Ball-Milling Synthesis of α-Bromoacrylates from Solvent-free *In-Situ* Prepared Ethyl Diethylbromophosphonate

Supporting information

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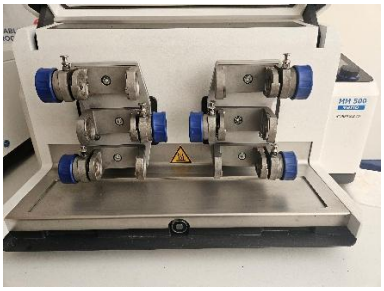
1- General Information

Mechanochemical reactions were performed with RETSCH® MIXER MILL MM 500. HWE reactions and Ullman type coupling functionalization reactions were carried out using 5 mm stainless steel balls and 1.5 mL steel jars. One-pot reactions were carried out using 7.5 mm stainless steel balls and 5 mL steel jars. Column chromatographies were carried out using silica gel (40-63 µm) supplied by VWR or Merck PTLC on silica gel 60 F254, 2 mm. Analytical thin layer chromatographies were performed on pre-coated silica gel aluminum plates with F-254 indicator (from Merck) and visualized by UV light (254 nm) and/or chemical stained with an aqueous $KMnO_4$ solution. ^{1}H (400 MHz), ^{13}C (101 MHz), ^{19}F (377 MHz) and ^{31}P NMR (162 MHz) spectra were recorded on a Bruker DXP 400 MHz spectrometer in $CDCl_3$. Chemical shifts (δ) are quoted in ppm relative to the residual solvent peak of $CDCl_3$ (^{1}H: δH = 7.26 ppm and ^{13}C: δC = 77.2 ppm). Coupling constants (*J*) are quoted in Hz. The following abbreviations were used to show multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, q = quadruplet, p = pentuplet, dd = doublet of doublets, ddd = doublet doublet doublet, td = triplet doublet, tt = triplet triplet, qd = quadruplet doublet. ***E*** and ***Z*** isomers were reported as a mixture and NMR peaks were attributed in ^{1}H and ^{19}F NMR. High Resolution Mass Spectrometry (HRMS) was carried out on a Waters LCP Premier XR spectrometer with a TOF analyzer.

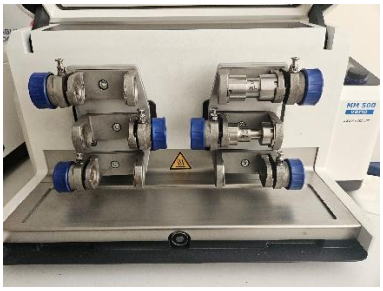
2- Materials

Cesium carbonate was purchased from Fluorochem and grinded using a mortar and pestle prior to the reaction. N-Bromosuccinimide (NBS) was purchased from Sigma Aldrich and recrystallized in water before use. N-Chlorosuccinimide (NCS), N-Iodosuccinimide (NIS), triethylphosphonoacetate, all the aldehydes derivatives were purchased from Fluorochem, Sigma Aldrich, Acros Organics, Fisher scientific, Alfa aesar, TCI.

MM500 vario :



MM 500 without Jars

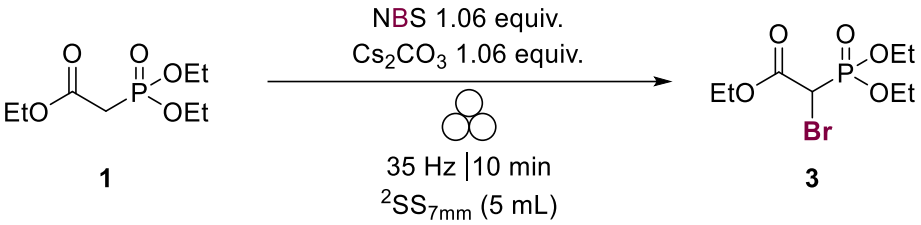


MM 500 with 1.5 and 5 mL Jars

1.5 and 5 mL jars

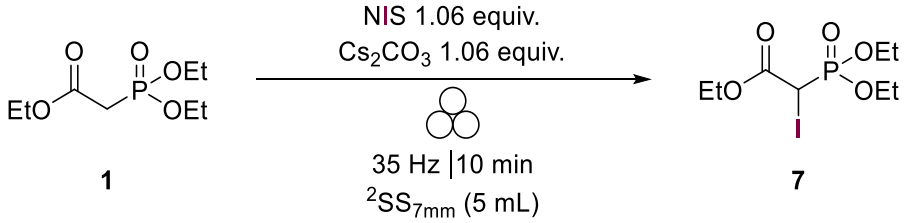
3- Preparation of phosphonates

a. Mechanochemical synthesis of ethyl 2-bromo-2-(diethoxyphosphoryl)acetate



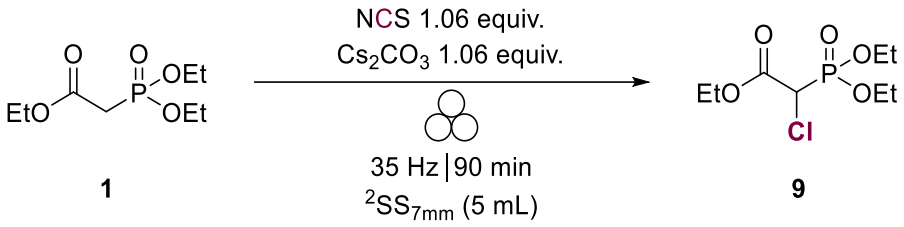
In a 5 mL stainless steel jar were added in that order triethylphosphonoacetate (112 mg, 0.50 mmol, 1.00 eq.), Cs_2CO_3 (174 mg, 0.53 mmol, 1.06 eq.), NBS (94.3 mg, 0.53 mmol, 1.06 eq.) and two 7 mm stainless steel balls. The jar was mounted on the mixer mill and milled at 35 Hz for 10 min. The jar was then opened and the reaction mixture collected with dichloromethane (DCM). The mixture was concentrated and the obtained residue was isolated by flash column chromatography (FCC) to afford the product as a colourless oil (87 mg, 57%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.36 (d, *J* = 14.0 Hz, 1H), 4.32 – 4.22 (m, 6H), 1.37 (t, *J* = 7.1 Hz, 6H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 64.7 (d, *J* = 6.7 Hz), 63.2, 36.7, 35.2, 16.5 (d, *J* = 5.9 Hz), 14.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 12.73 – 12.35 (m). **HRMS** (ESI^+) m/z: $[M+H]^+$ Calcd for $C_8H_{17}BrO_5P$: 302.9997. Found: 302.9999 (Δ = 0.7 ppm).

b. Mechanochemical synthesis of ethyl 2-iodo-2-(diethoxyphosphoryl)acetate



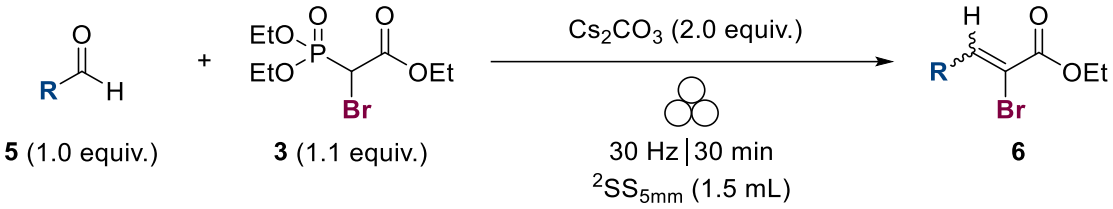
In a 5 mL stainless steel jar were added in that order triethylphosphonoacetate (112 mg, 0.50 mmol, 1.00 eq.), Cs_2CO_3 (174 mg, 0.53 mmol, 1.06 eq.), NIS (119 mg, 0.53 mmol, 1.06 eq.) and two 7 mm stainless steel balls. The jar was mounted on the mixer mill and milled at 35 Hz for 10 min. The jar was then opened and the reaction mixture collected with DCM. The mixture was concentrated and the obtained residue was isolated by FCC to afford the product as a yellow oil (98 mg, 56%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.39 (d, *J* = 12.9 Hz, 1H), 4.31 – 4.20 (m, 5H), 1.37 (t, *J* = 7.1 Hz, 6H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 64.5 (t, *J* = 6.2 Hz), 62.9, 16.4 (d, *J* = 6.0 Hz), 13.8, 7.6, 6.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 15.30 – 14.93 (m). **HRMS** (ESI^+) m/z: $[M+H]^+$ Calcd for $C_8H_{17}IO_5P$: 350.9858. Found: 350.9853 (Δ = -1.4 ppm).

c. Mechanochemical synthesis of ethyl 2-chloro-2-(diethoxyphosphoryl)acetate



In a 5 mL stainless steel jar were added in that order triethylphosphonoacetate (112 mg, 0.50 mmol, 1.00 eq.), Cs_2CO_3 (174 mg, 0.53 mmol, 1.06 eq.), NCS (70.8 mg, 0.53 mmol, 1.06 eq.) and two 7 mm stainless steel balls. The jar was mounted on the mixer mill and milled at 35 Hz for 90 min. The jar was then opened and the reaction mixture collected with DCM. The mixture was concentrated and the obtained residue was isolated by FCC to afford the product as a colourless oil (62 mg, 48%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.50 (d, *J* = 16.2 Hz, 1H), 4.35 – 4.19 (m, 6H), 1.42 – 1.27 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.9 (d, *J* = 1.2 Hz), 64.7 (d, *J* = 6.7 Hz), 63.1, 51.0, 49.5, 16.3 (d, *J* = 5.9 Hz), 14.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 12.38 (dp, *J* = 16.2, 8.1 Hz). **HRMS** (ESI$^+$) m/z: $[M+Na]^+$ Calcd for $C_8H_{13}ClO_5PNa$: 281.0322. Found: 281.0316 (Δ = -2.1 ppm).

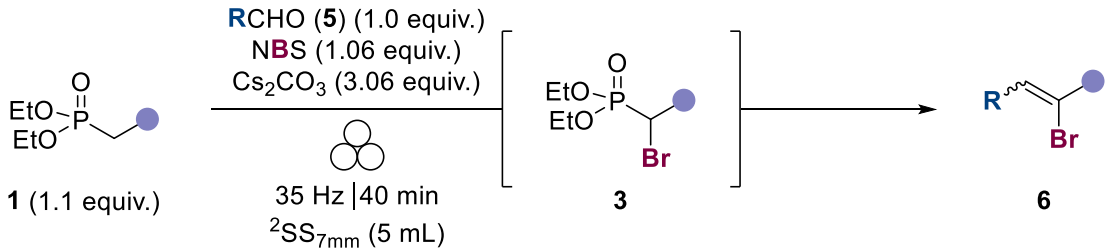
4- General procedure A for mechanochemical HWE reaction



To a 1.5 mL stainless steel jar, equipped with two 5 mm stainless steel balls, was added the aldehyde **5** (0.20 mmol, 1.0 equiv.), ethyl 2-bromo-2-(diethoxyphosphoryl)acetate **3** (0.22 mmol, 1.1 equiv.) and Cs_2CO_3 (0.40 mmol, 2.0 equiv.). The jar was closed and mounted on the mixer mill, then milled at 30 Hz for 30 min. Upon completion, the reaction mixture was washed out of the jar using DCM (10 mL), then filtered through a short silica gel plug, eluting with DCM (3 × 5 mL). The filtrate was concentrated under vacuum to give the corresponding product.

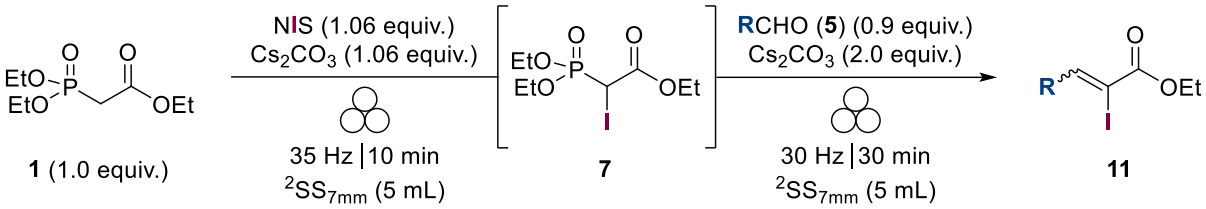
5- General one-pot procedures for the synthesis of halogenated alkenes

a. General procedure B: NBS as the halogen source



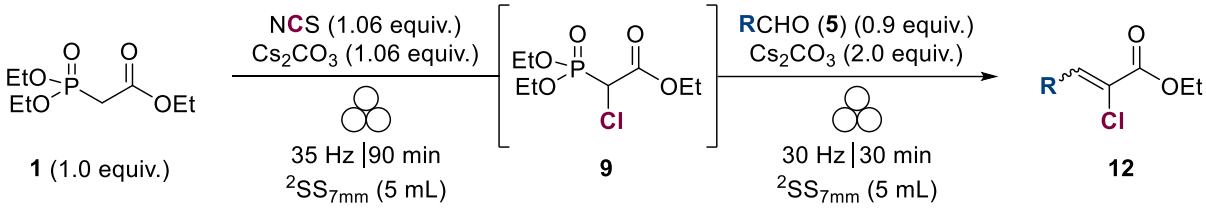
To a 5 mL stainless steel jar, was added **1** (1.1 equiv.), **5** (1.0 equiv.), Cs_2CO_3 (3.06 equiv.), NBS (1.06 equiv.) and two 7 mm stainless steel balls. The jar was closed and mounted on the mixer mill, then milled at 35 Hz for 40 minutes. Upon completion, the reaction mixture was washed out of the jar using DCM (10 mL), then filtered through a short silica gel plug, eluting with DCM (3 × 5 mL). The filtrate was concentrated under vacuum to give the corresponding product.

b. General procedure C: NIS as the halogen source



To a 5 mL stainless steel jar, was added triethylphosphonoacetate **1** (1.0 equiv.), Cs_2CO_3 (1.06 equiv.), NIS (1.06 equiv.) and two 7 mm stainless steel balls. The jar was closed and mounted on the mixer mill, then milled at 35 Hz for 10 minutes. The jar was opened and to the *in situ* formed ethyl 2-iodo-2-(diethoxyphosphoryl)acetate **7** (1.1 equiv.) were added the aldehyde **5** (1.0 equiv.) and Cs_2CO_3 (2.0 equiv.). The jar was closed and mounted on the mixer mill, then milled at 30 Hz for 30 minutes. Upon completion, the reaction mixture was washed out of the jar using DCM (10 mL), then filtered through a short silica gel plug, eluting with DCM (3 × 5 mL). The filtrate was concentrated under vacuum and isolated using reverse phase purification method to give the corresponding product.

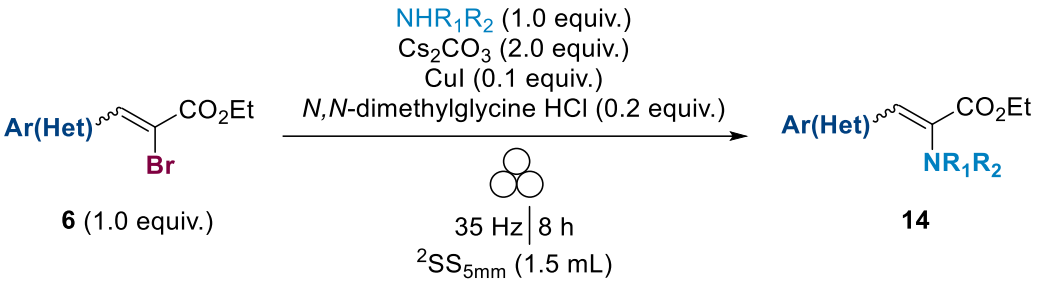
c. General procedure D: NCS as the halogen source



To a 5 mL stainless steel jar, was added triethylphosphonoacetate **1** (1.0 equiv.), Cs_2CO_3 (1.06 equiv.), NCS (1.06 equiv.) and two 7 mm stainless steel balls. The jar was closed and mounted on the mixer mill, then milled at 35 Hz for 90 minutes. The jar was opened and to the *in situ* formed ethyl 2-chloro-2-(diethoxyphosphoryl)acetate **9** (1.1 equiv.) were added the aldehyde **5** (1.0 equiv.) and Cs_2CO_3 (2.0 equiv.). The jar was closed and mounted on the mixer mill, then milled at 30 Hz for 30 minutes. Upon completion, the reaction mixture was washed out of the jar using DCM (10 mL), then filtered through a short silica gel plug, eluting with DCM (3 × 5 mL). The filtrate was concentrated under vacuum and isolated using reverse phase purification method to give the corresponding product.

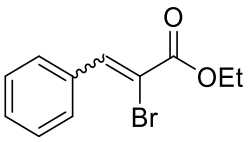
6- General procedures for post functionalization of bromoalkenes

a. General procedure E: ball-milling assisted Ullmann type coupling



In a 1.5 mL stainless steel jar charged with two 5 mm stainless steel balls were successively added **6** (0.250 mmol, 1.0 equiv.), the amine (0.250 mmol, 1.0 equiv.), N,N-dimethylglycine hydrochloride (6.98 mg, 0.050 mmol, 0.2 equiv.), copper iodide (4.76 mg, 0.025 mmol, 0.1 equiv.) and cesium carbonate (164 mg, 0.500 mmol, 2.0 equiv.). The jar was mounted on a mixer mill and milled at 35 Hz for 8 hours. The reaction mixture was collected with EtOAc and filtered through a short pad of silica, eluting with EtOAc. The mixture was concentrated and the residue was isolated by FCC to afford the product.

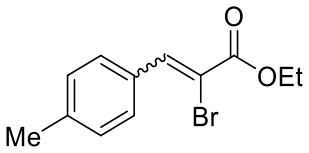
7- Products characterization



6a

Ethyl 2-bromoacrylate

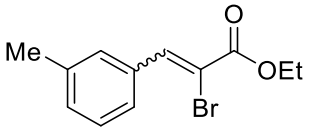
Following the general procedure **A**, the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6a** was obtained as a yellow oil (0.2 mmol scale: 40 mg, 77%, *E:*Z = 1:2.8; 3.0 mmol scale: 705 mg, 92%, *E:Z* = 1:2.9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (s, 0.72H, ***Z*** isomer), 7.90 – 7.81 (m, 1.46H, mixture of ***E*** and ***Z*** isomer), 7.47 – 7.40 (m, 2.22H, mixture of ***E*** and ***Z*** isomer), 7.37 – 7.27 (m, 1.47H, mixture of ***E*** and ***Z*** isomer), 4.36 (q, *J* = 7.1 Hz, 1.48H, ***Z*** isomer), 4.21 (q, *J* = 7.1 Hz, 0.52H, ***E*** isomer), 1.39 (t, *J* = 7.1 Hz, 2.23H, ***Z*** isomer), 1.18 (t, *J* = 7.1 Hz, 0.79H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.5, 163.4, 140.9, 139.7, 135.0, 133.9, 130.4, 130.3, 129.0, 128.5, 128.5, 128.2, 113.3, 111.9, 62.9, 62.4, 14.3, 13.8. **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{11}H_{11}BrO_2$: 253.99424. Found: 253.99487 (Δ = 2.48 ppm).



6b

Ethyl 2-bromo-3-(p-tolyl)acrylate

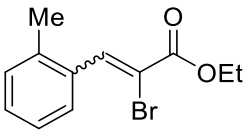
Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6b** was obtained as a yellow oil (43 mg, 81%, *E:Z* = 1:2.2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (s, 0.67H, ***Z*** isomer), 7.79 (d, *J* = 8.0 Hz, 1.38H, ***Z*** isomer), 7.31 (s, 0.30H, ***E*** isomer), 7.24 (d, *J* = 8.0 Hz, 1.35H, ***Z*** isomer), 7.19 (d, *J* = 8.1 Hz, 0.63H, ***E*** isomer), 7.13 (d, *J* = 8.0 Hz, 0.60H, ***E*** isomer), 4.35 (q, *J* = 7.1 Hz, 1.39H, ***Z*** isomer), 4.23 (q, *J* = 7.1 Hz, 0.61H, ***E*** isomer), 2.39 (s, 2.14H, ***Z*** isomer), 2.34 (s, 0.93H, ***E*** isomer), 1.38 (t, *J* = 7.1 Hz, 2.09H, ***Z*** isomer), 1.22 (t, *J* = 7.1 Hz, 1.04H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.7, 163.6, 140.9, 139.8, 139.2, 133.1, 132.1, 131.0, 130.5, 129.3, 129.2, 128.3, 112.1, 110.8, 62.8, 62.4, 21.7, 21.5, 14.4, 13.9. **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{12}H_{13}BrO_2$: 268.00989. Found: 268.00983 (Δ = -0.21 ppm).



6c

Ethyl 2-bromo-3-(m-tolyl)acrylate

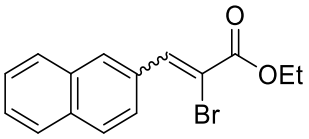
Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6c** was obtained as a yellow oil (45 mg, 84%, *E:Z* = 1:2.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (s, 0.66H, ***Z*** isomer), 7.79 (d, *J* = 8.2 Hz, 1.35H, ***Z*** isomer), 7.31 (s, 0.33H, ***E*** isomer), 7.24 (m, 1.34H, ***Z*** isomer), 7.19 (m, 0.60H, ***E*** isomer), 7.13 (m, 0.60H, ***E*** isomer), 4.35 (q, *J* = 7.1 Hz, 1.39H, ***Z*** isomer), 4.23 (q, *J* = 7.1 Hz, 0.61H, ***E*** isomer), 2.38 (s, 2.06H, ***Z*** isomer), 2.34 (s, 0.92H, ***E*** isomer), 1.38 (t, *J* = 7.1 Hz, 2.10H, ***Z*** isomer), 1.22 (t, *J* = 7.1 Hz, 1.11H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.6, 163.5, 141.1, 139.6, 138.2, 138.1, 134.9, 133.8, 131.1, 129.8, 128.9, 128.4, 127.5, 125.3, 113.0, 111.6, 62.9, 62.4, 21.5, 21.4, 14.3, 13.8. **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{12}H_{13}BrO_2$: 268.00989. Found: 268.00937 (Δ = -1.94 ppm).



6d

Ethyl 2-bromo-3-(o-tolyl)acrylate

Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6d** was obtained as a yellow oil (43 mg, 81%, *E:Z* = 1:2.0); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (s, 0.65H, ***Z*** isomer), 7.67 (m, 0.67H, ***Z*** isomer), 7.52 (s, 0.32H, ***E*** isomer), 7.33 – 7.11 (m, 3.88H, mixture of ***E*** and ***Z*** isomers), 4.37 (q, *J* = 7.1 Hz, 1.36H, ***Z*** isomer), 4.10 (q, *J* = 7.1 Hz, 0.64H, ***E*** isomer), 2.32 (s, 2.02H, ***Z*** isomer), 2.30 (s, 0.98H, ***E*** isomer), 1.40 (t, *J* = 7.1 Hz, 2.10H, ***Z*** isomer), 1.05 (t, *J* = 7.1 Hz, 1.01H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.9, 163.3, 140.8, 140.6, 137.1, 135.8, 135.2, 133.8, 130.3, 130.0, 129.5, 128.9, 128.8, 128.1, 125.7, 125.7, 115.9, 113.3, 62.9, 62.2, 20.0, 20.0, 14.3, 13.7. **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{12}H_{13}BrO_2$: 268.00989. Found: 268.00984 (Δ = -0.21 ppm).

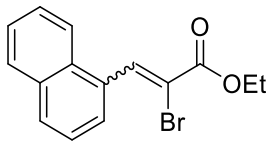


6e

Ethyl 2-bromo-3-(naphthalen-2-yl)acrylate

Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6e** was obtained as a white solid (51 mg, 84%, *E:Z* = 1:1.8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 – 8.35 (m, 1.25H, mixture of ***E*** and ***Z*** isomers), 8.01 – 7.95 (m, 0.66H, mixture of ***E*** and ***Z*** isomers), 7.93 – 7.74 (m, 3.41H, mixture of ***E*** and ***Z*** isomers),

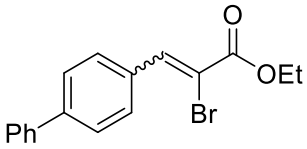
7.59 – 7.46 (m, 2.34H, mixture of ***E*** and ***Z*** isomers), 7.41 – 7.35 (m, 0.35H, mixture of ***E*** and ***Z*** isomers), 4.39 (q, *J* = 7.1 Hz, 1.29H, ***Z*** isomer), 4.24 (q, *J* = 7.1 Hz, 0.71H, ***E*** isomer), 1.42 (t, *J* = 7.1 Hz, 1.95H, ***Z*** isomer), 1.17 (t, *J* = 7.1 Hz, 1.09H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.6, 163.5, 140.9, 139.7, 134.0, 133.3, 133.1, 133.0, 132.4, 131.3, 131.2, 128.9, 128.4, 128.4, 128.1, 128.1, 127.8, 127.8, 127.6, 127.0, 126.8, 126.7, 126.7, 125.4, 113.4, 112.0, 62.9, 62.5, 14.4, 13.9. **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{15}H_{13}BrO_2$: 304.00989. Found: 304.00892 (Δ = -3.18 ppm).



6f

Ethyl 2-bromo-3-(naphthalen-1-yl)acrylate

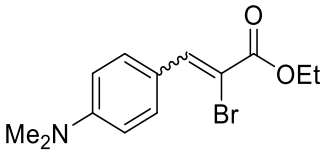
Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6f** was obtained as a colourless oil (57 mg, 94%, *E:Z* = 1:2.2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.76 (s, 0.66H, ***Z*** isomer), 8.00 – 7.82 (m, 4.10H, mixture of ***E*** and ***Z*** isomers), 7.61 – 7.49 (m, 2.76H, mixture of ***E*** and ***Z*** isomers), 7.45 – 7.35 (m, 0.64H, mixture of ***E*** and ***Z*** isomers), 4.43 (q, *J* = 7.1 Hz, 1.38H, ***Z*** isomer), 4.00 (q, *J* = 7.1 Hz, 0.63H, ***E*** isomer), 1.45 (t, *J* = 7.1 Hz, 2.11H, ***Z*** isomer), 0.86 (t, *J* = 7.1 Hz, 0.98H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.8, 163.2, 140.1, 139.6, 133.5, 133.4, 133.2, 131.7, 131.2, 130.8, 130.0, 129.2, 128.8, 128.6, 127.2, 126.8, 126.7, 126.4, 126.3, 126.0, 125.2, 125.2, 124.5, 124.1, 117.2, 114.8, 63.0, 62.2, 14.4, 13.5. **HRMS** (ESI): $[M+Na]^+$ Calcd for $C_{15}H_{13}BrO_2Na$: 326.9997. Found: 326.9995 (Δ = -0.6 ppm).



6g

Ethyl 3-([1,1'-biphenyl]-4-yl)-2-bromoacrylate

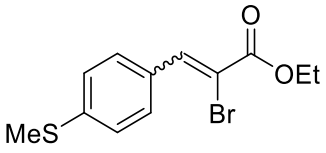
Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM and isolated by column chromatography (100% cyclohexane) on silica gel. The desired product **6g** was obtained as a white solid (33 mg, 50%, *E:Z* = 1:2.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (s, 0.67H, ***Z*** isomer), 7.97 (d, *J* = 8.3 Hz, 1.40H, ***Z*** isomer), 7.70 – 7.54 (m, 4.02H, mixture of ***Z*** and ***E*** isomer), 7.50 – 7.34 (m, 3.87H, mixture of ***Z*** and ***E*** isomer), 4.37 (q, *J* = 7.1 Hz, 1.39H, ***Z*** isomer), 4.26 (q, *J* = 7.1 Hz, 0.59H, ***E*** isomer), 1.41 (t, *J* = 7.1 Hz, 2.09H, ***Z*** isomer), 1.24 (t, *J* = 7.1 Hz, 0.97H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.6, 163.5, 143.0, 141.8, 140.5, 140.4, 140.3, 139.4, 133.9, 132.8, 131.0, 129.1, 129.0, 128.9, 128.1, 127.9, 127.2, 127.2, 113.1, 111.8, 62.9, 62.5, 14.4, 13.9. **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{17}H_{15}BrO_2$: 330.02554. Found: 330.02392 (Δ = -4.92 ppm).



6h

Ethyl 2-bromo-3-(4-(*N*,N-dimethylamino)phenyl)acrylate

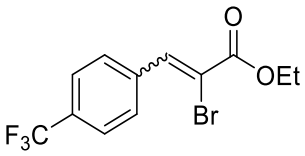
Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6h** was obtained as a yellow solid (37 mg, 62%, *E*:*Z* = 1:1.6); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (s, 0.59H, ***Z*** isomer), 7.94 – 7.86 (m, 1.20H, ***Z*** isomer), 7.31 – 7.25 (m, 1.86H, ***E*** isomer), 6.72 – 6.67 (m, 1.21H, ***Z*** isomer), 6.63 – 6.59 (m, 0.71H, ***E*** isomer), 4.36 – 4.24 (m, 2.00H, mixture of ***E*** and ***Z*** isomer), 3.04 (s, 3.62, ***Z*** isomer), 2.98 (s, 2.23, ***E*** isomer), 1.37 (t, *J* = 7.1 Hz, 1.93H, ***Z*** isomer), 1.29 (t, *J* = 7.1 Hz, 1.24H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.0, 164.2, 151.7, 151.0, 141.4, 140.9, 132.8, 130.7, 122.4, 121.2, 111.5, 111.3, 106.8, 106.2, 62.4, 62.1, 40.2, 40.1, 14.4, 14.1. **HRMS** (ESI^+) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{16}BrNO_2$: 320.0262. Found: 320.0260 (Δ = -0.6 ppm).



6i

Ethyl 2-bromo-3-(4-(methylthio)phenyl)acrylate

Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6i** was obtained as a yellow solid (54 mg, 90%, *E*:*Z* = 1:1.8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (s, 0.65H, ***Z*** isomer), 7.85 – 7.78 (m, 1.32H, ***Z*** isomer), 7.30 – 7.14 (m, 3.09H, mixture of ***E*** and ***Z*** isomers), 4.34 (q, *J* = 7.1 Hz, 1.33H, ***Z*** isomer), 4.24 (q, *J* = 7.1 Hz, 0.67H, ***E*** isomer), 2.50 (s, 1.98H, ***Z*** isomer), 2.47 (s, 1.03H, ***E*** isomer), 1.38 (t, *J* = 7.1 Hz, 2.00H, ***Z*** isomer), 1.23 (t, *J* = 7.1 Hz, 1.05H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.5, 163.5, 142.3, 140.4, 140.2, 139.4, 131.3, 130.9, 130.1, 128.9, 125.8, 125.4, 112.1, 111.0, 62.8, 62.4, 15.3, 15.1, 14.3, 13.9. **HRMS** (ESI): $[M+Na]^+$ Calcd for $C_{12}H_{13}BrO_2SNa$: 326.9997. Found: 326.9995 (Δ = -1.2 ppm).

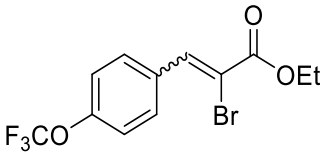


6j

Ethyl 2-bromo-3-(4-(trifluoromethyl)phenyl)acrylate

Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6j** was obtained as a yellow oil (49 mg, 76%, *E*:*Z* = 1:2.6); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (s, 0.68H, ***Z*** isomer), 7.91 (d, *J* = 8.3 Hz, 1.43H, ***Z*** isomer),

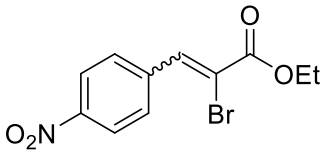
7.68 (d, *J* = 8.3 Hz, 1.43H, ***Z*** isomer), 7.59 (d, *J* = 8.3 Hz, 0.55H, ***E*** isomer), 7.42 – 7.36 (m, 0.82H, ***E*** isomer), 4.37 (q, *J* = 7.1 Hz, 1.44H, ***Z*** isomer), 4.21 (q, *J* = 7.1 Hz, 0.56H, ***E*** isomer), 1.39 (t, *J* = 7.1 Hz, 2.21H, ***Z*** isomer), 1.18 (t, *J* = 7.1 Hz, 0.91H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.9, 163.0, 139.3, 138.5, 138.4, 137.4, 131.6 (q, *J* = 32.7 Hz), 130.4, 128.5, 125.5 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 272.0 Hz), 123.9 (q, *J* = 272.4 Hz), 122.6, 116.0, 114.5, 63.2, 62.7, 14.3, 13.8. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.8 (s), -63.0 (s). **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{12}H_{10}BrF_3O_2$: 321.98163. Found: 321.98045 (Δ = -3.64 ppm).



6k

Ethyl 2-bromo-3-(4-(trifluoromethoxy)phenyl)acrylate

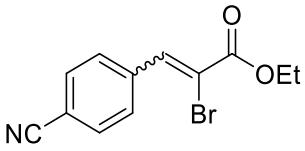
Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6k** was obtained as a yellow oil (62 mg, 91%, *E:Z* = 1:3.5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (s, 0.72H, ***Z*** isomer), 7.92 – 7.86 (m, 1.49H, ***Z*** isomer), 7.36 – 7.30 (m, 0.65H, ***E*** isomer), 7.30 – 7.23 (m, 1.61H, ***Z*** isomer), 7.17 (d, *J* = 8.2 Hz, 0.44H, ***E*** isomer), 4.35 (q, *J* = 7.1 Hz, 1.55H, ***Z*** isomer), 4.21 (q, *J* = 7.1 Hz, 0.45H, ***E*** isomer), 1.39 (t, *J* = 7.1 Hz, 2.43H, ***Z*** isomer), 1.18 (t, *J* = 7.1 Hz, 0.69H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.1, 163.2, 150.2 (q, *J* = 1.45 Hz), 149.5 (q, *J* = 2.11 Hz), 139.2, 138.5, 133.6, 132.4, 132.0, 129.9, 120.8, 120.7, 120.5 (q, *J* = 258.1 Hz), 114.3, 113.1, 63.1, 62.6, 14.3, 13.8. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -57.7 (s), -57.8 (s). **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{12}H_{10}BrF_3O_3$: 337.97654. Found: 337.97523 (Δ = -3.89 ppm).



6l

Ethyl 2-bromo-3-(4-nitrophenyl)acrylate

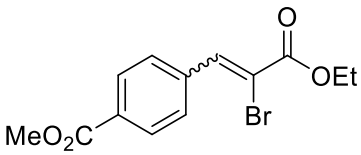
Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6l** was obtained as a yellow solid (49 mg, 82%, *E:Z* = 1:1.8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 – 8.21 (m, 1.93H, ***Z*** isomer), 8.19 (d, *J* = 8.6 Hz, 0.70H, ***E*** isomer), 7.95 (d, *J* = 8.7 Hz, 1.31H, ***Z*** isomer), 7.48 – 7.38 (m, 1.00H, ***E*** isomer), 4.37 (q, *J* = 7.1 Hz, 1.32H, ***Z*** isomer), 4.22 (q, *J* = 7.1 Hz, 0.68H, ***E*** isomer), 1.39 (t, *J* = 7.1 Hz, 2.01H, ***Z*** isomer), 1.20 (t, *J* = 7.1 Hz, 1.13H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.5, 162.7, 148.1, 147.6, 141.3, 140.2, 138.4, 137.7, 130.8, 129.1, 123.7, 123.7, 117.5, 115.9, 63.4, 62.9, 14.3, 13.8. **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{11}H_{10}BrNO_4$: 298.97932. Found: 298.97836 (Δ = -3.22 ppm)



6m

Ethyl 2-bromo-3-(4-cyanophenyl)acrylate

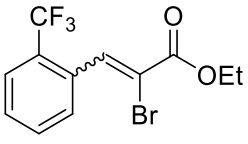
Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6m** was obtained as a white solid (49 mg, 87%, *E*:*Z* = 1:1.7); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (s, 0.61H, ***Z*** isomer), 7.89 (d, *J* = 8.2 Hz, 1.27H, ***Z*** isomer), 7.70 (d, *J* = 8.2 Hz, 1.25H, ***Z*** isomer), 7.62 (d, *J* = 8.0 Hz, 0.72H, ***E*** isomer), 7.42 – 7.33 (m, 1.07H, ***E*** isomer), 4.36 (q, *J* = 7.1 Hz, 1.28H, ***Z*** isomer), 4.21 (q, *J* = 7.1 Hz, 0.72H, ***E*** isomer), 1.38 (t, *J* = 7.1 Hz, 1.92H, ***Z*** isomer), 1.19 (t, *J* = 7.1 Hz, 1.16H, ***Z*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.6, 162.7, 139.4, 138.7, 138.3, 138.0, 132.2, 130.5, 128.8, 118.5, 118.4, 116.9, 115.4, 113.3, 112.4, 63.3, 62.8, 14.3, 13.8. **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{12}H_{10}BrNO_2$: 278.98949. Found: 278.98911 (Δ = -1.37 ppm).



6n

Methyl 4-(2-bromo-3-ethoxy-3-oxoprop-1-en-1-yl)benzoate

Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6n** was obtained as a white solid (48 mg, 77%, *E*:*Z* = 1:2.5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (s, 0.67H, ***Z*** isomer), 8.10 – 8.04 (m, 1.40H, ***Z*** isomer), 8.01 – 7.95 (m, 0.56H, ***E*** isomer), 7.86 (d, *J* = 8.3 Hz, 1.38H, ***Z*** isomer), 7.37 (s, 0.28H, ***E*** isomer), 7.32 (d, *J* = 8.1 Hz, 0.57H, ***E*** isomer), 4.35 (q, *J* = 7.1 Hz, 1.42H, ***Z*** isomer), 4.20 (q, *J* = 7.1 Hz, 0.58H, ***E*** isomer), 3.92 (s, 2.11H, ***Z*** isomer), 3.90 (s, 0.83H, ***E*** isomer), 1.38 (t, *J* = 7.1 Hz, 2.13H, ***Z*** isomer), 1.17 (t, *J* = 7.1 Hz, 0.86H, ***E*** isomer).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 166.5, 164.1, 163.1, 139.7, 139.3, 138.6, 138.2, 131.2, 130.3, 130.1, 129.7, 129.6, 128.1, 115.6, 114.1, 63.1, 62.6, 52.4, 52.3, 14.3, 13.8. **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{13}H_{13}BrO_4$: 311.99972. Found: 311.99848 (Δ = -3.96 ppm).

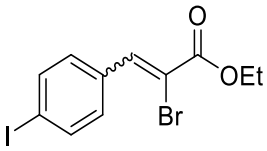


6o

Ethyl 2-bromo-3-(2-(trifluoromethyl)phenyl)acrylate

Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6o** was obtained as a colourless oil (51 mg, 79%,

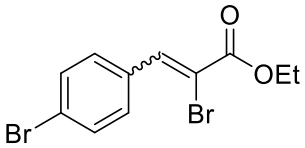
E:Z = 1:3.9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 – 8.35 (m, 0.72H, ***Z*** isomer), 7.76 – 7.65 (m, 2.01H, mixture of ***E*** and ***Z*** isomers), 7.64 – 7.57 (m, 0.79H, ***Z*** isomer), 7.52 – 7.41 (m, 1.21H, mixture of ***E*** and ***Z*** isomers), 7.31 – 7.27 (m, 0.21H, ***E*** isomer), 4.37 (q, *J* = 7.1 Hz, 1.60H, ***Z*** isomer), 4.04 (q, *J* = 7.1 Hz, 0.41H, ***E*** isomer), 1.39 (t, *J* = 7.1 Hz, 2.45H, ***Z*** isomer), 0.97 (t, *J* = 7.1 Hz, 0.63H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.0, 162.6, 138.7, 138.5, 134.8 – 134.7 (q, *J* = 2.05 Hz), 133.4 (q, *J* = 1.72 Hz), 131.7, 131.6, 130.5, 129.8, 129.2, 128.6 (q, *J* = 30.5 Hz), 128.6, 127.7 (q, *J* = 30.5 Hz), 126.1 (q, *J* = 5.4 Hz), 125.9 (q, *J* = 5.1 Hz), 124.0 (q, *J* = 273.6 Hz), 123.9 (q, *J* = 273.9 Hz), 118.3, 115.9, 63.2, 62.4, 14.2, 13.6. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -60.6 (s), -60.8 (s). **HRMS** (EI): $[M]^+$ Calcd for $C_{12}H_{10}BrF_3O_2$: 321.98163. Found: 321.98030 (Δ = -4.13 ppm).



6p

Ethyl 2-bromo-3-(4-iodophenyl)acrylate

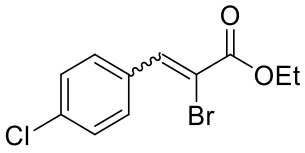
Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6p** was obtained as a yellow oil (61 mg, 80%, *E:Z* = 1:1.8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (s, 0.59H, ***Z*** isomer), 7.79 – 7.74 (m, 1.22H, ***Z*** isomer), 7.69 – 7.64 (m, 0.71H, ***E*** isomer), 7.60 – 7.55 (m, 1.24H, ***Z*** isomer), 7.26 (s, 0.50H, ***E*** isomer), 7.05 – 6.99 (m, 0.71H, ***E*** isomer), 4.34 (q, *J* = 7.1 Hz, 1.27H, ***Z*** isomer), 4.22 (q, *J* = 7.1 Hz, 0.72H, ***E*** isomer), 1.38 (t, *J* = 7.1 Hz, 1.97H, ***Z*** isomer), 1.21 (t, *J* = 7.1 Hz, 1.13H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.1, 163.2, 139.7, 138.8, 137.8, 137.7, 134.4, 133.3, 131.8, 129.9, 114.2, 112.8, 96.8, 95.1, 63.0, 62.6, 14.3, 13.9. **HRMS** (ESI): $[M+Na]^+$ Calcd for $C_{11}H_{10}BrIO_2Na$: 402.8807. Found: 402.8803 (Δ = -1.0 ppm).



6q

Ethyl 2-bromo-3-(4-bromophenyl)acrylate

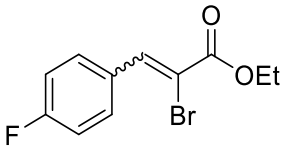
Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6q** was obtained as a colourless solid (58 mg, 87%, *E:Z* = 1:3.5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (s, 0.78H, ***Z*** isomer), 7.72 (d, *J* = 8.4 Hz, 1.64H, ***Z*** isomer), 7.56 (d, *J* = 8.4 Hz, 1.61H, ***Z*** isomer), 7.46 (d, *J* = 8.3 Hz, 0.45H, ***E*** isomer), 7.28 (s, 0.22H, ***E*** isomer), 7.16 (d, *J* = 8.3 Hz, 0.45H, ***E*** isomer), 4.35 (q, *J* = 7.1 Hz, 1.66H, ***Z*** isomer), 4.22 (q, *J* = 7.1 Hz, 0.47H, ***E*** isomer), 1.38 (t, *J* = 7.1 Hz, 2.49H, ***Z*** isomer), 1.21 (t, *J* = 7.1 Hz, 0.78H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.2 , 163.2, 139.6, 138.7, 133.9, 132.8, 131.8, 131.8, 131.7, 129.9, 124.6, 123.3, 114.1, 112.8, 63.0, 62.6, 14.3, 13.9. **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{11}H_{10}Br_2O_2$: 331.90476. Found: 331.90457 (Δ = -0.56 ppm).



6r

Ethyl 2-bromo-3-(4-chlorophenyl)acrylate

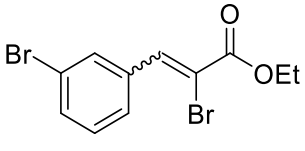
Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6r** was obtained as a colourless oil (49 mg, 85%, *E:Z* = 1:4.3); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (s, 0.76H, ***Z*** isomer), 7.83 – 7.75 (m, 1.59H, ***Z*** isomer), 7.43 – 7.36 (m, 1.57H, ***Z*** isomer), 7.32 – 7.28 (m, 0.57H, ***E*** isomer), 7.24 – 7.20 (m, 0.38H, ***E*** isomer), 4.27 (q, *J* = 7.1 Hz, 1.61H, ***Z*** isomer), 4.14 (q, *J* = 7.1 Hz, 0.39H, ***E*** isomer), 1.30 (t, *J* = 7.1 Hz, 2.41H, ***Z*** isomer), 1.14 (t, *J* = 7.1 Hz, 0.64H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.2, 163.3, 139.5, 138.7, 136.2, 135.0, 133.4, 132.3, 131.6, 129.6, 128.9, 128.8, 114.0, 112.7, 63.0, 62.6, 14.3, 13.9. **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{11}H_{10}BrClO_2$: 287.95527. Found: 287.95543 (Δ = 0.56 ppm).



6s

Ethyl 2-bromo-3-(4-fluorophenyl)acrylate

Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6s** was obtained as a yellow oil (52 mg, 96%, *E:Z* = 1:3.5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (s, 0.79H, ***Z*** isomer), 7.91 – 7.83 (m, 1.62H, ***Z*** isomer), 7.35 – 7.26 (m, 0.59H, ***E*** isomer), 7.11 (t, *J* = 8.6 Hz, 1.61H, ***Z*** isomer), 7.01 (t, *J* = 8.5 Hz, 0.44H, ***E*** isomer), 4.34 (q, *J* = 7.1 Hz, 1.64H, ***Z*** isomer), 4.22 (q, *J* = 7.1 Hz, 0.44H, ***E*** isomer), 1.38 (t, *J* = 7.1 Hz, 2.50H, ***Z*** isomer), 1.20 (t, *J* = 7.1 Hz, 0.73H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) 164.3, 163.6 (d, *J* = 252.3 Hz),163.4, 162.97 (d, *J* = 249.9 Hz), 139.6, 138.9, 132.6 (d, *J* = 8.6 Hz), 131.1 (d, *J* = 3.3 Hz), 130.3 (d, *J* = 8.4 Hz), 130.0 (d, *J* = 3.4 Hz), 115.7 (d, *J* = 21.8 Hz), 115.6 (d, *J* = 21.8 Hz), 113.0 (d, *J* = 2.0 Hz), 111.9 (d, *J* = 1.5 Hz), 63.0, 62.5, 14.3, 13.9. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -108.8 – -108.9 (m), -111.4 – -111.5 (m). **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{11}H_{10}BrFO_2$: 271.98482. Both isomers were found: 271.98581 (Δ = 3.65 ppm) and 271.98312 (Δ = -6.27 ppm).

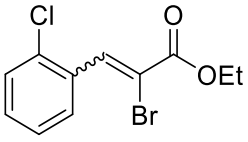


6t

Ethyl 2-bromo-3-(3-bromophenyl)acrylate

Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6t** was obtained as a colourless oil (53 mg, 79%,

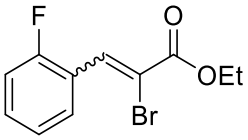
E:*Z* = 1:2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (s, 0.64H, ***Z*** isomer), 7.99 (s, 0.63H, ***Z*** isomer), 7.74 (d, *J* = 7.8 Hz, 0.66H, ***Z*** isomer), 7.54 (d, *J* = 8.0 Hz, 0.64H, ***Z*** isomer), 7.48 – 7.41 (m, 0.64H, ***E*** isomer), 7.33 – 7.27 (m, 0.98H, mixture of ***Z*** and ***E*** isomer), 7.20 (d, *J* = 5.1 Hz, 0.62H, ***E*** isomer), 4.35 (q, *J* = 7.1 Hz, 1.33H, ***Z*** isomer), 4.22 (q, *J* = 7.1 Hz, 0.66H, ***E*** isomer), 1.38 (t, *J* = 7.1 Hz, 2.04H, ***Z*** isomer), 1.20 (t, *J* = 7.1 Hz, 1.03H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.0, 163.1, 139.2, 138.1, 136.9, 135.9, 133.0, 132.9, 131.9, 131.1, 130.0, 130.0, 128.8, 126.8, 122.6, 122.5, 114.9, 113.7, 63.1, 62.7, 14.3, 13.9. **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{11}H_{10}Br_2O_2$: 331.90476. Found: 331.90367 (Δ = -3.26 ppm).



6u

Ethyl 2-bromo-3-(2-chlorophenyl)acrylate

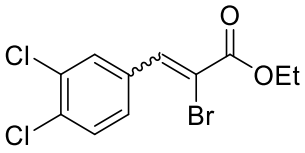
Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6u** was obtained as a yellow oil (55 mg, 95%, *E*:*Z* = 1:4.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (s, 0.75H, ***Z*** isomer), 7.88 (m, 0.79H, mixture of ***E*** and ***Z*** isomers), 7.54 (s, 0.18H, ***E*** isomer), 7.46 – 7.17 (m, 3.30H, mixture of ***E*** and ***Z*** isomers), 4.37 (q, *J* = 7.1 Hz, 1.64H, ***Z*** isomer), 4.13 (q, *J* = 7.1 Hz, 0.36H, ***E*** isomer), 1.39 (t, *J* = 7.1 Hz, 2.55H, ***Z*** isomer), 1.09 (t, *J* = 7.1 Hz, 0.58H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.5, 162.9, 138.3, 138.2, 134.5, 134.3, 132.9, 132.9, 130.8, 130.6, 130.0, 129.74, 129.69, 129.5, 126.6, 126.5, 116.8, 114.9, 63.1, 62.5, 14.3, 13.7. **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{11}H_{10}BrClO_2$: 287.95527. Found: 287.95411 (Δ = -4.02 ppm).



6v

Ethyl 2-bromo-3-(2-fluorophenyl)acrylate

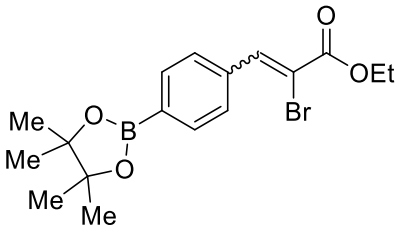
Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6v** was obtained as a yellow oil (49 mg, 89%, *E*:*Z* = 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (s, 0.84H, ***Z*** isomer), 8.12 (t, *J* = 7.6 Hz, 0.87H, ***Z*** isomer), 7.45 – 7.01 (m, 3.33H, mixture of ***E*** and ***Z*** isomers), 4.36 (q, *J* = 7.1 Hz, 1.78H, ***Z*** isomer), 4.20 (q, *J* = 7.1 Hz, 0.22H, ***E*** isomer), 1.39 (t, *J* = 7.1 Hz, 2.71H, ***Z*** isomer), 1.16 (t, *J* = 7.1 Hz, 0.35H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.8, 163.0, 160.8 (d, *J* = 252.6 Hz), 159.6 (d, *J* = 250.1 Hz), 133.6 (d, *J* = 4.6 Hz), 133.5 (d, *J* = 6.2 Hz), 131.9 (d, *J* = 8.7 Hz), 130.8 (d, *J* = 8.4 Hz), 130.0 (d, *J* = 1.7 Hz), 129.8 (d, *J* = 2.6 Hz), 124.0 (d, *J* = 3.6 Hz), 123.9 (d, *J* = 3.7 Hz), 123.3 (d, *J* = 13.9 Hz), 122.3 (d, *J* = 12.1 Hz), 116.2, 116.1, 115.8, 115.6, 63.1, 62.5, 14.3, 13.8. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -112.53 – -112.80 (m), -113.76 – -113.94 (m). **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{11}H_{10}BrFO_2$: 271.98482. Found: 271.98556 (Δ = 2.73 ppm).



6w

Ethyl 2-bromo-3-(3,4-dichlorophenyl)acrylate

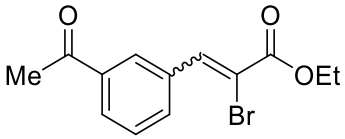
Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6w** was obtained as a yellow oil (61 mg, 94%, *E*:*Z* = 1:1.5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (s, 0.56H, ***Z*** isomer), 7.95 (m, 0.55H, ***Z*** isomer), 7.67 (m, 0.58H, ***Z*** isomer), 7.49 (d, *J* = 8.4 Hz, 0.57H, ***Z*** isomer), 7.40 (d, *J* = 5.3 Hz, 0.33H, ***E*** isomer), 7.39 (s, 0.38H, ***E*** isomer), 7.25 (s, 0.33H, ***E*** isomer), 7.14 – 7.10 (m, 0.36H, ***E*** isomer), 4.35 (q, *J* = 7.1 Hz, 1.21H, ***Z*** isomer), 4.24 (q, *J* = 7.1 Hz, 0.79H, ***E*** isomer), 1.38 (t, *J* = 7.1 Hz, 1.88H, ***Z*** isomer), 1.23 (t, *J* = 7.1 Hz, 1.26H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.8, 162.9, 138.2, 137.3, 134.8, 134.3, 133.8, 133.1, 132.9, 132.7, 131.8, 130.5, 130.5, 130.1, 129.4, 127.6, 115.3, 114.1, 63.2, 62.8, 14.3, 13.9. **HRMS** (EI): $[M]^+$ Calcd for $C_{11}H_9BrCl_2O_2$: 321.91630. Found: 321.91602 (Δ = -0.86 ppm).



6x

Ethyl 2-bromo-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate

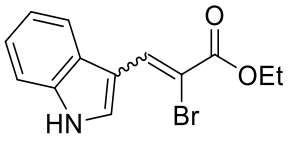
Following the general procedure **A** (0.2 mmol scale), using 1.3 equiv. of **3**, the reaction mixture was filtered through a pad of silica gel using DCM and isolated by column chromatography (5% EtOAc in cyclohexane) on silica gel. The desired product **6x** was obtained as a colourless oil (61 mg, 80%, *E*:*Z* = 1:1.8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (s, 0.61H, ***Z*** isomer), 7.84 (q, *J* = 8.2 Hz, 2.56H, ***Z*** isomer), 7.76 (d, *J* = 8.1 Hz, 0.74H, ***E*** isomer), 7.35 (s, 0.35H, ***E*** isomer), 7.28 – 7.24 (m, 0.91H, ***E*** isomer), 4.35 (q, *J* = 7.1 Hz, 1.27H, ***Z*** isomer), 4.21 (q, *J* = 7.1 Hz, 0.73H, ***E*** isomer), 1.41 – 1.32 (m, 14.08H, mixture of ***Z*** and ***E*** isomers), 1.19 (t, *J* = 7.1 Hz, 1.15H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.5, 163.4, 140.9, 139.4, 137.5, 136.4, 134.9, 134.8, 129.4, 127.4, 114.2, 112.6, 84.2, 84.1, 62.9, 62.5, 27.0, 25.0, 14.4, 13.9. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.92. **HRMS** (ESI): $[M+H]^+$ Calcd for $C_{17}H_{23}BBrO_4$: 381.0869. Found: 381.0873 (Δ = -1.0 ppm).



6y

Ethyl 3-(3-acetylphenyl)-2-bromoacrylate

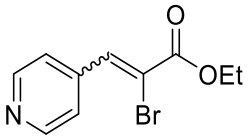
Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6y** was obtained as a colourless oil (48 mg, 81%, *E:Z* = 1:1.5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (s, 1.15H, ***Z*** isomer), 8.24 (s, 1.15H, ***Z*** isomer), 8.05 – 7.96 (m, 2.34H, mixture of ***E*** and ***Z*** isomers), 7.92 – 7.86 (m, 1.55H, mixture of ***E*** and ***Z*** isomers), 7.58 – 7.37 (m, 3.56H, mixture of ***E*** and ***Z*** isomers), 4.35 (q, *J* = 7.1 Hz, 2.40H, ***Z*** isomer), 4.21 (q, *J* = 7.1 Hz, 1.59H, ***E*** isomer), 2.63 (s, 3,56H, ***Z*** isomer), 2.58 (s, 2.44H, ***E*** isomer), 1.39 (t, *J* = 7.1 Hz, 3.61H, ***Z*** isomer), 1.18 (t, *J* = 7.1 Hz, 2.43H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.5, 197.4, 164.0, 163.1, 139.8, 138.9, 137.3, 137.3, 135.5, 134.4, 132.6, 130.2, 129.7, 128.9, 128.8, 128.7, 128.1, 114.9, 113.5, 63.1, 62.6, 26.8, 26.7, 14.3, 13.8. (EI^+) m/z: $[M]^+$ Calcd for $C_{13}H_{13}BrO_3$: 296.00481. Found: 296.00412 (Δ = -2.31 ppm).



6z

Ethyl 2-bromo-3-(1H-indol-3-yl)acrylate

Following the general procedure **A** (0.4 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6z** was obtained as a yellow oil (20 mg, 34%, *E:Z* > 1:20); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.64 (s, 1H), 8.54 (d, *J* = 2.9 Hz, 1H), 7.82 (d, *J* = 7.4 Hz, 1H), 7.48 – 7.40 (m, 1H), 7.33 – 7.24 (m, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.45 – 1.38 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.0, 135.4, 132.6, 127.9, 127.9, 123.7, 121.5, 118.6, 111.8, 111.7, 108.4, 62.5, 14.5. **HRMS** (ESI): $[M+H]^+$ Calcd for $C_{13}H_{13}NO_2Br$: 294.0130. Found: 294.0122 (Δ = -2.7 ppm).

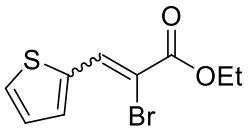


6aa

Ethyl 2-bromo-3-(pyridin-4-yl)acrylate

Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6aa** was obtained as a brown oil (43 mg, 83%, *E:Z* = 1:1.8); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 – 8.64 (m, 1.27H, mixture of ***Z*** and ***E*** isomers), 8.61 – 8.54 (m, 0.65H, ***E*** isomer), 8.10 (s, 0.56H, ***Z*** isomer), 7.66 – 7.57 (m, 1.14H, ***Z*** isomer), 7.43 – 7.38

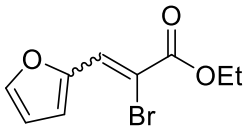
(m, 0.14H), 7.28 (s, 0.32H, ***E*** isomer), 7.18 – 7.11 (m, 0.63H, ***E*** isomer), 4.35 (q, *J* = 7.1 Hz, 1.34H, ***Z*** isomer), 4.20 (q, *J* = 7.1 Hz, 0.67H, ***E*** isomer), 1.38 (t, *J* = 7.1 Hz, 2.20H, ***Z*** isomer), 1.17 (t, *J* = 7.1 Hz, 1.00H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.6, 162.6, 150.3, 150.2, 150.1, 142.5, 141.4, 138.2, 137.0, 126.2, 123.6, 122.3, 118.0, 116.2, 63.3, 62.8, 62.7, 14.3, 14.1, 13.7. **HRMS** (ESI): $[M+H]^+$ Calcd for $C_{10}H_{11}BrNO_2$: 255.9973. Found: 255.9973 (Δ = 0 ppm).



6ab

Ethyl 2-bromo-3-(2-thienyl)-2-propenoate

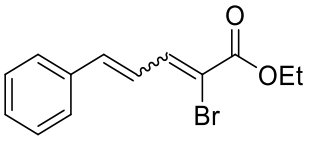
Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6ab** was obtained as a colourless oil (51 mg, 98%, *E:Z* = 1:1.9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (s, 0.63H, ***Z*** isomer), 7.63 (s, 0.32H, ***E*** isomer), 7.61 – 7.58 (m, 0.61H, ***Z*** isomer), 7.57 – 7.53 (m, 0.63H, ***Z*** isomer), 7.50 – 7.46 (m, 0.32H, ***E*** isomer), 7.31 – 7.28 (m, 0.33H, ***E*** isomer), 7.15 (dd, *J* = 5.1, 3.8 Hz, 0.63H, ***Z*** isomer), 7.03 (dd, *J* = 5.1, 3.7 Hz, 0.32H, ***E*** isomer), 4.39 – 4.28 (m, 2.00H, mixture of ***Z*** and ***E*** isomers), 1.41 – 1.34 (m, 3.00H, mixture of ***Z*** and ***E*** isomers). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.6, 163.3, 137.7, 137.0, 136.7, 135.1, 134.9, 134.5, 131.5, 131.2, 127.1, 126.9, 110.1, 107.3, 62.8, 62.6, 14.4, 14.2. **HRMS** (EI): $[M]^+$ Calcd for $C_9H_9BrO_2S$: 259.95066. Found: 259.95121 (Δ = 2.11 ppm).



6ac

Ethyl 2-bromo-3-(2-furanyl)-2-propenoate

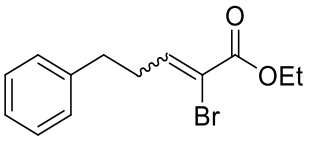
Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6ac** was obtained as a colourless oil (37 mg, 75%, *E:Z* = 1:3.0); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (s, 0.70H, ***Z*** isomer), 7.62 – 7.57 (m, 0.71H, ***Z*** isomer), 7.47 – 7.41 (m, 0.95H, mixture of ***Z*** and ***E*** isomers), 7.17 (s, 0.22H, ***E*** isomer), 7.02 – 6.98 (m, 0.23H, ***E*** isomer), 6.60 – 6.55 (m, 0.72H, ***Z*** isomer), 6.46 – 6.42 (m, 0.23H, ***E*** isomer), 4.37 – 4.28 (m, 2.00H, mixture of ***Z*** and ***E*** isomers), 1.40 – 1.32 (m, 3.03H, mixture of ***Z*** and ***E*** isomers). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.9, 163.2, 150.2, 149.5, 145.1, 144.3, 129.2, 128.6, 116.9, 115.1, 112.6, 112.4, 109.8, 107.8, 62.8, 62.4, 14.4, 14.2. **HRMS** (EI): $[M]^+$ Calcd for $C_9H_9BrO_3$: 243.97351. Found: 243.97267 (Δ = -3.43 ppm).



