Supplementary Information (SI) for Organic Chemistry Frontiers.
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Supplementary Information

1,2,3-Trifunctionalization of α,α-Disubstituted Vinyl Aldehydes Enabled by Radical 1,2-Migration of Formyl

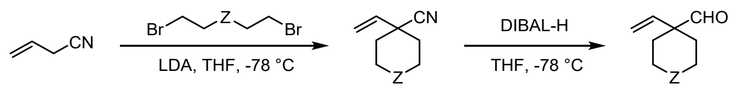
Contents

1. General Information

Unless otherwise noted, materials obtained from commercial suppliers were used directly without further purification. ^1H, ^{13}C, and ^{19}F NMR spectra were measured on a 600 MHz or 400 MHz NMR spectrometer. Chemical shifts are given in parts per million on the delta (δ) scale, and the coupling constants are given in hertz. ^1H NMR chemical shifts were determined relative to the internal standard tetramethylsilane (TMS) at 0.00 ppm, ^{13}C NMR shifts were determined relative to the residual solvent peaks of $CDCl_3$ at δ 77.00 ppm, and ^{19}F NMR chemical shifts were determined relative to outside standard $CFCl_3$ at δ 0.00 ppm. High-resolution mass spectrometry (HRMS) analysis was carried out using a TOF MS instrument with an ESI source. Flash column chromatography was carried out on the silica gel (200-300 mesh).

2. Synthesis of Starting Materials

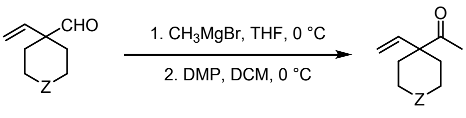
2.1 Synthesis of Allyl Aldehydes[1]



S1 1

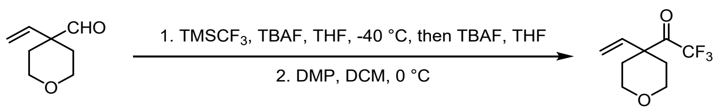
To a solution of diisopropylamine (24 mmol, 2.4 equiv) in 40 mL of dry THF was added dropwise *n*-BuLi (8.4 mL, 2.4 M in hexane, 2.0 equiv) at -78 °C under nitrogen atmosphere. After stirring at -78 °C for 1 h, 3-butenenitrile (10 mmol, 1.0 equiv) in dry THF (10 mL) and the dibromodate (20 mmol, 2.0 equiv) in dry THF (15 mL) were added dropwise slowly and kept at this temperature for another 10 h. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl solution, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 30:1) gave the desired product.

To a solution of the product (5 mmol, 1.0 equiv) in 10 mL of dry DCM was added dropwise DIBAL-H (7.5 mL, 1 M in hexane, 1.5 equiv) at -78 °C and kept at this temperature for another 4 h. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl solution, extracted with DCM, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 40:1) gave the desired product allyl aldehydes **1**.



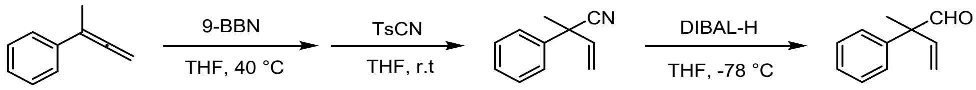
1 **1h, 1i**

To a solution of the **1** (5 mmol, 1.0 equiv) in 10 mL of dry THF was added dropwise CH_3MgBr (7.5 mL, 1 M in THF, 1.5 equiv) at 0 °C and kept at this temperature for another 2 h. The reaction mixture was quenched by addition of dilute hydrochloric acid, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was dissolved in 15 mL DCM and added DMP (6.5 mmol, 1.3 equiv) at 0 °C. After stirring at for 2 h at room temperature, the reaction mixture was quenched by addition of saturated aqueous $Na_2S_2O_3$ solution, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 10:1) gave the desired product (**1h, 1i**).



1b **1j**

To a solution of the **1b** (5 mmol, 1.0 equiv) in dry THF (10 mL) was added dropwise $TMSCF_3$ (10 mmol, 2.0 equiv) in dry THF (5 mL) and TBAF (0.5 mL, 1 M in THF, 0.1 equiv) in dry THF (1 mL) sequentially at -40 °C under nitrogen atmosphere. After stirring at for 4 h at -40 °C, the reaction mixture was quenched by addition of dilute hydrochloric acid, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was dissolved in 15 mL THF and added dropwise TBAF (7.5 mL, 1 M in THF, 1.5 equiv) at room temperature. After stirring at for 2 h at room temperature, the reaction mixture was quenched by addition of dilute hydrochloric acid, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was dissolved in 15 mL DCM and added DMP (6.5 mmol, 1.3 equiv) at 0 °C. After stirring at for 2 h at room temperature, the reaction mixture was quenched by addition of saturated aqueous $Na_2S_2O_3$ solution, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 10:1) gave the desired product **1j.**

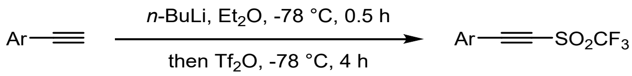


S2 **1f**

To a Schlenk flask containing **S2** (5 mmol, 1.0 equiv) in 5 mL of dry THF was added 9-BBN (1.3 mL, 0.5 M in THF, 1.05 equiv) under nitrogen atmosphere. The flask was immersed in an oil bath and heated at 40 °C for 4 h. After cooling to room temperature, the reaction mixture was added TsCN (5 mmol, 1.0 equiv) under nitrogen atmosphere. After stirring at for 10 h at room temperature, the reaction mixture was quenched by addition of saturated aqueous NH_4Cl solution, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 50:1) gave the desired product**.**

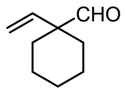
To a solution of the product (1.0 equiv) in 10 mL of dry DCM was added dropwise DIBAL-H (1 M in hexane, 1.5 equiv) at -78 °C and kept at this temperature for another 4 h. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl solution, extracted with DCM, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 60:1) gave the desired product **1f.**

2.2 Synthesis of Acetylenic Triflones[2]



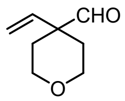
S3 **2**

To a solution of d alkyne **S3** (10 mmol, 1.0 equiv) in dry Et_2O (25 mL) was added dropwise *n*-BuLi (4.4 mL, 2.4 M in hexane, 1.05 equiv) at -78 °C under nitrogen atmosphere. After stirring at -78 °C for 30 min, triflic anhydride (1.9 mL, 11 mmol, 1.1 equiv) was added dropwise slowly and kept at this temperature for another 4 h. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl solution, extracted with Et_2O, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 50:1) gave the desired product acetylenic triflone **2**.



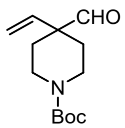
1a

1-vinylcyclohexane-1-carbaldehyde (**1a**)[3]: 871 mg, 63% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 9.30 (s, 1H), 5.61 (dd, J = 17.8, 10.8 Hz, 1H), 5.29 (d, J = 10.6 Hz, 1H), 5.13 (d, J = 17.8 Hz, 1H), 1.94-1.90 (m, 2H), 1.61-1.57 (m, 2H), 1.55-1.46 (m, 3H), 1.42-1.33 (m, 3H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 202.7, 138.8, 117.3, 53.4, 30.3, 25.7, 22.3; **HRMS (ESI)** m/z: $[M + NH_4]^+$ Calcd for $C_9H_{14}O + NH_4^+$: 156.1383; found 156.1390.



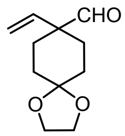
1b

4-vinyltetrahydro-2H-pyran-4-carbaldehyde (**1b**): 981 mg, 70% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.35 (s, 1H), 5.65 (dd, J = 17.6, 10.6 Hz, 1H), 5.39 (d, J = 10.6 Hz, 1H), 5.19 (d, J = 17.4 Hz, 1H), 3.81-3.76 (m, 2H), 3.59-3.53 (m, 2H), 2.06-2.00 (m, 2H), 1.80-1.73 (m, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 201.8, 136.4, 120.1, 64.4, 50.4, 30.2; **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_8H_{12}O_2+H^+$: 141.0910; found 141.0913.



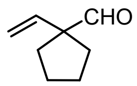
1c

tert-butyl 4-formyl-4-vinylpiperidine-1-carboxylate (**1c**): 1.6 g, 66% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.34 (s, 1H), 5.63 (dd, J = 17.6, 10.8 Hz, 1H), 5.39 (d, J = 10.8 Hz, 1H), 5.19 (d, J = 17.6 Hz, 1H), 3.64-3.60 (m, 2H), 3.24-3.18 (m, 2H), 2.02-1.96 (m, 2H), 1.71-1.65 (m, 2H), 1.45 (s, 9H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 201.9, 154.7, 136.9, 119.1, 79.7, 52.0, 40.6, 29.9, 28.4; **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{13}H_{21}NO_3+Na^+$: 262.1414; found 262.1412.



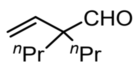
1d

8-vinyl-1,4-dioxaspiro[4.5]decane-8-carbaldehyde (**1d**): 687 mg, 70% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 10:1; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.33 (s, 1H), 5.62 (dd, J = 17.8, 10.8 Hz, 1H), 5.33 (d, J = 10.8 Hz, 1H), 5.17 (d, J = 17.8 Hz, 1H), 3.94 (s, 4H), 2.07-2.03 (m, 2H), 1.80-1.76 (m, 2H), 1.72-1.68 (m, 2H), 1.61-1.56 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 201.6, 137.3, 118.0, 108.2, 64.3, 52.4, 31.0, 27.8; **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{13}H_{21}NO_3$+Na^+: 219.0992; found 219.0989.



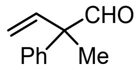
1e

1-vinylcyclopentane-1-carbaldehyde (**1e**): 943 mg, 76% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.35 (s, 1H), 5.82 (dd, J = 17.6, 10.8 Hz, 1H), 5.15 (d, J = 10.6 Hz, 1H), 5.03 (d, J = 17.6 Hz, 1H), 2.04-2.00 (m, 2H), 1.64-1.49 (m, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 200.8, 137.2, 115.0, 60.6, 31.3, 23.6; **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_8H_{12}O$+H^+: 125.0961; found 125.0960.



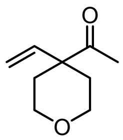
1f

2-propyl-2-vinylpentanal (**1f**): 1.1 g, 69% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.38 (s, 1H), 5.73 (dd, J = 17.8, 10.8 Hz, 1H), 5.30 (d, J = 11.0 Hz, 1H), 5.11 (d, J = 17.8 Hz, 1H), 1.61-1.57 (m, 4H), 1.24-1.19 (m, 4H), 0.91 (t, J = 7.4 Hz, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 203.5, 138.2, 116.9, 56.1, 35.0, 17.1, 14.7; **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{10}H_{18}O$+Na^+: 177.1250; found 177.1252.



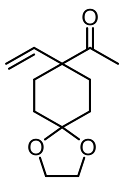
1g

2-methyl-2-phenylbut-3-enal (**1g**): 408 mg, 51% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.58 (s, 1H), 7.40-7.37 (m, 2H), 7.32-7.29 (m, 1H), 7.26-7.24 (m, 2H), 6.22 (dd, J = 17.6, 10.8 Hz, 1H), 5.42 (d, J = 10.8 Hz, 1H), 5.18 (d, J = 17.6 Hz, 1H), 1.54 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 198.4, 139.0, 137.4, 127.9, 126.4, 126.4, 116.4, 56.8, 19.1; **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{11}H_{12}O+H^+$: 161.0961; found 161.0961.



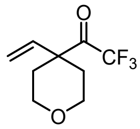
1h

1-(4-vinyltetrahydro-2H-pyran-4-yl)ethan-1-one (**1h**): 486 mg, 63% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 10:1; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 5.74 (dd, J = 17.6, 10.8 Hz, 1H), 5.34 (d, J = 10.8 Hz, 1H), 5.20 (d, J = 16.6 Hz, 1H), 3.74-3.70 (m, 2H), 3.62-3.58 (m, 2H), 2.12 (s, 3H), 2.09-2.04 (m, 2H), 1.81-1.76 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 208.9, 139.7, 117.6, 64.5, 52.8, 32.4, 25.3; **HRMS (ESI)** *m*/*z*: $[M + Na]^+$ Calcd for $C_9H_{14}O_2+Na^+$: 177.0886; found 177.0887.



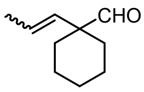
1i

1-(8-vinyl-1,4-dioxaspiro[4.5]decan-8-yl)ethan-1-one (**1i**): 725 mg, 69% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 10:1; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 5.73 (dd, J = 17.6, 10.8 Hz, 1H), 5.27 (d, J = 10.8 Hz, 1H), 5.18 (d, J = 17.6 Hz, 1H), 3.93 (s, 4H), 2.12 (s, 3H), 2.10-2.07 (m, 2H), 1.84-1.79 (m, 2H), 1.70-1.66 (m, 2H), 1.60-1.56 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 209.6, 139.9, 116.9, 108.3, 64.2, 54.3, 31.4, 29.7, 25.3; **HRMS (ESI)** *m*/*z*: $[M + Na]^+$ Calcd for $C_{12}H_{18}O_3+Na^+$: 233.1148; found 233.1147.



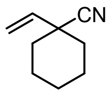
1j

2,2,2-trifluoro-1-(4-vinyltetrahydro-2H-pyran-4-yl)ethan-1-one (**1j**): 738 mg, 71% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 5.85 (dd, J = 17.6, 10.6 Hz, 1H), 5.48 (d, J = 10.8 Hz, 1H), 5.23 (d, J = 17.6 Hz, 1H), 3.79-3.73 (m, 2H), 3.67-3.61 (m, 2H), 2.22-2.16 (m, 2H), 1.95-1.89 (m, 2H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 191.3 (q, J = 31.4 Hz), 136.2, 120.3, 116.1 (q, J = 295.1 Hz), 63.9, 50.4, 32.2; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -71.45; **HRMS (ESI)** *m*/*z*: $[M + Na]^+$ Calcd for $C_9H_{11}F_3O_2$+Na^+: 231.0603; found 231.0605.



1k

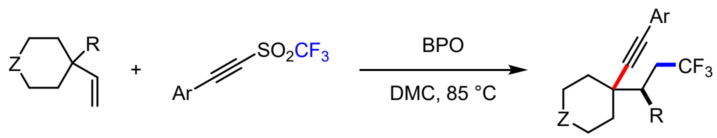
(Z/E)-1-(prop-1-en-1-yl)cyclohexane-1-carbaldehyde (**1k**): (Z/E=10/1) 2.1 g, 68% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 9.25 (s, 1H), 5.56-5.49 (m, 1H), 5.20 (d, J = 15.8 Hz, 1H), 1.91-1.87 (m, 2H), 1.72 (dd, J = 6.6, 1.4 Hz, 3H), 1.60-1.55 (m, 2H), 1.51-1.45 (m, 3H), 1.39-1.29 (m, 3H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 202.8, 131.6, 128.3, 52.5, 31.2, 25.7, 22.4, 18.5; **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{10}H_{16}O$ +H^+: 153.1274; found 153.1279.



1l

1-vinylcyclohexane-1-carbonitrile (**1l**): 959 mg, 71% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 5.69 (dd, J = 17.2, 10.2 Hz, 1H), 5.46 (d, J = 17.2 Hz, 1H), 5.19 (d, J = 10.4 Hz, 1H), 1.95-1.93 (m, 2H), 1.78-1.74 (m, 3H), 1.71-1.64 (m, 2H), 1.43 (td, J = 13.2, 3.6 Hz, 2H), 1.24-1.17 (m, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 139.0, 121.9, 115.1, 42.2, 35.9, 24.9, 22.8; **HRMS (ESI)** *m*/*z*: $[M + NH_4]^+$ Calcd for $C_9H_{13}N$+NH_4^+: 153.1386; found 153.1379.

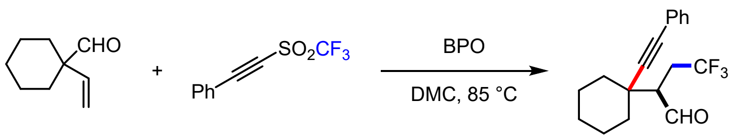
3. General Procedure for Radical 1,2,3-Tifunctionalization of Allyl Aldehyde Enabled by 1,2-Formyl Migration



1 **2** **3**

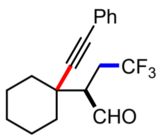
To a Schlenk flask containing **1** (0.2 mmol) and **2** (0.4 mmol) in 2 mL of DMC was added BPO (0.06 mmol, 30 mol%) under nitrogen atmosphere. The flask was immersed in an oil bath and heated at 85 °C for 10 h. Then the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. Column chromatography on silica gel gave the desired product.

Gram-Scale Synthesis of 3aa



1a **2a** **3aa**

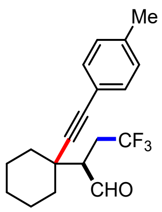
To a solution of BPO (581.4 mg, 2.4 mmol)) in 80 mL of DMC was added **1a** (1.1 g, 8 mmol) and **2a** (3.7 g, 16 mmol) under nitrogen atmosphere. The reaction mixture was immersed in an oil bath and heated at 85 °C for 10 h. Then the reaction mixture was quenched by water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 100:1) gave 1.4 g (57.8% yield) of **3aa** as a yellow oil.



3aa

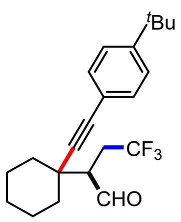
4,4,4-trifluoro-2-(1-(phenylethynyl)cyclohexyl)butanal (**3aa**): 43 mg, 70% yield, yellow oil. Flash column chromatography conditions: petroleum ethers/EtOAc = 150:1； **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.91 (d, J = 3.4 Hz, 1H), 7.45-7.39 (m, 2H), 7.34-7.30 (m, 3H), 3.01-2.86 (m, 1H), 2.65 (ddd, J = 10.2, 3.4, 1.8 Hz, 1H), 2.54-2.41 (m, 1H), 1.95-1.89 (m, 1H), 1.87-1.81 (m, 1H), 1.81-1.68 (m, 5H), 1.45 (td, J = 12.2, 4.0 Hz, 1H), 1.35 (td, J = 12.4, 3.6 Hz, 1H), 1.23-1.12 (m, 1H); **^{13}C**

NMR (151 MHz, CDCl$_3$) δ 201.3, 131.6, 128.4, 128.3, 126.6 (q, J = 276.4 Hz), 122.8, 90.1, 86.3, 54.4, 39.2, 35.7, 35.6, 29.6 (q, J = 29.2 Hz), 25.5, 22.7, 22.6; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -64.43; **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{18}H_{19}F_3O+Na^+$: 331.1280; found 331.1279.



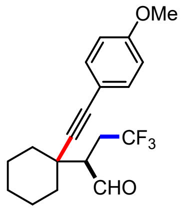
3ab

4,4,4-trifluoro-2-(1-(p-tolylethynyl)cyclohexyl)butanal (**3ab**): 42 mg, 65% yield, yellow oil. Flash column chromatography conditions: petroleum ethers/EtOAc = 150:1; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 9.90 (d, J = 3.4 Hz, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 2.97-2.88 (m, 1H), 2.63 (ddd, J = 10.2, 3.4, 2.2 Hz, 1H), 2.49-2.45 (m, 1H), 2.35 (s, 3H), 1.92-1.88 (m, 1H), 1.84-1.80 (m, 1H), 1.79-1.66 (m, 5H), 1.42 (td, J = 12.4, 3.6 Hz, 1H), 1.31 (td, J = 12.6, 3.6 Hz, 1H), 1.21-1.13 (m, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 201.4, 139.4, 131.5, 129.1, 126.5 (q, J =276.4 Hz), 119.7, 89.4, 86.4, 54.4, 39.1, 35.7, 35.6, 29.6 (q, J = 29.7 Hz), 25.6, 22.7, 22.6, 21.4; **^{19}F NMR (565 MHz, CDCl$_3$)** δ -64.42; **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{19}H_{21}F_3O+Na^+$: 345.1437; found 345.1434.



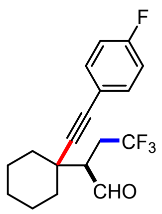
3ac

2-(1-((4-(tert-butyl)phenyl)ethynyl)cyclohexyl)-4,4,4-trifluorobutanal (**3ac**): 44 mg, 60% yield, yellow oil. Flash column chromatography conditions: petroleum ethers/EtOAc = 150:1； **^{1}H NMR (600 MHz, CDCl$_3$)** δ 9.90 (d, J = 3.4 Hz, 1H), 7.38-7.32 (m, 4H), 2.97-2.87 (m, 1H), 2.63 (ddd, J = 10.2, 3.4, 2.0 Hz, 1H), 2.52-2.43 (m, 1H), 1.92-1.89 (m, 1H), 1.85-1.81 (m, 1H), 1.79-1.66 (m, 5H), 1.42 (td, J = 12.6, 3.6 Hz, 1H), 1.31 (td, J = 12.4, 3.6 Hz,1H), 1.31(s, 9H), 1.21-1.13(m, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 201.4, 151.7, 131.4, 126.7 (q, J = 276.8 Hz), 125.4, 119.8, 89.4, 86.3, 54.5, 39.1, 35.8, 35.7, 34.8, 31.2, 29.6 (q, J = 29.2 Hz), 25.6, 22.7, 22.6; **^{19}F NMR (565 MHz, CDCl$_3$)** δ -64.41; **HRMS (ESI)** m/z: [M + Na]$^+$ Calcd for $C_{22}H_{27}F_3O$+Na$^+$: 387.1906; found 387.1904.



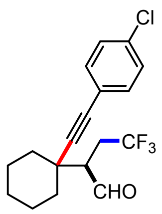
3ad

4,4,4-trifluoro-2-(1-((4-methoxyphenyl)ethynyl)cyclohexyl)butanal (**3ad**): 37 mg, 55% yield, yellow oil. Flash column chromatography conditions: petroleum ethers/EtOAc = 100:1； **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.90 (d, J = 3.8 Hz, 1H), 7.35 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H), 2.97-2.85 (m, 1H), 2.63 (ddd, J = 10.4, 3.8, 2.6 Hz, 1H), 2.50-2.43 (m, 1H), 1.94-1.87 (m, 1H), 1.84-1.80 (m, 1H), 1.78-1.62 (m, 5H), 1.42 (td, J = 12.0, 3.6 Hz, 1H), 1.35-1.28 (td, J = 12.6, 3.8 Hz, 1H), 1.23-1.16 (m, 1H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 201.5,159.6, 133.0, 126.5 (q, J = 277.9 Hz), 114.9, 113.9, 88.6, 86.1, 55.3, 54.44, 39.1, 35.8, 35.7, 29.6 (q, J = 29.2 Hz), 25.6, 22.7, 22.6; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -64.42; **HRMS (ESI)** m/z: [M + H]$^+$ Calcd for $C_{19}H_{21}F_3O_2$+H$^+$: 339.1566; found 339.1563.



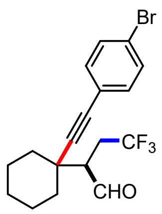
3ae

4,4,4-trifluoro-2-(1-((4-fluorophenyl)ethynyl)cyclohexyl)butanal (**3ae**): 40 mg, 61% yield, yellow oil. Flash column chromatography conditions: petroleum ethers/EtOAc = 150:1； **^{1}H NMR (600 MHz, CDCl$_3$)** δ 9.90 (d, J = 3.6 Hz, 1H), 7.42-7.37 (m, 2H), 7.04-6.98 (m, 2H), 2.99-2.85 (m, 1H), 2.65 (ddd, J = 10.2, 3.6, 2.8 Hz, 1H), 2.52-2.39 (m, 1H), 1.93-1.89 (m, 1H), 1.86-1.82 (m, 1H), 1.77-1.68 (m, 5H), 1.44 (td, J = 12.8, 4.4 Hz, 1H), 1.33 (td, J = 12.6, 4.0 Hz, 1H), 1.23-1.15 (m, 1H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 201.1, 162.5 (d, J = 250.5 Hz), 133.5 (d, J = 8.4 Hz), 126.6 (q, J = 277.9 Hz), 118.8 (d, J = 3.6 Hz), 115.6 (d, J = 21.9 Hz) , 89.8, 85.2, 54.3, 39.2, 35.6, 35.6, 29.6 (q, J = 29.5 Hz), 25.5, 22.7, 22.6; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -64.49, -110.89; **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}F_4O+H^+$: 327.1367; found 327.1372.



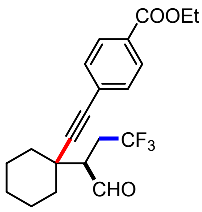
3af

2-(1-((4-chlorophenyl)ethynyl)cyclohexyl)-4,4,4-trifluorobutanal (**3af**): 50 mg, 73% yield, yellow oil. Flash column chromatography conditions: petroleum ethers/EtOAc = 150:1； **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.90 (d, J = 3.6 Hz, 1H), 7.36-7.26 (m, 4H), 2.99-2.85 (m,1H), 2.66 (ddd, J = 10.4, 3.6, 2.8 Hz, 1H), 2.50-2.39 (m, 1H), 1.92-1.89 (m, 1H), 1.86-1.82 (m, 1H), 1.78-1.64 (m, 5H), 1.44 (td, J = 12.8, 3.8 Hz, 1H), 1.34 (td, J = 12.8, 3.6 Hz, 1H), 1.22-1.12 (m, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 201.0, 134.4, 132.9, 128.7, 126.6 (q, J = 276.4 Hz), 121.2, 91.2, 85.2, 54.2, 39.3, 35.6, 35.5, 29.5 (q, J = 29.2 Hz), 25.5, 22.7, 22.6; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -64.48; **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{18}H_{18}ClF_3O+Na^+$: 365.0890; found 365.0890.



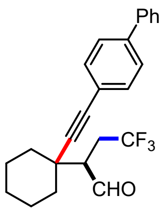
3ag

2-(1-((4-bromophenyl)ethynyl)cyclohexyl)-4,4,4-trifluorobutanal (**3ag**): 50 mg, 65% yield, yellow oil. Flash column chromatography conditions: petroleum ethers/EtOAc = 150:1； **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.90 (d, J = 3.6 Hz, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.8 Hz, 2H), 2.97-2.87 (m, 1H), 2.66 (ddd, J = 10.4, 3.4, 2.6 Hz, 1H), 2.49-2.40 (m, 1H), 1.92-1.89 (m, 1H), 1.86-1.82 (m, 1H), 1.77-1.68 (m, 5H), 1.44 (td, J = 12.8, 5.0 Hz, 1H), 1.34 (td, J = 12.8, 4.0 Hz, 1H), 1.22-1.15 (m, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 200.9, 133.1, 131.6, 126.6 (q, J = 276.9 Hz), 122.5, 121.7, 91.4, 85.3, 54.2, 39.3, 35.6, 35.5, 29.5 (q, J = 29.6 Hz), 25.5, 22.6, 22.7; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -64.49; **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}BrF_3O+H^+$: 387.0566; found 387.0570.



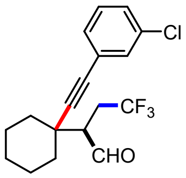
3ah

ethyl 4-((1-(4,4,4-trifluoro-1-oxobutan-2-yl)cyclohexyl)ethynyl)benzoate (**3ah**): 39 mg, 51% yield, yellow oil. Flash column chromatography conditions: petroleum ethers/EtOAc = 100:1； **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.91 (d, J = 3.8 Hz, 1H), 8.0 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 4.39 (q, J = 7.2 Hz, 2H), 2.98-2.89 (m, 1H), 2.68 (ddd, J = 10.2, 3.6, 2.8 Hz, 1H), 2.50-2.42 (m, 1H), 1.96-1.92 (m, 1H), 1.88-1.84 (m, 1H), 1.78-1.69 (m, 5H), 1.47 (td, J = 12.8, 4.4 Hz, 1H), 1.40 (t, J = 7.2 Hz, 3H), 1.36 (td, J = 12.8, 4.0 Hz, 1H), 1.22-1.17 (m, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 200.9, 166.0, 131.5, 130.0, 129.5, 127.3, 126.5 (q, J = 276.8 Hz), 93.2, 85.7, 61.2, 54.2, 39.4, 35.6, 35.5, 29.6 (q, J = 29.2 Hz), 25.5, 22.7, 22.6, 14.3; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -64.49; **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{21}H_{23}F_3O_3$+H^+: 381.1672; found 381.1676.



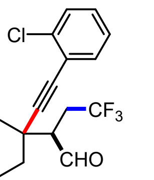
3ai

2-(1-([1,1'-biphenyl]-4-ylethynyl)cyclohexyl)-4,4,4-trifluorobutanal (**3ai**): 48 mg, 63% yield, corlorless liquid. Flash column chromatography conditions: petroleum ethers/EtOAc = 150:1； **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.93 (d, J = 3.6 Hz, 1H), 7.59-7.54 (m, 4H), 7.49-7.43 (m, 4H), 7.38-7.36 (m, 1H), 2.98-2.92 (m, 1H), 2.67 (ddd, J = 10.2, 3.0, 2.4 Hz, 1H), 2.51-2.46 (m, 1H), 1.95-1.92 (m, 1H), 1.88-1.84 (m, 1H), 1.81-1.68 (m, 5H), 1.45 (td, J = 12.4, 3.6 Hz, 1H), 1.34 (td, J = 12.6, 3.6 Hz, 1H), 1.22-1.18 (m, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 201.4, 141.3, 140.4, 132.2, 129.0, 127.8, 127.2, 127.1, 126.9 (q, J = 276.4 Hz), 121.8, 90.9, 86.3, 54.5, 39.4, 35.9, 35.8, 29.8 (q, J = 29.2 Hz), 25.7, 22.9, 22.8; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -64.41; **HRMS (ESI)** *m*/*z*: $[M + Na]^+$ Calcd for $C_{24}H_{23}F_3O$+Na^+: 407.1593; found 407.1589.



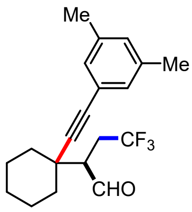
3aj

2-(1-((3-chlorophenyl)ethynyl)cyclohexyl)-4,4,4-trifluorobutanal (**3aj**): 38 mg, 55% yield, yellow oil. Flash column chromatography conditions: petroleum ethers/EtOAc = 150:1; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.90 (d, J = 3.6 Hz, 1H), 7.40 (s, 1H), 7.32-7.28 (m, 2H), 7.26-7.23 (m, 1H), 2.97-2.87 (m, 1H), 2.66 (ddd, J = 10.4, 3.6, 2.8 Hz, 1H), 2.49-2.40 (m, 1H), 1.94-1.89 (m, 1H), 1.87-1.81 (m, 1H), 1.77-1.68 (m, 5H), 1.45 (td, J = 12.8, 5.0 Hz, 1H), 1.34 (td, J = 12.8, 4.2 Hz, 1H), 1.22-1.11(m, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 200.9, 134.2, 131.5, 129.8, 129.6, 128.6, 126.3 (q, J = 276.4 Hz), 124.4, 91.5, 84.9, 54.2, 39.3, 35.6, 35.5, 29.6 (q, J = 29.2 Hz), 25.5, 22.7, 22.6; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -64.49; **HRMS (ESI)** *m*/*z*: $[M + Na]^+$ Calcd for $C_{18}H_{18}ClF_3O+Na^+$: 365.0890; found 365.0892.



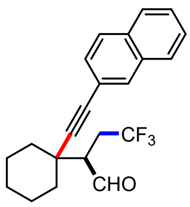
3ak

2-(1-((2-chlorophenyl)ethynyl)cyclohexyl)-4,4,4-trifluorobutanal (**3ak**): 24 mg, 35% yield, yellow oil. Flash column chromatography conditions: petroleum ethers/EtOAc = 150:1; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.91 (d, J = 4.0 Hz, 1H), 7.45 (dd, J = 7.4, 2.0 Hz, 1H), 7.40 (dd, J = 7.6, 1.6 Hz, 1H), 7.29-7.24 (m, 1H), 7.24-7.19 (m, 1H), 3.05-2.90 (m, 1H), 2.65 (ddd, J = 10.6, 3.6, 2.4 Hz, 1H), 2.58-2.46 (m, 1H), 2.00-1.92(m, 1H), 1.90-1.85 (m, 1H), 1.84-1.66 (m, 5H), 1.44 (td, J = 12.4, 3.4, 1H), 1.34 (td, J = 12.6, 3.6 Hz, 1H), 1.24-1.15 (m, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 201.3, 136.1, 133.3, 129.3, 129.3, 126.8 (q, J = 276.4 Hz), 126.5, 122.7, 95.7, 83.1, 54.4, 39.3, 35.7, 35.6, 29.7 (q, J = 29.2 Hz), 25.5, 22.7, 22.6; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -64.36; **HRMS (ESI)** *m*/*z*: $[M + Na]^+$ Calcd for $C_{18}H_{18}ClF_3O+Na^+$: 365.0890; found 365.0892.



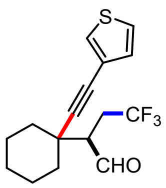
3al

2-(1-((3,5-dimethylphenyl)ethynyl)cyclohexyl)-4,4,4-trifluorobutanal (**3al**): 35 mg, 52% yield, yellow oil. Flash column chromatography conditions: petroleum ethers/EtOAc = 150:1； **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.90 (d, J = 3.8 Hz, 1H), 7.04 (s, 2H), 6.96 (s, 1H), 2.95-2.89 (m, 1H), 2.62 (ddd, J = 10.2, 3.6, 2.8 Hz, 1H), 2.49-2.44 (m, 1H), 2.29 (m, 6H), 1.91-1.88 (m, 1H), 1.84-1.80 (m, 1H), 1.79-1.66 (m, 5H), 1.42 (td, J = 12.4, 3.6, 1H), 1.31 (td, J = 12.6, 3.6 Hz, 1H), 1.22-1.13 (m, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 201.4, 137.9, 130.2, 129.3, 126.6 (q, J = 276.4 Hz), 121.8, 89.3, 86.6, 54.4, 39.7, 35.8, 35.7, 29.6 (q, J = 29.2 Hz), 25.6, 22.7, 22.6, 21.1; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -64.39; **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{20}H_{23}F_3O+H^+$: 337.1774; found 337.1774.



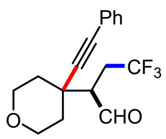
3am

4,4,4-trifluoro-2-(1-(naphthalen-2-ylethynyl)cyclohexyl)butanal (**3am**): 39 mg, 55% yield, corlorless liquid. Flash column chromatography conditions: petroleum ethers/EtOAc = 150:1； **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.95 (d, J = 3.6 Hz, 1H), 7.93 (s, 1H), 7.80-7.77 (m, 3H), 7.49-7.48 (m, 2H), 7.45 (d, J = 8.4 Hz, 1H), 3.00-2.95 (m, 1H), 2.69 (ddd, J = 10.4, 3.2, 2.4 Hz, 1H), 2.55-2.47 (m, 1H), 1.97-1.94 (m ,1H), 1.89-1.86 (m, 1H), 1.84-1.69 (m, 5H), 1.47 (td, J = 12.6, 3.6 Hz, 1H), 1.36 (td, J = 12.6, 3.6 Hz, 1H), 1.22-1.17 (m, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 201.3, 132.9, 132.8, 131.4, 128.4, 128.0, 127.8, 127.6, 126.7, 126.6, 126.6 ((q, J = 276.9 Hz), 120.0, 90.4, 86.7, 54.4, 39.3, 35.8, 35.7, 29.6 (q, J = 29.2 Hz), 25.6, 22.8, 22.7; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -64.40; **HRMS (ESI)** *m*/*z*: $[M + Na]^+$ Calcd for $C_{22}H_{21}F_3O+Na^+$: 381.1437; found 381.1429.



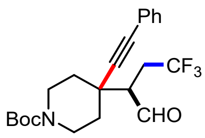
3an

4,4,4-trifluoro-2-(1-(thiophen-3-ylethynyl)cyclohexyl)butanal (**3an**): 15 mg, 24% yield, yellow oil. Flash column chromatography conditions: petroleum ethers/EtOAc = 100:1; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.89 (d, J = 3.8 Hz, 1H), 7.41-7.40 (m, 1H), 7.29-7.27 (m, 1H), 7.08 (d, J = 5.0 Hz, 1H), 2.96-2.85 (m, 1H), 2.63 (ddd, J = 10.4, 3.6, 2.6 Hz, 1H), 2.49-2.42 (m, 1H), 1.93-1.87 (m, 1H), 1.86-1.80 (m, 1H), 1.78-1.65 (m, 5H), 1.42 (td, J = 12.4, 4.2 Hz, 1H), 1.33 (td, J = 12.4, 4.0 Hz, 1H), 1.22-1.16 (m, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 201.2, 129.9, 128.5, 126.6 (q, J = 276.9 Hz), 125.4, 121.7, 89.7, 81.3, 54.3, 39.2, 35.7, 35.6, 29.6, (q, J = 29.2 Hz), 25.5, 22.6, 22.5; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -64.43; **HRMS (ESI)** *m*/*z*: [M + Na]$^+$ Calcd for $C_{16}H_{17}F_3OS$+Na$^+$: 337.0844; found 337.0845.



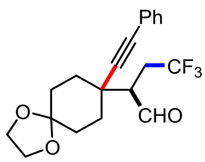
3ba

4,4,4-trifluoro-2-(4-(phenylethynyl)tetrahydro-2H-pyran-4-yl)butanal (**3ba**): 45 mg, 72% yield, yellow oil. Flash column chromatography conditions: petroleum ethers/EtOAc = 10:1; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.91 (d, J = 3.4 Hz, 1H), 7.45-7.40 (m, 2H), 7.37-7.31 (m, 3H), 3.96-3.91 (m, 2H), 3.86 (ddd, J = 20.6, 11.6, 2.2 Hz, 2H), 3.02-2.92 (m, 1H), 2.65 (ddd, J = 10.2, 3.6, 2.8 Hz, 1H), 2.49-2.41 (m, 1H), 1.85 (ddd, J = 13.2, 12.0, 4.6 Hz, 1H), 1.80-1.72 (m, 2H), 1.71-1.66 (m, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 200.4, 131.7, 128.8, 128.5, 126.4 (q, J = 276.8 Hz), 122.1, 88.1, 87.4, 64.4, 64.2, 54.4, 36.9, 35.9, 35.6, 29.3 (q, J = 29.8 Hz); **^{19}F NMR (565 MHz, $CDCl_3$)** δ -64.34; **HRMS (ESI)** *m*/*z*: [M + Na]$^+$ Calcd for $C_{17}H_{17}F_3O_2$+Na$^+$: 333.1073; found 333.1080.



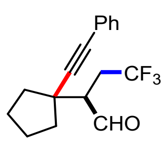
3ca

tert-butyl-4-(phenylethynyl)-4-(4,4,4-trifluoro-1-oxobutan-2-yl)piperidine-1-carboxylate (**3ca**): 47 mg, 57% yield, yellow oil. Flash column chromatography conditions: petroleum ethers/EtOAc = 2:1; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 9.91 (d, J = 3.4 Hz, 1H), 7.44-7.39 (m, 2H), 7.37-7.31 (m, 3H), 4.29-3.98 (m, 2H), 3.27-3.07 (m, 2H), 3.01-2.92 (m, 1H), 2.67 (ddd, J = 10.4, 3.6, 2.8 Hz, 1H), 2.49-2.41 (m, 1H), 1.91-1.74 (m, 2H), 1.64-1.63 (m, 1H), 1.51 (td, J = 12.8, 4.4 Hz, 1H), 1.46 (s, 9H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 200.5, 154.7, 131.8, 128.9, 128.6, 126.5 (q, J = 276.9 Hz), 122.1, 87.9, 87.8, 80.0, 54.1, 53.7, 40.9, 40.1, 38.1, 34.9, 29.5 (q, J = 29.2 Hz), 28.5 ; **^{19}F NMR (565 MHz, CDCl$_3$)** δ -64.43; **HRMS (ESI)** m/z: [M + Na]$^+$ Calcd for $C_{22}H_{26}F_3NO_3$+Na$^+$: 432.1757; found 432.1755.



3da

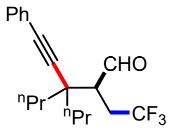
4,4,4-trifluoro-2-(8-(phenylethynyl)-1,4-dioxaspiro[4.5]decan-8-yl)butanal (**3da**): 48 mg, 66% yield, yellow oil. Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 9.93 (d, J = 3.4 Hz, 1H), 7.41-7.38 (m, 2H), 7.36-7.28 (m, 3H), 3.99-3.92 (m, 4H), 3.00-2.91 (m, 1H), 2.70 (ddd, J = 10.4, 3.6, 2.8 Hz, 1H), 2.50-2.40 (m, 1H), 2.11-2.03 (m, 2H), 1.92-1.84 (m, 2H), 1.80 (td, J = 13.0, 3.6 Hz, 1H), 1.76-1.66 (m, 3H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 200.6, 131.7, 128.5, 128.4, 126.5 (q, J = 276.4 Hz), 122.4, 107.7, 88.9, 86.1, 64.5, 64.3, 53.6, 38.2, 33.1, 32.9, 31.6, 31.5, 29.7 (q, J = 29.8 Hz); **^{19}F NMR (565 MHz, CDCl$_3$)** δ -64.56; **HRMS (ESI)** m/z: [M + Na]$^+$ Calcd for $C_{20}H_{21}F_3O_3$+Na$^+$: 389.1335; found 389.1331.



3ea

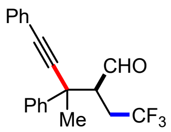
4,4,4-trifluoro-2-(1-(phenylethynyl)cyclopentyl)butanal (**3ea**): 33 mg, 56% yield, yellow oil.

Flash column chromatography conditions: petroleum ethers/EtOAc = 150:1; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 9.84 (d, J = 3.4 Hz, 1H), 7.37-7. 35 (m, 2H), 7.32-7.28 (m, 3H), 3.11-3.05 (m, 1H), 2.70 (ddd, J = 10.4, 3.6, 2.8 Hz, 1H), 2.44-2.35 (m, 1H), 2.14-2.05 (m, 2H), 2.01-1.90 (m, 2H), 1.85-1.72 (m, 3H), 1.69-1.64 (m, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 200.5, 131.6, 128.3, 128.2, 126.4 (q, J = 276.8 Hz), 122.8, 91.3, 84.2, 53.9, 44.4, 39.7, 38.6, 31.5 (q, J = 29.8 Hz), 24.2, 23.2; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -64.55; **HRMS (ESI)** *m/z*: [*M* + H]$^+$ Calcd for $C_{17}H_{17}F_3O+H^+$: 295.1304; Found 295.1314.



3fa

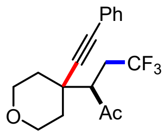
3-(phenylethynyl)-3-propyl-2-(2,2,2-trifluoroethyl)hexanal (**3fa**): 49 mg, 76% yield, yellow oil. Flash column chromatography conditions: petroleum ethers/EtOAc = 150:1; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 9.96 (d, J = 3.4 Hz, 1H), 7.40-7.39 (m, 2H), 7.33-7.30 (m, 3H), 2.96-2.87 (m, 2H), 2.37-2.29 (m, 1H), 1.57-1.47 (m, 8H), 0.96 (t, J = 7.0 Hz, 6H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 201.3, 131.6, 128.3, 128.2, 126.7 (q, J = 276.4 Hz), 122.8, 90.9, 85.8, 50.5, 41.3, 38.9, 38.6, 29.2 (q, J = 29.2 Hz), 17.7, 14.4, 14.3; **^{19}F NMR (565 MHz, CDCl$_3$)** δ -64.69; **HRMS (ESI)** *m/z*: [*M* + Na]$^+$ Calcd for $C_{19}H_{23}F_3O+Na^+$: 347.1593; found 347.1590.



3ga

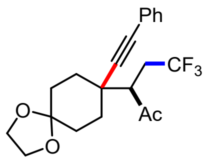
3-methyl-3,5-diphenyl-2-(2,2,2-trifluoroethyl)pent-4-ynal (**3ga,** both isomers)**:** 22 mg, 33% yield, yellow oil, 2:1 dr, determined by ^{19}F NMR analysis of the crude mixture. Flash column chromatography conditions: petroleum ethers/EtOAc = 100:1. Major isomer: **^{1}H NMR (600 MHz, CDCl$_3$)** δ 9.85 (d, J = 4.0 Hz, 1H), 7.59-7.57 (m, 2H), 7.52-7.49 (m, 2H), 7.42-7.40 (m, 1H), 7.37-7.31 (m, 5H), 3.00 (ddd, J = 11.0, 4.0, 2.0 Hz, 1H), 2.90-2.82 (m, 1H), 2.07-1.99 (m, 1H), 1.73 (s, 3H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 200.9, 141.8, 131.7, 129.0, 128.7, 128.5, 127.8, 126.3 (q, J = 276.9 Hz), 126.2, 122.3, 89.1, 87.7, 55.1, 42.2, 31.1 (q, J = 29.2 Hz) , 28.4; **^{19}F NMR (565 MHz,

$CDCl_3$) δ -64.29. Minor isomer: **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.54 (s, 1H), 7.62-7.60 (m, 2H), 7.48-7.46 (m, 2H), 7.44-7.42 (m, 2H), 7.38-7.36 (m, 4H), 3.14 (ddd, *J* = 11.2, 4.0, 2.2 Hz, 1H), 2.96-2.92 (m ,1H), 2.41-2.33 (m, 1H), 1.77 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 199.8, 141.3, 131.7, 128.9, 128.7, 128.4, 127.9, 126.4, (q, *J* = 277.1 Hz), 126.5, 122.4, 90.0, 87.0, 54.9, 42.3, 29.6 (q, *J* = 29.2 Hz), 27.2; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -64.70; Both isomers**: HRMS (ESI)** *m*/*z*: [*M* + Na]$^+$ Calcd for $C_{20}H_{17}F_3O$+Na^+: 353.1124; found 353.1124.



3ha

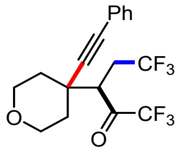
5,5,5-trifluoro-3-(4-(phenylethynyl)tetrahydro-2H-pyran-4-yl)pentan-2-one (**3ha**): 39 mg, 60% yield, white solid, mp 64-65 °C ; Flash column chromatography conditions: petroleum ethers/EtOAc = 10:1； **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.47-7.41 (m, 2H), 7.38-7.30 (m, 3H), 3.93-3.89 (m, 2H), 3.88-3.81 (m, 2H), 2.98 (d, *J* = 11.2 Hz, 1H), 2.85-2.79 (m, 1H), 2.51-2.42 (m, 1H), 2.36 (s, 3H), 1.90 (td, *J* = 12.6, 4.6 Hz, 1H), 1.82-1.79 (m, 1H), 1.63 (td, *J* =12.2, 4.6 Hz, 1H), 1.51-1.48 (m, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 207.7, 131.6, 128.6, 128.4, 126.7 (q, *J* = 276.9 Hz), 122.4, 89.3, 86.9, 64.7, 64.5, 54.3, 37.6, 35.4, 34.2, 32.8 (q, *J* = 28.6 Hz), 32.7; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -64.86; **HRMS (ESI)** *m*/*z*: [*M* + Na]$^+$ Calcd for $C_{18}H_{19}F_3O_2$+Na^+: 347.1229; found 347.1230.



3ia

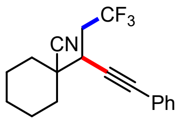
5,5,5-trifluoro-3-(8-(phenylethynyl)-1,4-dioxaspiro[4.5]decan-8-yl)pentan-2-one (**3ia**): 49 mg, 65% yield, colorless oil. Flash column chromatography conditions: petroleum ethers/EtOAc = 100:1； **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.43-7.39 (m, 2H), 7.34-7.28 (m, 3H), 3.97-3.91 (m, 4H), 3.00 (d, *J* =10.0 Hz, 1H), 2.86-2.79 (m, 1H), 2.51-2.42 (m, 1H), 2.36 (s, 3H), 2.10-2.02 (m, 2H), 1.98-1.94 (m, 1H), 1.85 (td, *J* = 12.8, 3.4 Hz, 1H), 1.74-1.67 (m, 2H), 1.67-1.58 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 208.2, 131.6, 128.3, 126.7 (q, *J* = 277.9 Hz), 122.7, 107.8, 89.9, 85.6, 64.4, 64.2, 53.7, 38.8, 33.4 (q, *J* = 28.8 Hz), 32.8, 32.7, 31.9, 31.8, 31.6; **^{19}F NMR (377 MHz, $CDCl_3$)** δ

-65.03; **HRMS (ESI)** *m*/*z*: [*M* + Na]$^+$ Calcd for $C_{21}H_{23}F_3O_3$+Na$^+$: 403.1491; found 403.1495.



3ja

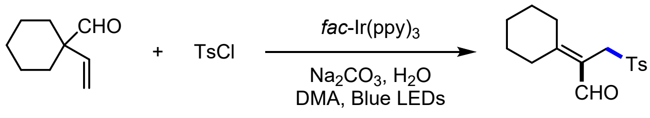
1,1,1,5,5,5-hexafluoro-3-(4-(phenylethynyl)tetrahydro-2H-pyran-4-yl)pentan-2-one (**3ja**): 46 mg, 61% yield, colorless oil. Flash column chromatography conditions: petroleum ethers/EtOAc = 10:1; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.48-7.43 (m, 2H), 7.38-7.31 (m, 3H), 3.97-3.91 (m, 2H), 3.89-3.81 (m, 2H), 3.52 (dd, *J* = 11.4, 1.8 Hz, 1H), 2.91-2.81 (m, 1H), 2.70-2.62 (m, 1H), 1.93 (td, *J* = 12.4, 4.6 Hz, 1H), 1.87-1.84 (m, 1H), 1.66 (td, *J* = 12.0, 4.4 Hz, 1H), 1.57-1.54 (m, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 192.6 (q, *J* = 36.4 Hz), 131.7, 128.8, 128.4, 125.8 (q, *J* = 276.8 Hz), 122.0, 114.8 (q, *J* =292.0 Hz) , 87.7, 87.5, 64.5, 64.3, 48.1, 39.5, 35.7, 33.9, 33.7 (q, *J* = 29.2 Hz); **^{19}F NMR (565 MHz, CDCl$_3$)** δ -65.24 (q, *J* = 2.7 Hz), -77.70 (q, *J* = 2.0 Hz); **HRMS (ESI)** *m*/*z*: [*M* + Na]$^+$ Calcd for $C_{18}H_{16}F_6O_2$+Na$^+$: 401.0947; found 401.0945.



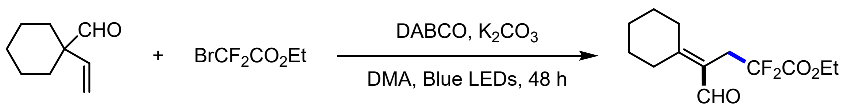
3la

1-(5,5,5-trifluoro-1-phenylpent-1-yn-3-yl)cyclohexane-1-carbonitrile (**3la**): 49 mg, 81% yield, colorless oil. Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.43-7.42 (m, 2H), 7.35-7.29 (m, 3H), 3.02 (dd, *J* = 11.2, 2.8 Hz, 1H), 2.66-2.59 (m, 1H), 2.58-2.50 (m, 1H), 2.15-2.12 (m, 1H), 2.02-2.19 (m, 1H), 1.86-1.77 (m, 3H), 1.69-1.63 (m, 3H), 1.62-1.55 (m, 1H), 1.24-1.17 (m, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 131.7, 128.6, 128.3, 126.0 (q, *J* = 277.5 Hz), 122.4, 121.4, 86.4, 84.5, 43.1, 35.8 (q, *J* = 28.6 Hz), 35.8, 34.1, 32.4, 25.0, 23.1, 22.9; **^{19}F NMR (565 MHz, CDCl$_3$)** δ -64.15; **HRMS (ESI)** *m*/*z*: [*M* + Na]$^+$ Calcd for $C_{18}H_{18}F_3N$+Na$^+$: 328.1284; found 328.1288.

4. Photocatalyzed 1,2,3-Trifunctionalization of α,α-Disubstituted Vinyl Aldehydes



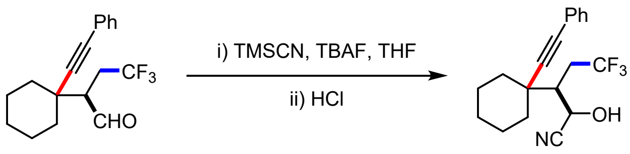
To a mixture of *fac*-Ir(ppy)$_3$ (0.004 mmol, 2 mol%), TsCl (0.3 mmol, 1.5 equiv), Na_2CO_3 (0.4 mmol, 2.0 equiv) and H_2O (0.4 mmol, 2.0 equiv) in 2 mL of DMA was added **1a** (0.2 mmol, 1.0 equiv) under nitrogen atmosphere. After 10 h of irradiation at a distance of ~5 cm (light intensity: 3.58 mW/cm^2 at 5 cm distance) with 30 W blue LEDs (GeAo Chemical lamps, 450 nm) at room temperature, the reaction mixture was quenched by water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 2:1) gave 52.0 mg (89% yield) of **2-cyclohexylidene-3-tosylpropanal** (**4**) as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.92 (s, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 4.24 (m, 2H), 2.80 (t, *J* = 5.8 Hz, 2H), 2.57 (t, *J* = 6.2 Hz, 2H), 2.43 (s, 3H), 1.87 - 1.81 (m, 2H), 1.79-1.74 (m, 2H), 1.72-1.66 (m, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 187.4, 171.1, 144.7, 136.4, 129.7, 128.6, 122.8, 51.7, 34.9, 30.1, 28.8, 28.2, 26.2, 21.8; **HRMS (ESI)** *m*/*z*: [*M* + Na]$^+$ Calcd for $C_{16}H_{20}O_3S+Na^+$: 315.1025; found 315.1021.



