Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Pd-Catalyzed Double-Heck and Heck-Suzuki Cascade Reaction of *N*-(*o*-Bromoaryl) CF_3-acrylamides

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1. General Information:

Experimental: All the inert condition reactions are performed in nitrogen atmosphere using Glove box and Schlenk techniques. Catalytic reactions were performed in commercially available 7 mL screw cap vials fitted with PTFE/silicone septa purchased from Sigma-Aldrich and 1.5 mL HPLC vials purchased from Shimadzu.

Chromatography: Analytical thin layer chromatography (TLC) was performed on Merck and GLR precoated silica gel 60 F_{254} plates, using UV light as the visualization agent. Chromatographic purification of products was accomplished by Column chromatography on Finar silica gel (100-200 mesh). The solvents were removed under reduced pressure using rotary evaporator to obtain the desired compounds.

Characterization: The compounds were characterized using ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, ESI-HRMS and GCMS. NMR spectra were recorded at Bruker Ascend 500 MHz for ^{1}H, 126 MHz for ^{13}C and 471 MHz for ^{19}F NMR and Jeol 400 MHz for ^{1}H, 101 MHz for ^{13}C and 376 MHz for ^{19}F NMR. MestReNova was used for data assessment. The chemical shift (δ) for ^{1}H, ^{13}C and ^{19}F NMR are given in ppm relative to internal standard/residual signals of the solvents (for ^{1}H NMR ($CHCl_3$ @ 7.260 ppm) for ^{13}C NMR ($CHCl_3$ @ 77.00 ppm) and tetramethylsilane @ 0 ppm). Coupling constants are given in Hertz. The following abbreviations are followed to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets; ddd, doublet of doublets of doublets; td, triplet of doublet; and dt, doublet of triplet; bs, broad singlet. The ^{13}C NMR of carbonyl appeared as a quartet in some cases or broad doublet in other cases due to CF_3 coupling.

High-resolution mass spectra (HRMS) were obtained using Waters Xevo-G2XQTOF instruments with the electrospray ionization (ESI) method. The Gas Chromatography-Mass spectrometry (GC-MS) analysis was performed using Shimadzu GCMS-TQ8040 NX spectrometer. Single crystal X-ray diffractions were recorded using Bruker AXS Smart Apex CCD diffractometer.

Materials: Chemicals like amines, carboxylic acids, methyl acrylate, ethyl acrylate, styrenes and phenylboronic acids were purchased from BLD Pharma, Spectrochem, GLR, TCI, Sigma-Aldrich, SRL chemical and used without further purification. Pd-catalysts were purchased from Sigma-Aldrich and Spectrochem. Oxalyl chloride was purchased from Spectrochem and distilled under N_2. Dry DME was purchased from Wako Pure Chemical Industries and used inside glove box without further drying. DCM, hexane, and ethyl acetate were purchased from Rankem and Finar (25 litre drums) and used after distillation for column chromatography. Dioxane was purchased

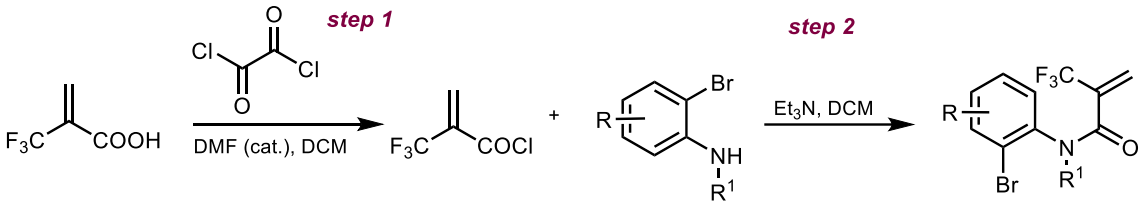
from SRL. DCM, MeCN, toluene and dioxane were dried by stirring over CaH_2 overnight and distilling under nitrogen atmosphere.

2. Synthesis of Starting Materials:

N-(*o*-haloaryl)-*N*-substituted trifluoromethyl acrylamide derivatives (**1a**-**1w**) were prepared according to the previous reports.[1-3] The characterization data of the known starting materials has been found consistent with the reported literature.

2.1. The synthesis of *N*-(2-bromoaryl)-*N*-substituted-2-(trifluoromethyl)acrylamides:

General procedure-1 (GP-1):



Scheme S1. Synthesis of *N*-(2-bromoaryl)-*N*-substituted-2-(trifluoromethyl)acrylamides.

Step 1: A two-necked round bottom flask equipped with a magnetic stir bar was charged with 2-(trifluoromethyl)acrylic acid (1.2−1.5 equiv) and dry DCM (0.5 M) was added under nitrogen atmosphere. The flask was then cooled to 0 °C using an ice bath and 2-4 drops of dry DMF were added. Afterwards, freshly distilled oxalyl chloride (1.2 equiv) was added dropwise to the solution. Then, the solution was allowed to attain room temperature slowly and stirred for 5-6 h. The acyl chloride was used for the next step without further purification.

Step 2: In a separate two-necked round-bottom flask equipped with a magnetic stir bar, 2-bromo *N*-substituted aniline (1.0 equiv), triethylamine (1.5 equiv), and dry DCM (0.5 M) were added under N_2 atmosphere and stirred for 1 h. Then, freshly prepared 2-(trifluoromethyl)acryloyl chloride (**Step 1**) was added dropwise for 10-15 min at 0 °C. The resultant mixture was allowed to warm up to room temperature and stirred overnight until the aniline was consumed completely (monitored by TLC). The reaction mixture was washed with water and extracted with DCM (3 times). The organic layer was washed with 1N HCl solution, 1N NaOH solution, and brine respectively. The final organic solution was dried over anhydrous Na_2SO_4, filtered, and concentrated in a rotary evaporator. The residue acrylamide was then purified by silica gel chromatography (100-200 mesh).

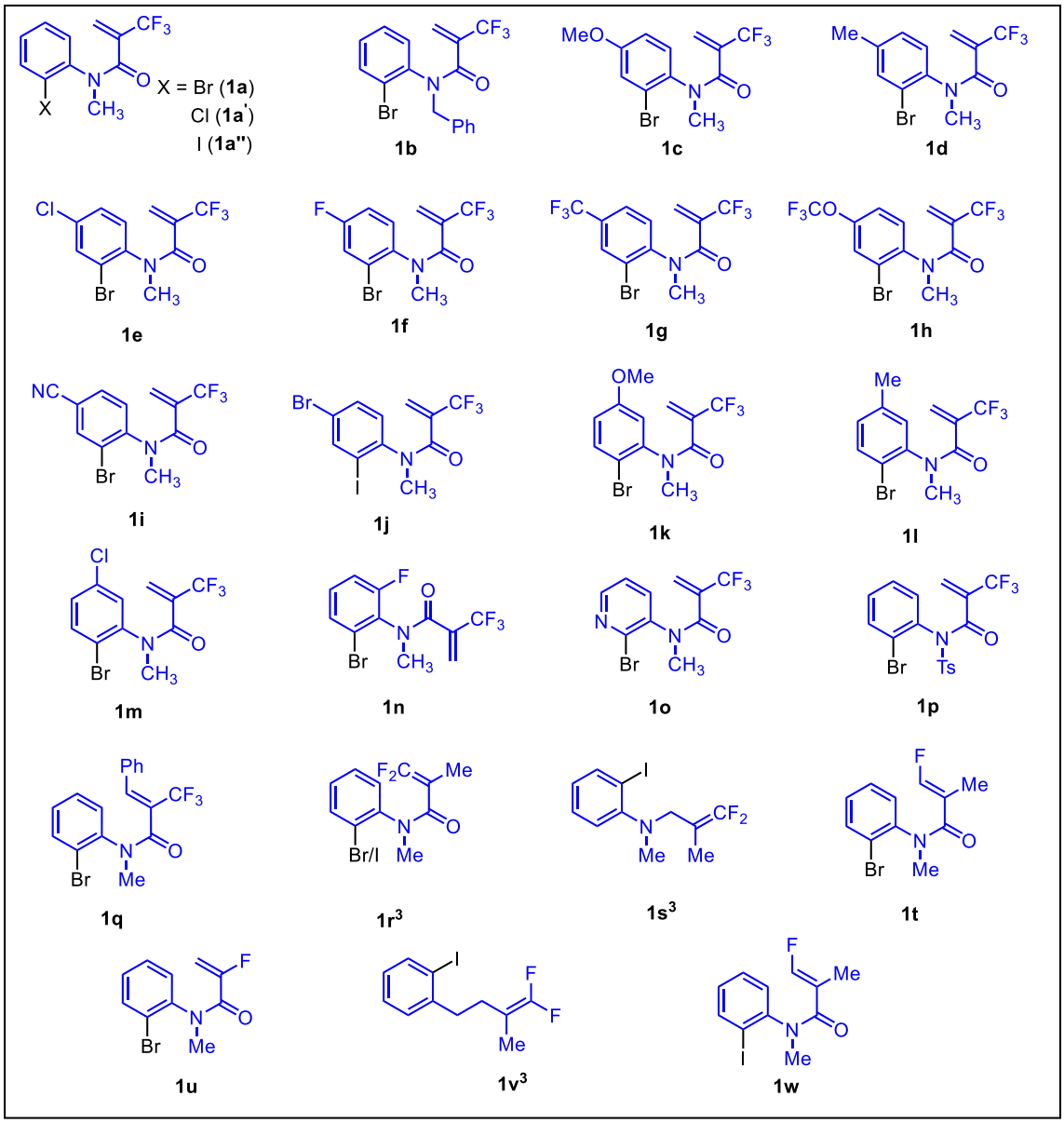
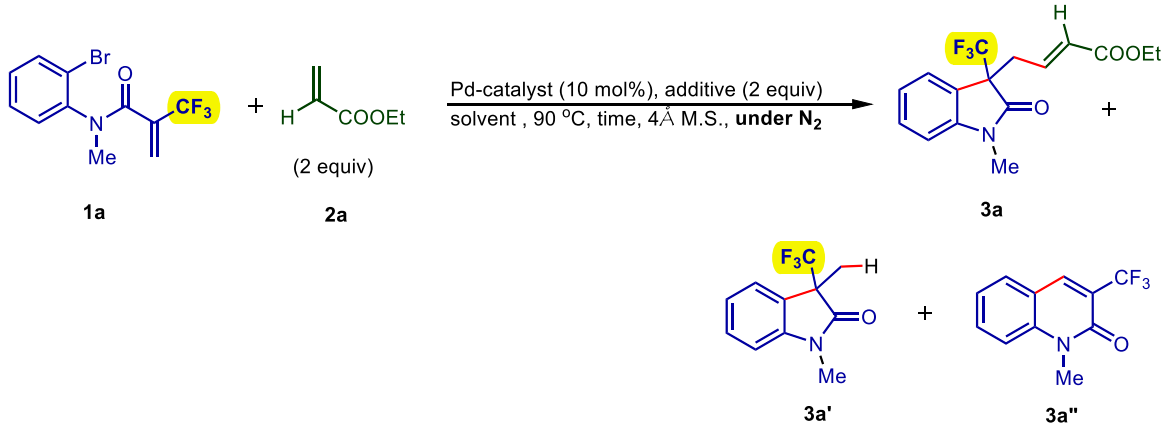


Figure S1. *N*-(2-haloaryl)-*N*-substituted-2-(trifluoromethyl)acrylamides.

3. Double Heck-type cyclization with alkenes:

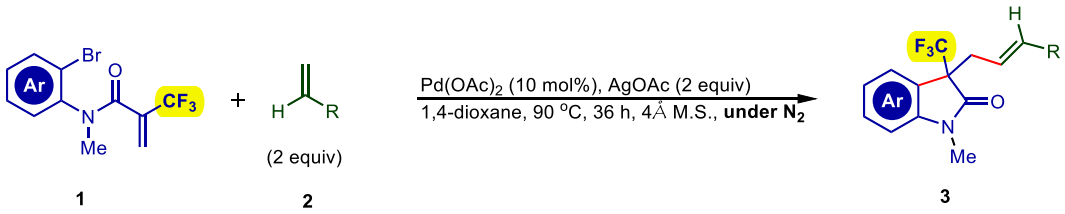
3.1. General Procedure for Optimization:



Scheme S2. Optimization of double Heck reaction of **1a** with ethyl acrylate.

General procedure-2 (GP-2): In a 7.0 mL reaction vial equipped with a magnetic bead, *N*-(2-bromophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (**1a**) (1 equiv), Pd-catalyst (10 mol%), additive (silver and non-silver salts) (2 equiv) and molecular sieves (4Å , 2 no.) were added. Then the reaction vial was introduced into glove box followed by addition of ethyl acrylate (**2a**) (2 equiv) and solvent (0.05 – 0.1 M) under N_2 atmosphere. Then, the reaction was sealed, taken outside and kept on stirring at desired temperature for 24–36 h. After completion of the reaction (monitored by TLC), the crude reaction mixture was filtered through a celite pad, and dried on sodium sulfate followed by high vacuum. Afterward, nitromethane (1 equiv) was added to the dried reaction mixture as an internal standard and crude ^{1}H NMR was recorded.

3.2. General Procedure for Reaction Setup:



Scheme S3. Scope study of double-Heck cyclization reaction of **1** with **2**.

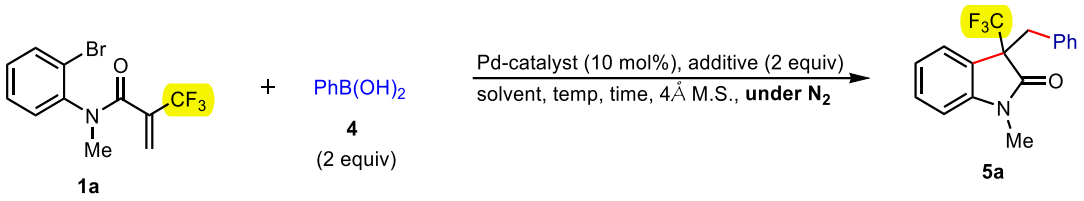
General procedure-3 (GP-3): In a 7.0 mL reaction vial equipped with a magnetic bead, acrylamide substrate (**1**) (1 equiv), $Pd(OAc)_2$ (10 mol%), AgOAc (2 equiv) and 4 Å molecular sieves (2 no.) were added. Next, the reaction vial was introduced into glove box followed by addition of alkene (**2**) (2 equiv) and dry dioxane (0.1 – 0.2 M). Then the reaction vial was sealed,

taken outside the glove box, and stirred in a pre-heated oil bath at 90 °C for 36 h. The crude reaction mixture was then purified by two successive silica gel column chromatography in different eluent systems (column 1: hexane-EtOAc; column 2: DCM-hexane or THF-$CHCl_3$-hexane).

4. Heck-Suzuki cascade with Phenyl Boronic Acids:

4.1. General Procedure for Optimization studies:

Table 1. Optimization studies of Pd catalyzed Heck-Suzuki cascade coupling reaction[a]

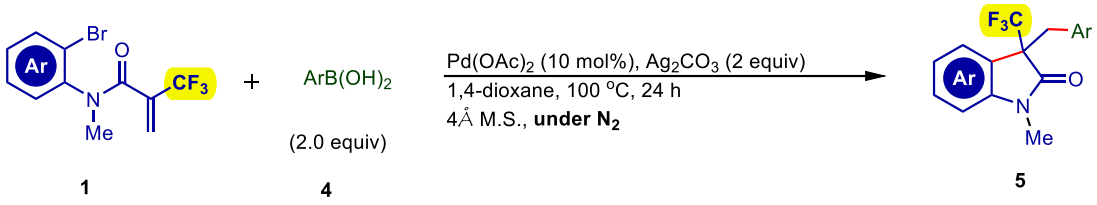


S. No.	Catalyst	Additive	Solvent	% Yield (3a)
1	$Pd(OAc)_2$	AgOAc	1,4-dioxane	71
2	$Pd(OAc)_2$	Ag_2CO_3	1,4-dioxane	77
3	$Pd(OAc)_2$	Ag(OTf)	1,4-dioxane	10[b]
4	$Pd(OAc)_2$	Ag_3PO_4	1,4-dioxane	07[b]
5	$Pd(OAc)_2$	K_3PO_4	1,4-dioxane	37[b]
6	$Pd(OAc)_2$	Cs_2CO_3	1,4-dioxane	57[b]

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), Pd-catalyst (10 mol%), additive (2.0 equiv), solvent, 100 °C, 24 h, isolated yield. [b]**1a** (0.025 mmol), **2a** (0.05 mmol), 100 °C, 24 h, crude ^{1}H-NMR yield with nitromethane as internal standard.

General procedure-4 (GP-4): In a 7.0 mL reaction vial equipped with a magnetic bead, *N*-(2-bromophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (**1a**) (1 equiv), Pd-catalyst (10 mol%), additive (silver and non-silver salts) (2 equiv), phenylboronic acid (2 equiv) and 4 Å molecular sieves (2 no.) were added. Then the rection vial was introduced into the glove box, followed by addition of solvent (0.1 M) under N_2 atmosphere. Then, the reaction was taken outside and kept on stirring at 100 °C for 24 h. After completion of the reaction (monitored by TLC), the crude reaction mixture was filtered through a celite pad and dried on sodium sulfate followed by high vacuum. Afterwards, nitromethane (1 equiv) was added to the dried reaction mixture as internal standard and crude ^{1}H NMR was recorded.

4.2. General Procedure for Reaction Setup:



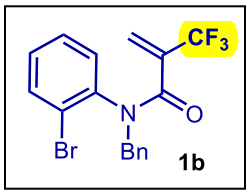
Scheme S4. Heck-Suzuki cyclization reaction of **1** with aryl boronic acids.

General procedure-5 (GP-5): In a 7.0 mL reaction vial equipped with a magnetic bead, acrylamide substrate (**1**) (1 equiv), $Pd(OAc)_2$ (10 mol%), Ag_2CO_3 (2 equiv), aryl boronic acid (2 equiv), and 4 Å molecular sieve (2 no.) were added. Next, the reaction vial was introduced into glove box and dry dioxane (0.1 M) was added in the reaction mixture. Then the reaction vial was sealed, taken outside the glove box and stirred in a pre-heated oil bath at 100 °C for 24 h. The crude reaction mixture was then purified by silica gel column chromatography.

5. Characterization:

5.1. Characterization of Starting Materials

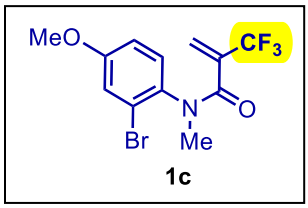
N-benzyl-*N*-(2-bromophenyl)-2-(trifluoromethyl)acrylamide (1b)



Following GP-1, amide coupling of CF_3-acrylic acid (560 mg, 4 mmol) with *N*-benzyl-2-bromo aniline (1.31 g, 5 mmol) afforded the desired amide **1b** (453 mg) in 29% yield as a yellow liquid; $R_f = 0.22$ (5% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, $J = 7.9$, 1.3 Hz, 1H), 7.27 – 7.21 (m, 3H), 7.21 – 7.10 (m, 4H), 6.66 (d, $J = 7.4$ Hz, 1H), 5.80 – 5.62 (m, 3H), 4.18 (d, $J = 14.3$ Hz, 1H); **^{13}C{1H} (126 MHz, $CDCl_3$)** δ 163.5, 139.7, 135.7, 134.2 (q, $J = 32.0$ Hz), 133.8, 131.9, 130.0, 129.2 (2C), 128.4 (2C), 128.2, 127.8, 123.9 (q, $J = 5.2$ Hz), 122.8, 121.3 (q, $J = 274.0$ Hz), 51.4; **^{19}F{1H} NMR (471 MHz, $CDCl_3$)** δ -64.3 ppm; **HRMS (ESI-TOF)** ***m/z***: $[M+H]^+$ calcd. for $C_{17}H_{13}F_3BrNO$: 384.0205, found 384.0210.

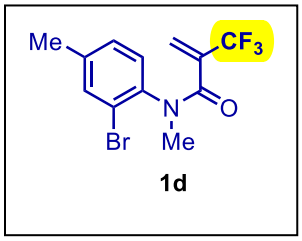
N-(2-Bromo-4-methoxyphenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (1c)



Following GP-1, amide coupling of CF_3-acrylic acid (1.1 g, 7.8 mmol) with 2-bromo-4-methoxy-*N*-methyl aniline (1.4 g, 6.5 mmol) afforded the desired amide **1c** (1.46 g) in 67% yield as a brown liquid; $R_f = 0.29$ (10% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, J = 2.7 Hz, 1H), 7.09 (d, J = 8.7 Hz, 1H), 6.84 (dd, J = 8.7, 2.8 Hz, 1H), 5.78 (s, 1H), 5.64 (s, 1H), 3.81 (s, 3H), 3.27 (s, 3H); **^{13}C{1H} (126 MHz, $CDCl_3$)** δ 163.9, 159.7, 134.8, 134.0 (q, J = 31.9 Hz), 130.2, 124.0 (q, J = 5.4 Hz), 122.9, 121.3 (q, J = 274.1 Hz), 118.8, 114.2, 55.6, 36.5; **^{19}F{1H} NMR (471 MHz, $CDCl_3$)** δ -64.4 ppm; **HRMS (ESI-TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{12}H_{11}BrF_3NO_2Na$: 359.9817, found 359.9818.

***N*-(2-Bromo-4-methylphenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (1d)**

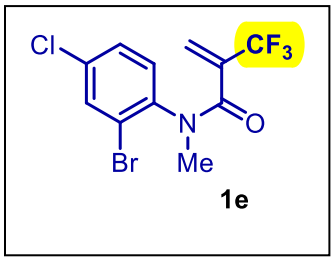


1d

Following GP-1, amide coupling of CF_3-acrylic acid (1.6 g, 11.26 mmol) with 2-bromo-4-methyl-*N*-methyl aniline (1.8 g, 9.4 mmol) afforded the desired amide **1d** (779 mg) in 26% yield as brown liquid; R_f = 0.40 (10% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.07 (d, J = 8.0 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 5.69 (s, 1H), 5.55 (s, 1H), 3.18 (s, 3H), 2.26 (s, 3H); **^{13}C{1H} (126 MHz, $CDCl_3$)** δ 163.4, 140.4, 139.4, 134.1, 133.7 (q, J = 31.8 Hz), 129.4, 129.3, 124.2 (q, J = 5.3 Hz), 121.8, 121.1 (q, J = 273.8 Hz), 36.2, 20.4; **^{19}F{1H} NMR (471 MHz, $CDCl_3$)** δ -64.4 ppm; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{12}H_{12}F_3BrNO$: 322.0049, found 322.0046.

***N*-(2-bromo-4-chlorophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (1e)**

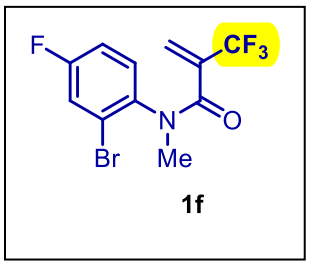


1e

Following GP-1, amide coupling of CF_3-acrylic acid (1.69 g, 12 mmol) with 2-bromo-4-chloro-*N*-methyl aniline (1.79 g, 8 mmol) afforded the desired amide **1e** (844 mg) in 30% yield as yellow liquid; R_f = 0.28 (5% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 1.9 Hz, 1H), 7.32 (d, J = 8.2 Hz, 1H), 7.12 (d, J = 8.3 Hz, 1H), 5.80 (s, 1H), 5.62 (s, 1H), 3.26 (s, 3H); **^{13}C{1H} (126 MHz, $CDCl_3$)** δ 163.5, 141.0, 135.1, 134.0 (q, J = 31.4 Hz), 133.6, 130.7, 129.2, 124.6 (bd, J = 4.0 Hz), 123.1, 121.2 (q, J = 274.1 Hz), 36.4; **^{19}F{1H} NMR (471 MHz, $CDCl_3$)** δ -64.4 ppm; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{11}H_9F_3ClBrNO$: 341.9503, found 341.9514.

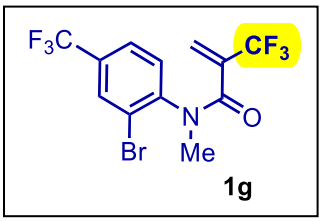
***N*-(2-bromo-4-fluorophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (1f)**



Following GP-1, amide coupling of CF_3-acrylic acid (840 mg, 6.0 mmol) with 2-bromo-4-fluoro-*N*-methyl aniline (1.0 g, 5.0 mmol) afforded the desired amide **1f** (731 mg) in 45% yield as yellow liquid; R_f = 0.20 (5% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 7.7, 2.6 Hz, 1H), 7.26 (dd, *J* = 8.4, 5.6 Hz, 1H), 7.11 (t, *J* = 8.1 Hz, 1H), 5.84 (s, 1H), 5.68 (s, 1H), 3.30 (s, 3H); **^{13}C{1H} (126 MHz, $CDCl_3$)** 163.3, 161.4 (d, *J* = 253.6 Hz), 138.4 (d, *J* = 3.5 Hz), 133.8 (q, *J* = 31.7 Hz), 130.9 (d, *J* = 9.1 Hz), 124.3 (q, *J* = 4.9 Hz), 122.9 (d, *J* = 10.1 Hz), 121.0 (q, *J* = 273.9 Hz), 120.8 (d, *J* = 25.6 Hz), 115.8 (d, *J* = 22.3 Hz), 36.1; **^{19}F{1H} NMR (471 MHz, $CDCl_3$)** δ -110.1, -64.5 ppm; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{11}H_9F_4BrNO$: 325.9798, found 325.9816.

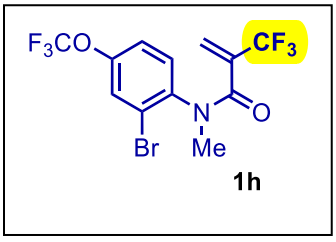
_N_-(2-Bromo-4-trifluoromethylphenyl)-_N_-methyl-2-(trifluoromethyl)acrylamide (1g)



Following GP-1, amide coupling of CF_3-acrylic acid (0.95 g, 6.8 mmol) with 2-bromo-4-trifluoromethyl-*N*-methyl aniline (1.4 g, 5.7 mmol) afforded the desired amide **1g** (945 mg) in 44% yield as yellow liquid; R_f = 0.24 (30% DCM in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.86 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 5.77 (s, 1H), 5.58 (s, 1H), 3.24 (s, 3H); **^{13}C{1H} NMR (126 MHz, $CDCl_3$)** *δ* 163.2, 145.5, 133.8 (q, *J* = 32.4 Hz), 131.9 (q, *J* = 33.2 Hz), 131.0, 130.5, 125.9 (q, *J* = 3.1 Hz), 125.0, 122.9, 122.5 (q, *J* = 273.1 Hz), 121.1 (q, *J* = 274.0 Hz), 36.0; **^{19}F{1H} NMR (471 MHz, $CDCl_3$)** *δ* -64.6, -63.1 ppm; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{12}H_9F_6BrNO$: 375.9766, found 375.9775.

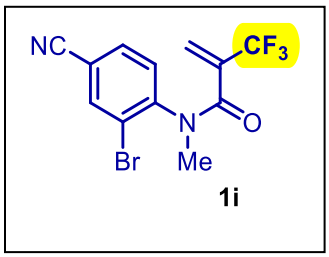
_N_-(2-Bromo-4-(trifluoromethoxy)phenyl)-_N_-methyl-2-(trifluoromethyl)acrylamide (1h)



Following GP-1, amide coupling of CF_3-acrylic acid (0.81 g, 5.80 mmol) with 2-bromo-4-trifluoromethoxy-*N*-methyl aniline (1.88 g, 6.96 mmol) afforded the desired amide **1h** (841 mg) in 37% yield as colorless liquid; R_f = 0.24 (30% DCM in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.46 (s, 1H), 7.26 − 7.10 (m, 2H), 5.76 (s, 1H), 5.59 (s, 1H), 3.22 (s, 3H); **^{13}C{1H} NMR (126 MHz, $CDCl_3$)** *δ* 163.4, 148.7, 140.9, 133.9 (q, *J* = 31.9 Hz), 130.9, 126.0, 124.6 (q, *J* = 4.4 Hz), 123.1, 121.13 (q, *J* = 274.0 Hz), 120.95, 120.1 (q, *J* = 274.0 Hz), 36.1; **^{19}F{1H} NMR (471 MHz, $CDCl_3$)** *δ* -64.6, -58.4 ppm; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{12}H_9F_6BrNO_2$: 391.9715, found 391.9734.

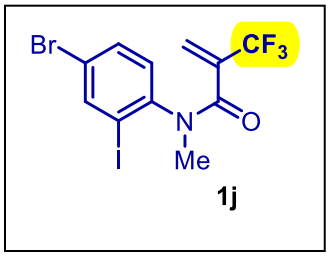
***N*-(2-Bromo-4-cyanophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (1i)**



Following GP-1, amide coupling of CF_3-acrylic acid (1.1 g, 8.0 mmol) with 2-bromo-4-cyano-*N*-methyl aniline (1.5 g, 6.6 mmol) afforded the desired amide **1i** (926 mg) in 42% yield as yellow liquid; $R_f = 0.18$ (15% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.67 (d, J = 7.9 Hz, 1H), 7.32 (bs, 1H), 5.85 (s, 1H), 5.62 (s, 1H), 3.31 (s, 3H); **^{13}C{1H} (126 MHz, $CDCl_3$)** δ 163.2, 146.5, 137.4, 133.9 (q, J = 32.1 Hz), 132.6, 130.8, 125.2, 123.3, 121.0 (q, J = 274.0 Hz), 116.2, 114.0, 36.3; **^{19}F{1H} NMR (471 MHz, $CDCl_3$)** δ -64.4 ppm; **GCMS-EI** (***m/z,*** relative intensity): 253 ((M-Br)$^+$, 99), 123 (100), 95 (24), 69 (19), 42 (84), 40 (34).

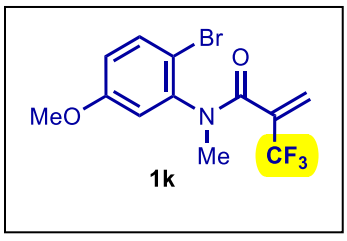
***N*-(4-bromo-2-iodophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (1j)**



Following GP-1, amide coupling of CF_3-acrylic acid (840 mg, 6.0 mmol) with 4-bromo-2-iodo-*N*-methyl aniline (1.56 g, 5.0 mmol) afforded the desired amide **1j** (1.42 g) in 65% yield as yellow liquid; $R_f = 0.28$ (5% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 2.2 Hz, 1H), 7.53 – 7.40 (m, 1H), 7.00 (d, J = 8.3 Hz, 1H), 5.77 (s, 1H), 5.63 (s, 1H), 3.19 (s, 3H); **^{13}C{1H} (126 MHz, $CDCl_3$)** δ 163.1, 144.6, 142.1, 133.5 (q, J = 31.0 Hz), 132.8, 130.2, 124.9 (q, J = 5.1 Hz), 122.5, 121.0 (q, J = 274.1 Hz), 99.3, 36.6; **^{19}F{1H} NMR (471 MHz, $CDCl_3$)** δ -64.1 ppm; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{11}H_9F_3BrNOI$: 433.8859, found 433.8877.

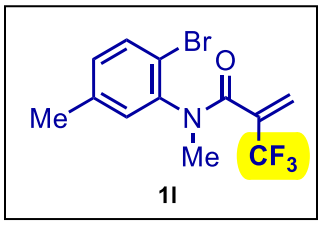
***N*-(2-Bromo-5-methoxyphenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (1k)**



Following GP-1, amide coupling of CF_3-acrylic acid (605 mg, 4.3 mmol) with 2-bromo-5-methoxy-*N*-methyl aniline (778 mg, 3.6 mmol) afforded the desired amide **1k** (592 mg) in 49% yield as a white solid $R_f = 0.18$ (5% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, J = 8.9 Hz, 1H), 6.78 (dd, J = 8.8, 2.7 Hz, 1H), 6.72 (s, 1H), 5.79 (s, 1H), 5.66 (s, 1H), 3.77 (s, 3H), 3.29 (s, 3H); **^{13}C{1H} NMR (126 MHz, $CDCl_3$)** δ 163.7, 159.9, 143.0, 134.2, 124.4 (q, J = 4.8 Hz), 121.4 (q, J = 274.0 Hz), 116.4, 115.2, 112.5, 55.6, 36.3; **^{19}F{1H} NMR (471 MHz, $CDCl_3$)** δ -64.4 ppm; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{12}H_{11}F_3BrNO_2$: 337.9998, found 337.9997.

***N*-(2-Bromo-5-methylphenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (1l)**

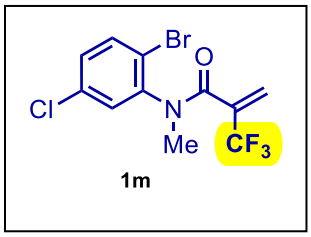


1l

Following GP-1, amide coupling of CF_3-acrylic acid (1.24 g, 8.83 mmol) with 2-bromo-5-methyl-*N*-methyl aniline (1.47 g, 7.36 mmol) afforded the desired amide **1l** (1.11 g) in 47% yield as yellow liquid; R_f = 0.5 (15% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.44 (d, *J* = 8.0 Hz, 1H), 7.04 – 6.91 (m, 2H), 5.72 (s, 1H), 5.59 (s, 1H), 3.23 (s, 3H), 2.25 (s, 3H); **^{13}C{1H} NMR (126 MHz, $CDCl_3$)** *δ* 163.5, 141.8, 139.3, 133.9 (q, *J* = 32.1 Hz), 133.4, 130.6, 130.4, 124.2 (q, *J* = 5.1 Hz), 121.2 (q, *J* = 273.8 Hz), 118.7, 36.2, 20.4; **^{19}F NMR{1H} (471 MHz, $CDCl_3$)** *δ* -64.5 ppm; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{12}H_{12}F_3BrNO$: 322.0049, found 322.0047.

***N*-(2-Bromo-5-chlorophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (1m)**

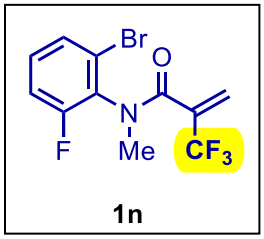


1m

Following GP-1, amide coupling of CF_3-acrylic acid (840 mg, 6.0 mmol) with 2-bromo-5-chloro-*N*-methyl aniline (1.10 g, 5.0 mmol) afforded the desired amide **1m** (925 mg) in 54% yield as a colorless liquid; R_f = 0.21 (5% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.4 Hz, 1H), 7.26 – 7.15 (m, 2H), 5.83 (s, 1H), 5.64 (s, 1H), 3.29 (s, 3H); **^{13}C{1H} NMR (126 MHz, $CDCl_3$)** δ 163.3, 143.1, 134.6, 134.3, 133.8 (q, *J* = 32.8 Hz), 130.1, 124.7 (bd, *J* = 3.7 Hz), 121.1 (q, *J* = 274.0 Hz), 120.5, 36.2; **^{19}F{1H} NMR (471 MHz, $CDCl_3$)** δ -64.4 ppm; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{11}H_9F_3ClBrNO$: 341.9503, found 341.9496.

***N*-(2-Bromo-6-fluorophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (1n)**



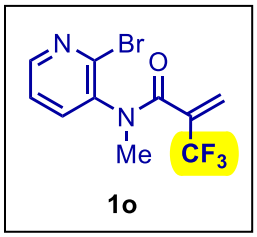
1n

Following GP-1, amide coupling of CF_3-acrylic acid (420 mg, 3.0 mmol) with 2-bromo-6-fluoro-*N*-methyl aniline (673 mg, 3.30 mmol) afforded the desired amide **1n** (509 mg) in 52% yield as a colorless liquid; R_f = 0.41 (5% EtOAc in hexane). The product contains rotamers in 82:18 (^{13}C NMR gave multiple peaks and it was difficult to clearly assign the corresponding peaks).

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.4 (dt, *J* = 8.1, 1.2 Hz, 1H), 7.23 (td, *J* = 8.3, 5.6 Hz, 1H), 7.13 (td, *J* = 8.7, 1.2 Hz, 1H), 5.87 (s, 1H), 5.71 (s, 1H), 3.28 (s, 3H);**^{19}F{1H} NMR (471 MHz, $CDCl_3$)** *δ* -

117.4, -115.7 (q, J = 7.4 Hz), -65.0, -63. 9 (d, J = 7.5 Hz); **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{11}H_9F_4BrNO$: 325.9798, found 325.9801.

***N*-(2-Bromopyridin-3-yl)-*N*-methyl-2-(trifluoromethyl)acrylamide (1o)**



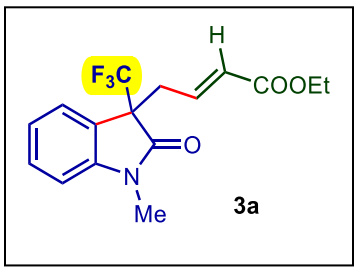
1o

Following GP-1, amide coupling of CF_3-acrylic acid (420 mg, 3.00 mmol) with 2-bromo-*N*-methylpyridin-3-amine (617 g, 3.30 mmol) afforded the desired amide **1o** (142 mg) in 15% yield as a colorless liquid; R_f = 0.21 (15% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 – 8.31 (m, 1H), 7.52 (d, J = 7.0 Hz, 1H), 7.35 (dd, J = 7.7, 4.7 Hz, 1H), 5.82 (s, 1H), 5.74 (s, 1H), 3.31 (s, 3H); **^{13}C{1H} NMR (126 MHz, $CDCl_3$)** δ 163.3, 149.6, 142.4, 139.6, 138.1, 133.8 (q, J = 34.0 Hz), 124.9 (bd, J = 3.1 Hz), 123.8, 121.0 (q, J = 274.8 Hz), 36.2; **^{19}F{1H} NMR (471 MHz, $CDCl_3$)** δ -64.5 ppm; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{10}H_9F_3BrN_2O$: 308.9845, found 308.9852.

5.2 Characterization of Products:

Ethyl (*E*)-4-(1-methyl-2-oxo-3-(trifluoromethyl)indolin-3-yl)but-2-enoate (3a)



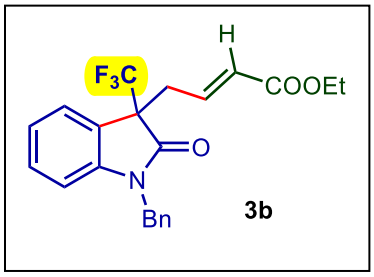
3a

Following GP-3, Heck coupling of *N*-(2-bromophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (31 mg, 0.10 mmol) with ethyl acrylate (21 μL, 0.20 mmol) afforded the desired oxindole **3a** (29 mg) in 88% yield as a yellow liquid; (column 1: hexane-EtOAc (90:10); column 2: DCM-hexane (50:50)); R_f = 0.22 (10% EtOAc in hexane). Reaction at 1.0 mmol scale in a 7 mL screw cap reaction vial afforded **3a** in 68% yield (223 mg). Reaction of **1a′** (*N*-(2-chlorophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide) (26 mg, 0.10 mmol) with **2a** (21 μl, 0.20 mmol) gave **3a** in 11% yield (3.6 mg) while **1a″** (*N*-(2-iodophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide) (35 mg, 0.10 mmol) with **2a** (21 μl, 0.20 mmol) gave **3a** in 75% yield (25 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.08 (td, J = 7.6, 0.9 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 6.32 (dt, J = 15.3, 7.6 Hz, 1H), 5.78 (dt, J = 15.5, 1.2 Hz, 1H), 4.02 (q, J = 7.1 Hz, 2H), 3.16 (s, 3H), 3.04 (ddd, J = 13.8, 8.0, 1.2 Hz, 1H), 2.95 (ddd, J = 13.9, 7.2, 1.4 Hz, 1H), 1.14 (t, J = 7.1 Hz, 3H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 170.2 (d, J = 2.4 Hz), 165.2, 144.0, 138.8, 130.3, 126.3, 124.8, 124.2 (q, J = 282.2 Hz), 123.2, 122.7 (d, J = 1.4 Hz), 108.7, 60.2, 55.7 (q, J = 26.8

Hz), 33.5 (q, J = 2.7 Hz), 26.4, 13.8.; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -72.1 ppm; **HRMS (ESI-TOF) *m/z***: [M+Na]$^+$ calcd. for $C_{16}H_{16}F_3NO_3Na$: 350.0974, found 350.0974.

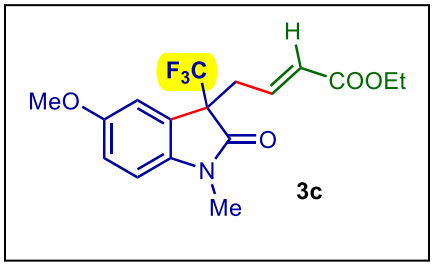
Ethyl (*E*)-4-(1-benzyl-2-oxo-3-(trifluoromethyl)indolin-3-yl)but-2-enoate (3b)



Following GP-3, Heck coupling of *N*-(2-bromophenyl)-*N*-benzyl-2-(trifluoromethyl)acrylamide (115 mg, 0.30 mmol) with ethyl acrylate (64 μL, 0.60 mmol) afforded the desired oxindole **3b** (78 mg) in 64% yield as a yellow liquid; (column 1: hexane-EtOAc (90:10); column 2: DCM-hexane (60:40)); R_f = 0.13 (10% EtOAc in hexane).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.39 (d, J = 7.4 Hz, 1H), 7.32 – 7.23 (m, 4H), 7.20 (d, J = 7.2 Hz, 2H), 7.11 (t, J = 7.6 Hz, 1H), 6.71 (d, J = 7.9 Hz, 1H), 6.45 – 6.33 (m, 1H), 5.89 (d, J = 15.5 Hz, 1H), 4.93 (q, J = 15.8 Hz, 2H), 4.10 (q, J = 7.1 Hz, 2H), 3.19 (dd, J = 13.7, 8.1 Hz, 1H), 3.05 (dd, J = 13.3, 6.4 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H); **^{13}C{1H} NMR (126 MHz, CDCl$_3$)** δ 170.6 (d, J = 1.7 Hz), 165.3, 143.3, 138.9, 134.7, 130.3, 128.8, 127.7, 126.9, 126.8, 125.0, 124.3 (q, J = 282.4 Hz), 123.4, 122.8, 110.0, 60.4, 55.9 (q, J = 26.8 Hz), 44.0, 33.7, 14.0; **^{19}F NMR (471 MHz, CDCl$_3$)** δ -72.2 ppm; **HRMS (ESI-TOF) *m/z:*** [M+H]$^+$ calcd. for $C_{22}H_{21}F_3NO_3$: 404.1468, found 404.1470.

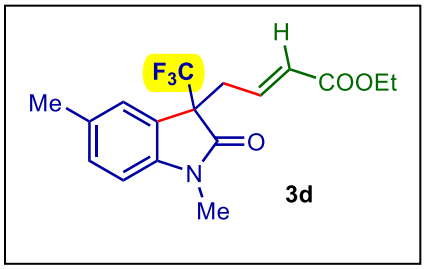
Ethyl (*E*)-4-(5-methoxy-1-methyl-2-oxo-3-(trifluoromethyl)indolin-3-yl)but-2-enoate (3c)



Following GP-3, Heck coupling of *N*-(2-bromo-4-methoxyphenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (101 mg, 0.30 mmol) with ethyl acrylate (64 μL, 0.60 mmol) afforded the desired oxindole **3c** (73 mg) in 68% yield as a colorless liquid; (column 1: hexane-EtOAc (90:10); column 2: DCM-hexane (60:40)); R_f = 0.14 (10% EtOAc in hexane).

^{1}H NMR (500 MHz, CDCl$_3$) δ 6.96 (s, 1H), 6.90 (dd, J = 8.5, 2.4 Hz, 1H), 6.78 (d, J = 8.5 Hz, 1H), 6.35 (dt, J = 15.3, 7.6 Hz, 1H), 5.84 (d, J = 15.5 Hz, 1H), 4.09 (q, J = 7.1 Hz, 2H), 3.80 (s, 3H), 3.19 (s, 3H), 3.09 (dd, J = 13.9, 8.2 Hz, 1H), 2.95 (dd, J = 13.9, 7.0 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H); **^{13}C{1H} NMR (101 MHz, CDCl$_3$)** δ 170.0 (q, J = 2.8 Hz), 165.4, 156.3, 138.9, 137.4, 126.4, 124.2 (q, J = 282.5 Hz), 124.0 (bd, J = 1.1 Hz), 114.5, 112.4, 109.2, 60.4, 56.1 (q, J = 28.9 Hz), 55.8, 33.7 (q, J = 2.8 Hz), 26.6, 14.0; **^{19}F NMR (471 MHz, CDCl$_3$)** δ -72.2 ppm; **HRMS (ESI-TOF) *m/z:*** [M+Na]$^+$ calcd. for $C_{17}H_{18}F_3NO_4Na$: 380.1080, found 380.1090.

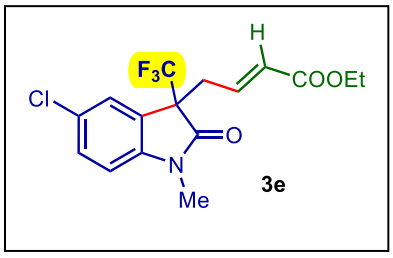
Ethyl (*E*)-4-(1,5-dimethyl-2-oxo-3-(trifluoromethyl)indolin-3-yl)but-2-enoate (3d)



Following GP-3, Heck coupling of *N*-(2-bromo-4-methylphenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (97 mg, 0.30 mmol) with ethyl acrylate (64 μL, 0.60 mmol) afforded the desired oxindole **3d** (79 mg) in 77% yield as a yellow liquid; (column 1: hexane-EtOAc (90:10); column 2: DCM-hexane (40:60)); R_f = 0.40 (10% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.18 (d, *J* = 10.4 Hz, 2H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.35 (dt, *J* = 15.3, 7.6 Hz, 1H), 5.84 (d, *J* = 15.5 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.20 (s, 3H), 3.08 (dd, *J* = 13.9, 8.2 Hz, 1H), 2.96 (dd, *J* = 13.9, 6.9 Hz, 1H), 2.36 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); **^{13}C{1H} NMR (126 MHz, $CDCl_3$)** *δ* 170.3 (d, *J* = 1.7 Hz), 165.4, 141.7, 139.1, 133.0, 130.7, 126.3, 125.6, 124.3 (q, *J* = 282.3 Hz), 122.8, 108.5, 60.3, 55.9 (q, *J* = 27.0 Hz), 33.7, 26.5, 21.0, 14.0; **^{19}F NMR (471 MHz, $CDCl_3$)** *δ* -72.2 ppm; **HRMS (ESI-TOF)** ***m/z:*** $[M+Na]^+$ calcd. for $C_{17}H_{18}F_3NO_3Na$: 364.1131, found 364.1142.

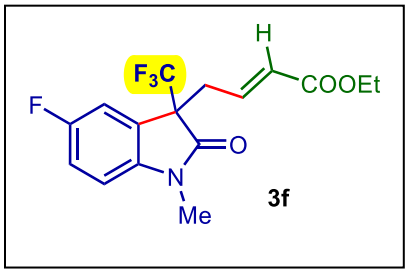
Ethyl (*E*)-4-(5-chloro-1-methyl-2-oxo-3-(trifluoromethyl)indolin-3-yl)but-2-enoate (3e)



Following GP-3, Heck coupling of *N*-(2-bromo-4-chlorophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (102 mg, 0.30 mmol) with ethyl acrylate (64 μL, 0.60 mmol) afforded the desired oxindole **3e** (76 mg) in 70% yield as a white solid; (column 1: hexane-EtOAc (90:10); column 2: DCM-hexane (60:40)); R_f = 0.17 (10% EtOAc in hexane); melting point: 54 °C.

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.37 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.34 (s, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.31 (dt, *J* = 15.2, 7.6 Hz, 1H), 5.84 (d, *J* = 15.5 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.20 (s, 3H), 3.10 (dd, *J* = 13.8, 8.1 Hz, 1H), 2.95 (dd, *J* = 13.8, 7.1 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H); **^{13}C{1H} NMR (126 MHz, $CDCl_3$)** *δ* 169.9 (bd, *J* = 1.7 Hz), 165.3, 142.7, 138.2, 130.5, 128.8, 126.9, 125.4, 124.4, 124.0 (q, *J* = 282.8 Hz), 109.8, 60.5, 56.0 (q, *J* = 26.8 Hz), 33.6 (bd, *J* = 1.4 Hz), 26.7, 14.0; **^{19}F NMR (471 MHz, $CDCl_3$)** *δ* -72.1 ppm; **HRMS (ESI-TOF)** ***m/z***: $[M+Na]^+$ calcd. for $C_{16}H_{15}F_3NO_3NaCl$: 384.0585, found 384.0589.

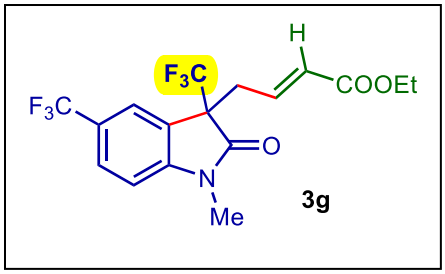
Ethyl (*E*)-4-(5-fluoro-1-methyl-2-oxo-3-(trifluoromethyl)indolin-3-yl)but-2-enoate (3f)



Following GP-3, Heck coupling of *N*-(2-bromo-4-fluorophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (98 mg, 0.30 mmol) with ethyl acrylate (64 μL, 0.60 mmol) afforded the desired oxindole **3f** (59 mg) in 57% yield as a colorless liquid; (column 1: hexane-EtOAc (90:10); column 2: DCM-hexane (60:40)); R_f = 0.14 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.16 – 7.06 (m, 2H), 6.87 – 6.77 (m, 1H), 6.32 (dt, *J* = 15.3, 7.6 Hz, 1H), 5.84 (d, *J* = 15.5 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.20 (s, 3H), 3.10 (ddd, *J* = 13.9, 8.0, 0.9 Hz, 1H), 2.95 (ddd, *J* = 13.9, 7.2, 1.1 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H); **^{13}C{1H} NMR (126 MHz, $CDCl_3$)** *δ* 170.0, 165.3, 159.3 (d, *J* = 242.8 Hz), 140.2, 138.3, 126.8, 124.3 (d, *J* = 8.1 Hz), 124.0 (q, *J* = 282.4 Hz), 116.9 (d, *J* = 23.5 Hz), 113.3 (d, *J* = 25.6 Hz), 109.5 (d, *J* = 8.1 Hz), 60.5, 56.2 (q, *J* = 27.1 Hz), 33.7, 26.7, 14.0; **^{19}F NMR (471 MHz, $CDCl_3$)** *δ* -118.7, -72.2 ppm; **HRMS (ESI-TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{16}H_{15}F_4NO_3Na$: 368.0880, found 368.0887.

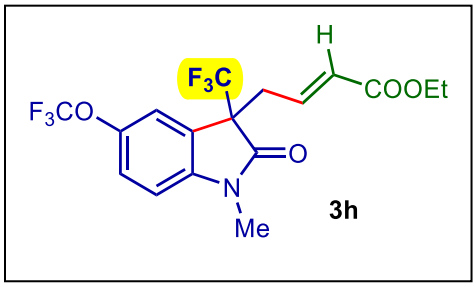
Ethyl (*E*)-4-(1-methyl-2-oxo-3,5-bis(trifluoromethyl)indolin-3-yl)but-2-enoate (3g)



Following GP-3, Heck coupling of *N*-(2-bromo-4-trifluoromethylphenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (113 mg, 0.30 mmol) with ethyl acrylate (64 μL, 0.60 mmol) afforded the desired oxindole **3g** (78 mg) in 66% yield as a colorless liquid; (column 1: hexane-EtOAc (90:10); column 2: DCM-hexane (60:40)); R_f = 0.16 (10% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.69 (bd, *J* = 8.1 Hz, 1H), 7.59 (s, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.30 (dt, *J* = 15.3, 7.6 Hz, 1H), 5.85 (d, *J* = 15.5 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.26 (s, 3H), 3.13 (dd, *J* = 13.8, 8.2 Hz, 1H), 3.01 (dd, *J* = 13.9, 7.0 Hz, 1H) 1.20 (t, *J* = 7.1 Hz, 3H); **^{13}C{1H} NMR (126 MHz, $CDCl_3$)** *δ* 170.3 (q, *J* = 1.8 Hz), 165.2, 147.1, 137.9, 128.3 (q, *J* = 3.8 Hz), 127.1, 125.8 (q, *J* = 33.3 Hz), 123.91 (q, *J* = 278.3 Hz), 123.90 (q, *J* = 282.7 Hz), 123.5, 122.1 (q, *J* = 3.4 Hz), 108.8, 60.5, 55.9 (q, *J* = 27.1 Hz), 33.6, 26.8, 14.0; **^{19}F NMR (471 MHz, $CDCl_3$)** *δ* -72.1, -61.7 ppm; **HRMS (ESI-TOF) *m/z:*** $[M+Na]^+$ calcd. for $C_{17}H_{15}F_6NO_3Na$: 418.0848, found 418.0848.

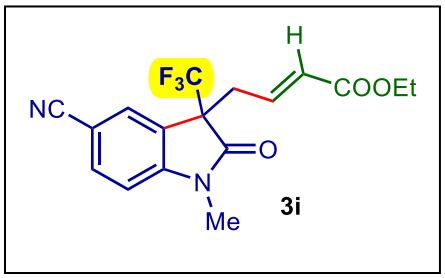
Ethyl (*E*)-4-(1-methyl-2-oxo-5-(trifluoromethoxy)-3-(trifluoromethyl)indolin-3-yl)but-2-enoate (3h)



Following GP-3, Heck coupling of *N*-(2-bromo-4-trifluoromethoxyphenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (118 mg, 0.30 mmol) with ethyl acrylate (64 μL, 0.60 mmol) afforded the desired oxindole **3h** (97 mg) in 79% yield as a colorless liquid; (column 1: hexane-EtOAc (90:10); column 2: DCM-hexane (60:40)); R_f = 0.14 (10% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.27 (d, *J* = 8.6 Hz, 1H), 7.24 (s, 1H), 6.88 (d, *J* = 8.5 Hz, 1H), 6.33 (dt, *J* = 15.4, 7.7 Hz, 1H), 5.82 (d, *J* = 15.5 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.22 (s, 3H), 3.08 (ddd, *J* = 13.9, 8.0, 1.0 Hz, 1H), 2.97 (ddd, *J* = 13.9, 7.3, 1.2 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H); **^{13}C{1H} NMR (126 MHz, $CDCl_3$)** *δ* 170.1 (q, *J* = 1.7 Hz), 165.2, 145.0 (q, *J* = 1.9 Hz), 142.8, 138.0, 127.1, 124.2, 123.9 (q, *J* = 282.4 Hz), 123.6, 120.4 (q, *J* = 257.3 Hz), 119.2, 109.4, 60.4, 56.1 (q, *J* = 27.1 Hz), 33.7 (bd, *J* = 1.7 Hz), 26.7, 14.0; **^{19}F NMR (471 MHz, $CDCl_3$)** *δ* -72.1, -58.6 ppm; **HRMS (ESI-TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{17}H_{15}F_6NO_4Na$: 434.0797, found 434.0818.

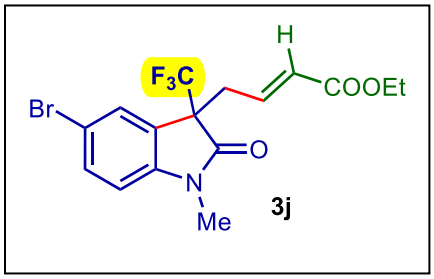
Ethyl (*E*)-4-(5-cyano-1-methyl-2-oxo-3-(trifluoromethyl)indolin-3-yl)but-2-enoate (3i)



Following GP-3, Heck coupling of *N*-(2-bromo-4-cyanophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (100 mg, 0.3 mmol) with ethyl acrylate (64 μL, 0.6 mmol) afforded the desired oxindole **3i** (75 mg) in 71% yield as a yellow solid; (column 1: hexane-EtOAc (80:20); column 2: DCM-hexane (90:10)); R_f = 0.05 (10% EtOAc in hexane); melting point: 114–116 °C.

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.72 (d, *J* = 8.2 Hz, 1H), 7.61 (s, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.27 (dt, *J* = 15.3, 7.6 Hz, 1H), 5.83 (d, *J* = 15.5 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.24 (s, 3H), 3.11 (dd, *J* = 13.9, 7.9 Hz, 1H), 2.98 (dd, *J* = 13.9, 7.3 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H); **^{13}C{1H} NMR (126 MHz, $CDCl_3$)** *δ* 170.0 (q, *J* = 1.4 Hz), 165.0, 147.8, 137.4, 135.5, 128.3, 127.2, 123.9, 123.6 (q, *J* = 282.7 Hz), 118.2, 109.4, 106.8, 60.5, 55.6 (q, *J* = 27.2 Hz), 33.4, 26.8, 14.0; **^{19}F NMR (471 MHz, $CDCl_3$)** *δ* -72.0 ppm; **HRMS (ESI-TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{17}H_{15}F_3N_2O_3Na$: 375.0927, found 375.0922.

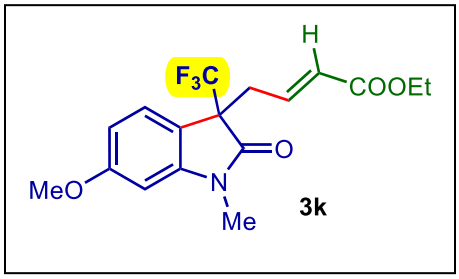
Ethyl (*E*)-4-(5-bromo-1-methyl-2-oxo-3-(trifluoromethyl)indolin-3-yl)but-2-enoate (3j)



Following GP-3, Heck coupling of *N*-(4-bromo-2-iodophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (43 mg, 0.10 mmol) with ethyl acrylate (43 μL, 0.40 mmol) afforded the desired oxindole **3j** (34 mg) in 84% yield as a colorless liquid; (column 1: hexane-EtOAc (90:10); column 2: DCM-hexane (50:50)); R_f = 0.20 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, J = 8.0, 1.7 Hz, 1H), 7.22 (dd, J = 8.0, 0.7 Hz, 1H), 7.04 (d, J = 1.7 Hz, 1H), 6.34 (dt, J = 15.4, 7.6 Hz, 1H), 5.84 (dt, J = 15.5, 1.3 Hz, 1H), 4.10 (q, J = 7.1 Hz, 2H), 3.21 (s, 3H), 3.08 (ddd, J = 13.9, 8.1, 1.3 Hz, 1H), 2.97 (ddd, J = 13.9, 7.2, 1.4 Hz, 1H), 1.22 (t, J = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 169.8, 165.3, 143.2, 138.2, 133.4, 128.1, 126.9, 124.8, 124.0 (q, J = 283.1 Hz), 116.0, 110.3, 60.5, 56.0 (q, J = 27.0 Hz), 33.6, 26.7, 14.0; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** δ -72.1 ppm; **HRMS (ESI-TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{16}H_{15}F_3NO_3NaBr$: 428.0080, found 428.0082.

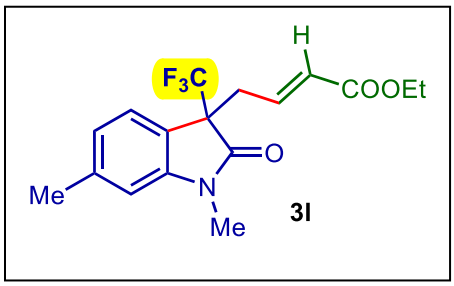
Ethyl (*E*)-4-(6-methoxy-1-methyl-2-oxo-3-(trifluoromethyl)indolin-3-yl)but-2-enoate (3k)



Following GP-3, Heck coupling of *N*-(2-bromo-5-methoxyphenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (101 mg, 0.30 mmol) with ethyl acrylate (64 μL, 0.60 mmol) afforded the desired oxindole **3k** (72 mg) in 67% yield as a yellow liquid; (column 1: hexane-EtOAc (90:10); column 2: DCM-hexane (60:40)); R_f = 0.16 (10% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, J = 8.3 Hz, 1H), 6.61 (dd, J = 8.3, 2.1 Hz, 1H), 6.44 (d, J = 2.0 Hz, 1H), 6.36 (dd, J = 15.4, 7.7 Hz, 1H), 5.83 (d, J = 15.5 Hz, 1H), 4.09 (q, J = 7.1 Hz, 2H), 3.83 (s, 3H), 3.19 (s, 3H), 3.04 (dd, J = 13.8, 8.2 Hz, 1H), 2.95 (dd, J = 13.9, 7.1 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H); **^{13}C{1H} NMR (126 MHz, $CDCl_3$)** δ 171.0 (bd, J = 1.9 Hz), 165.5, 161.7, 145.4, 139.3, 126.4, 125.8, 124.4 (q, J = 282.2 Hz), 114.5, 107.2, 96.8, 60.4, 55.6, 55.4 (q, J = 26.8 Hz), 33.8, 26.6, 14.1; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -72.4 ppm; **HRMS (ESI-TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{17}H_{18}F_3NO_4Na$: 380.1080, found 380.1085.

