

Palladium-Catalyzed Intermolecular Aryldifluoroalkylation of Alkynes

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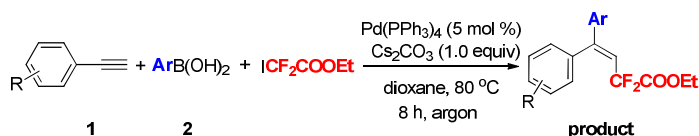
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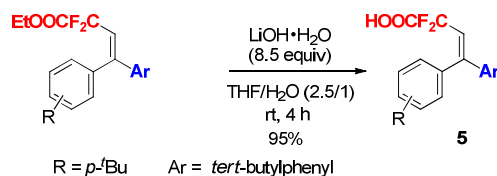
1. General Remarks

For Column chromatography, 200-300 mesh silica gel was employed. Analytical TLC was performed with silica gel GF254 plates. ^1H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) were recorded in CDCl_3 using TMS as internal standard. IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm^{-1} . All products were further characterized by high resolution mass spectra (HRMS); copies of their ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra are provided. Unless otherwise noted, reactions were carried out under an argon atmosphere. All solvents were dried under standard method.

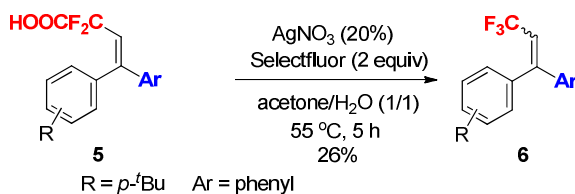
2. General experimental procedure



An oven-dried tube was charged with arylboronic acids **2** (0.4 mmol), Cs_2CO_3 (0.2 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (0.01 mmol). The tube was evacuated and backfilled with argon (repeated three times). Then, ethyl difluoroiodoacetate (0.3 mmol) dissolved in 1,4-dioxane (1.0 mL), and alkynes **1** (0.2 mmol) were added into the tube. The reaction mixture was stirring at 80°C for 8 h and extracted with DCM. The combined organic layers were washed with saturated brine, dried over Na_2SO_4 , concentrated in vacuum and purified by flash column chromatography (silica gel) to afford final the product.

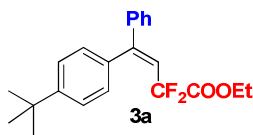


Aryldifluoromethylation product (0.3 mmol) and $\text{LiOH}\cdot\text{H}_2\text{O}$ (2.55 mmol) were stirred in a $\text{THF}/\text{H}_2\text{O}$ (2.5:1) mixture at room temperature for 4 h. The mixture was then acidified to pH 1 with a 35% HCl solution and extracted with diethyl ether (3×10 mL), and the combined organic layer was dried over Na_2SO_4 . After diethyl ether was removed under vacuum, the crude product **5** was crystallized in toluene.



To a Schlenk tube containing a magnetic stirrer bar was added the carboxylic acid **5** (1.0 equiv), Selectfluor (2.0 equiv) and silver nitrate (20 mol%). The Schlenk tube was closed with a rubber septum and equipped with a nitrogen balloon, and the system was purged with nitrogen. Acetone and water (1:1) were added and the reaction was stirred at 55 °C for 5 h, before diluting with water. The reaction mixture was extracted with DCM (3 × 10 mL), dried over MgSO₄ and concentrated in vacuo. The crude mixture was purified by flash column chromatography to afford product **6**.

3. Characterization Data of 3a-v, 4a-m, 5, 6, 8 and 9



(E)-ethyl 4-(4-(tert-butyl)phenyl)-2,2-difluoro-4-phenylbut-3-enoate, Oil, 82% yield (58.5 mg).

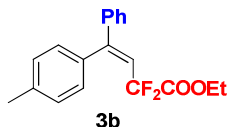
¹H NMR (400 MHz, CDCl₃) δ ppm 7.36 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.23 (m, 5H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.22 (t, *J* = 11.6 Hz, 1H), 3.82 (q, *J* = 7.2 Hz, 2H), 1.33 (s, 9H), 1.12 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ ppm 163.4 (t, *J* = 33.0 Hz), 151.6, 151.1 (t, *J* = 10.0 Hz), 140.8, 134.1, 129.6, 128.9, 128.3, 128.0, 124.8, 119.3 (t, *J* = 28.0 Hz), 112.6 (t, *J* = 244.0 Hz), 62.6, 34.6, 31.2, 13.6.

¹⁹F NMR (376 MHz, CDCl₃) δ ppm -89.9 (s, 2F).

IR (neat, cm⁻¹): 3368, 2962, 1771, 1637, 1305, 1106, 781.

HRMS (ESI) Calcd for C₂₂H₂₄F₂O₂: [M] + Na = 381.1637. Found: 381.1630.



(E)-ethyl 2,2-difluoro-4-phenyl-4-(p-tolyl)but-3-enoate, Oil, 81% yield (51.2 mg).

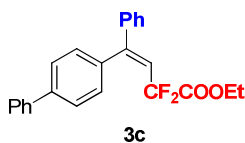
¹H NMR (400 MHz, CDCl₃) δ ppm 7.31 – 7.23 (m, 5H), 7.16 (d, *J* = 7.6 Hz 2H), 7.08 (t, *J* = 8.0 Hz, 2H), 6.23 (t, *J* = 11.6 Hz, 1H), 3.90 (q, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ ppm 163.5 (t, *J* = 34.0 Hz, COCF₂), 151.1 (t, *J* = 9.0 Hz, CCHCF₂), 140.7, 138.4, 134.1, 129.8, 129.0, 128.6, 128.3, 127.9, 119.2 (t, *J* = 28.0 Hz, CHCF₂), 112.6 (t, *J* = 244.0 Hz, CF₂), 62.7, 21.3, 13.6.

¹⁹F NMR (376 MHz, CDCl₃) δ ppm -90.7 (s, 2F).

IR (neat, cm⁻¹): 3366, 2985, 1771, 1637, 1305, 1102, 702.

HRMS (ESI) Calcd for $C_{19}H_{18}F_2O_2$: $[M] + Na = 339.1167$. Found: 339.1172.



(E)-ethyl 4-([1,1'-biphenyl]-4-yl)-2,2-difluoro-4-phenylbut-3-enoate, Oil, 80% yield (60.5 mg).

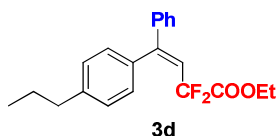
1H NMR (400 MHz, $CDCl_3$) δ ppm 7.63 – 7.58 (m, 4H), 7.44 (t, $J = 7.5$ Hz, 2H), 7.37 – 7.27 (m, 8H), 6.28 (t, $J = 12.0$ Hz, 1H), 3.92 (q, $J = 7.1$ Hz, 2H), 1.14 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 163.5 (t, $J = 34.0$ Hz), 150.7 (t, $J = 9.0$ Hz), 141.3, 140.5, 140.3, 136.1, 130.3, 129.1, 128.8, 128.4, 128.0, 127.6, 127.0, 126.6, 119.5 (t, $J = 28.0$ Hz), 112.6 (t, $J = 244.0$ Hz), 62.8, 13.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -90.8 (s, 2F).

IR (neat, cm^{-1}): 3512, 2984, 1770, 1636, 1305, 1102, 766.

HRMS (ESI) Calcd for $C_{24}H_{20}F_2O_2$: $[M] + Na = 401.1324$. Found: 401.1331.



(E)-ethyl 2,2-difluoro-4-phenyl-4-(4-propylphenyl)but-3-enoate, Oil, 77% yield (53.0 mg).

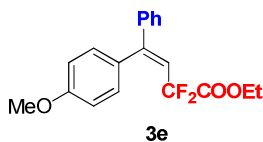
1H NMR (400 MHz, $CDCl_3$) δ ppm 7.33 – 7.23 (m, 5H), 7.16 (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 8.1$ Hz, 2H), 6.23 (t, $J = 11.6$ Hz, 1H), 3.87 (q, $J = 7.2$ Hz, 2H), 2.60 (t, $J = 7.2$ Hz, 2H), 1.70 – 1.61 (m, 2H), 1.14 (t, $J = 7.2$ Hz, 3H), 0.96 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 163.5 (t, $J = 33.0$ Hz), 151.2 (t, $J = 10.0$ Hz), 143.3, 140.8, 134.4, 129.8, 129.0, 128.3, 128.1, 128.0, 119.3 (t, $J = 28.0$ Hz), 112.7 (t, $J = 243.0$ Hz), 62.7, 37.8, 24.4, 13.8, 13.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -90.3 (s, 2F).

IR (neat, cm^{-1}): 3519, 2962, 1771, 1636, 1307, 1102, 738.

HRMS (ESI) Calcd for $C_{21}H_{22}F_2O_2$: $[M] + Na = 367.1480$. Found: 367.1475.



(E)-ethyl 2,2-difluoro-4-(4-methoxyphenyl)-4-phenylbut-3-enoate, Oil, 80% yield (53.1 mg).

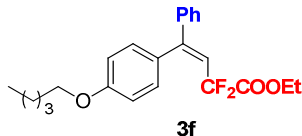
1H NMR (400 MHz, $CDCl_3$) δ ppm 7.33 – 7.28 (m, 3H), 7.27 – 7.24 (m, 2H), 7.13 (d, $J = 8.6$ Hz, 2H), 6.88 (d, $J = 8.6$ Hz, 2H), 6.20 (t, $J = 11.6$ Hz, 1H), 3.92 (q, $J = 7.2$ Hz, 2H), 3.82 (s, 3H), 1.16 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 163.5 (t, $J = 34.0$ Hz, $COCF_2$), 159.8, 150.8 (t, $J = 9.0$ Hz, $CCHCF_2$), 140.9, 131.3, 129.3, 129.0, 128.3, 128.0, 119.0 (t, $J = 28.0$ Hz, $CHCF_2$), 113.3, 111.4 (d, $J = 244.0$ Hz, CF_2), 62.7, 55.2, 13.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -90.2 (s, 2F).

IR (neat, cm^{-1}): 3414, 2977, 1638, 1451, 1247, 1046, 623.

HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{18}\text{F}_2\text{O}_3$: $[\text{M}] + \text{Na} = 355.1116$. Found: 355.1110.



(E)-ethyl 2,2-difluoro-4-(4-(pentyloxy)phenyl)-4-phenylbut-3-enoate, Oil, 73% yield (56.7 mg).

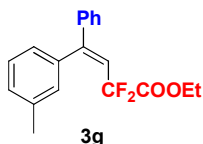
^1H NMR (400 MHz, CDCl_3) δ ppm 7.32 – 7.24 (m, 5H), 7.11 (d, $J = 8.4$ Hz, 2H), 6.86 (d, $J = 8.4$ Hz, 2H), 6.19 (t, $J = 11.6$ Hz, 1H), 3.97 (t, $J = 6.7$ Hz, 2H), 3.92 (q, $J = 7.2$ Hz, 2H), 1.83 – 1.76 (m, 2H), 1.45 – 1.38 (m, 4H), 1.16 (t, $J = 7.2$ Hz, 3H), 0.94 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.5 (t, $J = 34.0$ Hz), 159.5, 151.0 (t, $J = 10.0$ Hz), 141.0, 131.3, 129.1, 129.0, 128.3, 128.0, 119.0 (t, $J = 28.0$ Hz), 113.8, 112.7 (t, $J = 244.0$ Hz), 67.9, 62.7, 28.9, 28.2, 22.4, 14.0, 13.6.

^{19}F NMR (376 MHz, CDCl_3) δ ppm -90.1 (d, $J = 3.8$ Hz, 2F).

IR (neat, cm^{-1}): 3367, 2957, 1771, 1608, 1302, 1103, 834.

HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{26}\text{F}_2\text{O}_3$: $[\text{M}] + \text{Na} = 411.1742$. Found: 411.1749.



(E)-ethyl 2,2-difluoro-4-phenyl-4-(m-tolyl)but-3-enoate, Oil, 81% yield (51.2 mg).

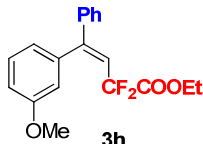
^1H NMR (400 MHz, CDCl_3) δ ppm 7.33 – 7.28 (m, 3H), 7.27 – 7.22 (m, 3H), 7.17 (d, $J = 7.6$ Hz, 1H), 7.00 (d, $J = 5.6$ Hz, 2H), 6.24 (t, $J = 11.6$ Hz, 1H), 3.89 (q, $J = 7.2$ Hz, 2H), 2.34 (s, 3H), 1.16 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.4 (t, $J = 34.0$ Hz), 151.1 (t, $J = 9.0$ Hz), 140.5, 137.6, 137.0, 130.3, 129.2, 129.0, 128.3, 127.9, 127.8, 127.0, 119.3 (t, $J = 28.0$ Hz), 112.5 (t, $J = 244.0$ Hz), 62.6, 21.3, 13.6.

^{19}F NMR (376 MHz, CDCl_3) δ ppm -90.8 (s, 2F).

IR (neat, cm^{-1}): 3570, 2984, 1772, 1637, 1307, 1104, 775.

HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{18}\text{F}_2\text{O}_2$: $[\text{M}] + \text{Na} = 339.1167$. Found: 339.1174.



(E)-ethyl 2,2-difluoro-4-(3-methoxyphenyl)-4-phenylbut-3-enoate, Oil, 76% yield (50.5 mg).

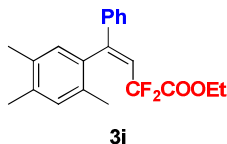
^1H NMR (400 MHz, CDCl_3) δ ppm 7.33 – 7.24 (m, 6H), 6.92 – 6.89 (m, 1H), 6.78 – 6.76 (m, 2H), 6.24 (t, $J = 12.0$ Hz, 1H), 3.94 (q, $J = 7.2$ Hz, 2H), 3.79 (s, 3H), 1.18 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.4 (t, $J = 33.0$ Hz), 159.1, 150.8 (t, $J = 9.0$ Hz), 140.2, 138.3, 129.1, 129.0, 128.3, 127.8, 122.2, 119.5 (t, $J = 28.0$ Hz), 115.3, 114.4, 111.3 (d, $J = 245.0$ Hz), 62.7, 55.2, 13.6.

^{19}F NMR (376 MHz, CDCl_3) δ ppm -91.0 (s, 2F).

IR (neat, cm^{-1}): 3513, 2962, 1770, 1599, 1256, 1103, 781.

HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{18}\text{F}_2\text{O}_3$: $[\text{M}] + \text{Na} = 355.1116$. Found: 355.1112.



(E)-ethyl 2,2-difluoro-4-phenyl-4-(2,3,5-trimethylphenyl)but-3-enoate, Oil, 89% yield (61.3 mg).

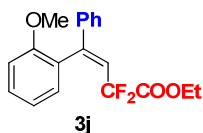
^1H NMR (400 MHz, CDCl_3) δ ppm 7.30 – 7.26 (m, 5H), 6.92 (d, $J = 18.0$ Hz, 2H), 6.34 (t, $J = 11.6$ Hz, 1H), 3.87 (q, $J = 6.8$ Hz, 2H), 2.24 (s, 6H), 1.91 (s, 3H), 1.17 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.4 (t, $J = 34.0$ Hz), 150.3 (t, $J = 10$ Hz), 139.3, 136.7, 133.7, 133.2, 133.1, 131.4, 128.9, 128.5, 127.9, 126.9, 119.6 (t, $J = 28.0$ Hz), 112.6 (t, $J = 244.0$ Hz), 62.6, 19.4, 19.1, 19.1, 13.5.

^{19}F NMR (376 MHz, CDCl_3) δ -90.7(d, $J = 274.5$ Hz, F), -94.7 (d, $J = 274.5$ Hz, F).

IR (neat, cm^{-1}): 3059, 2924, 1773, 1638, 1346, 1103, 766.

HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{22}\text{F}_2\text{O}_2$: $[\text{M}] + \text{Na} = 367.1480$. Found: 367.1475.



(E)-ethyl 2,2-difluoro-4-(2-methoxyphenyl)-4-phenylbut-3-enoate, Oil, 78% yield (51.8 mg).

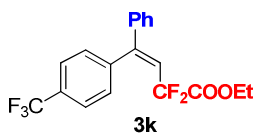
^1H NMR (400 MHz, CDCl_3) δ ppm 7.37 – 7.33 (m, 1H), 7.30 – 7.23 (m, 5H), 7.12 – 7.10 (m, 1H), 7.00 – 6.95 (m, 1H), 6.89 (d, $J = 8.4$ Hz, 1H), 6.33 (t, $J = 12.0$ Hz, 1H), 3.97 (q, $J = 7.2$ Hz, 2H), 3.64 (s, 3H), 1.21 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.4 (t, $J = 34.0$ Hz), 156.8, 147.2 (t, $J = 9.0$ Hz), 139.9, 131.2, 130.0, 128.7, 128.2, 126.9, 125.8, 120.1, 120.0 (t, $J = 27.0$ Hz), 112.6 (t, $J = 244.0$ Hz), 110.8, 62.6, 55.4, 13.7.

^{19}F NMR (376 MHz, CDCl_3) δ ppm -94.4 (s, 2F).

IR (neat, cm^{-1}): 3404, 2961, 1770, 1492, 1265, 1099, 740.

HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{18}\text{F}_2\text{O}_3$: $[\text{M}] + \text{Na} = 355.1116$. Found: 355.1122.



(E)-ethyl 2,2-difluoro-4-phenyl-4-(4-(trifluoromethyl)phenyl)but-3-enoate, Oil, 77% yield (57.0 mg).

^1H NMR (400 MHz, CDCl_3) δ ppm 7.67 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 6.0$ Hz, 5H), 7.28 – 7.25 (m, 2H), 6.36 (t, $J = 12.4$ Hz, 1H), 4.06 (q, $J = 7.2$ Hz, 2H), 1.24 (t, $J = 7.2$ Hz, 3H).

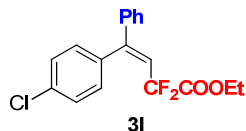
^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.5 (t, $J = 34.0$ Hz), 149.6 (t, $J = 8.0$ Hz), 141.0, 139.7, 130.3 (q, $J = 32.0$ Hz), 130.1, 129.4, 128.6, 127.7, 124.9 (q, $J = 4.0$ Hz),

124.0 (q, $J = 271.0$ Hz), 120.1 (t, $J = 27.0$ Hz, CHCF_2), 112.3 (t, $J = 246.0$ Hz), 63.0, 13.7.

^{19}F NMR (376 MHz, CDCl_3) δ ppm -62.7 (s, 3F).

IR (neat, cm^{-1}): 3231, 2989, 1773, 1618, 1325, 1127, 732.

HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{15}\text{F}_5\text{O}_2$: $[\text{M}] + \text{Na} = 393.0884$. Found: 393.0890.



(E)-ethyl 4-(4-chlorophenyl)-2,2-difluoro-4-phenylbut-3-enoate, Oil, 75% yield (50.4 mg).

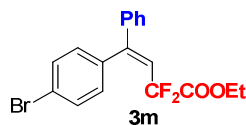
^1H NMR (400 MHz, CDCl_3) δ ppm 7.35 – 7.30 (m, 5H), 7.25 – 7.22 (m, 2H), 7.15 (d, $J = 8.4$ Hz, 2H), 6.26 (t, $J = 12.2$ Hz, 1H), 4.01 (q, $J = 7.2$ Hz, 2H), 1.21 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.5 (t, $J = 33.0$ Hz), 149.9 (t, $J = 8.0$ Hz), 140.1, 135.6, 134.7, 131.1, 129.3, 128.5, 128.2, 127.8, 119.8 (t, $J = 28.0$ Hz), 112.4 (t, $J = 245.0$ Hz), 62.9, 13.7.

^{19}F NMR (376 MHz, CDCl_3) δ ppm -91.9 (s, 2F).

IR (neat, cm^{-1}): 3503, 2985, 1770, 1637, 1306, 1100, 781.

HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{15}\text{ClF}_2\text{O}_2$: $[\text{M}] + \text{Na} = 359.0621$. Found: 359.0627.



(E)-ethyl 4-(4-bromophenyl)-2,2-difluoro-4-phenylbut-3-enoate, Oil, 74% yield (56.2 mg).

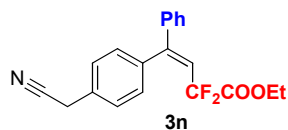
^1H NMR (400 MHz, CDCl_3) δ ppm 7.51 – 7.49 (m, 2H), 7.35 – 7.29 (m, 3H), 7.24 – 7.22 (m, 2H), 7.08 (d, $J = 8.4$ Hz, 2H), 6.27 (t, $J = 12.2$ Hz, 1H), 4.01 (q, $J = 7.2$ Hz, 2H), 1.21 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.4 (t, $J = 33.0$ Hz), 149.8 (t, $J = 9.0$ Hz), 139.9, 136.0, 131.4, 131.2, 129.3, 128.5, 127.8, 122.9, 119.7 (t, $J = 28.0$ Hz), 112.3 (t, $J = 245.0$ Hz), 63.0, 13.7.

^{19}F NMR (376 MHz, CDCl_3) δ ppm -91.9 (d, $J = 2.4$ Hz, 2F).

IR (neat, cm^{-1}): 3367, 2924, 2372, 1773, 1296, 1106, 777.

HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{15}\text{BrF}_2\text{O}_2$: $[\text{M}] + \text{Na} = 403.0116$. Found: 403.0113.



(E)-ethyl 4-(4-(2-cyanoethyl)phenyl)-2,2-difluoro-4-phenylbut-3-enoate, Oil, 70% yield (47.7 mg).

^1H NMR (400 MHz, CDCl_3) δ ppm 7.35 – 7.29 (m, 5H), 7.25 – 7.22 (m, 4H), 6.28 (t, $J = 12.4$ Hz, 1H), 4.01 (q, $J = 7.2$ Hz, 2H), 3.78 (s, 2H), 1.21 (t, $J = 7.2$ Hz, 3H).

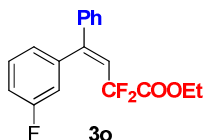
^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.4 (t, $J = 34.0$ Hz, COCF_2), 150.1 (t, $J = 8.0$

Hz, CCHCF₂), 140.0, 137.1, 130.4, 130.2, 129.2, 128.4, 127.7, 127.5, 119.5 (t, *J* = 27.0 Hz, CHCF₂), 117.5, 112.3 (t, *J* = 245.0 Hz, CF₂), 62.9, 23.3, 13.7.

¹⁹F NMR (376 MHz, CDCl₃) δ ppm -92.1 (s, 2F).

IR (neat, cm⁻¹): 3514, 2986, 2253, 1769, 1637, 1306, 1101, 737.

HRMS (ESI) Calcd for C₂₀H₁₇F₂NO₂: [M] + Na = 364.1120. Found: 364.1125.



(E)-ethyl 2,2-difluoro-4-(3-fluorophenyl)-4-phenylbut-3-enoate, Oil, 74% yield (47.4 mg).

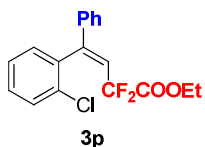
¹H NMR (400 MHz, CDCl₃) δ ppm 7.37 – 7.30 (m, 4H), 7.26 – 7.23 (m, 2H), 7.08 (td, *J* = 8.4, 2.0 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 9.2, 1H), 6.28 (t, *J* = 12.0 Hz, 1H), 4.02 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ ppm 163.4 (t, *J* = 34.0 Hz), 162.3 (d, *J* = 247.1 Hz), 149.6 (t, *J* = 9.0 Hz), 139.8, 139.2 (d, *J* = 8.0 Hz), 129.6 (d, *J* = 9.0 Hz), 129.3, 128.5, 127.7, 125.6 (d, *J* = 3.0 Hz), 119.9 (t, *J* = 28.0 Hz), 116.7 (d, *J* = 22.0 Hz), 115.5 (d, *J* = 21.0 Hz), 112.3 (t, *J* = 244.0 Hz), 62.9, 13.7.

¹⁹F NMR (376 MHz, CDCl₃) δ ppm -92.1 (d, *J* = 3.8 Hz, 2F).

IR (neat, cm⁻¹): 3493, 2986, 1771, 1584, 1258, 1102, 790.

HRMS (ESI) Calcd for C₁₈H₁₅F₃O₂: [M] + Na = 343.0916. Found: 343.0911.



(E)-ethyl 4-(2-chlorophenyl)-2,2-difluoro-4-phenylbut-3-enoate, Oil, 74% yield (49.7 mg).

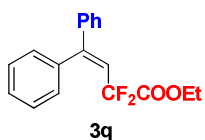
¹H NMR (400 MHz, CDCl₃) δ ppm 7.41 – 7.36 (m, 1H), 7.34 – 7.28 (m, 6H), 7.27 – 7.24 (m, 2H), 6.41 (dd, *J* = 13.4, 10.8 Hz, 1H), 4.12 – 4.00 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ ppm 163.2 (t, *J* = 34.0 Hz), 147.8 (t, *J* = 7.0 Hz), 138.4, 135.6, 133.3, 131.8, 129.9, 129.5, 129.2, 128.5, 126.9, 126.3, 120.6 (dd, *J* = 30.0, 25.0 Hz), 112.2 (t, *J* = 243.0 Hz), 63.0, 13.7.

¹⁹F NMR (376 MHz, CDCl₃) δ ppm -93.8 (dd, *J* = 272.6 Hz, 11.3 Hz), -95.8 (dd, *J* = 272.6 Hz, 11.3 Hz).

IR (neat, cm⁻¹): 3516, 2985, 1772, 1641, 1305, 1101, 762.

HRMS (ESI) Calcd for C₁₈H₁₅ClF₂O₂: [M] + Na = 359.0621. Found: 359.0616.



ethyl 2,2-difluoro-4,4-diphenylbut-3-enoate, Oil, 78% yield (47.1 mg).

¹H NMR (400 MHz, CDCl₃) δ ppm 7.37 – 7.35 (m, 3H), 7.33 – 7.29 (m, 3H), 7.26 – 7.23 (m, 2H), 7.21 – 7.19 (m, 2H), 6.27 (t, *J* = 12.0 Hz, 1H), 3.90 (q, *J* = 7.2 Hz, 2H),

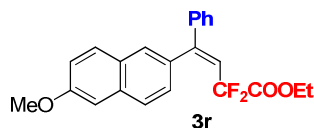
1.16 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.4 (t, $J = 34.0$ Hz), 150.9 (t, $J = 9.0$ Hz), 140.4, 137.0, 129.8, 129.0, 128.5, 128.3, 127.9, 127.8, 119.4 (t, $J = 28.0$ Hz), 112.5 (t, $J = 244.0$ Hz), 62.7, 13.6.

^{19}F NMR (376 MHz, CDCl_3) δ ppm -90.9 (d, $J = 3.4$ Hz, 2F).

IR (neat, cm^{-1}): 3519, 2985, 1771, 1637, 1358, 1102, 765.

HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{16}\text{F}_2\text{O}_2$: $[\text{M}] + \text{Na} = 325.1011$. Found: 325.1006.



(E)-ethyl 2,2-difluoro-4-(6-methoxynaphthalen-2-yl)-4-phenylbut-3-enoate, Oil, 55% yield (42.0 mg).

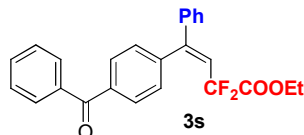
^1H NMR (400 MHz, CDCl_3) δ ppm 7.75 (d, $J = 9.2$ Hz, 1H), 7.68 (d, $J = 7.2$ Hz, 2H), 7.34 – 7.30 (m, 5H), 7.19 – 7.14 (m, 3H), 6.32 (td, $J = 11.2, 1.2$ Hz, 1H), 3.92 (s, 3H), 3.66 (q, $J = 7.2$ Hz, 2H), 0.96 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.4 (t, $J = 33.0$ Hz, COCF_2), 158.4, 151.1 (t, $J = 10.0$ Hz, CCHCF_2), 140.5, 134.4, 132.2, 129.8, 129.4, 129.1, 128.4, 128.1, 128.0, 127.8, 126.5, 119.7 (t, $J = 29.0$ Hz, CHCF_2), 119.3, 112.7 (t, $J = 243.0$ Hz, CF_2), 105.7, 62.6, 55.3, 13.4.

^{19}F NMR (376 MHz, CDCl_3) δ ppm -89.9 (s, 2F).

IR (neat, cm^{-1}): 3513, 2980, 1771, 1629, 1499, 1214, 855.

HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{20}\text{F}_2\text{O}_3$: $[\text{M}] + \text{Na} = 405.1273$. Found: 405.1278.



(E)-ethyl 4-(4-benzoylphenyl)-2,2-difluoro-4-phenylbut-3-enoate, Oil, 65% yield (52.8 mg).

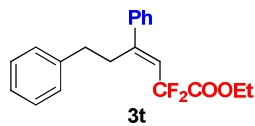
^1H NMR (400 MHz, CDCl_3) δ ppm 7.84 – 7.82 (m, 4H), 7.63 – 7.59 (m, 1H), 7.52 – 7.49 (m, 2H), 7.37 – 7.33 (m, 5H), 7.28 – 7.26 (m, 2H), 6.33 (t, $J = 12.4$ Hz, 1H), 4.06 (q, $J = 7.2$ Hz, 2H), 1.24 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ ppm 196.1, 163.4 (t, $J = 34.0$ Hz), 150.0 (t, $J = 8.0$ Hz), 141.4, 139.8, 137.4, 137.3, 132.6, 130.0, 129.6, 129.4, 128.5, 128.4, 127.8, 119.8 (t, $J = 27.0$ Hz), 112.3 (t, $J = 245.0$ Hz), 63.0, 13.8.

^{19}F NMR (376 MHz, CDCl_3) δ ppm -92.5 (s, 2F).

IR (neat, cm^{-1}): 3508, 2985, 1770, 1660, 1283, 1103, 703.

HRMS (ESI) Calcd for $\text{C}_{25}\text{H}_{20}\text{F}_2\text{O}_3$: $[\text{M}] + \text{Na} = 429.1273$. Found: 429.1277.



(E)-ethyl 2,2-difluoro-4,6-diphenylhex-3-enoate, Oil, 58% yield (38.3 mg).

^1H NMR (400 MHz, CDCl_3) δ ppm 7.40 – 7.37 (m, 5H), 7.28 – 7.24 (m, 2H), 7.19

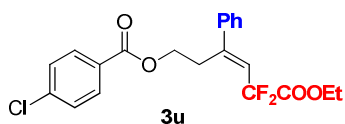
– 7.13 (m, 3H), 5.84 (t, $J = 14.4$ Hz, 1H), 4.32 (q, $J = 7.2$ Hz, 2H), 3.02 – 2.98 (m, 2H), 2.64 – 2.59 (m, 2H), 1.33 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ ppm 164.2 (t, $J = 35.0$ Hz), 152.2 (t, $J = 7.0$ Hz), 141.2, 140.4, 128.7, 128.6, 128.4, 128.3, 126.7, 126.0, 119.4 (t, $J = 26.0$ Hz), 112.9 (t, $J = 247.0$ Hz), 63.0, 34.9, 33.2, 13.9.

^{19}F NMR (376 MHz, CDCl_3) δ ppm -97.4 (d, $J = 9.4$ Hz, 2F).

IR (neat, cm^{-1}): 3511, 2930, 1765, 1535, 1296, 1087, 756.

HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{20}\text{F}_2\text{O}_2$: $[\text{M}] + \text{Na} = 353.1324$. Found: 353.1331.



(E)-ethyl 4-((3-(4-chlorophenyl)propanoyl)oxy)-2,2-difluoro-4-phenylbut-3-enoate, Oil, 45% yield (36.7 mg).

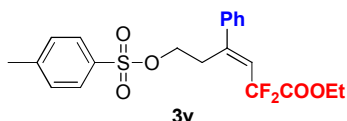
^1H NMR (400 MHz, CDCl_3) δ ppm 7.73 (d, $J = 8.8$, 2H), 7.41 – 7.26 (m, 7H), 5.94 (t, $J = 14.4$ Hz, 1H), 4.34 (q, $J = 7.2$ Hz, 4H), 3.23 (t, $J = 6.4$ Hz, 2H), 1.35 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ ppm 165.4, 164.1 (t, $J = 35.0$ Hz), 149.1 (t, $J = 6.0$ Hz), 140.3, 139.3, 130.9, 128.9, 128.8, 128.5, 128.4, 126.7, 121.3 (t, $J = 26.0$ Hz), 112.7 (t, $J = 248.0$ Hz), 63.5, 63.2, 30.3, 13.9.

^{19}F NMR (376 MHz, CDCl_3) δ ppm -90.5 (d, $J = 11.3$ Hz, 2F).

IR (neat, cm^{-1}): 3507, 2926, 1765, 1595, 1272, 1092, 760.

HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{19}\text{ClF}_2\text{O}_4$: $[\text{M}] + \text{Na} = 431.0832$. Found: 431.0841.



(E)-ethyl 2,2-difluoro-4-phenyl-6-(tosyloxy)hex-3-enoate, Oil, 48% yield (40.7 mg).

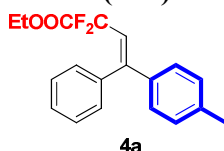
^1H NMR (400 MHz, CDCl_3) δ ppm 7.66 (d, $J = 8.4$ Hz, 2H), 7.34 – 7.30 (m, 3H), 7.28 – 7.26 (m, 2H), 7.24 – 7.22 (m, 2H), 5.89 (t, $J = 14.4$ Hz, 1H), 4.35 (q, $J = 7.2$ Hz, 2H), 3.97 (t, $J = 7.2$ Hz, 2H), 3.10 (t, $J = 7.2$ Hz, 2H), 2.43 (s, 3H), 1.36 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.8 (t, $J = 34.0$ Hz), 146.8 (t, $J = 6.0$ Hz), 144.6, 139.1, 132.8, 129.7, 129.0, 128.7, 127.8, 126.5, 122.1 (t, $J = 26.0$ Hz), 112.4 (t, $J = 247.0$ Hz), 67.8, 63.3, 30.4, 21.6, 13.9.

^{19}F NMR (376 MHz, CDCl_3) δ ppm -97.6 (d, $J = 11.3$ Hz, 2F).

IR (neat, cm^{-1}): 3459, 2985, 1739, 1373, 1244, 1047, 782.

HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{22}\text{F}_2\text{O}_5\text{S}$: $[\text{M}] + \text{Na} = 447.1048$. Found: 447.1057.



(Z)-ethyl 2,2-difluoro-4-phenyl-4-(p-tolyl)but-3-enoate, Oil, 84% yield (53.1 mg).

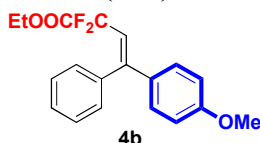
¹H NMR (400 MHz, CDCl₃) δ ppm 7.35 – 7.34 (m, 3H), 7.21 – 7.18 (m, 2H), 7.12 (q, *J* = 8.4 Hz, 4H), 6.24 (t, *J* = 12.0 Hz, 1H), 3.89 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ ppm 163.4 (t, *J* = 34.0 Hz), 150.8 (t, *J* = 9.0 Hz), 139.2, 137.6, 137.2, 129.8, 129.0, 128.4, 127.9, 127.7, 118.5 (t, *J* = 28.0 Hz), 112.6 (t, *J* = 244.0 Hz), 62.6, 21.1, 13.6.

¹⁹F NMR (376 MHz, CDCl₃) δ ppm -90.6 (s, 2F).

IR (neat, cm⁻¹): 3513, 2986, 1772, 1636, 1306, 1103, 765.

HRMS (ESI) Calcd for C₁₉H₁₈F₂O₂: [M] + Na = 339.1167. Found: 339.1173.



(Z)-ethyl 2,2-difluoro-4-(4-methoxyphenyl)-4-phenylbut-3-enoate, Oil, 81% yield (53.8 mg).

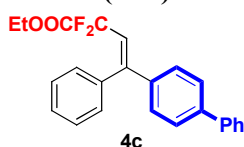
¹H NMR (400 MHz, CDCl₃) δ ppm 7.36 – 7.34 (m, 3H), 7.23 – 7.16 (m, 4H), 6.84 – 6.81 (m, 2H), 6.20 (t, *J* = 12.0 Hz, 1H), 3.89 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ ppm 163.5 (t, *J* = 34.0 Hz), 160.4, 150.4 (t, *J* = 9.0 Hz), 137.2, 132.8, 129.8, 129.1, 128.4, 127.9, 117.5 (t, *J* = 28.0 Hz), 113.7, 112.7 (t, *J* = 243.0 Hz), 62.6, 55.2, 13.6.

¹⁹F NMR (376 MHz, CDCl₃) δ ppm -90.4 (s, 2F).

IR (neat, cm⁻¹): 3516, 2984, 1771, 1605, 1253, 1101, 827.

HRMS (ESI) Calcd for C₁₉H₁₈F₂O₃: [M] + Na = 355.1116. Found: 355.1124.



(Z)-ethyl 4-([1,1'-biphenyl]-4-yl)-2,2-difluoro-4-phenylbut-3-enoate, Oil, 75% yield (56.7 mg).

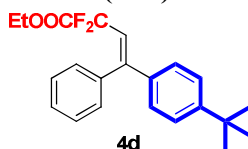
¹H NMR (400 MHz, CDCl₃) δ ppm 7.58 – 7.53 (m, 4H), 7.44 – 7.41 (m, 1H), 7.39 – 7.36 (m, 2H), 7.34 – 7.31 (m, 3H), 7.25 – 7.24 (m, 2H), 6.33 (t, *J* = 11.6 Hz, 1H), 3.92 (q, *J* = 7.2 Hz, 2H), 1.17 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ ppm 163.4 (t, *J* = 34.0 Hz), 150.5 (t, *J* = 9.0 Hz), 141.9, 140.2, 139.3, 137.0, 129.8, 128.8, 128.6, 128.3, 128.0, 127.6, 127.0, 119.3 (t, *J* = 28.4 Hz), 112.6 (t, *J* = 244.0 Hz), 62.7, 13.7.

¹⁹F NMR (376 MHz, CDCl₃) δ ppm -90.9 (d, *J* = 5.8 Hz, 2F).

IR (neat, cm⁻¹): 3512, 3000, 1770, 1664, 1322, 1101, 738.

HRMS (ESI) Calcd for C₂₄H₂₀F₂O₂: [M] + Na = 401.1324. Found: 401.1331.



(Z)-ethyl 4-(4-(tert-butyl)phenyl)-2,2-difluoro-4-phenylbut-3-enoate, Oil, 79%

yield (56.6 mg).

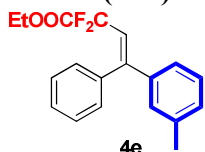
¹H NMR (400 MHz, CDCl₃) δ ppm 7.36 – 7.32 (m, 5H), 7.23 – 7.18 (m, 4H), 6.27 (t, *J* = 11.6 Hz, 1H), 3.90 (q, *J* = 7.2 Hz, 2H), 1.30 (s, 9H), 1.16 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ ppm 163.5 (t, *J* = 34.0 Hz), 152.4, 150.6 (t, *J* = 9.0 Hz), 137.4, 137.1, 129.8, 128.4, 127.9, 127.5, 125.3, 118.6 (t, *J* = 28.0 Hz), 112.6 (t, *J* = 244.0 Hz), 62.7, 34.6, 31.2, 13.6.

¹⁹F NMR (376 MHz, CDCl₃) δ ppm -90.9 (s, 2F).

IR (neat, cm⁻¹): 3366, 2964, 1772, 1638, 1305, 1103, 703.

HRMS (ESI) Calcd for C₂₂H₂₄F₂O₂: [M] + Na = 381.1637. Found: 381.1632.



(Z)-ethyl 2,2-difluoro-4-(3-methoxyphenyl)-4-phenylbut-3-enoate, Oil, 80% yield (50.6 mg).

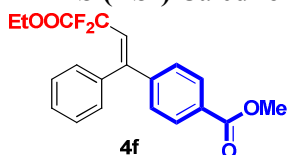
¹H NMR (400 MHz, CDCl₃) δ ppm 7.36 – 7.35 (m, 3H), 7.23 – 7.13 (m, 3H), 7.09 (s, 4H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.25 (t, *J* = 11.6 Hz, 1H), 3.89 (q, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ ppm 163.4 (t, *J* = 34.0 Hz), 151.1 (t, *J* = 9.0 Hz), 140.5, 138.0, 137.1, 129.8, 129.8, 128.5, 128.4, 128.2, 127.9, 125.1, 119.3 (t, *J* = 28.0 Hz), 112.5 (t, *J* = 243.0 Hz), 62.7, 21.3, 13.6.

¹⁹F NMR (376 MHz, CDCl₃) δ ppm -90.8 (s, 2F).

IR (neat, cm⁻¹): 3364, 2984, 1772, 1637, 1307, 1104, 781.

HRMS (ESI) Calcd for C₁₉H₁₈F₂O₂: [M] + Na = 339.1167. Found: 339.1175.



(Z)-methyl 4-(4-ethoxy-3,3-difluoro-4-oxo-1-phenylbut-1-en-1-yl)benzoate, Oil, 58% yield (41.8 mg).

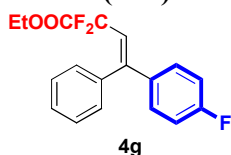
¹H NMR (400 MHz, CDCl₃) δ ppm 7.98 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.36 (m, 3H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.20 – 7.18 (m, 2H), 6.34 (t, *J* = 11.6 Hz, 1H), 3.92 (q, *J* = 7.2 Hz, 2H), 3.91 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ ppm 166.5, 163.2 (t, *J* = 34.0 Hz), 150.0 (t, *J* = 9.0 Hz), 144.7, 136.4, 130.5, 129.7, 129.6, 128.8, 128.1, 127.8, 121.2 (t, *J* = 28.0 Hz), 112.2 (t, *J* = 244.0 Hz), 62.8, 52.2, 13.6.

¹⁹F NMR (376 MHz, CDCl₃) δ ppm -91.4 (d, *J* = 5.8 Hz, 2F).

IR (neat, cm⁻¹): 3526, 2987, 1771, 1609, 1281, 1106, 740.

HRMS (ESI) Calcd for C₂₀H₁₈F₂O₄: [M] + Na = 383.1066. Found: 383.1073.



(Z)-ethyl 2,2-difluoro-4-(4-fluorophenyl)-4-phenylbut-3-enoate, Oil, 82% yield (52.5 mg).

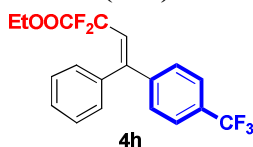
¹H NMR (400 MHz, CDCl₃) δ ppm 7.38 – 7.34 (m, 3H), 7.25 – 7.22 (m, 2H), 7.20 – 7.17 (m, 2H), 7.00 (t, *J* = 8.4 Hz, 2H), 6.22 (t, *J* = 11.6 Hz, 1H), 3.90 (q, *J* = 7.2 Hz, 2H), 1.16 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ ppm 163.34 (t, *J* = 34.0 Hz), 163.25 (d, *J* = 248.0 Hz), 149.9 (t, *J* = 9.0 Hz), 136.9, 136.6, 129.7, 129.6, 128.7, 128.1, 119.3 (t, *J* = 28.0 Hz), 115.3 (d, *J* = 21.0 Hz), 112.4 (t, *J* = 244.0 Hz), 62.7, 13.6.

¹⁹F NMR (376 MHz, CDCl₃) δ ppm -91.0 (s, 2F).

IR (neat, cm⁻¹): 3519, 2986, 1771, 1602, 1237, 1102, 831.

HRMS (ESI) Calcd for C₁₈H₁₅F₃O₂: [M] + Na = 343.0916. Found: 343.0921.



(Z)-ethyl 2,2-difluoro-4-phenyl-4-(4-(trifluoromethyl)phenyl)but-3-enoate, Oil, 61% yield (45.2 mg).

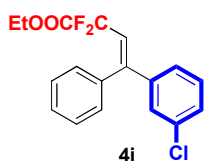
¹H NMR (400 MHz, CDCl₃) δ ppm 7.57 (d, *J* = 8.0 Hz, 2H), 7.40 – 7.36 (m, 5H), 7.20 – 7.18 (m, 2H), 6.32 (t, *J* = 11.6 Hz, 1H), 3.92 (q, *J* = 7.2 Hz, 2H), 1.17 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ ppm 163.2 (t, *J* = 33.0 Hz), 149.8 (t, *J* = 9.0 Hz), 144.0, 136.3, 131.8, 131.0 (q, *J* = 32.7 Hz), 129.7, 128.9, 128.2, 125.4 (q, *J* = 4.0 Hz), 123.9 (q, *J* = 270.0 Hz), 121.3 (t, *J* = 28.0 Hz), 112.2 (t, *J* = 244.0 Hz), 62.9, 13.6.

¹⁹F NMR (376 MHz, CDCl₃) δ ppm -62.7 (s, 3F).

IR (neat, cm⁻¹): 3367, 2987, 1771, 1639, 1326, 1067, 855.

HRMS (ESI) Calcd for C₁₉H₁₅F₅O₂: [M] + Na = 393.0884. Found: 393.0892.



(Z)-ethyl 4-(3-chlorophenyl)-2,2-difluoro-4-phenylbut-3-enoate, Oil, 74% yield (49.7 mg).

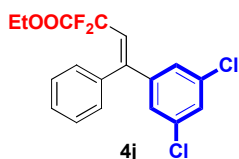
¹H NMR (400 MHz, CDCl₃) δ ppm 7.38 – 7.36 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.20 – 7.17 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.26 (t, *J* = 11.6 Hz, 1H), 3.91 (q, *J* = 7.2 Hz, 2H), 1.16 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ ppm 163.2 (t, *J* = 34.0 Hz), 149.7 (t, *J* = 9.0 Hz), 142.3, 136.3, 134.4, 129.7, 129.6, 129.0, 128.8, 128.1, 127.9, 126.1, 120.6 (t, *J* = 28.0 Hz), 112.2 (t, *J* = 244.0 Hz), 62.8, 13.6.

¹⁹F NMR (376 MHz, CDCl₃) δ ppm -91.3 (s, 2F).

IR (neat, cm⁻¹): 3505, 2985, 1772, 1566, 1307, 1104, 780.

HRMS (ESI) Calcd for C₁₈H₁₅ClF₂O₂: [M] + Na = 359.0621. Found: 359.0627.



(Z)-ethyl 4-(3,5-dichlorophenyl)-2,2-difluoro-4-phenylbut-3-enoate, Oil, 71% yield (52.6 mg).

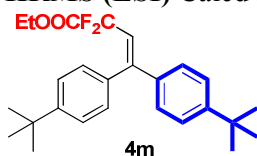
^1H NMR (400 MHz, CDCl_3) δ ppm 7.39 (d, $J = 5.2$ Hz, 3H), 7.34 (s, 1H), 7.18 – 7.16 (m, 2H), 7.13 (s, 1H), 6.26 (t, $J = 11.2$ Hz, 1H), 3.92 (q, $J = 7.2$ Hz, 2H), 1.17 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.0 (t, $J = 34.0$ Hz), 148.7 (t, $J = 9.0$ Hz), 143.5, 135.7, 135.1, 129.6, 129.1, 128.9, 128.3, 126.3, 121.6 (t, $J = 28.0$ Hz), 112.0 (t, $J = 244.0$ Hz), 62.9, 13.7.

^{19}F NMR (376 MHz, CDCl_3) δ ppm -91.7 (s, 2F).

IR (neat, cm^{-1}): 3520, 2984, 1773, 1560, 1306, 1105, 804.

HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{14}\text{Cl}_2\text{F}_2\text{O}_2$: $[\text{M}] + \text{Na} = 393.0231$. Found: 393.0239.



ethyl 4,4-bis(4-(tert-butyl)phenyl)-2,2-difluorobut-3-enoate, Oil, 78% yield (64.6 mg).

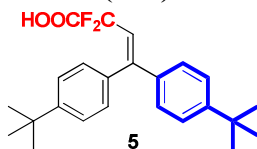
^1H NMR (400 MHz, CDCl_3) δ ppm 7.37 – 7.32 (m, 4H), 7.20 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 2H), 6.22 (t, $J = 11.6$ Hz, 1H), 3.83 (q, $J = 7.2$ Hz, 2H), 1.33 (s, 9H), 1.31 (s, 9H), 1.13 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.5 (t, $J = 34.0$ Hz), 152.2, 151.5, 150.8 (t, $J = 9.0$ Hz), 137.8, 134.2, 129.6, 127.6, 125.2, 124.8, 118.5 (t, $J = 28.0$ Hz), 112.8 (t, $J = 243.0$ Hz), 62.5, 34.7, 34.6, 31.3, 31.2, 13.7.

^{19}F NMR (376 MHz, CDCl_3) δ ppm -89.9 (s, 2F).

IR (neat, cm^{-1}): 3404, 2962, 1772, 1637, 1269, 1102, 829.

HRMS (ESI) Calcd for $\text{C}_{26}\text{H}_{32}\text{F}_2\text{O}_2$: $[\text{M}] + \text{Na} = 437.2263$. Found: 437.2271.



4,4-bis(4-(tert-butyl)phenyl)-2,2-difluorobut-3-enoic acid, 95% yield (110.0 mg).

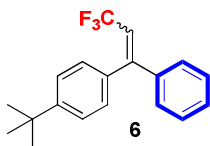
^1H NMR (400 MHz, CDCl_3) δ ppm 9.84 (s, 1H), 7.32 (d, $J = 6.4$ Hz, 4H), 7.19 (d, $J = 7.2$ Hz, 2H), 7.09 (d, $J = 7.2$ Hz, 2H), 6.22 (t, $J = 10.8$ Hz, 1H), 1.30 (s, 18H).

^{13}C NMR (100 MHz, CDCl_3) δ ppm 168.5 (t, $J = 34.0$ Hz), 152.4, 151.9, 151.7 (t, $J = 9.0$ Hz), 137.2, 133.8, 129.6, 127.5, 125.3, 124.8, 117.6 (t, $J = 27.0$ Hz), 112.5 (t, $J = 243.0$ Hz), 34.6, 31.2.

^{19}F NMR (376 MHz, CDCl_3) δ ppm -91.7 (s, 2F).

IR (neat, cm^{-1}): 3423, 2959, 1763, 1462, 1269, 1110, 835.

HRMS (ESI) Calcd for $\text{C}_{24}\text{H}_{28}\text{F}_2\text{O}_2$: $[\text{M}] + \text{H} = 387.2130$. Found: 387.2139.



1-(tert-butyl)-4-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)benzene, Oil, 26% yield (15.8 mg).

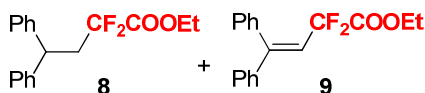
¹H NMR (400 MHz, CDCl₃) δ ppm **major**: 7.42 – 7.35 (m, 3H), 7.34 – 7.32 (m, 2H), 7.26 – 7.23 (m, 2H), 7.19 – 7.15 (m, 2H), 6.12 (q, *J* = 8.4 Hz, 1H), 1.31 (s, 9H). **minor**: 7.42 – 7.35 (m, 3H), 7.34 – 7.32 (m, 2H), 7.26 – 7.23 (m, 2H), 7.19 – 7.15 (m, 2H), 6.07 (q, *J* = 8.4 Hz, 1H), 1.35 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ ppm **major**: 152.8, 140.6, 137.0, 129.2, 129.1, 128.4, 128.3, 128.0, 125.4, 123.2 (q, *J* = 274.0 Hz), 114.6 (q, *J* = 33.0 Hz), 34.7, 31.2. **minor**: 151.5, 137.4, 134.2, 129.2, 128.9, 128.3, 128.1, 127.6, 124.9, 123.2 (d, *J* = 274.0 Hz), 115.1 (q, *J* = 34.0 Hz), 34.7, 31.3.

¹⁹F NMR (376 MHz, CDCl₃) δ ppm **major**: -55.4 (d, *J* = 2.2 Hz, 3F). **minor**: -55.5 (d, *J* = 2.2 Hz, 3F).