To a mixture of DABCO (0.4 mmol, 2.0 equiv) and K_2CO_3 (0.2 mmol, 1.0 equiv) in 2 mL of DMA was added **1a** (0.2 mmol, 1.0 equiv) under nitrogen atmosphere. After 48 h of irradiation at a distance of ~5 cm (light intensity: 3.58 mW/cm^2 at 5 cm distance) with 30 W blue LEDs (GeAo Chemical lamps, 450 nm) at room temperature, the reaction mixture was quenched by water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 10:1) gave 20.8 mg (40% yield) of **ethyl 4-cyclohexylidene-2,2-difluoro-5-oxopentanoate** (**5**) as a colorless liquid. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 10.2 (s, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 3.17 (t, *J* = 16.6 Hz, 2H), 2.80 (dd, *J* = 8.2, 6.0 Hz, 2H), 2.47 (dd, *J* = 8.2, 6.0 Hz, 2H), 1.78-1.74 (m, 4H), 1.70-1.67 (m, 2H), 1.36 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 189.3, 168.7, 164.1 (t, *J* = 29.9 Hz), 124.8, 115.1 (t, *J* = 252.0 Hz), 63.1, 34.3, 30.0, 29.9 (t, *J* = 24.7 Hz), 28.9, 28.2, 26.4, 14.1; **^{19}F NMR (377 MHz,

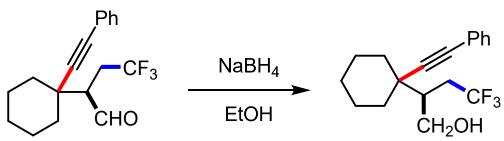
CDCl$_3$) δ -104.68; **HRMS (ESI)** *m/z*: [*M* + H]$^+$ Calcd for $C_{13}H_{18}F_2O_3$+H$^+$: 261.1297; found 261.1294.

5. Synthetic Utility



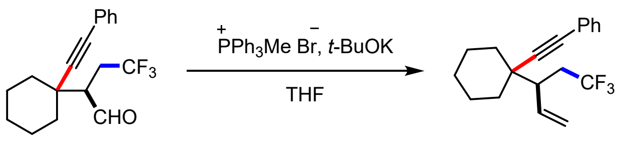
3aa **6**

To a solution of TMSCN (0.2 mmol, 1.0 equiv) in 2 mL of THF was added TBAF (20 μL, 1.0 M in THF, 0.1 equiv) and **3aa** (0.2 mmol, 1.0 equiv) at 0 °C under nitrogen atmosphere. After stirring at room temperature for 2 h, the reaction mixture was quenched by 1.0 M aqueous solution of HCl, extracted with EtOAc, dried over anhydrous Na_2SO_4, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 10:1) gave 52 mg (77% yield) of **5,5,5-trifluoro-2-hydroxy-3-(1-(phenylethynyl)cyclohexyl)pentanenitrile** (**6**) as a colorless liquid, dr = 2:1, determined by ^{19}F NMR analysis of the crude mixture. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.46-7.39 (m, 2H), 7.34-7.28 (m, 3H), 5.12-5.10 (m, 0.3H, minor), 5.00-4.98 (m, 0.6H, major), 3.20 (d, J = 4.6 Hz, 0.3H, minor), 3.01 (d, J = 6.8 Hz, 0.6H, major), 2.78-2.51 (m, 2H), 2.11 (dt, J = 9.4, 3.2 Hz, 1H), 2.07-1.95 (m, 2H), 1.83-1.69 (m, 5H), 1.54-1.40 (m, 1H), 1.34-1.27 (m, 1H), 1.26 -1.16 (m, 1H); **^{13}C NMR (101 MHz, CDCl$_3$, major)** δ 131.8, 128.6, 128.5, 126.8 (q, J = 277.5 Hz), 122.7, 118.9, 90.2, 87.4, 62.6, 46.7, 39.8, 36.3, 36.2, 32.7 (q, J = 29.5 Hz), 25.6, 23.1, 22.6; **^{13}C NMR (101 MHz, CDCl$_3$, minor)** δ 131.8, 128.8, 128.5, 126.7 (q, J = 277.4 Hz), 122.2, 118.7, 91.0, 87.5, 61.6, 46.5, 40.5, 36.2, 35.6, 30.3 (q, J = 30.0 Hz), 25.5, 23.1, 22.6; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -63.73; **HRMS (ESI)** *m/z*: [*M* + Na]$^+$ Calcd for $C_{19}H_{20}F_3NO$ +Na$^+$: 358.1389; found 358.1383.



3aa **7**

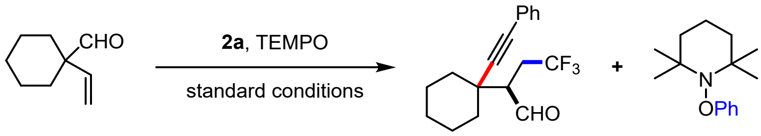
To a solution of **3aa** (0.2 mmol, 1.0 equiv) in 2 mL of EtOH was added $NaBH_4$ (0.1 mmol, 0.5 equiv). After stirring at room temperature for 2 h, EtOH was removed under reduced pressure. The reaction mixture was quenched by water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 10:1) gave 53 mg (85% yield) of **4,4,4-trifluoro-2-(1-(phenylethynyl)cyclohexyl)butan-1-ol** (**7**) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.41-7.38 (m, 2H), 7.31-7.28 (m, 3H), 4.06-4.03 (m, 1H), 3.86-3.82 (m, 1H), 2.62-2.58 (m, 1H), 2.48-2.39 (m, 1H), 2.02-1.99 (m, 1H), 1.97-1.93 (m, 2H), 1.79-1.66 (m, 6H), 1.36 (td, J = 12.6, 4.0 Hz, 1H), 1.27 (td, J = 12.4, 3.8 Hz, 1H), 1.23-1.15 (m, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 131.6, 128.3, 128.1, 127.6 (q, J = 276.4 Hz), 122.9, 92.6, 85.8, 62.1, 44.4, 39.2, 36.3, 35.8, 31.3 (q, J = 28.1 Hz), 25.8, 23.0, 22.7; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -64.19; **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{21}F_3O + H^+$: 311.1615; found 311.1617.



3aa **8**

To a solution of methyltriphenylphosphonium bromidethe (0.24 mmol, 1.2 equiv) in 2 mL of THF was added *t*-BuOK (0.3 mmol, 1.5 equiv) at 0 °C under nitrogen atmosphere. After stirring at for 2 h at room temperature, **3aa** was added dropwise slowly and kept at this temperature for another 8 h. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl solution, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. Column chromatography on silica gel (petroleum ethers) gave 49 mg (50% yield) of **((1-(5,5,5-trifluoropent-1-en-3-yl)cyclohexyl)ethynyl) benzene** (**8**) as a yellow liquid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.42-7.40 (m, 2H), 7.32-7.27 (m, 3H), 5.78 (dt, J = 19.2, 9.4 Hz, 1H), 5.18 (dd, J = 10.2, 1.8 Hz, 1H), 5.12 (dd, J = 17.0, 1.8 Hz, 1H), 2.66-2.58 (m, 1H), 2.34-2.24 (m, 2H), 1.88-1.81 (m, 2H), 1.76-1.62 (m, 5H), 1.31-1.25 (m, 1H), 1.19-1.13 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.0, 131.6, 128.3, 127.8, 127.3 (q, J = 277.5 Hz), 123.6, 118.2, 92.4, 84.8, 48.6, 39.8, 36.3, 35.4, 35.0 (q, J = 27.0 Hz), 25.9, 23.1, 23.0; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -62.70; **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{21}F_3 + H^+$: 307.1668; found 307.1667.

6. Mechanistic Experiments



1a **3aa, ND** **9**
Detected by HRMS

To a Schlenk flask containing **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv) and TEMPO (0.4 mmol, 2.0 equiv) in 2 mL of DMC was added BPO (0.06 mmol, 30 mol%) under nitrogen atmosphere. The flask was immersed in an oil bath and heated at 85 °C for 10 h. Then the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was analyzed by HRMS and **9** was detected while **3aa** was not observed.

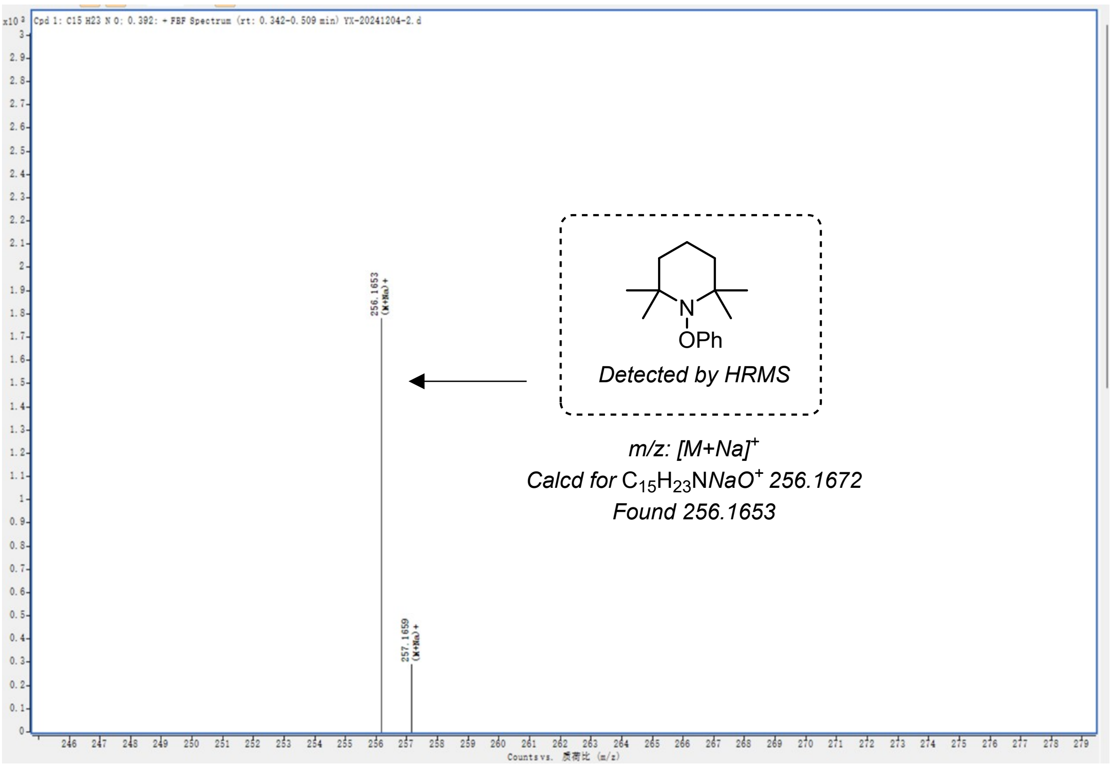
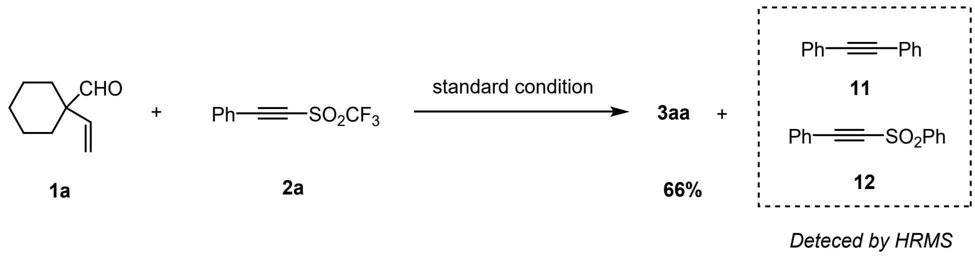


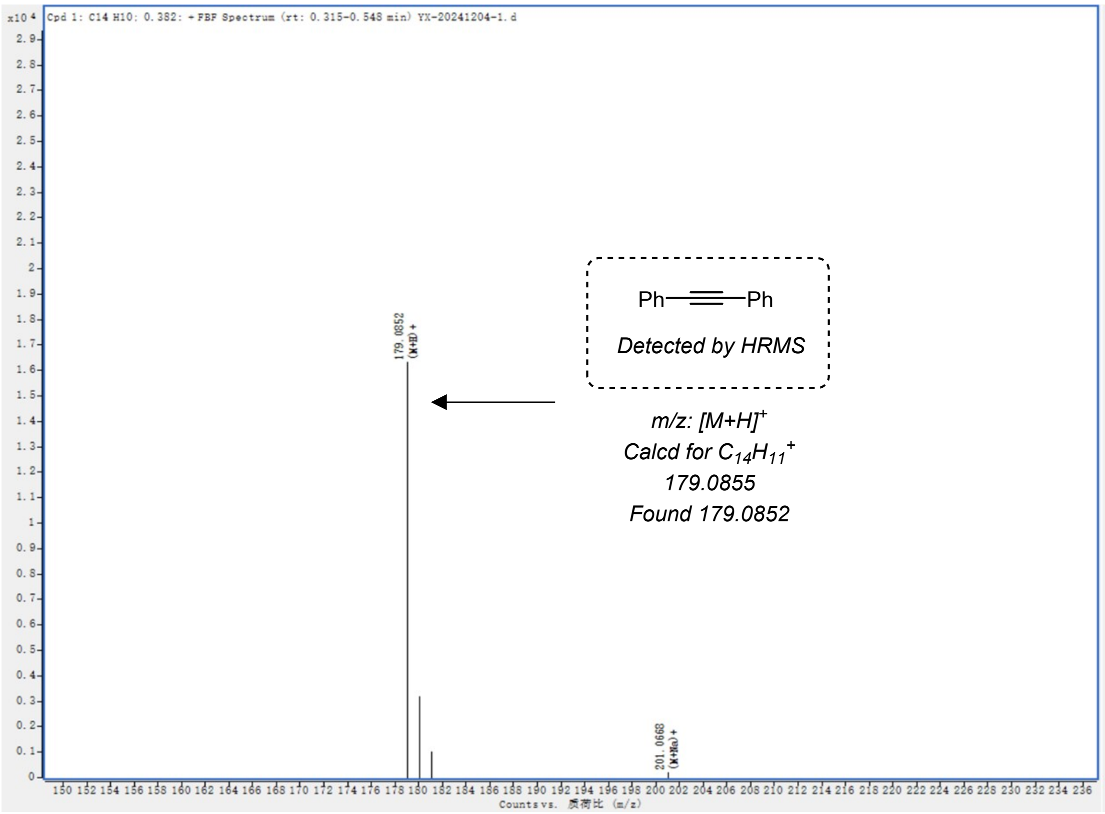
Figure S1. HRMS analysis of the radical-trapping experiment

5a **2a** **10, 70%**

To a Schlenk flask containing β-pinene (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv) in 2 mL of DMC was added BPO (0.06 mmol, 30 mol%) under nitrogen atmosphere. The flask was immersed in an oil bath and heated at 85 °C for 10 h. Then the reaction mixture was quenched by water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. Column chromatography on silica gel (petroleum ethers) gave 43 mg (70% yield) of **(3-methyl-3-(4-(2,2,2-trifluoroethyl)cyclohex-3-en-1-yl)but-1-yn-1-yl)benzene** (**10**) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** *δ* 7.45-7.38 (m, 2H), 7.33-7.26 (m, 3H), 5.69-5.69 (m, 1H), 2.76 (m, 2H), 2.28-2.24 (m, 1H), 2.22-2.00 (m, 4H), 1.53-1.48 (m, 1H), 1.47-1.40 (m, 1H), 1.29 (s, 3H), 1.27 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** *δ* 131.6, 128.9, 128.1, 127.5, 127.4 (q, *J* = 2.6 Hz), 126.2 (q, *J* = 278.7 Hz), 124.0, 96.1, 81.2, 43.3, 41.7 (q, *J* = 28.9 Hz), 34.6, 29.7, 27.8, 27.2, 26.9, 24.6 ; **^{19}F NMR (565 MHz, $CDCl_3$)** *δ* -64.76; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{21}F_3+Na^+$: 329.1488; found 329.1488.



To a Schlenk flask containing **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv) in 2 mL of DMC was added BPO (0.06 mmol, 30 mol%) under nitrogen atmosphere. The flask was immersed in an oil bath and heated at 85 °C for 10 h. The crude product was analyzed by HRMS. The compounds **11** and **12** was detected.[4]



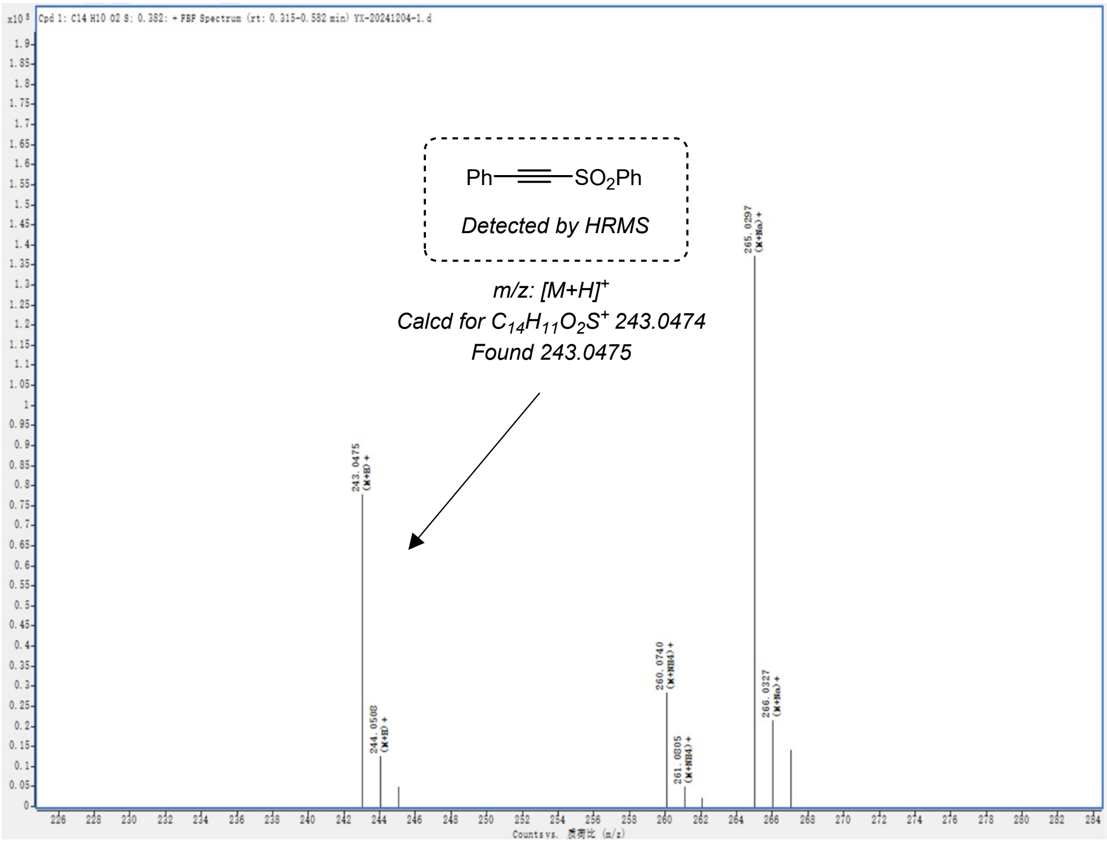
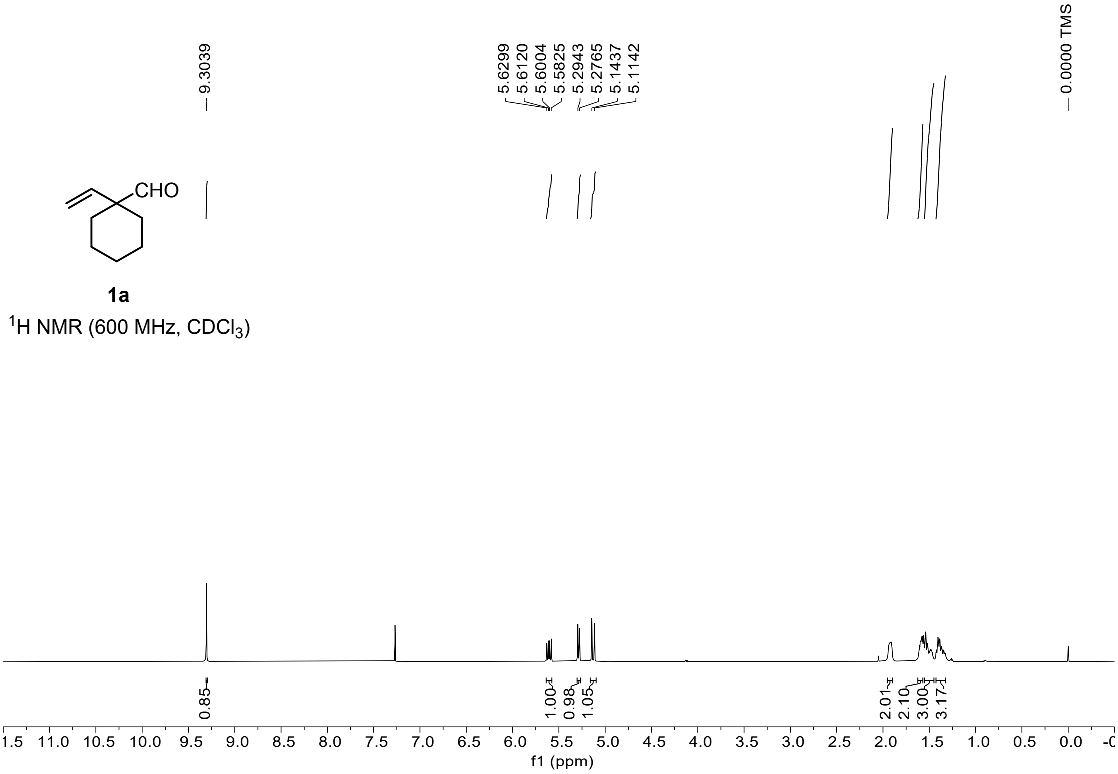
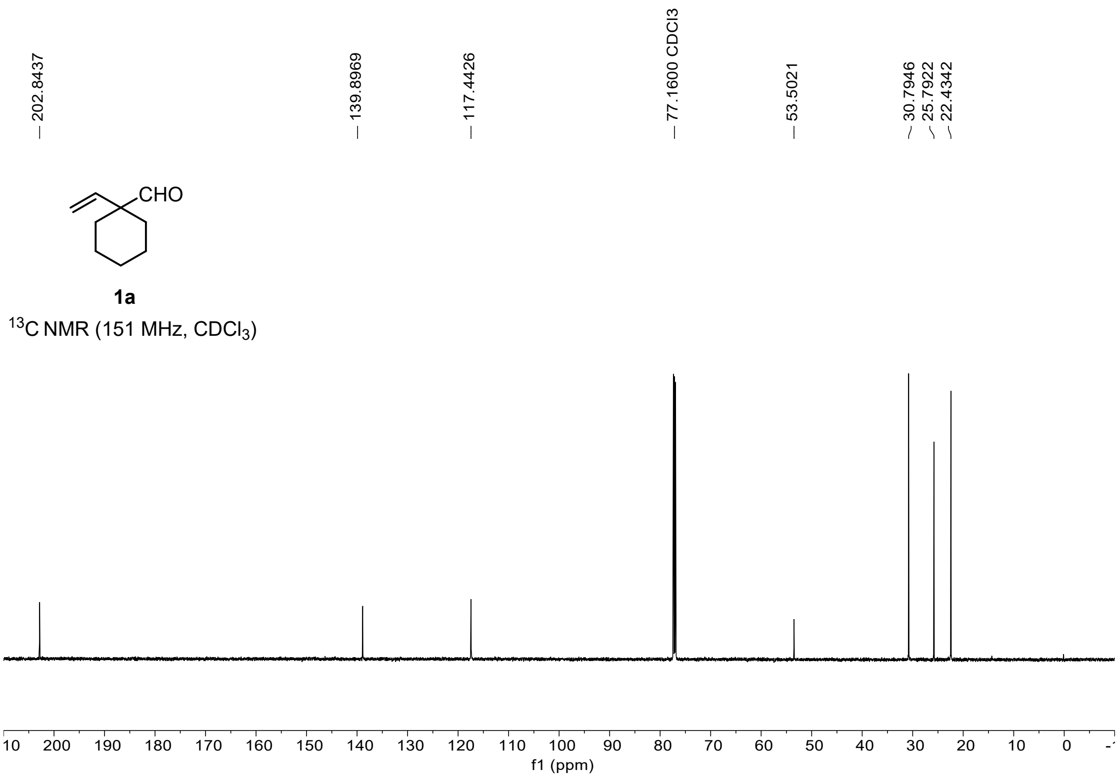
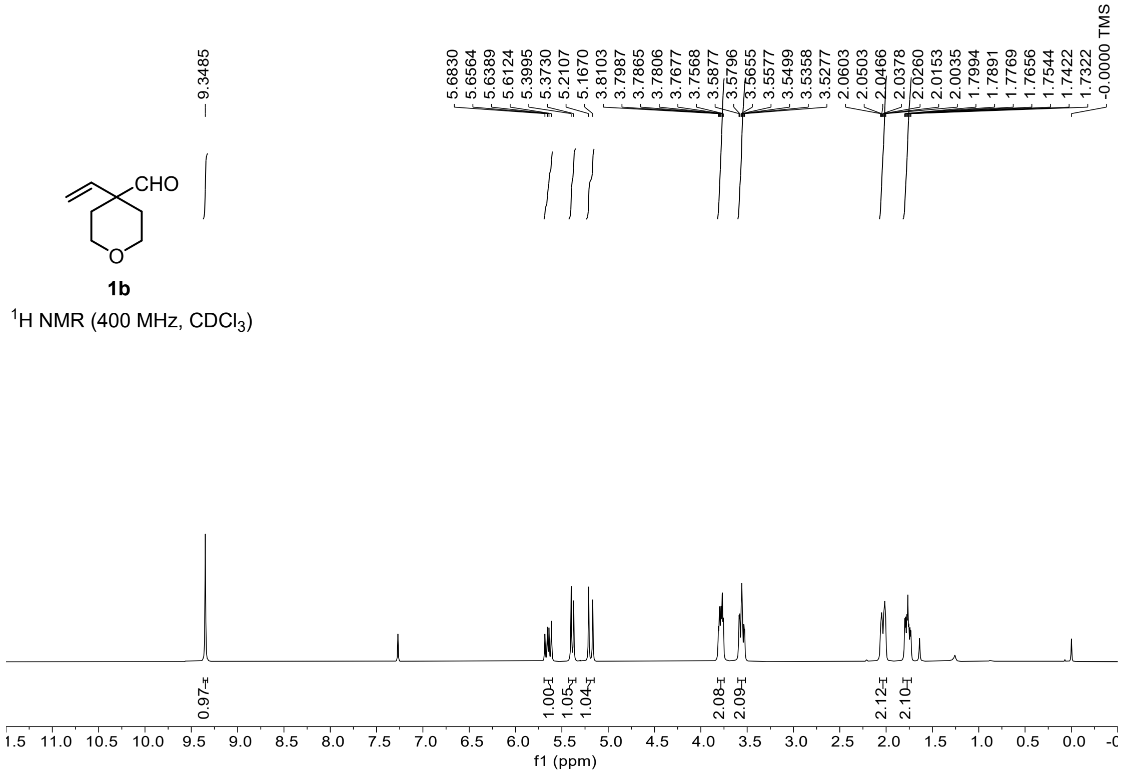


Figure S2. HRMS analysis of the model reaction

7. NMR Spectra

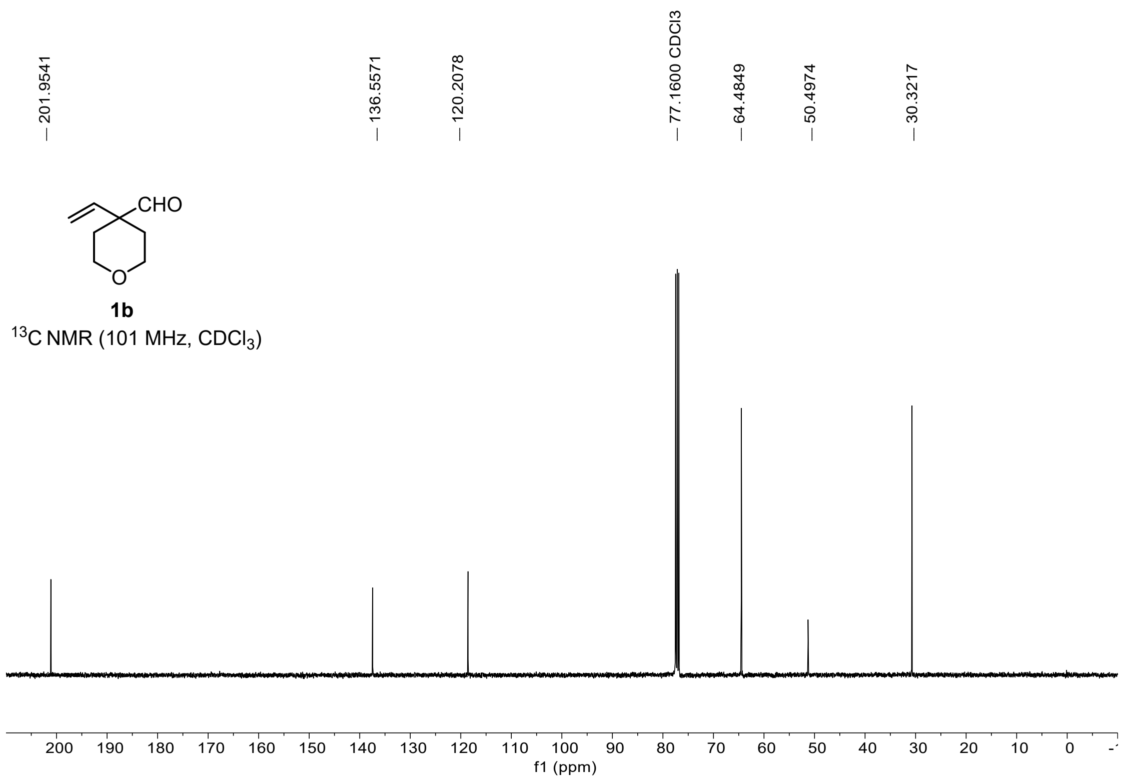






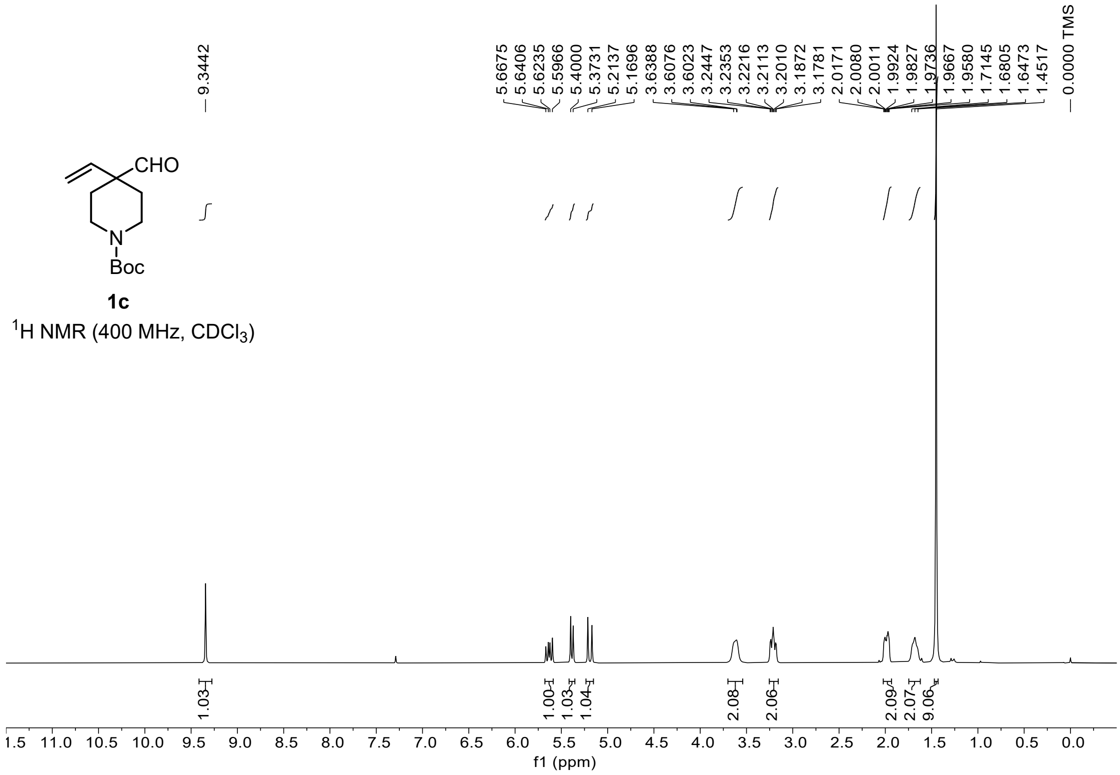
1b

^{1}H NMR (400 MHz, $CDCl_3$)

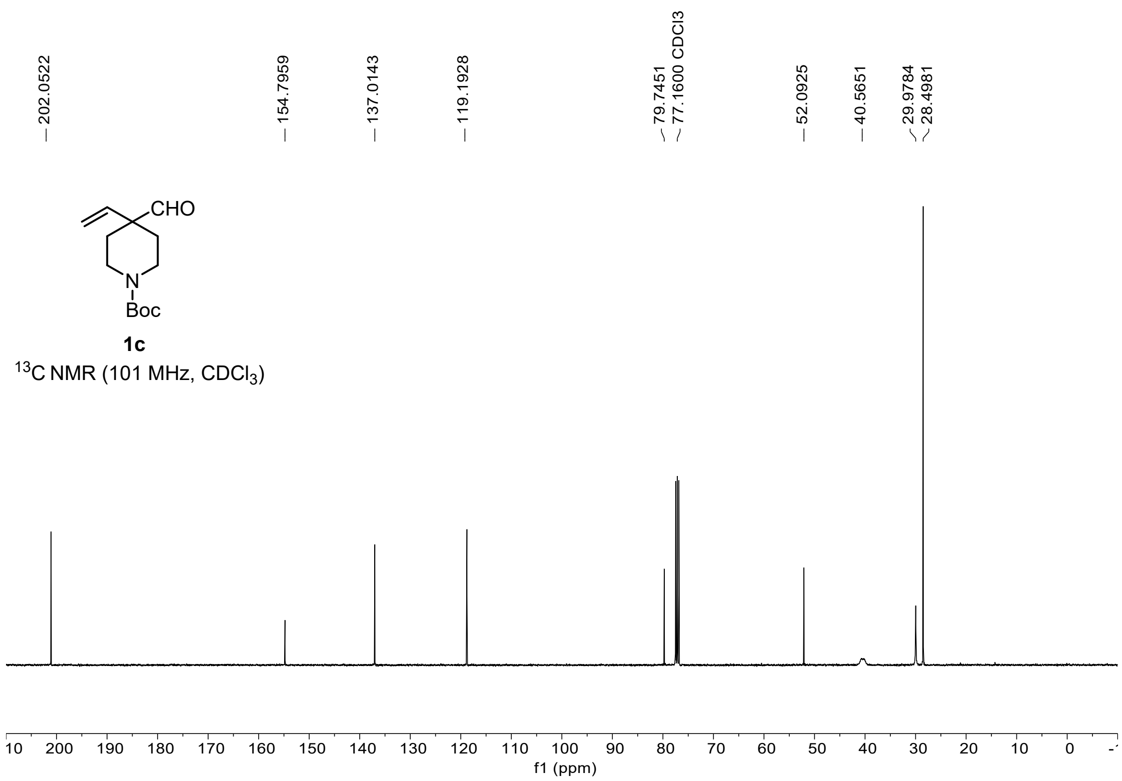


1b

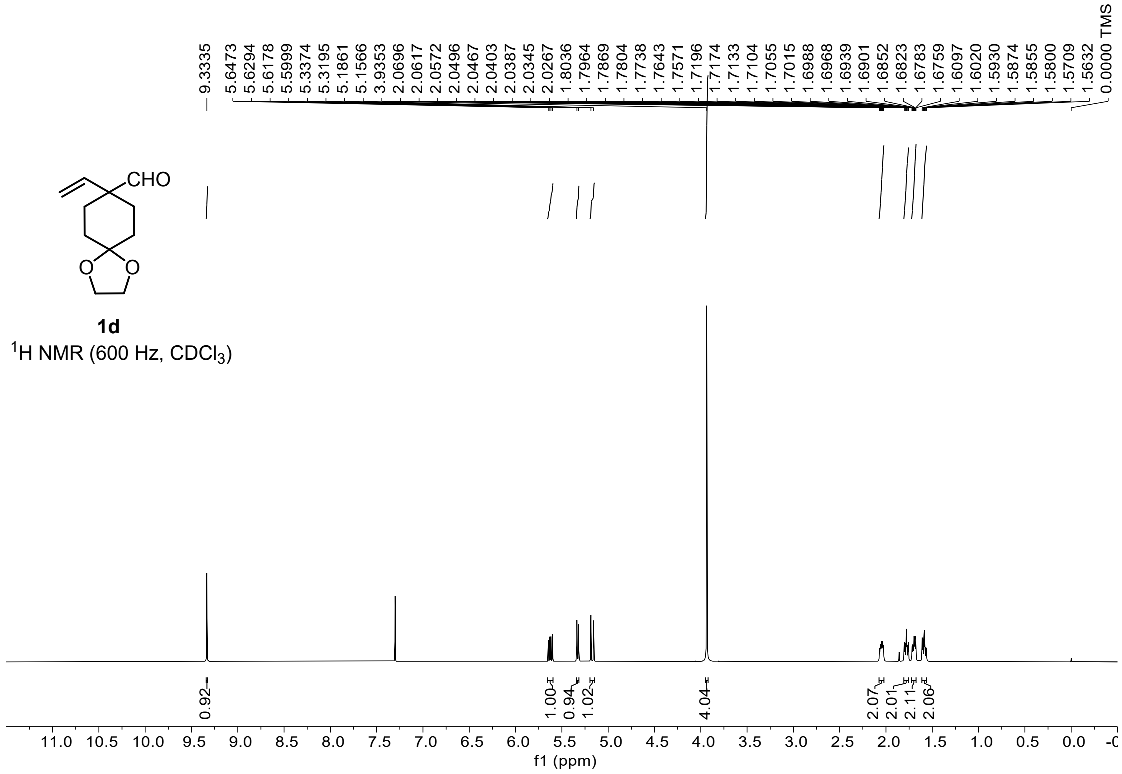
^{13}C NMR (101 MHz, $CDCl_3$)



9.3442
5.6675
5.6406
5.6235
5.5966
5.4000
5.3731
5.2137
5.1696
3.6388
3.6076
3.6023
3.2447
3.2353
3.2216
3.2113
3.2010
3.1872
3.1781
2.0171
2.0080
2.0011
1.9924
1.9827
1.9736
1.9667
1.9580
1.7145
1.6805
1.6473
1.4517
0.0000 TMS
CHO
N
Boc
1c
^{1}H NMR (400 MHz, $CDCl_3$)
1.03
1.00
1.03
1.04
2.08
2.06
2.09
2.07
9.06
f1 (ppm)

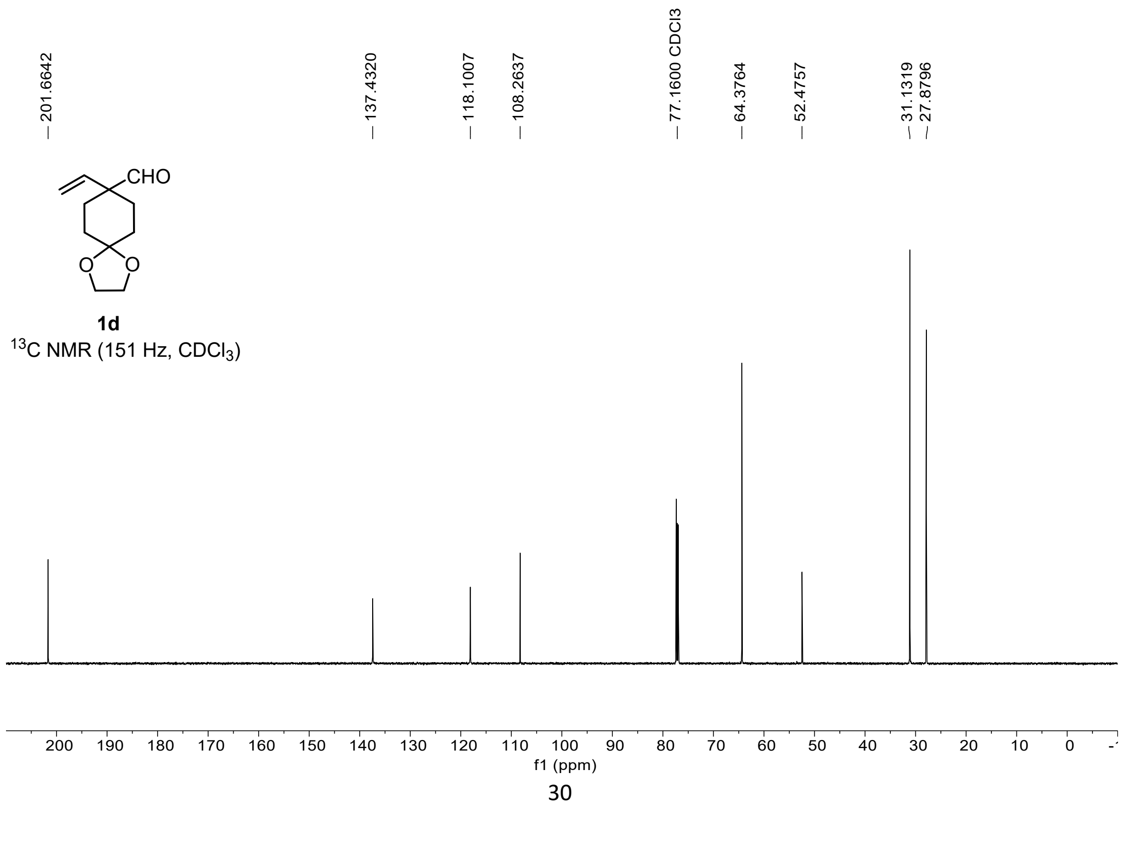


202.0522
154.7959
137.0143
119.1928
79.7451
77.1600 CDCl3
52.0925
40.5651
29.9784
28.4981
CHO
N
Boc
1c
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)



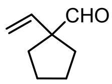
1d

^{1}H NMR (600 Hz, $CDCl_3$)



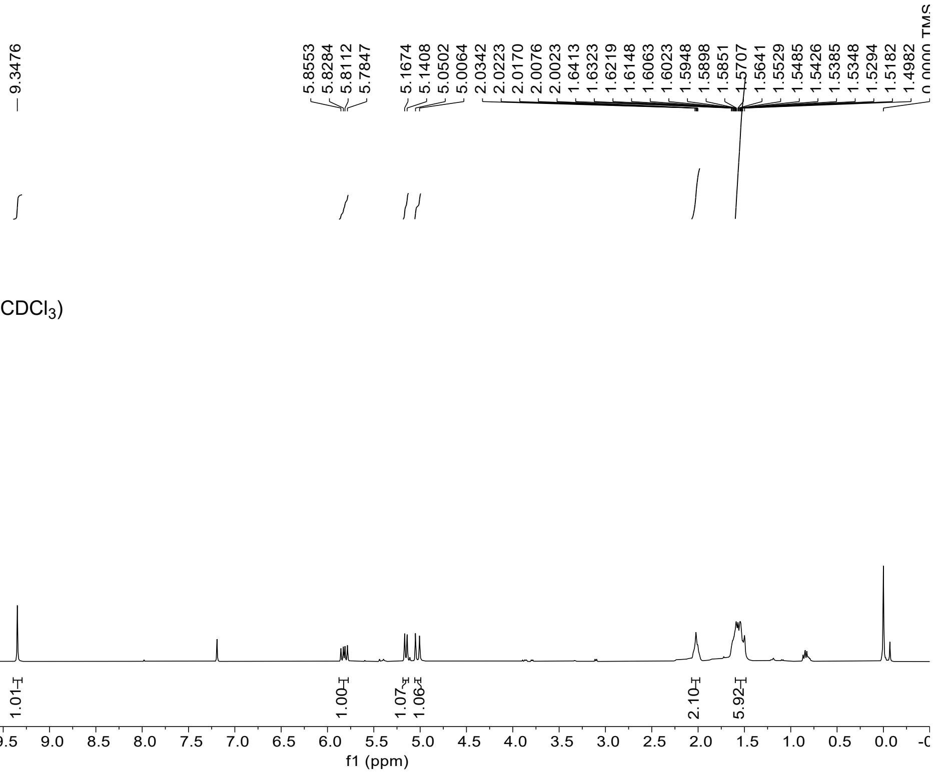
1d

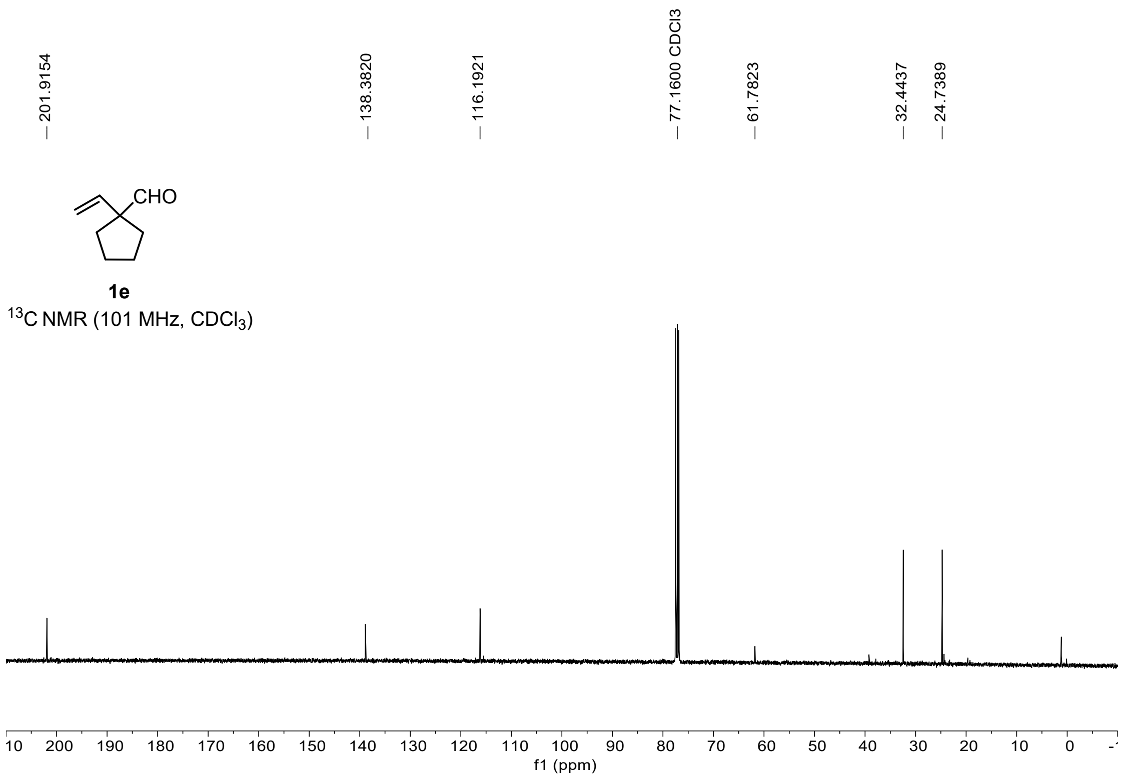
^{13}C NMR (151 Hz, $CDCl_3$)

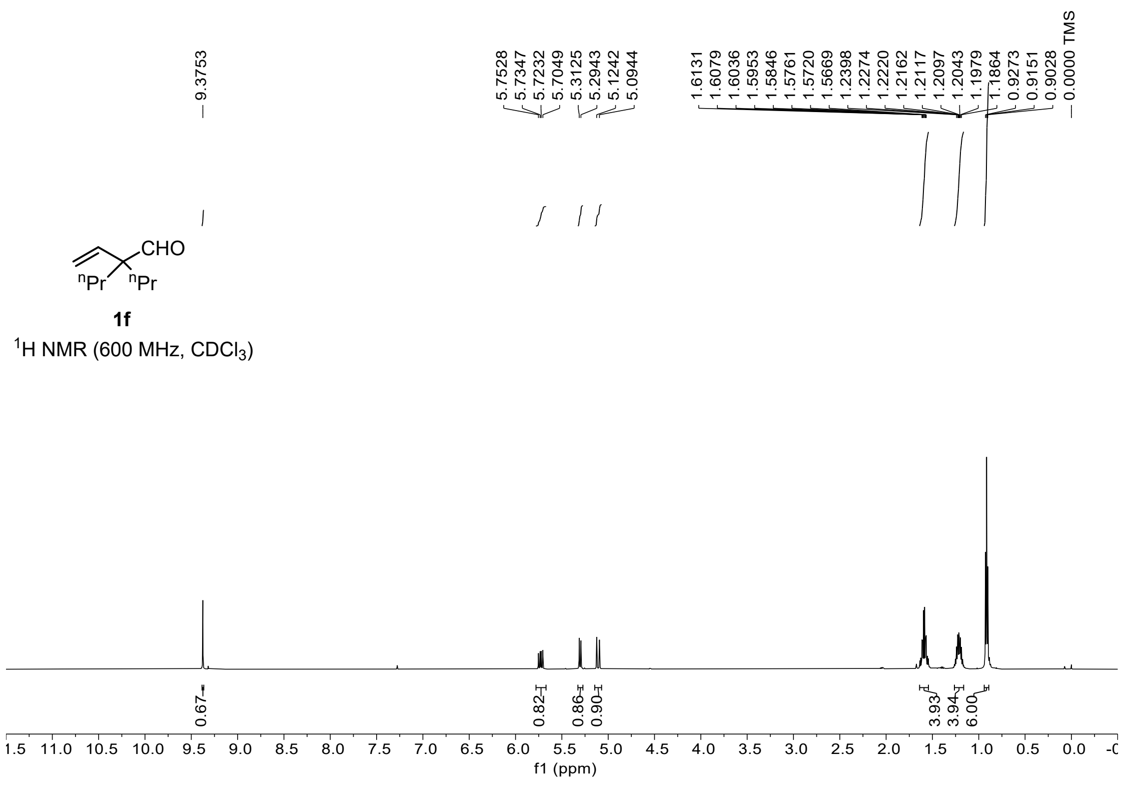


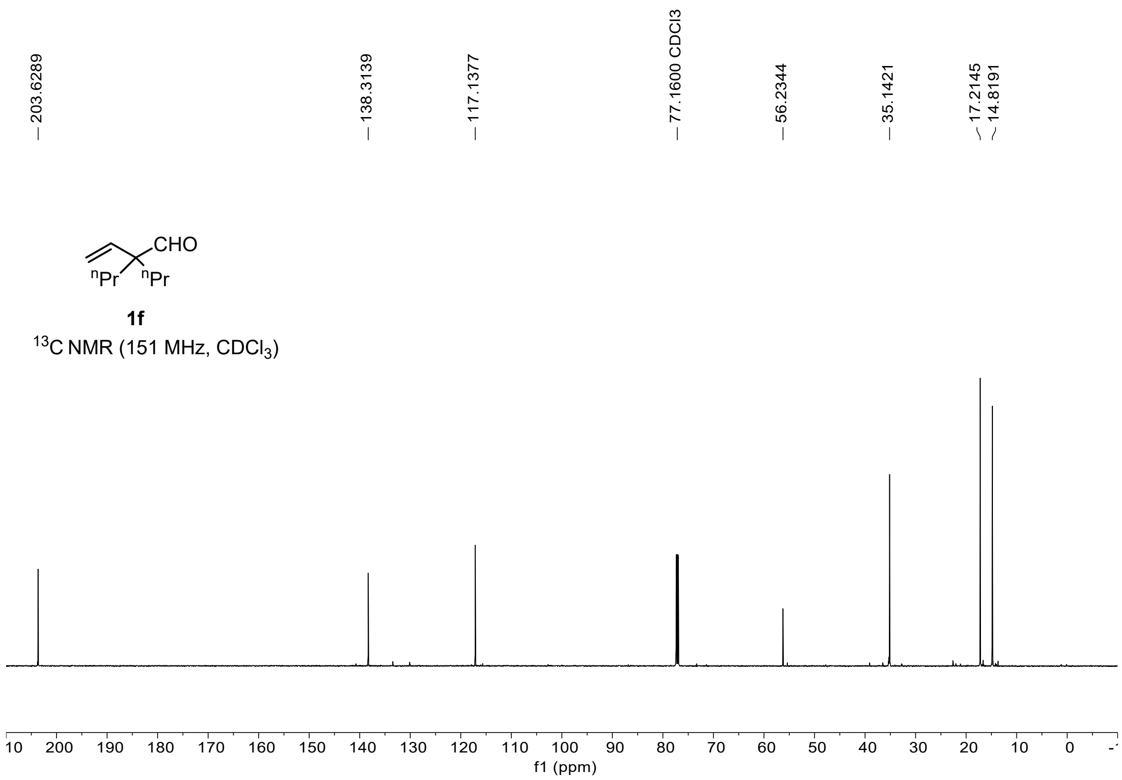
1e

^{1}H NMR (400 MHz, $CDCl_3$)



