N-Heterocyclic Carbene-Catalyzed Synthesis of α-Trifluoromethyl esters

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Supporting Information

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1. General information

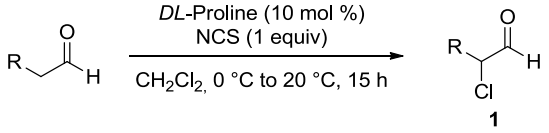
All reactions were carried out using oven-dried glassware and magnetic stirring under argon unless otherwise stated. Reaction temperatures are reported as the temperature of the bath surrounding the vessel. Analytical thin layer chromatography was performed on silica gel aluminum plates with F-254 indicator and visualized by UV light (254 nm) and/or chemical staining with a $KMnO_4$ solution or a phosphomolybdic acid solution. Flash column chromatography was performed using 0.040 – 0.063 nm silica gel. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker DXP 300 MHz spectrometer or on Bruker AV 400 MHz spectrometer. Coupling constants (*J*) are quoted in Hz. The following abbreviations were used to show the multiplicities: s: singlet, d: doublet, t: triplet, q: quadruplet, dd: doublet of doublet, m: multiplet. The residual solvent signals were used as references $CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm or relative to external $CFCl_3$, δ_F = 0 ppm). High-resolution mass spectra (HRMS) were recorded on Waters LCT Premier or on a Thermo Scientific Q-Exactive, Accela 1250 pump. IR spectra were recorded on a PerkinElmer Spectrum 100 or a Perkin-Elmer 1615 FT Infrared Spectrophotometer Model 60B. The wave numbers (ν) of recorded IR-signals (ATR) are quoted in cm^{-1}. Melting points were reported for new compounds, recorded on a Heizbank system kofler WME and were uncorrected.

2. Materials

Dichloromethane was purified by distillation over CaH_2. Methanol was purified by distillation over sodium. 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) was purchased from ACROS and used as received. The Umemoto reagent **C** was purchased from Apollo and used as received. The Togni's reagents (**A** and **B**)[1] and NHC precursors (**I**,[2a] **II**,[2b] **III**[2c] and **IV**[2d]) were prepared according to the literature procedures.

3. Synthesis of α-chloroaldehyde derivatives 1

a) General procedure for the chlorination reaction of aldehyde



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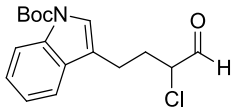
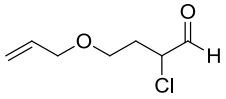
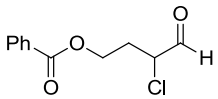
To a solution of an aldehyde derivative (12 mmol, 1.2 equiv) in dichloromethane (50 mL) at 0 °C was added under argon *DL*-Proline (1 mmol, 0.1 equiv) and *N*-chlorosuccinimide (NCS, 10 mmol, 1 equiv). The reaction mixture was slowly warmed-up to room temperature and stirred for 15 h. The reaction was monitored by ^{1}H NMR. If the starting aldehyde is not totally consumed, extra NCS was added by small portions until full conversion. To the resulting solution was added pentane (100 mL) and the precipitate was filtered off. The filtrate was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (petroleum ether/dichloromethane) to afford the desired α-chloro-aldehyde derivative **1**.



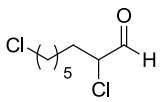
4-(1-Boc-indol-3-yl)-2-chlorobutanal 1j. General procedure from 4-(1-boc-indol-3-yl)butanal[3] (1.192 g, 4.15 mmol, 1.2 equiv) followed by flash column chromatography on silica gel (petroleum ether/dichloromethane, 50:50). **1j** was afforded as a yellow oil (1.023 g, 92%). R_f (petroleum ether/dichloromethane, 50:50): 0.42. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 9.55 (d, J = 1.8 Hz, 1H), 8.13 (d, J = 7.5 Hz, 1H), 7.54 (d, J = 7.2 Hz, 1H), 7.42 (s, 1H), 7.37-7.21 (m, 2H), 4.28-4.19 (m, 1H), 3.03-2.83 (m, 2H), 2.49-2.34 (m, 1H), 2.27-2.12 (m, 1H), 1.67 (s, 9H). **IR** (neat, cm^{-1}) ν: 2978, 1728, 1454, 1369, 1253, 1155, 1087, 908, 729. **HRMS** (ESI) calcd for $C_{17}H_{21}NO_3Cl$ *m/z* 322.1210 $[M+H]^+$. Found 322.1213. This compound was directly engaged under the standard conditions used for the trifluoromethylation reaction.



4-(Allyloxy)-2-chlorobutanal 1n. General procedure from 4-allyloxybutanal (486 mg, 3.8 mmol, 1.2 equiv) followed by flash column chromatography on silica gel (dichloromethane). **1n** was afforded as a yellow oil (452 mg, 88%). R_f (dichloromethane): 0.27. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 9.53 (d, J = 1.6 Hz, 1H), 5.97-5.79 (m, 1H), 5.33-5.14 (m, 2H), 4.46-4.38 (m, 1H), 3.96 (d, J = 5.5 Hz, 2H), 3.70-3.53 (m, 2H), 2.37-2.23 (m, 1H), 2.18-2.05 (m, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 194.4, 134.1, 116.4, 71.4, 64.6, 61.2, 32.4. **IR** (neat, cm^{-1}) ν: 3085, 2980, 2870, 1731, 1422, 1092, 995, 926, 609. **HRMS** (ESI) calcd for $C_7H_{12}ClO_2$ *m/z* 163.0526 $[M+H]^+$. Found 163.0525.

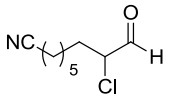


3-Chloro-4-oxobutyl benzoate 1p. General procedure from 4-(benzyloxy)butanal (700 mg, 3.64 mmol, 1.2 equiv) followed by flash column chromatography on silica gel (petroleum ether/dichloromethane). **1w** was afforded as a colorless liquid (405 mg, 59%). R_f (petroleum ether/dichloromethane, 70:30): 0.32. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.56 (d, J = 1.4 Hz, 1H), 8.00-7.98 (m, 2H), 7.57-7.53 (m, 1H), 7.44-7.41 (m, 2H), 4.57-4.41 (m, 3H), 2.56-2.47 (m, 1H), 2.29-2.21 (m, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 194.6, 166.2, 133.3, 129.7, 129.6, 128.5, 60.8, 60.6, 31.4. **IR** (neat, cm^{-1}) ν: 2942, 2292, 2257, 1733, 1703, 1455, 1371, 1204, 1102, 1030. **HRMS** (ESI) calcd for $C_{11}H_{12}ClO_3$ *m/z* 227.0469 $[M+H]^+$. Found: 227.0469.

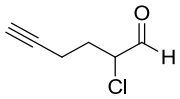


2,8-Dichlorooctanal 1s. General procedure from 8-chlorooctanal[4] (693 mg, 4.26 mmol,

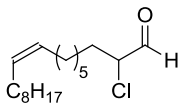
1.2 equiv) followed by flash column chromatography on silica gel (petroleum ether/dichloromethane, 50:50). **1s** was afforded as a yellow oil (451 mg, 64%). R_f (petroleum ether/dichloromethane, 50:50): 0.32. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 9.50 (d, J = 1.6 Hz, 1H), 4.20-4.12 (m, 1H), 3.53 (t, J = 5.5 Hz, 2H), 2.06-1.92 (m, 1H), 1.90-1.71 (m, 3H), 1.56-1.26 (m, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 194.7, 63.7, 44.7, 32.1, 31.5, 27.9, 26.3, 25.1. **IR** (neat, cm^{-1}) ν: 2936, 2860, 1732, 1463, 1282, 1057, 729, 650, 607. **HRMS** (EI) calcd for $C_8H_{14}ClO$ *m/z* 161.0733 $[M\text{-}Cl]^+$. Found 161.0734.



8-Chloro-9-oxononanenitrile 1u. General procedure from 9-oxononanenitrile[5] (734 mg, 4.8 mmol, 1.2 equiv) followed by flash column chromatography on silica gel (dichloromethane). **1u** was afforded as a yellow oil (631 mg, 84%). R_f (dichloromethane): 0.36. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 9.50 (d, J = 1.6 Hz, 1H), 4.20-4.12 (m, 1H), 2.35 (t, J = 1.6 Hz, 2H), 2.06-1.92 (m, 1H), 1.90-1.75 (m, 1H), 1.73-1.30 (m, 8H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 194.5, 119.4, 63.5, 31.0, 27.7, 27.5, 24.7, 24.6, 16.4. **IR** (neat, cm^{-1}) ν: 3441, 2936, 2861, 2246, 1731, 1463, 1059, 730, 605. **HRMS** (EI) calcd for $C_9H_{14}NO$ *m/z* 152.1075 $[M\text{-}Cl]^+$. Found 152.1074.

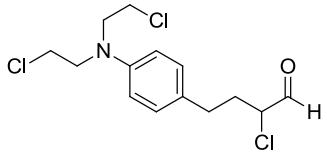


2-Chlorohex-5-ynal 1v. General procedure from hex-5-ynal[6] (327 mg, 3.4 mmol, 1.2 equiv) followed by flash column chromatography on silica gel (petroleum ether/dichloromethane, 30:70). **1v** was afforded as a yellow oil (155 mg, 42%). R_f (petroleum ether/dichloromethane, 30:70): 0.27. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 9.59 (d, J = 1.5 Hz, 1H), 4.47-4.40 (m, 1H), 2.50-2.43 (m, 2H), 2.33-2.19 (m, 1H), 2.05-1.91 (m, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 194.8, 81.8, 70.5, 62.6, 30.7, 15.1. **IR** (neat, cm^{-1}) ν: 3299, 2925, 1731, 1433, 1073, 999, 912, 733, 637. **HRMS** (EI) calcd for C_6H_7O *m/z* 95.0497 $[M\text{-}Cl]^+$. Found 95.0500.



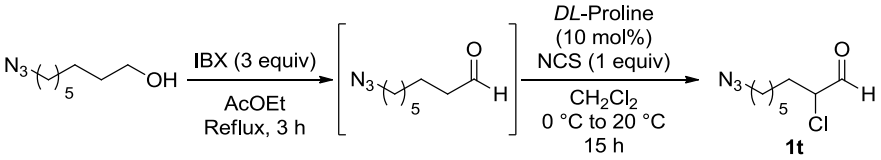
(*Z*)-2-Chlorooctadec-9-enal 1w. General procedure from (*Z*)-octadec-9-enal (1.14 g, 4.28 mmol, 1.2 equiv) followed by flash column chromatography on silica gel (petroleum ether/dichloromethane, 70:30). **1w** was afforded as a colorless liquid (818 mg, 76%). R_f (petroleum ether/dichloromethane, 70:30): 0.31. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 9.49 (s, 1H), 5.43-5.25 (m, 2H), 4.19-4.11 (m, 1H), 2.08-1.90 (m, 5H), 1.90-1.73 (m, 1H), 1.54-1.19 (m, 20H), 0.93-0.83 (m, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 195.36, 130.23, 129.62, 64.04, 32.14, 32.03, 29.87, 29.66, 29.64, 29.45, 29.44, 29.02, 28.95, 27.33, 27.18, 25.62, 22.80, 14.22. **IR** (neat, cm^{-1}) ν: 2923, 2854,

1735, 1464, 1378, 1059, 723. **HRMS** (EI) calcd for $C_{18}H_{33}O$ *m/z* 265.2531 $[M\text{-}Cl]^+$. Found 265.2535.



4-(4-(Bis(2-chloroethyl)amino)phenyl)-2-chlorobutanal 1y. General procedure from 4-(4-(bis(2-chloroethyl)amino)phenyl)butanal (432 mg, 1.5 mmol, 1.2 equiv) followed by flash column chromatography on silica gel (petroleum ether/dichloromethane). **1y** was afforded as a brownish liquid (212 mg, 53%). R_f (petroleum ether/dichloromethane, 70:30): 0.23. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.50 (d, *J* = 2.0 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 8.7 Hz, 2H), 4.14-4.10 (m, 1H), 3.73-3.69 (m, 4H), 3.65-3.60 (m, 4H), 2.83-2.66 (m, 2H), 2.30-2.21 (m, 1H), 2.12-2.03 (m, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.5, 143.8, 130.1, 130.0, 113.6, 63.2, 54.2, 40.1, 33.8, 30.5. **IR** (neat, cm^{-1}) *ν*: 3164, 3003, 2943, 2627, 2293, 2259, 2246, 1733, 1616, 1520, 1470, 1393, 1369, 1182, 1035. **HRMS** (ESI) calcd for $C_{14}H_{19}Cl_3ON$ *m/z* 322.0527 $[M+H]^+$. Found: 322.0524.

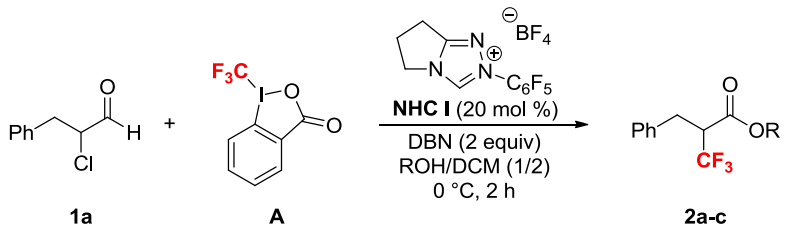
b) Synthesis of **1t** from the corresponding alcohol



8-Azido-2-chlorooctanal 1t. To a solution of 8-azidooctan-1-ol[7] (856 mg, 5 mmol, 1 equiv) in ethyl acetate (50 mL) was added under argon 2-iodoxybenzoic acid (IBX, 4.2 g, 15 mmol, 3 equiv). The reaction mixture was refluxed for 3 h and then cooled down to room temperature. The resulting solution was filtered, concentrated under vaccum and the residue was used in the next step without further purification.

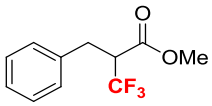
To solution of the crude mixture (684 mg, 4.05 mmol, 1 equiv) in dichloromethane (15 mL) was added at 0 °C under argon *DL*-proline (46 mg, 0.4 mmol, 10 mol %) and NCS (540 mg, 4.05 mmol, 1 equiv). The reaction mixture was slowly warmed to room temperature and stirred for 15 h. To the resulting solution was added pentane (30 mL) and the precipitate was filtered off. The filtrate was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (petroleum ether/dichloromethane, 1:1) to afford the desired α-chloroaldehyde derivative **1t** (606 mg, 59% over two steps). Note that the product was contaminated with 5% of the inseparable α,α-dichlorinated aldehyde. R_f (petroleum ether/dichloromethane, 50:50): 0.31. **^{1}H NMR** (300.1 MHz, $CDCl_3$) *δ* 9.49 (s, 1H), 4.21-4.11 (m, 1H), 3.31-3.21 (m, 2H), 2.07-1.91 (m, 1H), 1.90-1.73 (m, 1H), 1.66-1.34 (m, 8H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) *δ* 194.6, 63.6, 50.9, 31.4, 28.3, 28.1, 26.0, 25.0. **IR** (neat, cm^{-1}) *ν*: 2929, 2858, 2092, 1732, 1462, 1259, 729. **HRMS** (ESI) calcd for $C_8H_{15}ClN_3O$ *m/z* 204.0904 $[M+H]^+$. Found 204.0908.

4. General procedure for the synthesis of products 2a-d

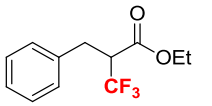


In an oven-dried tube equipped with a magnetic stirrer was added under argon the α-chloroaldehyde **1a**[8] (0.5 mmol, 1 equiv), the Togni's reagent **A** (0.75 mmol, 1.5 equiv), the **NHC I** (0.1 mmol, 20 mol %) and dichloromethane (1.65 mL). Once cooled to 0 °C, the alcohol (0.85 mL) was added to the reaction mixture. After stirring 5 min at 0 °C, DBN (1 mmol, 2 equiv) was added and the mixture was stirred at 0 °C for 2 h. Then, the crude mixture was diluted in dichloromethane (20 mL), washed with brine (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure (20 °C, 100 mbar). The residue was then purified by flash column chromatography on silica gel (petroleum ether/diethyl ether) to afford the desired trifluoromethylated ester derivative **2**.
CAUTION: α-trifluoromethylated ester derivatives might be volatile and were concentrated at 20 °C under 100 mbar.

5. Synthesis and characterization of products 2a-d

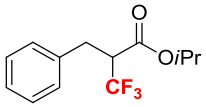


Methyl 2-benzyl-3,3,3-trifluoropropanoate 2a. General procedure from **1a** (84 mg, 0.5 mmol, 1 equiv) and MeOH (0.85 mL) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether, 98:2). **2a** was afforded as a pale yellow oil (77 mg, 66%). R_f (petroleum ether/diethyl ether, 98:2): 0.25. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.35-7.15 (m, 5H), 3.65 (s, 3H), 3.49-3.34 (m, 1H), 3.25-3.06 (m, 2H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 68.9 (d, J = 8.1 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 167.5 (q, J = 3.1 Hz), 136.3, 128.9, 128.9, 127.3, 124.5 (q, J = 280.5 Hz), 52.7, 52.5 (q, J = 27.2 Hz), 32.3 (q, J = 2.5 Hz). **IR** (neat, cm^{-1}) ν: 2961, 1750, 1439, 1266, 1152, 1113, 1020, 799, 700. **HRMS** (EI) calcd for $C_{11}H_{11}F_3O_2$ *m/z* 232.0711 $[M]^+$. Found 232.0705.

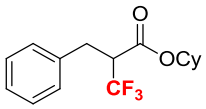


Ethyl 2-benzyl-3,3,3-trifluoropropanoate 2b. General procedure from **1a** (84 mg, 0.5 mmol, 1 equiv) and ethanol (0.85 mL) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether, 99:1). **2b** was afforded as a pale yellow oil (75 mg, 61%). R_f (petroleum ether/diethyl ether, 99:1): 0.18. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.35-7.15 (m, 5H), 4.10 (q, J = 7.1 Hz, 2H), 3.48-3.32 (m, 1H), 3.24-3.06 (m, 2H), 1.12 (t, J = 7.1 Hz, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 69.0 (d, J = 8.1 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 167.0 (q, J = 3.2 Hz), 136.3, 128.9, 128.8, 127.3, 124.6 (q,

J = 280.5 Hz), 61.8, 52.5 (q, *J* = 27.1 Hz), 32.3 (q, *J* = 2.6 Hz), 13.9. **IR** (neat, cm^{-1}) *ν*: 2986, 1744, 1375, 1268, 1151, 1110, 1017, 747, 699, 566. **HRMS** (EI) calcd for $C_{12}H_{13}F_3O_2$ *m/z* 246.0868 $[M]^+$. Found 246.0860.

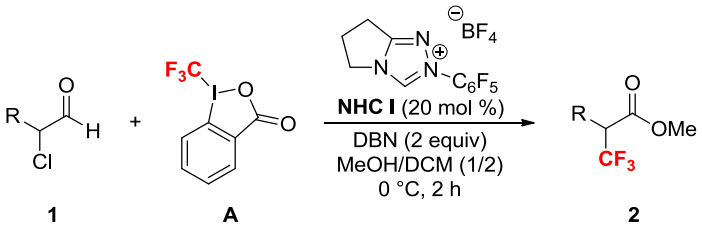


***iso*-Propyl 2-benzyl-3,3,3-trifluoropropanoate 2c.** General procedure from **1a** (84 mg, 0.5 mmol, 1 equiv) and *iso*-propanol (0.85 mL) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether, 99:1). **2c** was afforded as a pale yellow oil (53 mg, 41%). R_f (petroleum ether/diethyl ether, 99:1): 0.24. **^{1}H NMR** (300.1 MHz, $CDCl_3$) *δ* 7.34-7.14 (m, 5H), 4.98 (sept, *J* = 7.3 Hz, 1H), 3.44-3.29 (m, 1H), 3.23-3.05 (m, 2H), 1.17 (d, *J* = 7.3 Hz, 3H), 1.00 (d, *J* = 7.3 Hz, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) *δ* - 69.0 (d, *J* = 8.2 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) *δ* 166.5 (q, *J* = 3.1 Hz), 136.3, 129.0, 128.8, 127.3, 124.7 (q, *J* = 280.5 Hz), 69.7, 52.6 (q, *J* = 26.9 Hz), 32.3 (q, *J* = 2.5 Hz), 21.6, 21.5. **IR** (neat, cm^{-1}) *ν*: 2985, 1741, 1376, 1270, 1150, 1101, 995, 747, 699, 566. **HRMS** (EI) calcd for $C_{13}H_{15}F_3O_2$ *m/z* 260.1024 $[M]^+$. Found 260.1026.



Cyclohexyl 2-benzyl-3,3,3-trifluoropropanoate 2d. General procedure from **1a** (84 mg, 0.5 mmol, 1 equiv) and cyclohexanol (0.85 mL) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether, 99:1). **2d** was afforded as a pale yellow oil (44 mg, 29%). R_f (petroleum ether/diethyl ether, 98:2): 0.25. **^{1}H NMR** (300.1 MHz, $CDCl_3$) *δ* 7.35-7.16 (m, 5H), 4.80-4.69 (m, 1H), 3.47-3.31 (m, 1H), 3.24-3.05 (m, 2H), 1.82-1.07 (m, 10H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) *δ* - 69.0 (d, *J* = 8.1 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) *δ* 166.4 (q, *J* = 3.2 Hz), 136.4, 129.0, 128.8, 127.2, 124.7 (q, *J* = 280.6 Hz), 74.3, 52.7 (q, *J* = 27.0 Hz), 32.3 (q, *J* = 2.5 Hz), 31.3, 31.1, 25.3, 23.5, 23.4. **IR** (neat, cm^{-1}) *ν*: 2938, 1732, 1454, 1275, 1150, 1109, 1011, 893, 745, 698. **HRMS** (EI) calcd for $C_{16}H_{19}F_3O_2$ *m/z* 300.1337 $[M]^+$. Found 300.1343.

6. General procedure for the synthesis of products 2e-u

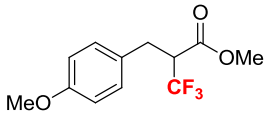


In an oven-dried tube equipped with a magnetic stirrer was added under argon the desired α-chloroaldehyde derivative **1** (0.5 mmol, 1 equiv), the Togni's reagent **A** (0.75 mmol, 1.5 equiv), the **NHC I** (0.1 mmol, 20 mol %) and dichloromethane (1.65 mL). Once cooled to 0 °C, methanol (0.85 mL) was added to the reaction mixture. After

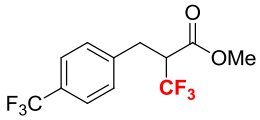
stirring 5 min at 0 °C, DBN (1 mmol, 2 equiv) was added and the mixture was stirred at 0 °C for 2 h. Then, the crude mixture was diluted in dichloromethane (20 mL), washed with brine (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure (20 °C, 100 mbar). The residue was then purified by flash column chromatography on silica gel (petroleum ether/diethyl ether) to afford the desired trifluoromethylated ester derivative **2**.

CAUTION: α-trifluoromethylated ester derivatives might be volatile and were concentrated at 20 °C under 100 mbar.

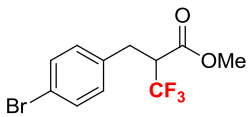
7. Synthesis and characterization of products 2e-u



Methyl 2-(4-methoxybenzyl)-3,3,3-trifluoropropanoate 2e. General procedure from **1e**[9] (99 mg, 0.5 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether, 97:3). **2e** was afforded as a pale yellow oil (98 mg, 75%). R_f (petroleum ether/ diethyl ether, 97:3): 0.21. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.10 (d, J = 8.2 Hz, 2H), 6.84 (d, J = 8.2 Hz, 2H), 3.79 (s, 3H), 3.65 (s, 3H), 3.44-3.27 (m, 1H), 3.20-2.99 (m, 2H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 68.9 (d, J = 8.1 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 167.5 (q, J = 3.2 Hz), 158.8, 129.9, 128.2, 124.5 (q, J = 280.6 Hz), 114.2, 55.2, 52.7 (q, J = 27.0 Hz), 52.6, 31.4 (q, J = 2.5 Hz). **IR** (neat, cm^{-1}) ν: 2959, 2843, 1747, 1614, 1515, 1440, 1366, 1248, 1106, 1034, 825. **HRMS** (EI) calcd for $C_{12}H_{13}F_3O_3$ *m/z* 262.0817 $[M]^+$. Found 262.0825.

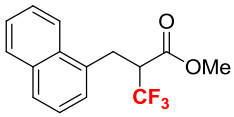


Methyl 2-[4-(trifluoromethyl)-benzyl]-3,3,3-trifluoropropanoate 2f. General procedure from **1f**[10] (118 mg, 0.5 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether, 97:3). **2f** was afforded as a pale yellow oil (79 mg, 53%). R_f (petroleum ether/ diethyl ether, 97:3): 0.23. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.58 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 3.67 (s, 3H), 3.50-3.35 (m, 1H), 3.32-3.11 (m, 2H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 63.1 (s), -68.8 (d, J = 7.9 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 167.1 (q, J = 3.0 Hz), 140.5, 129.8 (q, J = 32.6 Hz), 129.3, 125.9 (q, J = 3.8 Hz), 124.4 (q, J = 280.6 Hz), 124.2 (q, J = 271.8 Hz), 52.9, 52.1 (q, J = 27.6 Hz), 32.0 (q, J = 2.4 Hz). **IR** (neat, cm^{-1}) ν: 2966, 1750, 1615, 1440, 1323, 1221, 1157, 1106, 1067, 1020, 832, 599. **HRMS** (EI) calcd for $C_{12}H_{10}F_6O_2$ *m/z* 300.0585 $[M]^+$. Found 300.0584.

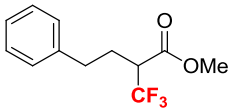


Methyl 2-(4-bromobenzyl)-3,3,3-trifluoropropanoate 2g. General procedure from **1g**[11] (124 mg, 0.5 mmol, 1 equiv) followed by flash column chromatography on silica

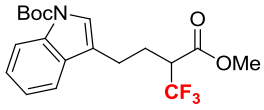
gel (petroleum ether/diethyl ether, 98.5:1.5). **2g** was afforded as a pale yellow oil (100 mg, 64%). R_f (petroleum ether/diethyl ether, 98.5:1.5): 0.26. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.43 (d, J = 8.1 Hz, 2H), 7.06 (d, J = 8.1 Hz, 2H), 3.66 (s, 3H), 3.45-3.28 (m, 1H), 3.21-3.00 (m, 2H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 68.9 (d, J = 8.0 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 167.2 (q, J = 3.1 Hz), 135.3, 132.0, 130.6, 124.3 (q, J = 280.7 Hz), 121.3, 52.8, 52.2 (q, J = 27.4 Hz), 31.6 (q, J = 2.6 Hz). **IR** (neat, cm^{-1}) ν: 2959, 1749, 1491, 1370, 1266, 1217, 1154, 1114, 1012, 802, 733, 518. **HRMS** (EI) calcd for $C_{11}H_{10}BrF_3O_2$ *m/z* 309.9816 $[M]^+$. Found 309.9808.



Methyl 3,3,3-trifluoro-2-(naphthalen-1-ylmethyl)propanoate 2h. General procedure from **1h**[11] (109 mg, 0.5 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether, 99:1). **2h** was afforded as a pale yellow solid (94 mg, 67%). R_f (petroleum ether/diethyl ether, 99:1): 0.14. **M.p.** 49-50 °C. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 7.7 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.62-7.48 (m, 2H), 7.43-7.30 (m, 2H), 3.72-3.54 (m, 6H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 68.9 (d, J = 7.7 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 167.6 (q, J = 3.1 Hz), 134.1, 132.1, 131.4, 129.3, 128.3, 127.5, 126.8, 126.0, 125.5, 124.7 (q, J = 280.6 Hz), 122.8, 52.7, 51.4 (q, J = 27.1 Hz), 29.5 (q, J = 2.5 Hz). **IR** (neat, cm^{-1}) ν: 2920, 1748, 1447, 1367, 1303, 1211, 1151, 1111, 798, 777, 576. **HRMS** (EI) calcd for $C_{15}H_{13}F_3O_2$ *m/z* 282.0868 $[M]^+$. Found 282.0868.

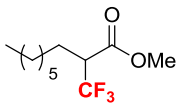


Methyl 2-(trifluoromethyl)-4-phenylbutanoate 2i. General procedure from **1i**[12] (91 mg, 0.5 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether, 98.5:0.5). **2i** was afforded as a pale yellow oil (82 mg, 67%). R_f (petroleum ether/diethyl ether, 97:3): 0.37. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.37-7.16 (m, 5H), 3.80 (s, 3H), 3.23-3.04 (m, 1H), 2.82-2.56 (m, 2H), 2.37-2.20 (m, 1H), 2.19-2.03 (m, 1H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 68.7 (d, J = 8.3 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 168.0 (q, J = 3.2 Hz), 139.9, 128.7, 128.6, 126.6, 124.8 (q, J = 280.0 Hz), 52.8, 49.6 (q, J = 27.6 Hz), 32.9, 27.8 (q, J = 2.0 Hz). **IR** (neat, cm^{-1}) ν: 2959, 1748, 1455, 1343, 1269, 1149, 1112, 1031, 910, 733, 699. **HRMS** (EI) calcd for $C_{12}H_{13}F_3O_2$ *m/z* 246.0868 $[M]^+$. Found 246.0860.

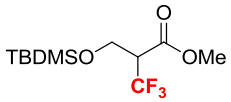


Methyl 4-(1-boc-indol-3-yl)-2-trifluoromethylbutanoate 2j. General procedure from **1j** (161 mg, 0.5 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether, 97:3). **2j** was afforded as yellow oil (98 mg, 51%). R_f

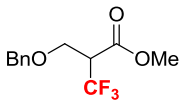
(petroleum ether/diethyl ether, 97:3): 0.21. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 8.13 (d, J = 8.3 Hz, 1H), 7.50 (d, J = 8.3 Hz, 1H), 7.39 (s, 1H), 7.36-7.21 (m, 2H), 3.79 (s, 3H), 3.30-3.14 (m, 1H), 2.89-2.65 (m, 2H), 2.42-2.12 (m, 2H), 1.67 (s, 9H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 68.5 (d, J = 8.3 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 167.9 (q, J = 3.1 Hz), 149.0, 135.7, 130.2, 124.8 (q, J = 280.0 Hz), 124.6, 123.0, 122.6, 118.8, 118.7, 115.5, 83.7, 52.8, 49.7 (q, J = 27.7 Hz), 28.3, 25.9 (q, J = 1.9 Hz), 22.3. **IR** (neat, cm^{-1}) ν: 2983, 1732, 1454, 1371, 1255, 1154, 1114, 909, 730. **HRMS** (ESI) calcd for $C_{19}H_{23}F_3NO_4$ *m/z* 386.1579 $[M+H]^+$. Found 386.1578.



Methyl 2-(trifluoromethyl)nonanoate 2k. General procedure from **1k**[13] (88 mg, 0.5 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether, 99.5:0.5). **2k** was afforded as a pale yellow oil (85 mg, 71%). R_f (petroleum ether/diethyl ether, 99:1): 0.54. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 3.76 (s, 3H), 3.18-3.00 (m, 1H), 1.98-1.66 (m, 2H), 1.38-1.16 (m, 10H), 0.92-0.81 (m, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 68.9 (d, J = 8.3 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 168.3 (q, J = 3.3 Hz), 124.9 (q, J = 279.8 Hz), 52.6, 50.4 (q, J = 27.5 Hz), 31.8, 29.2, 29.0, 26.9, 26.3 (q, J = 2.0 Hz), 22.7, 14.1. **IR** (neat, cm^{-1}) ν: 2929, 1751, 1438, 1270, 1161, 1106, 1041, 669. **HRMS** (EI) calcd for $C_{11}H_{19}F_3O_2$ *m/z* 240.1337 $[M]^+$. Found 240.1330.

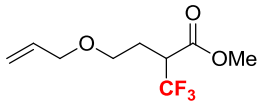


Methyl 2-[((*tert*-butyldimethylsilyl)oxy)methyl]-3,3,3-trifluoropropanoate 2l. General procedure from **1l**[14] (111 mg, 0.5 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether, 99:1). **2l** was afforded as a pale yellow oil (76 mg, 53%). R_f (petroleum ether/diethyl ether, 99:1): 0.29. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 4.12-3.96 (m, 2H), 3.88 (s, 3H), 3.44-3.29 (m, 1H), 0.86 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 66.9 (d, J = 8.5 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 166.8 (q, J = 3.1 Hz), 123.9 (q, J = 280.1 Hz), 59.4 (q, J = 3.1 Hz), 53.2 (q, J = 26.4 Hz), 52.7, 25.7, 18.2, -5.6, -5.7. **IR** (neat, cm^{-1}) ν: 2933, 2860, 1756, 1359, 1252, 1175, 1113, 904, 835, 778, 672. **HRMS** (ESI) calcd for $C_{11}H_{22}F_3O_3Si$ *m/z* 287.1290 $[M+H]^+$. Found 287.1288.

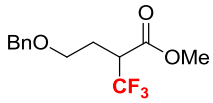


Methyl 2-[(benzyloxy)-methyl]-3,3,3-trifluoropropanoate 2m. General procedure from **1m**[12] (99 mg, 0.5 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether, 98:2). **2m** was afforded as a pale yellow oil (55 mg, 42%). R_f (petroleum ether/diethyl ether, 98:2): 0.17. **^{1}H NMR** (300.1 MHz, $CDCl_3$)

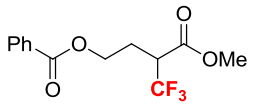
δ 7.41-7.27 (m, 5H), 4.56 (s, 2H), 3.99-3.79 (m, 5H), 3.57-3.42 (m, 1H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 67.0 (d, J = 8.5 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 166.5 (q, J = 3.1 Hz), 137.3, 128.6, 128.1, 127.8, 123.8 (q, J = 280.1 Hz), 73.6, 65.4 (q, J = 2.9 Hz), 53.0, 51.0 (q, J = 31.6 Hz). **IR** (neat, cm^{-1}) ν: 2959, 1752, 1439, 1245, 1173, 1116, 737, 698, 469. **HRMS** (EI) calcd for $C_{12}H_{13}F_3O_3$ *m/z* 262.0817 $[M]^+$. Found 262.0817.



Methyl 4-(allyloxy)-2-(trifluoromethyl)butanoate 2n. General procedure from **1n** (81 mg, 0.5 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether, 96:4). **2n** was afforded as a pale yellow oil (26 mg, 23%). R_f (petroleum ether/diethyl ether, 97:3): 0.19. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 5.94-5.78 (m, 1H), 5.31-5.14 (m, 2H), 3.96-3.91 (m, 2H), 3.77 (s, 3H), 3.57-3.29 (m, 3H) 2.27-2.00 (m, 2H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 68.9 (d, J = 8.6 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 168.1 (q, J = 3.2 Hz), 134.5, 125.0 (q, J = 279.8 Hz), 117.3, 72.0, 66.6, 52.8, 47.6 (q, J = 27.9 Hz), 26.6 (q, J = 2.1 Hz). **IR** (neat, cm^{-1}) ν: 2923, 1750, 1440, 1270, 1167, 1115, 927, 661. **HRMS** (ESI) calcd for $C_9H_{14}F_3O_3$ *m/z* 227.0895 $[M+H]^+$. Found 227.0894.

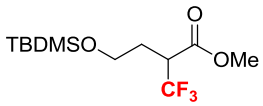


Methyl 4-(benzyloxy)-2-(trifluoromethyl)butanoate 2o. General procedure from **1o**[9] (106 mg, 0.5 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/ethyl acetate). **2o** was afforded as a pale yellow oil (87 mg, 63%). R_f (petroleum ether/ethyl acetate, 90:10): 0.37. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.38-7.28 (m, 5H), 4.52-4.45 (m, 2H), 3.70 (s, 3H), 3.60-3.55 (m, 1H), 3.52-3.36 (m, 2H), 2.28-2.19 (m, 1H), 2.14-2.06 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ - 68.4 (d, J = 8.7 Hz). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 168.0 (q, J = 3.2 Hz), 138.0, 128.5, 127.9, 127.8, 124.9 (q, J = 279.9 Hz), 73.2, 66.6, 52.7, 47.6 (q, J = 27.9 Hz), 26.6. **IR** (neat, cm^{-1}) ν: 3164, 3003, 2944, 2293, 2258, 1749, 1386, 1366, 1325, 1277, 1229, 1170, 1121, 1033. **HRMS** (EI) calcd for $C_{13}H_{15}O_3F_3Na$ *m/z* 299.0866 $[M+Na]^+$. Found 299.0865.

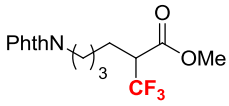


4,4,4-Trifluoro-3-(methoxycarbonyl)butyl benzoate 2p. General procedure from **1p** (113 mg, 0.5 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/ethyl acetate). **2p** was afforded as a pale yellow oil (92 mg, 63%). R_f (petroleum ether/ethyl acetate, 90:10): 0.30. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.02-8.00 (m, 2H), 7.59-7.56 (m, 1H), 7.47-7.43 (m, 2H), 4.46-4.33 (m, 2H), 3.72 (s, 3H), 3.41-3.31 (m, 1H), 2.48-2.39 (m, 1H), 2.32-2.24 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ - 68.4 (d, J = 8.5 Hz). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 167.5 (q, J = 3.1 Hz),

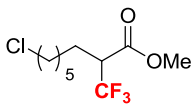
166.3, 133.4, 129.7, 128.8, 128.6, 124.6 (q, J = 279.9 Hz), 61.8, 53.0, 47.7 (q, J = 27.9 Hz), 25.7. **IR** (neat, cm^{-1}) ν: 2944, 2293, 2248, 1750, 1723, 1371, 1271, 1175, 1120, 1030. **HRMS** (EI) calcd for $C_{13}H_{13}O_4F_3Na$ *m/z* 313.0658 $[M+Na]^+$. Found 313.0657.



Methyl 4-[((*tert*-butyldimethylsilyl)oxy)-2ethyl]butanoate 2q. General procedure from **1q**[8] (118 mg, 0.5 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/ethyl acetate). **2q** was afforded as a pale yellow oil (88 mg, 59%). R_f (petroleum ether/ethyl acetate, 90:10): 0.46; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.76 (s, 3H), 3.74-3.68 (m, 1H), 3.63-3.56 (m, 1H), 3.43-3.33 (m, 1H), 2.15-2.07 (m, 1H), 2.02-1.94 (m, 1H), 0.88 (s, 9H), 0.03 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -68.3 (d, J = 8.7 Hz). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 168.1 (q, $J_{C\text{-}F}$ = 3.2 Hz), 125.1 (q, J = 279.9 Hz), 59.7, 52.7, 47.0 (q, J = 27.9 Hz), 29.2, 25.9, 18.4, -5.4, -5.5. **IR** (neat, cm^{-1}) ν: 3164, 3003, 2944, 2293, 2252, 1749, 1442, 1376, 1259, 1169, 1106, 1039. **HRMS** (EI) calcd for $C_{12}H_{23}O_3F_3NaSi$ *m/z* 323.1261 $[M+Na]^+$. Found 323.1260.

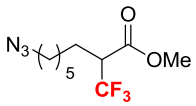


Methyl 6-(1,3-dioxoisoindolin-2-yl)-2-(trifluoromethyl)hexanoate 2r. General procedure from **1r**[15] (140 mg, 0.5 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether, 70:30). **2r** was afforded as a pale yellow oil (135 mg, 79%). R_f (petroleum ether/diethyl ether, 70:30): 0.33. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.87-7.81 (m, 2H), 7.76-7.68 (m, 2H), 3.76 (s, 3H), 3.72-3.63 (m, 2H), 3.18-3.01 (m, 1H), 2.03-1.63 (m, 4H), 1.47-1.31 (m, 2H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 68.8 (d, J = 8.2 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 168.3, 167.9 (q, J = 3.3 Hz), 134.0, 132.0, 124.6 (q, J = 279.9 Hz), 123.2, 52.6, 50.0 (q, J = 27.6 Hz), 37.3, 28.1, 25.6 (q, J = 2.1 Hz), 24.0. **IR** (neat, cm^{-1}) ν: 2947, 1707, 1397, 1169, 1129, 911, 718, 529. **HRMS** (EI) calcd for $C_{16}H_{16}F_3NO_4$ *m/z* 343.1031 $[M]^+$. Found 343.1035.

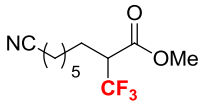


Methyl 8-chloro-2-(trifluoromethyl)octanoate 2s. General procedure from **1s** (99 mg, 0.5 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether, 98:2). **2s** was afforded as a pale yellow oil (94 mg, 72%). R_f (petroleum ether/diethyl ether, 96:4): 0.27. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.53 (t, J = 6.6 Hz, 2H), 3.18-3.02 (m, 1H), 2.00-1.70 (m, 4H), 1.50-1.31 (m, 6H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 68.8 (d, J = 8.3 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 168.2 (q, J = 3.2 Hz), 124.8 (q, J = 279.9 Hz), 52.7, 50.3 (q, J = 27.6 Hz), 45.0, 32.4, 28.5, 26.7, 26.5, 26.1 (q, J = 2.1 Hz). **IR** (neat, cm^{-1}) ν: 2939, 1749, 1438, 1264, 1167,

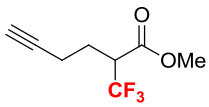
1113, 731, 651. **HRMS** (EI) calcd for $C_9H_{13}ClF_3O$ *m/z* 229.0607 $[M\text{-}CH_3O]^+$. Found 229.0610.



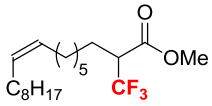
Methyl 8-azido-2-(trifluoromethyl)octanoate 2t. General procedure from **1t** (103 mg, 0.5 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether, 97:3). **2t** was afforded as a pale yellow oil (99 mg, 74%). R_f (petroleum ether/diethyl ether, 97:3): 0.17. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.26 (t, J = 6.9 Hz, 2H), 3.18-3.01 (m, 1H), 1.98-1.84 (m, 1H), 1.84-1.72 (m, 1H), 1.65-1.52 (m, 2H), 1.44-1.28 (m, 6H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 68.8 (d, J = 8.3 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 168.2 (q, J = 3.3 Hz), 124.8 (q, J = 279.9 Hz), 52.6, 51.4, 50.3 (q, J = 27.5 Hz), 28.7, 28.7, 26.7, 26.4, 26.1 (q, J = 2.1 Hz). **IR** (neat, cm^{-1}) ν: 2939, 2094, 1749, 1438, 1268, 1170, 1117, 912, 733, 670. **HRMS** (ESI) calcd for $C_{10}H_{17}F_3N_3O_2$ *m/z* 268.1273 $[M+H]^+$. Found 268.1270.