Ethyl (*E*)-4-(6-methyl-1-methyl-2-oxo-3-(trifluoromethyl)indolin-3-yl)but-2-enoate (3l)

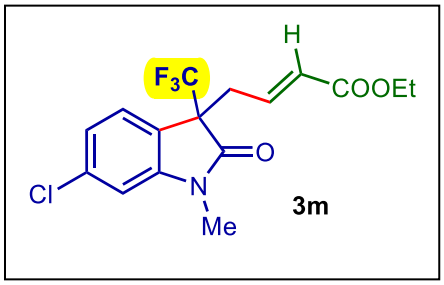


3l

Following GP-3, Heck coupling of *N*-(2-bromo-5-methylphenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (97 mg, 0.30 mmol) with ethyl acrylate (64 μL, 0.60 mmol) afforded the desired oxindole **3l** (71 mg) in 69% yield as a colorless liquid; (column 1: hexane-EtOAc (90:10); column 2: DCM-hexane (40:60)); R_f = 0.44 (10% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, J = 7.6 Hz, 1H), 6.93 (d, J = 7.6 Hz, 1H), 6.69 (s, 1H), 6.36 (dt, J = 15.3, 7.6 Hz, 1H), 5.82 (d, J = 15.5 Hz, 1H), 4.08 (q, J = 7.0 Hz, 2H), 3.19 (s, 3H), 3.05 (dd, J = 13.8, 8.2 Hz, 1H), 2.96 (dd, J = 13.8, 7.1 Hz, 1H), 2.39 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H); **^{13}C{1H} NMR (126 MHz, $CDCl_3$)** δ 170.7 (bd, J = 1.7 Hz), 165.4, 144.1, 140.8, 139.2, 126.3, 124.7, 124.3 (q, J = 282.3 Hz), 123.9, 119.8, 109.8, 60.3, 55.6 (q, J = 26.6 Hz), 33.7 (bd, J = 1.7 Hz), 26.5, 21.8, 14.0; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -72.3 ppm; **HRMS (ESI-TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{17}H_{18}F_3NO_3Na$: 364.1131, found 364.1135.

Ethyl (*E*)-4-(6-chloro-1-methyl-2-oxo-3-(trifluoromethyl)indolin-3-yl)but-2-enoate (3m)

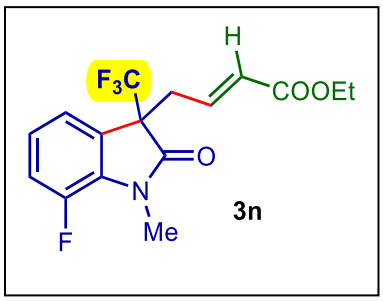


3m

Following GP-3, Heck coupling of *N*-(2-bromo-5-chlorophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (102 mg, 0.30 mmol) with ethyl acrylate (64 μL, 0.60 mmol) afforded the desired oxindole **3m** (73 mg) in 67% yield as a yellow liquid; (column 1: hexane-EtOAc (90:10); column 2: DCM-hexane (50:50)); R_f = 0.32 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, J = 8.0, 0.8 Hz, 1H), 7.12 (dd, J = 8.0, 1.9 Hz, 1H), 6.89 (d, J = 1.8 Hz, 1H), 6.34 (dt, J = 15.3, 7.6 Hz, 1H), 5.83 (dt, J = 15.4, 1.3 Hz, 1H), 4.10 (q, J = 7.1 Hz, 2H), 3.21 (s, J = 3.2 Hz, 3H), 3.08 (ddd, J = 13.9, 8.0, 1.3 Hz, 1H), 2.97 (ddd, J = 13.9, 7.2, 1.4 Hz, 1H), 1.22 (t, J = 7.1 Hz, 3H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 170.4 (q, J = 2.0 Hz), 165.3, 145.3, 138.4, 136.5, 126.8, 126.0, 124.0 (q, J = 282.5 Hz), 123.3, 121.2, 109.7, 60.5, 55.7 (q, J = 27.0 Hz), 33.6 (q, J = 2.1 Hz), 26.7, 14.1; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -72.0 ppm; **HRMS (ESI-TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{16}H_{15}F_3NO_3NaCl$: 384.0585, found 384.0585.

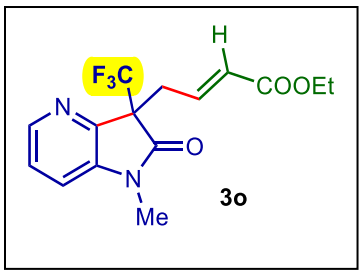
Ethyl (*E*)-4-(7-fluoro-1-methyl-2-oxo-3-(trifluoromethyl)indolin-3-yl)but-2-enoate (3n)



Following GP-3, Heck coupling of *N*-(2-bromo-6-fluorophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (65 mg, 0.20 mmol) with ethyl acrylate (43 μL, 0.40 mmol) afforded the desired oxindole **3n** (30 mg) in 44% yield as a yellow liquid; (column 1: hexane-EtOAc (90:10); column 2: DCM-hexane (40:60)); R_f = 0.42 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.05 (m, 3H), 6.35 (dt, *J* = 15.3, 7.6 Hz, 1H), 5.84 (d, *J* = 15.5 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.43 (d, *J* = 2.7 Hz, 3H), 3.10 (dd, *J* = 13.9, 8.2, 1H), 2.97 (dd, *J* = 13.8, 7.2, 1H), 1.22 (t, *J* = 7.1 Hz, 3H); **^{13}C{1H} NMR (126 MHz, $CDCl_3$)** δ 170.0 (bd, *J* = 1.2 Hz), 165.3, 147.7 (d, *J* = 245.1 Hz), 138.4, 131.0 (d, *J* = 9.1 Hz), 126.8, 125.5 (bs), 124.01 (q, *J* = 282.7 Hz), 123.97 (d, *J* = 6.5 Hz), 120.9 (bd, *J* = 3.0 Hz), 118.5 (d, *J* = 19.2 Hz), 60.5, 56.1 (q, *J* = 26.8 Hz), 33.8, 29.1 (d, *J* = 6.0 Hz), 14.1; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -135.0, -72.3 ppm; **HRMS (ESI-TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{16}H_{15}F_4NO_3Na$: 368.0880, found 368.0890.

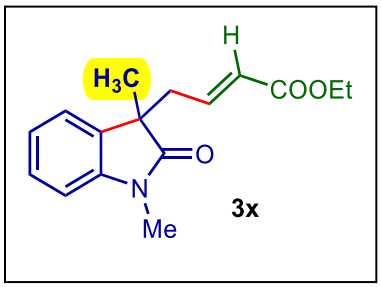
Ethyl (*E*)-4-(1-methyl-2-oxo-3-(trifluoromethyl)-2,3-dihydro-1H-pyrrolo[3,2-b]pyridin-3-yl)but-2-enoate (3o)



Following GP-3, Heck coupling of *N*-(2-bromopyridin-3-yl)-*N*-methyl-2-(trifluoromethyl)acrylamide (62 mg, 0.20 mmol) with ethyl acrylate (43 μL, 0.40 mmol) afforded the desired oxindole **3o** (26 mg) in 40% yield as a yellow liquid; (column 1: hexane-EtOAc (85:15); column 2: DCM-hexane (80:20)); R_f = 0.11 (20% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.31 (dd, *J* = 8.0, 5.1 Hz, 1H), 7.14 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.32 (dt, *J* = 15.4, 7.6 Hz, 1H), 5.84 (d, *J* = 15.5 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.25 (s, 3H), 3.28 – 3.20 (m, 1H), 3.16 (dd, *J* = 13.6, 7.9 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H); **^{13}C{1H} NMR (126 MHz, $CDCl_3$)** δ 169.0 (bd, *J* = 1.5 Hz), 165.4, 144.7, 144.1, 139.9, 138.3, 126.8, 124.7, 123.6 (q, *J* = 283.5 Hz), 115.1, 60.4, 56.0 (q, *J* = 26.6 Hz), 32.3 (bd, *J* = 1.6 Hz), 26.4, 14.1; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -71.4 ppm; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{15}H_{16}F_3N_2O_3$: 329.1108, found 329.1118.

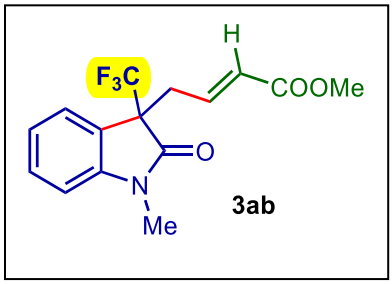
Ethyl (*E*)-4-(1,3-dimethyl-2-oxoindolin-3-yl)but-2-enoate (3x)[4]



Following GP-3, Heck coupling of *N*-(2-bromophenyl)-*N*-methylmethacrylamide (25 mg, 0.10 mmol) with ethyl acrylate (21 μL, 0.20 mmol) afforded the desired oxindole **3x** (23 mg) in 85% yield as a yellow liquid; R_f = 0.17 (10% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.28 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 6.62 (dt, *J* = 15.4, 7.7 Hz, 1H), 5.78 (d, *J* = 15.5 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.21 (s, 3H), 2.64 (d, *J* = 7.5 Hz, 2H), 1.40 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H).

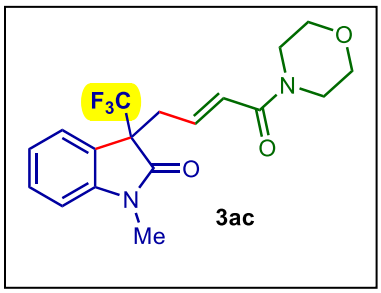
Methyl (*E*)-4-(1-methyl-2-oxo-3-(trifluoromethyl)indolin-3-yl)but-2-enoate (3ab)



Following GP-3, Heck coupling of *N*-(2-bromophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (62 mg, 0.20 mmol) with methyl acrylate (36 μL, 0.40 mmol) afforded the desired oxindole **3ab** (38 mg) in 62% yield as a yellow liquid; (column 1: hexane-EtOAc (90:10); column 2: DCM-hexane (60:40)); R_f = 0.14 (10% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.39 (t, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.37 (dt, *J* = 15.2, 7.5 Hz, 1H), 5.83 (d, *J* = 15.5 Hz, 1H), 3.62 (s, 3H), 3.21 (s, 3H), 3.08 (dd, *J* = 13.8, 8.1 Hz, 1H), 2.99 (dd, *J* = 13.8, 7.2 Hz, 1H); **^{13}C{1H} NMR (126 MHz, $CDCl_3$)** *δ* 170.4 (bd, *J* = 1.6 Hz), 165.8, 144.1, 139.3, 130.4, 126.0, 125.0, 124.3 (q, *J* = 282.5 Hz), 123.4, 122.9, 108.9, 55.8 (q, *J* = 26.8 Hz), 51.5, 33.7, 26.6; **^{19}F NMR (471 MHz, $CDCl_3$)** *δ* -72.2 ppm; **HRMS (ESI-TOF)** ***m/z***: $[M+Na]^+$ calcd. for $C_{15}H_{14}F_3NO_3Na$: 336.0818, found 336.0809.

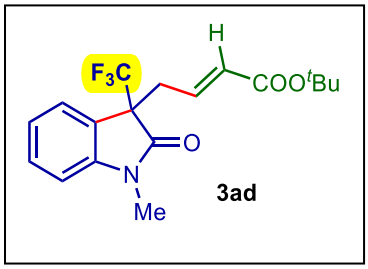
(*E*)-1-Methyl-3-(4-morpholino-4-oxobut-2-en-1-yl)-3-(trifluoromethyl)indolin-2-one (3ac)



Following GP-3, Heck coupling of *N*-(2-bromophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (62 mg, 0.20 mmol) with 1-morpholinoprop-2-en-1-one (56 mg, 0.40 mmol) afforded the desired oxindole **3ac** (40 mg) in 54% yield as a yellow liquid; (column 1: hexane-EtOAc (90:10); column 2: DCM-hexane (50:50)); R_f = 0.28 (10% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.13 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 6.26 – 6.10 (m, 2H), 3.66 – 3.49 (m, 6H), 3.31 (bs, 2H), 3.20 (s, 3H), 3.11 (dd, J = 13.5, 7.6 Hz, 1H), 2.98 (dd, J = 13.6, 6.0 Hz, 1H); **^{13}C{1H} NMR (126 MHz, $CDCl_3$)** δ 170.5, 164.6, 144.2, 136.0 (d, J = 4.5 Hz), 130.4, 125.9, 125.0, 124.3 (q, J = 282.4 Hz), 123.3 (d, J = 2.0 Hz), 123.0 (d, J = 3.2 Hz), 108.9 (d, J = 2.8 Hz), 66.6, 56.2 (q, J = 27.0 Hz), 46.1, 42.1, 34.1 (d, J = 1.7 Hz), 26.5 (d, J = 2.7 Hz); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -72.2 ppm; **HRMS (ESI-TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{18}H_{19}F_3N_2O_3Na$: 391.1240, found 391.1239.

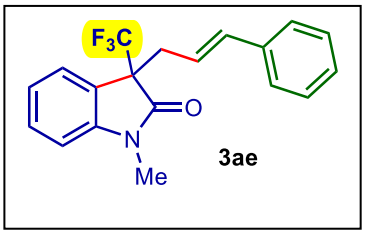
tert-Butyl (_E_)-4-(1-methyl-2-oxo-3-(trifluoromethyl)indolin-3-yl)but-2-enoate (3ad)



Following GP-3, Heck coupling of *N*-(2-bromophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (31 mg, 0.10 mmol) with *t*-butyl acrylate (29 μL, 0.20 mmol) afforded the desired oxindole **3ad** (34 mg) in 97% yield as a colorless liquid; (column 1: hexane-EtOAc (90:10); column 2: DCM-hexane (50:50)); R_f = 0.24 (10% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (t, J = 7.8 Hz, 1H), 7.36 (d, J = 7.4 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 6.23 (dt, J = 15.2, 7.5 Hz, 1H), 5.77 (d, J = 15.4 Hz, 1H), 3.22 (s, 3H), 3.05 (dd, J = 14.0, 8.3 Hz, 1H), 2.97 (dd, J = 14.0, 6.8 Hz, 1H), 1.39 (s, 9H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 170.5 (q, J = 2.7 Hz), 164.8, 144.1, 137.7, 130.4, 128.2, 125.0, 124.5 (q, J = 268.1 Hz), 123.4, 122.9 (d, J = 5.0 Hz), 108.8, 80.6, 55.9 (q, J = 26.8 Hz), 33.6 (q, J = 2.7 Hz), 28.0, 26.6; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -72.0 ppm; **HRMS (ESI-TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{18}H_{20}F_3NO_3Na$: 378.1287, found 378.1294.

3-Cinnamyl-1-methyl-3-(trifluoromethyl)indolin-2-one (3ae)

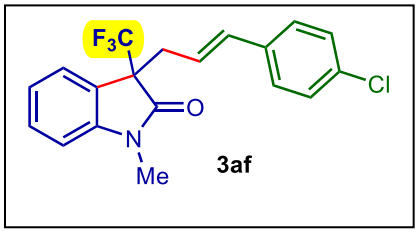


Following GP-3, Heck coupling of *N*-(2-bromophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (62 mg, 0.20 mmol) with styrene (46 μL, 0.40 mmol) afforded the desired oxindole **3ae** (43 mg) in 65% yield as a colorless liquid; (column 1: hexane-EtOAc (90:10); column 2: THF-$CHCl_3$-hexane (2:20:78)); R_f = 0.28 (5% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 7.3 Hz, 1H), 7.38 (td, J = 7.8, 0.9 Hz, 1H), 7.24 – 7.10 (m, 6H), 6.85 (d, J = 7.8 Hz, 1H), 6.39 (d, J = 15.7 Hz, 1H), 5.63 (dt, J = 15.3, 7.5 Hz, 1H), 3.19 (s, 3H), 3.10 (dd, J = 13.4, 8.6 Hz, 1H), 3.03 (dd, J = 12.4, 6.8 Hz, 1H); **^{13}C{1H} NMR (101 MHz,**

$CDCl_3$) δ 171.1, 144.2, 136.6, 135.5, 130.0, 128.4, 127.6, 126.2, 125.0 (q, J = 1.4 Hz), 124.5 (q, J = 281.7 Hz), 123.7 (q, J = 1.6 Hz), 123.1, 120.6, 108.6, 56.8 (q, J = 26.3 Hz), 34.9 (q, J = 2.6 Hz), 26.5; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -71.7 ppm; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{19}H_{17}F_3NO$: 332.1257, found 332.1277.

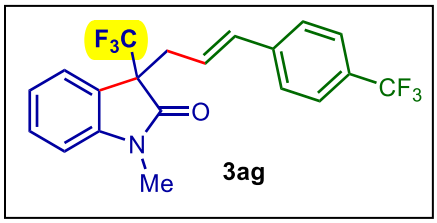
(*E*)-3-(3-(4-Chlorophenyl)allyl)-1-methyl-3-(trifluoromethyl)indolin-2-one (3af)



Following GP-3, Heck coupling of *N*-(2-bromophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (62 mg, 0.2 mmol) with 1-chloro-4-vinylbenzene (48 μL, 0.4 mmol) afforded the desired oxindole **3af** (42 mg) in 57% yield as a yellow liquid; (column 1: hexane-EtOAc (90:10); column 2: THF-$CHCl_3$-hexane (2:20:78)); R_f = 0.44 (10% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 –7.35 (m, 2H), 7.22 – 7.12 (m, 3H), 7.03 (bd, J = 7.4 Hz, 2H), 6.85 (d, J = 7.6 Hz, 1H), 6.33 (d, J = 15.6 Hz, 1H), 5.60 (dt, J = 14.8, 7.3 Hz, 1H), 3.18 (s, 3H), 3.08 (dd, J = 13.0, 8.5 Hz, 1H), 3.01 (dd, J = 13.2, 6.6 Hz, 1H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 171.0 (d, J = 2.6 Hz), 144.2, 135.0, 134.3, 133.3, 130.1, 128.6, 127.4, 125.0, 124.8 (q, J = 245.0 Hz), 123.2, 121.4, 108.6, 56.7 (q, J = 26.5 Hz), 34.8 (q, J = 2.9 Hz), 26.5 (one aromatic carbon peak merged with other peaks); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -71.7 ppm; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{19}H_{16}F_3NOCl$: 366.0867, found 366.0879.

(*E*)-1-Methyl-3-(trifluoromethyl)-3-(3-(4-(trifluoromethyl)phenyl)allyl)indolin-2-one (3ag)

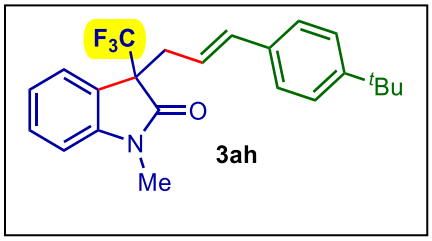


Following GP-3, Heck coupling of *N*-(2-bromophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (62 mg, 0.2 mmol) with 1-trifluoromethyl-4-vinylbenzene (59 μL, 0.4 mmol) in 1.5 mL reaction vial, afforded the desired oxindole **3ag** (51 mg) in 64% yield as a white solid; (column 1: hexane-EtOAc (90:10); column 2: THF-$CHCl_3$-hexane (1:10:89)); R_f = 0.40 (10% EtOAc in hexane); melting point = 60–62 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.3 Hz, 2H), 7.44 – 7.37 (m, 2H), 7.20 (d, J = 8.2 Hz, 2H), 7.16 (t, J = 7.6 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 6.42 (d, J = 15.8 Hz, 1H), 5.73 (dt, J = 15.4, 7.4 Hz, 1H), 3.19 (s, 3H), 3.12 (dd, J = 13.5, 8.3 Hz, 1H), 3.04 (dd, J = 13.9, 7.3 Hz, 1H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 170.9 (q, J = 2.8 Hz), 144.2, 139.9 (q, J = 1.6 Hz), 134.2, 130.2, 129.4

(q, J = 32.5 Hz), 126.3, 125.4 (q, J = 4.2 Hz), 125.0, 124.5 (q, J = 282.3 Hz), 124.1 (q, J = 263.3 Hz), 123.6, 123.5, 123.2, 108.6, 56.6 (q, J = 26.5 Hz), 34.8 (q, J = 2.5 Hz), 26.5; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -71.7, -62.6 ppm; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{20}H_{16}F_6NO$: 400.1131, found 400.1153.

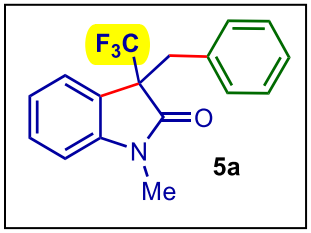
(*E*)-3-(3-(4-(tert-butyl)phenyl)allyl)-1-methyl-3-(trifluoromethyl)indolin-2-one (3ah)



Following GP-3, Heck coupling of *N*-(2-bromophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (62 mg, 0.2 mmol) with 1-(*tert*-butyl)-4-vinylbenzene (73 μL, 0.4 mmol) afforded the desired oxindole **3ah** (57 mg) in 73% yield as a colorless liquid; (column 1: hexane-EtOAc (90:10); column 2: THF-$CHCl_3$-hexane (2:20:78)); R_f = 0.38 (10% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 7.4 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.28 (d, J = 8.2 Hz, 2H), 7.17 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 8.3 Hz, 2H), 6.87 (d, J = 7.8 Hz, 1H), 6.40 (d, J = 15.7 Hz, 1H), 5.63 (dt, J = 15.4, 7.5 Hz, 1H), 3.22 (s, 3H), 3.12 (dd, J = 13.4, 8.3 Hz, 1H), 3.05 (dd, J = 13.4, 6.8 Hz, 1H), 1.30 (s, 9H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 171.7 (q, J = 1.9 Hz), 150.7, 144.2, 135.2, 133.9, 130.0, 126.0, 125.3, 125.0, 124.1 (q, J = 283.6 Hz), 123.8, 123.1, 119.8, 108.5, 56.8 (q, J = 26.1 Hz), 34.9 (q, J = 1.9 Hz), 34.5, 31.2, 26.5; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -71.7 ppm; **HRMS (ESI-TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{23}H_{24}F_3NONa$: 410.1702, found 410.1704.

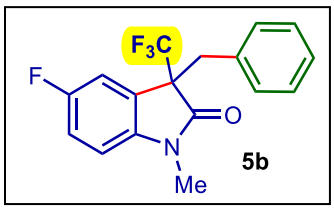
3-Benzyl-1-methyl-3-(trifluoromethyl)indolin-2-one (5a)[2]



Following GP-5, The reaction of *N*-(2-bromophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (31 mg, 0.1 mmol) with phenyl boronic acid (23.55 mg, 0.2 mmol) afforded the desired oxindole **5a** (24 mg) in 77% yield as a yellow liquid; R_f = 0.37 (10% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, J = 7.5 Hz, 1H), 7.28 (td, J = 7.8, 1.2 Hz, 1H), 7.12 (td, J = 7.6, 0.8 Hz, 1H), 7.08 – 6.99 (m, 3H), 6.86 – 6.81 (m, 2H), 6.59 (d, J = 7.8 Hz, 1H), 3.62 (d, J = 12.9 Hz, 1H), 3.32 (d, J = 12.9 Hz, 1H), 2.94 (s, 3H); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -71.6 ppm.

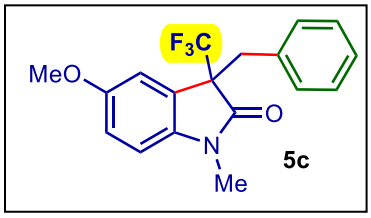
3-Benzyl-5-fluoro-1-methyl-3-(trifluoromethyl)indolin-2-one (5b)



Following GP-5, the reaction of *N*-(2-bromo-4-fluorophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (65 mg, 0.2 mmol) with phenyl boronic acid (50 mg, 0.4 mmol) afforded the desired oxindole **5b** (45 mg) in 70% yield as a white solid; R_f = 0.28 (5% EtOAc in hexane); melting point: 104 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, J = 7.8, 1.4 Hz, 1H), 7.09 – 7.01 (m, 3H), 6.98 (td, J = 8.8, 2.6 Hz, 1H), 6.88 – 6.82 (m, 2H), 6.51 (dd, J = 8.6, 4.1 Hz, 1H), 3.62 (d, J = 13.0 Hz, 1H), 3.28 (d, J = 13.0 Hz, 1H), 2.93 (s, 3H); **^{13}C{1H} NMR (126 MHz, $CDCl_3$)** δ 170.5, 159.0 (d, J = 241.8 Hz), 140.2 (d, J = 2.0 Hz), 132.4, 129.9, 127.8, 127.3, 125.0 (d, J = 8.6 Hz), 122.2 (q, J = 282.4 Hz), 116.3 (d, J = 23.5 Hz), 113.4 (d, J = 25.5 Hz), 108.9 (d, J = 8.1 Hz), 58.6 (q, J = 27.0 Hz, splitting is not clear), 37.3 (q, J = 1.9 Hz), 26.2; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -119.5, -71.5 ppm; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{17}H_{14}F_4NO$: 324.1006, found 324.1024.

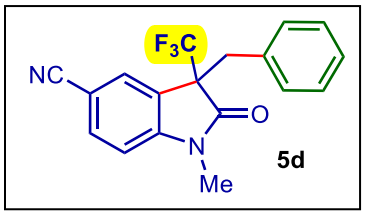
3-Benzyl-5-methoxy-1-methyl-3-(trifluoromethyl)indolin-2-one (5c)[2]



Following GP-5, the reaction of *N*-(2-bromo-4-methoxyphenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (34 mg, 0.1 mmol) with phenyl boronic acid (25 mg, 0.2 mmol) afforded the desired oxindole **5c** (23 mg) in 68% yield as a yellow solid; R_f = 0.17 (5% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 – 7.01 (m, 4H), 6.86 (d, J = 6.9 Hz, 2H), 6.80 (dd, J = 8.5, 2.5 Hz, 1H), 6.49 (d, J = 8.5 Hz, 1H), 3.82 (s, 3H), 3.59 (d, J = 13.0 Hz, 1H), 3.29 (d, J = 13.0 Hz, 1H), 2.91 (s, 3H); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -71.5 ppm.

3-Benzyl-1-methyl-2-oxo-3-(trifluoromethyl)indoline-5-carbonitrile (5d)

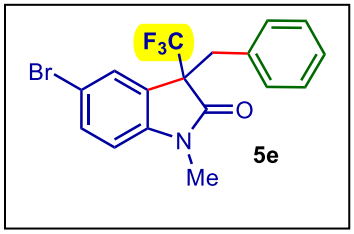


Following GP-5, the reaction of *N*-(2-bromo-4-cyanophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (67 mg, 0.2 mmol) with phenyl boronic acid (49 mg, 0.4 mmol) and AgOAc as additive afforded the desired oxindole **5d** (43 mg) in 65% yield as a white solid; R_f = 0.10 (10% EtOAc in hexane); melting point: 144–146 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.60 (dd, J = 8.2, 1.6 Hz, 1H), 7.12 – 7.02 (m, 3H), 6.84 – 6.76 (m, 2H), 6.66 (d, J = 8.2 Hz, 1H), 3.64 (d, J = 13.0 Hz, 1H), 3.31 (d, J = 13.0 Hz, 1H), 2.98 (s, 3H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 170.6 (q, J = 2.6 Hz), 147.8, 135.0, 131.8, 129.7,

128.6 (q, *J* = 1.4 Hz), 128.0, 127.6, 124.7, 124.0 (q, *J* = 282.4 Hz), 118.6, 108.8, 106.1, 58.0 (q, *J* = 26.5 Hz), 37.3 (q, *J* = 2.6 Hz), 26.4; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -71.2 ppm; **GCMS-EI** (***m/z,*** relative intensity): 330.0 (M^+, 20), 91.0 (100), 65.0 (18).

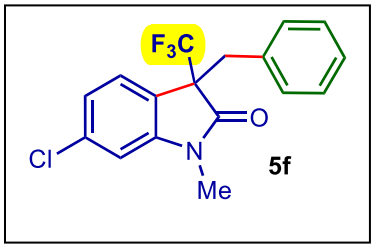
3-Benzyl-5-bromo-1-methyl-3-(trifluoromethyl)indolin-2-one (5e)[2]



Following GP-5, the reaction of *N*-(4-bromo-2-iodophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (43 mg, 0.1 mmol) with phenyl boronic acid (49 mg, 0.4 mmol) afforded the desired oxindole **5e** (25 mg) in 66% yield as a colorless liquid; R_f = 0.42 (5% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.40 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.12 – 7.02 (m, 3H), 6.84 (d, *J* = 7.0 Hz, 2H), 6.46 (d, *J* = 8.3 Hz, 1H), 3.61 (d, *J* = 13.0 Hz, 1H), 3.28 (d, *J* = 13.0 Hz, 1H), 2.91 (s, 3H); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -71.4 ppm.

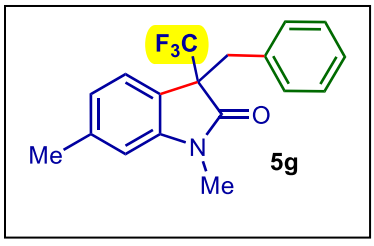
3-Benzyl-6-chloro-1-methyl-3-(trifluoromethyl)indolin-2-one (5f)[2]



Following GP-5, the reaction of *N*-(2-bromo-5-chlorophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (34 mg, 0.1 mmol) with phenyl boronic acid (25 mg, 0.2 mmol) afforded the desired oxindole **5f** (26 mg) in 78% yield as a yellow liquid; R_f = 0.19 (5% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 1H), 7.12 – 7.02 (m, 4H), 6.83 (d, *J* = 7.3 Hz, 2H), 6.60 (d, *J* = 1.6 Hz, 1H), 3.60 (d, *J* = 13.0 Hz, 1H), 3.29 (d, *J* = 13.0 Hz, 1H), 2.93 (s, 3H); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -71.5 ppm.

3-Benzyl-1,6-dimethyl-3-(trifluoromethyl)indolin-2-one (5g)

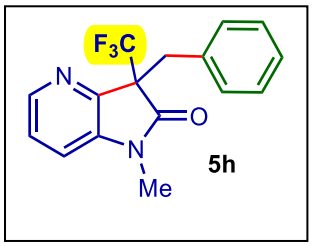


Following GP-5, the reaction of *N*-(2-bromo-5-methylphenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (64 mg, 0.2 mmol) with phenyl boronic acid (49 mg, 0.4 mmol) and AgOAc as additive afforded the desired oxindole **5g** (45 mg) in 70% yield as a yellow liquid; R_f = 0.35 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.6 Hz, 1H), 7.10 – 7.00 (m, 3H), 6.94 –6.91 (m, 1H), 6.87 – 6.82 (m, 2H), 6.42 (s, 1H), 3.58 (d, *J* = 12.9 Hz, 1H), 3.30 (d, *J* = 12.9 Hz, 1H), 2.92 (s,

3H), 2.33 (s, 3H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 171.1 (q, J = 2.7 Hz), 144.1, 140.2, 133.0, 130.0, 127.7, 127.0, 124.7 (q, J = 283.1 Hz, only 3 peaks are visible other may be merged), 124.9, 123.3, 120.5, 109.2, 58.0 (q, J = 26.1 Hz), 37.1 (q, J = 2.7 Hz), 26.1, 21.8; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -71.6 ppm; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{18}H_{17}F_3NO$: 320.1257, found 320.1266.

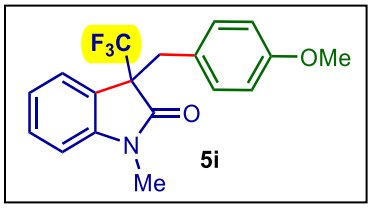
3-Benzyl-1-methyl-3-(trifluoromethyl)-1,3-dihydro-2H-pyrrolo[3,2-b]pyridin-2-one (5h)



Following GP-5, the reaction of *N*-(2-bromopyridin-3-yl)-*N*-methyl-2-(trifluoromethyl)acrylamide (62 mg, 0.2 mmol) with phenyl boronic acid (49 mg, 0.4 mmol) and AgOAc as additive afforded the desired oxindole **5h** (22 mg) in 36% yield as a yellow solid; R_f = 0.22 (15% EtOAc in hexane); melting point: 113–114 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (dd, J = 5.1, 1.2 Hz, 1H), 7.18 (dd, J = 8.0, 5.1 Hz, 1H), 7.06 – 6.96 (m, 3H), 6.85 – 6.78 (m, 3H), 3.64 (d, J = 12.7 Hz, 1H), 3.60 (d, J = 12.5 Hz, 1H), 2.93 (s, 3H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 169.4 (q, J = 2.4 Hz), 145.4, 143.5, 139.9, 132.6, 129.8, 127.8, 127.2, 124.2, 123.8 (q, J = 282.0 Hz), 114.6, 58.4 (q, J = 26.0 Hz), 36.1 (q, J = 2.6 Hz), 25.8; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -70.7 ppm; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{16}H_{14}F_3N_2O$: 307.1053, found 307.1058.

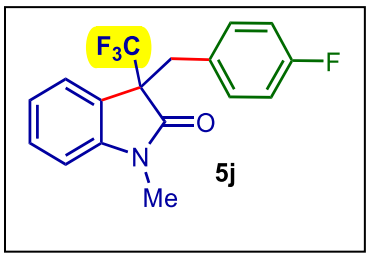
3-(4-Methoxybenzyl)-1-methyl-3-(trifluoromethyl)indolin-2-one (5i)[2]



Following GP-5, the reaction of *N*-(2-bromophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (31 mg, 0.1 mmol) with 4-methoxyphenyl boronic acid (30 mg, 0.2 mmol), with AgOAc as additive afforded the desired oxindole **5i** (21 mg) in 62% yield as a yellow liquid; R_f = 0.25 (5% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 7.4 Hz, 1H), 7.24 (d, J = 9.5 Hz, 1H), 7.08 (t, J = 7.4 Hz, 1H), 6.71 (d, J = 8.5 Hz, 2H), 6.57 (d, J = 7.8 Hz, 1H), 6.52 (d, J = 8.5 Hz, 2H), 3.64 (s, 3H), 3.52 (d, J = 13.1 Hz, 1H), 3.23 (d, J = 13.1 Hz, 1H), 2.92 (s, 3H); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -71.5 ppm.

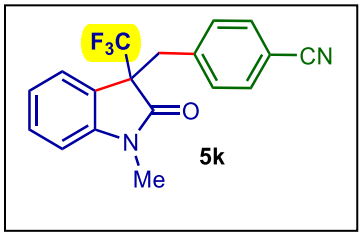
3-(4-Fluorobenzyl)-1-methyl-3-(trifluoromethyl)indolin-2-one (5j)



Following GP-5, the reaction of *N*-(2-bromophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (62 mg, 0.2 mmol) with 4-fluorophenyl boronic acid (56 mg, 0.4 mmol) afforded the desired oxindole **5j** (31 mg) in 48% yield as a white solid; $R_f = 0.38$ (10% EtOAc in hexane); melting point: 120 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, $J = 7.5$ Hz, 1H), 7.29 (td, $J = 7.8$, 1.2 Hz, 1H), 7.13 (td, $J = 7.6$, 1.0 Hz, 1H), 6.82 – 6.76 (m, 2H), 6.74 – 6.67 (m, 2H), 6.62 (d, $J = 7.8$ Hz, 1H), 3.59 (d, $J = 13.1$ Hz, 1H), 3.28 (d, $J = 13.0$ Hz, 1H), 2.96 (s, 3H); **^{13}C{1H} NMR (126 MHz, $CDCl_3$)** δ 170.7 (bd, $J = 1.8$ Hz), 162.0 (d, $J = 245.8$ Hz), 144.1, 131.5 (d, $J = 8.0$ Hz), 130.0, 128.6 (d, $J = 3.3$ Hz), 125.1, 124.6 (q, $J = 282.2$ Hz), 123.4, 122.9, 114.6 (d, $J = 21.3$ Hz), 108.4, 58.1 (q, $J = 26.0$ Hz), 36.4 (q, $J = 1.9$ Hz), 26.1; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -115.3, -71.6 ppm; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{17}H_{14}F_4NO$: 324.1006, found 324.1042.

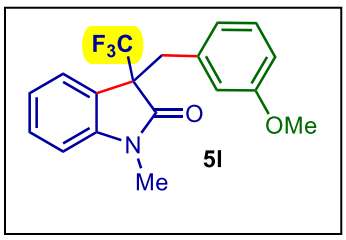
4-((1-Methyl-2-oxo-3-(trifluoromethyl)indolin-3-yl)methyl)benzonitrile (5k)



Following GP-5, the reaction of *N*-(2-bromophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (62 mg, 0.2 mmol) with 4-cyanophenyl boronic acid (59 μL, 0.4 mmol), with AgOAc as additive afforded the desired oxindole **5k** (14 mg) in 21% yield as a mixture with **3a"** (9.8 mg) in 1:1 ratio; $R_f = 0.12$ (10% EtOAc in hexane). The yield is given based on the ^{1}H NMR of the mixture. After multiple attempts, we were unable to isolate the product in its pure form due to elution with a six-membered cyclic product (**3a"**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, $J = 7.5$ Hz, 1H), 7.32 – 7.28 (m, 3H), 7.15 (td, $J = 7.6$, 0.7 Hz, 1H), 6.98 – 6.92 (m, 2H), 6.64 (d, $J = 7.9$ Hz, 1H), 3.66 (d, $J = 12.8$ Hz, 1H), 3.36 (d, $J = 12.8$ Hz, 1H), 2.96 (s, 3H); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -71.7, -66.1 (possibly six membered cyclic product) ppm.

3-(3-Methoxybenzyl)-1-methyl-3-(trifluoromethyl)indolin-2-one (5l)



Following GP-5, the reaction of *N*-(2-bromophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (62 mg, 0.2 mmol) with 3 methoxyphenyl boronic acid (61 mg, 0.4 mmol) afforded the desired oxindole **5l** (38 mg) in 56% yield as a yellow liquid; $R_f = 0.21$ (10% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, J = 7.9 Hz, 1H), 7.29 (td, J = 7.9, 1.7 Hz, 1H), 7.13 (t, J = 7.8 Hz, 1H), 6.94 (t, J = 8.0 Hz, 1H), 6.61 (dd, J = 8.8, 3.6 Hz, 2H), 6.47 (d, J = 7.9 Hz, 1H), 6.32 (t, J = 2.6 Hz, 1H), 3.59 (d, J = 12.9 Hz, 1H), 3.56 (s, 3H), 3.29 (d, J = 13.0 Hz, 1H), 2.96 (s, 3H); **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 170.8 (q, J = 2.6 Hz), 158.9, 144.2, 134.3, 129.9, 128.7, 125.2, 124.7 (q, J = 286.8 Hz), 123.6 (bs), 122.7, 122.4, 114.6, 113.5, 108.4, 58.1 (q, J = 26.2 Hz), 55.0, 37.3 (q, J = 2.8 Hz), 26.2; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -71.5 ppm; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{18}H_{17}F_3NO_2$: 336.1206, found 336.1220.

6. Ligand Screening for 1q, 1r, 1t:

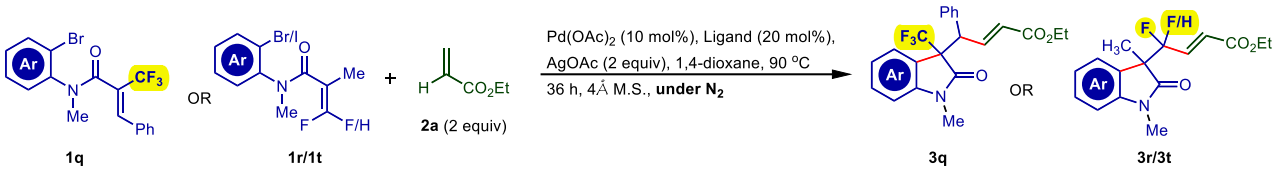


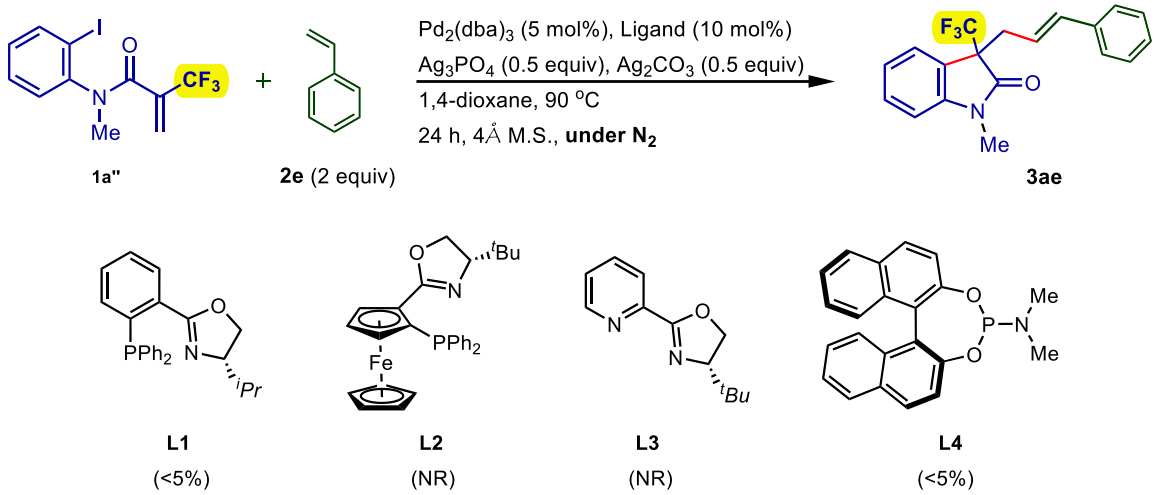
Table 2: Screening of unsuccessful substrates in presence of ligands.

S. No.	Starting material	Ligand	Observation
1	**1q**	Xphos	No product
2	**1q**	Sphos	No product
3	**1r**	Xphos	No product
4	**1r**	Brettphos	No product
5	**1r**	Sphos	No product
6	**1t**	Xphos	No product
7	**1t**	Sphos	<10% **3t** along with **3t'** as major product

Reaction condition: **1** (0.025 mmol), **2a** (0.05 mmol), Pd-catalyst (10 mol%), ligand (20 mol%) AgOAc (2.0 equiv), 1,4-dioxane (0.5 mL), 90 °C, 36 h, under N_2, analyzed by ^{19}FNMR and GC-MS.

7. Optimization of Chiral Ligands for Enantioselective Reaction:

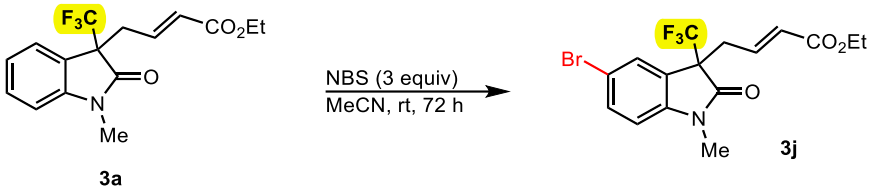
In a 7 mL reaction vial equipped with a magnetic bead, $Pd_2(dba)_3$ (5 mol%), ligand (10 mol%) and 4Å molecular sieves were added and the vial was introduced in glove box followed by addition of 1,4-dioxane. After 30 minutes of stirring inside glove box, *N*-(2-iodophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (**1a**'') (0.025 mmol), Ag_3PO_4 (0.5 equiv), Ag_2CO_3 (0.5 equiv) and styrene (**2e**) (2.0 equiv) were added and closed the vial. The vial was taken outside and stirred at 90 °C for 24 h. After completion of the reaction time, product formation was monitored by ^{19}FNMR and TLC. Due to low conversion, the reaction was not subjected to HPLC for determination of *ee*.



Scheme S5: Enantioselective double Heck cyclization of **1a**" with **2e**.

8. Synthetic Applications:

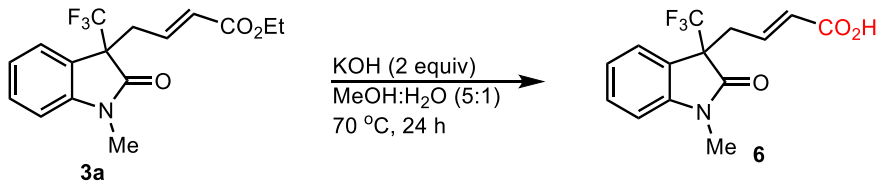
8.1 Bromination of 3a using NBS:[5]



Scheme S6: Bromination of **3a** using NBS.

Compound **3a** (65 mg, 0.2 mmol) and *N*-bromosuccinimide (107 mg, 0.6 mmol) were taken in a 7 ml reaction vial equipped with a magnetic stir bar. Then the reaction vial was taken inside glove box and dry MeCN (2.0 mL) was added to the reaction mixture, vial was sealed and taken outside followed by stirring at room temperature for 72 h. After that, the reaction mixture was purified on silica gel column chromatography (Hexane:Ethyl acetate = 9:1, R_f = 0.19) to afford the desired brominated product **3j** (76 mg, 93%) as yellow liquid.

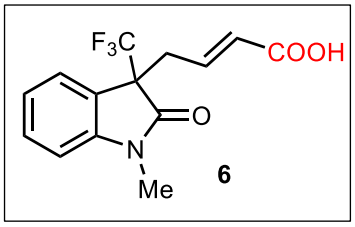
8.2 Hydrolysis of 3a using KOH:[6]



Scheme S7: Hydrolysis of **3a** in alkaline medium.

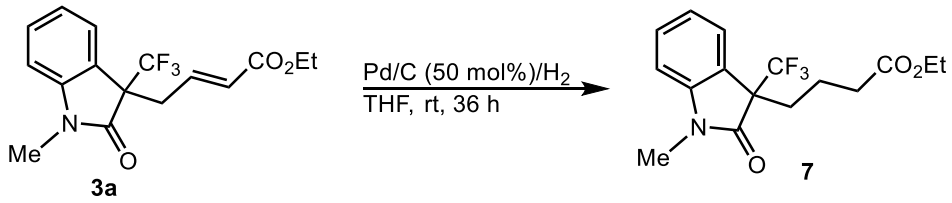
Compound **3a** (28 mg, 0.086 mmol) and KOH (10 mg, 0.17 mmol) were taken in a 7 mL reaction vial equipped with a magnetic stir bar. Then, MeOH (1 mL) and H_2O (0.2 mL) were added sequentially, the vial was sealed and kept for stirring at 70 ^oC for 24 h. After cooling to room temperature, the reaction mixture was acidified with 1 mL of 3N HCl and concentrated, followed by water addition and extraction with EtOAc. The final organic solution was purified on column chromatography (DCM:MeOH = 95:5, R_f = 0.22) to afford the desired acid **6** (21 mg, 81%) as yellow solid with melting point: 92 ^oC.

(*E*)-4-(1-Methyl-2-oxo-3-(trifluoromethyl)indolin-3-yl)but-2-enoic acid (6):



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (td, J = 7.7, 0.7 Hz, 1H), 7.36 (d, J = 7.4 Hz, 1H), 7.14 (t, J = 7.4 Hz, 1H), 6.89 (d, J = 7.9 Hz, 1H), 6.45 (dt, J = 15.4, 7.6 Hz, 1H), 5.81 (d, J = 15.5 Hz, 1H), 3.23 (s, 3H), 3.11 (dd, J = 14.1, 8.2 Hz, 1H), 3.01 (dd, J = 13.7, 7.0 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 170.4 (q, J = 2.4 Hz), 169.9, 144.1, 141.8, 130.5, 130.3, 125.7, 125.0 (bd, J = 1.2 Hz), 124.3 (q, J = 282.0 Hz), 123.5, 108.9, 55.7 (q, J = 26.8 Hz), 33.8 (q, J = 2.5 Hz), 26.6; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** δ -72.1 ppm; **HRMS (ESI-TOF) *m/z***: $[M+H]^+$ calcd. for $C_{14}H_{13}F_3NO_3$: 300.0842, found 300.0844.

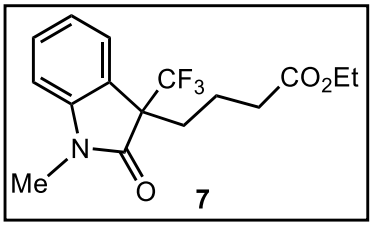
8.3 Reduction of 3a using Pd/C:



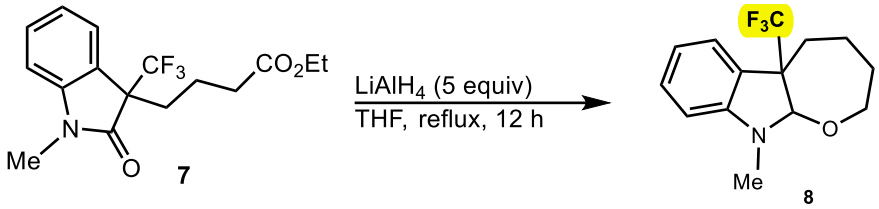
Scheme S8: Reduction of **3a** using palladium activated on charcoal.

The substituted oxindole (**3a**) (65 mg, 0.2 mmol) was taken in a Schlenk flask, equipped with magnetic stir bar. Then, palladium on activated charcoal (11 mg, 0.1 mmol) was introduced in the flask, followed by addition of 6 mL dry THF. The reaction mixture was stirred for 36 h at room temperature under H_2 gas pressure using a rubber balloon. Then, the crude reaction mixture was purified by celite filteration to give the desired product **7** in quantitative yield and directly utilized for next step.

Ethyl 4-(1-methyl-2-oxo-3-(trifluoromethyl)indolin-3-yl)butanoate (7): The product **7** was obtained in 36 h with quantitative yield as colorless liquid (Hexane:Ethyl acetate = 90:10, R_f = 0.23).



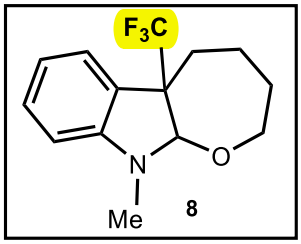
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 4.07 (q, *J* = 7.0 Hz, 2H), 3.25 (s, 3H), 2.35 – 2.09 (m, 4H), 1.35 – 1.28 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.18 – 1.12 (m, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 172.6, 171.3 (bd, *J* = 1.8 Hz), 144.4, 130.0, 124.8, 124.7 (q, *J* = 282.3 Hz), 123.8, 123.3, 108.6, 60.4, 56.6 (q, *J* = 26.5 Hz), 33.6, 30.2, 26.5, 18.8, 14.1; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** δ -72.5 ppm**; HRMS (ESI-TOF) *m/z***: [M+H$^+$] calcd. for $C_{16}H_{19}F_3NO_3$: 330.1312, found 330.1326.



Scheme S9: Reduction of **7** using $LiAlH_4$.

The reaction of crude **7** with $LiAlH_4$ (38 mg, 5 equiv) in dry THF (4 mL) at 66 °C for 12 hours afforded **8** (36 mg, 66%) as the colorless liquid; R_f = 0.67 (Hexane).

10-Methyl-5a-(trifluoromethyl)-3,4,5,5a,10,10a-hexahydro-2H-oxepino[2,3-b]indole (8):



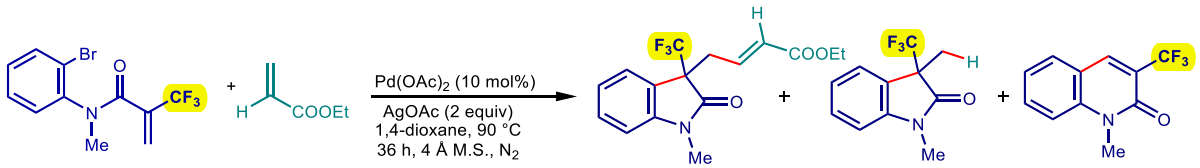
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 5.23 (s, 1H), 3.61 – 3.51 (m, 1H), 3.34 (t, *J* = 11.7 Hz, 1H), 2.92 (s, 3H), 2.28 – 2.17 (m, 2H), 1.80 – 1.56 (m, 3H), 1.52 – 1.43 (m, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 150.9, 130.0, 127.3 (q, *J* = 282.8 Hz), 125.2, 123.3, 117.1, 104.6, 95.6 (bd, *J* = 2.0 Hz), 63.7, 59.7 (q, *J* = 23.4 Hz), 31.1, 30.2, 28.3, 23.2; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** δ -76.2**; GCMS-EI** (***m/z,*** relative intensity): 271 (M$^+$, 83), 241 (58), 212 (62), 200 (56), 172 (55), 144 (53), 131 (33), 42 (100), 40 (41).

9. Mechanistic Investigation:

To gain insight into the mechanism, a few control experiments were performed (Table 3). In a 7 mL vial equipped with a magnetic bead, CF_3-acrylamide substrate (**1a**) (0.05 mmol), $Pd(OAc)_2$ (10 mol%), AgOAc (0.1 mmol) and 4 Å molecular sieves (2 no.) were added. Then the reaction vial was introduced inside glove box, followed by addition of ethylacrylate (**2a**) (0.1 mmol) and dry dioxane (0.5 mL) and closed the vial. The vial was taken outside and stirred in a pre-heated oil bath at 90 °C for 36 h. After that, the reaction mixture was cooled to room temperature and dried on high vacuum. The reaction mixture was analyzed by crude ^{19}F NMR.

9.1. Control Experiments:

Table 3. Control experiments[a]



S. No.	1a	2a	$Pd(OAc)_2$	AgOAc	1a(%)	3a (%)	3a' (%)	3a''
1	✓	✓	✓	×	88	8	<2	<2
2	✓	×	✓	✓	85	-	~5	<2
3	✓	×	✓	×	>95	-	<2	-

[a]Reaction condition: **1a** (0.025 mmol), **2a** (0.05 mmol), Pd-catalyst (10 mol%), AgOAc (2.0 equiv), 1,4-dioxane (0.5 mL), 90 °C, 36 h, conversion based on crude ^{19}F-NMR relative to **1a**.

10. X-Ray Structural Analysis:

To obtain crystals, a saturated solution of the compound was kept in ethyl acetate at room temperature. Colorless crystals were observed after 2-3 days. A suitable crystal was selected and visualised on a Bruker APEX-II CCD diffractometer. The crystal was kept at 301.00 K during data collection. Using olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the olex2.refine refinement package using Gauss-Newton minimisation. The crystal structure was drawn on diamond-3 software.

Crystal Structure of compound 3e:

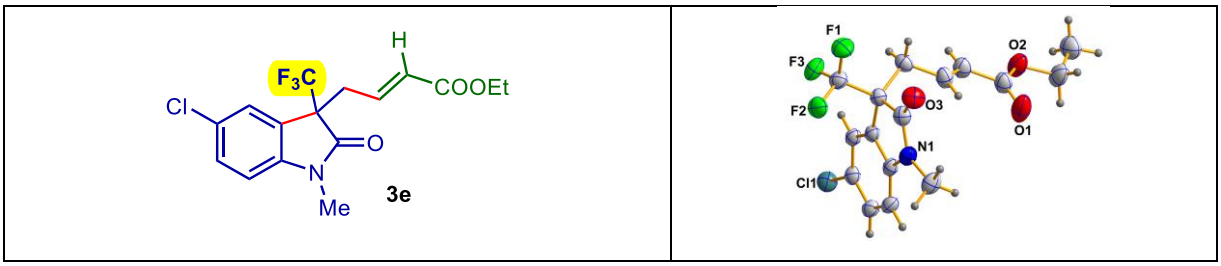


Figure S2: Crystal Structure of compound **3e**.

Table 4: Crystal data and structure refinement for 3e:

Empirical formula	**$C_{16}H_{15}ClF_3NO_3$**
CCDC	**2305839**
Formula weight	361.750
Temperature/K	298.00
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	17.315(3)
b/Å	7.8480(15)
c/Å	12.8208(19)
α/°	90
β/°	103.384(5)
γ/°	90
Volume/Å^3	1694.9(5)
Z	4
ρ_{calc}(g/cm^3)	1.418
μ/mm^{-1}	0.270
F(000)	744.0
Crystal size/mm^3	0.39 × 0.27 × 0.18
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.84 to 52.76
Index ranges	-21 ≤ h ≤ 21, -9 ≤ k ≤ 9, -16 ≤ l ≤ 15
Reflections collected	31293
Independent reflections	3469 [R_{int} = 0.0399, R_{sigma} = 0.0226]
Data/restraints/parameters	3469/0/219
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0398, wR_2 = 0.1100
Final R indexes [all data]	R_1 = 0.0514, wR_2 = 0.1226
Largest diff. peak/hole/ e Å^{-3}	0.38/-0.26

Crystal Structure of compound 3i:

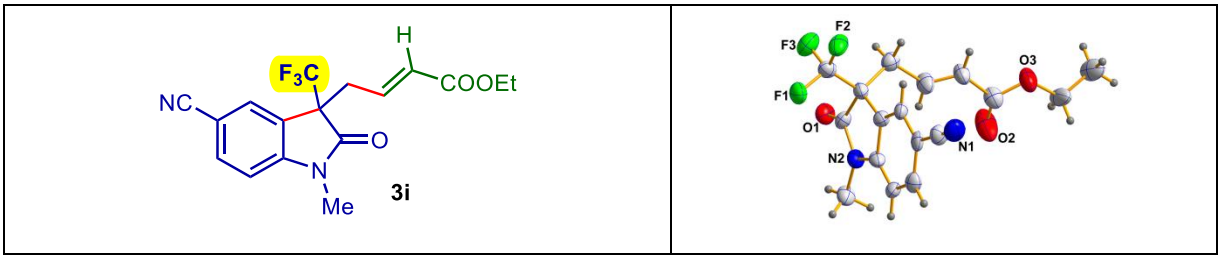


Figure S3: Crystal Structure of compound **3i**.

Table 5: Crystal data and structure refinement for 3i:

Empirical formula	**$C_{17}H_{15}F_3N_2O_3$**
CCDC	**2305840**
Formula weight	352.315
Temperature/K	302.00
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	17.1833(6)
b/Å	7.8190(3)
c/Å	12.9026(4)
α/°	90
β/°	100.059(1)
γ/°	90
Volume/Å^3	1706.9(1)
Z	4
ρ_{calc}(g/cm^3)	1.371
μ/mm^{-1}	0.116
F(000)	728.0
Crystal size/mm^3	0.44 × 0.36 × 0.28
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.82 to 52.78
Index ranges	-21 ≤ h ≤ 21, -9 ≤ k ≤ 9, -16 ≤ l ≤ 16
Reflections collected	55495
Independent reflections	3500 [R_{int} = 0.0629, R_{sigma} = 0.0250]
Data/restraints/parameters	3500/0/228
Goodness-of-fit on F^2	1.130
Final R indexes [I>=2σ (I)]	R_1 = 0.0511, wR_2 = 0.1290
Final R indexes [all data]	R_1 = 0.0893, wR_2 = 0.1679
Largest diff. peak/hole/ e Å^{-3}	0.36/-0.29

Crystal Structure of compound 3ag:

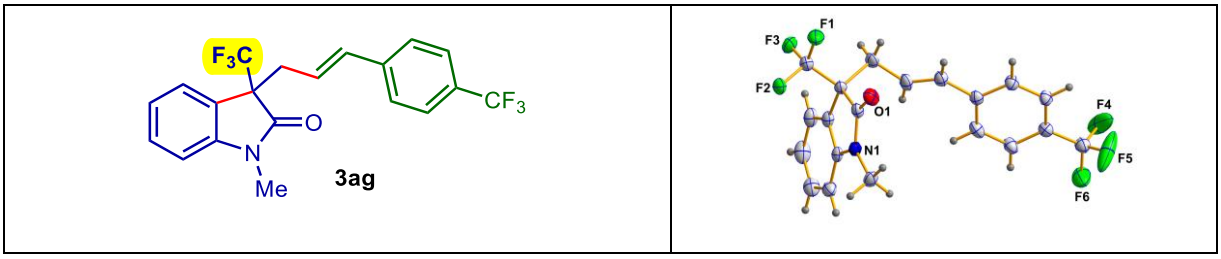


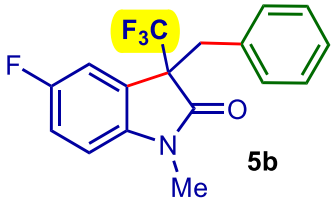
Figure S4: Crystal Structure of compound **3ag**.

