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Supporting Information

Silver-Mediated Direct Trifluoromethoxylation of α-Diazo Esters by $^{-}OCF_3$ Anion

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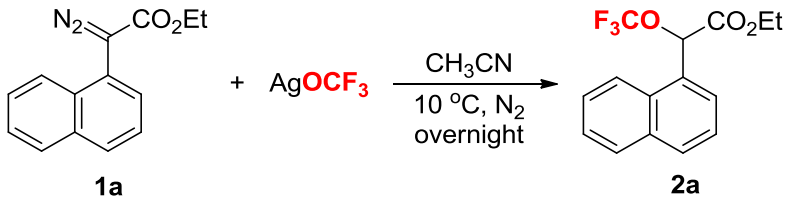
1. General Considerations

All reactions were carried out under a nitrogen atmosphere. Unless otherwise specified, NMR spectra were recorded in $CDCl_3$ on a 500 or 400 MHz (for ^1H), 471 or 376 MHz (for ^{19}F), or 126 or 100 MHz (for ^{13}C) spectrometer. All chemical shifts were reported in ppm relative to TMS (^1H NMR, 0 ppm) and $PhCF_3$ (^{19}F NMR, -63.0 ppm) as internal or external standards. The HPLC experiments were carried out on a Waters e2695 instrument (column: J&K, RP-C18, 5 μm, 4.6 × 150 mm), and the yields of the products were determined by using the corresponding pure compounds as the external standards. The coupling constants were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Melting points were measured and uncorrected. MS experiments were performed on a TOF-Q ESI or CI/EI instrument. $AgOCF_3$ was synthesized and used in CH_3CN solutions (0.5 M or 1.0 M) according to the literature.[1] Other $Q^+[OCF_3]^-$ salts were prepared *in situ* from the corresponding anhydrous fluorides according to the literature.[2] Solvents were dried before use according to the literature.[3] 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) was sublimated before use according to the literature.[4] Other reagents used in the reactions were all purchased from commercial sources and used without further purification.

2. Screening the optimized reaction conditions for silver-mediated trifluoromethoxylation of 1a

Table 1 Trifluoromethoxylation of **1a** by $AgOCF_3$



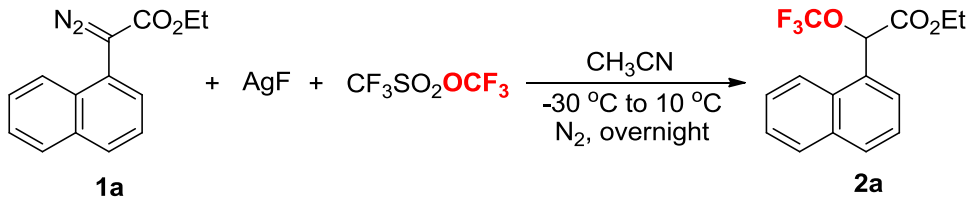
1a **2a**

Entry	**1a** : $AgOCF_3$ [a]	Conditions [b]	Yield (**2a**, %) [c]
1	1 : 2	Method A	43
2	2 : 1	Method A	36

3	1 : 4	Method A	53
4	1 : 4	Method A at -30 ^{o}C, then warmed to 10 ^{o}C	53
5	1 : 4	Method A at 25 ^{o}C	58
6	1 : 2	Method B	20
7	1 : 2	Method C	38
8 [d]	1 : 2	Method C	36
9 [d]	1 : 3	Method C	45
10 [d]	**1 : 4**	**Method C**	**60 (56)**
11	1 : 2	Method D	37
12	1 : 2	Method E	41

[a] The molar ratio of **1a** and $AgOCF_3$. The reactions were run on a 0.1 or 0.5 mmol scale of **1a** and the solutions of $AgOCF_3$ (0.5 or 1.0 M) in CH_3CN were used. [b] Reaction conditions: *Method A*: the $AgOCF_3$ solution was added into a mixture of **1a** and CH_3CN in one portion via syringe. *Method B*: the $AgOCF_3$ solution was added dropwise into a mixture of **1a** and CH_3CN. *Method C*: a solution of **1a** in CH_3CN was added into $AgOCF_3$ in one portion via syringe. *Method D*: a solution of **1a** in CH_3CN was added dropwise into $AgOCF_3$. *Method E*: The solutions of **1a** and $AgOCF_3$ in CH_3CN were simultaneously added dropwise into a flask. All reactions (for Methods A, B, C, D, and E) were conducted at 10 ^{o}C under a N_2 atmosphere overnight. [c] The yield was determined by HPLC using **2a** as the external standard (t_R = 7.71 min, λ_{max} = 221.6 nm, methanol/water = 75 : 25 (v / v)). Isolated yield is reported in parenthesis. [d] The neat **1a** was used instead of its solution**.**

Table 2 Trifluoromethoxylation of **1a** by $CF_3SO_2OCF_3$ in the presence of AgF



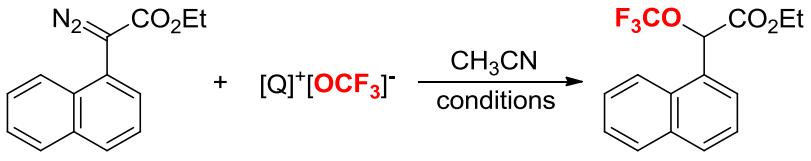
1a **2a**

Entry	**1a** : AgF : $CF_3SO_2OCF_3$ [a]	Conditions [b]	Yields (**2a**, %) [c]

1	1 : 2 : 8	Method A	58
2	1 : 2 : 8	Method B	77
3	1 : 1 : 8	Method B	36
4	1 : 3 : 8	Method B	84
5	1 : 4 : 8	Method B	80
6	1 : 5 : 8	Method B	92 (90)
7	1 : 6 : 8	Method B	93
8	1 : 3 : 3	Method B	49
9	1 : 3 : 4.5	Method B	69
10	1 : 3 : 6	Method B	77 (74)
11	1 : 2 : 5	Method B	76 (75)
12	1 : 0 : 5	Method B	0
13 [d]	1 : 2 : 8	Method B at 10 ^{o}C	89
14 [d]	1 : 2 : 8	Method C	76
15 [d]	1 : 2 : 8	Method C at 10 ^{o}C	83
16 [d]	1 : 5 : 8	Method C at 10 ^{o}C	92

[a] The molar ratio of **1a**, AgF, and $CF_3SO_2OCF_3$. The reactions were run on a 0.1 or 0.5 mmol scale of **1a**. [b] Reaction conditions: *Method A*: A solution of **1a** in CH_3CN was added into a mixture of AgF, $CF_3SO_2OCF_3$, and CH_3CN at -30 ^{o}C in one portion via syringe under a N_2 atmosphere. *Method B*: $CF_3SO_2OCF_3$ was added into a mixture of **1a**, AgF, and CH_3CN at -30 ^{o}C in one portion via syringe under a N_2 atmosphere. *Method C*: AgF was added into a mixture of **1a**, $CF_3SO_2OCF_3$, and CH_3CN at -30 ^{o}C in one portion. After 5 mins, the reaction mixtures (for *Methods A, B,* and *C*) were gradually warmed to 10 ^{o}C overnight. [c] The yield was determined by HPLC using **2a** as the external standard (t_R = 7.71 min, λ_{max} = 221.6 nm, methanol/water = 75 : 25 (v / v)). Isolated yield is reported in parenthesis. [d] The reaction is severe, which releases a great quantity of gases.

Table 3 Trifluoromethoxylation of **1a** by other *in situ* generated $Q^+[OCF_3]^-$ salts in the presence or absence of silver additives [a]



1a **2a**

Entry	$Q^+[OCF_3]^-$	Silver additives	Yield (**2a**, %) [b]
1	$[TAS][OCF_3]$	-	0
2	$Cs[OCF_3]$	-	0
3	$K[OCF_3]$	-	0
4	$[Me_4N][OCF_3]$	-	1
5	$[Me_4N][OCF_3]$	AgOTf (2.0)	1
6	$[Me_4N][OCF_3]$	$AgSbF_6$ (2.0)	0
7	$[Me_4N][OCF_3]$	$AgNO_3$ (2.0)	0
8	$[Me_4N][OCF_3]$	Ag_2CO_3 (2.0)	32
9	$[Me_4N][OCF_3]$	Ag_2O (2.0)	23

[a] Reaction conditions: $Q^+[OCF_3]^-$ was prepared *in situ* by addition of $CF_3SO_2OCF_3$ (0.8 mmol) into a mixture of Q^+F^- (0.2 mmol) and CH_3CN (1.0 mL) at -30 ^oC in one portion via syringe under a N_2 atmosphere. After 2 h, the reaction mixture was warmed to 0 ^oC followed by addition of a solution of **1a** (0.1 mmol) in CH_3CN (0.5 mL) or a solution of **1a** (0.1 mmol) in CH_3CN (0.5 mL) and the silver additive (0.2 mmol). The mixture was then warmed to 10 ^oC overnight. [b] The yield was determined by ^{19}F NMR using $PhCF_3$ as an internal standard.

3. Synthesis of $CF_3SO_2OCF_3$ [5]

A three-necked flask was changed with CF_3SO_3H (205.0 g, 120 mL, 1.37 mol) and a condenser with vigorous stirring. Anhydrous P_2O_5 (32.0 g, 0.23 mol) was added slowly and the mixture was heated at 120 ^oC for about 3 h, then at 130 ^oC for 1 h and at 150 ^oC for another 2 h. The product ($CF_3SO_2OCF_3$, TFMT) was collected by bubbling into an aqueous NaOH solution (50.0 g NaOH in 800 mL water) at -10 ^oC. The bottom layer was separated from the NaOH solution and distilled with anhydrous P_2O_5 to give 45 mL of $CF_3SO_2OCF_3$ as a colorless liquid (b.p. 21 ^oC, 1.79 g/mL (20 ^oC, 760 Torr), 80.6 g,

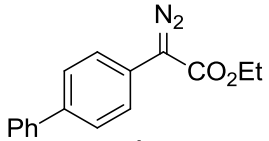
54%), which was stored over anhydrous P_2O_5 for further use in a freezer (-30 ^oC). ^{19}F NMR (471 MHz, $CDCl_3$) δ -53.0 (s, 3F), -73.6 (s, 3F).

4. General procedures for the synthesis of α-diazo esters

4.1. General procedure for the preparation of alkyl α-diazo arylacetates (1a-cc) [6]

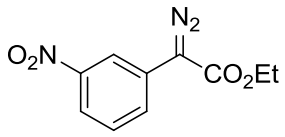
1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 2.28 g, 15.0 mmol) was added slowly into a solution of benzoylated ester (10.0 mmol) and *p*-toluenesulfonyl azide (TsN_3, 2.37 g, 12.0 mmol) in CH_3CN (20 mL) at 0 ℃ with stirring. The mixture was reacted at room temperature overnight, quenched by water (100 mL), and extracted with DCM (3 × 30 mL). The combined organic layers were washed with water (50 mL), dried over anhydrous Na_2SO_4, and concentrated to dryness under the reduced pressure. The residual was purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 20 : 1 (v / v) as eluent to give the title compounds.

The unknown α-diazo esters were fully characterized below.



1o

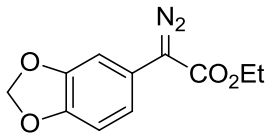
Ethyl 2-([1,1'-biphenyl]-4-yl)-2-diazoacetate (**1o**), red solid, 76% yield. M.p.: 90-91 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 7.65-7.56 (m, 6H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 4.37 (q, *J* = 7.0 Hz, 2H), 1.37 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 140.4, 138.6, 128.9, 127.6, 127.4, 126.9, 124.6, 124.3, 61.1, 14.5. IR (KBr): 3425, 3362, 3250, 3057, 3029, 3005, 2981, 2938, 2908, 2088, 1699, 1608, 1520, 1488, 1371, 1341, 1242, 1166, 1050, 1036, 849, 821, 761, 697 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_{15}N_2O_2]^+$ ($[M + H]^+$): 267.1128, found: 267.1114.



1p

Ethyl 2-diazo-2-(3-nitrophenyl)acetate (**1p**), yellow solid, 77% yield. M.p.: 57-58 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz,

1H), 7.55 (t, *J* = 8.0 Hz, 1H), 4.37 (q, *J* = 7.5 Hz, 2H), 1.37 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 148.8, 129.8, 129.0, 128.6, 120.3, 118.2, 61.5, 14.4. IR (KBr): 3438, 3122, 3095, 2993, 2912, 2098, 1696, 1688, 1571, 1522, 1457, 1377, 1346, 1238, 1176, 1164, 1094, 1049, 917, 897, 881, 805, 742, 718, 671 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{10}H_{10}N_3O_4]^+$ ($[M + H]^+$): 236.0666, found: 236.0695.



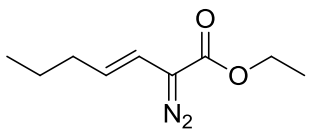
1r

Ethyl 2-(benzodioxol-5-yl)-2-diazoacetate (**1r**), red solid, 85% yield. M.p.: 49-51 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (s, 1H), 6.87-6.82 (m, 2H), 5.96 (s, 2H), 4.32 (q, *J* = 7.0 Hz, 2H), 1.33 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 148.4, 146.0, 118.8, 117.8, 108.8, 105.8, 101.3, 61.0, 14.5. IR (KBr): 3418, 3346, 3127, 2994, 2977, 2929, 2910, 2127, 2086, 1693, 1509, 1495, 1478, 1450, 1375, 1336, 1276, 1236, 1157, 1105, 1038, 936, 896, 875, 814, 792, 736, 679 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{11}H_{10}N_2O_4Na]^+$ ($[M + Na]^+$): 257.0533, found: 257.0519.

4.2. General procedure for the preparation of α-diazo vinylacetates (3a-e) [7,8]

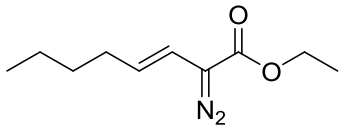
1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 1.83 g, 12.0 mmol) was added slowly into a solution of (*E*)-alk-3-enoate (10.0 mmol) and *p*-toluenesulfonyl azide (TsN_3, 2.37 g, 12.0 mmol) in CH_3CN (20 mL) at 0 ℃ with stirring. The mixture was reacted at room temperature overnight, quenched by water (100 mL), and extracted with DCM (3 × 30 mL). The combined organic layers were washed with water (50 mL), dried over anhydrous Na_2SO_4, and concentrated to dryness under the reduced pressure. The residual was purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 20 : 1 (v / v) as eluent to give the title compounds.

The new products were fully characterized below.



3b

Ethyl (*E*)-2-diazohept-3-enoate (**3b**), red oil, 76 % yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 (d, *J* = 15.7 Hz, 1H), 5.30 (dt, *J* = 15.7 Hz, *J* = 7.1 Hz, 1H), 4.26 (q, *J* = 7.0 Hz, 2H), 2.14 (q, *J* = 7.0 Hz, 2H), 1.41 (m, 2H), 1.29 (t, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.7, 125.5, 111.9, 61.0, 34.9, 22.7, 14.5, 13.6. IR (KBr): 3287, 3188, 3143, 3103, 2961, 2933, 2873, 2097, 1705, 1465, 1393, 1372, 1335, 1314, 1267, 1213, 1173, 1136, 1099, 1044, 1024, 985, 952, 780, 739 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_9H_{15}N_2O_2]^+$ ($[M + H]^+$): 183.1128, found: 183.1148.



3c

Ethyl (*E*)-2-diazooct-3-enoate (**3c**), red oil, 62 % yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 (d, *J* = 15.7 Hz, 1H), 5.31 (dt, *J* = 15.7 Hz, *J* = 7.0 Hz, 1H), 4.26 (q, *J* = 7.0 Hz, 2H), 2.17 (q, *J* = 6.8 Hz, 2H), 1.40-1.26 (m, 7H), 0.90 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.7, 125.7, 111.7, 61.0, 32.5, 31.7, 22.1, 14.4, 13.8. IR (KBr): 2959, 2930, 2873, 2859, 2079, 1738, 1705, 1646, 1466, 1394, 1372, 1314, 1259, 1200, 1172, 1136, 1101, 1032, 952, 738 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{10}H_{16}N_2O_2Na]^+$ ($[M + Na]^+$): 219.1104, found: 219.1117.

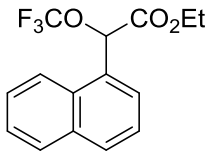
5. Typical procedures for silver-mediated trifluoromethoxylation of α-diazo esters

5.1. Trifluoromethoxylation of 1a by $AgOCF_3$

In a nitrogen-filled glovebox, an oven-dried tube (20 mL) was charged with $AgOCF_3$ (0.5 mol/L in CH_3CN, 4.0 mL, 2.0 mmol) with vigorous stirring. Then **1a** (0.12 g, 0.5 mmol) was added in one portion. The mixture was reacted at 10 ^{o}C overnight and quenched by water (30 mL) outside of glovebox (*Caution! This should be carried out in a fume hood because of the rapid release of gasses*). The resulting mixture was extracted with DCM (2 × 30 mL). The organic layers were washed with water (50 mL), dried over anhydrous Na_2SO_4, and concentrated under the reduced pressure. The residual was purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 20 : 1 (v / v) as eluent to give 84 mg of **2a** (56% yield).

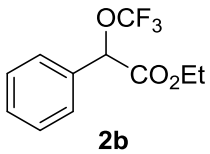
5.2 Trifluoromethoxylation of 1a-cc and 3a-f by $CF_3SO_2OCF_3$ in the presence of AgF

Under a N_2 atmosphere, an oven-dried tube (20 mL) was charged with AgF (0.127 g, 1.0 mmol) and cooled to -30 ^oC with stirring. A solution of α-diazo ester (0.5 mmol) in CH_3CN (2.5 mL) was introduced via syringe. Then $CF_3SO_2OCF_3$ (0.3 mL, 1.79 g/mL, 2.5 mmol) was added in one portion via syringe. After 5 mins, the reaction mixture was gradually warmed to 10 ^oC overnight, quenched by water (30 mL) (*Caution! This should be carried out in a fume hood because of the rapid release of gasses*), and extracted with DCM (2 × 30 mL). The organic layers were washed with water (50 mL), dried over anhydrous Na_2SO_4, and concentrated under the reduced pressure. The residual was purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 20 : 1 (v / v) as eluent to give the trifluoromethoxylated products.



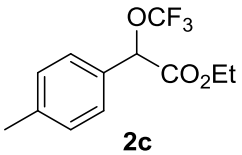
2a

Ethyl 2-(naphthalen-1-yl)-2-(trifluoromethoxy)acetate (**2a**), colorless oil, 119 mg, 75% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.5 Hz, 1H), 7.91 (t, *J* = 7.5 Hz, 2H), 7.66 (d, *J* = 7.0 Hz, 1H), 7.60 (t, *J* = 7.1 Hz, 1H), 7.54 (t, *J* = 7.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 6.15 (s, 1H), 4.25 (m, 1H), 4.18 (m, 1H), 1.18 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 133.9, 130.5, 130.3. 129.3, 128.9, 127.1, 127.0, 126.1, 125.1, 123.3, 121.5 (q, *J* = 258.4 Hz), 75.6 (q, *J* = 3.7 Hz), 51.4, 13.7. IR (KBr): 3055, 2985, 2942, 2906, 2876, 1761, 1514, 1466, 1447, 1394, 1371, 1346, 1275, 1225, 1152, 1087, 1059, 1021, 955, 901, 891, 799, 791, 776, 740 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{15}H_{13}F_3O_3$: 298.0817, found: 298.0817.



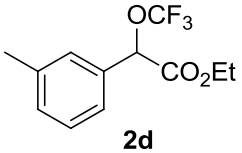
2b

Ethyl 2-phenyl-2-(trifluoromethoxy)acetate (**2b**), colorless oil, 77 mg, 62% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (m, 2H), 7.42-7.40 (m, 3H), 5.53 (s, 1H), 4.24 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.3 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 133.2, 129.7, 128.9, 127.1, 121.4 (q, *J* = 258.4 Hz), 77.0 (q, *J* = 2.8 Hz), 62.2, 13.9. IR (KBr): 3072, 3038, 2978, 2966, 2928, 2856, 1764, 1745, 1498, 1458, 1373, 1263, 1226, 1180, 1152, 1058, 1025, 799, 732, 697 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{11}H_{11}F_3O_3$: 248.0660, found: 248.0660.



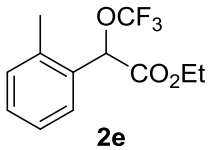
2c

Ethyl 2-(*p*-tolyl)-2-(trifluoromethoxy)acetate (**2c**), colorless oil, 79 mg, 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.49 (s, 1H), 4.23 (m, 2H), 2.37 (s, 3H), 1.25 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 139.8, 130.3, 129.6, 127.1, 121.4 (q, *J* = 258.4 Hz), 76.9 (q, *J* = 2.6 Hz), 62.1, 21.2, 13.9. IR (KBr): 2982, 2963, 2932, 2908, 2860, 1764, 1746, 1516, 1448, 1374, 1281, 1262, 1225, 1180, 1151, 1052, 1022, 806 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{12}H_{13}F_3O_3$: 262.0817, found: 262.0813.



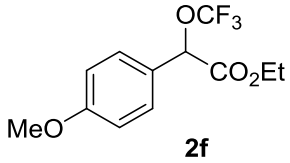
2d

Ethyl 2-(m-tolyl)-2-(trifluoromethoxy)acetate (**2d**), colorless oil, 69 mg, 53% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.16 (m, 3H), 7.13 (d, *J* = 7.5 Hz, 1H), 5.41 (s, 1H), 4.16 (m, 2H), 2.29 (s, 3H), 1.17 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 138.8, 133.1, 130.5, 128.8, 127.6, 124.2, 121.4 (q, *J* = 258.4 Hz), 77.0 (m), 62.1, 21.3, 13.9. IR (KBr): 3064, 2985, 2943, 2909, 2841, 1762, 1604, 1590, 1493, 1468, 1459, 1440, 1375, 1262, 1225, 1150, 1096, 1049, 1023, 964, 900, 854, 784, 741, 692 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{12}H_{14}F_3O_3]^+$ ([M + H]$^+$): 263.0890, found: 263.0905.



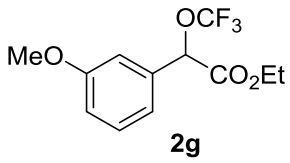
2e

Ethyl 2-(*o*-tolyl)-2-(trifluoromethoxy)acetate (**2e**), colorless oil, 109 mg, 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.5 Hz, 1H), 7.31-7.21 (m, 3H), 5.76 (s, 1H), 4.24 (m, 2H), 2.45 (s, 3H), 1.24 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.3 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 136.2, 131.9, 130.9, 129.6, 127.6, 126.6, 121.5 (q, *J* = 258.4 Hz), 74.2 (q, *J* = 2.8 Hz), 62.1, 19.1, 13.9. IR (KBr): 3070, 3029, 2986, 2941, 2910, 2876, 1764, 1744, 1607, 1494, 1466, 1448, 1374, 1282, 1225, 1151, 1053, 1023, 902, 743 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{12}H_{13}F_3O_3$: 262.0817, found: 262.0815.



2f

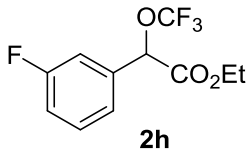
Ethyl 2-(4-methoxyphenyl)-2-(trifluoromethoxy)acetate (**2f**), colorless oil, 101 mg, 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 5.48 (s, 1H), 4.23 (m, 2H), 3.82 (s, 3H), 1.25 (t, *J* = 7.5 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.1 (s, 3F). ^{13}C NMR(126 MHz, $CDCl_3$) δ 167.7, 160.7, 128.7, 125.3, 121.4 (q, *J* = 265.7 Hz), 114.3, 76.7 (m), 62.1, 55.3, 13.9. IR (KBr): 2985, 2941, 2910, 2842, 1761, 1613, 1588, 1516, 1466, 1445, 1395, 1374, 1252, 1225, 1178, 1151, 1116, 1032, 957, 902, 872, 852, 835, 810, 797, 751, 641, 547 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{12}H_{13}F_3O_4$: 278.0766, found: 278.0759.



2g

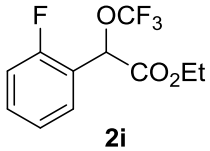
Ethyl 2-(3-methoxyphenyl)-2-(trifluoromethoxy)acetate (**2g**), colorless oil, 81 mg, 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 1H),

6.99 (m, 1H), 6.93 (dd, *J* = 8.2 Hz, *J* = 1.8 Hz, 1H), 5.49 (s, 1H), 4.24 (m, 2H), 3.82 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.3 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 159.9, 134.5, 129.9, 121.4 (q, *J* = 258.4 Hz), 119.3, 115.4, 112.3, 76.8 (q, *J* = 2.8 Hz), 62.2, 55.3, 13.9. IR (KBr): 2985, 2965, 2928, 2873, 1763, 1611, 1490, 1466, 1448, 1373, 1355, 1264, 1225, 1194, 1154, 1097, 1049, 1025, 969, 896, 854, 787, 759, 740, 696, 569 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{12}H_{13}F_3O_4$: 278.0766, found: 278.0765.



2h

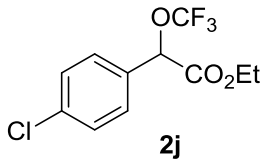
Ethyl 2-(3-fluorophenyl)-2-(trifluoromethoxy)acetate (**2h**), colorless oil, 51 mg, 38% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (m, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 9.3 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 5.54 (s, 1H), 4.27 (m, 2H), 1.27 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.5 (s, 3F), -111.5 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 162.8 (d, *J* = 248.3 Hz), 135.4 (d, *J* = 8.2 Hz), 130.6 (d, *J* = 8.2 Hz), 122.6 (d, *J* = 2.8 Hz), 121.4 (q, *J* = 258.4 Hz), 116.7 (d, *J* = 20.9 Hz), 114.1 (d, *J* = 23.6 Hz), 76.1 (m), 62.4, 13.9. IR (KBr): 3073, 2987, 2942, 2911, 1765, 1748, 1618, 1596, 1491, 1453, 1374, 1263, 1227, 1195, 1156, 1095, 1062, 1023, 972, 899, 876, 787, 744, 686 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{11}H_{10}F_4O_3$: 266.0566, found: 266.0555.



2i

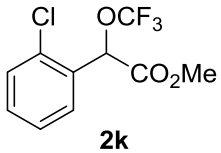
Ethyl 2-(2-fluorophenyl)-2-(trifluoromethoxy)acetate (**2i**), colorless oil, 117 mg, 88% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (t, *J* = 7.2 Hz, 1H), 7.40 (q, *J* = 6.9 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 9.2 Hz, 1H), 5.87 (s, 1H), 4.26 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.6 (s, 3F), -117.8 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 160.0 (d, *J* = 250.2 Hz), 131.7 (d, *J* = 8.2 Hz), 128.8 (d, *J* = 1.8 Hz), 124.7 (d, *J* = 3.7 Hz), 121.2 (d, *J* = 13.7 Hz), 121.4 (q, *J* = 258.4 Hz), 115.9 (d, *J* = 20.9 Hz), 70.4 (m), 62.4, 13.9. IR (KBr): 3080, 2987, 2942, 2909, 2877, 1766, 1619,

1593, 1496, 1461, 1375, 1268, 1227, 1156, 1100, 1062, 1022, 945, 902, 853, 823, 758, 648 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{11}H_{10}F_4O_3$: 266.0566, found: 266.0564.



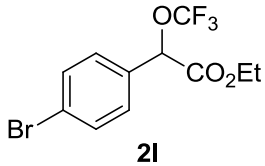
2j

Ethyl 2-(4-chlorophenyl)-2-(trifluoromethoxy)acetate (**2j**), colorless oil, 100 mg, 71% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.38 (m, 4H), 5.50 (s, 1H), 4.23 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.3 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 135.8, 131.8, 129.2, 128.4, 121.4 (q, *J* = 258.4 Hz), 76.2 (q, *J* = 2.8 Hz), 62.4, 13.9. IR (KBr): 2986, 2941, 2911, 2876, 1764, 1599, 1494, 1414, 1374, 1279, 1260, 1227, 1179, 1155, 1094, 1063, 1017, 904, 874, 831, 766, 621 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{11}H_{10}ClF_3O_3$: 282.0271, found: 282.0264.



2k

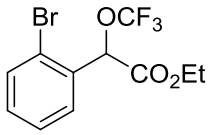
Methyl 2-(2-chlorophenyl)-2-(trifluoromethoxy)acetate (**2k**), colorless oil, 72 mg, 54% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 6.8 Hz, 1H), 7.43 (d, *J* = 7.3 Hz, 1H), 7.34 (m, 2H), 6.08 (s, 1H), 3.78 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.5 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 133.4, 131.6, 131.0, 129.9, 128.9, 127.5, 121.4 (q, *J* = 257.9 Hz), 73.2 (q, *J* = 2.7 Hz), 53.1. IR (KBr): 3070, 3007, 2959, 2930, 2853, 1769, 1595, 1577, 1480, 1447, 1439, 1366, 1274, 1259, 1225, 1156, 1069, 1051, 1040, 1012, 990, 755 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{10}H_8ClF_3O_3$: 268.0114, found: 268.0111.



2l

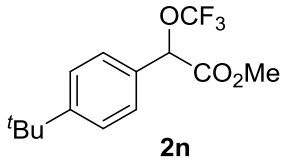
Ethyl 2-(4-bromophenyl)-2-(trifluoromethoxy)acetate (**2l**), colorless oil, 128 mg, 79% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.36 (m, 4H), 5.50 (s, 1H), 4.23 (m, 2H), 1.24

(t, J = 7.0 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.3 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 135.8, 131.8, 129.2, 128.4, 121.4 (q, J = 258.4 Hz), 76.2 (q, J = 2.8 Hz), 62.4, 13.9. IR (KBr): 3069, 3038, 2986, 2941, 2905, 1763, 1598, 1494, 1468, 1458, 1414, 1375, 1261, 1225, 1179, 1154, 1093, 1063, 1016, 968, 873, 828, 777, 698 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{11}H_{11}BrF_3O_3]^+$ (M + H^+): 326.9838, found: 326.9833.



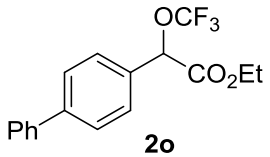
2m

Ethyl 2-(2-bromophenyl)-2-(trifluoromethoxy)acetate (**2m**), colorless oil, 119 mg, 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 8.1 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.40 (t, J = 7.7 Hz, 1H), 7.29 (t, J = 8.1 Hz, 1H), 6.09 (s, 1H), 4.27 (m, 2H), 1.27 (t, J = 7.0 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.3 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 133.4, 133.2, 131.1, 129.0, 128.1, 123.3, 121.4 (q, J = 259.3 Hz), 75.6 (q, J = 2.6 Hz), 62.4, 13.9. IR (KBr): 3068, 2986, 2941, 2910, 2876, 1764, 1591, 1573, 1475, 1444, 1374, 1357, 1274, 1225, 1185, 1156, 1096, 1066, 1025, 947, 902, 753 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{11}H_{10}BrF_3O_3$: 325.9765, found: 325.9760.



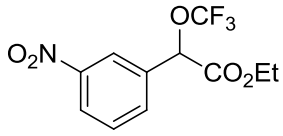
2n

Methyl 2-(4-(tert-butyl)phenyl)-2-(trifluoromethoxy)acetate (**2n**), colorless oil, 97 mg, 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 5.53 (s, 1H), 3.78 (s, 3H), 1.32 (s, 9H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.3 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 153.0, 130.0, 126.9, 125.9, 121.4 (q, J = 258.4 Hz), 52.9, 34.7, 31.2. IR (KBr): 3037, 2963, 2909, 2871, 1769, 1751, 1614, 1518, 1462, 1439, 1366, 1262, 1226, 1151, 1107, 1058, 1018, 872, 828, 801, 776 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{14}H_{17}F_3O_3$: 290.1130, found: 290.1119.



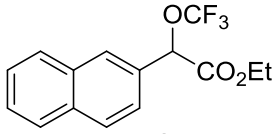
2o

Ethyl 2-([1,1'-biphenyl]-4-yl)-2-(trifluoromethoxy)acetate (**2o**), white solid, 124 mg, 77% yield. M.p.: 47-48 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 5.60 (s, 1H), 4.28 (m, 2H), 1.29 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 142.7, 140.2, 132.1, 128.9, 127.8, 127.7, 127.5, 127.2, 121.5 (q, *J* = 258.0 Hz), 76.8 (m), 62.3, 14.0. IR (KBr): 3060, 3034, 2984, 2965, 2939, 2910, 2875, 1762, 1744, 1613, 1602, 1568, 1521, 1488, 1449, 1413, 1373, 1354, 1260, 1224, 1178, 1149, 1096, 1055, 1021, 903, 874, 839, 810, 760, 737, 697 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{17}H_{19}F_3NO_3]^+$ ($[M + NH_4]^+$): 342.1312, found: 342.1311.



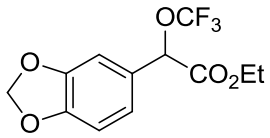
2p

Ethyl 2-(3-nitrophenyl)-2-(trifluoromethoxy)acetate (**2p**), colorless oil, 37 mg, 27% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.29 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.63 (t, *J* = 8.1 Hz, 1H), 5.63 (s, 1H), 4.27 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.5 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 148.5, 135.3, 132.7, 130.1, 124.6, 122.1, 121.3 (q, *J* = 259.4 Hz), 75.6 (q, *J* = 2.8 Hz), 62.8, 13.9. IR (KBr): 2963, 2925, 2854, 1761, 1659, 1632, 1536, 1469, 1447, 1412, 1372, 1353, 1261, 1094, 1021, 864, 801, 732, 699 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{11}H_{11}F_3NO_5]^+$ ($[M + H]^+$): 294.0584, found: 294.0603.



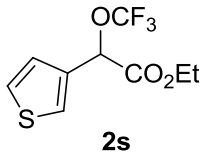
2q

Ethyl 2-(naphthalen-2-yl)-2-(trifluoromethoxy)acetate (**2q**), white solid, 100 mg, 67% yield. M.p.: 30-31 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.91-7.86 (m, 3H), 7.59-7.53 (m, 3H), 5.72 (s, 1H), 4.26 (m, 2H), 1.25 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 133.7, 133.0, 130.6, 129.0, 128.3, 127.8, 127.1, 127.0, 126.8, 123.8, 121.5 (q, *J* = 258.4 Hz), 77.2 (q, *J* = 2.8 Hz), 62.3, 13.9. IR (KBr): 3061, 2963, 2907, 2875, 2856, 1766, 1603, 1511, 1467, 1446, 1372, 1348, 1261, 1227, 1096, 1020, 889, 861, 804, 752 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{15}H_{13}F_3O_3Na]^+$ ($[M + Na]^+$): 321.0709, found: 321.0725.



2r

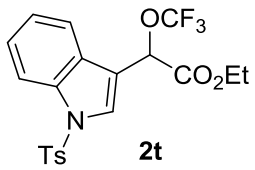
Ethyl 2-(benzo[d][1,3]dioxol-5-yl)-2-(trifluoromethoxy)acetate (**2r**), colorless oil, 105 mg, 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 (s, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 5.99 (s, 2H), 5.42 (s, 1H), 4.23 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 148.9, 148.2, 126.8, 121.5, 121.4 (q, *J* = 258.4 Hz), 108.5, 107.4, 101.5, 76.8 (q, *J* = 2.8 Hz), 62.2, 13.9. IR (KBr): 3080, 2987, 2940, 2907, 2783, 1761, 1611, 1506, 1493, 1449, 1373, 1349, 1248, 1225, 1180, 1152, 1105, 1040, 933, 899, 866, 854, 808, 770, 754, 679, 652 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{12}H_{11}F_3O_5Na]^+$ ($[M + Na]^+$): 315.0451, found: 315.0439.



2s

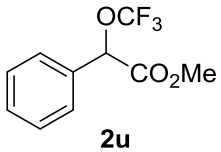
Ethyl 2-(thiophen-3-yl)-2-(trifluoromethoxy)acetate(**2s**), colorless oil, 70 mg, 55% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 2.1 Hz, 1H), 7.36 (dd, *J* = 4.9 Hz, *J* = 3.2 Hz, 1H), 7.16 (d, *J* = 5.0 Hz, 1H), 5.64 (s, 1H), 4.27 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.4 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 133.4, 127.0, 125.9, 124.9, 121.4 (q, *J* = 258.0 Hz), 73.2 (q, *J* = 2.7 Hz), 62.3, 14.0. IR (KBr):

3111, 2984, 2959, 2925, 2854, 1764, 1467, 1448, 1419, 1394, 1373, 1349, 1270, 1224, 1152, 1096, 1084, 1055, 1025, 968, 930, 900, 846, 787, 724, 713, 692, 643 cm^{-1}. HRMS-ESI (m/z) calcd for $C_9H_9F_3O_3S$ (M^+): 254.0225, found: 254.0212.



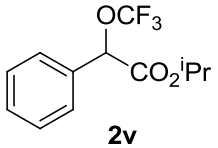
2t

Ethyl 2-(1-tosyl-1H-indol-3-yl)-2-(trifluoromethoxy)acetate(**2t**), colorless oil, 198 mg, 90% yield. A mixture of petroleum ether / ethyl acetate = 5 : 1 (v / v) was used as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.2, 2H), 7.67 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.22-7.16 (m, 3H), 5.69 (s, 1H), 4.17 (m, 2H), 2.28 (s, 3H), 1.16 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.4 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 145.5, 135.1, 134.9, 130.1, 127.7, 127.0, 126.0, 125.5, 123.8, 121.4 (q, *J* = 258.4 Hz), 120.3, 114.7, 113.7, 71.1 (q, *J* = 2.7 Hz), 62.5, 21.6, 13.9. IR (KBr): 3361, 3112, 2982, 2922, 2851, 1761, 1659, 1633, 1597, 1566, 1494, 1469, 1448, 1375, 1278, 1259, 1223, 1190, 1176, 1123, 1099, 1085, 1047, 1021, 981, 898, 853, 813, 748, 704, 666, 599 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{20}H_{18}F_3NO_5SNa]^+$ ($[M + Na]^+$): 464.0750, found: 464.0759.



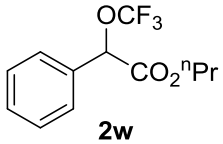
2u

Methyl 2-phenyl-2-(trifluoromethoxy)acetate (**2u**), colorless oil, 70 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (m, 2H), 7.42-7.40 (m, 3H), 5.56 (s, 1H), 3.77 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -59.3 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 133.1, 129.7, 128.9, 127.1, 121.4 (q, *J* = 259.4 Hz), 76.8 (q, *J* = 2.6 Hz), 52.9. IR (KBr): 3070, 3039, 3019, 2961, 2903, 1768, 1589, 1498, 1458, 1439, 1366, 1261, 1227, 1151, 1084, 1059, 1031, 1015, 989, 942, 865, 799, 735, 697, 648 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{10}H_9F_3O_3$: 234.0504, found: 234.0510.



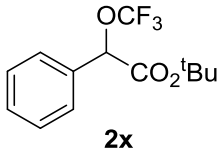
2v

Isopropyl 2-phenyl-2-(trifluoromethoxy)acetate (**2v**), colorless oil, 79 mg, 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (m, 2H), 7.40-7.39 (m, 3H), 5.49 (s, 1H), 5.08 (m, 1H), 1.27 (d, *J* = 6.2 Hz, 3H), 1.16 (d, *J* = 6.3 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.1, 133.3, 129.6, 128.9, 127.0, 121.5 (q, *J* = 258.4 Hz), 77.1 (q, *J* = 2.8 Hz), 70.1, 21.5, 21.3. IR (KBr): 3070, 3038, 2986, 2940, 2881, 1759, 1740, 1495, 1468, 1458, 1377, 1262, 1226, 1180, 1152, 1105, 1058, 1030, 1017, 970, 920, 867, 832, 735, 697 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{12}H_{13}F_3O_3$: 262.0817, found: 262.0814.



2w

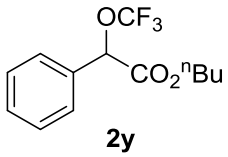
Propyl 2-phenyl-2-(trifluoromethoxy)acetate(**2w**), colorless oil, 69 mg, 53% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (m, 2H), 7.40 (m, 3H), 5.54 (s, 1H), 4.14 (t, *J* = 6.5 Hz, 2H), 1.63 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.3 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.6, 133.3, 129.7, 128.9, 127.0, 121.4 (q, *J* = 257.5 Hz), 76.9 (q, *J* = 2.7 Hz), 67.6, 21.8, 10.0. IR (KBr): 3070, 3039, 2971, 2941, 2902, 2884, 2859, 1765, 1746, 1498, 1458, 1393, 1381, 1363, 1262, 1227, 1177, 1152, 1107, 1084, 1059, 1032, 1004, 979, 936, 865, 795, 733, 697, 649 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{12}H_{13}F_3O_3Na]^+$ (M + Na^+): 285.0709, found: 285.0712.



2x

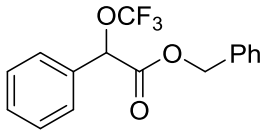
Tert-butyl 2-phenyl-2-(trifluoromethoxy)acetate (**2x**), colorless oil, 124 mg, 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (m, 2H), 7.40 (m, 3H), 5.41 (s, 1H), 1.43 (s, 9H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.6, 133.6,

129.4, 128.8, 127.0, 121.5 (q, J = 257.4 Hz), 83.3, 77.3 (m), 27.7. IR (KBr): 3070, 3038, 2982, 2964, 2931, 2873, 2856, 1759, 1489, 1478, 1458, 1396, 1371, 1262, 1228, 1150, 1106, 1085, 1060, 1030, 960, 899, 867, 839, 800, 750, 697 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_{16}F_3O_3]^+$ ($[M + H]^+$): 277.1046, found: 277.1045.



