Electronic Supplementary Material (ESI) for ChemComm.


# Highly Selective γ-Alkoxylation, γ-Amination and γ-Alkylation of Unbiased Enals by Means of Photoredox Catalysis

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# Supporting Information

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# I. General methods

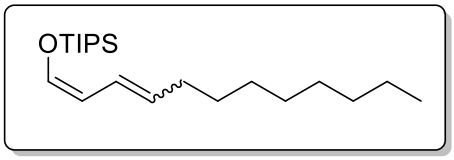
Each reaction was carried out under argon in a freshly distilled solvent, unless otherwise noted. All chemicals were purchased from Sigma-Aldrich, Fluorochem, TCI or Alfa Aesar and were used without further purification. Organic solvents were purchased from Sigma-Aldrich. Visible light irradiations were performed with a Flexled INSPIRE LED lamp (3.45 W/m; $\lambda$ = 465 nm). Reactions were monitored by thin-layer chromatography on silica gel 60 F254. Unless otherwise noted, yields refer to materials purified by column chromatography. Flash chromatography was conducted on silica gel 60 (40-63 μm) at medium pressure (300 mbar). $^{1}H$ and $^{19}F$ NMR spectra were recorded with a Bruker AC-200 spectrometer. $^{13}C$ NMR spectra were recorded with a Bruker AC-300 spectrometer at 75 MHz using a broadband decoupled mode with the multiplicities obtained using a DEPT sequence. Unless otherwise noted, NMR experiments were carried out in $CDCl_3$, for which chemical shifts ($\delta$) are reported in parts per million (ppm) with reference to $CHCl_3$ ($^{1}H$: 7.26; $^{13}C$: 77.07) and $CFCl_3$ ($^{19}F$: 0). Coupling constants (*J*) are reported in Hertz (Hz). High-resolution electrospray mass spectra in the positive ion mode were obtained with a Xevo Q-Tof WATERS spectrometer.
*N*-alkoxypyridinium and aminopyridinium salts were prepared following known procedures.[1]

## II. Synthesis of silyloxydienes

**General procedure A (GP A):**

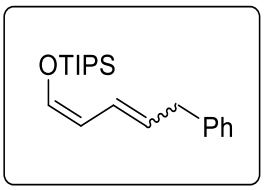
To a solution of the corresponding enal (1 equiv) in $CH_2Cl_2$ (0.25 M) at room temperature, was added triethylamine (1.8 equiv) and TIPSOTf (1.2 equiv). The mixture was stirred at rt for 1h, and was quenched with 5% $NaHCO_3$ solution. After extraction with EtOAc, the organic phases were dried over anhydrous $MgSO_4$ and the solvents were removed in vacuo. Purification on silica gel flash chromatography (eluent: petroleum ether/EtOAc + 0.5% of $Et_3N$) afforded the corresponding silylated dienol ether.

**(Dodeca-1,3-dien-1-yloxy)triisopropylsilane 1a**




Prepared according the GP A.
*E/Z* ratio: 43:57
**$^1$H NMR (300 MHz, $CDCl_3$) δ:** 6.62 major, 6.56 minor (d, *J* = 11 Hz, 1H), 6.01 - 5.91 (m, 1H), 5.86 major, 5.70 minor (t, *J* = 11 Hz, 1H), 5.44 minor (dt, *J* = 15 Hz, *J* = 7 Hz, 1H), 5.19 major (dt, *J* = 10 Hz, *J* = 7.5 Hz, 1H), 2.10 major, 2.03 minor (q, *J* = 7 Hz, 2H), 1.28 (m, 12H), 1.24 – 1.06 (m, 21H), 0.89 (t, *J* = 7 Hz, 3H).
**$^{13}$C NMR (75 MHz, $CDCl_3$) δ:** 145.2 major & 143.4 minor, 129.4 minor & 127.4 major, 126.0 minor & 124.4 major, 113.5 minor & 109.3 major, 33.1, 32.1, 29.9, 29.8, 29.7 (2C), 29.5 (2C), 29.4, 27.9, 22.9, 17.83 (6C TIPS), 14.26, 12.11 (3C TIPS).
**HRMS (ASAP-TOF):** Calcd for $C_{21}H_{43}OSi$ $[M+H]^+$: 339.3083; Found: 339.3075.

**Triisopropyl-5-phenylpenta-1,3-dien-1-yl)oxy)silane (1b)**

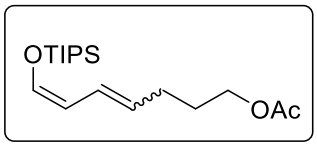



Prepared according the GP A.
*E/Z* ratio: 40:60
**$^1$H NMR (300 MHz, $CDCl_3$) δ:** 7.36 (m, 2H), 7.28 (m, 3H), 6.79 major & 6.68 minor (d, *J* = 11 Hz, 1H), 6.18 major & 5.82 minor (t, *J* = 11 Hz, 1H), 6.12 – 6.01 (m, 1H), 5.68 minor (dt, *J* = 15 Hz, *J* = 7 Hz, 1H) & 5.44 major (dm, *J* = 10 Hz, 1H), 3.55 major & 3.47 minor (d, *J* = 7.0 Hz, 2H), 1.33 – 1.16 (m, 21H).
**$^{13}$C NMR (75 MHz, $CDCl_3$) δ:** 146.3 major & 144.3 minor, 141.4 major & 141.1 minor, 128.7, 128,5 (2C), 128,4, 127.6, 127.2, 126,0, 125,9, 125,5, 125.0, 113.2 minor & 108.9 major,39.3 minor & 34.1 major, 17.8 (6C TIPS), 12.1 (3C TIPS).
**HRMS (ASAP-TOF):** Calcd for $C_{22}H_{37}OSi$ $[M+H]^+$: 317.2301; Found: 317.2295.

**Triisopropyl((6Z)-nona-1,3,6-trien-1-yl)oxy)silane (1c)**

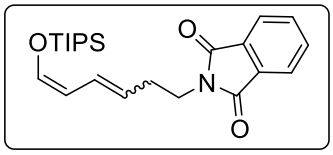

Prepared according the GP A.
*E/Z* ratio: 35:65
**$^{1}$H NMR (200 MHz, $CDCl_3$) δ:** 6.64 major, 6.57 minor (d, *J* = 11 Hz, 1H), 6.05 – 5.65 (m, 2H), 5.49 – 5.09 (m, 3H), 2.84 (m, 2H), 2.08 (m, 2H), 1.28 – 1.06 (m, 21H), 0.98 (m, 3H).
**$^{13}$C NMR (75 MHz, $CDCl_3$) δ:** 145.7 (major) & 143.8, 132.3 & 131.9 (major), 127.4, 126.9, 126.4, 125.0, 124.7, 113.3 & 109.0 (major), 30.5 & 26.0 (major), 20.7 (major) & 20.6, 17.8 (6C TIPS), 14.4, 12.1 (3C TIPS).
**HRMS (ASAP-TOF):** Calcd for $C_{18}H_{35}OSi$ $[M+H]^+$: 295.2457; Found: 295.2468.

**7-((triisopropylsilyl)oxy)hepta-4,6-dien-1-yl acetate (1d)**



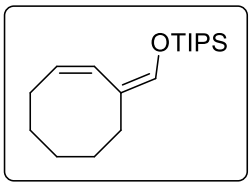

Prepared according the GP A.
*E/Z* ratio: 48.52
**$^{1}$H NMR (300 MHz, $CDCl_3$) δ:** 6.60 & 6.54 (d, *J* = 11 Hz, 1H), 5.89 (m, 2H), 5.66 (t, *J* = 10 Hz, 1H), 5.38 minor (dt, *J* = 15 Hz, *J* = 7 Hz, 1H) & 5.12 major (dm, *J* = 10 Hz, 1H), 4.04 (t, *J* = 6.6 Hz, 2H), 2.12 (m, 2H), 2.02 & 2.01 (s, 3H), 1.68 (q, *J* = 7 Hz, 2H), 1.18 – 1.04 (m, 21H).
**$^{13}$C NMR (75 MHz, $CDCl_3$) δ:** 171.0, 145.6 (major) & 143.8 (minor), 127.1 (minor) & 127.0 (major), 125.6 (major) & 124.9 (minor), 113.0 (minor) & 108.8 (major), 64.0 (minor) & 63.9 (major), 29.1 (minor) & 28.5 (major), 23.9, 20.8, 17.6 (6C TIPS), 11.9 (3C TIPS).
**HRMS (ASAP-TOF):** Calcd for $C_{18}H_{35}O_3Si$ $[M+H]^+$: 327.2355; Found: 327.2346.

**2-(6-((triisopropylsilyl)oxy)hexa-3,5-dien-1-yl)isoindoline-1,3-dione (1e)**



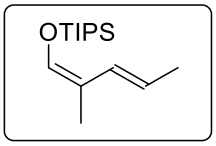

Prepared according the GP A.
*E/Z* ratio: 43:57
**$^{1}$H NMR (200 MHz, $CDCl_3$) δ:** 7.82 (m, 2H), 7.69 (m, 2H), 6.56 & 6.50 (d, *J* = 9 Hz, 1H), 6.01 – 5.86 (m, 1H), 5.65 (t, *J* = 11 Hz, 1H), 5.38 (dt, *J* = 15 Hz, *J* = 7 Hz, 1H) & 5.15 (dm, *J* = 10 Hz, 1H), 3.73 (m, 2H), 2.46 (m, 2H), 1.13 – 1.01 (m, 21H).
**$^{13}$C NMR (75 MHz, $CDCl_3$) δ:** 168.3 major & 168.2 minor, 146.3, 144.4, 133.7 (2C), 132,1, 129.1, 127.5, 123,5, 123,0 (2C), 121.4, 112.9, 108.4, 37.8 minor & 37.5 major, 31.9 & 26.9, 17.6 (6C TIPS), 11.9 minor & 11.8 major (3C TIPS).
**HRMS (ASAP-TOF):** Calcd for $C_{23}H_{34}NO_3Si$ $[M+H]^+$: 400.2308; Found: 400.2319.

**(((Z)-cyclooct-2-en-1-ylidene)methoxy)triisopropylsilane (1f)**



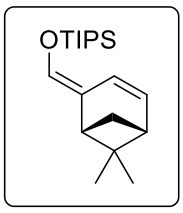

Prepared according the GP A.
One diastereomer.
**$^{1}$H NMR (300 MHz, $CDCl_3$) δ:** 6.50 (s, 1H), 5.99 (d, *J* = 11 Hz, 1H), 5.27 (dm, *J* = 11 Hz, 1H), 2.68 (t, *J* = 7 Hz, 2H), 2.43 (m, 2H), 1.66 – 1.52 (m, 6H), 1.22 – 1.06 (m, 21H).
**$^{13}$C NMR (75 MHz, $CDCl_3$) δ:** 142.3, 132.8, 122.7, 122.3, 28.4, 27.5, 26.1, 23.9, 22.9, 17.8 (6C TiPS), 12.1 (3C TiPS).
**HRMS (ASAP-TOF):** Calcd for $C_{18}H_{35}OSi$ $[M+H]^+$: 295.2457; Found: 295.2450.

