Electronic Supplementary Material (ESI) for Chemical Communications


# Supporting Information

## Room Temperature Decarboxylative Trifluoromethylation of α,β-Unsaturated Carboxylic Acids by Photoredox Catalysis

Pan Xu,[a] Ablimit Abdukader,[a] Kaidong Hu,[a] Yixiang Cheng,[a] and Chengjian Zhu*[a,b]

*(State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University Nanjing 210093 E-mail: cjzhu@nju.edu.cn)*

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## General Information

All reactions were carried out under nitrogen atmosphere unless otherwise noted. All reagents and solvents were obtained from commercial suppliers and used without further purification. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. $^{1}H$ NMR ,$^{13}C$ NMR spectra and $^{19}F$ NMR spectra were recorded on 400 MHz spectrometer at room temperature. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. Abbreviations for signal couplings are: s, singlet; d, doublet; t, triplet; m, multiplet. High resolution mass spectra were obtained on a high–resolution mass spectrometer in the EI, ESI mode. Togni reagent were prepared according to the literature[1]. The 35W fluorescent light bulb was directly got from the supermarket (daylight, energy saving, 220 V, 50 Hz). Some acids **1** were prepared through the wittig reaction.

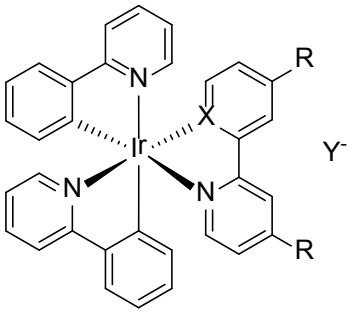
## General experimental details

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1a-x** (0.2 mmol), *fac*-Ir(ppy)$_3$ (0.01 equiv), Togni's reagent (1.5 equiv), $CH_3COONa$ (2 equiv) and DMSO (1 mL). The tube was degassed by alternating vacuum evacuation (5 min) and $N_2$ backfill three times. The tube was placed at a distance (app.5 cm) from 35W fluorescent light bulb, and the resulting yellow solution was stirred at ambient temperature under visible-light irradiation. When the reaction finished, the mixture was diluted with ethyl acetate and added to a separatory funnel containing 10 mL saturated $K_2CO_3$ solution. The layers were separated and the aqueous layer was extracted with ethyl acetate (3x10 mL). The combined organic layers were washed with saturated brine, dried ($Na_2SO_4$) and filtered. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel to afford the oxindoles **2a-x**.

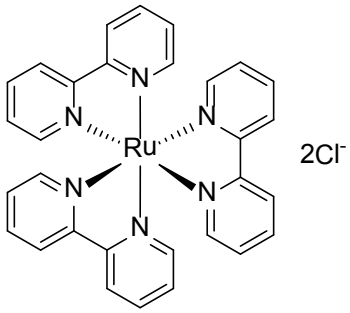
## Optimization of the Reaction Conditions [a]

| Entry | Photocatalyst | additives | solvent | Yield(%)[b] |
|---|---|---|---|---|
| 1 | **3a**(1 %) | - | DMF | 30 |
| 2 | **3a**(1 %) | - | DCM | 22 |
| 3 | **3a**(1 %) | | $CH_3OH$ | 25 |
| 4 | **3a**(1 %) | - | $CH_3CN$ | 13 |
| 5 | **3a**(1 %) | - | DMSO | 65 |
| 6 | **3b**(1 %) | - | DMSO | 19 |
| 7 | **3c**(1 %) | - | DMSO | 26 |

| | | | | |
|---|---|---|---|---|
| 8 | **4a**(1 %) | - | DMSO | 22 |
| 9 | **3a**(1 %) | $CH_3CH_2ONa$ (2 equiv) | DMSO | 62 |
| 10 | **3a**(1 %) | t-BuOK (2 equiv) | DMSO | 36 |
| 11 | **3a**(1 %) | $NaH_2PO_4$ (2 equiv) | DMSO | 63 |
| 12 | **3a**(1 %) | NaOH(2 equiv) | DMSO | trace |
| 13 | **3a**(1 %) | $Et_3N$(2 equiv) | DMSO | 39 |
| 14 | **3a**(1 %) | TsOH(2 equiv) | DMSO | trace |
| 15 | **3a**(1 %) | $CH_3COOK$(2 equiv) | DMSO | 78 |
| 16 | **3a**(1 %) | $CH_3COONa$(2 equiv) | DMSO | 83(75)[c] |
| 17 | **3a**(1 %) | $CH_3COONa$(3 equiv) | DMSO | 82 |
| 18 | **3a**(1 %) | $CH_3COONa$(1 equiv) | DMSO | 76 |
| 19 | **3a**(5 %) | $CH_3COONa$(2 equiv) | DMSO | 76 |
| 20 | - | $CH_3COONa$(2 equiv) | DMSO | N.P |
| 21[d] | **3a**(1 %) | $CH_3COONa$(2 equiv) | DMSO | N.P |




**3a:**R=H; X=C (*fac*)
**3b**:R=H; X=N; Y=$PF_6$
**3c**:R=t-Bu; X=N; Y=$BF_4$

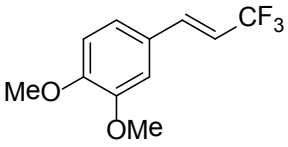



**4a**

[a] Reaction conditions: **1a** (0.2 mmol), Togni reagent (0.3 mmol), additives (0.4 mmol), photocatalyst (1 mol%), solvent (1 mL), 35 W fluorescent light bulb, 18h, rt. [b] Determined by $^{19}F$ NMR analysis of the reaction mixture using perfluorobenzene as an internal standard. [d] In the dark. DMF = *N,N*-dimethylformamide; DCM = dichloromethane; DMSO = dimethylsulfoxide.

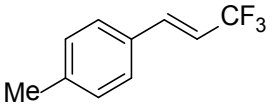
## Characterization data of compounds

(E)-1,2-dimethoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2a**[2a]



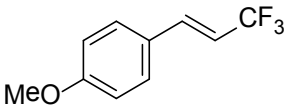

$R_f$= 0.3 ( EA/PE = 1:15), Yield 75%, yellow liquid. E/Z=95/5. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.08 (dd, $J$ = 1.6 Hz, 16.0 Hz, 1H), 7.01 (d, $J$ = 8.0 Hz, 1H), 6.96 (s, 1H), 6.86 (d, $J$ = 8.0 Hz, 1H), 6.07 (dq, $J$ = 6.8 Hz, 16.0 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ 150.7, 149.2, 137.4 (q, $J$ = 6.7 Hz), 126.3, 123.9 (q, $J$ = 6.7 Hz), 121.6, 113.6 (q, $J$ = 33.5 Hz), 110.0, 109.3, 55.9, 55.8 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): δ -62.83 ppm.

(E)-1-methyl-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2b**[2a]



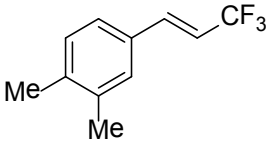

$R_f$ = 0.9 (Hexane), Yield 78%, colorless liquid. E/Z=97/3. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.34 (d, $J$ = 8.0 Hz, 2H), 7.19 (d, $J$ = 8.0 Hz, 2H), 7.11 (dq, $J$ = 2.0 Hz, 16.0 Hz, 1H), 6.15 (dq, $J$ = 6.4 Hz, 16.0 Hz, 1H), 2.37 (s, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ 140.3, 137.6 (q, $J$ = 6.2 Hz), 130.6, 129.6, 127.5, 123.8 (q, $J$ = 267.1 Hz), 114.8 (q, $J$ = 33.2 Hz), 21.4 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): δ -63.12 ppm.

(E)-1-methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2c**[2a]



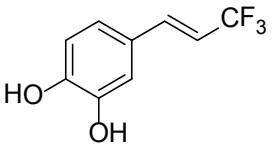

$R_f$ = 0.7 ( EA/PE = 1:10 ), Yield 83%. white solid. E/Z=99/1. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.39 (d, $J$ = 8.4 Hz, 2H), 7.08 (d, $J$ = 17.2 Hz, 1H), 6.90 (d, $J$ = 8.4 Hz, 2H), 6.06 (dq, $J$ = 6.4 Hz, 16.0 Hz, 1H), 3.83 (s, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ 161.1, 137.1 (q, $J$ = 7.1 Hz), 129.0, 126.1, 123.9 (q, $J$ = 267.7 Hz), 114.3, 113.5 (q, $J$ = 33.5 Hz), 55.4 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): δ -62.87 ppm.

(E)-1,2-dimethyl-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2d**



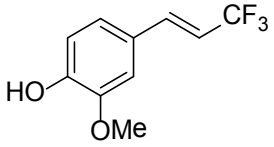

$R_f$ = 0.6 ( Hexane ), Yield 73%, colorless liquid. E/Z=94/6. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.22 (s, 1H), 7.18 (d, $J$ = 8.0 Hz, 1H), 7.13 (d, $J$ = 8.0 Hz, 1H), 7.08 (dq, $J$ = 2.4 Hz, 16.4 Hz, 1H) , 7.08 (dq, $J$ = 6.8 Hz, 16.0 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ139.0, 137.7 (q, $J$ = 7.1 Hz ), 137.2, 131.1, 130.2, 128.7, 125.1, 123.9 ( q, $J$ = 267.3 Hz), 114.6 (q, $J$ = 33.4 Hz), 19.7(2C) ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): δ = -63.07 ppm. HRMS (EI) m/z calcd for $C_{11}H_{11}F_3$ $[M]^+$: 200.0807; found: 200.0816.

(E)-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene-1,2-diol **2e**[2a]



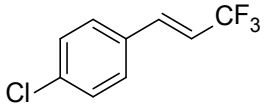

$R_f$ = 0.4 ( EA/PE = 1:1 ), Yield 83%, yellow liquid. E/Z=93/7 . $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 6.96-7.06 (m, 2H), 6.90-6.93 (m, 1H), 6.86-6.88 (d, $J$ = 8.0 Hz, 1H), 6.01 (dq, $J$ = 6.4 Hz, 16.0 Hz, 1H), 5.72 (s, 1H), 5.59 (s, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ145.4, 143.7, 137.0 (q, $J$ = 7.0 Hz), 126.9, 123.8 (q, $J$ = 267.0 Hz), 121.7, 115.6, 113.9, 113.9 (q, $J$ = 33.5 Hz)ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): δ = -62.92 ppm.

(E)-2-methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)phenol **2f**[2a]



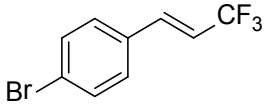
$R_f$ = 0.4 ( DCE/Hexane = 1/2 ), Yield 80%, colorless liquid. E/Z=96/4. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.06 (dd, $J$ = 2.0 Hz, 16.0 Hz 1H), 6.99 (dd, $J$ = 1.6 Hz, 8.0Hz, 1H), 6.94-6.96 (m, 1H), 6.90-6.94 (m, 1H), 6.05 (dq, $J$ = 6.4 Hz, 16.4 Hz, 1H), 3.92 (s, 3H)ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ147.5, 146.8, 137.5 (q, $J$ = 5.8 Hz), 125.9, 124.0 (q, $J$ = 267.1 Hz), 122.1, 114.7, 113.4 (q, $J$ = 33.3 Hz), 109.0, 56.0 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): δ -63.80 ppm.

(E)-1-chloro-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2g**[2b]



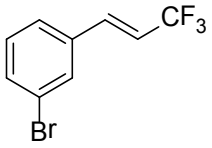
$R_f$ = 0.9 (Hexane), Yield 70%, colorless liquid. E/Z=98/2. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.37-7.40 (m ,4H), 7.10 (d, $J$ = 16.0 Hz, 1H), 6.18 (dq, $J$ = 6.4 Hz, 16.4 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ 136.4 (q, $J$ = 6.5 Hz), 136.0, 131.9, 129.2, 128.7, 123.4 (q, $J$ = 267.5 Hz), 116.4 (q, $J$ = 34.0 Hz) ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): δ -63.45 ppm.

(E)-1-bromo-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2h**[2b]



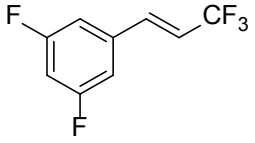
$R_f$ = 0.8 ( Hexane ), Yield 80%, colorless liquid. E/Z=95/5. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.53 (d, $J$ = 8.4 Hz, 2H), 7.26 (d, $J$ = 8.0 Hz, 2H), 7.09 (d, $J$ = 16.0 Hz, 1H), 6.20 (dq, $J$ = 6.4 Hz, 16.4 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ 138.2, 136.5 (q, $J$ = 7.6 Hz), 132.2, 129.0, 124.3, 123.4 (q, $J$ = 267.4 Hz), 116.6 (q, $J$ = 34.8 Hz)ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): δ -63.49 ppm.

(E)-1-bromo-3-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2i**



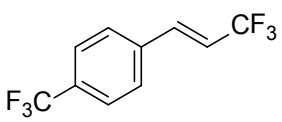
$R_f$ = 0.8 ( Hexane ), Yield 68%, colorless liquid. E/Z=99/1. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.60 (s, 1H), 7.51 (d, $J$ = 8.4 Hz, 1H), 7.37 (d, $J$ = 7.6 Hz, 1H), 7.25-7.29 (m, 1H), 7.49 ( dq, $J$ = 2.0 Hz, 16.0 Hz, 1H ), 6.21 (dq, $J$ = 6.4 Hz, 16.0 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ136.2 (q, $J$ = 7.0 Hz ), 135.5, 130.5, 130.4, 126.2, 123.3 ( q, $J$ = 267.6 Hz), 123.1, 117.4 (q, $J$ = 33.1 Hz), 19.7 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): δ = -63.61 ppm. HRMS (EI) m/z calcd for $C_9H_6BrF_3$ $[M]^+$: 249.9599; found: 249.9602.

(E)-1,3-difluoro-5-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2j**[2b]



$R_f$ = 0.9 ( Hexane ), Yield 84%, colorless liquid. E/Z=96/4. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.07 (dd，$J$ = 2.0 Hz，16.0 Hz, 1H), 6.94-7.00 (m, 2H), 6.81-6.87 (m, 1H), 6.22 (dq, $J$ = 6.4 Hz, 16.4 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ163.32 (d, $J$ = 248.5 Hz), 136.6 (t, $J$ = 9.5 Hz), 135.6, 123.0 (q, $J$ = 267.3 Hz), 118.6 (q, $J$ = 34.6 Hz), 110.4 (d, $J$ = 25.5 Hz), 105.3 (t, $J$ = 25.3 Hz) ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): δ = -63.87，-108.78 ppm.

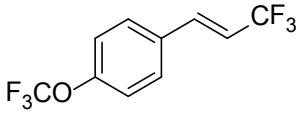
(E)-1-(trifluoromethyl)-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2k**[2b]



$R_f$ = 0.8 (Hexane), Yield 76%, colorless liquid. E/Z=98/2. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.66 (d, $J$ = 8.4 Hz, 2H), 7.56 (d, $J$ = 8.4 Hz, 2H), 7.18 (dd, $J$ = 2.4 Hz, 16.4 Hz), 6.29 (dq, $J$ = 6.4, 16.0 Hz 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ 136.9, 136.3 (q, $J$ = 6.1 Hz), 131.9 (q, $J$ = 32.7 Hz),

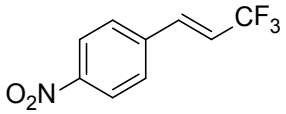
127.8, 126.0 (q, $J$ = 3.8 Hz), 123.9 (q, $J$ = 270.3 Hz), 123.2 (q, $J$ = 267.0 Hz), 118.5 (q, $J$ = 34.3 Hz)ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): δ -62.97, -63.86 ppm.

(E)-1-(trifluoromethoxy)-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2l**[2b]



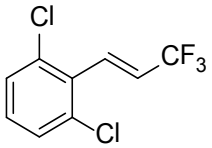
$R_f$ = 0.8 ( PE/EA = 1:10 ), Yield 87%, colorless liquid. E/Z=99/1. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.49 (d, $J$ = 8.4 Hz, 2H), 7.24 (d, $J$ = 8.0 Hz, 2H), 7.14 (dd, $J$ = 2.4 Hz, 16.4 Hz, 1H), 6.19 (dq, $J$ = 6.4 Hz, 16.0 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ150.3, 136.2 (q, $J$ = 5.9 Hz), 132.0, 129.0, 123.3 (q, $J$ = 267.1 Hz), 121.3, 120.4 (q, $J$ = 256.3 Hz), 116.9 (q, $J$ = 33.3 Hz) ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): δ -57.84, -63.55 ppm.

(E)-1-nitro-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2m**[2c]



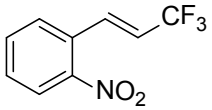
$R_f$ = 0.4 ( DCE/Hexane = 1/20 ), Yield 78%, yellow solid. E/Z=98/2. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.27 (d , $J$ = 8.4 Hz, 2H), 7.63 (d, $J$ = 8.4 Hz, 2H), 7.23 (dq, $J$ = 2.0 Hz, 16.0 Hz, 1H), 6.37 (dq, $J$ = 6.0 Hz, 16.4 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ 148.5, 139.5, 135.4 (q, $J$ = 5.7 Hz), 128.3, 125.5 (q, $J$ = 268.3 Hz), 124.2, 118.4 (q, $J$ = 34.2 Hz) ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): δ -63.98 ppm.

(E)-1,3-dichloro-2-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2n**



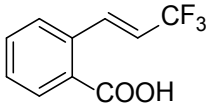
$R_f$ = 0.8 ( Hexane ), Yield 83%, colorless liquid. E/Z=99/1. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.28 (d, $J$ = 8.4 Hz, 2H), 7.14-7.19 (m, 1H), 7.11-7.14 (m, 1H), 6.31 (dq, $J$ = 6.4 Hz, 16.4 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ134.7 (q, $J$ = 5.9 Hz), 131.5 (q, $J$ = 7.2 Hz), 130.9, 130.0, 128.8, 122.8 (q, $J$ = 269.5 Hz), 124.5 (q, $J$ = 33.1 Hz)ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): δ -64.75 ppm. HRMS (EI) m/z calcd for $C_9H_5Cl_2F_3$ $[M]^+$: 239.9715; found: 239.9716.

(E)-1-nitro-2-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2o**



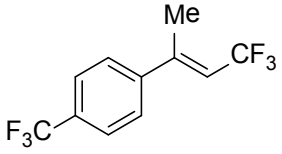
$R_f$ = 0.4 ( EA/PE = 1:10 ), Yield 86%, yellow liquid. E/Z=99/1. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.09 (d, $J$ = 8.4 Hz, 1H), 7.71-7.74 (m, 1H), 7.67-7.70 (m, 1H), 7.59-7.61 (m, 1H), 7.56-7.59 (m, 1H), 6.16 (dq, $J$ = 6.4 Hz, 16.0 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ134.3(q, $J$ = 5.9 Hz), 133.8, 130.7, 130.4, 129.8, 129.3, 125.1, 122.7 (q, $J$ = 268.1 Hz), 120.6 (q, $J$ = 33.2 Hz) ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): δ -64.09 ppm.

(E)-2-(3,3,3-trifluoroprop-1-en-1-yl)benzoic acid **2p**[2a]



$R_f$ = 0.3 ( PE/EA = 1:5 ), Yield 59%, colorless liquid. E/Z=95/5. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.14 (d, $J$ = 8.4 Hz, 1H), 8.08-8.12 (m, 1H), 7.60-7.64(m, 1H), 7.56 (d, $J$ = 6.8 Hz, 1H), 7.48-7.52 (m, 1H), 6.08 (dq, $J$ = 6.4 Hz, 16.0 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ170.8, 137.4 (q, $J$ = 6.8 Hz), 136.5, 133.4, 131.8, 129.5, 128.2, 128.0, 123.2 (q, $J$ = 267.5 Hz), 118.6 (q, $J$ = 33.0 Hz) ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): δ -63.62 ppm.

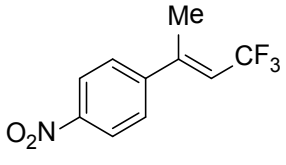
(E)-1-(4,4,4-trifluorobut-2-en-2-yl)-4-(trifluoromethyl)benzene **2q**



$R_f$ = 0.8 ( EA/PE = 1:20 ), Yield 80%, colorless liquid. E/Z=97/3. $^1$H NMR

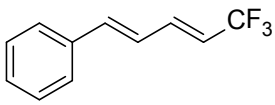
(400 MHz, $CDCl_3$): $\delta$ = 7.64 (d, $J$ = 8.0 Hz, 2H), 7.52 (d, $J$ = 8.4 Hz, 2H), 5.91 (q, $J$ = 8.4 Hz, 1H), 2.31 (s, 3H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$): δ147.9 (q, $J$ = 6.2 Hz ), 144.4, 131.1 (q, $J$ = 32.5 Hz ), 126.5, 125.6 (q, $J$ = 3.9 Hz), 123.9 (q, $J$ = 270.5 Hz ), 123.3 (q, $J$ = 269.2 Hz ), 117.7 (q, $J$ = 34.9 Hz ), 17.4 ppm; $^{19}F$ NMR (376 MHz, $CDCl_3$): δ = -57.51, -62.80 ppm. HRMS (EI) m/z calcd for $C_{11}H_8F_6$ $[M]^+$: 254.0525; found: 254.0523.

(E)-1-nitro-4-(4,4,4-trifluorobut-2-en-2-yl)benzene **2r**



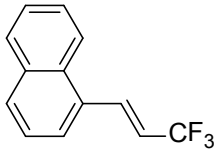

$R_f$ = 0.4 ( PE/EA= 0.4 ), Yield 66%, yellow liquid. E/Z=96/4. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 8.17 (d, $J$ = 8.4 Hz, 2H), 7.51 (d, $J$ = 8.4 Hz, 2H), 5.90 (q, $J$ = 8.0 Hz, 1H), 2.26(s, 3H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$): δ148.0, 147.2 (q, $J$ = 5.7 Hz), 147.1, 127.1, 123.9, 123.1 (q, $J$ = 269.6 Hz), 118.9 (q, $J$ = 34.5 Hz), 17.5 ppm; $^{19}F$ NMR (376 MHz, $CDCl_3$): δ -57.65 ppm. HRMS (EI) m/z calcd for $C_{10}H_8F_3NO_2$ $[M]^+$: 231.0502; found: 231.0506.

((1E,3E)-5,5,5-trifluoropenta-1,3-dien-1-yl)benzene **2s**[2a]



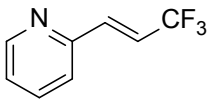

$R_f$ = 0.9 ( Hexane ), Yield 50%, colorless liquid. E/Z=98/2. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.44 (d, $J$ = 6.8 Hz, 2H), 7.35-7.39 (m, 2H), 7.31-7.33 (m, 1H), 6.88-6.95 (m, 1H), 6.83 (d, $J$ = 15.6 Hz, 1H), 6.77 (dd, $J$ = 9.6 Hz, 15.6 Hz, 1H), 5.80 (dq, $J$ = 6.8 Hz, 15.2 Hz, 1H ) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$): δ139.3, 137.5 (q, $J$ = 5.9 Hz), 135.8, 129.0, 128.8, 127.0, 124.9, 123.5(q, $J$ = 267.1 Hz), 118.3 (q, $J$ = 33.3 Hz) ppm; $^{19}F$ NMR (376 MHz, $CDCl_3$): δ -63.20 ppm.