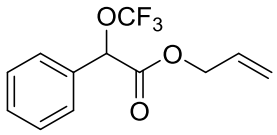
2y

Butyl 2-phenyl-2-(trifluoromethoxy)acetate (**2y**), colorless oil, 113 mg, 82% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.46 (m, 2H), 7.40 (m, 3H), 5.53 (s, 1H), 4.18 (t, J = 6.5 Hz, 2H), 1.59 (m, 2H), 1.29 (m, 2H), 0.87 (t, J = 7.3 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.3 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.6, 133.3, 129.7, 128.9, 127.0, 121.4 (q, J = 257.5 Hz), 76.9 (q, J = 2.8 Hz), 66.0, 30.4, 18.8, 13.5. IR (KBr): 3070, 3038, 2963, 2935, 2877, 2853, 1765, 1745, 1498, 1468, 1458, 1390, 1364, 1263, 1226, 1152, 1084, 1062, 1030, 1019, 964, 894, 866, 802, 732, 697 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{13}H_{15}F_3O_3$: 276.0973, found: 276.0981.



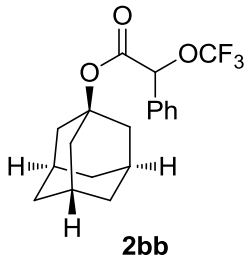
2z

Benzyl 2-phenyl-2-(trifluoromethoxy)acetate (**2z**), colorless oil, 119 mg, 77% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 (m, 2H), 7.39-7.37 (m, 3H), 7.31-7.30 (m, 3H), 7.22 (m, 2H), 5.58 (s, 1H), 5.22 (d, J = 12.4 Hz, 1H), 5.22 (d, J = 12.4 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.4, 134.8, 133.1, 129.8, 129.0, 128.6, 128.6, 128.1, 127.1, 121.5 (q, J = 258.4 Hz), 76.9 (q, J = 2.7 Hz), 67.7. IR (KBr): 3093, 3068, 3037, 2958, 2856, 1764, 1498, 1457, 1382, 1362, 1282, 1263, 1226, 1152, 1082, 1061, 1030, 1003, 969, 864, 735, 696 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{16}H_{13}F_3O_3$: 310.0817, found: 310.0815.



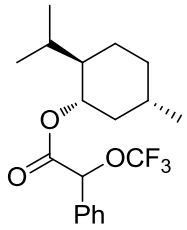
2aa

Allyl 2-phenyl-2-(trifluoromethoxy)acetate (**2aa**), colorless oil, 91 mg, 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (m, 2H), 7.42-7.41 (m, 3H), 5.85 (m, 1H), 5.57 (s, 1H), 5.24 (dd, *J* = 11.4 Hz, *J* = 1.2 Hz, 1H), 5.21 (dm, *J* = 4.6 Hz, 1H), 4.67 (m, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.3 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.2, 133.1, 130.9, 129.7, 128.9, 127.1, 121.4 (q, *J* = 257.5 Hz), 119.0, 76.9 (q, *J* = 2.8 Hz), 66.4. IR (KBr): 3071, 3038, 2961, 2880, 1765, 1650, 1498, 1458, 1416, 1374, 1263, 1227, 1153, 1085, 1059, 1031, 986, 939, 865, 797, 736, 697 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{12}H_{11}F_3O_3$: 260.0660, found: 260.0658.



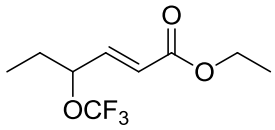
2bb

Adamantan-1-yl 2-phenyl-2-(trifluoromethoxy)acetate (**2bb**), colorless oil, 118 mg, 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (m, 2H), 7.40-7.39 (m, 3H), 5.40 (s, 1H), 2.15 (m, 3H), 2.06 (m, 6H), 1.64 (m, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.0 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.2, 133.8, 129.4, 128.8, 127.0, 121.5 (q, *J* = 258.4 Hz), 83.3, 77.2 (m), 41.0, 36.0, 30.9. IR (KBr): 3068, 3037, 2915, 2855, 1758, 1736, 1498, 1457, 1367, 1355, 1346, 1325, 1315, 1286, 1260, 1226, 1177, 1151, 1104, 1083, 1051, 966, 936, 903, 863, 814, 801, 741, 696 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{21}F_3O_3K]^+$ ($[M + K]^+$): 393.1074, found: 393.1095.



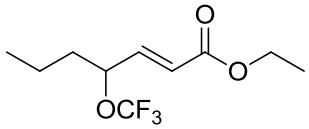
2cc

(*1S,2R,5S*)-2-Isopropyl-5-methylcyclohexyl 2-phenyl-2-(trifluoromethoxy)acetate (**2cc**), colorless oil, 127 mg, 71% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (m, 2H), 7.40 (m, 3H), 5.52 (s, 0.53H), 5.49 (s, 0.47H), 4.78 (td, *J* = 10.8 Hz, *J* = 4.3 Hz, 0.53H), 4.69 (td, *J* = 10.9 Hz, *J* = 4.2 Hz, 0.47H), 1.83-1.74 (m, 1H), 1.68-1.66 (m, 2H), 1.47-1.27 (m, 3H), 1.05-0.94 (m, 2H), 0.91 (d, *J* = 6.7 Hz, 2H), 0.86 (dd, *J* = 6.5 Hz, *J* = 3.8 Hz, 4H), 0.69 (dd, *J* = 9.8 Hz, *J* = 7.8 Hz, 3H), 0.49 (d, *J* = 6.8 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.1 (s, 1.4F). -59.3 (s, 1.6F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.22, 167.17, 133.51, 133.22, 129.63, 129.53, 128.80, 128.78, 127.17, 126.85, 121.48 (q, *J* = 258.4 Hz), 121.46 (q, *J* = 257.5 Hz), 77.11 (m), 77.05 (m), 76.56, 76.39, 47.01, 46.90, 40.51, 40.04, 34.09, 34.07, 31.40, 31.33, 26.14, 25.60, 23.31, 23.07, 21.91, 21.87, 20.61, 20.49, 16.01, 15.65. IR (KBr): 3069, 3038, 2959, 2930, 2872, 1760, 1739, 1498, 1457, 1388, 1371, 1262, 1227, 1177, 1150, 1096, 1059, 1038, 981, 963, 917, 866, 802, 739, 696 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{19}H_{25}F_3O_3$: 358.1756, found: 358.1767.



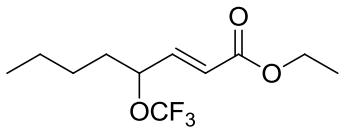
4a

Ethyl (*E*)-4-(trifluoromethoxy)hex-2-enoate (**4a**), colorless oil, 100 mg, 89% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 (dd, *J* = 15.7 Hz, *J* = 5.7 Hz, 1H), 6.04 (dd, *J* = 15.7 Hz, *J* = 1.1 Hz, 1H), 4.68 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.76 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.3 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.4 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.7, 143.7, 122.7, 121.5 (q, *J* = 255.7 Hz), 78.5 (q, *J* = 2.6 Hz), 60.7, 27.6, 14.1, 8.8. IR (KBr): 2981, 2942, 2907, 2884, 1726, 1666, 1596, 1465, 1370, 1314, 1273, 1223, 1181, 1145, 1097, 1039, 980, 854, 813 cm^{-1}. HRMS-EI (m/z) calcd. for $C_9H_{13}F_3O_3$: 226.0817, found: 226.0812.



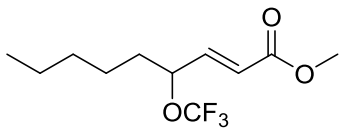
4b

Ethyl (*E*)-4-(trifluoromethoxy)hept-2-enoate (**4b**), colorless oil, 86 mg, 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 (dd, *J* = 15.8 Hz, *J* = 5.7 Hz, 1H), 6.02 (d, *J* = 15.7 Hz, 1H), 4.73 (q, *J* = 5.8 Hz, 1H), 4.21 (q, *J* = 7.0 Hz, 2H), 1.69 (m, 2H), 1.43 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.4 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.7, 144.0, 122.5, 121.5 (q, *J* = 255.7 Hz), 77.2 (q, *J* = 2.7 Hz), 60.7, 36.5, 17.8, 14.1, 13.5. IR (KBr): 2965, 2939, 2878, 1727, 1667, 1468, 1369, 1263, 1219, 1180, 1146, 1083, 1040, 980, 898, 864, 807 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{10}H_{15}F_3O_3$: 240.0973, found: 240.0983.



4c

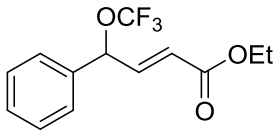
Ethyl (*E*)-4-(trifluoromethoxy)oct-2-enoate (**4c**), colorless oil, 119 mg, 94% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 (dd, *J* = 15.7 Hz, *J* = 5.6 Hz, 1H), 6.02 (d, *J* = 15.7 Hz, 1H), 4.72 (q, *J* = 5.9 Hz, 1H), 4.21 (q, *J* = 7.0 Hz, 2H), 1.71 (m, 2H), 1.39-1.32 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 6.5 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.4 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 144.0, 122.5, 121.5 (q, *J* = 256.5 Hz), 77.4 (q, *J* = 2.8 Hz), 60.7, 34.2, 26.6, 22.2. 14.1, 13.7. IR (KBr): 2962, 2936, 2875, 1728, 1667, 1468, 1370, 1263, 1223, 1179, 1147, 1097, 1040, 981, 930, 864, 847, 805 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{11}H_{17}F_3O_3Na]^+$ ($[M + Na]^+$): 277.1022, found: 277.1046.



4d

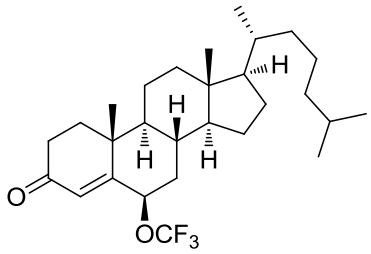
Methyl (*E*)-4-(trifluoromethoxy)non-2-enoate (**4d**), colorless oil, 115 mg, 91% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 (dd, *J* = 15.7 Hz, *J* = 5.7 Hz, 1H), 6.04 (d, *J* = 15.7 Hz,

1H), 4.73 (q, *J* = 6.1 Hz, 1H), 3.76 (s, 3H), 1.70 (m, 2H), 1.39 (m, 2H), 1.35-1.25 (m, 4H), 0.89 (t, *J* = 5.9 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.3 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.1, 144.3, 122.1, 121.5 (q, *J* = 256.5 Hz), 77.4 (q, *J* = 2.8 Hz), 51.8, 34.4, 31.3, 24.1, 22.4, 13.9. IR (KBr): 2957, 2933, 2864, 1732, 1668, 1645, 1460, 1437, 1379, 1315, 1271, 1221, 1203, 1172, 1146, 1094, 1040, 1015, 979, 873, 807 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{11}H_{18}F_3O_3]^+$ ($[M + H]^+$): 255.1203, found: 255.1206.



4e

Ethyl (*E*)-4-phenyl-4-(trifluoromethoxy)but-2-enoate (**4e**), colorless oil, 112 mg, 82 % yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.38 (m, 3H), 7.34 (d, *J* = 7.6 Hz, 2H), 6.99 (dd, *J* = 15.5 Hz, *J* = 5.1 Hz, 1H), 6.12 (d, *J* = 15.7 Hz, 1H), 5.73 (d, *J* = 5.0 Hz, 1H), 4.21 (q, *J* = 7.0 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.6, 143.1, 136.0, 129.3, 129.0, 127.0, 122.5, 121.6 (q, *J* = 257.5 Hz), 78.6 (q, *J* = 2.8 Hz), 60.9, 14.2. IR (KBr): 3068, 3036, 2985, 2939, 2907, 2876, 1724, 1664, 1496, 1457, 1393, 1370, 1311, 1266, 1223, 1177, 1150, 1097, 1070, 1034, 978, 894, 863, 832, 765, 698 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{13}H_{13}F_3O_3$ (M^+): 274.0817, found: 274.0831.



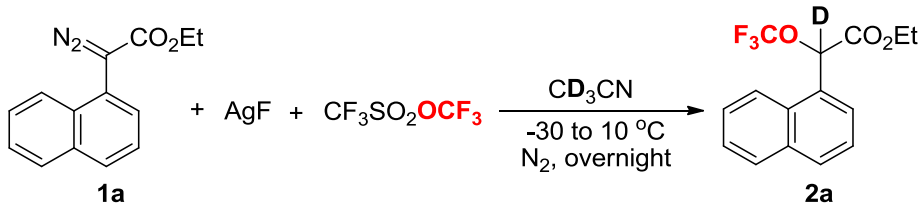
4f

(*6R,8S,9S,10R,13R,14S,17R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-6-(trifluoromethoxy)-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a] phenanthren-3-one (**4f**),[8] 22.5 mg, 48% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.87 (s, 1H), 4.75 (m, 1H), 2.54 (td, *J* = 17.0 Hz, *J* = 4.9 Hz, 1H), 2.40 (dm, *J* = 17.0 Hz, 1H), 2.16-2.06 (m, 3H), 1.86 (m, 2H), 1.73 (td, *J* = 14.7 Hz, *J* = 4.0 Hz, 1H), 1.60 (m, 1H), 1.55-

1.48 (m, 3H), 1.35-1.26 (m, 9H), 1.20-1.09 (m, 6H), 1.01 (m, 2H), 0.92 (d, J = 6.4 Hz, 3H), 0.87 (d, J = 6.4 Hz, 6H), 0.75 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -57.6 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$): 199.7, 161.4, 128.6, 79.4 (q, J = 2.7 Hz), 56.1, 55.6, 53.5, 42.5, 39.5, 38.1, 37.3, 37.2, 36.1, 35.7, 34.1, 30.9, 30.0, 28.1, 28.0, 24.0, 23.8, 22.8, 22.6, 20.9, 18.6, 18.6, 12.0. IR (KBr): 2950, 2869, 1689, 1467, 1382, 1366, 1278, 1262, 1231, 1216, 1143, 1071, 914, 801 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{28}H_{43}F_3O_2Na]^+$ ([M + Na]$^+$): 491.3107, found: 491.3111.

6. Control experiments

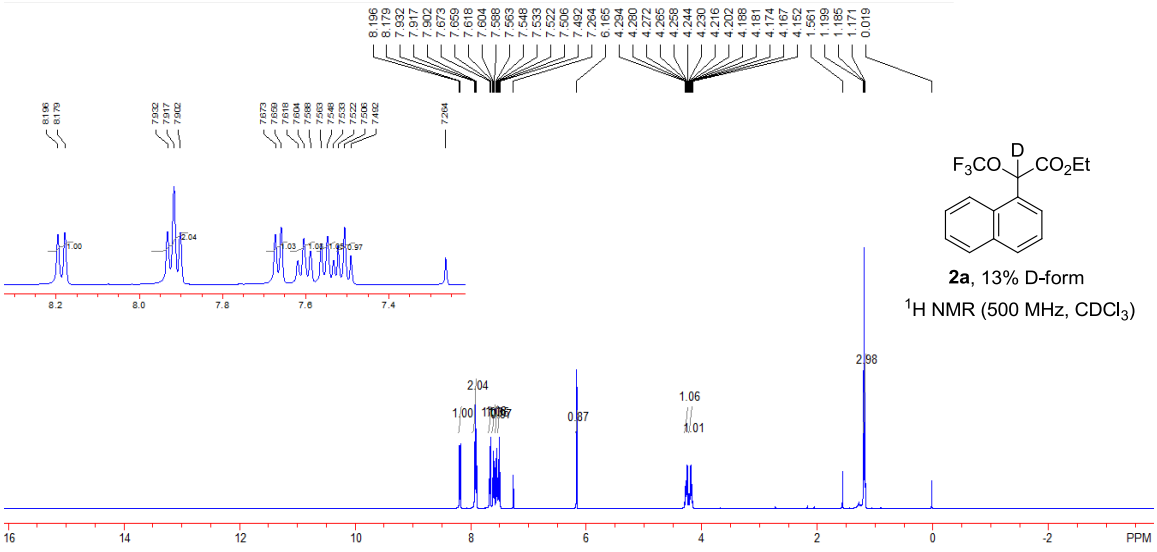
6.1. Trifluoromethoxylation of 1a by $CF_3SO_2OCF_3$ / AgF in CD_3CN



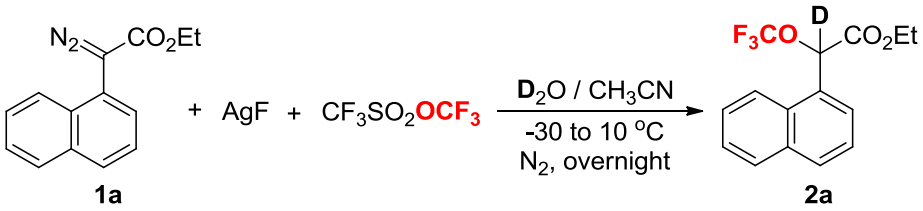
80 % isolated yield of **2a**, 13% D-form

The typical procedure in **5.2.** was used.

2a, 48.0 mg, 80% yield, 13% D-form. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, J = 8.5 Hz, 1H), 7.92 (t, J = 7.5 Hz, 2H), 7.67 (d, J = 7.0 Hz, 1H), 7.60 (t, J = 7.0 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.9 Hz, 1H), 6.17 (s, 0.87 H), 4.26 (m, 1H), 4.18 (m, 1H), 1.19 (t, J = 7.0 Hz, 3H).



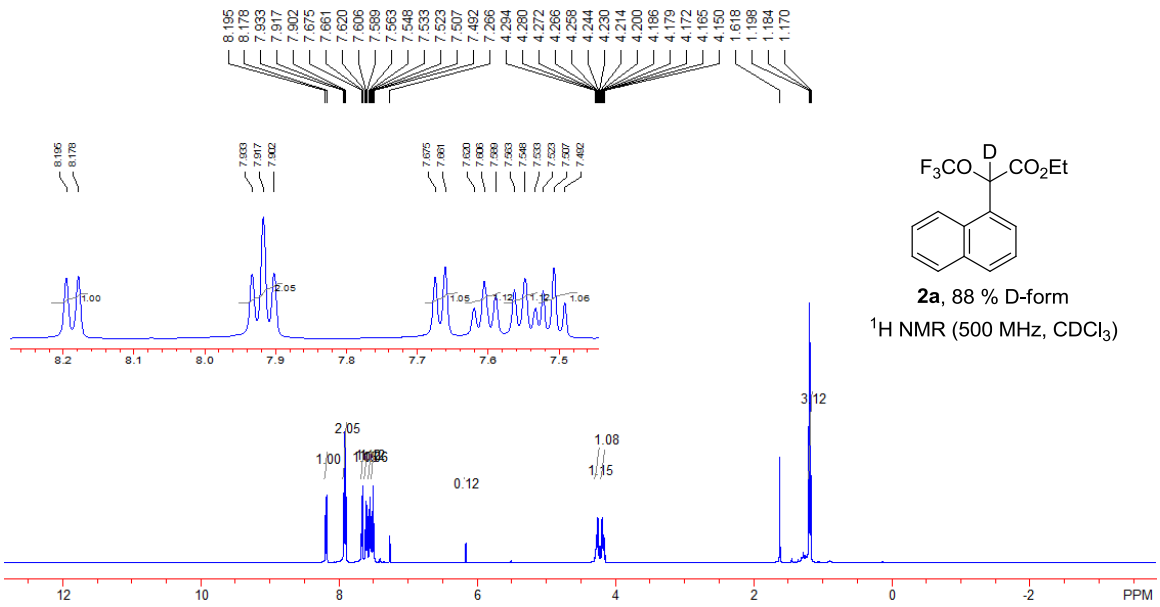
6.2. Trifluoromethoxylation of 1a by $CF_3SO_2OCF_3$ / AgF in CH_3CN with D_2O



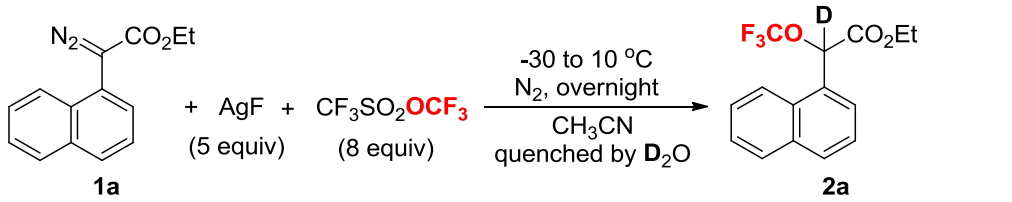
1a **2a**

33% isolated yield, 88% D-form

Under a nitrogen atmosphere, an oven-dried tube (20 mL) was charged with AgF (127 mg, 1.0 mmol,) and cooled to -30 ^{o}C with stirring. A solution of **1a** (48 mg, 0.2 mmol) and D_2O 4 μL (4.0 mg, 0.22 mmol) in CH_3CN (1.0 mL) were added in one portion via syringe. Then $CF_3SO_2OCF_3$ (0.20 mL, 1.6 mmol) was introduced in one portion via syringe. After 5 mins, the reaction mixture was gradually warmed to 10 ^{o}C overnight, quenched by water (30 mL), and extracted with DCM (2 × 30 mL). The organic layers were washed with water (50 mL), dried over anhydrous Na_2SO_4, and concentrated under the reduced pressure. The residual was purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 20 : 1 as eluent to give **2a** as a colorless liquid (20.0 mg, 0.067 mmol, 33 % yield, 88 % D-form). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.5 Hz, 1H), 7.92 (t, *J* = 7.5 Hz, 2H), 7.67 (d, *J* = 7.0 Hz, 1H), 7.61 (t, *J* = 7.0 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 6.17 (s, 0.12H), 4.26 (m, 1H), 4.18 (m, 1H), 1.18 (t, *J* = 7.0 Hz, 3H).



6.3. Trifluoromethoxylation of 1a by $CF_3SO_2OCF_3$ / AgF in CH_3CN and quenched by D_2O

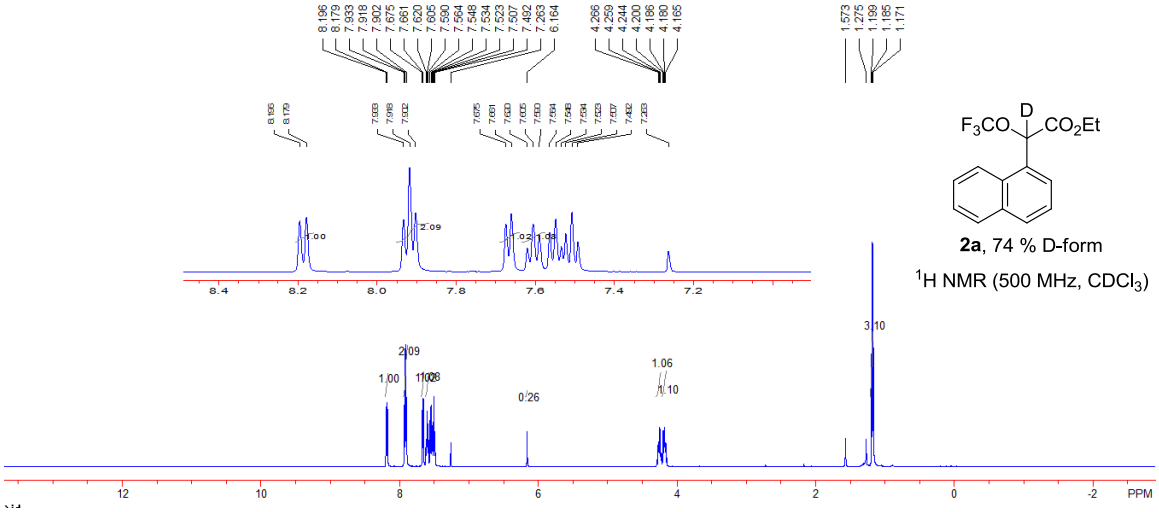


1a **2a**

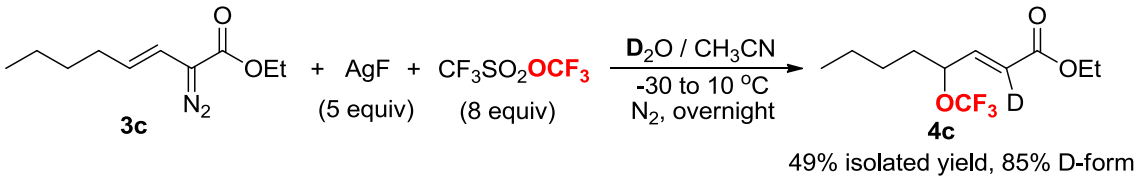
91% isolated yield, 74% D-form

Under a nitrogen atmosphere, an oven-dried tube (20 mL) was charged with AgF (127 mg, 1.0 mmol) and cooled to -30 ^oC with stirring. A solution of **1a** (48 mg, 0.2 mmol) in CH_3CN (1.0 mL) was added in one portion via syringe. Then $CF_3SO_2OCF_3$ (0.20 mL, 1.6 mmol) was introduced in one portion via syringe. After 5 mins, the reaction mixture was gradually warmed to 10 ^oC overnight and quenched by D_2O (0.1 mL). Water (30 mL) was added and the mixture was extracted with DCM (2 × 30 mL). The organic layers were washed with water (50 mL), dried over anhydrous Na_2SO_4, and concentrated under the reduced pressure. The residual was purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 20 : 1 as eluent to give **2a** as a colorless liquid (54.5 mg, 0.18 mmol, 91 % yield, 74 % D-form). ^1H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.5 Hz, 1H), 7.92 (t, *J* = 7.5 Hz, 2H), 7.67 (d, *J* = 7.0 Hz, 1H), 7.61 (t, *J* = 7.0 Hz, 1H),

7.55 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.0 Hz, 1H), 6.16 (s, 0.26 H), 4.26 (m, 1H), 4.18 (m, 1H), 1.19 (t, *J* = 7.0 Hz, 3H).



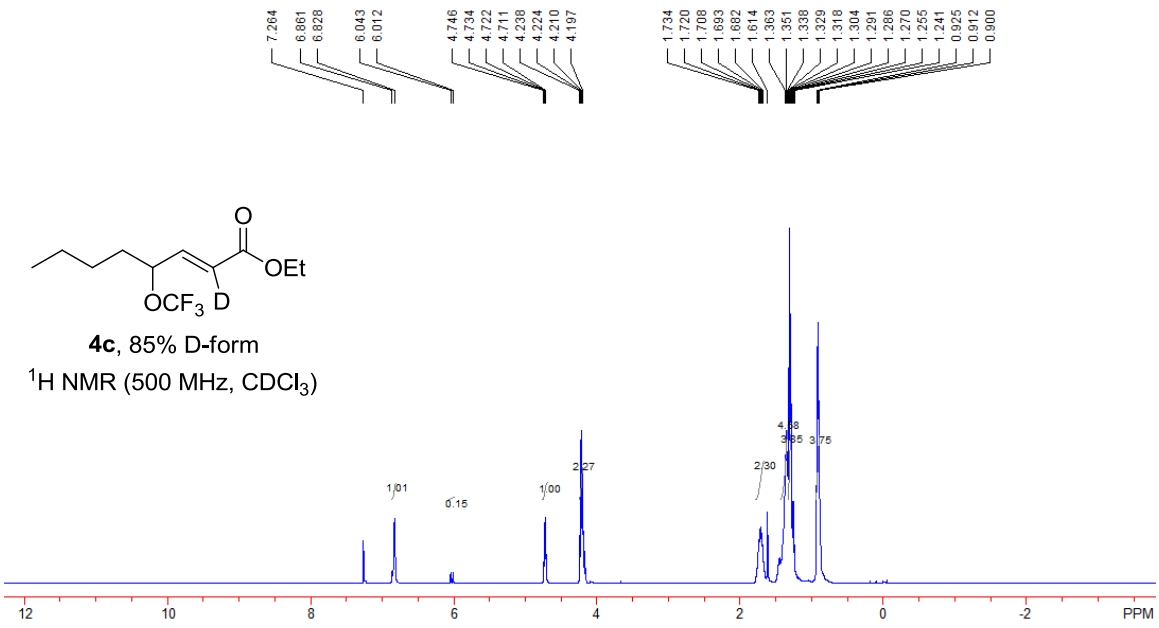
6.4. Trifluoromethoxylation of 3c by $CF_3SO_2OCF_3$ / AgF in CH_3CN with D_2O



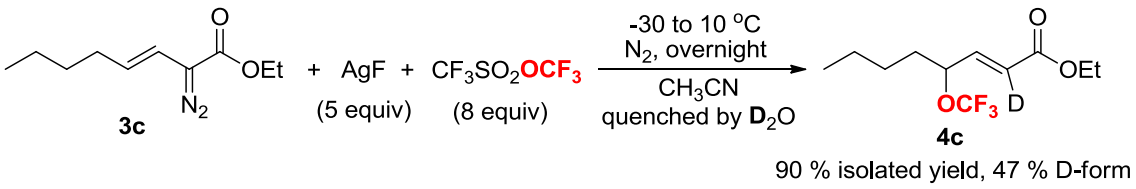
49% isolated yield, 85% D-form

The procedure in **6.2.** was used for **3c**.

4c, 25.0 mg, 0.098 mmol, 49 % yield, 85 % D-form. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 (m, 1H), 6.03 (d, *J* = 15.7 Hz, 0.15 H), 4.73 (q, *J* = 6.1 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.71 (m, 2H), 1.36-1.32 (m, 4H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 6.7 Hz, 3H).

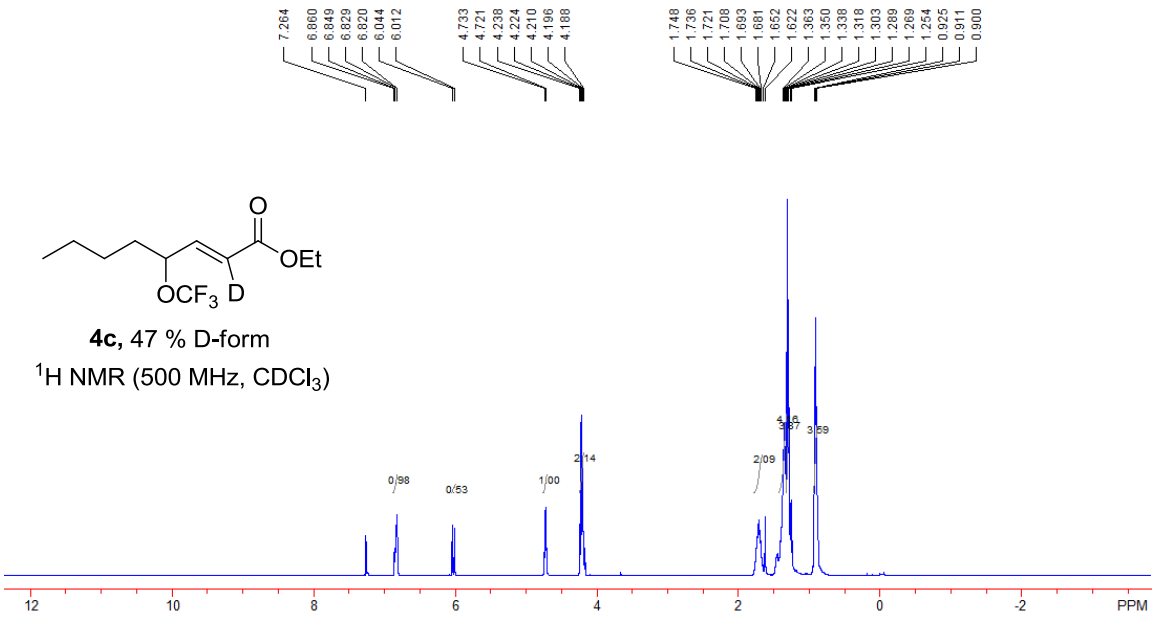


6.5. Trifluoromethoxylation of 3c by $CF_3SO_2OCF_3$ / AgF in CH_3CN and quenched by D_2O

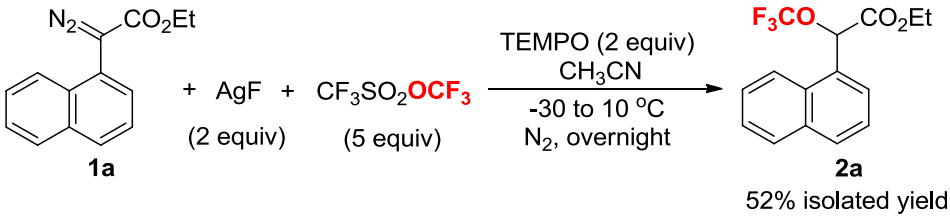


The procedure in **6.3.** was used for **3c**.

4c, 46.0 mg, 0.18 mmol, 90 % yield, 47 % D-form. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84 (m, 1H), 6.03 (d, *J* = 15.7 Hz, 0.53 H), 4.73 (q, *J* = 6.2 Hz, 1H), 4.22 (q, *J* = 7.0 Hz, 2H), 1.71 (m, 2H), 1.36-1.32 (m, 4H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 6.7 Hz, 3H).



6.6. Trifluoromethoxylation of 1a by $CF_3SO_2OCF_3$ / AgF in CH_3CN in the presence of TEMPO



Under a nitrogen atmosphere, an oven-dried tube (20 mL) was charged with AgF (127 mg, 1.0 mmol) and TEMPO (156 mg, 1.0 mmol), and cooled to -30 ^{o}C with stirring. A solution of **1a** (120 mg, 0.5 mmol) in CH_3CN (2.5 mL) was added in one portion via syringe. Then $CF_3SO_2OCF_3$ (0.3 mL, 2.5 mmol) was introduced in one portion via syringe. After 5 mins, the reaction mixture was gradually warmed to 10 ^{o}C overnight, quenched by water (30 mL), and extracted with DCM (2 × 30 mL). The organic layers were washed with water (50 mL), dried over anhydrous Na_2SO_4, and concentrated under the reduced pressure. The residual was purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 20 : 1 as eluent to give **2a** as a colorless liquid (77.0 mg, 0.26 mmol, 52% yield).

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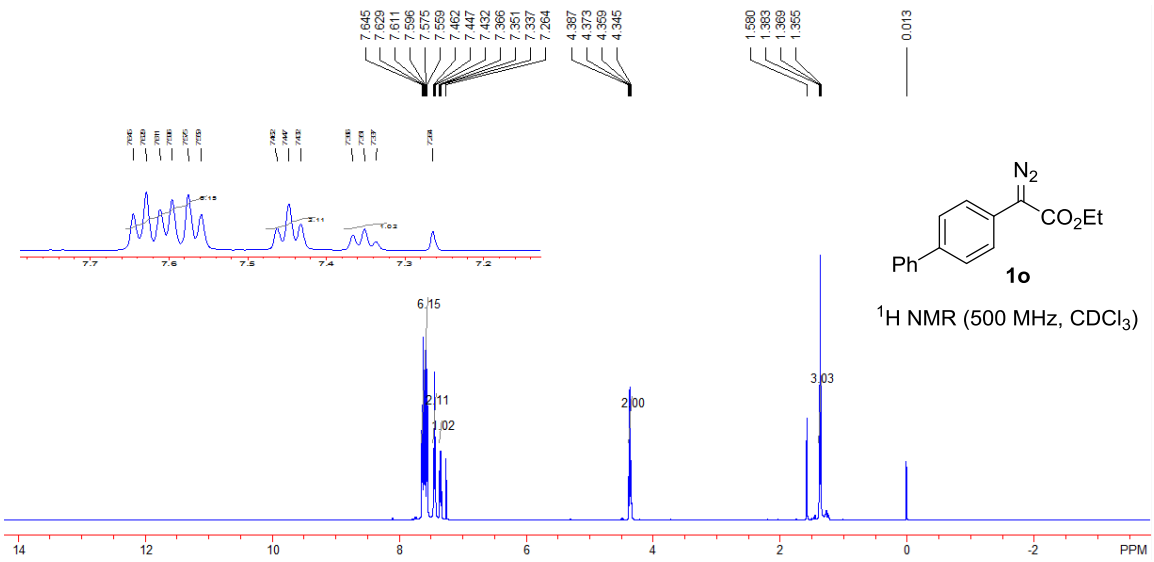
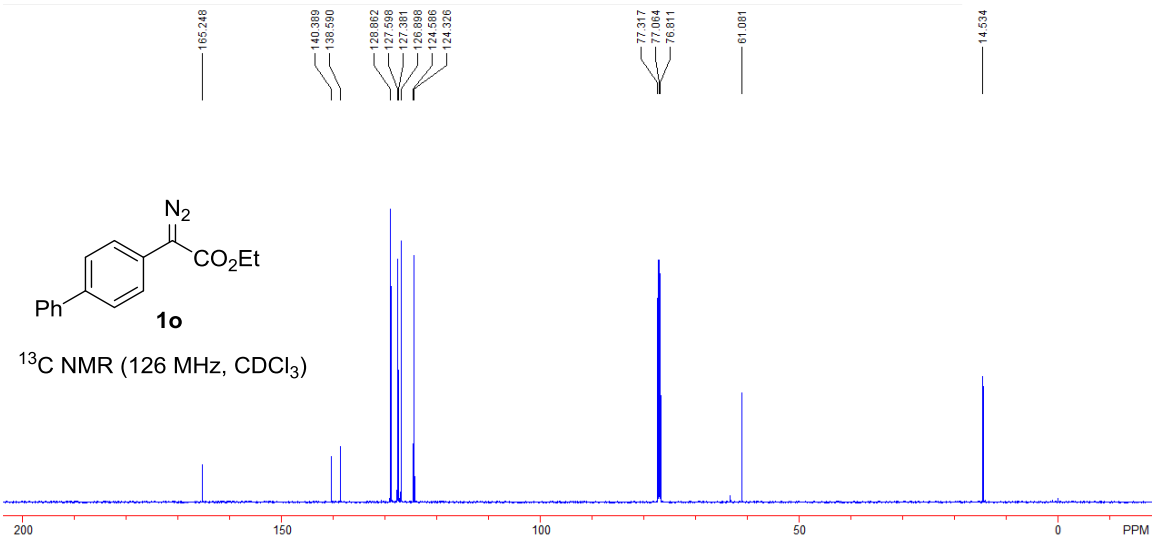
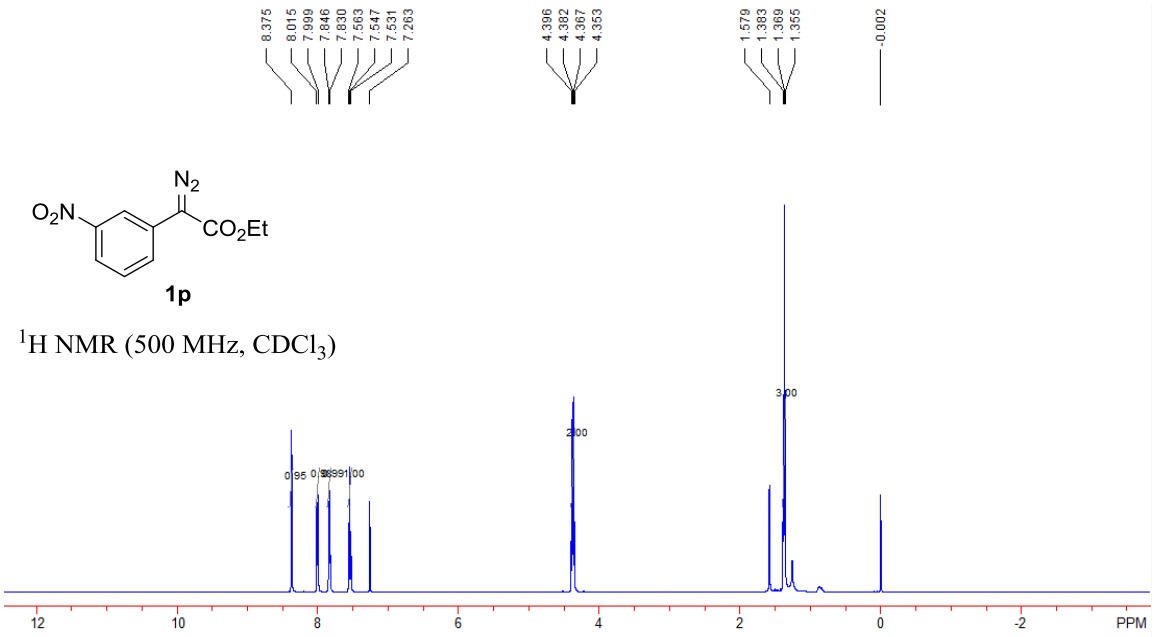
7. NMR spectra of 1o, 1p, 1r, 3b, and 3c