IR (neat, cm⁻¹): 3364, 2963, 1641, 1365, 1272, 1131, 699.

HRMS (ESI) Calcd for C₁₉H₁₉F₃: [M] + Na = 327.1331. Found: 327.1337.



¹H NMR (400 MHz, CDCl₃) δ ppm **major**: 7.81 – 7.79 (m, 2H), 7.60 – 7.56 (m, 1H), 7.37 – 7.16 (m, 7H), 6.27 (t, *J* = 11.6 Hz, 1H), 3.90 (q, *J* = 7.2 Hz, 2H), 1.16 (t, *J* = 7.2 Hz, 3H). **minor**: 7.52 – 7.44 (m, 2H), 7.39 – 7.15 (m, 8H), 4.27 (t, *J* = 7.2 Hz, 1H), 3.83 (q, *J* = 7.2 Hz, 2H), 2.93 (td, *J* = 15.2, 7.2 Hz, 2H), 1.15 (t, *J* = 7.2 Hz, 3H).

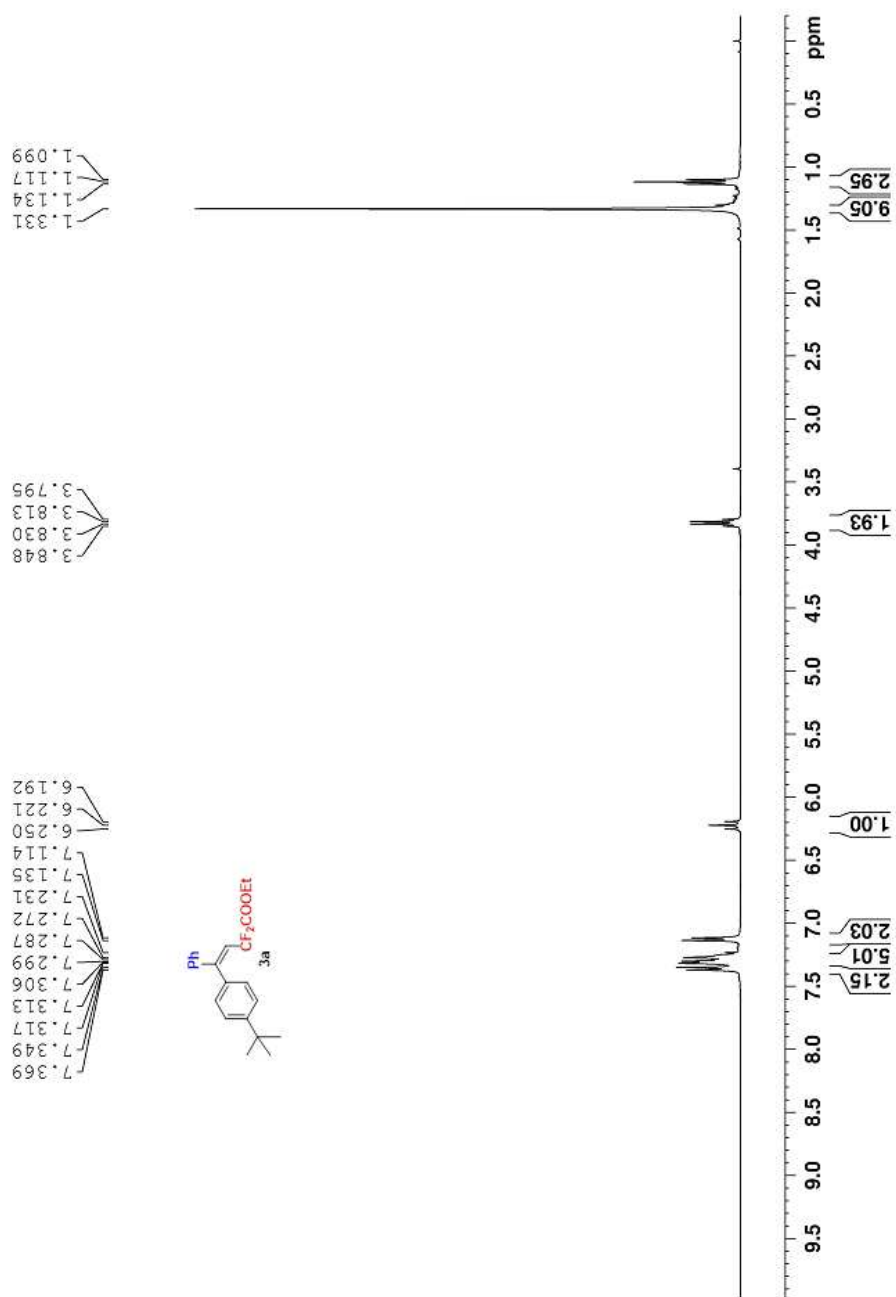
¹³C NMR (100 MHz, CDCl₃) δ ppm **major**: 163.7 (t, *J* = 32.0 Hz), 151.0 (t, *J* = 9.0 Hz), 142.9, 140.5, 132.34, 129.8, 129.1, 128.6, 128.2, 127.7, 119.5 (t, *J* = 28.0 Hz), 112.5 (t, *J* = 244.0 Hz), 62.7, 13.6. **minor**: 163.4 (t, *J* = 32.0 Hz), 137.6 (s), 137.1 (s), 132.4 (s), 130.0 (s), 128.4 (s), 128.0 (s), 127.9 (s), 126.7 (s), 115.6 (t, *J* = 249.0 Hz), 62.6 (s), 44.8 (t, *J* = 5.0 Hz), 40.2 (t, *J* = 23.0 Hz), 13.6 (s).

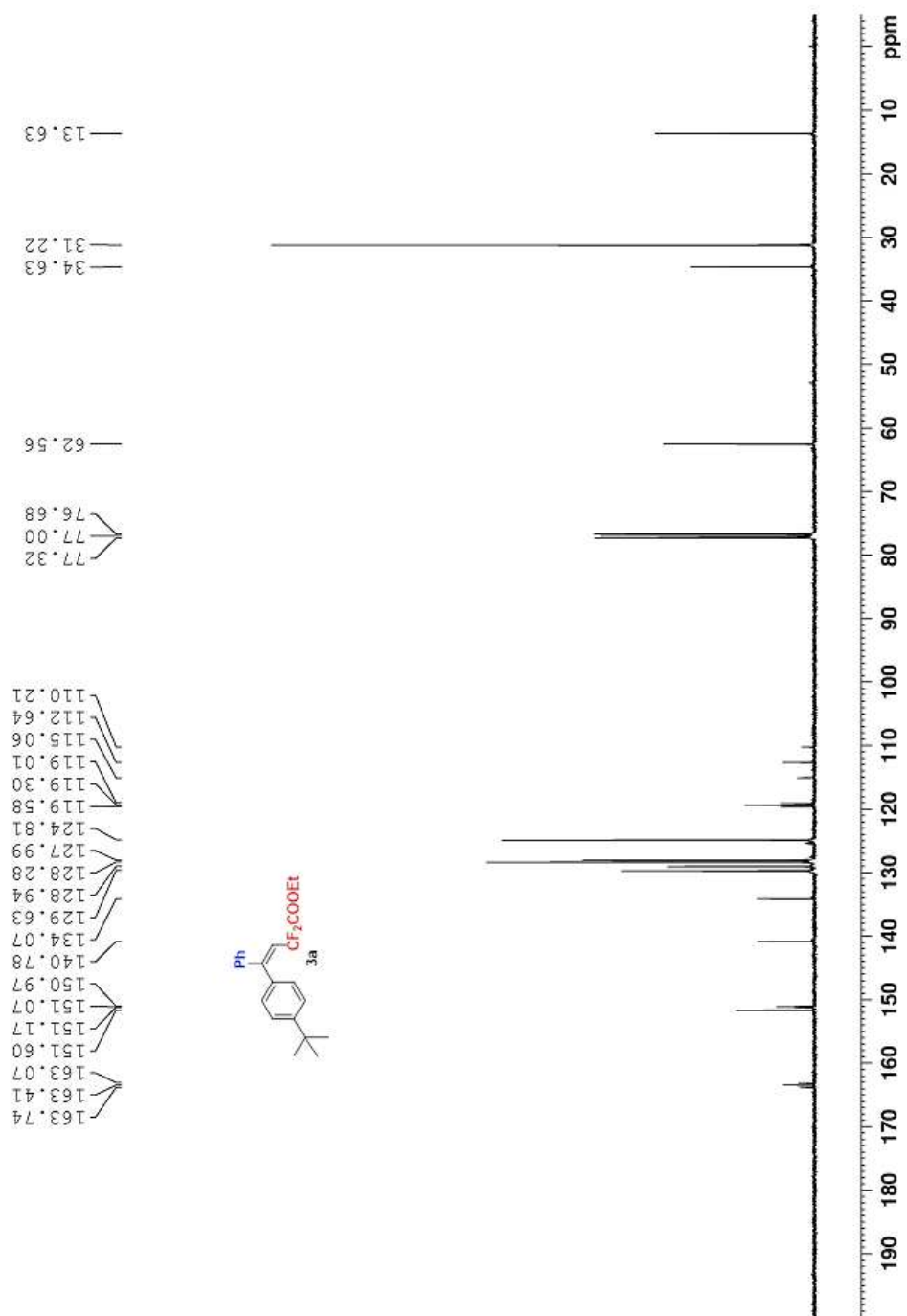
¹⁹F NMR (376 MHz, CDCl₃) δ ppm **major**: -91.0 (d, *J* = 11.3 Hz, 2F). **minor**: -103.4 (t, *J* = 15.0 Hz, 2F).

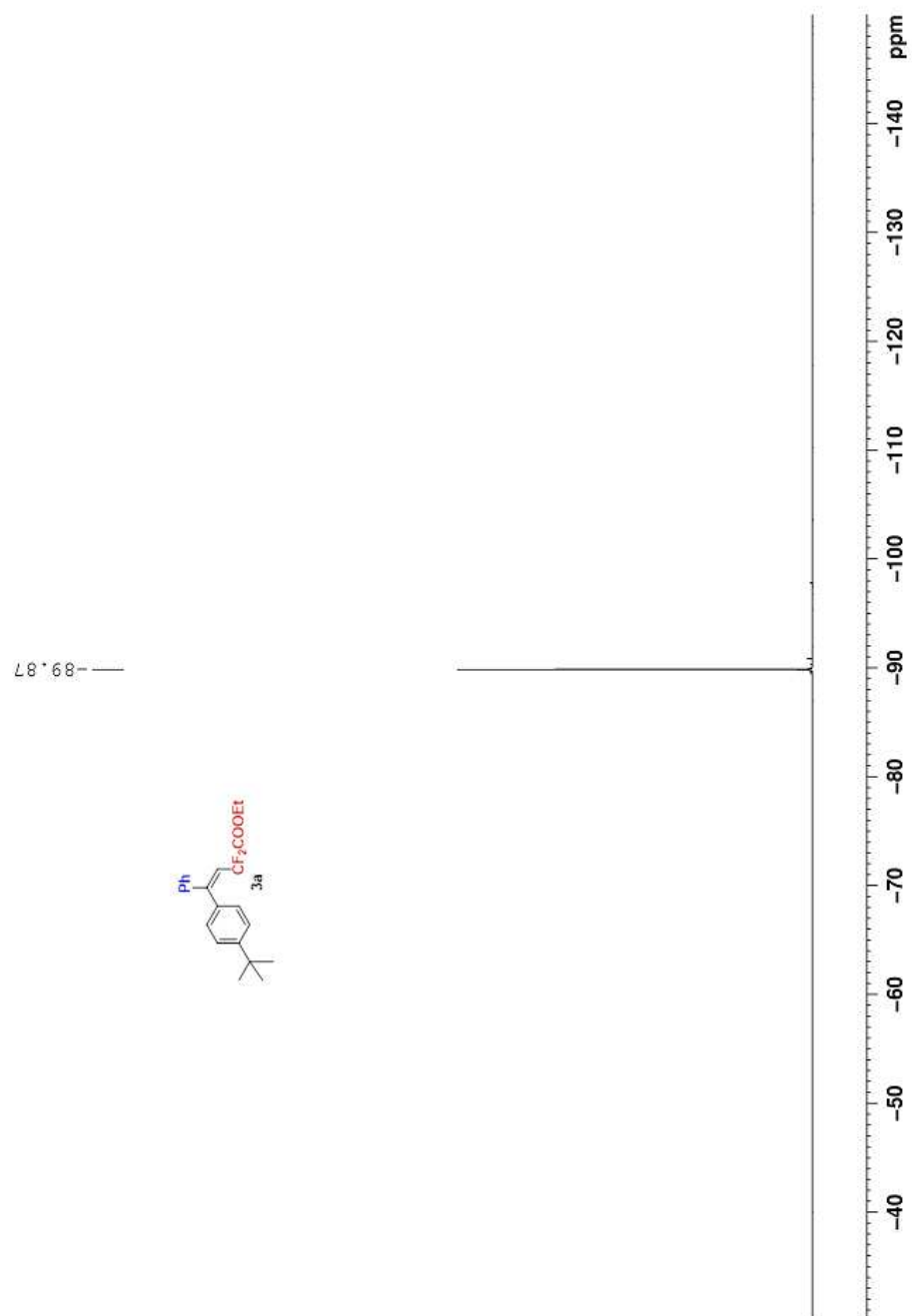
IR (neat, cm⁻¹): 3304, 2985, 1769, 1660, 1278, 1068, 739.

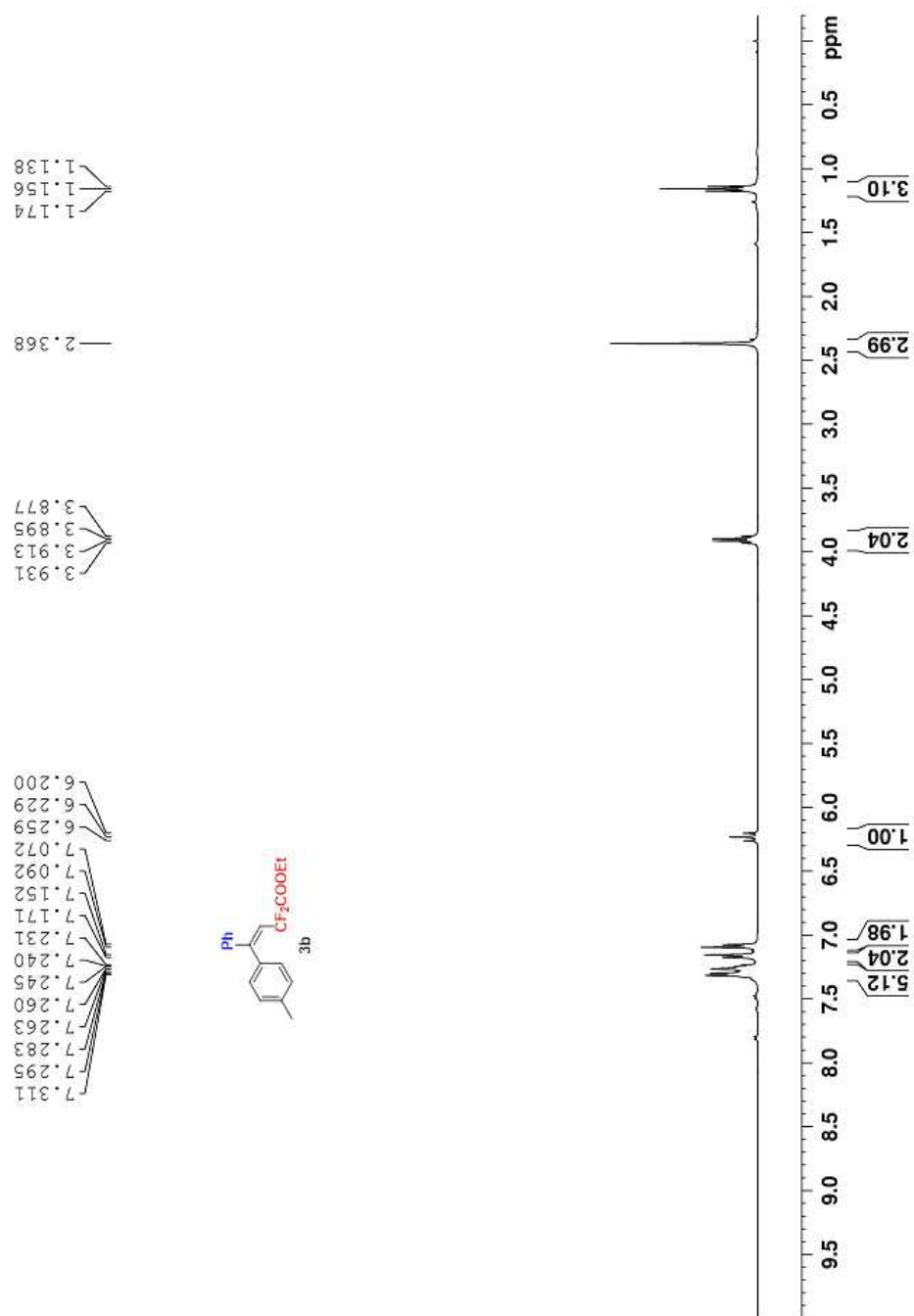
HRMS (ESI) Calcd for C₁₈H₁₆F₂O₂/C₁₈H₁₈F₂O₂: [M] + Na = 325.1011/327.1167. Found: 325.1016/327.1171.

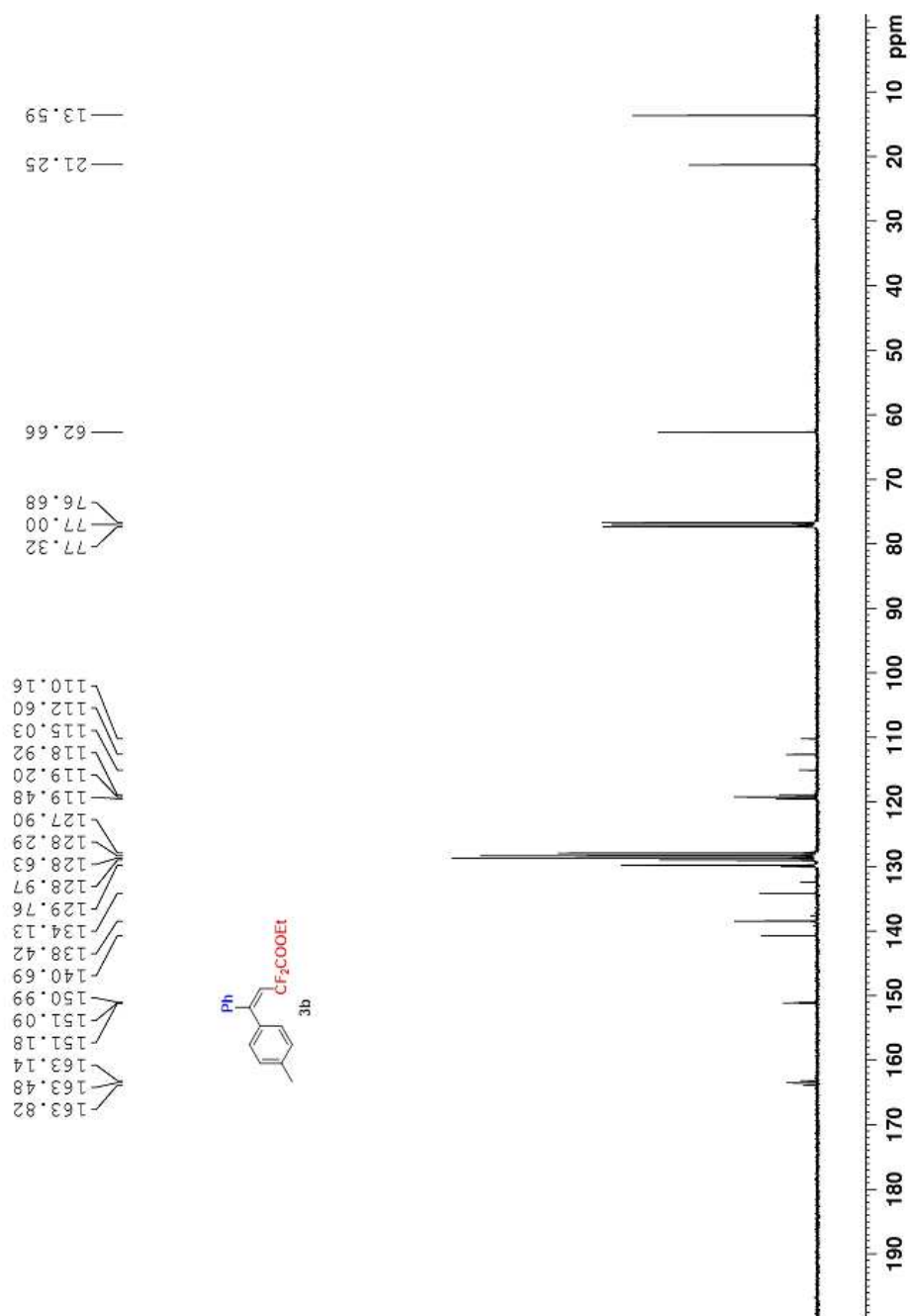
**4, ^1H NMR, ^{13}C NMR, ^{19}F NMR Spectra for Substrates 3a-v, 4a-m,
5, 6, 8, 9 and 1D-NOESY for Product 3u**

