Supplementary Information

Metal-Catalyst-Free Approach for the Synthesis of Deoxybenzoins Using γ-Aryl-β-Ketoesters and Benzoyl Chlorides

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1. General information

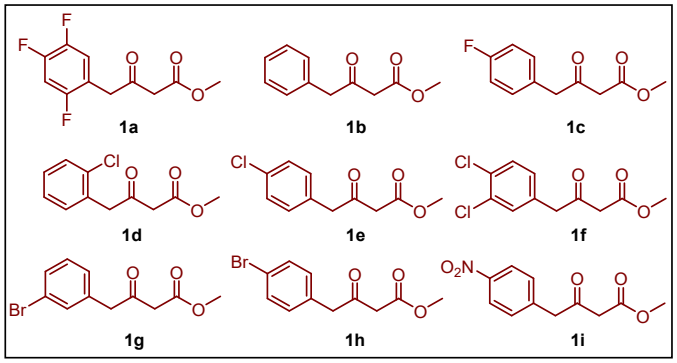
1.1 Practical considerations:

Unless otherwise specified, all reactions were carried out in oven-dried reaction vessels with magnetic stirring under an argon atmosphere. All reactions were performed in round-bottom flasks with rubber septa. All experiments were monitored by analytical thin-layer chromatography (TLC). TLC was performed on pre-coated silica gel plates (0.254mm silica gel 60-F plates). After elution, the plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining iodine and anisaldehyde solution and charring on a hot plate. Solvents were removed in a vacuum and heated with a water bath at 35 °C. Silica gel finer than 230-400 mesh was used for flash column chromatography. Columns were packed as a slurry of silica gel in petroleum ether and equilibrated with the ethyl acetate solvent mixture prior to use. The compounds were loaded as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with an air pump.

1.2 Instrumentation:

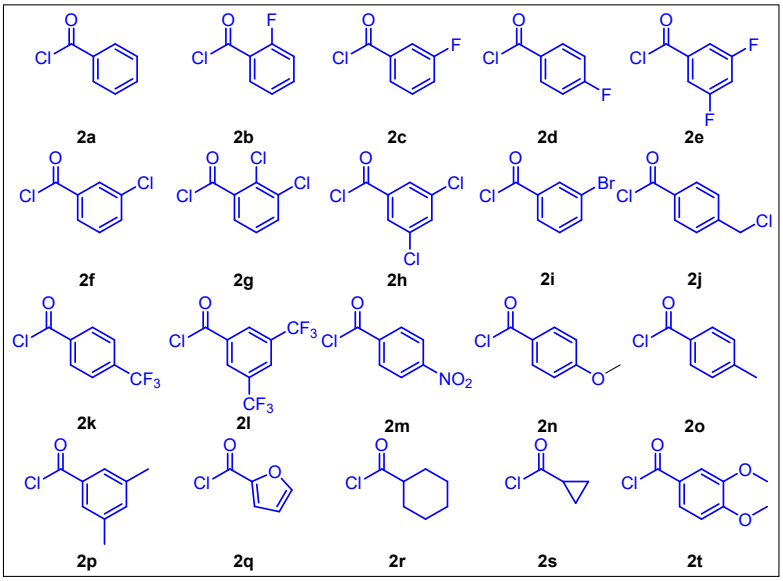
All NMR spectra were obtained at ambient temperature using Bruker Advance NMR spectrometer operating at 400 or 500 MHz for ^{1}H-NMR and 100 or 125 MHz for ^{13}C-NMR at room temperature using $CDCl_3$ as solvents. The chemical shifts (δ) are reported in ppm and coupling constants (*J*) are given in Hz. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.27 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. Signal multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. The known products were characterized by comparing to the corresponding ^{1}H NMR and ^{13}C NMR from the literature. High-resolution mass spectrometry data were obtained on a micro TOF-Q II (hybrid quadrupolar/time-of-flight) API US system by electrospray ionization (ESI) in the positive ion mode using a Bruker instrument. Liquid Chromatography-Mass Spectrometry (LC-MS/MS) data were acquired using a Waters Xevo TQ-S Cronos Triple Quadrupole Mass Spectrometer, operating in positive ion mode with electrospray ionization (ESI).

γ-aryl-β-ketoester used in the study[1, 2]



Note: The starting materials (1a – 1h) [1] and 1i[2] were synthesized from a known literature procedure. The starting materials 2a – 2t were commercially available.

Benzoyl chlorides used in the study



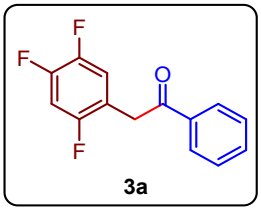
Experimental Procedure

General Procedure A

Methyl 3-oxo-4-(2,4,5-trifluorophenyl)butanoate (0.8124 mmol, 1 equiv) was stirred with the potassium carbonate (1.62 mmol, 2 equiv) in 1,4-dioxane (3 mL) at room temperature for 5 min. Benzoyl Chloride (1.6247 mmol, 2 equiv) was added slowly drop-wise, and the reaction mixture was stirred at 90 °C until benzoyl chloride was completely consumed (monitored by TLC). Typically starting materials were fully consumed within 5 hours. After 6 hours, the reaction mixture was diluted with ethyl acetate, saturated aqueous sodium chloride solution, and transferred to a separatory funnel. The aqueous layer was extracted with ethyl acetate twice, and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude residue was purified by flash column chromatography. The resulting product was then analyzed by ^{1}H NMR, ^{13}C NMR, LC-MS\MS and HRMS to verify the identity and purity. ^{19}F NMR was also reported in the case that compounds have fluorine atom(s).

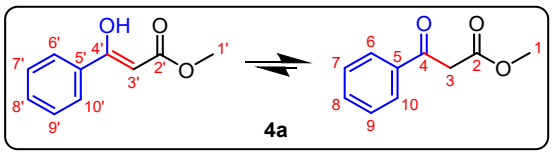
Characterization data of substrate

1-phenyl-2-(2,4,5-trifluorophenyl)ethan-1-one (3a)



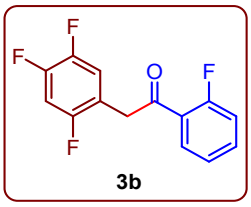
3a prepared from Methyl 3-oxo-4-(2,4,5-trifluorophenyl)butanoate (**1a**) (0.20 gm, 0.8124 mmol, 1 equiv) and benzoyl chloride (**2a**) (0.188 ml, 1.62 mmol, 2 equiv) using K_2CO_3 (0.225 gm, 1.62 mmol, 2 equiv) according to general procedure A, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate: petroleum ether mixture (1 : 9) as eluent to afford the title compound 3a and 4a as a minor product. 3a was obtained as a white solid (0.167 gm, 0.668 mmol, yield: 82%) M.P. 85–87 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.92 - 7.95 (m, 2H), 7.50 - 7.55 (m, 1H), 7.39 - 7.45 (m, 2H), 7.00 (ddd, *J* = 10.22, 8.66, 6.88 Hz, 1H), 6.87 (td, *J* = 9.57, 6.63 Hz, 1H), 4.19 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 195.3, 156 (ddd, *J* = 244.90, 9.16, 3.05 Hz) 149.3 (ddd, *J* = 250.24, 14.50, 12.97 Hz), 146.6 (ddd, *J* = 244.90, 12.21, 3.82 Hz) 136.1, 133.6, 128.8, 128.3, 119.4 (dd, *J* = 20.60, 6.10, 1.53 Hz), 118 (ddd, *J* = 18.31,6.1, 4.58 Hz) 105.4 (dd, *J* = 28.23, 20.60 Hz), 37.8 ppm; **HRMS (ESI)**: Exact mass calcd for $C_{14}H_{10}F_3O$ $[M+H]^+$: 251.0678, found 251.0676.

Methyl 3-oxo-3-phenylpropanoate (4a)



4a obtained as a yellow oil (0.022 gm, 0.337 mmol, yield: 15%); **^{1}H NMR $CDCl_3$, 400 MHz) Keto/enol mixture of 4a:** δ = 12.50 (s, 1H of enol), 7.97 - 7.93 (m, 2H, H6, H10), 7.80 - 7.76 (m, 2H, H6', H10'), 7.64 - 7.58 (m, 1H, H8), 7.52 - 7.47 (m, 2H, H7, H9), 7.46 - 7.39 (m, 3H, H7', H8', H9'), 5.68 (s, 1H, CH of enol), 4.02 (s, 2H, CH_2 of keto), 3.81 (s, 3H, OCH_3 of enol), 3.76 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 192.4 (C4), 173.5 (C4'), 171.5 (C2'), 168.0 (C2), 135.9 (C5), 133.8 (C5'), 133.3 (C8'), 131.3 (C8), 128.8 (C7, C9), 128.5 (C6, C10, C7', C9'), 126.1 (C6', C10'), 87.1 (C3'), 52.5 (C1), 51.4 (C1'), 45.7 (C3) ppm; **HRMS (ESI)**: Exact mass calcd for $C_{10}H_{11}O_3$ $[M+H]^+$: 179. 0703, found 179.0697.

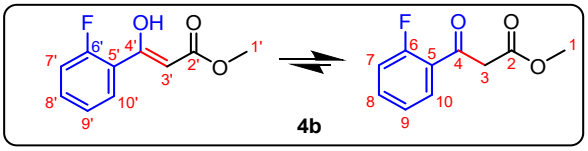
1-(2-fluorophenyl)-2-(2,4,5-trifluorophenyl)ethan-1-one (3b)



3b prepared from **1a** (0.20 gm, 0.8124 mmol, 1 equiv) and **2b** (0.18 ml, 1.62 mmol, 2 equiv) using K_2CO_3 (0.225 gm, 1.62 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate

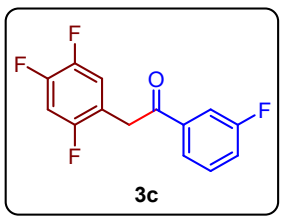
: petroleum ether mixture (1 : 9) as eluent to afford the title compound **3b** as a major product and **4b** as a minor product, **3b** obtained as a white solid (0.151 gm, 0.563 mmol, yield: 74%) M.P. 87–89 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.82 (t, *J* = 7.6 Hz, 1H), 7.43 - 7.54 (m, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.10 (dd, *J* = 11.3, 8.4 Hz, 1H), 6.92 - 7.03 (m, 1H), 6.87 (td, *J* = 9.5, 6.6 Hz, 1H), 4.19 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 193.5, 162.1 (s, *J* = 254.82 Hz), 156 (ddd, *J* = 244.90, 9.16, 3.05 Hz) 149.3 (ddd, *J* =250.24, 14.50, 12.97 Hz), 146.6 (ddd, *J* = 244.90, 12.21, 3.82 Hz), 135.2, 130.9, 124.7, 119.4 (dd, *J* = 20.60, 6.10, 1.53 Hz), 116.9, 105.4 (dd, *J* = 28.23, 20.60 Hz), 42.8 ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_9OF_4$ $[M+H]^+$: 269.0584, found 269.0580.

Methyl 3-(2-fluorophenyl)-3-oxopropanoate (4b)



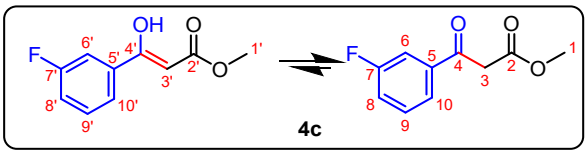
4b obtained as a colourless oil (0.032 gm, 0.163 mmol, yield: 20%); **^{1}H NMR ($CDCl_3$, 400MHz) Keto/enol mixture of 4b:** δ = 12.61 (s, 1H of OH), 7.92 - 7.98 (m, 1H, H10), 7.91 - 7.86 (m, 1H, H10'), 7.55 - 7.61 (m, 1H, H8) 7.25 - 7.21 (m, 1H, H8'), 7.27 (t, *J* = 7.6 Hz, 1H, H7), 7.25 - 7.21 (m, 1H, H7'), 7.16 (dd, *J* = 11.5, 8.4 Hz, 1H, H9), 7.14 - 7.09 (m, 1H, H9'), 5.88 (s, 1H, H3'), 4.02 (d, *J* = 3.5 Hz, 2H of H2), 3.82 (s, 3H OCH_3 of enol) 3.77 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 190.2 (d, *J* = 3.82 Hz, C4). 173.7 (C4'), 167.9 (d, *J* = 2.29 Hz, C6), 166.3 (d, *J* = 4.58 Hz, C6'), 163.5 (C2), 162.02 (C2'), 160.9 (C5), 159.4 (C5'), 135.6 (d, *J* = 9.15 Hz, C8), 132.4 (d, *J* = 9.15 Hz, C8'), 131.0 (d, *J* = 1.53 Hz, C10'),129.2 (C9) 125 (d, *J* = 3.05 Hz, C10), 124.3 (d, *J* = 12.21 Hz, C9') 116.7 (d, *J* = 24.41 Hz, C7), 116.4 (d, *J* = 22.89 Hz, C7'), 92.2 (d, *J* = 14.50 Hz, C3'), 52.4 (C1), 51.6 (C1'), 49.7 (d, *J* = 7.63 Hz, C3); **HRMS (ESI):** Exact mass calcd for $C_{10}H_9FO_3Na$ $[M+Na]^+$: 219.0428, found 219.0421.

1-(3-fluorophenyl)-2-(2,4,5-trifluorophenyl)ethan-1-one (3c)



3c prepared from **1a** (0.2 gm, 0.8124 mmol, 1 equiv) and **2c** (0.2 ml, 1.62 mmol, 2 equiv) using K_2CO_3 (0.225 gm, 1.62 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3c** as a major product and **4c** as a minor product. **3c** found as white solid (0.155 gm, 0.578 mmol, yield: 76%) M.P. 91–93 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.73 (d, *J* = 7.8 Hz, 1H), 7.62 (td, *J* = 2.0, 9.4 Hz, 1H), 7.42 (dt, *J* = 5.5, 8.0 Hz, 1H), 7.24 (dt, *J* = 2.6, 8.2 Hz, 1H), 7.06 - 6.94 (m, 1H), 6.89 (dt, *J* = 6.6, 9.5 Hz, 1H), 4.18 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 194.1, 156 (ddd, *J* = 244.90, 9.16, 2.29 Hz), 149.3 (ddd, *J* = 250.24, 13.73, 12.21 Hz), 146.6 (ddd, *J* = 244.90, 12.21, 3.82 Hz), 138 (d, *J* = 6.87 Hz), 130.6 (d, *J* = 7.63 Hz), 124.1 (d, *J* = 3.05 Hz), 121 (d, *J* = 21.36 Hz), 119.4 (ddd, *J* = 20.60, 6.10, 1.53 Hz), 117.5 (ddd, *J* = 18.31, 5.34, 3.81 Hz), 115.1 (d, *J* = 20.60 Hz), 105.3 (dd, *J* = 28.23, 20.60, Hz), 38.0 ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_9OF_4$ $[M+H]^+$: 269.0584, found 269.0580.

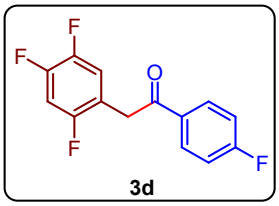
Methyl 3-(3-fluorophenyl)-3-oxopropanoate (4c)



4c

4c obtained as colourless oil (0.024 gm, 0.122 mmol, yield:15%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto/enol mixture of 4c:** δ = 12.40 (s, 1H, enol OH), 7.65 (d, *J* = 7.8 Hz, 1H, H10), 7.58 - 7.55 (m, 1H, 10'), 7.56 (td, *J* = 2.0, 9.3 Hz, 1H, H9), 7.48 (d, *J* = 7.9 Hz, 1H, H9'), 7.44 - 7.36 (m, 1H, H8), 7.32 (dt, *J* = 8.0, 5.8 Hz, 1H, H8'), 7.27 - 7.20 (m, 1H, H6), 7.09 (dt, *J* = 8.3, 2.5 Hz, 1H, H6'), 5.59 (s, 1H, H3'), 3.92 (s, 2H, H3), 3.69 (s, 3H, OCH_3 of keto), 3.74 (s, 3H, OCH_3 of enol) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 191.2 (d, *J* = 2.29 Hz, C4), 173.3 (C4'), 169.9 (d, *J* = 2.29 Hz, C2'),167.6 (C2), 164.1 (C7), 161.6 (C7'), 137.9 (d, *J* = 6.1 Hz, C5), 135.6 (d, *J* = 7.63 Hz, C5'), 130.6 (d, *J* = 7.63 Hz, C9), 130.2 (d, *J* = 7.63 Hz, C9'), 124.3 (d, *J* = 3.05 Hz, C10), 121.7 (d, *J* = 3.05 Hz, C10'), 120.8 (d, *J* = 21.36 Hz, C8), 118.2 (d, *J* = 20.6 Hz, C8'), 115.2 (d, *J* = 22.89 Hz, C6), 113.1 (d, *J* = 23.65 Hz, C6'), 87.9 (C3'), 52.6 (C1), 51.6 (C1'), 45.8 (C3) ppm; **^{19}F NMR ($CDCl_3$, 375 MHz)** δ -111.26, -112.31 ppm; **HRMS (ESI)**: Exact mass calcd for $C_{10}H_9FO_3Na$ $[M+Na]^+$: 219.0428, found 219.0421.

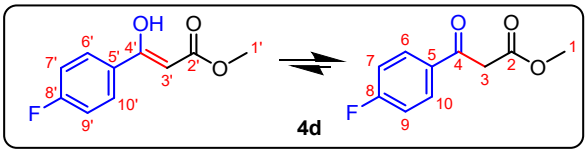
1-(4-fluorophenyl)-2-(2,4,5-trifluorophenyl)ethan-1-one (3d)



3d

3d prepared from **1a** (0.2 gm, 0.8124 mmol, 1 equiv) and **2d** (0.19 ml, 1.62 mmol, 2 equiv) using K_2CO_3 (0.225gm, 1.62 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3d** as a major product and **4d** as a minor product. **3d** found as white solid (0.168 gm, 0.627 yield: 77%) M.P. 77–79 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.11 - 8.01 (m, 2H), 7.22 - 7.14 (m, 2H), 7.09 (ddd, *J* = 10.0, 8.7, 6.9 Hz, 1H), 6.97 (td, *J* = 9.6, 6.6 Hz, 1H), 4.25 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 193.8, 167.3, 164.8, 156 (ddd, *J* = 244.90, 9.16, 3.05 Hz) 149.3 (ddd, *J* = 250.24, 14.50, 12.97 Hz), 146.6 (ddd, *J* = 244.90, 12.21, 3.82), 132.4 (d, *J* = 3.05), 131 (d, *J* = 9.92), 119.4 (ddd, *J* = 19, 6.10, 1.53 Hz), 117.5 (ddd, *J* = 19.07, 6.1, 4.81 Hz), 116.1 (d, *J* = 21.36 Hz), 105.3 (dd, *J* = 28.23, 20.60 Hz), 37.8 ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_9OF_4$ $[M+H]^+$: 269.0584, found 269.0591.

Methyl 3-(4-fluorophenyl)-3-oxopropanoate (4d)

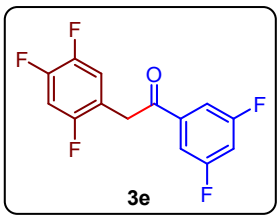


4d

4d obtained as a colourless oil (0.021 gm, 0.107 mmol yield: 13%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto/enol mixture of 4d:** δ =12.44 (s, 1H, enol OH), 7.88 (t, *J* = 5.9 Hz, 2H, H6, H10), 7.67 (t, *J* = 6.0 Hz, 2H, H6', H10'), 7.05 (t, *J* = 7.9 Hz, 2H, H7, H9), 7.00 (br. s., 2H, H7', H9'), 5.52 (s, 1H, H3'), 3.90 (s, 2H, H3), 3.70 (s, 3H, OCH_3 of enol) 3.65 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 189.8 (C4), 173.0 (C4'), 167.6 (C2), 166.9

(C2'), 137.4 (C5'), 135.6 (C5), 133.1-131.7 (m, C8, C8', C9'), 128.5 (d, J = 3.0 Hz, C10'), 126.9 (m, C6), 126.1 (d, J = 3.05 Hz, C10) 124.5 (m, C6), 124.3 (d, J = 23.65, C9), 121.6 (d, J = 23.65 Hz, C7'), 118.7 (d, J = 22.89 Hz, C7), 89.4 (C3'), 52.8 (C1'), 51.9 (C1), 45.6 (C3) ppm; **HRMS (ESI):** Exact mass calcd for $C_{10}H_9FO_3Na$ $[M+Na]^+$: 219.0428 found 219.0421.

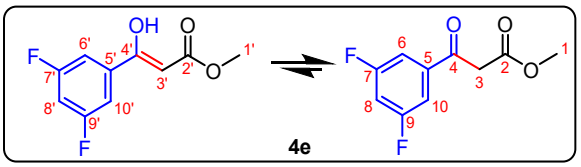
1-(3,5-difluorophenyl)-2-(2,4,5-trifluorophenyl)ethan-1-one (3e)



3e

3e prepared from **1a**, (0.2 gm, 0.8124 mmol, 1 equiv) and **2e**, (0.2 ml, 1.62 mmol, 1 equiv) using K_2CO_3 (0.225 gm, 1.62 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3e** as a major product and **4e** as a minor product. **3e** obtained as a white solid (0.175 gm, 0.611 mmol, yield: 75%) M.P. 89–91 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.47 - 7.58 (m, 2H), 7.03 - 7.12 (m, 2H), 6.98 (td, J = 9.6, 6.6 Hz, 1H), 4.23 ppm (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 192.9, 164.3 (d, J = 11.44), 161.8 (d, J = 12.21 Hz), 156 (ddd, J = 244.90, 9.16, 3.05 Hz) 149.3 (ddd, J = 250.24, 14.50, 12.97 Hz), 146.6 (ddd, J = 244.90, 12.21, 3.82 Hz), 138.8 (t, J = 15.26, 7.63 Hz), 119.4 (ddd, J = 19, 6.10, 1.53 Hz), 117.5 (ddd, J = 19.07, 6.1, 4.81 Hz), 111.3 (m, J = 25.94, 19.07, 7.63 Hz), 109.3 (t, J = 51.12, 25. 18 Hz), 105.3 (dd, J = 28.23, 21.36 Hz), 38.1 ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_8F_5O$ $[M+H]^+$: 287.0490, found 287.0487.

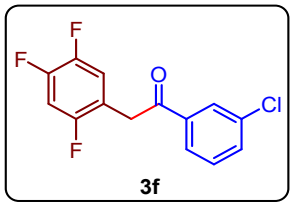
Methyl 3-(3,5-difluorophenyl)-3-oxopropanoate (4e)



4e

4e obtained as a colourless oil (0.028 gm, 0.130 mmol, yield: 16%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto/enol mixture of 4e:** δ =12.38 (s, 1H enol OH), 7.38 (d, J = 6.6 Hz, 2H, H6, H10), 7.24 - 7.18 (m, 2H, H6', H10'), 7.21 (d, J = 7.3 Hz, 1H, H8), 6.88 - 6.80 (m, 1H, H8'), 5.57 (s, 1H, H3'), 3.90 (s, 2H, H3),3.75 (s, 3H, OCH_3 of enol), 3.70 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 190.0 (C4), 173.1 (C4'), 168.5 (t, J = 6.1, 3.05Hz, C2'), 167.2 (C2), 164.4 (dd, J = 12.21, 9.16 Hz, C9, C9'), 161.88 (m, C7, C7'), 138.7 (t, J = 15.26 7.63, C5), 136.6 (t, J = 19.07, 9.92 Hz, C5') 111.6 (m, C10), 109.5 (m, C6, C10, C8), 106.5 (t, J = 51.12, 25.94 Hz, C8'), 88.6 (C3'), 52.8 (C1'), 51.8 (C1), 45.7 (C3) ppm; **HRMS (ESI):** Exact mass calcd for $C_{10}H_7F_2O_3$ $[M\ \ H]^+$: 213.0358, found 213.0363.

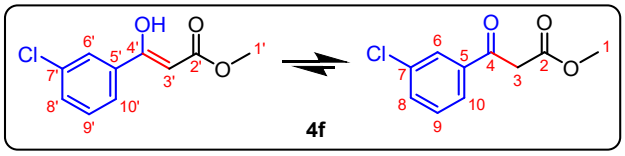
1-(3-chlorophenyl)-2-(2,4,5-trifluorophenyl)ethan-1-one (3f)



3f

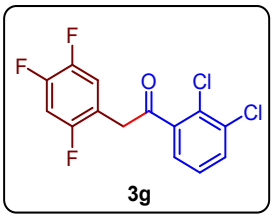
3f obtained from **1a** (0.20 gm, 0.8124 mmol, 1 equiv) and **2f** (0.2 ml, 1.62 mmol, 2 equiv) using K_2CO_3 (0.225 gm, 1.62 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3f** as a major product and **4f** as a minor product, **3f** found as a white solid (0.169 gm, 0.595 mmol, yield: 73%) M.P. 85–87 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.99 (s, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.54 - 7.64 (m, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.07 (dd, *J* = 8.4, 1.4 Hz, 1H), 6.97 (td, *J* = 9.5, 6.7 Hz, 1H), 4.26 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 193.0, 156 (ddd, *J* = 244.90, 9.16, 3.05 Hz), 149.3 (ddd, *J* =250.24, 14.50, 12.97 Hz), 146.6 (ddd, *J* = 244.90, 12.21, 3.82 Hz), 136.5, 134.1, 132.5, 129.1, 127.4, 125.3, 118.2 (m, *J* = 25.18, 20.06, 6.87, 5.34 Hz), 116.4 (ddd, *J* = 18.31, 6.1, 4.58 Hz), 105.3 (dd, *J* = 28.23, 21.36 Hz), 37 ppm; **^{19}F NMR ($CDCl_3$, 375 MHz)** δ -118.4 (dd, *J* = 11.84 Hz), -134.56 (dd, *J* = 23.67 Hz), -142.56 (dd, *J* =15.79 Hz) ppm; **HRMS (ESI)**: Exact mass calcd for $C_{14}H_8OF_3Cl$ $[M+H]^+$: 285.0289, found 285.0290.

Methyl 3-(3-chlorophenyl)-3-oxopropanoate (4f)



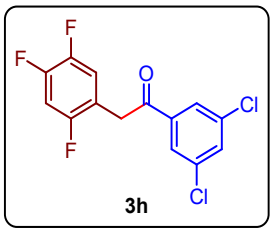
4f obtained as a colourless oil (0.035 gm, 0.165 mmol, yield: 20%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto/enol mixture of 4f :** δ = 12.48 (s, 1H, enol OH), 7.93 (s, 1H, H6), 7.82 (d, *J* = 7.8 Hz, 1H, H10), 7.77 (s, 1H, H6), 7.65 (d, *J* = 7.9 Hz, 1H, H10'), 7.59 (d, *J* = 8.0 Hz, 1H, H8), 7.45 (t, *J* = 7.8 Hz, 1H, H9), 7.43 (s, 1H, H8'), 7.37 (d, *J* = 7.9 Hz, 1H, H9'), 5.67 (s, 1H, H3'), 4.00 (s, 2H, H3), 3.82 (s, 3H, OCH_3 of enol), 3.77 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 191.2 (C4), 173.3 (C4'), 169.8 (C2), 167.6 (C2'), 137.4 (C5), 135.2 (C7), 135.2 (C7'), 134.8 (C8), 133.8 (C5'), 131.2 (C9), 130.2 (C9'), 129.9 (C6), 128.6 (C8'), 126.7 (C10), 126.3 (C6'), 124.2 (C10'), 87.9 (C3'), , 52.7 (C1'), 51.6 (C1), 45.7 (C3) ppm; **HRMS (ESI):** Exact mass calcd for $C_{10}H_9O_3ClNa$ $[M+Na]^+$: 235.0127, found 235.0132.

1-(2,3-dichlorophenyl)-2-(2,4,5-trifluorophenyl)ethan-1-one (3g)



3g prepared from **1a** (0.2 gm, 0.8124 mmol, 1 equiv) and **2g** (0.22 ml, 1.62 mmol, 2 equiv) using K_2CO_3 (0.225 gm, 1.62 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3g** as a major product and unseparable mixture as a minor product. **3g** obtained as a white solid (0.177 gm, 0.5566 mmol, yield: 68%), M.P. 91–93°C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.59 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.28 - 7.36 (m, 2H), 7.13 (dd, *J* = 16.3, 9.3 Hz, 1H), 6.96 (td, *J* = 9.4, 6.6 Hz, 1H), 4.21 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 198.1, 156 (ddd, *J* = 244.90, 9.16, 3.05 Hz), 149.3 (ddd, *J* =250.24, 14.50, 12.97 Hz), 146.6 (ddd, *J* = 244.90, 12.21, 3.82 Hz), 141.0, 134.3, 132.6, 128.9, 127.9, 126.5, 119.3 (m, *J* = 25.18, 19.84, 18.31, 4.58 Hz), 116.4 (ddd, *J* = 18.31, 6.1, 4.58 Hz), 105.3 (dd, *J* = 28.23, 21.36 Hz), 42.2 ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_7Cl_2F_3O$ $[M+H]^+$ 317.9899, found 318.9908.

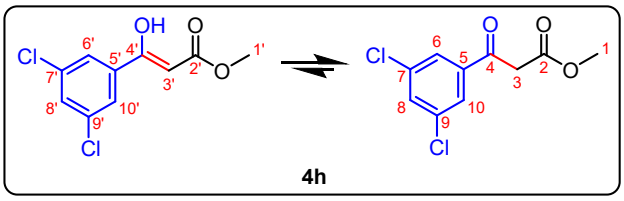
1-(3,5-dichlorophenyl)-2-(2,4,5-trifluorophenyl)ethan-1-one (3h)



3h

3h prepared from **1a** (0.2 gm, 0.8124 mmol, 1 equiv) and **2h** (0.23 ml, 1.62 mmol, 2 equiv) using K_2CO_3 (0.225 gm, 1.62 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3h** as a major product and **4h** as a minor product. **3h** obtained as a White solid (0.187 gm, 0.588 mmol, yield: 72%), M.P. 90–92 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.86 (d, *J* = 1.9 Hz, 2H), 7.59 (t, *J* = 1.8 Hz, 1H), 7.13 - 6.90 (m, 2H), 4.23 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 192.9, 156 (ddd, *J* = 244.90, 9.16, 3.05 Hz) 149.3 (ddd, *J* =250.24, 14.50, 12.97 Hz), 146.6 (ddd, *J* = 244.90, 12.21, 3.82 Hz), 138.4, 135.9, 133.3, 126.7, 119.3 (m, *J* = 25.18, 19.84, 18.31, 4.58 Hz), 116.4 (ddd, *J* = 18.31, 6.1, 4.58 Hz), 105.3 (dd, *J* = 28.23, 21.36, Hz), 38.1 ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_7Cl_2F_3O$ $[M+H]^+$: 318.9826, found 318.9899.

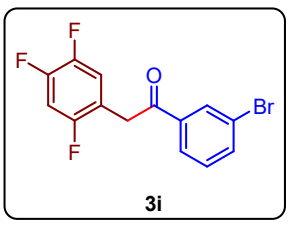
Methyl 3-(3,5-dichlorophenyl)-3-oxopropanoate (4h)



4h

4h found as a colourless oil (0.032 gm, 0.13 mmol, yield 16%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto/enol mixture of 4h**: δ = 12.44 (s, 1H, enol OH), 7.80 - 7.76 (m, 2H, H6, H10), 7.64 - 7.60 (m, 2H, H6', H10'), 7.59 - 7.56 (m, 1H, H8), 7.44 - 7.41 (m, 1H, H8'), 5.64 (s, 1H, H3'), 3.97 (s, 2H, H3), 3.81 (s, 3H, OCH_3 of enol), 3.77 (s, 3H, OCH_3 of keto); **^{13}C NMR ($CDCl_3$, 100 MHz**): δ = 190.3 (C4), 173.3 (C4'), 168.5 (C2), 167.4 (C2'), 138.5 (C5), 136.5 (C7), 136.1 (C7'), 135.6 (C9), 133.9 (C9'), 133.7 (C8), 131.2 (C5'), 130.1 (C8'), 128.6 (C10), 127.2 (C10'), 126.4 (C6), 124.8 (C6'), 89 (C3'), 53 (C1'), 52 (C1), 45.8 (C3) ppm; **HRMS (ESI):** Exact mass calcd for $C_{10}H_8O_3Cl_2$ $[M+H]^+$ 246.9923, found 246.9921.

1-(3-bromophenyl)-2-(2,4,5-trifluorophenyl)ethan-1-one (3i)

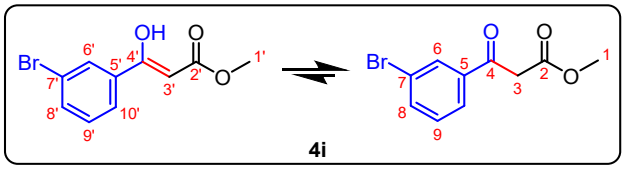


3i

3i prepared from **1a** (0.2 gm, 0.8124 mmol, 1 equiv) and **4i** (0.21 ml, 1.62 mmol, 2 equiv) using K_2CO_3 (0.225 gm, 1.62 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3i** as a major product and **4i** as a minor product. **3i** found as a white solid (0.201 gm, 0.613 mmol, yield: 75%) M.P. 92–

94 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.15 (t, *J* = 1.6 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.69 - 7.77 (m, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.02 - 7.13 (m, 1H), 6.97 (td, *J* = 9.6, 6.6 Hz, 1H), 4.25 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 194.0, 156 (ddd, *J* = 244.90, 9.16, 3.05 Hz) 149.3 (ddd, *J* = 250.24, 14.50, 12.97 Hz), 146.6 (ddd, *J* = 244.90, 12.21, 3.82 Hz), 137.8, 136.5, 131.4, 130.4, 126.8, 123.2, 119.3 (m, *J* = 25.18, 19.84, 18.31, 4.58 Hz), 116.4 (ddd, *J* = 18.31, 6.1, 4.58 Hz), 105.3 (dd, *J* = 28.23, 21.36, Hz), 37.9 ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_8OBrF_3$ $[M+H]^+$: 327.9783, found 328.9779.

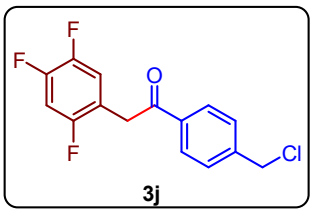
Methyl 3-(3-bromophenyl)-3-oxopropanoate (4i)



4i

4i obtained as a colourless oil (0.042 gm, 0.164 mmol, yield: 20%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto/enol mixture of 4i:** δ = 12.46 (s, 1H, enol OH), 8.07 (t, *J* = 1.8 Hz, 1H, H6), 7.91 (t, *J* = 1.8 Hz, 1H, H6'), 7.86 (dt, *J* = 7.8, 1.3 Hz, 1H, H10), 7.68 (dt, *J* = 7.9, 1.3 Hz, 1H, H10'), 7.72 (ddd, *J* = 8.0, 1.9, 0.9 Hz, 1H, H8), 7.60 - 7.55 (m, 1H, H8'), 7.37 (t, *J* = 7.9 Hz, 1H, H9), 7.31 - 7.27 (m, 1H, H9'), 5.65 (s, 1H, H3'), 3.98 (s, 2H, H3), 3.81 (s, 3H, OCH_3 of enol), 3.76 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** 191.03 (C4), 173.25 (C4'), 169.6 (C2), 167.5 (C2') 137.6 (C5), 136.6 (C5'), 135.2 (C8), 134 (C8'), 131.4 (C6), 130.3 (C6'), 130 (C9), 129.1 (C9'), 127 (C10), 124.6 (C10'), 123.1 (C7), 122.7 (C7'), 87.95 (C3'), 52.59 (C1'), 51.59 (C1), 45.58 (C3) ppm; **HRMS (ESI):** Exact mass calcd for $C_{10}H_9O_3BrNa$ $[M+Na]^+$: 278.9627, found 278.9622.

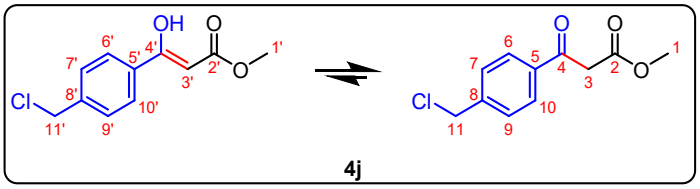
1-(4-(chloromethyl)phenyl)-2-(2,4,5-trifluorophenyl)ethan-1-one (3J)



3j

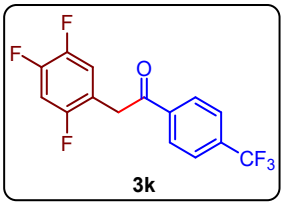
3J prepared from **1a** (0.2 gm, 0.8124 mmol, 1 equiv) and **2J** (0.23 ml, 1.62 mmol, 2 equiv) using K_2CO_3 (0.225 gm, 1.62 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3J** as a major product and **4J** as a minor product. **3J** found as a white solid (0.158 gm, 0.530 mmol, yield: 65%), M.P. 90–92 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.97 - 8.08 (m, *J* = 8.4 Hz, 2H), 7.47 - 7.58 (m, *J* = 8.3 Hz, 2H), 7.04 - 7.13 (m, 1H), 6.96 (td, *J* = 9.6, 6.6 Hz, 1H), 4.63 (s, 2H), 4.27 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 194.7, 156 (ddd, *J* = 244.90, 9.16, 3.05 Hz), 149.3 (ddd, *J* = 250.24, 14.50, 12.97 Hz), 146.6 (ddd, *J* = 244.90, 12.21, 3.82 Hz), 143.0, 135.9, 128.9, 128.8, 119.3 (m, *J* = 25.18, 19.84, 18.31, 4.58 Hz), 116.4 (ddd, *J* = 18.31, 6.1, 4.58 Hz), 105.3 (dd, *J* = 28.23, 21.36, Hz), 45.2, 37.9 ppm; **HRMS (ESI):** Exact mass calcd for $C_{15}H_{10}OClF_3$ $[M+H]$+: 298.0445 found 299.0441

Methyl 3-(4-(chloromethyl)phenyl)-3-oxopropanoate (4J)



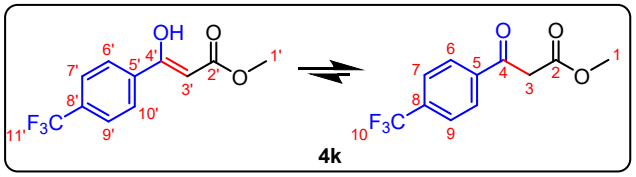
4J obtained as a colourless oil (0.037 gm, 0.163 mmol, yield: 20%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto/enol mixture of 4J**: δ = 12.41 (s, 1H, enol OH), 7.89 - 7.80 (m, *J* = 7.9 Hz, 2H, H7,H9), 7.72 - 7.63 (m, *J* = 7.9 Hz, 2H, H7', H9'), 7.47 - 7.38 (m, *J* = 8.0 Hz, 2H, H6, H10), 7.33 - 7.38 (m, *J* = 8.0 Hz, 2H, H6', H10'), 5.60 (s, 1H, H3'), 4.53 (s, 2H, H11), 4.52 (s, 2H, H11'), 3.92 (s, 2H, H3), 3.72 (s, 3H, OCH_3 of enol), 3.67 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 191.7 (C4), 173.3(C4'), 170.6(C2), 167.7(C2'), 143.1 (C8'), 140.5 (C8'), 135.6 (C5), 133.3 (C5'), 130.9 (C6), 128.9 (C6'), 128.8 (C10, C7), 128.8 (C10'), 128.6 (C9), 128.6 (C9'), 126.4 (C7'), 87.3 (C3'), 52.4 (C1'), 51.4 (C1), 48.1 (C3), 45.6 (C11), 45.1 (C11') ppm; **HRMS (ESI):** Exact mass calcd for $C_{11}H_{11}O_3ClNa$ $[M+Na]^+$: 249.0289, found 249.0282.

1-(4-(trifluoromethyl)phenyl)-2-(2,4,5-trifluorophenyl)ethan-1-one (3k)



3k prepared from (**1a**) (0.2 gm, 0.8124 mmol, 1 equiv) and 4-(trifluoromethyl)benzoyl chloride (**2f**) (0.24 ml, 1.62 mmol, 2 equiv) using K_2CO_3 (0.225 gm, 1.62 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3k** as a major product and **4k** as a minor product. **3k** found as a White solid (0.181 gm, 0.569 mmol, yield: 70%), M.P. 89–91 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.03 - 8.21 (m, *J* = 8.3 Hz, 2H), 7.67 - 7.85 (m, *J* = 8.3 Hz, 2H), 7.04 - 7.14 (m, 1H), 6.98 (td, *J* = 9.6, 6.6 Hz, 1H), 4.31 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** □= 194.4, 156 (ddd, *J* = 244.90, 9.16, 3.05 Hz) 149.3 (ddd, *J* = 250.24, 14.50, 12.97 Hz), 146.6 (ddd, *J* = 244.90, 12.21, 3.82 Hz), 138.6, 135.4 (q, *J* = 32.81 Hz), 128.7, 126.1 (q, 3.81 Hz), 124.8, 122.1, 119.3 (m, *J* = 25.18, 19.84, 18.31, 4.58 Hz), 116.4 (ddd, *J* = 18.31, 6.1, 4.58 Hz), 105.3 (dd, *J* = 28.23, 21.36 Hz), 38.2 ppm; **HRMS (ESI):** Exact mass calcd for $C_{15}H_8F_6O$ $[M+H]^+$: 319.0552 found 319.0543.

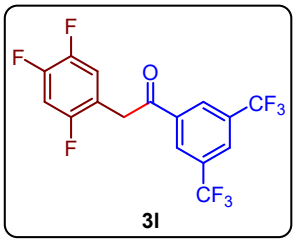
Methyl 3-oxo-3-(4-(trifluoromethyl)phenyl)propanoate (4k)



4k obtained as a colourless oil (0.044 gm, 0.179 mmol, yield: 22%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto/enol mixture of 4k:** δ = 12.41 (s, 1H, enol OH), 8.01 - 7.95 (m, *J* = 7.9 Hz, 2H, C7, C9), 7.83 - 7.77 (m, *J* = 7.9 Hz, 2H, C7', C9'), 7.71 - 7.64 (m, *J* = 7.8 Hz, 2H, C6, C10), 7.62 - 7.57 (m, *J* = 7.9 Hz, 2H, C6', C10'), 5.65 (s, 1H, H3'), 3.96 (s, 2H, H3), 3.75 (s, 3H,

OCH_3 of enol), 3.69 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 191.4 (C4), 173.2 (C4'), 169.6 (C2), 167.4 (C2'), 138.5 (C5), 136.8 (C5'), 134.9 (C8), 133.0 (C8'), 132.7 (C6), 128.9 (C10), 126.4 (C6'), 125.9 (C10'), 125.9 (C7), 125.6 (C7'), 125.6 (C9), 125.5 (C9'), 125.5 (C11), 122.4 (C11'), 88.7 (C3'), 52.6 (C1'), 51.6 (C1), 45.8 (C3) ppm; **HRMS (ESI):** Exact mass calcd for $C_{11}H_9F_3O_3Na$ $[M+Na]^+$: 269.0396, found 269.0385.

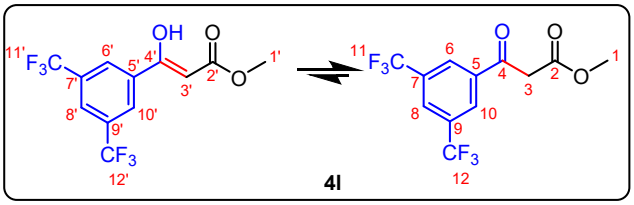
1-(3,5-bis(trifluoromethyl)phenyl)-2-(2,4,5-trifluorophenyl)ethan-1-one (3l)



3l

3l prepared from methyl **1a** (0.2 gm, 0.8124 mmol, 1 equiv) and **2l** (0.29 ml, 1.62 mmol, 2 equiv) using K_2CO_3 (0.225 gm, 1.62 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3l** as a major product and **4l** as a minor product. **3l** obtained as a white solid (0.210 gm, 0.544 mmol, yield: 67%), M.P. 79 81 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.46 (s, 2H), 8.13 (s, 1H), 7.10 (dd, *J* = 16.7, 8.7 Hz, 1H), 7.00 (td, *J* = 9.5, 6.6 Hz, 1H), 4.34 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 192.6, 156 (ddd, *J* = 244.90, 9.16, 3.05 Hz) 149.3 (ddd, *J* = 250.24, 14.50, 12.97 Hz), 146.6 (ddd, *J* = 244.90, 12.21, 3.82 Hz), 137.4, 132.6 (q, *J* = 34.33 Hz), 128.3 (d, *J* = 3.05 Hz), 126.8 (m, *J* = 3.82 Hz), 124.1, 121.4, 119.3 (m, *J* = 25.18, 19.84, 18.31, 4.58 Hz), 118.7, 116.4 (ddd, *J* = 18.31, 6.1, 4.58 Hz), 105.3 (dd, *J* = 28.23, 21.36 Hz), 38.2 ppm; **HRMS (ESI):** Exact mass calcd for $C_{16}H_6F_9O$ [M H]$^+$: 385.0269 found 385.0286.

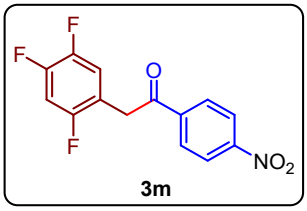
Methyl 3-(3,5-bis(trifluoromethyl)phenyl)-3-oxopropanoate (4l)



4l

4l obtained as a colourless oil (0.046 gm, 0.146 mmol, yield 18%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto/enol mixture of 4l:** δ = 12.56 (s, 1H, enol OH), 8.39 (s, 2H, H6', H10'), 8.21 (s, 2H, H6, H10), 8.11 (br. s., 1H, H8'), 7.97 (br. s., 1H, H8), 5.79 (s, 1H, H3'), 4.08 (s, 2H, H3), 3.85 (s, 3H, OCH_3 of enol), 3.78 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 189.8 (C4), 173.0 (C4'), 167.6 (C2), 166.8 (C2'), 137.4 (C5), 135.6 (C7), 133.2 (C7'), 132.7 (C9), 132.5 (C9'), 132.4 (C6'), 132.1 (C5'), 131.7 (C10), 128.6 (C10'), 128.5 (C8), 126.9 (m, C11), 126.1 (C11'), 124.5 (C12), 124.1 (C12'), 121.6 (C8'), 89.4 (C3'), 52.8 (C1'), 51.9 (C1), 45.6 (C3) ppm; **HRMS (ESI):** Exact mass calcd for $C_{12}H_7F_6O_3$ [M H]$^+$: 313.0294 found 313.0309.

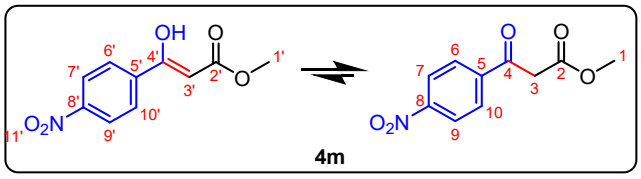
1-(4-nitrophenyl)-2-(2,4,5-trifluorophenyl)ethan-1-one (3m):



3m

3m prepared from **1a** (0.2 gm, 0.8124 mmol, 1 equiv) and **2m**, (0.301 gm, 1.62 mmol, 2 equiv) using K_2CO_3 (0.225 gm, 1.62 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3m** as a major product and **4m** as a minor product, **3m** found as a white solid (0.144 gm, 0.488 mmol, yield: 60%) M.P. 100 102°C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.35 (d, *J* = 7.9 Hz, 2 H), 8.18 (d, *J* = 7.9 Hz, 2H), 7.05 - 7.15 (m, 1H), 6.94 - 7.04 (m, 1H), 4.33 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 193.9, 156 (ddd, *J* = 244.90, 9.16, 3.05 Hz) 149.3 (ddd, *J* = 250.24, 14.50, 12.97 Hz), 146.6 (ddd, *J* = 244.90, 12.21, 3.82 Hz), 140.4, 129.4, 124.1, 119.3 (m, *J* = 25.18, 19.84, 18.31, 4.58 Hz), 118.7, 116.4 (ddd, *J* = 18.31, 6.1, 4.58 Hz), 105.3 (dd, *J* = 28.23, 21.36, Hz), 38.4 ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_7F_3NO_3$ [M H]$^+$: 294.0373, found 294.0387.

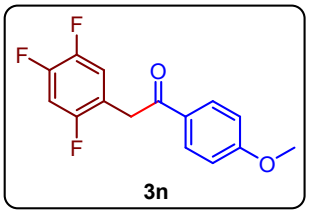
Methyl 3-(4-nitrophenyl)-3-oxopropanoate (4m)



4m

4m obtained as a white solid (0.060 gm, 0.269 mmol, yield 33%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto/enol mixture of 4m**: δ = 12.48 (s, 1H, enol OH), 8.33 (d, *J* = 8.8 Hz, 2H, H7, H9), 8.15 - 8.07 (m, 2H, H7', H9'), 8.27 (d, *J* = 8.9 Hz, 2H, H6, H10), 7.93 (d, *J* = 8.9 Hz, 2H, H6', H10'), 5.77 (s, 1H, H3), 4.06 (s, 2H, H3), 3.84 (s, 3H, OCH_3 of enol), 3.77 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 190.9 (C4), 173.0 (C4'), 168.4 (C2), 167.1 (C2'), 150.7 (C8), 149.3 (C8'), 140.3 (C5), 139.2 (C5'), 129.6 (C6), 129.3 (C6'), 127.0 (C10, C10'), 123.9 (C7, C9), 123.8 (C7', C9'), 89.9 (C3'), 52.8 (C1'), 51.8 (C1), 45.9 (C3) ppm; **HRMS (ESI):** Exact mass calcd for $C_{10}H_8NO_5$ [M H]$^+$: 222.0397, found 222.0404.

1-(4-methoxyphenyl)-2-(2,4,5-trifluorophenyl)ethan-1-one (3n)

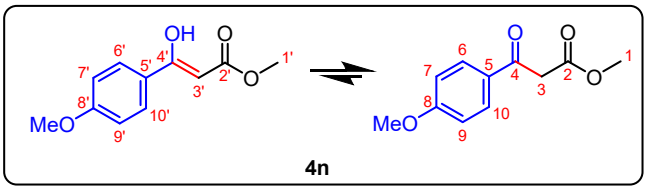


3n

3n prepared from **1a** (0.2 gm, 0.8124 mmol, 1 equiv) and **2n**, (0.24 ml, 1.62 mmol, 2 equiv) using K_2CO_3 (0.225 gm, 1.62 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3n** as a major product and **4n** as a minor product. **3n** found as a white solid (0.155 gm, 0.553 mmol, yield: 68%), M.P. 60 62 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.94 - 8.06 (m, 2H), 7.09 (ddd, *J* = 10.1, 8.8, 7.0 Hz, 1H), 6.89 - 7.01 (m, 3H), 4.22 (s, 2H), 3.85 - 3.91 (m, 3H) ppm; **^{13}C NMR ($CDCl_3$, 100**

MHz): δ = 193.9, 163.9, 156 (ddd, *J* = 244.90, 9.16, 3.05 Hz) 149.3 (ddd, *J* = 250.24, 14.50, 12.97 Hz), 146.6 (ddd, *J* = 244.90, 12.21, 3.82 Hz), 130.7, 129.2, 119.3 (m, *J* = 25.18, 19.84, 18.31, 4.58 Hz), 118.7, 116.4 (ddd, *J* = 18.31, 6.1, 4.58 Hz), 114, 105.3 (dd, *J* = 28.23, 21.36 Hz), 55.5, 37.4 ppm; **HRMS (ESI):** Exact mass calcd for $C_{15}H_{12}O_2F_3$ $[M+H]^+$: 281.0784, found 281.0778.

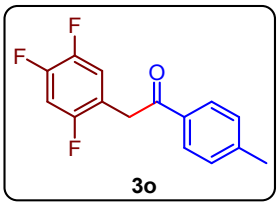
Methyl 3-(4-methoxyphenyl)-3-oxopropanoate (4n)



4n

4n obtained as a colourless oil (0.042 gm, 0.201 mmol, yield 25%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto enol mixture of 4n:** δ = 7.88 - 7.95 (m, *J* = 8.8 Hz, 2H, H6, H10), 6.91 - 6.97 (m, *J* = 8.9 Hz, 2H, H7, H9), 3.96 (s, 2H, H3), 3.86 (s, 3H), 3.74 (s, 3H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 190.8 (C4), 168.2 (C4'), 164.0 (C8), 130.9 (C6), 129.0 (C10), 127.8 (C7), 113.9 (C9), 55.5 (OCH_3 of C8), 52.4 OCH_3 of C1), 45.5 (C3) ppm; **HRMS (ESI):** Exact mass calcd for $C_{11}H_{13}O_4$ $[M+H]^+$: 209.0808, found 209.0803.

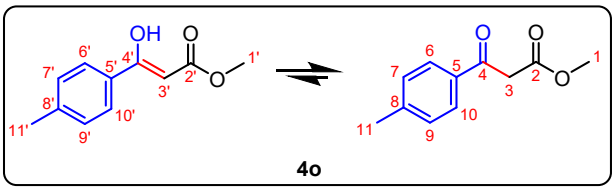
1-(p-tolyl)-2-(2,4,5-trifluorophenyl)ethan-1-one (3o)



3o

3o prepared from **1a** (0.2 gm, 0.8124 mmol, 1 equiv) and **2o** (0.21 ml, 1.62 mmol, 2 equiv) using K_2CO_3 (0.225 gm, 1.62 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3o** as a major product and, **4o** as a minor product, **3o** found as a white solid (0.151 gm, 0.5719 mmol, yield: 70%), M.P. 100 102 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.97 - 7.97 (m, *J* = 8.1 Hz, 2H), 7.28 - 7.34 (m, *J* = 8.1 Hz, 2H), 7.02 - 7.15 (m, 1H), 6.95 (td, *J* = 9.5, 6.7 Hz, 1H), 4.26 (s, 2 H), 2.44 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 195.0, 156 (ddd, *J* = 244.90, 9.16, 3.05 Hz) 149.3 (ddd, *J* = 250.24, 14.50, 12.97 Hz), 146.6 (ddd, *J* = 244.90, 12.21, 3.82 Hz), 144.6, 133.6, 129.5, 128.7, 128.5, 119.3 (m, *J* = 25.18, 19.84, 18.31, 4.58 Hz), 118.4 (ddd, *J* = 18.31, 6.1, 4.58 Hz), 105.3 (dd, *J* = 28.23, 21.36 Hz), 37.7, 21.7 ppm; **^{19}F NMR ($CDCl_3$)** δ -118.60 (d, *J* = 15.79) -135.16 (d, *J* = 23.67) -1423(d, *J* = 15.78) ppm; **HRMS (ESI):** Exact mass calcd for $C_{15}H_{12}F_3O$ $[M+H]^+$: 265.0835, found 265.0836.

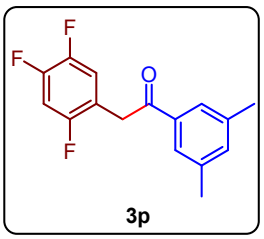
Methyl 3-oxo-3-(p-tolyl)propanoate (4o)



4o

4o obtained as a colourless oil (0.035 gm, 0.1822 mmol, yield: 22%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto enol mixture of 4o:** δ = 12.50 (s, 1H, enol OH), 7.88 - 7.81 (m, *J* = 7.6 Hz, 2H, C7, C9), 7.70 - 7.64 (m, *J* = 7.6 Hz, 2H, C7', C9'), 7.31 - 7.24 (m, *J* = 7.9 Hz, 2H, C6, C10), 7.25 - 7.18 (m, *J* = 7.9 Hz, 2H, C6', C10'), 5.64 (s, 1H, H3'), 3.98 (s, 2H, H3),3.79 (s, 3H, OCH_3 of enol), 3.74 (s, 3H, OCH_3 of keto), 2.41 (s, 3H, H11), 2.39 (s, 3H, C11'); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 192.0 (C4), 173.6 (C4'), 171.7 (C2), 168.1 (C2'), 144.8 (C8), 141.8 (C8'), 133.5 (C5), 130.8 (C5'), 130.5 (C7), 129.5 (C7', C10), 129.3 (C9), 128.9 (C9'), 128.7 (C6, C10'), 126.0 (C6'), 86.3 (C3'), 52.4 (C1), 51.4 (C1'), 45.6 (C3), 21.7 (C11), 21.5 (C11'); **HRMS (ESI):** Exact mass calcd for $C_{11}H_{13}O_3$ $[M+H]^+$: 193.0859, found 193.0853.

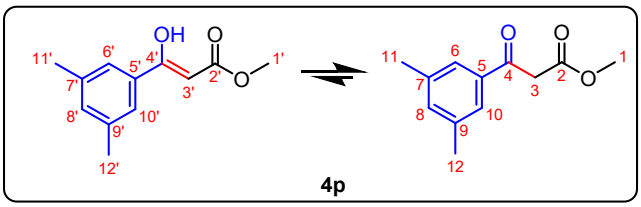
1-(3,5-dimethylphenyl)-2-(2,4,5-trifluorophenyl)ethan-1-one (3p)



3p

3p prepared from methyl **1a** (0.2 gm, 0.8124 mmol, 1 equiv) and **2p** (0.22 ml, 1.62 mmol, 2 equiv) using K_2CO_3 (0.225 gm, 1.62 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3p** as a major product and **4p** as a minor product. **3p** found as a white solid (0.153 gm, 0.550 mmol, yield: 71%), M.P. 76 78 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.63 (s, 2H), 7.25 (s, 1H), 7.01 - 7.14 (m, 1H), 6.96 (td, *J* = 9.6, 6.6 Hz, 1H), 4.26 (s, 2H), 2.40 (s, 6H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 195.7, 156 (ddd, *J* = 244.90, 9.16, 3.05 Hz) 149.3 (ddd, *J* = 250.24, 14.50, 12.97 Hz), 146.6 (ddd, *J* = 244.90, 12.21, 3.82 Hz), 138.5, 136.2, 135.3, 126.1, 119.3 (m, *J* = 25.18, 19.84, 18.31, 4.58 Hz), 118.4 (ddd, *J* = 18.31, 6.1, 4.58 Hz), 105.3 (dd, *J* = 28.23, 21.36 Hz), 38.0, 21.3 ppm; **HRMS (ESI):** Exact mass calcd for $C_{16}H_{14}OF_3$ $[M+H]^+$: 279.0991, found 279.0987.

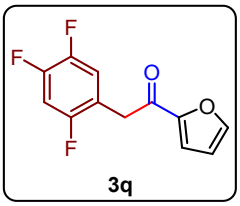
Methyl 3-(3,5-dimethylphenyl)-3-oxopropanoate (4p)



4p

4p obtained as a colourless oil (0.034 gm, 0.165 mmol, yield: 22%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto enol mixture of 4p:** δ =12.48 (s, 1H, enol OH) 7.55 (br. s., 2H, H6, H10), 7.40 (br. s., 2H, H6', H10'), 7.24 (br. s., 1H, H9), 7.11 (br. s., 1 H), 5.65 (s, 1H, H3'), 3.99 (s, 2H, H3), 3.80 (br. s., 3H, OCH_3 of enol), 3.76 (s, 3H, OCH_3 of keto), 2.38 (br. s., 6H, H11, H12), 2.35 (br. s., 6H, H11', H12'); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 192.83 (C4), 173.7 (C4'), 172 (C2') 168.1 (C2), 138.5 (C9), 136.1 (C9), 135.5 (C7), 133 (C7), 131.8 (C5), 131.6 (C5'), 129.5 (C8), 128.7 (C8)', 128.7 (C6), 127.0 (C6'), 126.3 (C10), 123.9 (C10'), 86.9 (C3'), 52.5 (C1'), 51.4 (C1), 45.7 (C3), 21.3 (C11', C12'), 21.2 (C11, C12) ppm; **HRMS (ESI):** Exact mass calcd for $C_{12}H_{15}O_3$ $[M+H]^+$: 207.1016, found 207.1009.

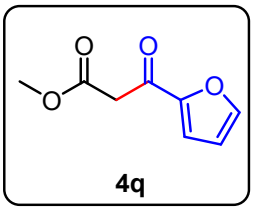
1-(furan-2-yl)-2-(2,4,5-trifluorophenyl)ethan-1-one (3q)



3q

3q prepared from **1a** (0.2 gm, 0.8124 mmol, 1 equiv) and **2q** (0.16 ml, 1.62 mmol, 2 equiv) using K_2CO_3 (0.225 gm, 1.62 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3q** as a major product and inseparable mixture as a minor product, **3q** as a white solid (0.391 gm, 1.629 mmol, yield: 80%), M.P. 68 70 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.69 - 7.59 (m, 1H), 7.30 (d, *J* = 3.5 Hz, 1H), 7.13 (ddd, *J* = 6.9, 8.8, 10.1 Hz, 1H), 6.95 (dt, *J* = 6.6, 9.6 Hz, 1H), 6.58 (dd, *J* = 1.7, 3.6 Hz, 1H), 4.13 (s, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 184.4, 156 (ddd, *J* = 244.90, 9.16, 3.05 Hz) 149.3 (ddd, *J* = 250.24, 14.50, 12.97 Hz), 146.6 (ddd, *J* = 244.90, 12.21, 3.82 Hz), 119.3 (m, *J* = 25.18, 19.84, 18.31, 4.58 Hz), 118.4 (ddd, *J* = 18.31, 6.1, 4.58 Hz), 105.3 (dd, *J* = 28.23, 21.36, Hz), 37.5 ppm; **^{19}F NMR ($CDCl_3$, 375 MHz)** δ = -118.50 (d, *J* = 15.79 Hz), -134.86 (d, *J* = 19.73 Hz), -142.85 (d, *J* = 15.78 Hz) ppm; **HRMS (ESI):** Exact mass calcd for $C_{12}H_8F_3O_2$ $[M+H]^+$: 241.0471, found 241.0476.

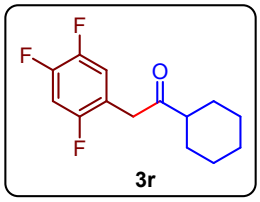
Methyl 3-(furan-2-yl)-3-oxopropanoate (4q)



4q

4q obtained as a colourless oil (0.021 gm, 0.125 mmol, yield: 15%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ = 7.54 (s, 1H), 7.21 (d, *J* = 3.8 Hz, 1H), 6.47 - 6.53 (m, 1H), 3.80 (s, 2H), 3.67 (s, 3H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 180.9, 167.4, 151.9, 147.1, 144.9, 143.5, 143.3, 118.4, 112.8, 112.1, 112.0, 111.6, 110.4, 109.4, 52.7, 52.5, 52.4, 45.2, 29.7 ppm; **HRMS (ESI):** Exact mass calcd for $C_8H_9O_4$ $[M+H]^+$: 169.0495, found 169.0491.

1-cyclohexyl-2-(2,4,5-trifluorophenyl)ethan-1-one (3r)

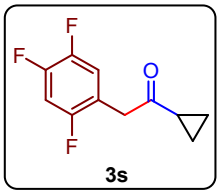


3r

3a prepared from **1a** (0.2 gm, 0.8124 mmol, 1 equiv) and **2r** (0.22 ml, 1.62 mmol, 2 equiv) using K_2CO_3 (0.225 gm, 1.62 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3r** as a major product and unseprable mixture of minor product, **3r** as a colourless oil (0.137 gm, 0.534 mmol, yield: 66%); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 6.95 (ddd, *J* = 6.9, 8.7, 10.2 Hz, 1H), 6.85 (dt, *J* = 6.6, 9.6 Hz, 1H), 3.76 (s, 2H), 1.92 (tt, *J* = 4.6, 7.8 Hz, 1H), 1.01 (quin, *J* = 3.8 Hz, 2H), 0.86 (qd, *J* = 3.7, 7.4 Hz, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz)** δ = 205.9, 156 (ddd, *J* = 244.90, 9.16, 3.05 Hz) 149.3 (ddd, *J* = 250.24, 14.50, 12.97 Hz), 146.6 (ddd, *J* = 244.90, 12.21, 3.82

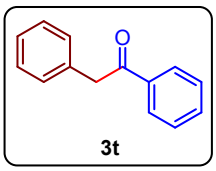
Hz), 119.3 (m, J = 25.18, 19.84, 18.31, 4.58 Hz), 118.4 (ddd, J = 18.31, 6.1, 4.58 Hz), 105.3 (dd, J = 28.23, 21.36, Hz), 42.5, 20.3, 11.4 ppm; **^{19}F NMR ($CDCl_3$, 375 MHz)** δ -118.70, -118.7 (dd, J = 13.87, 3.47 Hz), -135. (dd, J = 22.54, 3.47 Hz), -143.00 (dd, J = 20.80, 15.6 Hz) ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_{14}F_3O$ [M H]$^+$: 256.0991, found 255.1004.

1-cyclopropyl-2-(2,4,5-trifluorophenyl)ethan-1-one (3s)



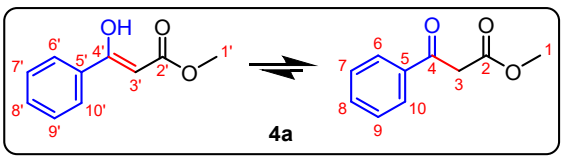
3s prepared from **1a** (0.2 gm, 0.8124 mmol, 1 equiv) and **2s**, (0.147 ml, 1.62 mmol, 2 equiv) using K_2CO_3 (0.225 gm, 1.62 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3s** as a major product and unseprable mixture as a minor product, **3a** as a colourless oil (0.096 gm, 0.448 mmol, yield: 55%); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.02 - 6.91 (m, 1H), 6.86 (dt, J = 6.7, 9.5 Hz, 1H), 3.81 - 3.73 (m, 2H), 1.96 - 1.88 (m, 1H), 1.01 (quin, J = 3.8 Hz, 2H), 0.86 (qd, J = 3.7, 7.5 Hz, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 206.0, 156 (ddd, J = 244.90, 9.16, 3.05 Hz), 149.3 (ddd, J =250.24, 14.50, 12.97 Hz), 146.6 (ddd, J = 244.90), 119.3 (m, J = 25.18, 19.84, 18.31, 4.58 Hz), 118.4 (ddd, J = 18.31, 6.1, 4.58 Hz), 105.3 (dd, J = 28.23, 21.36, Hz), 42.6, 20.3, 16.0, 11.7, 11.5, 9.4 ppm; **HRMS (ESI):** Exact mass calcd for $C_{11}H_{10}F_3O$ [M+H]$^+$ 215.0678, found 215.0674.

1, 2-diphenylethan-1-one (3t)



3t prepared from **1b** (0.2 gm, 1.04 mmol, 1 equiv) and **2a** (0.24 ml, 2.08 mmol, 2 equiv) using K_2CO_3 (0.288 gm, 2.08 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3t** as a major product and **4a** as a minor product, **3t** found as a white solid (0.133 gm, 0.678 mmol, yield: 65%), M.P. 48 50 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.93 (d, J = 8.0 Hz, 2H), 7.51 - 7.43 (m, 1H), 7.42 - 7.33 (m, 2H), 7.28 - 7.11 (m, 5H), 4.20 (s, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 195.8, 134.6, 132.6, 131.3, 127.6, 126.8, 126.8, 126.7, 125, 43.6 ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_{13}O$ [M+H]$^+$: 196.0961, found 197.0959.

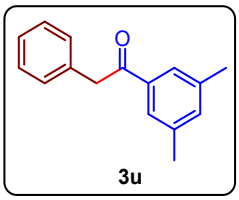
Methyl 3-oxo-3-phenylpropanoate (4a)



4a found as a yellowish oil (0.028 gm, 0.157 mmol, yield: 15%); **^{1}H NMR $CDCl_3$, 400 MHz) Keto/enol mixture of 4a:** δ = 12.50 (s, 1H of enol), 7.97 - 7.93 (m, 2H, H6, H10), 7.80 - 7.76

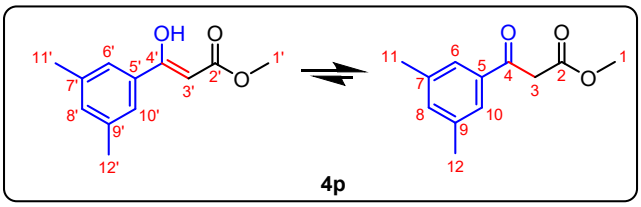
(m, 2H, H6', H10'), 7.64 - 7.58 (m, 1H, H8), 7.52 - 7.47 (m, 2H, H7, H9), 7.46 - 7.39 (m, 3H, H7', H8', H9'), 5.68 (s, 1H, CH of enol), 4.02 (s, 2H, CH_2 of keto), 3.81 (s, 3H, OCH_3 of enol), 3.76 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 192.4 (C4), 173.5 (C4'), 171.5 (C2'), 168.0 (C2), 135.9 (C5), 133.8 (C5'), 133.3 (C8'), 131.3 (C8), 128.8 (C7, C9), 128.5 (C6, C10, C7', C9'), 126.1 (C6', C10'), 87.1 (C3'), 52.5 (C1), 51.4 (C1'), 45.7 (C3) ppm; **HRMS (ESI)**: Exact mass calcd for $C_{10}H_{11}O_3$ $[M+H]^+$: 179. 0703, found 179.0697.

1-(3,5-dimethylphenyl)-2-phenylethan-1-one (3u)



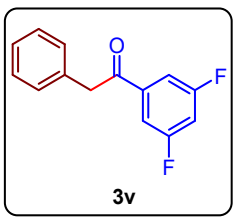
3u prepared from **1b** (0.2 gm, 1.04 mmol, 1 equiv) and benzoyl chloride **2p** (0.3 ml, 2.08 mmol, 2 equiv) using K_2CO_3 (0.288 gm, 2.08 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3u** as a major product and **4p** as a minor product, **3u** found as a colourless oil (0.152 gm, 0.678 mmol, yield: 65%); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.54 (s, 2H), 7.24 (dd, *J* = 7.8, 6.9 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 3H), 7.11 (s, 1H), 4.18 (s, 2H), 2.23 - 2.32 (m, 6H) ppm; **^{13}C NMR ($CDCl_3$, 100MHz):** δ = 198.1, 138.3, 136.8, 134.9, 134.8, 129.5, 128.7, 126.8, 126.4, 45.5, 21.3 ppm; **HRMS (ESI):** Exact mass calcd for $C_{16}H_{17}O$ $[M+H]^+$: 225.1274, found 225.1270.

Methyl 3-(3,5-dimethylphenyl)-3-oxopropanoate (4p)



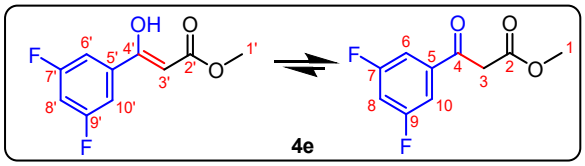
4p obtained as a colourless oil (0.034 gm, 0.165 mmol, yield: 22%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto enol mixture of 4p:** δ =12.48 (s, 1H, enol OH) 7.55 (br. s., 2H, H6, H10), 7.40 (br. s., 2H, H6', H10'), 7.24 (br. s., 1H, H9), 7.11 (br. s., 1 H), 5.65 (s, 1H, H3'), 3.99 (s, 2H, H3), 3.80 (br. s., 3H, OCH_3 of enol), 3.76 (s, 3H, OCH_3 of keto), 2.38 (br. s., 6H, H11, H12), 2.35 (br. s., 6H, H11', H12'); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 192.83 (C4), 173.7 (C4'), 172 (C2') 168.1 (C2), 138.5 (C9), 136.1 (C9), 135.5 (C7), 133 (C7), 131.8 (C5), 131.6 (C5'), 129.5 (C8), 128.7 (C8)', 128.7 (C6), 127.0 (C6'), 126.3 (C10), 123.9 (C10'), 86.9 (C3'), 52.5 (C1'), 51.4 (C1), 45.7 (C3), 21.3 (C11', C12'), 21.2 (C11, C12) ppm; **HRMS (ESI):** Exact mass calcd for $C_{12}H_{15}O_3$ $[M+H]^+$: 207.1016, found 207.1009.

(3,5-difluorophenyl)-2-phenylethan-1-one (3v)



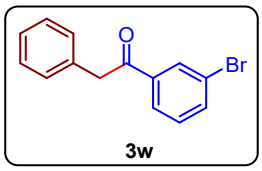
3v prepared from **1b** (0.2 gm, 1.04 mmol) and **2e**, 0.26 ml, 2.08 mmol) using K_2CO_3 (0.288 gm, 2.08 mmol according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3v** as a major product and **4e** as a minor product, **3v** found as a white solid (0.152 gm, 0.655 mmol, yield: 63%), M.P. 50 - 52 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.46 - 7.39 (m, 2H), 7.30 - 7.24 (m, 2H), 7.23 - 7.14 (m, 3H), 6.96 - 6.88 (m, 1H), 4.16 (s, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 195.1, 163 (dd, *J* =251.01, 11.44 Hz), 139.4(t, *J* =14.01, 7.63 Hz), 133.5, 129.4, 128.9, 127.3, 111.3 (m, *J* = 25.94, 19.07, 7.63), 108.5 (t, *J* = 51.12, 25. 18), 45.7 ppm; **^{19}F NMR ($CDCl_3$, 375 MHz)** δ -107.86 ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_{11}OF_2$ $[M+H]^+$: 233.0772 found 233.0771.

Methyl 3-(3,5-difluorophenyl)-3-oxopropanoate (4e)



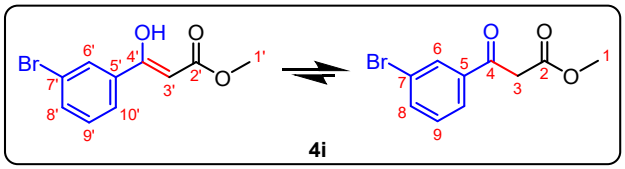
4e obtained as a colourless oil (0.028 gm, 0.130 mmol, yield: 16%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto/enol mixture of 4e:** δ =12.38 (s, 1H enol OH), 7.38 (d, *J* = 6.6 Hz, 2H, H6, H10), 7.24 - 7.18 (m, 2H, H6', H10'), 7.21 (d, *J* = 7.3 Hz, 1H, H8), 6.88 - 6.80 (m, 1H, H8'), 5.57 (s, 1H, H3'), 3.90 (s, 2H, H3),3.75 (s, 3H, OCH_3 of enol), 3.70 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 190.0 (C4), 173.1 (C4'), 168.5 (t, *J* = 6.1, 3.05Hz, C2'), 167.2 (C2), 164.4 (dd, *J* = 12.21, 9.16 Hz, C9, C9'), 161.88 (m, C7, C7'), 138.7 (t, *J* = 15.26 7.63, C5), 136.6 (t, *J* = 19.07, 9.92 Hz, C5') 111.6 (m, C10), 109.5 (m, C6, C10, C8), 106.5 (t, *J* = 51.12, 25.94 Hz, C8'), 88.6 (C3'), 52.8 (C1'), 51.8 (C1), 45.7 (C3) ppm; **HRMS (ESI):** Exact mass calcd for $C_{10}H_7F_2O_3$ $[M\ H]^+$: 213.0358, found 213.0363.

1-(3-bromophenyl)-2-phenylethan-1-one (3w)



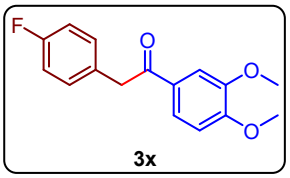
3w prepared from **1b** (0.2 gm, 1.04 mmol, 1 equiv) and **2i** (0.27 ml, 2.08 mmol, 2 equiv) using K_2CO_3 (0.288 gm, 2.08 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3w** as a major product and **4i** as a minor product, **3w** as a white solid (0.192 gm, 0.700 mmol, yield: 67%) M.P. 80 83 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.04 (s, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.38 - 7.09 (m, 6H), 4.15 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 196.2, 138.3, 136.0, 134.0, 131.6, 130.3, 129.5, 128.8, 127.2, 127.1, 123.1, 45.6 ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_{12}OBr$ $[M\ H]^+$: 275.0086, found 275.0062.

Methyl 3-(3-bromophenyl)-3-oxopropanoate (4i)



4i obtained as a colourless oil (0.042 gm, 0.164 mmol, yield: 20%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto/enol mixture of 4i:** δ = 12.46 (s, 1H, enol OH), 8.07 (t, *J* = 1.8 Hz, 1H, H6), 7.91 (t, *J* = 1.8 Hz, 1H, H6'), 7.86 (dt, *J* = 7.8, 1.3 Hz, 1H, H10), 7.68 (dt, *J* = 7.9, 1.3 Hz, 1H, H10'), 7.72 (ddd, *J* = 8.0, 1.9, 0.9 Hz, 1H, H8), 7.60 - 7.55 (m, 1H, H8'), 7.37 (t, *J* = 7.9 Hz, 1H, H9), 7.31 - 7.27 (m, 1H, H9'), 5.65 (s, 1H, H3'), 3.98 (s, 2H, H3), 3.81 (s, 3H, OCH_3 of enol), 3.76 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** 191.03 (C4), 173.25 (C4'), 169.6 (C2), 167.5 (C2') 137.6 (C5), 136.6 (C5'), 135.2 (C8), 134 (C8'), 131.4 (C6), 130.3 (C6'), 130 (C9), 129.1 (C9'), 127 (C10), 124.6 (C10'), 123.1 (C7), 122.7 (C7'), 87.95 (C3'), 52.59 (C1'), 51.59 (C1), 45.58 (C3) ppm; **HRMS (ESI):** Exact mass calcd for $C_{10}H_9O_3BrNa$ $[M+Na]^+$: 278.9627, found 278.9622.

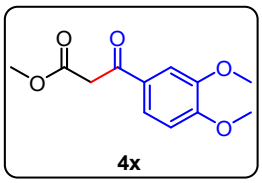
1-(3,4-dimethoxyphenyl)-2-(4-fluorophenyl)ethan-1-one (3x)



3x

3x prepared from **1c** (0.2 gm, 0.9514 mmol, 1 equiv) and **2t** (0.229 gm, 1.9 mmol, 2 equiv) using K_2CO_3 (0.263 gm, 1.9 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3x** as a major product and **4t** as a minor product, **3x** as a white solid (0.175 gm, 0.638 mmol, yield: 67%), M.P. 104 106 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.66 (d, *J* = 8.4 Hz, 1H), 7.56 (s, 1H), 7.31 - 7.17 (m, 2H), 7.07 - 6.96 (m, 2H), 6.90 (d, *J* = 8.4 Hz, 1H), 4.23 (s, 2H), 3.93 (s, 3H), 3.95 (s, 3H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz**): δ = 196.1, 161.8 (d, *J* = 245.67 Hz), 153.5, 149.2, 130.9, 130.9, 130.7, 130.7, 129.6, 123.3, 115.6, 115.4, 110.6, 110.0, 56.1, 56.0, 44.1 ppm; **HRMS (ESI):** Exact mass calcd for $C_{16}H_{15}FO_3$ $[M+H]^+$: 274.1078, found 275.1073.

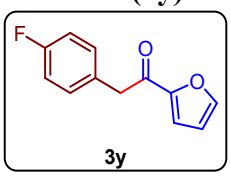
Methyl 3-(3,4-dimethoxyphenyl)-3-oxopropanoate(4t)



4x

4k obtained as a colourless oil (0.043 gm, 0.180 mmol, yield: 19%); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.63 - 7.49 (m, 2H), 6.90 (d, *J* = 7.9 Hz, 1H), 3.98 (s, 2H), 3.95 (s, 3H), 3.93 (s, 3 H), 3.75 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 189.0, 166.2, 152.0, 147.3, 127.3, 121.7, 108.4, 108.2, 75.5, 75.2, 74.8, 54.2, 54.1, 50.5, 43.5 ppm; **HRMS (ESI):** Exact mass calcd for $C_{12}H_{15}O_5$ $[M+H]^+$: 239.0914, found 239.0912.

2-(4-fluorophenyl)-1-(furan-2-yl)ethan-1-one (3y)

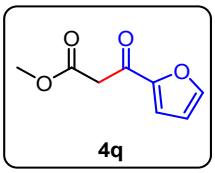


3y

3y prepared from **1c** (0.2 gm, 0.9514 mmol, 1 equiv) **2q** (0.19 ml, 1.9 mmol, 2 equiv) using K_2CO_3 (0.263 gm, 1.9 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate :

petroleum ether mixture (1 : 9) as eluent to afford the title compound **3y** as a major product and **4q** as a minor product, **3y** found as a white solid (0.143 gm, 0.699 mmol, yield: 73%) M.P**.** 49 51 °C; **^{1}H NMR ($CDCl_3$, 400MHz):** δ = 7.59 (s, 1H), 7.31 - 7.16 (m, 3H), 7.00 (t, *J* = 7.9 Hz, 2H), 6.58 - 6.48 (m, 1H), 4.09 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100MHz):** δ = 186.4, 161.9 (d, *J* = 244.90), 152.3, 146.7, 131.1, 131.0, 129.7(d, *J* = 3.05), 117.9, 115.6, 115.4, 112.5, 44.4 ppm; **HRMS (ESI):** Exact mass calcd for $C_{12}H_{10}FO_2$ $[M+H]^+$: 205.0659, found 205.0664.

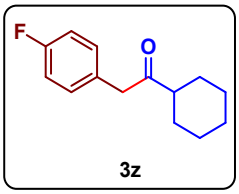
Methyl 3-(furan-2-yl)-3-oxopropanoate (4q)



4q

4q obtained as a colourless oil (0.021 gm, 0.125 mmol, yield: 15%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ = 7.54 (s, 1H), 7.21 (d, *J* = 3.8 Hz, 1H), 6.47 - 6.53 (m, 1H), 3.80 (s, 2H), 3.67 (s, 3H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 180.9, 167.4, 151.9, 147.1, 144.9, 143.5, 143.3, 118.4, 112.8, 112.1, 112.0, 111.6, 110.4, 109.4, 52.7, 52.5, 52.4, 45.2, 29.7 ppm; **HRMS (ESI):** Exact mass calcd for $C_8H_9O_4$ $[M+H]^+$: 169.0495, found 169.0491.

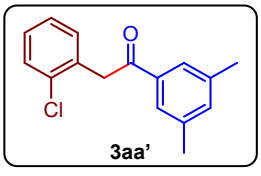
1-cyclohexyl-2-(4-fluorophenyl)ethan-1-one (3z)



3z

3y prepared from **1c** (0.2 gm, 0.8124 mmol, 1 equiv) **2r** (0.47 ml, 1.62 mmol, 2 equiv) using K_2CO_3 (0.263 gm, 1.62 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3z** as a major product and unseperable mixture as a minor product, **3z** found as a colorless oil (0.134 gm, 0.609 mmol yield: 64%); **^{1}H NMR (400 MHz, ($CDCl_3$, 400 MHz)** δ = 7.18 - 7.09 (m, 2H), 7.04 - 6.95 (m, 2H), 3.70 (s, 2H), 2.50 - 2.38 (m, 1H), 1.87 - 1.73 (m, 5H), 1.42 - 1.18 (m, 6H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz)** δ = 211.0, 161.9 (d, *J* = 244.90), 131.0, 130.9, 130.1, 130.1, 115.5, 115.3, 50.3, 46.8, 28.5, 25.8, 25.8, 25.6 ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_{16}OF$ $[M\ \ H]^+$: 219.1180, found 219.1183.

2-(2-chlorophenyl)-1-(3,5-dimethylphenyl)ethan-1-one (3aa')

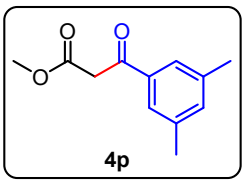


3aa'

3aa' prepared from **1d** (0.2 gm, 0.8824 mmol, 1 equiv) and benzoyl chloride **2p** (0.26 ml, 1.76 mmol, 2 equiv) using K_2CO_3 (0.244 gm, 1.76 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3aa'** as a major product and **4p** as a minor product, **3aa'** found as a white solid

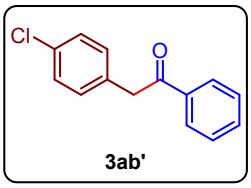
(0.137 gm, 0.531mmol, yield: 60%), M.P. 52 54 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.65 (s, 2H), 7.23 (d, *J* = 4.1 Hz, 4H), 4.40 (s, 2H), 2.38 (s, 6H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 196.7, 138.3, 136.8, 135.0, 134.5, 133.4, 131.7, 129.5, 128.5, 126.9, 126.1, 43.3, 21.3 ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_{16}OF$ $[M+H]^+$: 259.0884, found 259.0885.