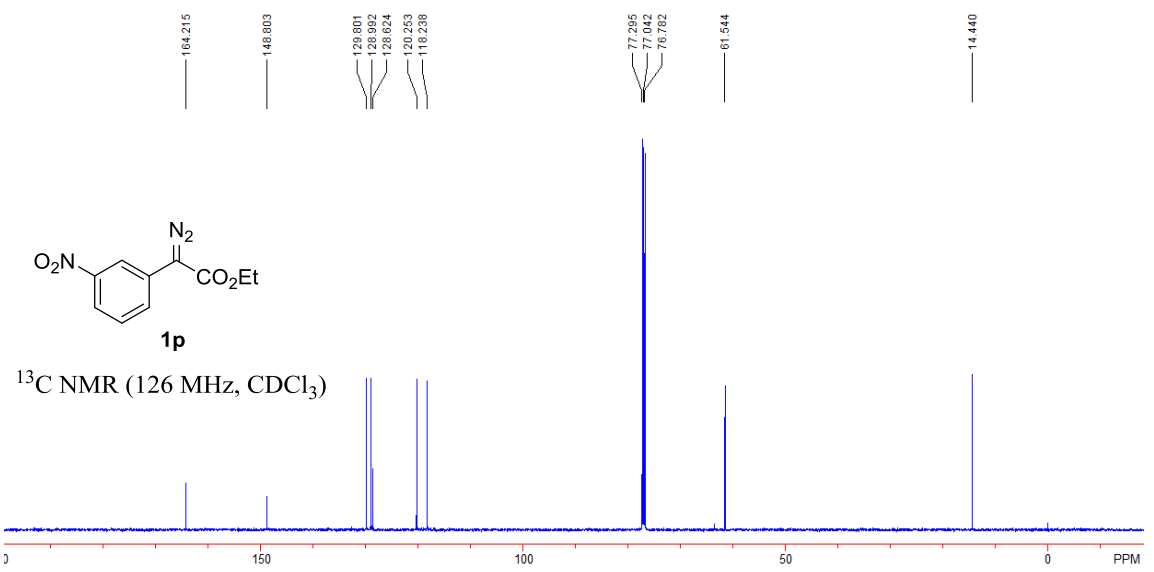






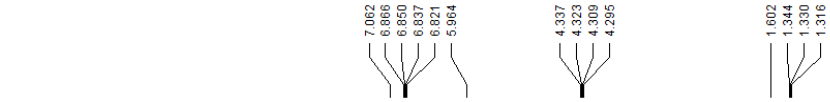
1p

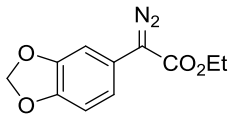
^{1}H NMR (500 MHz, $CDCl_3$)



1p

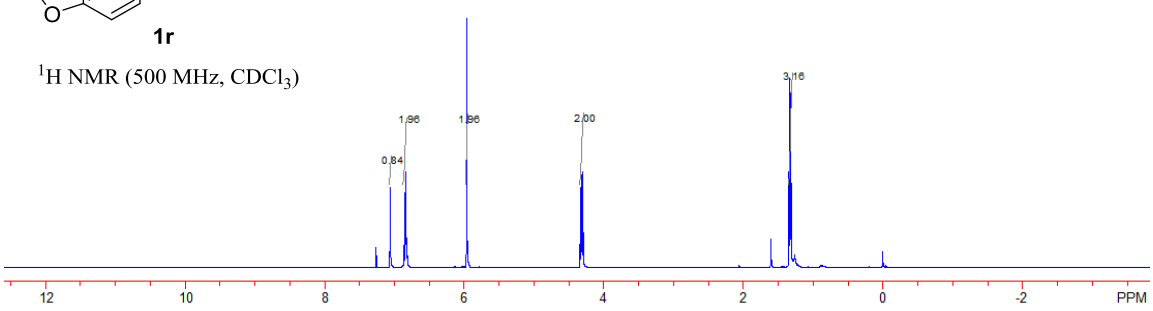
^{13}C NMR (126 MHz, $CDCl_3$)

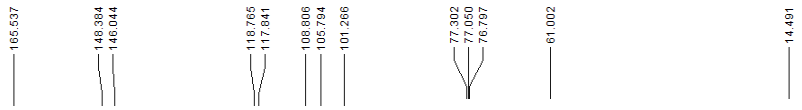


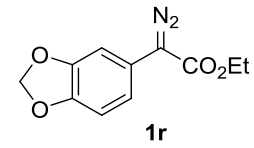


1r

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

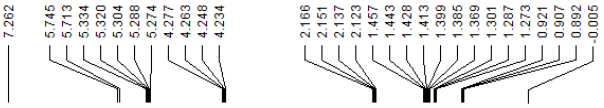


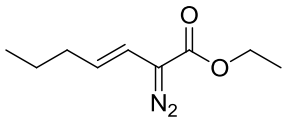




1r

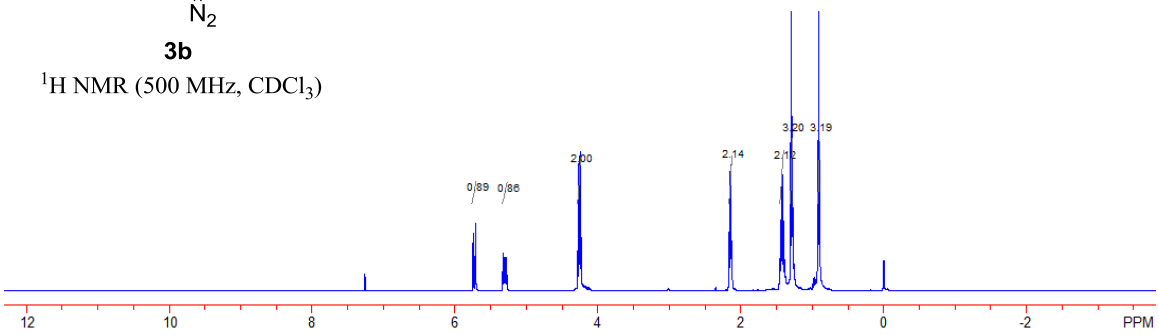
^{13}C NMR (126 MHz, $CDCl_3$)

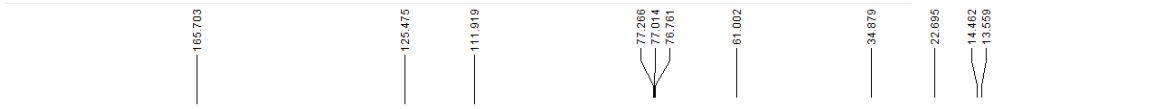


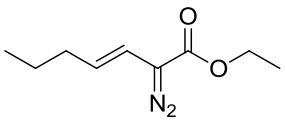


3b

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

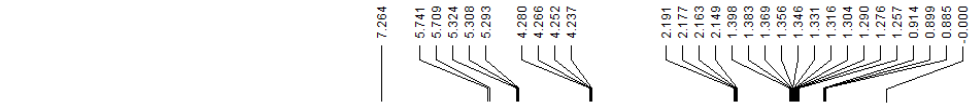


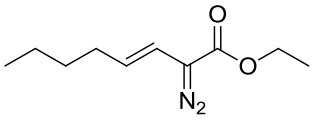




3b

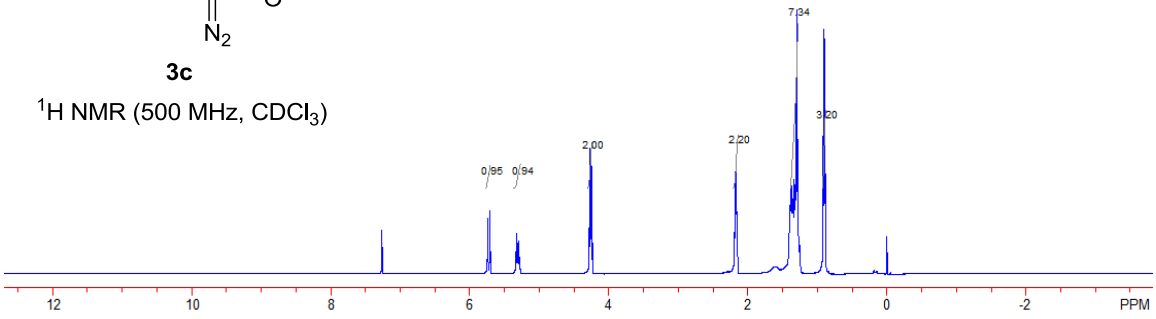
^{13}C NMR (126 MHz, $CDCl_3$)

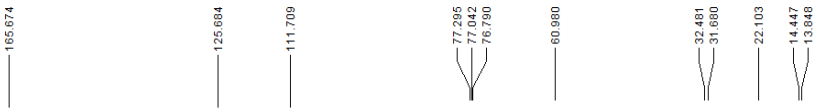


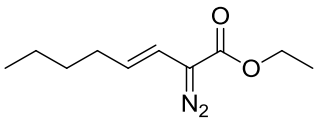


3c

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

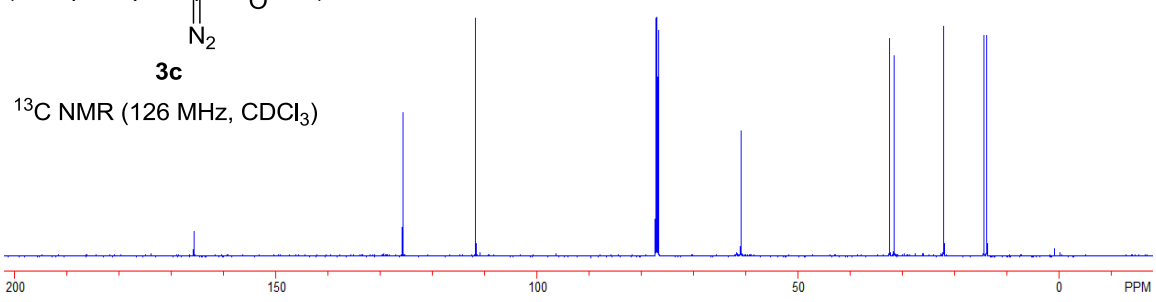




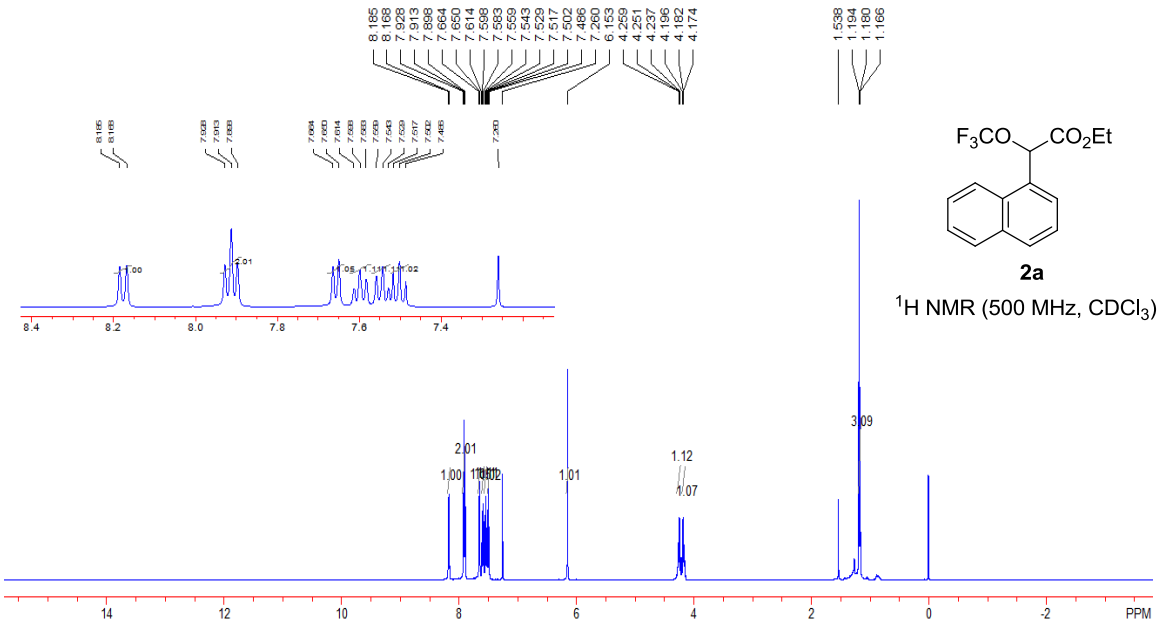


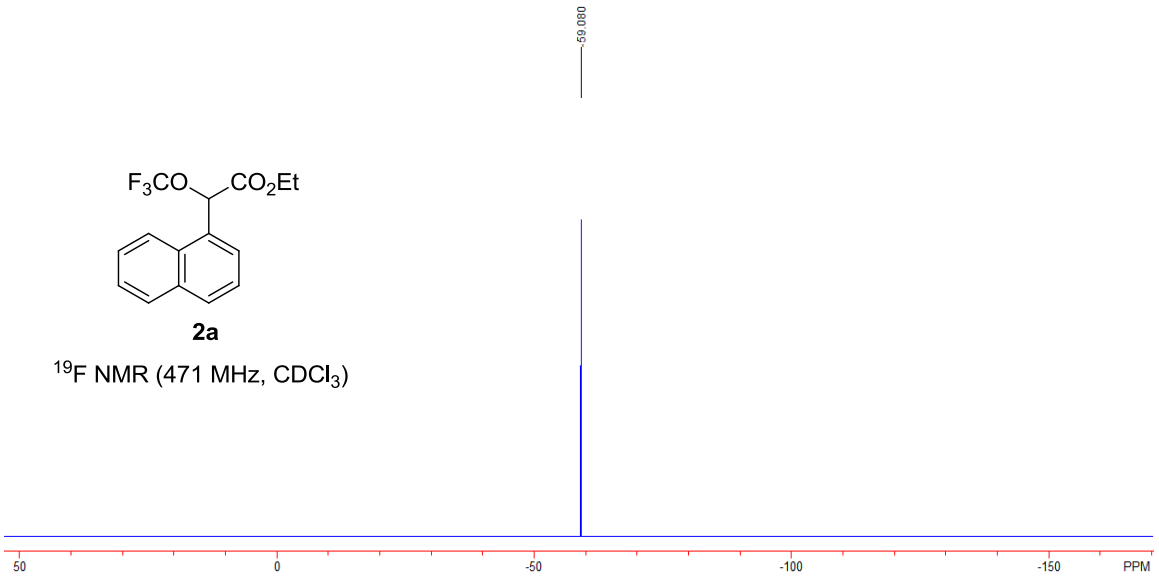
3c

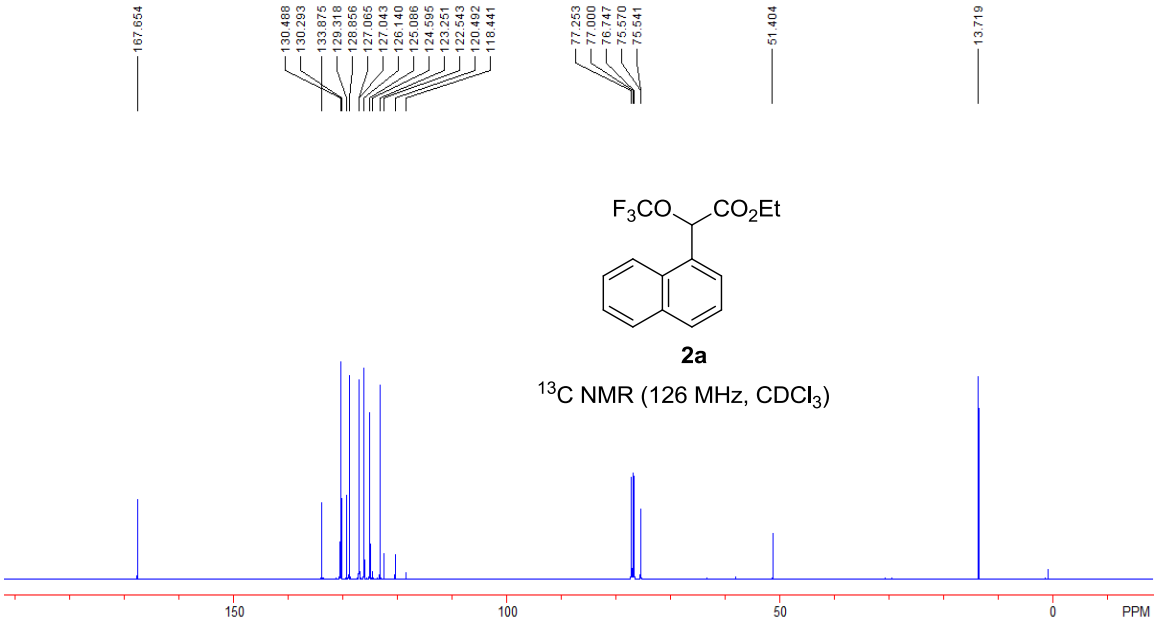
^{13}C NMR (126 MHz, $CDCl_3$)



8. NMR spectra of 2 and 4

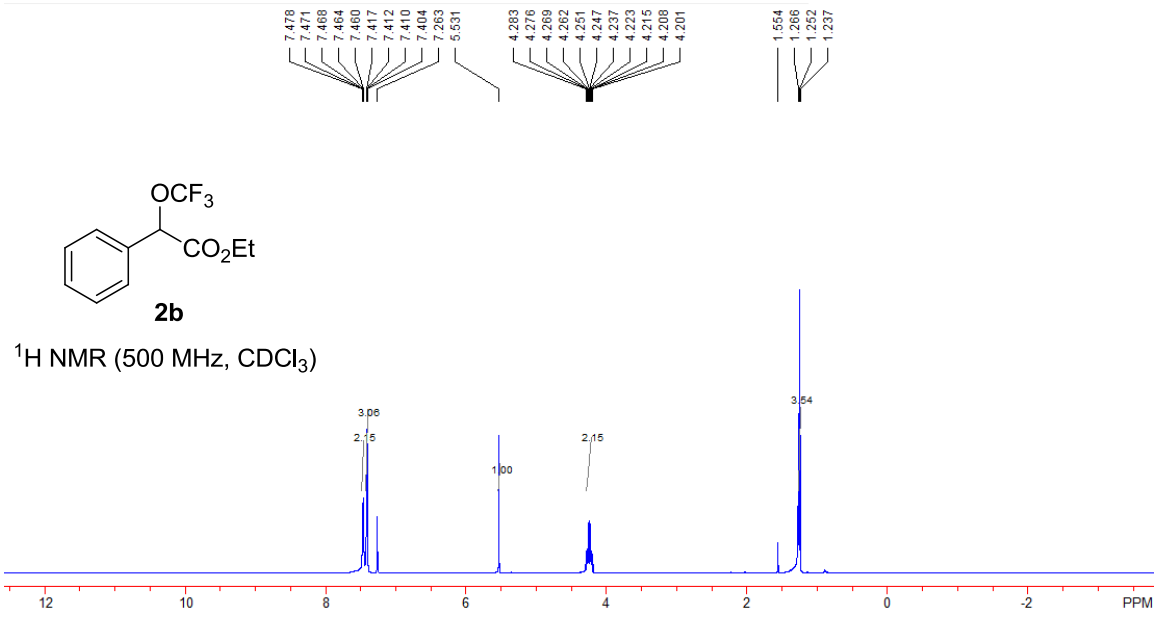






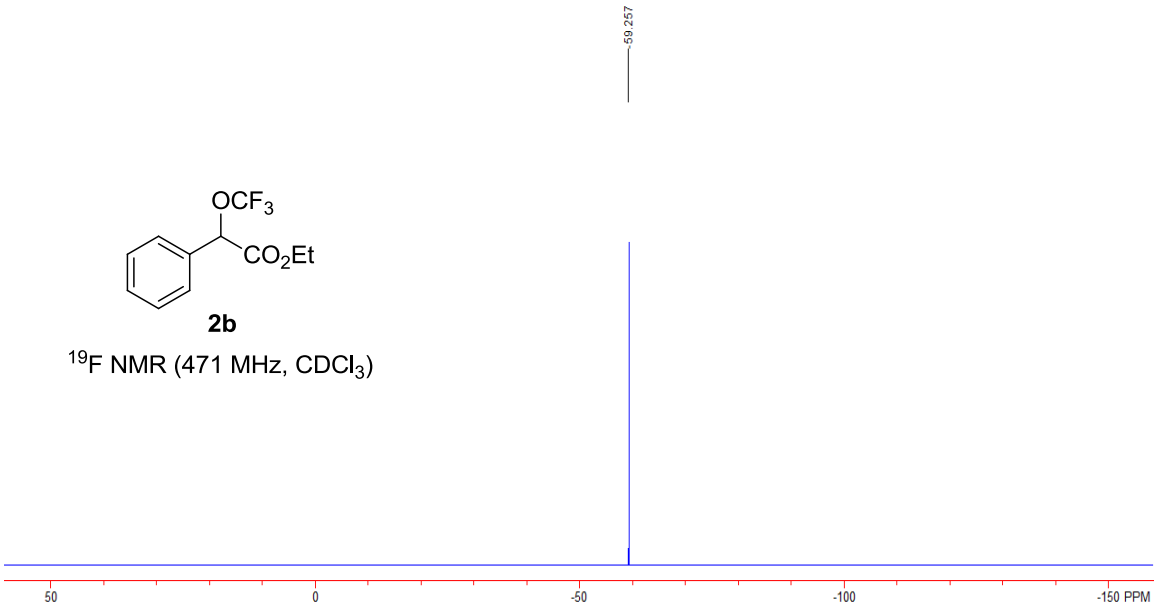
2a

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



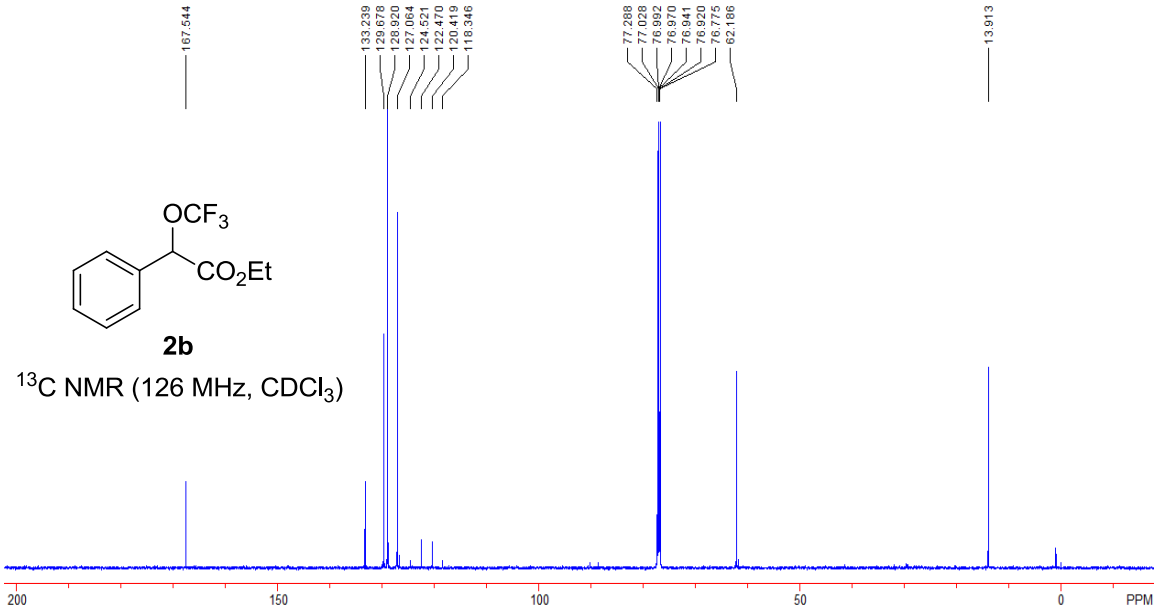
2b

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



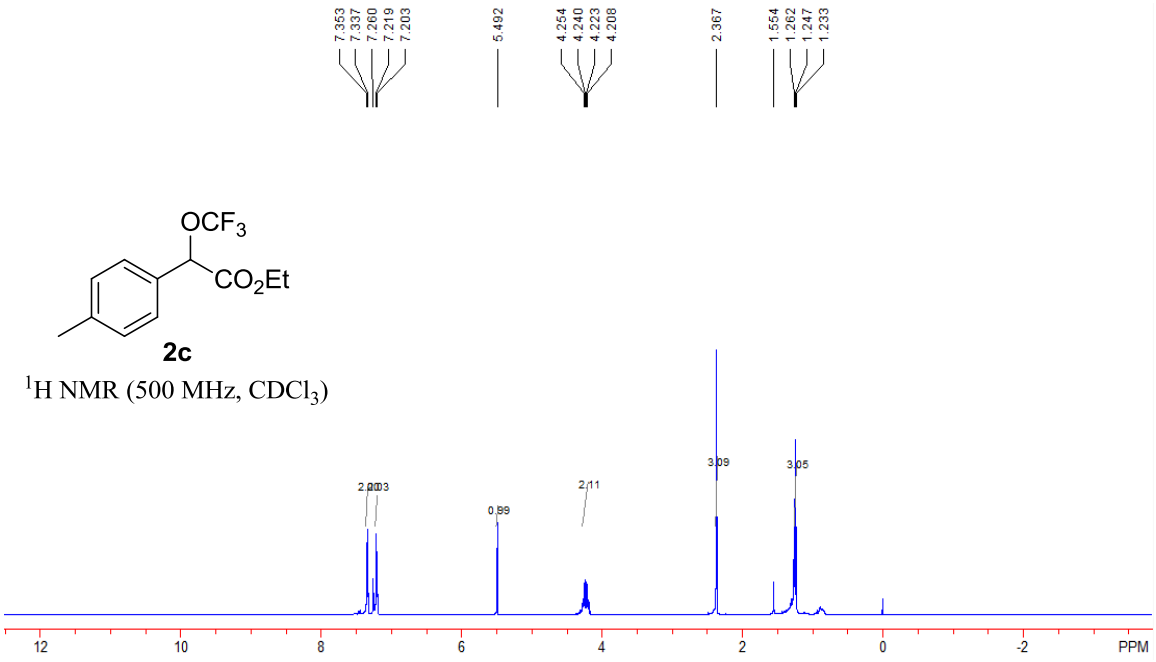
2b

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



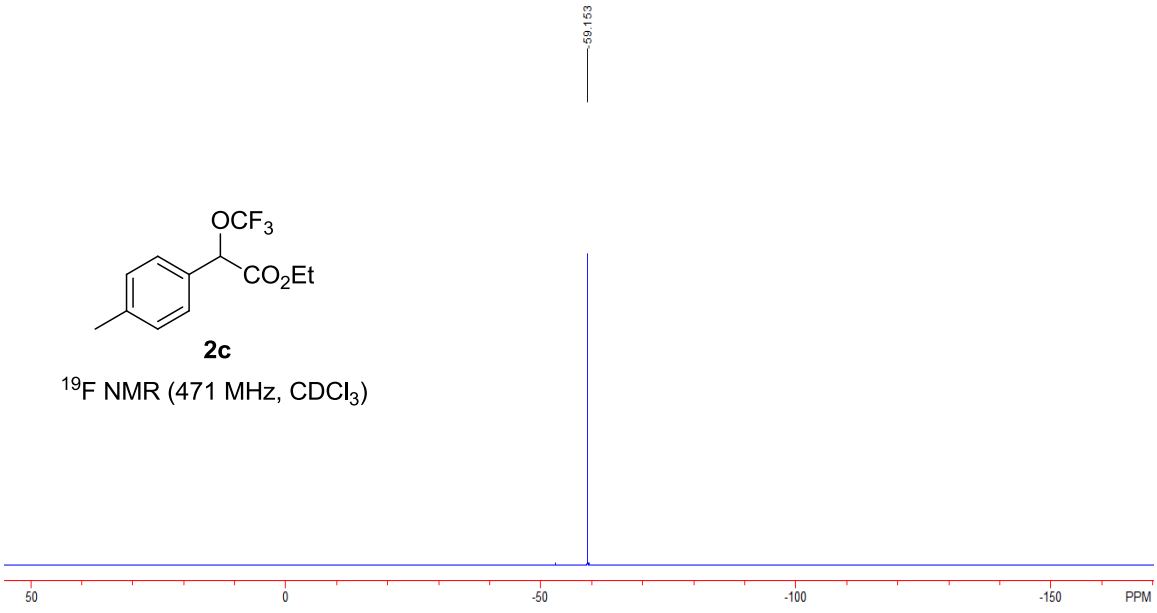
2b

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



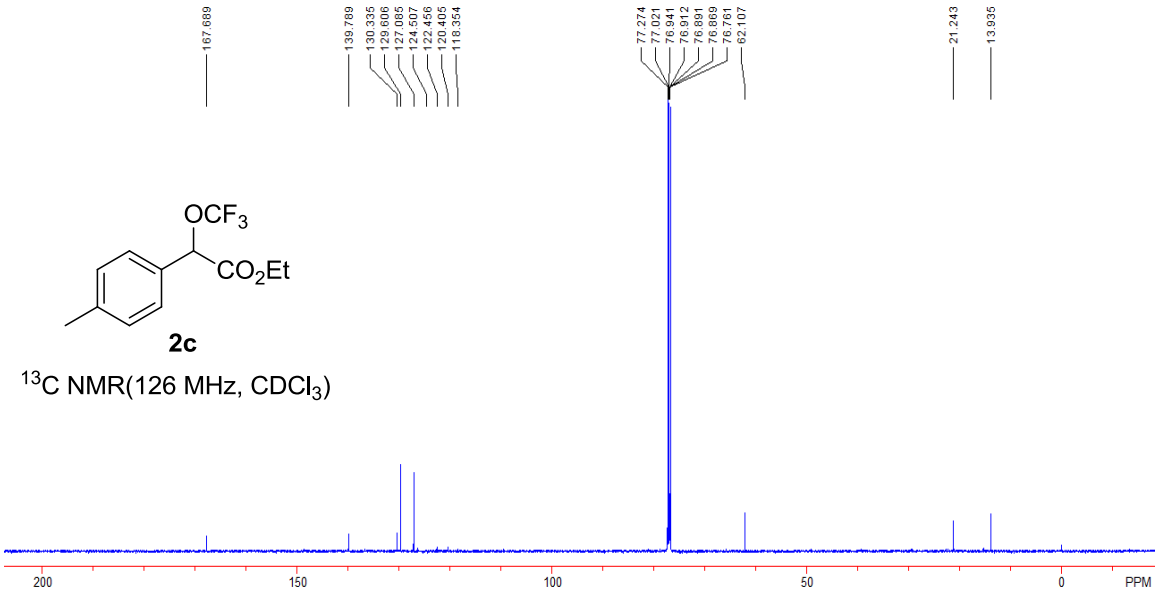
2c

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



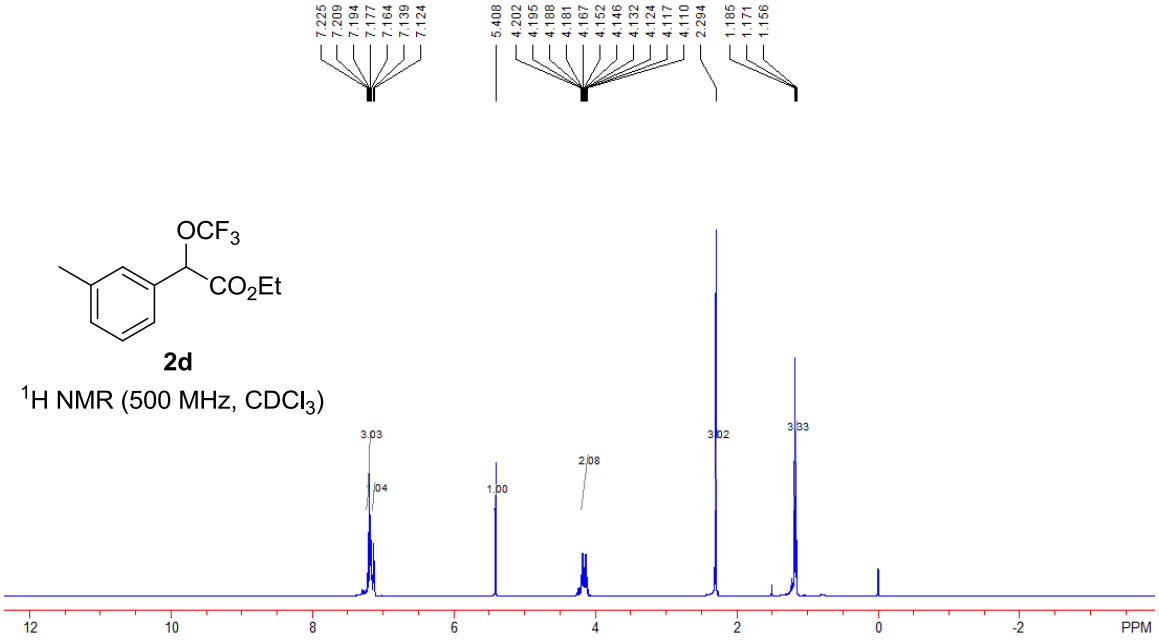
2c

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



2c

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



2d

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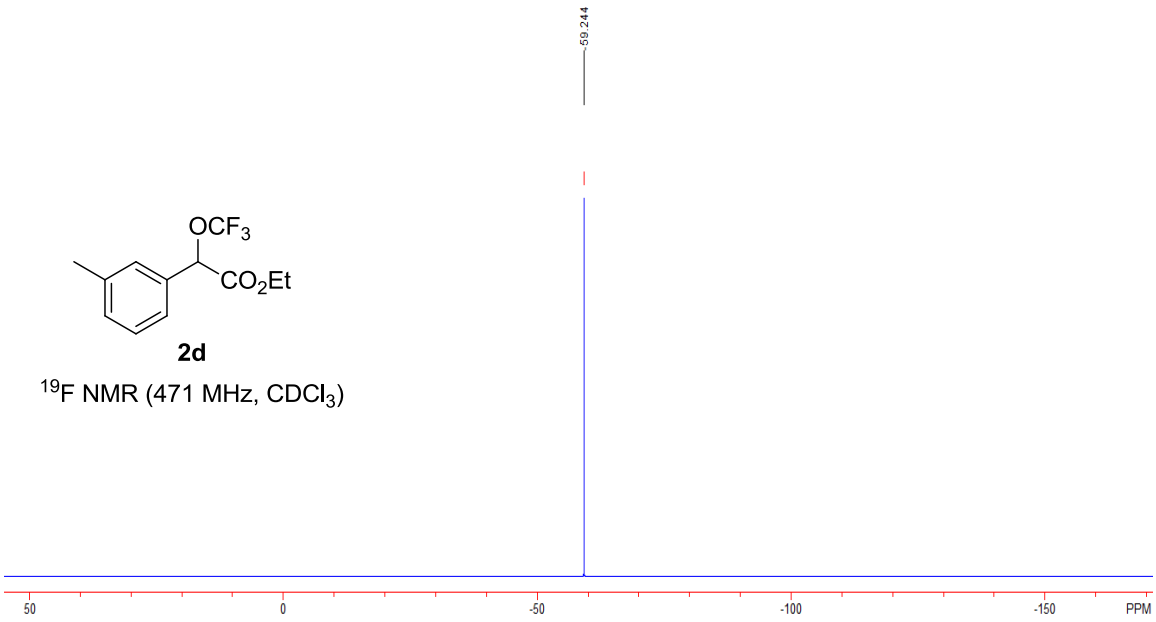
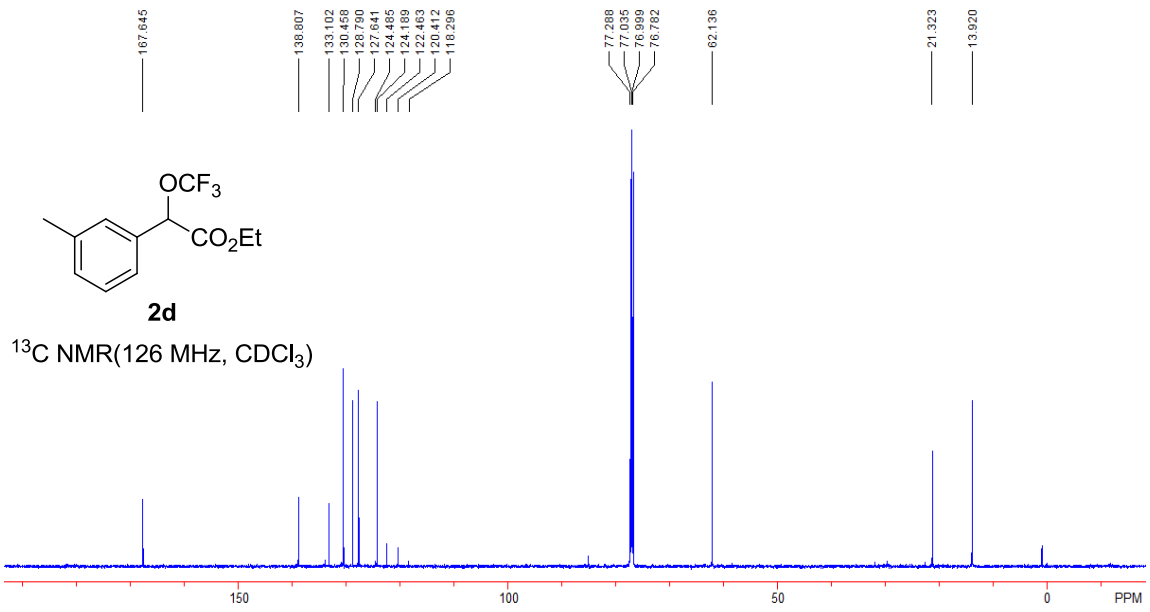


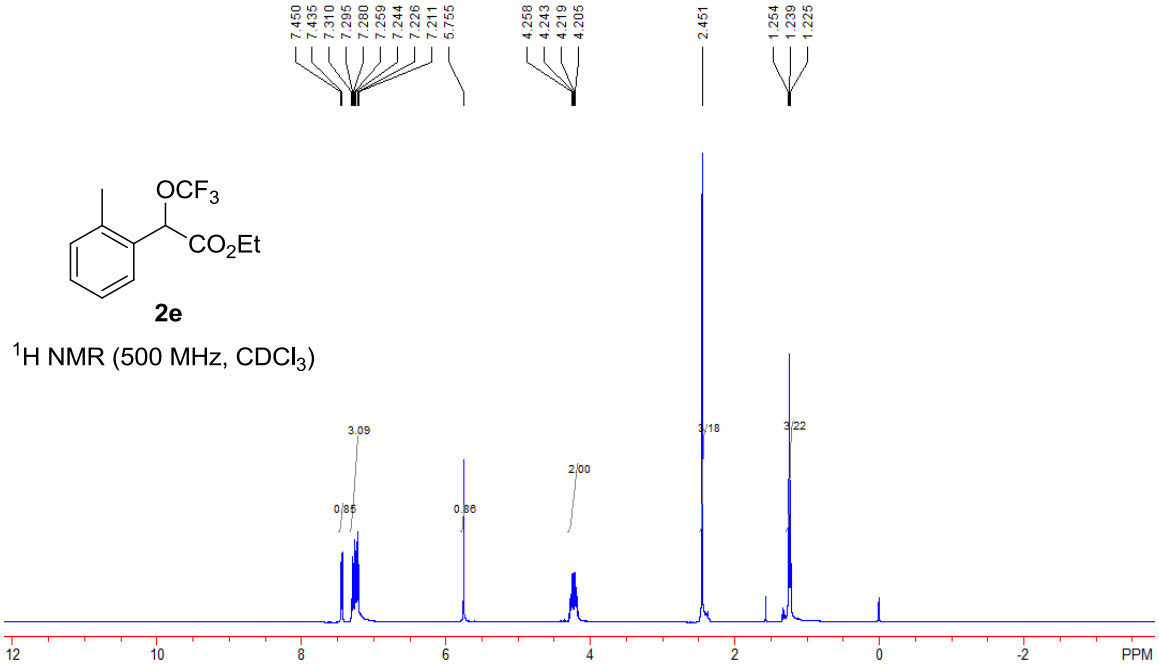
2d

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



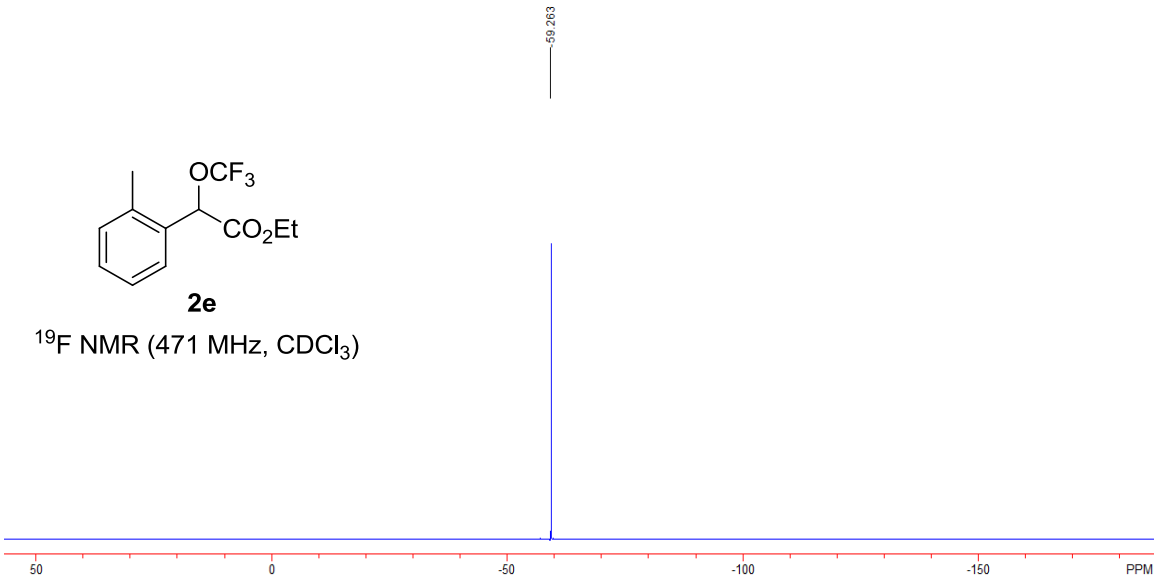
2d

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



2e

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



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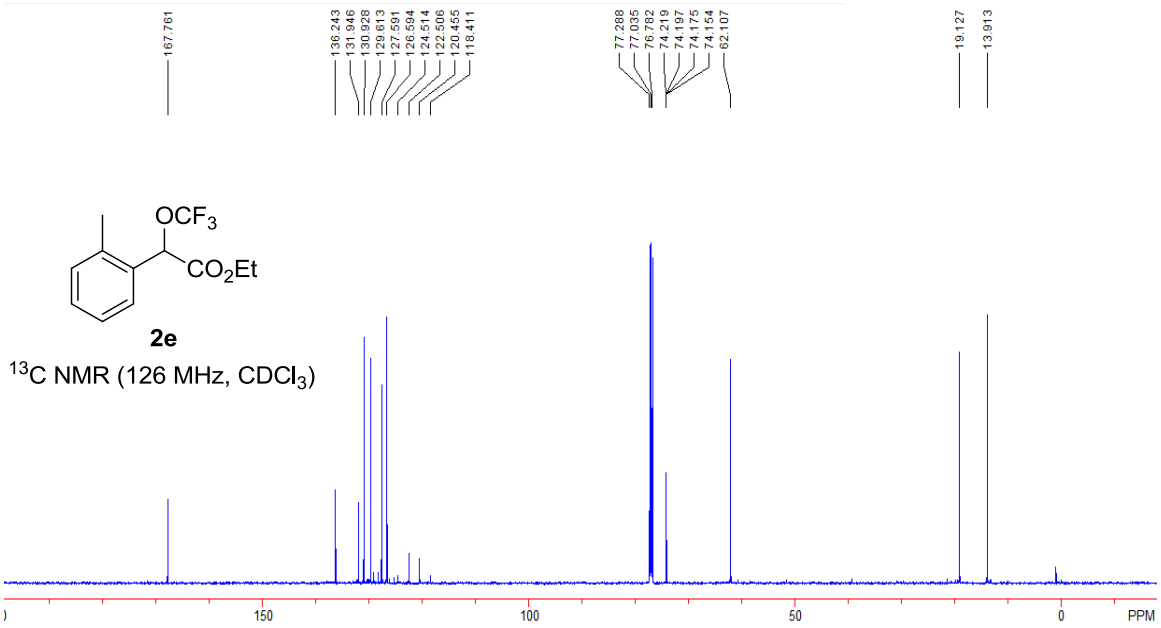