**Triisopropyl((2-methylpenta-1,3-dien-1-yl)oxy)silane (1g)**



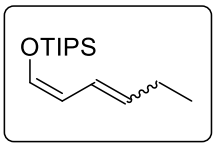

Prepared according the GP A.
One diastereomer.
**$^{1}$H NMR (300 MHz, $CDCl_3$) δ:** 6.44 (s, 1H), 5.99 (d, *J* = 15 Hz, 1H), 5.45 (dq, *J* = 15 Hz, *J* = 7 Hz, 1H), 1.77 (d, *J* = 7 Hz, 3H), 1.74 (s, 3H), 1.21 – 1.03 (m, 21 H).
**$^{13}$C NMR (75 MHz, $CDCl_3$) δ:** 140.0, 131.1, 119.3, 117.3, 18.3, 17.7 (6C TIPS), 11.9 (3C TIPS), 9.3.
**HRMS (ASAP-TOF):** Calcd for $C_{15}H_{31}OSi$ $[M+H]^+$: 255.2144; Found: 255.2140.

**(((1R,5R)-6,6-dimethylbicyclo[3.1.1]hept-3-en-2-ylidene)methoxy)triisopropylsilane (1h)**



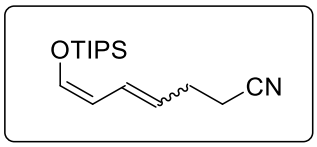

Prepared according the GP A.
One diastereoisomer.
**$^{1}$H NMR (300 MHz, $CDCl_3$) δ:** 6.33 (s, 1H), 6.02 (dd, *J* = 8 Hz, *J* = 6 Hz, 1H), 5.88 (d, *J* = 8 Hz, 1H), 3.17 (m, 1H), 2.48 (m, 1H), 2.27 (m, 1H), 1.36 (s, 3H), 1.33 (m, 1H), 1.20 – 1.06 (m, 21H), 0.84 (s, 3H).
**$^{13}$C NMR (75 MHz, $CDCl_3$) δ:** 135.0, 132.6, 126.5, 124.0, 43.7, 42.6, 41.3, 34.1, 26.4, 22.8, 17.9 (6C TIPS), 12.1 (3C TIPS).
**HRMS (ASAP-TOF):** Calcd for $C_{19}H_{35}OSi$ $[M+H]^+$: 307.2457; Found: 307.2441.

**triisopropyl(((1Z)-2-methylpenta-1,3-dien-1-yl)oxy)silane (1i)**



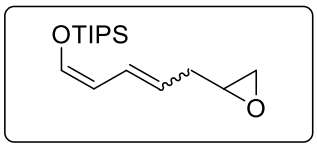

Prepared according the GP A.
*E/Z* ratio: 40:60
**$^{1}$H NMR (300 MHz, $CDCl_3$) δ:** 6.63 major, 6.57 minor (d, *J* = 11 Hz, 1H), 5.90 - 5.80 (m, 1H), 5.97 major, 5.71 minor (t, *J* = 11 Hz, 1H), 5.49 minor (dt, *J* = 15 Hz, *J* = 7 Hz, 1H), 5.19 major (dt, *J* = 10 Hz, *J* = 7.5 Hz, 1H), 2.20 – 1.99 (m, 2H), 1.21 – 1.05 (m, 21H), 0.99 (t, *J* = 7.5 Hz, 3H).
**$^{13}$C NMR (75 MHz, $CDCl_3$) δ:** 147.2 major & 145.5 minor, 130.7 minor & 128.7 major, 125.0 minor & 123.8 major, 113.3 minor & 109.0 major, 25.8 minor & 21.0 major, 17.7 (6C TIPS), 14.3 major & 13.8 minor, 12.0 (3C TIPS).
**HRMS (ASAP-TOF):** Calcd for $C_{15}H_{31}OSi$ $[M+H]^+$: 255.2144; Found: 255.2138.

**7-((triisopropylsilyl)oxy)hepta-4,6-dienenitrile (1j)**



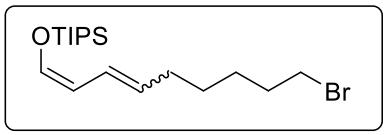

Prepared according the GP A.
*E/Z* ratio: 62:38
**$^{1}$H NMR (300 MHz, $CDCl_3$) δ:** 6.67 minor & 6.61 major (d, *J* = 11 Hz, 1H), 6.00 (m, 1H), 5.86 minor & 5.67 major (t, *J* = 11 Hz, 1H), 5.38 major (dm, *J* = 15 Hz, 1H) & 5.13 minor (dm, *J* = 10 Hz, 1H), 2.39 (m, 2H), 1.13 – 1.03 (m, 21 H).
**$^{13}$C NMR (75 MHz, $CDCl_3$) δ:** 147.2 minor & 145.5 major, 129.6 major & 127.9 minor, 123.2 major & 121.1 minor, 119.5, 112.4 major & 108.1 minor, 28.8, 23.8, 17.7 (6C TIPS), 12.0 (3C TIPS).
**HRMS (ASAP-TOF):** Calcd for $C_{16}H_{30}NOSi$ $[M+H]^+$: 280.2097; Found: 280.2098.

**Triisopropyl-5-(oxiran-2-yl)penta-1,3-dien-1-yl)oxy)silane (1k)**



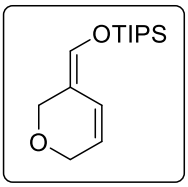

Prepared according the GP A.
*E/Z* ratio: 54:46
**$^{1}$H NMR (300 MHz, $CDCl_3$) δ:** 6.66 minor & 6.59 major (d, *J* = 11 Hz, 1H), 6.06 – 5.96 (m, 1H), 6.01 minor & 5.70 major (t, *J* = 11 Hz, 1H), 5.41 major (dt, *J* = 15 Hz, *J* = 7 Hz, 1H) & 5.18 minor (dm, *J* = 10 Hz, 1H), 2.96 (m, 1H), 2.73 (m, 1H), 2.52 - 2.23 (m, 3H), 1.22 – 1.06 (m, 21H).
**$^{13}$C NMR (75 MHz, $CDCl_3$) δ:** 146.6 minor & 144.8 major, 129.3 major & 127.5 minor, 122.1 major & 119.6 minor, 112.9 major & 108.7 minor, 51.8 major & 51,7 minor, 46.8, 35.8, 30.7, 17.8 (6C TIPS), 12.1 (3C TIPS).
**HRMS (ASAP-TOF):** Calcd for $C_{16}H_{31}O_2Si$ $[M+H]^+$: 283.2093; Found: 283.2102.

**((9-bromonona-1,3-dien-1-yl)oxy)triisopropylsilane (1l)**



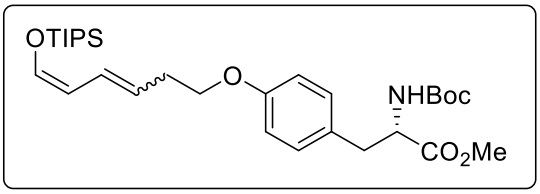

Prepared according the GP A.
*E/Z* ratio: 50:50
**$^1$H NMR (300 MHz, $CD_3CN$) δ:** 6.70 & 6.63 (d, *J* = 11 Hz, 1H), 5.95 & 5.64 (t, *J* = 11 Hz, 1H), 5.91 (m, 1H), 5.43 (dt, *J* = 15 Hz, *J* = 7 Hz, 1H) & 5.17 (dm, *J* = 10 Hz, 1H), 3.46 (t, *J* = 7 Hz, 2H), 2.08 (m, 2H), 1.83 (q, *J* = 7 Hz, 2H), 1.40 (m, 4H), 1.23 – 1.02 (m, 21H).
**$^{13}$C NMR (75 MHz, $CD_3CN$) δ:** 146.6 & 144.7, 129.6 & 127.4, 127.3 & 125.6, 114.2 & 110.0, 35.3, 33.5 & 33.5, 33.3 & 29.6, 39.5 & 28.4, 28.4 & 28.1, 18.0 (6C TIPS), 12.7 (3C TIPS).
**HRMS (ASAP-TOF):** Calcd for $C_{18}H_{36}BrOSi$ $[M+H]^+$: 375.1719; Found: 375.1722.

**((2H-pyran-3(6H)-ylidene)methoxy)triisopropylsilane (1m)**




Prepared according the GP A.
One diastereomer.
**$^1$H NMR (300 MHz, $CDCl_3$) δ :** 6.27 (s, 1H), 6.10 (dm, *J* = 11 Hz, 1H), 5.58 (dm, *J* = 10 Hz, 1H), 4.46 (m, 2H), 4.18 (m, 2H), 1.19 – 1.05 (m, 21H).
**$^{13}$C NMR (75 MHz, $CDCl_3$) δ :** 137.1, 123.4, 122.4, 115.2, 65.8, 63.0, 17.8 (6C TIPS), 12.0 (3C TIPS).
**HRMS (ASAP-TOF):** Calcd for $C_{15}H_{29}O_2Si$ $[M+H]^+$: 269.1937; Found: 269.1936.

**Methyl 2-((tert-butoxycarbonyl)amino)-3-(4-((6-((triisopropylsilyl)oxy)hexa-3,5-dien-1-yl)oxy)phenyl)propanoate (1n)**




Prepared according the GP A.
*E/Z* ratio: 60:40
**$^1$H NMR (200 MHz, $CDCl_3$) δ:** 6.99 (d, *J* = 8 Hz, 2H), 6.79 (d, *J* = 8 Hz, 2H), 6.58 (m, 1H), 6.09 – 5.93 (m, 1H), 5.99 minor (m, 1H), 5.69 major (t, *J* = 11 Hz, 1H), 5.46 major (dt, *J* = 15 Hz, *J* = 7 Hz, 1H), 5.20 minor (m, 1H), 5.02 (d, *J* = 8 Hz, 1H), 4.50 (m, 1H), 3.91 (t, *J* = 7 Hz, 2H), 3.67 (s, 3H), 2.99 (m, 2H), 2.52 (m, 2H), 1.39 (s, 9H), 1.22 – 1.02 (m, 21H).
**$^{13}$C NMR (75 MHz, $CDCl_3$) δ:** 172.4, 158.0, 155.1, 146.1 minor & 144.4 major, 130.2 (2C), 128.7, 127.9 major & 127.0 minor, 123.6 major & 121.2 minor, 114.6 (2C), 113.0 major & 108.8 minor, 79.7, 67.7 major & 67.4 minor, 54.6, 52.1, 37.4, 32.8 major & 27.9 minor, 28.3 (3C), 17.7 (6C TIPS), 11.9 (3C TIPS).
**HRMS (ASAP-TOF):** Calcd for $C_{30}H_{50}NO_6Si$ $[M+H]^+$: 548.3407; Found: 548.3413.