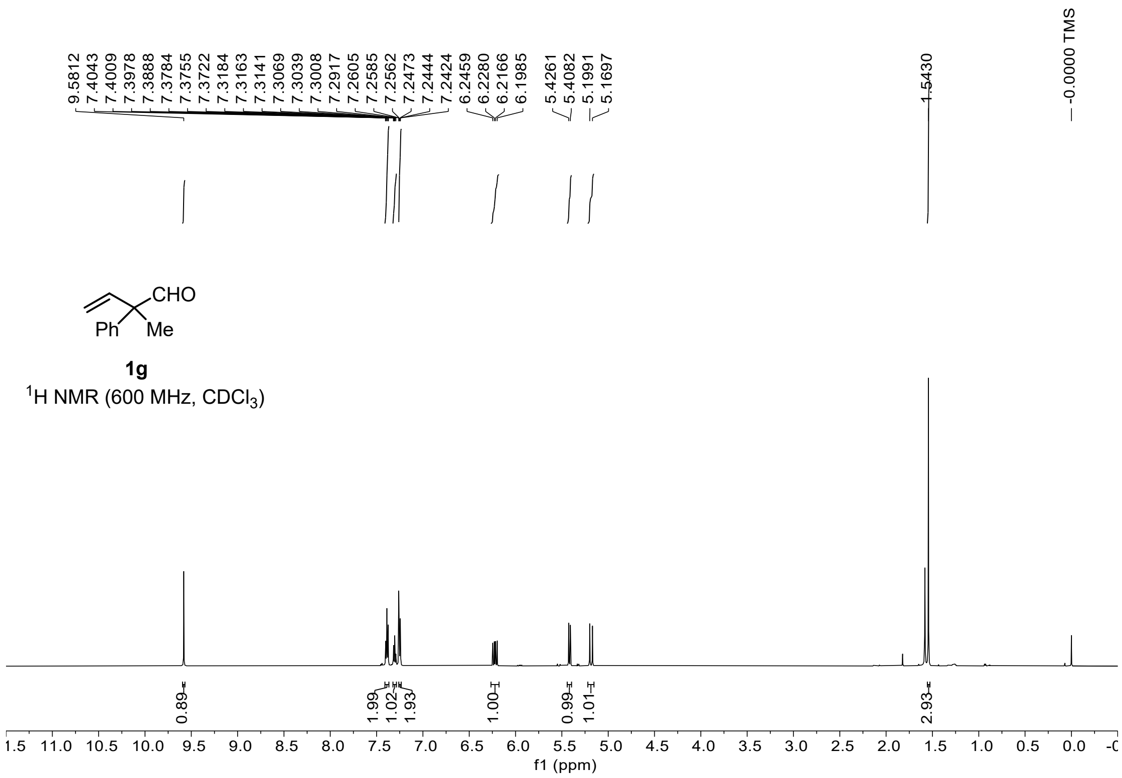

201.9154
138.3820
116.1921
77.1600 CDCl3
61.7823
32.4437
24.7389
CHO
1e
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

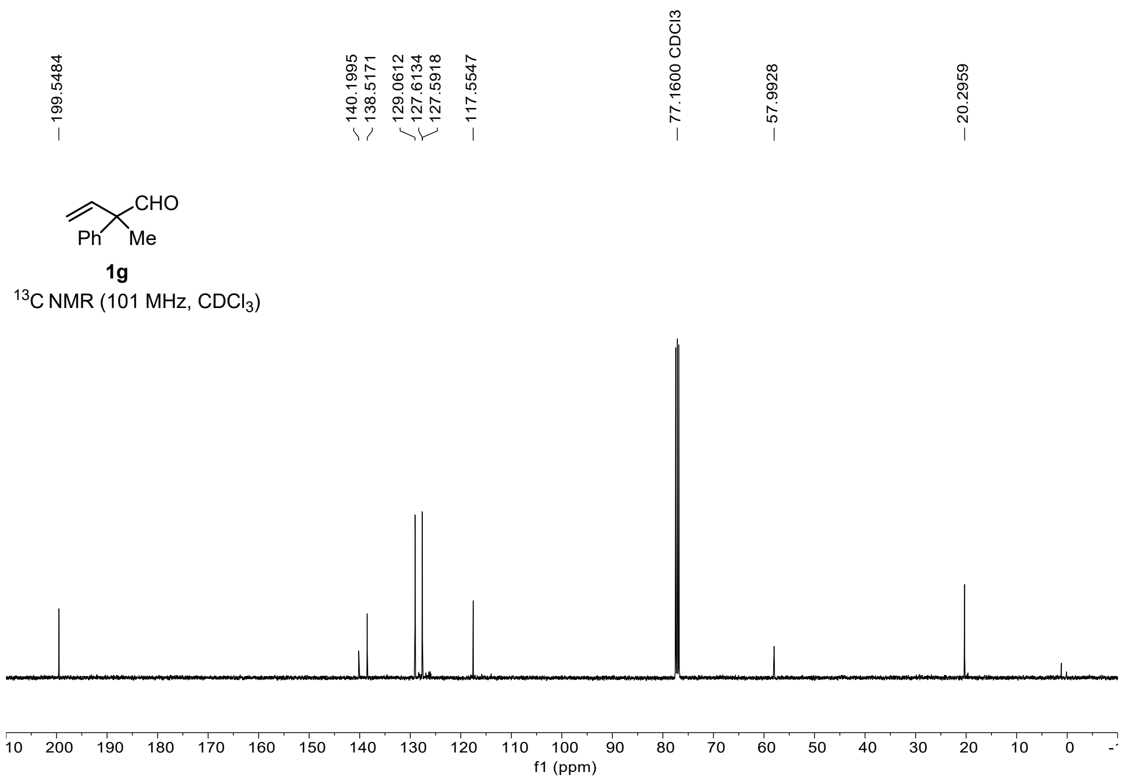

9.3753
5.7528
5.7347
5.7232
5.7049
5.3125
5.2943
5.1242
5.0944
1.6131
1.6079
1.6036
1.5953
1.5846
1.5761
1.5720
1.5669
1.2398
1.2274
1.2220
1.2162
1.2117
1.2097
1.2043
1.1979
1.1864
0.9273
0.9151
0.9028
0.0000 TMS
CHO
^{n}Pr ^{n}Pr
1f
^{1}H NMR (600 MHz, CDCl$_3$)
0.67
0.82
0.86
0.90
3.93
3.94
6.00
f1 (ppm)



1f

^{13}C NMR (151 MHz, $CDCl_3$)


9.5812
7.4043
7.4009
7.3978
7.3888
7.3784
7.3755
7.3722
7.3184
7.3163
7.3141
7.3069
7.3039
7.3008
7.2917
7.2605
7.2585
7.2562
7.2473
7.2444
7.2424
6.2459
6.2280
6.2166
6.1985
5.4261
5.4082
5.1991
5.1697
1.5430
-0.0000 TMS
CHO
Ph
Me
1g
1H NMR (600 MHz, CDCl3)
0.89
1.99
1.02
1.93
1.00
0.99
1.01
2.93
f1 (ppm)


199.5484
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129.0612
127.6134
127.5918
117.5547
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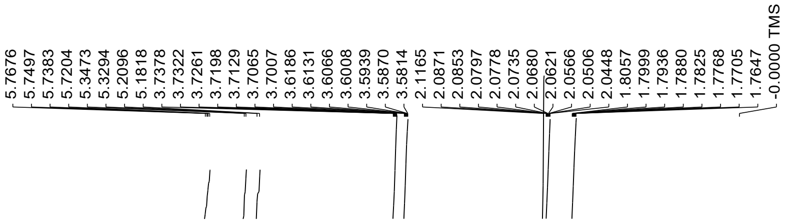
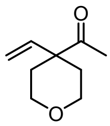
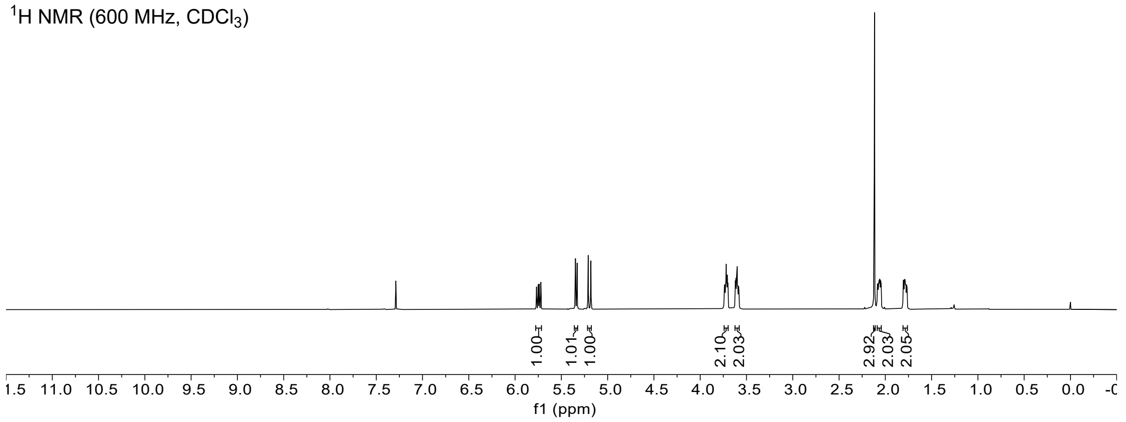
57.9928
20.2959
CHO
Ph
Me
1g
13C NMR (101 MHz, CDCl3)
f1 (ppm)

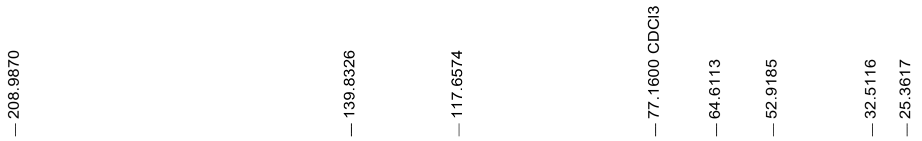


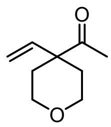


1h

^{1}H NMR (600 MHz, $CDCl_3$)

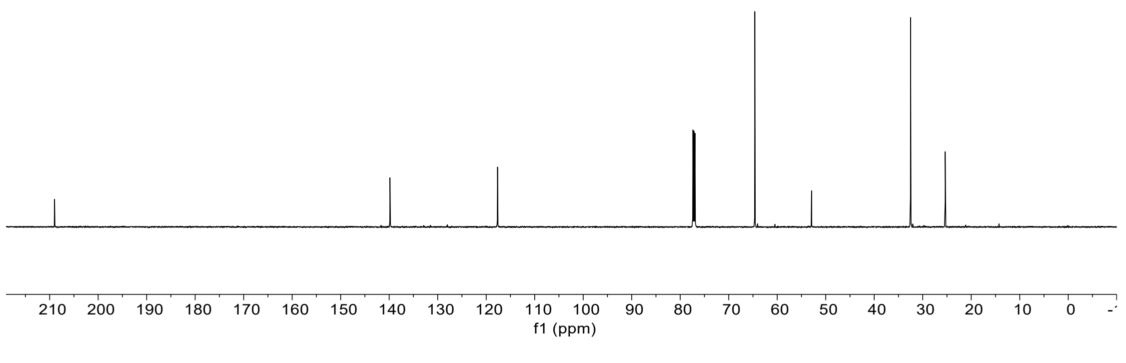


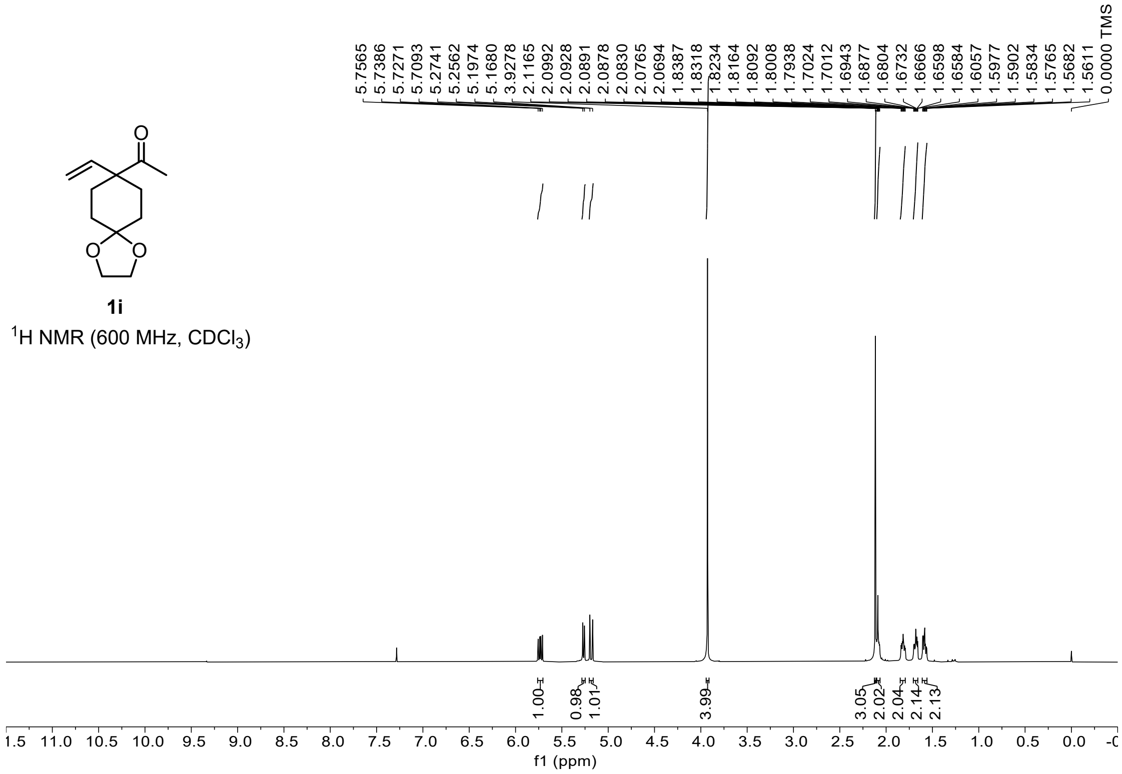




1h

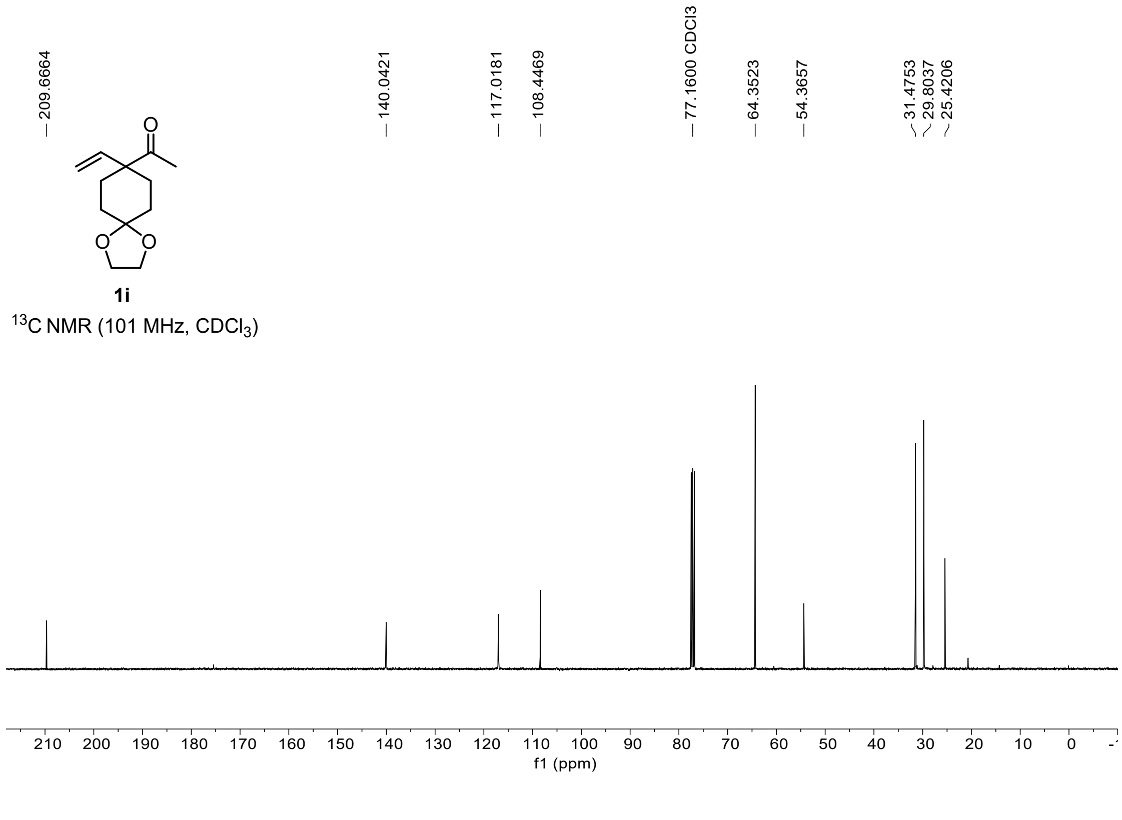
^{13}C NMR (151 MHz, $CDCl_3$)





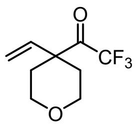
1i

^{1}H NMR (600 MHz, $CDCl_3$)



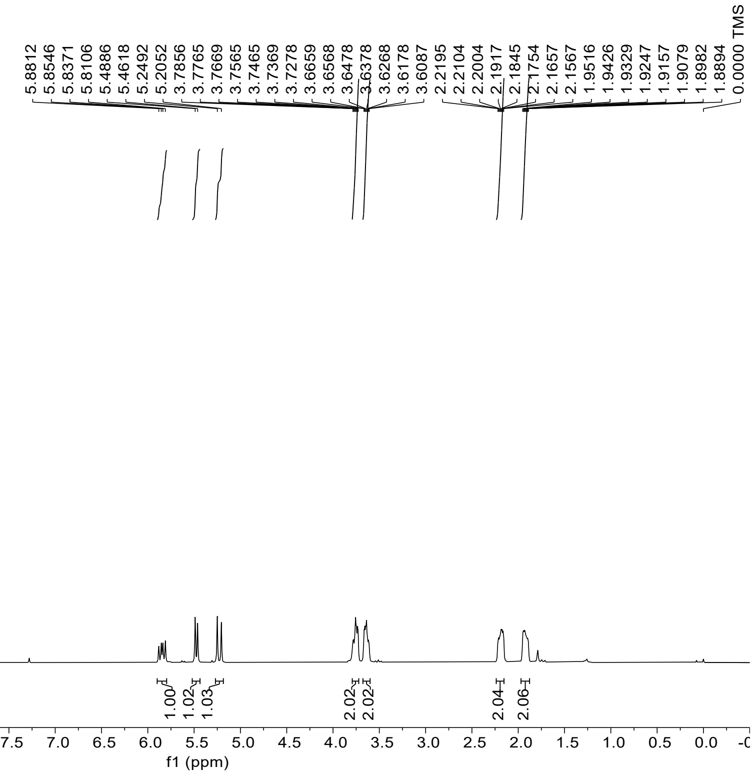
1i

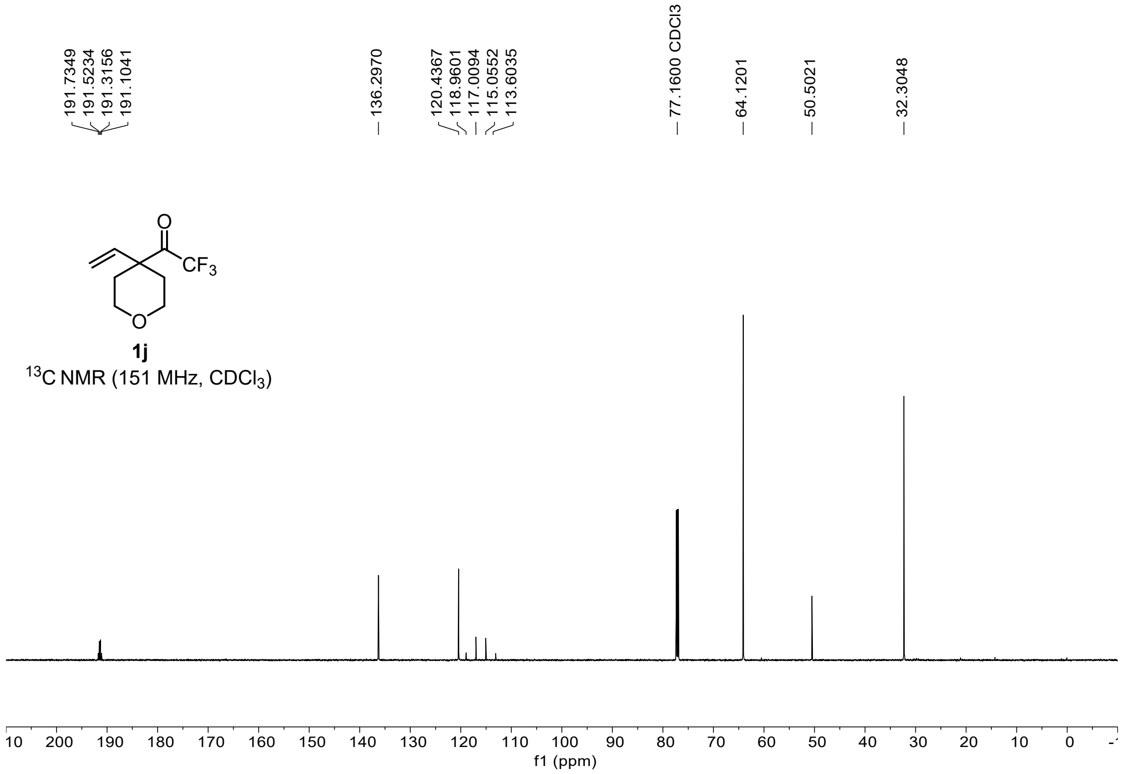
^{13}C NMR (101 MHz, $CDCl_3$)

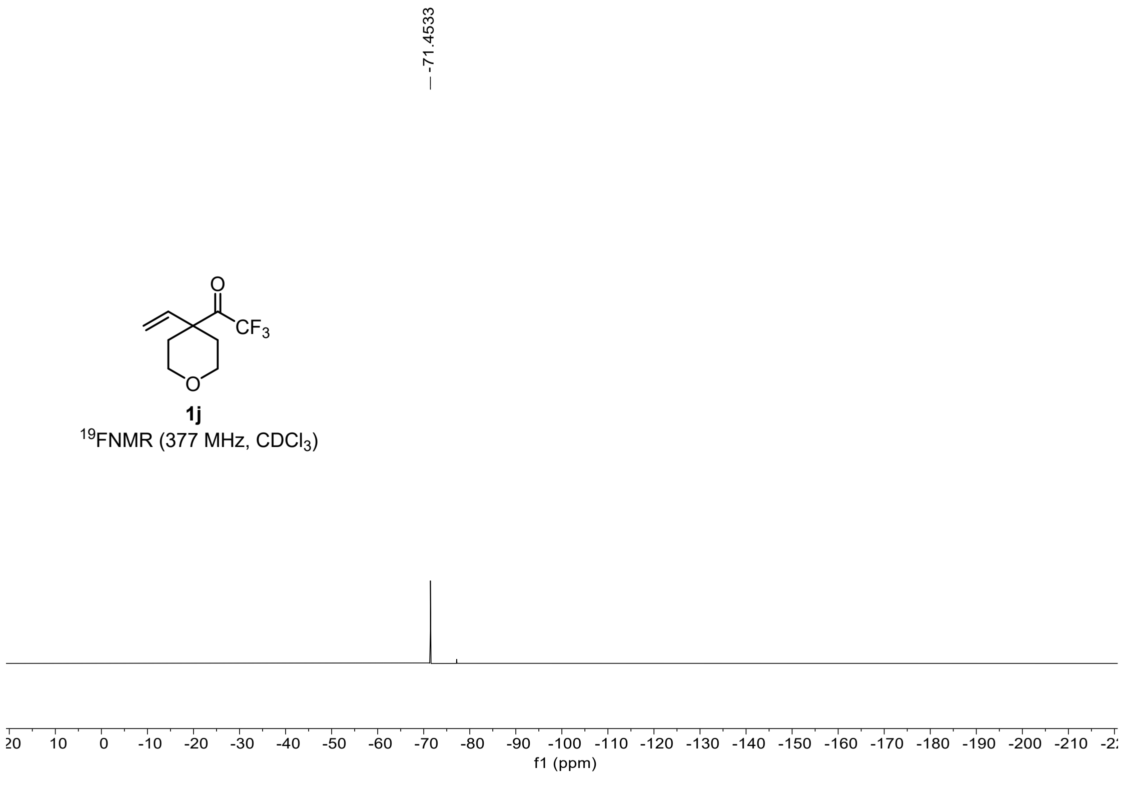


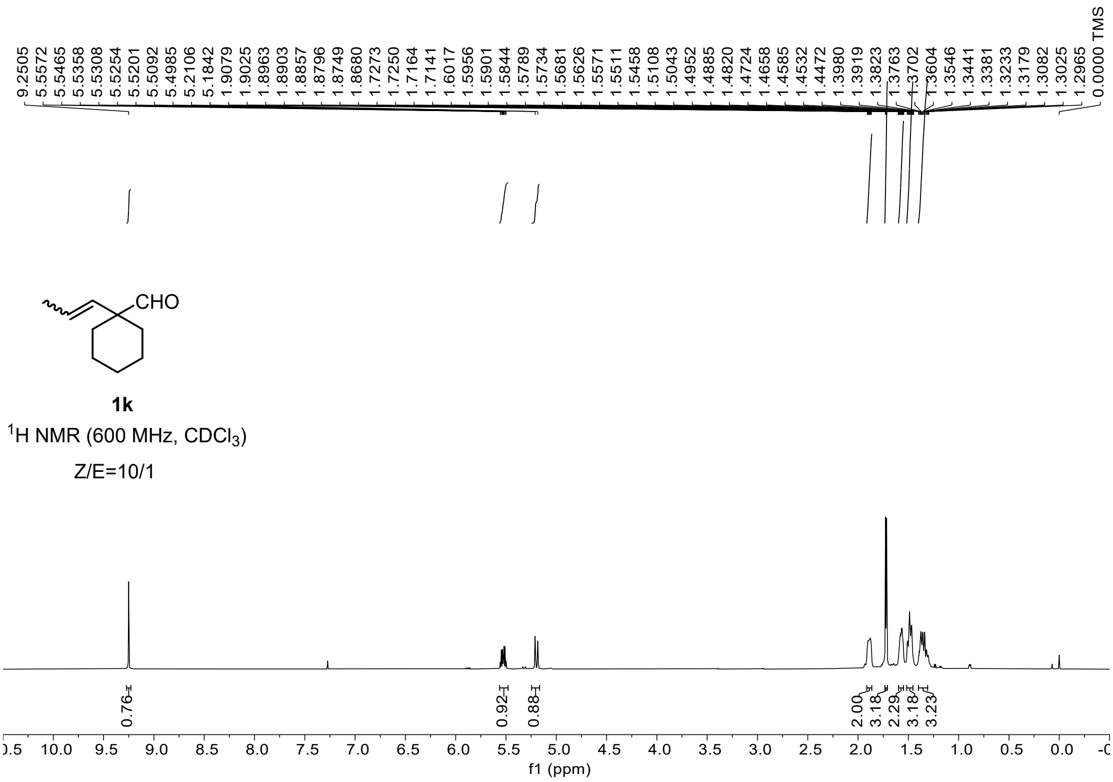
1j

^1H NMR (400 MHz, $CDCl_3$)




191.7349
191.5234
191.3156
191.1041
136.2970
120.4367
118.9601
117.0094
115.0552
113.6035
77.1600 CDCl3
64.1201
50.5021
32.3048
O
CF3
O
1j
13C NMR (151 MHz, CDCl3)
f1 (ppm)


-71.4533
O
CF3
O
1j
19FNMR (377 MHz, CDCl3)
f1 (ppm)

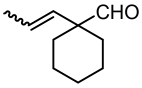


1k

^1H NMR (600 MHz, $CDCl_3$)

Z/E=10/1

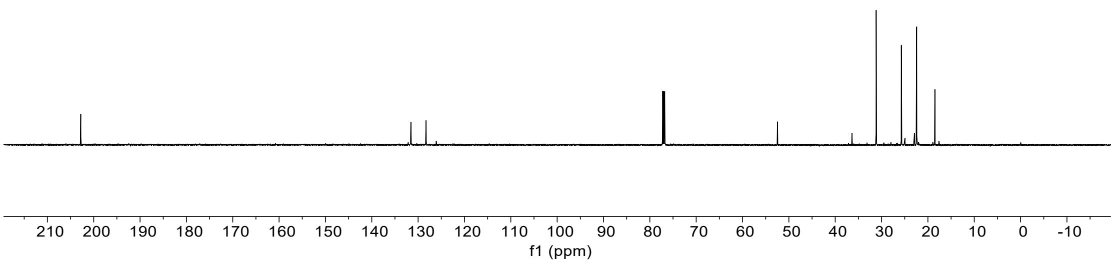
202.7957
131.5632
128.2817
52.4552
31.1587
25.7370
22.4264
18.4996



1k

^{13}C NMR (151 MHz, $CDCl_3$)

Z/E=10/1



5.7146
5.6975
5.6860
5.6689
5.4773
5.4487
5.2004
5.1831
1.9542
1.9502
1.9351
1.9322
1.9262
1.7794
1.7733
1.7664
1.7620
1.7520
1.7487
1.7427
1.7137
1.7083
1.7028
1.6955
1.6914
1.6879
1.6822
1.6749
1.6704
1.6662
1.6610
1.6495
1.6440
1.6353
1.4533
1.4472
1.4313
1.4253
1.4096
1.4036
1.2362
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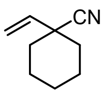
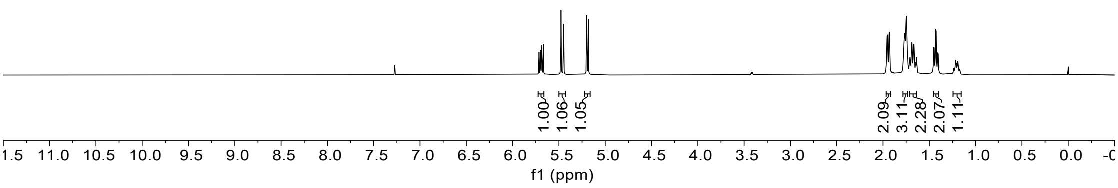
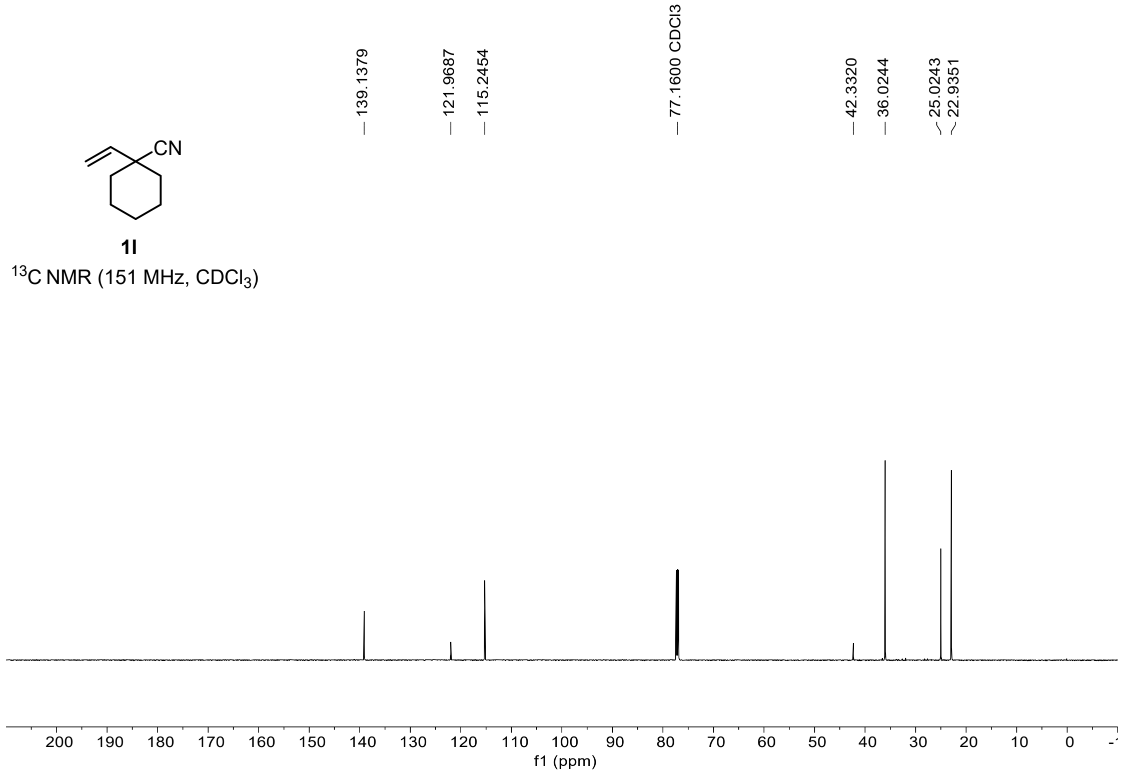
1.1715
0.0000 TMS



1l

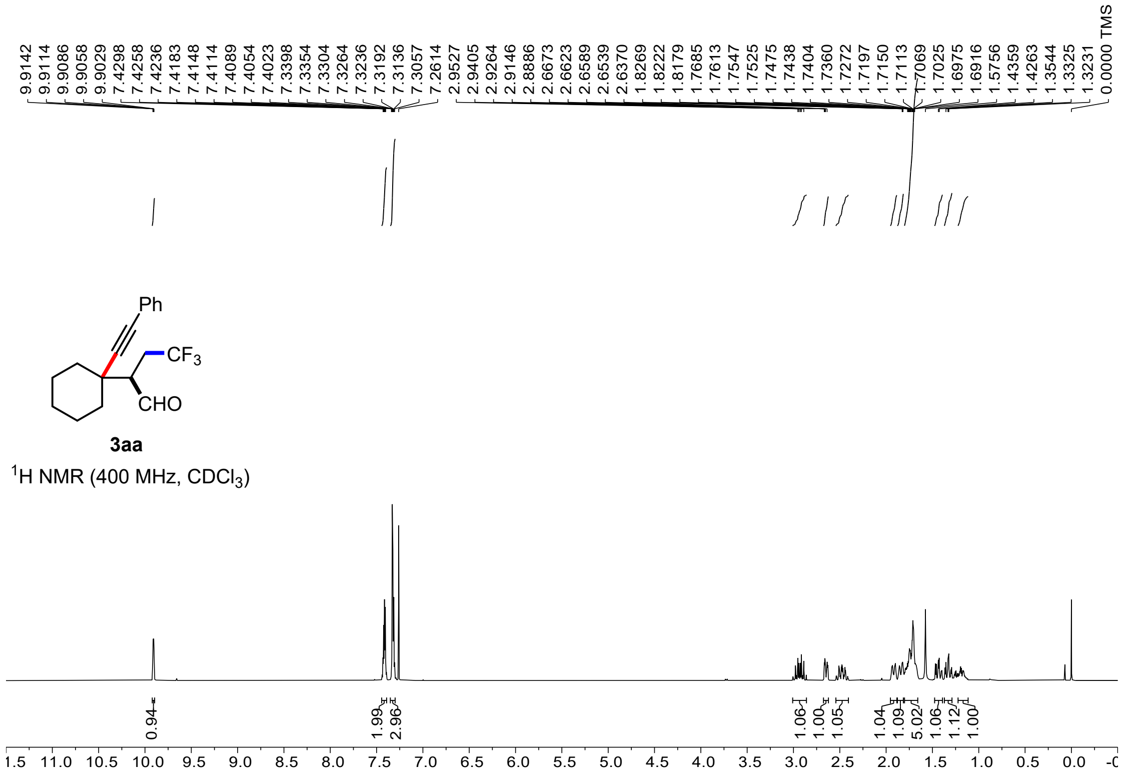
^{1}H NMR (600 MHz, $CDCl_3$)





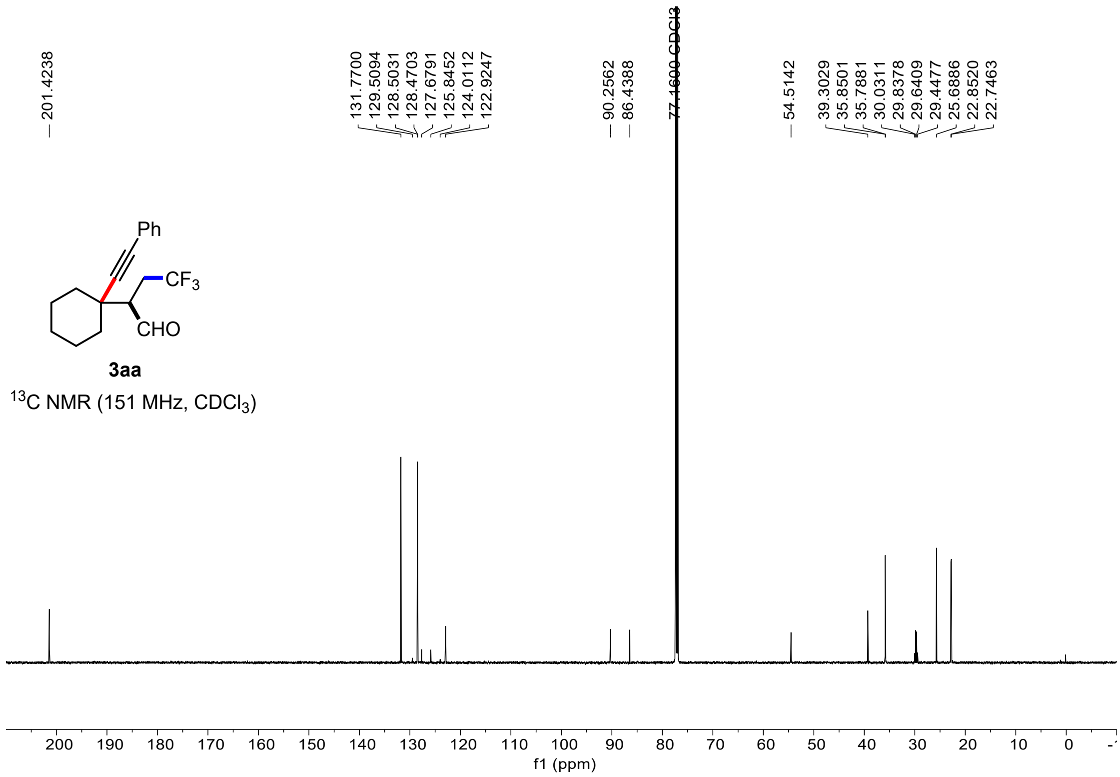
1l

^{13}C NMR (151 MHz, $CDCl_3$)



3aa

^{1}H NMR (400 MHz, $CDCl_3$)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125.8452
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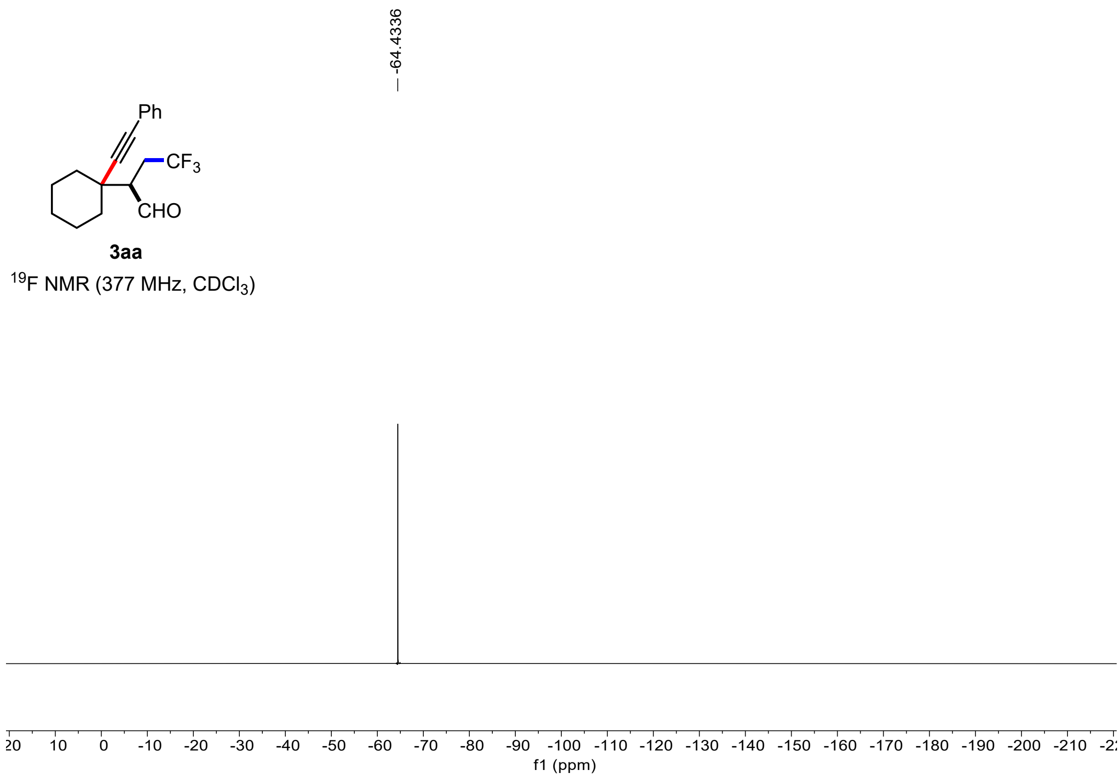
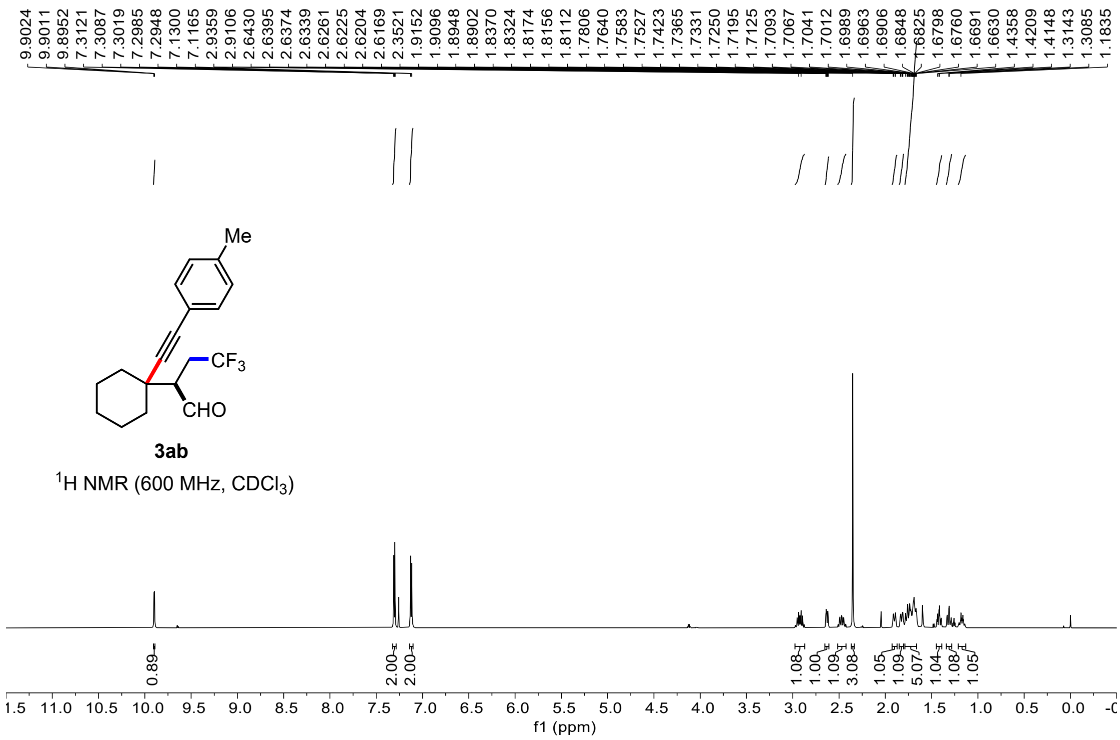
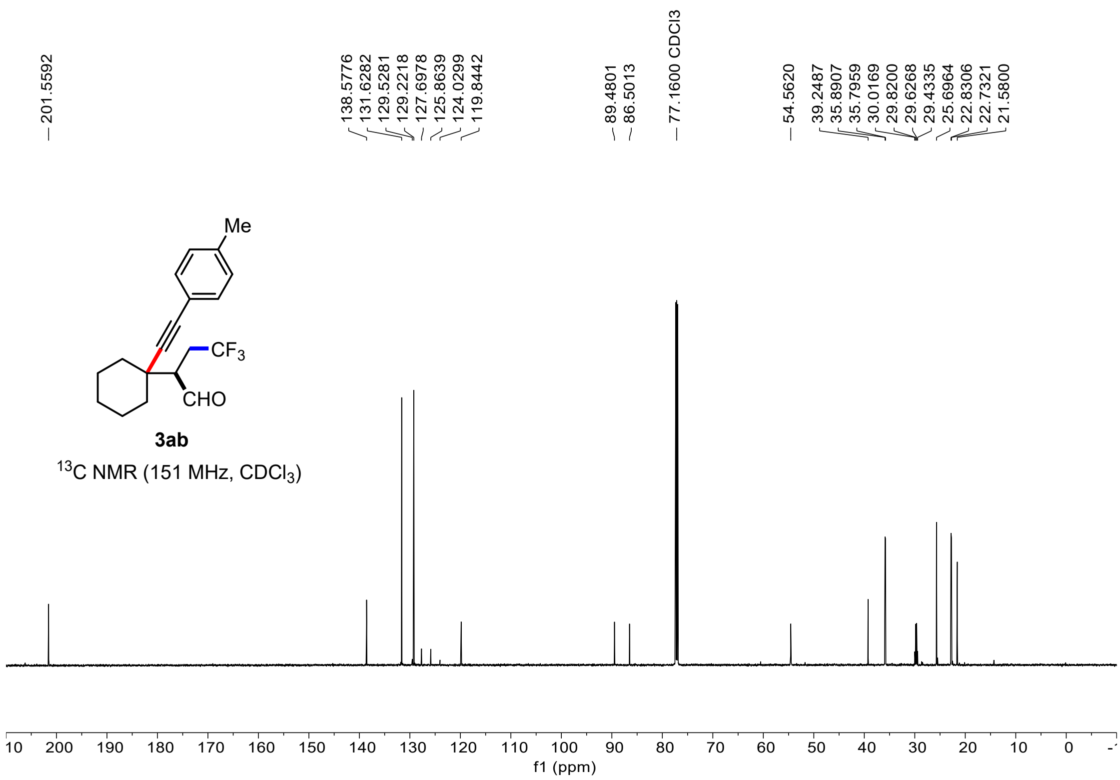
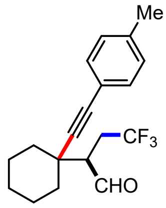
122.9247
90.2562
86.4388
77.1600 CDCl3
54.5142
39.3029
35.8501
35.7881
30.0311
29.8378
29.6409
29.4477
25.6886
22.8520
22.7463
Ph
CF3
CHO
3aa
^{13}C NMR (151 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-64.4336
Ph
CF3
CHO
3aa
^{19}F NMR (377 MHz, CDCl$_3$)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

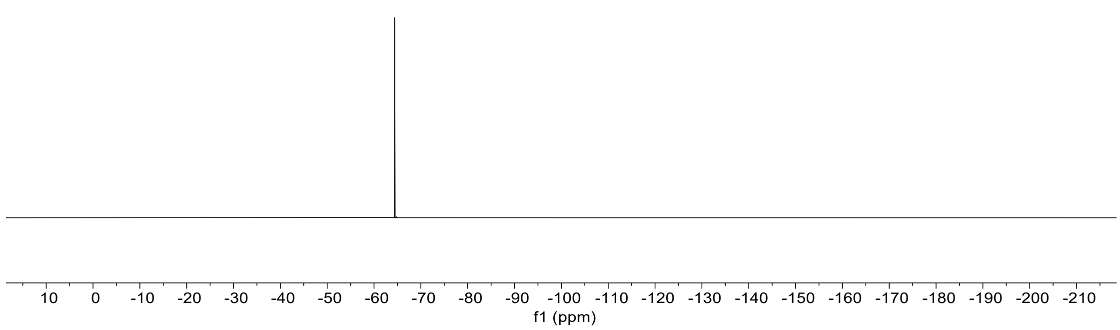

Me
CF3
CHO
3ab
1H NMR (600 MHz, CDCl3)
f1 (ppm)

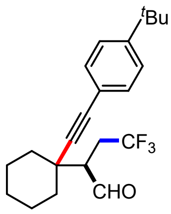

Me
CF3
CHO
3ab
13C NMR (151 MHz, CDCl3)
f1 (ppm)



3ab

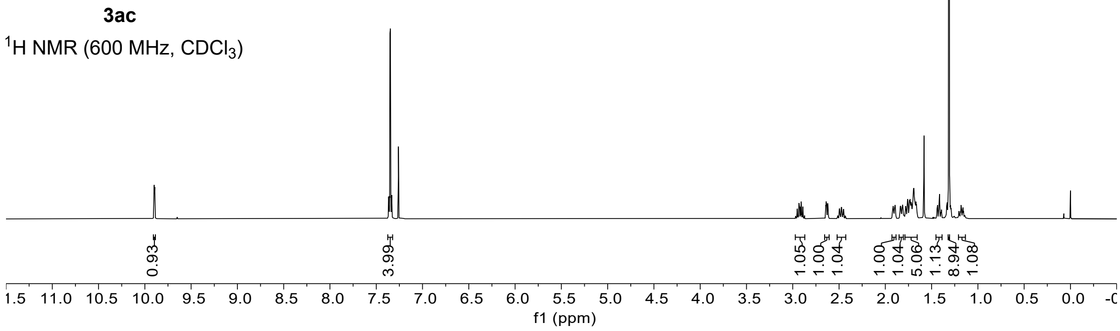
^{19}F NMR (565 MHz, $CDCl_3$)