2e

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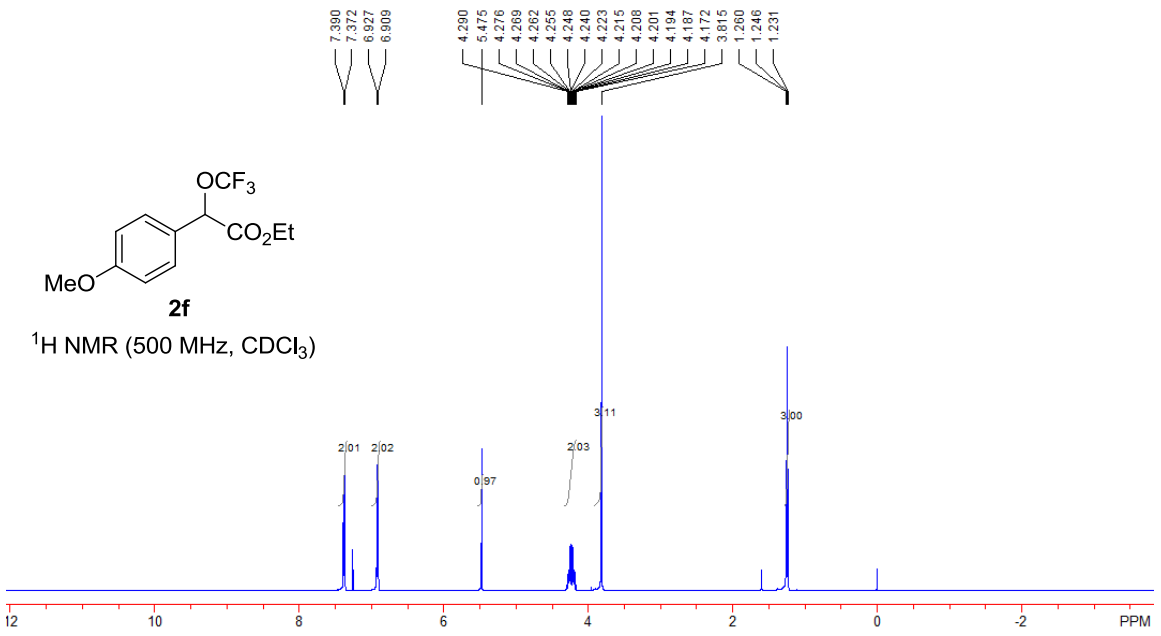

2f

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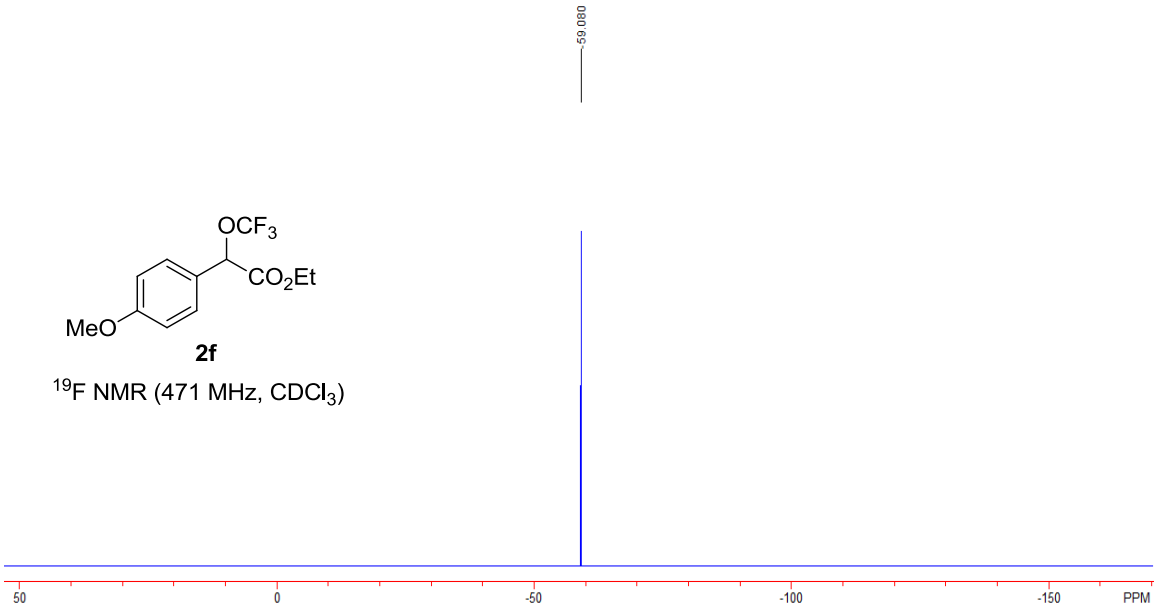

2f

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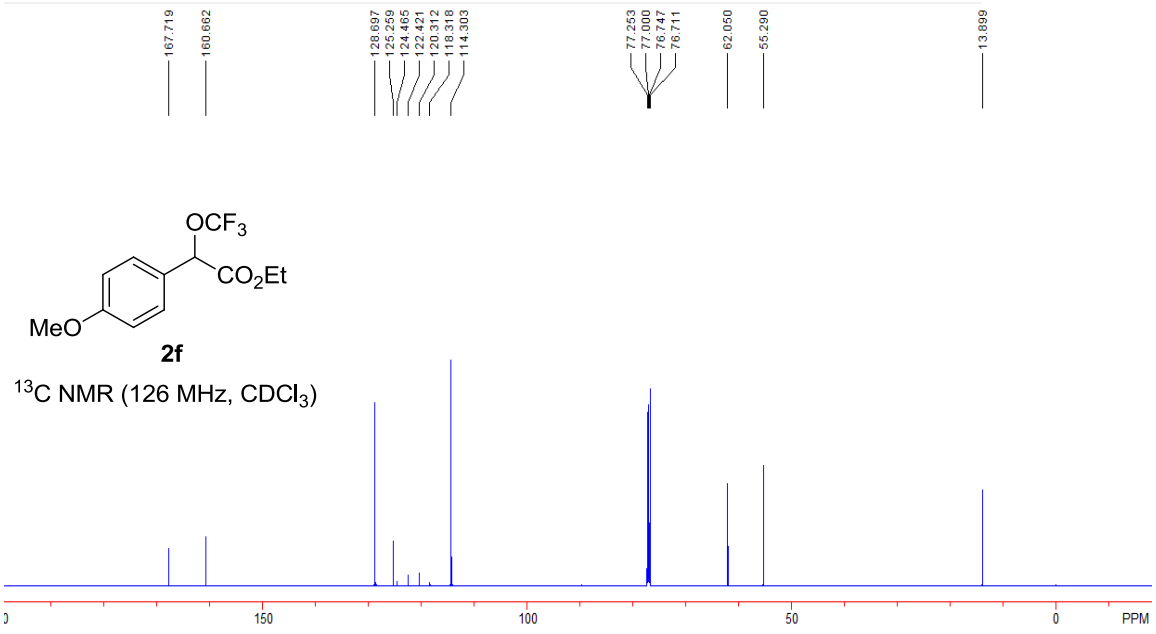

2f

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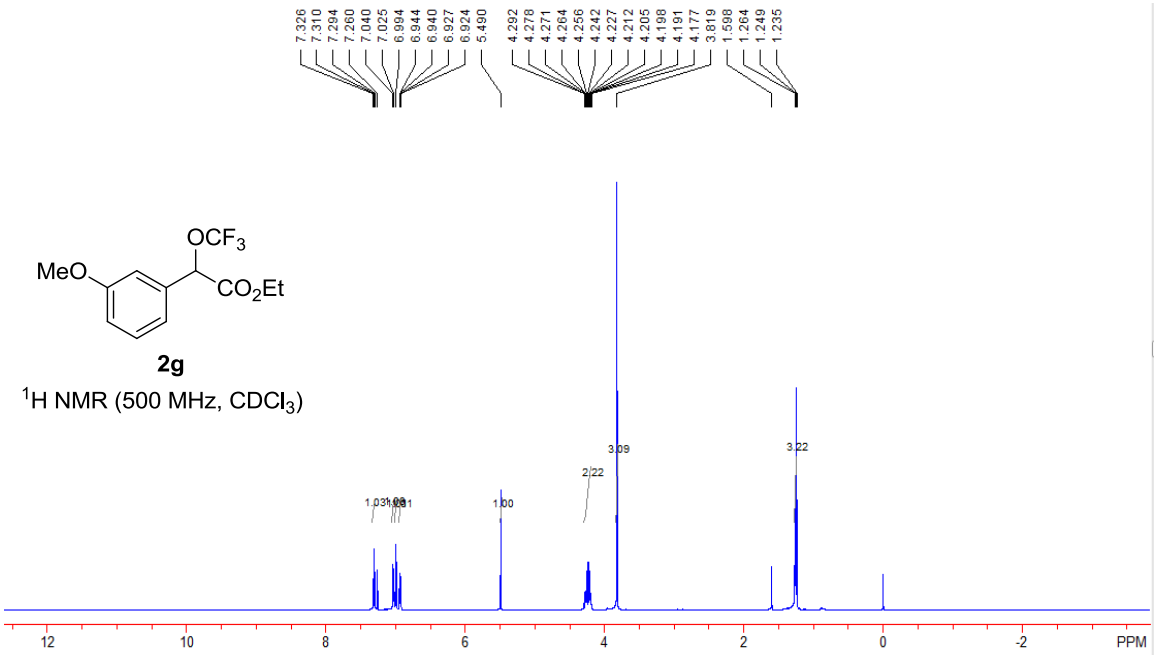
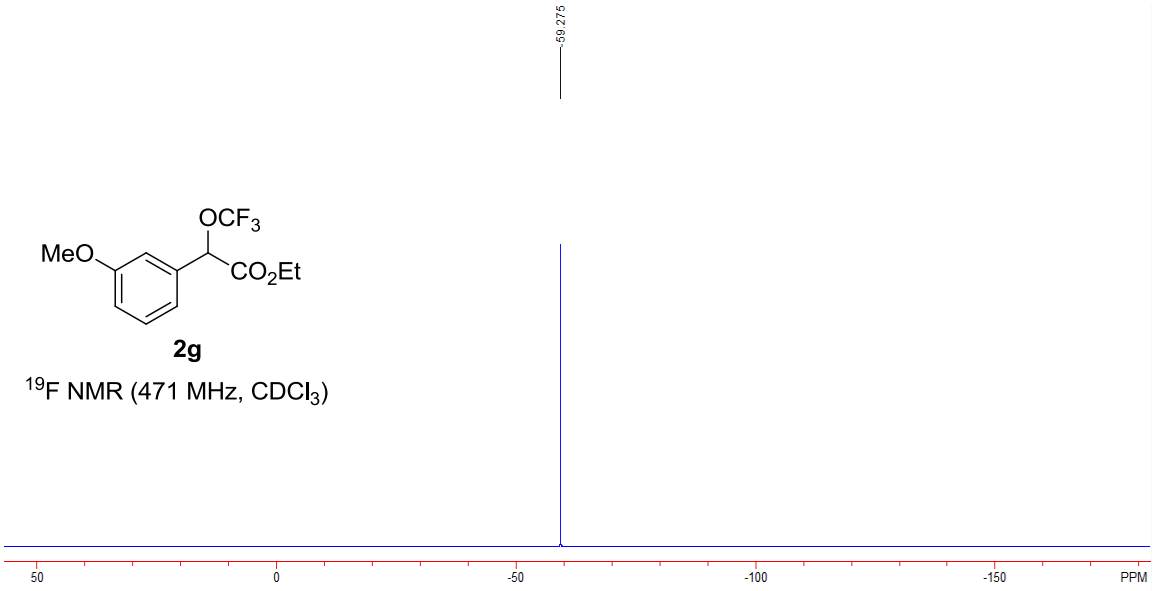


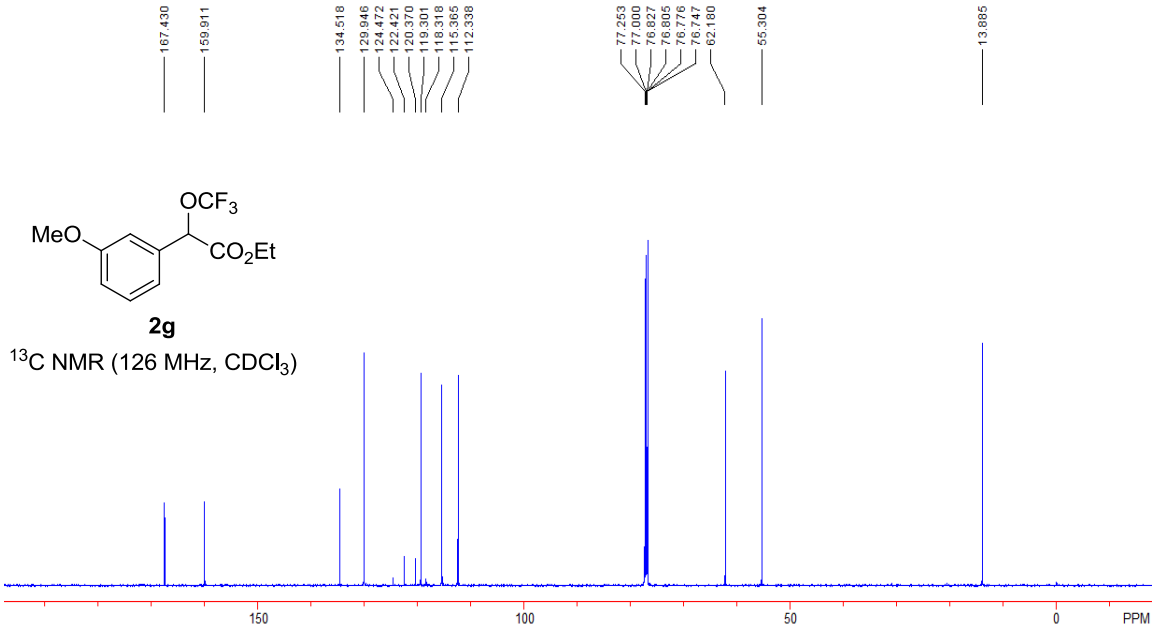
2g

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



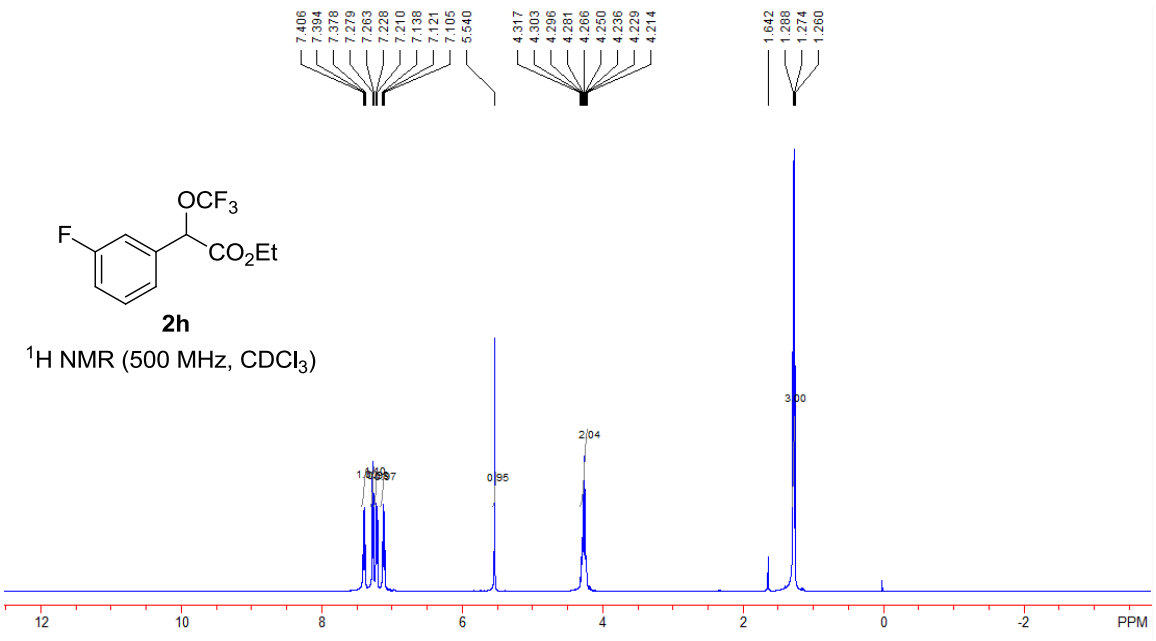
2g

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



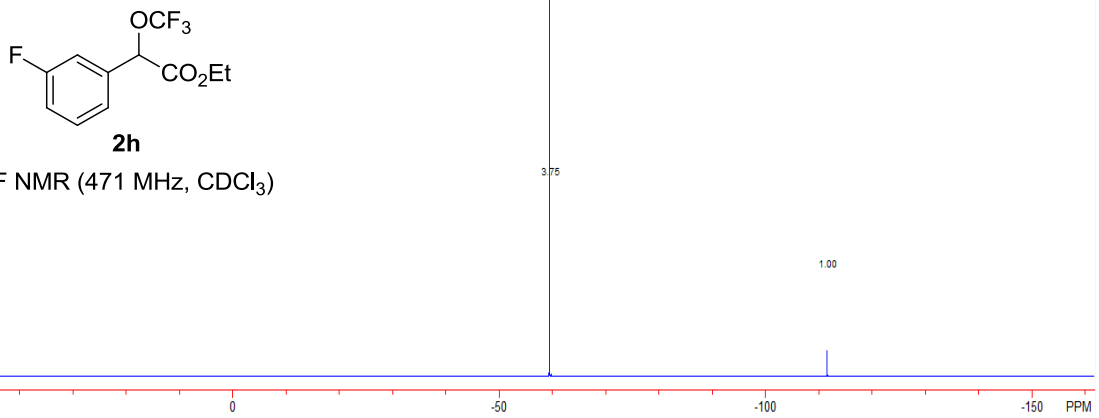
2g

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



2h

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



2h

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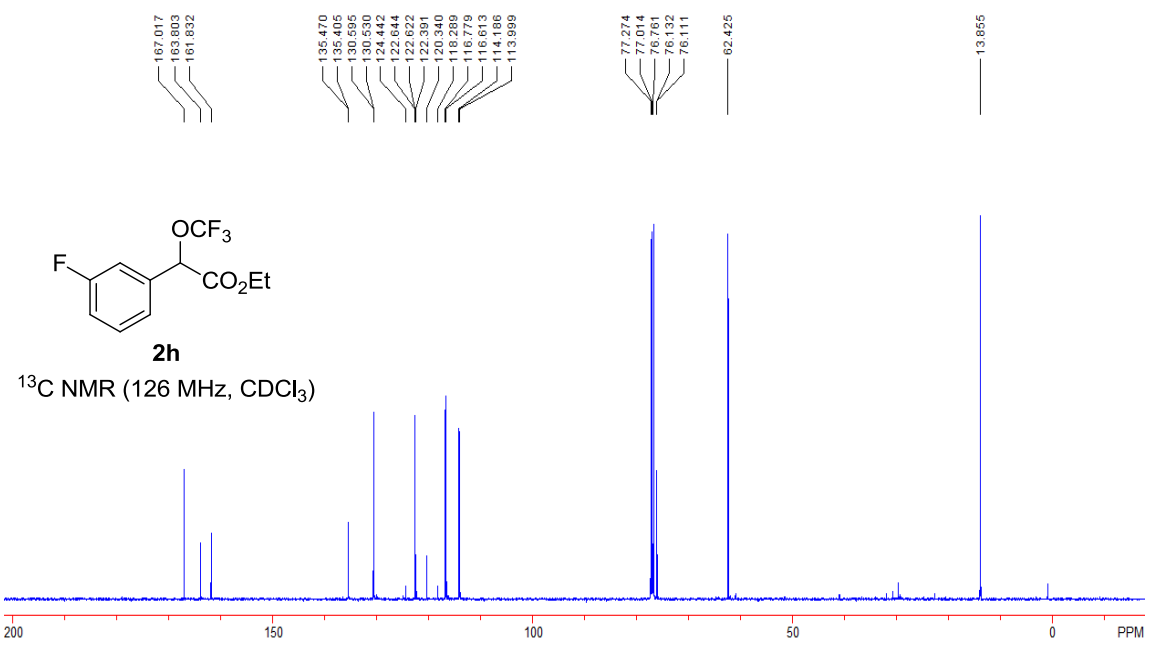
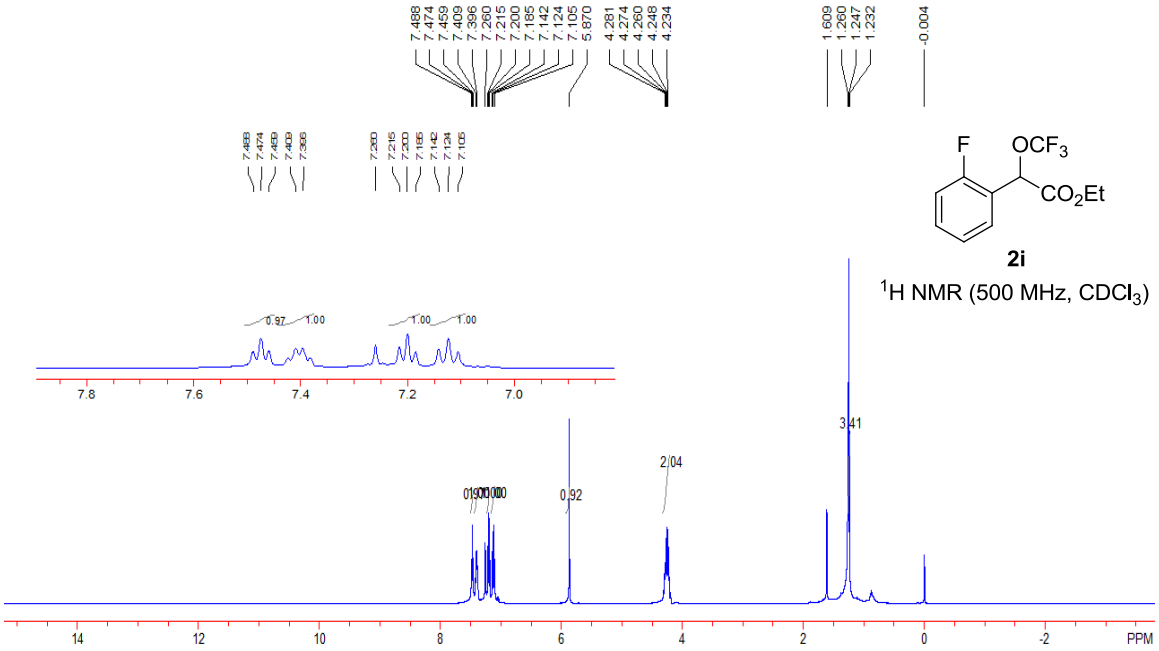


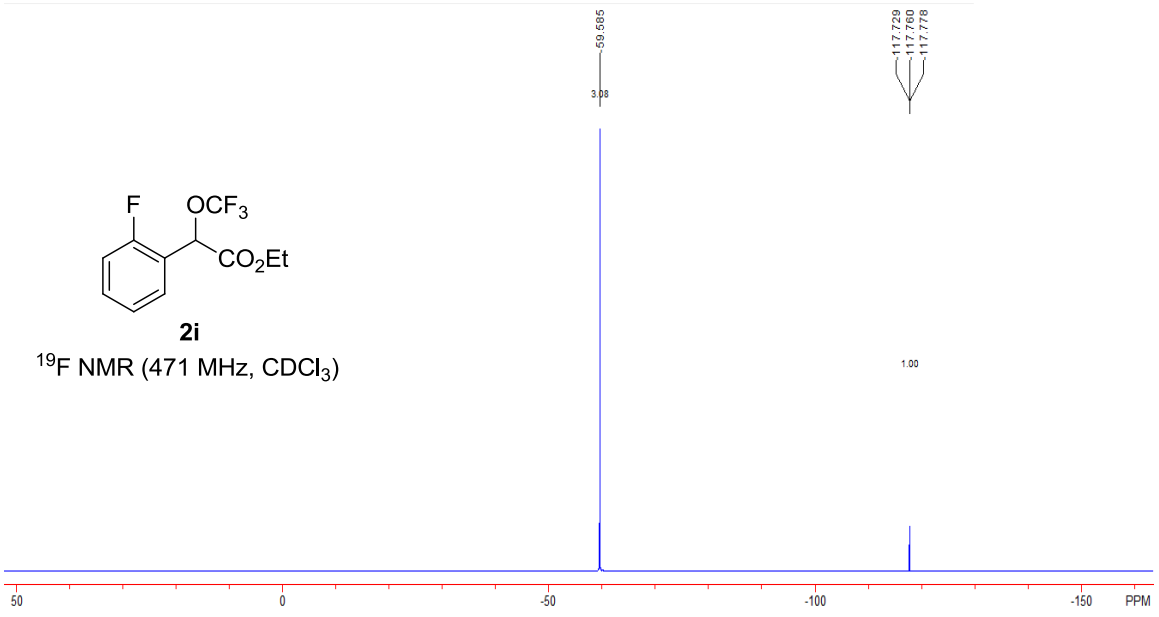
2h

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



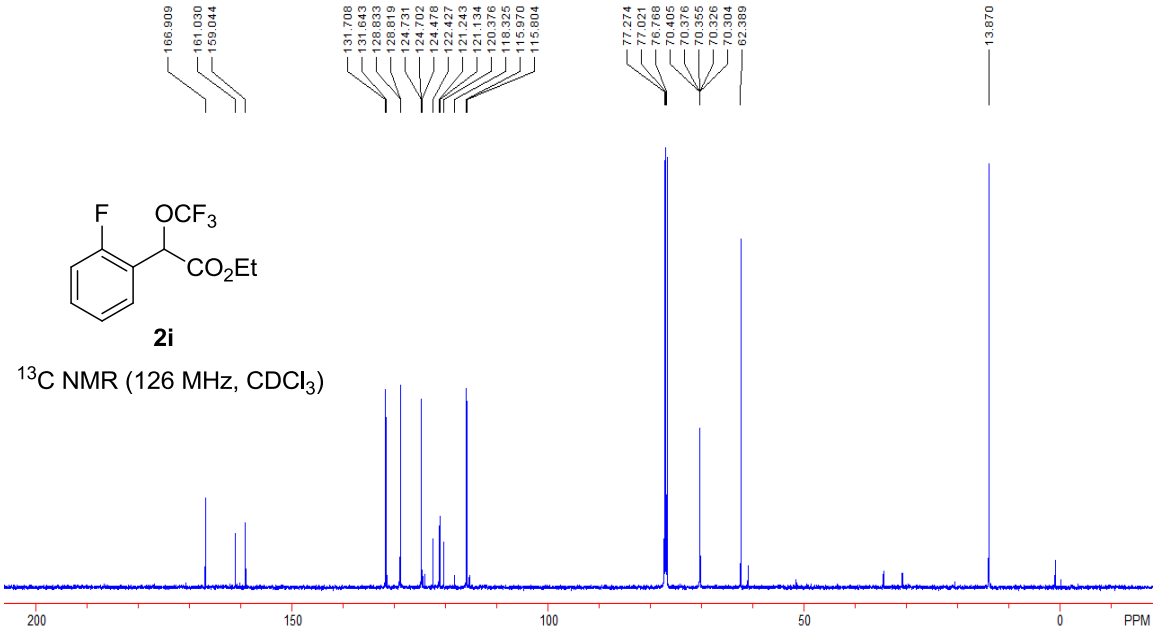
2i

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



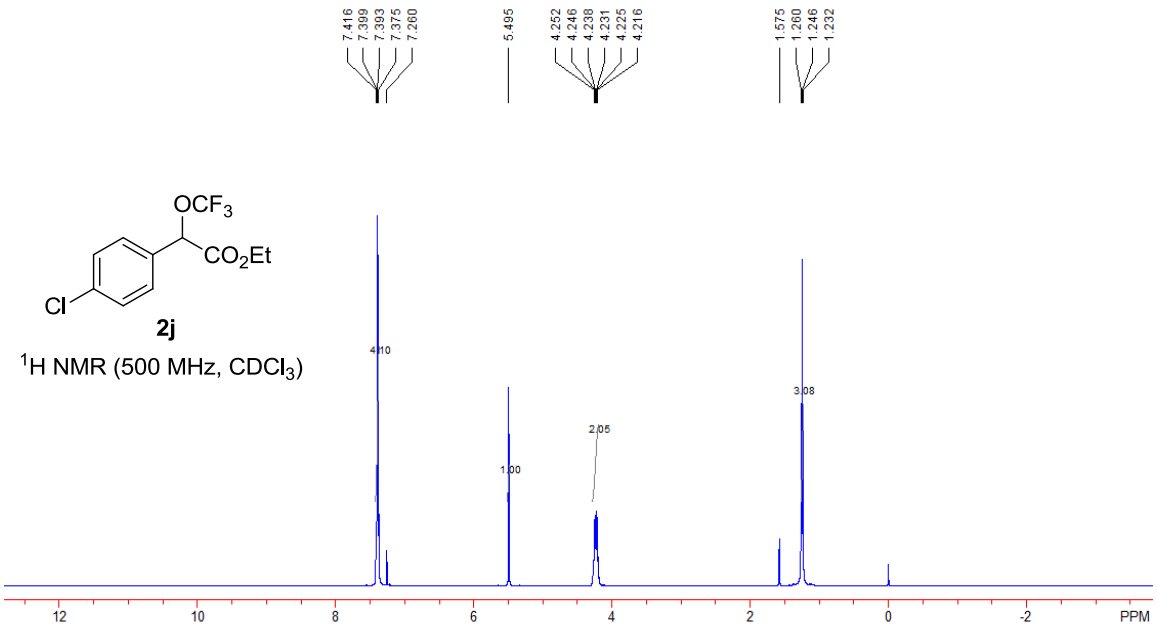
2i

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



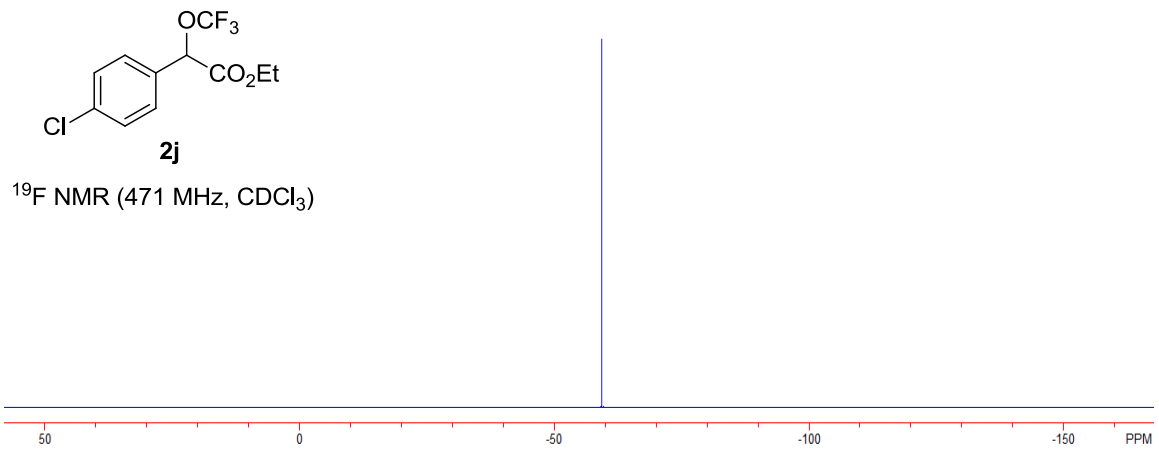
2i

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



2j

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



2j

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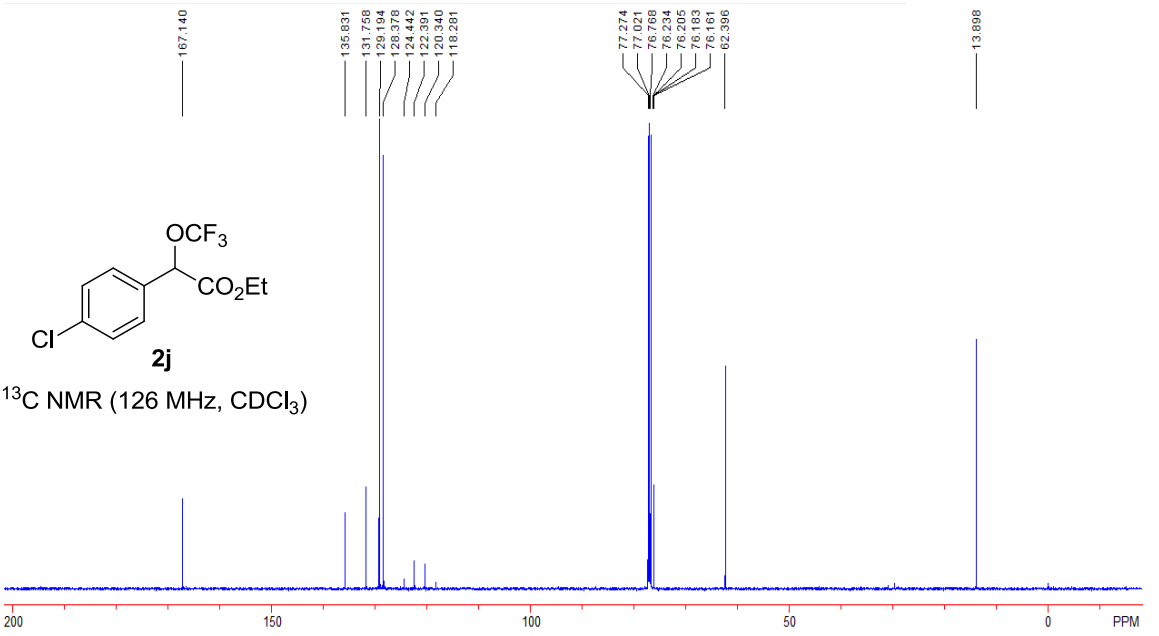

2j

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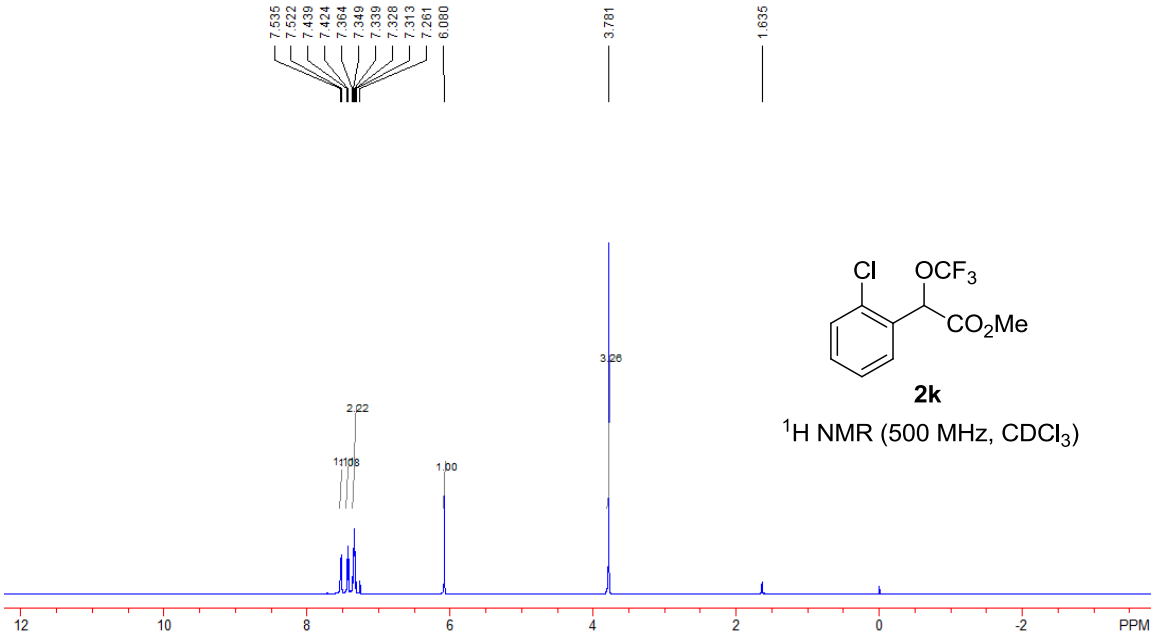
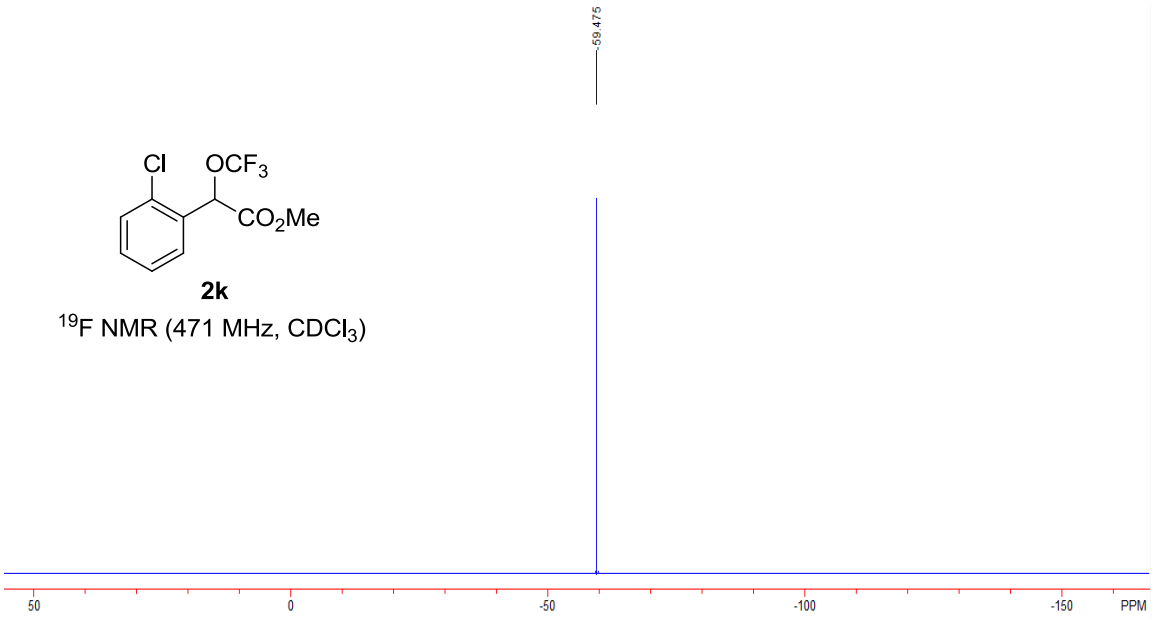