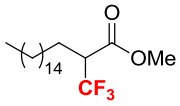
Methyl 8-cyano-2-(trifluoromethyl)octanoate 2u. General procedure from **1u** (94 mg, 0.5 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether, 70:30). **2u** was afforded as a pale yellow oil (94 mg, 75%). R_f (petroleum ether/diethyl ether, 70:30): 0.27. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 3.79 (s, 3H), 3.19-3.02 (m, 1H), 2.34 (t, J = 7.0 Hz, 2H), 1.99-1.30 (m, 10H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 68.8 (d, J = 8.3 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 168.0 (q, J = 3.2 Hz), 124.7 (q, J = 279.8 Hz), 119.7, 52.6, 50.1 (q, J = 27.6 Hz), 28.2, 28.2, 26.4, 25.9 (q, J = 2.2 Hz), 25.1, 16.9. **IR** (neat, cm^{-1}) ν: 2941, 2252, 1748, 1438, 1268, 1117, 911, 729. **HRMS** (EI) calcd for $C_{11}H_{15}F_3NO_2$ *m/z* 250.1055 $[M-H]^+$. Found 250.1056.



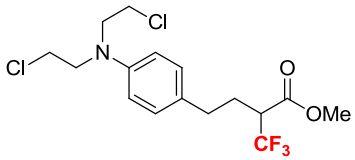
Methyl 2-(trifluoromethyl)hex-5-ynoate 2v. General procedure from **1v** (65 mg, 0.5 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether, 97:3). **2v** was afforded as a pale yellow oil (38 mg, 39%). R_f (petroleum ether/diethyl ether, 97:3): 0.30. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.45-3.29 (m, 1H), 2.44-1.92 (m, 5H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 68.6 (d, J = 8.4 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 167.6 (q, J = 3.1 Hz), 124.7 (q, J = 280.0Hz), 81.6, 70.4, 52.9, 48.9 (q, J = 27.9 Hz), 25.1 (q, J = 2.2 Hz), 16.2. **IR** (neat, cm^{-1}) ν: 3315, 2959, 1748, 1439, 1272, 1158, 1114, 1043, 735, 640. **HRMS** (ESI) calcd for $C_8H_{10}F_3O_2$ *m/z* 195.0633 $[M+H]^+$. Found 195.0627.



(*Z*)-Methyl 2-(trifluoromethyl)octadec-9-enoate 2w. General procedure from **1w** (151 mg, 0.5 mmol, 1 eq.) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether, 99.5:0.5). **2w** was afforded as a pale yellow oil (98 mg, 54%). R_f (petroleum ether/diethyl ether, 99.5:0.5): 0.15. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 5.42-5.27 (m, 2H), 3.78 (s, 3H), 3.18-3.02 (m, 1H), 2.06-1.71 (m, 6H), 1.38-1.23 (m, 20H), 0.92-0.83 (m, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 68.9 (d, J = 8.3 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 168.3 (q, J = 3.3 Hz), 130.3, 129.7, 124.8 (q, J = 279.8 Hz), 52.7, 50.4 (q, J = 27.5 Hz), 32.1, 29.90, 29.69, 29.67, 29.48, 29.47, 29.16, 28.99, 27.36, 27.22, 26.90, 26.3 (q, J = 2.0 Hz), 22.8, 14.2. **IR** (neat, cm^{-1}) ν: 2925, 2856, 1753, 1438, 1268, 1168, 1114, 725. **HRMS** (EI) calcd for $C_{20}H_{35}F_3O_2$ *m/z* 364.2589 $[M]^+$. Found 364.2596.



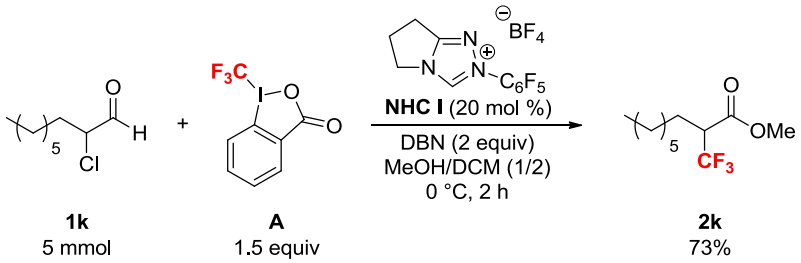
Methyl 2-(trifluoromethyl)octadecanoate 2x. General procedure from **1x**[16] (152 mg, 0.5 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether, 99.5:0.5). **2x** was afforded as a pale yellow oil (127 mg, 69%). R_f (petroleum ether/diethyl ether, 99.5:0.5): 0.28. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.18-3.02 (m, 1H), 1.98-1.68 (m, 2H), 1.39-1.20 (m, 28H), 0.88 (t, J = 6.9 Hz, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 68.9 (d, J = 8.4 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 168.4 (q, J = 3.4 Hz), 124.8 (q, J = 279.9 Hz), 52.7, 50.4 (q, J = 27.6 Hz), 32.1, 29.86, 29.85, 29.84, 29.83, 29.82, 29.79, 29.73, 29.62, 29.53, 29.37, 29.26, 26.93, 26.3 (q, J = 2.1 Hz), 22.9, 14.3. **IR** (neat, cm^{-1}) ν: 2923, 2854, 1754, 1466, 1270, 1168, 1112, 735. **HRMS** (EI) calcd for $C_{20}H_{37}F_3O$ *m/z* 366.2746 $[M]^+$. Found 366.2761.



Methyl 4-(4-(bis(2-chloroethyl)amino)phenyl)-2-(trifluoromethyl)butanoate 2y. General procedure from **1y** (161 mg, 0.5 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/ethyl acetate). **2y** was afforded as a brownish oil (131 mg, 68%). R_f (petroleum ether/ethyl acetate, 90:10): 0.32. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.06 (d, J = 8.6 Hz, 2H), 6.63 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H), 3.73-3.69 (m, 4H), 3.65-3.61 (m, 4H), 3.18-3.08 (m, 1H), 2.68-2.61 (m, 1H), 2.54-2.47 (m, 1H), 2.26-2.17 (m, 1H), 2.08-2.00 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ - 68.1 (d, J = 8.5 Hz). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 168.1 (q, J = 3.4 Hz, 1H), 144.7, 129.8, 129.0, 124.8 (q, J = 279.9 Hz), 112.4, 53.7, 52.8, 49.5 (d, J = 27.9 Hz), 40.5, 31.7, 28.1. **IR** (neat, cm^{-1}) ν: 3164, 3002, 2944, 2294, 2252, 2247, 1749, 1592, 1510, 1442, 1375, 1260, 1169, 1040. **HRMS** (ESI) calcd for $C_{16}H_{21}Cl_2F_3NO_2$ *m/z* 386.0896 $[M+H]^+$.

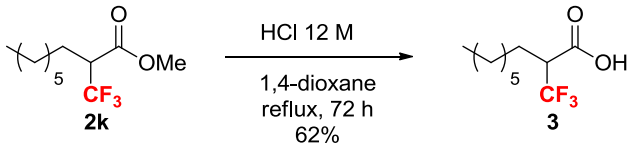
Found 386.0899.

8. Scale-up synthesis of 2k



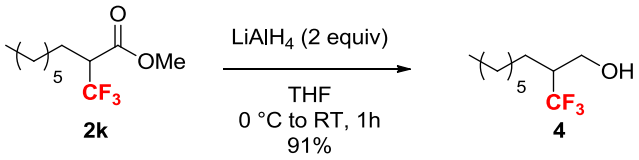
Methyl 2-(trifluoromethyl)nonanoate 2k. In a oven-dried 50 mL round bottom flask equipped with a magnetic stirrer, was added under argon the α-chloroaldehyde derivative **1k**[13] (884 mg, 5.0 mmol, 1 equiv), the Togni's reagent **A** (2.37 g, 7.5 mmol, 1.5 equiv), **NHC I** (363 mg, 1.0 mmol, 20 mol %) and dichloromethane (16.5 mL). Once cooled to 0 °C, methanol (8.5 mL) was added to the reaction mixture. After stirring 5 min at 0 °C, DBN (1.24 mL, 10 mmol, 2 equiv) was added and the reaction mixture was stirred at 0 °C for 2 h. The crude mixture was diluted in dichloromethane (100 mL), washed with brine (100 mL), dried over $MgSO_4$ and concentrated under reduced pressure (20 °C, 100 mbar). The residue was then purified by column chromatography on silica gel (petroleum ether/diethyl ether, 99.5:0.5) to afford the desired trifluoromethylated ester derivative **2k** (877 mg, 73%). Analytical data were identical to those of compound **2k** obtained on 0.5 mmol scale (cf pages S10).
CAUTION: α-trifluoromethylated ester derivatives might be volatile and were concentrated at 20 °C under 100 mbar.

9. Post-functionalization reactions - Synthesis of derivatives 3-4



2-(Trifluoromethyl)nonanoic acid 3. In a tube equipped with a magnetic stirrer, an aqueous HCl 12 M (0.5 mL) solution was added to a solution of trifluoromethylated ester **2k** (60 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (0.5 mL). The tube was sealed and the reaction mixture was heated at 100 °C for 3 days. After cooling to room temperature, water (20 mL) was added. The aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure (20 °C, 100 mbar). The residue was then purified by flash column chromatography on silica gel (petroleum ether/diethyl ether, 50:50) to afford the desired trifluoromethylated acid derivative **3** as a yellowish liquid (35 mg, 62%). R_f (petroleum ether/diethyl ether, 50:50): 0.16. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 8.51 (br s, 1H), 3.22-3.06 (m, 1H), 2.00-1.74 (m, 2H), 1.48-1.21 (m, 10H), 0.92-0.82 (m, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 68.7 (d, J = 8.2 Hz). **^{13}C NMR** (75.5 MHz,

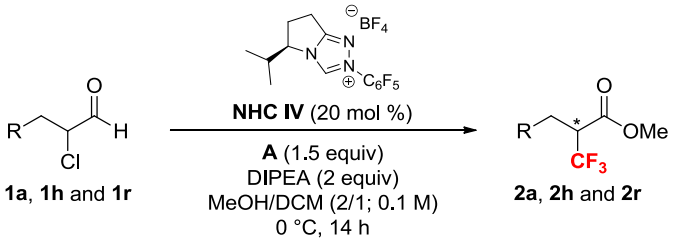
$CDCl_3$) δ 173.5, 124.7 (q, J = 280.2 Hz), 50.4 (q, J = 26.2 Hz), 31.8, 29.2, 29.0, 26.9, 26.3 (q, J = 1.7 Hz), 22.7, 14.2. **IR** (neat, cm^{-1}) ν: 2928, 1724, 1425, 1263, 1164, 1130, 923, 662. **HRMS** (ESI) calcd for $C_{10}H_{16}F_3O_2$ *m/z* 225.1108 $[M-H]^-$. Found 225.1096.



2-(Trifluoromethyl)nonan-1-ol 4. In an oven-dried tube equipped with a magnetic stirrer, a solution of trifluoromethylated ester **2k** (120 mg, 0.5 mmol, 1 equiv) in THF (0.5 mL) was slowly added at 0 °C to a solution of $LiAlH_4$ (38 mg, 1 mmol, 2 equiv) in THF (0.5 mL). The reaction mixture was stirred at 0 °C for 1h then carefully quenched using NaOH 1M (10 mL). The aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure (20 °C, 100 mbar). The desired trifluoromethylated alcohol derivative **4** was obtained as a colorless liquid (97 mg, 91%). R_f (petroleum ether/diethyl ether, 90:10): 0.22. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 3.88-3.74 (m, 2H), 2.31-2.12 (m, 1H), 1.68-1.19 (m, 13H), 0.88 (t, J = 7.0 Hz, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ - 69.7 (d, J = 9.4 Hz). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 128.1 (q, J = 280.5 Hz), 59.9 (q, J = 3.0 Hz), 45.6 (q, J = 23.9 Hz), 31.9, 29.7, 29.2, 27.0, 24.8 (q, J = 2.2 Hz), 22.7, 14.1. **IR** (neat, cm^{-1}) ν: 3359, 2927, 1468, 1253, 1134, 1035, 605. **HRMS** (ESI) calcd for $C_{10}H_{17}F_3$ *m/z* 194.1282 $[M-H_2O]^+$. Found 194.1281.

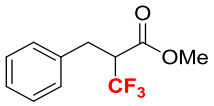
10. Asymmetric approach

General asymmetric trifluoromethylation procedure:

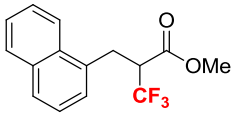


In a oven-dried tube equipped with a magnetic stirrer, was added under argon the α-chloroaldehyde derivative **1** (0.2 mmol, 1 equiv), the Togni's reagent **A** (0.3 mmol, 1.5 equiv) and the **NHC IV**[2d] (0.04 mmol, 20 mol %) and dichloromethane (0.65 mL). Once cooled to 0 °C, methanol (1.35 mL) was added to the reaction mixture. After stirring 5 min at 0 °C, DIPEA (0.4 mmol, 2 equiv) was added and the reaction mixture was stirred at 0 °C for 14 h. Then, the crude mixture was diluted in dichloromethane (20 mL), washed with brine (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure (20 °C, 100 mbar). The residue was then purified by flash column chromatography on silica gel (petroleum ether/diethyl ether) to afford the desired trifluoromethylated ester derivative **2**.

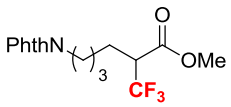
CAUTION: α-trifluoromethylated ester derivatives might be volatile and were concentrated at 20 °C under 100 mbars.



Methyl 2-benzyl-3,3,3-trifluoropropanoate 2a. General asymmetric trifluoromethylation procedure from **1a**[8] (17 mg, 0.1 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether = 98:2). **2a** was afforded as a pale yellow oil (8 mg, yield = 34%, ee = 78%). Analytical data were identical to those of racemic **2a** (cf page S6). HPLC: rt (majo) = 4.4 min, rt (mino) = 4.7 min (CHIRALPAK® AS-H; flowrate = 1.0 mL min^{-1}; heptane/2-propanol 99:1; 20 °C, 209 nm); $[\alpha]_D^{20}$ = + 45.0 (c 0.44, $CHCl_3$).



Methyl 3,3,3-trifluoro-2-(naphthalen-1-ylmethyl)propanoate 2h. General asymmetric trifluoromethylation procedure from **1h**[11] (44 mg, 0.2 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether = 98:2). **2h** was afforded as a pale yellow solid (20 mg, yield = 35%, ee = 81%). Analytical data were identical to those of racemic **2h** (cf pages S9). HPLC: rt (majo) = 4.6 min, rt (mino) = 5.0 min (CHIRALPAK® AS-H; flowrate = 1.0 mL min^{-1}; heptane/2-propanol 99:1; 20 °C, 222 nm); $[\alpha]_D^{20}$ = + 118.5 (c 1.0, $CHCl_3$).



Methyl 6-(1,3-dioxoisoindolin-2-yl)-2-(trifluoromethyl)hexanoate 2r. General asymmetric trifluoromethylation procedure from **1r**[15] (49 mg, 0.2 mmol, 1 equiv) followed by flash column chromatography on silica gel (petroleum ether/diethyl ether = 70:30). **2o** was afforded as a pale yellow oil (39 mg, yield = 57%, ee = 74%). Analytical data were identical to those of racemic **2o** (cf page S12). HPLC: rt (majo) = 17.7 min, rt (mino) = 19.0 min (CHIRALPAK® AS-H; flowrate = 1.0 mL min^{-1}; heptane/2-propanol 97:3; 20 °C, 216 nm); $[\alpha]_D^{20}$ = + 16.2 (c 1.0, $CHCl_3$).

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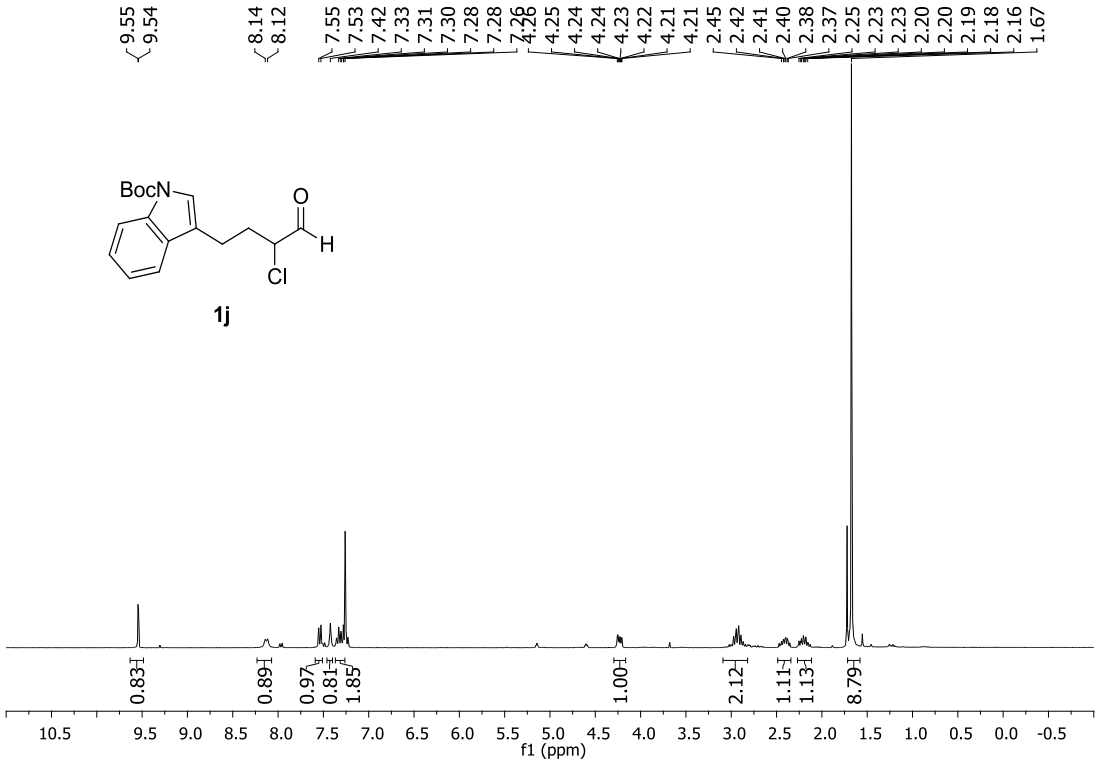
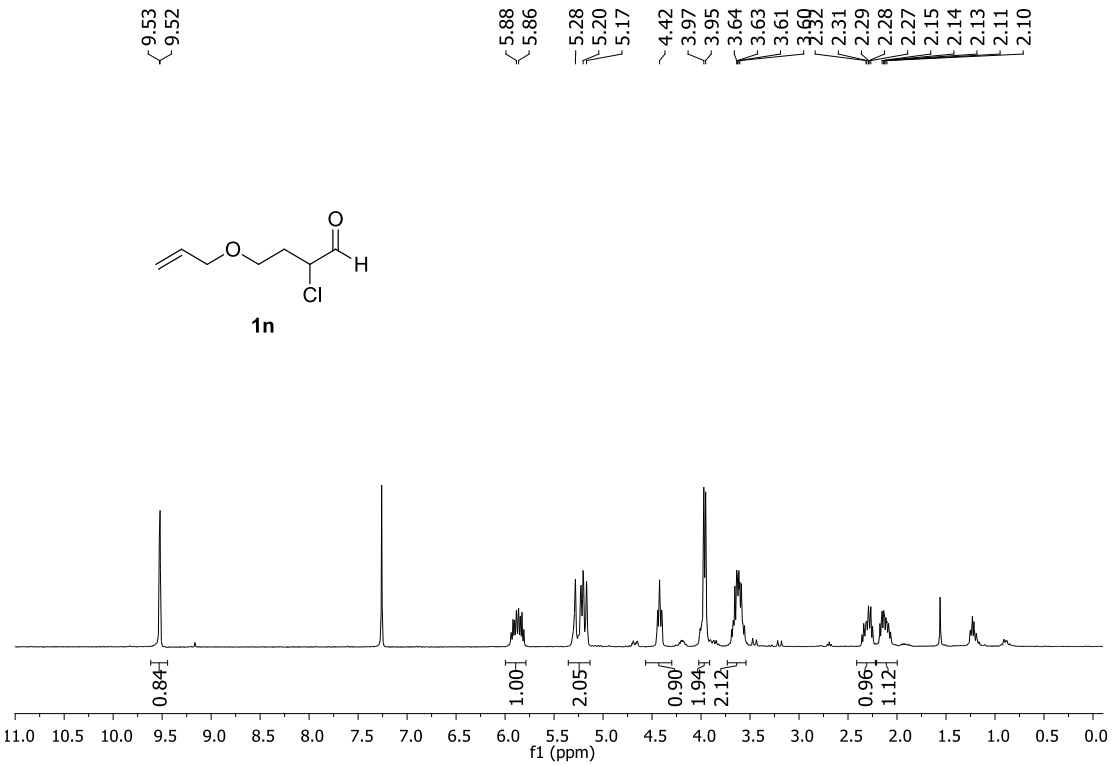
12. NMR spectra

^{1}H NMR Spectrum ($CDCl_3$, 300 MHz)



^{1}H NMR Spectrum ($CDCl_3$, 300 MHz)



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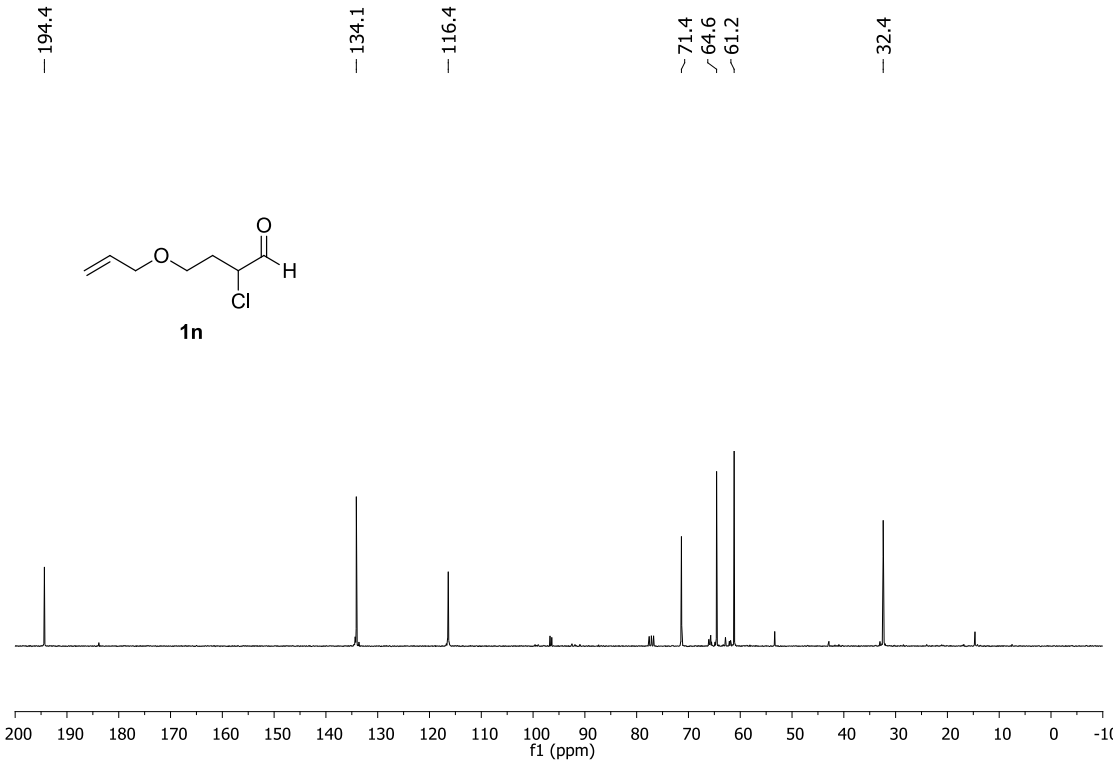
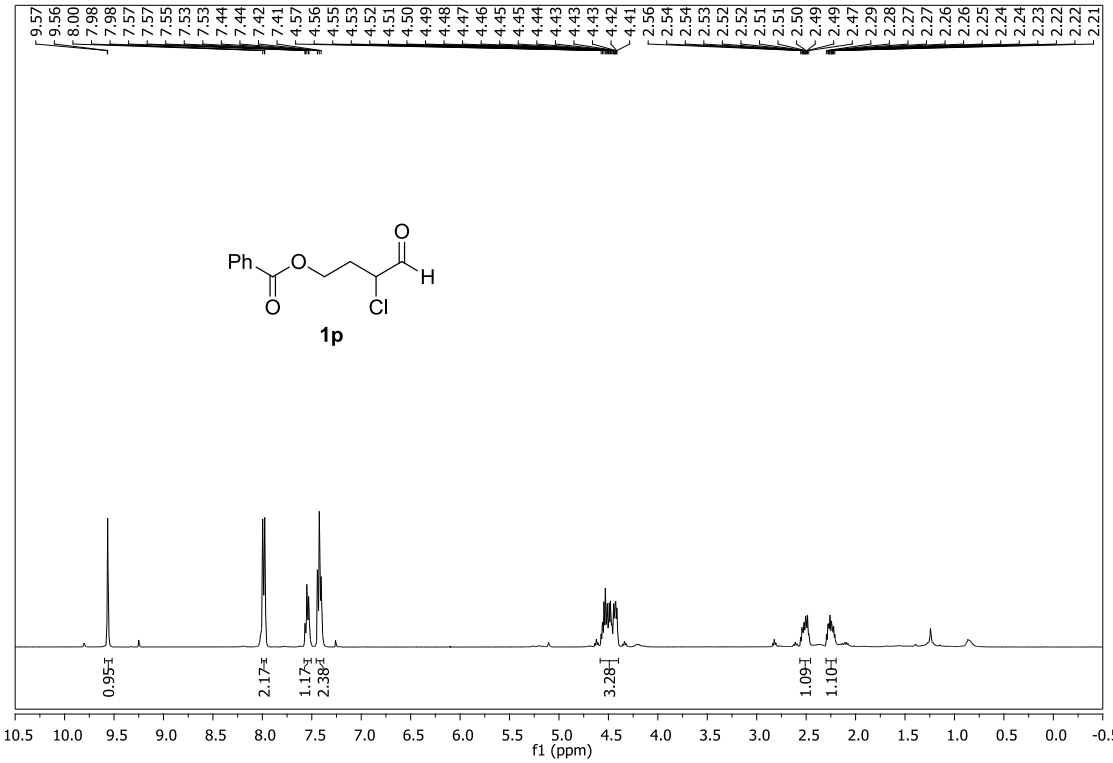


^{1}H NMR Spectrum ($CDCl_3$, 400 MHz)



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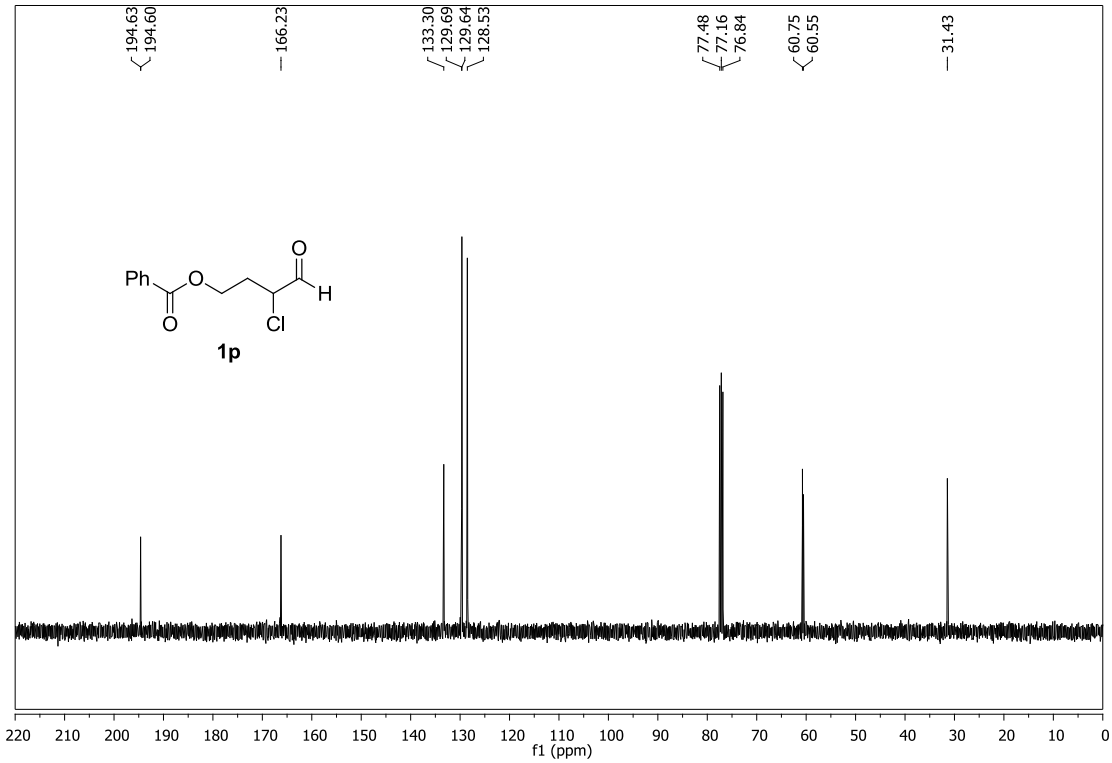

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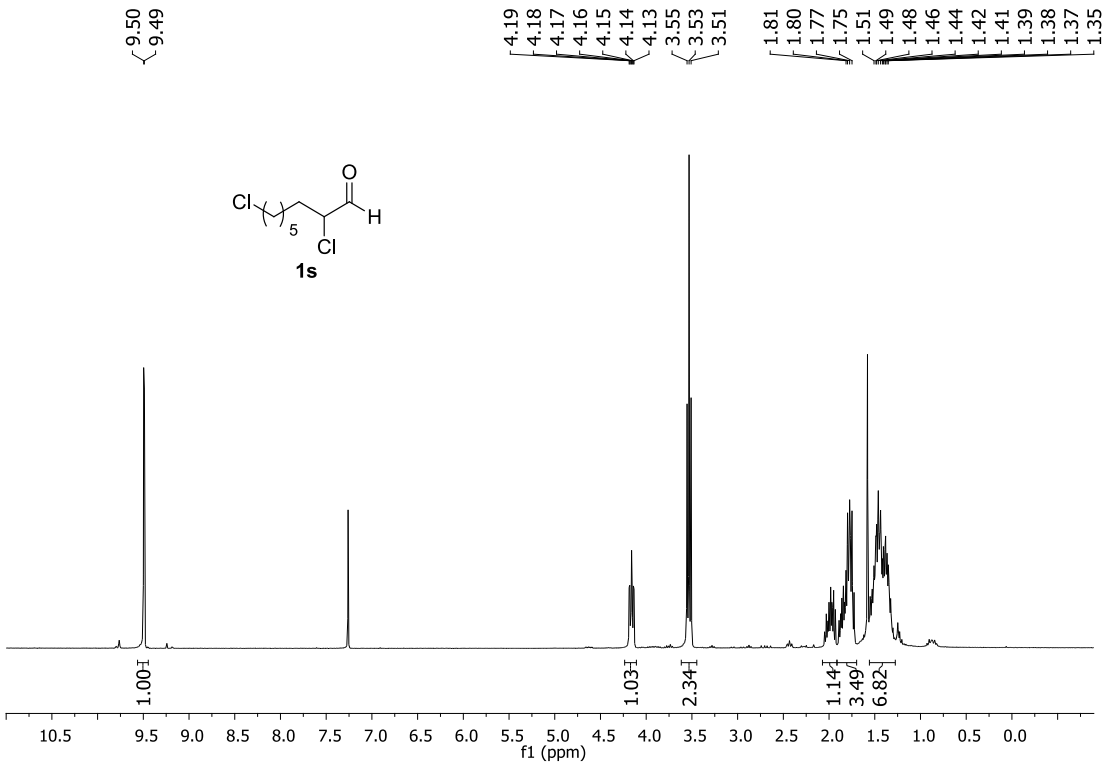

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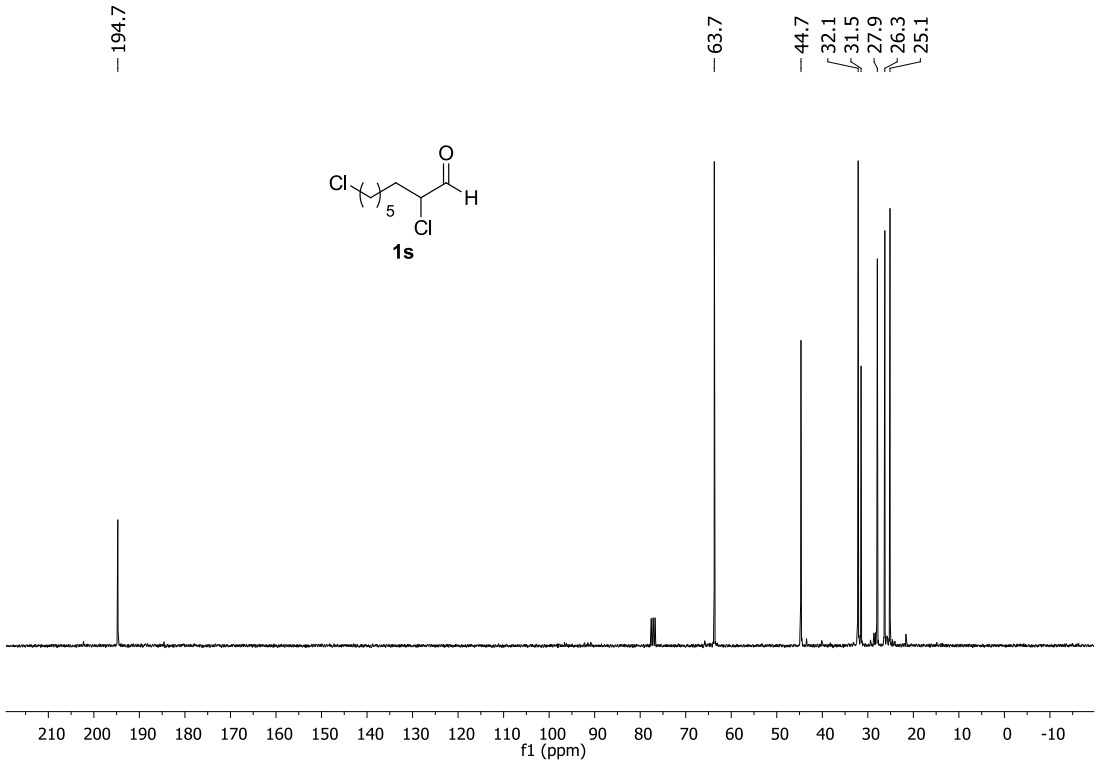

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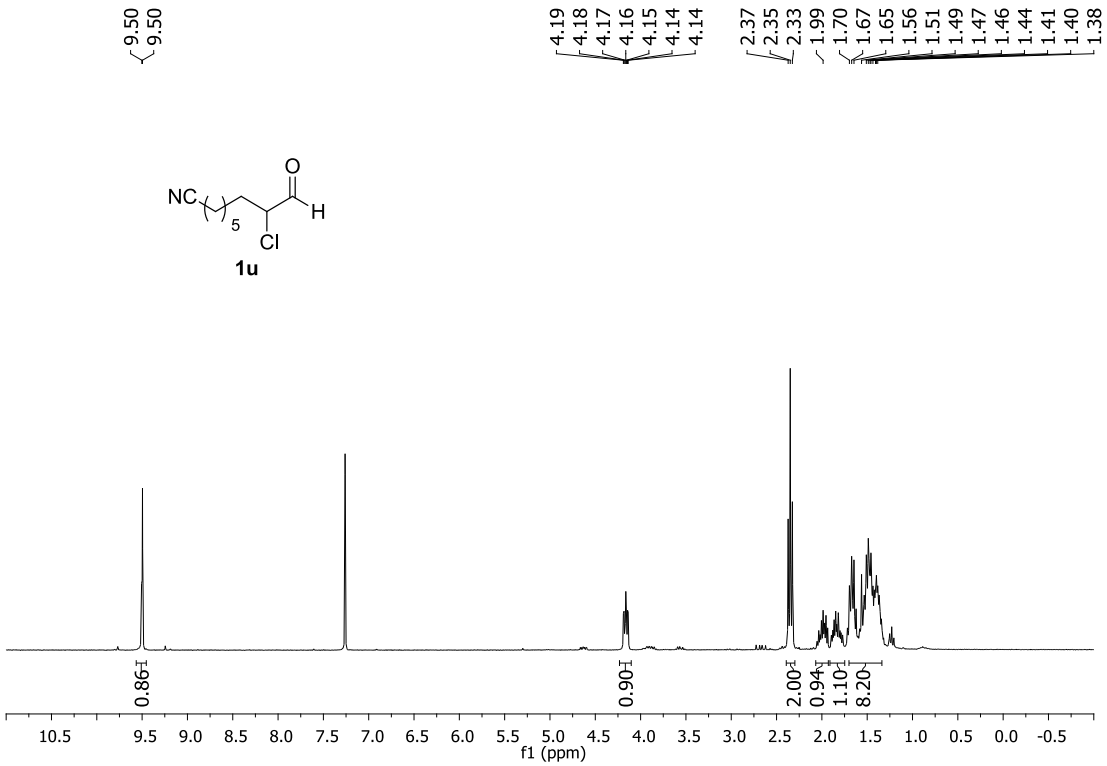

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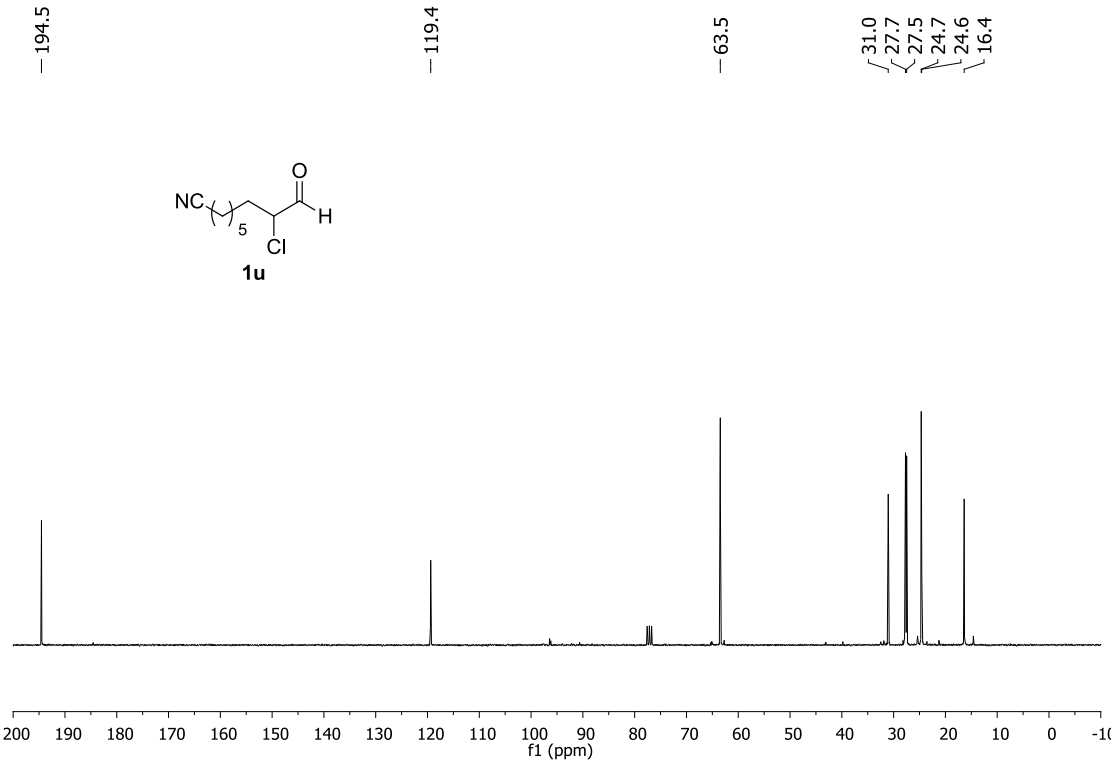

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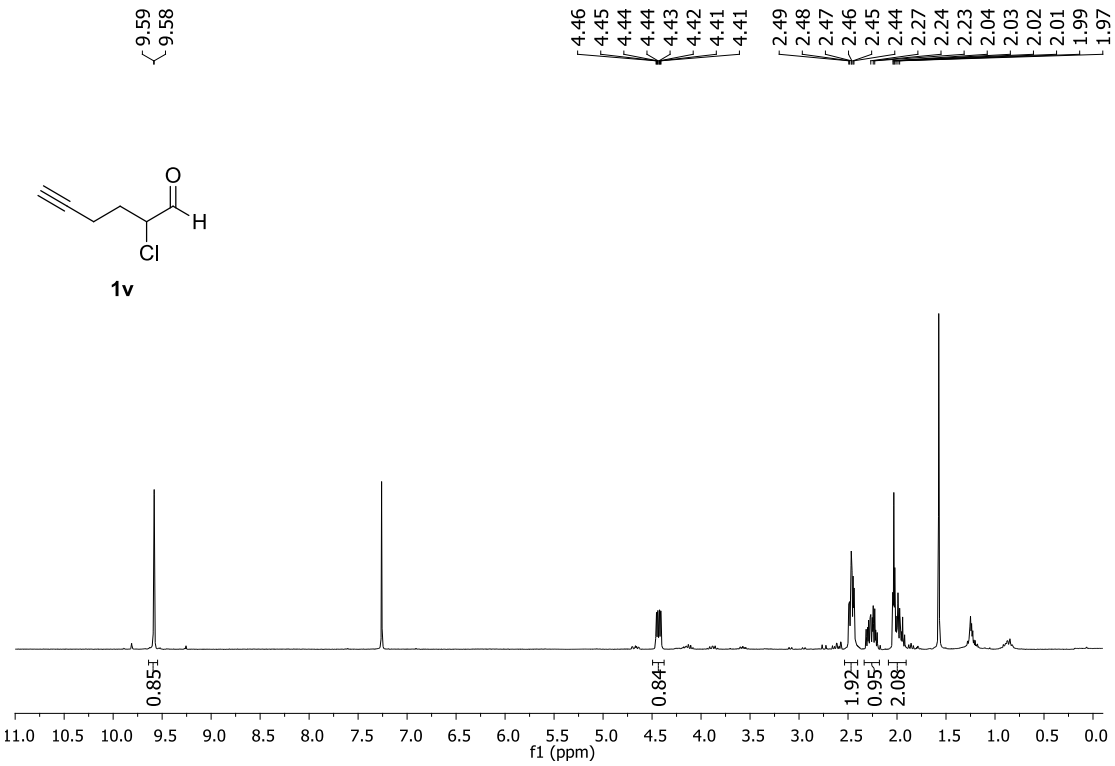