6ad

Ethyl 2-bromo-5-phenylpenta-2,4-dienoate

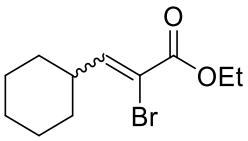
Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6ad** was obtained as a yellow oil (40 mg, 71%, *E:Z* = 1:2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 10.6 Hz, 0.80H, ***Z*** isomer), 7.78 (d, *J* = 11.4 Hz, 0.17H, ***E*** isomer), 7.55 – 7.45 (m, 2.01H, mixture of ***E*** and ***Z*** isomers), 7.37 – 7.23 (m, 3.46H, mixture of ***E*** and ***Z*** isomers), 7.18 (d, *J* = 10.3 Hz, 0.23H, ***E*** isomer), 7.14 (d, *J* = 10.3 Hz, 0.46H, ***Z*** isomer), 7.09 – 7.01 (m, 0.68H, mixture of ***E*** and ***Z*** isomers), 6.76 (d, *J* = 15.6 Hz, 0.31H, mixture of ***E*** and ***Z*** isomers), 4.36 – 4.26(m, 1.99H, mixture of ***E*** and ***Z*** isomers), 1.43 – 1.34 (m, 3.03H, mixture of ***E*** and ***Z*** isomers). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.1, 163.0, 146.1, 142.8, 141.5, 141.3, 136.2, 136.0, 129.7, 129.4, 129.0, 129.0, 127.7, 127.6, 125.4, 125.0, 114.5, 111.2, 62.6, 62.3, 14.4, 14.3. **HRMS** (ESI): $[M+Na]^+$ Calcd for $C_{13}H_{13}BrO_2Na$: 302.9997. Found: 302.9998 (Δ = 0.3 ppm).



6ae

Ethyl 2-bromo-5-phenylpent-2-enoate

Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6ae** was obtained as a colourless oil (39 mg, 68%, *E:Z* = 1:4.0); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2.80H, mixture of ***E*** and ***Z*** isomers), 7.25 – 7.16 (m, 2.92H, mixture of ***E*** and ***Z*** isomers), 6.70 (t, *J* = 7.3 Hz, 0.21H, ***E*** isomer), 4.27 (m, 2.00H, mixture of ***E*** and ***Z*** isomers), 2.81 (m, 2.46H, mixture of ***E*** and ***Z*** isomers), 2.67 (m, 1.58H, mixture of ***E*** and ***Z*** isomers), 1.33 (m, 2.97H, mixture of ***E*** and ***Z*** isomers). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9, 162.5, 147.3, 145.0, 140.7, 140.6, 128.7, 128.6, 128.5, 128.4, 126.4, 126.4, 117.1, 112.0, 62.5, 62.2, 34.9, 33.9, 33.7, 33.1, 14.3, 14.2. **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{13}H_{15}BrO_2$: 282.02554. Found: 282.02519 (Δ = -1.24 ppm).

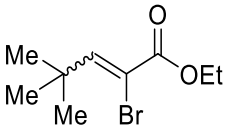


6af

Ethyl 2-bromo-3-cyclohexylacrylate

Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6af** was obtained as a colourless oil (38 mg, 72%,

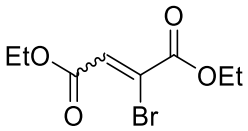
E:*Z* = 1:2.3); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 9.2 Hz, 0.70H, ***Z*** isomer), 6.47 (d, *J* = 10.1 Hz, 0.30H, ***E*** isomer), 4.26 (q, *J* = 7.1 Hz, 2.04H, mixture of ***Z*** and ***E*** isomer), 2.99 – 2.87 (m, 0.30H, ***E*** isomer), 2.63 – 2.50 (m, 0.72H, ***Z*** isomer), 1.76 – 1.67 (m, 5.43H, mixture of ***Z*** and ***E*** isomer), 1.43 – 1.04 (m, 8.60H, mixture of ***Z*** and ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.1, 162.9, 153.3, 150.5, 114.4, 110.0, 62.5, 62.2, 41.3, 40.6, 32.3, 30.8, 25.9, 25.8, 25.5, 25.4, 14.3, 14.2. **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{11}H_{17}BrO_2$: 260.04119. Found: 260.04062 (Δ = -2.21 ppm).



6ag

Ethyl 2-bromo-4,4-dimethylpent-2-enoate

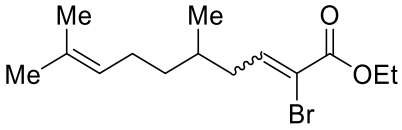
Following the general procedure **A** (0.4 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6ag** was obtained as a white powder (24 mg, 26%, *E*:*Z* = 1:3.2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (s, 0.68H, ***Z*** isomer), 6.17 (s, 0.22H, ***E*** isomer), 4.26 (q, *J* = 7.1 Hz, 1.94H, mixture of ***E*** and ***Z*** isomers), 1.37 – 1.30 (m, 3.18H, mixture of ***E*** and ***Z*** isomers), 1.27 (s, 6.99H, ***Z*** isomer), 1.11 (s, 2.20H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.4, 163.4, 153.9, 147.4, 113.3, 107.4, 62.7, 62.2, 36.3, 34.2, 29.4, 28.9, 14.3, 14.0. **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_9H_{15}BrO_2$: 234.02554. Found: 234.02654 (Δ = 4.26 ppm).



6ah

Diethyl 2-bromobut-2-enedioate

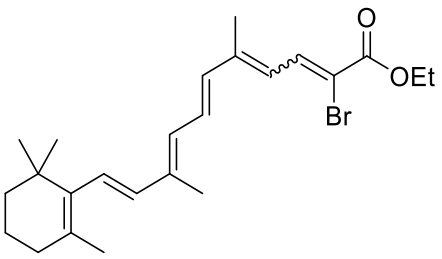
Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6ah** was obtained as an orange oil (25 mg, 49%, *E*:*Z* = 2.2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (s, 0.26H, ***E*** isomer), 6.47 (s, 0.58H, ***Z*** isomer), 4.40 – 4.26 (m, 2.71H, mixture of ***E*** and ***Z*** isomers), 4.20 (q, *J* = 7.1 Hz, 1.31H, ***Z*** isomer), 1.40 – 1.23 (m, 6.14H, mixture of ***E*** and ***Z*** isomers). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.84, 163.82, 163.1, 162.0, 130.9, 127.5, 126.7, 125.4, 63.6, 63.0, 61.7, 61.7, 14.2, 14.2, 14.1, 13.9. **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{18}H_{11}BrO_4$: 249.98407. Found: 249.98529 (Δ = 4.87 ppm).



6ai

Ethyl 2-bromo-5,9-dimethyldeca-2,8-dienoate

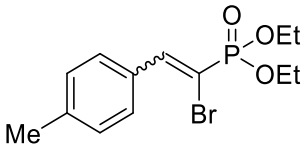
Following the general procedure **A** (0.2 mmol scale), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6ai** was obtained as a colourless oil (47 mg, 77%, *E:Z* = 1:4.1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.2 Hz, 0.74H, ***Z*** isomer), 6.66 (t, *J* = 7.8 Hz, 0.18H, ***E*** isomer), 5.12 – 5.04 (m, 0.93H, mixture of ***E*** and ***Z*** isomers), 4.31 – 4.22 (m, 1.92H, mixture of ***E*** and ***Z*** isomers), 2.49 (ddd, *J* = 15.3, 7.5, 5.9 Hz, 0.21H, ***E*** and ***Z*** isomer), 2.43 – 2.30 (m, 1.02H, mixture of ***E*** and ***Z*** isomers), 2.21 (dt, *J* = 15.1, 7.5 Hz, 0.80H, ***Z*** isomer), 2.07 – 1.92 (m, 2.09H, mixture of ***E*** and ***Z*** isomers), 1.79 – 1.65 (m, 3.85H, mixture of ***E*** and ***Z*** isomers), 1.60 (s, *J* = 7.6 Hz, 3.06H, mixture of ***E*** and ***Z*** isomers), 1.42 – 1.30 (m, 4.06H, mixture of ***E*** and ***Z*** isomers), 1.29 – 1.17 (m, 1.20H, mixture of ***E*** and ***Z*** isomers), 1.02 – 0.82 (m, 3.43H, mixture of ***E*** and ***Z*** isomers). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.1, 162.6, 147.7, 145.3, 131.7, 131.6, 124.5, 124.4, 117.1, 111.6, 62.5, 62.1, 39.4, 38.5, 36.9, 36.8, 32.9, 32.2, 25.8, 25.8, 25.6, 25.6, 19.8, 19.6, 17.81, 17.8, 14.3, 14.2. **HRMS** (EI^+) m/z: $[M]^+$ Calcd for $C_{14}H_{23}BrO_2$: 302.08814. Found: 302.08665 (Δ = -0.21 ppm).



6aj

Ethyl (6E,8E,10E)-2-bromo-5,9-dimethyl-11-(2,6,6-trimethylcyclohex-1-en-1-yl)undeca-2,4,6,8,10-pentaenoate

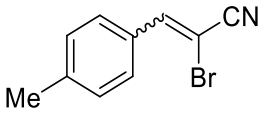
Following the general procedure **A** (0.2 mmol), the reaction mixture was filtered through a pad of silica gel using DCM. The desired product **6aj** was obtained as a brown oil (38 mg, 44%, *E:Z* = 1:2.2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 – 7.30 (m, 1.18H, mixture of ***E*** and ***Z*** isomers), 7.17 – 6.81 (m, 1.30H, mixture of ***E*** and ***Z*** isomers), 6.53 – 6.10 (m, 4.08H, mixture of ***E*** and ***Z*** isomers), 4.38 – 4.20 (m, *J* = 7.1, 3.9 Hz, 2.00H, mixture of ***E*** and ***Z*** isomers), 2.26 – 0.94 (m, 24.26H, mixture of ***E*** and ***Z*** isomers). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.5, 163.3, 147.0, 145.9, 144.9, 141.8, 139.8, 139.3, 138.8, 137.9, 137.6, 137.6, 136.9, 136.5, 136.1, 135.6, 130.7, 130.4, 130.3, 130.2, 130.0, 129.7, 129.2, 128.8, 128.6, 128.3, 127.6, 126.8, 125.6, 114.0, 113.3, 110.4, 62.4, 62.2, 39.8, 34.4, 33.3, 29.1, 27.0, 21.9, 21.5, 19.4, 14.4, 14.3, 14.2, 13.1, 13.0, 12.9. **HRMS** (ESI^+) m/z: $[M+H]^+$ Calcd for $C_{24}H_{34}BrO_2$: 433.1742. Found: 433.1729 (Δ = -3.0 ppm).



6ak

Diethyl *P*-[1-bromo-2-(4-methylphenyl)ethenyl]phosphonate

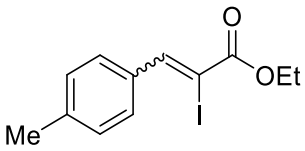
Following the general procedure **B** (0.5 mmol), the reaction mixture was filtered through a pad of silica gel using DCM and isolated by column chromatography (15% EtOAc in cyclohexane) on silica gel. The desired product **6ak** was obtained as a colourless oil (38 mg, 43%, *E:Z* = 1:1.1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 16.3 Hz, 0.47H, ***Z*** isomer), 7.85 (d, *J* = 37.7 Hz, 0.47H, ***E*** isomer), 7.76 (d, *J* = 8.1 Hz, 0.97H, ***Z*** isomer), 7.39 (d, *J* = 8.0 Hz, 0.95H, ***E*** isomer), 7.23 (d, *J* = 8.0 Hz, 0.97H, ***Z*** isomer), 7.15 (d, *J* = 8.0 Hz, 0.96H, ***E*** isomer), 4.26 – 3.95 (m, 4.00H, mixture of ***Z*** and ***E*** isomer), 2.38 (s, 1.55H, ***Z*** isomer), 2.34 (s, 1.41H, ***E*** isomer), 1.39 (td, *J* = 7.1, 0.6 Hz, 3.13H, ***Z*** isomer), 1.21 (td, *J* = 7.1, 0.6 Hz, 2.90H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.6 (d, *J* = 13.1 Hz), 144.9 (d, *J* = 16.8 Hz), 140.8, 139.5, 130.2, 129.4 (d, *J* = 1.2 Hz), 129.3, 128.8, 63.4 (d, *J* = 6.0 Hz), 63.3 (d, *J* = 5.2 Hz), 21.7, 21.5, 16.4 (d, *J* = 6.6 Hz), 16.2 (d, *J* = 6.7 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 10.97 (m), 8.10 – 7.06 (m). **HRMS** (EI): $[M]^+$ Calcd for $C_{13}H_{18}BrO_3P$: 332.01769. Both isomers were found: 332.01811 (Δ = 1.26 ppm) and 332.01725 (Δ = -1.33 ppm).



6al

2-bromo-3-(4-methylphenyl)-2-propenenitrile

Following the general procedure **B** (0.5 mmol), the reaction mixture was filtered through a pad of silica gel using DCM and isolated by column chromatography on silica gel. The desired product **6al** was obtained as a colourless oil (8 mg, 27%, *E:Z* = 1:5.7); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 0.28H, ***Z*** isomer), 7.64 (s, 0.15H, ***Z*** isomer), 7.60 (d, *J* = 8.2 Hz, 1.69H, ***E*** isomer), 7.52 (s, 0.84H, ***E*** isomer), 7.26 – 7.21 (m, 1.89H, mixture of ***Z*** and ***E*** isomer), 2.40 – 2.36 (m, 3.00H, mixture of ***Z*** and ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.2, 145.5, 142.23, 142.21, 133.6, 130.2, 130.0, 129.8, 129.6, 128.8, 117.4, 116.1, 85.7, 83.4, 21.8, 21.7. **HRMS** (EI): $[M]^+$ Calcd for $C_{10}H_8BrN$: 220.98401. Found: 220.98494 (Δ = 4.21 ppm).

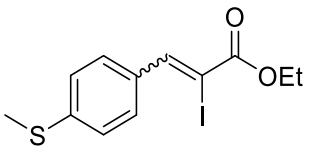


11a

Ethyl-2-iodo-3-(4-methylphenyl)-2-propenoate

Following the general procedure **C** (0.3 mmol scale), the reaction mixture was isolated with a preparatory TLC (5% EtOAc in cyclohexane). The desired product **11a** was obtained as a yellow

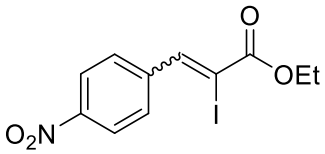
oil (28 mg, 38%, *E:Z* = 1:2.6); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (s, 0.67H, ***Z*** isomer), 7.72 (d, *J* = 8.1 Hz, 1.39H, ***Z*** isomer), 7.45 (s, 0.27H, ***E*** isomer), 7.26 – 7.21 (m, 1.38H, ***Z*** isomer), 7.17 – 7.10 (m, 1.09H, ***E*** isomer), 4.34 (q, *J* = 7.1 Hz, 1.44H, ***Z*** isomer), 4.22 (q, *J* = 7.1 Hz, 0.56H, ***E*** isomer), 2.38 (s, 2.14H, ***Z*** isomer), 2.33 (s, 0.83H, ***E*** isomer), 1.38 (t, *J* = 7.1 Hz, 2.25H, ***Z*** isomer), 1.21 (t, *J* = 7.1 Hz, 0.99H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 164.0, 148.0, 146.4, 140.7, 139.3, 133.8, 132.6, 129.8, 129.2, 129.1, 128.0, 89.8, 83.3, 63.1, 62.4, 21.7, 21.5, 14.4, 13.8. **HRMS** (EI): $[M]^+$ Calcd for $C_{12}H_{13}IO_2$: 315.99602. Found: 315.99541 (Δ = -1.93 ppm).



11b

Ethyl 2-iodo-3-(4-(methylthio)phenyl)acrylate

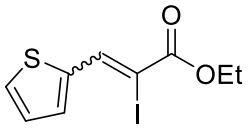
Following the general procedure **C** (0.5 mmol scale), the reaction mixture was isolated by reverse phase purification on C18. The desired product **11b** was obtained as a yellow oil (53 mg, 39%, *E:Z* = 1:2.2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (s, 0.65H, ***Z*** isomer), 7.83 – 7.72 (m, *J* = 8.4 Hz, 1.35H, ***Z*** isomer), 7.43 (s, 0.29H, ***E*** isomer), 7.31 – 7.22 (m, 1.98H, mixture of ***E*** and ***Z*** isomers), 7.23 – 7.11 (m, 1.23H, mixture of ***E*** and ***Z*** isomers), 4.34 (q, *J* = 7.1 Hz, 1.38H, ***Z*** isomer), 4.23 (q, *J* = 7.1 Hz, 0.62H, ***E*** isomer), 2.52 (s, 2.06H, ***Z*** isomer), 2.48 (s, 0.93H, ***E*** isomer), 1.38 (t, *J* = 7.1 Hz, 2.09H, ***Z*** isomer), 1.23 (t, *J* = 7.1 Hz, 1.02H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.3, 163.9, 147.2, 145.8, 142.1, 140.4, 133.0, 131.5, 130.2, 128.5, 125.7, 125.3, 89.5, 83.6, 63.1, 62.4, 15.3, 15.1, 14.3, 13.8. **HRMS** (EI): $[M]^+$ Calcd for $C_{12}H_{13}IO_2S$: 347.96809. Found: 347.96787 (Δ = -0.65 ppm).



11c

Ethyl 2-iodo-3-(4-nitrophenyl)acrylate

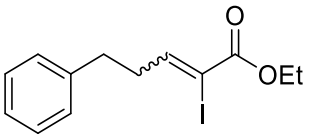
Following the general procedure **C** (0.5 mmol scale), the reaction mixture was isolated by reverse phase purification on C18. The desired product **11c** was obtained as a yellow oil (64 mg, 48%, *E:Z* = 1:1.7). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 – 8.24 (m, 1.84H, ***Z*** isomer), 8.18 (d, *J* = 8.8 Hz, 0.73H, ***E*** isomer), 7.85 (d, *J* = 8.5 Hz, 1.17H, ***Z*** isomer), 7.56 (s, 0.35H, ***E*** isomer), 7.41 (d, *J* = 8.5 Hz, 0.74H, ***E*** isomer), 4.36 (q, *J* = 7.1 Hz, 1.25H, ***Z*** isomer), 4.22 (q, *J* = 7.1 Hz, 0.75H, ***E*** isomer), 1.39 (t, *J* = 7.1 Hz, 1.85H, ***Z*** isomer), 1.20 (t, *J* = 7.1 Hz, 1.12H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.4, 163.2, 148.1, 147.6, 145.7, 144.2, 142.6, 142.4, 130.1, 128.7, 123.8, 123.7, 96.1, 89.4, 63.6, 62.9, 14.3, 13.8. **HRMS** (EI): $[M]^+$ Calcd for $C_{11}H_{10}INO_4$: 346.96545. Both isomers were found: 346.96395 (Δ = -4.31 ppm) and 346.96535 (Δ = -0.29 ppm).



11d

Ethyl 2-iodo-3-(2-thienyl)-2-propenoate

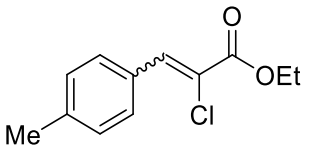
Following the general procedure **C** (0.5 mmol scale), the reaction mixture was isolated by reverse phase purification on C18. The desired product **11d** was obtained as a colourless oil (64 mg, 54%, *E:Z* = 1:2.3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (s, 0.65H, ***Z*** isomer), 7.74 (s, 0.28H, ***E*** isomer), 7.64 – 7.59 (m, 0.69H, ***Z*** isomer), 7.56 (d, *J* = 5.1 Hz, 0.67H, ***Z*** isomer), 7.44 (d, *J* = 4.9 Hz, 0.28H, ***E*** isomer), 7.25 – 7.15 (m, 0.98H, mixture of ***Z*** and ***E*** isomer), 7.00 (dd, *J* = 5.1, 3.7 Hz, 0.30H, ***E*** isomer), 4.38 – 4.27 (m, 2.00H, mixture of ***E*** and ***Z*** isomers), 1.41 – 1.31 (m, 3.00H, mixture of ***E*** and ***Z*** isomers). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.9, 164.0, 142.6, 141.45, 138.9, 138.9, 135.9, 133.9, 130.9, 130.1, 127.1, 126.8, 86.5, 80.1, 63.0, 62.7, 14.4, 14.1. **HRMS** (EI): $[M]^+$ Calcd for $C_9H_9IO_2S$: 307.93679. Both isomers were found: 307.93560 (Δ = -1.20 ppm) and 307.93623 (Δ = -1.82 ppm).



11e

Ethyl 2-iodo-5-phenylpent-2-enoate

Following the general procedure **C** (0.5 mmol scale), the reaction mixture was isolated by reverse phase purification on C18. The desired product **11e** was obtained as a yellow oil (53 mg, 42%, *E:Z* = 1:4.7). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.16 (m, 6.31H, mixture of ***E*** and ***Z*** isomers), 6.96 – 6.89 (m, 0.15H, ***E*** isomer), 4.33 – 4.18 (m, 2.00H, mixture of ***E*** and ***Z*** isomers), 2.91 – 2.75 (m, 2.41H, mixture of ***E*** and ***Z*** isomers), 2.71 – 2.58 (m, 1.65H, mixture of ***E*** and ***Z*** isomers), 1.36 – 1.29 (m, 3.00H, mixture of ***E*** and ***Z*** isomers). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.8, 162.9, 154.7, 151.9, 140.6, 140.6, 128.7, 128.6, 128.5, 126.4, 126.3, 96.1, 85.6, 62.8, 62.3, 38.8, 35.0, 34.8, 33.6, 14.3, 14.2. **HRMS** (EI): $[M]^+$ Calcd for $C_{13}H_{15}IO_2$: 330.01167. Found: 330.01201 (Δ = 1.04 ppm).

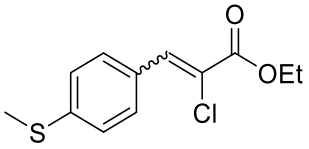


12a

Ethyl-2-chloro-3-(4-methylphenyl)-2-propenoate

Following the general procedure **D** (0.3 mmol scale), the reaction mixture was isolated with a preparatory TLC (5% EtOAc in cyclohexane). The desired product **12a** was obtained as a yellow oil (28 mg, 69%, *E:Z* = 1:2.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (s, 0.68H, ***Z*** isomer), 7.76 (d, *J* = 8.2 Hz,

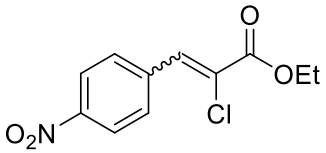
1.39H, ***Z*** isomer), 7.26 – 7.12 (m, 2.84H, mixture of ***Z*** and ***E*** isomers), 4.35 (q, *J* = 7.1 Hz, 1.41H, ***Z*** isomer), 4.23 (q, *J* = 7.1 Hz, 0.59H, ***E*** isomer), 2.39 (s, 2.14H, ***Z*** isomer), 2.35 (s, 0.89H, ***E*** isomer), 1.39 (t, *J* = 7.1 Hz, 2.12H, ***Z*** isomer), 1.22 (t, *J* = 7.1 Hz, 0.94H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.9, 163.7, 140.8, 139.2, 137.2, 137.0, 131.1, 130.9, 130.3, 129.4, 129.1, 128.7, 122.2, 121.3, 62.6, 62.3, 21.7, 21.5, 14.4, 13.9. **HRMS** (EI): $[M]^+$ Calcd for $C_{12}H_{13}ClO_2$: 224.06041. Found: 224.05976 (Δ = -2.89 ppm).



12b

Ethyl 2-chloro-3-(4-(methylthio)phenyl)acrylate

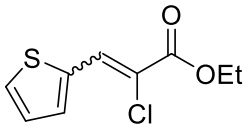
Following the general procedure **D** (0.5 mmol scale), the reaction mixture was isolated by reverse phase purification on C18. The desired product **12b** was obtained as a yellow oil (61 mg, 80%, *E:Z* = 1:2.2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (s, 0.67H, ***Z*** isomer), 7.83 – 7.77 (m, 1.37H, ***Z*** isomer), 7.30 – 7.24 (m, 2.06H, mixture of ***Z*** and ***E*** isomer), 7.22 – 7.17 (m, 0.63H, ***E*** isomer), 7.15 (s, 0.29H, ***E*** isomer), 4.36 (q, *J* = 7.1 Hz, 1.38H, ***Z*** isomer), 4.25 (q, *J* = 7.1 Hz, 0.62H, ***E*** isomer), 2.52 (s, 2.05H, ***Z*** isomer), 2.49 (s, 0.95H, ***E*** isomer), 1.40 (t, *J* = 7.1 Hz, 2.10H, ***Z*** isomer), 1.25 (t, *J* = 7.1 Hz, 0.98H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.7, 163.6, 142.3, 140.3, 136.8, 136.4, 131.1, 130.3, 129.4, 129.2, 125.7, 125.5, 122.4, 121.3, 62.6, 62.3, 15.4, 15.1, 14.3, 13.9. **HRMS** (EI): $[M]^+$ Calcd for $C_{12}H_{13}ClO_2S$: 256.03248. Found: 256.03269 (Δ = 0.83 ppm).



12c

Ethyl 2-chloro-3-(4-nitrophenyl)acrylate

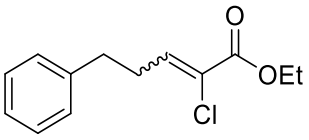
Following the general procedure **D** (0.5 mmol scale), the reaction mixture was isolated by reverse phase purification on C18. The desired product **12c** was obtained as a yellow oil (34 mg, 45%, *E:Z* = 1:4.4). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 – 8.23 (m, 1.62H, ***Z*** isomer), 8.21 – 8.16 (m, 0.37H, ***E*** isomer), 7.99 – 7.90 (m, 2.41H, ***Z*** isomer), 7.48 – 7.42 (m, 0.34H, ***E*** isomer), 7.25 (s, 0.16H, ***E*** isomer), 4.37 (q, *J* = 7.1 Hz, 1.63H, ***Z*** isomer), 4.21 (q, *J* = 7.1 Hz, 0.37H, ***E*** isomer), 1.40 (t, *J* = 7.1 Hz, 2.46H, ***Z*** isomer), 1.19 (t, *J* = 7.1 Hz, 0.54H, ***E*** isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9, 162.7, 148.1, 147.7, 140.5, 139.2, 135.0, 134.4, 131.2, 129.4, 126.8, 126.2, 123.8, 123.6, 63.2, 62.8, 14.3, 13.8. **HRMS** (EI): $[M]^+$ Calcd for $C_{11}H_{10}ClNO_4$: 255.02984. Found: 255.02902 (Δ = -3.21 ppm).



12d

Ethyl 2-chloro-3-(2-thienyl)-2-propenoate

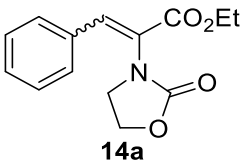
Following the general procedure **D** (0.5 mmol scale), the reaction mixture was isolated by reverse phase purification on C18. The desired product **12b** was obtained as a colourless oil (22 mg, 35%, *E:Z* = 1:2.7). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (s, 0.69H, ***Z*** isomer), 7.64 – 7.57 (m, 0.69H, ***Z*** isomer), 7.55 – 7.48 (m, 0.96H, mixture of ***E*** and ***Z*** isomers), 7.45 (s, 0.25H, ***E*** isomer), 7.35 – 7.29 (m, 0.26H, ***E*** isomer), 7.15 (dd, *J* = 5.1, 3.8 Hz, 0.70H, ***Z*** isomer), 7.05 (dd, *J* = 5.1, 3.7 Hz, 0.25H, ***E*** isomer), 4.42 – 4.30 (m, 2.00H, mixture of ***E*** and ***Z*** isomers), 1.45 – 1.34 (m, 3.00H, mixture of ***E*** and ***Z*** isomers). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.3, 163.2, 136.8, 136.0, 135.3, 134.3, 134.0, 131.9, 131.6, 130.8, 127.2, 126.9, 119.3, 118.1, 62.6, 62.4, 14.4, 14.3. **HRMS** (EI): $[M]^+$ Calcd for $C_9H_9ClO_2S$: 216.00118. Both isomers were found: 216.00107 (Δ = -0.52 ppm) and 216.00098 (Δ = -0.93 ppm).



12e

Ethyl 2-chloro-5-phenylpent-2-enoate

Following the general procedure **D** (0.5 mmol scale), the reaction mixture was isolated by preparatory TLC (5% EtOAc in cyclohexane). The desired product **12e** was obtained as a yellow oil (12 mg, 17%, *E:Z* = 1:4.0). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2.06H, mixture of ***E*** and ***Z*** isomers), 7.24 – 7.16 (m, 2.87H, mixture of ***E*** and ***Z*** isomers), 7.10 (t, *J* = 7.1 Hz, 0.80H, ***Z*** isomer), 6.46 (t, *J* = 7.7 Hz, 0.20H, ***E*** isomer), 4.32 – 4.22 (m, 2.00H, mixture of ***E*** and ***Z*** isomers), 2.93 – 2.63 (m, 4.16H, mixture of ***E*** and ***Z*** isomers), 1.36 – 1.30 (m, 3.39H, mixture of ***E*** and ***Z*** isomers). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 162.6, 143.7, 141.2, 140.7, 140.7, 128.7, 128.6, 128.6, 128.4, 126.5, 126.4, 125.5, 62.4, 62.1, 35.0, 33.8, 31.6, 31.2, 14.3, 14.3. **HRMS** (EI): $[M]^+$ Calcd for $C_{13}H_{15}ClO_2$: 238.07606. Found: 238.07599 (Δ = -0.29 ppm).

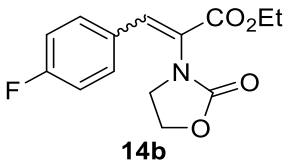


14a

Ethyl 2-(2-oxooxazolidin-3-yl)-3-phenylpropanoate

Following the general procedure **E**, the desired product **14a** was obtained as a yellowish oil (42 mg, 65%, *E:Z* > 1:20); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.37 (m, 5H), 6.19 (s, 1H), 4.55 – 4.45 (m, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.82 – 3.73 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$)

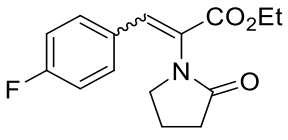
δ 164.7, 156.3, 147.5, 134.6, 130.9, 129.1, 127.3, 114.7, 62.7, 60.7, 46.4, 14.3. **HRMS** (ESI): $[M+H]^+$ Calcd for $C_{14}H_{15}NO_4$: 261.10011. Found: 261.10055 (Δ = 1.68 ppm).



14b

Ethyl 3-(4-fluorophenyl)-2-(2-oxooxazolidin-3-yl)propanoate

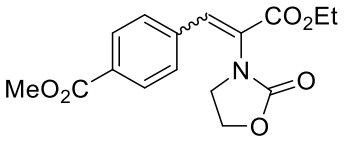
Following the general procedure **E**, the desired product **14b** was obtained as a yellowish oil (39 mg, 56%, *E:Z* > 1:20). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.44 (m, 2H), 7.15 – 7.06 (m, 2H), 6.13 (s, 1H), 4.54 – 4.45 (m, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.81 – 3.72 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.6, 164.4 (d, J = 252.1 Hz), 156.3, 146.6, 130.8 (d, *J* = 3.1 Hz), 129.4 (d, *J* = 8.6 Hz), 116.4, 116.2, 114.5 (d, *J* = 1.1 Hz), 62.7, 60.8, 46.4, 14.3. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -108.9 – -109.1 (m). **HRMS** (ESI): $[M+Na]^+$ Calcd for $C_{14}H_{14}NO_4NaF$: 302.0805. Found: 302.0805 (Δ = 0.0 ppm).



14c

Ethyl 3-(4-fluorophenyl)-2-(2-oxopyrrolidin-1-yl)propanoate

Following the general procedure **E**, the desired product **14c** was obtained as a yellowish oil (13 mg, 19%, *E:Z* > 1:20). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.39 (m, 2H), 7.13 – 7.04 (m, 2H), 6.20 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.54 (t, *J* = 7.0 Hz, 2H), 2.58 (t, *J* = 8.0 Hz, 2H), 2.25 – 2.10 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.4, 164.6, 164.3 (d, *J* = 251.4 Hz), 147.1, 131.1, 129.2 (d, *J* = 8.5 Hz), 116.2 (d, *J* = 21.9 Hz), 115.0 (d, *J* = 1.1 Hz), 60.6, 49.2, 31.8, 19.3, 14.4. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -109.6 – -109.7 (m). **HRMS** (ESI): $[M+H]^+$ Calcd for $C_{15}H_{17}FNO_3$: 278.1192. Found: 278.1183 (Δ = -3.2 ppm).



14d

Methyl 4-(3-ethoxy-3-oxo-2-(2-oxooxazolidin-3-yl)prop-1-en-1-yl)benzoate

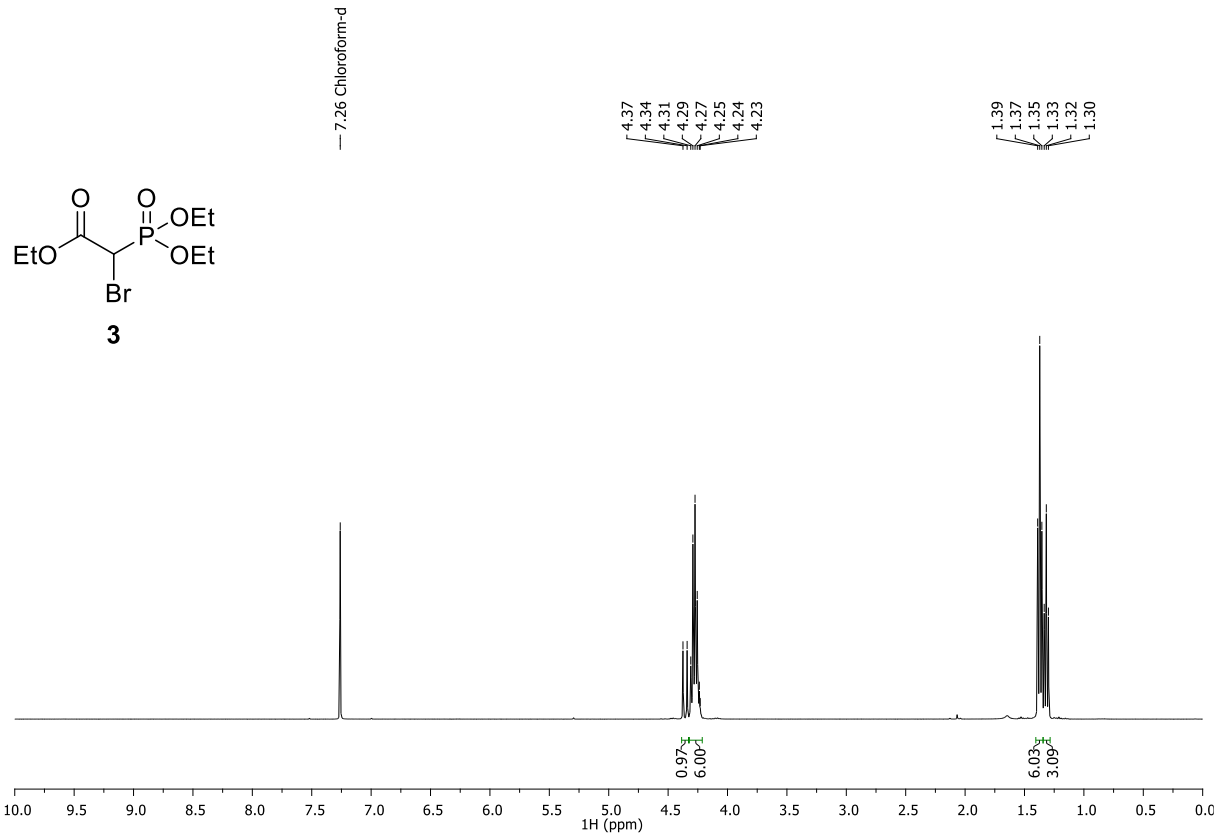
Following the general procedure **E**, the desired product **14d** was obtained as a yellowish oil (26 mg, 67%, *E:Z* > 1:20). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.8 Hz, 2.00H), 7.58 (d, *J* = 8.4 Hz, 1.90H), 6.27 (s, 0.86H), 4.53 (t, *J* = 7.9 Hz, 1.89H), 4.24 (q, *J* = 7.1 Hz, 1.97H), 3.93 (s, 2.99H), 3.79 (t, *J* = 7.9 Hz, 1.90H), 1.31 (t, *J* = 7.1 Hz, 2.97H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.3, 164.4, 156.3,

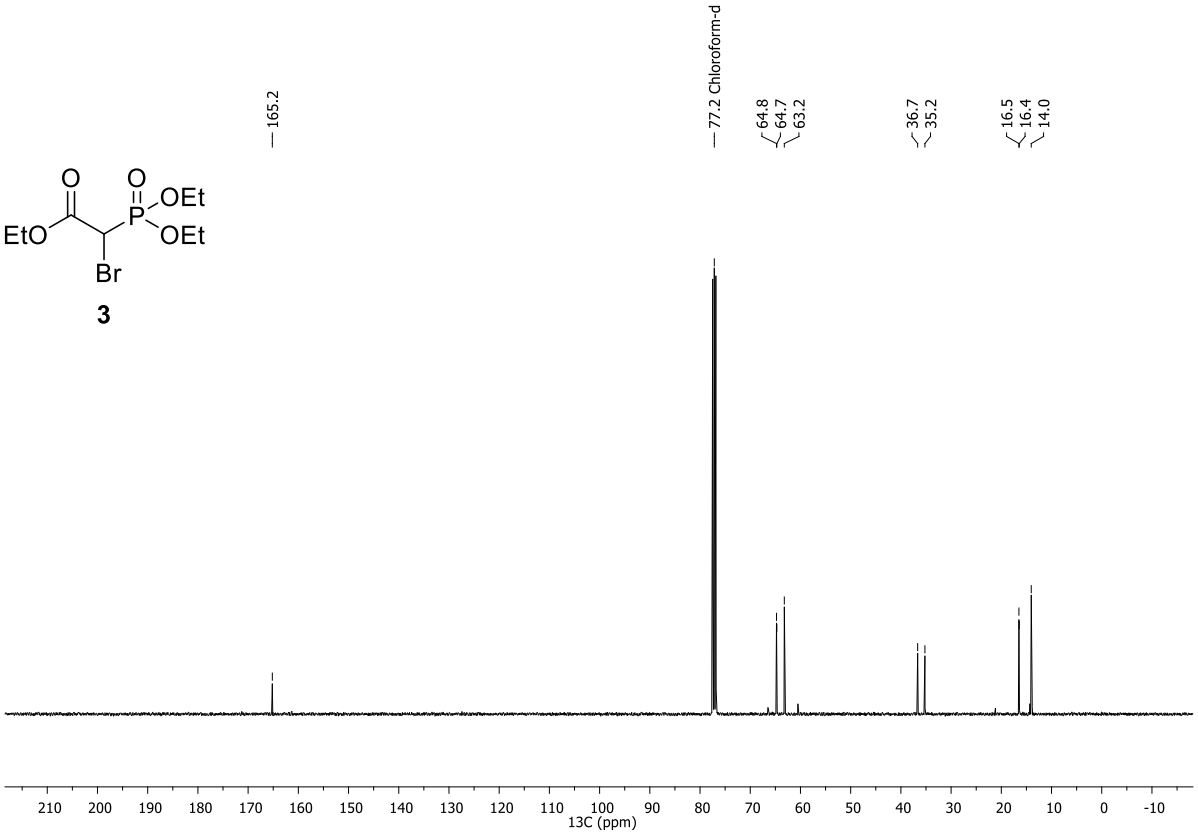
146.5, 139.0, 132.3, 130.3, 127.3, 116.5, 62.8, 61.0, 52.5, 46.4, 14.3. **HRMS** (ESI): $[M+Na]^+$ Calcd for $C_{16}H_{17}NO_6Na$: 34.0954. Found: 342.0955 (Δ = 0.3 ppm).

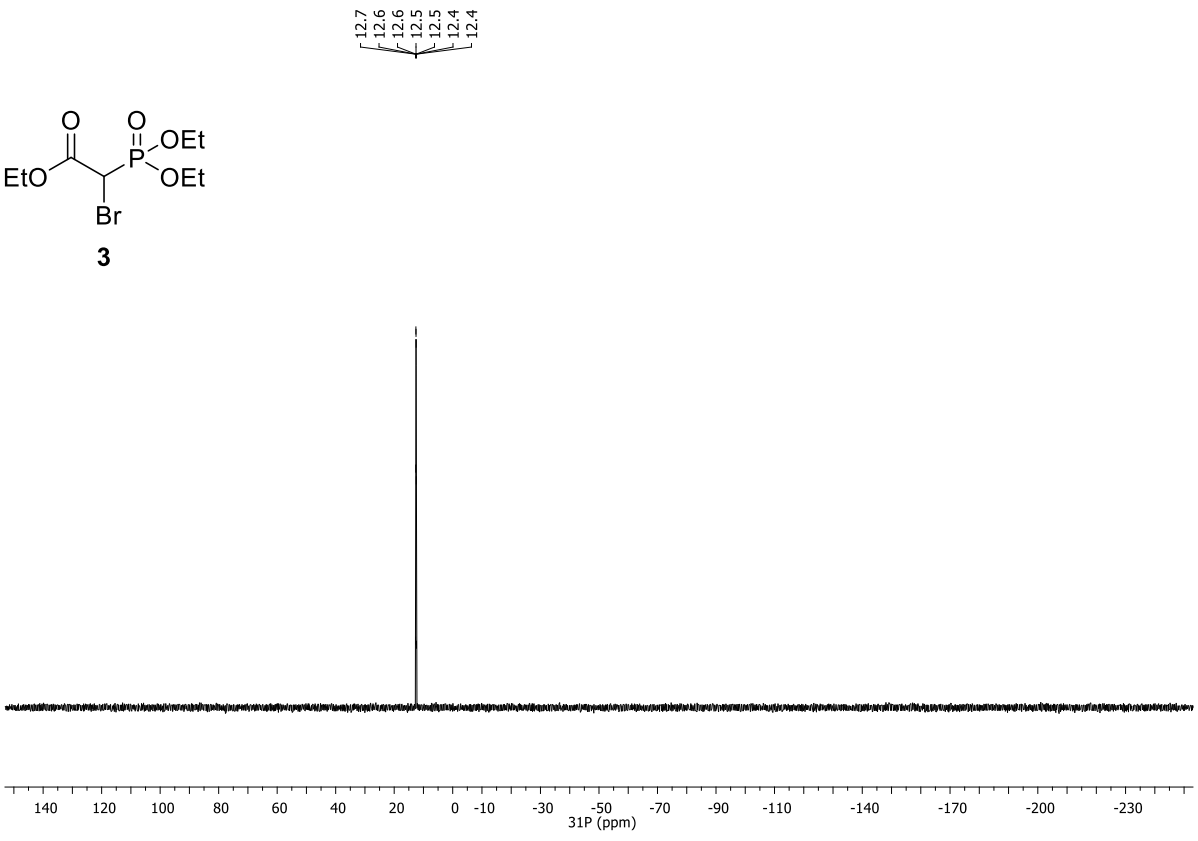
NMR spectra

NMR spectra of phosphonates

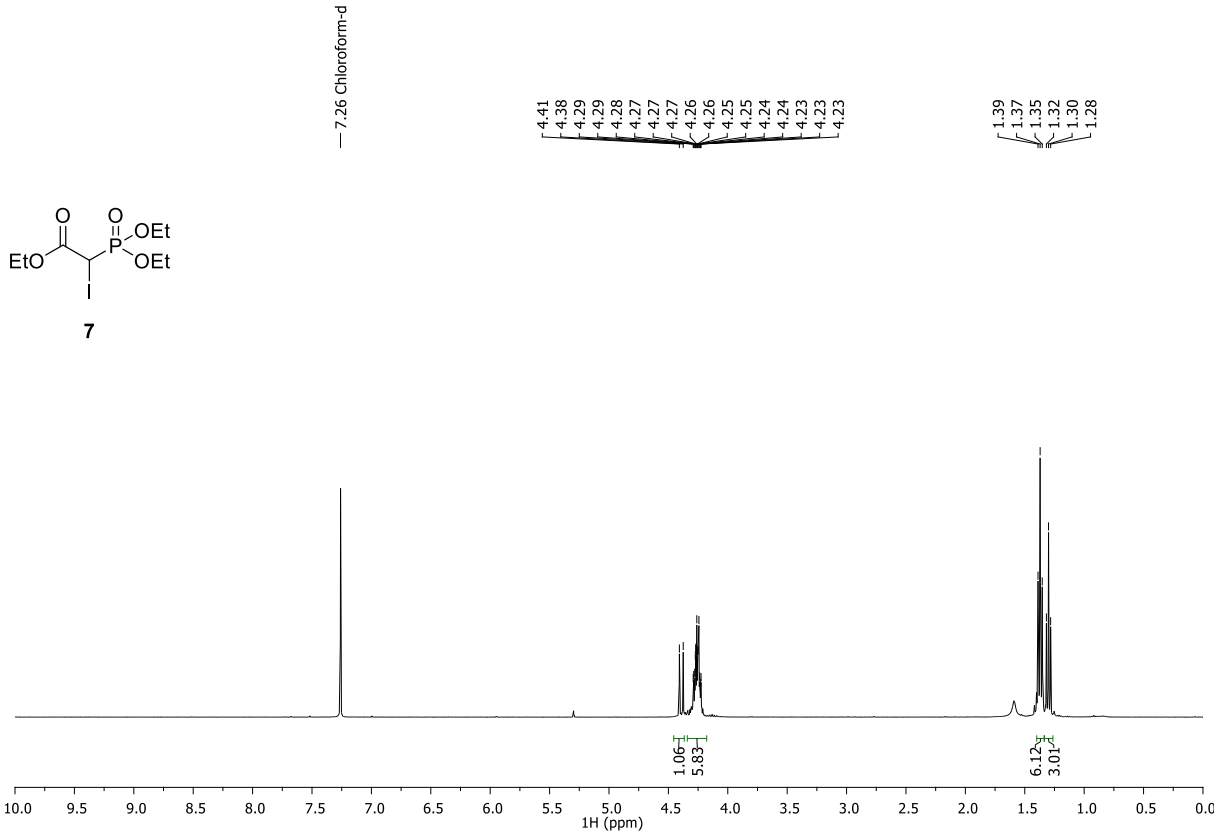
^{1}H, ^{13}C and ^{31}P NMR spectra of ethyl 2-bromo-2-(diethoxyphosphoryl)acetate **3** in $CDCl_3$

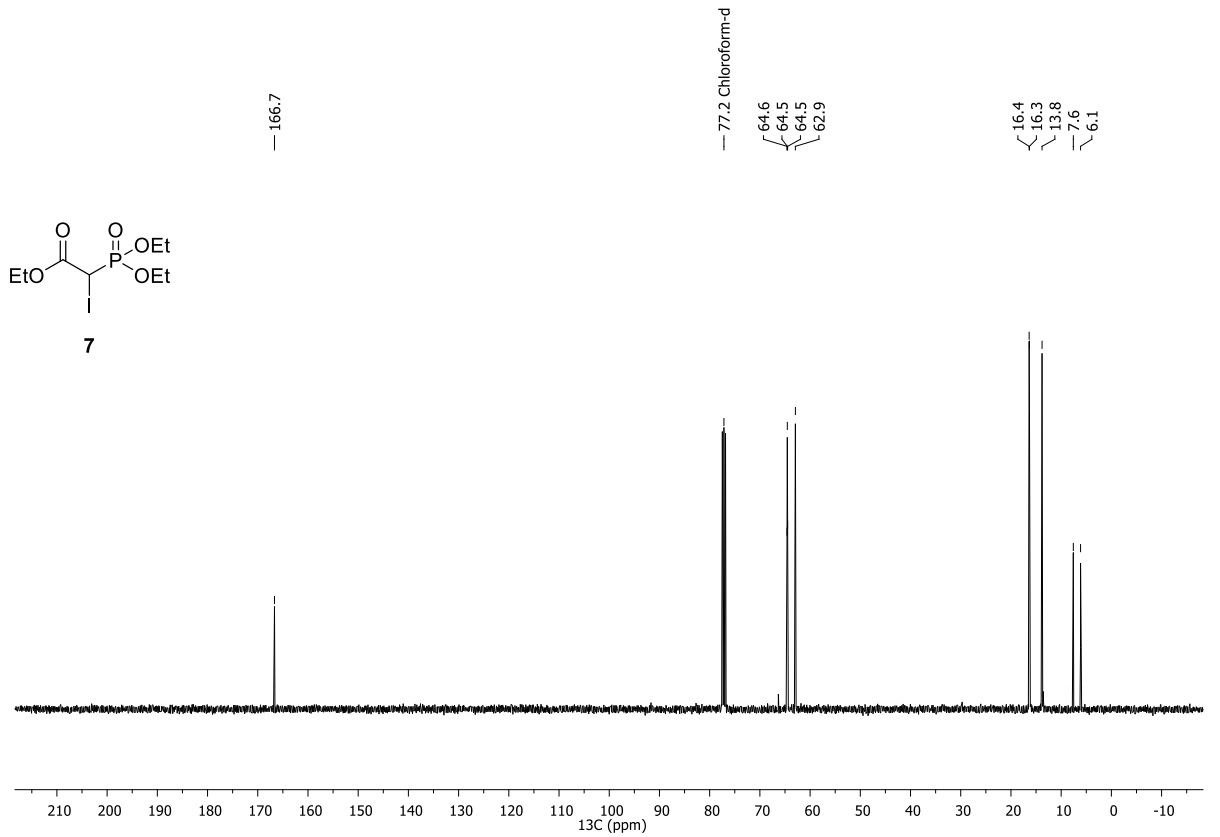


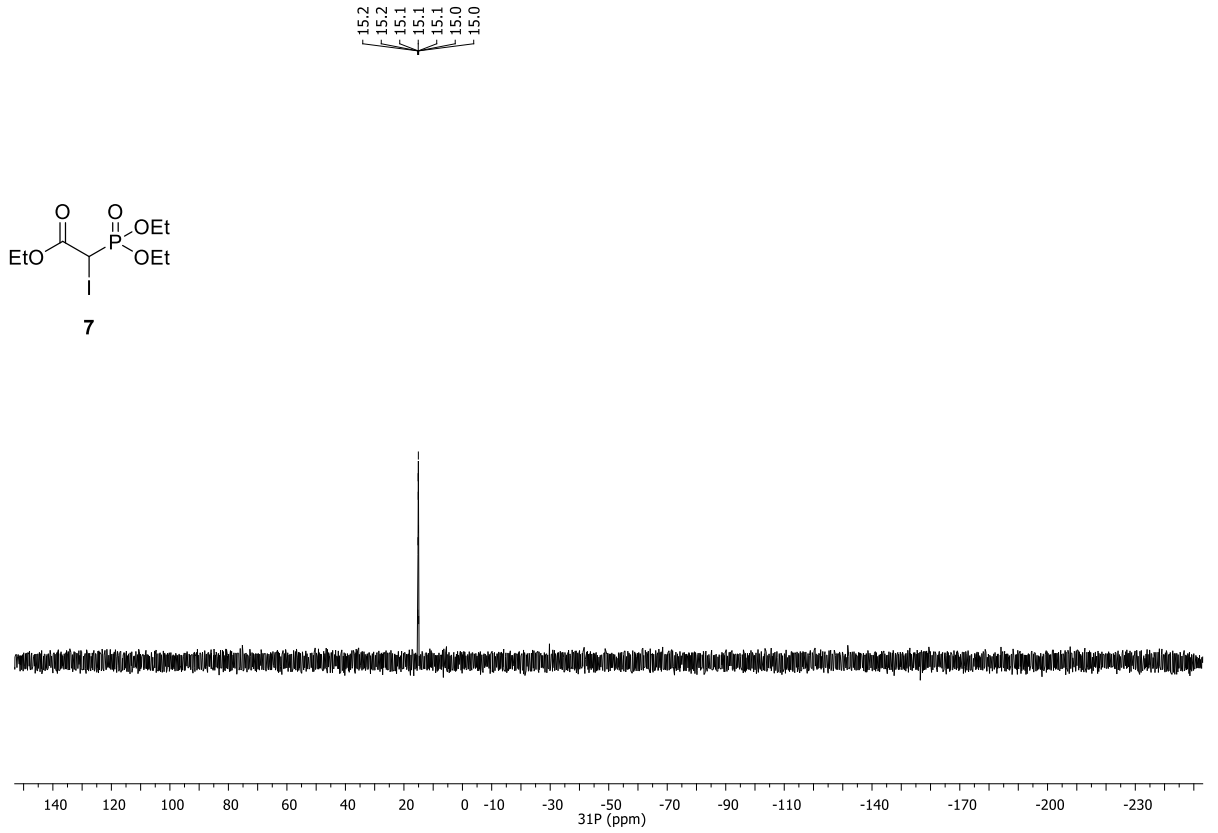

165.2
77.2 Chloroform-d
64.8
64.7
63.2
36.7
35.2
16.5
16.4
14.0
O
O
OEt
EtO
P
OEt
Br
3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)


12.7
12.6
12.6
12.5
12.5
12.4
12.4
O
O
OEt
EtO
P
OEt
Br
3
140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -110 -140 -170 -200 -230
31P (ppm)

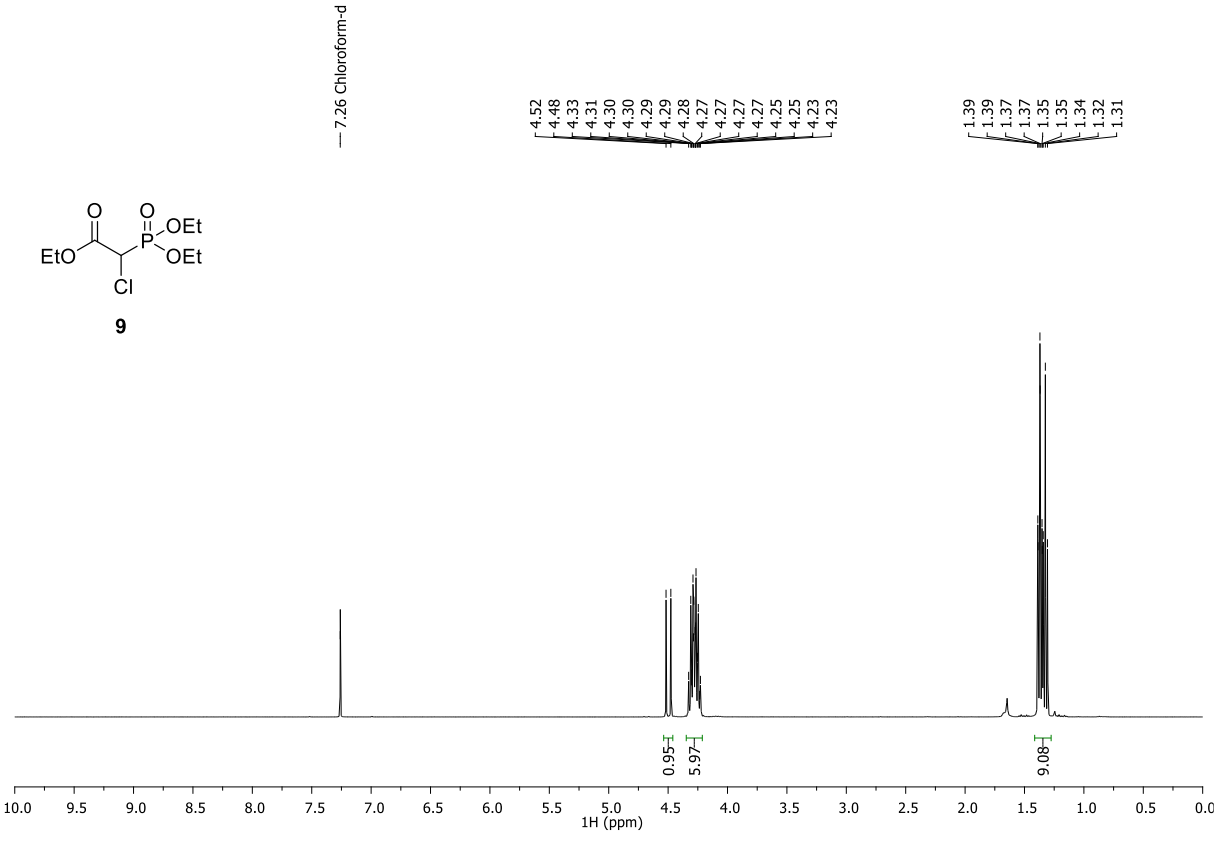
^{1}H, ^{13}C and ^{31}P NMR spectra of ethyl 2-iodo-2-(diethoxyphosphoryl)acetate **7** in $CDCl_3$

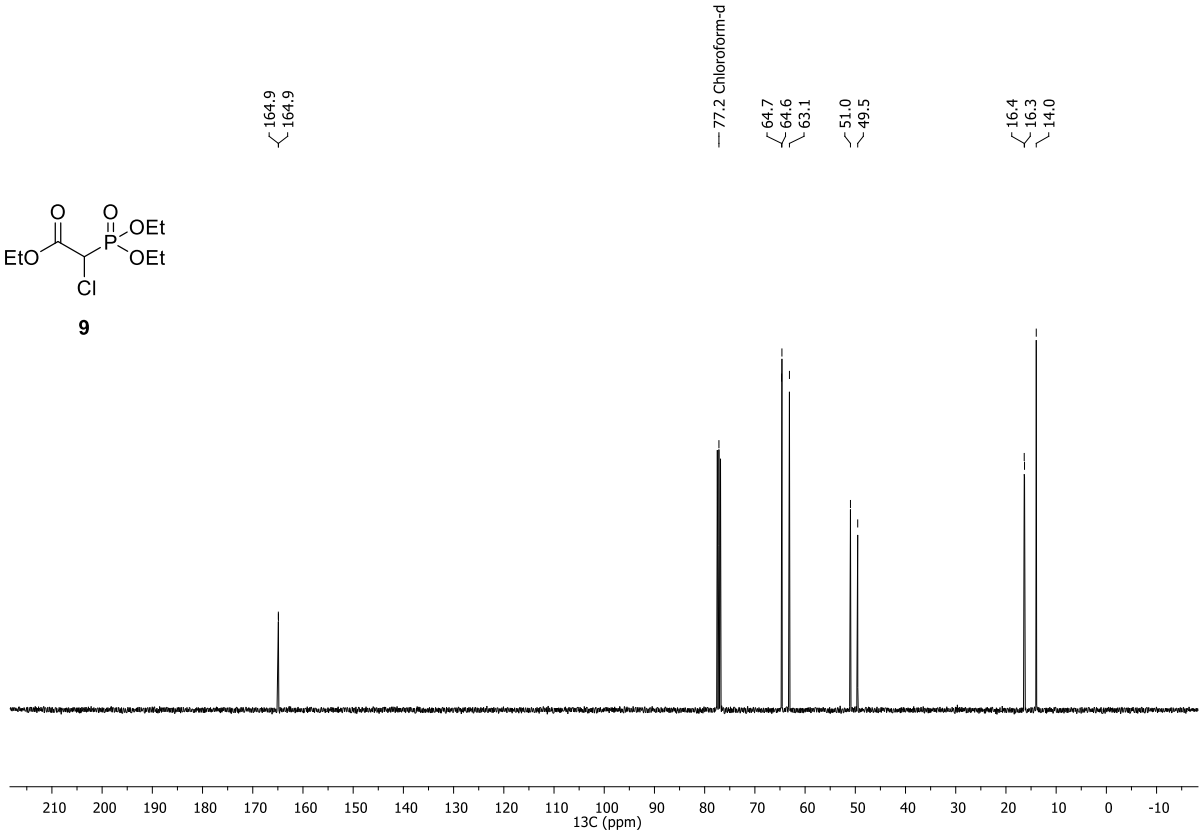


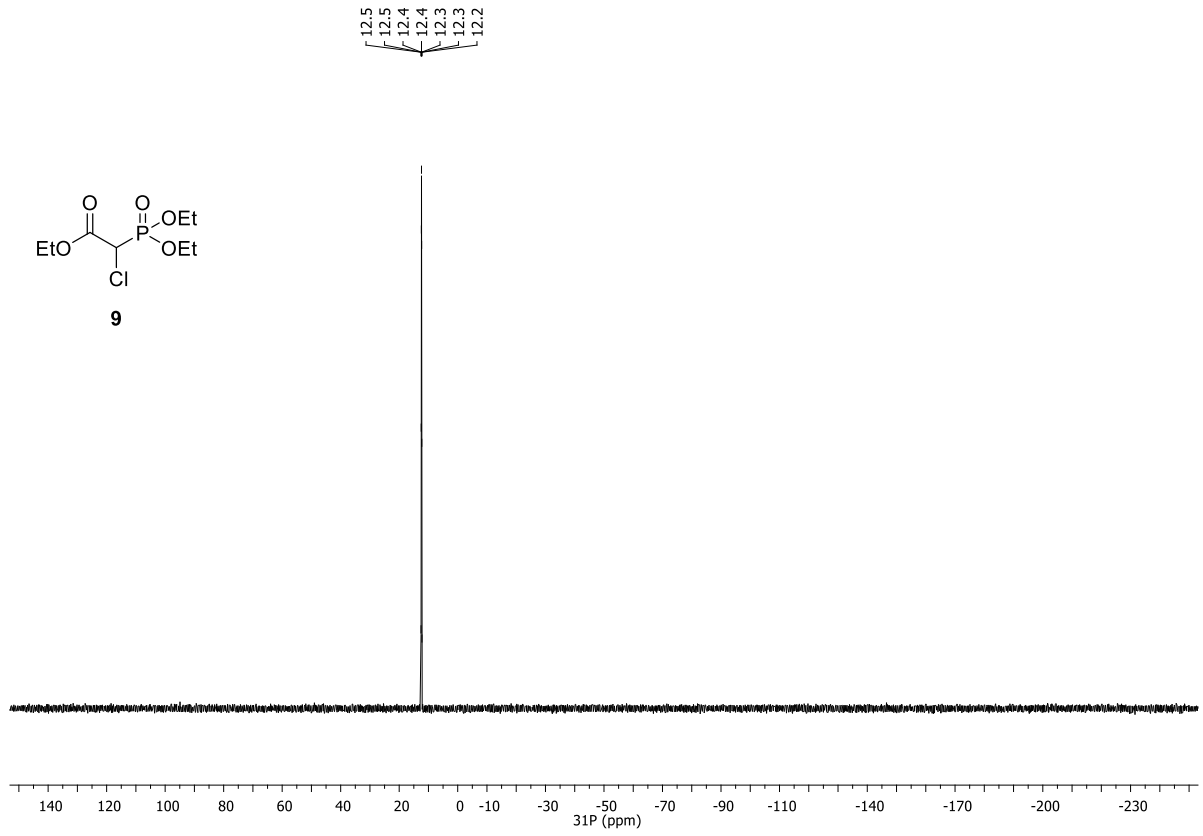




^{1}H, ^{13}C and ^{31}P NMR spectra of ethyl 2-chloro-2-(diethoxyphosphoryl)acetate **9** in $CDCl_3$