(E)-1-(3,3,3-trifluoroprop-1-en-1-yl)naphthalene **2t**[2d]



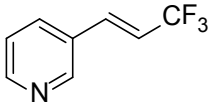

$R_f$ = 0.8 ( Hexane ), Yield 73%, colorless liquid. E/Z=94/6. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 8.05 (d，$J$ = 8.4 Hz, 1H), 7.95 (dq, $J$ = 2.0 Hz, 15.6 Hz, 1H), 7.85-7.90 (m, 2H), 7.63 (d，$J$ = 7.2 Hz, 1H), 7.52-7.60 (m, 2H), 7.49( m, 1H ), 6.26 (dq, $J$ = 6.4 Hz, 16.0 Hz, 1H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$): δ135.2 (q, $J$ = 7.4 Hz), 133.6, 131.1, 131.0, 130.2, 128.8, 127.0, 126.3, 125.4, 124.9, 123.4 (q, $J$ = 266.3 Hz ), 123.2, 118.8 (q, $J$ = 33.2 Hz) ppm; $^{19}F$ NMR (376 MHz, $CDCl_3$): δ = -63.41 ppm.

(E)-2-(3,3,3-trifluoroprop-1-en-1-yl)pyridine **2u**[2c]




$R_f$ = 0.4 ( EA/PE = 1:15), Yield 79%, yellow liquid. E/Z=97/3. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 8.64 (d, $J$ = 4.0 Hz, 1H), 7.71-7.75 (m, 1H), 7.35 (d, $J$ = 7.6 Hz 1H), 7.27-7.30 (m, 1H), 7.18 (dq, $J$ = 2.0 Hz, 15.6 Hz, 1H), 6.82 (dq, $J$ = 6.8 Hz, 15.6 Hz, 1H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 151.7, 150.0, 137.0, 136.7 (q, $J$ = 6.1 Hz), 124.4, 124.3, 123.5 (q, $J$ = 267.2 Hz), 120.0 (q, $J$ = 34.6 Hz) ppm; $^{19}F$ NMR (376 MHz, $CDCl_3$): δ -63.91 ppm.

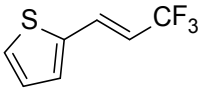
(E)-3-(3,3,3-trifluoroprop-1-en-1-yl)pyridine **2v**[2b]




$R_f$ = 0.4 ( EA/PE = 1:5 ), Yield 60%, yellow liquid. E/Z=98/2. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 8.71 (s , $J$ = 4.0 Hz, 1H), 8.63 (d, $J$ = 3.6 Hz, 1H), 7.82 (d, $J$ = 7.6 Hz, 1H), 7.37 (dd, $J$ = 4.8 Hz, 7.6 Hz, 1H), 7.17 (dd, $J$ = 2.0 Hz, 16.4 Hz, 1H),

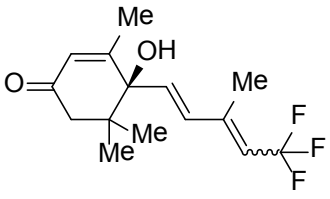
6.32 (dq, *J* = 6.4 Hz, 16.4 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ 150.5, 148.8, 134.3, 134.2 (q, *J* = 5.8 Hz), 129.5, 124.0, 123.0 (q, *J* = 266.8 Hz), 118.4 (q, *J* = 34.2 Hz) ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): δ -63.86 ppm.

(E)-2-(3,3,3-trifluoroprop-1-en-1-yl)thiophene **2w**[2a]




$R_f$ = 0.7 (Hexane), Yield 52%, colorless liquid. E/Z= 85/15. $^1$H NMR (400 MHz, $CDCl_3$): *δ* = 7.35 (d, *J* = 5.2 Hz, 1H), 7.25 (dd, *J* = 2.0 Hz, 15.6 Hz, 1H), 7.19 (d, *J* = 3.2 Hz, 1H), 7.04 (dd, *J* = 3.6 Hz, 4.8 Hz, 1H), 6.02 (dq, *J* = 6.4 Hz, 16.0 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ 138.0, 130.5 (q, *J* = 5.9 Hz), 130.0, 127.9, 127.7, 123.4 (q, *J* = 267.3 Hz), 114.3 (q, *J* = 33.9 Hz) ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): δ -63.10 ppm.

(S)-4-hydroxy-3,5,5-trimethyl-4-((1E)-5,5,5-trifluoro-3-methylpenta-1,3-dien-1-yl)cyclohex-2-enone **2x**




$R_f$ = 0.3 (EA/PE=1/5), Yield 69%, colorless liquid. E/Z= 72/28. $^1$H NMR (400 MHz, $CDCl_3$) of (E,E)-product : *δ* = 6.39 (d, *J* = 15.6 Hz, 1H), 6.04 (d, *J* = 15.6 Hz, 1H), 5.94 (s, 1H), 5.67 (q, *J* = 8.4 Hz, 1H), 2.46 (d, *J* =17.2 Hz, 1H), 2.30 (d, *J* =16.8 Hz, 1H), 2.01 (s, 3H), 1.90 (s, 3H), 1.11 (s, 3H), 1.02 (s, 3H) ppm; $^1$H NMR (400 MHz, $CDCl_3$) of (E,Z)-product: *δ* = 6.91 (d, *J* = 16.0 Hz, 1H), 6.06 (d, *J* = 16.0 Hz, 1H), 5.94 (s, 1H), 5.57 (q, *J* = 8.0 Hz, 1H), 2.46 (d, *J* =17.2 Hz, 1H), 2.30 (d, *J* =16.8 Hz, 1H), 1.98 (s, 3H), 1.90 (s, 3H), 1.11 (s, 3H), 1.02 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl3): δ197.5, 161.9，144.3 (q, J = 5.5 Hz，(E)-product), 143.1 (q, J = 5.3 Hz，(Z)-product)，133.8, 132.5, 127.2，123.3 (q, J =269.5 Hz), 119.4 (q, J = 33.4 Hz, (E)-product), 117.4 (q, J = 33.4 Hz, (Z)-product), 79.5，49.7，41.5，24.3 ((E)-product)，23.0 ((E)-product)，20.4( (Z)-product), 18.8 ((Z)-product))，19.0，13.8 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): δ -55.59 (E, Z), -56.76(E,E) ppm.

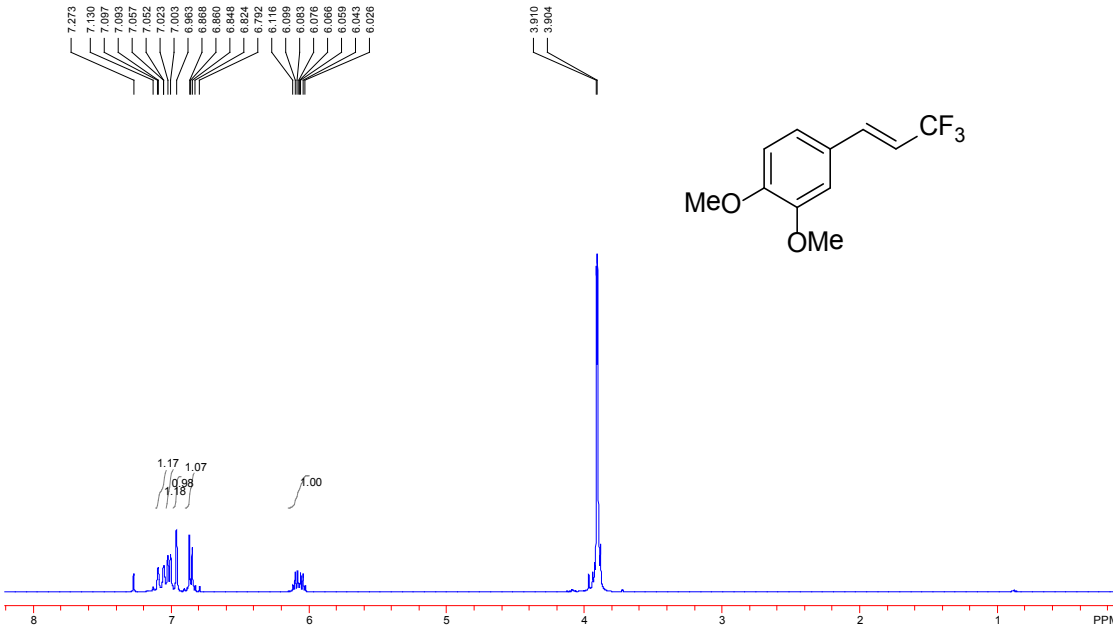
# References:

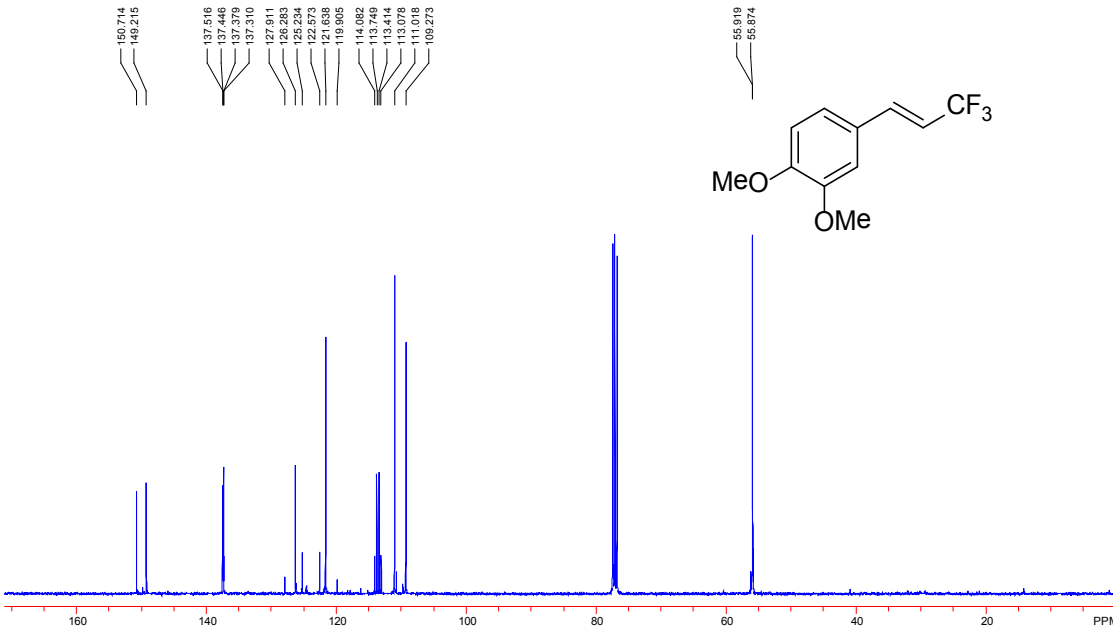
(1) Eisenberger, P; Gischig, S; Togni, A. *Chem. Eur. J.* **2006**, *12*, 2579.

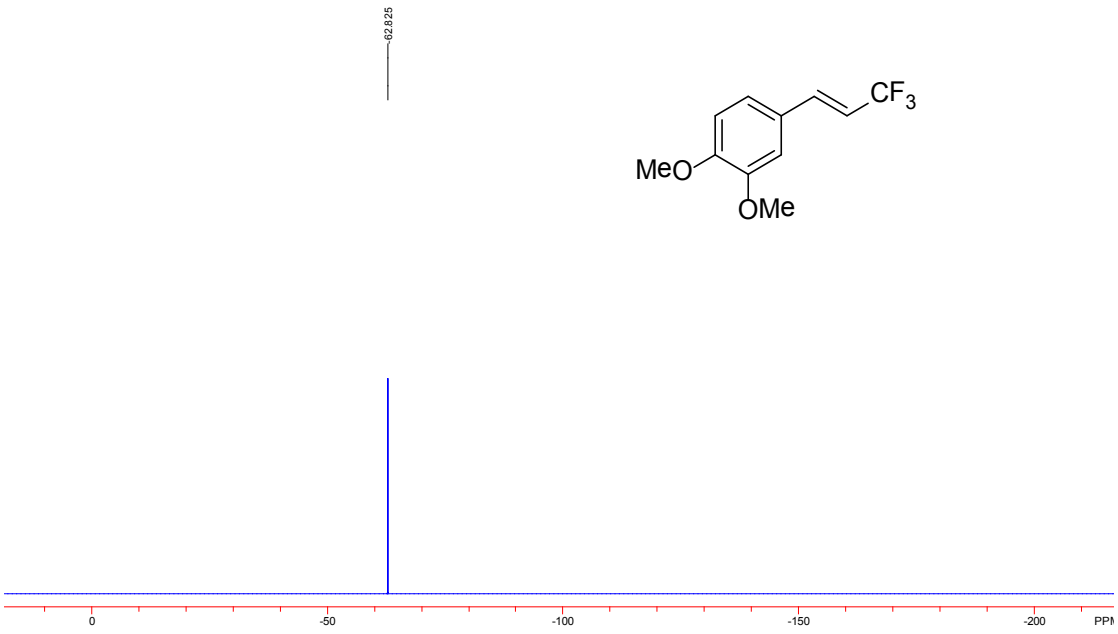
(2) (a) Li, Z.; Cui, Z.; Liu, Z. *Org. Lett.* **2013**,*15*, 406. (b) Yasu, Y.; Koike, T.; Akita, M. *Chem. Commun.* **2013**, *49*, 2037. (c) Hanamoto, T.; Morita, N.; Shindo, K. *Eur. J. Org. Chem.* **2003**, 4279. (d) Masaaki, O.; Miyuu, T.; Akari. I.; Shiho, N.; Atsushi, T.; Kazuyuki, S.; Akira, A. *Org. Lett.* **2012**,*14*, 1146.

## Copies $^{1}H$ NMR, $^{13}C$ NMR, NOESY $^{1}H$ NMR

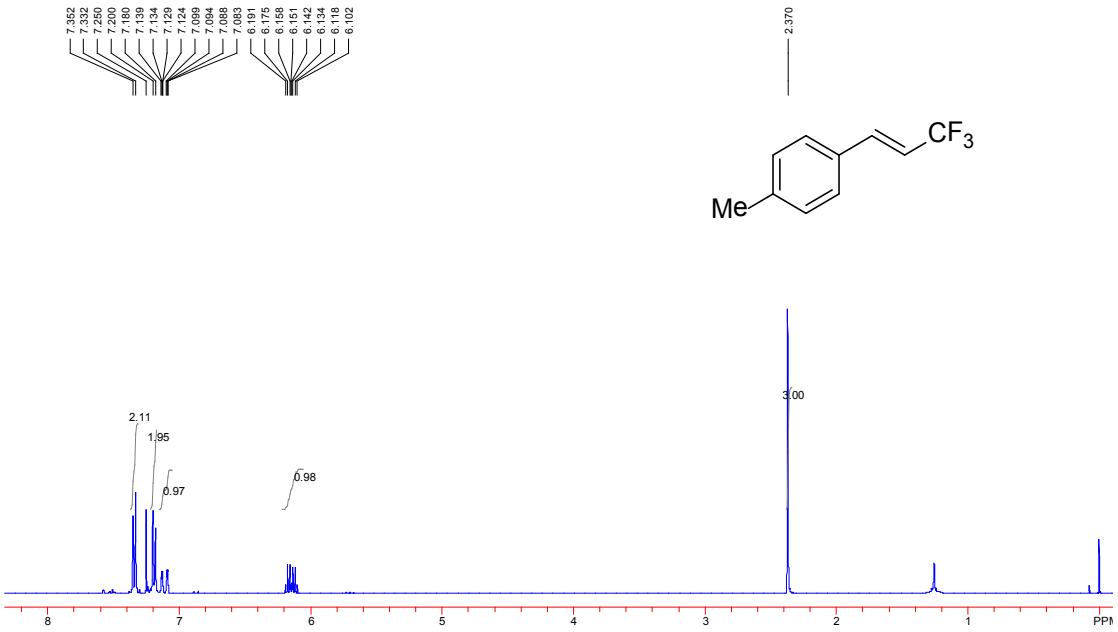
(E)-1,2-dimethoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2a**