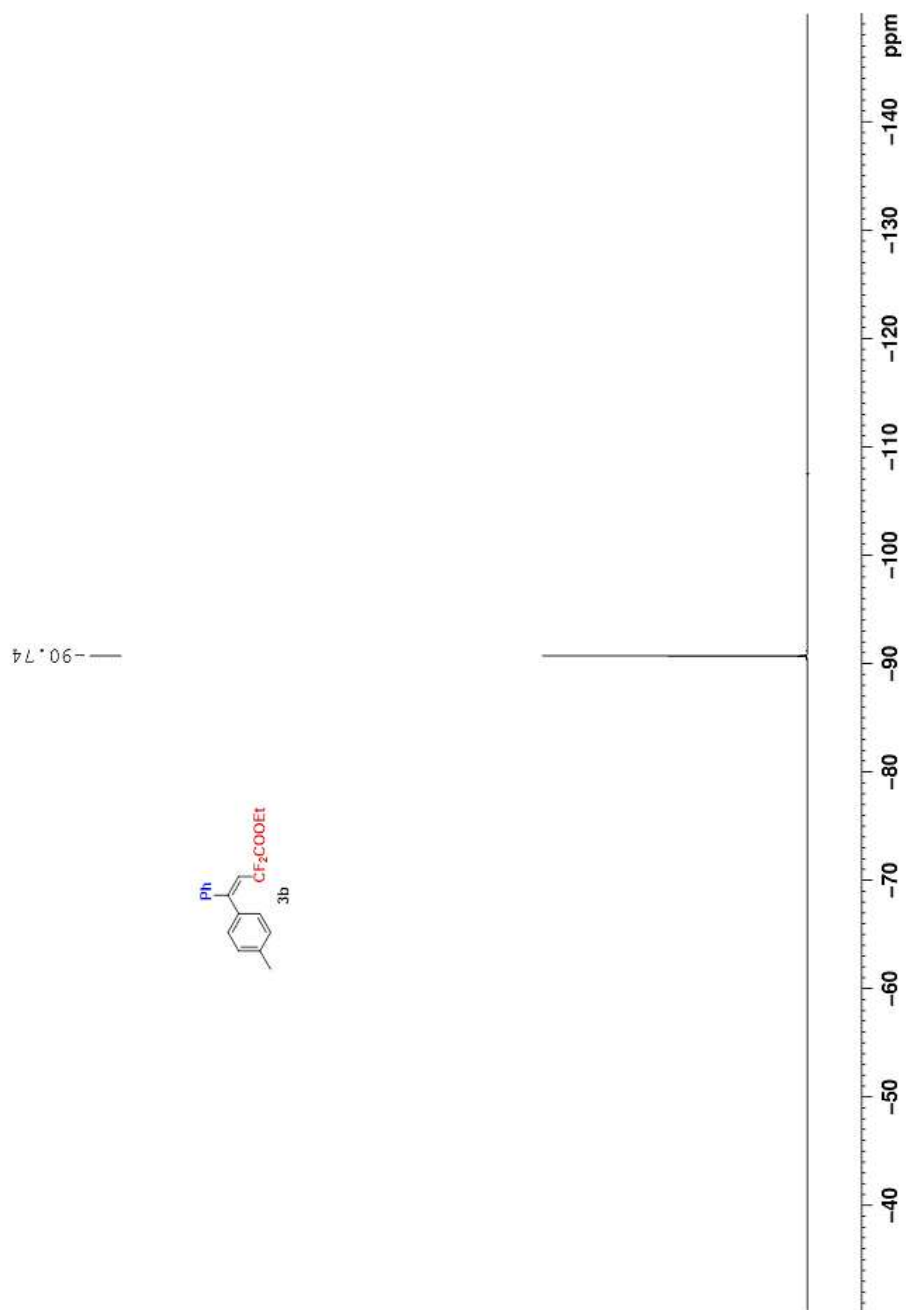


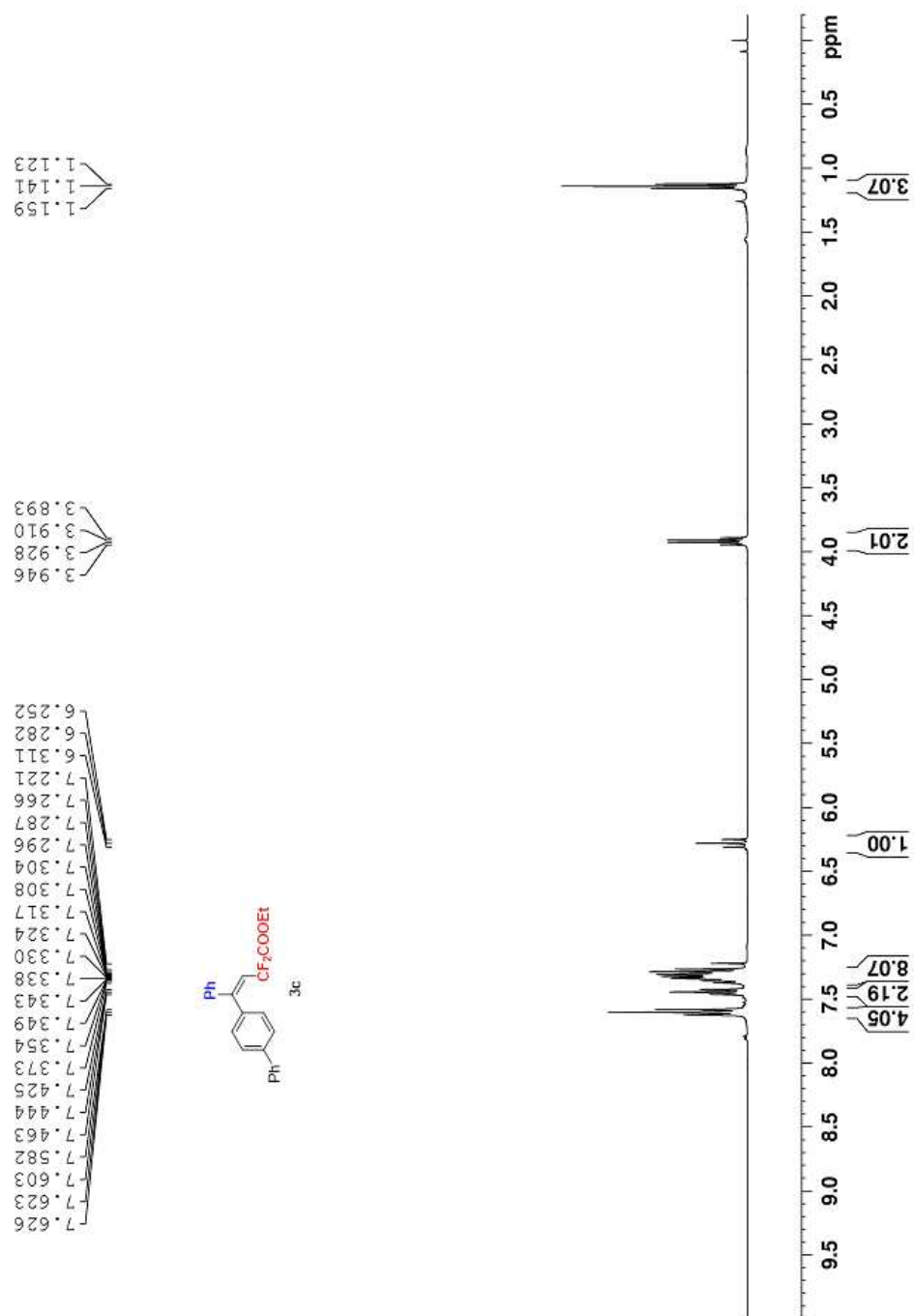


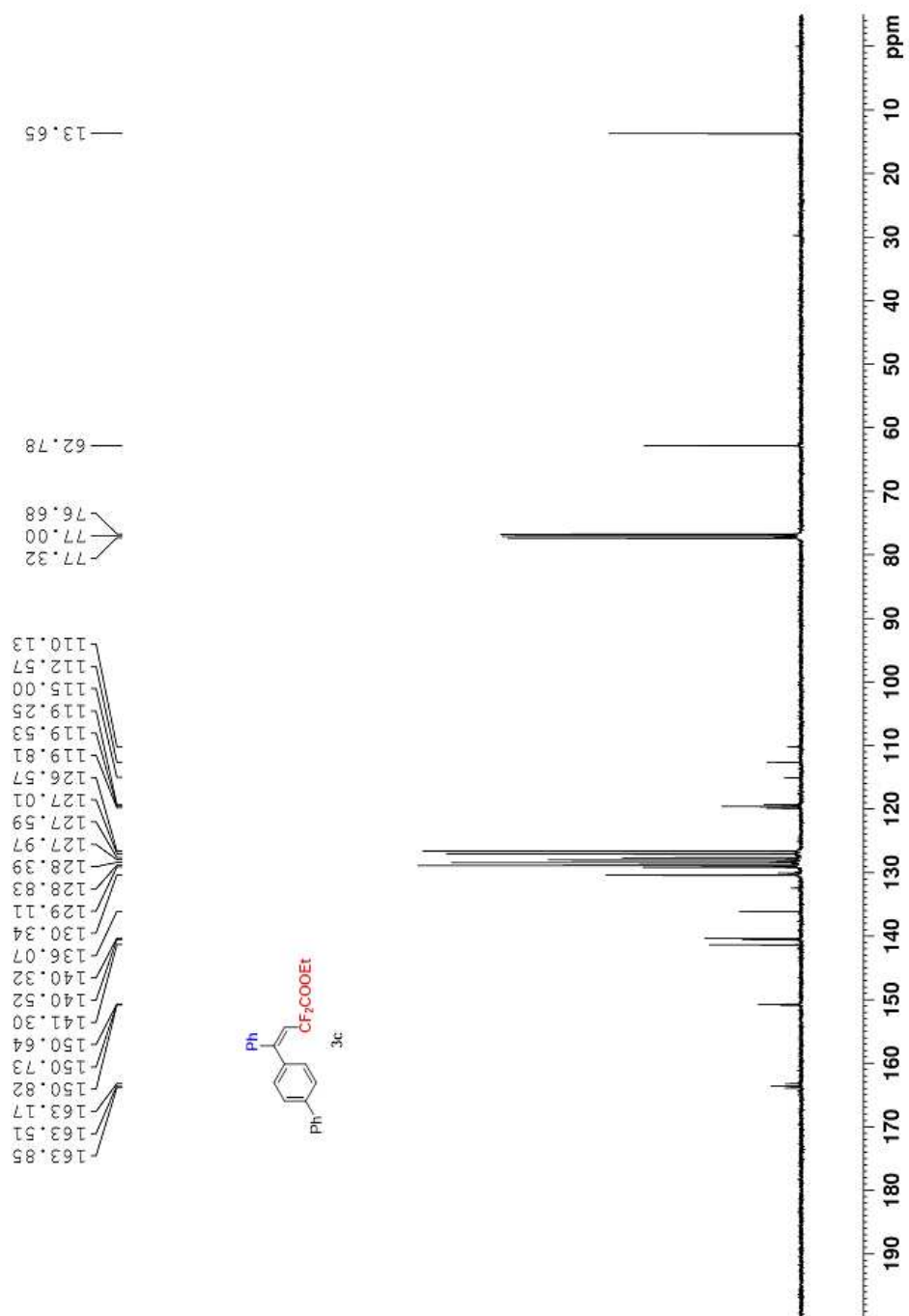




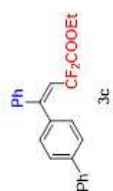


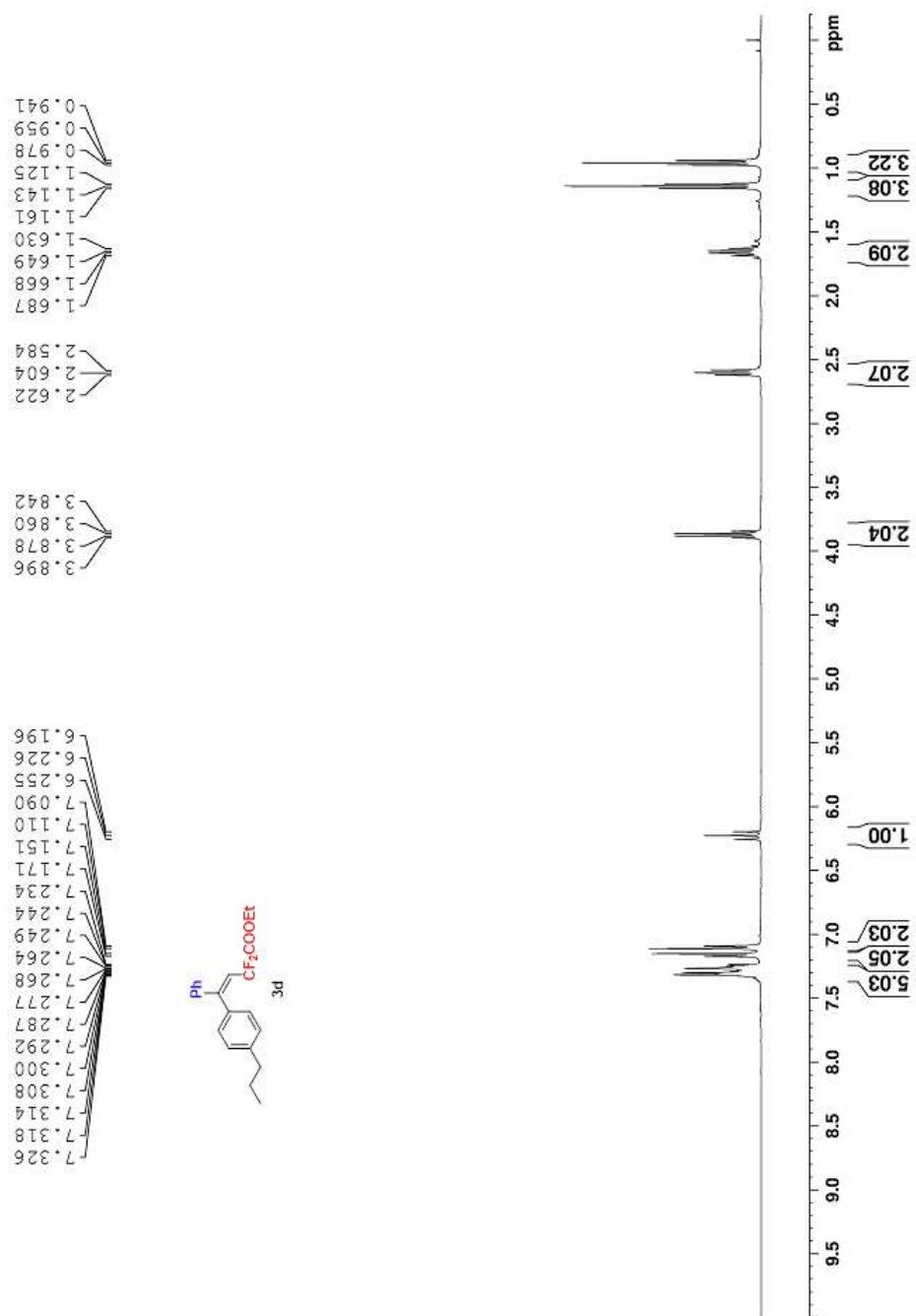


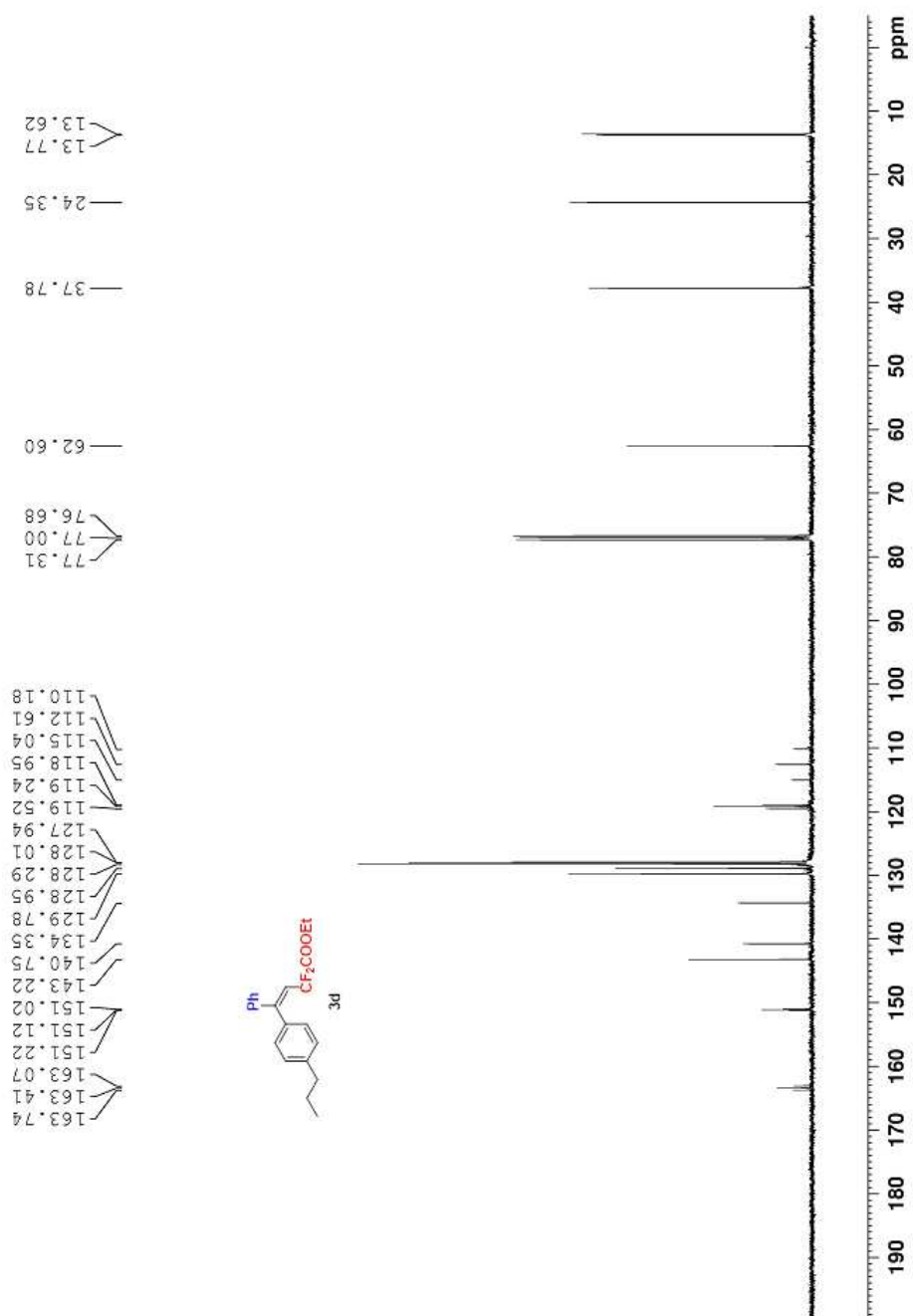


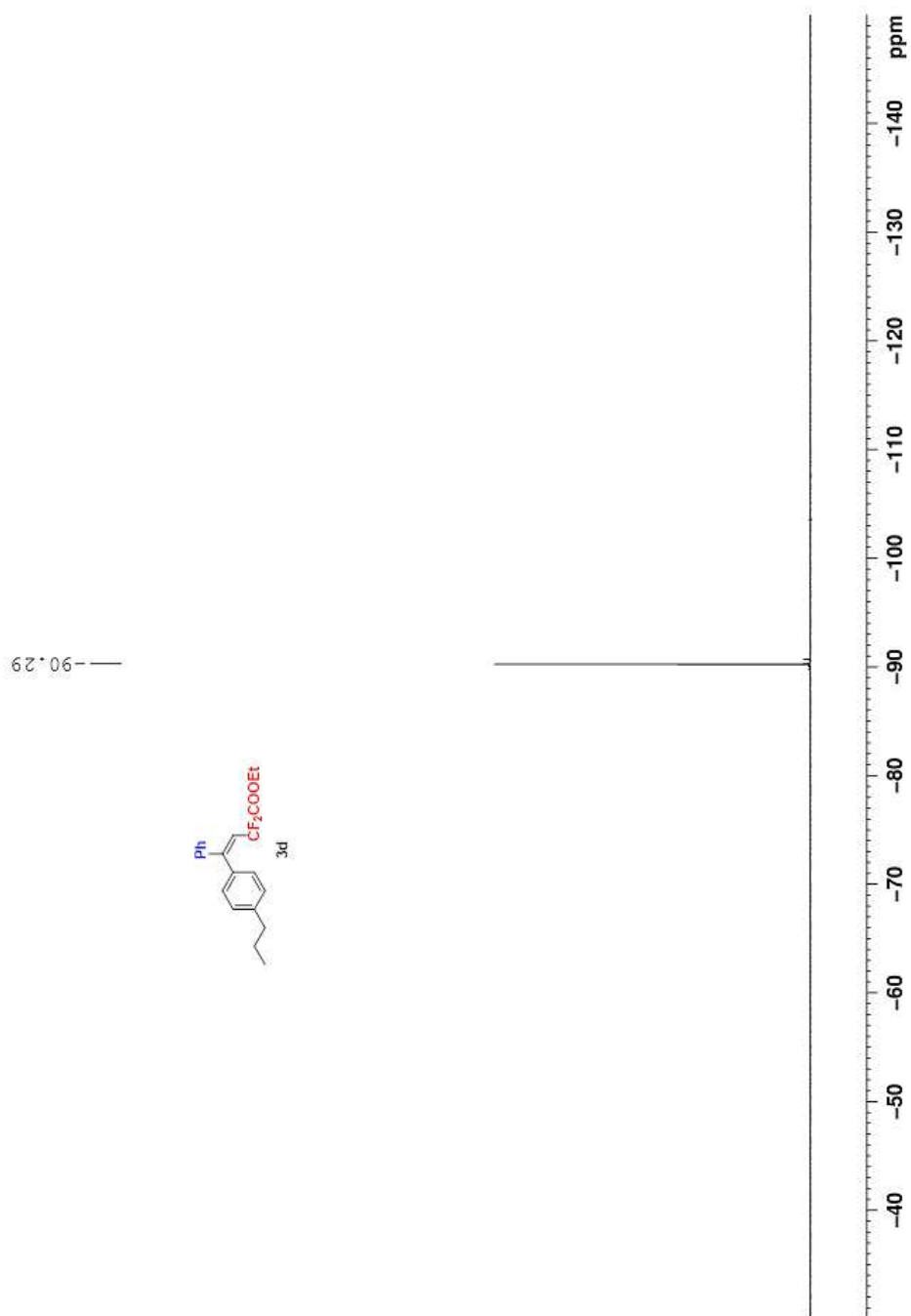


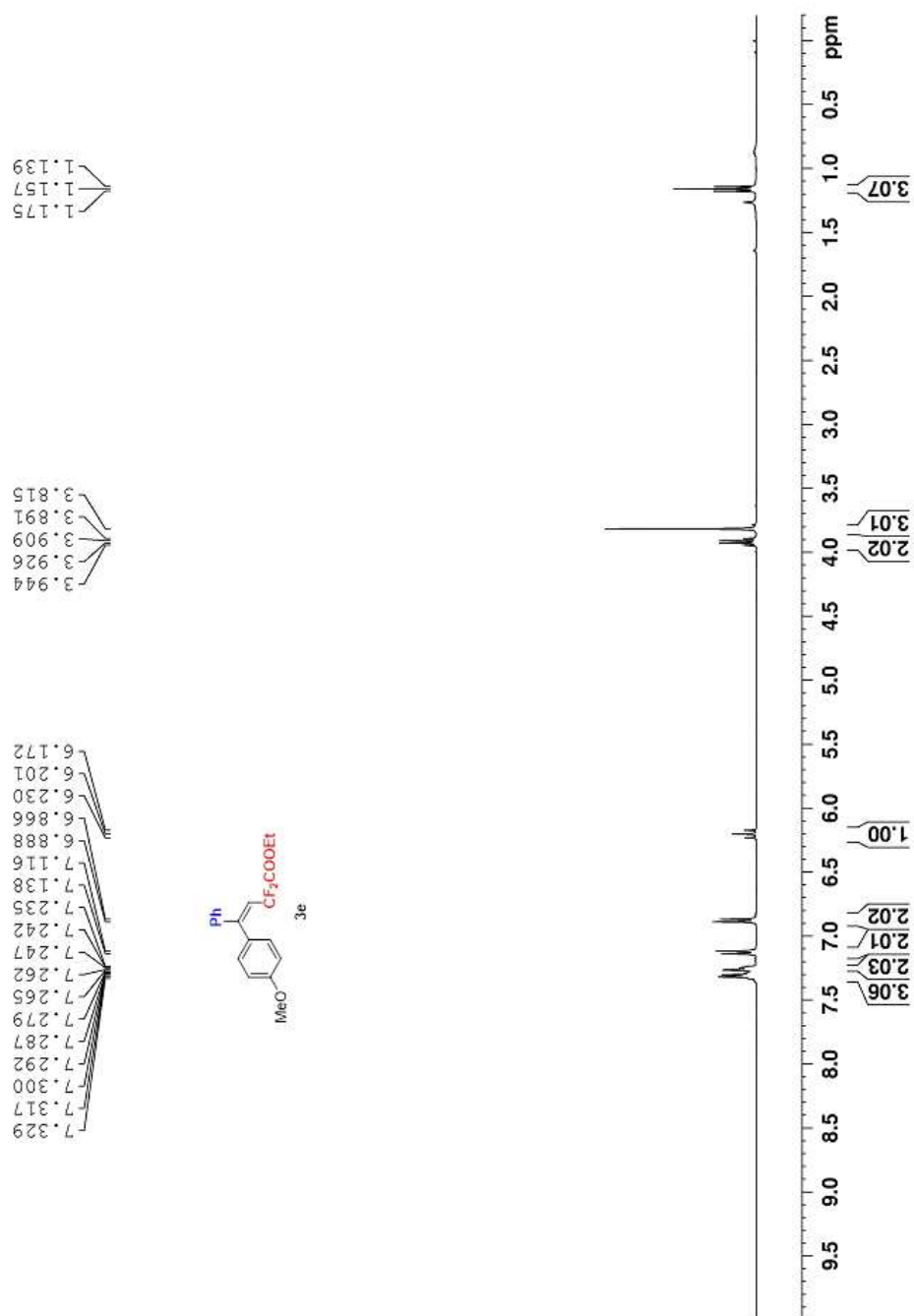
08'06—

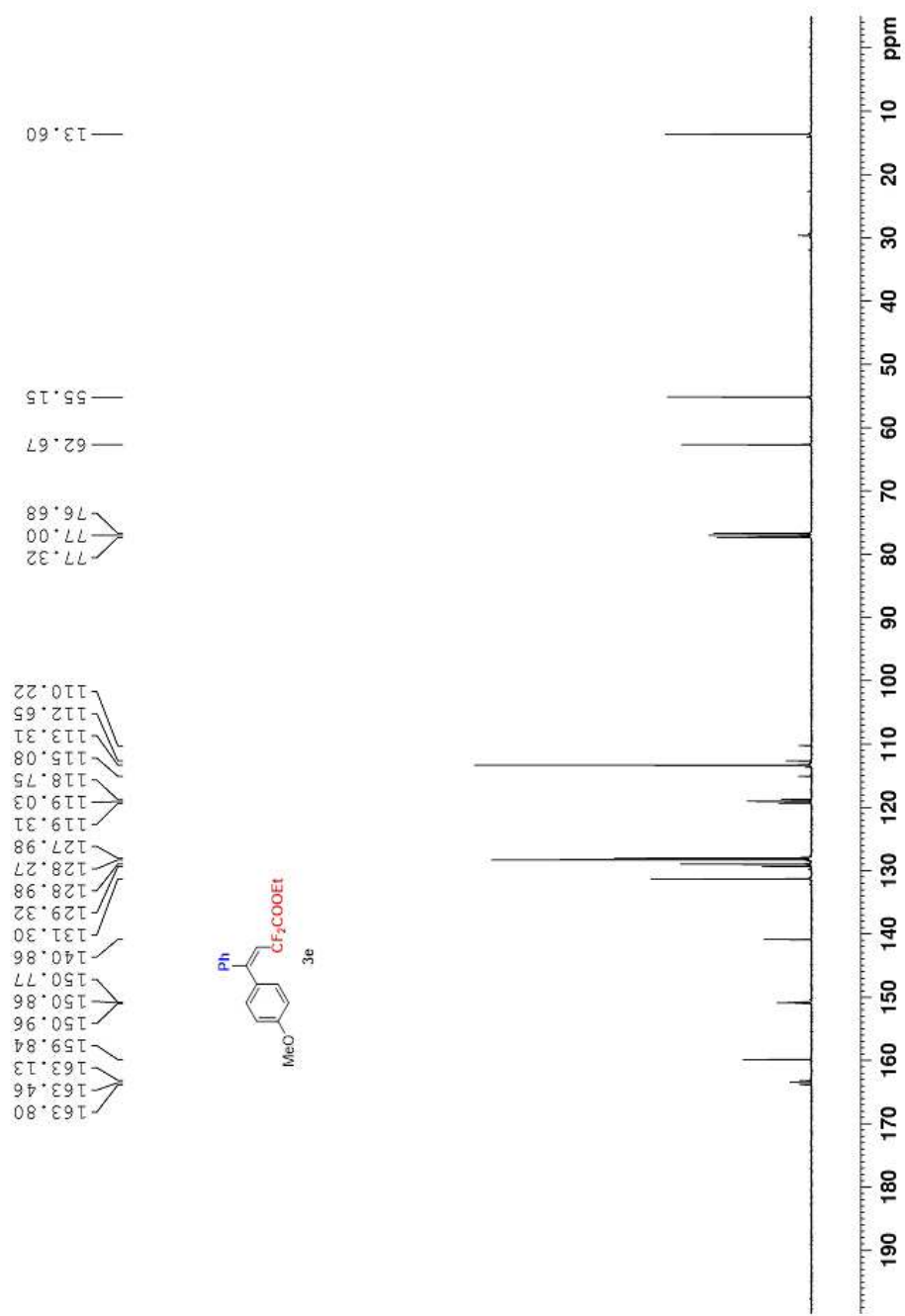


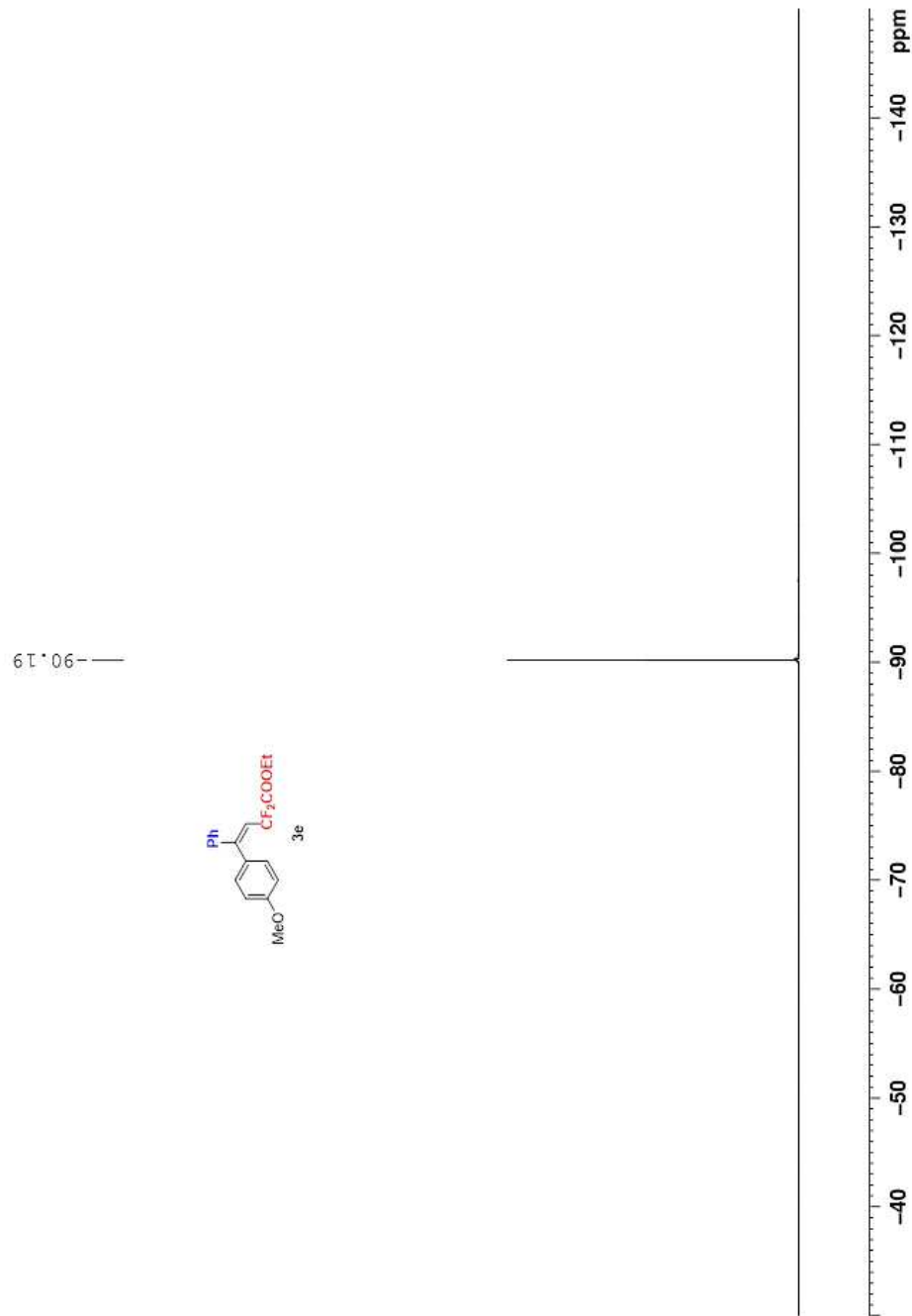


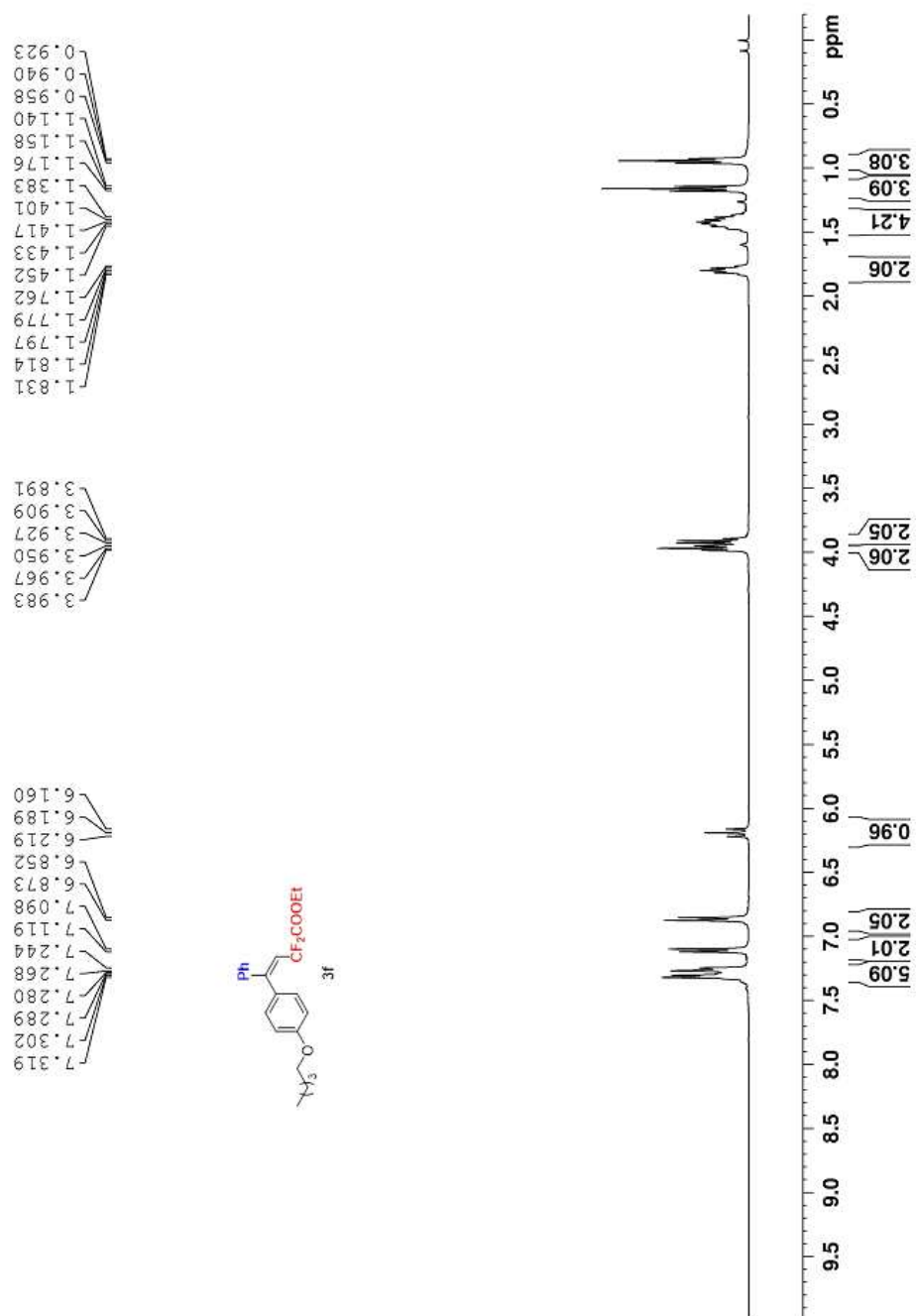


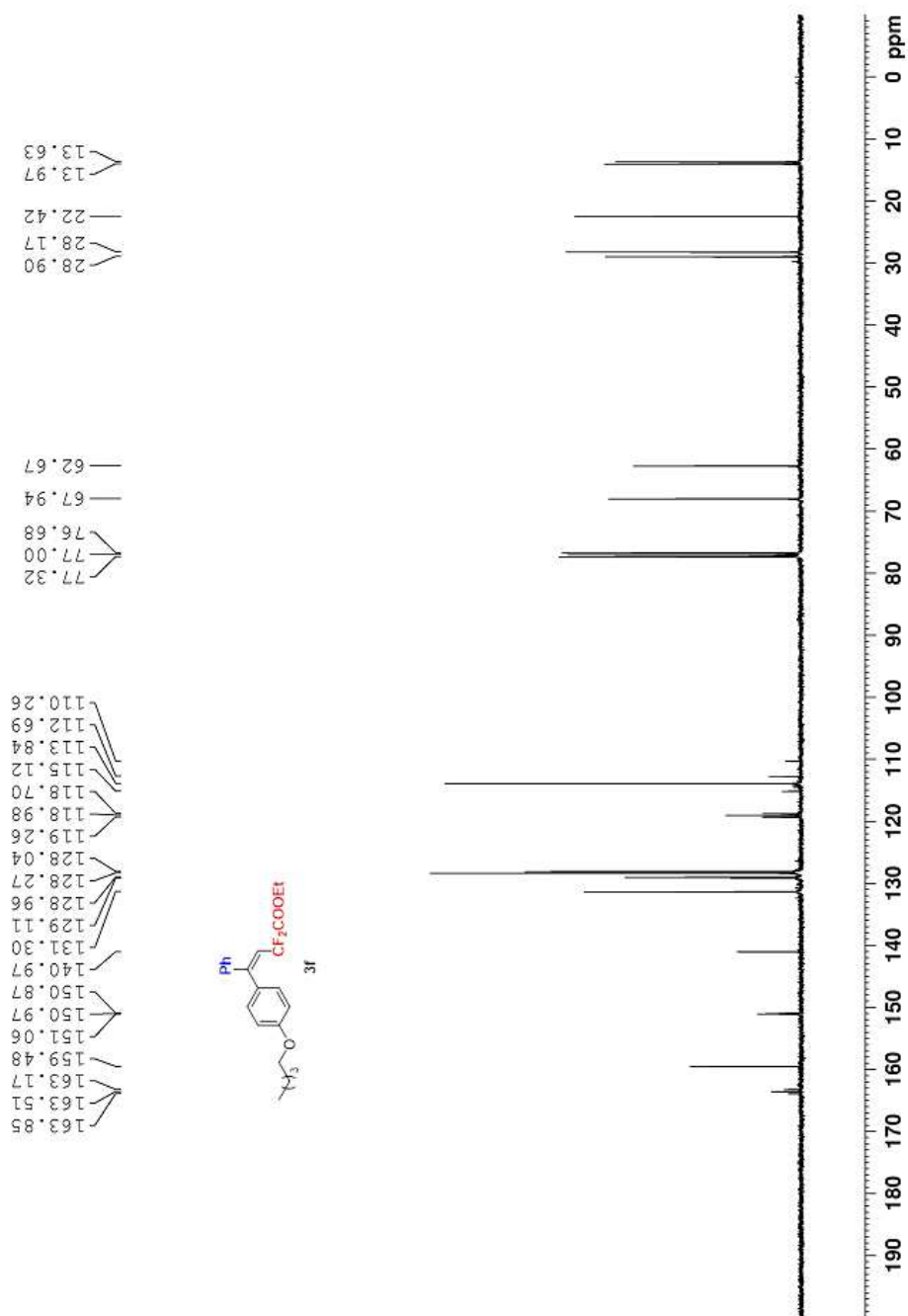


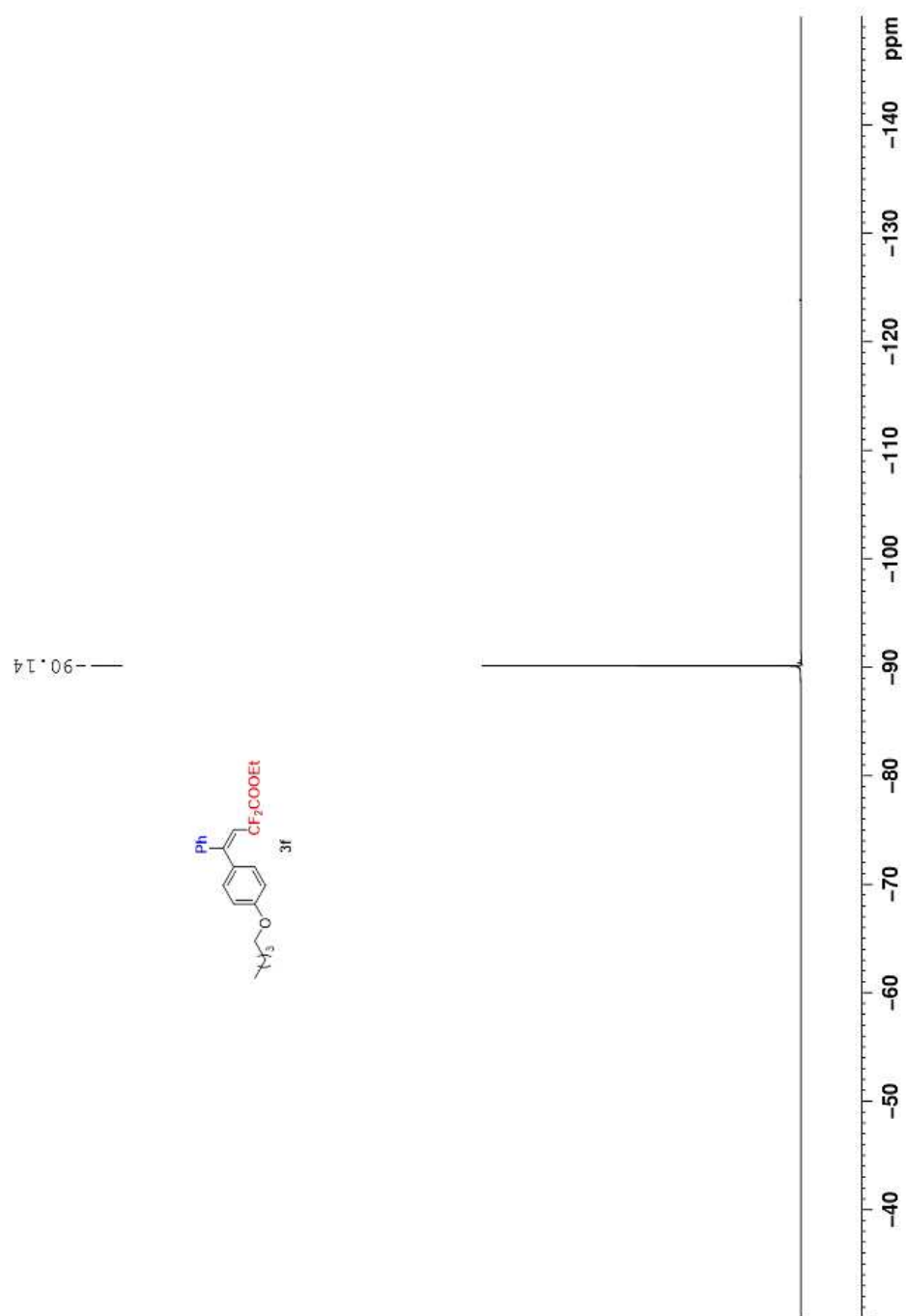


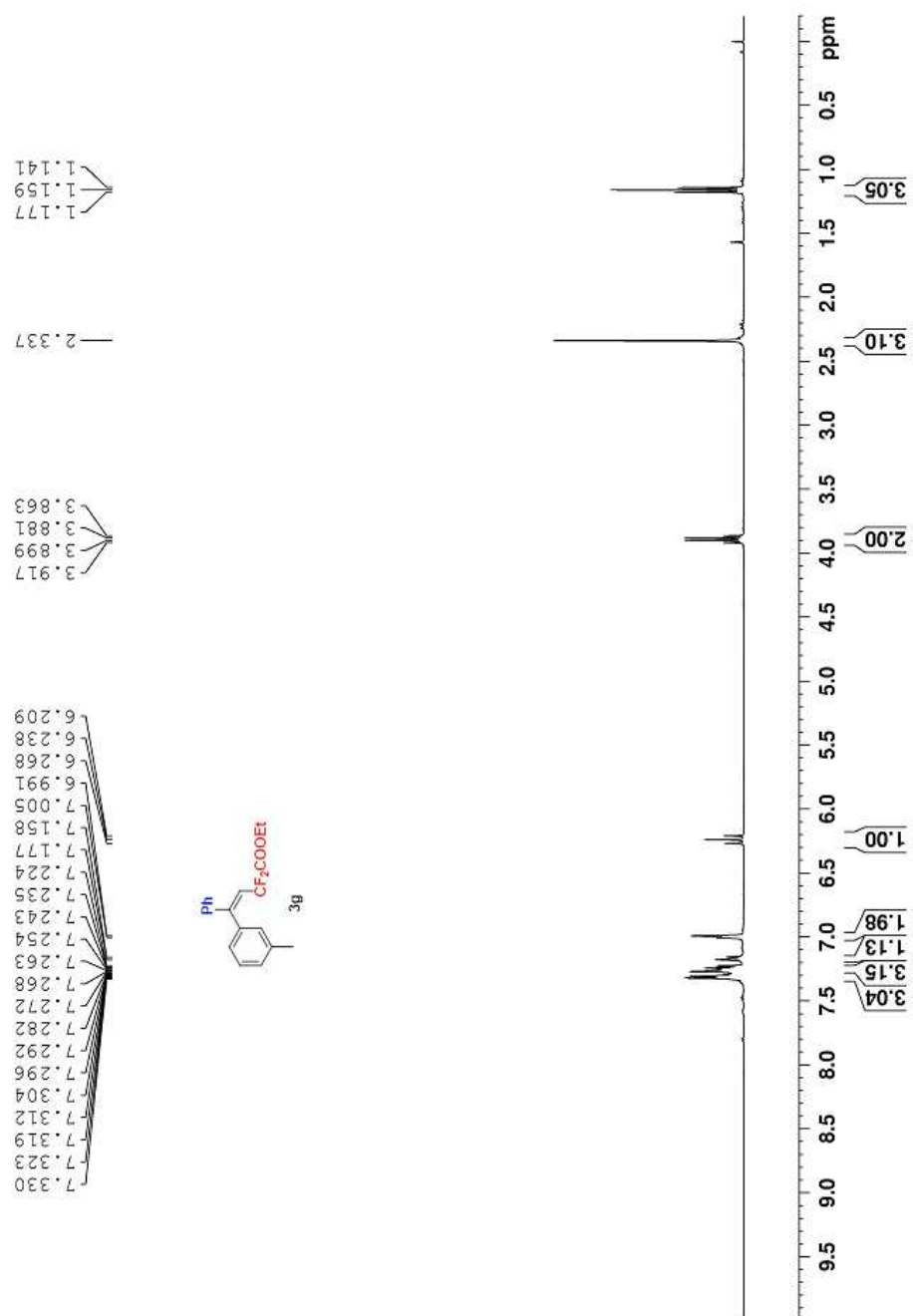


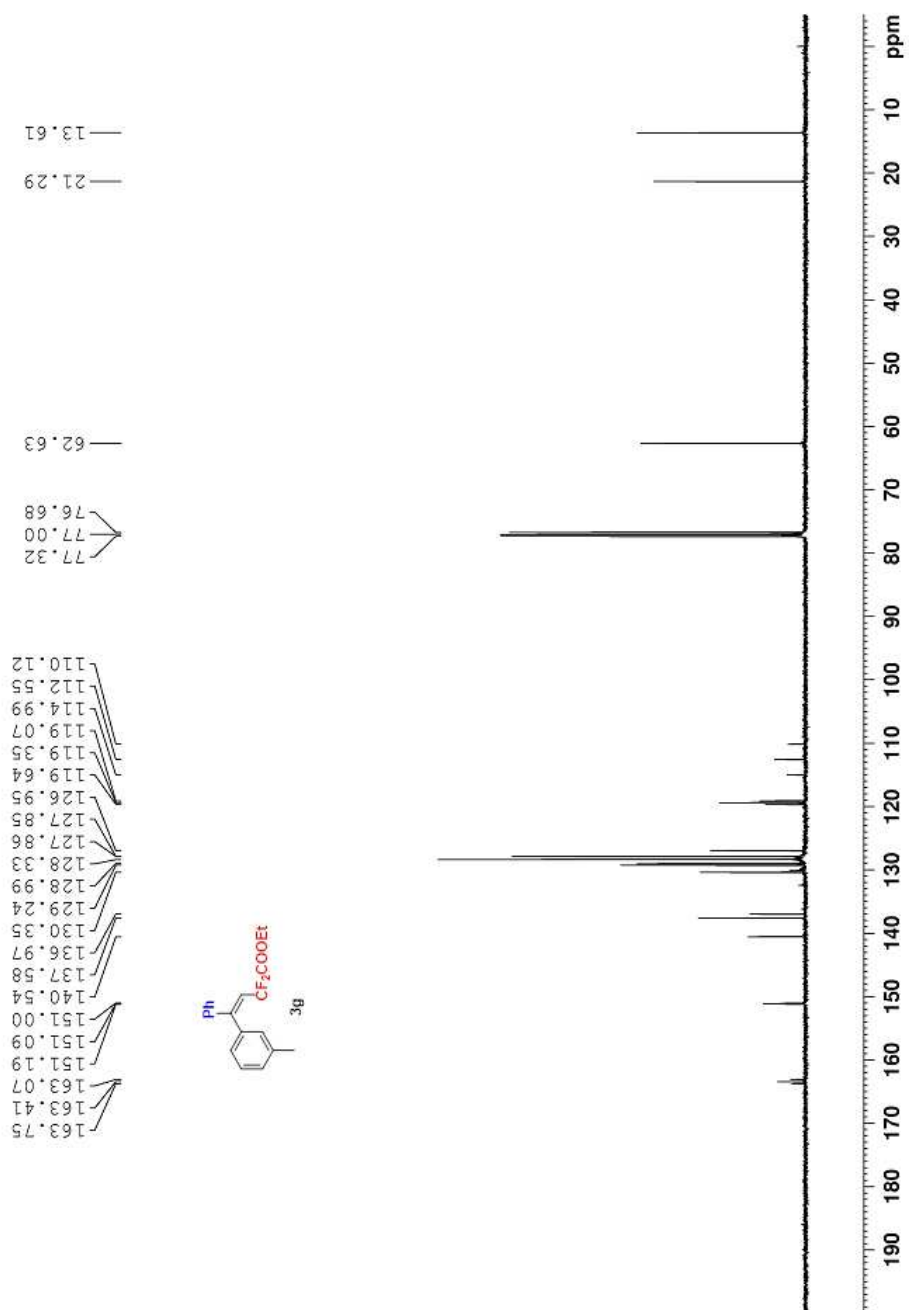


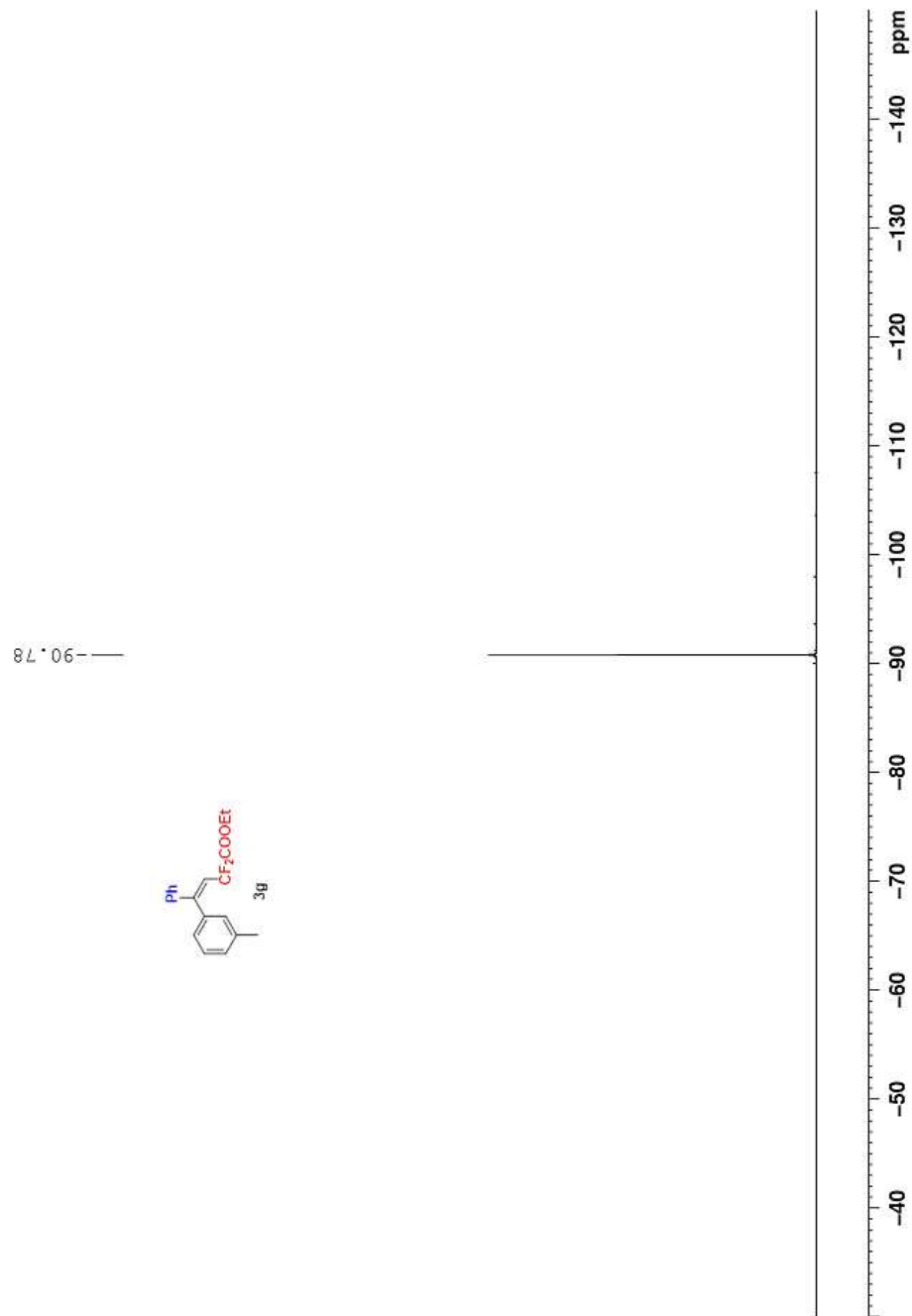


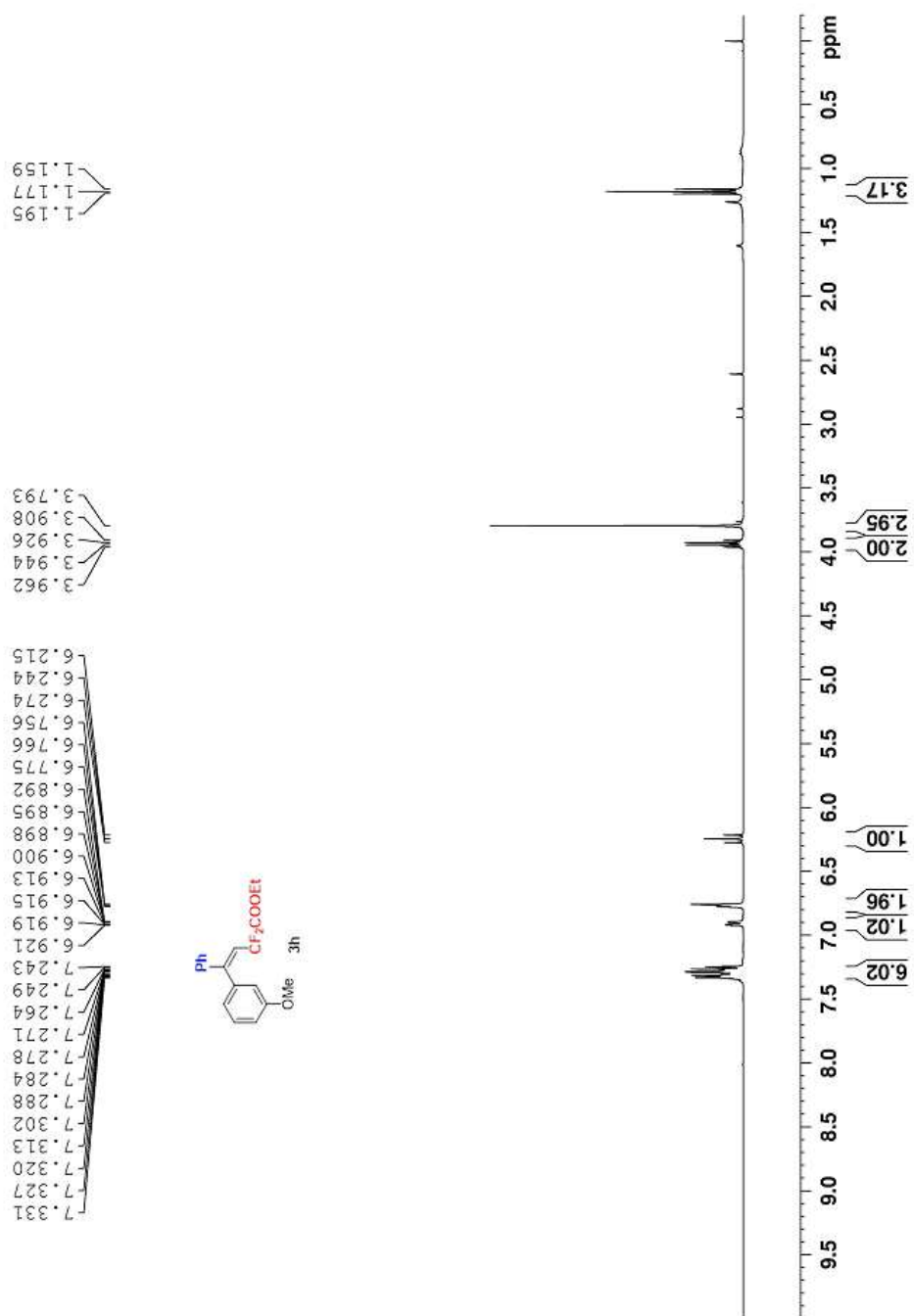


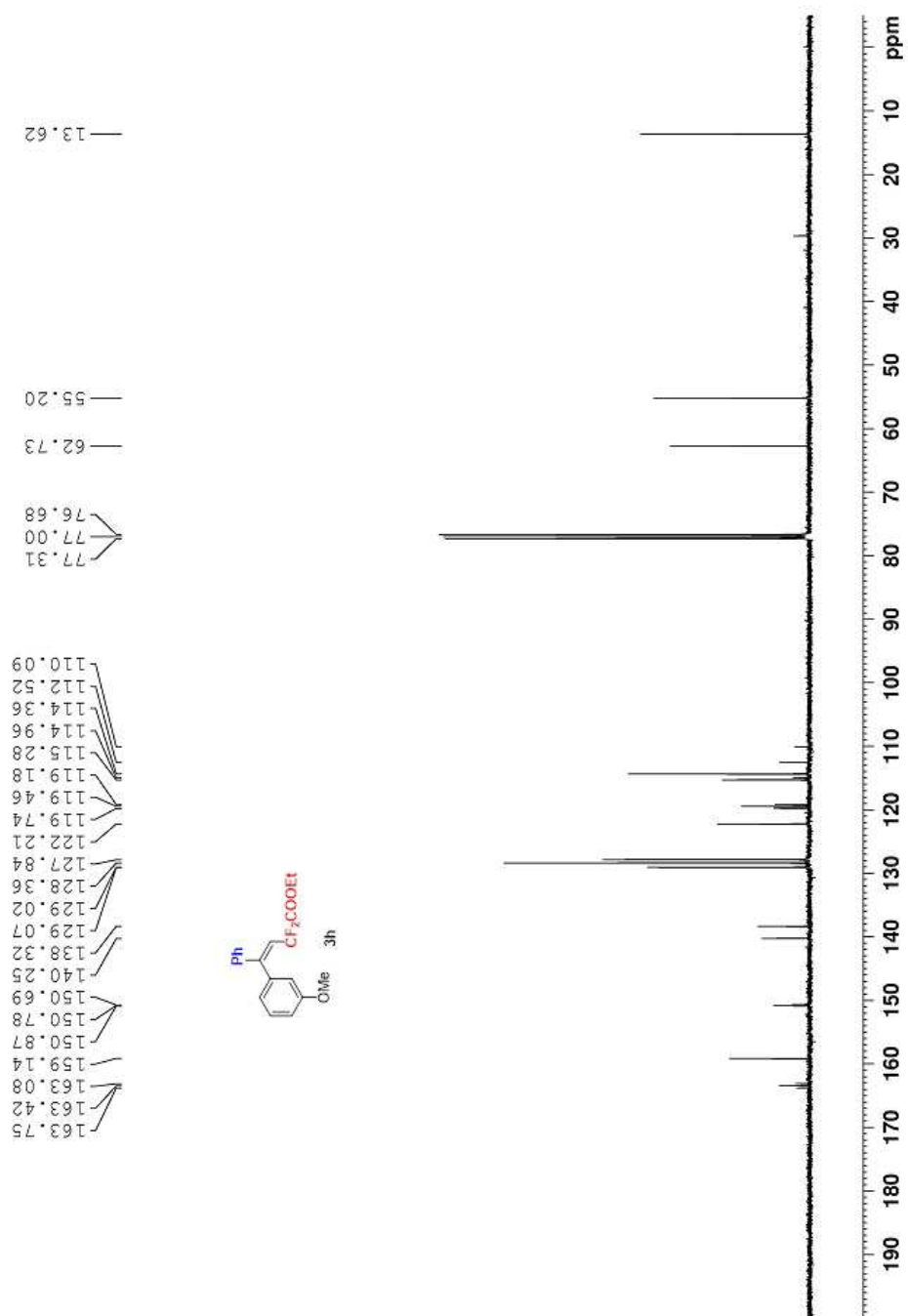


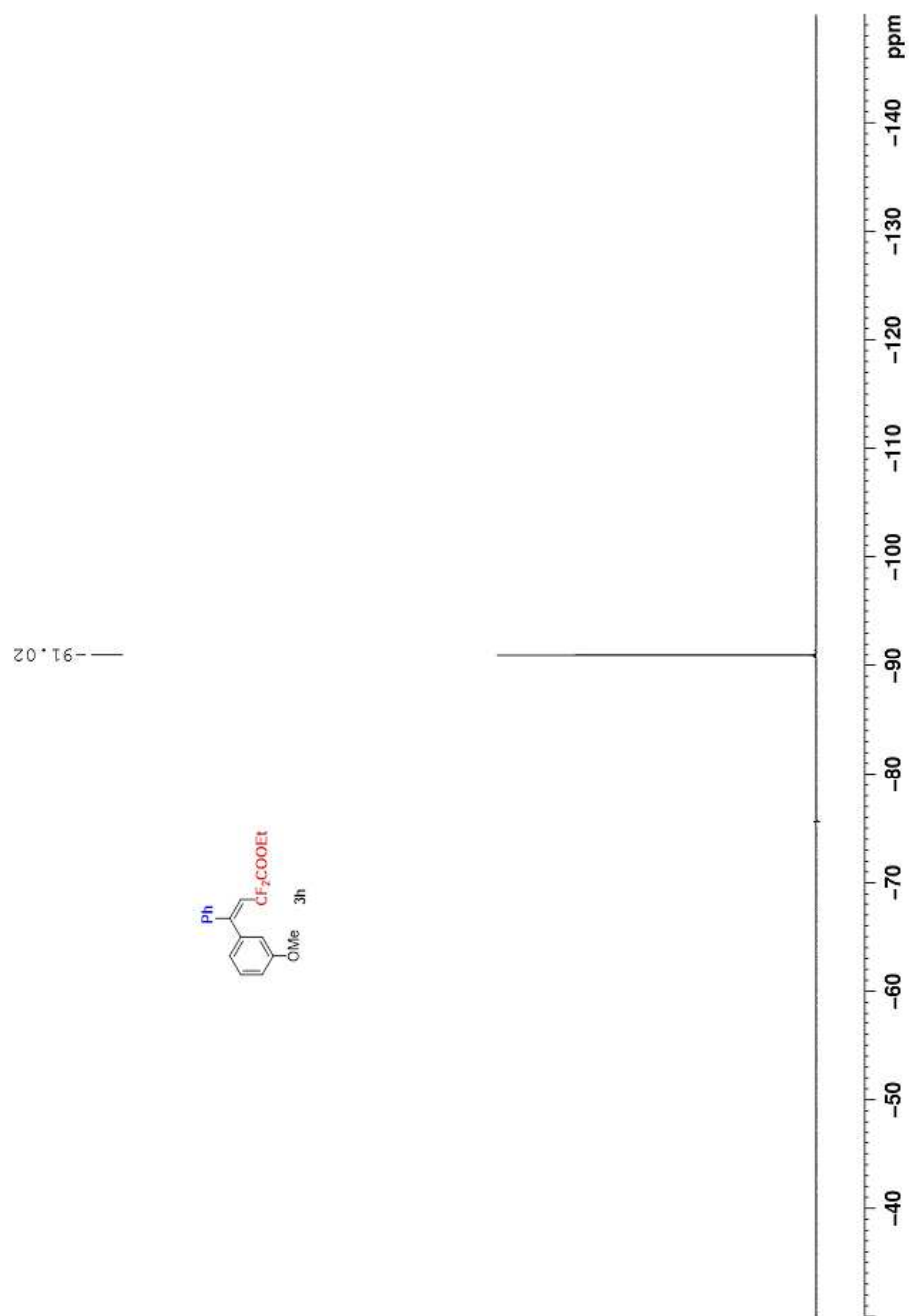


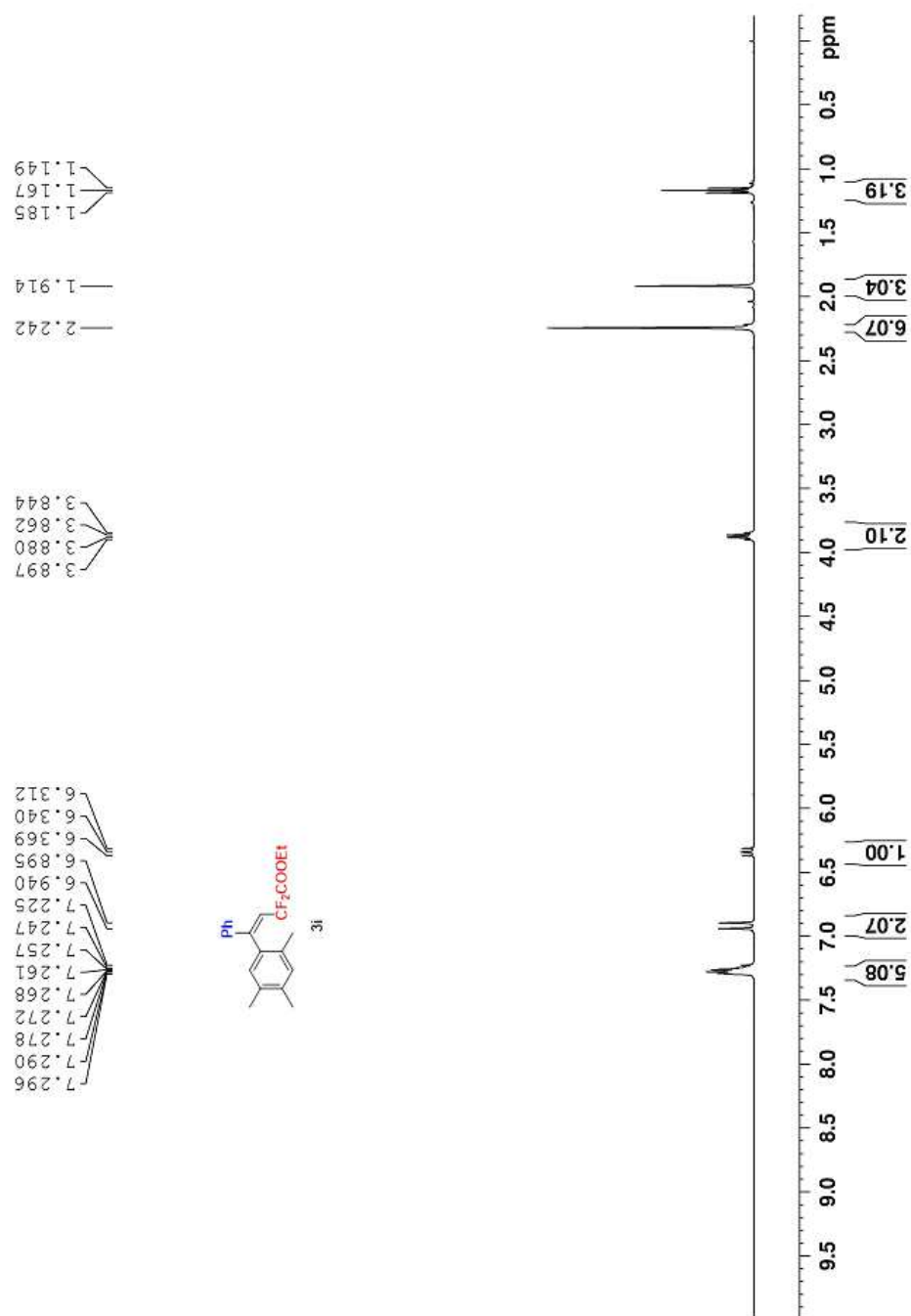


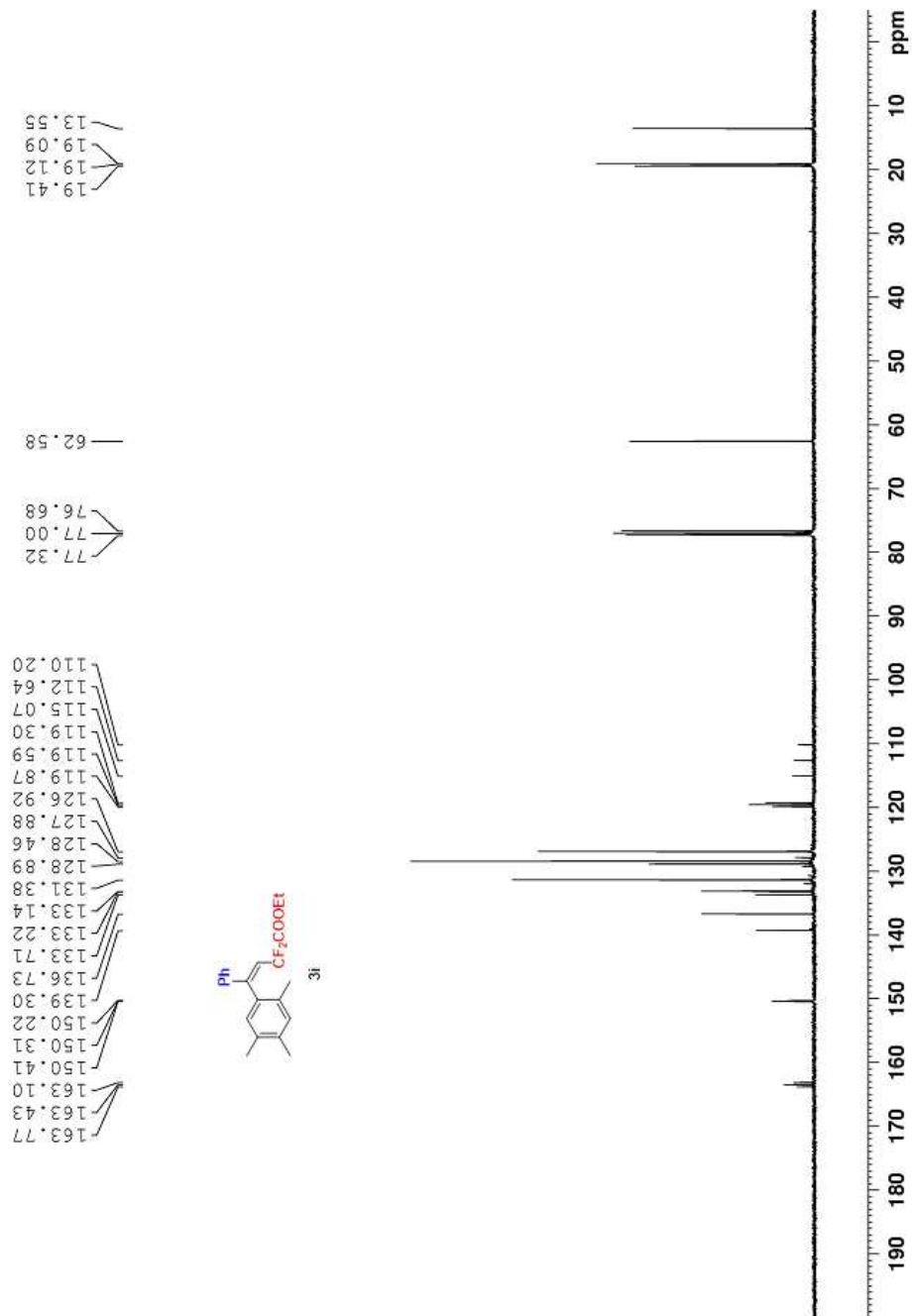