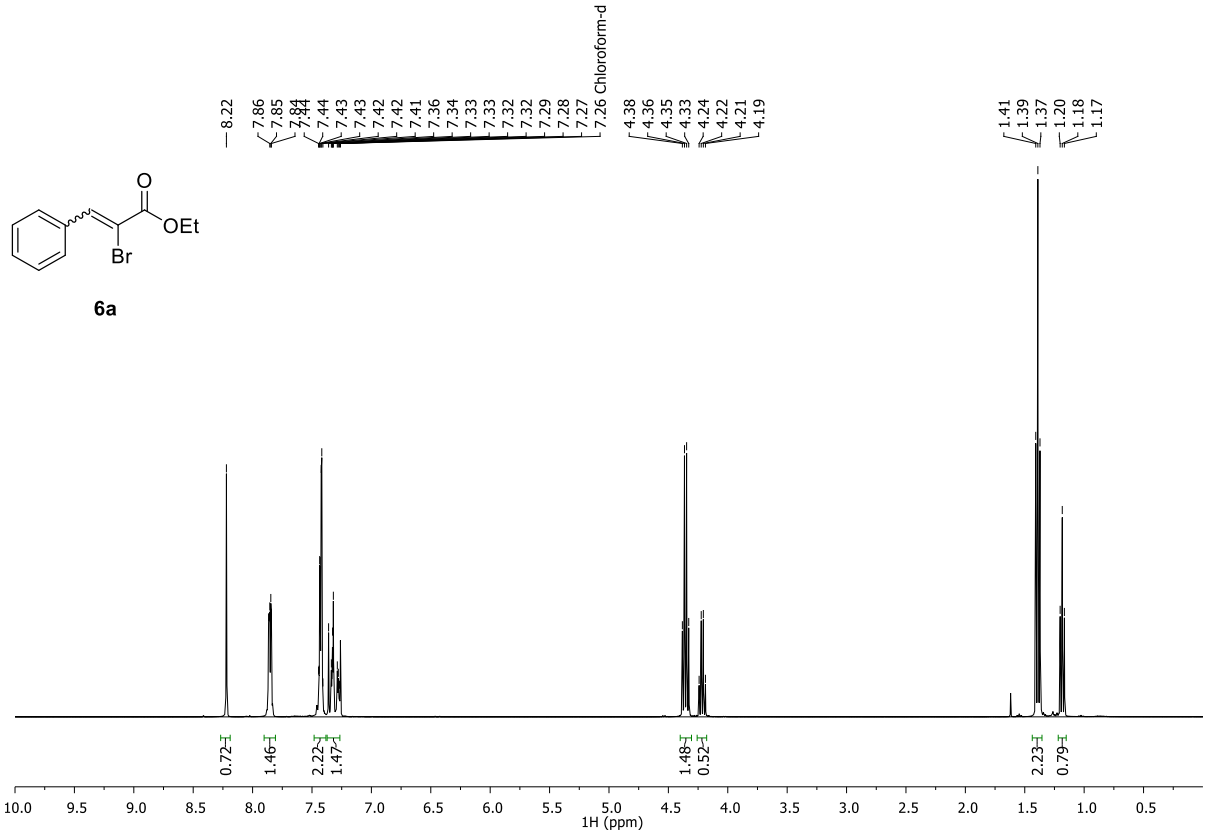


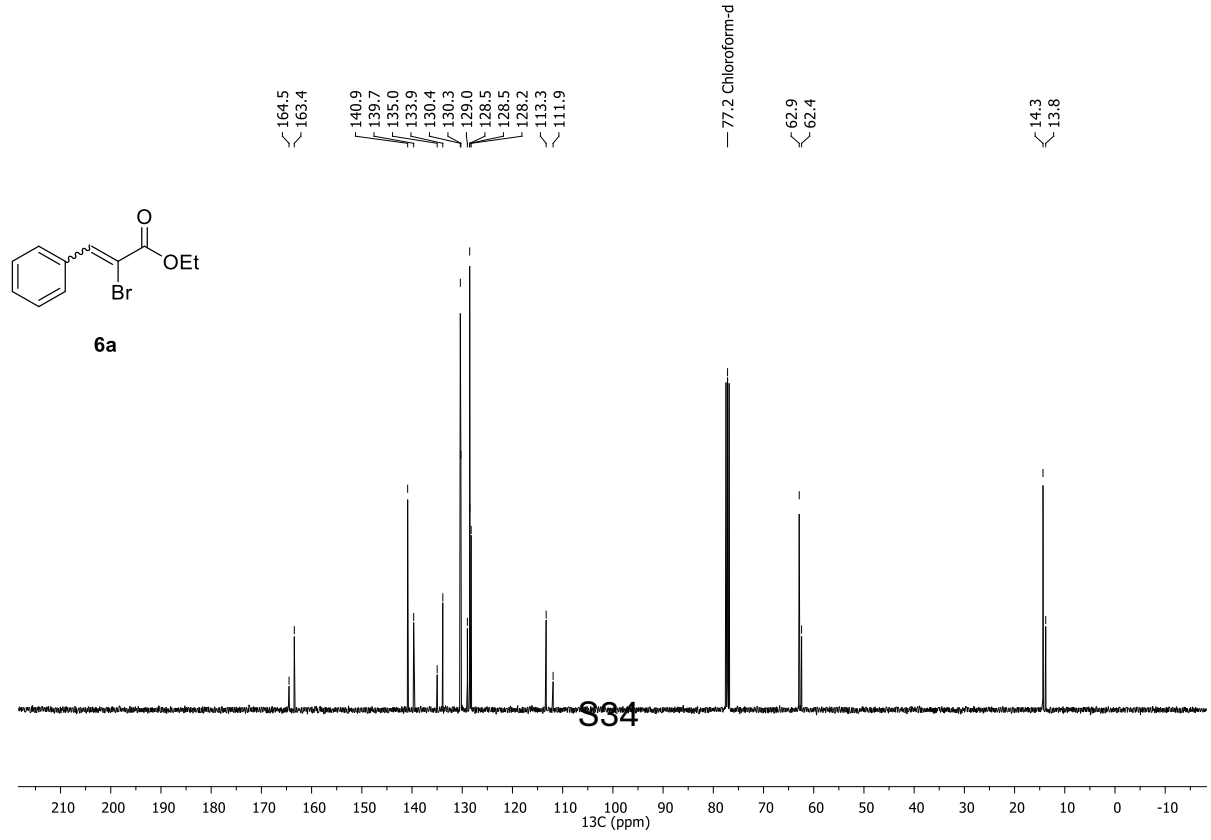

164.9
164.9
77.2 Chloroform-d
64.7
64.6
63.1
51.0
49.5
16.4
16.3
14.0
O
O
OEt
EtO
P
OEt
Cl
9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)


12.5
12.5
12.4
12.4
12.3
12.3
12.2
O
O
OEt
EtO
P
OEt
Cl
9
140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -110 -140 -170 -200 -230
31P (ppm)

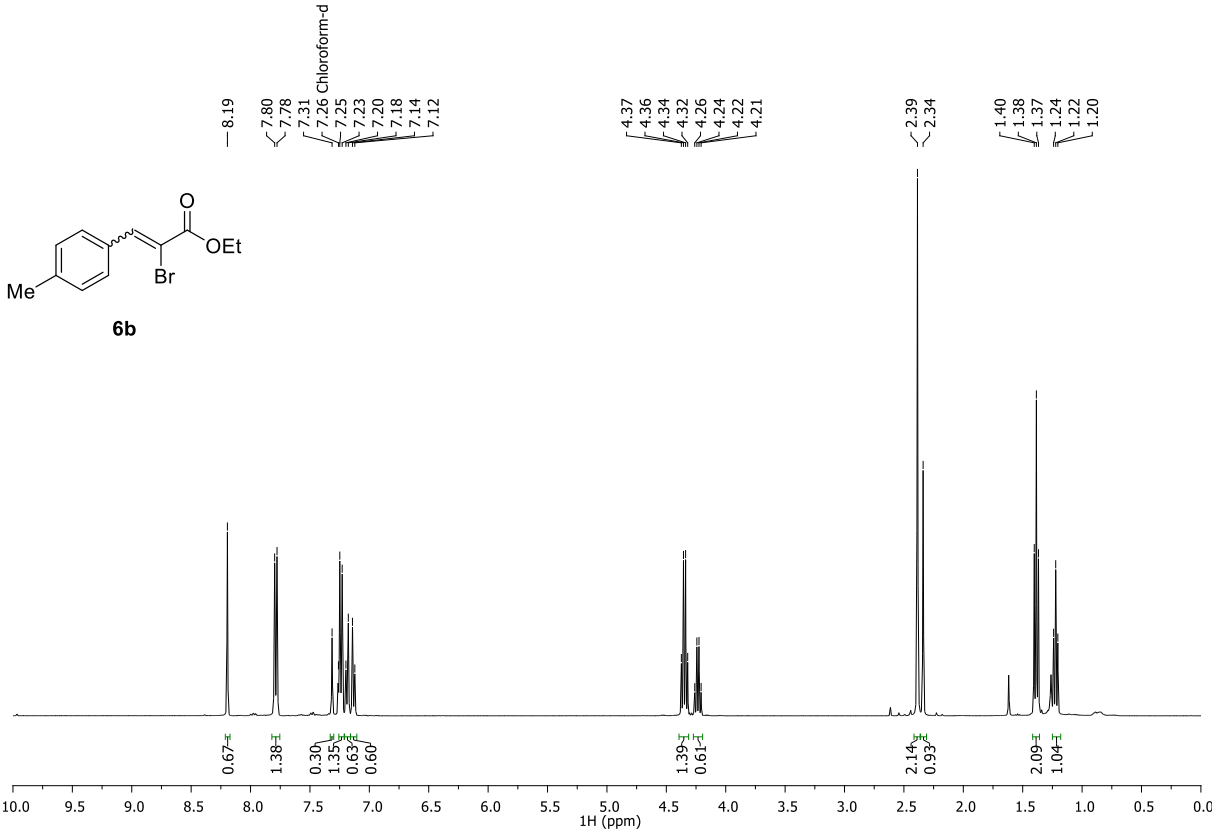
NMR spectra of bromoalkenes

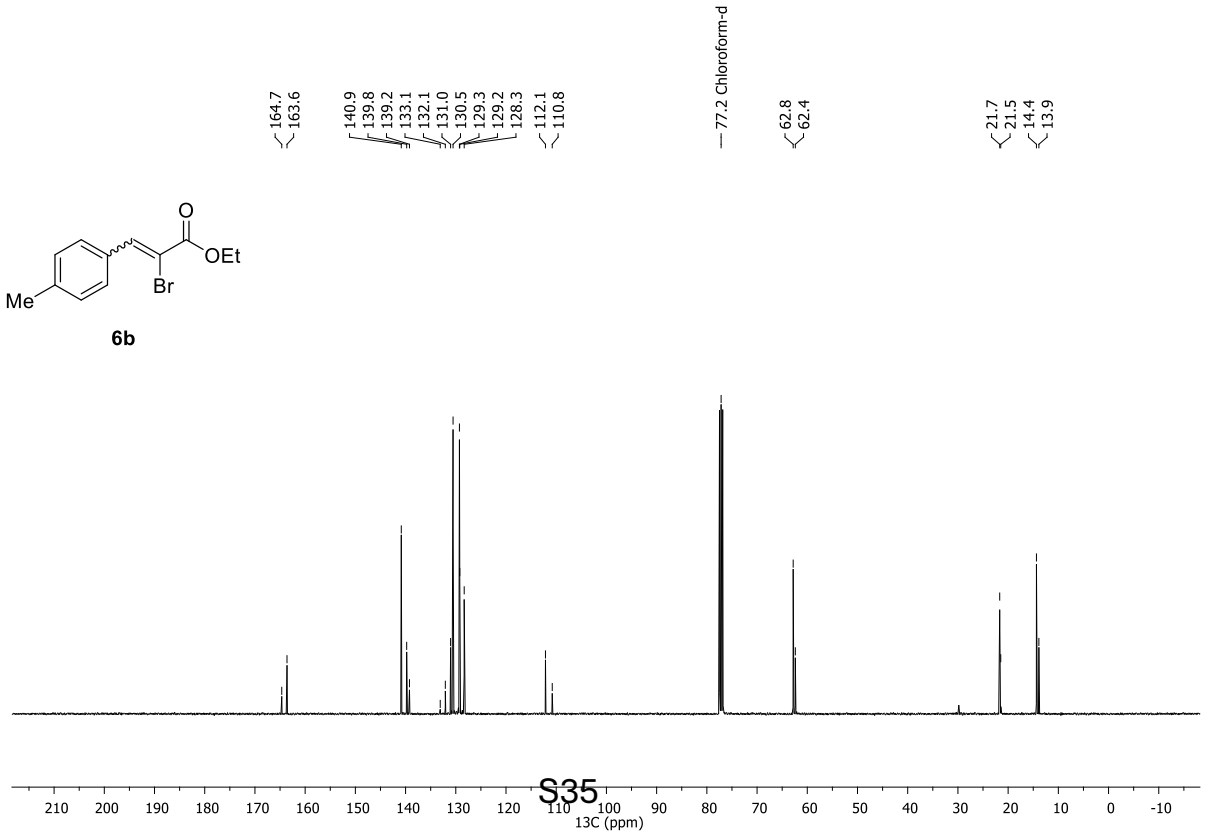
^{1}H and ^{13}C NMR spectra of ethyl 2-bromoacrylate **6a** in $CDCl_3$



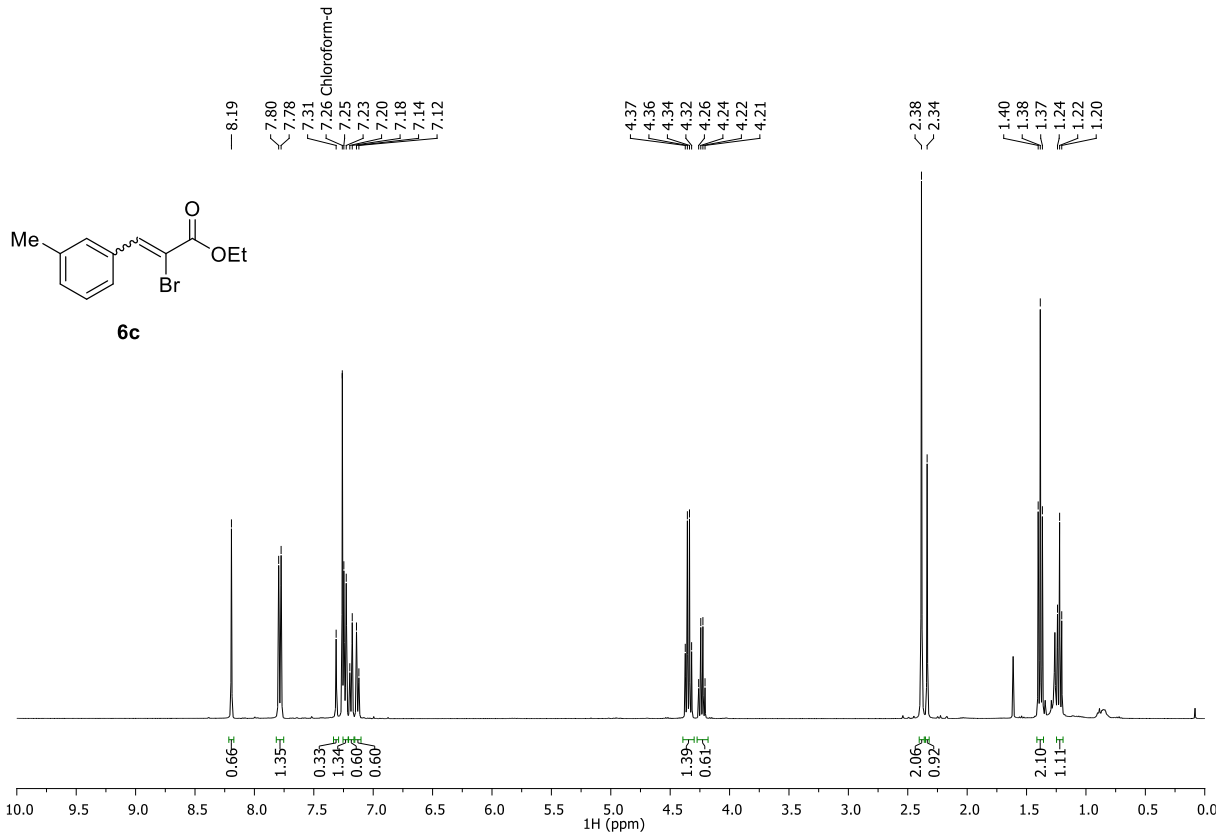


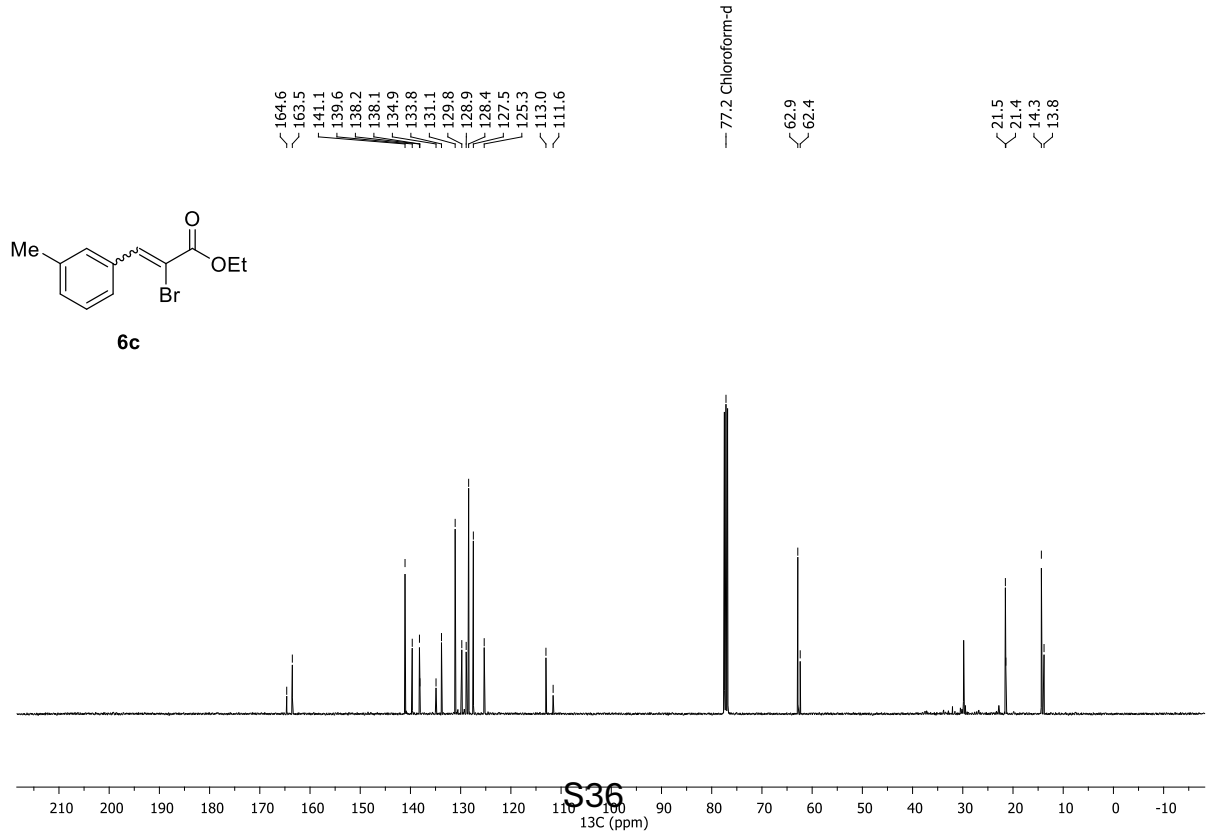
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-3-(p-tolyl)acrylate **6b** in $CDCl_3$



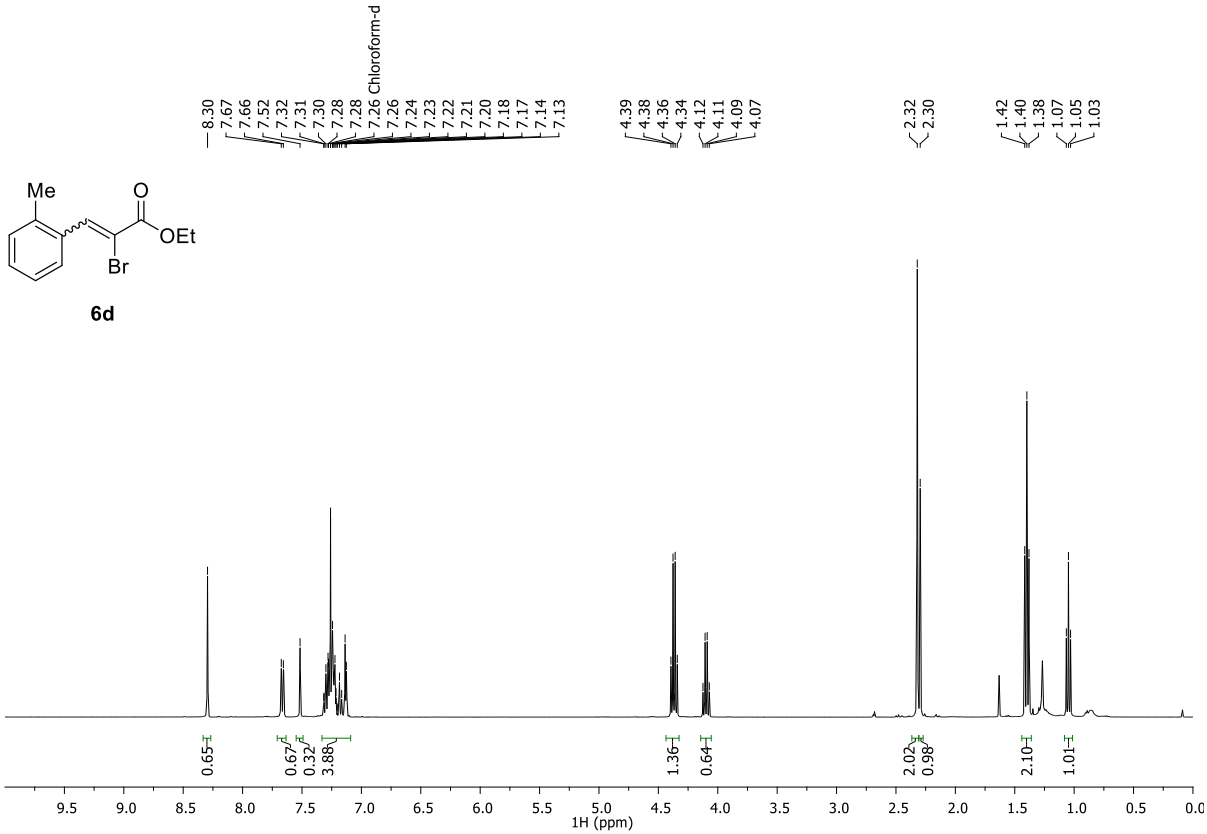


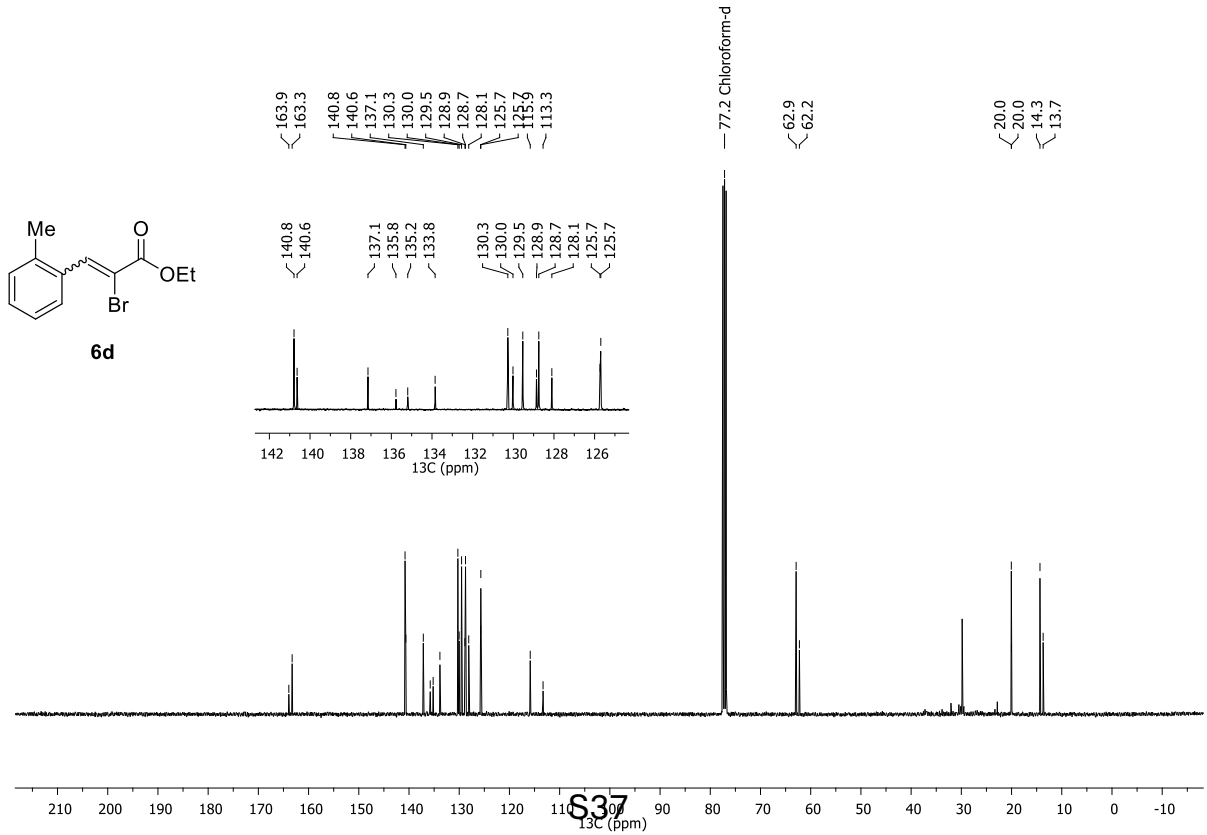
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-3-(m-tolyl)acrylate **6c** in $CDCl_3$



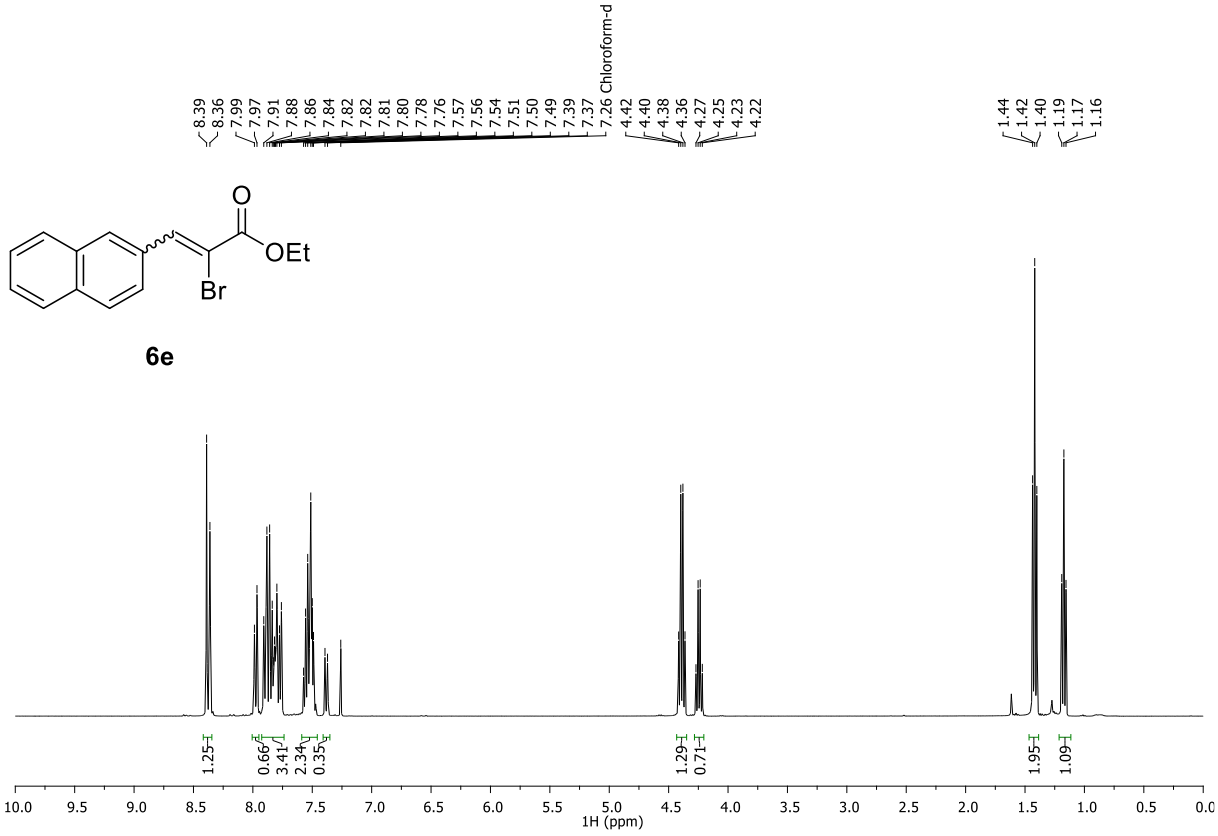


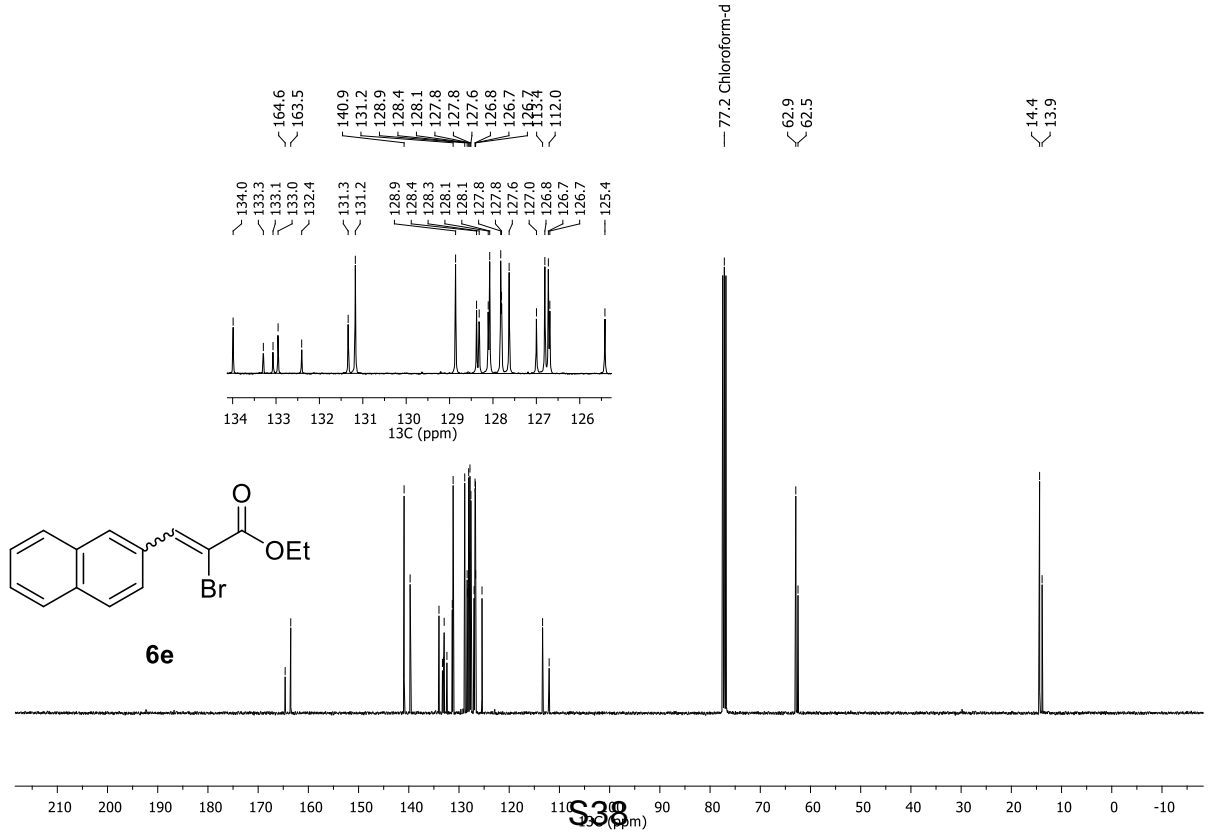
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-3-(o-tolyl)acrylate **6d** in $CDCl_3$



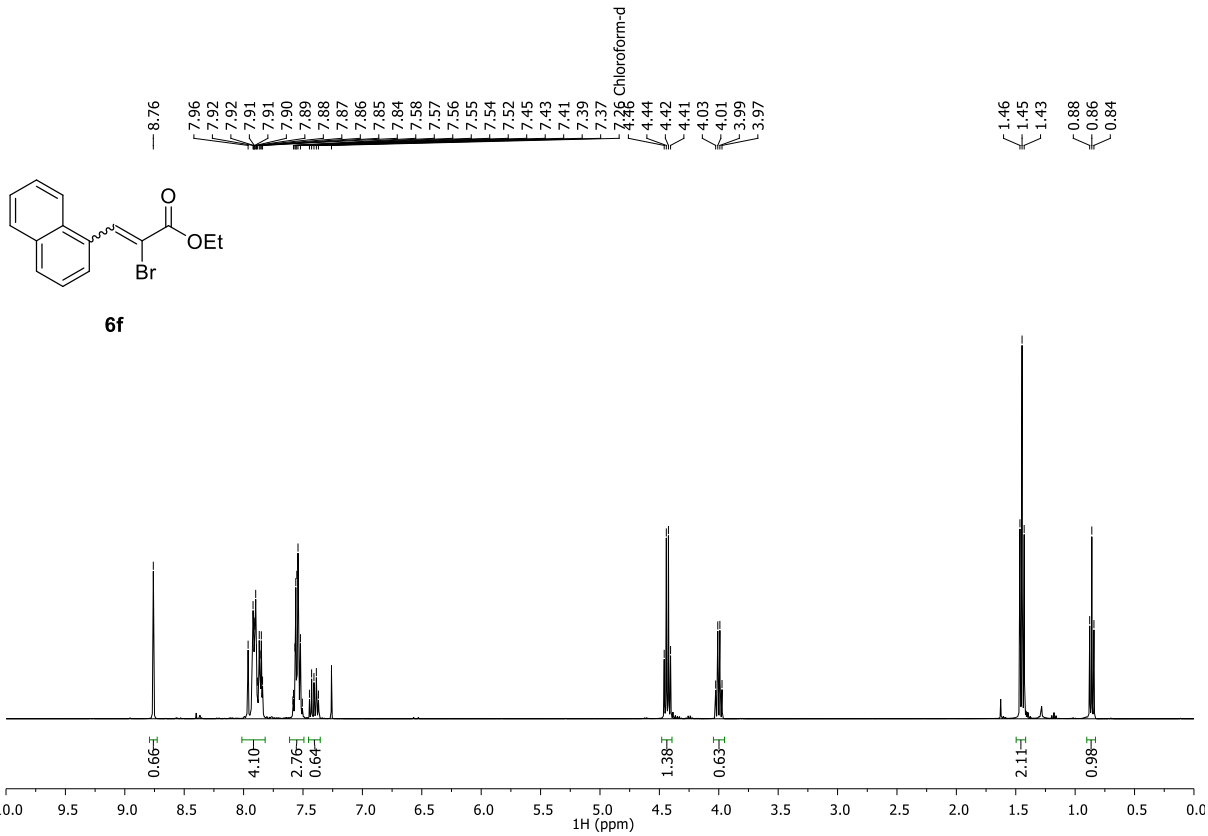


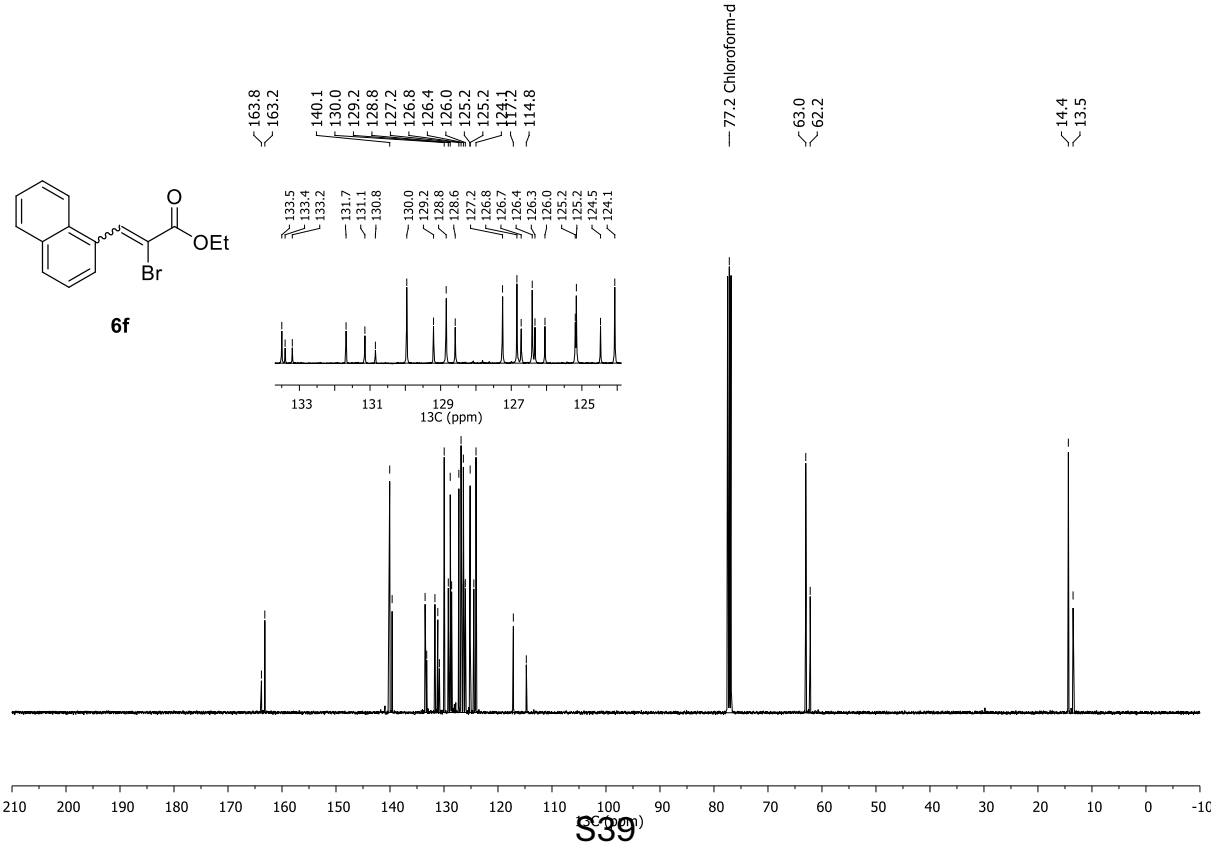
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-3-(naphthalen-2-yl)acrylate **6e** in $CDCl_3$



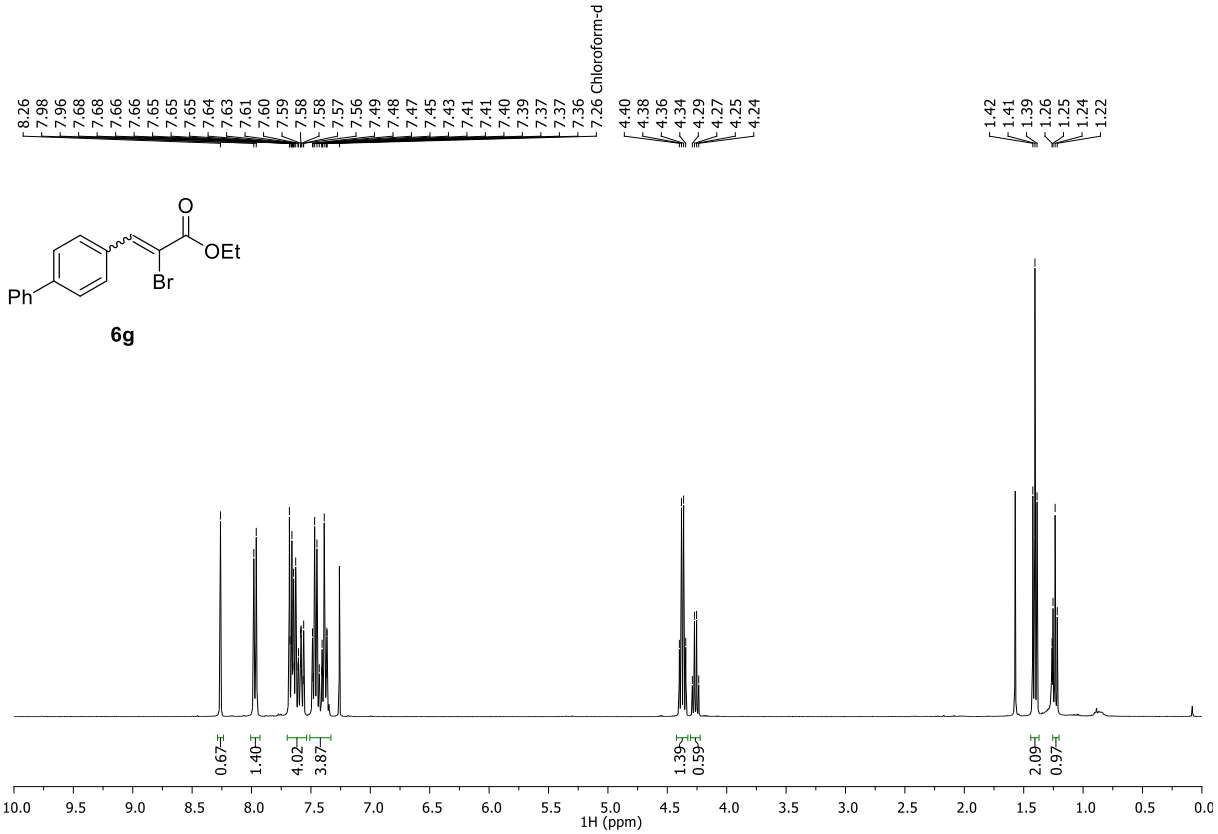


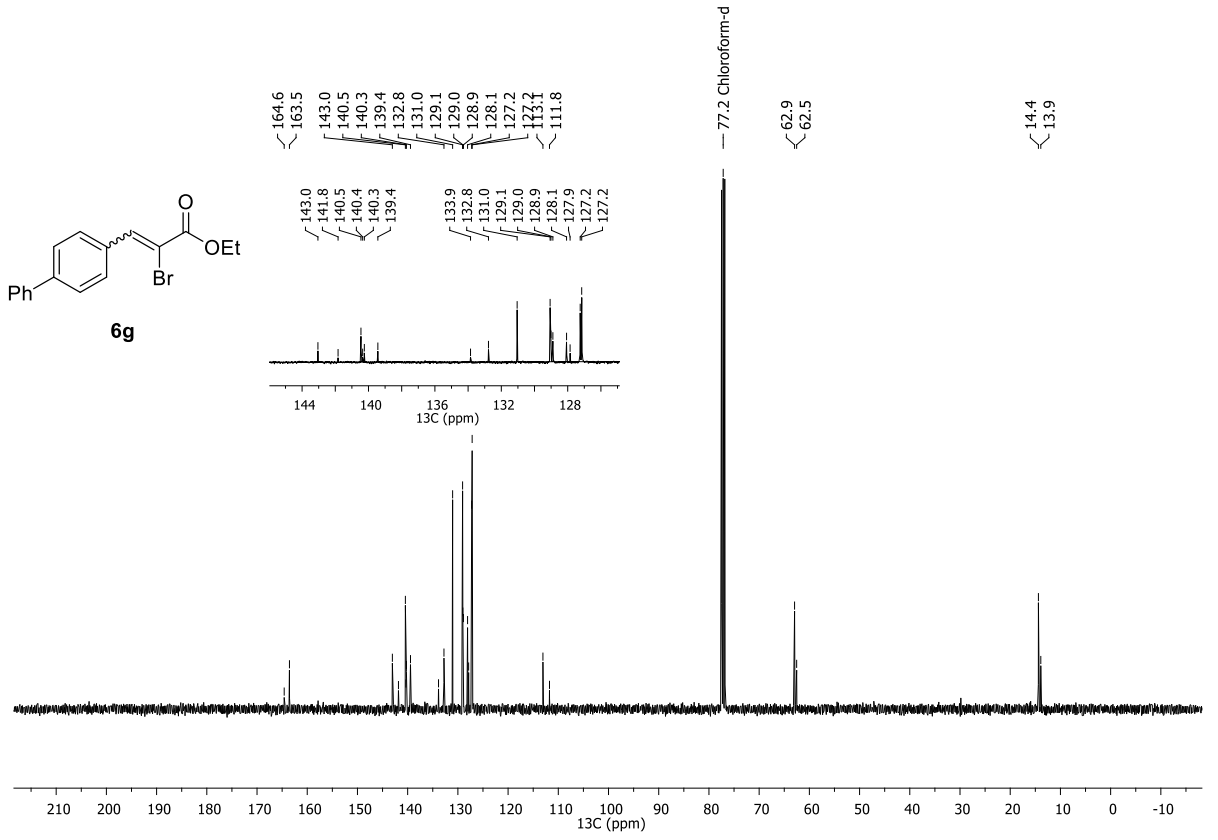
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-3-(naphthalen-1-yl)acrylate **6f** in $CDCl_3$



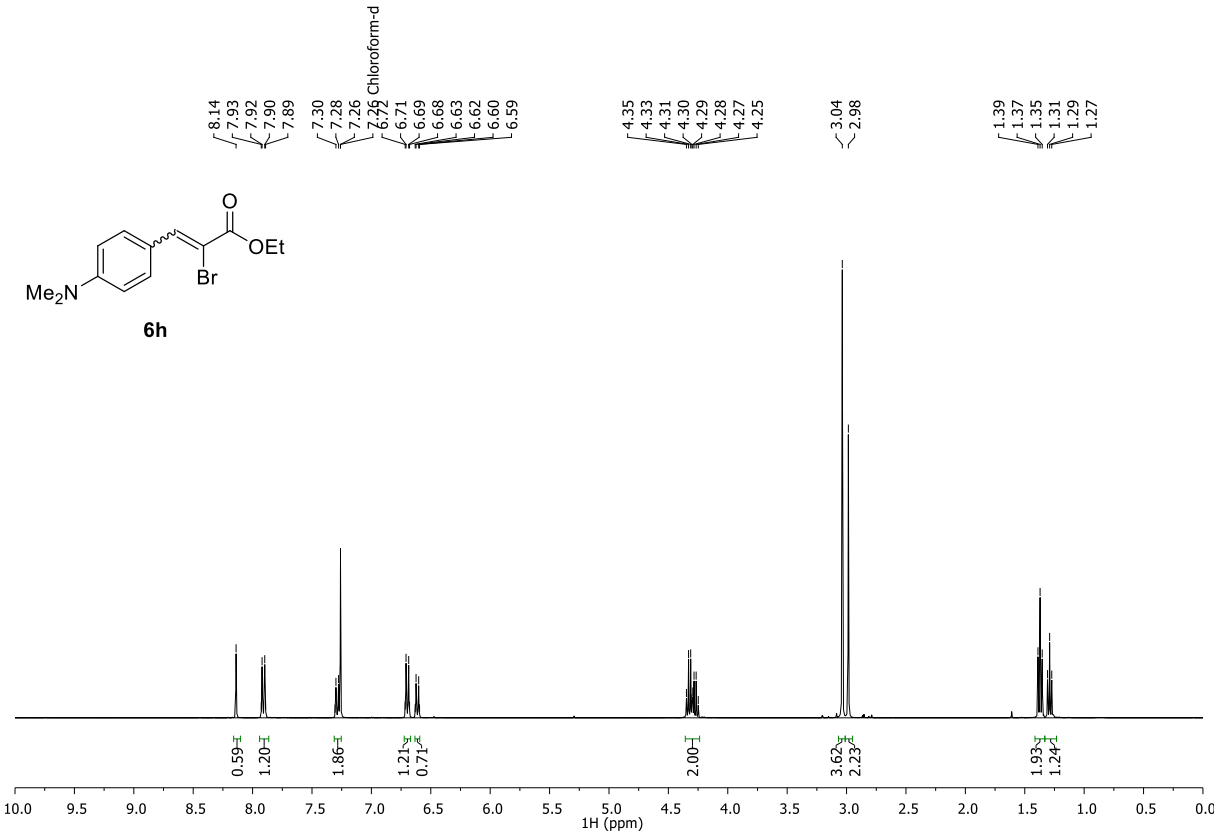


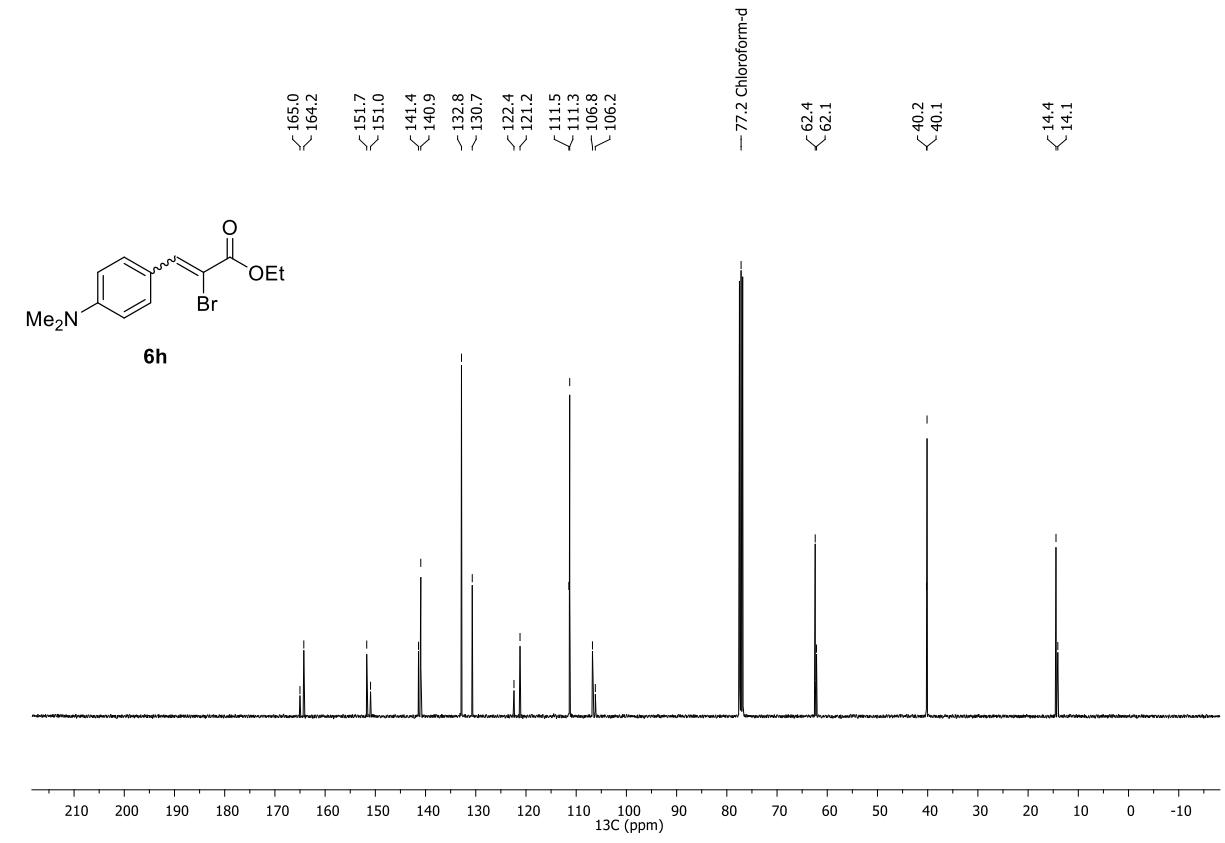
^{1}H and ^{13}C NMR spectra of ethyl 3-([1,1'-biphenyl]-4-yl)-2-bromoacrylate **6g** in $CDCl_3$



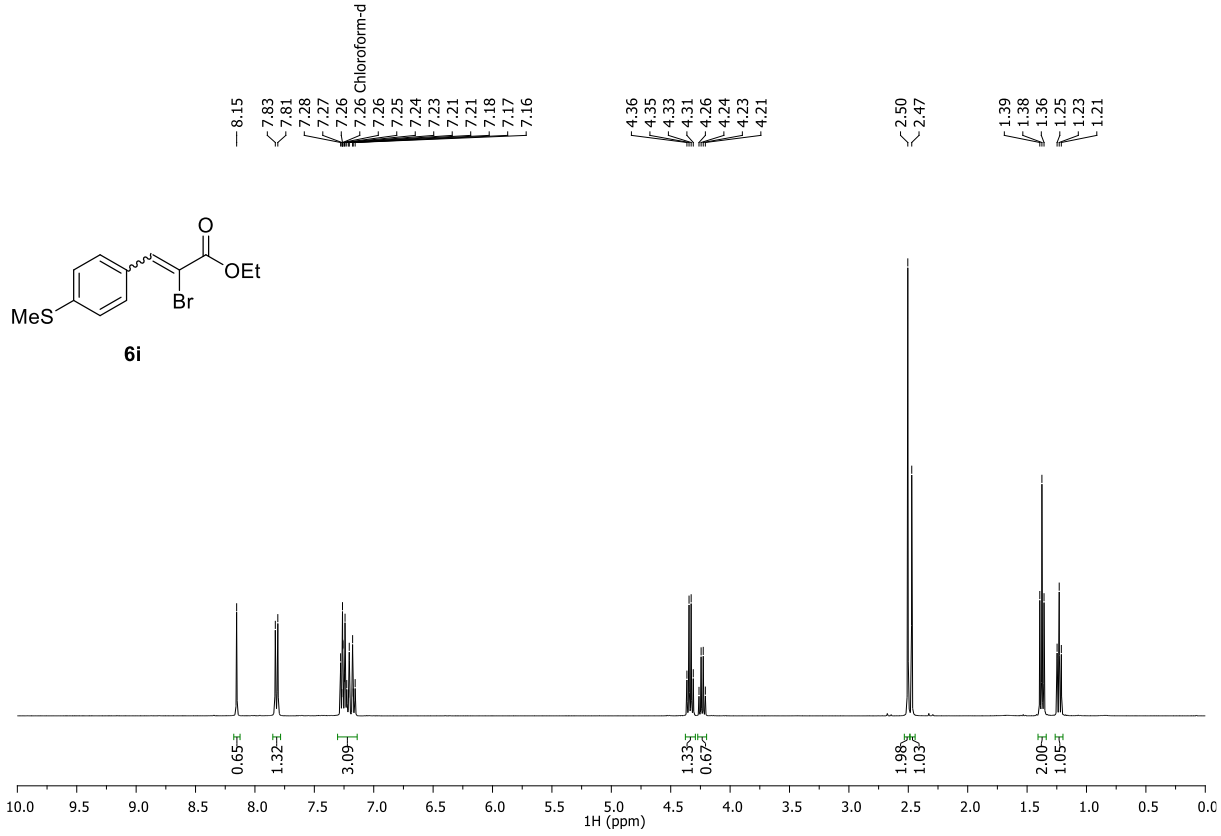


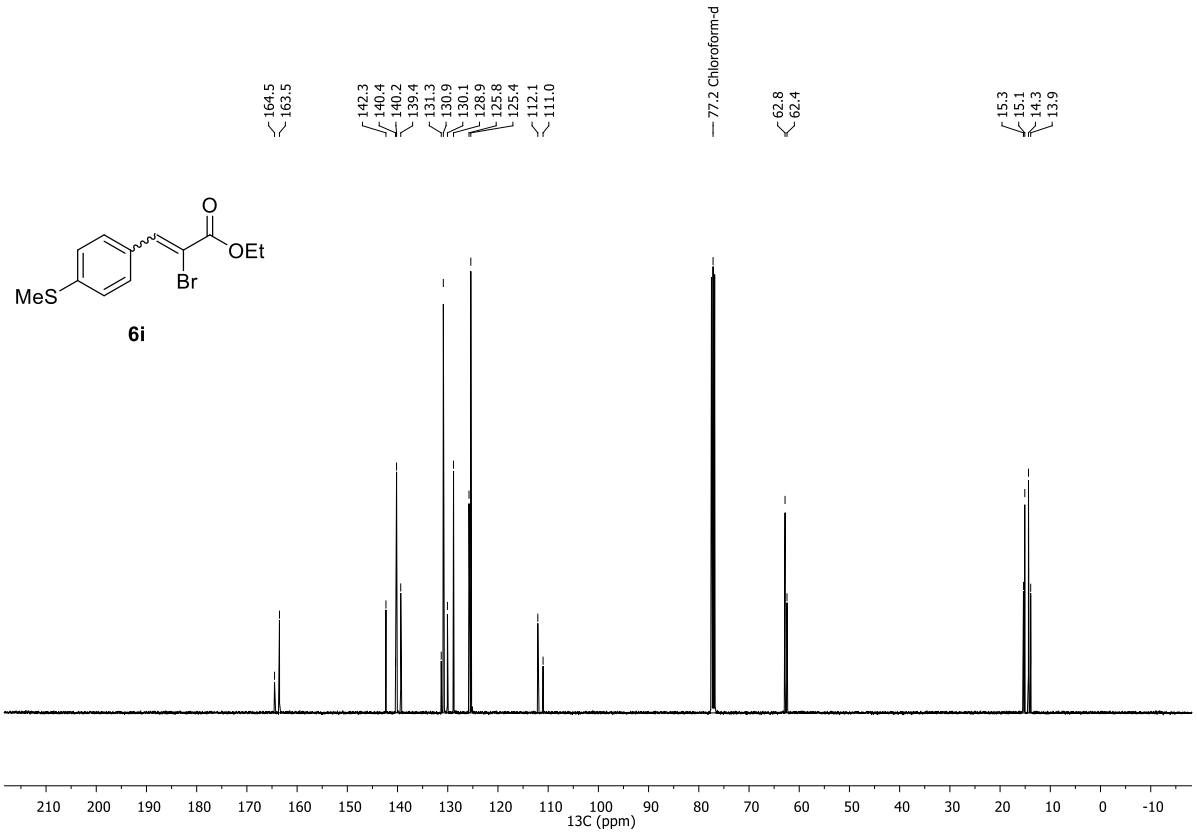
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-3-(4-(dimethylamino)phenyl)acrylate **6h** in $CDCl_3$