Table 6: Crystal data and structure refinement for 3ag:

Empirical formula	**$C_{20}H_{15}F_6NO$**
CCDC	**2305841**
Formula weight	399.338
Temperature/K	298.00
Crystal system	Triclinic
Space group	P-1
a/Å	7.2546(3)
b/Å	7.7811(3)
c/Å	17.2128(7)
α/°	99.301(1)
β/°	94.304(1)
γ/°	105.274(2)
Volume/$Å^3$	917.91(7)
Z	2
$\rho_{calc}(g/cm^3)$	1.445
μ/mm^{-1}	0.131
F(000)	408.4
Crystal size/mm^3	0.44 × 0.32 × 0.18
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.84 to 52.78
Index ranges	-9 ≤ h ≤ 9, -9 ≤ k ≤ 9, -21 ≤ l ≤ 21
Reflections collected	29651
Independent reflections	3745 [R_{int} = 0.0361, R_{sigma} = 0.0207]
Data/restraints/parameters	3745/0/254
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0836, wR_2 = 0.2710
Final R indexes [all data]	R_1 = 0.0942, wR_2 = 0.2859

Largest diff. peak/hole/ e Å^{-3}	0.87/-0.62

Crystal Structure of compound 5b:



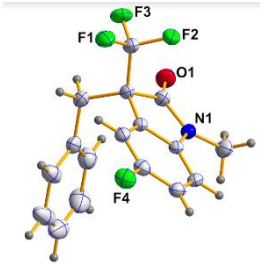


Figure S5: Crystal Structure of compound **5b**.

Table 7: Crystal data and structure refinement for 5b:

Empirical formula	**$C_{17}H_{13}F_4NO$**
CCDC	**2305843**
Formula weight	323.28
Temperature/K	298.00
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	15.167(1)
b/Å	7.6889(5)
c/Å	13.1968(8)
α/°	90
β/°	99.510(3)
γ/°	90
Volume/Å^3	1517.83(17)
Z	4
ρ_{calc}(g/cm^3)	1.415
μ/mm^{-1}	0.122
F(000)	664.6
Crystal size/mm^3	0.38 × 0.24 × 0.18
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.44 to 52.92
Index ranges	-19 ≤ h ≤ 19, -9 ≤ k ≤ 9, -16 ≤ l ≤ 16
Reflections collected	43483
Independent reflections	3127 [R_{int} = 0.0489, R_{sigma} = 0.0309]
Data/restraints/parameters	3127/0/209

Goodness-of-fit on F^2	1.092
Final R indexes [I>=2σ (I)]	R_1 = 0.0441, wR_2 = 0.1197
Final R indexes [all data]	R_1 = 0.0665, wR_2 = 0.1409
Largest diff. peak/hole/ e $Å^{-3}$	0.14/-0.21

Crystal Structure of compound 5j:

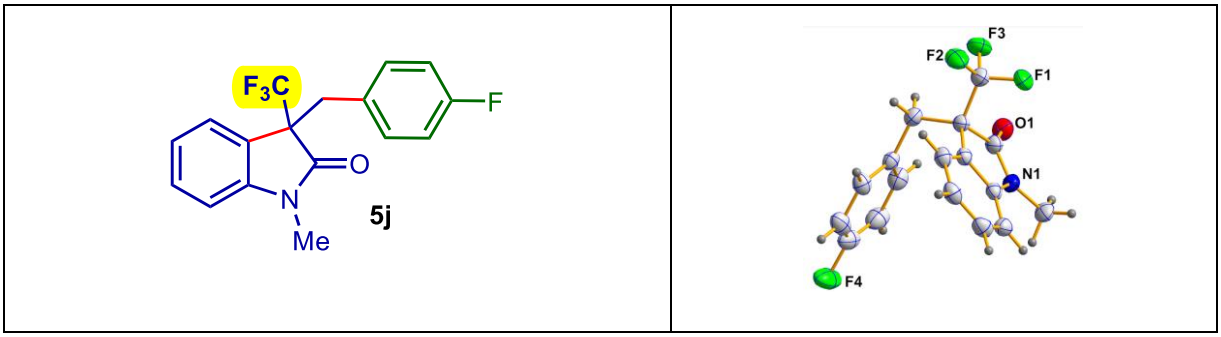


Figure S6: Crystal Structure of compound **5j**.

Table 8: Crystal data and structure refinement for 5j:

Empirical formula	**$C_{17}H_{13}F_4NO$**
CCDC	**2305844**
Formula weight	323.292
Temperature/K	297.00
Crystal system	Orthorhombic
Space group	$Pna2_1$
a/Å	12.9186(8)
b/Å	7.4826(6)
c/Å	15.3993(11)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	1488.57(18)
Z	4
ρ_{calc}(g/cm^3)	1.443
μ/mm^{-1}	0.124
F(000)	664.6
Crystal size/mm^3	0.32 × 0.23 × 0.15
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.3 to 52.68

Index ranges	-14 ≤ h ≤ 16, -9 ≤ k ≤ 9, -19 ≤ l ≤ 19
Reflections collected	15643
Independent reflections	3033 [R_{int} = 0.0346, R_{sigma} = 0.0269]
Data/restraints/parameters	3033/1/209
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0340, wR_2 = 0.0826
Final R indexes [all data]	R_1 = 0.0408, wR_2 = 0.0878
Largest diff. peak/hole/ e $Å^{-3}$	0.12/-0.15

11. References:

1. X. Bai, C. Wu, S. Ge and Y. Lu, Pd/Cu-Catalyzed Enantioselective Sequential Heck/Sonogashira Coupling: Asymmetric Synthesis of Oxindoles Containing Trifluoromethylated Quaternary Stereogenic Centers, *Angew. Chem. Int. Ed.,* 2020, **59**, 2764–2768.

2. R. Shaw, N. Sihag, S. Jain, R. Sharma and M. R. Yadav, Photoinduced Alkyl/Aryl Radical Cascade for the Synthesis of Quaternary CF_3-Containing Oxindoles and Indoline Alkaloids, *J. Org. Chem.,* 2023, **88**, 5652–5660.

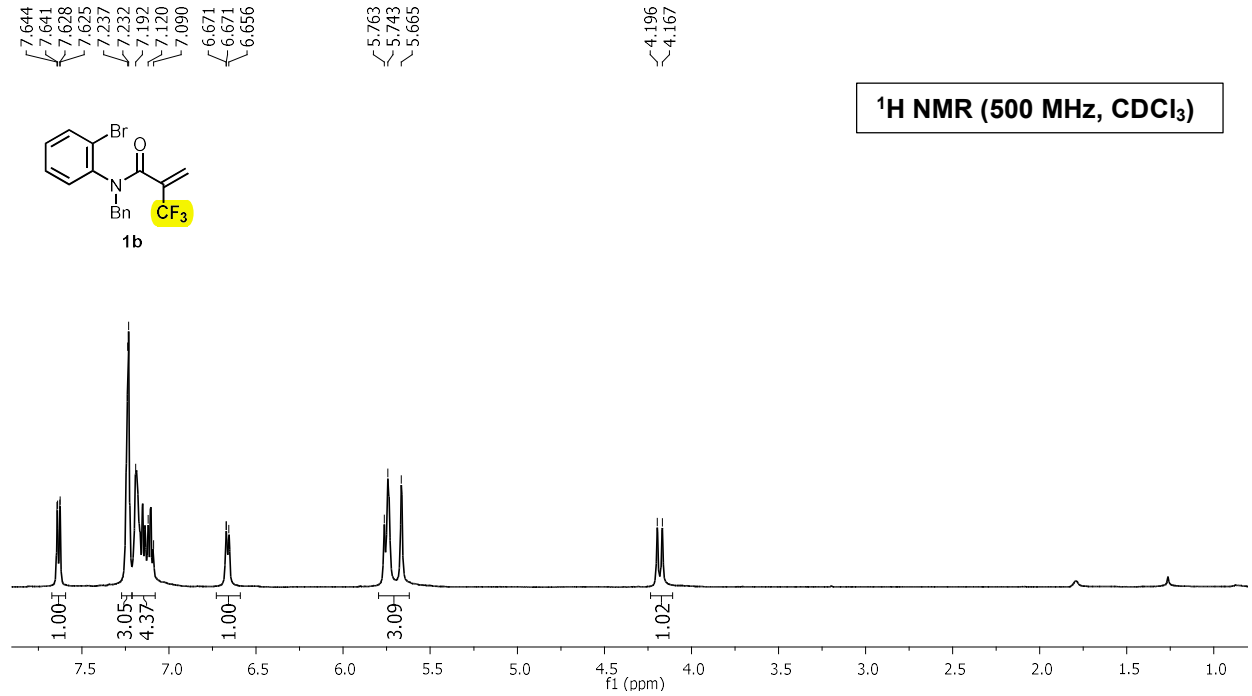
3. Y. Li, G. Sun, X. He, H. Lv and B. Gao, Palladium-catalyzed intramolecular annulation of difluoroalkenes to difluoro-and trifluoromethylated indane analogs, *J. Fluor. Chem.*, 2023, **268**, 110115.

4. X. Wu, Z. Tang, C. Zhang, C. Wang, L. Wu, J. Qu and Y. Chen, Pd-Catalyzed Regiodivergent Synthesis of Diverse Oxindoles Enabled by the Versatile Heck Reaction of Carbamoyl Chlorides, *Org. Lett.*, 2020, **22**, 3915–3921.

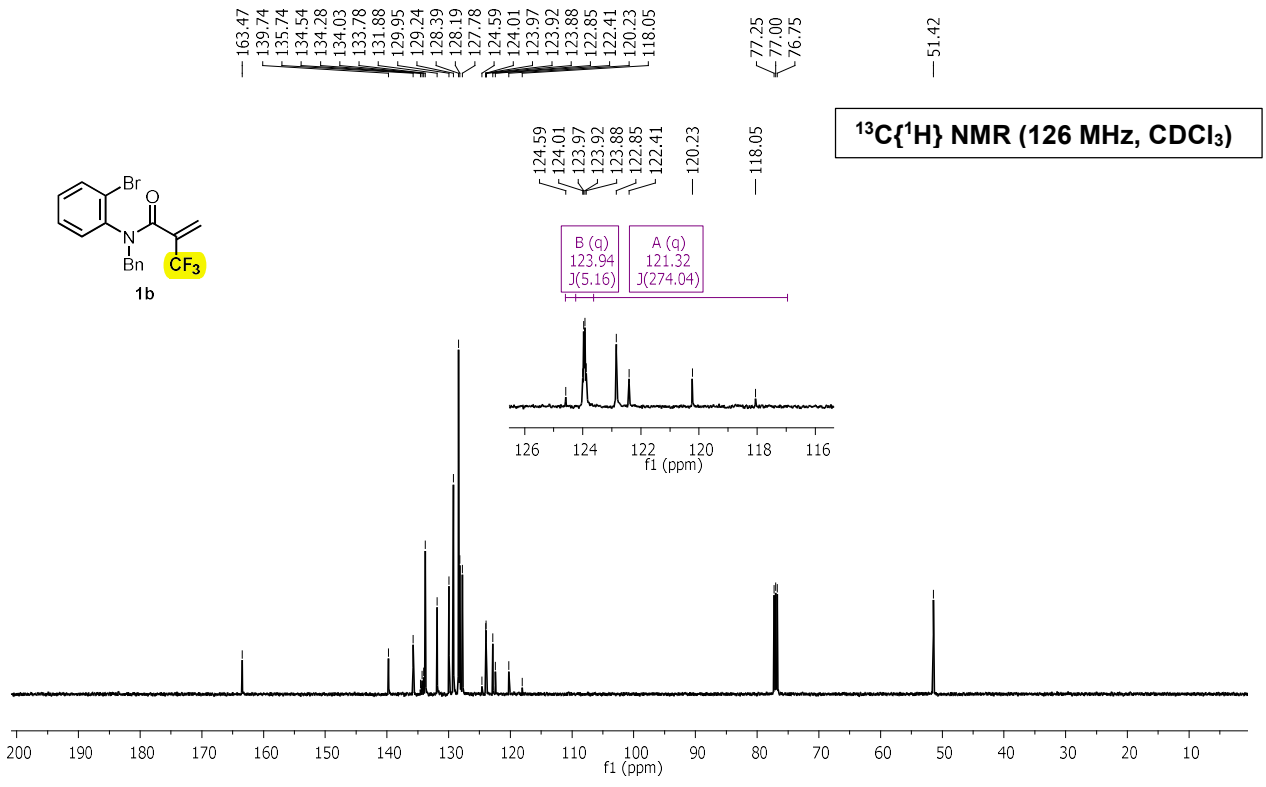
5. H. Lv, X. Xu, J. Li, X. Huang, G. Fang and L. Zheng, Mechanochemical Divergent Syntheses of Oxindoles and α-Arylacylamides via Controllable Construction of C−C and C−N Bonds by Copper and Piezoelectric Materials, *Angew. Chem. Int. Ed*., 2022, **61**, e202206420.

6. Q. Bouazzaoui, K. Rousée, J. K. Mulengi, X. Pannecoucke, J. P. Bouillon and S. C. Bonnaire, Synthesis of α-Fluorinated Acrylates by a Palladium-Catalyzed Decarboxylative Olefination Reaction, *Eur. J. Org. Chem*., 2018, 3705–3715.

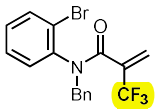
^{1}H, ^{13}C, ^{19}F NMR spectra of starting materials and products:



^{1}H NMR (500 MHz, $CDCl_3$)

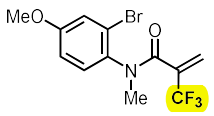


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



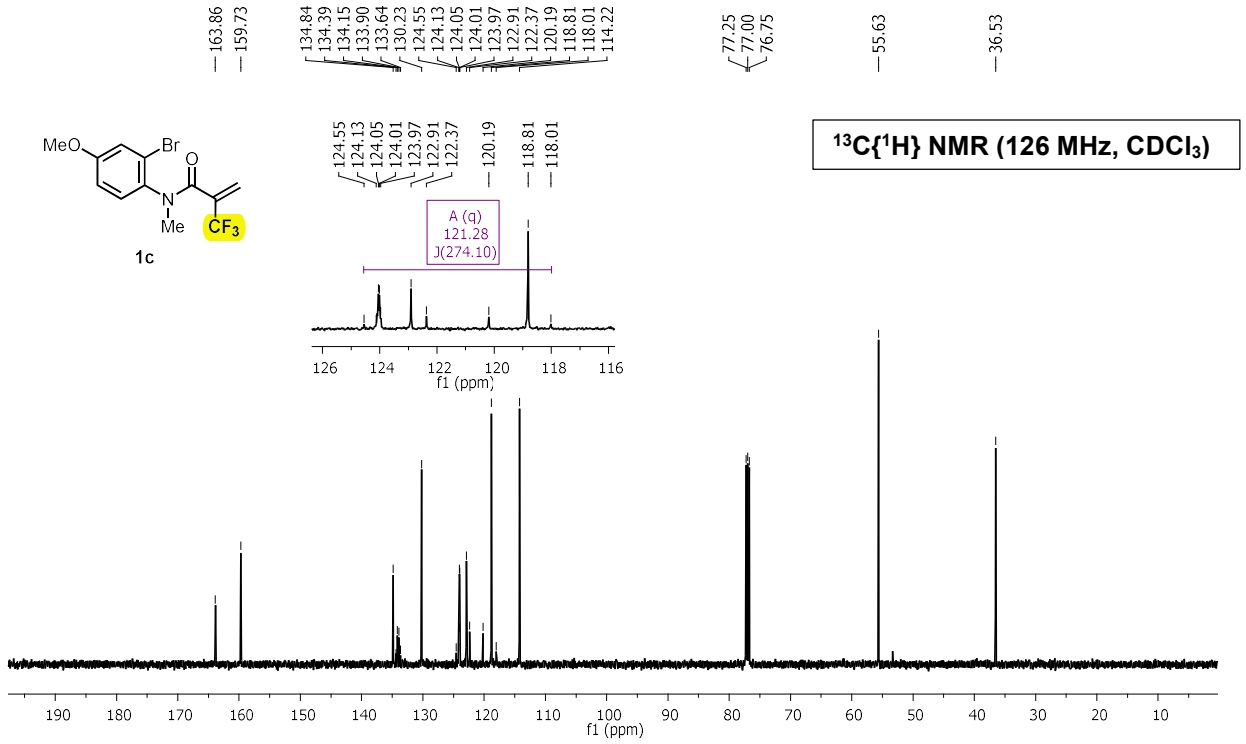
1b

$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

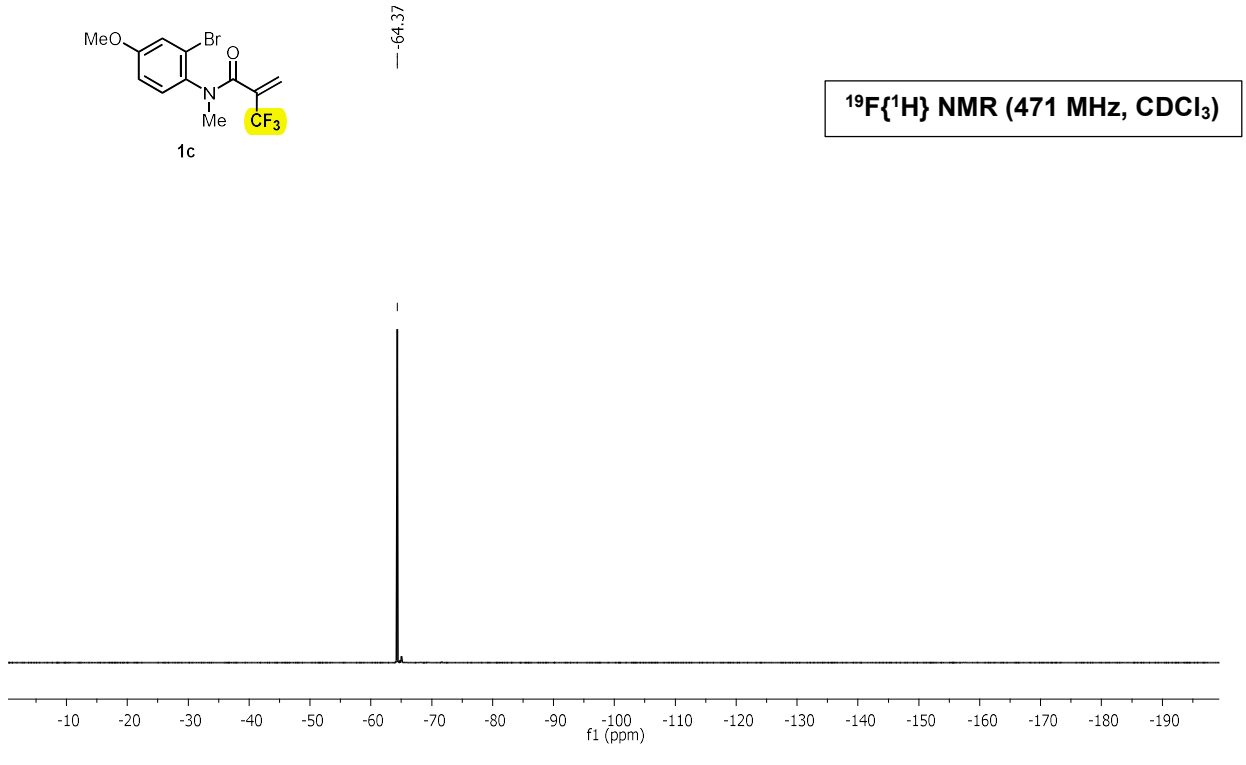


1c

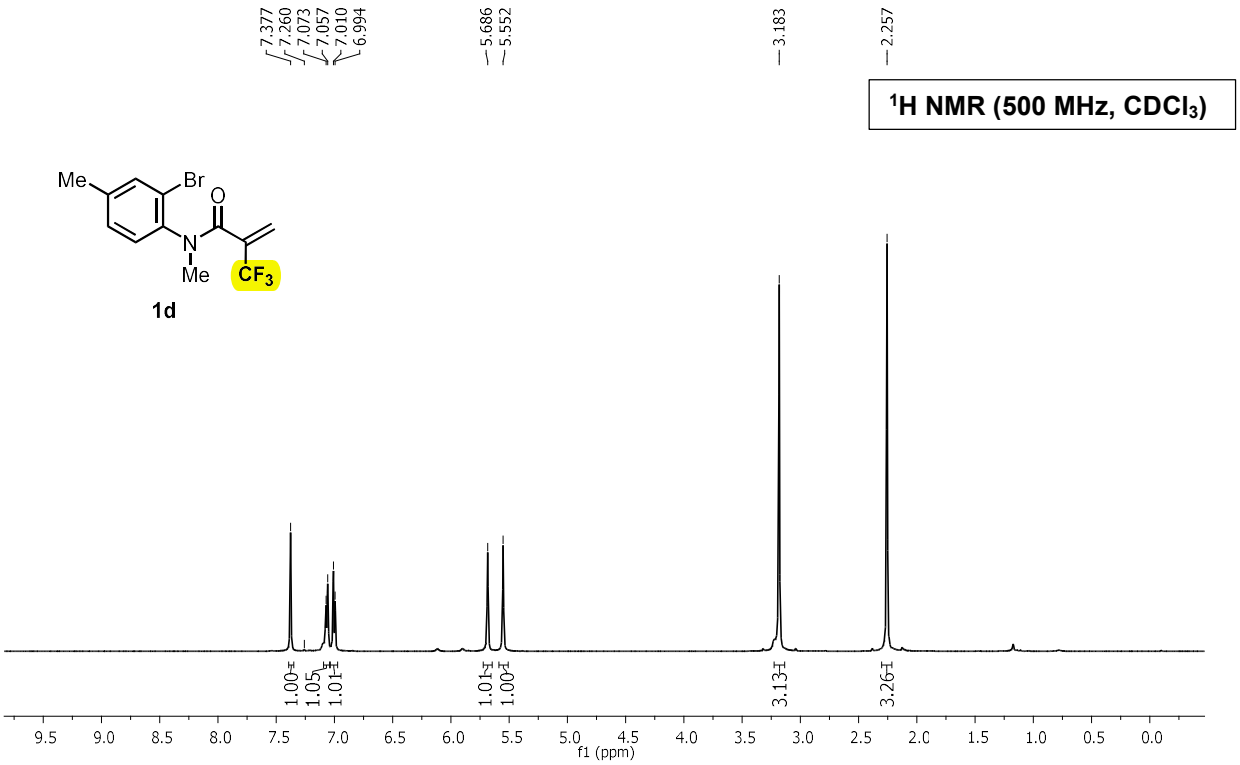
^{1}H NMR (500 MHz, $CDCl_3$)

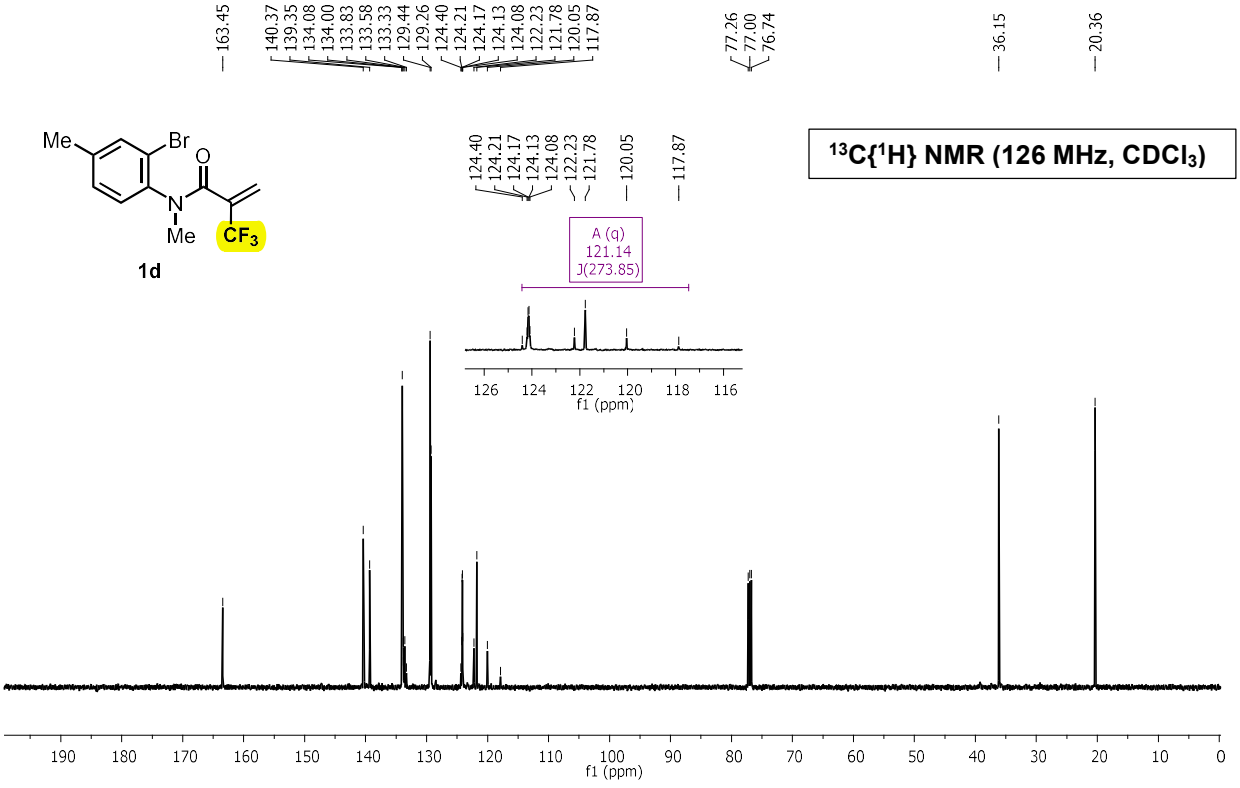


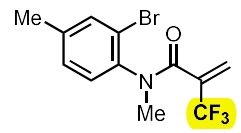
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

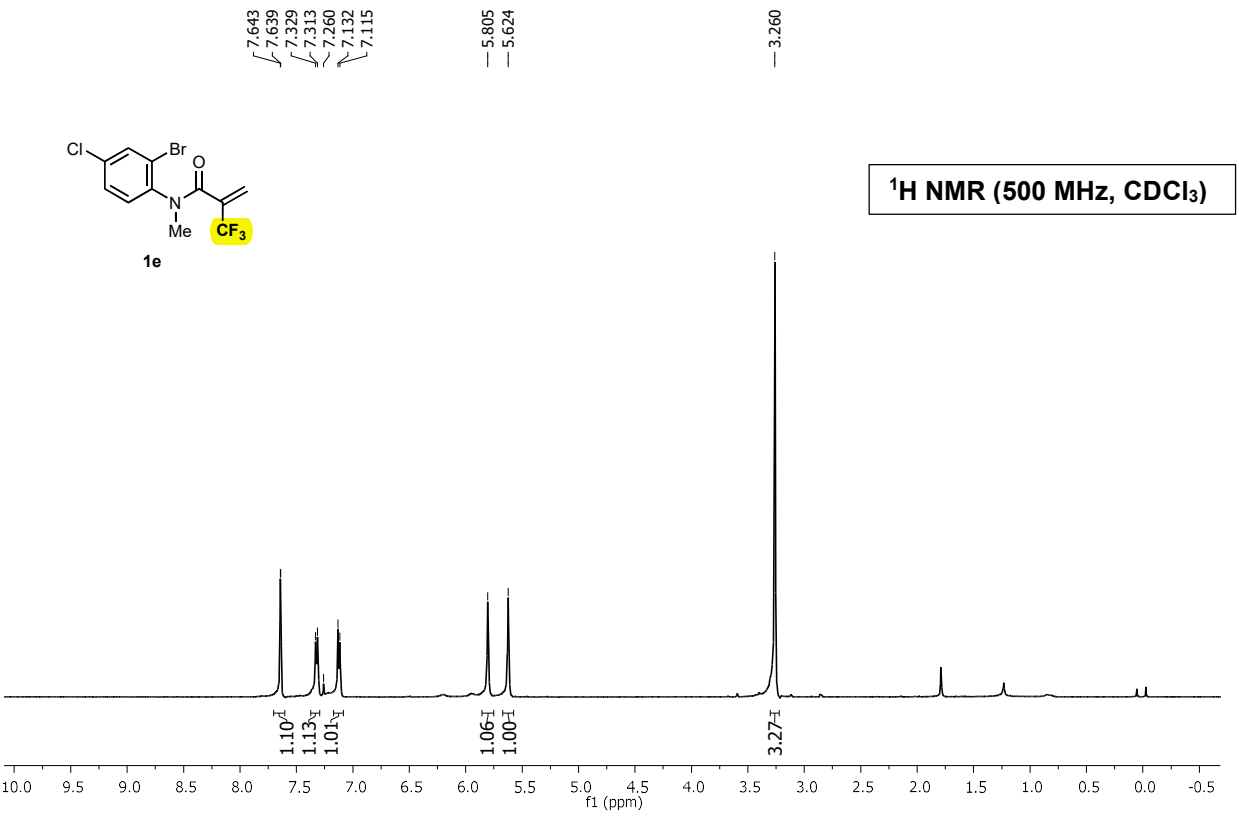

7.377
7.260
7.073
7.057
7.010
6.994
5.686
5.552
3.183
2.257
1H NMR (500 MHz, CDCl3)
Me
Br
O
N
Me
CF3
1d
1.00
1.05
1.01
1.01
1.00
3.13
3.26
f1 (ppm)


163.45
140.37
139.35
134.08
134.00
133.83
133.58
133.33
129.44
129.26
124.40
124.21
124.17
124.13
124.08
122.23
121.78
120.05
117.87
77.26
77.00
76.74
36.15
20.36
13C{1H} NMR (126 MHz, CDCl3)
Me
Br
O
N
Me
CF3
1d
A (q)
121.14
J(273.85)
f1 (ppm)
f1 (ppm)



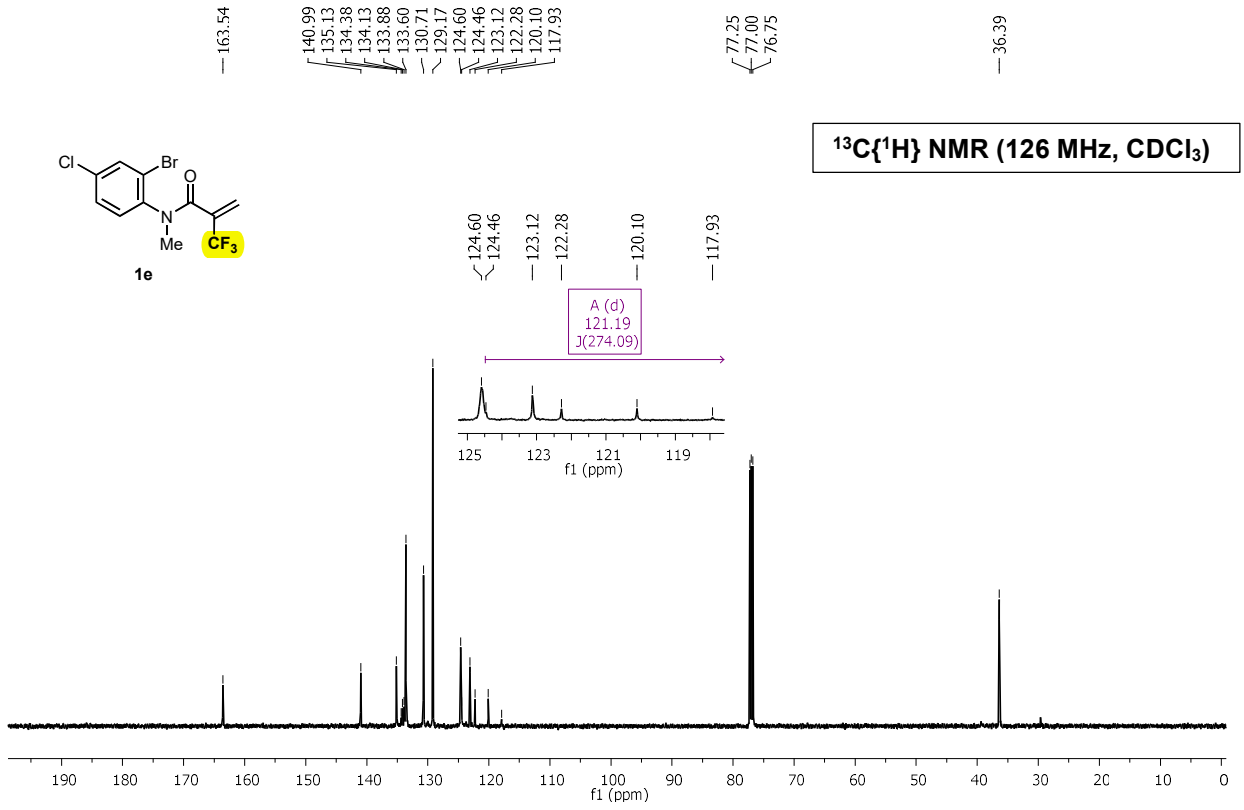
1d

$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

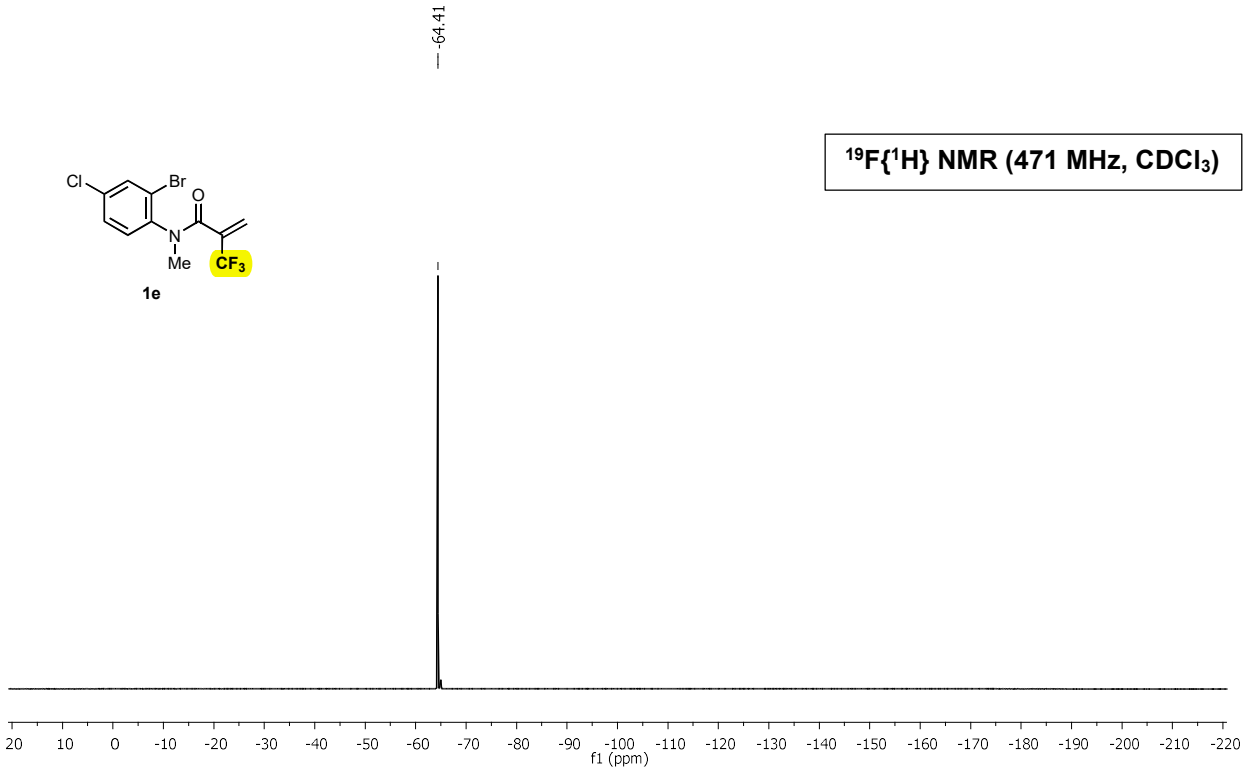


1e

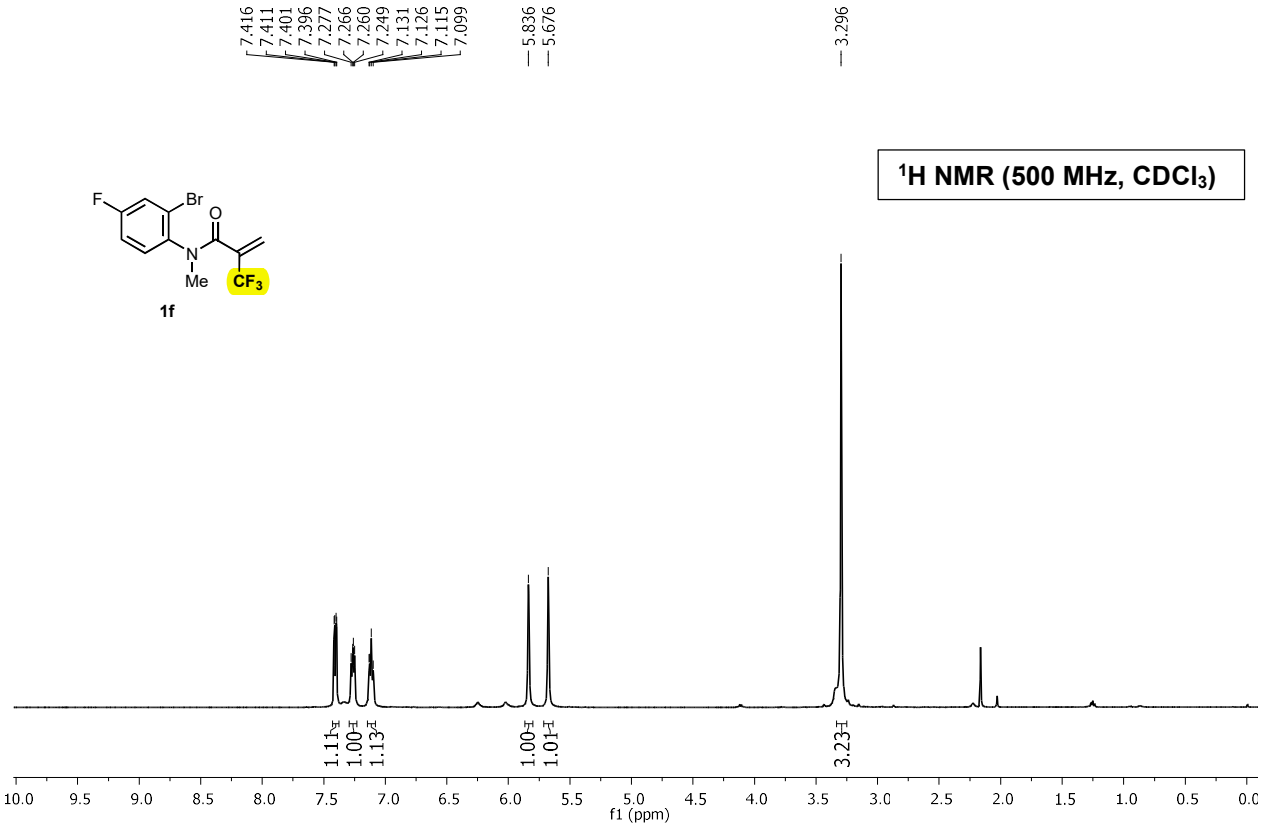
^{1}H NMR (500 MHz, $CDCl_3$)

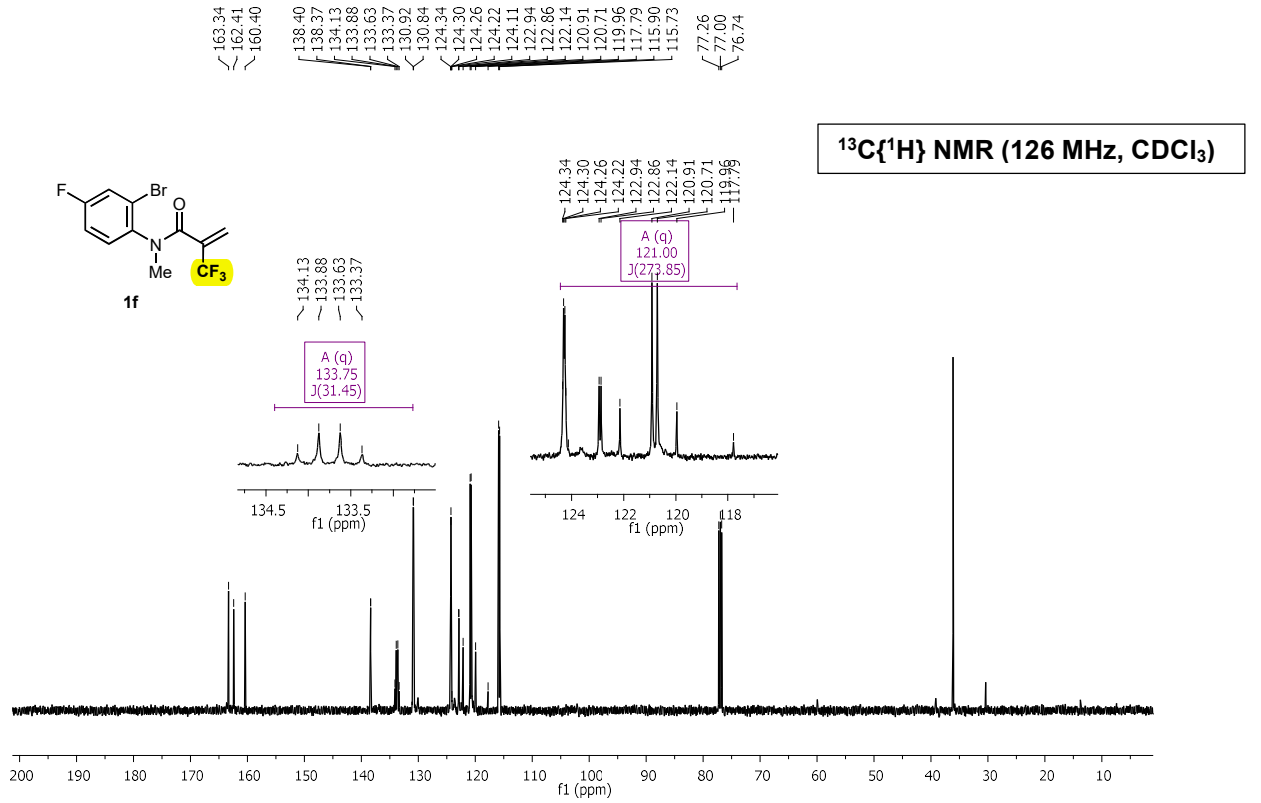


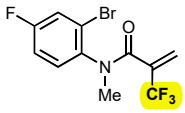
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

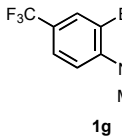

7.416
7.411
7.401
7.396
7.277
7.266
7.260
7.249
7.131
7.126
7.115
7.099
5.836
5.676
3.296
F
Br
O
N
Me
CF3
1f
1H NMR (500 MHz, CDCl3)
1.11
1.00
1.13
1.00
1.01
3.23
f1 (ppm)


163.34
162.41
160.40
138.40
138.37
134.13
133.88
133.63
133.37
130.92
130.84
124.34
124.30
124.26
124.22
124.11
122.94
122.86
122.14
120.91
120.71
119.96
117.79
115.90
115.73
77.26
77.00
76.74
F
Br
O
N
Me
CF3
1f
13C{1H} NMR (126 MHz, CDCl3)
A (q)
133.75
J(31.45)
A (q)
121.00
J(273.85)
f1 (ppm)
f1 (ppm)



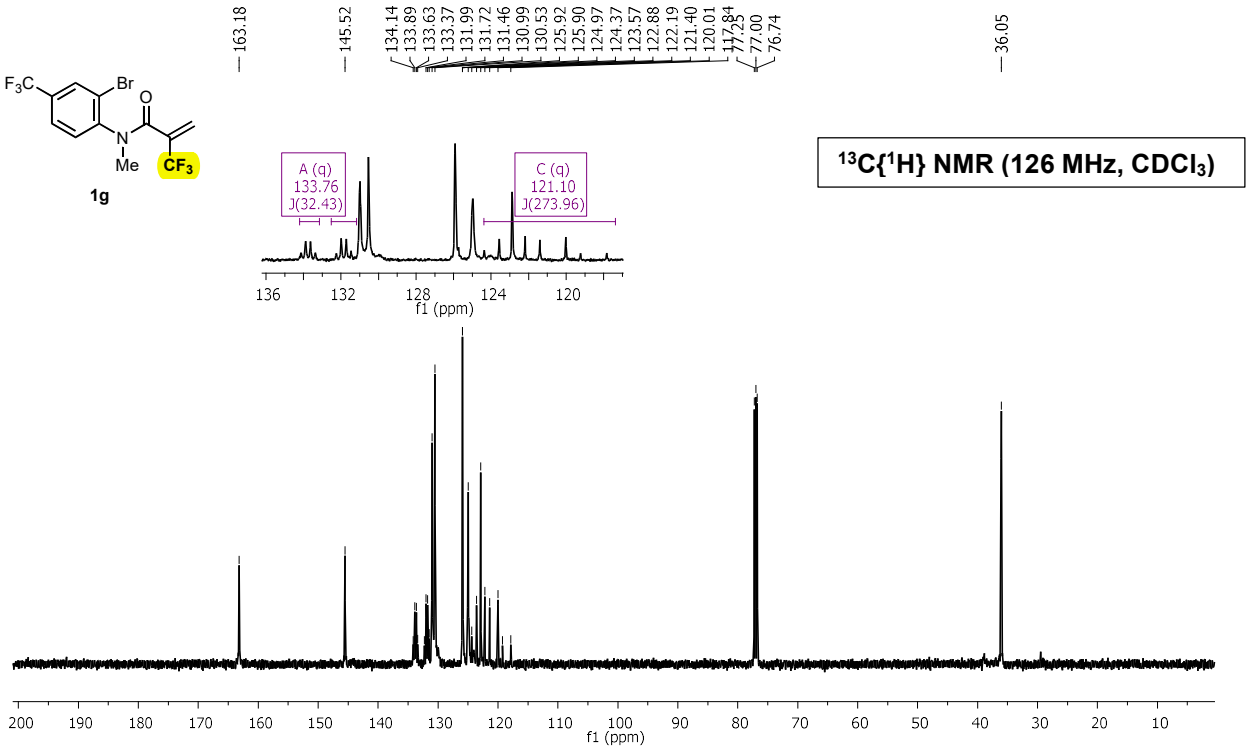
1f

$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

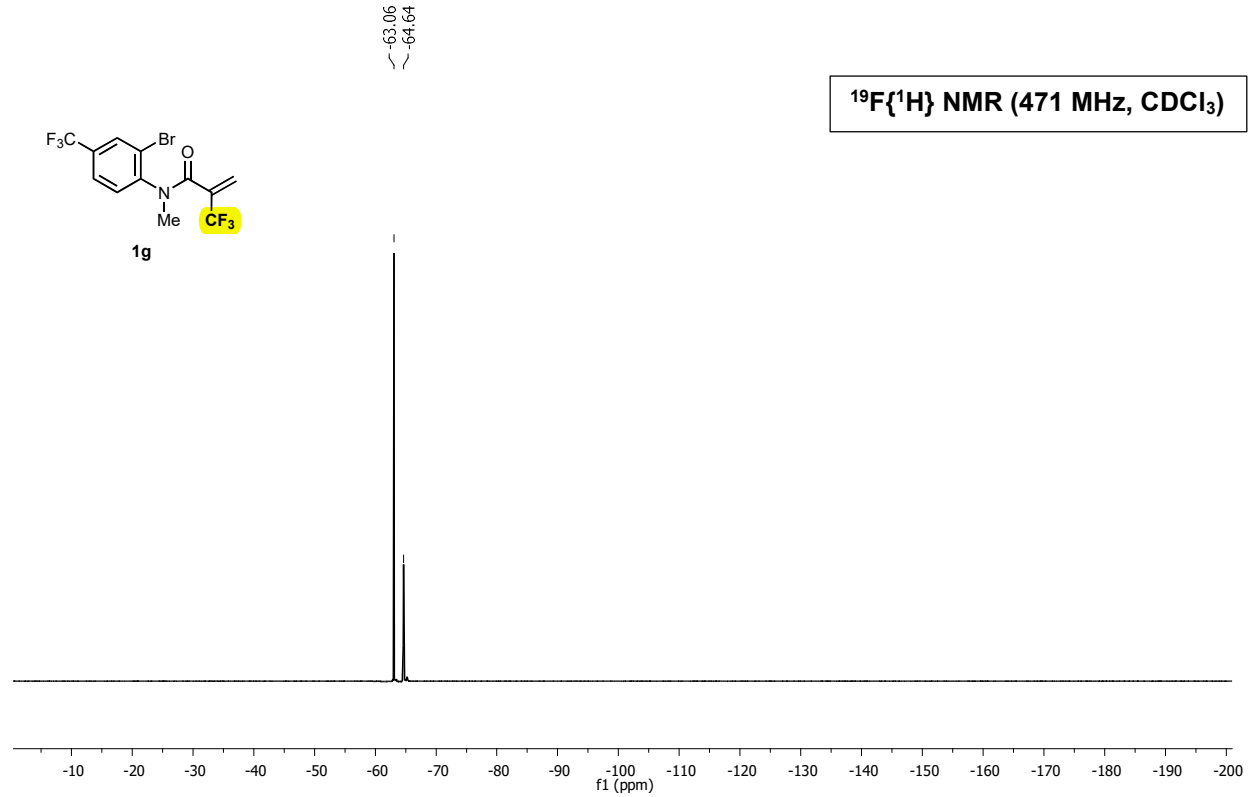


1g

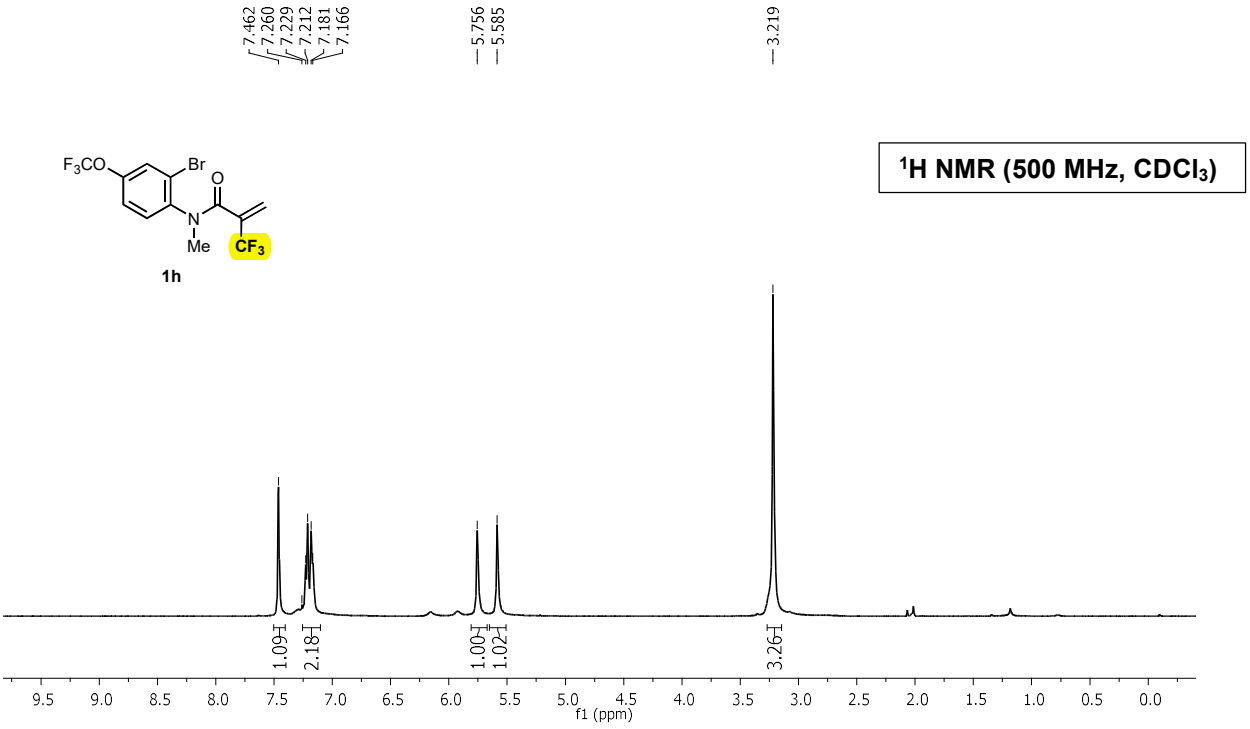
^{1}H NMR (500 MHz, $CDCl_3$)

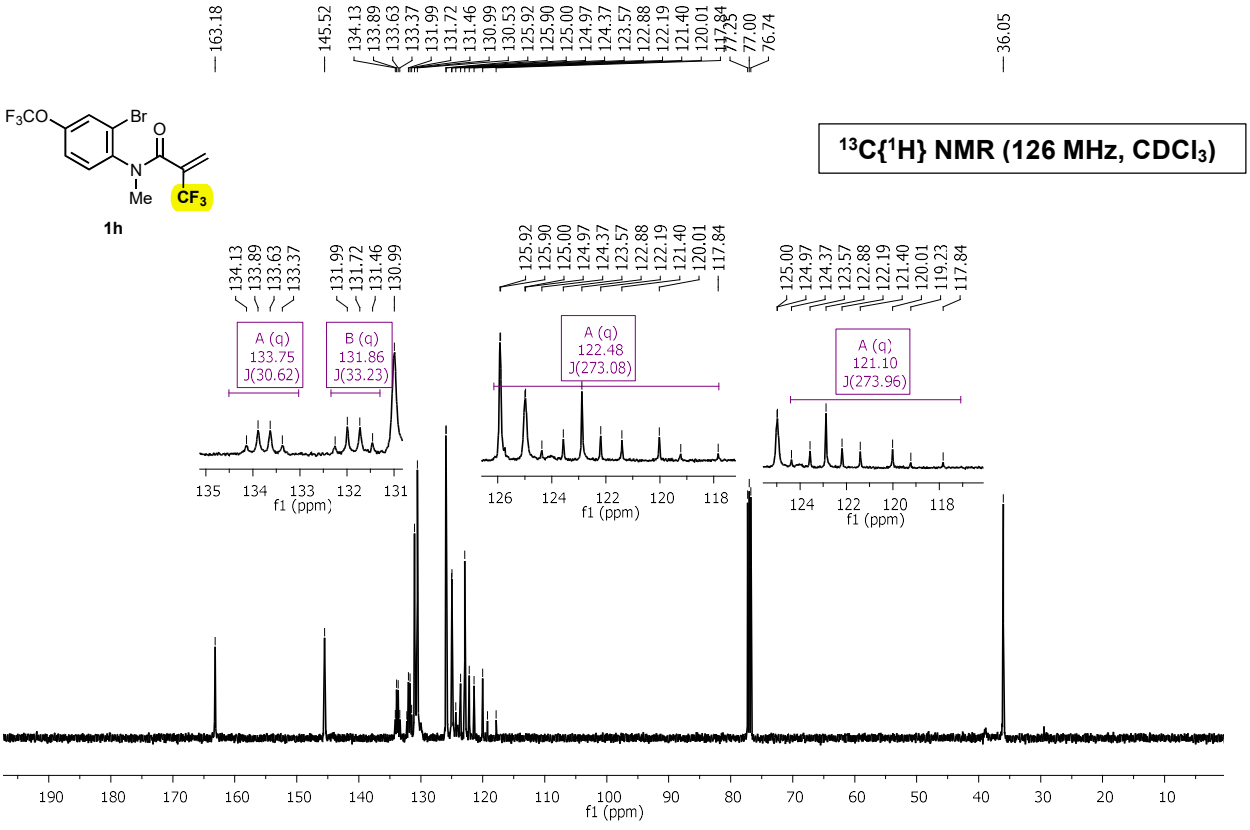


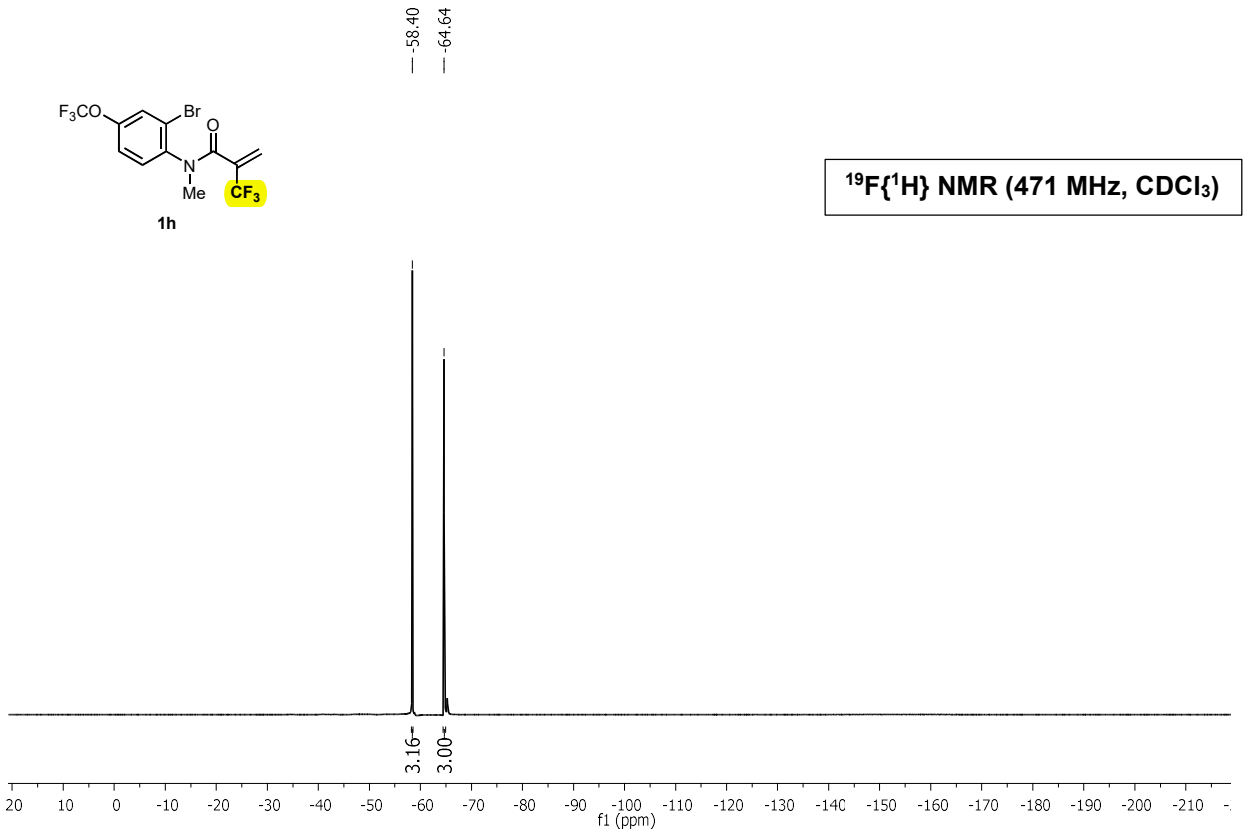
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