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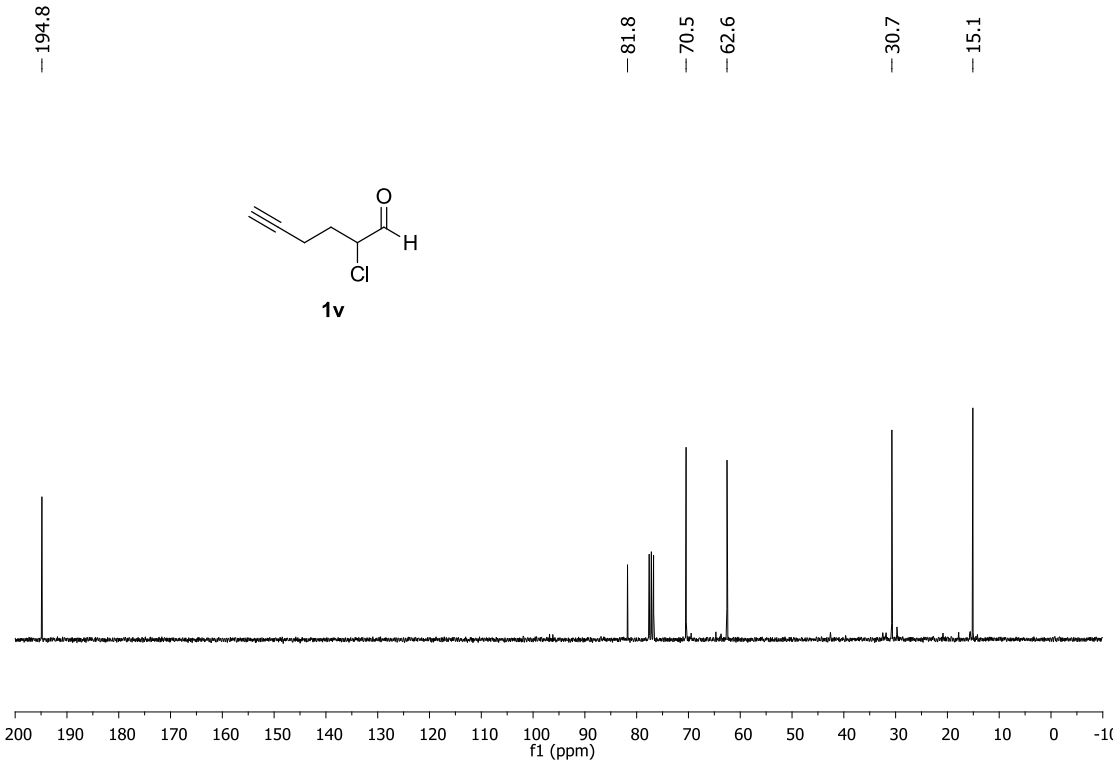

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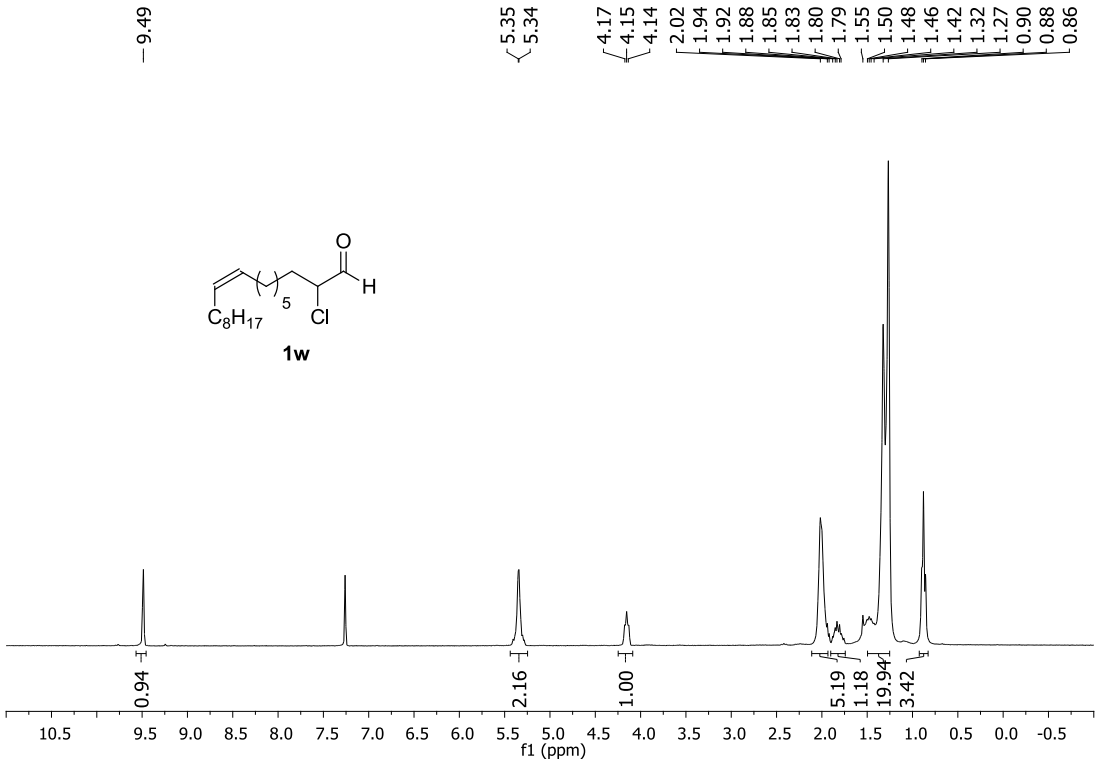
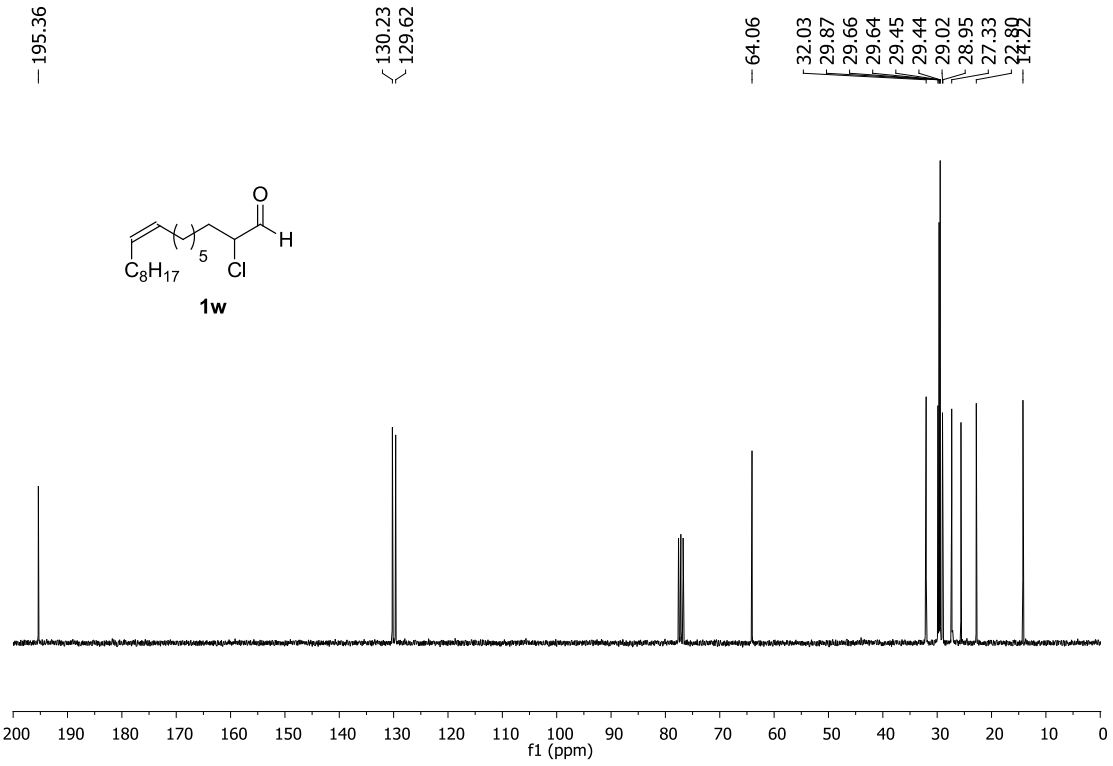
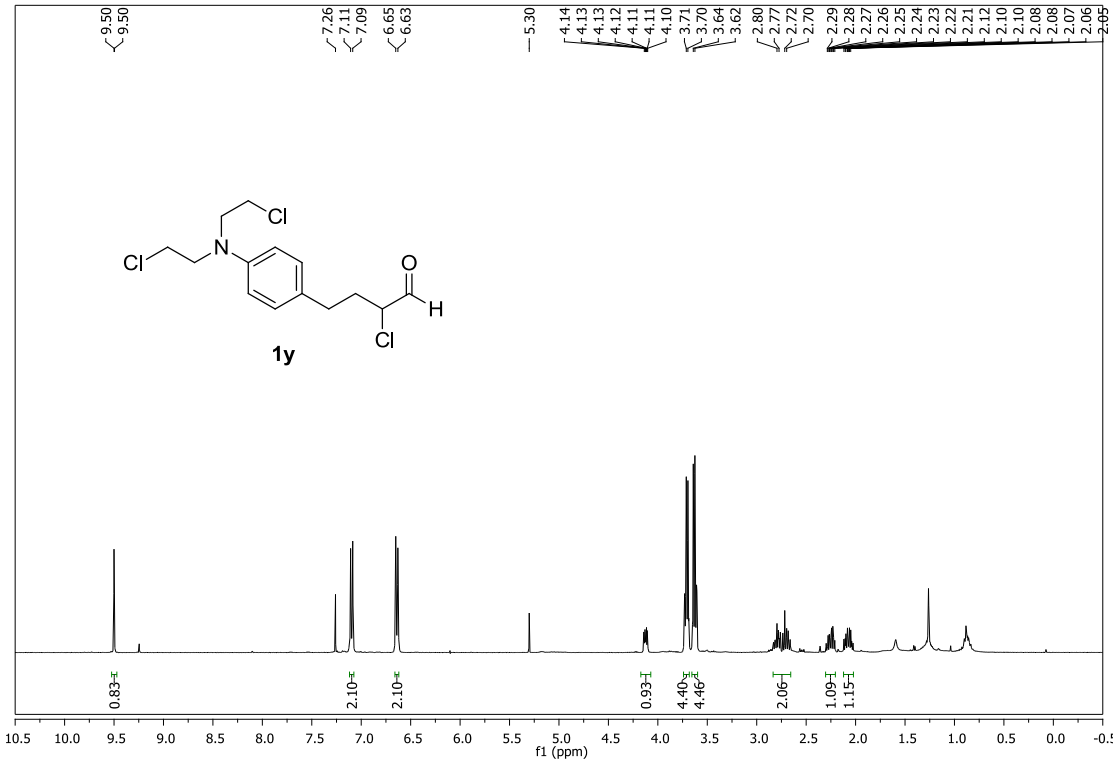


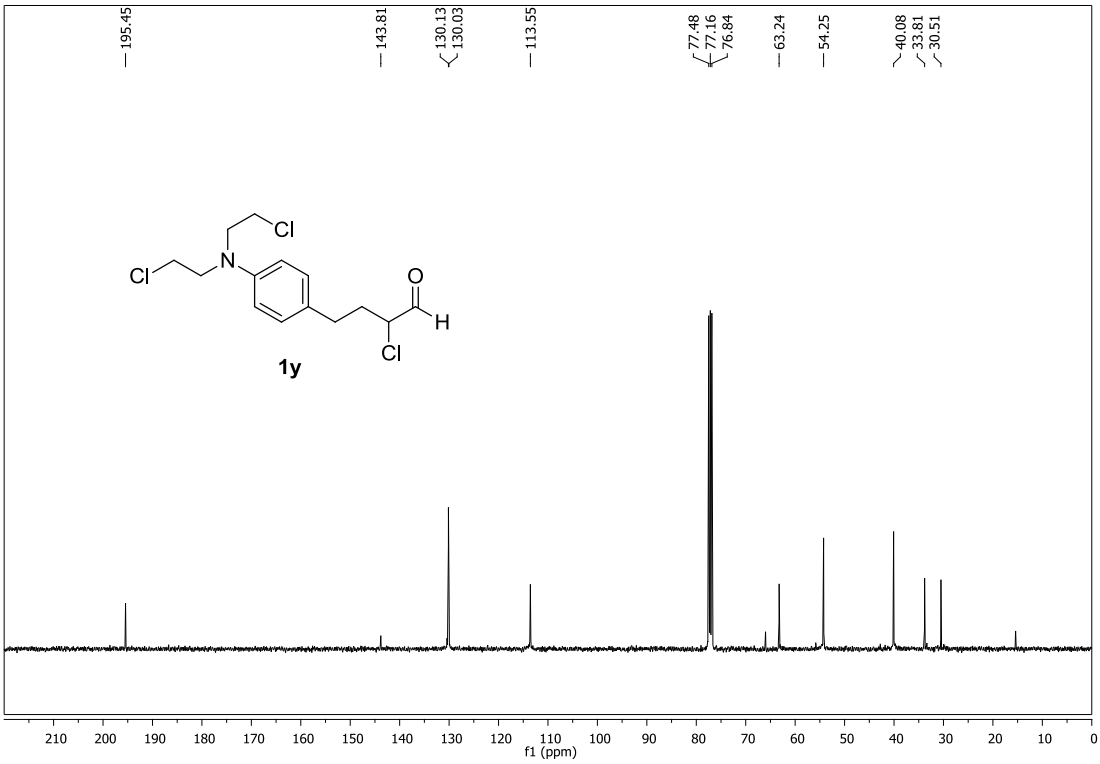
^{13}C NMR Spectrum ($CDCl_3$, 75 MHz)



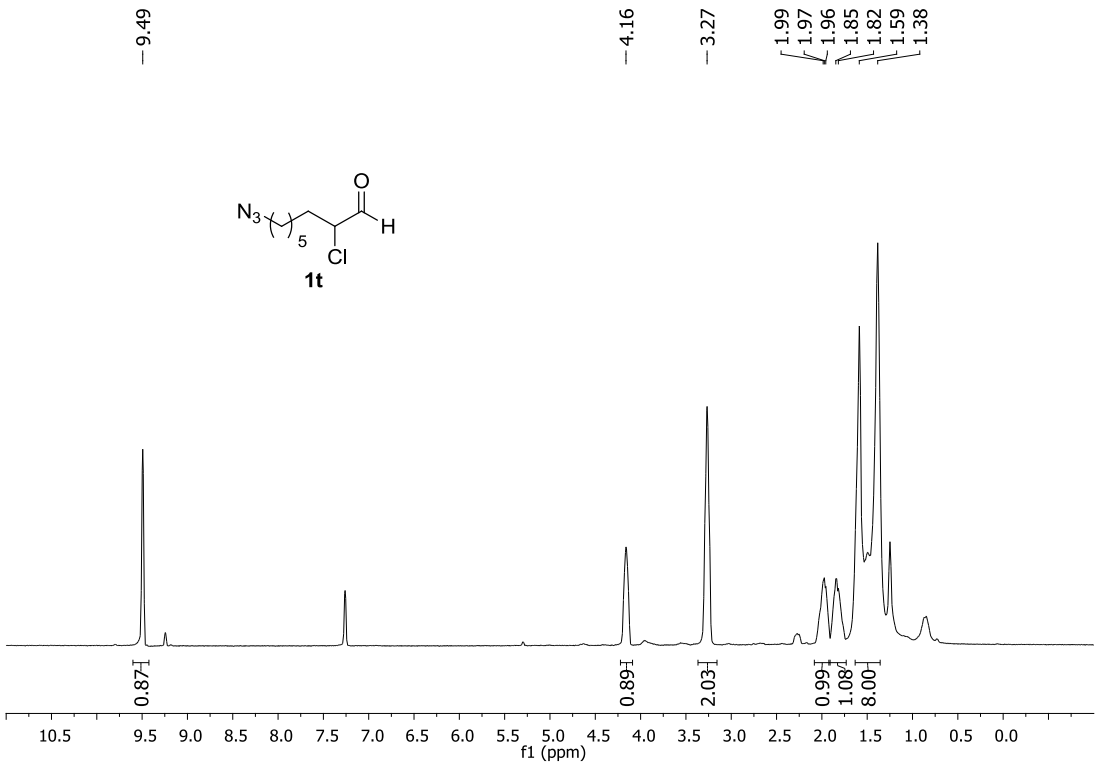
^{1}H NMR Spectrum ($CDCl_3$, 400 MHz)



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



^{1}H NMR Spectrum ($CDCl_3$, 300 MHz)



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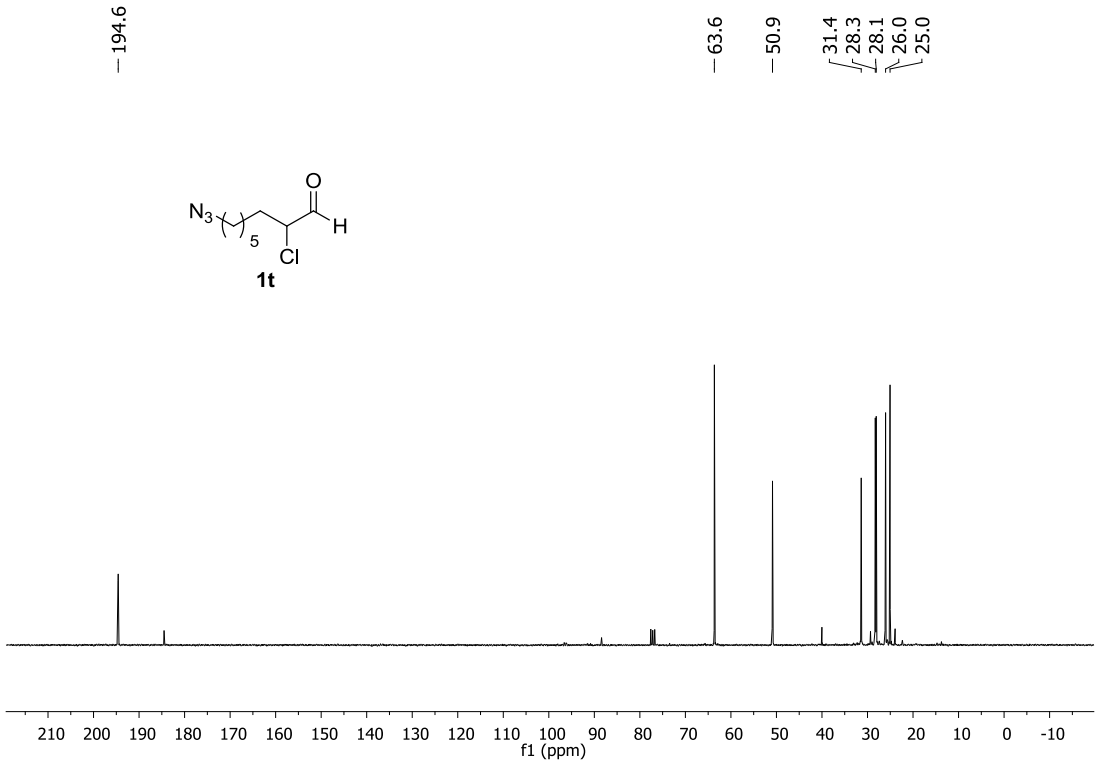

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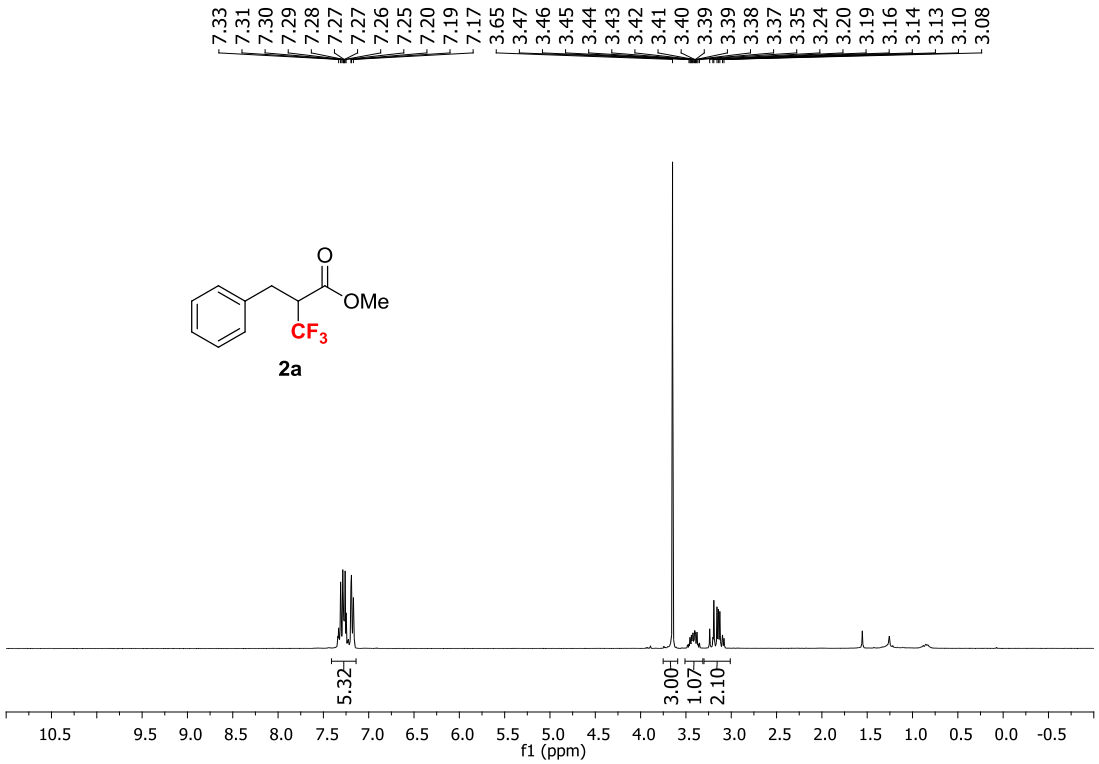
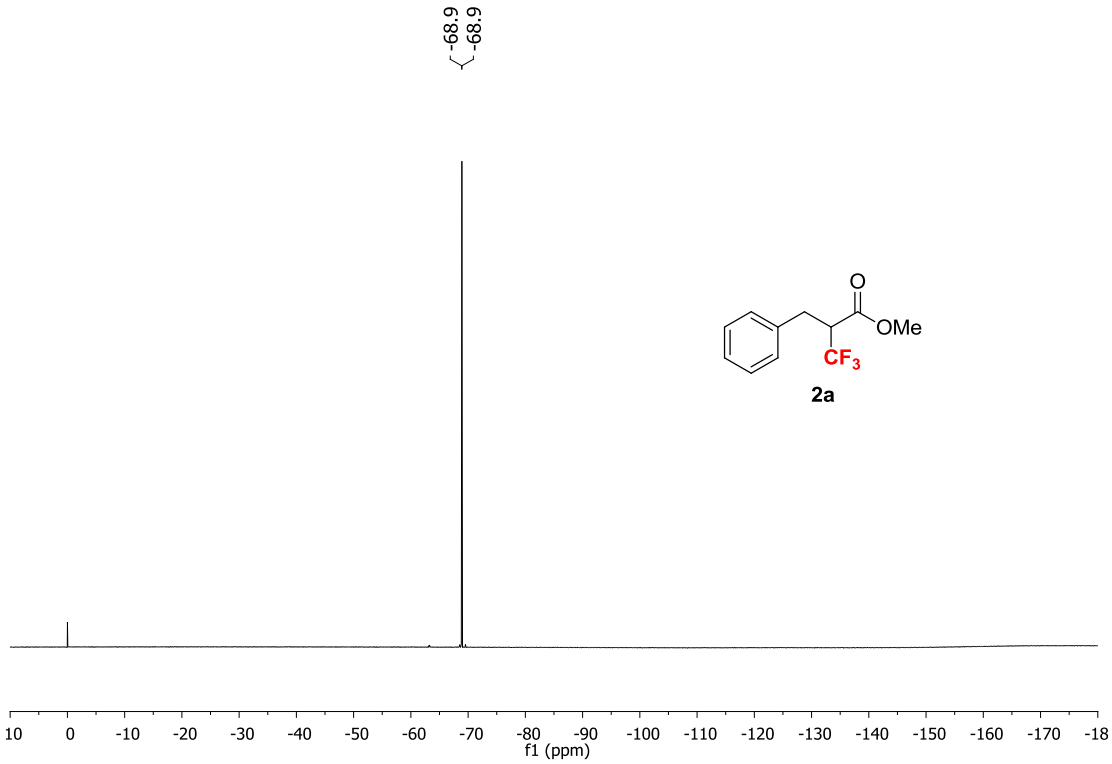


^{19}F NMR Spectrum ($CDCl_3$, 282 MHz)



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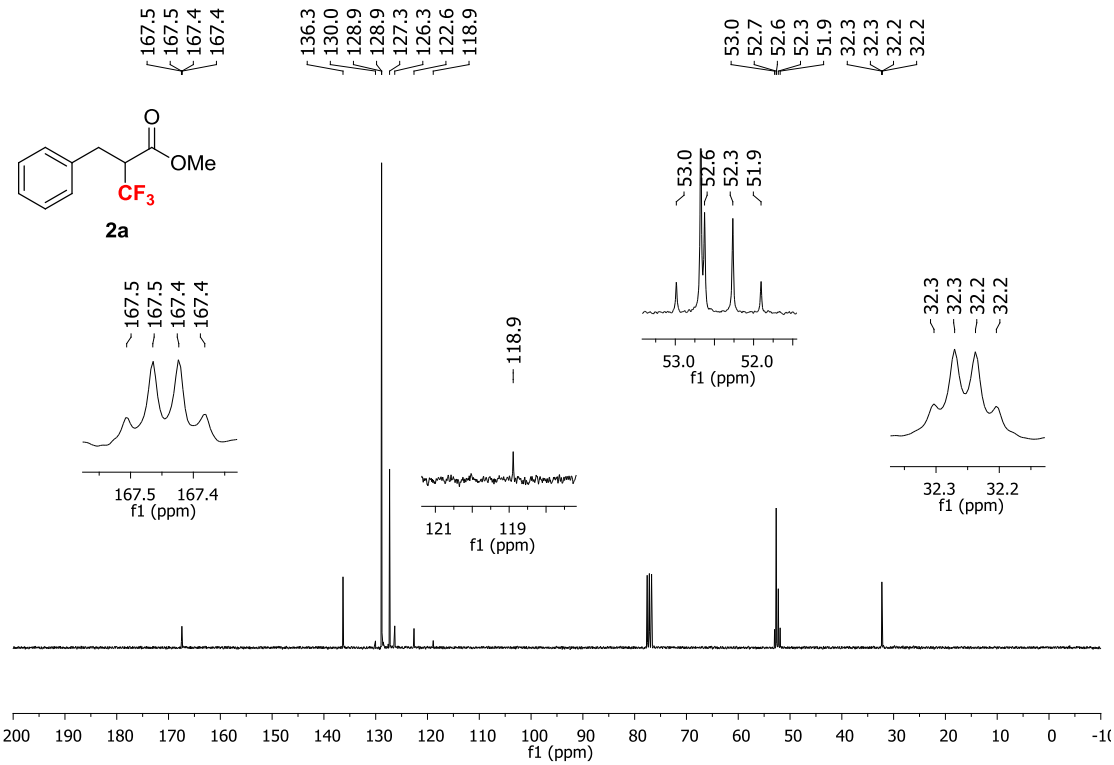

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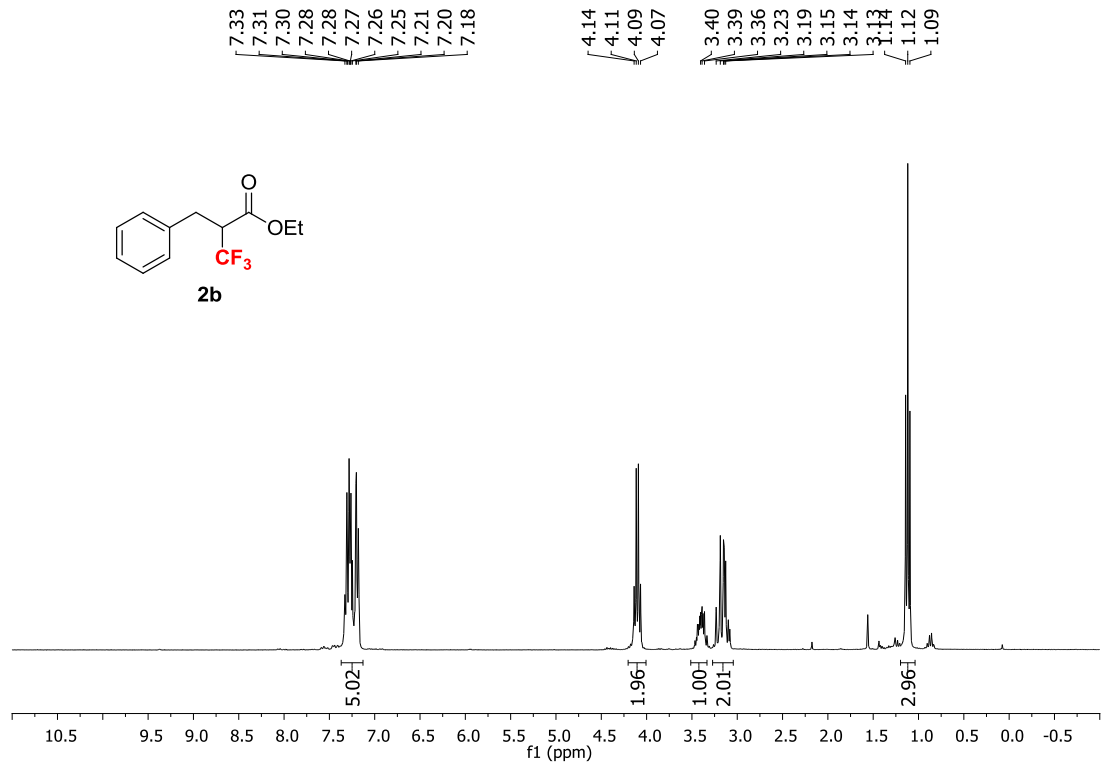

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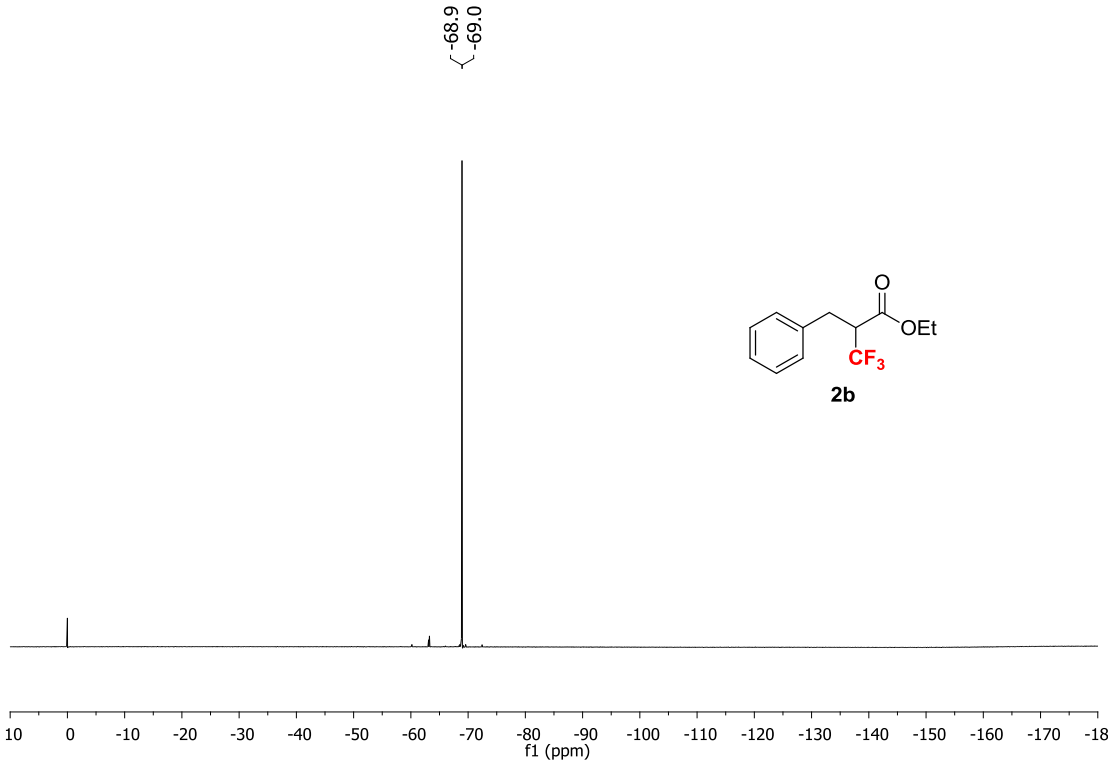

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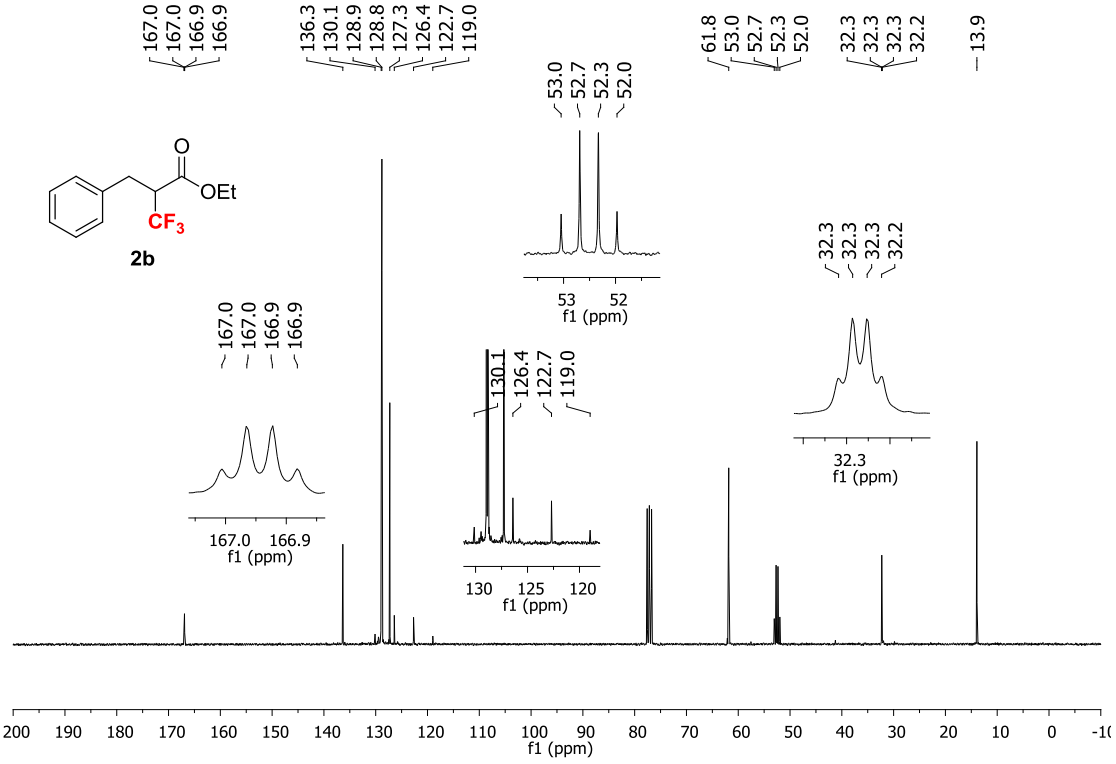

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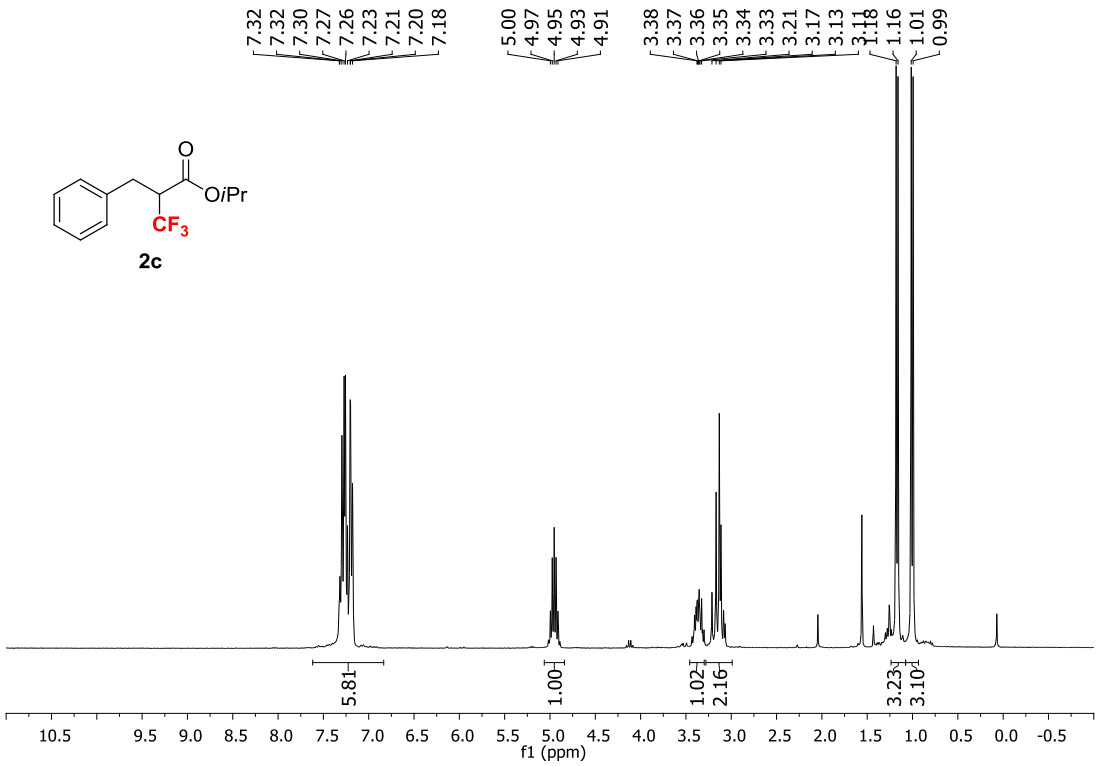

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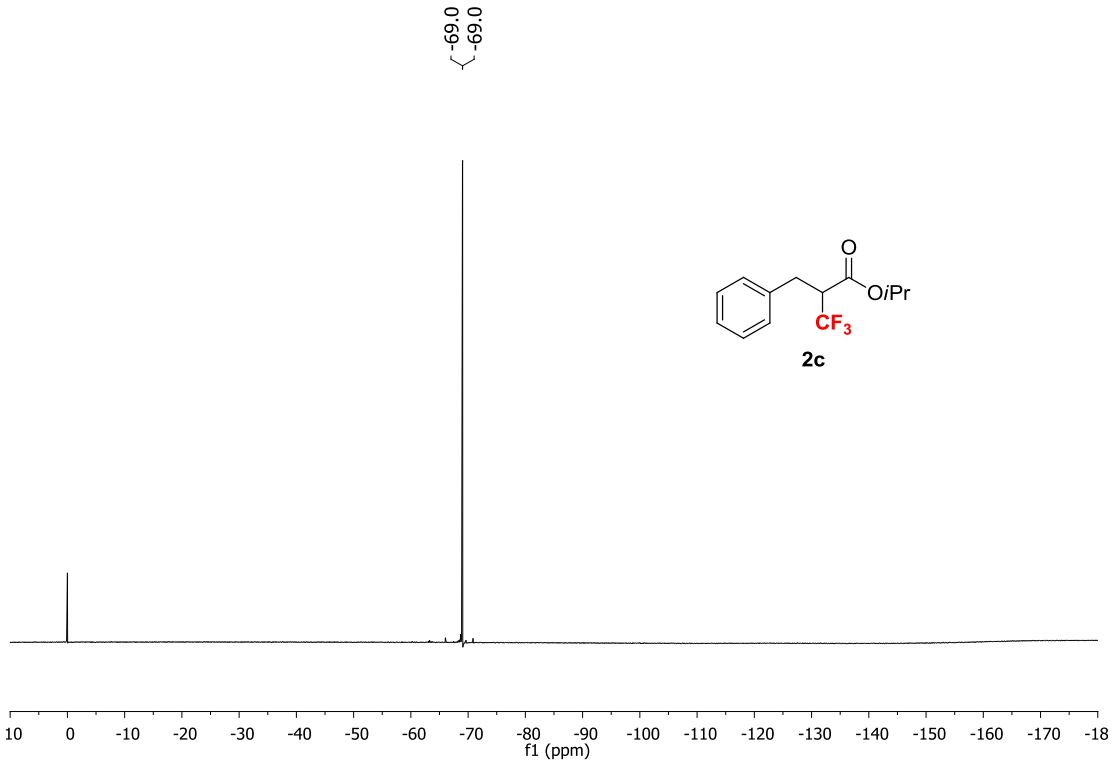

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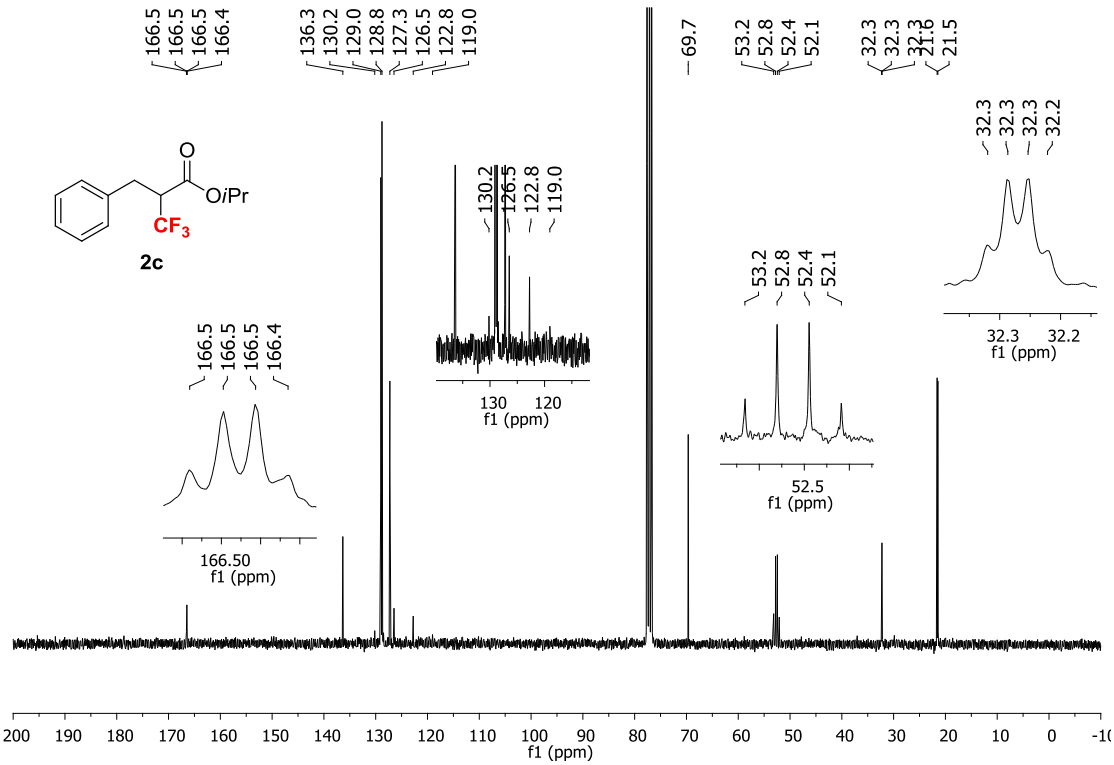