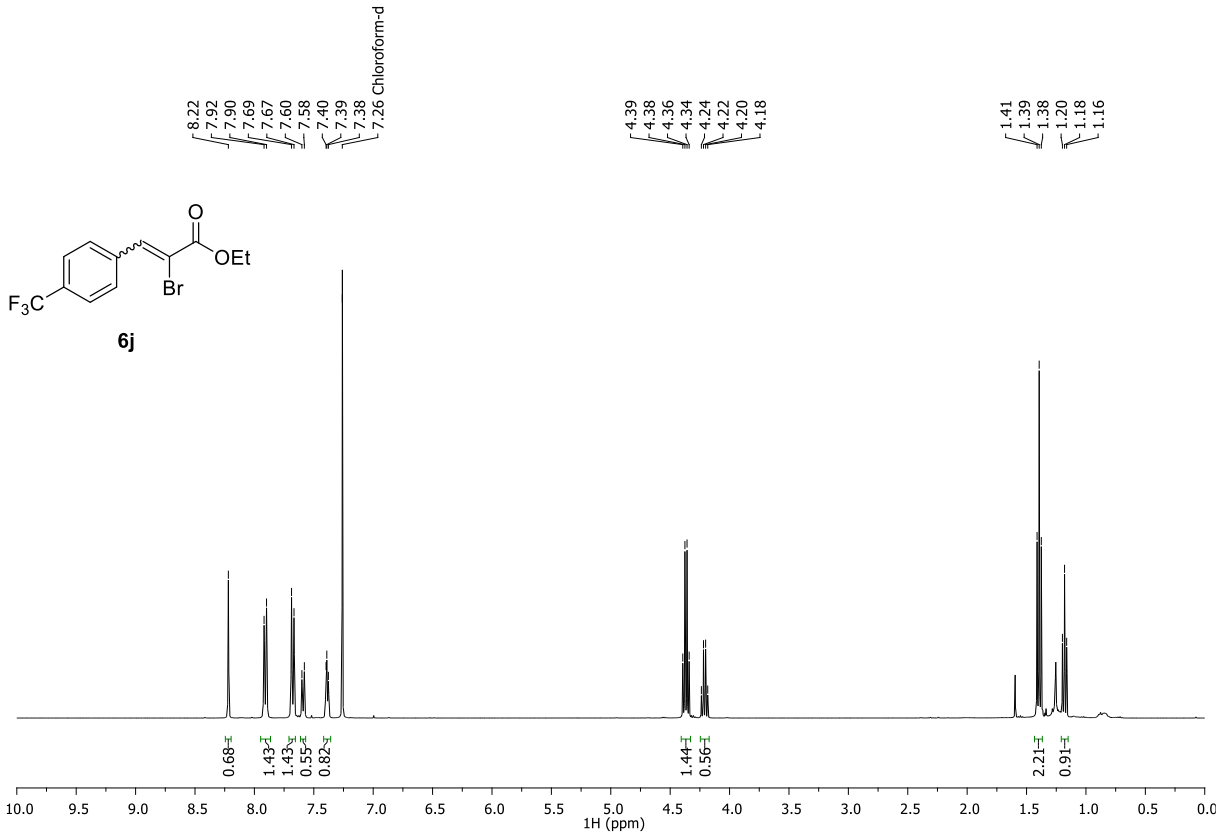


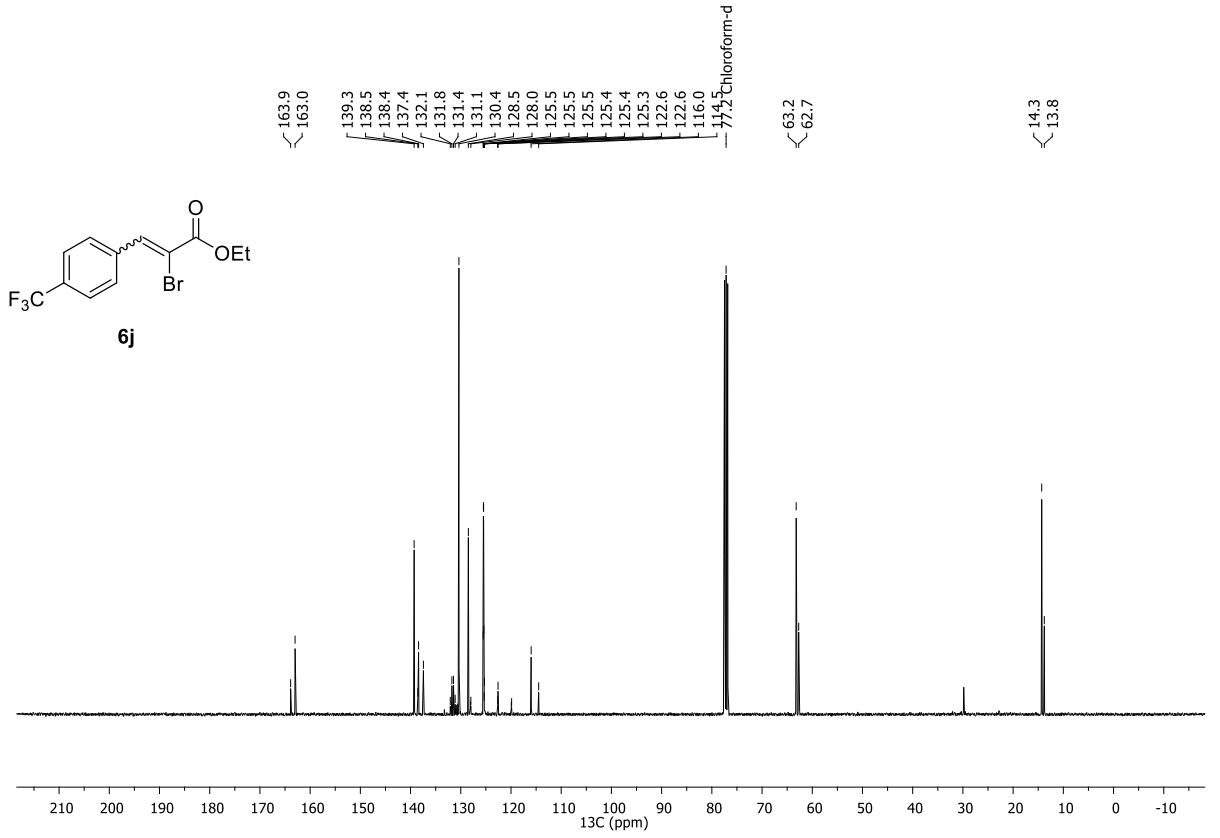
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-3-(4-(methylthio)phenyl)acrylate **6i** in $CDCl_3$

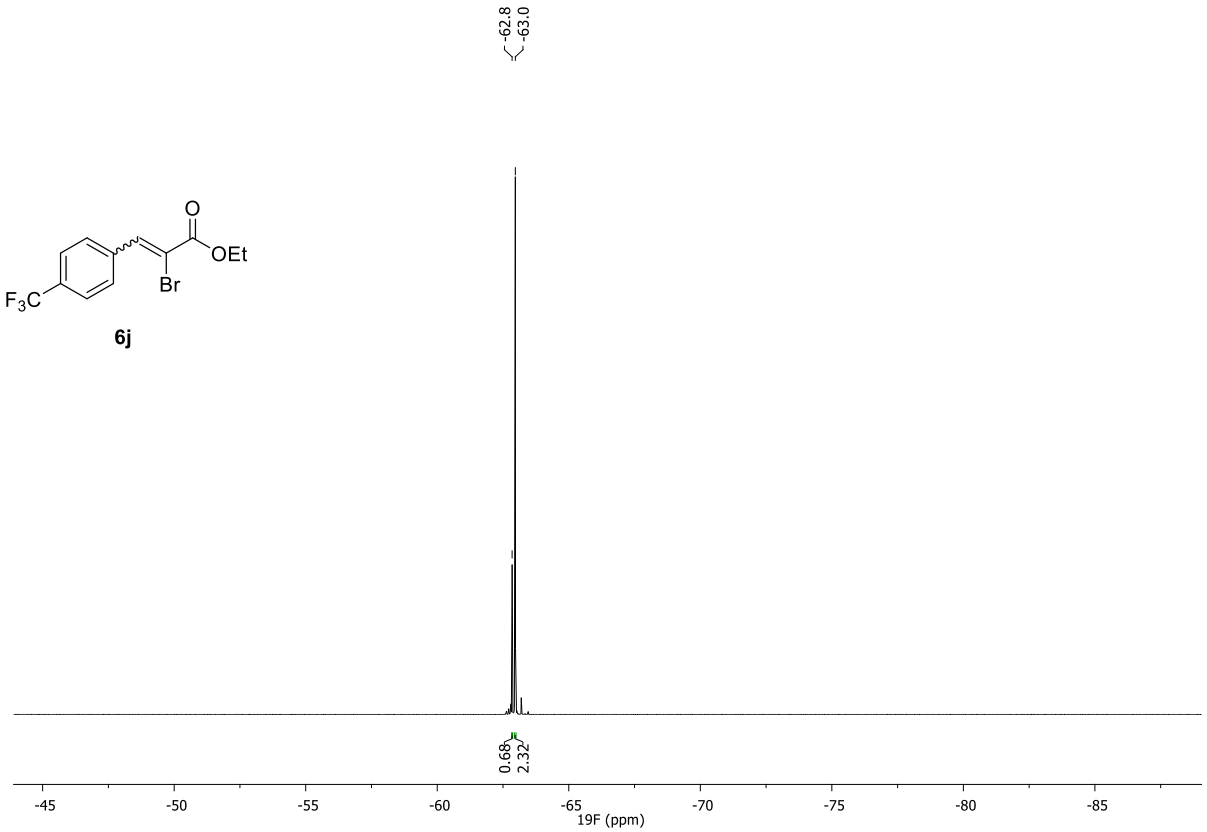




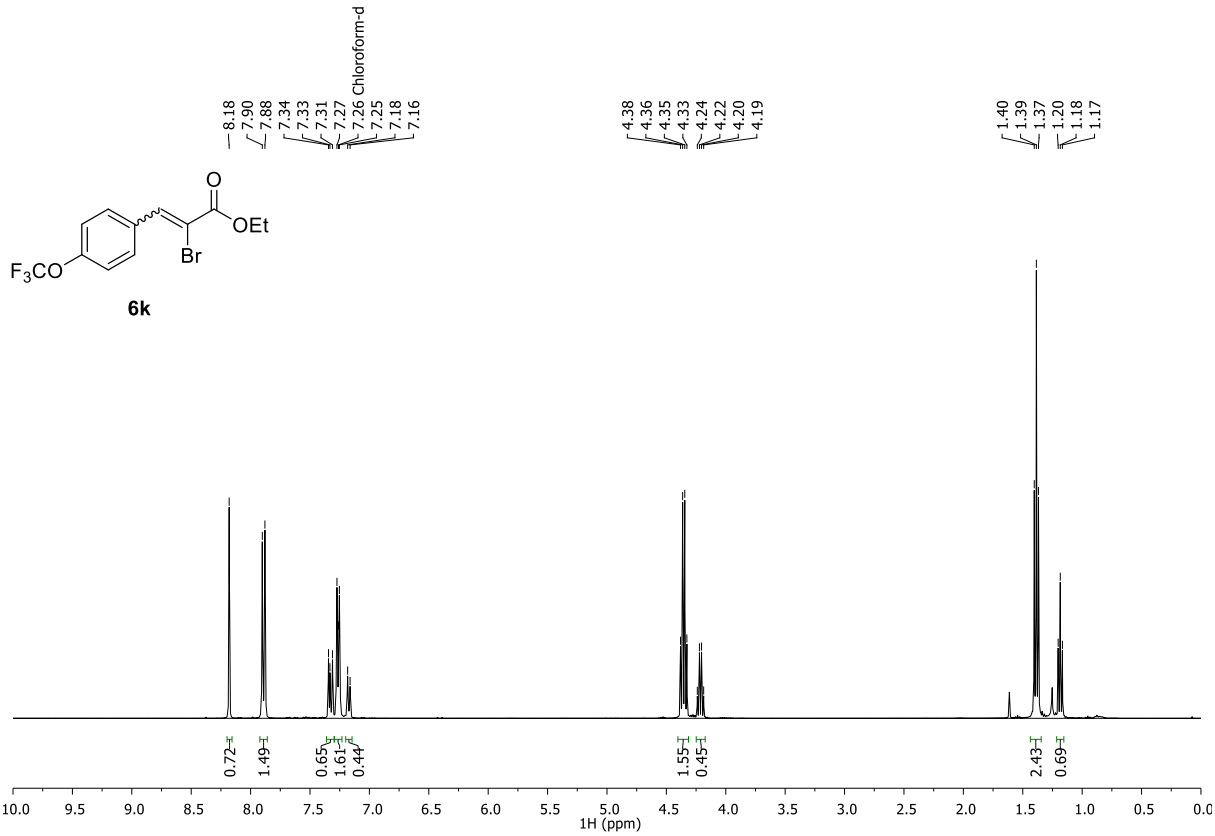
^{1}H, ^{13}C NMR and ^{19}F spectra of ethyl 2-bromo-3-(4-(trifluoromethyl)phenyl)acrylate **6j** in $CDCl_3$

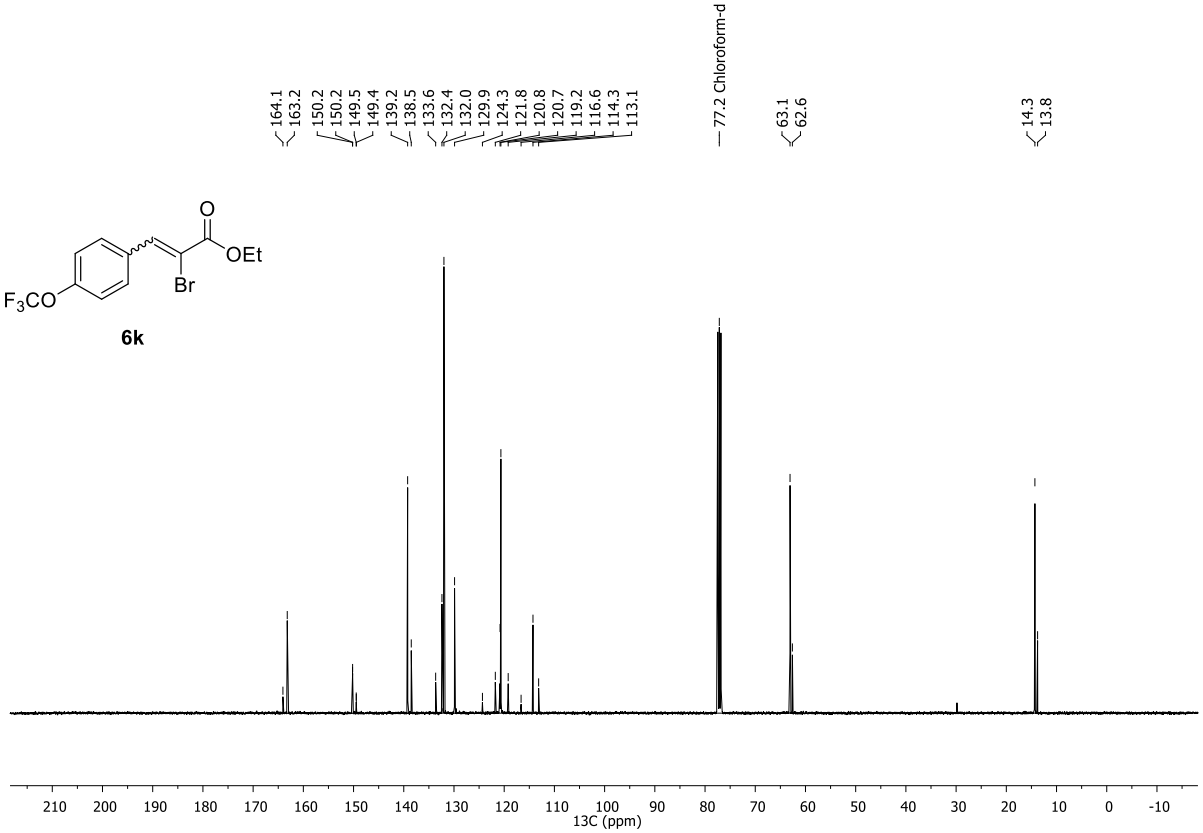






^{1}H,^{13}C NMR and ^{19}F spectra of ethyl 2-bromo-3-(4-(trifluoromethoxy)phenyl)acrylate **6k** in $CDCl_3$




164.1
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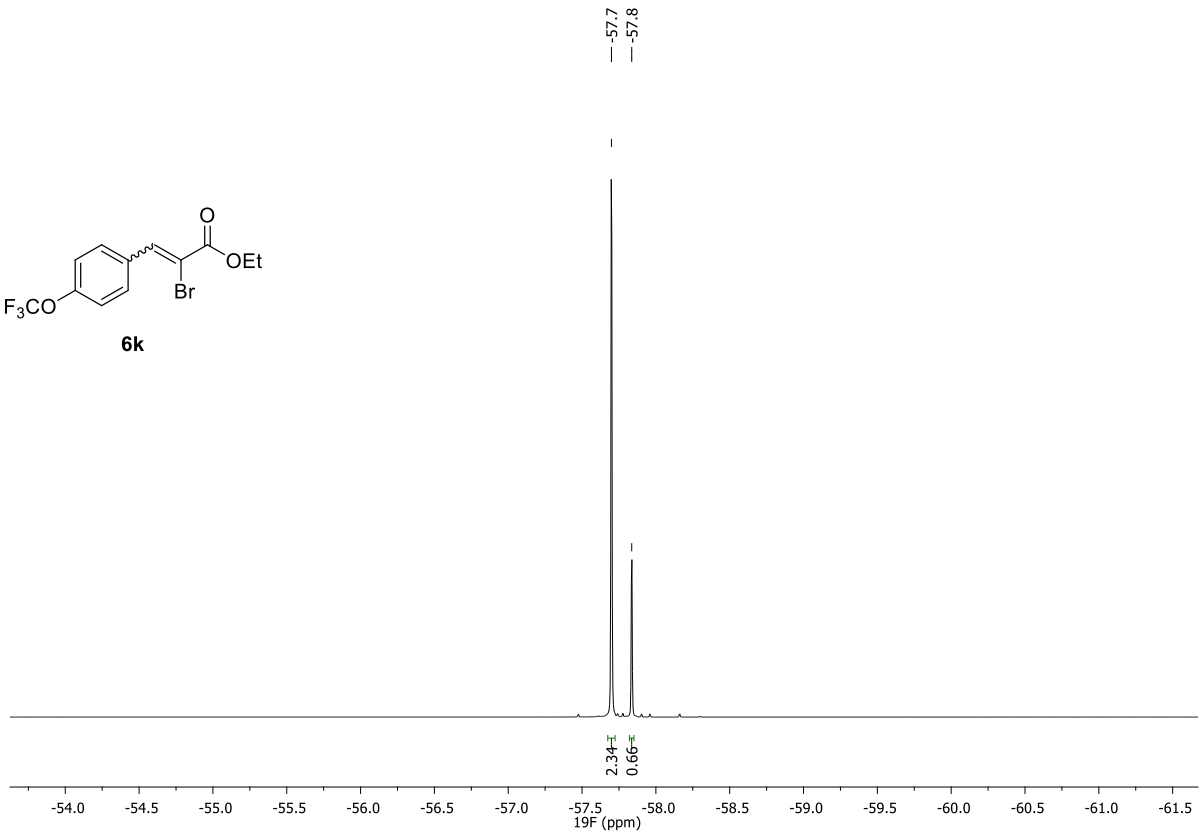
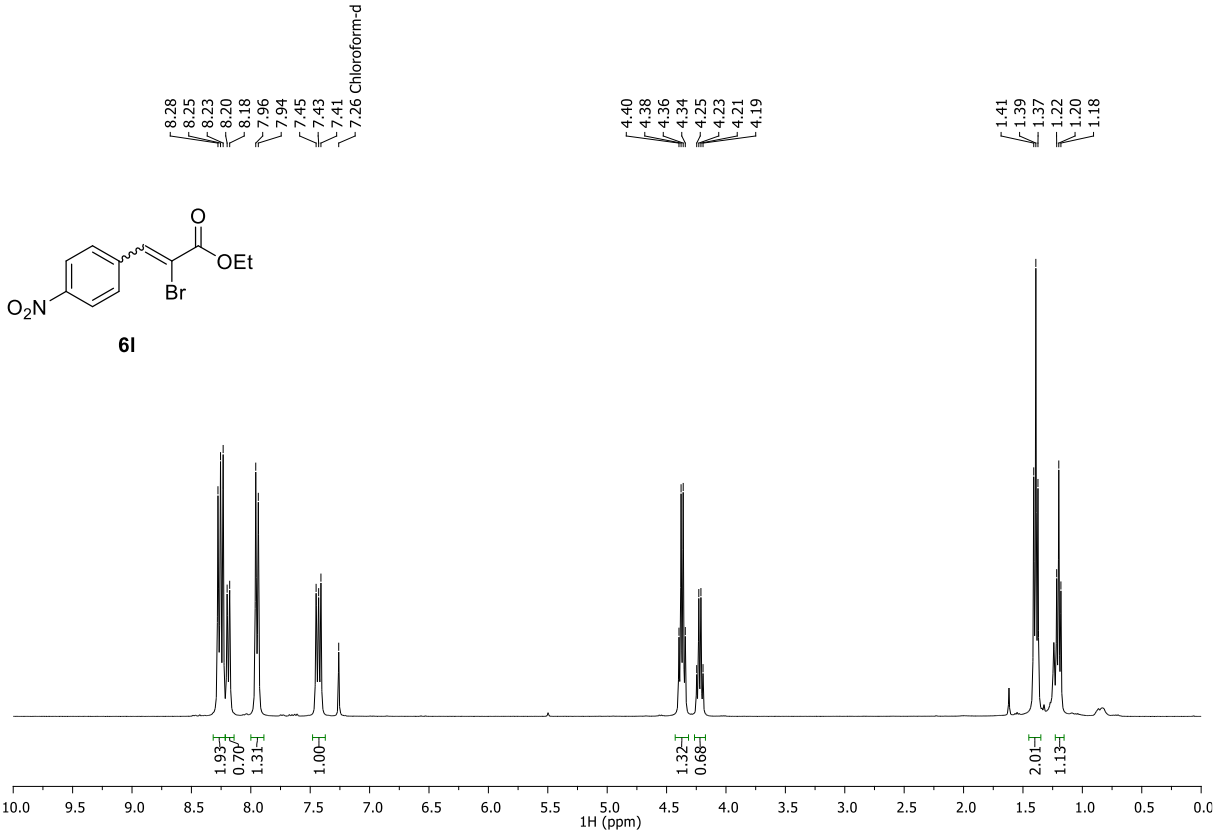
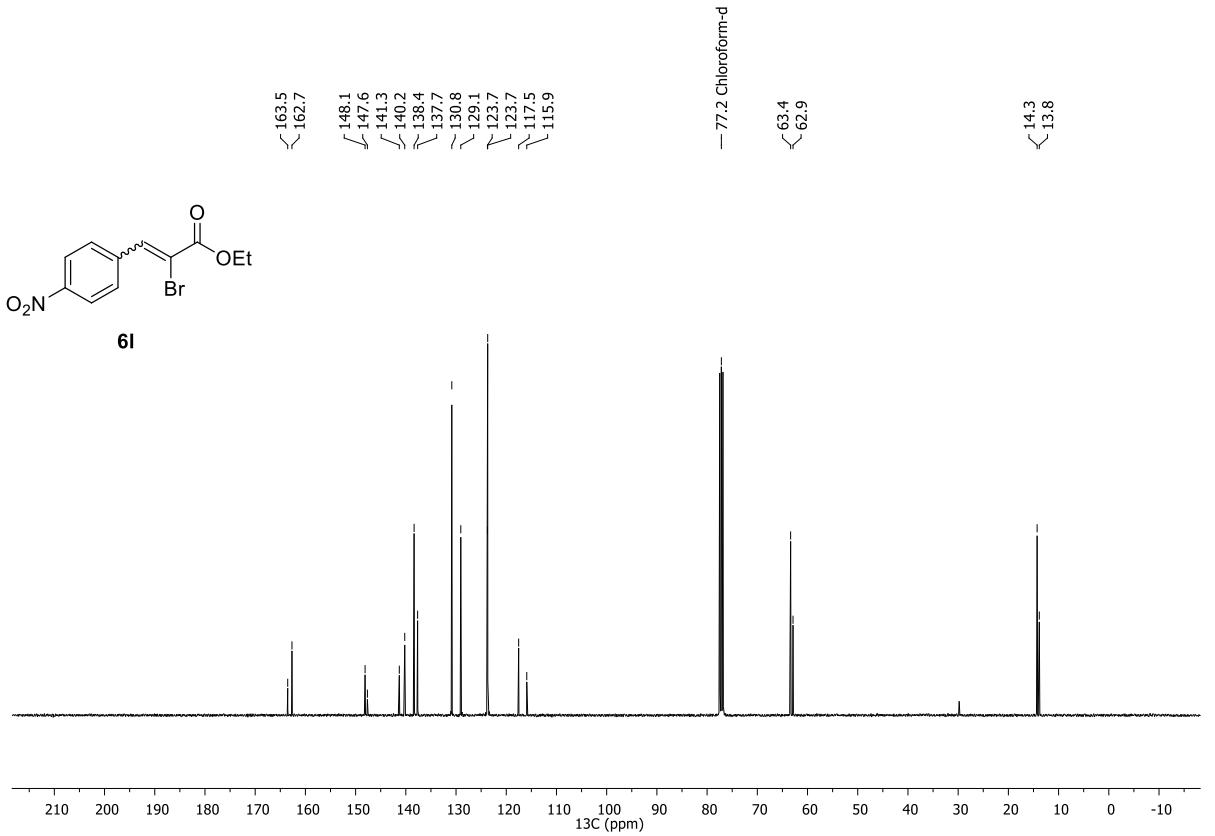
150.2
150.2
149.5
149.4
139.2
138.5
133.6
132.4
132.0
129.9
124.3
121.8
120.8
120.7
119.2
116.6
114.3
113.1
77.2 Chloroform-d
63.1
62.6
14.3
13.8
O
OEt
Br
F3CO
6k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)

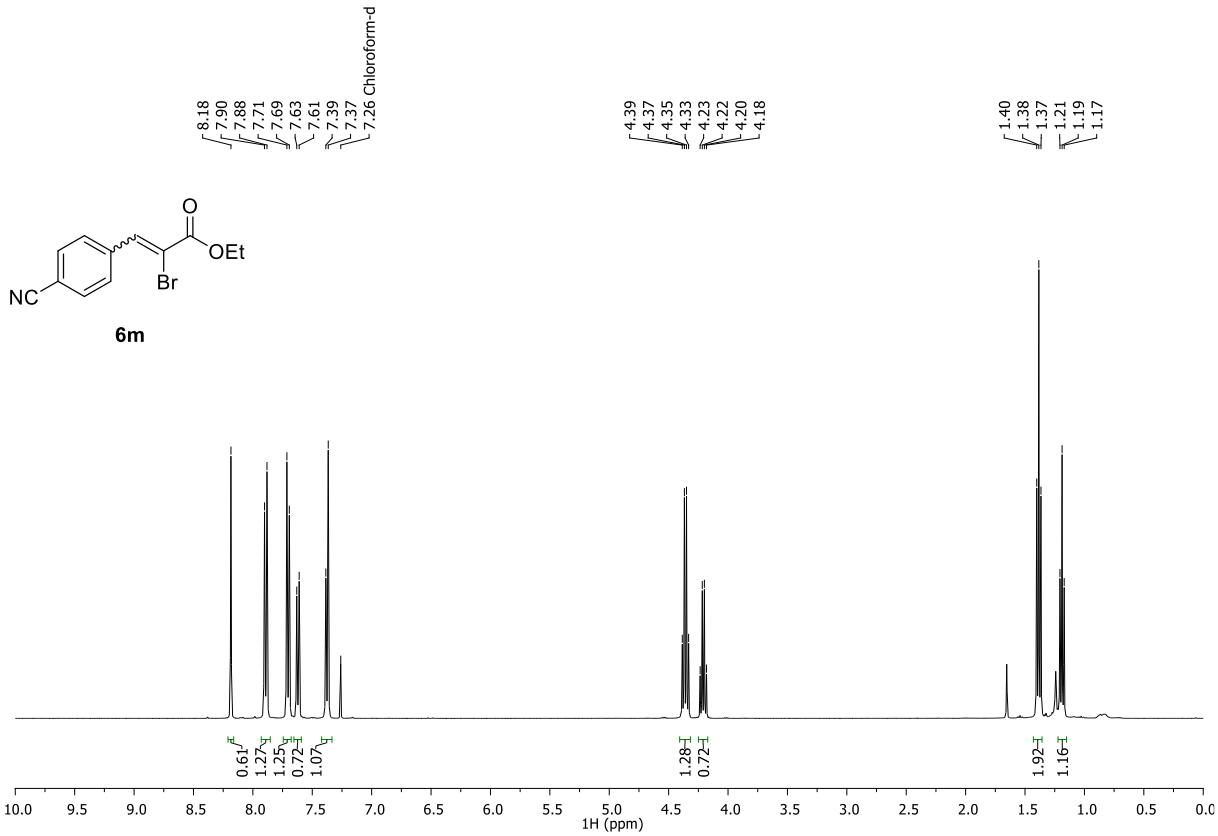

-57.7
-57.8
O
OEt
Br
F3CO
6k
2.34
0.66
-54.0 -54.5 -55.0 -55.5 -56.0 -56.5 -57.0 -57.5 -58.0 -58.5 -59.0 -59.5 -60.0 -60.5 -61.0 -61.5
19F (ppm)

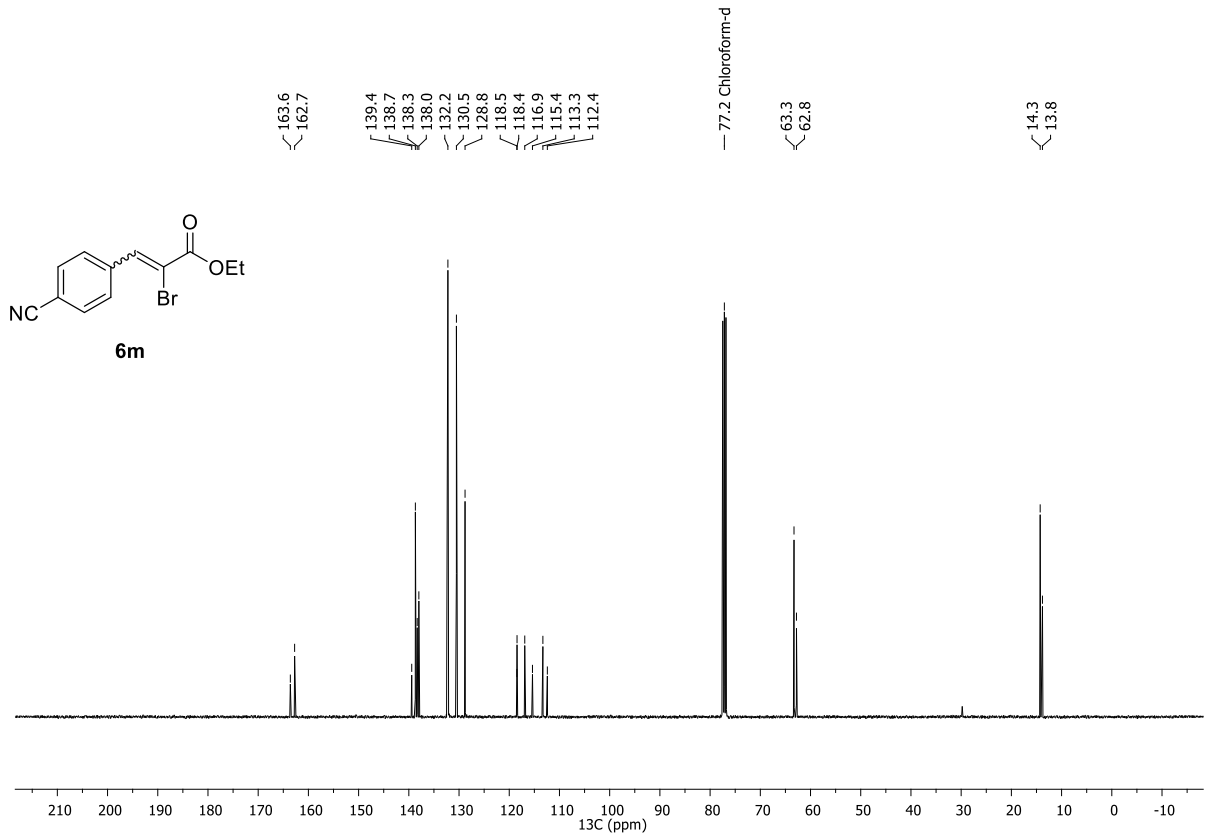
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-3-(4-nitrophenyl)acrylate **6l** in $CDCl_3$



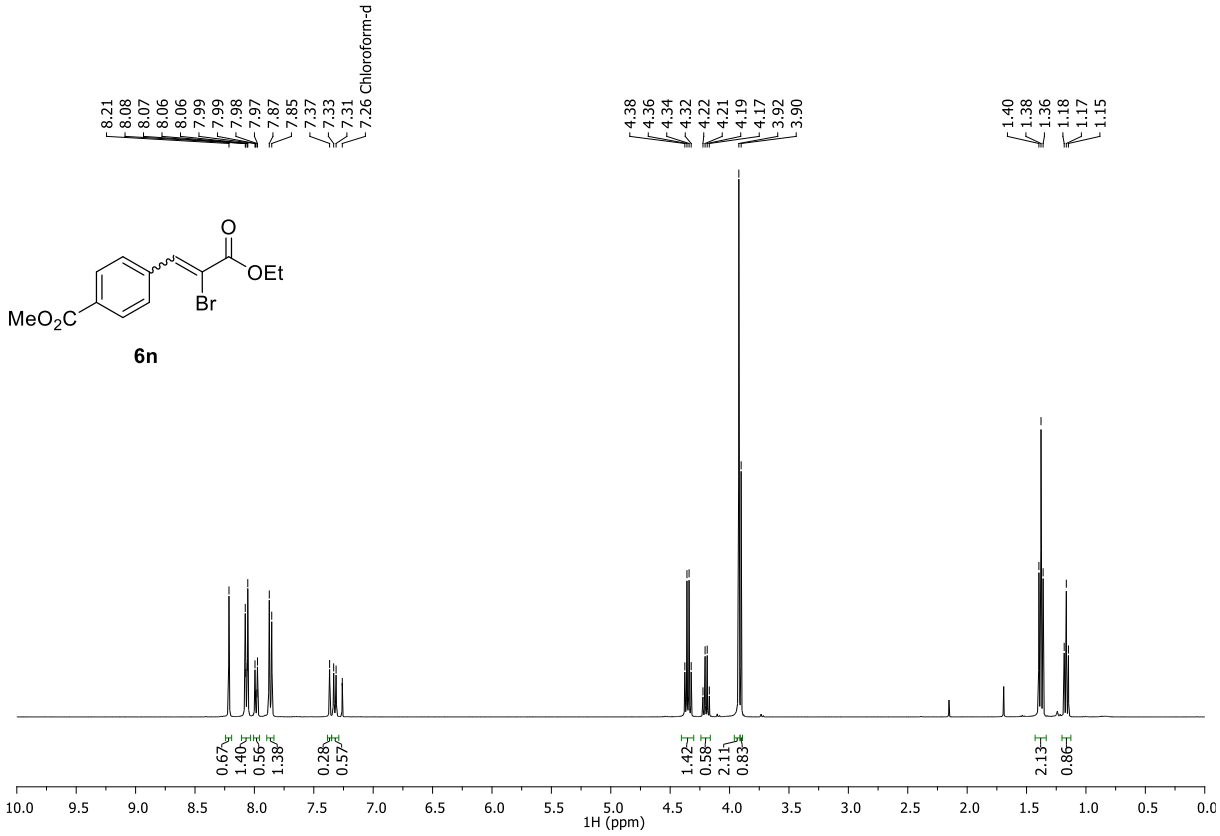


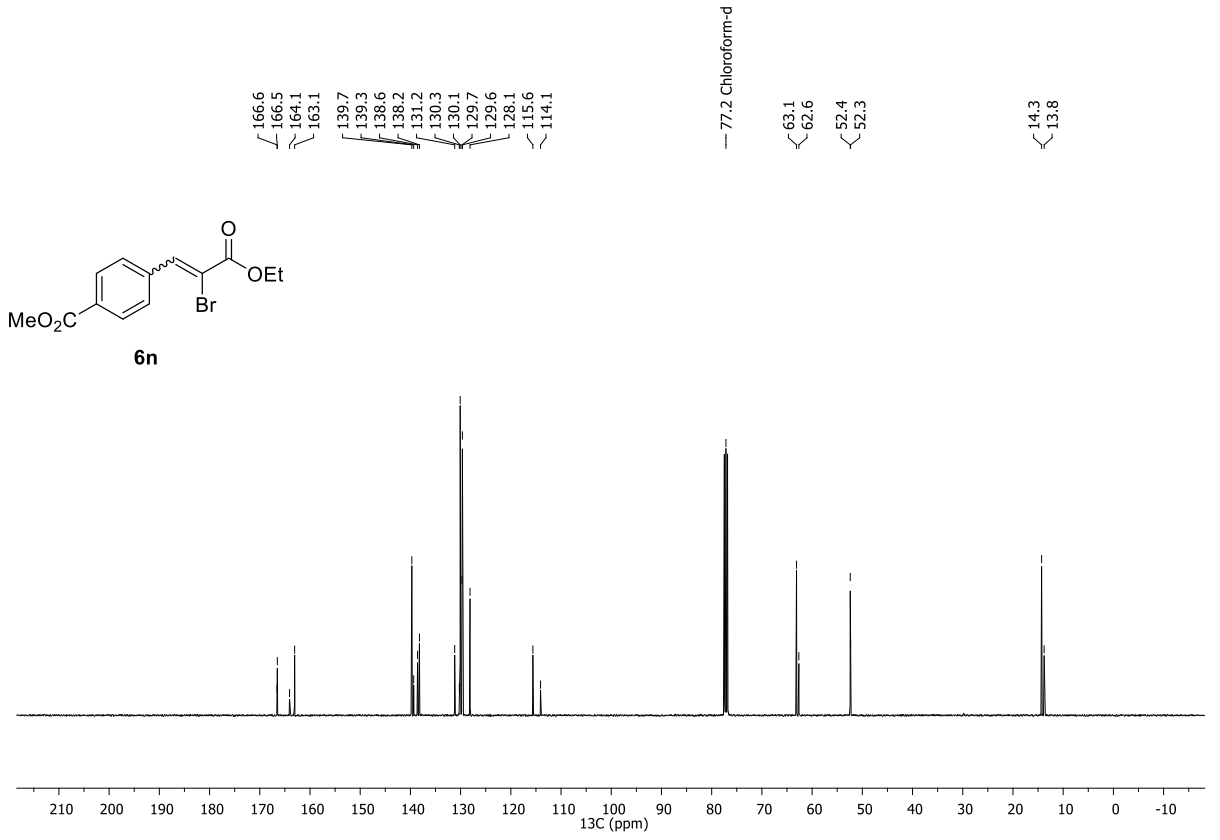
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-3-(4-cyanoophenyl)acrylate **6m** in $CDCl_3$



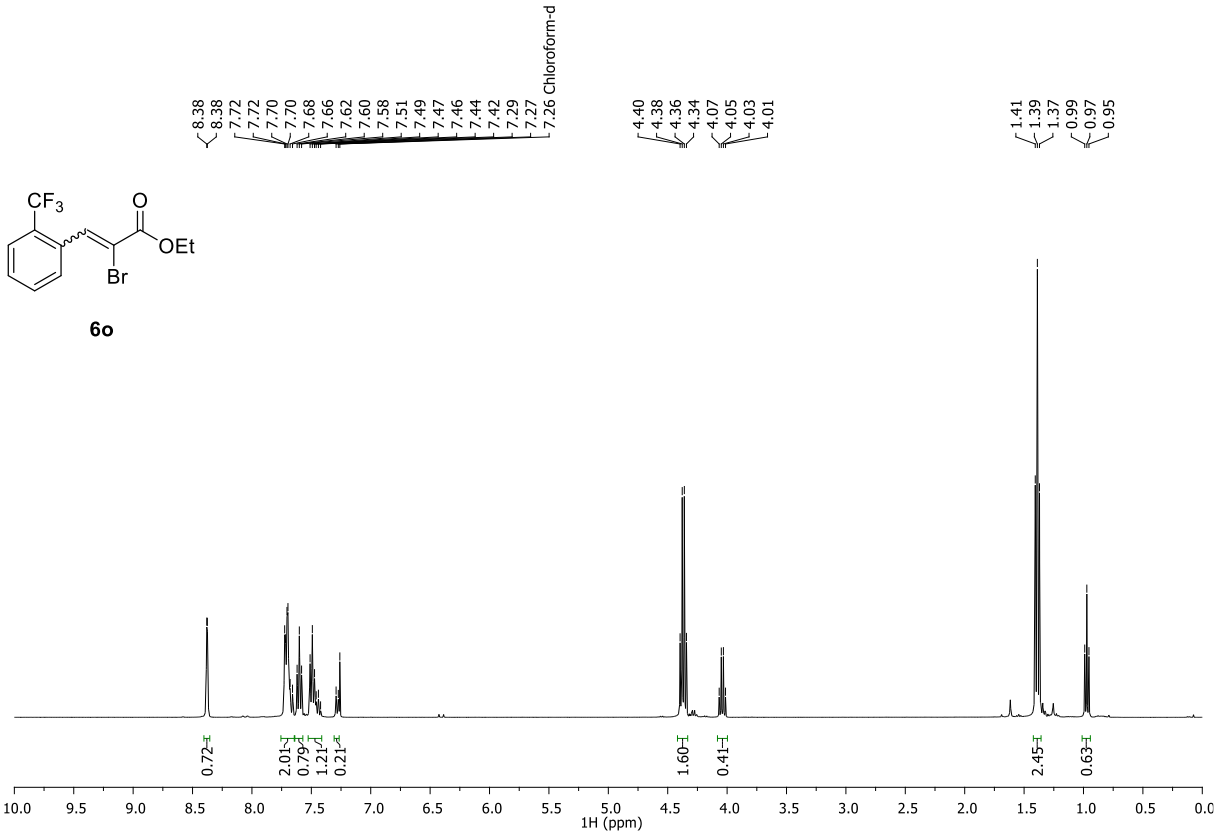


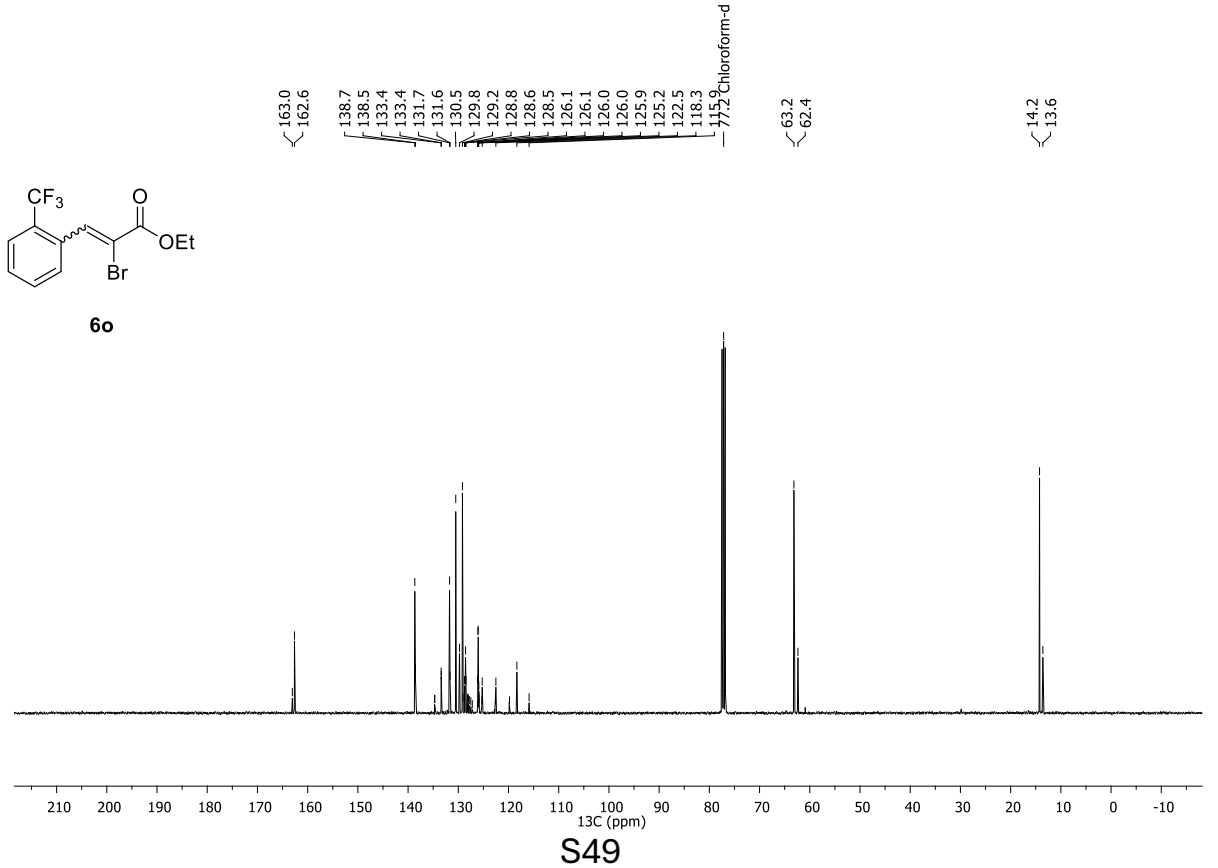
^{1}H and ^{13}C NMR spectra of methyl 4-(2-bromo-3-ethoxy-3-oxoprop-1-en-1-yl)benzoate **6n** in $CDCl_3$

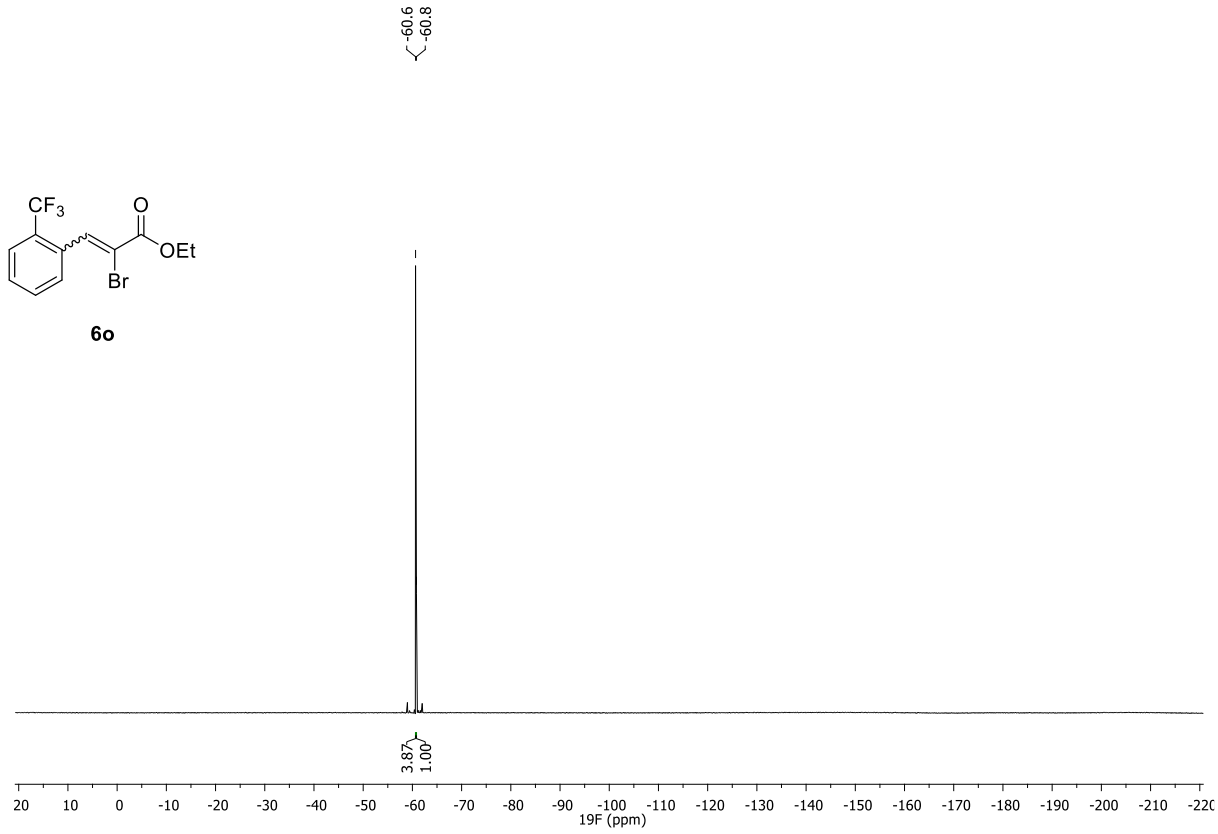




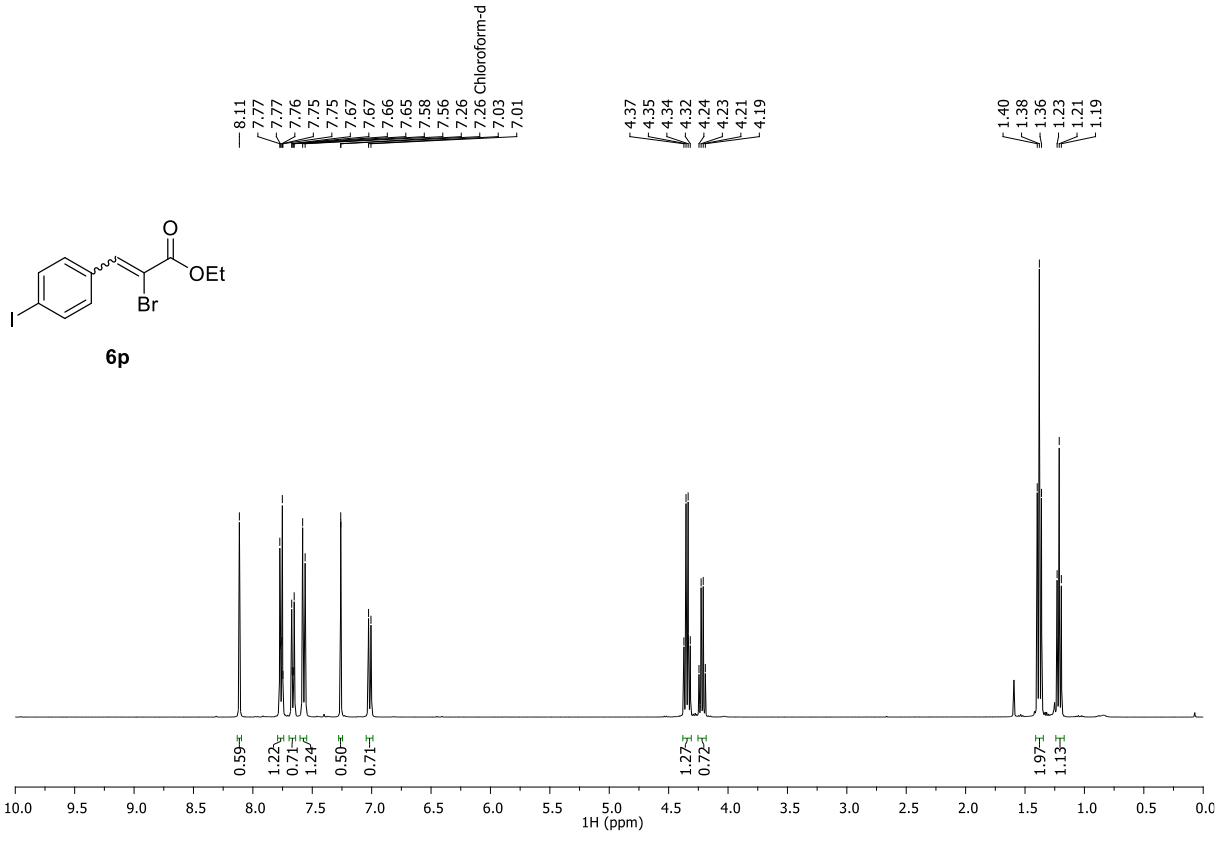
^{1}H, ^{13}C and ^{19}F NMR spectra of ethyl 2-bromo-3-(2-(trifluoromethyl)phenyl)acrylate **6o** in $CDCl_3$

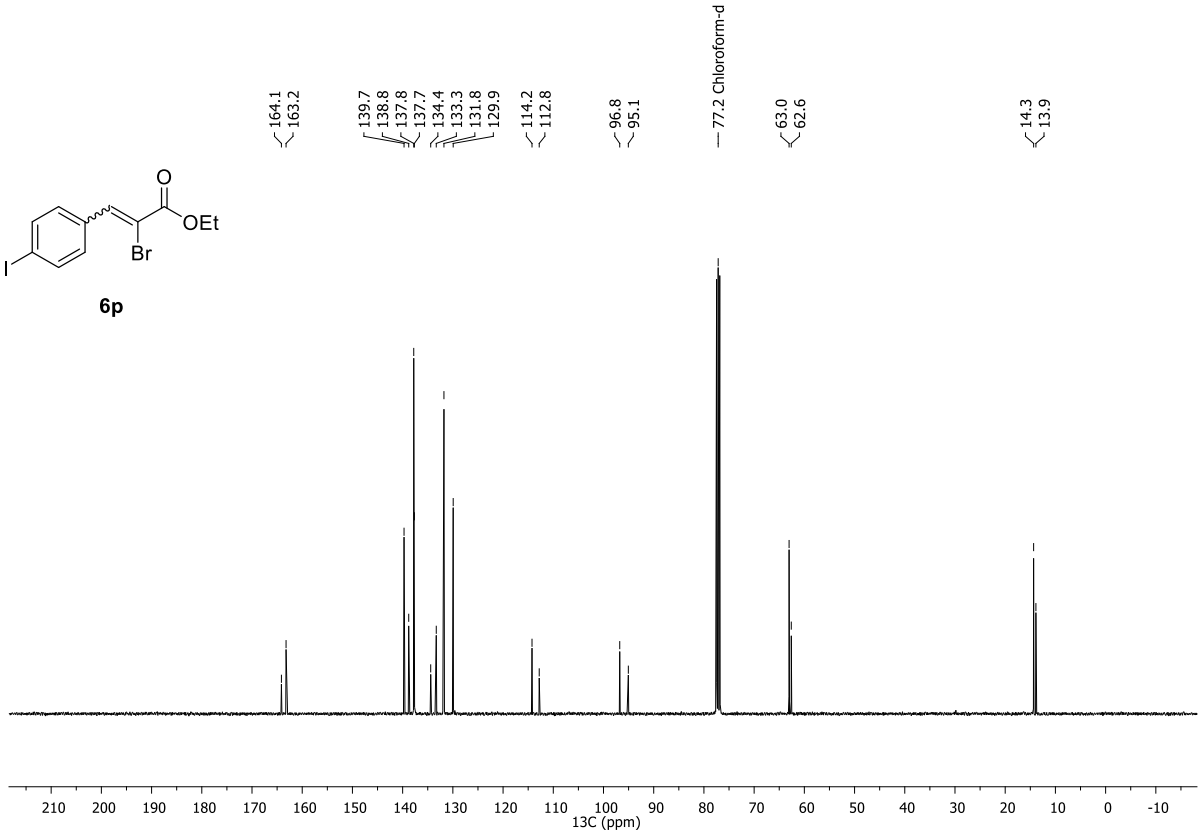




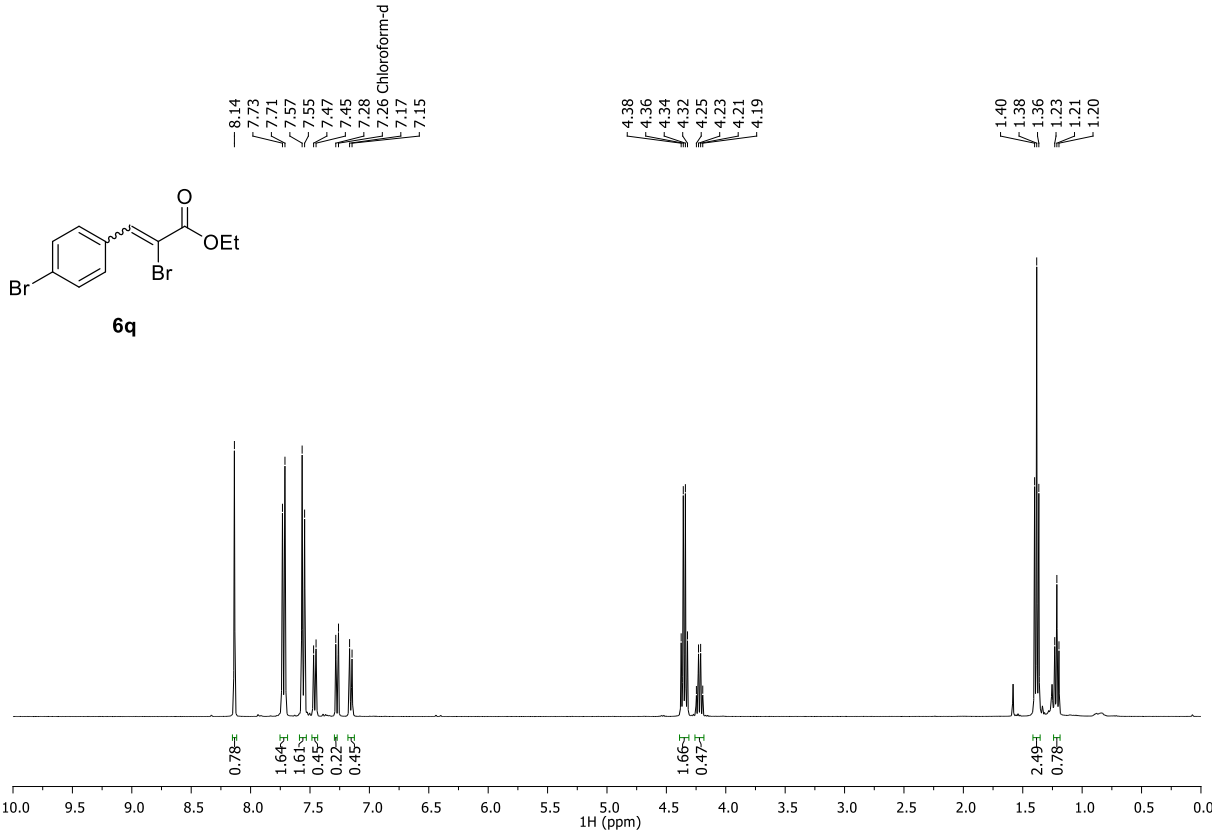


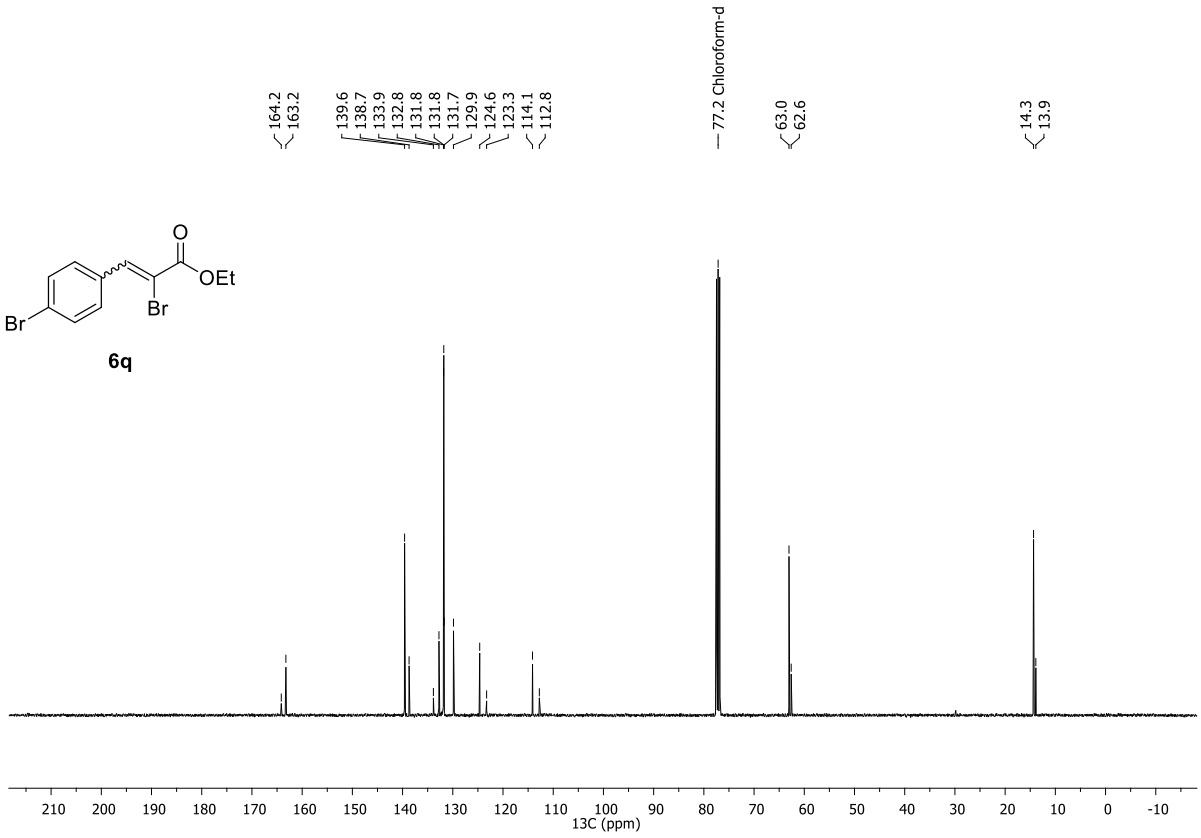
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-3-(4-iodophenyl)acrylate **6p** in $CDCl_3$