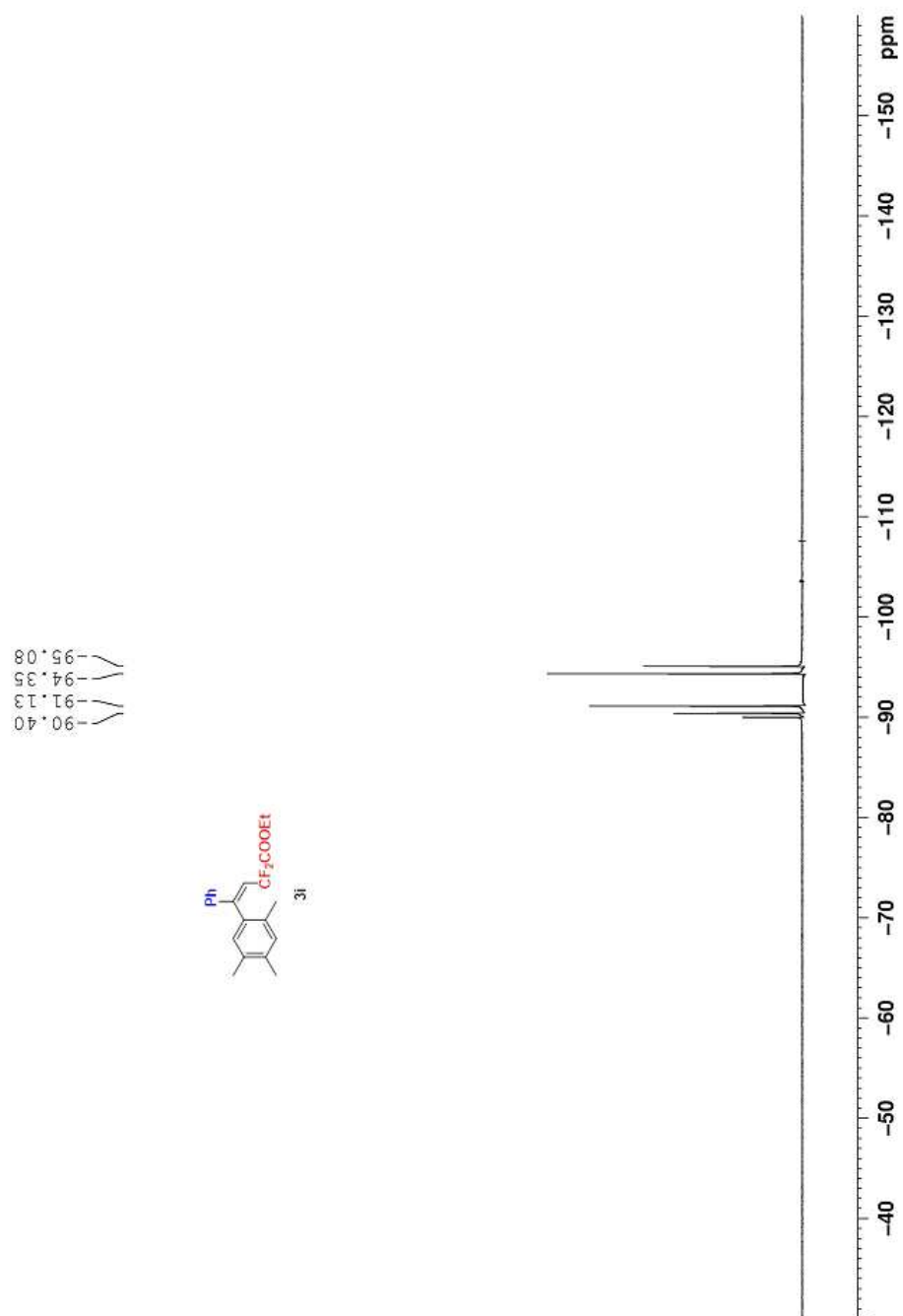


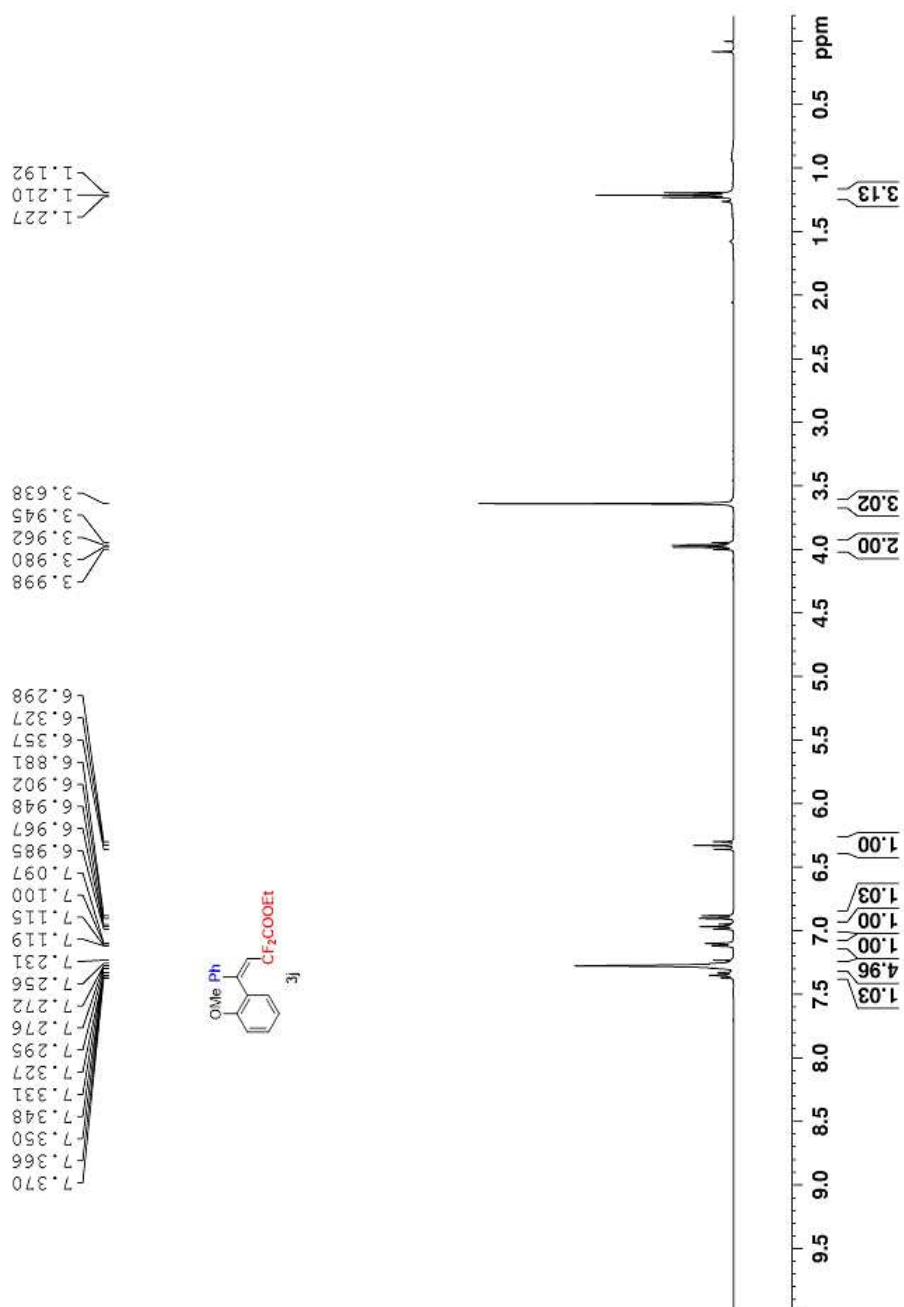


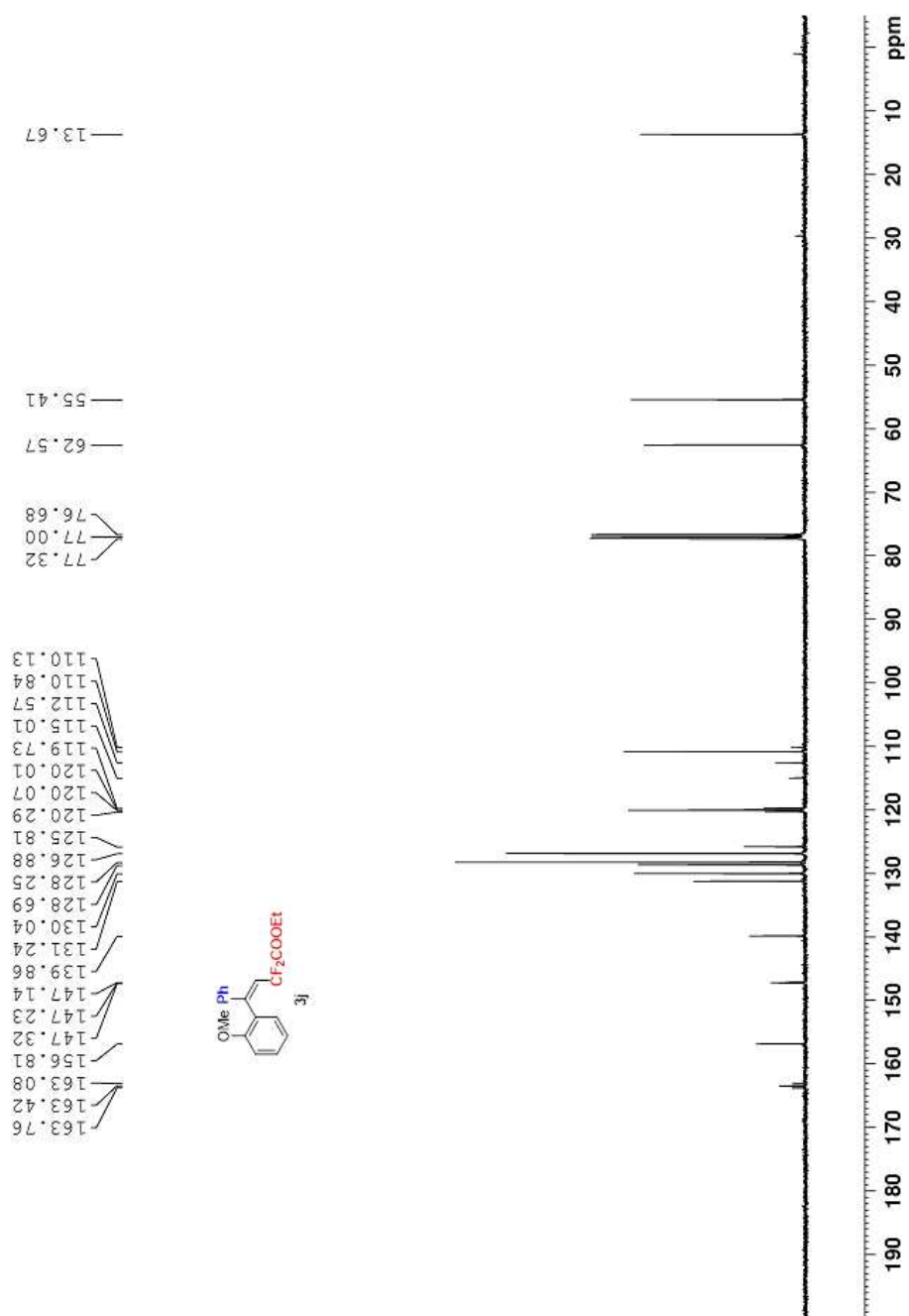


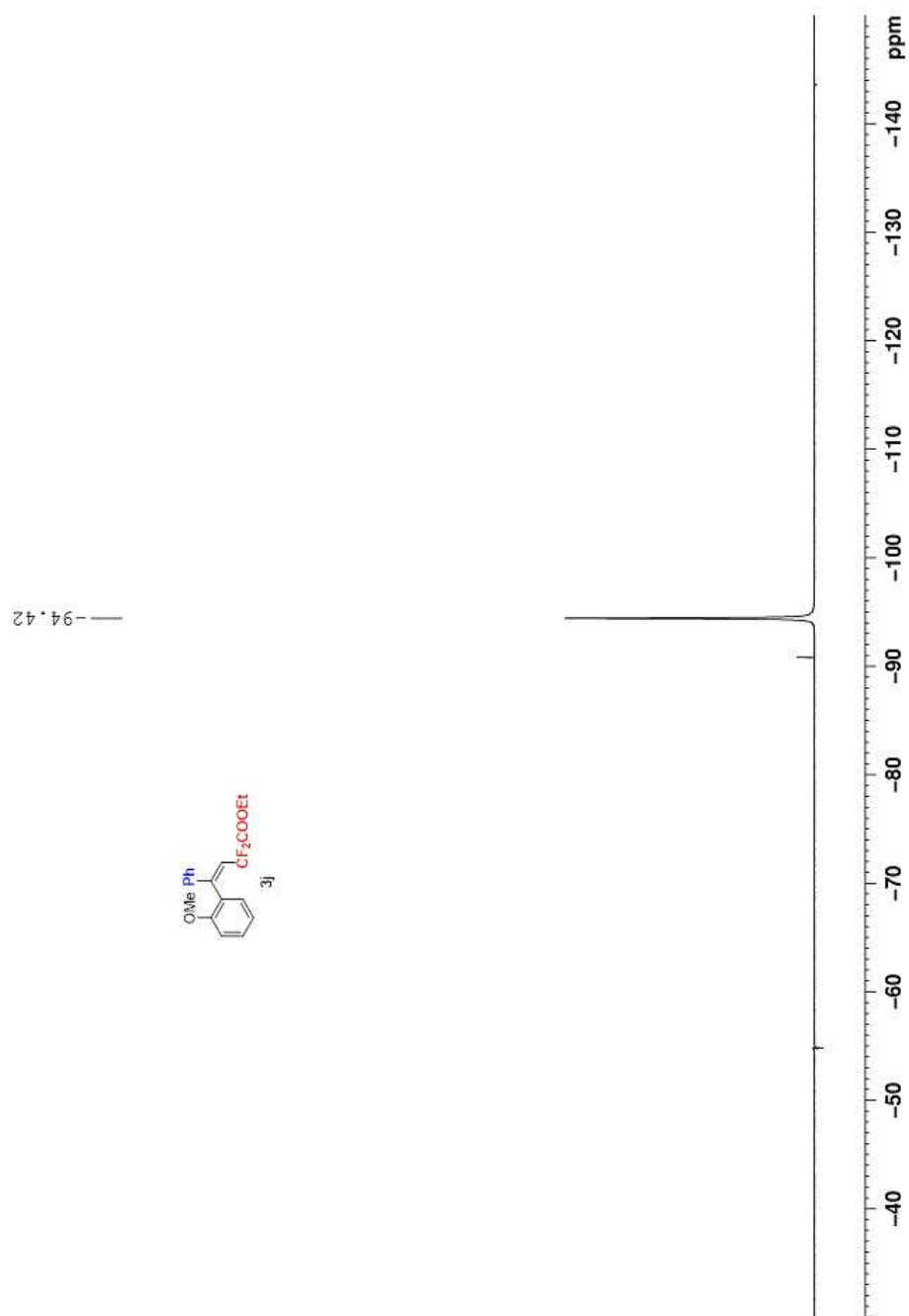


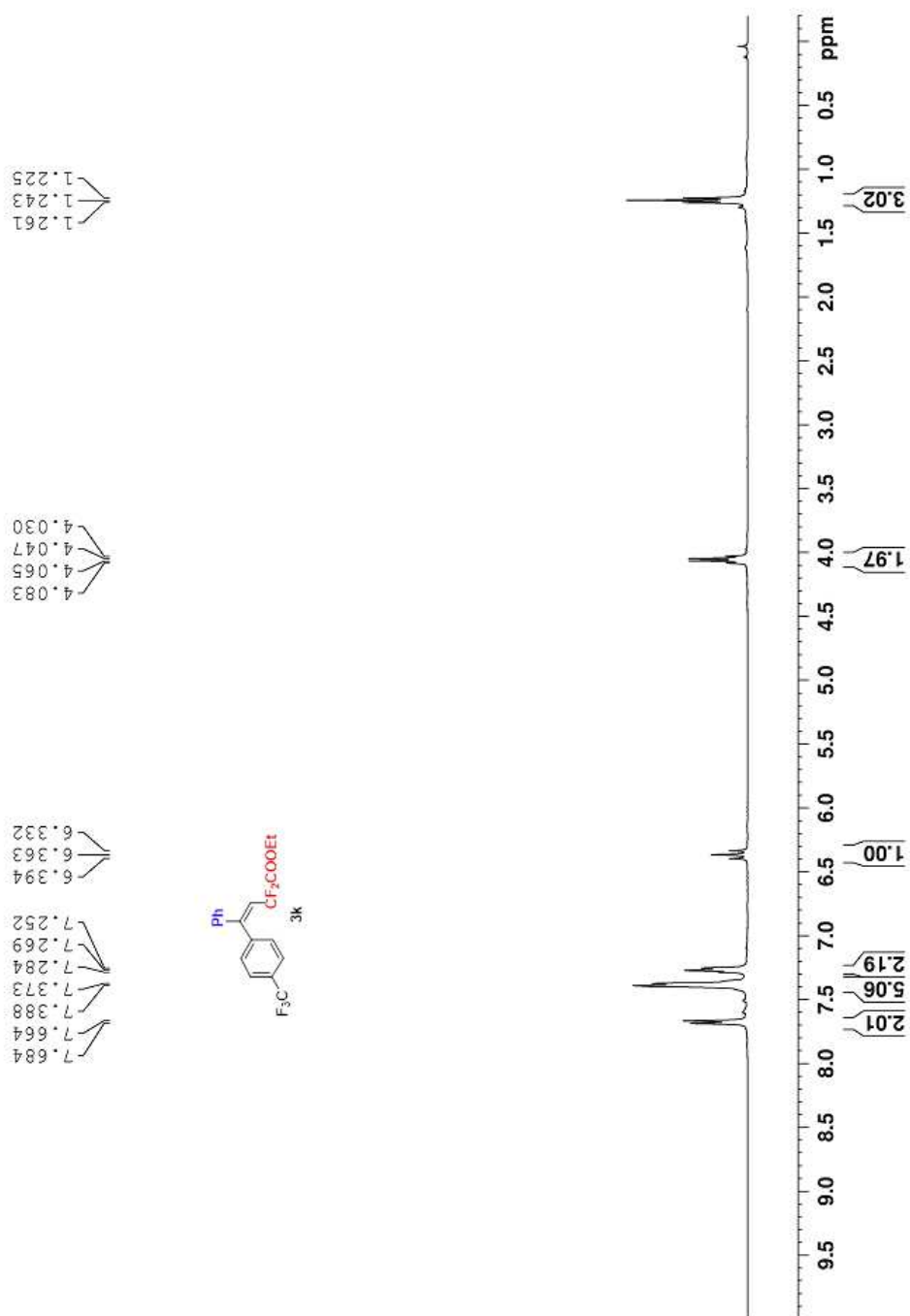


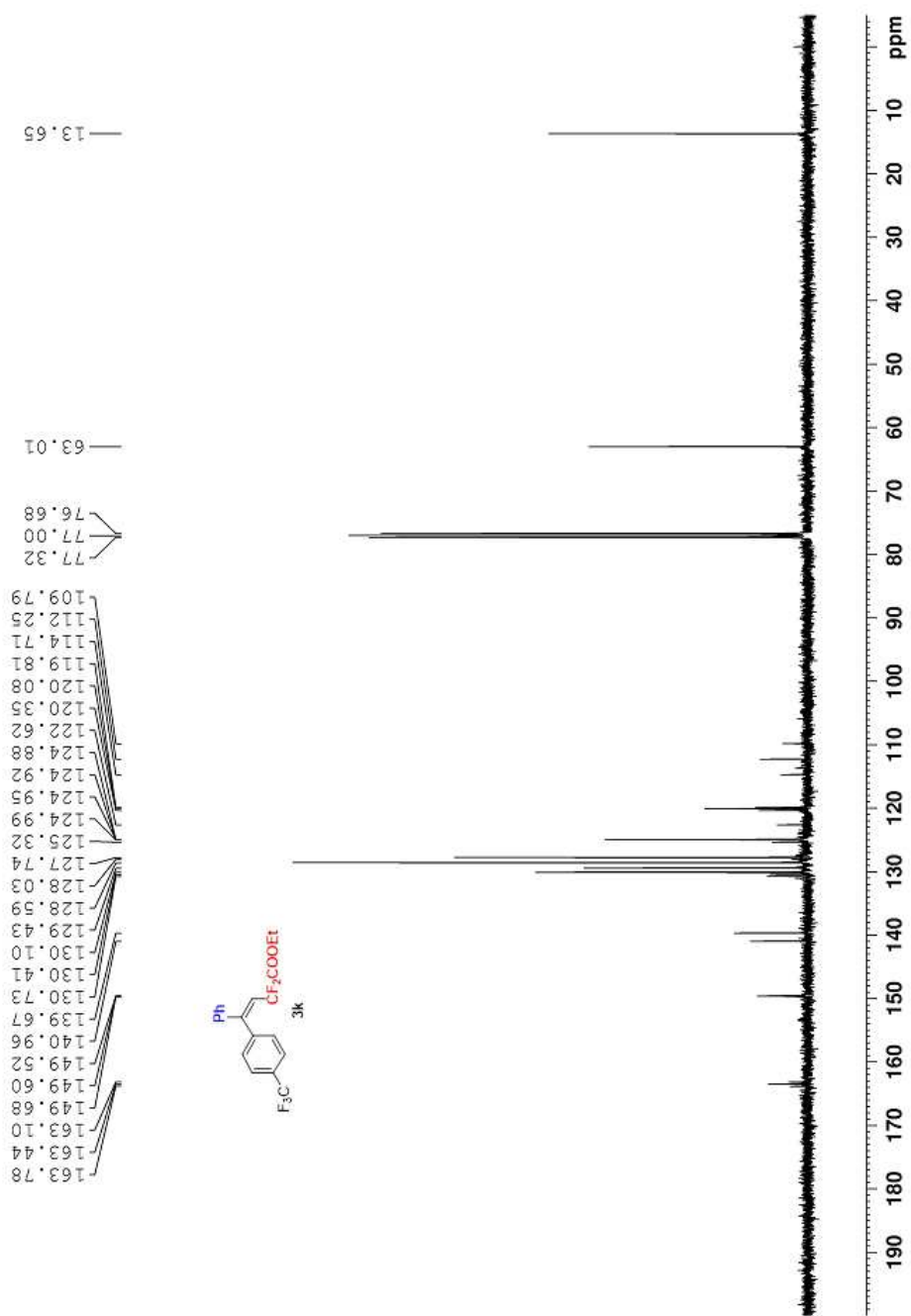




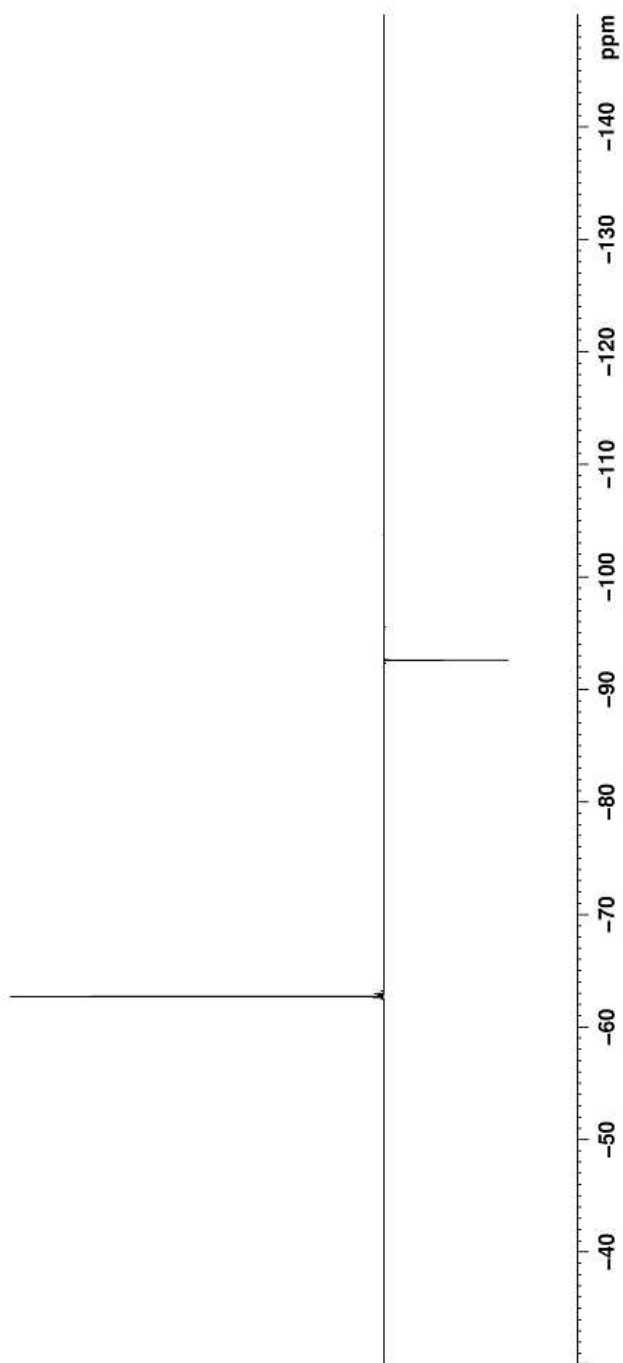
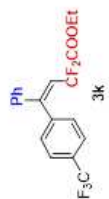


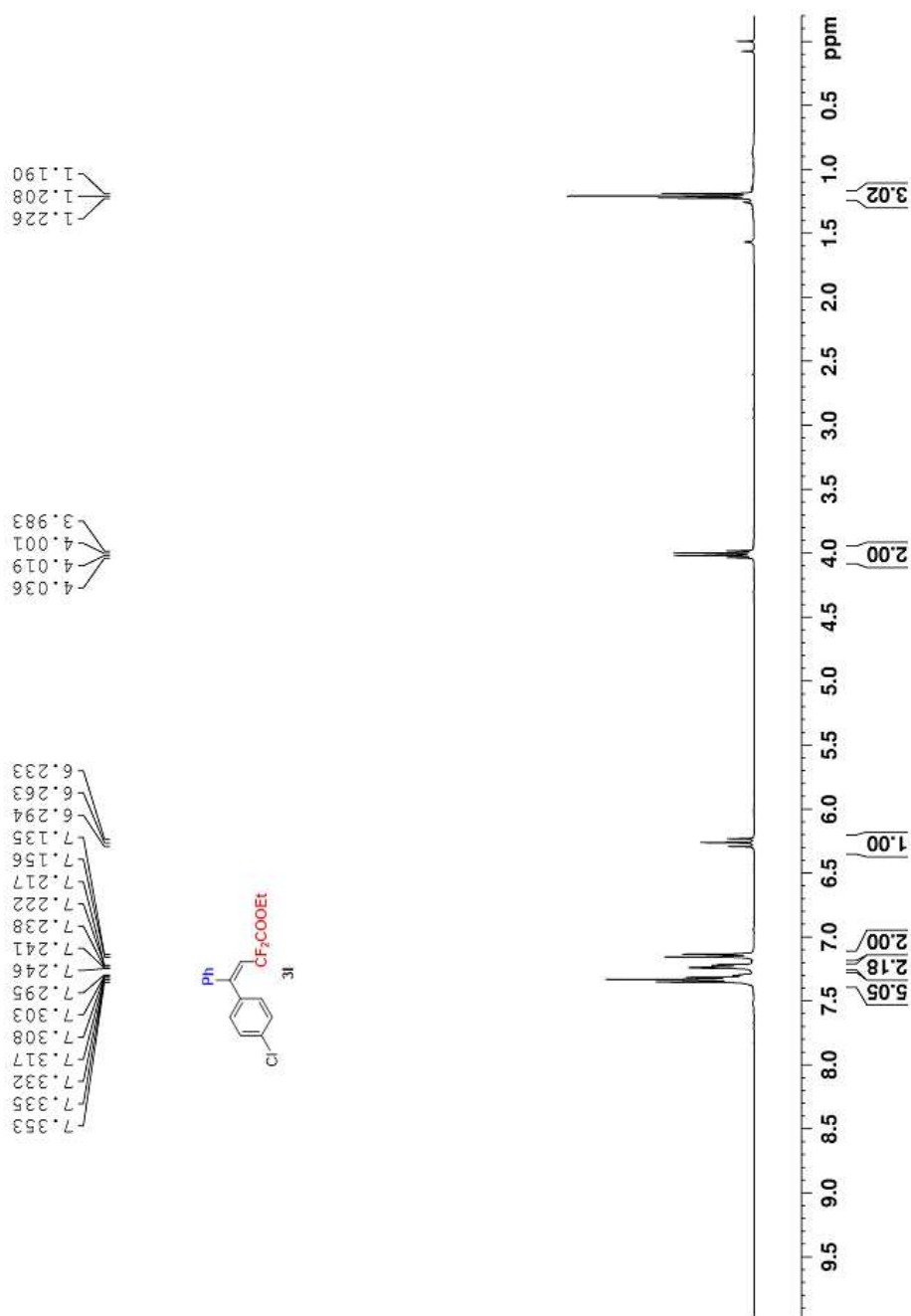


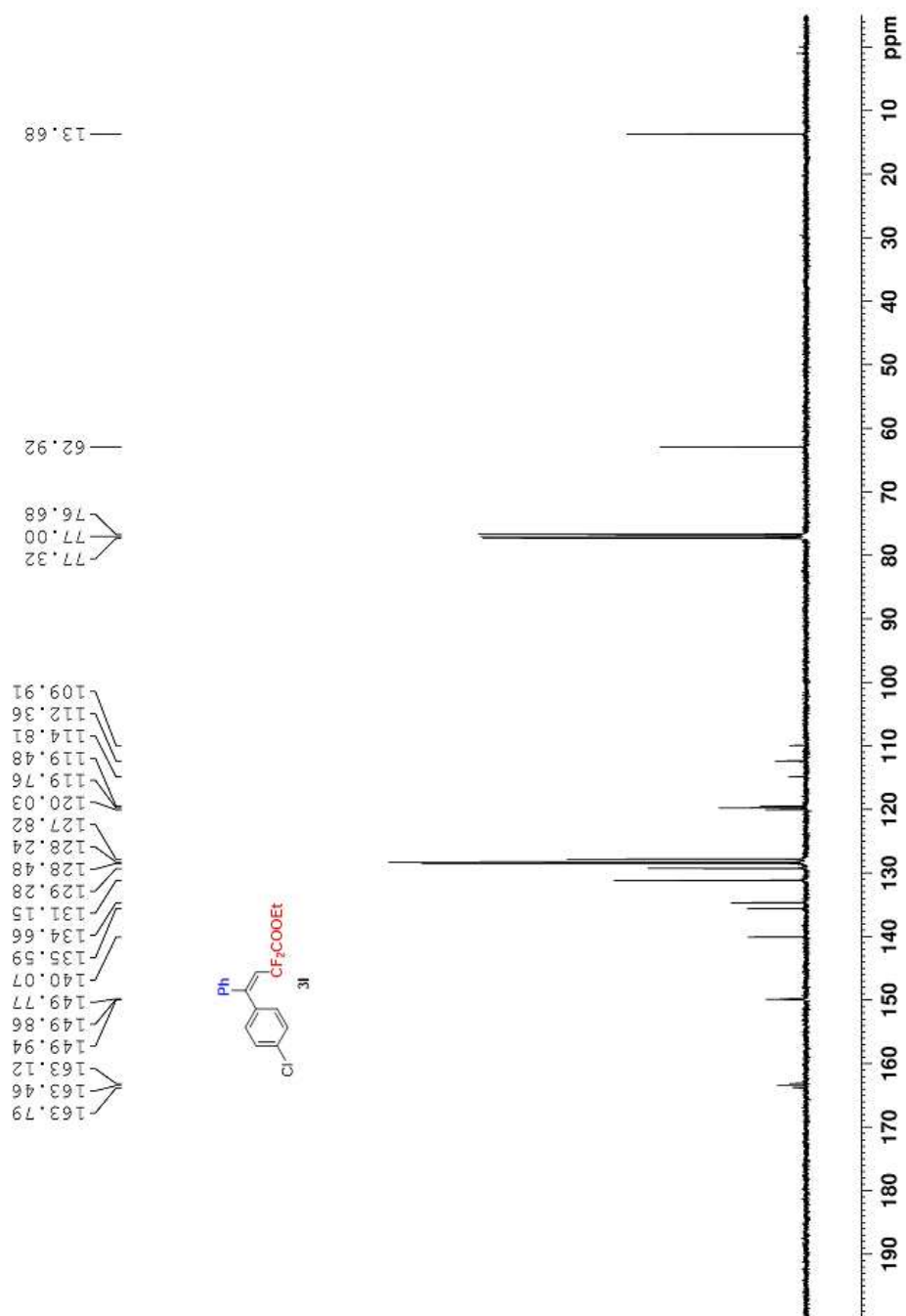


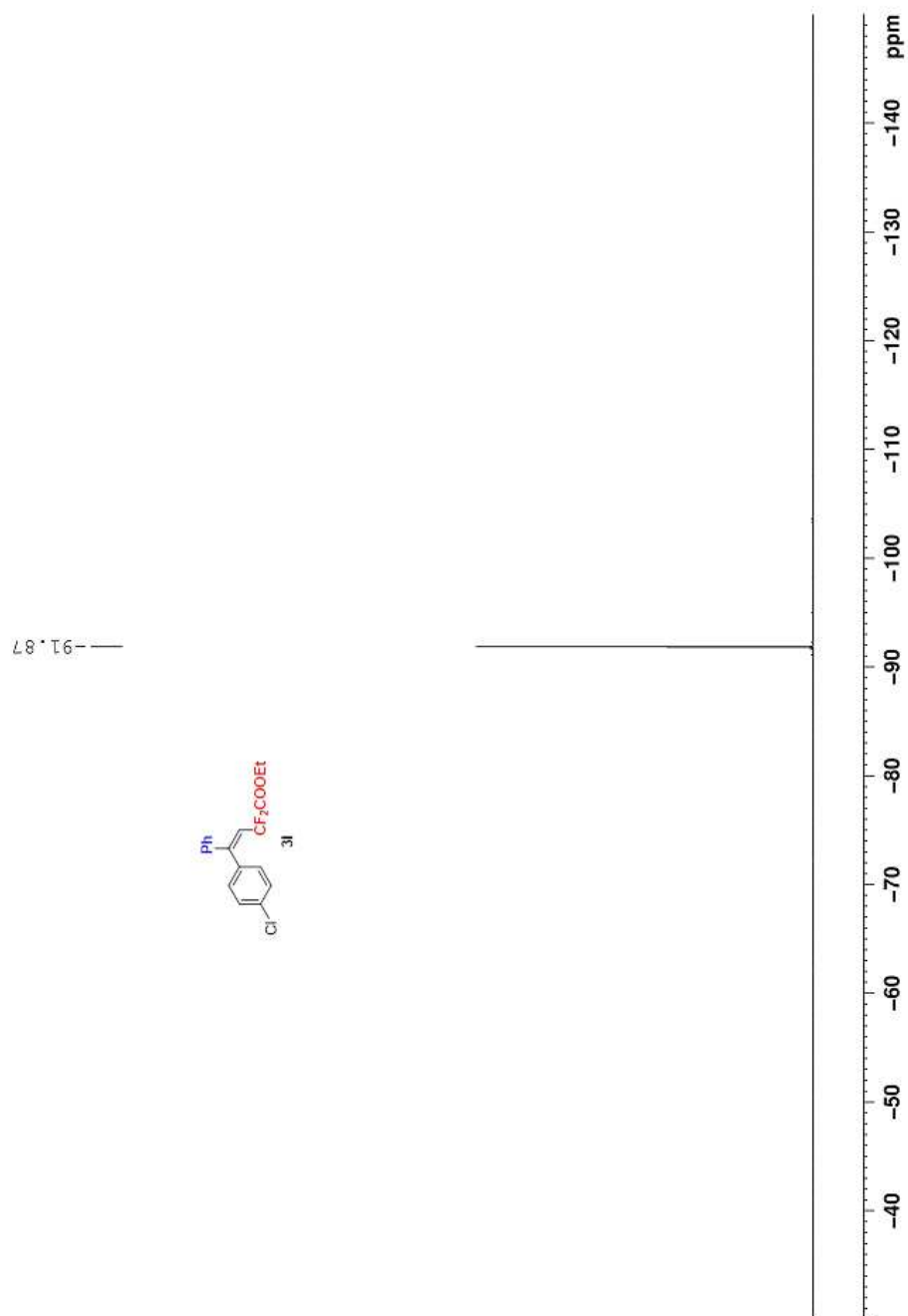


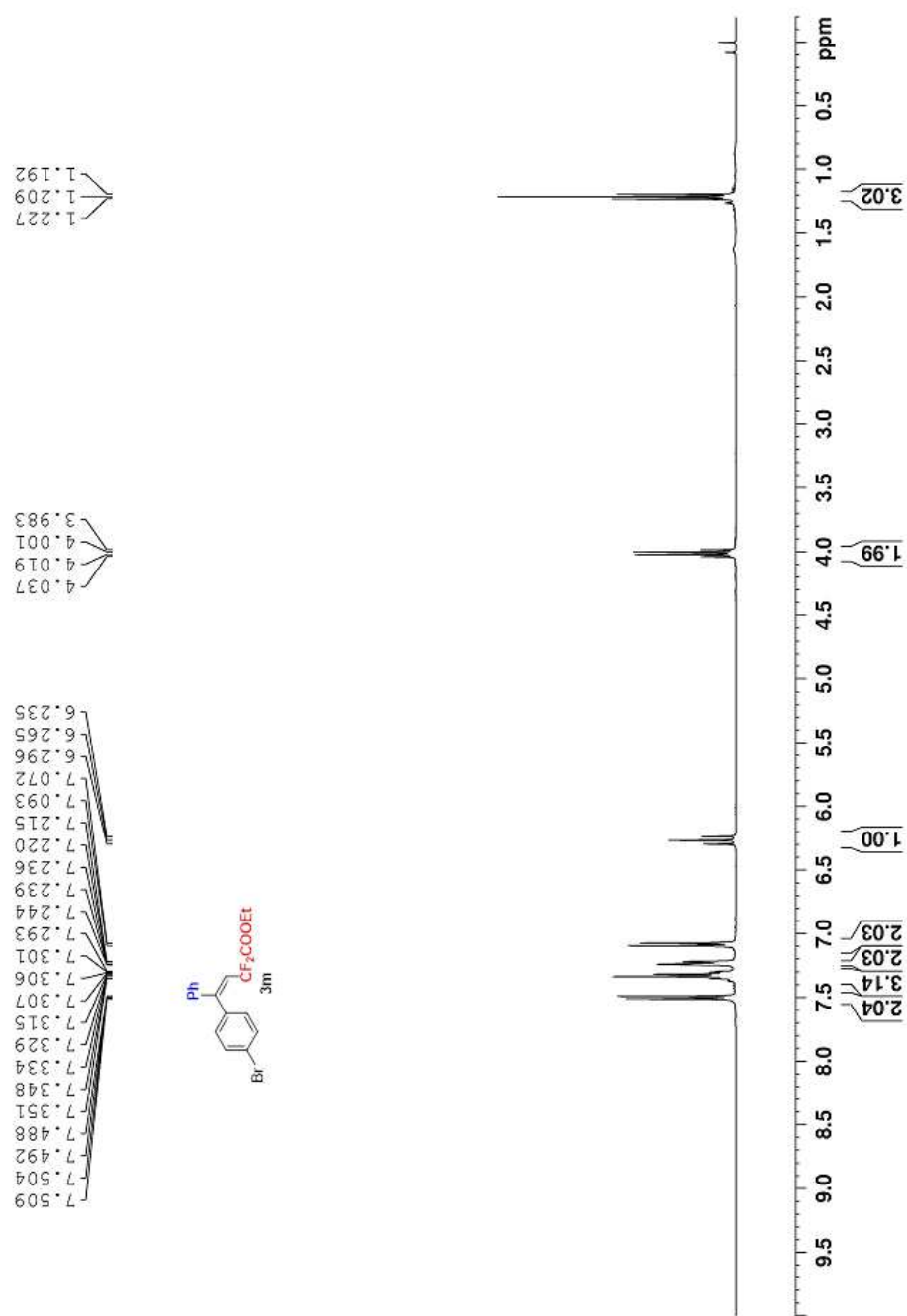
—62.72

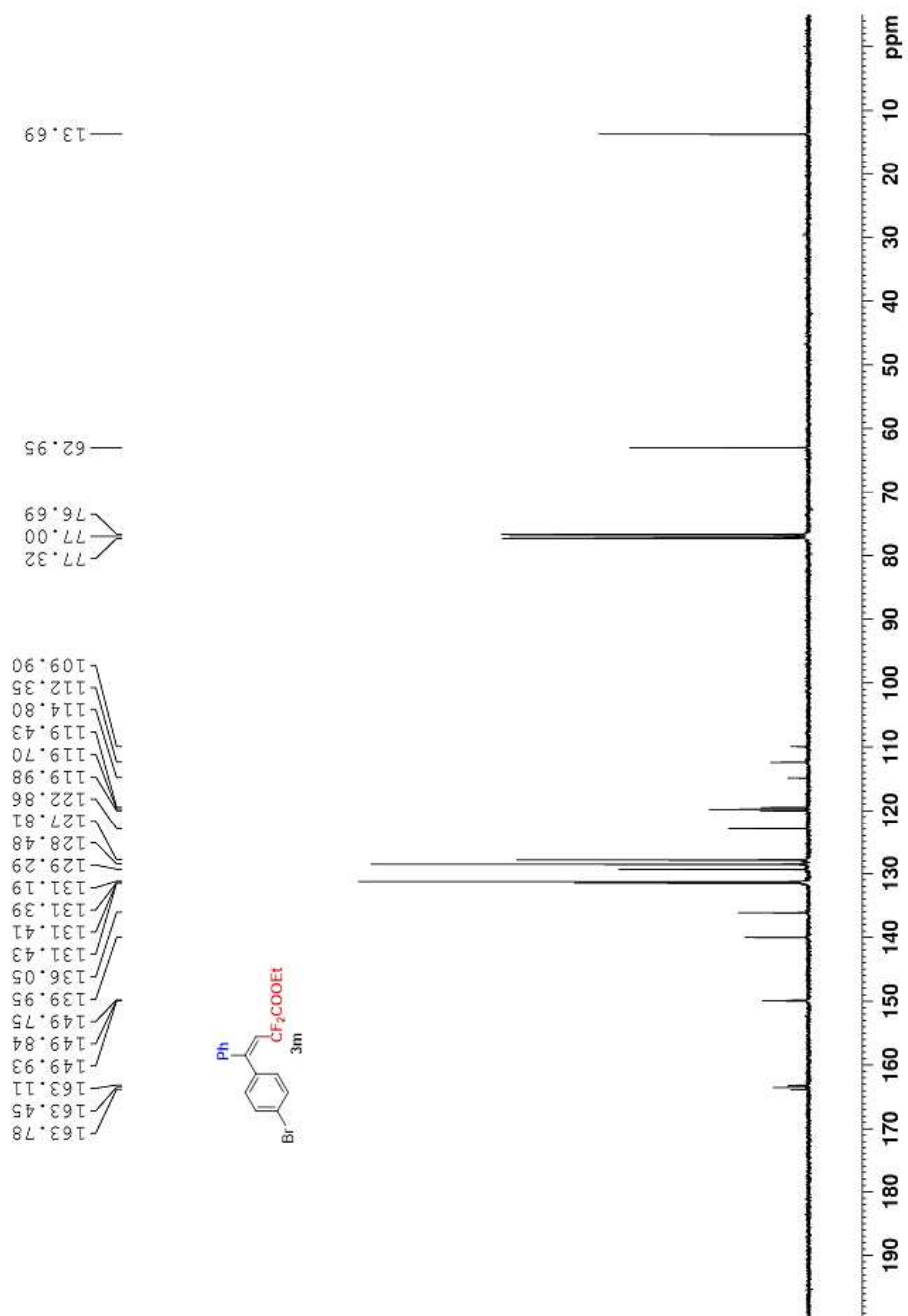


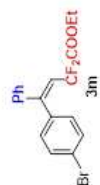


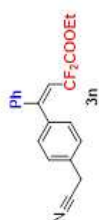
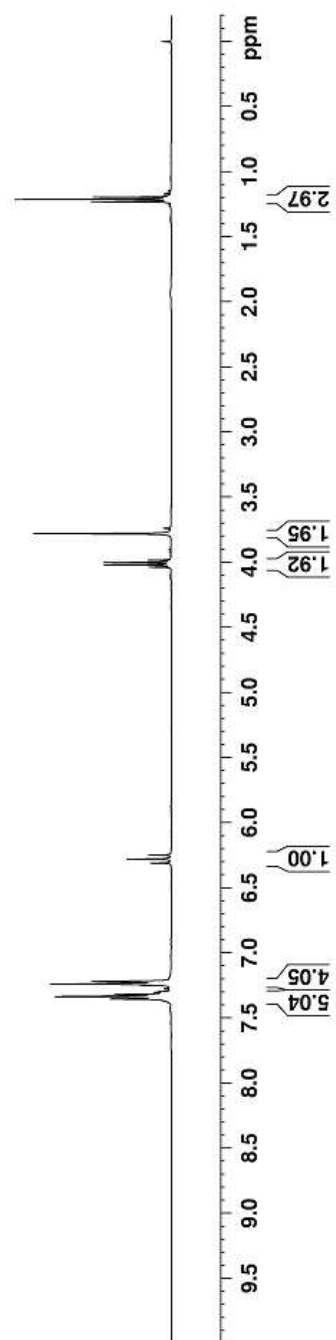








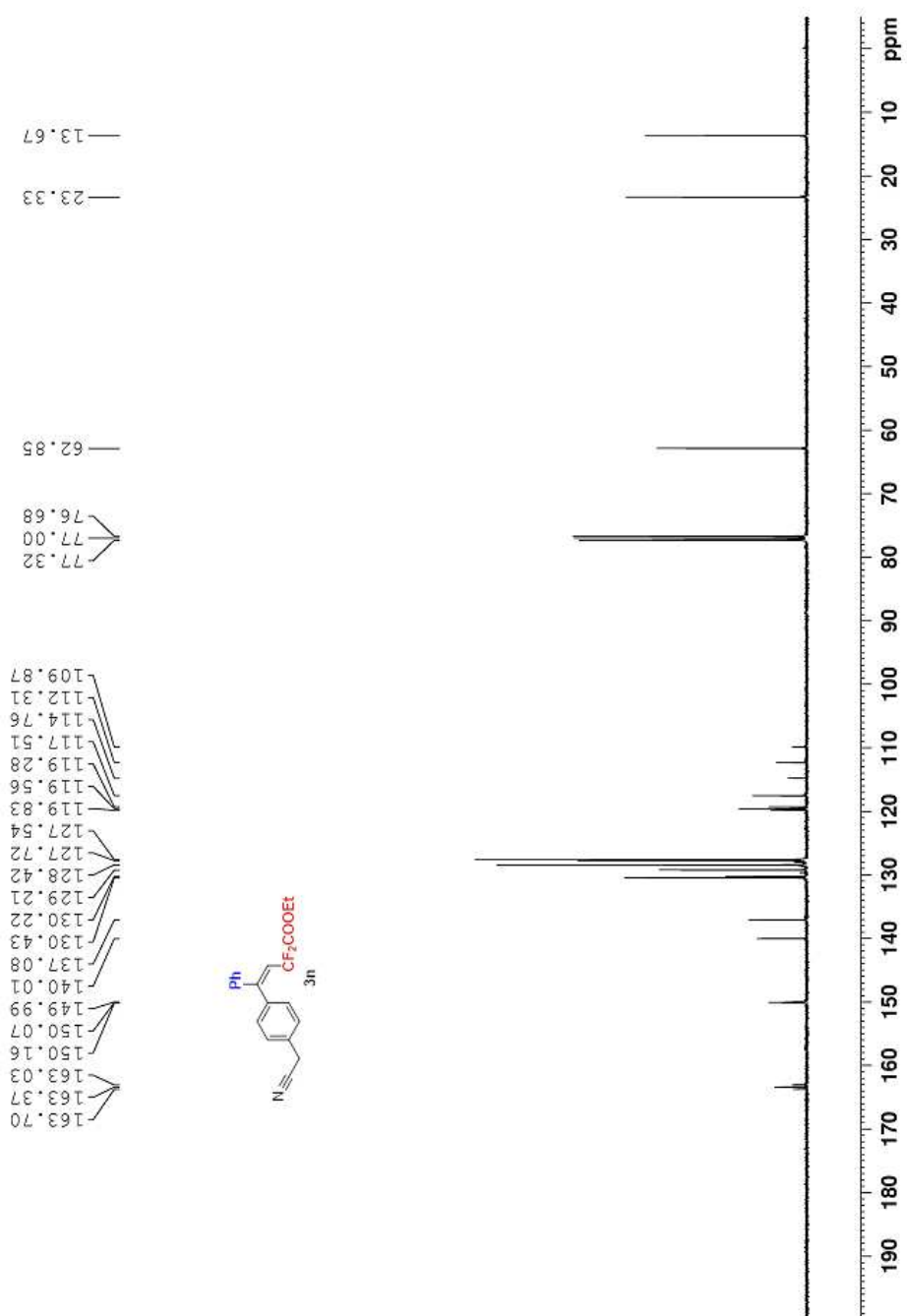


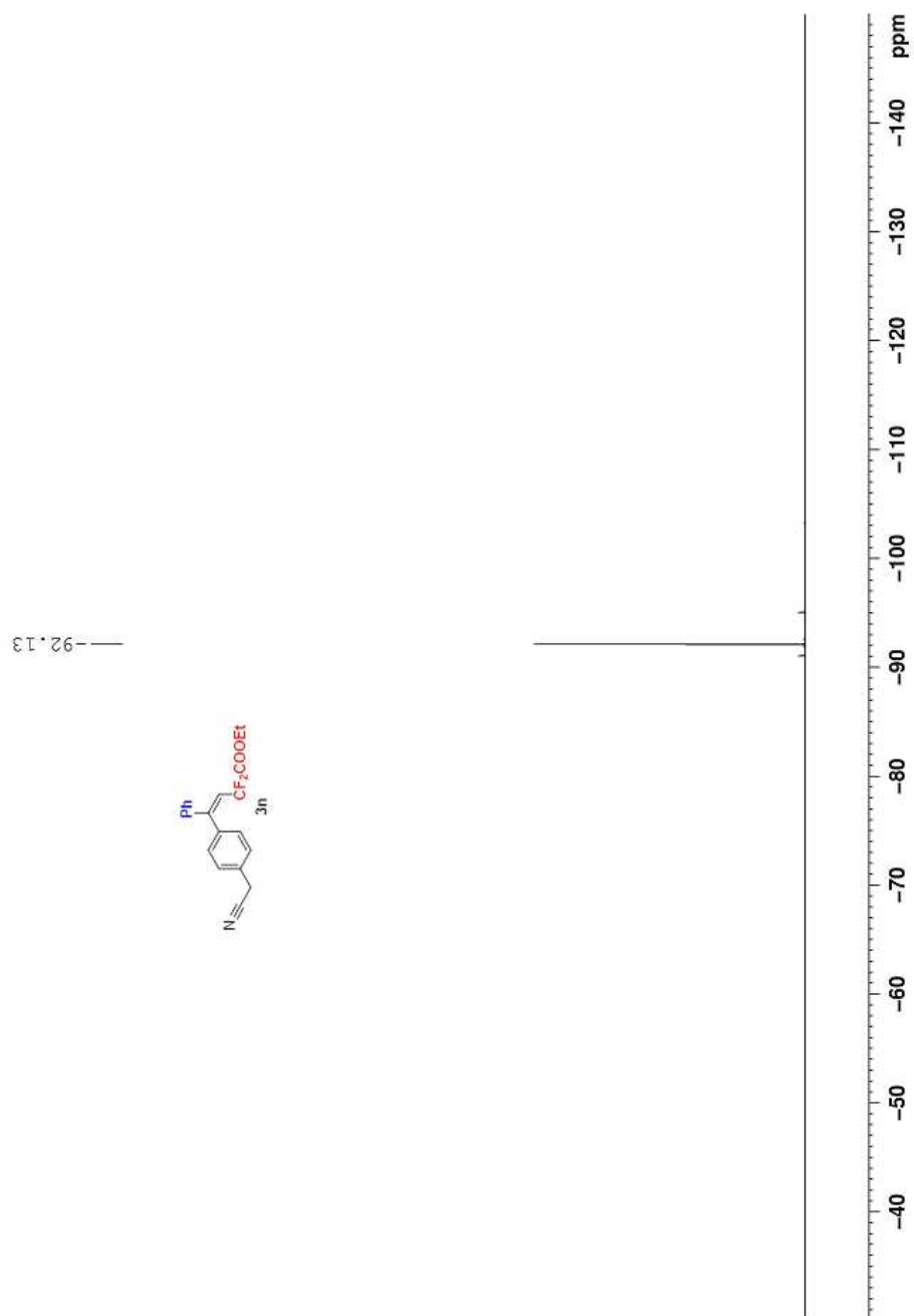


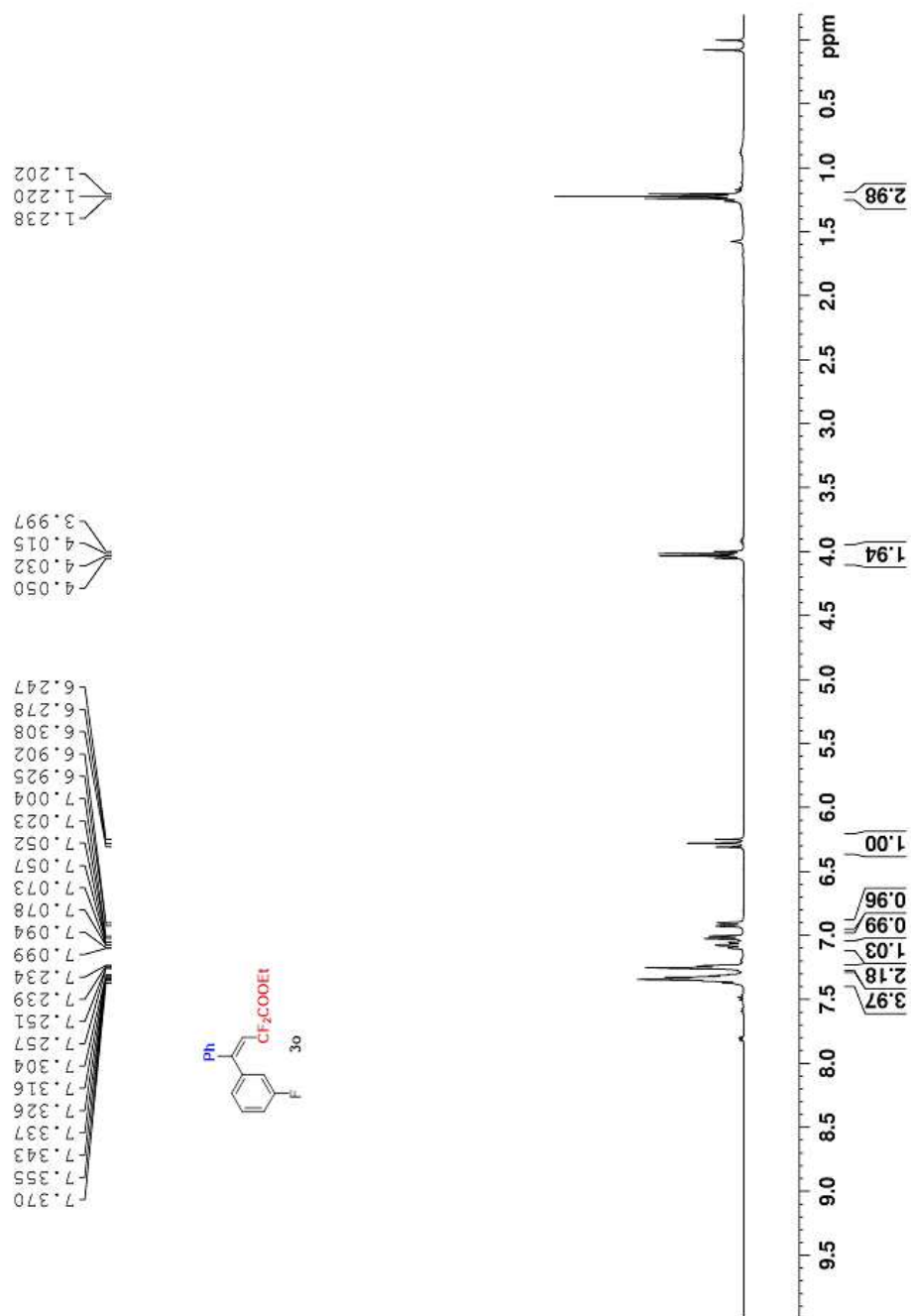
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1.212
1.195