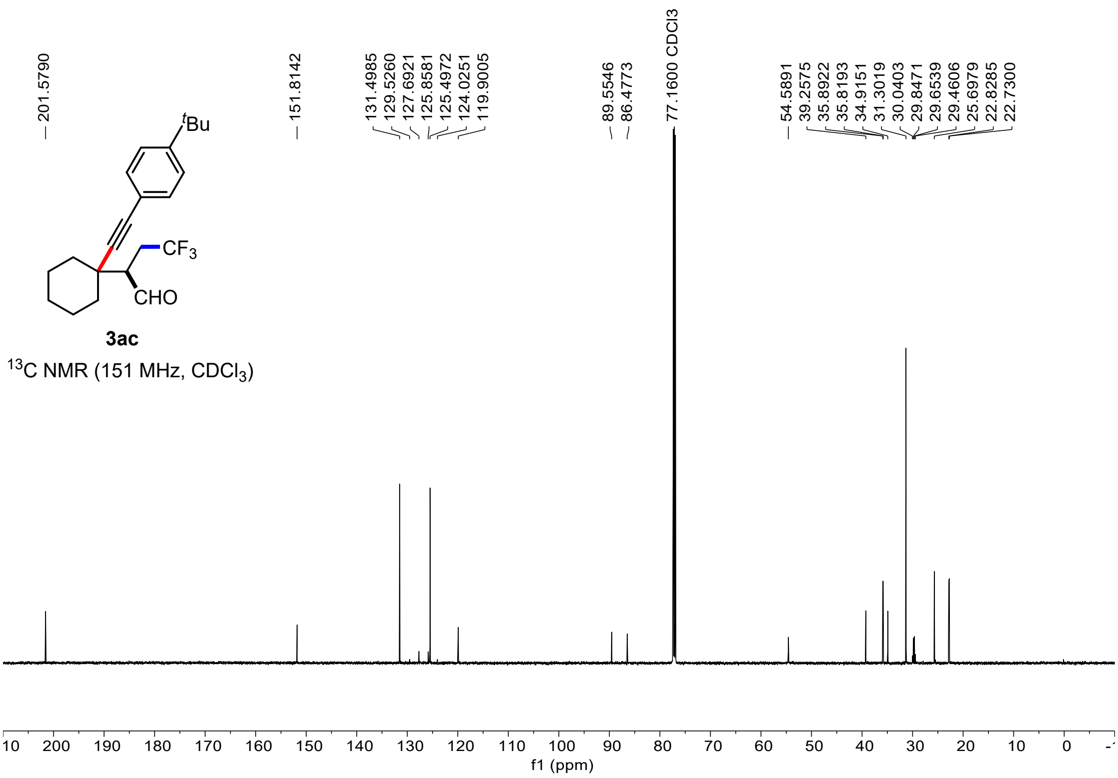




3ac

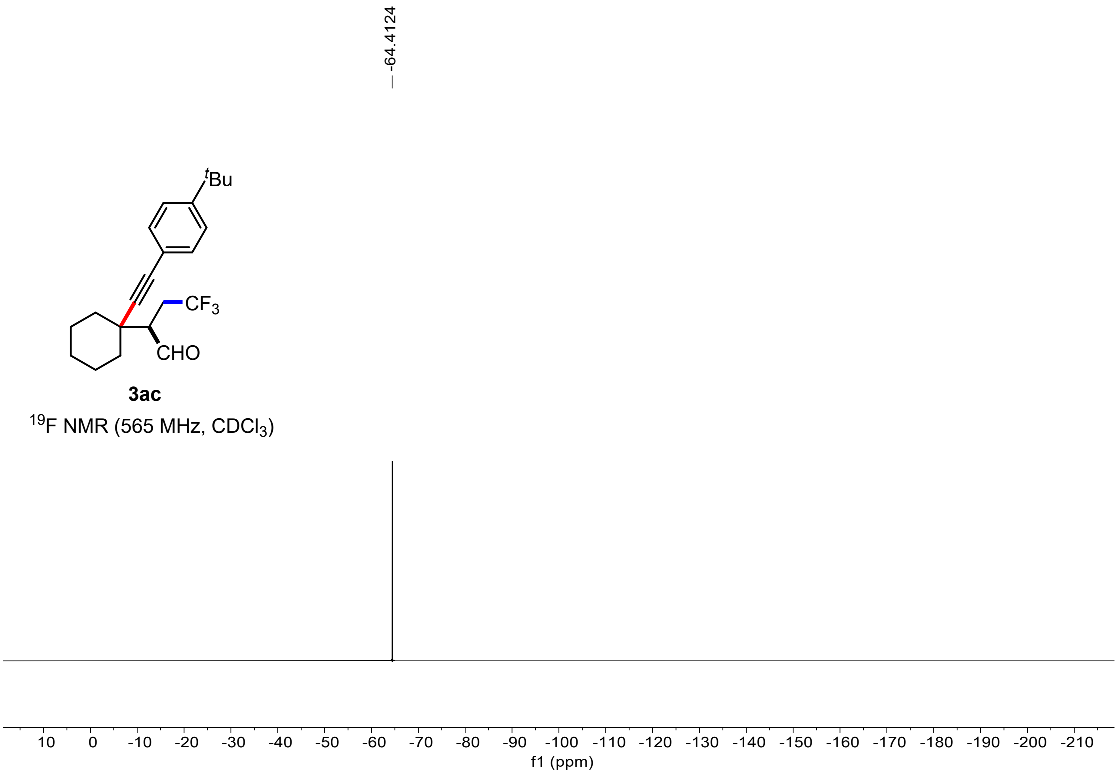
^{1}H NMR (600 MHz, $CDCl_3$)





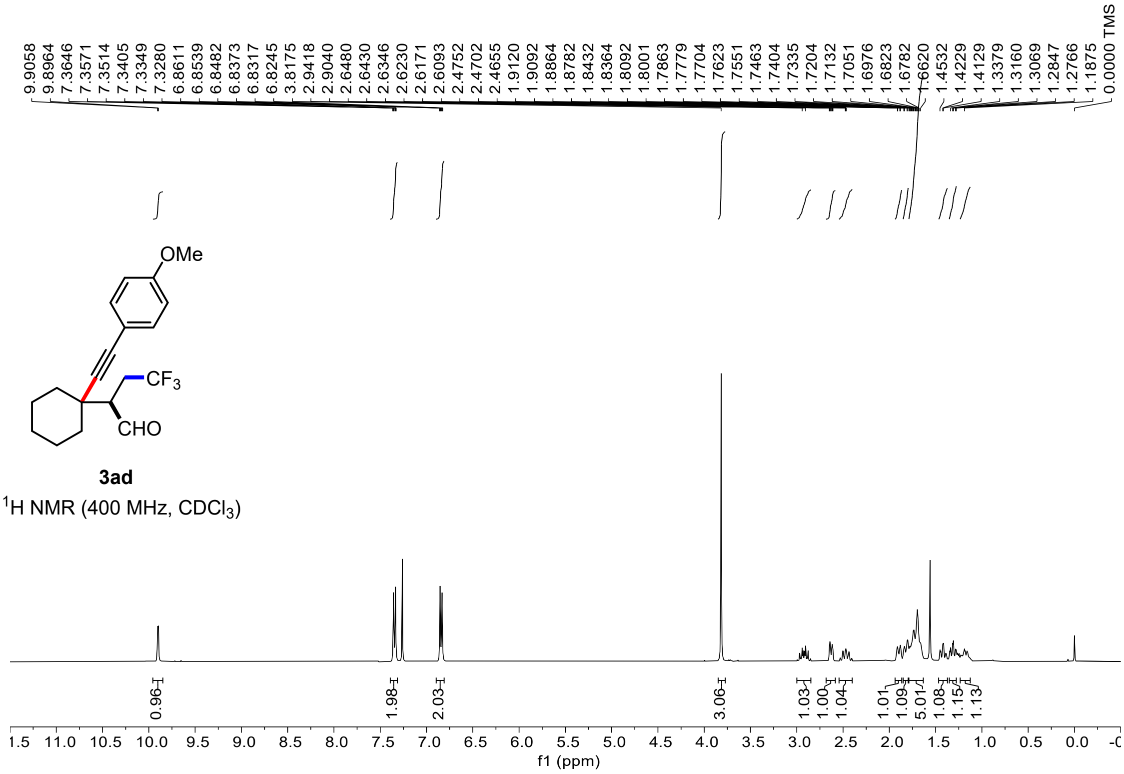
3ac

^{13}C NMR (151 MHz, $CDCl_3$)



3ac

^{19}F NMR (565 MHz, $CDCl_3$)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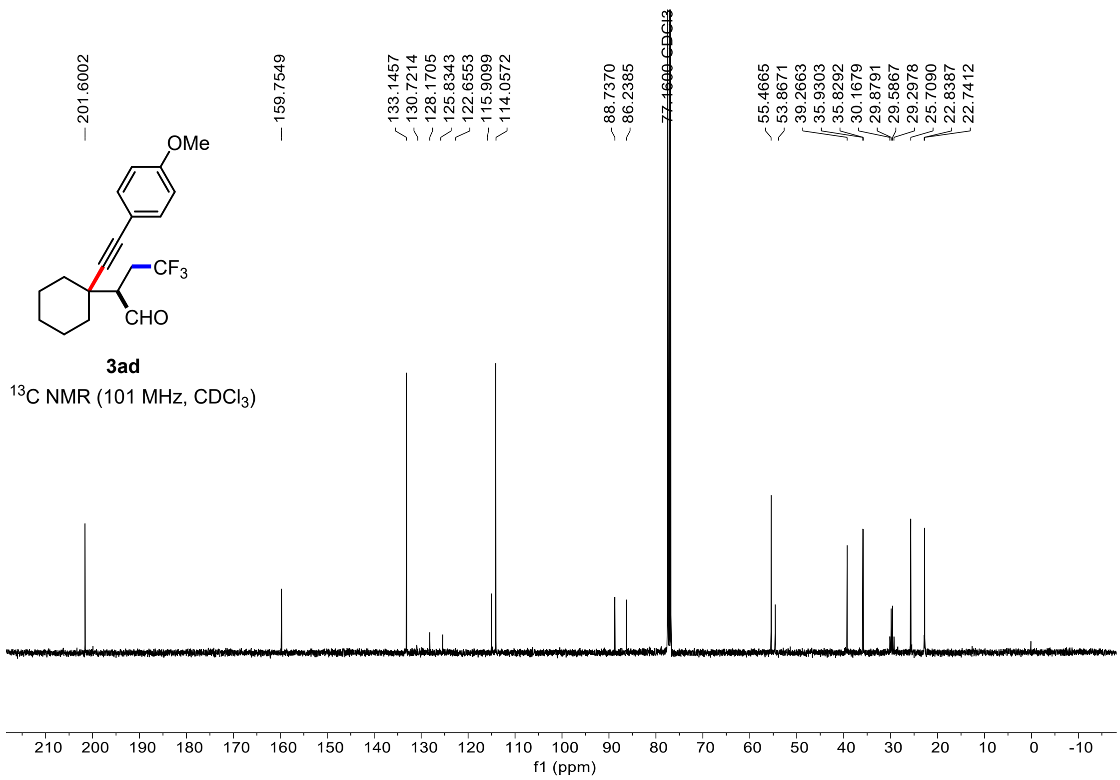
6.8539
6.8482
6.8373
6.8317
6.8245
3.8175
2.9418
2.9040
2.6480
2.6430
2.6346
2.6230
2.6171
2.6093
2.4752
2.4702
2.4655
1.9120
1.9092
1.8864
1.8782
1.8432
1.8364
1.8092
1.8001
1.7863
1.7779
1.7704
1.7623
1.7551
1.7463
1.7404
1.7335
1.7204
1.7132
1.7051
1.6976
1.6823
1.6782
1.6620
1.4532
1.4229
1.4129
1.3379
1.3160
1.3069
1.2847
1.2766
1.1875
0.0000 TMS
OMe
CF3
CHO
3ad
1H NMR (400 MHz, CDCl3)
0.96
1.98
2.03
3.06
1.03
1.00
1.04
1.01
1.09
5.01
1.08
1.15
1.13
f1 (ppm)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128.1705
125.8343
122.6553
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114.0572
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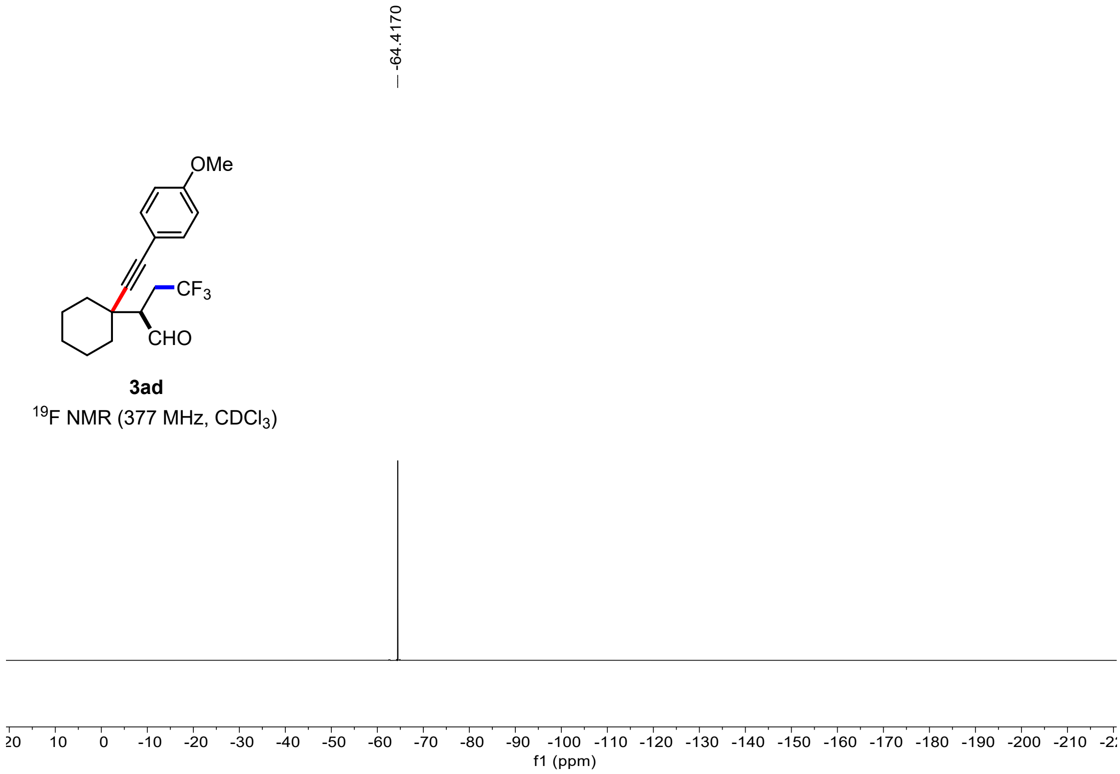
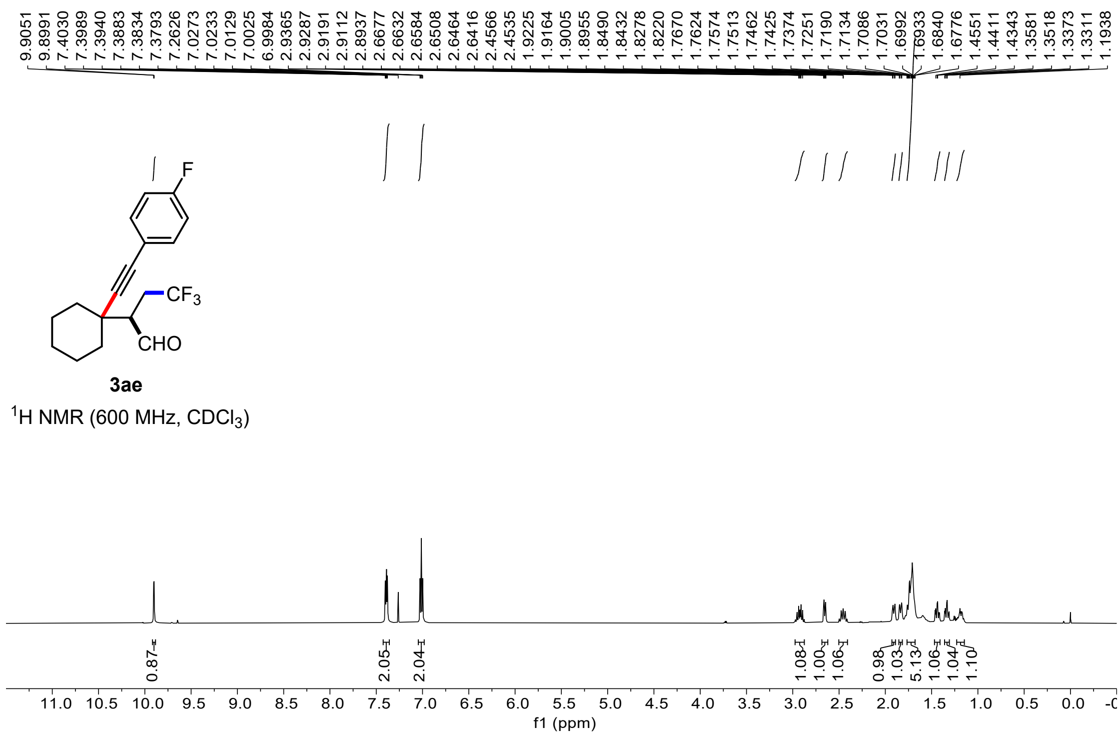
86.2385
77.1600 CDCl3
55.4665
53.8671
39.2663
35.9303
35.8292
30.1679
29.8791
29.5867
29.2978
25.7090
22.8387
22.7412
OMe
CF3
CHO
3ad
13C NMR (101 MHz, CDCl3)
f1 (ppm)



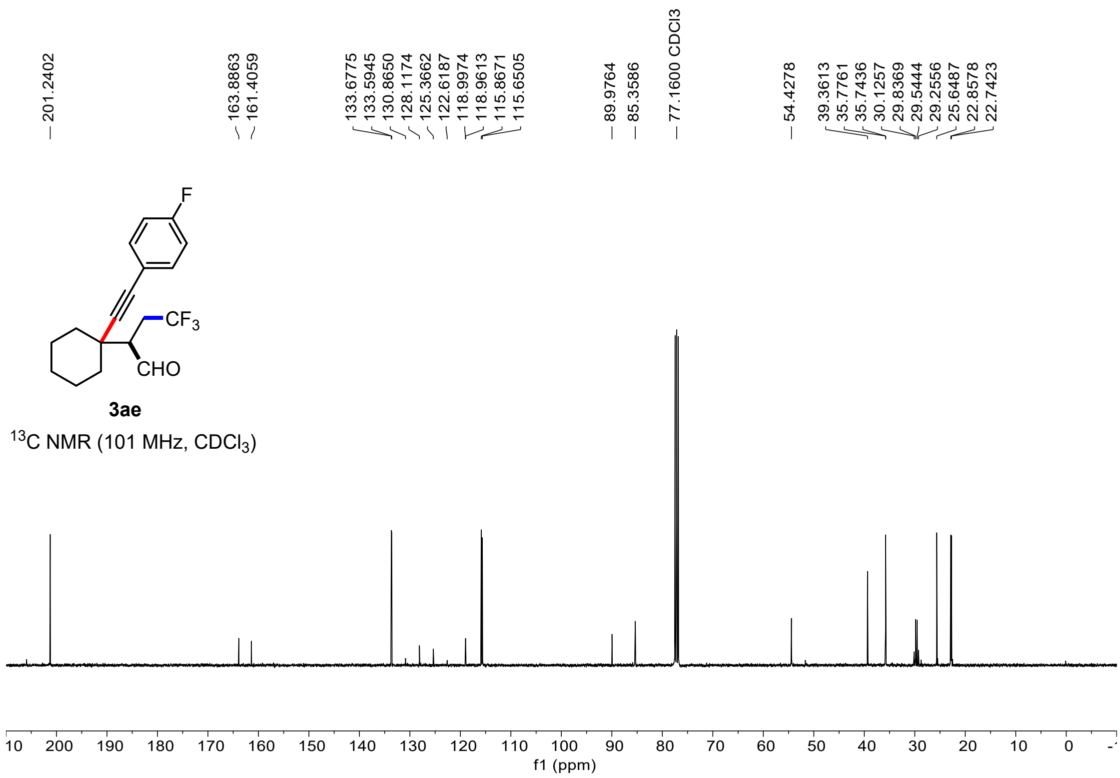
3ad

^{19}F NMR (377 MHz, $CDCl_3$)



3ae

^{1}H NMR (600 MHz, $CDCl_3$)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128.1174
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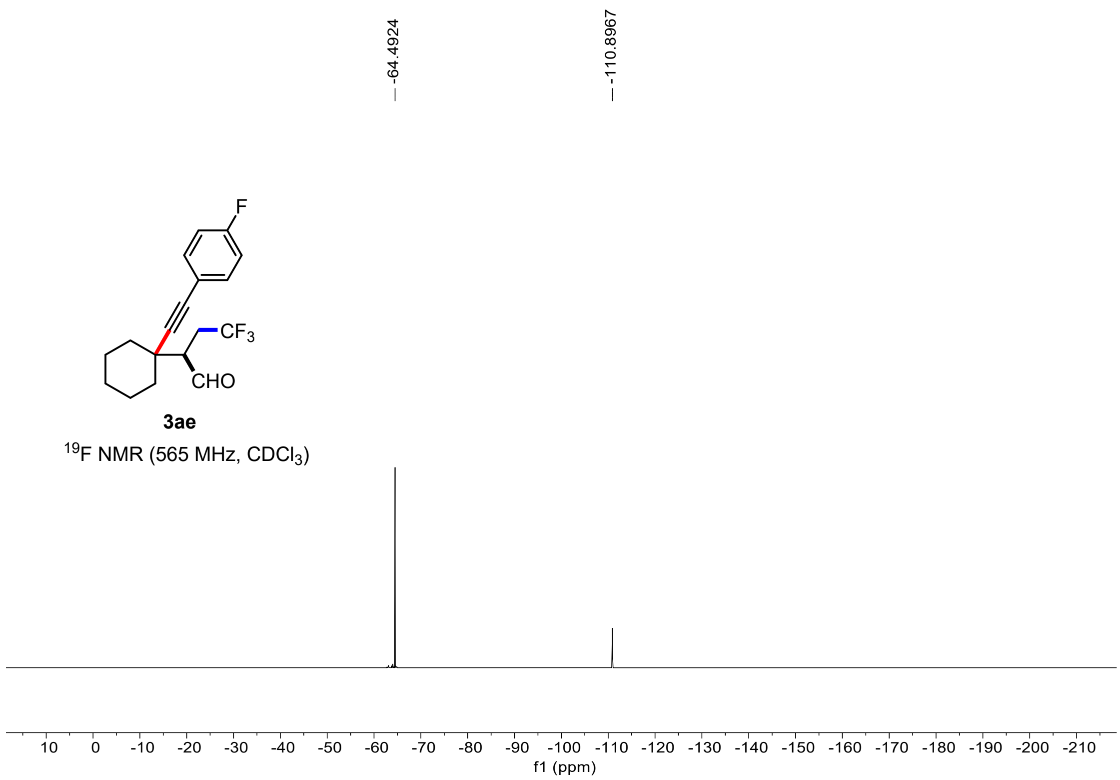
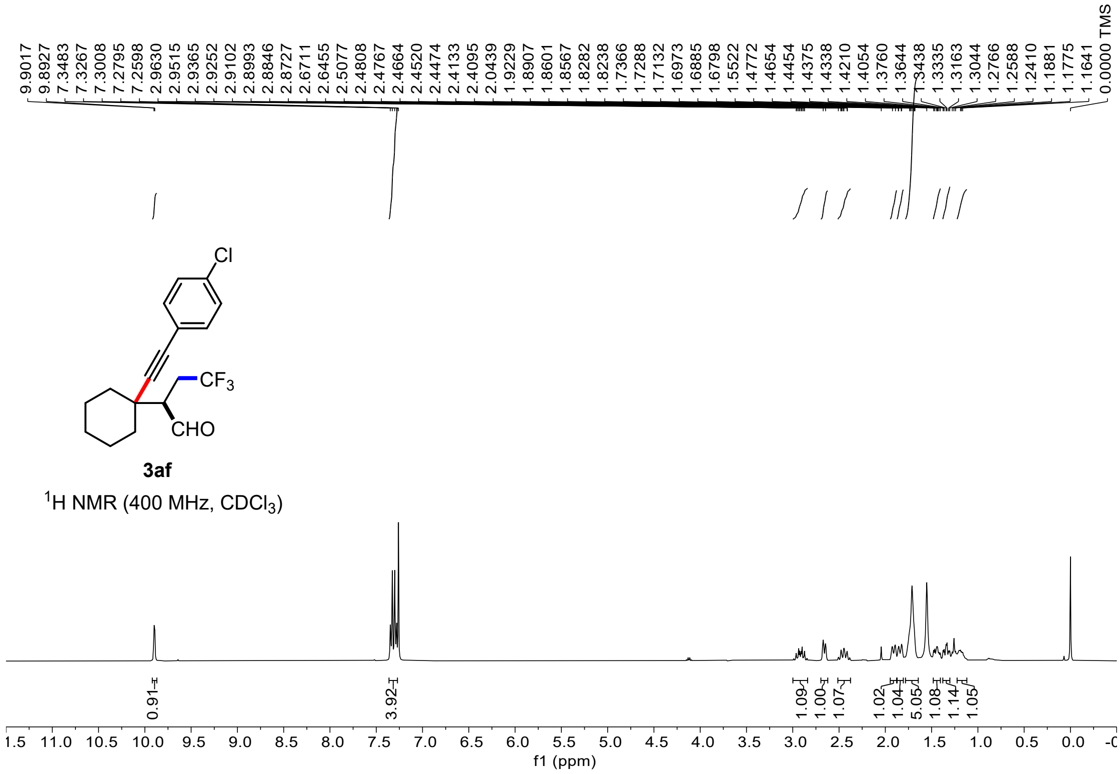
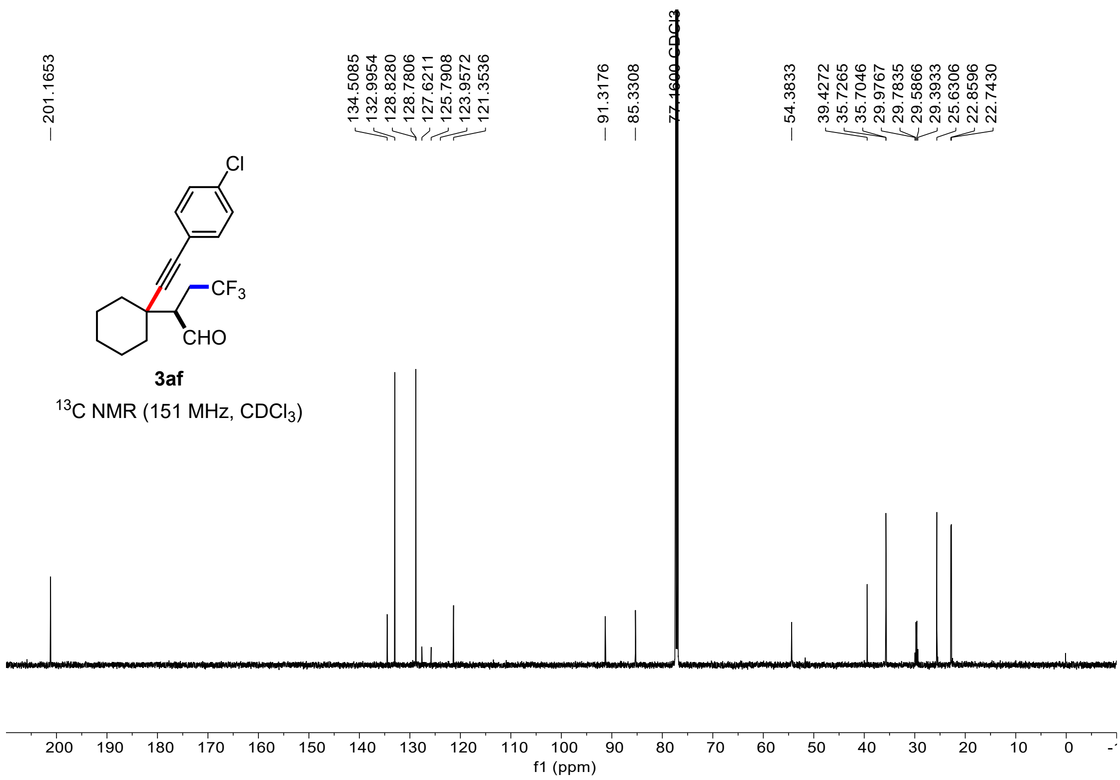
118.9613
115.8671
115.6505
89.9764
85.3586
77.1600 CDCl3
54.4278
39.3613
35.7761
35.7436
30.1257
29.8369
29.5444
29.2556
25.6487
22.8578
22.7423
F
CF3
CHO
3ae
13C NMR (101 MHz, CDCl3)
f1 (ppm)

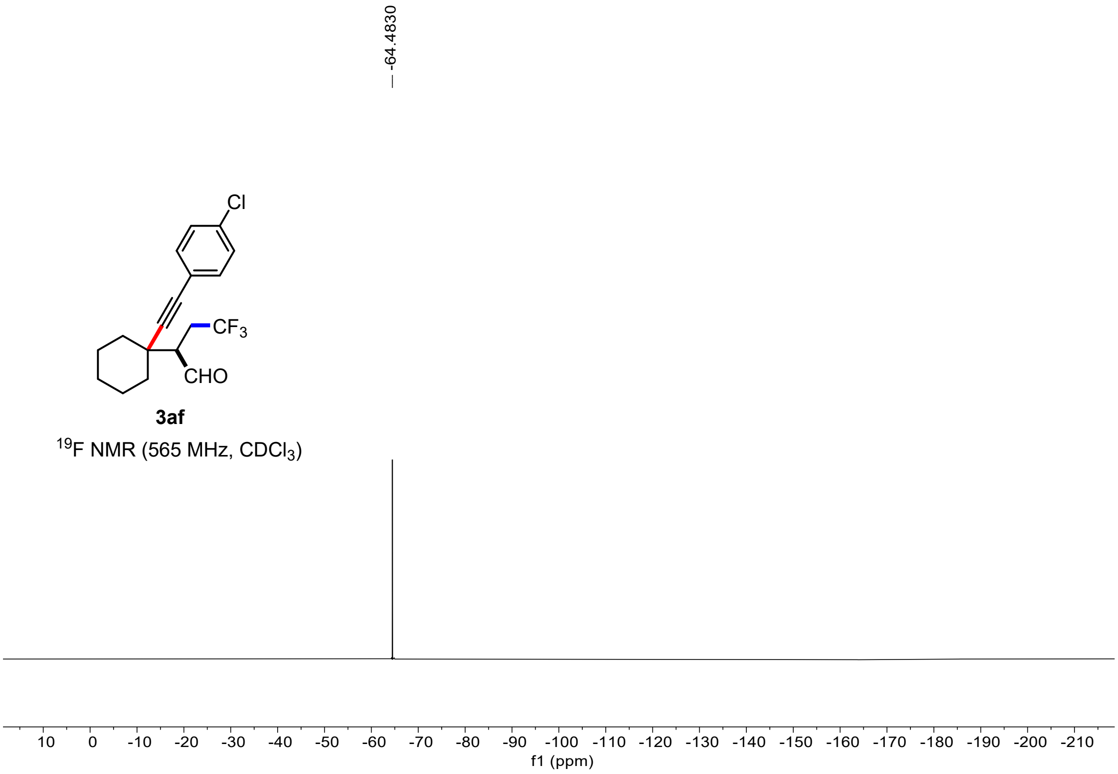

-64.4924
-110.8967
F
CF3
CHO
3ae
19F NMR (565 MHz, CDCl3)
f1 (ppm)



3af
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

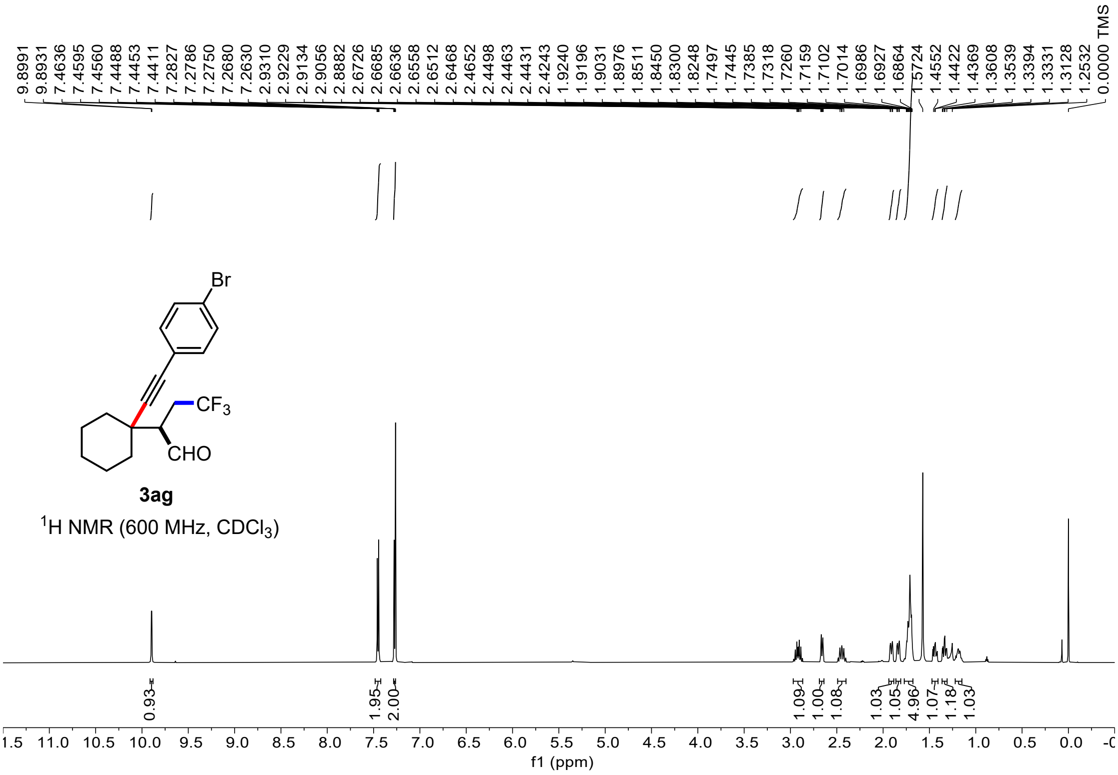


3af
^{13}C NMR (151 MHz, CDCl$_3$)
f1 (ppm)



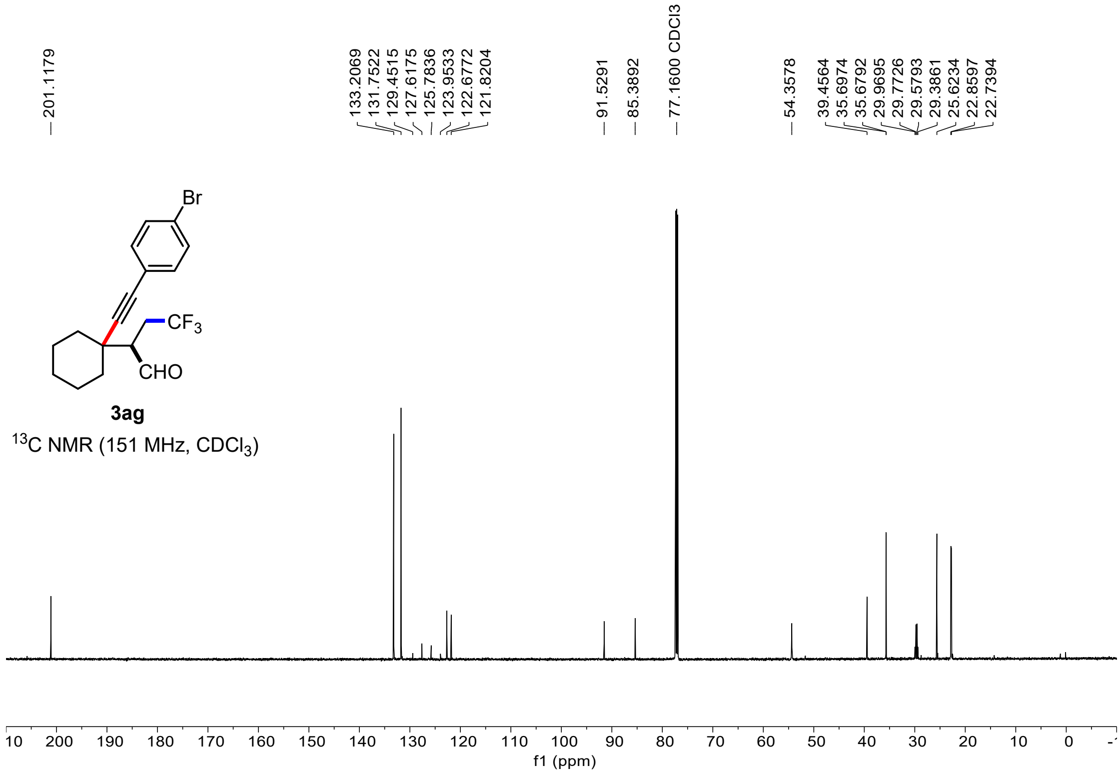
3af

^{19}F NMR (565 MHz, $CDCl_3$)



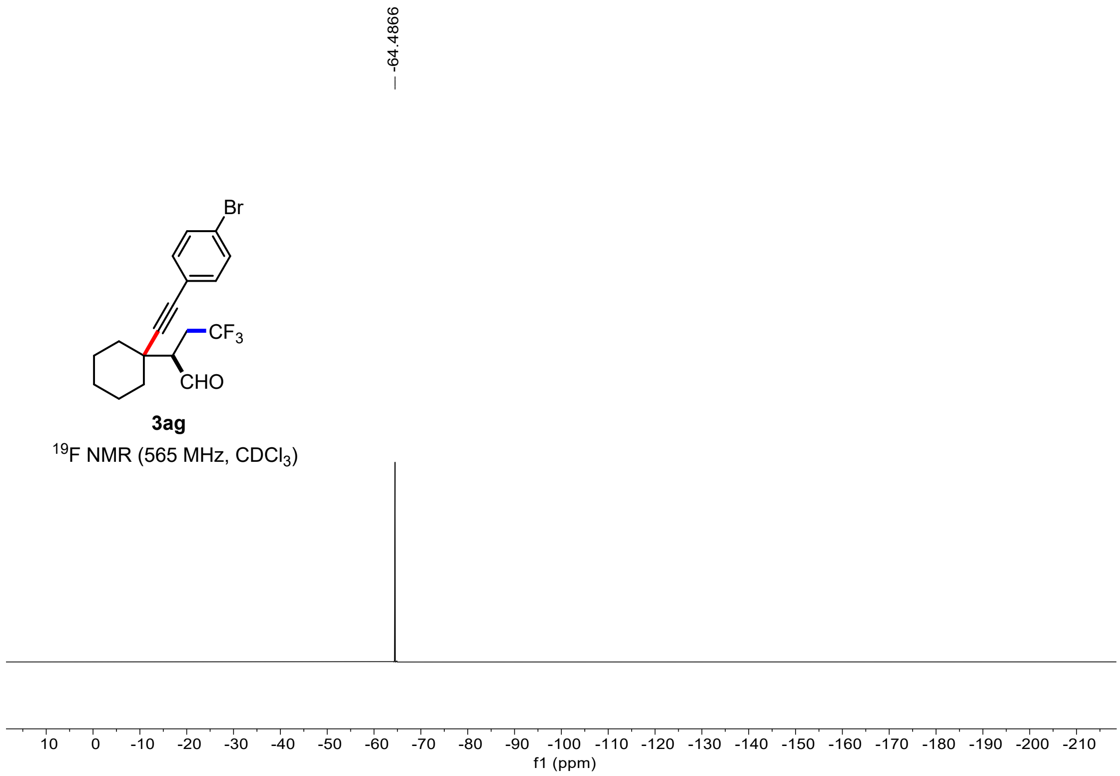
3ag

^{1}H NMR (600 MHz, $CDCl_3$)



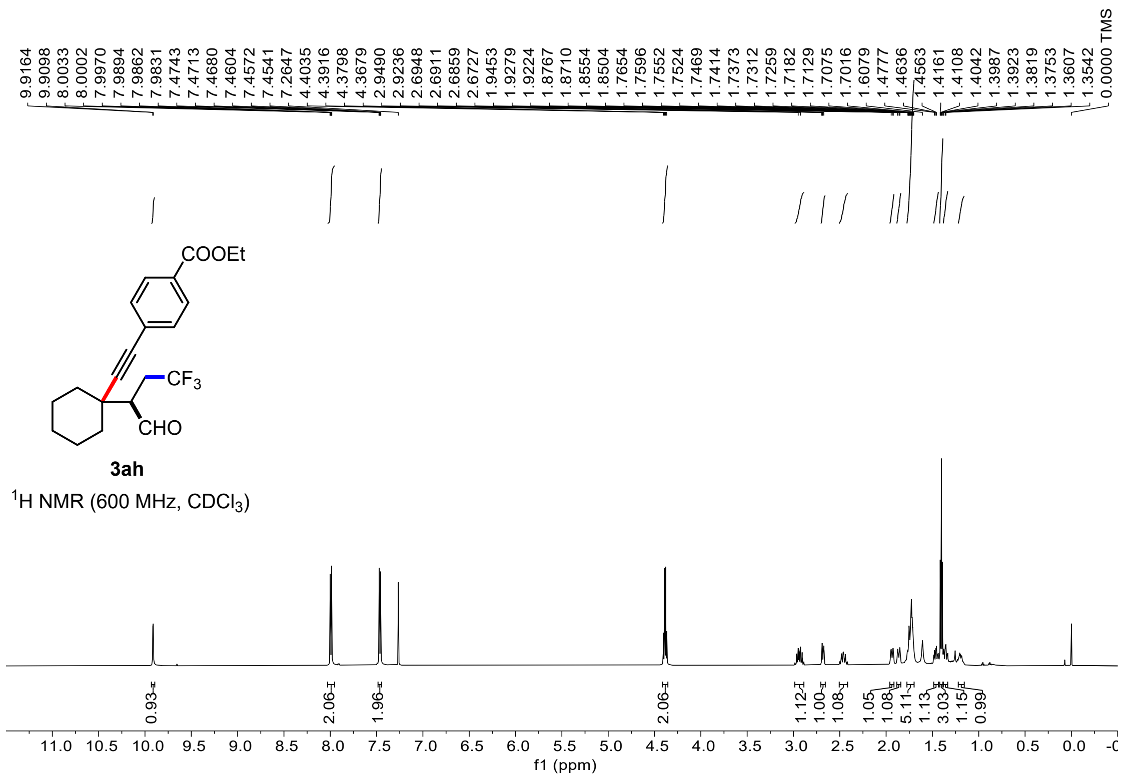
3ag

^{13}C NMR (151 MHz, $CDCl_3$)



3ag

^{19}F NMR (565 MHz, $CDCl_3$)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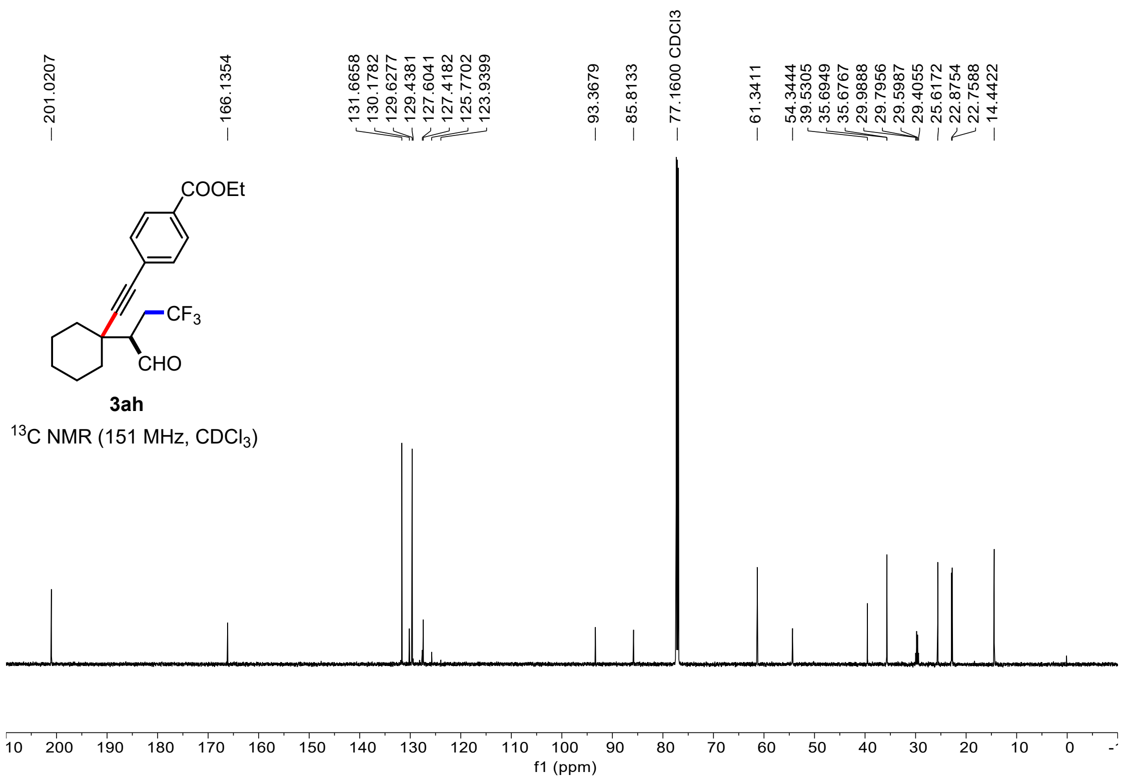
7.4604
7.4572
7.4541
7.2647
4.4035
4.3916
4.3798
4.3679
2.9490
2.9236
2.6948
2.6911
2.6859
2.6727
1.9453
1.9279
1.9224
1.8767
1.8710
1.8554
1.8504
1.7654
1.7596
1.7552
1.7524
1.7469
1.7414
1.7373
1.7312
1.7259
1.7182
1.7129
1.7075
1.7016
1.6079
1.4777
1.4636
1.4563
1.4161
1.4108
1.4042
1.3987
1.3923
1.3819
1.3753
1.3607
1.3542
0.0000 TMS
COOEt
CF3
CHO
3ah
1H NMR (600 MHz, CDCl3)
0.93
2.06
1.96
2.06
1.12
1.00
1.08
1.05
1.08
5.11
1.13
3.03
1.15
0.99
f1 (ppm)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129.6277
129.4381
127.6041
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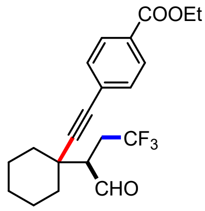
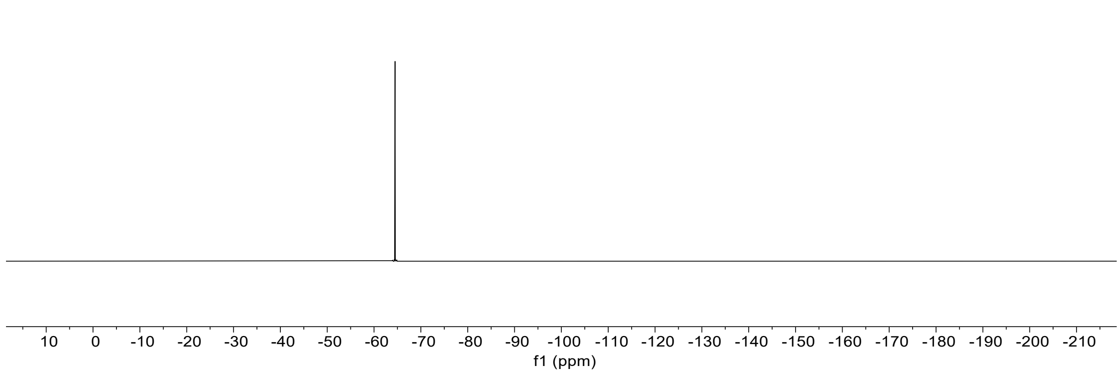
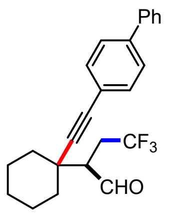
125.7702
123.9399
93.3679
85.8133
77.1600 CDCl3
61.3411
54.3444
39.5305
35.6949
35.6767
29.9888
29.7956
29.5987
29.4055
25.6172
22.8754
22.7588
14.4422
COOEt
CF3
CHO
3ah
13C NMR (151 MHz, CDCl3)
f1 (ppm)



3ah

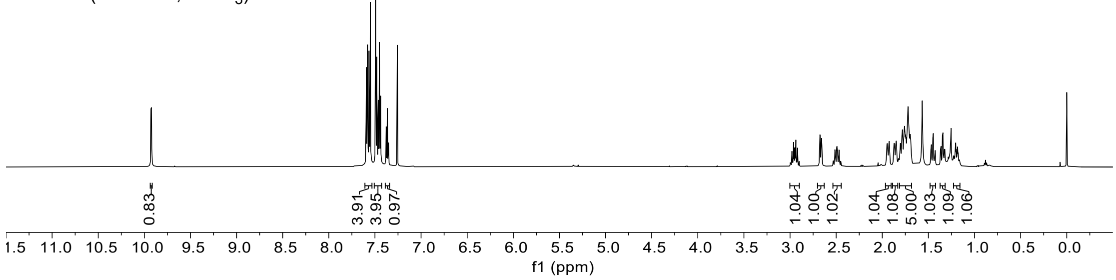
^{19}F NMR (565 MHz, $CDCl_3$)

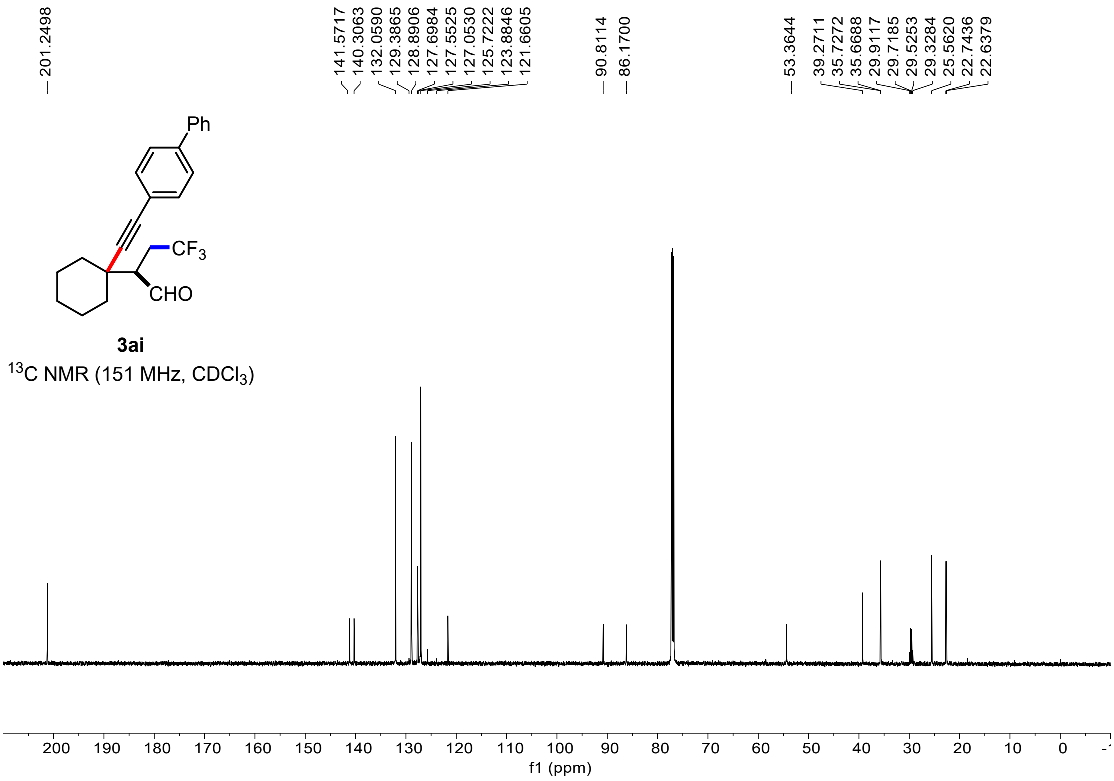




3ai

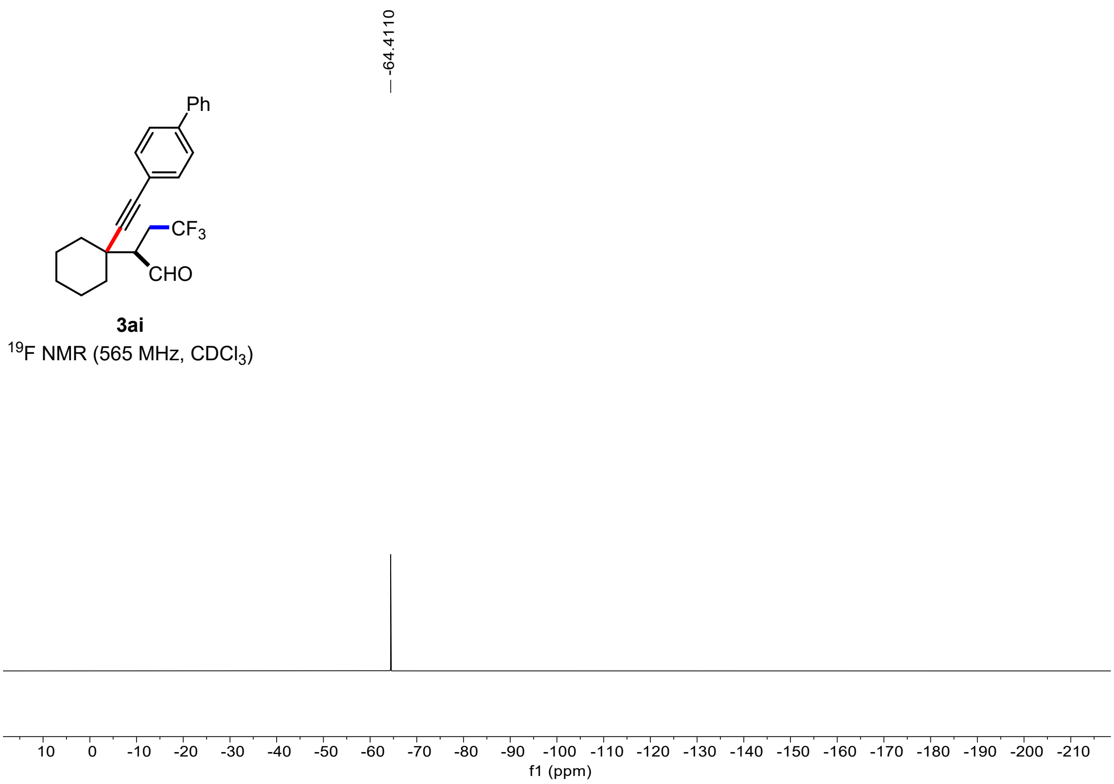
^{1}H NMR (600 MHz, $CDCl_3$)