## III. Synthesis of radical sources

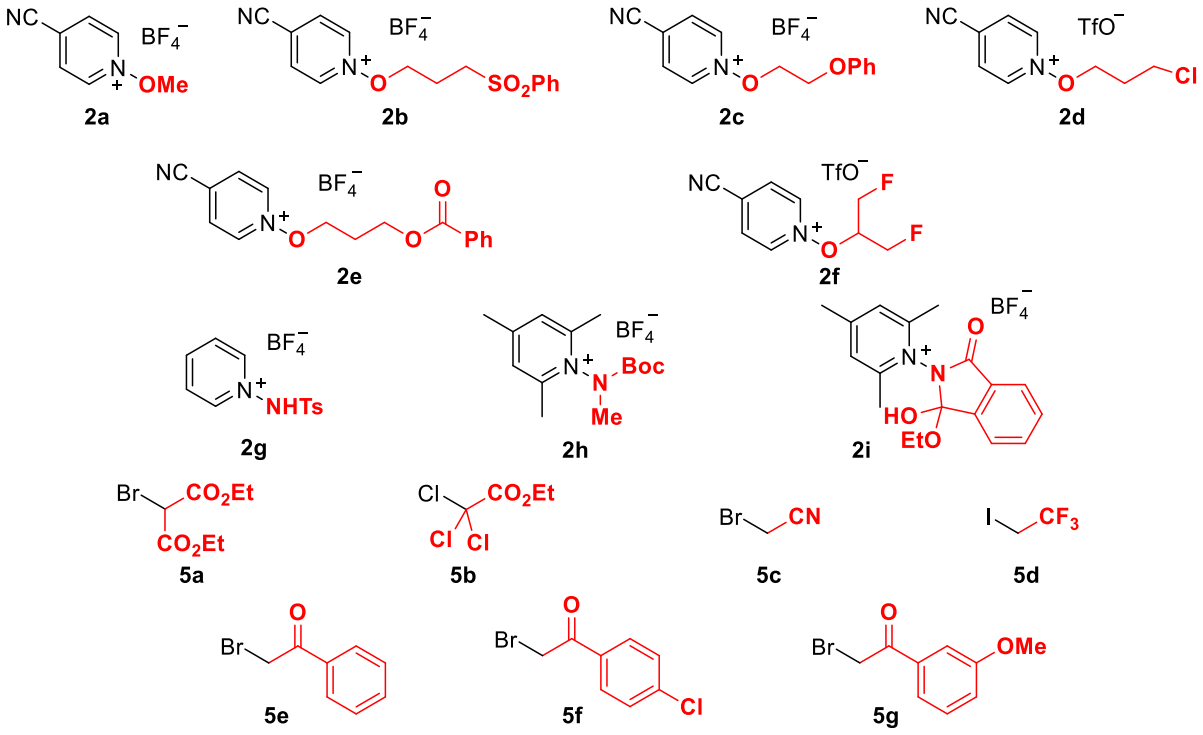



*Figure S1. Scope of radical sources used in this study*

*N*-alkoxypyridinium **2a-2f** and aminopyridinium salts **2g-2h** were prepared following known procedures.[1]Alkyl halides **5a-5g** are commercailly available.

**Synthesis of 1-(1-ethoxy-1-hydroxy-3-oxoisoindolin-2-yl)-2,4,6-trimethylpyridin-1-ium tetrafluoroborate 2i**

2,4,6-Trimethylpyrylium tetrafluoroborate (3 mmol, 1 equiv.) was suspended in EtOH (10mL) then N-aminophthalimide (3 mmol, 1 equiv.) was slowly introduced. The reaction mixture was stirred at reflux overnight. $Et_2O$ was added once the reaction mixture has cooled down and was left stirring at room temperature for 30 minutes. The precipitate was filtered and washed with $Et_2O$. The product was obtained as a white solid in 89% yield.

**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 11.21 (s, 1H), 7.95 (d, *J* = 7.1 Hz, 1H), 7.80 (d, *J* = 7.2 Hz, 1H), 7.73-7.59 (m, 2H), 7.52 (s, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.89 (s, 6H), 2.60 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 166.2, 165.7, 160.4, 158.3, 132.4, 132.2, 132.0, 131.4, 130.5, 127.9, 127.7, 61.9, 22.2, 19.6, 14.2.

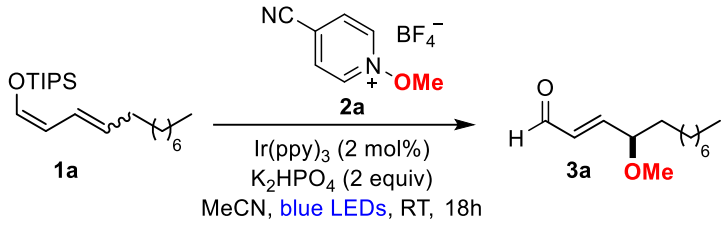
**$^{19}$F NMR (188 MHz, $CDCl_3$) δ (ppm):** -152.18, -152.23.

**HRMS (TOF MS ES+) $C_{18}H_{21}O_3N_2$ $[M+H]^+$**: requires 313.1552; found 313.1545.

**m. p.:** 173 – 175 °C

## IV. Optimization of the reaction conditions

**Table S1.** Survey of reaction conditions for the photoredox-catalyzed γ-alkoxylation of silyloxydiene **1a**.




| Entry | Photocatalyst | Additive (1 equiv) | Solvent | Yield [%][a,b] |
|---|---|---|---|---|
| 1 | $Ru(bpy)_3(PF_6)_2$ | $K_2HPO_4$ | MeCN | 59 |
| 2 | Eosin Y | $K_2HPO_4$ | MeCN | 33 |
| 3 | *fac*-$Ir(ppy)_3$ | $K_2HPO_4$ | MeCN | 75 (71)[c] |
| 4 | *fac*-$Ir(ppy)_3$ | $K_2CO_3$ | MeCN | 25 |
| 5 | *fac*-$Ir(ppy)_3$ | $Na_2HPO_4$ | MeCN | 41 |
| 6 | *fac*-$Ir(ppy)_3$ | none | MeCN | 31[d] |
| 7 | *fac*-$Ir(ppy)_3$ | $K_2HPO_4$ | Acetone | 11 |
| 8[e] | *fac*-$Ir(ppy)_3$ | $K_2HPO_4$ | MeCN | 0 |
| 9 | none | $K_2HPO_4$ | MeCN | 6 |

[a] General conditions: **1a** (0.2 mmol), **2a** (0.36 mmol), photocatalyst (2 mol%) and additive (2 equiv) in 2 mL of solvent irradiated with 5W blue LEDs at RT for 18 h. [b] Yields determined by $^1H$ NMR spectroscopy using 1,4-dicyanobenzene as an internal standard. [c] Yield into brackets refers to chromatographically pure product. [d] 40% of (*E*)-2-dodecenal was formed during the reaction. Bpy = 2,2-bipyridine; ppy = 2-phenylpyridine. [e] In the dark.

# V. General procedures of γ-functionalization reactions

**General procedure GP B: γ-alkoxylation**

A test-tube was charged with substrate **1** (0.20 mmol), *N*-alkoxypyridinium salt **2** (0.36 mmol), *fac*-Ir(ppy)$_3$ **2a** (2 mol%) and $K_2HPO_4$ (0.4 mmol). MeCN (2 mL) was added and argon was bubbled into the solution during 5 min. Then the mixture was irradiated with 5W blue LEDs strip for 18 h. After completion, the solvent was removed *in vacuo*, and the crude product was purified by preparative TLC to afford the desired pure γ-alkoxylated product **3**.

**General procedure GP C: γ-amination**

A test-tube was charged with substrate **1** (0.20 mmol), *N*-aminopyridinium salt **2** (0.30 mmol), *fac*-Ir(ppy)$_3$ **2a** (2 mol%) and $K_2HPO_4$ (0.40 mmol). MeCN (3 mL) was added and argon was bubbled into the solution during 5 min. Then the mixture was irradiated with 5W blue LEDs strip for 18 h. After completion, the solvent was removed *in vacuo*, and the crude product was purified by preparative TLC to afford the desired pure γ-aminated product **4**.

**General procedure GP D: γ-alkylation**

A test-tube was charged with substrate **1** (0.20 mmol), the source of C-centered radical **5** (0.30 mmol), *fac*-Ir(ppy)$_3$ **2a** (2 mol%) and $K_2CO_3$ (0.40 mmol). $CDCl_3$ (2 mL) was added and argon was bubbled into the solution during 5 min. Then the mixture was irradiated with 5W blue LEDs strip for 18 h. After completion, the solvent was removed *in vacuo*, and the crude product was purified by preparative TLC to afford the desired pure γ-alkylated product **6**.

**Gram-scale experiment:**

A 200 mL test-tube was charged with substrate **1a** (8 mmol, 2.7 g), diethyl bromomalonate **5a** (4 mmol, 0.96 g), *fac*-Ir(ppy)$_3$ **2a** (0.08 mmol, 52 mg) and $K_2CO_3$ (8 mmol, 1.11 g). $CHCl_3$ (40 mL) was added and argon was bubbled into the solution during 5 min. Then the mixture was irradiated with 5W blue LEDs strip for 18 h. After completion, the solvent was removed *in vacuo*, and the crude product was purified by flash chromatography (pentane/EtOAc) to afford the desired pure γ-alkylated product **6a** (450 mg, 53% yield).

## VI. Stern-Volmer experiments

Rates of quenching ($k_q$) were determined using Stern-Volmer kinetics:

$$I_0/I = k_q\tau_0[\text{quencher}] + 1$$

Where $I_0$ is the luminescene intensity without the quencher, I is the intensity with the quencher, and $\tau_0$ is the excited state lifetime of the photocatalyst ($\tau_0$ = 1.9 µs for $Ir(ppy)_3$).

The following stock solutions were prepared in distilled MeCN (or $CHCl_3$) and degassed by three freeze-pump-thaw cycles.