2k

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



2k

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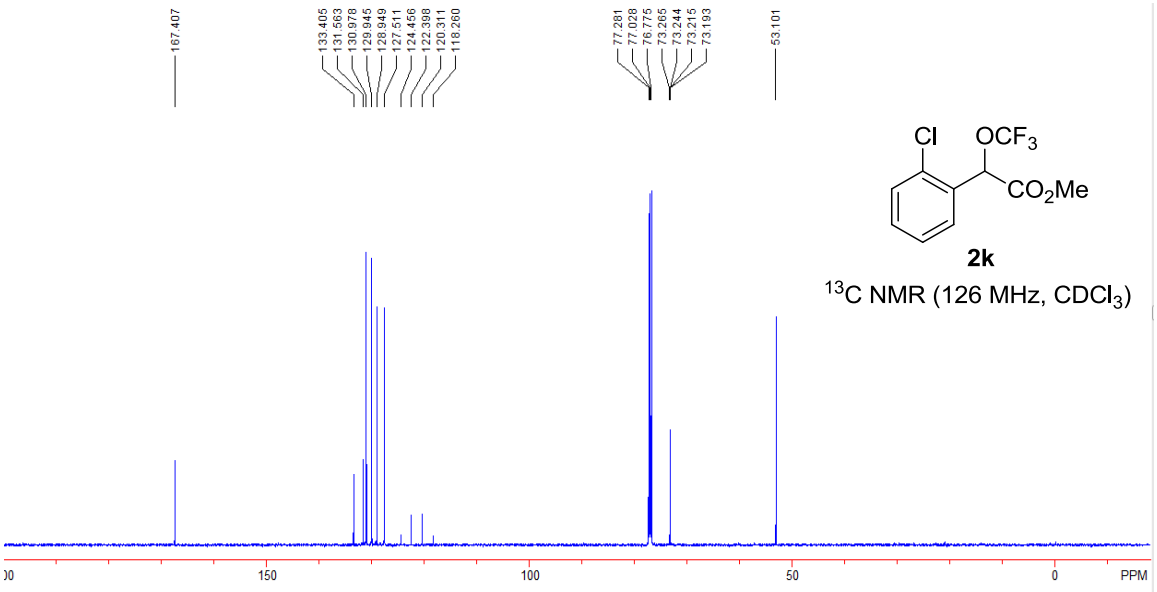
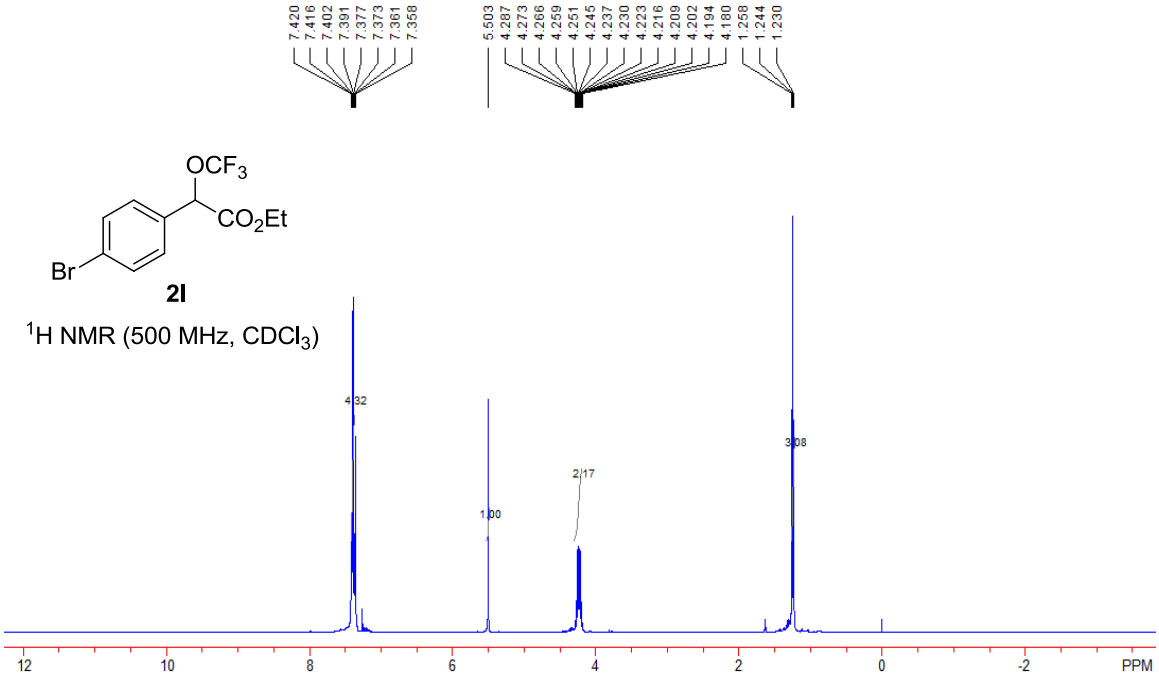


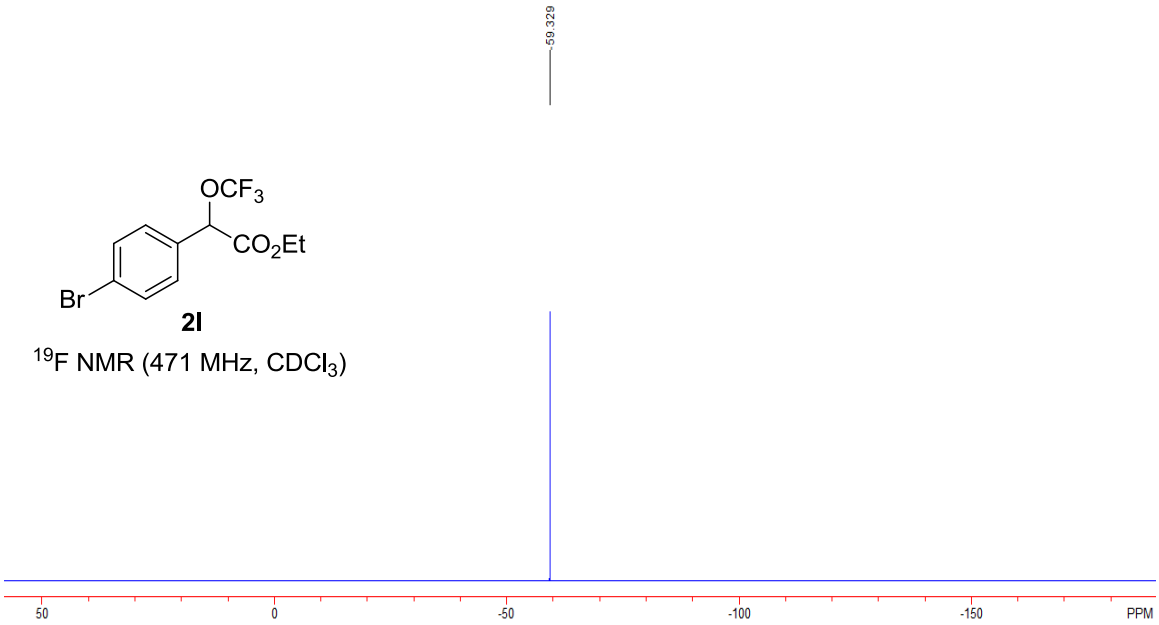
2k

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



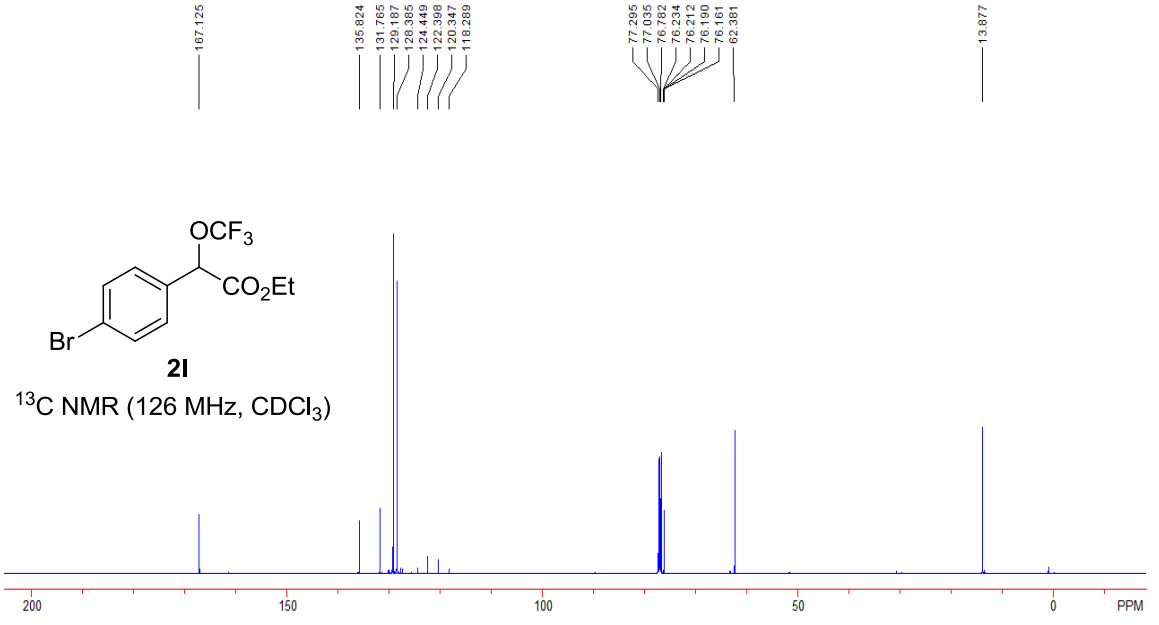
2l

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



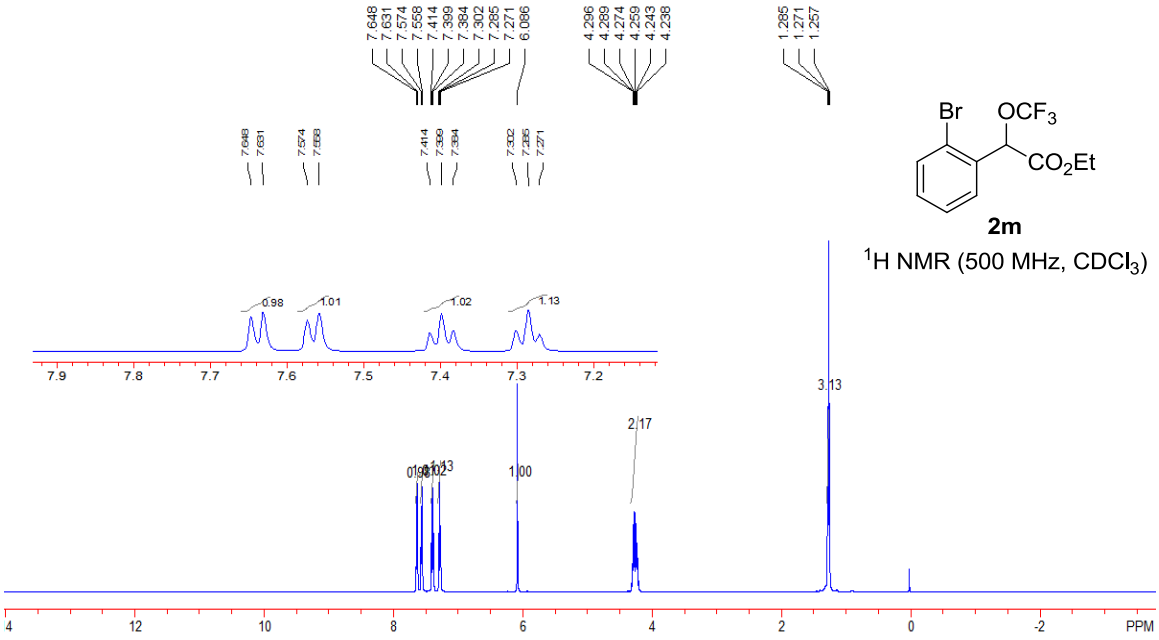
2l

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



2l

^{13}C NMR (126 MHz, $CDCl_3$)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7.558
7.414
7.399
7.384
7.302
7.285
7.271
6.086
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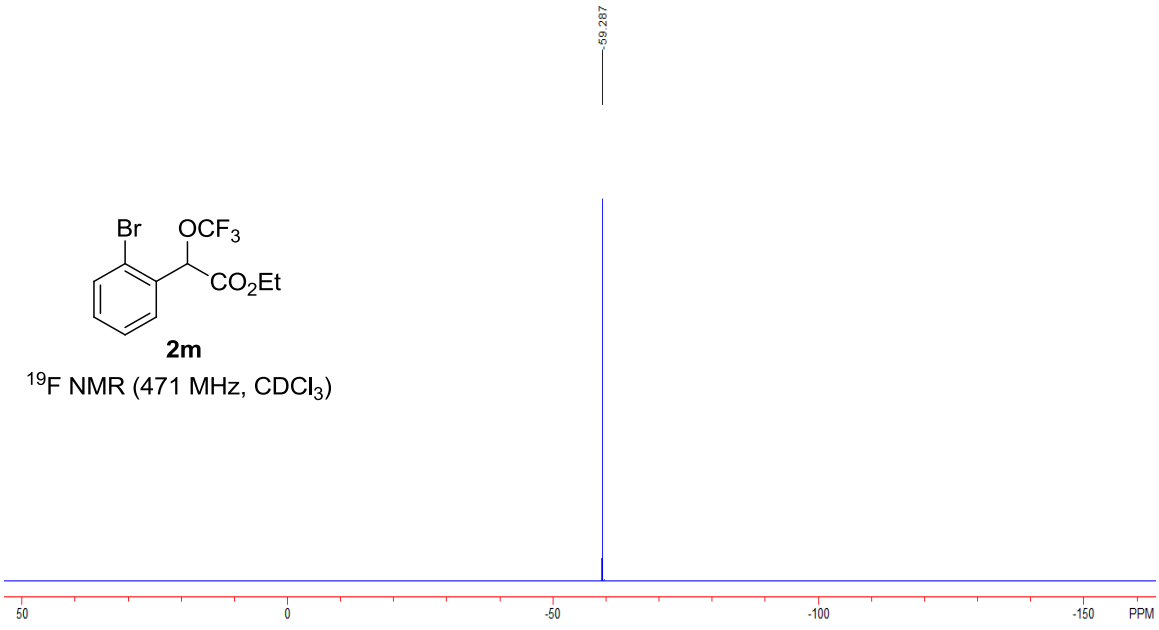
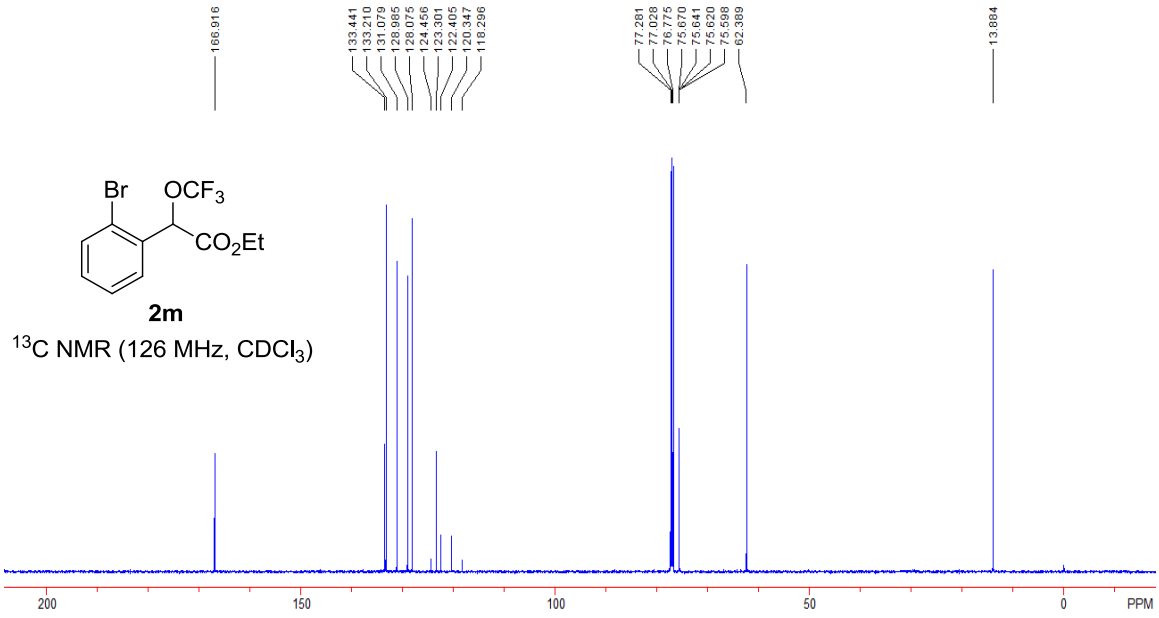
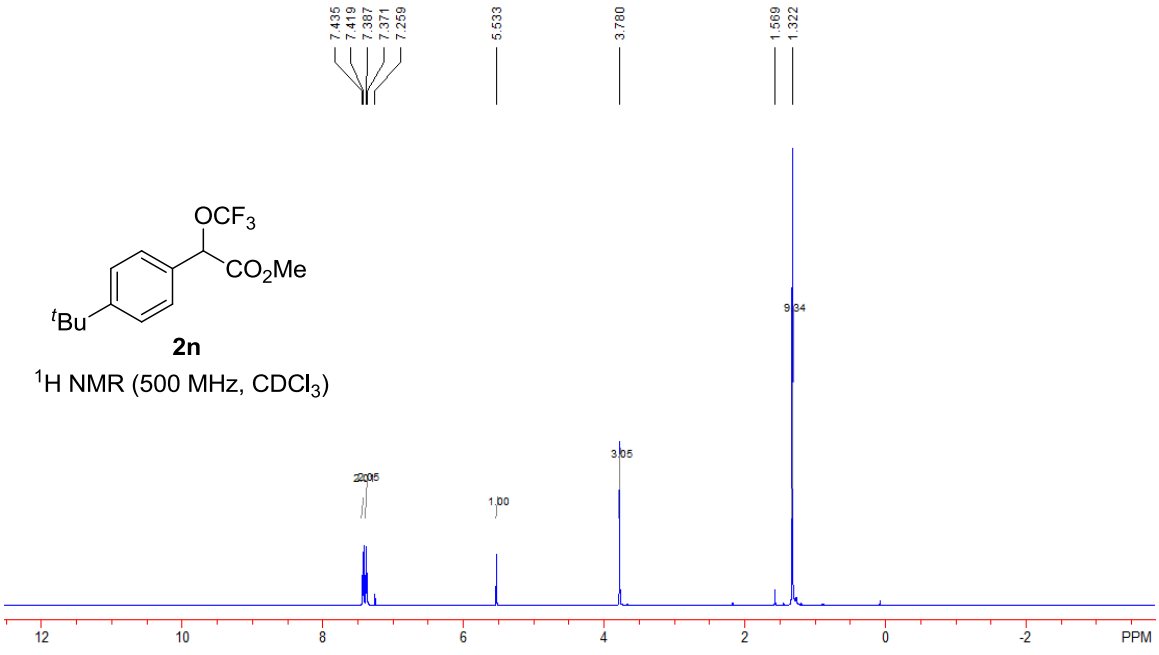
4.289
4.274
4.259
4.243
4.238
1.285
1.271
1.257
0.98
1.01
1.02
1.13
3.13
2.17
1.00
Br
OCF3
CO2Et
2m
1H NMR (500 MHz, CDCl3)
PPM


-59.287
Br
OCF3
CO2Et
2m
19F NMR (471 MHz, CDCl3)
PPM



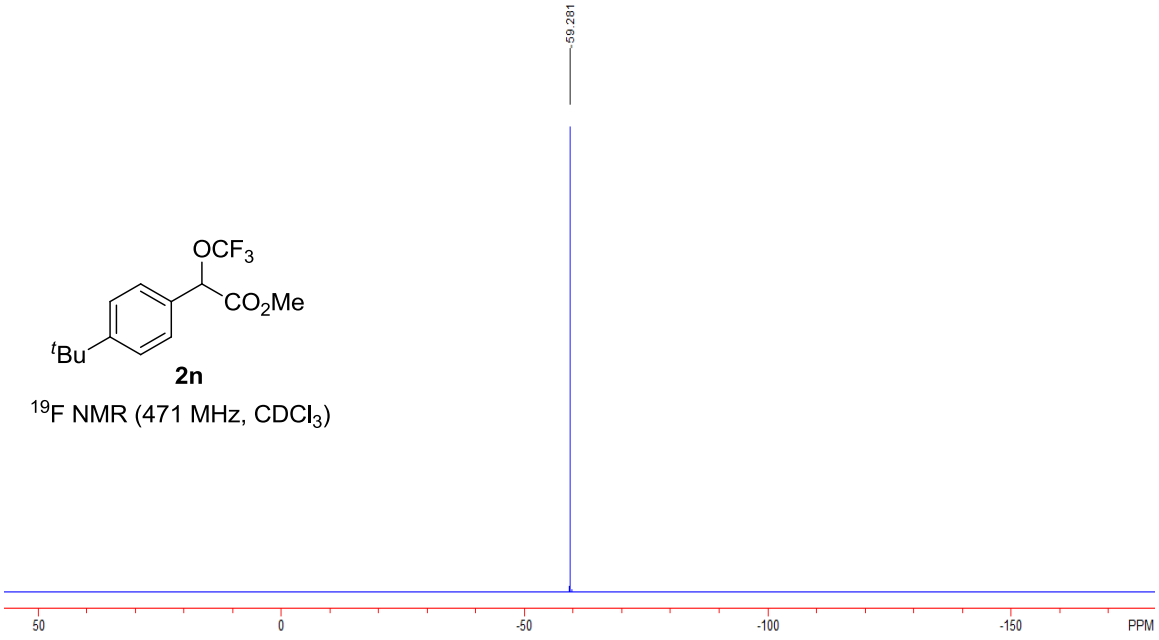
2m

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



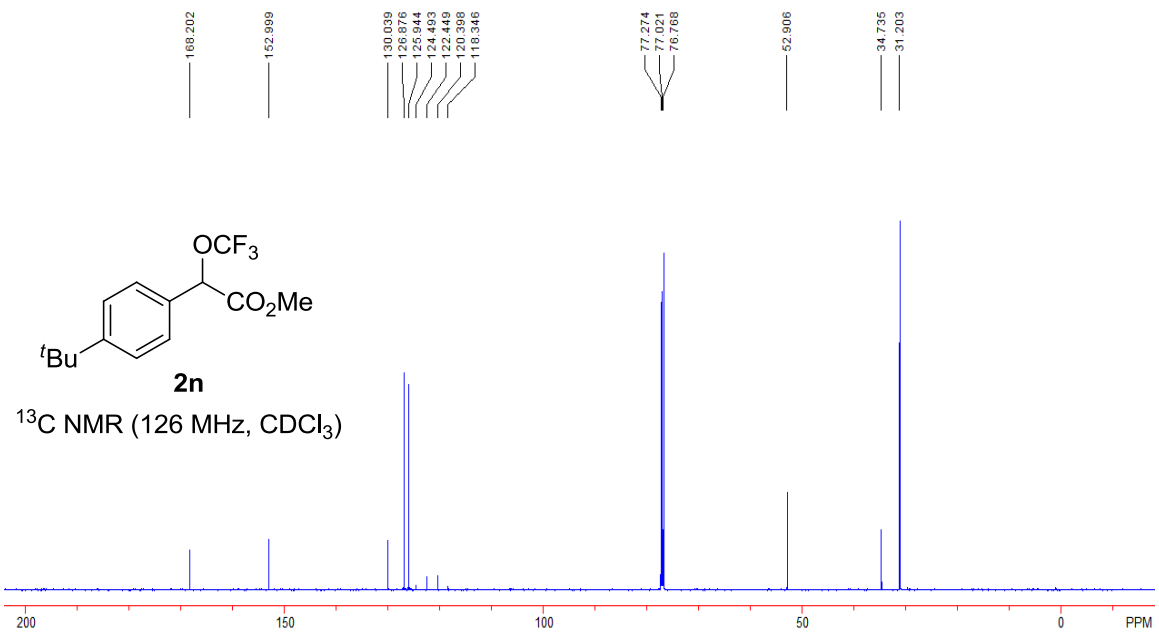
2n

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



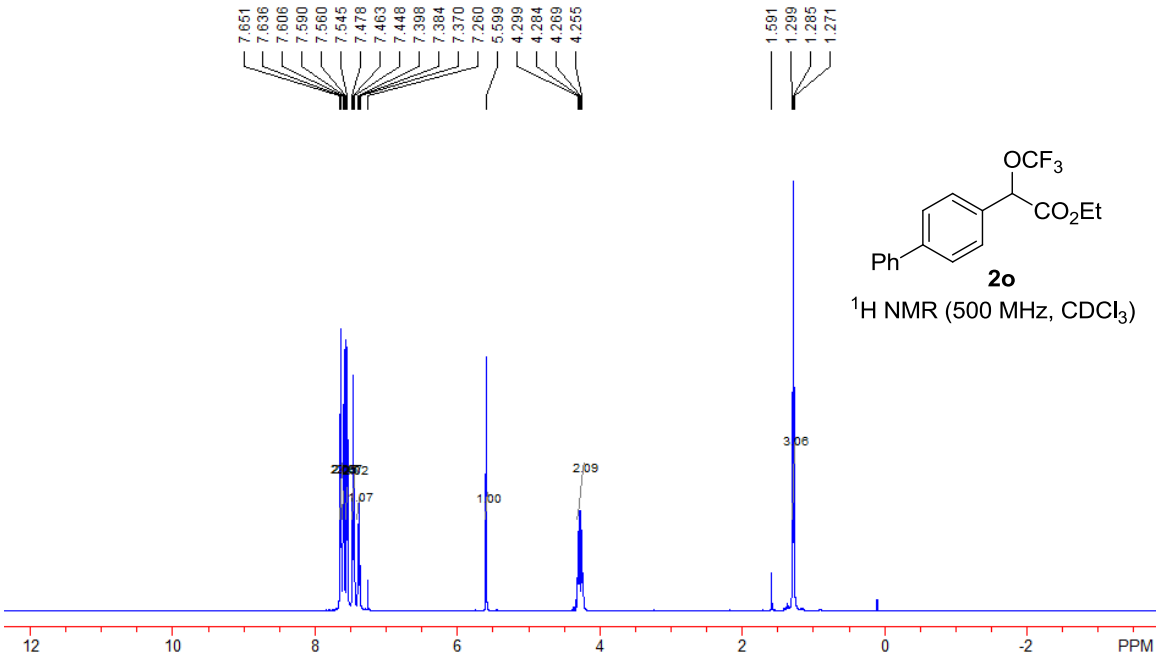
2n

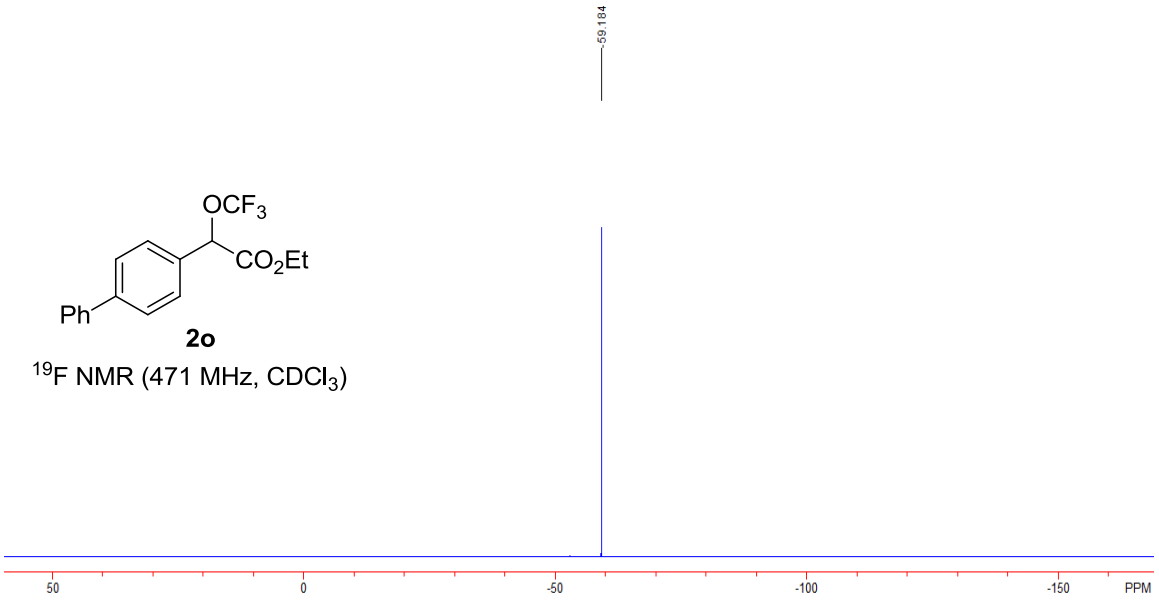
^{19}F NMR (471 MHz, $CDCl_3$)



2n

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


7.651
7.636
7.606
7.590
7.560
7.545
7.478
7.463
7.448
7.398
7.384
7.370
7.260
5.599
4.299
4.284
4.269
4.255
1.591
1.299
1.285
1.271
OCF3
CO2Et
Ph
2o
1H NMR (500 MHz, CDCl3)
3.06
2.09
1.00
1.07
12
10
8
6
4
2
0
-2
PPM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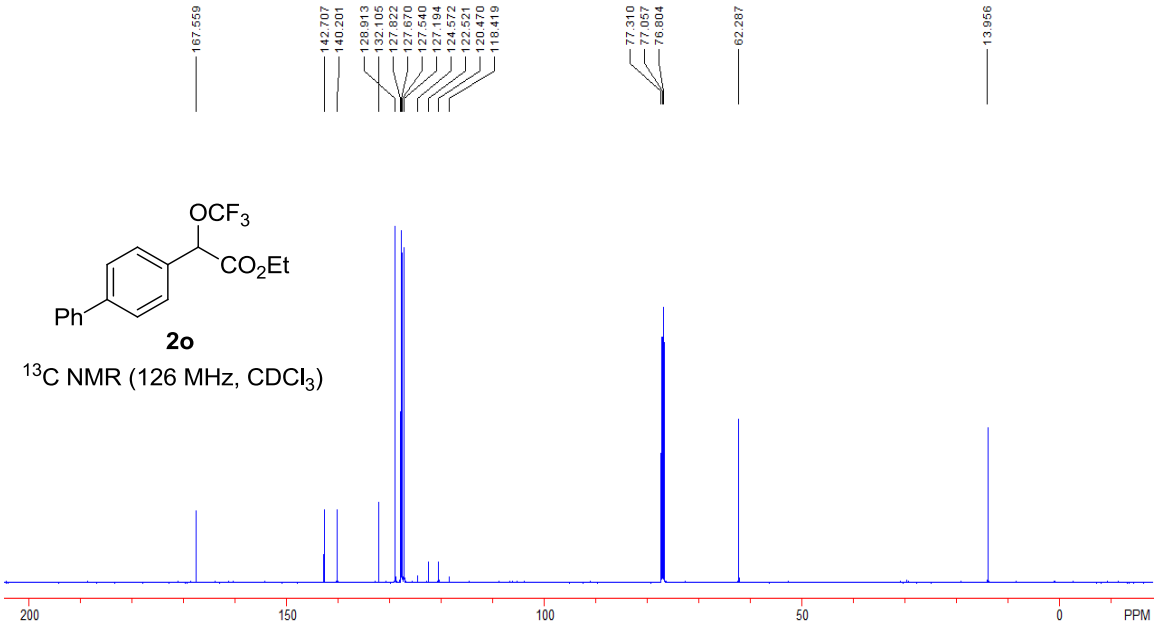
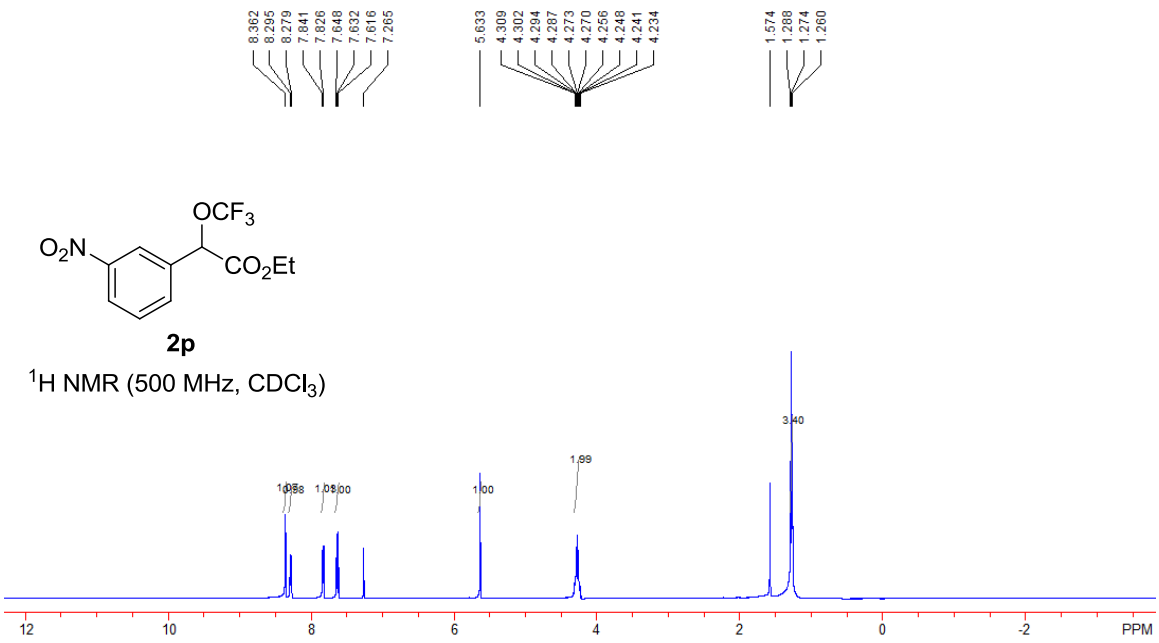
OCF3
CO2Et
Ph
2o
19F NMR (471 MHz, CDCl3)
50
0
-50
-100
-150
PPM