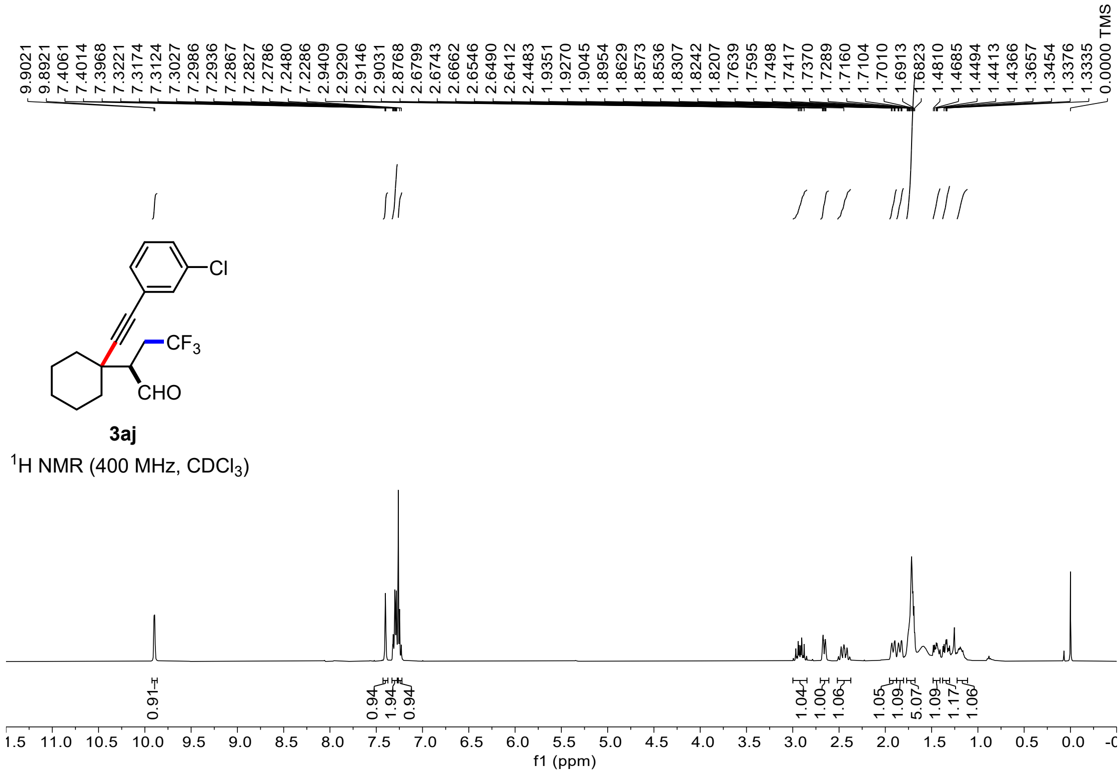
3ai

^{13}C NMR (151 MHz, $CDCl_3$)



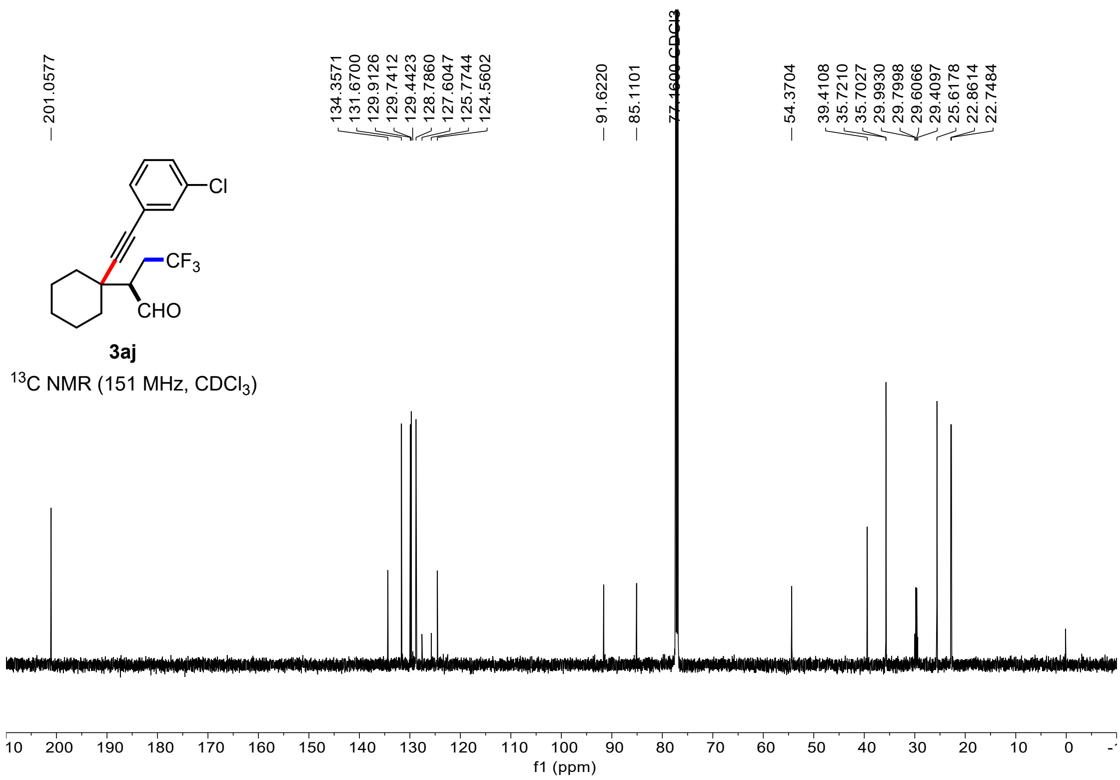
3ai

^{19}F NMR (565 MHz, $CDCl_3$)



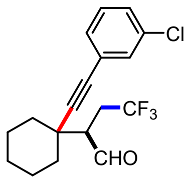
3aj

^{1}H NMR (400 MHz, $CDCl_3$)



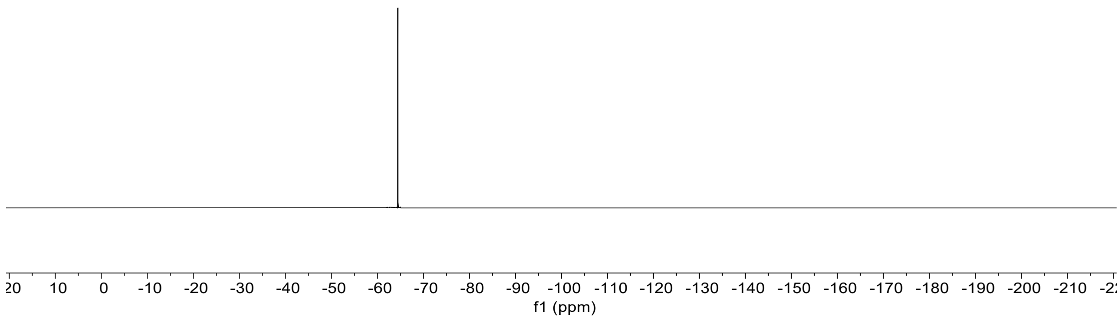
3aj

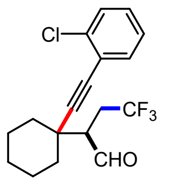
^{13}C NMR (151 MHz, $CDCl_3$)



3aj

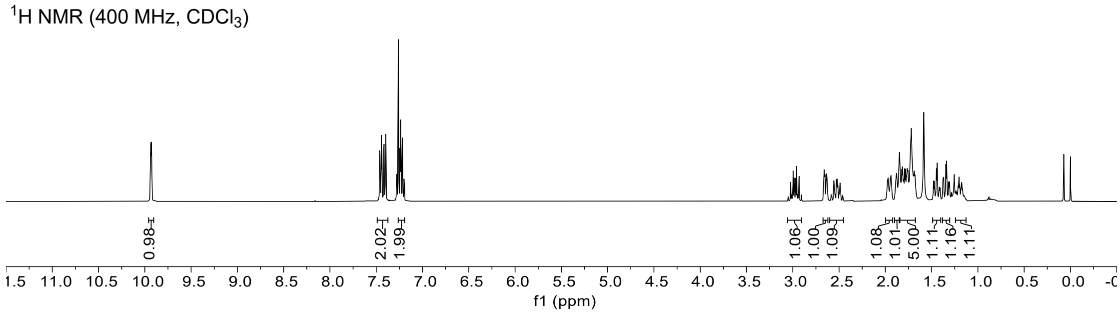
^{19}F NMR (377 MHz, $CDCl_3$)

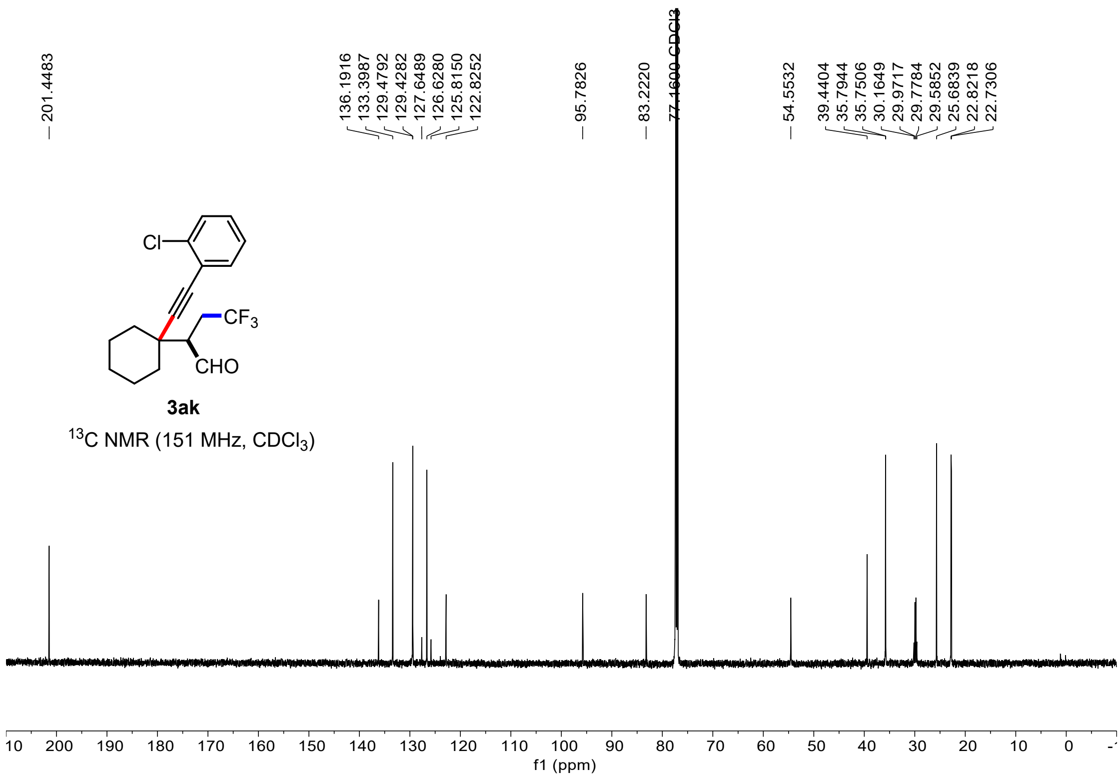




3ak

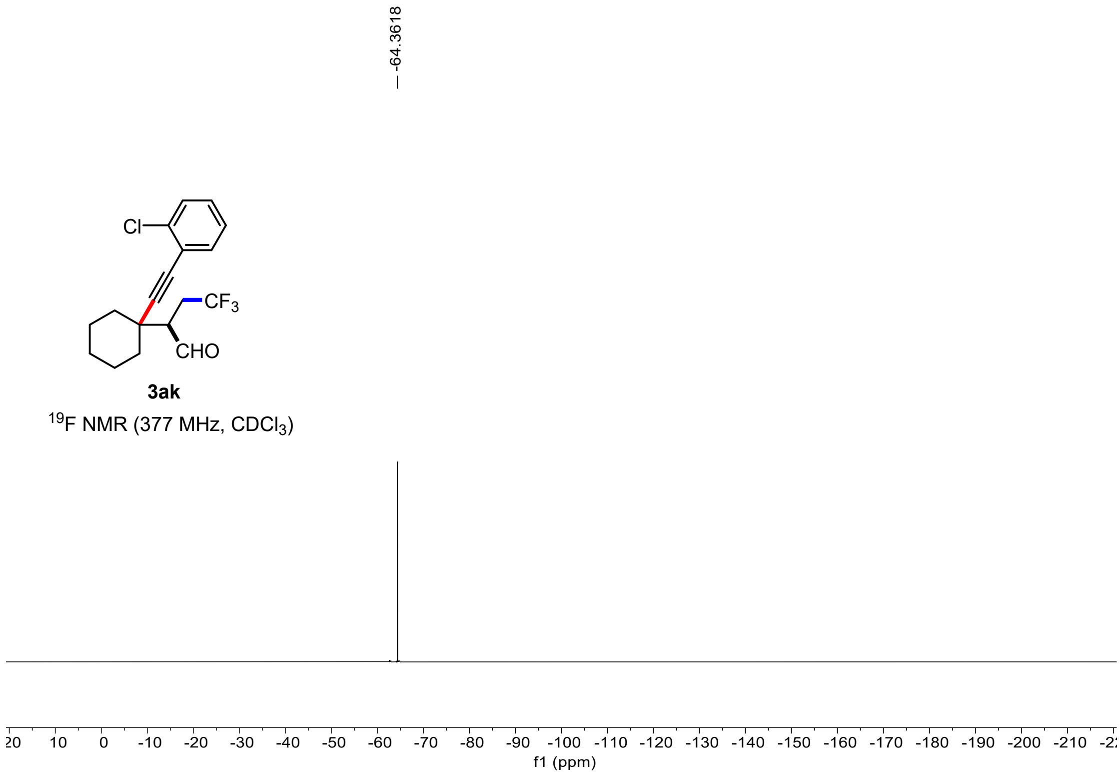
^1H NMR (400 MHz, $CDCl_3$)





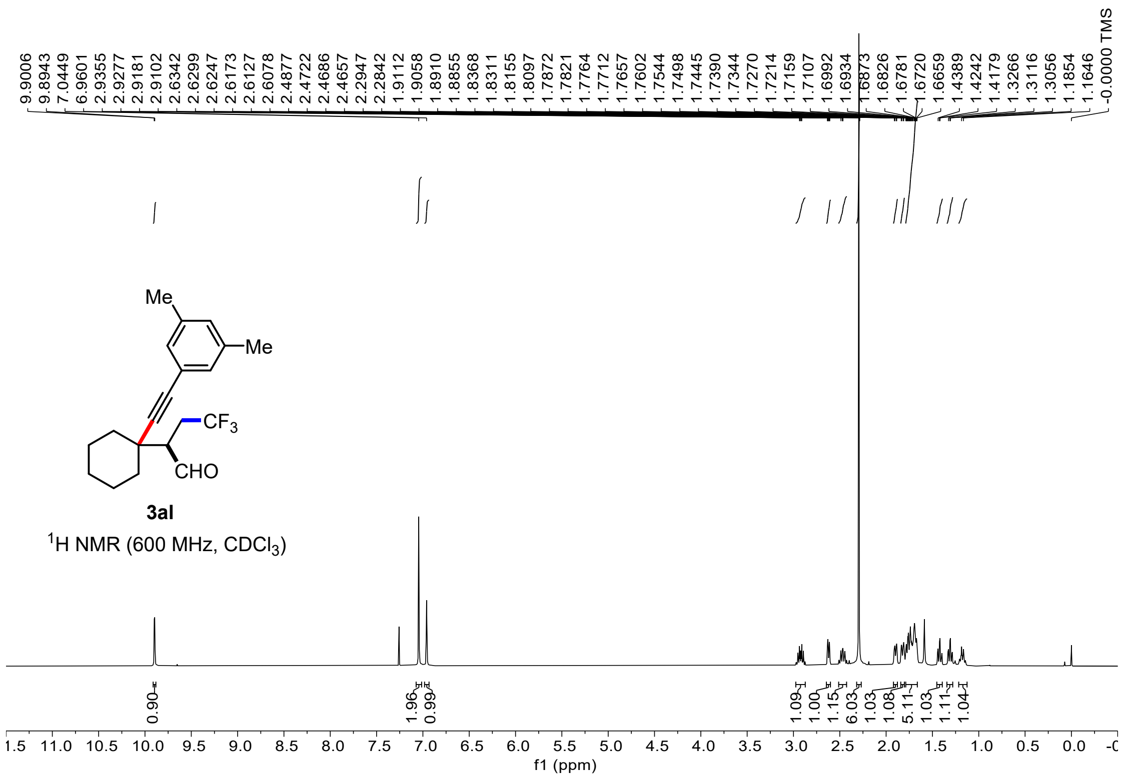
3ak

^{13}C NMR (151 MHz, $CDCl_3$)



3ak

^{19}F NMR (377 MHz, $CDCl_3$)



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2.6173
2.6127
2.6078
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1.9112
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1.8910
1.8855
1.8368
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1.8155
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1.7214
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1.6873
1.6826
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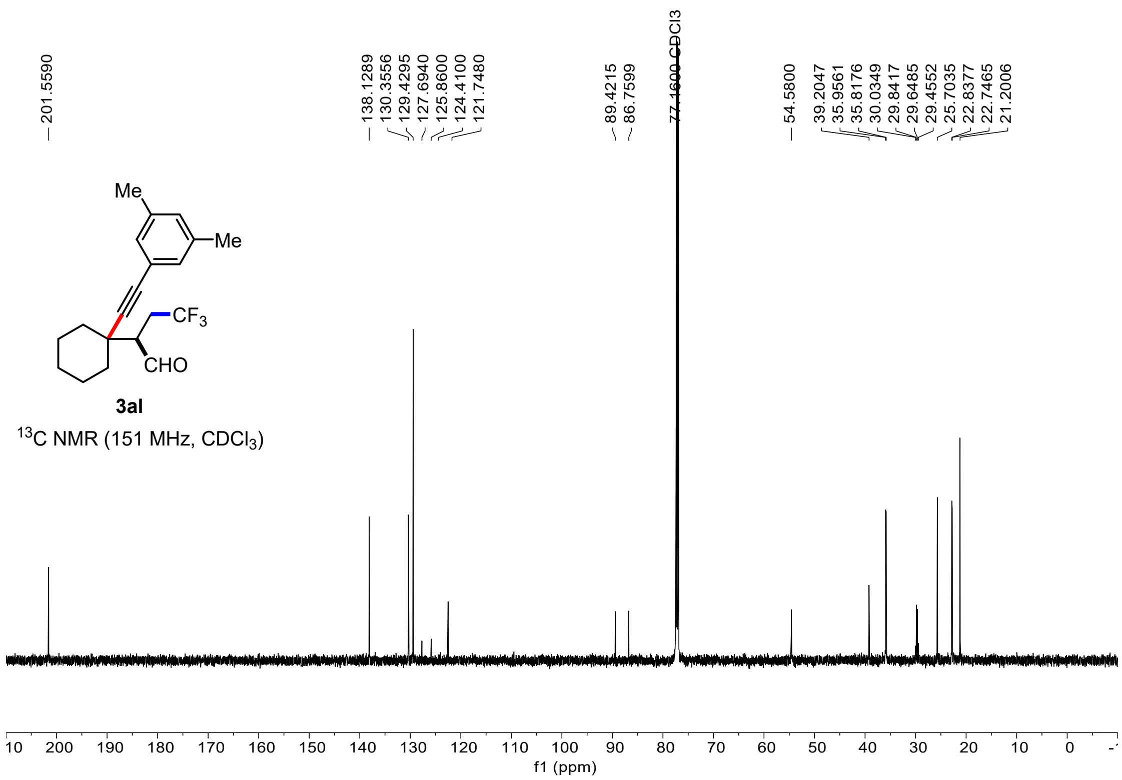
1.4179
1.3266
1.3116
1.3056
1.1854
1.1646
-0.0000 TMS
Me
Me
CF3
CHO
3al
1H NMR (600 MHz, CDCl3)
0.90
1.96
0.99
1.09
1.00
1.15
6.03
1.03
1.08
5.11
1.03
1.11
1.04
f1 (ppm)



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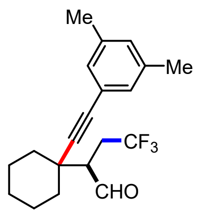
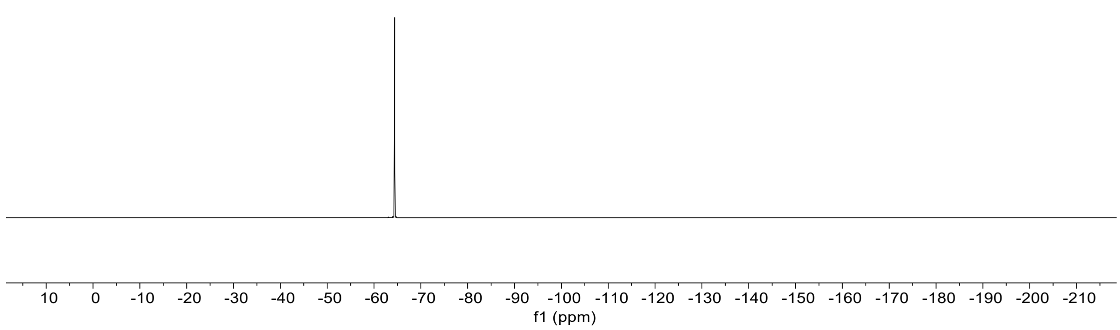
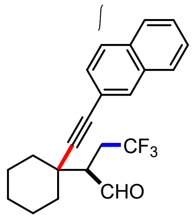
54.5800
39.2047
35.9561
35.8176
30.0349
29.8417
29.6485
29.4552
25.7035
22.8377
22.7465
21.2006
Me
Me
CF3
CHO
3al
13C NMR (151 MHz, CDCl3)
f1 (ppm)



3al

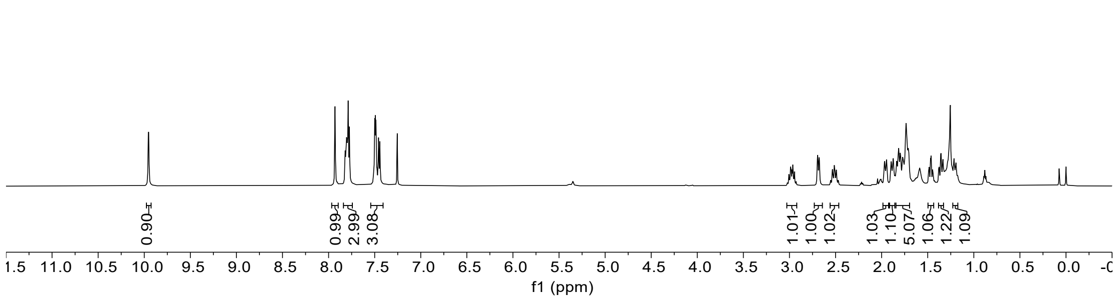
^{19}F NMR (565 MHz, $CDCl_3$)

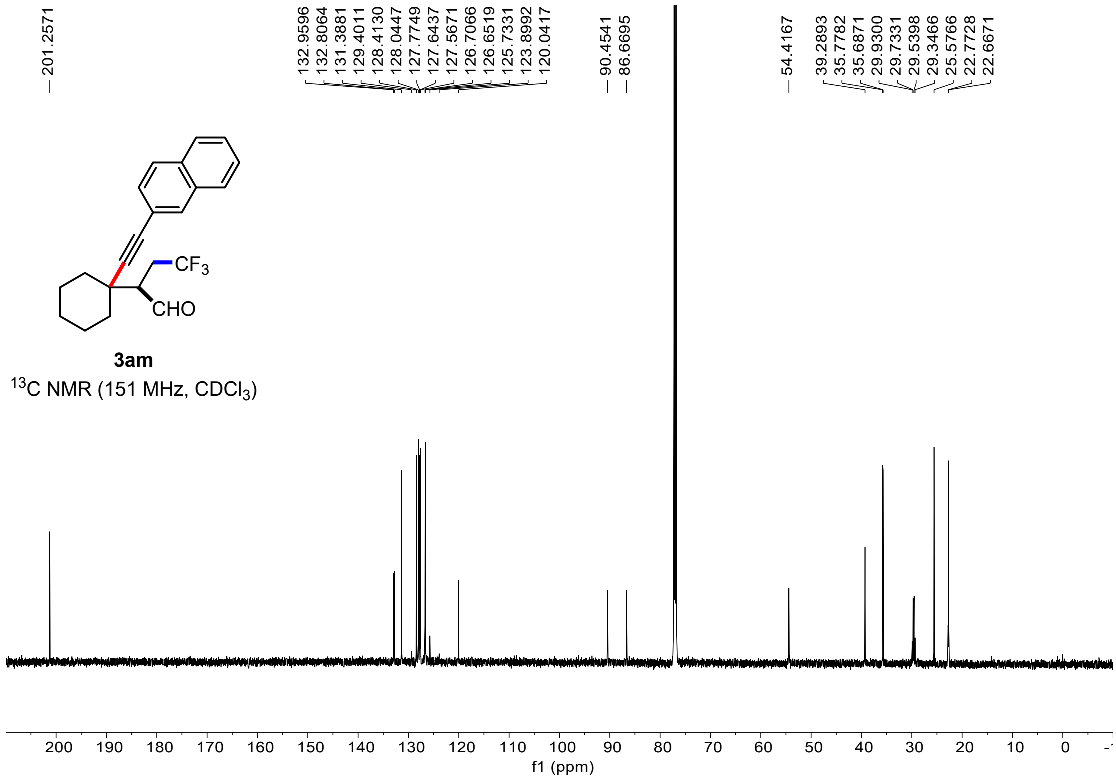




3am

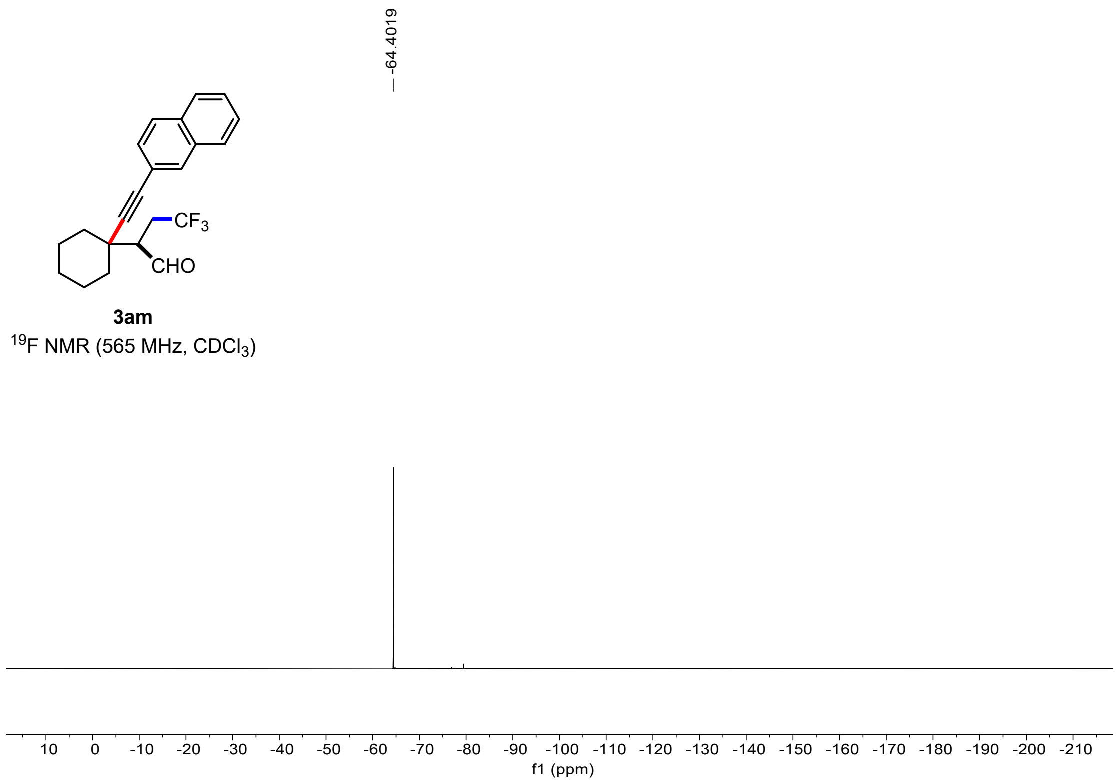
^{1}H NMR (600 MHz, $CDCl_3$)





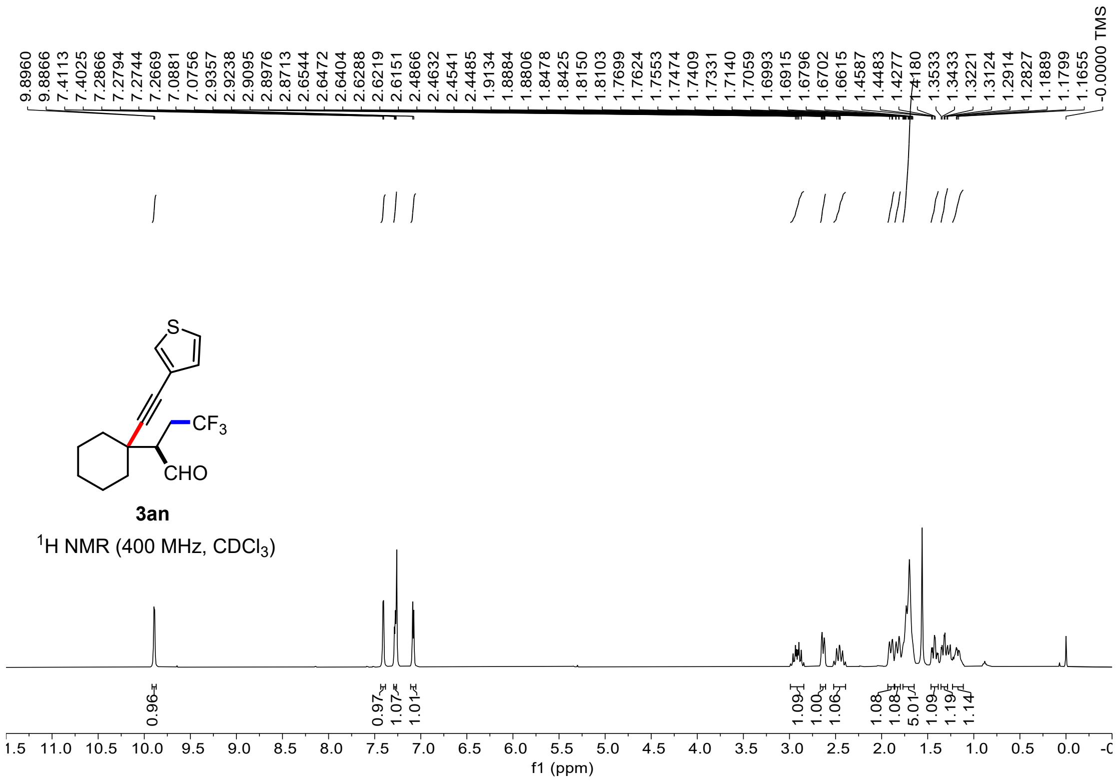
3am

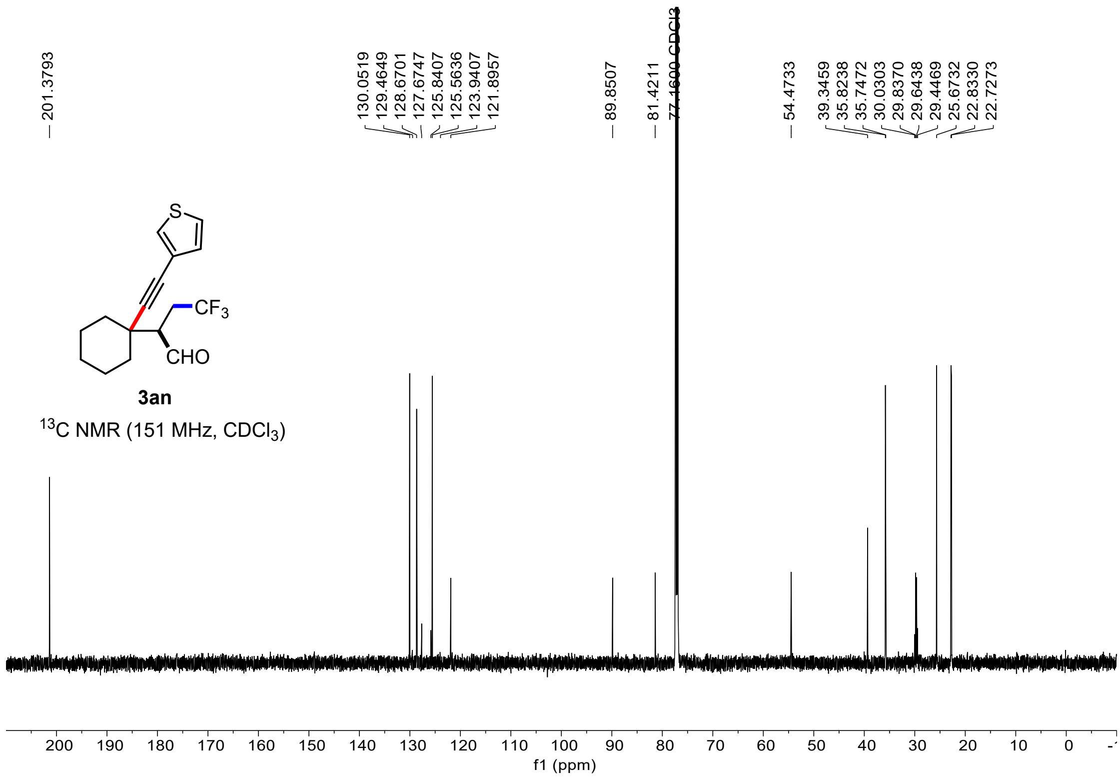
^{13}C NMR (151 MHz, $CDCl_3$)

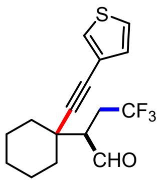


3am

^{19}F NMR (565 MHz, $CDCl_3$)

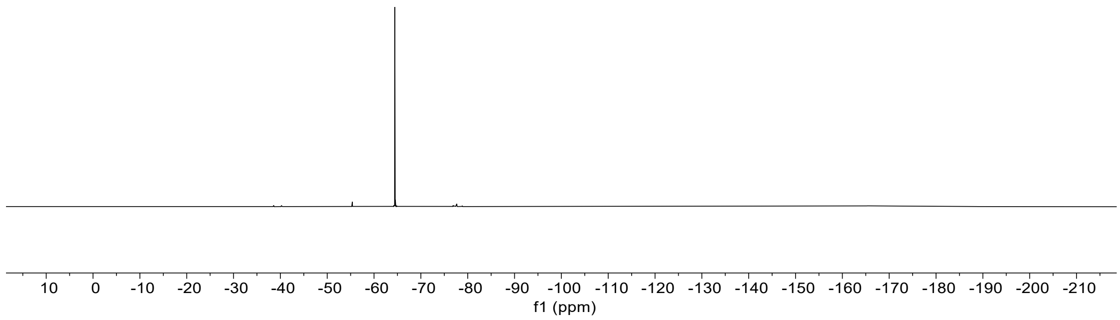

9.8960 9.8866 7.4113 7.4025 7.2866 7.2794 7.2744 7.2669 7.0881 7.0756 2.9357 2.9238 2.9095 2.8976 2.8713 2.6544 2.6472 2.6404 2.6288 2.6219 2.6151 2.4866 2.4632 2.4541 2.4485 1.9134 1.8884 1.8806 1.8478 1.8425 1.8150 1.8103 1.7699 1.7624 1.7553 1.7474 1.7409 1.7331 1.7140 1.7059 1.6993 1.6915 1.6796 1.6702 1.6615 1.4587 1.4483 1.4277 1.4180 1.3533 1.3433 1.3221 1.3124 1.2914 1.2827 1.1889 1.1799 1.1655 -0.0000 TMS
S
CF3
CHO
3an
1H NMR (400 MHz, CDCl3)
0.96
0.97
1.07
1.01
1.09
1.00
1.06
1.08
1.08
5.01
1.09
1.19
1.14
f1 (ppm)

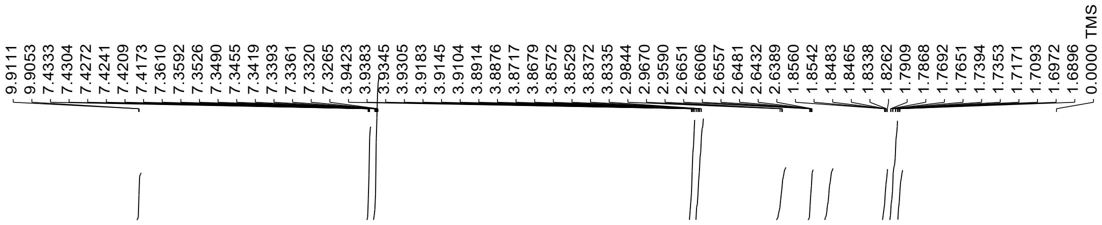

201.3793
130.0519 129.4649 128.6701 127.6747 125.8407 125.5636 123.9407 121.8957
89.8507
81.4211
77.1600 CDCl3
54.4733
39.3459 35.8238 35.7472 30.0303 29.8370 29.6438 29.4469 25.6732 22.8330 22.7273
S
CF3
CHO
3an
13C NMR (151 MHz, CDCl3)
f1 (ppm)

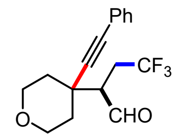


3an

^{19}F NMR (565 MHz, $CDCl_3$)

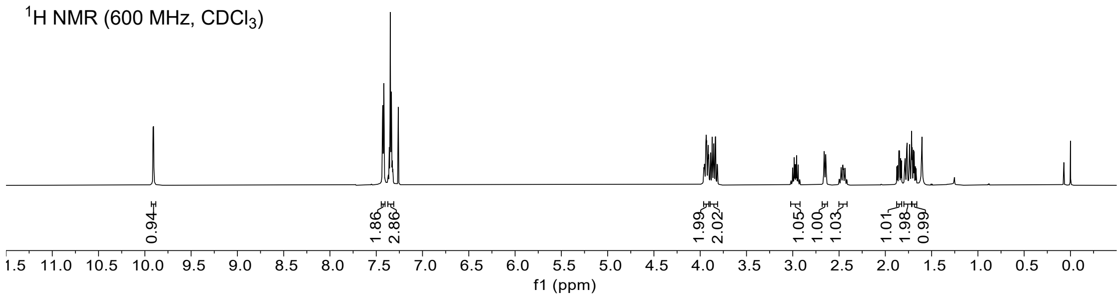


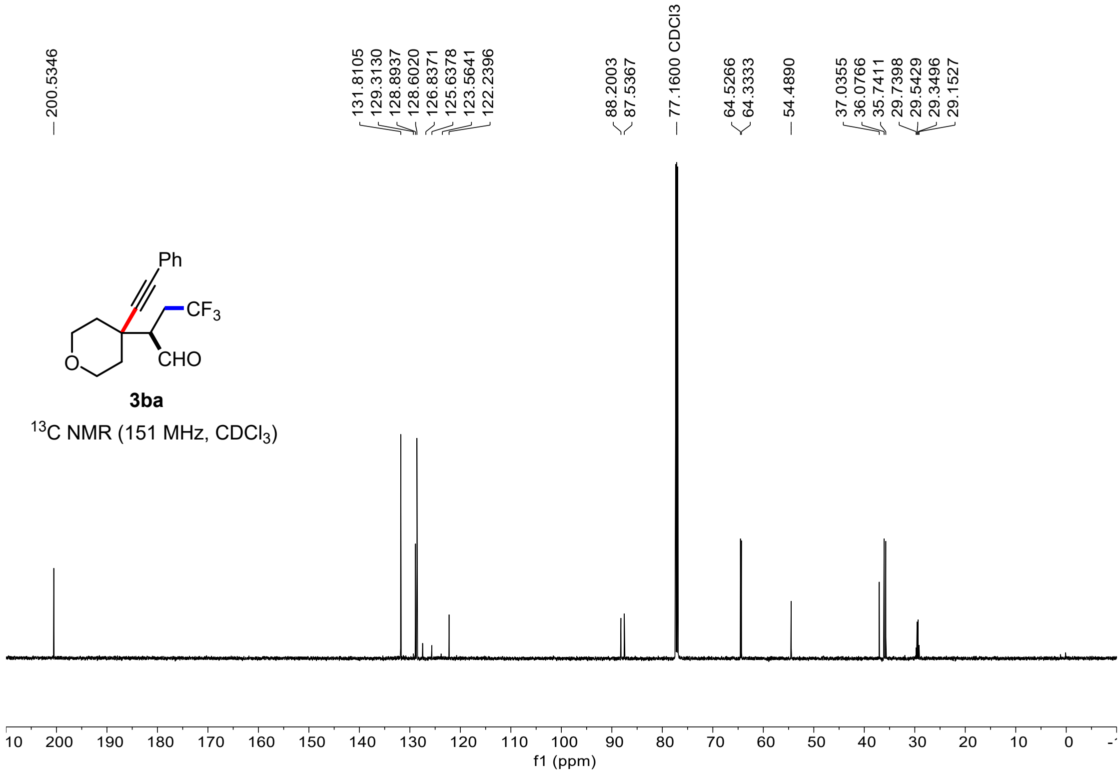




3ba

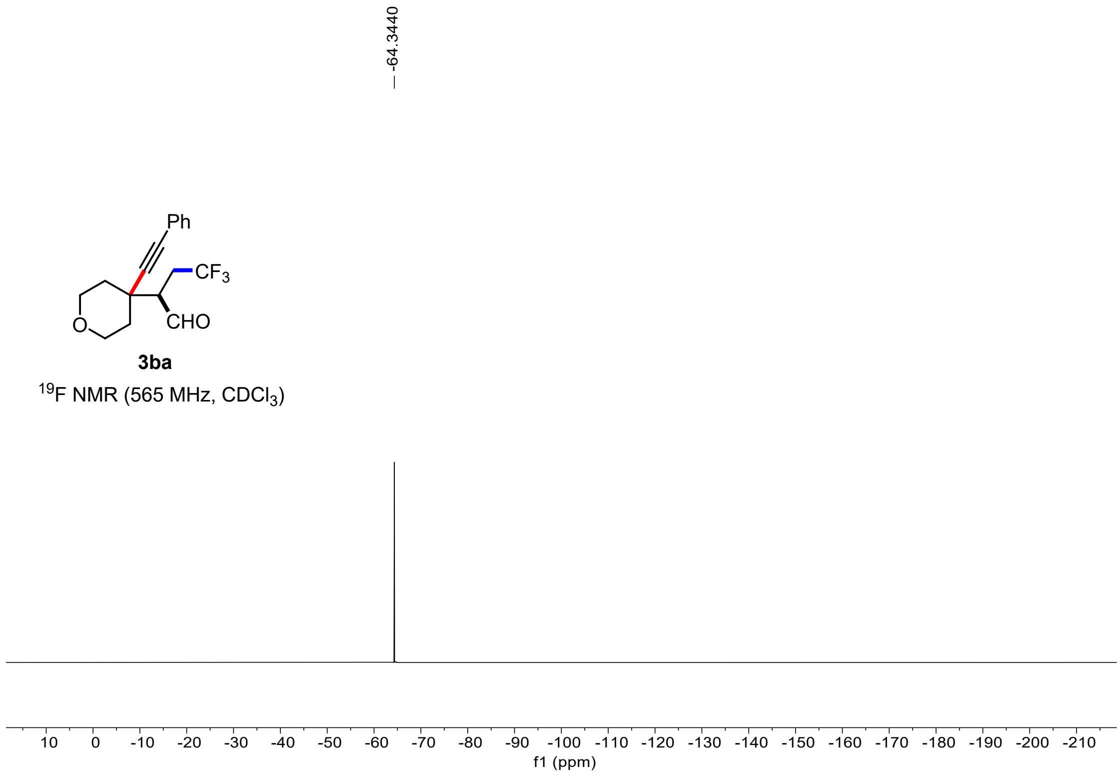
^{1}H NMR (600 MHz, $CDCl_3$)





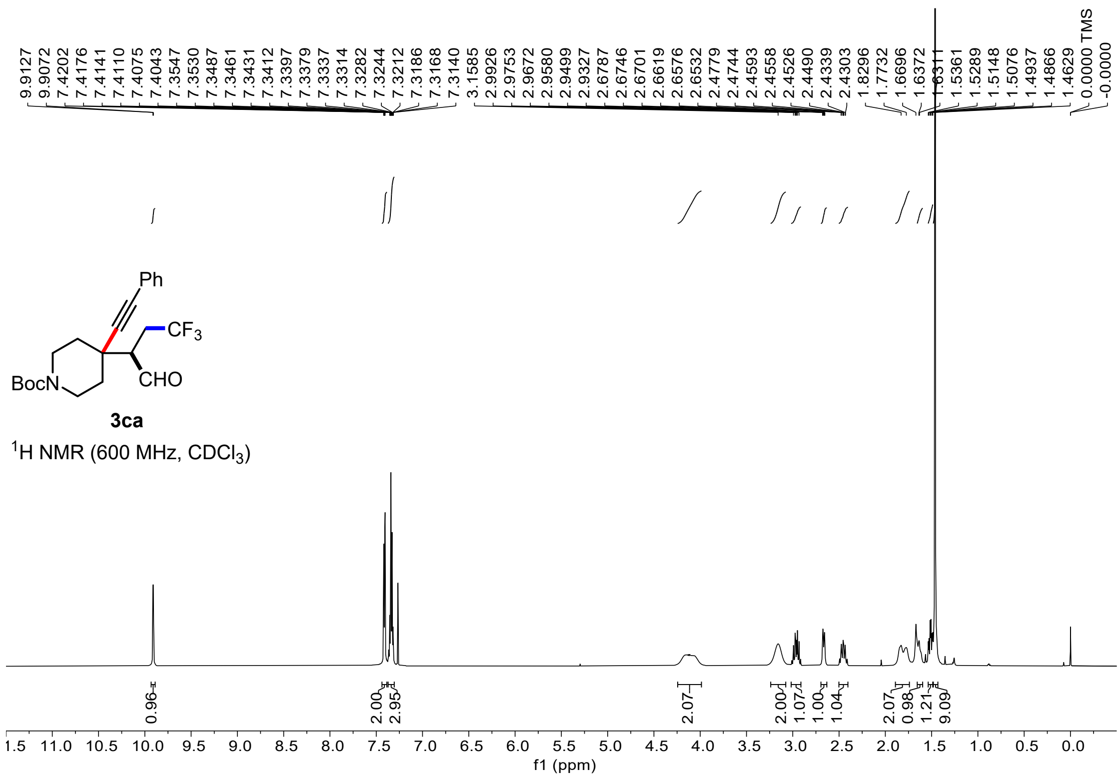
3ba

^{13}C NMR (151 MHz, $CDCl_3$)



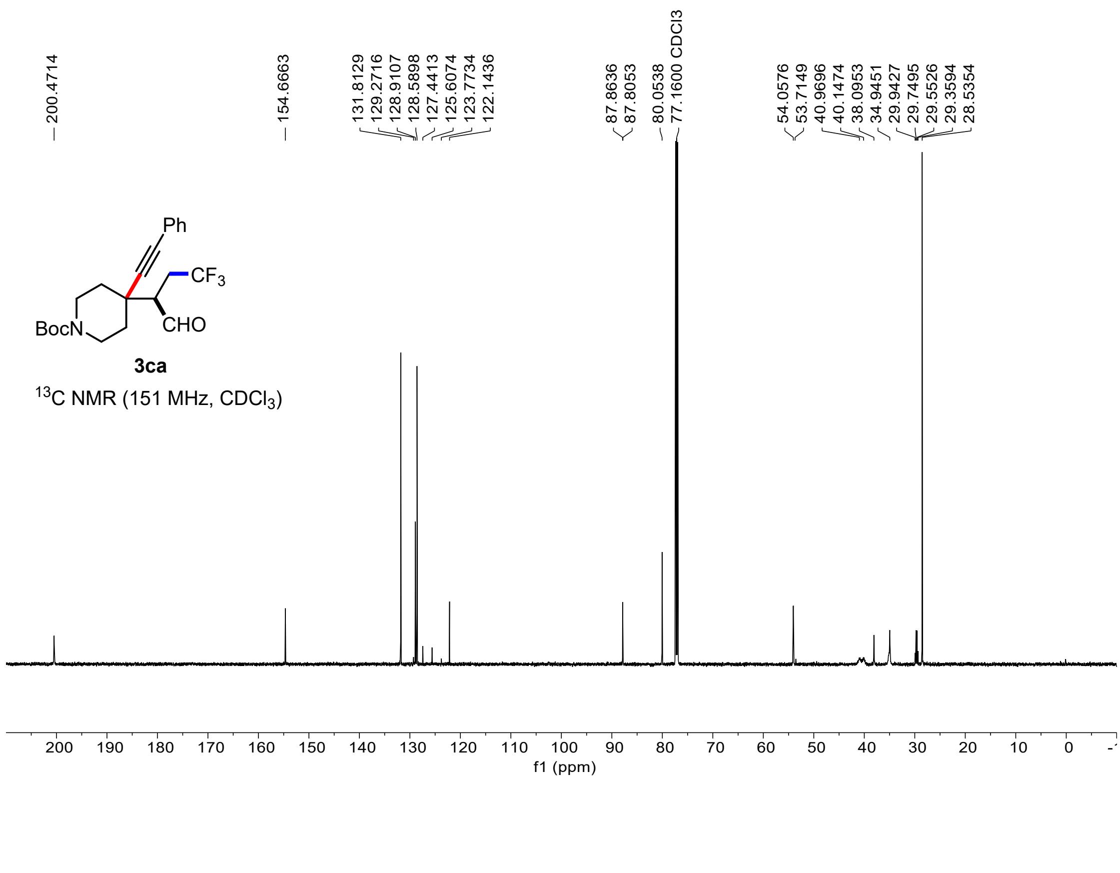
3ba

^{19}F NMR (565 MHz, $CDCl_3$)



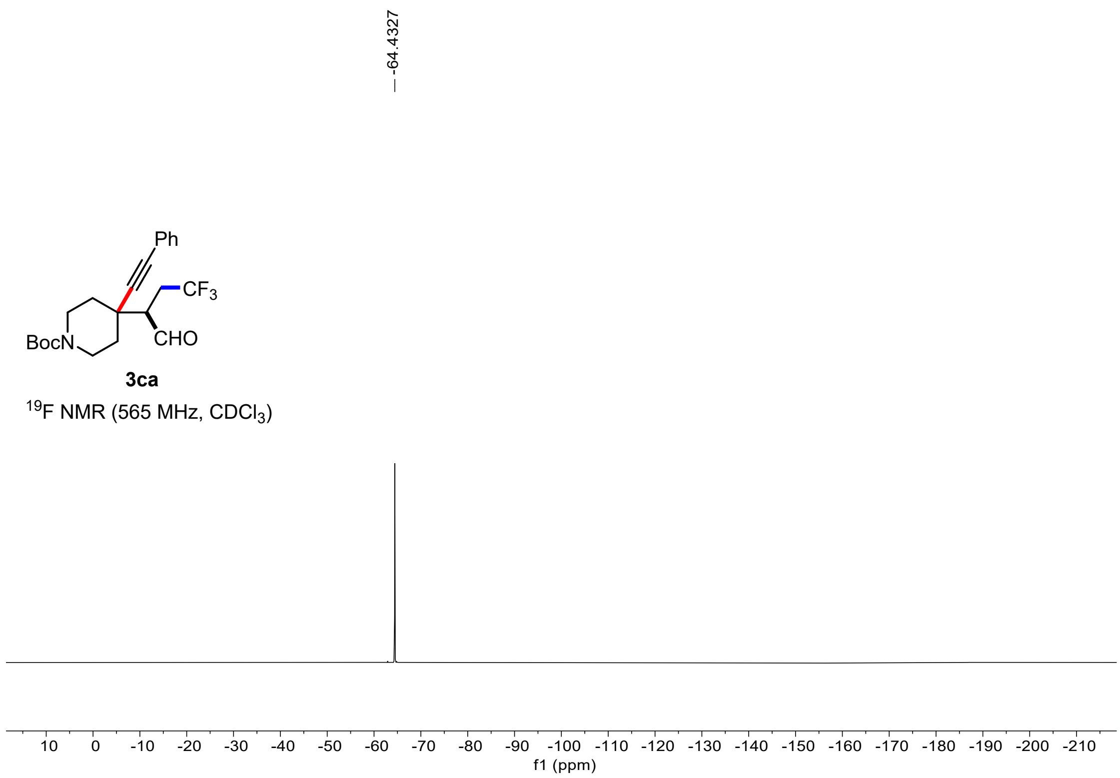
3ca

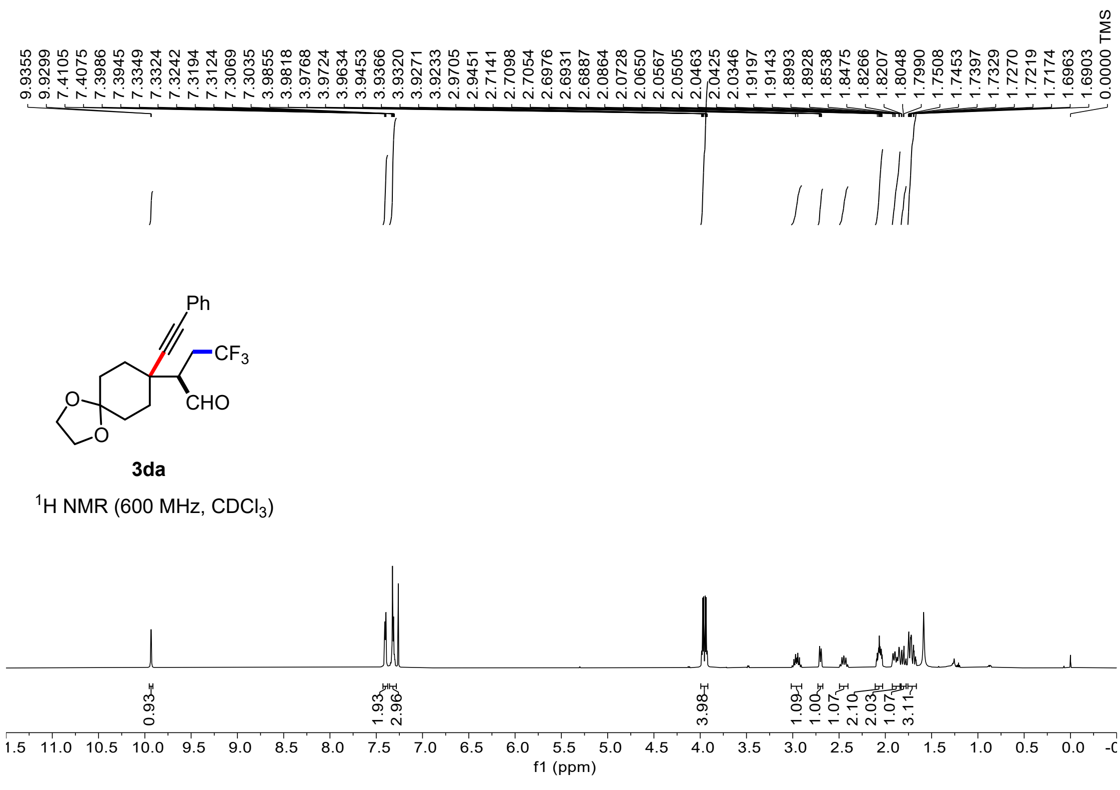
^{1}H NMR (600 MHz, CDCl$_3$)