**General procedure:** A stock solution of $Ir(ppy)_3$ was prepared by dissolving $Ir(ppy)_3$ (25 µmol) in 10 mL of MeCN (or $CHCl_3$). Of this solution, 0.1 mL were further diluted with MeCN (or $CHCl_3$) to give a total voume of 10 mL. Concentration of [**Ir**] = 2.5 x $10^{-5}$ M. A stock solution of **2** (or **5**) was prepared by dissolving **2** (or **5**) (30 µmol) in 10 mL of MeCN (or $CHCl_3$). Concentration of [**2**] or [**5**] = 3 x $10^{-3}$ M. A stock solution of **1a** was prepared by dissolving **1a** (30 µmol) in 10 mL of MeCN (or $CHCl_3$). Concentration of [**1a**] = 3 x $10^{-3}$ M. For each experiment, 6 samples were prepared in the dark. Quartz cuvettes (3.5 mL) were filled with photocatalyst stock solution (0.3 mL), reagent stock solution (0 mL, 0.2 mL, 0.4mL, 0.6 mL, 0.8 mL, 1.0 mL) and MeCN (or $CHCl_3$) (2.7 mL, 2.5 mL, 2.3 mL, 2.1 mL, 1.9 mL, 1.7 mL) to obtain a total volume of 3 mL. The final concentrations were [**Ir**] = 2.5 $10^{-6}$ M and [quencher] = 2 x $10^{-4}$ M, 4 x $10^{-4}$ M, 6 x $10^{-4}$ M, 8 x $10^{-4}$ M, 1 x $10^{-3}$ M. For each sample, emission spectra were acquired between 470 nm and 650 nm (excitation at 450 nm).

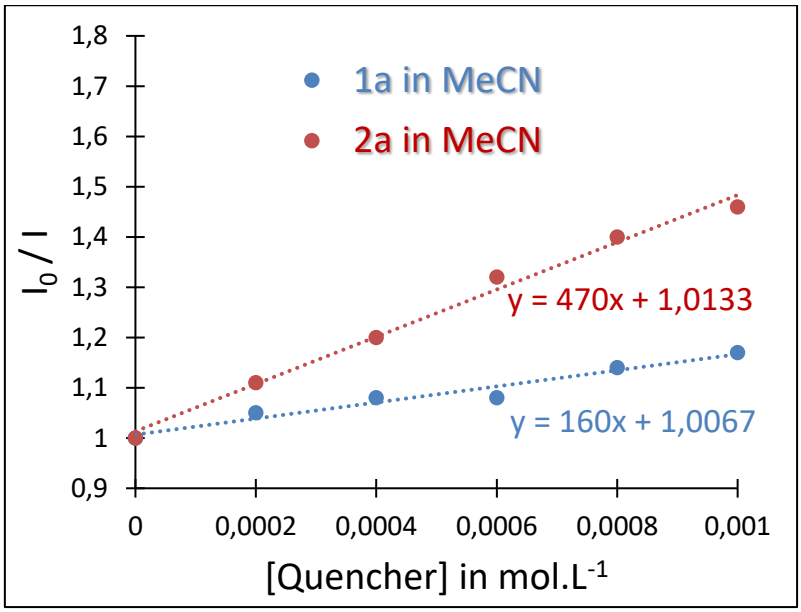



*Figure S2. Stern-Volmer experiments in MeCN*

For *N*-methoxypyridinium salt **2a**, $k_q$ = 2.5 $10^8$ $M^{-1}.s^{-1}$ in MeCN.
For silyl dienol ether **1a**, $k_q$ = 8.4 $10^7$ $M^{-1}.s^{-1}$ in MeCN

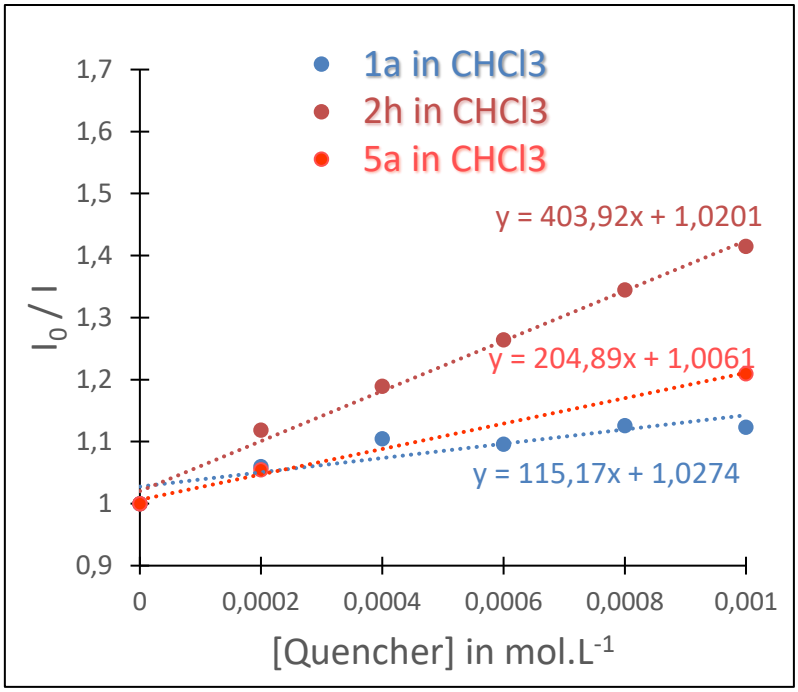



*Figure S3. Stern-Volmer experiments in $CHCl_3$.*

For *N*-aminopyridinium salt **2h**, $k_q = 2.1\ 10^8\ M^{-1}.s^{-1}$ in $CHCl_3$.
For diethyl bromomalonate **5a**, $k_q = 1.1\ 10^8\ M^{-1}.s^{-1}$ in $CHCl_3$.
For silyl dienol ether **1a**, $k_q = 6.1\ 10^7\ M^{-1}.s^{-1}$ in $CHCl_3$.

## VII. Quantum yield measurement

The photon flux was determined by standard ferrioxalate actinometry.[2]

**Solutions needed:**

*0.05 M sulfuric acid stock solution:*
In a 100 mL volumetric flask, 0.281 mL of concentrated sulfuric acid (17.8 M) was added to 90 mL deionized water. Then, water was added until the 100 mL graduation mark was reached.

*Ferrioxolate solution:*
A 0.15 M solution of potassium ferrioxolate was prepared in a 25 mL volumetric flask by dissolving potassium ferrioxolate ($K_3FeC_2O_4*3H_2O$) (1.842 g, 3.75 mmol) with the 0.05 M sulfuric acid solution. The solution was prepared and stored in the dark.

*Developer solution:*
22.5 g of sodium acetate trihydrate was dissolved in 100 mL of 0.5 M sulfuric acid. 1 g of 1,10-phenantroline was added to this solution. Store the solution in the dark.

**Typical Experiment carried out under dark:**

*Figure S4 Prizmatix FC5-LED*

200 μL of 0.15 M aqueous potassium ferrioxalate was transferred to a 5 mm thin wall NMR tube followed by the placement of the coaxial insert. Then the sample was irradiated with 445 nm LED (Prizmatix FC5-LED) at room temperature. The procedure was repeated with different irradiations times for different samples.
100 $\mu$L aliquots of the solution were taken from each solution and added immediately to 3 mL of a developer solution of sodium acetate and 1,10-phenanthroline and the flask was quickly wrapped in aluminum foil. Concurrently, a "blank" sample was prepared by diluting 100 $\mu$L of the stock solution (kept in the dark) into 3 mL of developer solution. The solutions were left in the dark for 30 min - 1 hr, becoming bright red. The solutions were transferred to a cuvette and the absorbance spectrum of the $Fe(phen)_3^{2+}$ complex was obtained. The absorbance at 510 nm (ε = 11,100 $M^{-1}.cm^{-1}$) was measured for every sample.

**Data analysis:**

To calculate photon flux from your chemical actinometry data, first determine the number of $Fe^{2+}$ ions produced by ferrioxolate photo-degradation:

$$moles\ Fe^{2+} = \frac{\Delta A_{510\,nm}\, V_1\, V_3}{\varepsilon_{510\,nm}\, l\, V_2}$$

$\Delta A$ = difference in absorbance at 510 nm between sample and 'blank'
l = path length of cuvette (0,2 cm)
$\varepsilon$ = Extinction coefficient of $Fe(phen)_3$ complex at 510 nm (ε = 11,100 $M^{-1}.cm^{-1}$)

$V_1$ = total volume of irradiated solution (200 µL)
$V_2$ = volume of aliquot taken from $V_1$ (100 µL)
$V_3$ = the volume that $V_2$ is diluted into (3 mL)

The photon flux can be determined:

$$photon\ flux = \frac{moles\ of\ Fe^{2+}}{\Phi_{448nm} \times t \times F}$$

with:
$F_{450nm}$ = 1.01 (reported literature value)[3]
t = time of irradiation (seconds)
F = mean fraction of light absorbed by the ferrioxalate solution (F ≈ 1 at 450 nm at 0.15 M ferrioxolate).

The linear dependence of $Fe^{2+}$ accumulation on LED irradiation time at 445 nm is plotted:

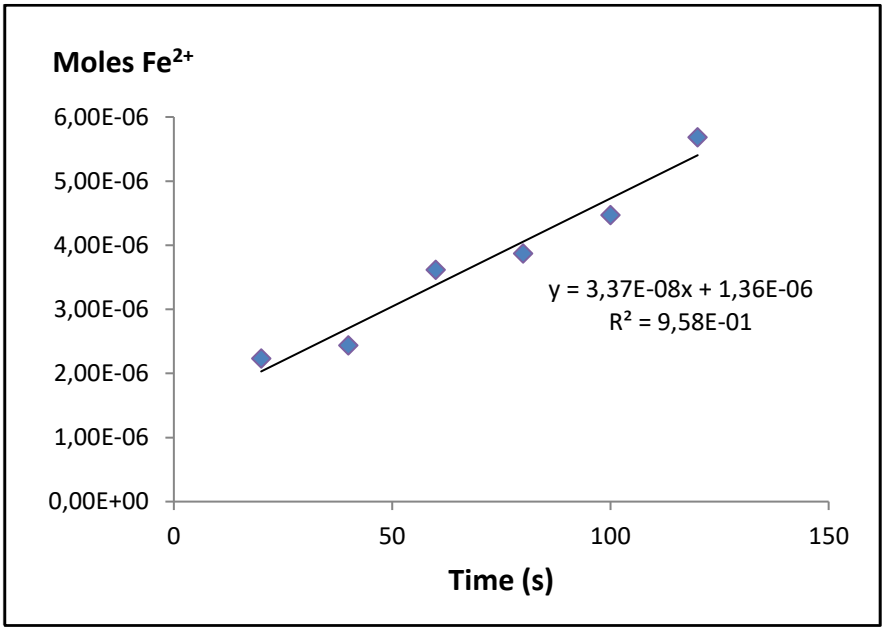



*Figure S5: linear dependence of $Fe^{2+}$ accumulation on LED irradiation time at 445 nm*

From the slope of the linear regression line, we finally find the photon flux:

**Photon flux = $3.37.10^{-8}$ mol.$s^{-1}$**

## Quantum yield measurement

$$\Phi = (\text{rate of substrate conversion})/(\text{absorbed photon flux})$$

The rate of substrate conversion was measured by analyzing the reaction mixture as a function of time thanks to *in situ* NMR irradiation.