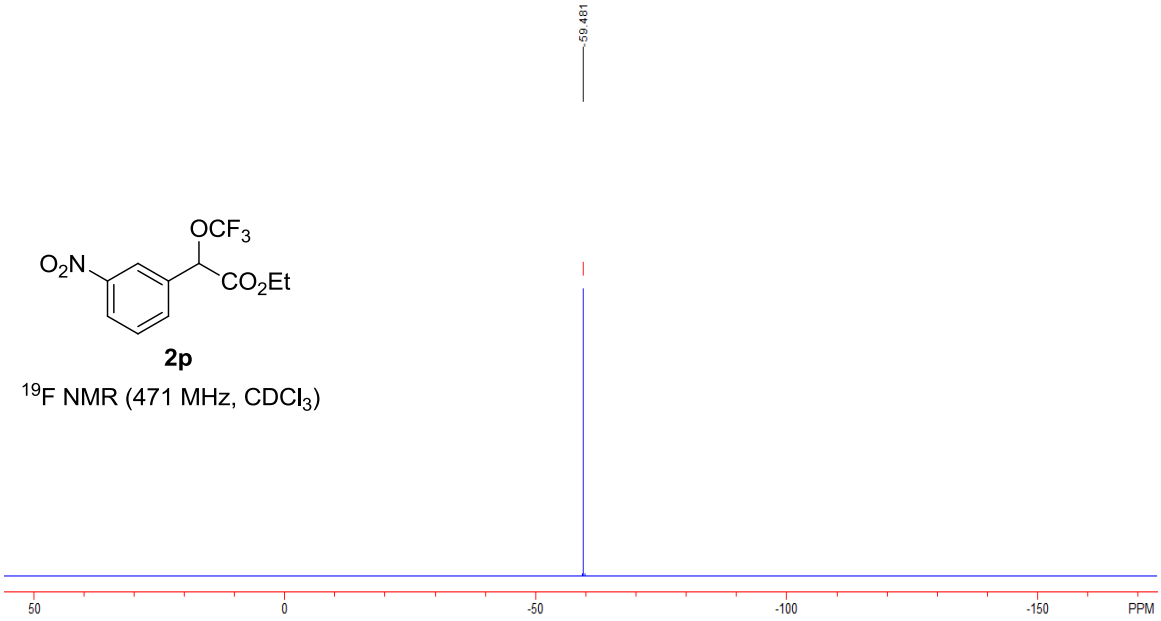
2o

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



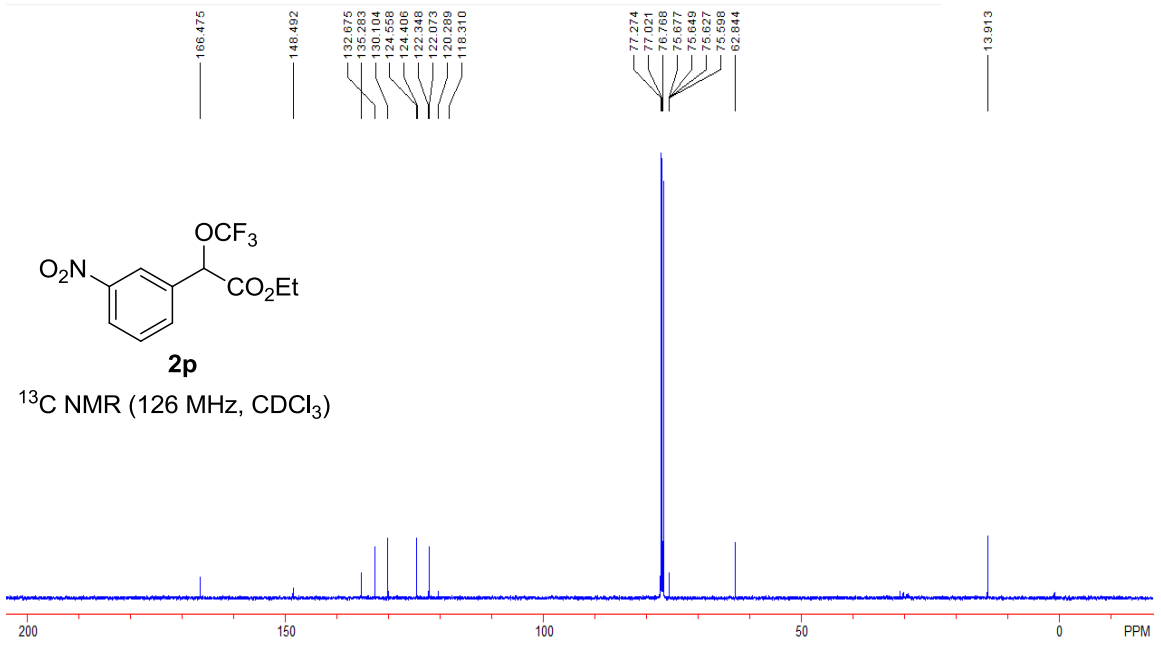
2p

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



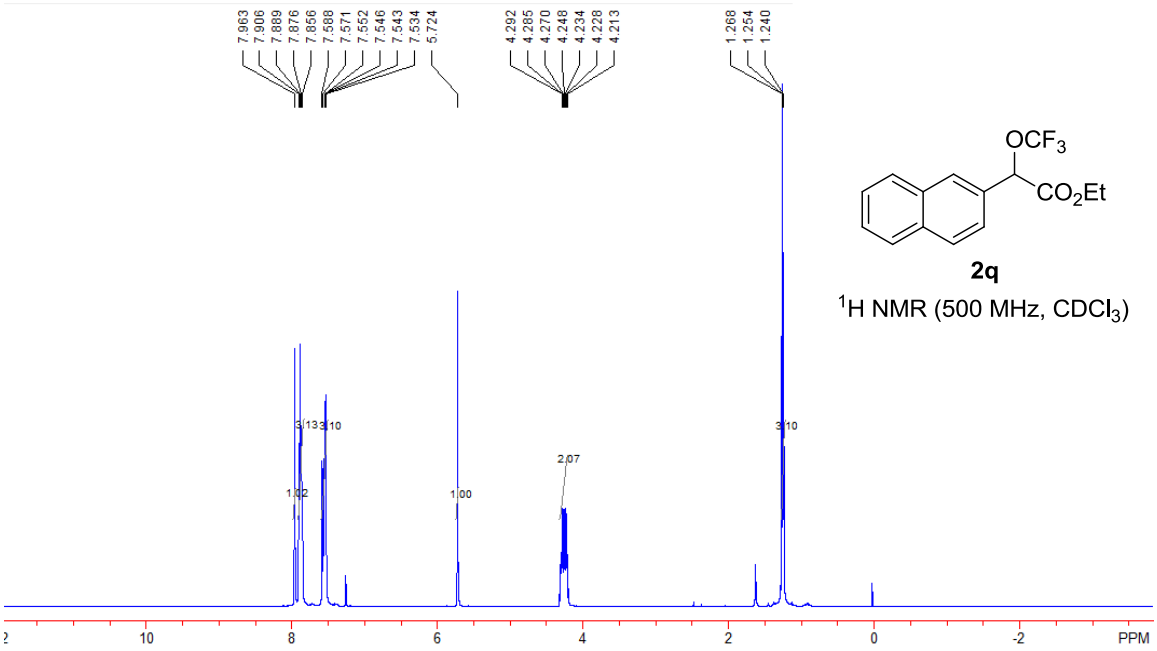
2p

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



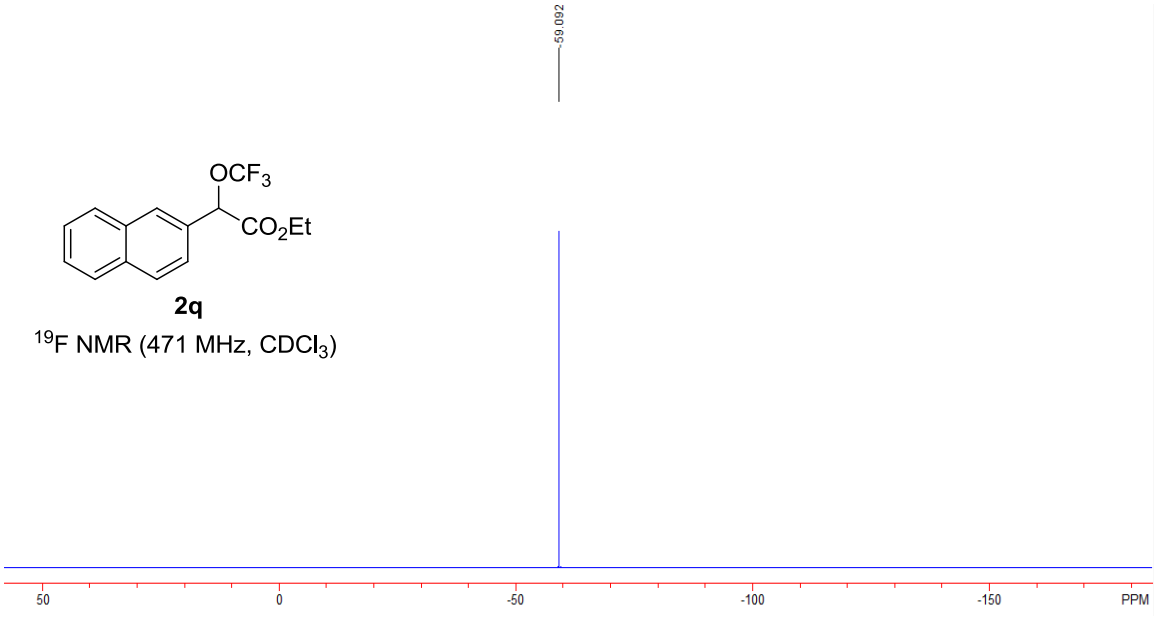
2p

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



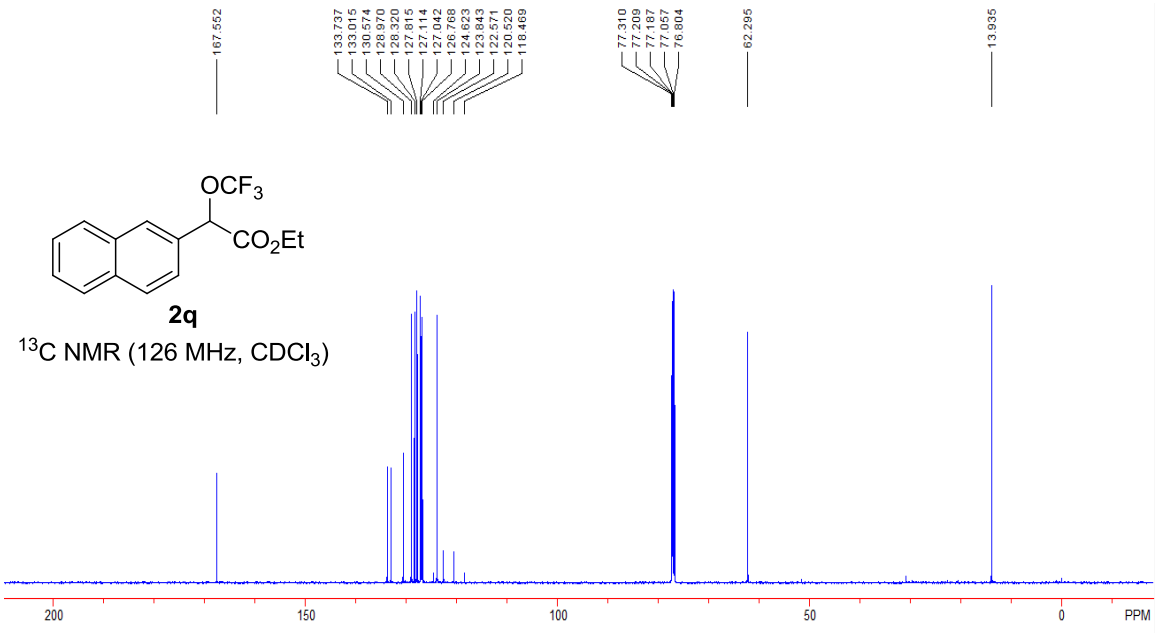
2q

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



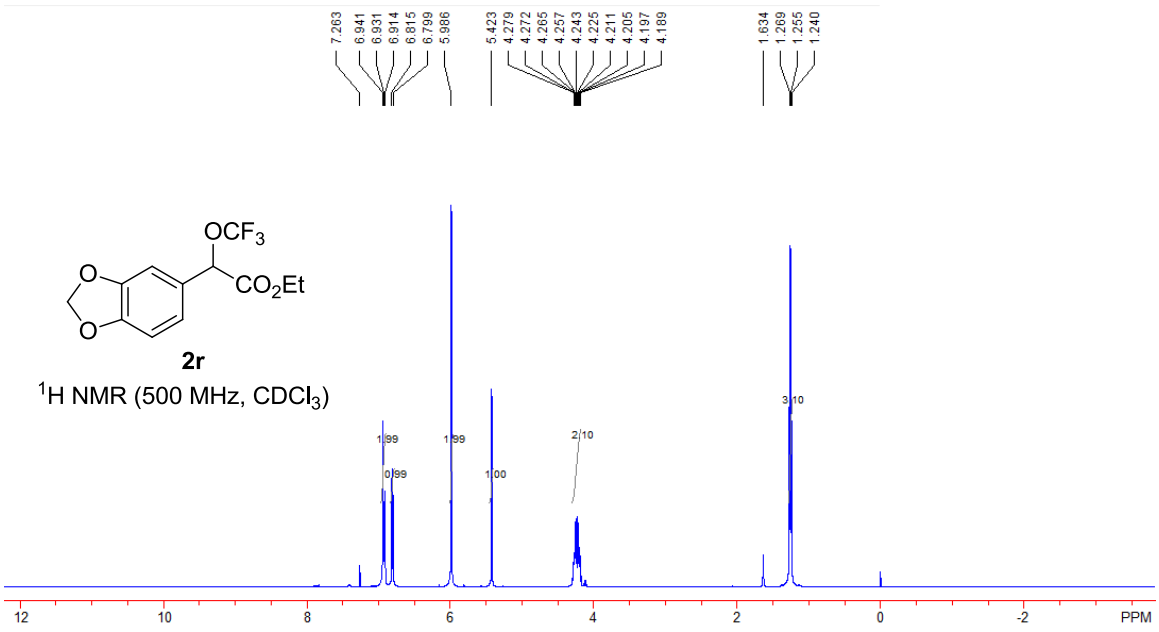
2q

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



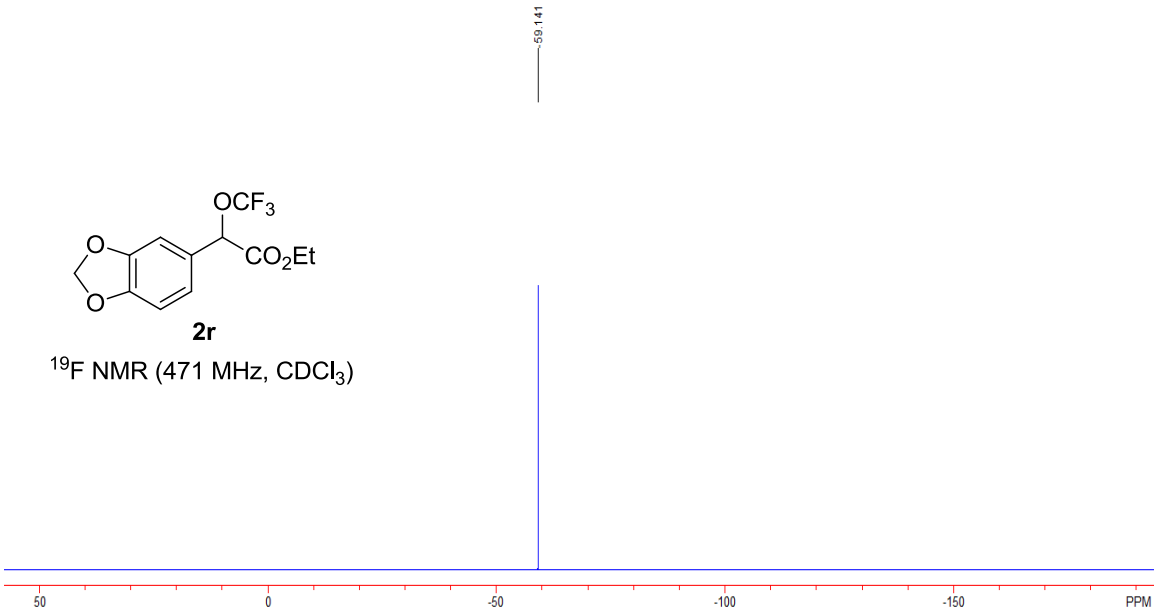
2q

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



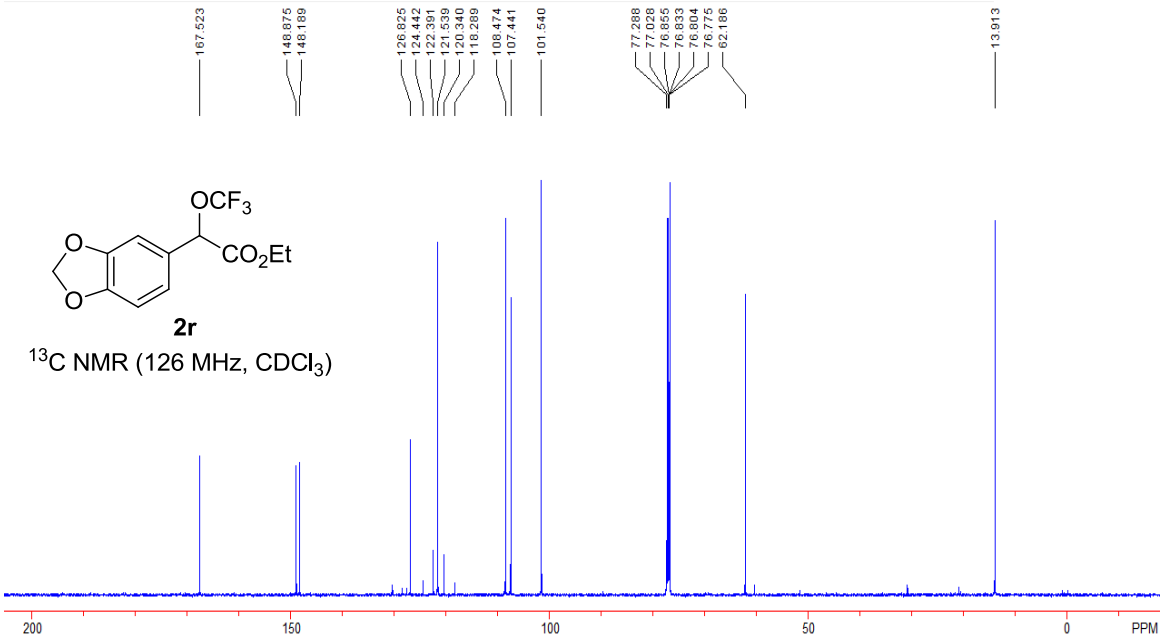
2r

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



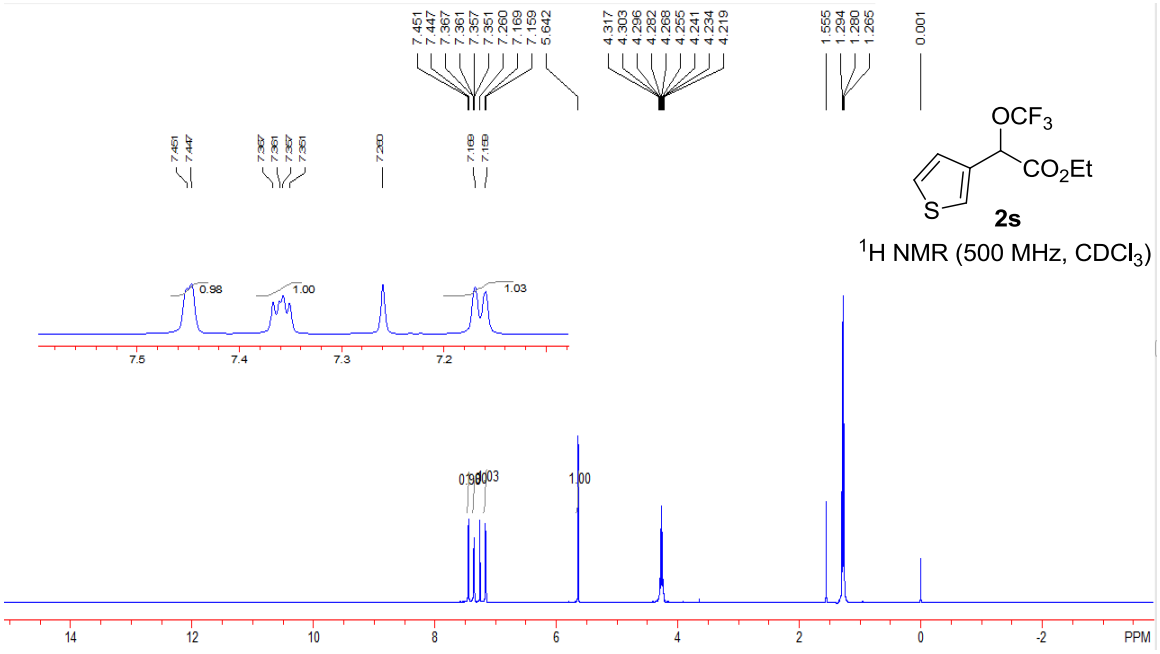
2r

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

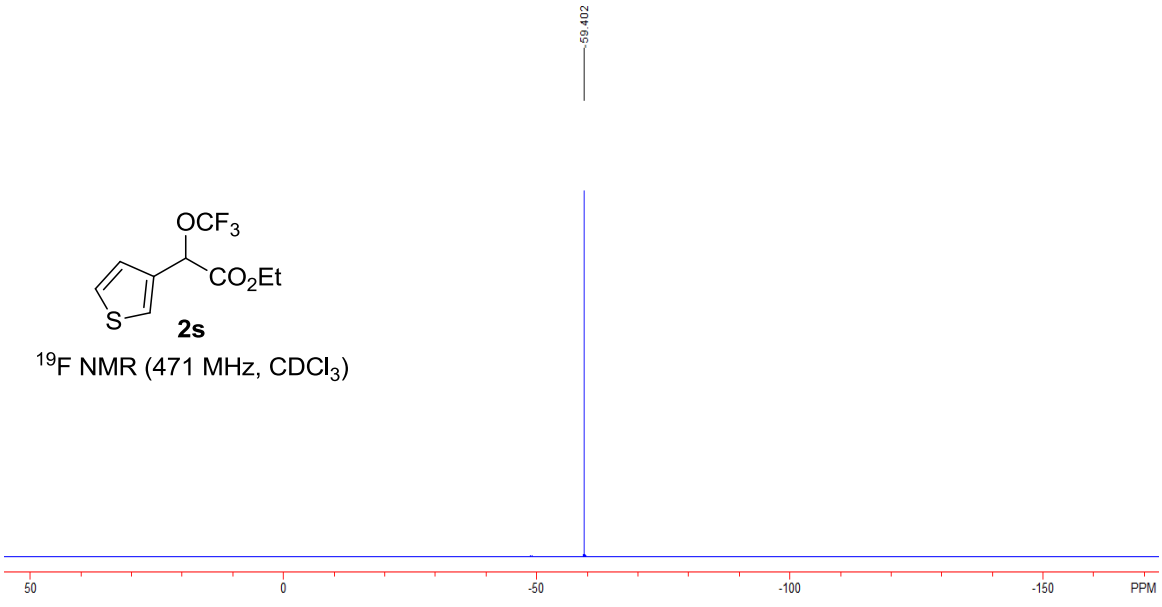


2r

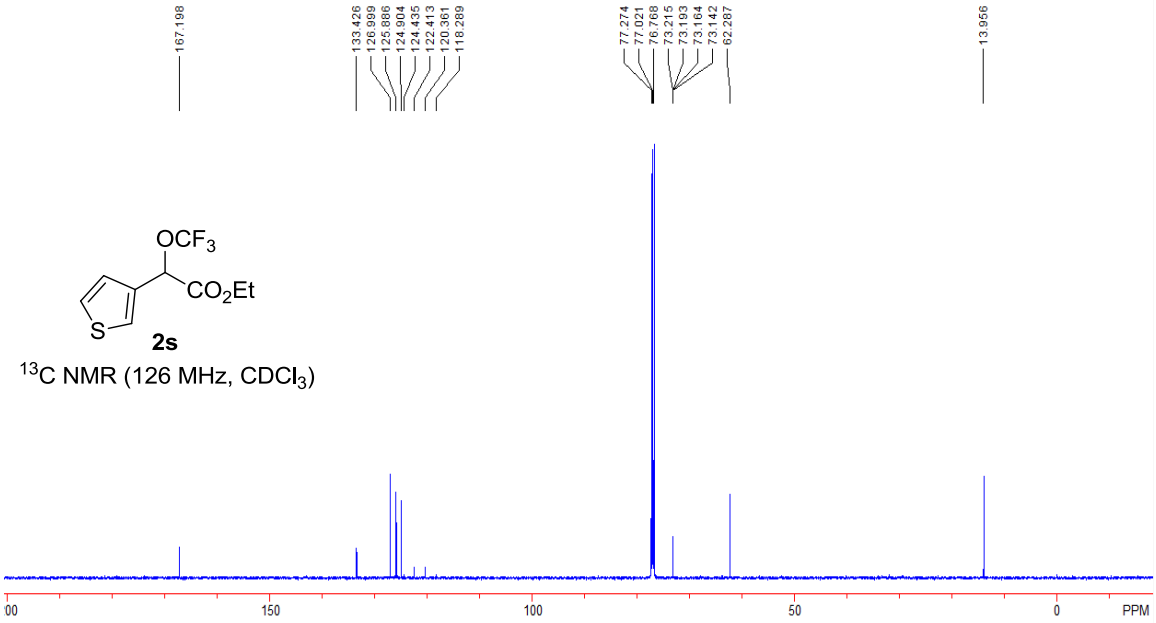
^{13}C NMR (126 MHz, $CDCl_3$)

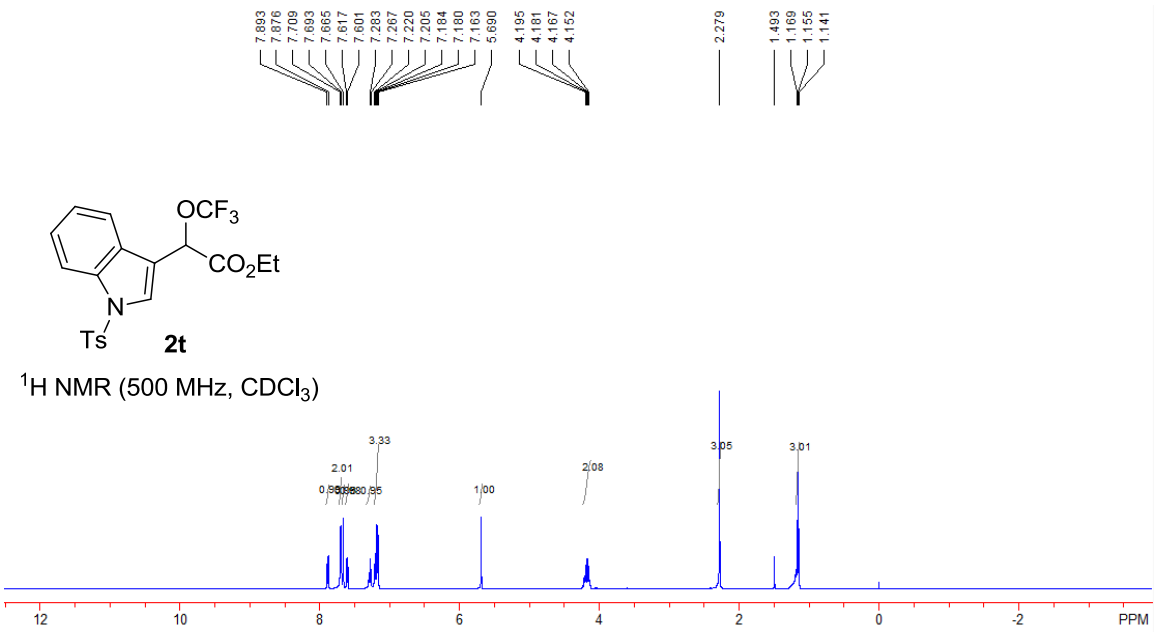


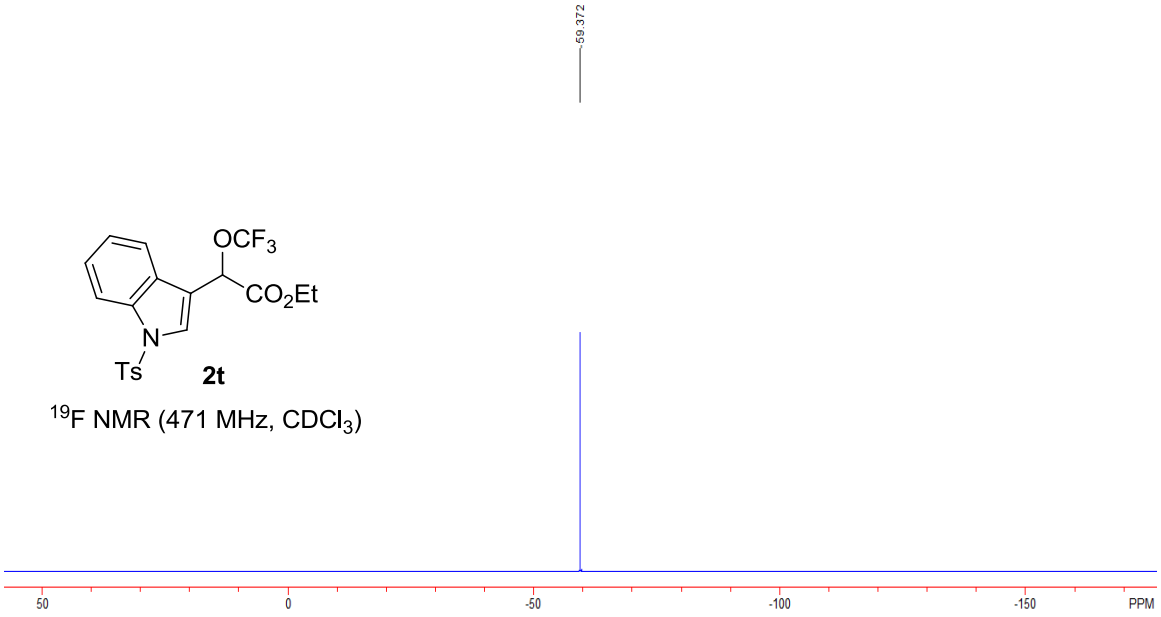
^{1}H NMR (500 MHz, $CDCl_3$)



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

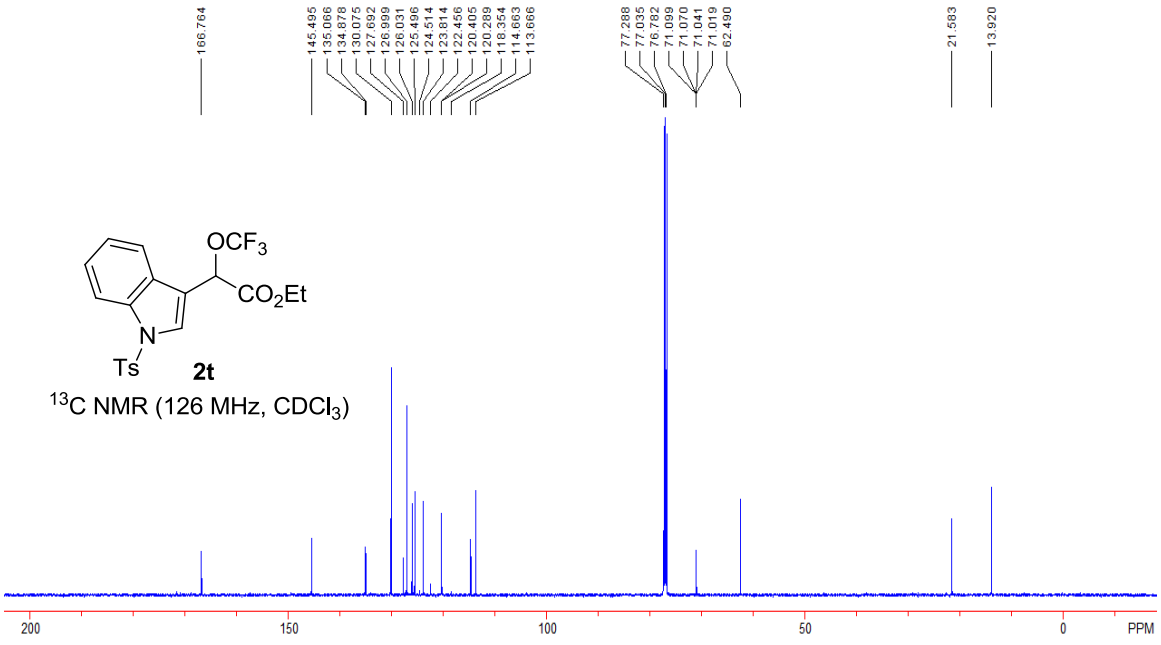

167.198
133.426
126.999
125.886
124.904
124.435
122.413
120.361
118.289
77.274
77.021
76.768
73.215
73.193
73.164
73.142
62.287
13.956
OCF3
CO2Et
S
2s
13C NMR (126 MHz, CDCl3)
150
100
50
0
PPM


7.893
7.876
7.709
7.693
7.665
7.617
7.601
7.283
7.267
7.220
7.205
7.184
7.180
7.163
5.690
4.195
4.181
4.167
4.152
2.279
1.493
1.169
1.155
1.141
OCF3
CO2Et
N
Ts
2t
1H NMR (500 MHz, CDCl3)
3.33
2.01
1.00
2.08
3.05
3.01
12
10
8
6
4
2
0
-2
PPM



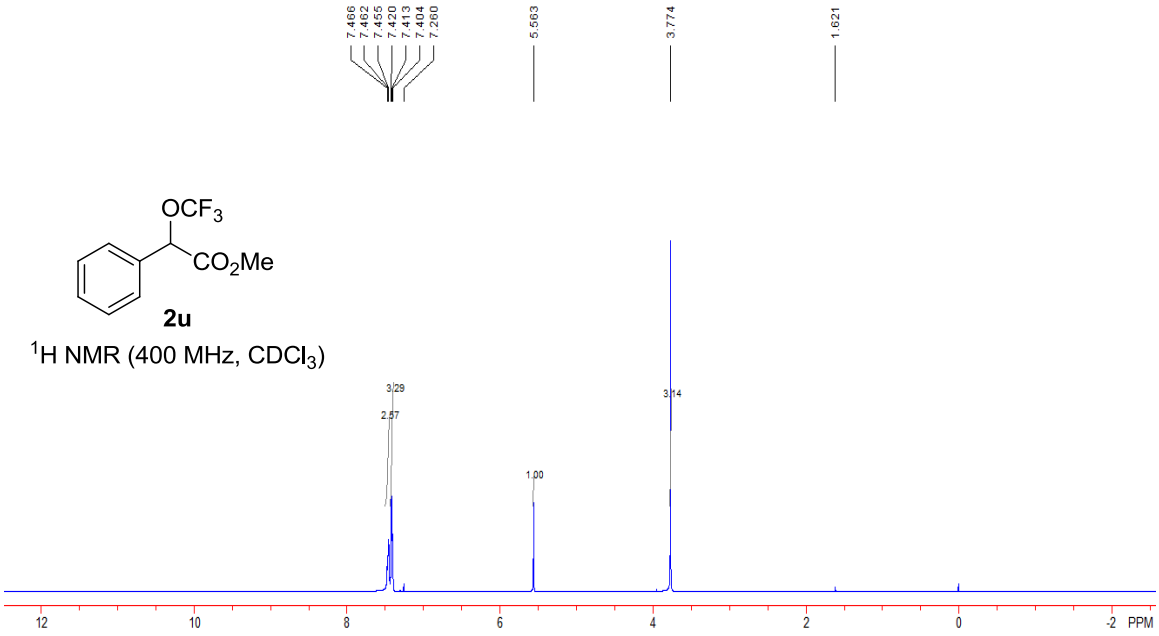
2t

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



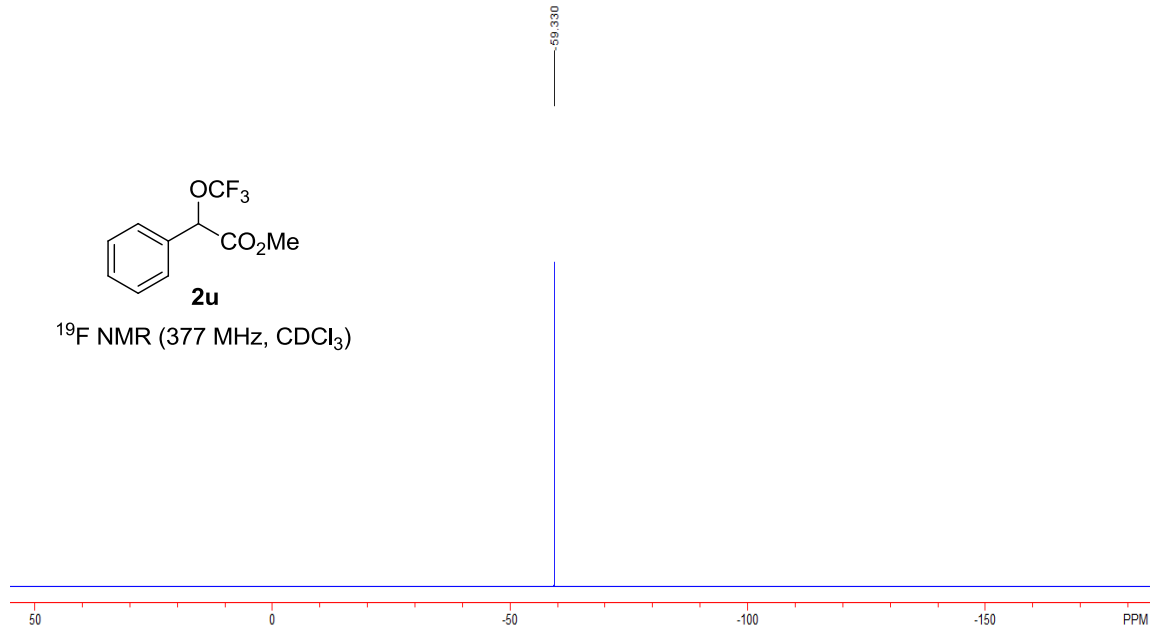
2t

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



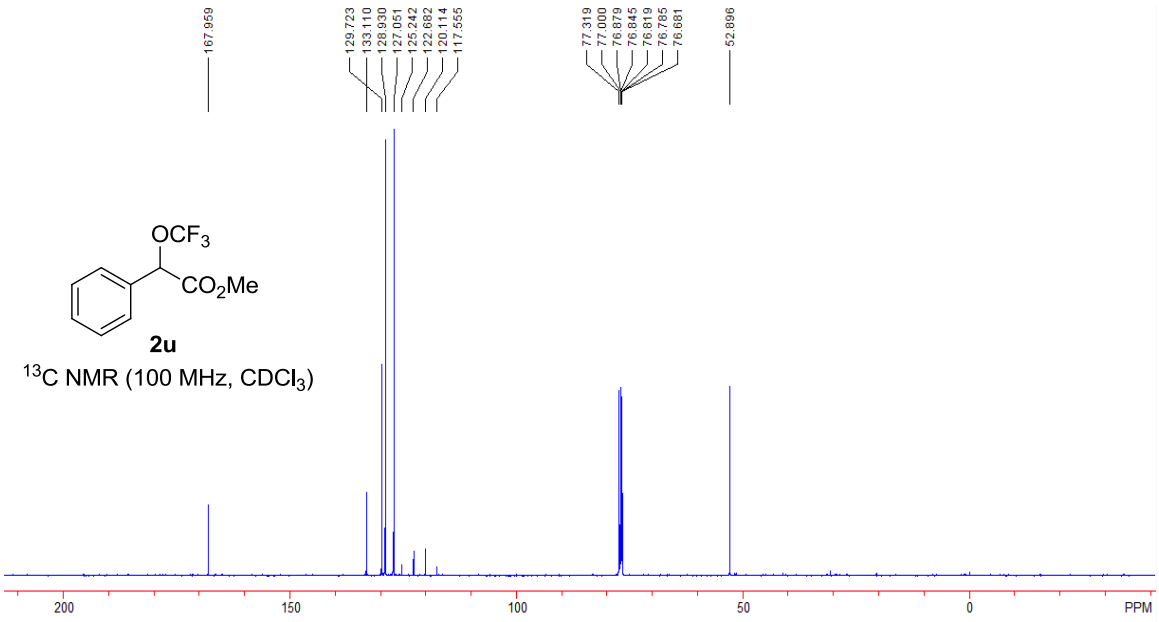
2u

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



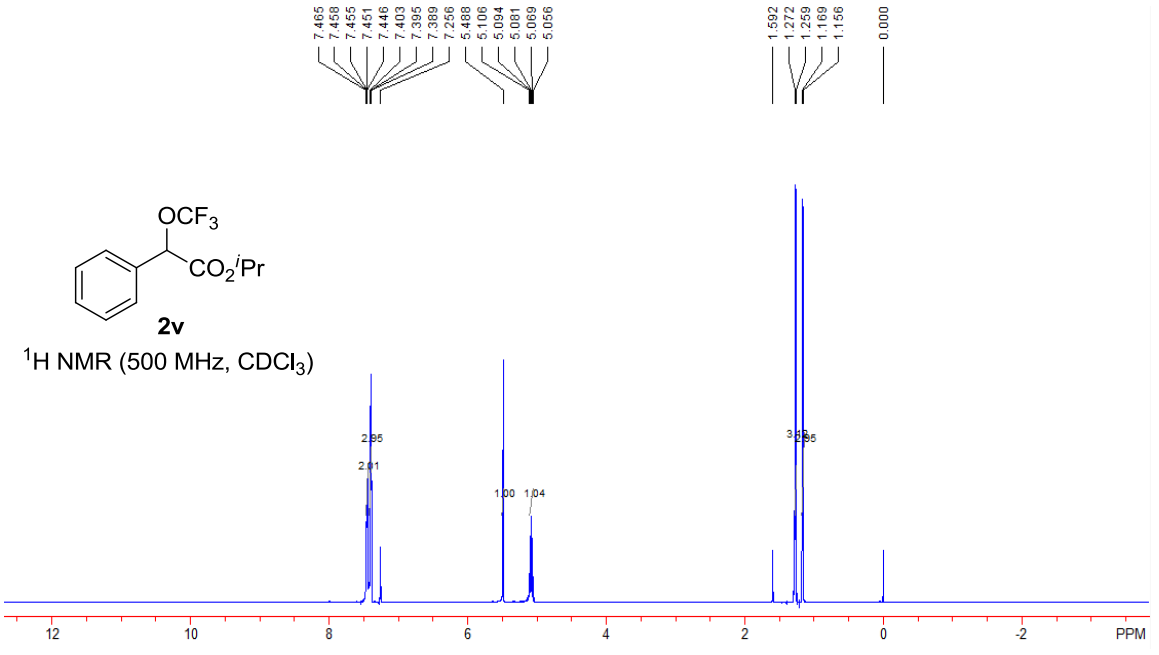
2u

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



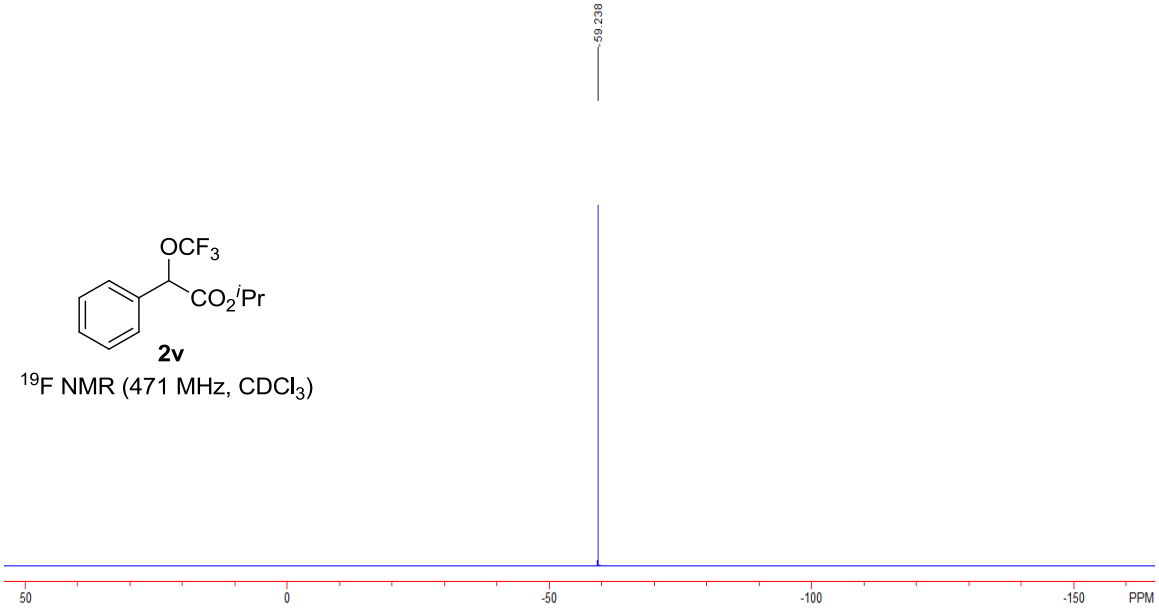
2u

^{13}C NMR (100 MHz, $CDCl_3$)



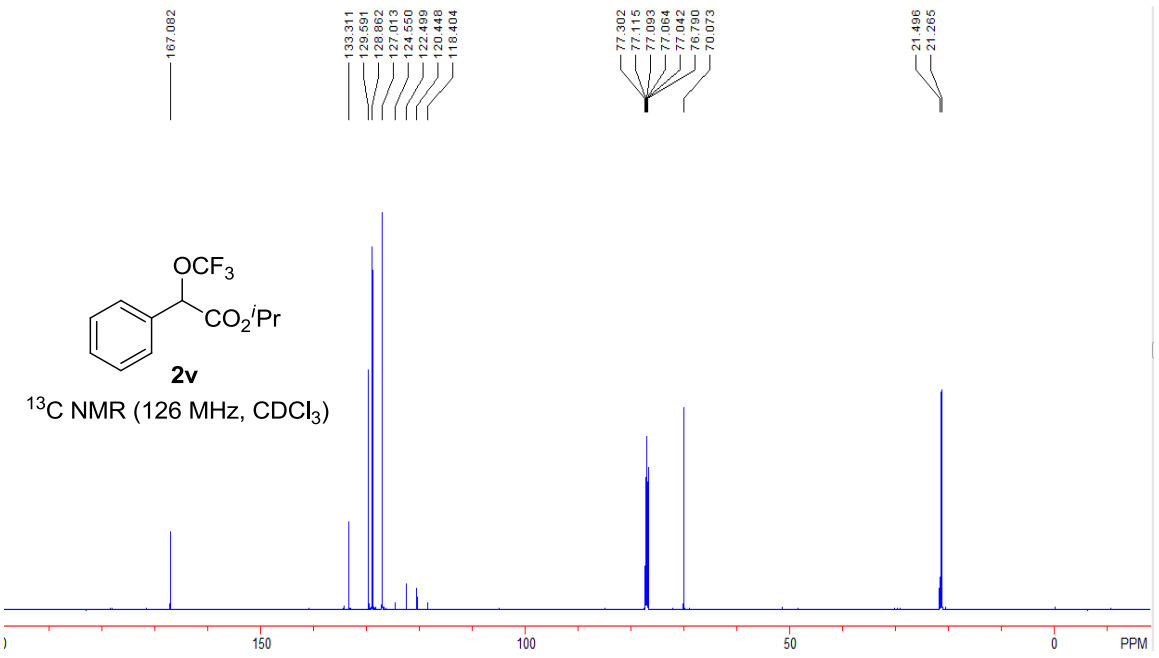
2v

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



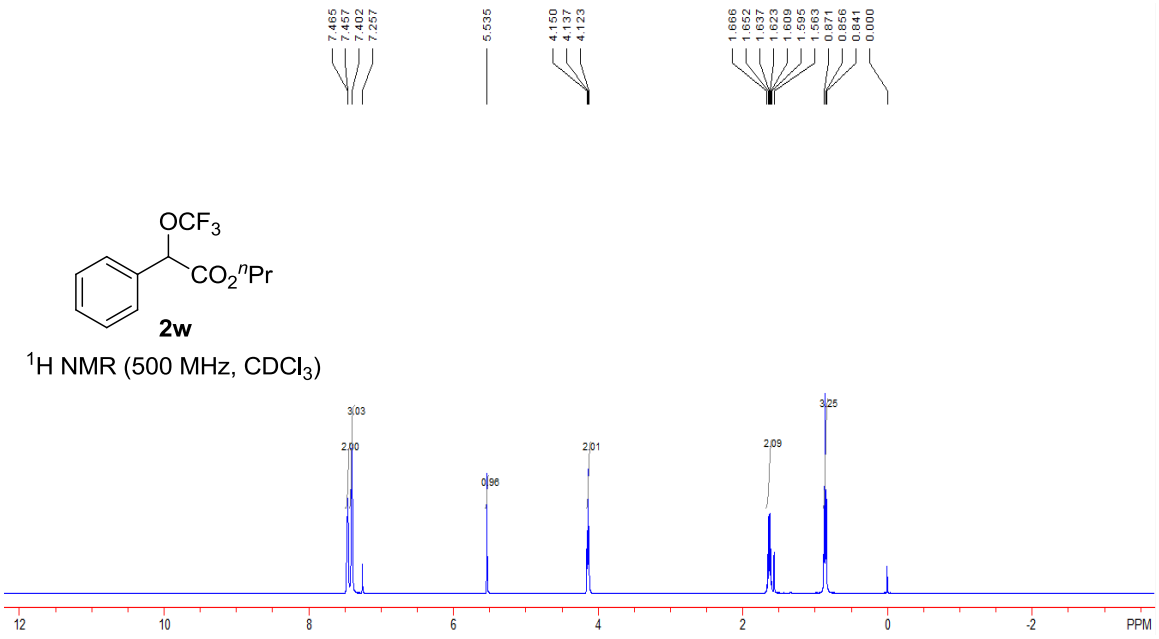
2v

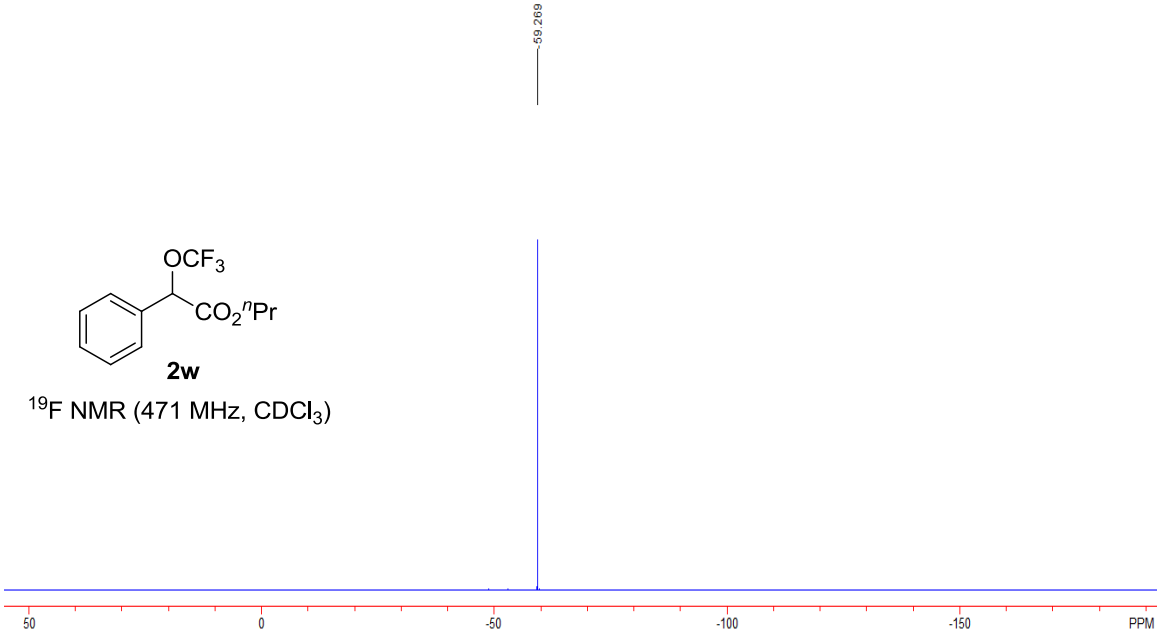
^{19}F NMR (471 MHz, $CDCl_3$)