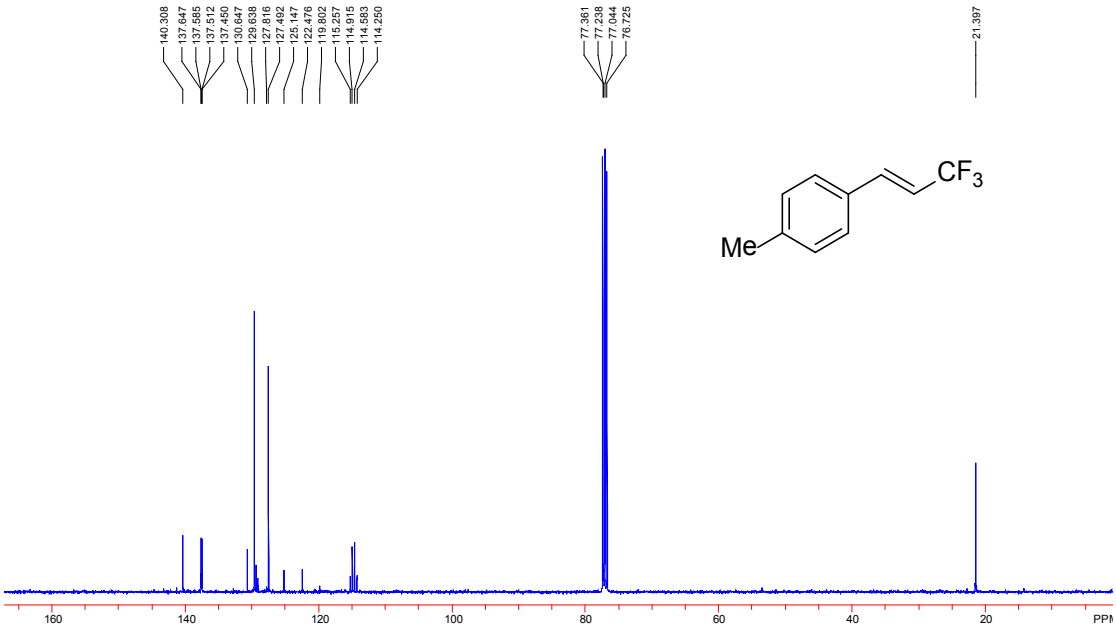


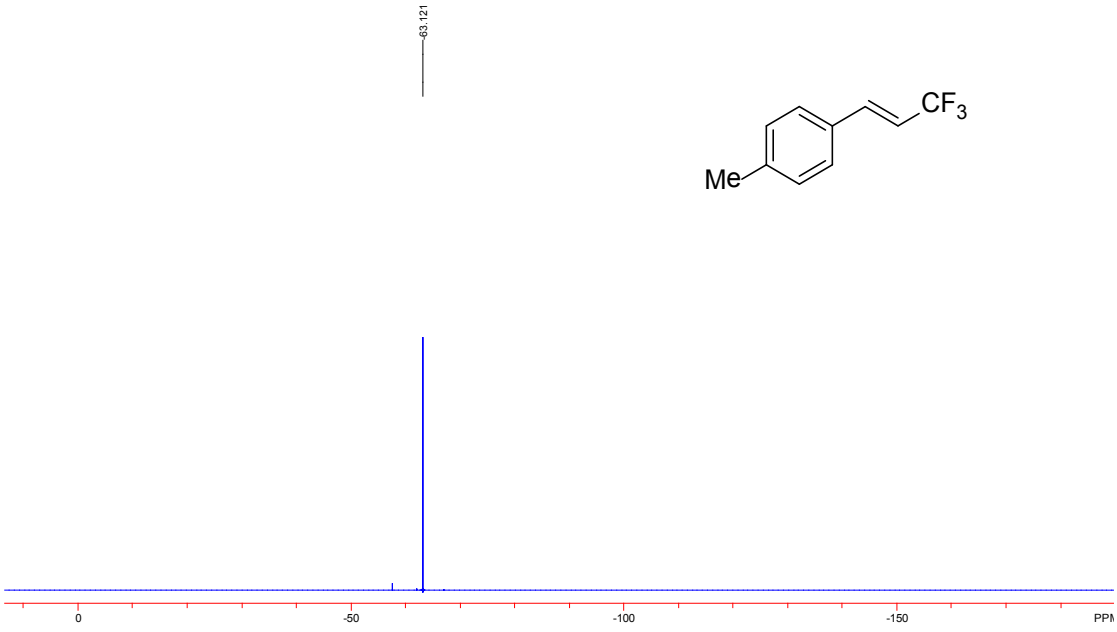





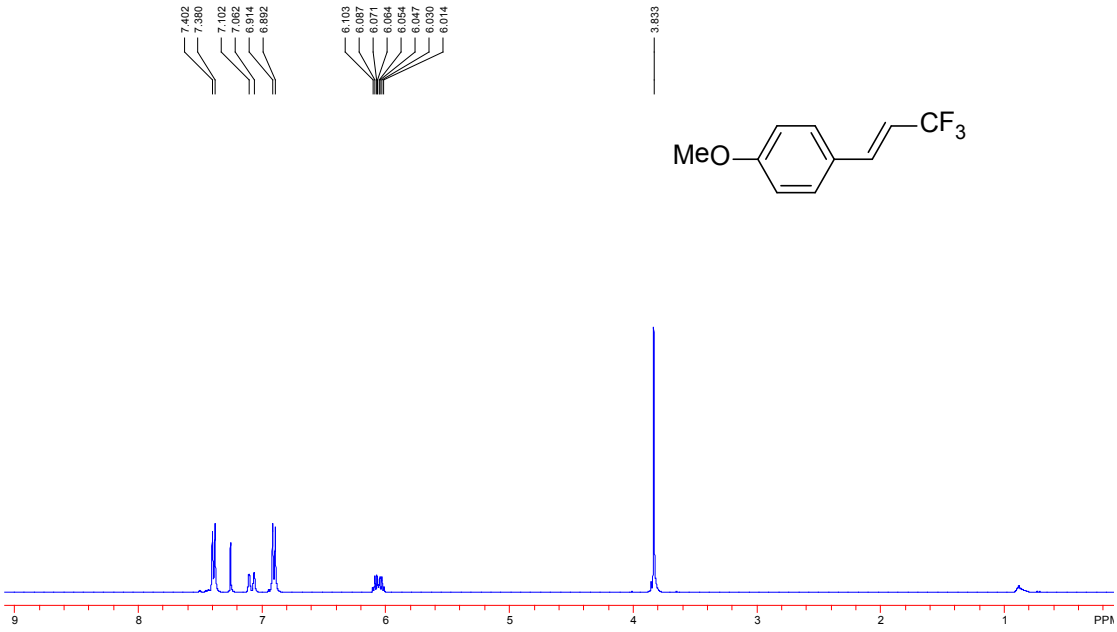

(E)-1-methyl-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2b**

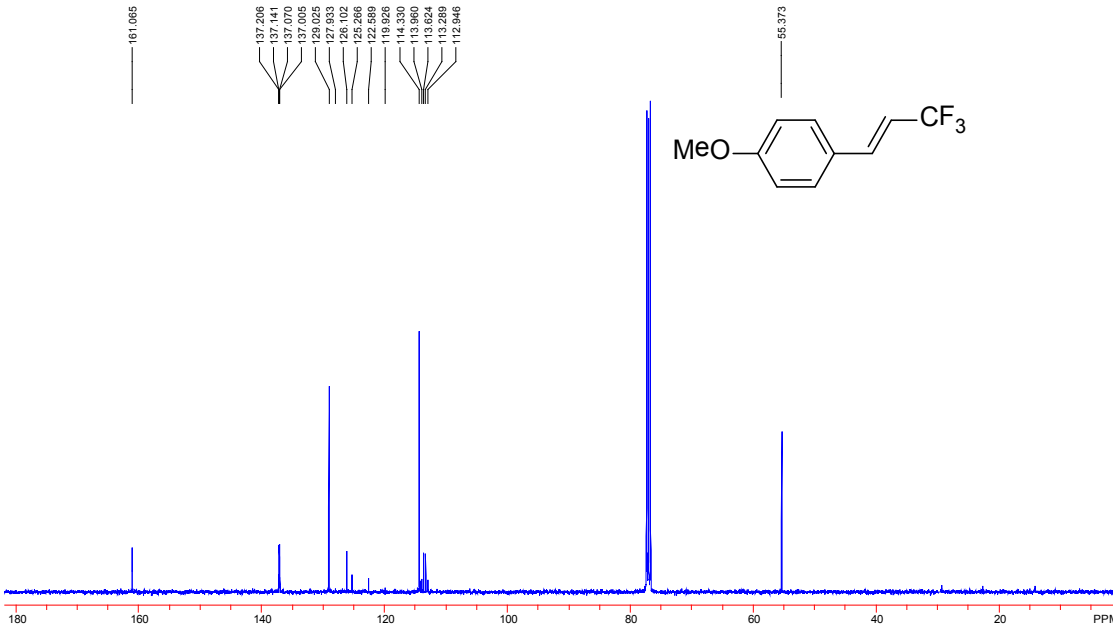


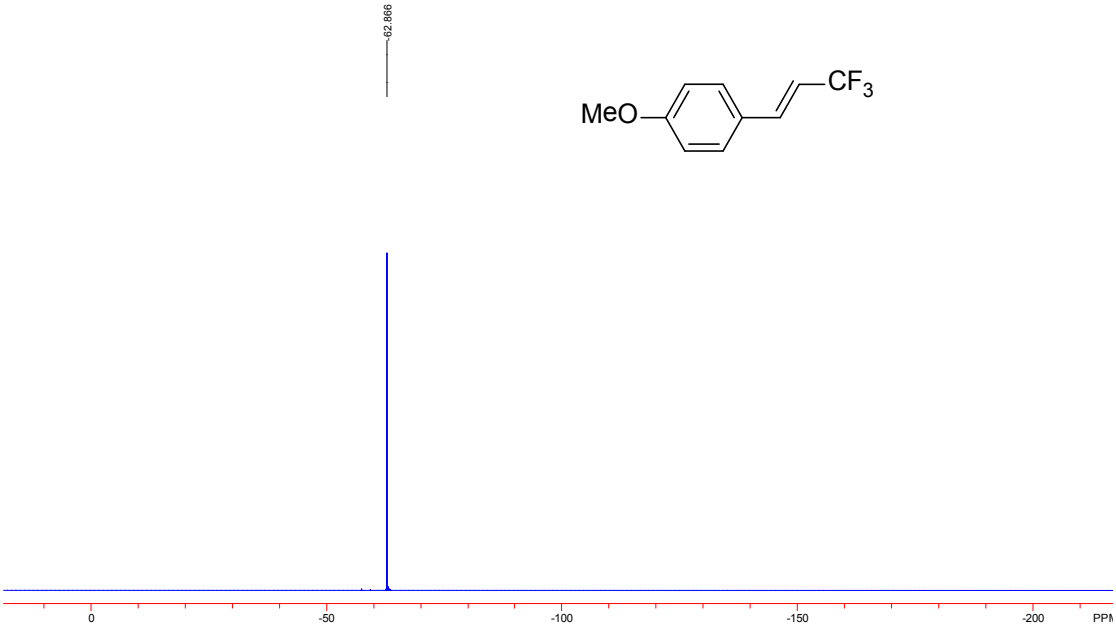


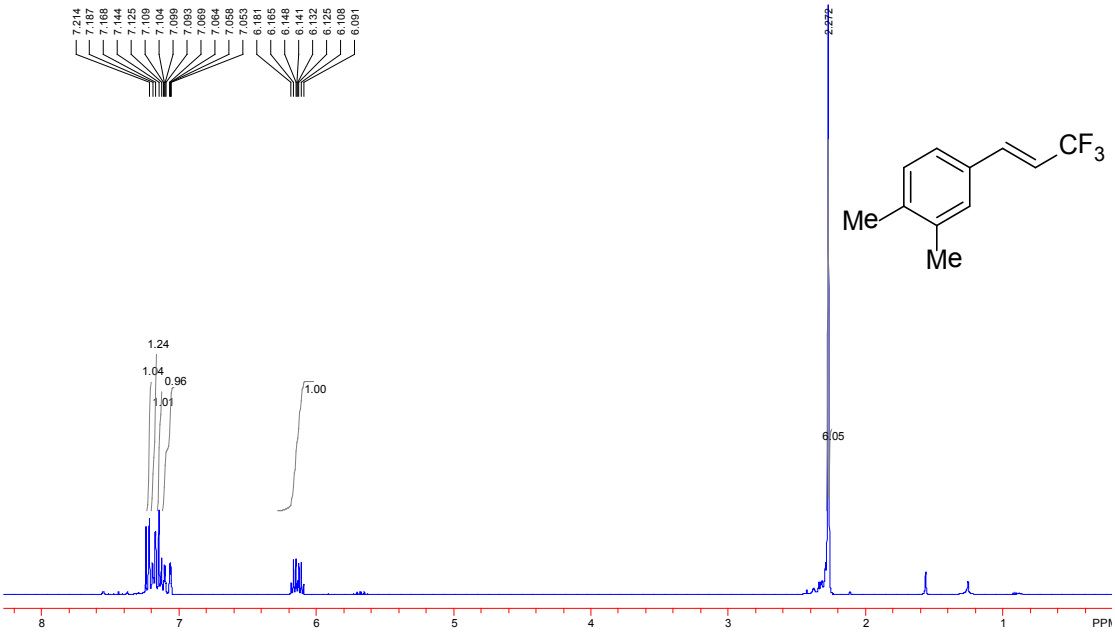
(E)-1-methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2c**

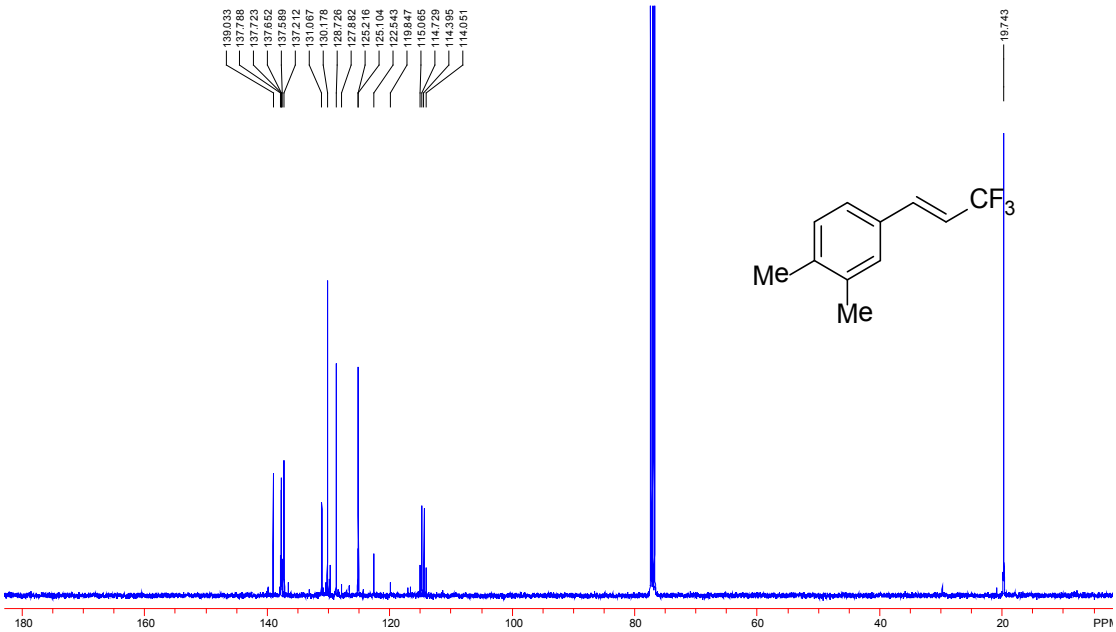


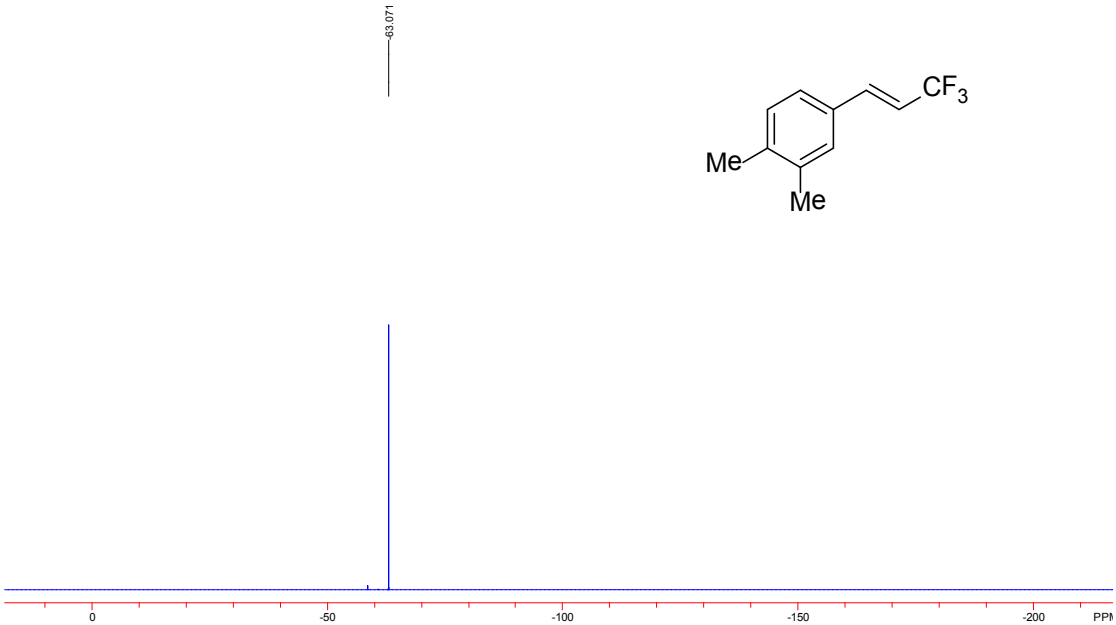





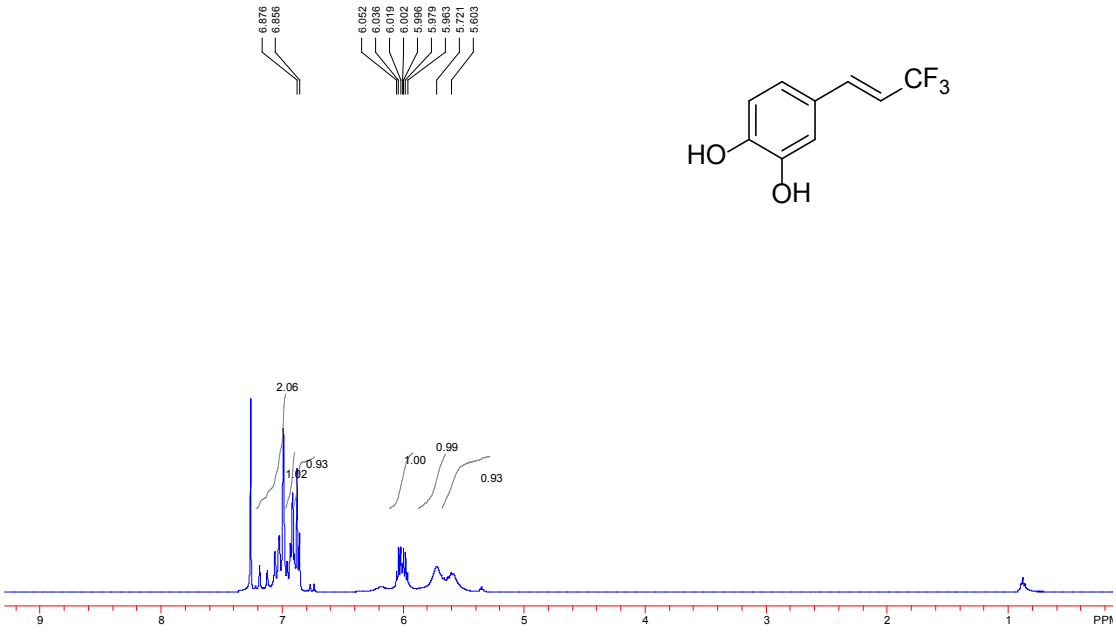

(E)-1,2-dimethyl-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2d**

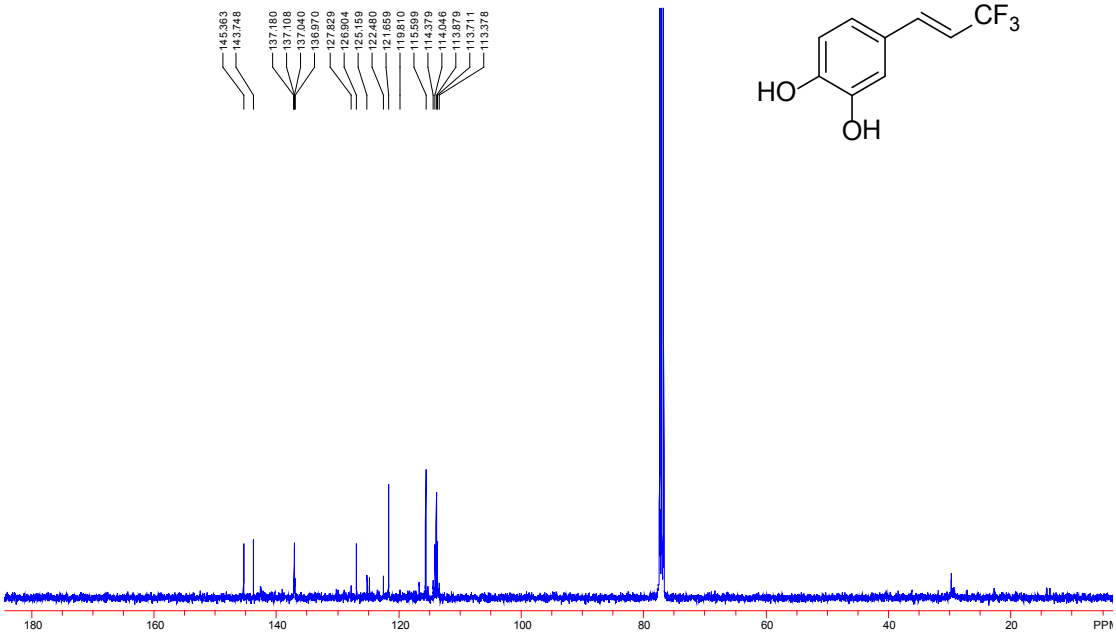


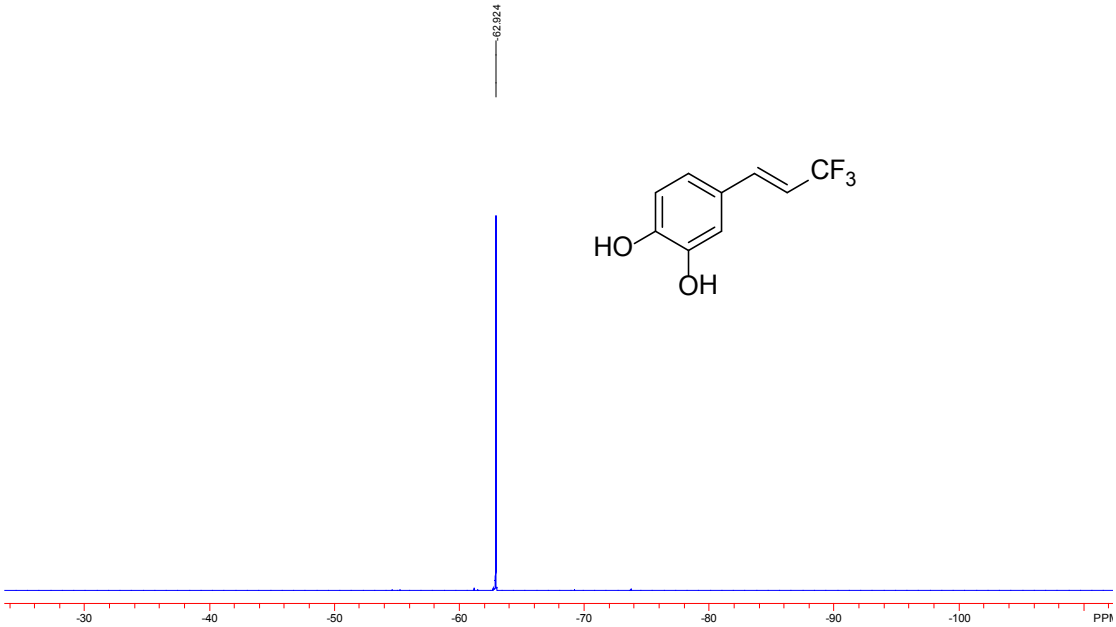


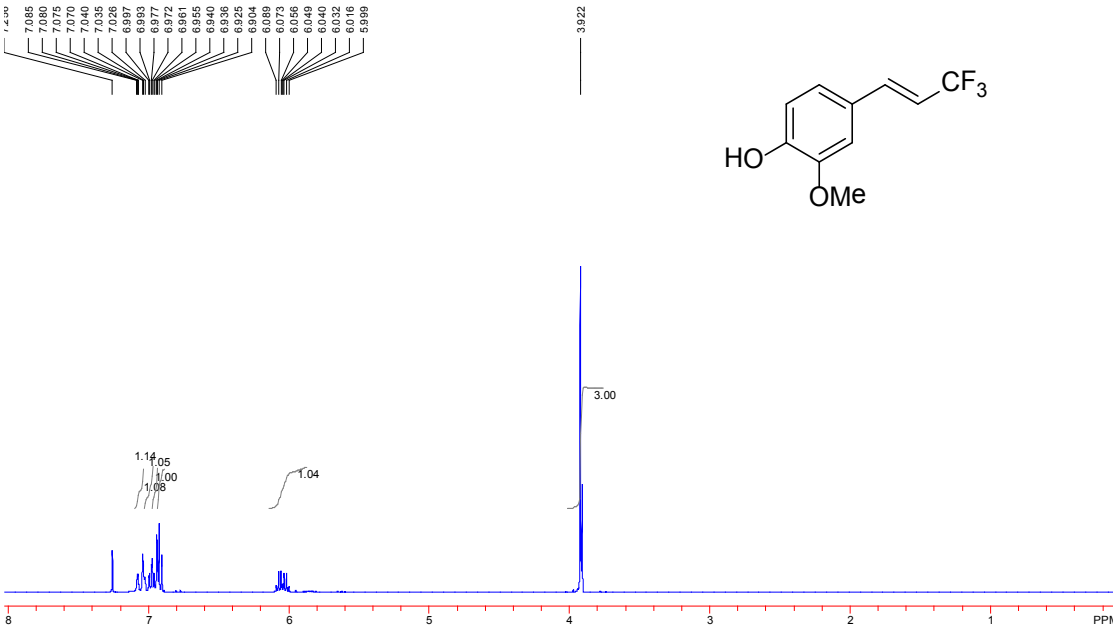
(E)-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene-1,2-diol **2e**