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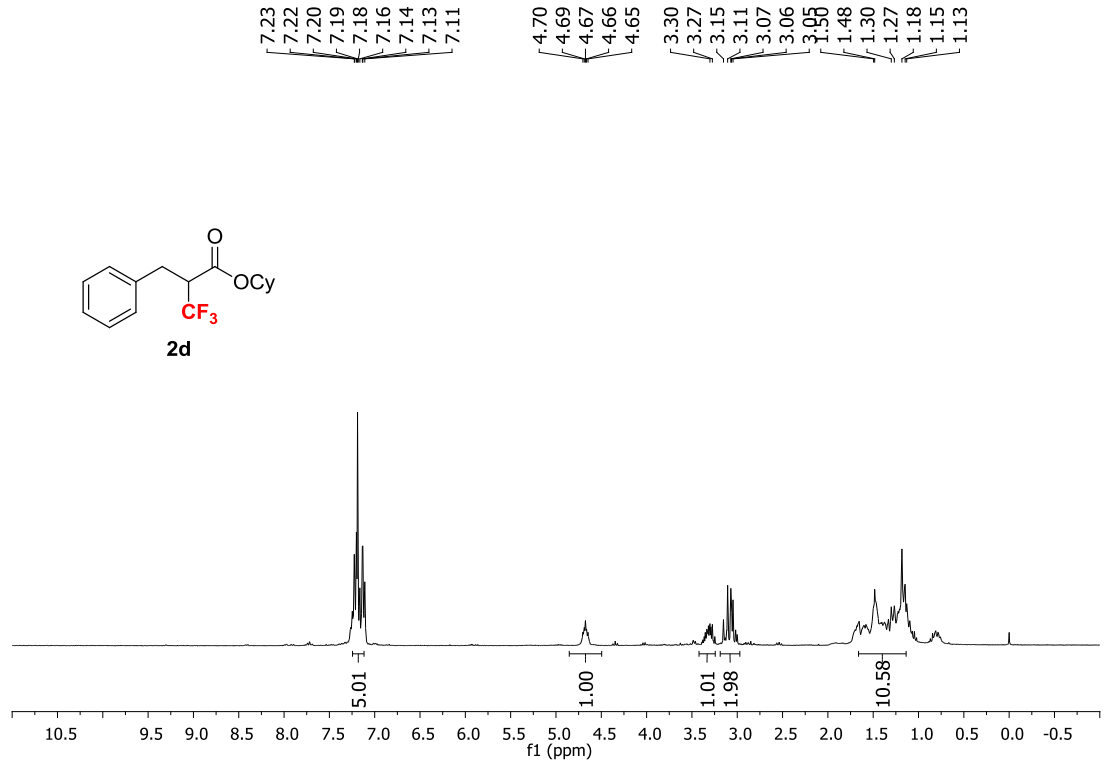

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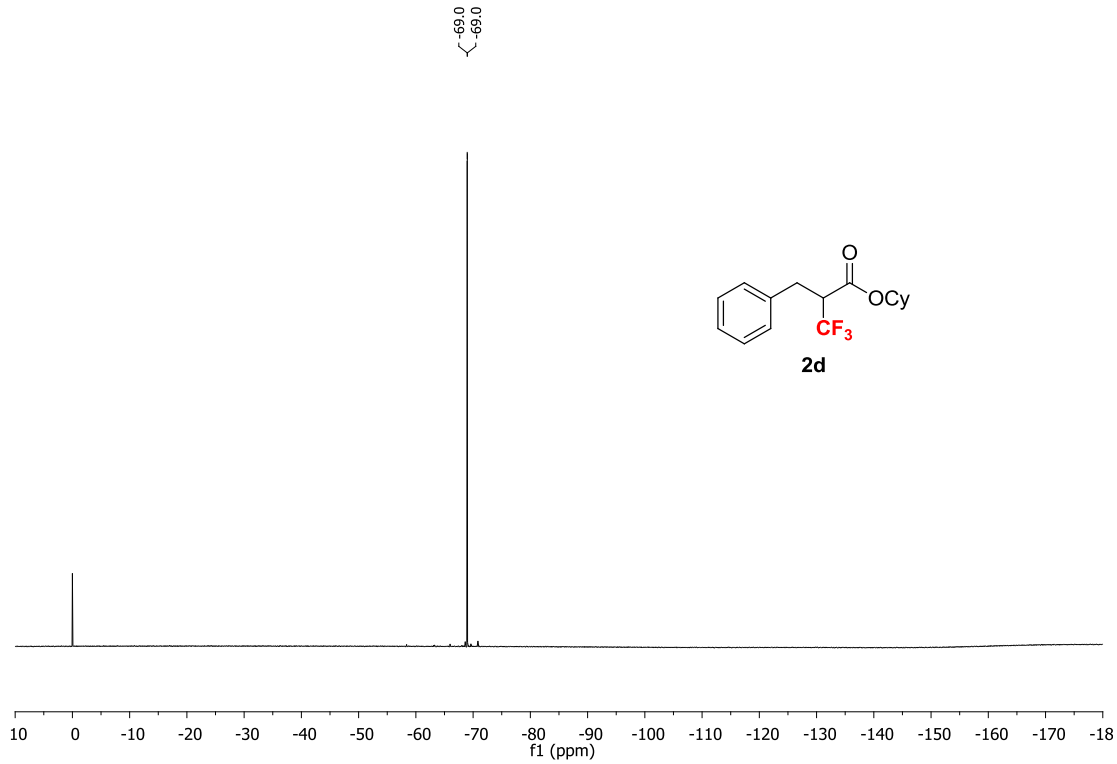

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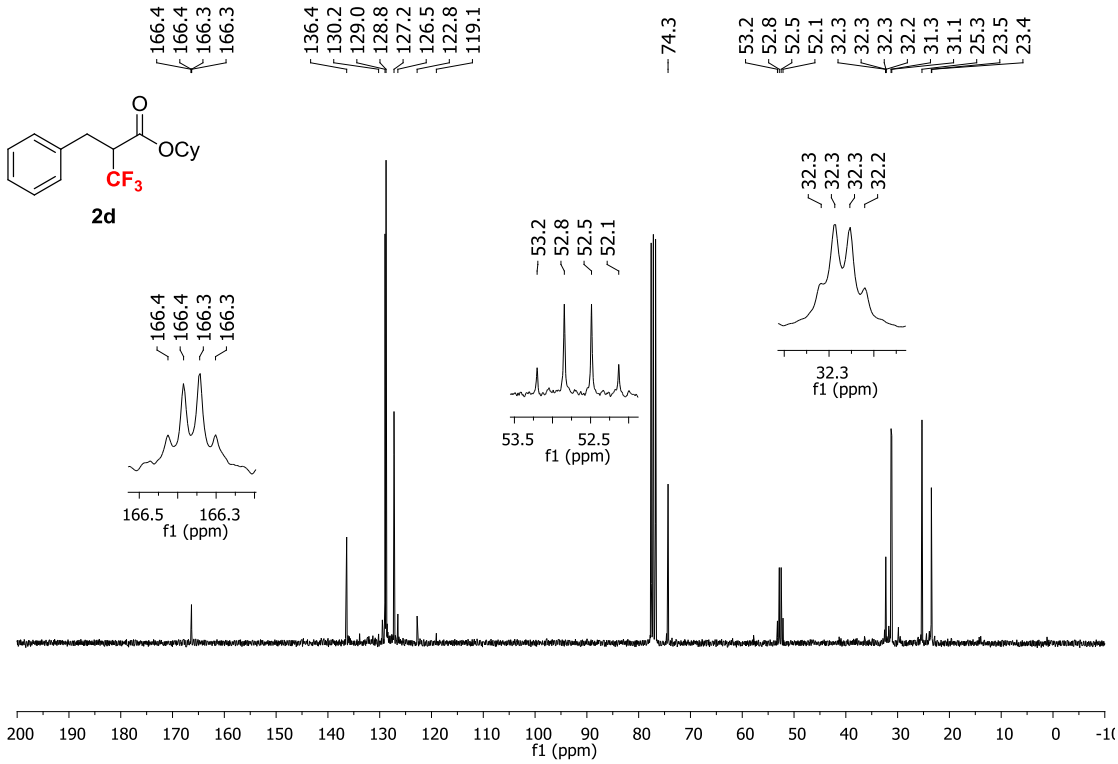

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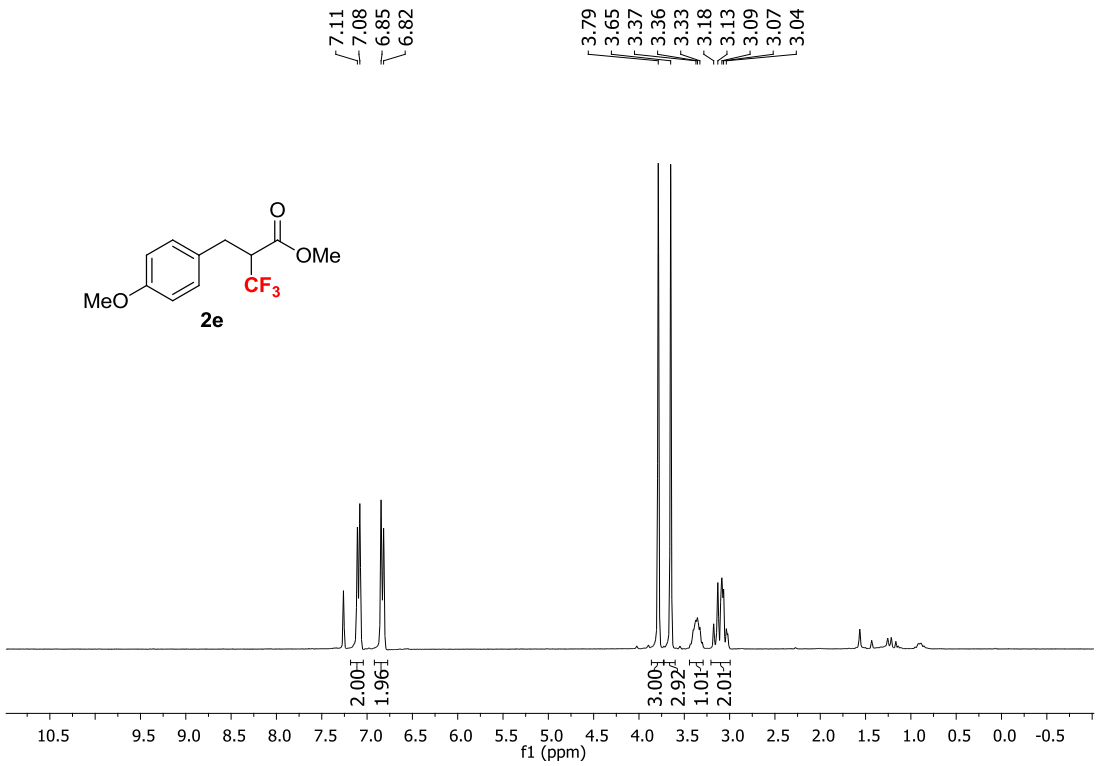

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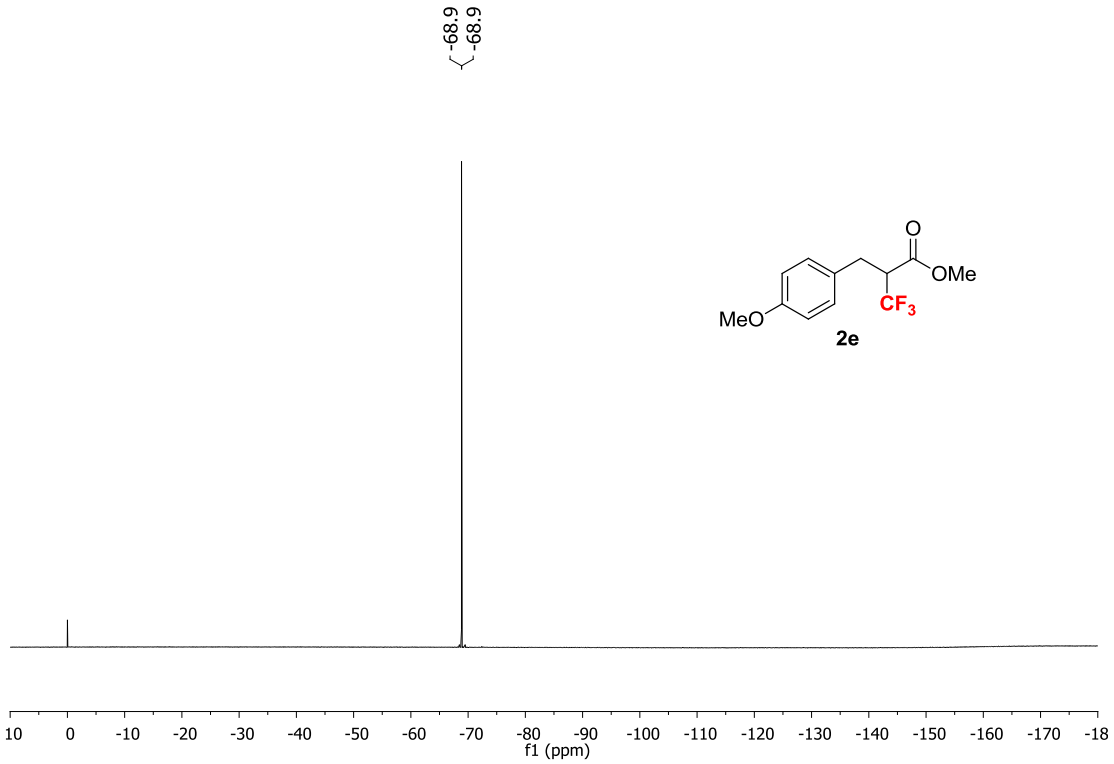

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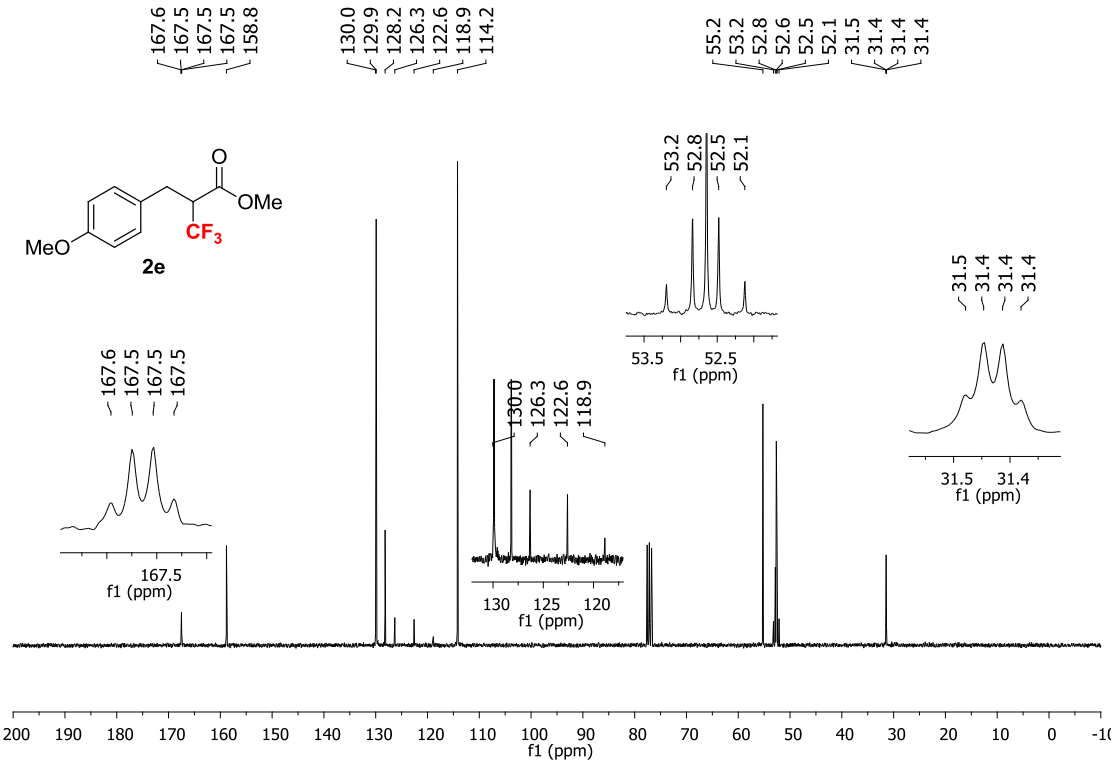

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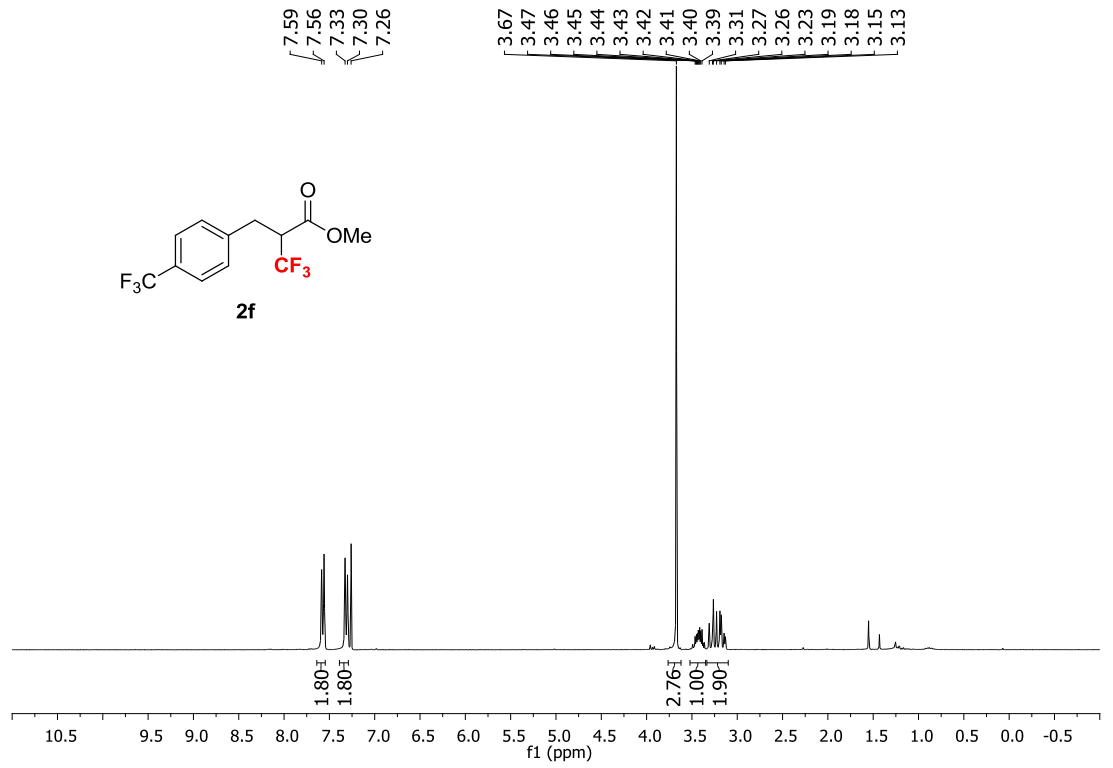

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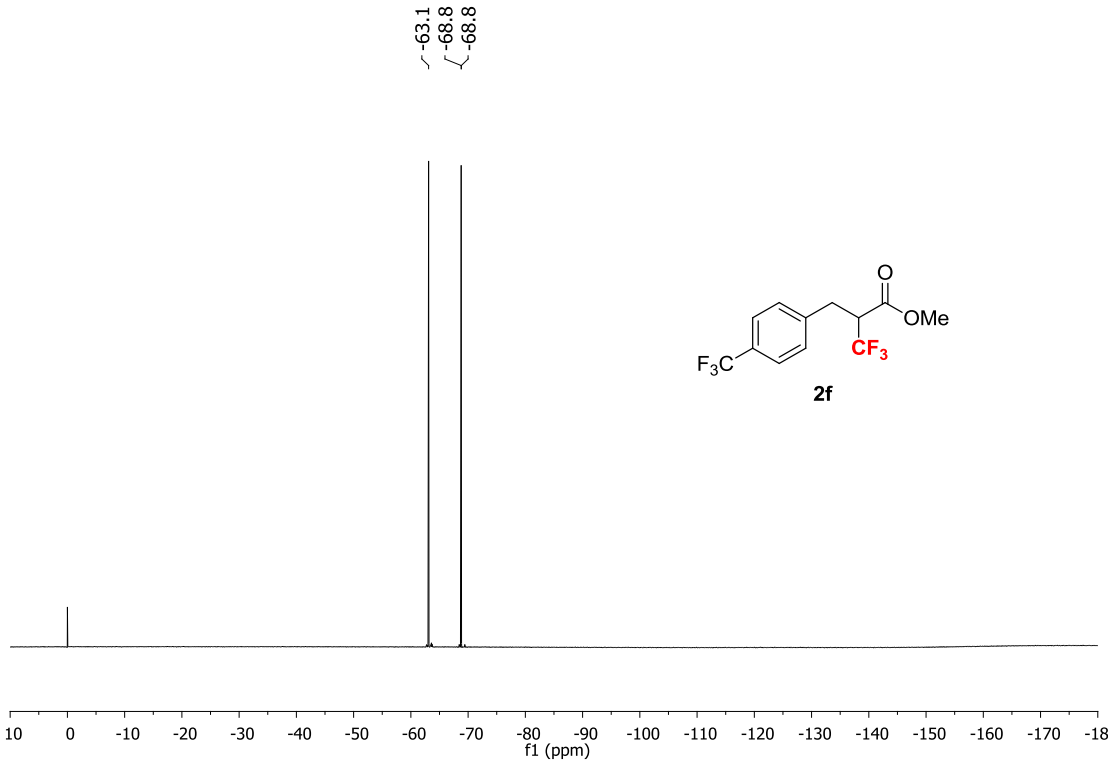

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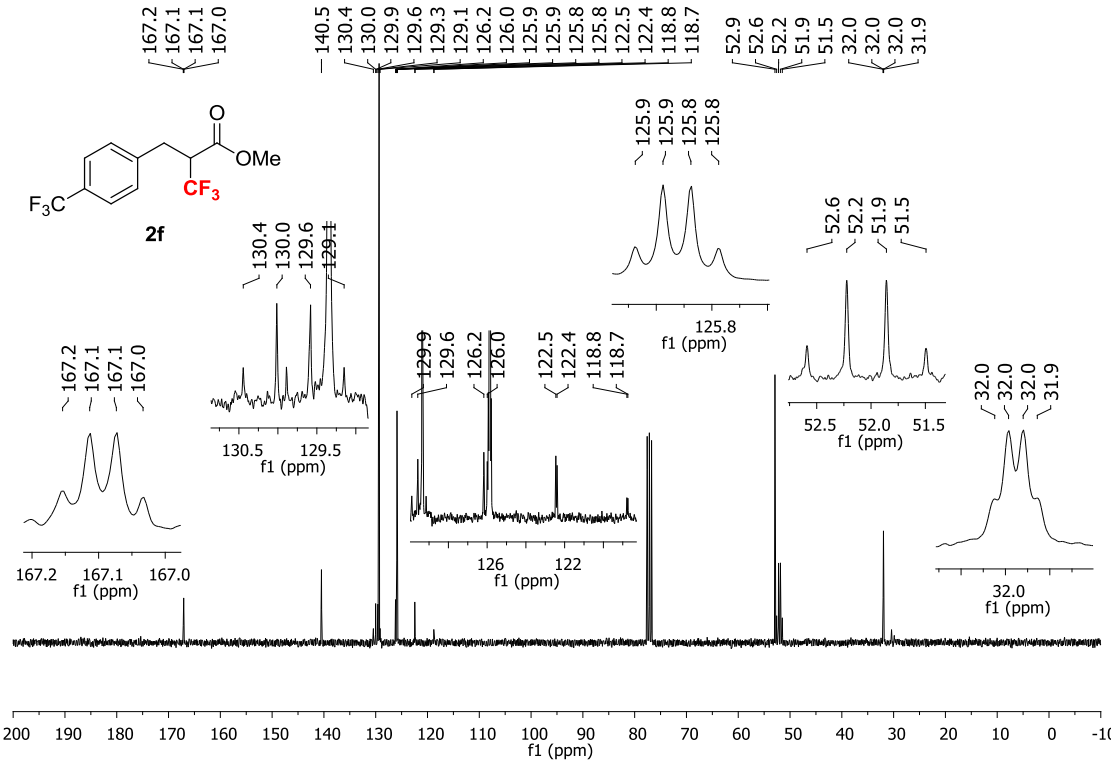

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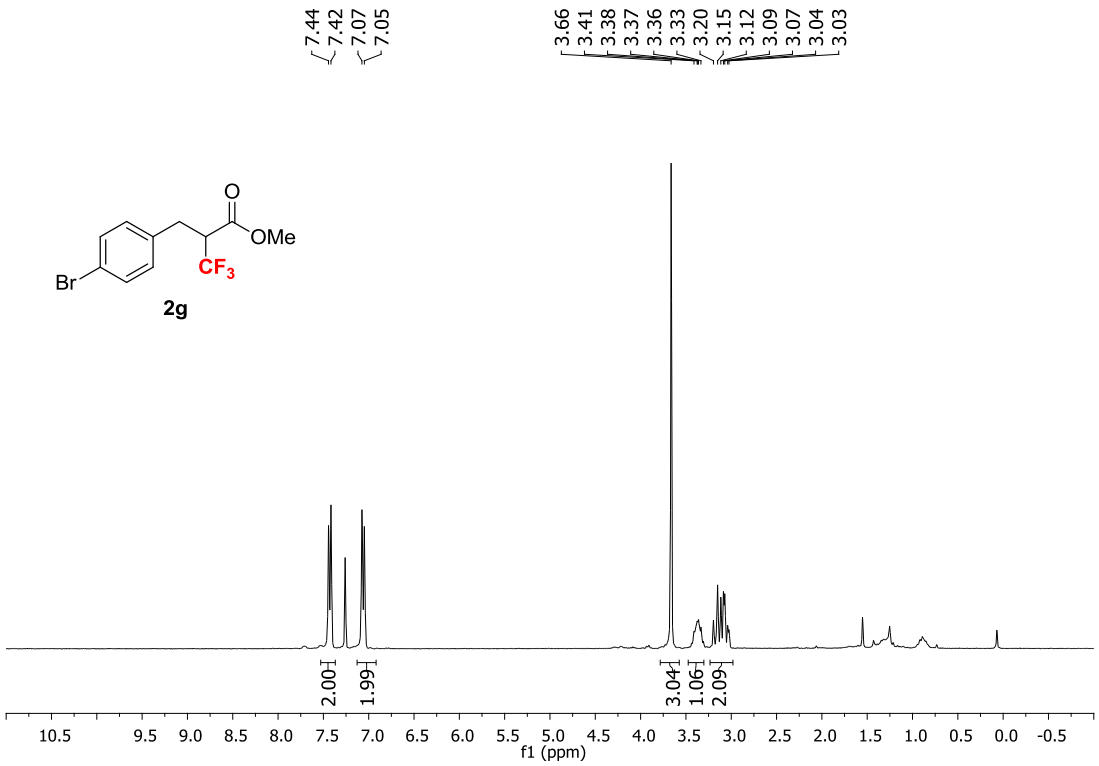

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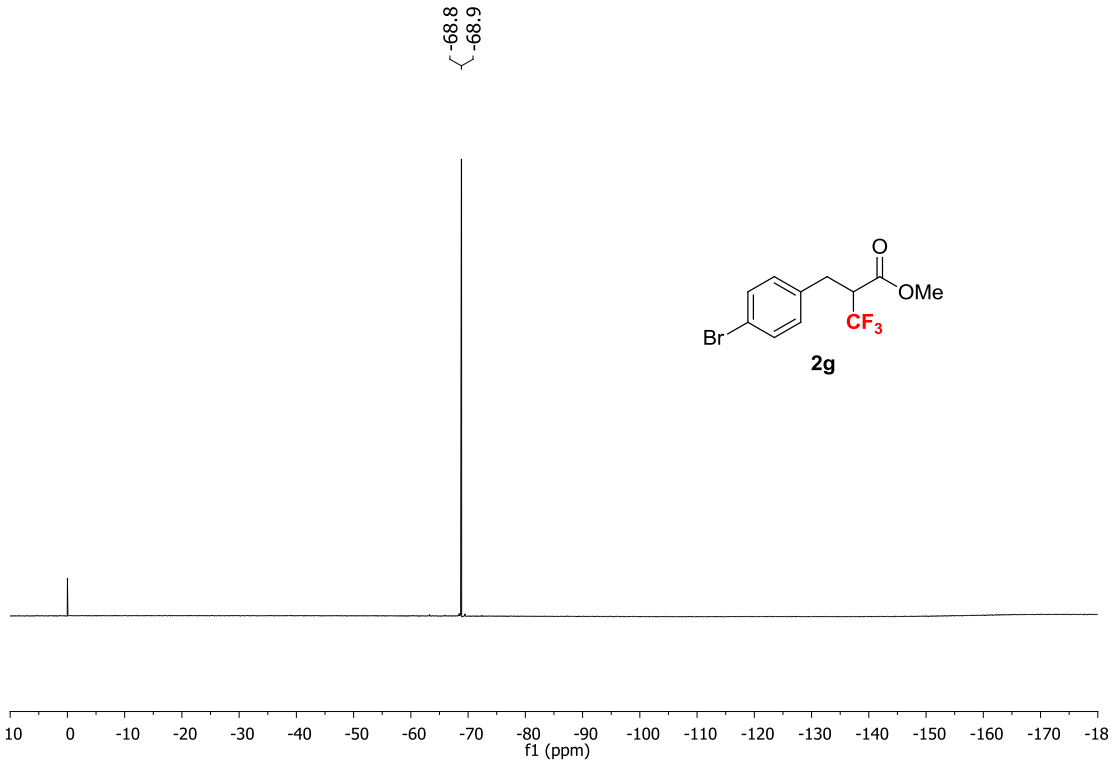

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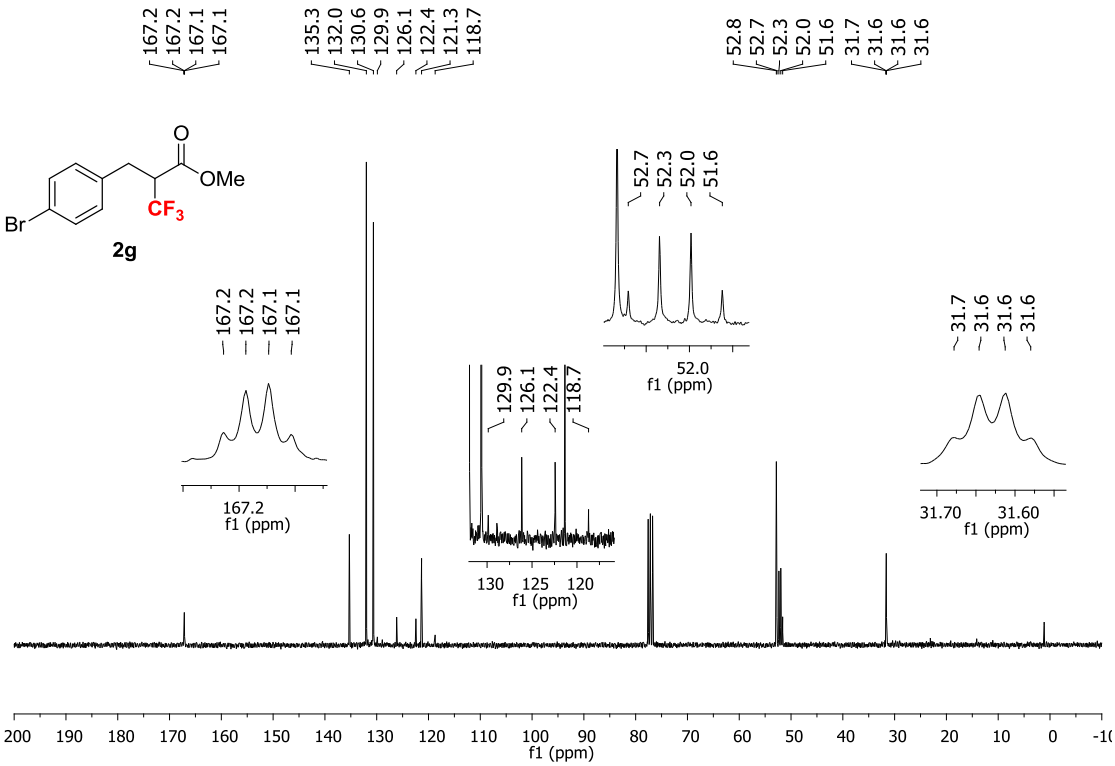

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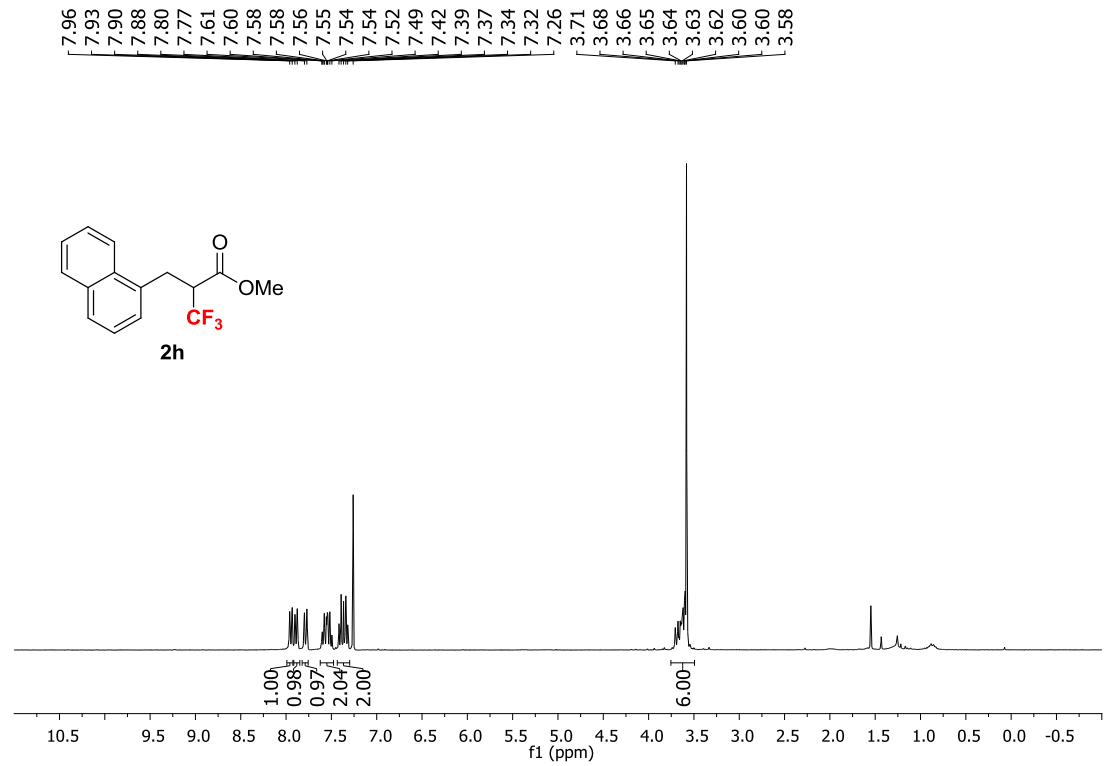

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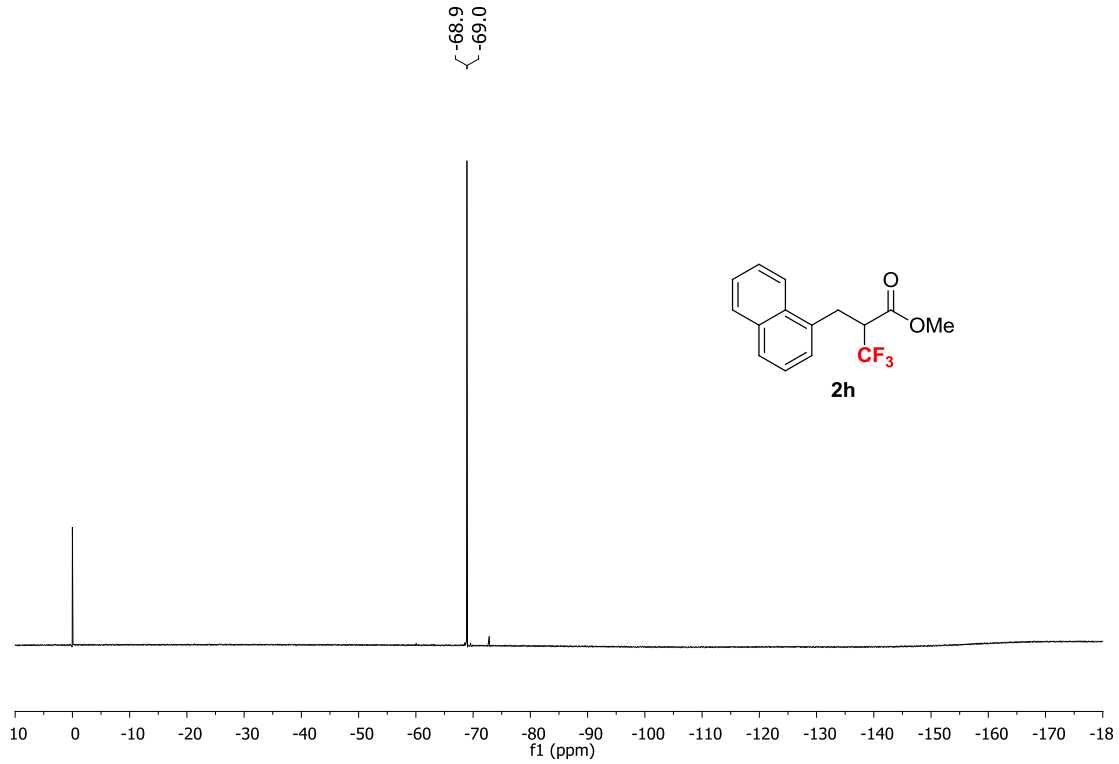

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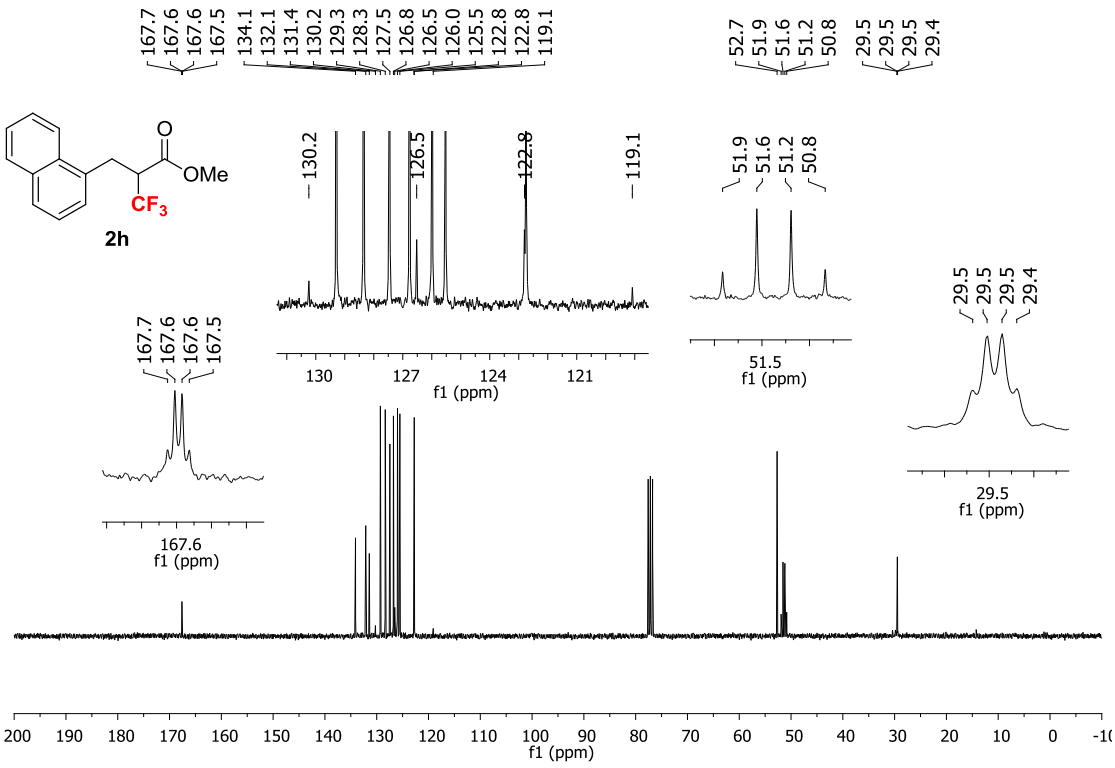

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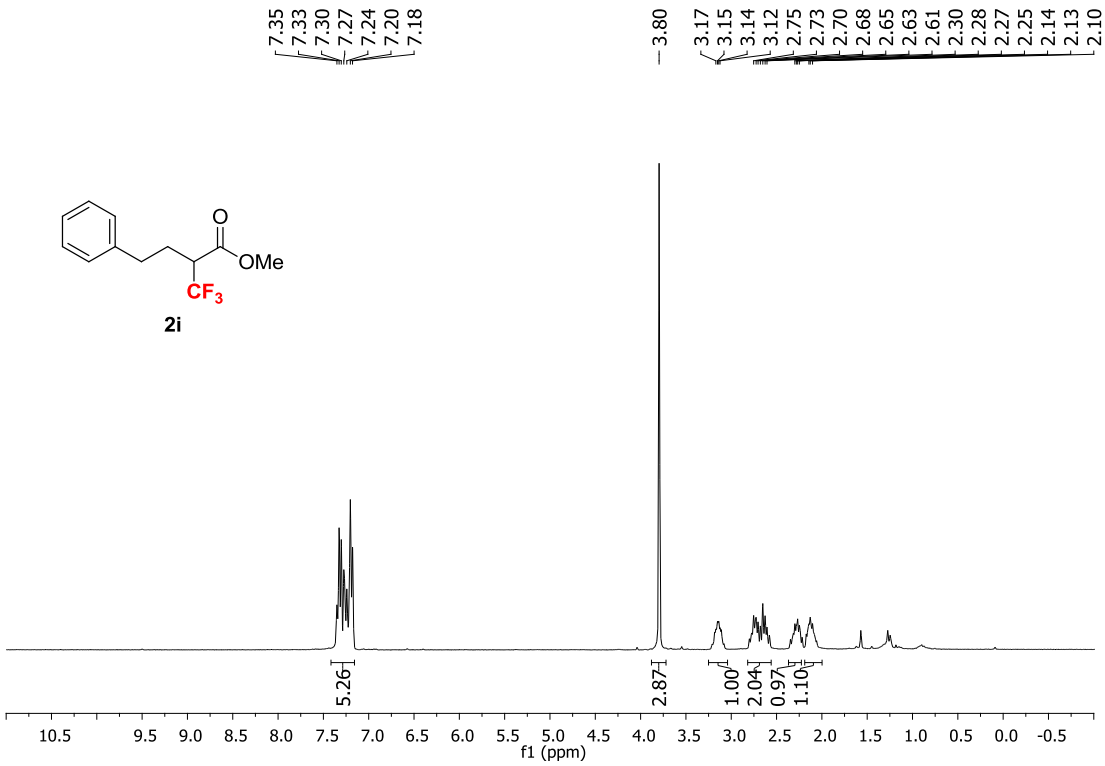