Methyl 3-(3,5-dimethylphenyl)-3-oxopropanoate(4p)



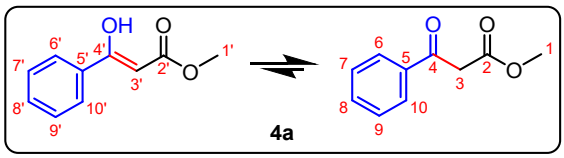
4p obtained as a colourless oil (0.034 gm, 0.165 mmol, yield: 22%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto enol mixture of 4p:** δ =12.48 (s, 1H, enol OH) 7.55 (br. s., 2H, H6, H10), 7.40 (br. s., 2H, H6', H10'), 7.24 (br. s., 1H, H9), 7.11 (br. s., 1 H), 5.65 (s, 1H, H3'), 3.99 (s, 2H, H3), 3.80 (br. s., 3H, OCH_3 of enol), 3.76 (s, 3H, OCH_3 of keto), 2.38 (br. s., 6H, H11, H12), 2.35 (br. s., 6H, H11', H12'); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 192.83 (C4), 173.7 (C4'), 172 (C2') 168.1 (C2), 138.5 (C9), 136.1 (C9), 135.5 (C7), 133 (C7), 131.8 (C5), 131.6 (C5'), 129.5 (C8), 128.7 (C8)', 128.7 (C6), 127.0 (C6'), 126.3 (C10), 123.9 (C10'), 86.9 (C3'), 52.5 (C1'), 51.4 (C1), 45.7 (C3), 21.3 (C11', C12'), 21.2 (C11, C12) ppm; **HRMS (ESI):** Exact mass calcd for $C_{12}H_{15}O_3$ $[M+H]^+$: 207.1016, found 207.1009.

2-(4-chlorophenyl)-1-phenylethan-1-one (3ab')



3ab' prepared from **1e** (0.2 gm, 0.8823 mmol, 1 equiv) and benzoyl chloride **2a** (0.2 ml, 1.76 mmol, 2 equiv) using K_2CO_3 (0.244 gm, 1.76 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3ab'** as a major product and **4a** as a minor product, **3ab'** found as a white solid (0.139 gm, 0.604, yield: 68%), M.P. 125 127 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.01 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.35 - 7.28 (m, *J* = 8.4 Hz, 2H), 7.24 - 7.17 (m, *J* = 8.4 Hz, 2H), 4.27 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 197.1, 136.4, 133.4, 133.0, 132.9, 130.9, 128.8, 128.7, 128.5, 77.4, 77.1, 76.7, 44.7 ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_{12}OCl$ [M+H]+: 231.0571, found 231.0568.

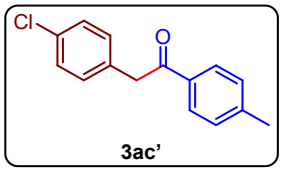
Methyl 3-oxo-3-phenylpropanoate (4a)



4a found as a yellow oil (0.024 gm, 0.134 mmol, yield: 15%); **^{1}H NMR $CDCl_3$, 400 MHz) Keto/enol mixture of 4a:** δ = 12.50 (s, 1H of enol), 7.97 - 7.93 (m, 2H, H6, H10), 7.80 - 7.76 (m, 2H, H6', H10'), 7.64 - 7.58 (m, 1H, H8), 7.52 - 7.47 (m, 2H, H7, H9), 7.46 - 7.39 (m, 3H, H7', H8', H9'), 5.68 (s, 1H, CH of enol), 4.02 (s, 2H, CH_2 of keto), 3.81 (s, 3H, OCH_3 of enol),

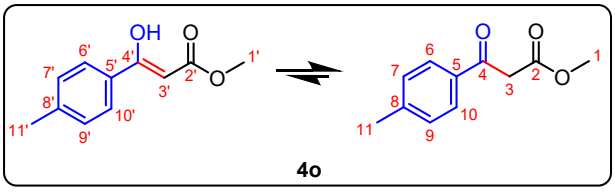
3.76 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 192.4 (C4), 173.5 (C4'), 171.5 (C2'), 168.0 (C2), 135.9 (C5), 133.8 (C5'), 133.3 (C8'), 131.3 (C8), 128.8 (C7, C9), 128.5 (C6, C10, C7', C9'), 126.1 (C6', C10'), 87.1 (C3'), 52.5 (C1), 51.4 (C1'), 45.7 (C3) ppm; **HRMS (ESI)**: Exact mass calcd for $C_{10}H_{11}O_3$ $[M+H]^+$: 179. 0703, found 179.0697.

12-(4-chlorophenyl)-1-(p-tolyl)ethan-1-one (3ac')



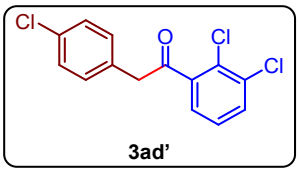
3ac' prepared from **1e** (0.2 gm, 0.824 mmol, 1 equiv) and **2o** (0.23 ml, 1.76 mmol, 2 equiv) using K_2CO_3 (0.244 gm, 1.76 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3ac'** as a major product and **4o** as a minor product, **3ac'** found as a white solid (0.156 gm, 0.639 mmol, yield: 72%), M.P. 105 107 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.89 (d, *J* = 7.9 Hz, 2H), 7.51 - 7.22 (m, 4H), 7.18 (d, *J* = 8.1 Hz, 2H), 4.22 (s, 2H), 2.40 (s, 3H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 196.8, 144.3, 133.9, 133.2, 132.8, 130.9, 129.4, 128.8, 128.7, 44.6, 21.7 ppm; **HRMS (ESI)**: Exact mass calcd for $C_{15}H_{12}OCl$ [M H]$^+$: 243.0571, found 243.0581.

Methyl 3-oxo-3-(p-tolyl)propanoate (4o)



4o obtained as a colourless oil (0.035 gm, 0.1822 mmol, yield: 22%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto enol mixture of 4o:** δ = 12.50 (s, 1H, enol OH), 7.88 - 7.81 (m, *J* = 7.6 Hz, 2H, C7, C9), 7.70 - 7.64 (m, *J* = 7.6 Hz, 2H, C7', C9'), 7.31 - 7.24 (m, *J* = 7.9 Hz, 2H, C6, C10), 7.25 - 7.18 (m, *J* = 7.9 Hz, 2H, C6', C10'), 5.64 (s, 1H, H3'), 3.98 (s, 2H, H3),3.79 (s, 3H, OCH_3 of enol), 3.74 (s, 3H, OCH_3 of keto), 2.41 (s, 3H, H11), 2.39 (s, 3H, C11'); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 192.0 (C4), 173.6 (C4'), 171.7 (C2), 168.1 (C2'), 144.8 (C8), 141.8 (C8'), 133.5 (C5), 130.8 (C5'), 130.5 (C7), 129.5 (C7', C10), 129.3 (C9), 128.9 (C9'), 128.7 (C6, C10'), 126.0 (C6'), 86.3 (C3'), 52.4 (C1), 51.4 (C1'), 45.6 (C3), 21.7 (C11), 21.5 (C11'); **HRMS (ESI):** Exact mass calcd for $C_{11}H_{13}O_3$ [M+H]+: 193.0859, found 193.0853.

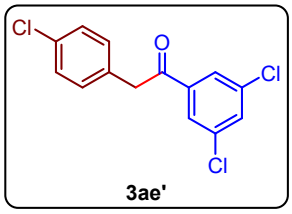
2-(4-chlorophenyl)-1-(2,3-dichlorophenyl)ethan-1-one (3ad')



3ad' prepared from **1e** (0.2 gm, 0.8823 mmol, 1 equiv) and **2g** (0.24 ml, 1.76 mmol, 2 equiv) using K_2CO_3 (0.244 gm, 1.76 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3ad'** as a major product and unidentified mixture as a minor product, **3ac'** found as a white solid (0.153 gm, 0.153

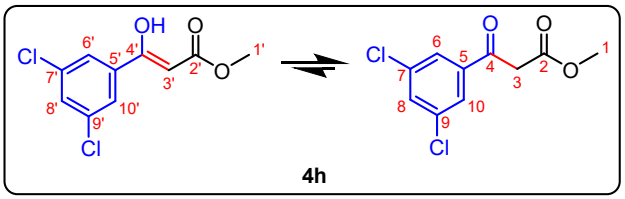
mmol, yield: 58%), M.P. 88 - 91 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.53 (d, *J* = 7.8 Hz, 1H), 7.34 - 7.10 (m, 6H), 4.17 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 199.9, 141.5, 134.1, 133.3, 132.3, 131.6, 131.1, 128.9, 128.7, 127.8, 126.5, 48.9 ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_{10}Cl_3O$ $[M+H]^+$: 298.9792, found 298.9686.

2-(4-chlorophenyl)-1-(3,5-dichlorophenyl)ethan-1-one (3ae')



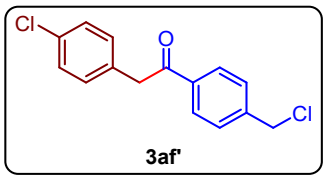
3ae' prepared from **1e** (0.2 gm, 0.8823 mmol, 1 equiv) and benzoyl chloride **2h** (0.25 ml, 1.76 mmol, 2 equiv) using K_2CO_3 (0.244 gm, 1.76 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3ae'** as a major product and **4h** as a minor product, **3ae'** found as a white solid (0.174 mg, 0.583 mmol, yield: 66%), M.P. 97 99 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.75 (d, *J* = 1.6 Hz, 2H), 7.51 - 7.43 (m, 1H), 7.28 - 7.21 (m, *J* = 8.4 Hz, 2H), 7.14 - 7.02 (m, *J* = 8.3 Hz, 2H), 4.13 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 194.6, 138.7, 135.8, 133.3, 133.1, 131.8, 130.9, 129, 126.9, 44.8 ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_9Cl_3O$ [M H]$^+$: 296.9635, found 296.9656.

Methyl 3-(3,5-dichlorophenyl)-3-oxopropanoate (4h)



4h obtained as a colourless oil (0.032 gm, 0.130 mmol, yield 16%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto/enol mixture of 4h**: δ = 12.44 (s, 1H, enol OH), 7.80 - 7.76 (m, 2H, H6, H10), 7.64 - 7.60 (m, 2H, H6', H10'), 7.59 - 7.56 (m, 1H, H8), 7.44 - 7.41 (m, 1H, H8'), 5.64 (s, 1H, H3'), 3.97 (s, 2H, H3), 3.81 (s, 3H, OCH_3 of enol), 3.77 (s, 3H, OCH_3 of keto); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 190.3 (C4), 173.3 (C4'), 168.5 (C2), 167.4 (C2'), 138.5 (C5), 136.5 (C7), 136.1 (C7'), 135.6 (C9), 133.9 (C9'), 133.7 (C8), 131.2 (C5'), 130.1 (C8'), 128.6 (C10), 127.2 (C10'), 126.4 (C6), 124.8 (C6'), 89 (C3'), 53 (C1'), 52 (C1), 45.8 (C3) ppm; **HRMS (ESI):** Exact mass calcd for $C_{10}H_8O_3Cl_2$ $[M+H]^+$ 246.9923, found 246.9921.

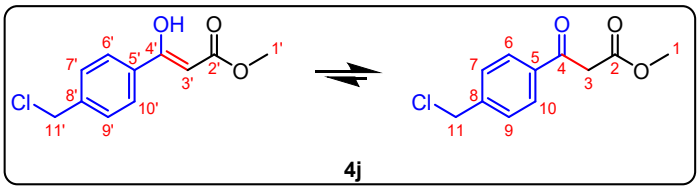
1-(4-(chloromethyl)phenyl)-2-(4-chlorophenyl)ethan-1-one (3af'):



3af' prepared from **1e** (0.2 gm, 0.8823 mmol, 1 equiv) and **2J** (0.218 ml, 1.76 mmol, 2 equiv) using K_2CO_3 (0.244 gm, 1.76 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate

: petroleum ether mixture (1 : 9) as eluent to afford the title compound **3af'** as a major product and **4j** as a minor product, **3af'** found as a white solid (0.153 gm, 0.550 mmol, yield: 62%), M.P. 115 117 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.08 - 7.87 (m, *J* = 7.4 Hz, 2 H), 7.63 - 7.40 (m, *J* = 7.8 Hz, 2 H), 7.40 - 7.24 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2 H), 4.61 (s, 2H), 4.26 ppm (s, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 196.5, 142.7, 136.2, 133.0, 132.8, 130.9, 129.0, 128.8, 45.2, 44.8 ppm; **HRMS (ESI):** Exact mass calcd for $C_{15}H_{12}Cl_2O$ [M H]$^+$ 277.0181, found = 277.0193.

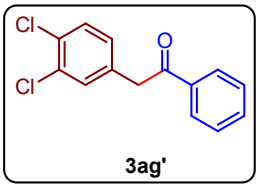
Methyl 3-(4-(chloromethyl)phenyl)-3-oxopropanoate (4J)



4j

4J obtained as a colourless oil (0.037 gm, 0.163 mmol, yield: 20%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto/enol mixture of 4J**: δ = 12.41 (s, 1H, enol OH), 7.89 - 7.80 (m, *J* = 7.9 Hz, 2H, H7,H9), 7.72 - 7.63 (m, *J* = 7.9 Hz, 2H, H7', H9'), 7.47 - 7.38 (m, *J* = 8.0 Hz, 2H, H6, H10), 7.33 - 7.38 (m, *J* = 8.0 Hz, 2H, H6', H10'), 5.60 (s, 1H, H3'), 4.53 (s, 2H, H11), 4.52 (s, 2H, H11'), 3.92 (s, 2H, H3), 3.72 (s, 3H, OCH_3 of enol), 3.67 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 191.7 (C4), 173.3(C4'), 170.6(C2), 167.7(C2'), 143.1 (C8'), 140.5 (C8'), 135.6 (C5), 133.3 (C5'), 130.9 (C6), 128.9 (C6'), 128.8 (C10, C7), 128.8 (C10'), 128.6 (C9), 128.6 (C9'), 126.4 (C7'), 87.3 (C3'), 52.4 (C1'), 51.4 (C1), 48.1 (C3), 45.6 (C11), 45.1 (C11') ppm; **HRMS (ESI):** Exact mass calcd for $C_{11}H_{11}O_3ClNa$ [M Na]$^+$: 249.0289, found 249.0282.

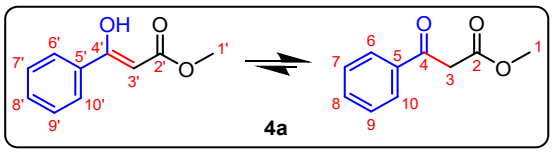
2-(3,4-dichlorophenyl)-1-phenylethan-1-one (3ag'):



3ag'

3ag' prepared from **1f** (0.2 gm, 0.766 mmol, 1 equiv) and **2a** (0.17 ml, 1.53 mmol, 2 equiv) using K_2CO_3 (0212 gm, 1.53 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3ag'** as a major product and **4a** as a minor product, **3ag'** as a white solid (0.132 gm, 0.497 mmol, yield: 65%), M.P. 89 91 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.01 (d, *J* = 7.9 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.45 - 7.32 (m, 2H), 7.11 (d, *J* = 8.1 Hz, 1H), 4.26 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 196.4, 136.2, 134.6, 133.6, 132.6, 131.6, 131.2, 130.5, 129.1, 128.8, 128.5, 44.2 ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_{11}Cl_2O[M+H]^+$: = 265.0181, found 265.0179.

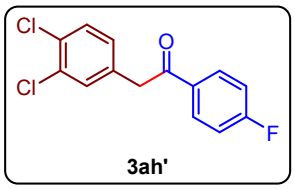
Methyl 3-oxo-3-phenylpropanoate (4a)



4a

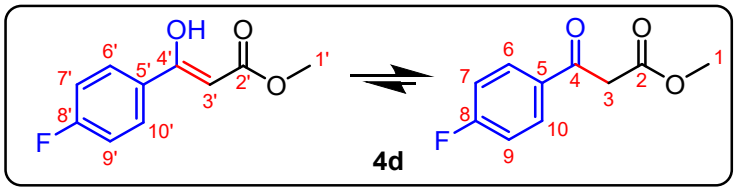
4a obtained as a yellow oil (0.021 gm, 0.117 mmol, yield: 15.4%); **^{1}H NMR CDCl$_3$, 400 MHz) Keto/enol mixture of 4a:** δ = 12.50 (s, 1H of enol), 7.97 - 7.93 (m, 2H, H6, H10), 7.80 - 7.76 (m, 2H, H6', H10'), 7.64 - 7.58 (m, 1H, H8), 7.52 - 7.47 (m, 2H, H7, H9), 7.46 - 7.39 (m, 3H, H7', H8', H9'), 5.68 (s, 1H, CH of enol), 4.02 (s, 2H, CH_2 of keto), 3.81 (s, 3H, OCH_3 of enol), 3.76 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR (CDCl$_3$, 100 MHz):** δ = 192.4 (C4), 173.5 (C4'), 171.5 (C2'), 168.0 (C2), 135.9 (C5), 133.8 (C5'), 133.3 (C8'), 131.3 (C8), 128.8 (C7, C9), 128.5 (C6, C10, C7', C9'), 126.1 (C6', C10'), 87.1 (C3'), 52.5 (C1), 51.4 (C1'), 45.7 (C3) ppm; **HRMS (ESI)**: Exact mass calcd for $C_{10}H_{11}O_3$ $[M+H]^+$: 179. 0703, found 179.0697.

2-(3,4-dichlorophenyl)-1-(4-fluorophenyl)ethan-1-one (3ah'):



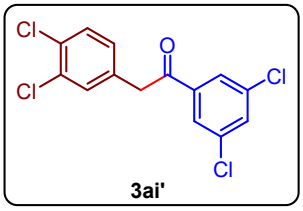
3ah' prepared from methyl **1f** (0.2 gm, 0.766 mmol, 1 equiv) and **2d** (0.18 ml, 153 mmol, 2 equiv) using K_2CO_3 (0.212 gm, 1.53 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3ah'** as a major product and **4d** as a minor product, **3ah'** found as a white solid (0.147 gm, 0.554 mmol, yield 68%), M.P. 82 84 °C; **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 8.02 - 7.88 (m, 2H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 1.9 Hz, 1H), 7.08 (t, *J* = 8.6 Hz, 2H), 7.01 (dd, *J* = 1.8, 8.2 Hz, 1H), 4.15 (s, 2H) ppm; **^{13}C NMR (CDCl$_3$, 100 MHz):** δ = 194.9, 166 (d, *J* = 255.5 Hz), 134.3, 132.6 (t, *J* = 3.05, 6.1 Hz), 131.5, 131.3 (d, *J* = 9.16 Hz), 131.1, 130.6, 129.0, 116.1, 115.9, 44.2 ppm; **HRMS (ESI)**: Exact mass calcd for $C_{14}H_{10}Cl_2FO$ $[M+H]^+$: 283.0087, found 283.0084.

Methyl 3-(4-fluorophenyl)-3-oxopropanoate (4d)



4d found as a colourless oil (0.021 gm, 0.107 mmol, yield: 14%); **^{1}H NMR (CDCl$_3$, 400 MHz) Keto/enol mixture of 4d:** δ =12.44 (s, 1H, enol OH), 7.88 (t, *J* = 5.9 Hz, 2H, H6, H10), 7.67 (t, *J* = 6.0 Hz, 2H, H6', H10'), 7.05 (t, *J* = 7.9 Hz, 2H, H7, H9), 7.00 (br. s., 2H, H7', H9'), 5.52 (s, 1H, H3'), 3.90 (s, 2H, H3), 3.70 (s, 3H, OCH_3 of enol) 3.65 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR (CDCl$_3$, 100 MHz):** δ = 189.8 (C4), 173.0 (C4'), 167.6 (C2), 166.9 (C2'), 137.4 (C5'), 135.6 (C5), 133.1-131.7 (m, C8, C8', C9'), 128.5 (d, *J* = 3.0 Hz, C10'), 126.9 (m, C6), 126.1 (d, *J* = 3.05 Hz, C10) 124.5 (m, C6), 124.3 (d, *J* = 23.65, C9), 121.6 (d, *J* = 23.65 Hz, C7'), 118.7 (d, *J* = 22.89 Hz, C7), 89.4 (C3'), 52.8 (C1'), 51.9 (C1), 45.6 (C3) ppm; **HRMS (ESI):** Exact mass calcd for $C_{10}H_9FO_3Na$ $[M+Na]^+$: 219.0428 found 219.0421.

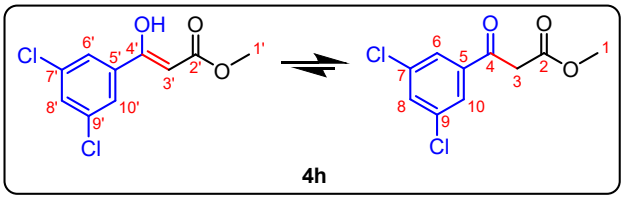
2-(3,4-dichlorophenyl)-1-(3,5-dichlorophenyl)ethan-1-one (3ai')



3ai'

3ai' prepared from **1f** (0.2 gm, 0.766 mmol, 1 equiv) and **2h** (0.22 ml, 1.53 mmol, 2 equiv) using K_2CO_3 (0.212 gm, 1.53 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3ai**' as a major product and **4h** as a minor product, **3a** found as a white solid. 0.130 gm, 0.490 mmol, yield: 64%), M.P**.** 58 60 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.84 (s, 2H), 7.58 (s, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.34 (s, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 4.21 ppm (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100MHz):** δ = 193.9, 138.6, 135.9, 133.4, 133.2, 132.8, 131.6, 131.5, 130.7, 129.0, 126.8, 44.3 ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_7Cl_3O^{37}Cl$ $[M-H]^+$: 332.9216 found 332.9226.

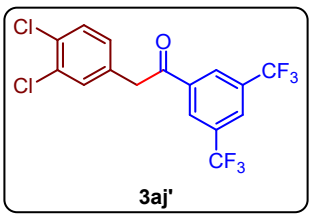
Methyl 3-(3,5-dichlorophenyl)-3-oxopropanoate (4h)



4h

4h found as a colourless oil (0.032 gm, 0.129 mmol, yield 17%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto/enol mixture of 4h**: δ = 12.44 (s, 1H, enol OH), 7.80 - 7.76 (m, 2H, H6, H10), 7.64 - 7.60 (m, 2H, H6', H10'), 7.59 - 7.56 (m, 1H, H8), 7.44 - 7.41 (m, 1H, H8'), 5.64 (s, 1H, H3'), 3.97 (s, 2H, H3), 3.81 (s, 3H, OCH_3 of enol), 3.77 (s, 3H, OCH_3 of keto); **^{13}C NMR ($CDCl_3$, 100 MHz**): δ = 190.3 (C4), 173.3 (C4'), 168.5 (C2), 167.4 (C2'), 138.5 (C5), 136.5 (C7), 136.1 (C7'), 135.6 (C9), 133.9 (C9'), 133.7 (C8), 131.2 (C5'), 130.1 (C8'), 128.6 (C10), 127.2 (C10'), 126.4 (C6), 124.8 (C6'), 89 (C3'), 53 (C1'), 52 (C1), 45.8 (C3) ppm; **HRMS (ESI):** Exact mass calcd for $C_{10}H_8O_3Cl_2$ $[M+H]^+$: 246.9923, found 246.9921.

1-(3,5-bis(trifluoromethyl)phenyl)-2-(3,4-dichlorophenyl)ethan-1-one (3aJ')

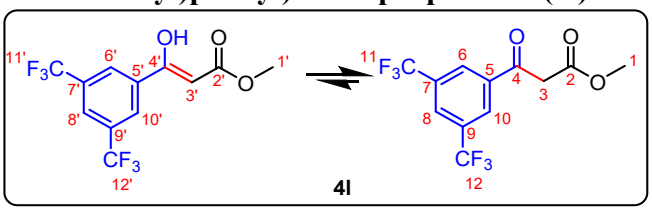


3aj'

3aJ' prepared from **1f** (0.2 gm, 0.766 mmol, 1 equiv) and **2l** (0.28 ml, 1.53 mmol, 2 equiv) using K_2CO_3 (0.212 gm, 1.53 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3aJ**' as a major product and **4l** as a minor product, **3aJ**' found as a white solid (0.184 gm, 0.458 mmol, yield: 60%), M.P. 58 60 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.02 - 7.88 (m, 2H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 1.9 Hz, 1H), 7.08 (t, *J* = 8.6 Hz, 2H), 7.01 (dd, *J* = 1.8, 8.2 Hz, 1H), 4.15 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz**):δ = 193.6, 137.6, 133.1, 132.9, (d, *J* = 2.29) 132.8, 132.5, 132.1, 131.8, 131.6, 130.8, 129.0, 128.4 (d, *J* = 2.29) 126.7(m, *J* = 1.53, 5.34, 9.16,

12.21, 16.02) 124.1, 121.4, 118.7, 44.4 ppm; **HRMS (ESI):** Exact mass calcd for $C_{16}H_7OCl_2F_6$ $[M-H]^+$: 398.9773, found 398.9797.

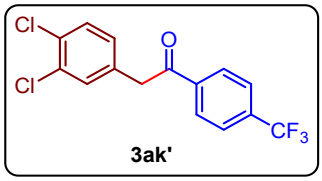
Methyl 3-(3,5-bis(trifluoromethyl)phenyl)-3-oxopropanoate (4l)



4l

4l obtained as a colourless oil (0.043 gm, 0.137 mmol, yield 18%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto/enol mixture of 4l:** δ = 12.56 (s, 1H, enol OH), 8.39 (s, 2H, H6', H10'), 8.21 (s, 2H, H6, H10), 8.11 (br. s., 1H, H8'), 7.97 (br. s., 1H, H8), 5.79 (s, 1H, H3'), 4.08 (s, 2H, H3), 3.85 (s, 3H, OCH_3 of enol), 3.78 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 189.8 (C4), 173.0 (C4'), 167.6 (C2), 166.8 (C2'), 137.4 (C5), 135.6 (C7), 133.2 (C7'), 132.7 (C9), 132.5 (C9'), 132.4 (C6'), 132.1 (C5'), 131.7 (C10), 128.6 (C10'), 128.5 (C8), 126.9 (m, C11), 126.1 (C11'), 124.5 (C12), 124.1 (C12'), 121.6 (C8'), 89.4 (C3'), 52.8 (C1'), 51.9 (C1), 45.6 (C3) ppm; **HRMS (ESI):** Exact mass calcd for $C_{12}H_7F_6O_3$ $[M - H]^+$: 313.0294 found 313.0309.

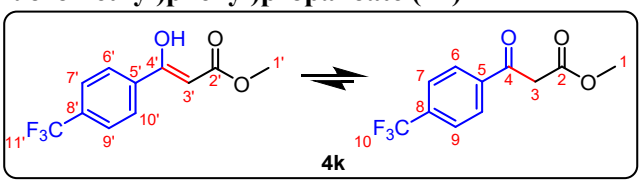
2-(3,4-dichlorophenyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (3ak')



3ak'

3ak' prepared from **1f** (0.2 gm, 0.766 mmol, 1 equiv) and **2k** (0.23 ml, 1.53 mmol, 2 equiv) using K_2CO_3 (0.212 gm, 1.53 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3ak'** as a major product and **4k** as a minor product, **3ak'** found as a white solid (0.174 gm, 0. 522 mmol, yield: 68%), M.P. 87 89 °C; **^{1}H NMR ($CDCl_3$, 400MHz):** δ = 8.06 - 7.95 (m, *J* = 7.8 Hz, 2H), 7.72 - 7.61 (m, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.27 (s, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 4.19 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 195.4, 138.8, 135.0, 134.7, 133.8, 132.8, 131.5, 130.6, 129.0, 128.8, 126.0, 125.9, 125.9, 125.9, 44.5 ppm; **HRMS (ESI):** Exact mass calcd for $C_{15}H_8F_3OCl_2$ $[M - H]^+$:330.9899 found 330.9914.

Methyl 3-oxo-3-(4-(trifluoromethyl)phenyl)propanoate (4k)

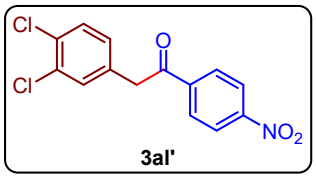


4k

4k obtained as a colourless oil (0.042 gm, 0.170 mmol, yield: 22%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto/enol mixture of 4k:** δ = 12.41 (s, 1H, enol OH), 8.01 - 7.95 (m, *J* = 7.9 Hz, 2H, C7, C9), 7.83 - 7.77 (m, *J* = 7.9 Hz, 2H, C7', C9'), 7.71 - 7.64 (m, *J* = 7.8 Hz, 2H, C6, C10), 7.62 - 7.57 (m, *J* = 7.9 Hz, 2H, C6', C10'), 5.65 (s, 1H, H3'), 3.96 (s, 2H, H3), 3.75 (s, 3H, OCH_3 of enol), 3.69 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 191.4 (C4), 173.2 (C4'), 169.6 (C2), 167.4 (C2'), 138.5 (C5), 136.8 (C5'), 134.9 (C8), 133.0 (C8'),

132.7 (C6), 128.9 (C10), 126.4 (C6'), 125.9 (C10'), 125.9 (C7), 125.6 (C7'), 125.6 (C9), 125.5 (C9'), 125.5 (C11), 122.4 (C11'), 88.7 (C3'), 52.6 (C1'), 51.6 (C1), 45.8 (C3) ppm; **HRMS (ESI):** Exact mass calcd for$C_{11}H_9F_3O_3Na$ $[M+Na]^+$: 269.0396, found 269.0385.

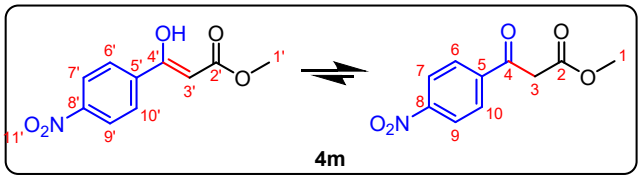
2-(3,4-dichlorophenyl)-1-(4-nitrophenyl)ethan-1-one (3al')



3al'

3al' prepared from **1f** (0.2 gm, 0.766 mmol, 1 equiv) and **2m** (0.202 gm, 1.56 mmol, 2 equiv) using K_2CO_3 (0.212 gm, 1.56 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3al'** as a major product and **4m** as a minor product, **3al'** found as a white solid (0.133 gm, 0.429 mmol, yield: 56%), M.P. 105 107 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.37 - 8.28 (m, *J* = 8.6 Hz, 2H), 8.19 - 8.08 (m, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.39 - 7.30 (m, 1H), 7.10 (dd, *J* = 1.6, 8.3 Hz, 1H), 4.31 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100MHz):** δ = 194.9, 150.6, 140.6, 133.4, 132.9, 131.7, 131.5, 130.7, 129.5, 129.0, 124.0, 77.4, 77.0, 76.7, 44.7 ppm; **HRMS (ESI):** Exact mass calcd for$C_{14}H_{10}Cl_2O_3N$ $[M+H]^+$: 310.0032, found 310.0012.

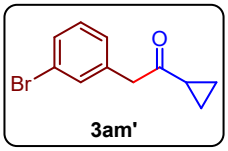
Methyl 3-(4-nitrophenyl)-3-oxopropanoate (4m)



4m

4m obtained as a white solid (0.036 gm, 0.161 mmol, yield: 21%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto/enol mixture of 4m**: δ = 12.48 (s, 1H, enol OH), 8.33 (d, *J* = 8.8 Hz, 2H, H7, H9), 8.15 - 8.07 (m, 2H, H7', H9'), 8.27 (d, *J* = 8.9 Hz, 2H, H6, H10), 7.93 (d, *J* = 8.9 Hz, 2H, H6', H10'), 5.77 (s, 1H, H3), 4.06 (s, 2H, H3), 3.84 (s, 3H, OCH_3 of enol), 3.77 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 190.9 (C4), 173.0 (C4'), 168.4 (C2), 167.1 (C2'), 150.7 (C8), 149.3 (C8'), 140.3 (C5), 139.2 (C5'), 129.6 (C6), 129.3 (C6'), 127.0 (C10, C10'), 123.9 (C7, C9), 123.8 (C7', C9'), 89.9 (C3'), 52.8 (C1'), 51.8 (C1), 45.9 (C3) ppm; **HRMS (ESI):** Exact mass calcd for $C_{10}H_8NO_5$ $[M-H]^+$: 222.0397, found 222.0404.

2-(4-bromophenyl)-1-cyclopropylethan-1-one (3am')

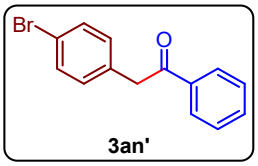


3am'

3am' prepared from **1g** (0.2 gm, 0.7377 mmol, 1 equiv) and **2s** (0.133 ml, 1.48 mmol, 2 equiv) using K_2CO_3 (0.204 gm, 1.48 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3al'** as a major product and unidentified mixture as a minor product, **3am'** found as a white solid (0.099 gm, 0.415 mmol, yield: 56%), M.P. 105 107 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.44 - 7.35 (m, 2H), 7.26 - 7.12 (m, 2H), 3.81 (s, 2H), 1.97 (dt, *J* = 7.8, 3.8 Hz, 1H), 1.06 (quin, *J* = 3.7 Hz, 2H),

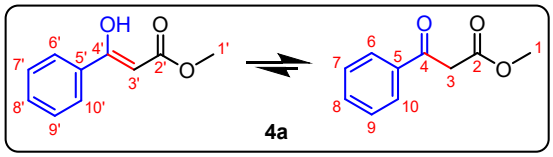
0.89 (dq, *J* = 7.5, 3.5 Hz, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 207.4, 136.6, 132.6, 130.1, 130.1, 128.2, 122.6, 50.0, 20.3, 11.6, 11.5 ppm; **HRMS (ESI):** Exact mass calcd for $C_{11}H_{12}{}^{81}BrO$ $[M+H]^+$ 241.0046, found 241.0040.

2-(4-bromophenyl)-1-phenylethan-1-one (3an')



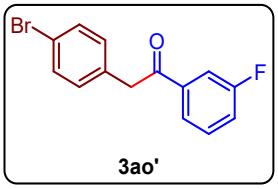
3an' prepared from **1h** (0.2 gm, 0.7377 mmol, 1 equiv) and **2a** (0.17 ml, 1.48 mmol, 2 equiv) using K_2CO_3 (0.204 gm, 1.48 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3an'** as a major product and **4a** as a minor product, **3an'** found as a white solid (0.138 gm, 0.501 mmol, yield: 68%), M.P. 131 133 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.07 7.94 (m, *J* = 8.0 Hz, 2H), 7.61 7.54 (m, 1H), 7.42 - 7.54 (m, 4H), 7.08 - 7.22 (m, *J* = 8.1 Hz, 2H), 4.25 ppm (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 197.1, 136.4, 133.4, 133.0, 132.9, 130.9, 128.8, 128.7, 128.5, 77.4, 77.1, 76.7, 44.7 ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_{12}{}^{81}BrO$ $[M+H]^+$ 277.0046, found 277.0047.

Methyl 3-oxo-3-phenylpropanoate (4a)



4a found as a yellowish oil (0.022 gm, 0.123 mmol, yield: 17%); **^{1}H NMR $CDCl_3$, 400 MHz) Keto/enol mixture of 4a:** δ = 12.50 (s, 1H of enol), 7.97 - 7.93 (m, 2H, H6, H10), 7.80 - 7.76 (m, 2H, H6', H10'), 7.64 - 7.58 (m, 1H, H8), 7.52 - 7.47 (m, 2H, H7, H9), 7.46 - 7.39 (m, 3H, H7', H8', H9'), 5.68 (s, 1H, CH of enol), 4.02 (s, 2H, CH_2 of keto), 3.81 (s, 3H, OCH_3 of enol), 3.76 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 192.4 (C4), 173.5 (C4'), 171.5 (C2'), 168.0 (C2), 135.9 (C5), 133.8 (C5'), 133.3 (C8'), 131.3 (C8), 128.8 (C7, C9), 128.5 (C6, C10, C7', C9'), 126.1 (C6', C10'), 87.1 (C3'), 52.5 (C1), 51.4 (C1'), 45.7 (C3) ppm; **HRMS (ESI)**: Exact mass calcd for $C_{10}H_{11}O_3$ $[M+H]^+$: 179. 0703, found 179.0697.

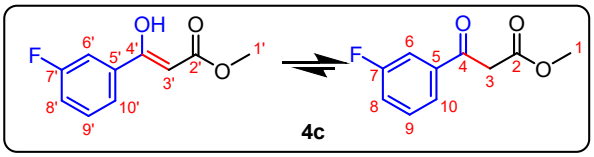
2-(4-bromophenyl)-1-(3-fluorophenyl)ethan-1-one (3ao')



3ao' prepared from **1h** (0.2 gm, 0.7377 mmol, 1 equiv) and **2c** (0.18 ml, 1.48 mmol, 2 equiv) using K_2CO_3 (0.204 gm, 1.48 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3ao'** as a major product and **4c** as a minor product, **3ao'** found as a white solid (0.152 gm, 0.518 mmol, yield: 70%), M.P. 59 61 °C; **^{1}H NMR $CDCl_3$, 400 MHz):** δ = 8.03 (dd, *J* = 8.3, 5.7 Hz, 2sH), 7.46 (d, *J*

= 8.1 Hz, 2H), 7.20 - 7.08 (m, 4H), 4.22 ppm (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 195.4, 167.1, 164.6, 133.3, 132.8, 132.8, 131.8, 131.2, 131.2, 131.1, 121.1, 116.0, 115.8, 44.7 ppm; **HRMS (ESI)**: Exact mass calcd for $C_{14}H_9OBrF$ [M H]$^+$: 290.9815, found 290.9837.

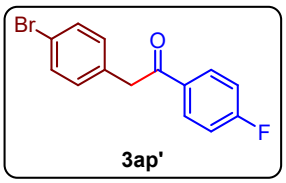
Methyl 3-(3-fluorophenyl)-3-oxopropanoate (4c)



4c

4c obtained as colourless oil (0.022 gm, 0.112 mmol, yield: 15%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto/enol mixture of 4c:** δ = 12.40 (s, 1H, enol OH), 7.65 (d, *J* = 7.8 Hz, 1H, H10), 7.58 - 7.55 (m, 1H, 10'), 7.56 (td, *J* = 2.0, 9.3 Hz, 1H, H9), 7.48 (d, *J* = 7.9 Hz, 1H, H9'), 7.44 - 7.36 (m, 1H, H8), 7.32 (dt, *J* = 8.0, 5.8 Hz, 1H, H8'), 7.27 - 7.20 (m, 1H, H6), 7.09 (dt, *J* = 8.3, 2.5 Hz, 1H, H6'), 5.59 (s, 1H, H3'), 3.92 (s, 2H, H3), 3.69 (s, 3H, OCH_3 of keto), 3.74 (s, 3H, OCH_3 of enol) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 191.2 (d, *J* = 2.29 Hz, C4), 173.3 (C4'), 169.9 (d, *J* = 2.29 Hz, C2'),167.6 (C2), 164.1 (C7), 161.6 (C7'), 137.9 (d, *J* = 6.1 Hz, C5), 135.6 (d, *J* = 7.63 Hz, C5'), 130.6 (d, *J* = 7.63 Hz, C9), 130.2 (d, *J* = 7.63 Hz, C9'), 124.3 (d, *J* = 3.05 Hz, C10), 121.7 (d, *J* = 3.05 Hz, C10'), 120.8 (d, *J* = 21.36 Hz, C8), 118.2 (d, *J* = 20.6 Hz, C8'), 115.2 (d, *J* = 22.89 Hz, C6), 113.1 (d, *J* = 23.65 Hz, C6'), 87.9 (C3'), 52.6 (C1), 51.6 (C1'), 45.8 (C3) ppm; **^{19}F NMR ($CDCl_3$, 375 MHz)** δ -111.26, -112.31 ppm; **HRMS (ESI)**: Exact mass calcd for $C_{10}H_9FO_3Na$ [M+Na]$^+$: 219.0428, found 219.0421.

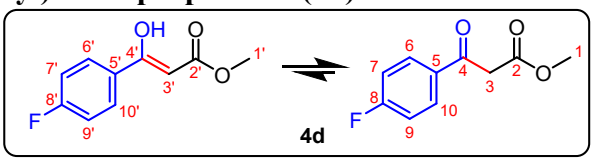
2-(4-bromophenyl)-1-(4-fluorophenyl)ethan-1-one (3ap')



3ap'

We prepared **3ap'** from **1h** (0.2 gm, 0.7377 mmol, 1 equiv) and **2d** (0.17 ml, 1.48 mmol, 2 equiv) using K_2CO_3 (0.204 gm, 1.48 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3ap'** as a major product and **4c** as a minor product, **3ao'** found as a white solid (0.154 gm, 0.525 mmol, yield: 71%), M.P. 131 133 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.77 (d, *J* = 7.63 Hz, 1H), 7.66 (d, *J* = 8.63 Hz, 1 H), 7.44 (m, 3H), 7.27 (m, 1H), 7.12 (d, *J* = 7.63 Hz, 2H), 4.95 (m, 1H), 4.21 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 195.7 (d, *J* = 2.29 Hz), 162.8 (d, 247.85), 138.5(d, 6.1 Hz), 133.0, 131.9, 131.2, 130.5(d, 7.6 Hz), 124.3, (d, 3 Hz), 121.2, 120.5(d, 6.1 Hz), 115.4(d, 22.1 Hz), 44.9 ppm; **HRMS (ESI)**: Exact mass calcd for $C_{14}H_{10}O^{81}BrF$ [M+H]$^+$: 294.9951, found 294.9952.

Methyl 3-(4-fluorophenyl)-3-oxopropanoate (4d)

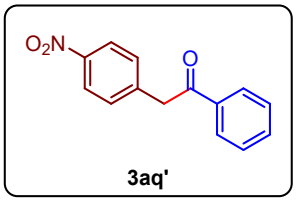


4d

4d obtained as a colourless oil (0.019 gm, 0.0968 mmol, yield: 13%); **^{1}H NMR ($CDCl_3$, 400 MHz) Keto/enol mixture of 4d:** δ =12.44 (s, 1H, enol OH), 7.88 (t, *J* = 5.9 Hz, 2H, H6, H10),

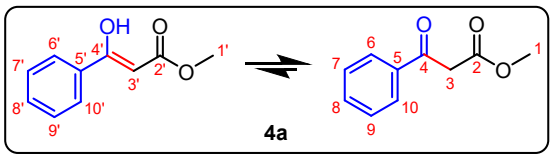
7.67 (t, J = 6.0 Hz, 2H, H6', H10'), 7.05 (t, J = 7.9 Hz, 2H, H7, H9), 7.00 (br. s., 2H, H7', H9'), 5.52 (s, 1H, H3'), 3.90 (s, 2H, H3), 3.70 (s, 3H, OCH_3 of enol) 3.65 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 189.8 (C4), 173.0 (C4'), 167.6 (C2), 166.9 (C2'), 137.4 (C5'), 135.6 (C5), 133.1-131.7 (m, C8, C8', C9'), 128.5 (d, J = 3.0 Hz, C10'), 126.9 (m, C6), 126.1 (d, J = 3.05 Hz, C10) 124.5 (m, C6), 124.3 (d, J = 23.65, C9), 121.6 (d, J = 23.65 Hz, C7'), 118.7 (d, J = 22.89 Hz, C7), 89.4 (C3'), 52.8 (C1'), 51.9 (C1), 45.6 (C3) ppm; **HRMS (ESI):** Exact mass calcd for $C_{10}H_9FO_3Na$ $[M+Na]^+$: 219.0428 found 219.0421.

2-(4-nitrophenyl)-1-phenylethan-1-one (3aq')



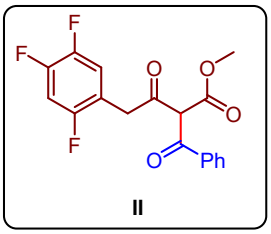
3aq' prepared from **1i** (0.20 gm, 8431 mmol, 1 equiv) and **2a** (0.17 ml, 1.69 mmol, 2 equiv) using K_2CO_3 (0.233 gm, 1.69 mmol, 2 equiv) according to general procedure **A**, purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **3aq'** as a major product and **4a** as a minor product, **3aq'** as a white solid (0.165 gm, 0.684 mmol, yield: 81%), M.P. 134 136 °C; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ = 8.26 - 8.14 (m, J = 8.4 Hz, 2H), 8.07 - 7.96 (m, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H), 7.47 - 7.41 (m, J = 8.6 Hz, 2H), 4.43 (s, 2H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 195.0, 146.0, 141.0, 135.1, 132.7, 129.6, 127.9, 127.4, 122.7, 76.3, 76.2, 76.0, 75.7, 43.9 ppm; **HRMS (ESI):** Exact mass calcd for $C_{14}H_{12}NO_3$ $[M+H]^+$: 242.0812 found 242.0808.

Methyl 3-o0.165xo-3-phenylpropanoate (4a)



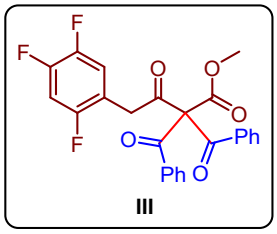
4a found as a yellowish oil (0.018 mg, 0.101mmol, yield: 12%); **^{1}H NMR $CDCl_3$, 400 MHz) Keto/enol mixture of 4a:** δ = 12.50 (s, 1H of enol), 7.97 - 7.93 (m, 2H, H6, H10), 7.80 - 7.76 (m, 2H, H6', H10'), 7.64 - 7.58 (m, 1H, H8), 7.52 - 7.47 (m, 2H, H7, H9), 7.46 - 7.39 (m, 3H, H7', H8', H9'), 5.68 (s, 1H, CH of enol), 4.02 (s, 2H, CH_2 of keto), 3.81 (s, 3H, OCH_3 of enol), 3.76 (s, 3H, OCH_3 of keto) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 192.4 (C4), 173.5 (C4'), 171.5 (C2'), 168.0 (C2), 135.9 (C5), 133.8 (C5'), 133.3 (C8'), 131.3 (C8), 128.8 (C7, C9), 128.5 (C6, C10, C7', C9'), 126.1 (C6', C10'), 87.1 (C3'), 52.5 (C1), 51.4 (C1'), 45.7 (C3) ppm; **HRMS (ESI)**: Exact mass calcd for $C_{10}H_{11}O_3$ $[M+H]^+$: 179. 0703, found 179.0697.

Methyl 2-benzoyl-3-oxo-4-(2,4,5-trifluorophenyl)butanoate (II)



II obtained from Methyl 3-oxo-4-(2,4,5-trifluorophenyl)butanoate (**1a**) (0.812 mmol, 1 equiv) was stirred with the potassium carbonate (0.812 mmol, 1 equiv) in 1,4-dioxane (2 mL) stirred at room temperature for 5 min then benzoyl chloride (0.812 mmol, 1 equiv) was added slowly drop-wise, and the reaction mixture was stirred at room temperature until benzoyl chloride was completely consumed (monitored by TLC). Purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **I** as a white solid (0.030 gm, 0.066 mmol, yield: 20%), M.P. 101 104 °C; **^{1}H NMR CDCl$_3$, 400 MHz):** δ = 7.99 - 7.85 (m, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.27 - 7.20 (m, 1H), 6.86 (dt, *J* = 6.6, 9.6 Hz, 1H), 6.01 (s, 1H), 4.33 (s, 2H), 3.80 (s, 3H) ppm; **^{13}C NMR (CDCl$_3$, 100 MHz):** δ = 166.2, 163.7, 162.7, , 156 (ddd, *J* = 244.90, 9.16, 3.05 Hz) 149.3 (ddd, *J* = 250.24, 14.50, 12.97 Hz), 146.6 (ddd, *J* = 244.90, 12.21, 3.82 Hz) 134.0, 130.0, 128.7, 128.5, 118.9, 118.7, 111.3, 105.5 (dd, *J* = 28.23, 20.6 Hz), 105.1, 51.8, 29.4ppm; **^{19}F NMR (CDCl$_3$, 375 MHz)** δ -118.84 (dd, *J* = 11.84 Hz), -135.12 (dd, *J* = 23.67 Hz), -142.56 (dd, *J* =15.79 Hz) ppm; **HRMS (ESI)**: Exact mass calcd for $C_{18}H_{14}O_4F_3$ $[M+H]^+$: 351.0839, found 351.0854.

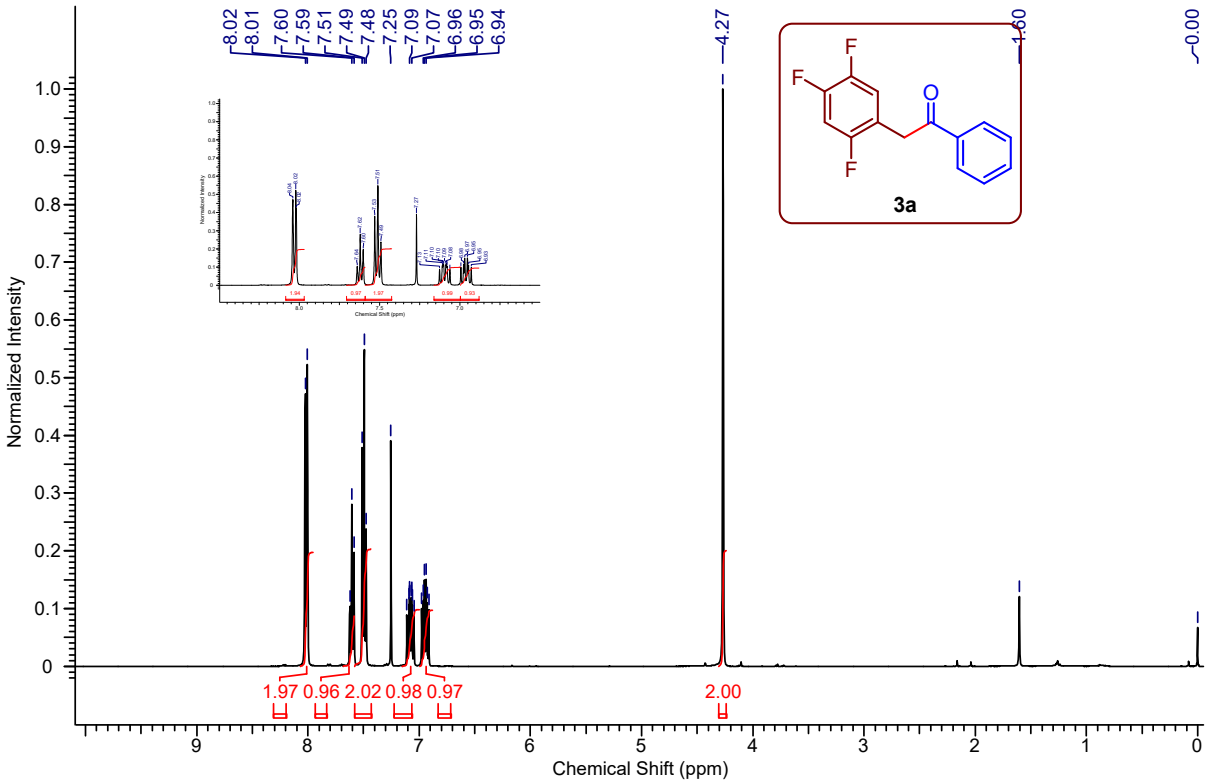
Methyl 2,2-dibenzoyl-3-oxo-4-(2,4,5-trifluorophenyl)butanoate (III)



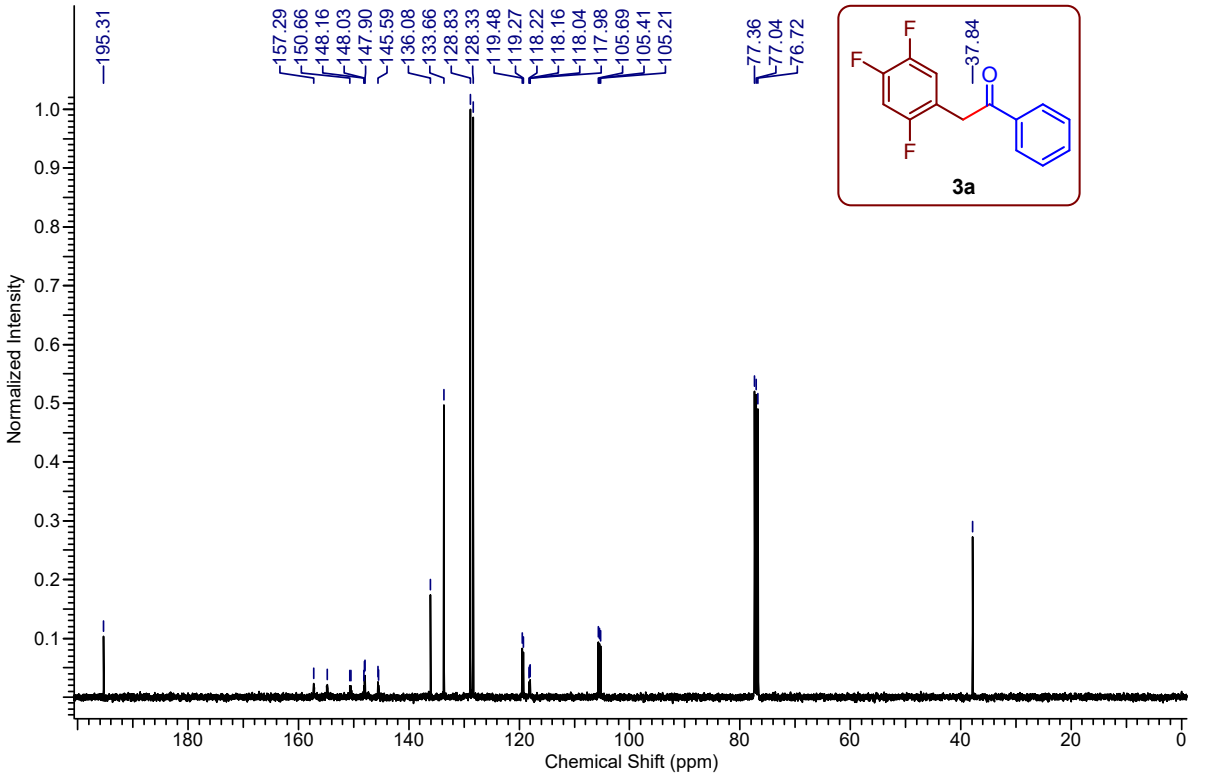
III

III obtained from Methyl 3-oxo-4-(2,4,5-trifluorophenyl)butanoate (**1a**) (0.812 mmol, 1 equiv) was stirred with the potassium carbonate (0.812 mmol, 1 equiv) in 1,4-dioxane (2 mL) stirred at room temperature for 5 min then benzoyl chloride (0.812 mmol, 1 equiv) was added slowly drop-wise, and the reaction mixture was stirred at room temperature until benzoyl chloride was completely consumed (monitored by TLC). Purification of crude product was carried out by silica gel flash column chromatography using ethyl acetate : petroleum ether mixture (1 : 9) as eluent to afford the title compound **I** as a white solid (0.030 gm, 0.066 mmol, yield: 20%), M.P. 101 104 °C; **^{1}H NMR CDCl$_3$, 400 MHz)** δ = 7.90 - 7.85 (m, 2H), 7.61 - 7.57 (m, 2H), 7.55 - 7.45 (m, 2H), 7.43 - 7.37 (m, 2H), 7.35 - 7.29 (m, 1H), 7.29 - 7.24 (m, 3H), 4.52 (s, 2H), 3.74 (s, 3H) ppm; **^{13}C NMR (CDCl$_3$, 100 MHz):** δ = 195.3, 166.2, 163.2, 161.4, 156 (ddd, *J* = 244.90, 9.16, 3.05 Hz) 149.3 (ddd, *J* = 250.24, 14.50, 12.97 Hz), 146.6 (ddd, *J* = 244.90, 12.21, 3.82 Hz) 136.1, 134.0, 133.8, 130.4, 129.9, 129.1, 128.8, 128.7, 128.5, 128.4, 128.2, 127.6, 124.3, 119.2(m), 105.5 (dd, *J* = 28.23, 20.6 Hz), 52.6, 29.9 ppm; **^{19}F NMR (CDCl$_3$, 375 MHz)** δ -118.32 (dd, *J* = 11.84 Hz), -134.56 (dd, *J* = 23.67 Hz), -142.22 (dd, *J* =15.79 Hz) ppm; **HRMS (ESI)**: Exact mass calcd for $C_{25}H_{18}O_5F_3$ $[M+H]^+$: 455.1101, found 455.1113.

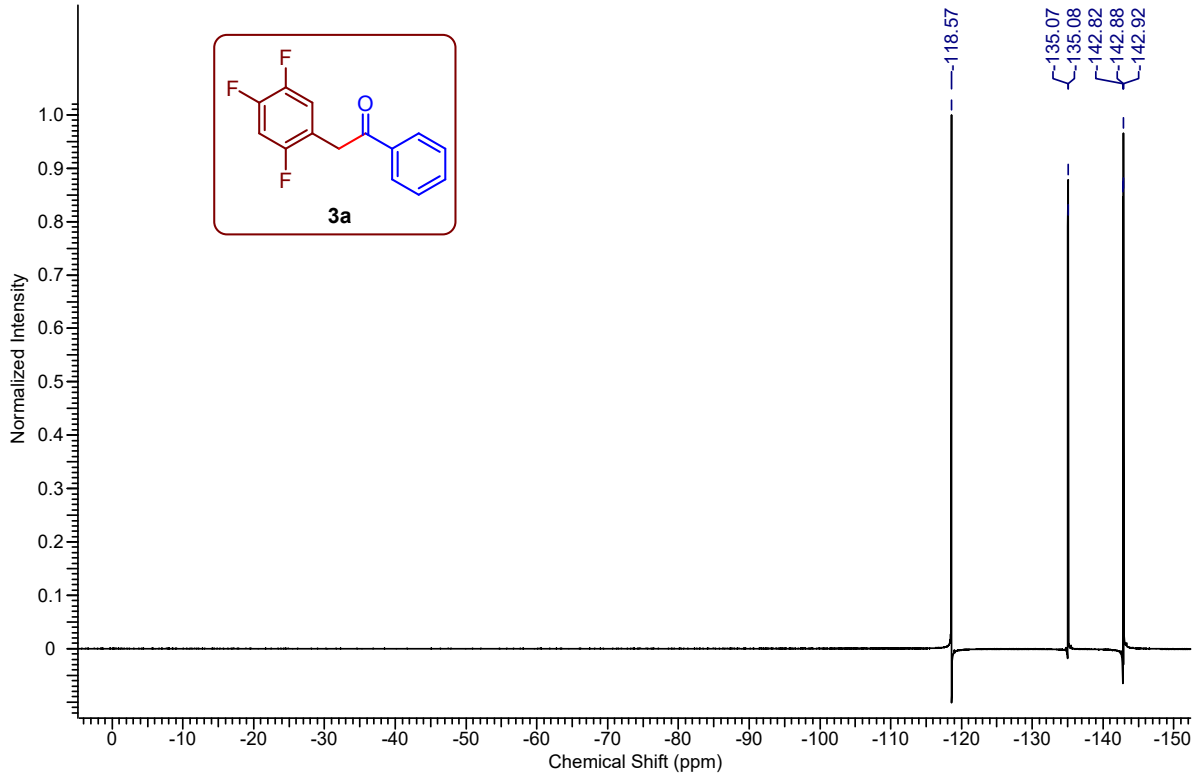
4. Copies of ^{1}H and ^{13}C NMR spectra of all products:



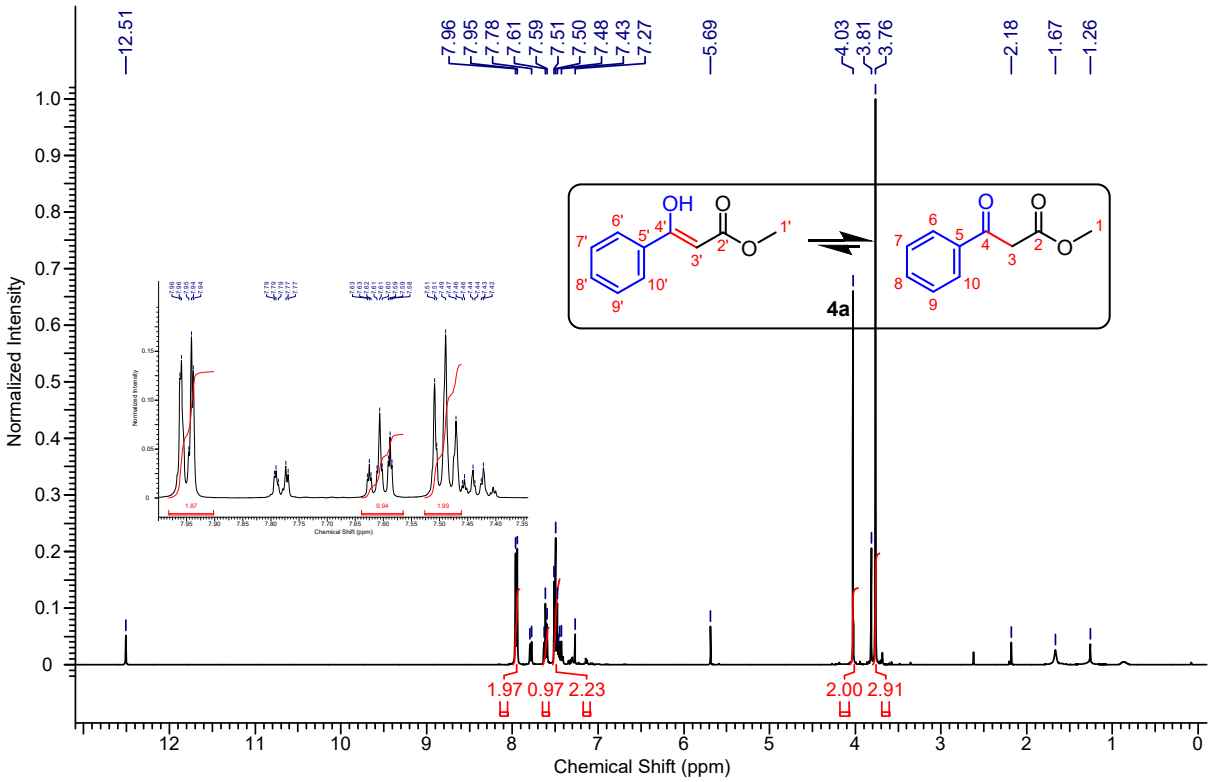
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3a



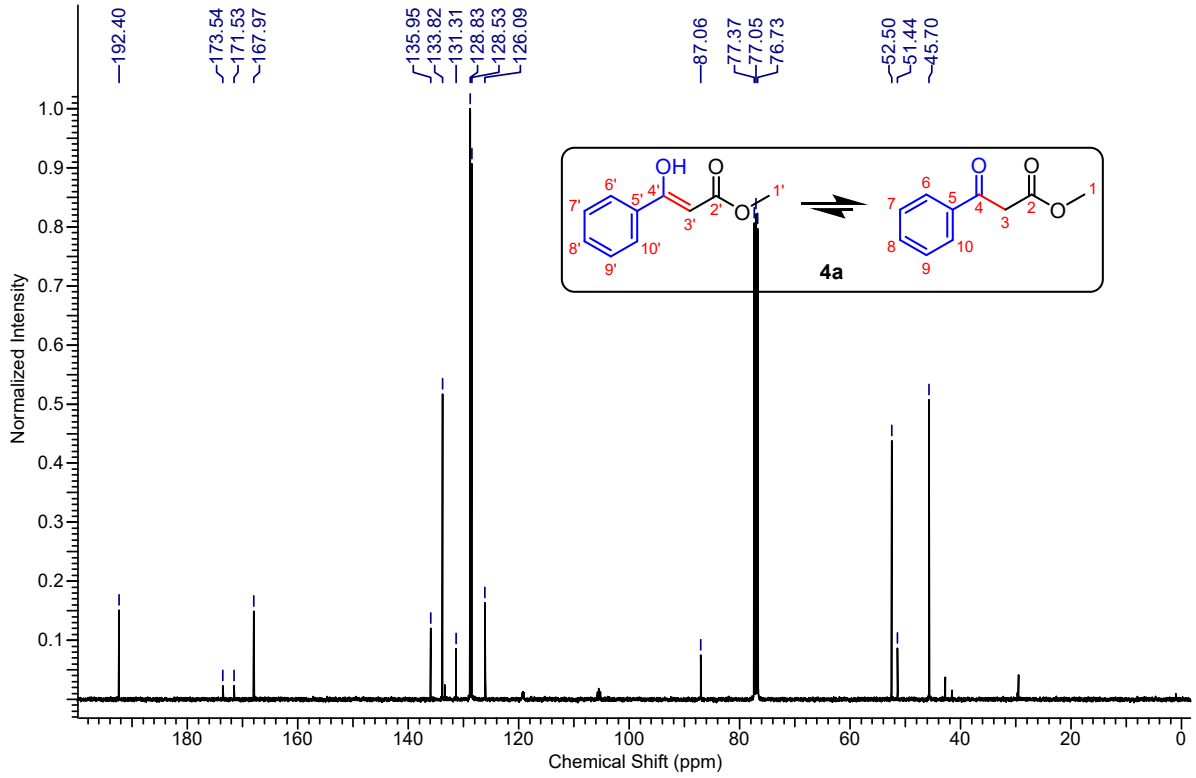
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3a



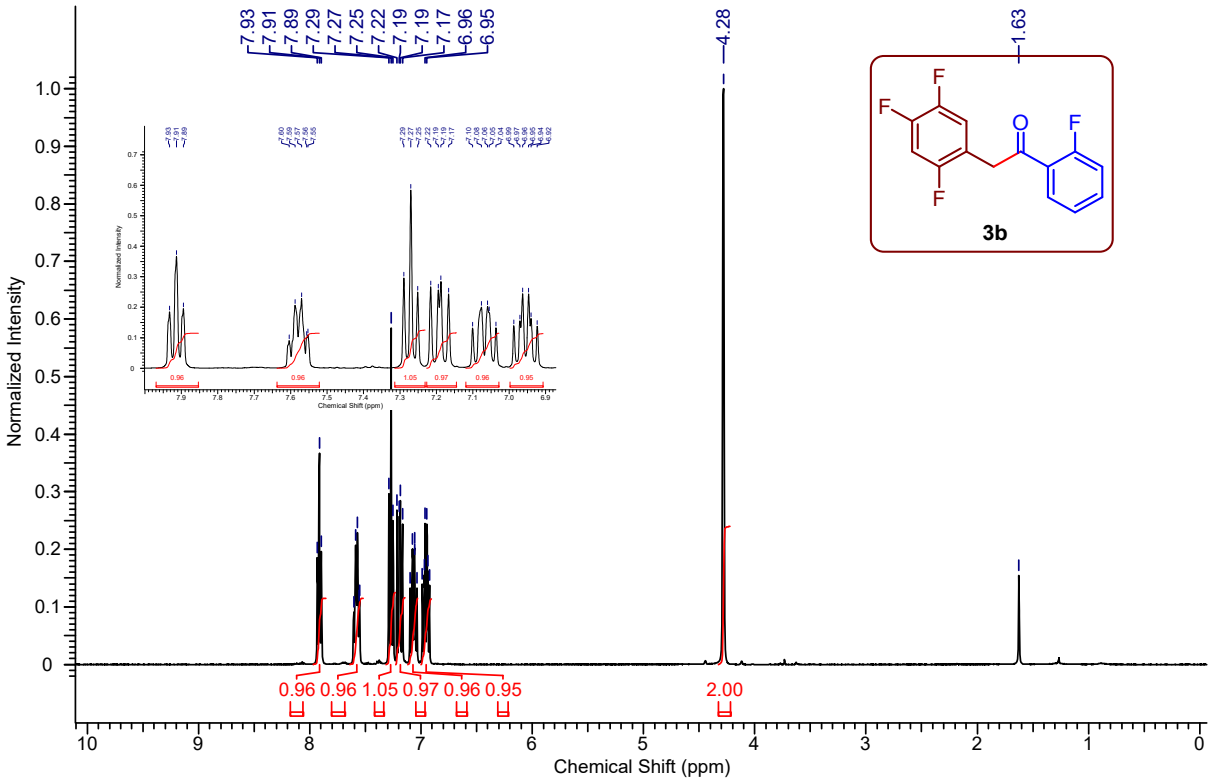
^{19}F NMR (375 MHz, $CDCl_3$) Spectrum of 3a



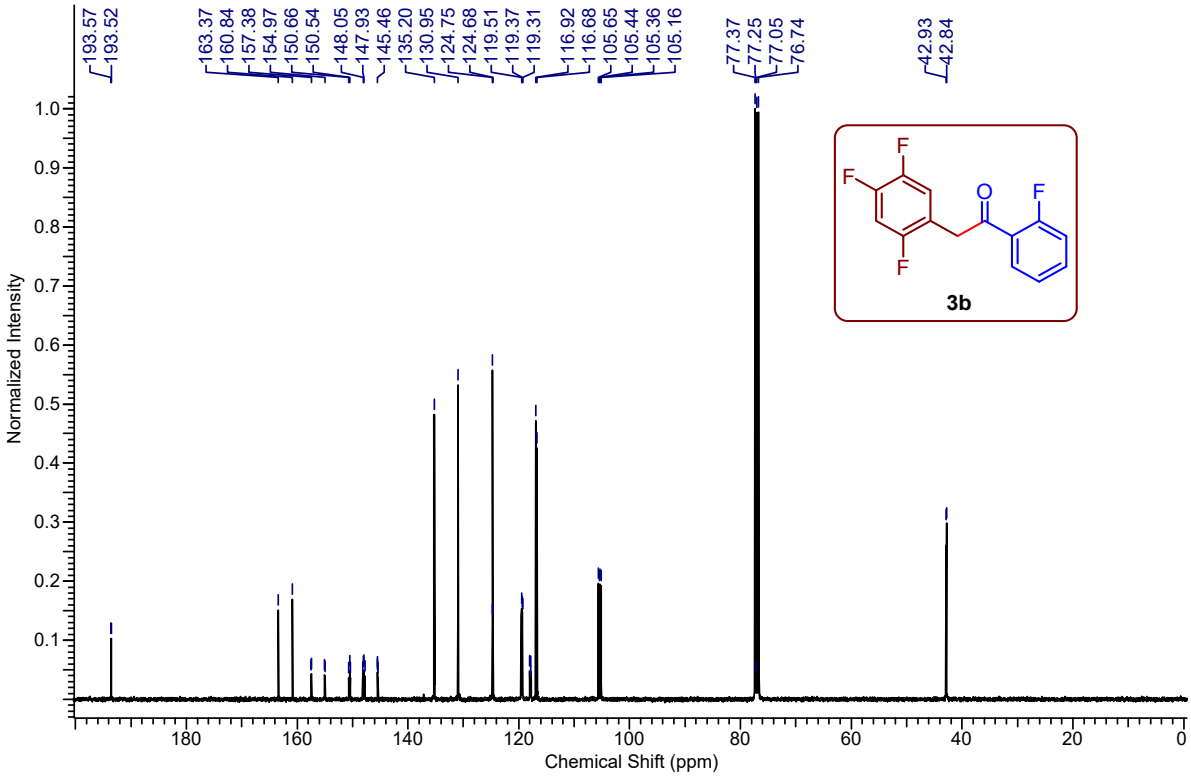
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4a



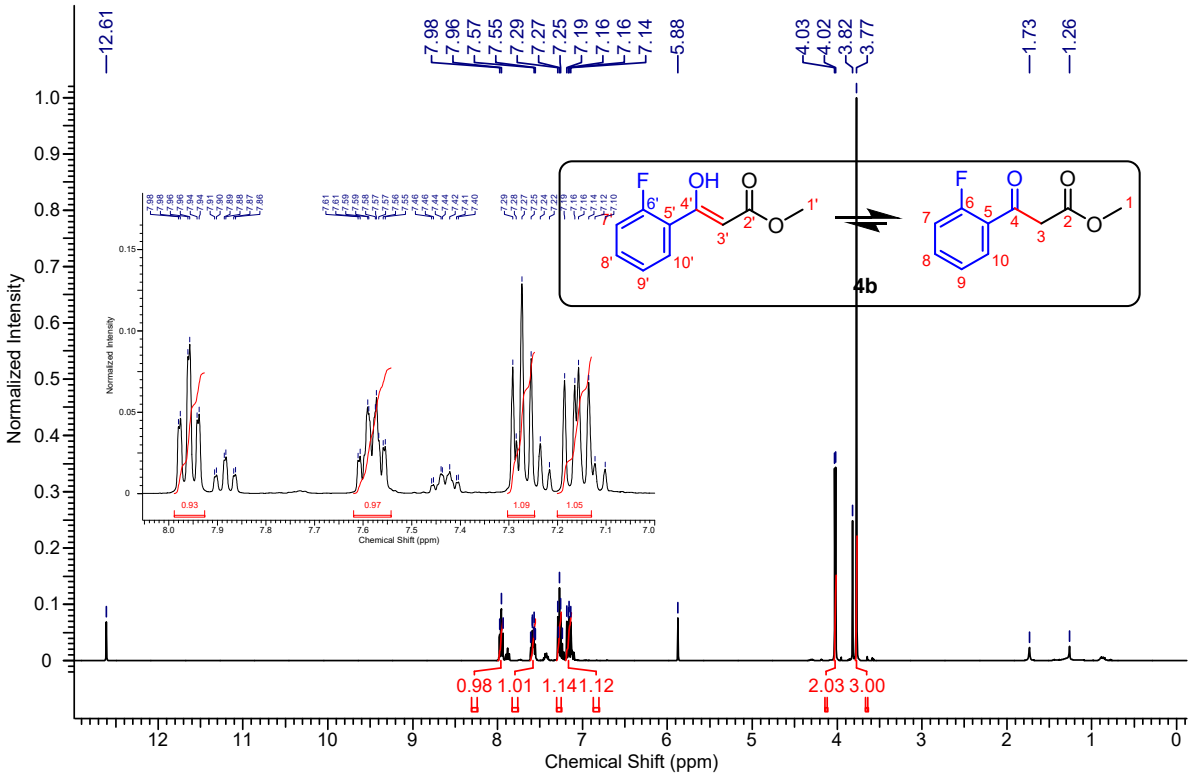
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4a



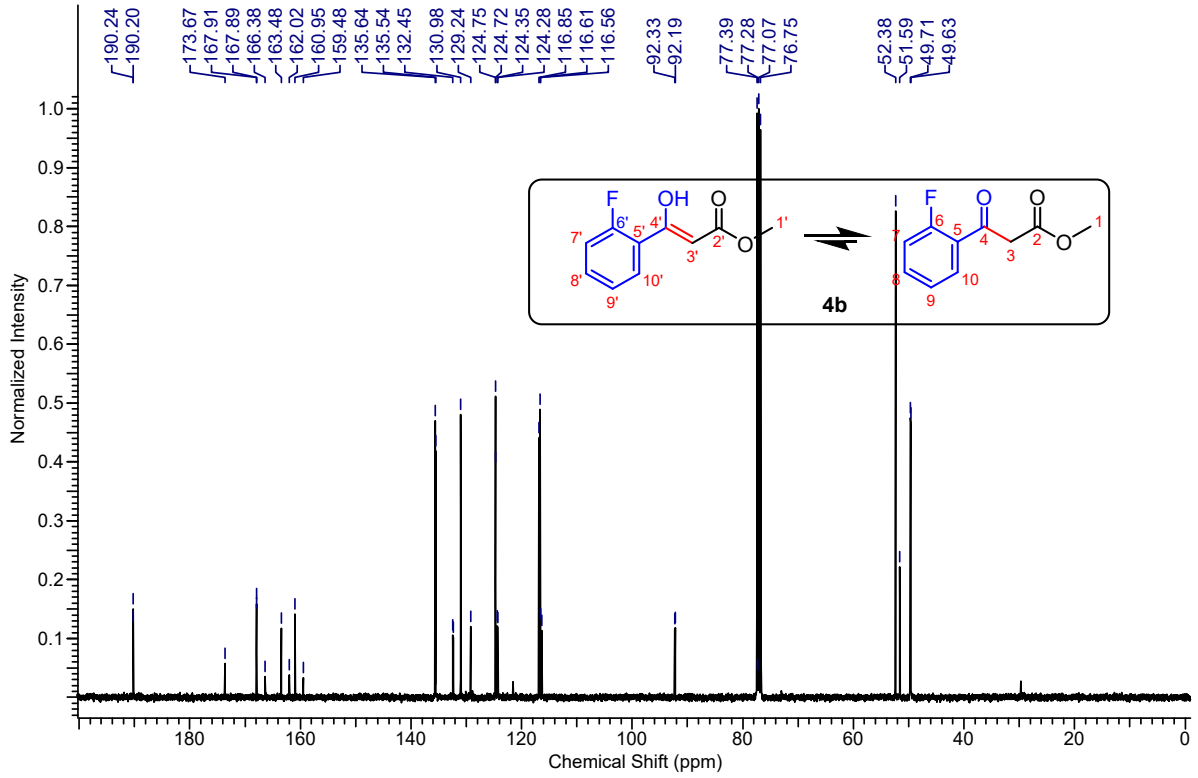
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3b



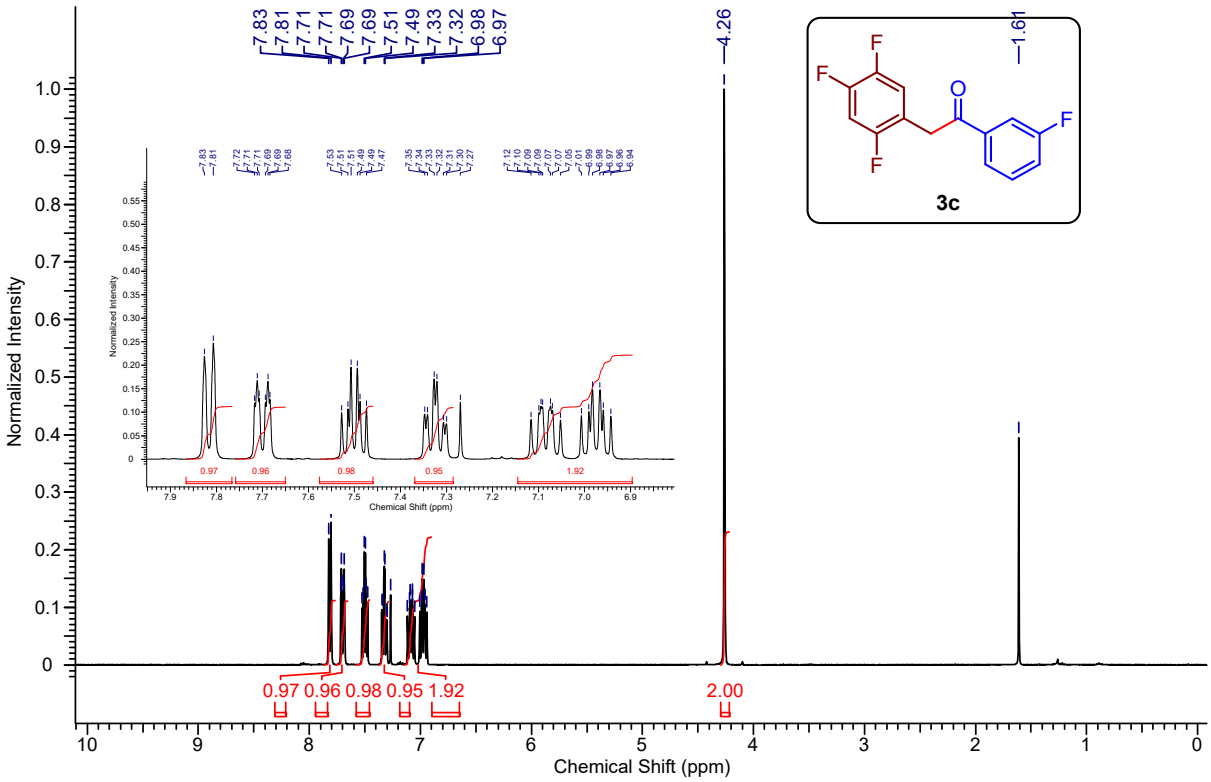
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3b



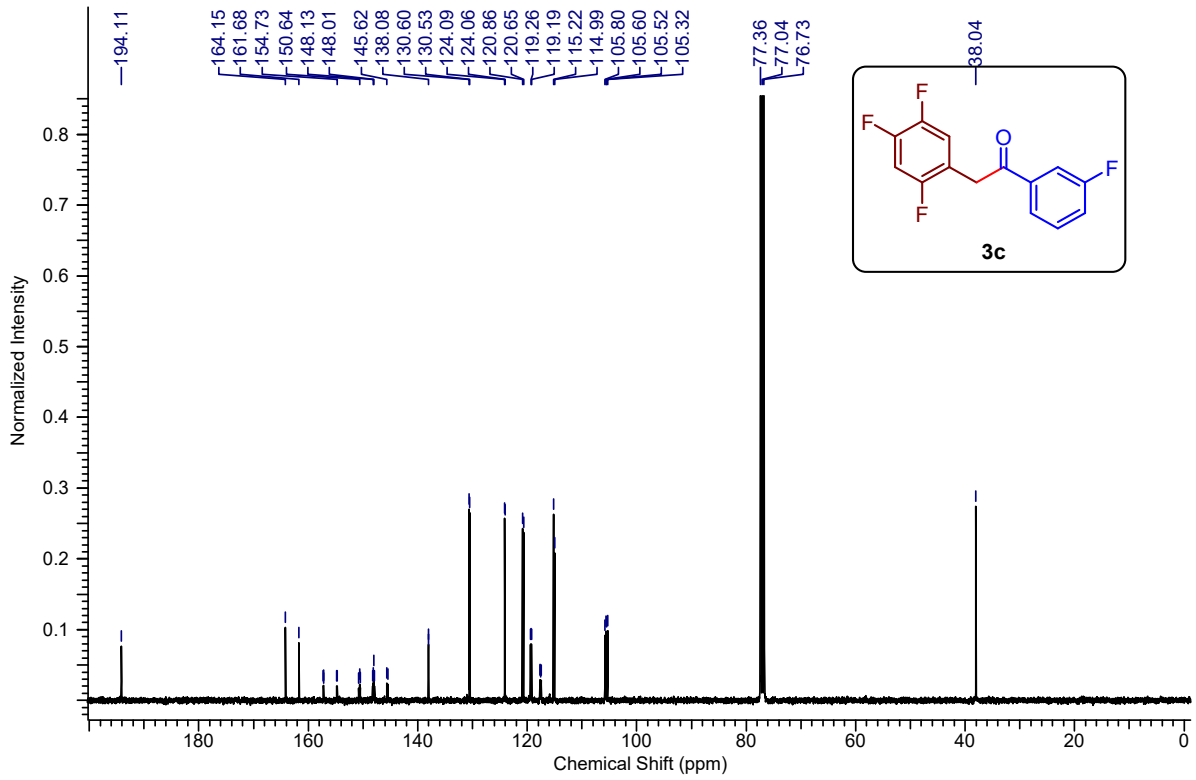
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4b