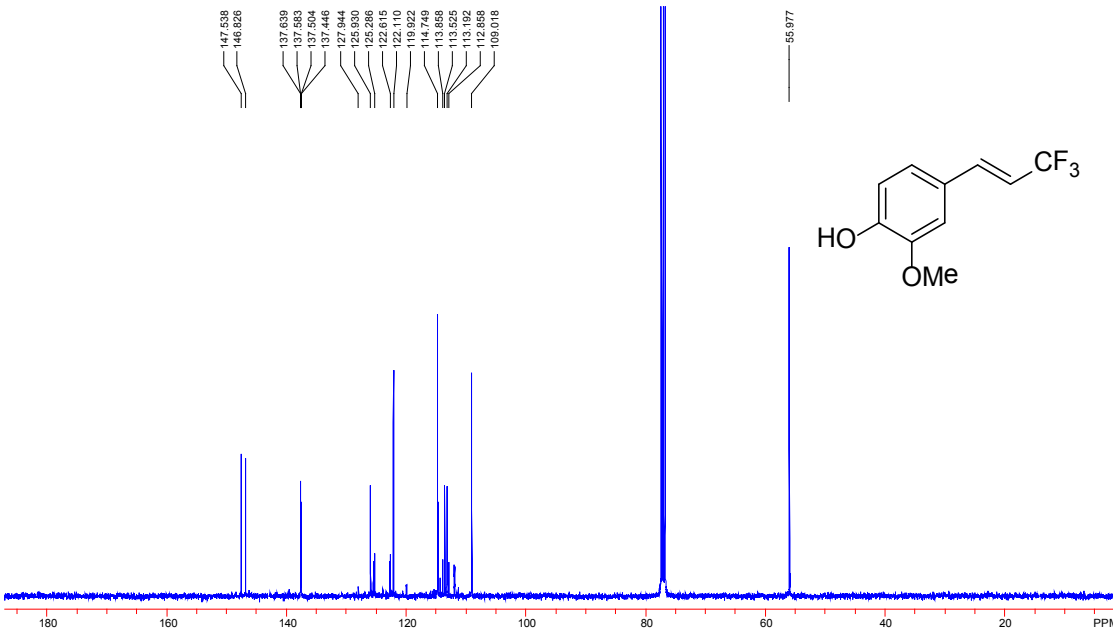


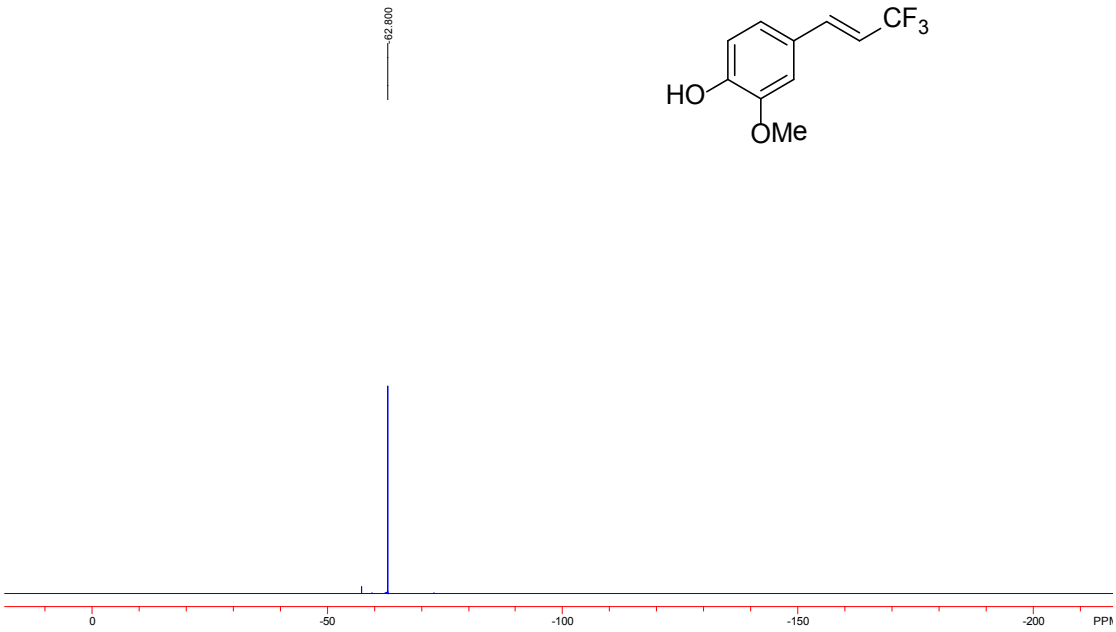





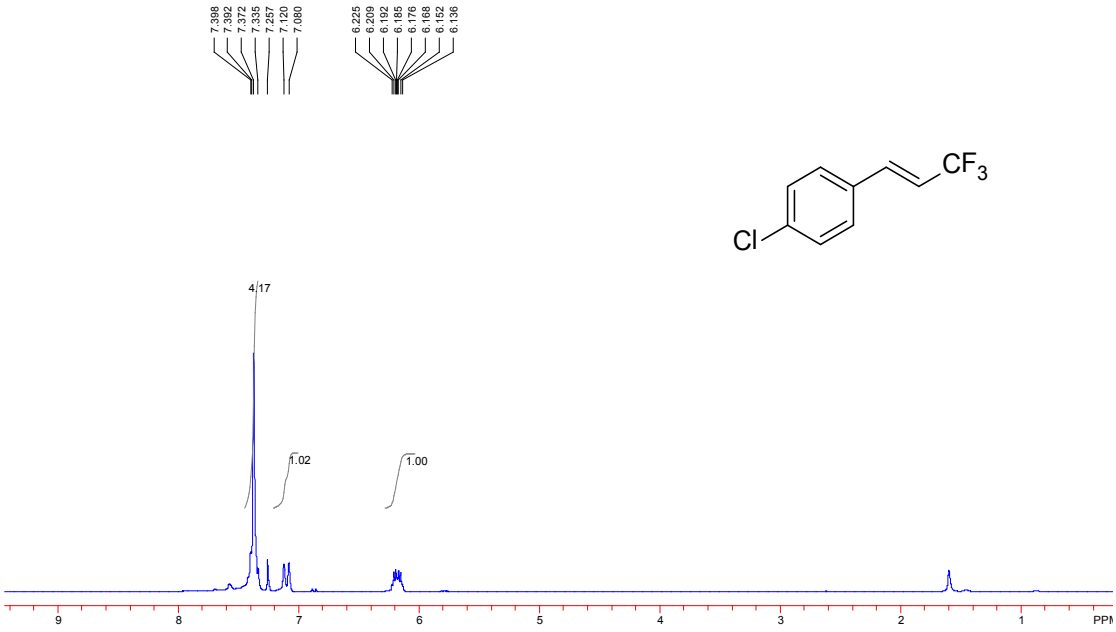

(E)-2-methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)phenol **2f**

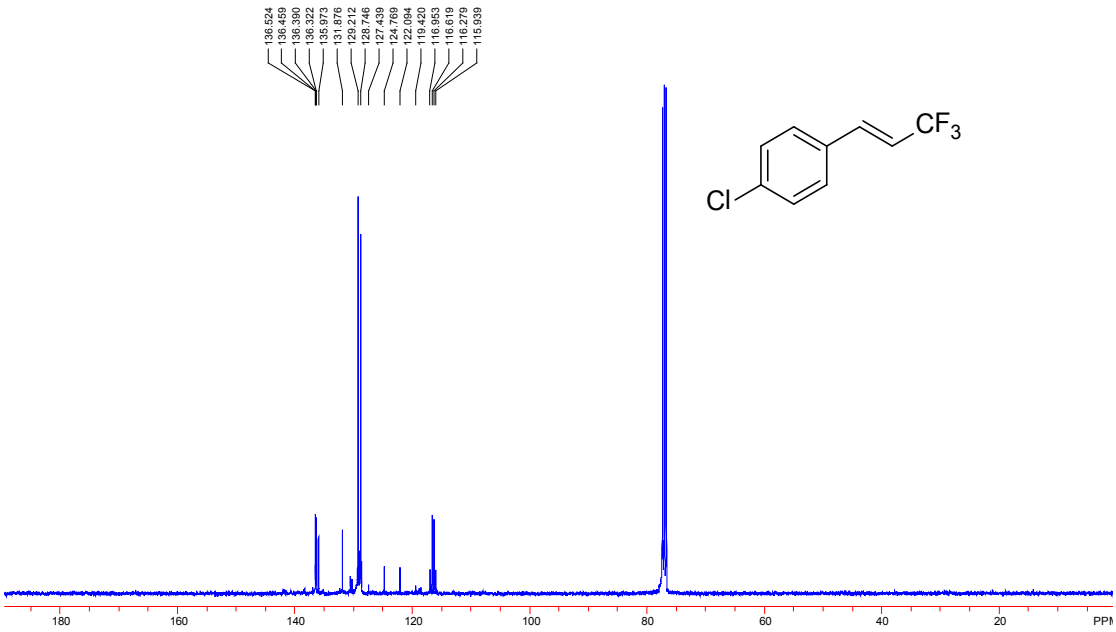


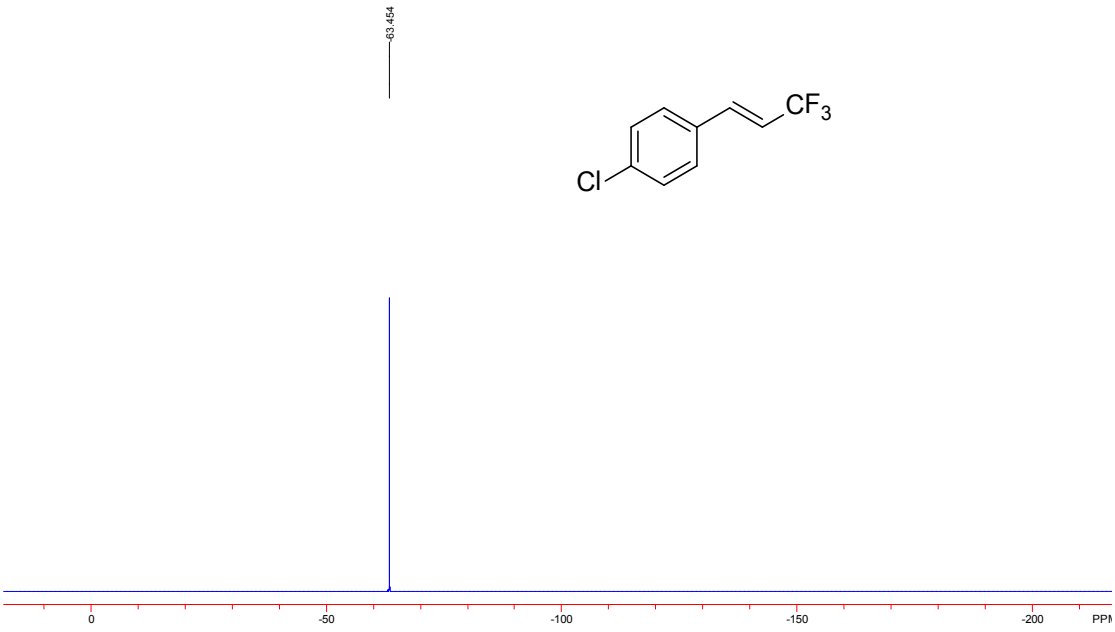


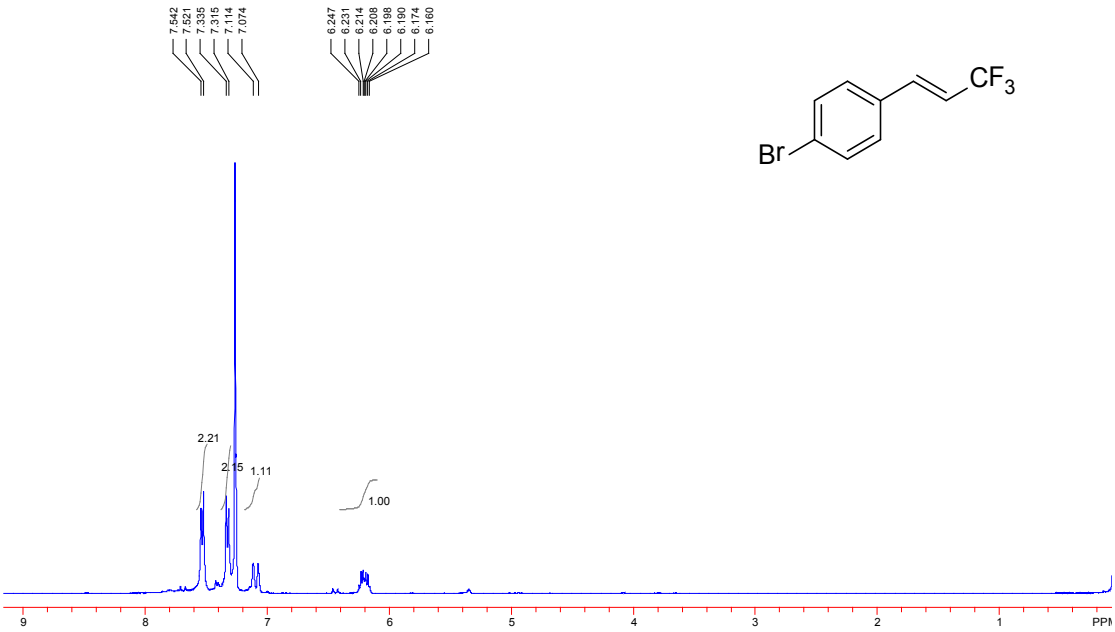
(E)-1-chloro-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2g**

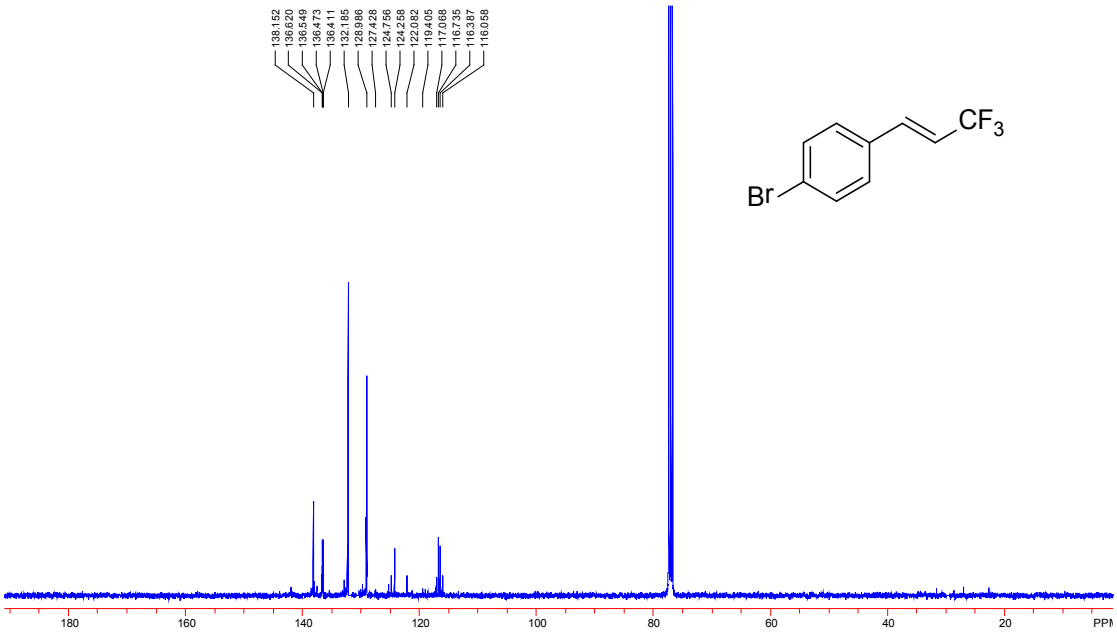


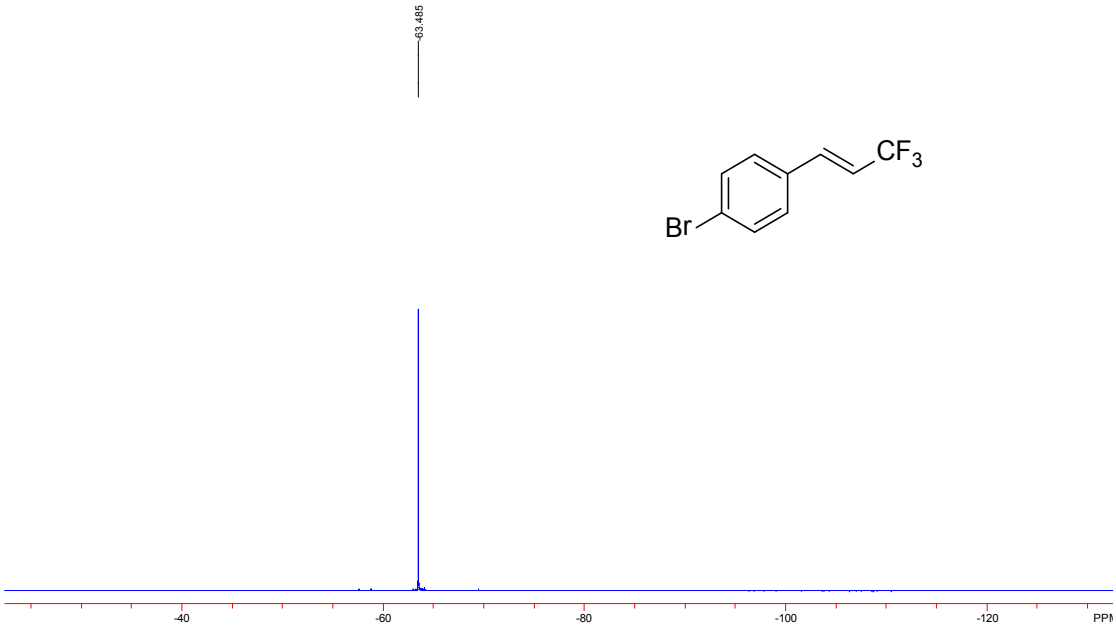





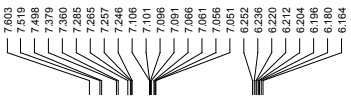

(E)-1-bromo-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2h**

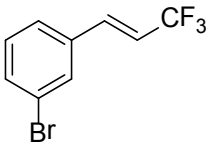


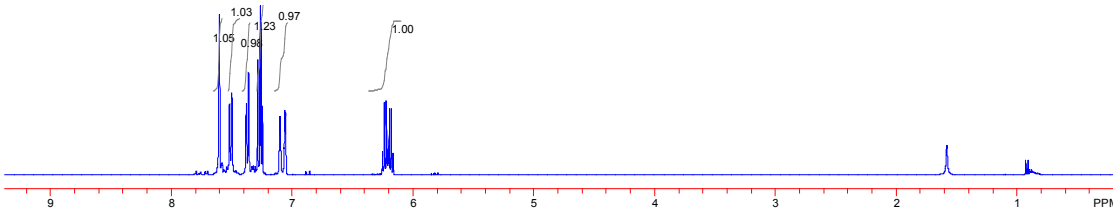


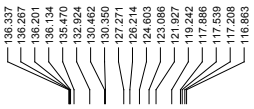



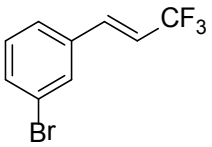
(E)-1-bromo-3-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2i**