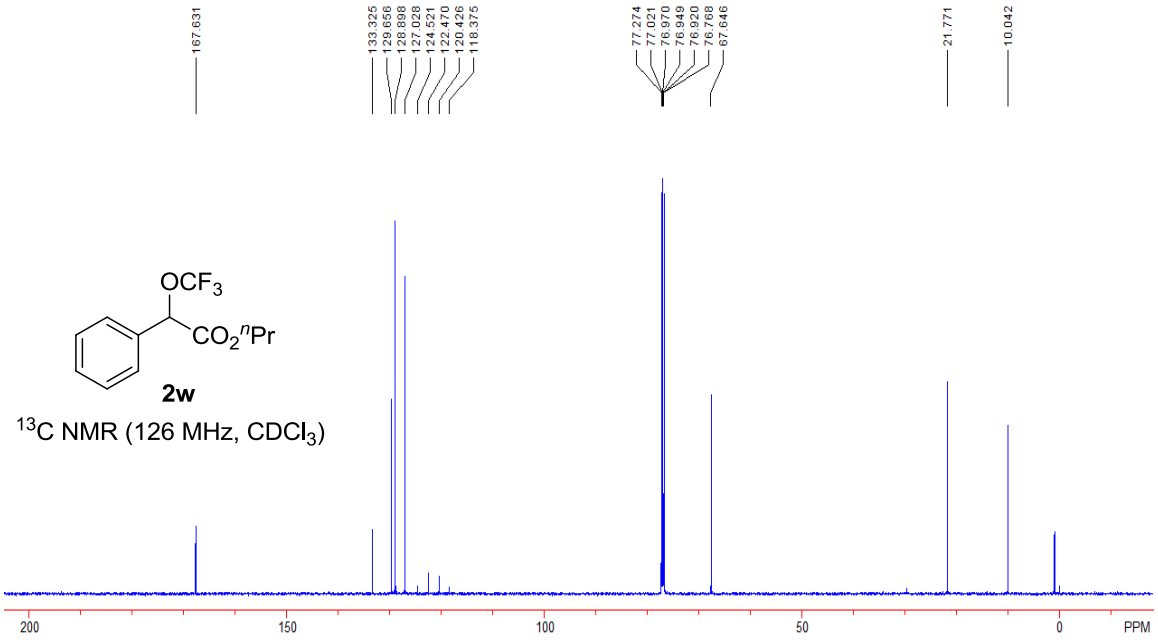


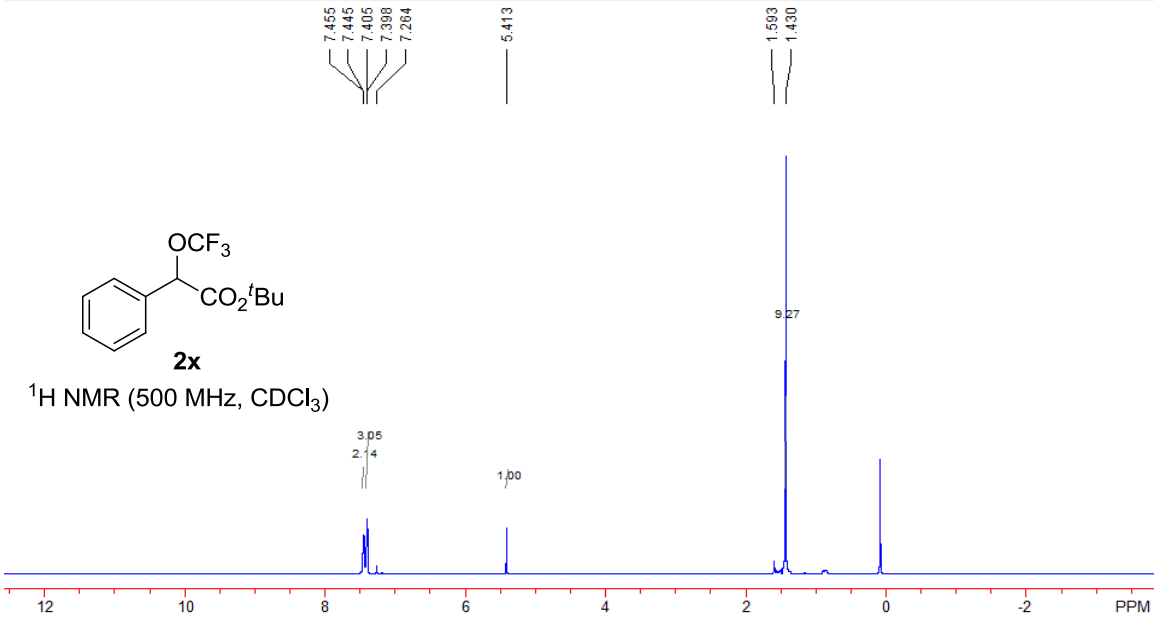
2v

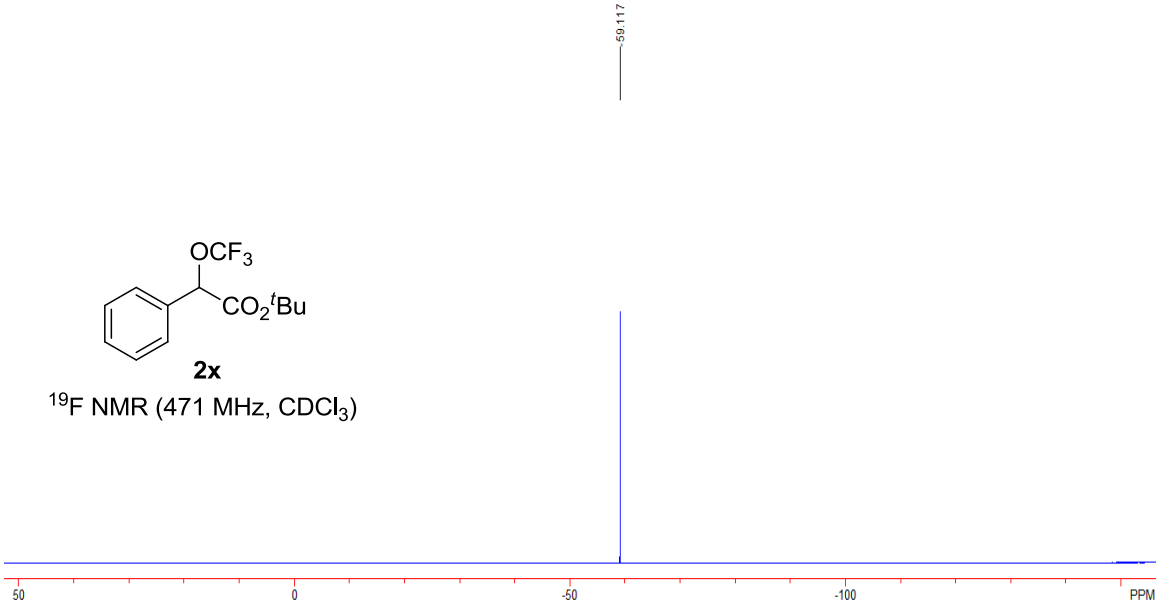
^{13}C NMR (126 MHz, $CDCl_3$)

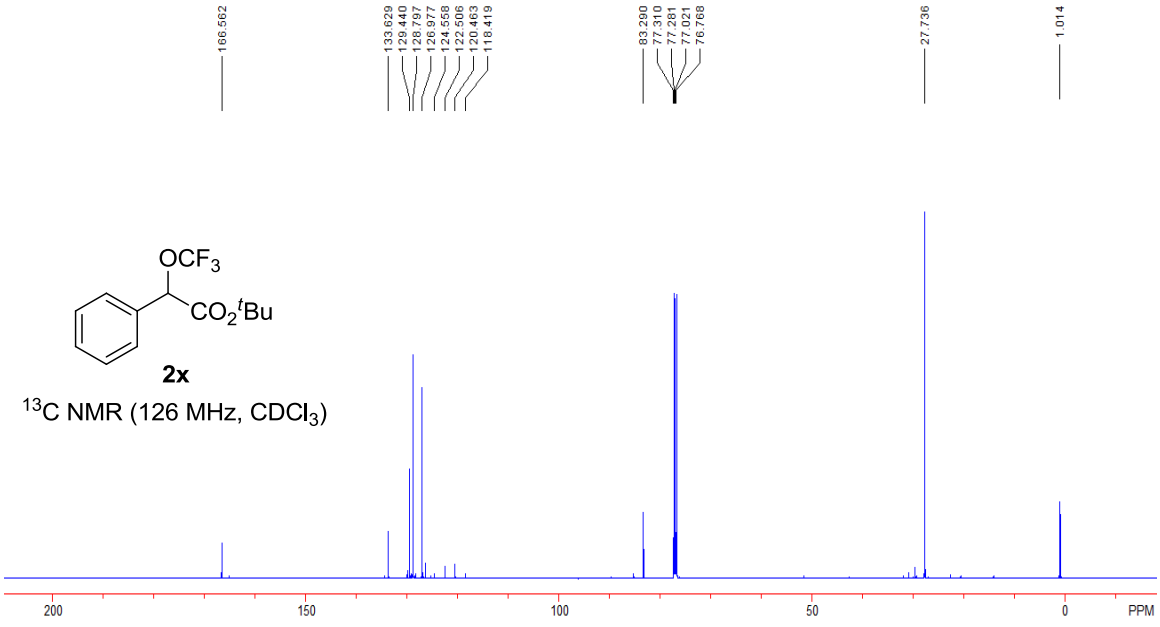

7.465
7.457
7.402
7.257
5.535
4.150
4.137
4.123
1.666
1.652
1.637
1.623
1.609
1.595
1.563
0.871
0.856
0.841
0.000
OCF3
CO2nPr
2w
1H NMR (500 MHz, CDCl3)
3.03
2.00
0.96
2.01
2.09
3.25
12
10
8
6
4
2
0
-2
PPM

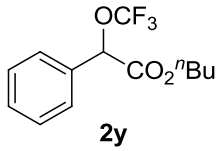

-59.269
OCF3
CO2nPr
2w
19F NMR (471 MHz, CDCl3)
50
0
-50
-100
-150
PPM


167.631
133.325
129.656
128.898
127.028
124.521
122.470
120.426
118.375
77.274
77.021
76.970
76.949
76.920
76.768
67.646
21.771
10.042
OCF3
CO2nPr
2w
13C NMR (126 MHz, CDCl3)
200
150
100
50
0
PPM


7.455
7.445
7.405
7.398
7.264
5.413
1.593
1.430
OCF3
CO2tBu
2x
1H NMR (500 MHz, CDCl3)
3.05
2.14
1.00
9.27
12
10
8
6
4
2
0
-2
PPM

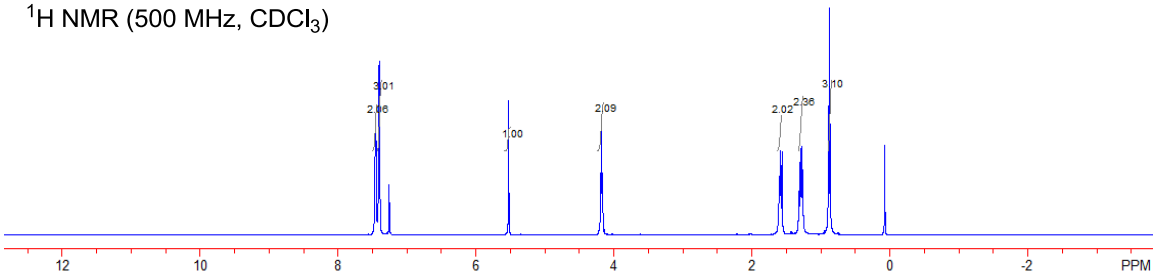

59.117
OCF3
CO2tBu
2x
19F NMR (471 MHz, CDCl3)
50
0
-50
-100
PPM

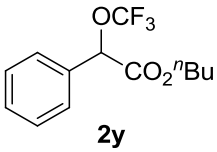

166.562
133.629
129.440
128.797
126.977
124.558
122.506
120.463
118.419
83.290
77.310
77.281
77.021
76.768
27.736
1.014
OCF3
CO2tBu
2x
13C NMR (126 MHz, CDCl3)
200
150
100
50
0
PPM



2y

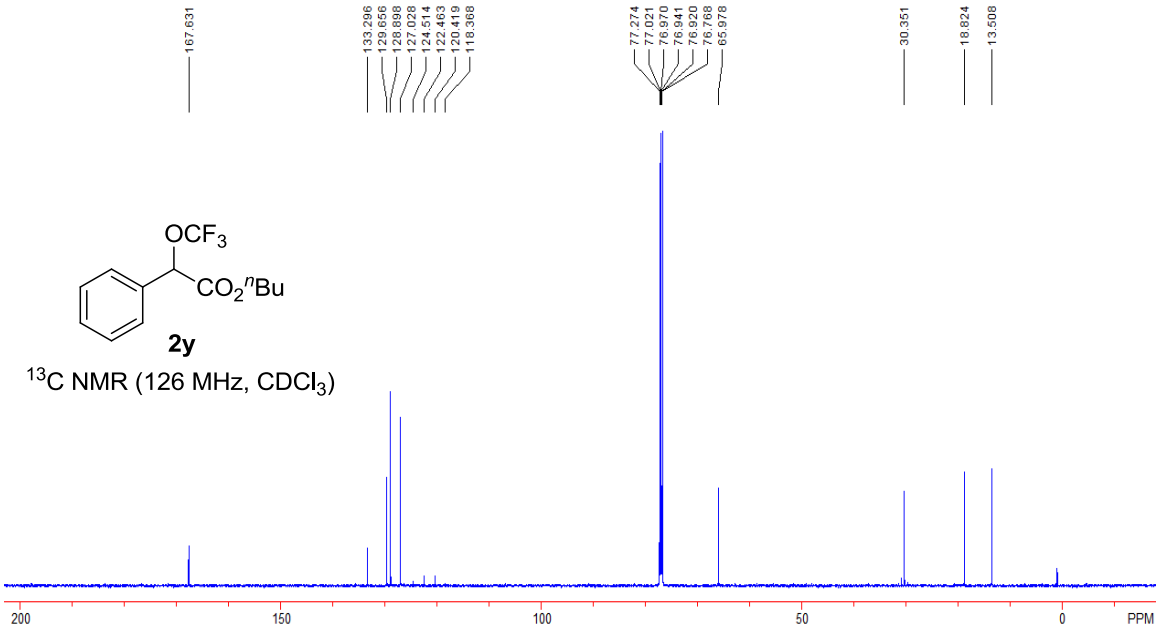
^{1}H NMR (500 MHz, $CDCl_3$)

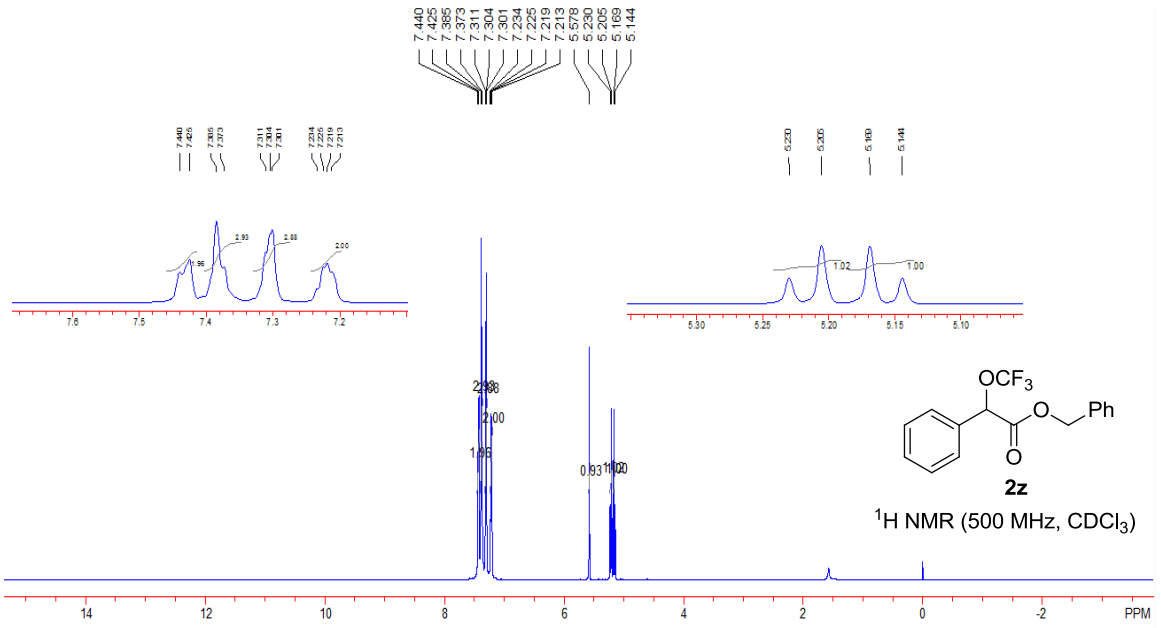


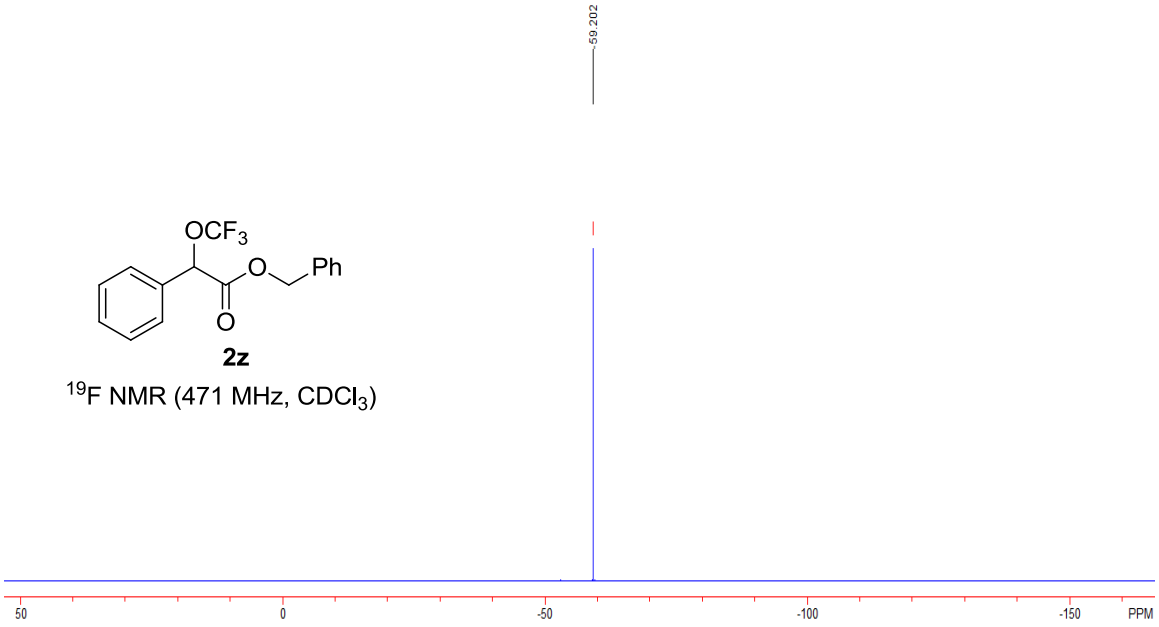


2y

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

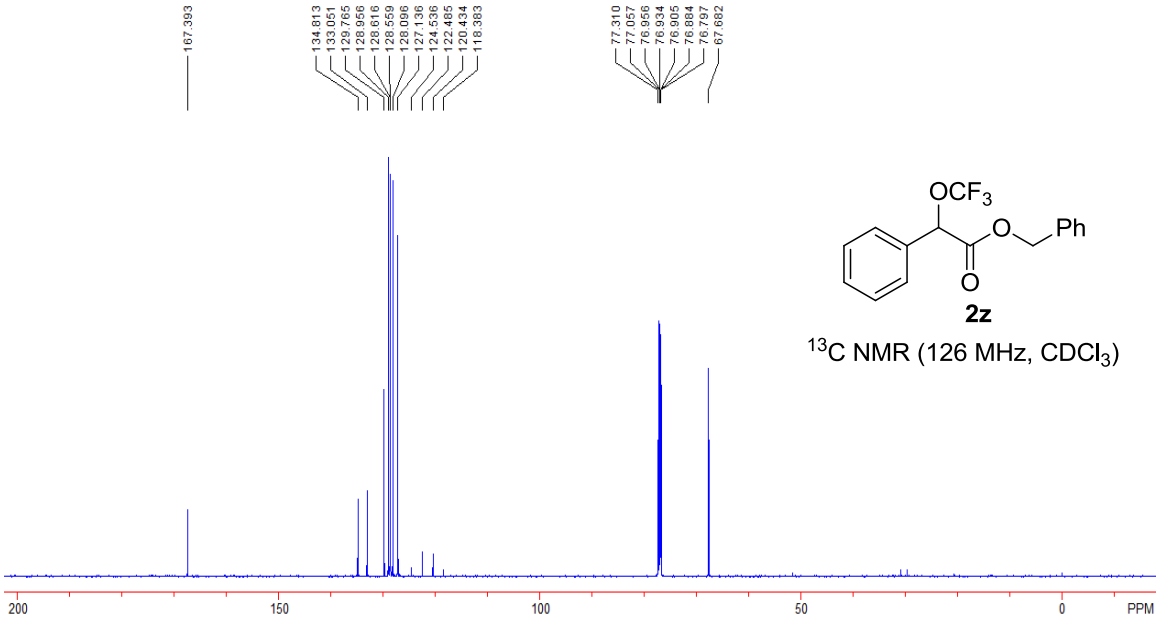

167.631
133.296
129.656
128.898
127.028
124.514
122.463
120.419
118.368
77.274
77.021
76.970
76.941
76.920
76.768
65.978
30.351
18.824
13.508
OCF3
CO2nBu
2y
13C NMR (126 MHz, CDCl3)
200
150
100
50
0
PPM


7.440
7.425
7.385
7.373
7.311
7.304
7.301
7.234
7.225
7.219
7.213
5.578
5.230
5.205
5.169
5.144
2.93
2.88
2.00
1.02
1.00
2.98
2.00
1.06
0.93
1.00
OCF3
O
Ph
O
2z
1H NMR (500 MHz, CDCl3)
14
12
10
8
6
4
2
0
-2
PPM