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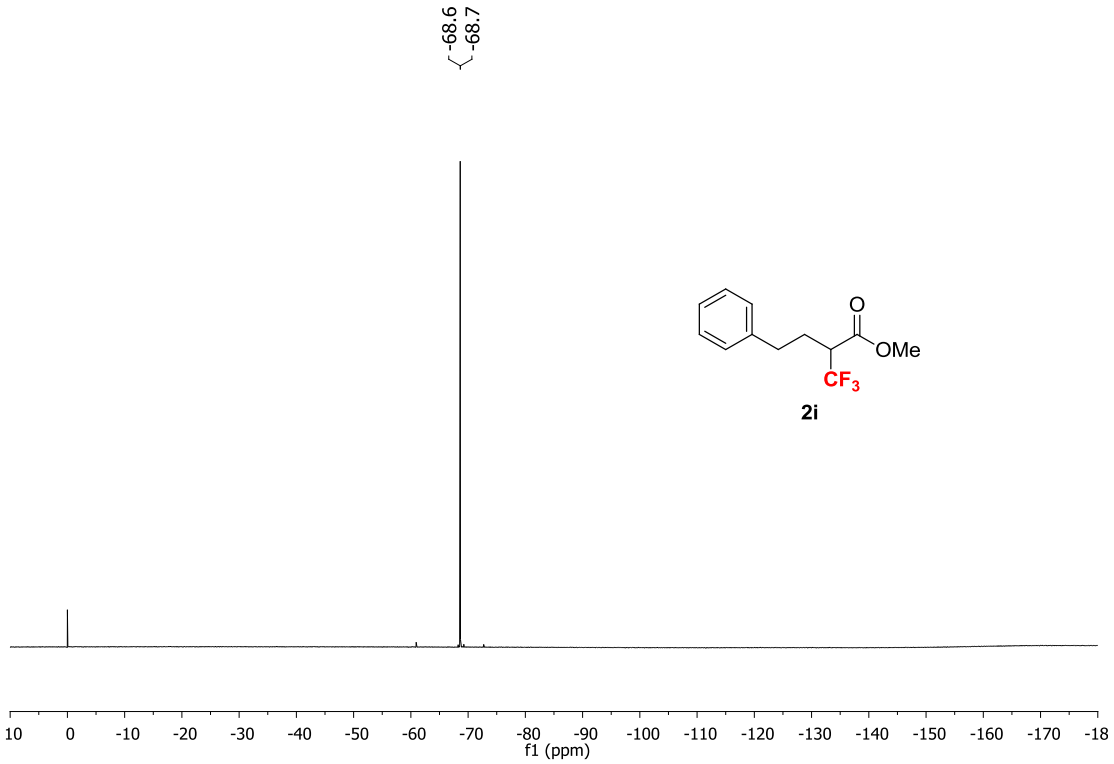
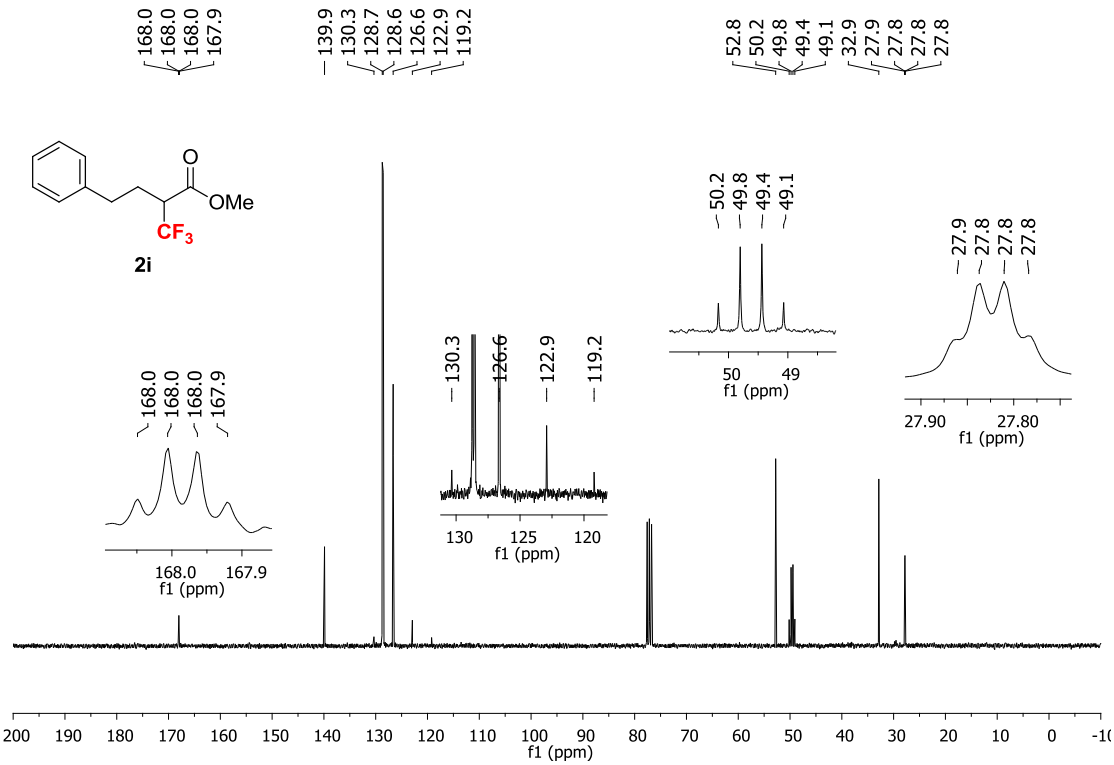
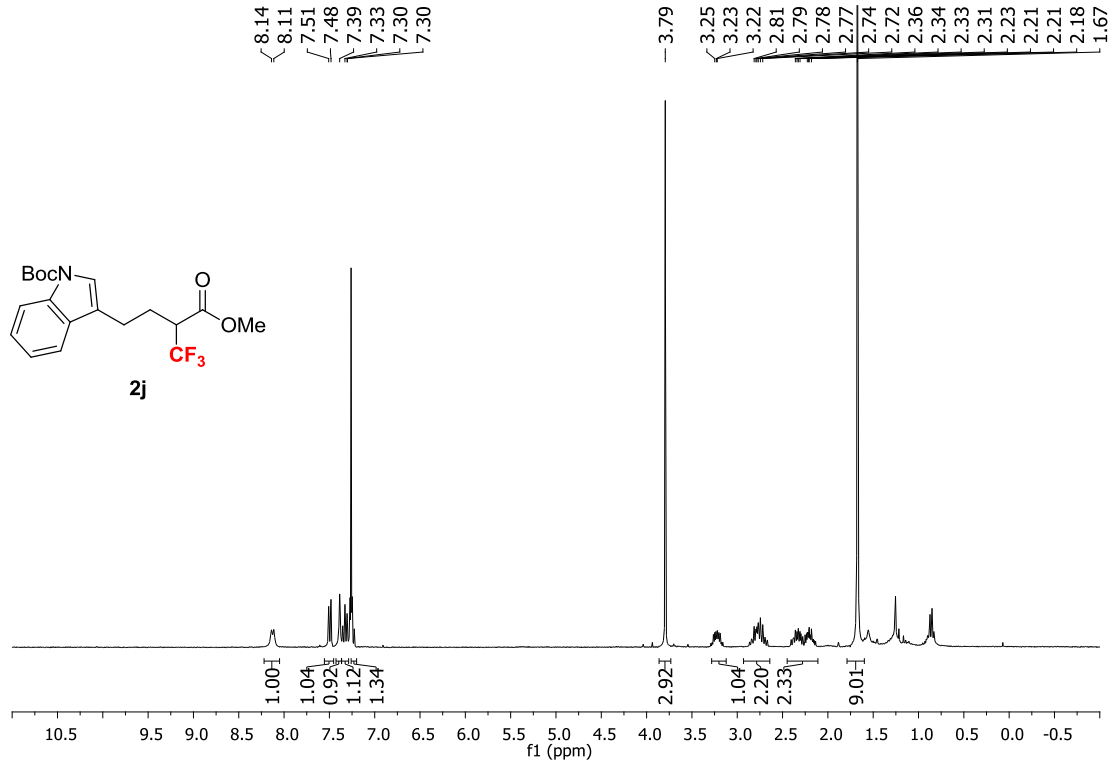


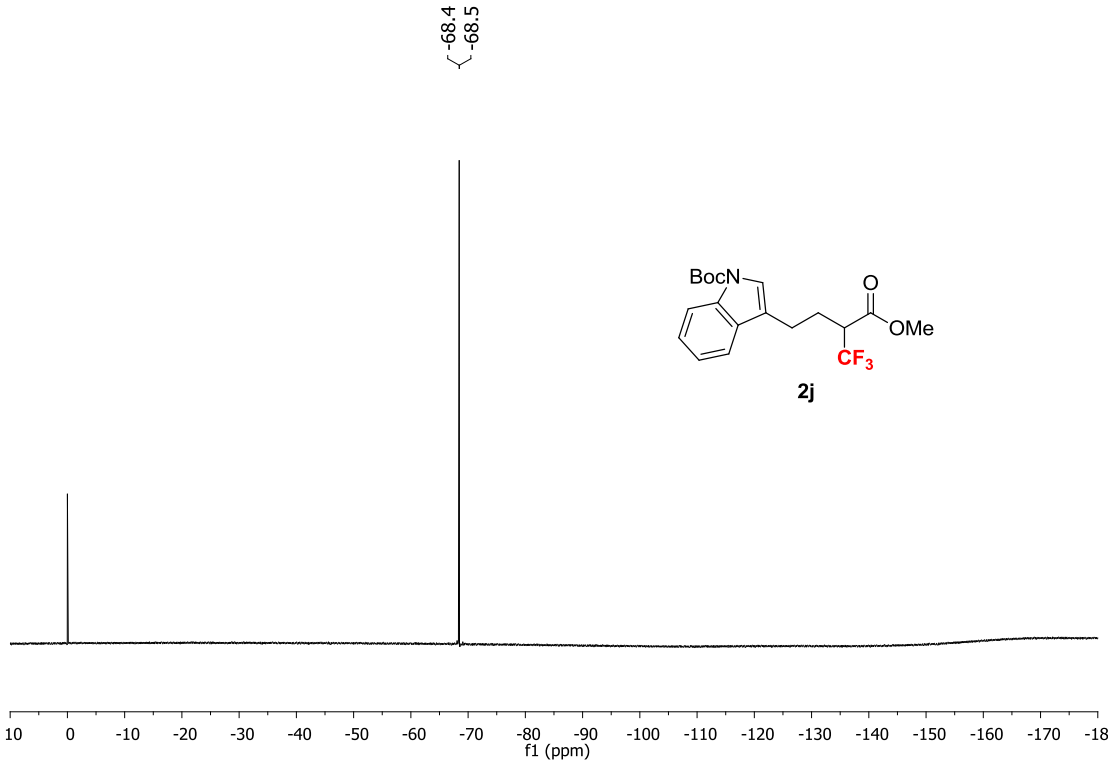
^{13}C NMR Spectrum ($CDCl_3$, 75 MHz)



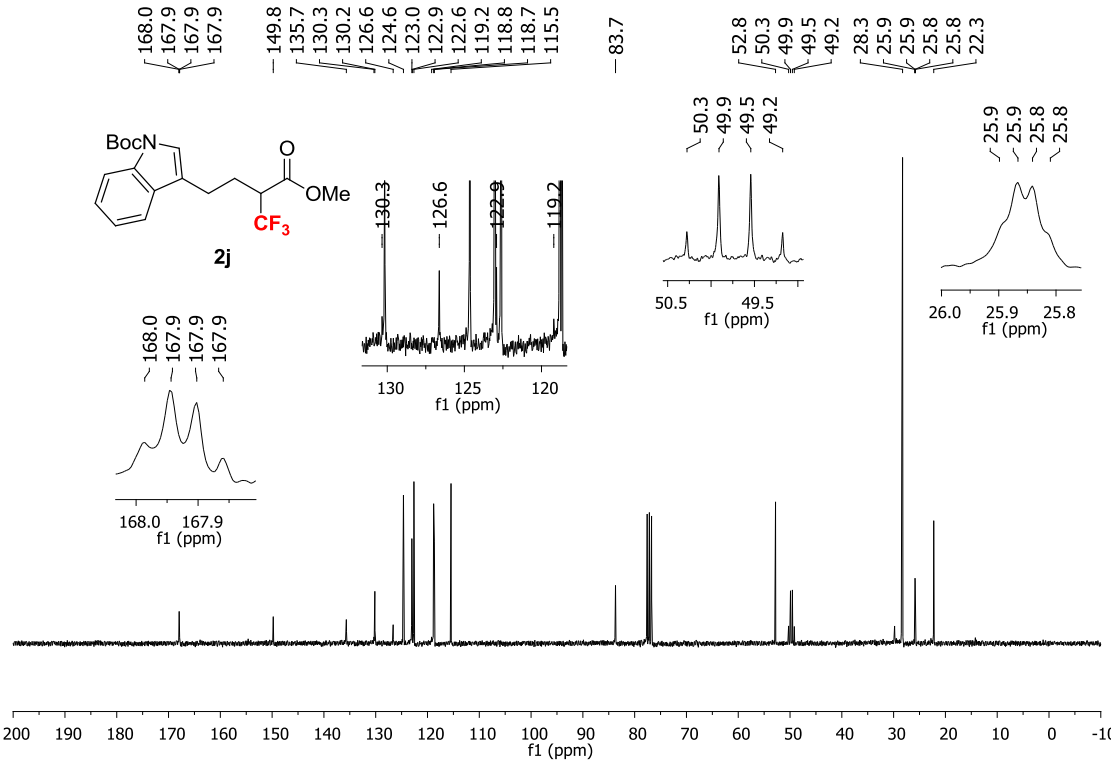
^{1}H NMR Spectrum ($CDCl_3$, 300 MHz)



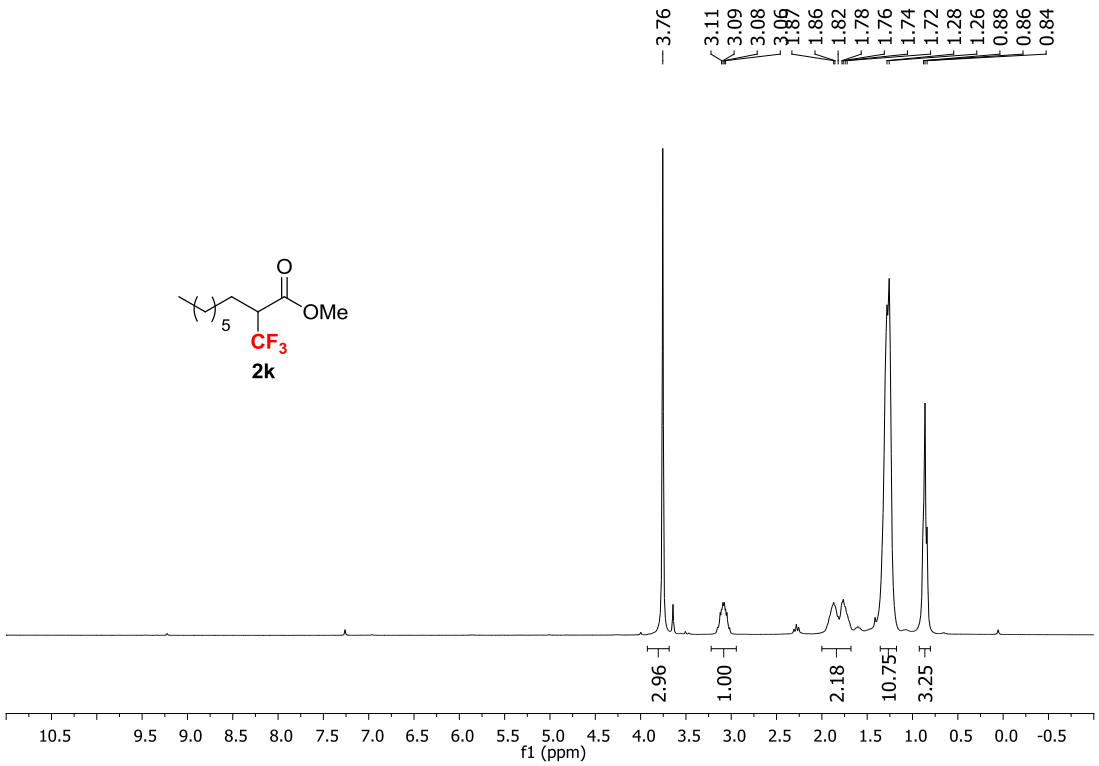
^{19}F NMR Spectrum ($CDCl_3$, 282 MHz)



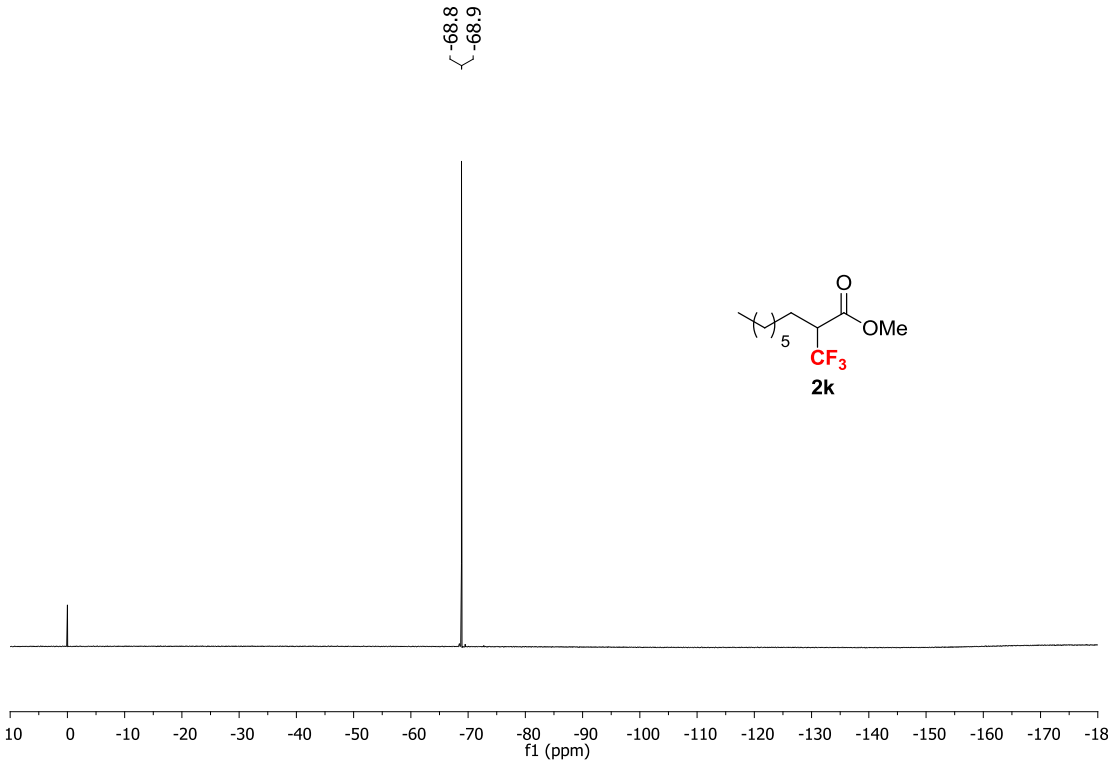
^{13}C NMR Spectrum ($CDCl_3$, 75 MHz)



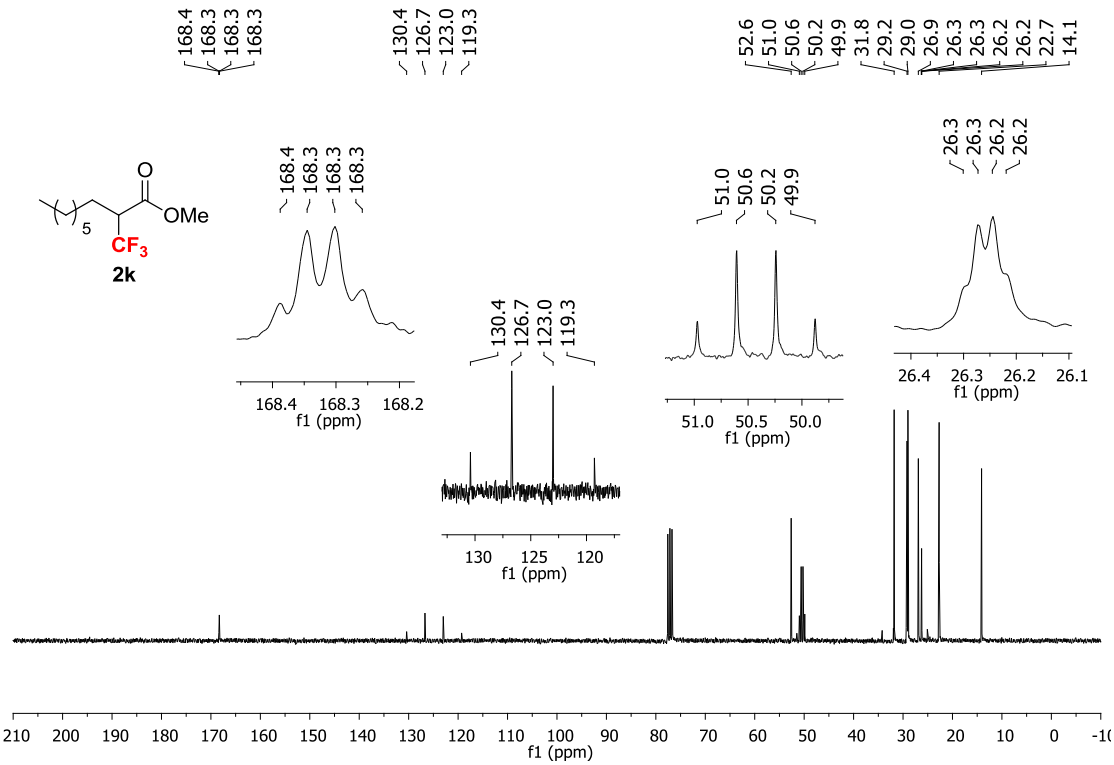
^{1}H NMR Spectrum ($CDCl_3$, 300 MHz)



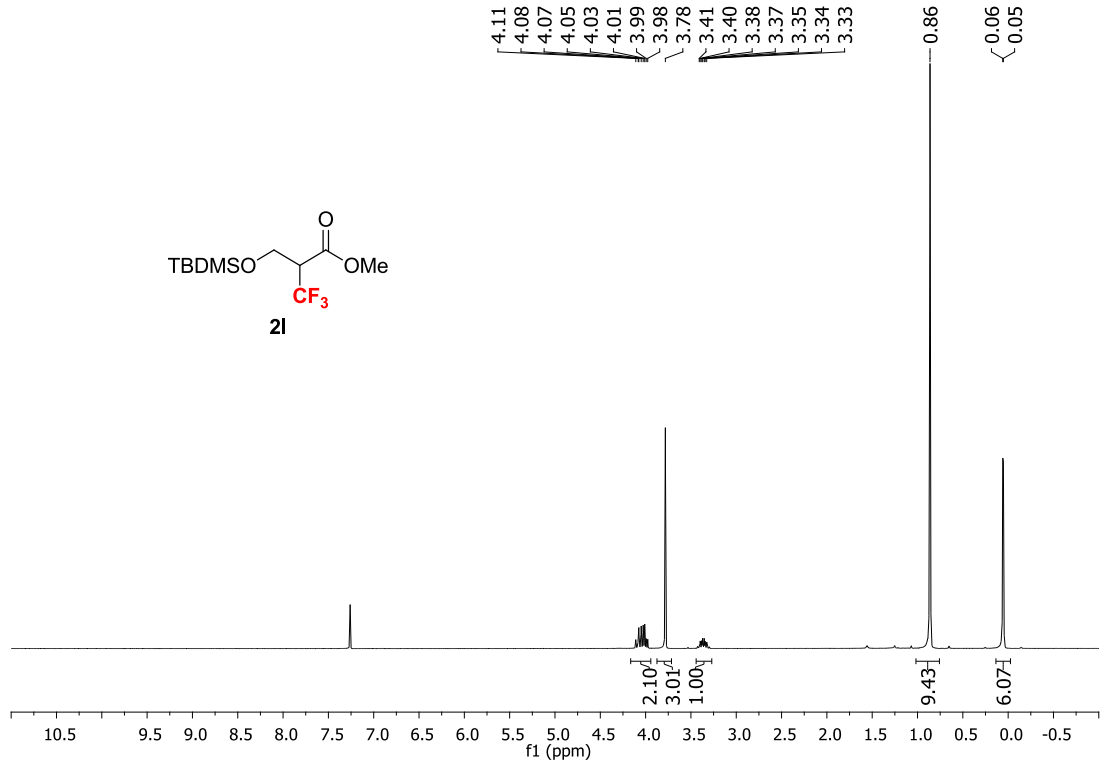
^{19}F NMR Spectrum ($CDCl_3$, 282 MHz)



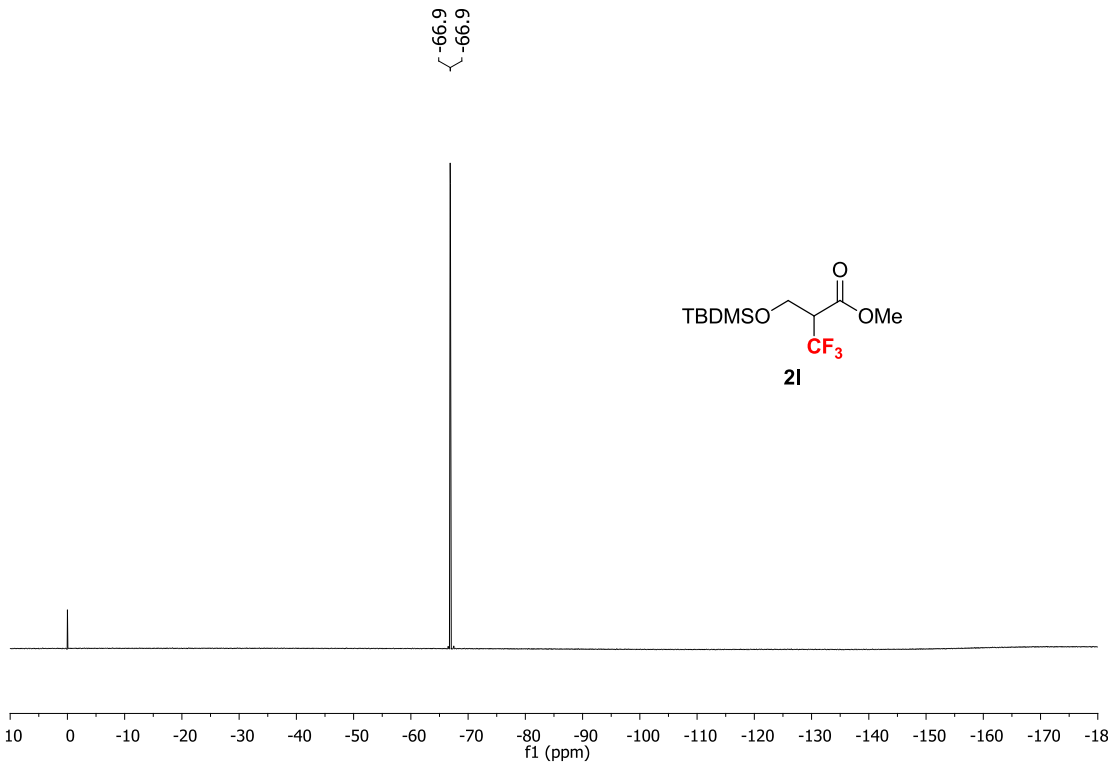
^{13}C NMR Spectrum ($CDCl_3$, 75 MHz)



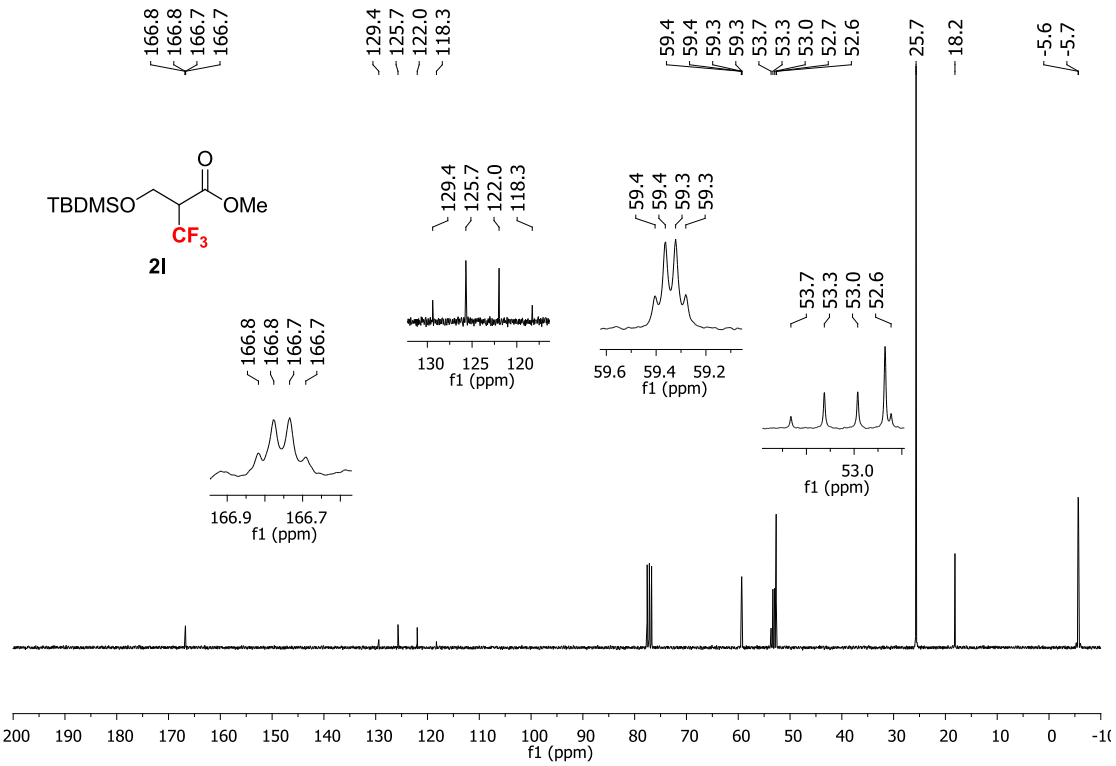
^{1}H NMR Spectrum ($CDCl_3$, 300 MHz)



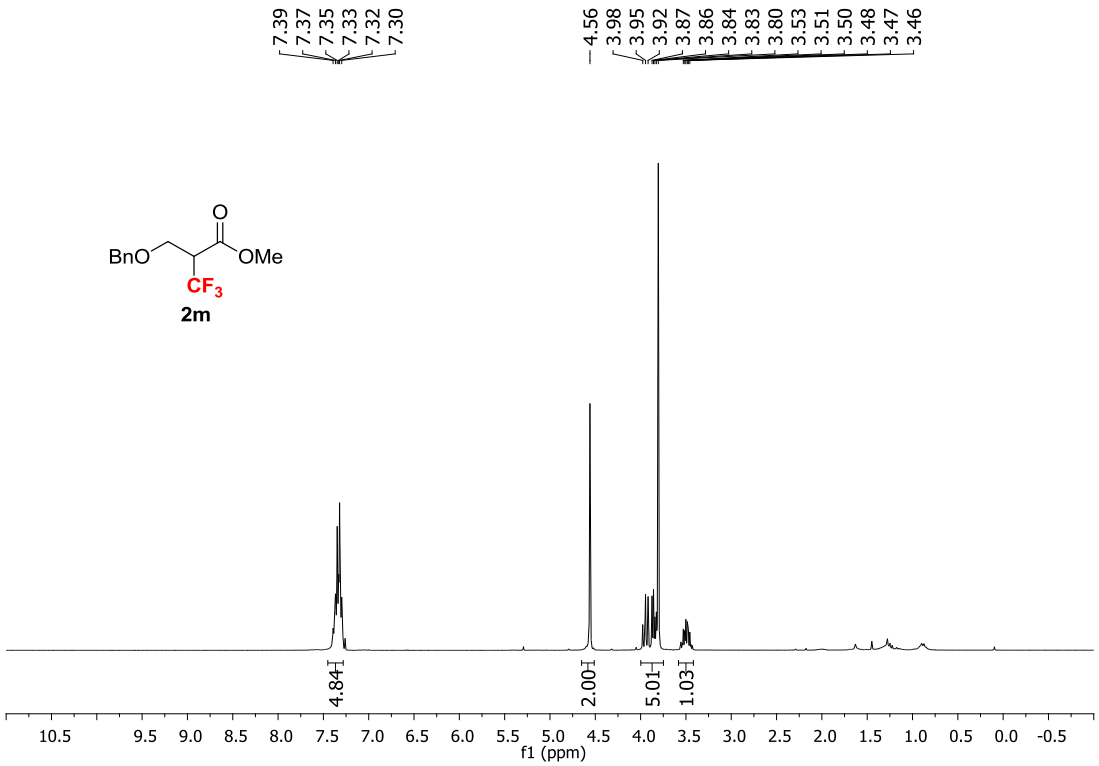
^{19}F NMR Spectrum ($CDCl_3$, 282 MHz)



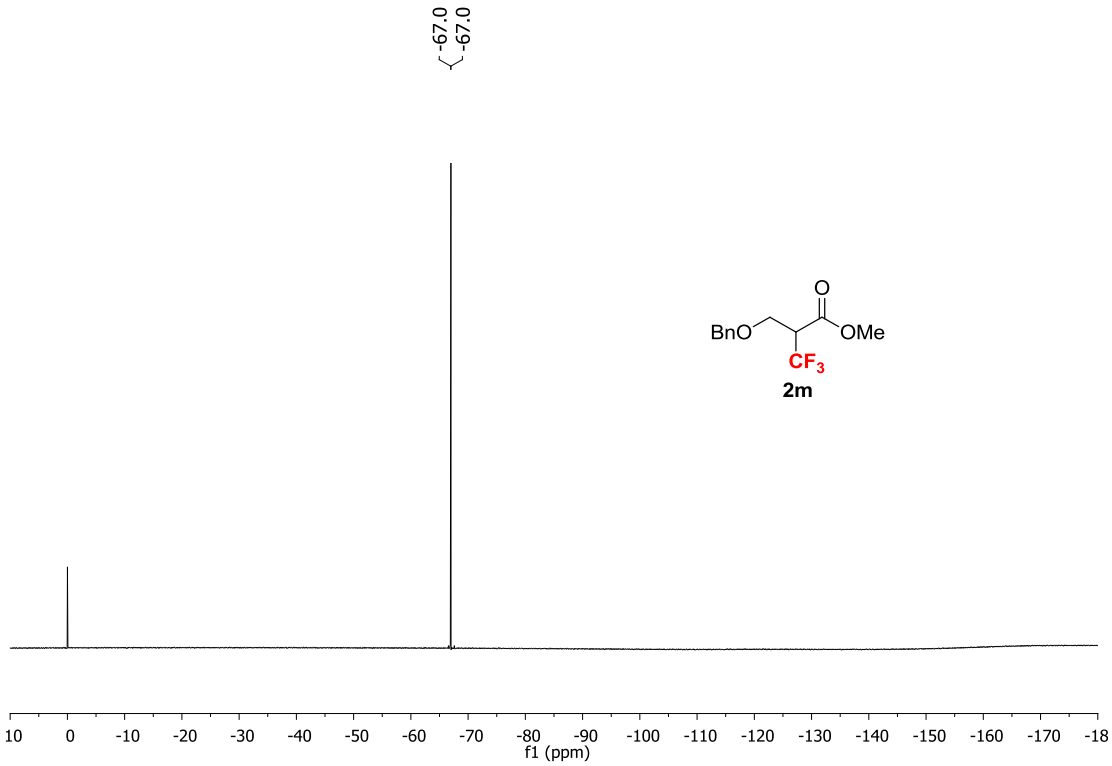
^{13}C NMR Spectrum ($CDCl_3$, 75 MHz)



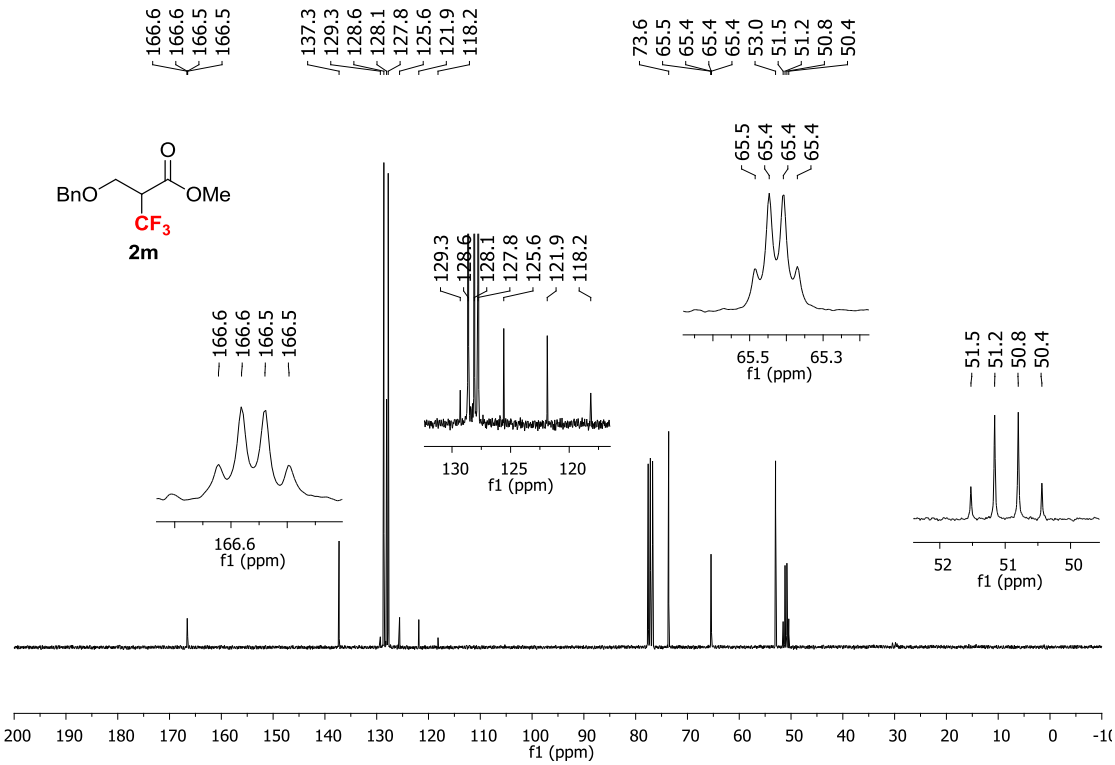
^{1}H NMR Spectrum ($CDCl_3$, 300 MHz)



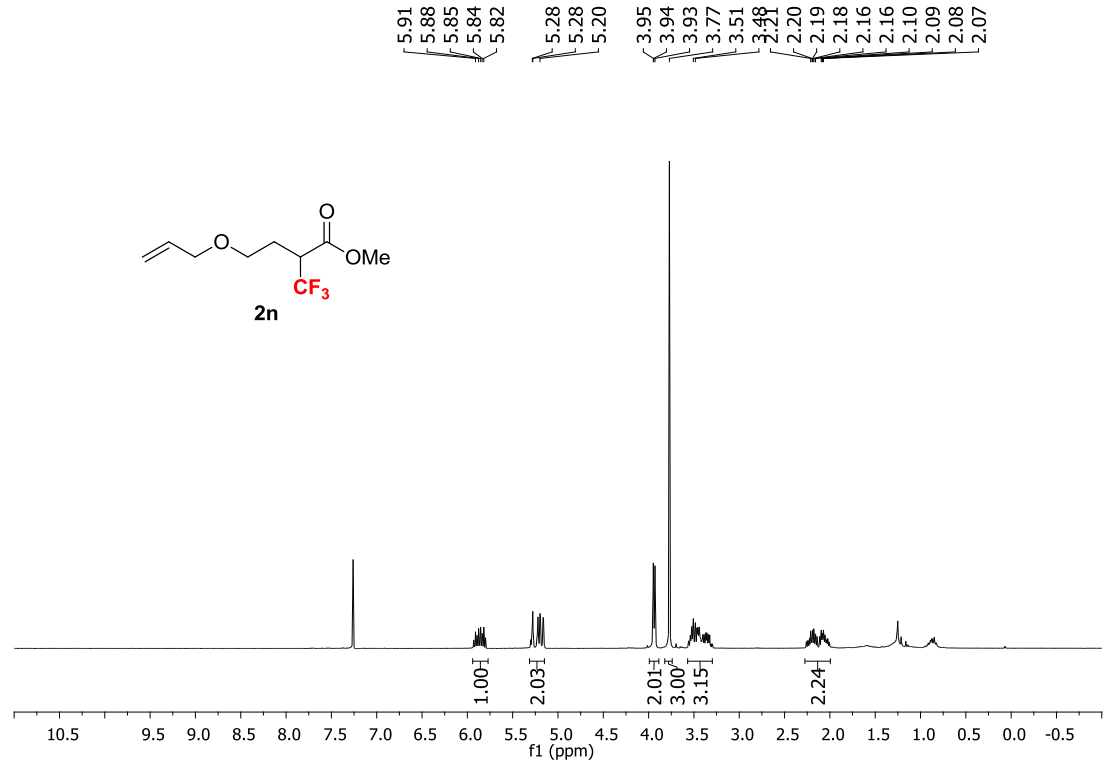
^{19}F NMR Spectrum ($CDCl_3$, 282 MHz)