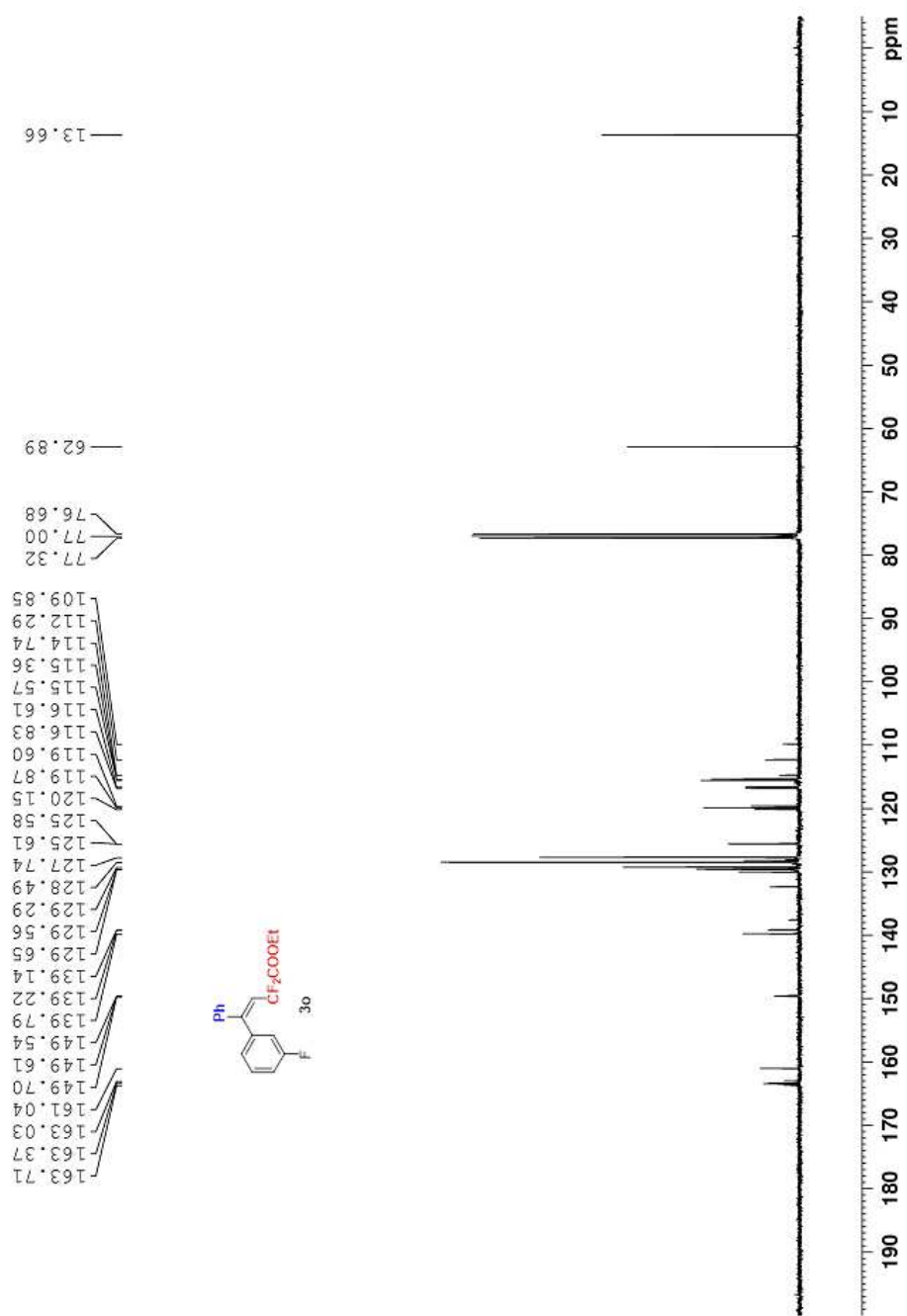
4.037
4.019
4.001
3.983
3.780

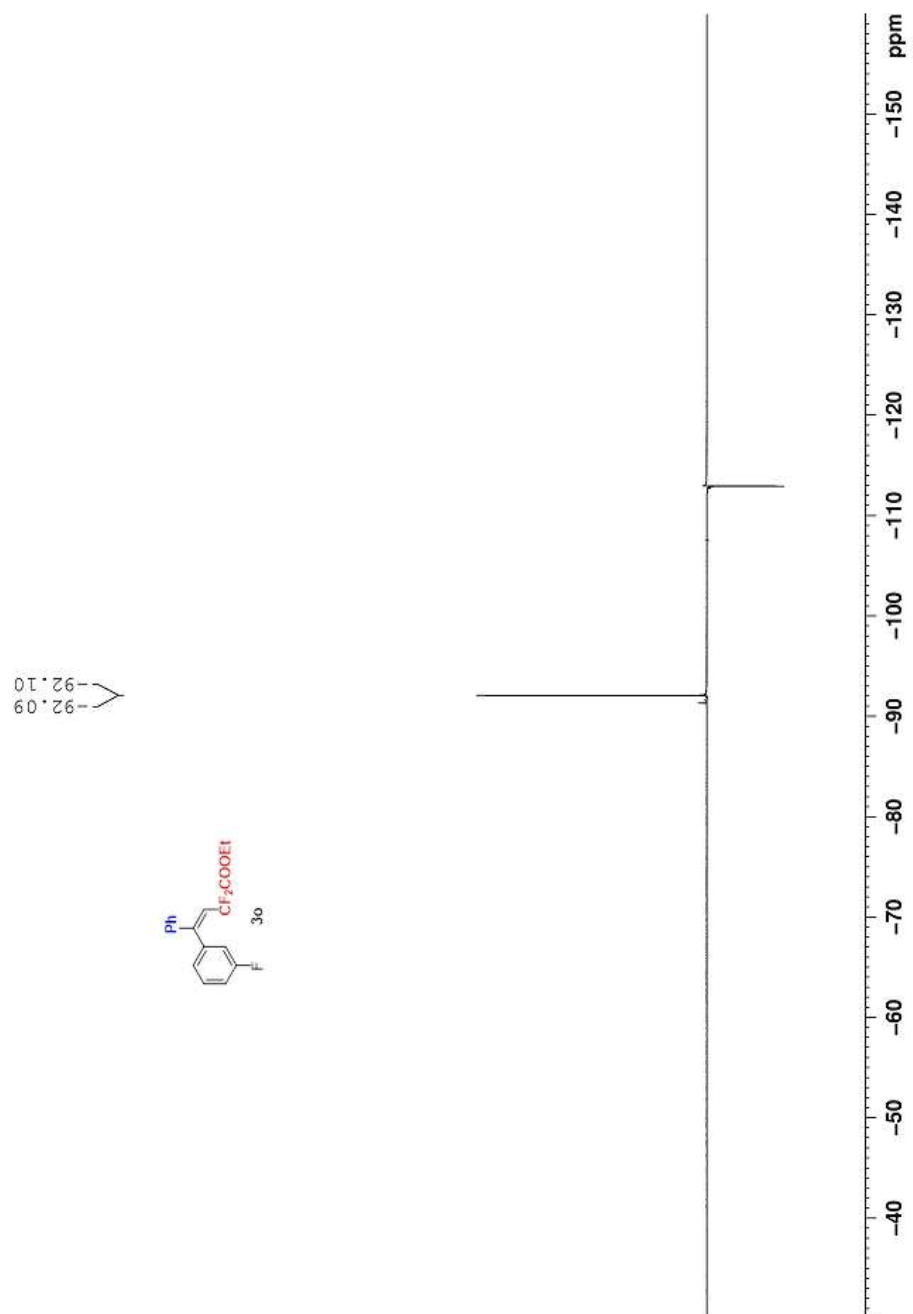
7.354
7.337
7.319
7.310
7.305
7.297
7.250
7.239
7.219
6.310
6.279
6.248

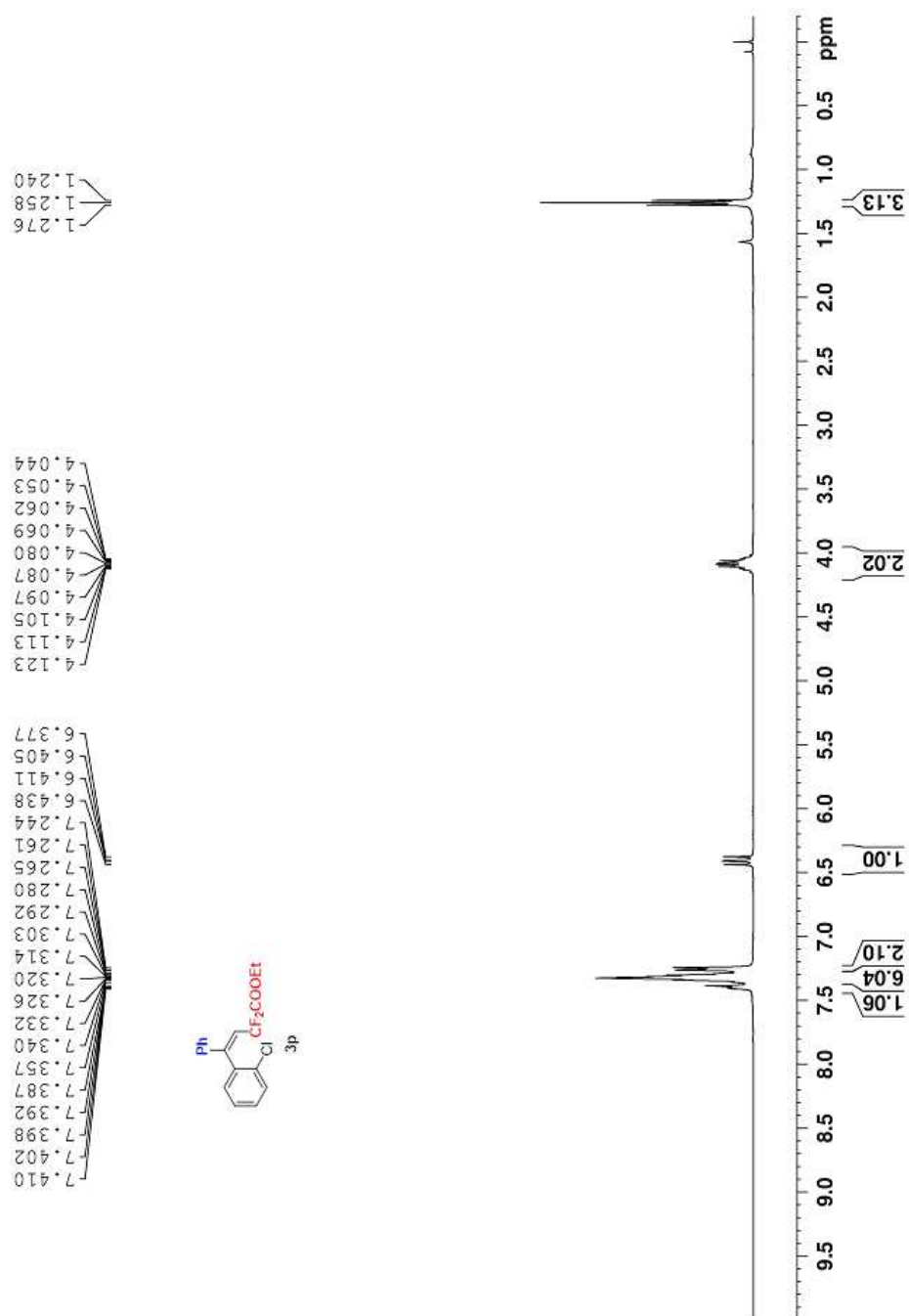


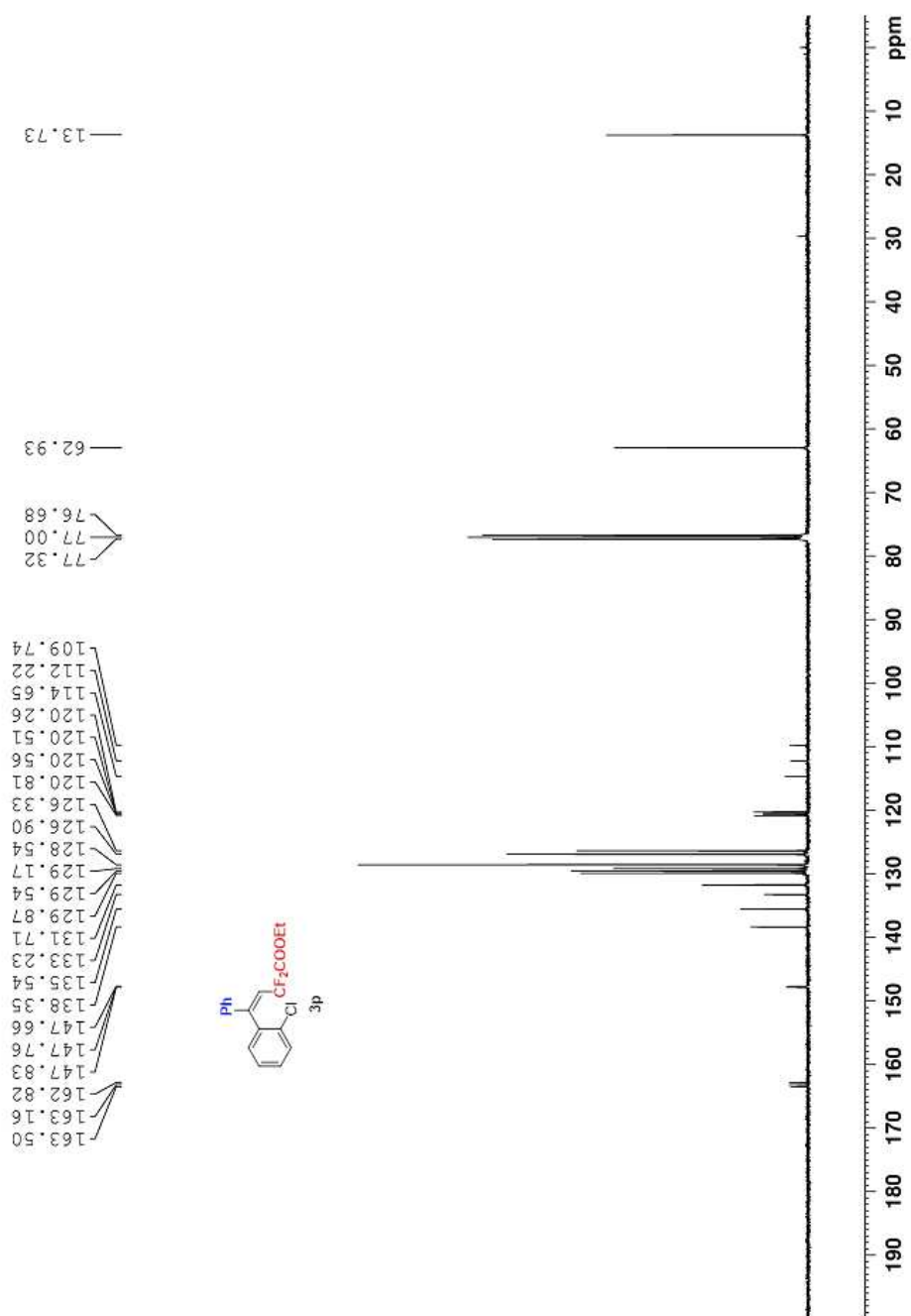


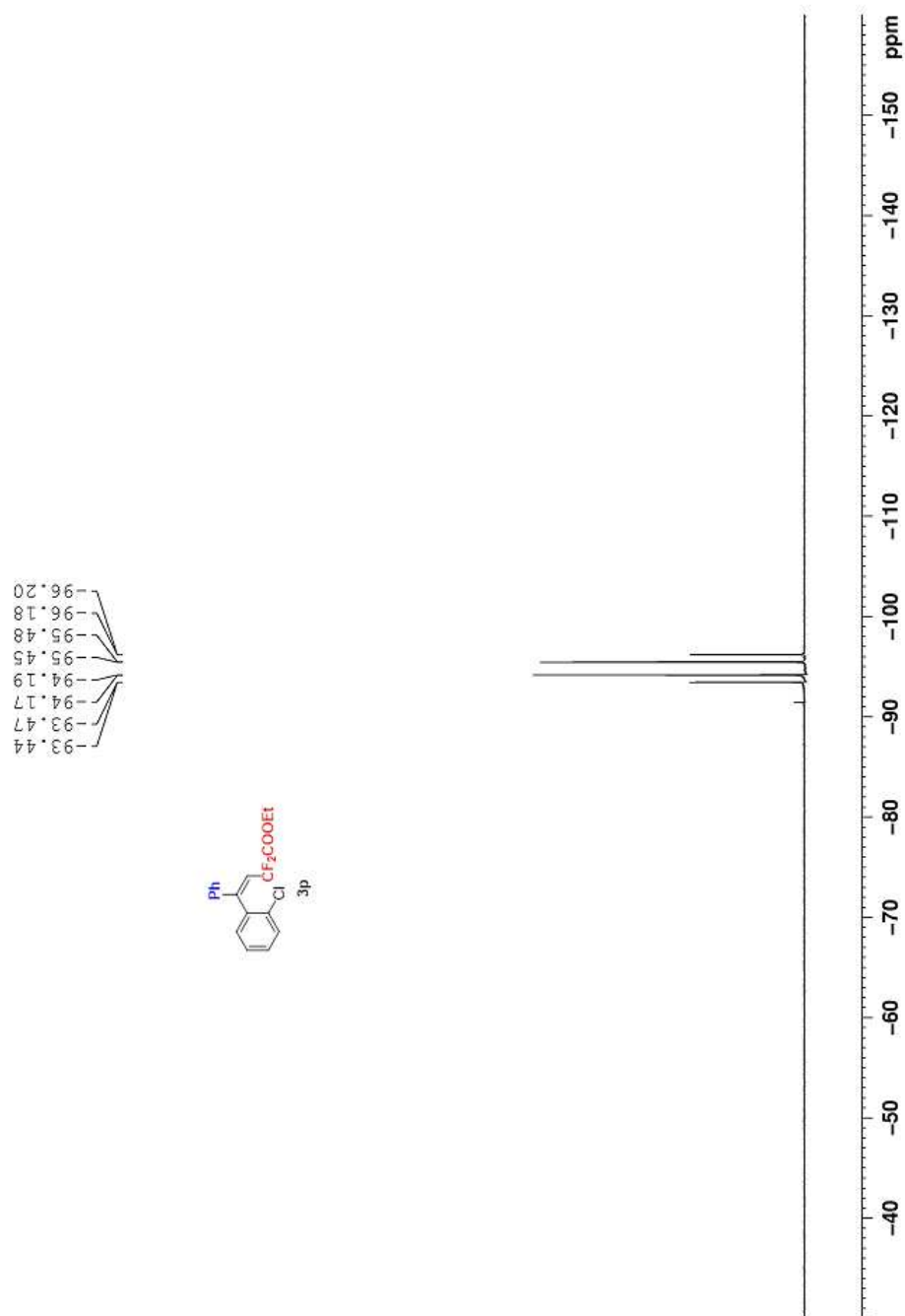


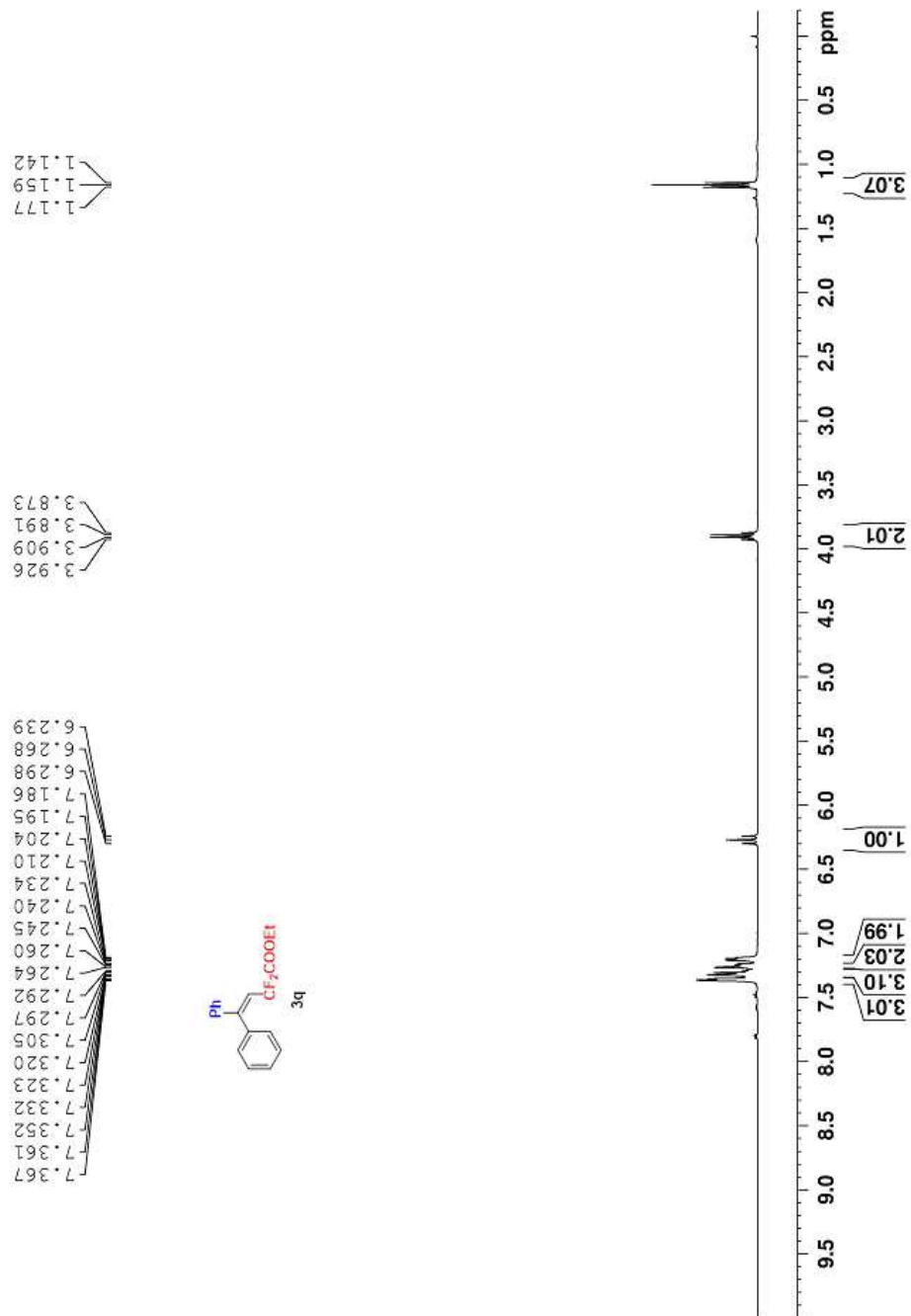


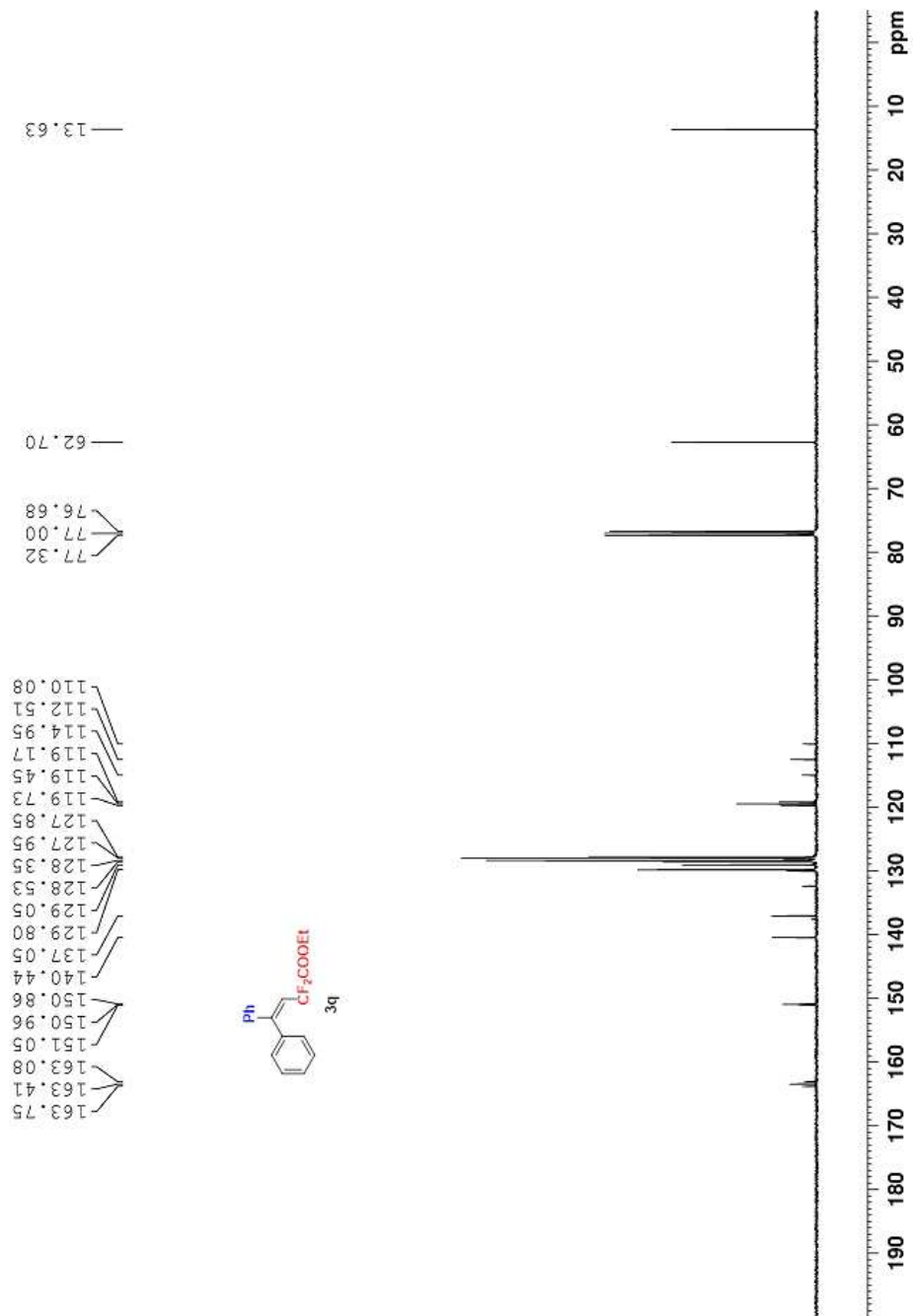




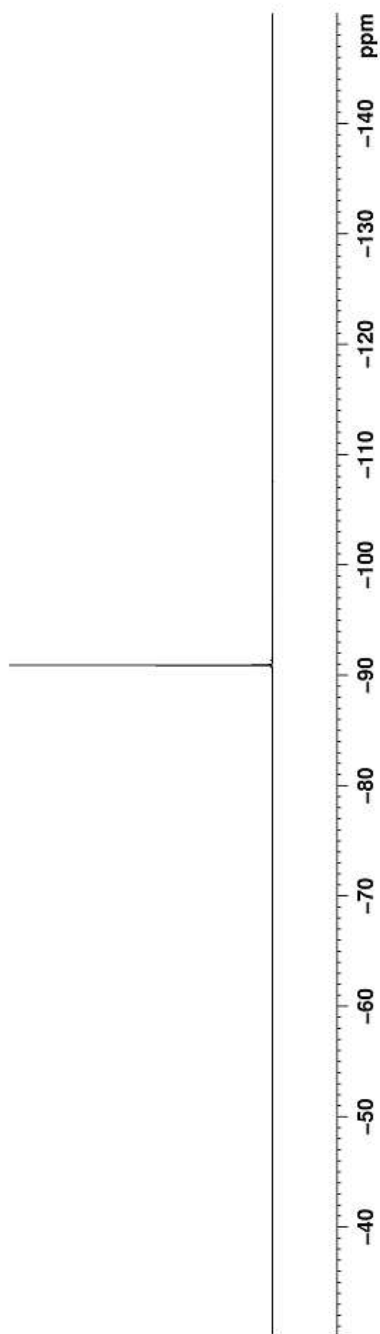
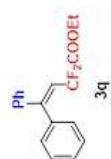


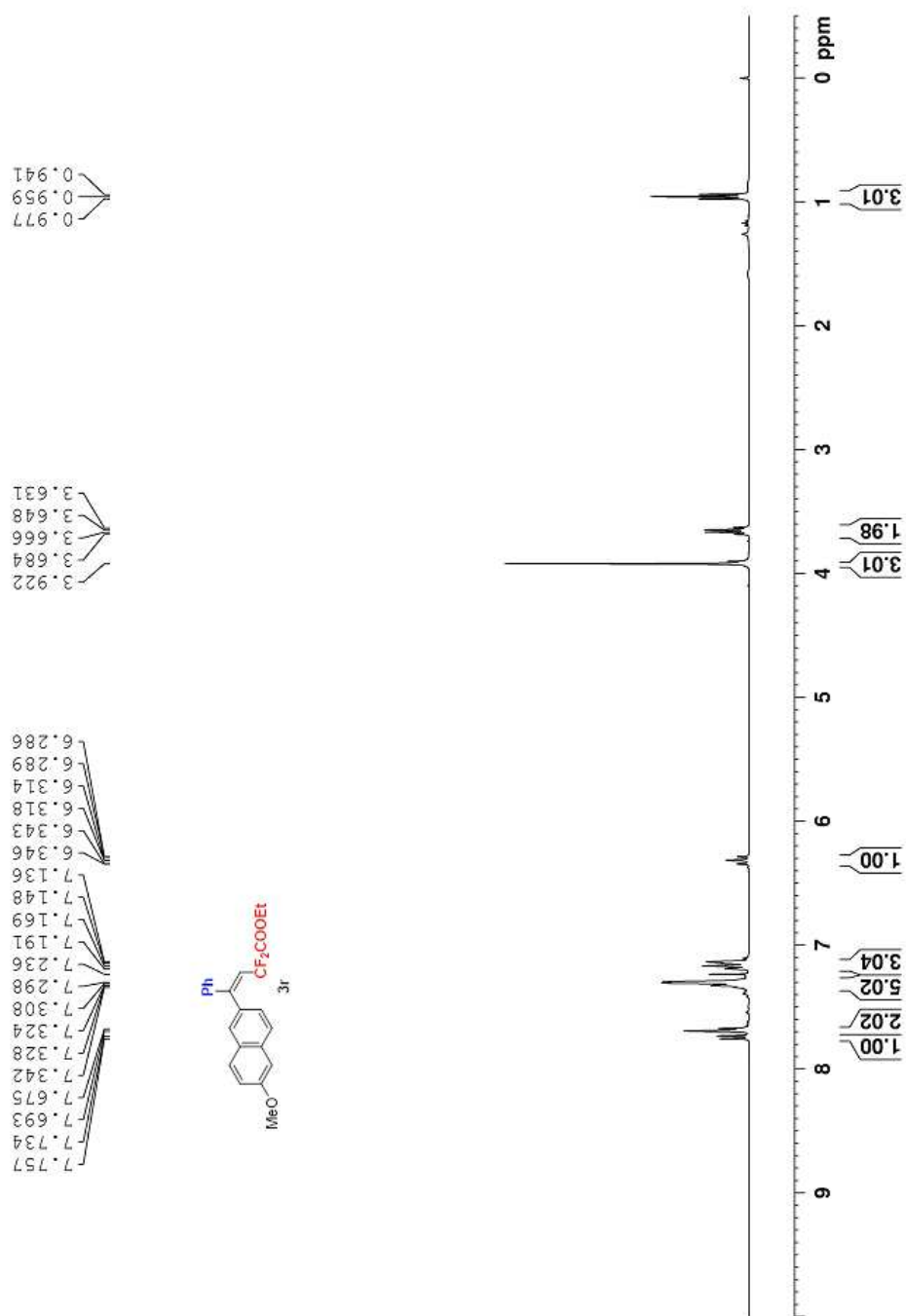


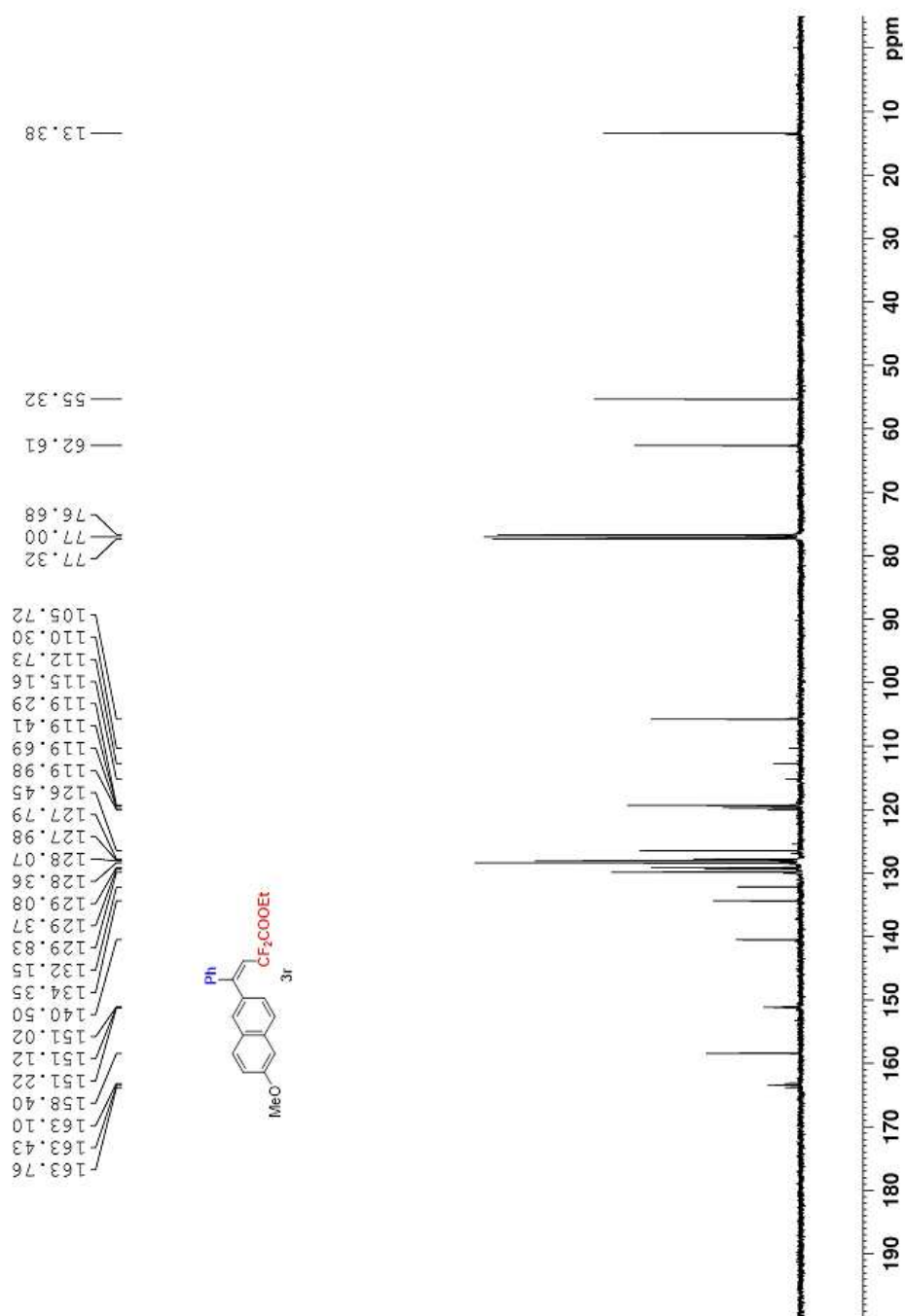




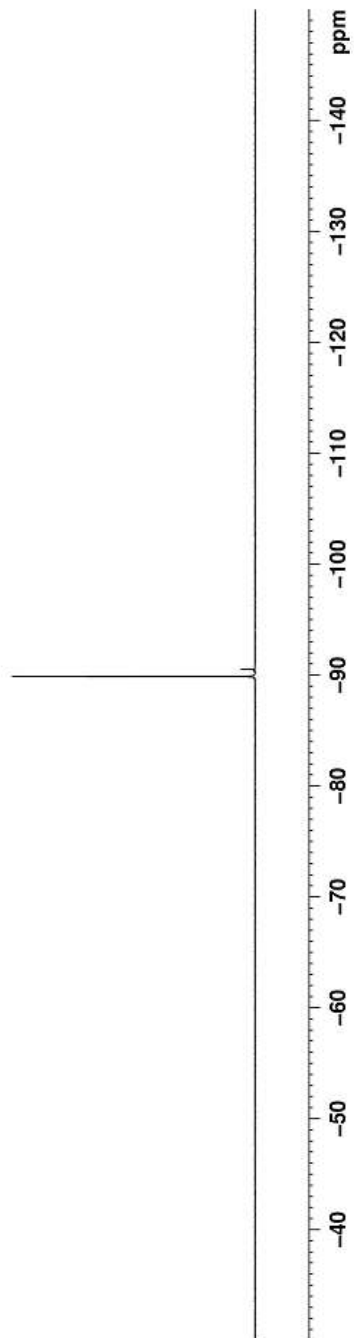
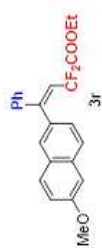
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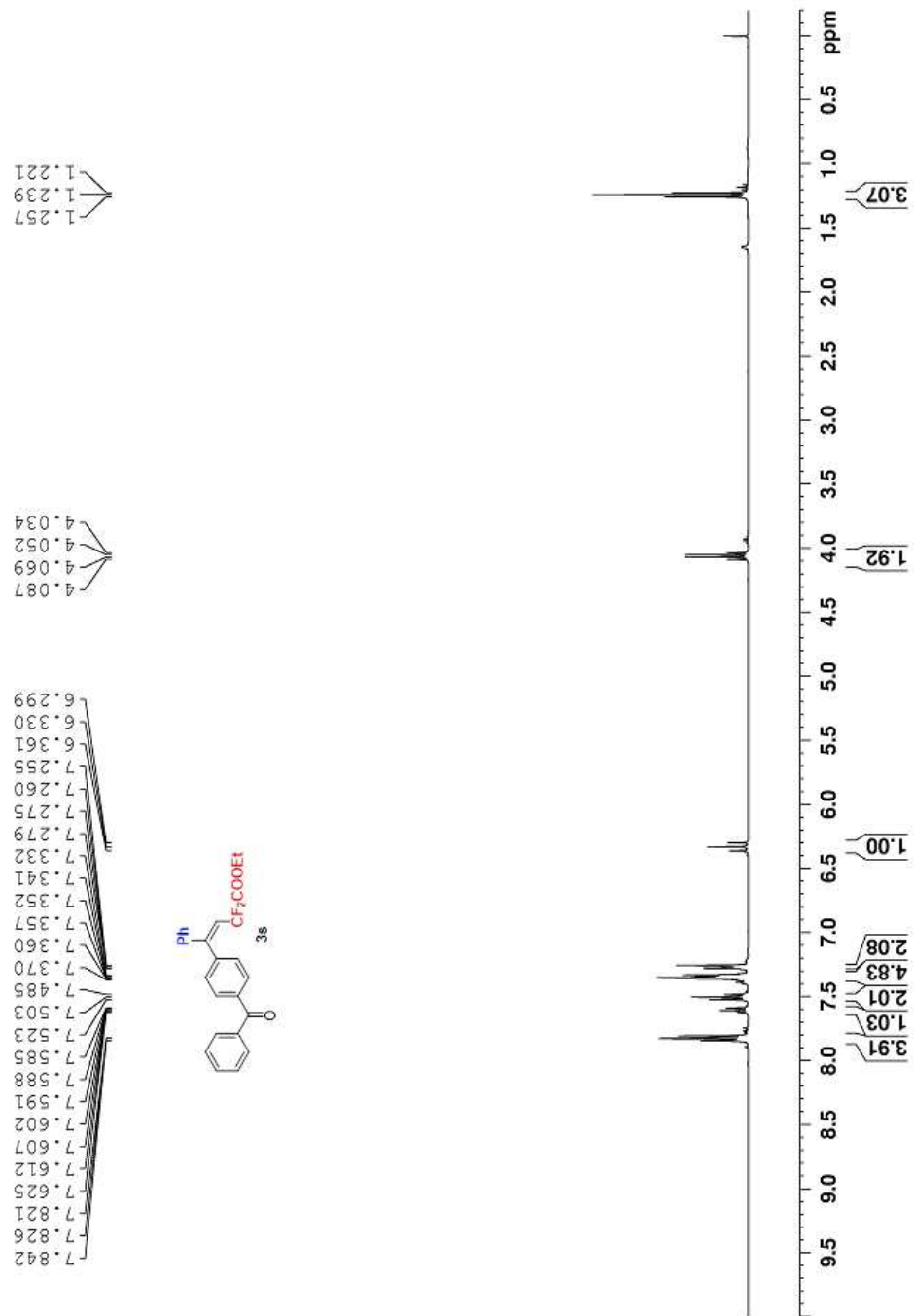


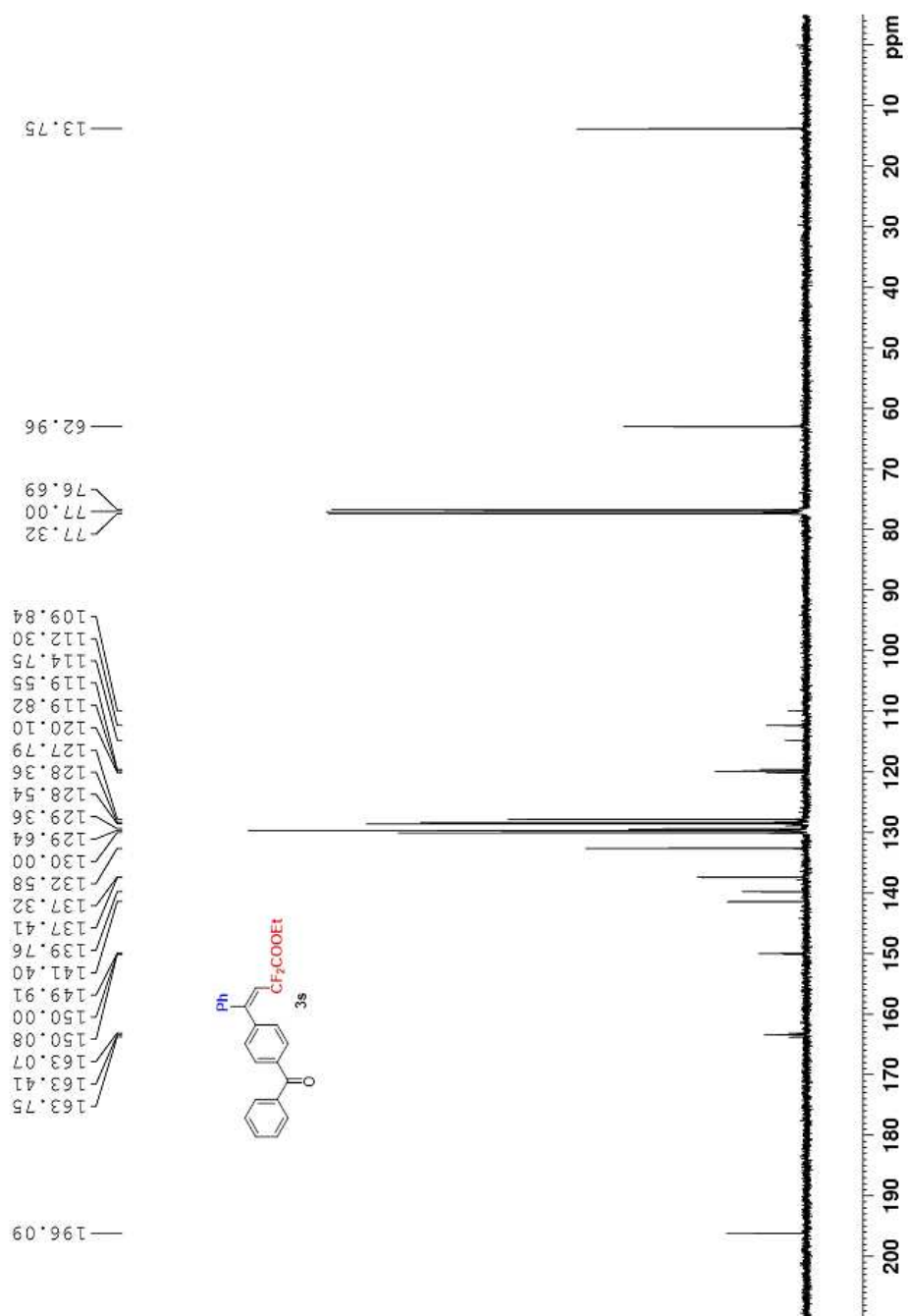


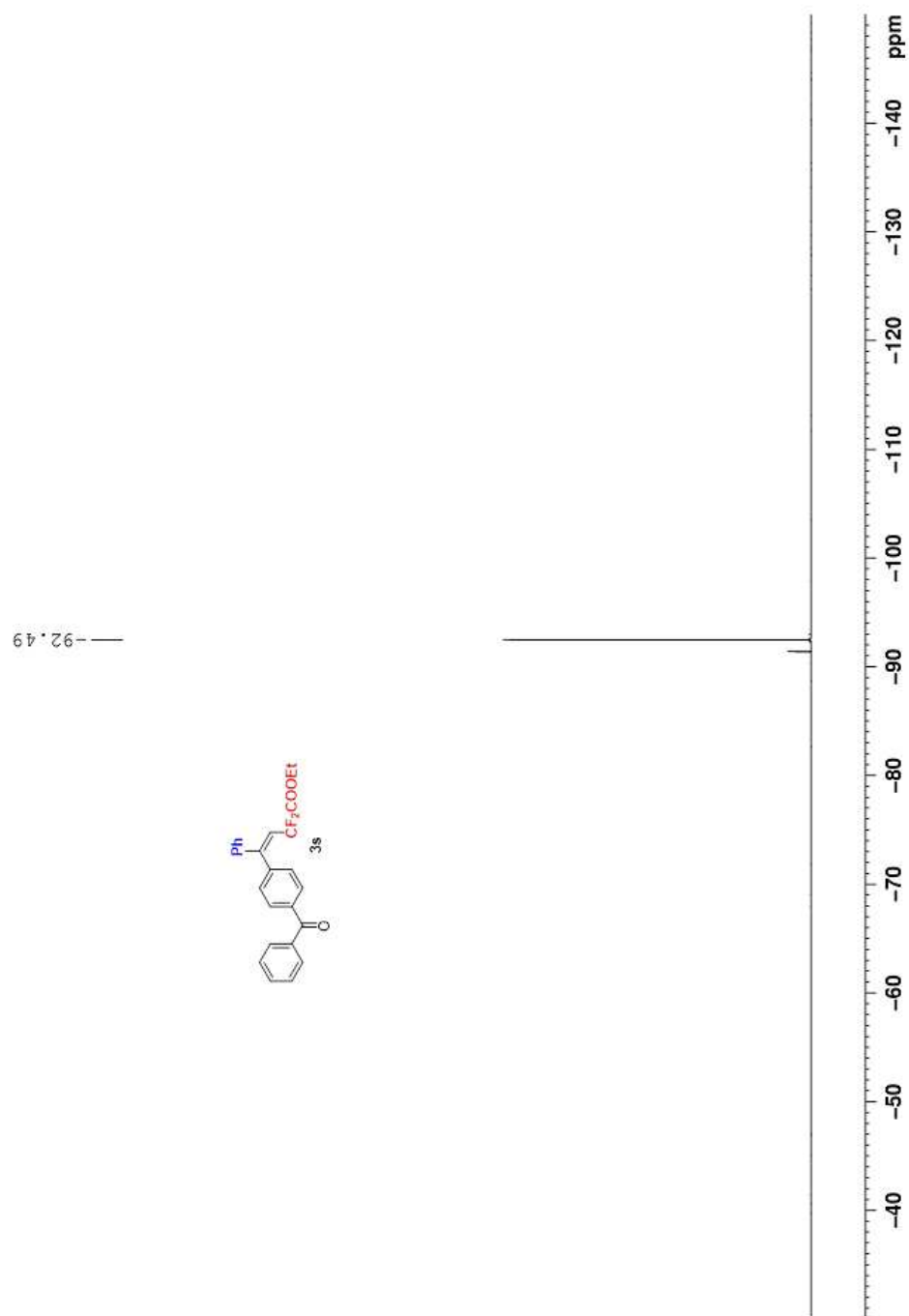


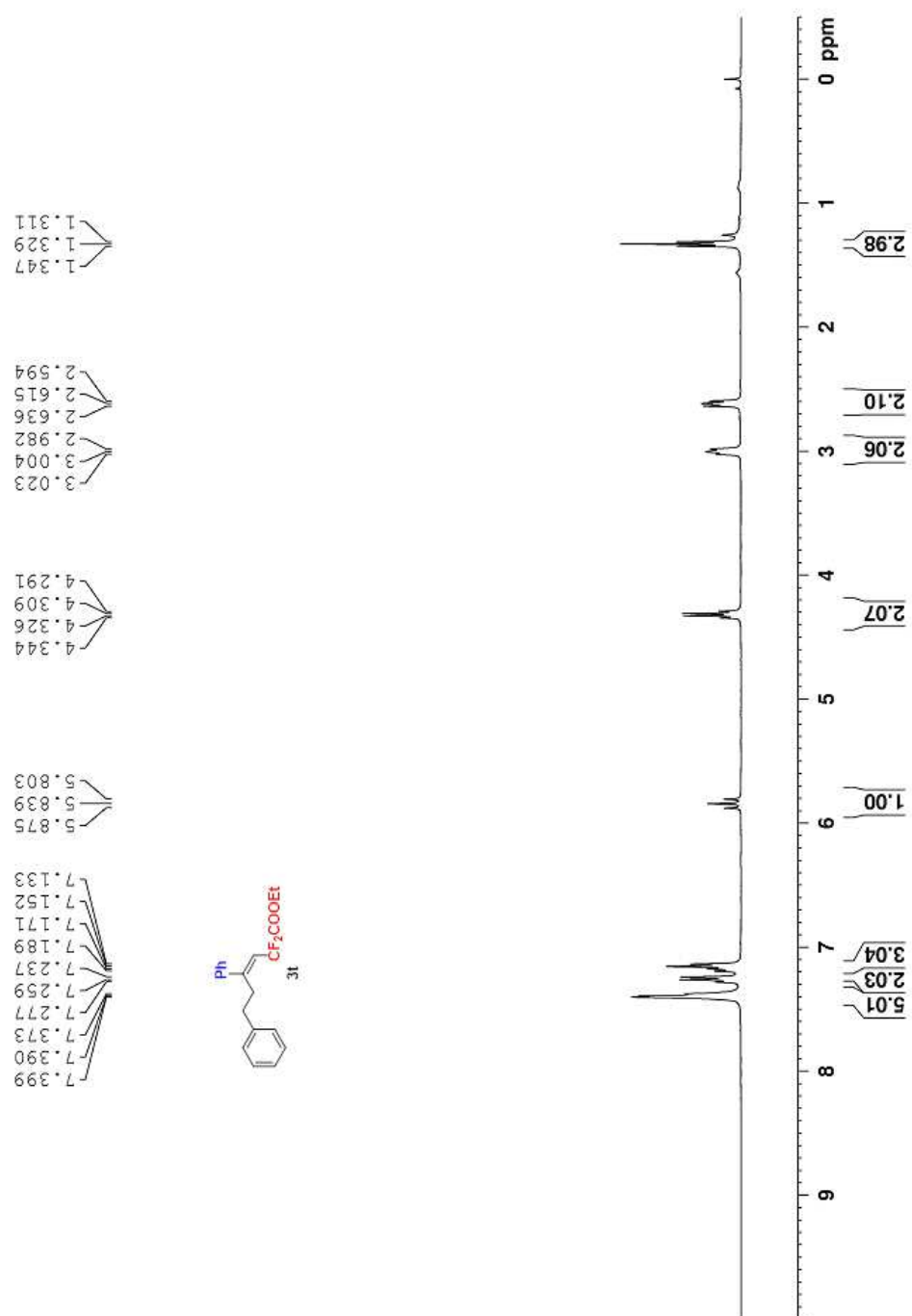
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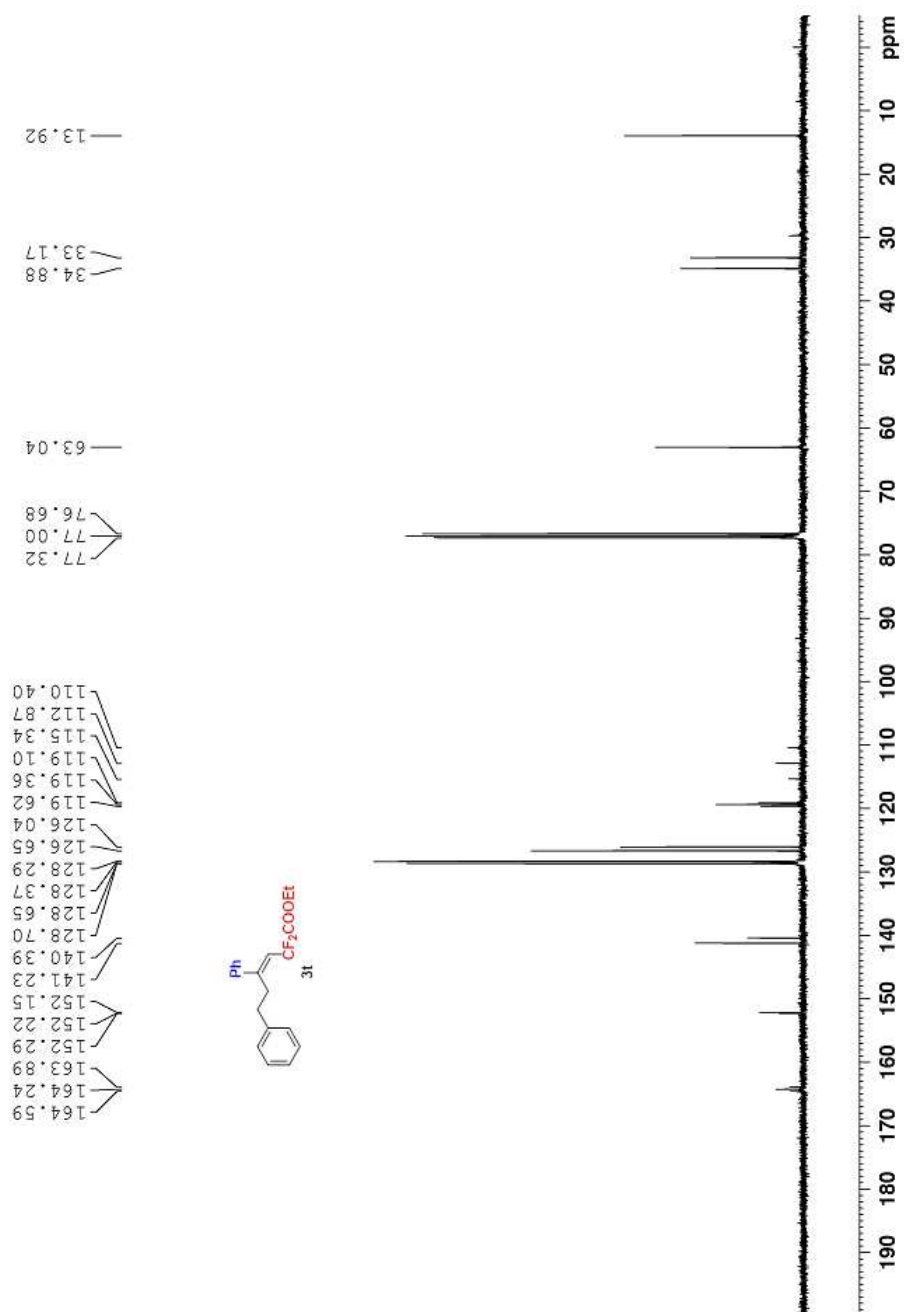