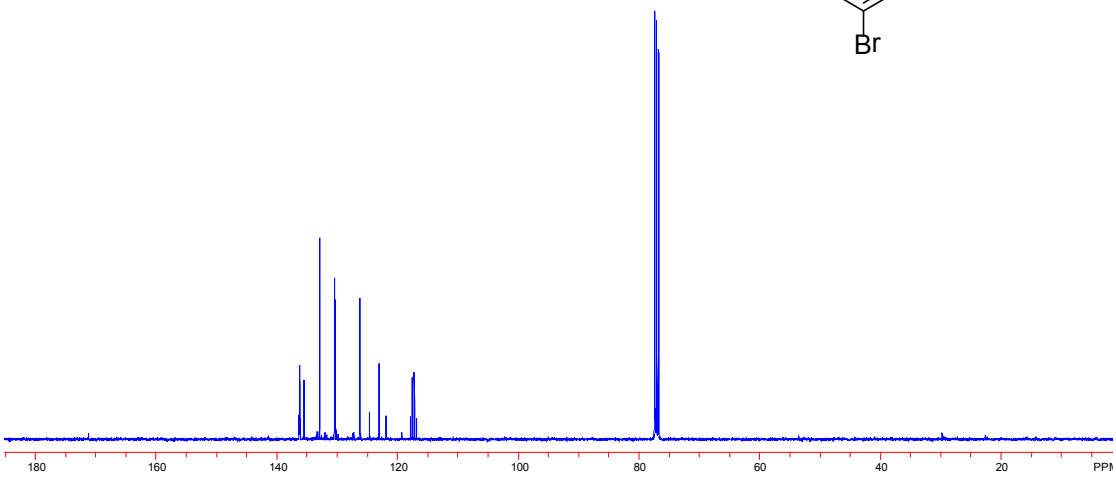


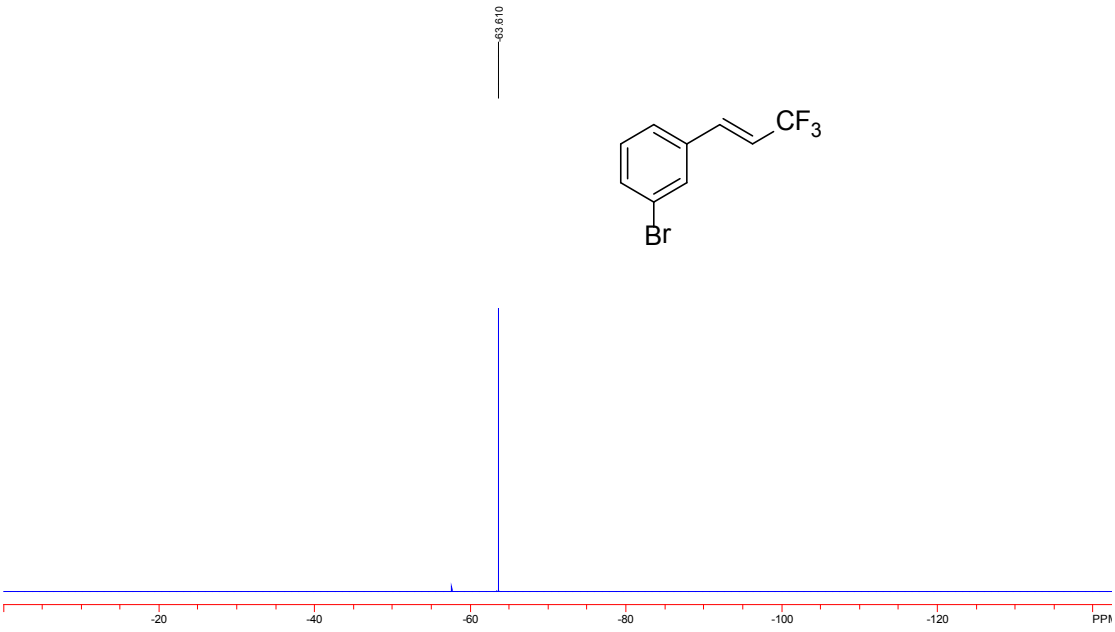



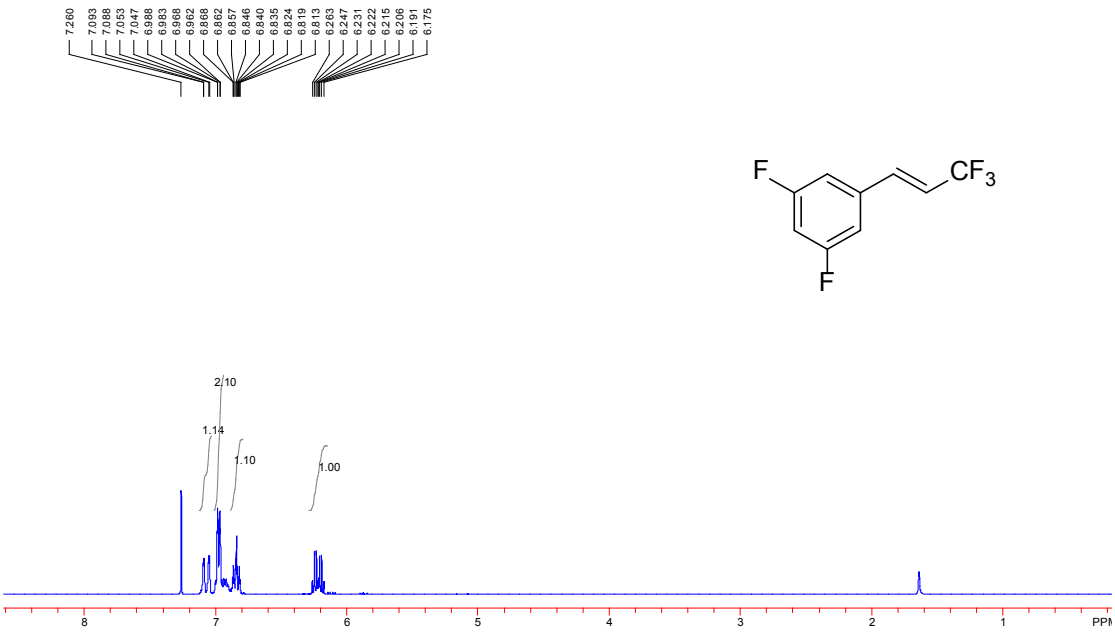



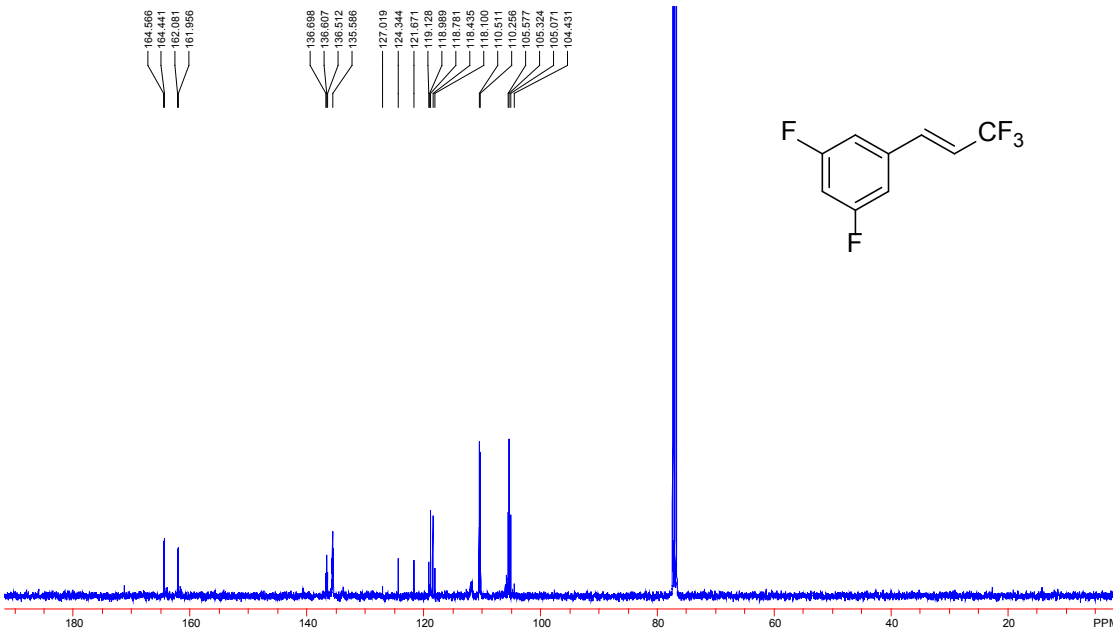



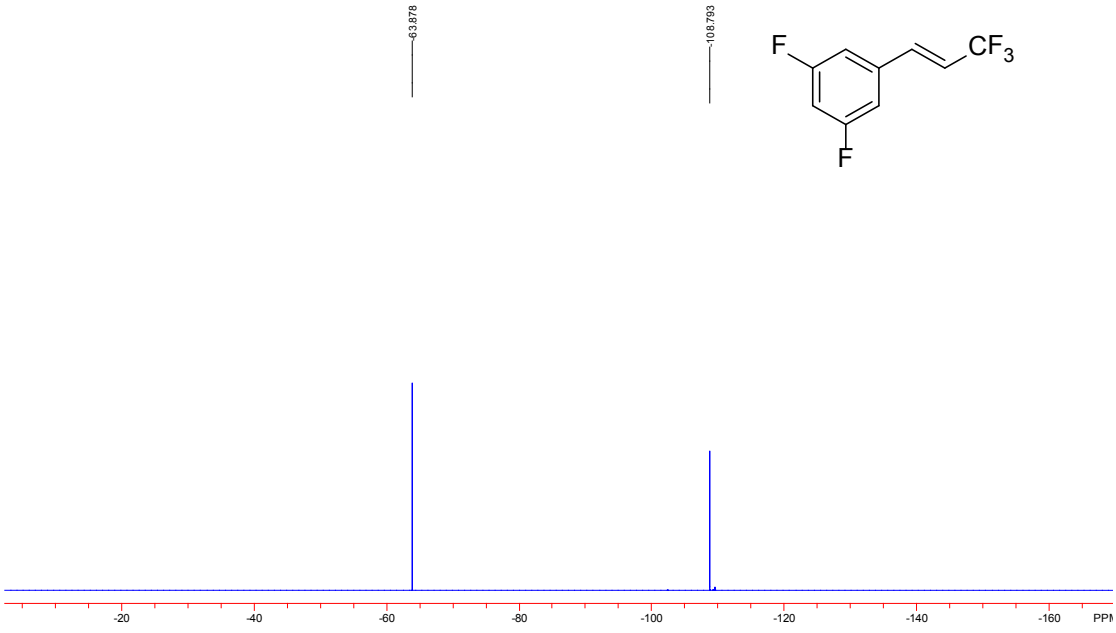





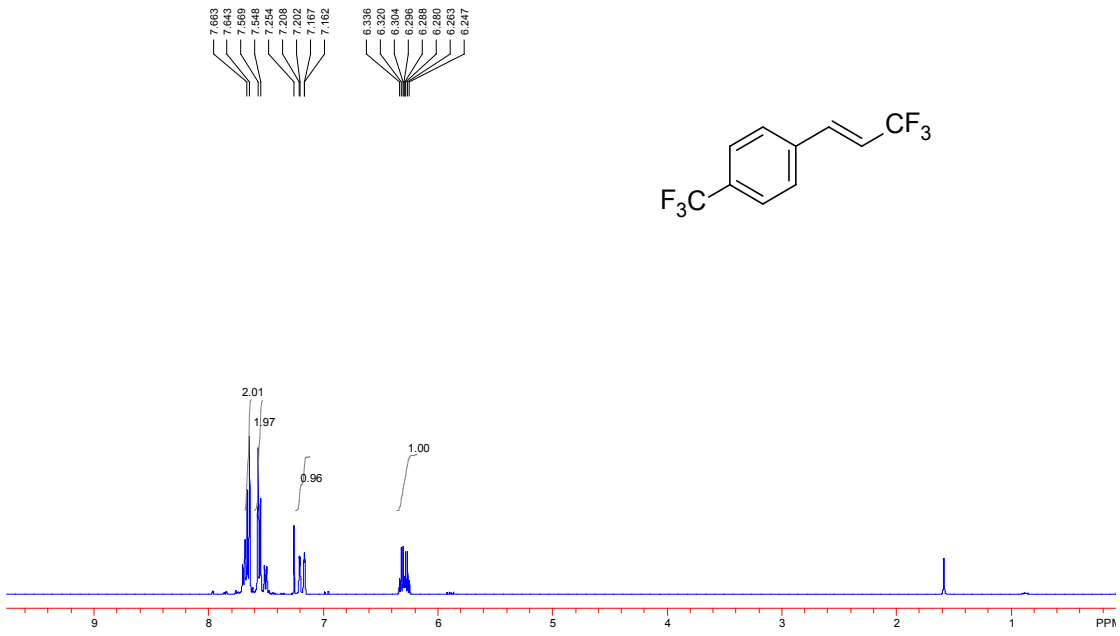

(E)-1,3-difluoro-5-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2j**

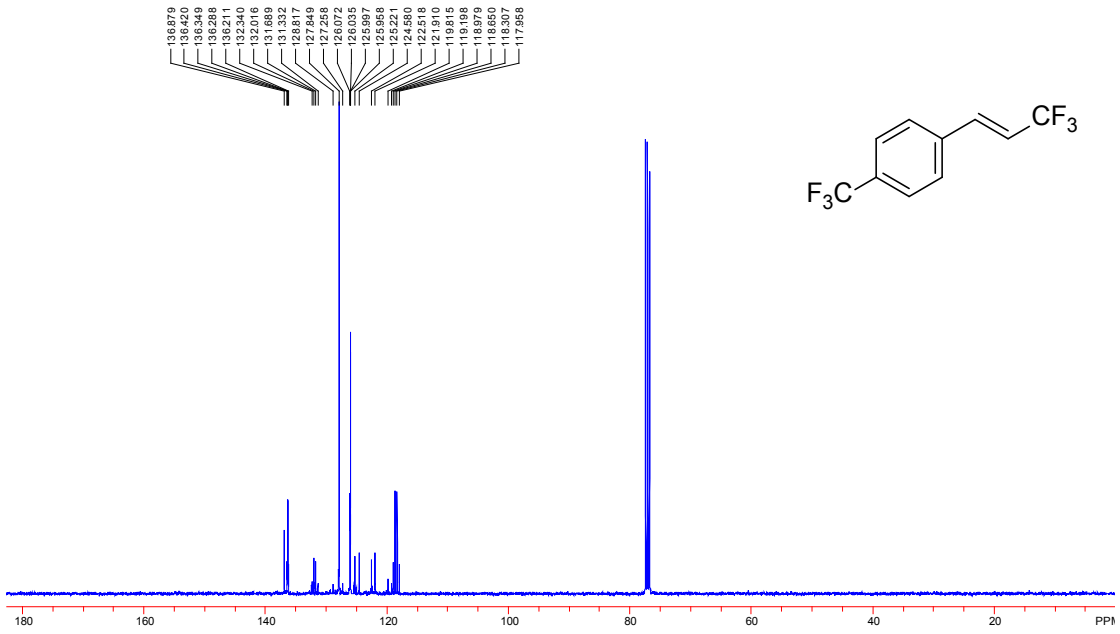


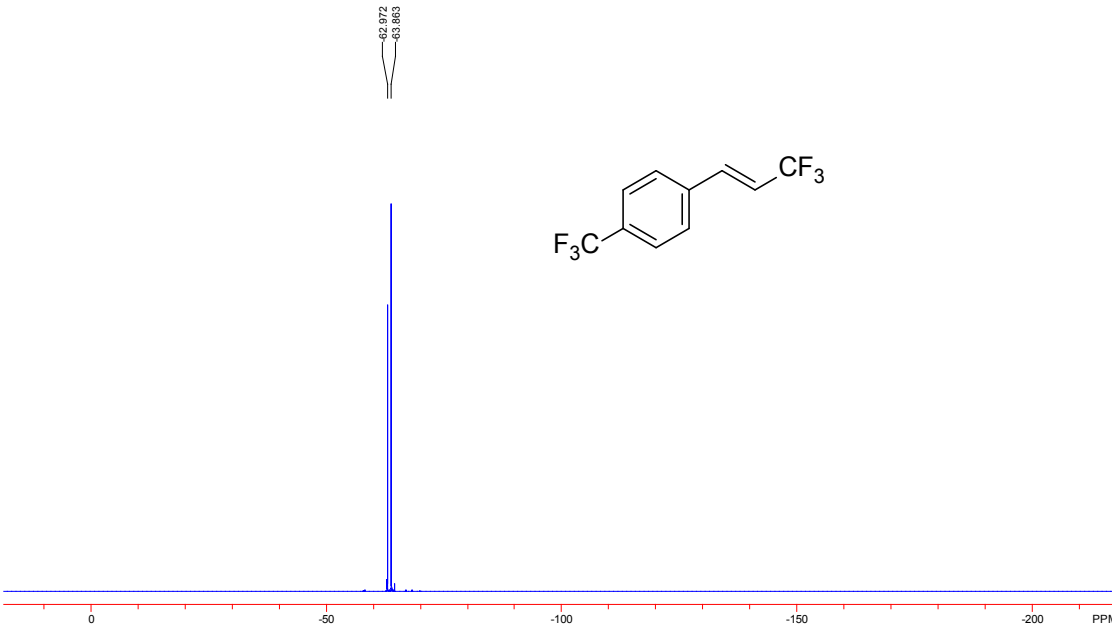


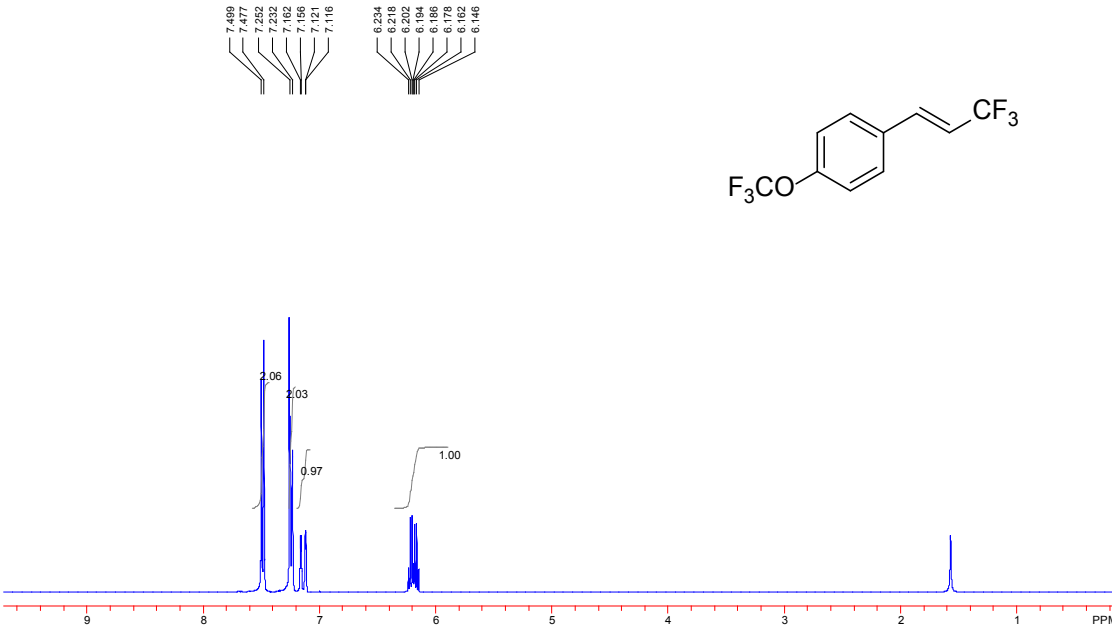
(E)-1-(trifluoromethyl)-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2k**

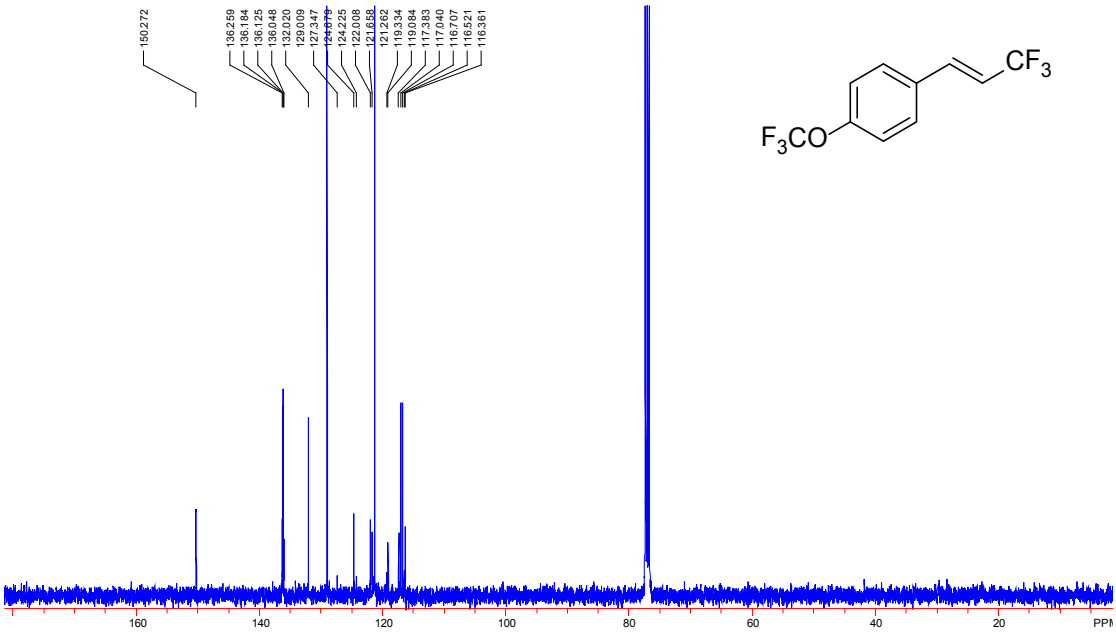




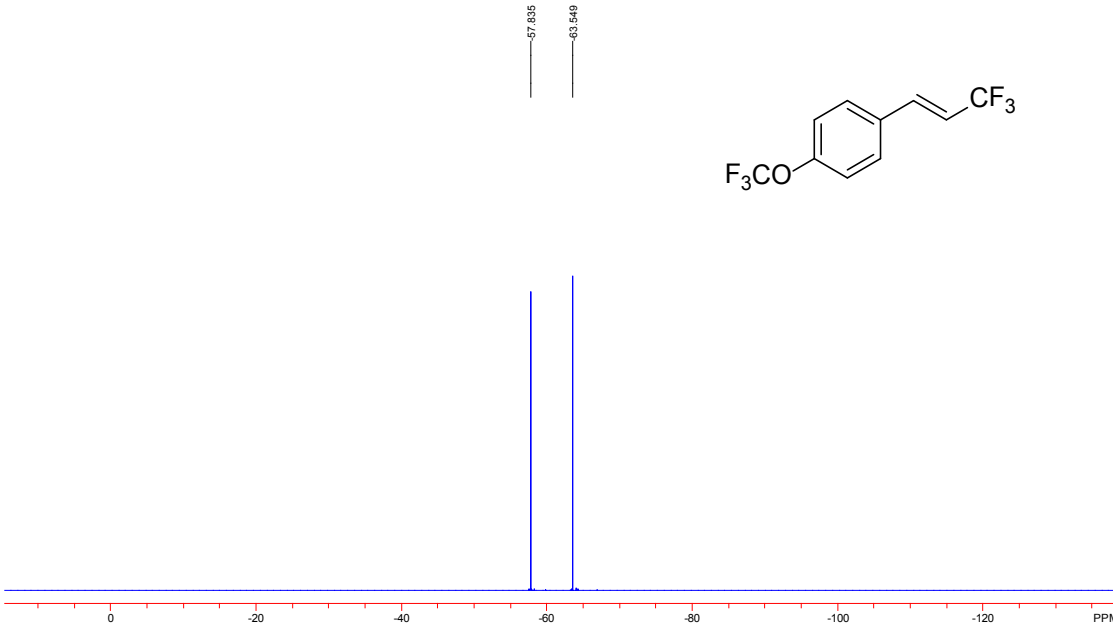

(E)-1-(trifluoromethoxy)-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2l**



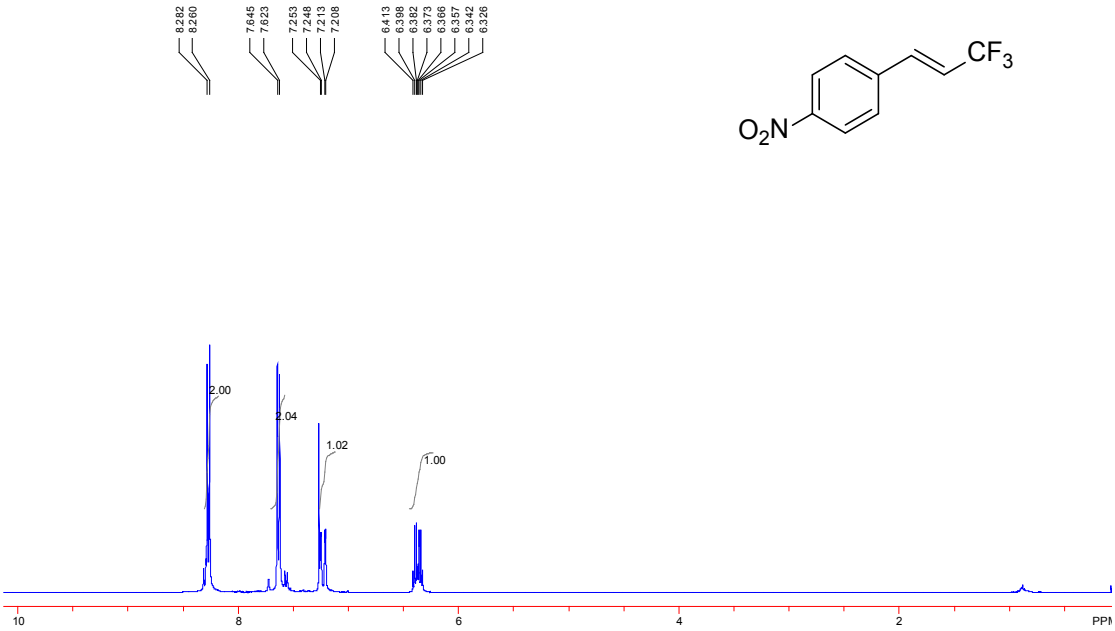


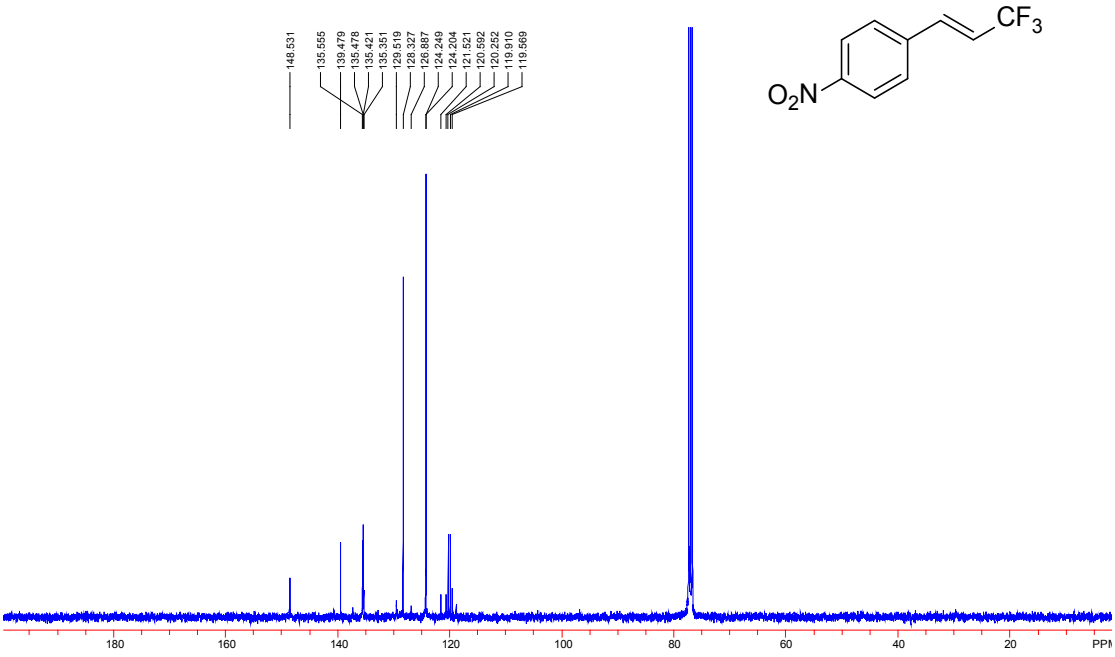


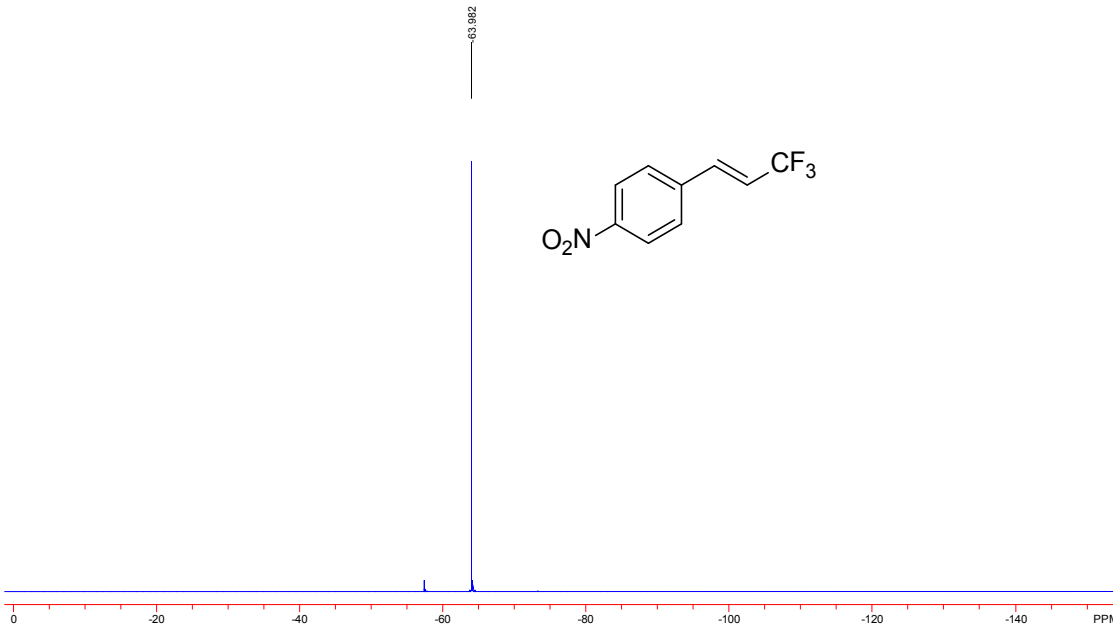




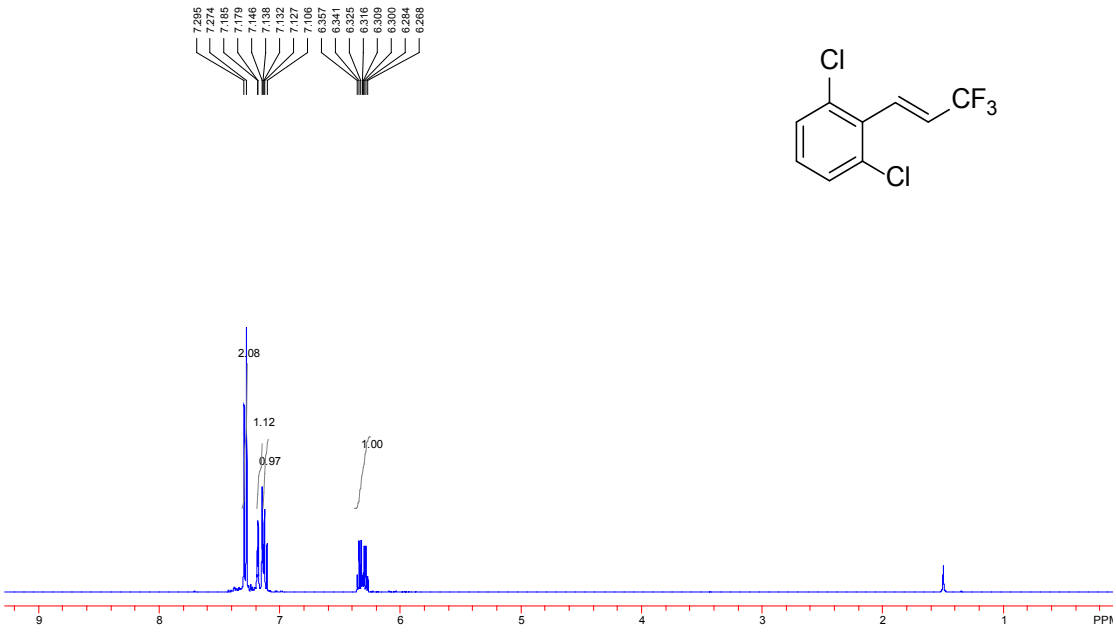
(E)-1-nitro-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2m**