**General procedure**: A solution of bromomalonate **5a** or *N*-alkoxypyridinium **2a** (0.15 mmol), silyloxydiene **1a** (0.1 mmol), 2,6-lutidine (0.2 mmol) and the photocatalyst *fac*-Ir(ppy)$_3$ (2 mol%) in $CDCl_3$ (1 mL) was prepared and 0.2 mL of this solution was introduced in an NMR tube and the mixture was degassed with argon.
Excitation was performed at 445 nm and substrate conversion was periodically determined (after 300 seconds) by comparison of the integration of $^1$H NMR silylated dienol ether **1a** peak and nitrobenzene peak, used as internal standard (Brucker AC-300).

The substrate conversions (as well as the product **6a** formation) were then plotted against time (see Figure S6):

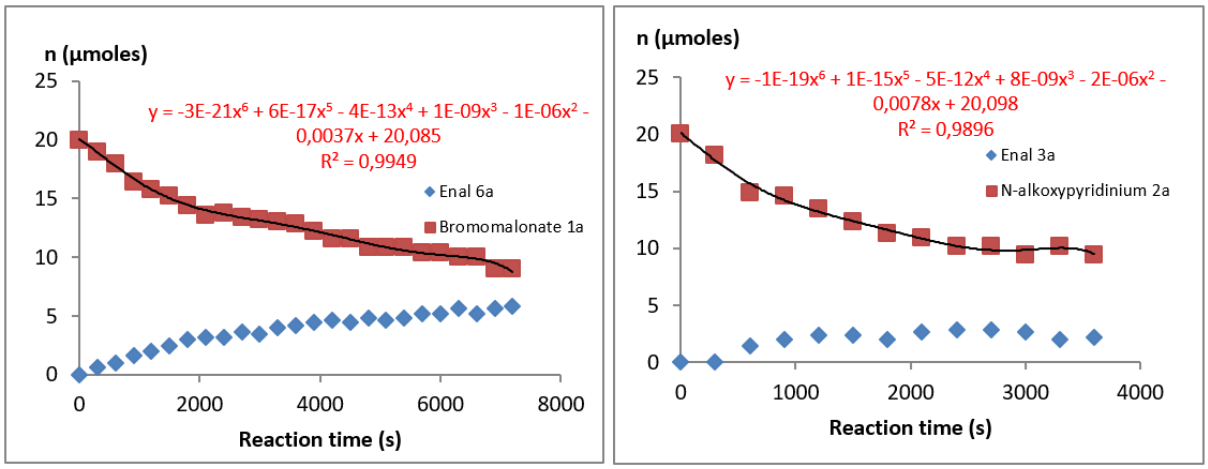



*Figure S6: Quantity of starting material or product **6a/3a** versus time. The plots are fitted to a 6th order polynomial*

The derivatives of the polynomials of Figure S5 are used to calculate the rate of substrate conversion.

Then the absorbed photon flux has to be calculated. Note that in the case of NMR experiments with an optical fiber, the path length of irradiated solution is very small (0.06 cm) and the fraction (f) of light absorbed by this solution has to be first calculated using the equation below, where A is the measured absorbance at 445 nm.

$$\mathbf{f = 1 - 10^{-A}}$$

with $A = \varepsilon_{445nm}.l.[Ir]$

The molar absorptivities $\varepsilon_{445nm}$ of Ir(ppy)$_3$ in MeCN and in $CHCl_3$ were measured to be 2753 $M^{-1}.cm^{-1}$ and 5634 $M^{-1}.cm^{-1}$ respectively thanks to the absorbance spectra of solutions of Ir(ppy)$_3$ in MeCN and in $CHCl_3$ at a known concentration (see Figure S7).

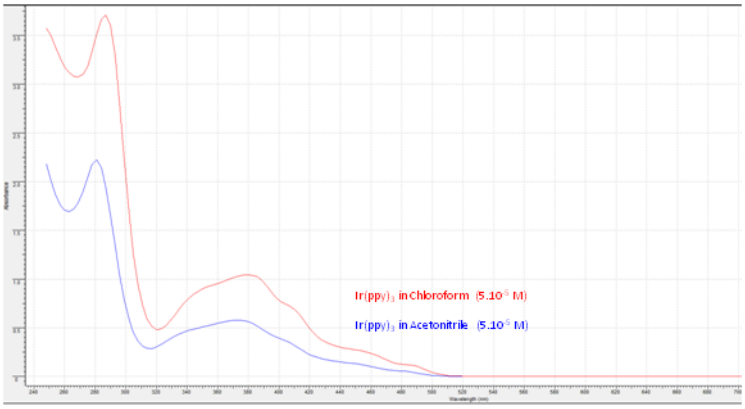



*Figure S7: Absorbance of a solution of $Ir(ppy)_3$ in $CHCl_3$ and in ACN ($5.10^{-5}$ M)*

With this value of $\varepsilon_{445nm}$, and the value of the concentration of $Ir(ppy)_3$ photocatalyst for the irradiated sample ($2.10^{-3}$ M), the fraction f of light absorbed were calculated:

$$\mathbf{f_{MeCN} = 0.51}$$

$$\mathbf{f_{CHCl3} = 0.79}$$

Then, absorbed photon flux in MeCN = photon flux • $f_{MeCN}$ = $\mathbf{1.72.10^{-8}\ mol.s^{-1}}$

And absorbed photon flux in $CHCl_3$ = photon flux • $f_{CHCl3}$ = $\mathbf{2.66.10^{-8}\ mol.s^{-1}}$

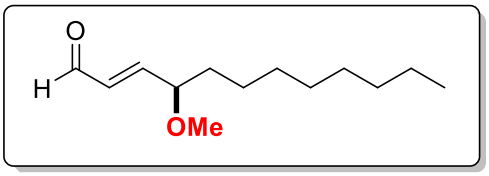
Finally, the quantum yields of the reactions can be calculated. The initial values are

$$\mathbf{\Phi_{\textit{N}\text{-alkoxypyridinium 2a}} = 0.45}$$

$$\mathbf{\Phi_{Bromomalonate\ 5a} = 0.14}$$

## VIII. Characterization of new compounds

### (*E*)-4-Methoxydodec-2-enal 3a



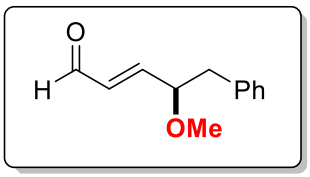

Synthesized according to GP B. m = 30.0 mg, 71% yield, colourless oil.

**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.59 (d, 7.9 Hz, 1H), 6.68 (dd, 15.9 and 6.1 Hz, 1H), 6.24 (dd, 15.9 and 7.9 Hz, 1H), 3.85 (q, 6.4 Hz, 1H), 3.33 (s, 3H), 1.64-1.54 (m, 2H), 1.34-1.21 (m, 12H), 0.88 (t, 6.4 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.4, 157.1, 132.4, 80.6, 57.3, 34.7, 31.9, 29.5, 29.5, 29.2, 25.1, 22.7, 14.1.

**EI-HRMS (positive ion) $C_{13}H_{25}O_2$ $[M+H]^+$:** requires 213.1855; found 213.1845.

### (*E*)-4-Methoxy-5-phenylpent-2-enal 3b



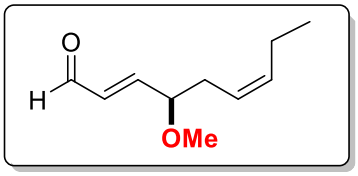

Synthesized according to GP B. m = 27 mg, 71% yield, colourless oil.

**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.59 (d, 7.7 Hz, 1H), 7.37-7.22 (m, 5H), 6.71 (dd, 15.9 and 5.9 Hz, 1H), 6.23 (dd, 15.9 and 7.9 Hz, 1H), 4.14 (q, 6.3 Hz, 1H), 3.37 (s, 3H), 3.05 (dd, 13.8 and 6.7 Hz, 1H), 2.87 (dd, 13.8 and 6.4 Hz, 1H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.3, 156.0, 136.9, 132.7, 129.4, 128.5, 126.8, 81.5, 57.6, 41.3.

**EI-HRMS (positive ion) $C_{12}H_{15}O_2$ $[M+H]^+$:** requires 191.1072; found 191.1076.

### (2*E*,6*Z*)-4-Methoxynona-2,6-dienal 3c



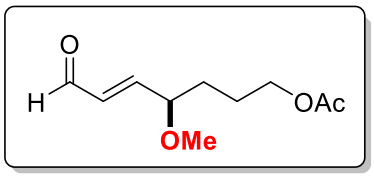

Synthesized according to GP B. m = 25 mg, 74% yield, colourless oil.

**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.58 (d, 7.9 Hz, 1H), 6.69 (dd, 15.6 and 5.9 Hz, 1H), 6.26 (dd, 15.6 and 7.9 Hz, 1H), 5.57-5.46 (m, 1H), 5.37-5.27 (m, 1H), 3.90 (q, 6.1 Hz, 1H), 3.35 (s, 3H), 2.47-2.31 (m, 2H), 2.07-1.97 (m, 2H), 0.95 (t, 7.4 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.4, 156.5, 135.0, 132.6, 122.6, 80.3, 57.4, 32.3, 20.8, 14.1.

**EI-HRMS (positive ion) $C_{10}H_{17}O_2$ $[M+H]^+$:** requires 169.2435; found 169.2432.

**(*E*)-4-Methoxy-7-oxohept-5-en-1-yl acetate 3d**



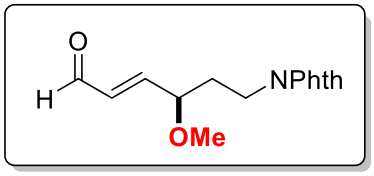

Synthesized according to GP B. m = 28 mg, 70% yield, colourless oil.

**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.59 (d, 7.7 Hz, 1H), 6.67 (dd, 15.9 and 5.9 Hz, 1H), 6.25 (dd, 15.9 and 7.9 Hz, 1H), 4.12 (t, 6.1 Hz, 2H), 3.89 (q, 5.7 Hz, 1H), 3.33 (s, 3H), 1.76-1.62 (m, 4H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.3, 171.2, 156.3, 132.7, 79.9, 64.0, 57.1, 31.1, 24.4, 21.0.