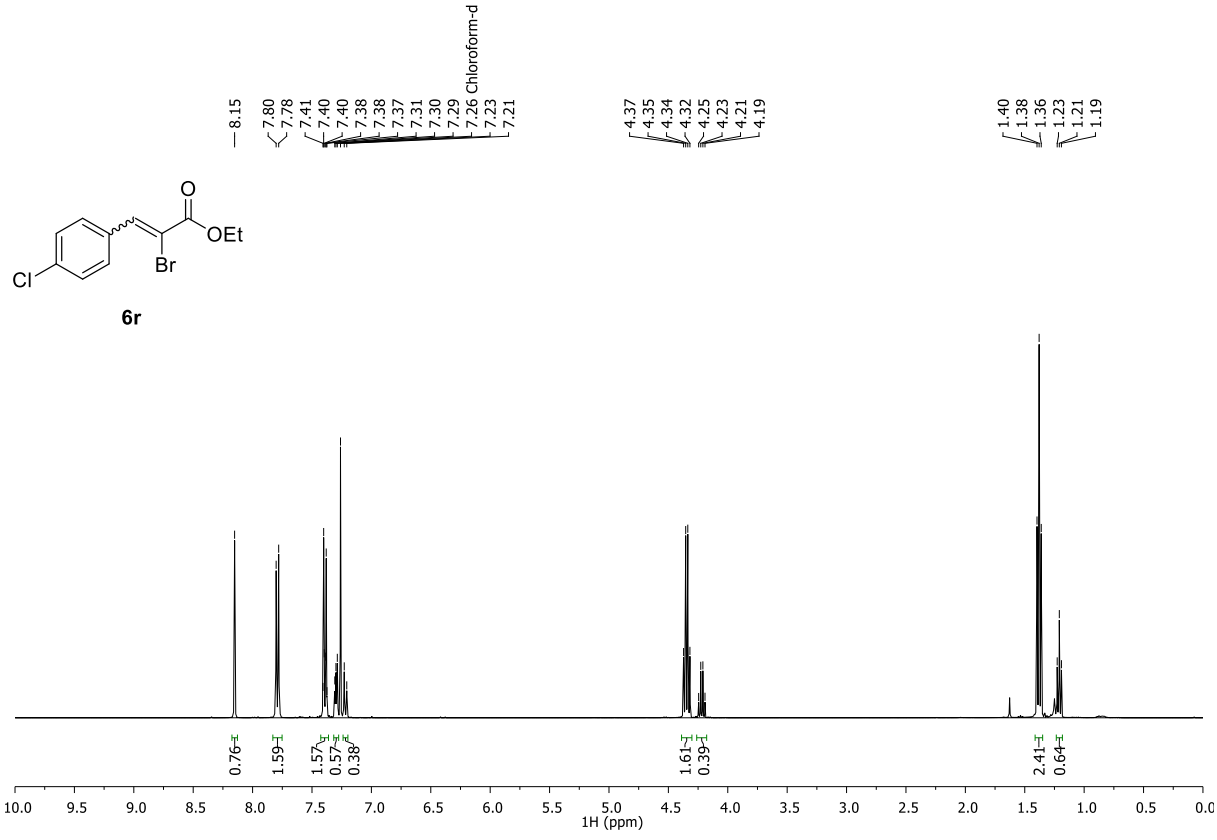


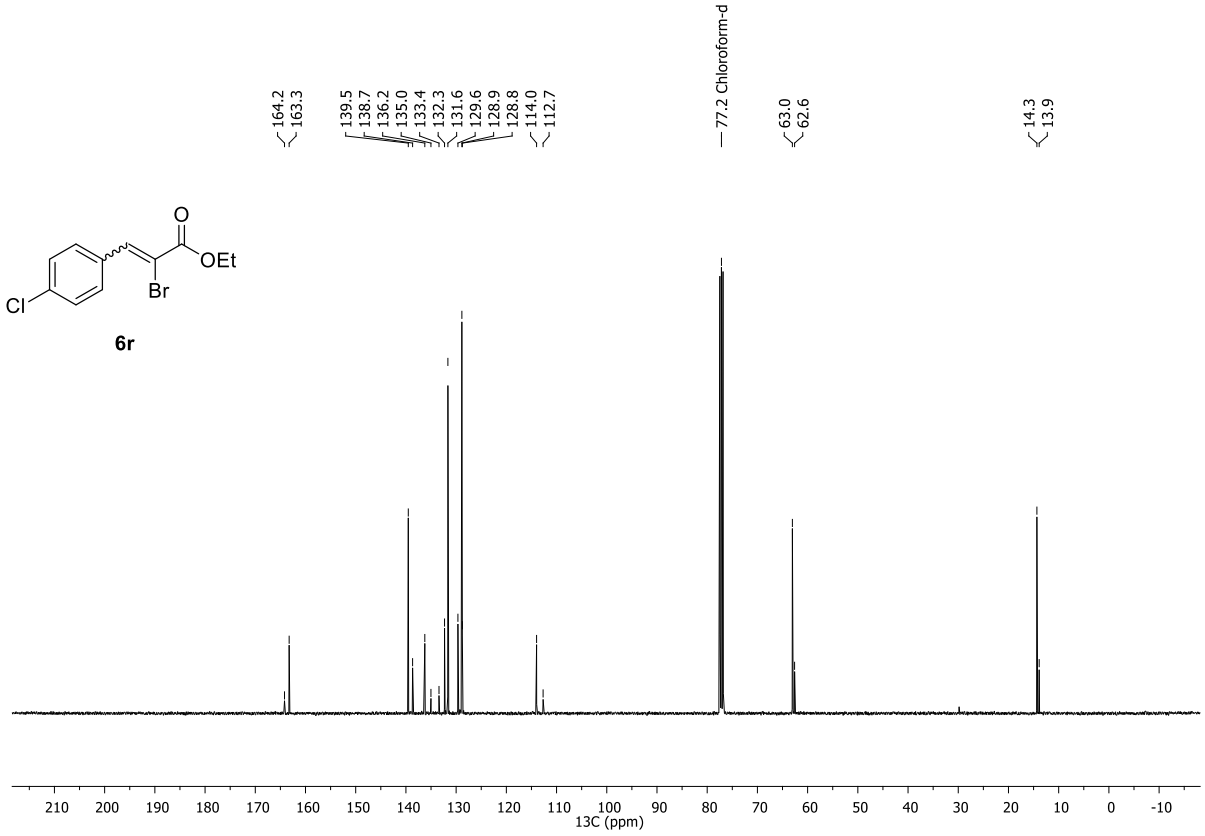
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-3-(4-bromophenyl)acrylate **6q** in $CDCl_3$



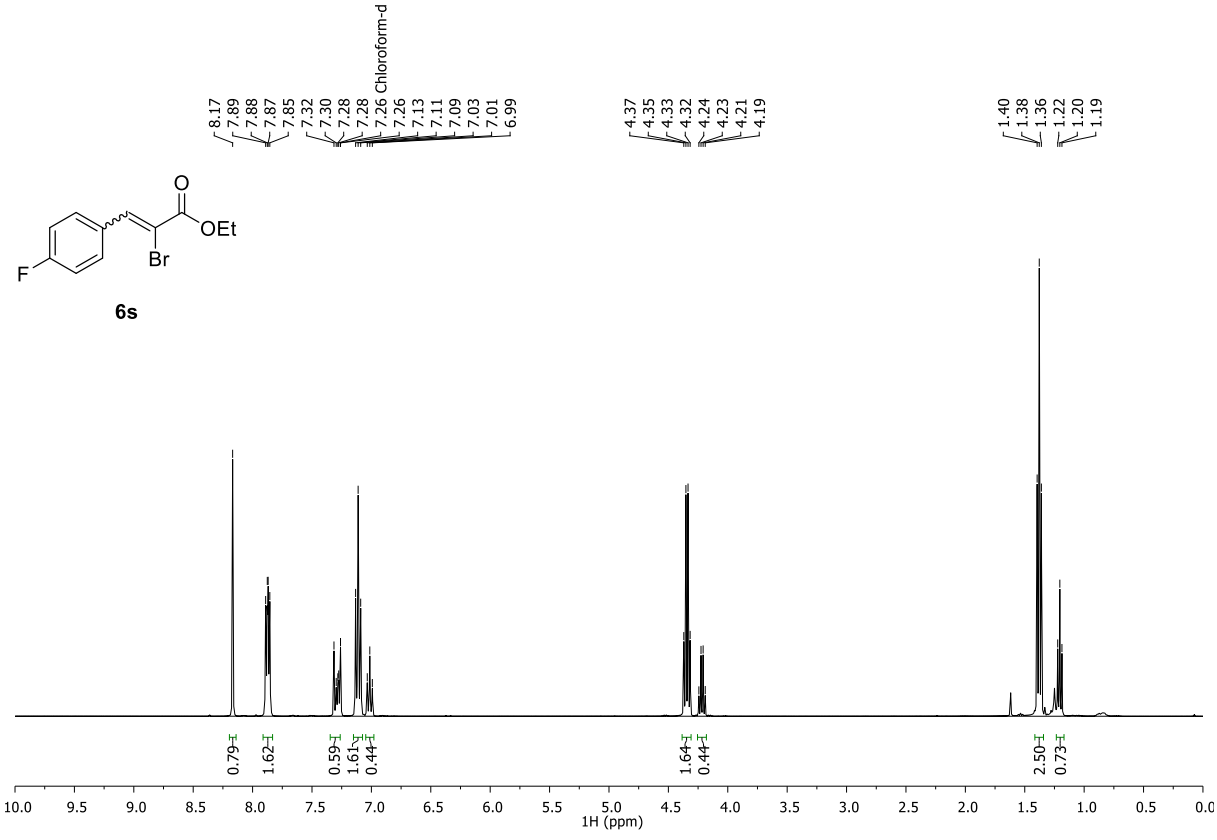


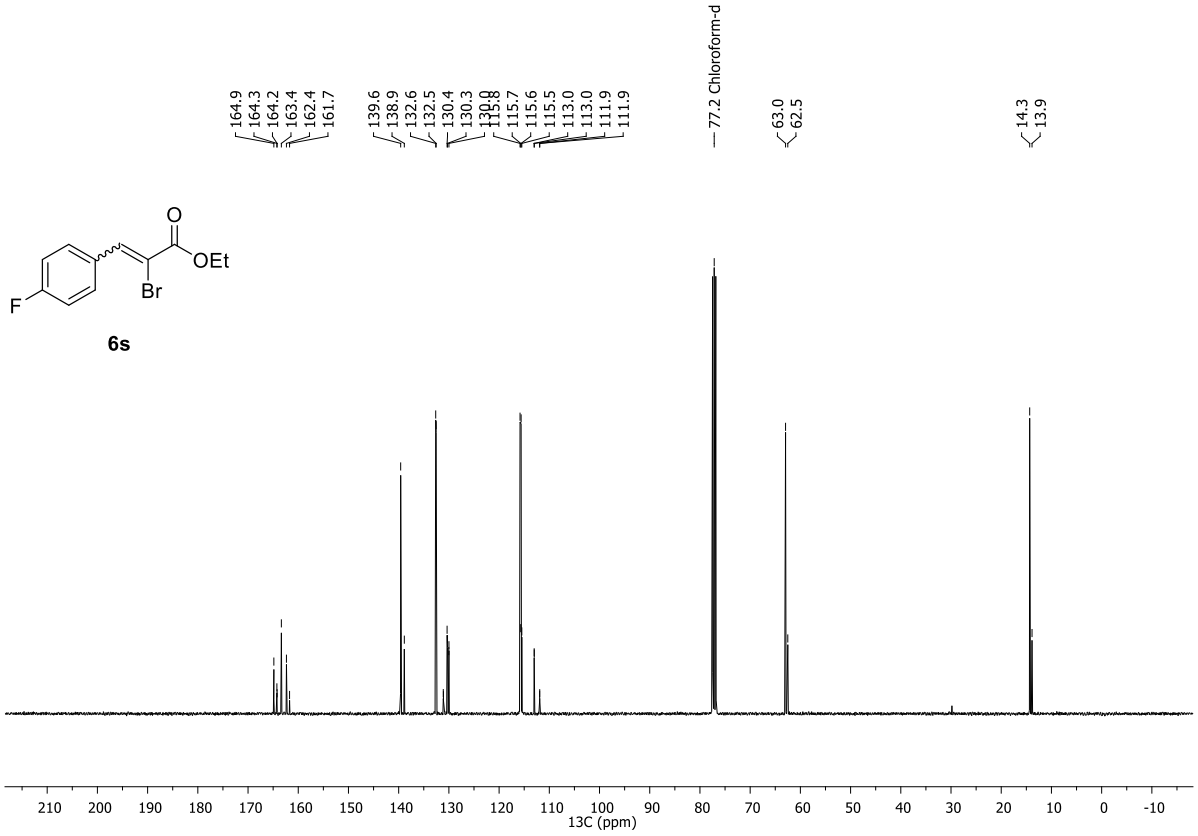
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-3-(4-chlorophenyl)acrylate **6r** in $CDCl_3$





^{1}H, ^{13}C and ^{19}F NMR spectra of ethyl 2-bromo-3-(4-iodophenyl)acrylate **6s** in $CDCl_3$




164.9
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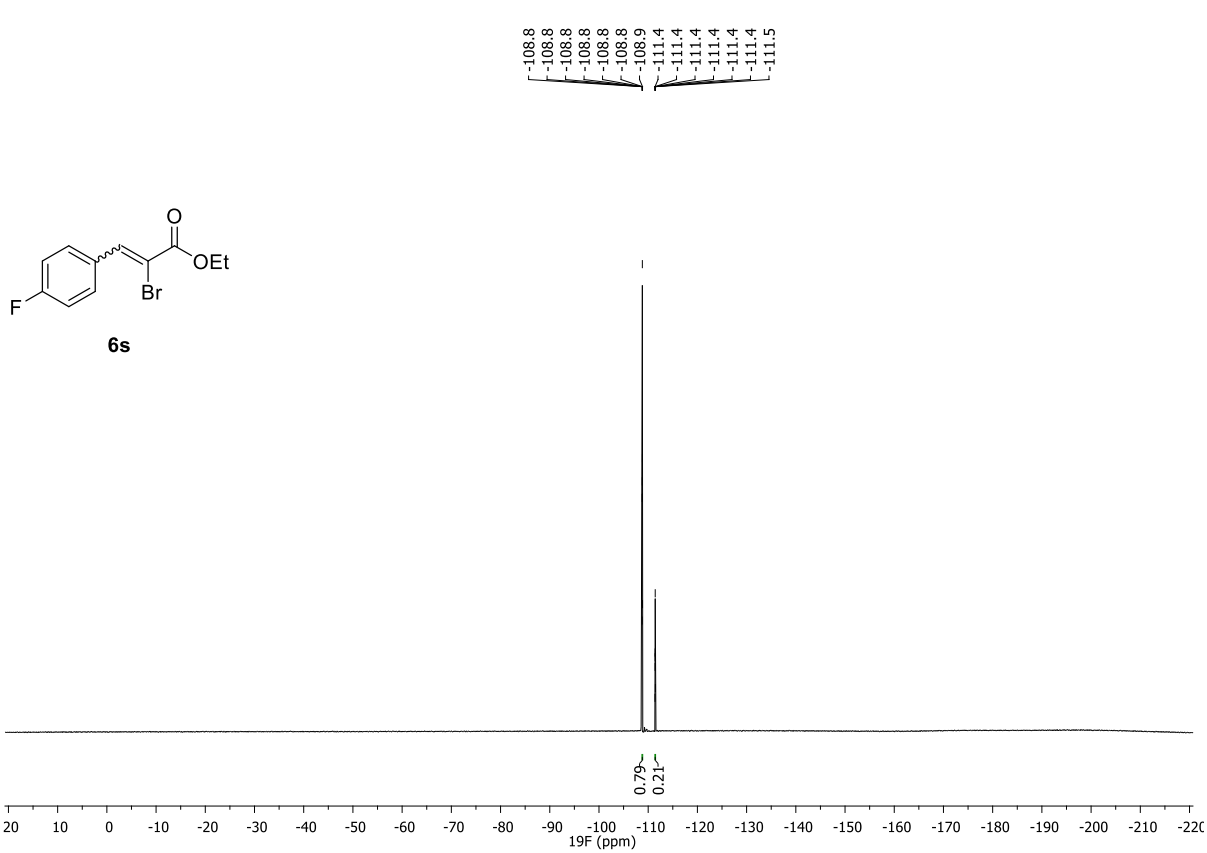
132.5
130.4
130.3
130.0
115.8
115.7
115.6
115.5
113.0
113.0
111.9
111.9
77.2 Chloroform-d
63.0
62.5
14.3
13.9
O
OEt
Br
F
6s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)


-108.8
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-108.8
-108.8
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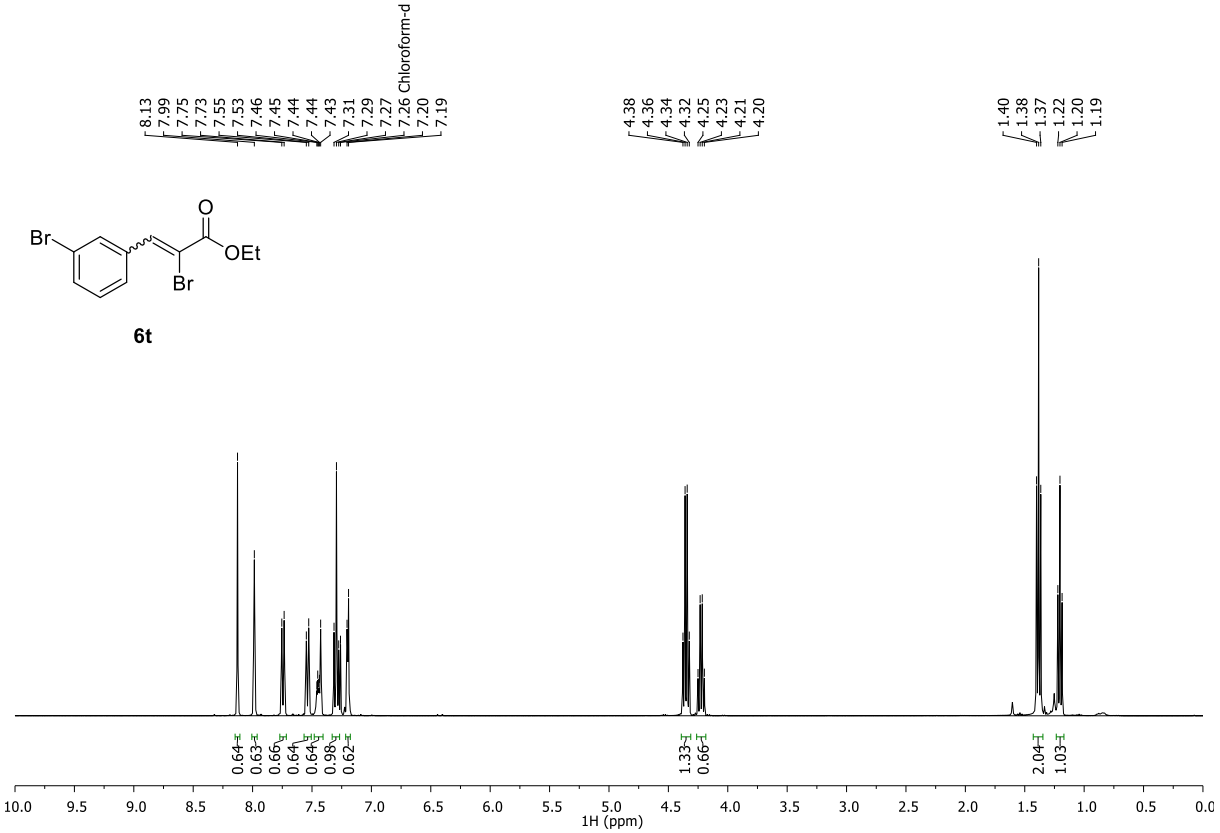
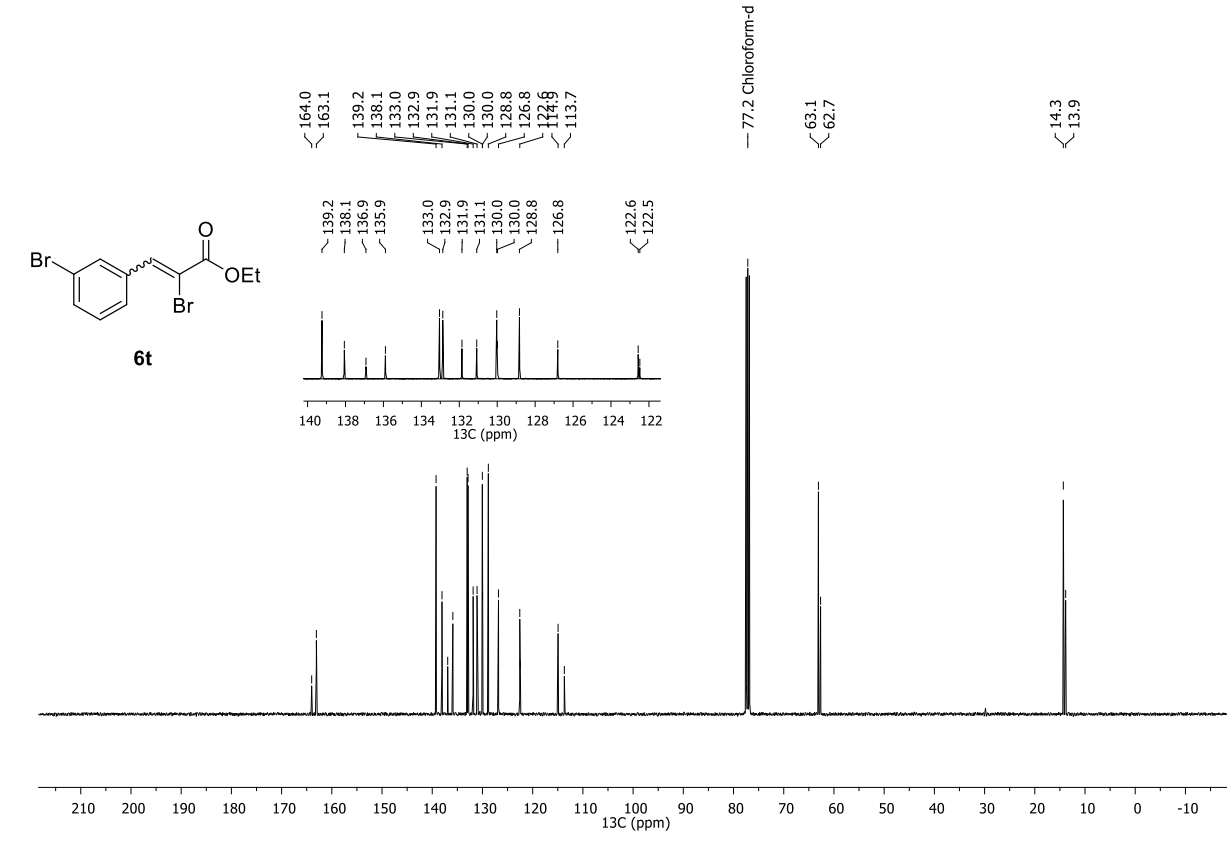
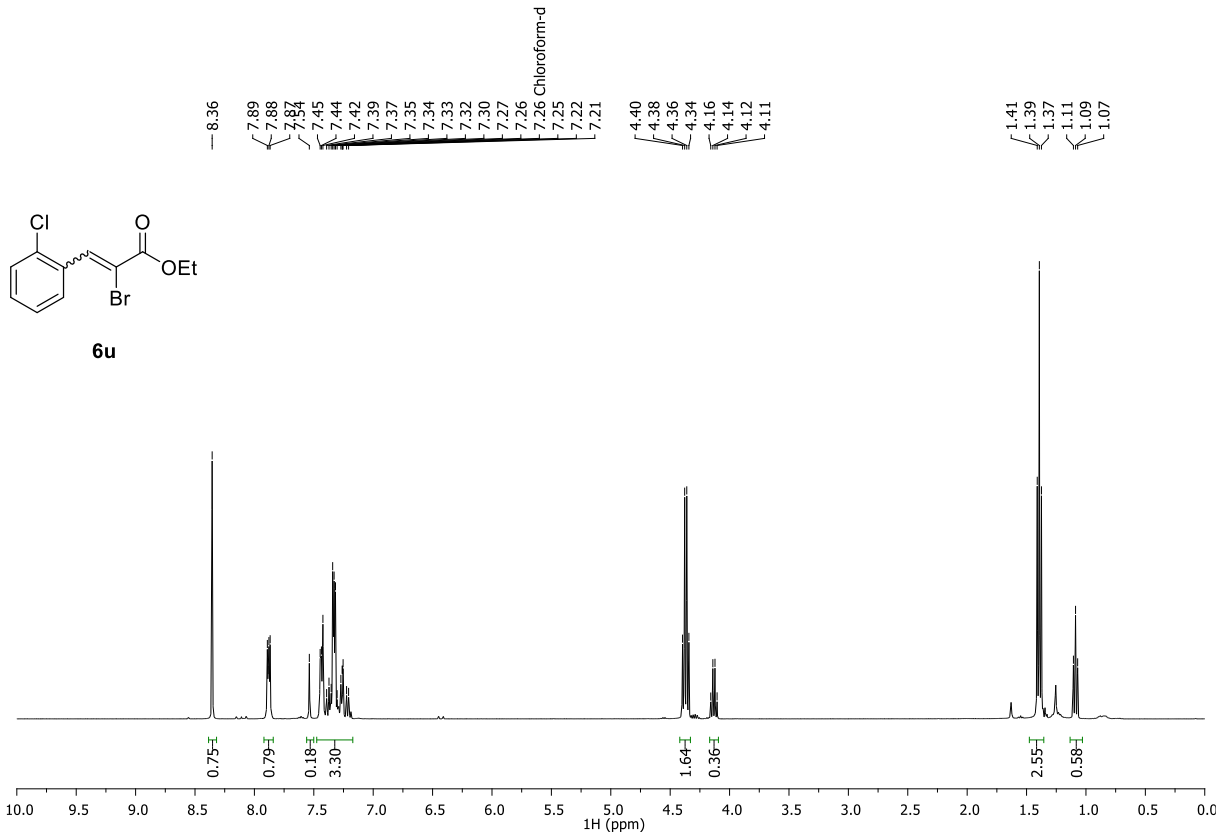
-108.8
-108.9
-111.4
-111.4
-111.4
-111.4
-111.4
-111.5
O
OEt
Br
F
6s
0.79
0.21
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
19F (ppm)

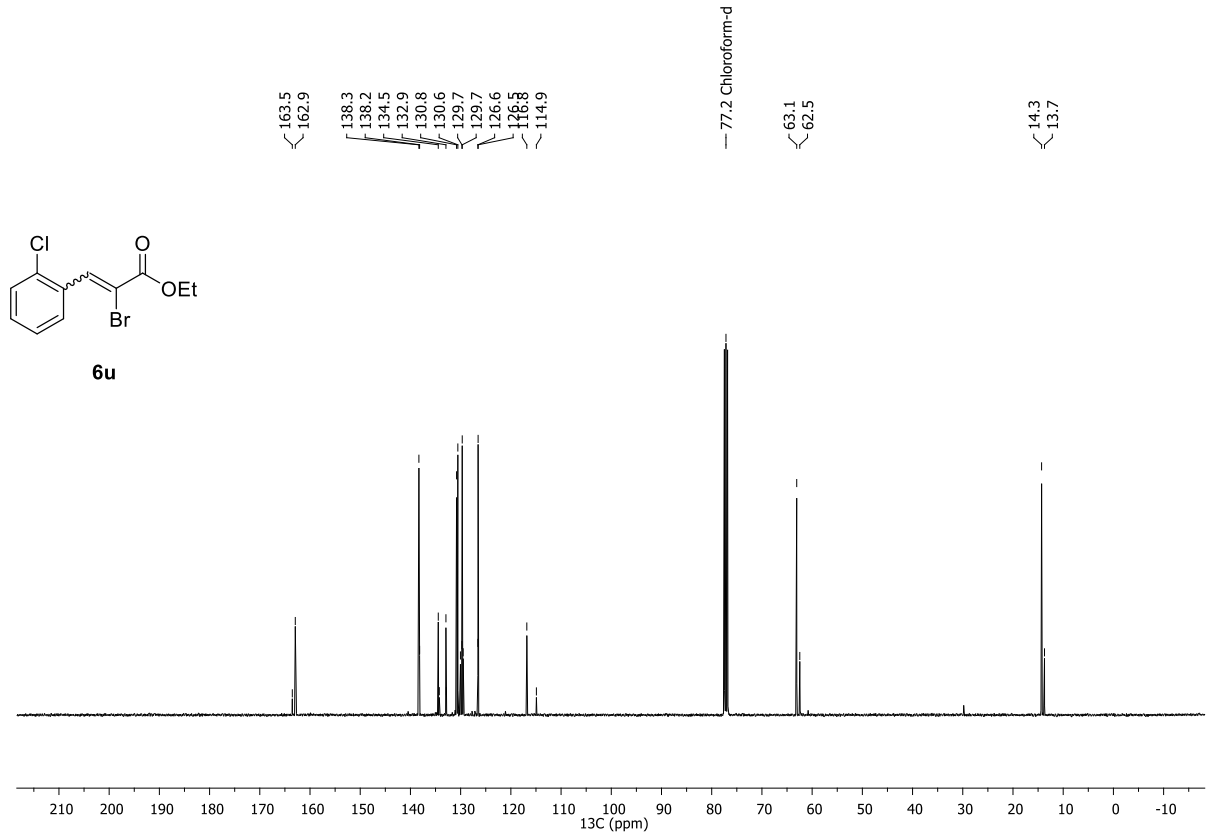
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-3-(3-bromophenyl)acrylate **6t** in $CDCl_3$



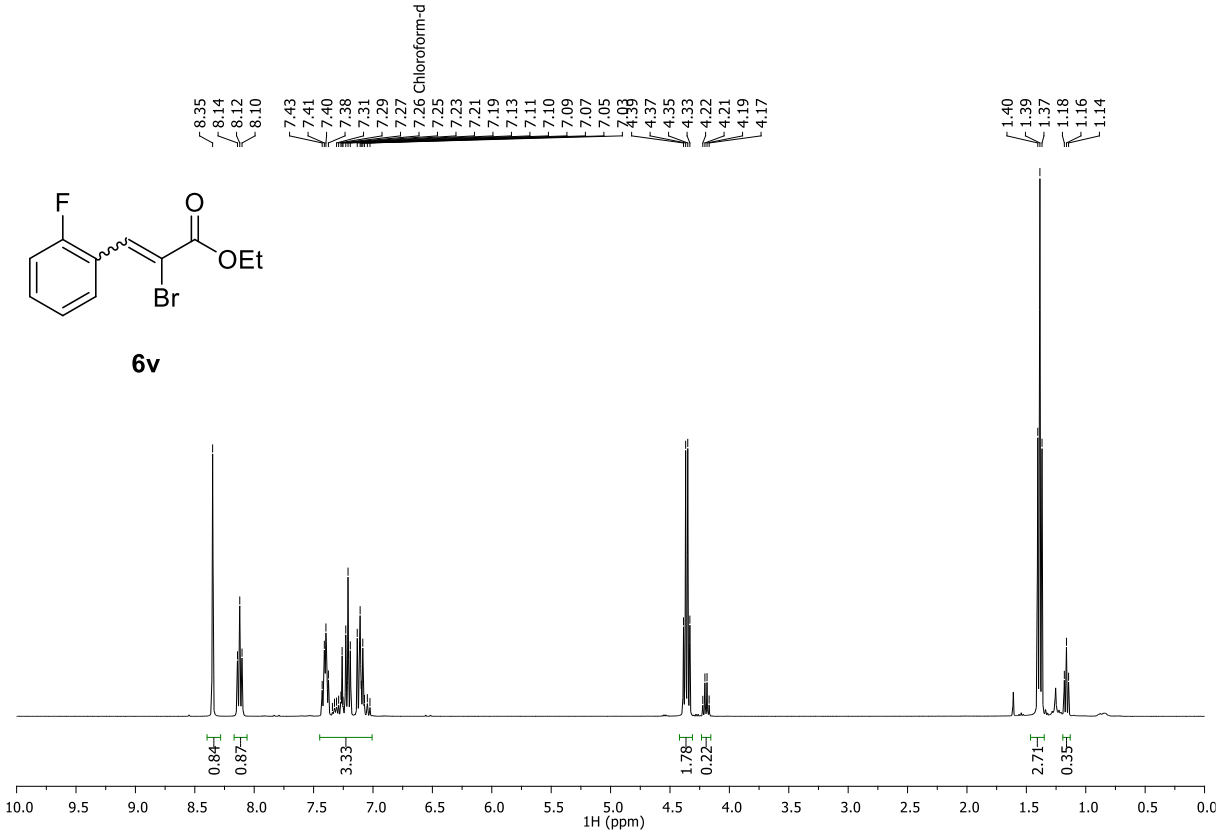


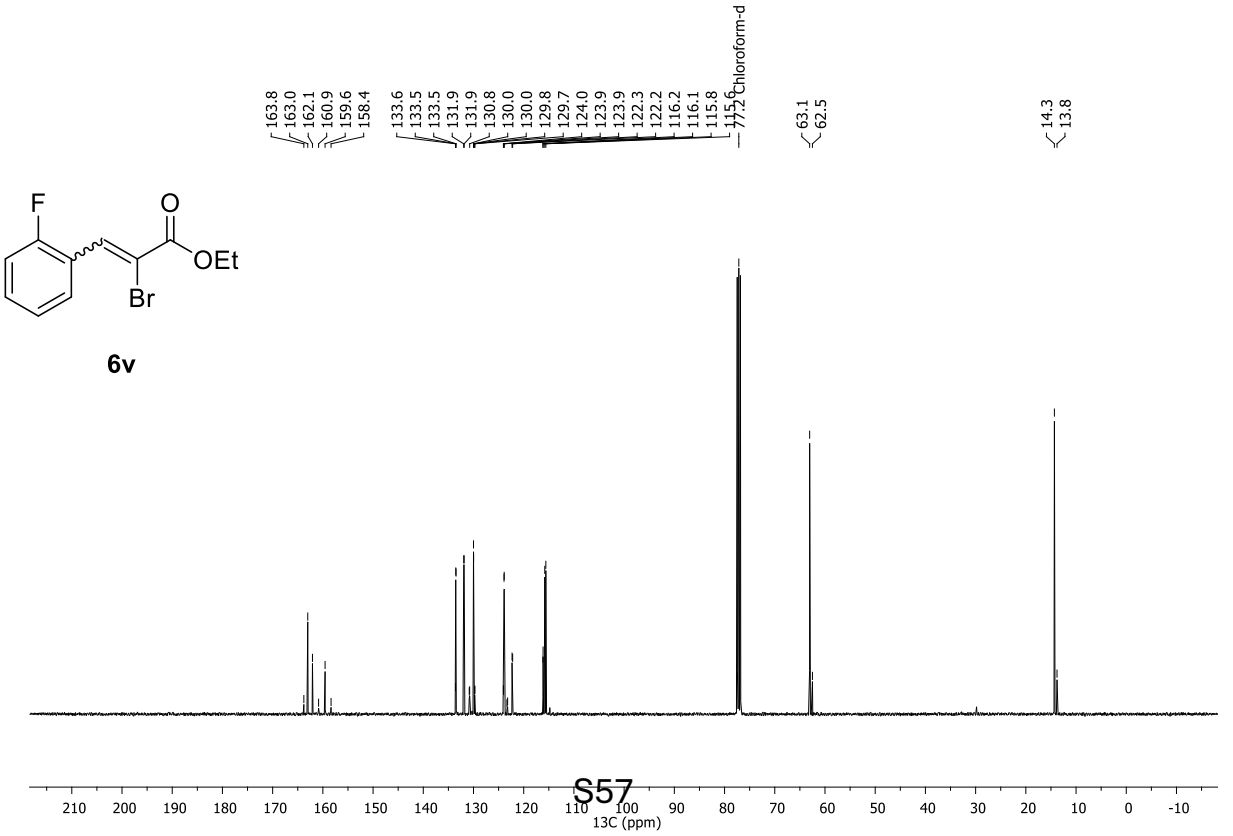
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-3-(2-chlorophenyl)acrylate **6u** in $CDCl_3$

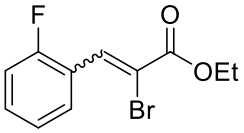




^{1}H, ^{13}C and ^{19}F NMR ethyl 2-bromo-3-(2-fluorophenyl)acrylate **6v** in $CDCl_3$

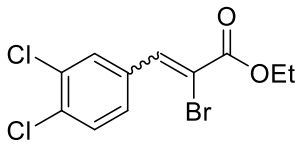




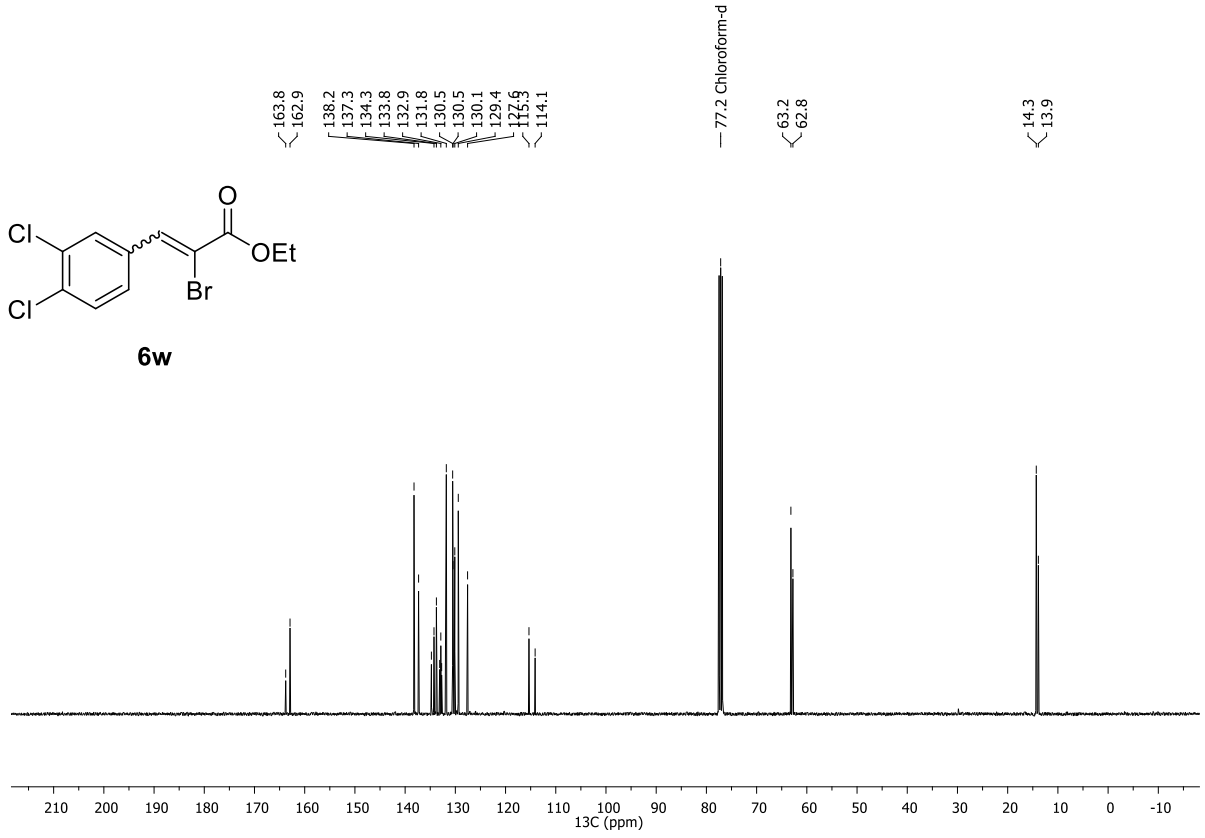


6v

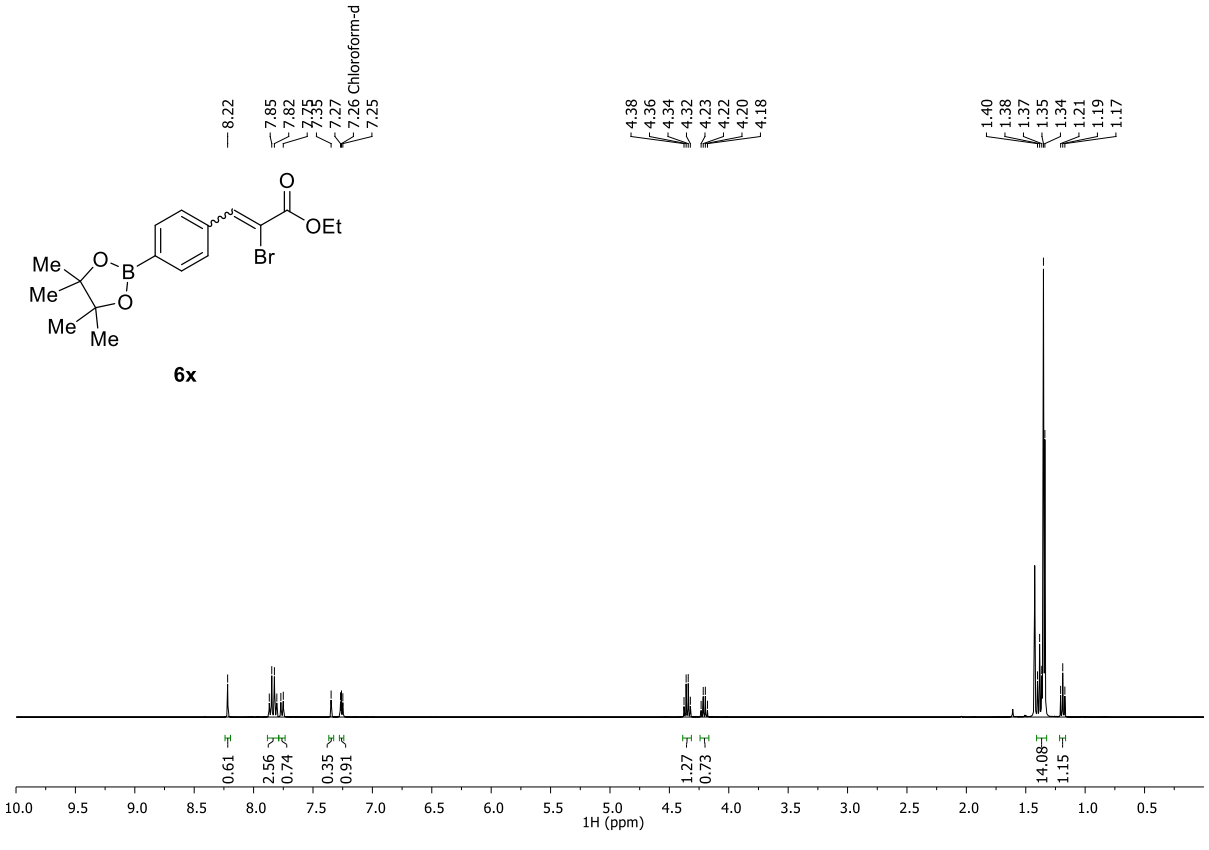
^{1}H and ^{13}C NMR ethyl 2-bromo-3-(3,4-dichlorophenyl)acrylate **6w** in $CDCl_3$

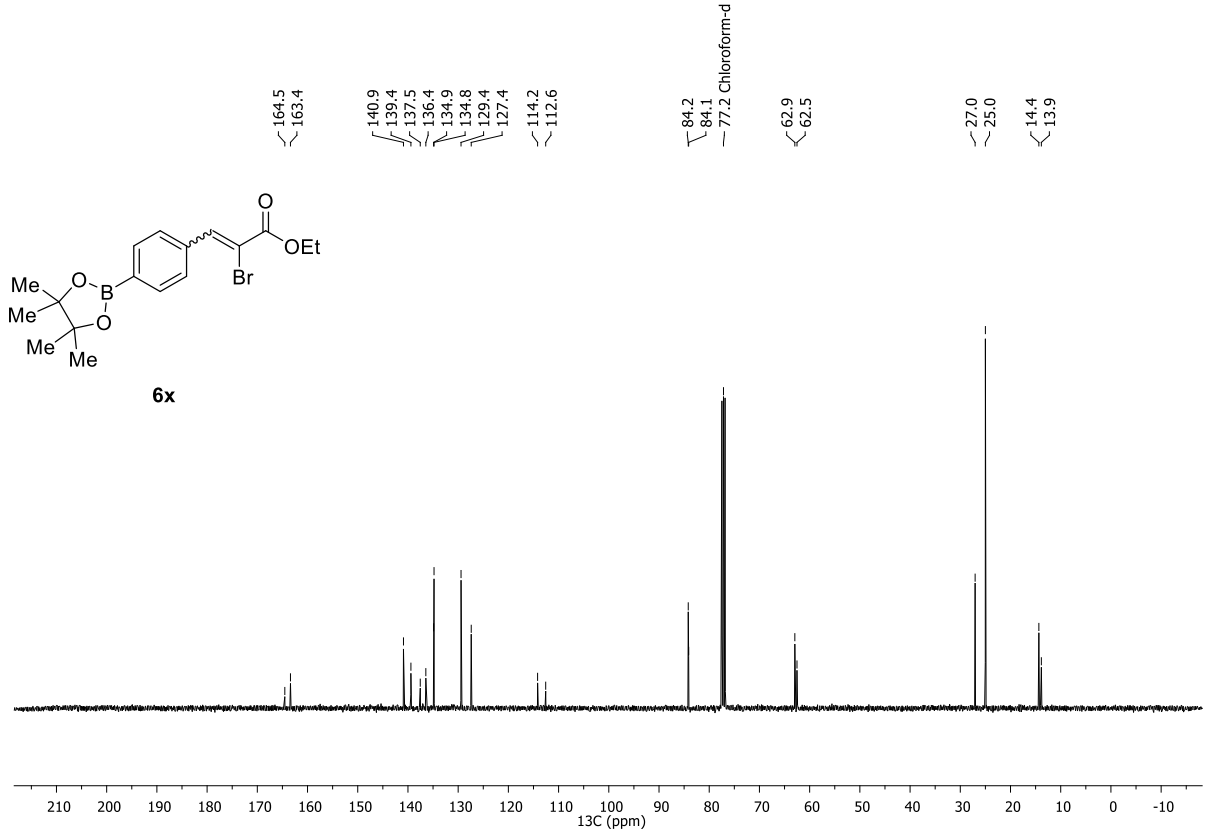


6w

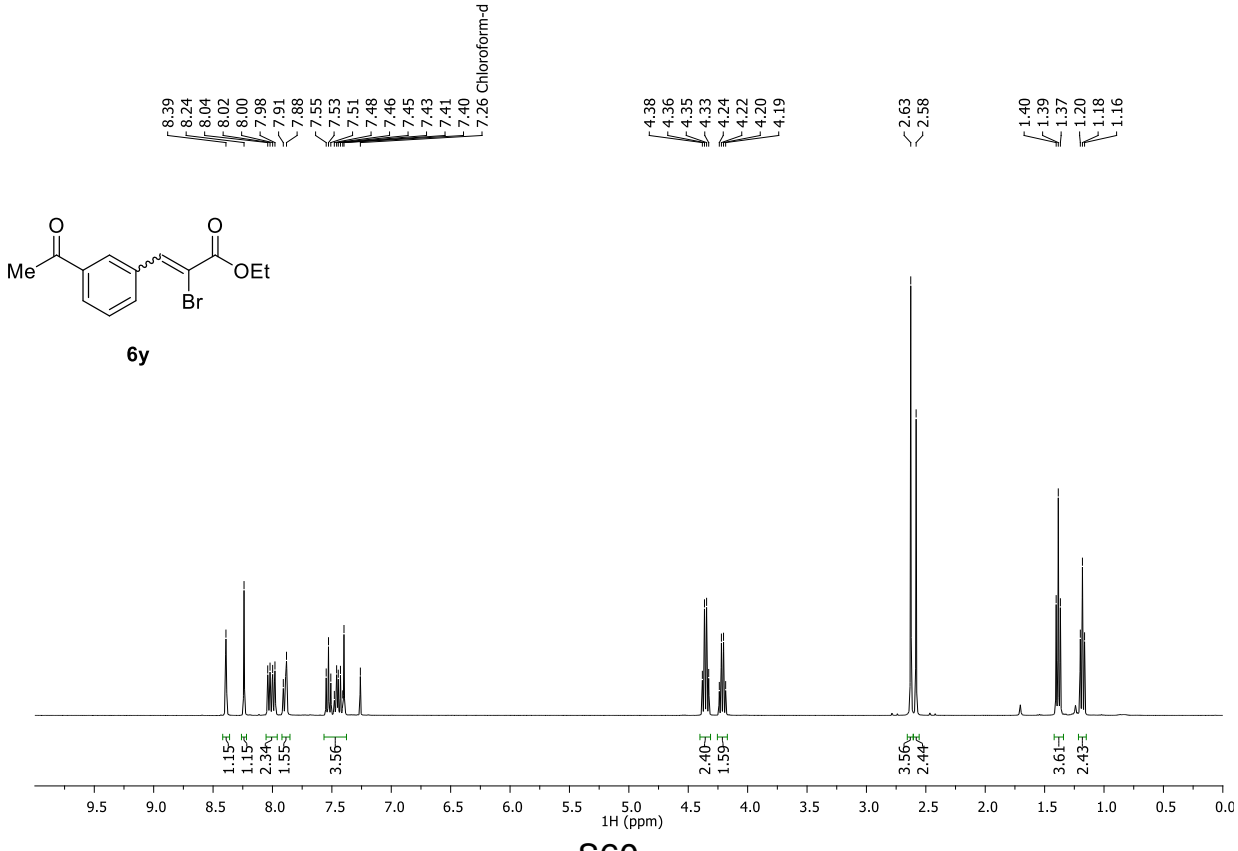


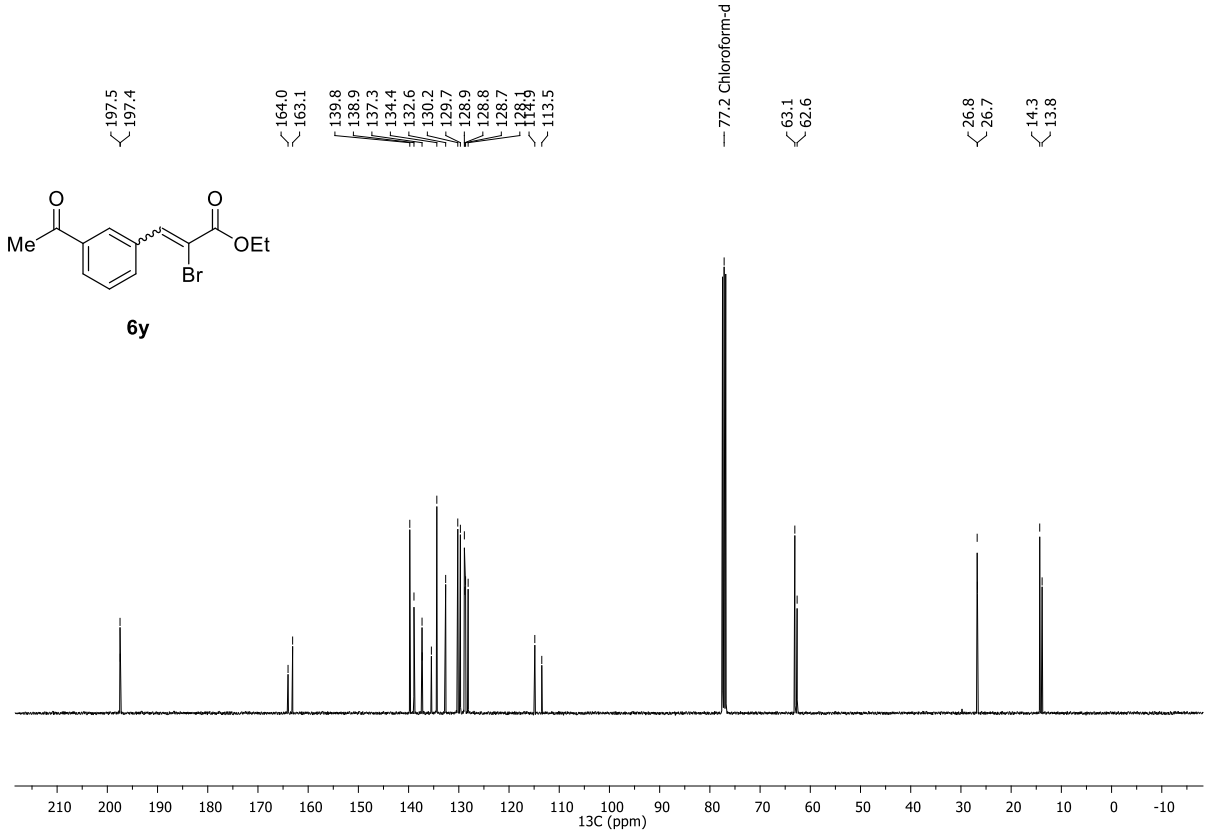
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate **6x** in $CDCl_3$





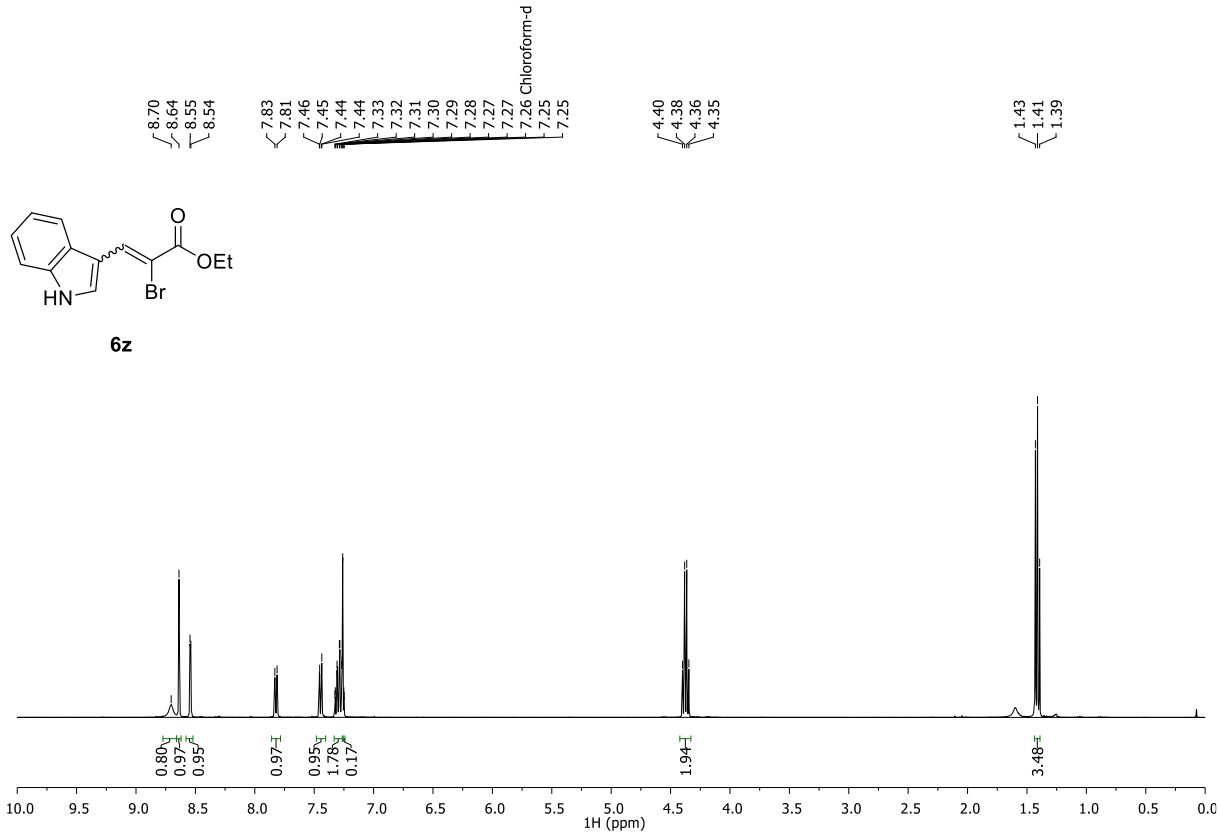
^{1}H and ^{13}C NMR spectra of ethyl 3-(3-acetylphenyl)-2-bromoacrylate **6y** in $CDCl_3$



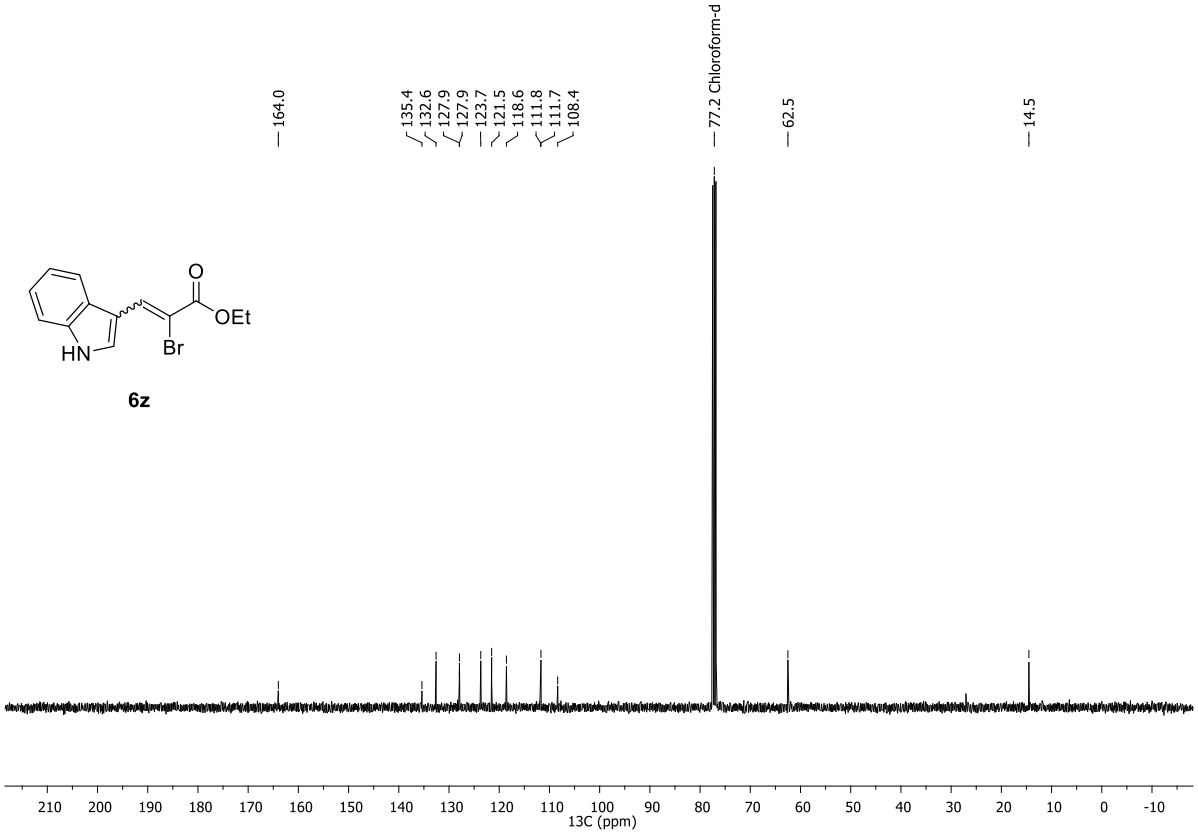


6y

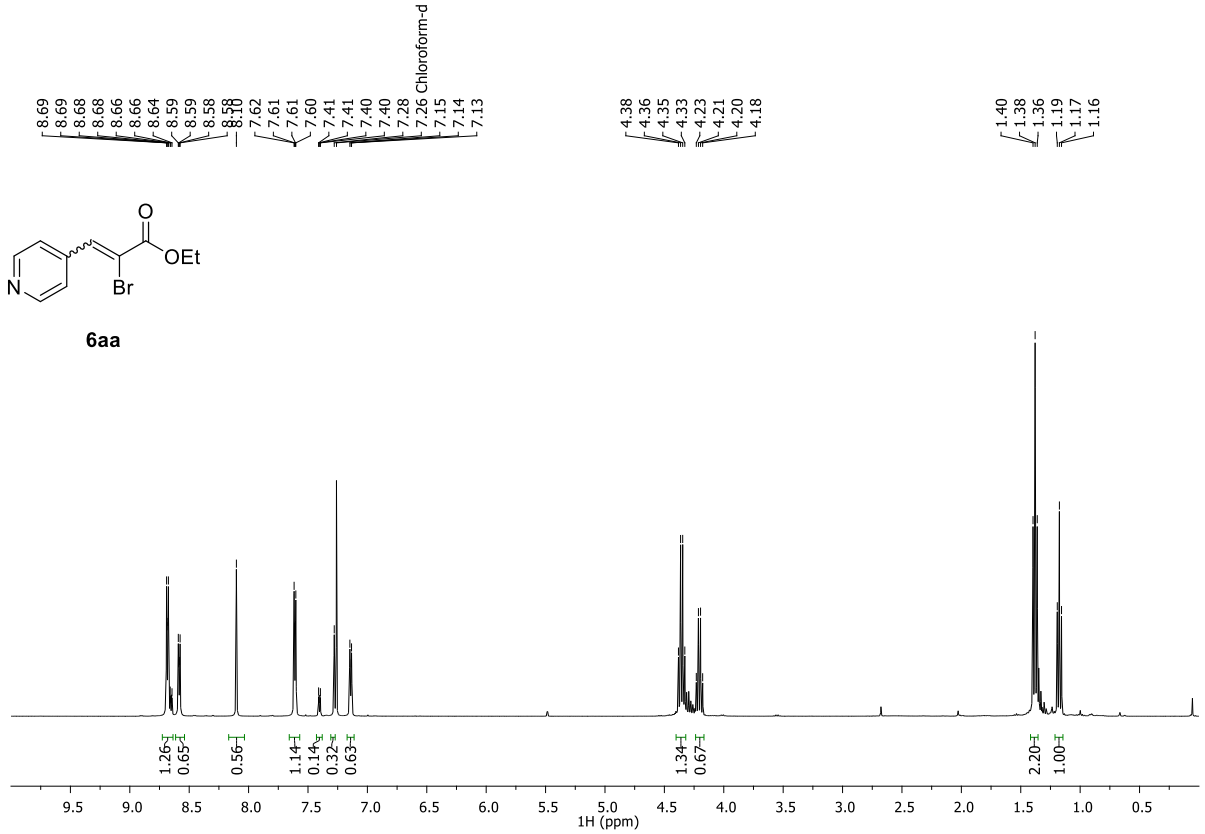
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-3-(1H-indol-3-yl)acrylate **6z** in $CDCl_3$