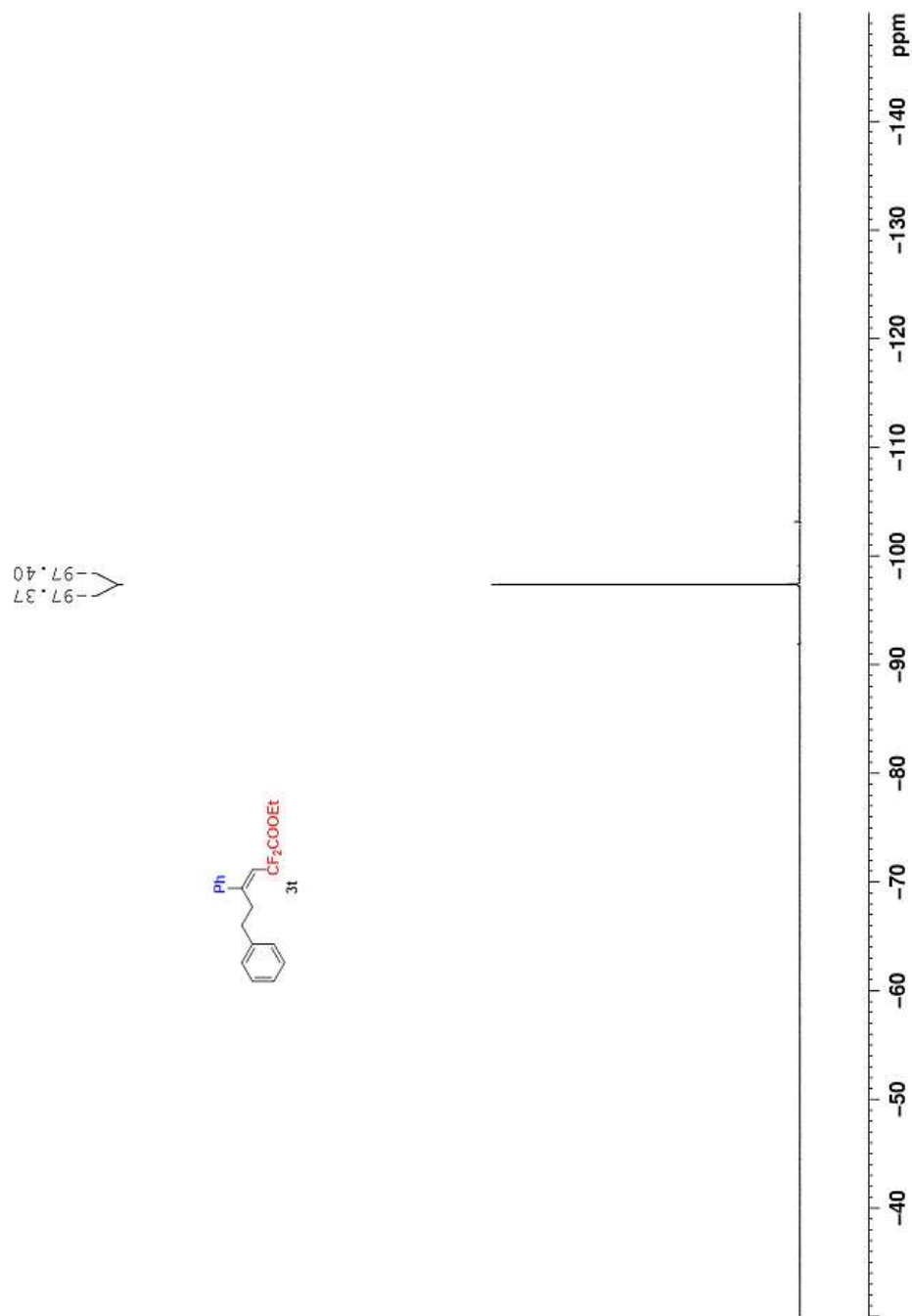


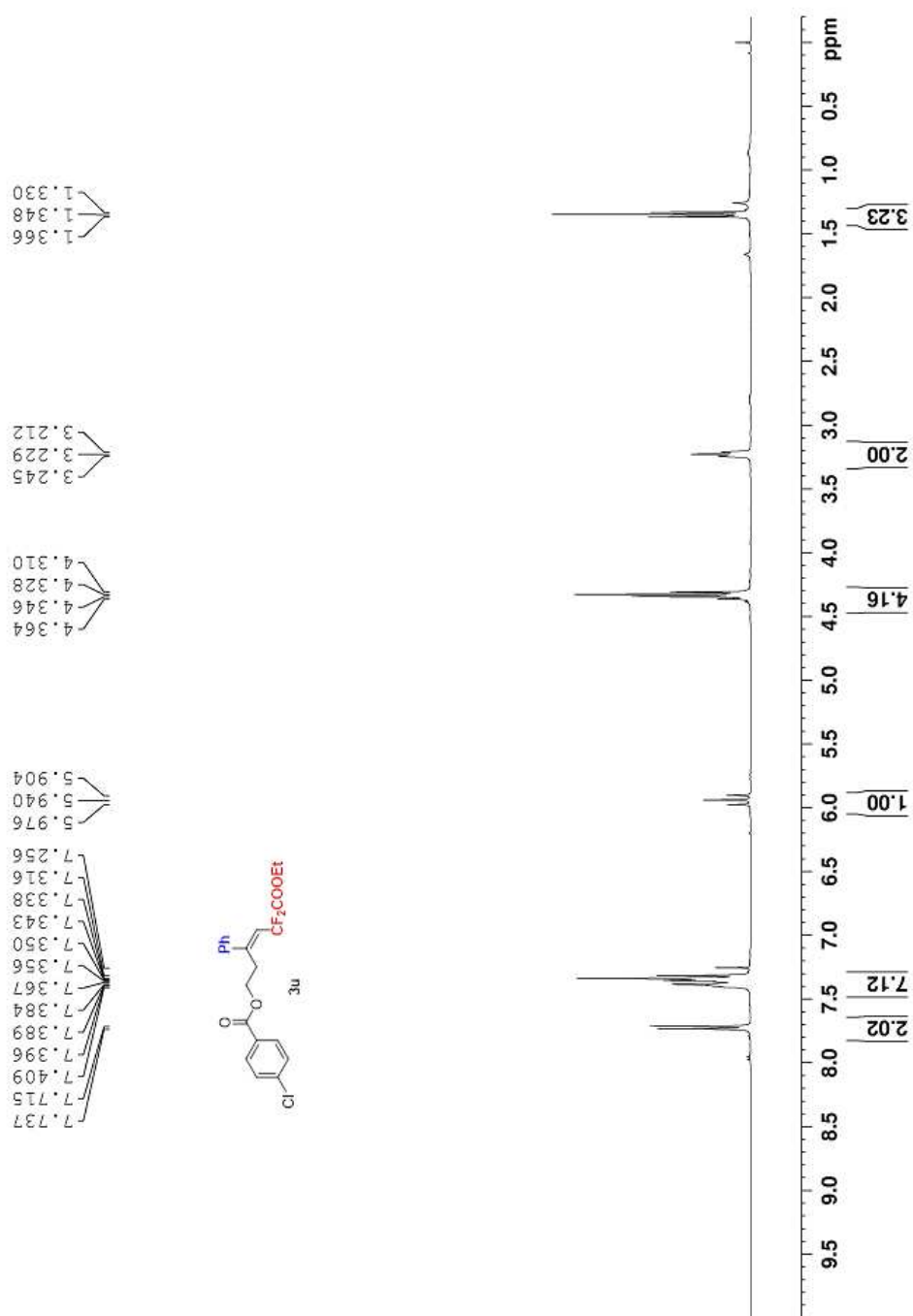


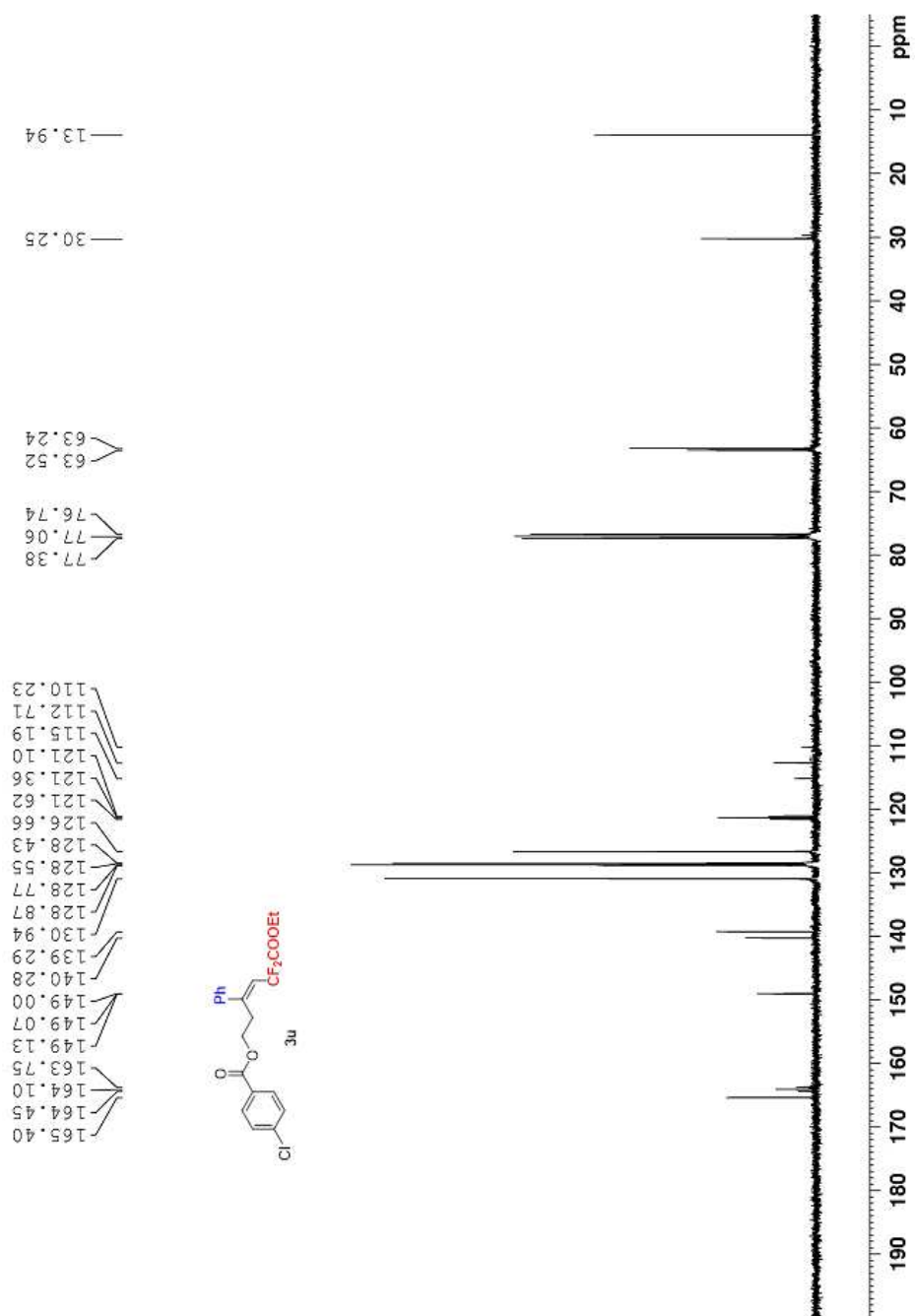




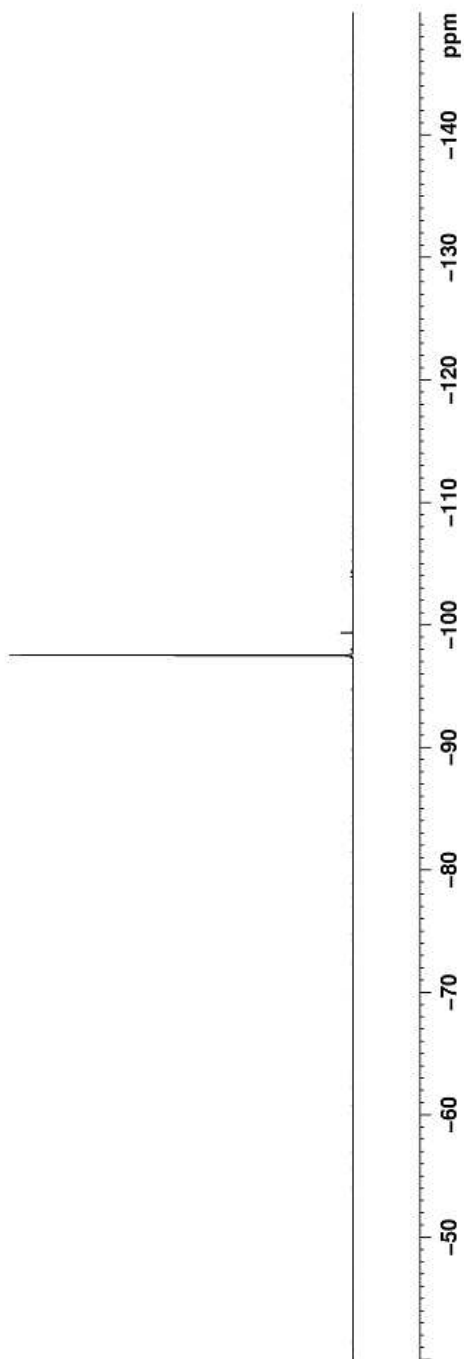
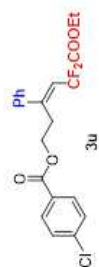


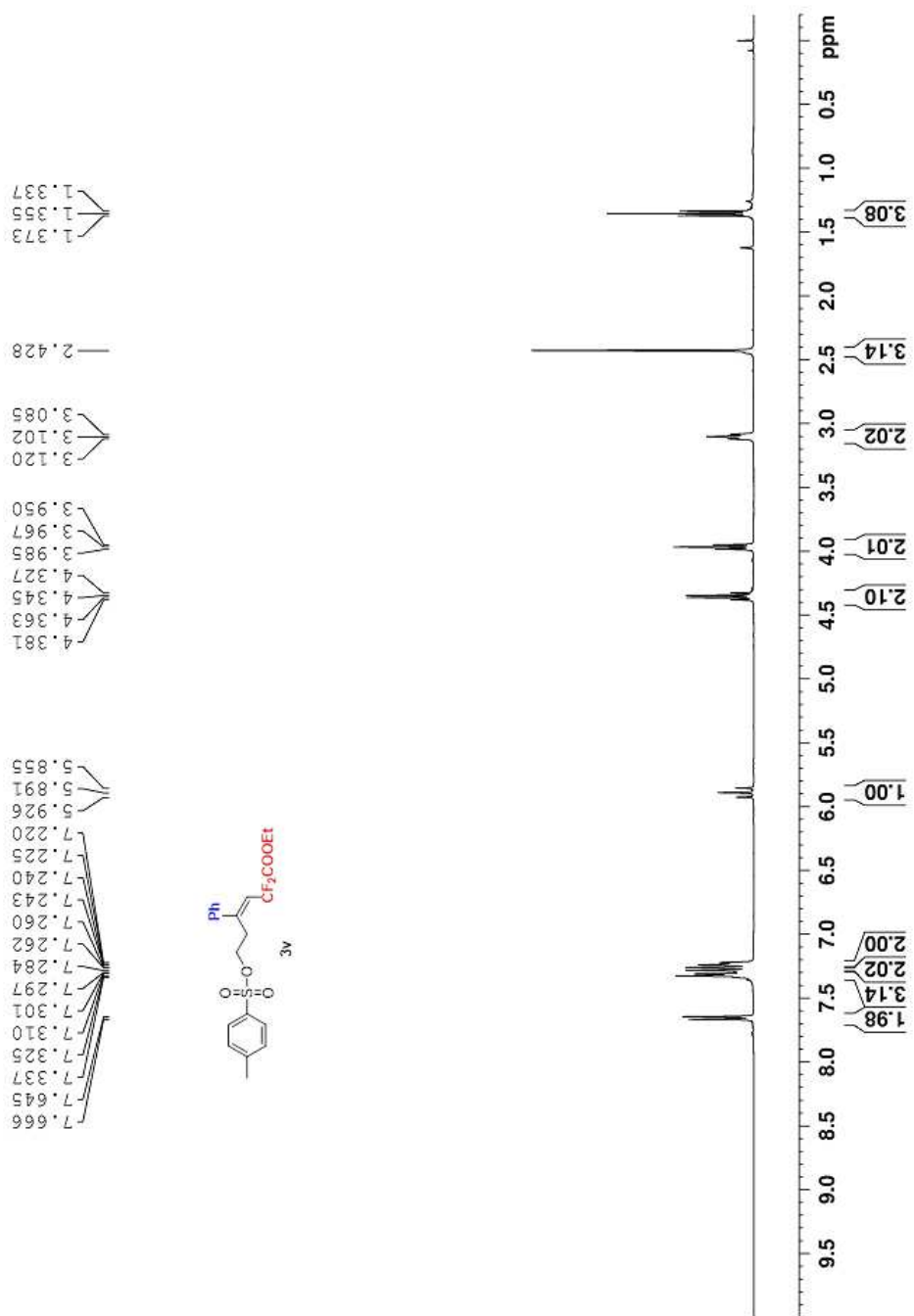


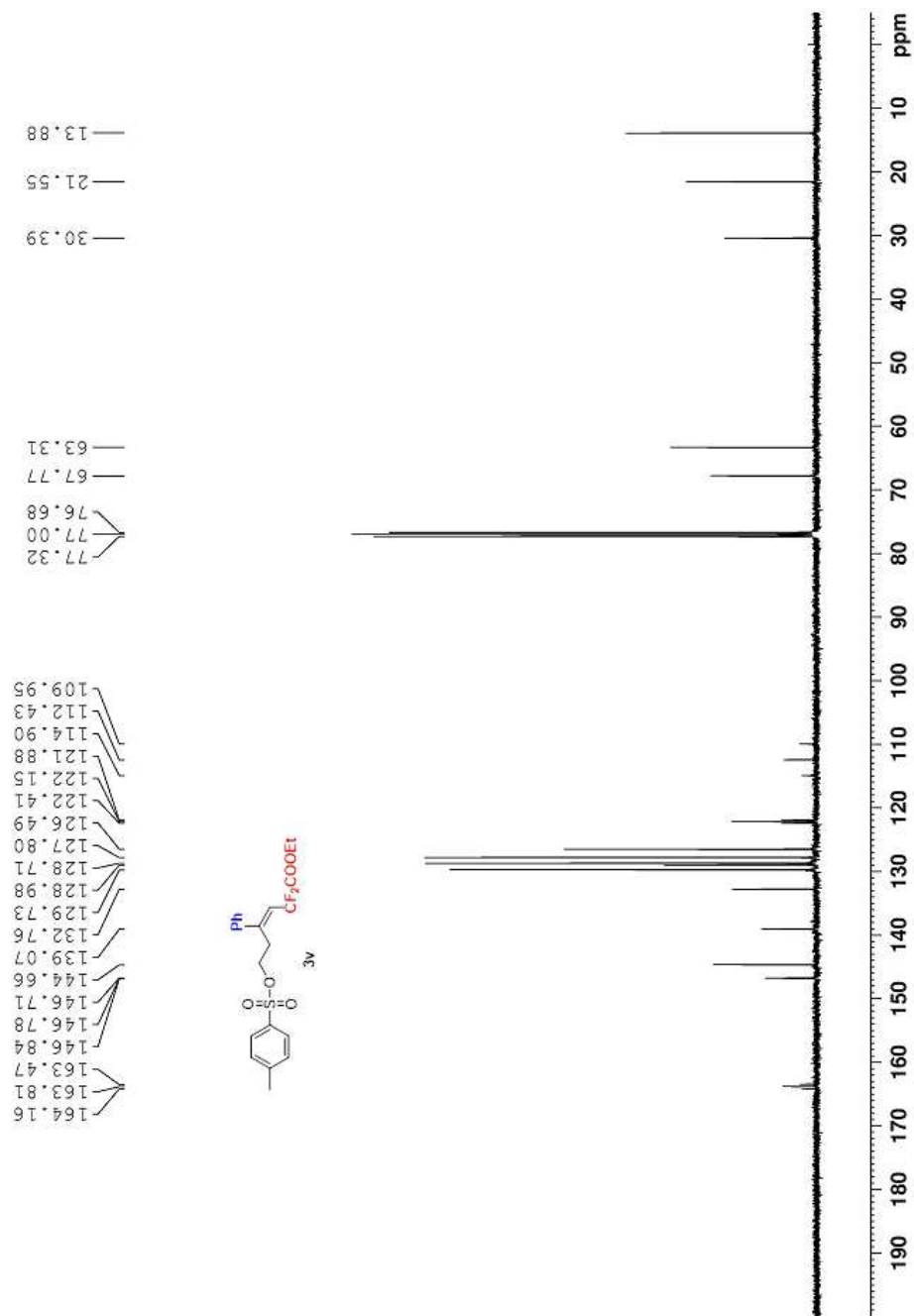


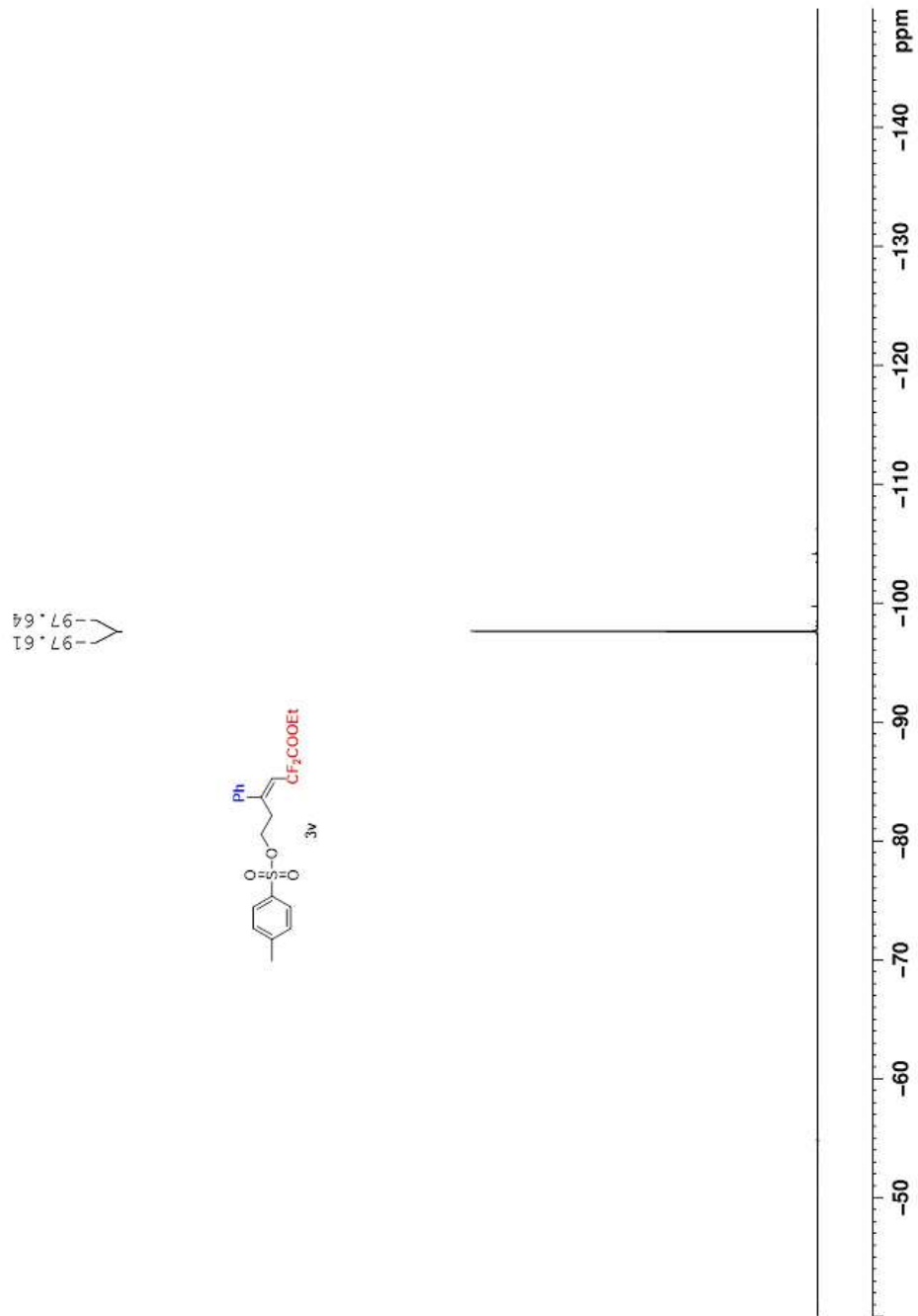


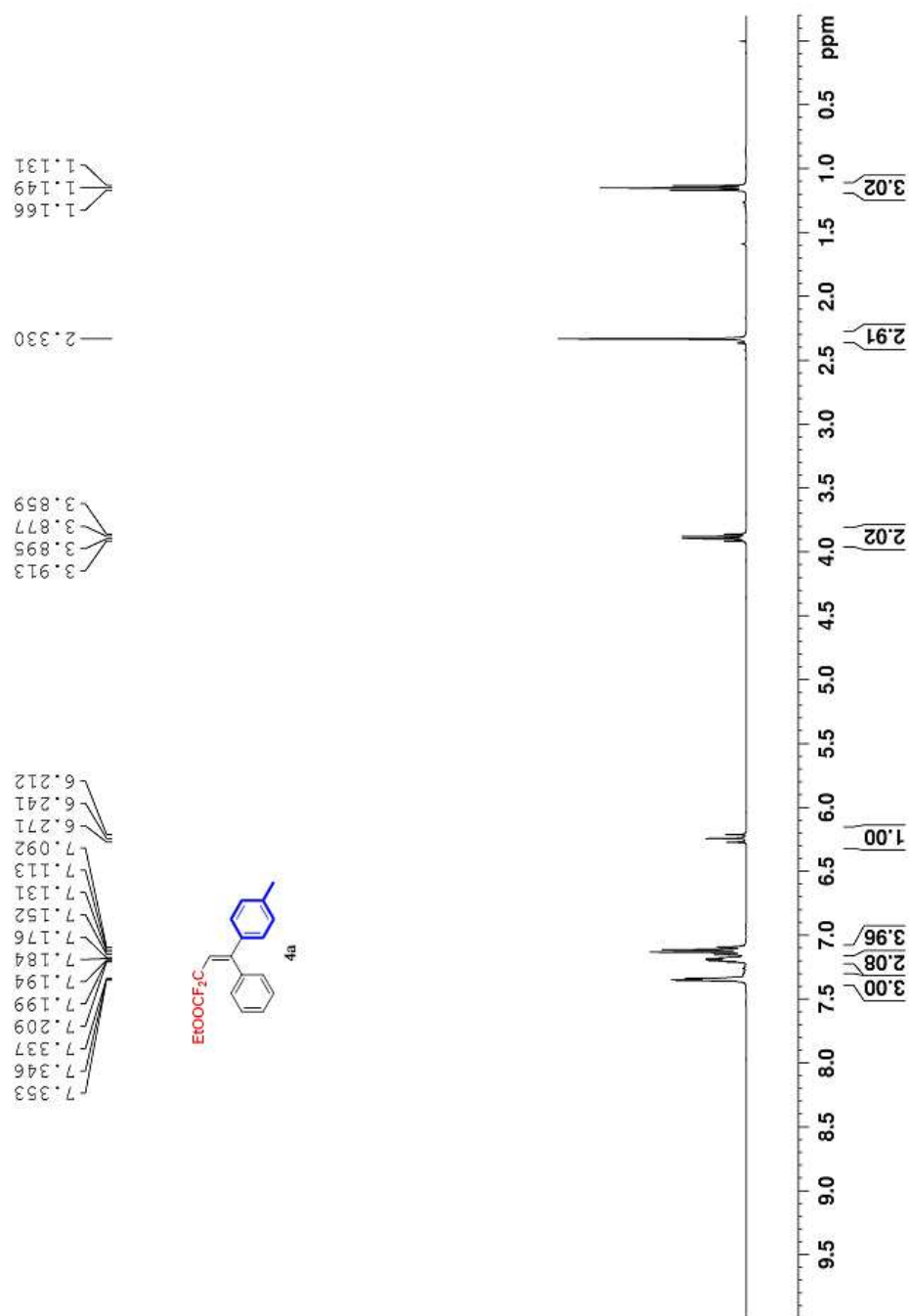
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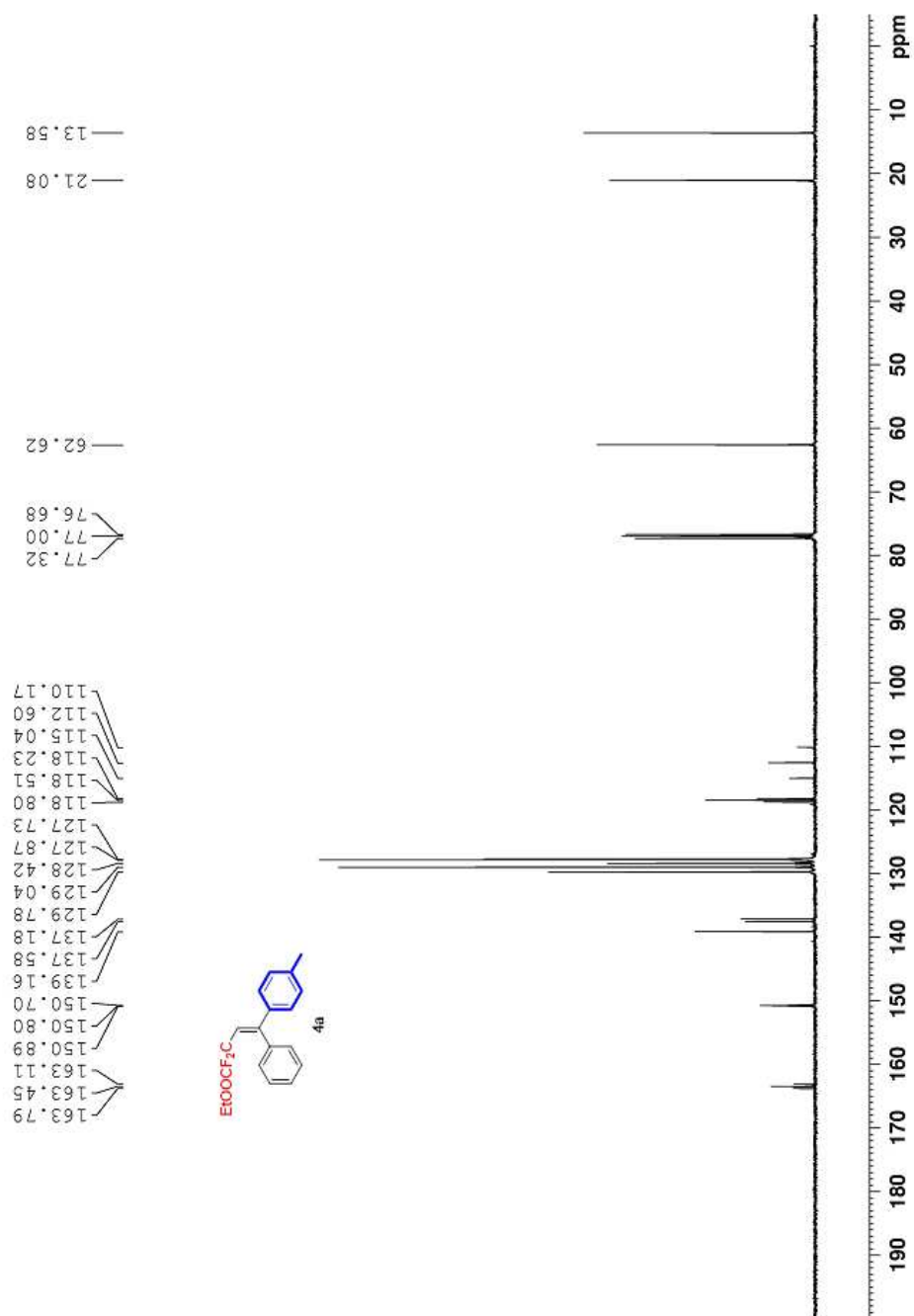


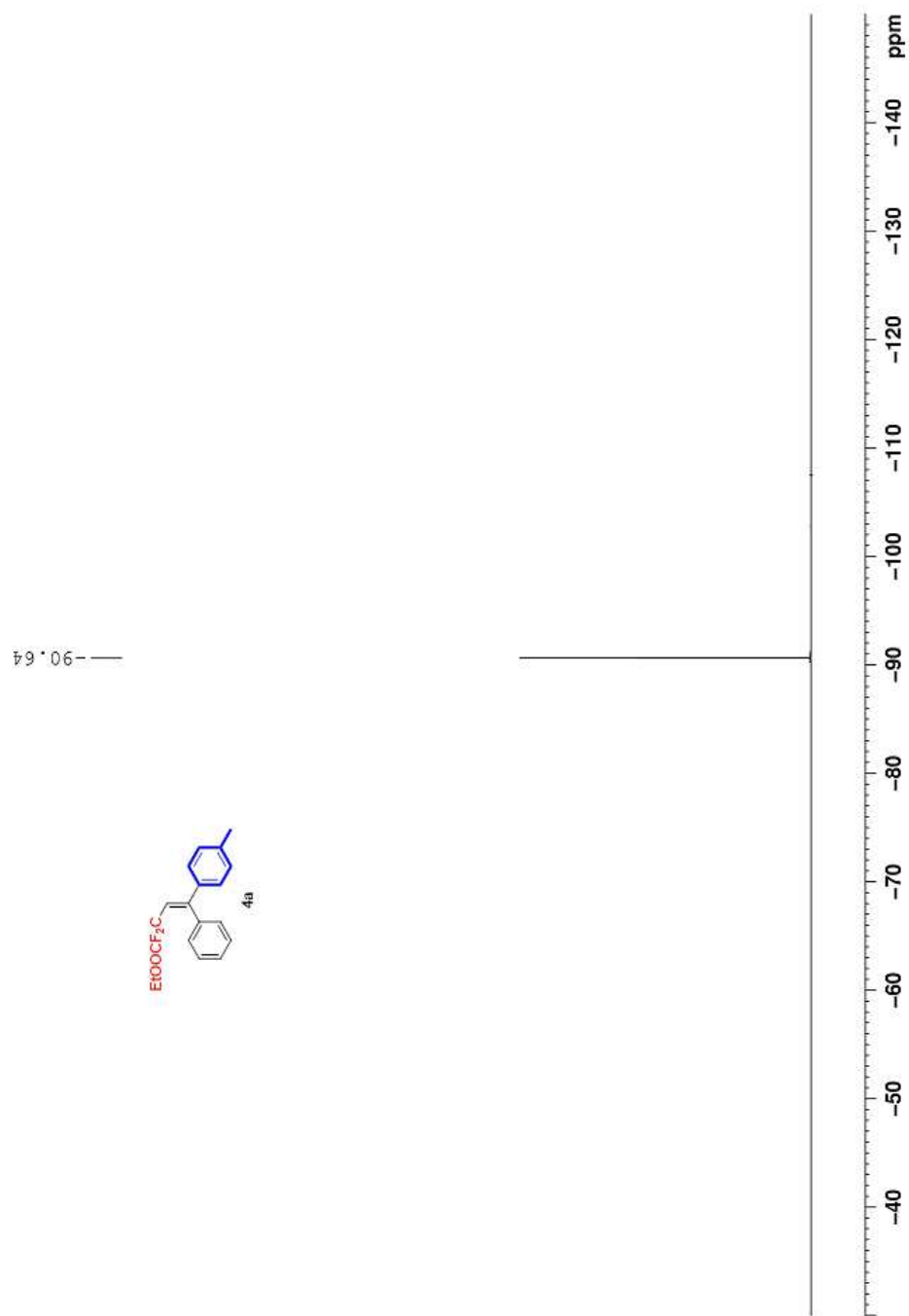


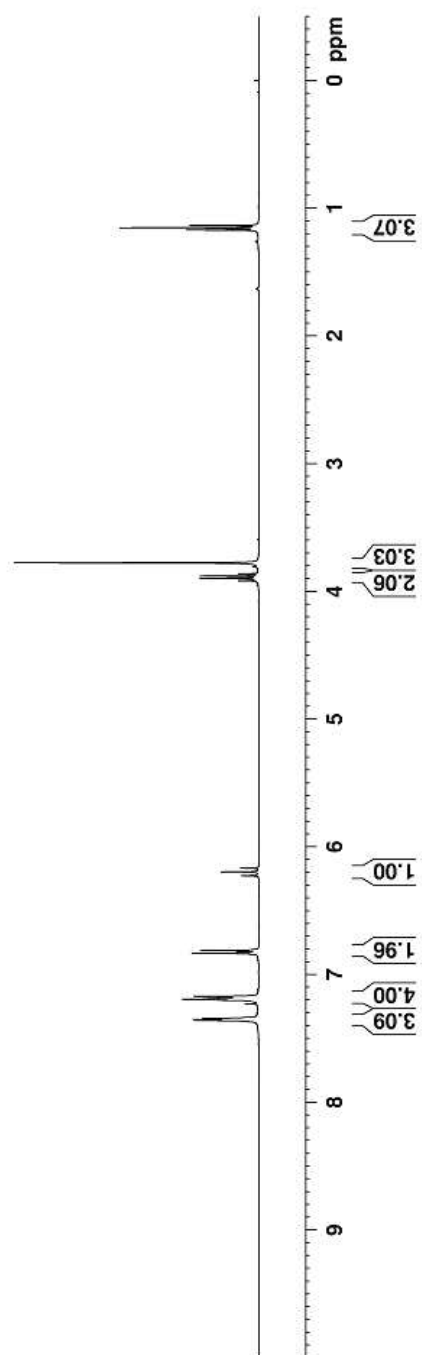








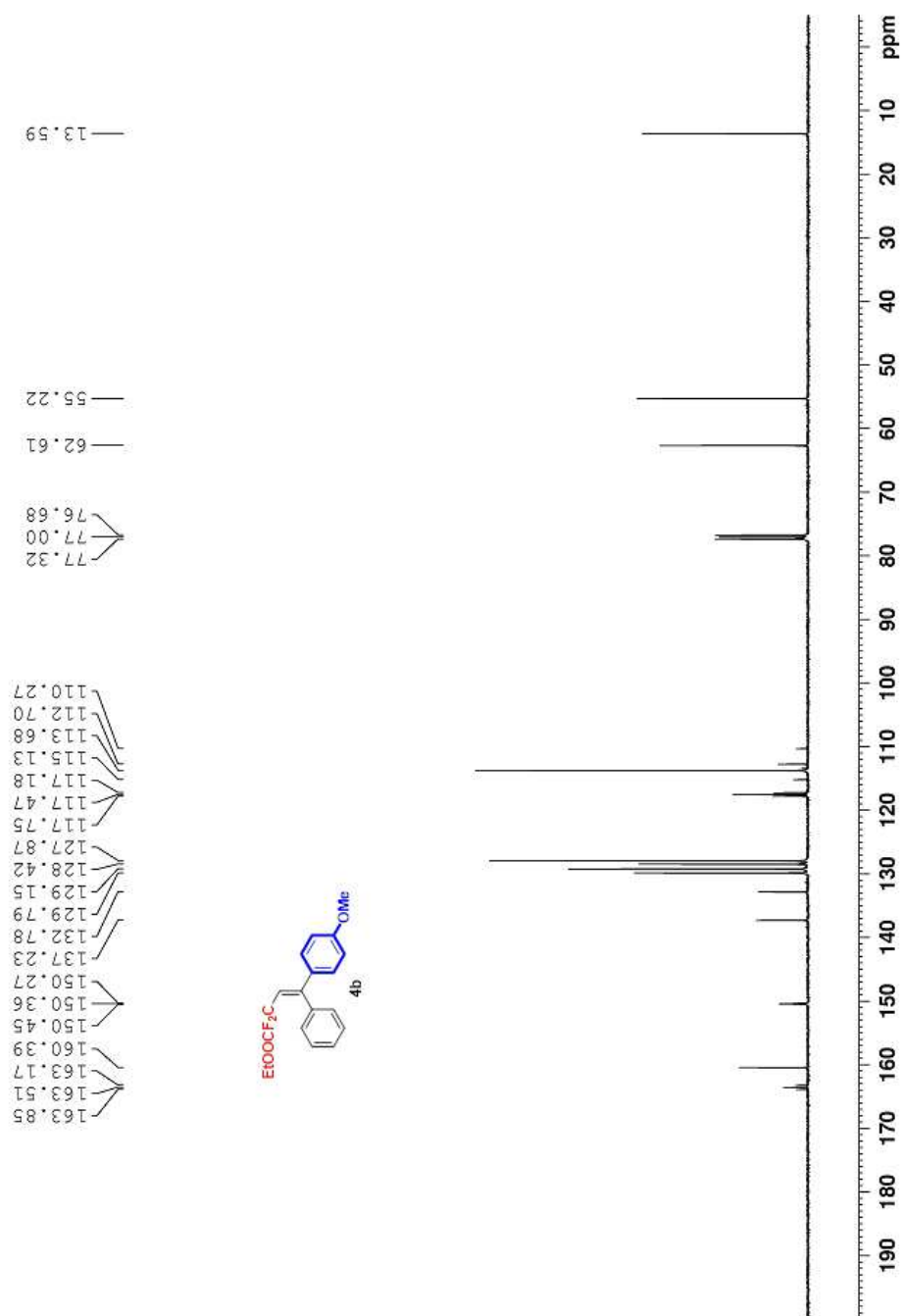


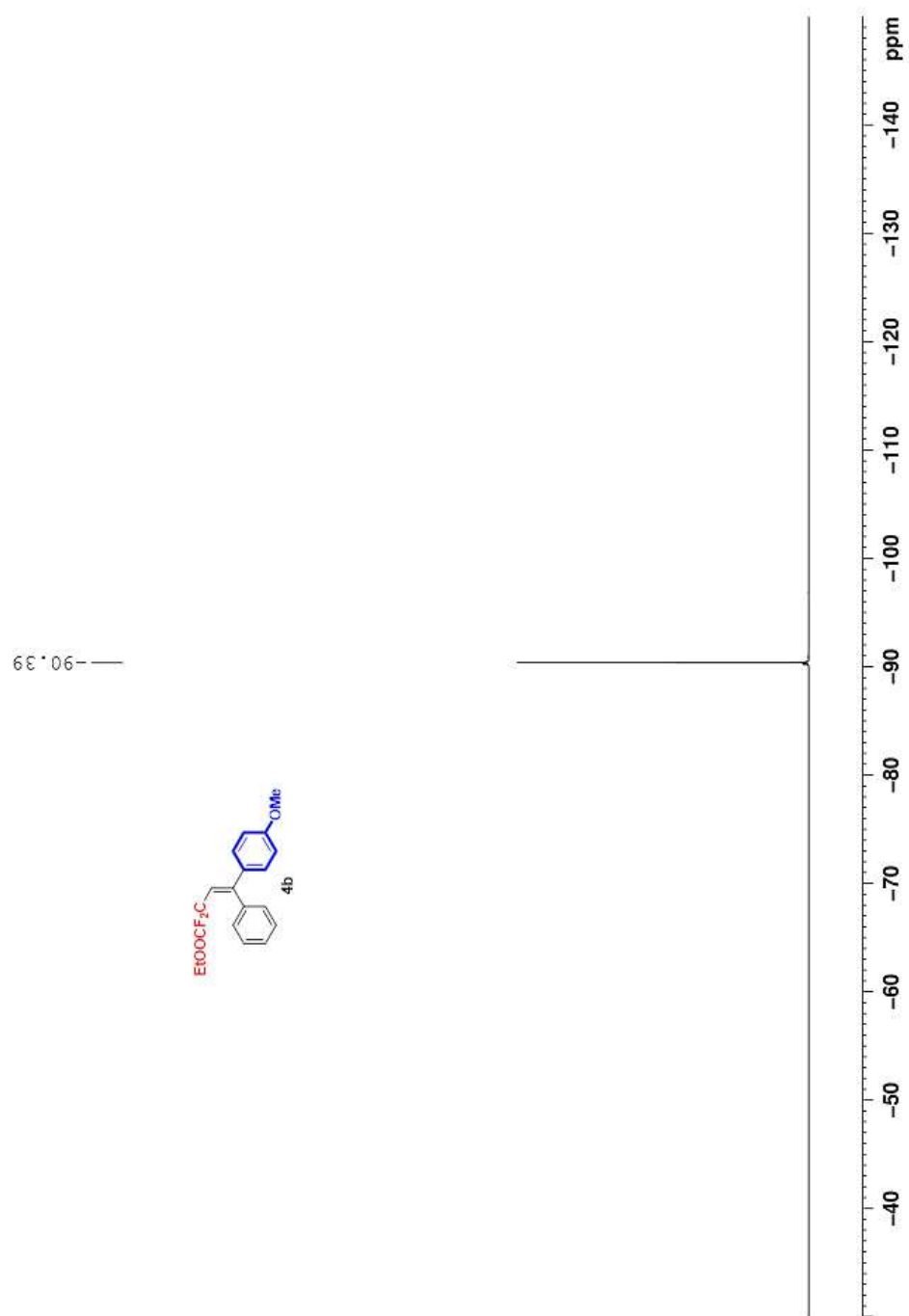


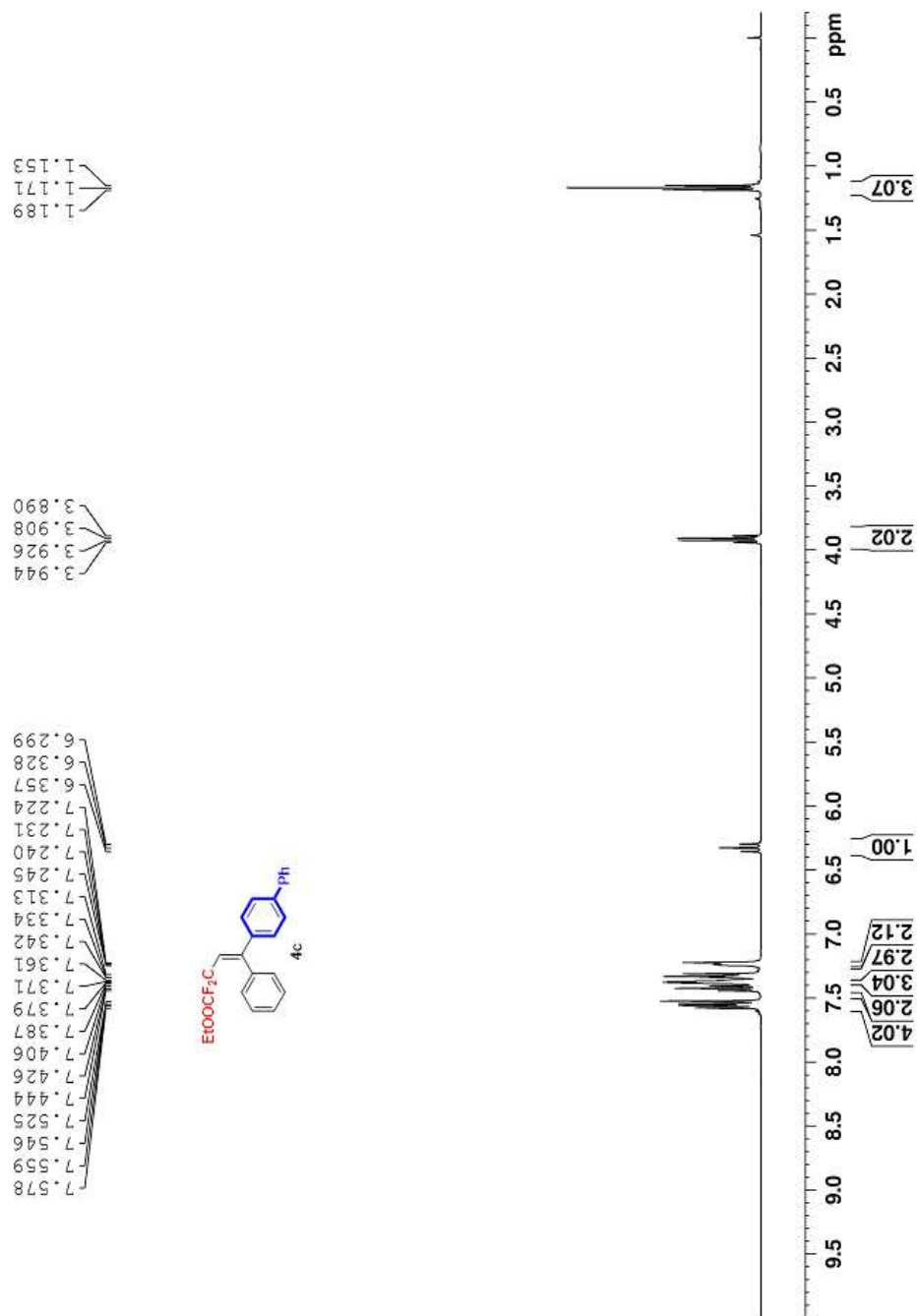
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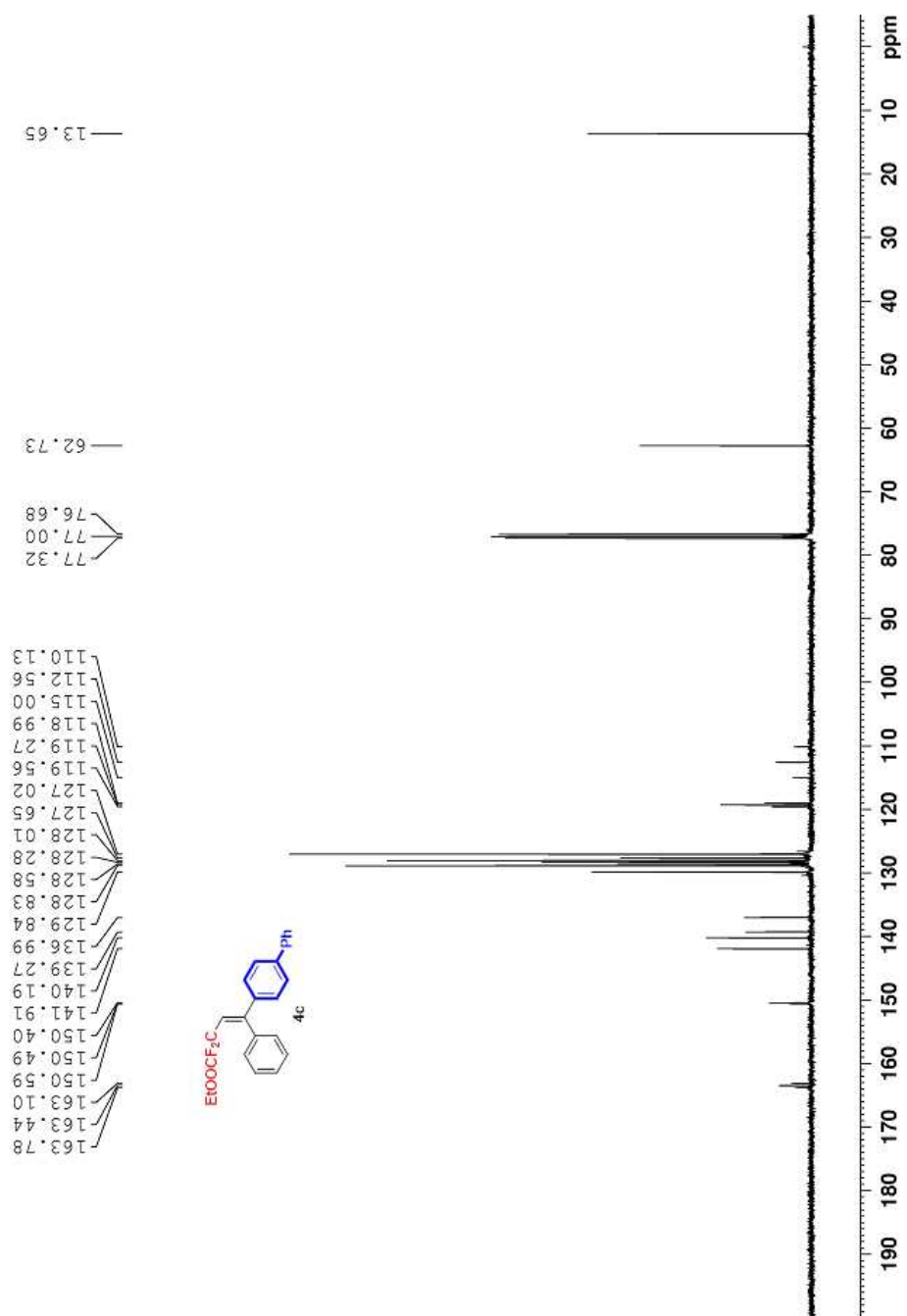
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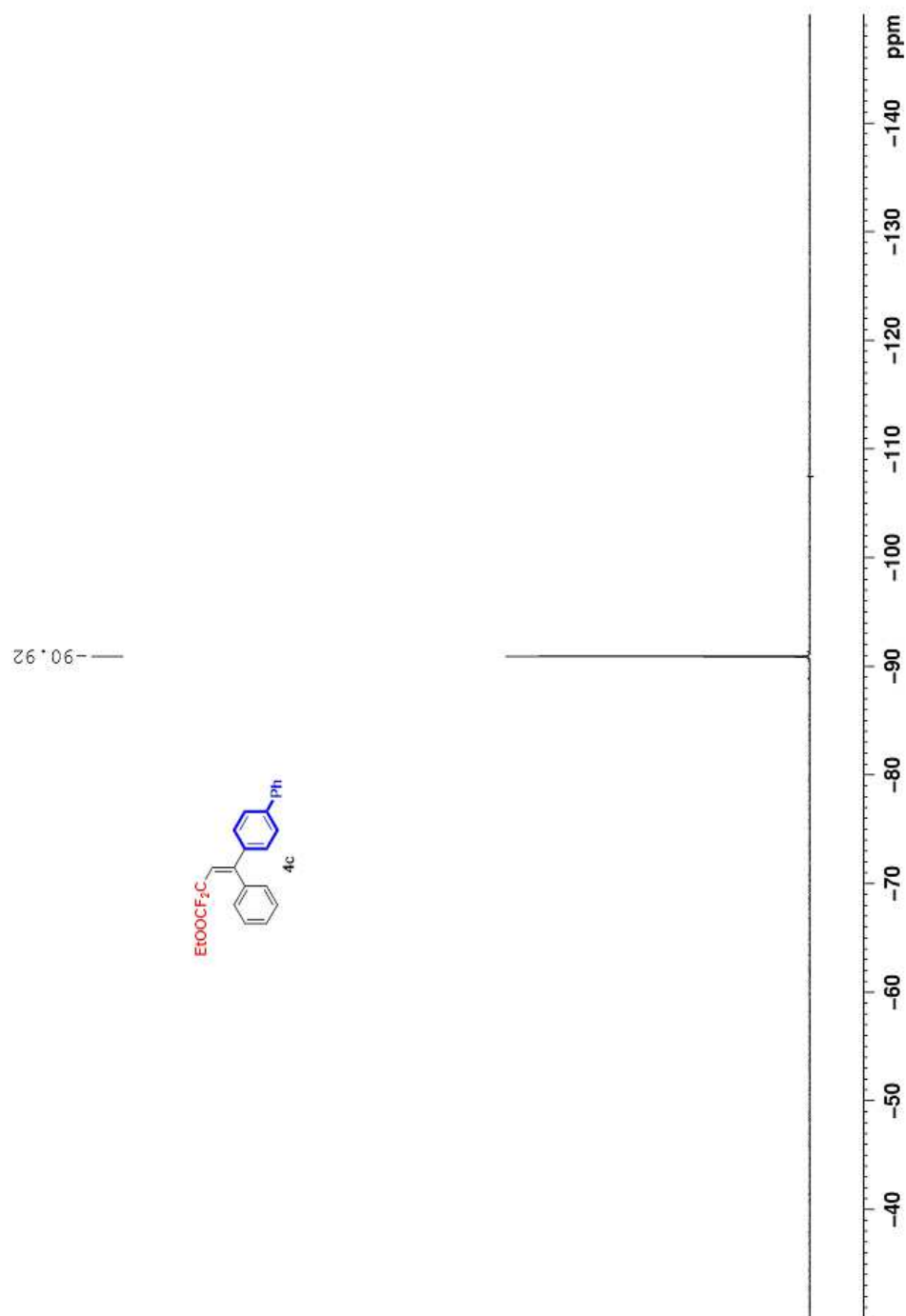
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6.196
6.167