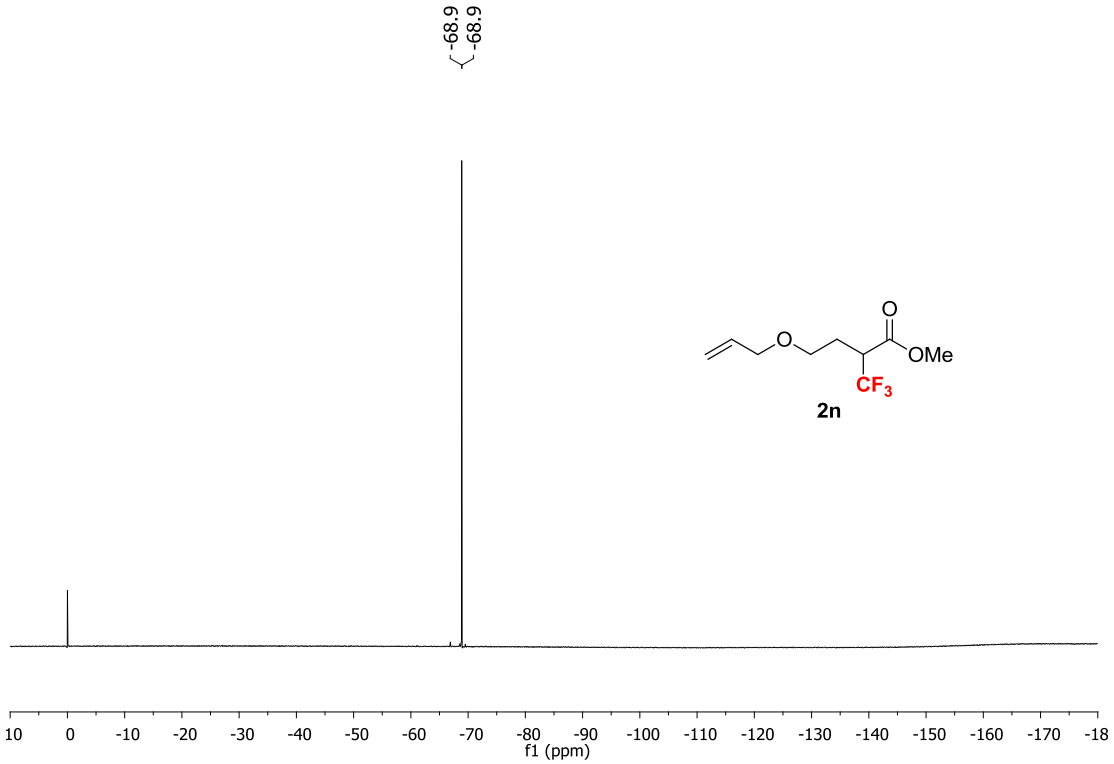
^{13}C NMR Spectrum ($CDCl_3$, 75 MHz)



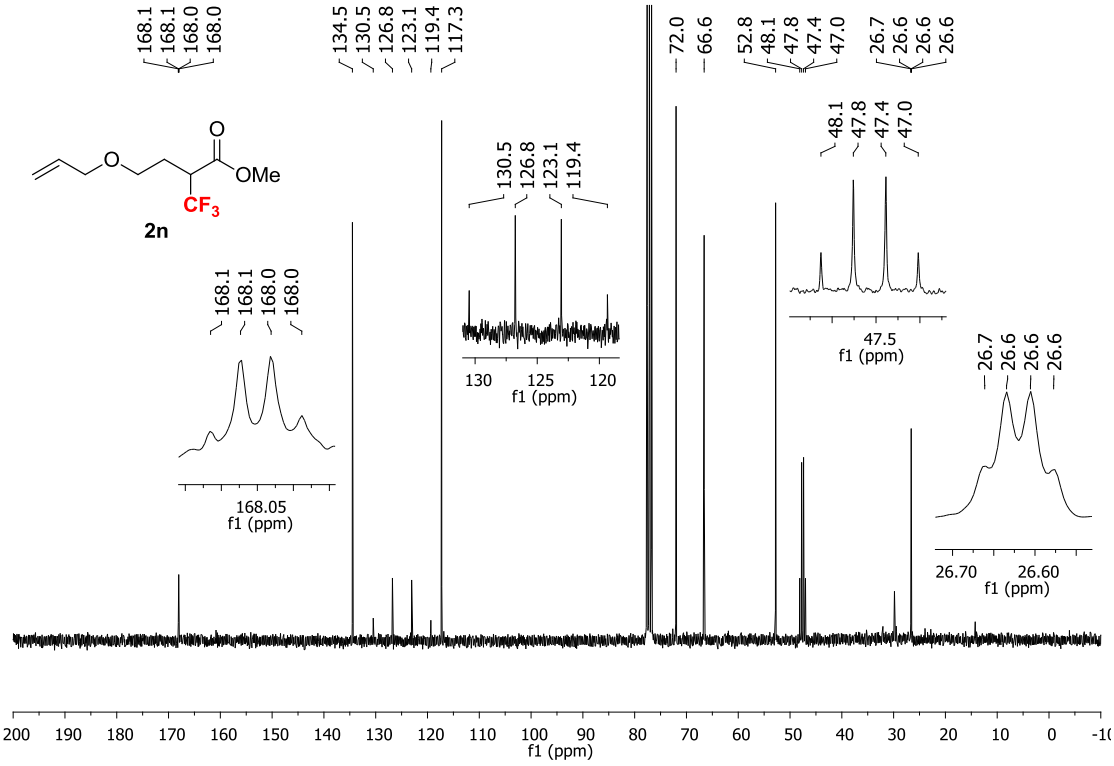
^{1}H NMR Spectrum ($CDCl_3$, 300 MHz)



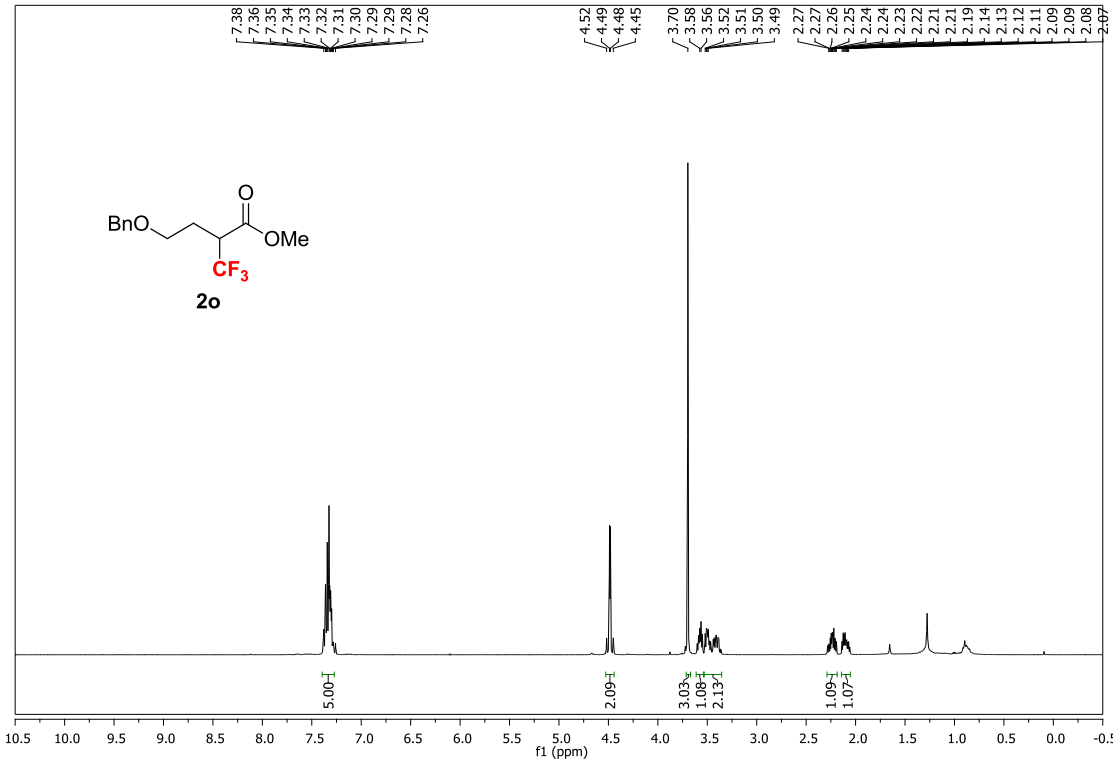
^{19}F NMR Spectrum ($CDCl_3$, 282 MHz)



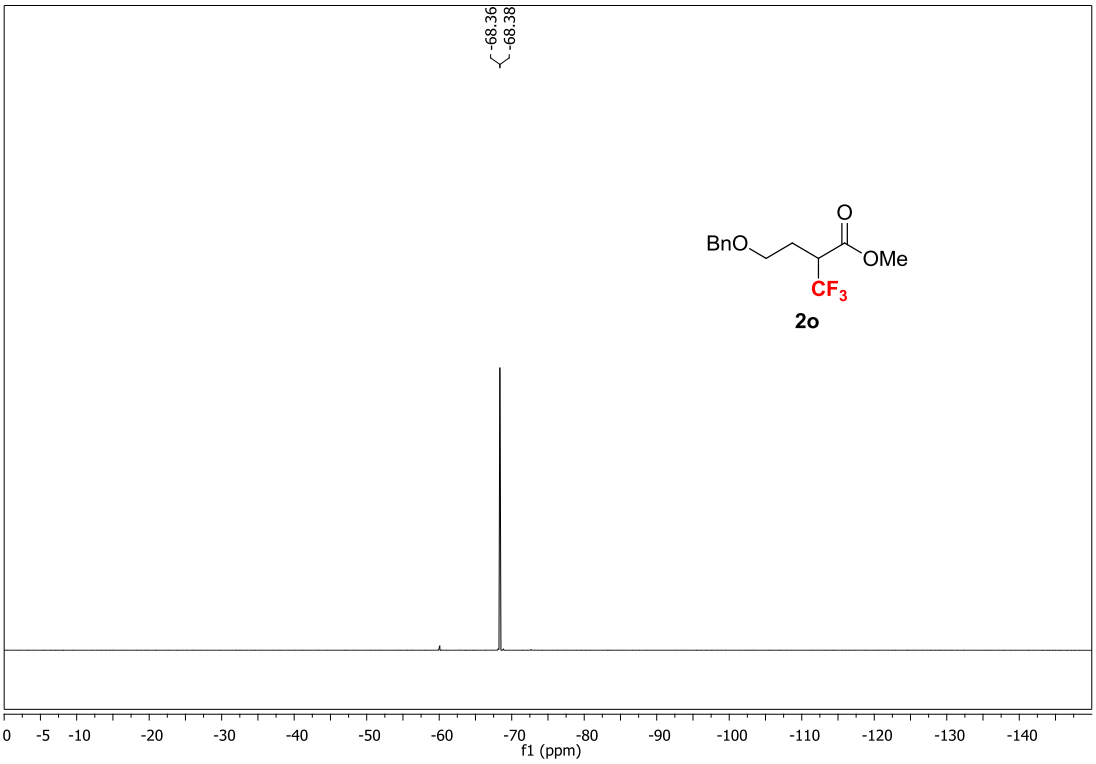
^{13}C NMR Spectrum ($CDCl_3$, 75 MHz)



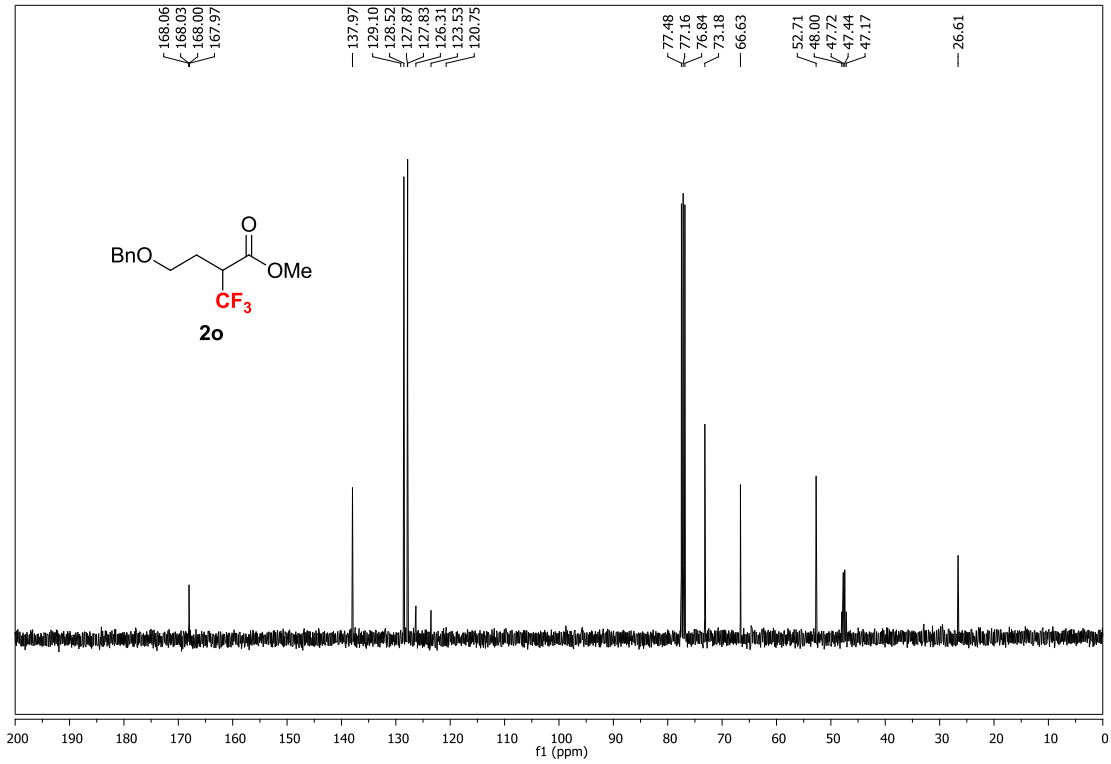
^{1}H NMR Spectrum ($CDCl_3$, 400 MHz)



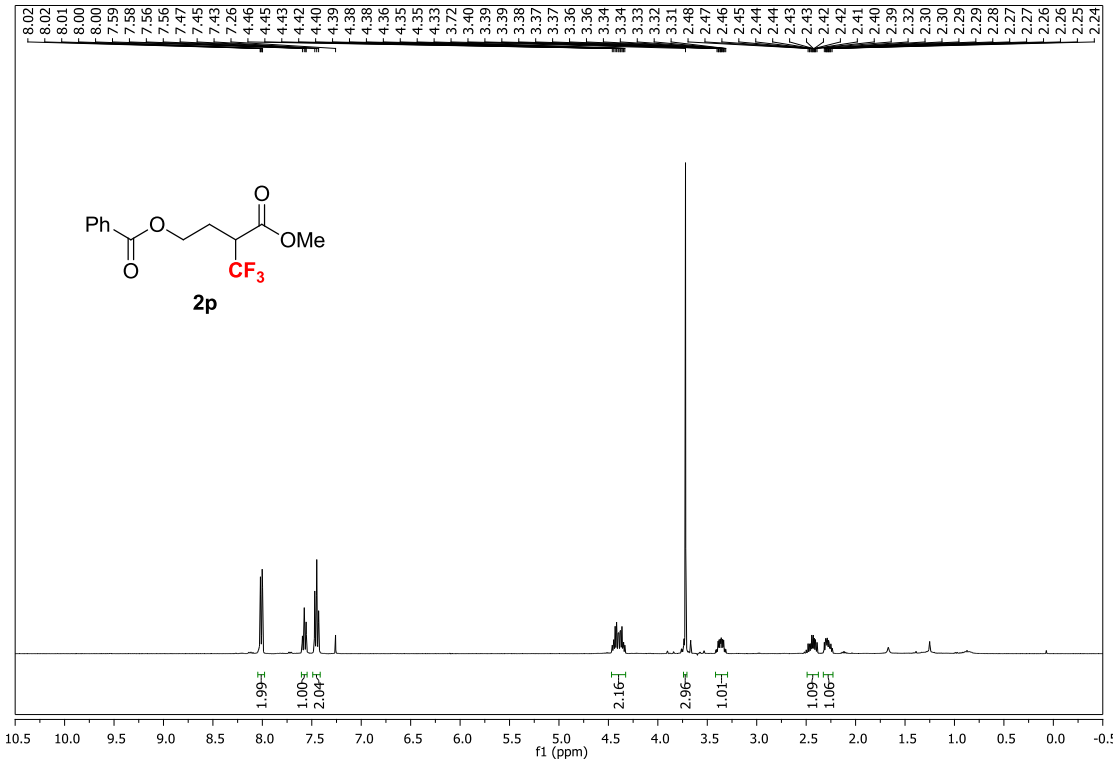
^{19}F NMR Spectrum ($CDCl_3$, 376 MHz)



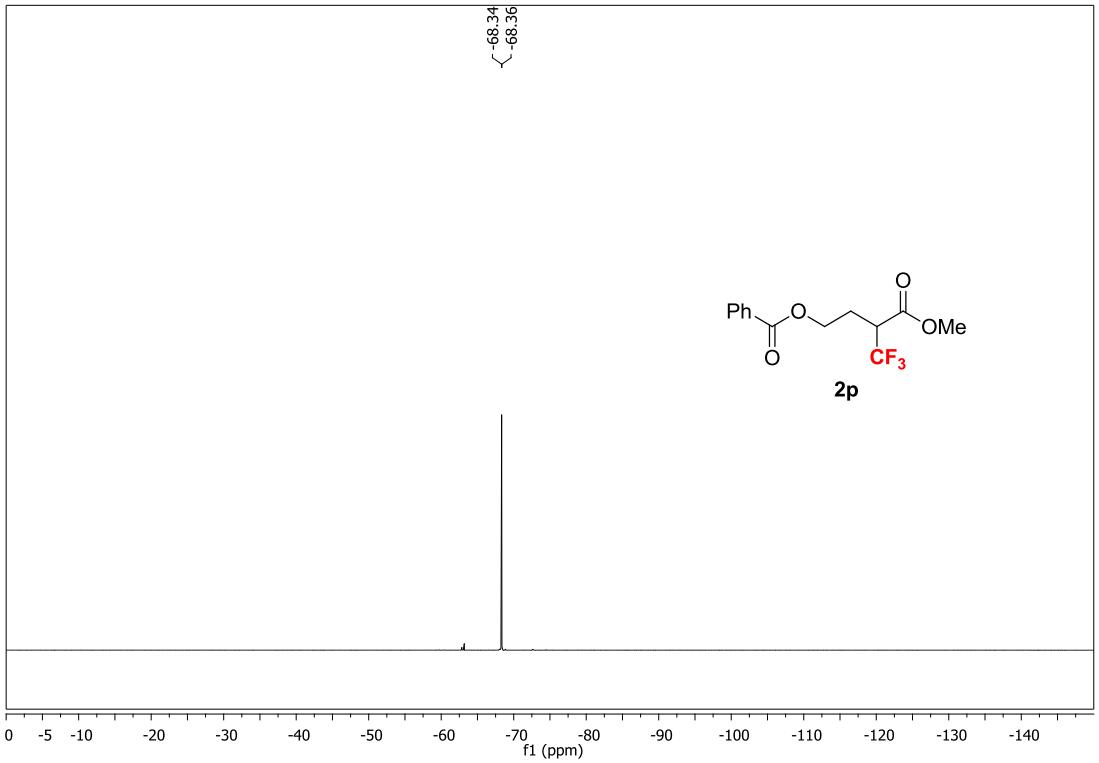
^{13}C NMR Spectrum ($CDCl_3$, 100 MHz)



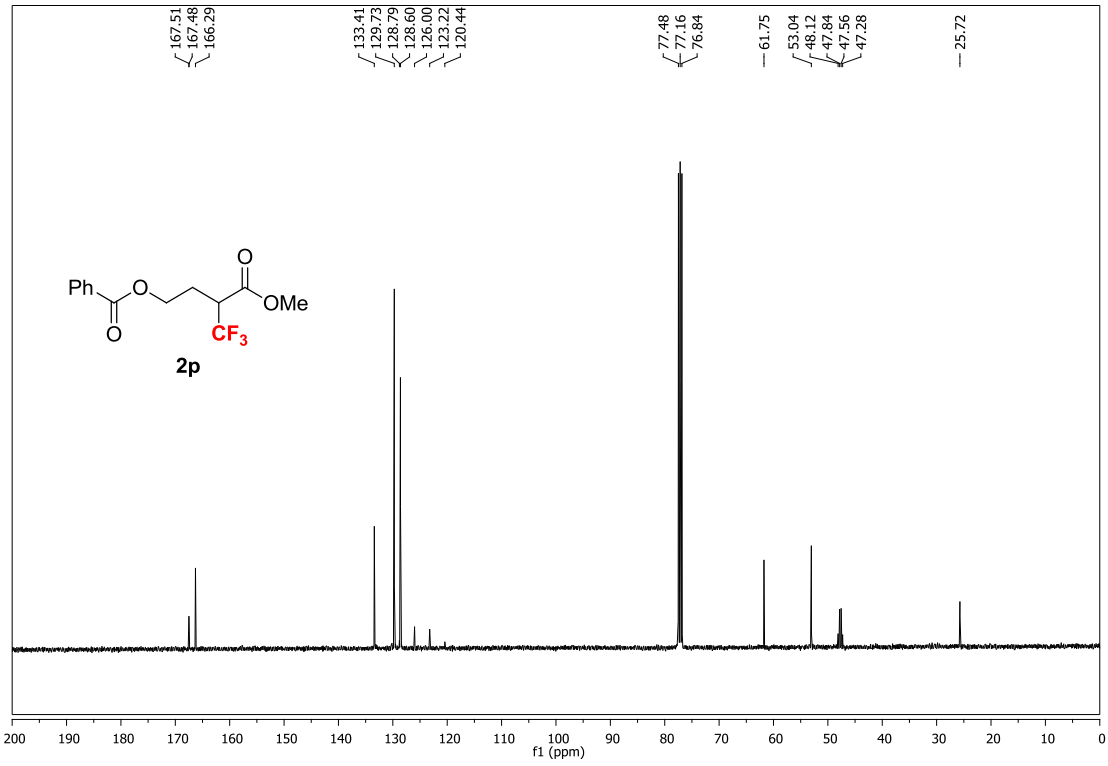
^{1}H NMR Spectrum ($CDCl_3$, 400 MHz)



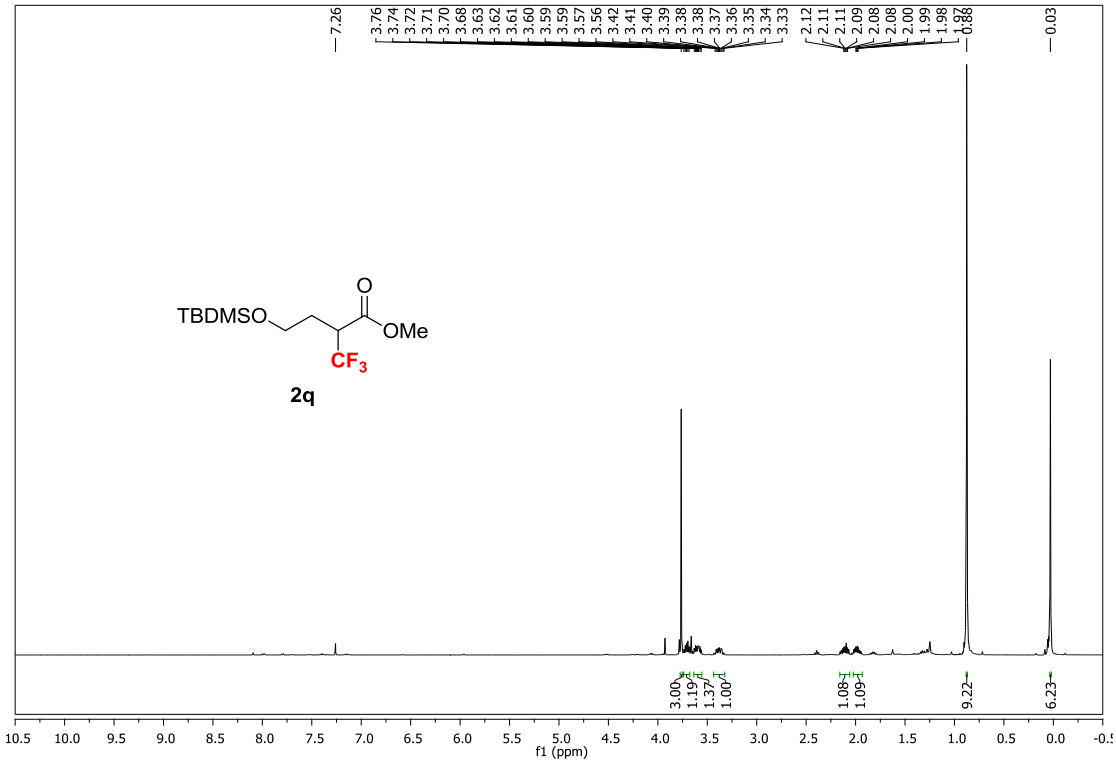
^{19}F NMR Spectrum ($CDCl_3$, 376 MHz)



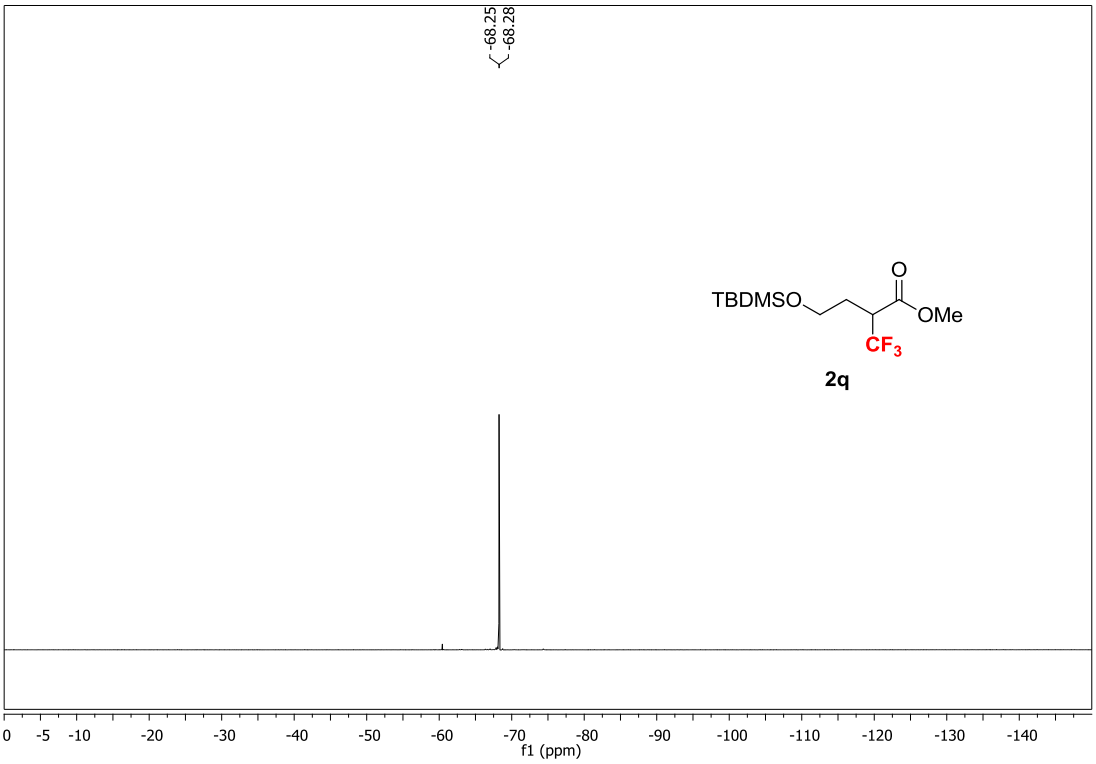
^{13}C NMR Spectrum ($CDCl_3$, 100 MHz)



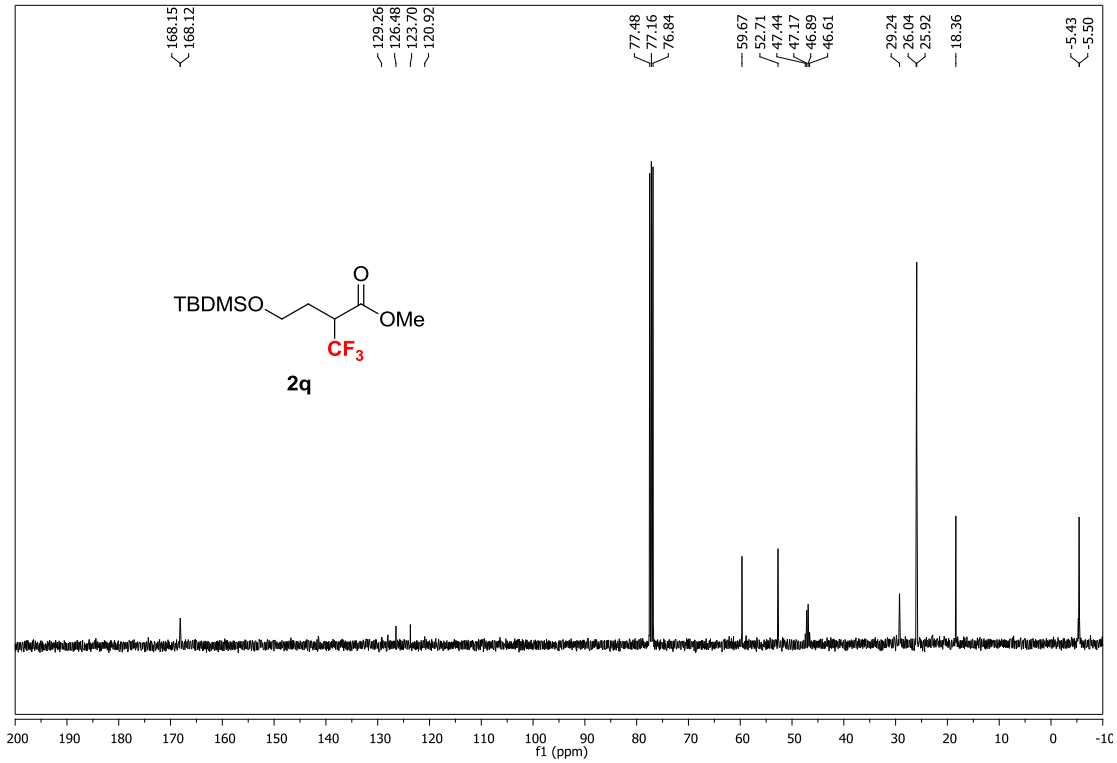
^{1}H NMR Spectrum ($CDCl_3$, 400 MHz)



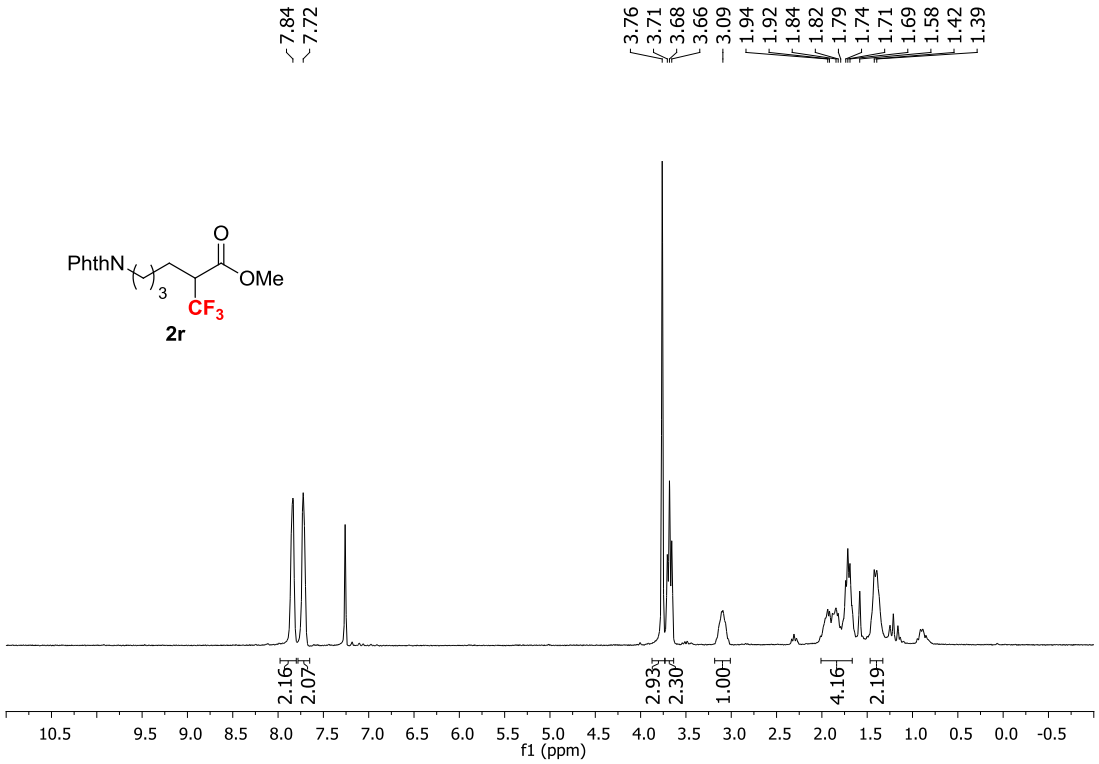
^{19}F NMR Spectrum ($CDCl_3$, 376 MHz)



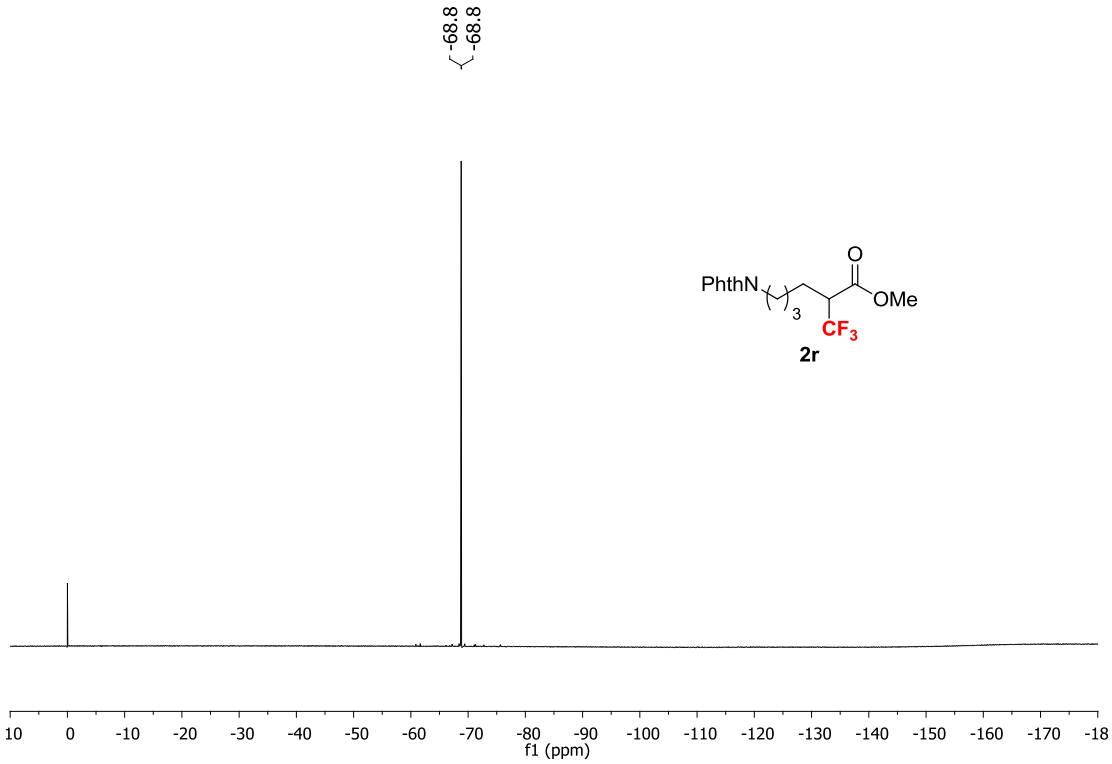
^{13}C NMR Spectrum ($CDCl_3$, 100 MHz)



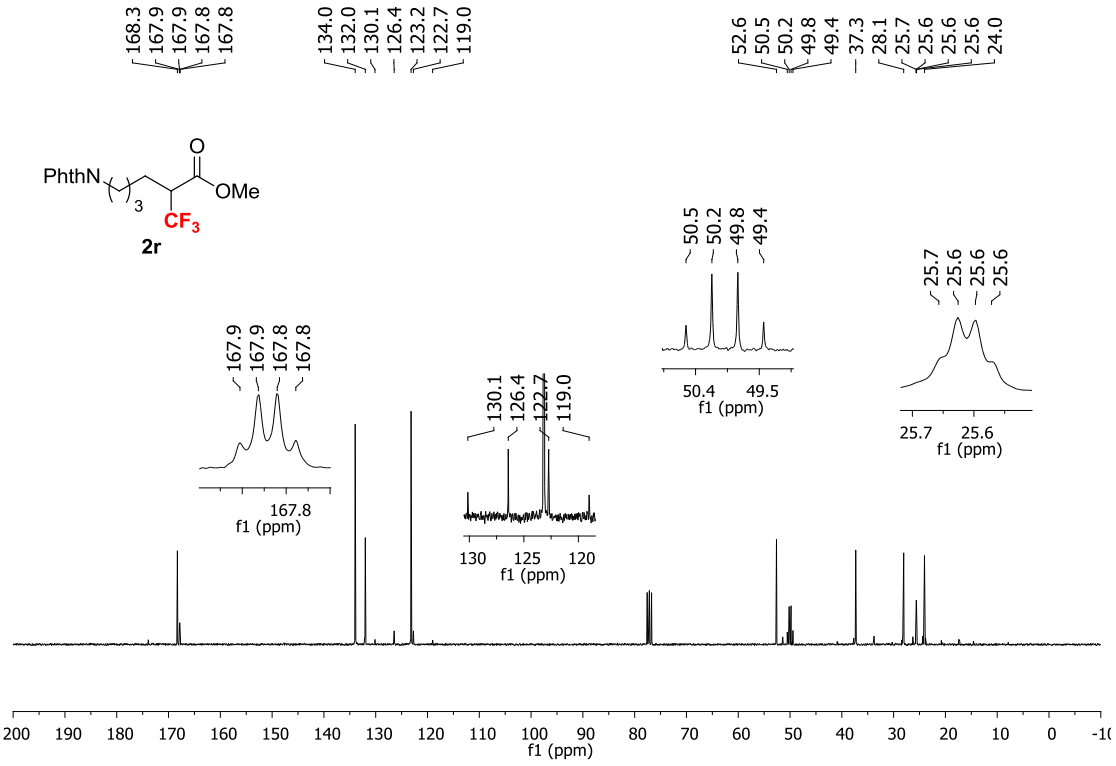
^{1}H NMR Spectrum ($CDCl_3$, 300 MHz)



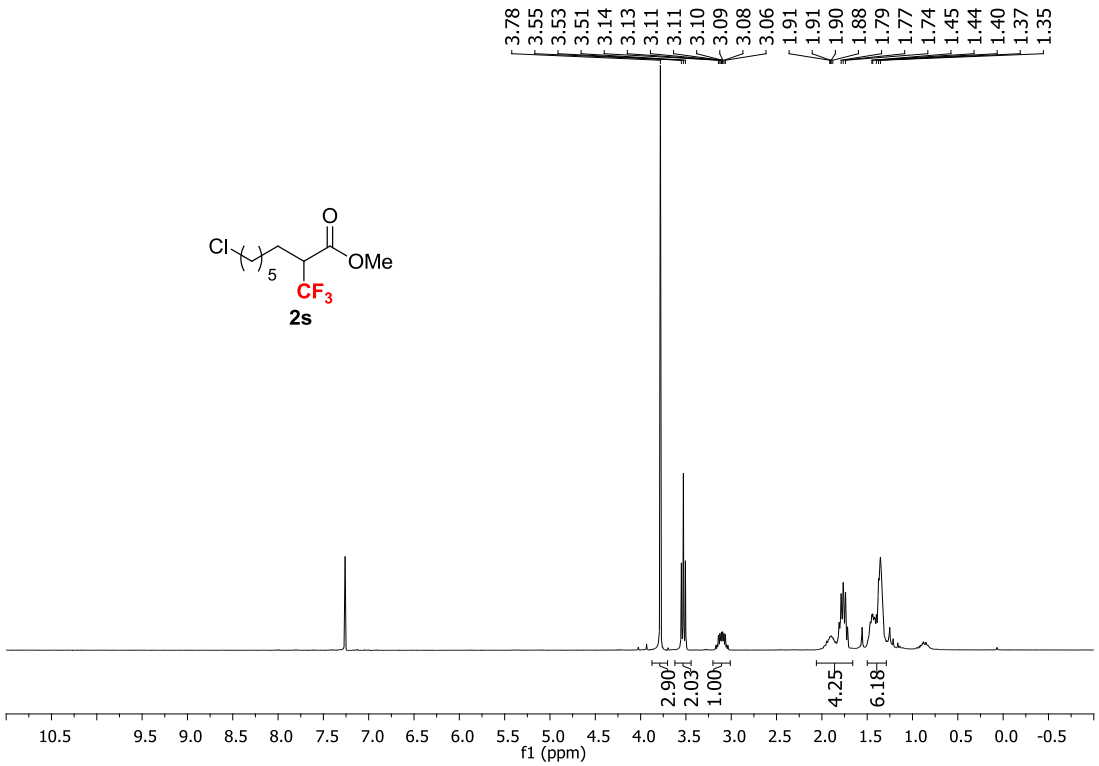
^{19}F NMR Spectrum ($CDCl_3$, 282 MHz)