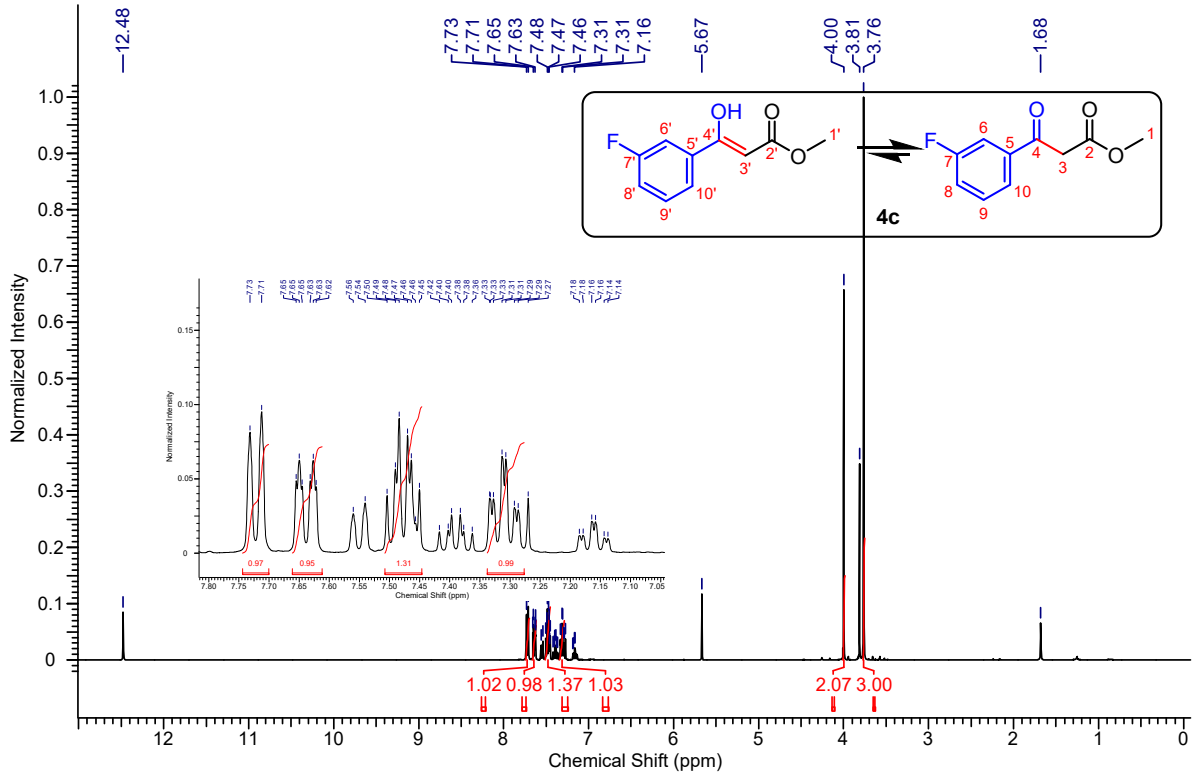
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4b



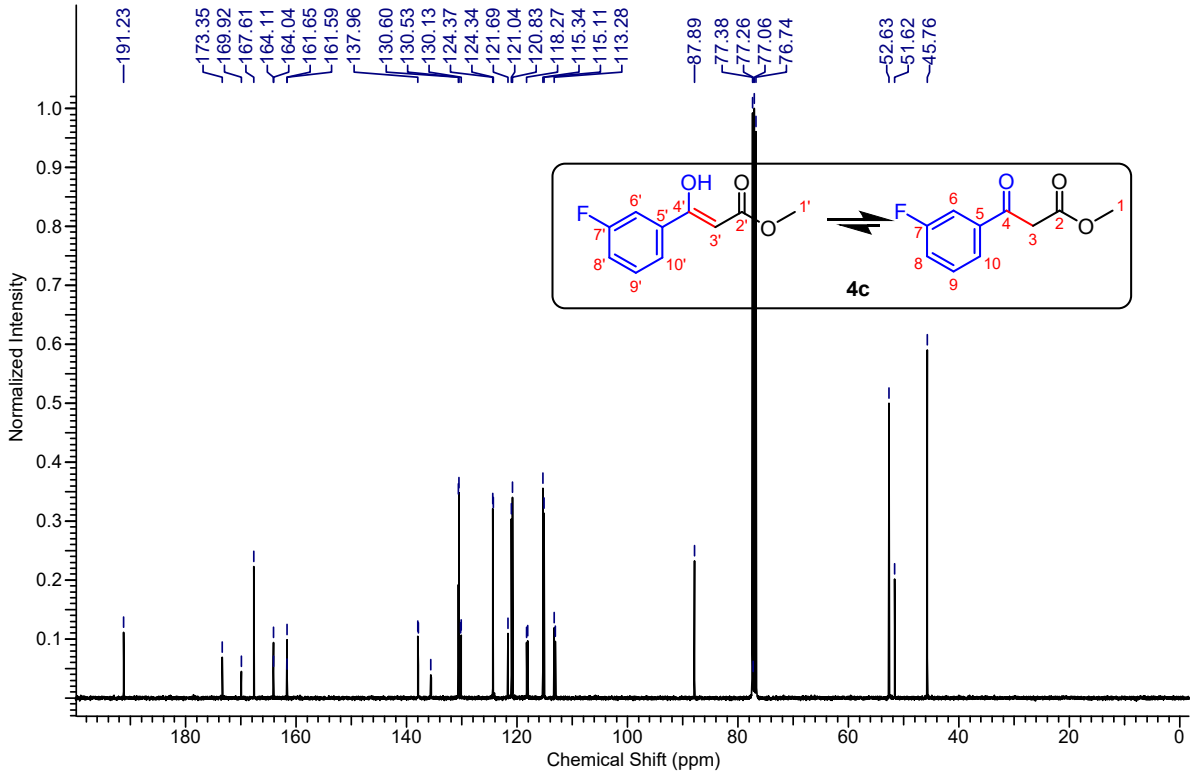
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3c



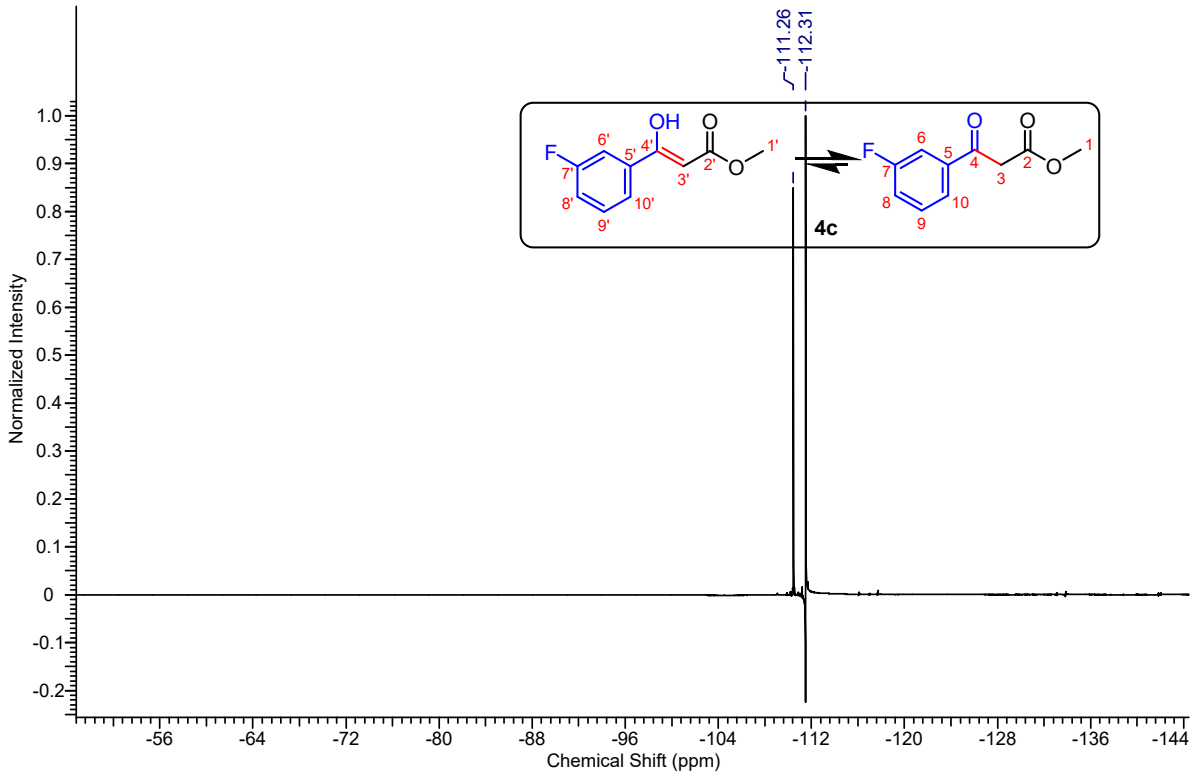
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 3c



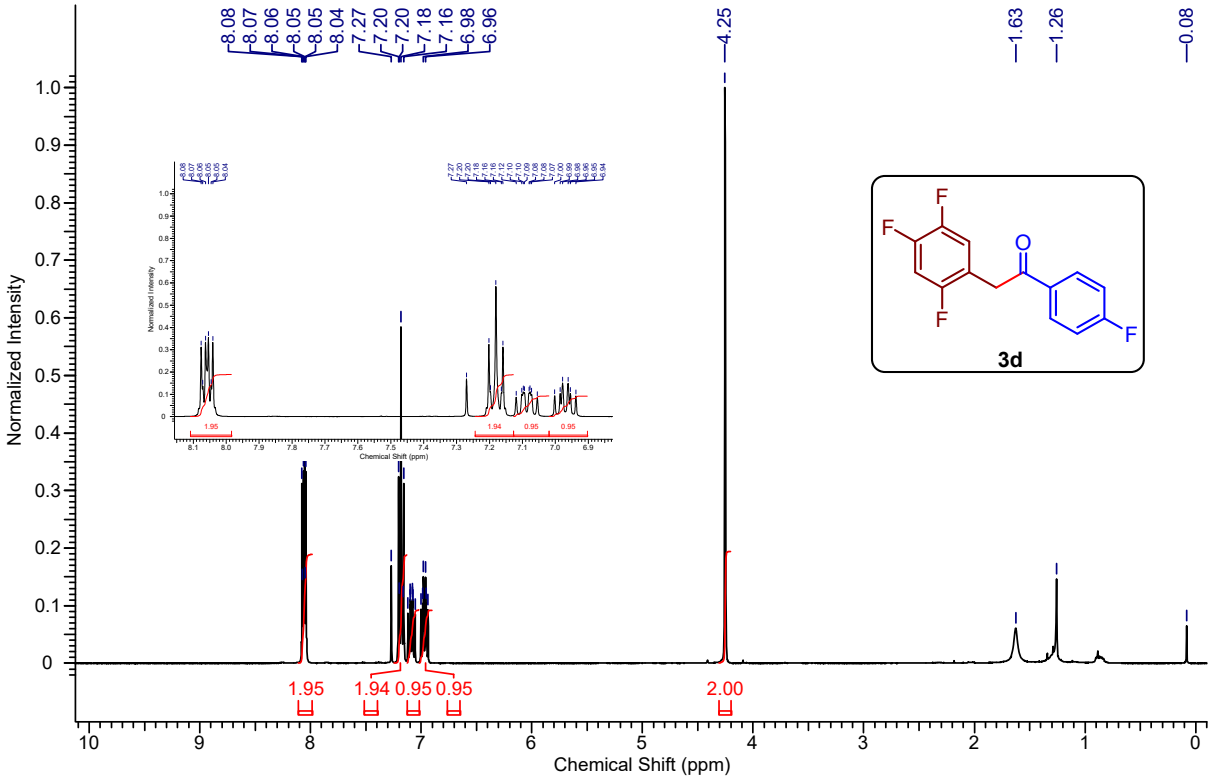
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4c



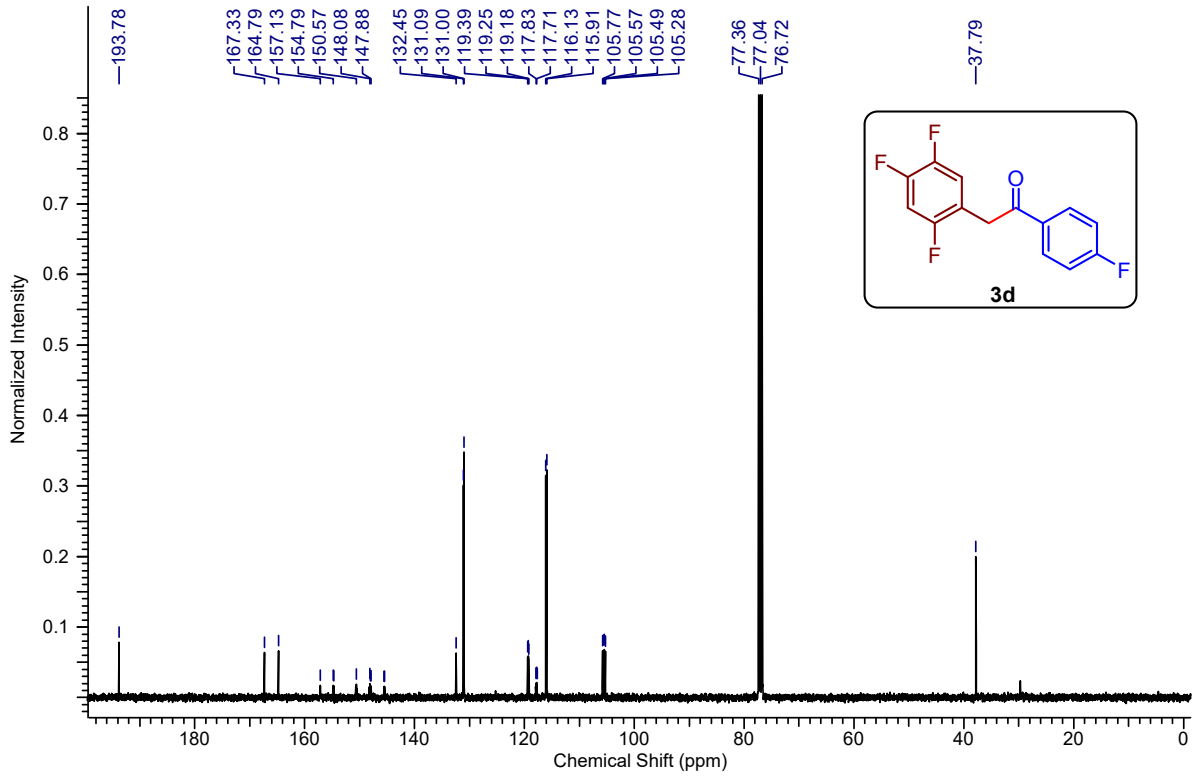
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4c



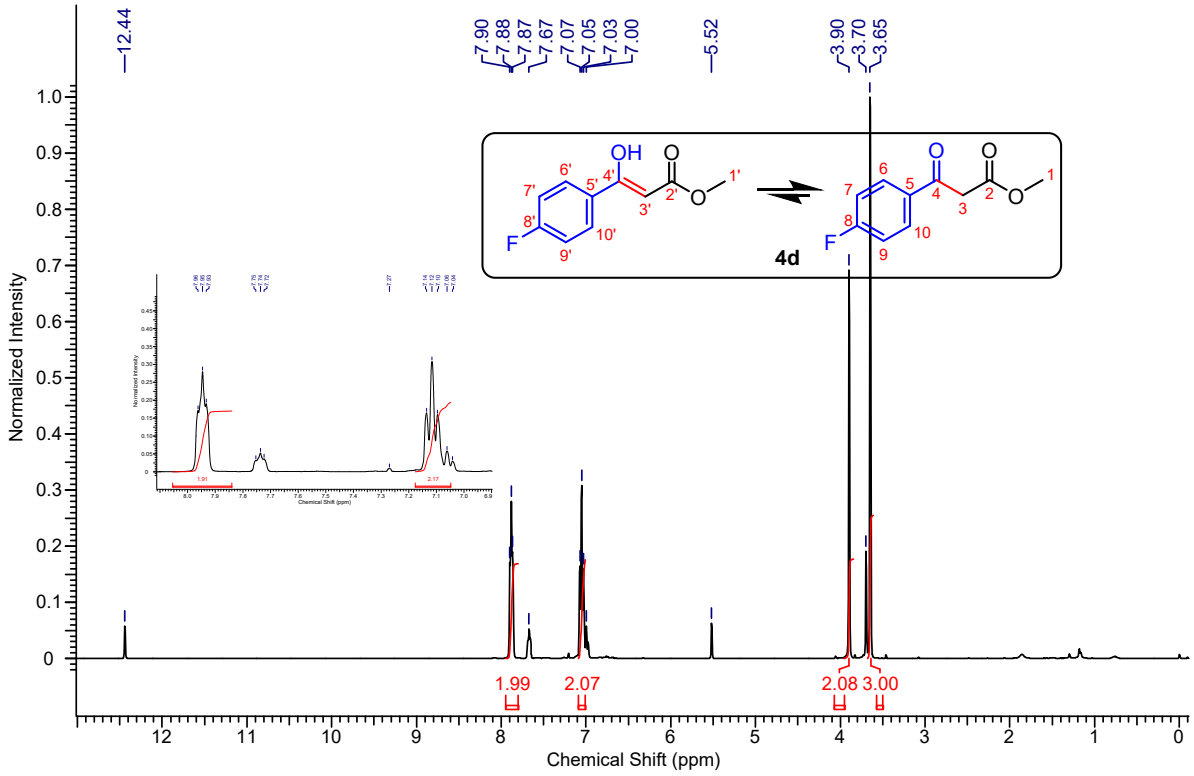
^{19}F NMR (375 MHz, $CDCl_3$) Spectrum of 4c



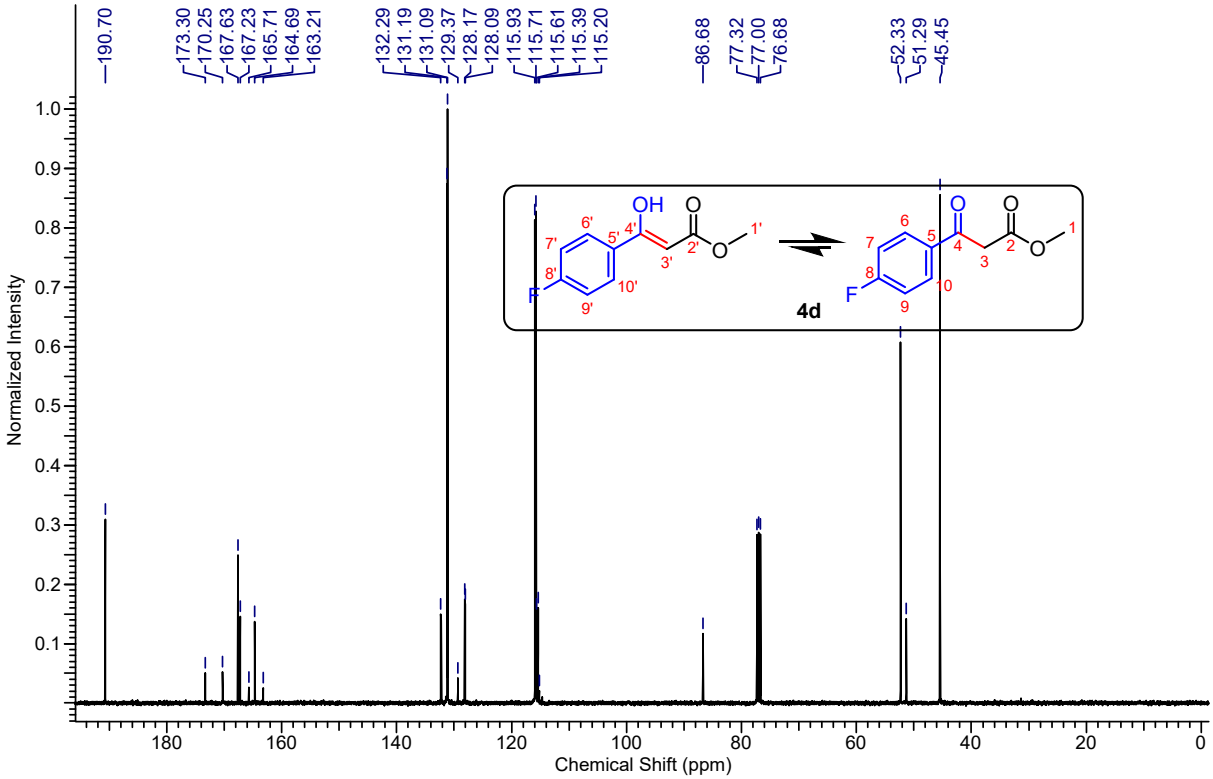
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3d



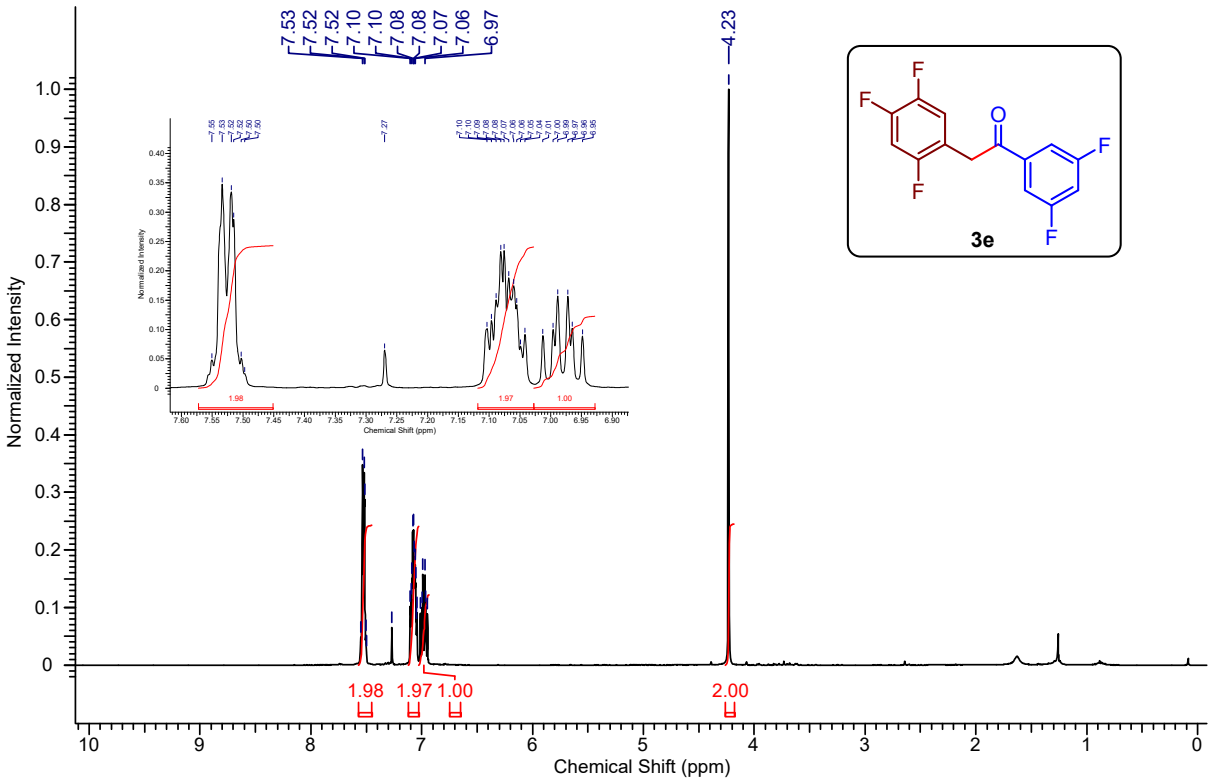
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4c



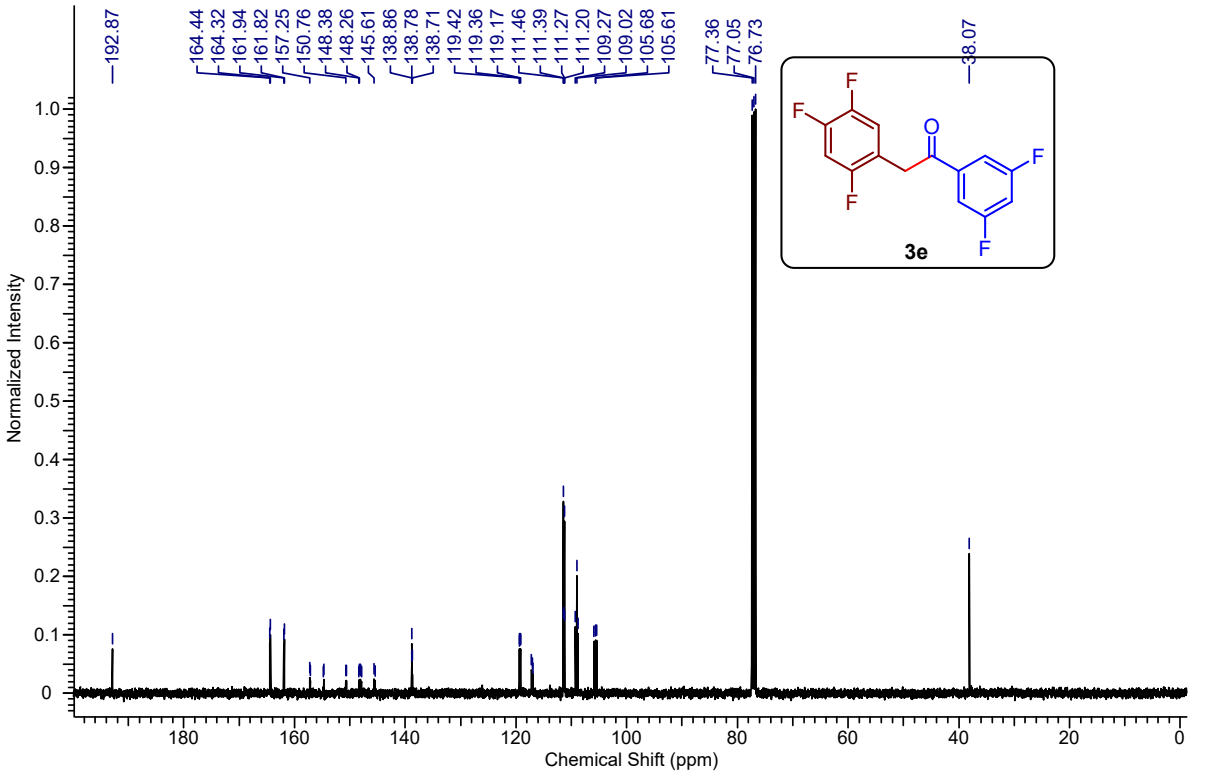
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4d



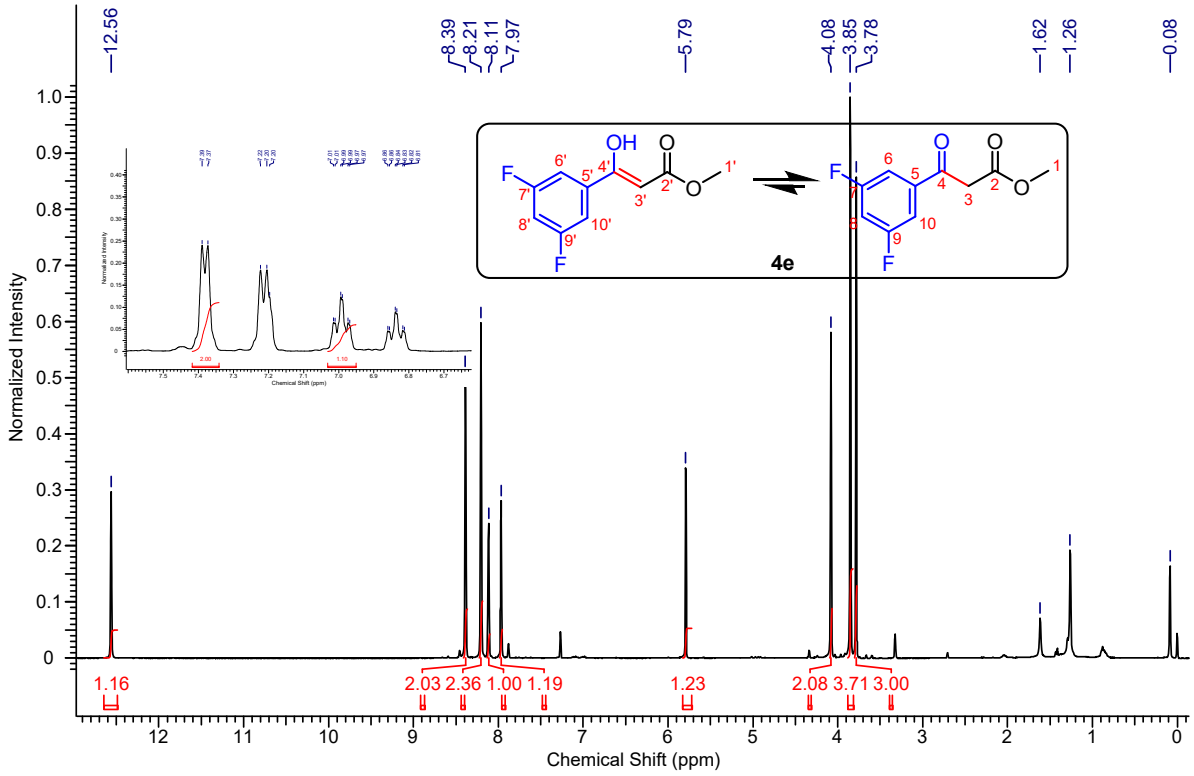
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4d



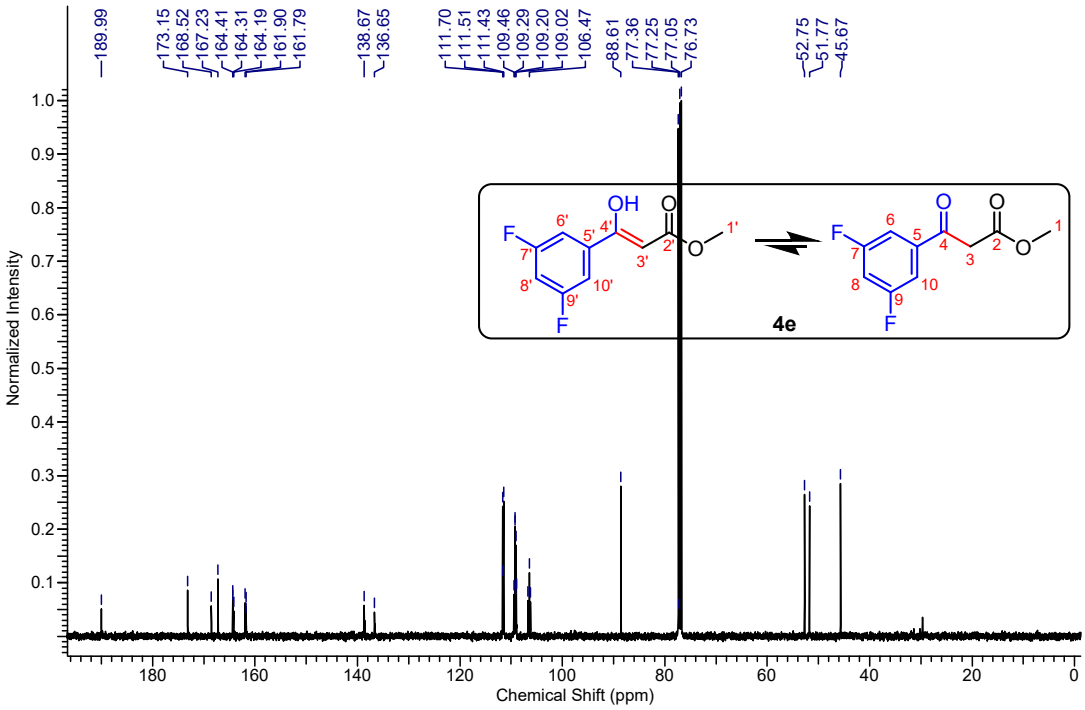
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3e



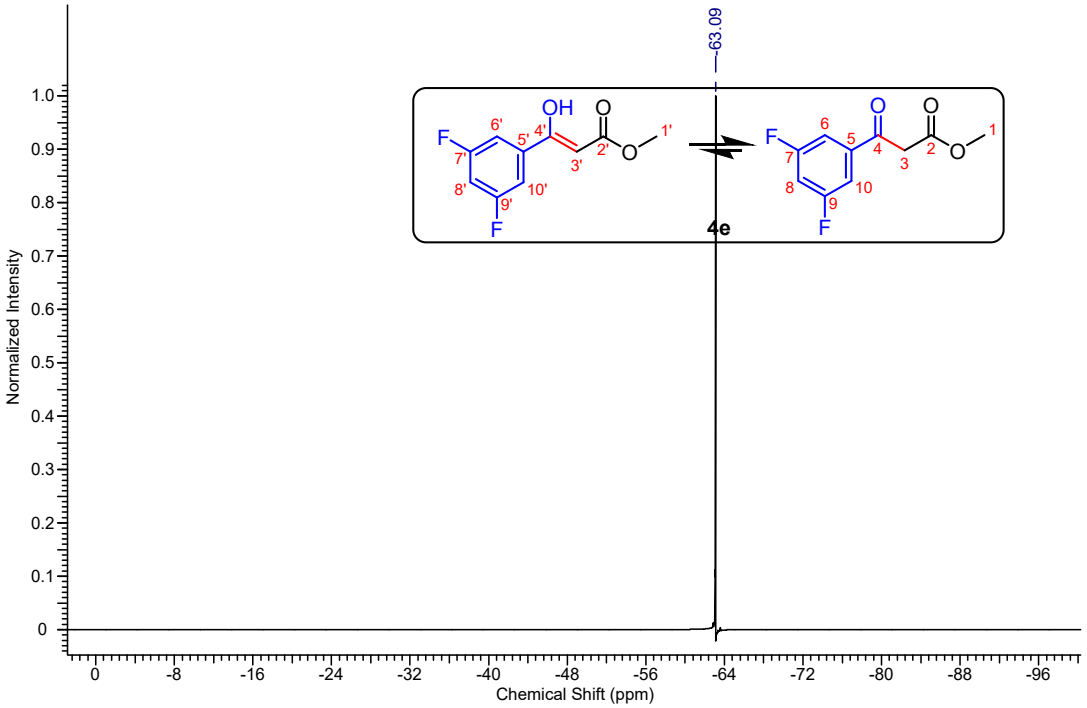
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3e



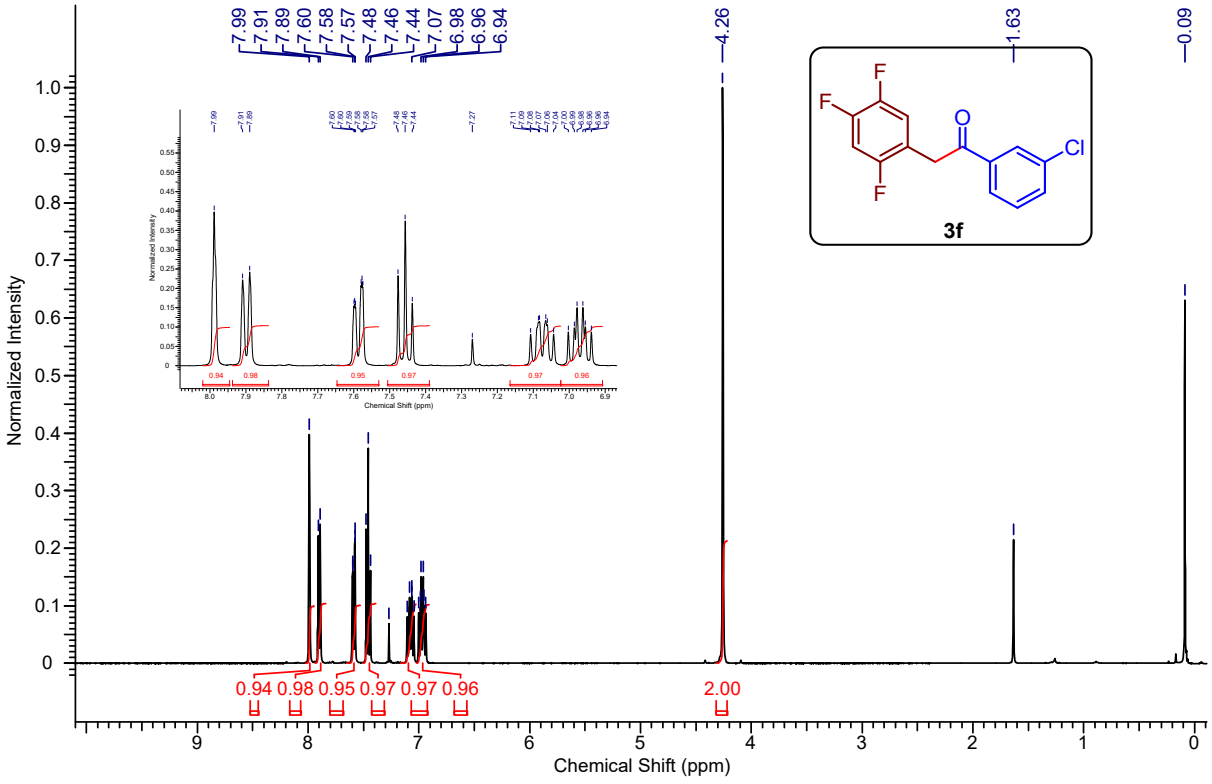
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4e



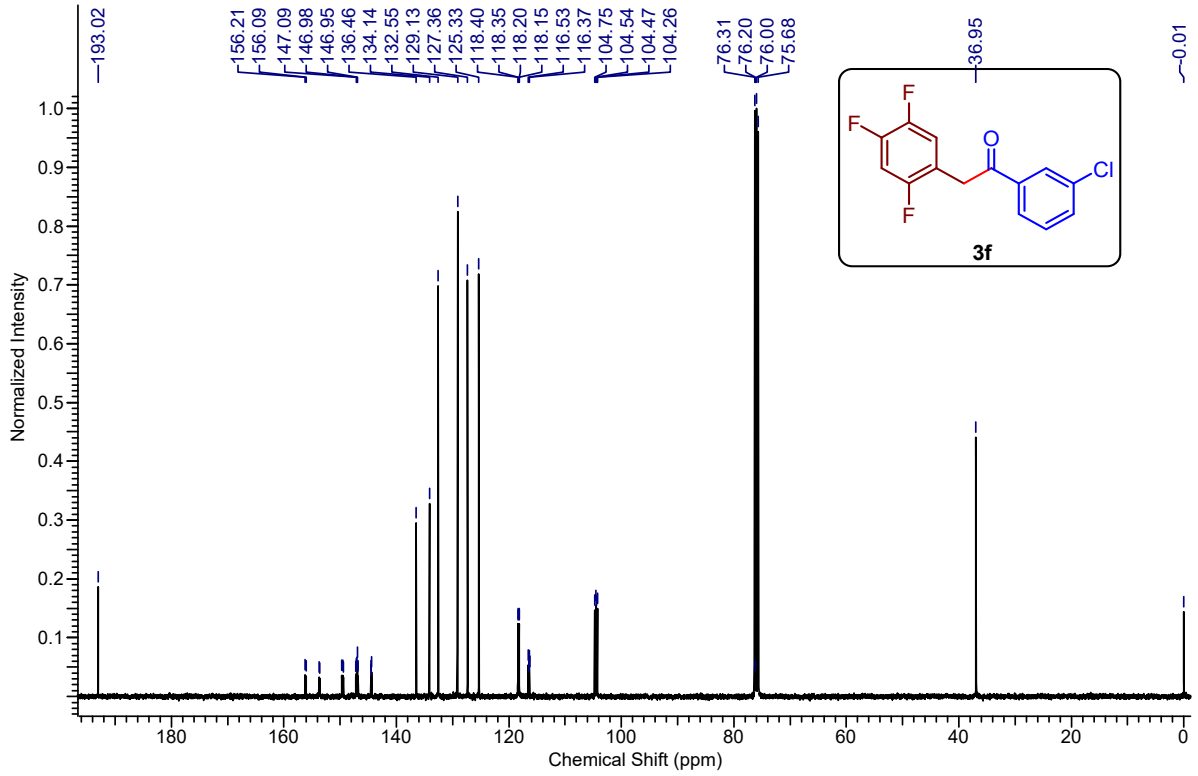
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4e



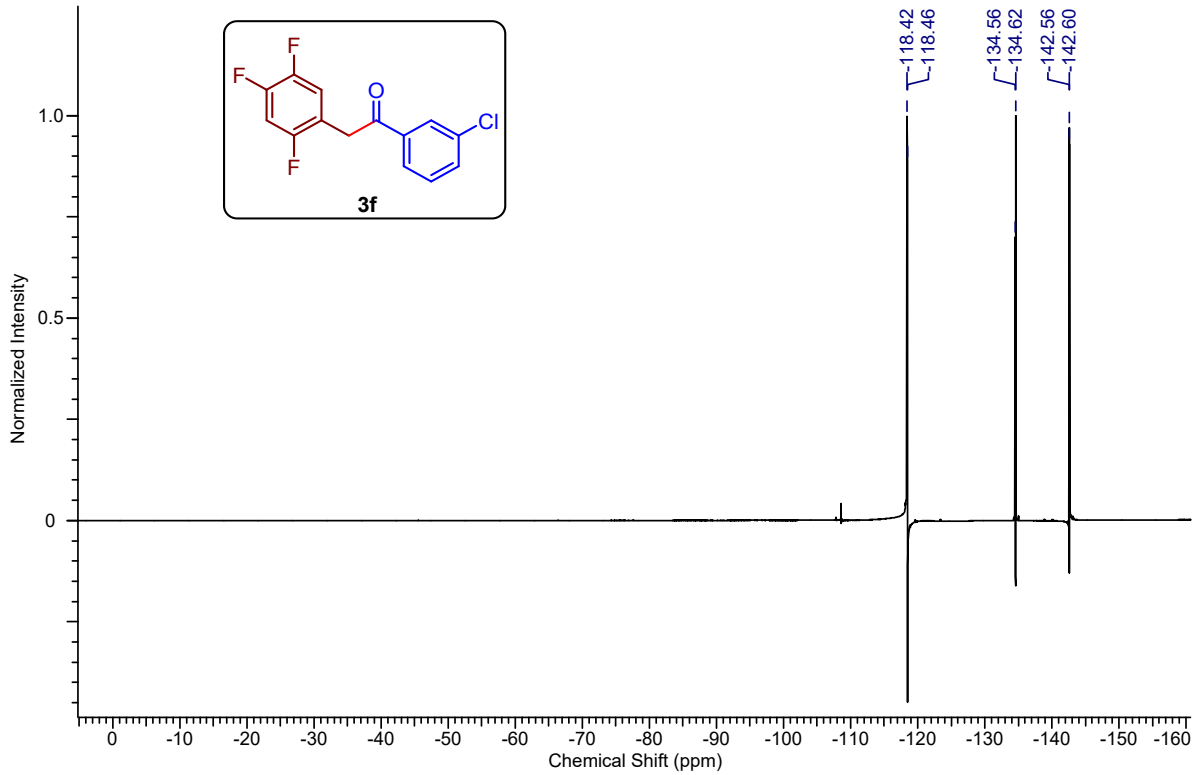
^{19}F NMR (375 MHz, $CDCl_3$) Spectrum of 4e



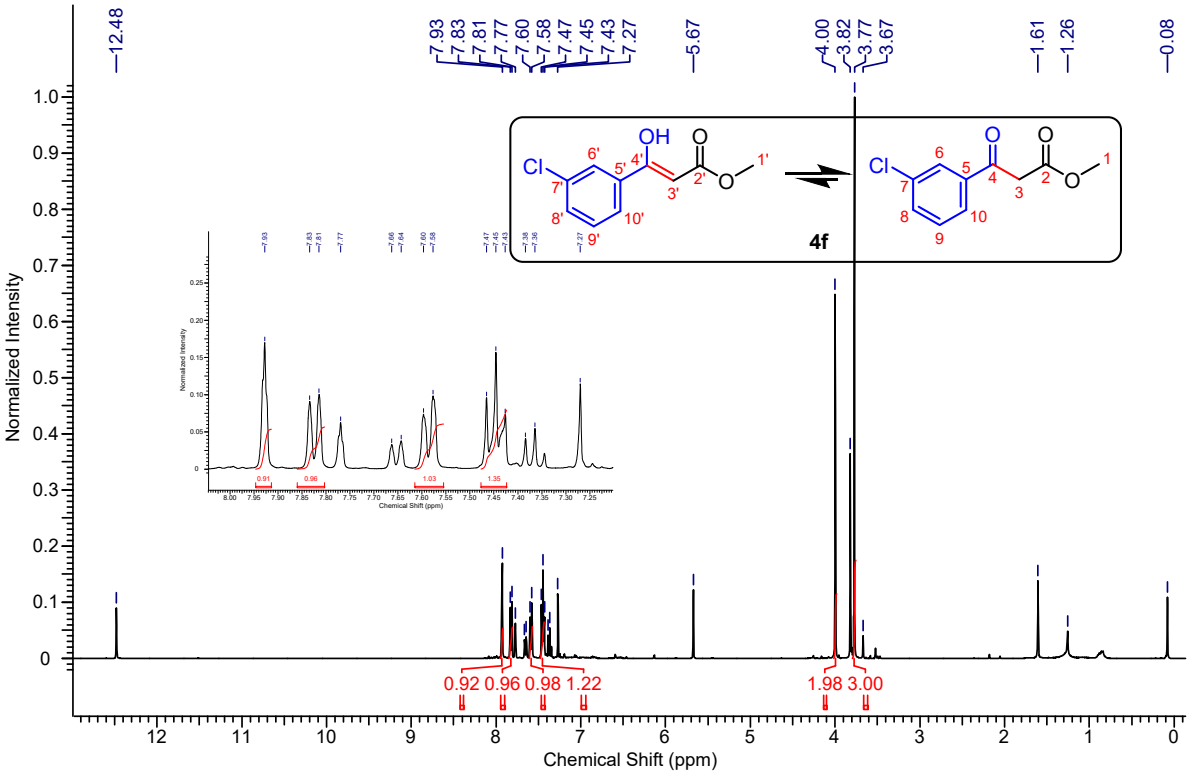
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3f



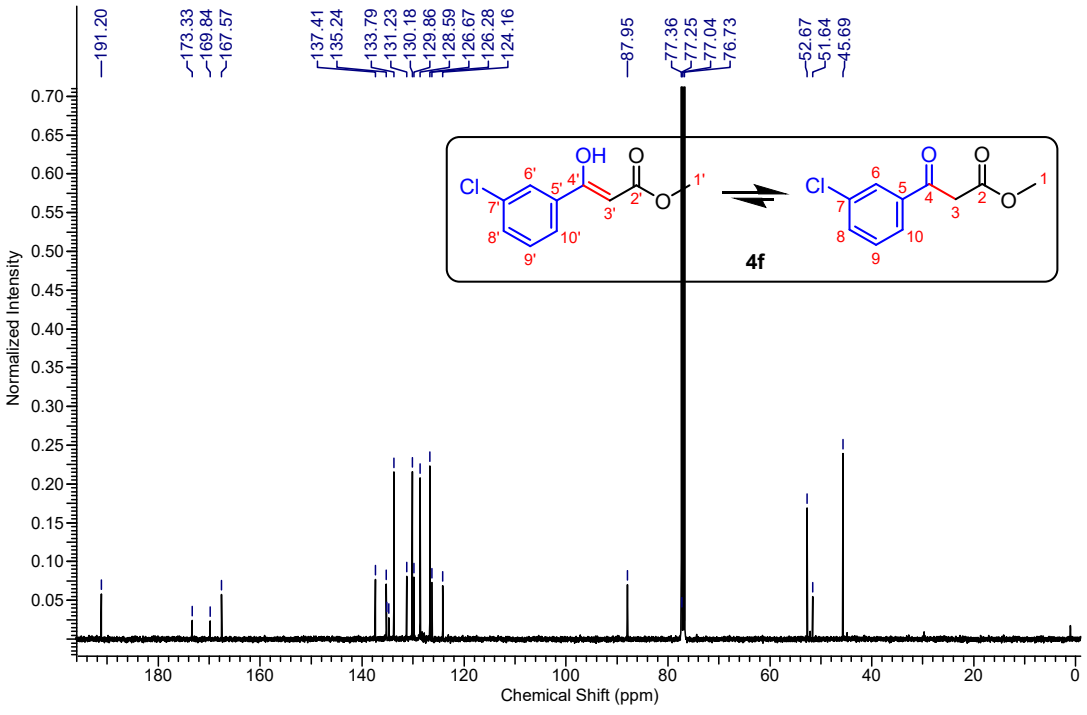
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3f



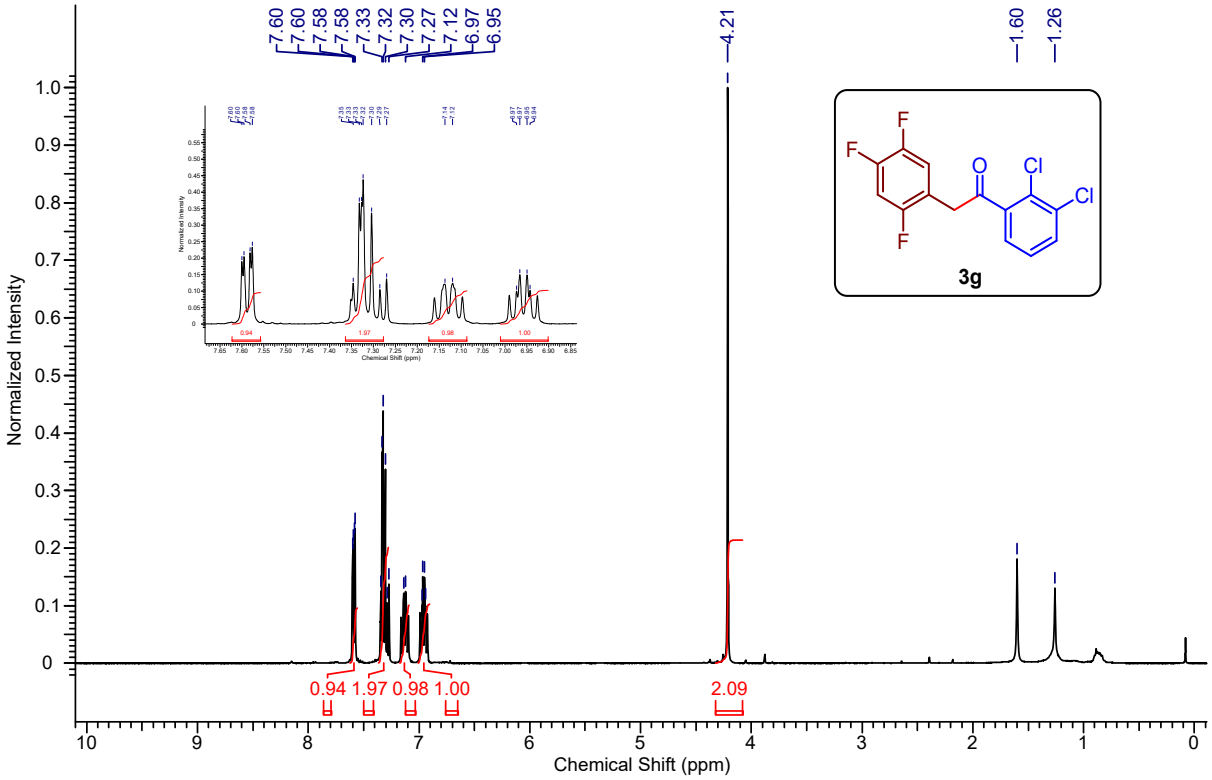
^{19}F NMR (375 MHz, $CDCl_3$) Spectrum of 3f



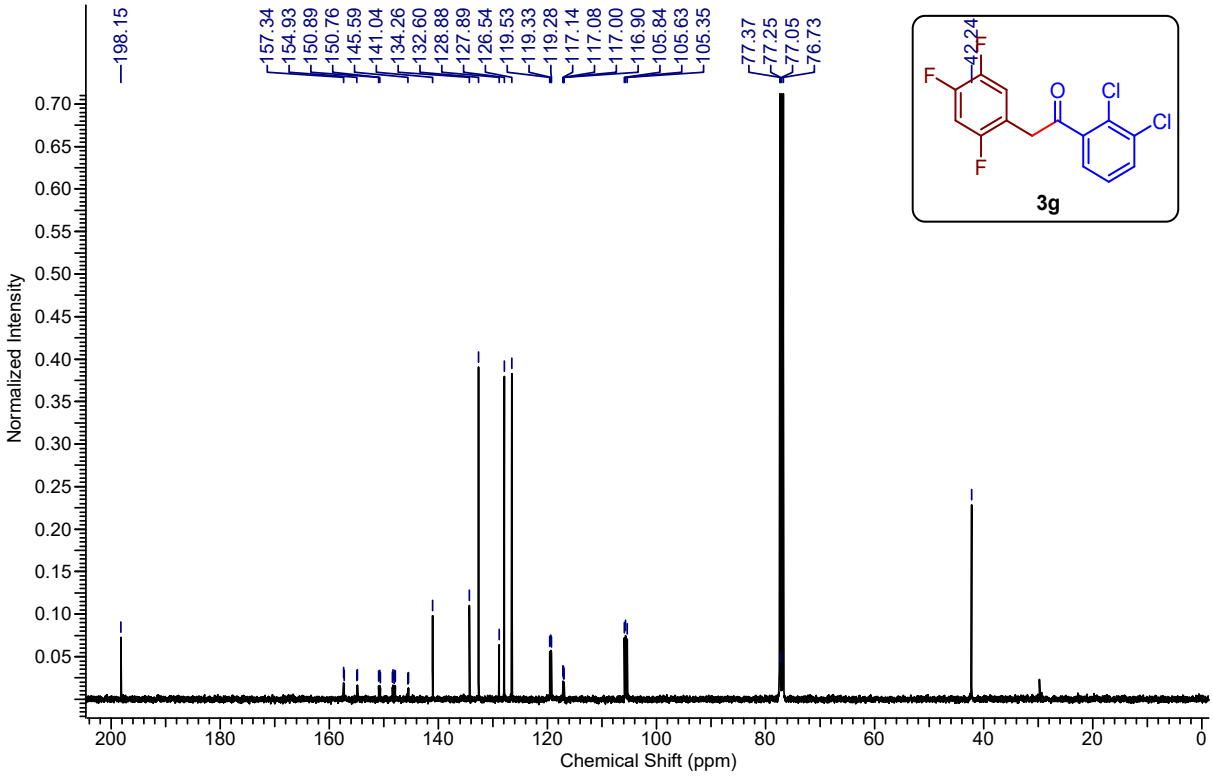
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4f



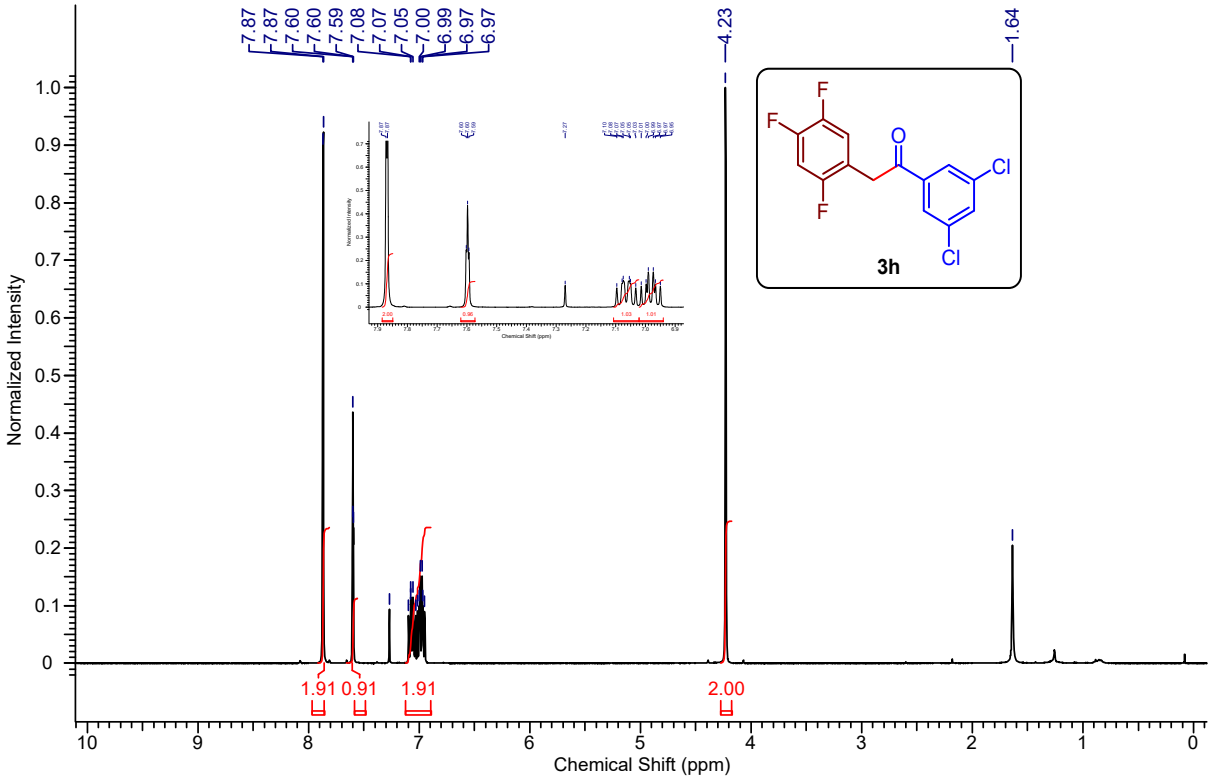
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4f



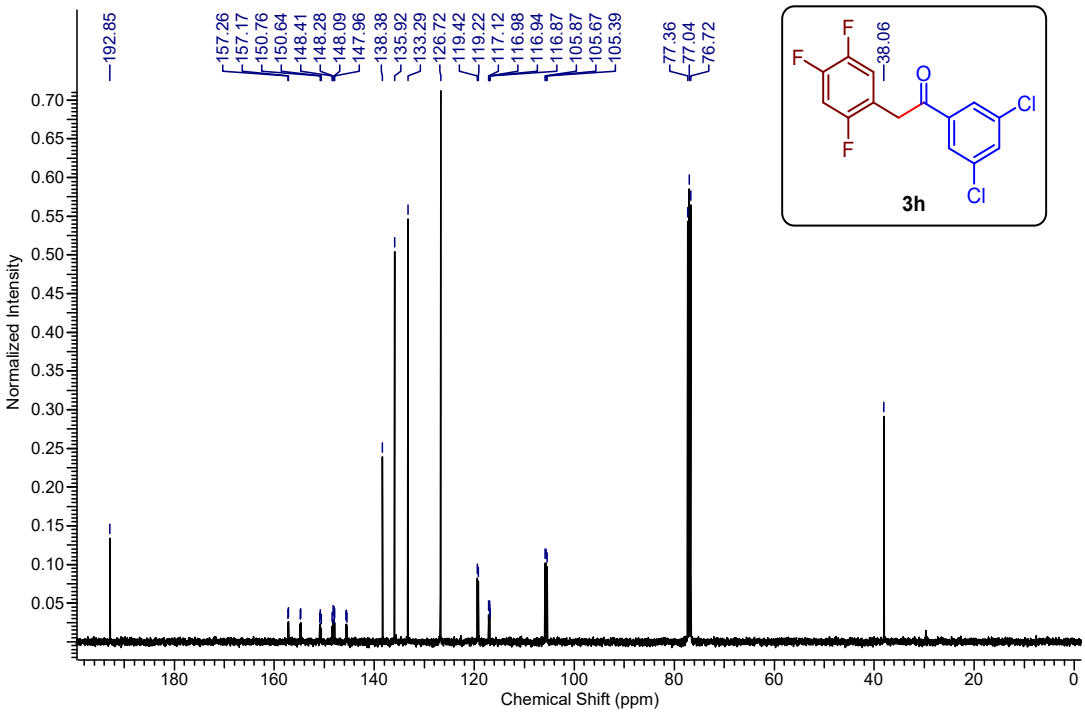
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3g



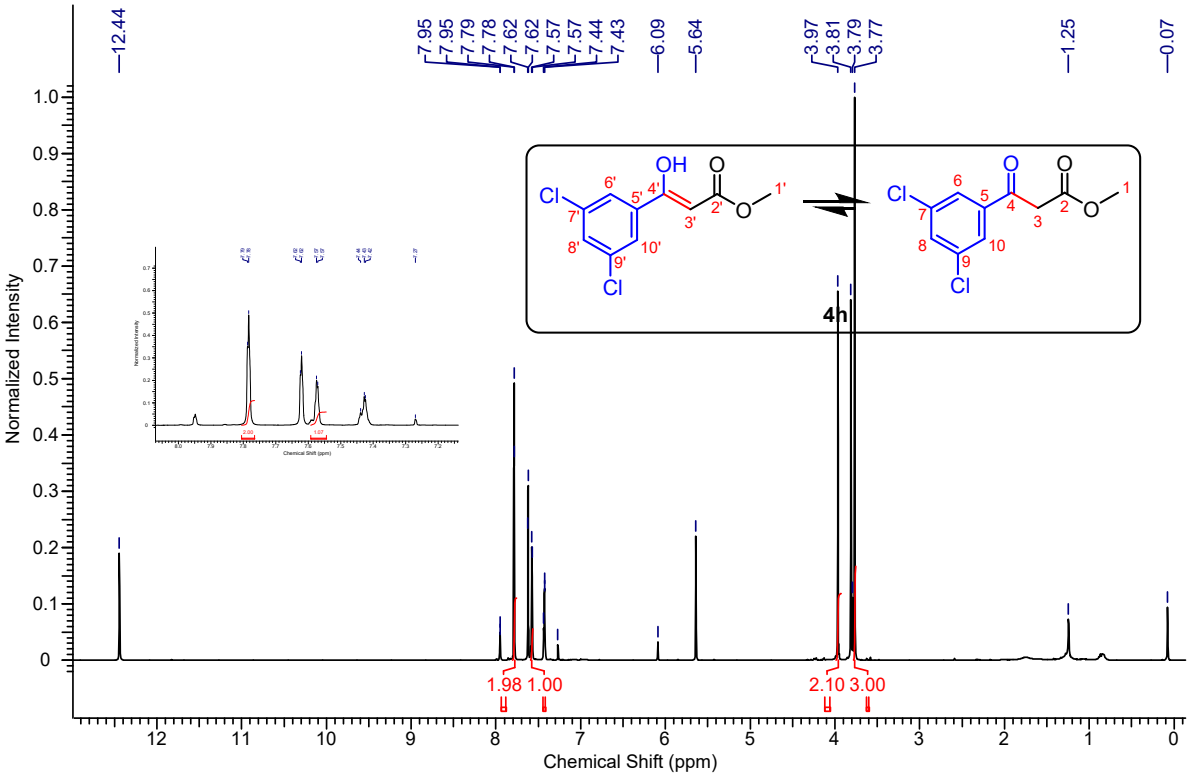
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3g



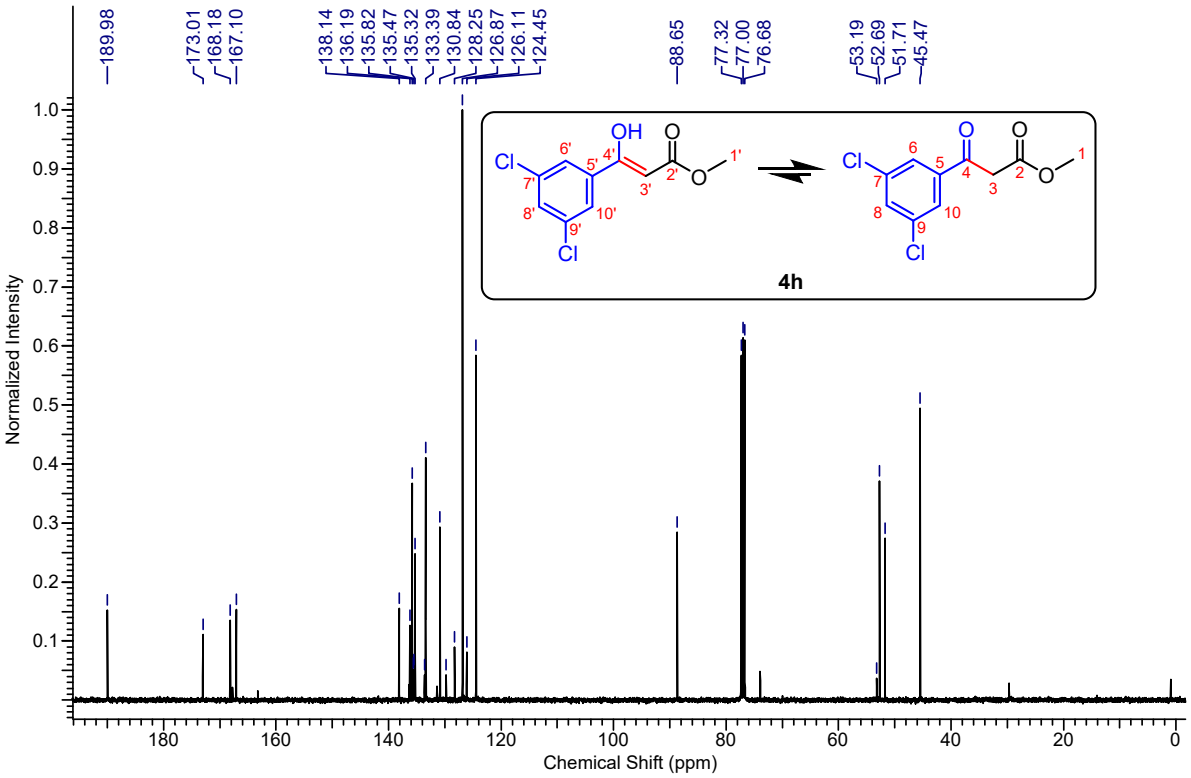
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3h



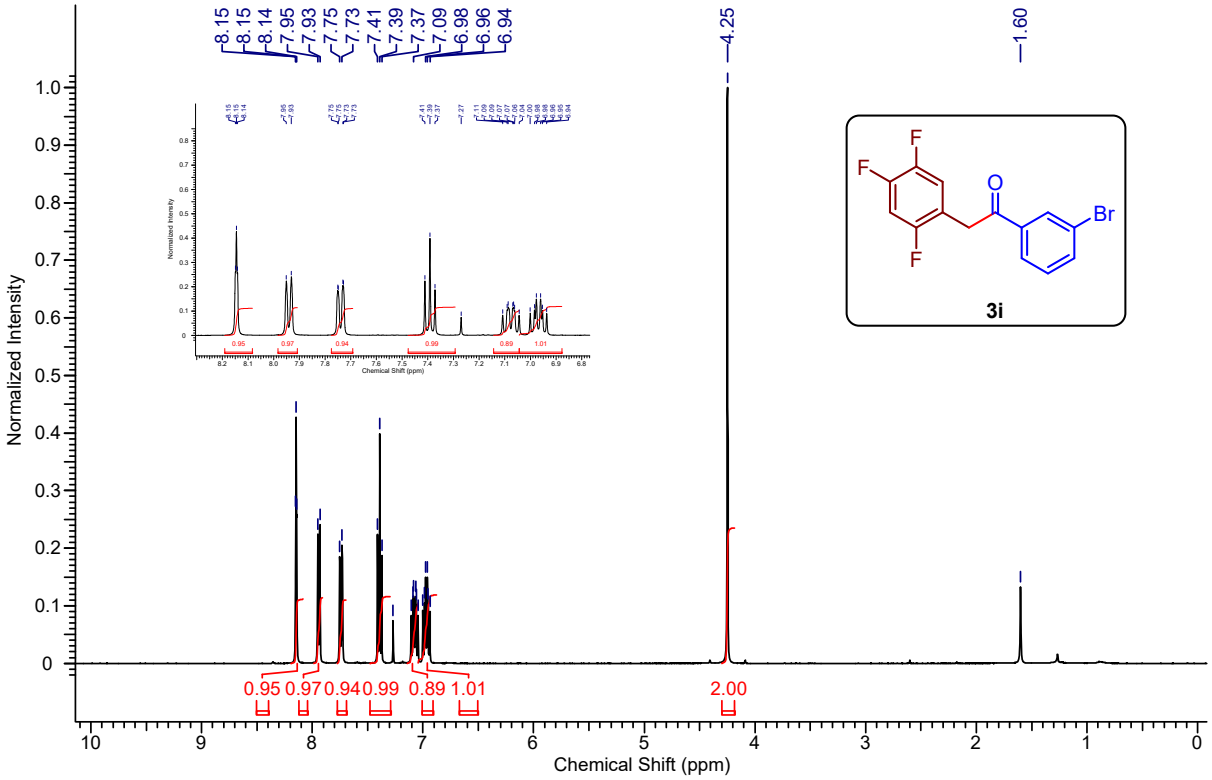
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3h



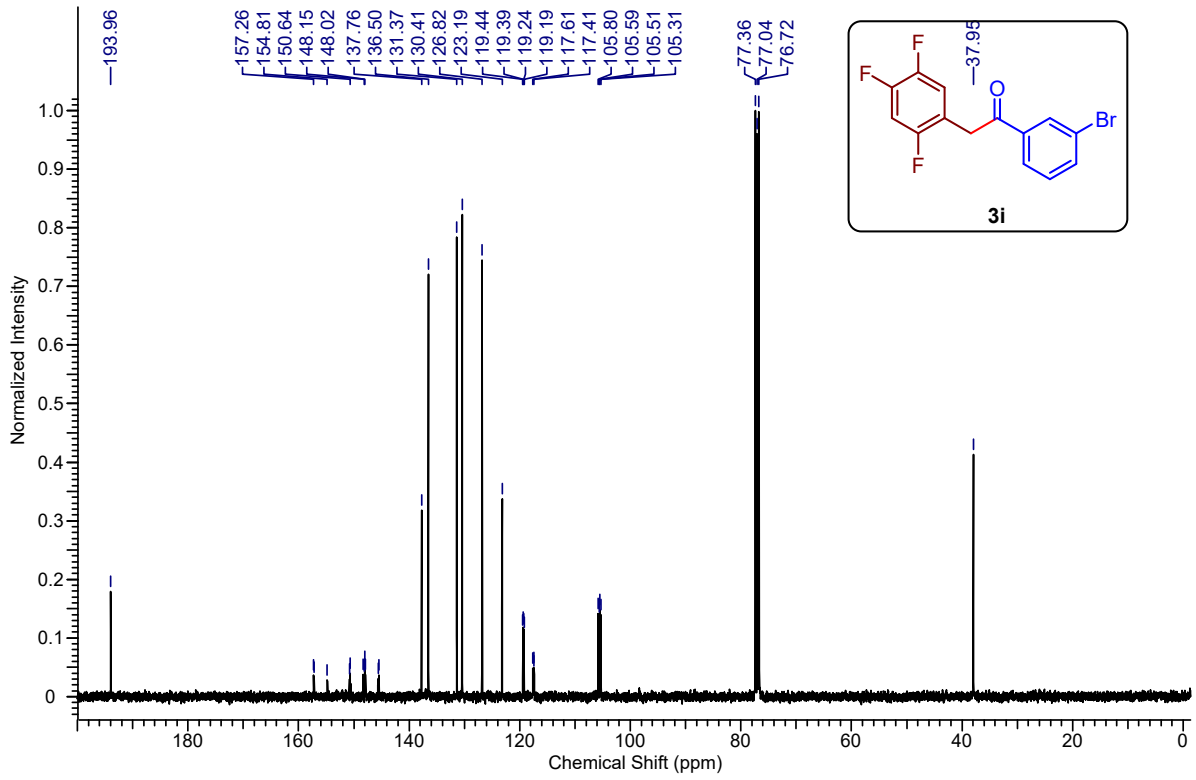
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4h



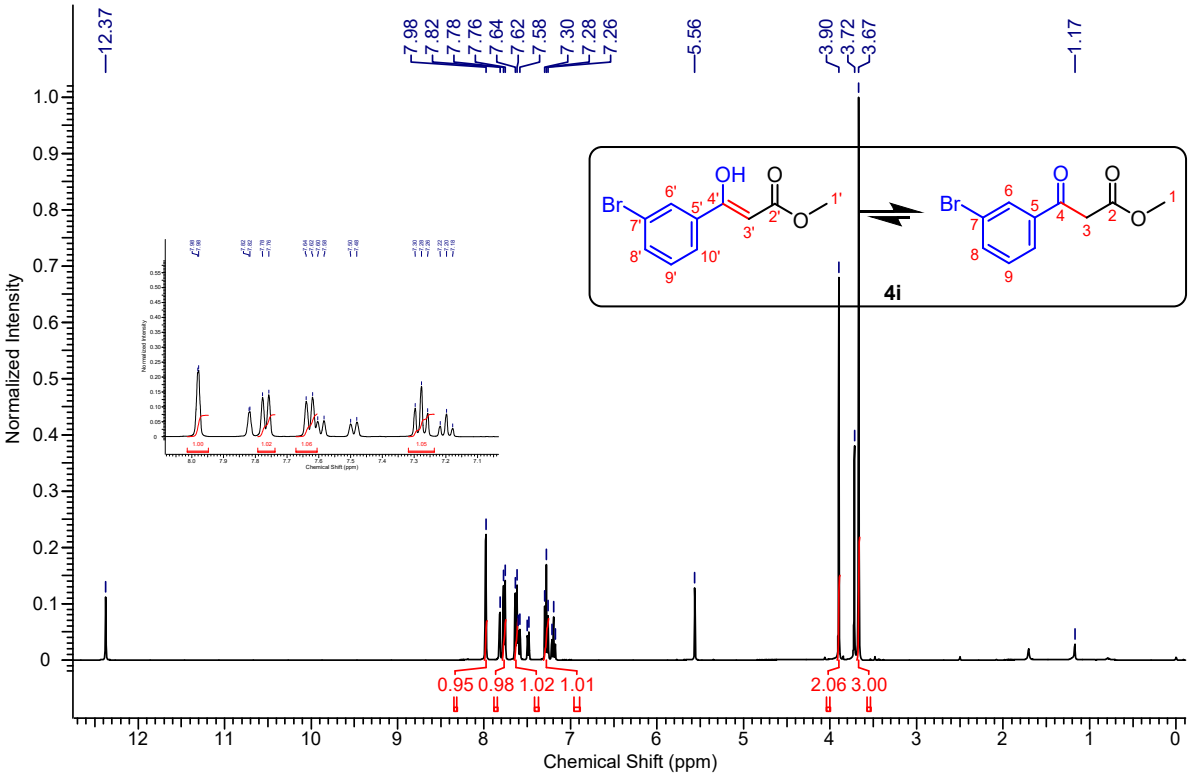
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4h



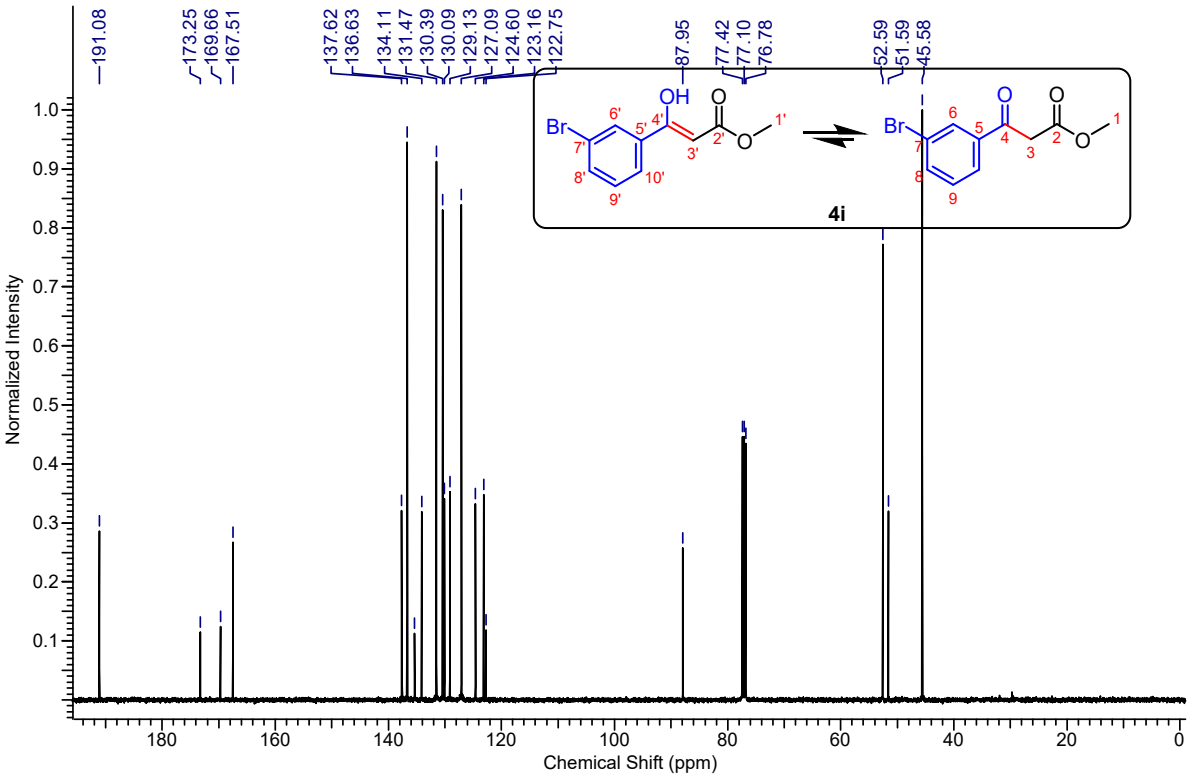
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3i



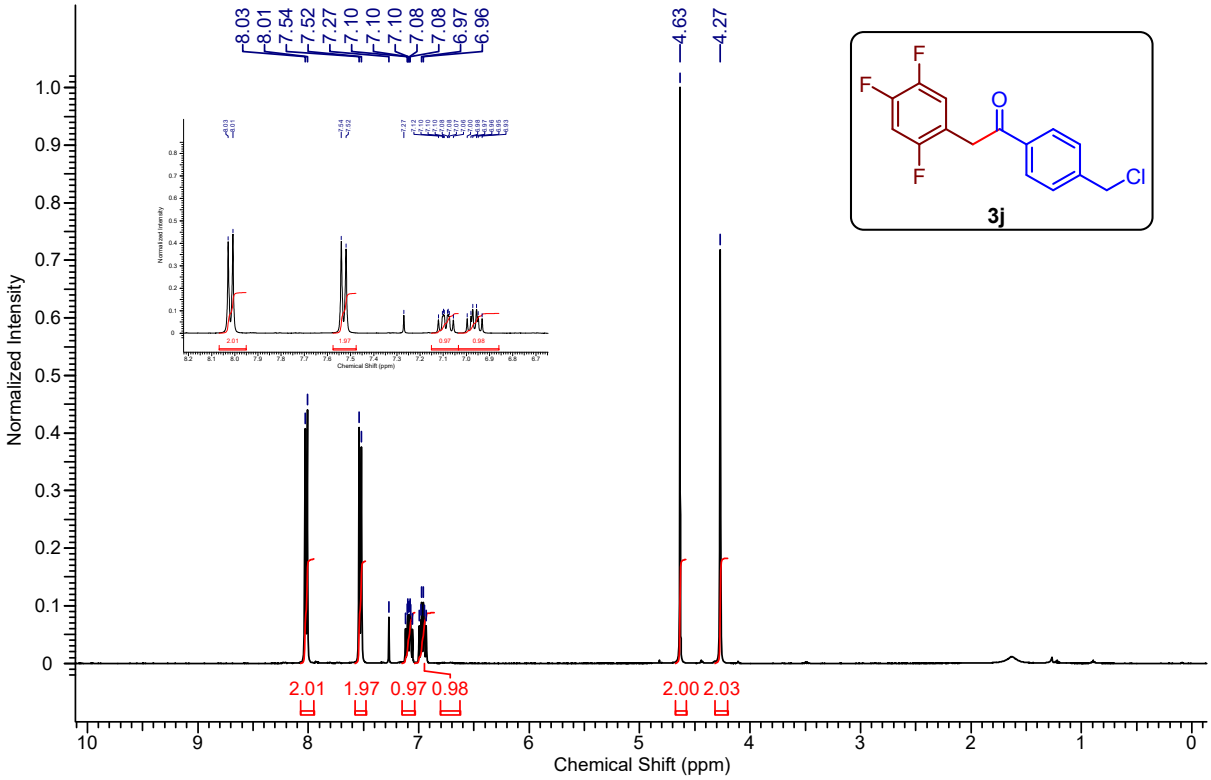
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3i



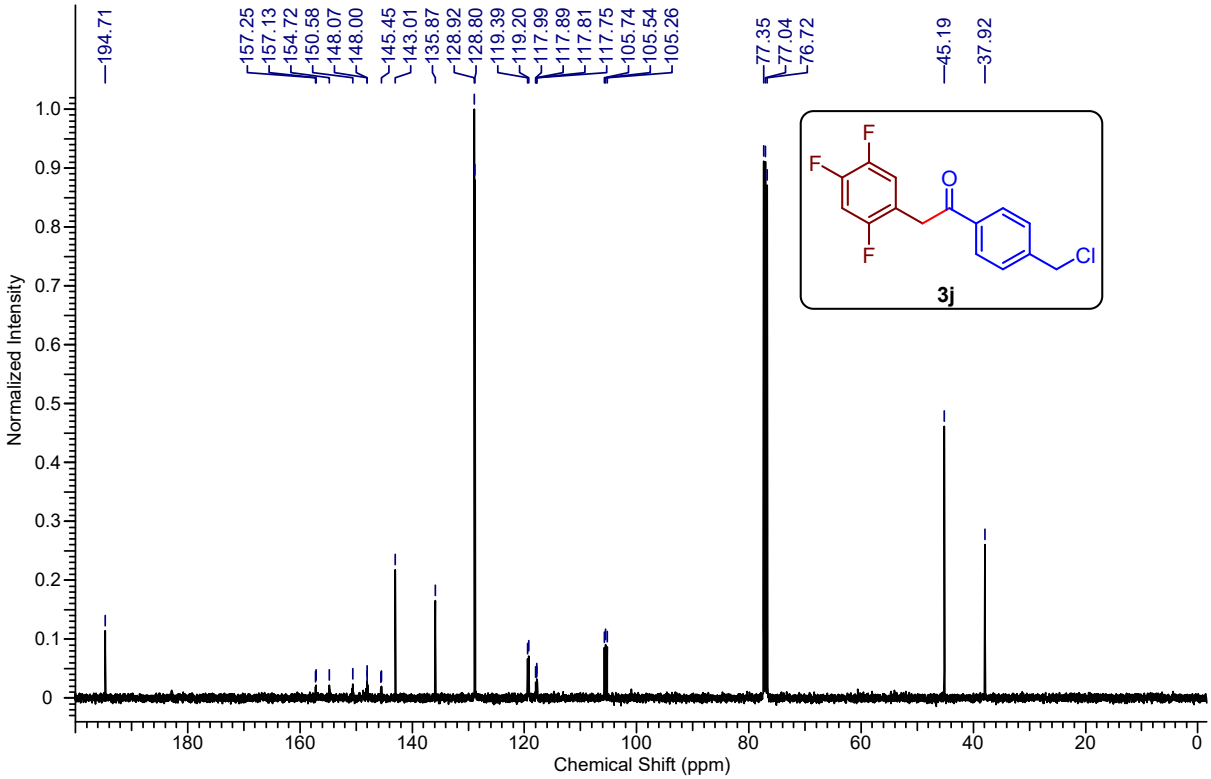
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4i