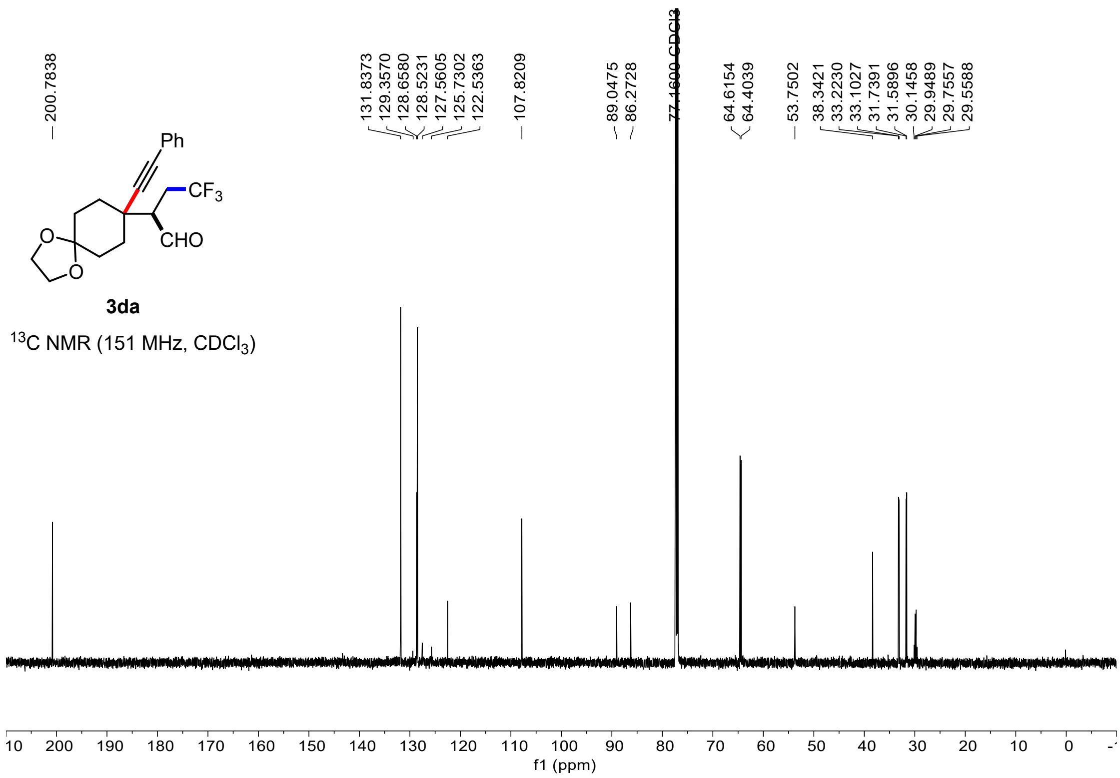


3ca

^{13}C NMR (151 MHz, CDCl$_3$)



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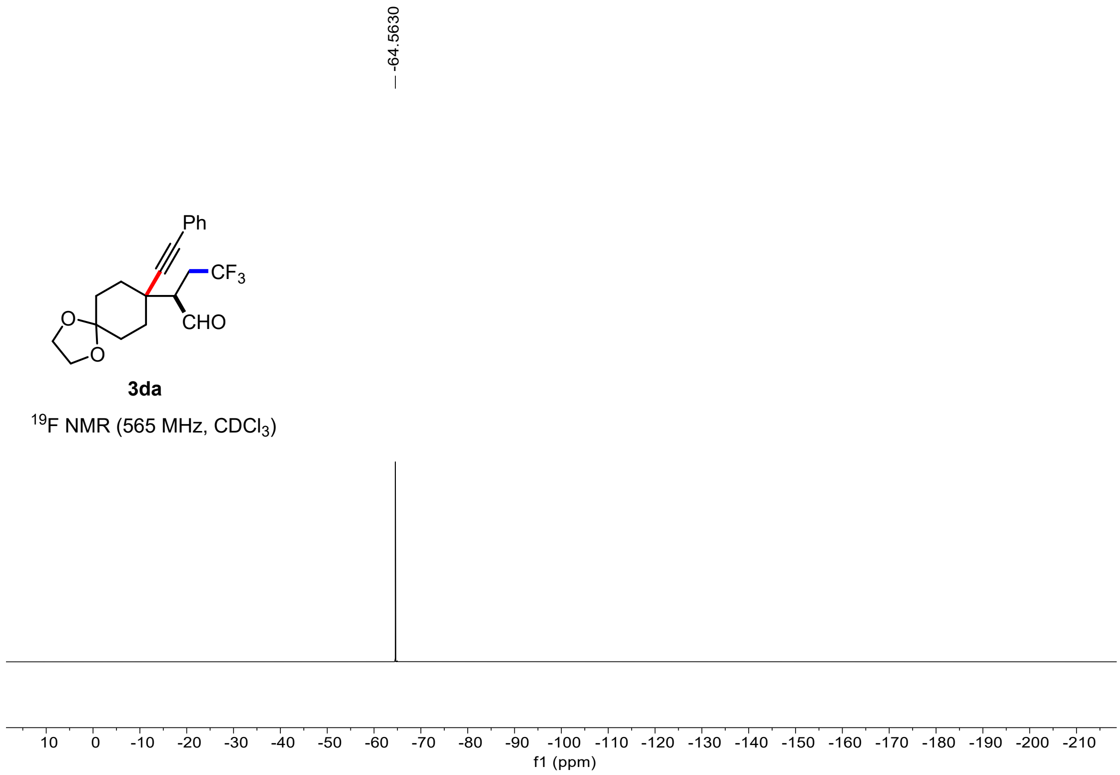
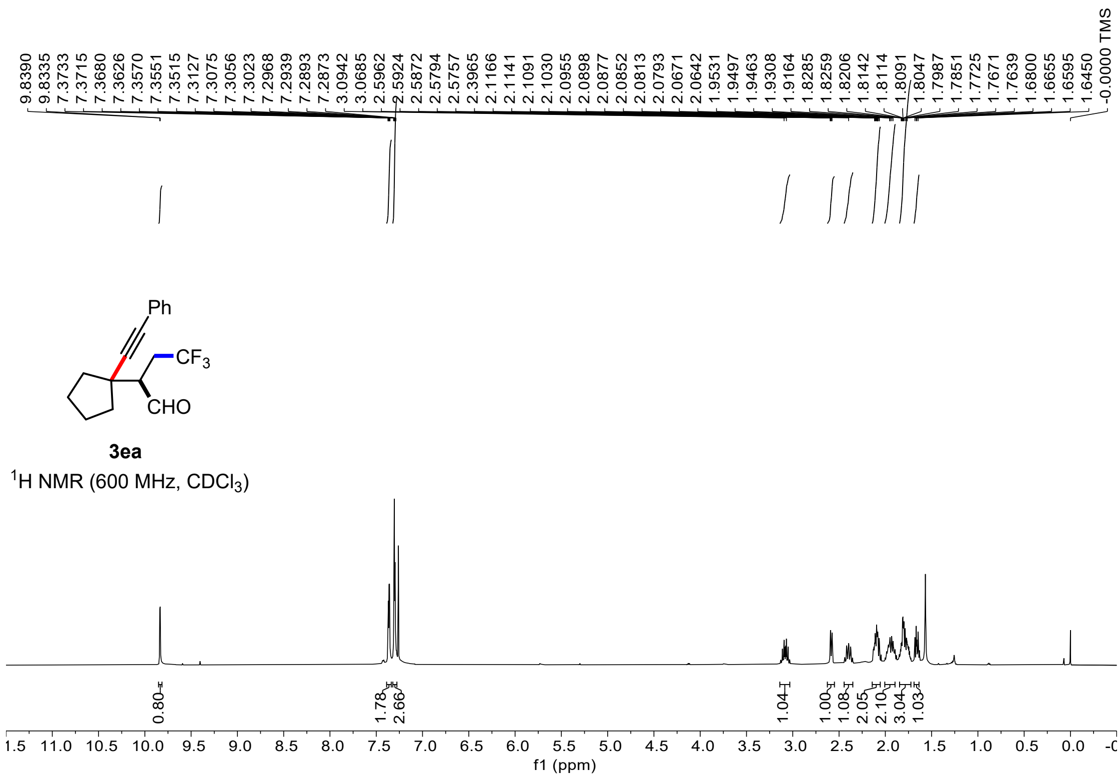
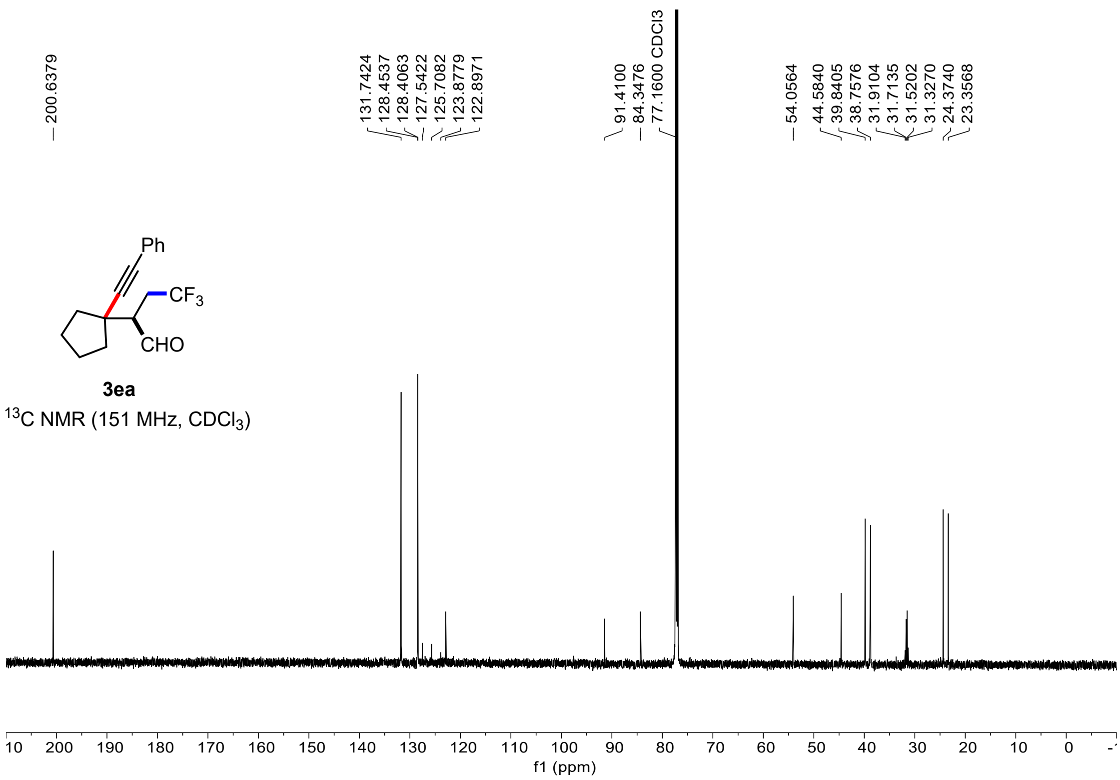
131.8373
129.3570
128.6580
128.5231
127.5605
125.7302
122.5363
107.8209
89.0475
86.2728
77.1600 CDCl3
64.6154
64.4039
53.7502
38.3421
33.2230
33.1027
31.7391
31.5896
30.1458
29.9489
29.7557
29.5588
Ph
CF3
CHO
O
O
3da
13C NMR (151 MHz, CDCl3)
f1 (ppm)


-64.5630
Ph
CF3
CHO
O
O
3da
19F NMR (565 MHz, CDCl3)
f1 (ppm)



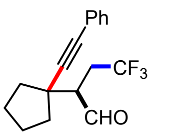
3ea

^{1}H NMR (600 MHz, $CDCl_3$)



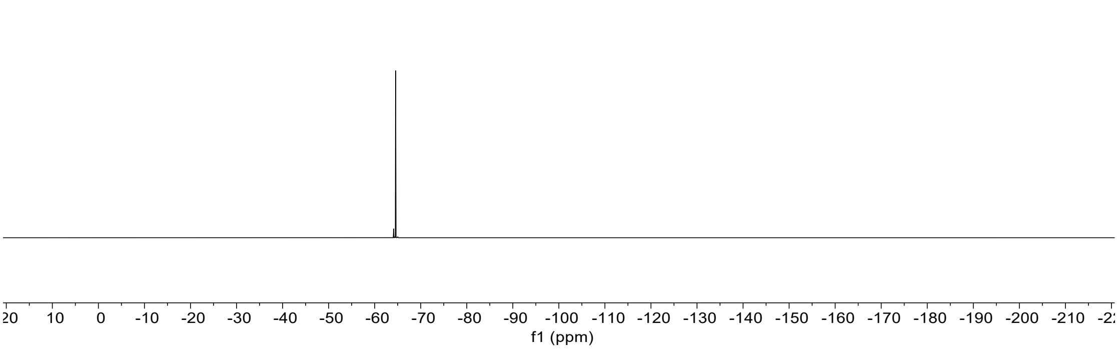
3ea

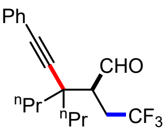
^{13}C NMR (151 MHz, $CDCl_3$)



3ea

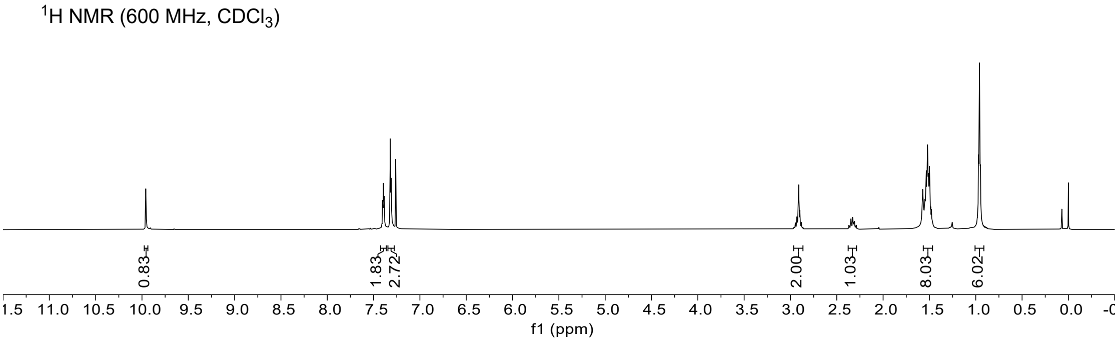
^{19}F NMR (377 MHz, $CDCl_3$)





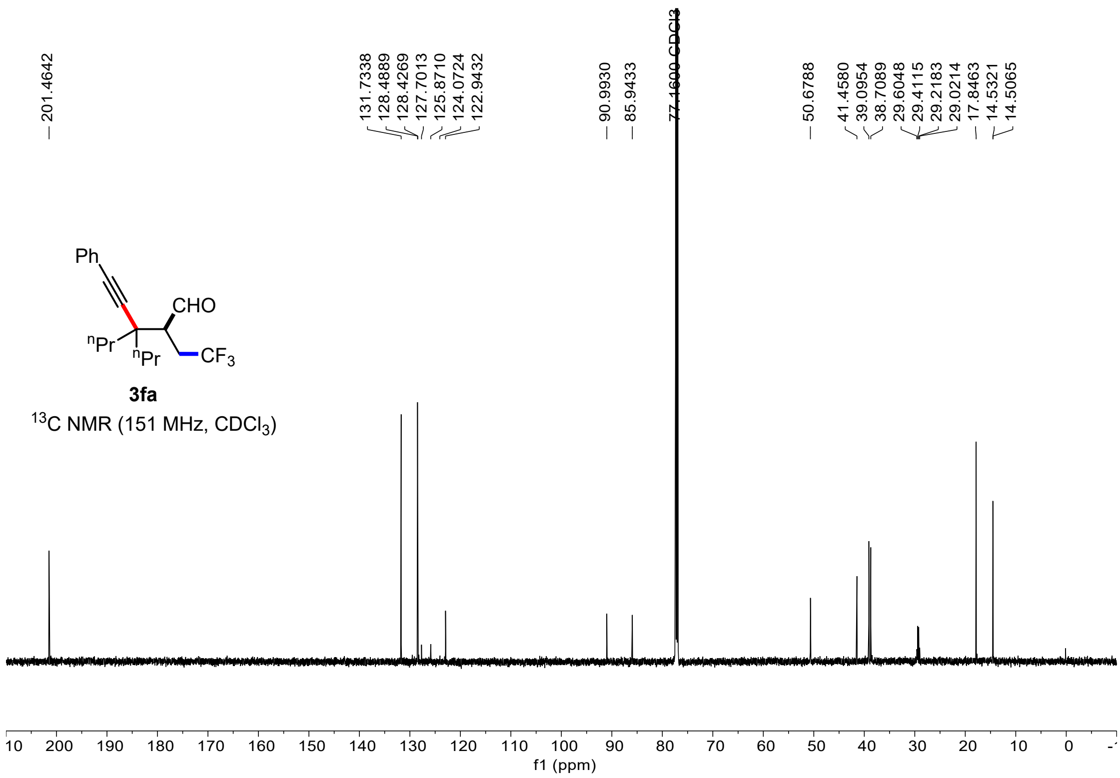
3fa

^{1}H NMR (600 MHz, $CDCl_3$)



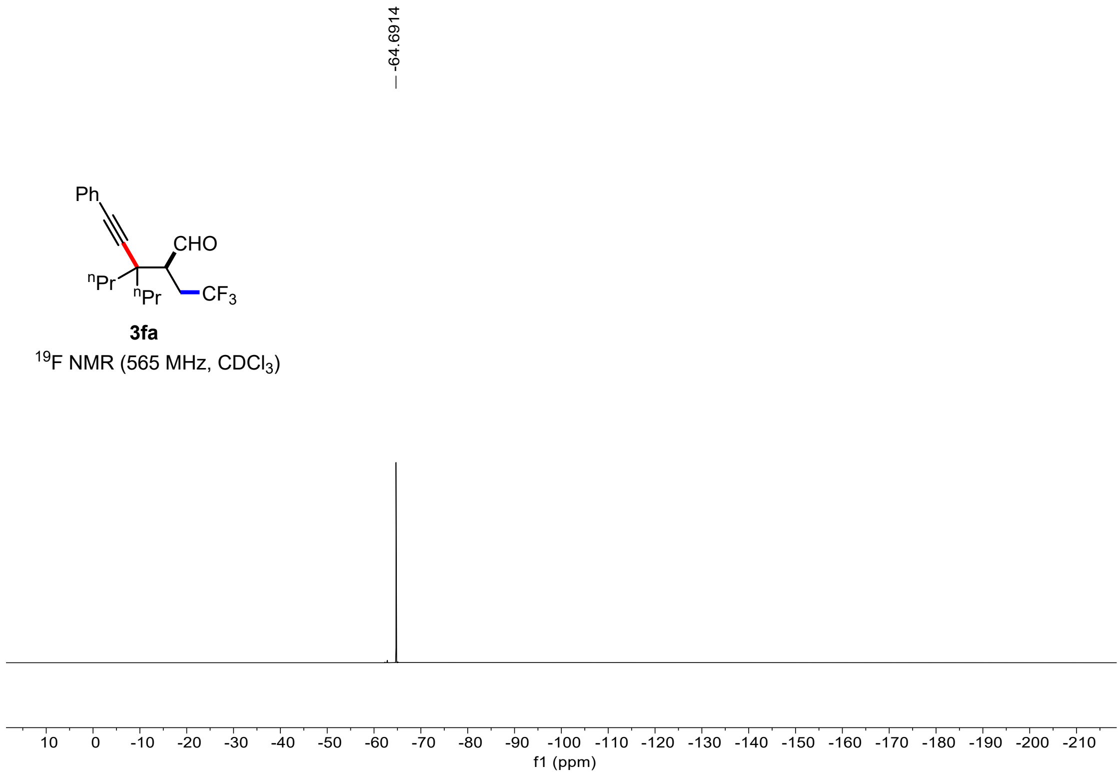
3fa

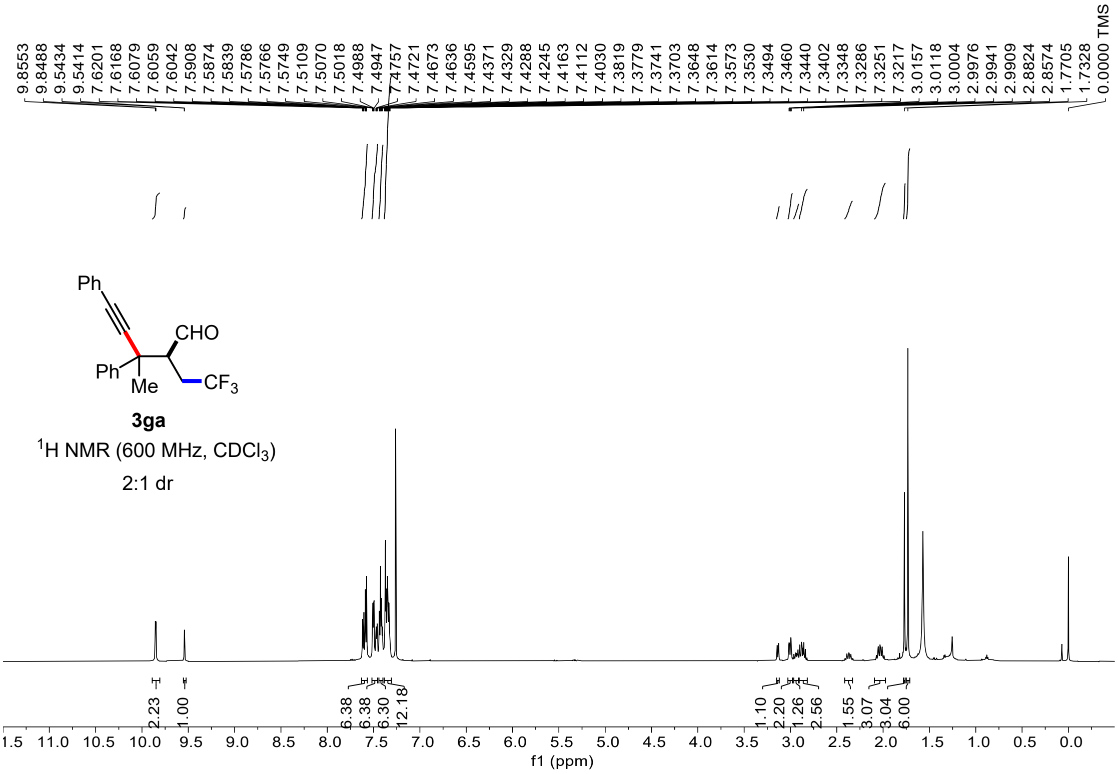
^{13}C NMR (151 MHz, $CDCl_3$)

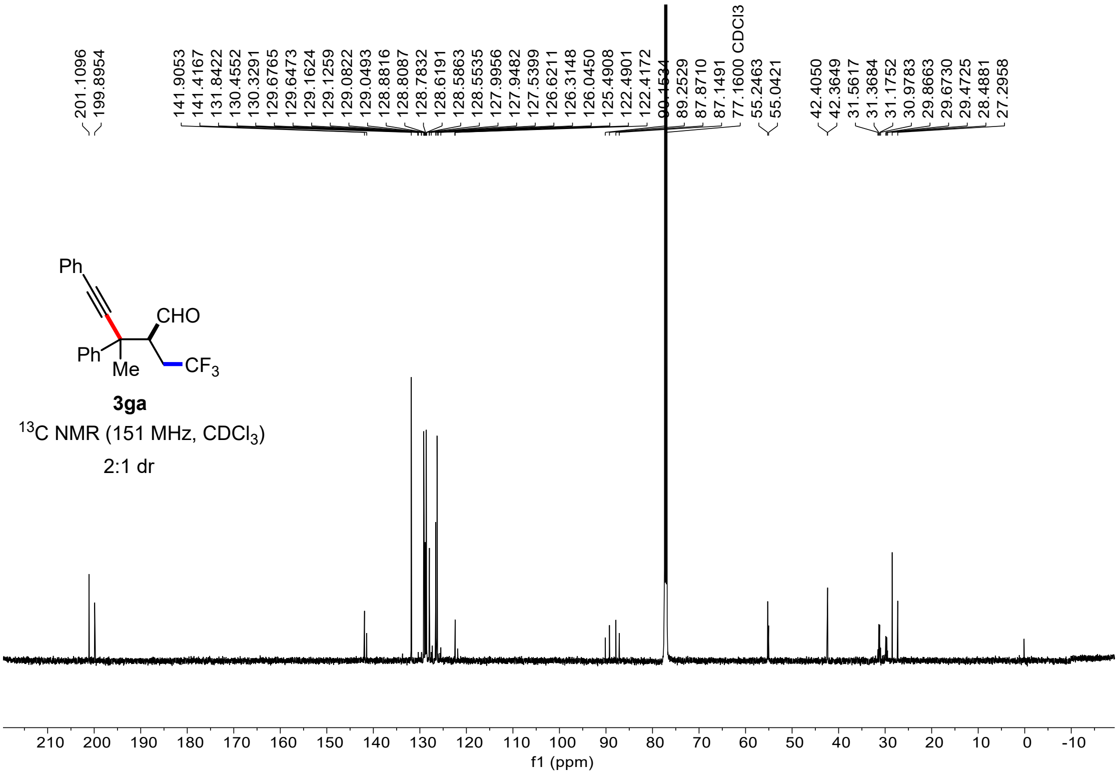


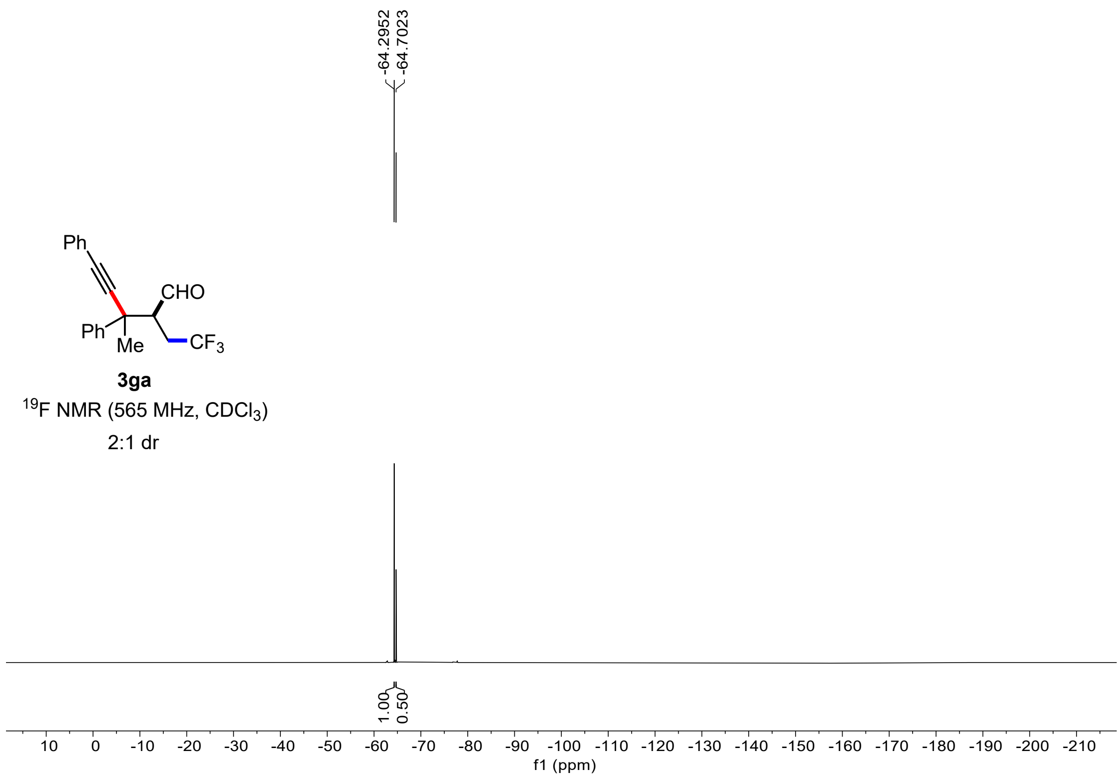
3fa

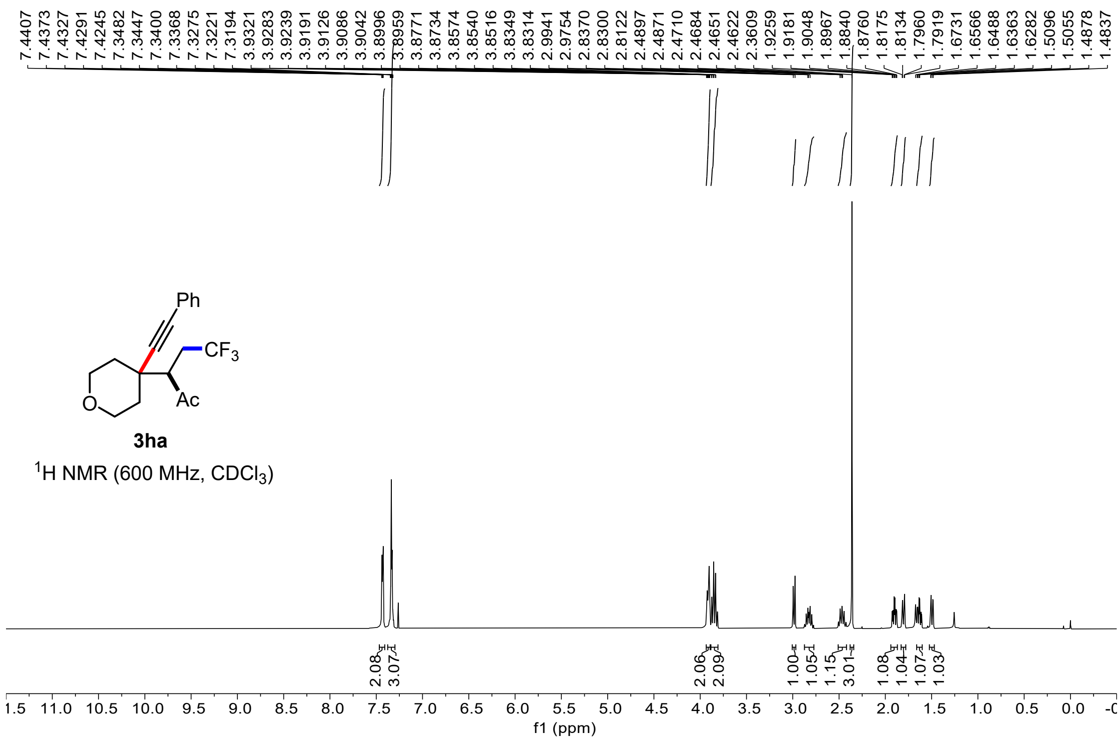
^{19}F NMR (565 MHz, $CDCl_3$)

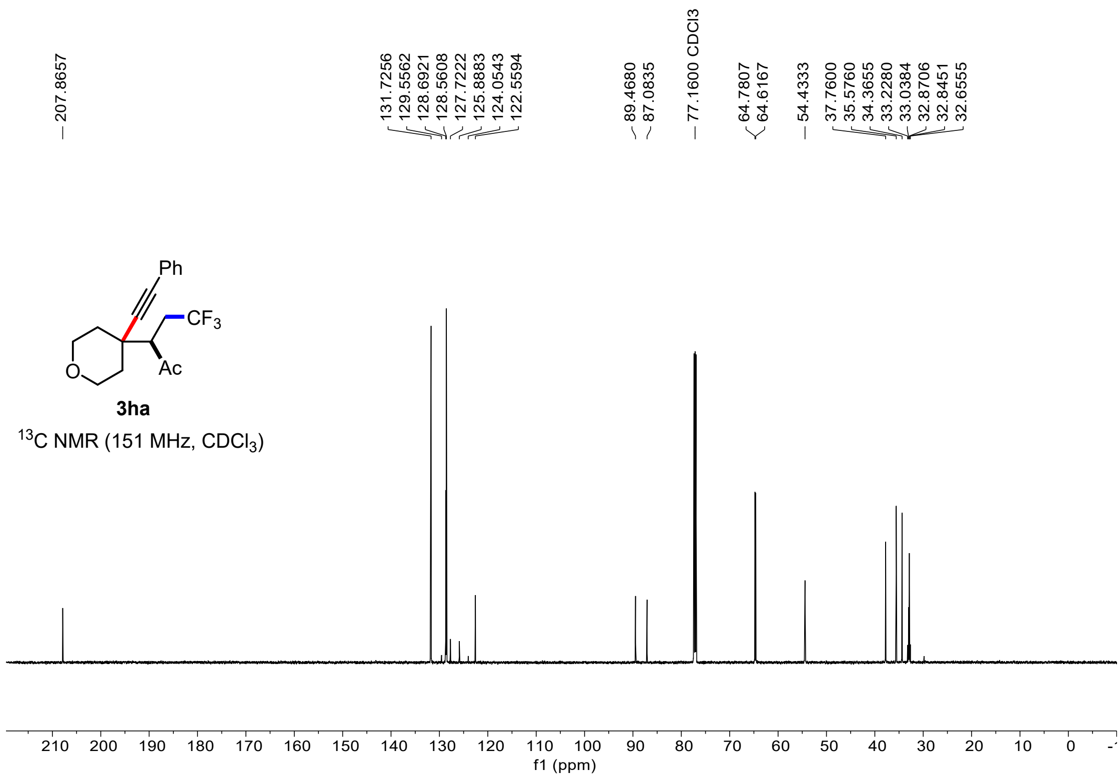



9.8553 9.8488 9.5434 9.5414 7.6201 7.6168 7.6079 7.6059 7.6042 7.5908 7.5874 7.5839 7.5786 7.5766 7.5749 7.5109 7.5070 7.5018 7.4988 7.4947 7.4757 7.4721 7.4673 7.4636 7.4595 7.4371 7.4329 7.4288 7.4245 7.4163 7.4112 7.4030 7.3819 7.3779 7.3741 7.3703 7.3648 7.3614 7.3573 7.3530 7.3494 7.3460 7.3440 7.3402 7.3348 7.3286 7.3251 7.3217 3.0157 3.0118 3.0004 2.9976 2.9941 2.9909 2.8824 2.8574 1.7705 1.7328 0.0000 TMS
Ph
CHO
Ph
Me
CF_3
3ga
^1H NMR (600 MHz, $CDCl_3$)
2:1 dr
2.23 1.00 6.38 6.38 6.30 12.18 1.10 2.20 1.26 2.56 1.55 3.07 3.04 6.00
f1 (ppm)


201.1096 199.8954 141.9053 141.4167 131.8422 130.4552 130.3291 129.6765 129.6473 129.1624 129.1259 129.0822 129.0493 128.8816 128.8087 128.7832 128.6191 128.5863 128.5535 127.9956 127.9482 127.5399 126.6211 126.3148 126.0450 125.4908 122.4901 122.4172 90.1534 89.2529 87.8710 87.1491 77.1600 CDCl3 55.2463 55.0421 42.4050 42.3649 31.5617 31.3684 31.1752 30.9783 29.8663 29.6730 29.4725 28.4881 27.2958
Ph
CHO
Ph
Me
CF_3
3ga
^{13}C NMR (151 MHz, $CDCl_3$)
2:1 dr
f1 (ppm)

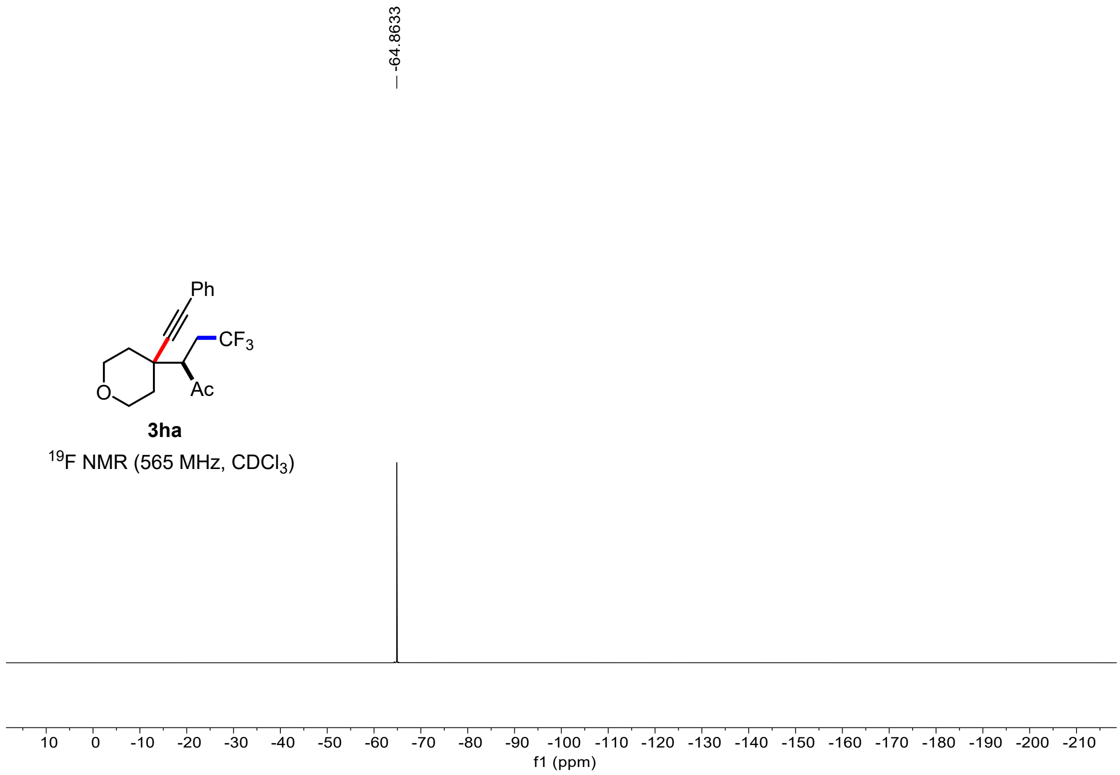

-64.2952
-64.7023
Ph
CHO
Ph
Me
CF3
3ga
19F NMR (565 MHz, CDCl3)
2:1 dr
1.00
0.50
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.4407 7.4373 7.4327 7.4291 7.4245 7.3482 7.3447 7.3400 7.3368 7.3275 7.3221 7.3194 3.9321 3.9283 3.9239 3.9191 3.9126 3.9086 3.9042 3.8996 3.8959 3.8771 3.8734 3.8574 3.8540 3.8516 3.8349 3.8314 2.9941 2.9754 2.8370 2.8300 2.8122 2.4897 2.4871 2.4710 2.4684 2.4651 2.4622 2.3609 1.9259 1.9181 1.9048 1.8967 1.8840 1.8760 1.8175 1.8134 1.7960 1.7919 1.6731 1.6566 1.6488 1.6363 1.6282 1.5096 1.5055 1.4878 1.4837
Ph
CF3
O
Ac
3ha
1H NMR (600 MHz, CDCl3)
2.08
3.07
2.06
2.09
1.00
1.05
1.15
3.01
1.08
1.04
1.07
1.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



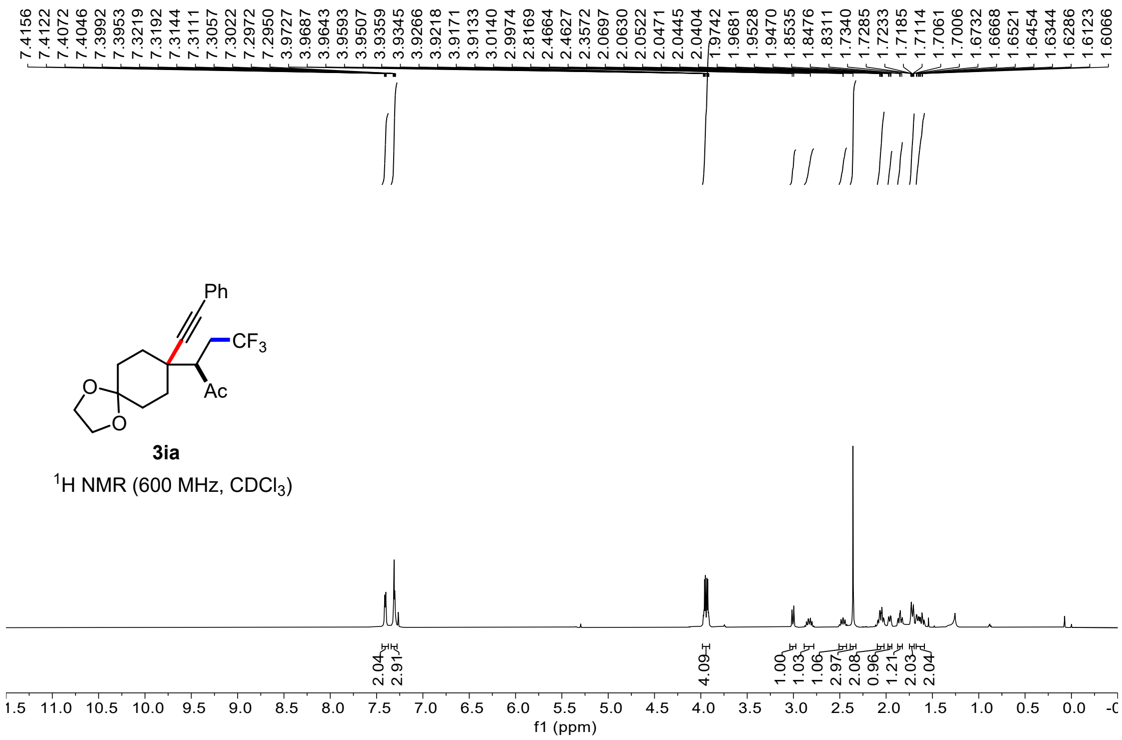
3ha

^{13}C NMR (151 MHz, $CDCl_3$)



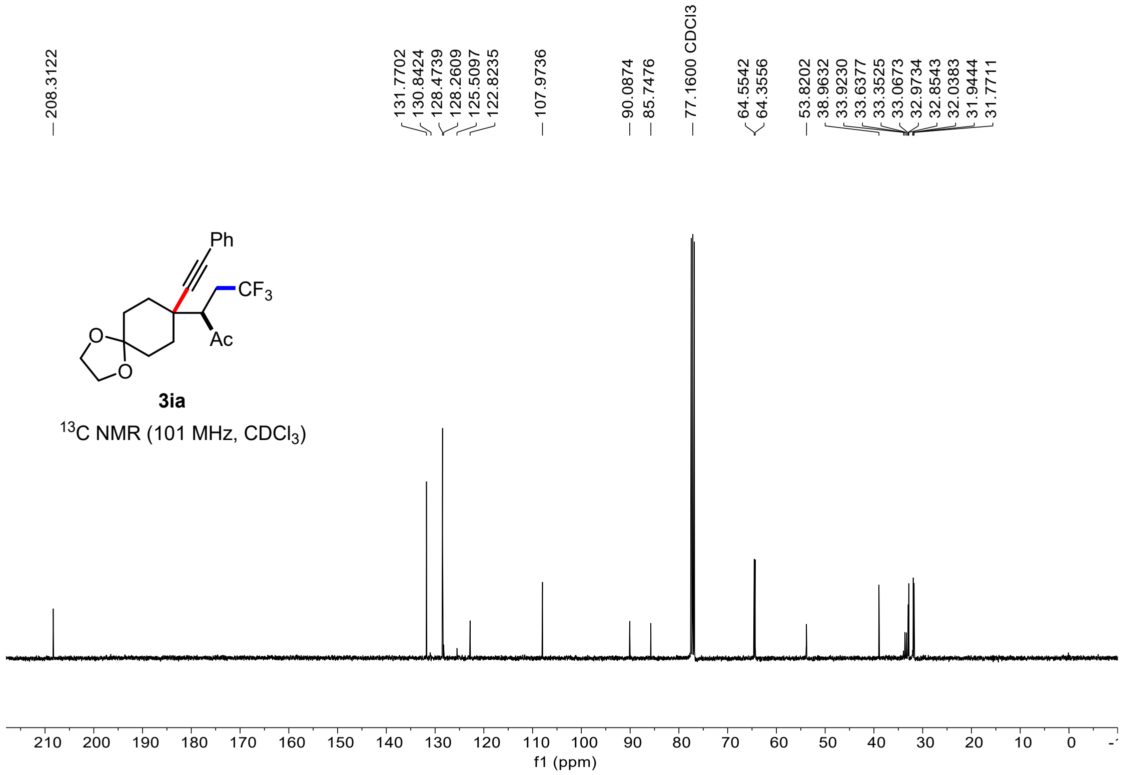
3ha

^{19}F NMR (565 MHz, $CDCl_3$)



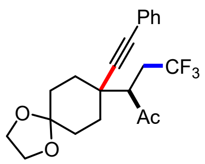
3ia

^{1}H NMR (600 MHz, $CDCl_3$)



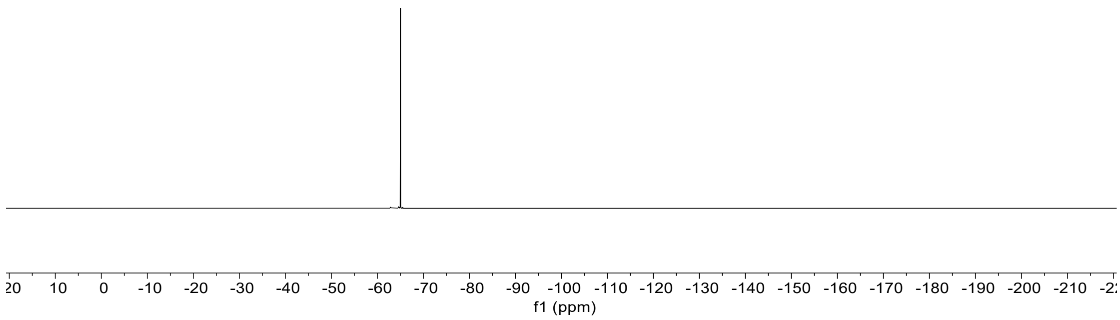
3ia

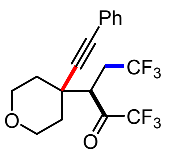
^{13}C NMR (101 MHz, $CDCl_3$)



3ia

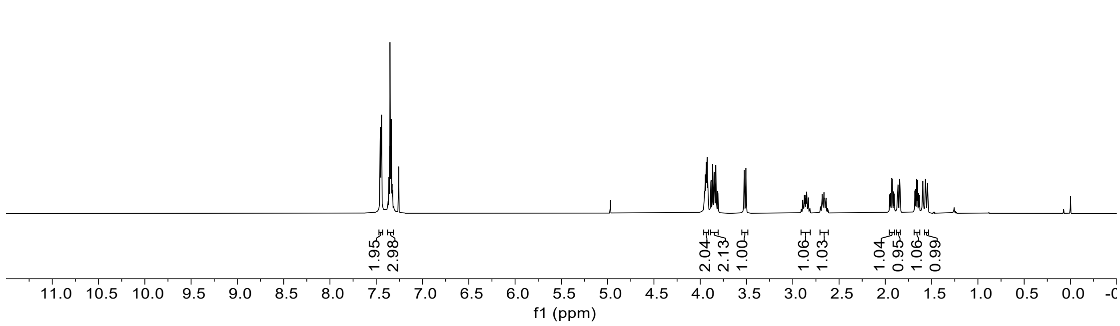
^{19}F NMR (377 MHz, $CDCl_3$)

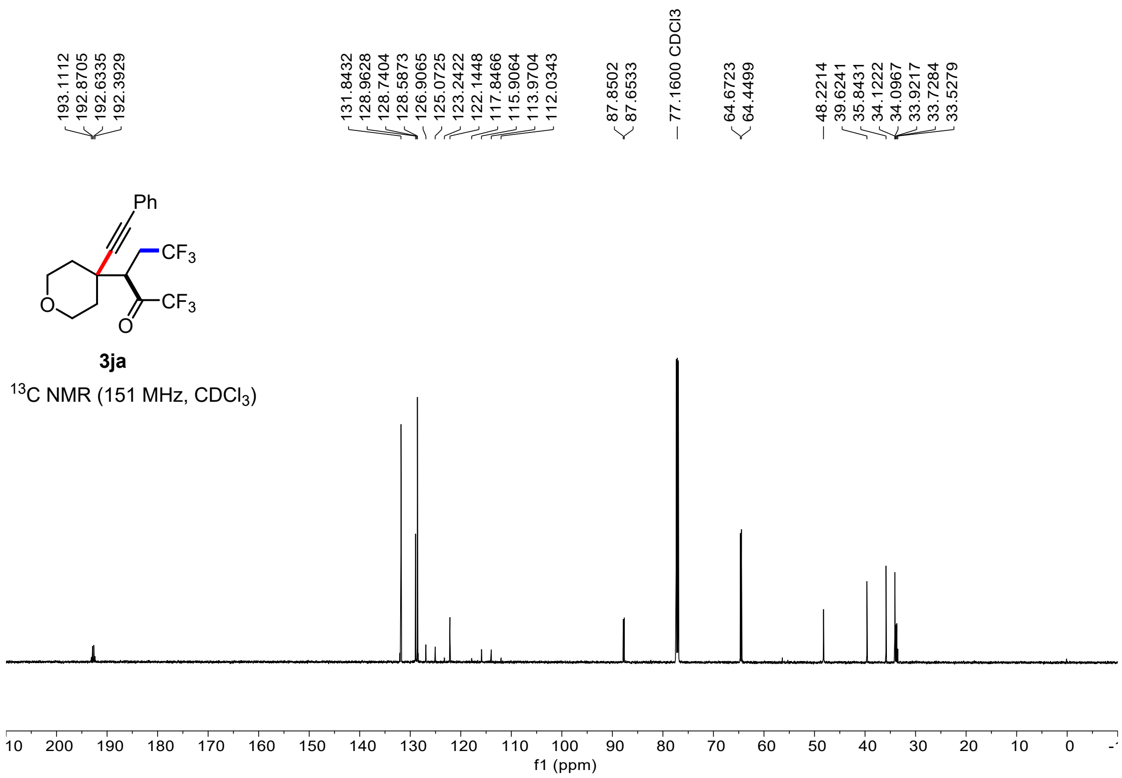




3ja

^{1}H NMR (600 MHz, $CDCl_3$)