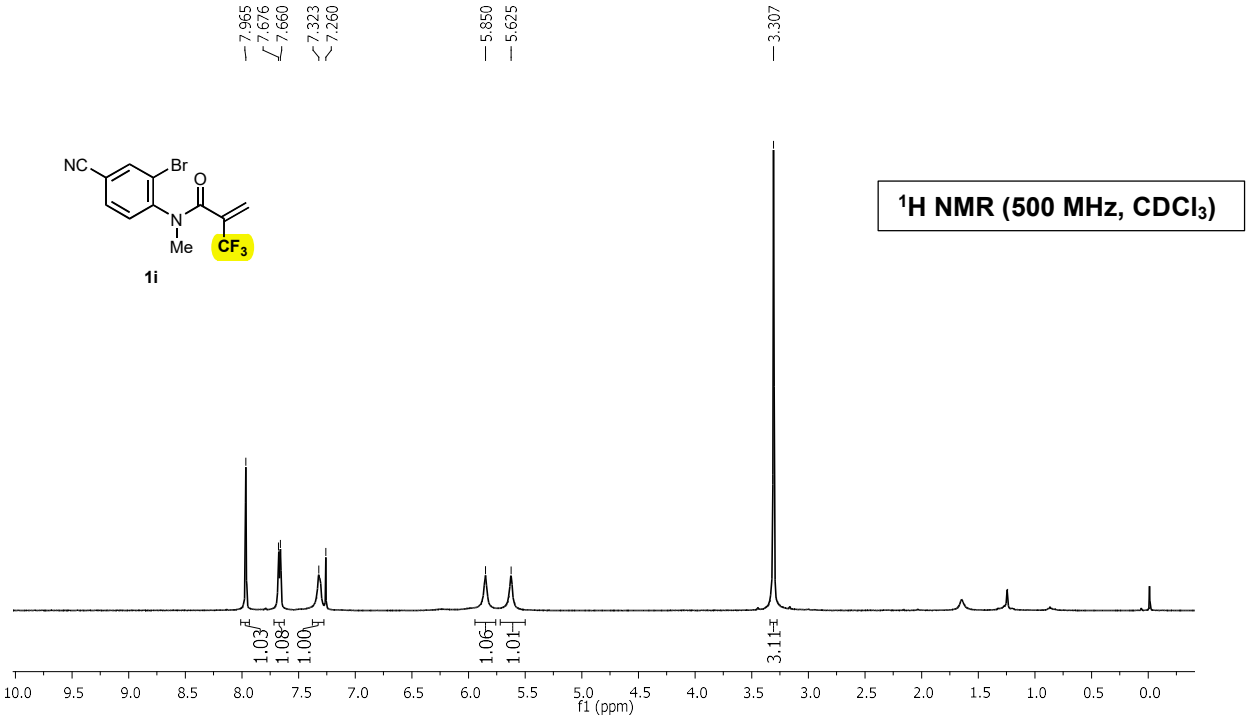


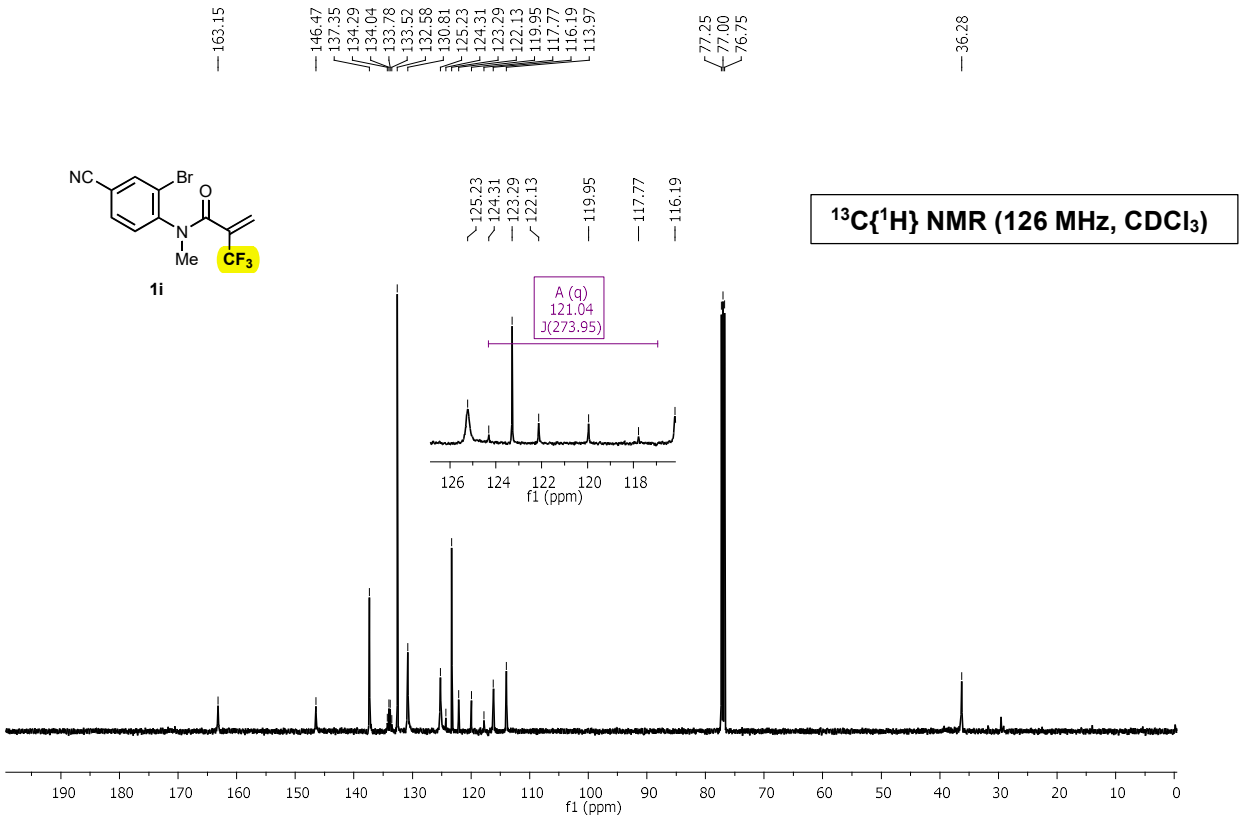
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)


7.462
7.260
7.229
7.212
7.181
7.166
5.756
5.585
3.219
F3CO
Br
O
N
Me
CF3
1h
1H NMR (500 MHz, CDCl3)
1.09
2.18
1.00
1.02
3.26
f1 (ppm)

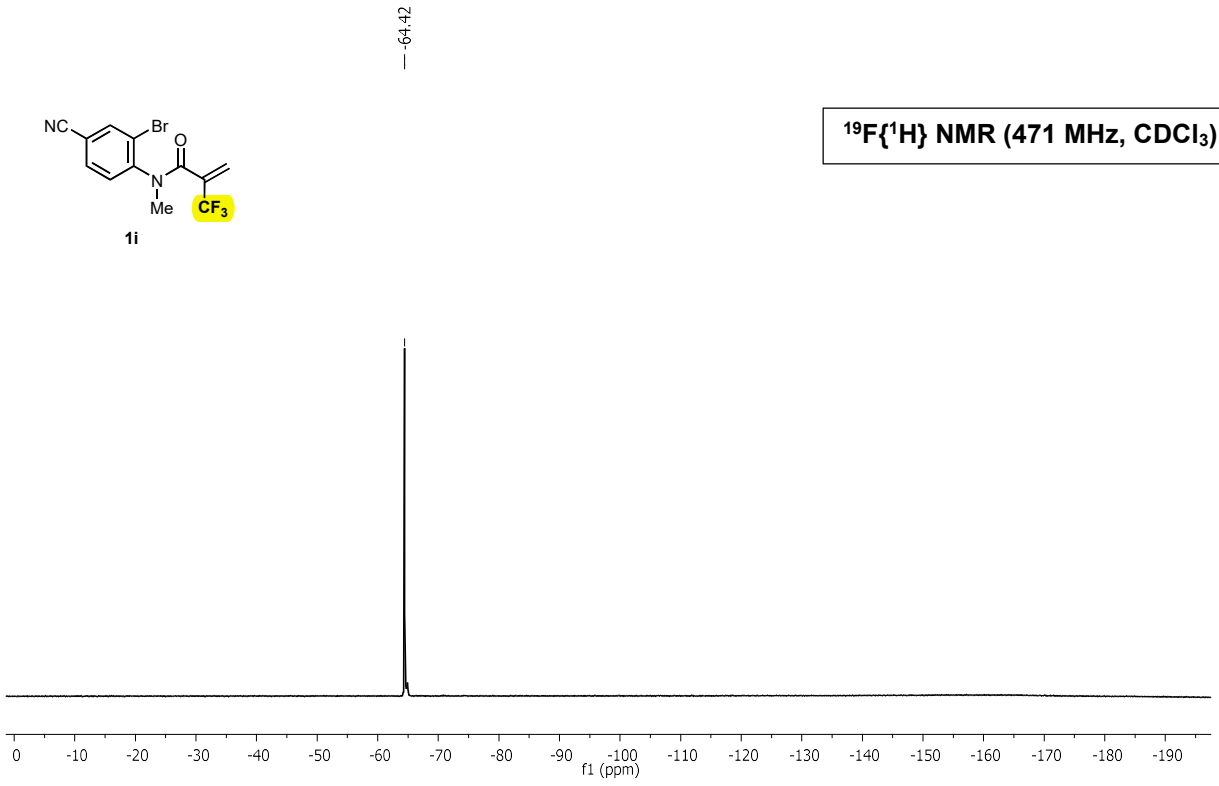

163.18
145.52
134.13
133.89
133.63
133.37
131.99
131.72
131.46
130.99
130.53
125.92
125.90
125.00
124.97
124.37
123.57
122.88
122.19
121.40
120.01
117.84
77.00
76.74
36.05
F3CO
Br
O
N
Me
CF3
1h
13C{1H} NMR (126 MHz, CDCl3)
A (q)
133.75
J(30.62)
B (q)
131.86
J(33.23)
A (q)
122.48
J(273.08)
A (q)
121.10
J(273.96)
f1 (ppm)


-58.40
-64.64
F3CO
Br
O
N
Me
CF3
1h
19F{1H} NMR (471 MHz, CDCl3)
3.16
3.00
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)

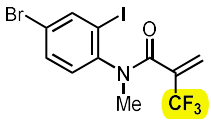

7.965
7.676
7.660
7.323
7.260
5.850
5.625
3.307
NC
Br
O
N
Me
CF3
1i
1H NMR (500 MHz, CDCl3)
1.03
1.08
1.00
1.06
1.01
3.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

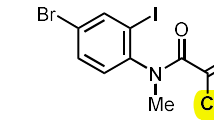


$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



1j

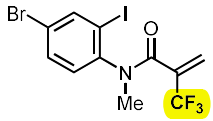
^{1}H NMR (500 MHz, $CDCl_3$)



1j

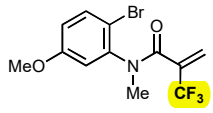
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

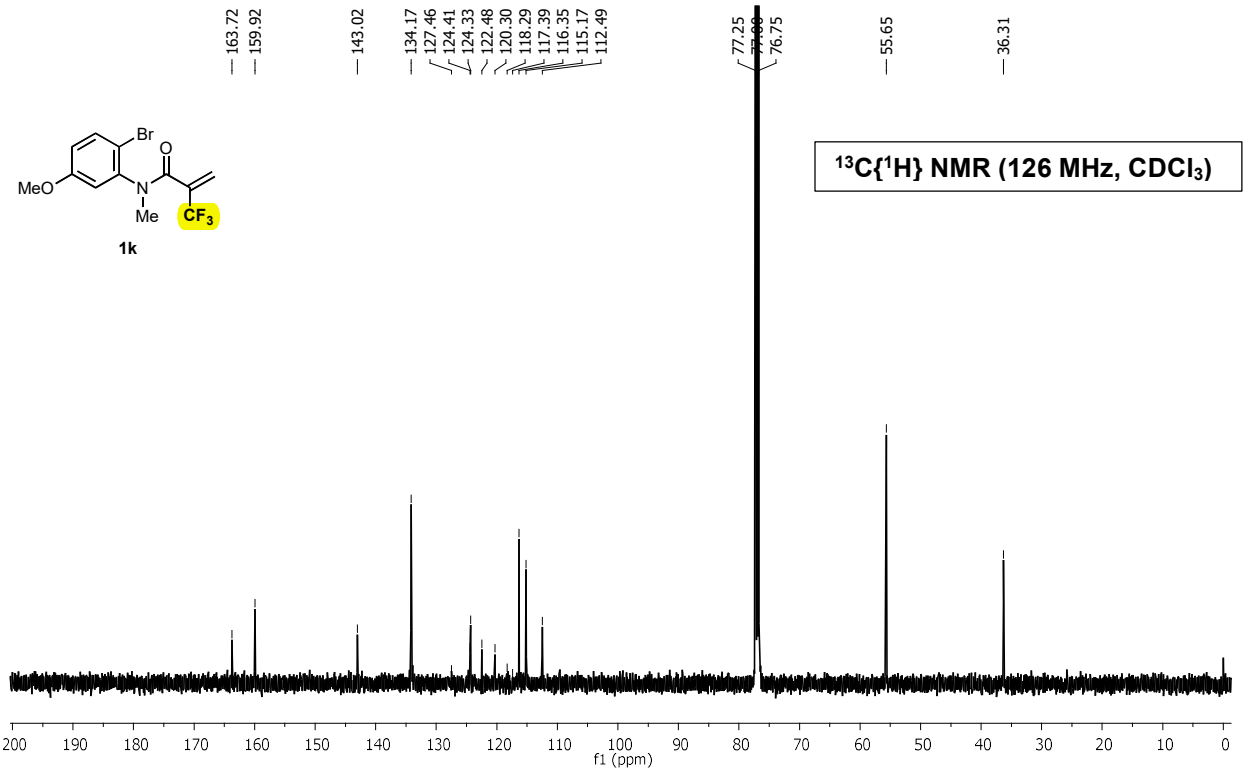


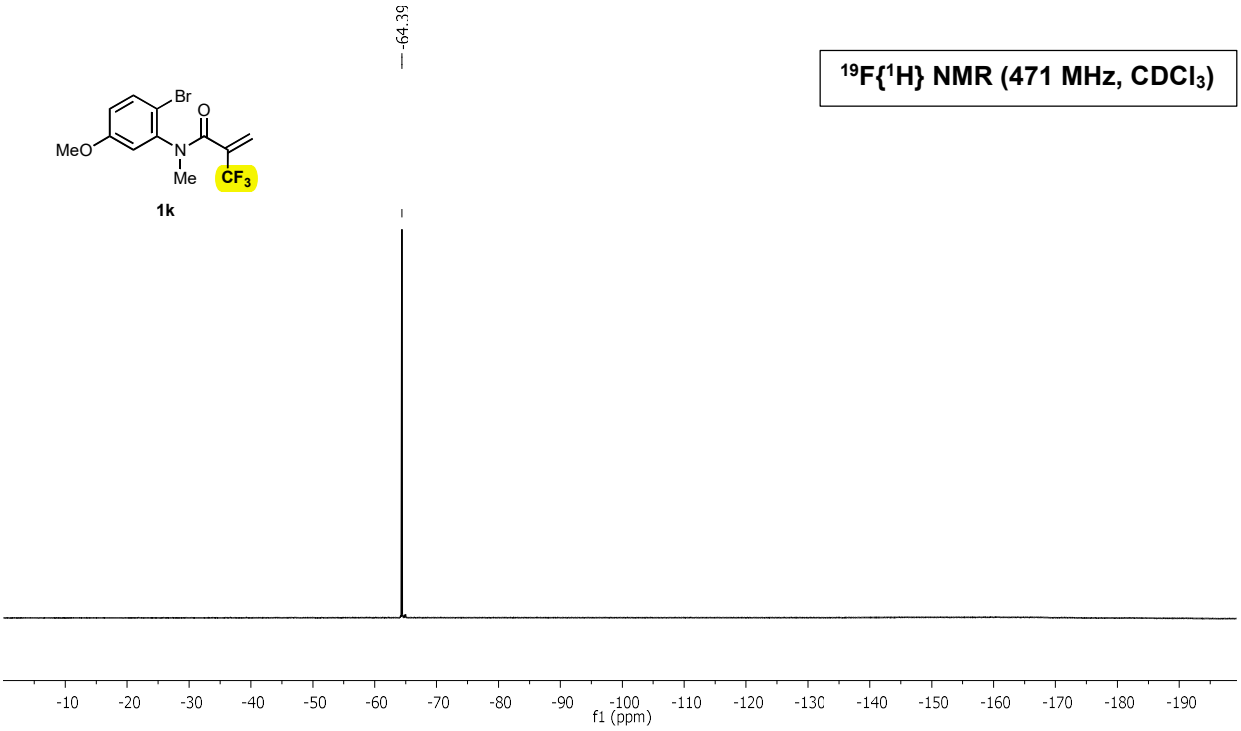
1j

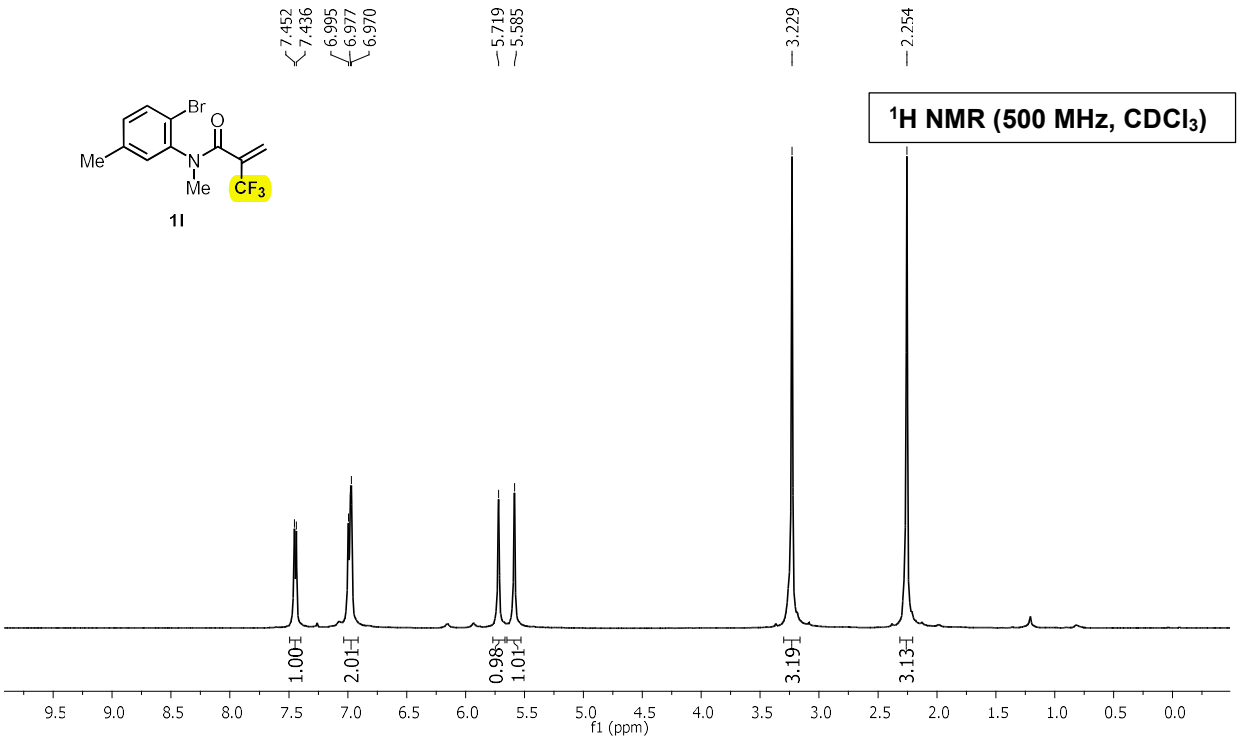
^{1}H NMR (500 MHz, $CDCl_3$)

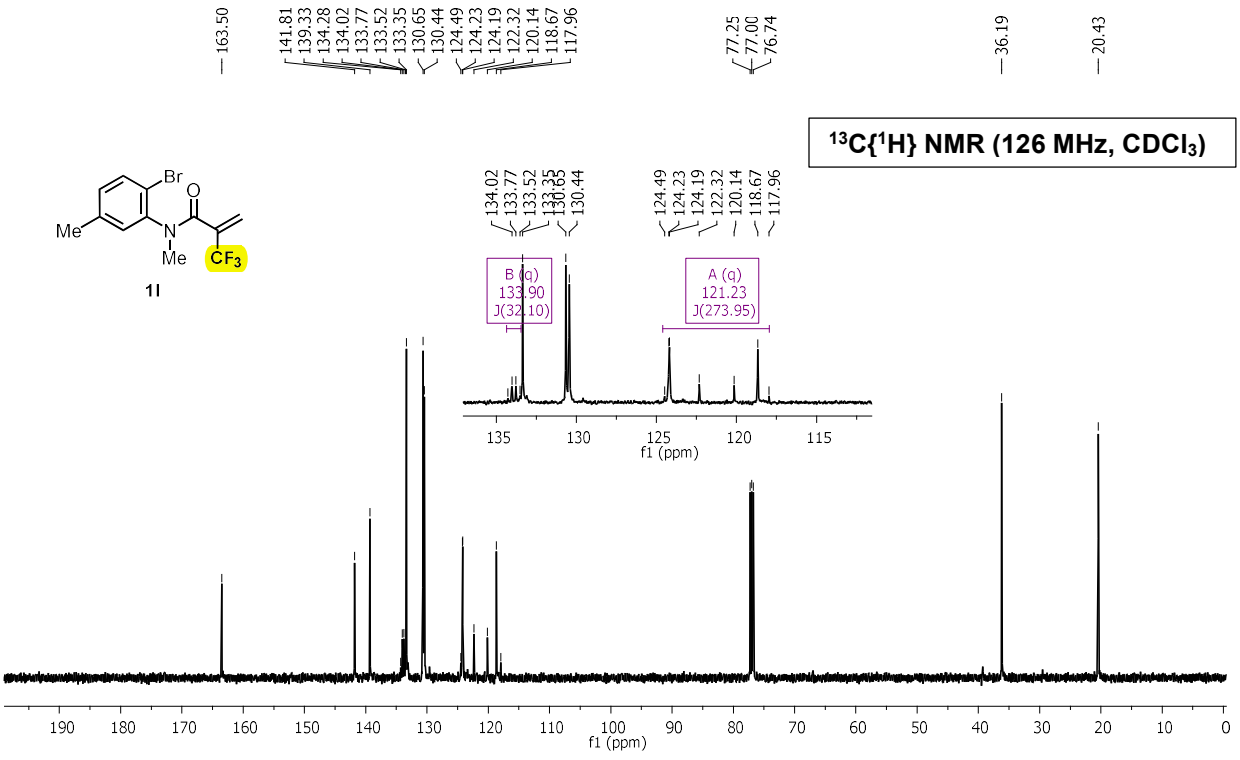


1k

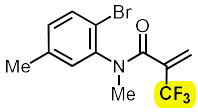

163.72
159.92
143.02
134.17
127.46
124.41
124.33
122.48
120.30
118.29
117.39
116.35
115.17
112.49
77.25
77.00
76.75
55.65
36.31
Br
O
MeO
N
Me
CF3
1k
13C{1H} NMR (126 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-64.39
Br
O
MeO
N
Me
CF3
1k
19F{1H} NMR (471 MHz, CDCl3)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


7.452
7.436
6.995
6.977
6.970
5.719
5.585
3.229
2.254
Br
O
Me
N
Me
CF3
1l
1H NMR (500 MHz, CDCl3)
1.00
2.01
0.98
1.01
3.19
3.13
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)

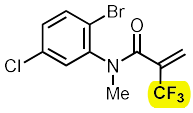

163.50
141.81
139.33
134.28
134.02
133.77
133.52
133.35
130.65
130.44
124.49
124.23
124.19
122.32
120.14
118.67
117.96
77.25
77.00
76.74
36.19
20.43
13C{1H} NMR (126 MHz, CDCl3)
Br
O
Me
N
Me
CF3
1l
B (q)
133.90
J(32.10)
A (q)
121.23
J(273.95)
135 130 125 120 115
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

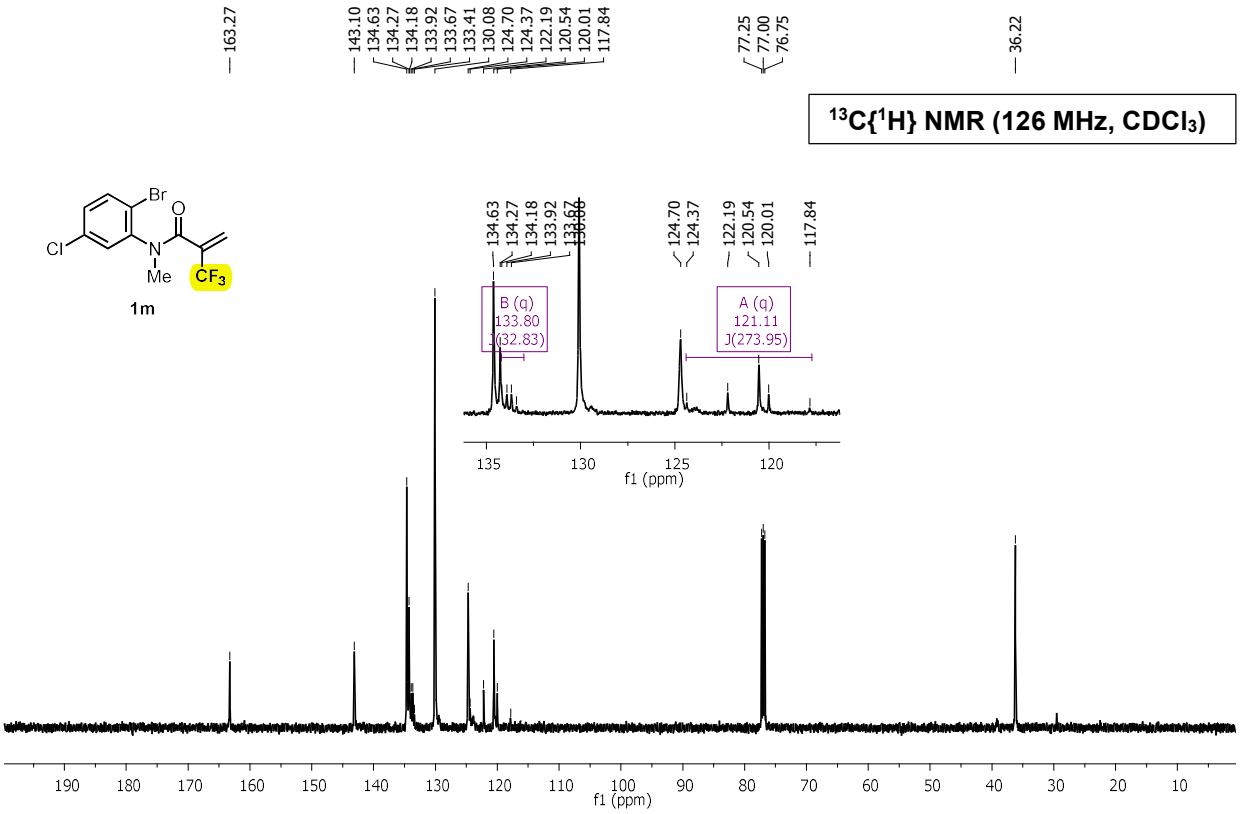


1l

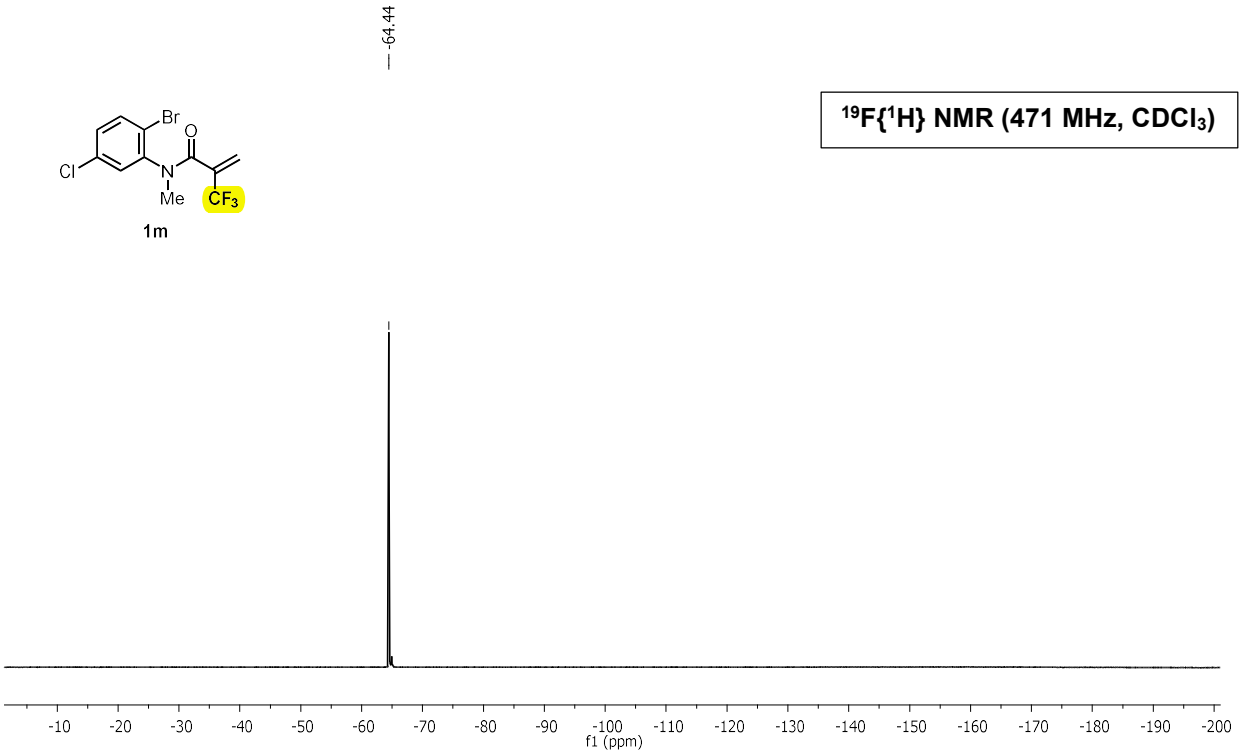
^{1}H NMR (500 MHz, $CDCl_3$)



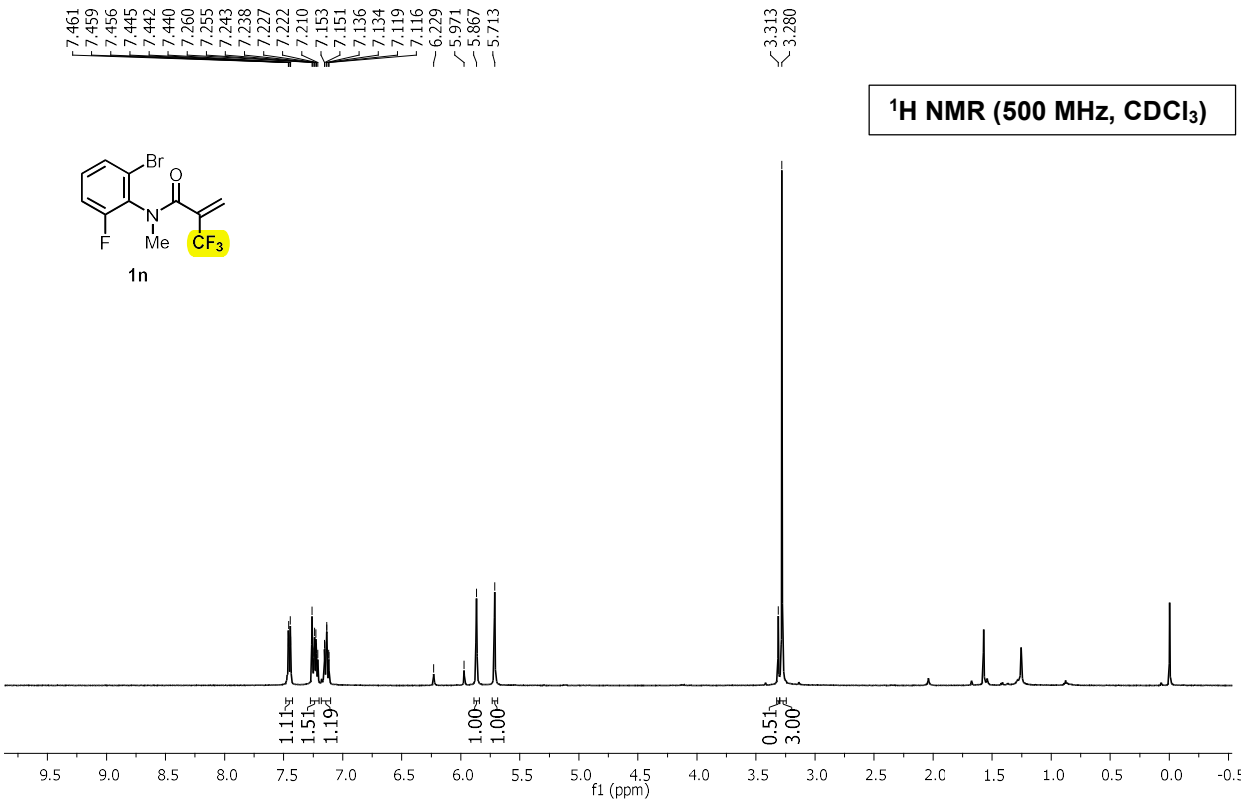
1m

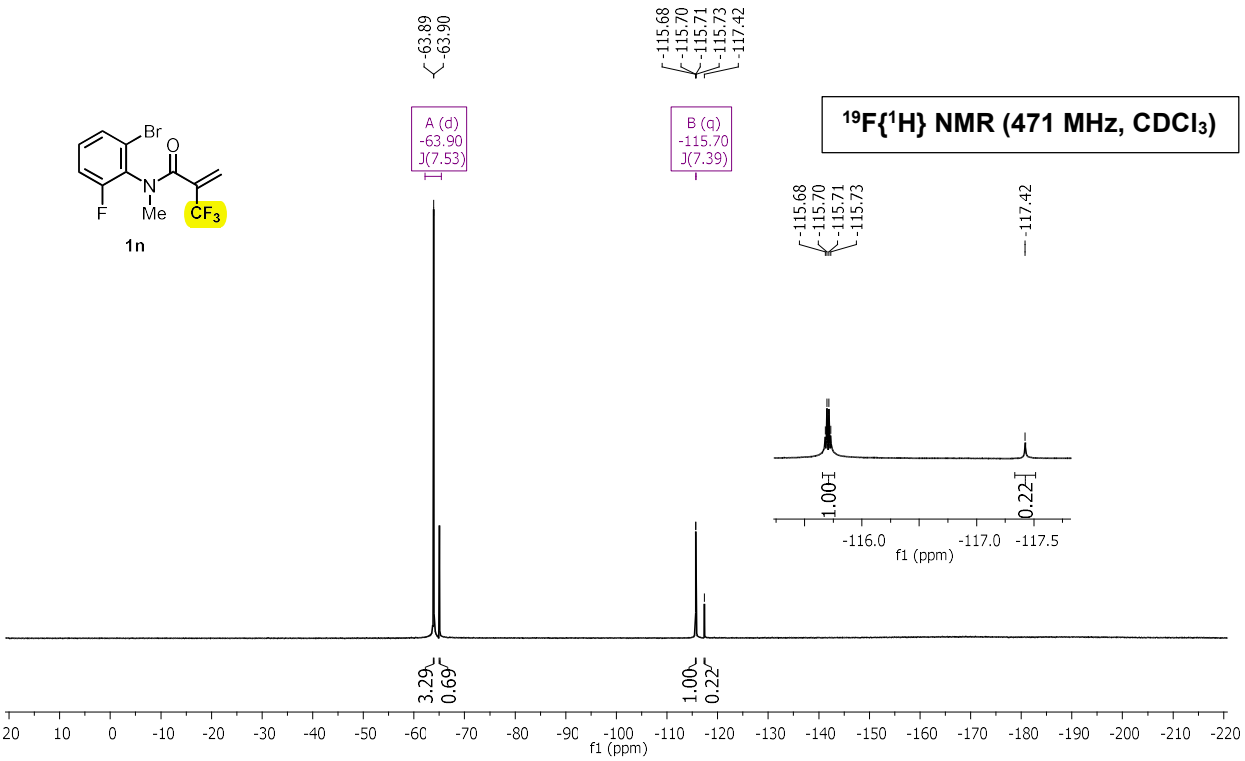


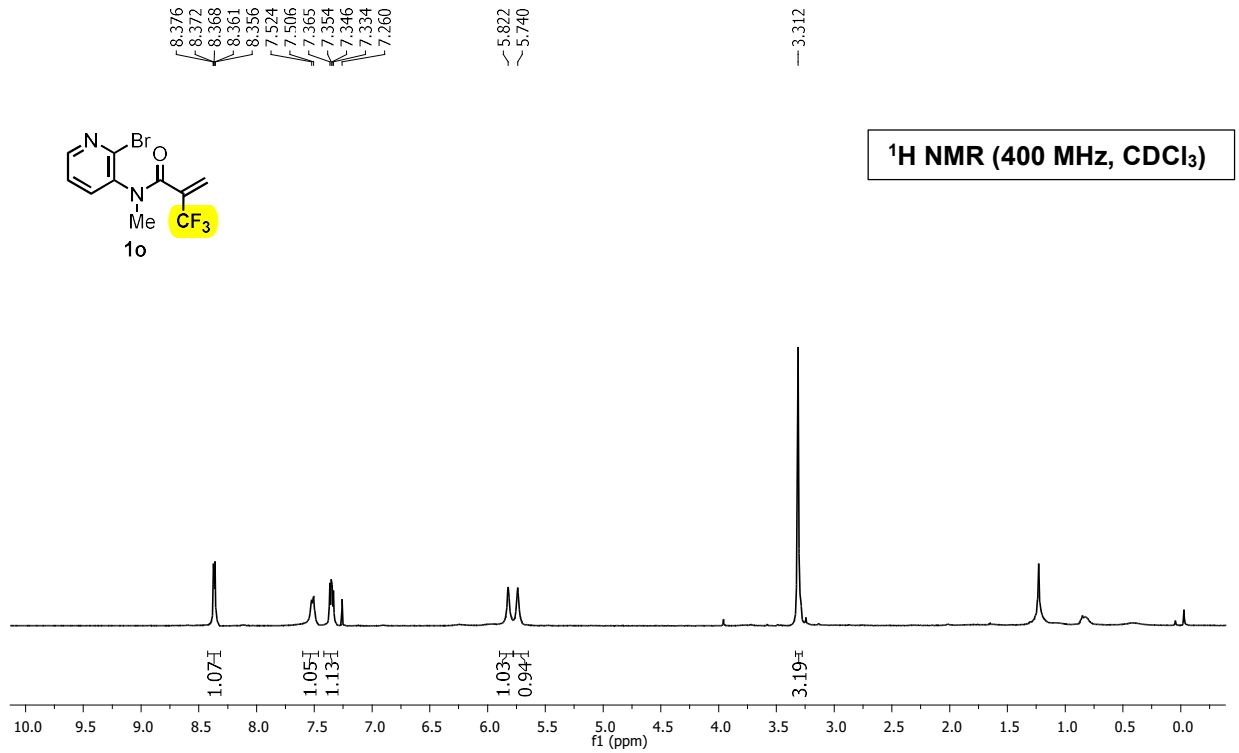
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



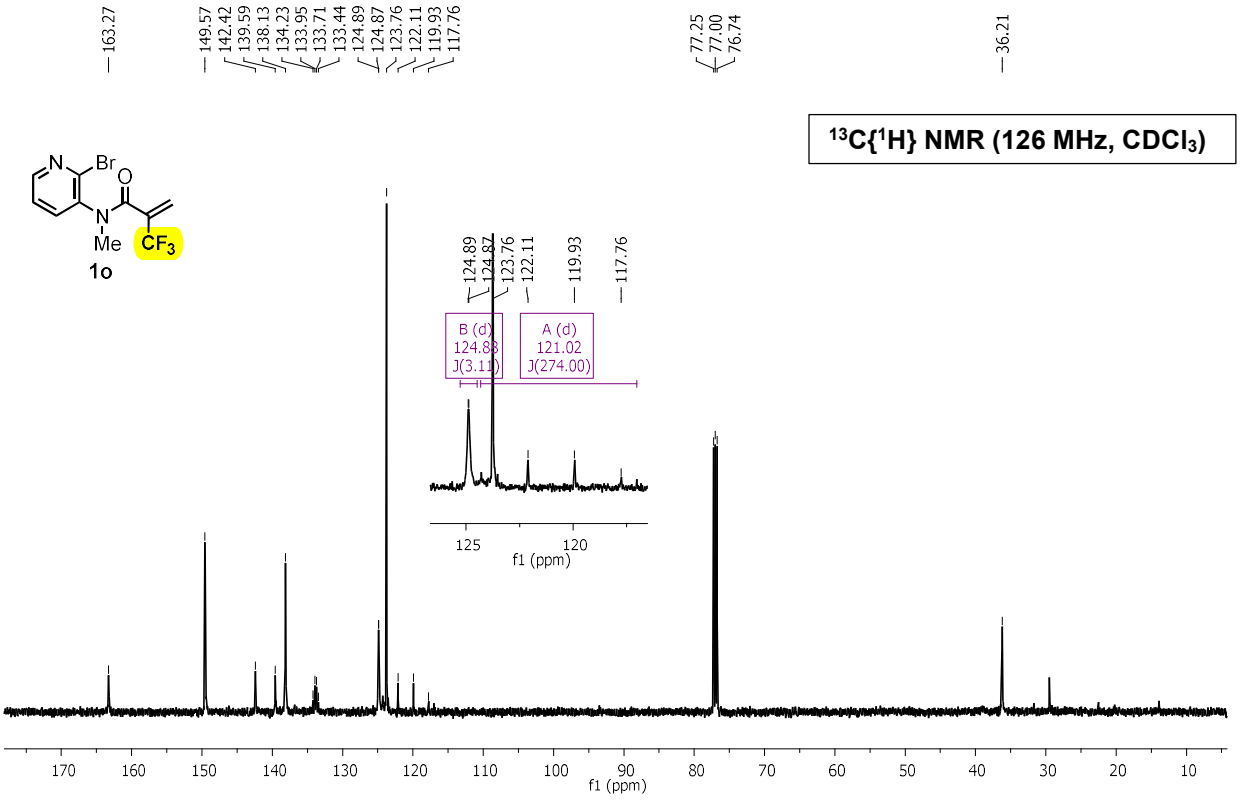
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)


7.461
7.459
7.456
7.445
7.442
7.440
7.260
7.255
7.243
7.238
7.227
7.222
7.210
7.153
7.151
7.136
7.134
7.119
7.116
6.229
5.971
5.867
5.713
3.313
3.280
1H NMR (500 MHz, CDCl3)
Br
O
N
Me
F
CF3
1n
1.11
1.51
1.19
1.00
1.00
0.51
3.00
f1 (ppm)


-63.89
-63.90
-115.68
-115.70
-115.71
-115.73
-117.42
19F{1H} NMR (471 MHz, CDCl3)
A (d)
-63.90
J(7.53)
B (q)
-115.70
J(7.39)
Br
O
N
Me
F
CF3
1n
1.00
0.22
-116.0
-117.0
-117.5
f1 (ppm)
3.29
0.69
1.00
0.22
f1 (ppm)

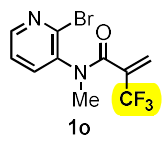


^{1}H NMR (400 MHz, $CDCl_3$)



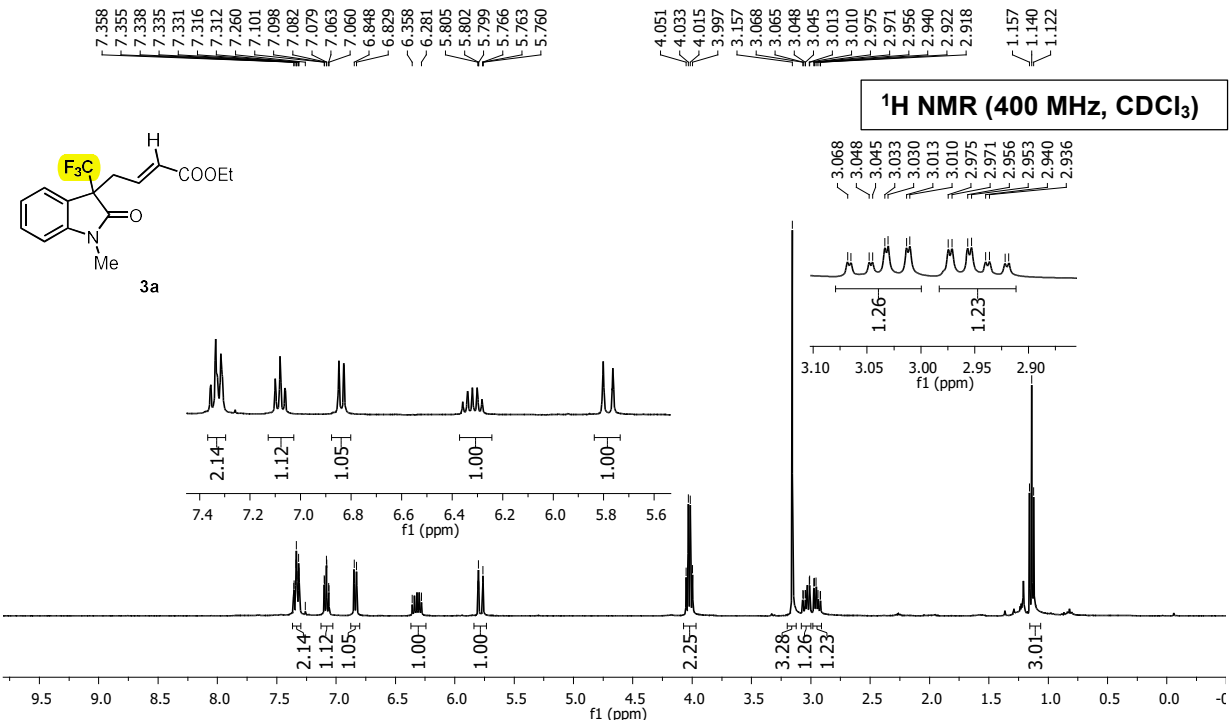
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

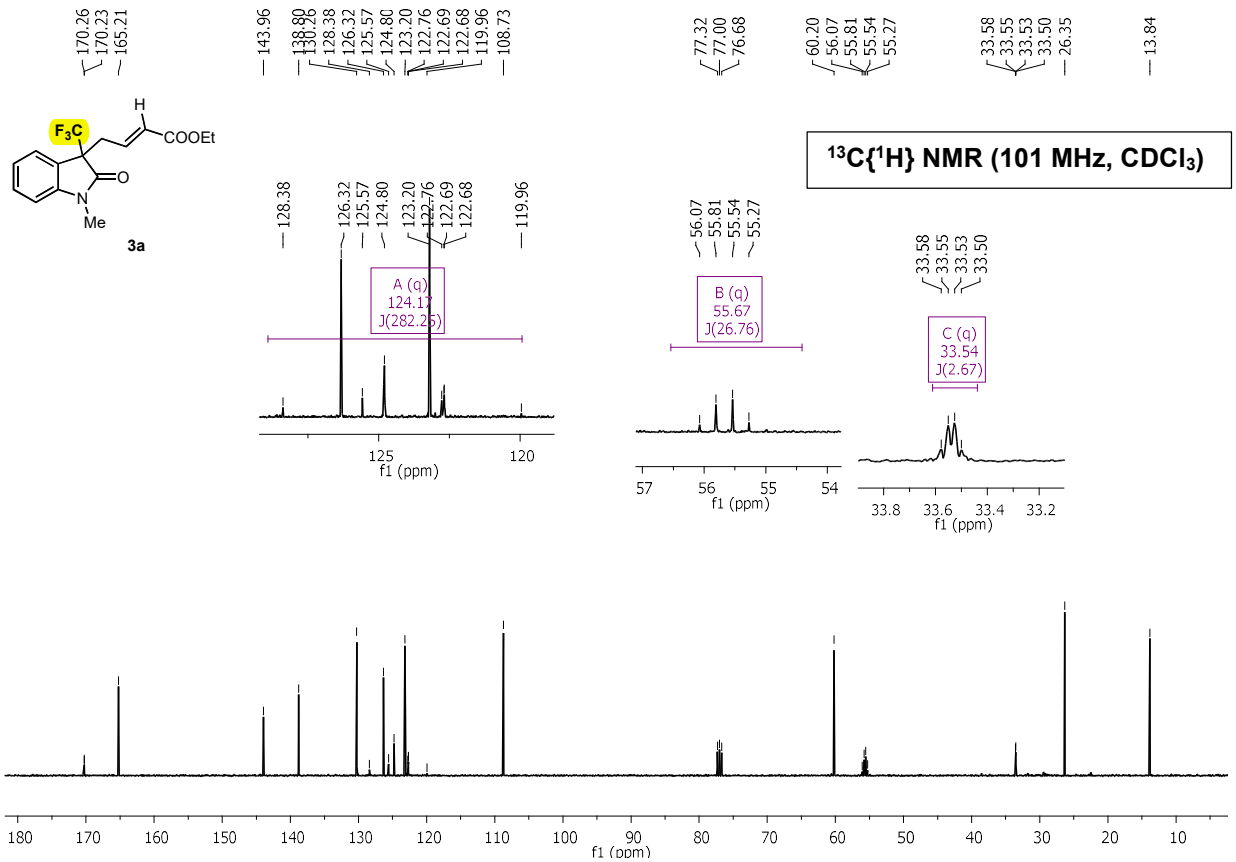


1o

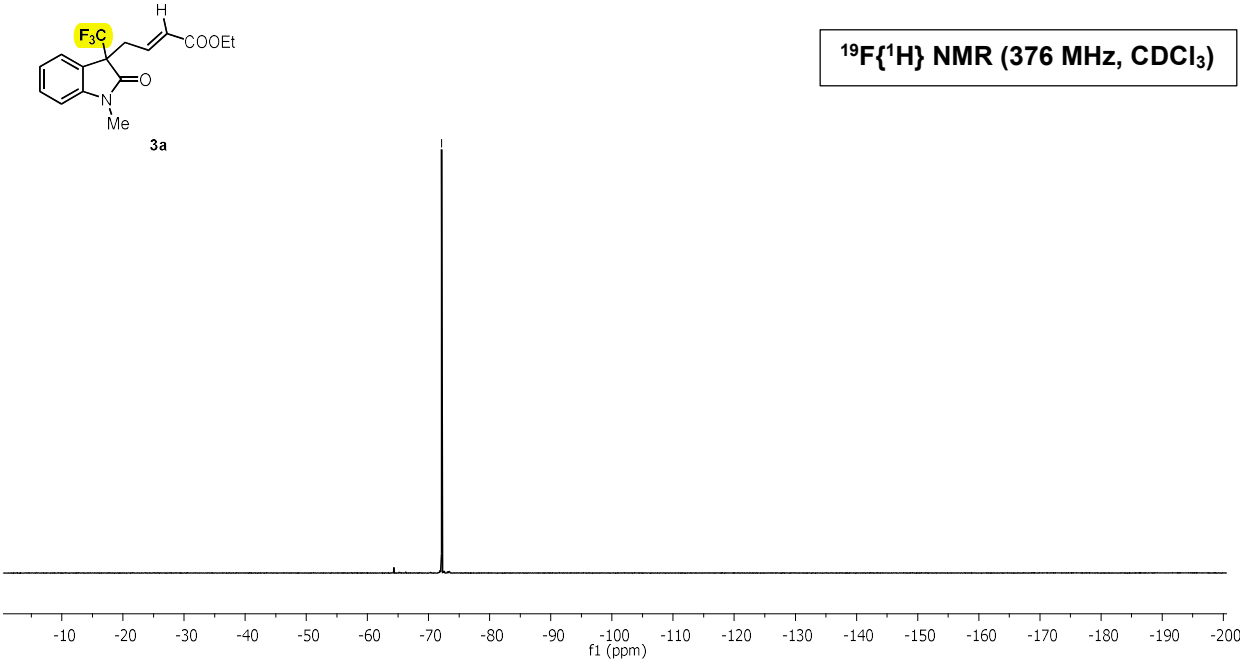
^{1}H NMR (400 MHz, $CDCl_3$)

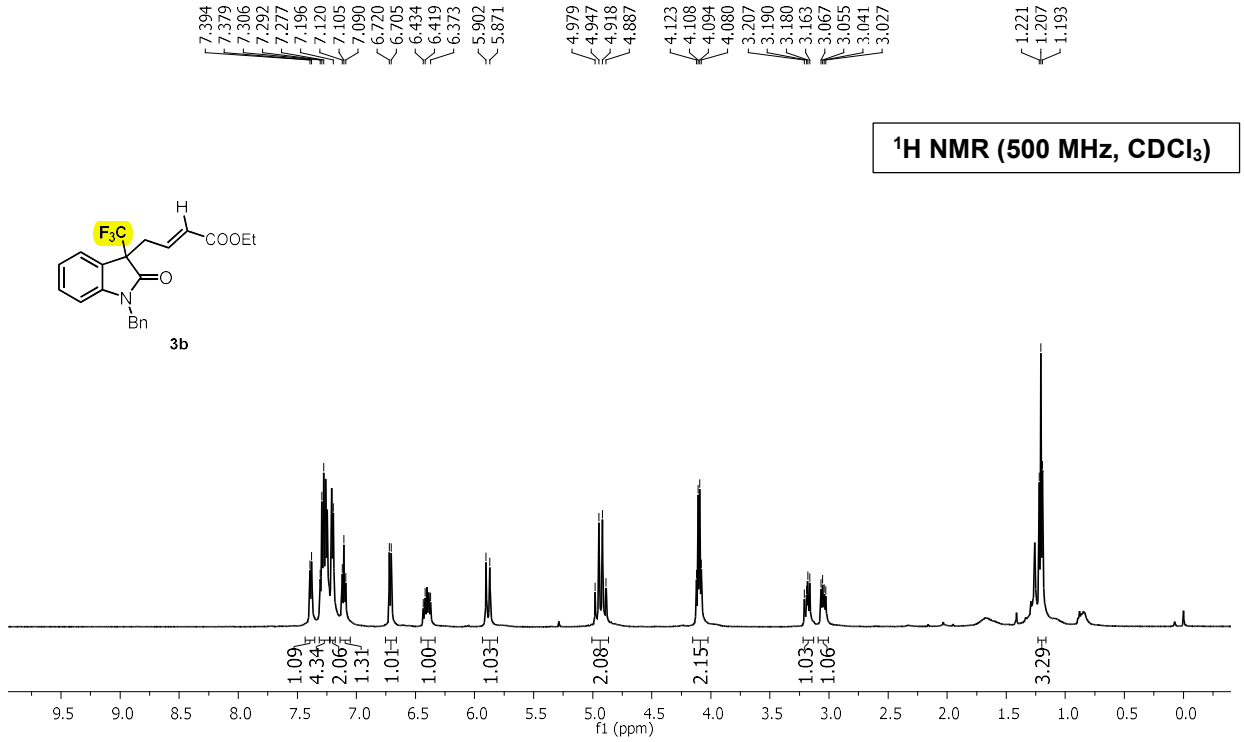


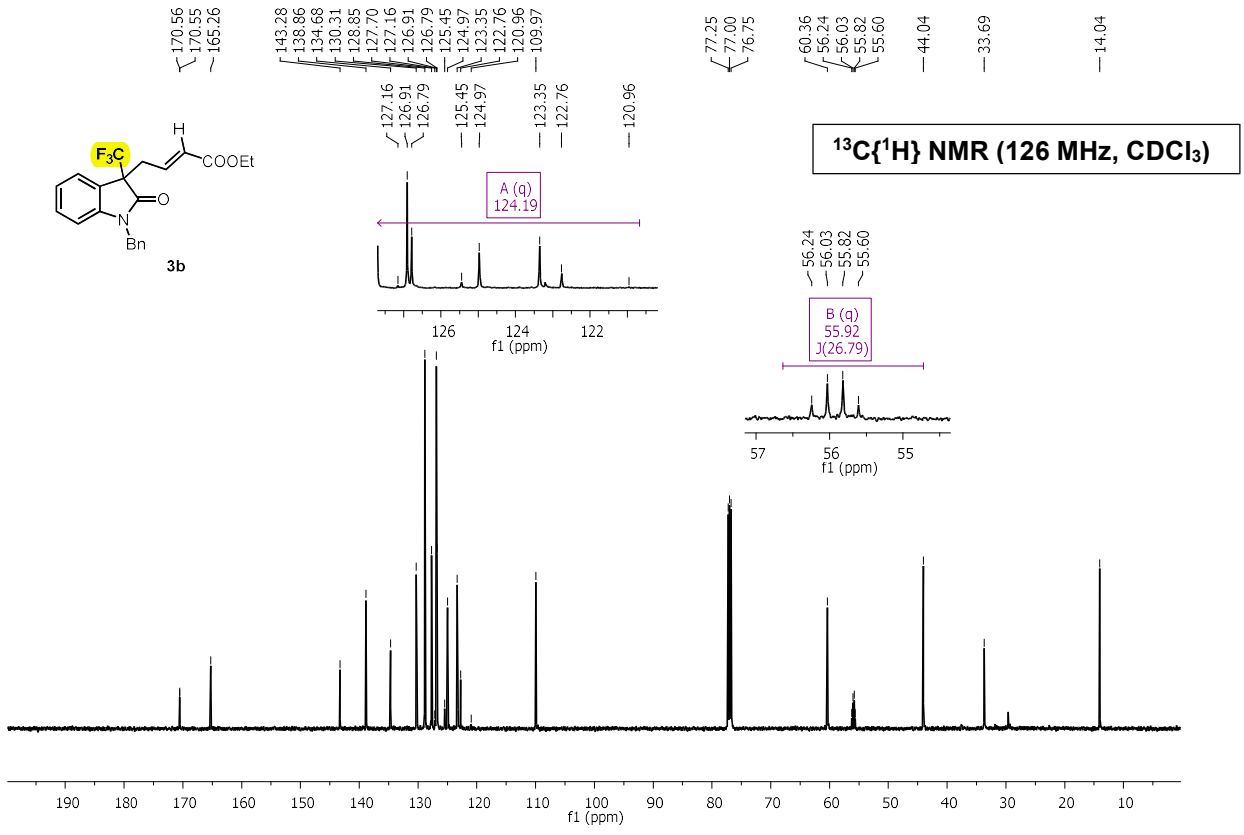
3a

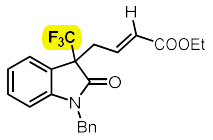

170.26
170.23
165.21
143.96
138.80
138.26
130.36
128.38
126.32
125.57
124.80
123.20
122.76
122.69
122.68
119.96
108.73
77.32
77.00
76.68
60.20
56.07
55.81
55.54
55.27
33.58
33.55
33.53
33.50
26.35
13.84
F3C
H
COOEt
O
N
Me
3a
13C{1H} NMR (101 MHz, CDCl3)
A (q)
124.17
J(282.25)
B (q)
55.67
J(26.76)
C (q)
33.54
J(2.67)
f1 (ppm)

f1 (ppm)


-72.13
F3C
H
COOEt
O
N
Me
3a
19F{1H} NMR (376 MHz, CDCl3)
f1 (ppm)

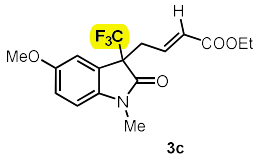

7.394
7.379
7.306
7.292
7.277
7.196
7.120
7.105
7.090
6.720
6.705
6.434
6.419
6.373
5.902
5.871
4.979
4.947
4.918
4.887
4.123
4.108
4.094
4.080
3.207
3.190
3.180
3.163
3.067
3.055
3.041
3.027
1.221
1.207
1.193
1H NMR (500 MHz, CDCl3)
F3C
H
COOEt
O
N
Bn
3b
1.09
4.34
2.06
1.31
1.01
1.00
1.03
2.08
2.15
1.03
1.06
3.29
f1 (ppm)


170.56
170.55
165.26
143.28
138.86
134.68
130.31
128.85
127.70
127.16
126.91
126.79
125.45
124.97
123.35
122.76
120.96
109.97
77.25
77.00
76.75
60.36
56.24
56.03
55.82
55.60
44.04
33.69
14.04
13C{1H} NMR (126 MHz, CDCl3)
A (q)
124.19
B (q)
55.92
J(26.79)
f1 (ppm)