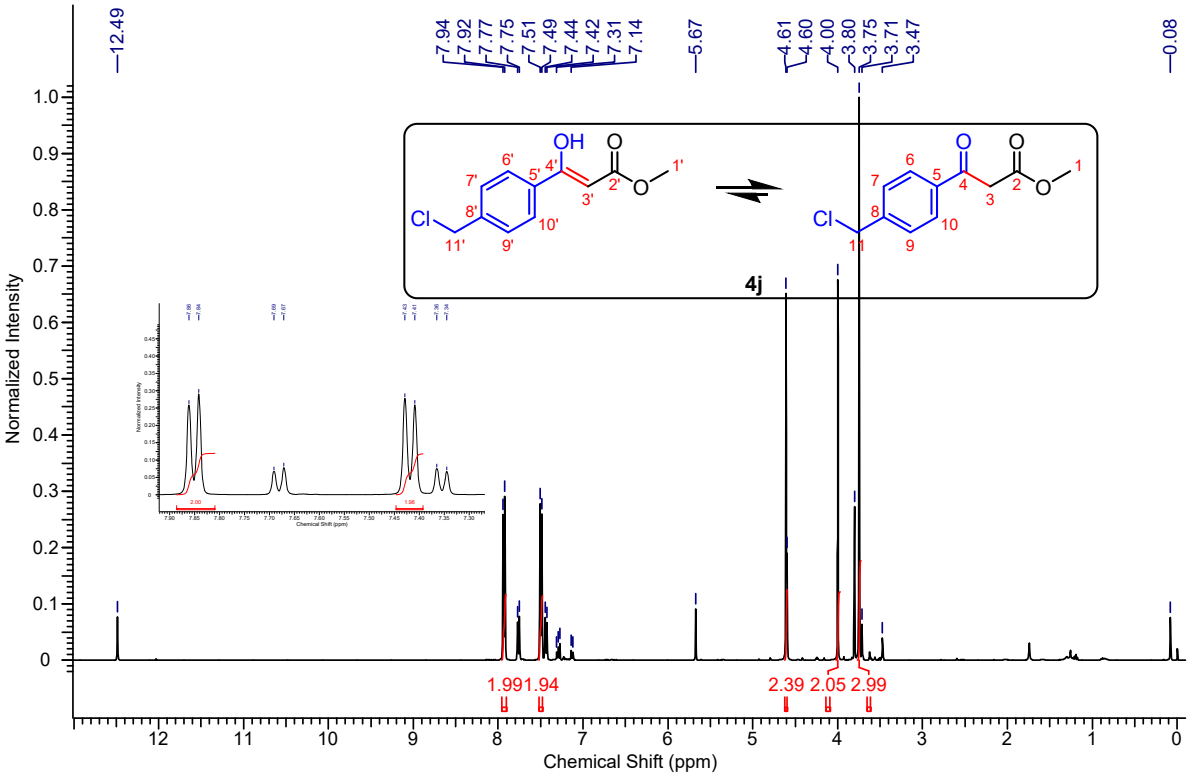
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4i



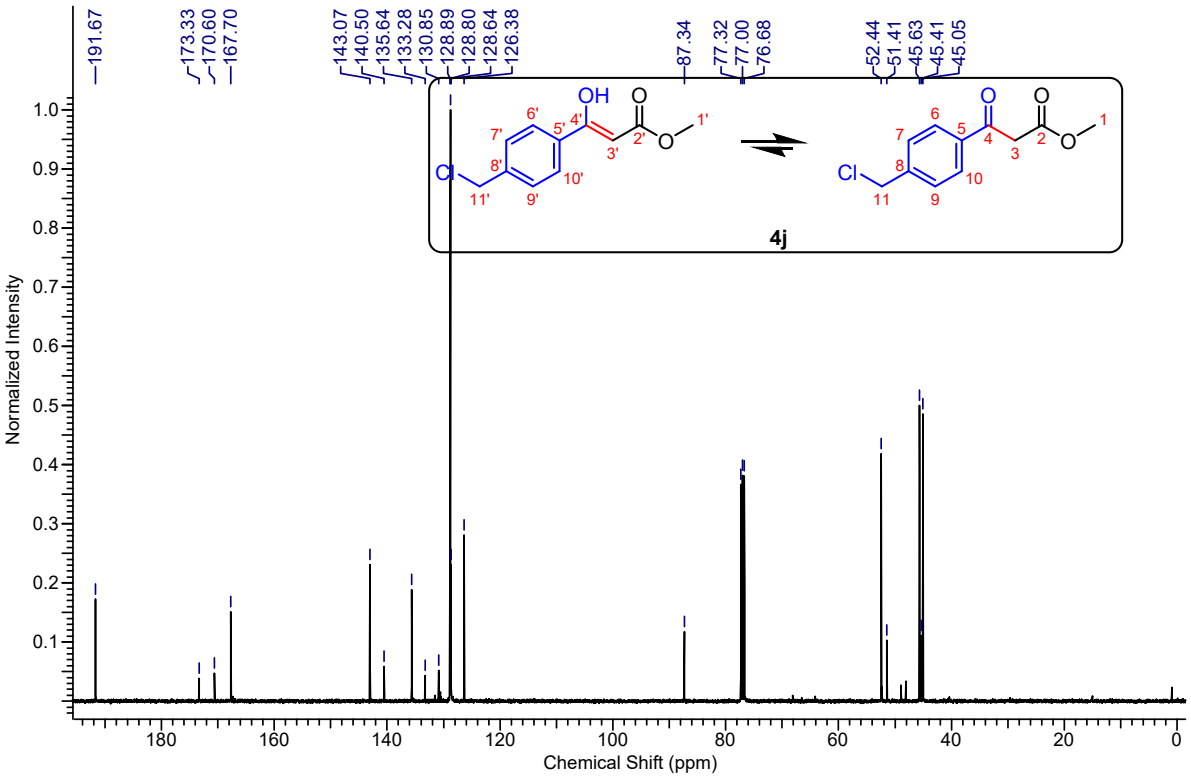
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3J



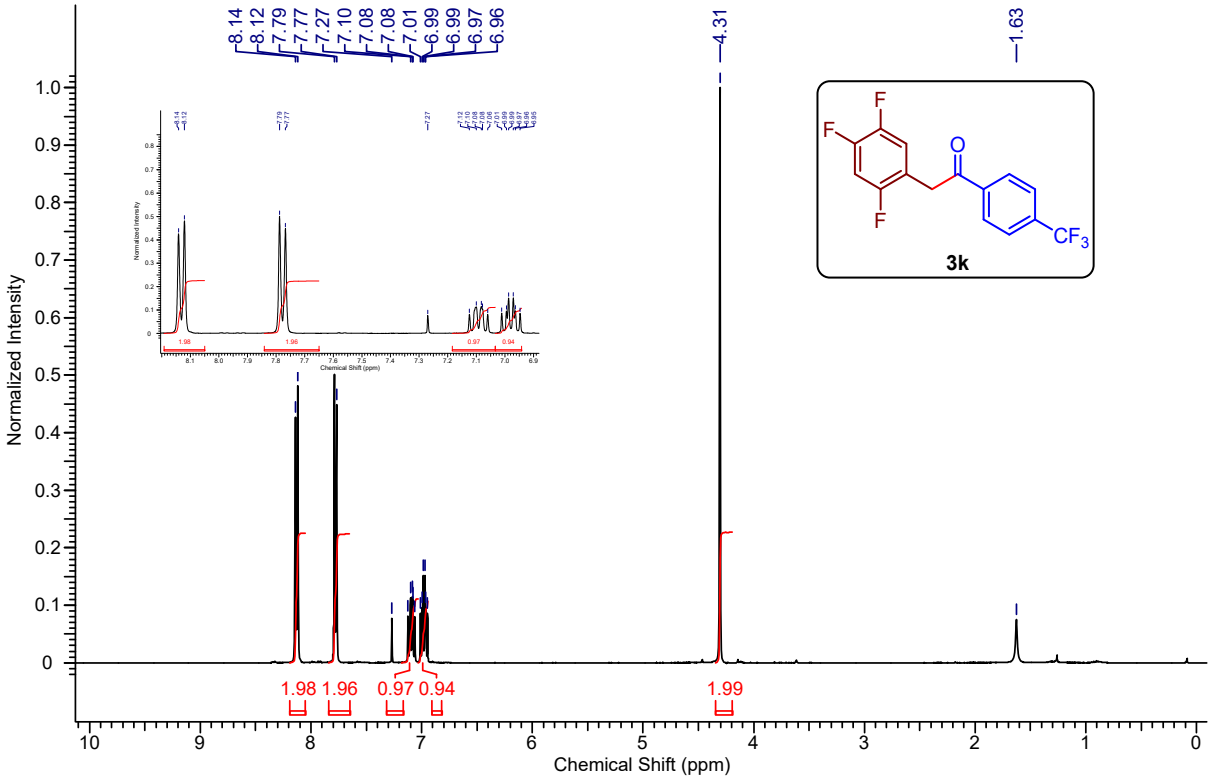
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3J



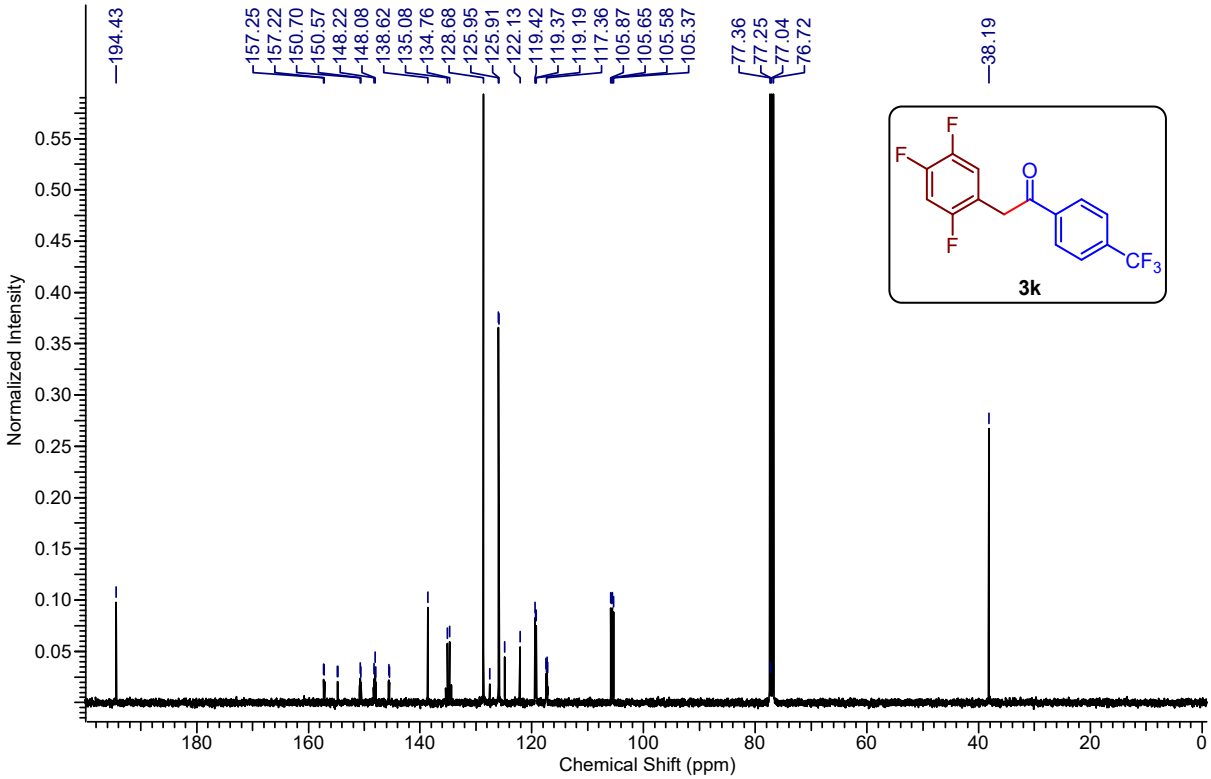
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4J



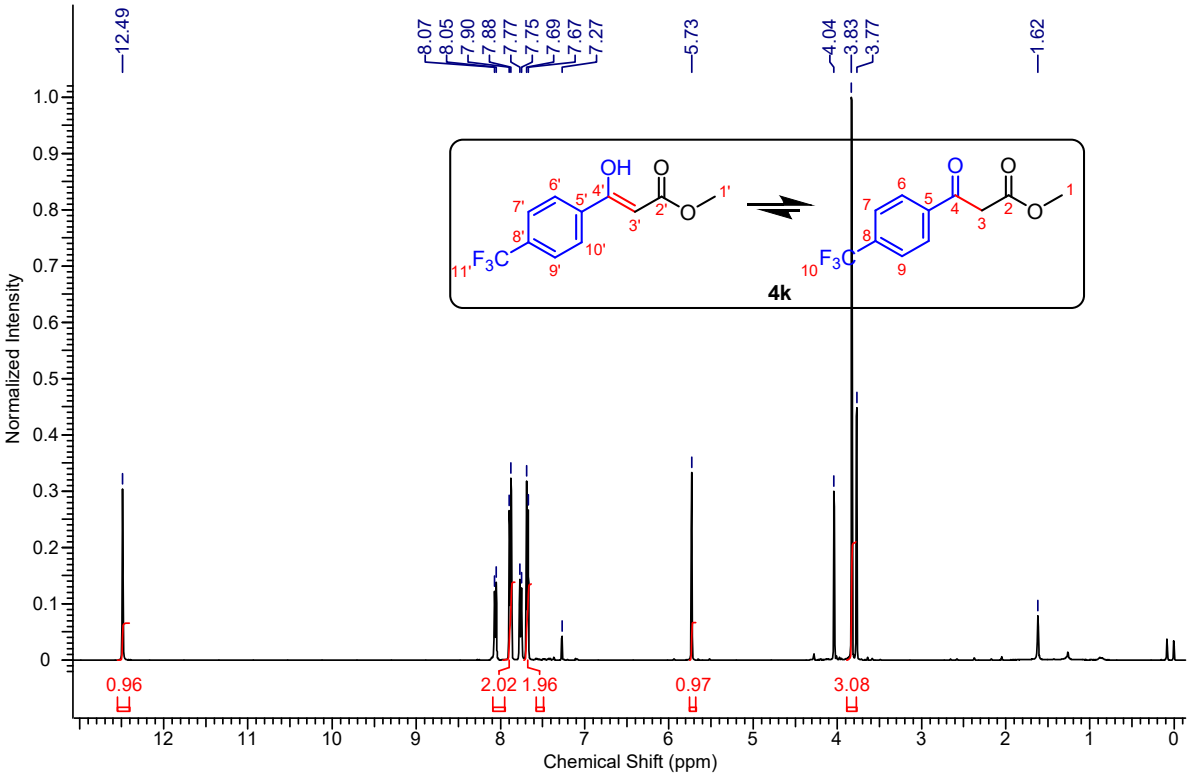
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4J



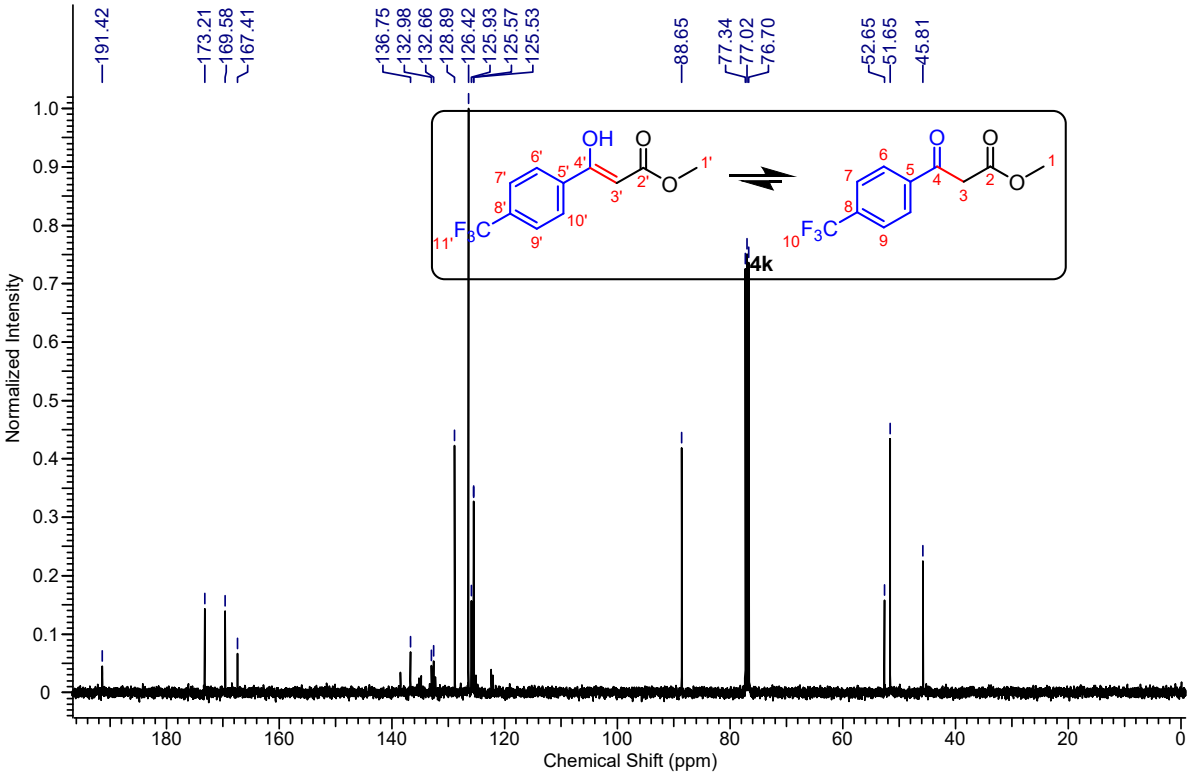
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3k



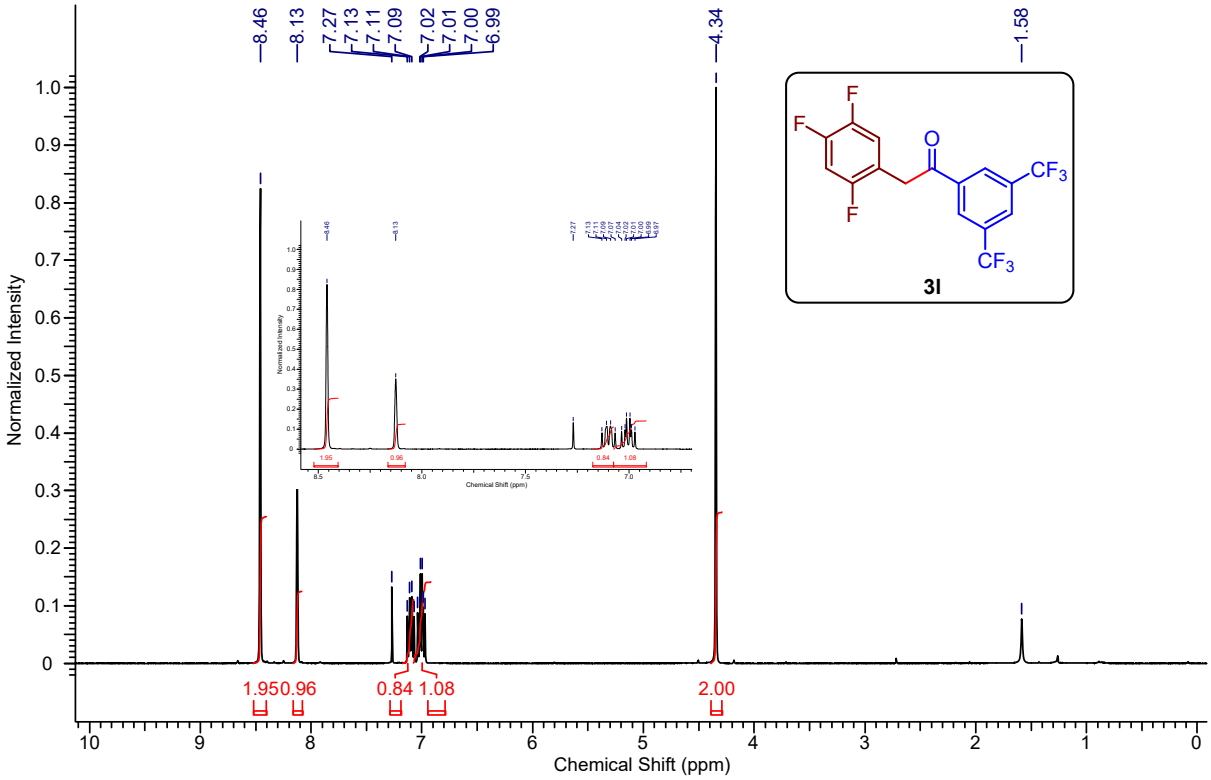
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3k



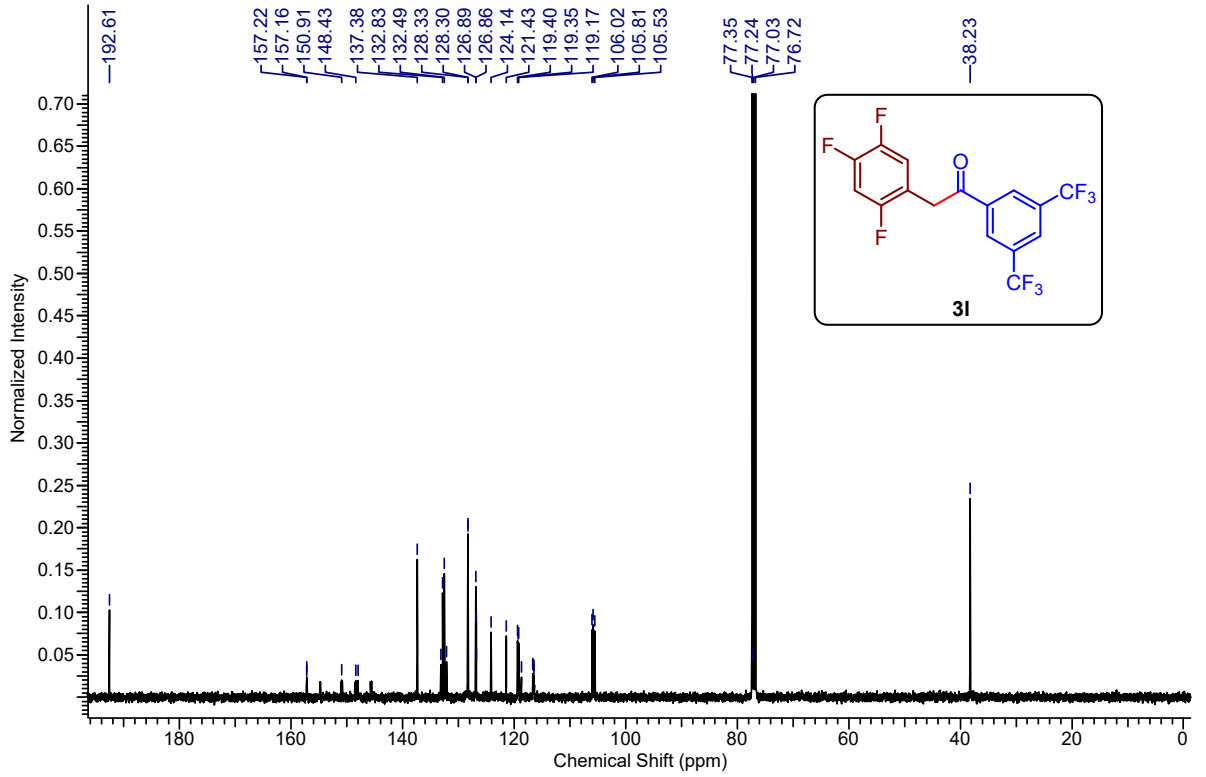
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4k



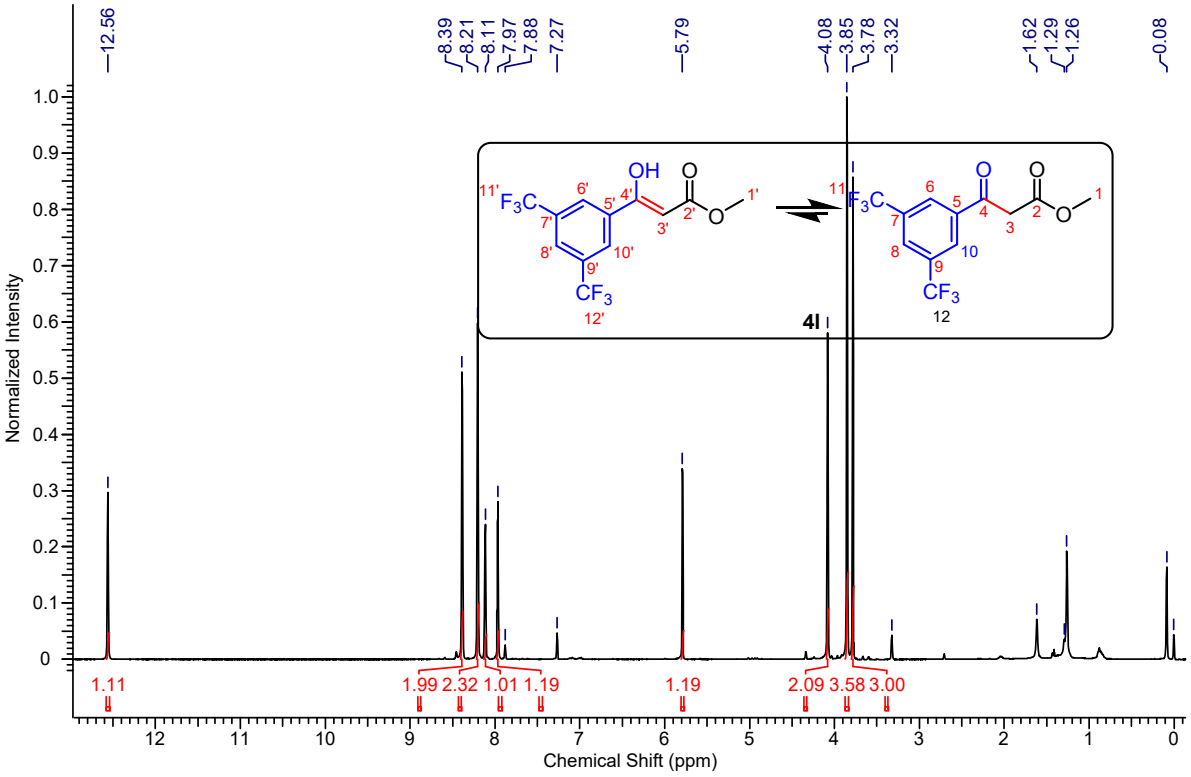
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4k



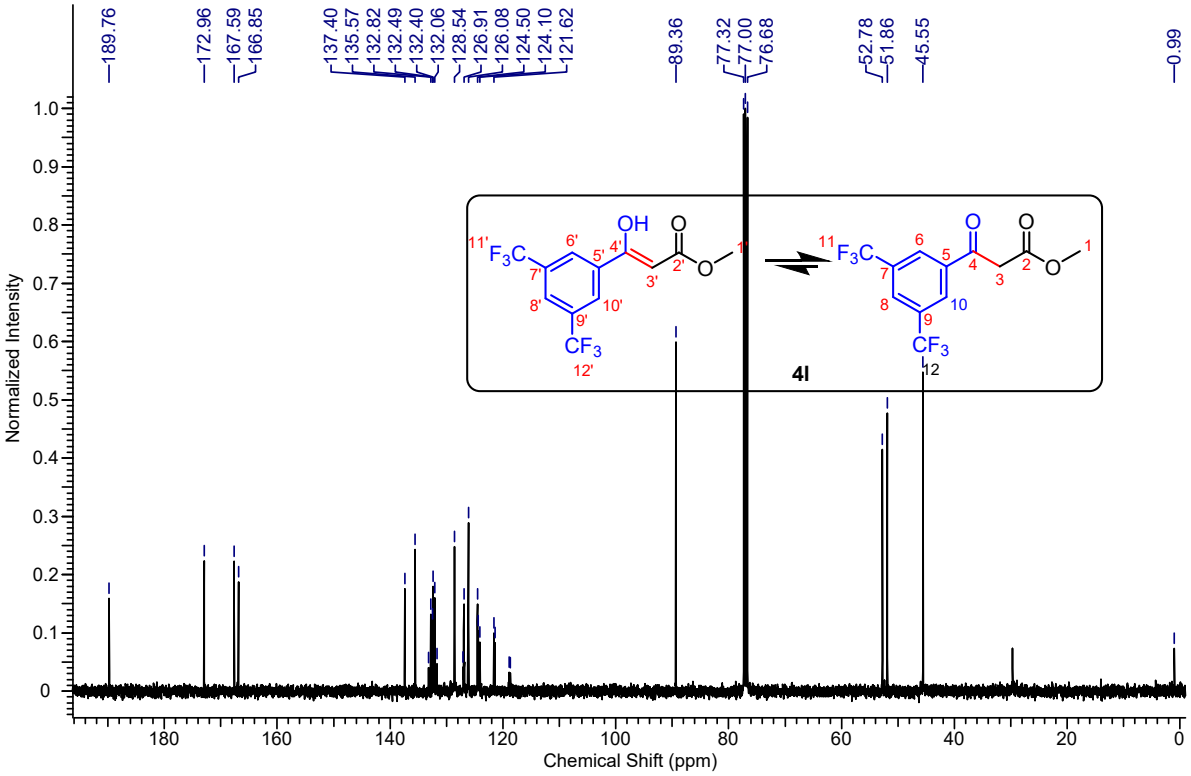
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3l



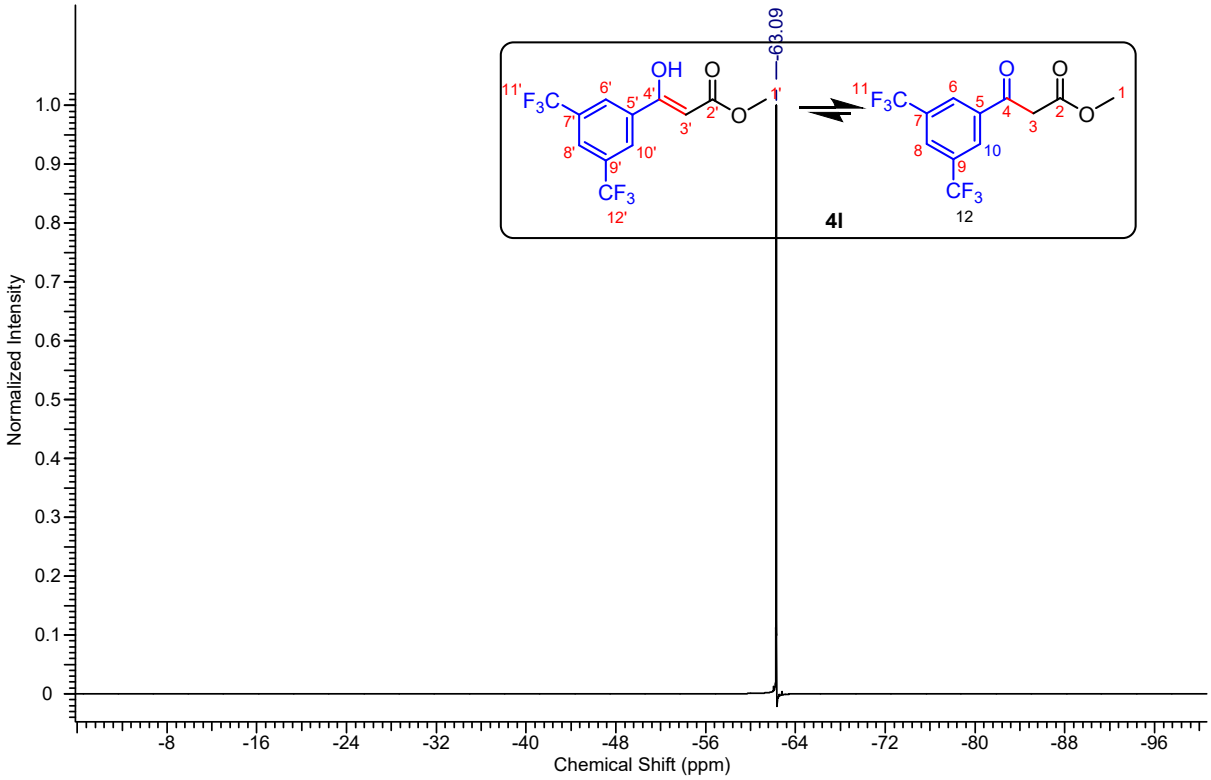
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3l



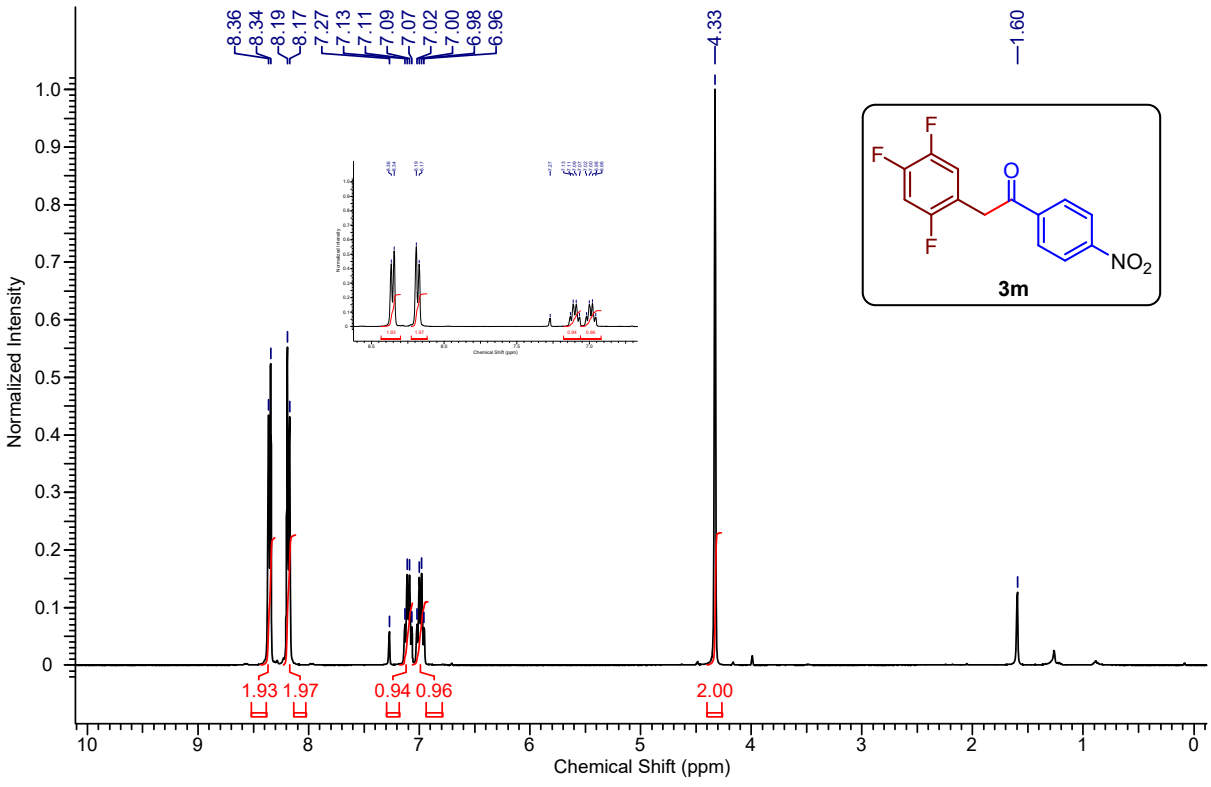
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4l



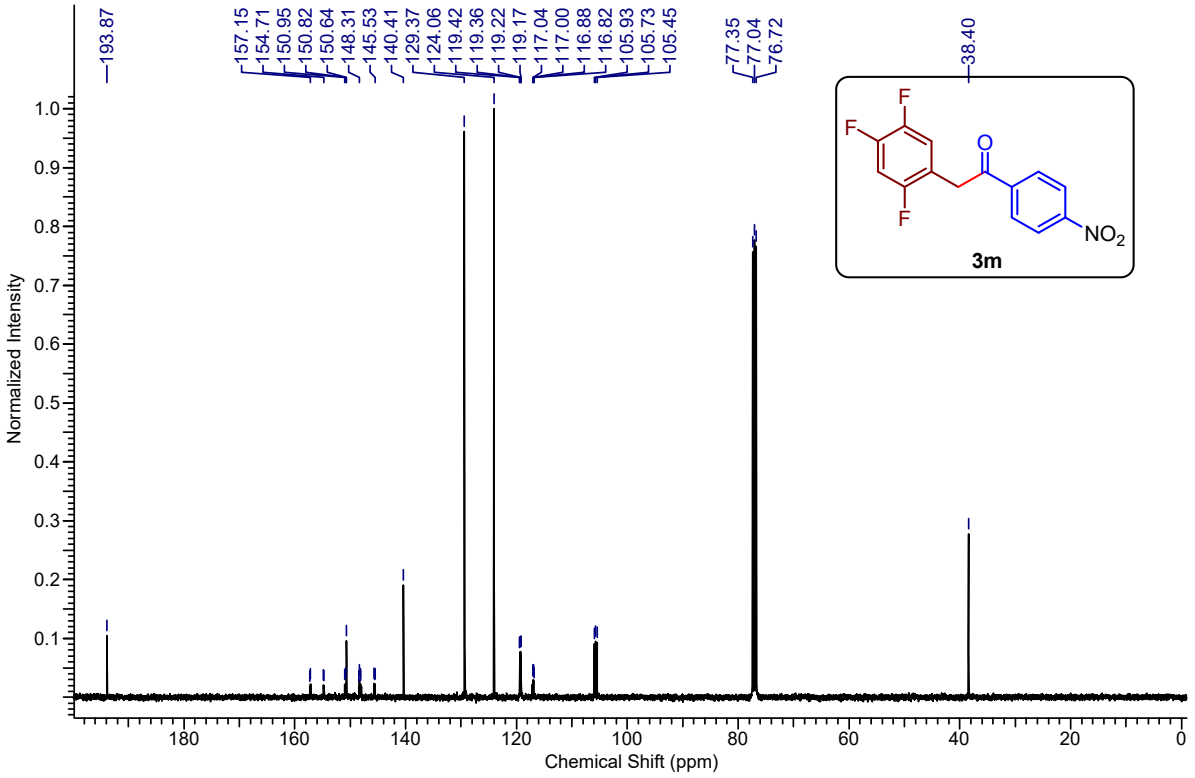
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4l



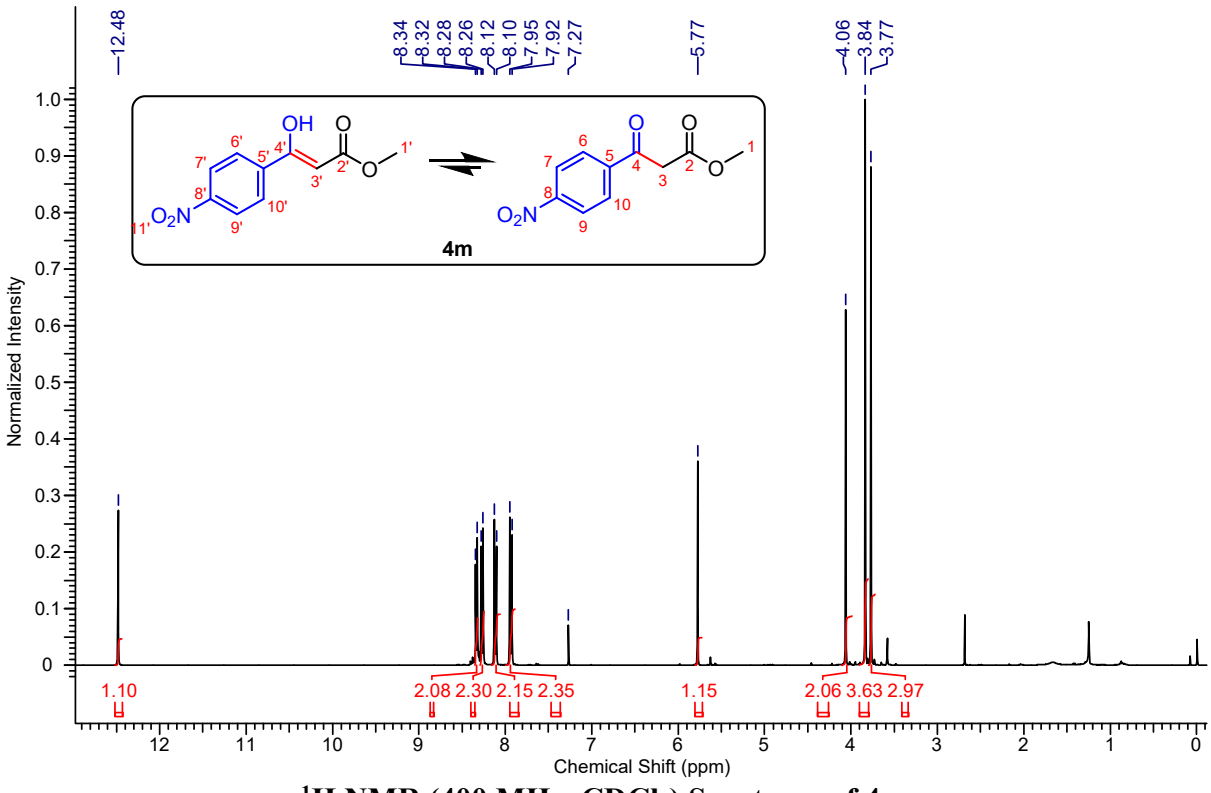
^{19}F NMR (375 MHz, $CDCl_3$) Spectrum of 4l



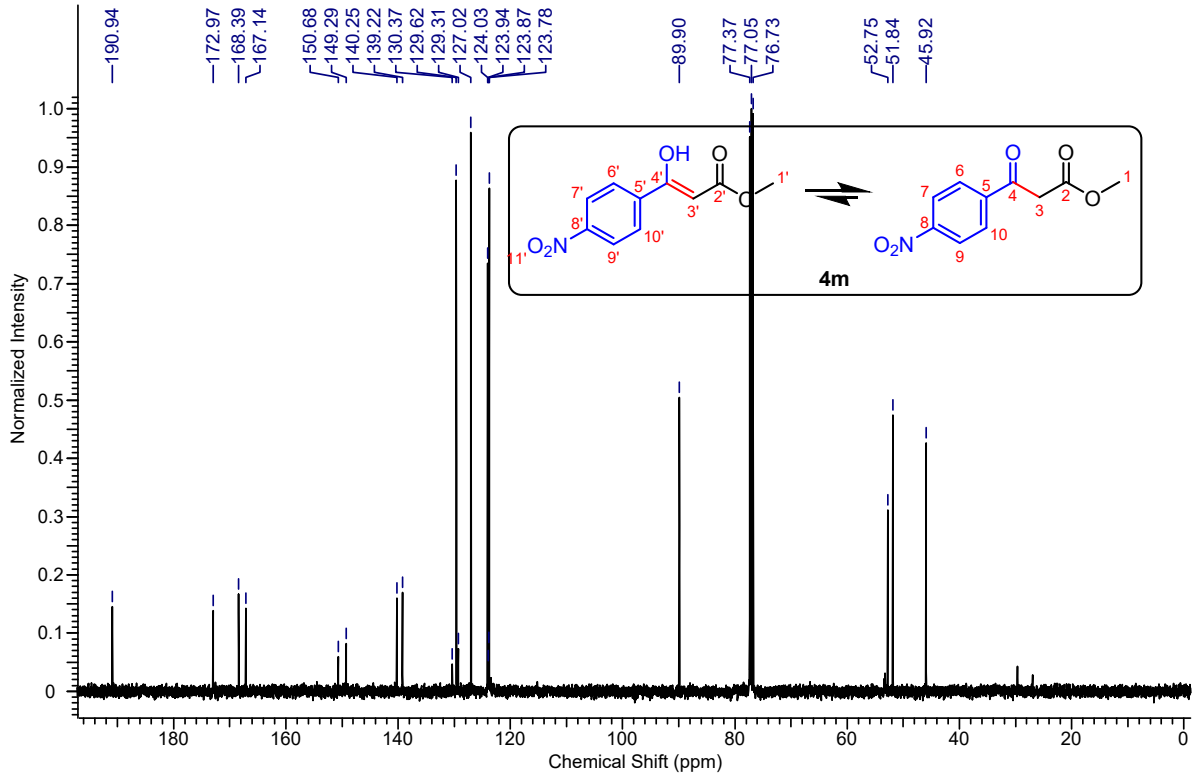
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3m



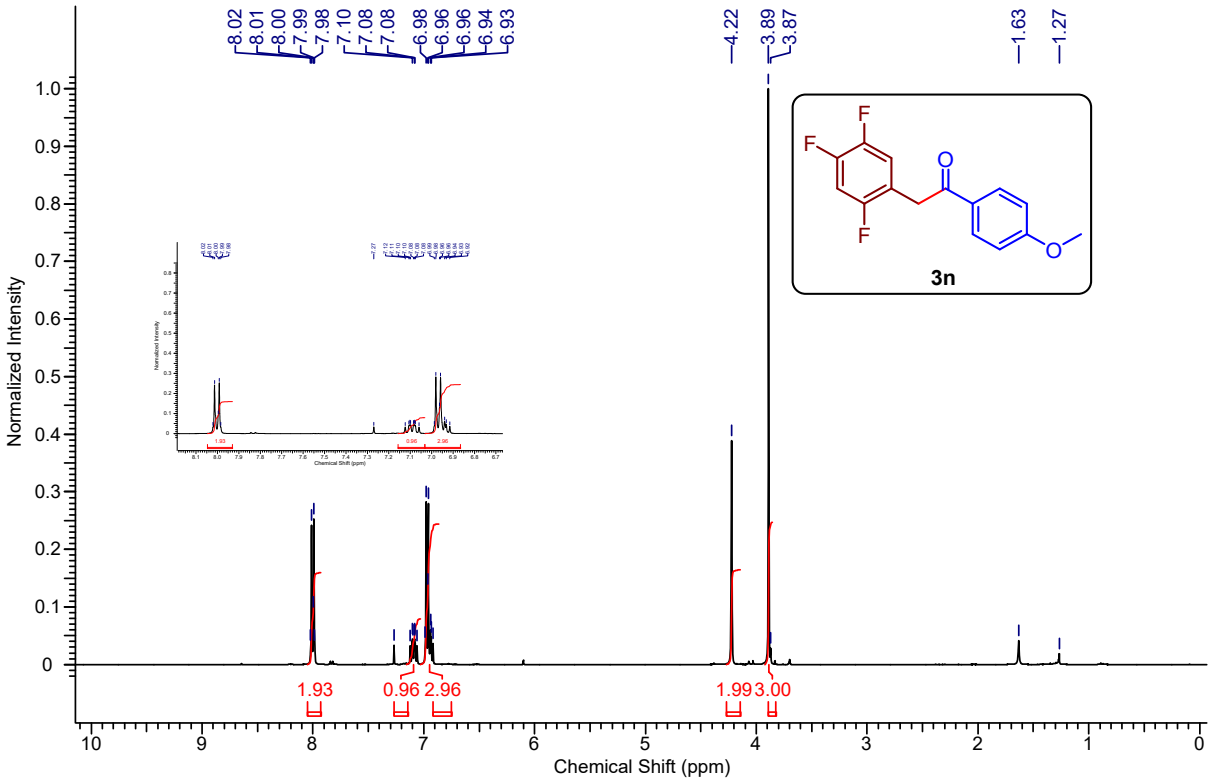
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3m



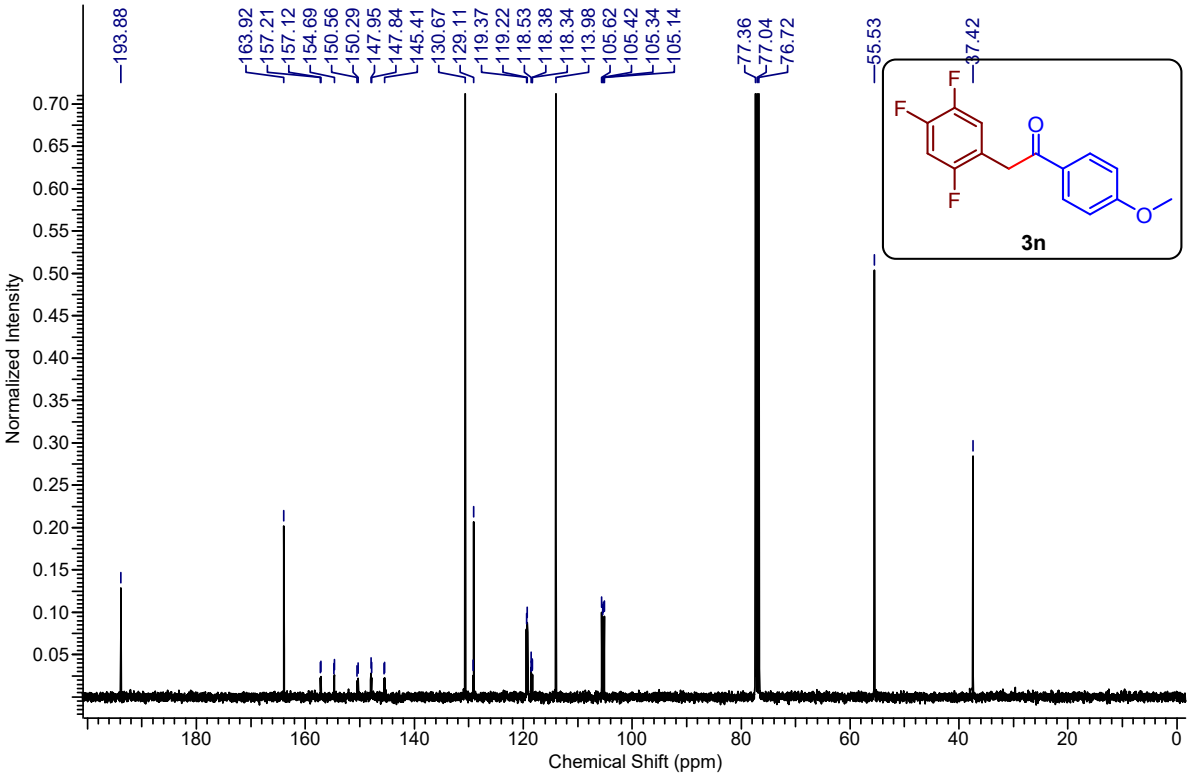
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4m



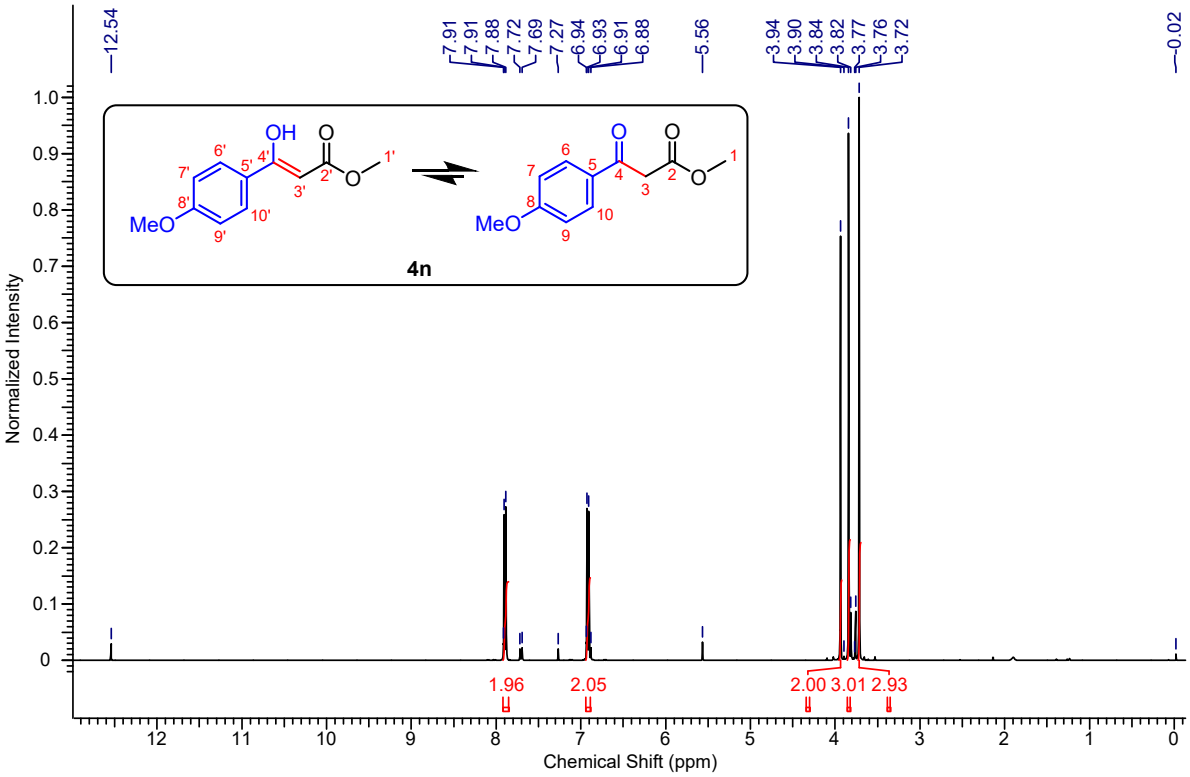
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4m



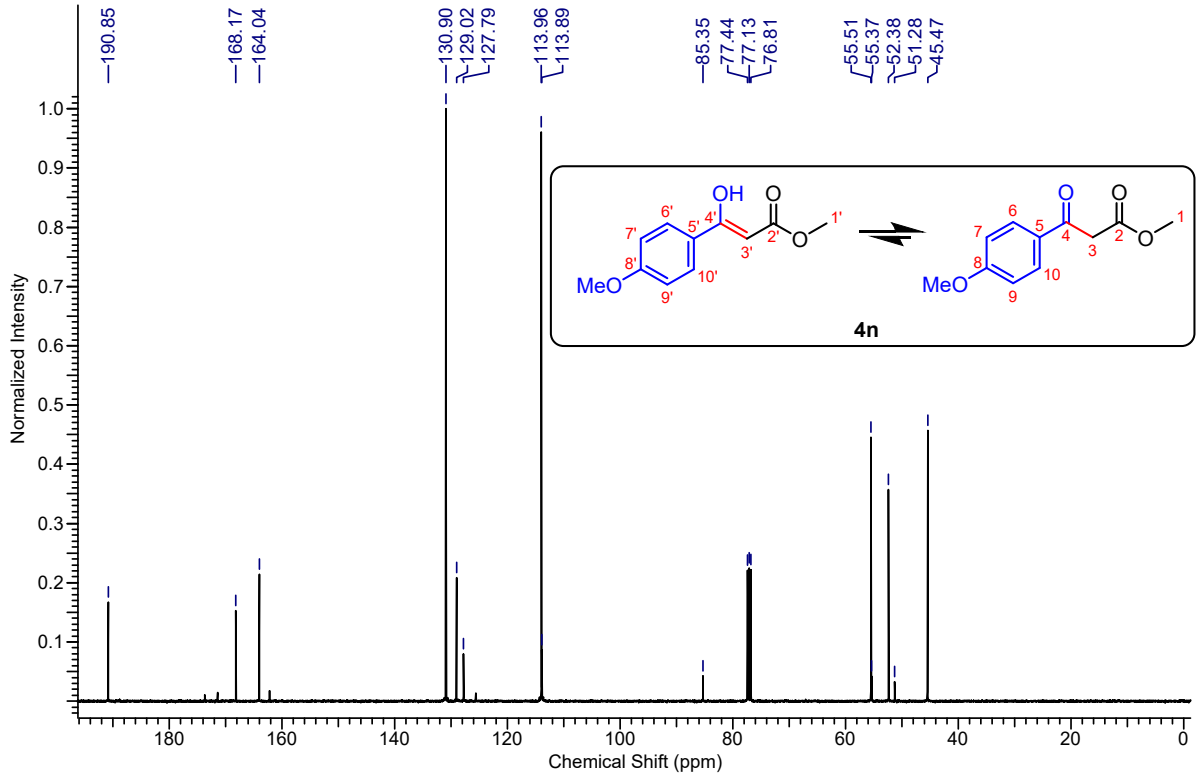
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3n



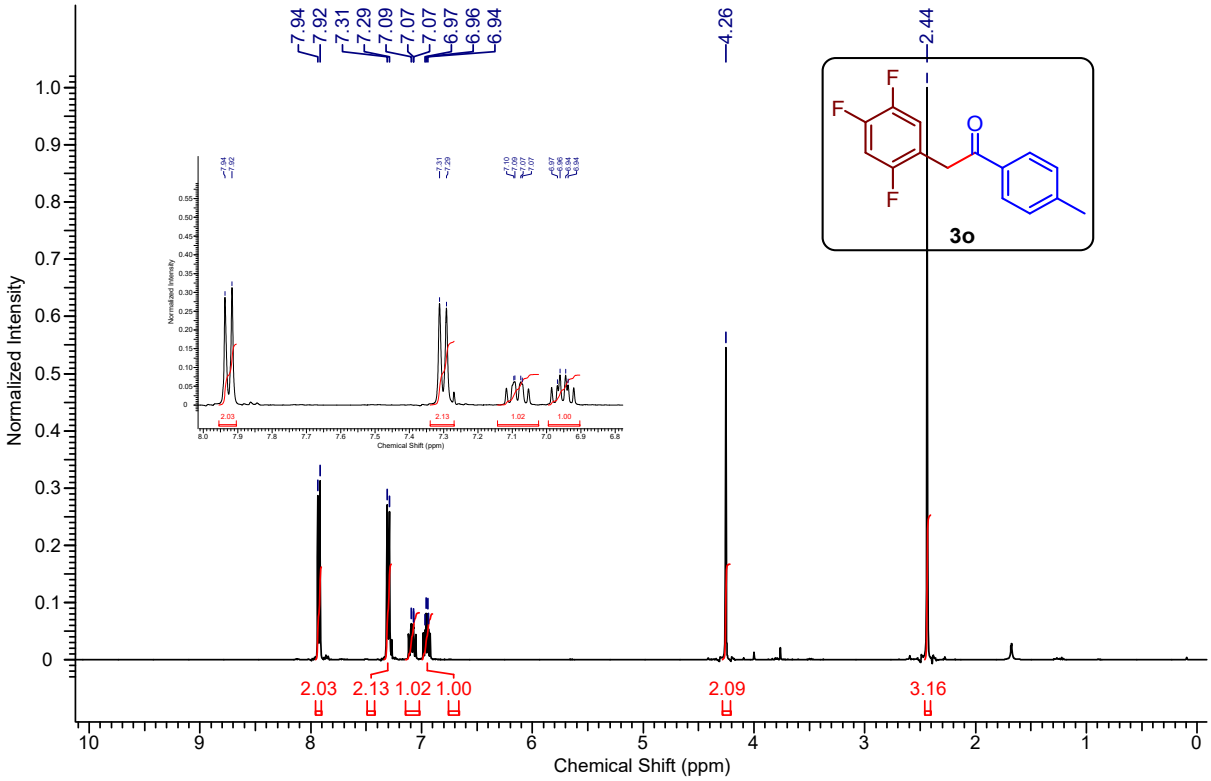
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3n



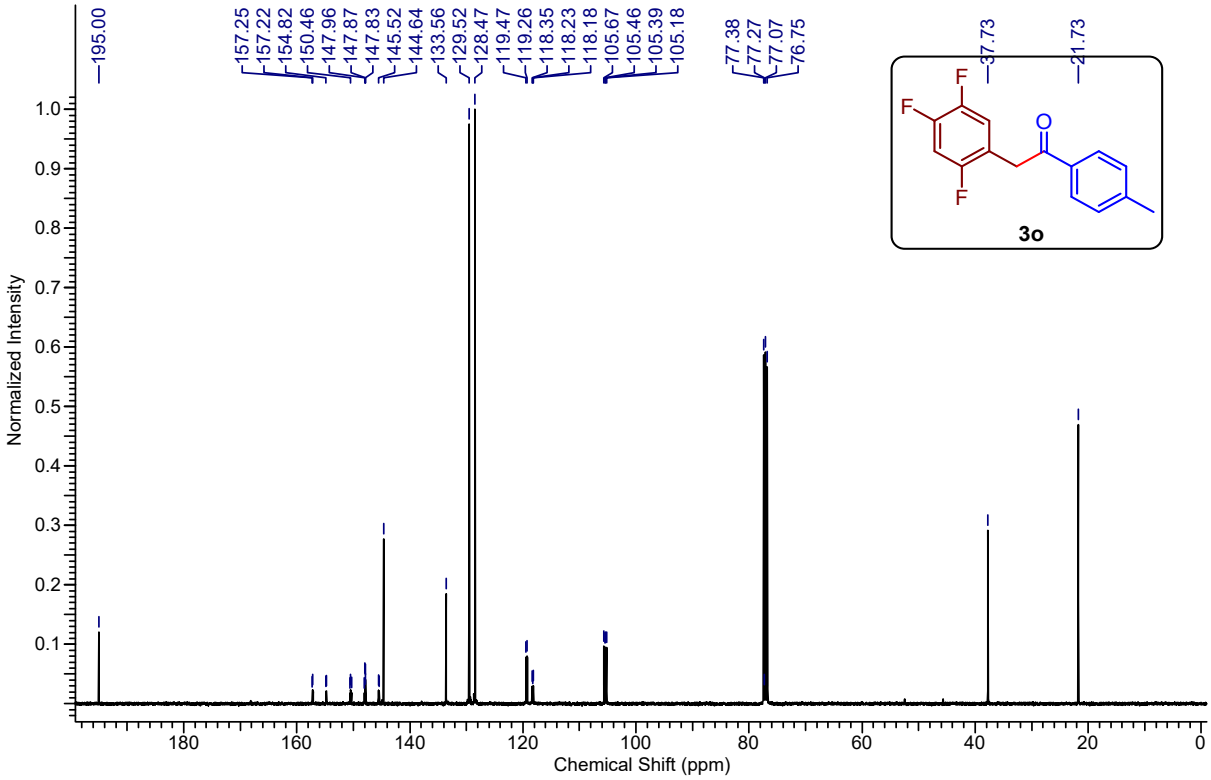
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4n



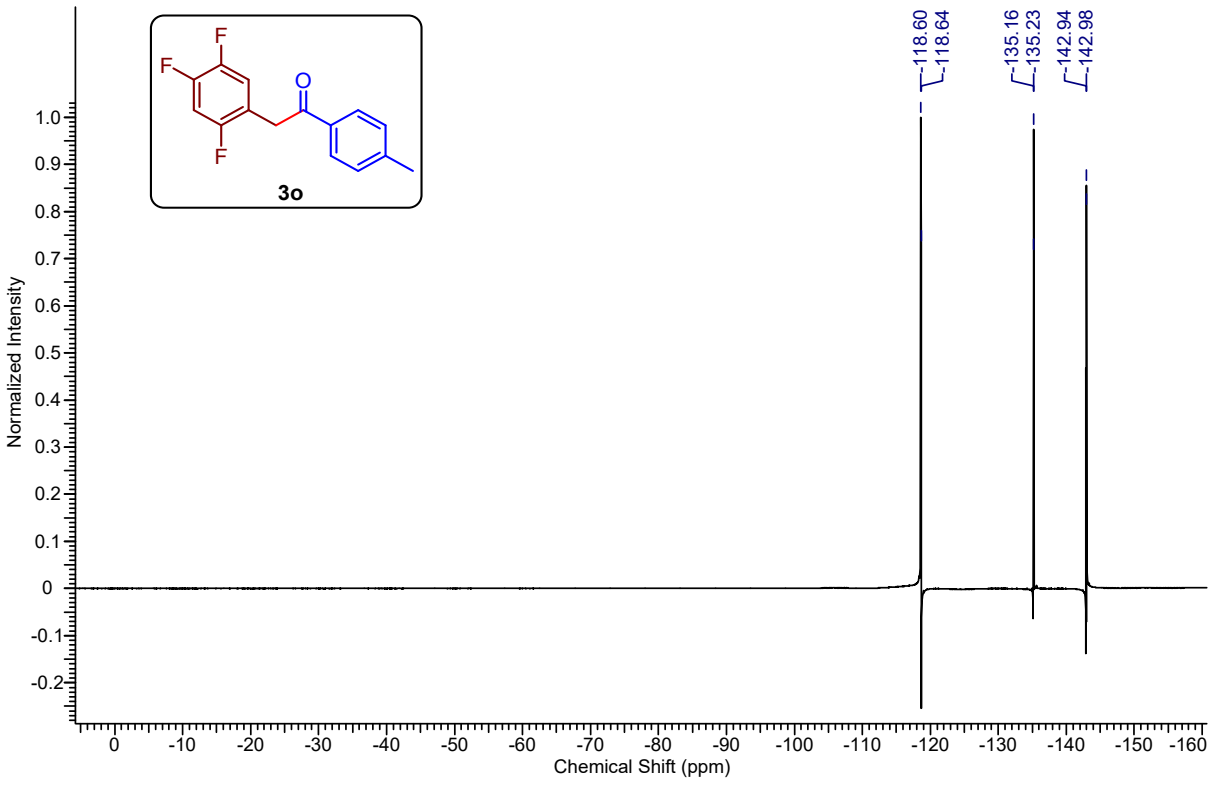
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3n



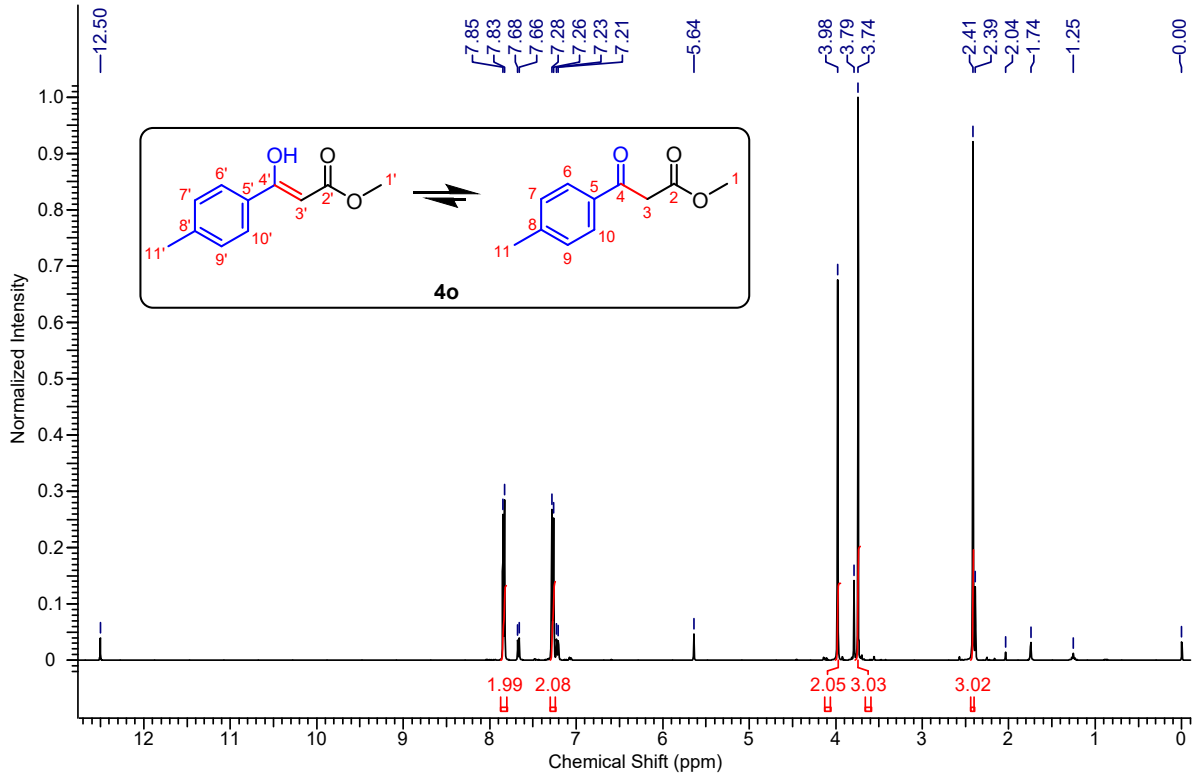
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3o



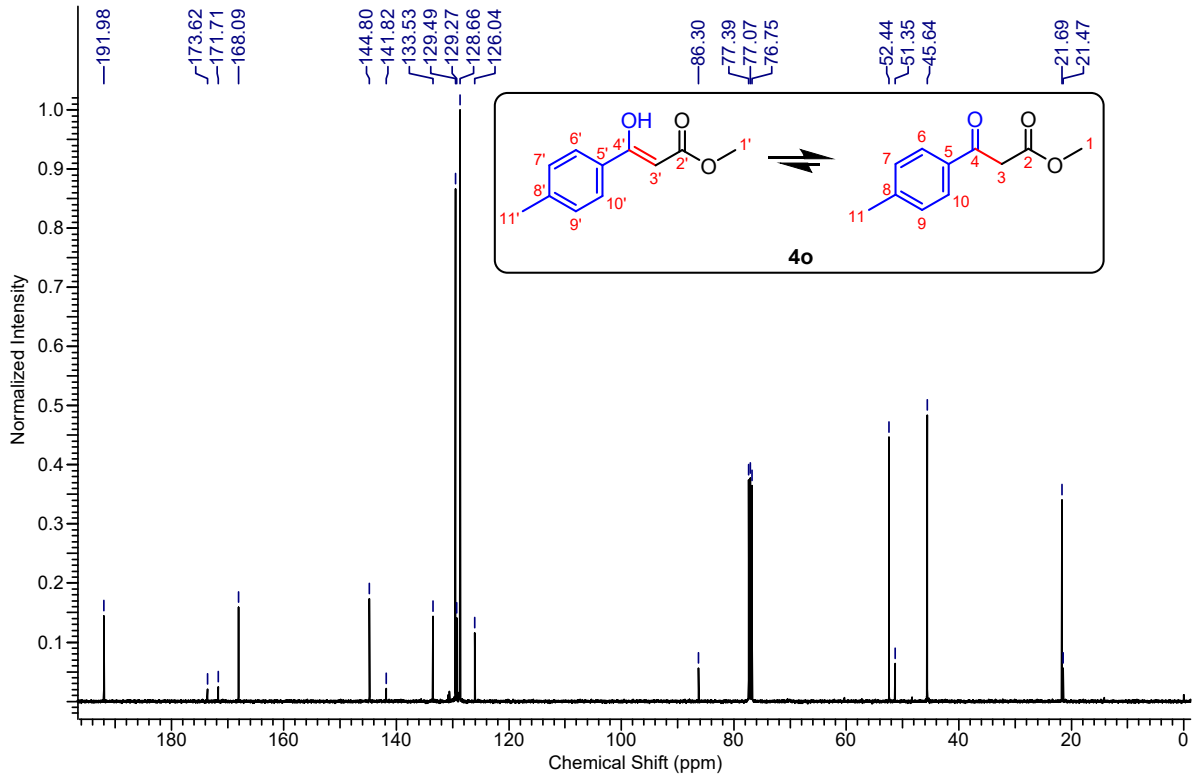
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3o



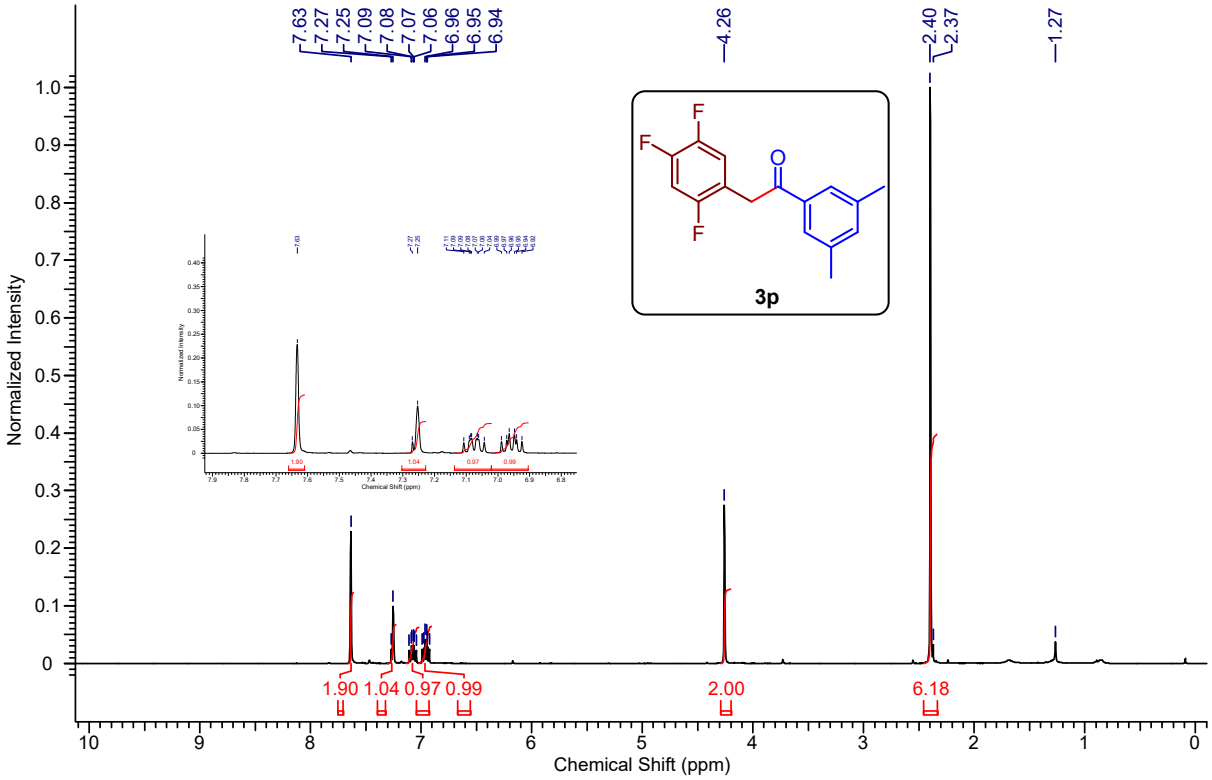
^{19}F NMR (375 MHz, $CDCl_3$) Spectrum of 3o



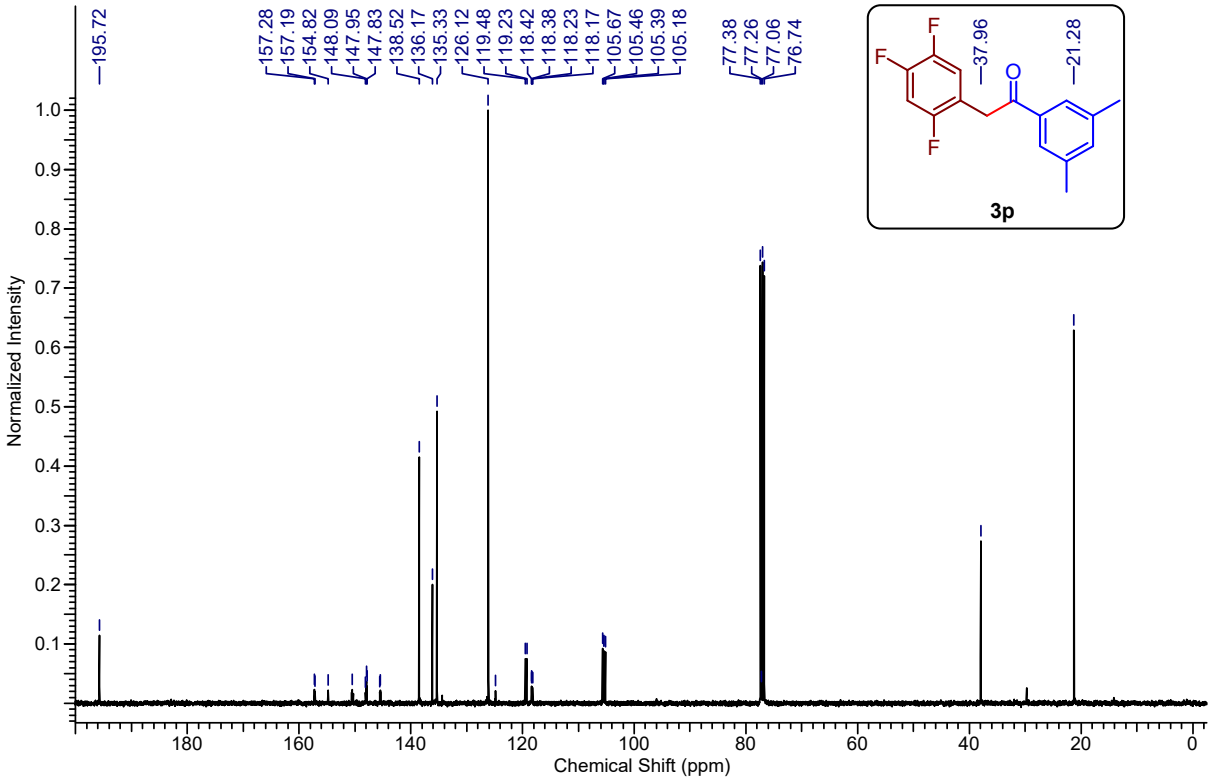
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4o



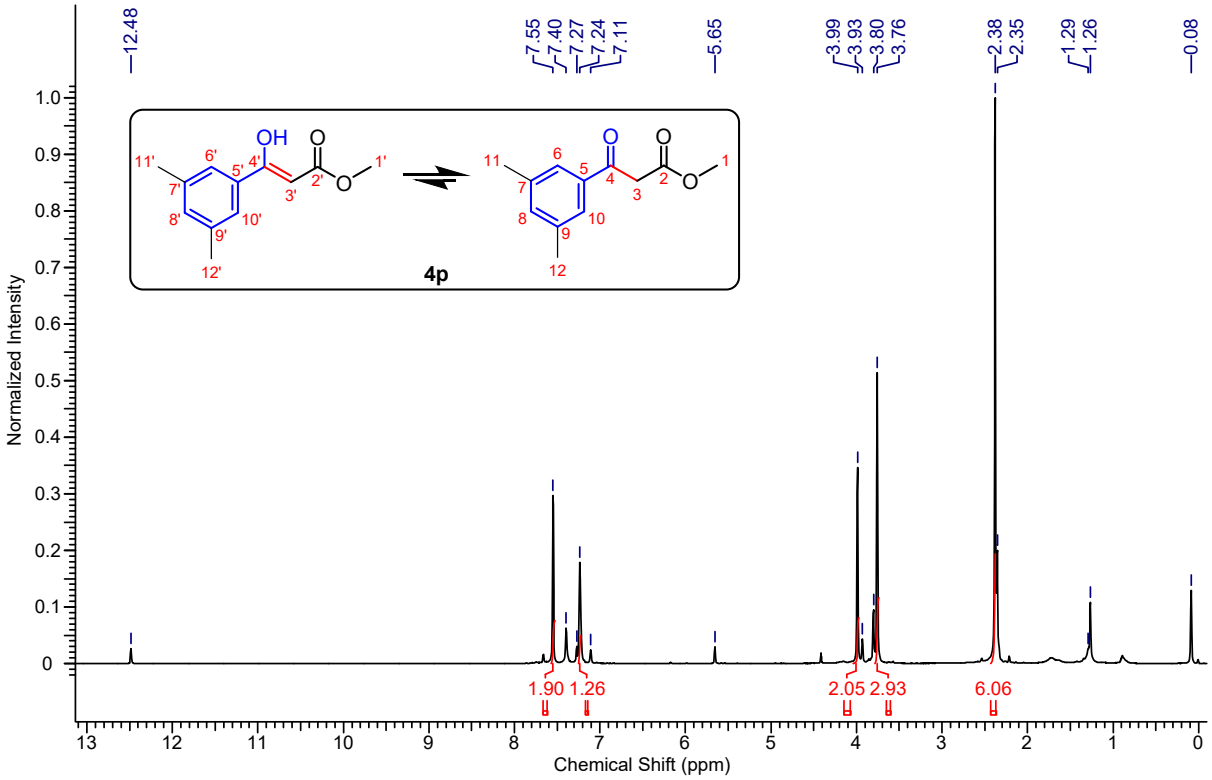
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4o



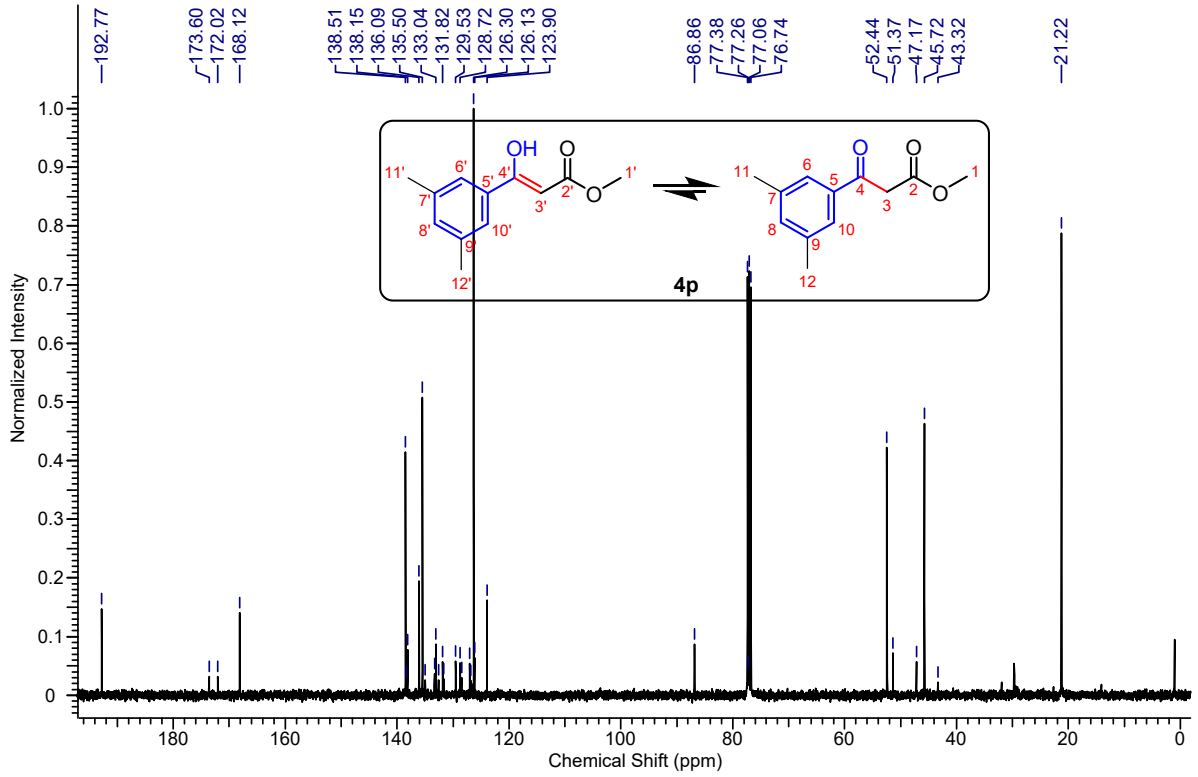
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3p



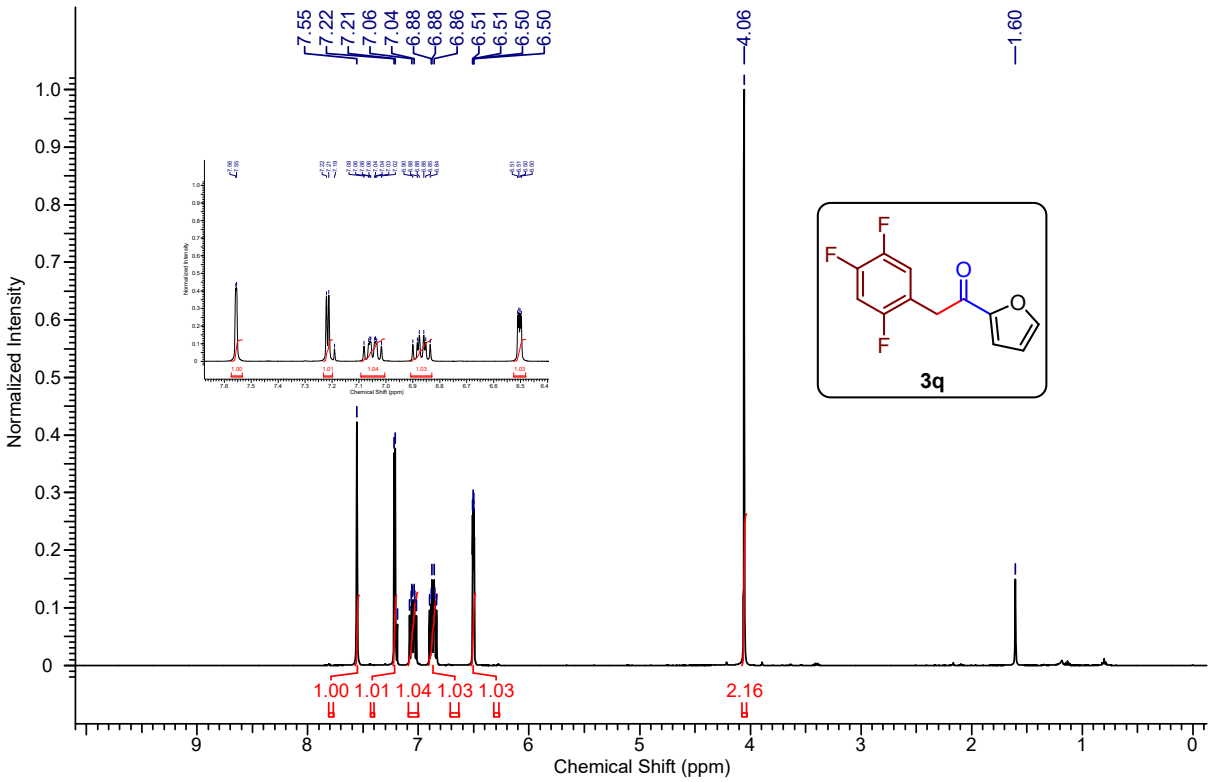
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3p