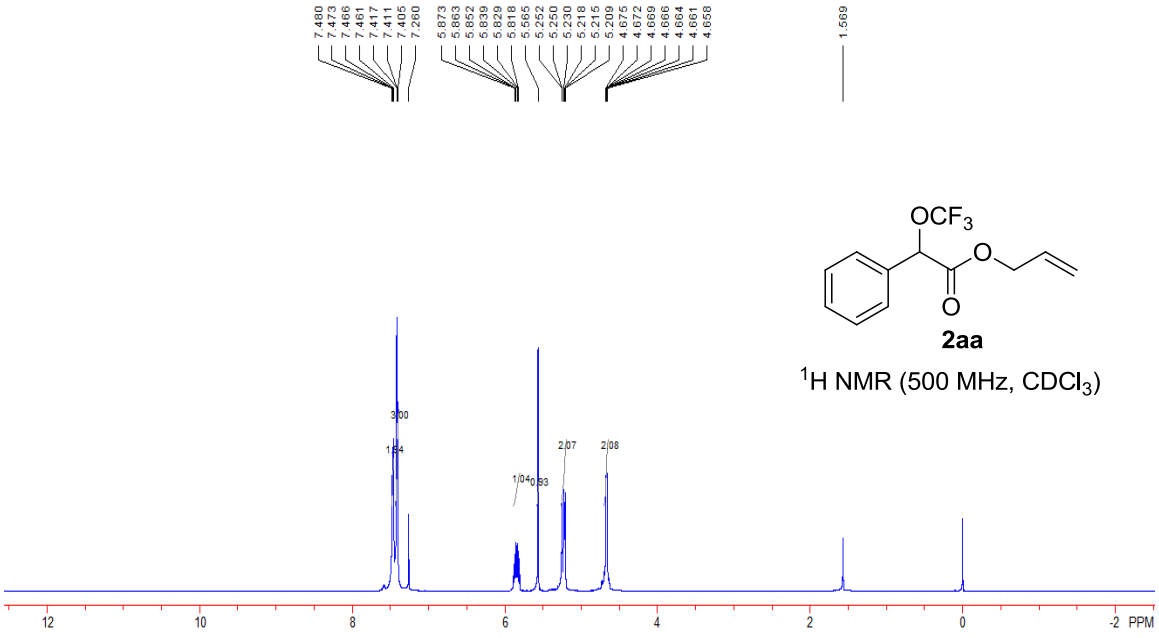
2z

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



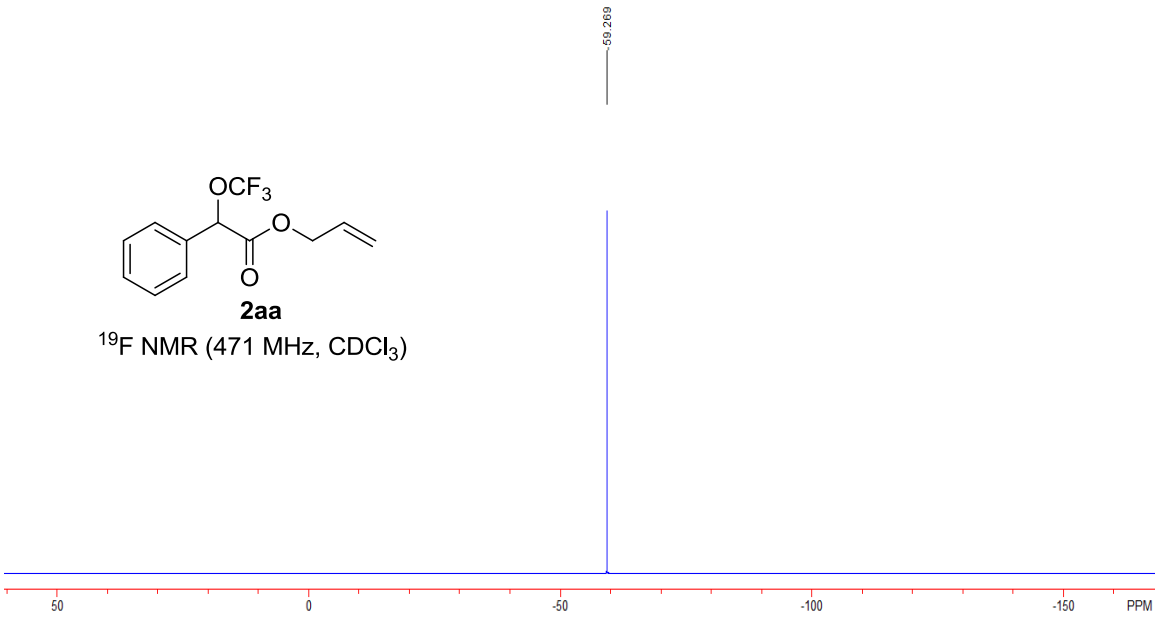
2z

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



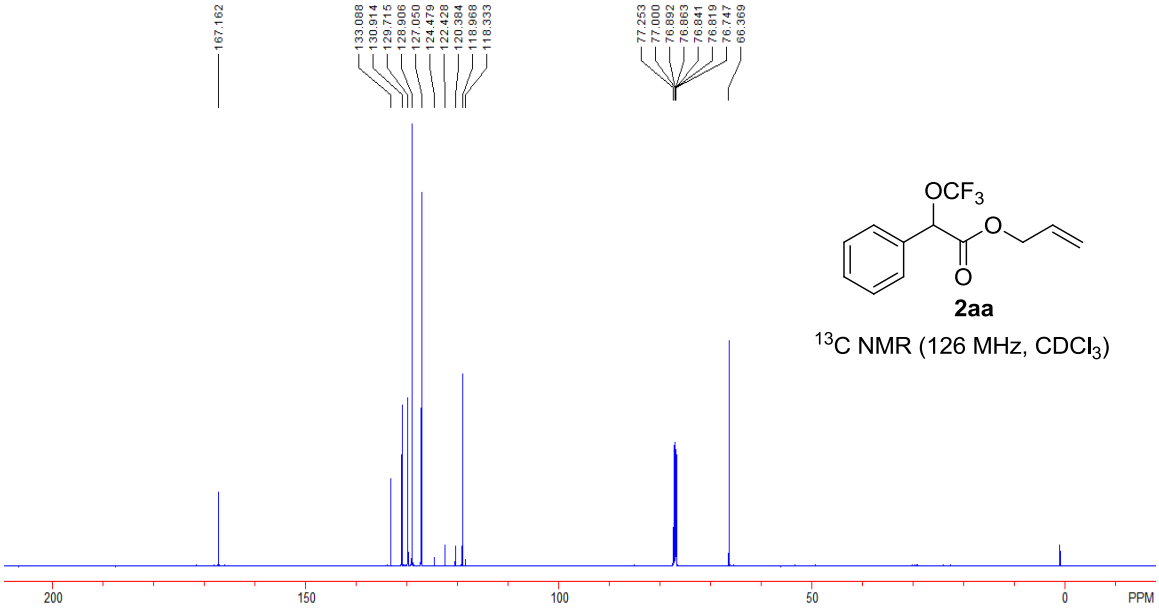
2aa

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



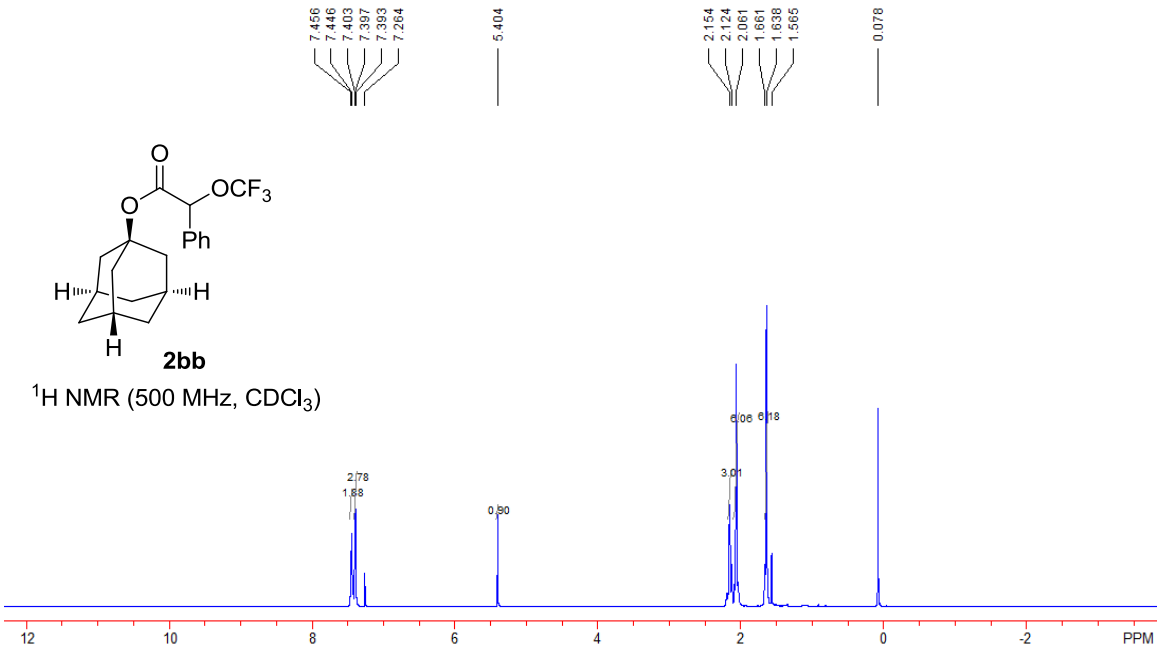
2aa

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



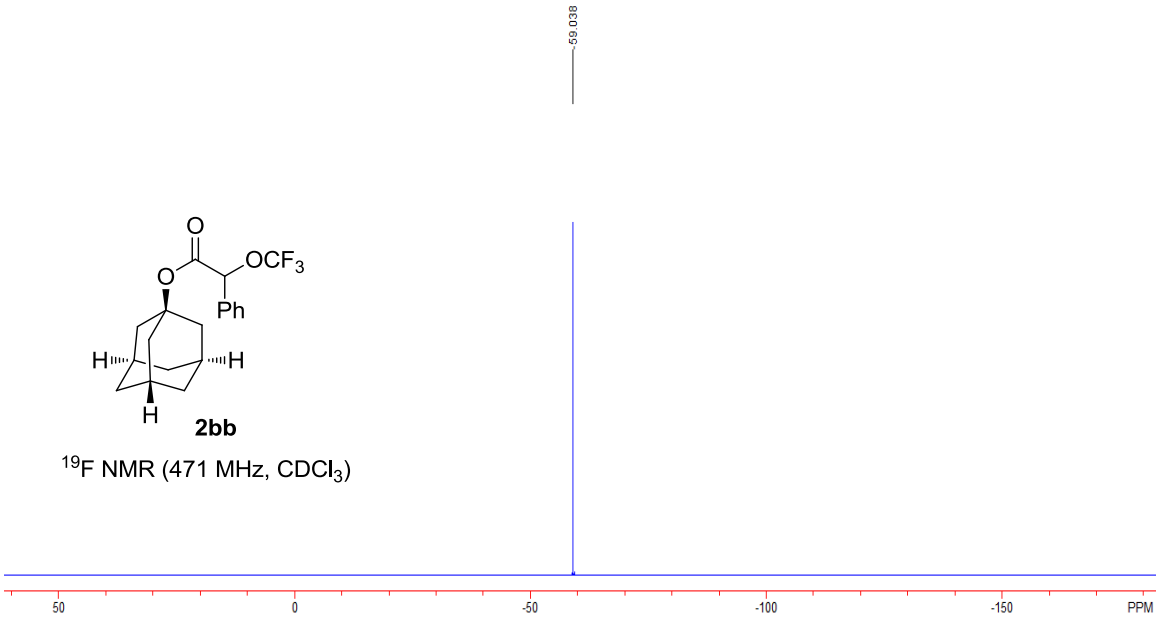
2aa

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



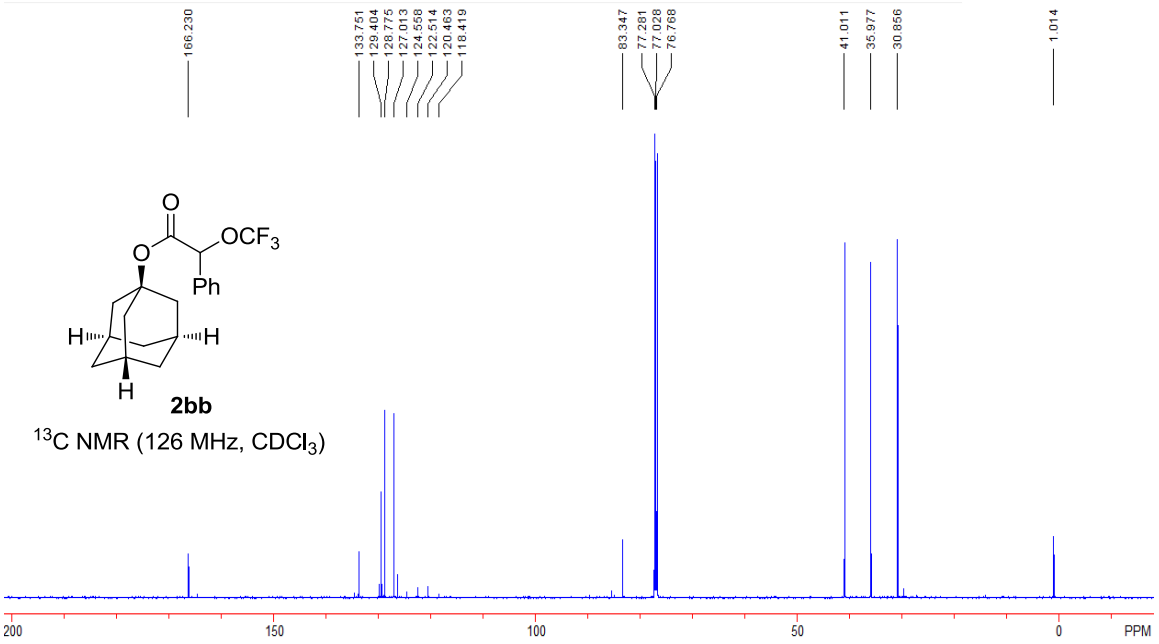
2bb

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



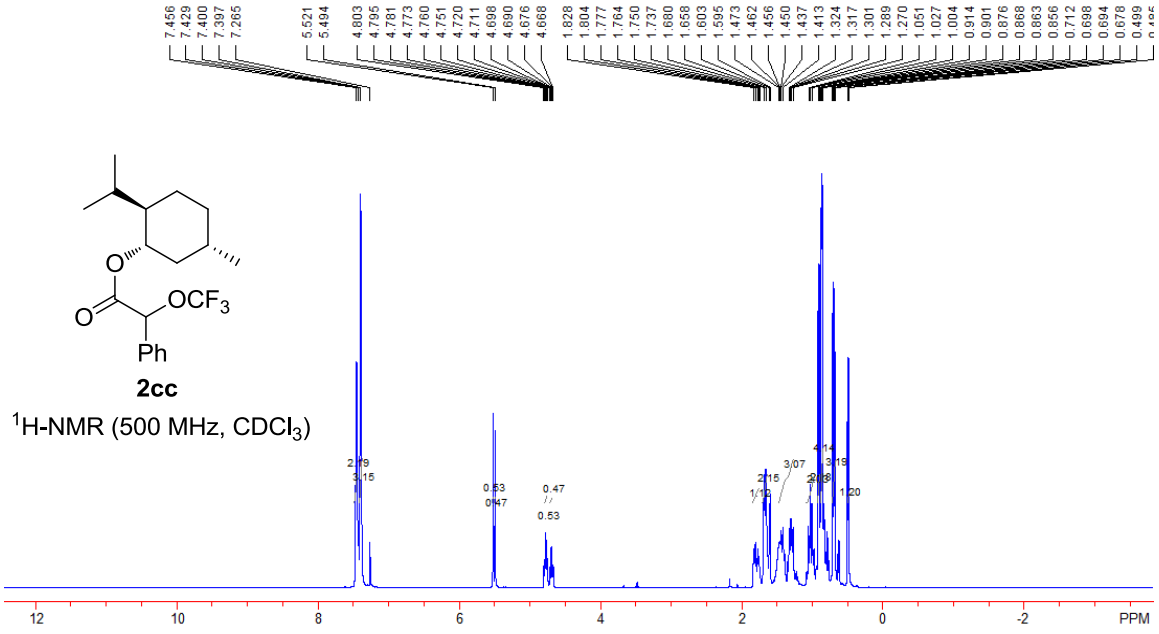
2bb

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



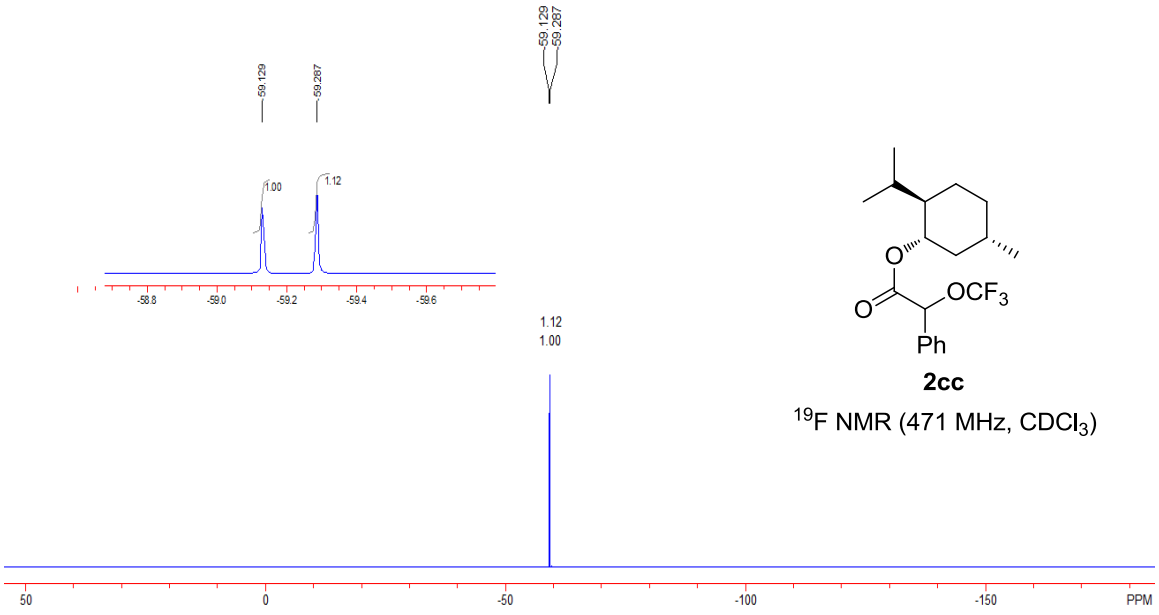
2bb

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



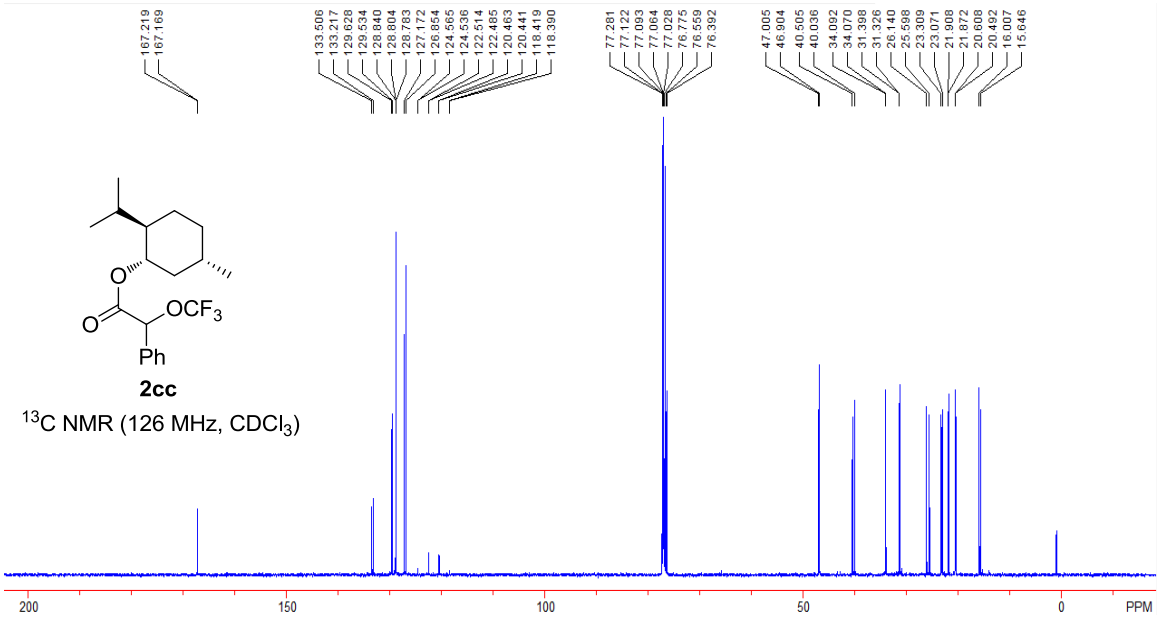
2cc

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



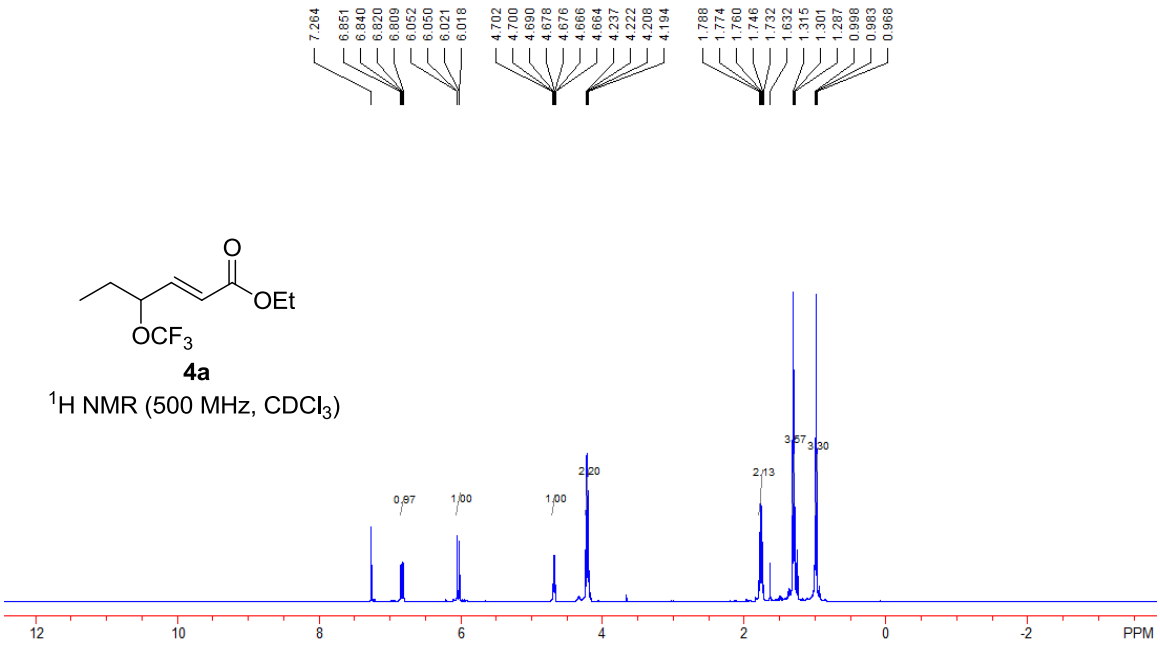
2cc

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



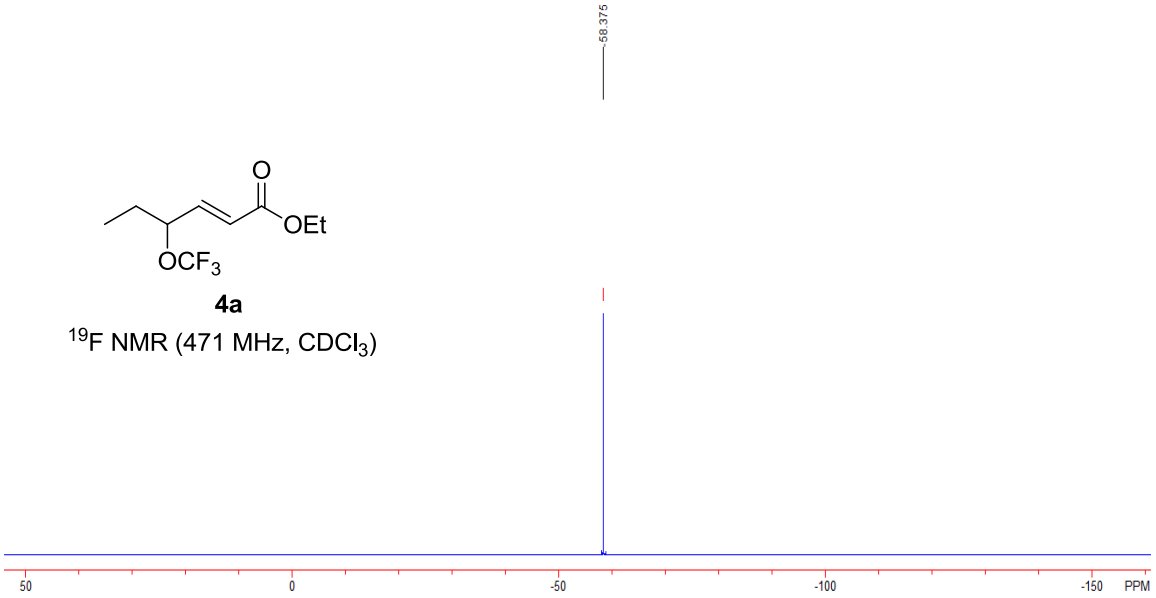
2cc

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



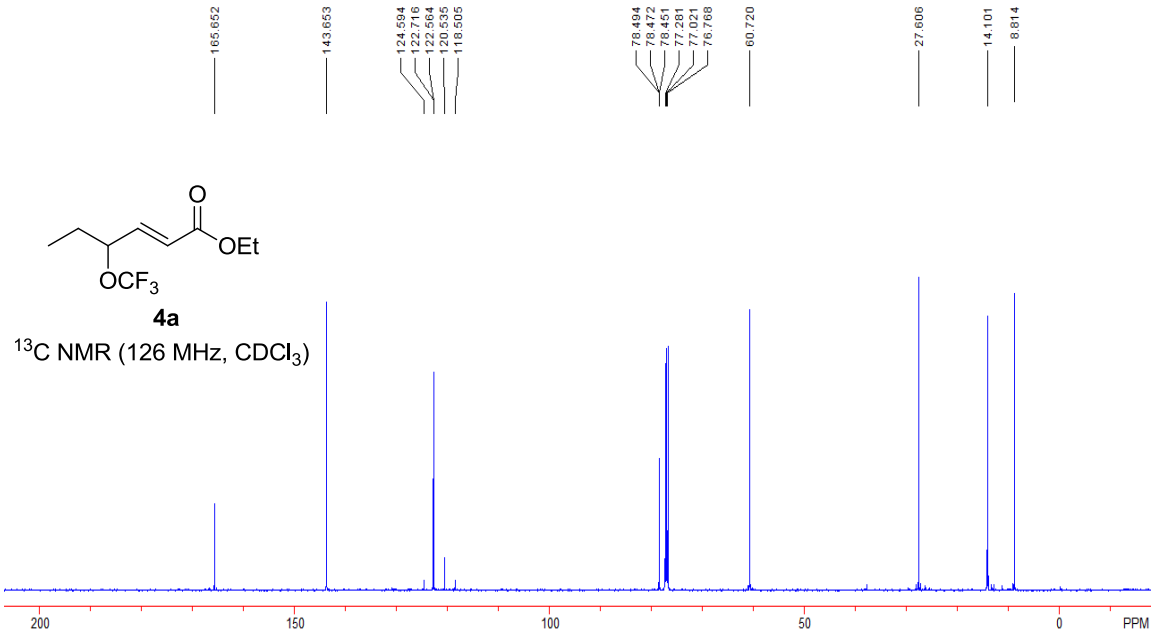
4a

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



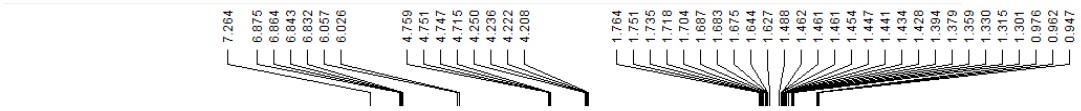
4a

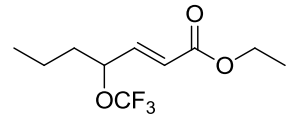
^{19}F NMR (471 MHz, $CDCl_3$)



4a

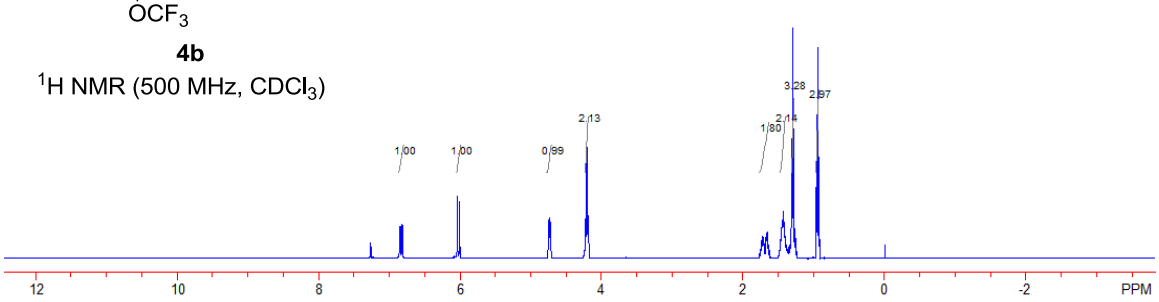
^{13}C NMR (126 MHz, $CDCl_3$)

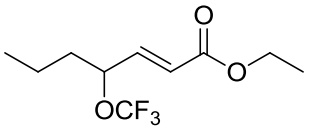




4b

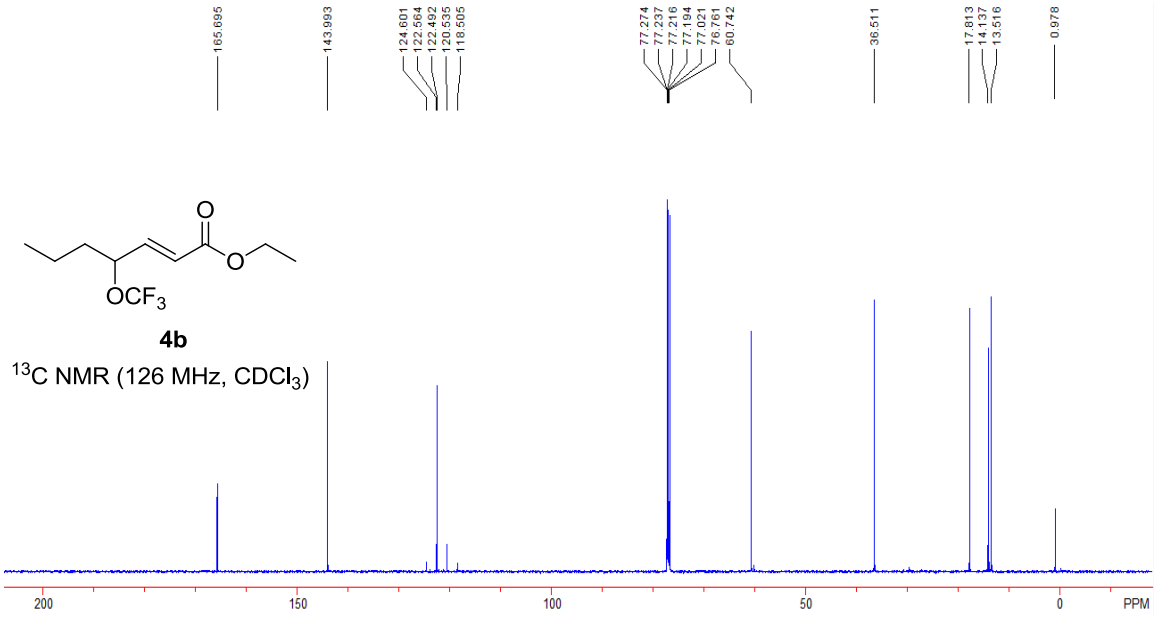
^{1}H NMR (500 MHz, $CDCl_3$)





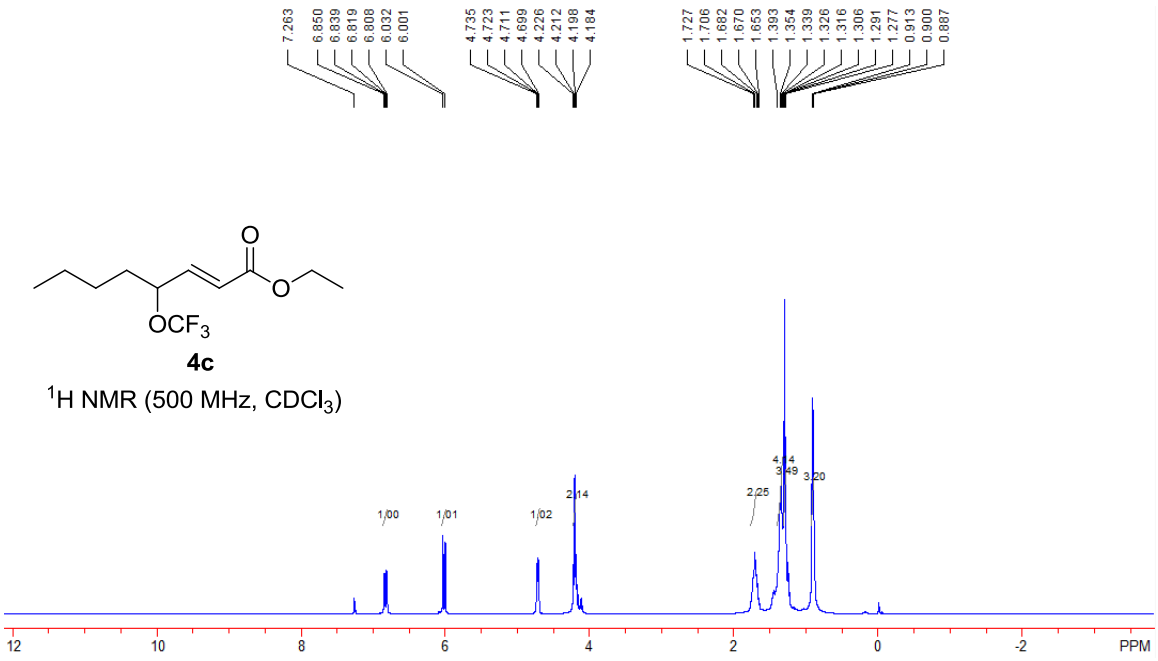
4b

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



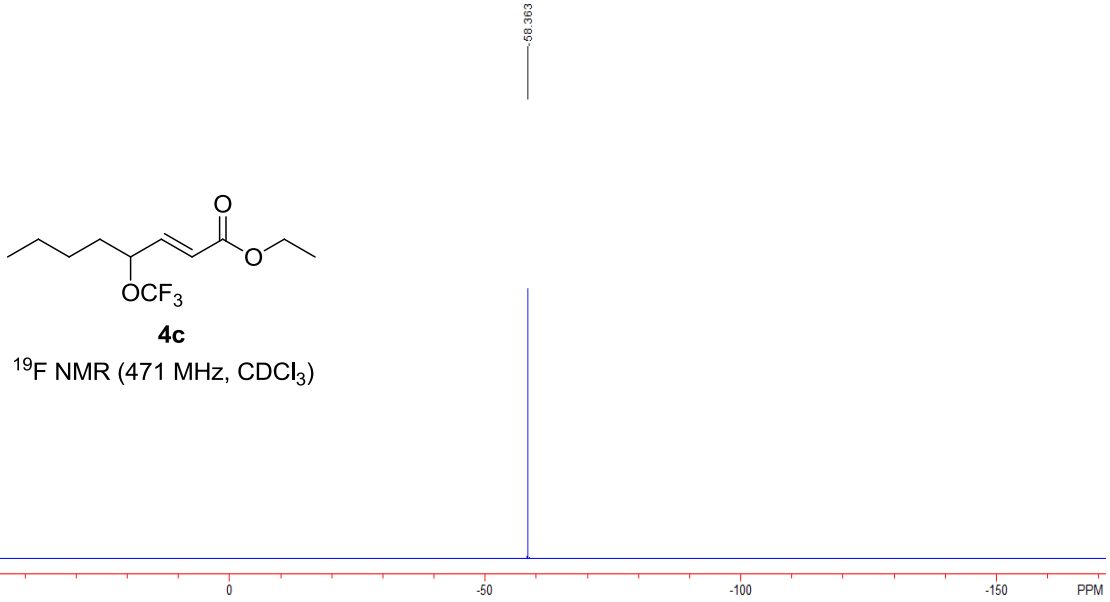
4b

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



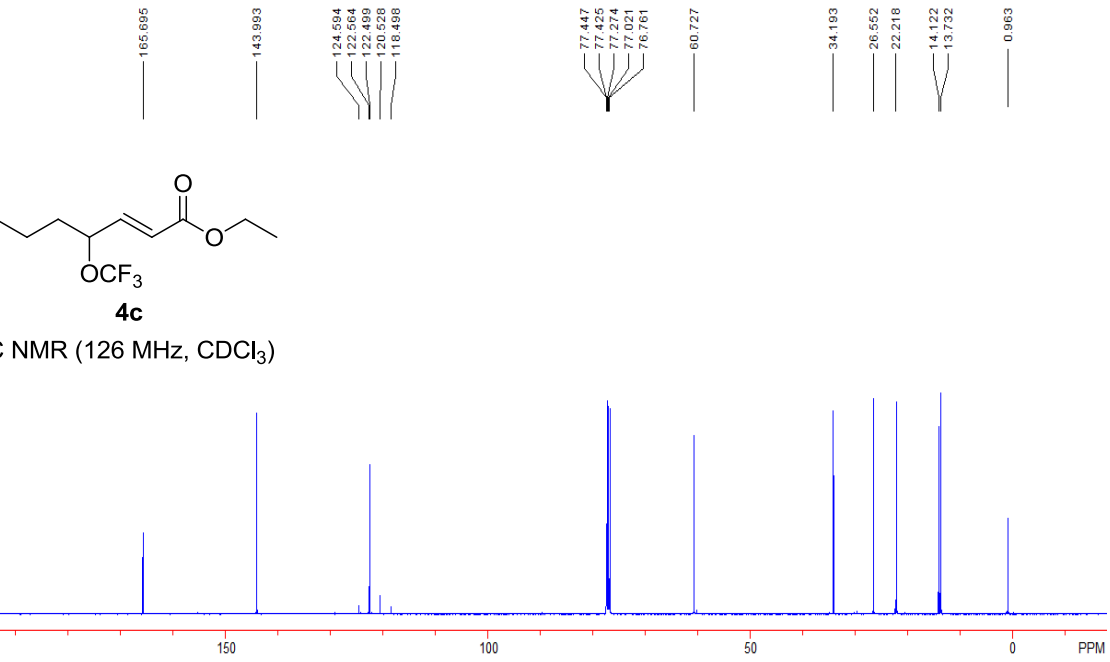
4c

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



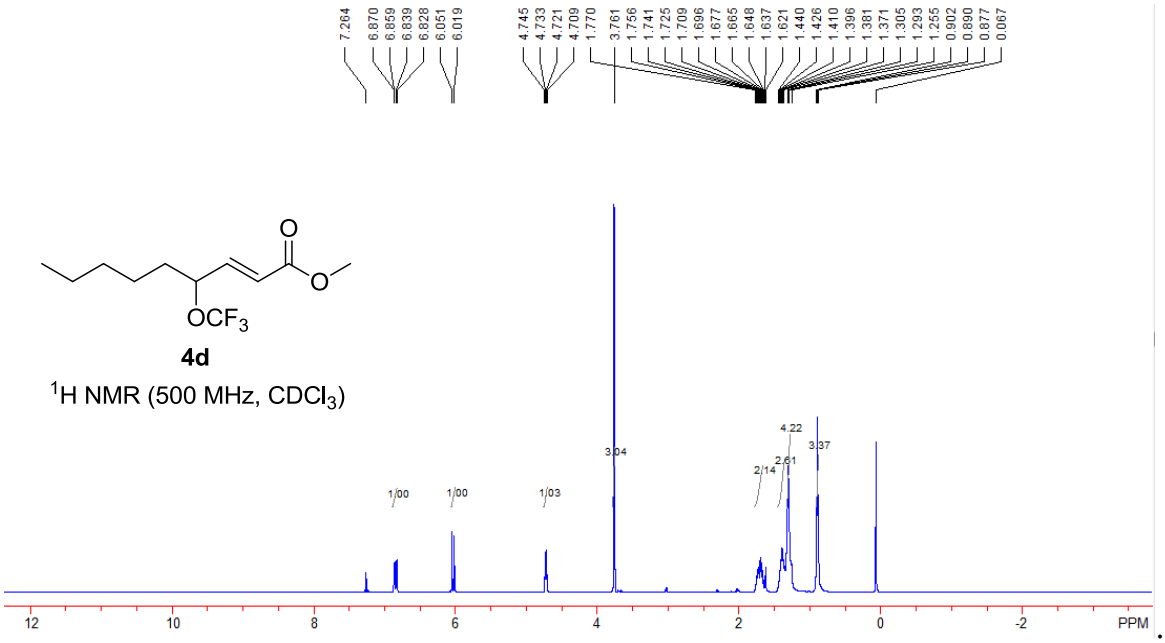
4c

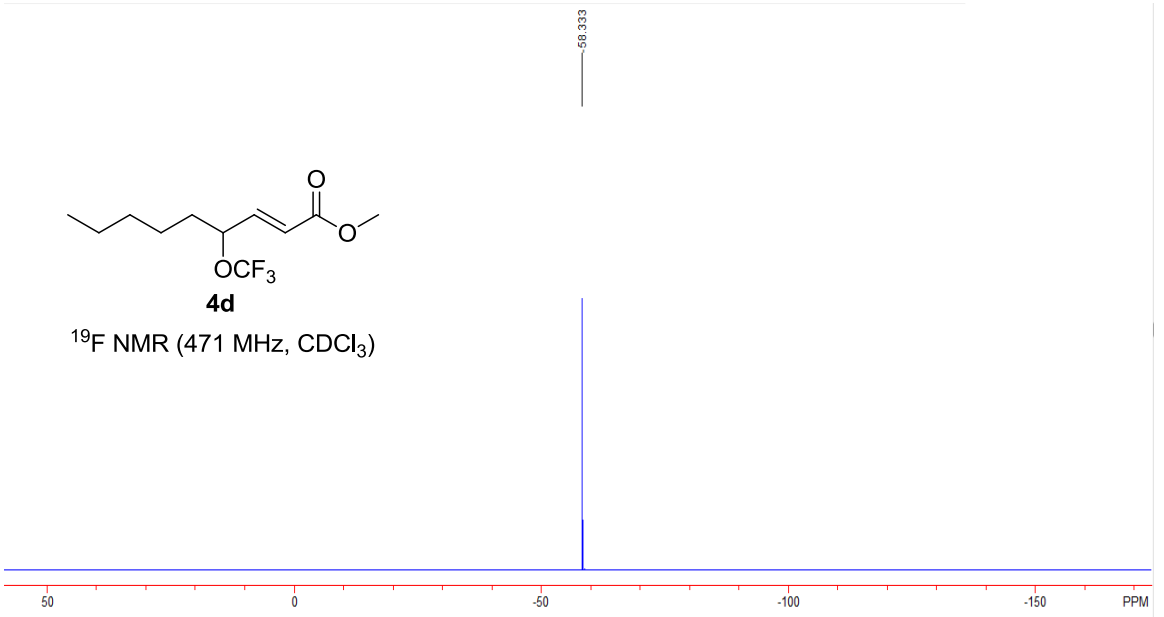
^{19}F NMR (471 MHz, $CDCl_3$)

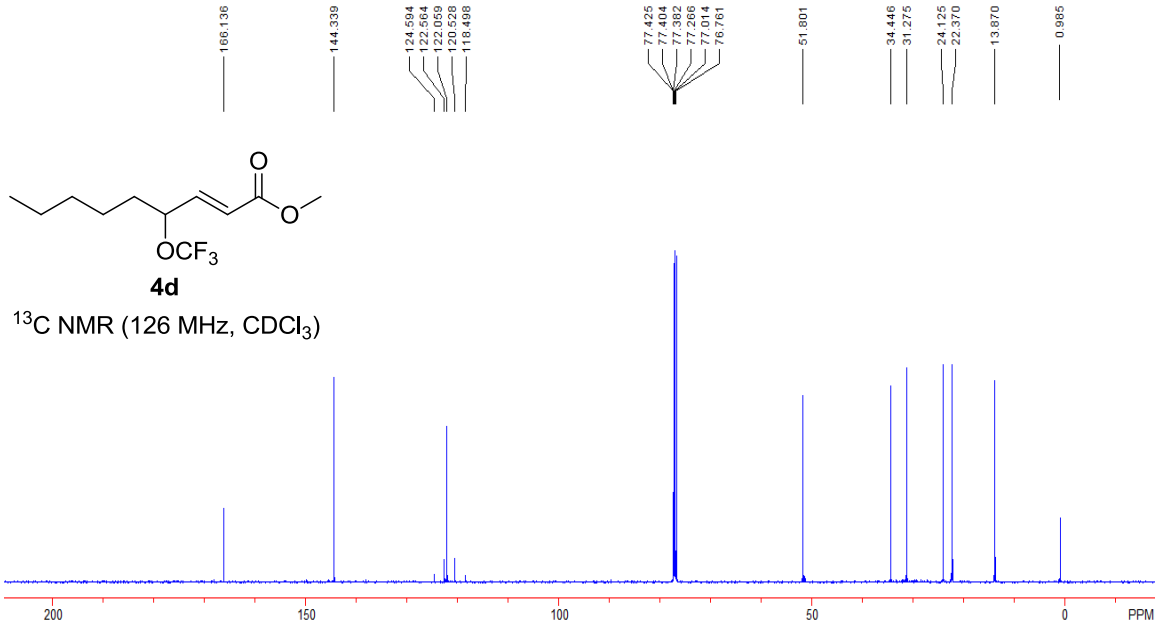


4c

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

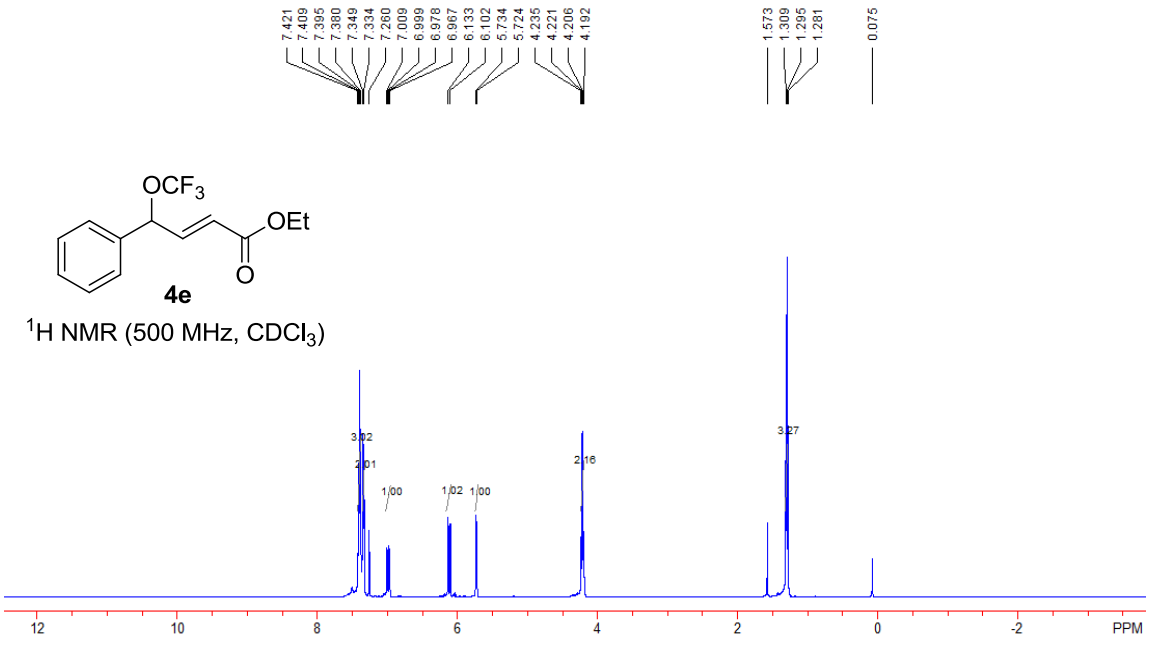

7.264
6.870
6.859
6.839
6.828
6.051
6.019
4.745
4.733
4.721
4.709
1.770
3.761
1.756
1.741
1.725
1.709
1.696
1.677
1.665
1.648
1.637
1.621
1.440
1.426
1.410
1.396
1.381
1.371
1.305
1.293
1.255
0.902
0.890
0.877
0.067
O
O
OCF3
4d
1H NMR (500 MHz, CDCl3)
1.00
1.00
1.03
3.04
2.14
2.61
4.22
3.37
12
10
8
6
4
2
0
-2
PPM


-58.333
O
O
OCF3
4d
19F NMR (471 MHz, CDCl3)
50
0
-50
-100
-150
PPM



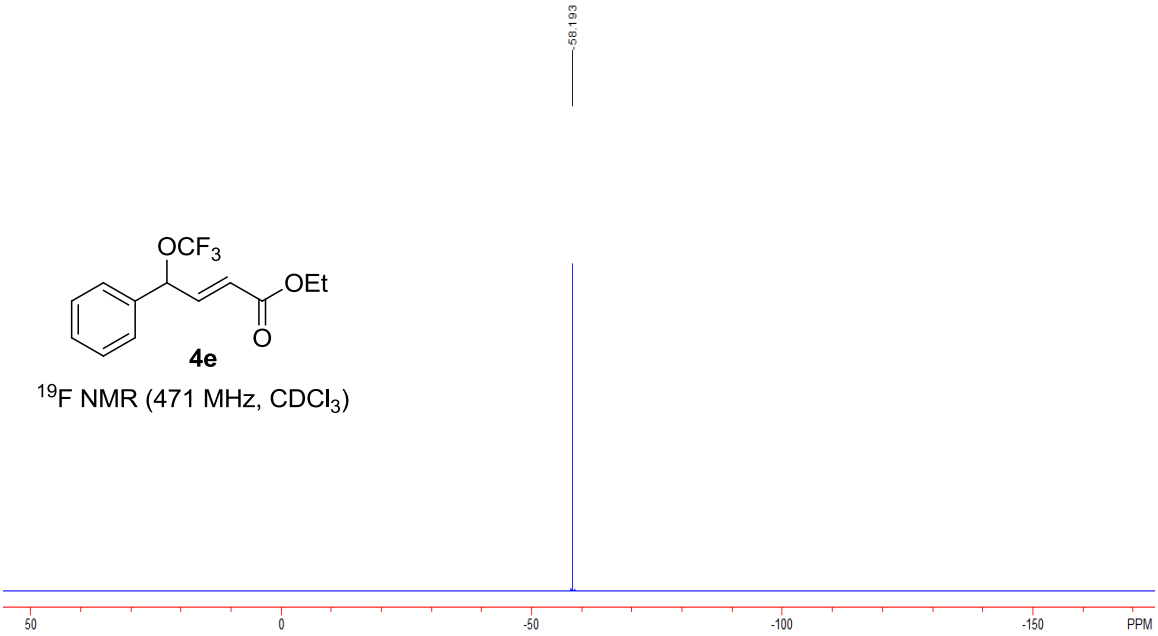
4d

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



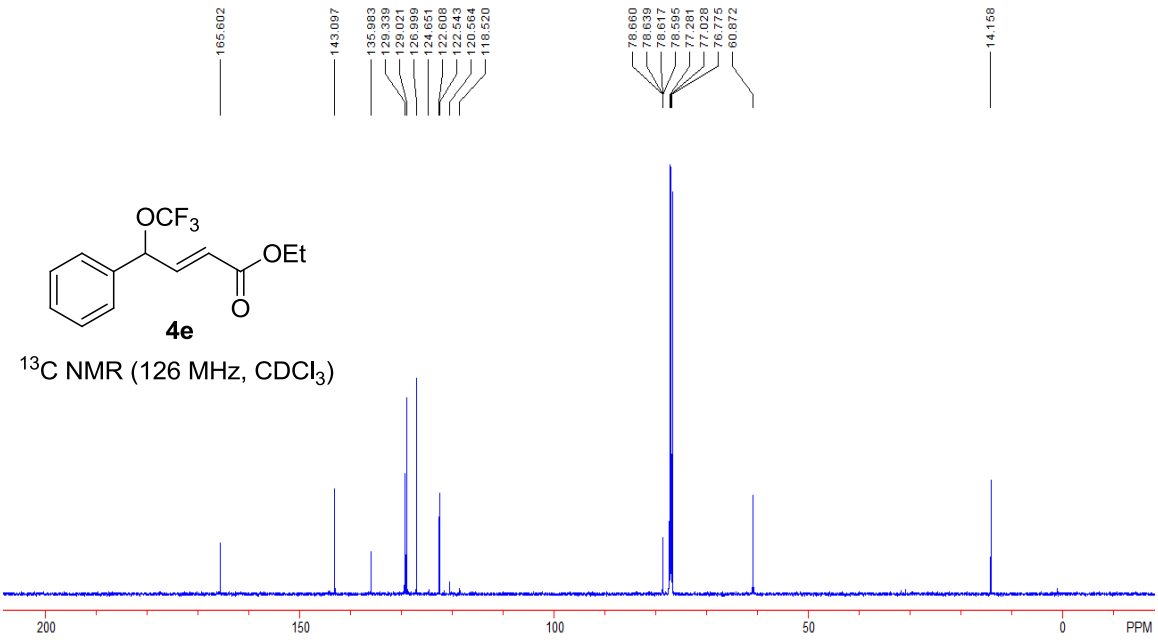
4e

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



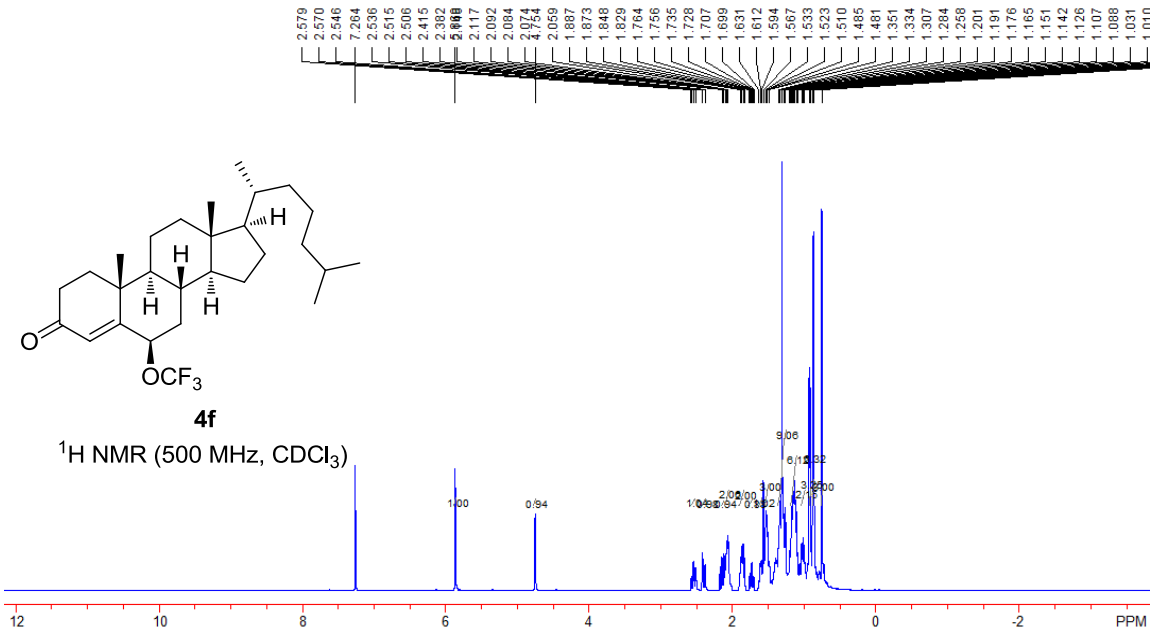
4e

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

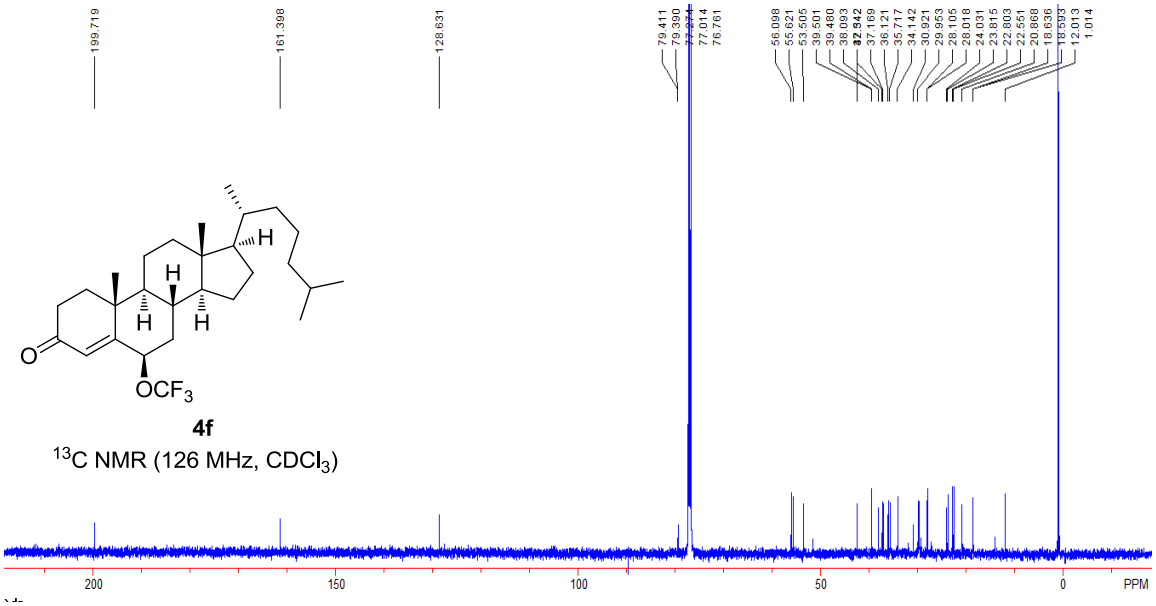


4e

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


2.579
2.570
2.546
7.264
2.536
2.515
2.506
2.415
2.382
2.117
2.092
2.084
2.074
1.754
2.059
1.887
1.873
1.848
1.829
1.764
1.756
1.735
1.728
1.707
1.699
1.631
1.612
1.594
1.567
1.533
1.523
1.510
1.485
1.481
1.351
1.334
1.307
1.284
1.258
1.201
1.191
1.176
1.165
1.151
1.142
1.126
1.107
1.088
1.031
O
H
H
H
H
OCF3
4f
1H NMR (500 MHz, CDCl3)
1.00
0.94
9.06
12
10
8
6
4
2
0
-2
PPM


-57.621
O
H
H
H
H
OCF3
4f
19F NMR (471 MHz, CDCl3)
50
0
-50
-100
-150
PPM



4f

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