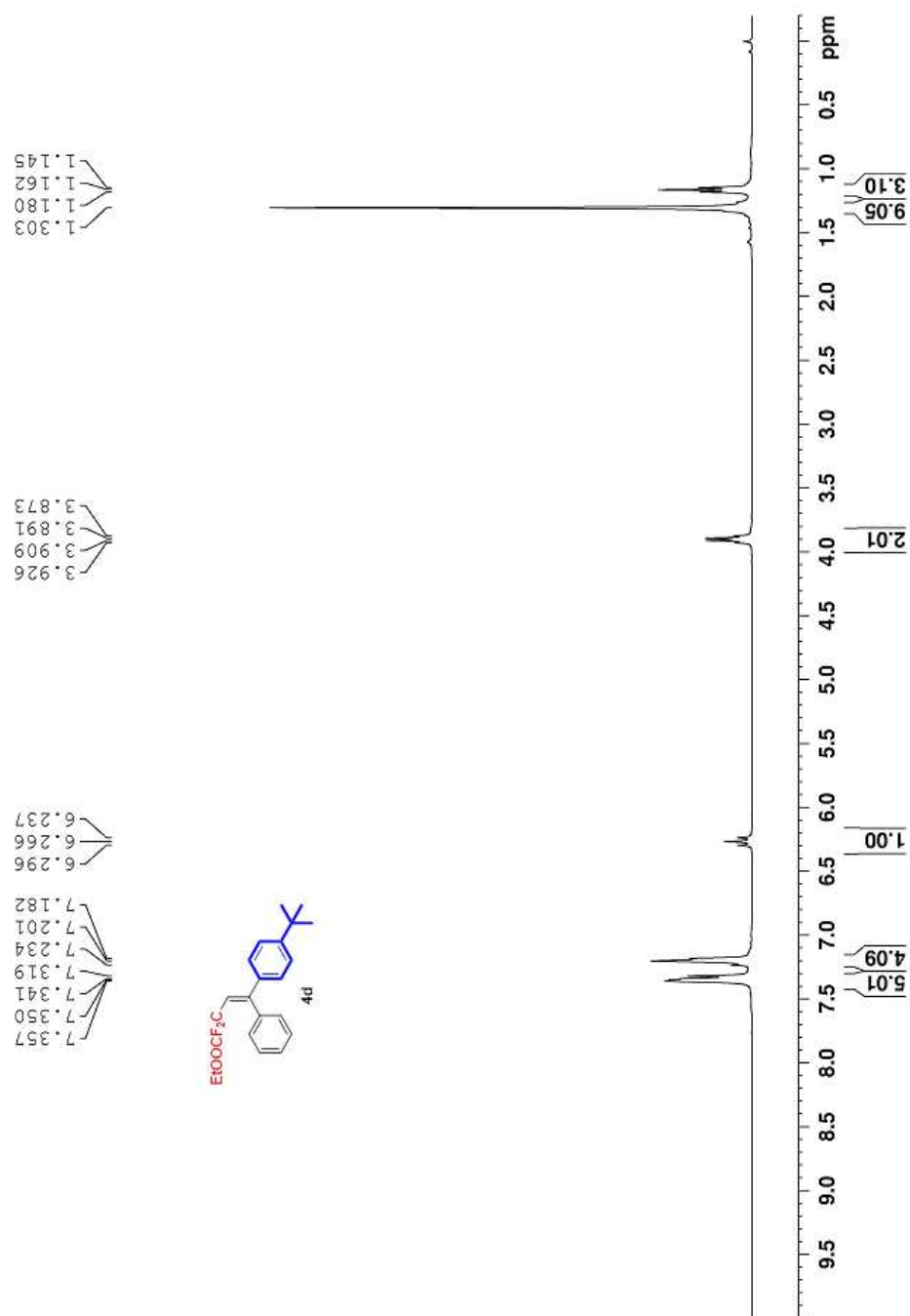


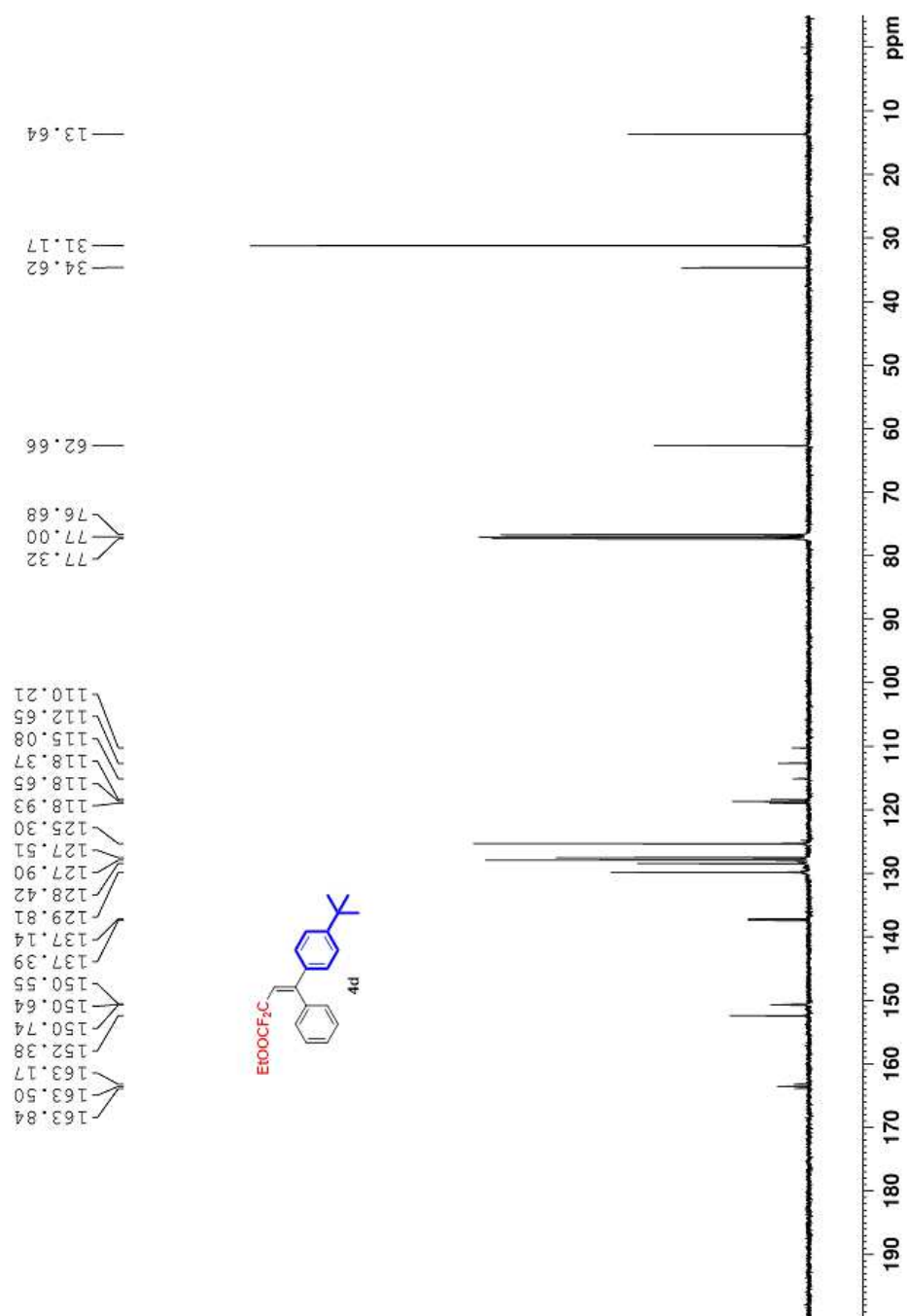


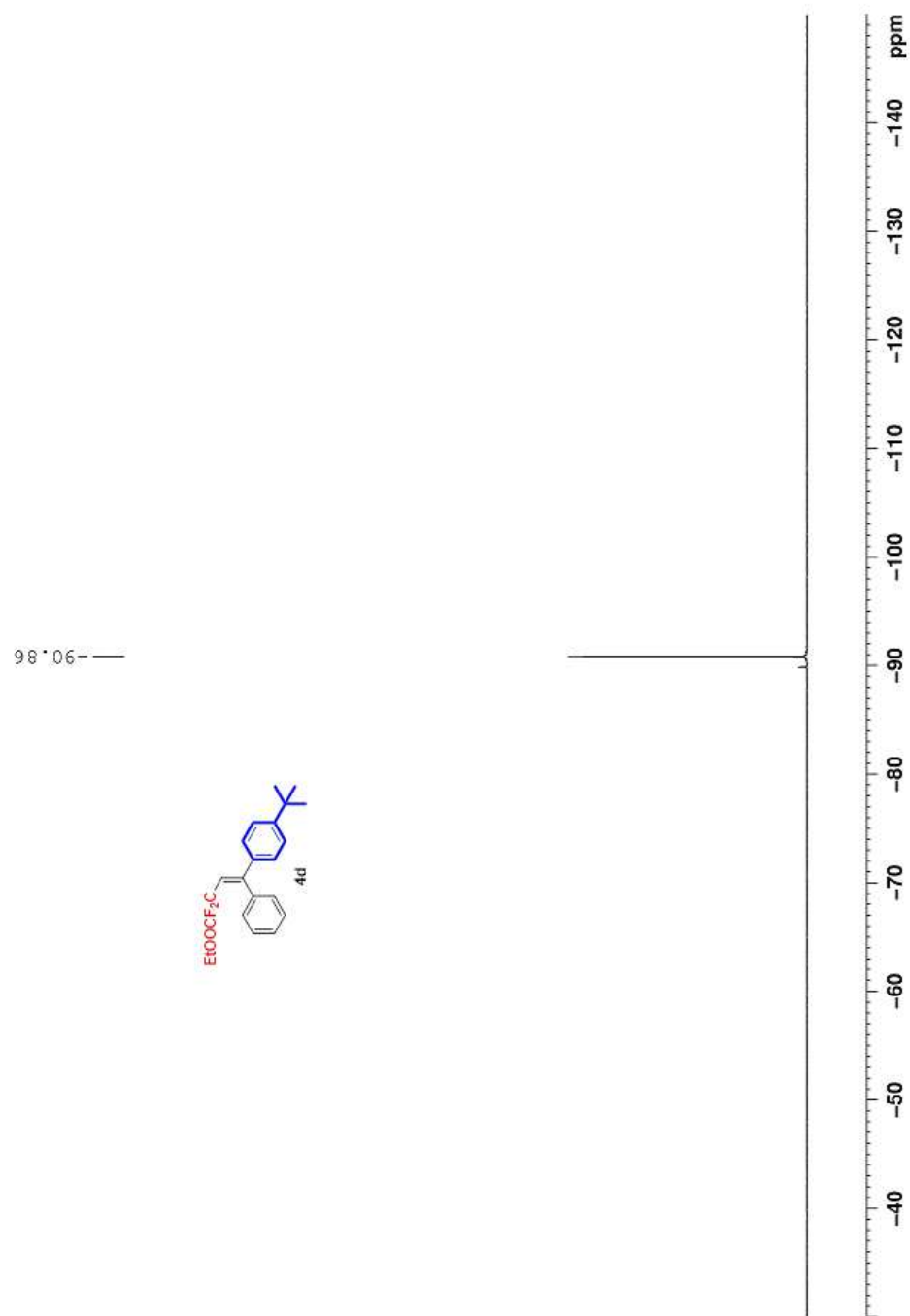


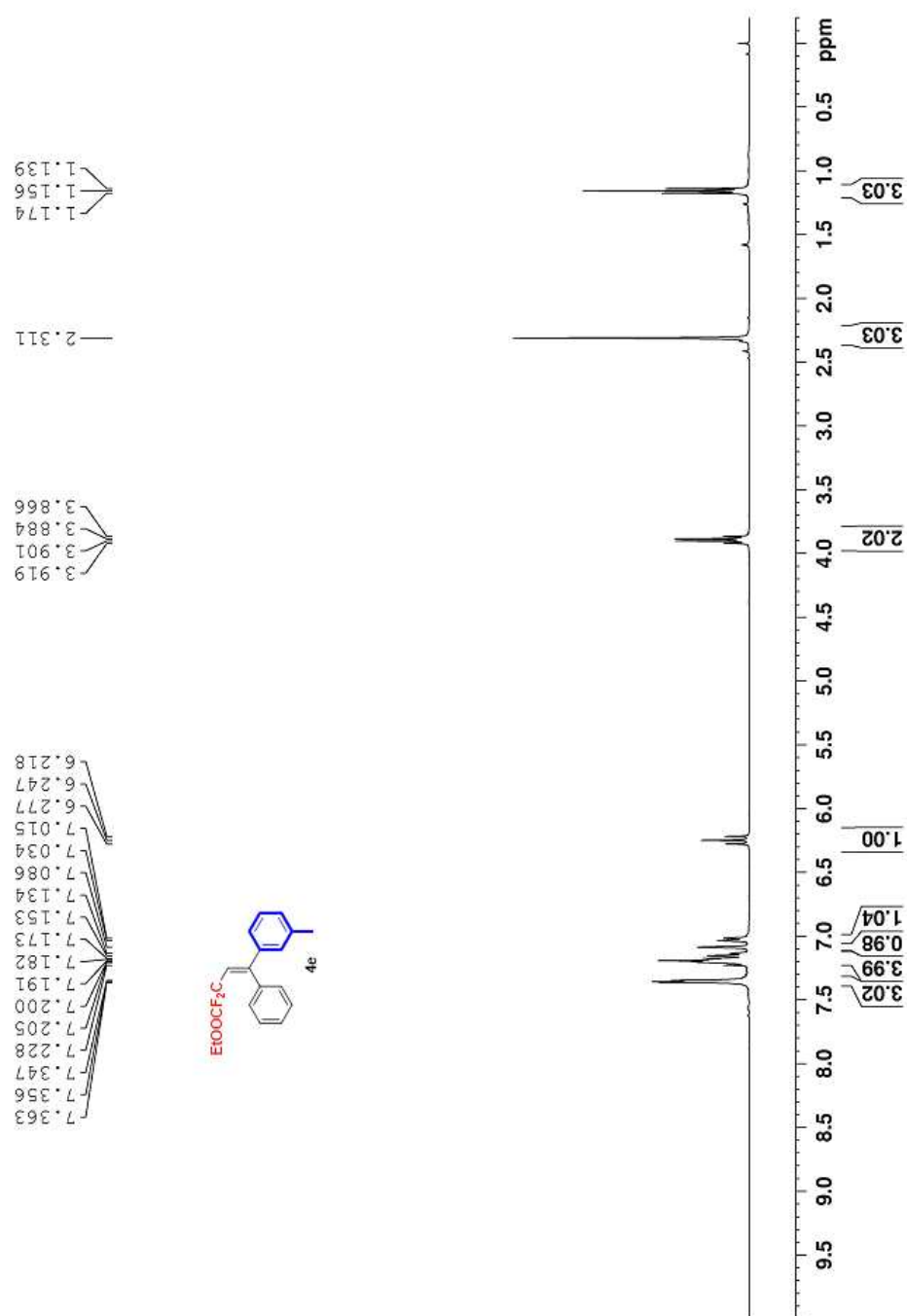


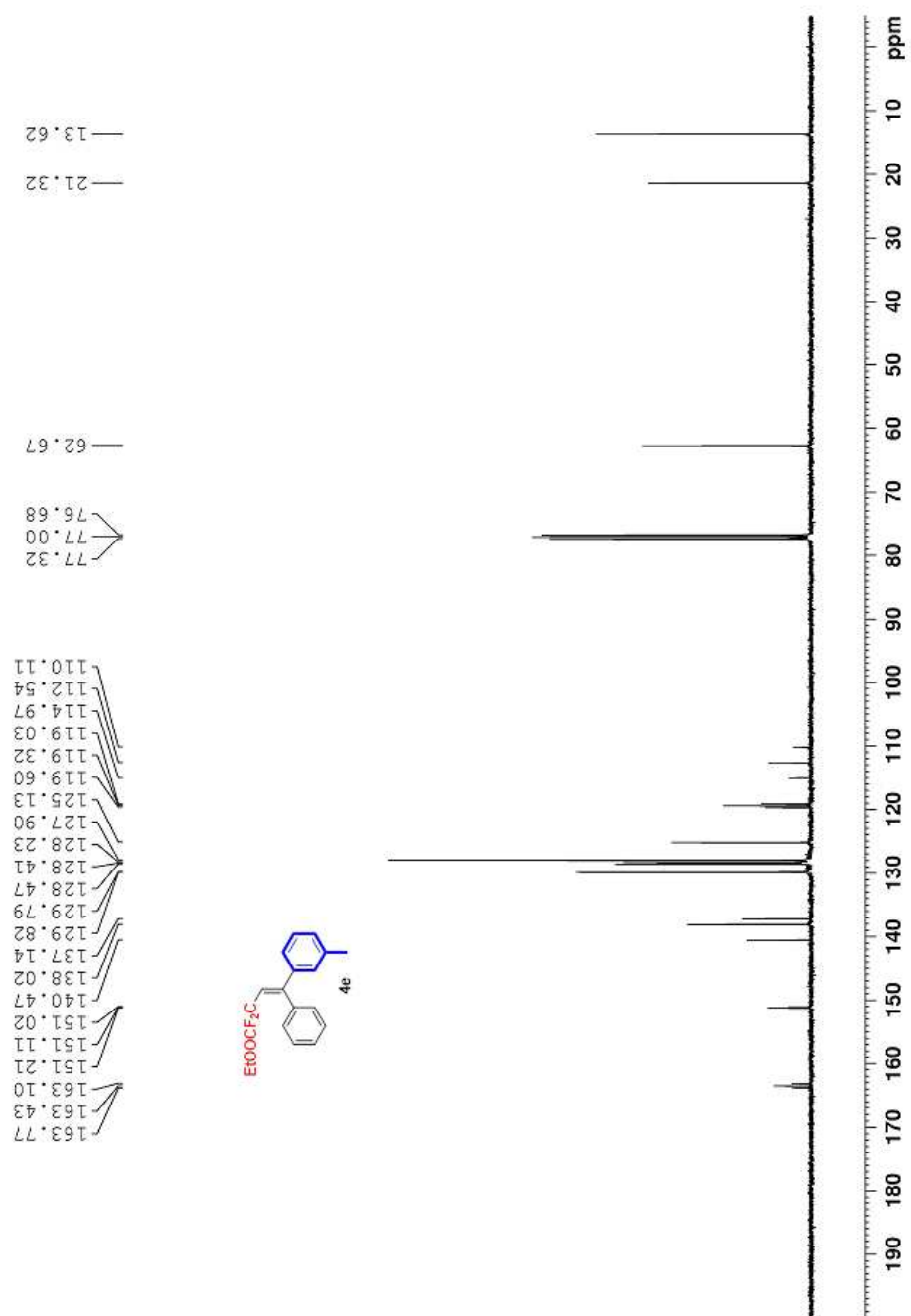


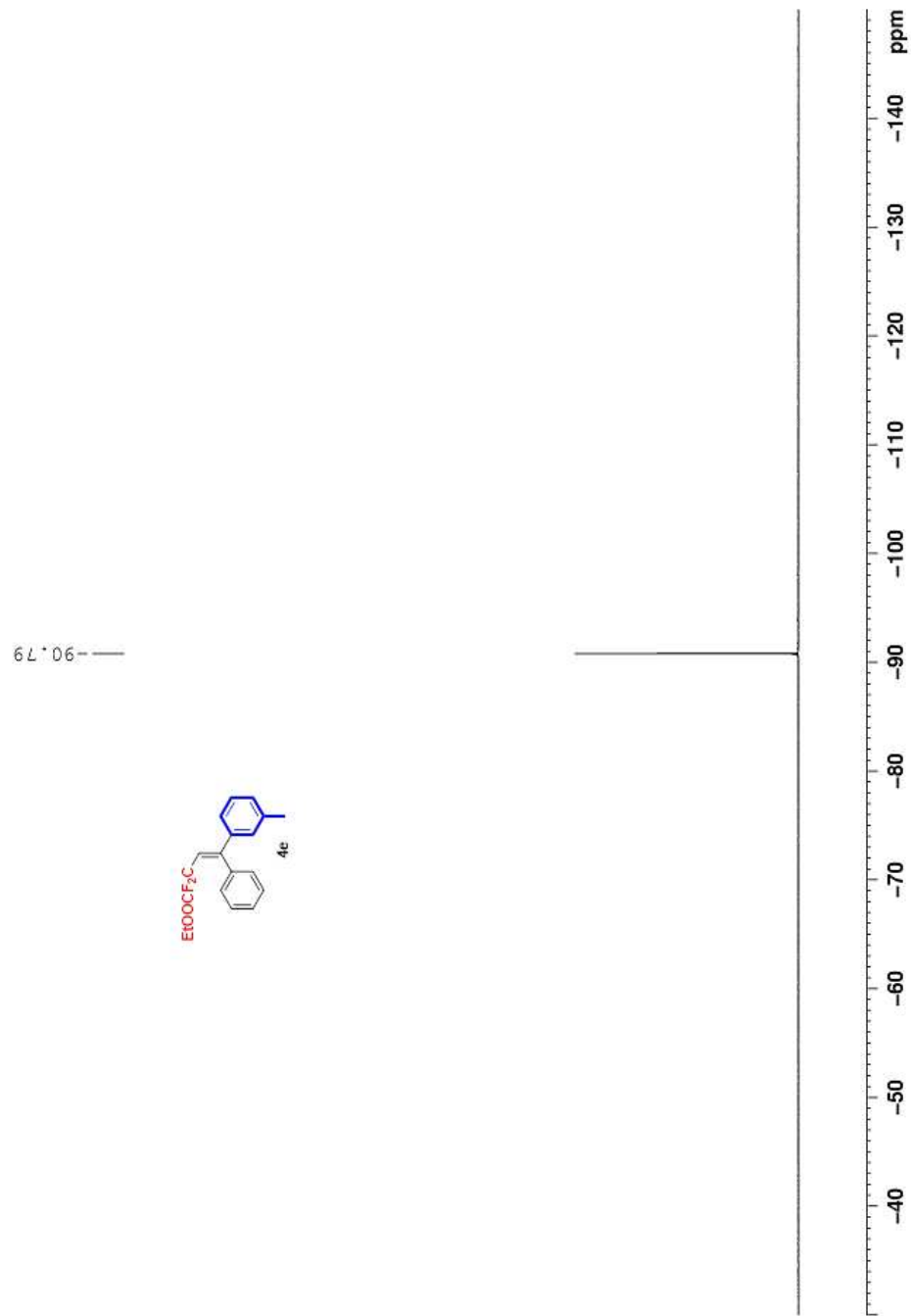


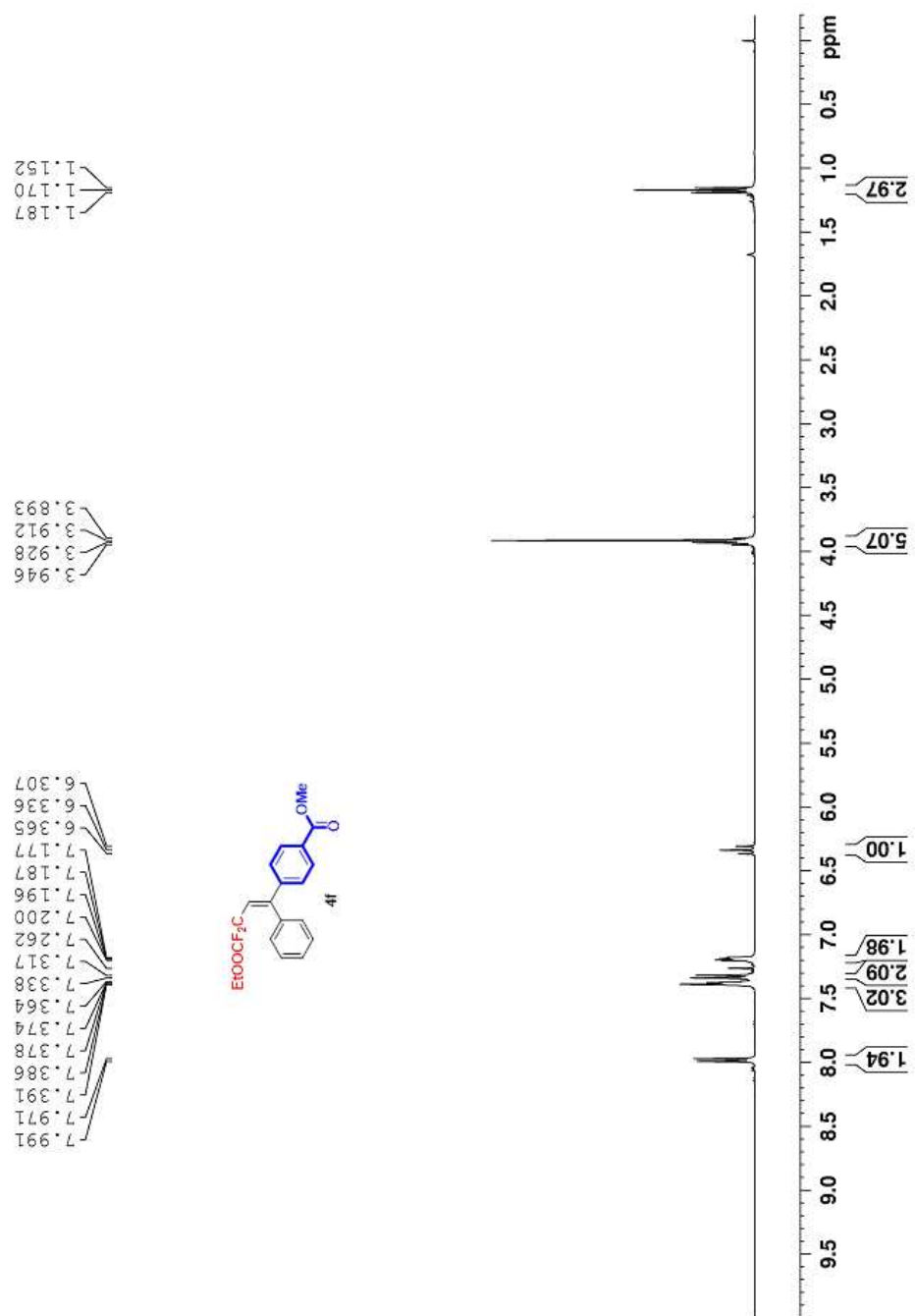


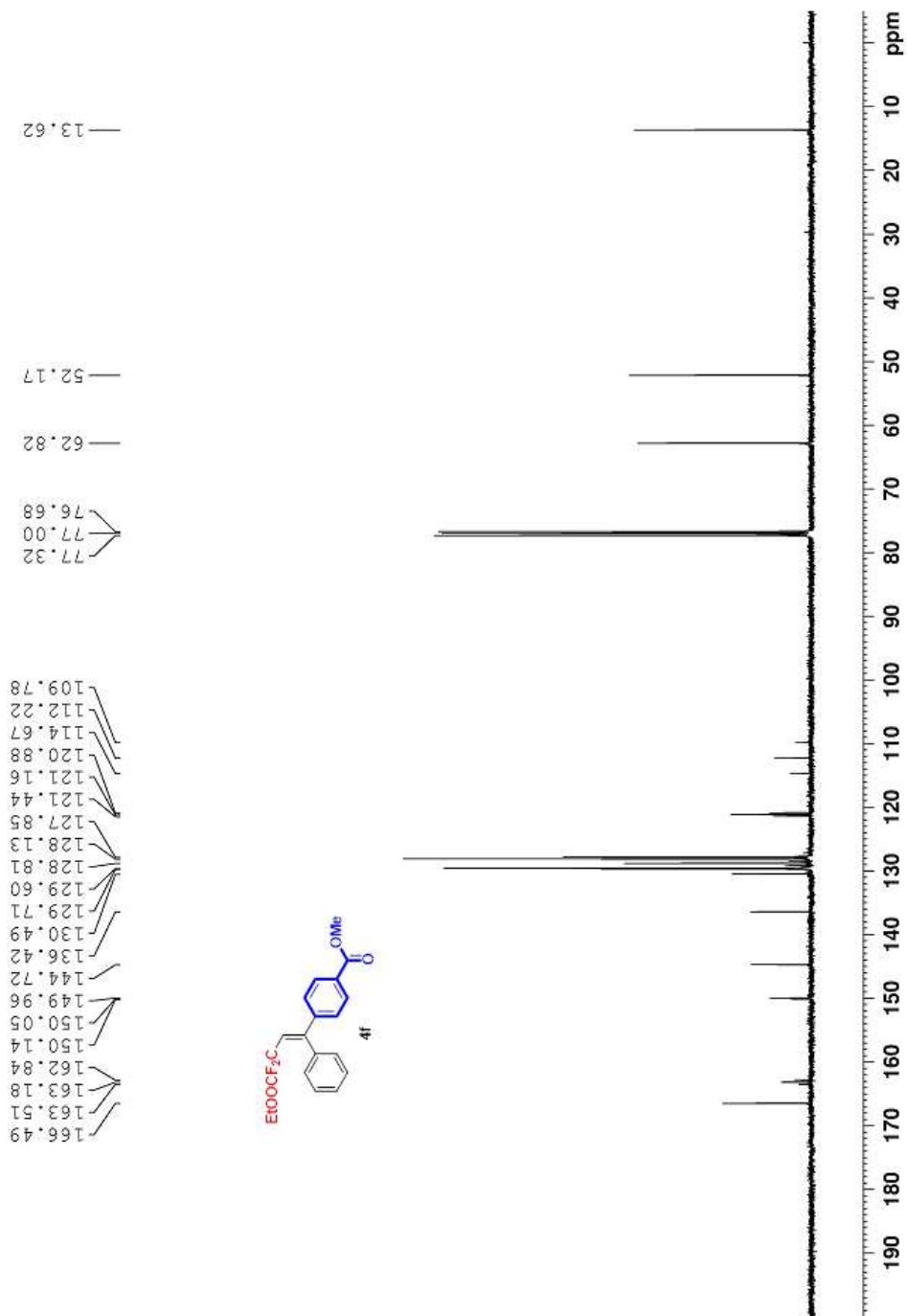


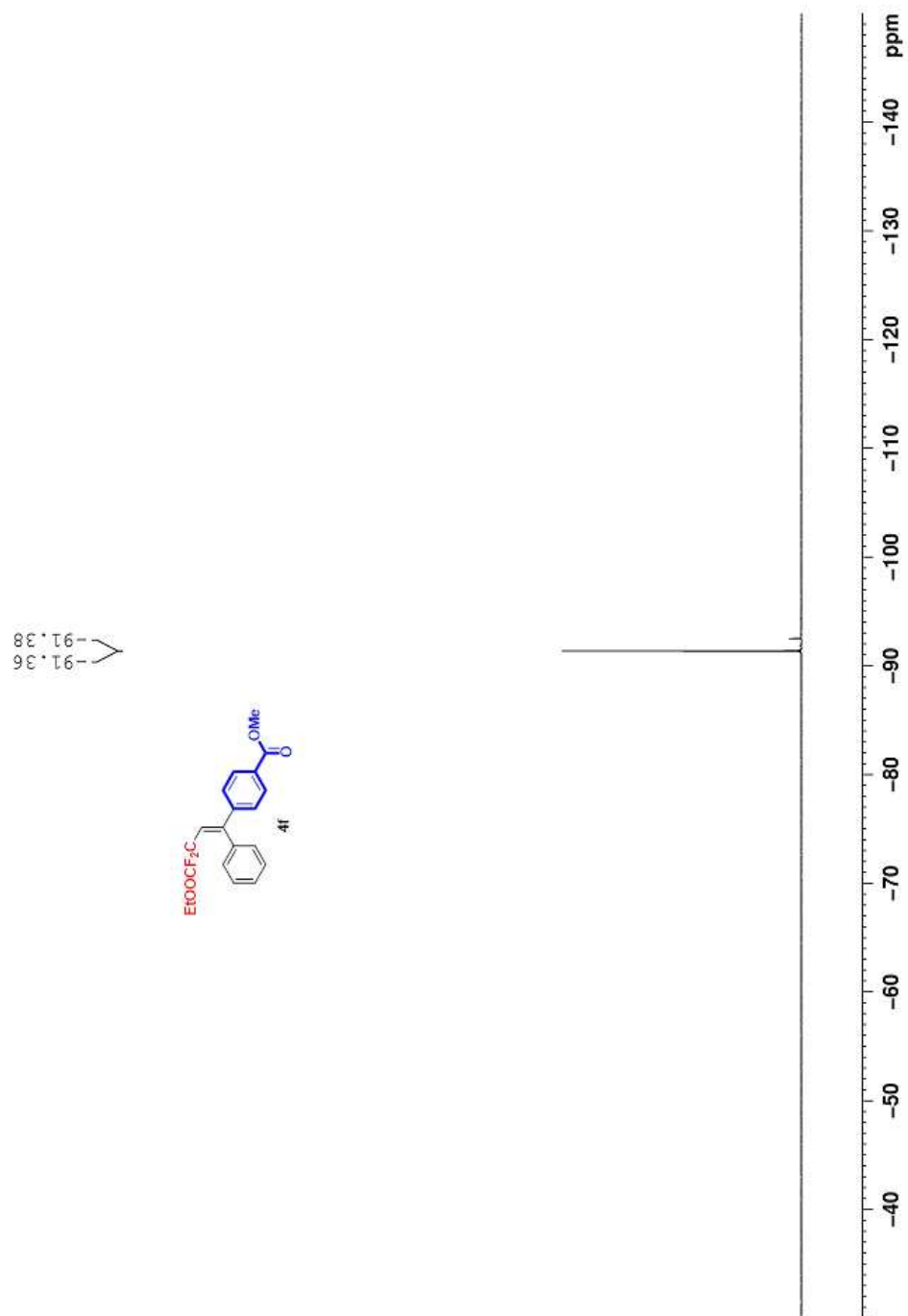


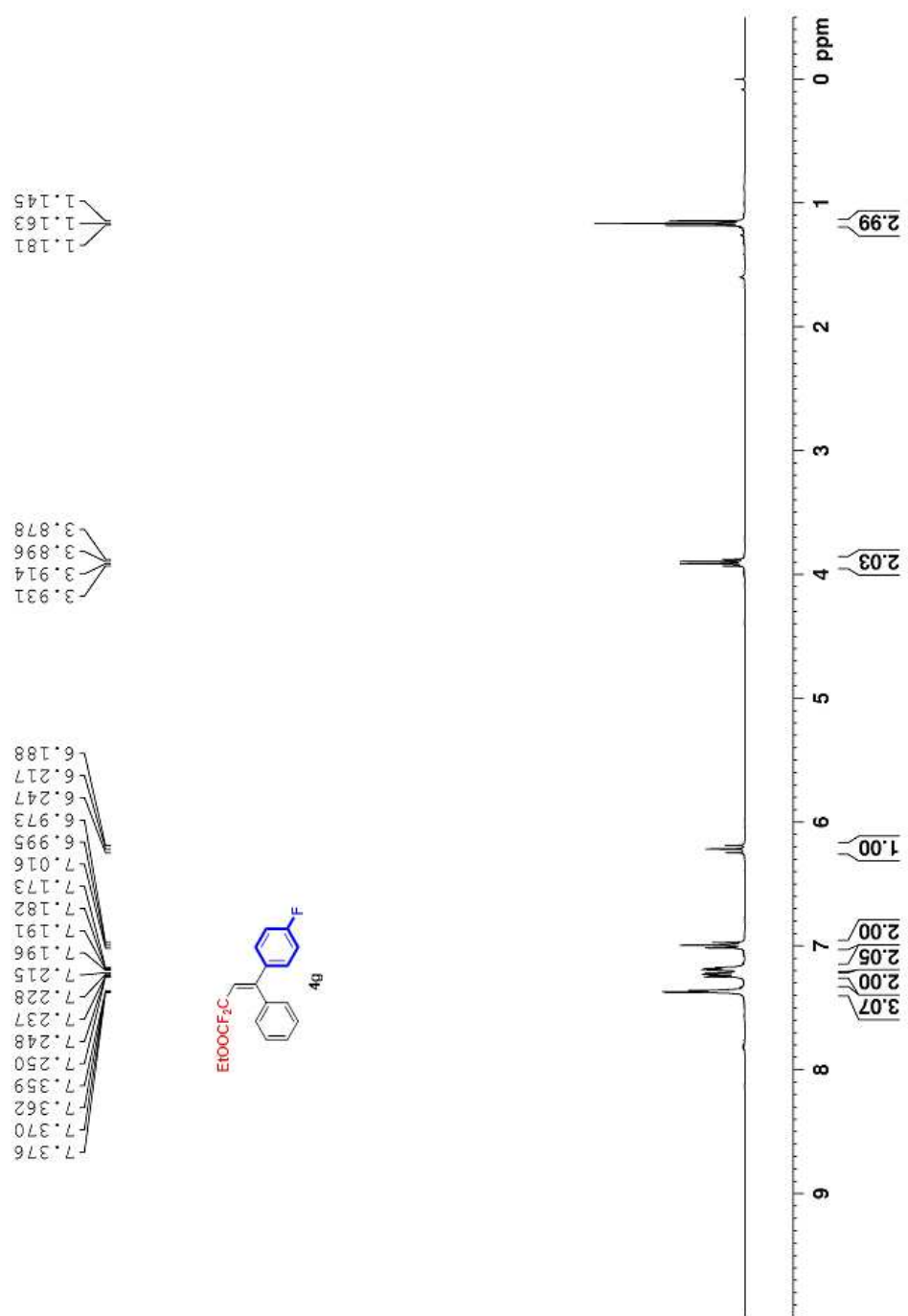


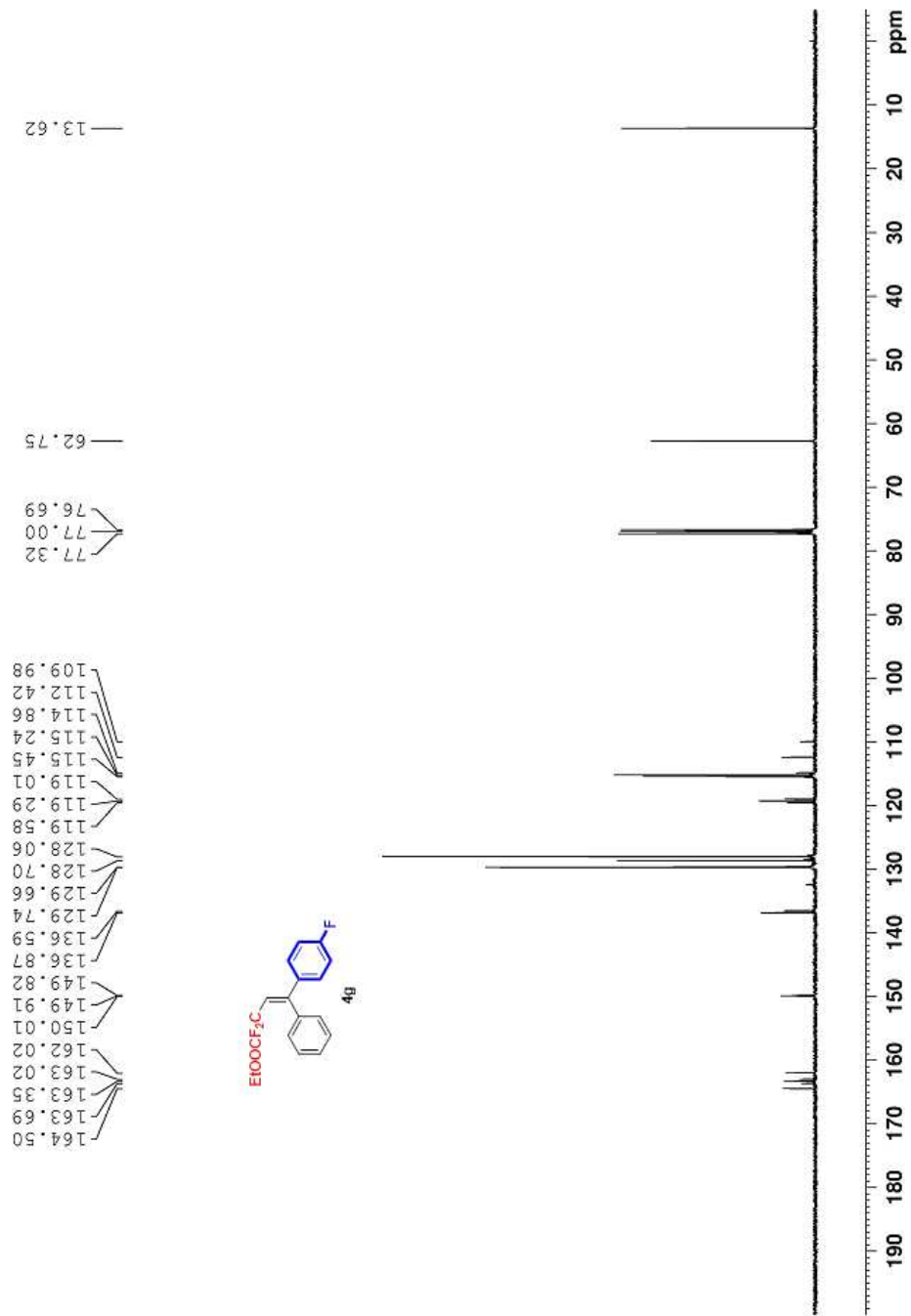




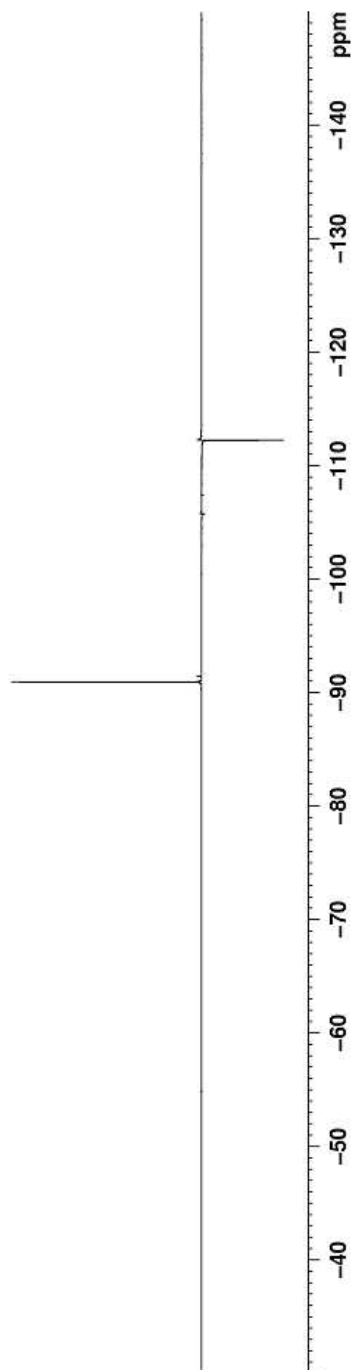


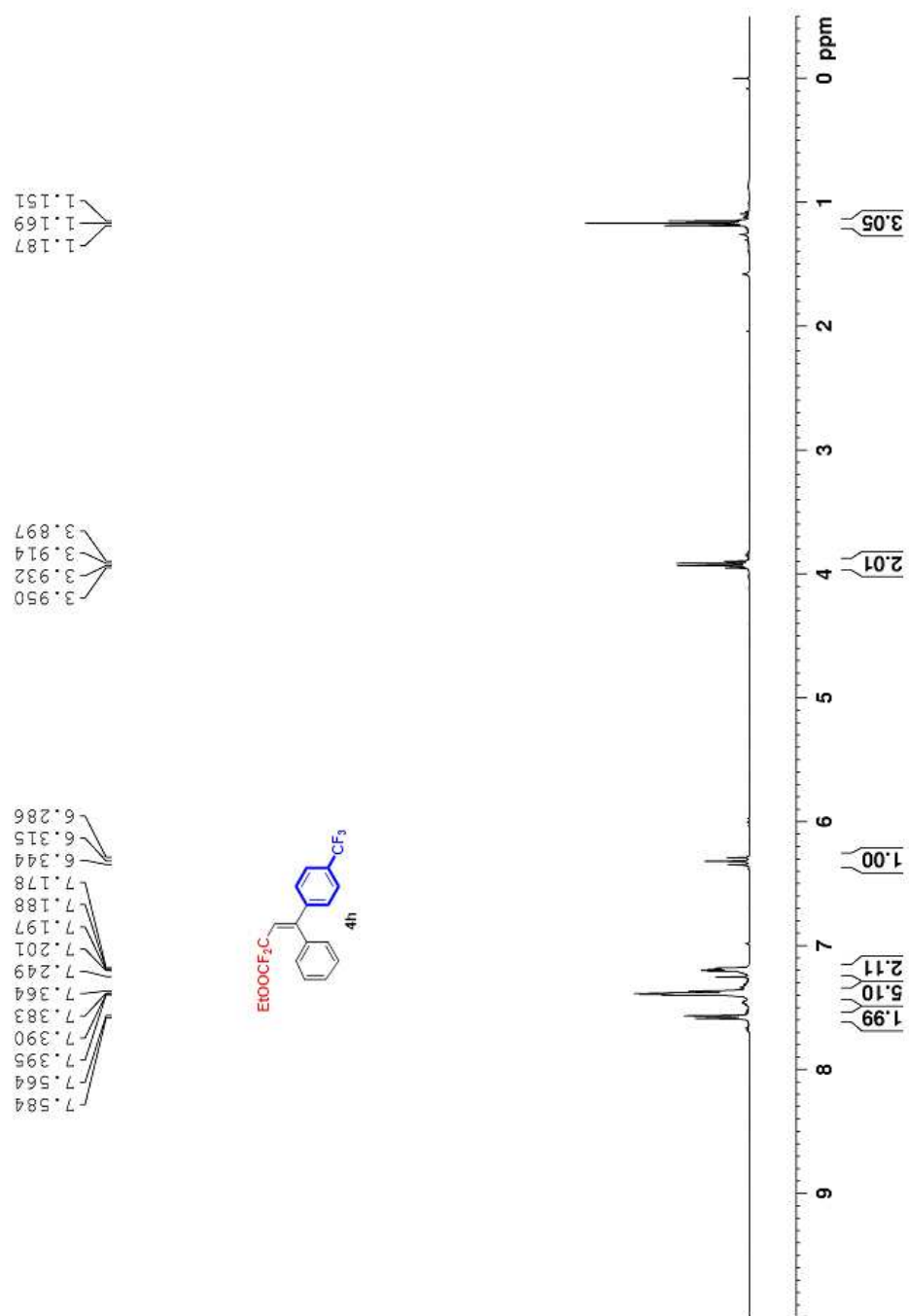


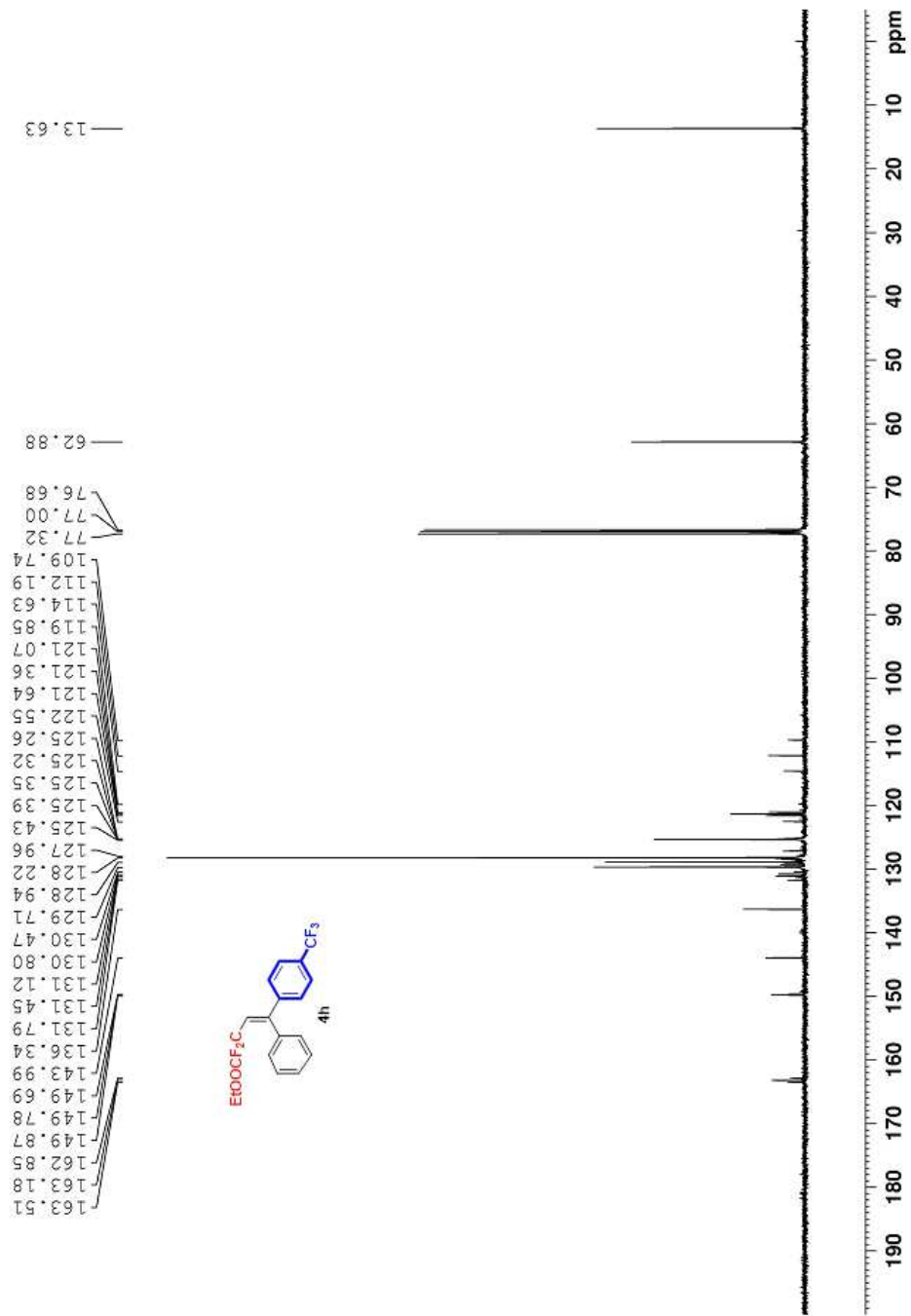




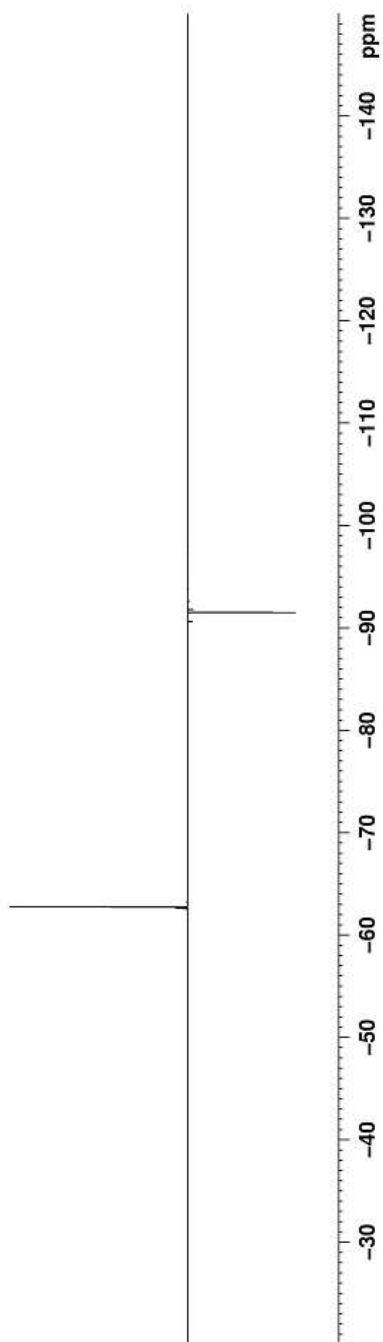
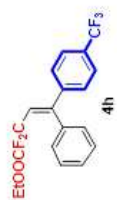