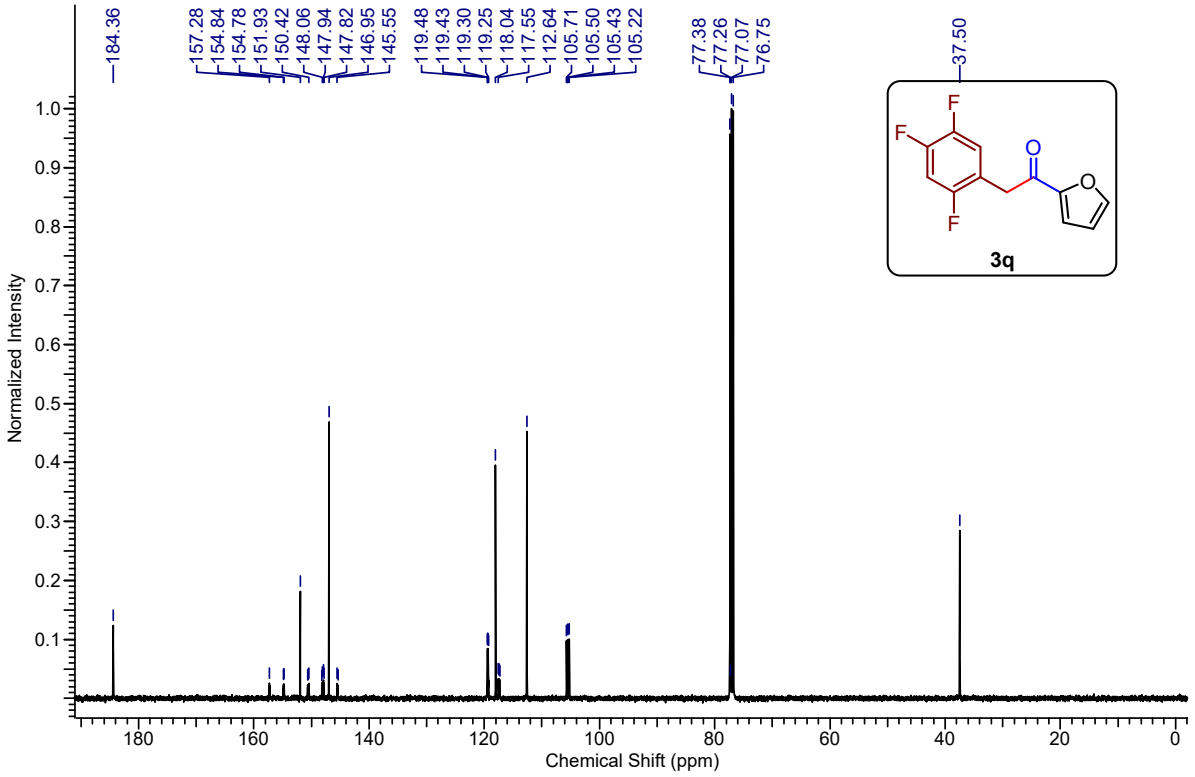
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4p



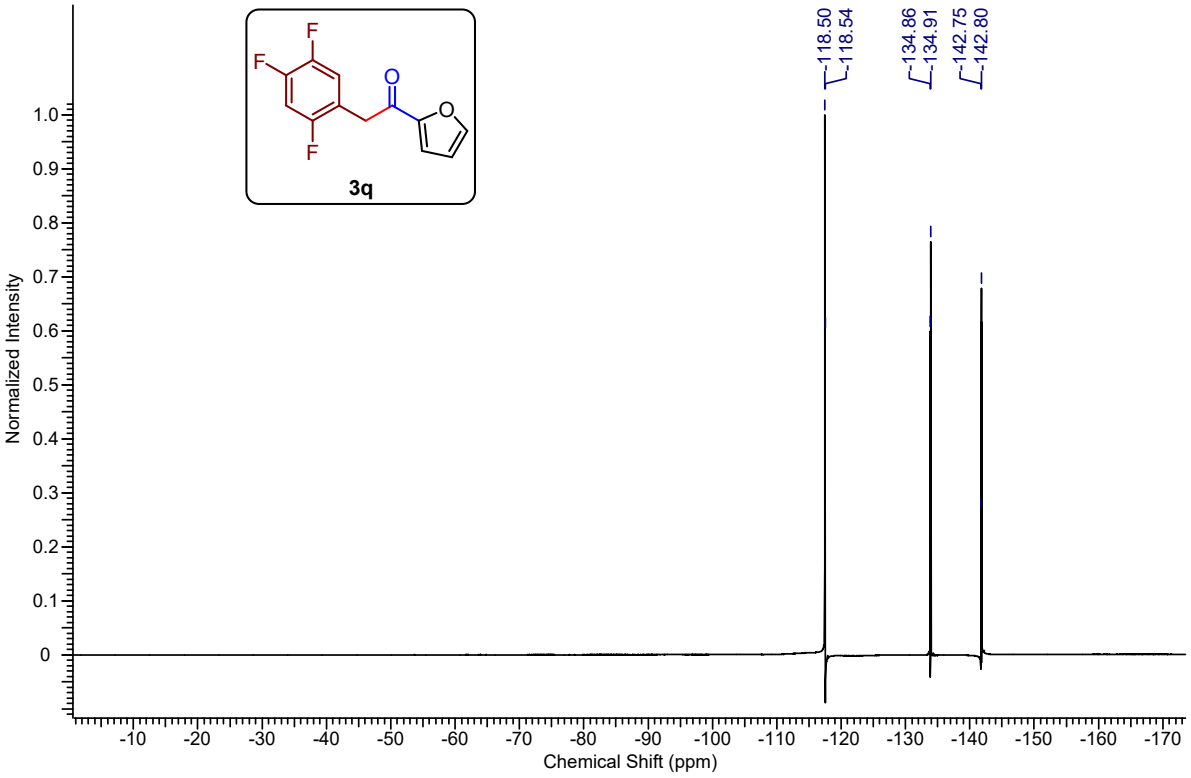
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4p



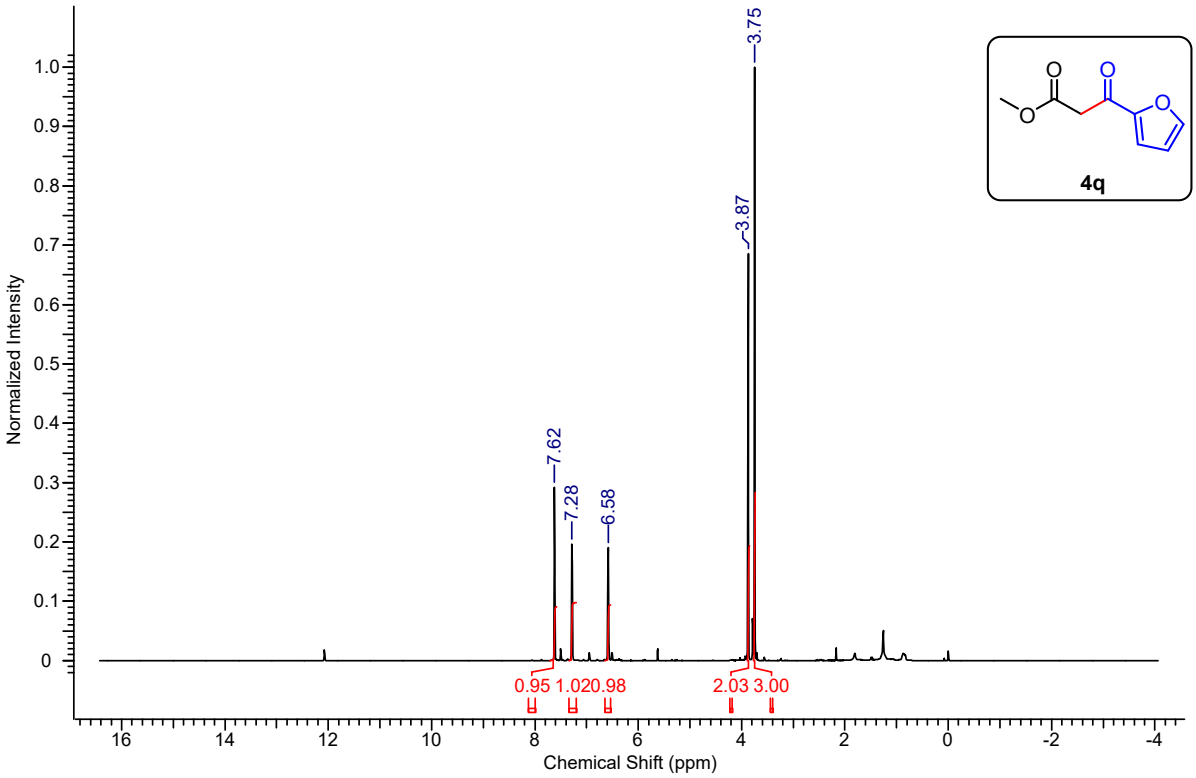
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3q



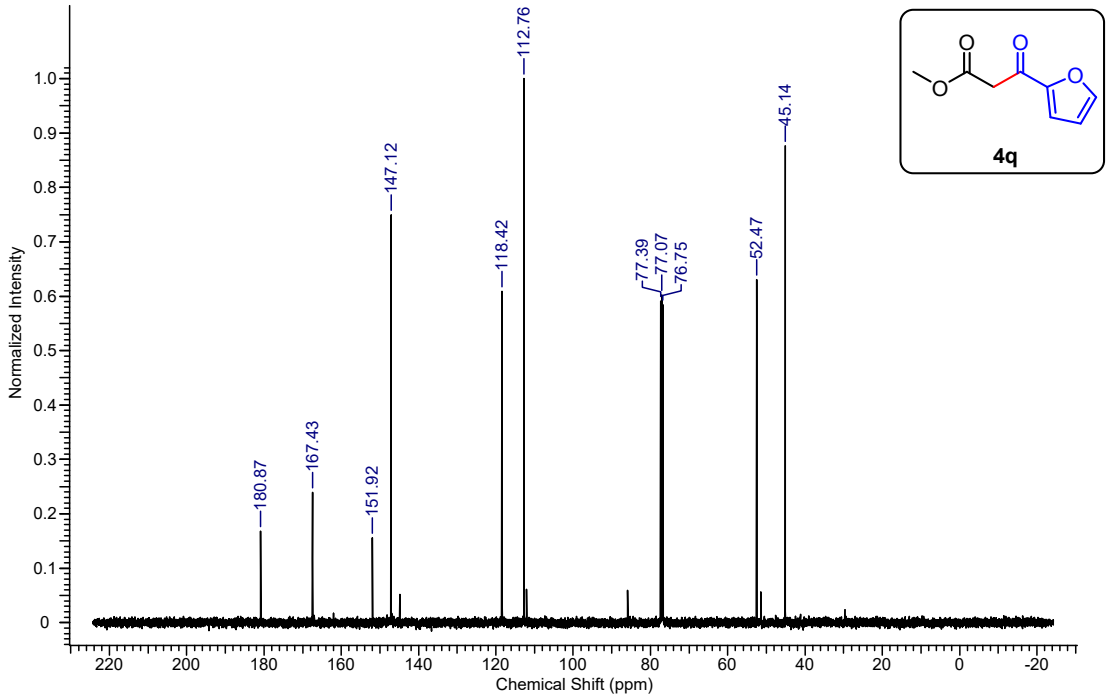
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3q



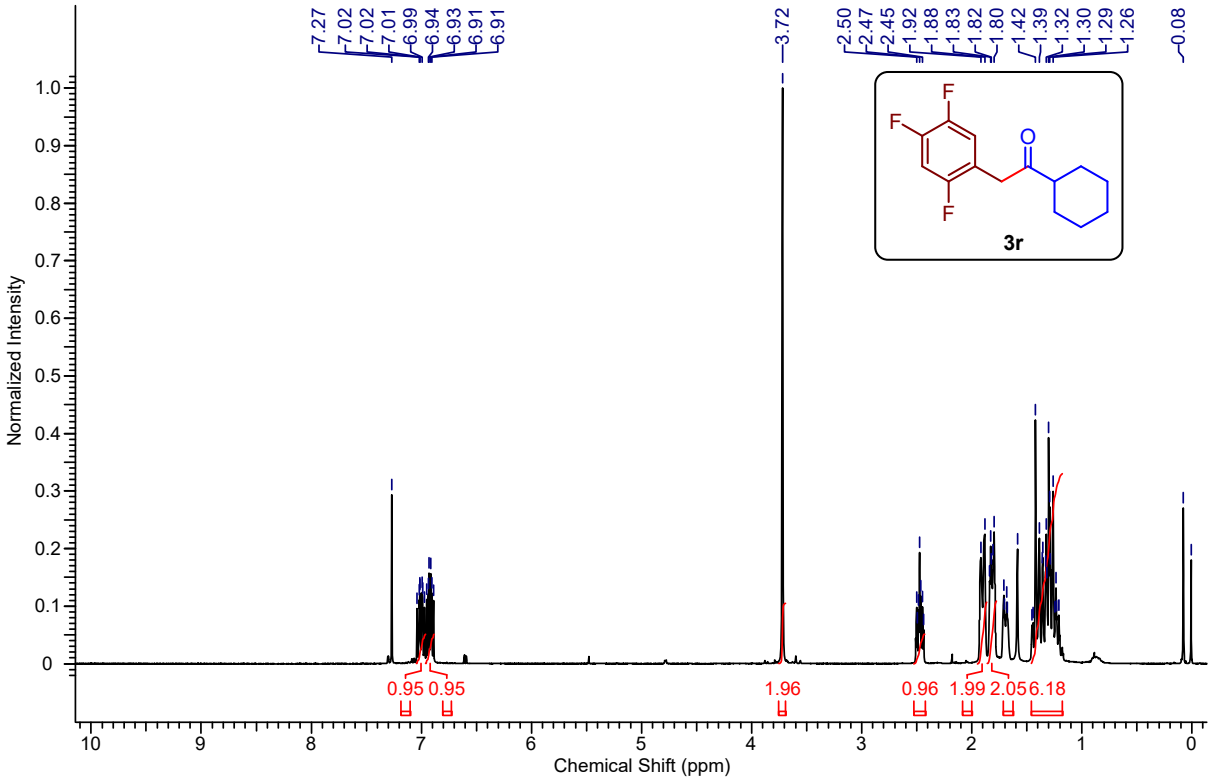
^{19}F NMR (375 MHz, $CDCl_3$) Spectrum of 3q



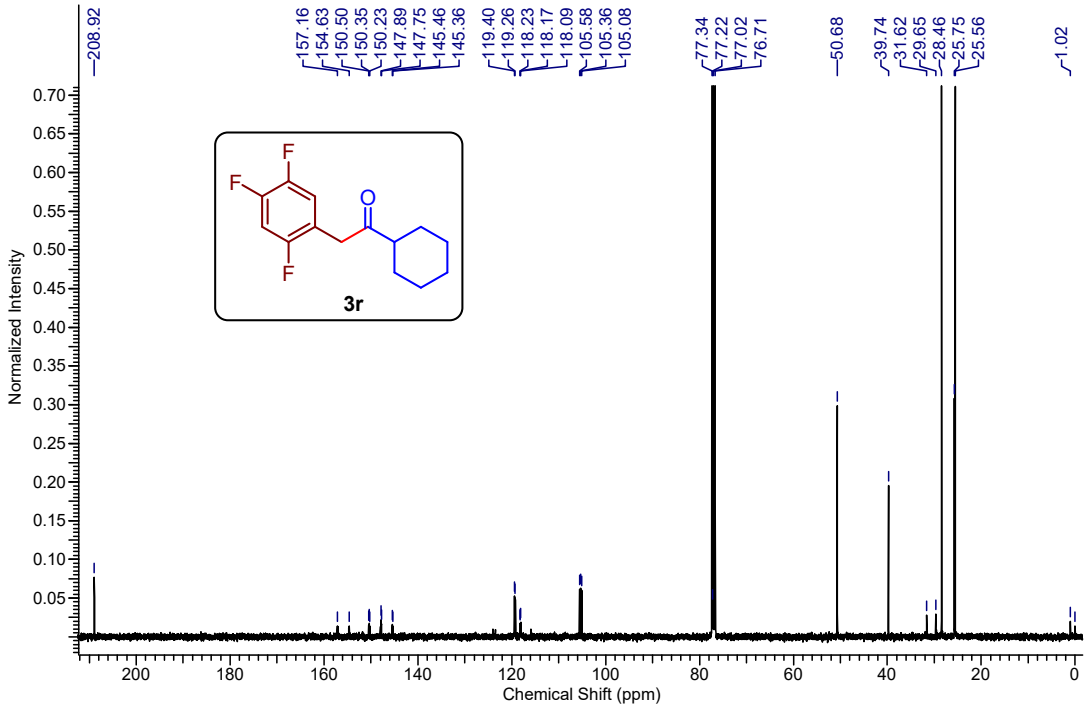
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4q



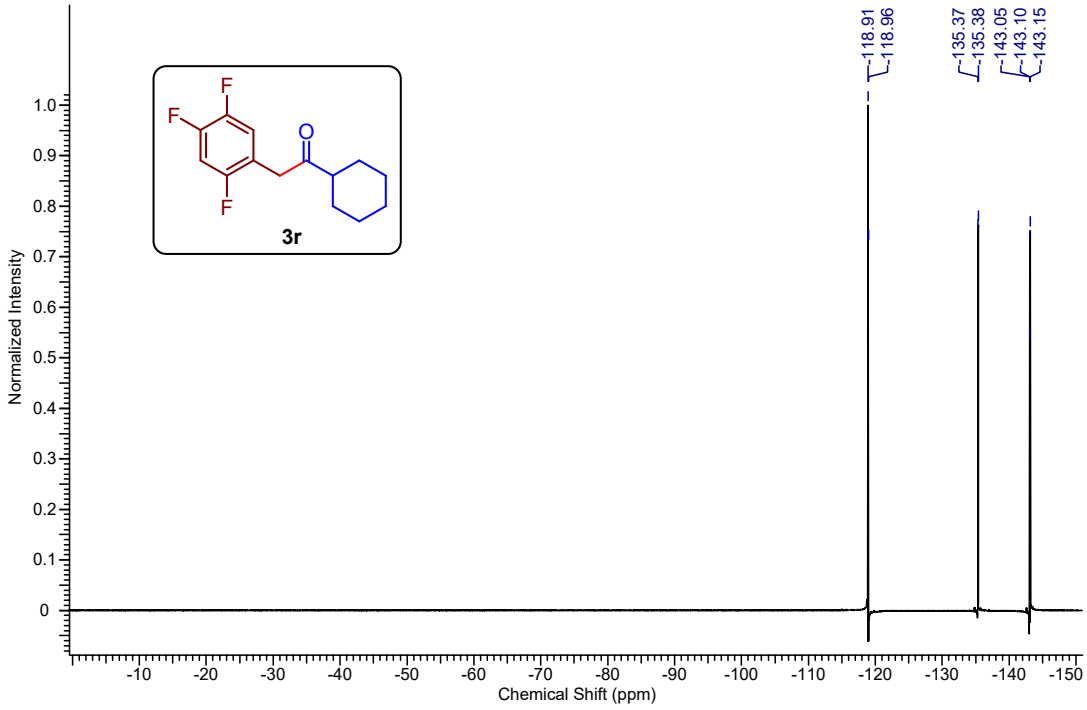
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4q



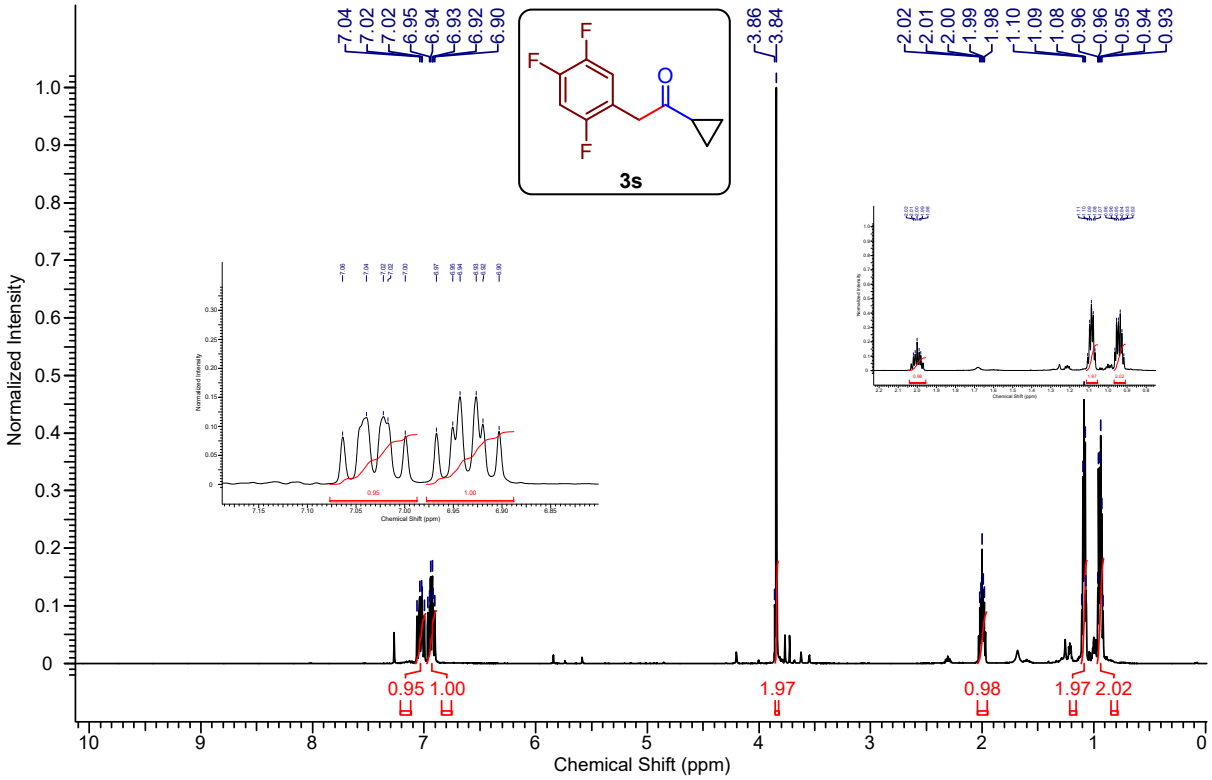
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3r



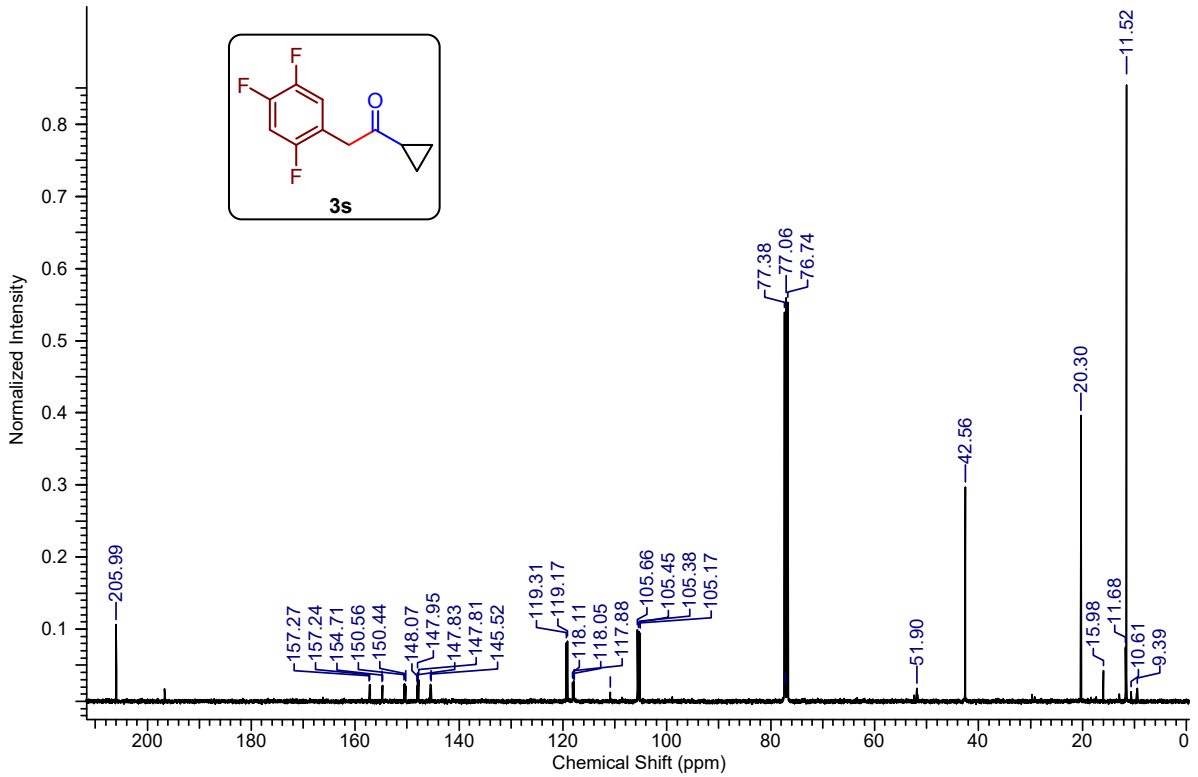
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3r



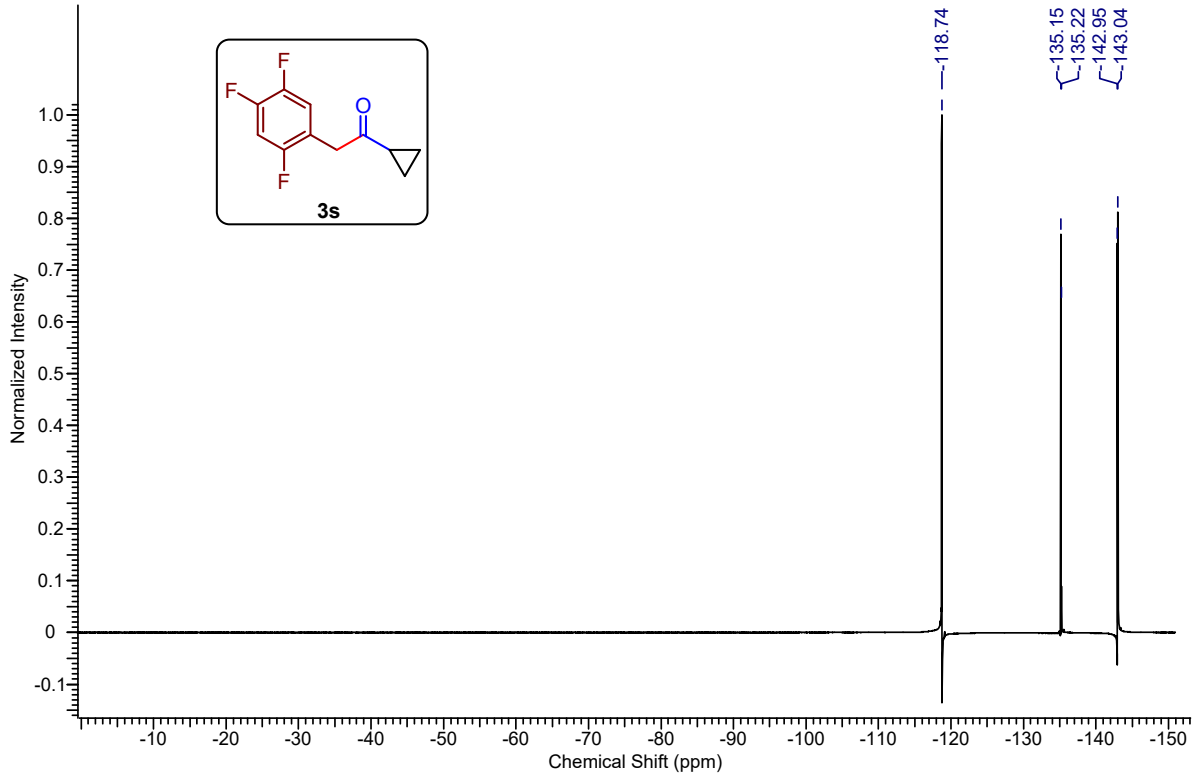
^{19}F NMR (375 MHz, $CDCl_3$) Spectrum of 3r



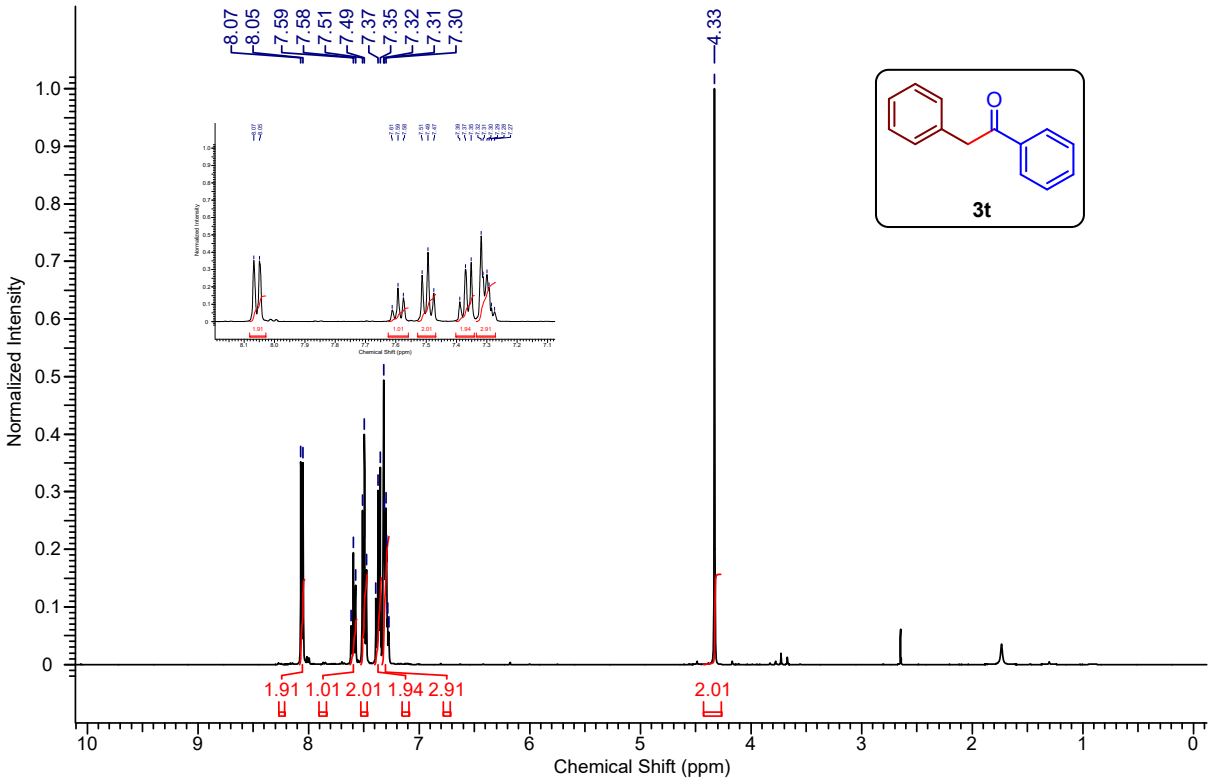
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3s



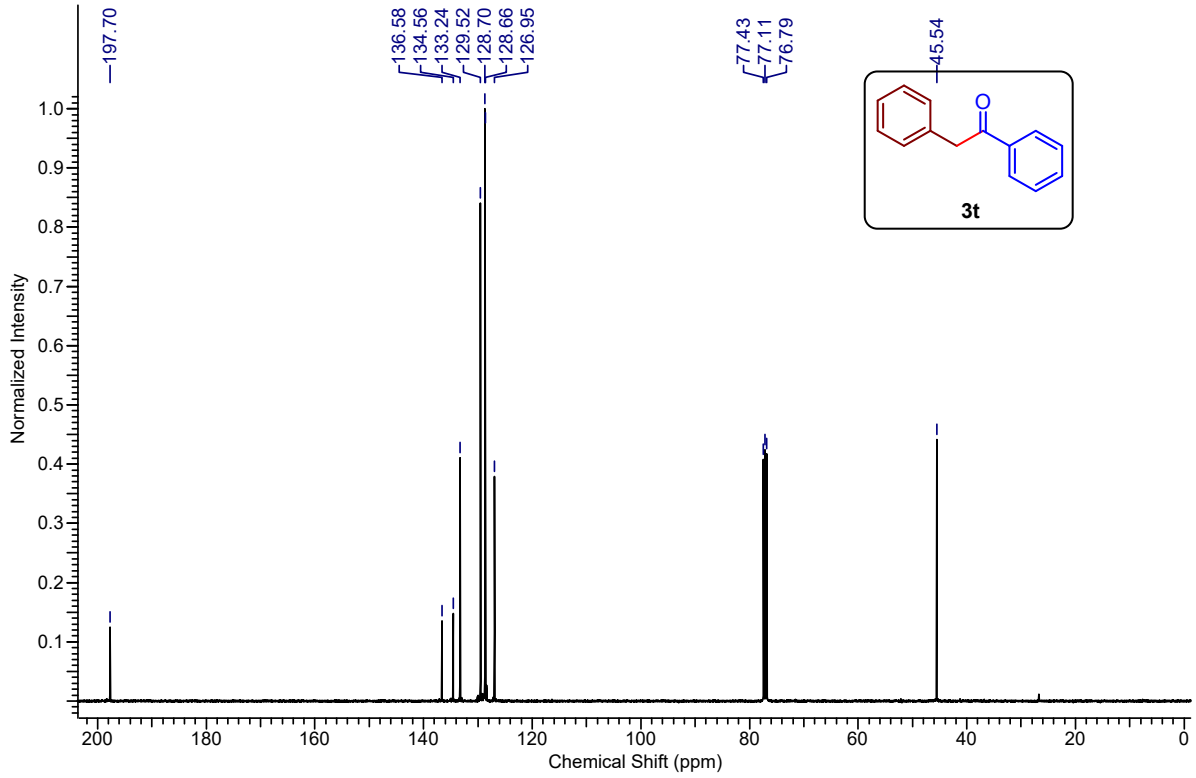
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3s



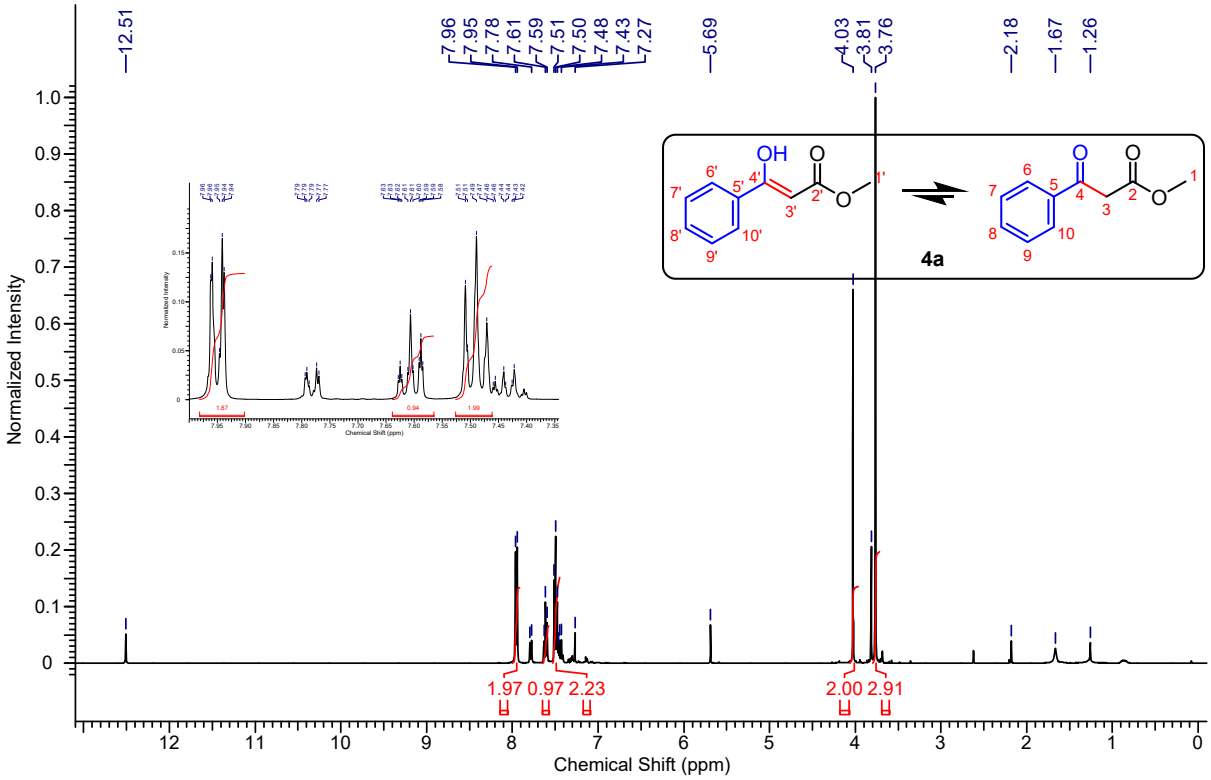
^{19}F NMR (375 MHz, $CDCl_3$) Spectrum of 3s



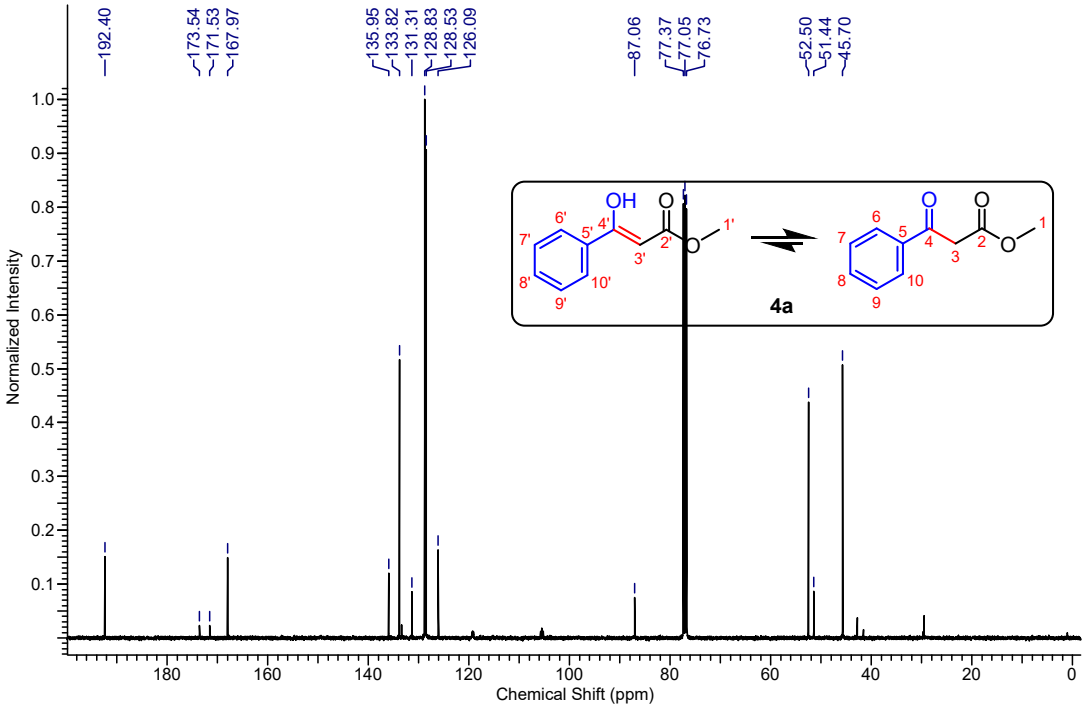
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3t



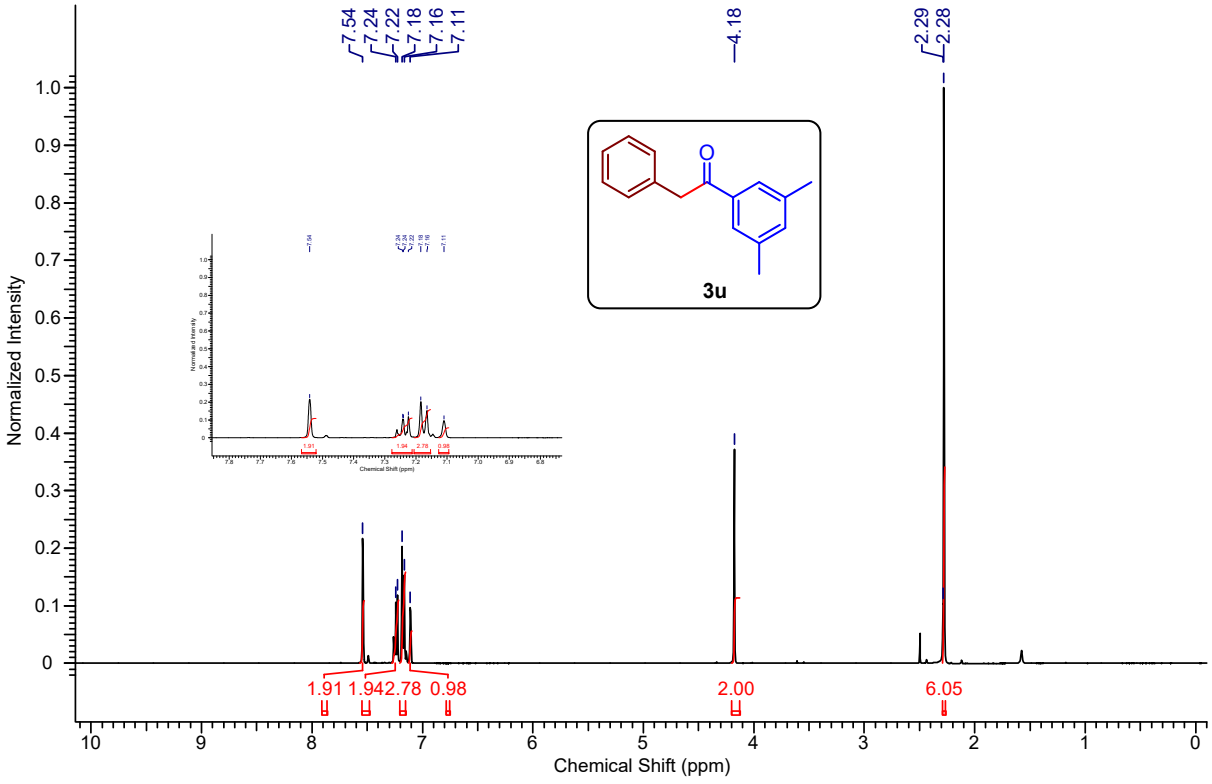
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3t



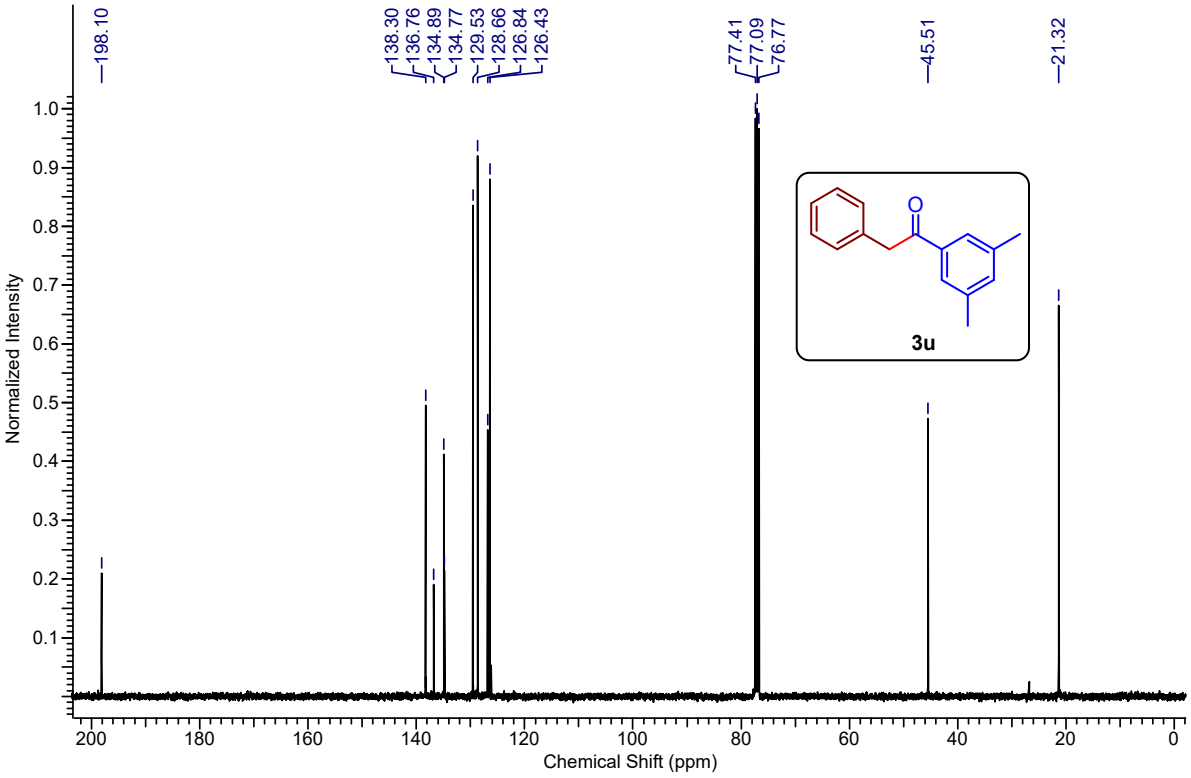
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4a



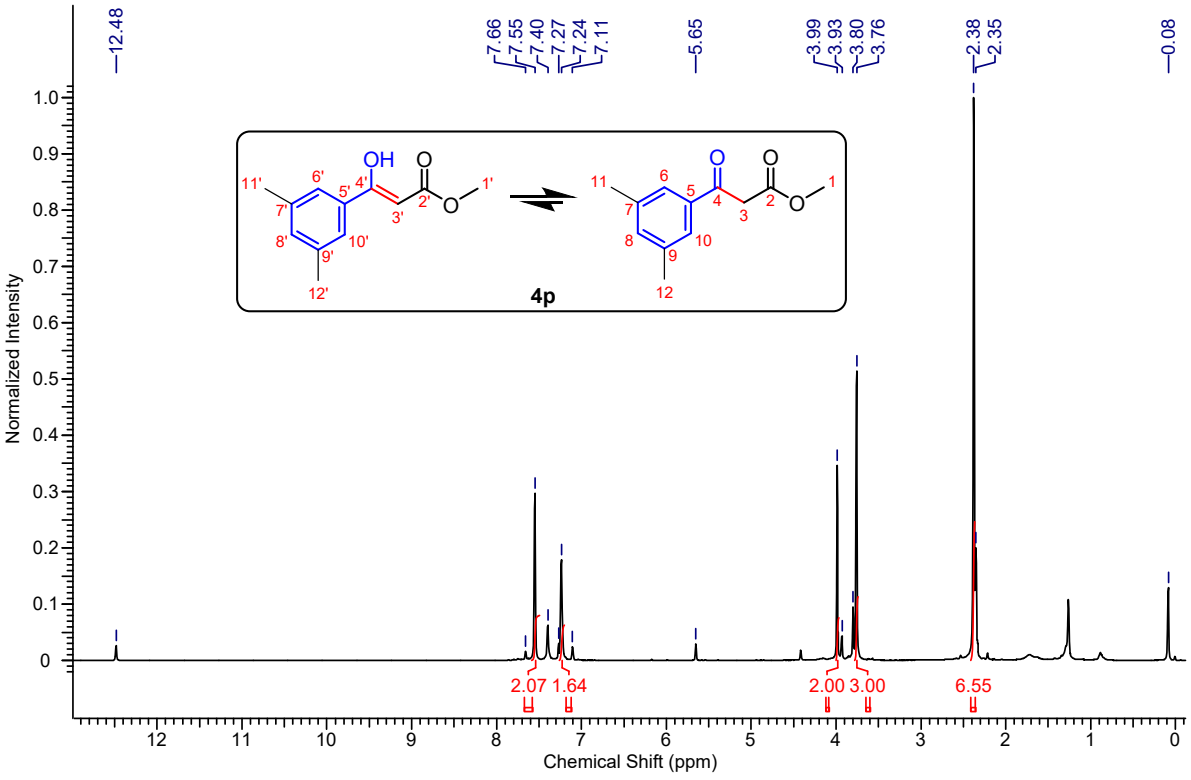
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4a



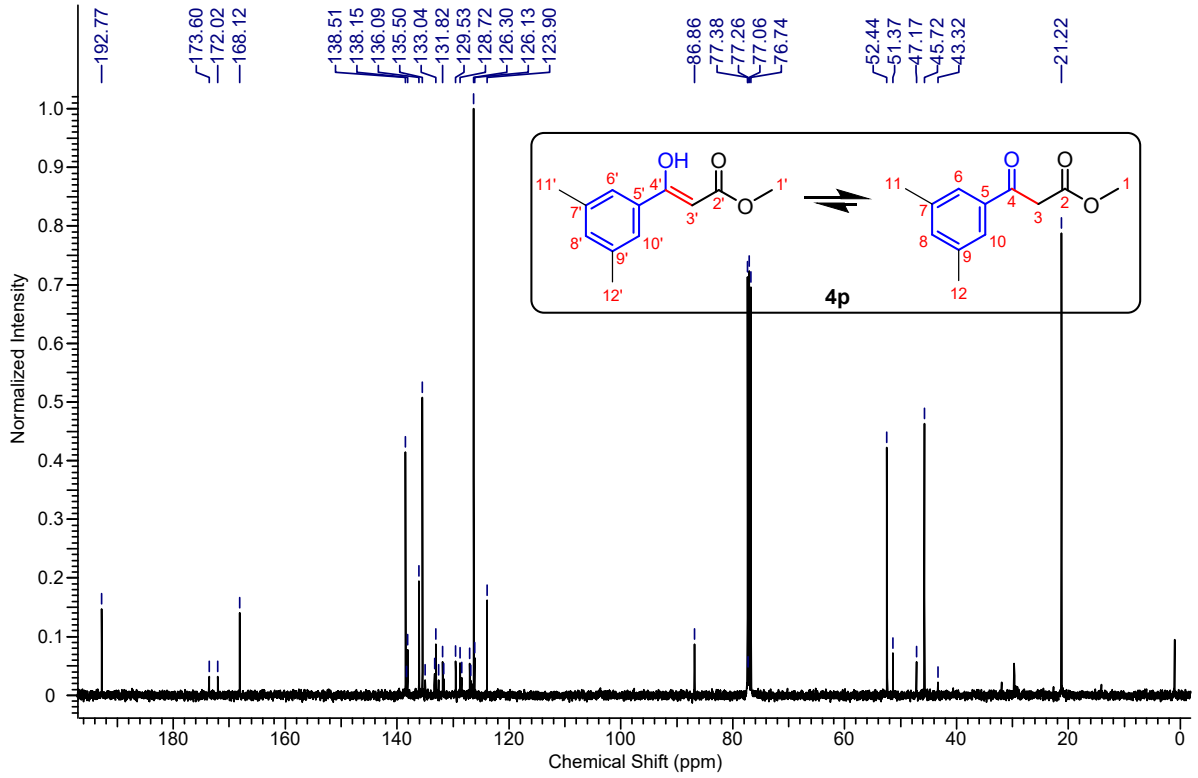
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3u



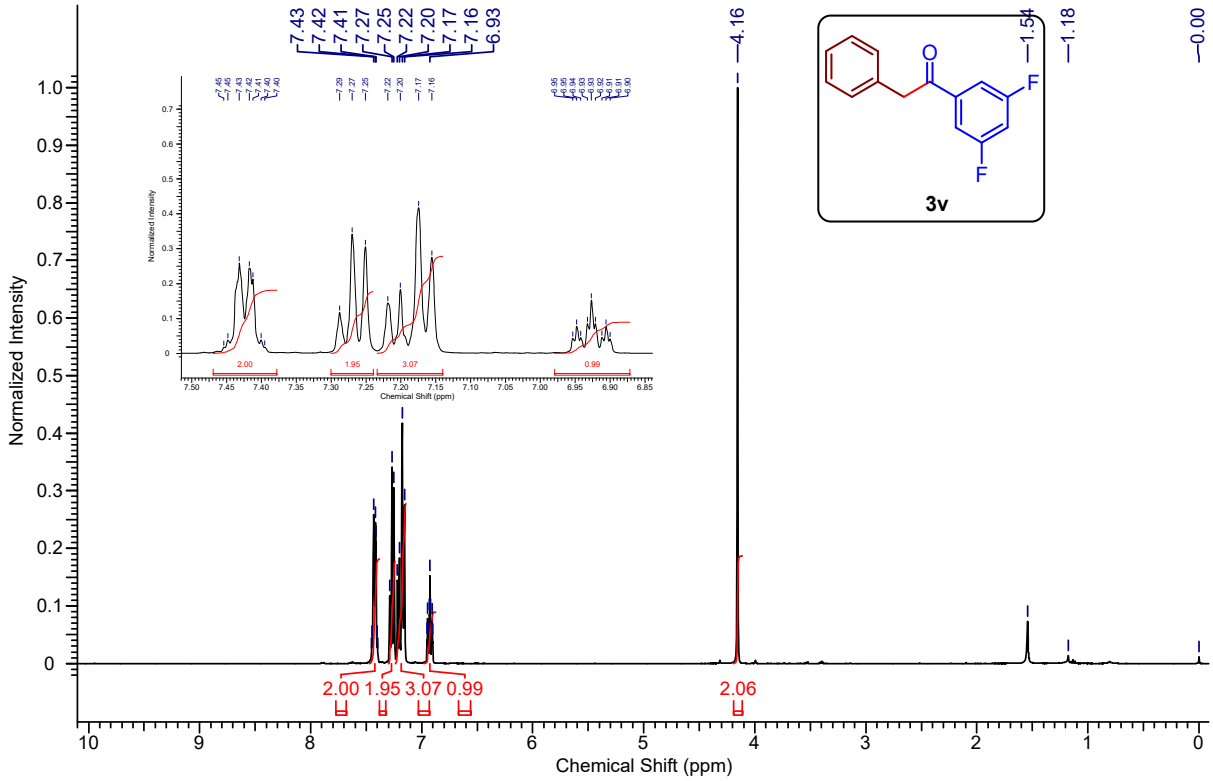
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3u



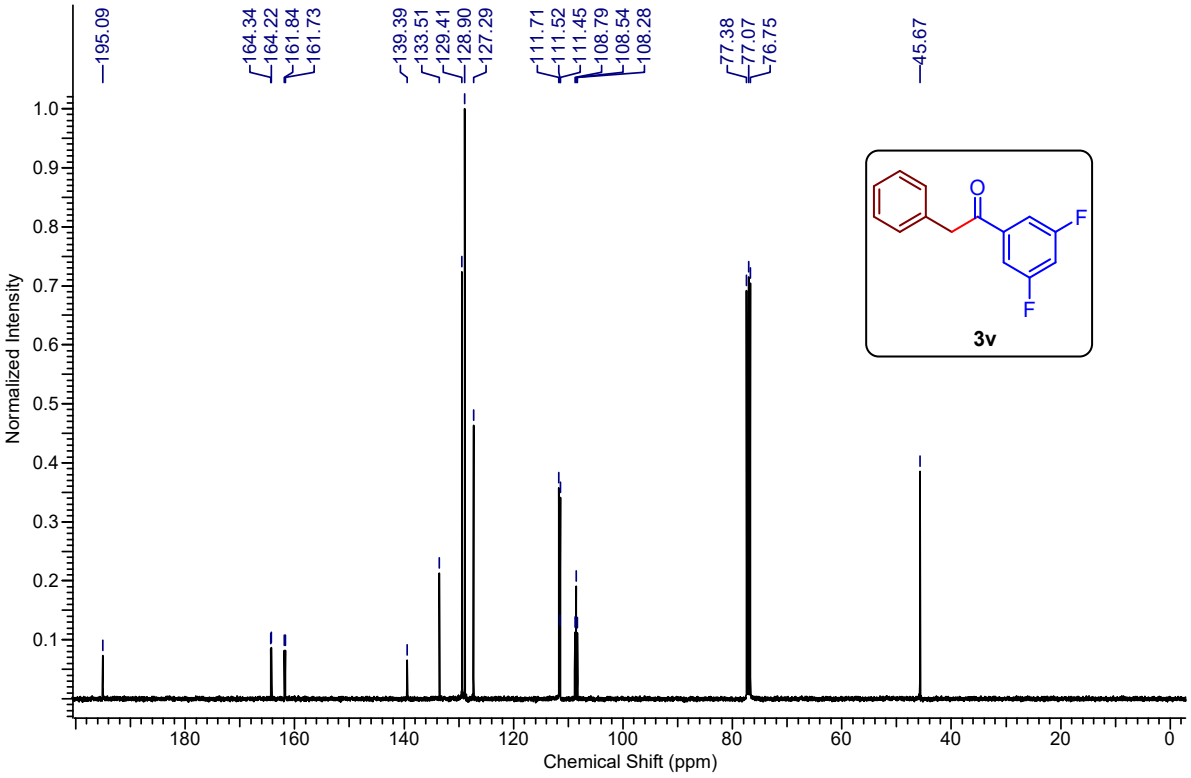
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4p



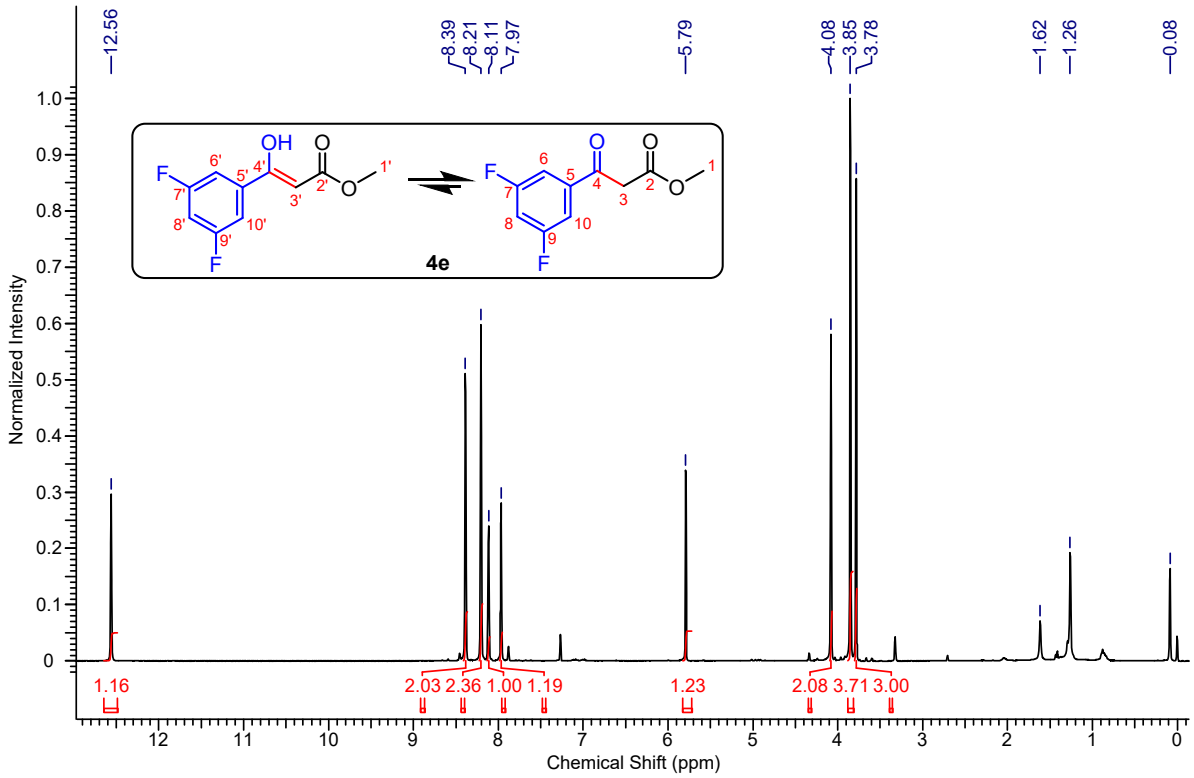
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4p



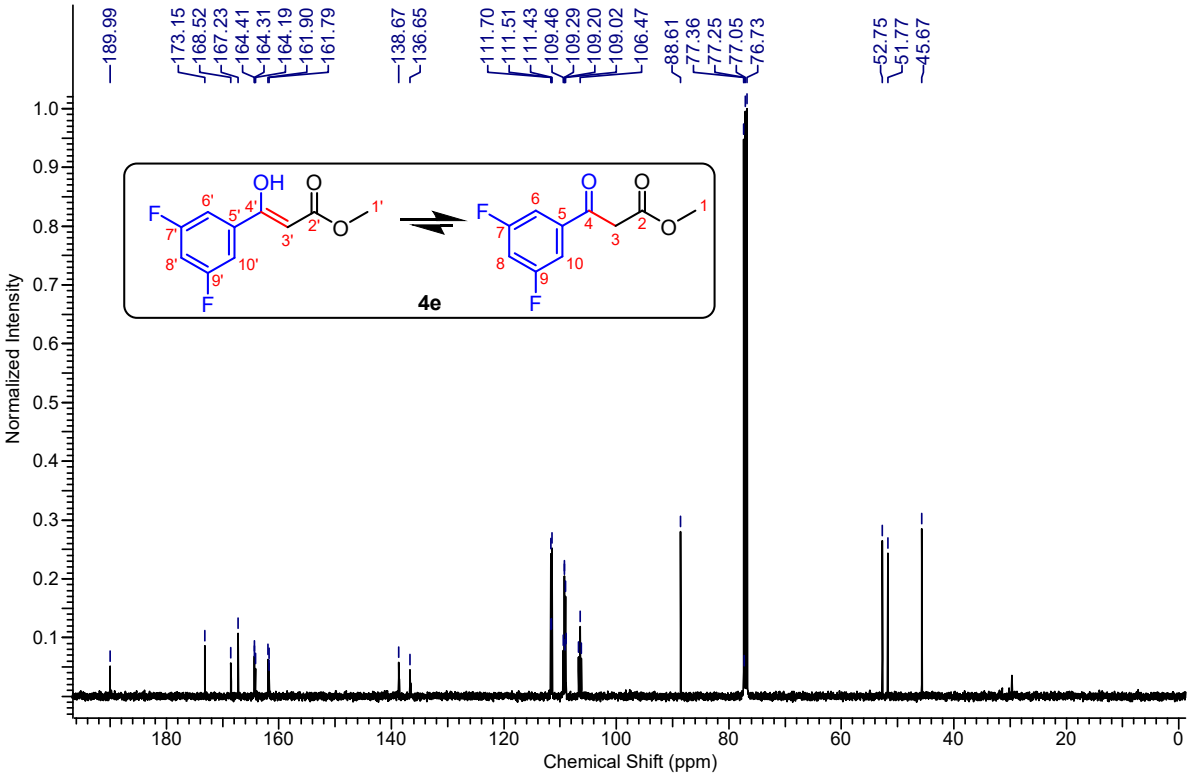
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3v



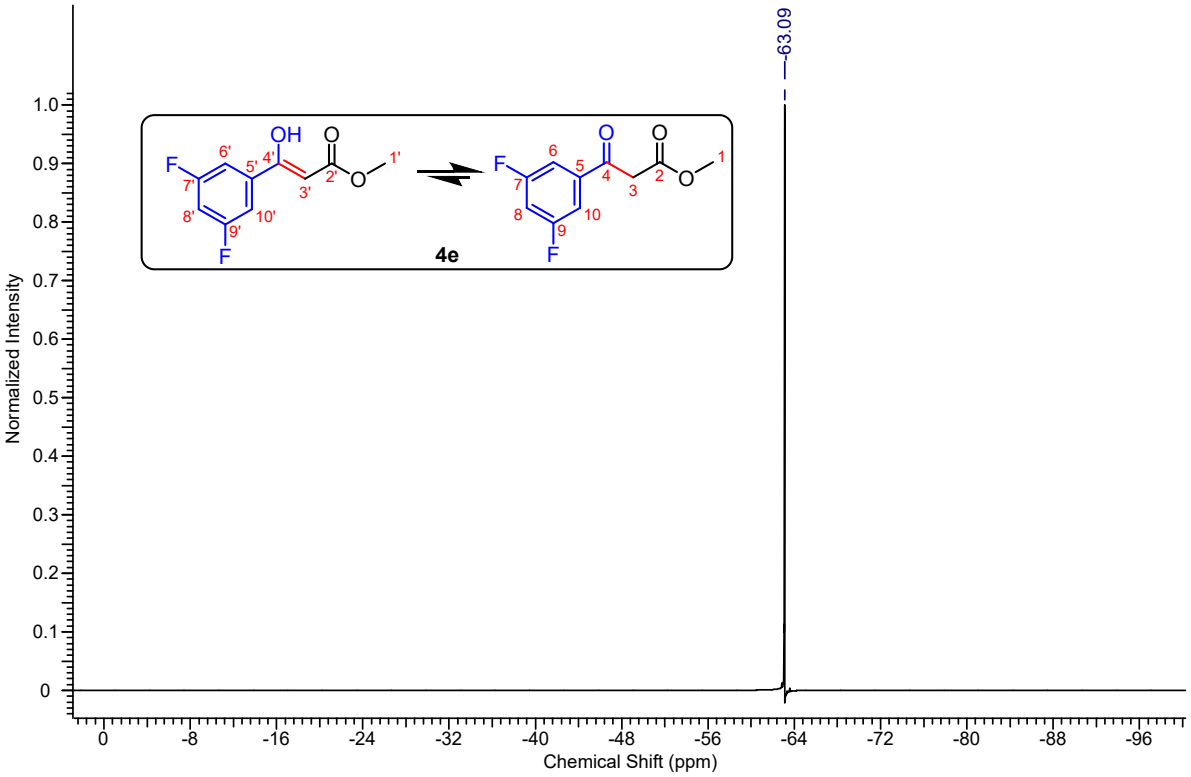
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3v



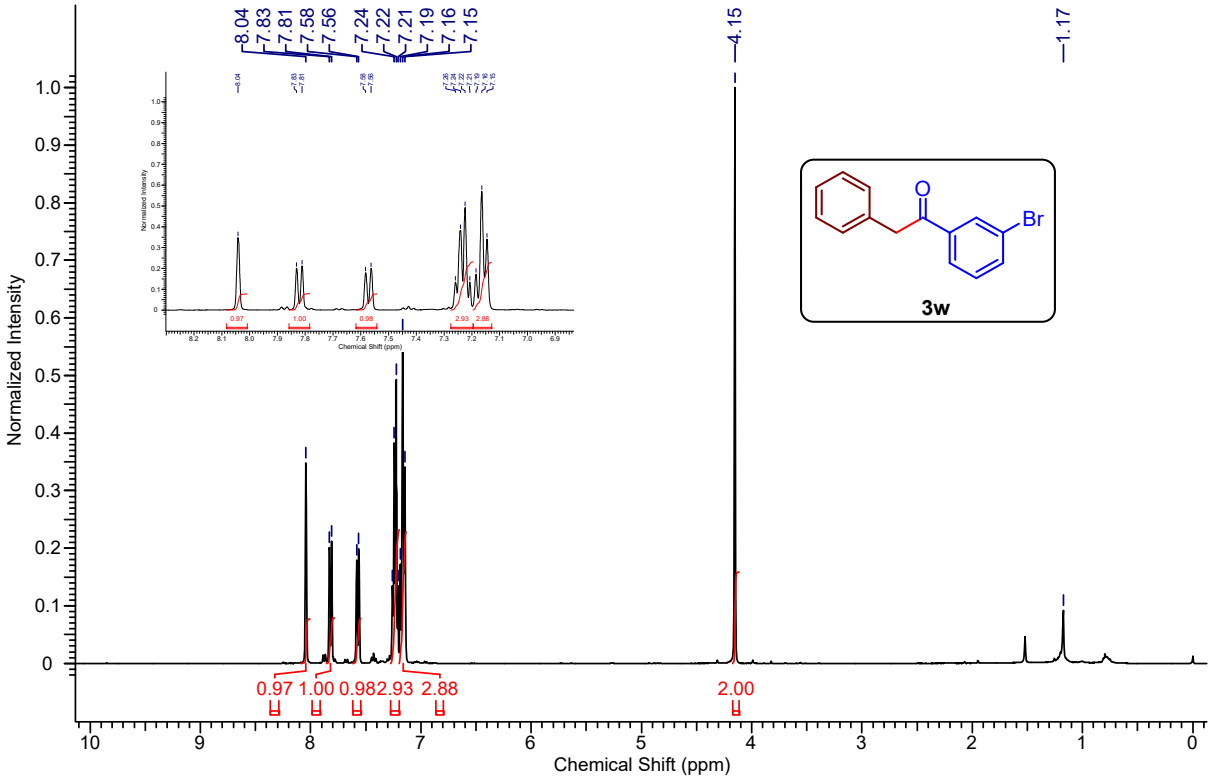
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4e



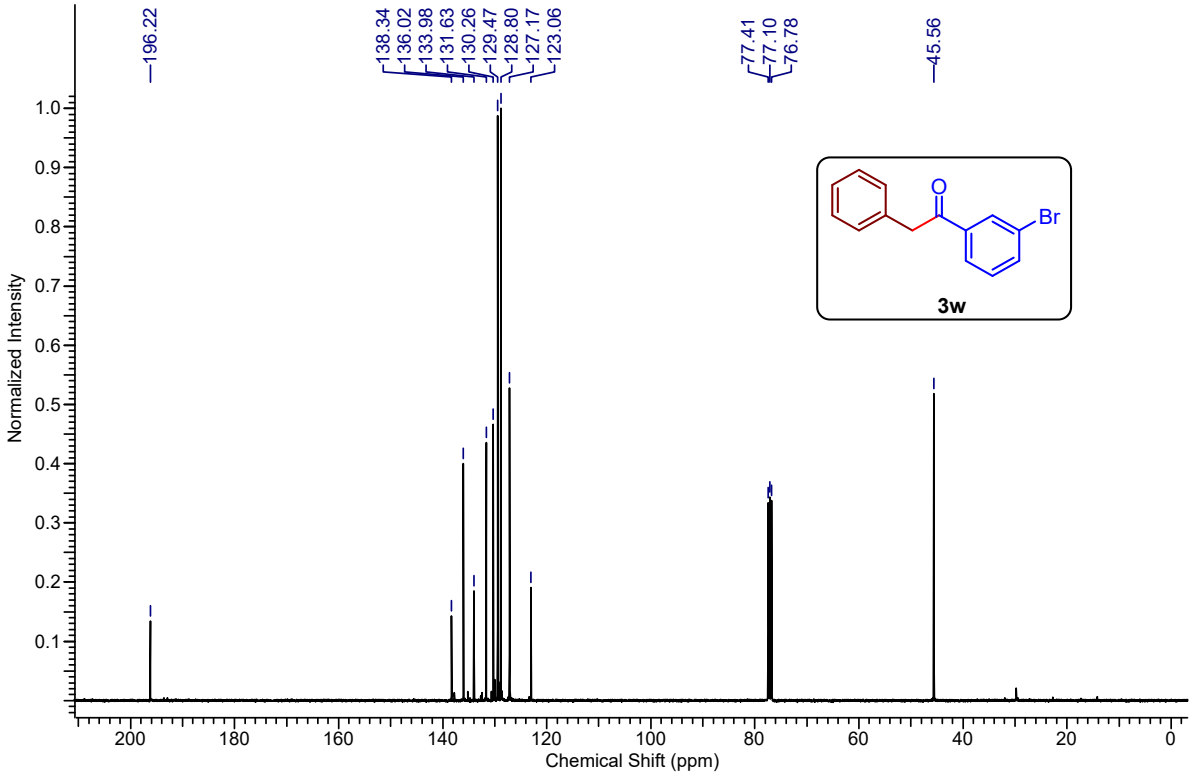
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4e



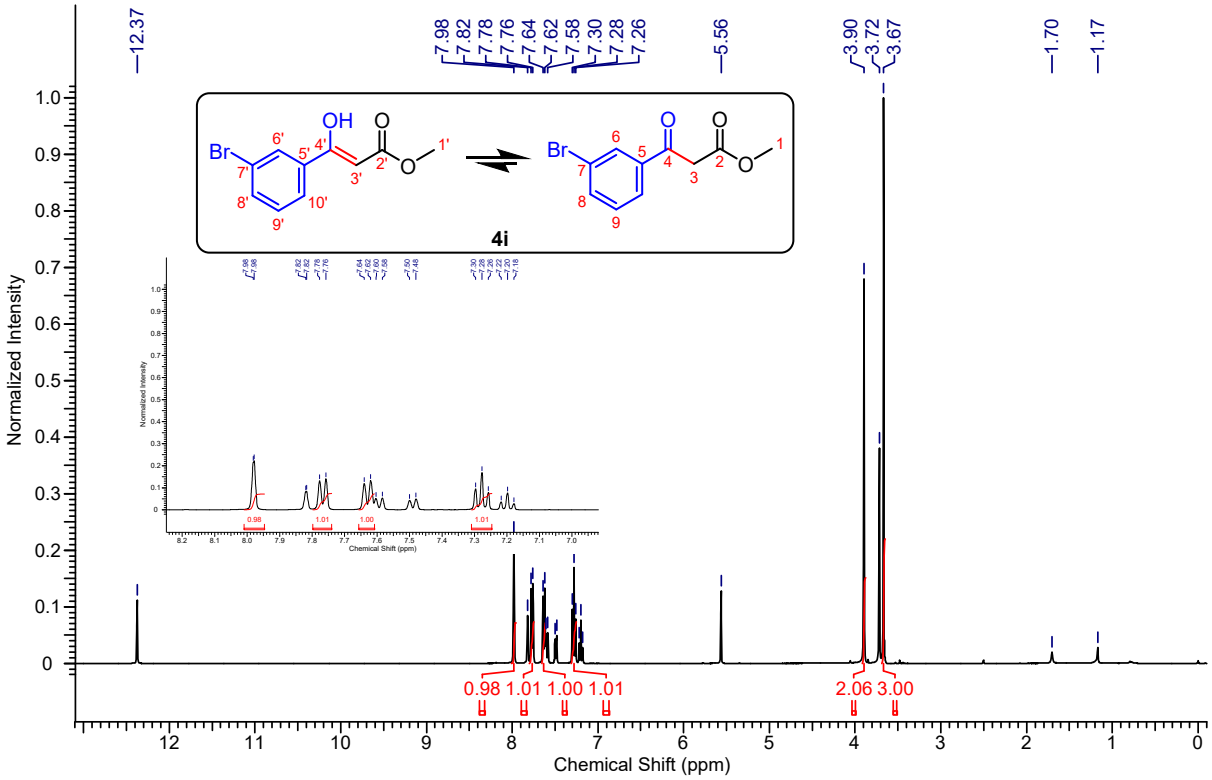
^{19}F NMR (375 MHz, $CDCl_3$) Spectrum of 4e



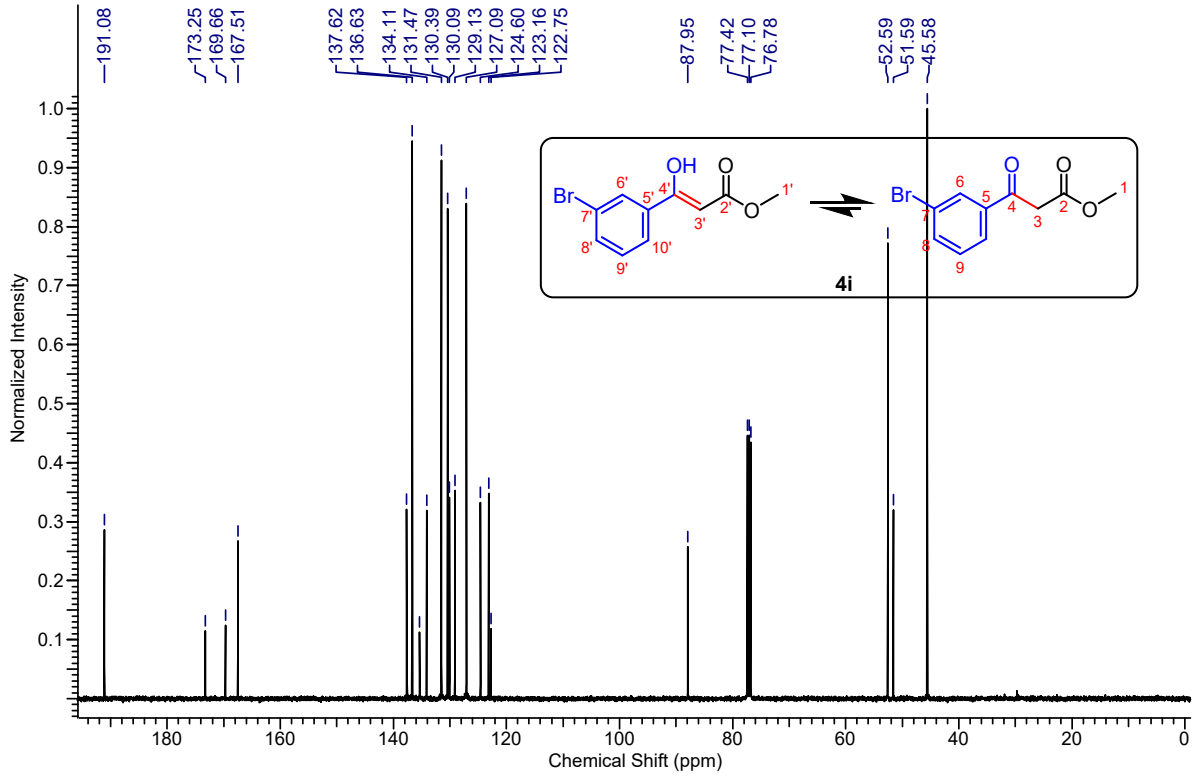
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3w



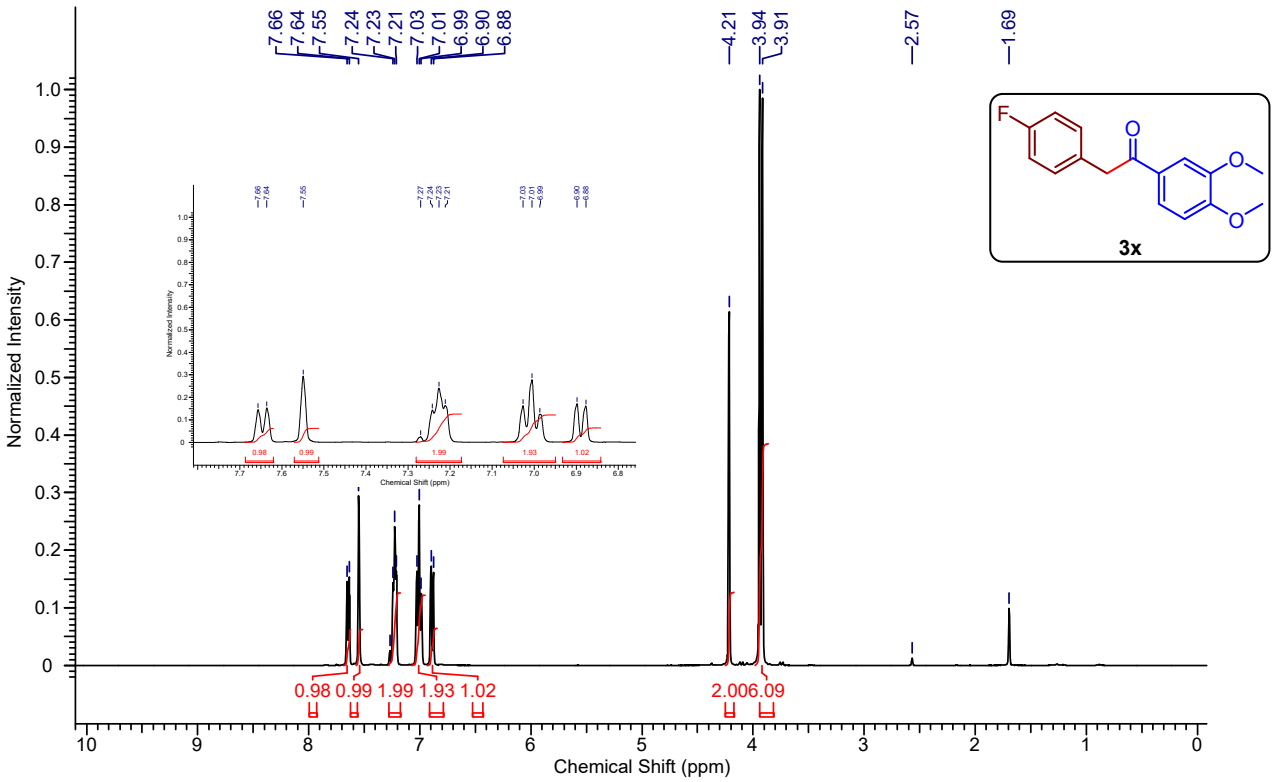
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3w



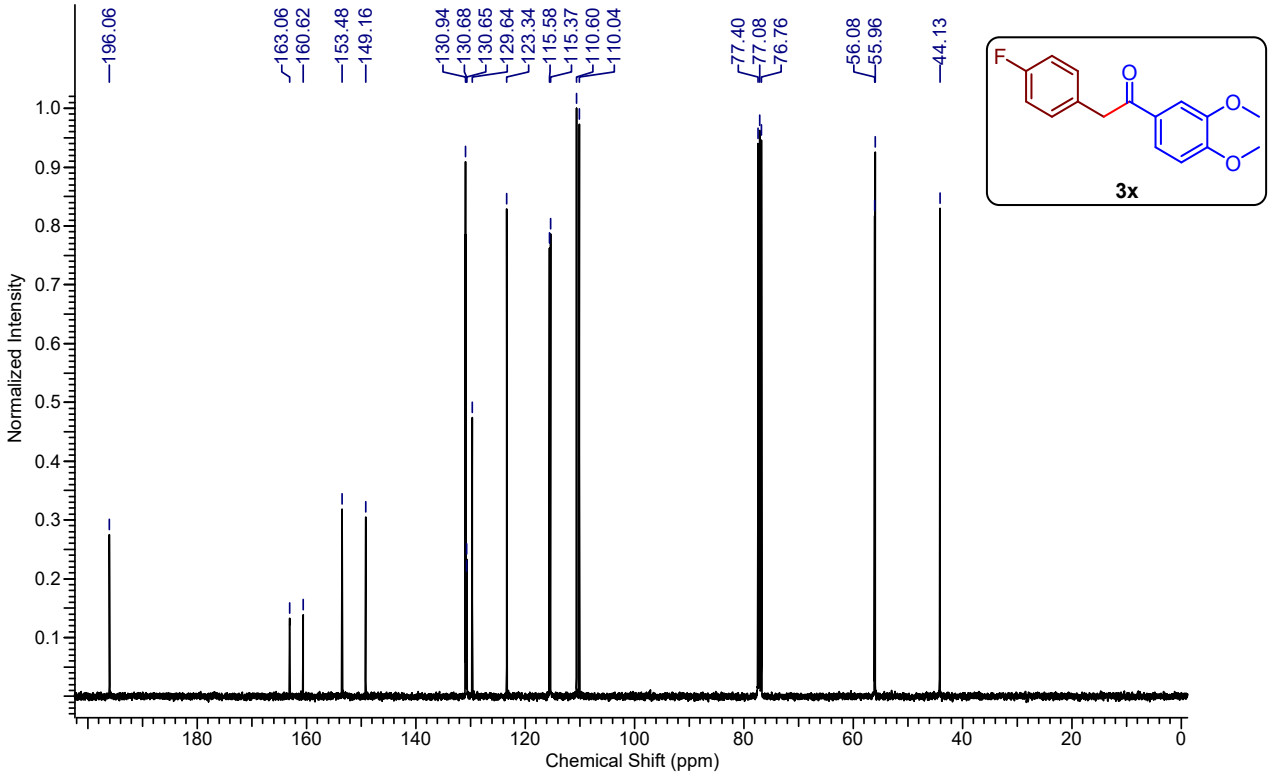
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4i