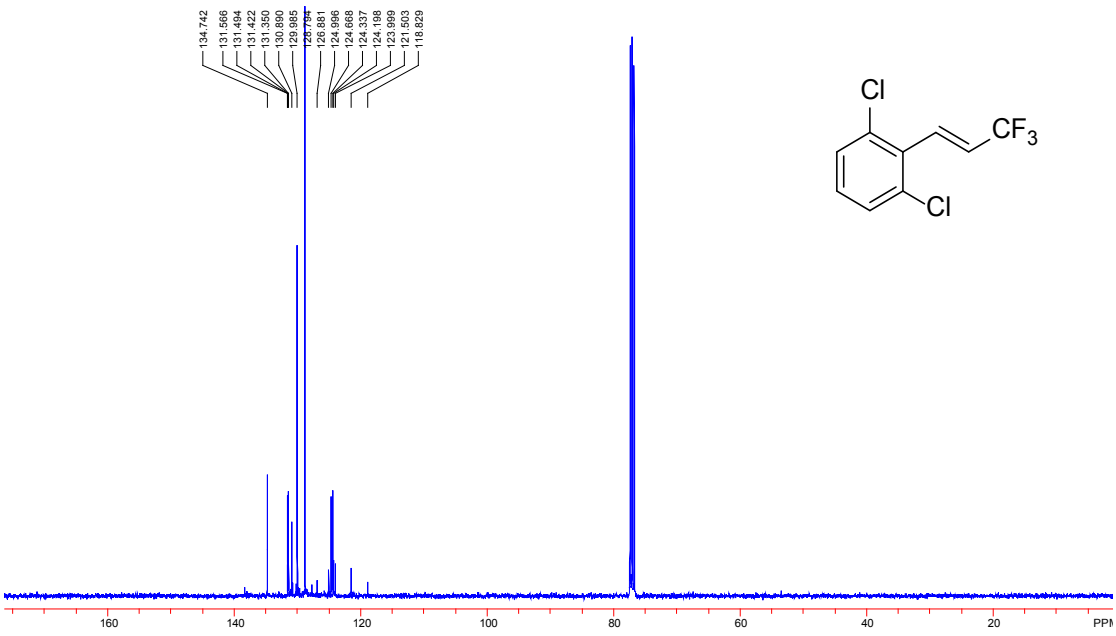


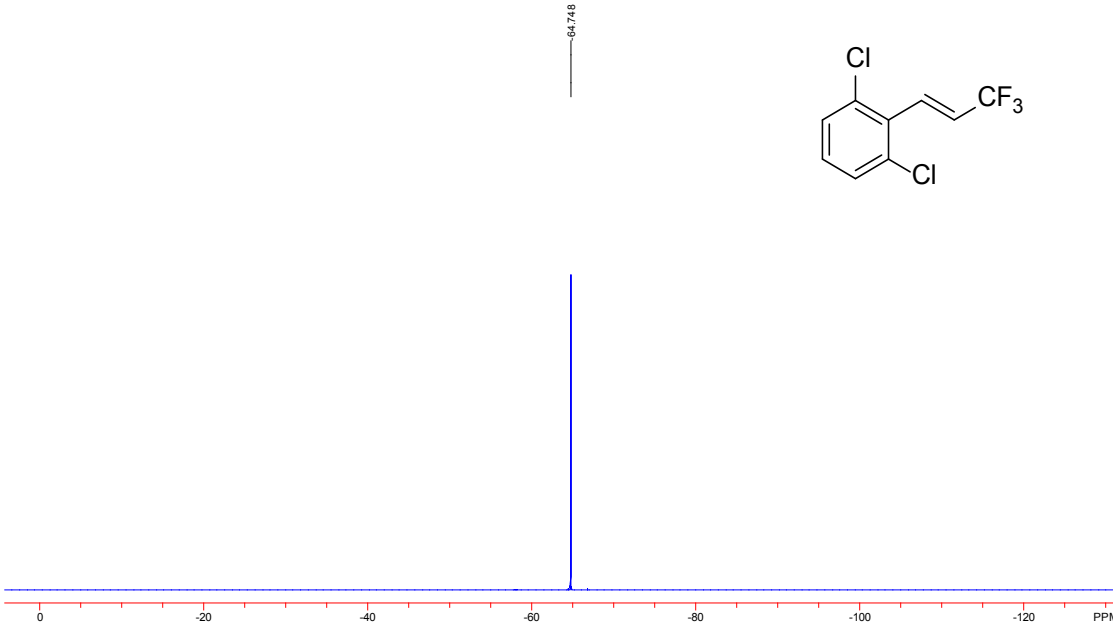





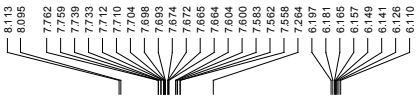

(E)-1,3-dichloro-2-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2n**

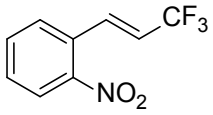


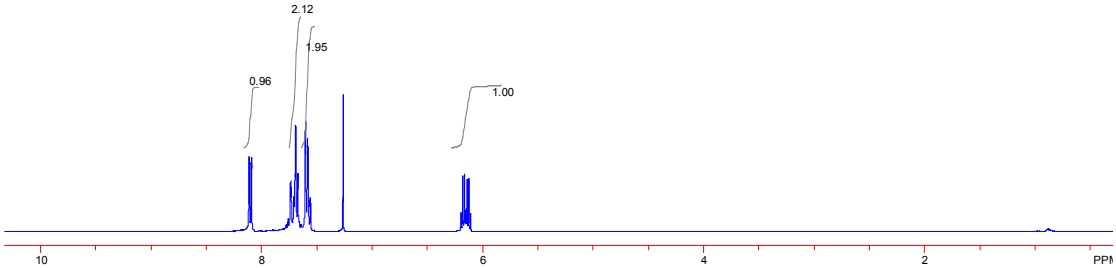


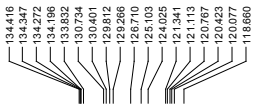



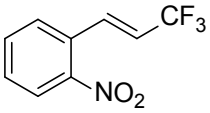
(E)-1-nitro-2-(3,3,3-trifluoroprop-1-en-1-yl)benzene **2o**

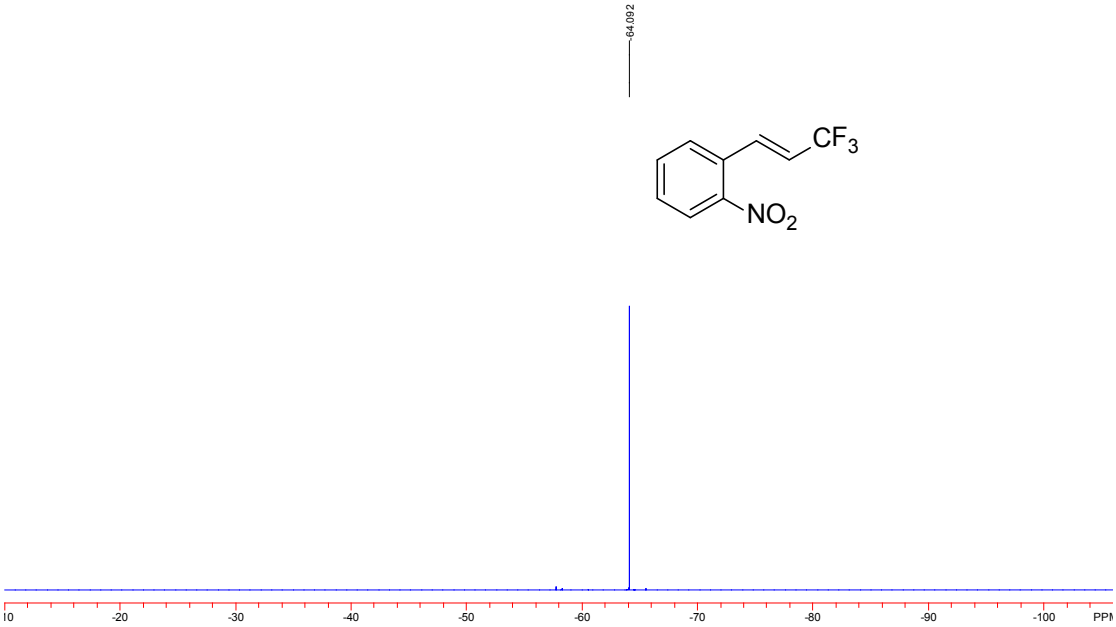


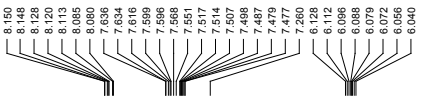



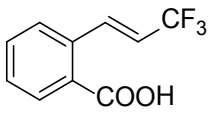



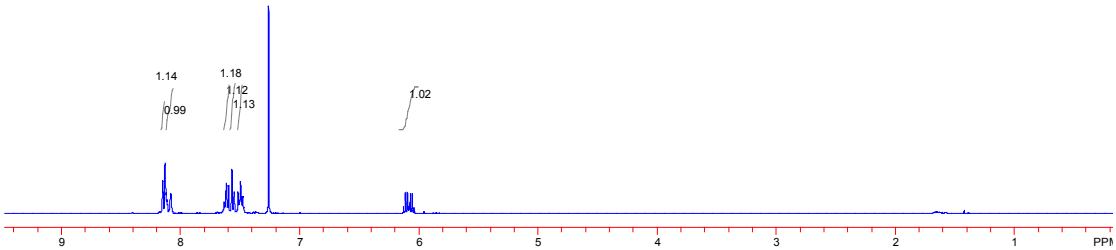



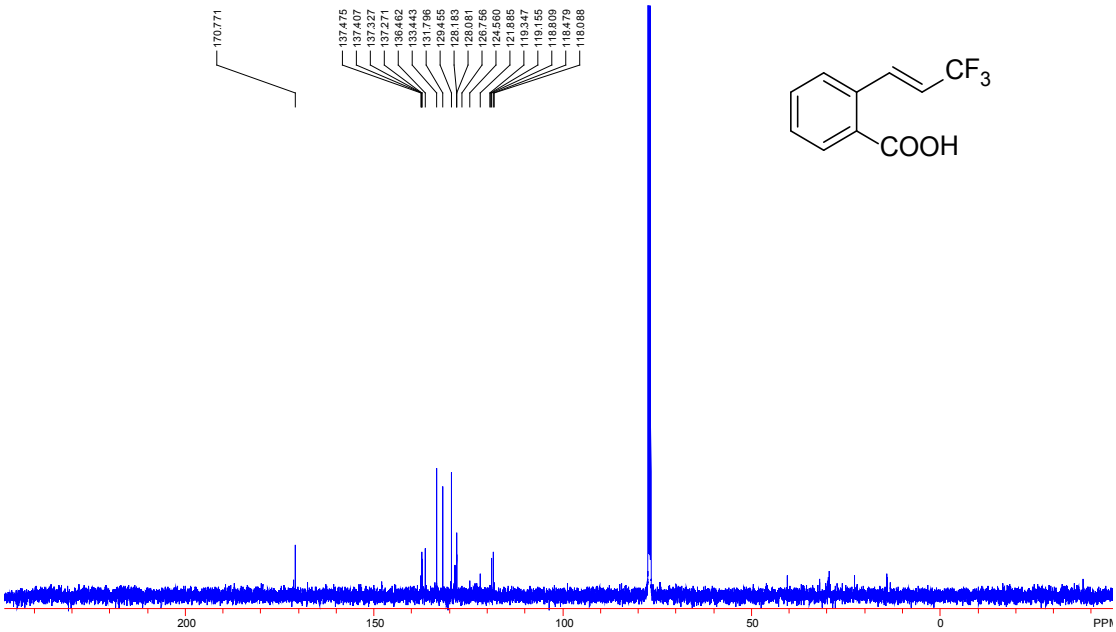


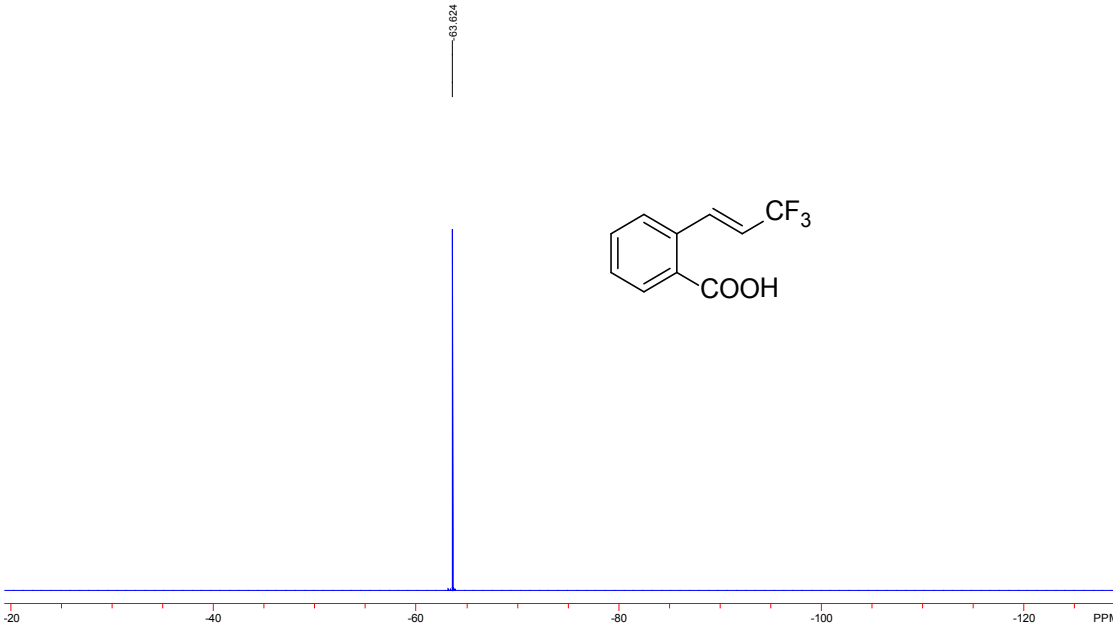

(E)-2-(3,3,3-trifluoroprop-1-en-1-yl)benzoic acid **2p**



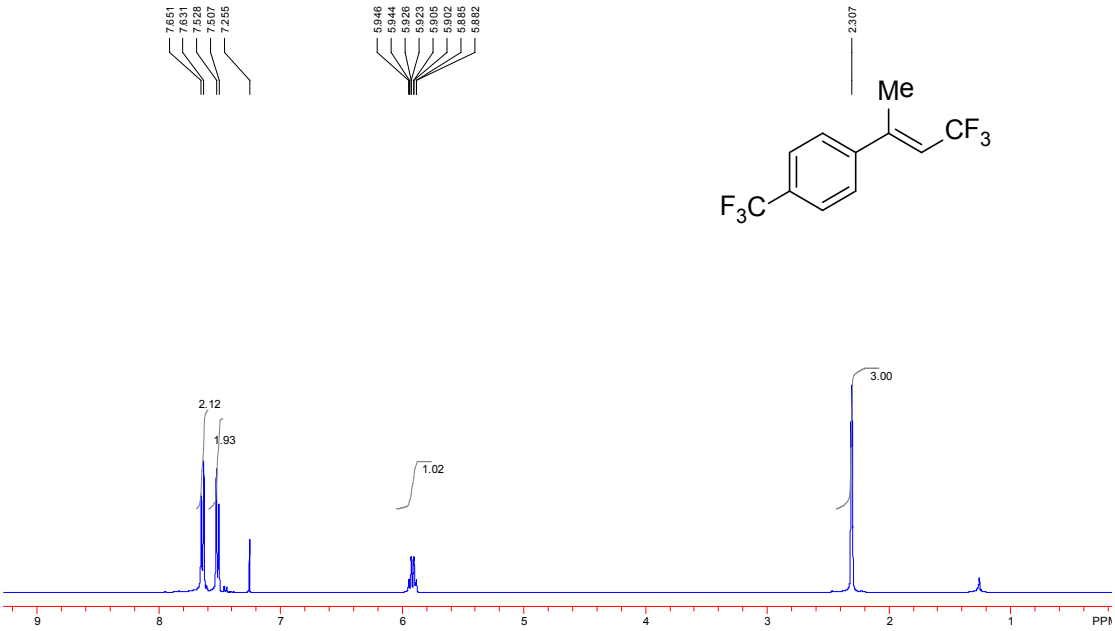



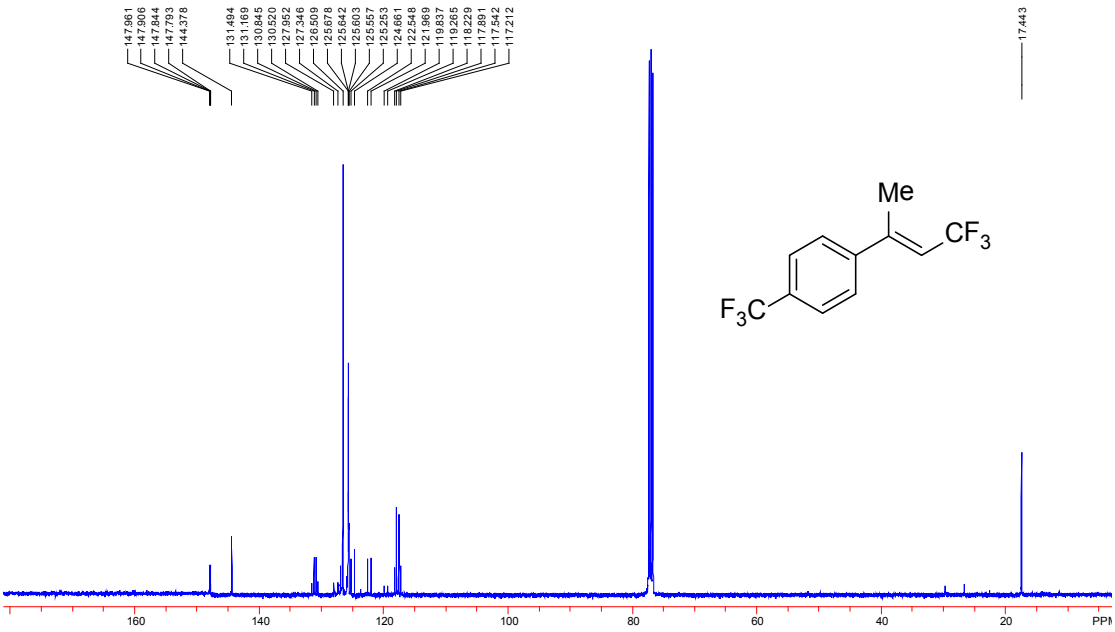



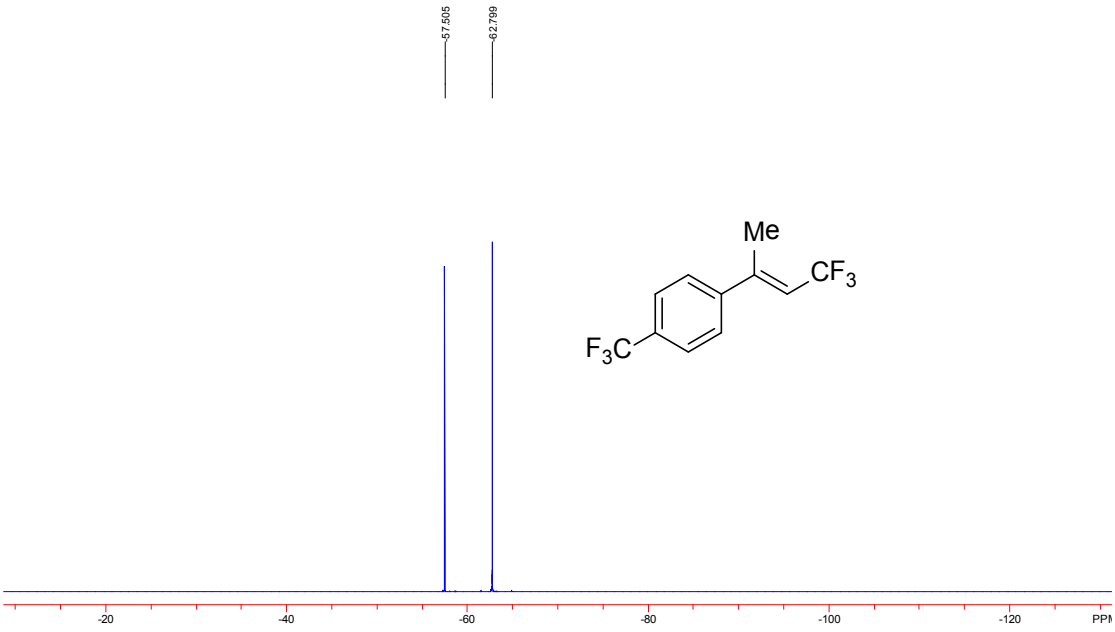


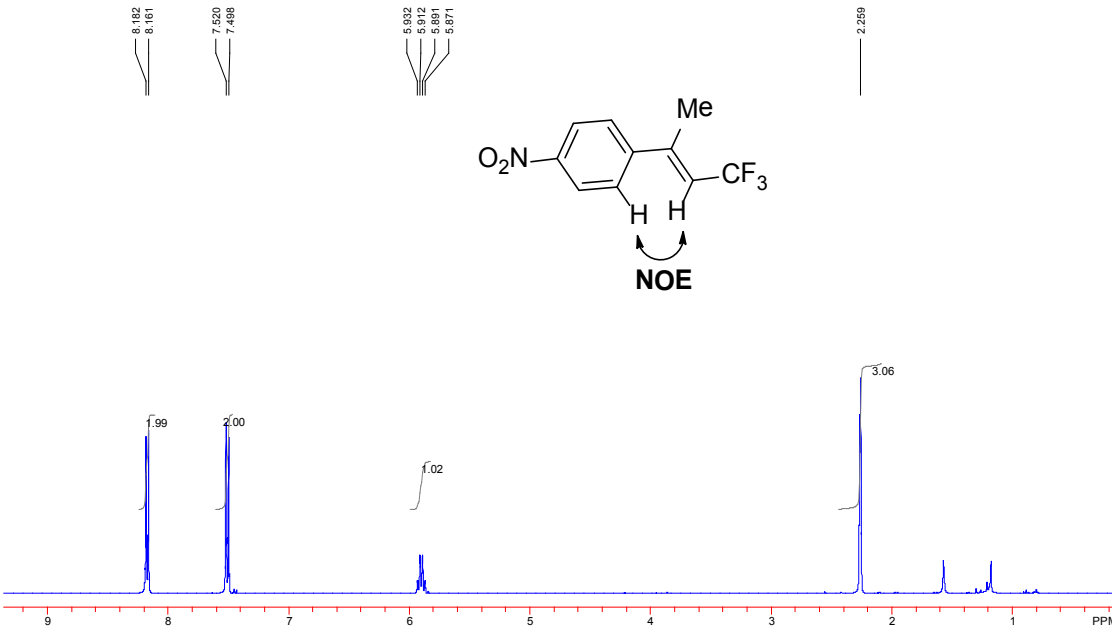
(E)-1-(4,4,4-trifluorobut-2-en-2-yl)-4-(trifluoromethyl)benzene **2q**