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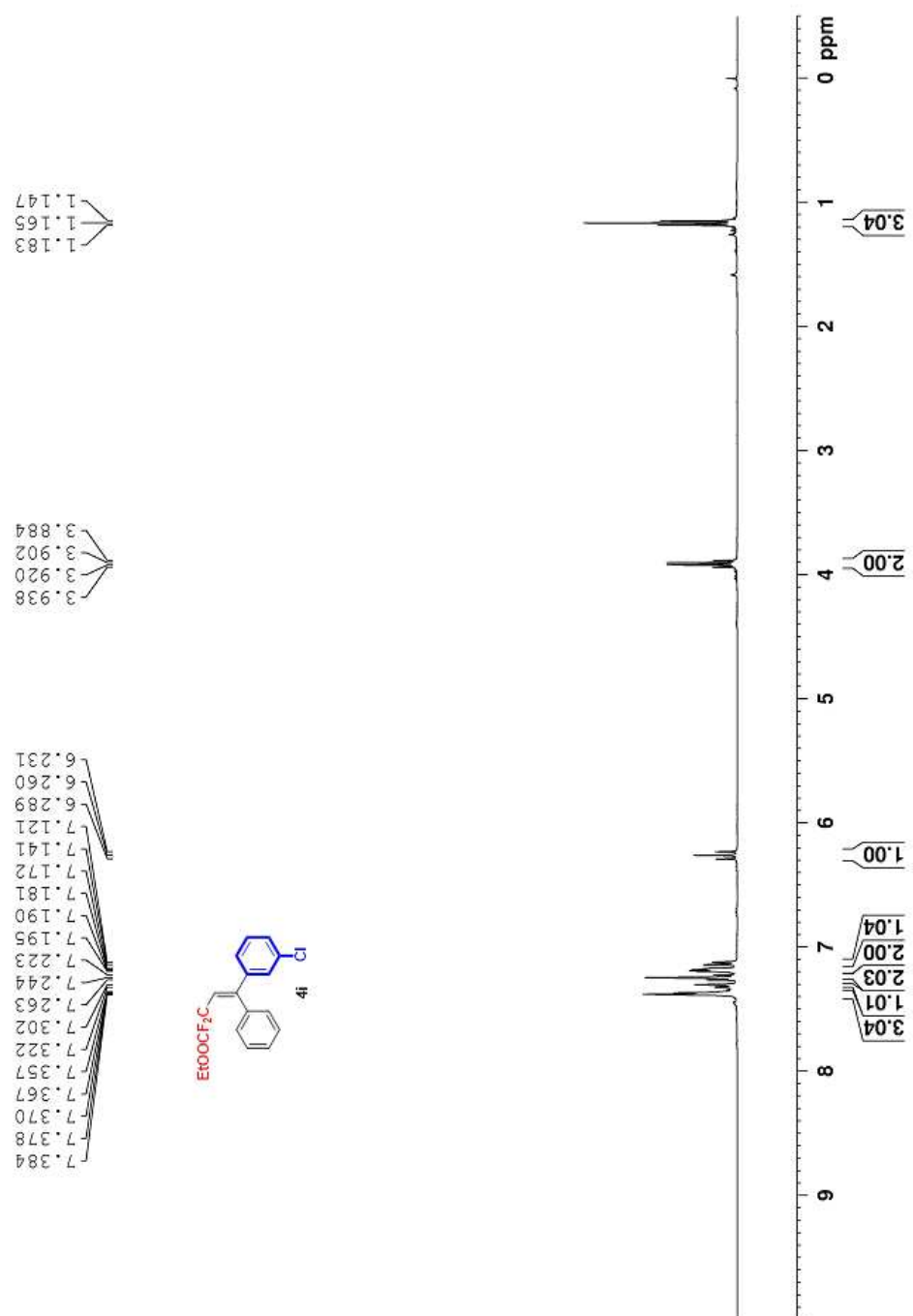


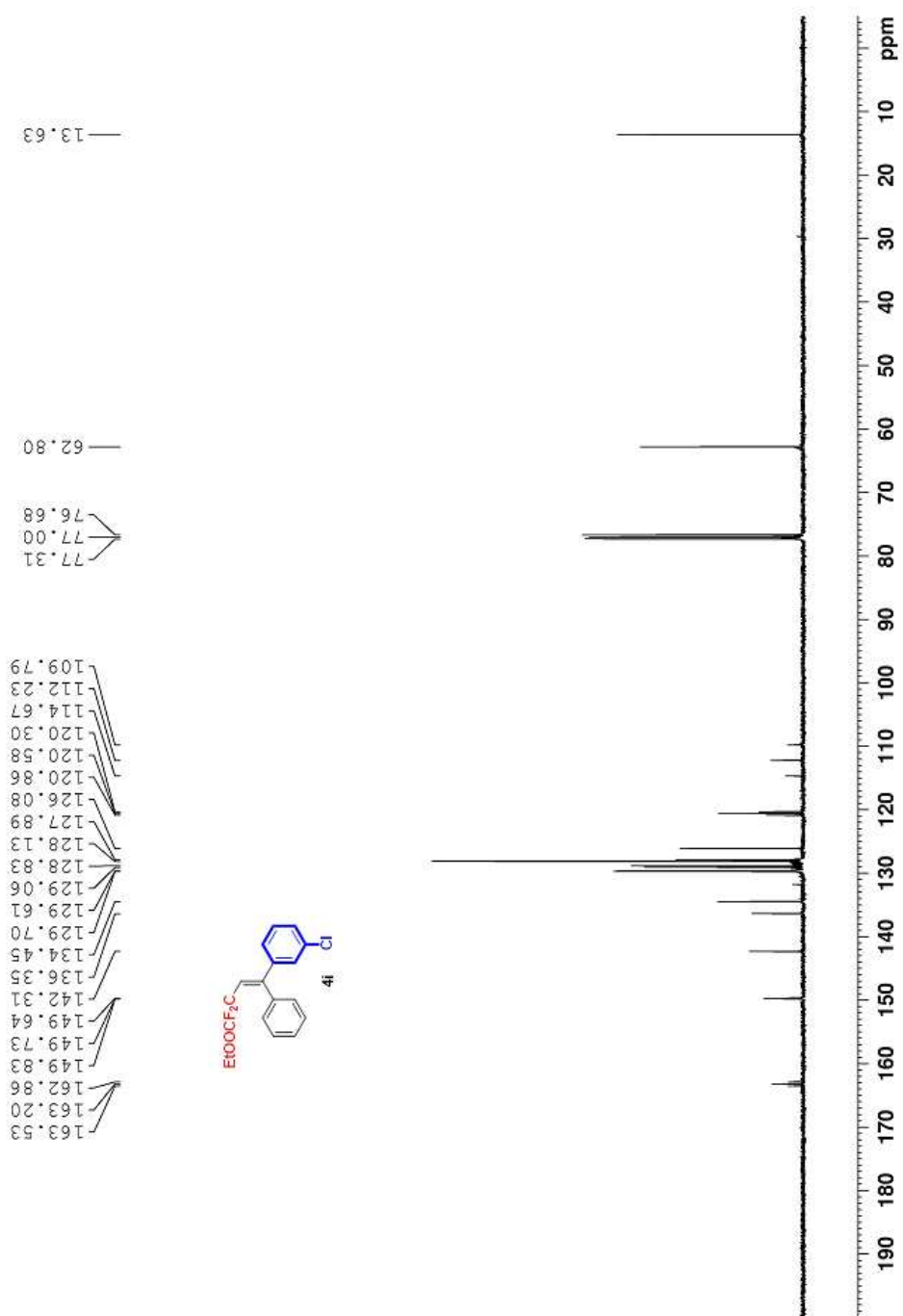


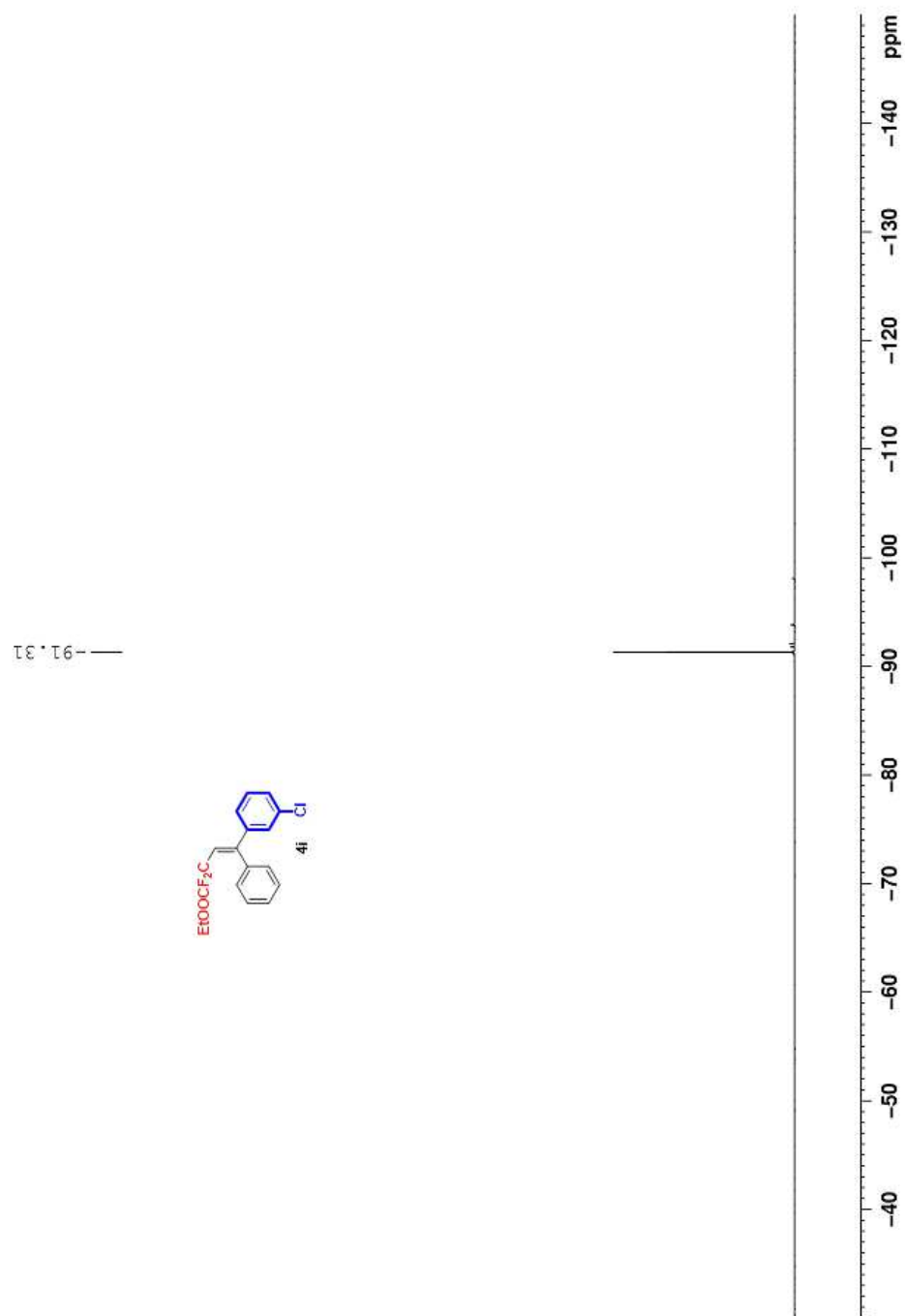


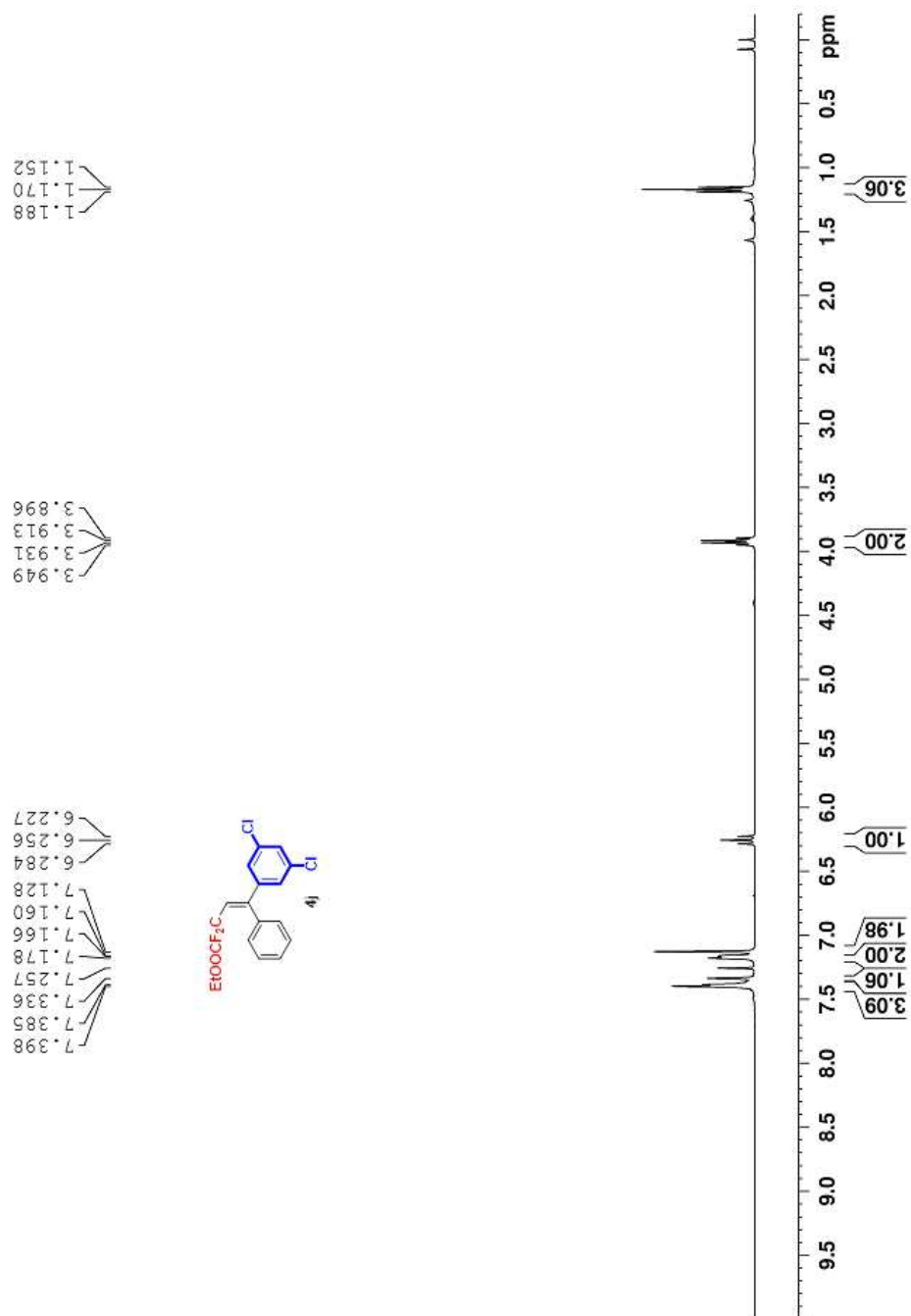
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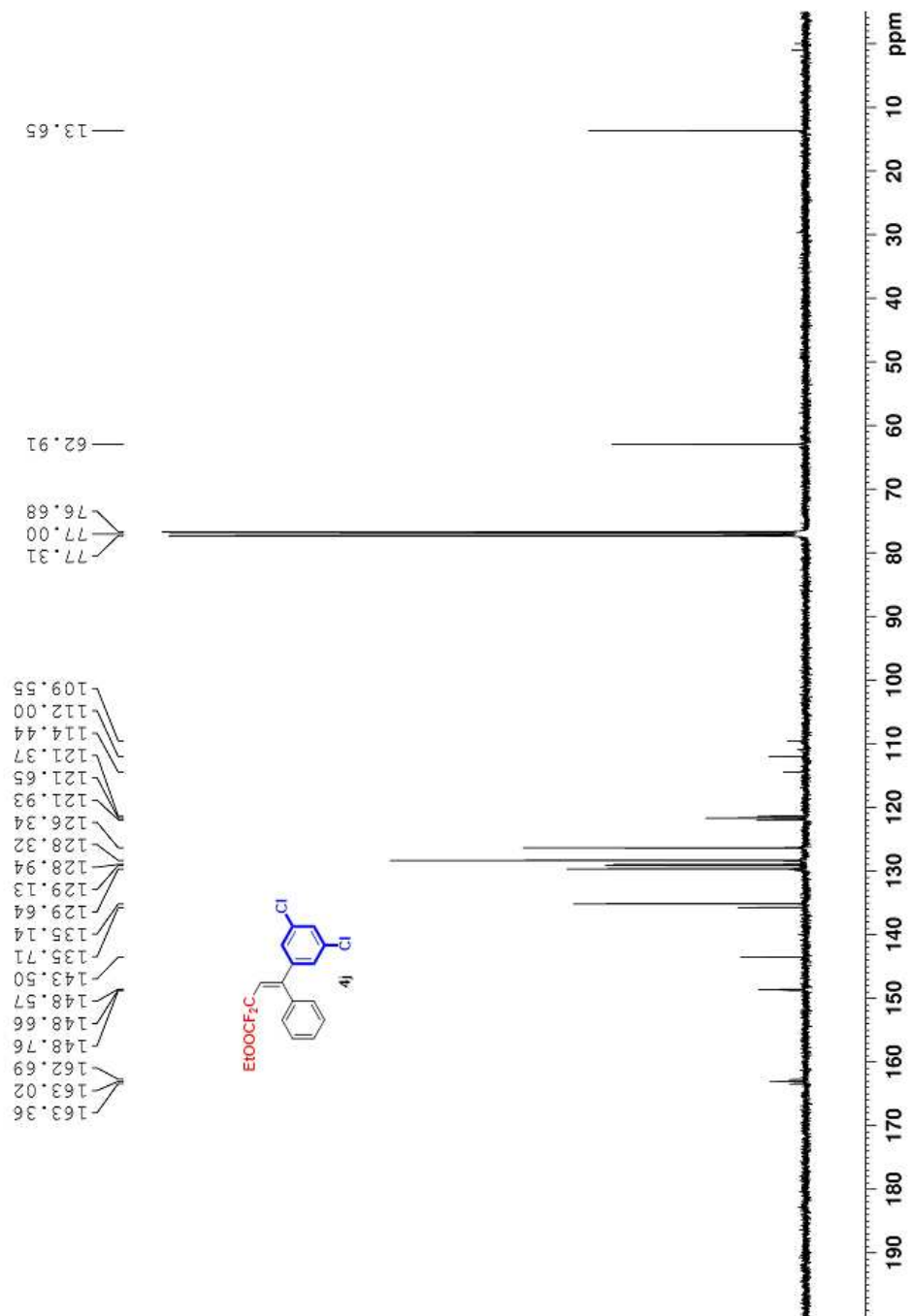


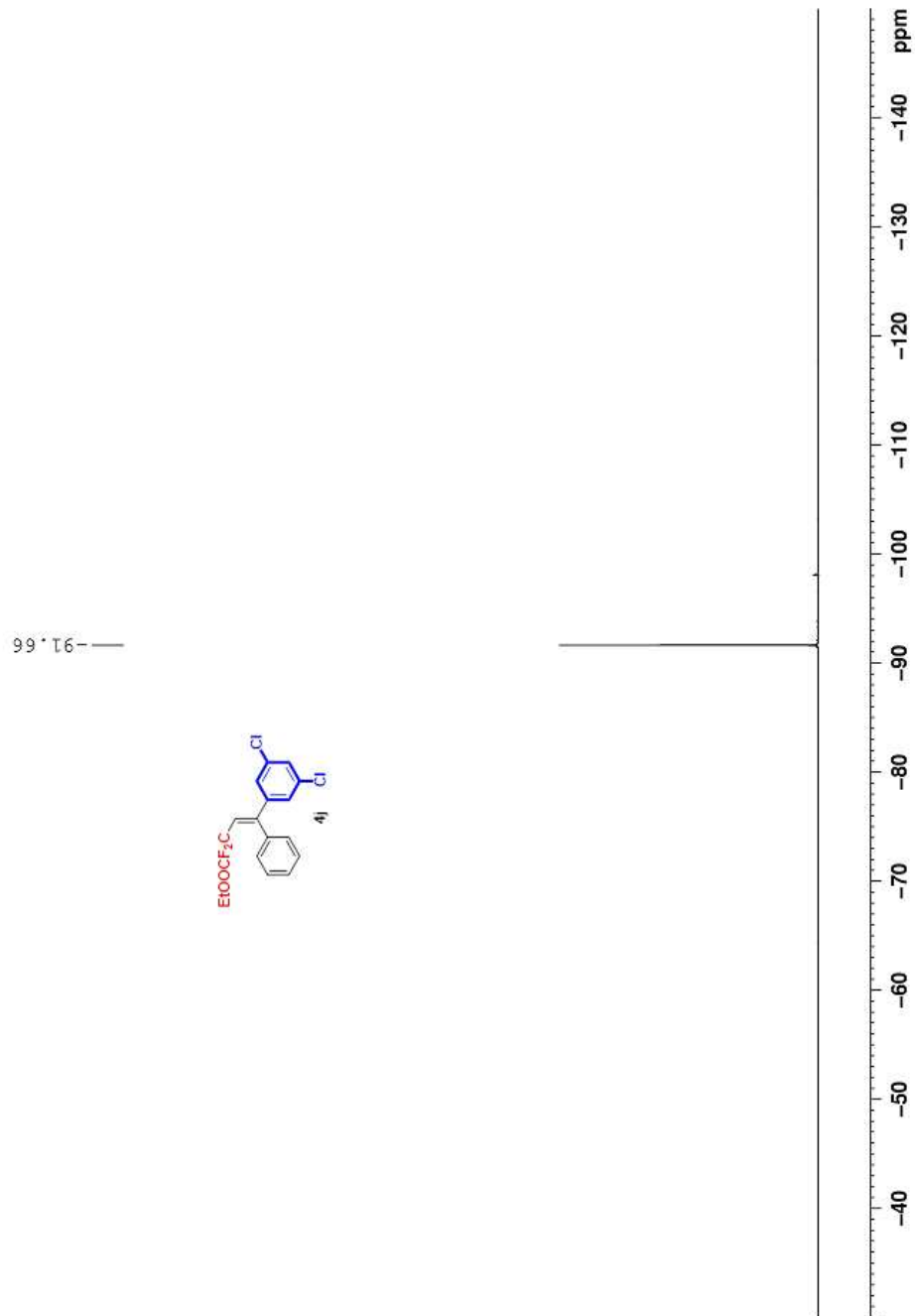


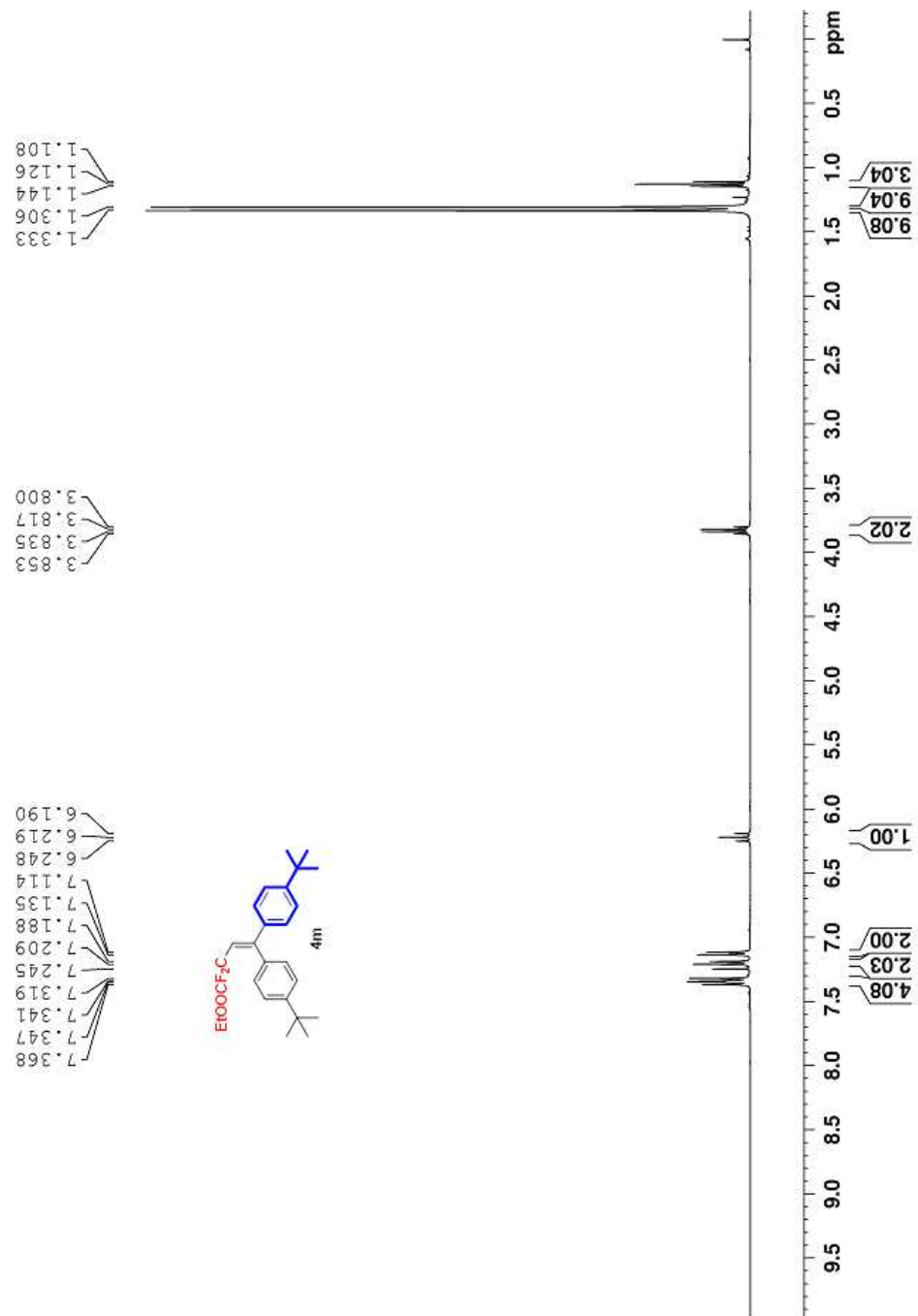


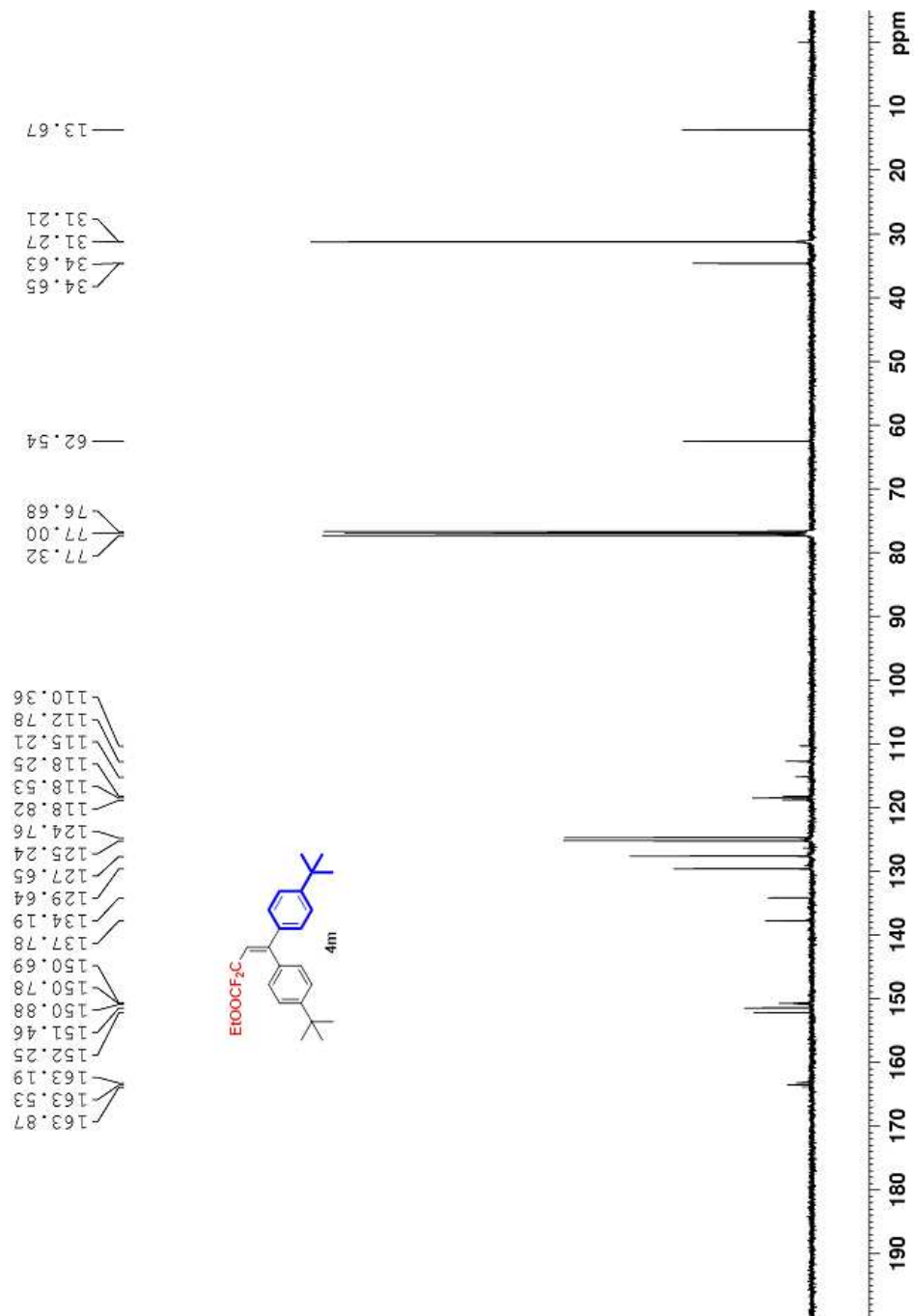


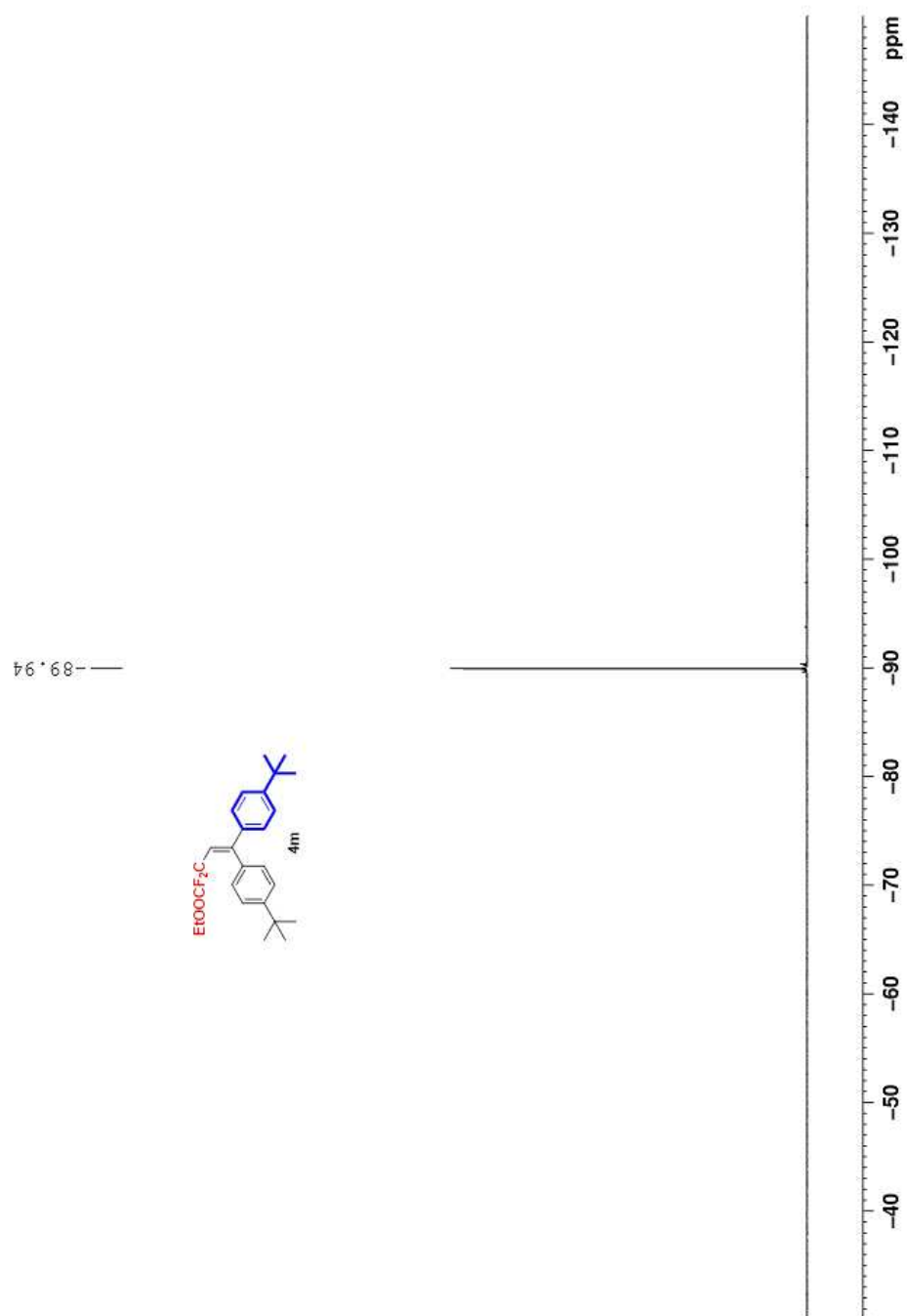


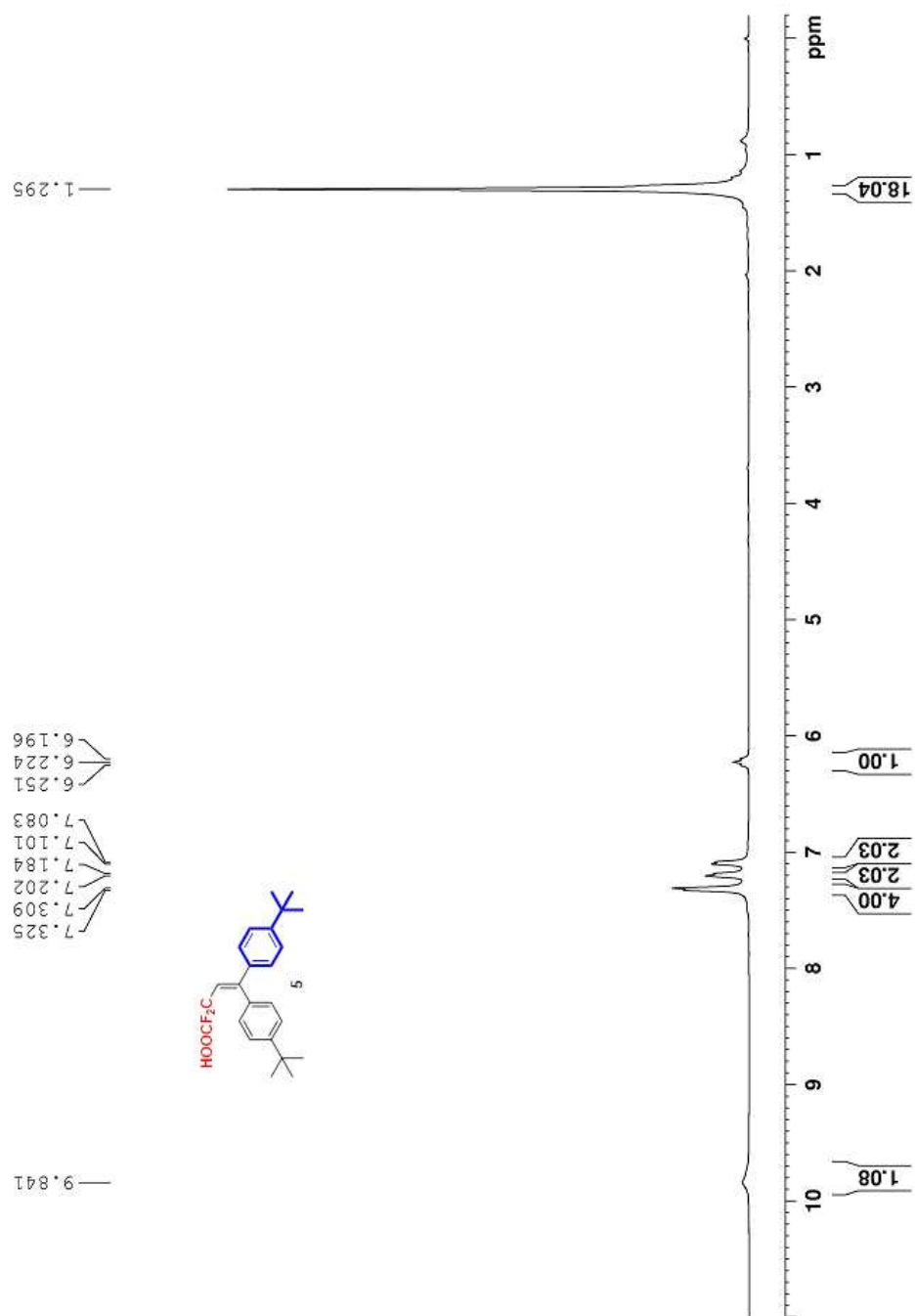


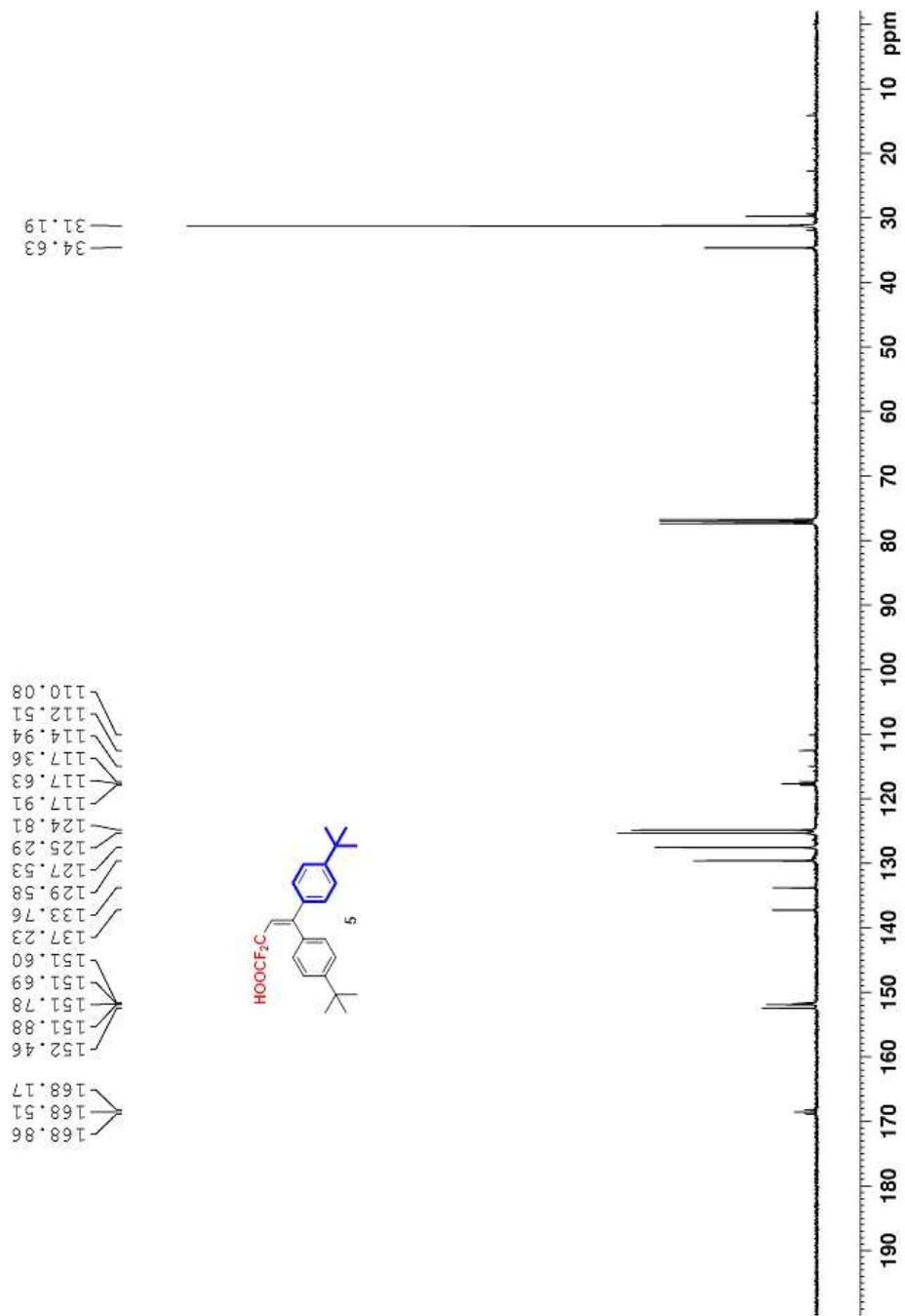






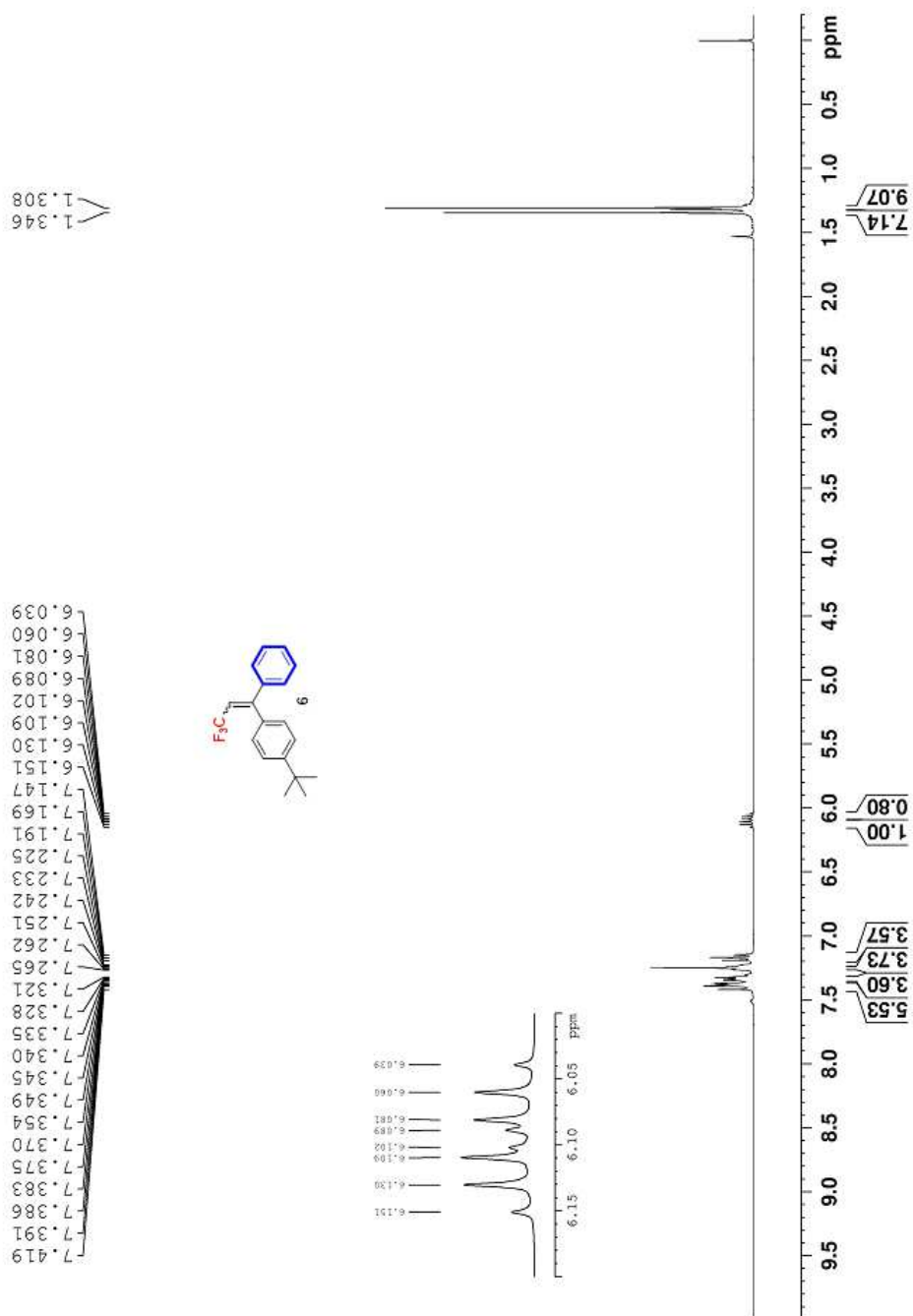


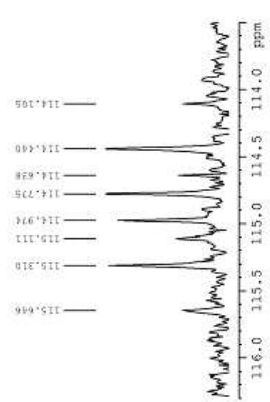




—91.65







55.5
55.4
55.3
55.2
55.1
55.0
54.9
54.8