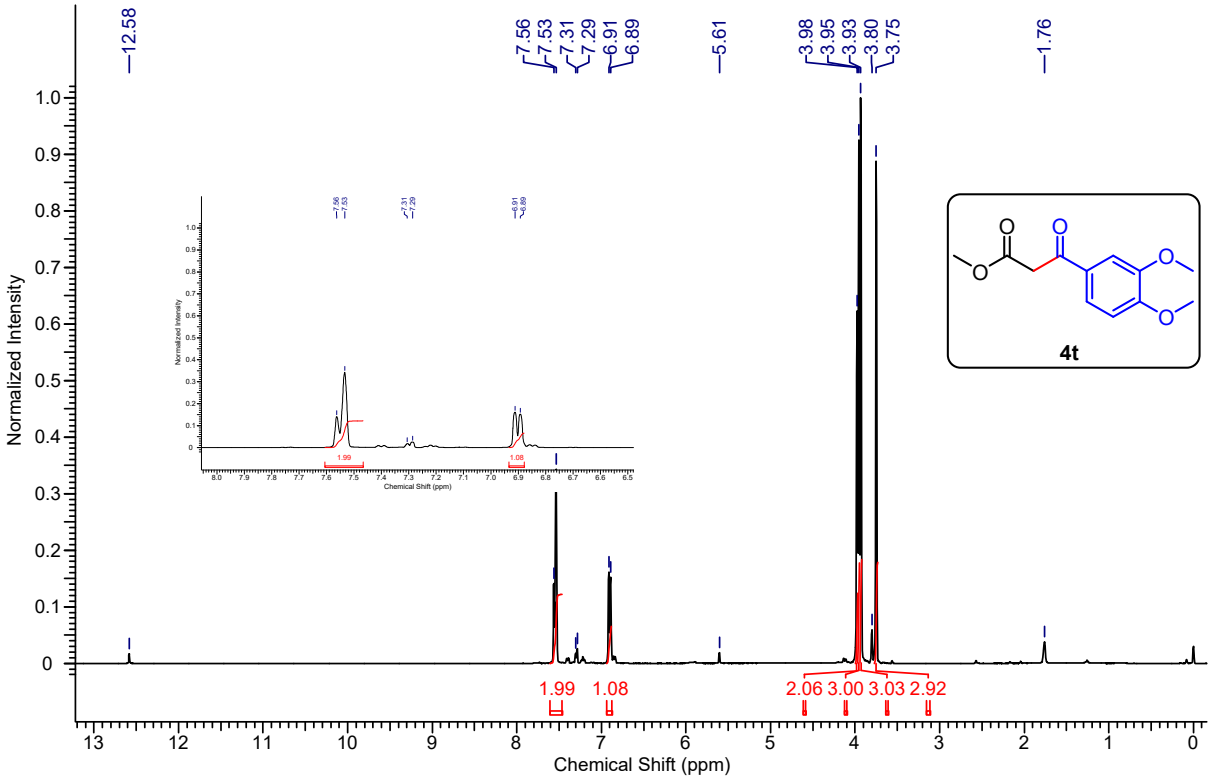
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4i



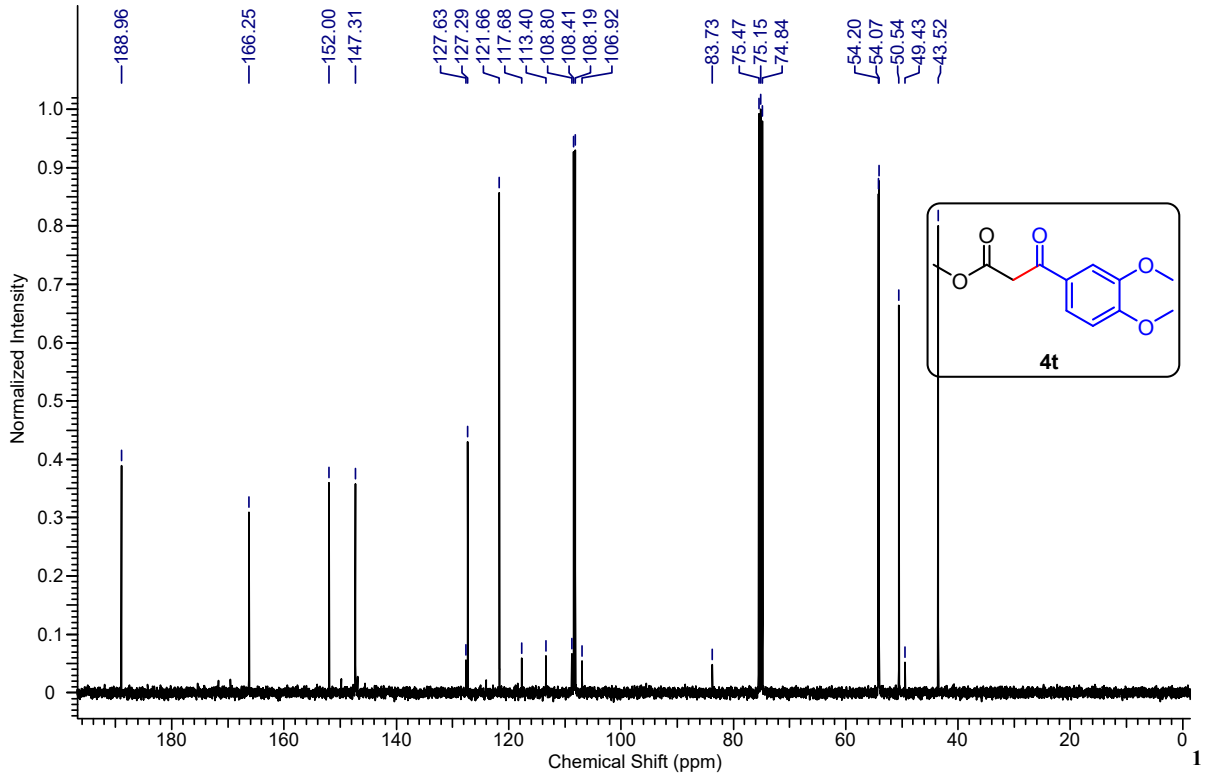
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3x



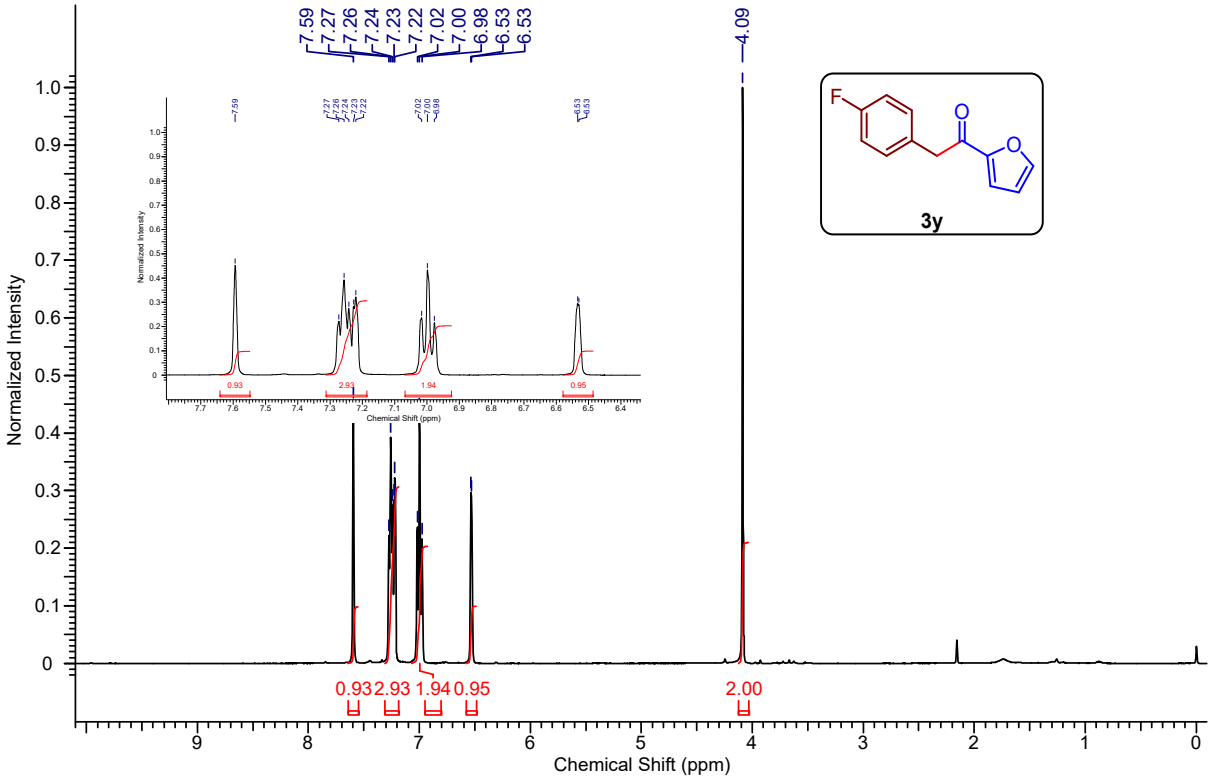
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3x



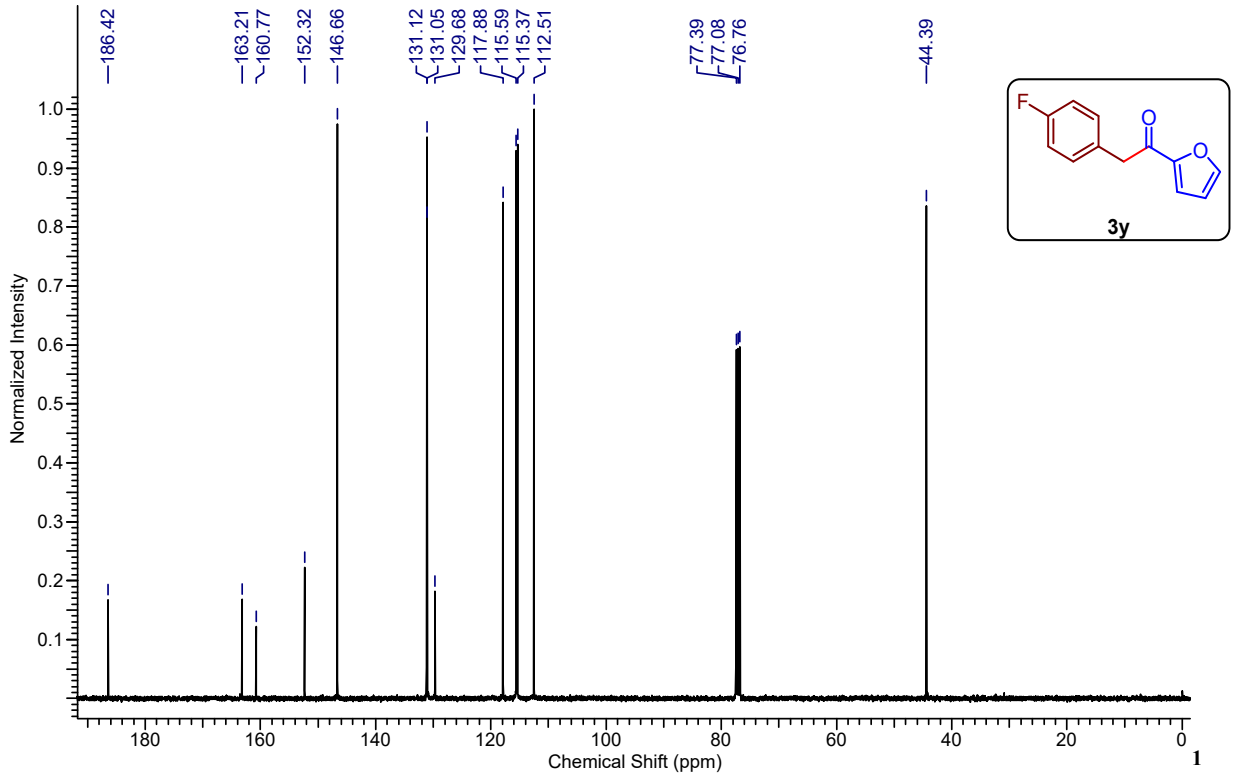
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4x



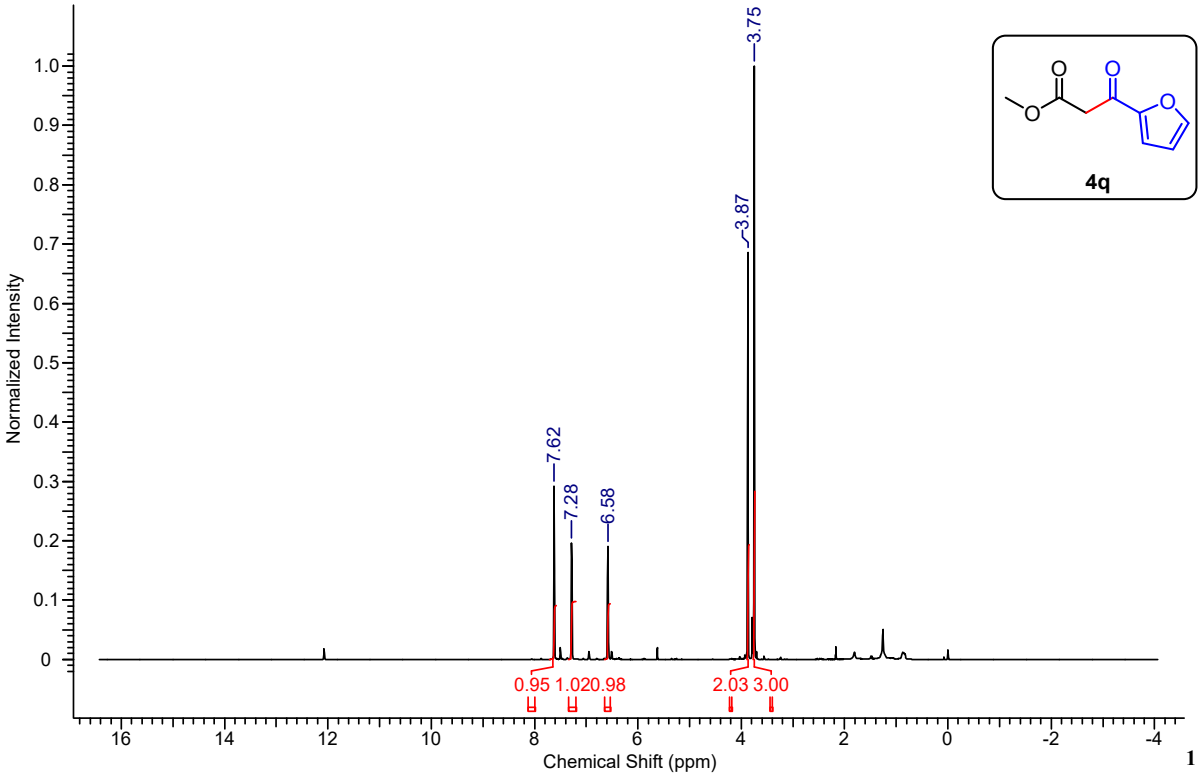
^{3}C NMR (100 MHz, $CDCl_3$) Spectrum of 4t



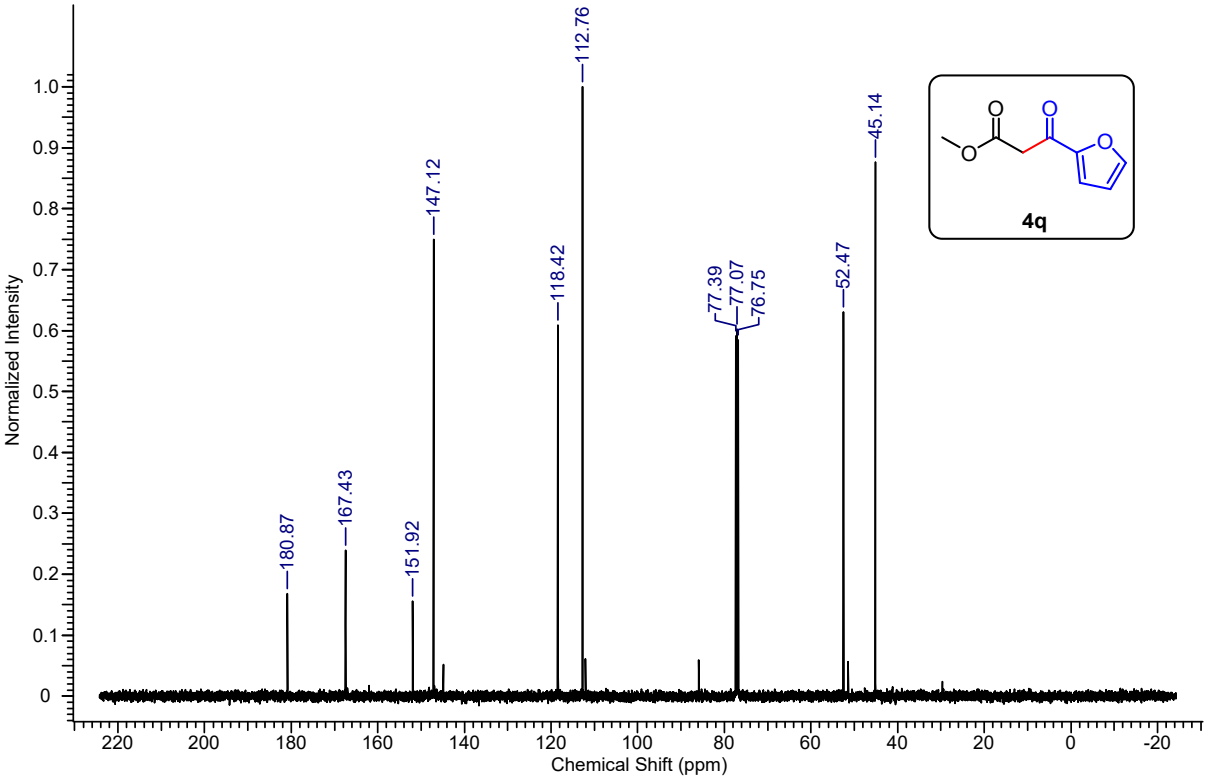
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3y



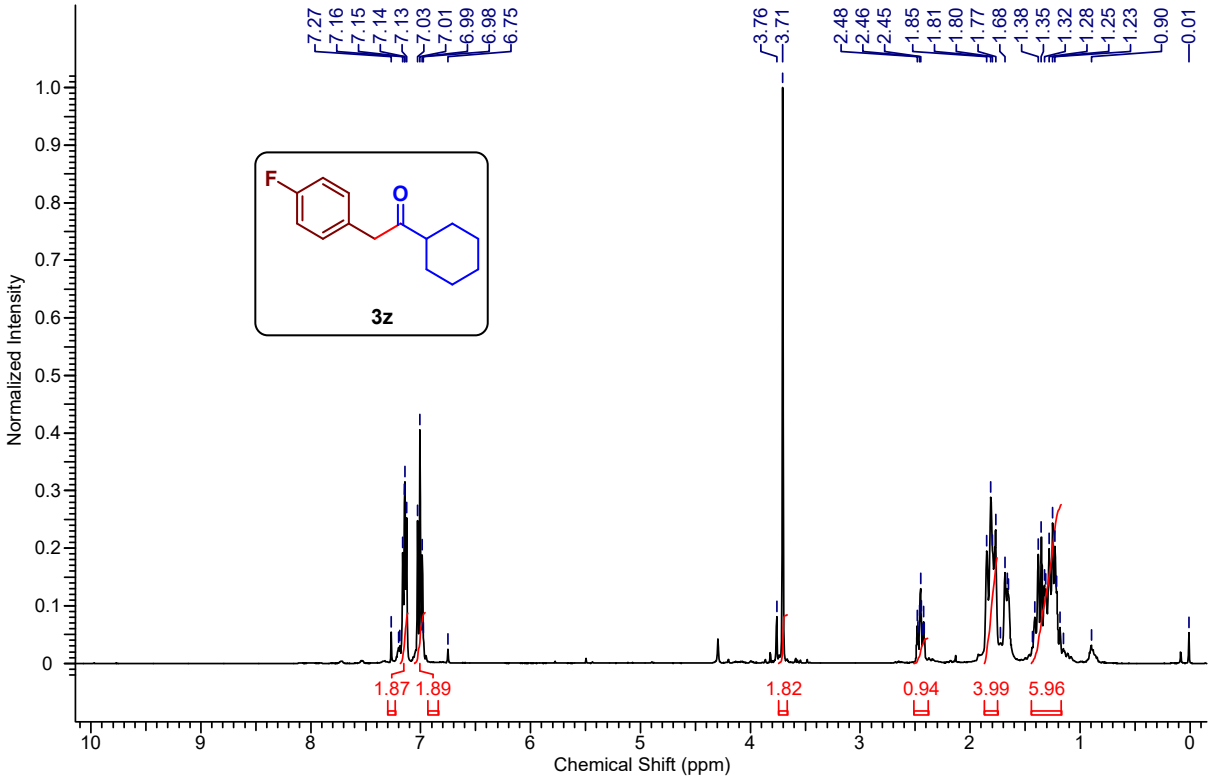
^{3}C NMR (100 MHz, $CDCl_3$) Spectrum of 3y



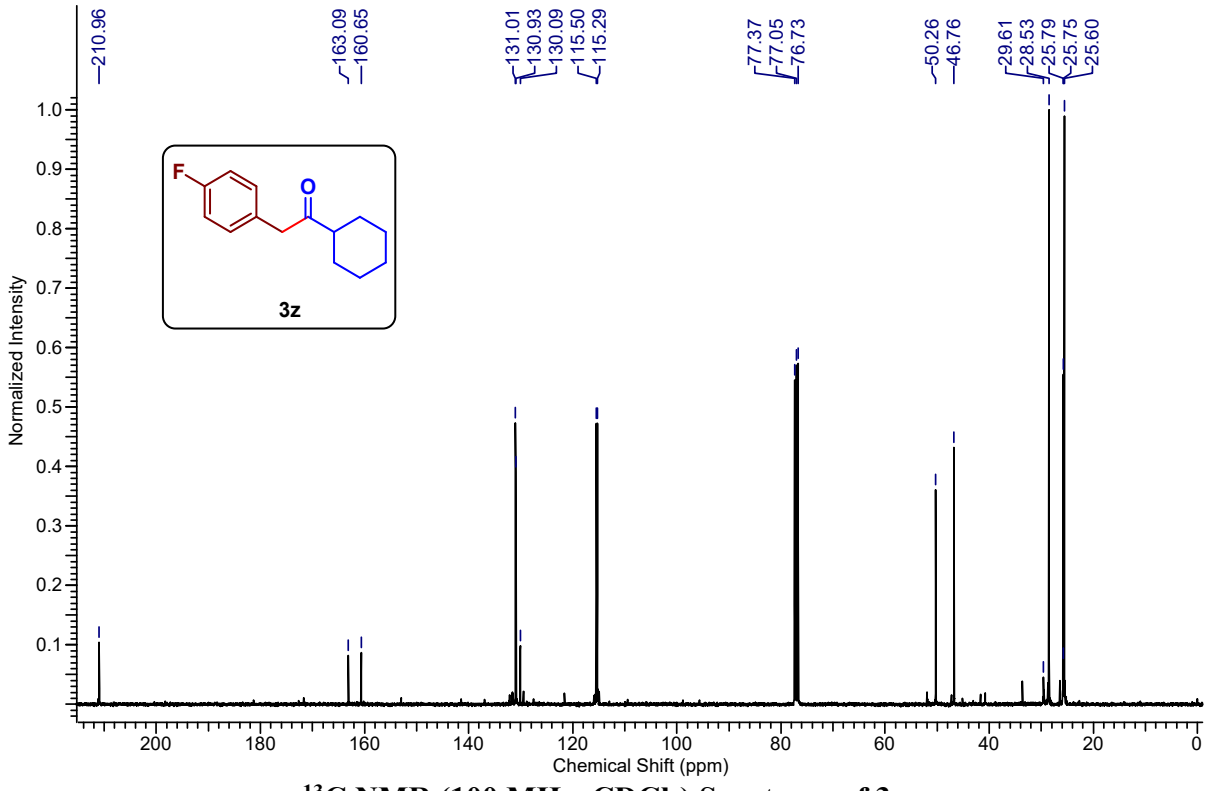
H NMR (400 MHz, $CDCl_3$) Spectrum of 4q



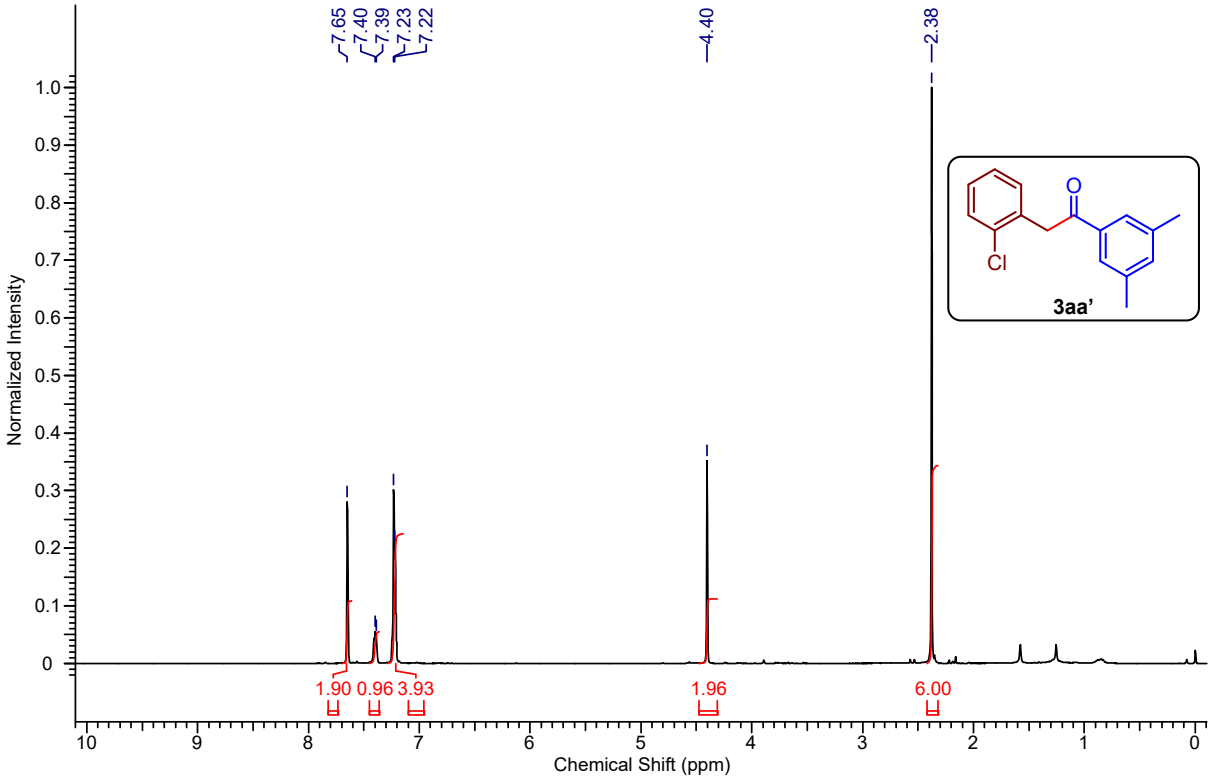
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4q



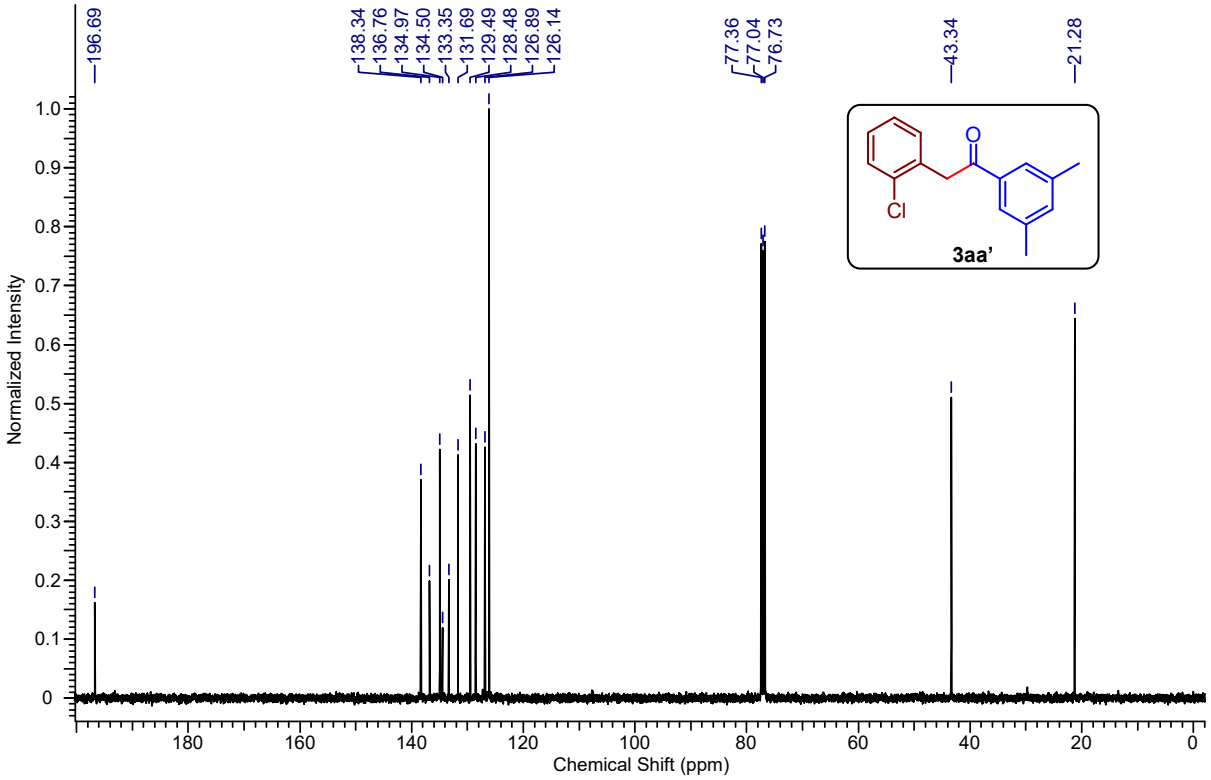
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3z



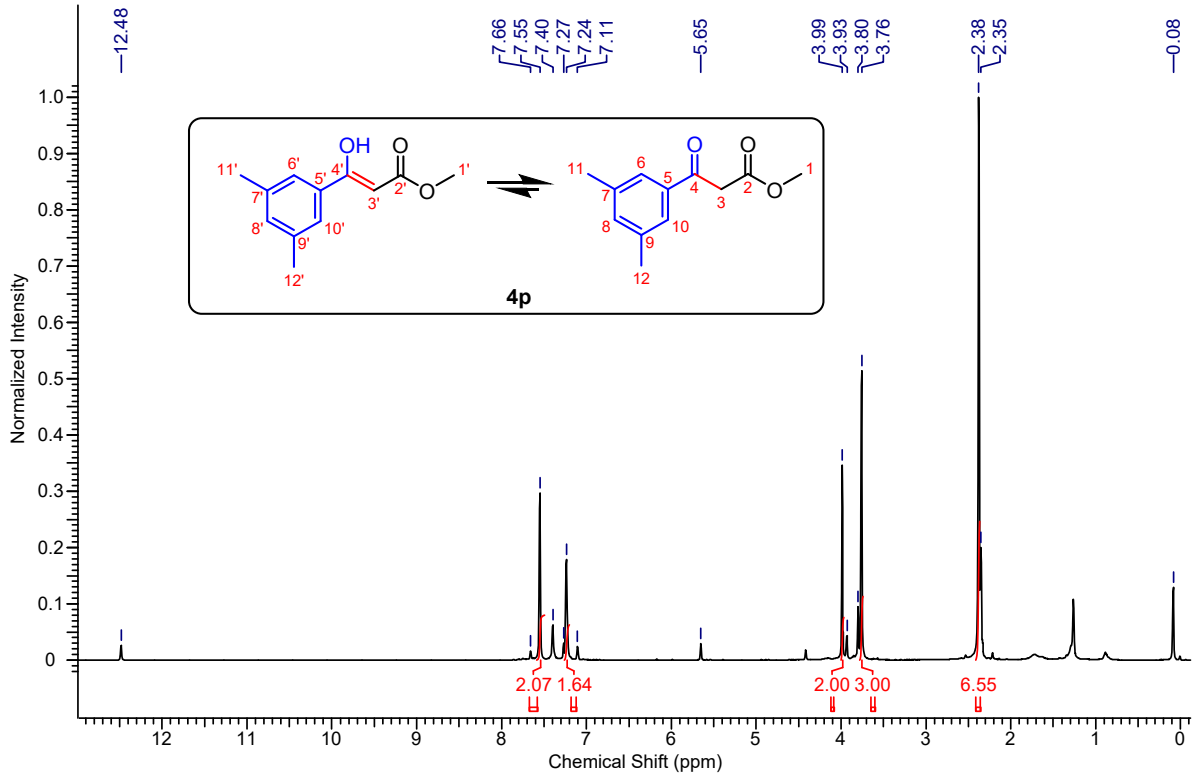
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3z



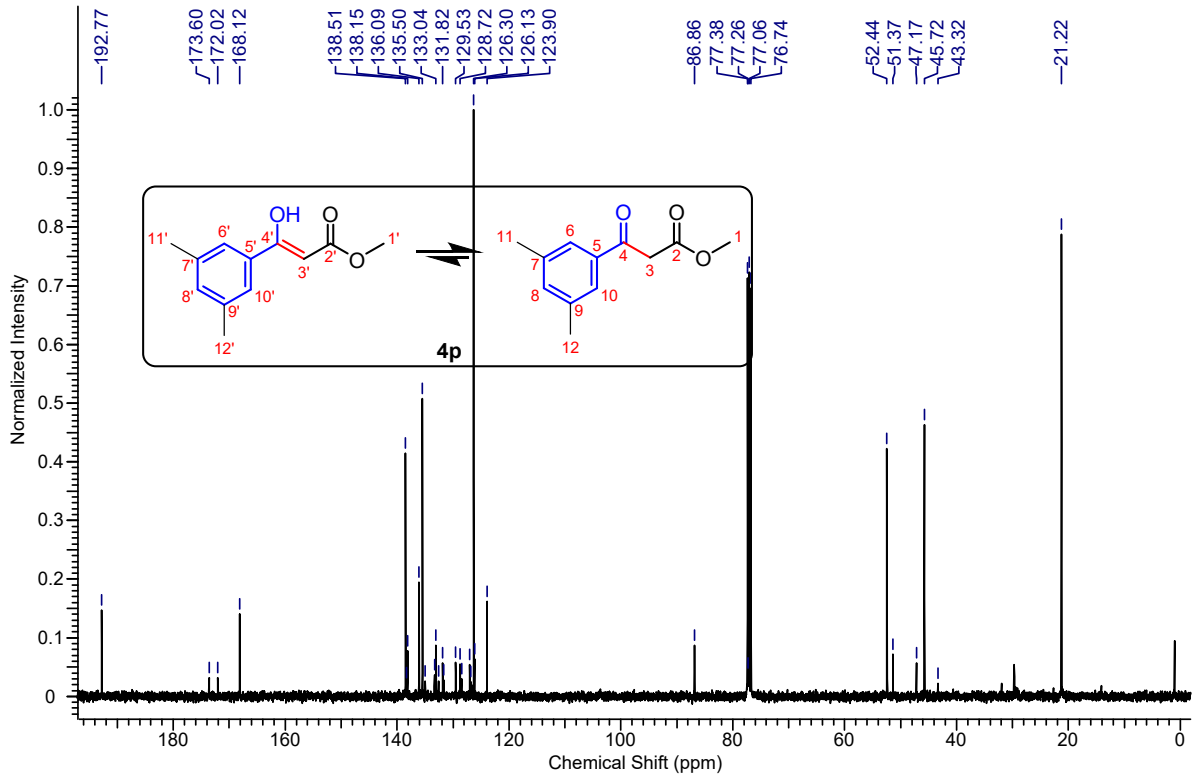
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3aa'



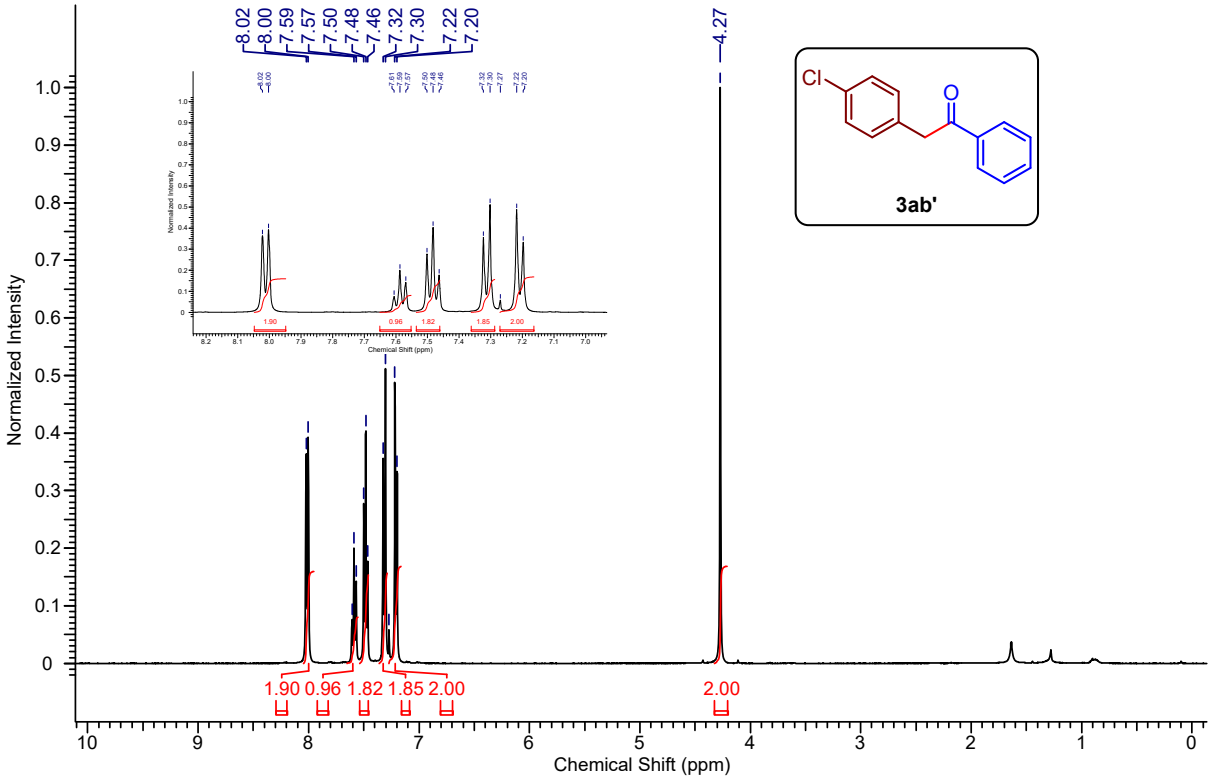
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3aa'



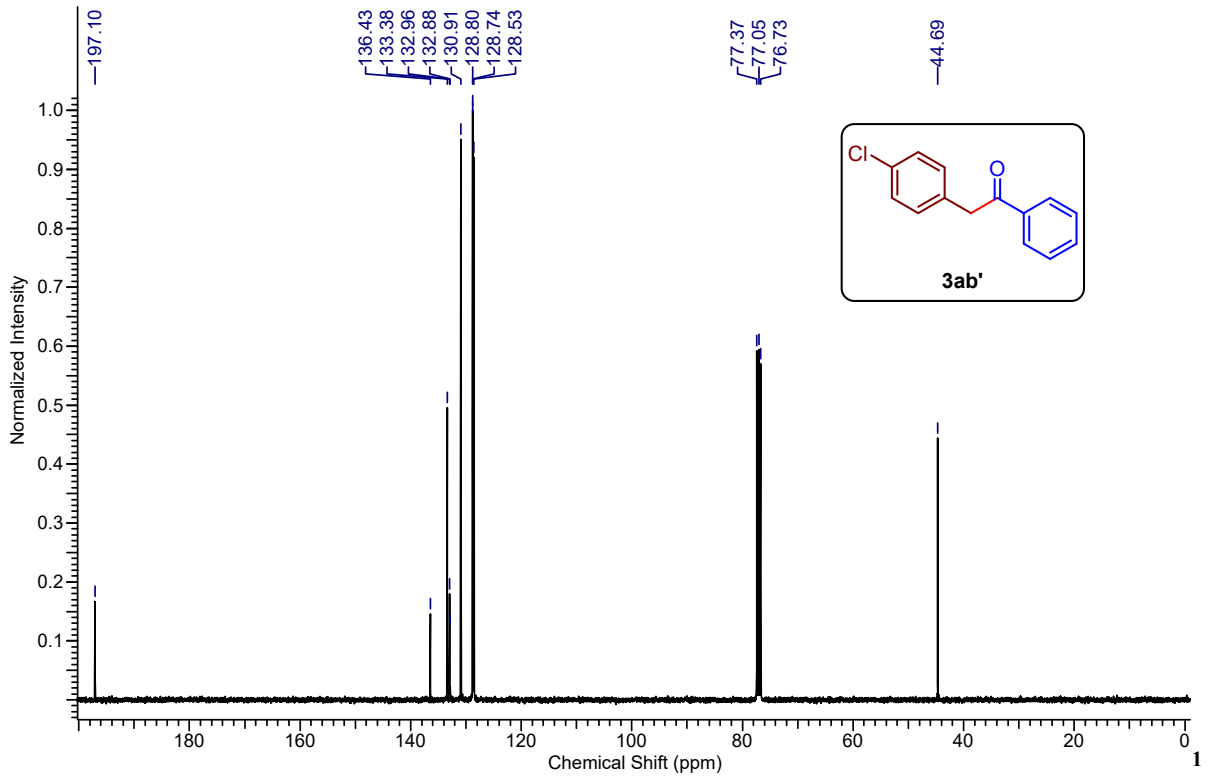
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4p



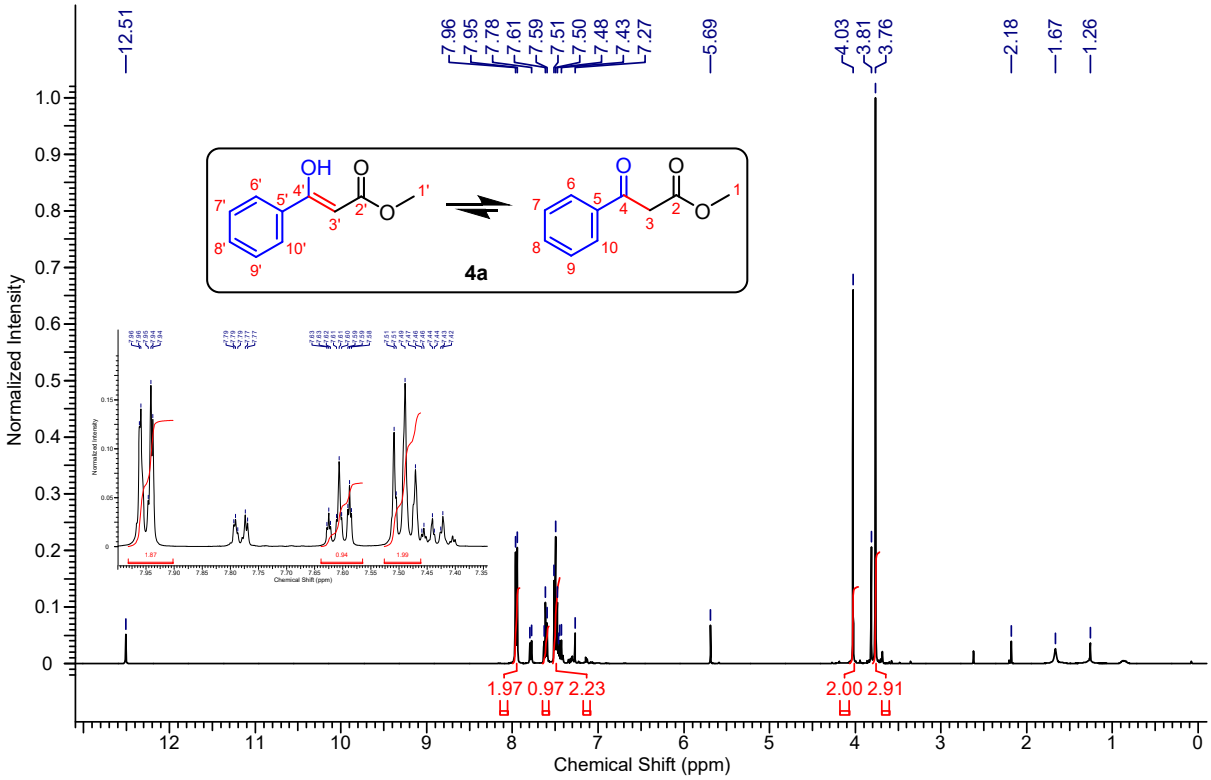
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4p



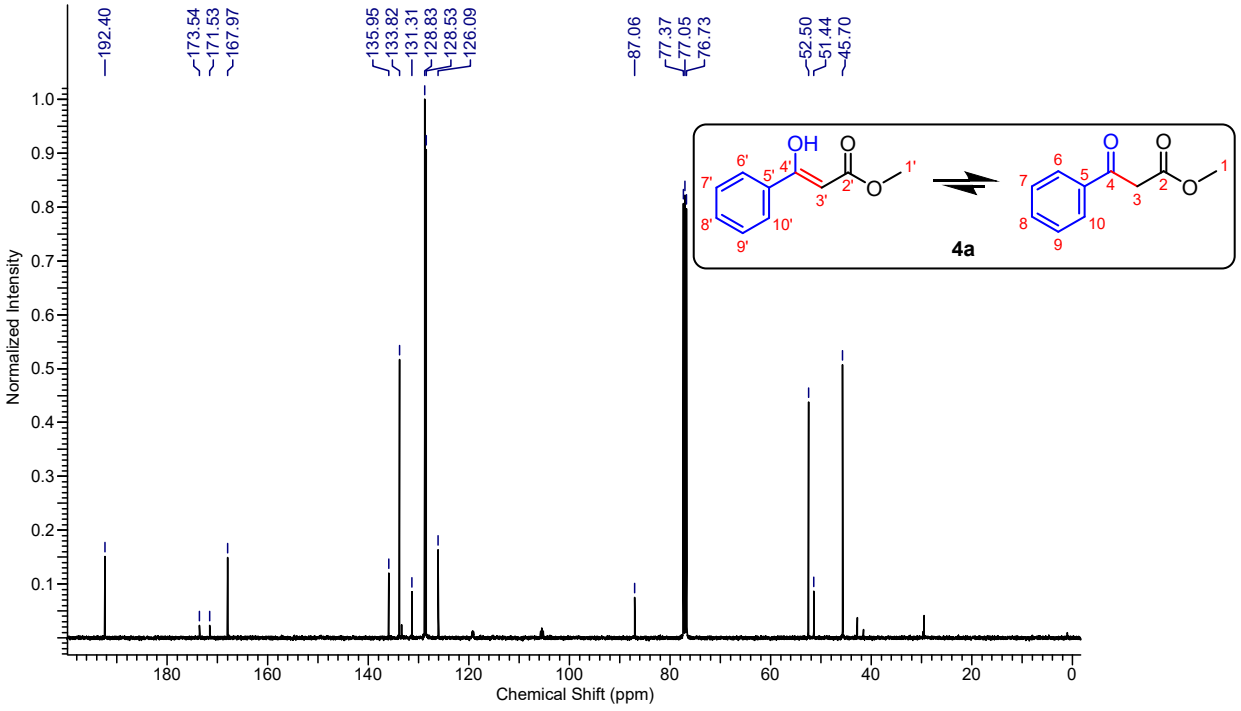
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3ab'



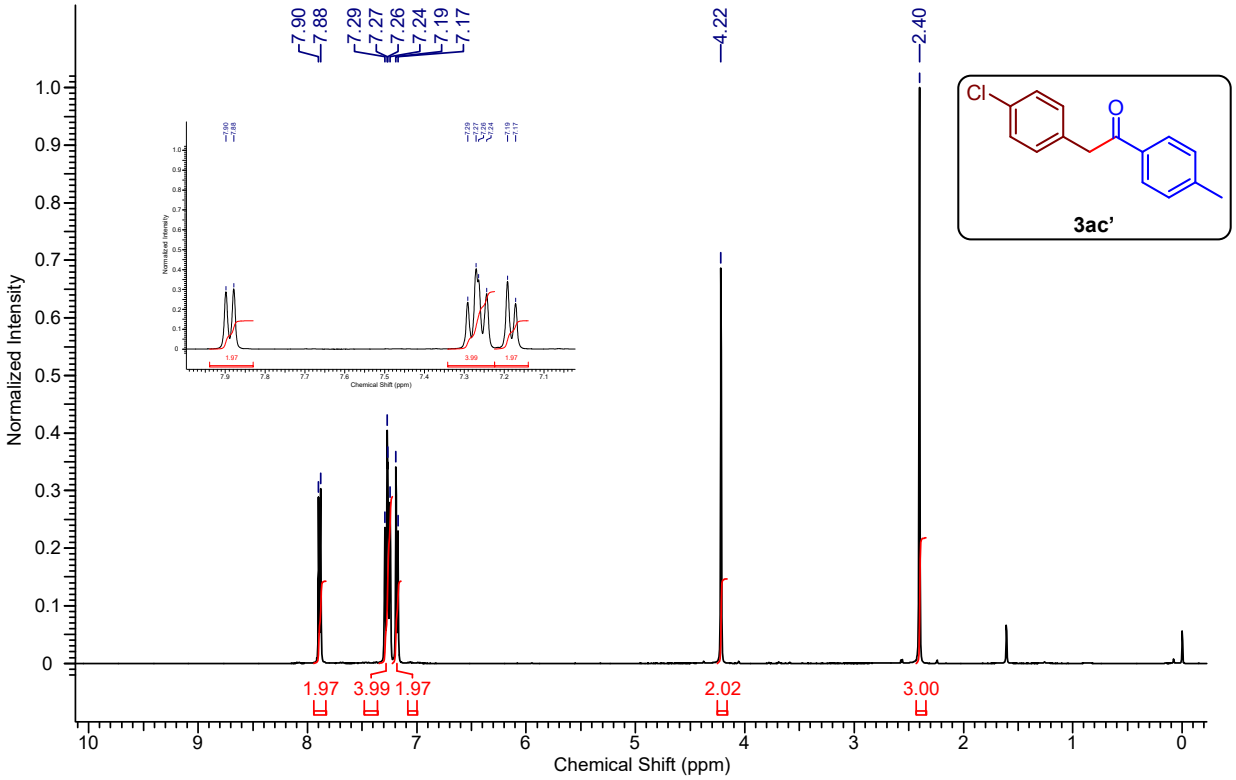
^{3}C NMR (100 MHz, $CDCl_3$) Spectrum of 3ab'



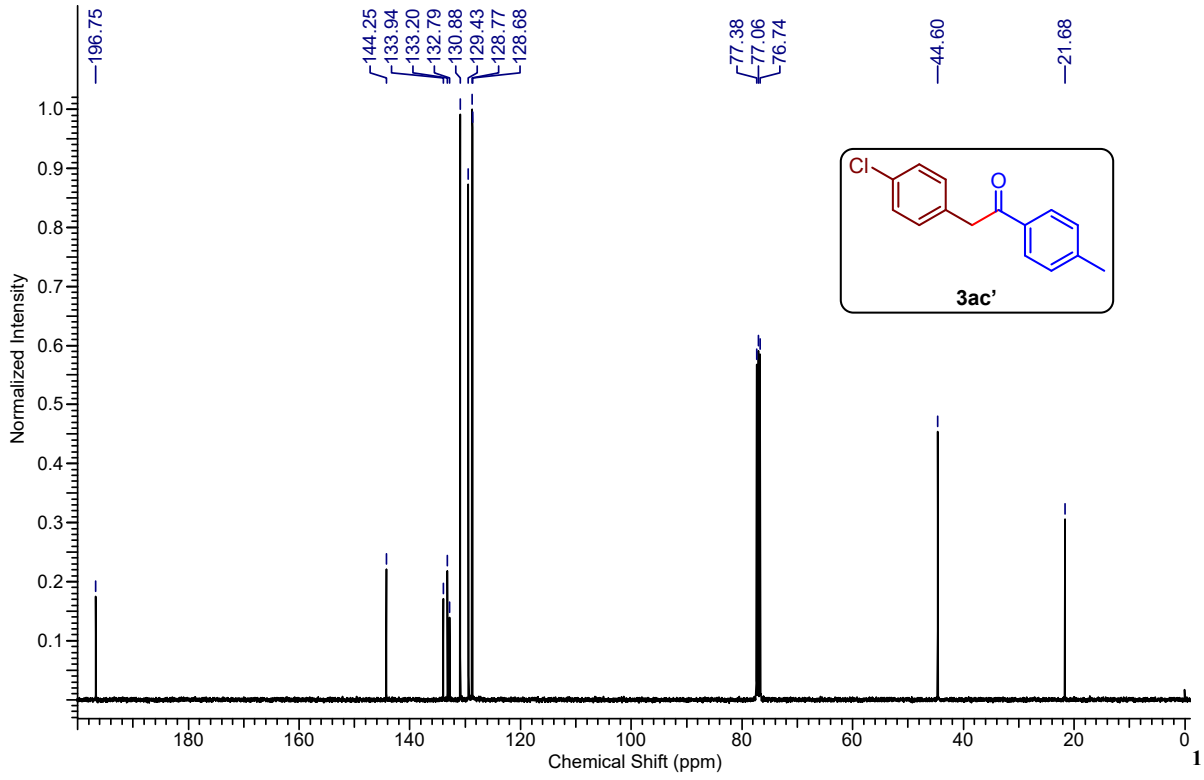
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4a



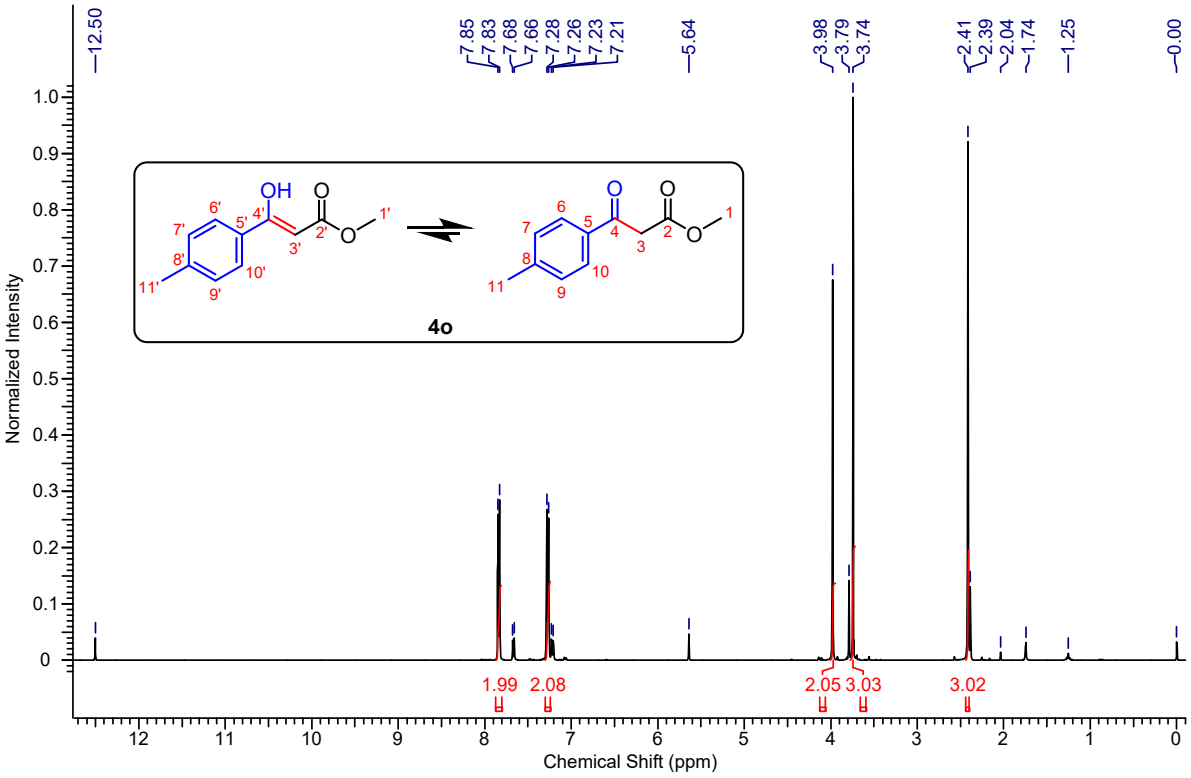
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4a



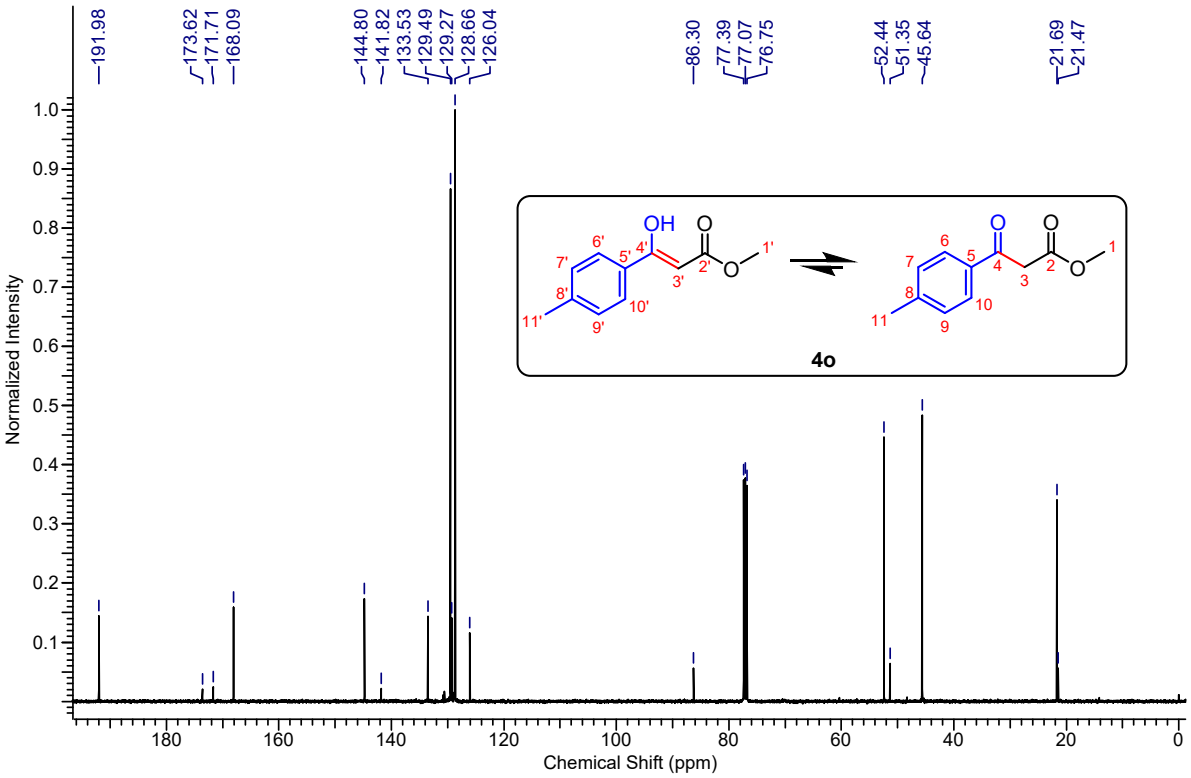
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3ac'



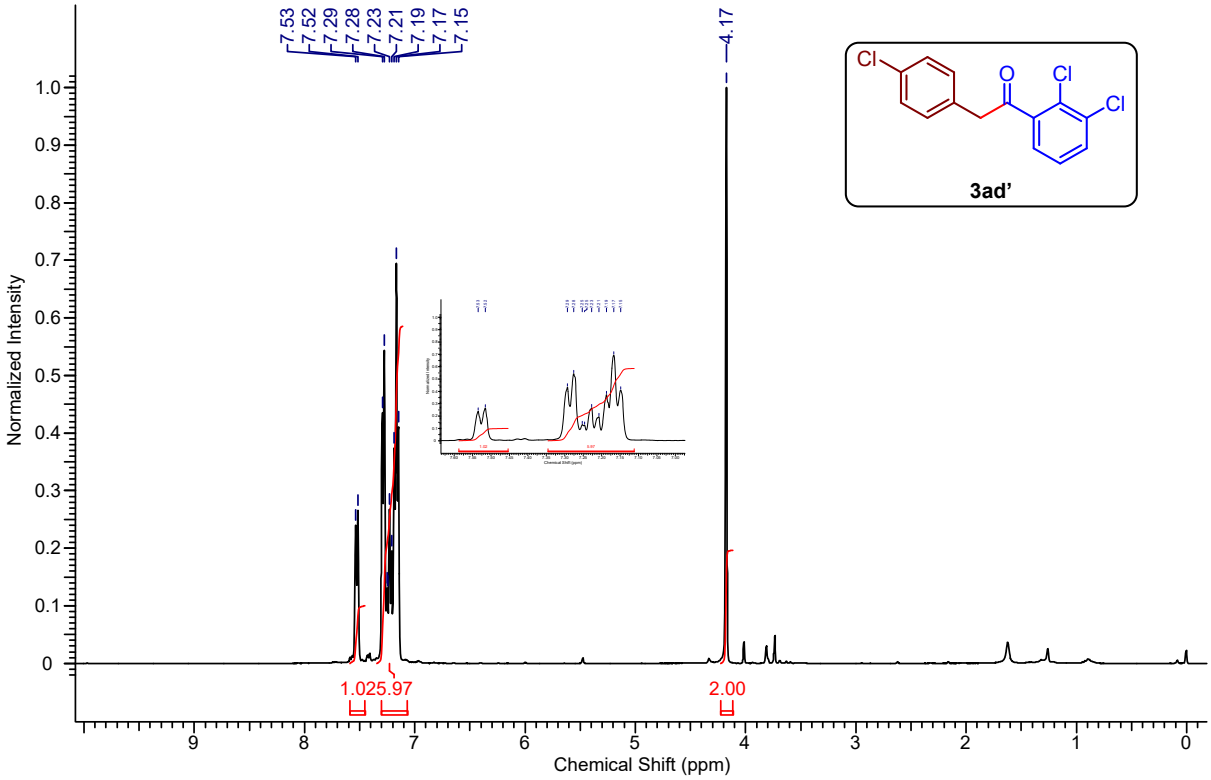
^{3}C NMR (100 MHz, $CDCl_3$) Spectrum of 3ac'



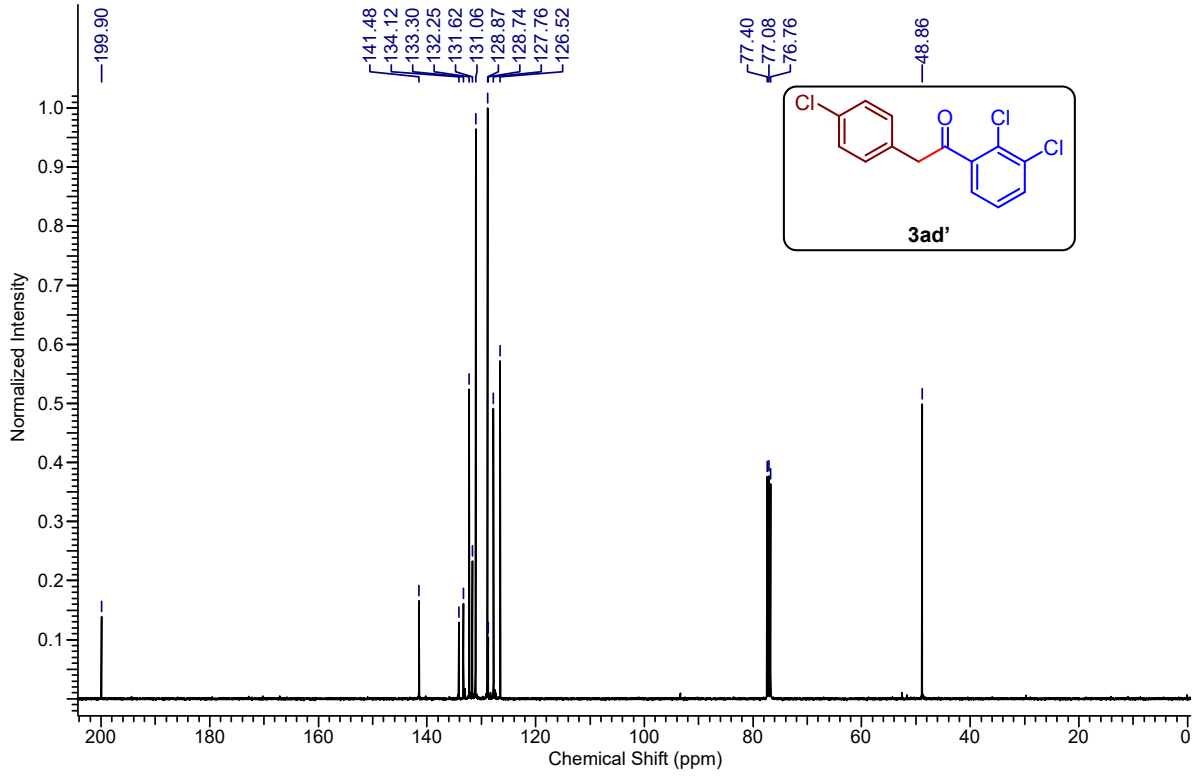
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4o



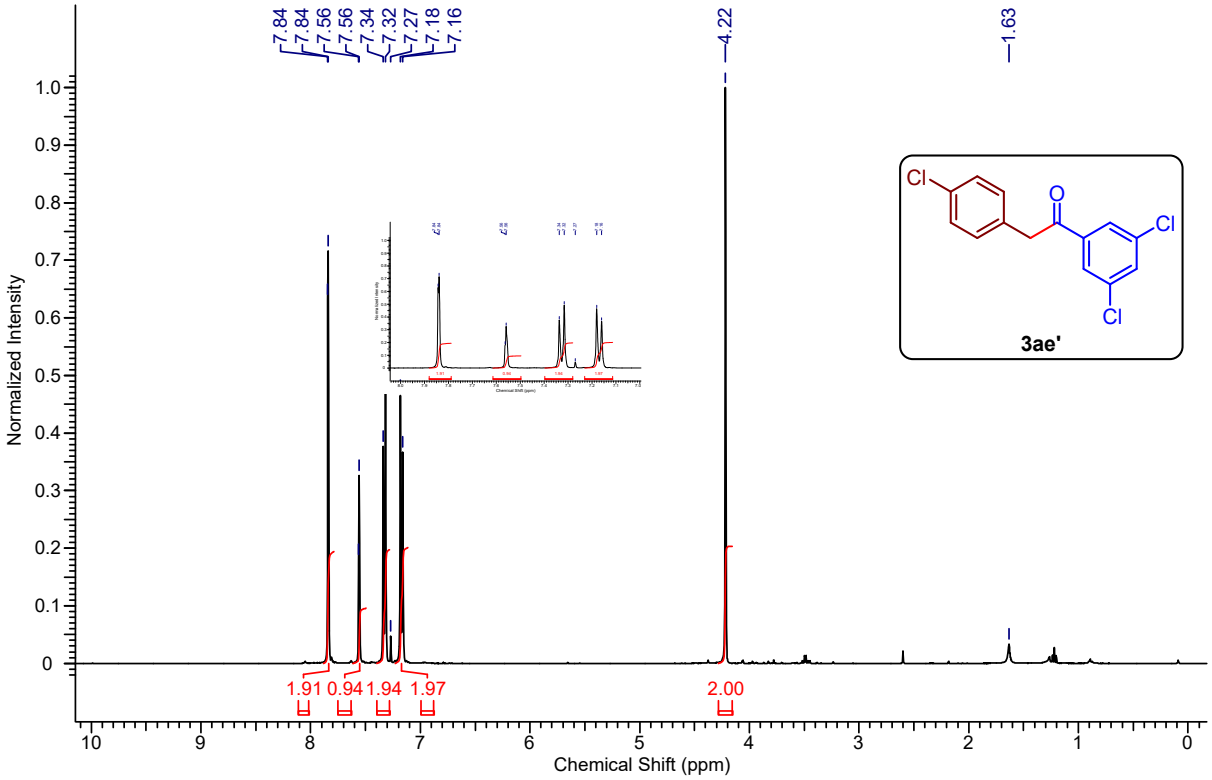
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4o



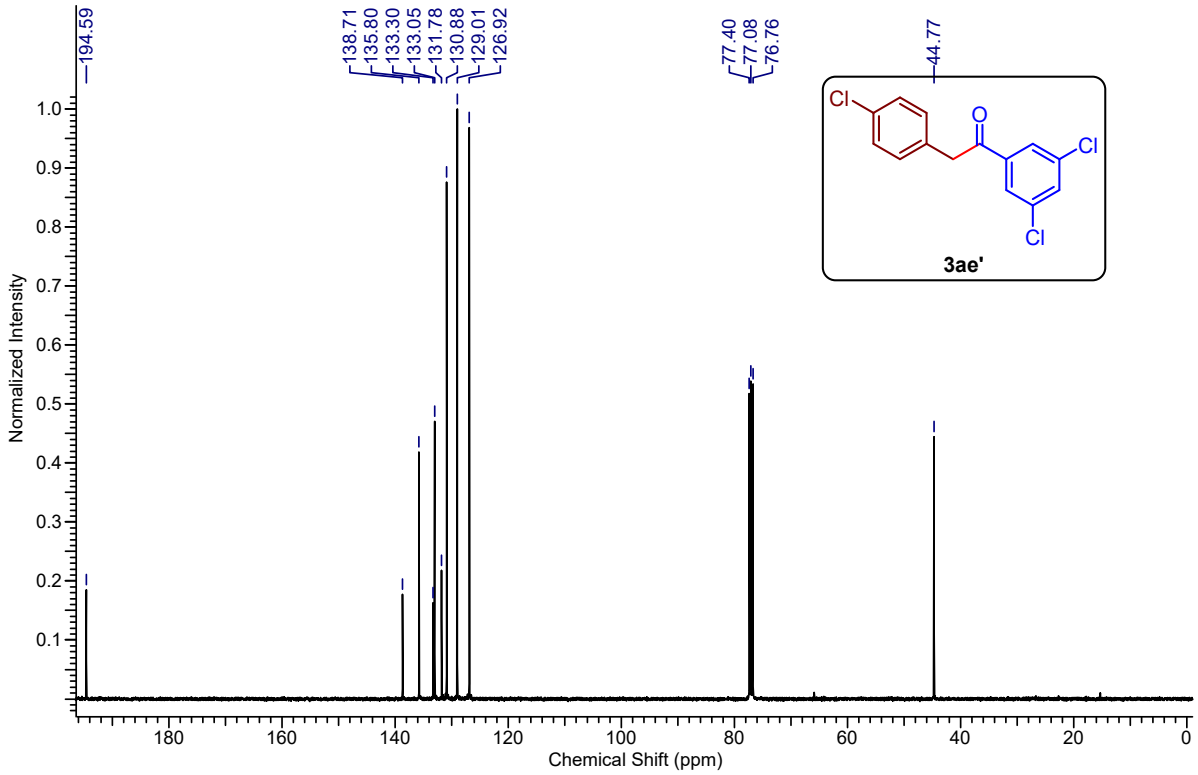
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3ad'



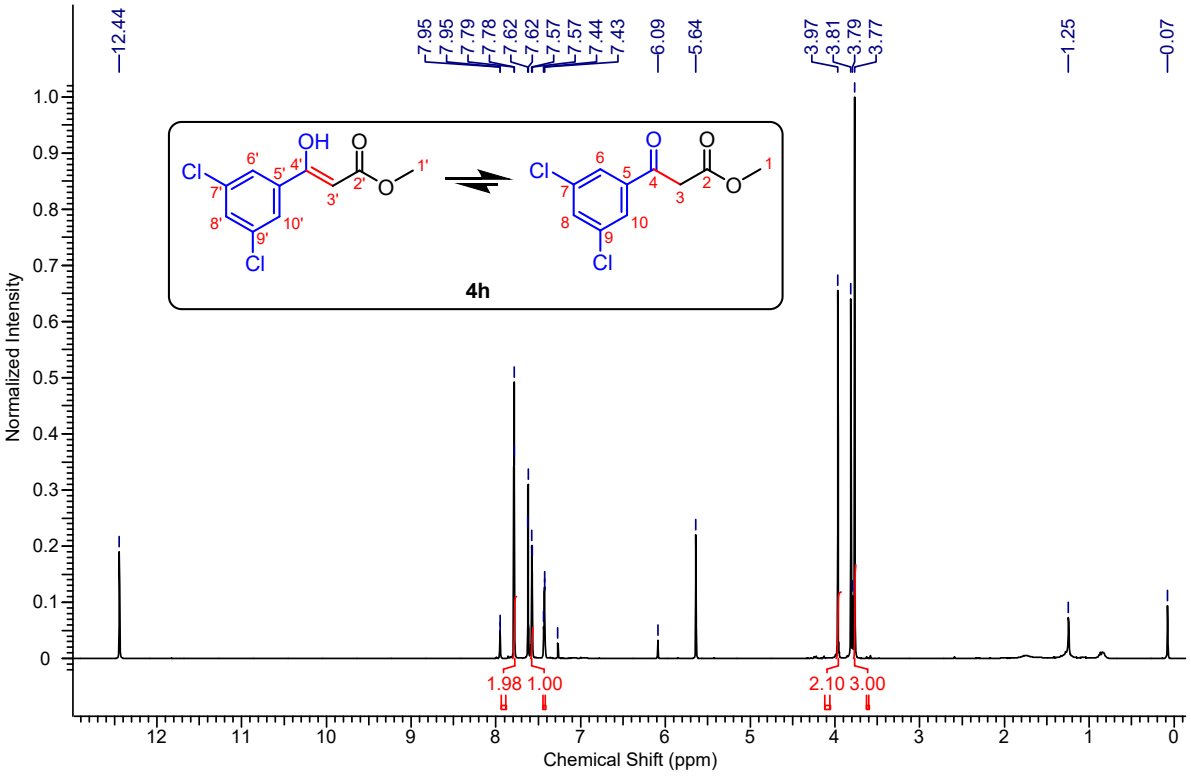
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3ad'



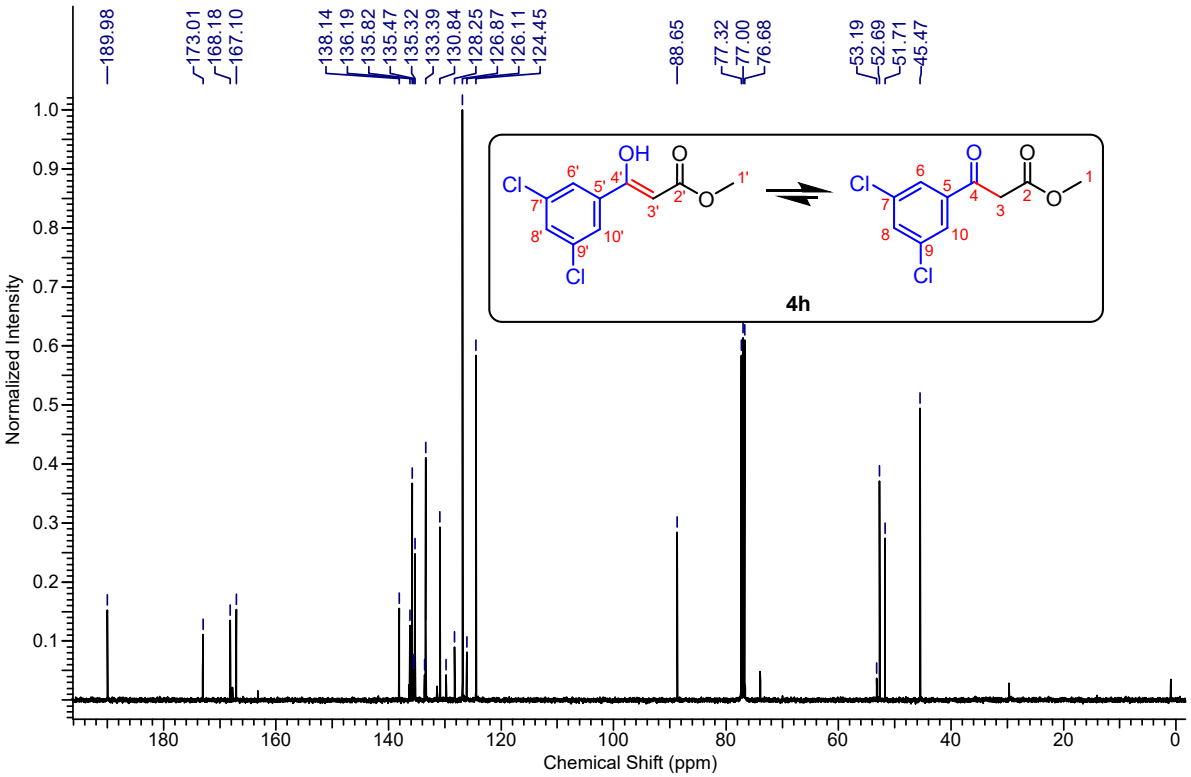
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3ae'



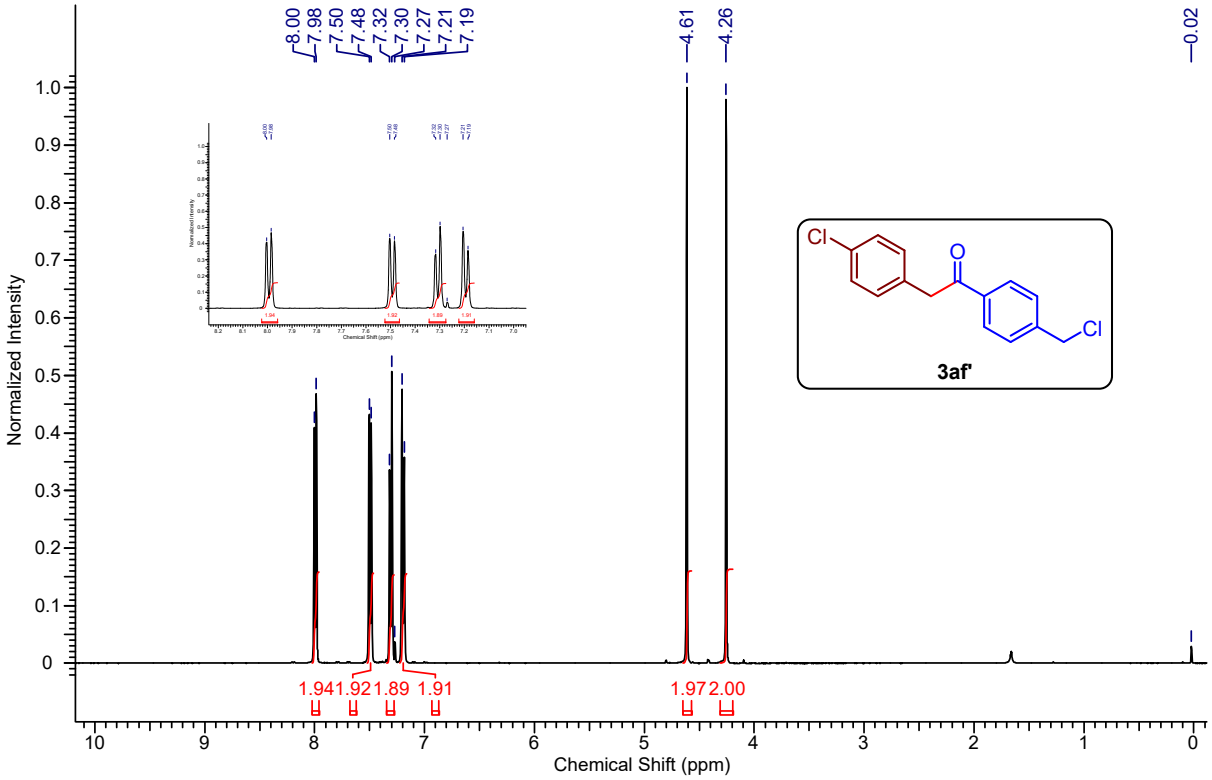
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3ae'



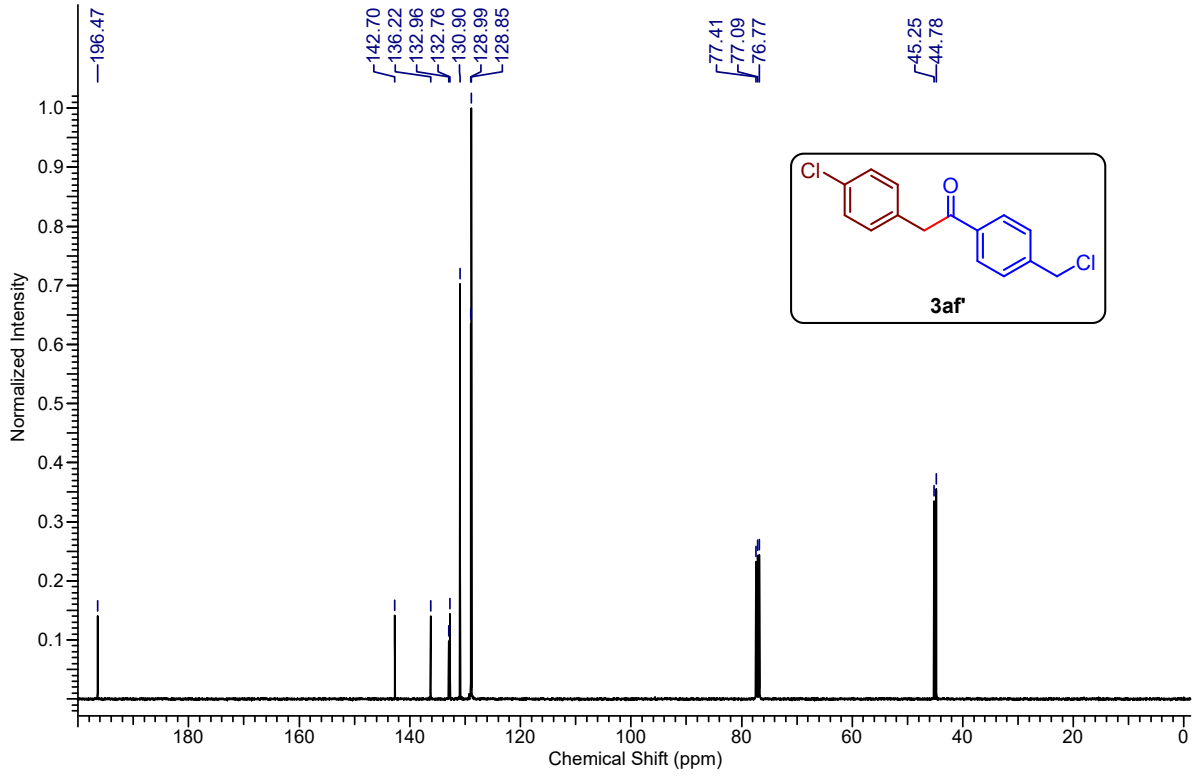
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4h