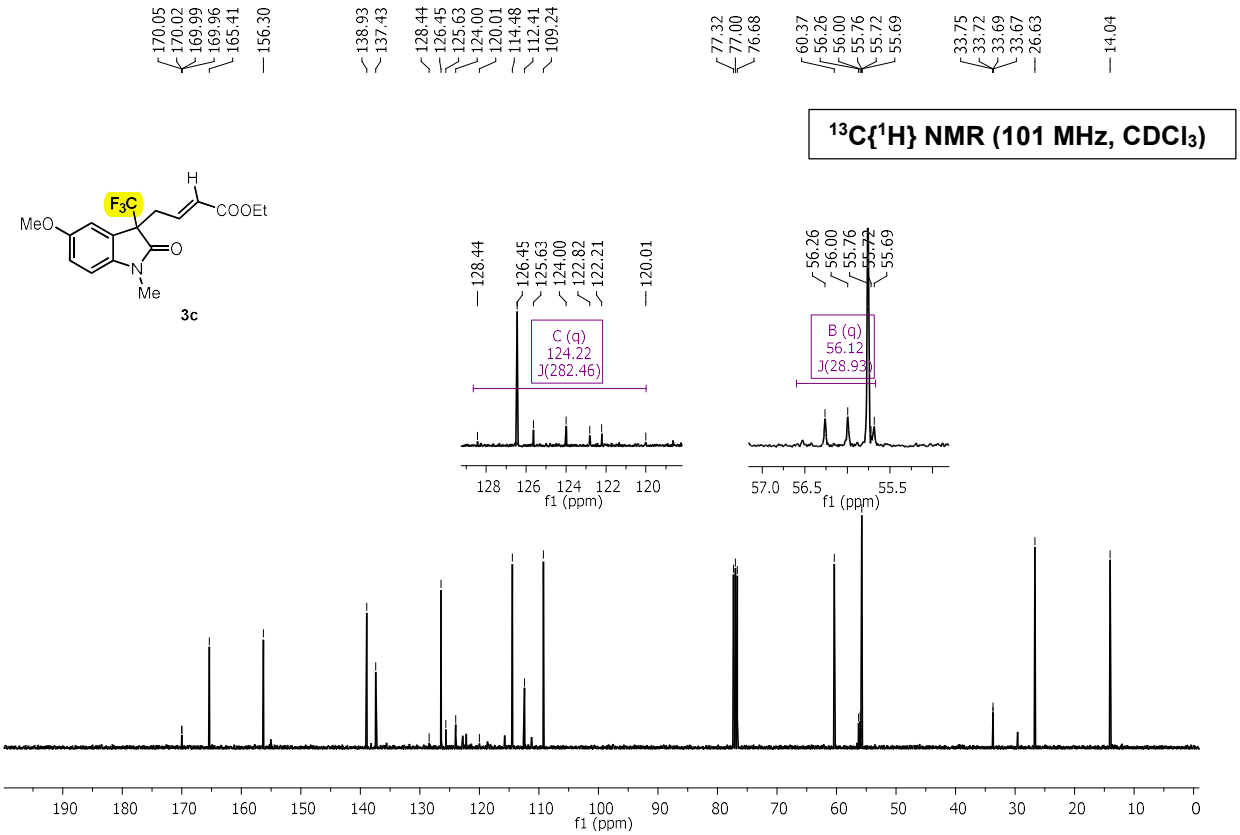
3b

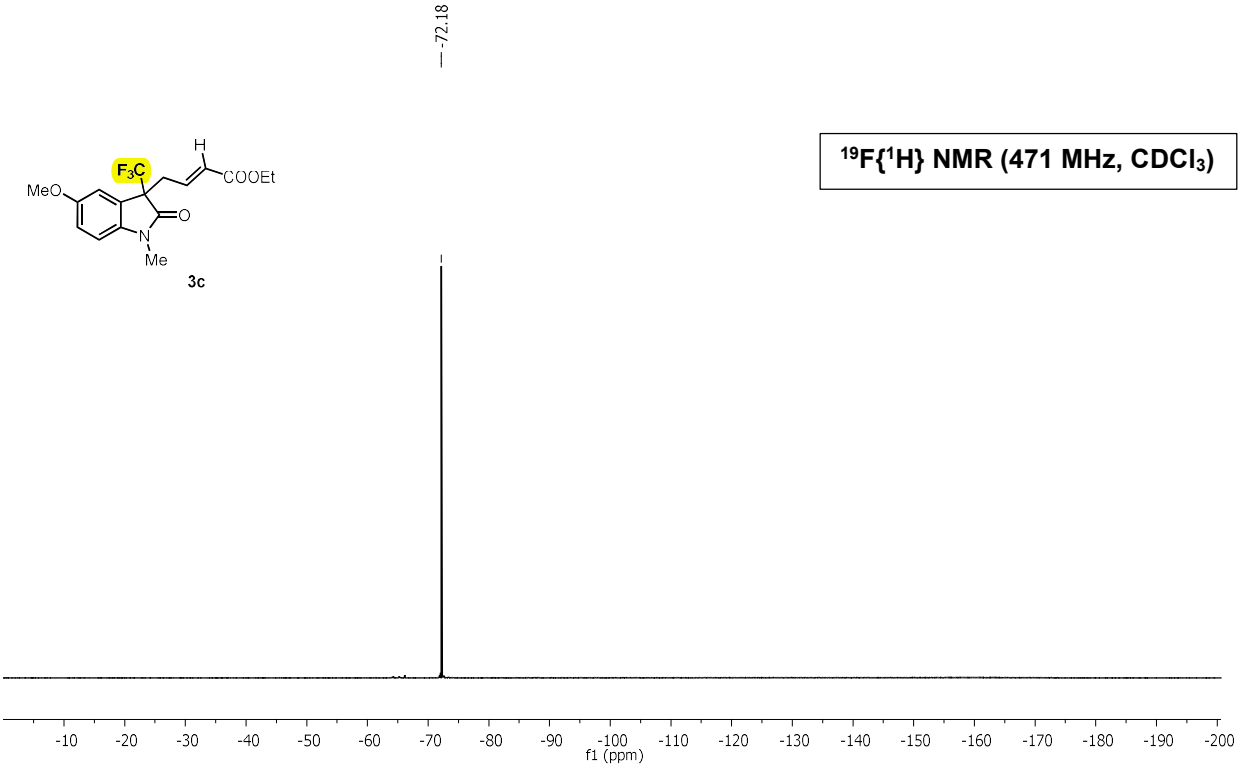
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

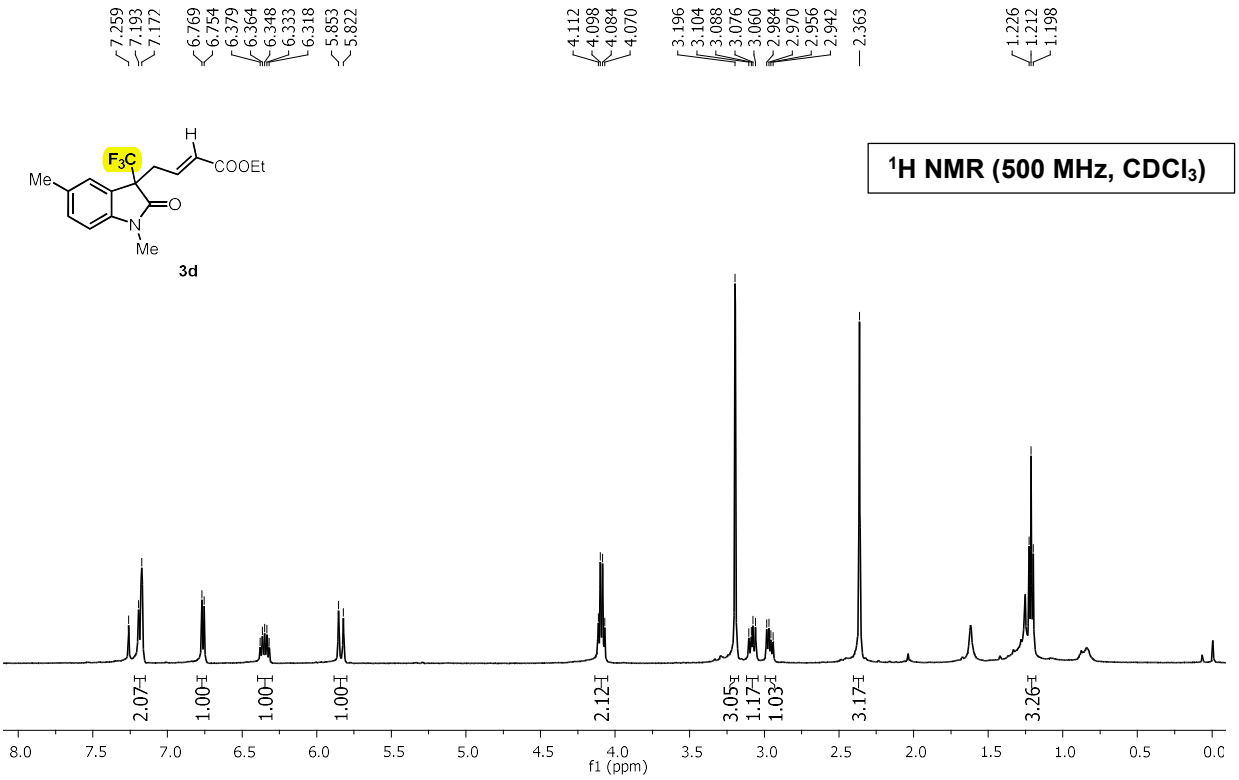


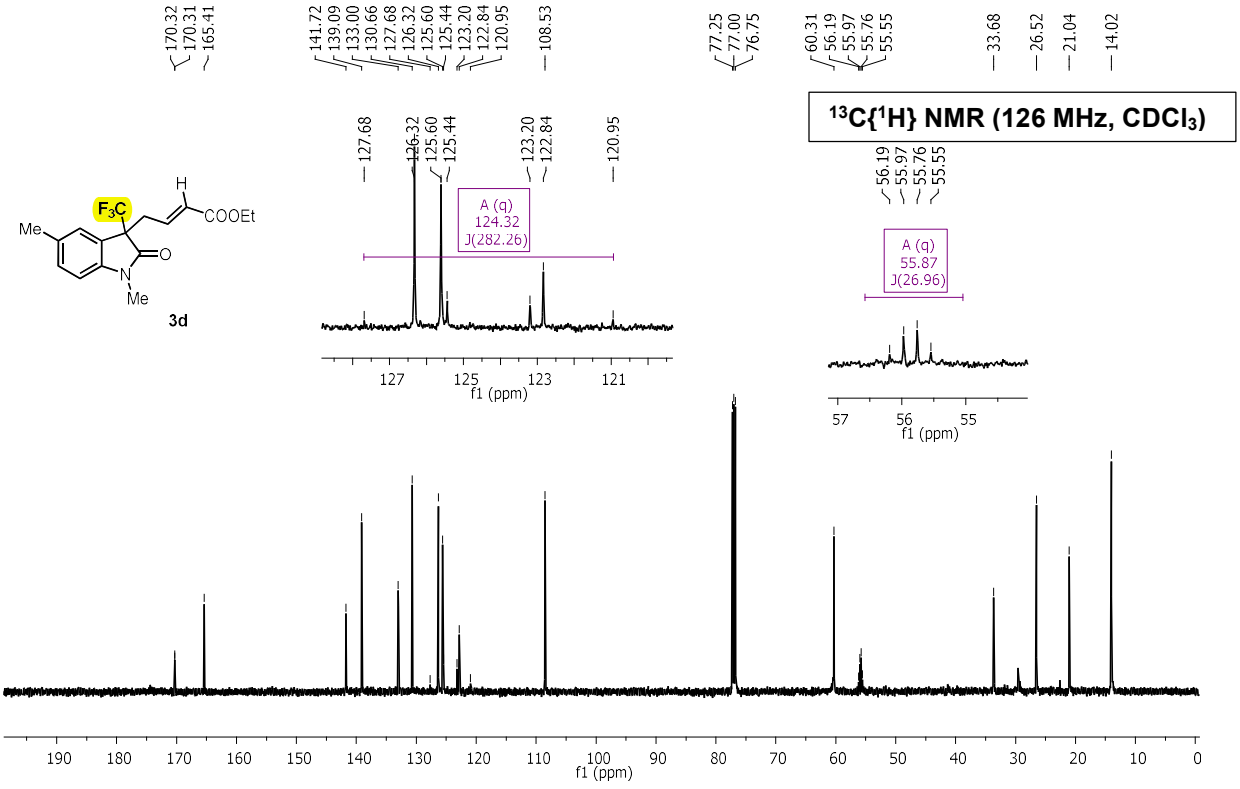
3c

^{1}H NMR (500 MHz, $CDCl_3$)

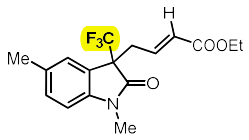

170.05
170.02
169.99
169.96
165.41
156.30
138.93
137.43
128.44
126.45
125.63
124.00
120.01
114.48
112.41
109.24
77.32
77.00
76.68
60.37
56.26
56.00
55.76
55.72
55.69
33.75
33.72
33.69
33.67
26.63
14.04
13C{1H} NMR (101 MHz, CDCl3)
F3C
H
COOEt
MeO
O
N
Me
3c
128.44
126.45
125.63
124.00
122.82
122.21
120.01
C (q)
124.22
J(282.46)
56.26
56.00
55.76
55.72
55.69
B (q)
56.12
J(28.93)
f1 (ppm)
f1 (ppm)
f1 (ppm)


-72.18
19F{1H} NMR (471 MHz, CDCl3)
F3C
H
COOEt
MeO
O
N
Me
3c
f1 (ppm)

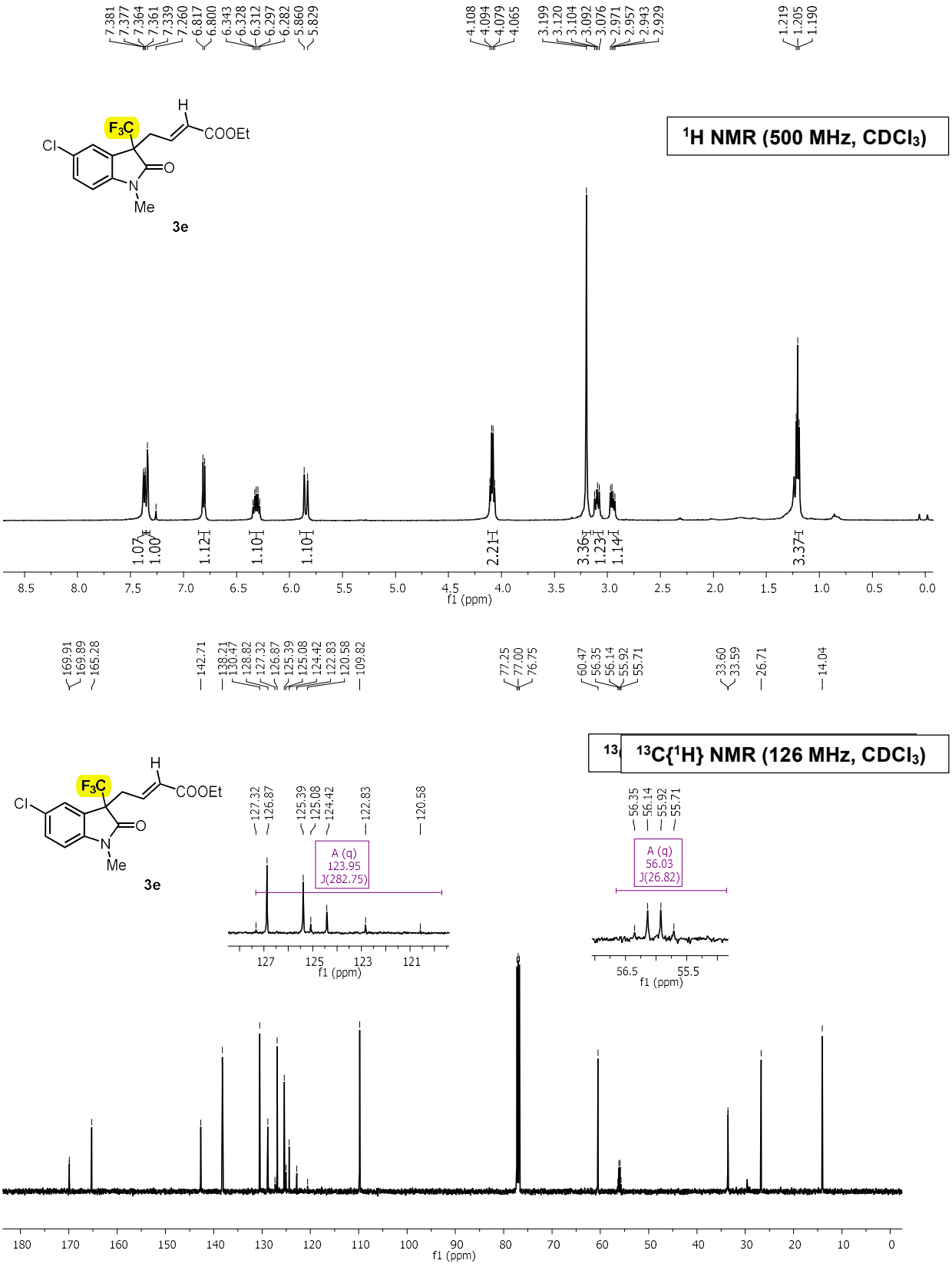

7.259
7.193
7.172
6.769
6.754
6.379
6.364
6.348
6.333
6.318
5.853
5.822
4.112
4.098
4.084
4.070
3.196
3.104
3.088
3.076
3.060
2.984
2.970
2.956
2.942
2.363
1.226
1.212
1.198
F3C
H
COOEt
Me
O
N
Me
3d
1H NMR (500 MHz, CDCl3)
2.07
1.00
1.00
1.00
2.12
3.05
1.17
1.03
3.17
3.26
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

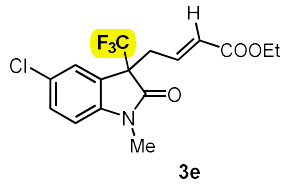

170.32
170.31
165.41
141.72
139.09
133.00
130.66
127.68
126.32
125.60
125.44
123.20
122.84
120.95
108.53
77.25
77.00
76.75
60.31
56.19
55.97
55.76
55.55
33.68
26.52
21.04
14.02
13C{1H} NMR (126 MHz, CDCl3)
F3C
H
COOEt
Me
O
N
Me
3d
127.68
126.32
125.60
125.44
123.20
122.84
120.95
A (q)
124.32
J(282.26)
127
125
123
121
f1 (ppm)
56.19
55.97
55.76
55.55
A (q)
55.87
J(26.96)
57
56
55
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



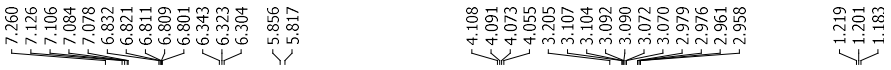
3d

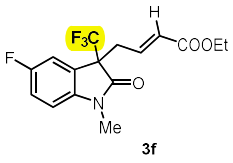

7.381
7.377
7.364
7.361
7.339
7.260
6.817
6.800
6.343
6.328
6.312
6.297
6.282
5.860
5.829
4.108
4.094
4.079
4.065
3.199
3.120
3.104
3.092
3.076
2.971
2.957
2.943
2.929
1.219
1.205
1.190
H
F3C
COOEt
Cl
O
N
Me
3e
1H NMR (500 MHz, CDCl3)
1.07
1.00
1.12
1.10
1.10
2.21
3.36
1.23
1.14
3.37
f1 (ppm)
169.91
169.89
165.28
142.71
138.21
130.47
128.82
127.32
126.87
125.39
125.08
124.42
122.83
120.58
109.82
77.25
77.00
76.75
60.47
56.35
56.14
55.92
55.71
33.60
33.59
26.71
14.04
13C{1H} NMR (126 MHz, CDCl3)
A (q)
123.95
J(282.75)
A (q)
56.03
J(26.82)
f1 (ppm)



3e

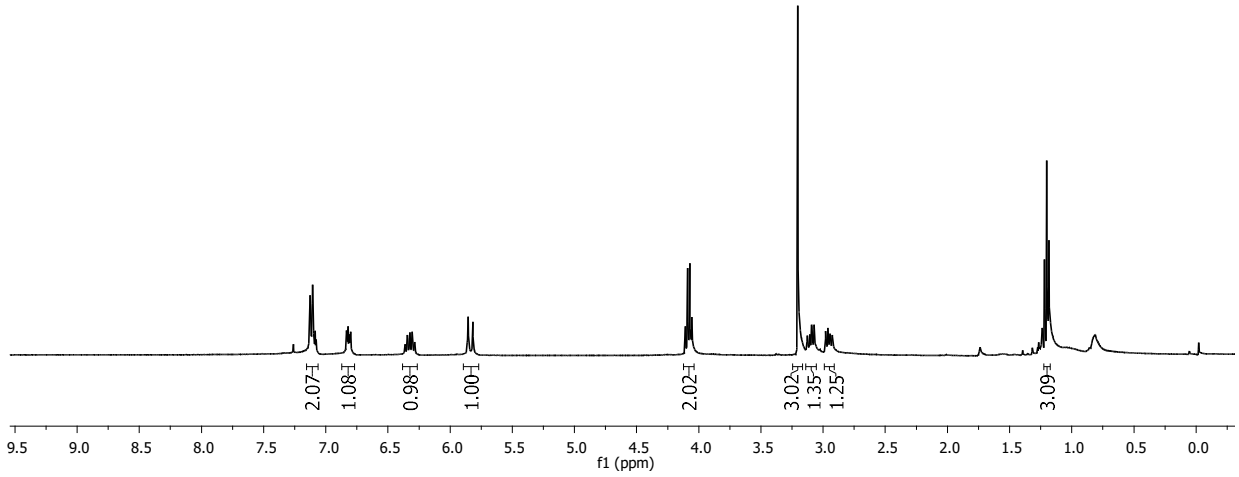
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

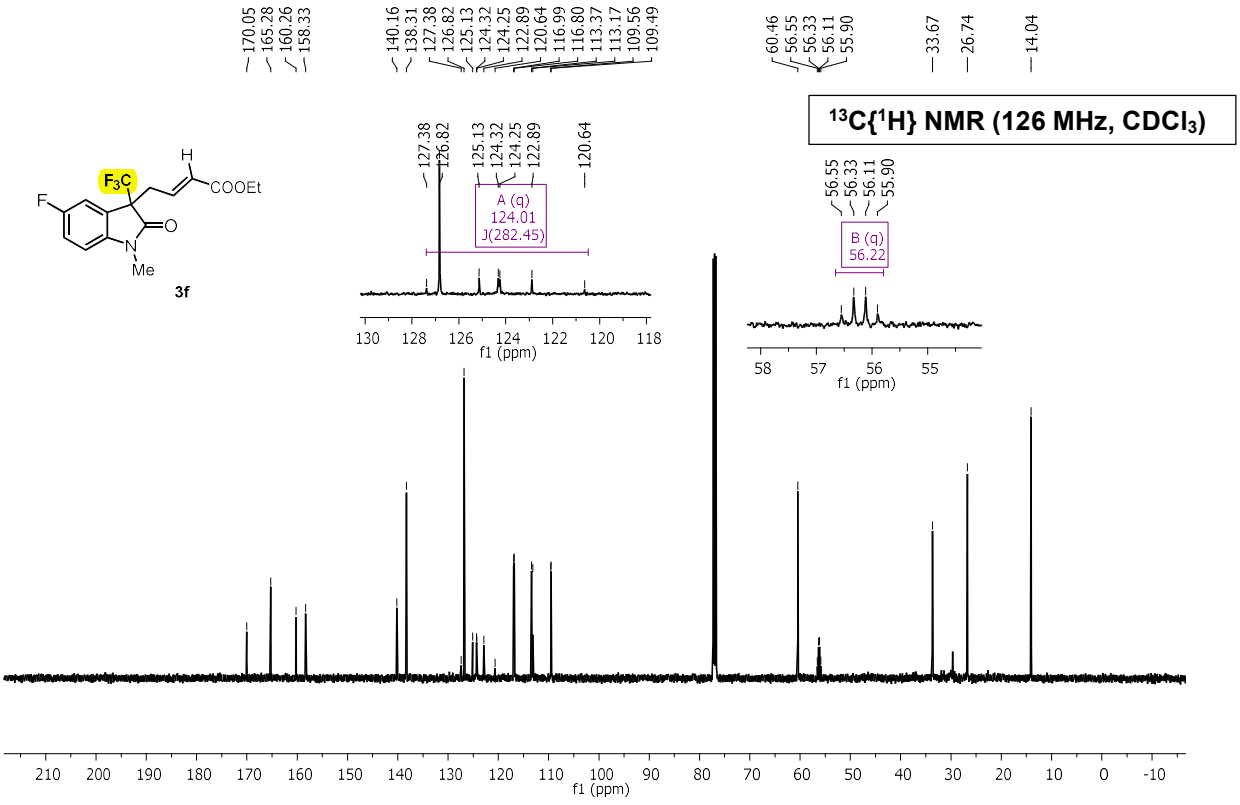




3f

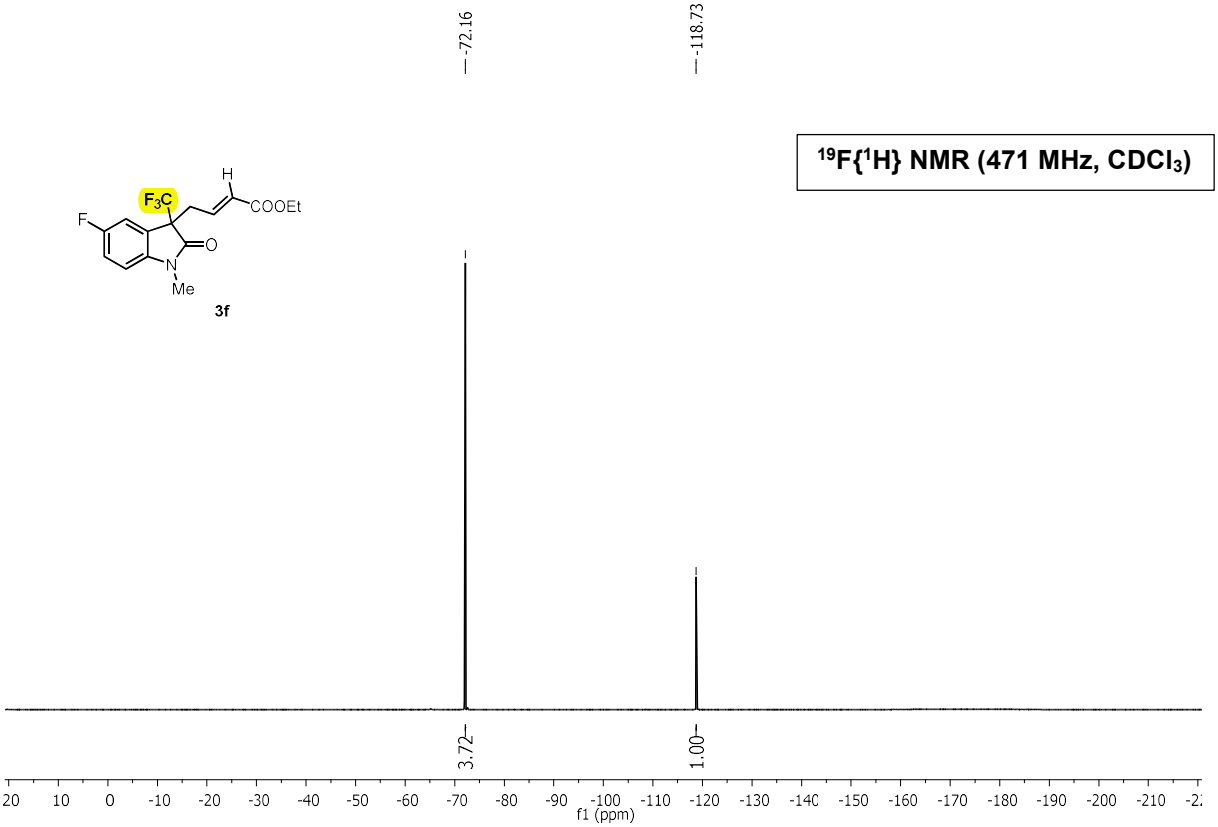
^{1}H NMR (400 MHz, $CDCl_3$)





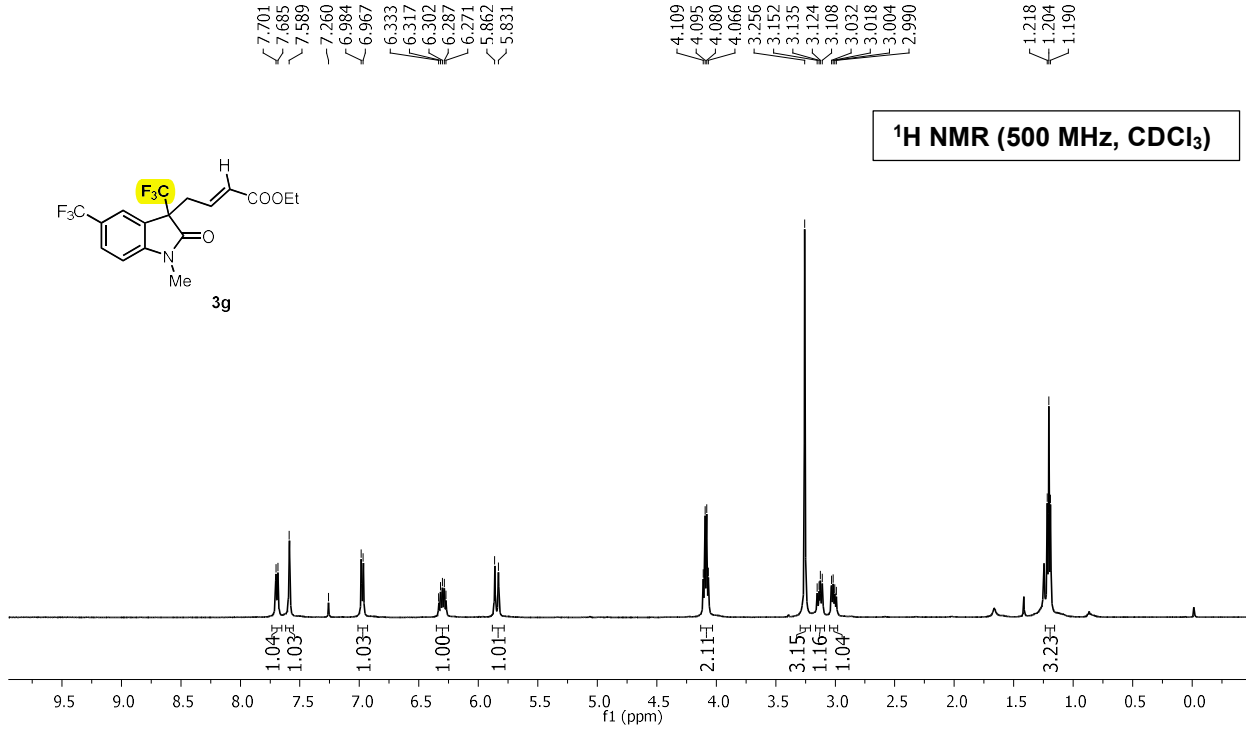
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

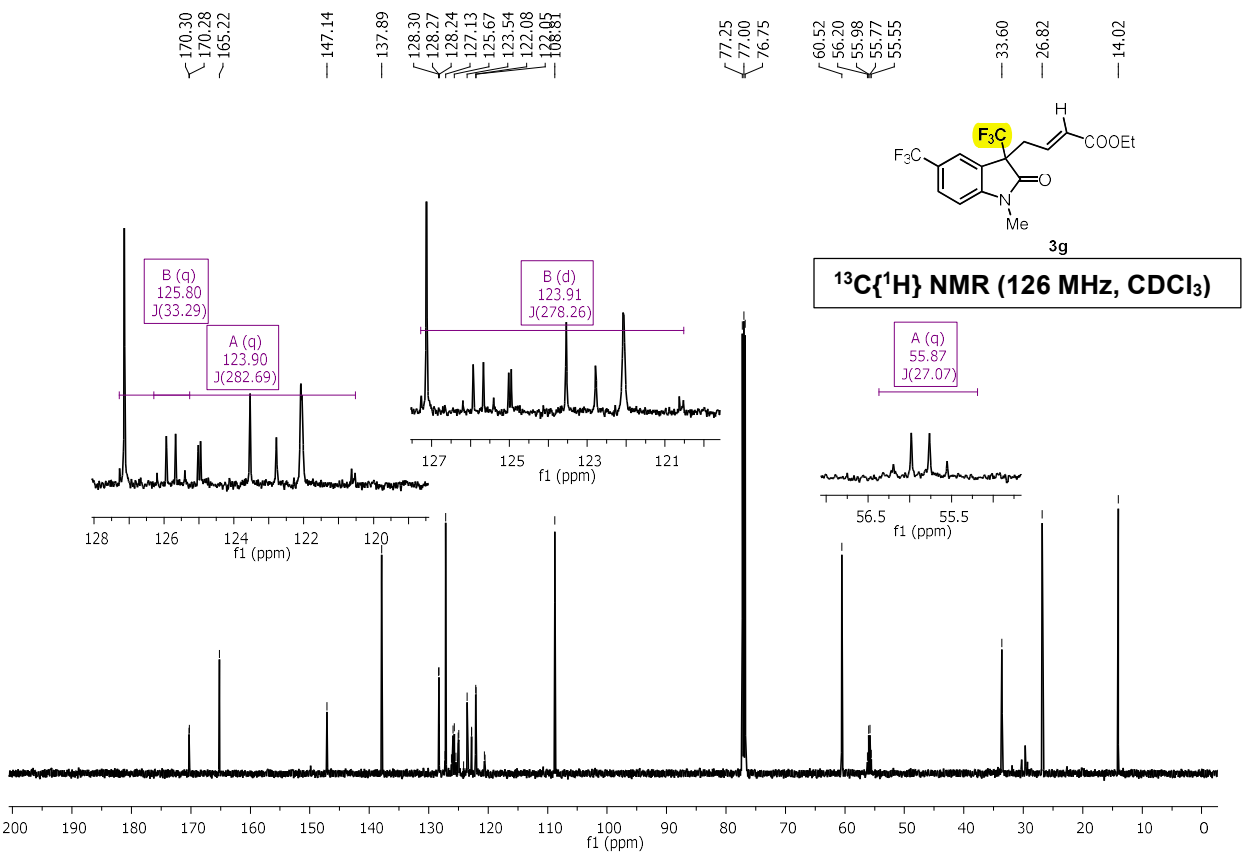
3f

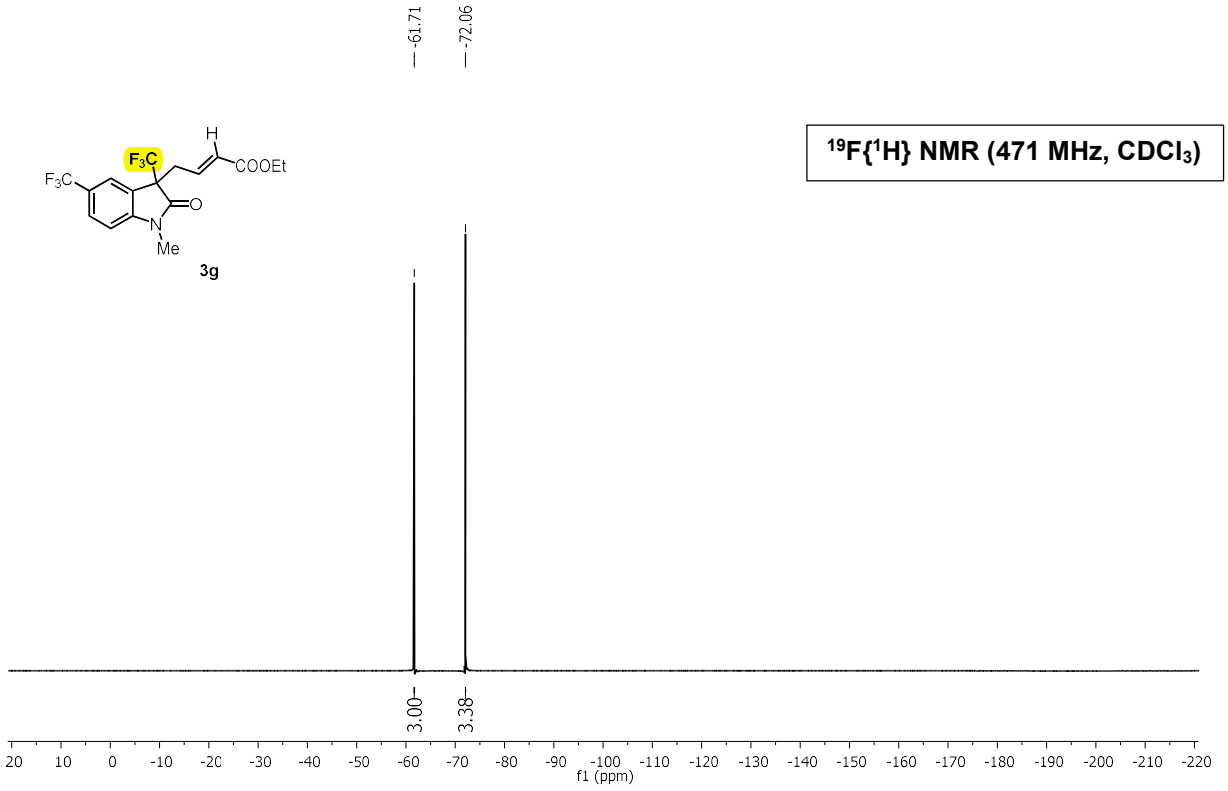


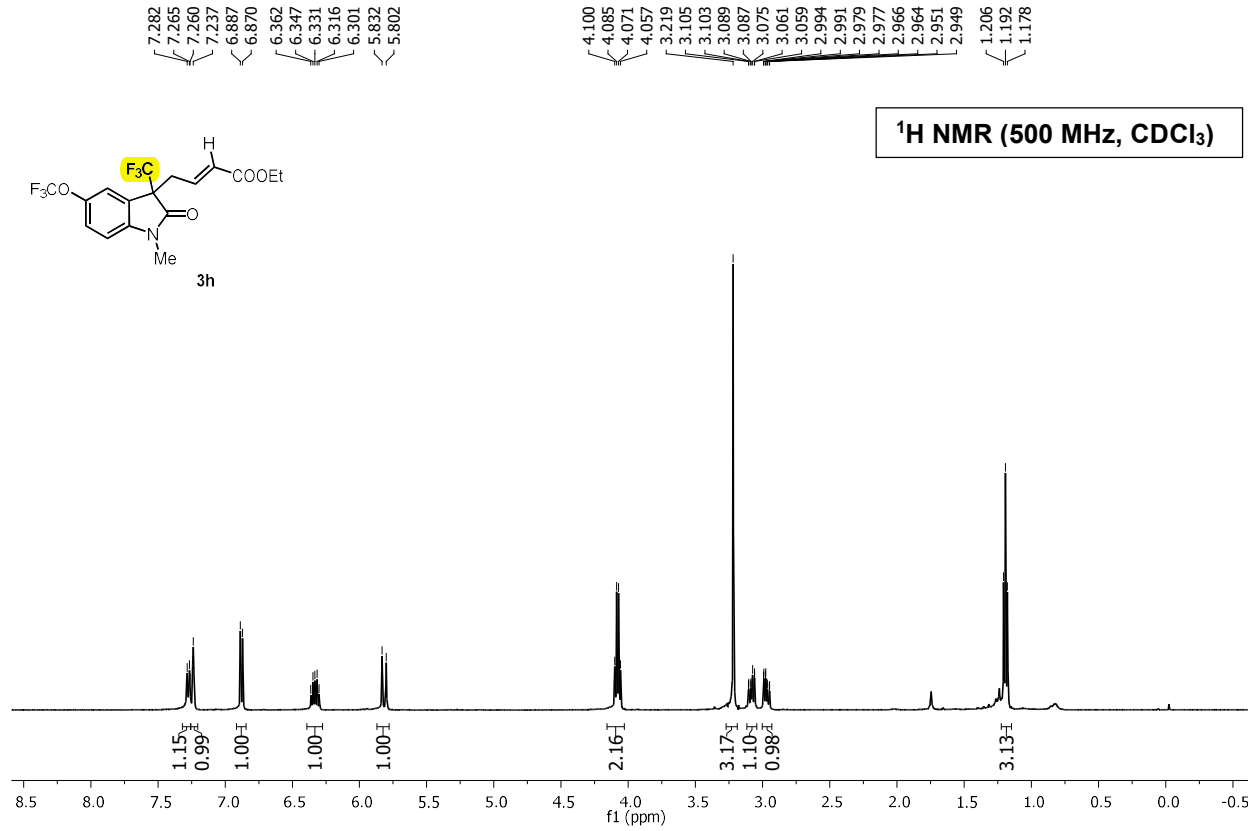
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

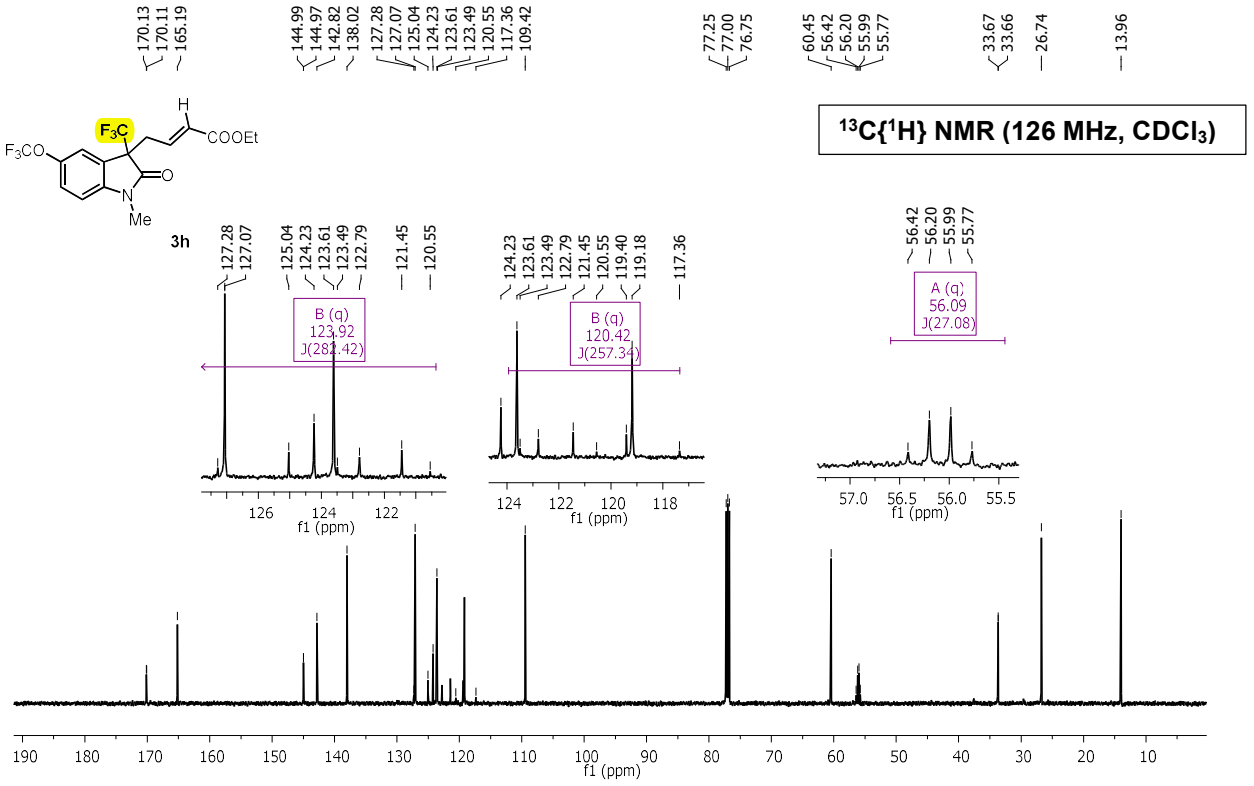
3f

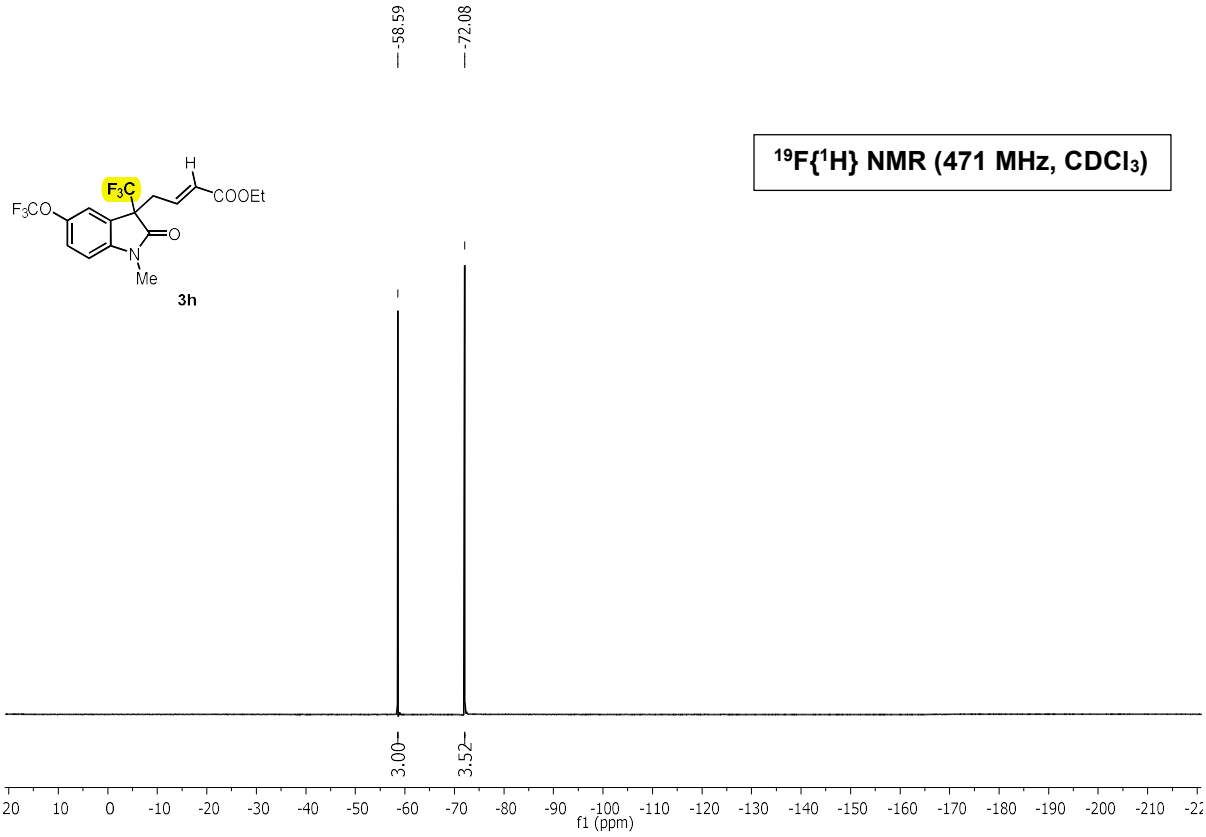

7.701
7.685
7.589
7.260
6.984
6.967
6.333
6.317
6.302
6.287
6.271
5.862
5.831
4.109
4.095
4.080
4.066
3.256
3.152
3.135
3.124
3.108
3.032
3.018
3.004
2.990
1.218
1.204
1.190
1H NMR (500 MHz, CDCl3)
F3C
H
COOEt
F3C
O
N
Me
3g
1.04
1.03
1.03
1.00
1.01
2.11
3.15
1.16
1.04
3.23
f1 (ppm)


170.30
170.28
165.22
147.14
137.89
128.30
128.27
128.24
127.13
125.67
123.54
122.08
122.05
108.81
77.25
77.00
76.75
60.52
56.20
55.98
55.77
55.55
33.60
26.82
14.02
F3C
H
COOEt
F3C
O
N
Me
3g
13C{1H} NMR (126 MHz, CDCl3)
B (q)
125.80
J(33.29)
A (q)
123.90
J(282.69)
B (d)
123.91
J(278.26)
A (q)
55.87
J(27.07)
f1 (ppm)

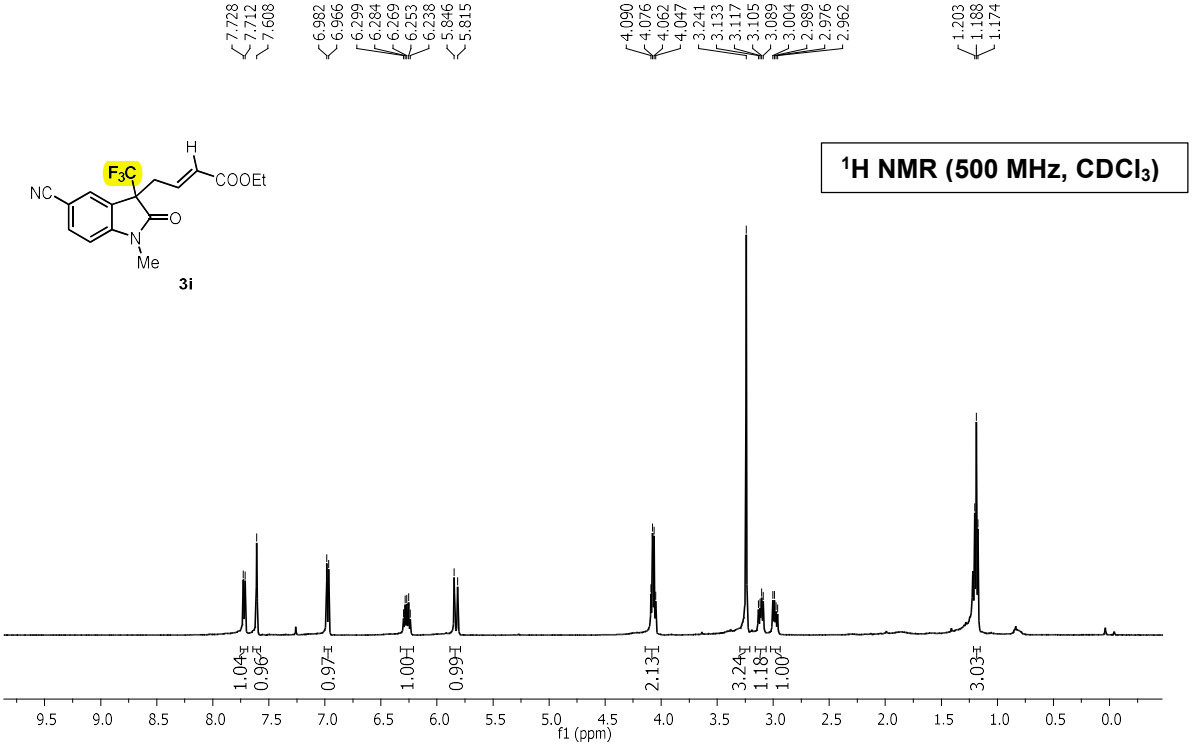

-61.71
-72.06
H
F3C
COOEt
F3C
O
N
Me
3g
19F{1H} NMR (471 MHz, CDCl3)
3.00
3.38
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)


7.282
7.265
7.260
7.237
6.887
6.870
6.362
6.347
6.331
6.316
6.301
5.832
5.802
4.100
4.085
4.071
4.057
3.219
3.105
3.103
3.089
3.087
3.075
3.061
3.059
2.994
2.991
2.979
2.977
2.966
2.964
2.951
2.949
1.206
1.192
1.178
1H NMR (500 MHz, CDCl3)
F3C
H
COOEt
F3CO
O
N
Me
3h
1.15
0.99
1.00
1.00
1.00
2.16
3.17
1.10
0.98
3.13
f1 (ppm)

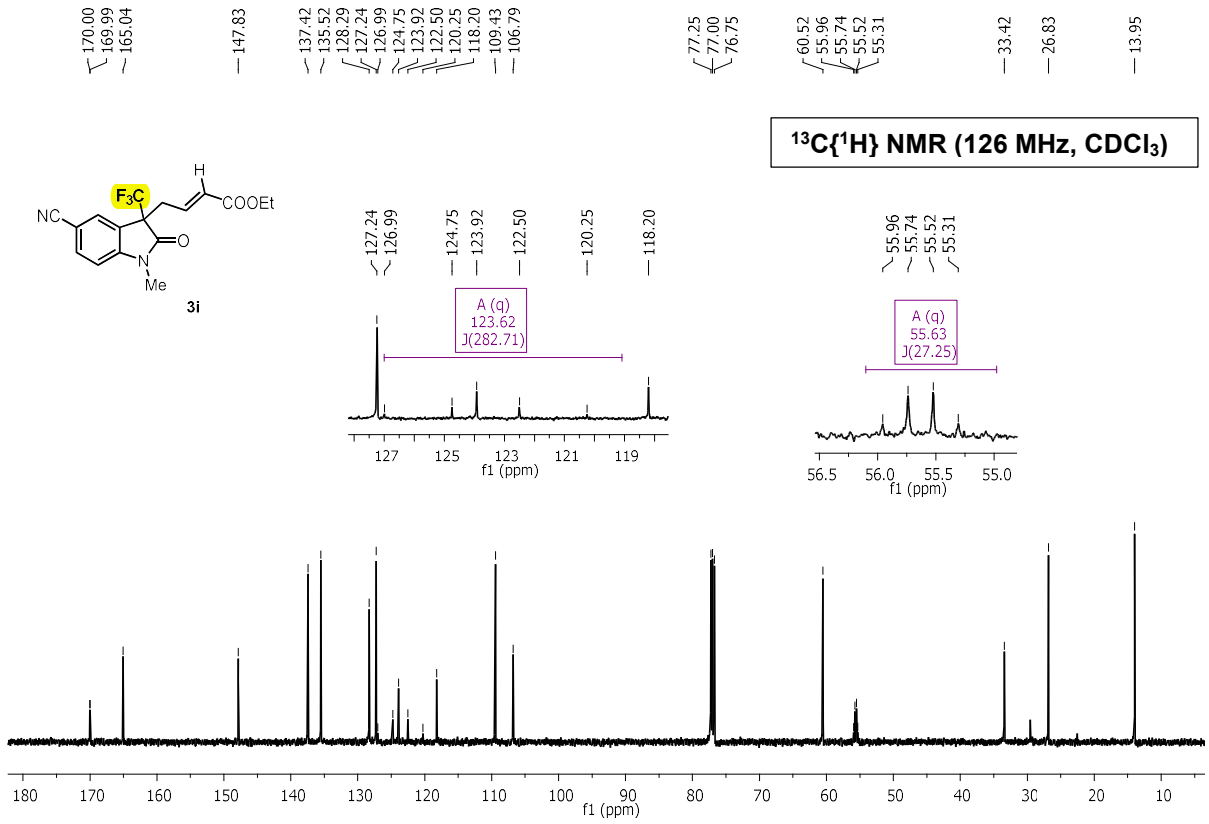

170.13
170.11
165.19
144.99
144.97
142.82
138.02
127.28
127.07
125.04
124.23
123.61
123.49
120.55
117.36
109.42
77.25
77.00
76.75
60.45
56.42
56.20
55.99
55.77
33.67
33.66
26.74
13.96
13C{1H} NMR (126 MHz, CDCl3)
F3C
H
COOEt
F3CO
O
N
Me
3h
B (q)
123.92
J(282.42)
B (q)
120.42
J(257.34)
A (q)
56.09
J(27.08)
f1 (ppm)

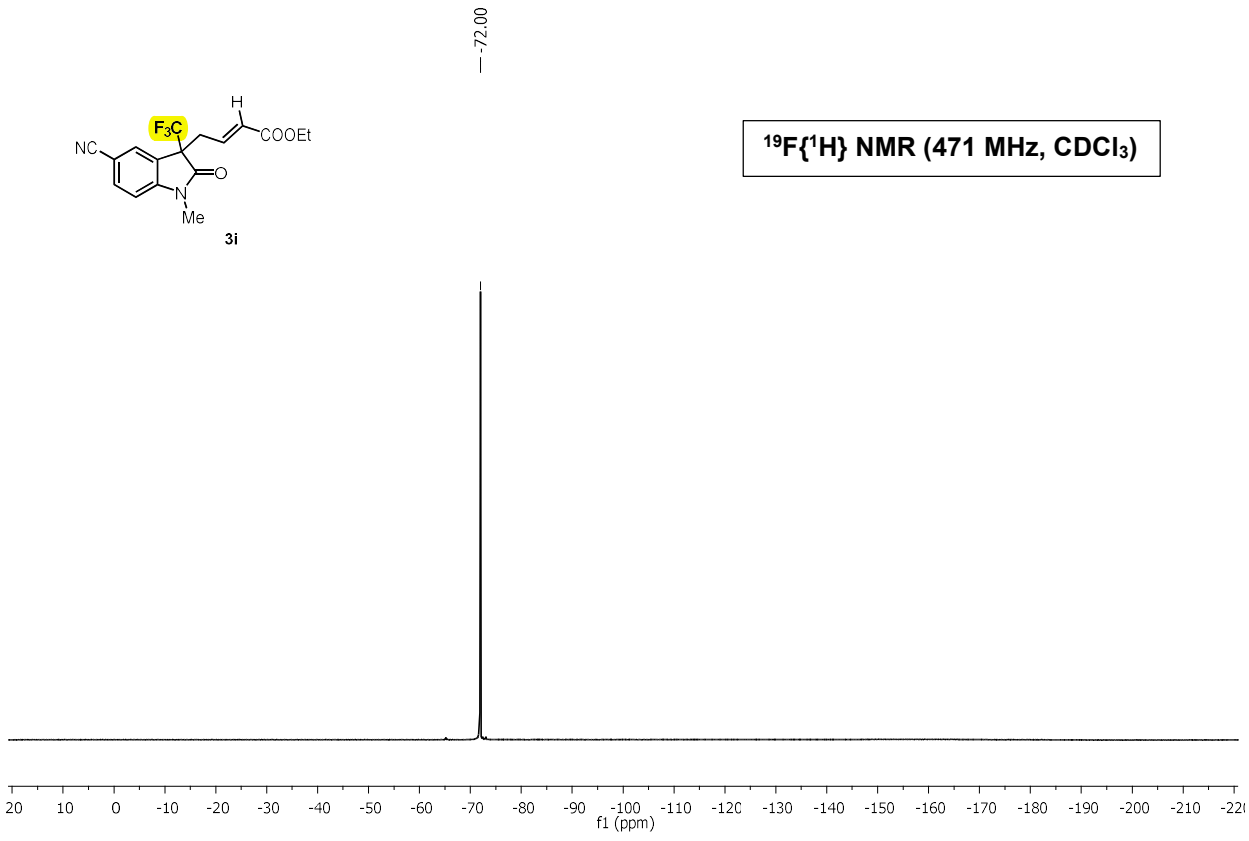


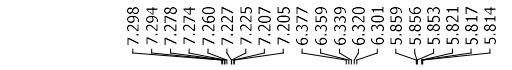
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



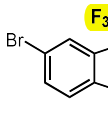
^{1}H NMR (500 MHz, $CDCl_3$)


170.00
169.99
165.04
147.83
137.42
135.52
128.29
127.24
126.99
124.75
123.92
122.50
120.25
118.20
109.43
106.79
77.25
77.00
76.75
60.52
55.96
55.74
55.52
55.31
33.42
26.83
13.95
13C{1H} NMR (126 MHz, CDCl3)
F3C
H
COOEt
NC
O
N
Me
3i
127.24
126.99
124.75
123.92
122.50
120.25
118.20
A (q)
123.62
J(282.71)
127
125
123
121
119
f1 (ppm)
55.96
55.74
55.52
55.31
A (q)
55.63
J(27.25)
56.5
56.0
55.5
55.0
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

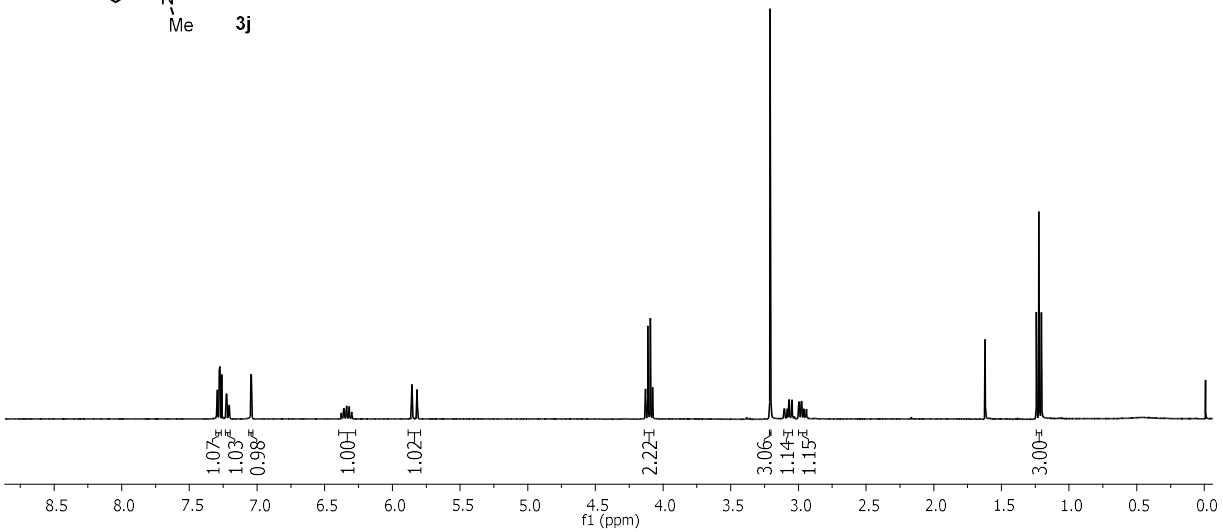

-72.00
F3C
H
COOEt
NC
O
N
Me
3i
19F{1H} NMR (471 MHz, CDCl3)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