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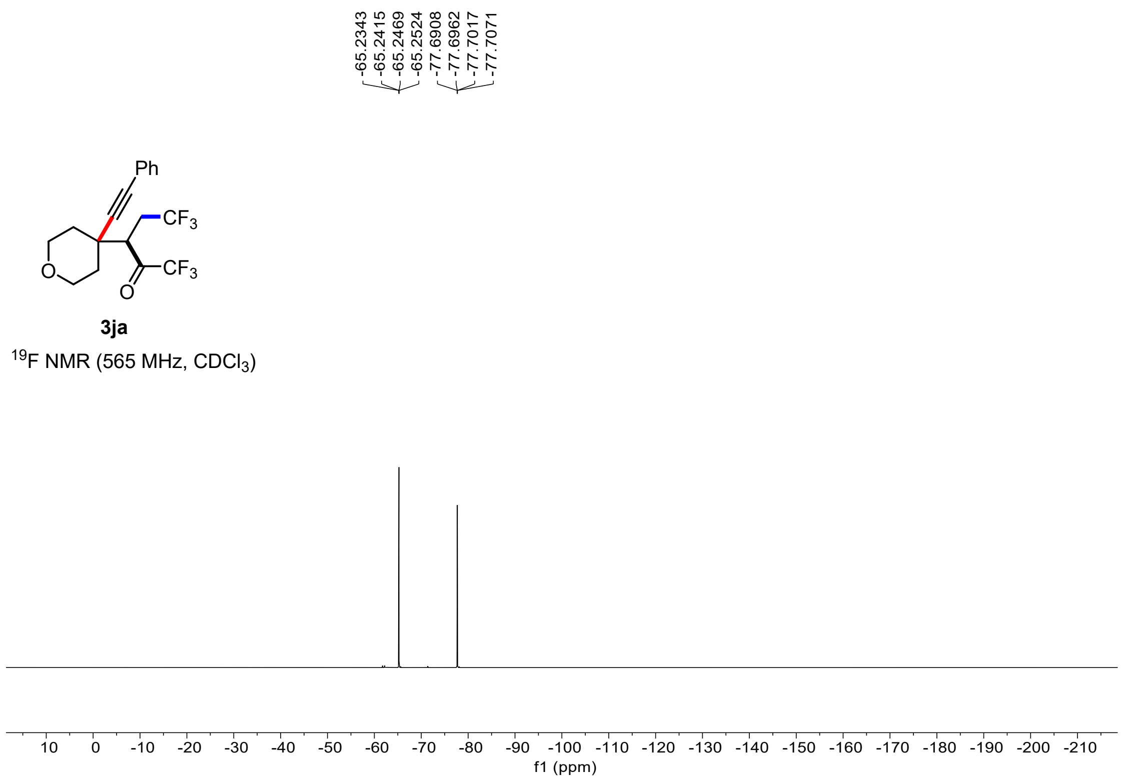
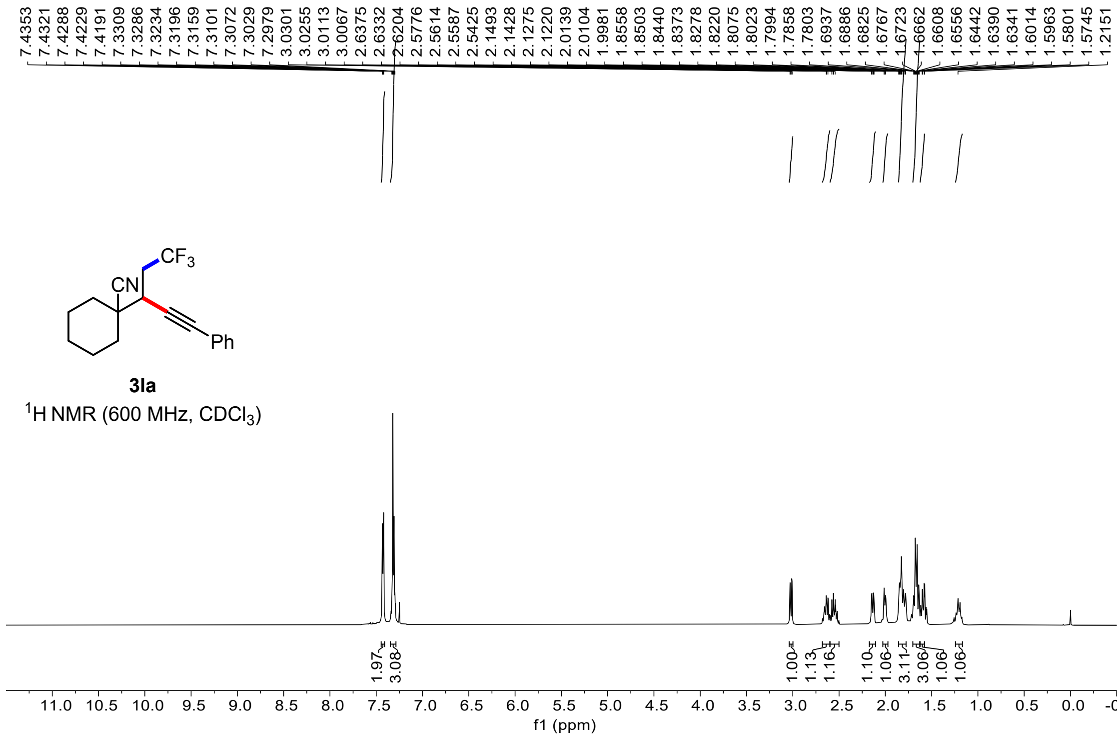
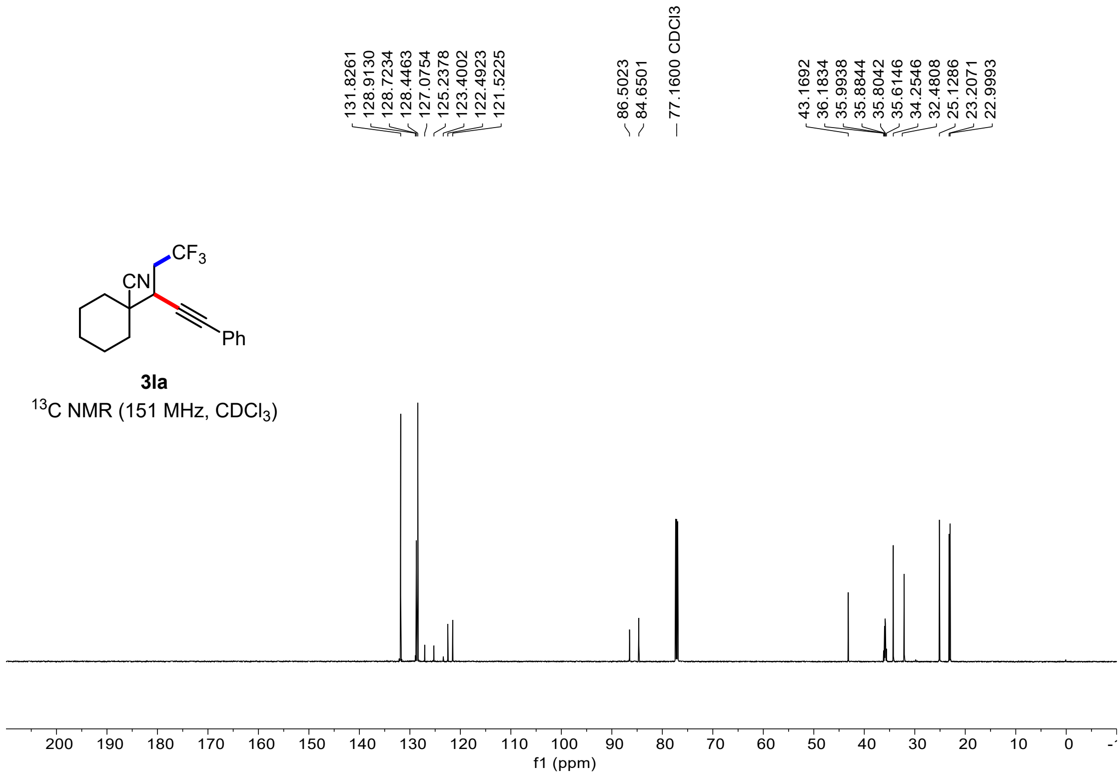
192.8705
192.6335
192.3929
131.8432
128.9628
128.7404
128.5873
126.9065
125.0725
123.2422
122.1448
117.8466
115.9064
113.9704
112.0343
87.8502
87.6533
77.1600 CDCl3
64.6723
64.4499
48.2214
39.6241
35.8431
34.1222
34.0967
33.9217
33.7284
33.5279
Ph
CF3
O
CF3
O
3ja
13C NMR (151 MHz, CDCl3)
f1 (ppm)


-65.2343
-65.2415
-65.2469
-65.2524
-77.6908
-77.6962
-77.7017
-77.7071
Ph
CF3
O
CF3
O
3ja
19F NMR (565 MHz, CDCl3)
f1 (ppm)



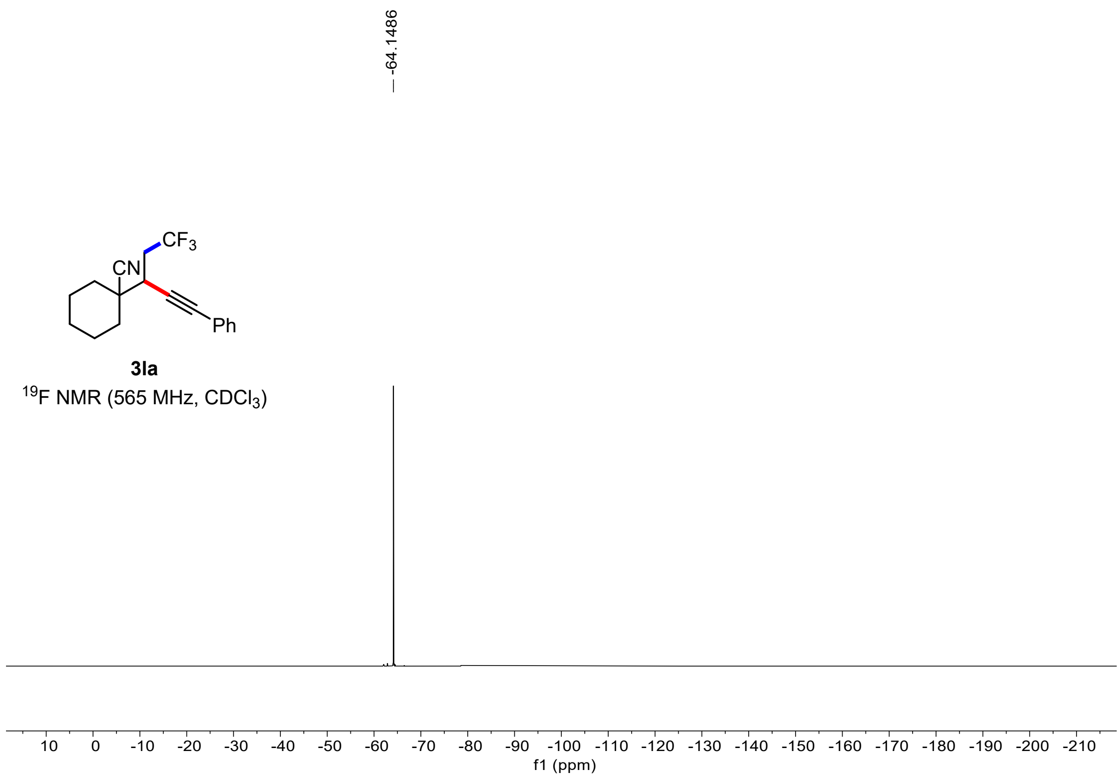
3la

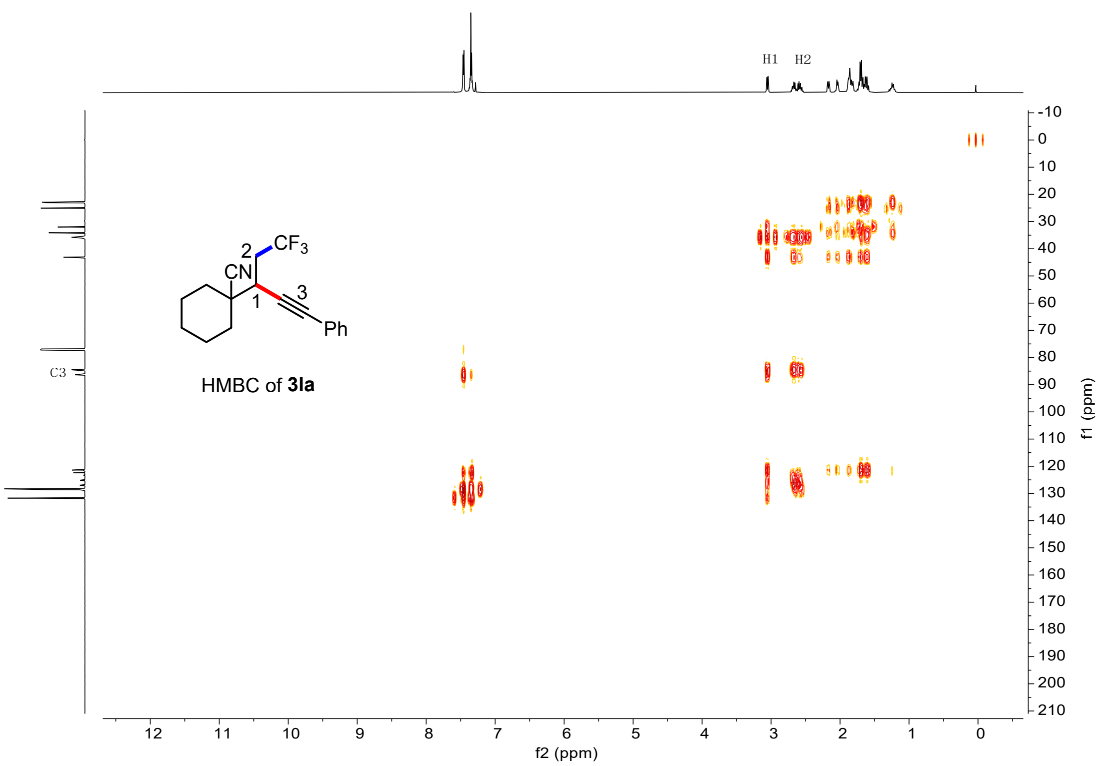
^1H NMR (600 MHz, $CDCl_3$)

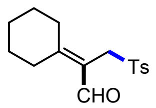


3la

^{13}C NMR (151 MHz, $CDCl_3$)

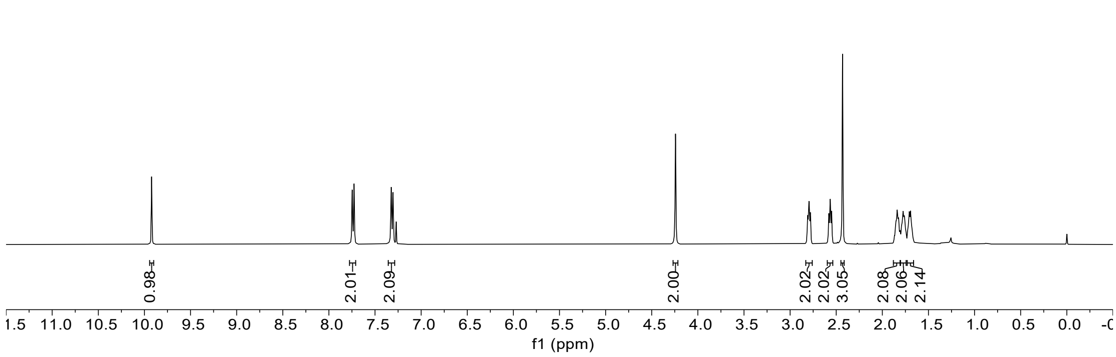

-64.1486
CF3
CN
Ph
3la
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

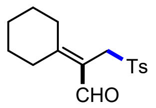

H1 H2
2
CF3
CN
1
3
Ph
HMBC of 3la
C3
12 11 10 9 8 7 6 5 4 3 2 1 0
f2 (ppm)
-10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210
f1 (ppm)



4

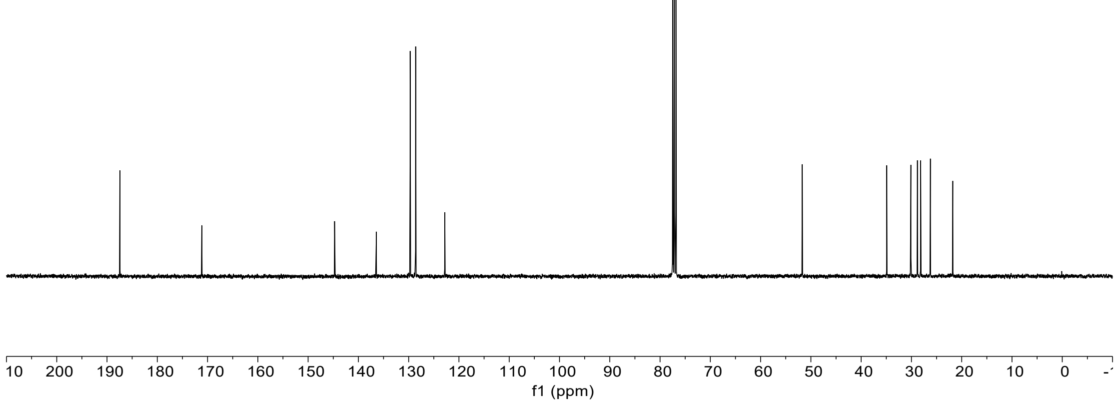
^{1}H NMR (400 MHz, $CDCl_3$)

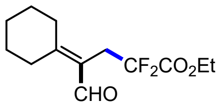




4

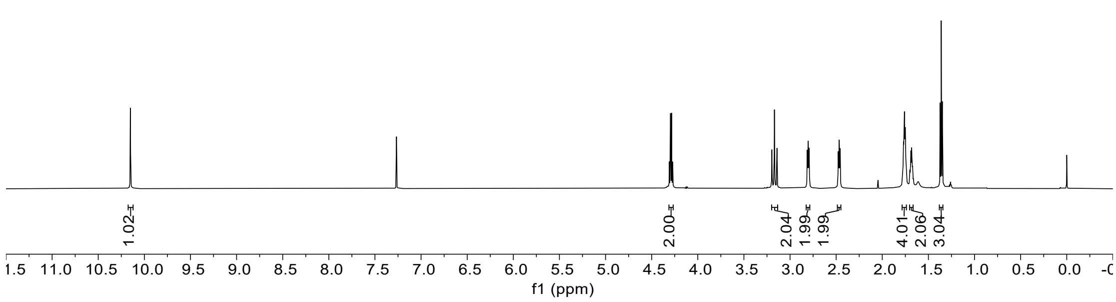
^{13}C NMR (101 MHz, $CDCl_3$)

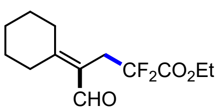




5

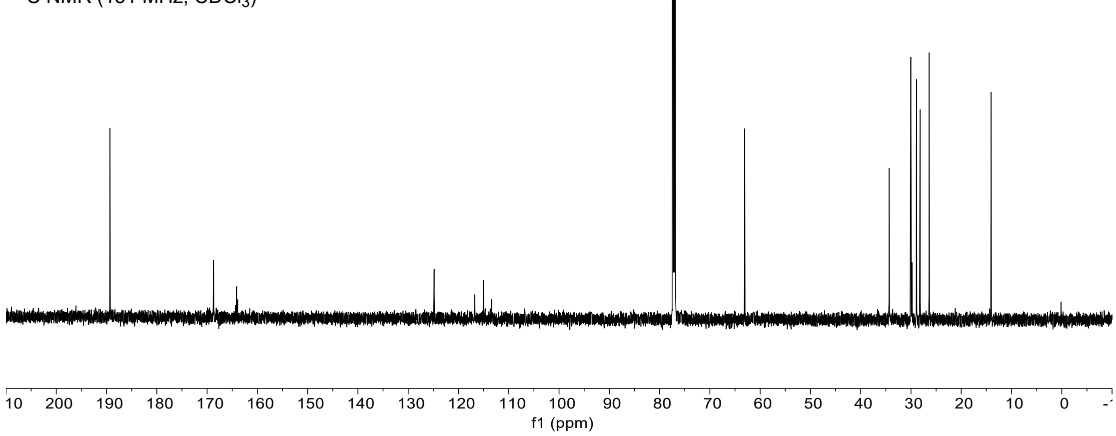
^{1}H NMR (600 MHz, $CDCl_3$)

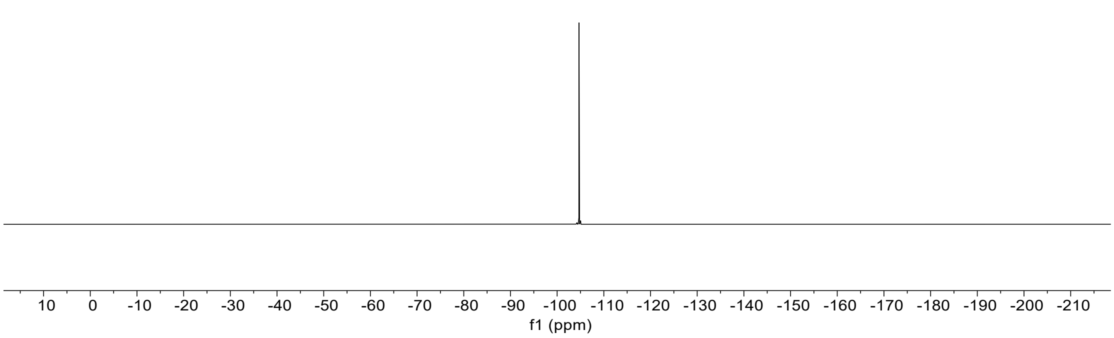


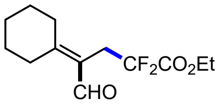


5

^{13}C NMR (151 MHz, $CDCl_3$)

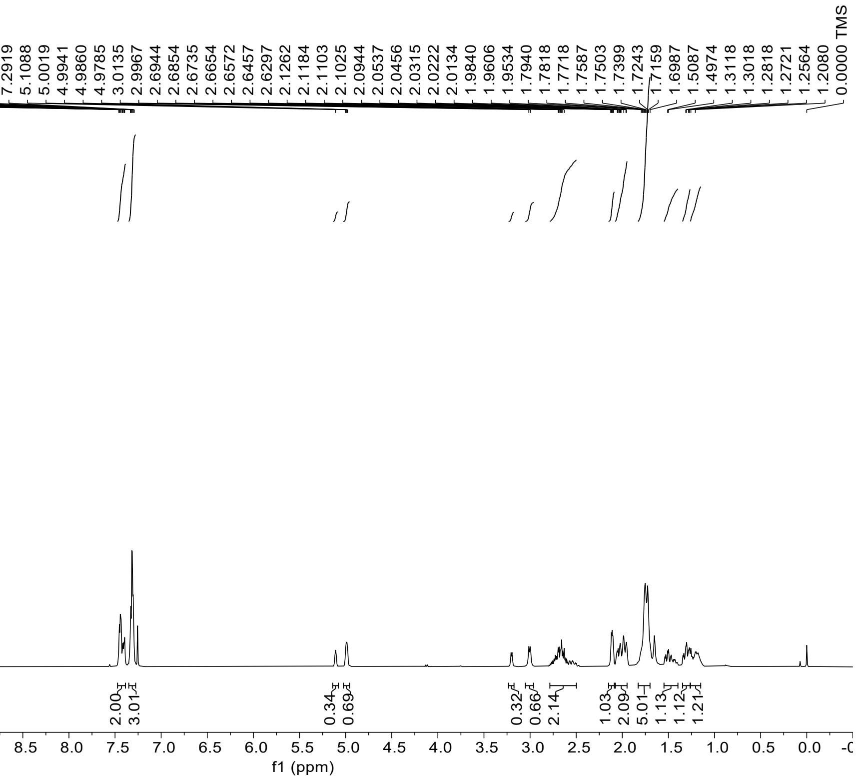


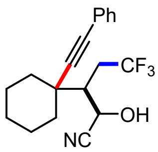




5

^{19}F NMR (377 MHz, $CDCl_3$)

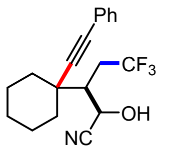




6

^{1}H NMR (400 MHz, $CDCl_3$)

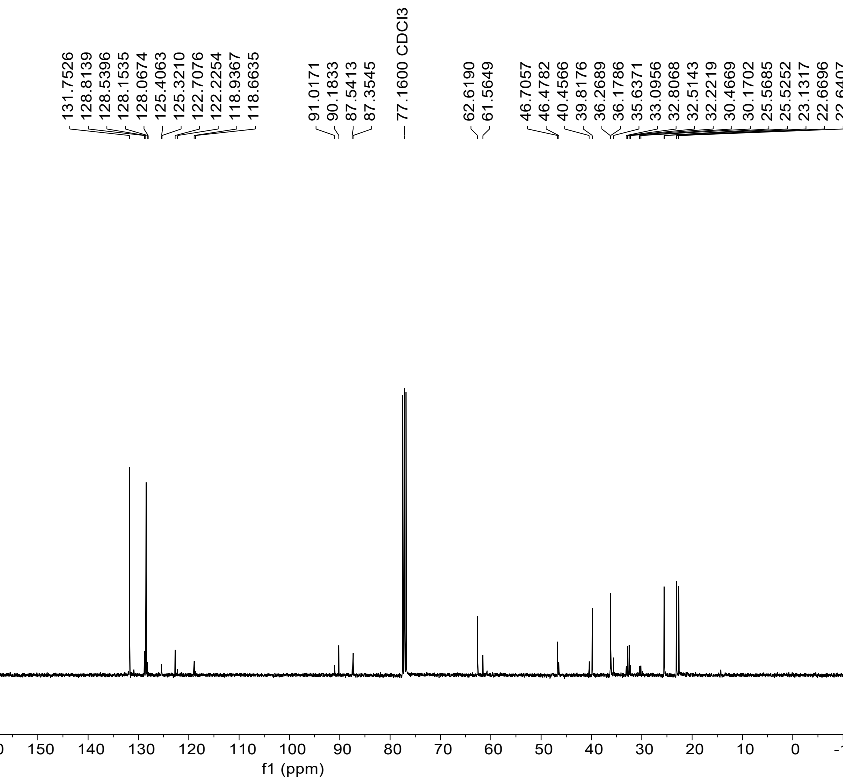
2:1 dr

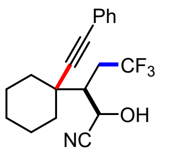


6

^{13}C NMR (101 MHz, $CDCl_3$)

2:1 dr

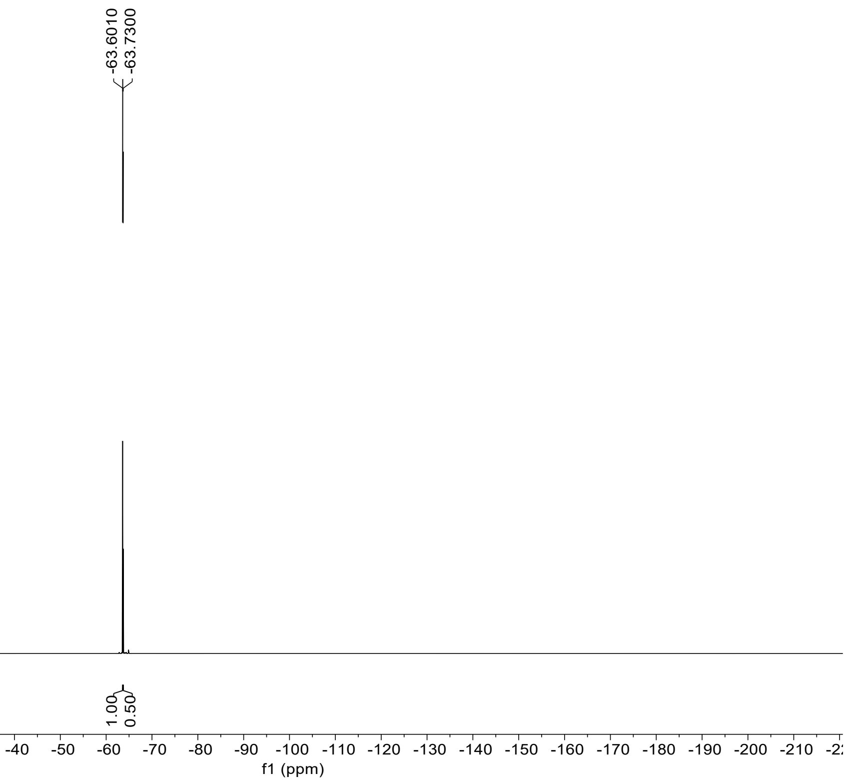


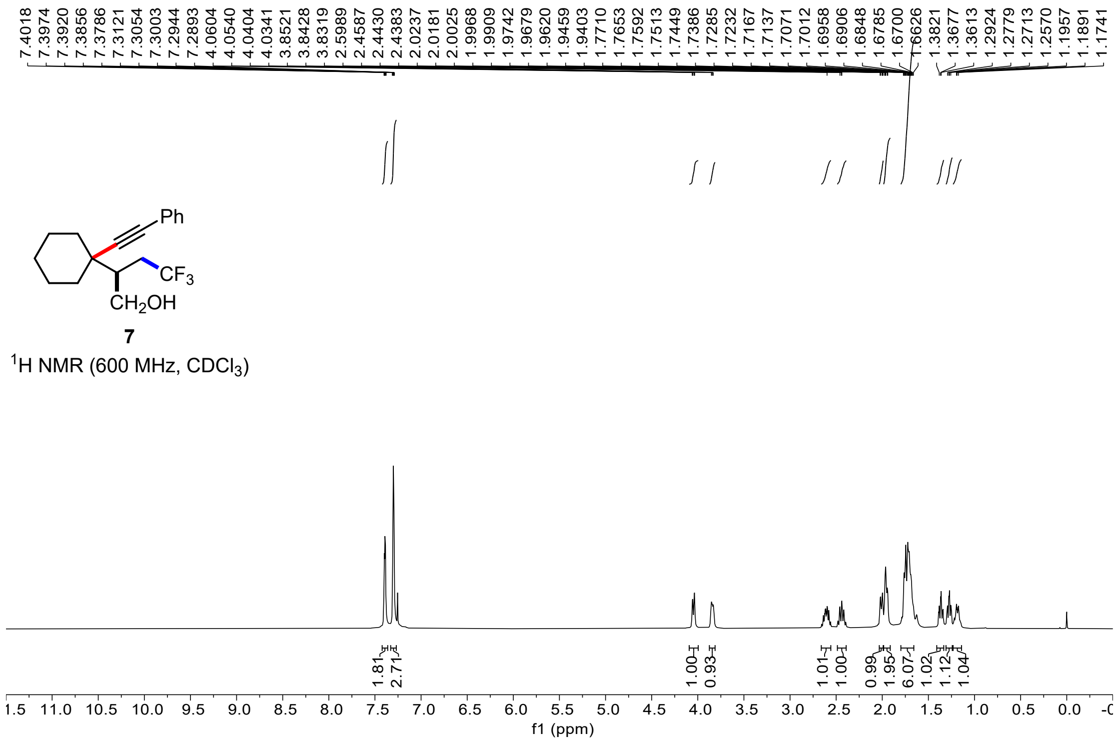


6

^{19}F NMR (377 MHz, $CDCl_3$)

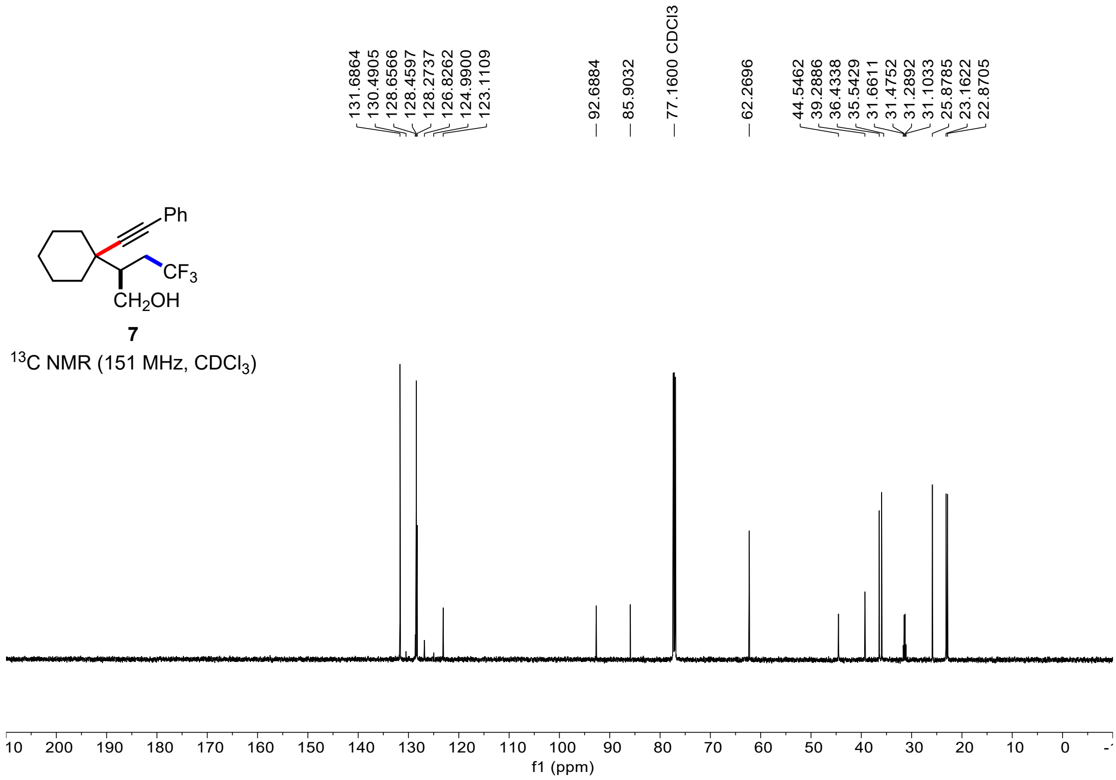
2:1 dr





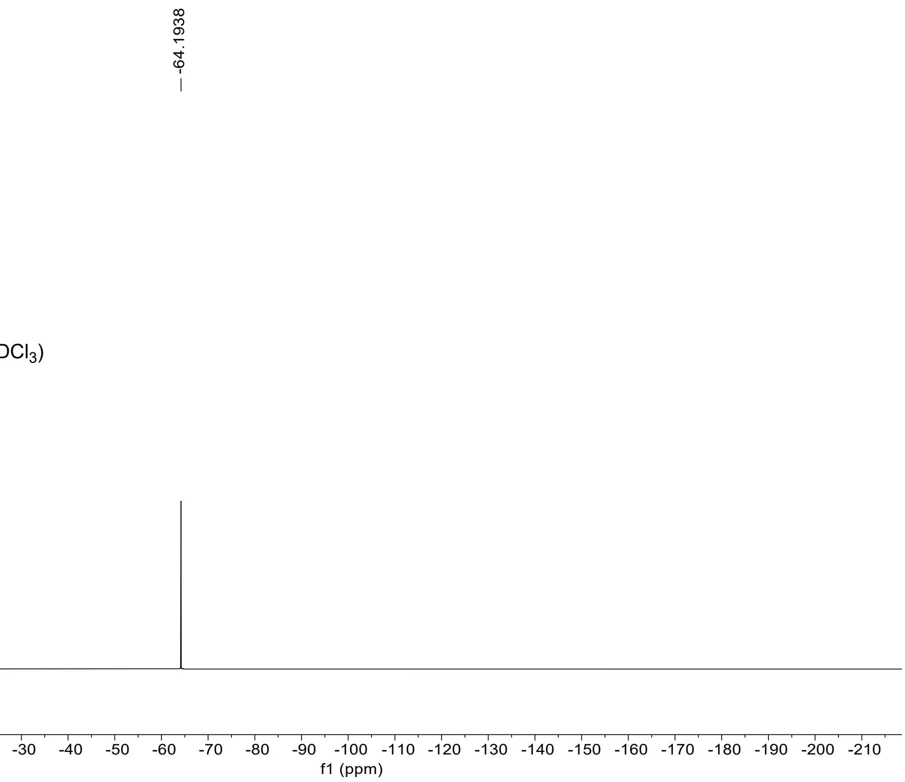
7

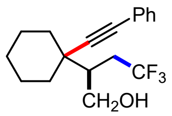
^{1}H NMR (600 MHz, $CDCl_3$)



7

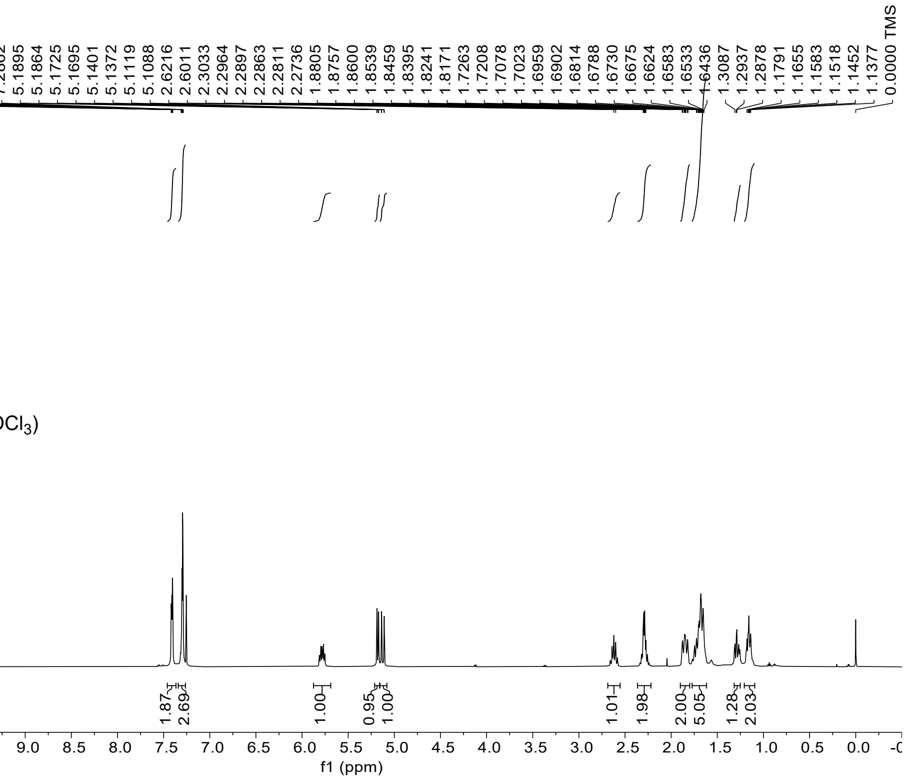
^{13}C NMR (151 MHz, $CDCl_3$)

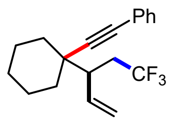




7

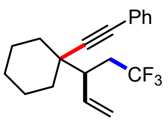
^{19}F NMR (565 MHz, $CDCl_3$)





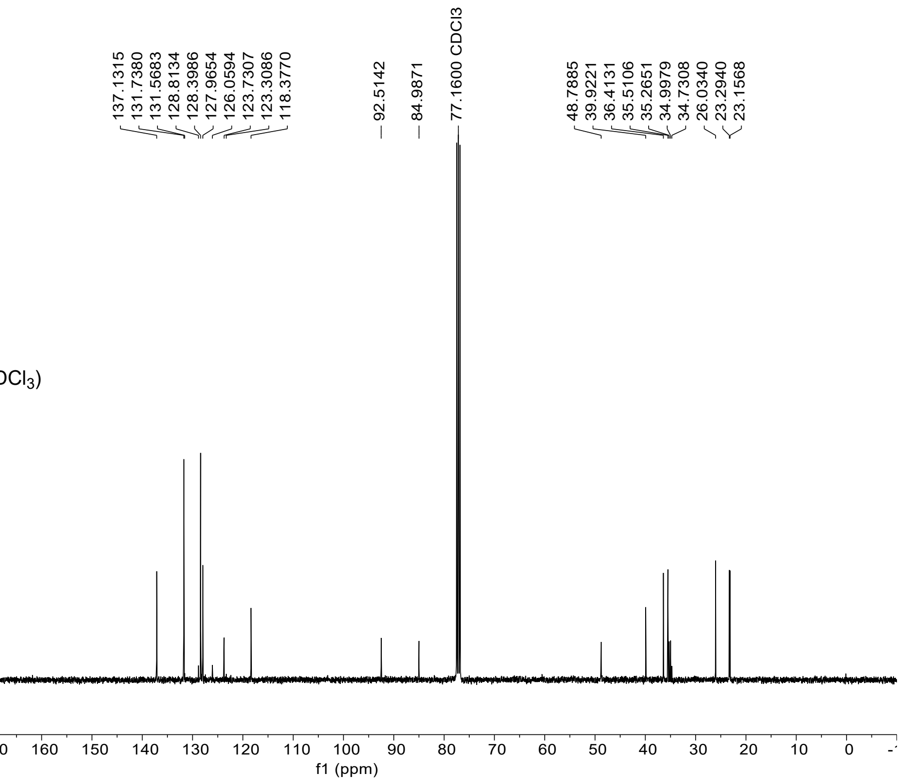
8

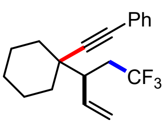
^{1}H NMR (600 MHz, $CDCl_3$)



8

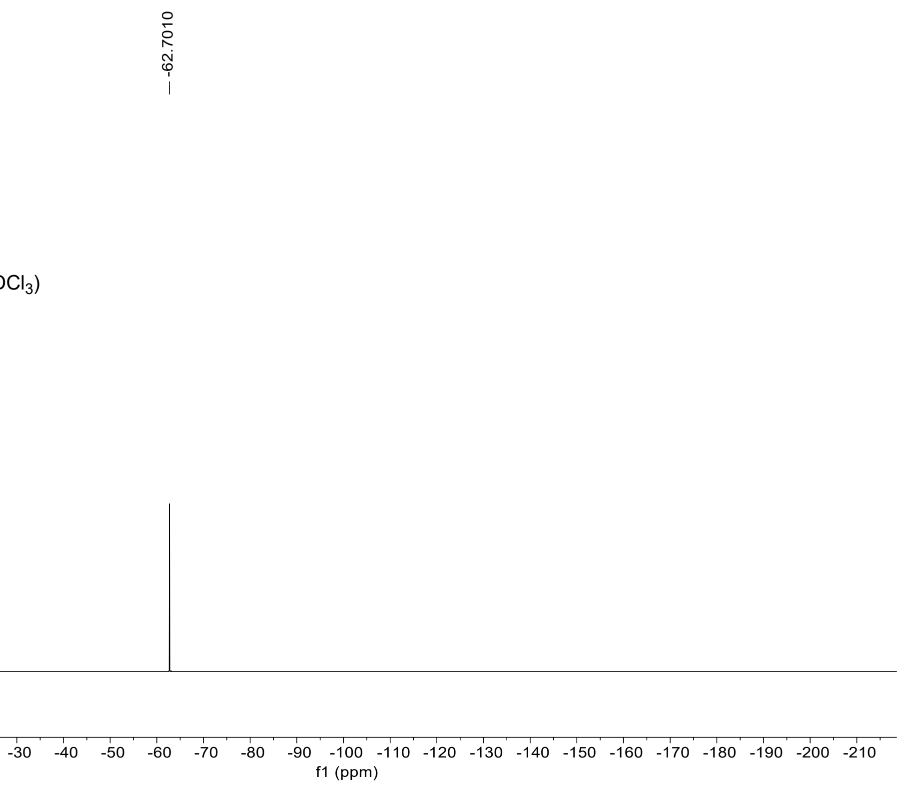
^{13}C NMR (101 MHz, $CDCl_3$)

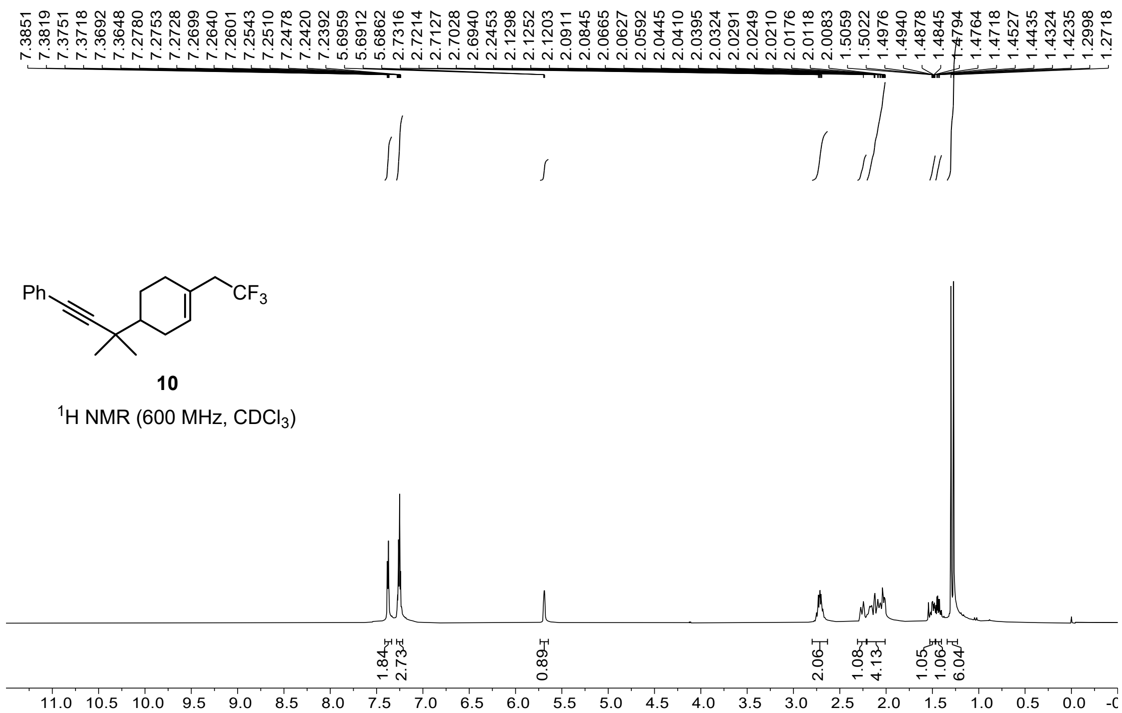




8

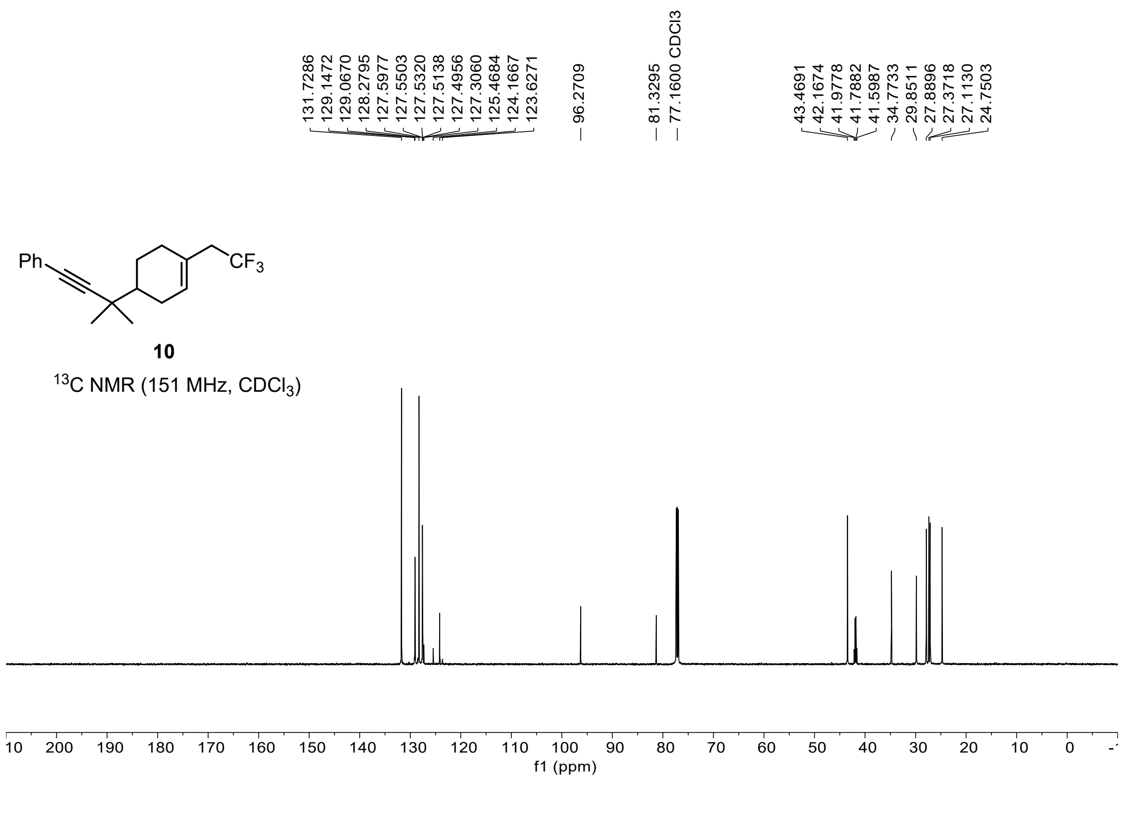
^{19}F NMR (565 MHz, $CDCl_3$)





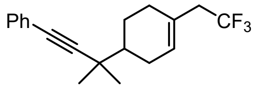
10

^{1}H NMR (600 MHz, $CDCl_3$)



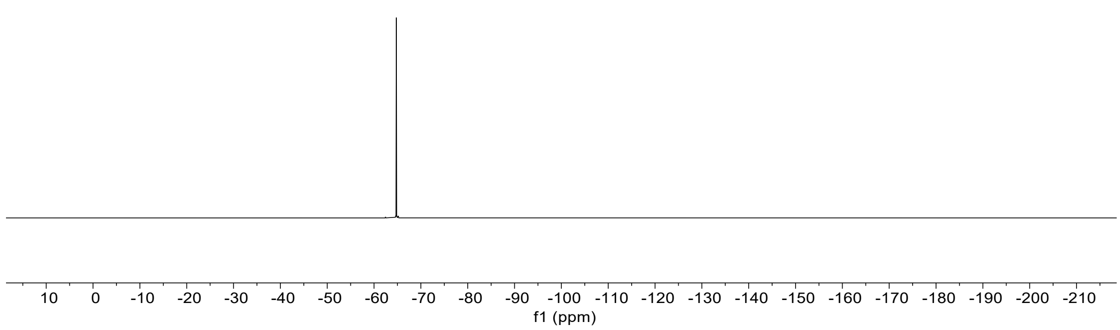
10

^{13}C NMR (151 MHz, $CDCl_3$)



10

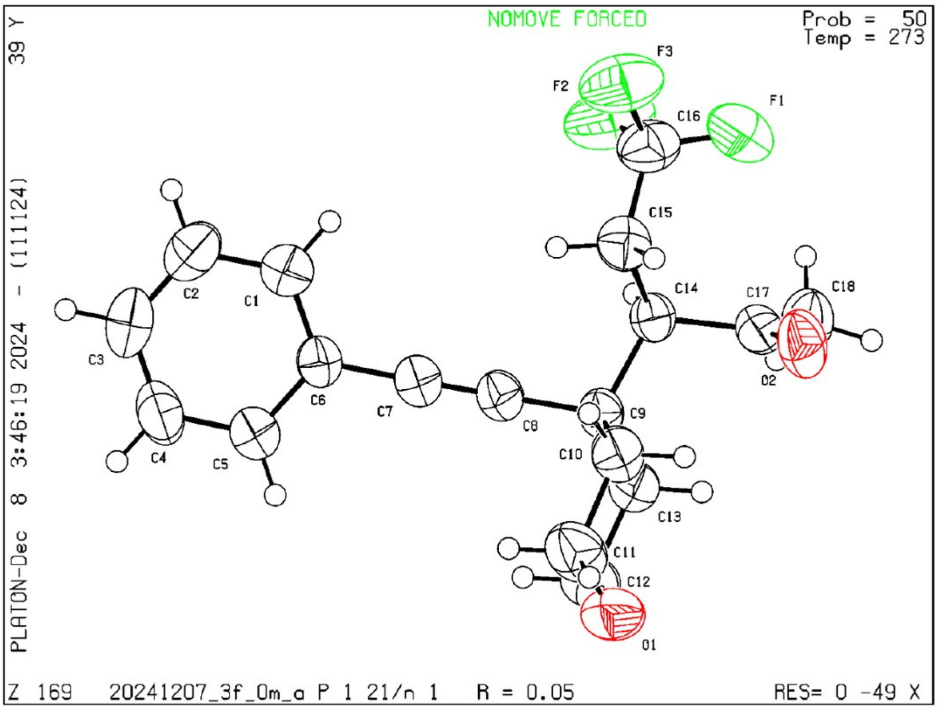
^{19}F NMR (565 MHz, $CDCl_3$)



8. X Ray Crystallographic Data

The crystal of **3ha** was recrystallized in petroleum ether and dichloromethane via slow evaporation at room temperature. Crystallographic data for the structure **3ha** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2409040.