**EI-HRMS (positive ion) $C_9H_{13}O_3$ $[M+H-MeOH]^+$:** requires 169.0865; found 169.0861.

**(*E*)-6-(1,3-Dioxoisoindolin-2-yl)-4-methoxyhex-2-enal 3e**



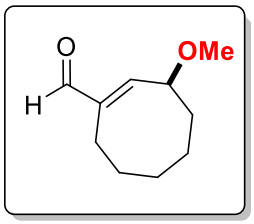

Synthesized according to GP B. m = 41 mg, 75% yield, white gum.

**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.56 (d, 7.7 Hz, 1H), 7.89-7.80 (m, 2H), 7.77-7.68 (m, 2H), 6.68 (dd, 15.9 and 5.9 Hz, 1H), 6.27 (dd, 15.9 and 7.7 Hz, 1H), 3.93 (q, 6.3 Hz, 1H), 3.88-3.78 (m, 2H), 3.32 (s, 3H), 1.97 (q, 6.7 Hz, 2H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.2, 168.4, 155.5, 134.1, 132.7, 132.1, 123.3, 78.2, 57.5, 34.4, 33.3.

**EI-HRMS (positive ion) $C_{15}H_{16}NO_4$ $[M+H]^+$:** requires 274.1079; found 274.1080.

**3-Methoxycyclooct-1-ene-1-carbaldehyde 3f**



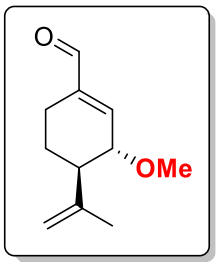

Synthesized according to GP B. m = 20 mg, 60% yield, colourless oil.

**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.45 (s, 1H), 6.55 (d, 7.2 Hz, 1H), 4.37-4.23 (m, 1H), 3.37 (s, 3H), 2.82-2.69 (m, 1H), 2.17-1.96 (m, 2H), 1.77-1.36 (m, 7H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 189.7, 152.3, 140.0, 75.4, 53.5, 31.8, 24.9, 22.4, 19.8, 19.0.

**EI-HRMS (positive ion) $C_{10}H_{17}O_2$ $[M+H]^+$:** requires 169.1223; found 169.1225.

**3-Methoxy-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carbaldehyde 3g**



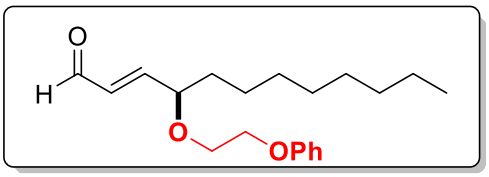

Synthesized according to GP B. m = 15 mg, 42% yield, colourless oil.

**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.52 (s, 1H), 6.78 (s, 1H), 4.88 (s, 1H), 4.81 (s, 1H), 4.06-4.02 (m, 1H), 3.45 (s, 3H), 2.40-2.27 (m, 2H), 2.22-2.12 (m, 1H), 1.88-1.80 (m, 1H), 1.79 (s, 3H), 1.69-1.61 (m, 1H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.8, 148.1, 146.1, 142.3, 111.8, 78.3, 56.8, 46.9, 26.2, 21.6, 20.3.

**EI-HRMS (positive ion) $C_{11}H_{17}O_2$ $[M+H]^+$:** requires 181.1229; found 181.1224.

**(*E*)-4-(2-Phenoxyethoxy)dodec-2-enal 3h**



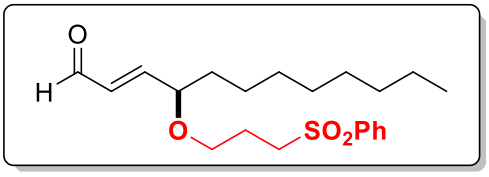

Synthesized according to GP B. m = 34 mg, 71% yield, colourless oil.

**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.54 (d, 7.9 Hz, 1H), 7.91 (d, 7.4 Hz, 2H), 7.67 (t, 7.4 Hz, 1H), 7.61-7.55 (m, 2H), 6.63 (dd, 15.9 and 6.1 Hz, 1H), 6.14 (dd, 15.9 and 7.9 Hz, 1H), 3.89 (q, 6.1 Hz, 1H), 3.56-3.47 (m, 1H), 3.44-3.36 (m, 1H), 3.25-3.17 (m, 2H), 2.04-1.94 (m, 2H), 1.60-1.47 (m, 2H), 1.33-1.19 (m, 12H), 0.88 (t, 6.5 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.5, 158.7, 157.3, 132.2, 129.5, 121.0, 114.6, 79.6, 68.2, 67.4, 34.8, 31.9, 29.5, 29.5, 29.3, 25.2, 22.7, 14.2.

**EI-HRMS (positive ion) $C_{20}H_{31}O_3$ $[M+H]^+$:** requires 319.2273; found 319.2288.

**(*E*)-4-(3-((λ1-oxidanyl)(oxo)(phenyl)-l5-sulfanyl)propoxy)dodec-2-enal 3i**




Synthesized according to GP B. m = 36.5 mg, 48% yield, white solid.

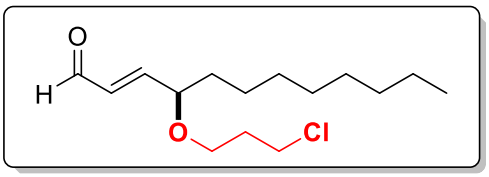
**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.54 (d, 7.9 Hz, 1H), 7.91 (d, 7.4 Hz, 2H), 7.67 (t, 7.4 Hz, 1H), 7.61-7.55 (m, 2H), 6.63 (dd, 15.9 and 6.1 Hz, 1H), 6.14 (dd, 15.9 and 7.9 Hz, 1H), 3.89 (q, 6.1 Hz, 1H), 3.56-3.47 (m, 1H), 3.44-3.36 (m, 1H), 3.25-3.17 (m, 2H), 2.04-1.94 (m, 2H), 1.60-1.47 (m, 2H), 1.33-1.19 (m, 12H), 0.88 (t, 6.5 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.3, 156.9, 139.1, 133.8, 132.2, 129.4, 128.1, 79.2, 67.0, 53.4, 34.6, 31.9, 29.5, 29.5, 29.3, 25.1, 23.5, 22.7, 14.2.

**EI-HRMS (positive ion) $C_{21}H_{33}SO_4$ $[M+H]^+$:** requires 381.2100; found 381.2101.

**m.p. (°C)** 102-104

**(*E*)-4-(3-Chloropropoxy)dodec-2-enal 3j**



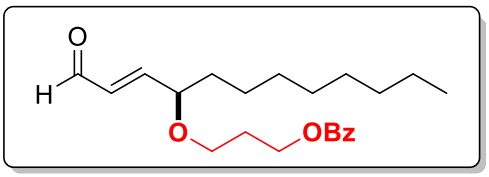

Synthesized according to GP B. m = 32 mg, 58% yield, colourless oil.

**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.58 (d, 7.9 Hz, 1H), 6.70 (dd, 15.9 and 5.9 Hz, 1H), 6.24 (dd, 15.9 and 7.9 Hz, 1H), 3.96 (q, 6.1 Hz, 1H), 3.66 (t, 6.4 Hz, 2H), 3.63-3.57 (m, 1H), 3.53-3.46 (m, 1H), 2.06-1.99 (m, 2H), 1.65-1.55 (m, 2H), 1.37-1.19 (m, 12H), 0.88 (t, 6.5 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.4, 157.4, 132.1, 79.2, 65.8, 41.8, 34.7, 32.9, 31.9, 29.5, 29.5, 29.2, 25.1, 22.7, 14.1.

**EI-HRMS (positive ion) $C_{15}H_{28}ClO_2$ $[M+H]^+$:** requires 275.1778; found 275.1781.

**(*E*)-3-((1-Oxododec-2-en-4-yl)oxy)propyl benzoate 3k**



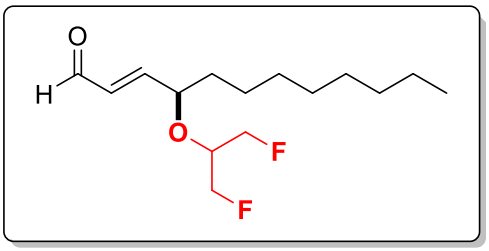

Synthesized according to GP B. m = 21 mg, 45% yield, colourless oil.

**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.54 (d, 7.7 Hz, 1H), 8.03 (d, 7.4 Hz, 2H), 7.56 (t, 7.4 Hz, 1H), 7.44 (t, 7.4 Hz, 2H), 6.69 (dd, 15.9 and 5.9 Hz, 1H), 6.23 (dd, 15.9 and 7.9 Hz, 1H), 4.44 (t, 6.4 Hz, 2H), 3.96 (q, 6.1 Hz, 1H), 3.66-3.59 (m, 1H), 3.54-3.47 (m, 1H), 2.5 (quint, 6.1 Hz, 2H), 1.65-1.53 (m, 2H), 1.37-1.20 (m, 12H), 0.87 (t, 6.5 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.4, 166.5, 157.4, 133.0, 132.2, 130.3, 129.6, 128.4, 79.2, 66.0, 62.0, 34.8, 31.9, 29.5, 29.5, 29.3, 29.3, 25.1, 22.7, 14.1.

**EI-HRMS (positive ion) $C_{22}H_{32}NaO_4$ $[M+Na]^+$:** requires 383.2198; found 383.2190.

**(*E*)-4-((1,3-Difluoropropan-2-yl)oxy)dodec-2-enal 3l**




Synthesized according to GP B. m = 36 mg, 65% yield, colourless oil.

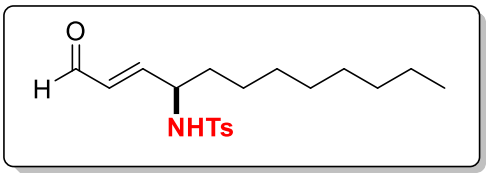
**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.59 (d, 7.9 Hz, 1H), 6.70 (dd, 15.9 and 6.1 Hz, 1H), 6.26 (dd, 15.9 and 7.7 Hz, 1H), 4.62-4.52 (m, 2H), 4.45-4.35 (m, 2H), 4.23 (q, 6.2 Hz, 1H), 3.82 (tquint, 17.4 and 4.9 Hz, 1H), 1.71-1.52 (m, 2H), 1.46-1.22 (m, 12H), 0.88 (t, 6.5 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.2, 156.3, 132.4, 81.9 (d, 172.9 Hz), 81.8 (d, 172.9 Hz), 79.0, 75.4 (t, 19.8 Hz), 35.1, 31.8, 29.5, 29.5, 29.2, 25.1, 22.7, 14.1.