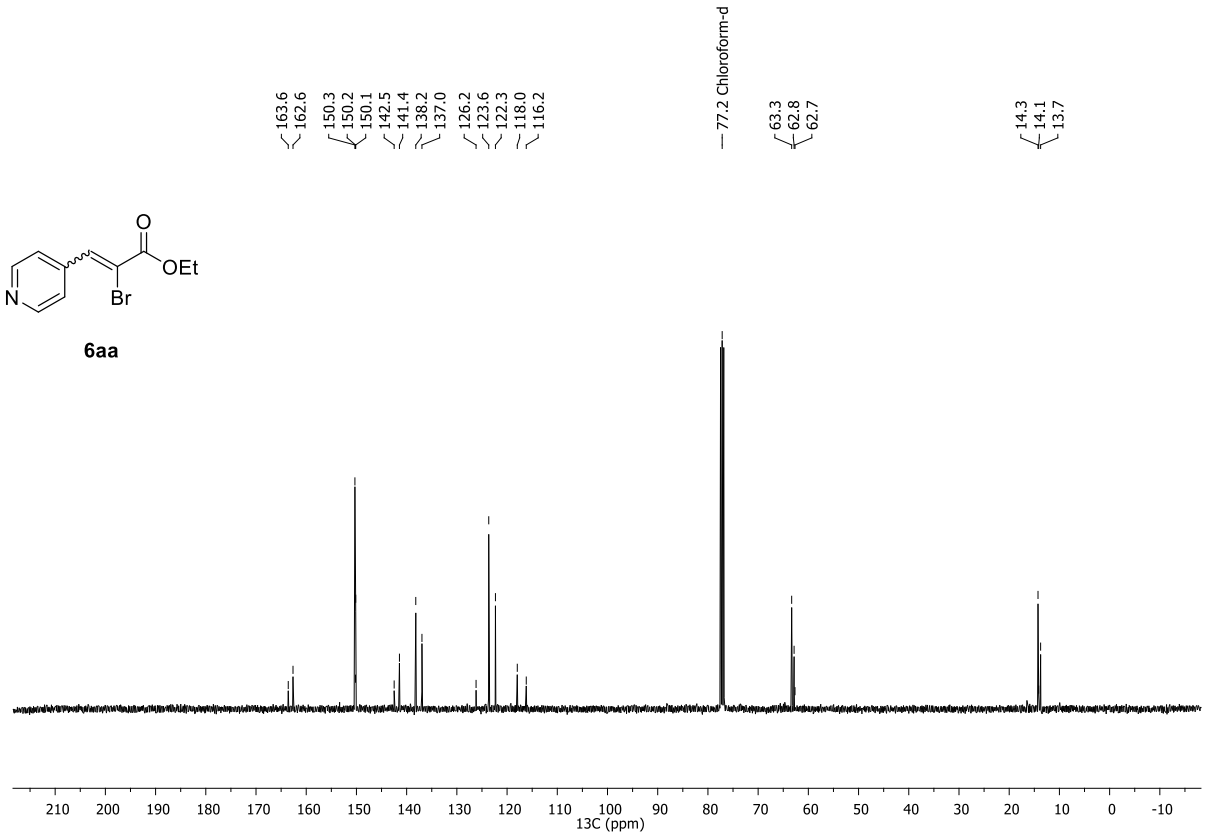


6z

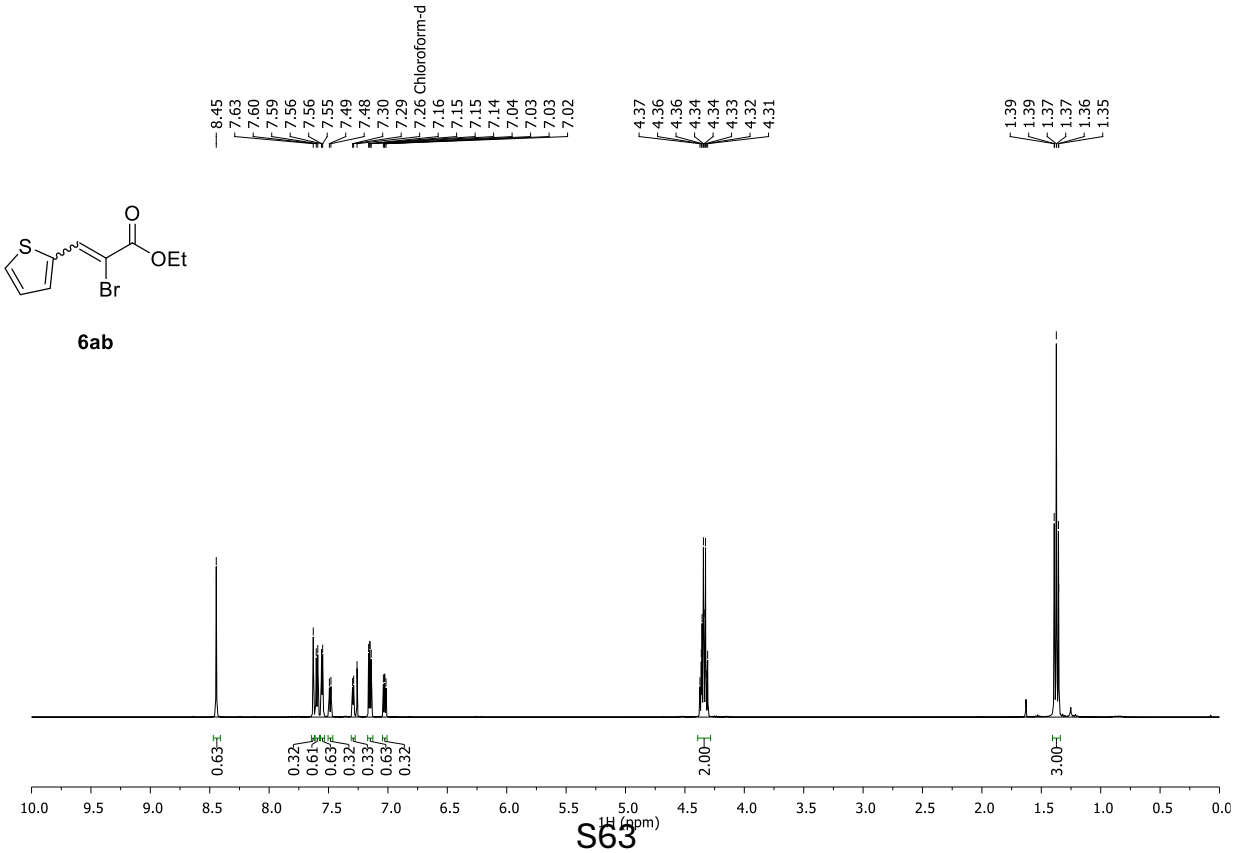


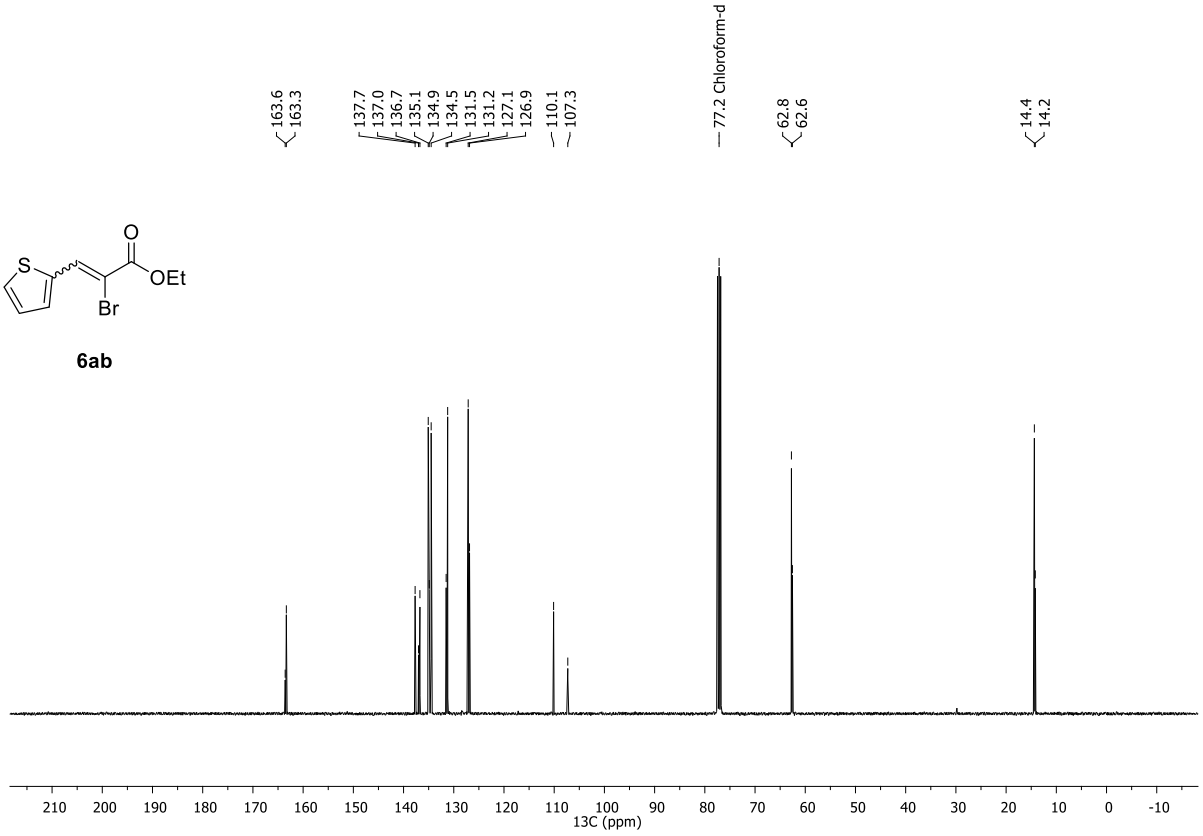
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-3-(pyridin-4-yl)acrylate **6aa** in $CDCl_3$



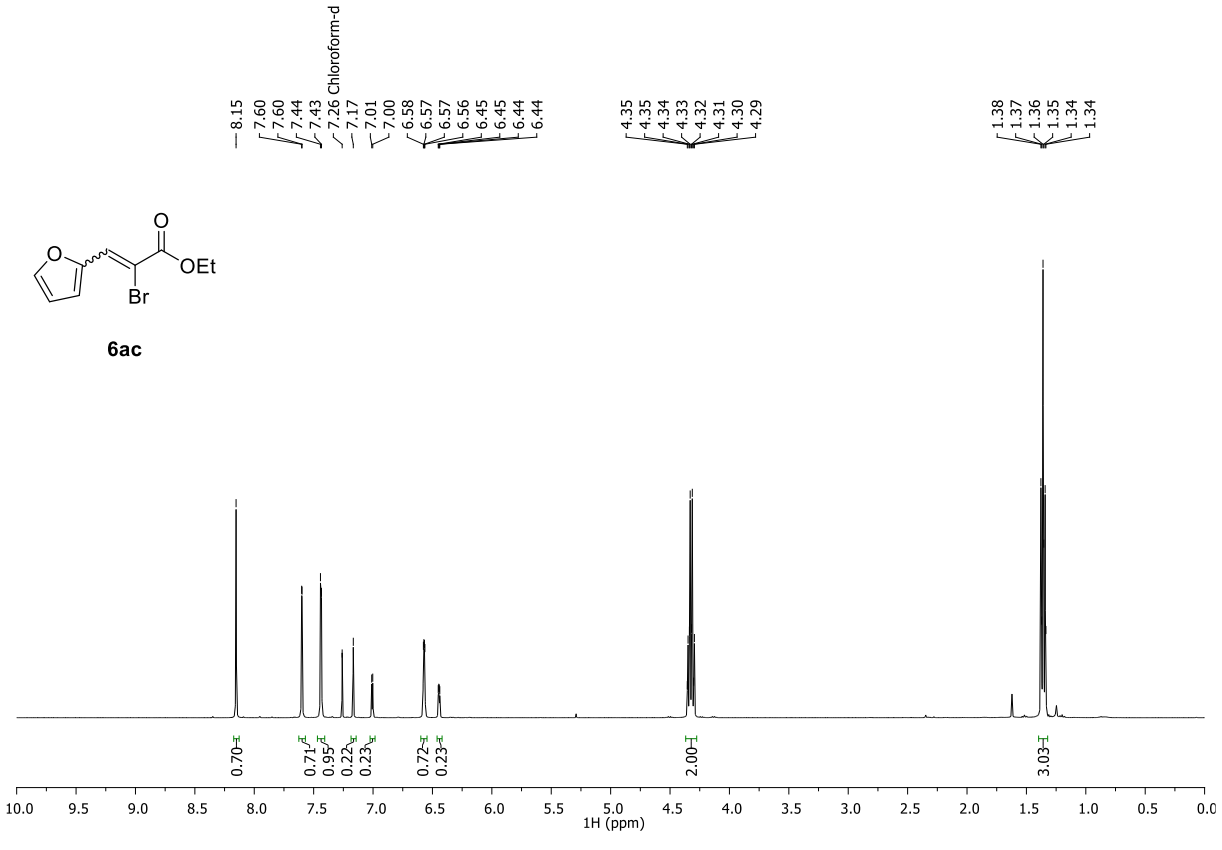


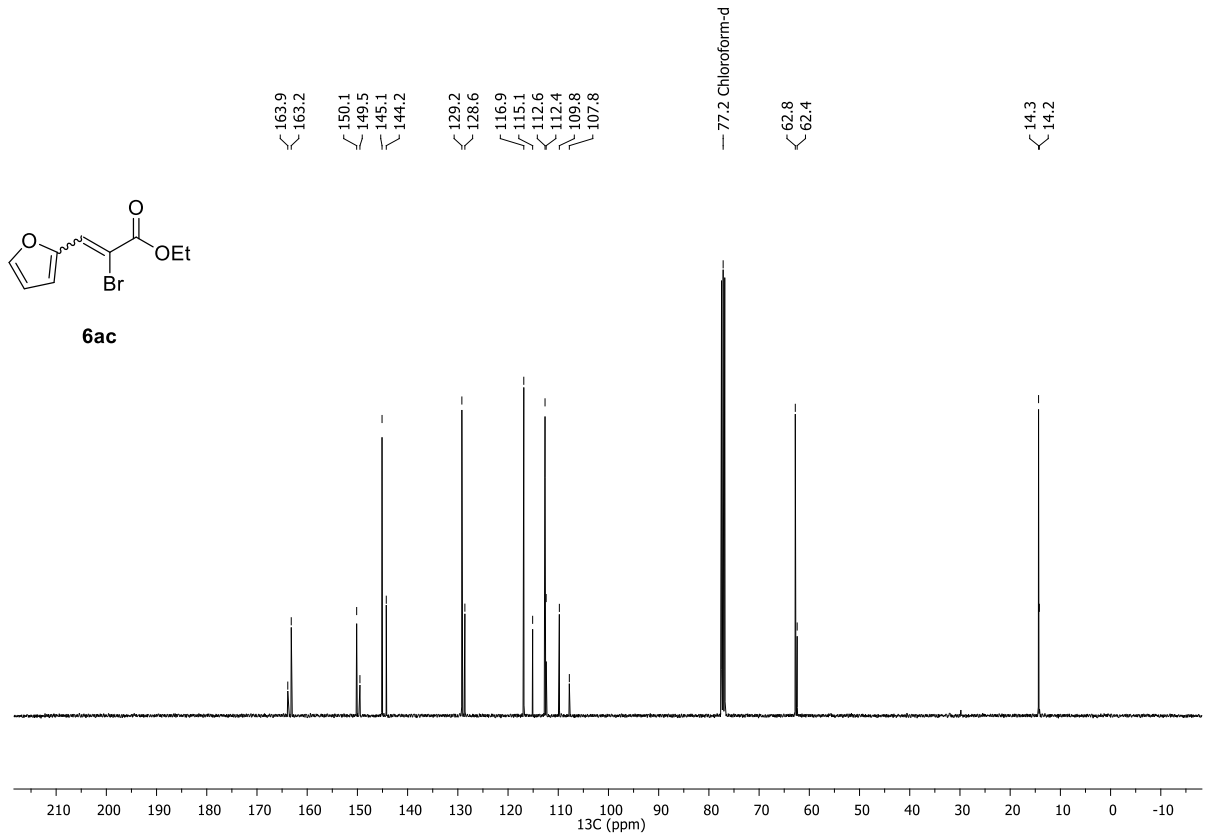
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-3-(2-thienyl)-2-propenoate **6ab** in $CDCl_3$



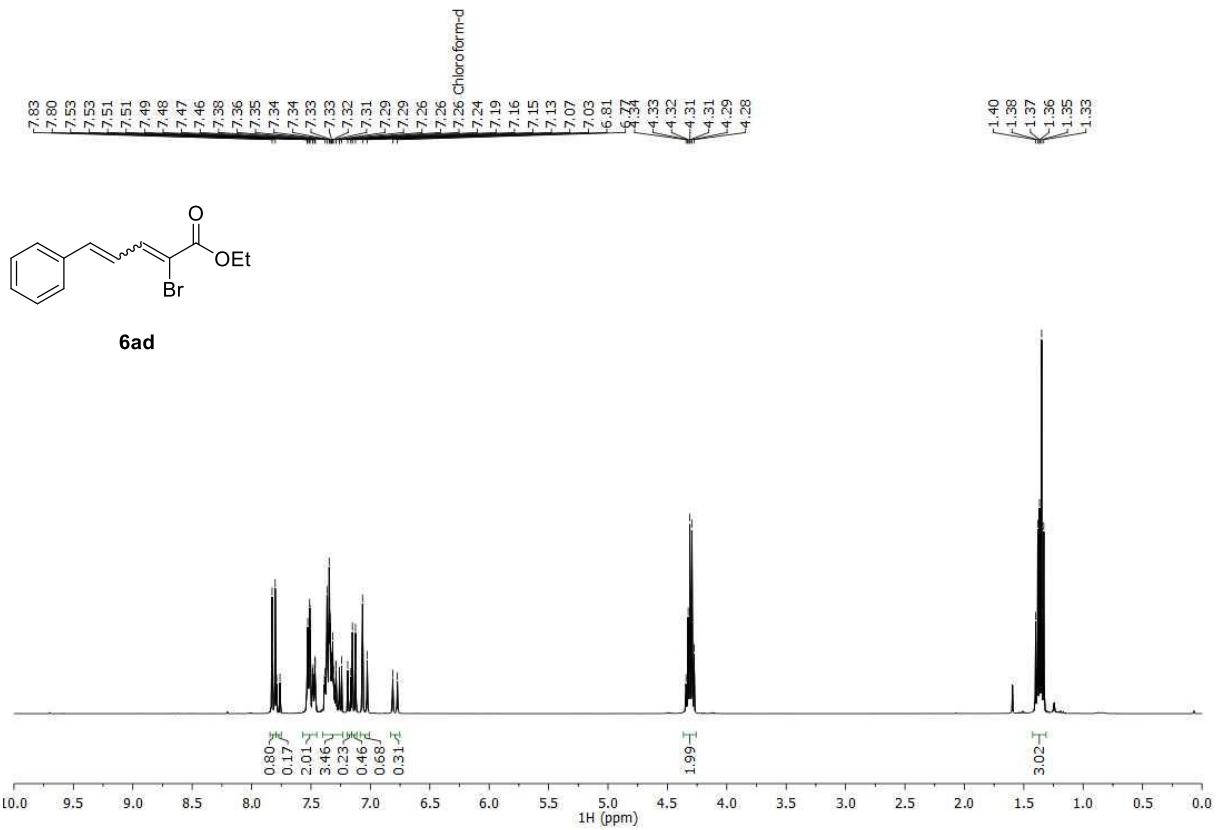


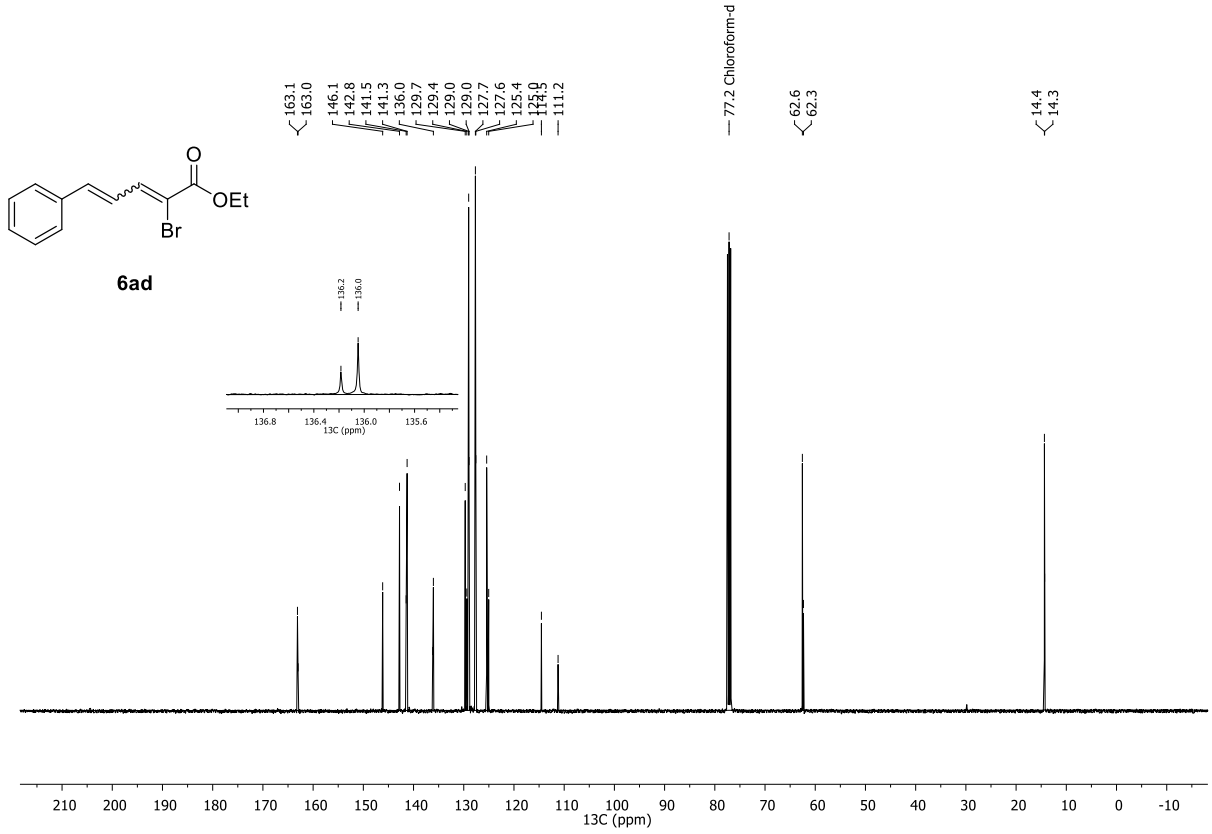
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-3-(2-furanyl)-2-propenoate **6ac** in $CDCl_3$



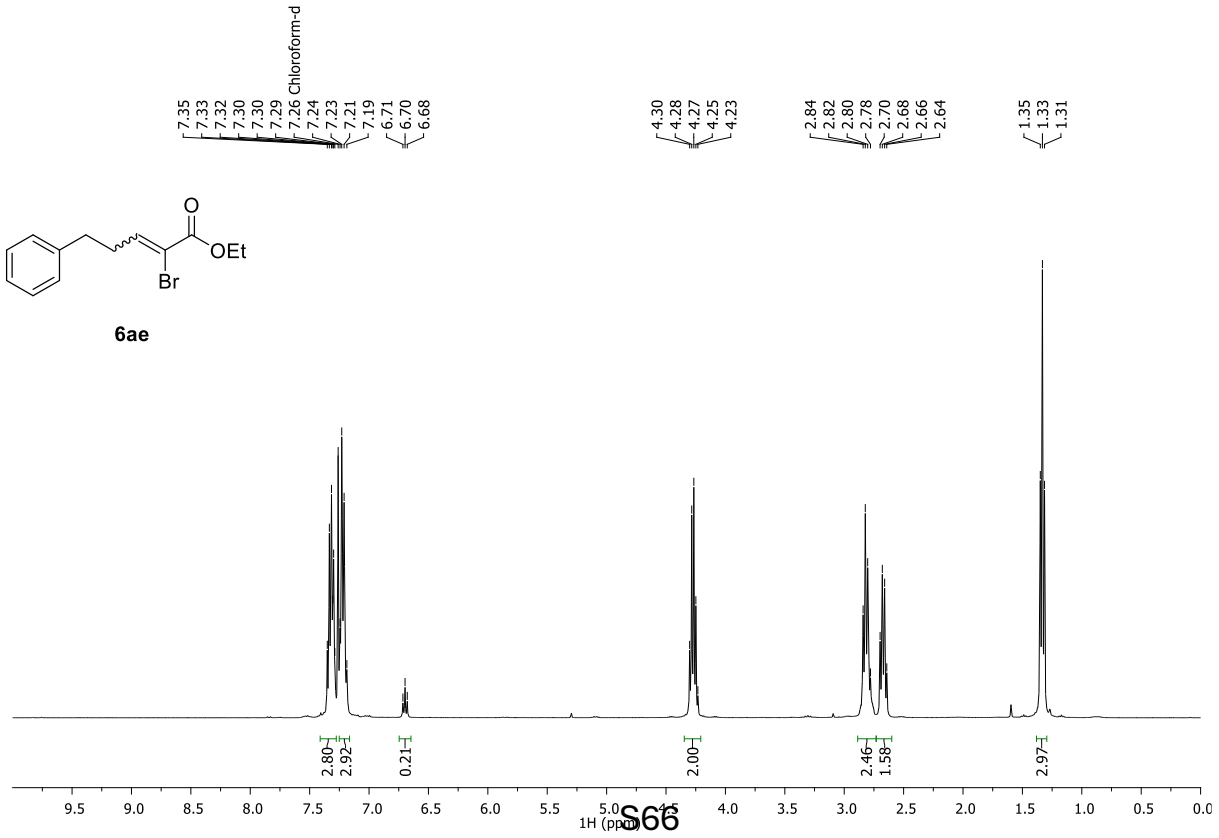


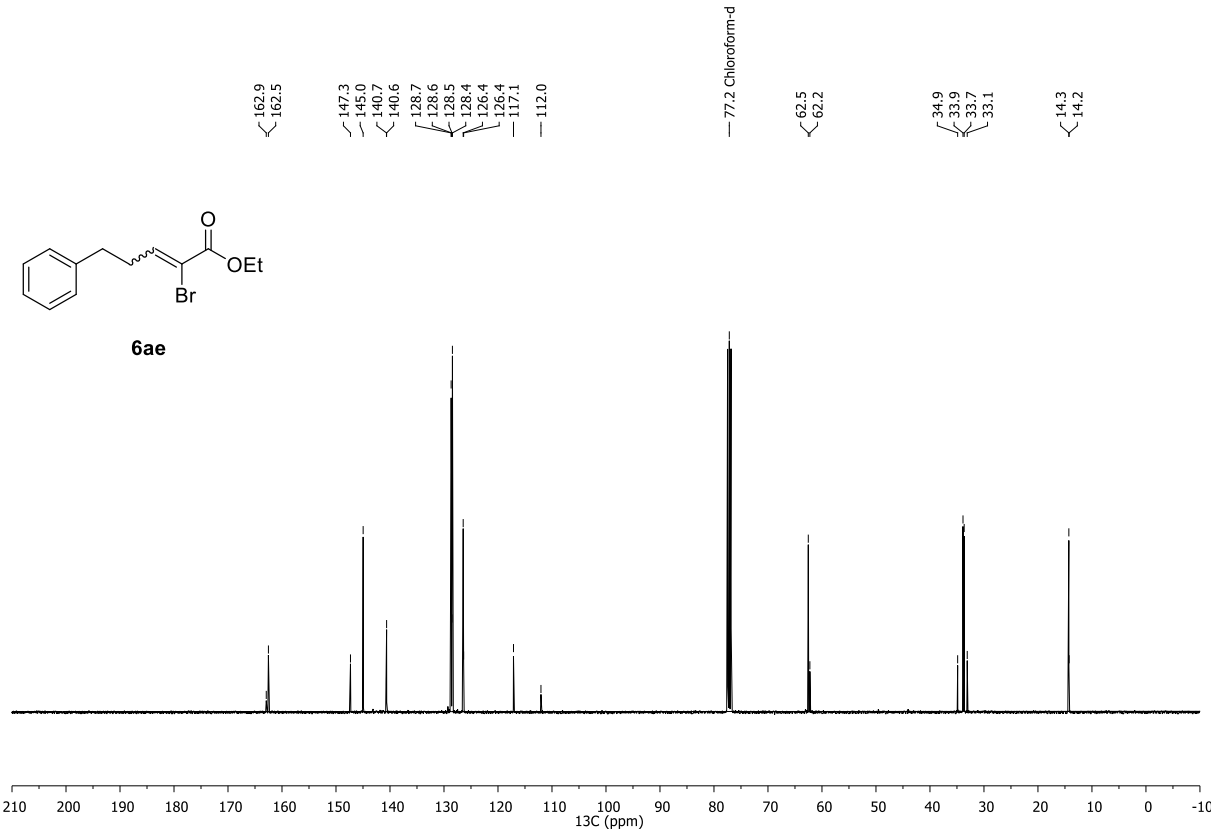
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-5-phenylpenta-2,4-dienoate **6ad** in $CDCl_3$



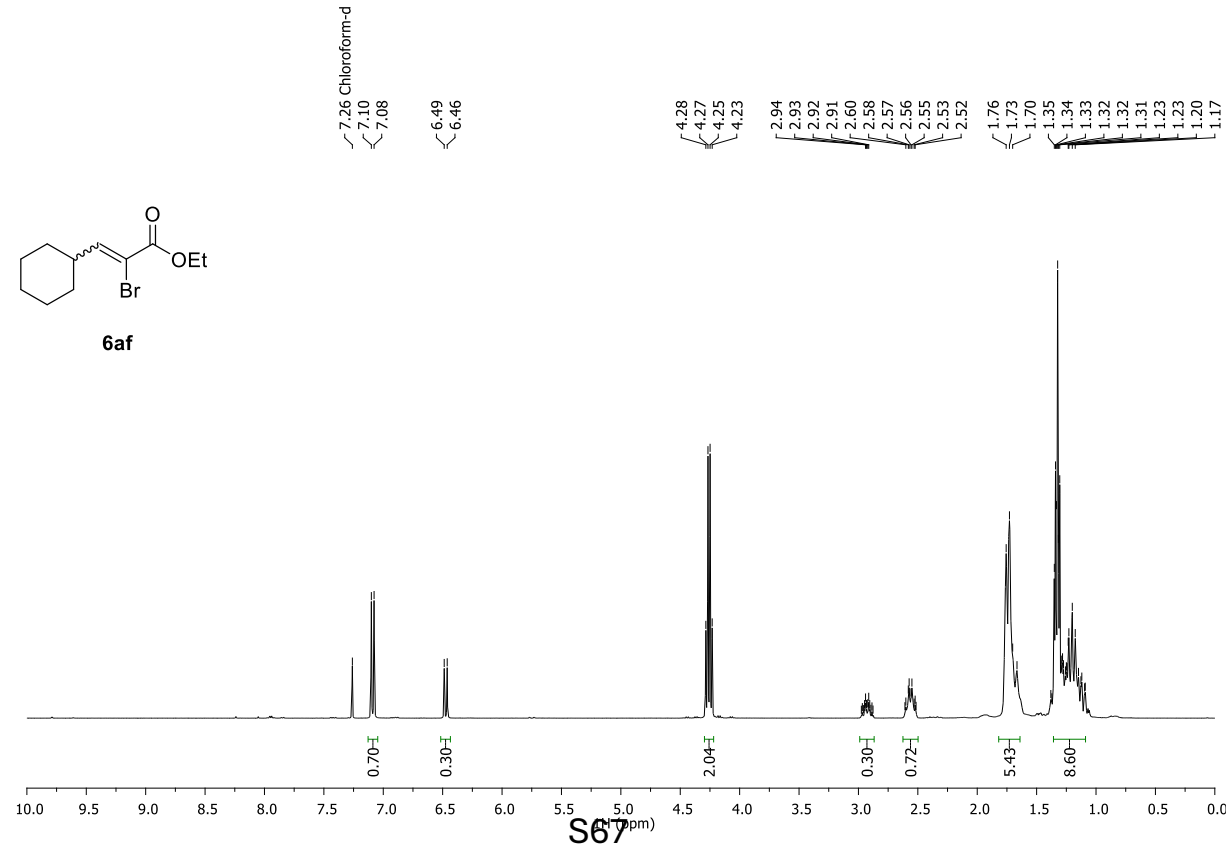


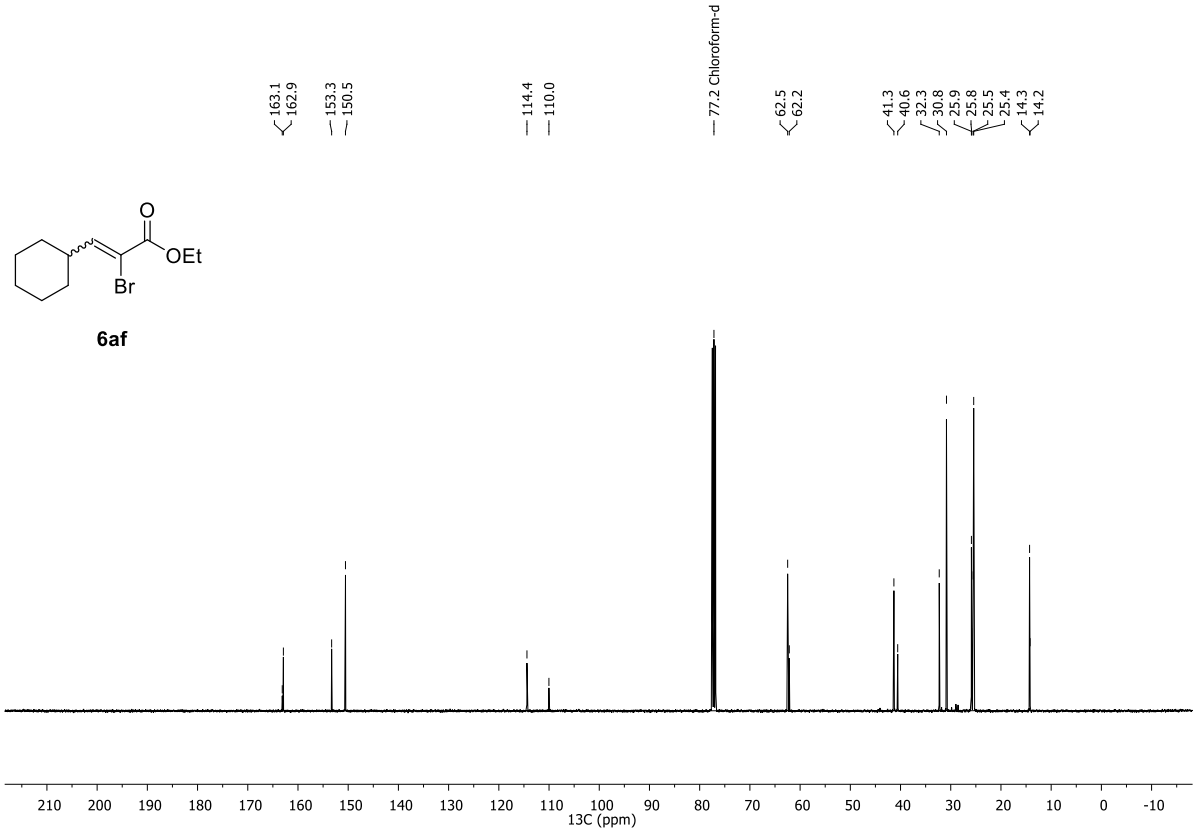
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-5-phenylpent-2-enoate **6ae** in $CDCl_3$



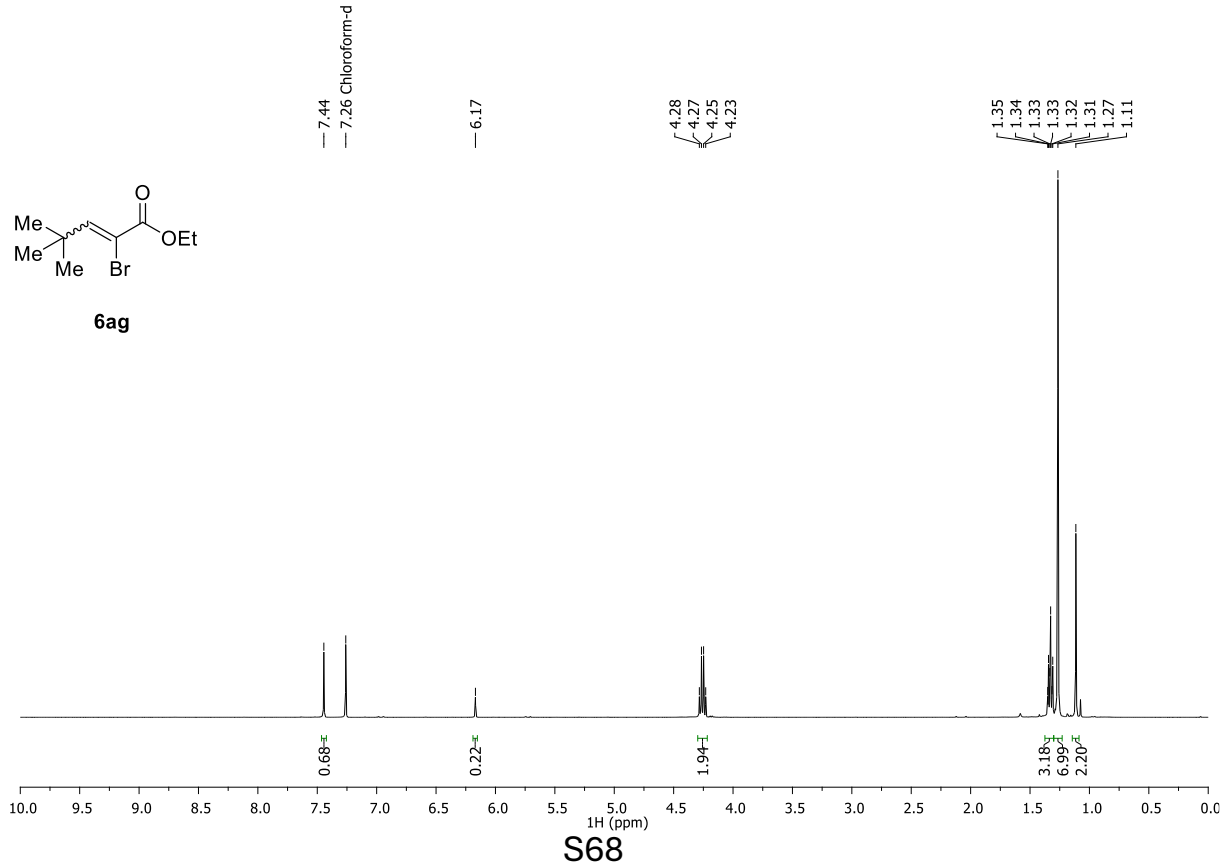


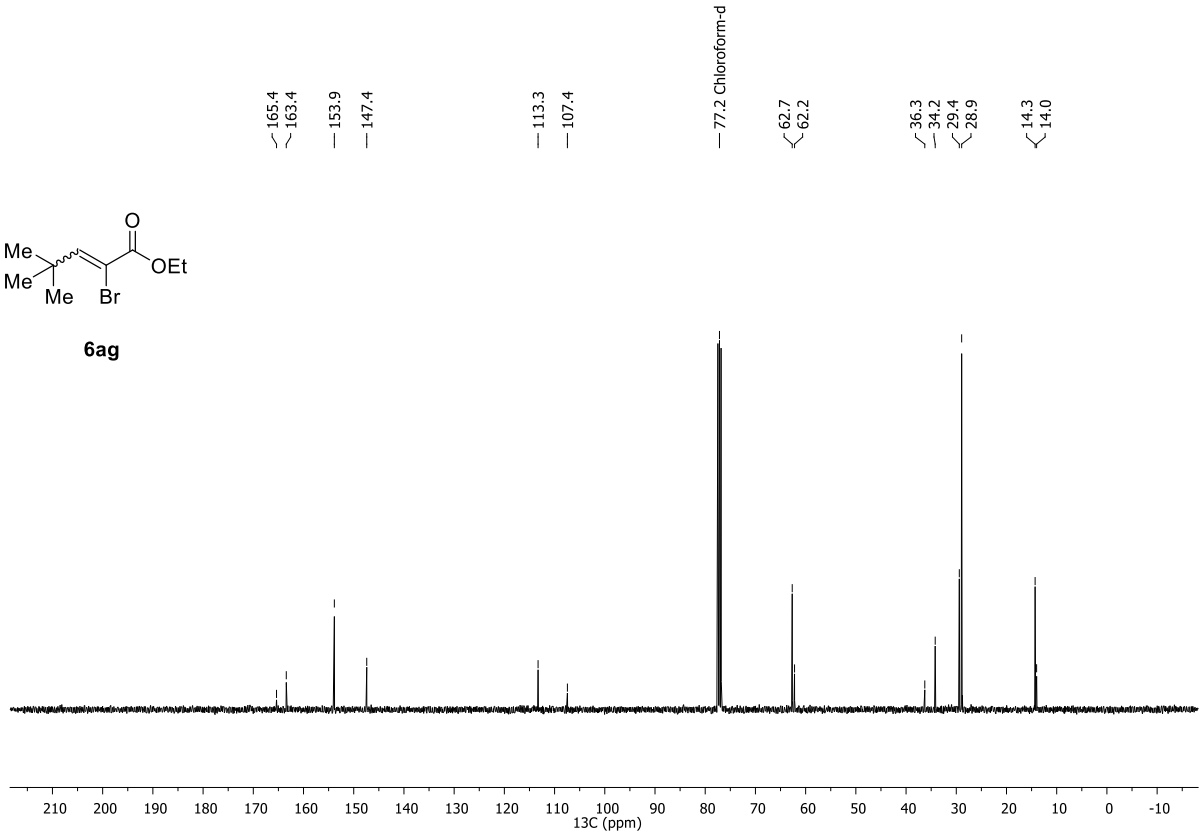
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-3-cyclohexylacrylate **6af** in $CDCl_3$



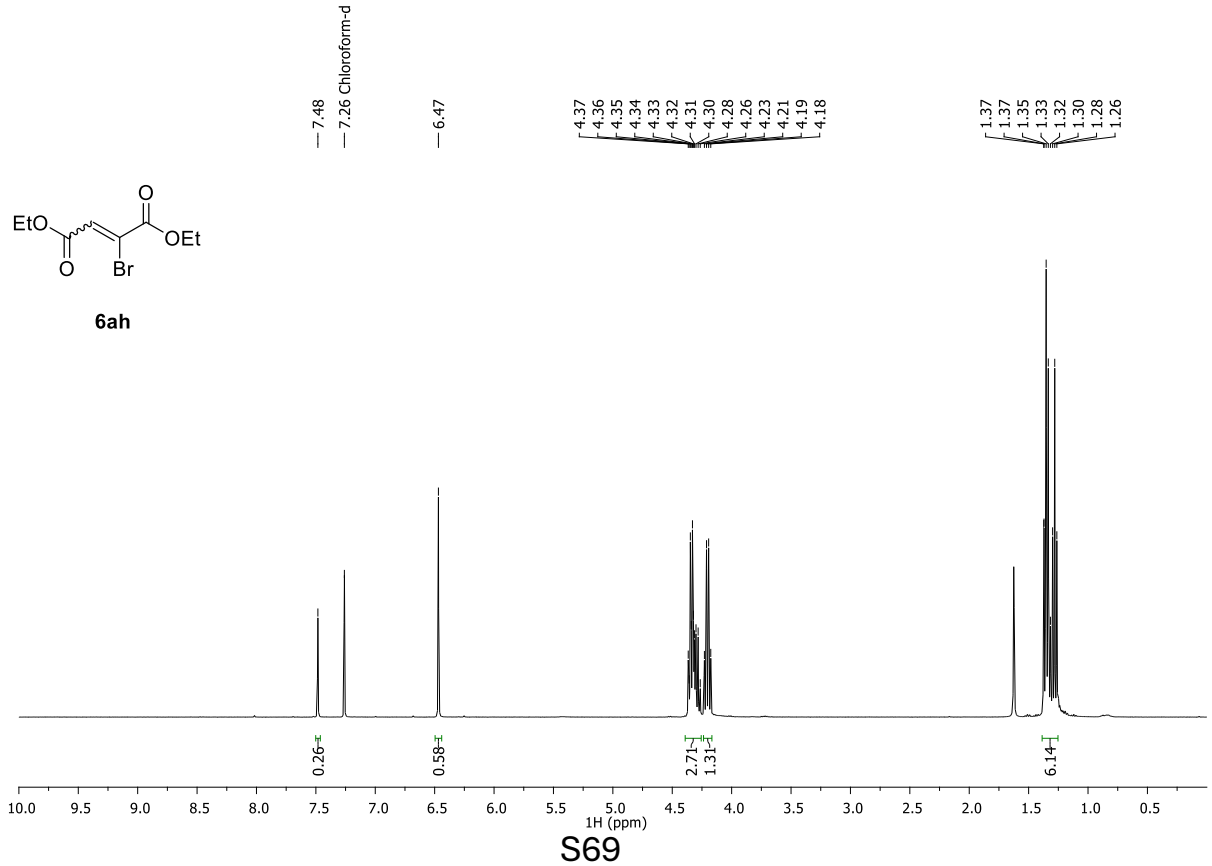


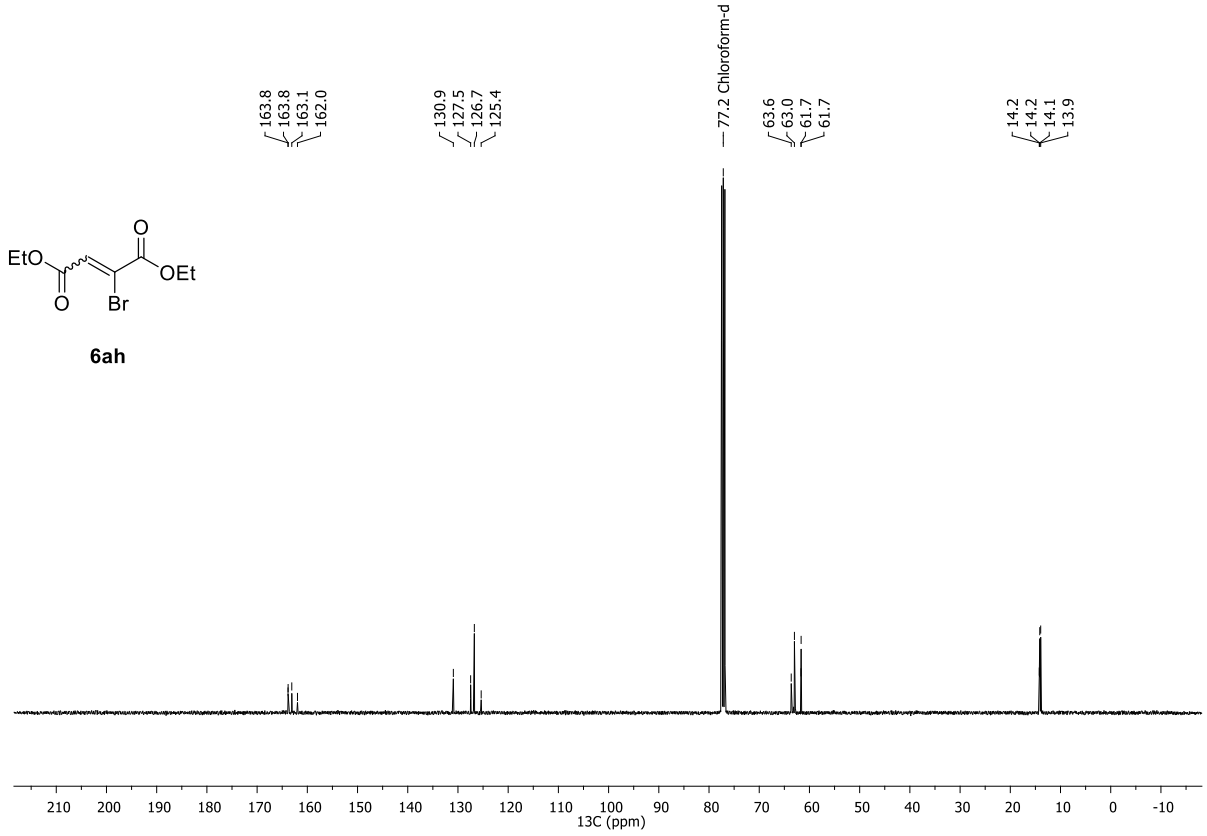
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-4,4-dimethylpent-2-enoate **6ag** in $CDCl_3$



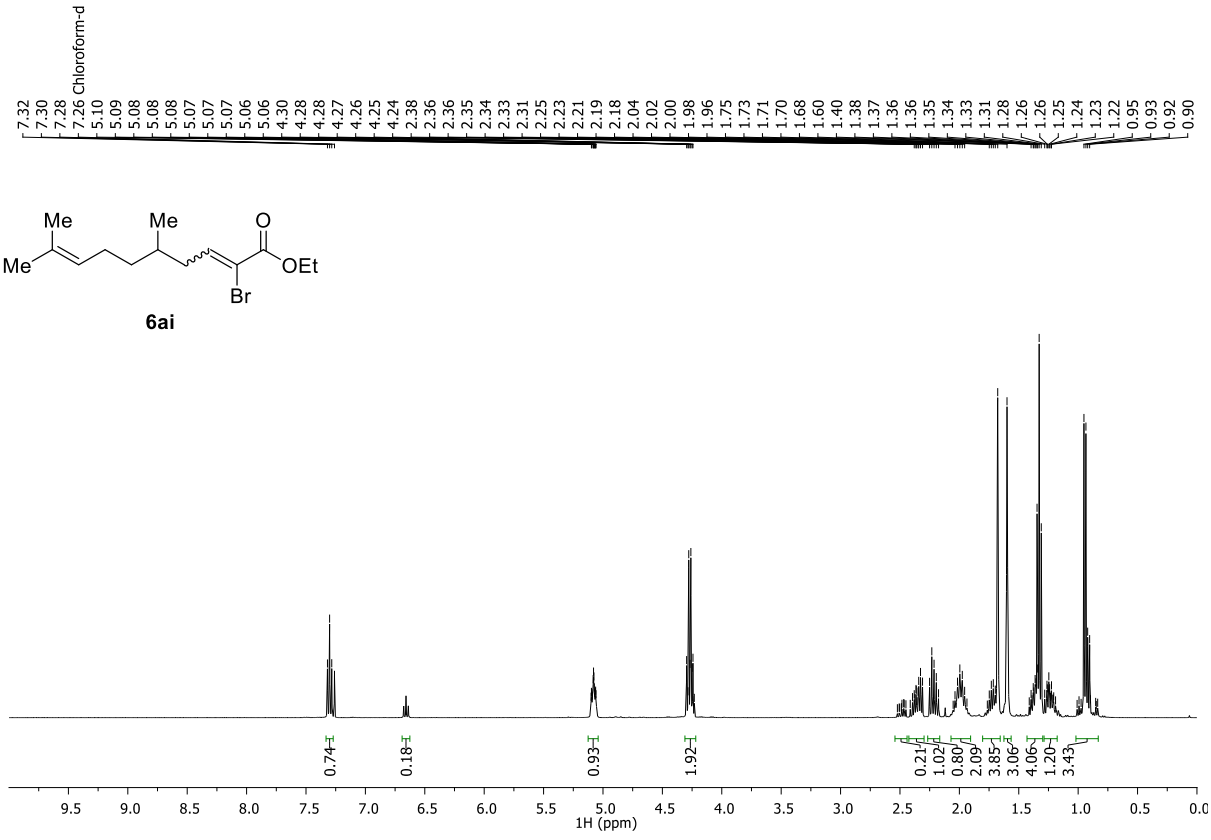


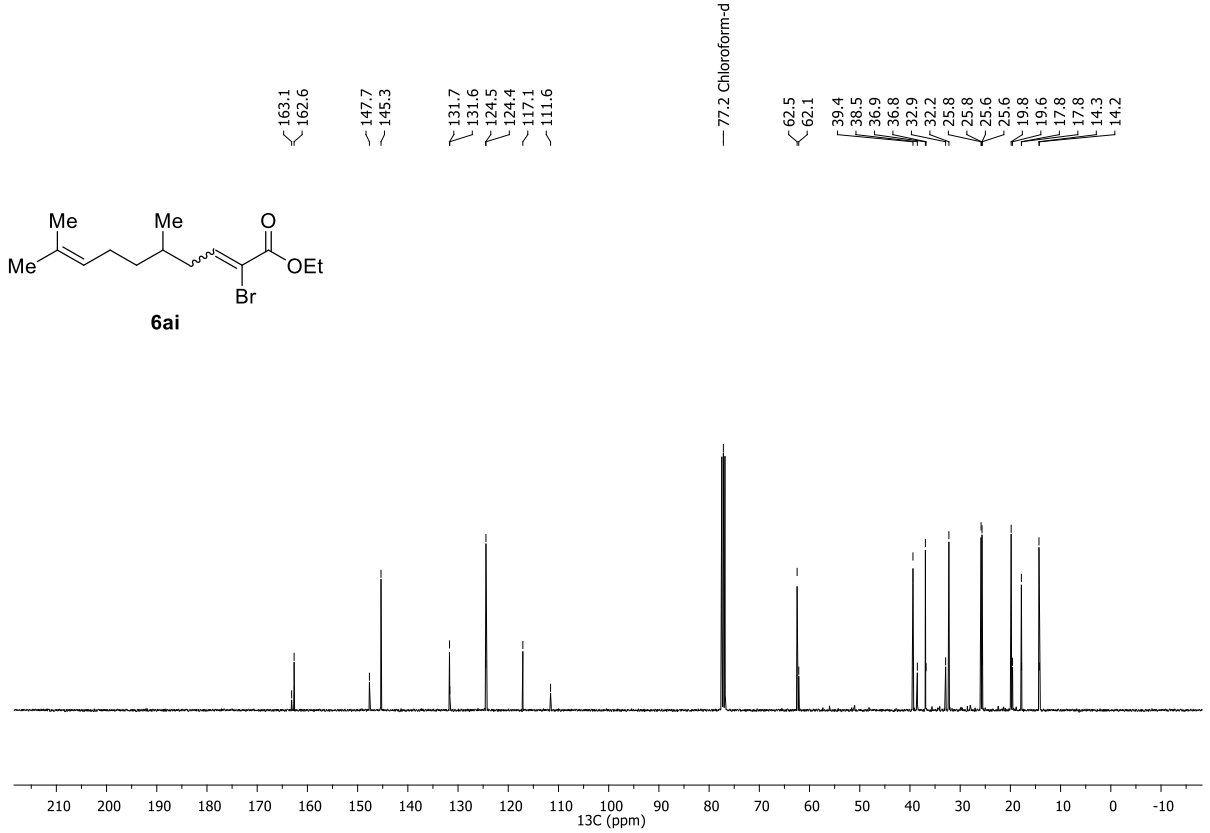
^{1}H and ^{13}C NMR spectra of diethyl 2-bromobut-2-enedioate **6ah** in $CDCl_3$



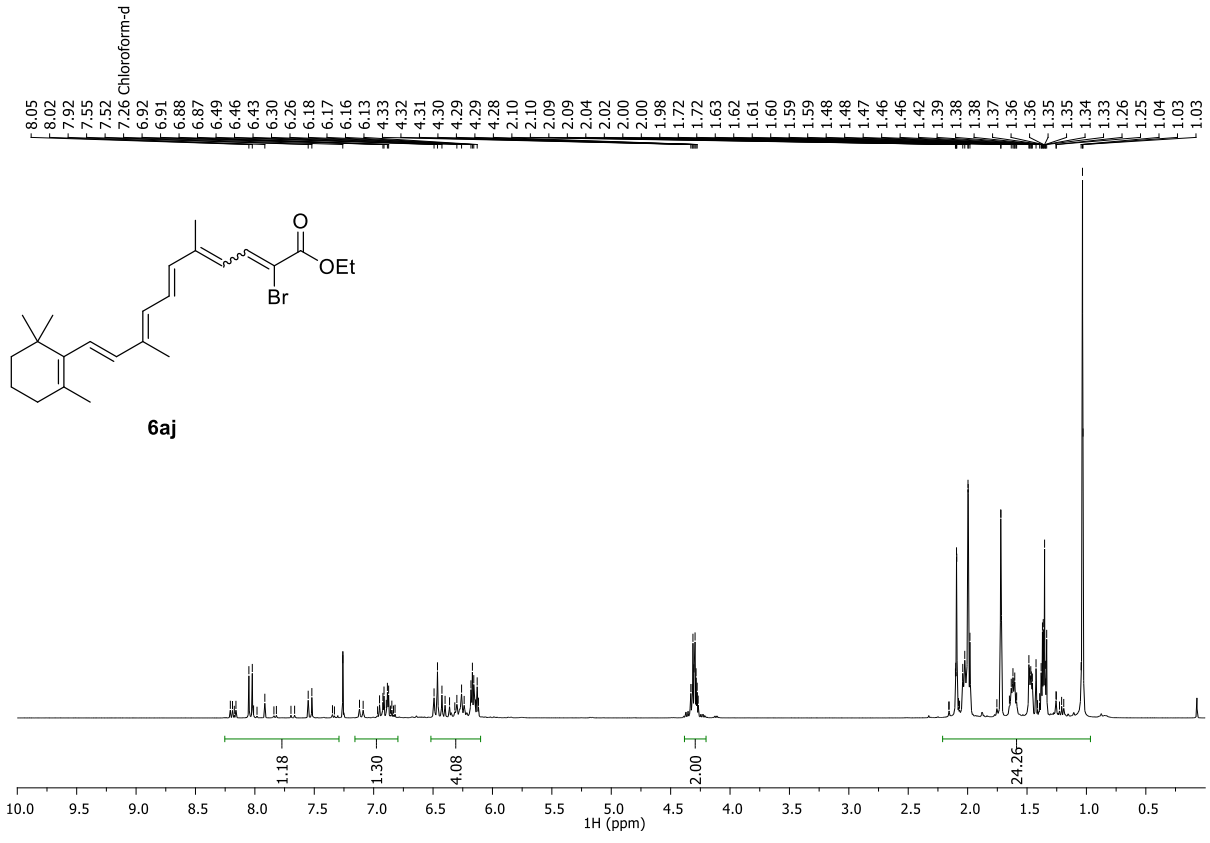


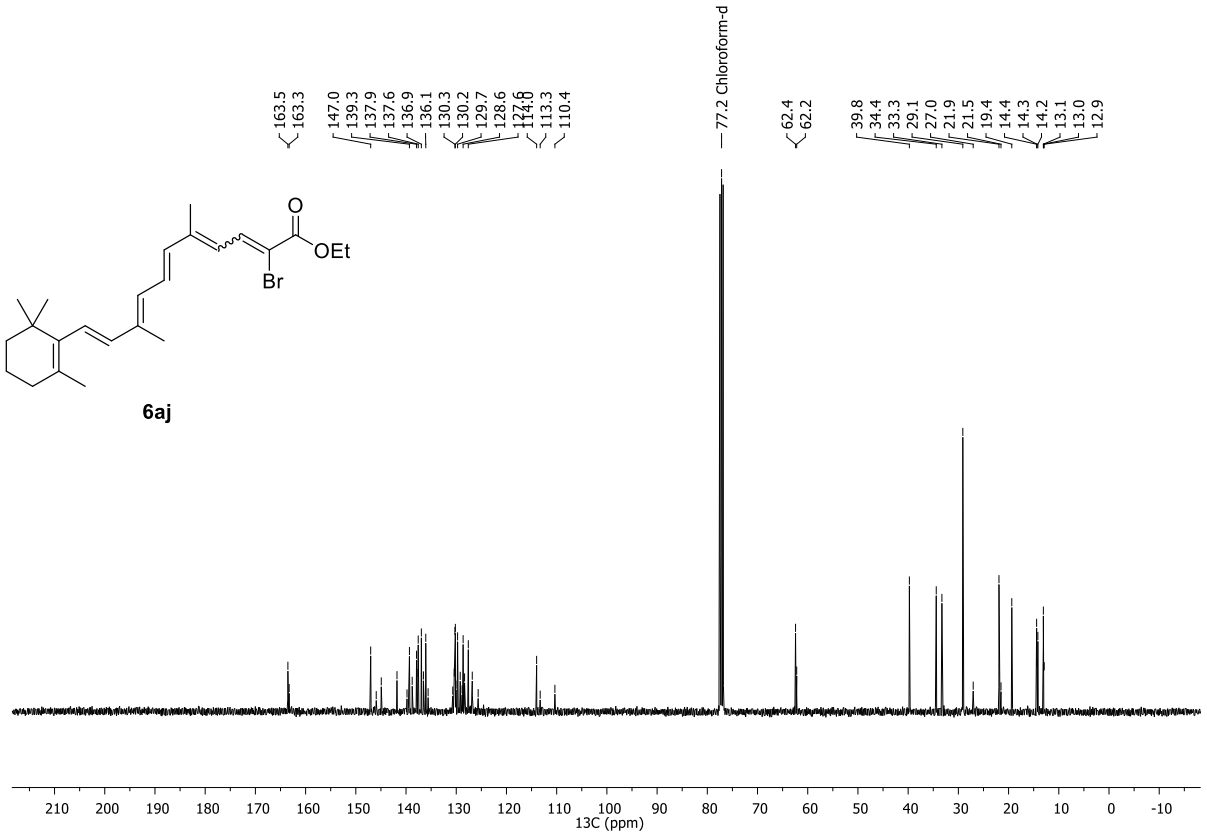
^{1}H and ^{13}C NMR spectra of ethyl 2-bromo-5,9-dimethyldeca-2,8-dienoate **6ai** in $CDCl_3$