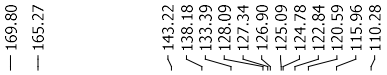


^{1}H NMR (400 MHz, $CDCl_3$)

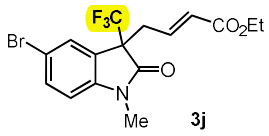


3j

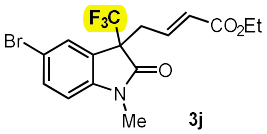




^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

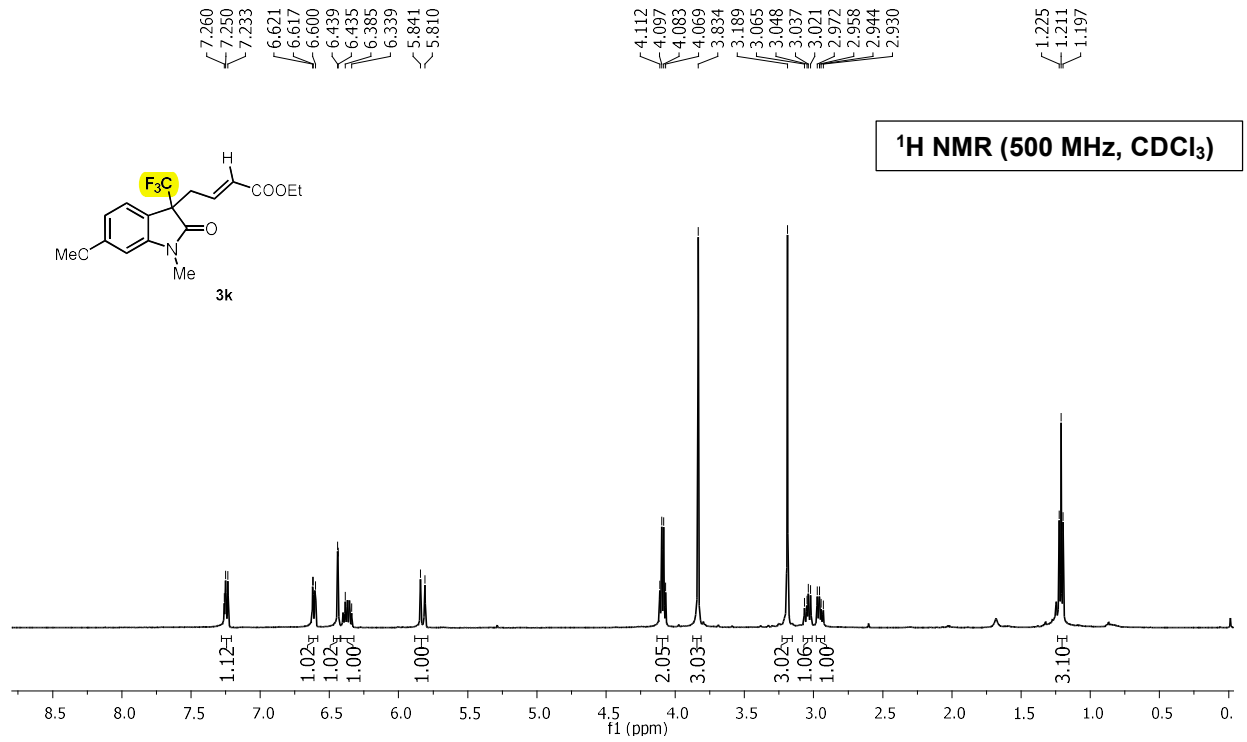


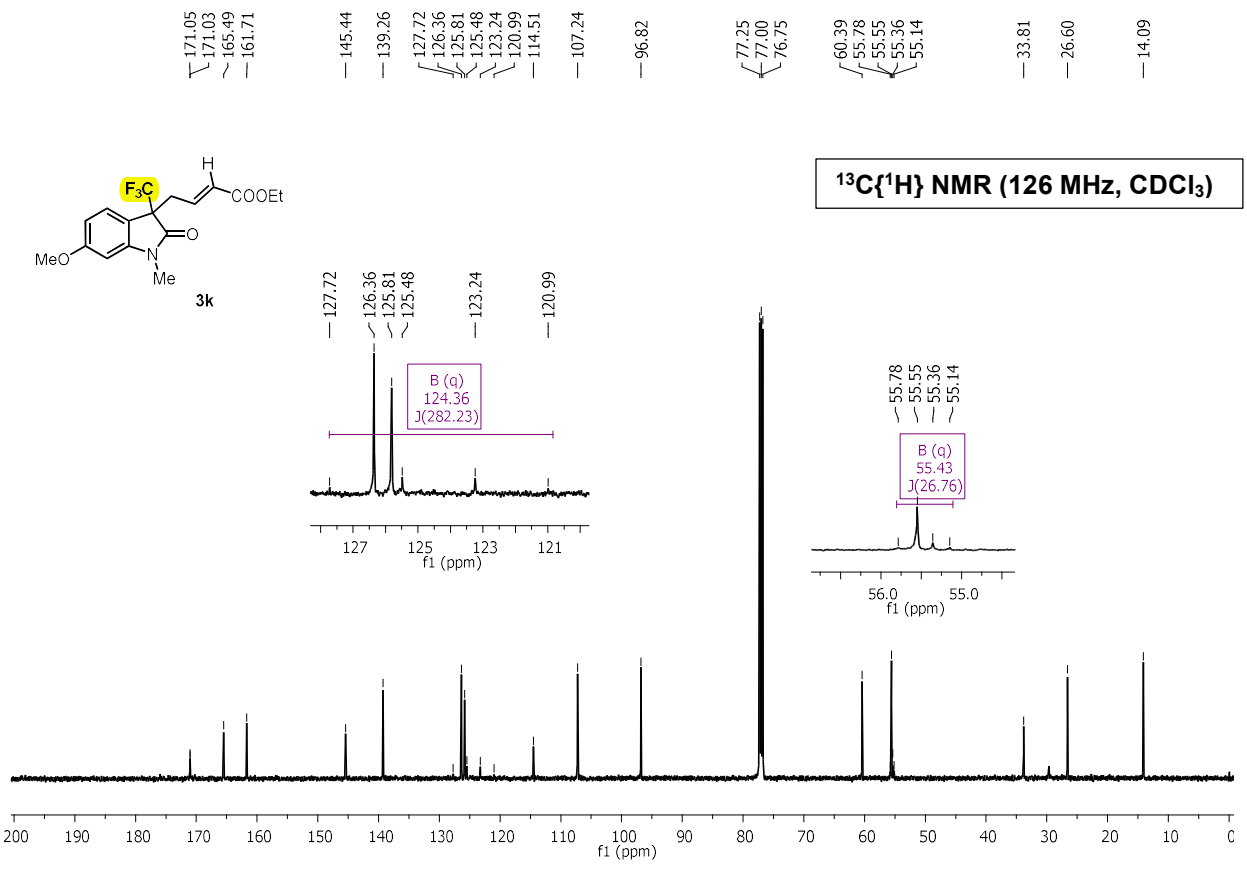
3j



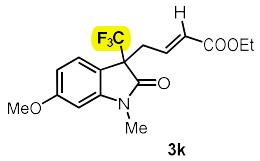
3j

$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)


7.260
7.250
7.233
6.621
6.617
6.600
6.439
6.435
6.385
6.339
5.841
5.810
4.112
4.097
4.083
4.069
3.834
3.189
3.065
3.048
3.037
3.021
2.972
2.958
2.944
2.930
1.225
1.211
1.197
1H NMR (500 MHz, CDCl3)
F3C
H
COOEt
O
MeO
N
Me
3k
1.12
1.02
1.02
1.00
1.00
2.05
3.03
3.02
1.06
1.00
3.10
f1 (ppm)

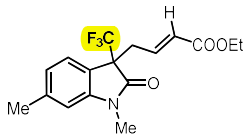

171.05
171.03
165.49
161.71
145.44
139.26
127.72
126.36
125.81
125.48
123.24
120.99
114.51
107.24
96.82
77.25
77.00
76.75
60.39
55.78
55.55
55.36
55.14
33.81
26.60
14.09
13C{1H} NMR (126 MHz, CDCl3)
F3C
H
COOEt
O
MeO
N
Me
3k
127.72
126.36
125.81
125.48
123.24
120.99
B (q)
124.36
J(282.23)
127
125
123
121
f1 (ppm)
55.78
55.55
55.36
55.14
B (q)
55.43
J(26.76)
56.0
55.0
f1 (ppm)
f1 (ppm)

$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

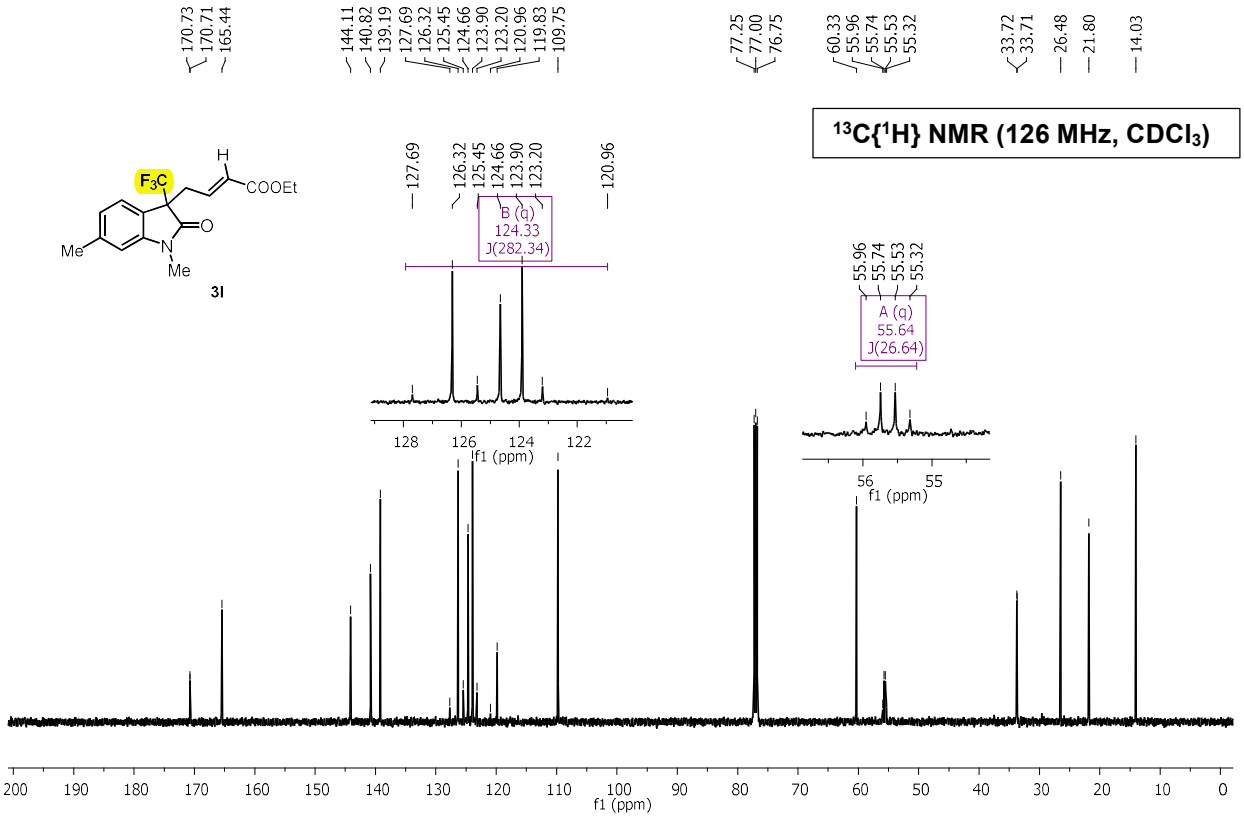


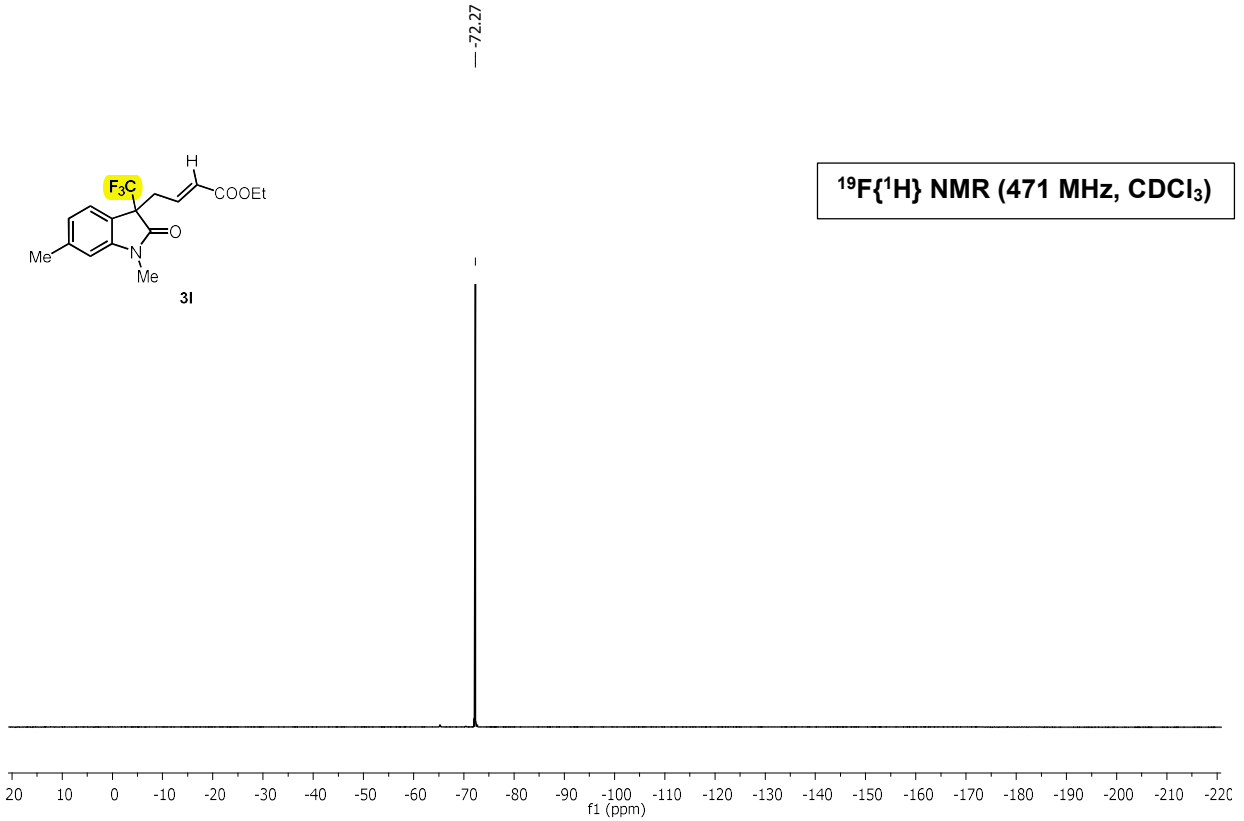
3k

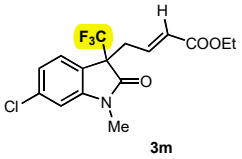
^{1}H NMR (500 MHz, $CDCl_3$)



3l

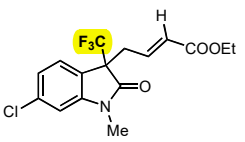

170.73
170.71
165.44
144.11
140.82
139.19
127.69
126.32
125.45
124.66
123.90
123.20
120.96
119.83
109.75
77.25
77.00
76.75
60.33
55.96
55.74
55.53
55.32
33.72
33.71
26.48
21.80
14.03
13C{1H} NMR (126 MHz, CDCl3)
F3C
H
COOEt
O
N
Me
Me
3l
B (q)
124.33
J(282.34)
A (q)
55.64
J(26.64)
f1 (ppm)


-72.27
19F{1H} NMR (471 MHz, CDCl3)
F3C
H
COOEt
O
N
Me
Me
3l
f1 (ppm)



3m

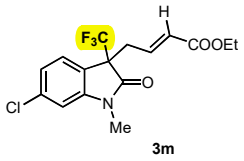
^{1}H NMR (400 MHz, $CDCl_3$)



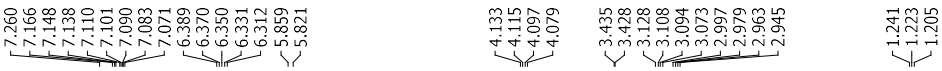
3m

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)

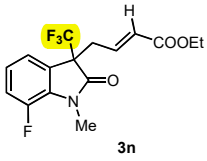
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



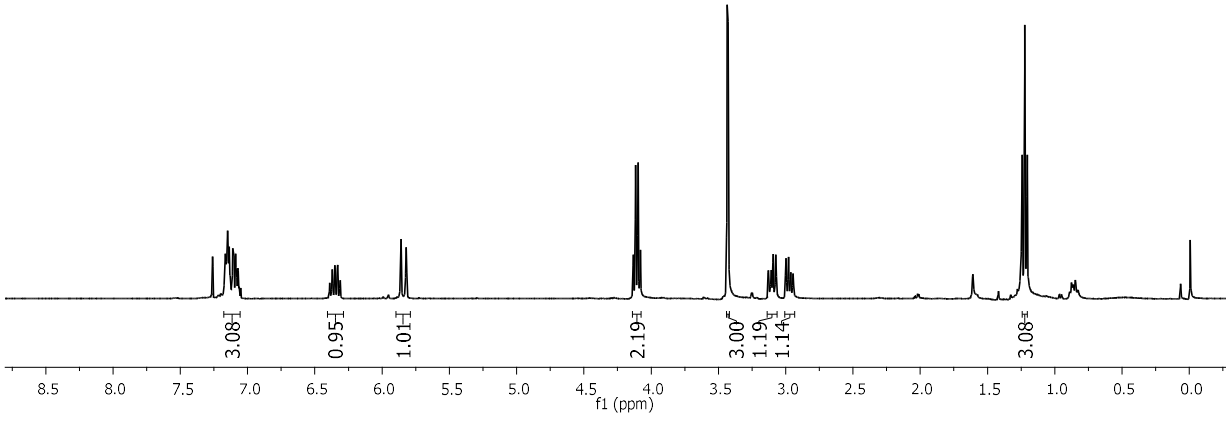
3m

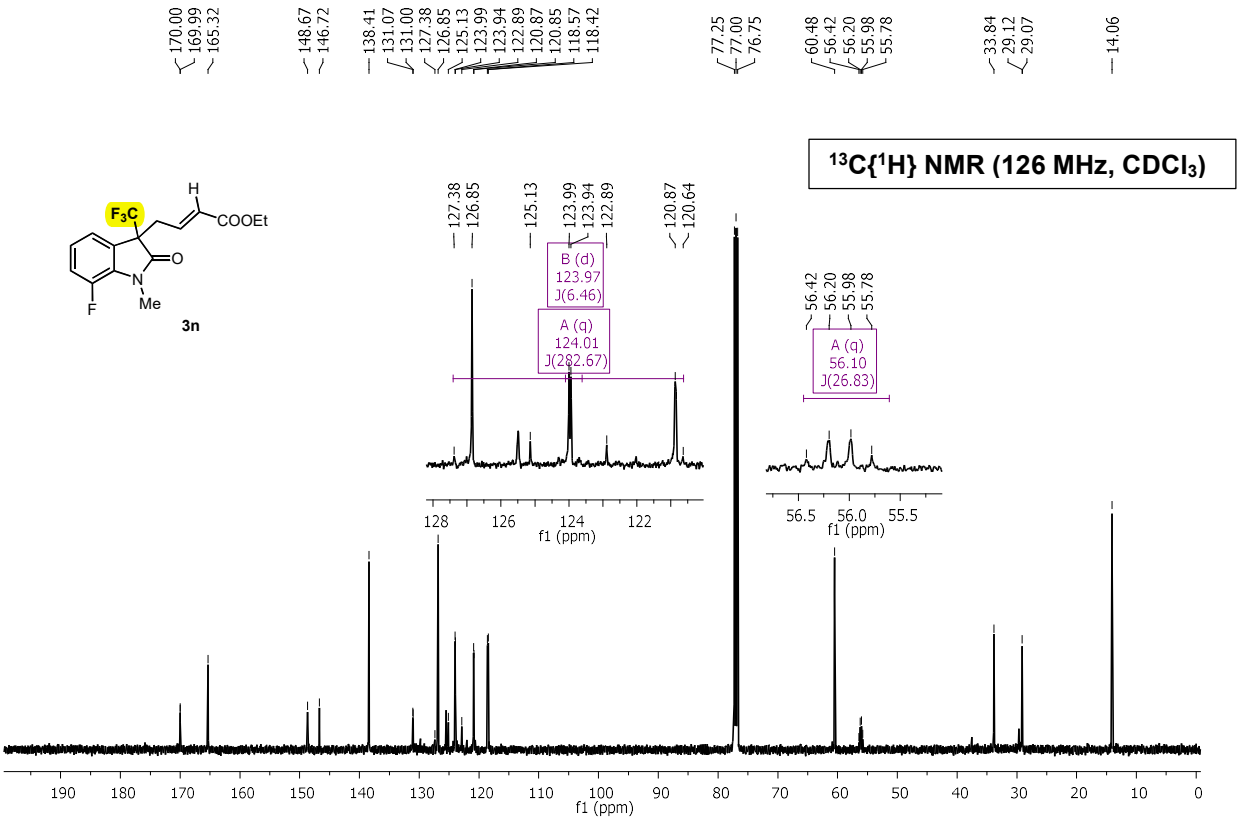


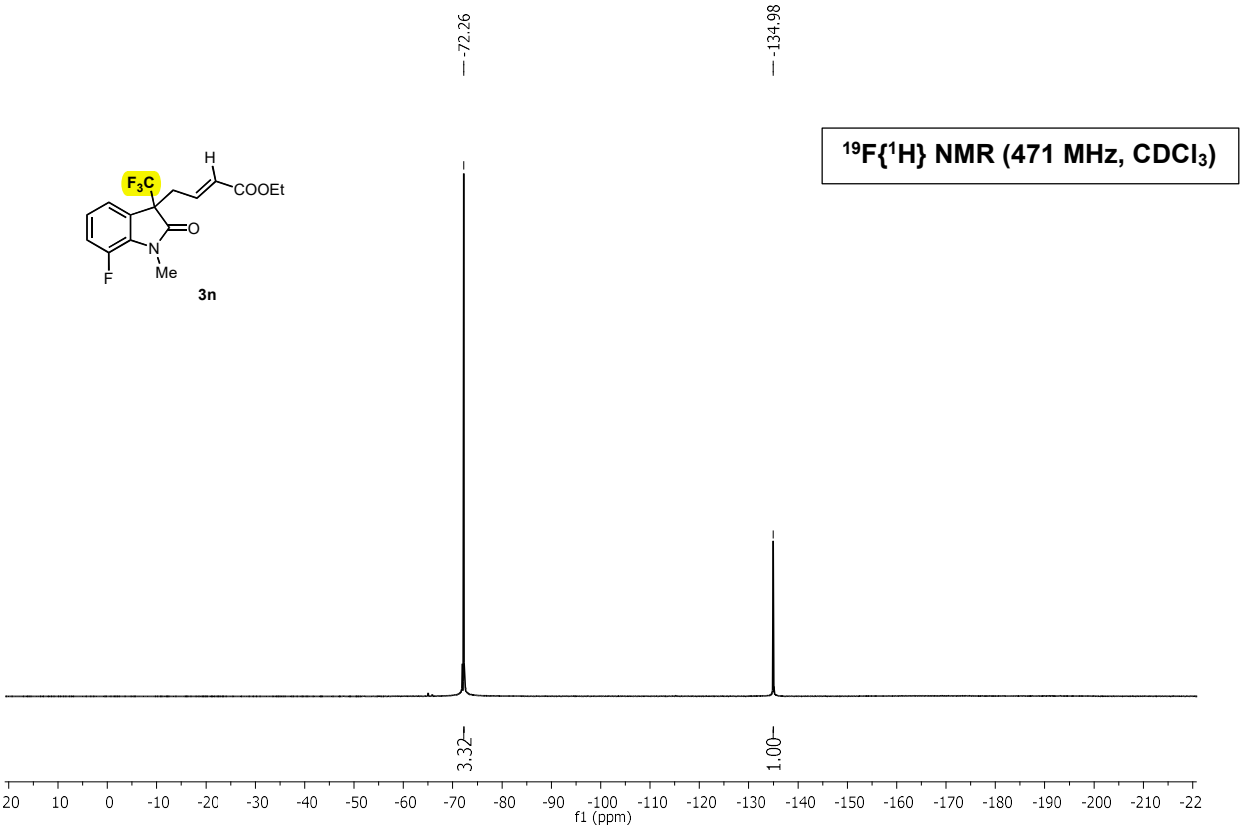
^{1}H NMR (400 MHz, $CDCl_3$)



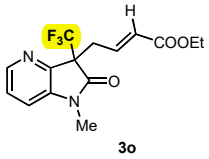
3n




170.00
169.99
165.32
148.67
146.72
138.41
131.07
131.00
127.38
126.85
125.13
123.99
123.94
122.89
120.87
120.85
118.57
118.42
77.25
77.00
76.75
60.48
56.42
56.20
55.98
55.78
33.84
29.12
29.07
14.06
13C{1H} NMR (126 MHz, CDCl3)
F3C
H
COOEt
O
N
Me
F
3n
127.38
126.85
125.13
123.99
123.94
122.89
120.87
120.64
B (d)
123.97
J(6.46)
A (q)
124.01
J(282.67)
56.42
56.20
55.98
55.78
A (q)
56.10
J(26.83)
128
126
124
122
f1 (ppm)
56.5
56.0
55.5
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

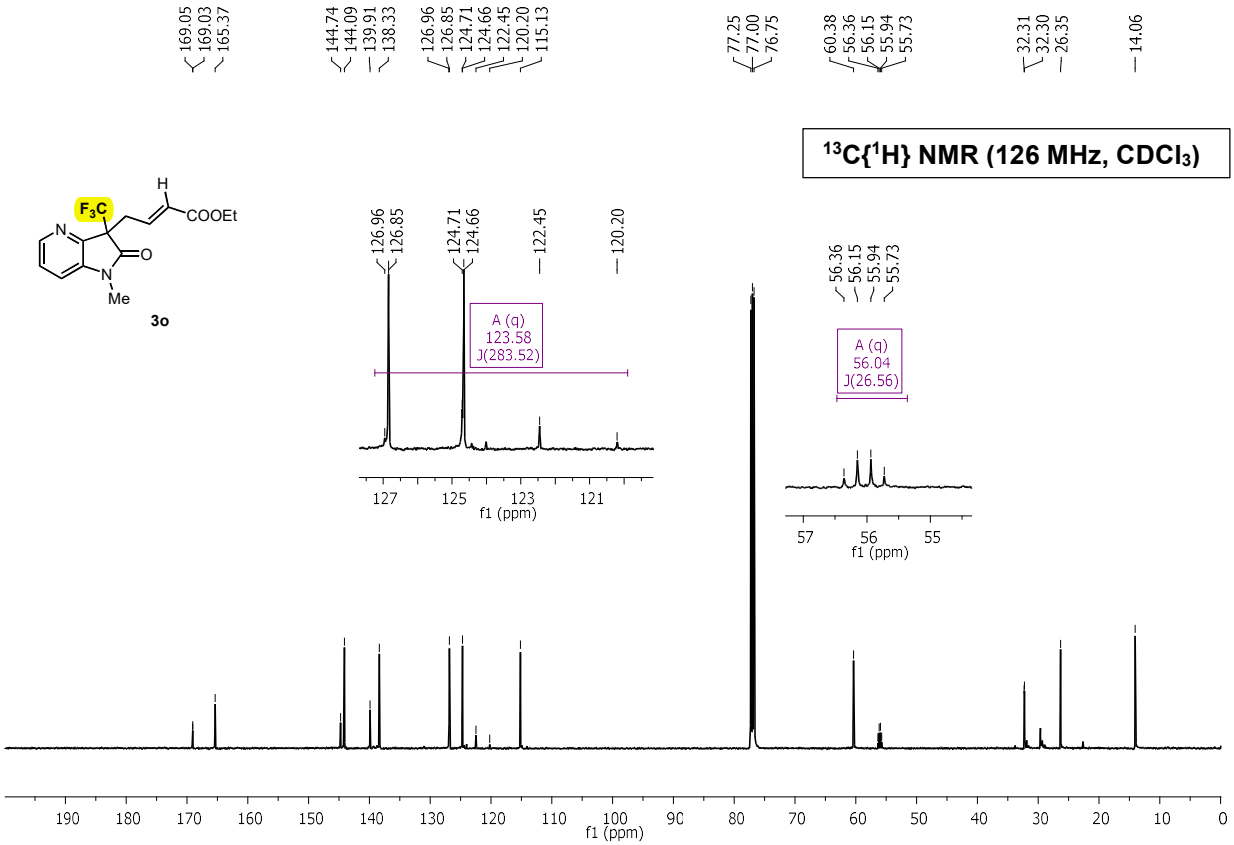

-72.26
-134.98
19F{1H} NMR (471 MHz, CDCl3)
F3C
H
COOEt
O
N
Me
F
3n
3.32
1.00
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-22
f1 (ppm)

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



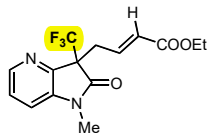
3o

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



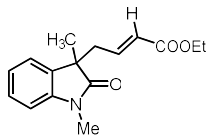
H
F3C
COOEt
N
O
N
Me

3o



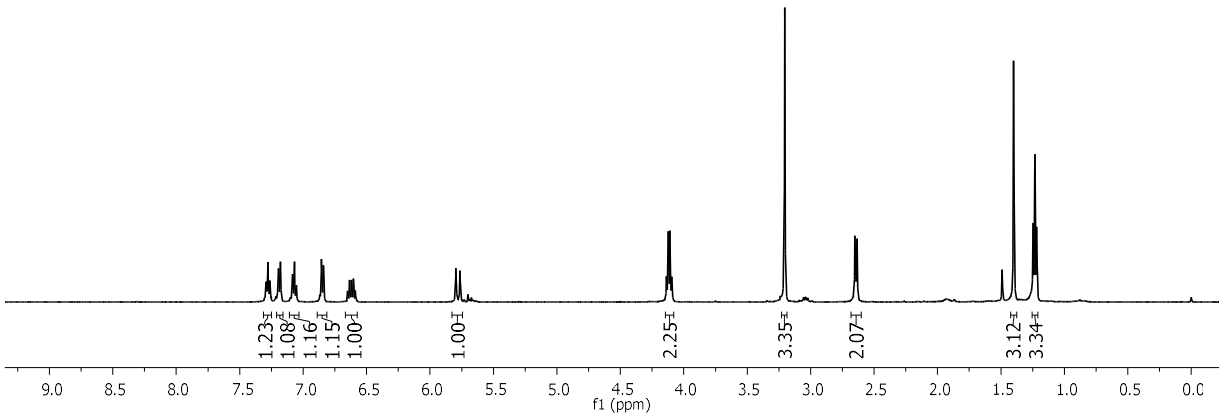
3o

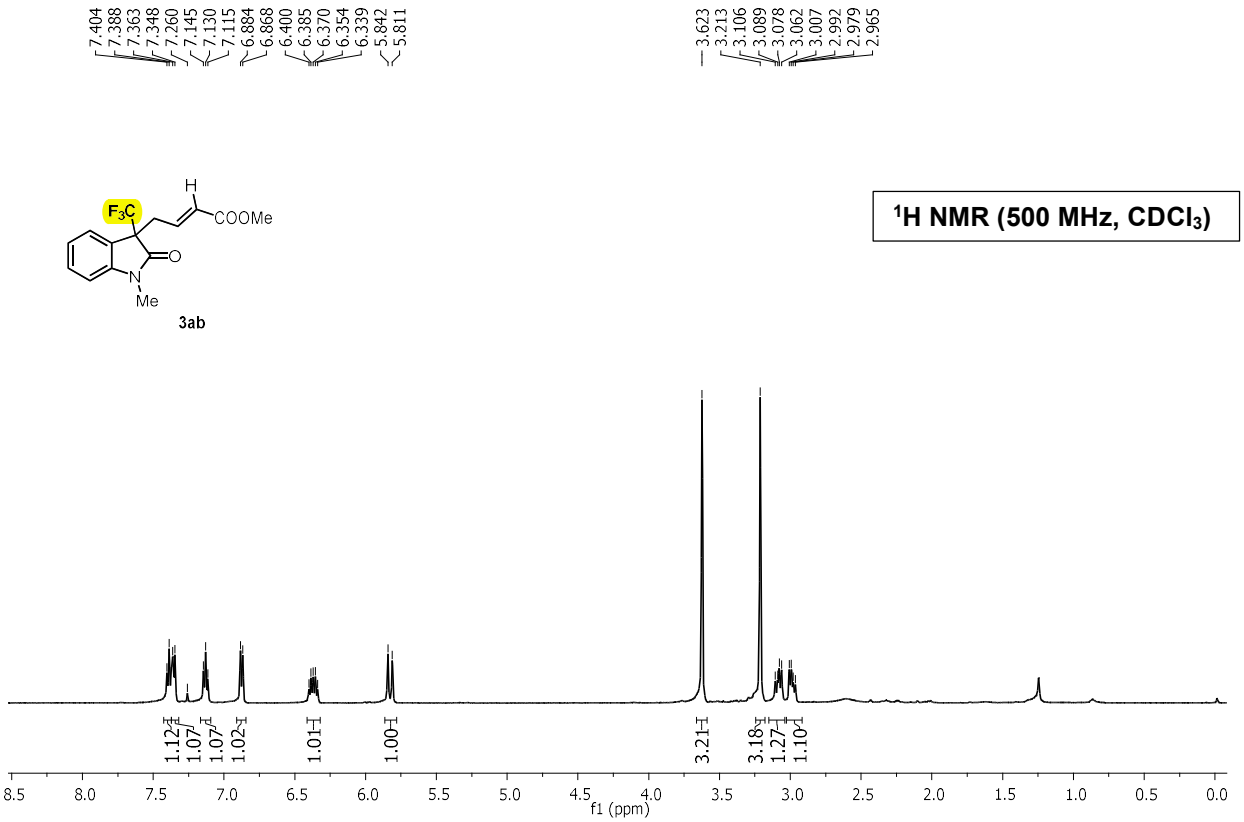
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

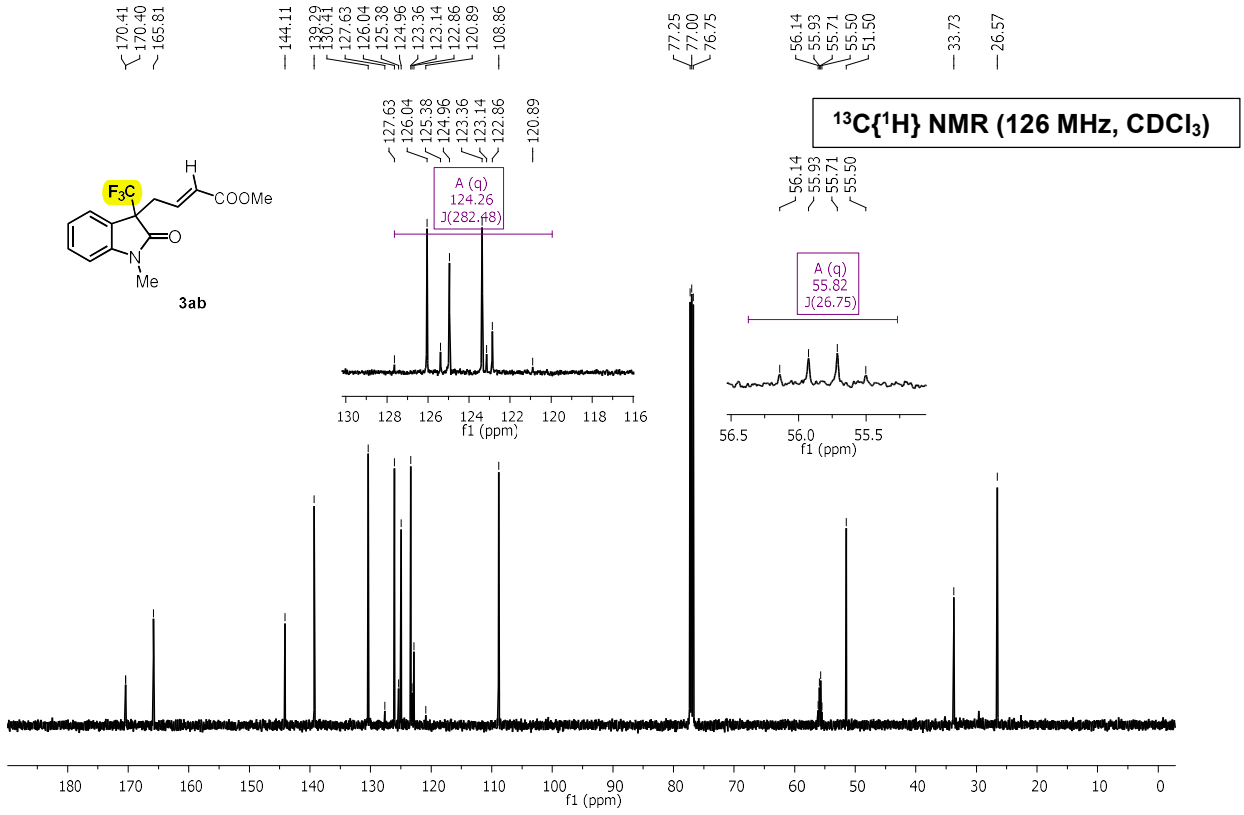


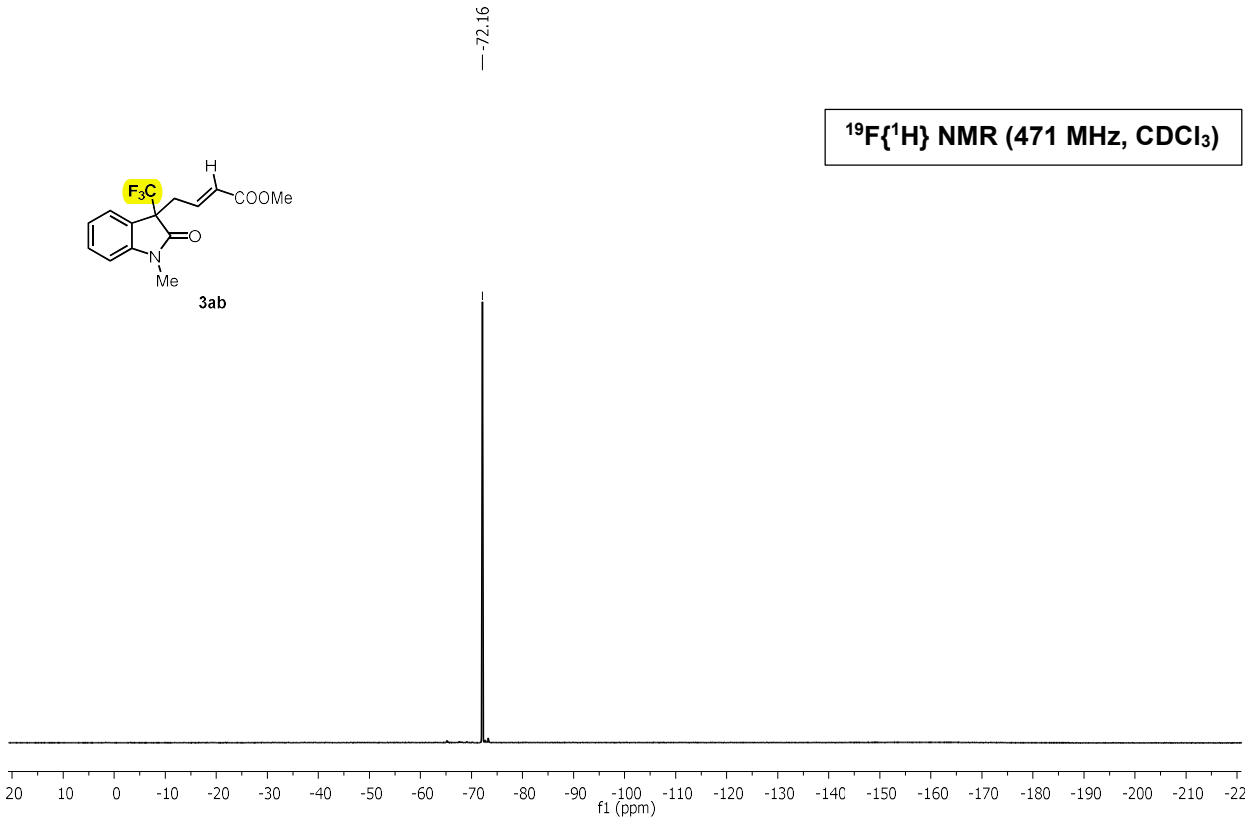
3x

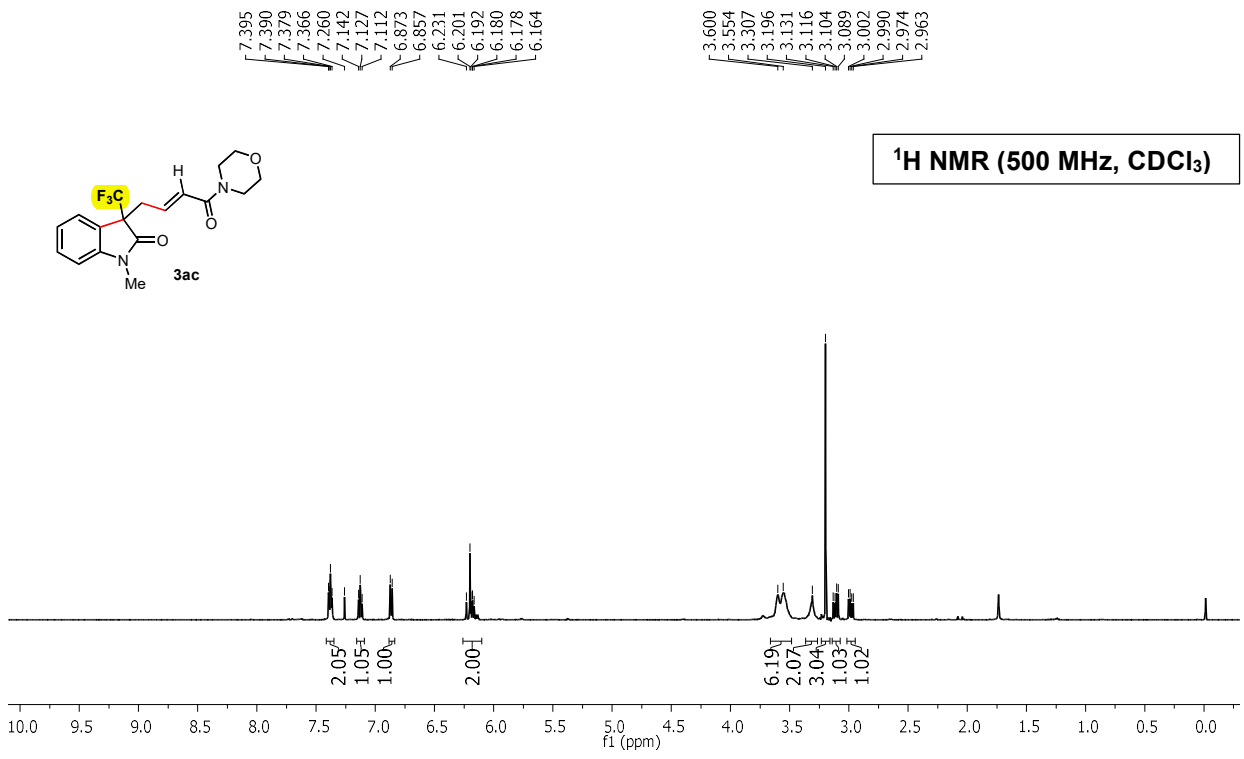
^{1}H NMR (500 MHz, $CDCl_3$)

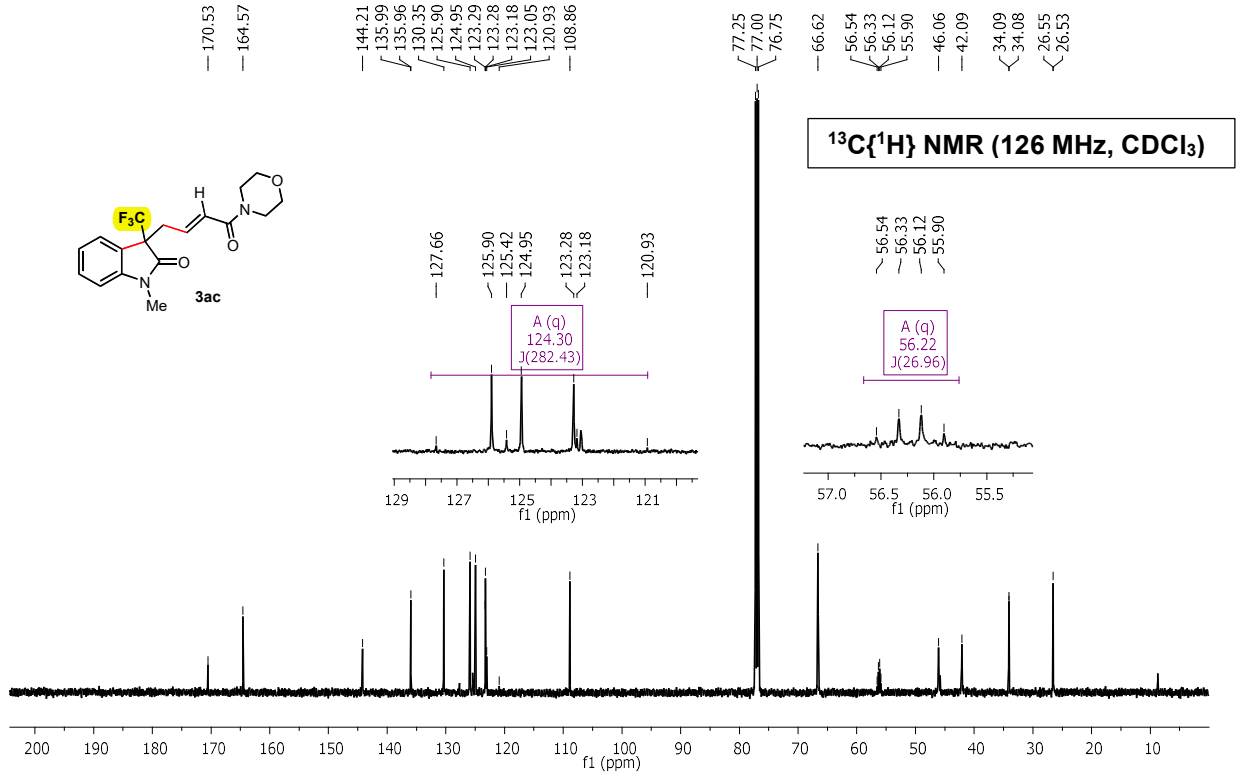



7.404
7.388
7.363
7.348
7.260
7.145
7.130
7.115
6.884
6.868
6.400
6.385
6.370
6.354
6.339
5.842
5.811
3.623
3.213
3.106
3.089
3.078
3.062
3.007
2.992
2.979
2.965
F3C
H
COOMe
O
N
Me
3ab
1H NMR (500 MHz, CDCl3)
1.12
1.07
1.07
1.02
1.01
1.00
3.21
3.18
1.27
1.10
f1 (ppm)

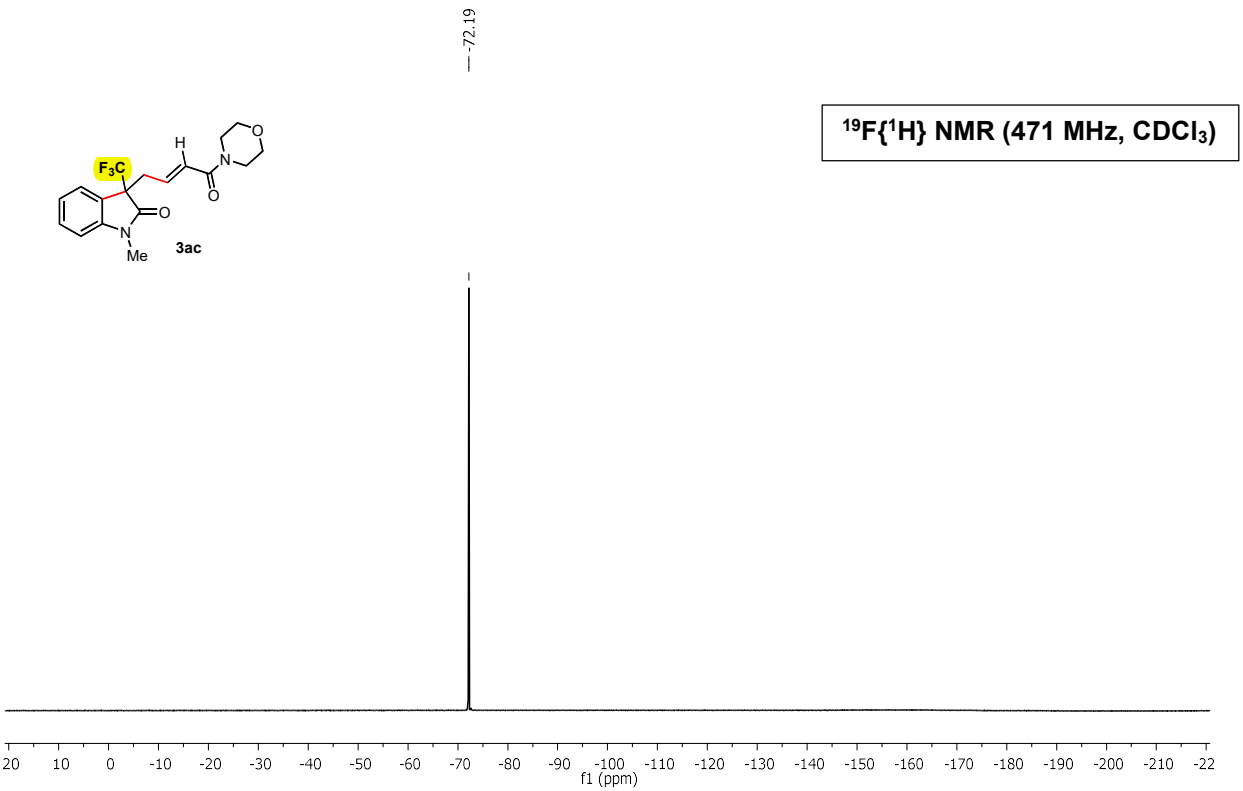

170.41
170.40
165.81
144.11
139.29
130.41
127.63
126.04
125.38
124.96
123.36
123.14
122.86
120.89
108.86
77.25
77.00
76.75
56.14
55.93
55.71
55.50
51.50
33.73
26.57
F3C
H
COOMe
O
N
Me
3ab
13C{1H} NMR (126 MHz, CDCl3)
A (q)
124.26
J(282.48)
A (q)
55.82
J(26.75)
f1 (ppm)


-72.16
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)
F_3C
H
COOMe
O
N
Me
3ab
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

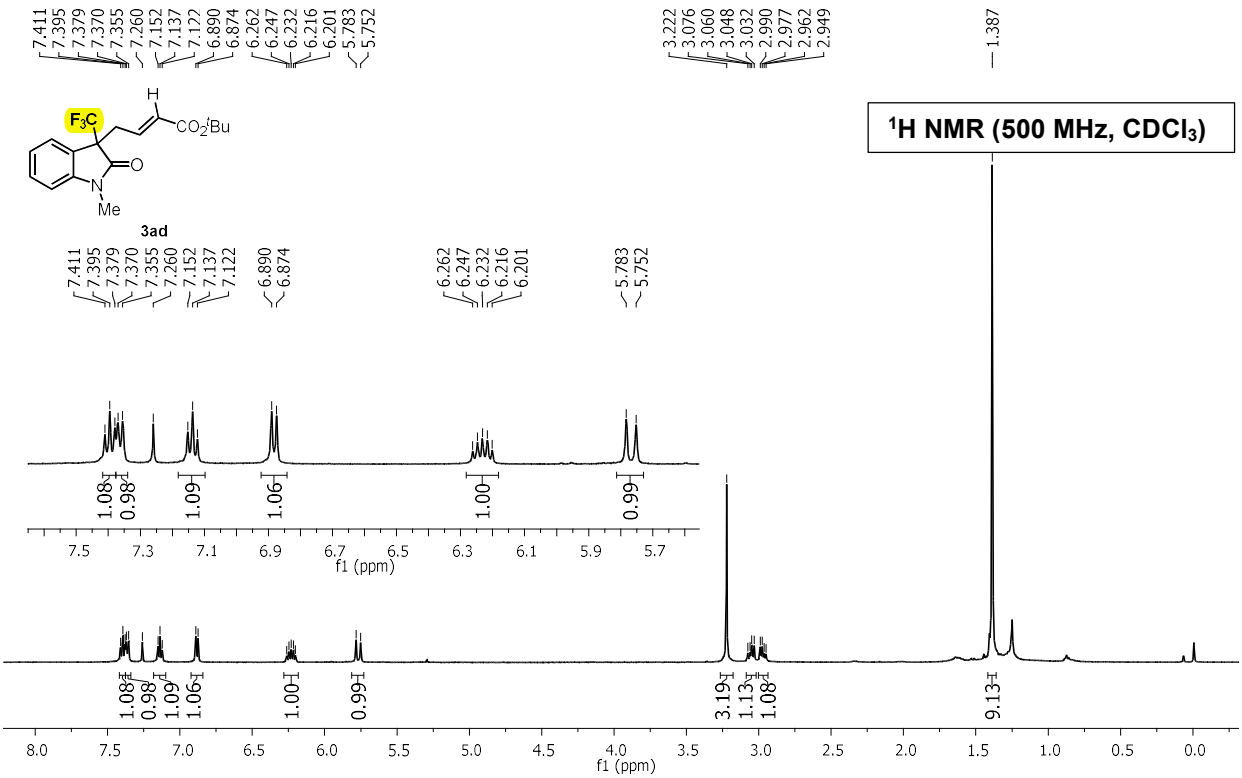

7.395
7.390
7.379
7.366
7.260
7.142
7.127
7.112
6.873
6.857
6.231
6.201
6.192
6.180
6.178
6.164
3.600
3.554
3.307
3.196
3.131
3.116
3.104
3.089
3.002
2.990
2.974
2.963
^{1}H NMR (500 MHz, $CDCl_3$)
F_3C
H
O
N
O
O
N
Me
3ac
2.05
1.05
1.00
2.00
6.19
2.07
3.04
1.03
1.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 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)

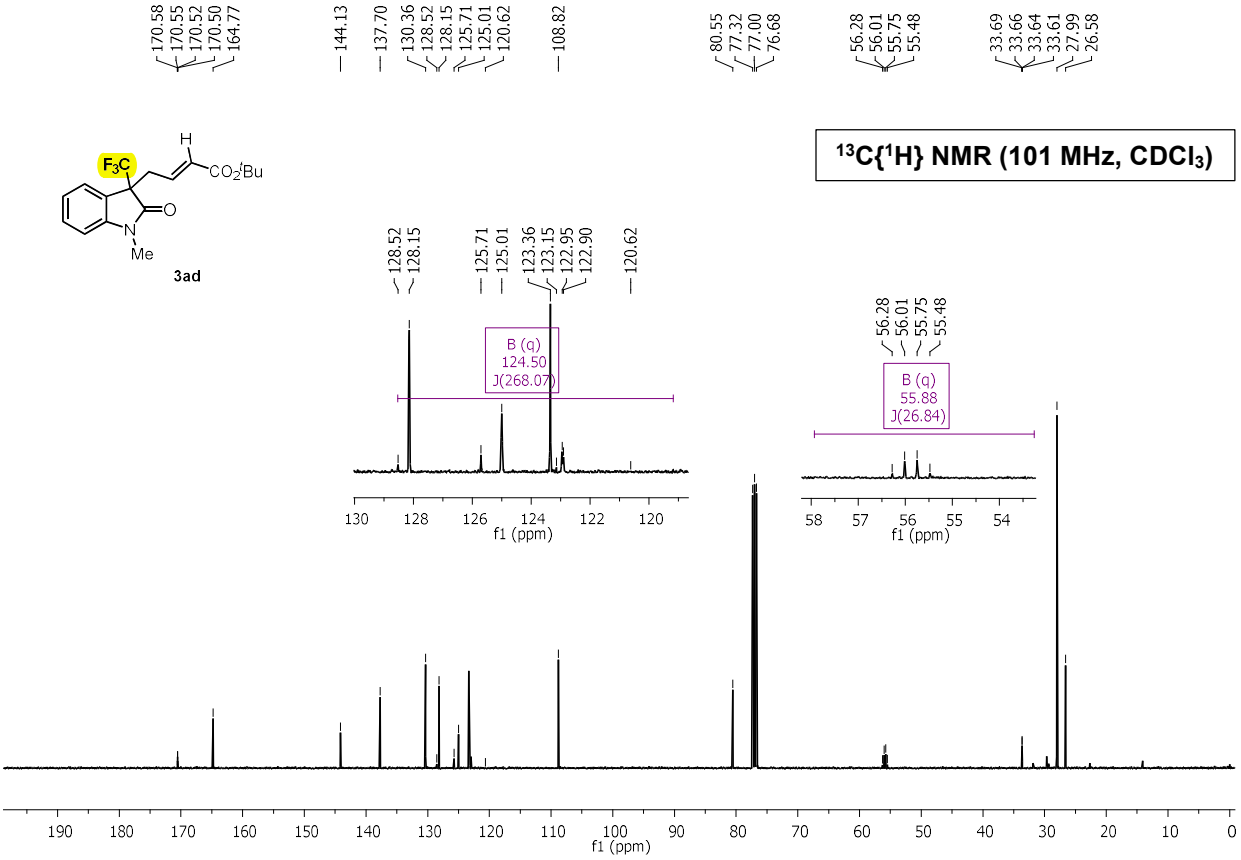


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

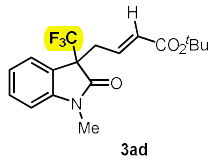


$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

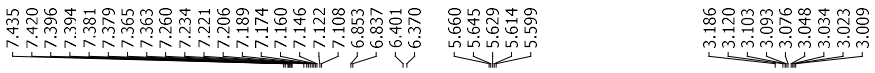

7.411
7.395
7.379
7.370
7.355
7.260
7.152
7.137
7.122
6.890
6.874
6.262
6.247
6.232
6.216
6.201
5.783
5.752
3.222
3.076
3.060
3.048
3.032
2.990
2.977
2.962
2.949
1.387
F3C
CO2tBu
H
O
N
Me
3ad
1H NMR (500 MHz, CDCl3)
1.08
0.98
1.09
1.06
1.00
0.99
3.19
1.13
1.08
9.13
f1 (ppm)


170.58
170.55
170.52
170.50
164.77
144.13
137.70
130.36
128.52
128.15
125.71
125.01
120.62
108.82
80.55
77.32
77.00
76.68
56.28
56.01
55.75
55.48
33.69
33.66
33.64
33.61
27.99
26.58
F3C
CO2tBu
H
O
N
Me
3ad
13C{1H} NMR (101 MHz, CDCl3)
B (q)
124.50
J(268.07)
B (q)
55.88
J(26.84)
f1 (ppm)