**$^{19}$F NMR (188 MHz, $CDCl_3$) δ (ppm):** -230.65 (td, 47.4 and 17.4 Hz, 1F), -231.00 (td, 47.4 and 17.4 Hz, 1F).

**EI-HRMS (positive ion) $C_{15}H_{27}O_2F_2$ $[M+H]^+$:** requires 277.1979; found 277.1967.

**(*E*)-4-Methyl-*N*-(1-oxododec-2-en-4-yl)benzenesulfonamide 4a**



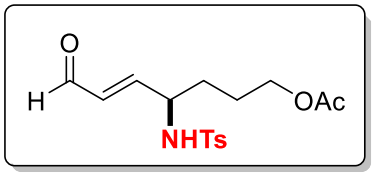

Synthesized according to GP C. m = 38 mg, 54% yield, colourless oil.

**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.36 (d, 7.4 Hz, 1H), 7.72 (d, 8.2 Hz, 2H), 7.29 (d, 8.2 Hz, 2H), 6.49 (dd, 15.6 and 6.4 Hz, 1H), 6.01 (dd, 15.6 and 7.7 Hz, 1H), 5.00 (d, 7.9 Hz, 1H), 3.98 (quint, 6.9 Hz, 1H), 2.41 (s, 3H), 1.52 (q, 6.3 Hz, 2H), 1.29-1.12 (m, 12H), 0.87 (t, 6.8 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 192.9, 155.6, 144.0, 137.4, 132.1, 129.8, 127.2, 54.8, 34.8, 31.8, 29.3, 29.2, 29.1, 25.2, 22.7, 21.6, 14.1.

**EI-HRMS (negative ion) $C_{19}H_{28}NSO_3$ $[M-H]^-$:** requires 350.1790; found 350.1788.

**(*E*)-4-((4-Methylphenyl)sulfonamido)-7-oxohept-5-en-1-yl acetate 4b**



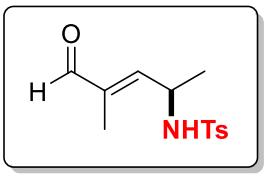

Synthesized according to GP C. m = 30 mg, 44% yield, colourless oil.

**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.36 (d, 7.4 Hz, 1H), 7.72 (d, 7.9 Hz, 2H), 7.29 (d, 7.9 Hz, 2H), 6.45 (dd, 15.6 and 6.1 Hz, 1H), 5.97 (dd, 15.6 and 7.7 Hz, 1H), 4.92 (d, 8.2 Hz, 1H), 4.11-3.96 (m, 3H), 2.41 (s, 3H), 2.03 (s, 3H), 1.71-1.60 (m, 4H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 192.6, 171.1, 154.4, 141.1, 137.3, 132.3, 129.9, 127.2, 63.4, 54.5, 31.4, 24.7, 21.6, 20.9.

**EI-HRMS (positive ion) $C_{16}H_{20}NSO_4$ $[M+H-H_2O]^+$:** requires 322.1113; found 322.1113.

**(*E*)-4-Methyl-*N*-(4-methyl-5-oxopent-3-en-2-yl)benzenesulfonamide 4c**



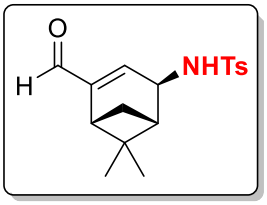

Synthesized according to GP C. m = 23 mg, 43% yield, colourless oil.

**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.14 (s, 1H), 7.70 (d, 7.7 Hz, 2H), 7.27 (d, 7.7 Hz, 2H), 6.01 (d, 9.0 Hz, 1H), 4.81 (d, 6.1 Hz, 1H), 4.36 (sext, 7.2 Hz, 1H), 2.41 (s, 3H), 1.65 (s, 3H), 1.26 (d, 6.7 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 194.4, 152.3, 144.0, 138.5, 137.4, 129.7, 127.3, 47.8, 21.6, 20.9, 9.2.

**EI-HRMS (positive ion) $C_{13}H_{18}NSO_3$ $[M+H]^+$:** requires 268.1007; found 268.0997.

***N*-(4-Formyl-6,6-dimethylbicyclo[3.1.1]hept-3-en-2-yl)-4-methylbenzenesulfonamide 4d**




Synthesized according to GP C. m = 38 mg, 60% yield, dr = 4.5:1, colourless oil.

**Major diastereomer:**

**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.40 (s, 1H), 7.79 (d, 7.9 Hz, 2H), 7.33 (d, 7.9 Hz, 2H), 6.31 (d, 1.0 Hz, 1H), 5.15 (d, 9.2 Hz, 1H), 4.16 (dt, 9.0 and 2.5 Hz, 1H), 2.82 (t, 5.6 Hz, 1H), 2.45 (s, 3H), 2.40-2.32 (m, 1H), 2.10-2.03 (m, 1H), 1.30 (s, 3H), 1.02 (d, 9.7 Hz, 1H), 0.72 (s, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 191.1, 151.4, 144.0, 143.5, 137.5, 129.7, 127.1, 56.2, 47.2, 44.4, 38.0, 35.1, 25.8, 22.7, 20.5.

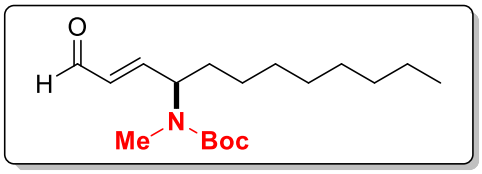
**Minor diastereomer:**

**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.43 (s, 1H), 7.79 (d, 7.9 Hz, 2H), 7.30 (d, 7.9 Hz, 2H), 6.40 (d, 1.3 Hz, 1H), 5.11 (d, 9.2 Hz, 1H), 4.31 (dt, 8.7 and 2.5 Hz, 1H), 2.79 (t, 5.6 Hz, 1H), 2.55-2.48 (m, 1H), 2.45 (s, 3H), 2.20-2.15 (m, 1H), 1.31 (s, 3H), 1.20 (d, 9.7 Hz, 1H), 0.85 (s, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 191.1, 152.1, 143.9, 142.8, 137.9, 130.0, 127.0, 53.8, 46.2, 44.4, 38.1, 28.5, 25.8, 21.6, 20.5.

**EI-HRMS (positive ion) $C_{17}H_{22}NSO_3$ $[M+H]^+$:** requires 320.1320; found 320.1320.

**(E)-*Tert*-butyl methyl(1-oxododec-2-en-4-yl)carbamate 4e**



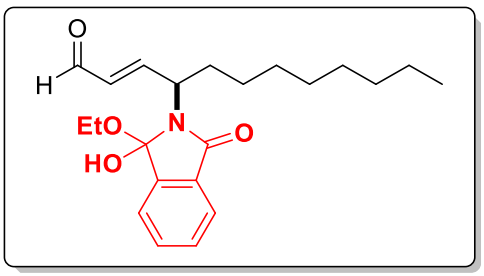

Synthesized according to GP C. m = 10 mg, 41% NMR yield, 21% isolated yield, light yellow oil.

**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.56 (d, *J* = 7.7 Hz, 1H), 6.72 (dd, *J* = 15.8, 4.0 Hz, 1H), 6.09 (dd, *J* = 15.8, 7.7 Hz, 1H), 5.03-4.64 (m, 1H), 2.69 (s, 3H), 1.74-1.54 (m, 2H), 1.46 (s, 9H), 1.38-1.15 (m, 12H), 0.87 (t, *J* = 6.0 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** (some signals are missing due to signal broadening) 193.6, 156.5, 132.1, 80.2, 31.9, 29.5, 29.2, 29.2, 28.4, 26.0, 22.7, 14.1.

**EI-HRMS (positive ion) $C_{18}H_{33}NO_3Na$ $[M+Na]^+$:** requires 334.2350, found 334.2358.

**(*E*)-4-(1-Ethoxy-1-hydroxy-3-oxoisoindolin-2-yl)dodec-2-enal 4f**

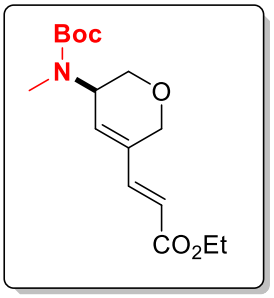



Synthesized according to GP C. m = 16 mg, 42% NMR yield, 29% isolated yield, light yellow oil.

**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.61 (d, *J* = 7.7 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.59-7.45 (m, 3H), 6.88 (dd, *J* = 15.8, 4.6 Hz, 1H), 6.32 (dd, *J* = 15.8, 7.7 Hz, 1H), 6.09 (d, *J* = 8.0 Hz, 1H), 4.98-4.85 (m, 1H), 4.35 (q, *J* = 7.0 Hz, 2H), 1.83-1.59 (m, 2H), 1.51-1.19 (m, 15H), 0.89 (t, *J* = 5.7 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.4, 168.9, 166.6, 156.8, 137.7, 131.9, 131.5, 130.2, 129.9, 129.6, 127.8, 61.7, 50.8, 34.1, 31.8, 29.4, 29.4, 29.2, 25.8, 22.7, 14.2, 14.1.

**Ethyl (*E*)-3-(5-((tert-butoxycarbonyl)(methyl)amino)-5,6-dihydro-2H-pyran-3-yl)acrylate 4g'**



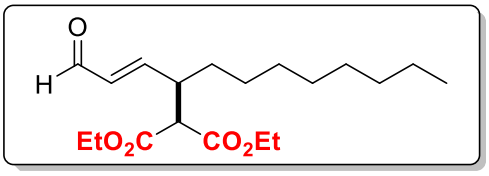

Synthesized according to GP C. At the end of the reaction, carbethoxymethylene)triphenylphosphorane (5 equiv.) was added and the mixture was stirred at room temperature overnight. 45% NMR yield of the aldehyde, 17% isolated overall yield as the ester (m = 8 mg), light yellow oil.

**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.22 (d, *J* = 16.2 Hz, 1H), 6.09 (broad s, 1H), 5.73 (d, *J* = 16.2 Hz, 1H), 4.88-4.57 (m, 1H), 4.40-4.11 (m, 4H), 3.90-3.65 (m, 2H), 2.79 (s, 3H), 1.46 (s, 9H), 1.30 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** (some signals are missing due to signal broadening) 166.6, 142.1, 137.6, 132.9, 117.6, 80.1, 68.2, 67.3, 64.5, 60.6, 50.2, 48.6, 30.9, 28.4, 17.7, 14.3.