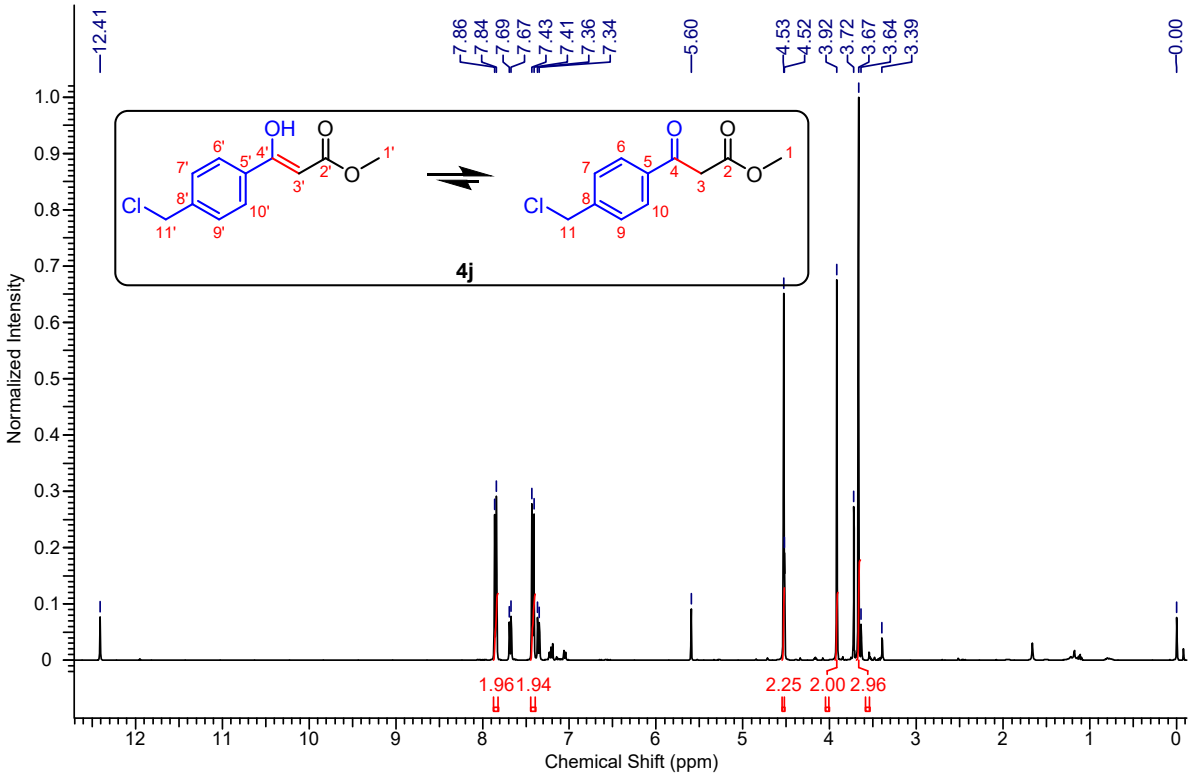
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4h



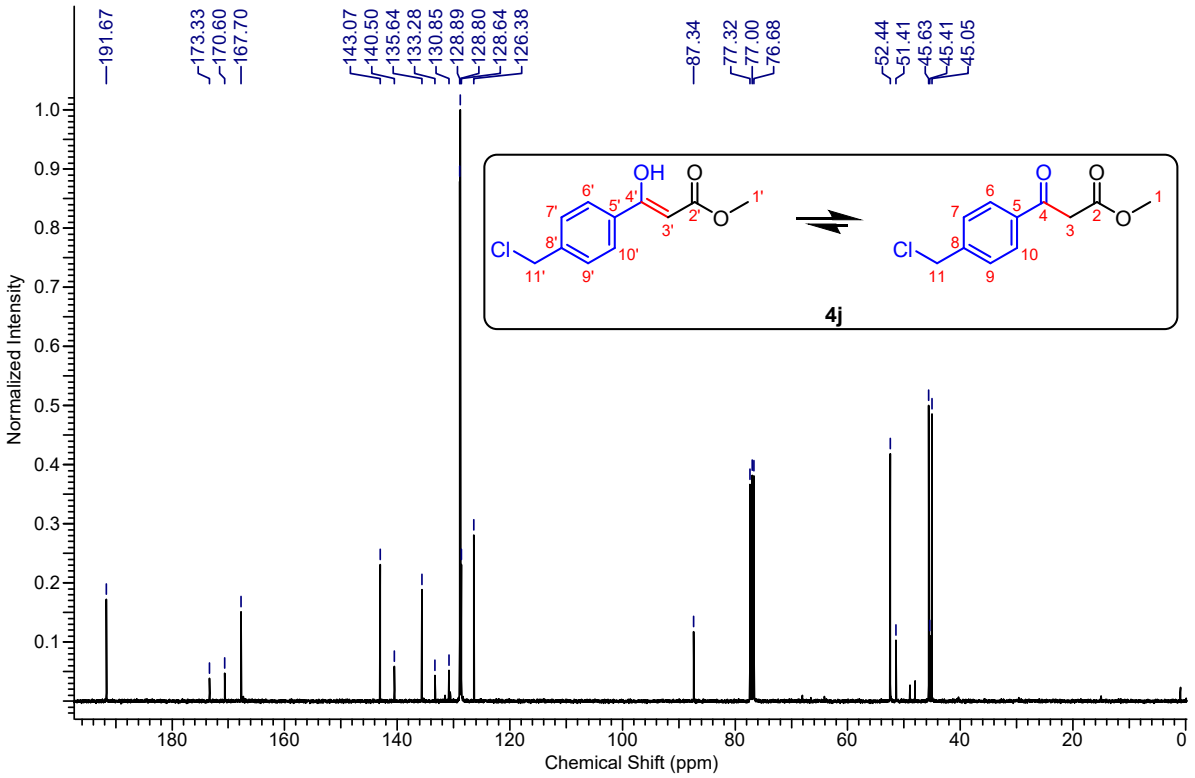
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3af'



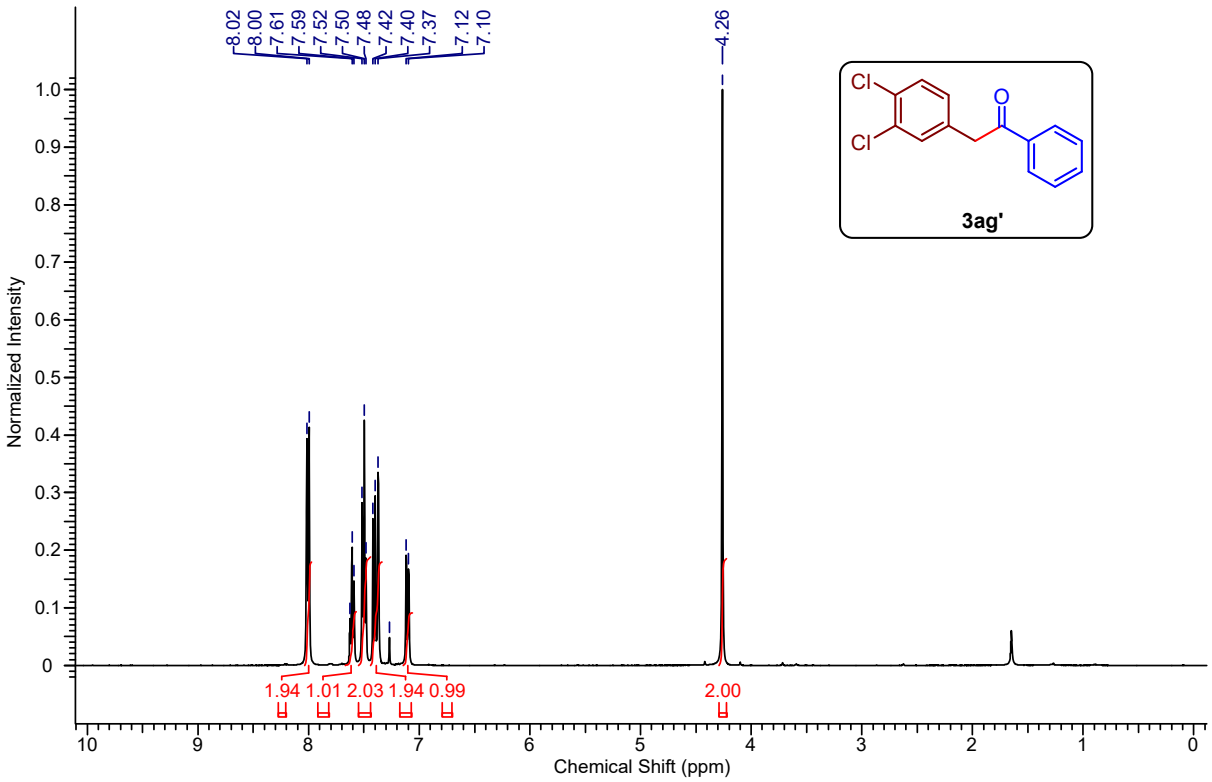
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3af'



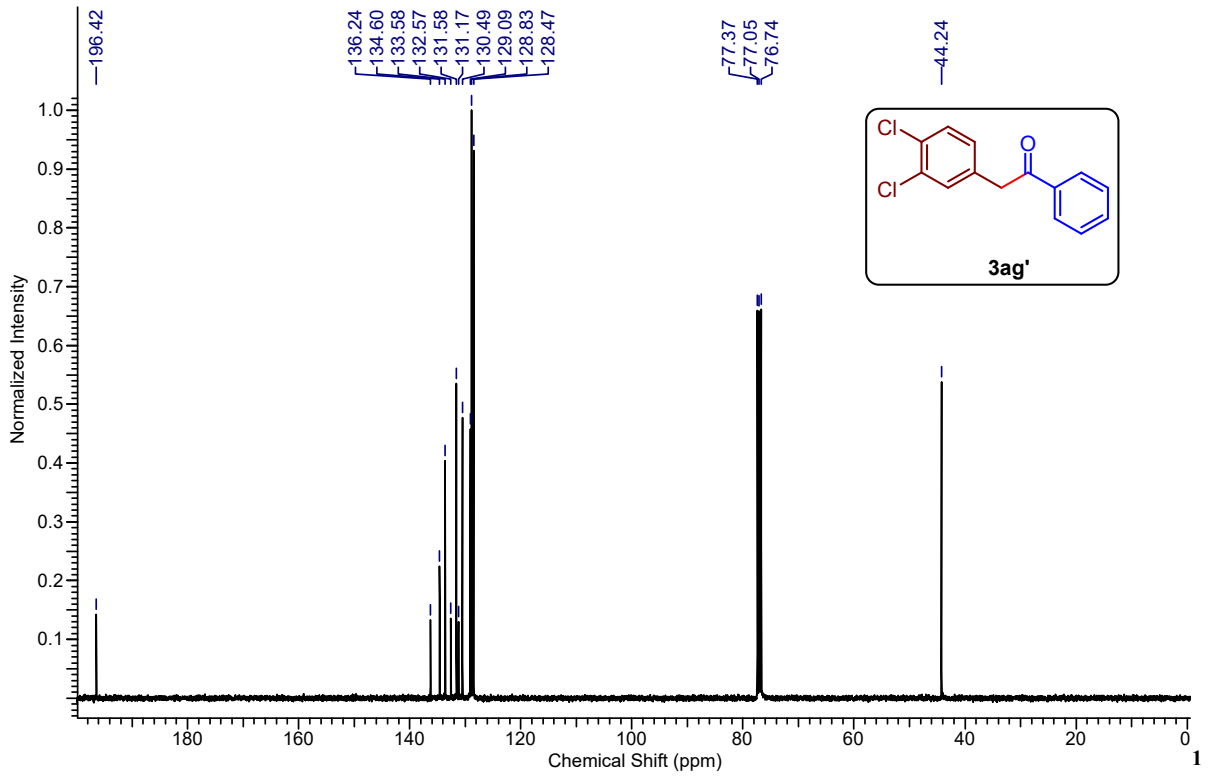
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4J



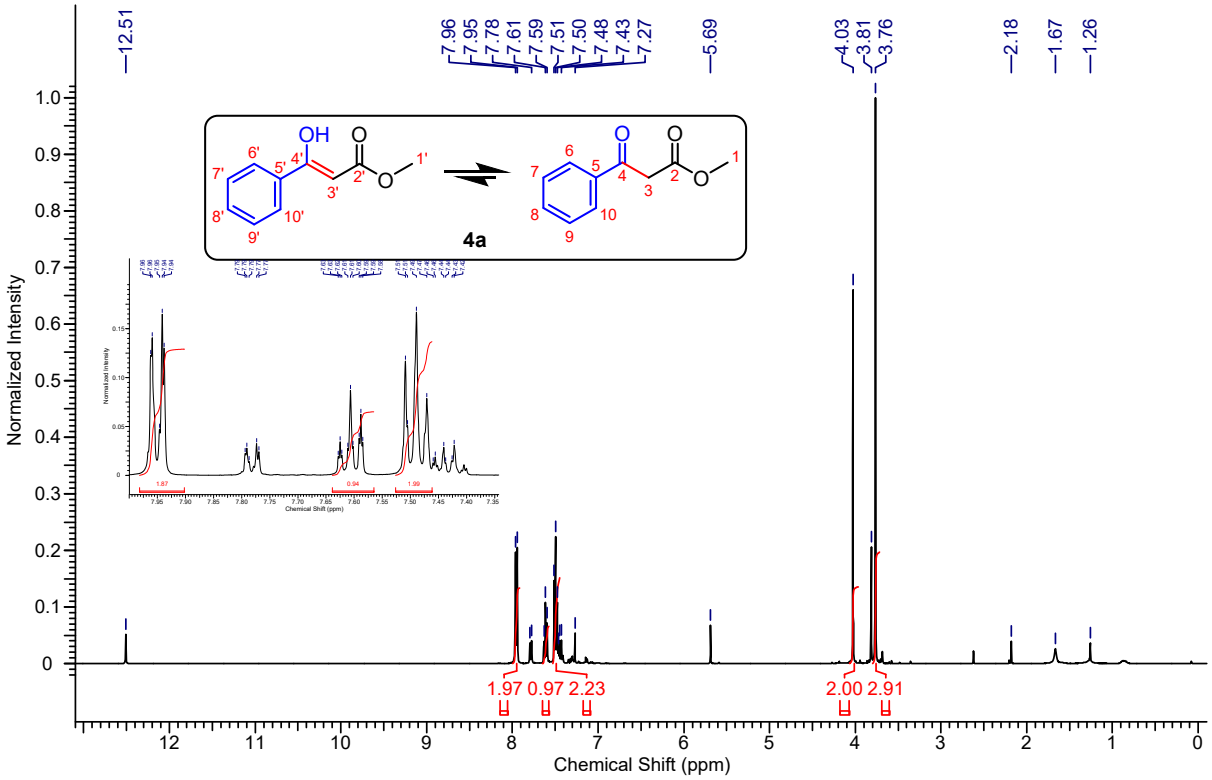
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4J



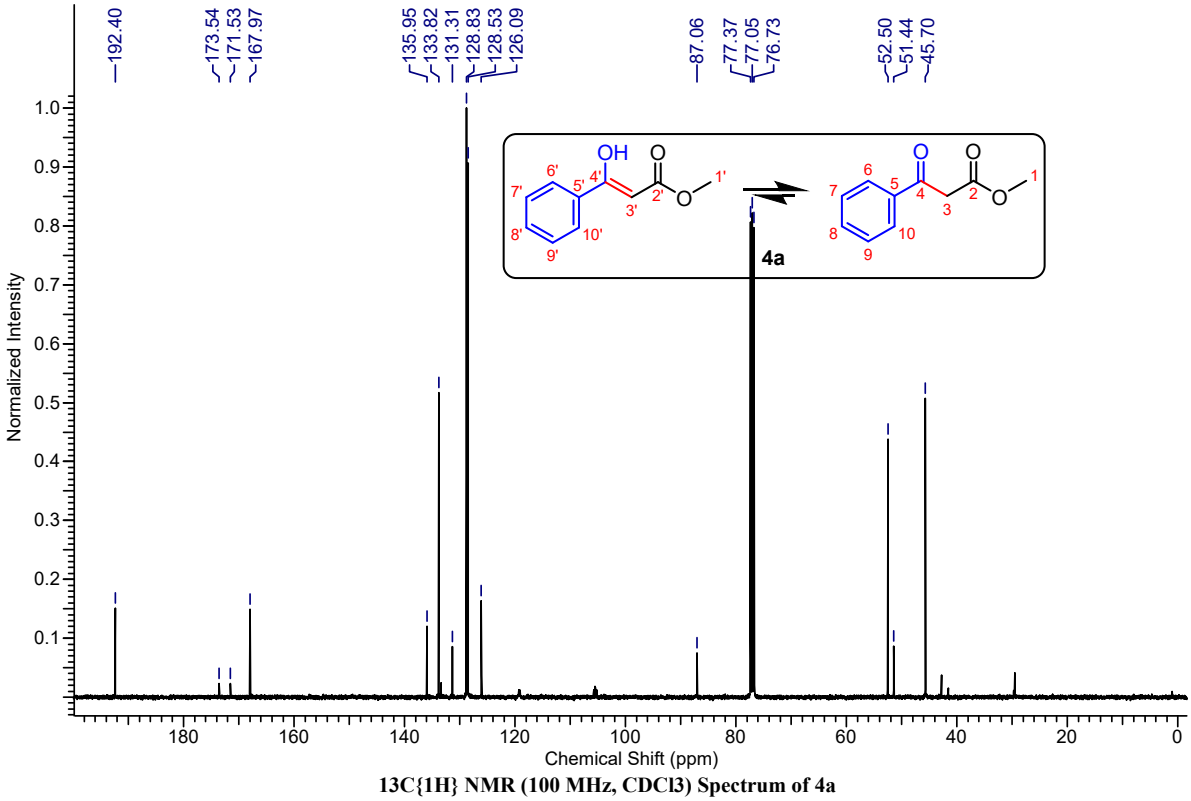
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3ag'



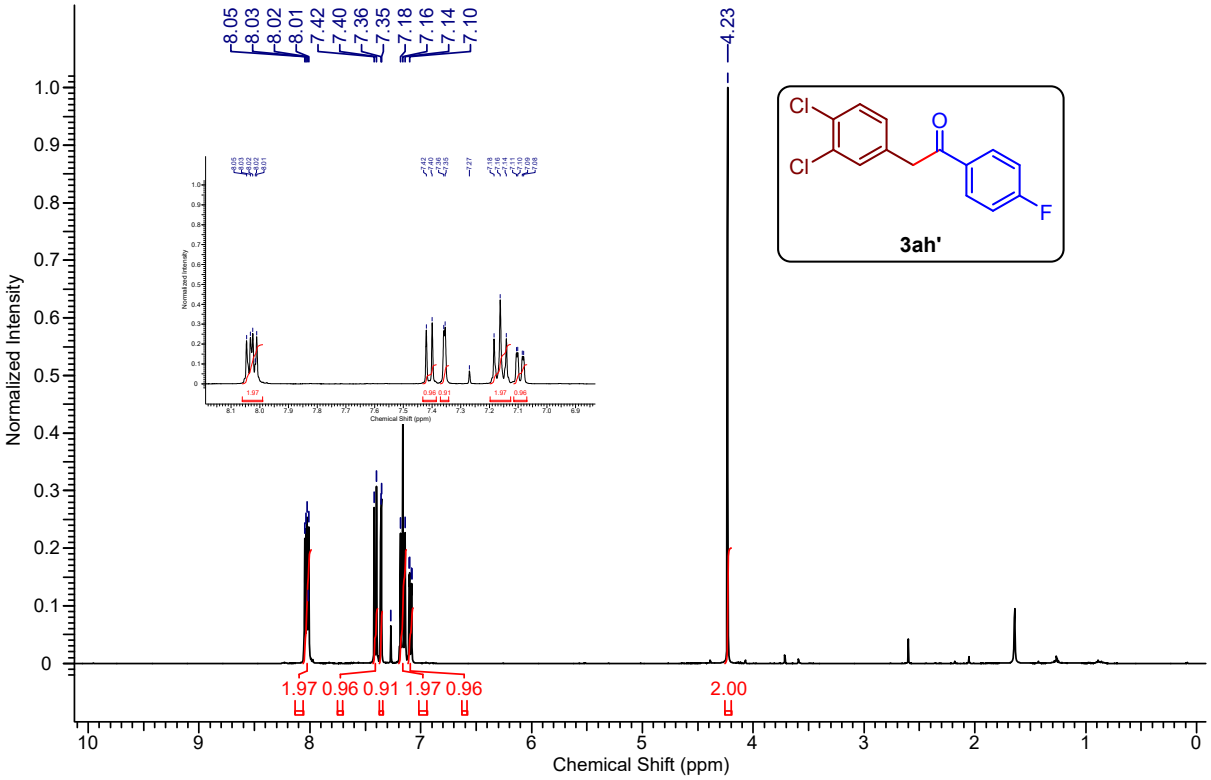
^{3}C NMR (100 MHz, $CDCl_3$) Spectrum of 3ag'



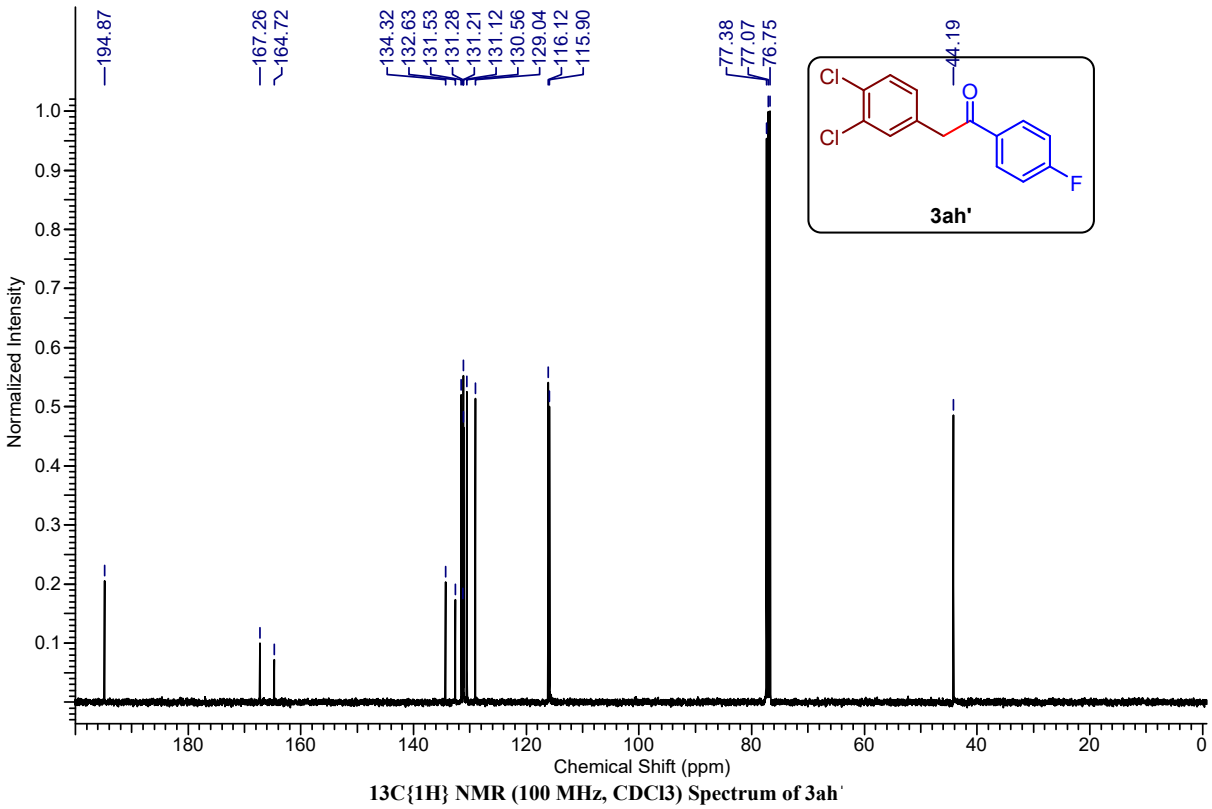
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4a



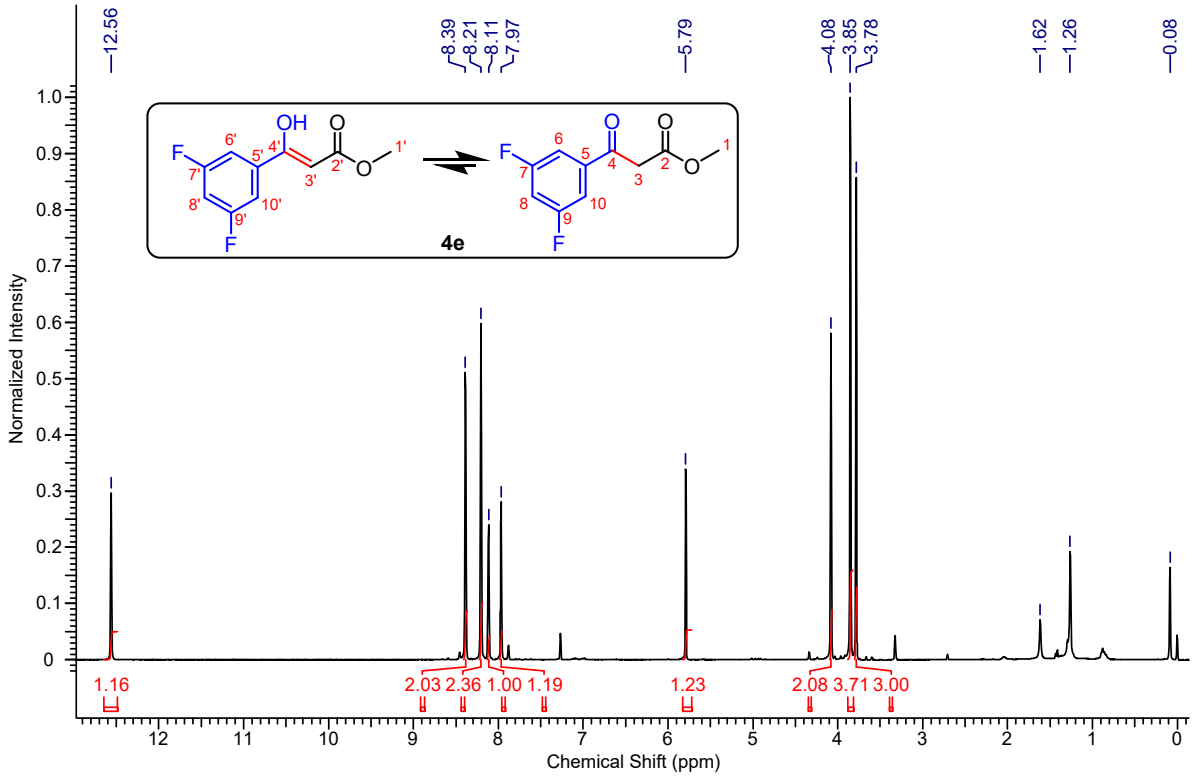
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 4a



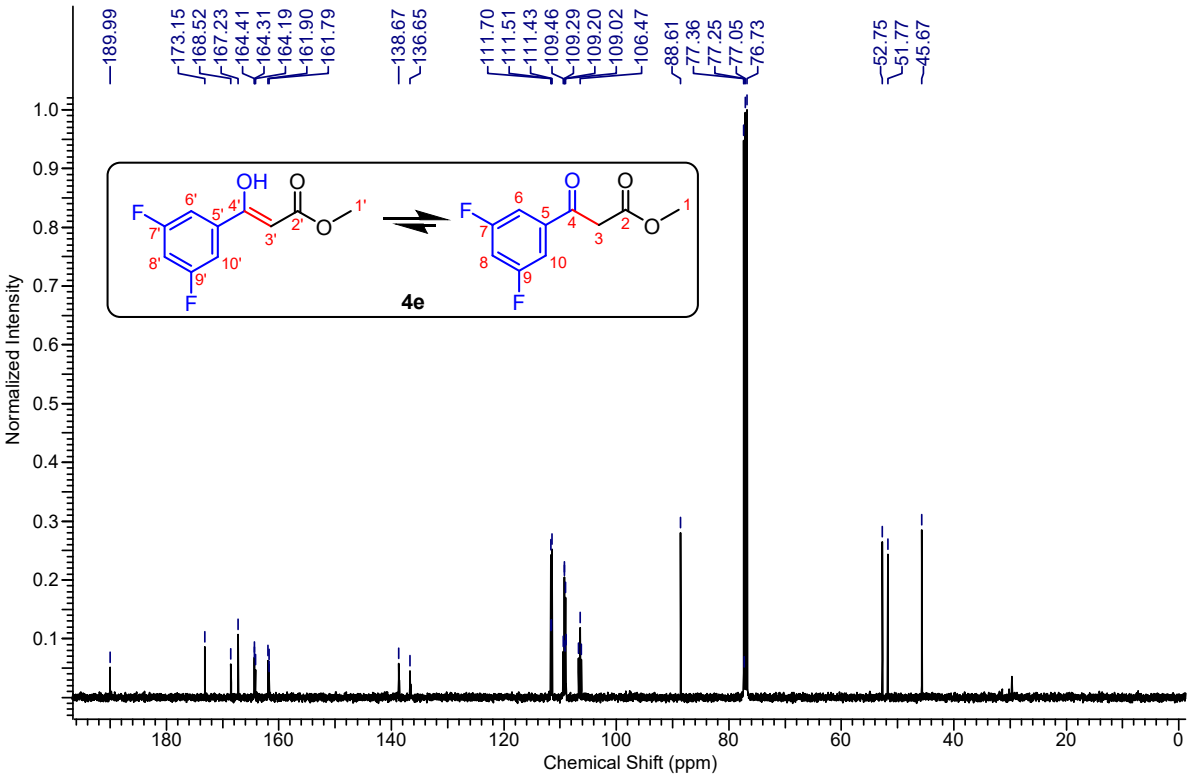
1H NMR (400 MHz, CDCl3) Spectrum of 3ah'



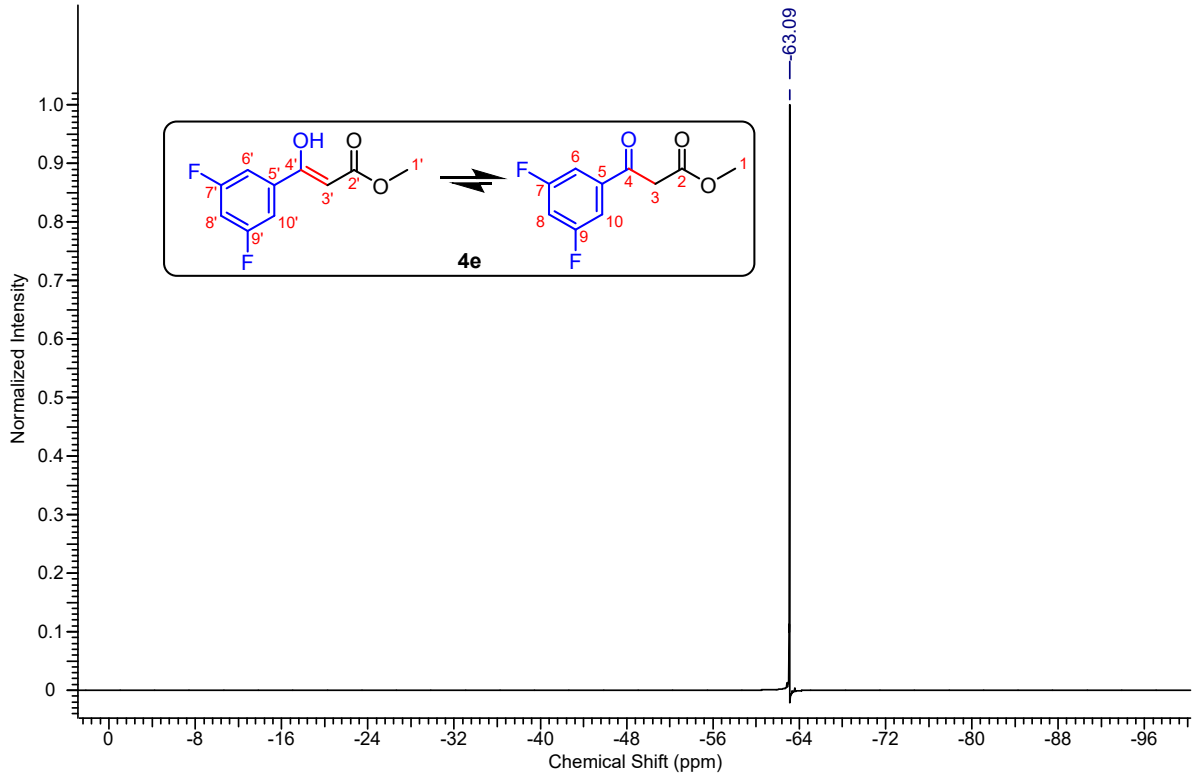
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 3ah'



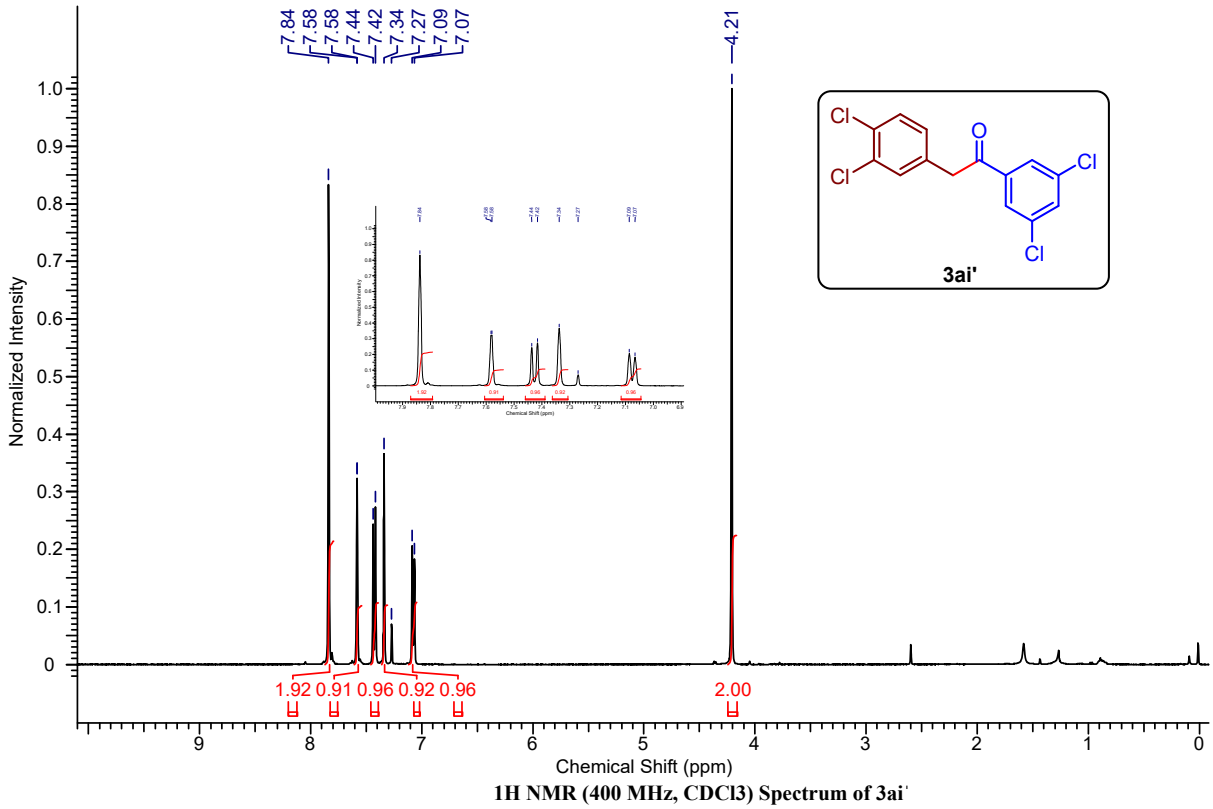
1H NMR (400 MHz, CDCl3) Spectrum of 4e



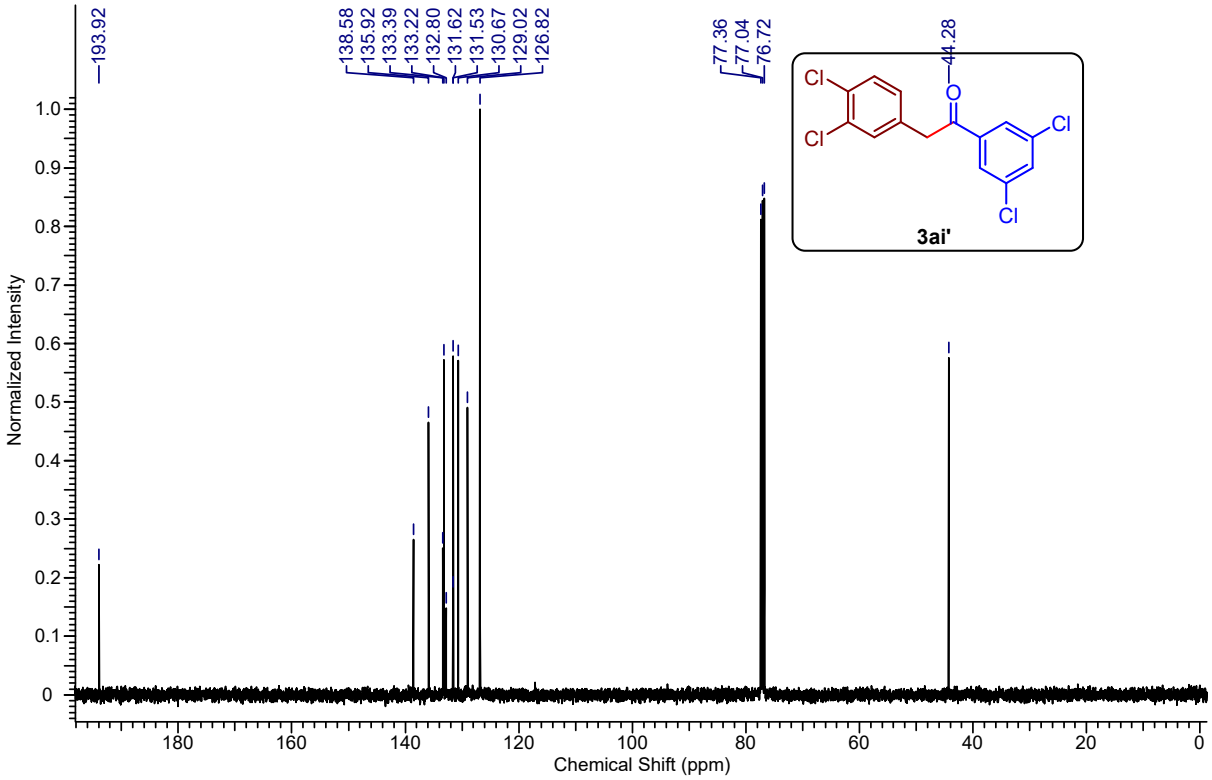
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 4e



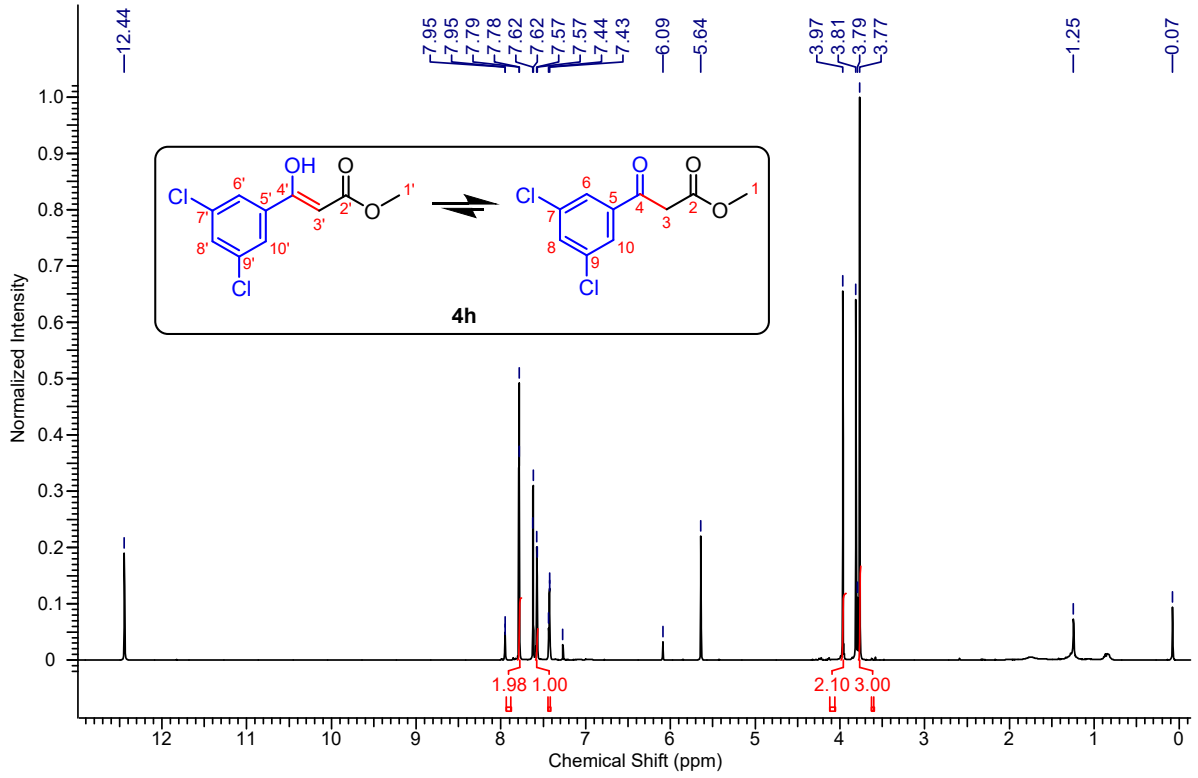
19F NMR (375 MHz, CDCl3) Spectrum of 4e



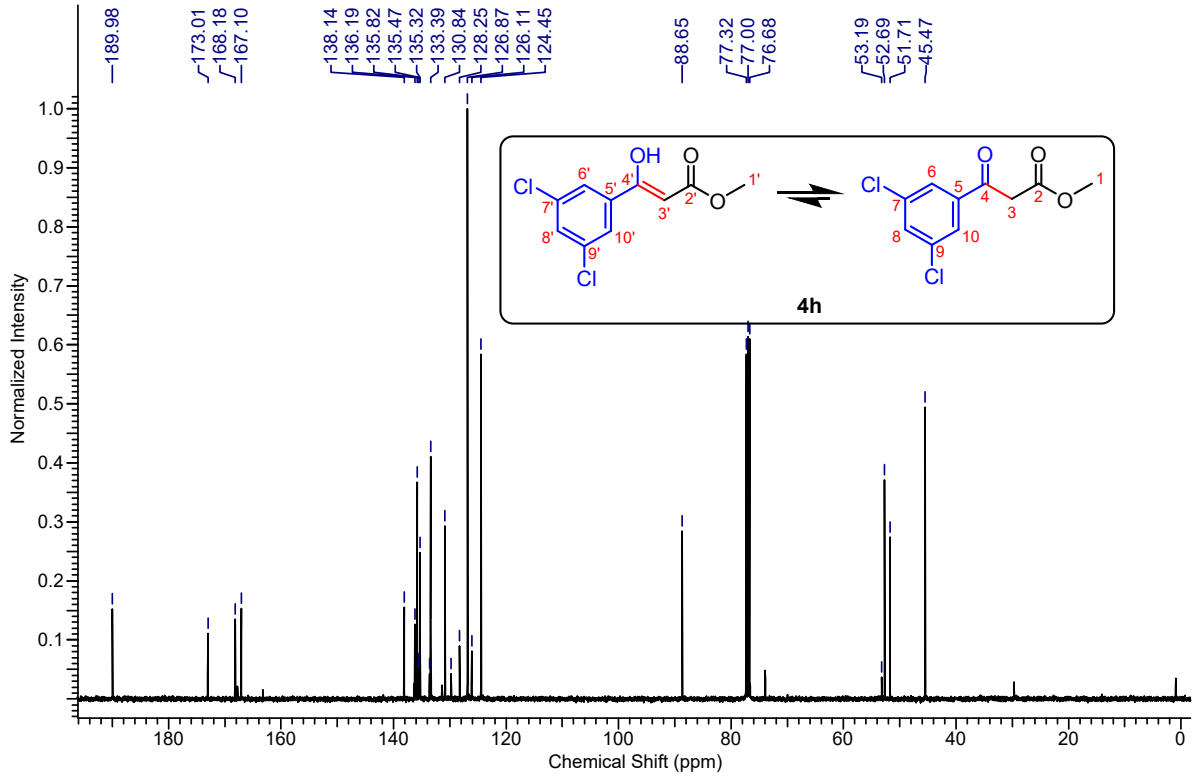
1H NMR (400 MHz, CDCl3) Spectrum of 3ai'



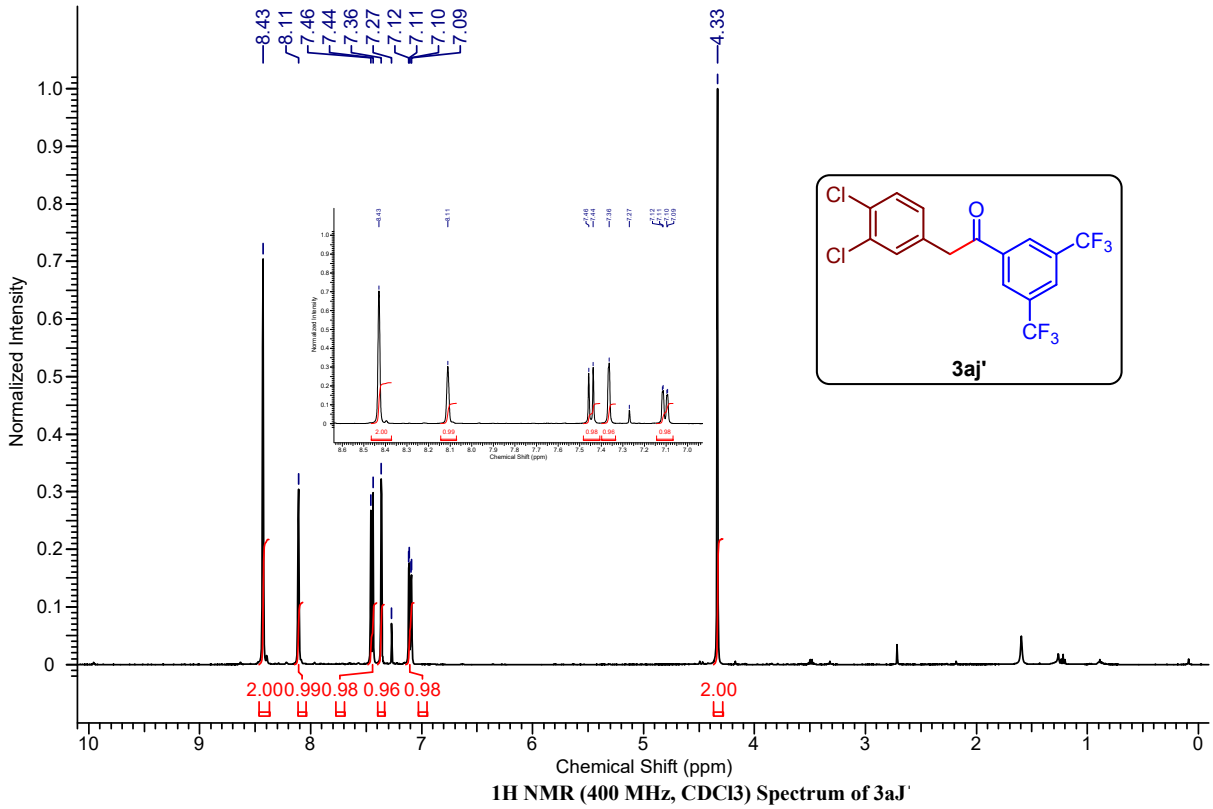
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 3ai



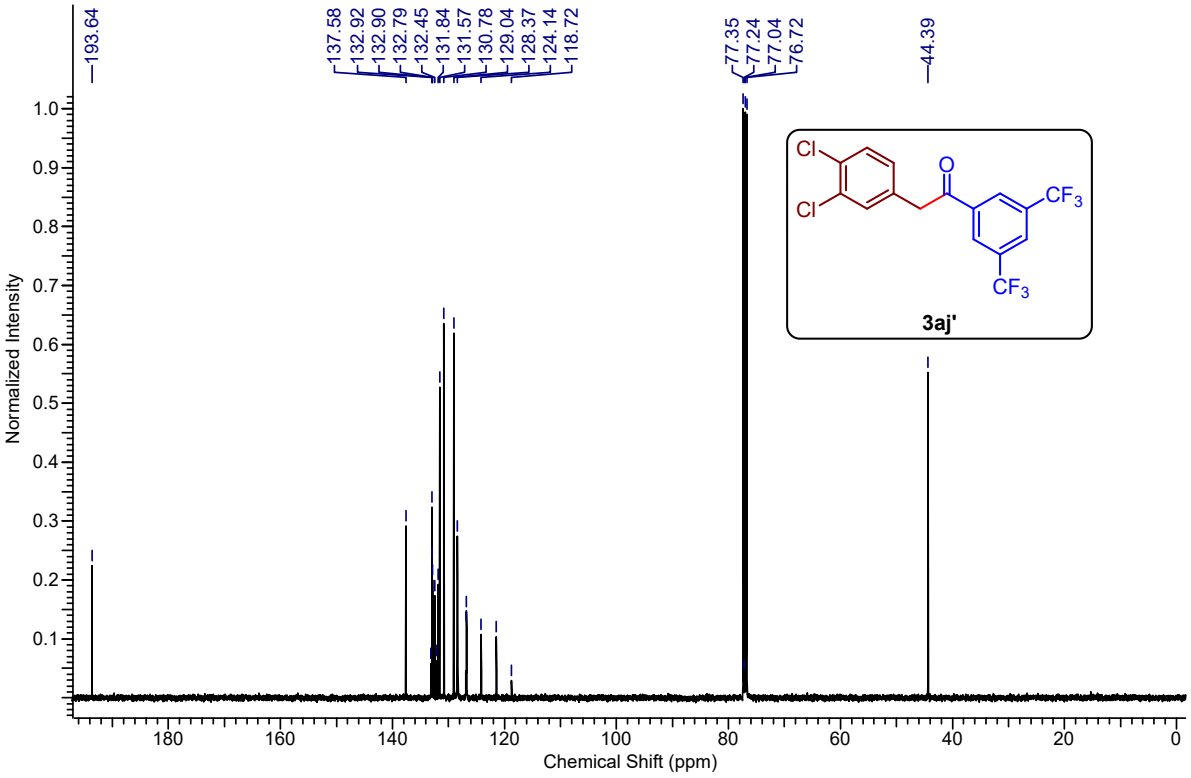
1H NMR (400 MHz, CDCl3) Spectrum of 4h



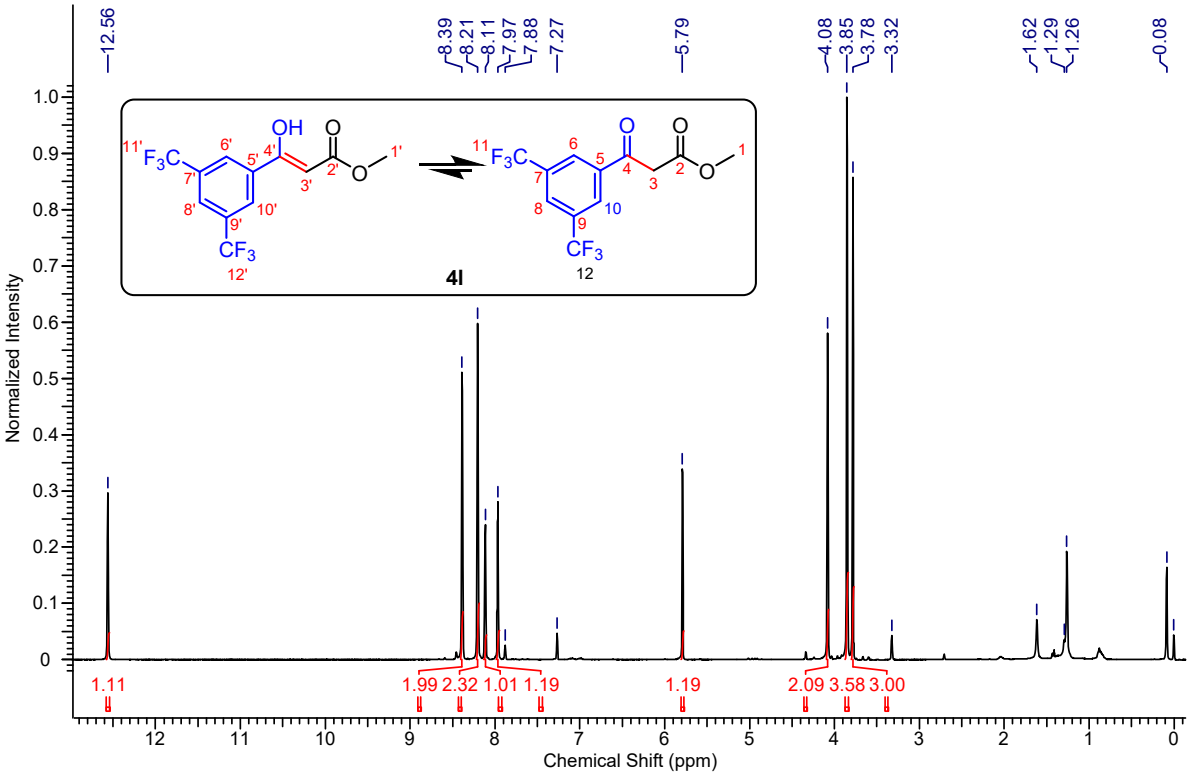
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 4h



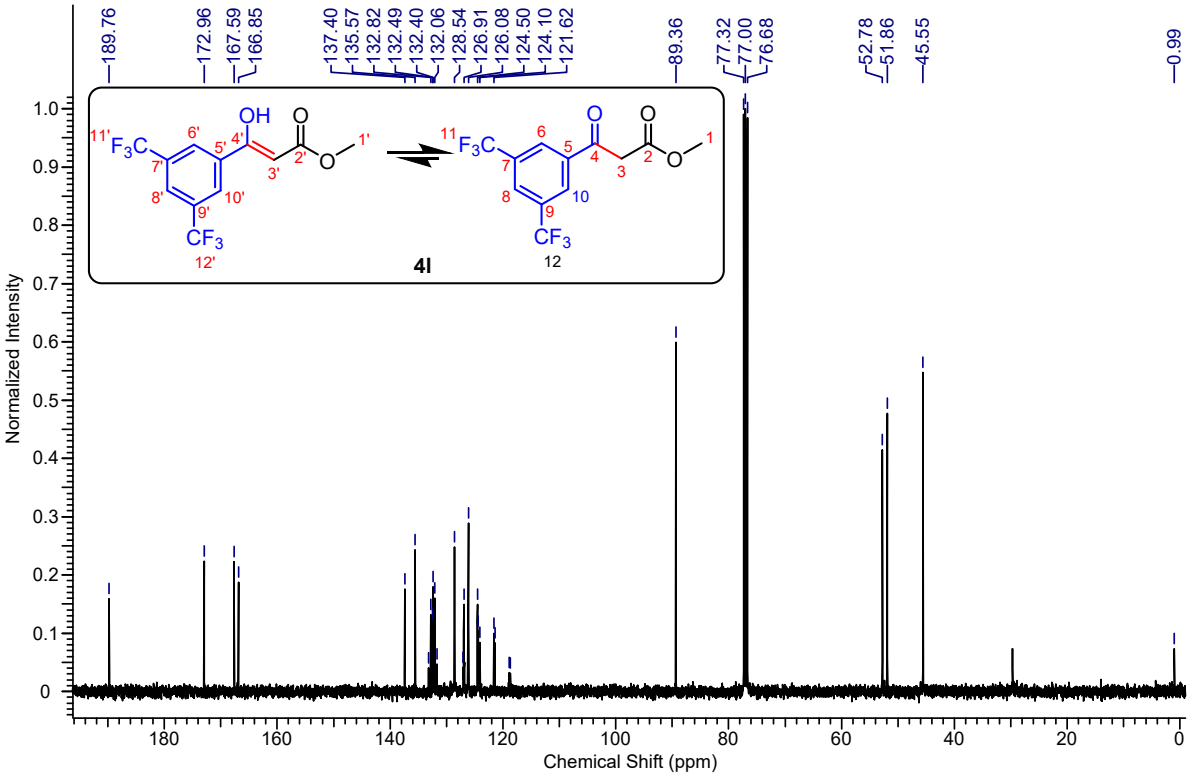
1H NMR (400 MHz, CDCl3) Spectrum of 3aj'



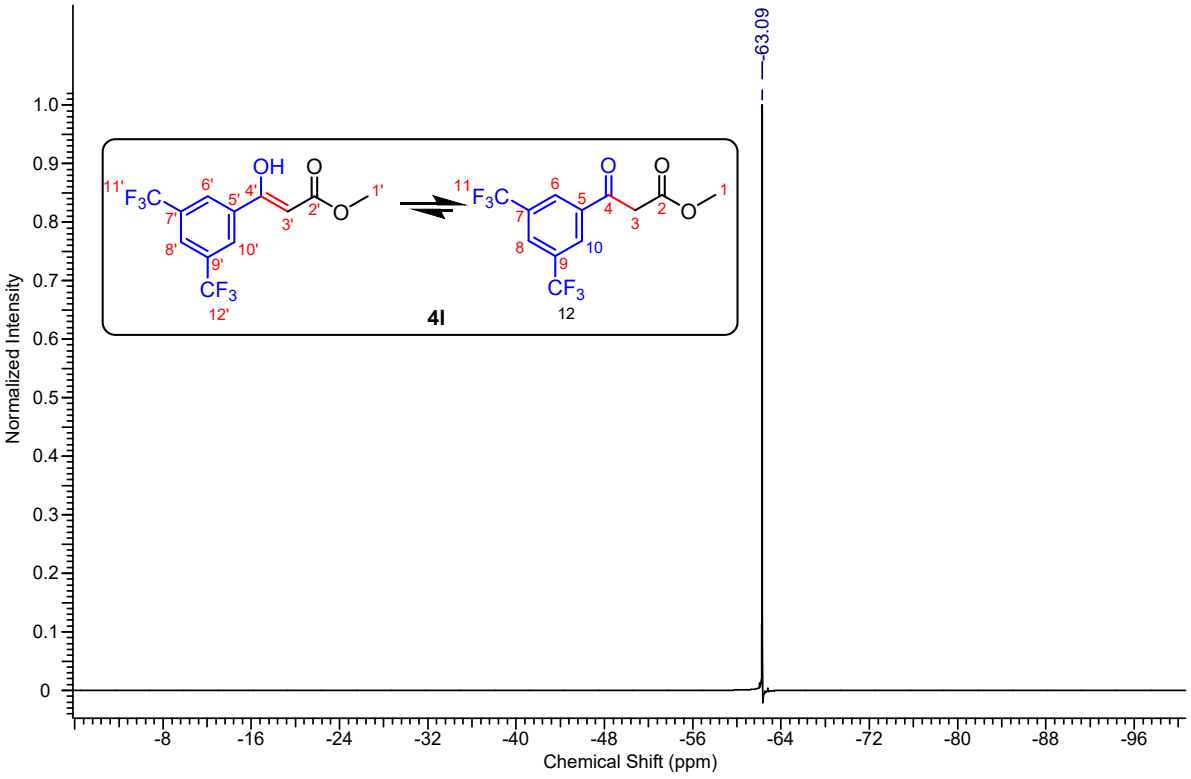
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 3aJ'



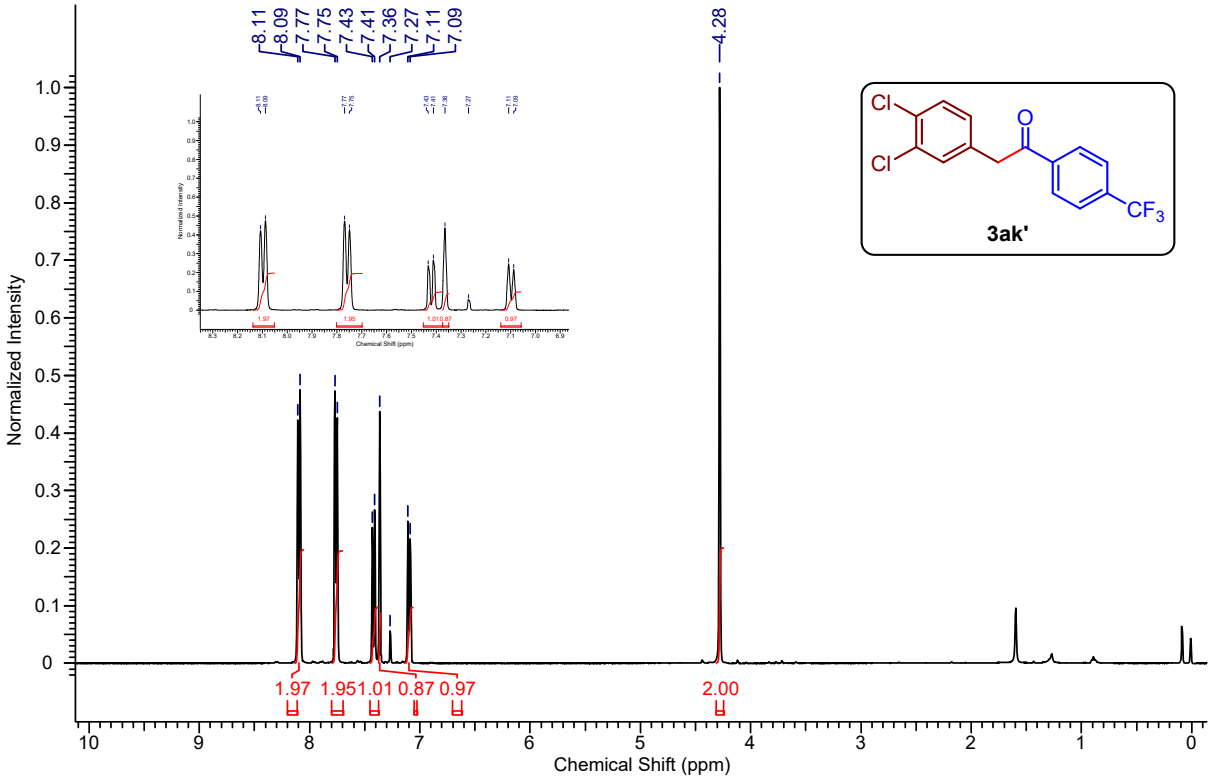
1H NMR (400 MHz, CDCl3) Spectrum of 4l



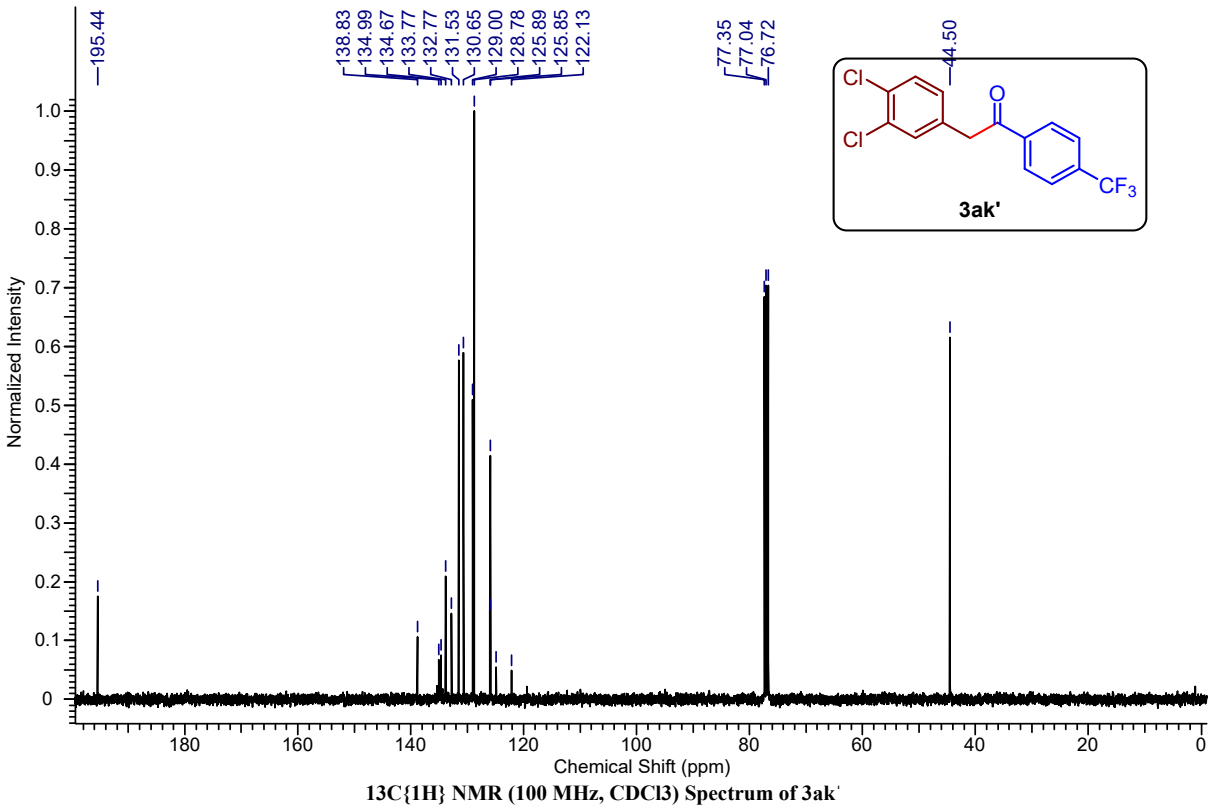
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 4l



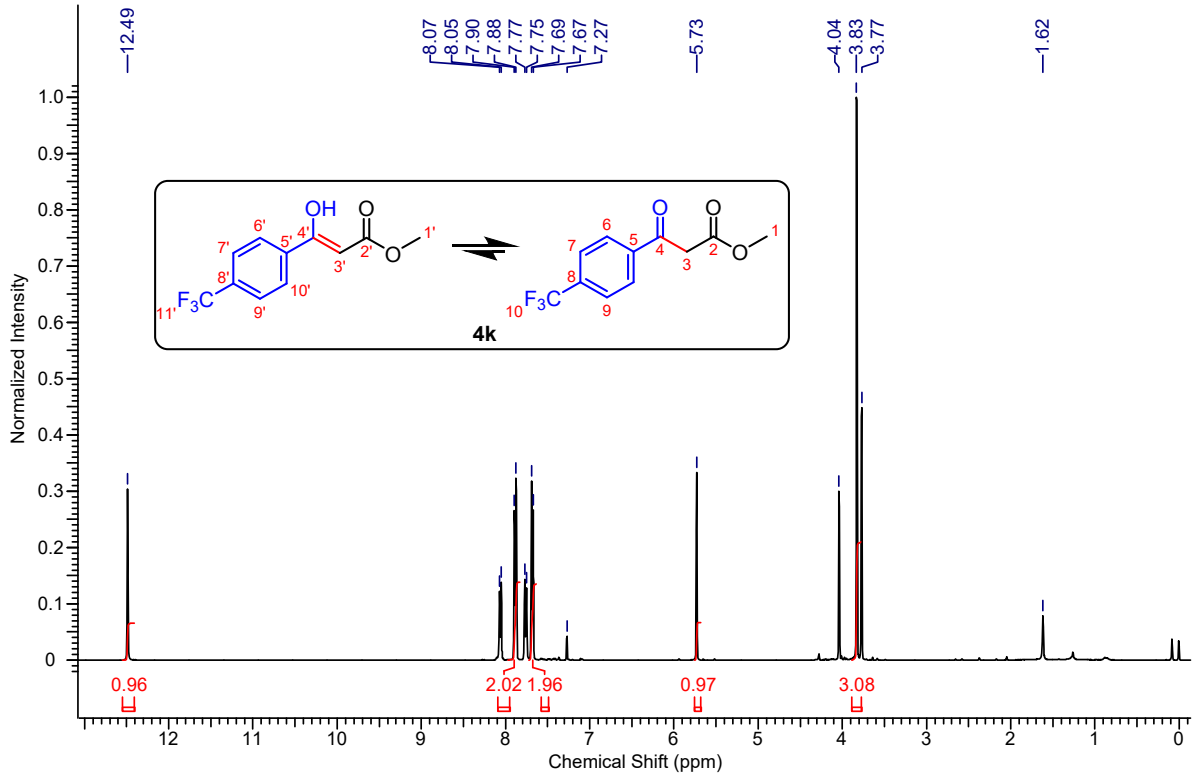
19F NMR (375 MHz, CDCl3) Spectrum of 4l



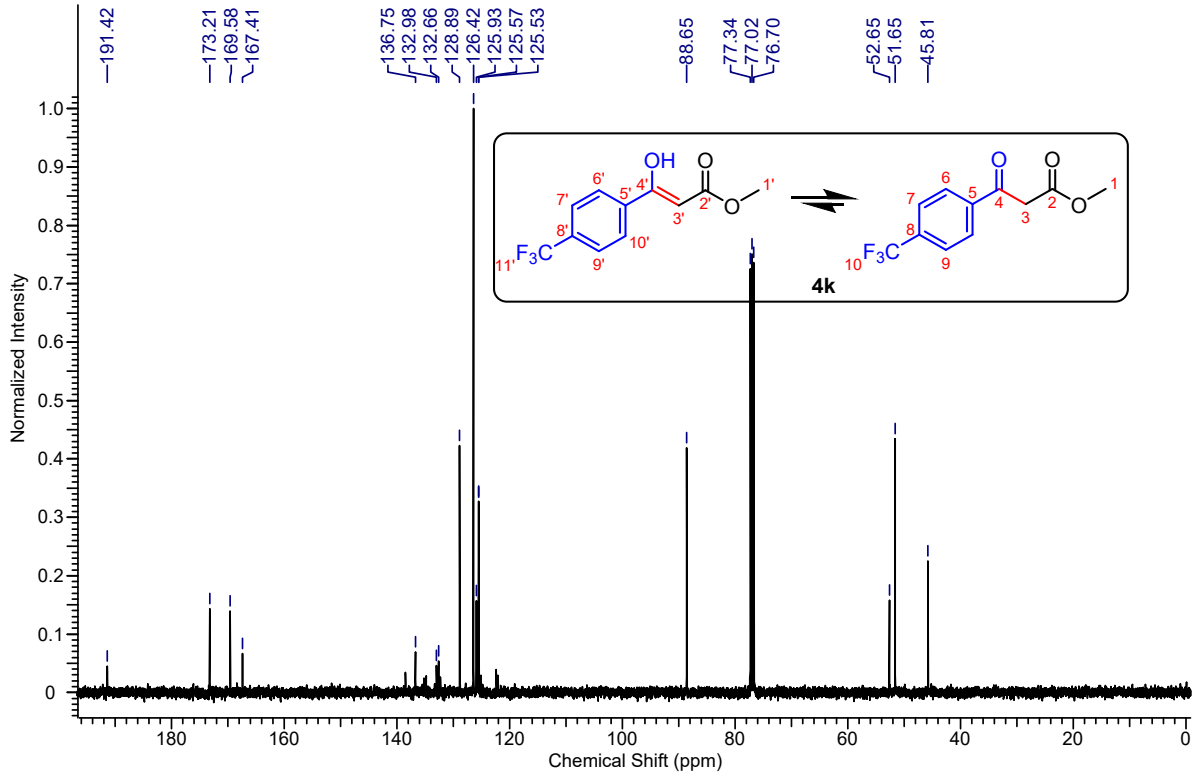
1H NMR (400 MHz, CDCl3) Spectrum of 3ai'



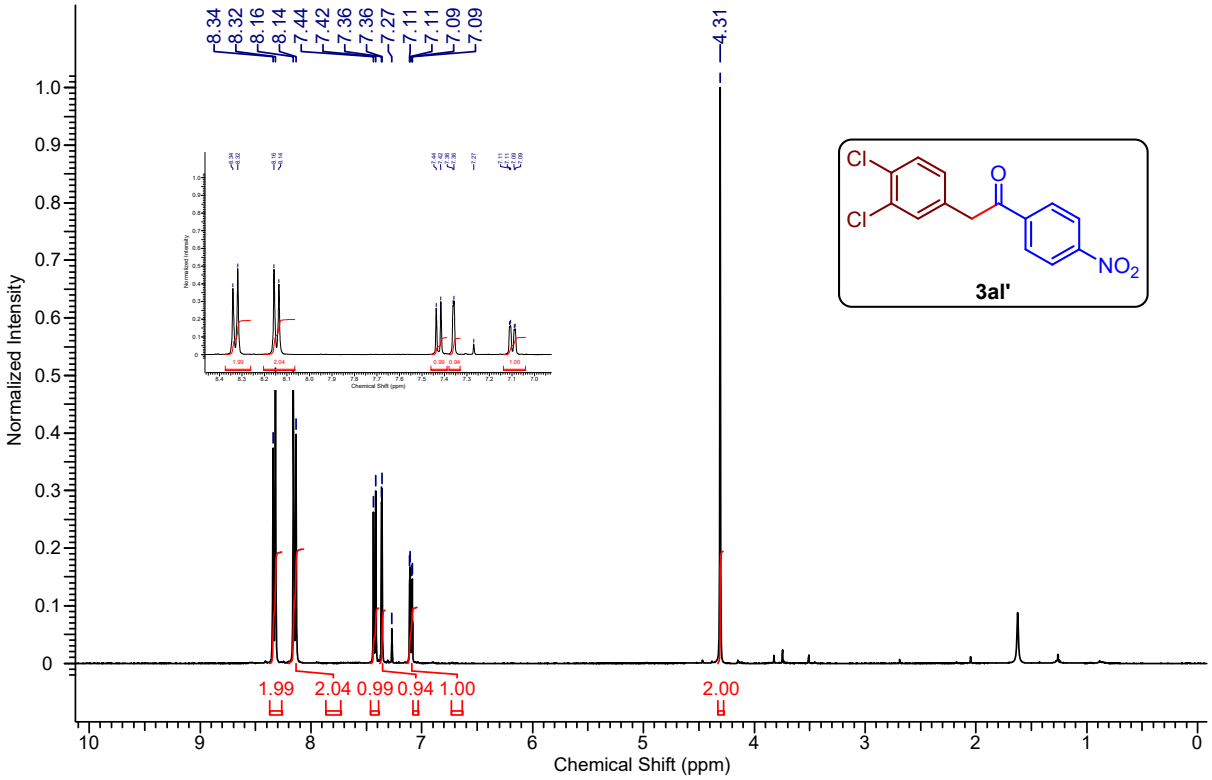
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 3ak'



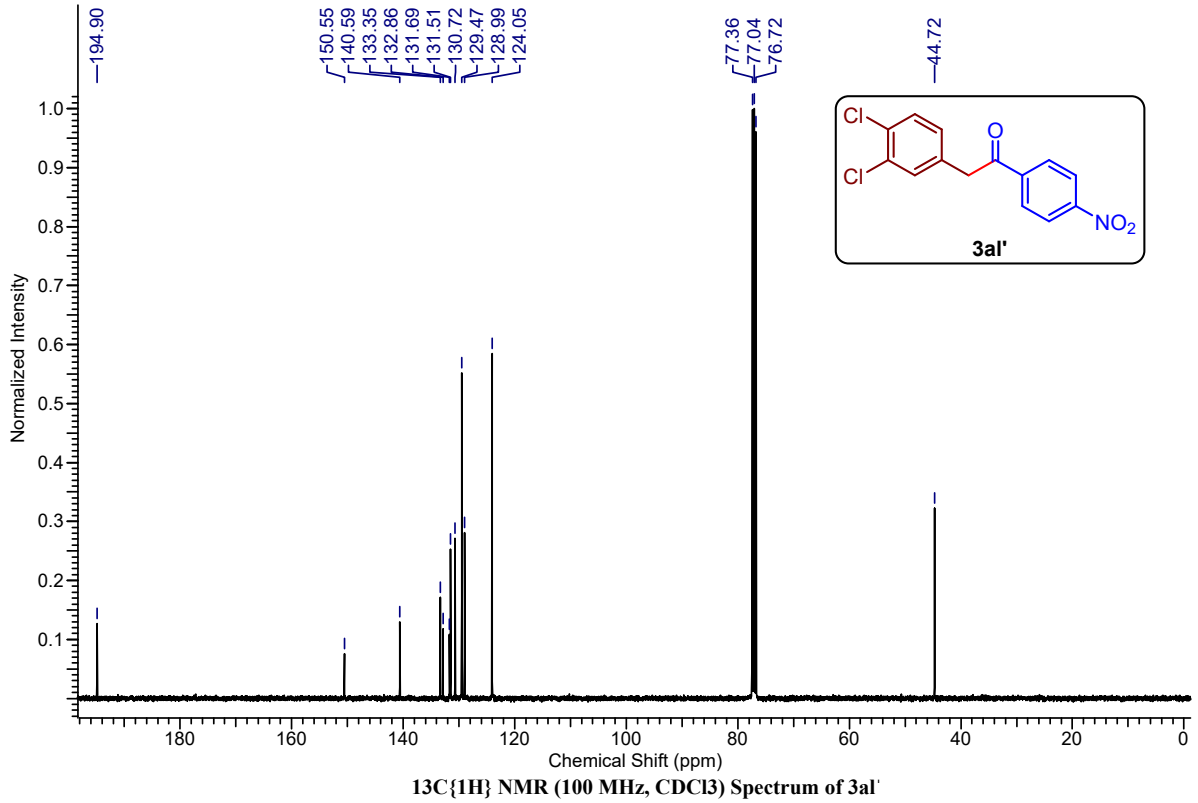
1H NMR (400 MHz, CDCl3) Spectrum of 4k



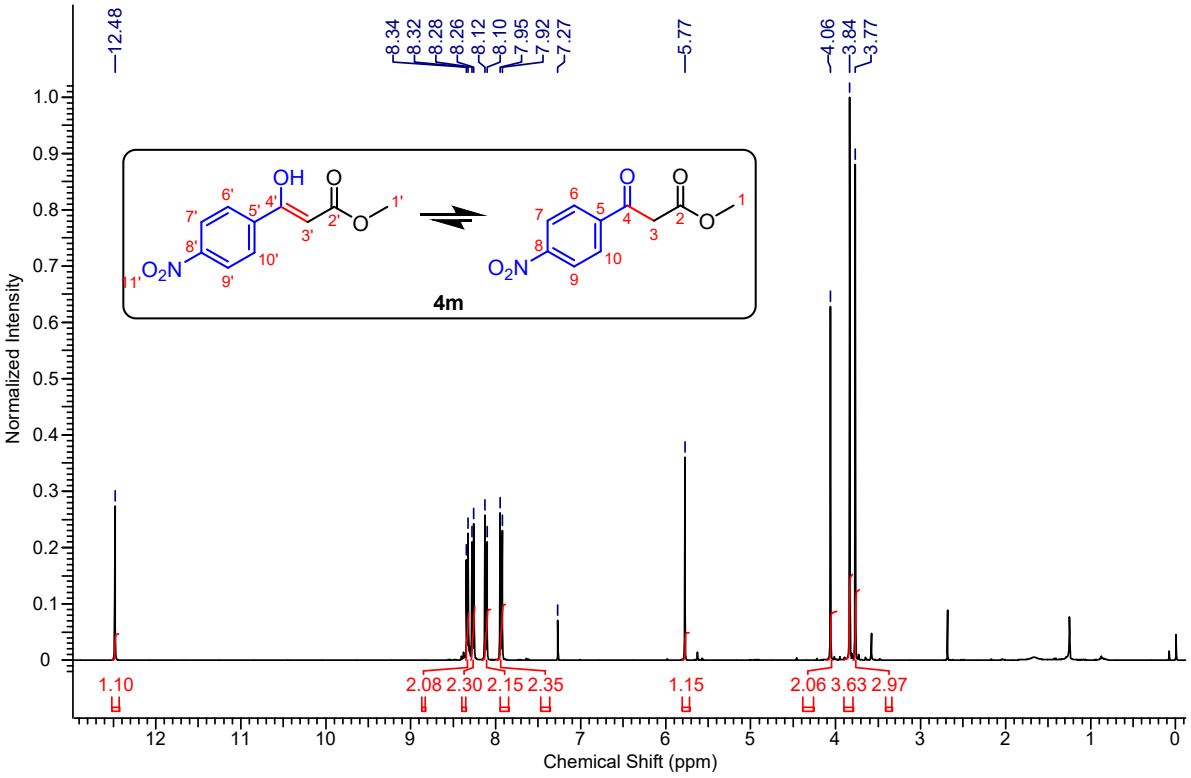
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 4k



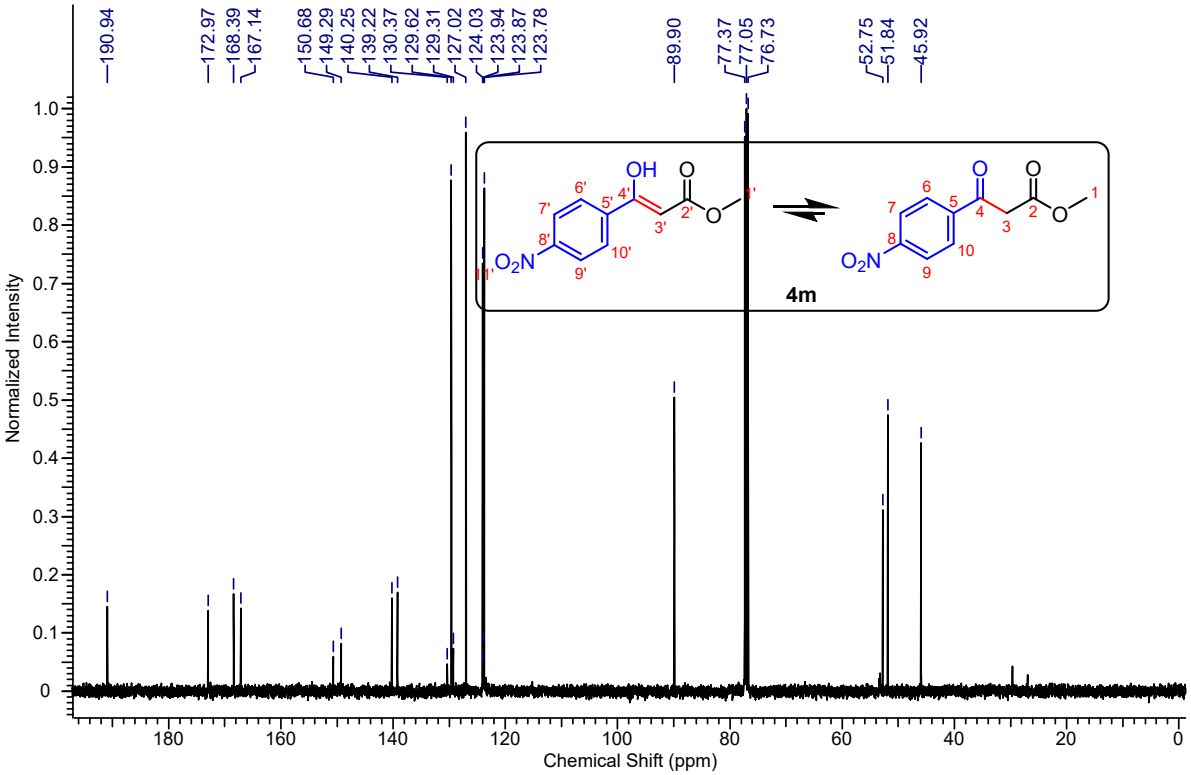
1H NMR (400 MHz, CDCl3) Spectrum of 3al'