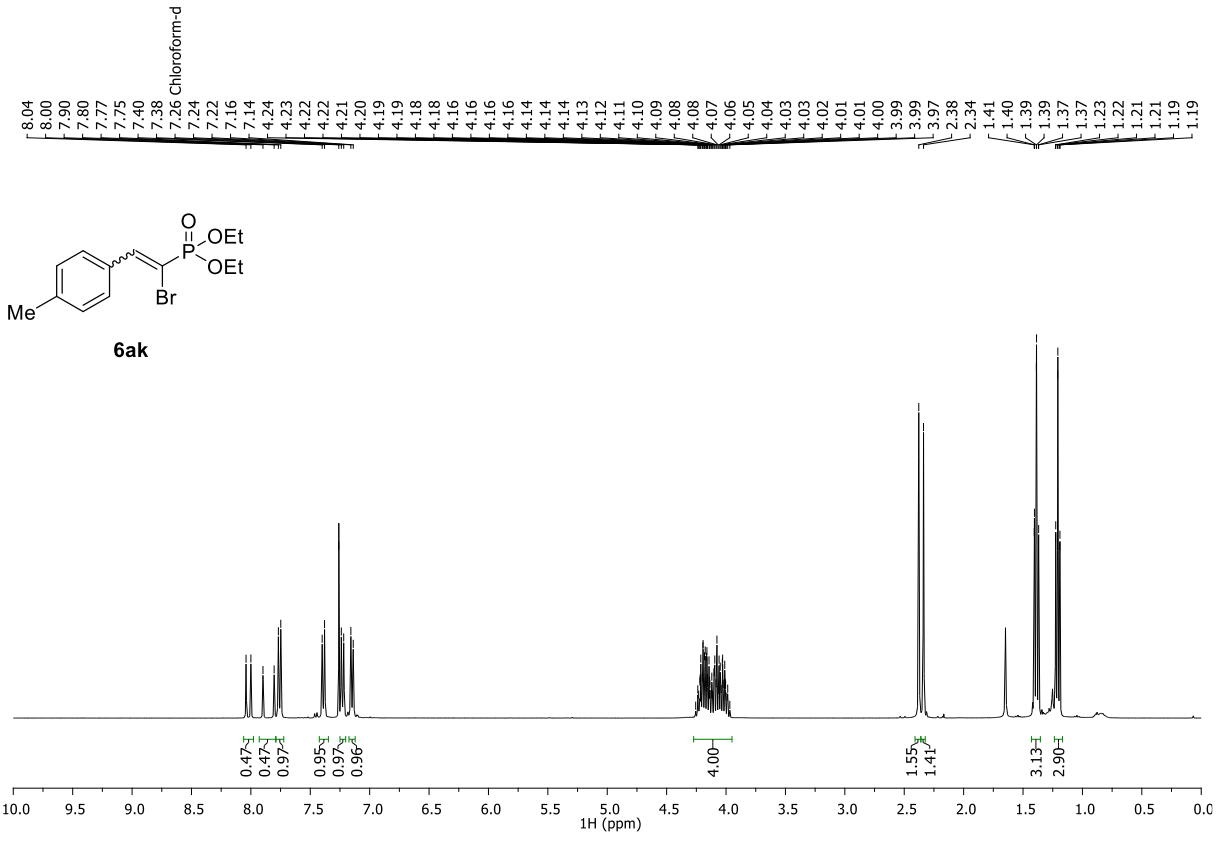


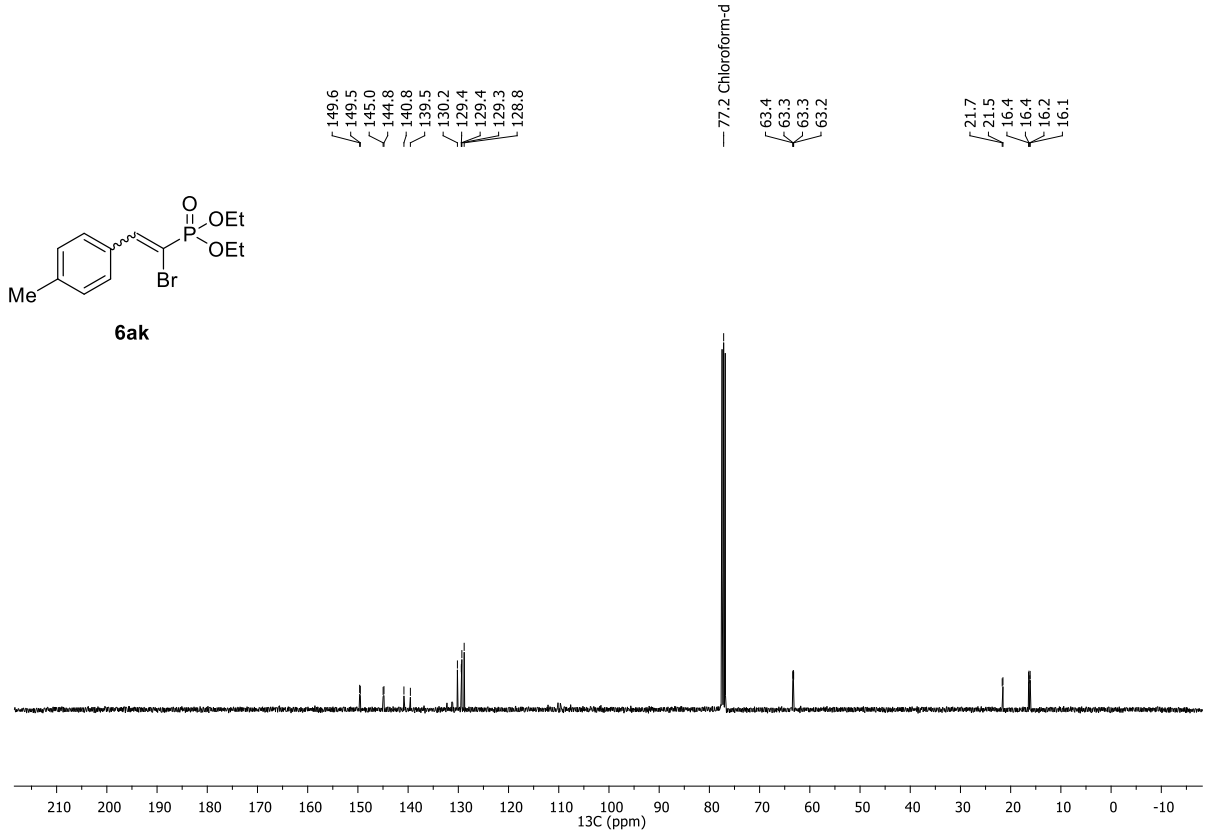
^{1}H and ^{13}C NMR spectra of ethyl (6E,8E,10E)-2-bromo-5,9-dimethyl-11-(2,6,6-trimethylcyclohex-1-en-1-yl)undeca-2,4,6,8,10-pentaenoate **6aj** in $CDCl_3$



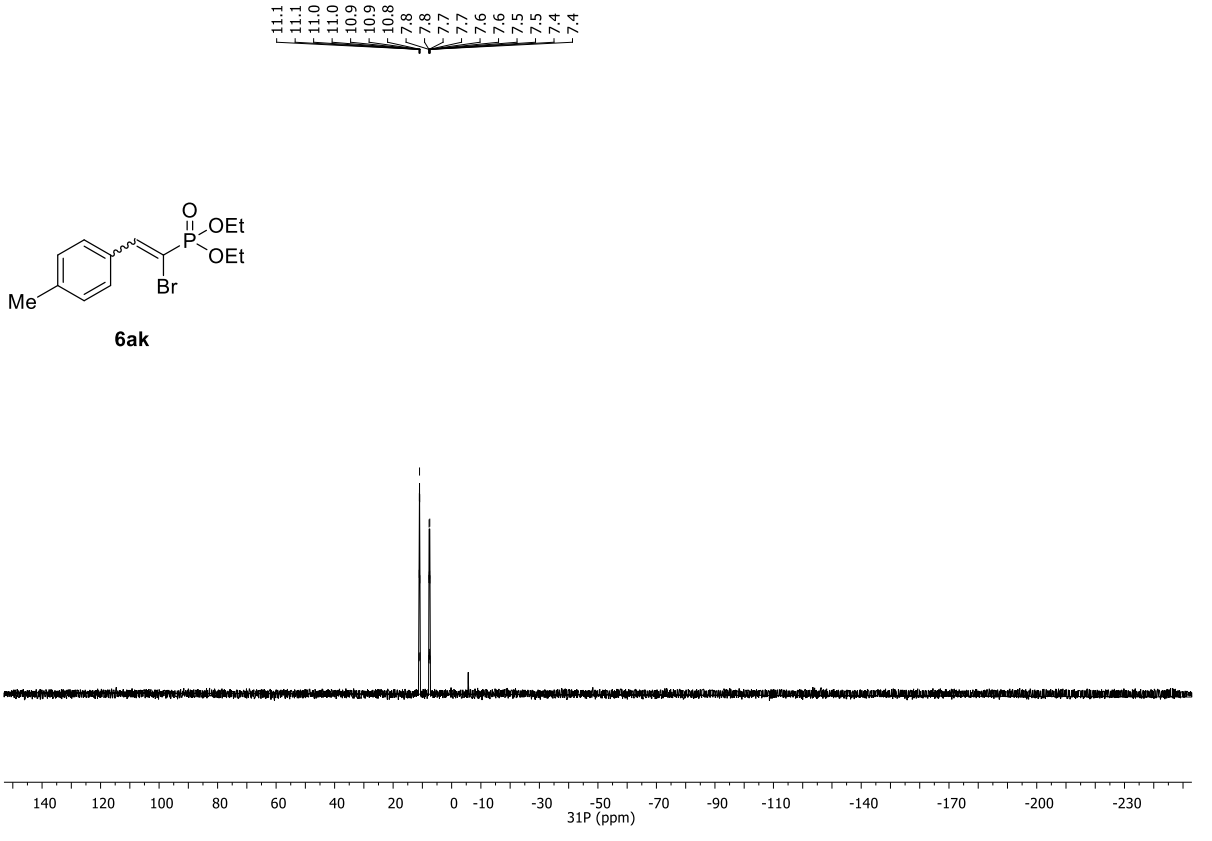


^{1}H, ^{13}C and ^{31}P NMR spectra of diethyl *P*-[1-bromo-2-(4-methylphenyl)ethenyl]phosphonate **6ak** in $CDCl_3$



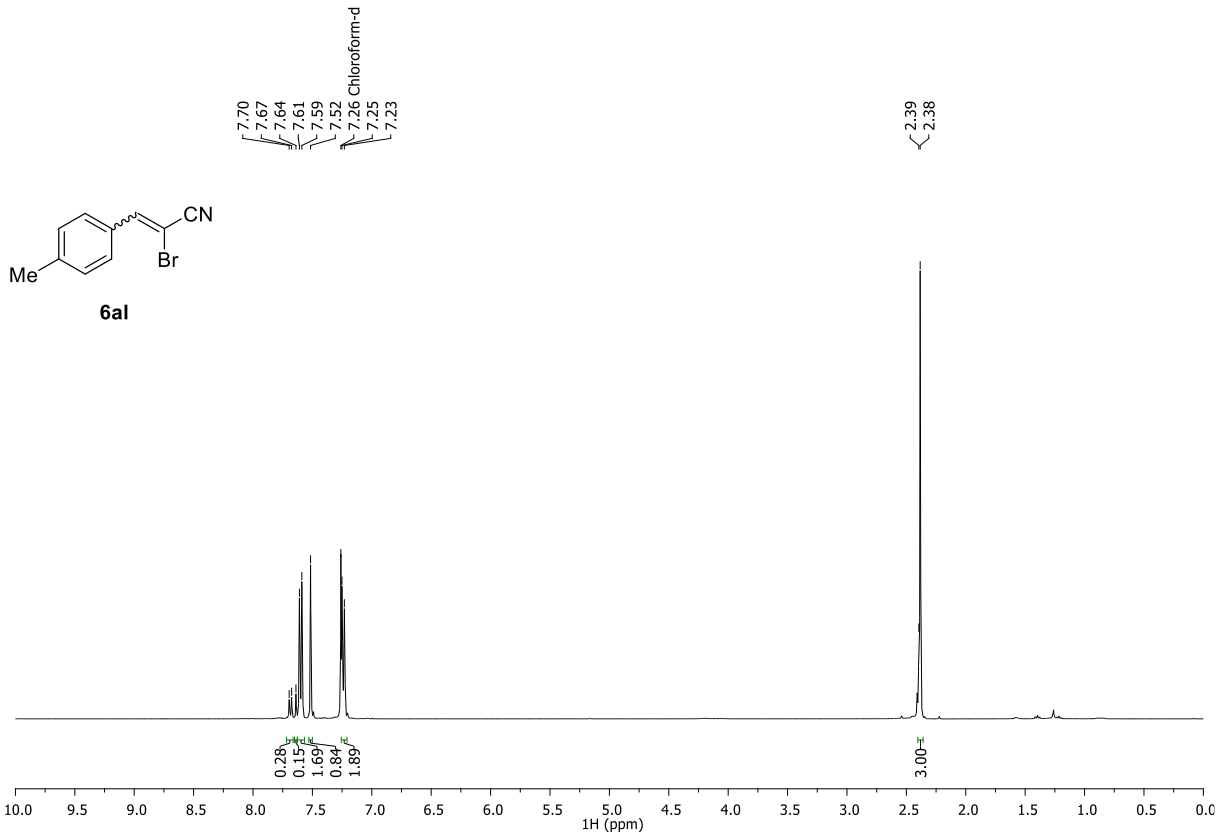

149.6
149.5
145.0
144.8
140.8
139.5
130.2
129.4
129.4
129.3
128.8
77.2 Chloroform-d
63.4
63.3
63.3
63.2
21.7
21.5
16.4
16.4
16.2
16.1
O
OEt
P
OEt
Br
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)

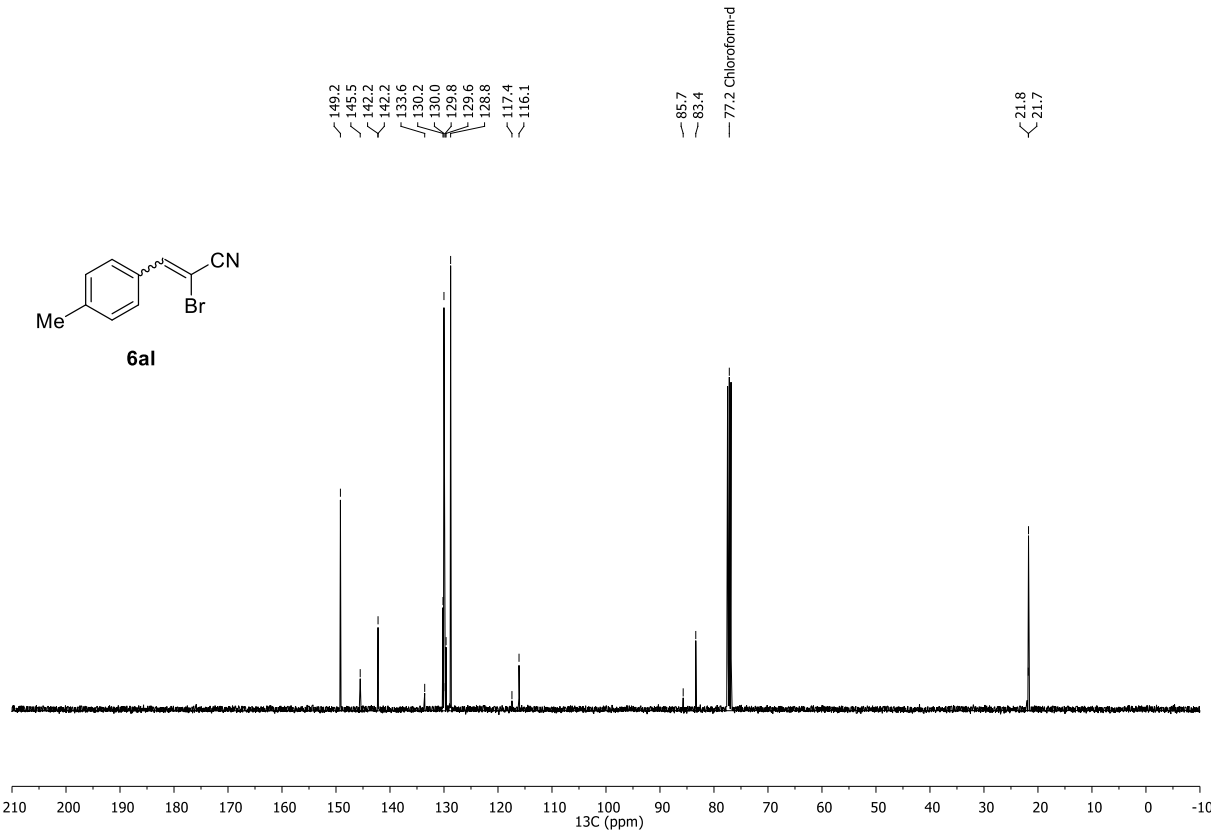
6ak


11.1
11.1
11.0
11.0
10.9
10.9
10.8
7.8
7.8
7.7
7.7
7.6
7.6
7.5
7.5
7.4
7.4
O
OEt
P
OEt
Br
Me
140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -110 -140 -170 -200 -230
31P (ppm)

6ak

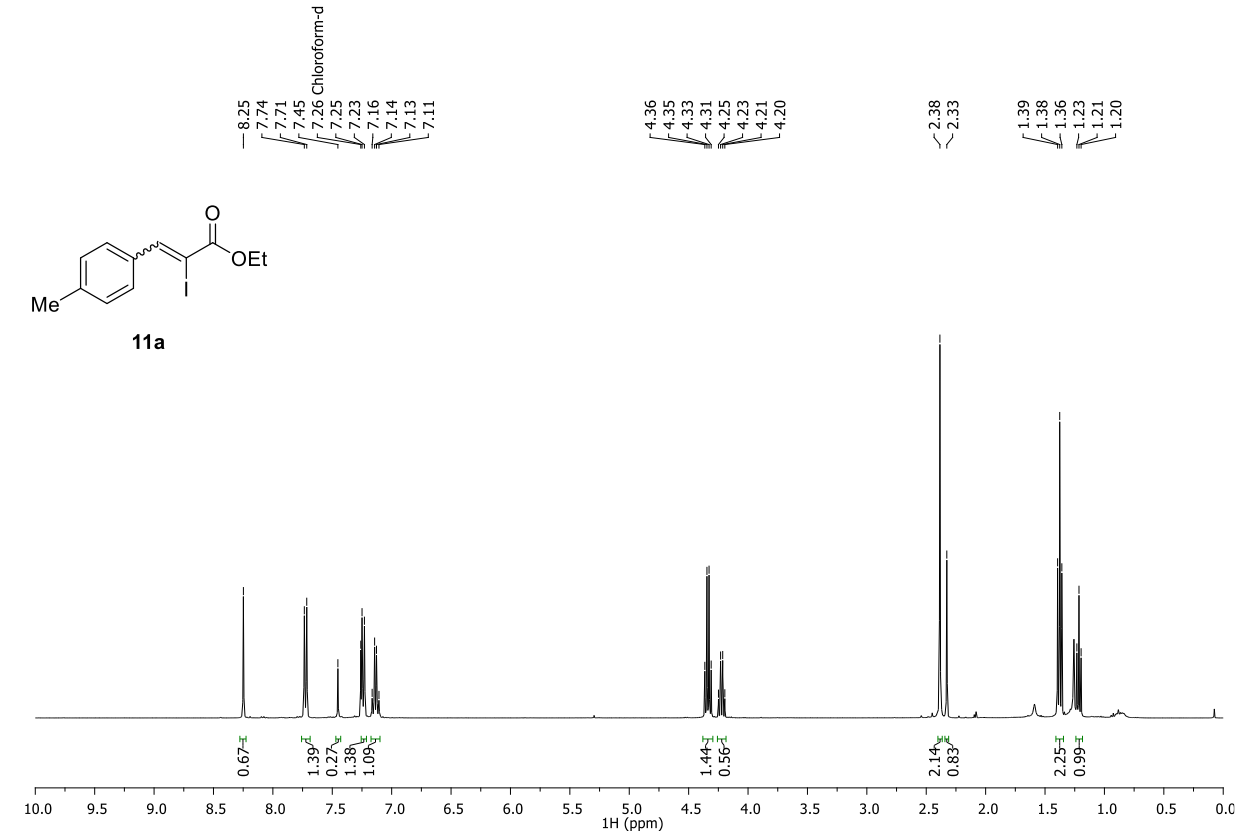
^{1}H and ^{13}C NMR spectra of 2-bromo-3-(4-methylphenyl)-2-propenenitrile **6al** in $CDCl_3$

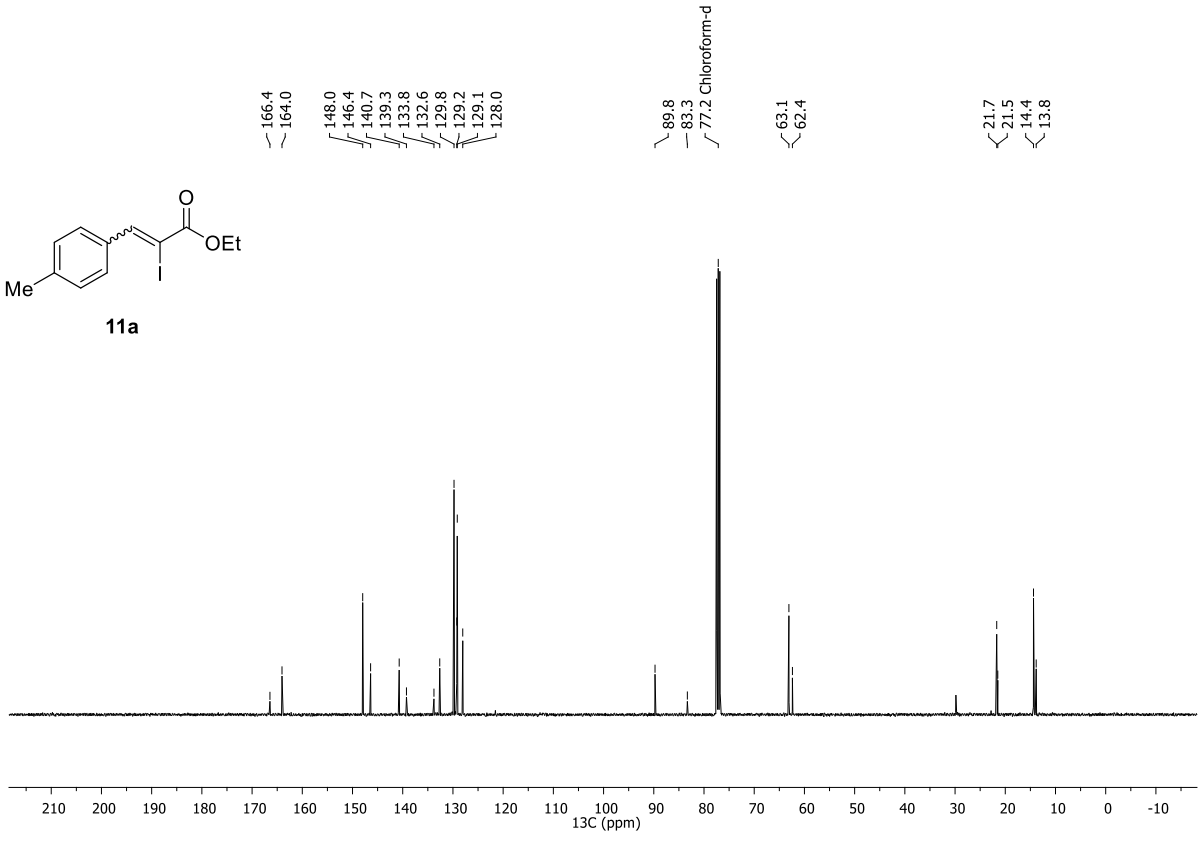




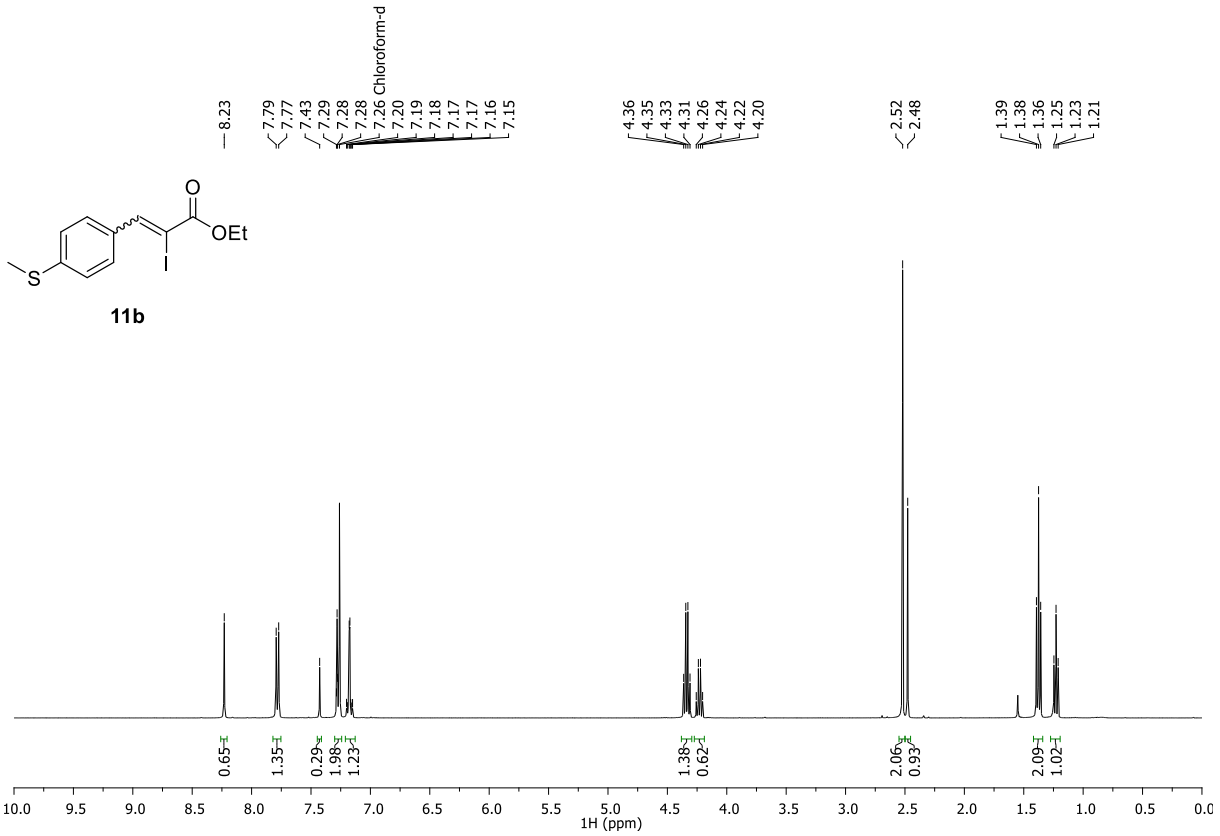
NMR spectra of iodoalkenes

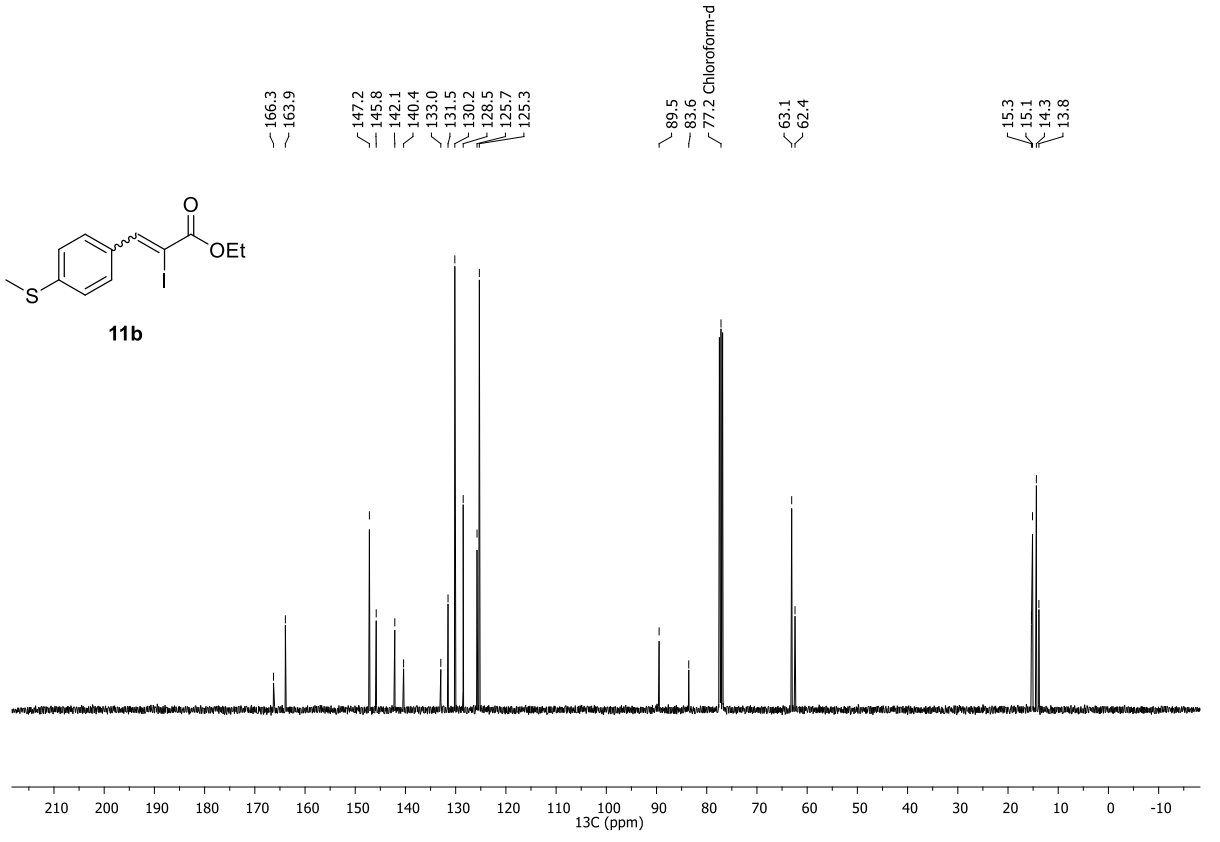
^{1}H and ^{13}C NMR spectra of ethyl-2-iodo-3-(4-methylphenyl)-2-propenoate **11a** in $CDCl_3$



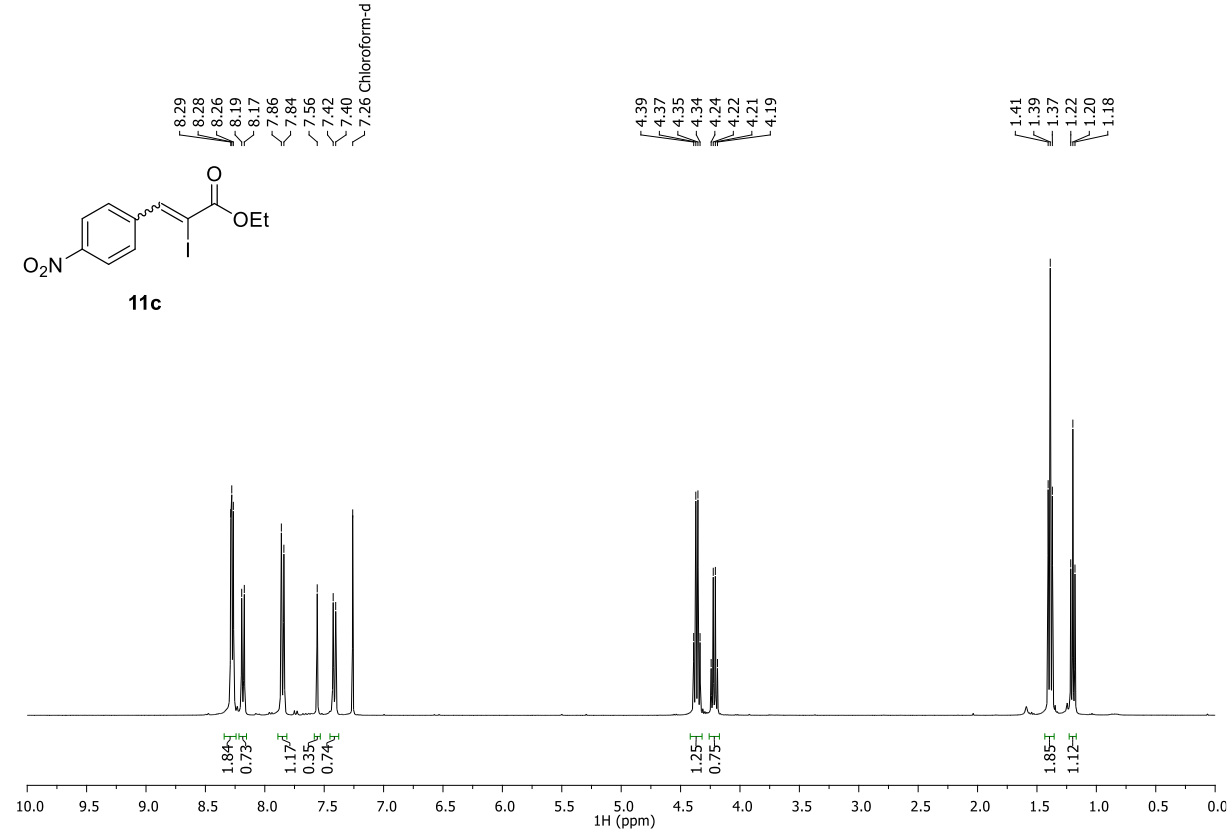


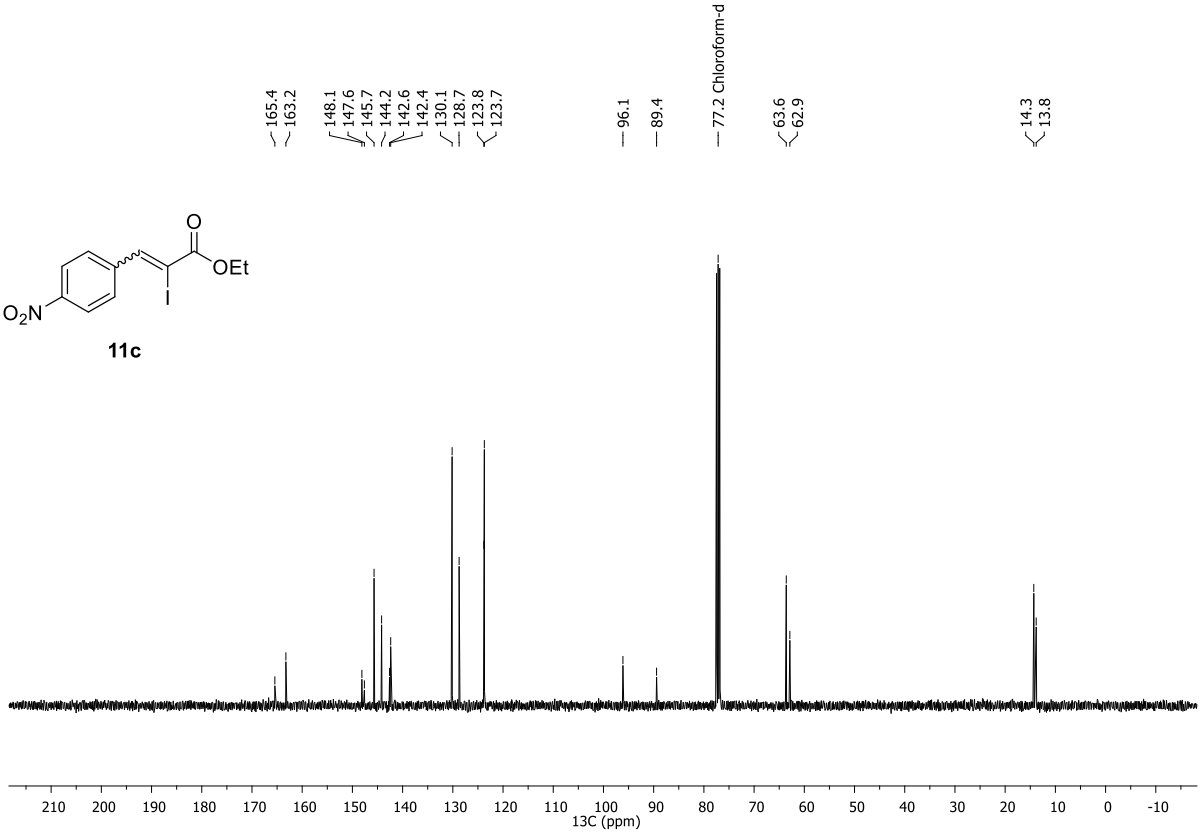
^{1}H and ^{13}C NMR spectra of ethyl 2-iodo-3-(4-(methylthio)phenyl)acrylate **11b** in $CDCl_3$



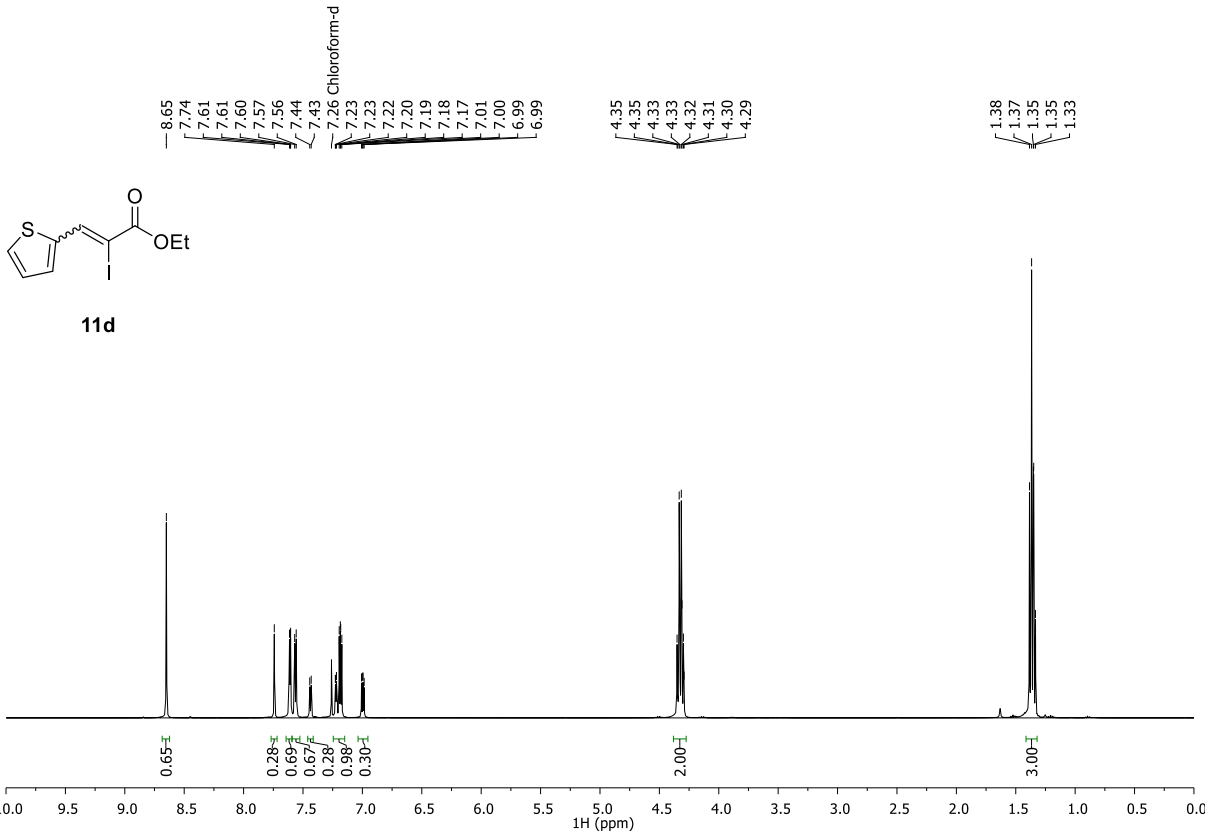


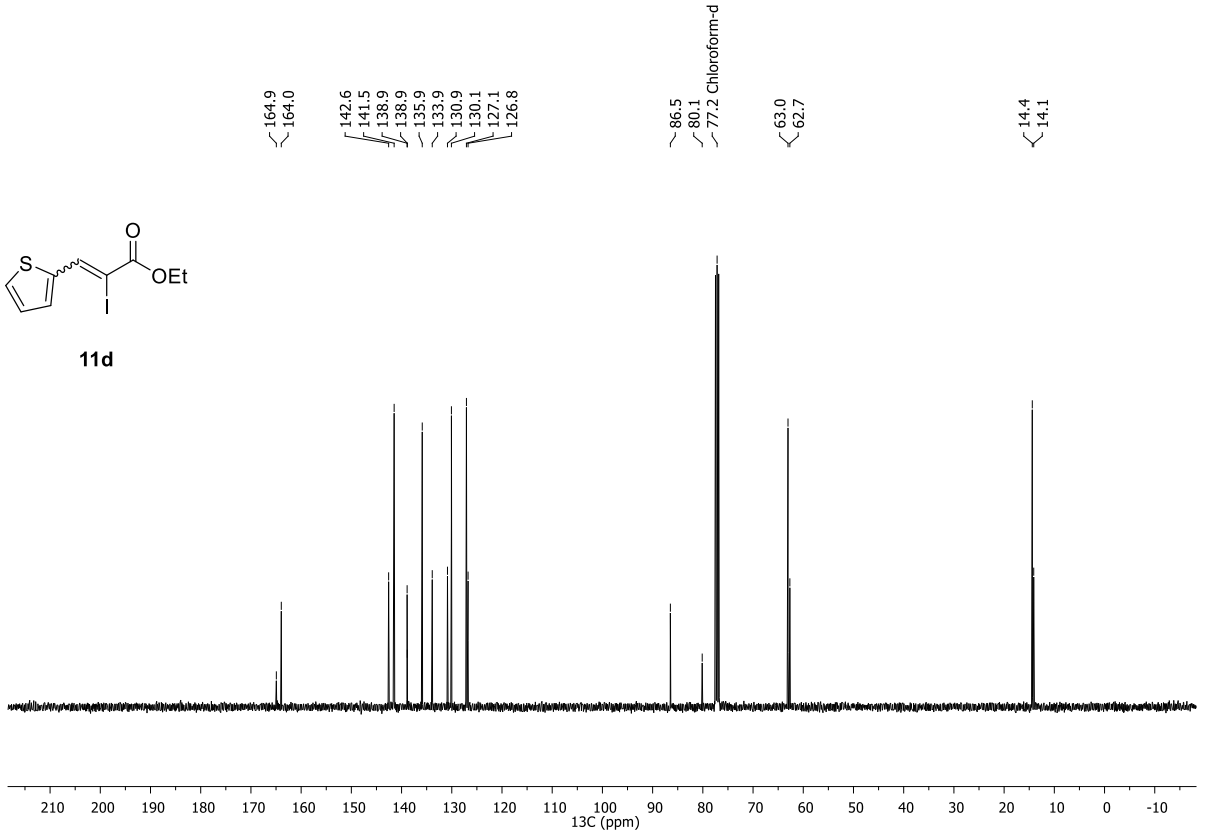
^{1}H and ^{13}C NMR spectra of ethyl 2-iodo-3-(4-nitrophenyl)acrylate **11c** in $CDCl_3$



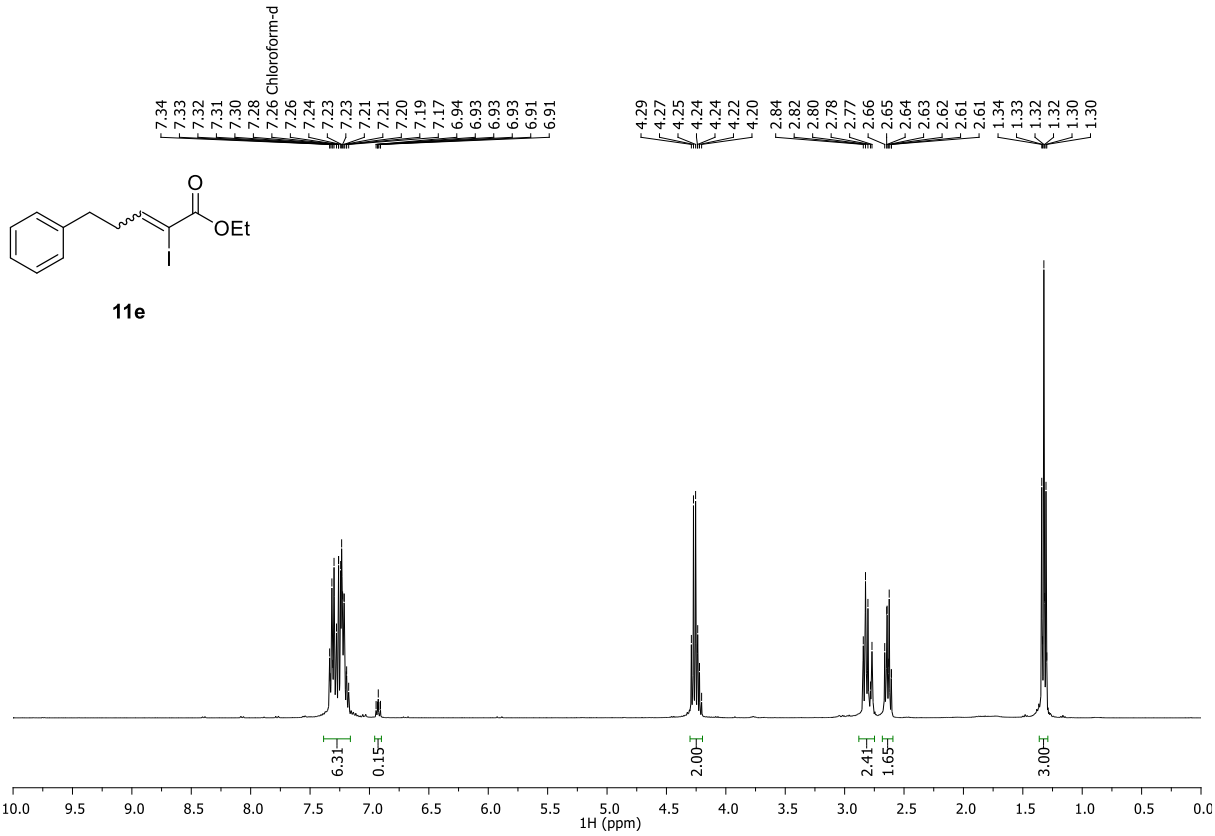


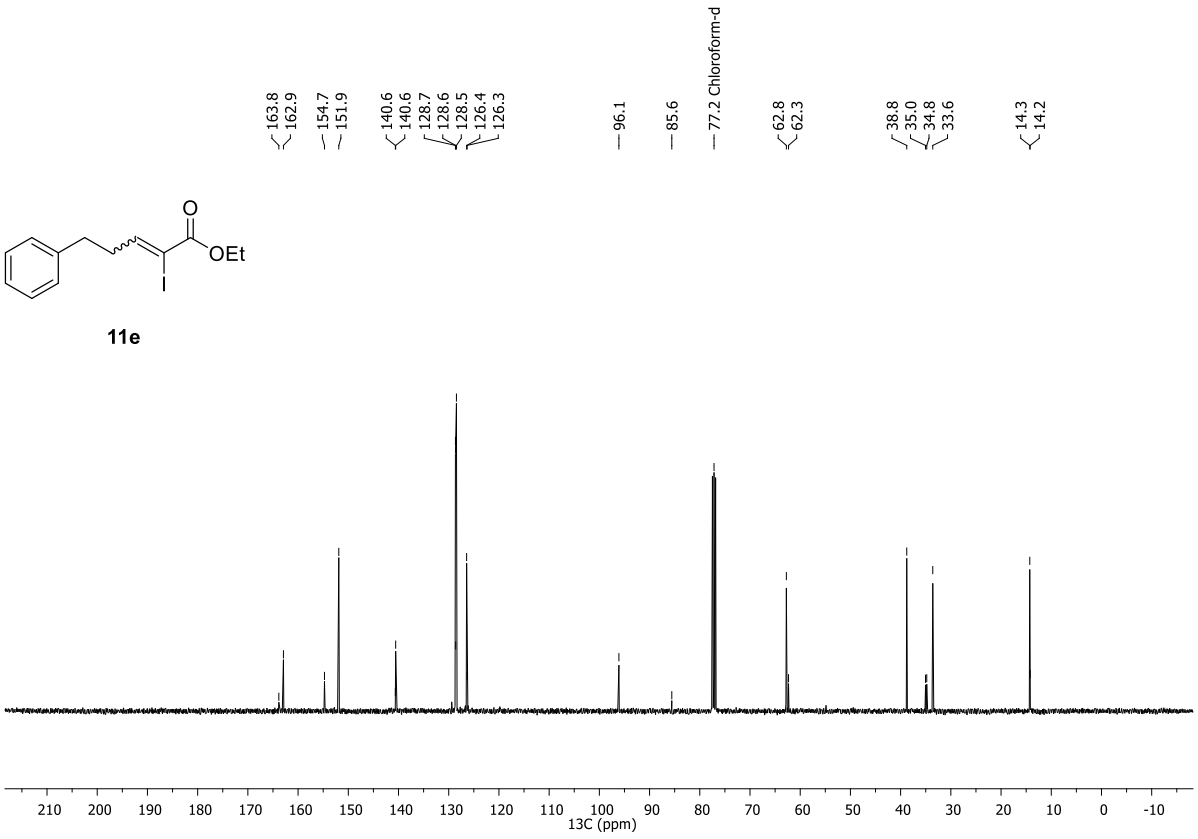
^{1}H and ^{13}C NMR spectra of ethyl 2-iodo-3-(2-thienyl)-2-propenoate **11d** in $CDCl_3$





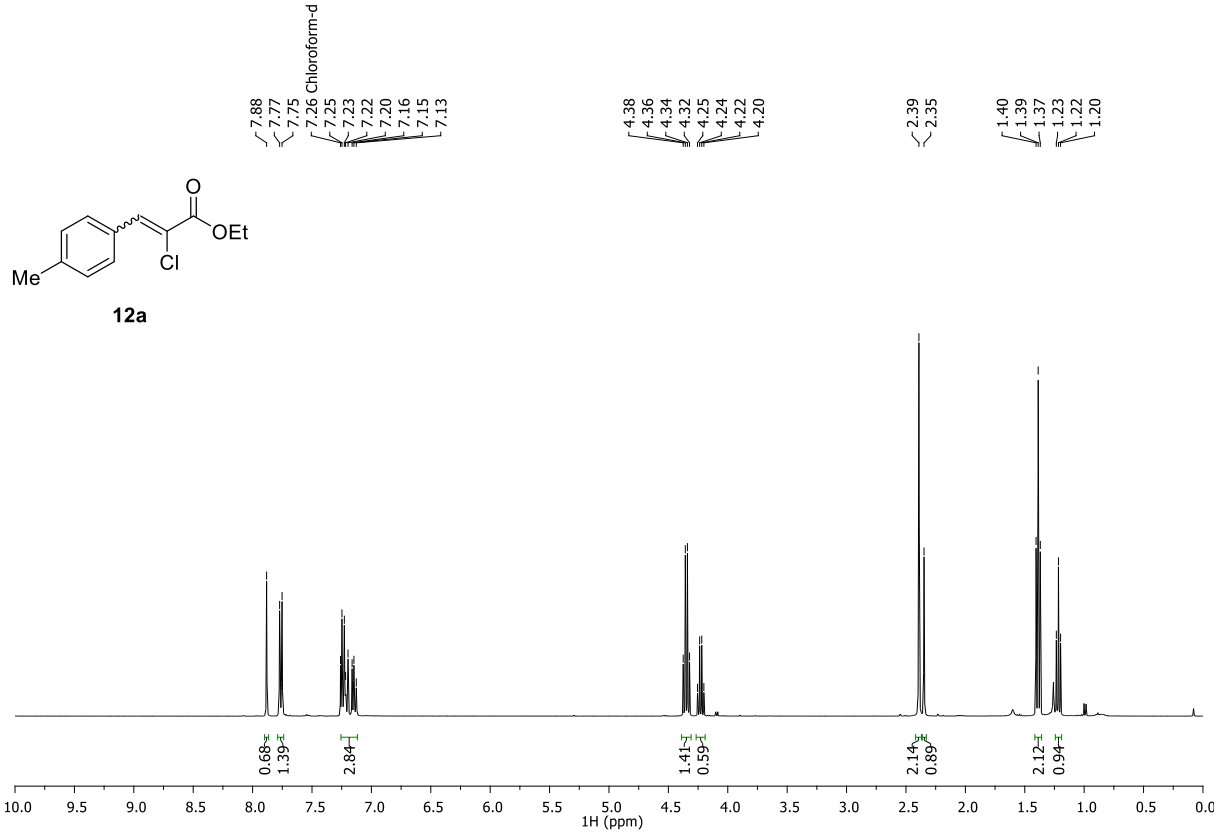
^{1}H and ^{13}C NMR spectra of ethyl 2-iodo-5-phenylpent-2-enoate **11e** in $CDCl_3$

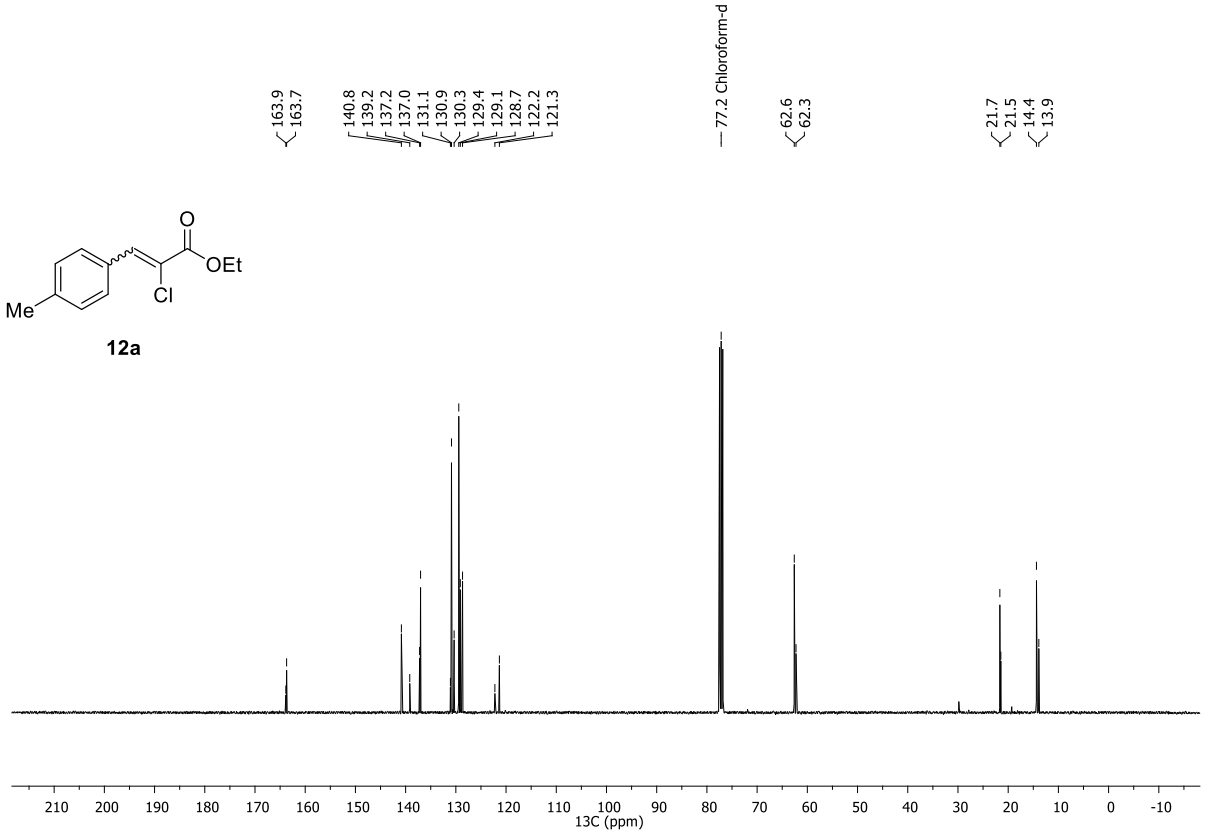




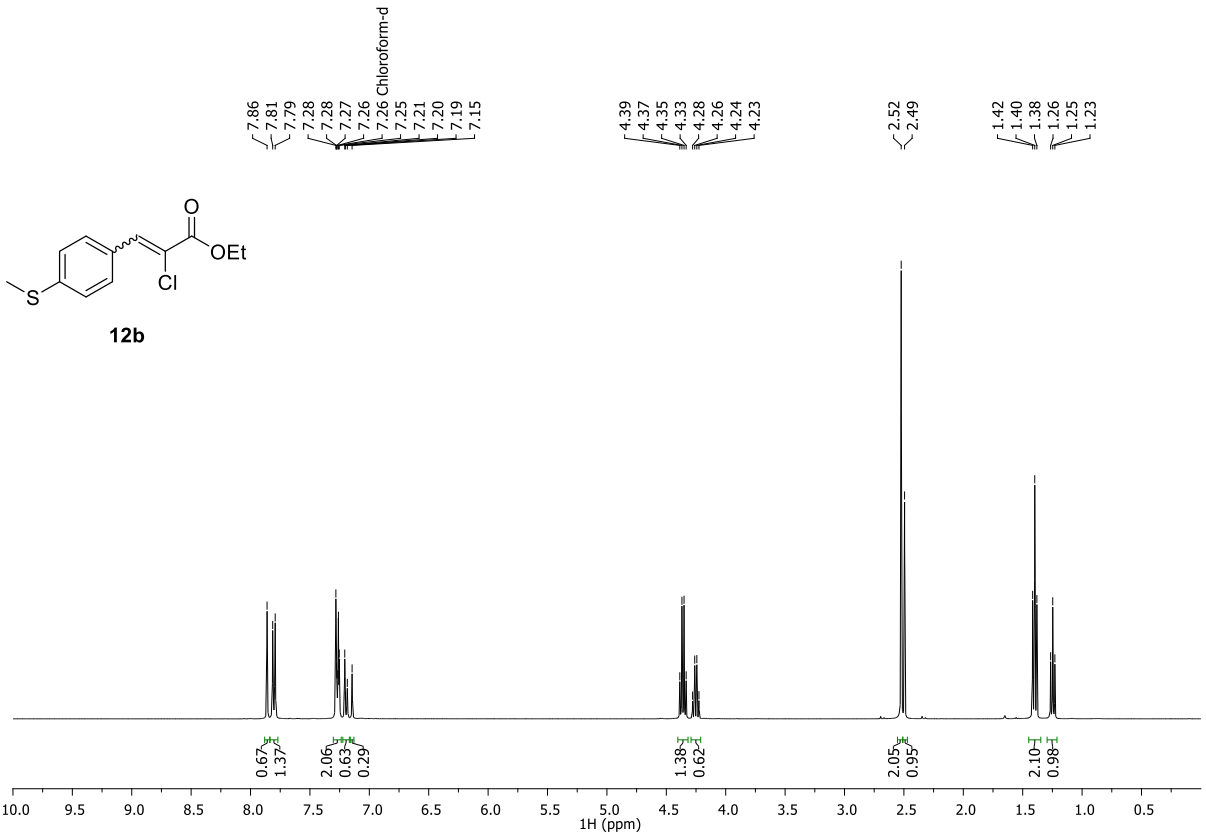
NMR spectra of chloroalkenes

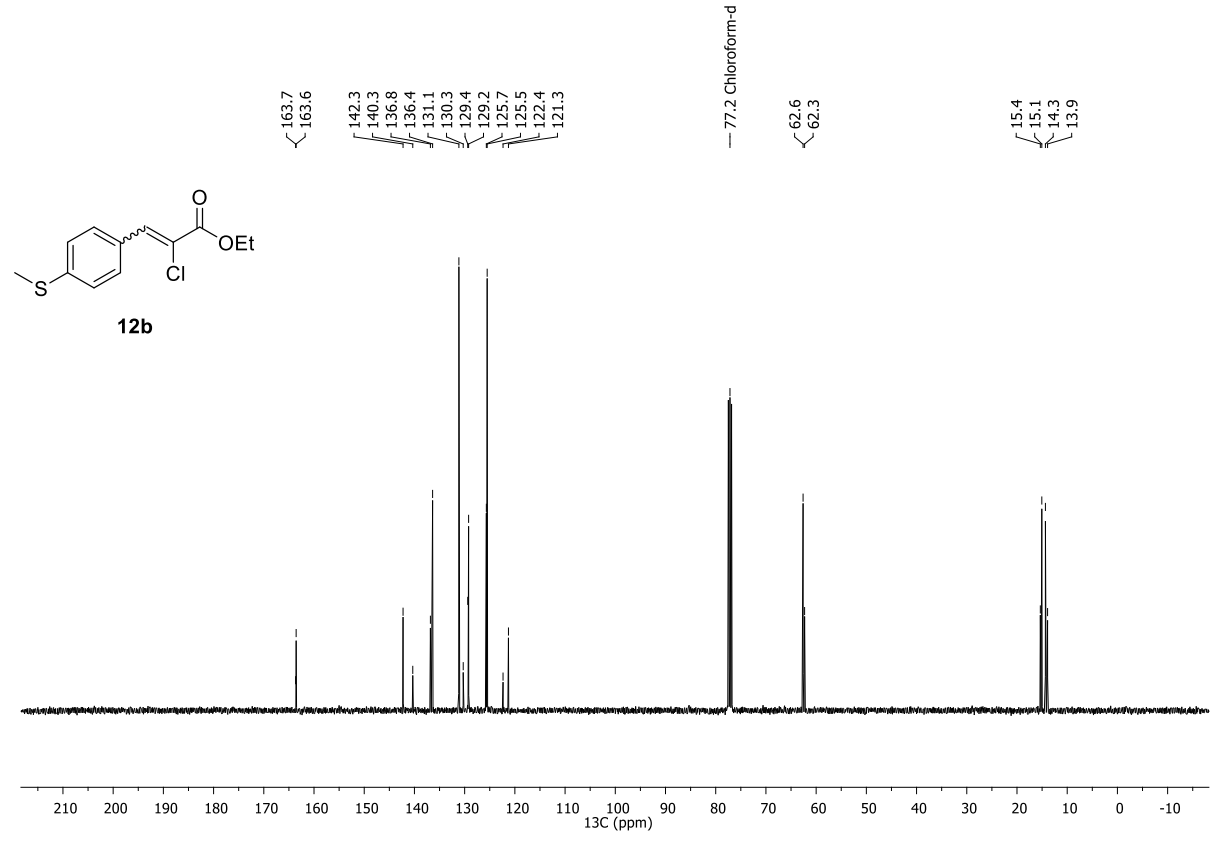
^{1}H and ^{13}C NMR spectra of ethyl-2-chloro-3-(4-methylphenyl)-2-propenoate **12a** in $CDCl_3$