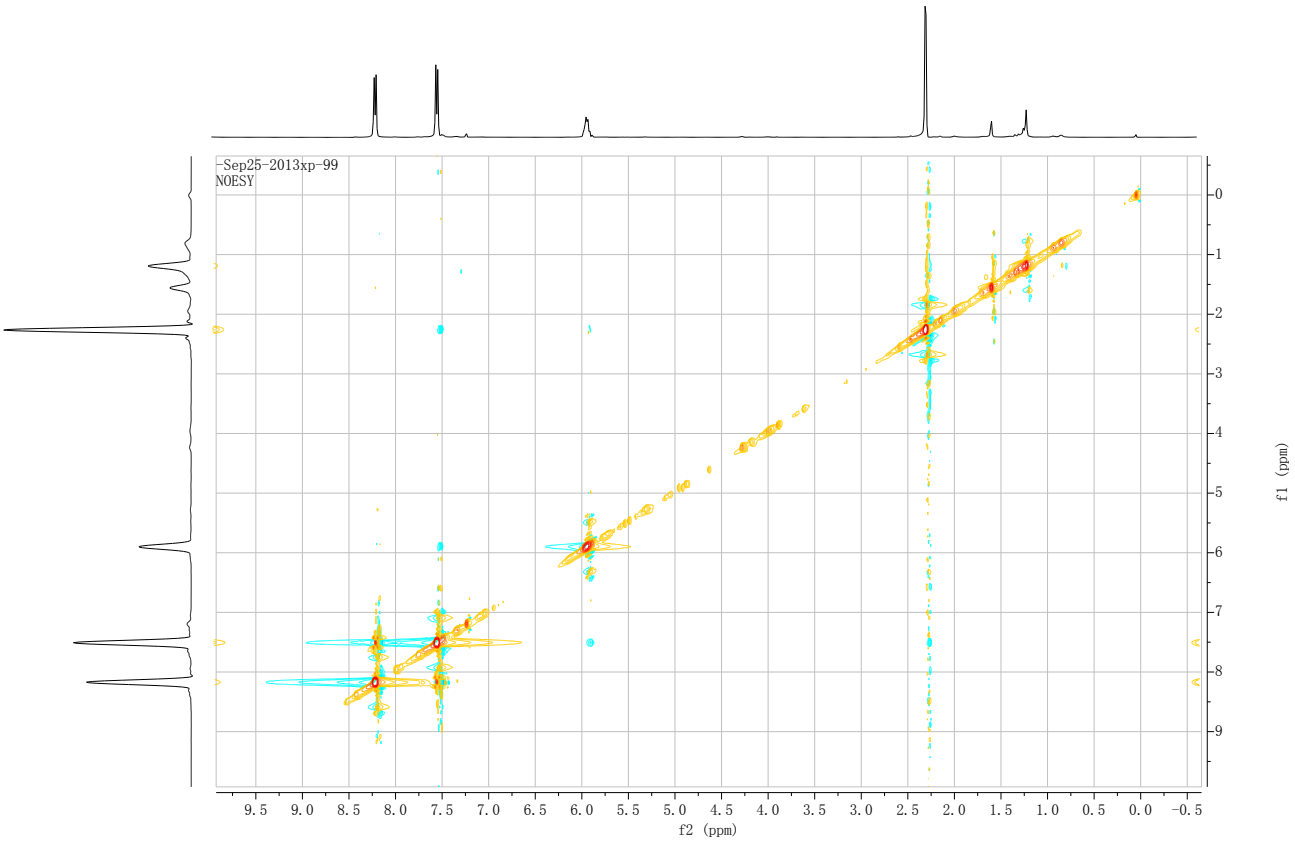


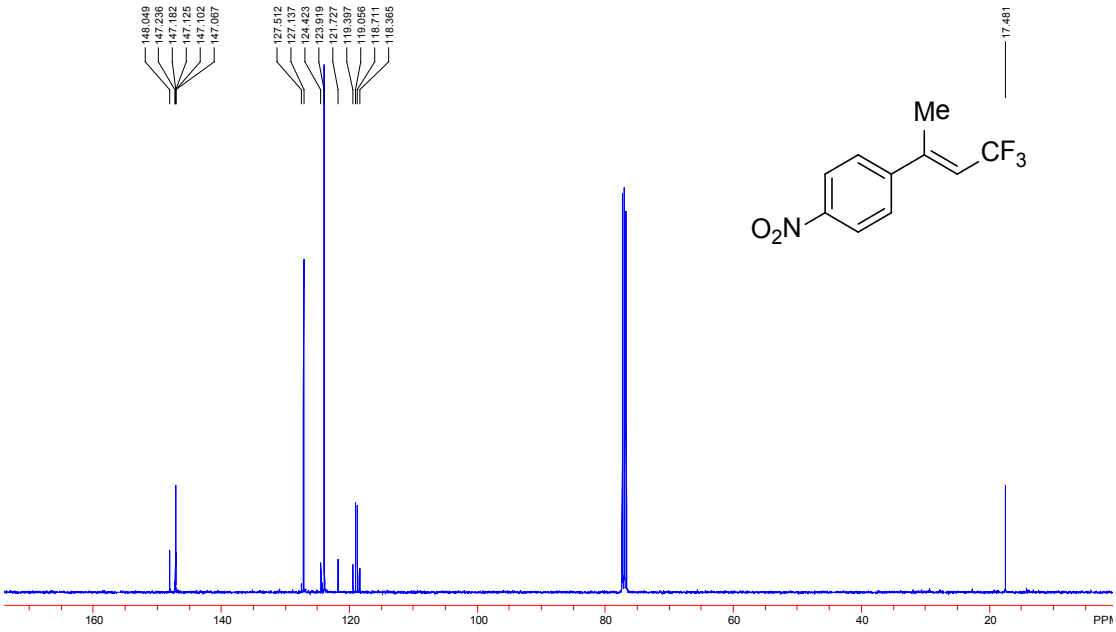



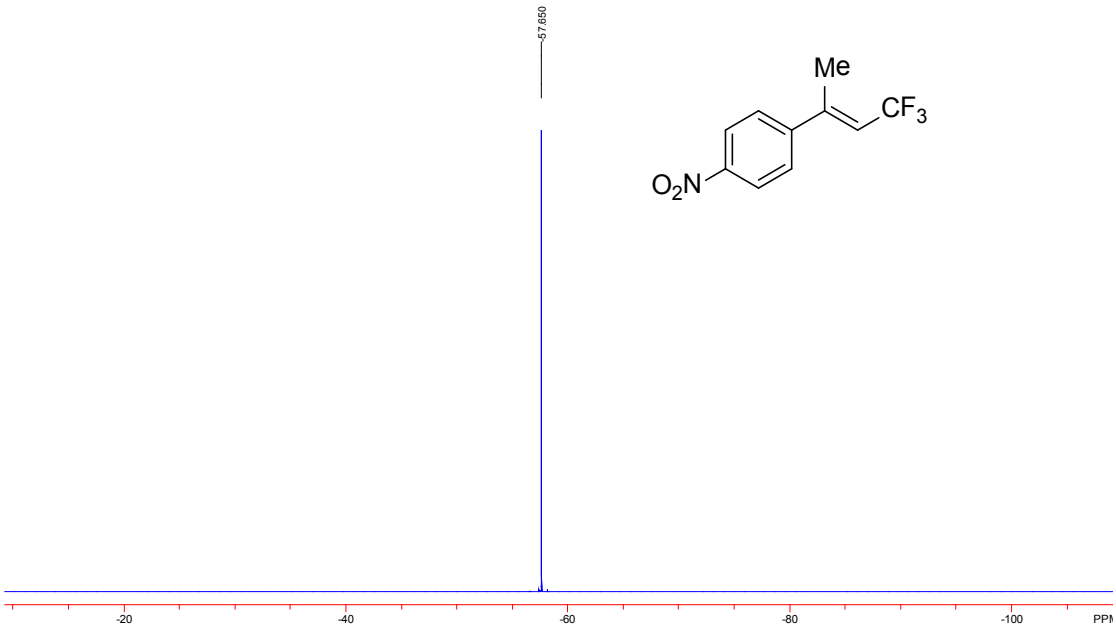



(E)-1-nitro-4-(4,4,4-trifluorobut-2-en-2-yl)benzene **2r**

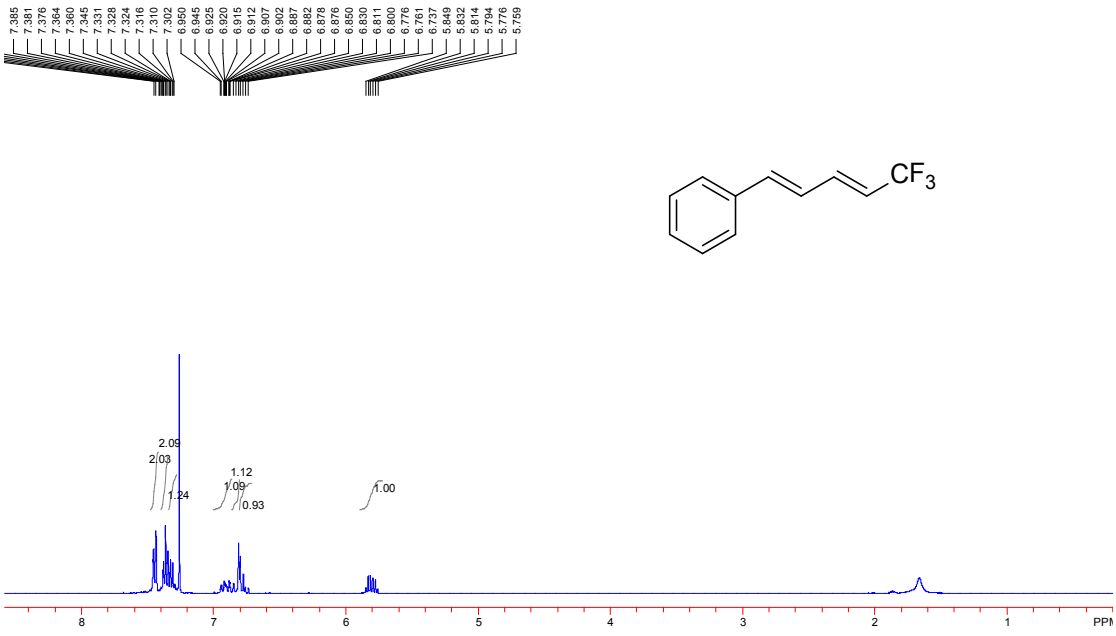


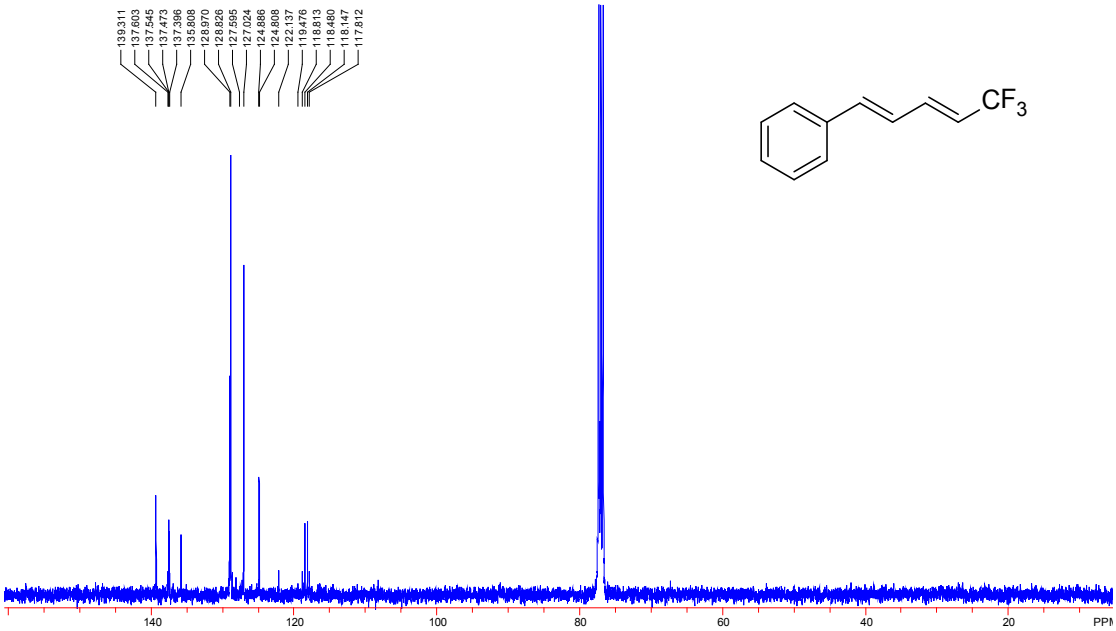


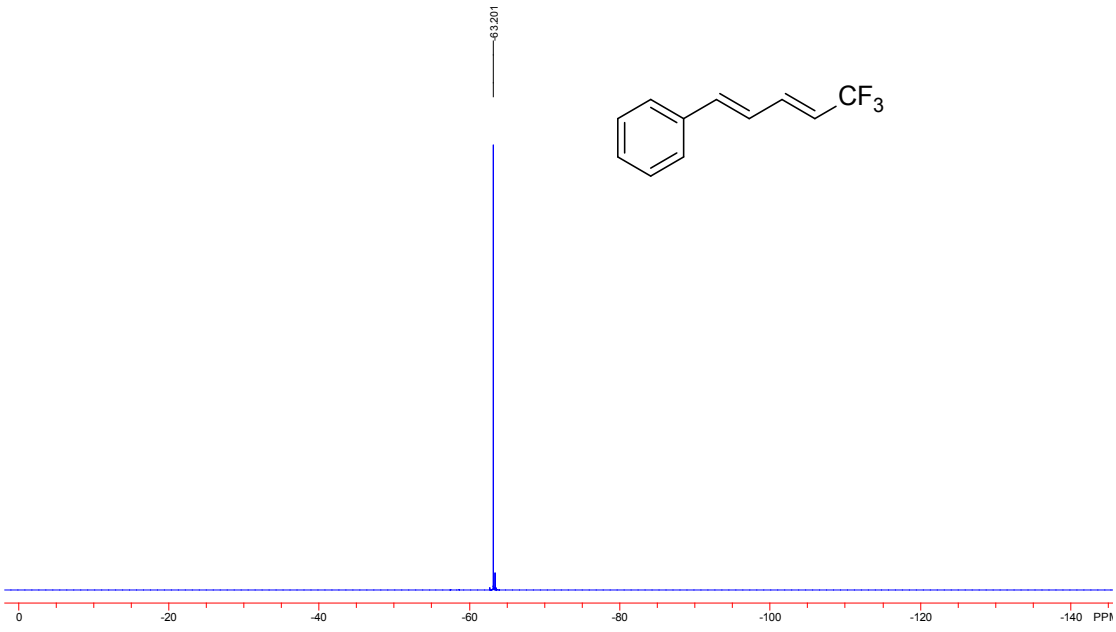





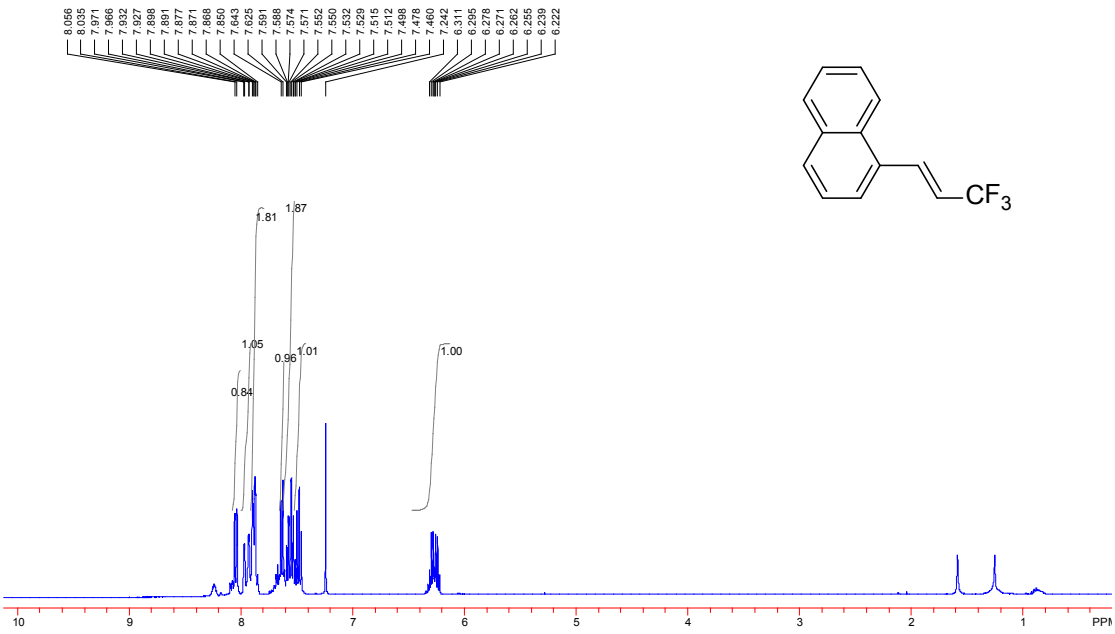

((1E,3E)-5,5,5-trifluoropenta-1,3-dien-1-yl)benzene **2s**

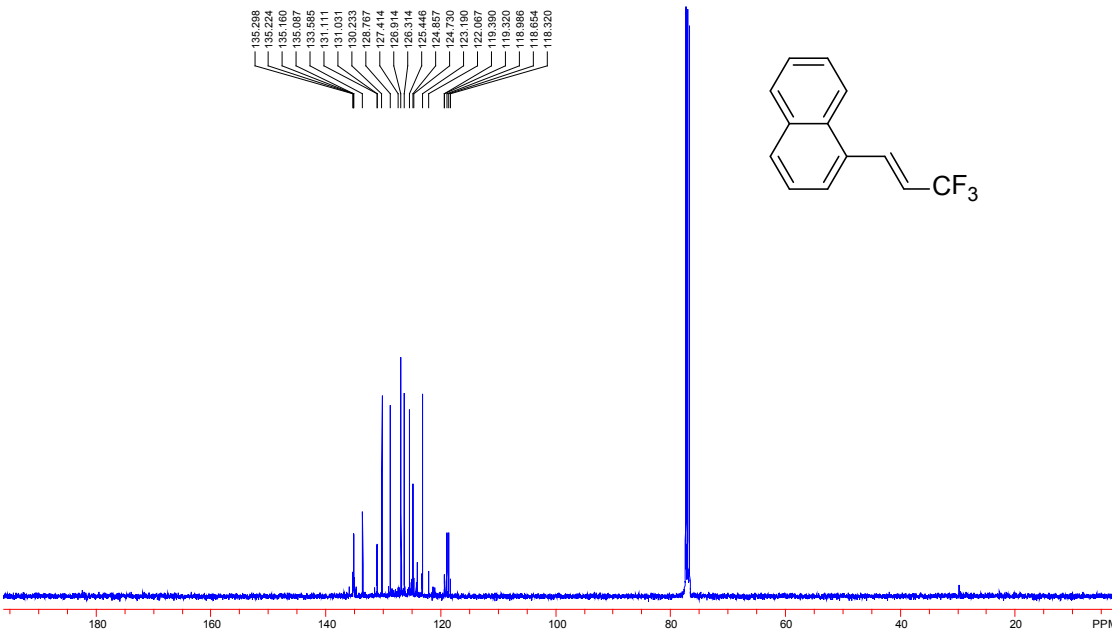


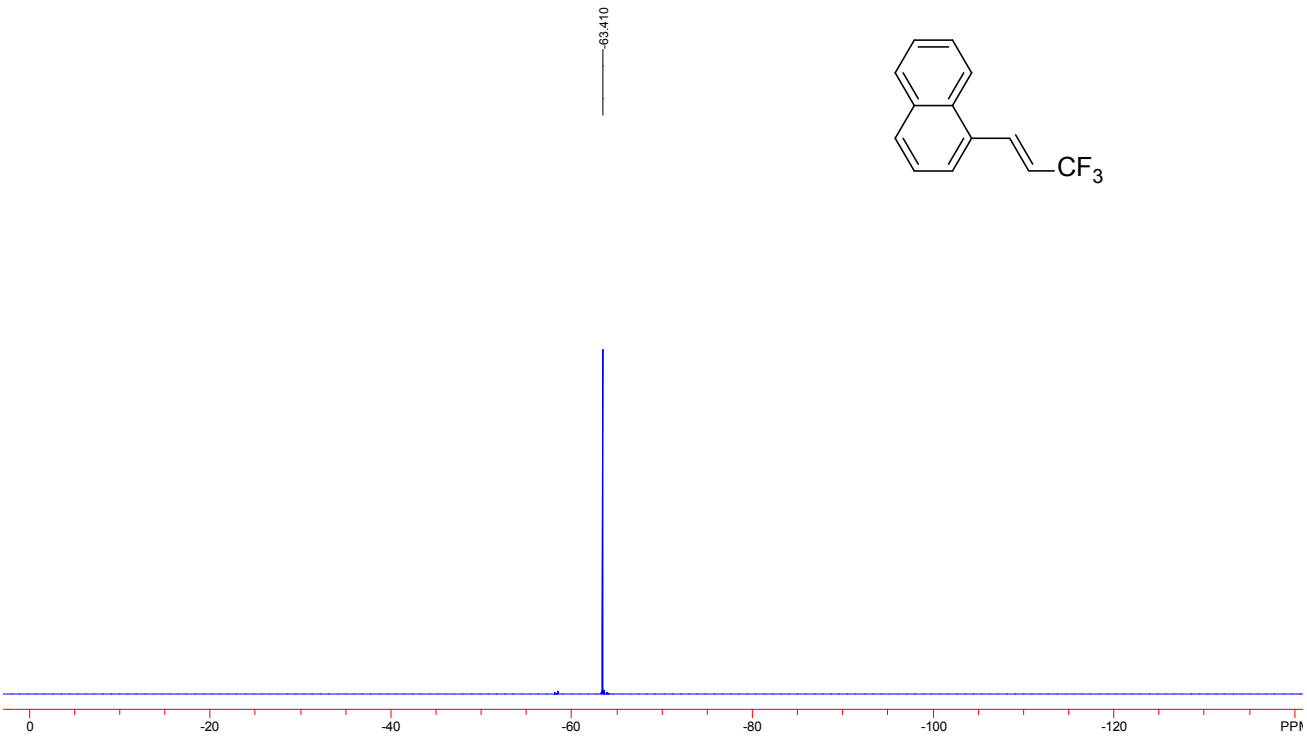


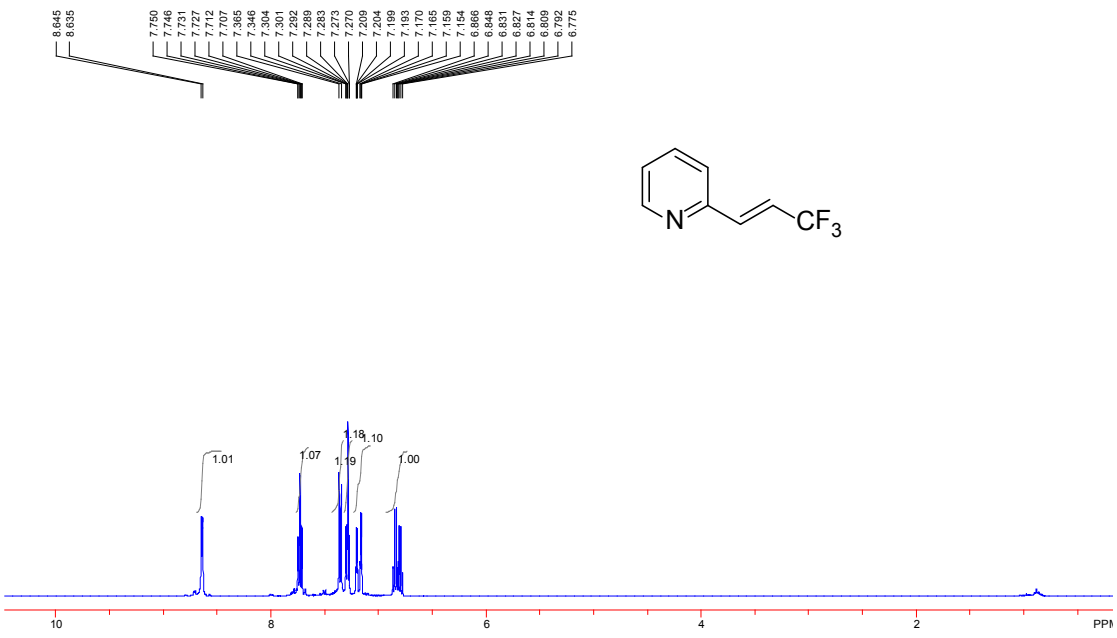
(E)-1-(3,3,3-trifluoroprop-1-en-1-yl)naphthalene **2t**