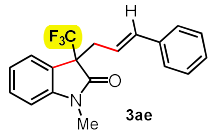
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



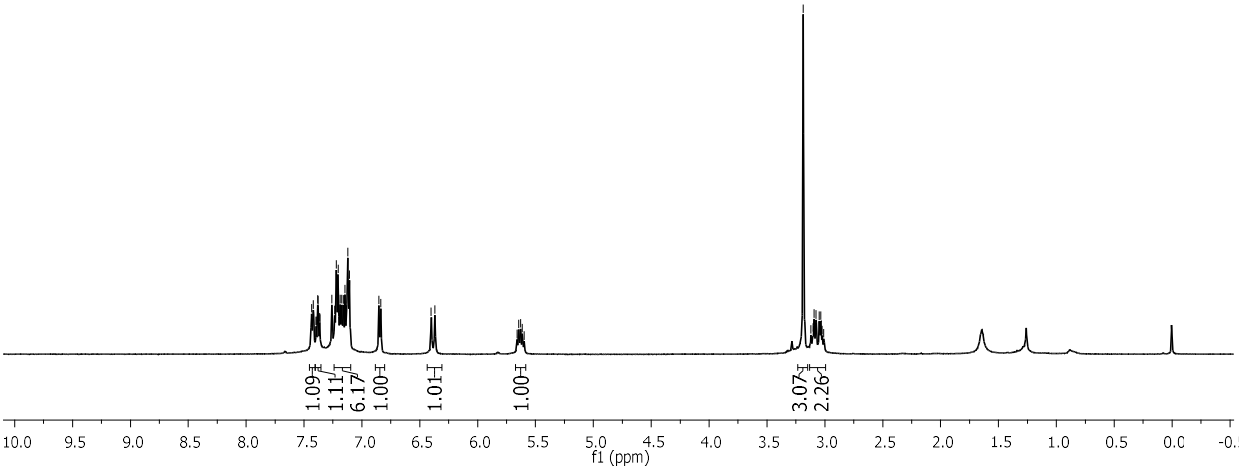
3ad

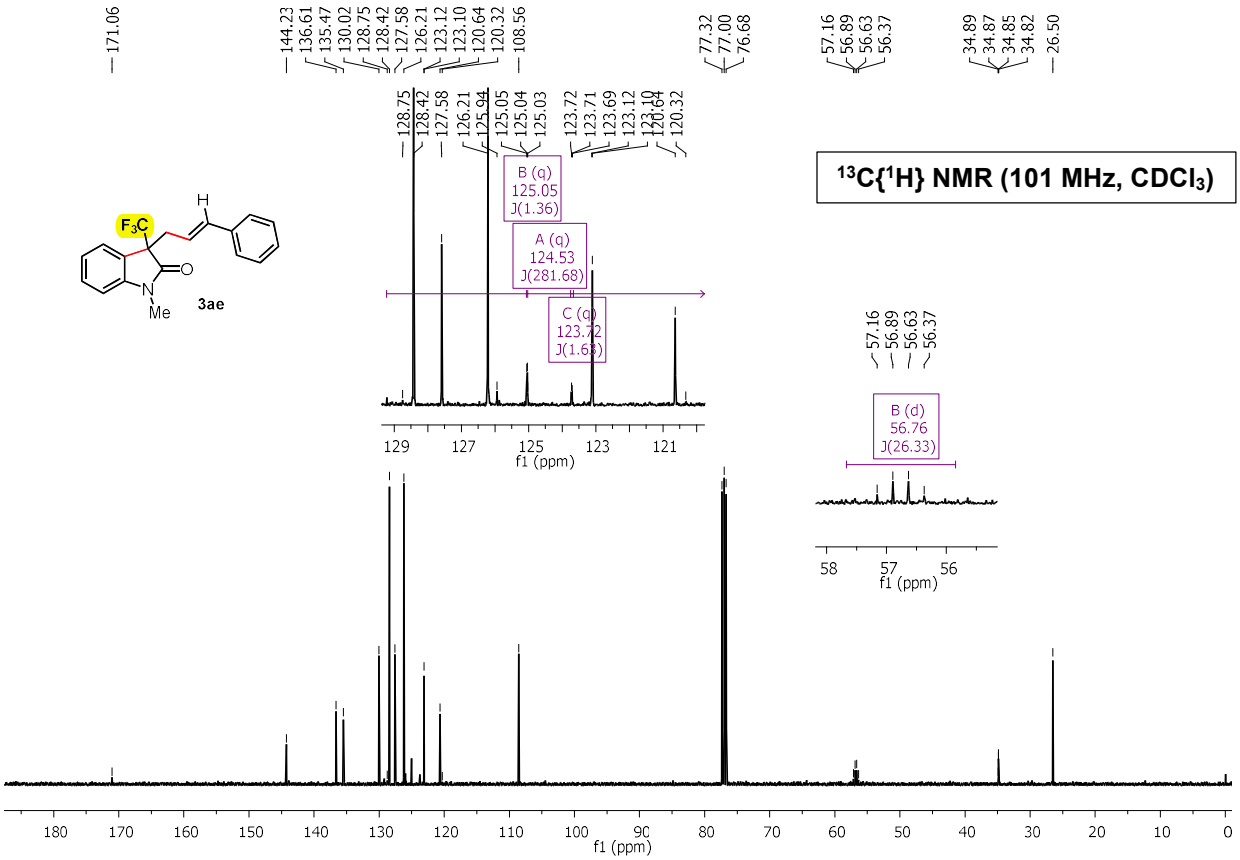


^{1}H NMR (500 MHz, $CDCl_3$)

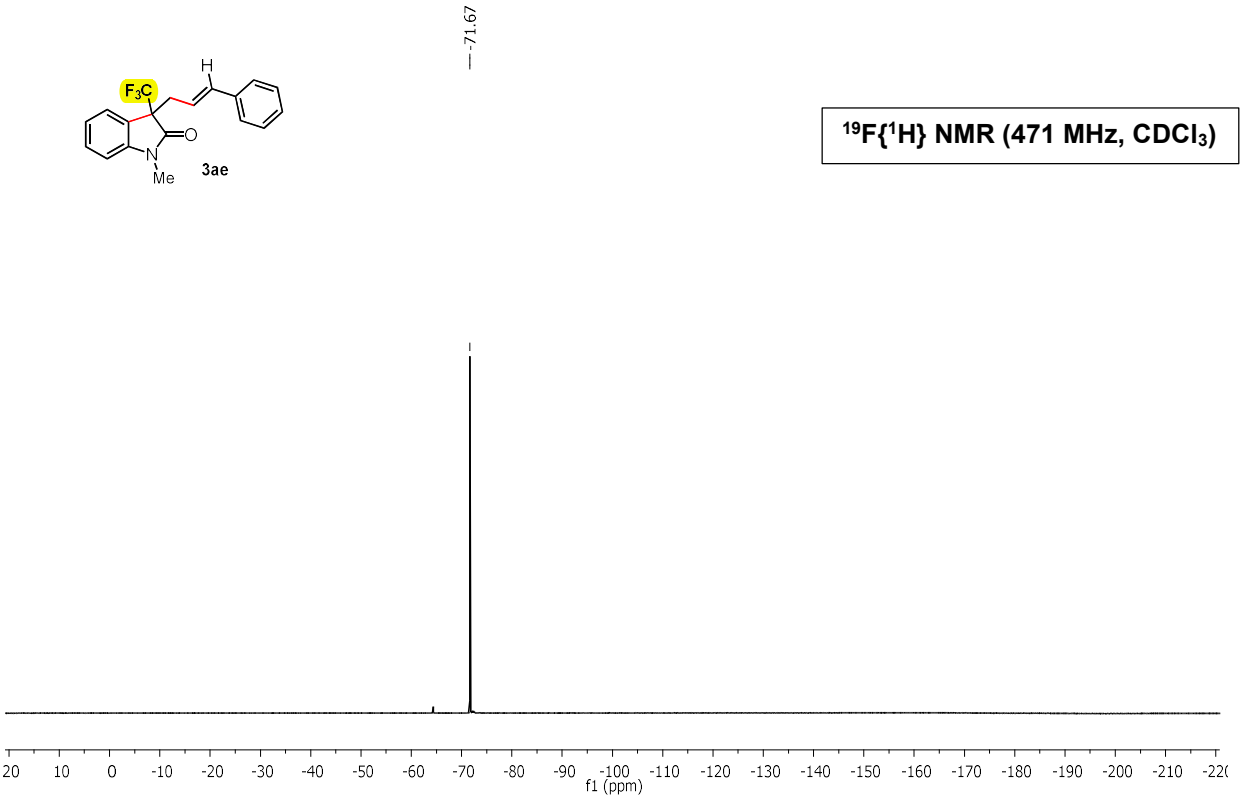


3ae

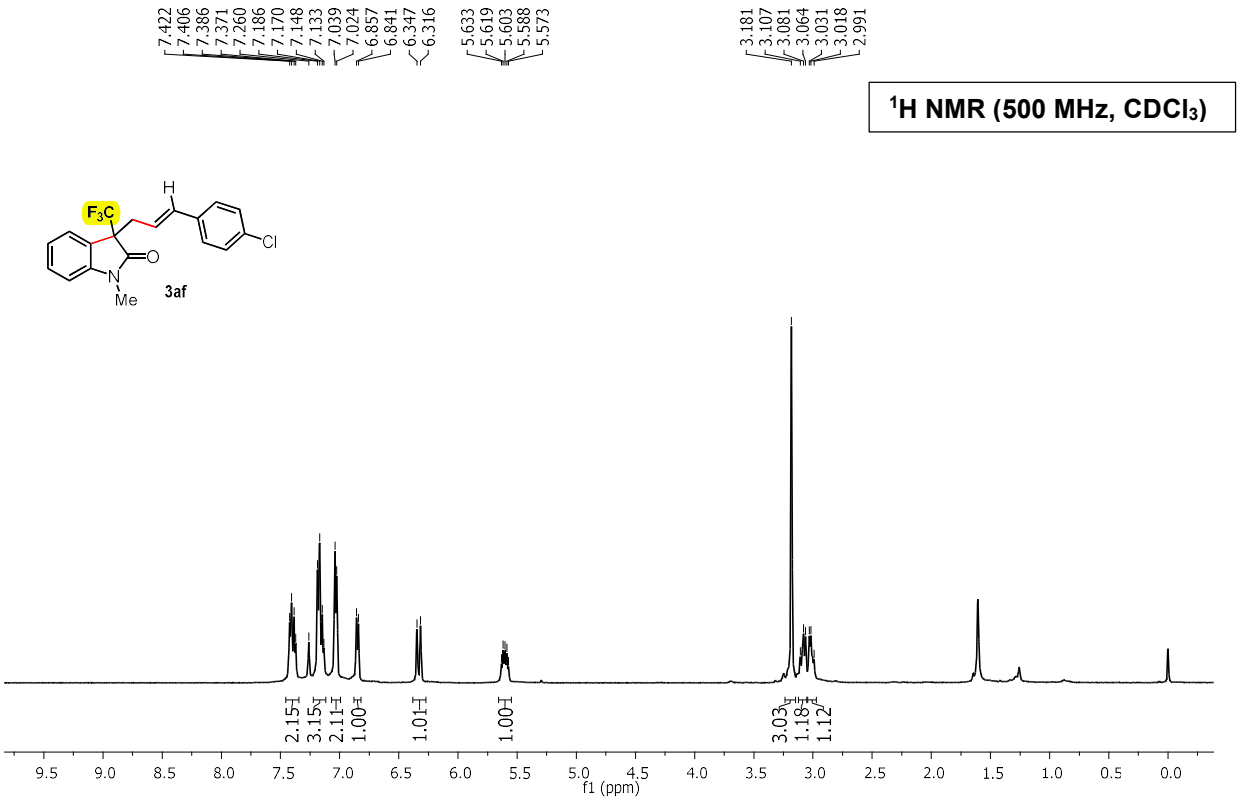




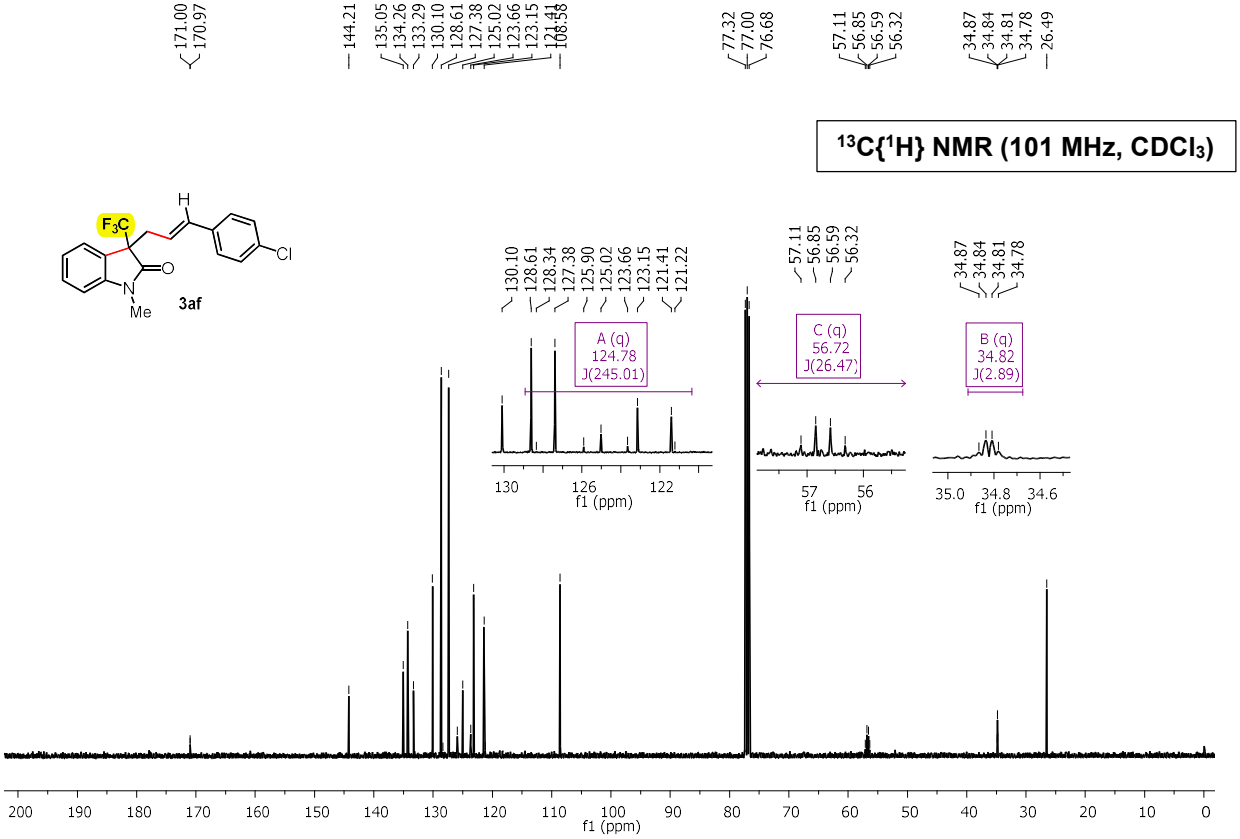
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



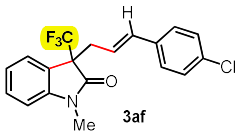
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

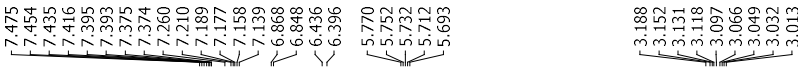


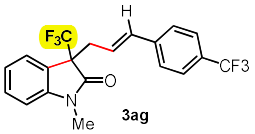
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



3af

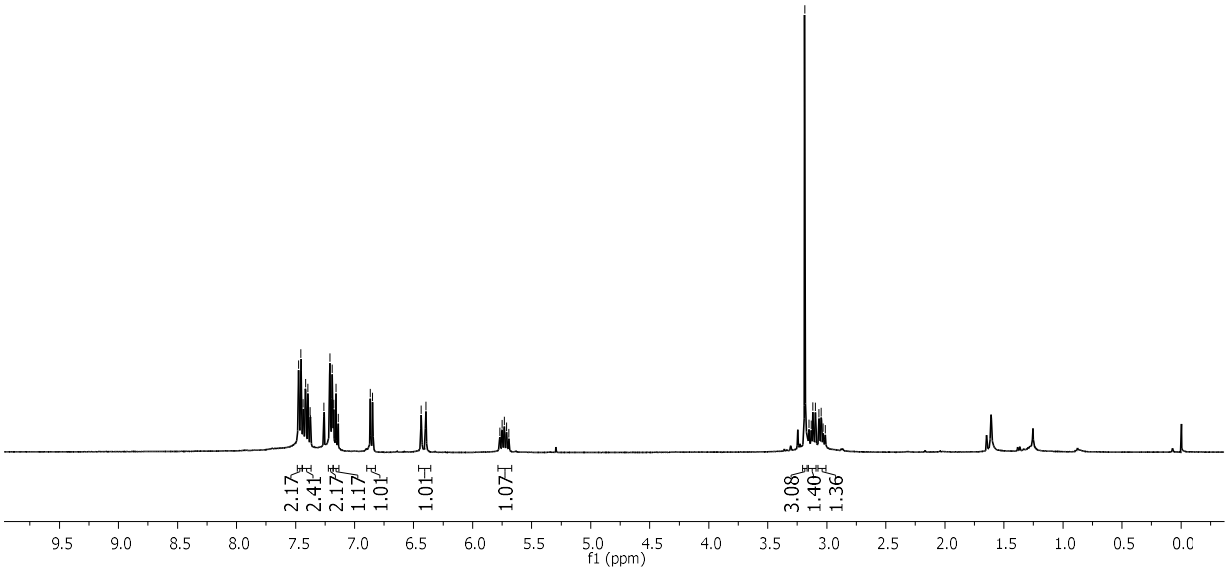
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

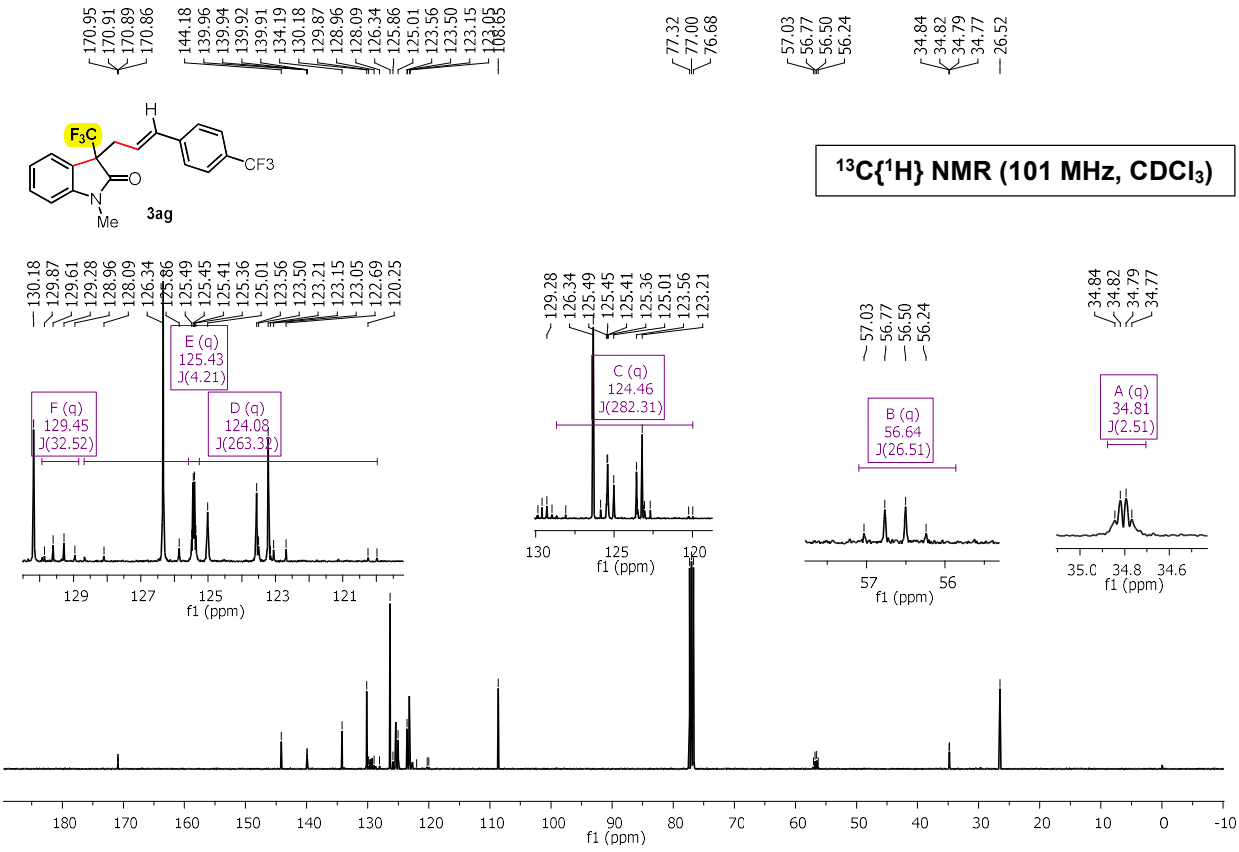




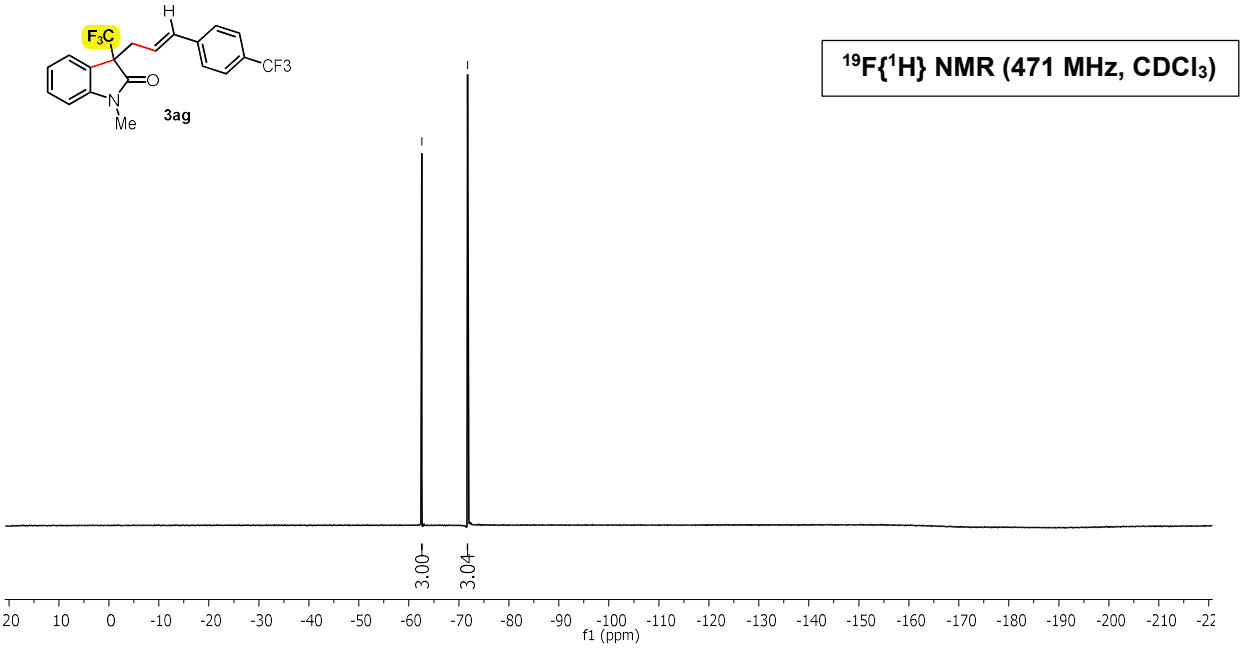
3ag

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



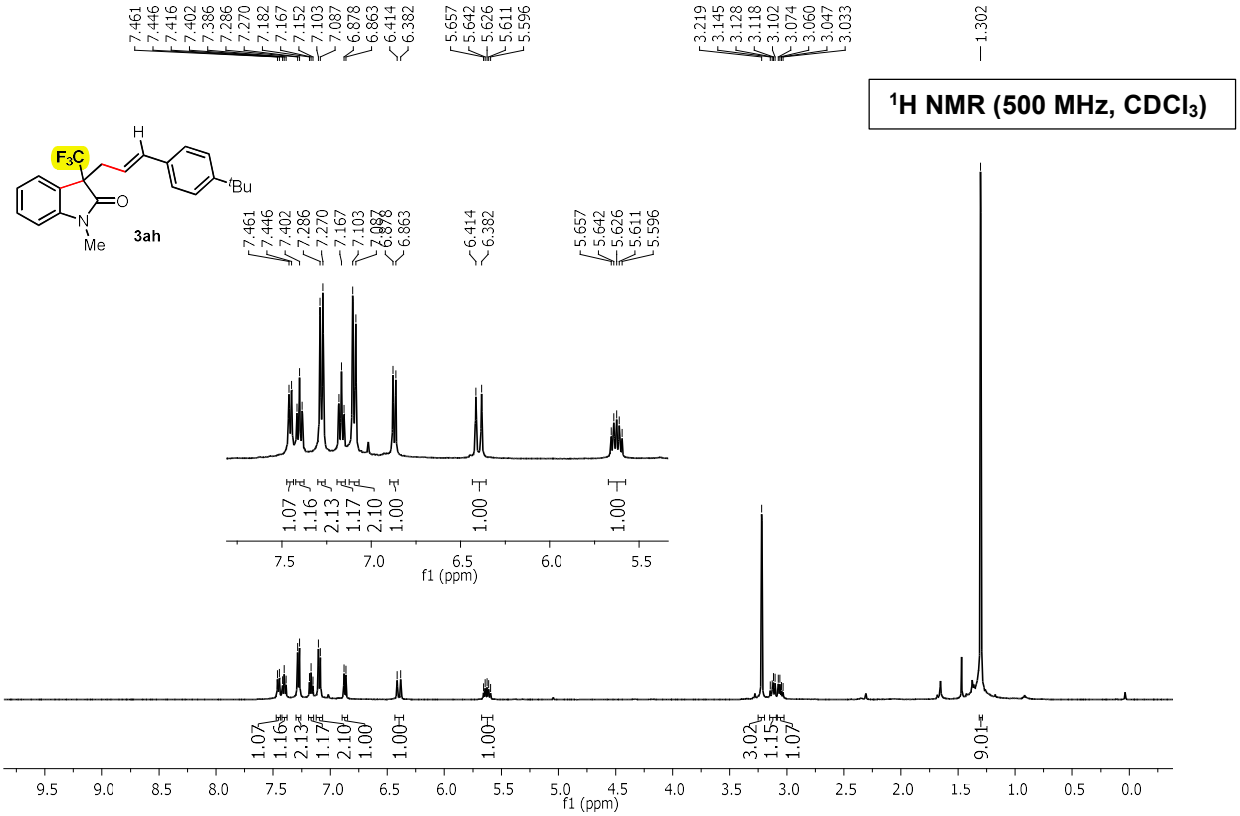


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

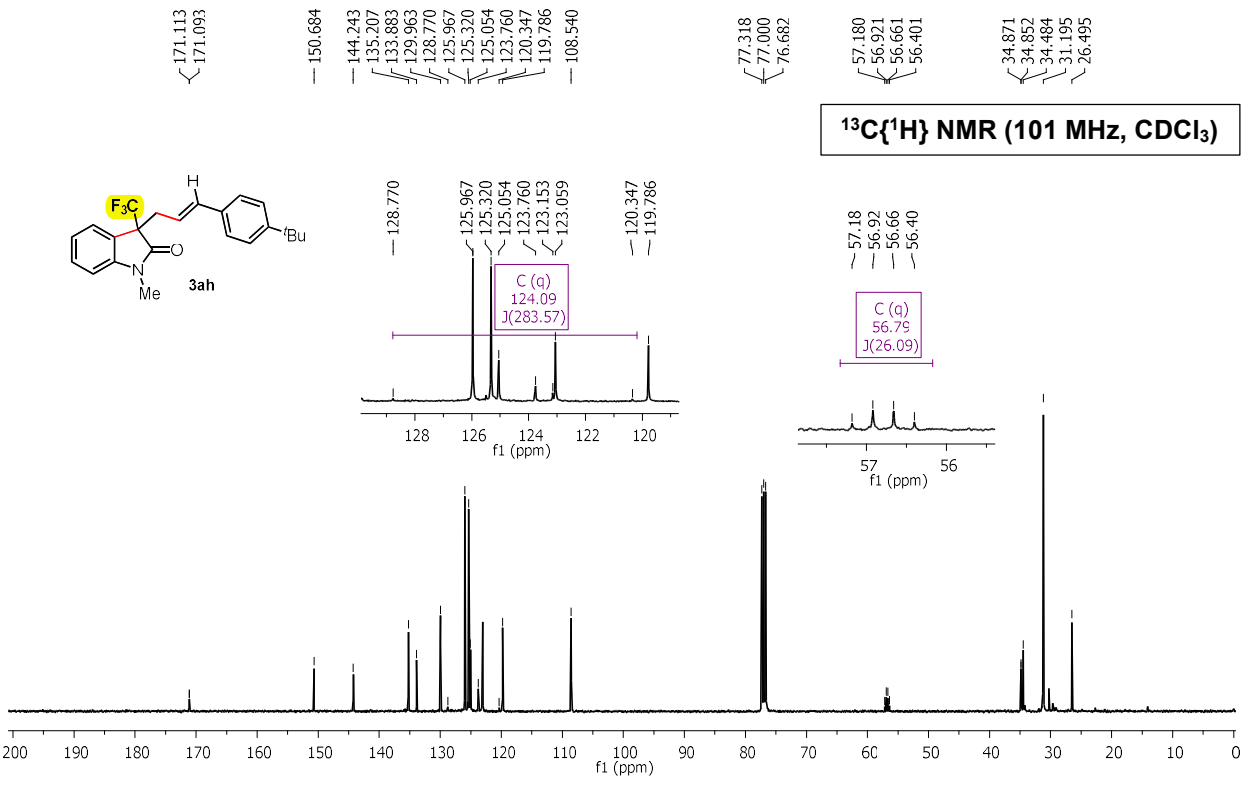


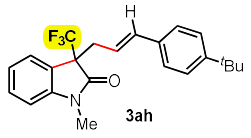
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

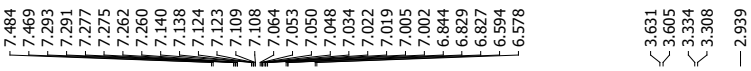


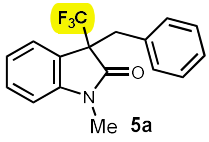
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)





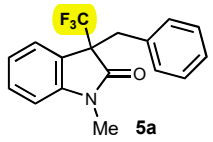
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



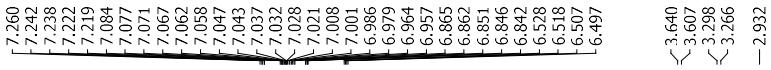


^{1}H NMR (500 MHz, $CDCl_3$)

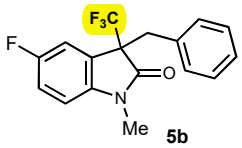
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



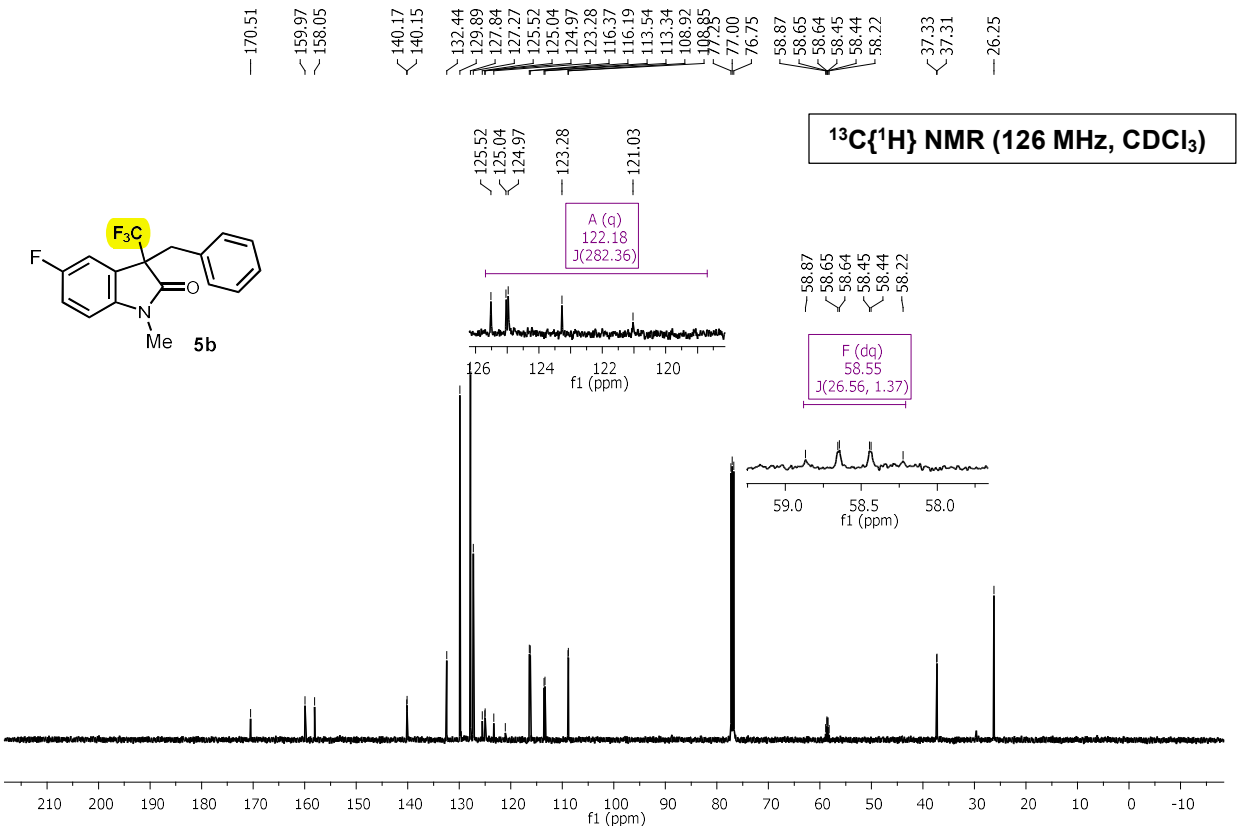
5a



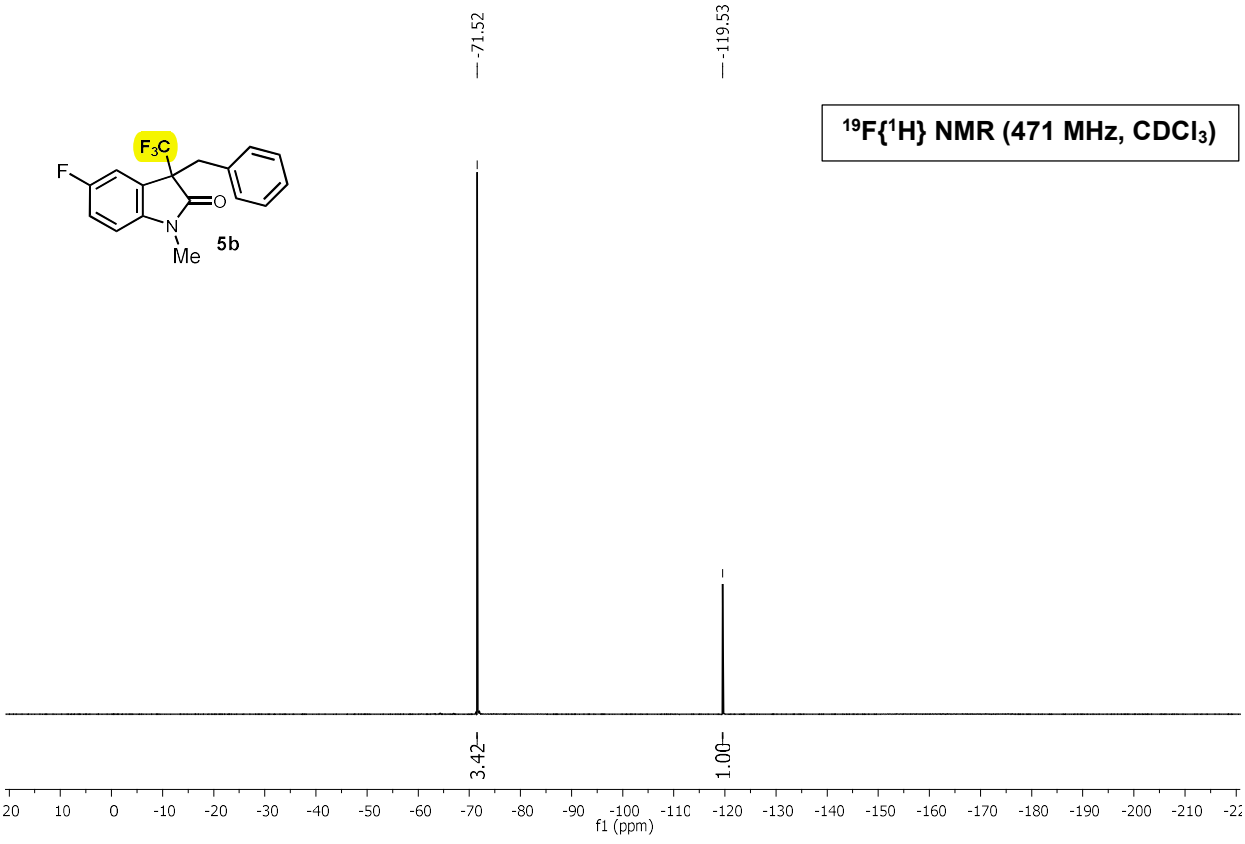
^{1}H NMR (400 MHz, $CDCl_3$)



5b

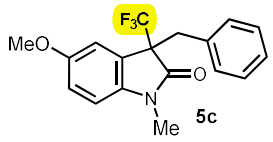


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

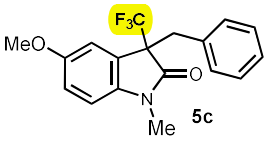


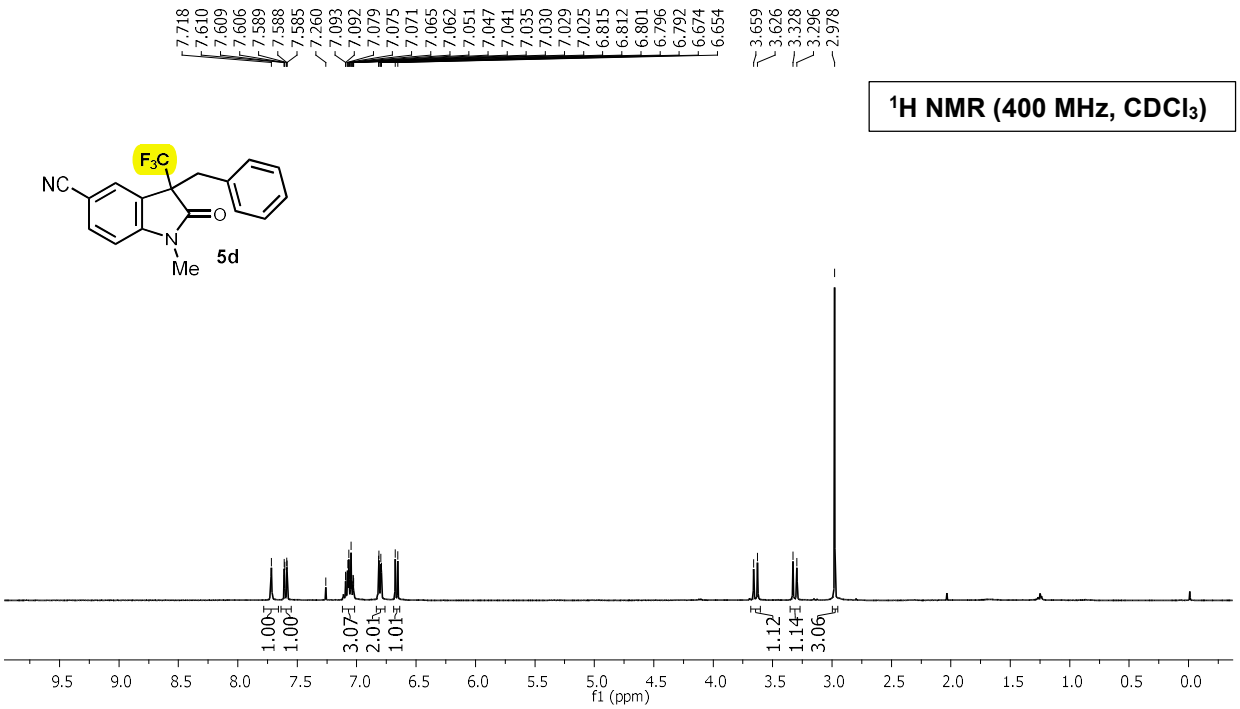
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

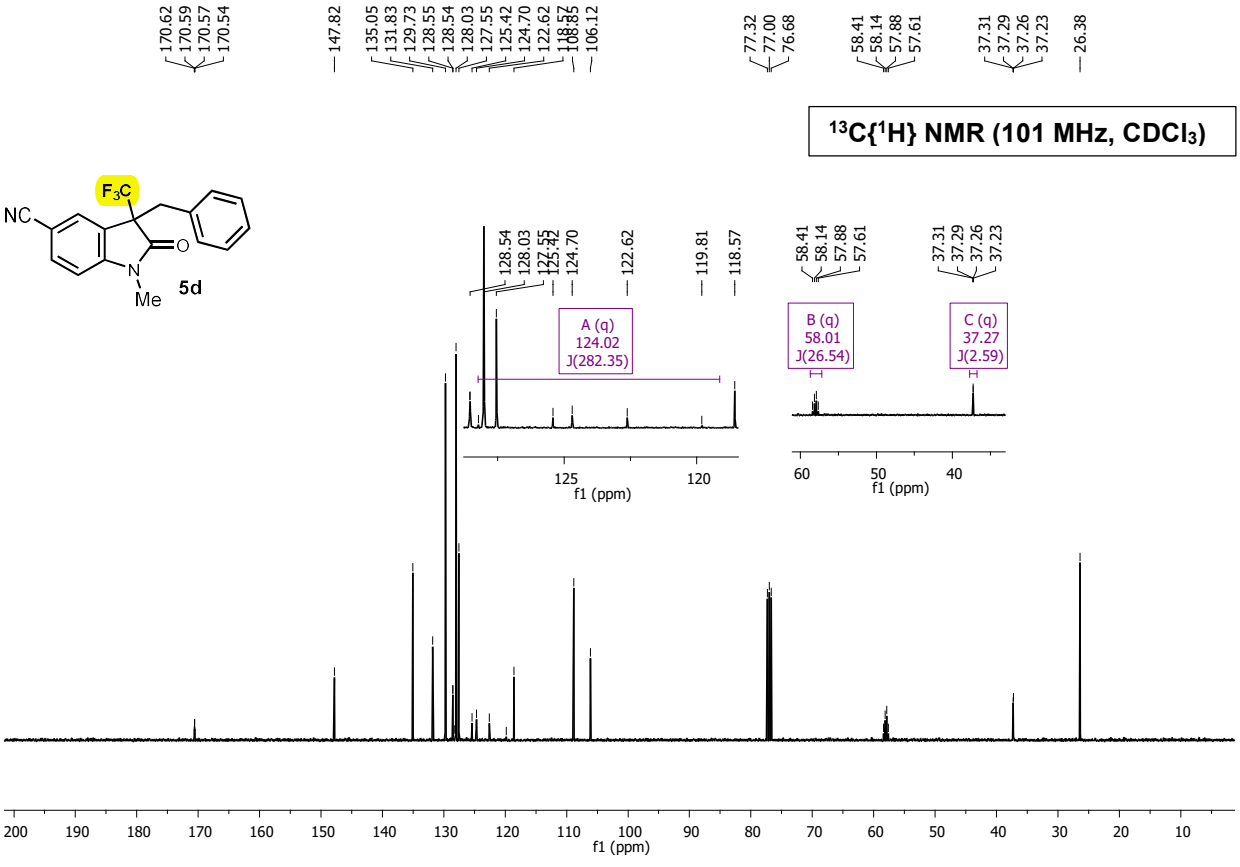
^{1}H NMR (500 MHz, $CDCl_3$)



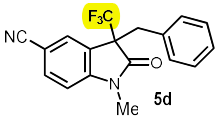
^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)




7.718
7.610
7.609
7.606
7.589
7.588
7.585
7.260
7.093
7.092
7.079
7.075
7.071
7.065
7.062
7.051
7.047
7.041
7.035
7.030
7.029
7.025
6.815
6.812
6.801
6.796
6.792
6.674
6.654
3.659
3.626
3.328
3.296
2.978
1H NMR (400 MHz, CDCl3)
F3C
NC
O
N
Me
5d
1.00
1.00
3.07
2.01
1.01
1.12
1.14
3.06
f1 (ppm)

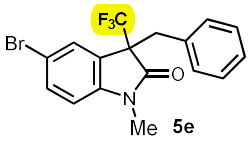

170.62
170.59
170.57
170.54
147.82
135.05
131.83
129.73
128.55
128.54
128.03
127.55
125.42
124.70
122.62
106.12
77.32
77.00
76.68
58.41
58.14
57.88
57.61
37.31
37.29
37.26
37.23
26.38
13C{1H} NMR (101 MHz, CDCl3)
F3C
NC
O
N
Me
5d
128.54
128.03
124.70
122.62
119.81
118.57
58.41
58.14
57.88
57.61
37.31
37.29
37.26
37.23
A (q)
124.02
J(282.35)
B (q)
58.01
J(26.54)
C (q)
37.27
J(2.59)
f1 (ppm)

$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

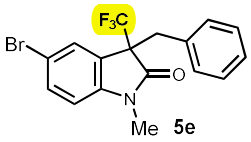


5d

^{1}H NMR (500 MHz, $CDCl_3$)

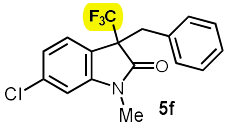


5e



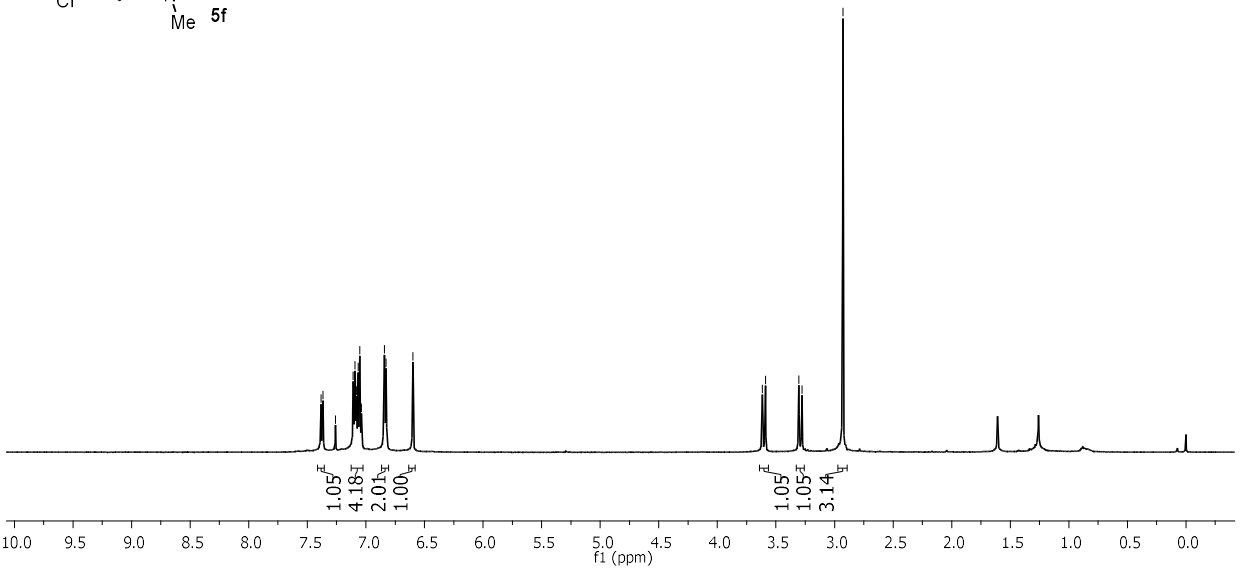
5e

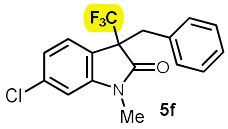
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



5f

^{1}H NMR (500 MHz, $CDCl_3$)

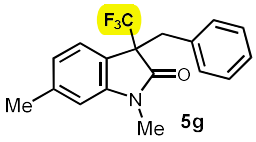




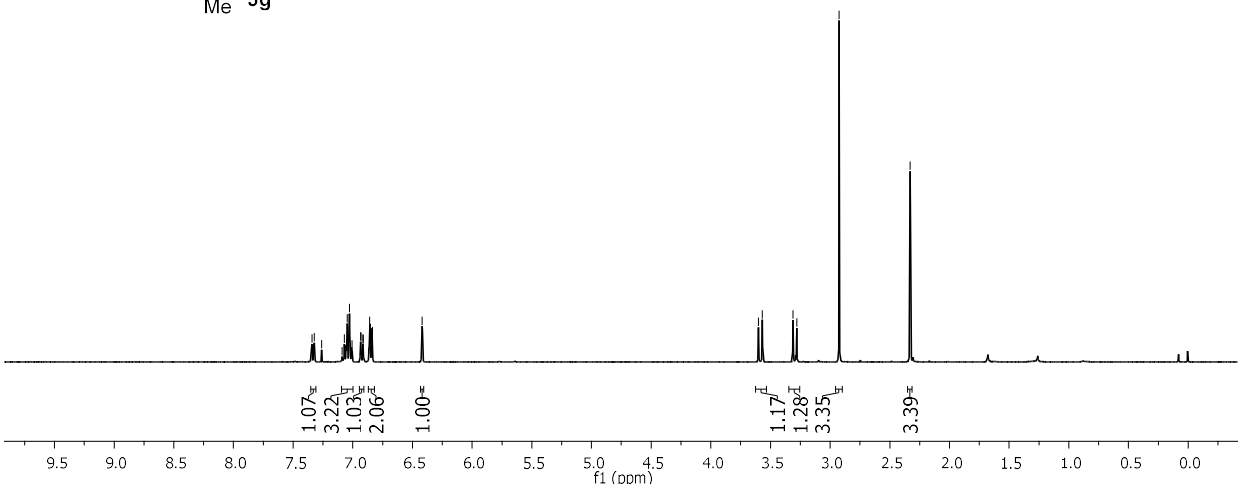
5f

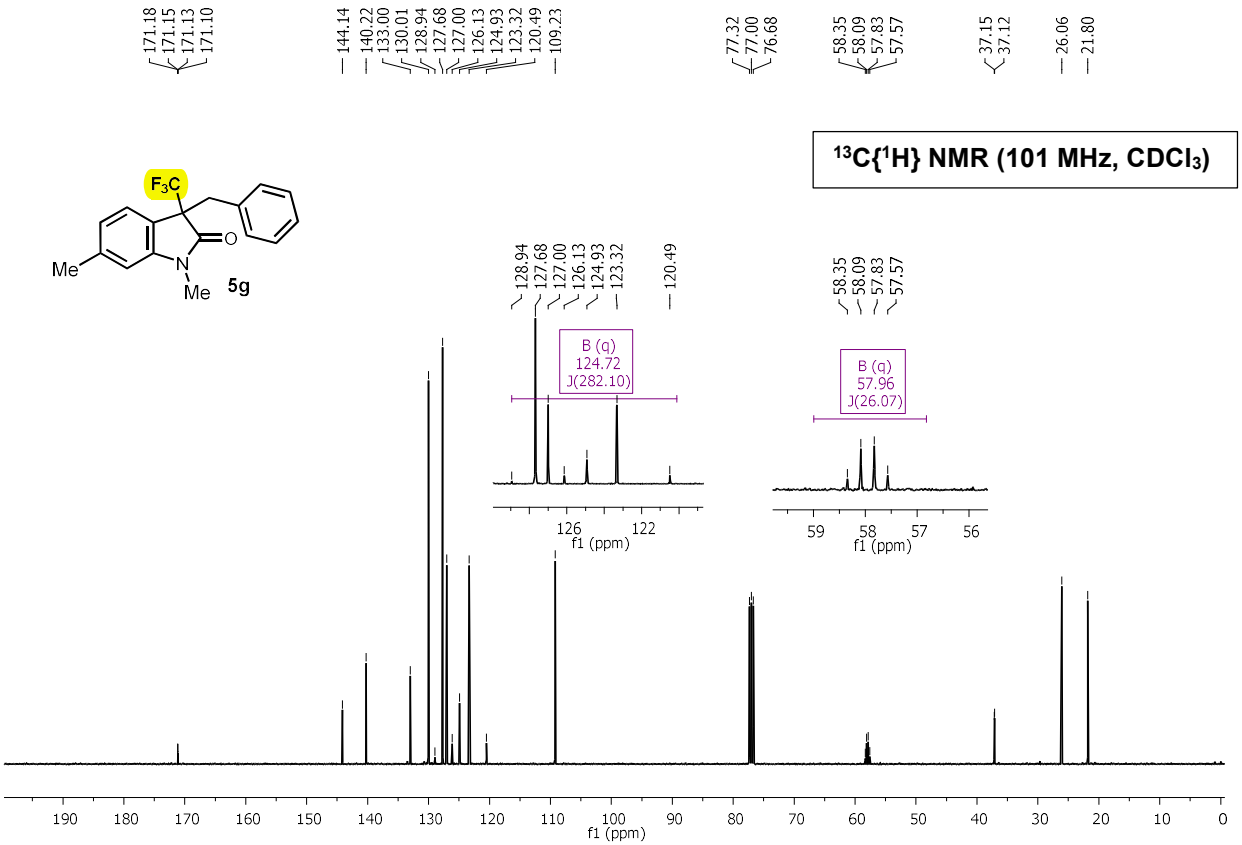
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

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

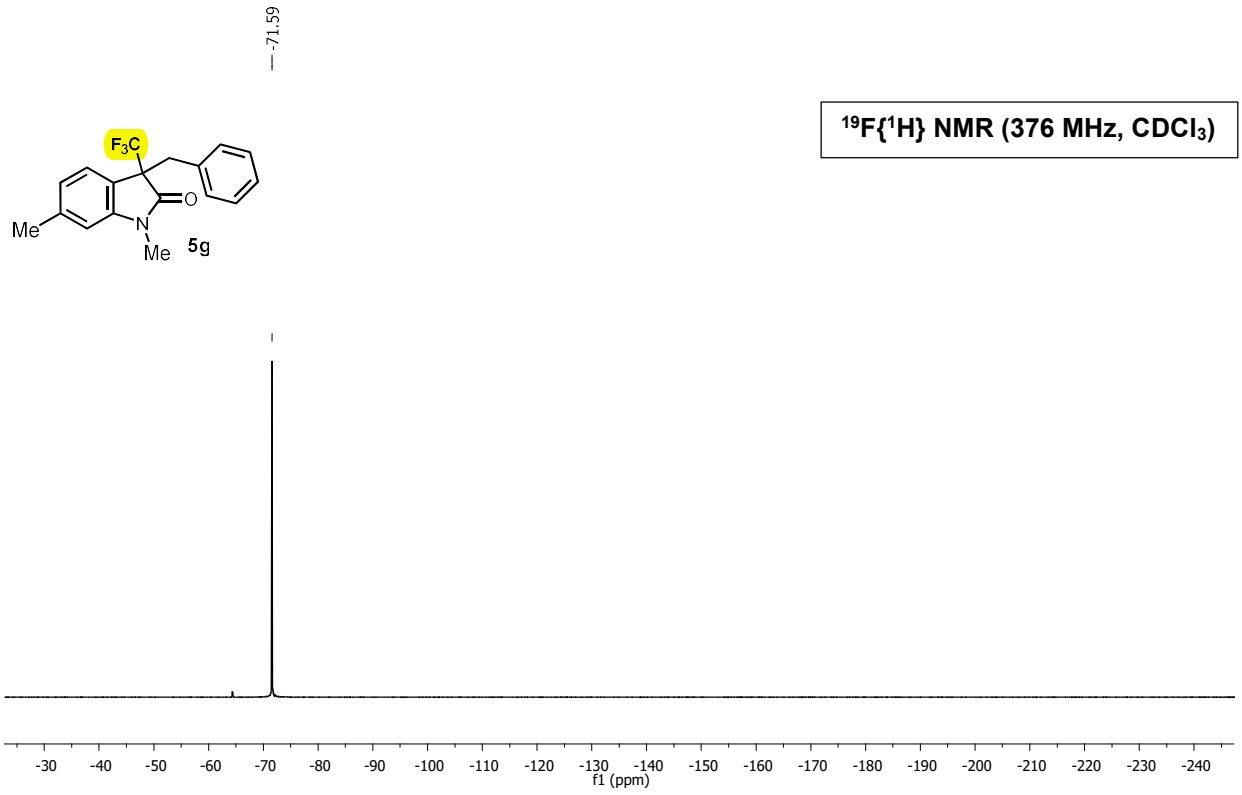


5g

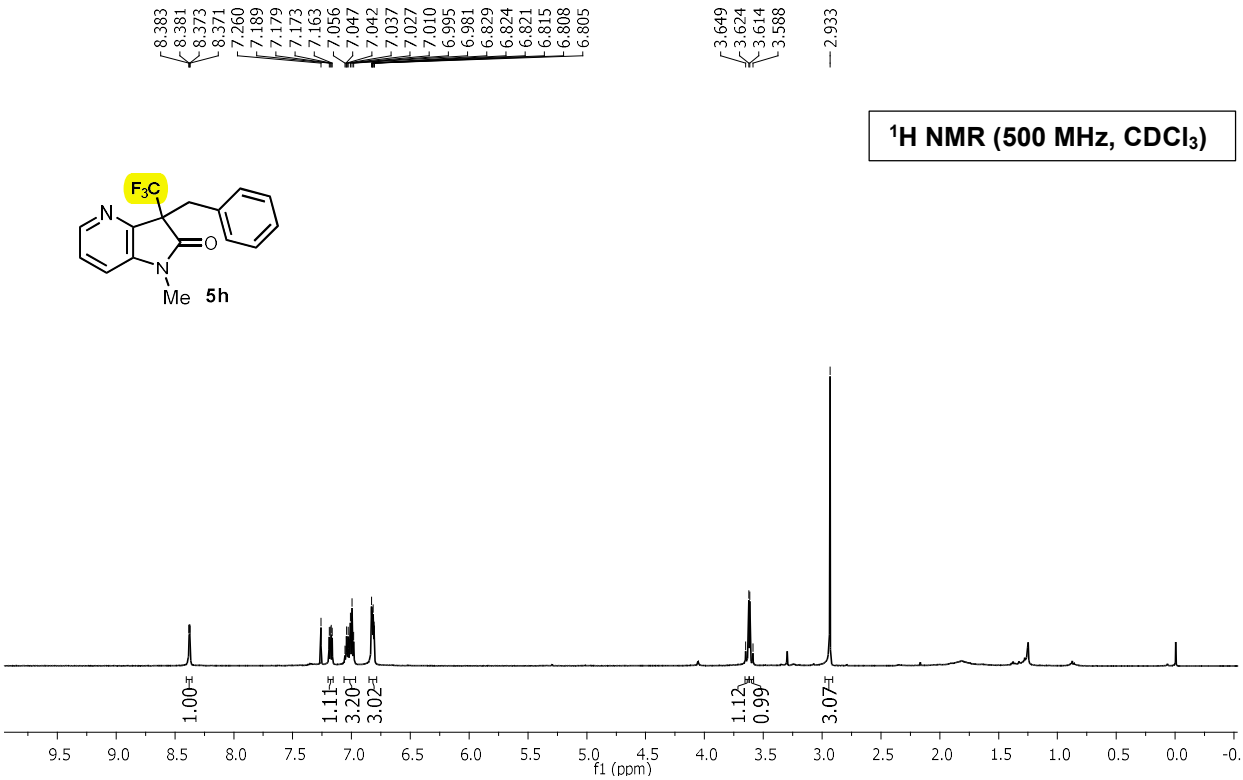


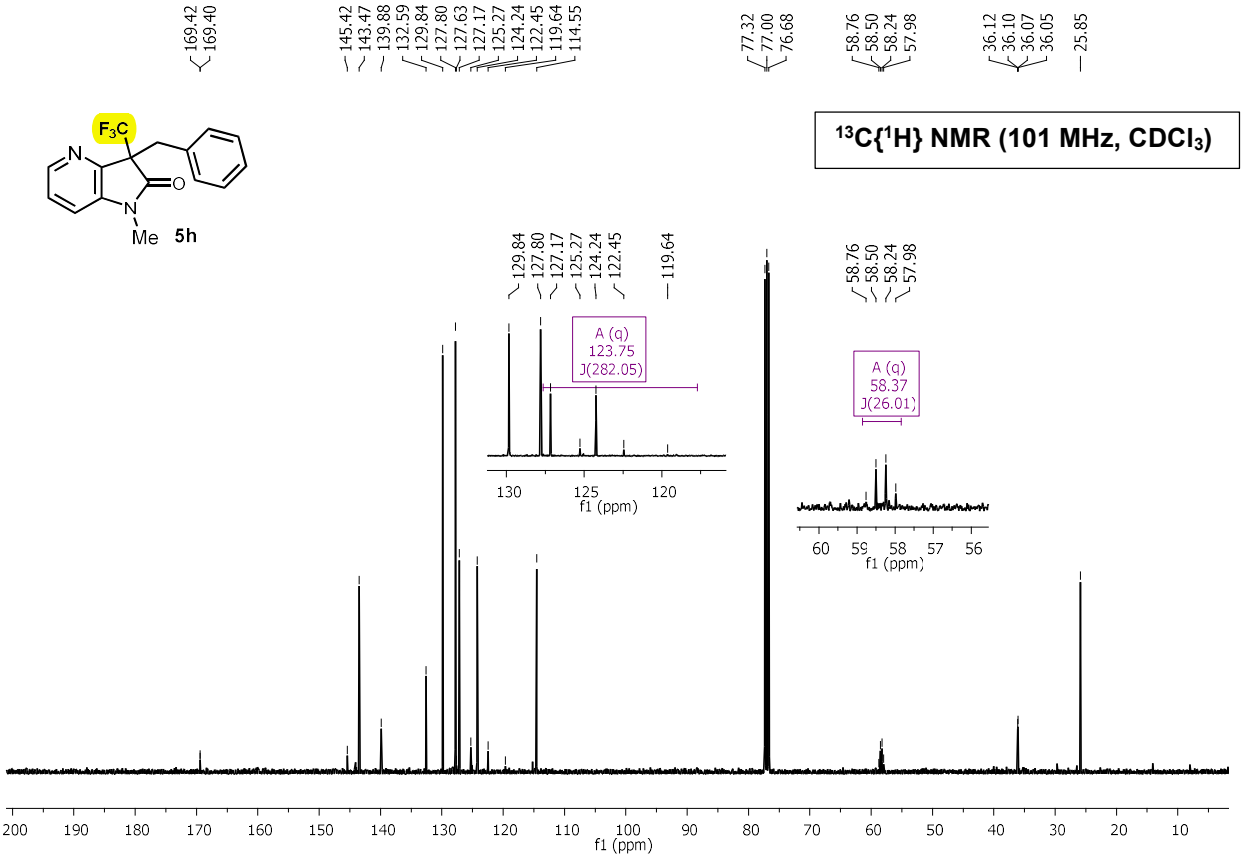


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

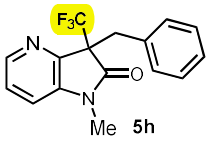


$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)