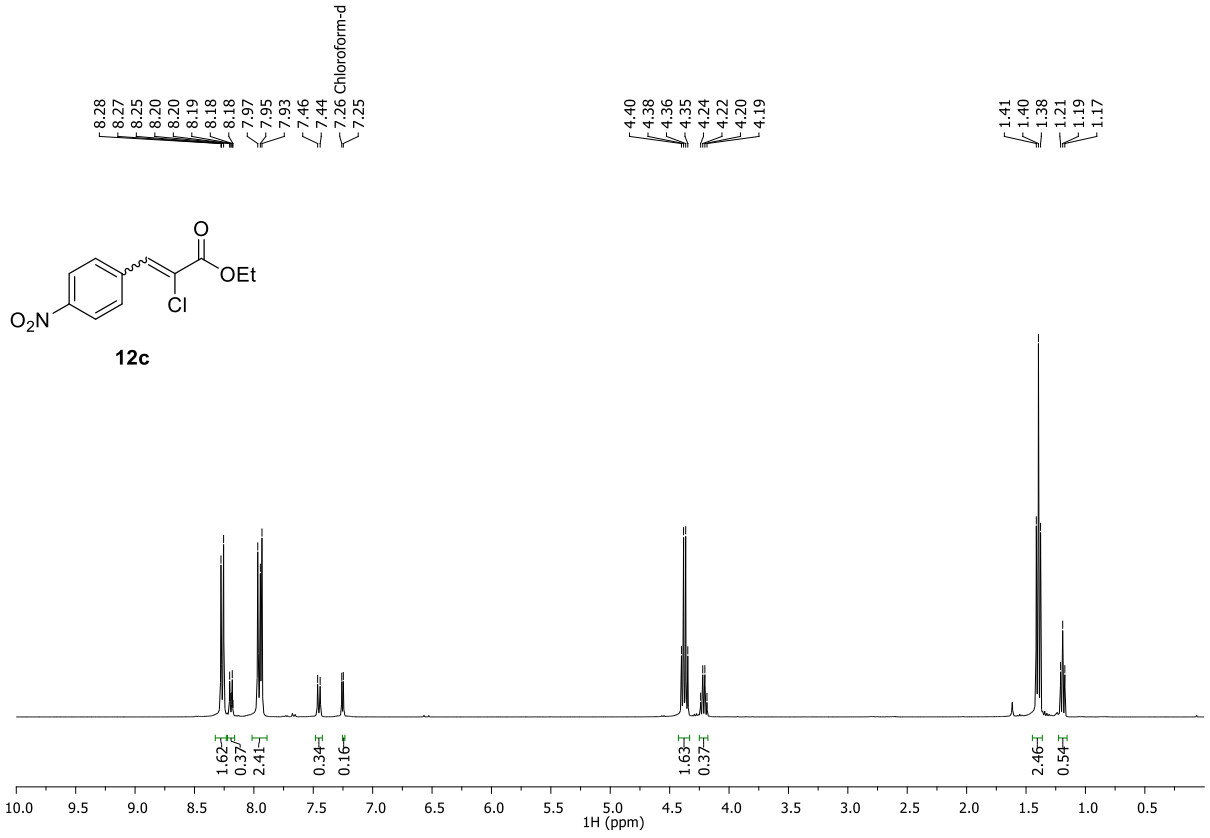


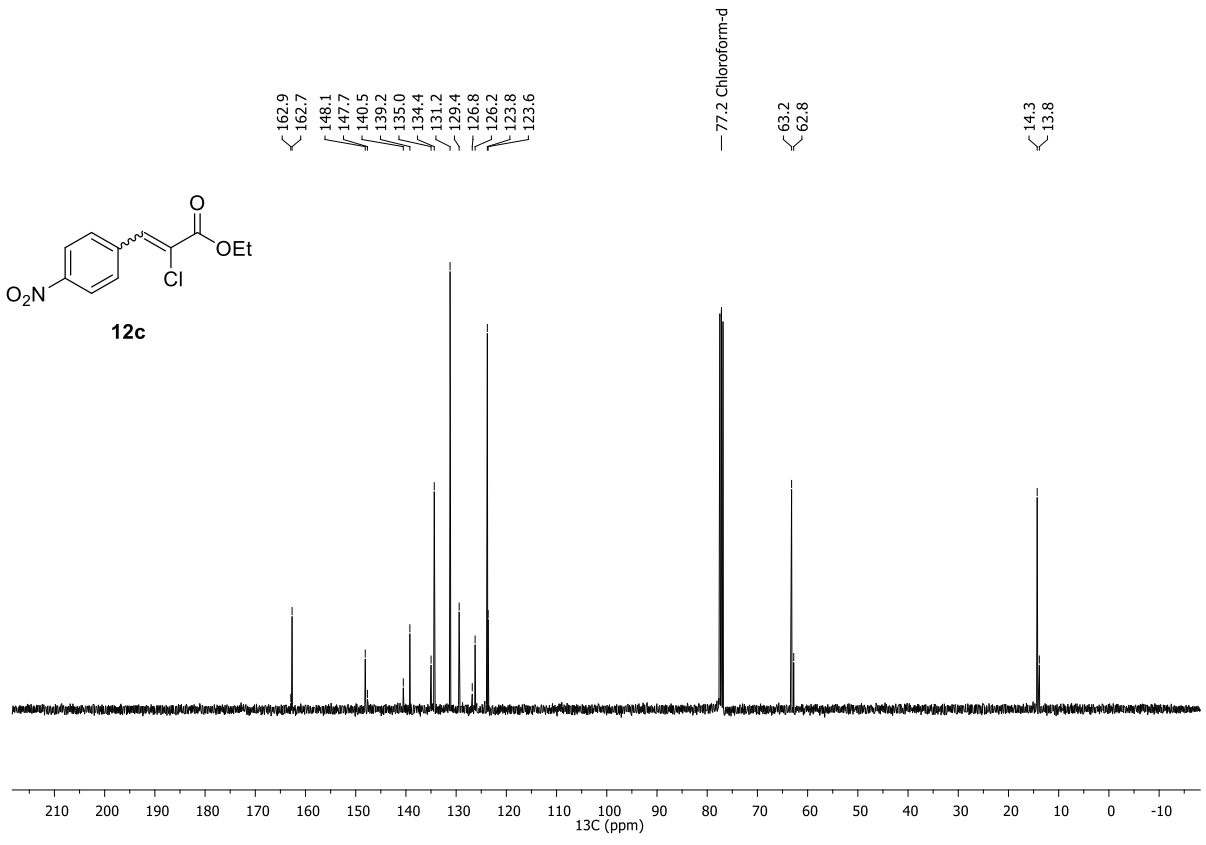
^{1}H and ^{13}C NMR spectra of ethyl 2-chloro-3-(4-(methylthio)phenyl)acrylate **12b** in $CDCl_3$



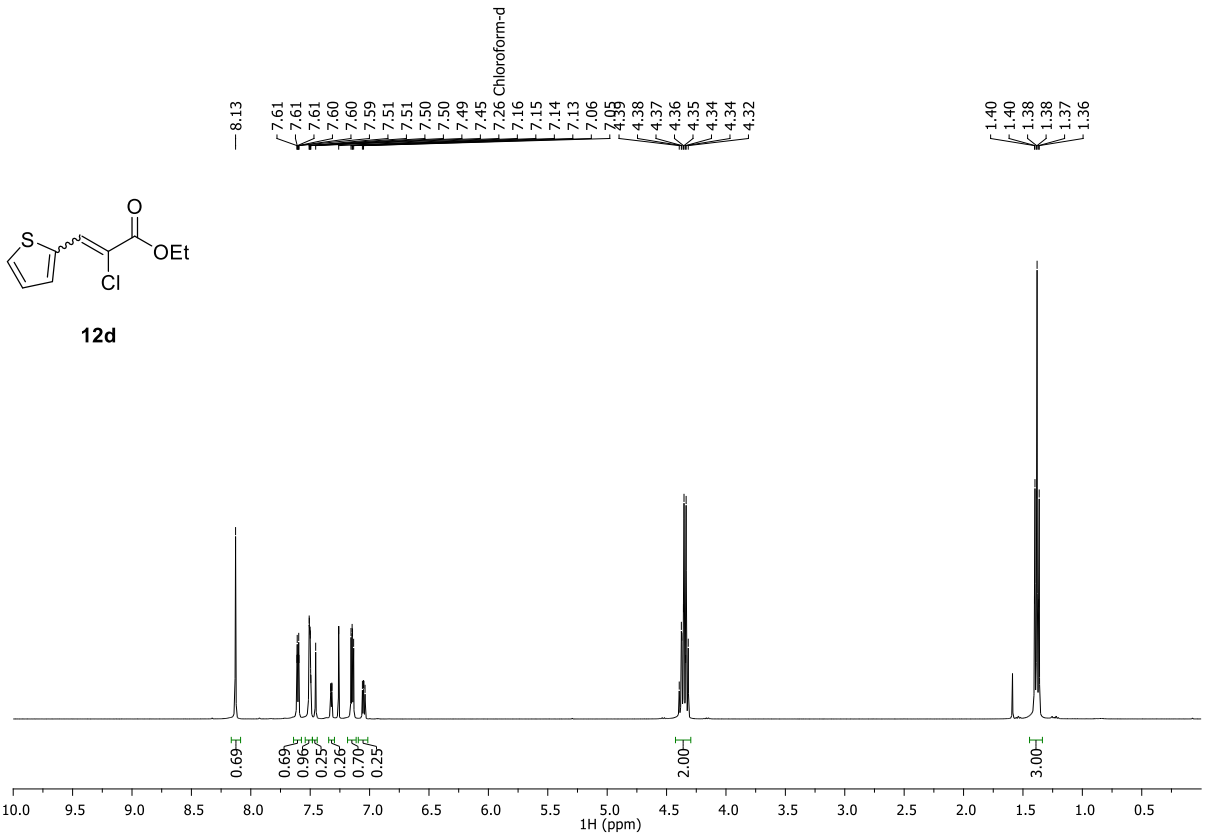


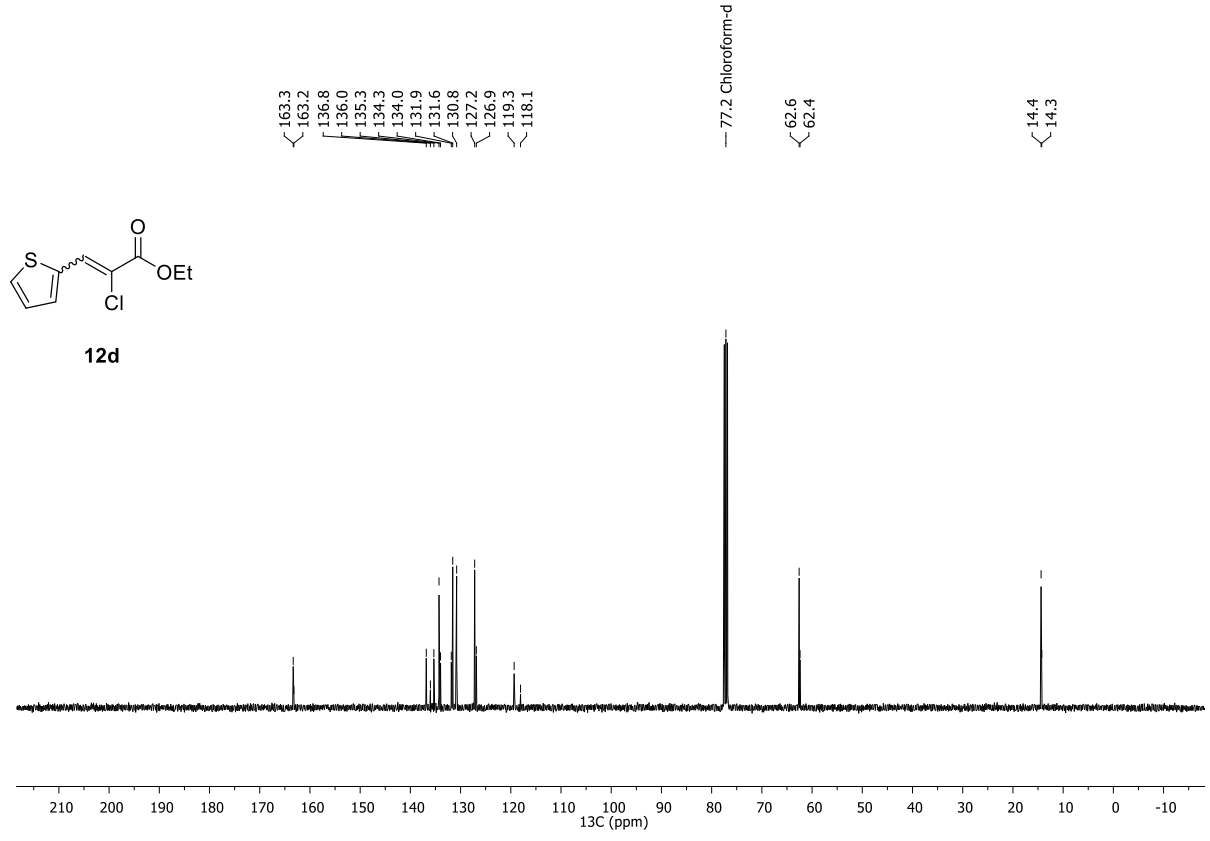
^{1}H and ^{13}C NMR spectra of ethyl 2-chloro-3-(4-nitrophenyl)acrylate **12c** in $CDCl_3$



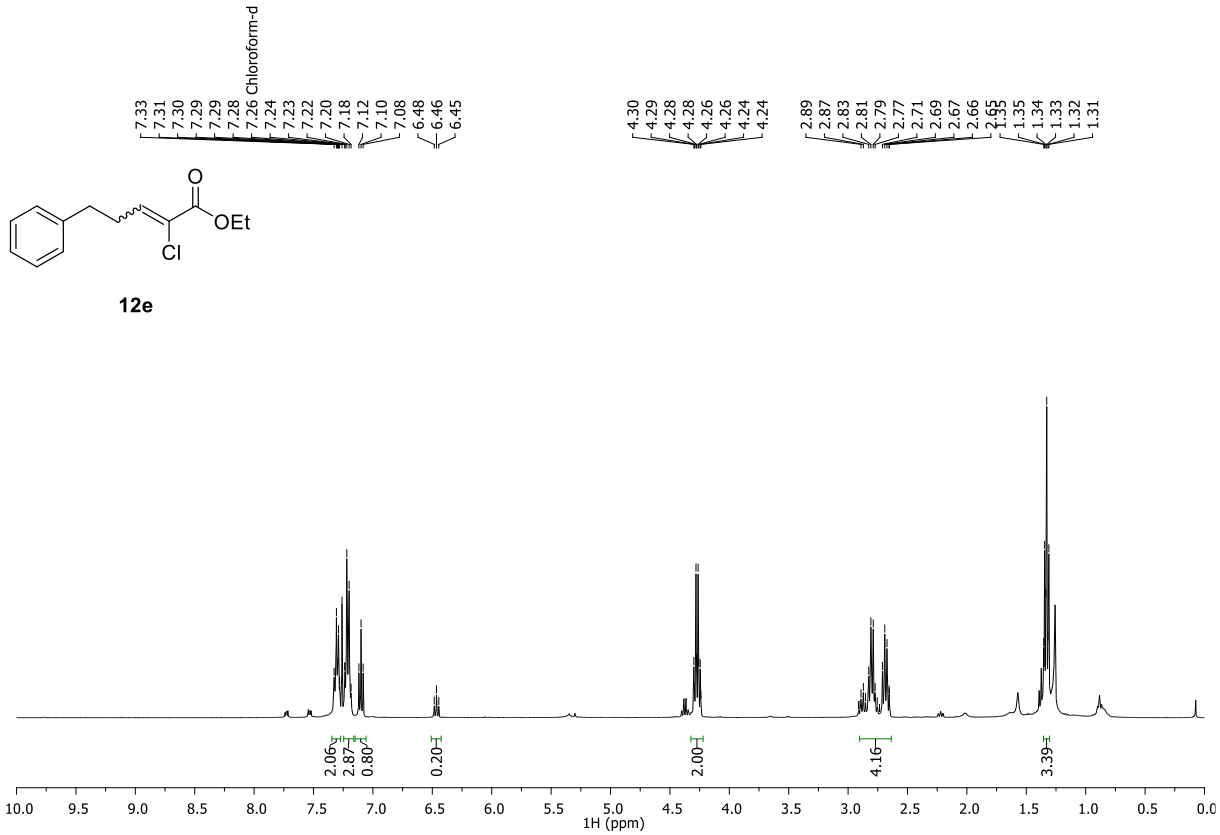


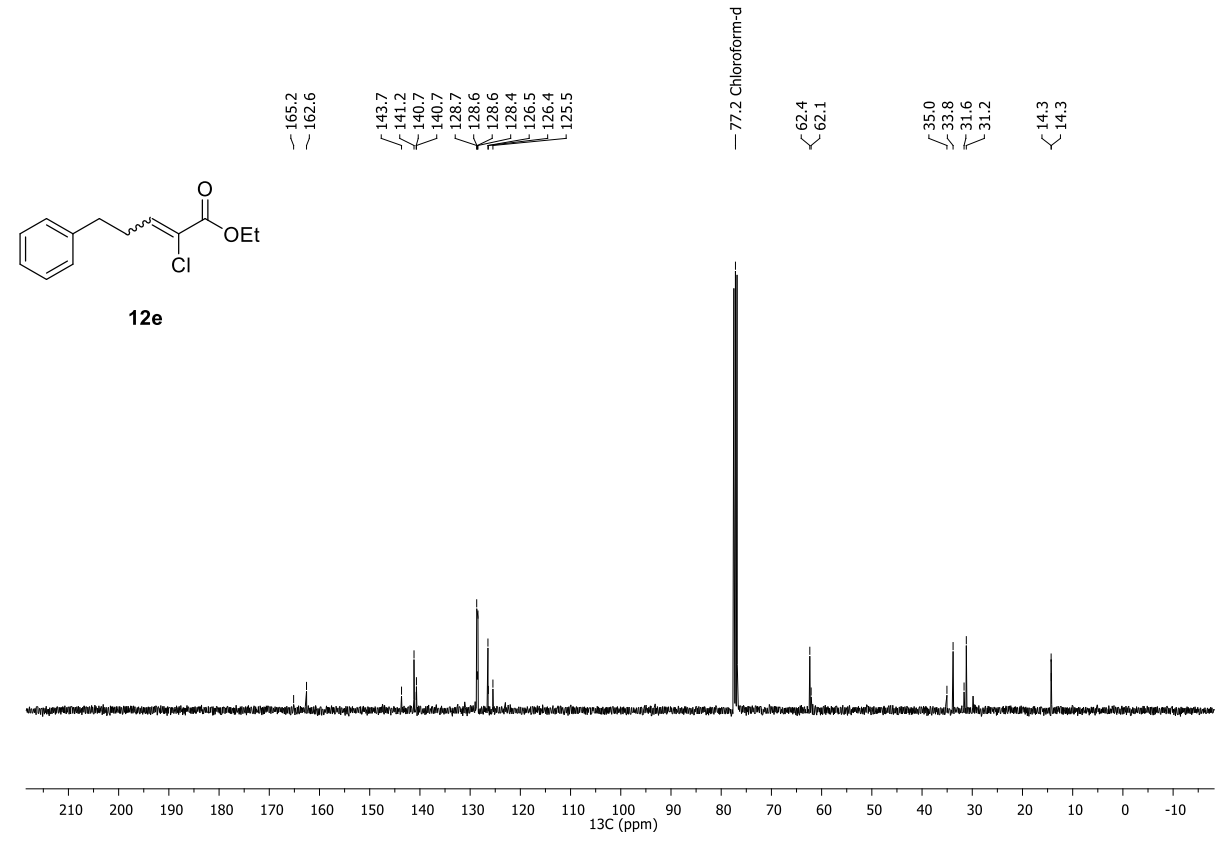
^{1}H and ^{13}C NMR spectra of ethyl 2-chloro-3-(2-thienyl)-2-propenoate **12d** in $CDCl_3$





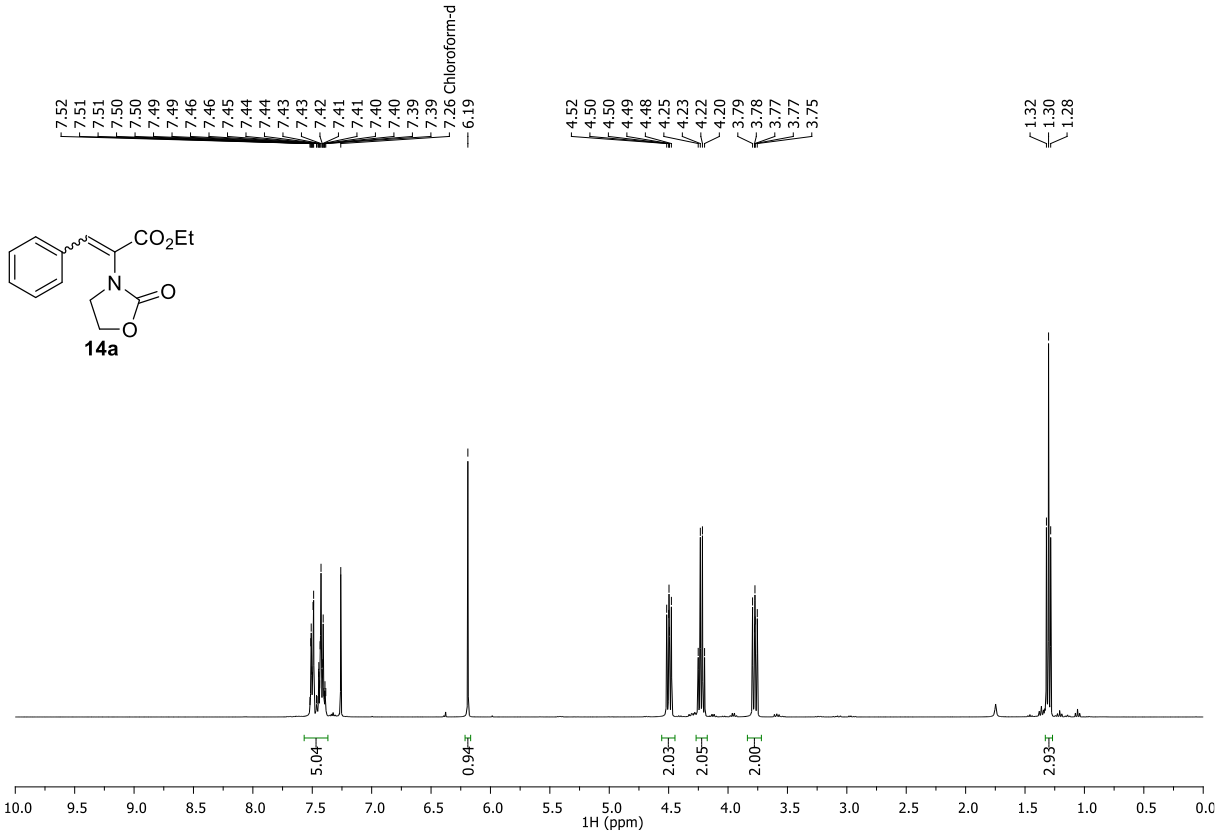
^{1}H and ^{13}C NMR spectra of ethyl 2-iodo-5-phenylpent-2-enoate **12e** in $CDCl_3$

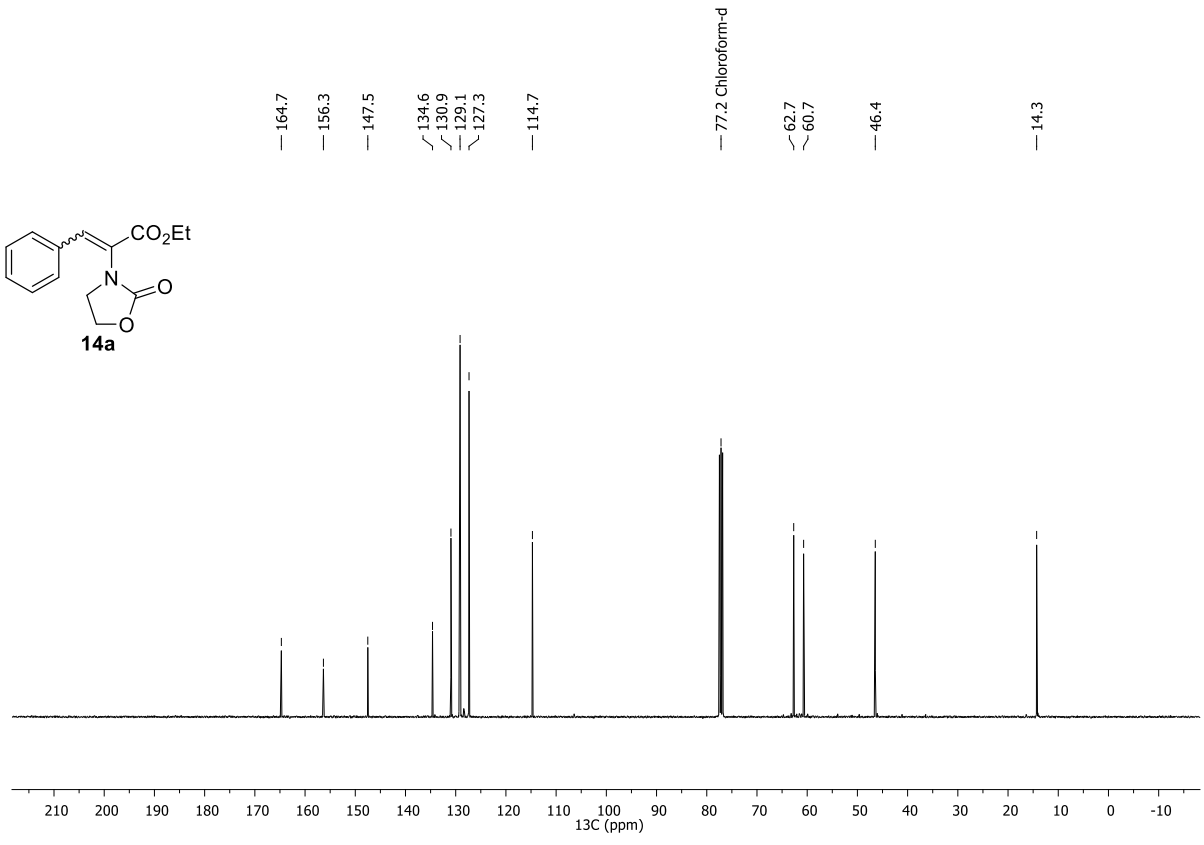




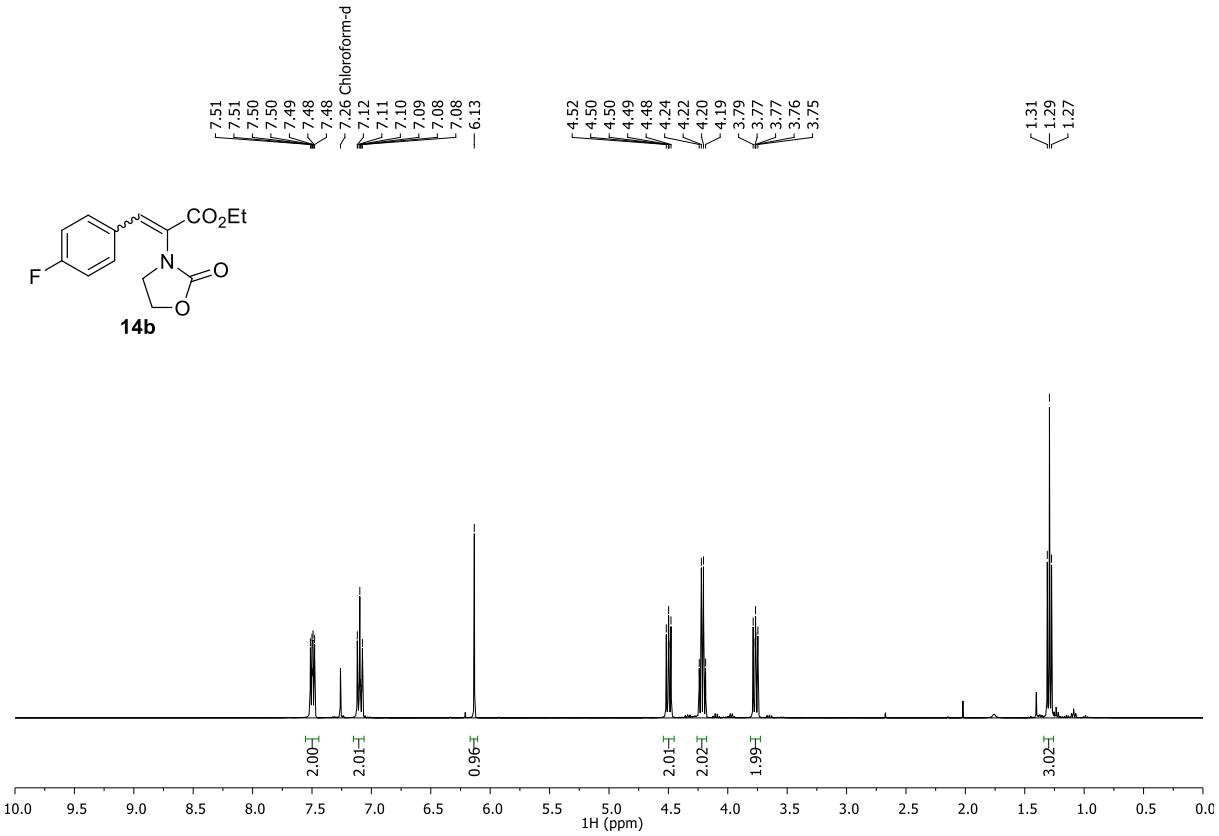
NMR spectra of products of Ullman type coupling

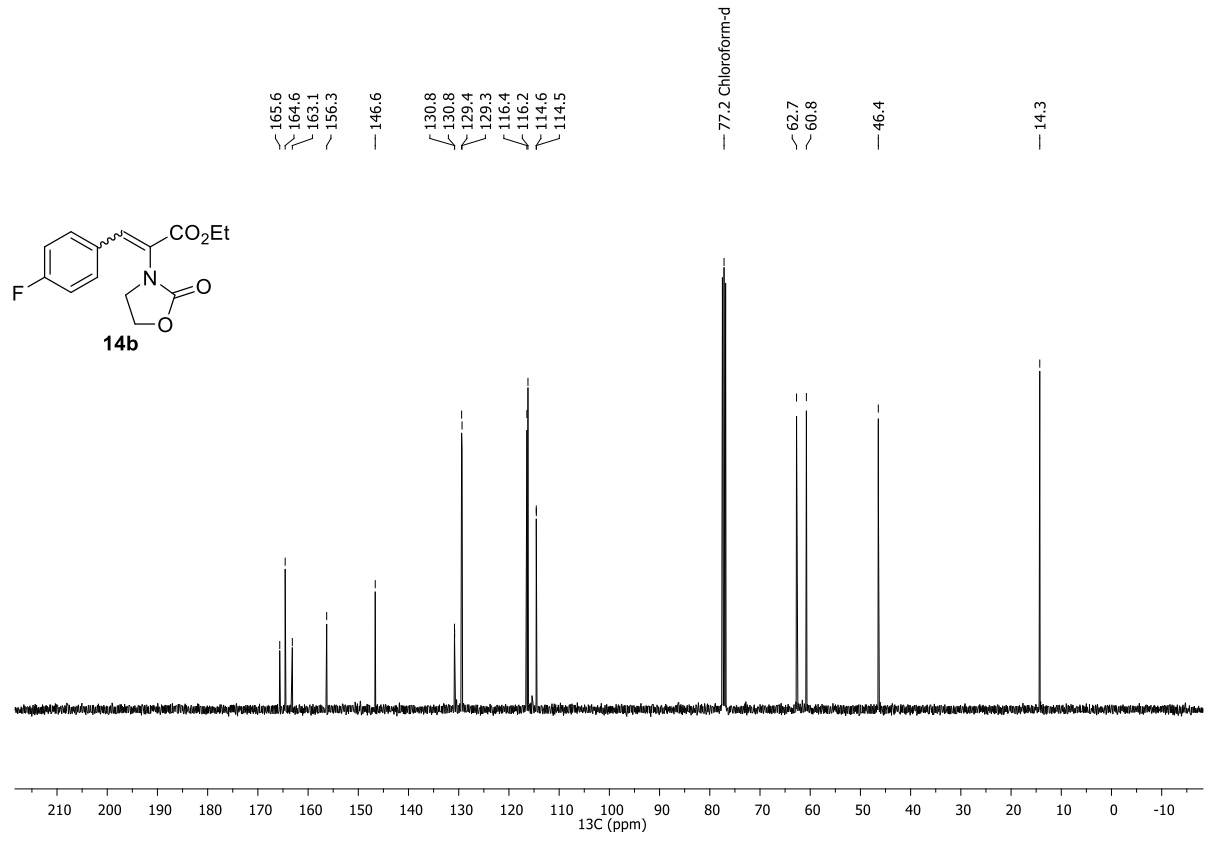
^{1}H and ^{13}C NMR spectra of ethyl 2-(2-oxooxazolidin-3-yl)-3-phenylpropanoate **14a** in $CDCl_3$

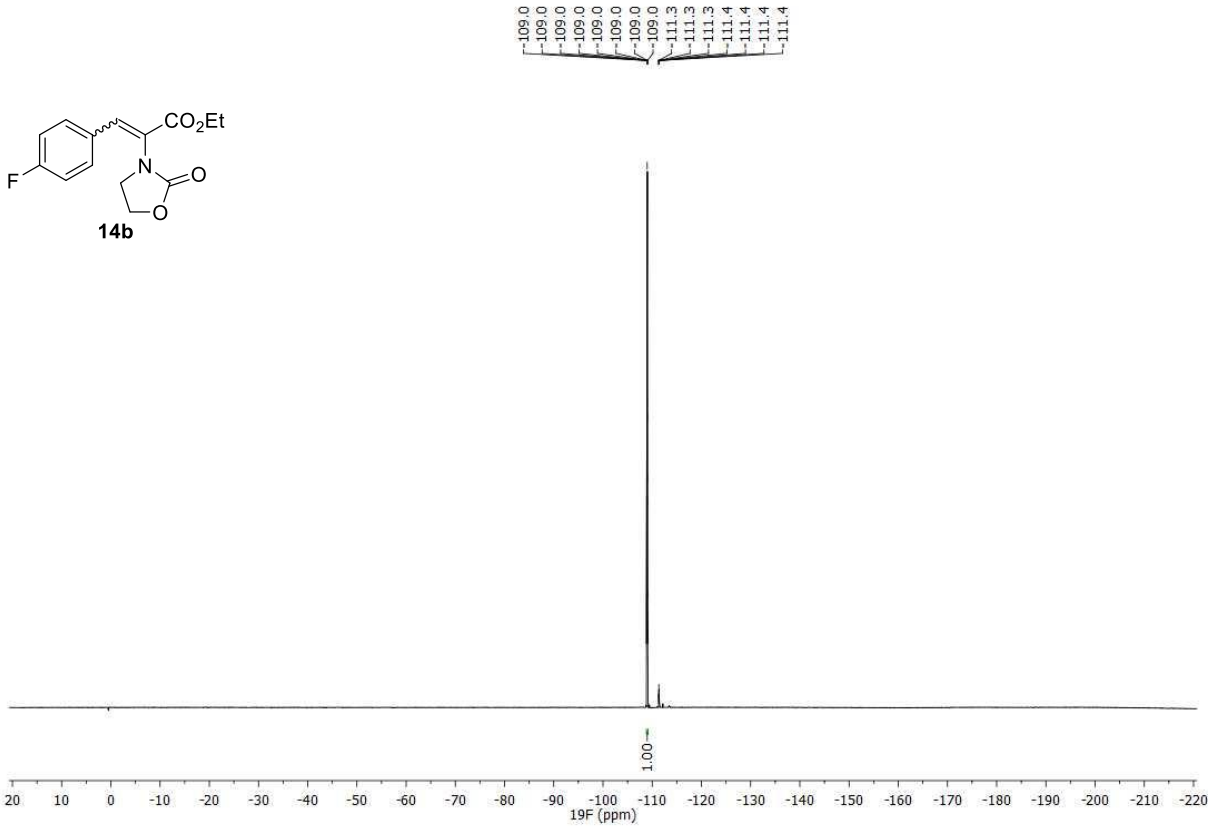


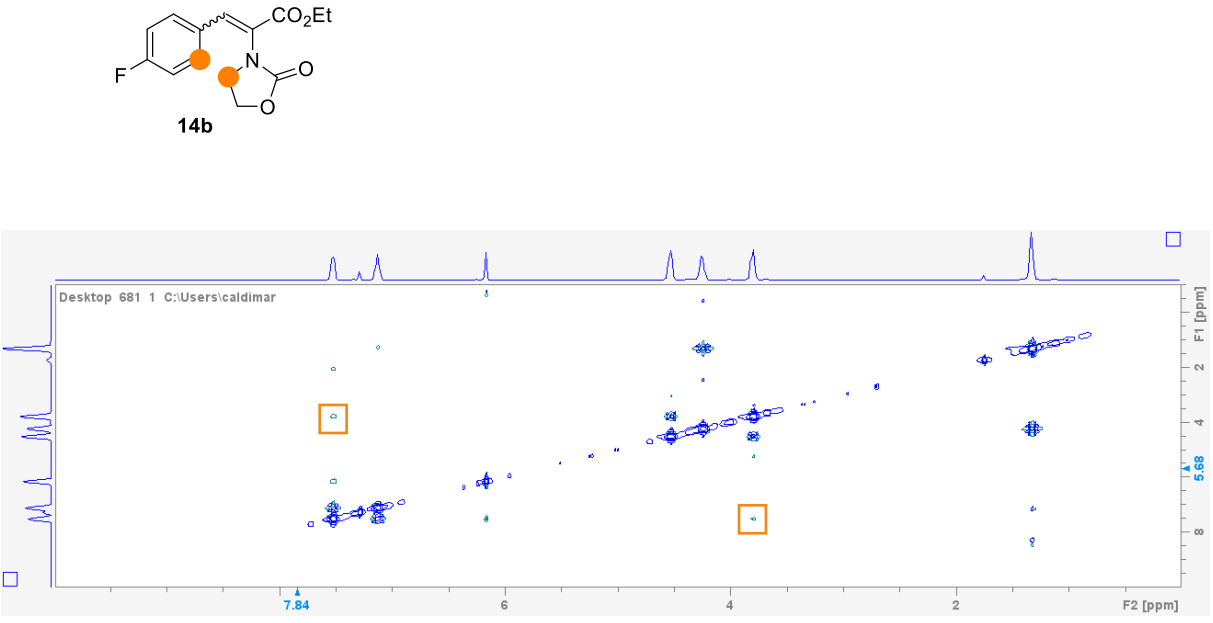


^{1}H, ^{13}C and ^{19}F NMR spectra of ethyl 3-(4-fluorophenyl)-2-(2-oxooxazolidin-3-yl)propanoate **14b** in $CDCl_3$

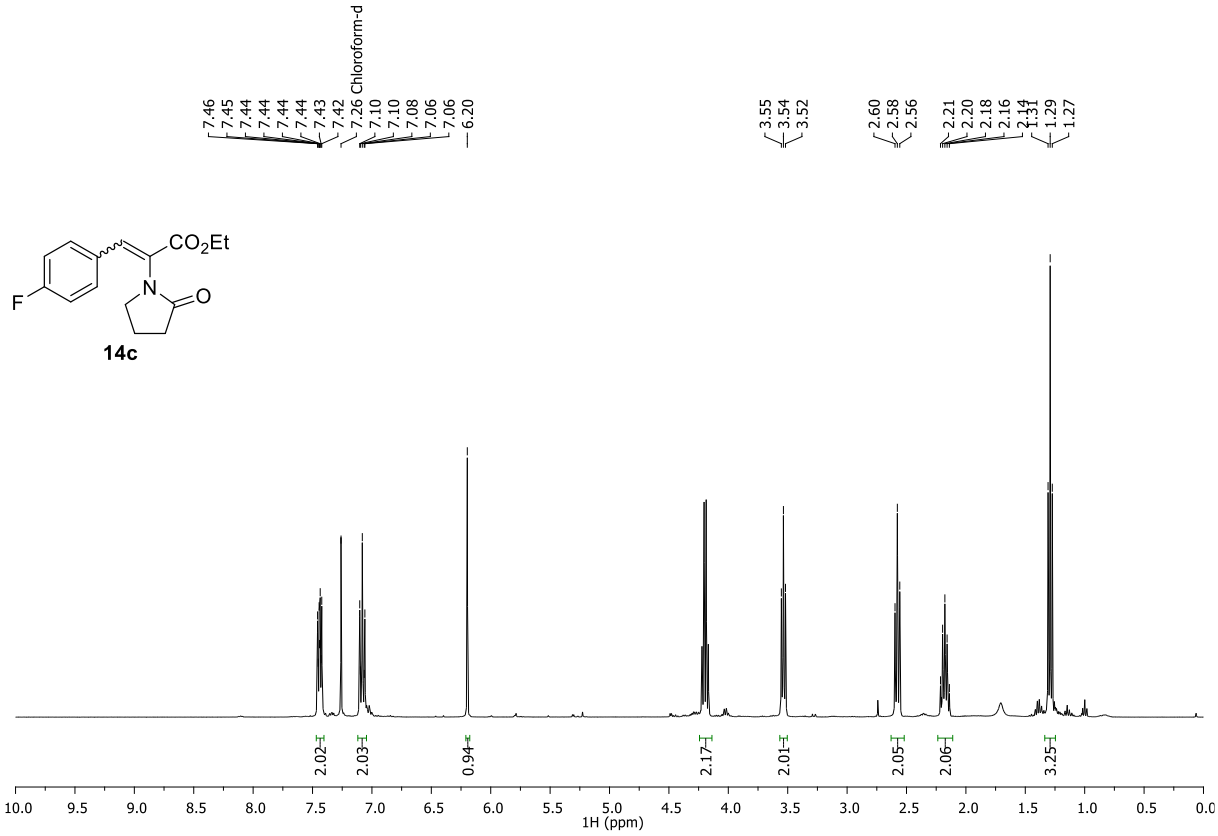


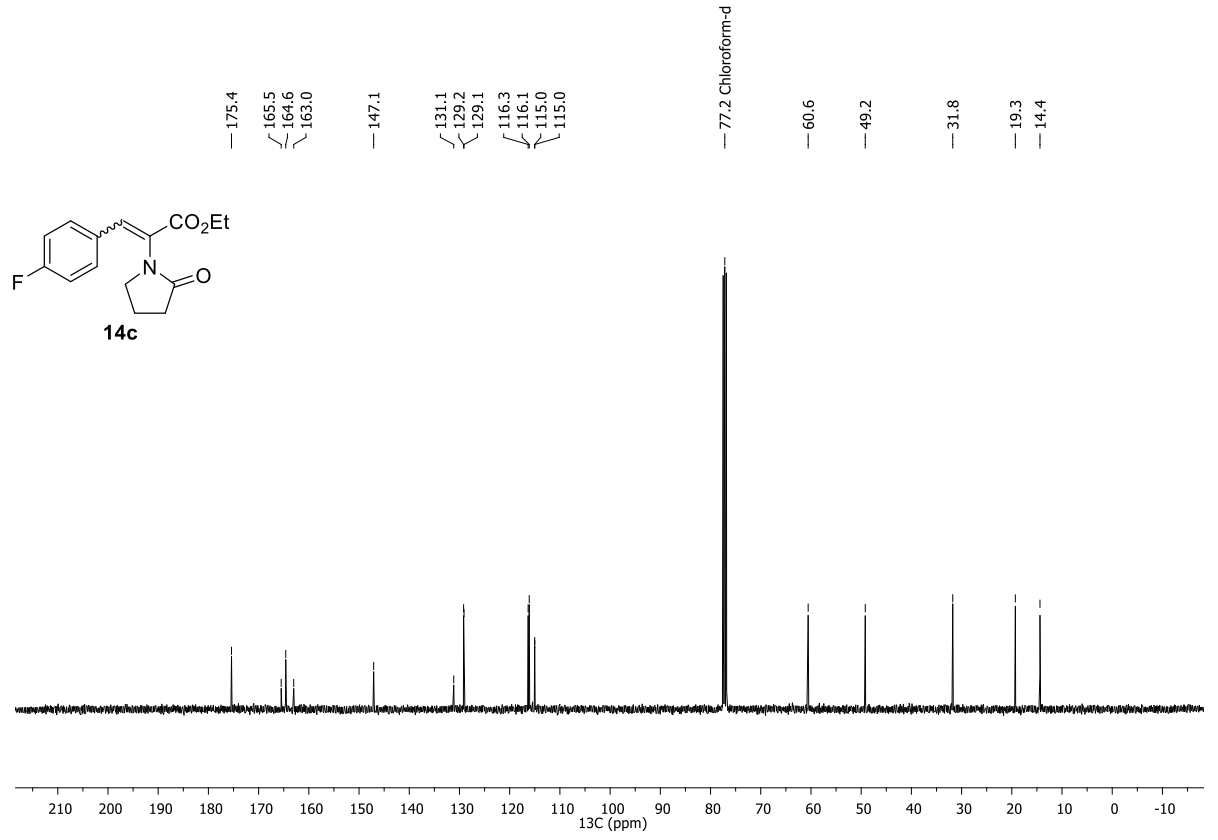


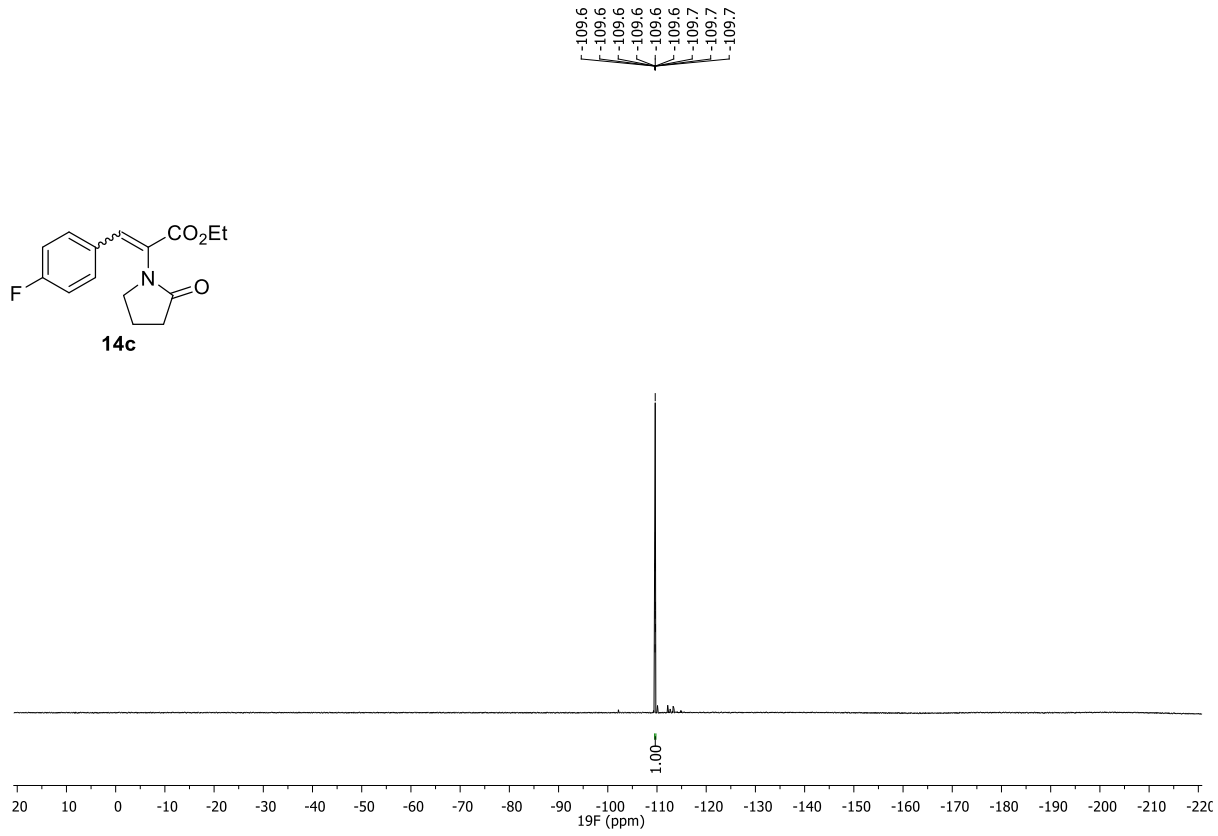

109.0
109.0
109.0
109.0
109.0
109.0
109.0
111.3
111.3
111.4
111.4
111.4
111.4
CO2Et
F
N
O
O
14b
1.00
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
19F (ppm)


CO2Et
F
N
O
O
14b
Desktop 681 1 C:\Users\caldimar
F1 [ppm]
2
4
5.68
8
7.84
6
4
2
F2 [ppm]

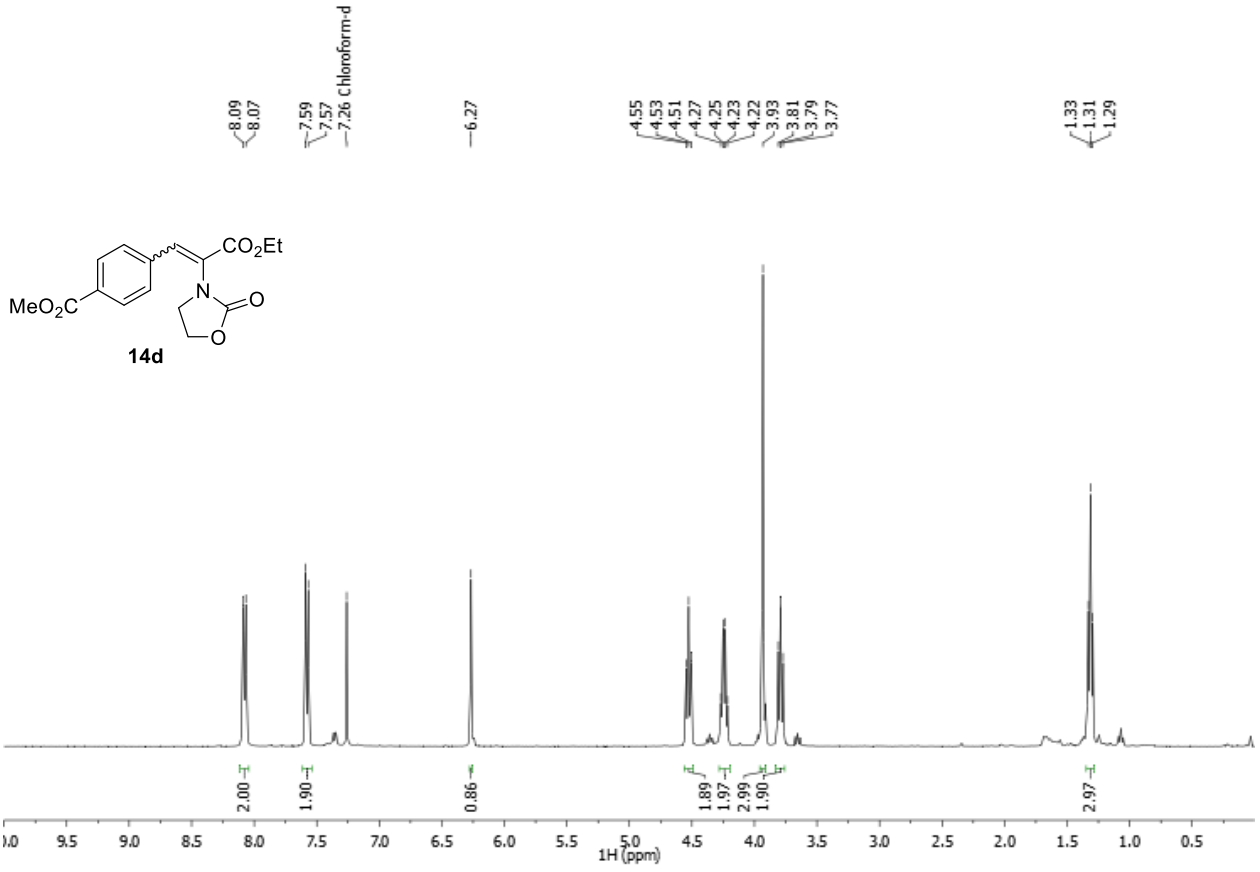
^{1}H, ^{13}C and ^{19}F NMR spectra of ethyl 3-(4-fluorophenyl)-2-(2-oxopyrrolidin-1-yl)propanoate **14c** in $CDCl_3$

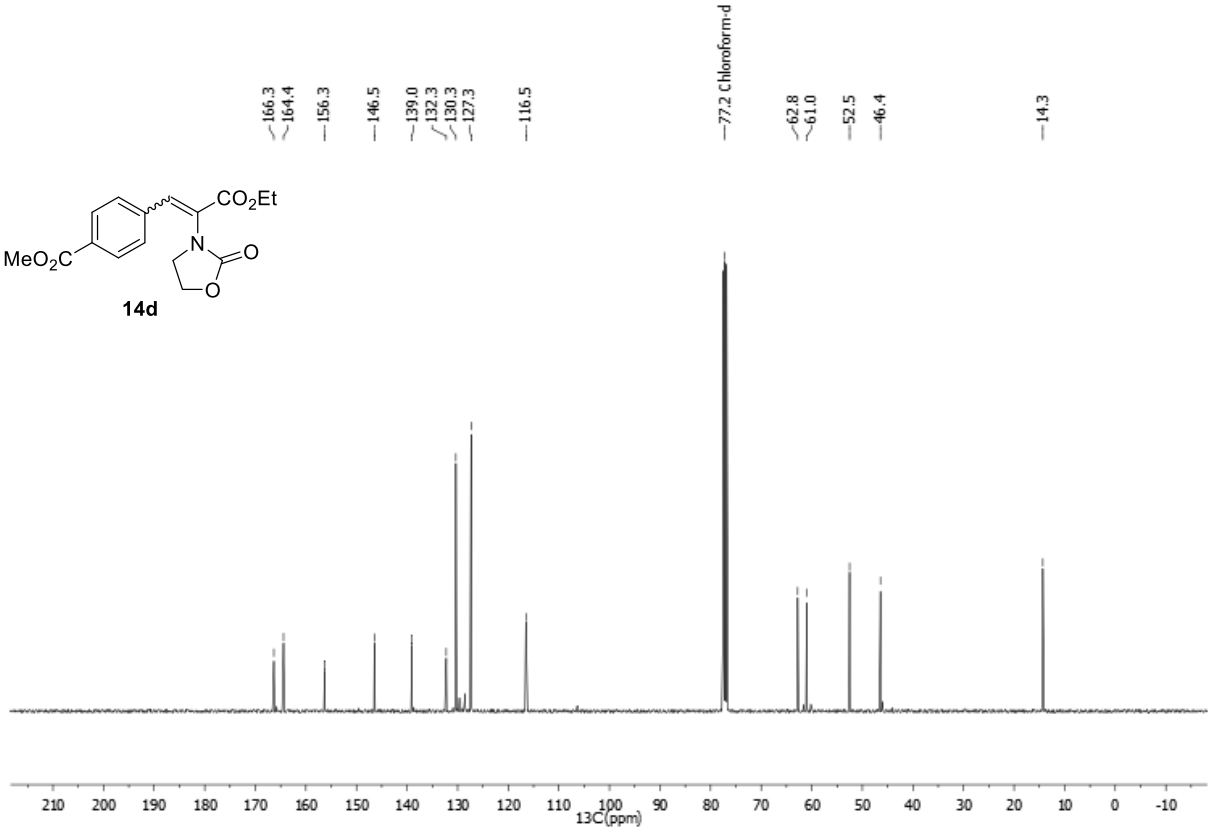


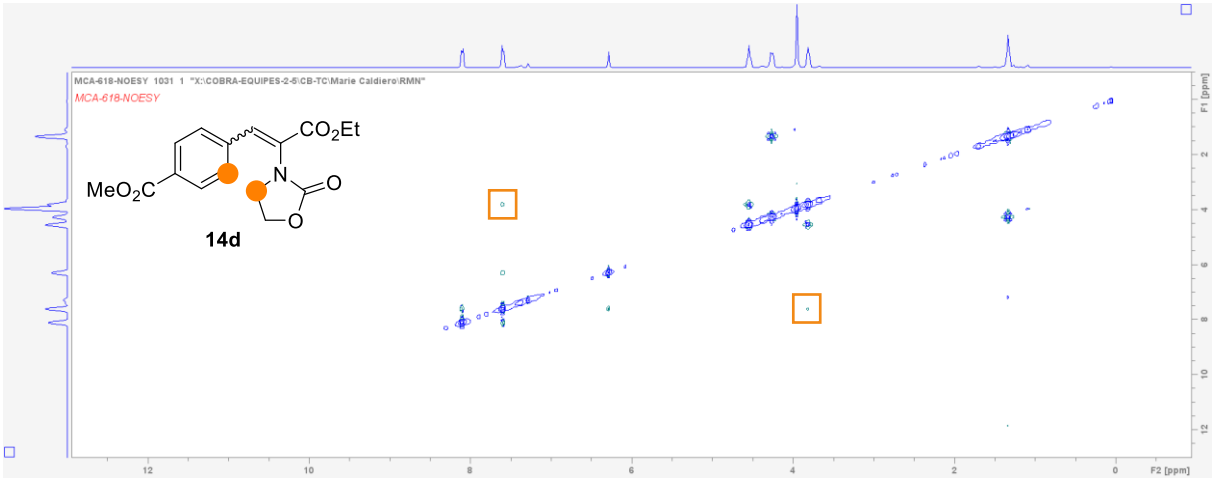




^{1}H, ^{13}C and NOESY NMR spectra of methyl 4-(3-ethoxy-3-oxo-2-(2-oxooxazolidin-3-yl)prop-1-en-1-yl)benzoate **14d** in $CDCl_3$




166.3
164.4
156.3
146.5
139.0
132.3
130.3
127.3
116.5
77.2 Chloroform-d
62.8
61.0
52.5
46.4
14.3
MeO2C
CO2Et
N
O
O
14d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C(ppm)


MCA-618-NOESY 1031 1 "X:\COBRA-EQUIPES-2-5\CB-TC\Marie Caldiero\RMN"
MCA-618-NOESY
MeO2C
CO2Et
N
O
O
14d
F1 [ppm]
F2 [ppm]
12 10 8 6 4 2 0