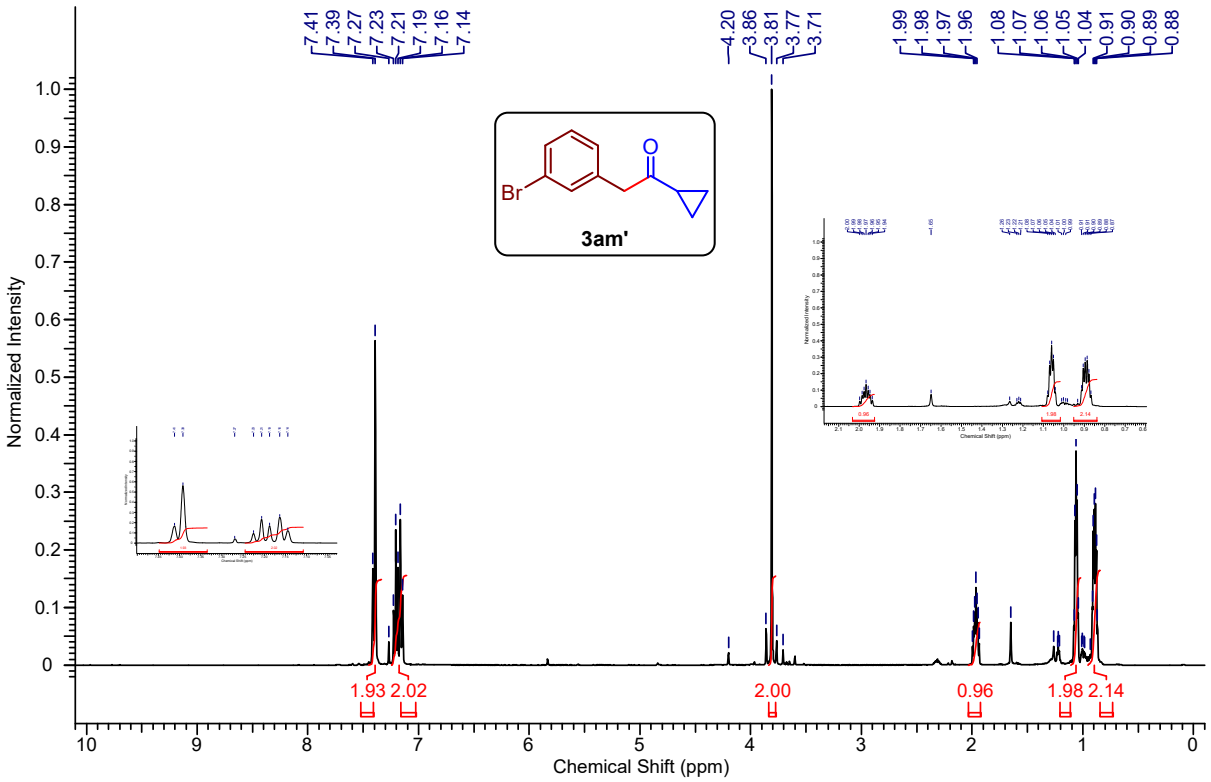
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 3al'



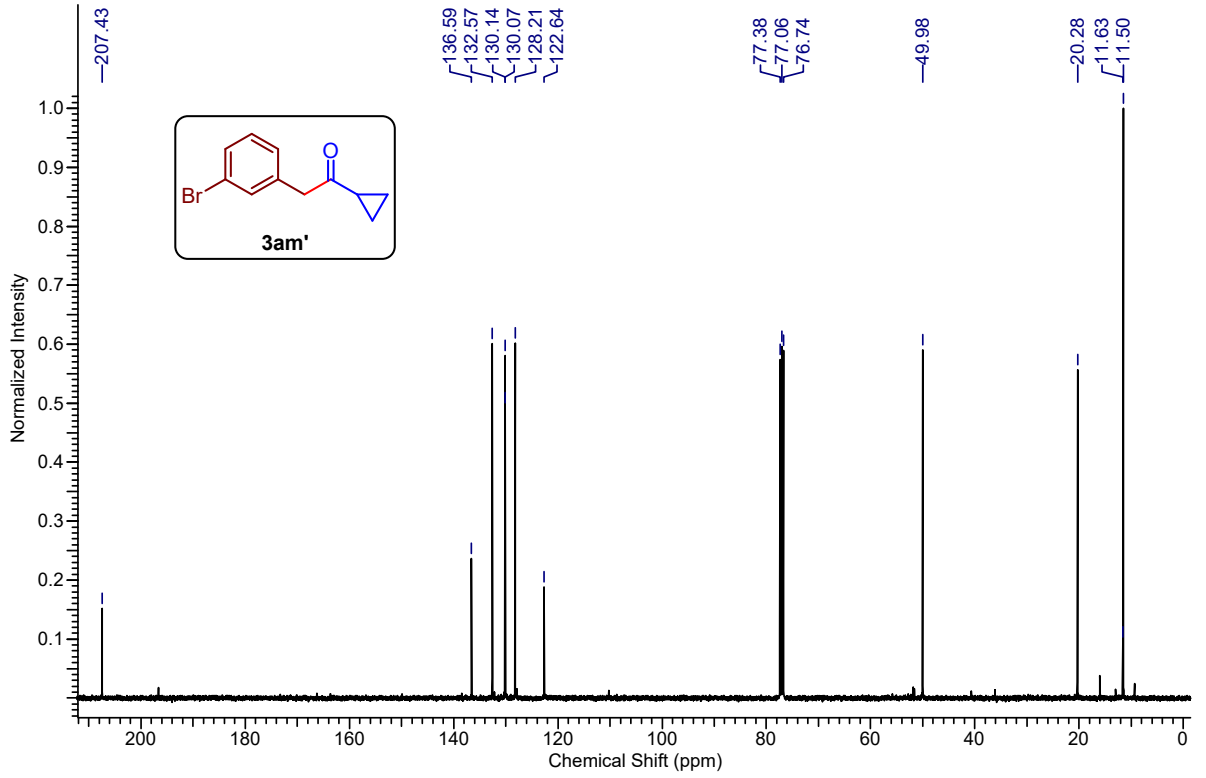
1H NMR (400 MHz, CDCl3) Spectrum of 4m



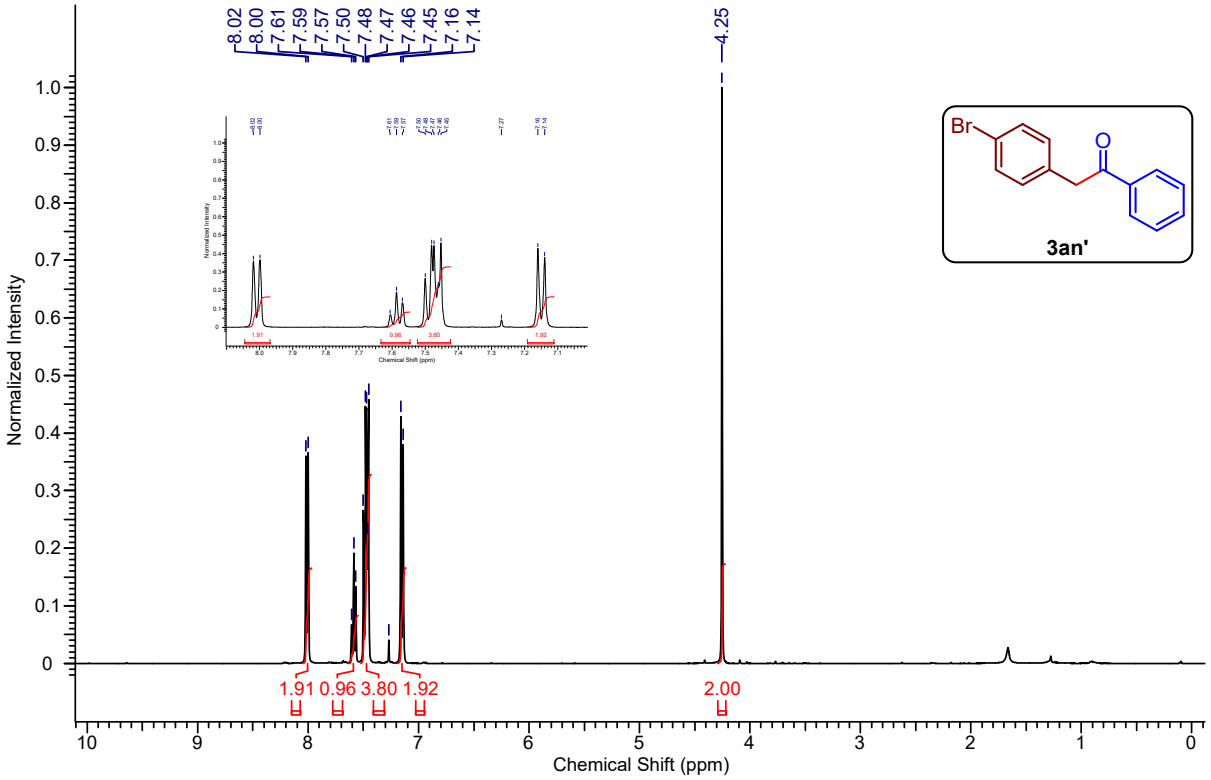
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 4m



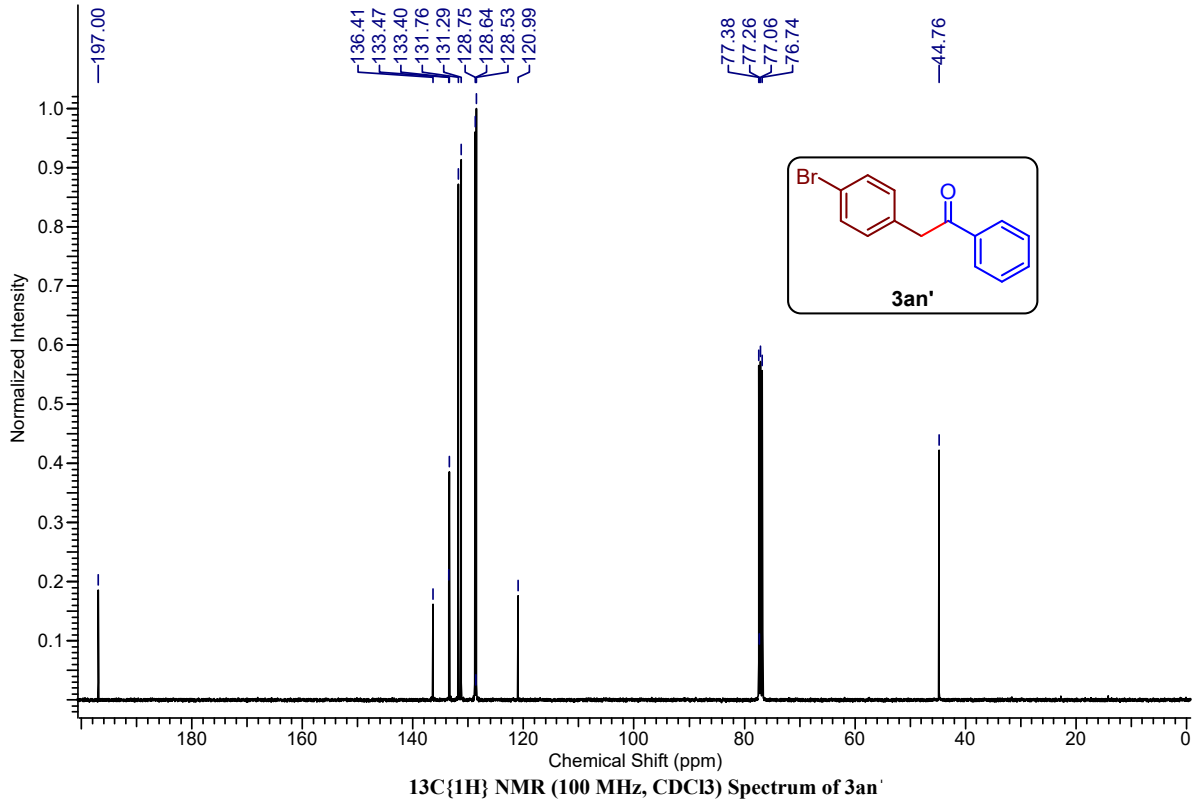
1H NMR (400 MHz, CDCl3) Spectrum of 3ao'



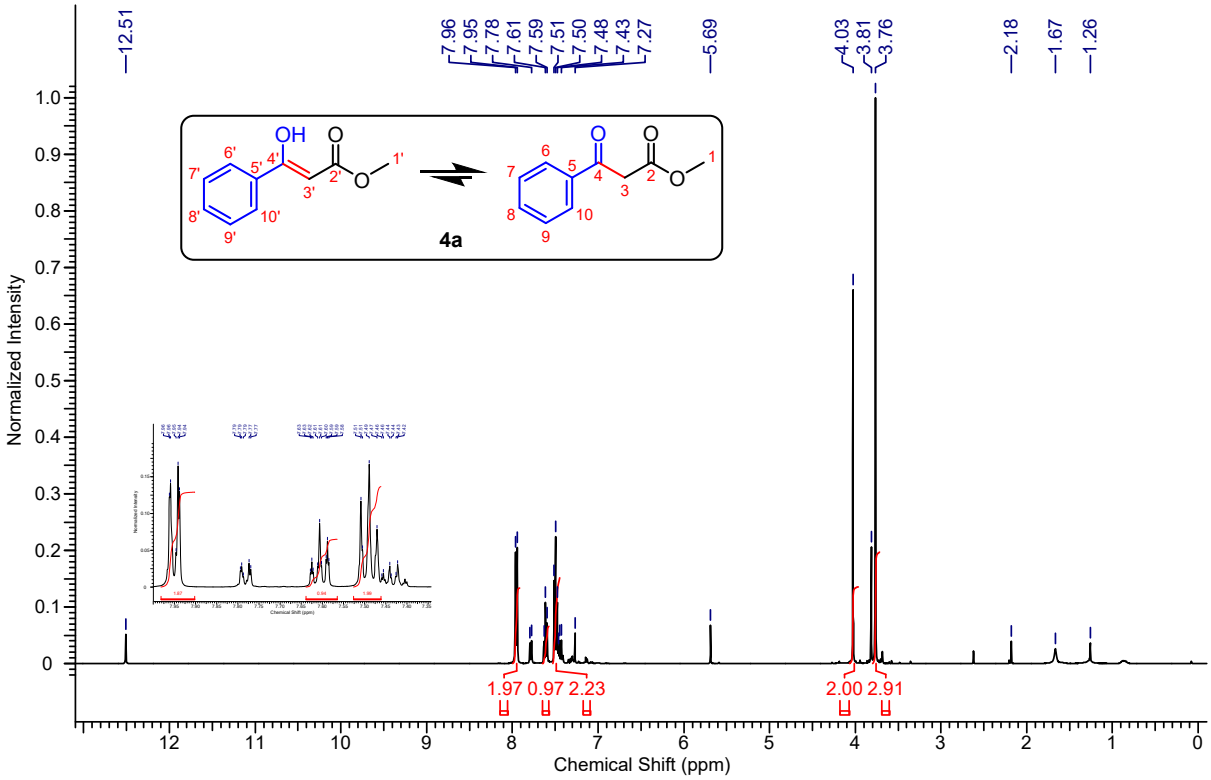
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 3am'



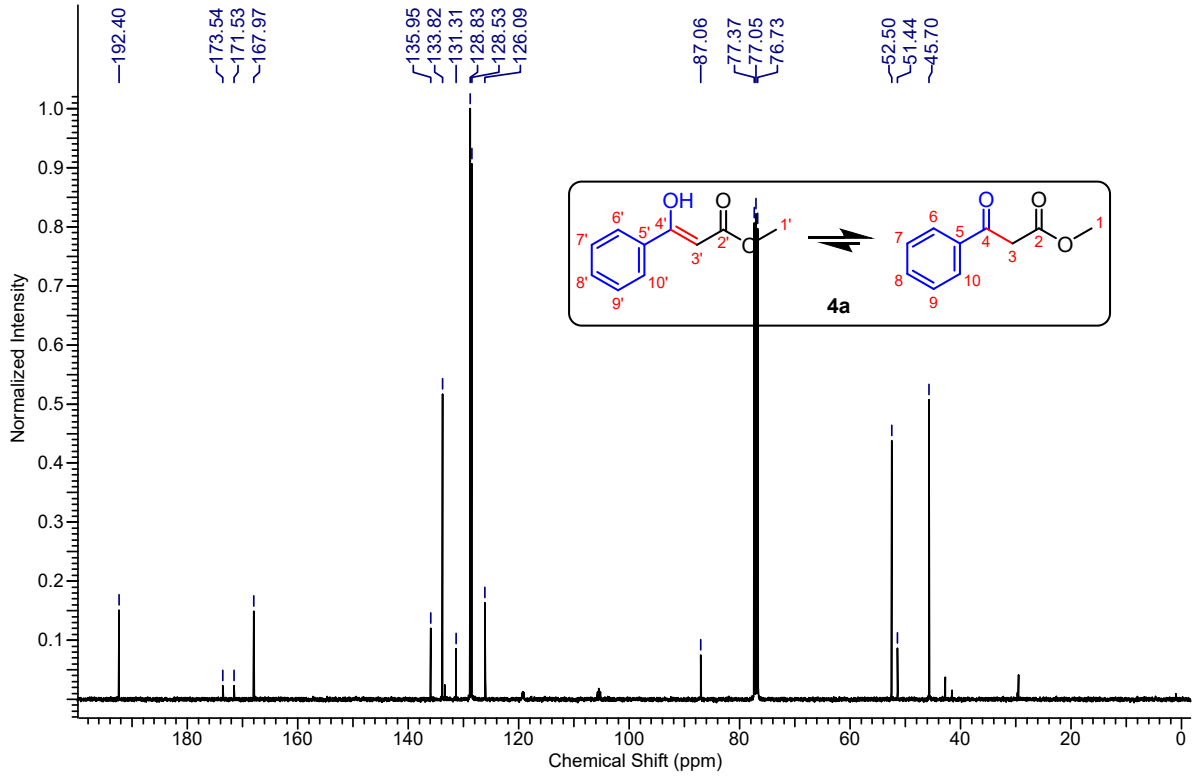
1H NMR (400 MHz, CDCl3) Spectrum of 3an'



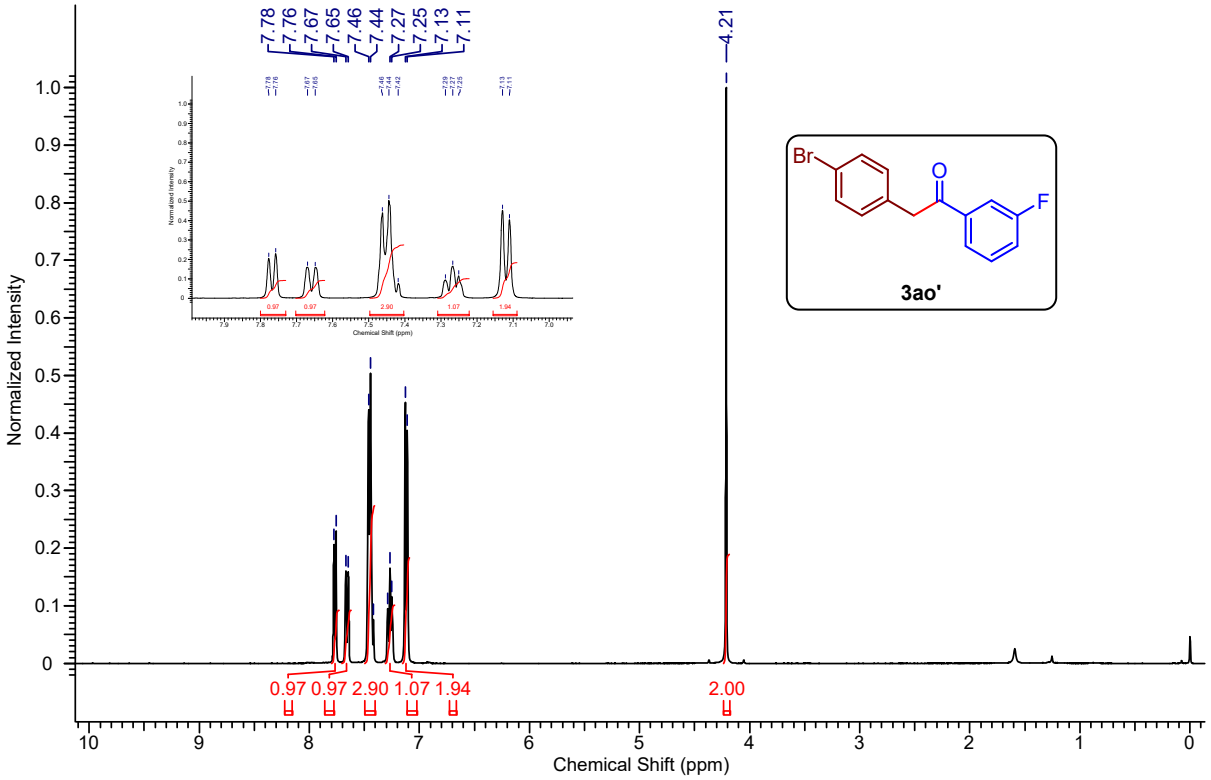
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 3an'



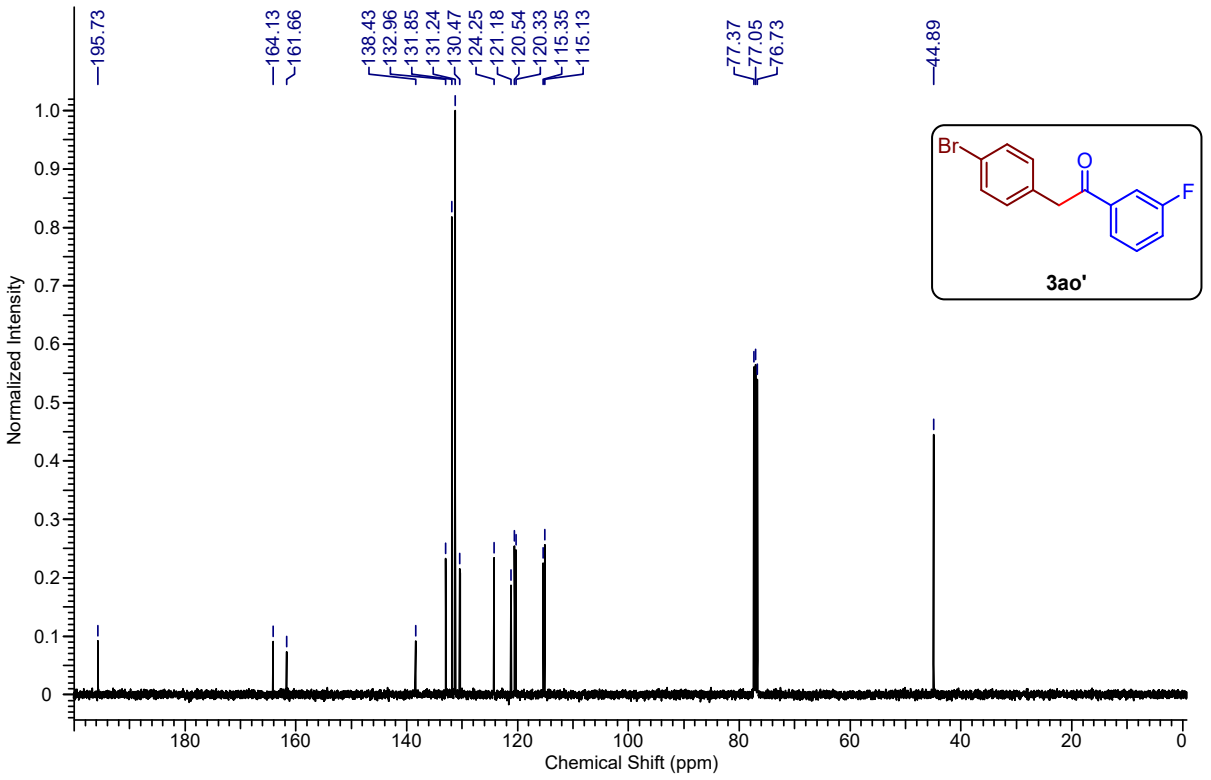
1H NMR (400 MHz, CDCl3) Spectrum of 4a



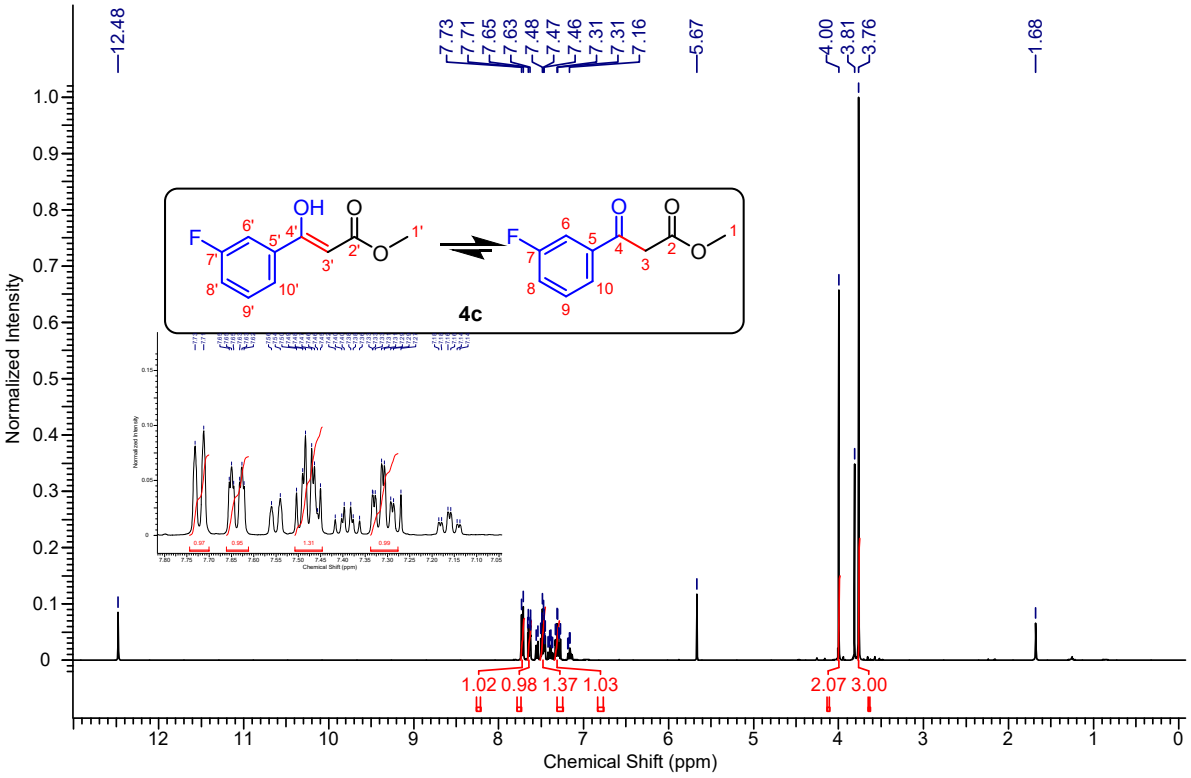
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 4a



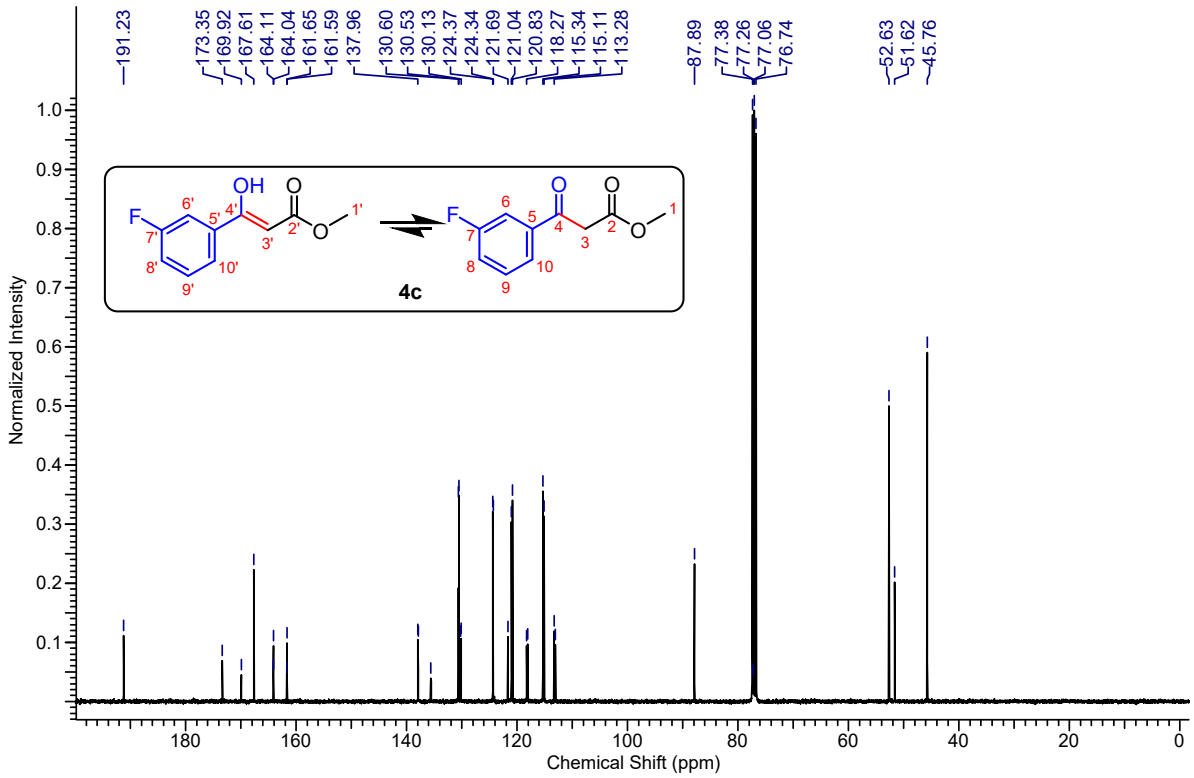
1H NMR (400 MHz, CDCl3) Spectrum of 3ao'



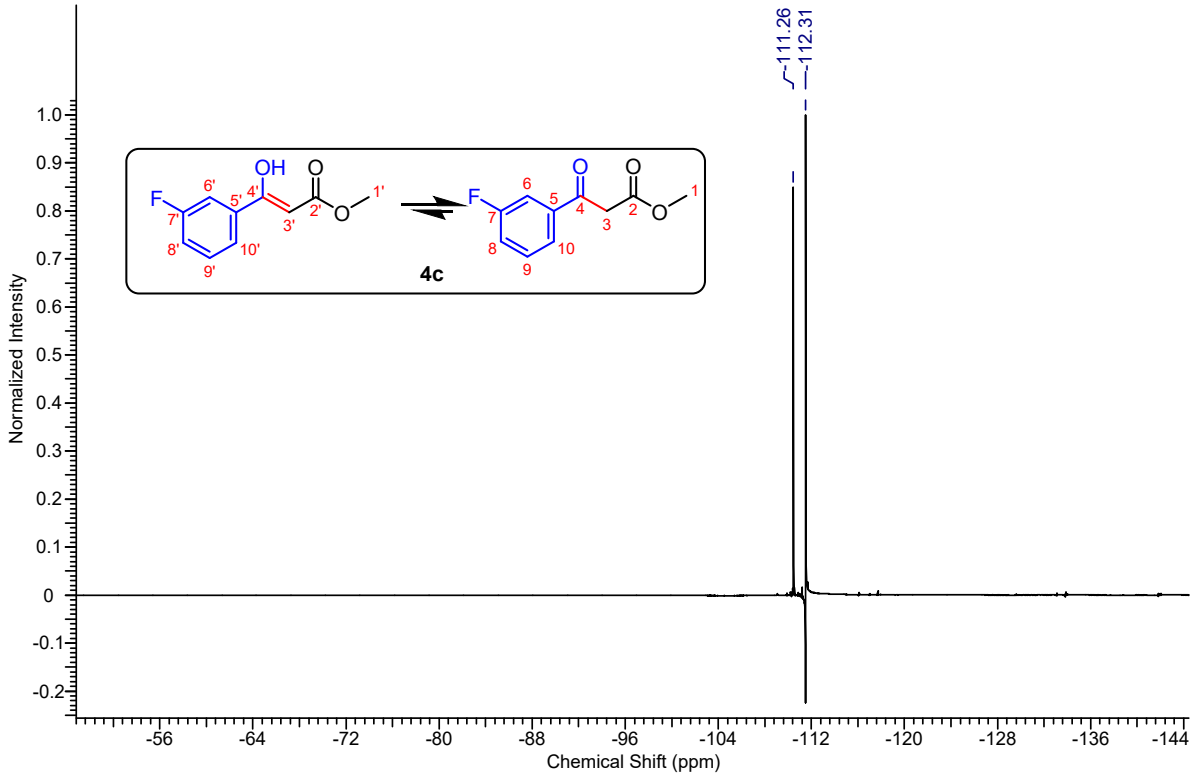
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 3ao'



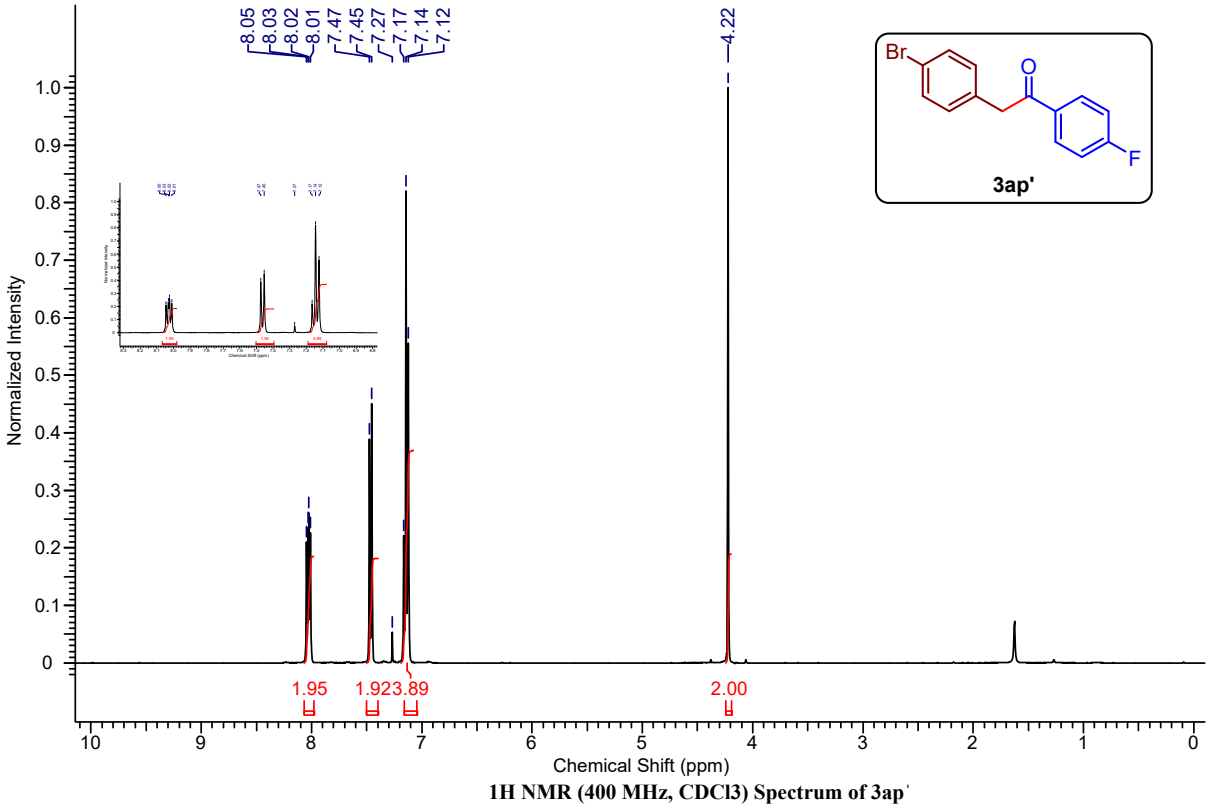
1H NMR (400 MHz, CDCl3) Spectrum of 4c



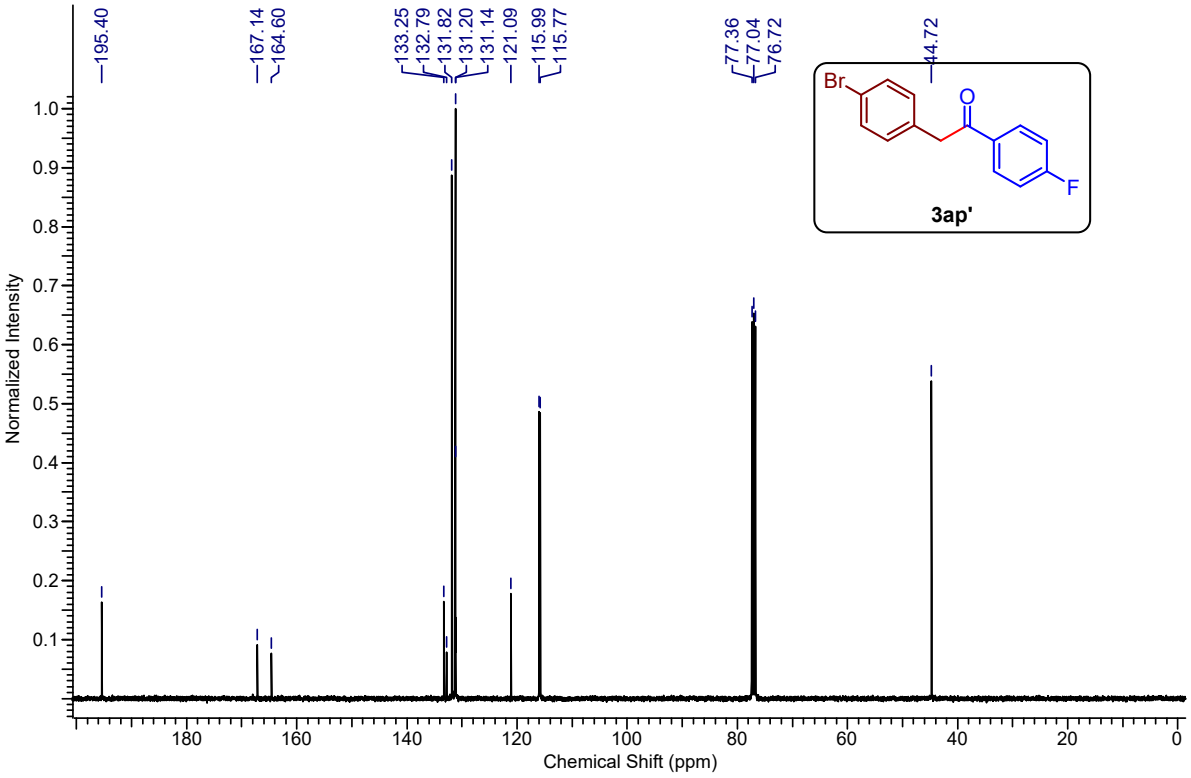
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 4c



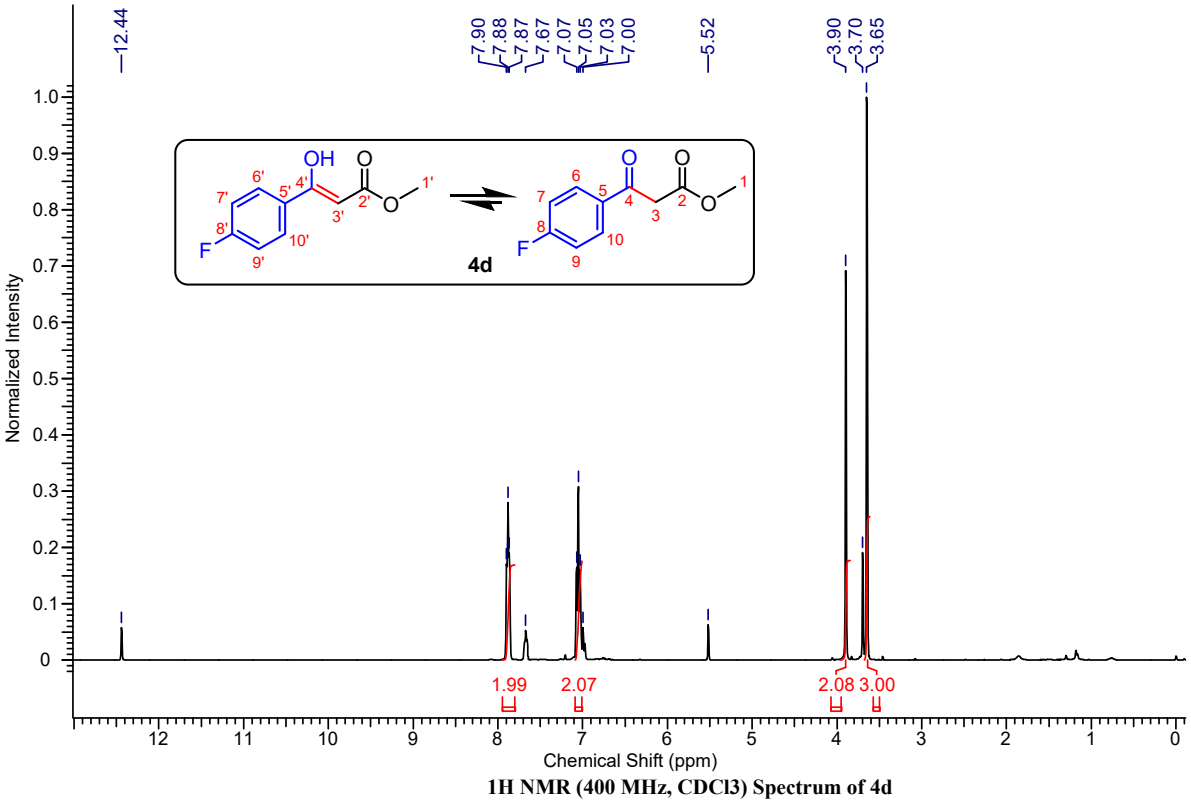
19F NMR (375 MHz, CDCl3) Spectrum of 4c



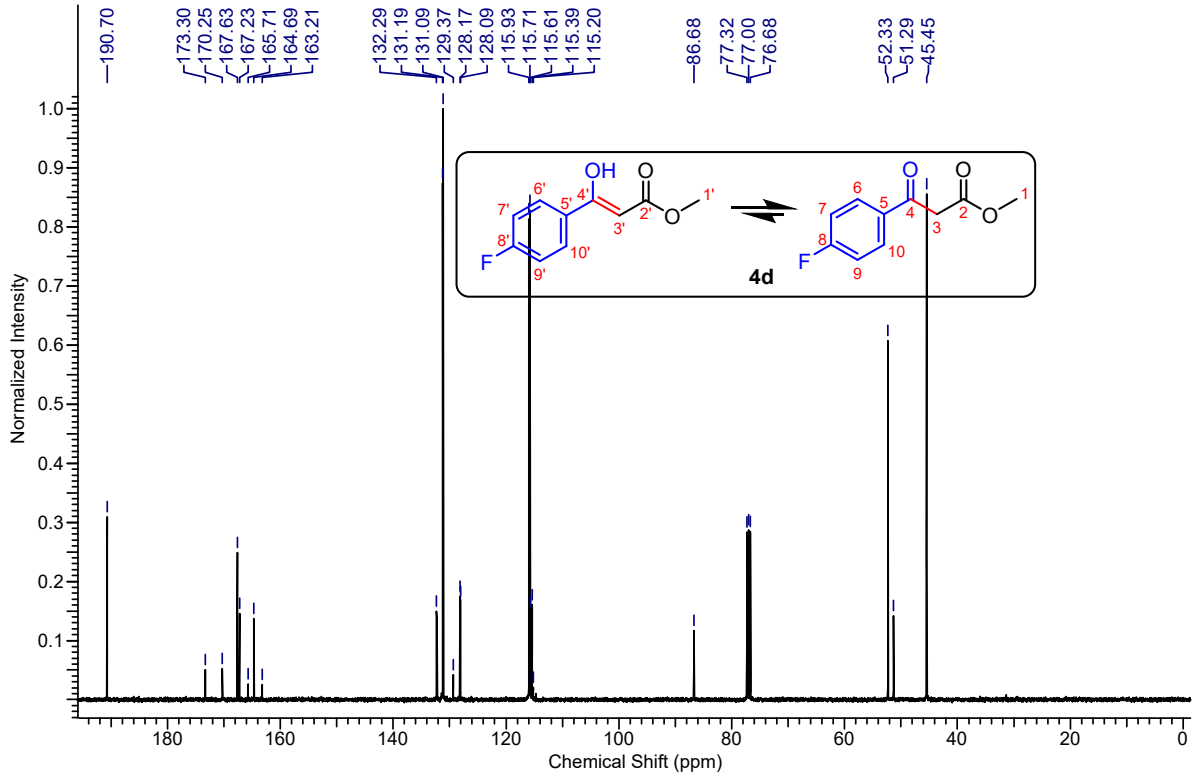
1H NMR (400 MHz, CDCl3) Spectrum of 3ap'



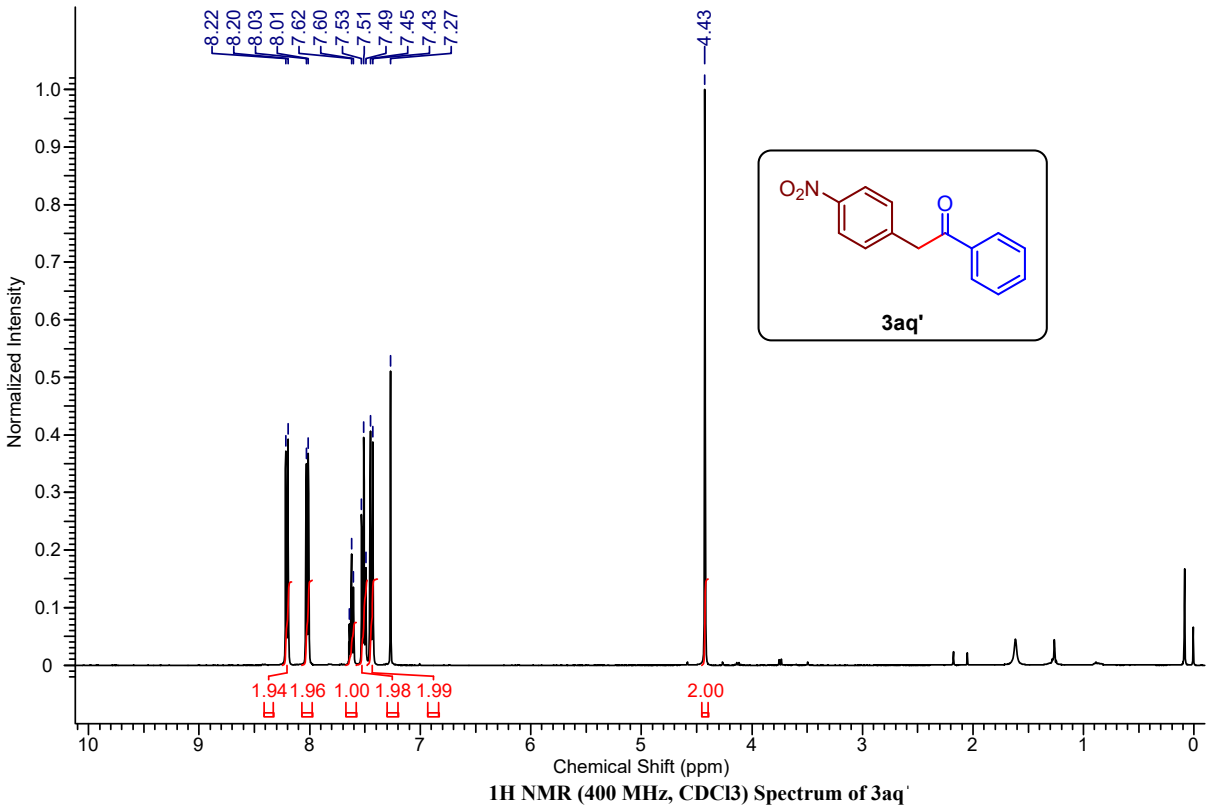
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 3ap'



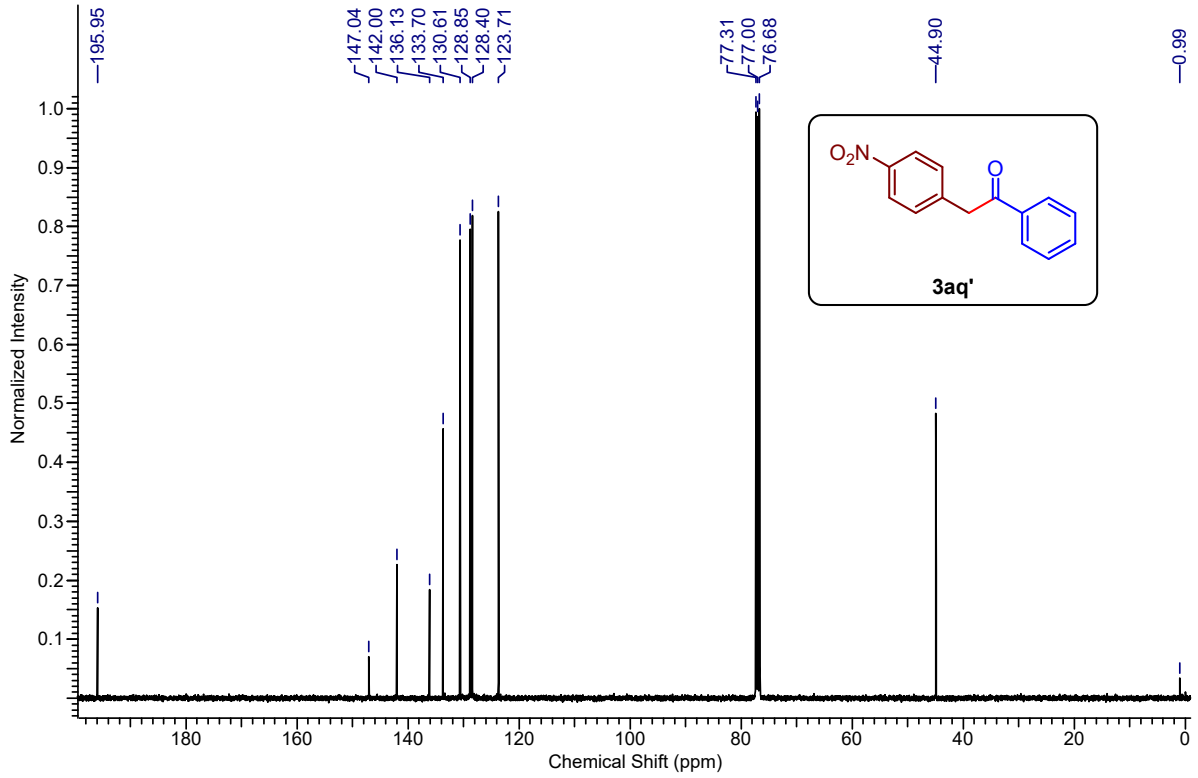
1H NMR (400 MHz, CDCl3) Spectrum of 4d



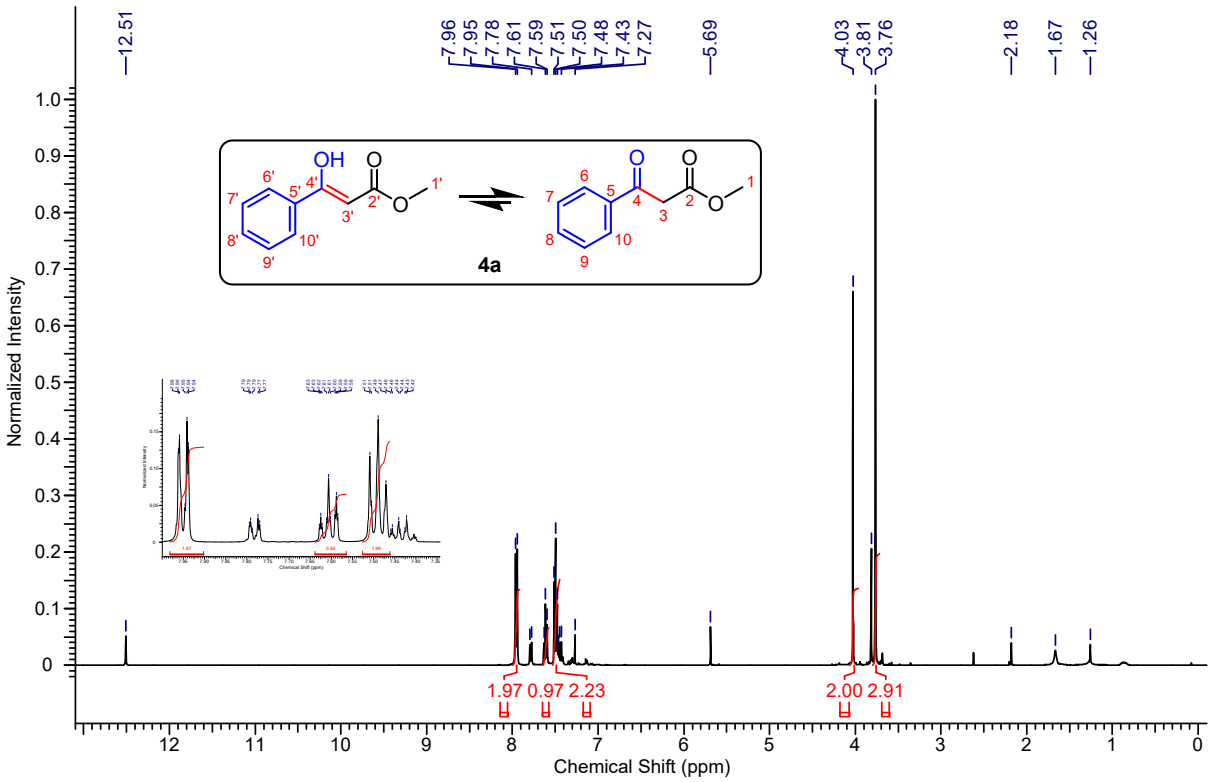
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 4d



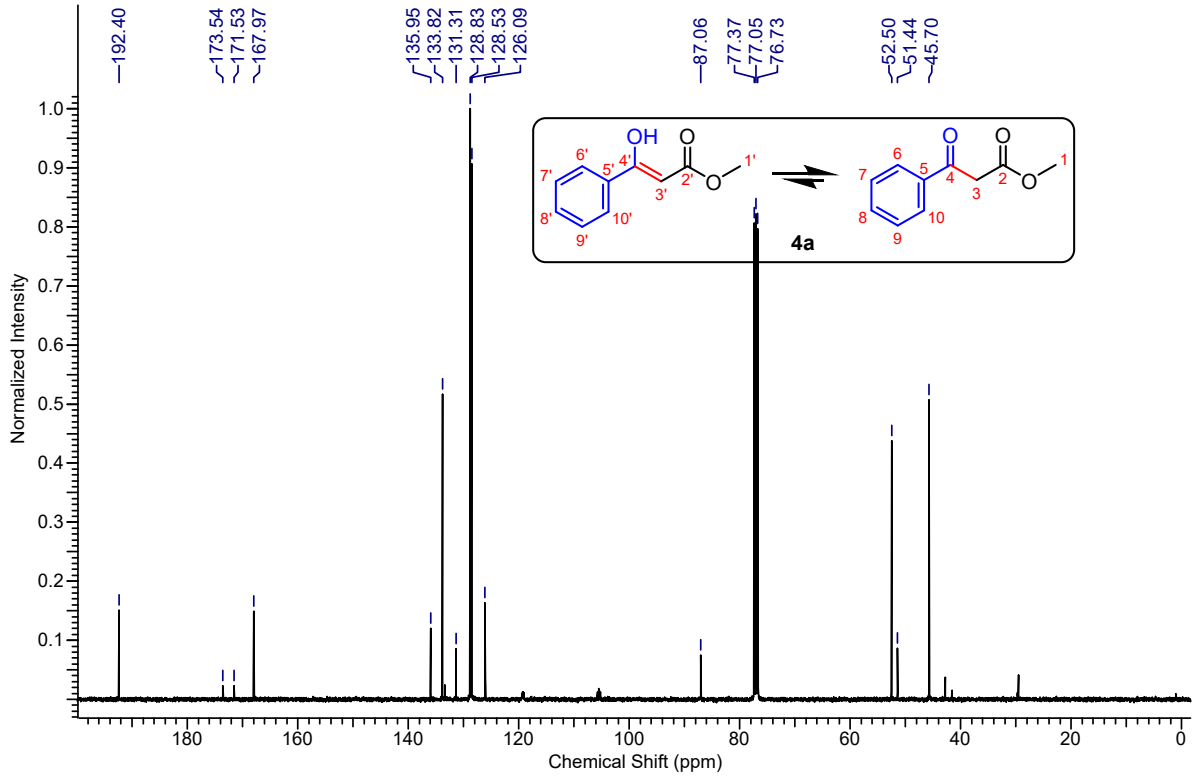
1H NMR (400 MHz, CDCl3) Spectrum of 3aq'



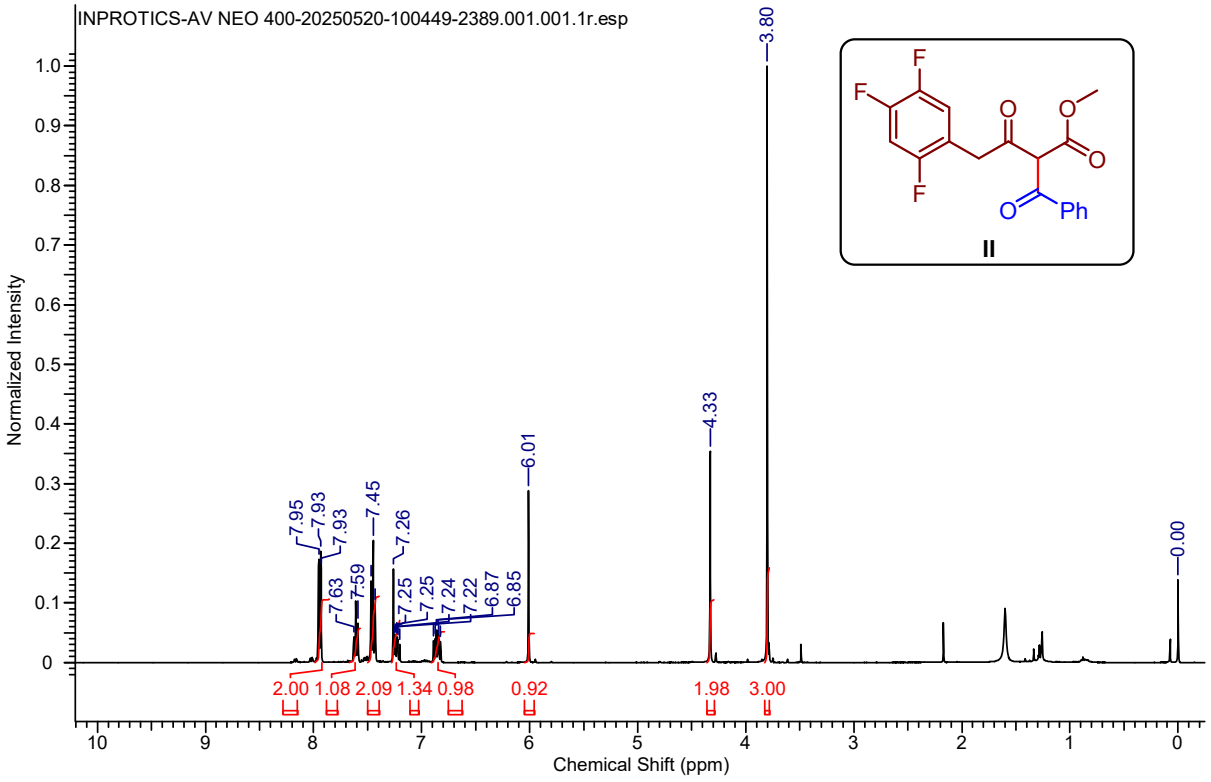
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 3aq'



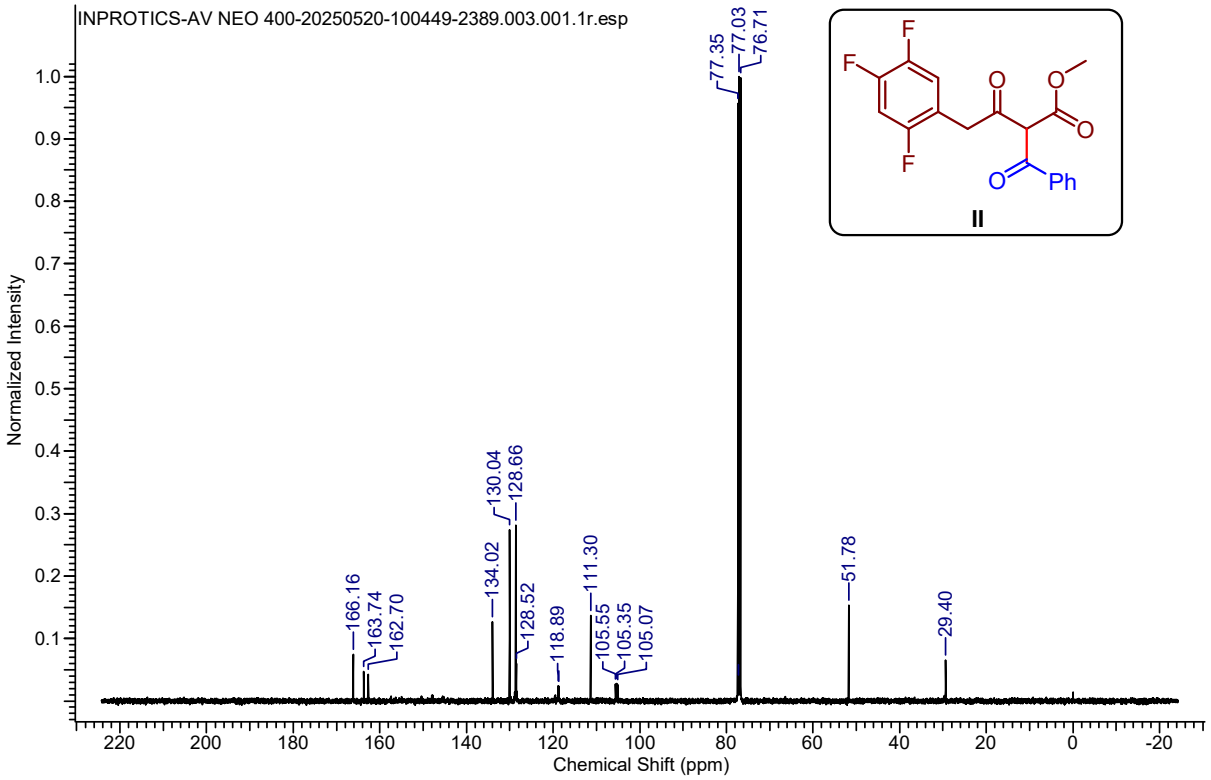
1H NMR (400 MHz, CDCl3) Spectrum of 4a



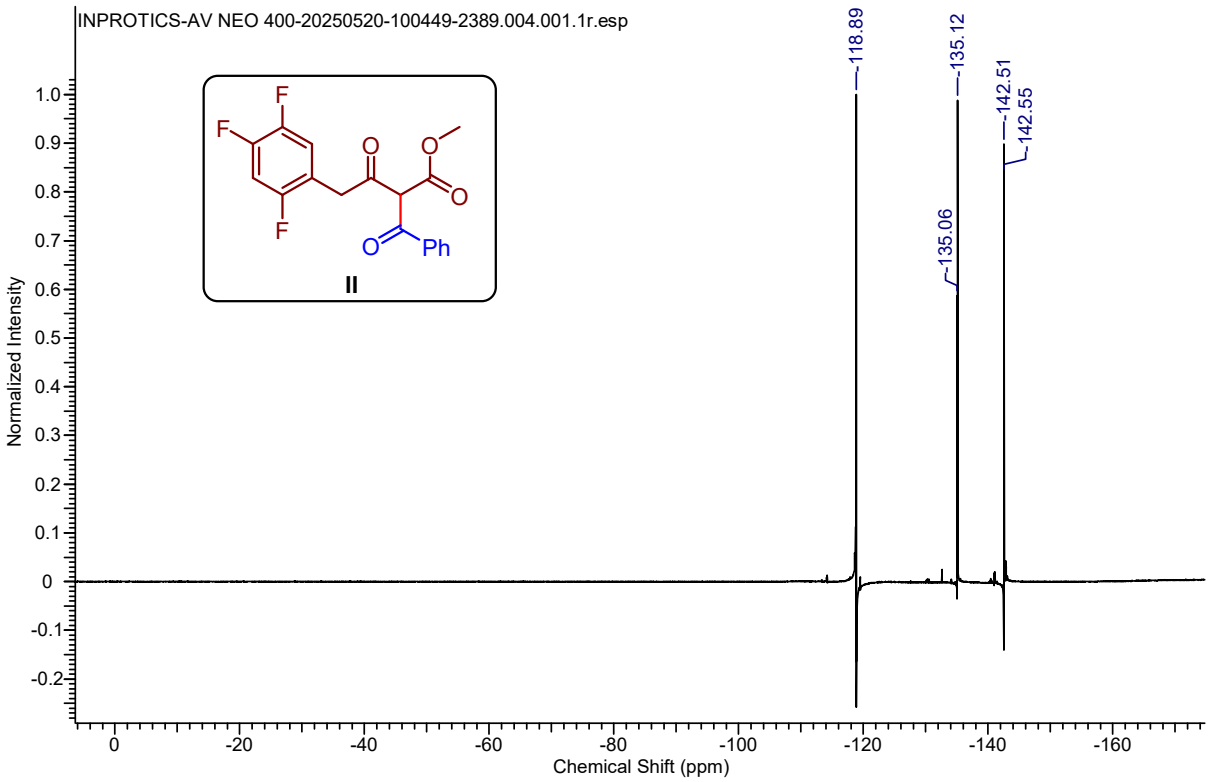
13C{1H} NMR (100 MHz, CDCl3) Spectrum of 4a



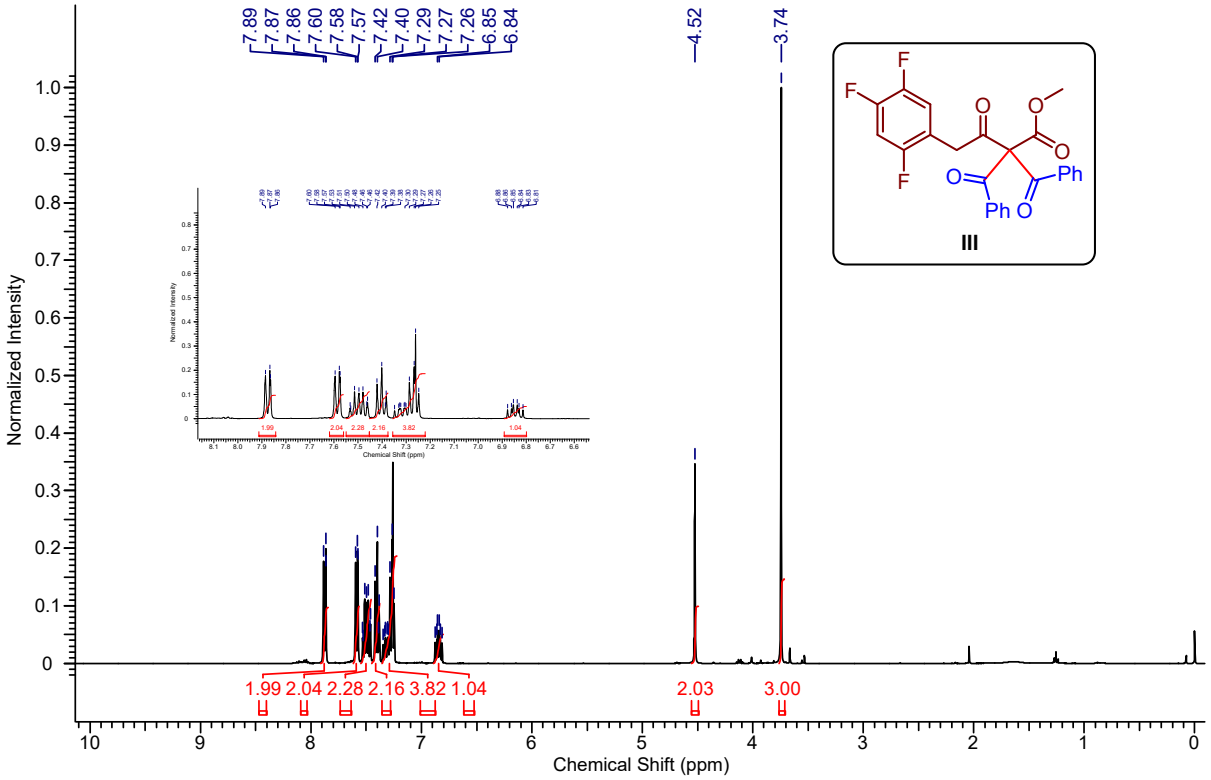
1H NMR (400 MHz, CDCl3) Spectrum of intermediate II



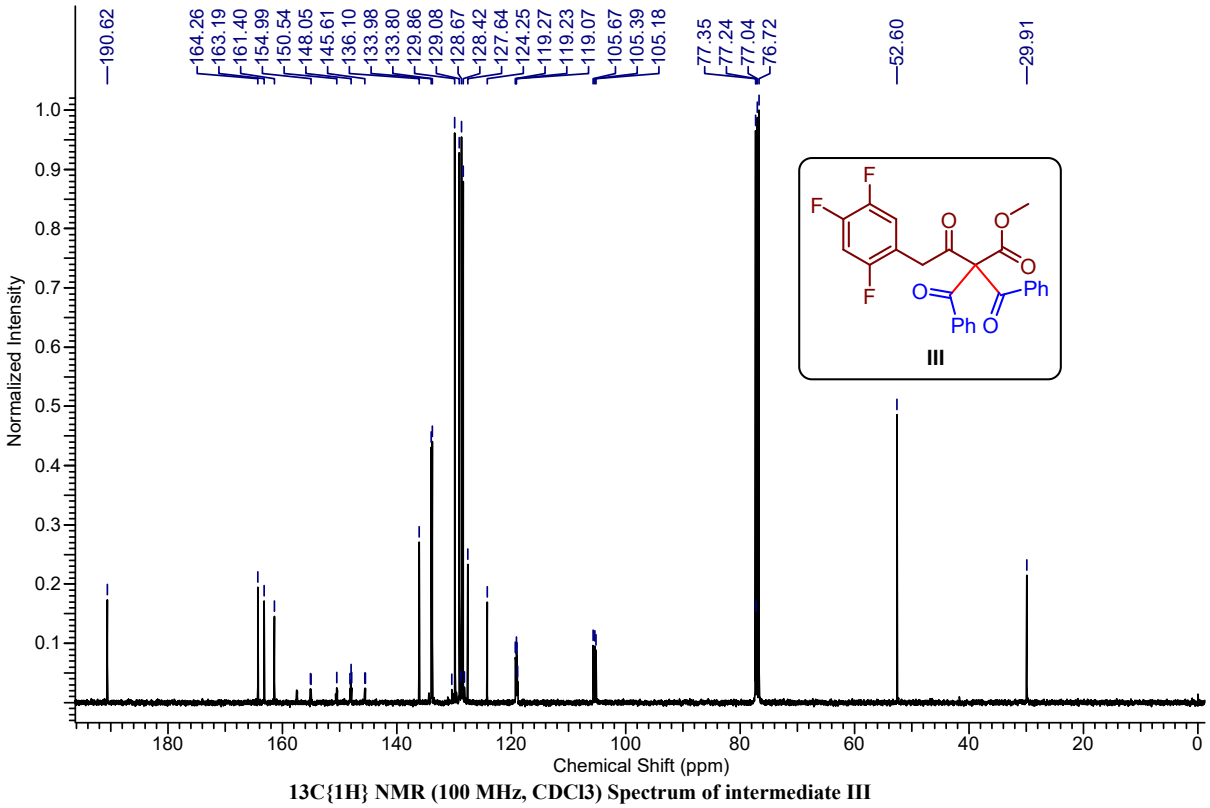
13C{1H} NMR (100 MHz, CDCl3) Spectrum of II



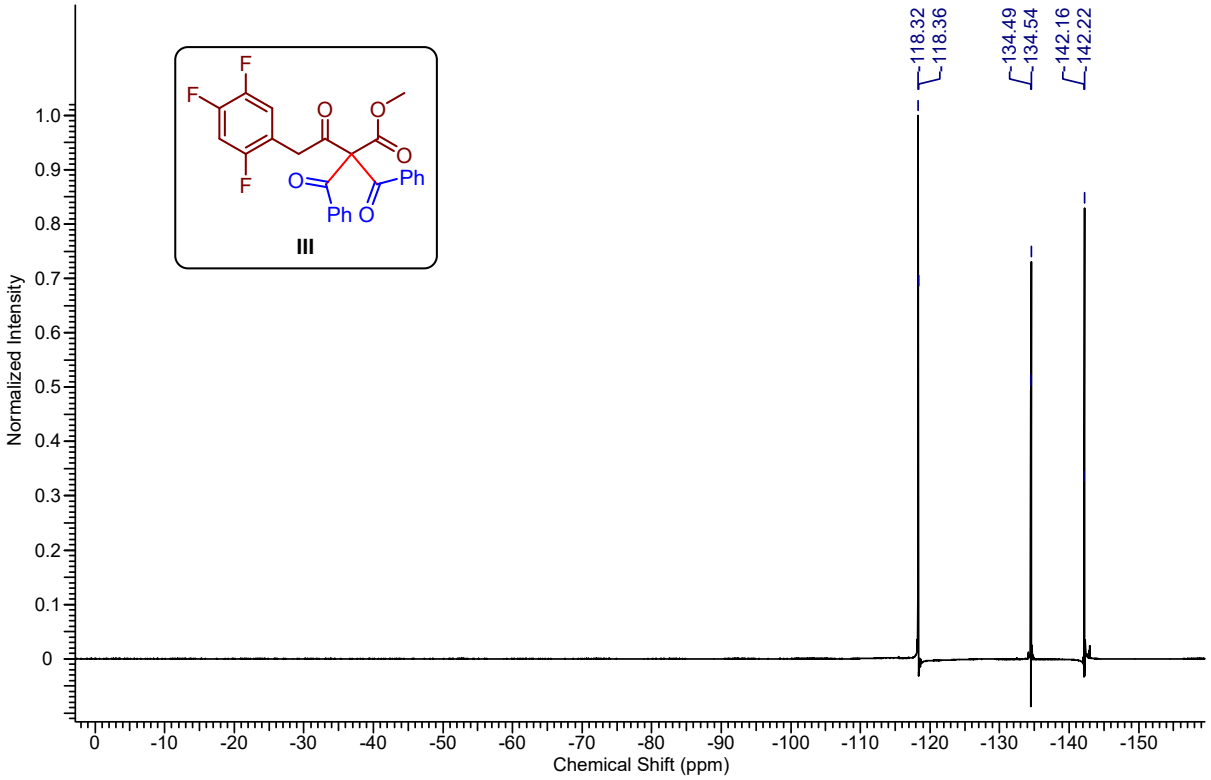
19F NMR (375 MHz, CDCl3) Spectrum of II



1H NMR (400 MHz, CDCl3) Spectrum of intermediate III

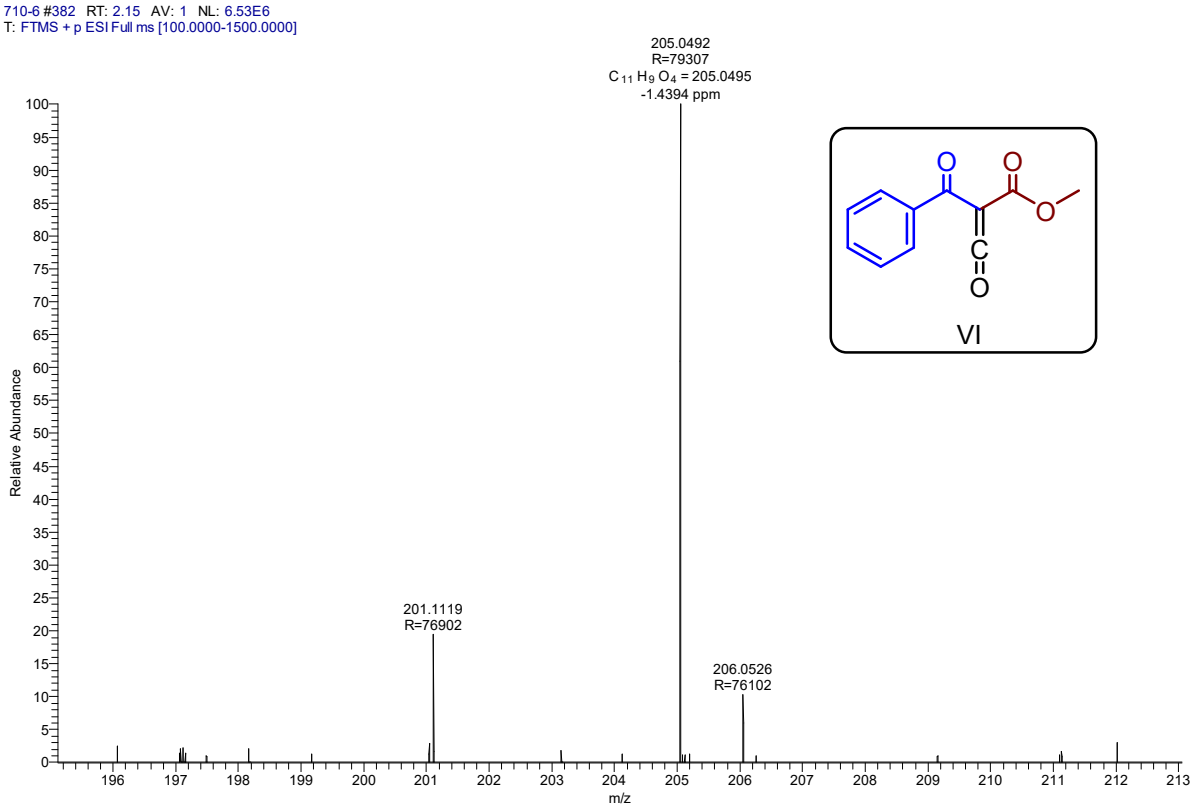


13C{1H} NMR (100 MHz, CDCl3) Spectrum of intermediate III



19F NMR (375 MHz, CDCl3) Spectrum of III

Control experiment HRMS data



HRMS data for compound VI

5. X-ray crystallographic data

SC-XRD: The single crystals of **ISSC218A**, **ISSC270A** and **ISSC276A** were obtained from the Ethyl acetate solvent by the slow evaporation method. The single crystal X-ray diffraction measurements were performed to determine the crystal structure at 100 K using APEX3 (Bruker, 2016**.** Bruker D8 VENTURE Kappa Duo PHOTON II CPAD) diffractometer having graphite-monochromatized (MoKα (0.71073)). The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of unit cell parameters and an orientation matrix were calculated from 36 frames, and the cell refinement was performed by SAINT-Plus (Bruker, 2016). An optimized strategy used for data collection consisted of different sets of φ and ω scans with 0.5° steps φ/ω. The data were collected with a time frame of 10 sec by setting the sample to detector distance fixed at 40 cm. All the data points were corrected for Lorentzian, polarization, and absorption effects using SAINT-Plus and SADABS programs (Bruker, 2016). SHELXS-97 (Sheldrick, 2008) was used for structure solution, and full-matrix least-squares refinement on F^2.[3, 4] The molecular graphics of ORTEP diagrams were performed by Mercury software. The crystal symmetry of the components was cross-checked by running the cif files through PLATON (Spek, 2020) software and notified that no additional symmetry was observed. The Encifer software was used to correct the cif files.

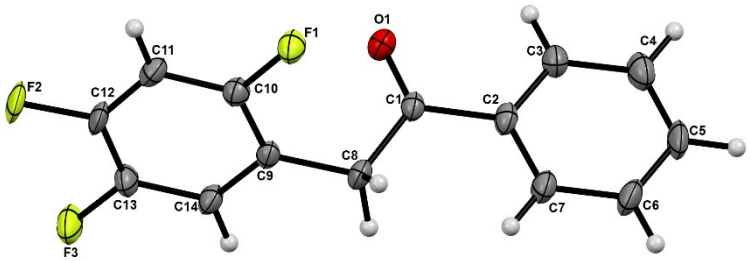


Figure 1. ORTEP diagram of compound **ISSC218A**, the asymmetric unit contains one molecule of **ISSC218A**. Herein, the ellipsoids are drawn with a 50% probability.

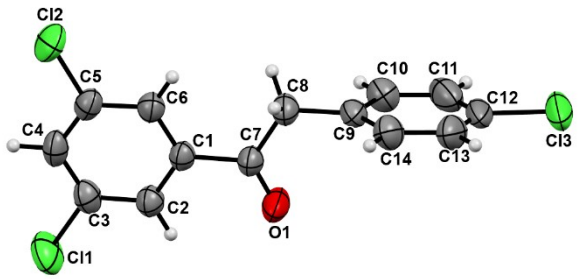


Figure 2. ORTEP diagram of compound **ISSC270A**, the asymmetric unit contains one molecule of **ISSC270A**. Herein, the ellipsoids are drawn with a 50% probability.

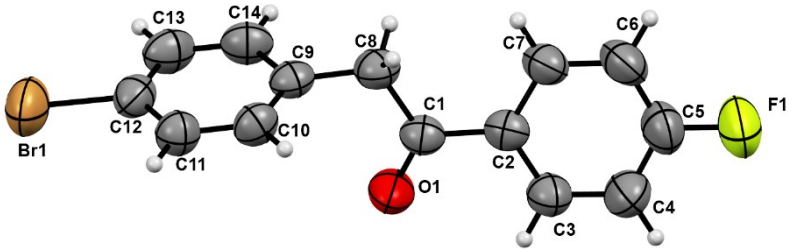


Figure 3. ORTEP diagram of compound **ISSC276A**, the asymmetric unit contains one molecule of **ISSC276A**. Herein, the ellipsoids are drawn with a 50% probability.

Table 1. Crystallographic information details of compounds, **ISSC218A, ISSC270A** and **ISSC276A**.

Crystal data	**ISSC218A**	**ISSC270A**	**ISSC276A**
Chemical formula	$C_{14}H_9F_3O$	$C_{14}H_9Cl_3O$	$C_{14}H_{10}BrFO$
Formula weight (M_r)	250.21	299.56	293.13
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P*2$_1$/*c*	*P*2$_1$/*n*	*C*$_2$/*c*
Te**M.P.** erature T (K)	100	298	298
a (Å)	12.821 (5)	11.9460 (3)	28.7831 (18)
b (Å)	8.643 (3)	8.9801 (2)	10.6380 (6)
c (Å)	10.145 (4)	12.6848 (3)	8.1073 (5)
α (°)	90	90	90
β (°)	98.224 (12)	99.683 (1)	99.183 (2)
γ (°)	90	90	90
Z	4	4	8
Volume (Å^3)	1112.6 (7)	1341.39 (6)	2450.6 (3)
Source of radiation	Mo*K*α (0.71073)	Mo*K*α (0.71073)	Mo*K*α (0.71073)
D_{calc} (g cm^{-3})	1.494	1.483	1.589
Crystal size (mm)	0.22 × 0.12 × 0.09	0.22 × 0.11 × 0.09	0.21 × 0.12 × 0.1
μ (mm^{-1})	0.13	0.67	3.35
Data collection			
Diffractometer	Bruker D8 VENTURE Kappa Duo PHOTON II CPAD	Bruker D8 VENTURE Kappa Duo PHOTON II CPAD	Bruker D8 VENTURE Kappa Duo PHOTON II CPAD
Absorption correction	Multi-scan (SADABS**.** Bruker, 2016)	Multi-scan (SADABS**.** Bruker, 2016)	Multi-scan (SADABS**.** Bruker, 2016)
No. of measured, independent and observed [I > 2σ(I)] reflections	11854, 2426, 1446	65556, 2831, 2632	66323, 2639, 1941
Theta range (°)	2.85-24.86	2.79-27.50	2.87-26.83
R_{int}	0.100	0.045	0.068
Refinement			
R[F^2 > 2σ (F^2)], wR(F^2)	0.064, 0.172	0.044, 0.109	0.046, 0.120
GOF on F^2	1.03	1.06	1.06
No. of independent reflections	2426	2831	2639

No. of parameters	164	164	154
F_000	512	608	
No. of restraints	0	0	0
H-atom treatment	Constr	Constr	Constr
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e A^{-3})	0.39, −0.30	0.37, −0.58	0.63, −0.55
CCDC number	2284931	2284932	2284933

Table 2. Hydrogen-bond geometry (A˚, °) of **ISSC218A** and **ISSC270A** are given as below.

Name of the co**M.P.** ound	*D*–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
ISSC218A	C8−H8A•••O1	0.9900	2.5600	3.507(4)	159
	C8−H8B•••O1	0.9900	2.4300	3.235(3)	138
	C14−H14•••O1	0.9500	2.5600	3.417(4)	150
ISSC270A	C4−H4•••O1	0.9300	2.3800	3.2068(1)	148

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