8.383
8.381
8.373
8.371
7.260
7.189
7.179
7.173
7.163
7.056
7.047
7.042
7.037
7.027
7.010
6.995
6.981
6.829
6.824
6.821
6.815
6.808
6.805
3.649
3.624
3.614
3.588
2.933
1H NMR (500 MHz, CDCl3)
F3C
N
O
N
Me
5h
1.00
1.11
3.20
3.02
1.12
0.99
3.07
f1 (ppm)

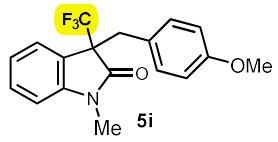

169.42
169.40
145.42
143.47
139.88
132.59
129.84
127.80
127.63
127.17
125.27
124.24
122.45
119.64
114.55
77.32
77.00
76.68
58.76
58.50
58.24
57.98
36.12
36.10
36.07
36.05
25.85
13C{1H} NMR (101 MHz, CDCl3)
F3C
N
O
N
Me
5h
129.84
127.80
127.17
125.27
124.24
122.45
119.64
A (q)
123.75
J(282.05)
58.76
58.50
58.24
57.98
A (q)
58.37
J(26.01)
f1 (ppm)

$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

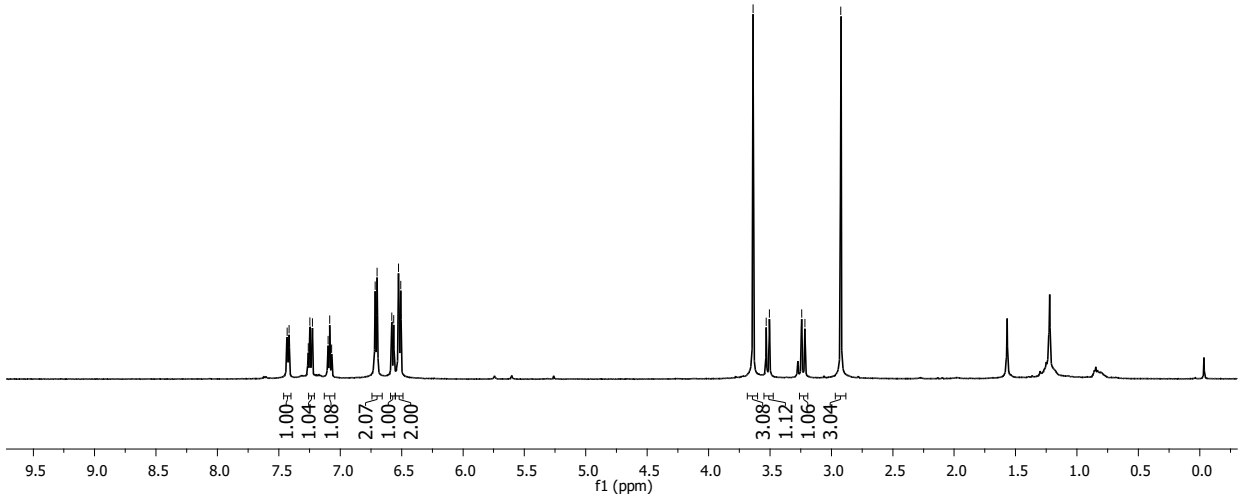


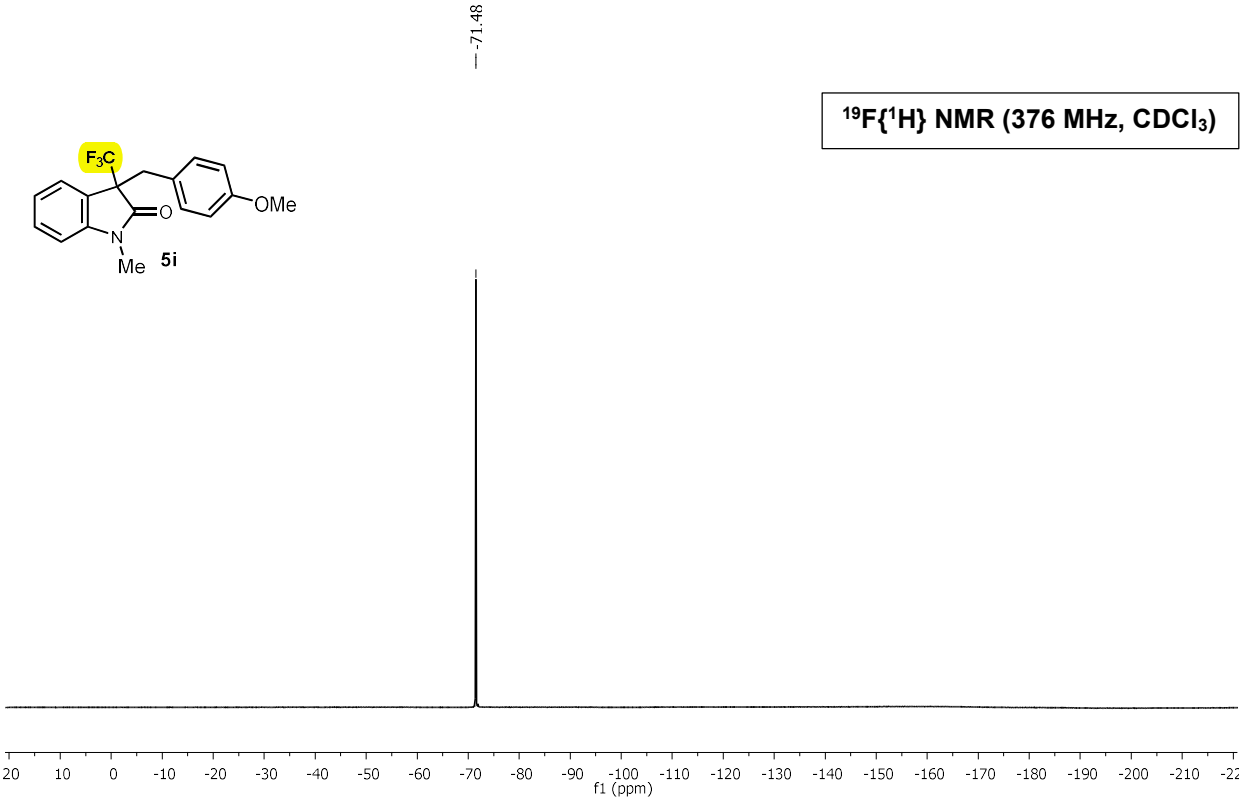
5h

^{1}H NMR (500 MHz, $CDCl_3$)

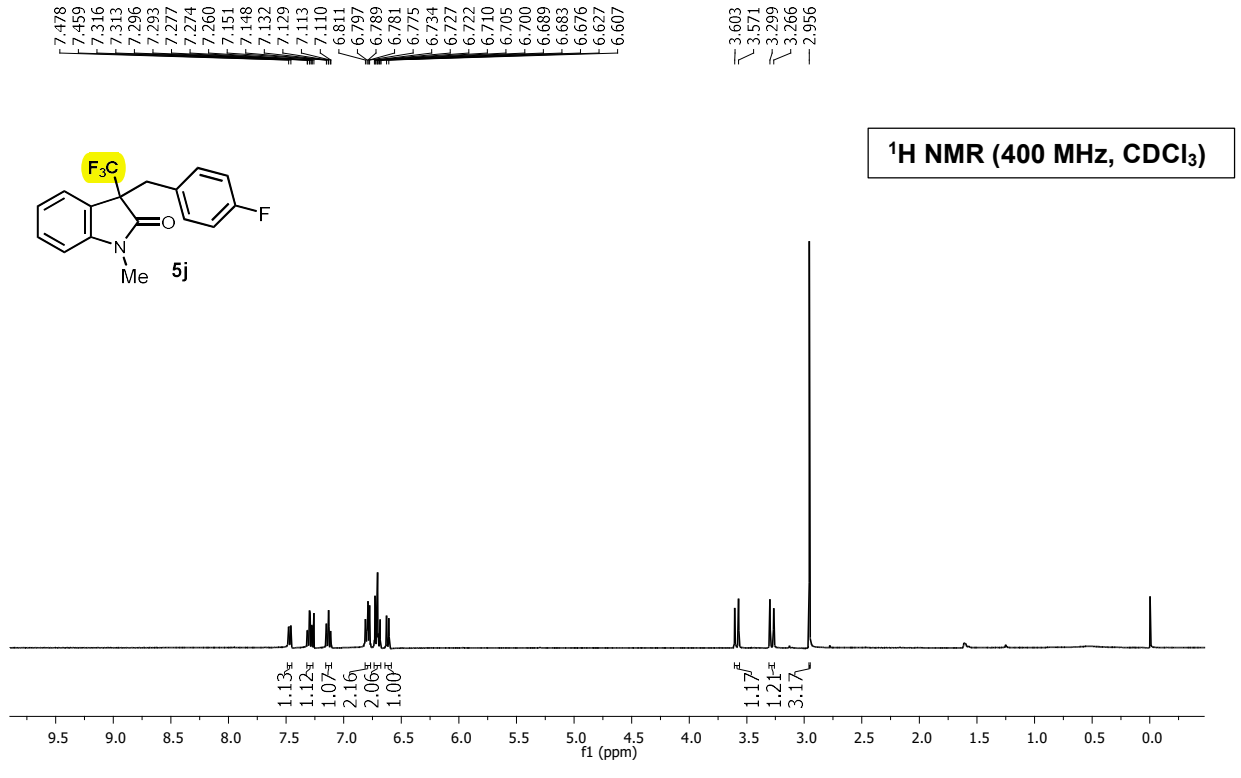


5i

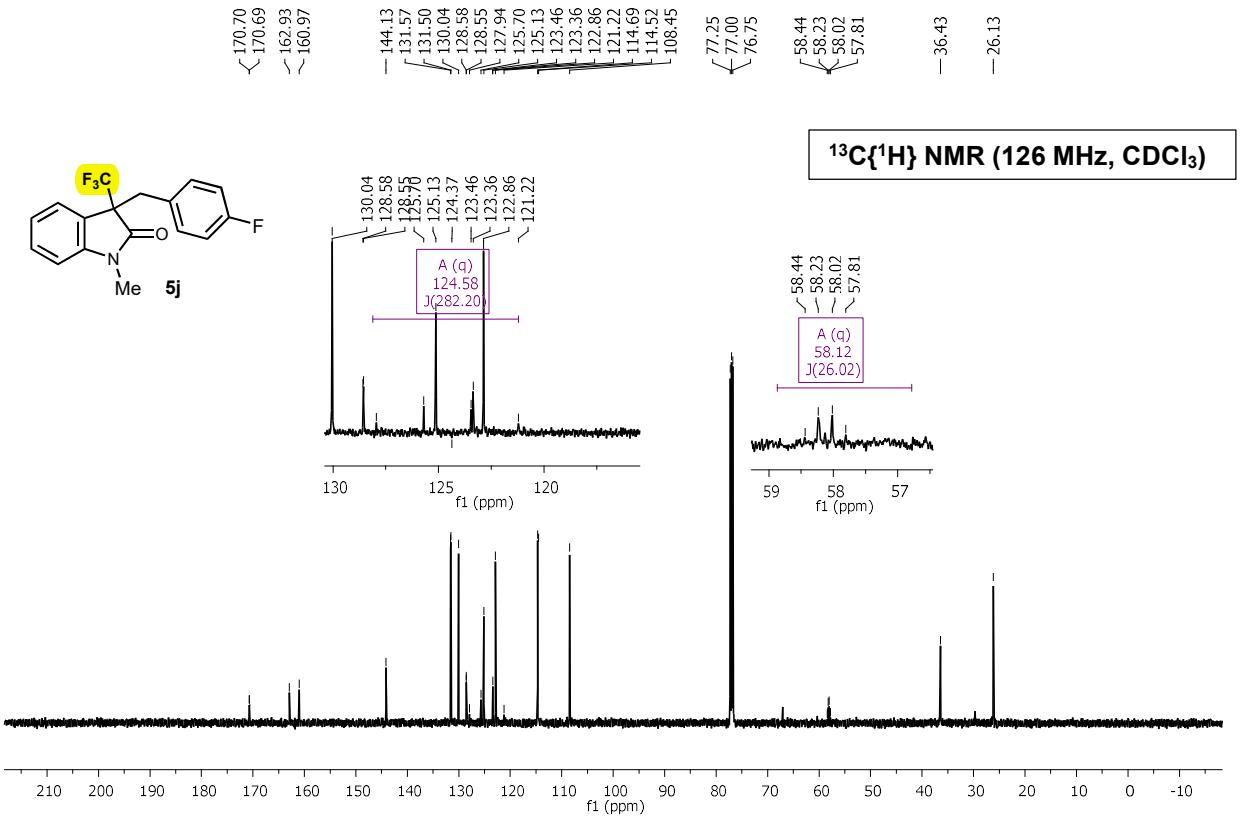




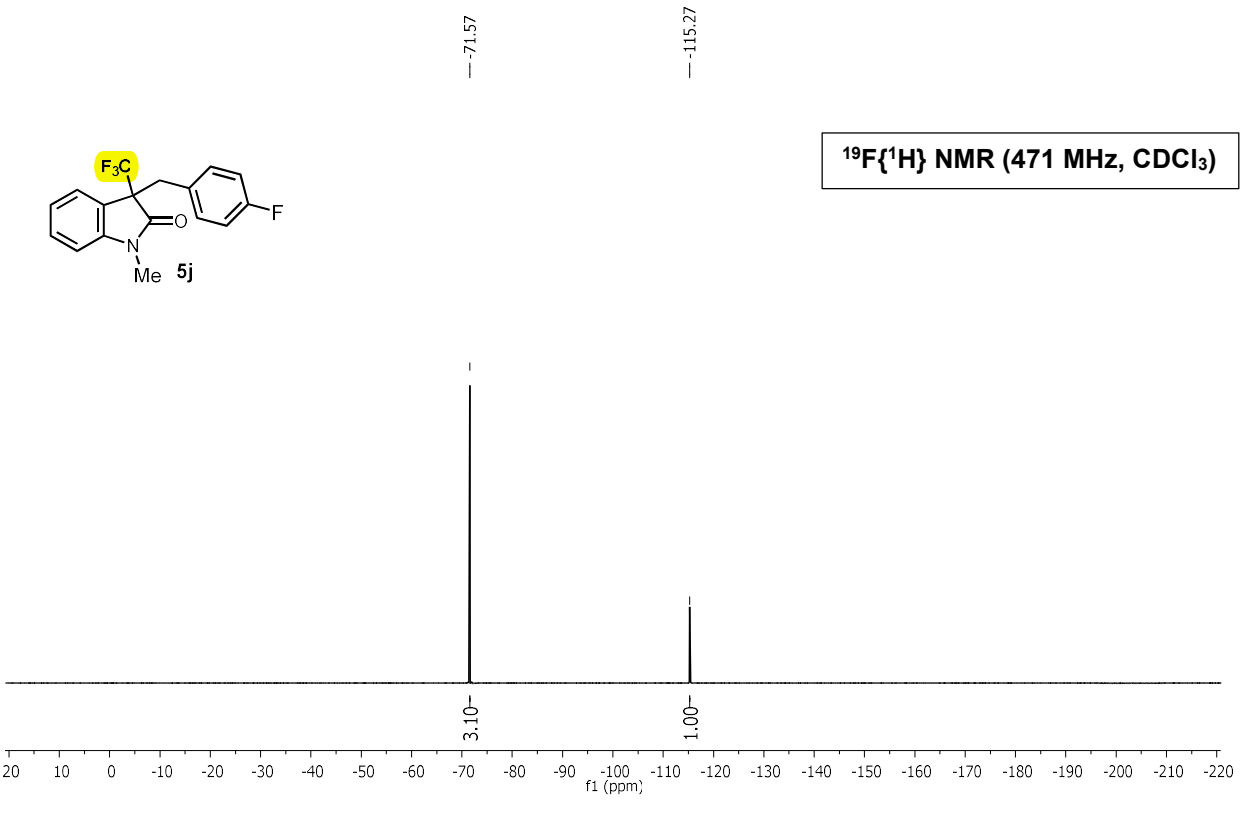
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



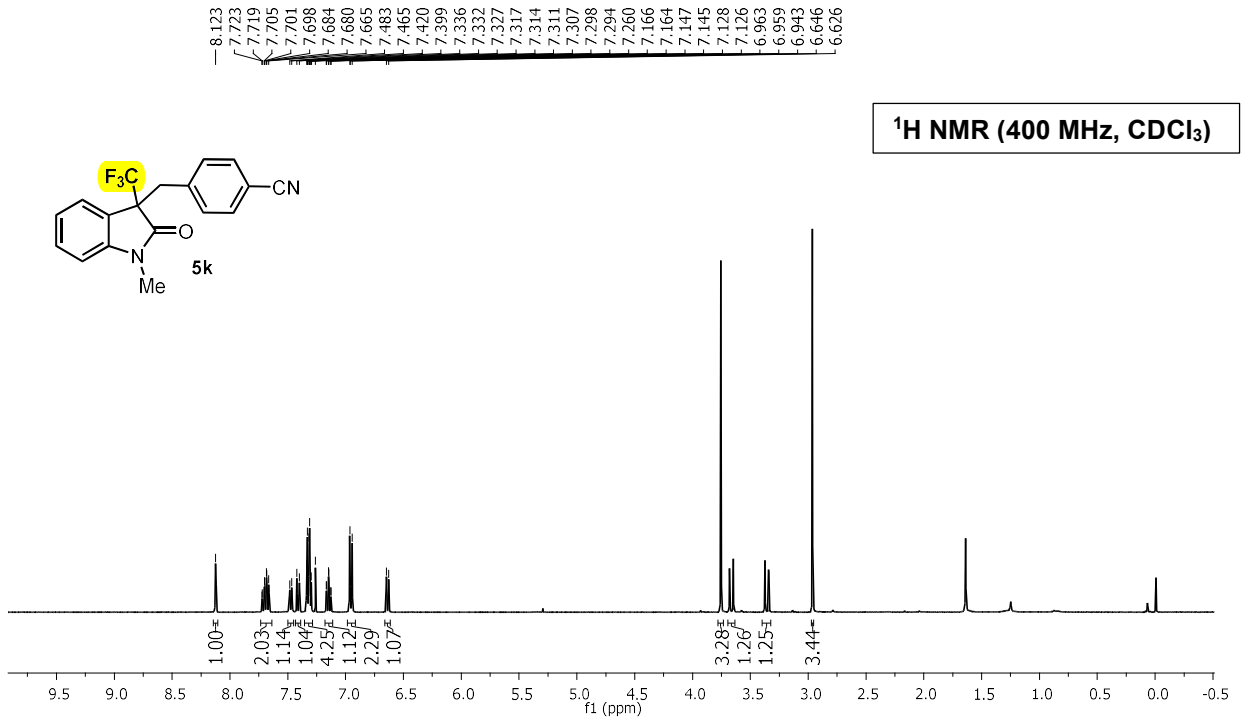
^{1}H NMR (400 MHz, $CDCl_3$)

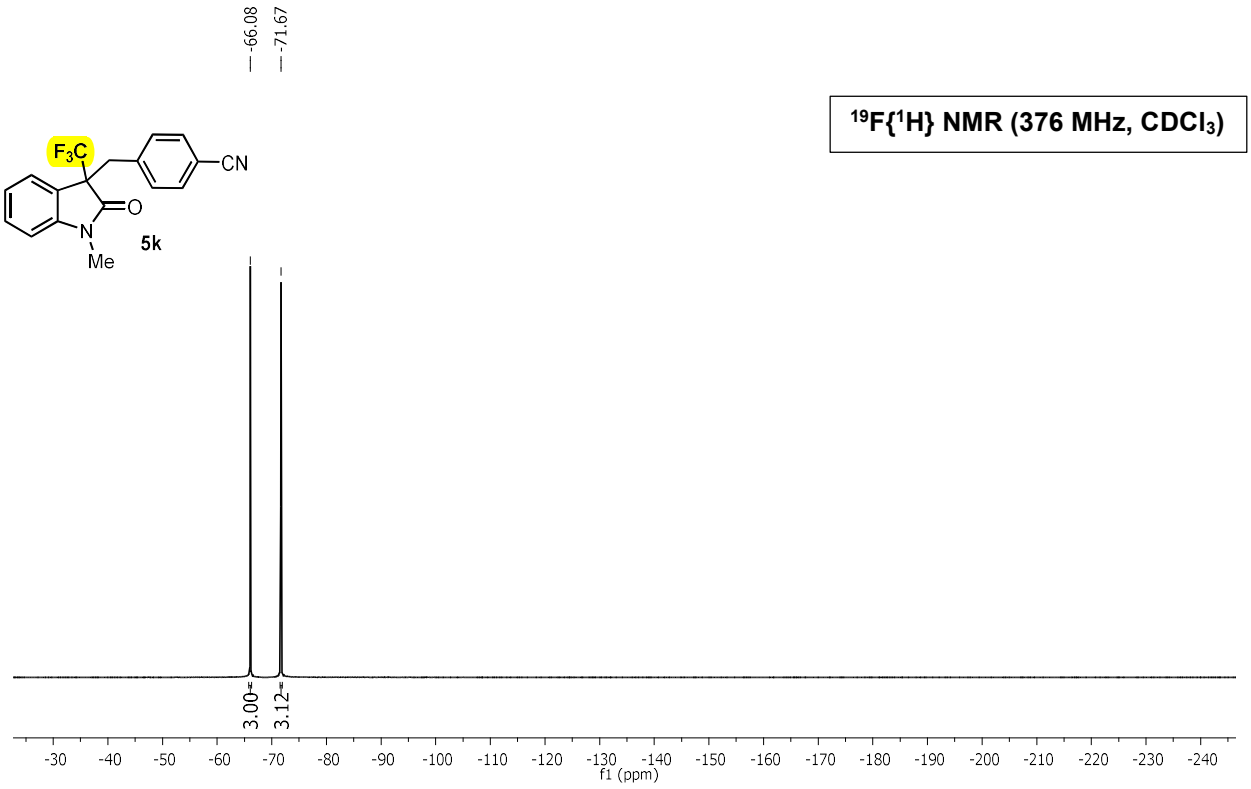


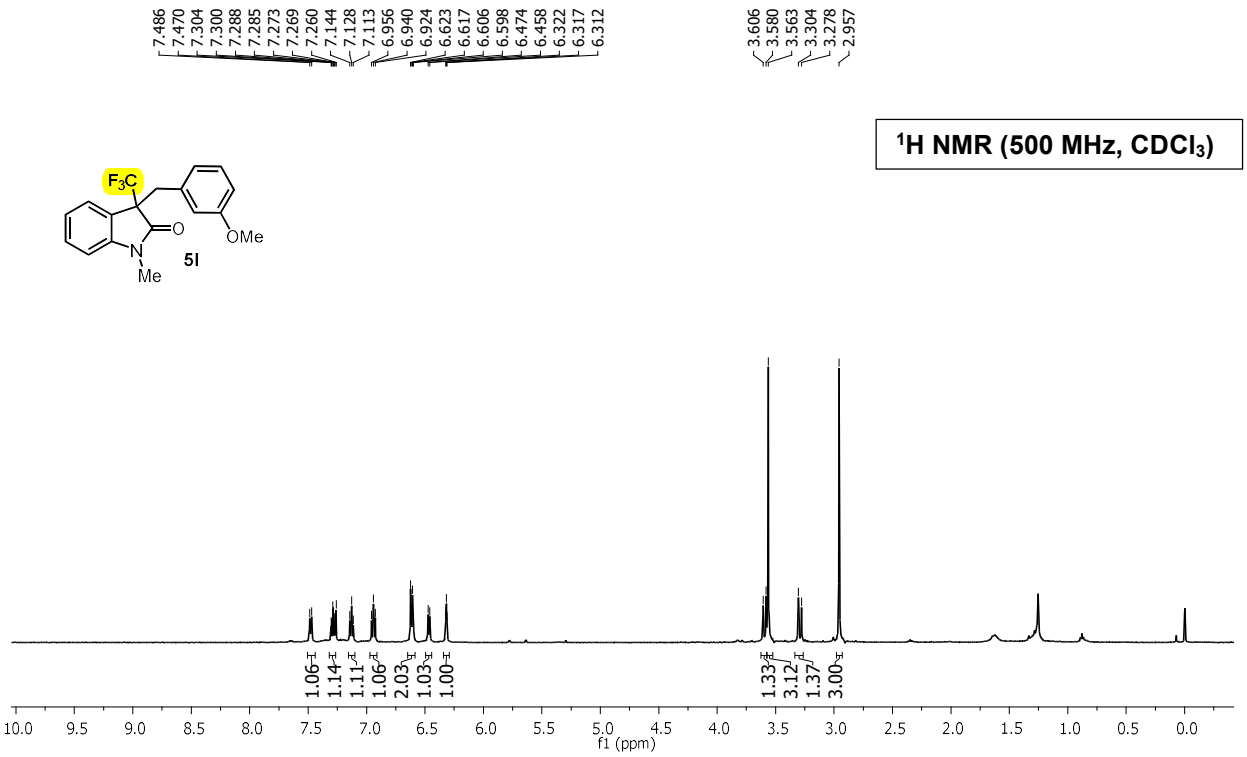
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

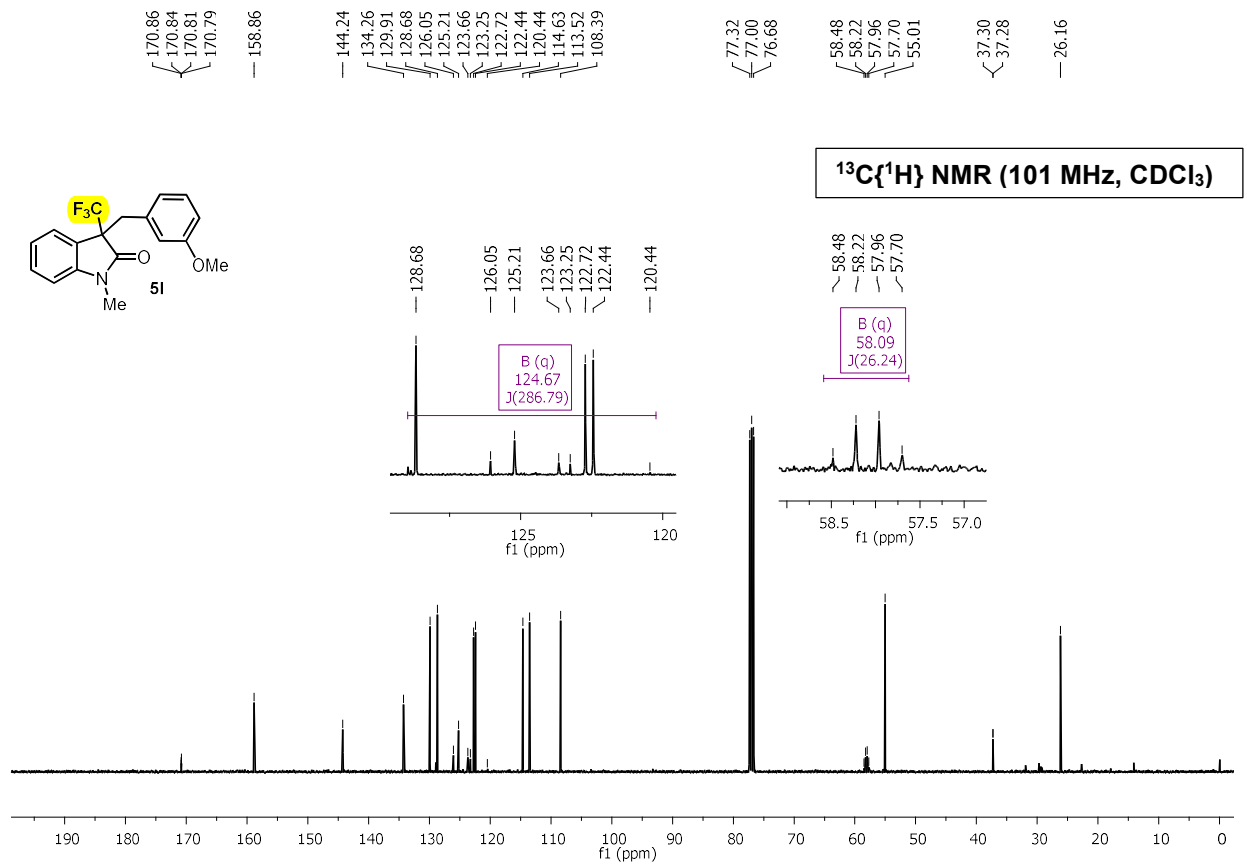


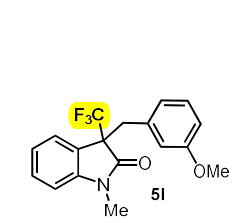
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)


8.123
7.723
7.719
7.705
7.701
7.698
7.684
7.680
7.665
7.483
7.465
7.420
7.399
7.336
7.332
7.327
7.317
7.314
7.311
7.307
7.298
7.294
7.260
7.166
7.164
7.147
7.145
7.128
7.126
6.963
6.959
6.943
6.646
6.626
1H NMR (400 MHz, CDCl3)
F3C
CN
O
N
Me
5k
1.00
2.03
1.14
1.04
4.25
1.12
2.29
1.07
3.28
1.26
1.25
3.44
f1 (ppm)


-66.08
-71.67
19F{1H} NMR (376 MHz, CDCl3)
F3C
CN
O
N
Me
5k
3.00
3.12
f1 (ppm)


7.486
7.470
7.304
7.300
7.288
7.285
7.273
7.269
7.260
7.144
7.128
7.113
6.956
6.940
6.924
6.623
6.617
6.606
6.598
6.474
6.458
6.322
6.317
6.312
3.606
3.580
3.563
3.304
3.278
2.957
1H NMR (500 MHz, CDCl3)
F3C
O
N
Me
OMe
5l
1.06
1.14
1.11
1.06
2.03
1.03
1.00
1.33
3.12
1.37
3.00
f1 (ppm)

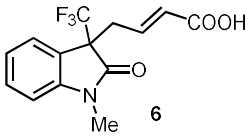

170.86
170.84
170.81
170.79
158.86
144.24
134.26
129.91
128.68
126.05
125.21
123.66
123.25
122.72
122.44
120.44
114.63
113.52
108.39
77.32
77.00
76.68
58.48
58.22
57.96
57.70
55.01
37.30
37.28
26.16
13C{1H} NMR (101 MHz, CDCl3)
F3C
O
N
Me
OMe
5l
128.68
126.05
125.21
123.66
123.25
122.72
122.44
120.44
B (q)
124.67
J(286.79)
58.48
58.22
57.96
57.70
B (q)
58.09
J(26.24)
f1 (ppm)
f1 (ppm)



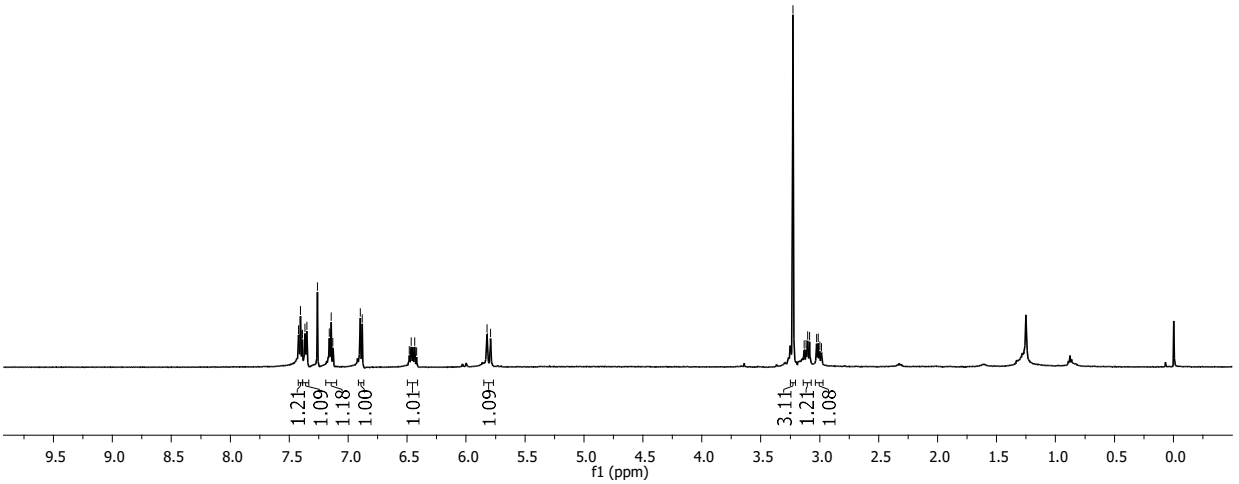
5l

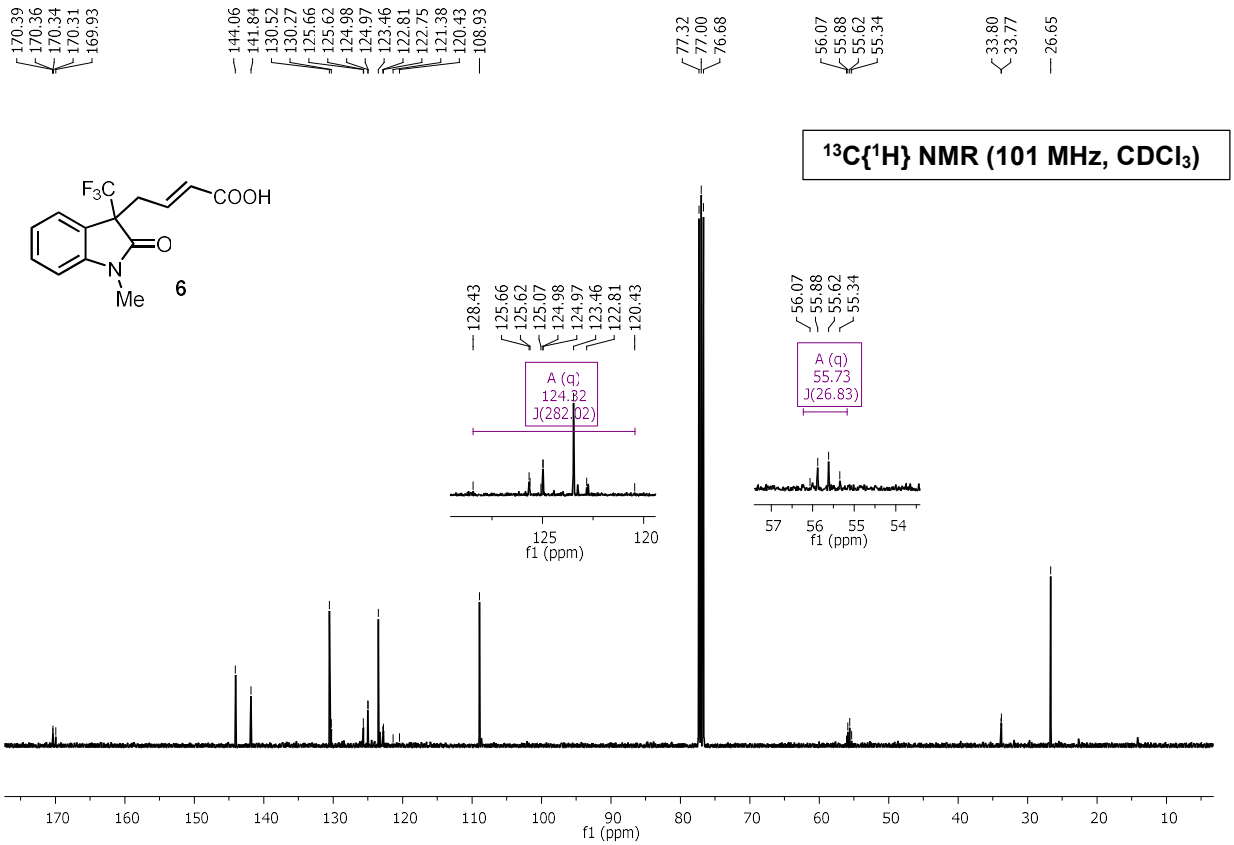
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

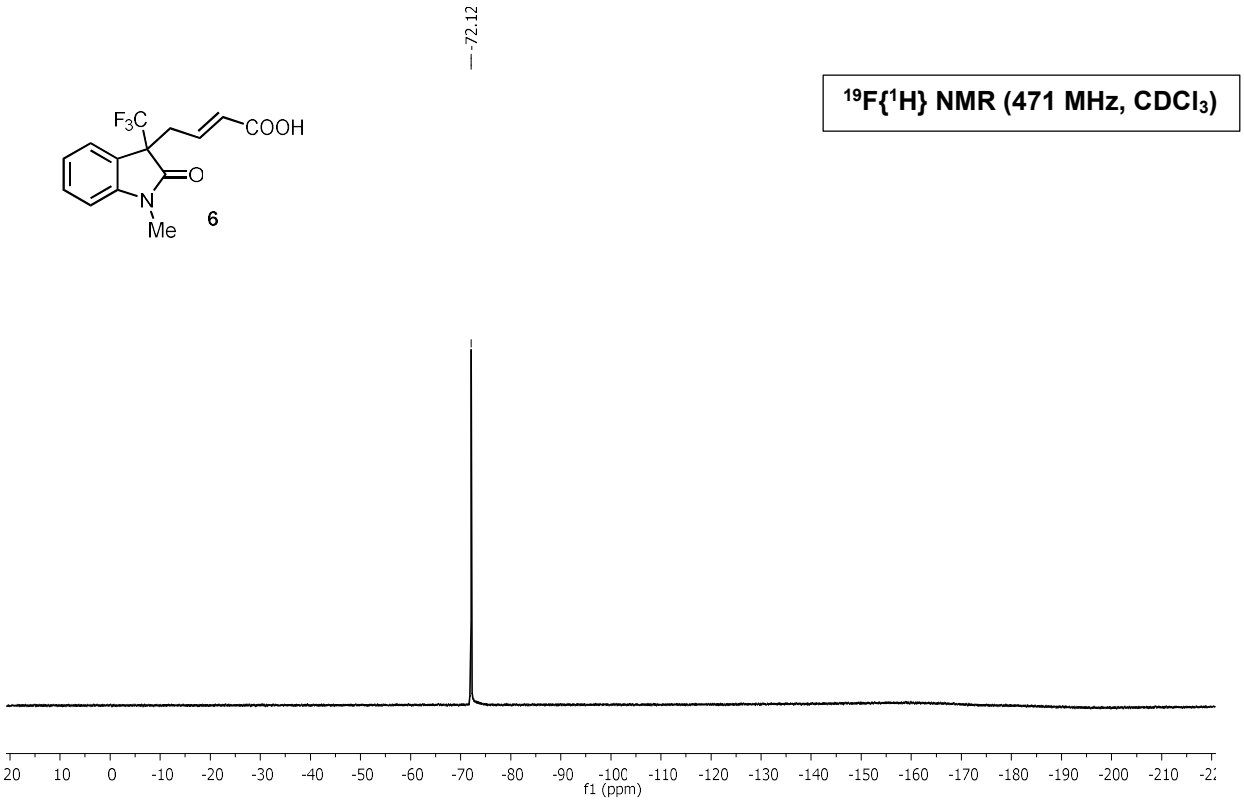
^{1}H NMR (500 MHz, $CDCl_3$)

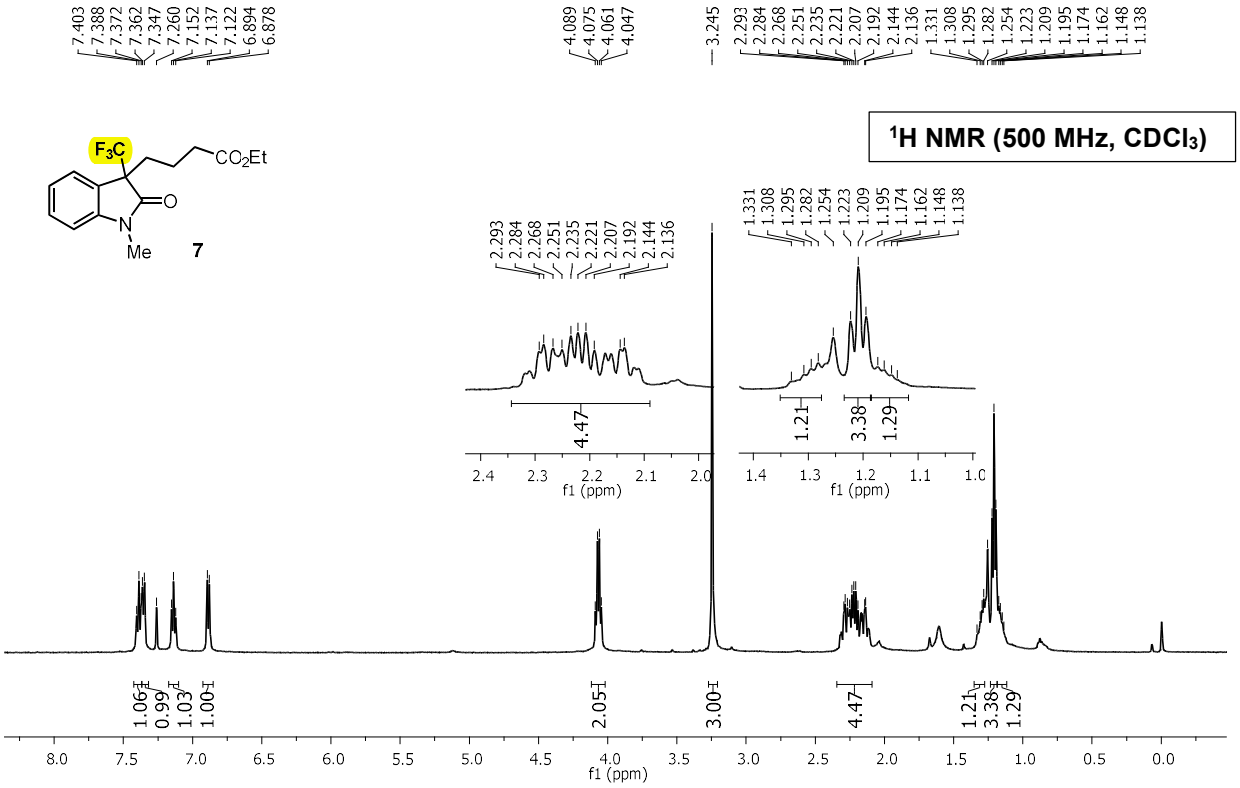


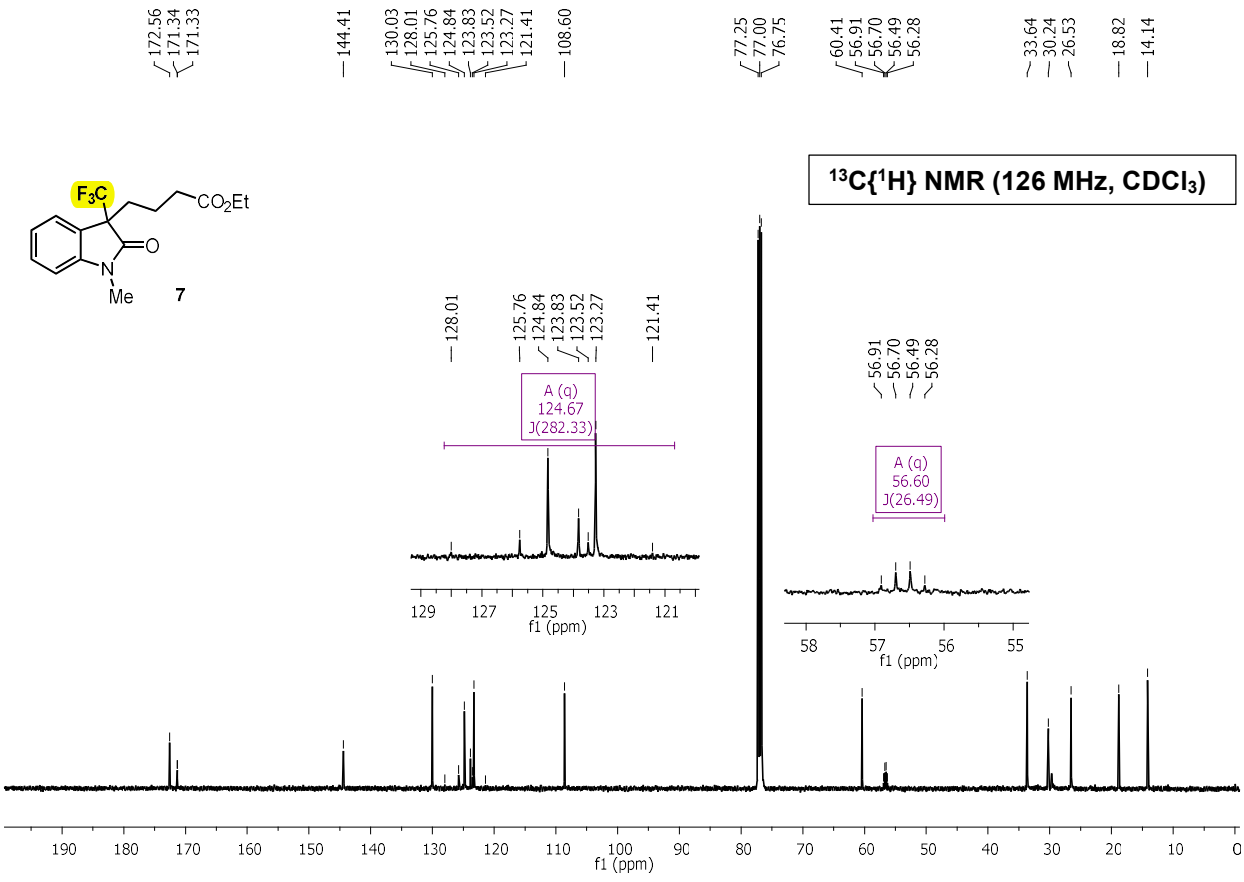
6

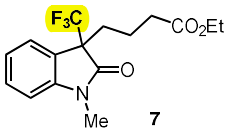



170.39
170.36
170.34
170.31
169.93
144.06
141.84
130.52
130.27
125.66
125.62
124.98
124.97
123.46
122.81
122.75
121.38
120.43
108.93
77.32
77.00
76.68
56.07
55.88
55.62
55.34
33.80
33.77
26.65
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)
F_3C
COOH
O
N
Me
6
128.43
125.66
125.62
125.07
124.98
124.97
123.46
122.81
120.43
A (q)
124.32
J(282.02)
56.07
55.88
55.62
55.34
A (q)
55.73
J(26.83)
f1 (ppm)
f1 (ppm)
f1 (ppm)


-72.12
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)
F_3C
COOH
O
N
Me
6
f1 (ppm)

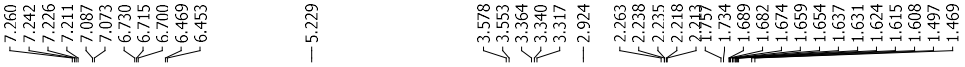

7.403
7.388
7.372
7.362
7.347
7.260
7.152
7.137
7.122
6.894
6.878
4.089
4.075
4.061
4.047
3.245
2.293
2.284
2.268
2.251
2.235
2.221
2.207
2.192
2.144
2.136
1.331
1.308
1.295
1.282
1.254
1.223
1.209
1.195
1.174
1.162
1.148
1.138
F3C
CO2Et
O
N
Me
7
1H NMR (500 MHz, CDCl3)
4.47
1.21
3.38
1.29
f1 (ppm)
1.06
0.99
1.03
1.00
2.05
3.00
4.47
1.21
3.38
1.29

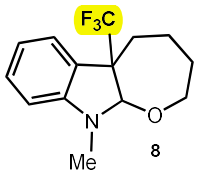

172.56
171.34
171.33
144.41
130.03
128.01
125.76
124.84
123.83
123.52
123.27
121.41
108.60
77.25
77.00
76.75
60.41
56.91
56.70
56.49
56.28
33.64
30.24
26.53
18.82
14.14
13C{1H} NMR (126 MHz, CDCl3)
F3C
CO2Et
O
N
Me
7
128.01
125.76
124.84
123.83
123.52
123.27
121.41
A (q)
124.67
J(282.33)
56.91
56.70
56.49
56.28
A (q)
56.60
J(26.49)
f1 (ppm)



7

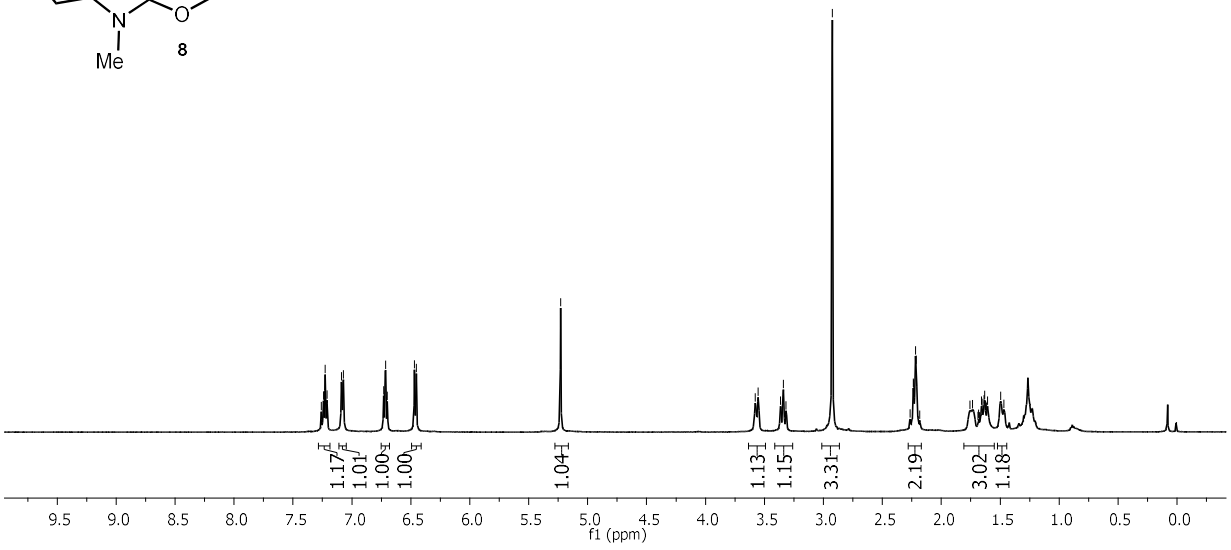
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)

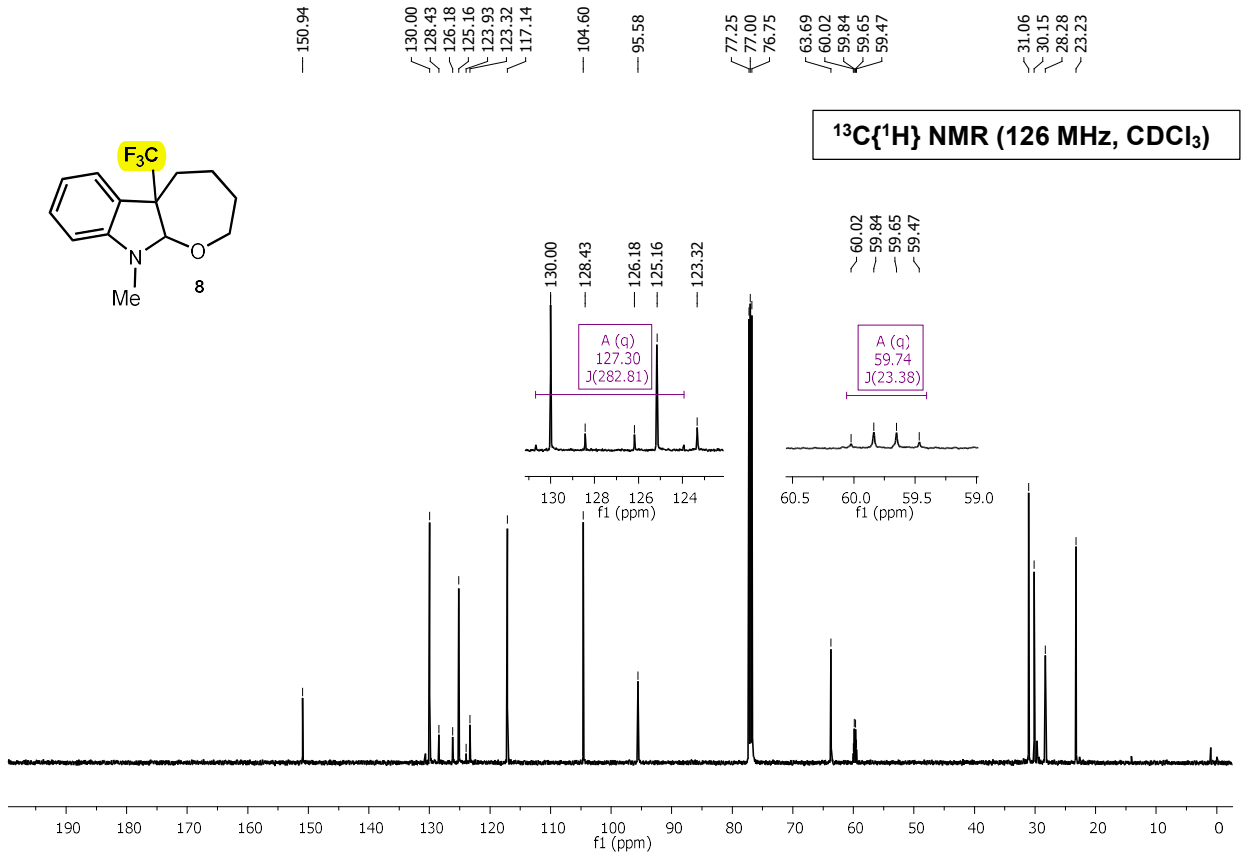


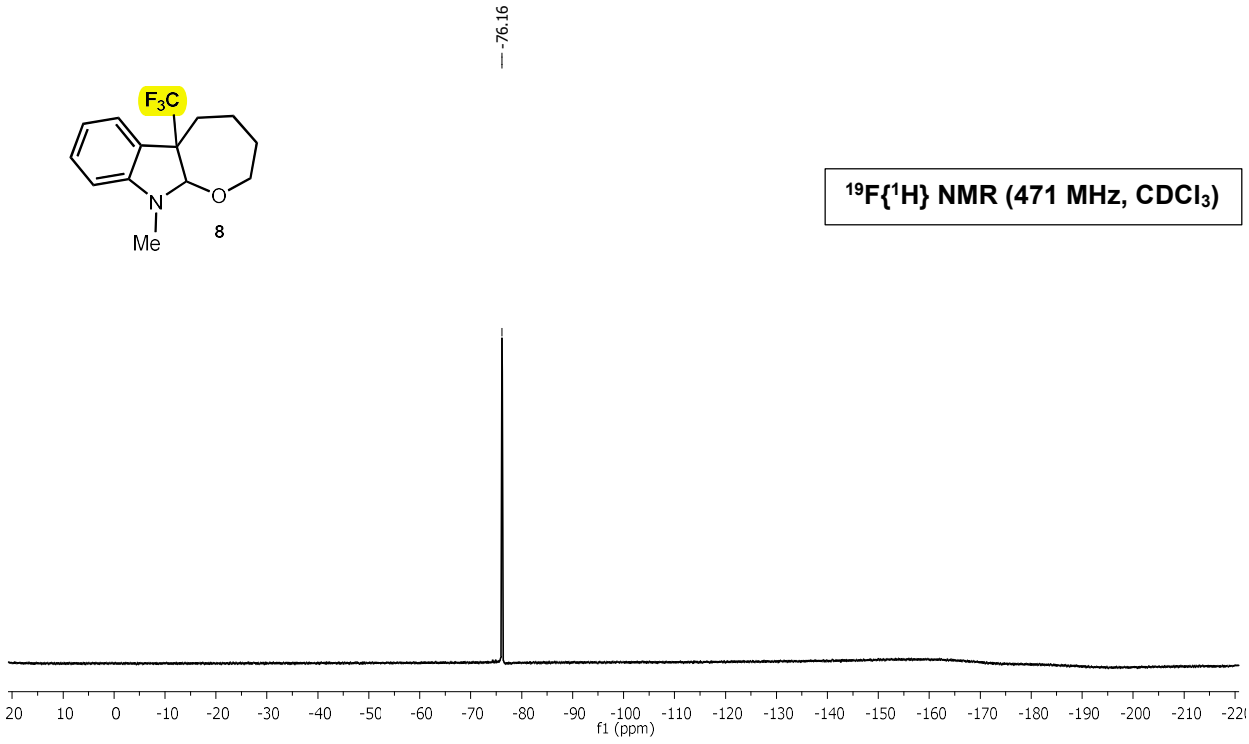


8

^{1}H NMR (500 MHz, $CDCl_3$)




150.94
130.00
128.43
126.18
125.16
123.93
123.32
117.14
104.60
95.58
77.25
77.00
76.75
63.69
60.02
59.84
59.65
59.47
31.06
30.15
28.28
23.23
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)
F_3C
N
O
Me
8
A (q)
127.30
J(282.81)
A (q)
59.74
J(23.38)
f1 (ppm)


-76.16
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)
F_3C
N
O
Me
8
f1 (ppm)