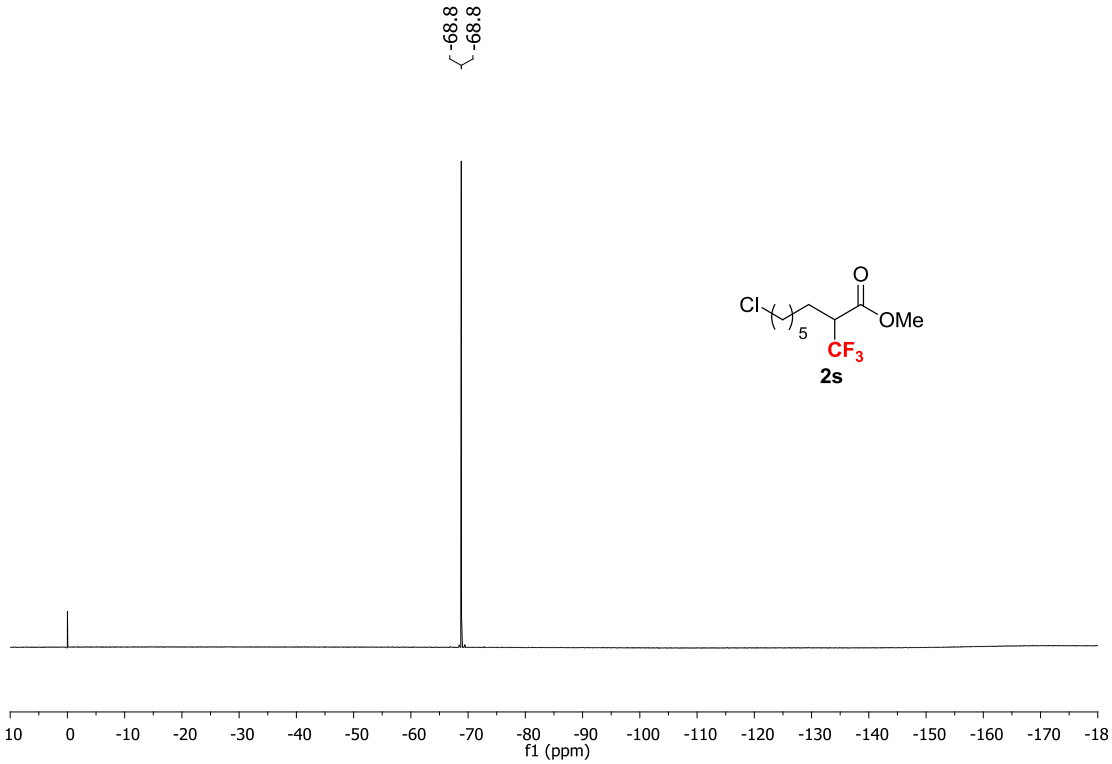
^{13}C NMR Spectrum ($CDCl_3$, 75 MHz)



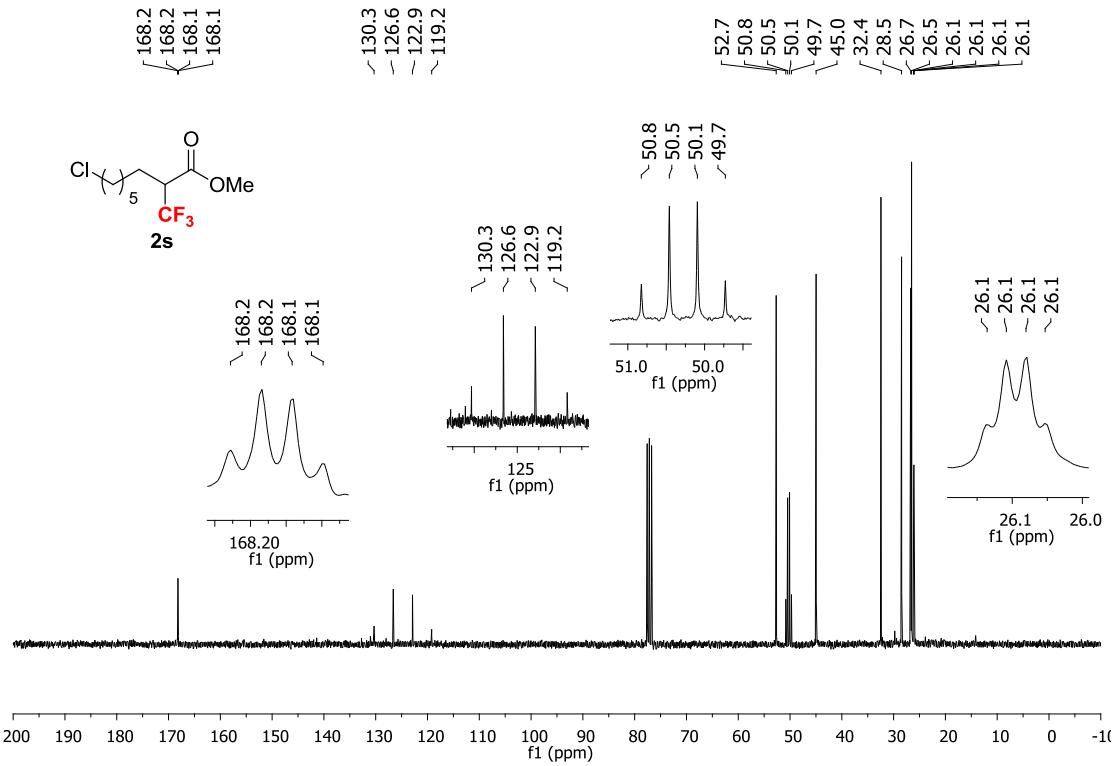
^{1}H NMR Spectrum ($CDCl_3$, 300 MHz)



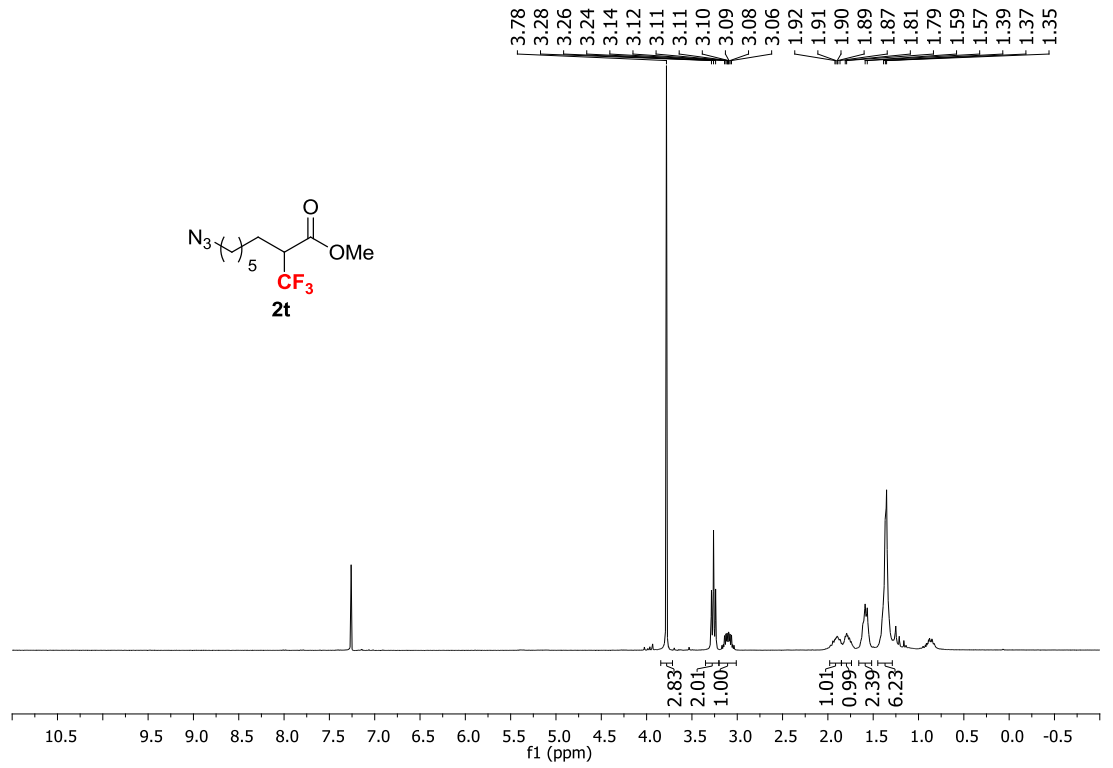
^{19}F NMR Spectrum ($CDCl_3$, 282 MHz)



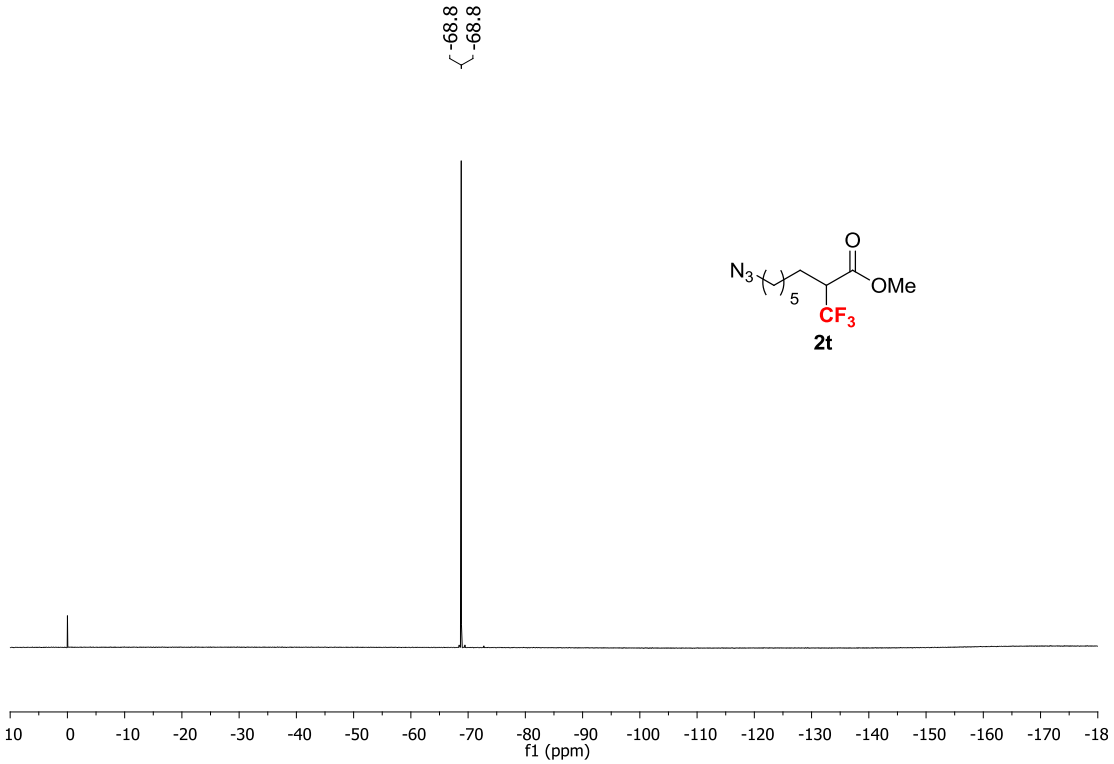
^{13}C NMR Spectrum ($CDCl_3$, 75 MHz)



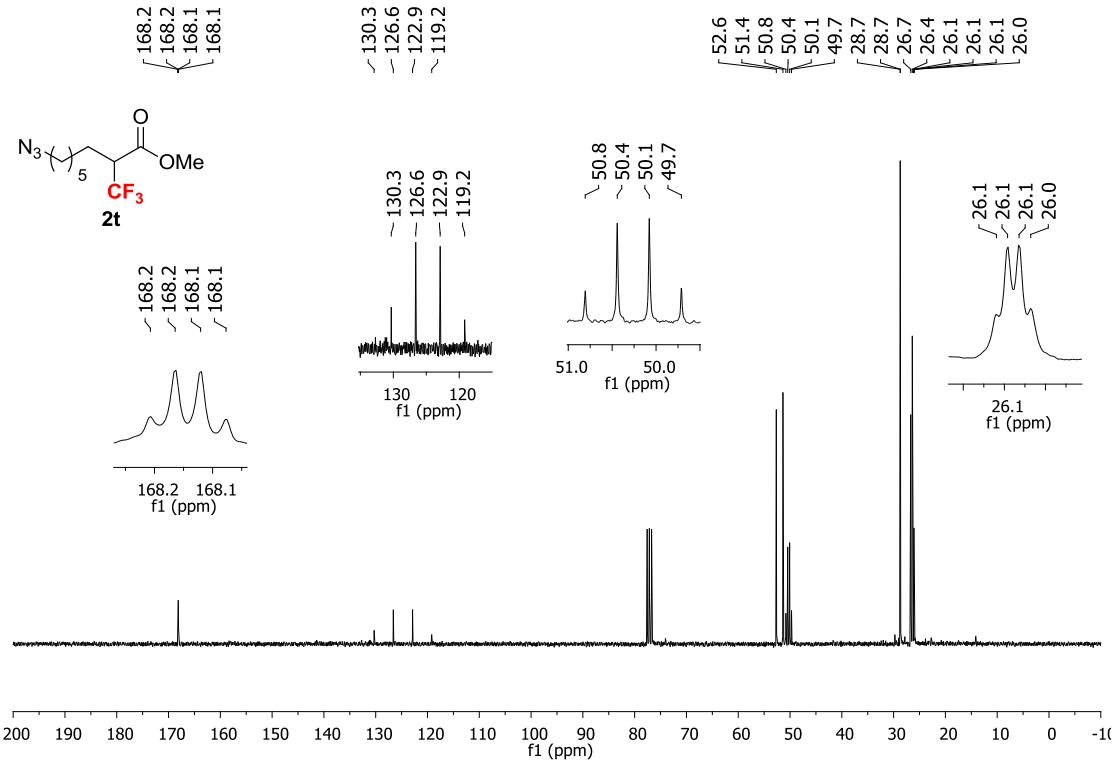
^{1}H NMR Spectrum ($CDCl_3$, 300 MHz)



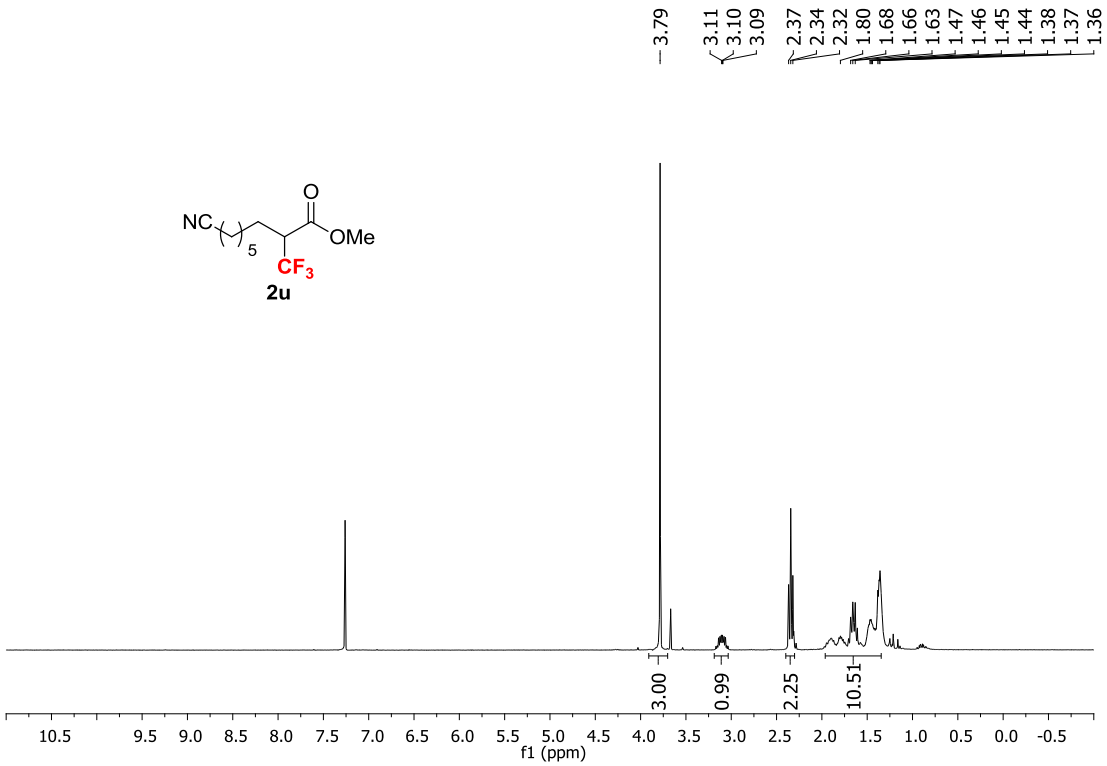
^{19}F NMR Spectrum ($CDCl_3$, 282 MHz)



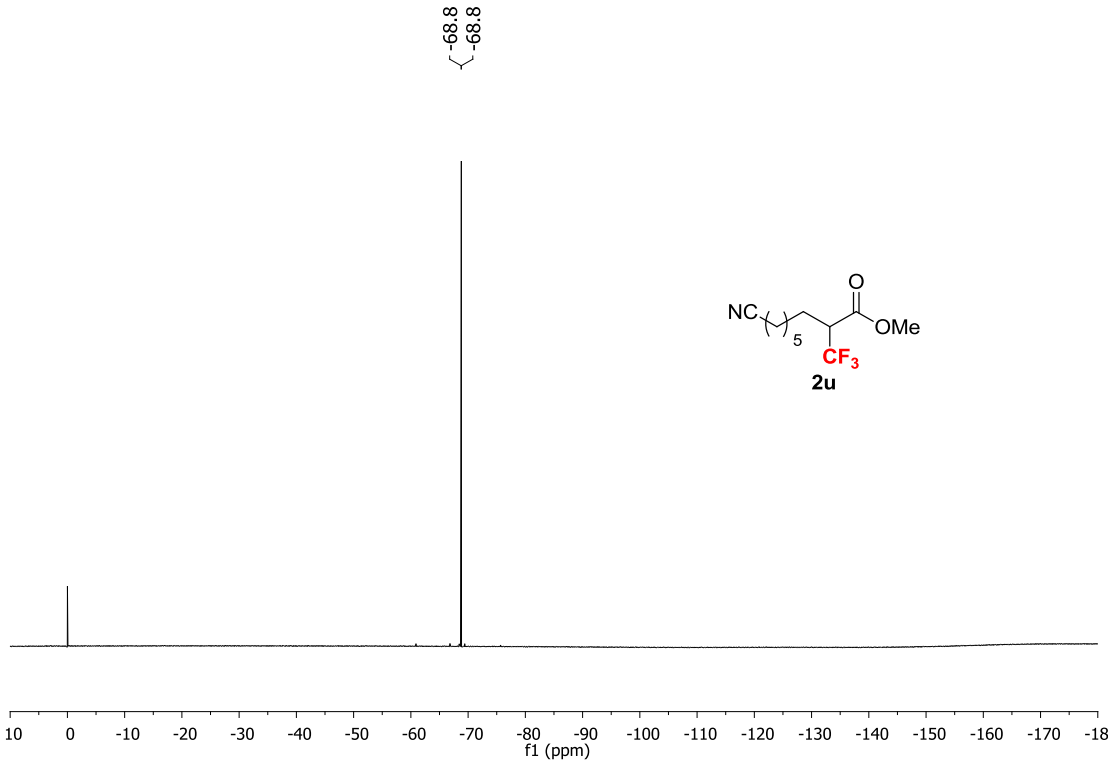
^{13}C NMR Spectrum ($CDCl_3$, 75 MHz)



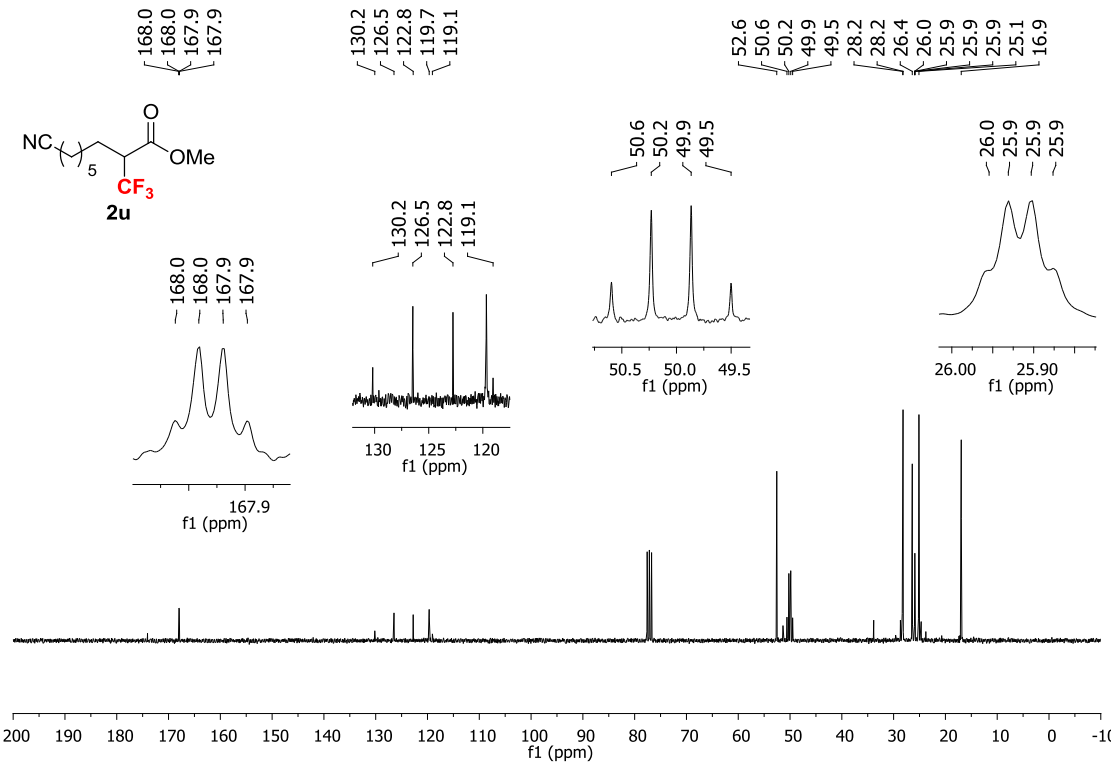
^{1}H NMR Spectrum ($CDCl_3$, 300 MHz)



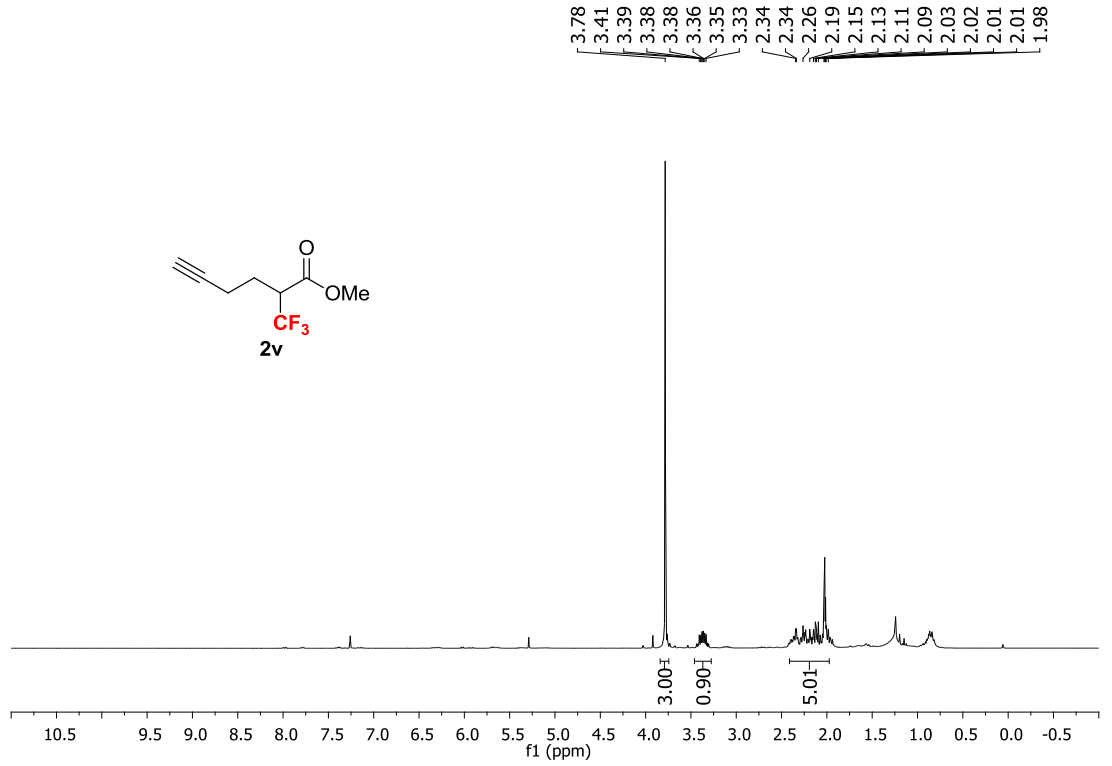
^{19}F NMR Spectrum ($CDCl_3$, 282 MHz)



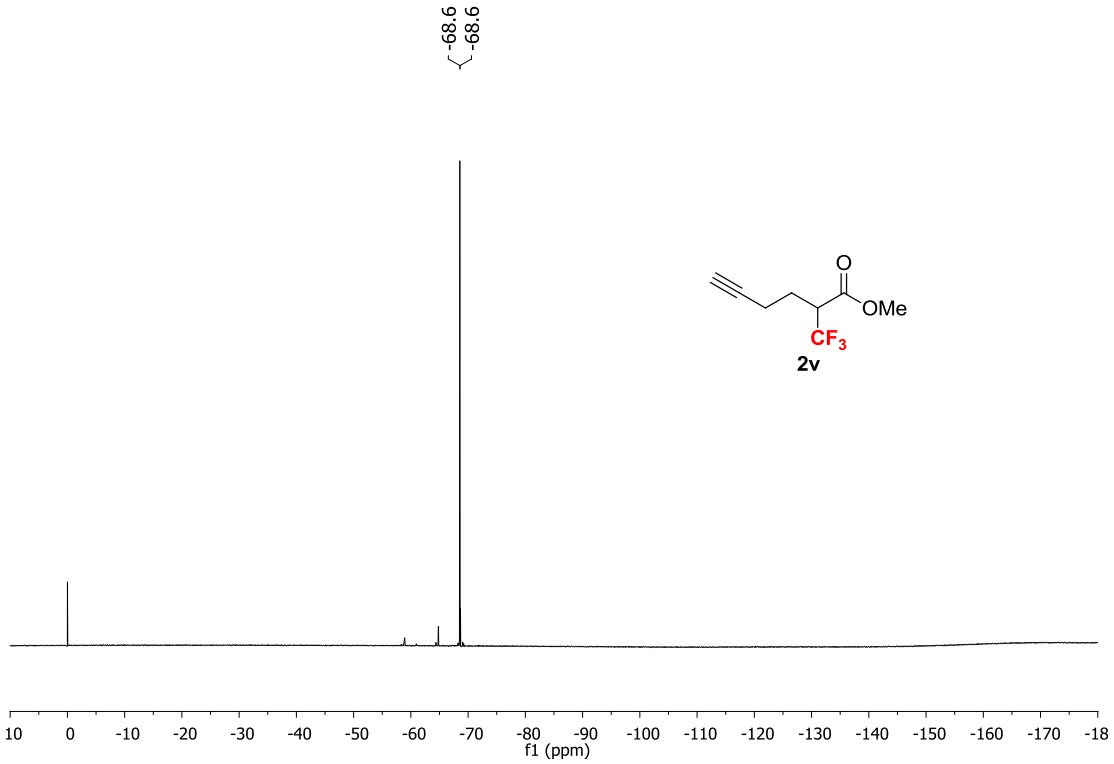
^{13}C NMR Spectrum ($CDCl_3$, 75 MHz)



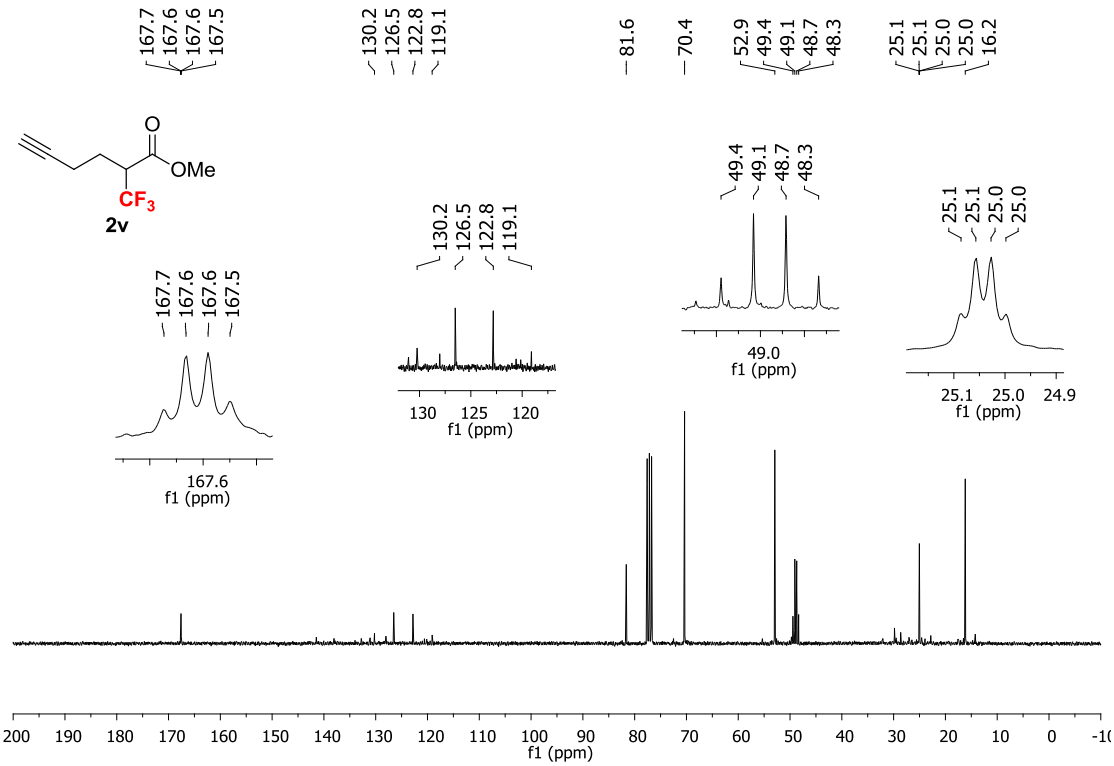
^{1}H NMR Spectrum ($CDCl_3$, 300 MHz)



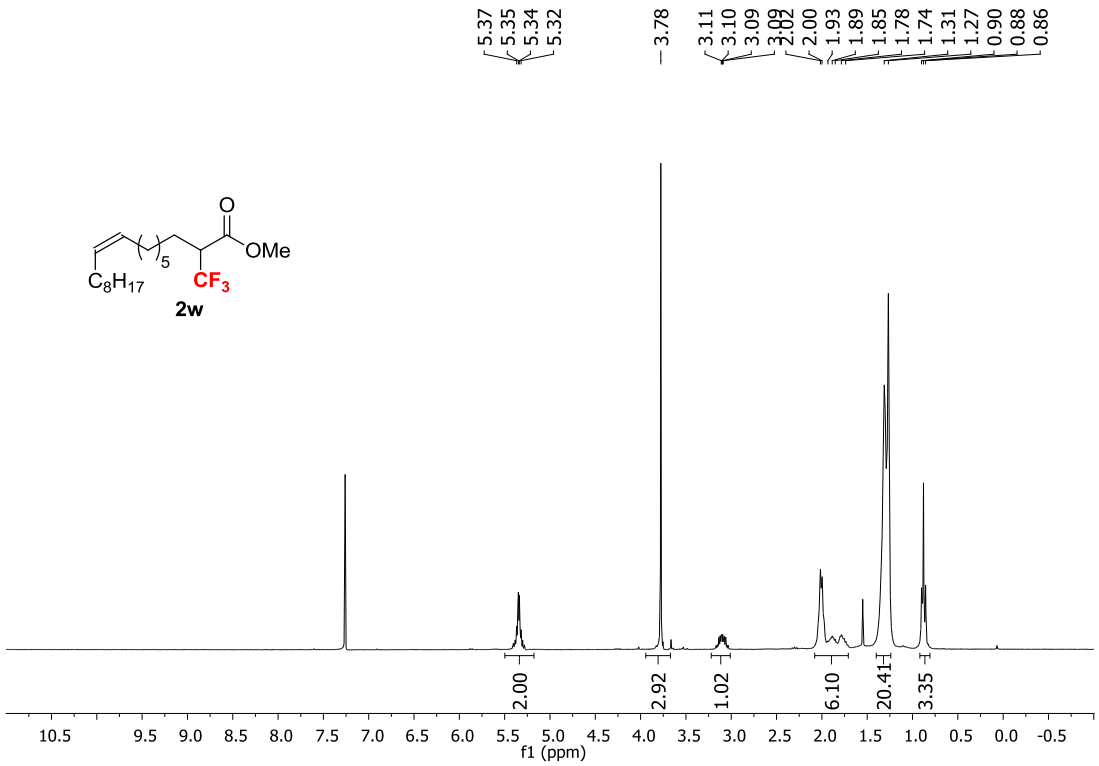
^{19}F NMR Spectrum ($CDCl_3$, 282 MHz)



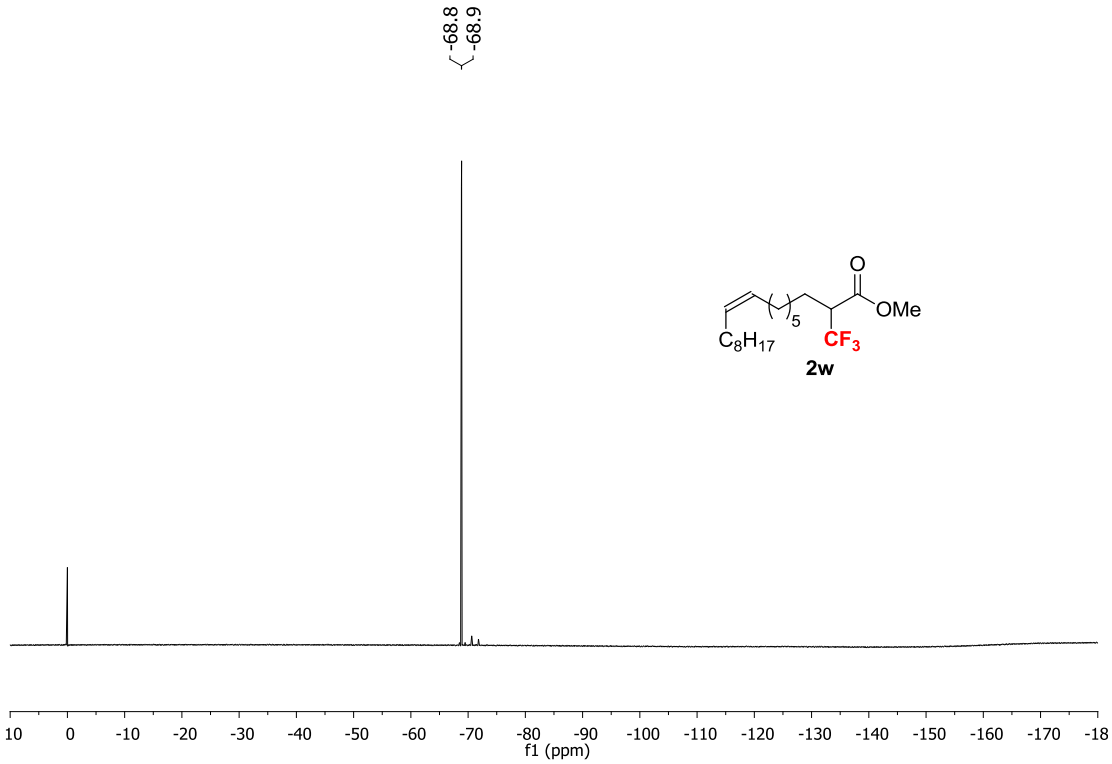
^{13}C NMR Spectrum ($CDCl_3$, 75 MHz)



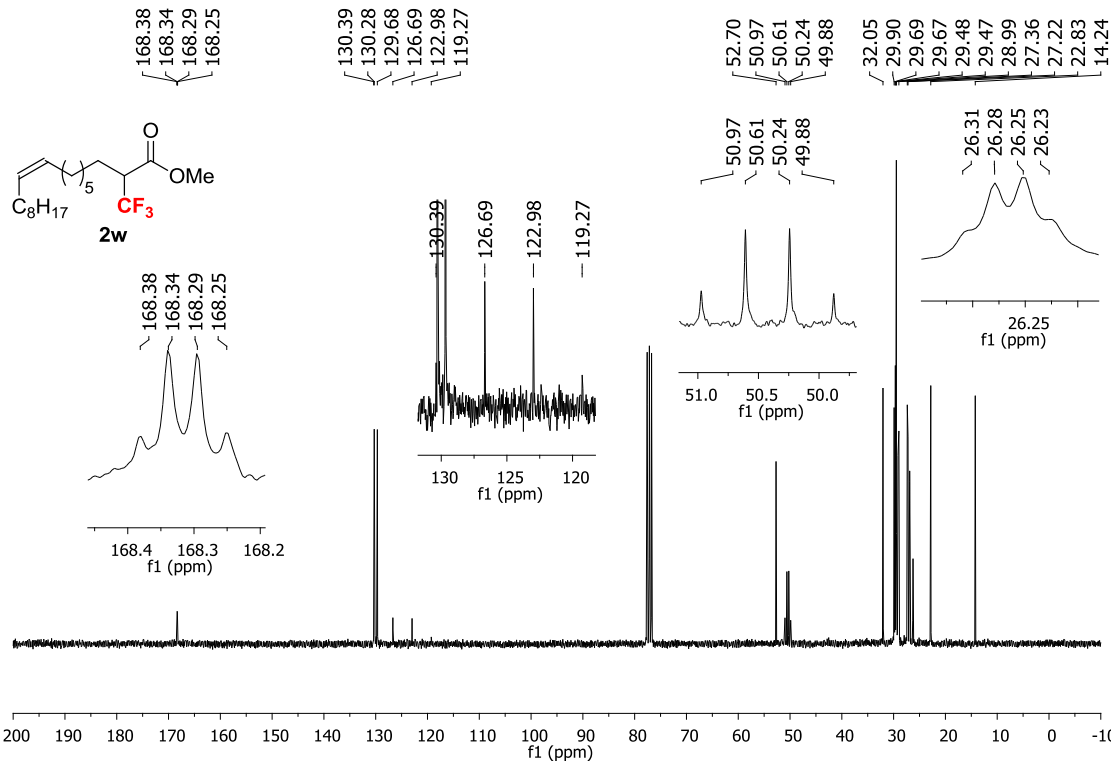
^{1}H NMR Spectrum ($CDCl_3$, 300 MHz)



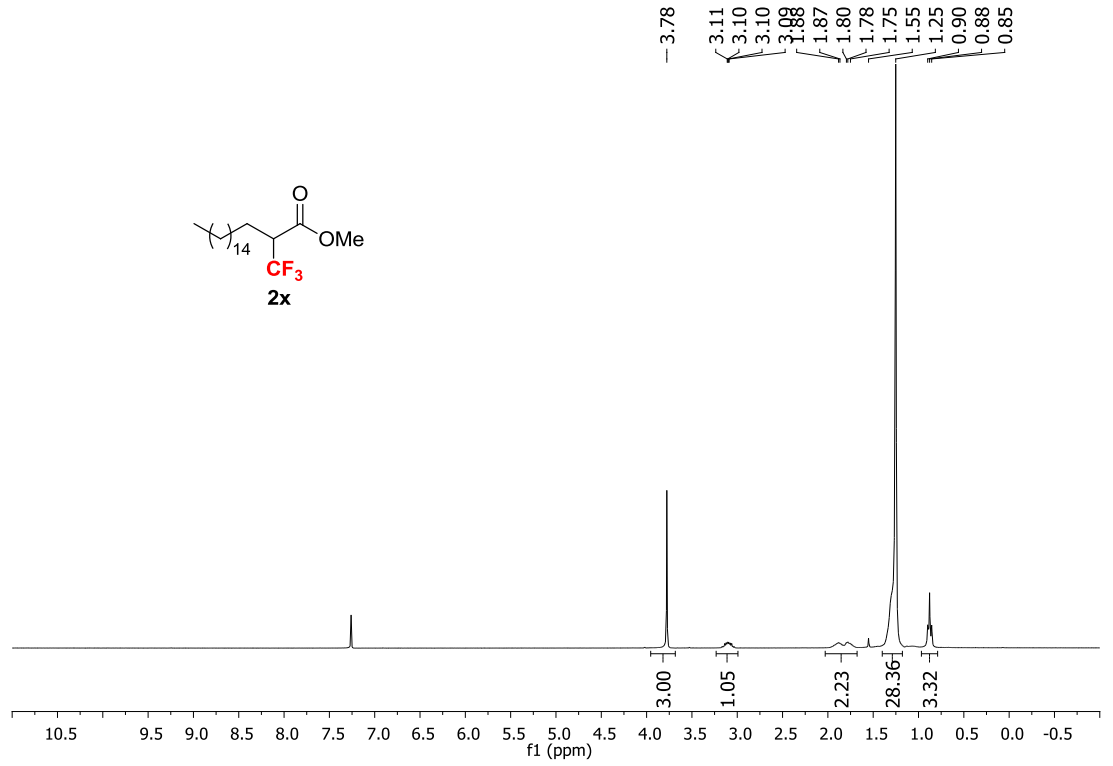
^{19}F NMR Spectrum ($CDCl_3$, 282 MHz)



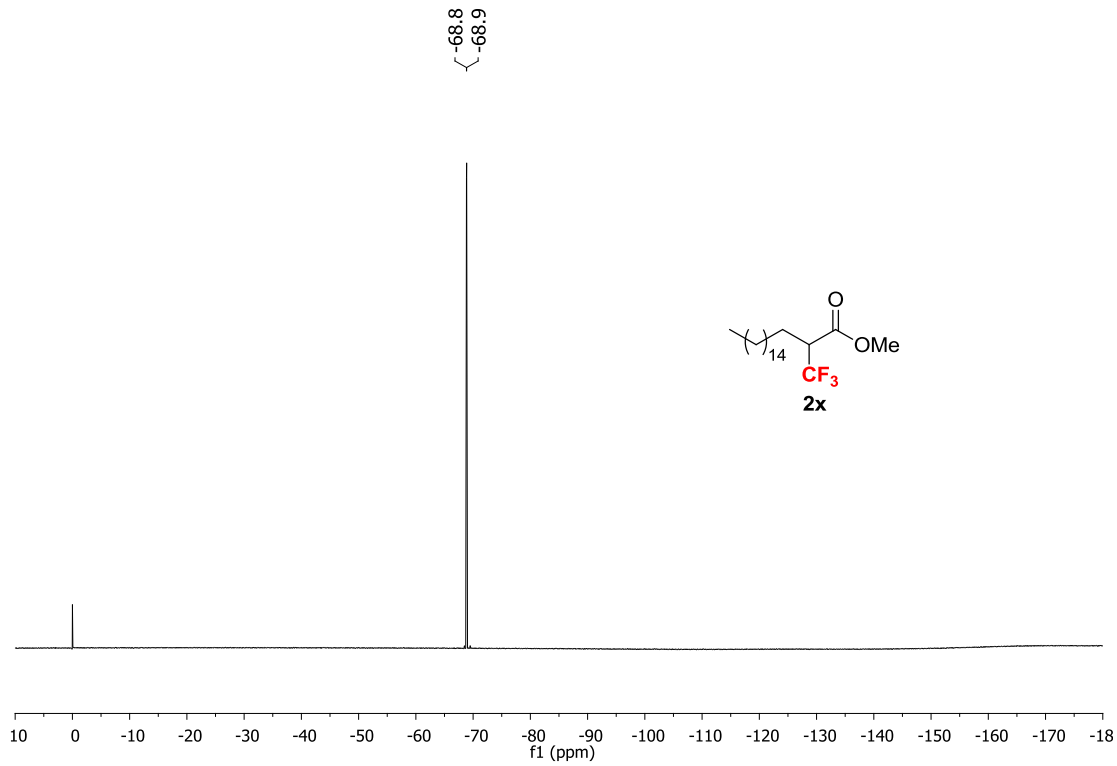
^{13}C NMR Spectrum ($CDCl_3$, 75 MHz)