Datablock 20241207_3f_0m_a - ellipsoid plot



Crystal data and structure refinement for compound **3ha**

Empirical formula	$C_{18}H_{19}F_3O_2$
Formula weight	324.33
Temperature/K	273.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.5172(14)
b/Å	9.3987(10)
c/Å	13.5553(14)
α/°	90
β/°	106.810(5)
γ/°	90
Volume/Å^3	1648.5(3)
Z	4
ρ_{calc}g/cm^3	1.307
μ/mm^{-1}	0.906
F(000)	680.0
Crystal size/mm^3	0.38 × 0.34 × 0.26
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	10.964 to 136.646
Index ranges	$-16 \le h \le 16$, $-11 \le k \le 11$, $-16 \le l \le 16$
Reflections collected	21741

Independent reflections	3011[R_{int} = 0.0586, R_{sigma} = 0.0341]
Data/restraints/parameters	3011/0/209
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0483, wR_2 = 0.1177
Final R indexes [all data]	R_1 = 0.0609, wR_2 = 0.1293
Largest diff. peak/hole / e Å^{-3}	0.22/-0.22

9. Computational Data

Computational details: All density functional theory (DFT) calculations were performed using Gaussian 16.[5] Geometry optimizations and frequencies were calculated at the M06-2X-D3/def2-SVP-SMD(CH_2Cl_2) level of theory.[6,7] Frequency calculations confirmed that optimized structures are minima (no imaginary frequency) or transition structures (one imaginary frequency). To obtain more accurate electronic energies, single-point energy calculations were performed at the M06-2X-D3/6-Def2-TZVP-SMD(CH_2Cl_2) level of theory with the optimized structures. Structures were generated using CYLview.[8]

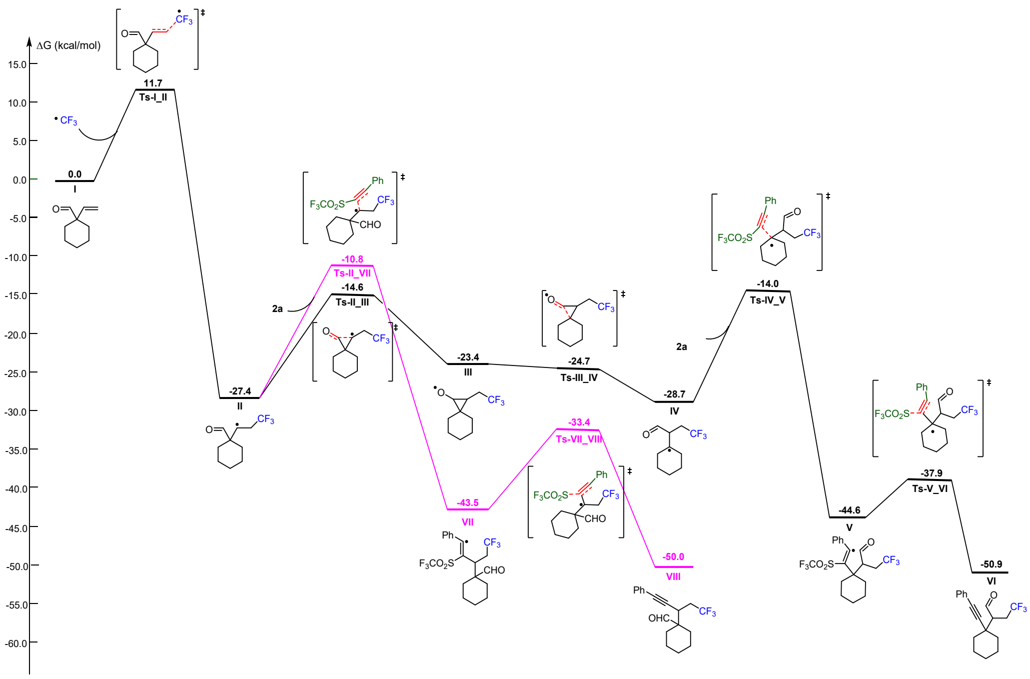


Figure S3. Calculated Gibbs free energy profile for the reactions of **1a** and **2a.**

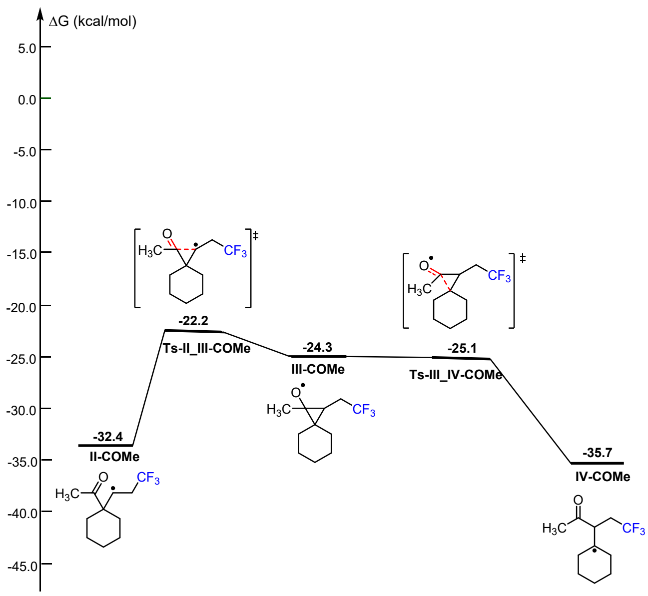


Figure S4. Calculated Gibbs free energy profile for the reactions of **1i** and **2a.**

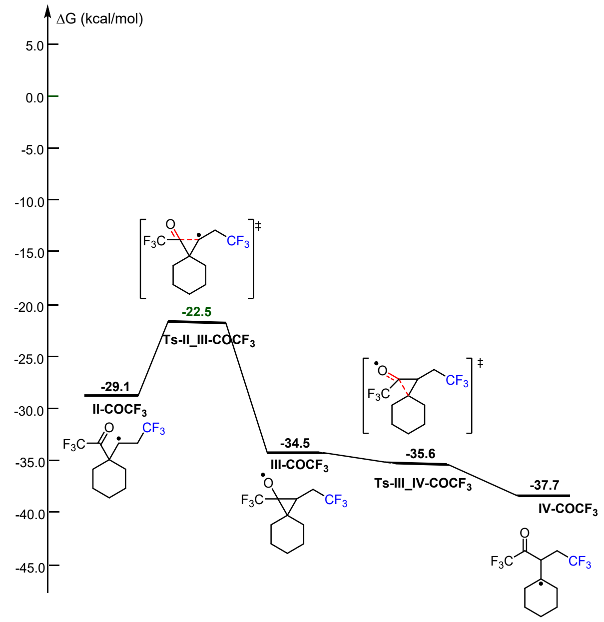


Figure S5. Calculated Gibbs free energy profile for the reactions of **1j** and **2a.**

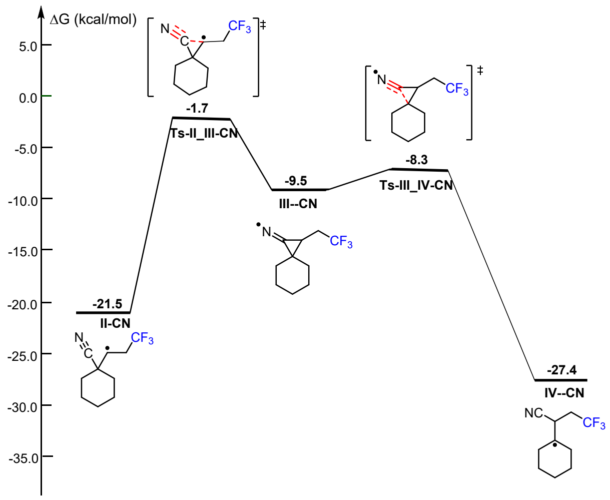


Figure S6. Calculated Gibbs free energy profile for the reactions of **1k** and **2a.**

The calculated Cartesian coordinates and energies of structures.

I

C	0.64218	1.16008	-0.9437
O	0.31657	2.3025	-0.75847
H	1.09432	0.84212	-1.91648
C	1.98424	-0.10578	0.5694
C	2.81209	-1.11433	0.29398
H	2.34167	0.72807	1.18597
H	3.8311	-1.12013	0.68795
H	2.51207	-1.96789	-0.31871
C	0.5526	0.04143	0.09055
C	0.02251	-1.21973	-0.6044
C	-0.3478	0.45542	1.26578
C	-1.44784	-1.07904	-0.99869
H	0.14229	-2.06971	0.08823
H	0.63868	-1.4411	-1.49113
C	-1.82247	0.55584	0.87381
H	-0.22799	-0.2977	2.06266
H	0.00914	1.416	1.66706
C	-2.31399	-0.72934	0.21017
H	-1.79512	-2.01096	-1.46949
H	-1.55166	-0.28469	-1.7601
H	-2.42467	0.78385	1.76636
H	-1.95534	1.39898	0.17674

H	-3.36761	-0.62571	-0.09067
H	-2.26863	-1.5584	0.93799

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -426.564876072 hartree

ZPG = 0.178326 hartree

II

C	0.54062	0.85261	0.49123
C	1.73506	0.84247	-0.40538
H	0.64059	1.3355	1.4665
C	2.77335	-0.16011	0.03804
H	1.48363	0.59598	-1.44636
H	2.24417	1.81994	-0.40406
F	3.8564	-0.12882	-0.7452
F	3.18699	0.0698	1.28969
F	2.30854	-1.4157	0.01005
C	-0.80339	-0.9006	-0.74845
C	-1.73582	0.25628	1.30555
C	-2.21245	-1.37998	-1.09669
H	-0.28318	-1.66602	-0.15002
H	-0.2116	-0.75644	-1.66653
C	-3.12996	-0.269	0.96341
H	-1.23835	-0.44109	2.00045
H	-1.80552	1.23021	1.81319
C	-3.05866	-1.56696	0.16111
H	-2.15124	-2.31841	-1.66791
H	-2.70091	-0.64033	-1.75682
H	-3.70169	-0.42102	1.89142
H	-3.67031	0.49217	0.3781
H	-4.07059	-1.90802	-0.10525
H	-2.6066	-2.35901	0.78343
C	-0.83169	0.40359	0.07401
C	-1.31745	1.54383	-0.82264
O	-2.13042	2.37328	-0.50868
H	-0.81014	1.58996	-1.81871

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -764.227565001 hartree

ZPG = 0.185885 hartree

III

C	2.49602	-0.96558	-1.26981
C	1.68854	0.33852	-1.2532
C	2.19479	0.61052	1.21106
C	3.00023	-0.69498	1.18879
C	3.58692	-0.95601	-0.19851
H	2.35249	1.18259	-1.5036
H	0.89141	0.32129	-2.00612
H	1.81399	-1.81403	-1.08797
H	2.93506	-1.11515	-2.26745
H	2.86866	1.4605	1.01235
H	1.73463	0.76934	2.19757
H	3.79739	-0.64994	1.94568
H	2.33562	-1.53025	1.46846
H	4.31754	-0.16343	-0.43588
H	4.13665	-1.90921	-0.20572
C	1.13307	0.56361	0.13413
C	-0.21238	0.13797	0.50416
H	-0.36512	-0.09545	1.56291
C	-1.14643	-0.55169	-0.45378
C	-2.56869	-0.49683	0.03118
H	-0.88363	-1.61422	-0.56767
H	-1.12574	-0.07593	-1.4419
F	-3.01678	0.7573	0.14919
F	-2.71396	-1.07145	1.23406
F	-3.39628	-1.13288	-0.80454
C	-0.01759	1.69981	0.28703
H	0.08989	2.2785	1.22101
O	-0.46032	2.23333	-0.77329

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -764.221663904 hartree

ZPG = 0.189036 hartree

IV

C	3.99218	-0.49053	-0.0446
C	3.408	0.31677	1.11245
C	2.08912	0.98609	0.7099
C	1.12847	0.01811	0.0884
C	1.67219	-0.90925	-0.9571
C	2.99817	-1.54655	-0.52246
H	1.62149	1.48335	1.57402
H	3.22355	-0.35881	1.96467
H	4.12209	1.08043	1.45492
H	4.2309	0.19029	-0.88083
H	4.93681	-0.96624	0.25978
H	0.94306	-1.69214	-1.21382
H	1.85425	-0.3386	-1.89281
H	2.80207	-2.25408	0.30089
H	3.41854	-2.12937	-1.35557

H	2.31389	1.79377	-0.01892
C	-0.33836	0.36042	0.14483
H	-0.56358	0.77962	1.13891
C	-0.51714	1.49151	-0.85827
O	-0.4223	2.65707	-0.5766
H	-0.66644	1.16178	-1.91652
C	-1.26191	-0.81608	-0.16083
C	-2.69091	-0.50377	0.18039
H	-0.97144	-1.70336	0.41928
H	-1.23742	-1.08254	-1.22781
F	-3.51203	-1.50541	-0.14641
F	-3.12871	0.58844	-0.46758
F	-2.8624	-0.26759	1.48624

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -764.230275425 hartree

ZPG = 0.186438 hartree

V

S	0.48262	1.88836	0.74513
O	0.87565	2.2113	2.1075
O	-0.64845	2.56863	0.12535
C	1.94801	2.38755	-0.30422
F	1.94507	3.70573	-0.3353
F	3.07524	1.96466	0.2311
F	1.83256	1.92136	-1.53395
C	0.36278	0.09111	0.4882
C	1.43365	-0.4935	0.04291
C	2.59136	-1.05626	-0.4659
C	2.73985	-1.23018	-1.87211
C	3.64759	-1.45798	0.40068
C	3.90293	-1.78699	-2.37653
H	1.92779	-0.92755	-2.53494
C	4.79898	-2.01369	-0.13139
H	3.53776	-1.3154	1.47667
C	4.93521	-2.18136	-1.51555
H	4.01134	-1.91968	-3.45405
H	5.60633	-2.31903	0.53595
H	5.84704	-2.61918	-1.92386
C	-2.02081	-0.12307	-0.31688
H	-2.28104	0.931	-0.14281
C	-1.31579	-0.19308	-1.66332
H	-0.74252	0.71757	-1.94992
O	-1.32775	-1.16407	-2.37395
C	-3.29149	-0.97088	-0.33189
H	-3.12706	-1.91142	-0.87447
H	-3.64685	-1.20683	0.68007
C	-4.41619	-0.24375	-1.01479
F	-4.08403	0.16461	-2.24793
F	-5.50061	-1.0143	-1.13665
F	-4.78935	0.85102	-0.33881
C	0.02065	-2.54885	2.03073
C	-0.51416	-2.01948	3.35991
C	-0.62957	-0.49657	3.33558
C	-1.5115	-0.02747	2.17892
C	-1.01063	-0.53485	0.81167
C	-0.83711	-2.06621	0.85947
H	-1.04905	-0.12492	4.28219
H	-1.51131	-2.45372	3.54892
H	0.13565	-2.34051	4.18766
H	1.06598	-2.22547	1.90162
H	0.03307	-3.64895	2.03021
H	-2.53334	-0.41325	2.32363
H	-1.59944	1.07061	2.16969
H	-1.83941	-2.50581	0.97481
H	-0.43729	-2.42654	-0.10188
H	0.37239	-0.04641	3.23823

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -1958.35378480 hartree

ZPG = 0.300422 hartree

VI

C	0.17241	4.09917	-0.63392
C	0.10697	3.02104	-1.71206
C	1.0403	1.85434	-1.39529
C	0.79575	2.33915	1.06305
C	-0.13441	3.50526	0.73798
H	0.95745	1.09193	-2.18217
H	-0.92758	2.64689	-1.79513
H	0.3727	3.43774	-2.69512
H	1.18537	4.53776	-0.62085
H	-0.52742	4.91638	-0.86462
H	0.54146	1.91983	2.0475
H	1.83734	2.69855	1.12337
H	-1.18011	3.1537	0.76006
H	-0.04098	4.27069	1.52272
H	2.08548	2.20807	-1.38362
C	1.85688	0.15803	0.31862
H	2.82602	0.6791	0.28555

C	1.67184	-0.34635	1.73765
O	2.36953	-0.01757	2.65974
H	0.81401	-1.04684	1.8859
C	1.85667	-1.01271	-0.66608
C	3.03176	-1.92966	-0.47245
H	1.90909	-0.66013	-1.70404
H	0.94629	-1.62204	-0.5592
F	3.01877	-2.93721	-1.34948
F	3.04738	-2.48006	0.75216
F	4.19981	-1.29427	-0.62149
C	0.75992	1.2216	-0.00949
C	-2.96299	-0.56573	-0.0048
C	-3.09805	-1.93836	-0.27281
C	-4.10901	0.19872	0.27245
C	-4.35773	-2.53168	-0.26237
H	-2.20843	-2.53252	-0.4884
C	-5.36472	-0.40269	0.28018
H	-4.00397	1.26458	0.4816
C	-5.4926	-1.76705	0.0136
H	-4.45388	-3.59848	-0.4711
H	-6.24972	0.19787	0.49693
H	-6.47834	-2.23521	0.0212
C	-0.56887	0.5799	-0.01123
C	-1.66322	0.05311	-0.01125

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -1072.09375838 hartree

ZPG = 0.282367 hartree

VII

C	1.50389	-1.16206	-2.16461
O	0.67187	-0.59517	-2.8285
H	1.94645	-2.11476	-2.5361
C	1.35396	1.80015	-1.24241
C	1.03595	3.08191	-0.52259
H	2.36724	1.93099	-1.64462
H	0.65846	1.70061	-2.08463
F	1.08135	4.12746	-1.35369
F	-0.191	3.0794	0.02703
F	1.89783	3.33192	0.46903
C	1.28263	0.57534	-0.31714
H	1.79365	0.84661	0.61982
S	-0.67244	0.74494	1.73544
O	-2.01463	1.3023	1.72467
O	0.42215	1.39529	2.44218
C	-0.88985	-0.90075	2.59282
F	-1.58244	-0.69447	3.69589
F	-1.54634	-1.74657	1.81684
F	0.28452	-1.41686	2.90451
C	-0.16903	0.29184	0.04697
C	-1.16356	-0.1186	-0.68564
C	-2.43551	-0.46796	-1.12681
C	-2.84563	-1.82717	-1.17047
C	-3.33469	0.54543	-1.55635
C	-4.11446	-2.14839	-1.62695
H	-2.15559	-2.60538	-0.84147
C	-4.59697	0.19796	-2.01023
H	-3.01845	1.5885	-1.51174
C	-4.99374	-1.14427	-2.04941
H	-4.42689	-3.19341	-1.65572
H	-5.28555	0.97989	-2.33428
H	-5.98978	-1.40786	-2.40787
C	2.03717	-0.67837	-0.83198
C	3.54218	-0.34032	-1.01263
C	1.89322	-1.80916	0.21766
C	4.4454	-1.55817	-1.21917
H	3.86026	0.18962	-0.09804
H	3.67368	0.35973	-1.85087
C	2.81242	-3.01185	0.00206
H	2.12834	-1.35898	1.19742
H	0.84372	-2.14043	0.26411
C	4.27187	-2.58171	-0.10202
H	5.48906	-1.2138	-1.27019
H	4.22874	-2.0344	-2.18968
H	2.67332	-3.71301	0.83843
H	2.52438	-3.55796	-0.91129
H	4.91955	-3.45396	-0.27554
H	4.58657	-2.13141	0.85536

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -1958.35238289 hartree

ZPG = 0.300776 hartree

VIII

C	-1.69841	-0.85279	1.5115
O	-2.39599	-0.48997	2.42271
H	-0.76471	-1.43439	1.70822
C	-1.12363	1.87105	0.34441
C	-0.248	2.98691	-0.16349
H	-2.15487	2.22211	0.21326

H	-0.92914	1.77008	1.42225
F	-0.65197	4.16548	0.32603
F	1.03736	2.85312	0.18081
F	-0.28437	3.08661	-1.49877
C	-0.92984	0.53878	-0.39699
H	-1.13473	0.71846	-1.46632
C	0.45737	0.06075	-0.28771
C	1.60883	-0.30987	-0.19649
C	2.98394	-0.71912	-0.08683
C	3.33415	-2.07796	-0.1511
C	3.98921	0.24733	0.08658
C	4.66911	-2.45955	-0.04385
H	2.55255	-2.8276	-0.28543
C	5.32114	-0.14366	0.1927
H	3.7127	1.30176	0.1361
C	5.66414	-1.49554	0.12784
H	4.93443	-3.51685	-0.0948
H	6.09689	0.61207	0.32676
H	6.70927	-1.79843	0.21131
C	-1.96579	-0.54972	0.04467
C	-3.4007	-0.04202	-0.15786
C	-1.71974	-1.8309	-0.77416
C	-4.45699	-1.13099	0.04495
H	-3.47565	0.35873	-1.1837
H	-3.60526	0.78473	0.53588
C	-2.77951	-2.9012	-0.5213
H	-1.72041	-1.55413	-1.84236
H	-0.71675	-2.22439	-0.54742
C	-4.17925	-2.3655	-0.80764
H	-5.44965	-0.71547	-0.18489
H	-4.47401	-1.42105	1.108
H	-2.5629	-3.78433	-1.14062
H	-2.7254	-3.23337	0.53133
H	-4.93636	-3.1409	-0.61651
H	-4.25327	-2.10033	-1.87679

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -1072.09230206 hartree

ZPG = 0.282351 hartree

Ts-I_II

C	1.09174	1.03333	1.30389
C	2.58471	-0.31084	0.03323
H	1.76892	0.8636	2.14425
H	1.35249	1.84467	0.61556
F	2.75866	0.21542	-1.16185
F	2.08833	-1.52456	-0.072
F	3.72673	-0.3401	0.68752
C	-0.11513	0.42922	1.25919
H	-0.36012	-0.31612	2.02241
C	-1.13248	2.18264	-0.10496
O	-0.88817	2.67574	-1.17449
H	-1.37776	2.82381	0.77719
C	-1.15146	0.69208	0.18501
C	-2.56882	0.35847	0.70928
C	-0.86022	-0.10592	-1.09857
C	-2.78856	-1.14579	0.87576
H	-3.30403	0.74857	-0.01544
H	-2.74187	0.88578	1.66124
C	-1.07072	-1.60615	-0.90466
H	-1.53921	0.2624	-1.88556
H	0.16287	0.11701	-1.43809
C	-2.48923	-1.90029	-0.41867
H	-3.82492	-1.32632	1.19888
H	-2.14014	-1.53368	1.67899
H	-0.87022	-2.13207	-1.85041
H	-0.34494	-1.9906	-0.16905
H	-2.62863	-2.98167	-0.26897
H	-3.20954	-1.58864	-1.1951

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -764.161947251 hartree

ZPG = 0.182595 hartree

Ts-II_III

C	3.41667	0.68885	0.35296
C	3.86945	-0.76508	0.12528
C	2.679	-1.69585	-0.1628
C	1.56794	-0.95454	-0.90819
C	2.01871	0.73663	0.96283
H	3.00644	-2.5694	-0.74456
H	4.5815	-0.7995	-0.71346
H	4.41138	-1.13238	1.01022
H	1.99594	0.14726	1.89367
H	3.39305	1.23337	-0.60505
H	1.98248	-0.50828	-1.82698
H	0.78068	-1.65215	-1.2241
H	1.72169	1.76375	1.21473
H	4.1345	1.21955	0.99446
H	2.2662	-2.0861	0.78132

C	0.99957	0.16073	-0.02071
C	-0.37147	0.05897	0.49273
H	-0.60445	0.64608	1.38516
C	-1.41174	-0.8958	0.0095
C	-2.79833	-0.31393	0.09433
H	-1.41266	-1.81292	0.62545
H	-1.25139	-1.20234	-1.03305
F	-2.94212	0.75575	-0.69578
F	-3.10492	0.07735	1.33679
F	-3.72391	-1.2034	-0.27659
C	0.23508	1.24999	-0.8089
O	0.24077	2.44809	-0.51356
H	-0.22221	0.88127	-1.75136

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -764.208495427 hartree

ZPG = 0.187131 hartree

Ts-III_IV

C	-3.36144	1.03664	0.41077
C	-3.90895	-0.14109	-0.39346
C	-2.92383	-1.3083	-0.39105
C	-1.55703	-0.89324	-0.94284
C	-1.99887	1.48599	-0.12191
H	-2.78314	-1.66776	0.64223
H	-4.87894	-0.46119	0.01572
H	-4.09132	0.18066	-1.43383
H	-2.12892	1.92743	-1.12943
H	-3.24993	0.73296	1.46546
H	-0.84024	-1.71859	-0.84918
H	-1.64993	-0.66195	-2.0214
H	-1.56142	2.27413	0.50922
H	-4.06378	1.88292	0.39126
H	-3.31832	-2.15088	-0.97777
C	-1.03565	0.3414	-0.26625
C	0.39299	0.55198	-0.011
H	0.67217	1.60648	0.09891
C	1.43475	-0.30618	-0.69175
C	2.81446	0.03706	-0.20569
H	1.42637	-0.16807	-1.78239
H	1.27161	-1.36778	-0.46578
F	3.74361	-0.74277	-0.76746
F	2.93127	-0.10416	1.12013
F	3.14995	1.30454	-0.48647
O	-0.08742	-1.2372	1.57803
C	-0.18702	-0.02914	1.29498
H	-0.54468	0.71994	2.02608

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -764.223508087 hartree

ZPG = 0.187707 hartree

Ts-V_VI

S	0.47413	1.339	1.47803
O	1.12128	0.99572	2.7473
O	-0.67787	2.25477	1.46214
C	1.79009	2.30512	0.53507
F	1.77631	3.5548	0.95221
F	2.97749	1.77909	0.75606
F	1.52524	2.27568	-0.7598
C	0.33138	-0.56862	0.13153
C	1.4719	-0.72271	-0.34034
C	2.80608	-0.77582	-0.80424
C	3.14283	-0.22152	-2.05847
C	3.80894	-1.36164	-0.00093
C	4.46031	-0.25929	-2.49516
H	2.36237	0.23196	-2.67129
C	5.12137	-1.39121	-0.45254
H	3.54017	-1.77988	0.97047
C	5.44887	-0.8418	-1.69613
H	4.72214	0.16868	-3.46374
H	5.89759	-1.84176	0.16741
H	6.48258	-0.86693	-2.04468
C	-2.04088	-0.08151	-0.45757
H	-2.05655	0.85752	0.11883
C	-1.45767	0.24498	-1.82589
H	-0.68042	1.04219	-1.83745
O	-1.77666	-0.31965	-2.83857
C	-3.45918	-0.63007	-0.59982
H	-3.53384	-1.2865	-1.477
H	-3.78154	-1.19179	0.28629
C	-4.45361	0.48272	-0.77936
F	-4.13943	1.28639	-1.80517
F	-5.68271	0.01349	-1.01109
F	-4.53192	1.2638	0.30617
C	-0.27125	-3.48138	0.47023
C	-0.60717	-3.4927	1.96152
C	-0.54123	-2.08935	2.56434
C	-1.44753	-1.12802	1.79873
C	-1.07908	-1.05459	0.30091

C	-1.13887	-2.48194	-0.29536
H	-0.84654	-2.11043	3.62081
H	-1.62839	-3.88865	2.09793
H	0.07169	-4.17216	2.49807
H	0.79357	-3.23254	0.33293
H	-0.41591	-4.48262	0.03805
H	-2.48701	-1.48361	1.86901
H	-1.4426	-0.12405	2.25022
H	-2.18917	-2.81026	-0.24039
H	-0.85969	-2.45131	-1.35975
H	0.49505	-1.71175	2.54419

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -1958.33898321 hartree

ZPG = 0.297109 hartree

Ts-II_VII

C	-3.34987	0.613	-1.81406
C	-4.41673	-0.37295	-2.32341
C	-3.98577	-1.83227	-2.10785
C	-3.16941	-1.97626	-0.82621
C	-1.81022	-1.18759	-0.90161
C	-1.95635	-0.00298	-1.8946
H	-4.8657	-2.49048	-2.06598
H	-5.36839	-0.18552	-1.80292
H	-4.60717	-0.20426	-3.3943
H	-1.77819	-0.36337	-2.92195
H	-3.54942	0.8895	-0.76652
H	-3.75019	-1.57578	0.02103
H	-2.97097	-3.03477	-0.59519
H	-1.18175	0.74475	-1.67976
H	-3.3822	1.55034	-2.38771
H	-3.38007	-2.1798	-2.9598
C	-0.79601	-2.15054	-1.48121
O	0.23014	-2.5055	-0.96096
H	-1.08413	-2.54829	-2.48563
C	-1.01709	-1.6578	1.53934
C	-1.13617	-1.0391	2.90218
H	-1.62497	-2.58021	1.54878
H	0.02901	-1.96981	1.39492
F	-0.6448	-1.83353	3.85748
F	-0.47655	0.12684	2.98404
F	-2.40953	-0.7777	3.22736
C	-1.45805	-0.70707	0.47401
H	-2.01058	0.1794	0.79635
S	0.08989	2.17406	0.65601
O	0.61865	2.60126	1.93454
O	-1.31355	2.35283	0.33309
C	0.99335	3.17427	-0.62613
F	0.60169	4.42701	-0.50659
F	2.29398	3.09431	-0.43442
F	0.69694	2.73111	-1.83419
C	0.65937	0.59698	0.27303
C	1.66455	-0.05165	-0.01464
C	2.76995	-0.88002	-0.3518
C	3.03285	-1.18757	-1.69961
C	3.59602	-1.39282	0.66545
C	4.11609	-1.99732	-2.01928
H	2.38219	-0.78919	-2.47922
C	4.67305	-2.20588	0.32987
H	3.38221	-1.14856	1.707
C	4.93484	-2.50776	-1.00842
H	4.32261	-2.23636	-3.06346
H	5.31339	-2.6062	1.11715
H	5.78219	-3.14542	-1.26577

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -1958.28565304 hartree

ZPG = 0.294118 hartree

Ts-VII_VIII

C	2.93902	-2.02175	-0.7512
C	4.42393	-1.74131	-1.06135
C	4.62282	-0.3513	-1.6819
C	3.69256	0.67033	-1.03283
C	2.18827	0.3471	-1.28864
C	2.03026	-1.1588	-1.62216
H	5.66723	-0.02789	-1.56641
H	5.01384	-1.81728	-0.13523
H	4.8185	-2.5057	-1.74742
H	2.2889	-1.31869	-2.68174
H	2.71392	-1.81943	0.30858
H	3.86712	0.66073	0.05585
H	3.92591	1.69029	-1.37654
H	0.97629	-1.45063	-1.51807
H	2.70442	-3.08391	-0.90971
H	4.42697	-0.38466	-2.76537
C	1.75121	1.10772	-2.52215
O	0.80548	1.84803	-2.60112
H	2.39902	0.91909	-3.4137

C	1.49044	2.22052	0.33253
C	0.73719	2.58762	1.58647
H	2.54591	2.45721	0.52098
H	1.11825	2.86612	-0.47245
F	1.19115	3.73101	2.10695
F	-0.57392	2.75493	1.37791
F	0.8535	1.64778	2.53858
C	1.3623	0.73235	-0.03578
H	1.8063	0.16455	0.79764
S	-0.39249	-0.91579	1.76945
O	-1.57789	-0.47023	2.50479
O	0.84615	-1.28024	2.47588
C	-0.92674	-2.53657	0.99449
F	-1.14511	-3.42653	1.94312
F	-2.03291	-2.36062	0.29584
F	0.03039	-2.9768	0.19503
C	-0.06986	0.34009	-0.13924
C	-1.19986	0.41944	-0.65282
C	-2.54714	0.44421	-1.0776
C	-3.01406	-0.46553	-2.05066
C	-3.43417	1.38352	-0.50807
C	-4.34499	-0.42771	-2.44388
H	-2.3229	-1.19112	-2.482
C	-4.76256	1.40747	-0.91223
H	-3.06253	2.07563	0.24867
C	-5.21917	0.50589	-1.87796
H	-4.70803	-1.13015	-3.19541
H	-5.44951	2.13108	-0.47125
H	-6.2642	0.52932	-2.1912

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -1958.33166005 hartree

ZPG = 0.296133 hartree

II-CN

C	0.5168	1.30212	0.14808
C	1.72272	0.9489	-0.65353
H	0.63263	2.00674	0.97442
C	2.55682	-0.13838	-0.01392
H	1.47647	0.60309	-1.66734
H	2.38882	1.81956	-0.74451
F	3.66836	-0.38304	-0.71261
F	2.93283	0.18482	1.22761
F	1.8914	-1.30077	0.07738
C	-1.84506	1.69244	-0.04488
N	-2.63965	2.52852	-0.09774
C	-0.82389	0.62127	0.02762
C	-0.96059	-0.26976	-1.22657
C	-1.10485	-0.22842	1.29995
C	-2.31022	-0.98269	-1.28319
H	-0.15323	-1.01673	-1.17666
H	-0.79678	0.33668	-2.13022
C	-2.44982	-0.94792	1.23334
H	-0.28471	-0.96112	1.36656
H	-1.04245	0.42011	2.18647
C	-2.55637	-1.81097	-0.02286
H	-2.34278	-1.62213	-2.17749
H	-3.11593	-0.23733	-1.39803
H	-2.57649	-1.56171	2.13741
H	-3.26427	-0.2032	1.23927
H	-3.54392	-2.29334	-0.0712
H	-1.80634	-2.61894	0.02977

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -743.151363514 hartree

ZPG = 0.177077 hartree

III-CN

C	-2.45611	-0.87139	-1.28965
C	-0.97257	-0.75742	-0.93415
C	-1.61992	-0.04566	1.42319
C	-3.09642	-0.17665	1.05023
C	-3.29898	-1.20826	-0.05972
H	-0.59353	-1.73272	-0.58374
H	-0.38423	-0.47543	-1.81849
H	-2.79266	0.09159	-1.71121
H	-2.59222	-1.63273	-2.07194
H	-1.25353	-0.99198	1.85919
H	-1.46975	0.74328	2.1752
H	-3.68455	-0.44465	1.94048
H	-3.46086	0.80622	0.70469
H	-3.00879	-2.20546	0.31485
H	-4.3631	-1.26768	-0.33316
C	-0.78195	0.24313	0.19123
C	-0.71547	1.70373	-0.22813
N	-1.26997	2.65202	-0.74565
C	0.49552	1.03581	0.36446
C	1.72152	0.84128	-0.49509
H	0.69436	1.34593	1.3965
H	1.46301	0.61713	-1.53826

H	2.34626	1.745	-0.4857
C	2.56882	-0.29148	0.01848
F	3.66742	-0.45989	-0.7221
F	1.90855	-1.45675	0.01335
F	2.97101	-0.0835	1.27831

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -743.125662016 hartree

ZPG = 0.177631 hartree

IV-CN

C	4.00279	-0.33806	-0.15561
C	3.42193	-0.07628	1.23217
C	2.07426	0.64513	1.14074
C	1.1313	-0.018	0.18462
C	1.67678	-0.47285	-1.13456
C	3.03499	-1.1685	-0.99524
H	1.60653	0.7331	2.13423
H	3.28064	-1.04003	1.74962
H	4.11841	0.51783	1.84189
H	4.19169	0.6255	-0.66096
H	4.97248	-0.85156	-0.07256
H	0.96267	-1.13171	-1.65202
H	1.79942	0.41773	-1.78834
H	2.88872	-2.14799	-0.50962
H	3.45249	-1.36352	-1.99398
H	2.25319	1.68594	0.79431
C	-0.32869	0.36749	0.28078
H	-0.57972	0.51254	1.34443
C	-1.27569	-0.68676	-0.31062
C	-2.70651	-0.48262	0.1052
H	-0.97193	-1.67901	0.05142
H	-1.24813	-0.6925	-1.40829
F	-3.50079	-1.42043	-0.41658
F	-3.18499	0.70366	-0.28869
F	-2.85517	-0.53661	1.43465
C	-0.50876	1.68431	-0.3693
N	-0.57032	2.71014	-0.89479

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -743.152572963 hartree

ZPG = 0.175853 hartree

Ts-II_III-CN

C	0.433	-0.23424	0.58904
H	0.67762	-1.04506	1.281
C	1.48295	0.79555	0.31359
C	2.83456	0.1679	0.09886
H	1.58621	1.4935	1.16218
H	1.25908	1.38941	-0.58321
F	2.8488	-0.64903	-0.95775
F	3.22367	-0.55752	1.15563
F	3.7752	1.09515	-0.10585
C	-0.41628	-0.84637	-0.80517
N	-0.14004	-1.46536	-1.78214
C	-1.01997	-0.04697	0.27385
C	-2.00176	-0.81936	1.15354
C	-1.54713	1.32677	-0.13319
C	-3.37032	-0.92472	0.48511
H	-2.08273	-0.2661	2.10463
H	-1.59217	-1.81406	1.38274
C	-2.92179	1.20357	-0.79025
H	-1.61745	1.93122	0.78735
H	-0.84275	1.83078	-0.80835
C	-3.90823	0.45445	0.10477
H	-4.0705	-1.44194	1.15752
H	-3.27869	-1.54543	-0.42262
H	-3.30315	2.20651	-1.03203
H	-2.81193	0.66305	-1.74602
H	-4.88047	0.35731	-0.40077
H	-4.08211	1.04148	1.02331

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -743.121526545 hartree

ZPG = 0.175958 hartree

Ts-III_IV-CN

C	3.3537	-0.95633	-0.42448
C	3.89888	0.42954	-0.0821
C	2.89182	1.22707	0.74491
C	1.5487	1.35951	0.01937
C	2.0197	-0.85803	-1.1683
H	2.71946	0.71018	1.70416
H	4.8495	0.33854	0.46452
H	4.11852	0.97626	-1.01616
H	2.18774	-0.40676	-2.16579
H	3.1942	-1.52389	0.50806
H	0.81694	1.86834	0.66222
H	1.67988	1.99123	-0.8809
H	1.58667	-1.85544	-1.33729
H	4.07822	-1.5205	-1.03012

H	3.28634	2.22685	0.97886
C	1.04423	0.01437	-0.42622
C	-0.41792	-0.33232	-0.45182
H	-0.65284	-1.14838	-1.1471
C	-1.48954	0.73936	-0.39945
C	-2.8414	0.15147	-0.09922
H	-1.55788	1.24598	-1.37262
H	-1.28414	1.48993	0.37381
F	-3.78854	1.09278	-0.07903
F	-2.86831	-0.46201	1.08874
F	-3.20825	-0.75595	-1.01279
C	0.1517	-0.82979	0.80688
N	0.40058	-1.27641	1.88123

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -743.121917399 hartree

ZPG = 0.175825 hartree

II-COCF3

C	-1.39706	-0.89952	-0.50134
O	-1.10632	-1.85305	-1.16958
C	0.90099	-0.08733	-0.68902
C	1.67071	-1.08869	0.10232
H	1.256	0.13614	-1.69774
C	3.14592	-0.78975	0.10107
H	1.35092	-1.13123	1.15343
H	1.55754	-2.10541	-0.31646
F	3.84087	-1.71611	0.76859
F	3.64785	-0.74203	-1.13912
F	3.42223	0.39095	0.67229
C	-2.77488	-0.95356	0.21441
F	-3.53417	-1.90058	-0.31203
F	-3.44406	0.19707	0.14192
F	-2.59666	-1.23998	1.50573
C	-0.49706	0.32048	-0.31538
C	-0.98947	1.41352	-1.30436
C	-0.56734	0.87777	1.12961
C	-0.16745	2.69462	-1.15924
H	-2.04835	1.63498	-1.1039
H	-0.92105	1.01895	-2.32988
C	0.2714	2.14763	1.26572
H	-1.61291	1.12216	1.37242
H	-0.24317	0.11304	1.85091
C	-0.19095	3.21678	0.27648
H	-0.56155	3.45377	-1.85132
H	0.87505	2.50054	-1.46087
H	0.19555	2.52249	2.2972
H	1.33302	1.90824	1.08817
H	0.43722	4.11585	0.36337
H	-1.22106	3.51929	0.53332

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -1101.31225049 hartree

ZPG = 0.187755 hartree

III-COCF3

C	2.58076	-2.1108	-0.74471
C	1.73942	-0.96141	-1.31124
C	2.21842	0.4117	0.75688
C	3.0587	-0.74657	1.31489
C	3.66532	-1.58959	0.19584
H	2.38178	-0.2973	-1.91209
H	0.95257	-1.33821	-1.97404
H	1.9214	-2.80456	-0.19543
H	3.02469	-2.6793	-1.57497
H	2.86597	1.09512	0.18527
H	1.76909	0.97898	1.58098
H	3.84451	-0.33669	1.96609
H	2.41442	-1.38168	1.94631
H	4.37595	-0.97118	-0.37881
H	4.2391	-2.4271	0.61979
C	1.15944	-0.15245	-0.1709
C	-0.18074	-0.42095	0.34801
C	-0.06457	0.83464	-0.60243
H	-0.34853	-0.11934	1.38683
O	-0.45594	0.75888	-1.80551
C	-1.06665	-1.52983	-0.15367
C	-2.50552	-1.27336	0.20453
H	-0.78128	-2.48942	0.30195
H	-1.01437	-1.62789	-1.24453
F	-2.95094	-0.11812	-0.30181
F	-2.68826	-1.20855	1.53009
F	-3.30385	-2.24055	-0.25388
C	-0.13305	2.22396	0.02721
F	-1.23591	2.8485	-0.37726
F	-0.15397	2.21027	1.36378
F	0.90771	2.97687	-0.34423

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -1101.31263377 hartree

ZPG = 0.190195 hartree

IV-COCF3

C	4.1969	-0.56469	-0.26929
C	3.65836	-0.71006	1.15193
C	2.27778	-0.05583	1.28783
C	1.33036	-0.51944	0.22229
C	1.83974	-0.51816	-1.18681
C	3.22716	-1.17014	-1.28114
H	1.8518	-0.24147	2.28597
H	3.57374	-1.78177	1.39838
H	4.35167	-0.26413	1.88027
H	4.33971	0.50625	-0.49742
H	5.18369	-1.04431	-0.35428
H	1.14057	-1.01638	-1.87311
H	1.92999	0.52953	-1.5414
H	3.12938	-2.25127	-1.08605
H	3.61318	-1.0595	-2.30527
H	2.40449	1.04398	1.20437
C	-0.13293	-0.59547	0.5806
H	-0.22112	-1.0552	1.57747
C	-0.55836	0.84607	0.82629
O	-0.7456	1.31454	1.91563
C	-1.006	-1.38634	-0.39696
C	-2.46339	-1.29727	-0.04331
H	-0.71617	-2.44578	-0.36306
H	-0.91435	-1.04129	-1.43284
F	-3.22048	-2.02272	-0.86544
F	-2.90478	-0.02589	-0.12322
F	-2.71734	-1.70918	1.20204
C	-0.56548	1.83913	-0.36019
F	-1.5547	2.7091	-0.22882
F	-0.6901	1.24128	-1.54419
F	0.58444	2.51833	-0.37431

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -1101.31584838 hartree

ZPG = 0.188228 hartree

Ts-II_III-COCF3

C	0.754	-0.1389	0.71638
H	1.01293	-0.05704	1.77525
C	1.81538	-0.70107	-0.17785
C	3.05178	0.16322	-0.0832
H	1.52414	-0.71854	-1.23367
H	2.11341	-1.71625	0.12331
F	3.54651	0.20483	1.15795
F	2.79737	1.42847	-0.44157
F	4.02129	-0.28654	-0.88087
C	-1.0131	-0.73872	0.79902
O	-1.45815	-0.87621	1.94298
C	-1.31574	-1.88847	-0.18089
F	-2.44281	-1.62906	-0.85297
F	-1.50268	-3.01813	0.48806
F	-0.36487	-2.11784	-1.09065
C	-0.4374	0.60568	0.28905
C	-0.82959	1.76698	1.20052
C	-0.61754	0.93521	-1.19211
C	-2.2318	2.28097	0.88993
H	-0.08824	2.56613	1.03238
H	-0.7457	1.45047	2.24817
C	-2.00817	1.50272	-1.48718
H	0.15345	1.68493	-1.43879
H	-0.42195	0.06489	-1.83211
C	-2.35186	2.68073	-0.57884
H	-2.46555	3.13194	1.54667
H	-2.96476	1.48821	1.11889
H	-2.05572	1.80106	-2.5449
H	-2.75813	0.70848	-1.34507
H	-3.36722	3.04316	-0.79818
H	-1.66063	3.51646	-0.78433

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -1101.30249454 hartree

ZPG = 0.188664 hartree

Ts-III_IV-COCF3

C	3.26997	-0.22535	0.92037
C	3.73842	-1.33255	-0.02194
C	2.71916	-1.57913	-1.13219
C	1.3387	-1.92086	-0.56241
C	1.87983	-0.52834	1.48646
H	2.61895	-0.67232	-1.75262
H	4.71573	-1.07176	-0.4546
H	3.88074	-2.26416	0.55283
H	1.94147	-1.43114	2.1258
H	3.23073	0.72969	0.37241
H	0.6091	-2.05296	-1.36923
H	1.39433	-2.87539	-0.00569
H	1.51471	0.28196	2.12795
H	3.98045	-0.0934	1.74922

H	3.0544	-2.39097	-1.79375
C	0.8822	-0.88035	0.41873
C	-0.52693	-0.47443	0.52632
H	-0.75591	0.02719	1.47369
C	-1.64069	-1.35999	0.01138
C	-2.96624	-0.65736	0.11634
H	-1.70886	-2.28931	0.59382
H	-1.48935	-1.61141	-1.04575
F	-3.95737	-1.39879	-0.38433
F	-2.96801	0.50635	-0.54532
F	-3.28899	-0.37761	1.38618
O	-0.02832	0.28799	-1.74034
C	0.04632	0.49221	-0.51744
C	0.41993	1.91103	-0.09854
F	0.49581	2.08846	1.22201
F	-0.50472	2.75795	-0.55575
F	1.58728	2.28371	-0.62653

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -1101.31321698 hartree

ZPG = 0.189006 hartree

II-COMe

C	1.78492	1.43956	-0.22336
O	2.46022	1.60842	-1.21144
C	-0.56924	1.02807	-0.42669
C	-1.78034	0.98848	0.44316
H	-0.66032	1.51438	-1.40174
C	-2.76122	-0.07804	0.01262
H	-1.54243	0.78895	1.49728
H	-2.33435	1.93847	0.39277
F	-3.85109	-0.092	0.78663
F	-3.17549	0.10242	-1.24638
F	-2.2291	-1.30814	0.06854
C	1.89501	2.36104	0.96816
H	2.44135	3.26601	0.67692
H	0.90414	2.6227	1.36564
H	2.45181	1.85184	1.77034
C	0.72783	0.31275	-0.15496
C	0.75873	-0.38954	1.21381
C	0.98356	-0.71755	-1.27634
C	2.05309	-1.17461	1.42588
H	-0.09406	-1.08679	1.25345
H	0.60852	0.33818	2.02552
C	2.25629	-1.53564	-1.05408
H	0.11094	-1.39128	-1.30601
H	1.0281	-0.18994	-2.23966
C	2.25824	-2.20619	0.31814
H	2.02958	-1.66445	2.411
H	2.91264	-0.48031	1.43966
H	2.34989	-2.28978	-1.85052
H	3.13162	-0.87206	-1.13923
H	3.19884	-2.75576	0.47522
H	1.4419	-2.94809	0.36386

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -803.546539986 hartree

ZPG = 0.214186 hartree

III-COMe

C	2.51098	-1.55315	-0.87337
C	1.69433	-0.32975	-1.30735
C	2.20081	0.79443	0.89845
C	3.02001	-0.43401	1.32248
C	3.60783	-1.16082	0.1149
H	2.3533	0.37452	-1.84241
H	0.89603	-0.61234	-2.00265
H	1.83791	-2.28798	-0.39886
H	2.94271	-2.04005	-1.76058
H	2.86801	1.53134	0.42059
H	1.75519	1.26725	1.7831
H	3.81587	-0.11974	2.0141
H	2.36278	-1.12384	1.87916
H	4.32979	-0.49696	-0.39144
H	4.16635	-2.05108	0.44114
C	1.13561	0.37279	-0.09024
C	-0.22076	0.11685	0.38752
C	-0.06318	1.48641	-0.40394
H	-0.38144	0.29686	1.4559
O	-0.43611	1.50424	-1.61419
C	-1.13542	-0.90398	-0.23572
C	-2.563	-0.67565	0.17668
H	-0.86736	-1.92557	0.07333
H	-1.10336	-0.84433	-1.33038
F	-3.00826	0.53318	-0.18459
F	-2.72455	-0.76193	1.50541
F	-3.38445	-1.57683	-0.37207
C	-0.05656	2.77311	0.39364
H	0.69213	3.47018	-0.01184
H	-1.04681	3.23993	0.28622

H	0.13929	2.6208	1.46111

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -803.534409860 hartree

ZPG = 0.214872 hartree

IV-COMe

C	-4.04662	-0.57685	0.0958
C	-3.45367	-0.08345	-1.22252
C	-2.15981	0.70589	-0.98696
C	-1.19275	-0.05136	-0.12825
C	-1.74264	-0.65194	1.13006
C	-3.03851	-1.43059	0.86218
H	-1.6875	0.98247	-1.942
H	-3.23155	-0.95235	-1.86482
H	-4.17853	0.54197	-1.76488
H	-4.33045	0.29255	0.71502
H	-4.96771	-1.14983	-0.09065
H	-1.00401	-1.30061	1.62426
H	-1.97765	0.15848	1.85288
H	-2.80025	-2.32917	0.26828
H	-3.46683	-1.77638	1.81494
H	-2.42096	1.6632	-0.48794
C	0.27864	0.20135	-0.33017
H	0.47049	0.23608	-1.41471
C	0.53829	1.63364	0.16543
O	0.47829	2.55884	-0.61014
C	1.17778	-0.85633	0.30822
C	2.59409	-0.76245	-0.18453
H	0.81896	-1.86371	0.05197
H	1.20634	-0.781	1.40396
F	3.38894	-1.65223	0.41753
F	3.12824	0.45001	0.03824
F	2.688	-0.98288	-1.50107
C	0.77171	1.84005	1.64143
H	1.80988	1.56536	1.88291
H	0.61723	2.89708	1.889
H	0.11055	1.20328	2.24641

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -803.549902412 hartree

ZPG = 0.212272 hartree

Ts-II_III-COMe

C	-0.43782	0.05135	0.73324
H	-0.67351	0.80272	1.49083
C	-1.5216	-0.9254	0.40819
C	-2.85223	-0.25592	0.18852
H	-1.65697	-1.61825	1.25736
H	-1.30521	-1.53934	-0.47532
F	-2.83217	0.57995	-0.85619
F	-3.23243	0.46341	1.25103
F	-3.81662	-1.15115	-0.04481
C	0.40125	0.97041	-0.60523
O	0.54022	2.17911	-0.3335
C	-0.01272	0.55842	-2.00338
H	-0.68806	1.32645	-2.40192
H	0.88573	0.52988	-2.64018
H	-0.50289	-0.41854	-2.06996
C	0.97546	-0.10105	0.38922
C	1.97373	0.49454	1.37424
C	1.4758	-1.39947	-0.23227
C	3.34683	0.67499	0.73165
H	2.04834	-0.19537	2.23253
H	1.58785	1.45178	1.74689
C	2.86369	-1.22167	-0.85174
H	1.52568	-2.15158	0.575
H	0.77447	-1.78947	-0.98158
C	3.86009	-0.64145	0.15053
H	4.05687	1.07422	1.47147
H	3.26398	1.42644	-0.07212
H	3.22106	-2.1885	-1.23688
H	2.78609	-0.54208	-1.71758
H	4.8395	-0.49498	-0.32957
H	4.01139	-1.36466	0.97102

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -803.530956359 hartree

ZPG = 0.214784 hartree

Ts-III_IV-COMe

C	3.01734	-0.49376	1.32467
C	3.60962	-1.17838	0.09476
C	2.51743	-1.54028	-0.91035
C	1.69892	-0.30218	-1.30635
C	2.19639	0.74892	0.937
H	2.95319	-1.99548	-1.81225
H	4.33255	-0.49711	-0.38636
H	4.16798	-2.07839	0.39338
H	1.74487	1.1921	1.83378
H	3.8101	-0.19978	2.02864

H	2.36111	0.41619	-1.81858	F	-2.67703	-0.92333	1.48427
H	0.90022	-0.56278	-2.01015	F	-3.38538	-1.55524	-0.44495
H	2.86924	1.49946	0.4884	F	-3.0445	0.53274	-0.0515
H	2.35941	-1.20228	1.85611	O	-0.41472	1.60002	-1.60475
H	1.84418	-2.29157	-0.46307	C	-0.11759	1.53852	-0.38668
C	1.14552	0.35259	-0.06774	C	-0.0373	2.80129	0.44202
C	-0.24526	0.1667	0.35164	H	0.1663	2.6121	1.5021
H	-0.41499	0.29874	1.42635	H	0.7319	3.47618	0.03836
C	-1.14682	-0.84534	-0.31236	H	-1.00861	3.31255	0.36214
C	-2.56293	-0.6971	0.1672				
H	-0.83336	-1.87683	-0.09462				
H	-1.15612	-0.69673	-1.39944				

M06-2X-D3-SMD(CH2Cl2)/def2-TZVP: E = -803.534967700 hartree

ZPG = 0.214219 hartree

10. References

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