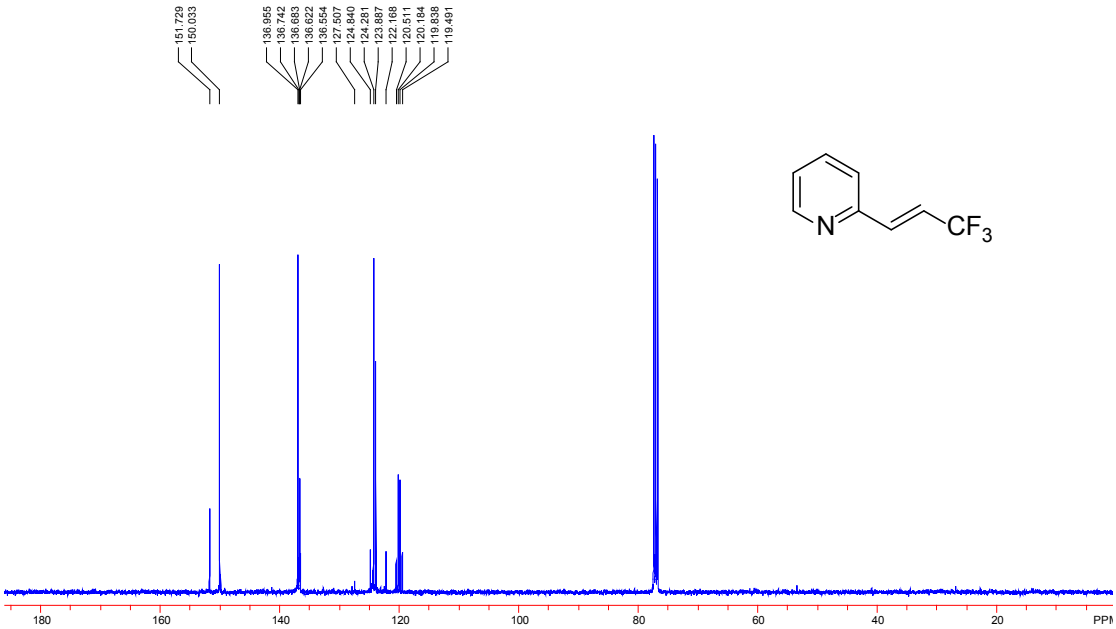


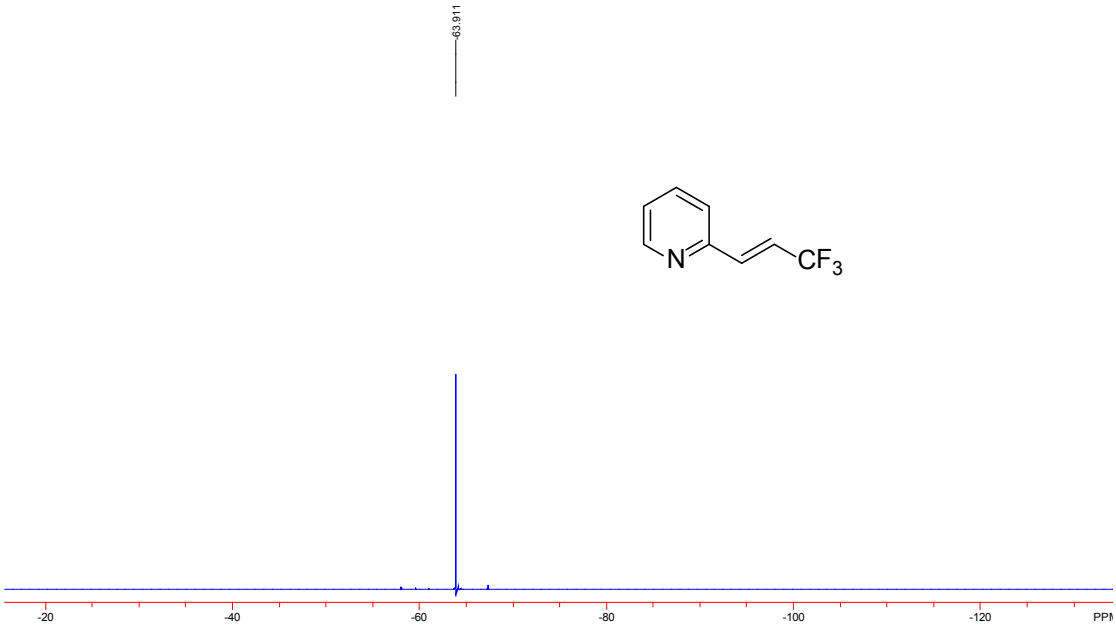





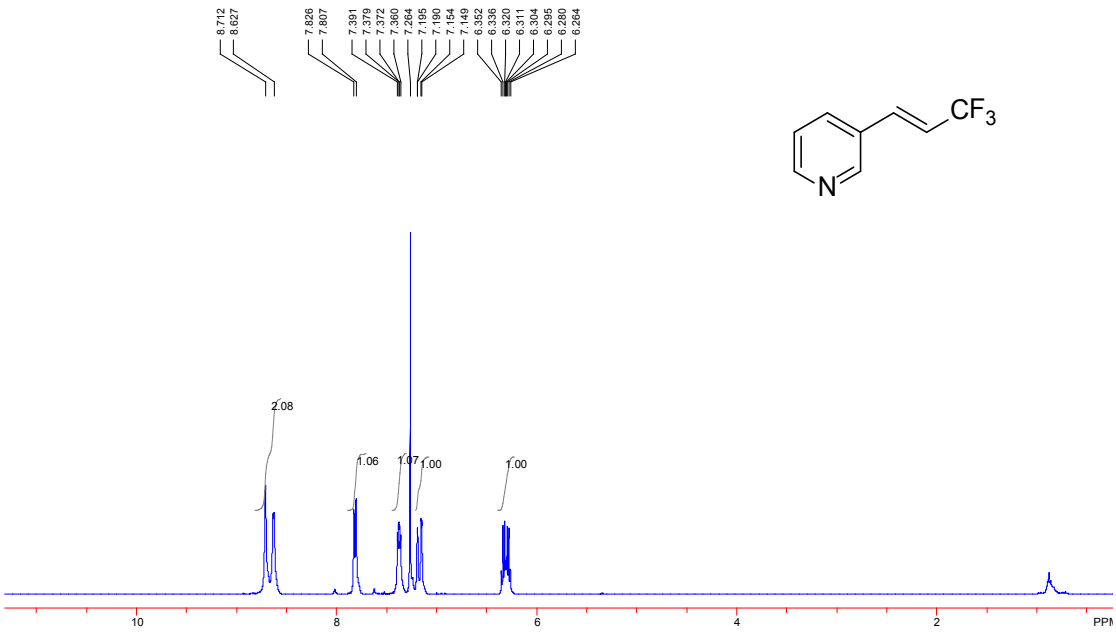

(E)-2-(3,3,3-trifluoroprop-1-en-1-yl)pyridine **2u**

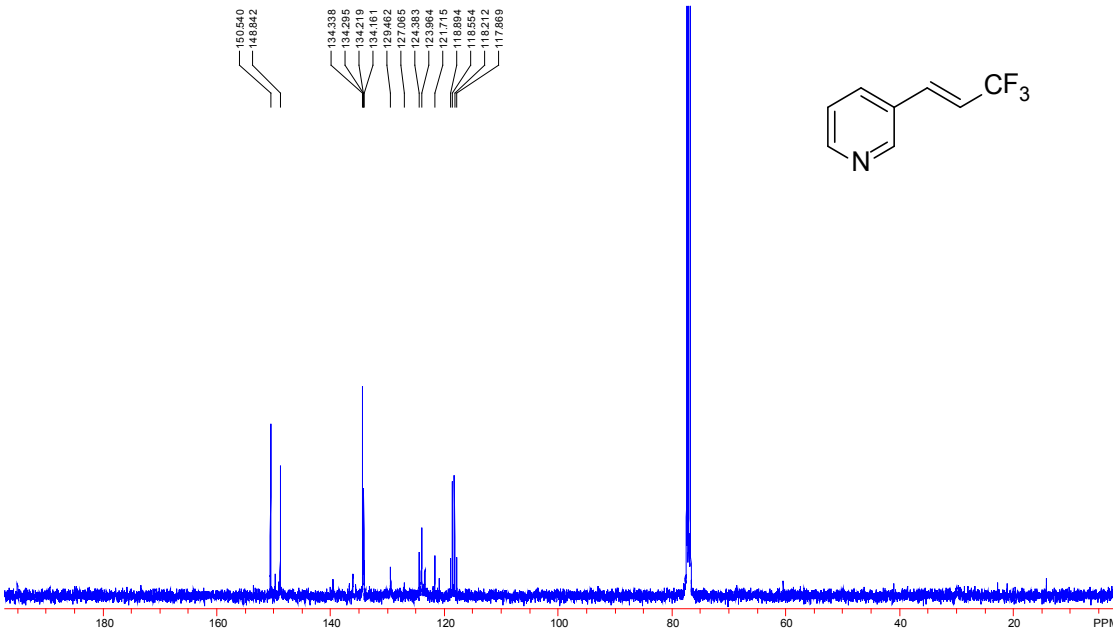


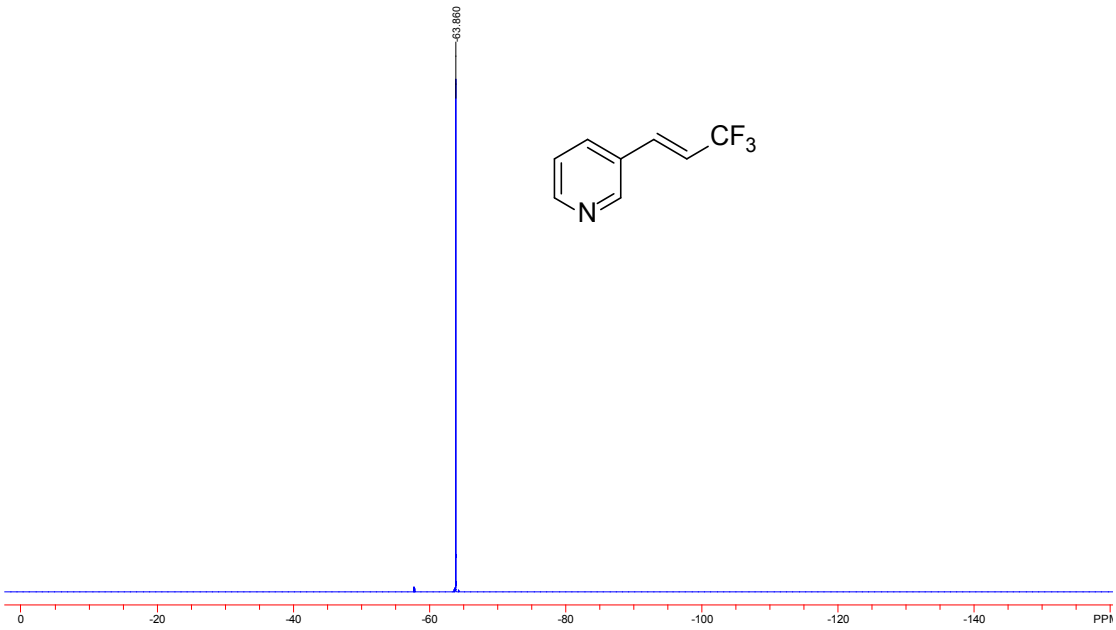


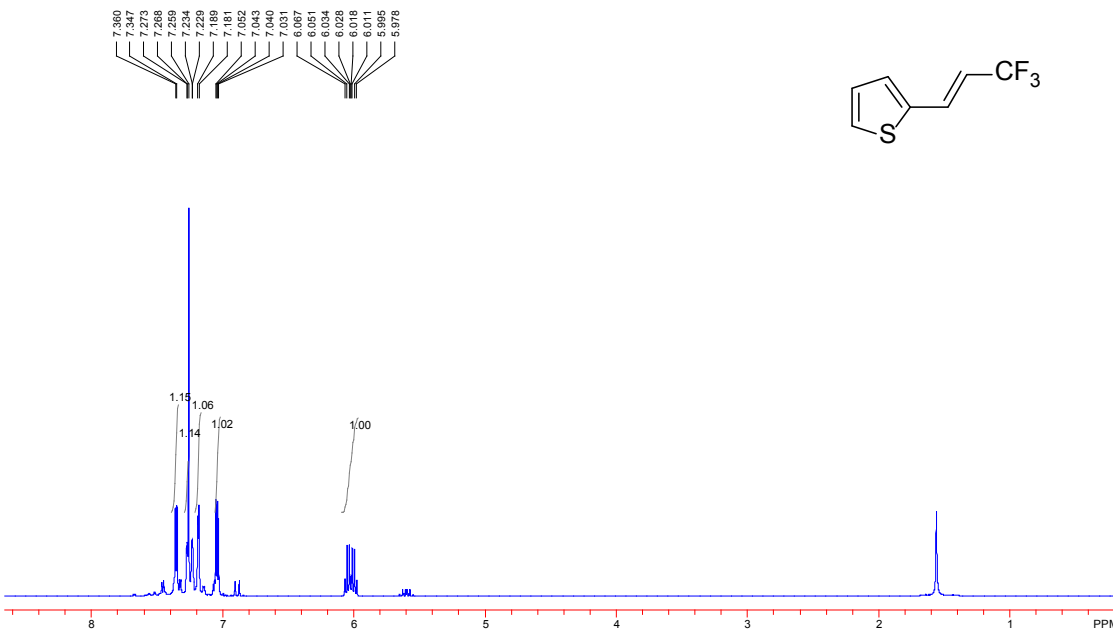
(E)-3-(3,3,3-trifluoroprop-1-en-1-yl)pyridine **2v**

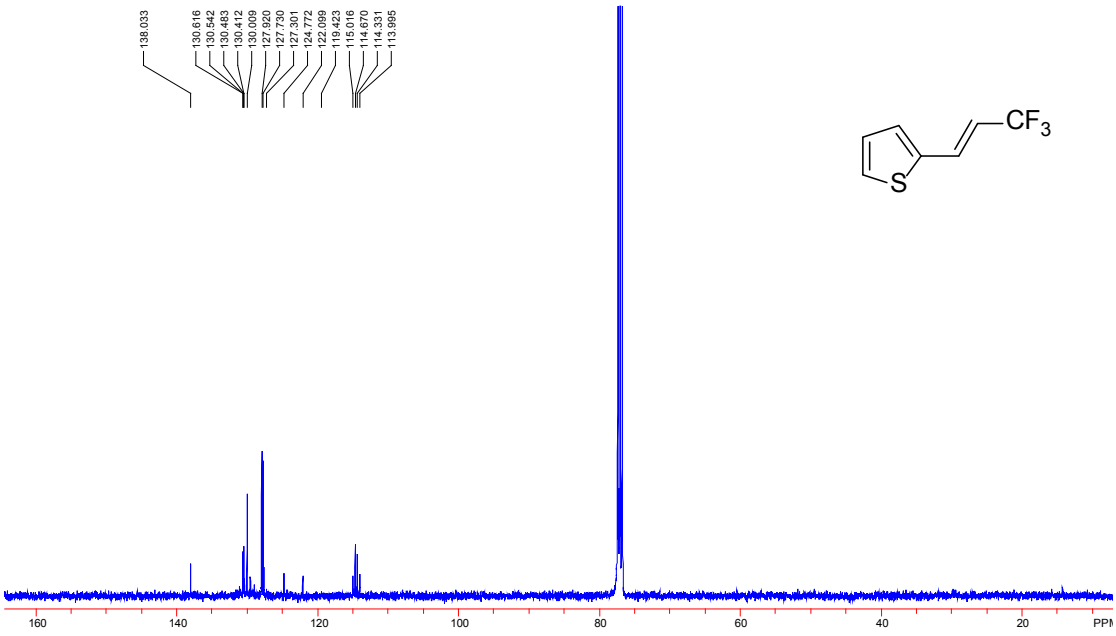


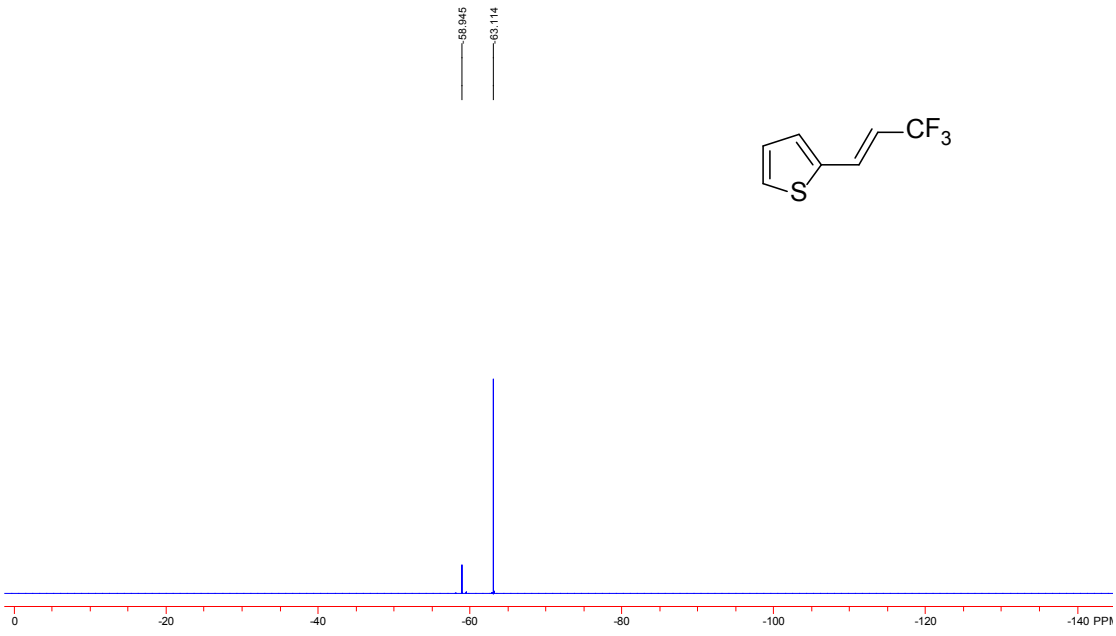






(E)-2-(3,3,3-trifluoroprop-1-en-1-yl)thiophene **2w**





(S)-4-hydroxy-3,5,5-trimethyl-4-((1E)-5,5,5-trifluoro-3-methylpenta-1,3-dien-1-yl)cyclohex-2-enone

**2x**