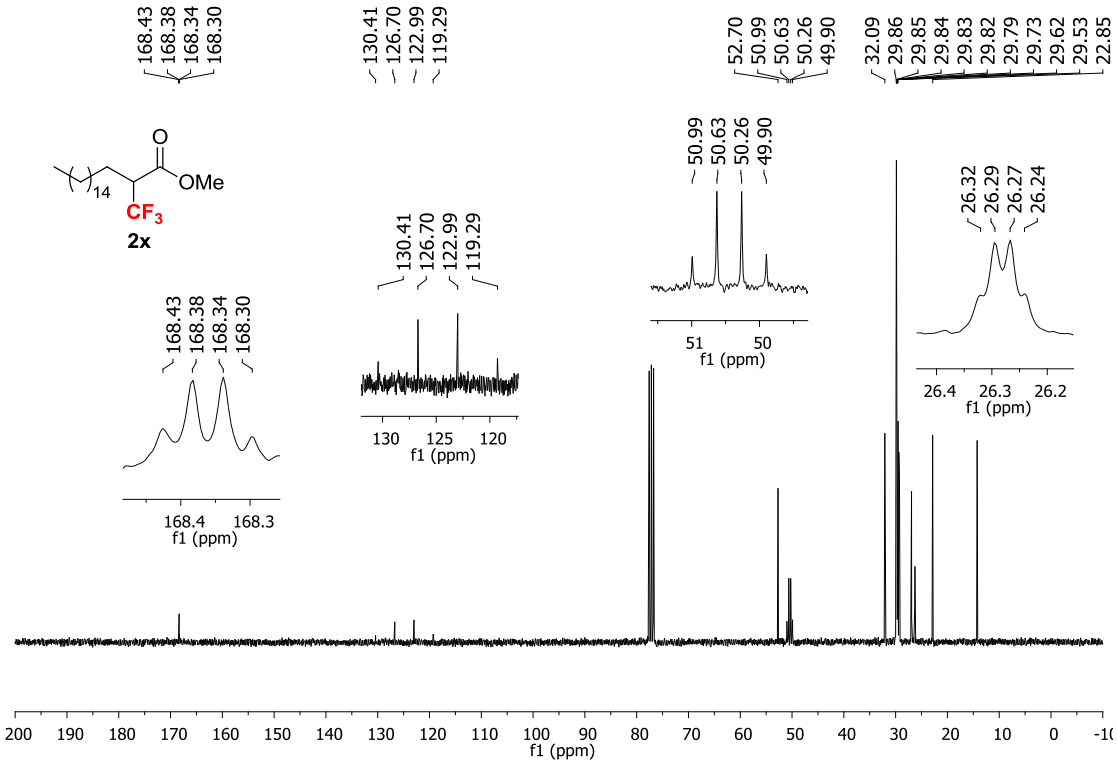
^{1}H NMR Spectrum ($CDCl_3$, 300 MHz)



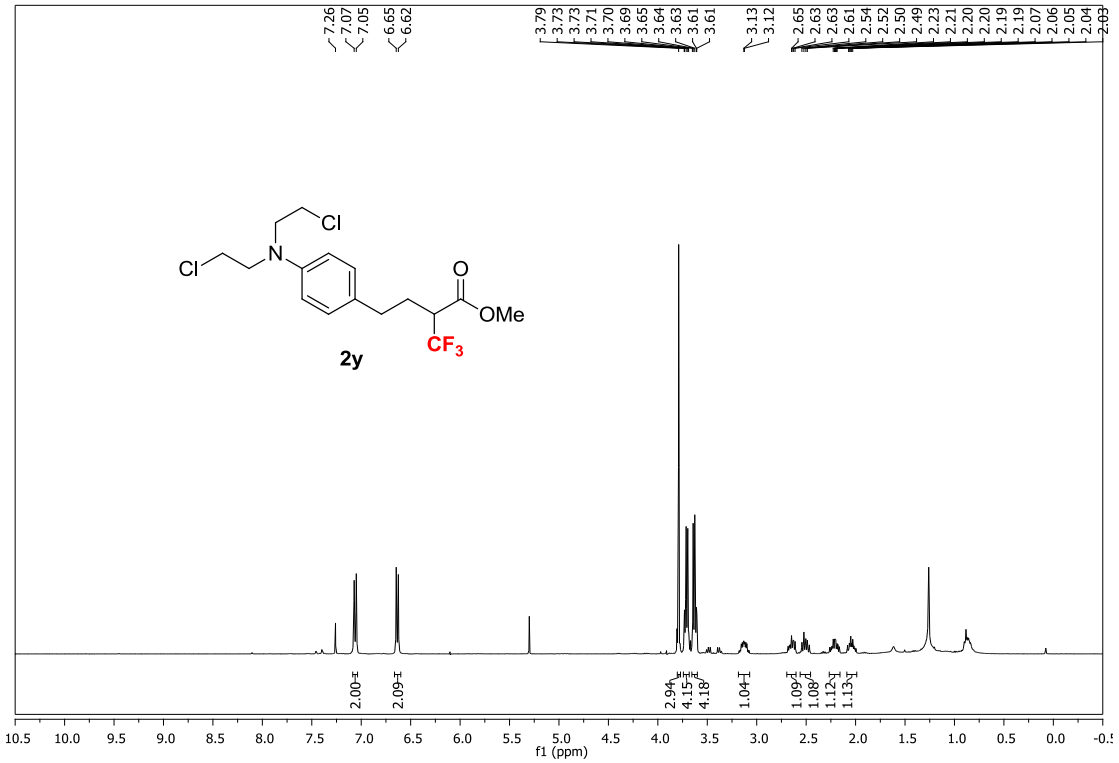
^{19}F NMR Spectrum ($CDCl_3$, 282 MHz)



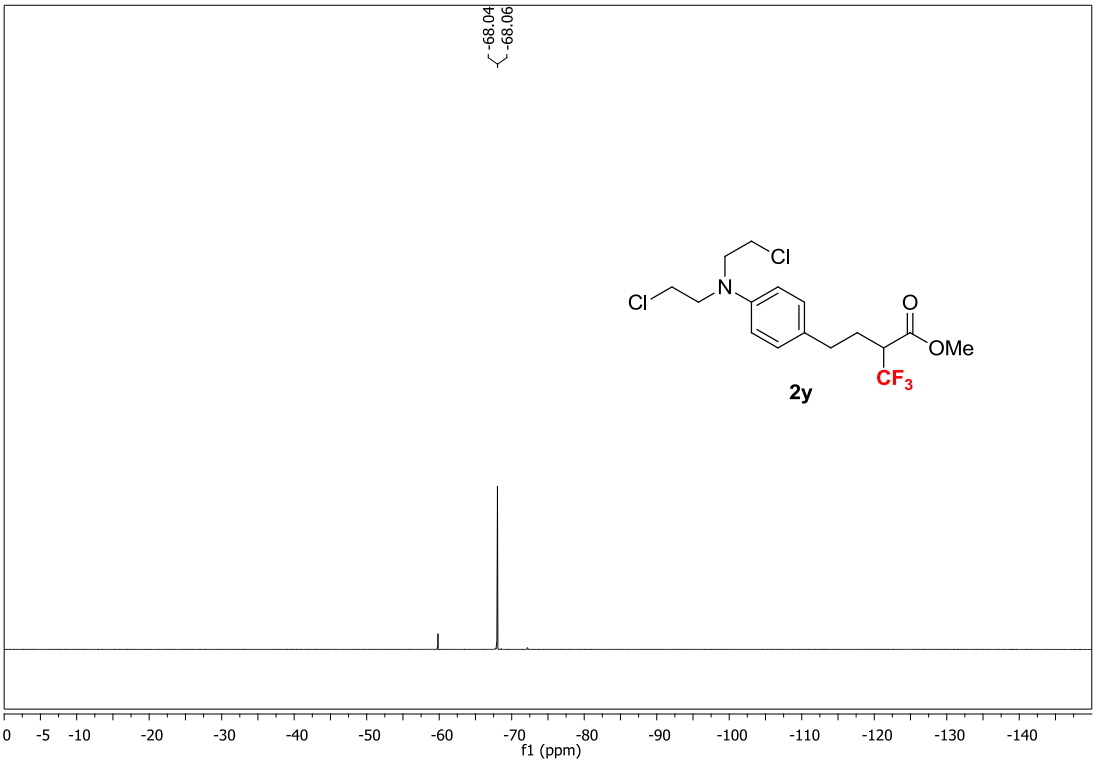
^{13}C NMR Spectrum ($CDCl_3$, 75 MHz)



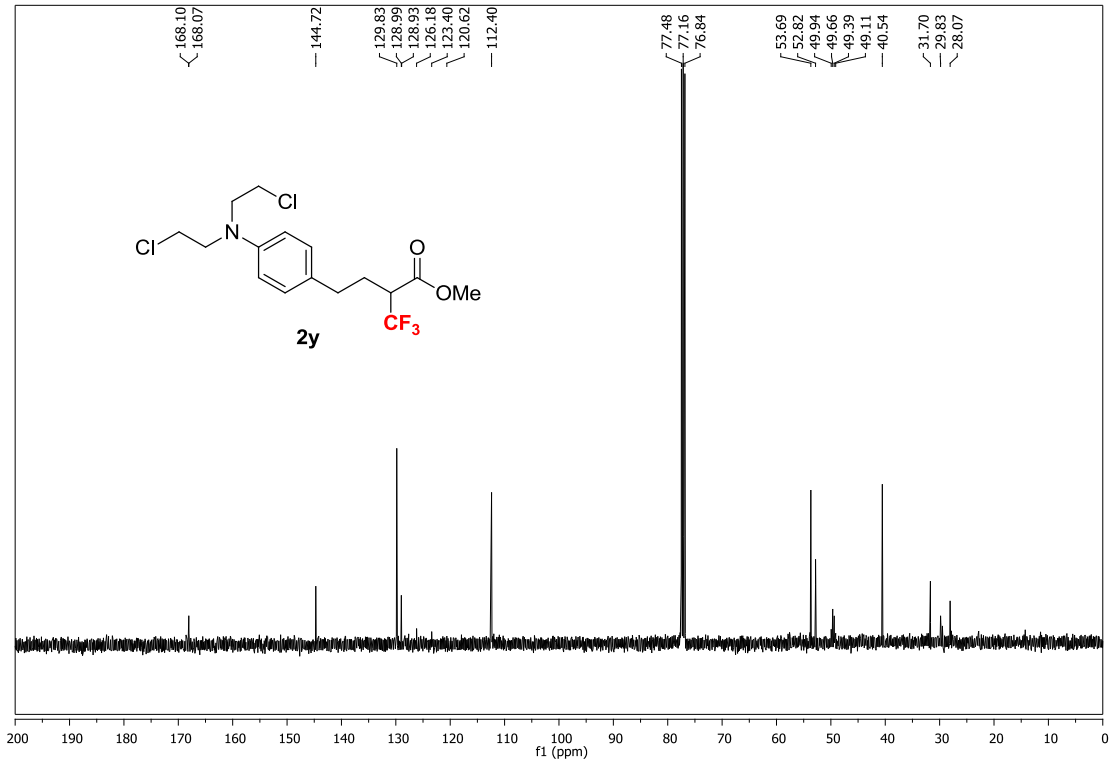
^{1}H NMR Spectrum ($CDCl_3$, 400 MHz)



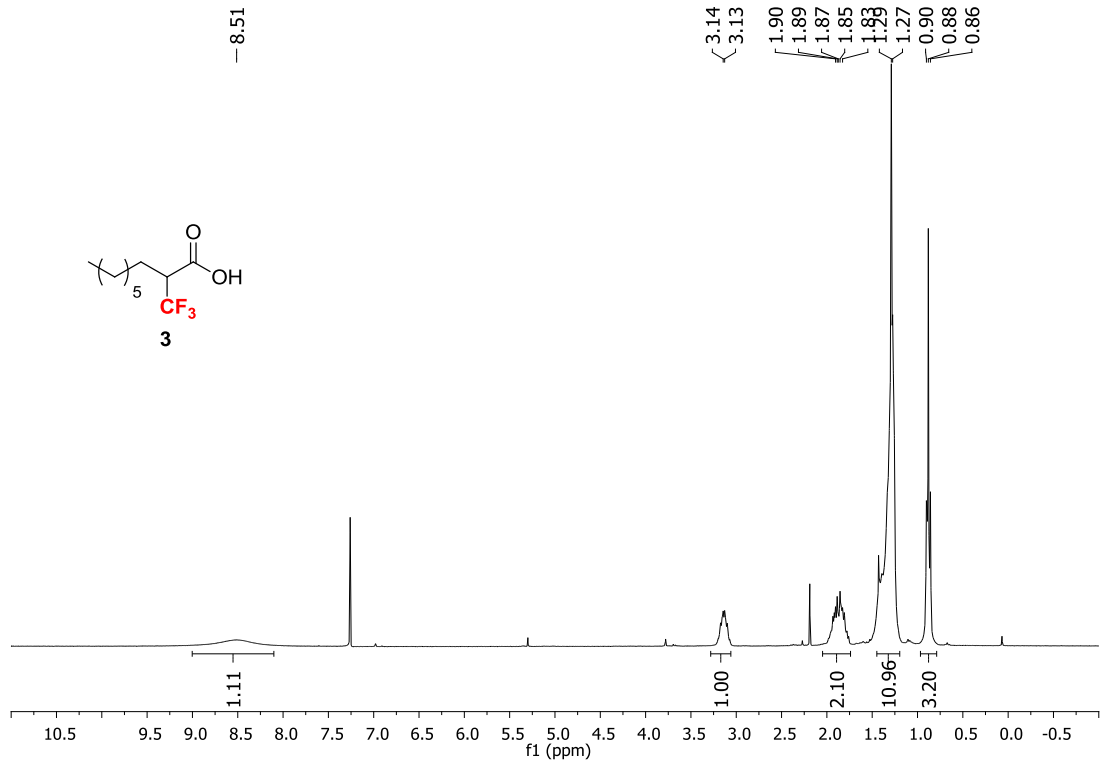
^{19}F NMR Spectrum ($CDCl_3$, 376 MHz)



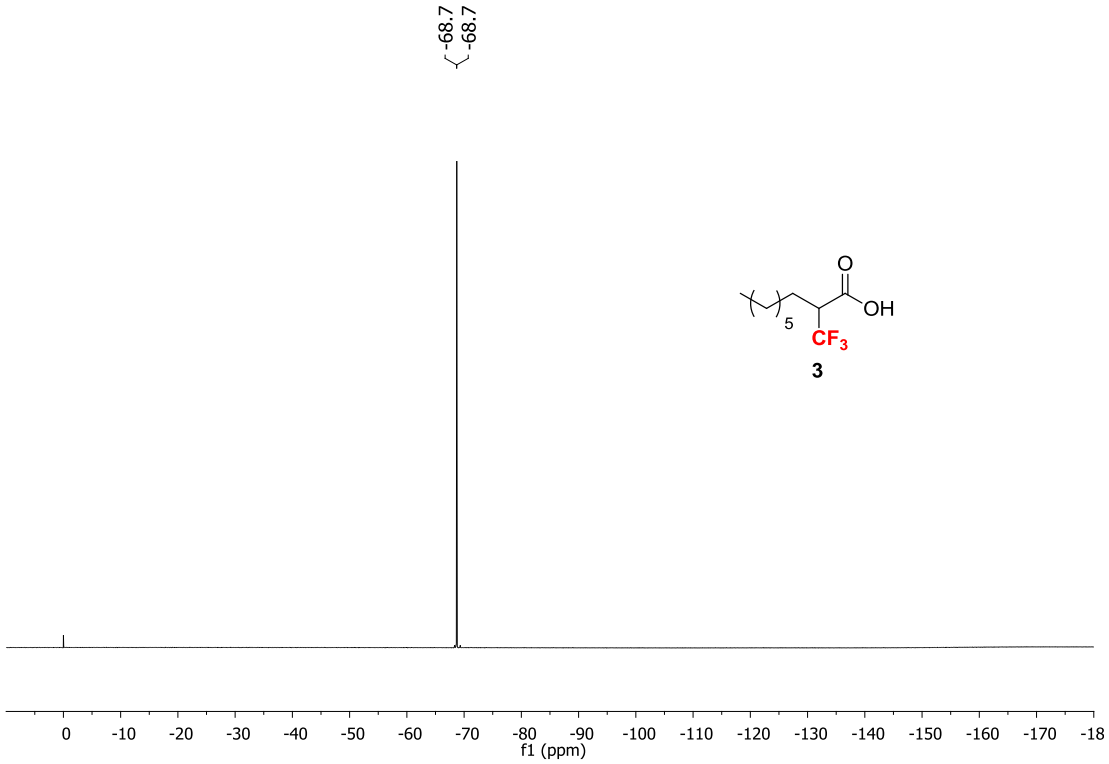
^{13}C NMR Spectrum ($CDCl_3$, 100 MHz)



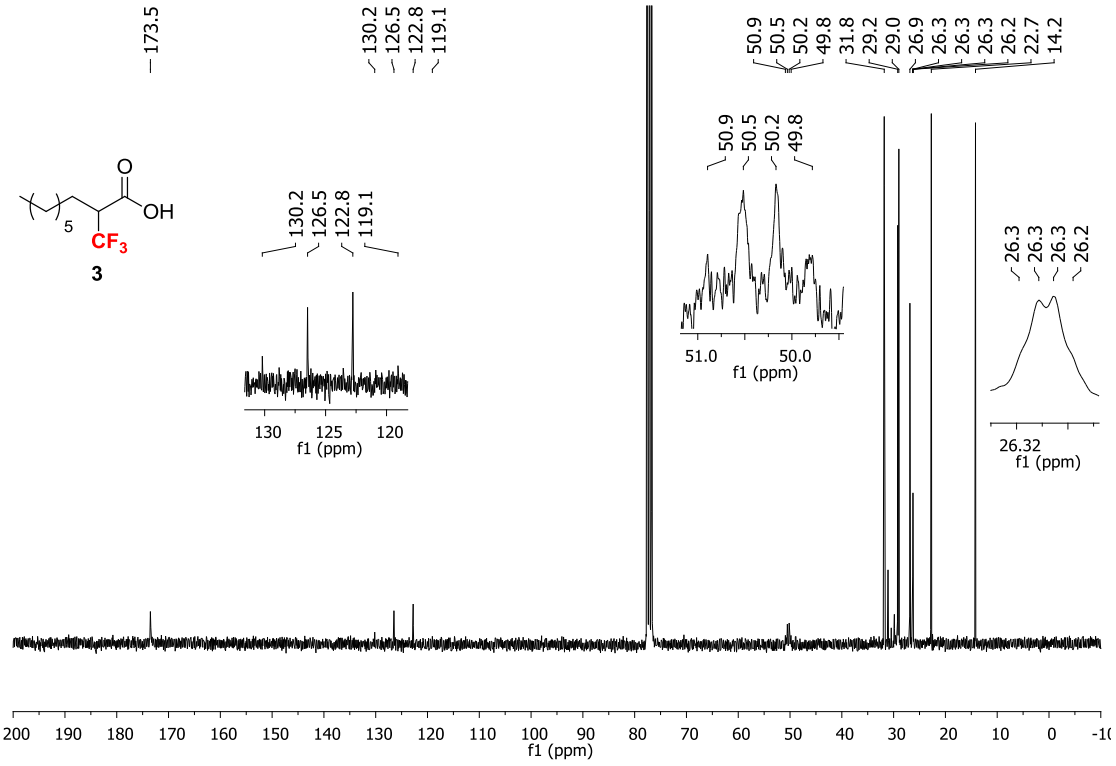
^{1}H NMR Spectrum ($CDCl_3$, 300 MHz)



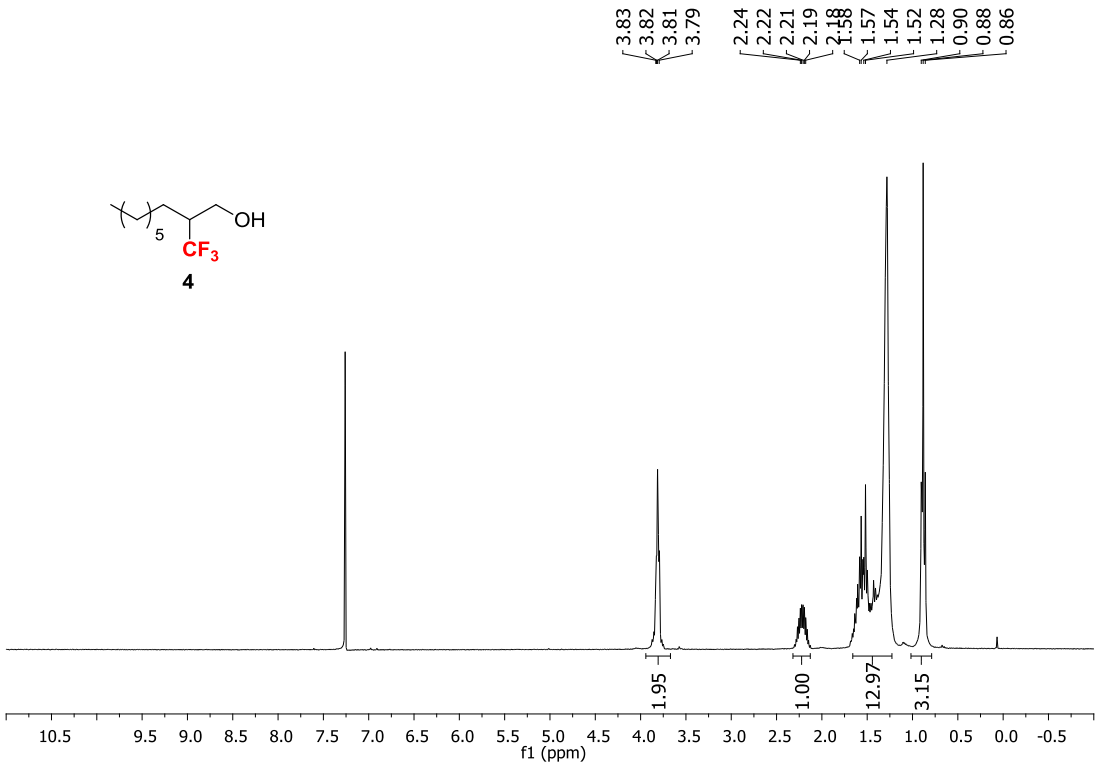
^{19}F NMR Spectrum ($CDCl_3$, 282 MHz)



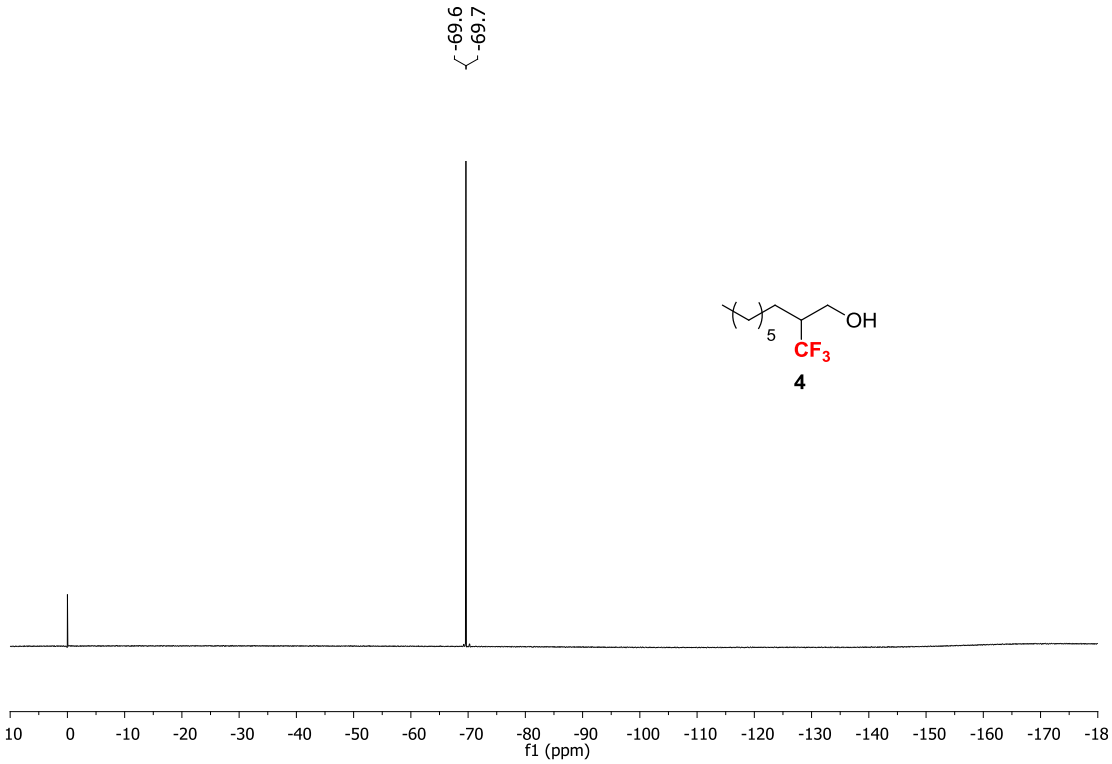
^{13}C NMR Spectrum ($CDCl_3$, 75 MHz)



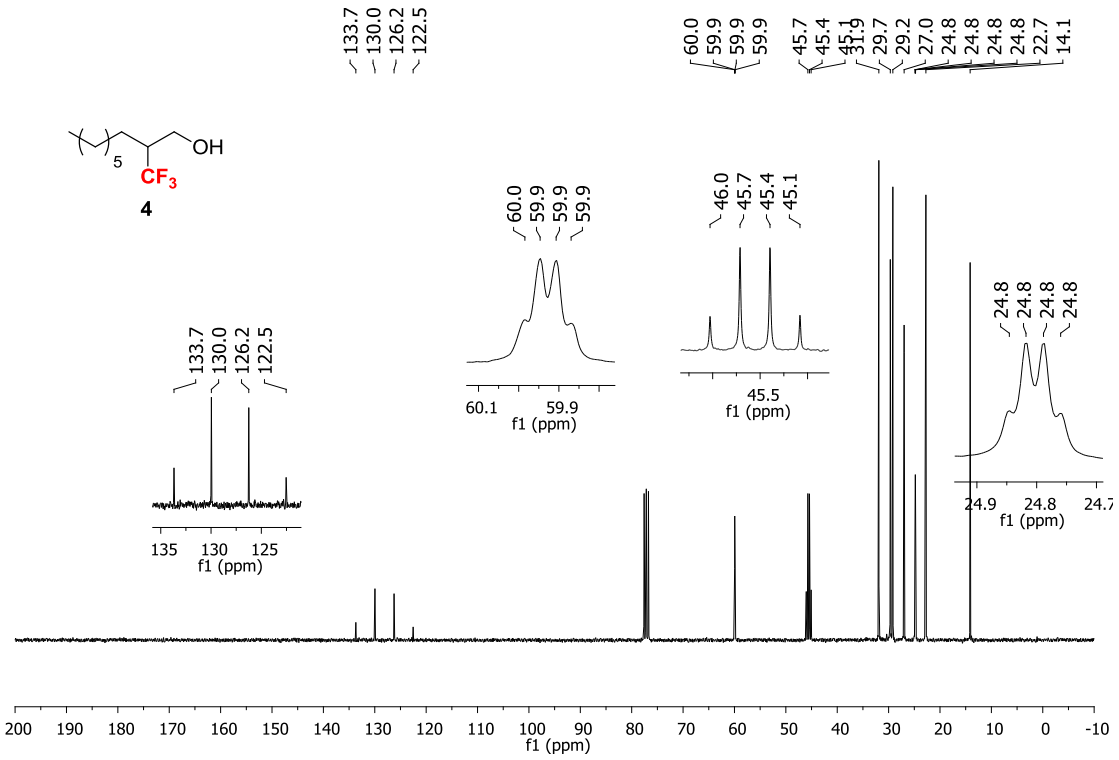
^{1}H NMR Spectrum ($CDCl_3$, 300 MHz)



^{19}F NMR Spectrum ($CDCl_3$, 282 MHz)



^{13}C NMR Spectrum ($CDCl_3$, 75 MHz)

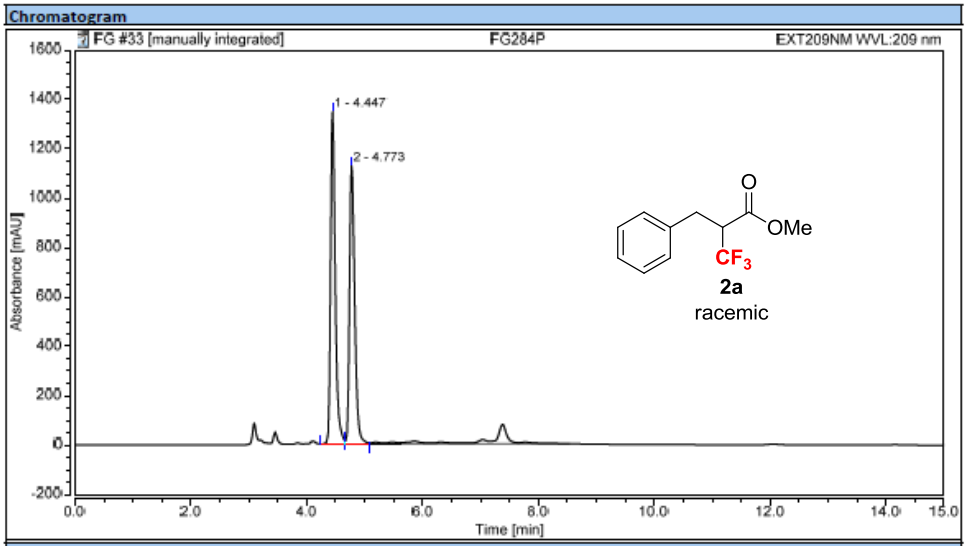


13. HPLC Chromatograms

Injection Details

Injection Name:	FG284P	*Run Time (min):*	40.00
Vial Number:	RB1	*Injection Volume:*	5.00
Injection Type:	Unknown	*Channel:*	EXT209NM
Calibration Level:	ash hept/IPA 99/1 20° 1ml/min	*Wavelength:*	n.a.
Instrument Method:	99A-1C	*Bandwidth:*	n.a.
Processing Method:	methode traitement	*Dilution Factor:*	1.0000
Injection Date/Time:	10/juil./17 19:24	*Sample Weight:*	1.0000

Chromatogram



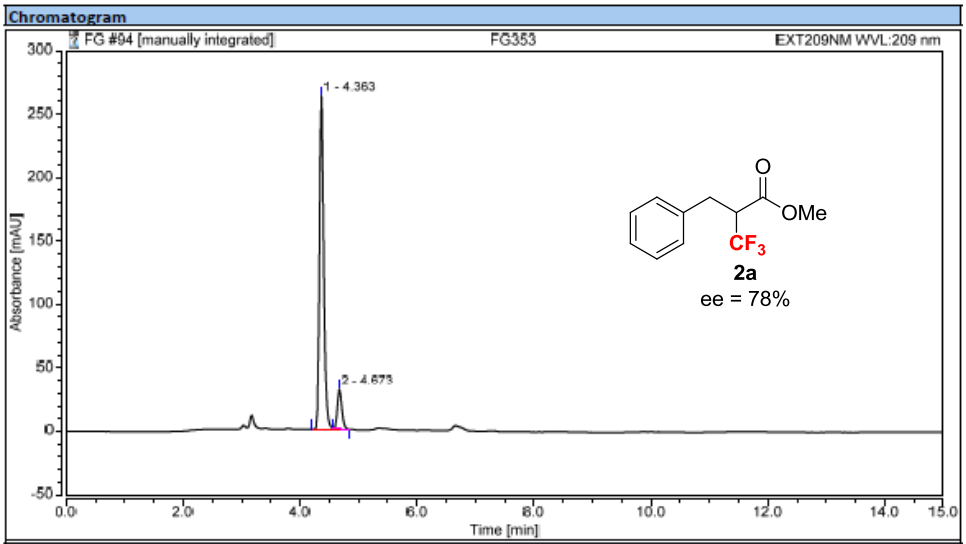
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.447	125.866	1345.920	51.84	54.45	n.a.
2		4.773	116.933	1125.845	48.16	45.55	n.a.
Total:			**242.799**	**2471.766**	**100.00**	**100.00**	

Injection Details

Injection Name:	FG353	*Run Time (min):*	15.00
Vial Number:	BA1	*Injection Volume:*	5.00
Injection Type:	Unknown	*Channel:*	EXT209NM
Calibration Level:	ash hept/IPA 99/1 20° 1ml/min	*Wavelength:*	n.a.
Instrument Method:	99A-1C	*Bandwidth:*	n.a.
Processing Method:	methode traitement	*Dilution Factor:*	1.0000
Injection Date/Time:	28/sept./17 16:09	*Sample Weight:*	1.0000

Chromatogram



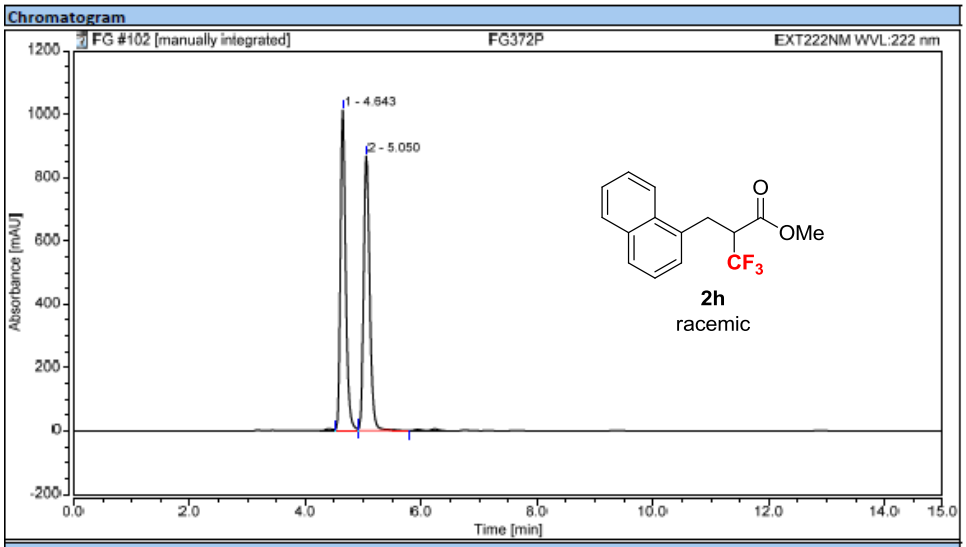
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.363	22.311	262.937	89.05	89.28	n.a.
2		4.673	2.742	31.562	10.95	10.72	n.a.
Total:			**25.053**	**294.499**	**100.00**	**100.00**	

Injection Details

Injection Name:	FG372P	*Run Time (min):*	15.00
Vial Number:	BC2	*Injection Volume:*	5.00
Injection Type:	Unknown	*Channel:*	EXT222NM
Calibration Level:	ash hept/IPA 99/1 20° 1ml/min	*Wavelength:*	n.a.
Instrument Method:	99A-1C	*Bandwidth:*	n.a.
Processing Method:	methode traitement	*Dilution Factor:*	1.0000
Injection Date/Time:	19/oct./17 13:41	*Sample Weight:*	1.0000

Chromatogram



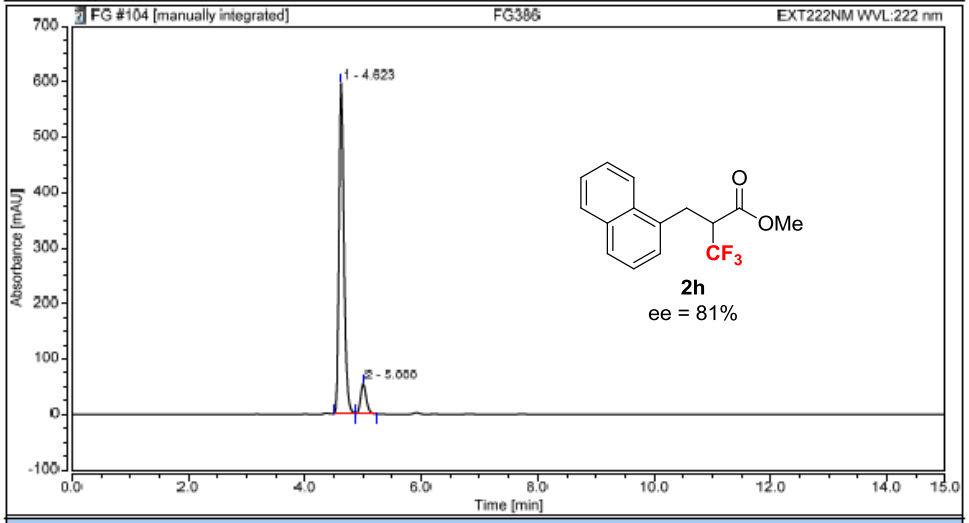
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.643	106.402	1011.828	49.87	53.88	n.a.
2		5.050	106.948	866.179	50.13	46.12	n.a.
Total:			**213.350**	**1878.006**	**100.00**	**100.00**	

Injection Details

Injection Name:	FG386	*Run Time (min):*	15.00
Vial Number:	BC4	*Injection Volume:*	1.00
Injection Type:	Unknown	*Channel:*	EXT222NM
Calibration Level:	ash hept/IPA 99/1 20° 1ml/min	*Wavelength:*	n.a.
Instrument Method:	99A-1C	*Bandwidth:*	n.a.
Processing Method:	methode traitement	*Dilution Factor:*	1.0000
Injection Date/Time:	19/oct./17 14:12	*Sample Weight:*	1.0000

Chromatogram

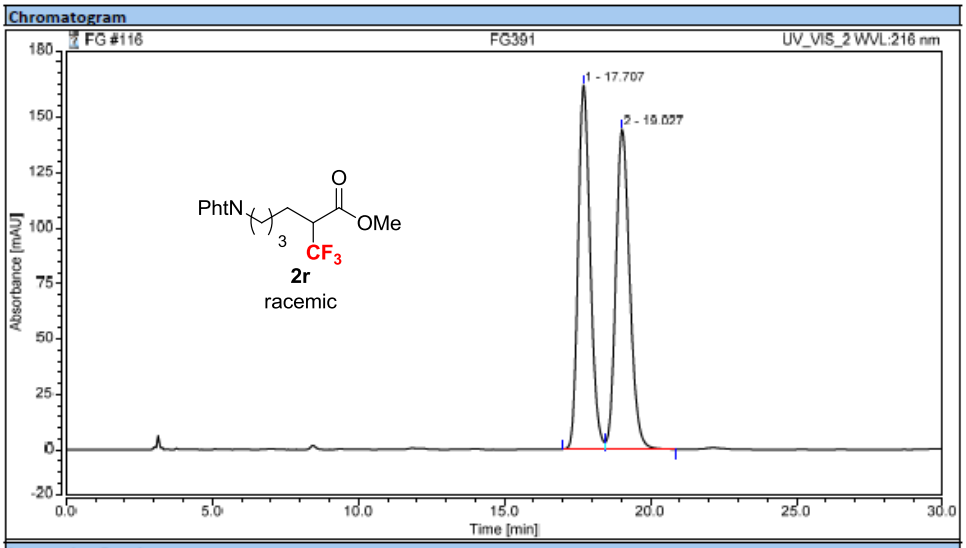


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.623	58.915	596.303	90.61	91.59	n.a.
2		5.000	6.104	54.720	9.39	8.41	n.a.
Total:			**65.019**	**651.023**	**100.00**	**100.00**	

Injection Details			
Injection Name:	**FG391**	*Run Time (min):*	**30.00**
Vial Number:	**RA2**	*Injection Volume:*	**5.00**
Injection Type:	**Unknown**	*Channel:*	**UV_VIS_2**
Calibration Level:	**ash hept/IPA 97/3 20° 1ml/min**	*Wavelength:*	**216**
Instrument Method:	**97A-3C**	*Bandwidth:*	**2**
Processing Method:	**methode traitement**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**01/déc./17 15:36**	*Sample Weight:*	**1.0000**

Chromatogram

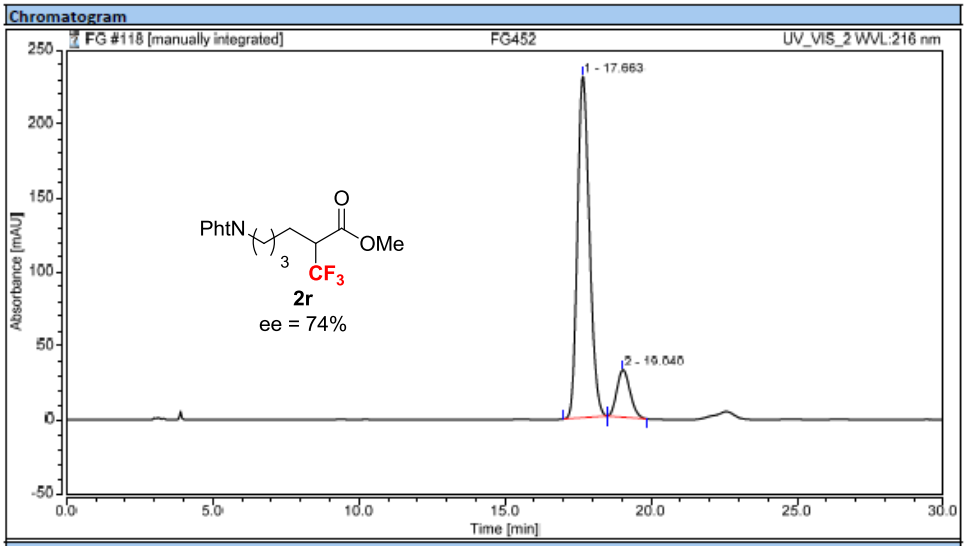


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.707	78.790	164.171	49.71	53.19	n.a.
2		19.027	79.716	144.468	50.29	46.81	n.a.
Total:			**158.506**	**308.639**	**100.00**	**100.00**	

Injection Details			
Injection Name:	**FG452**	*Run Time (min):*	**30.00**
Vial Number:	**RA3**	*Injection Volume:*	**1.00**
Injection Type:	**Unknown**	*Channel:*	**UV_VIS_2**
Calibration Level:	**ash hept/IPA 97/3 20° 1ml/min**	*Wavelength:*	**216**
Instrument Method:	**97A-3C**	*Bandwidth:*	**2**
Processing Method:	**methode traitement**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**01/déc./17 16:23**	*Sample Weight:*	**1.0000**

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.663	109.969	230.741	86.79	87.80	n.a.
2		19.040	16.731	32.072	13.21	12.20	n.a.
Total:			**126.700**	**262.814**	**100.00**	**100.00**	