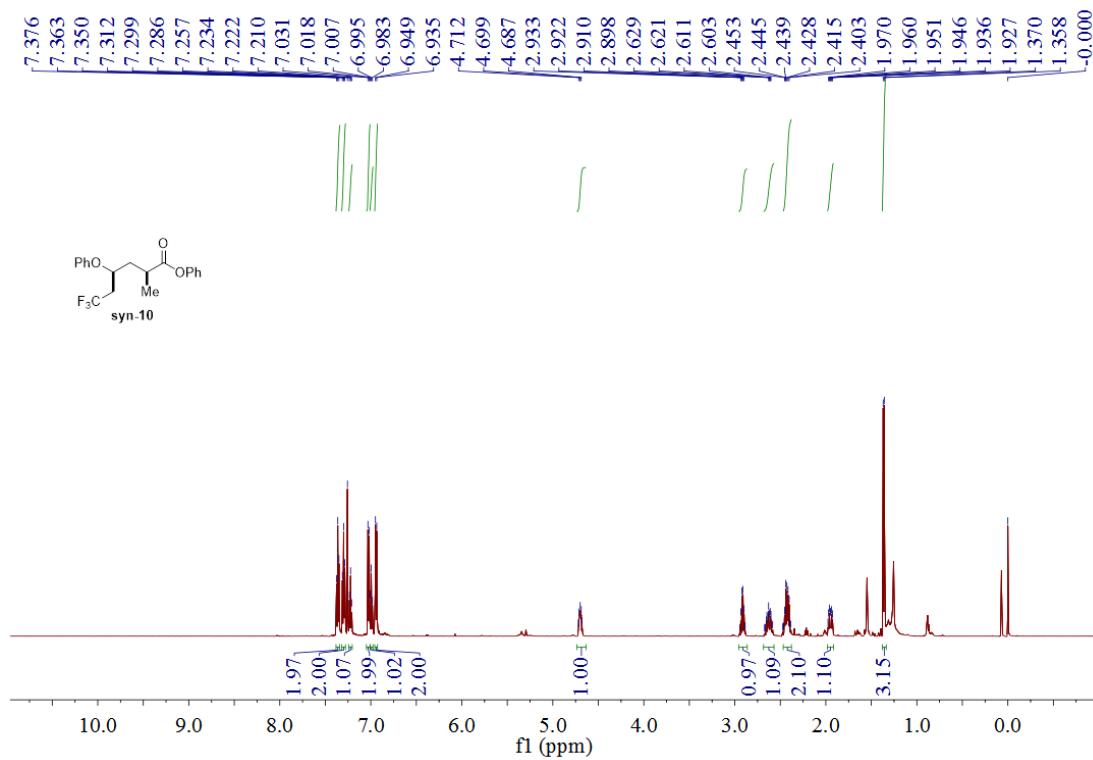


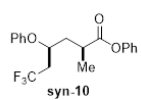












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-63.012
-63.041