**EI-HRMS (positive ion) $C_{16}H_{26}NO_5$ $[M+H]^+$**: requires 312.1811; found 312.1811.

**Diethyl (*E*)-2-(1-oxododec-2-en-4-yl)malonate 6a**



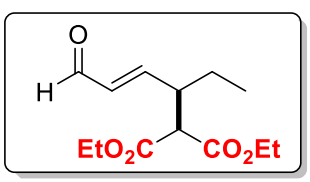

Synthesized according to GP D. m = 51 mg, 75% yield, colourless oil.

**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.51 (d, 7.9 Hz, 1H), 6.80 (dd, 15.6 and 9.2 Hz, 1H), 6.12 (dd, 15.6 and 7.9 Hz, 1H), 4.20 (q, 7.2 Hz, 2H), 4.17 (q, 7.2 Hz, 2H), 3.48 (d, 7.7 Hz, 1H), 3.11-2.99 (m, 1H), 1.59-1.43 (m, 2H), 1.30-1.19 (m, 18H), 0.86 (t, 6.5 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.7, 167.8, 167.6, 157.2, 134.4, 61.8, 61.6, 55.8, 42.5, 31.9, 31.8, 29.4, 29.3, 29.2, 27.1, 22.7, 14.1.

**EI-HRMS (positive ion) $C_{29}H_{33}O_5$ $[M+H]^+$:** requires 341.2328; found 341.2323.

**Diethyl (*E*)-2-(6-oxohex-4-en-3-yl)malonate 6b**



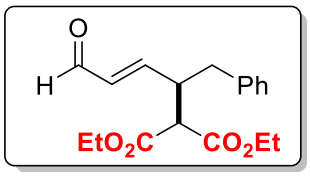
Synthesized according to GP D. m = 35 mg, 68% yield, colourless oil.

**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.51 (d, 7.7 Hz, 1H), 6.80 (dd, 15.6 and 9.2 Hz, 1H), 6.13 (dd, 15.6 and 7.9 Hz, 1H), 4.20 (q, 7.2 Hz, 2H), 4.17 (q, 7.2 Hz, 2H), 3.50 (d, 7.7 Hz, 1H), 3.03-2.93 (m, 1H), 1.70-1.61 (m, 1H), 1.55-1.45 (m, 1H), 1.26 (t, 7.2 Hz, 3H), 1.23 (t, 7.2 Hz, 3H), 0.91 (t, 7.4 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.6, 167.8, 167.6, 156.8, 134.5, 61.8, 61.6, 55.5, 44.0, 25.0, 14.1, 11.6.

**EI-HRMS (positive ion) $C_{13}H_{20}O_5Na$ $[M+Na]^+$:** requires 279.1208; found 279.1201.

**Diethyl (*E*)-2-(5-oxo-1-phenylpent-3-en-2-yl)malonate 6c**



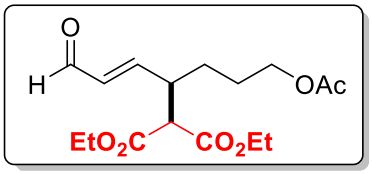

Synthesized according to GP D. m =53 mg, 84% yield, colourless oil.

**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.44 (d, 7.7 Hz, 1H), 7.32-7.20 (m, 3H), 7.14 (d, 7.4 Hz, 2H), 6.88 (dd, 15.9 and 8.7 Hz, 1H), 5.97 (dd, 15.9 and 7.7 Hz, 1H), 4.20 (q, 7.2 Hz, 4H), 3.52 (d, 6.7 Hz, 1H), 3.36 (quint, 7.5 Hz, 1H), 2.97 (dd, 13.6 and 6.1 Hz, 1H), 2.79 (dd, 13.6 and 8.2 Hz, 1H), 1.26 (t, 7.2 Hz, 6H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.5, 167.8, 167.6, 156.1, 137.7, 134.2, 129.2, 128.7, 126.9, 61.9, 61.7, 54.6, 44.0, 38.1, 14.1.

**EI-HRMS (positive ion) $C_{18}H_{23}O_5$ $[M+H]^+$:** requires 319.1545; found 319.1551.

**Diethyl (*E*)-2-(7-acetoxy-1-oxohept-2-en-4-yl)malonate 6d**



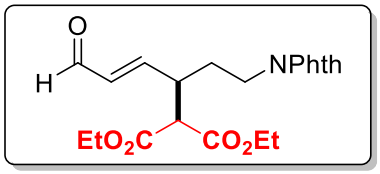

Synthesized according to GP D. m = 54 mg, 82% yield, colourless oil.

**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.51 (d, 7.7 Hz, 1H), 6.79 (dd, 15.9 and 9.2 Hz, 1H), 6.13 (dd, 15.9 and 7.9 Hz, 1H), 4.20 (q, 7.2 Hz, 2H), 4.16 (q, 7.2 Hz, 2H), 4.03 (t, 5.1 Hz, 1H), 3.48 (d, 7.4 Hz, 1H), 3.11-3.01 (m, 1H), 2.02 (s, 3H), 1.68-1.52 (m, 4H), 1.25 (t, 6.9 Hz, 3H), 1.23 (t, 6.9 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.4, 171.0, 167.5, 167.4, 156.0, 134.7, 63.7, 61.9, 61.7, 55.7, 42.1, 28.3, 26.3, 20.9, 14.1.

**EI-HRMS (positive ion) $C_{16}H_{24}O_7Na$ $[M+Na]^+$:** requires 351.1420; found 351.1425.

**Diethyl (*E*)-2-(1-(1,3-dioxoisoindolin-2-yl)-6-oxohex-4-en-3-yl)malonate 6e**




Synthesized according to GP D. m = 41 mg, 51% yield, white solid.

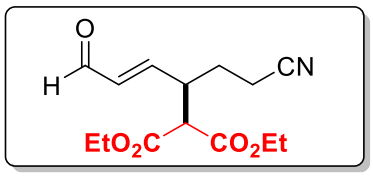
**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.51 (d, 7.7 Hz, 1H), 7.91-7.83 (m, 2H), 7.79-7.72 (m, 2H), 6.88 (dd, 15.9 and 9.2 Hz, 1H), 6.27 (dd, 15.9 and 7.7 Hz, 1H), 4.22 (q, 7.2 Hz, 2H), 4.19 (q, 7.2 Hz, 2H), 3.73 (t, 6.9 Hz, 2H), 3.59 (d, 7.2 Hz, 1H), 3.21-3.11 (m, 1H), 2.10-1.93 (m, 2H), 1.27 (t, 7.2 Hz, 3H), 1.26 (t, 7.2 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.3, 168.2, 167.3, 167.3, 155.1, 134.9, 134.1, 132.0, 123.4, 62.0, 61.8, 55.5, 40.0, 35.7, 30.6, 14.1.

**EI-HRMS (positive ion) $C_{21}H_{24}NO_7$ $[M+H]^+$:** requires 402.1553; found 402.1547.

**m.p. (°C)** 72-74

**Diethyl (*E*)-2-(1-cyano-6-oxohex-4-en-3-yl)malonate 6f**



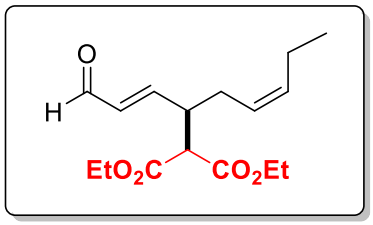

Synthesized according to GP D. m = 24 mg, 43% yield, colourless oil.

**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.55 (d, 7.7 Hz, 1H), 6.78 (dd, 15.9 and 9.5 Hz, 1H), 6.22 (dd, 15.9 and 7.7 Hz, 1H), 4.23 (q, 7.2 Hz, 2H), 4.20 (q, 7.2 Hz, 2H), 3.52 (d, 6.9 Hz, 1H), 3.23-3.12 (m, 1H), 2.46-2.24 (m, 2H), 2.11-2.00 (m, 1H), 1.95-1.83 (m, 1H), 1.28 (t, 7.2 Hz, 3H), 1.26 (t, 7.2 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 192.8, 167.1, 153.1, 135.7, 118.3, 62.2, 62.1, 55.3, 41.4, 27.4, 15.4, 14.1.

**EI-HRMS (positive ion) $C_{14}H_{19}O_5Na$ $[M+Na]^+$:** requires 304.1161; found 304.1158.

**Diethyl 2-(2*E*,6*Z*)-1-oxonona-2,6-dien-4-yl)malonate 6g**



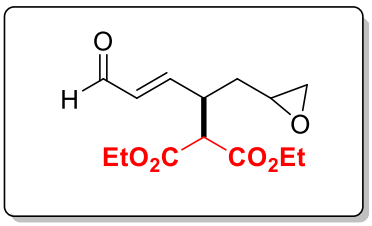

Synthesized according to GP D. m = 48 mg, 81% yield, colourless oil.

**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.48 (d, 7.9 Hz, 1H), 6.86 (dd, 15.6 and 8.7 Hz, 1H), 6.10 (dd, 15.6 and 7.9 Hz, 1H), 5.55-5.45 (m, 1H), 5.28-5.17 (m, 1H), 4.20 (q, 7.2 Hz, 2H), 4.17 (q, 7.2 Hz, 2H), 3.55 (d, 7.4 Hz, 1H), 3.16-3.06 (m, 1H), 2.43-2.22 (m, 2H), 1.99 (quint, 7.4 Hz, 1H), 1.26 (t, 6.9 Hz, 3H), 1.23 (t, 6.9 Hz, 3H), 0.93 (t, 7.4 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.6, 167.9, 167.6, 156.6, 135.3, 134.1, 124.0, 61.8, 61.6, 54.8, 42.5, 29.5, 20.7, 14.1.

**EI-HRMS (positive ion) $C_{16}H_{25}O_4Na$ $[M+Na]^+$:** requires 319.1521; found 319.1509.

**Diethyl 2-((*E*)-1-(oxiran-2-yl)-5-oxopent-3-en-2-yl)malonate 6h**




Synthesized according to GP D. m = 45 mg, 80% yield, dr = 1.1:1, colourless oil.

**Major diastereomer:**

**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.53 (d, 7.7 Hz, 1H), 6.94 (dd, 15.9 and 7.7 Hz, 1H), 6.20 (dd, 15.9 and 7.9 Hz, 1H), 4.20 (q, 7.2 Hz, 2H), 4.17 (q, 7.2 Hz, 2H), 3.59 (d, 7.2 Hz, 1H), 3.38-3.25 (m, 1H), 2.94-2.87 (m, 1H), 2.79-2.72 (m, 1H), 2.49-2.42 (m, 1H), 1.98-1.88 (m, 1H), 1.76-1.64 (m, 1H), 1.26 (t, 6.9 Hz, 3H), 1.24 (t, 6.9 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.5, 167.4, 167.4, 155.8, 134.1, 62.0, 61.9, 55.1, 50.1, 46.7, 40.5, 35.0, 14.1.

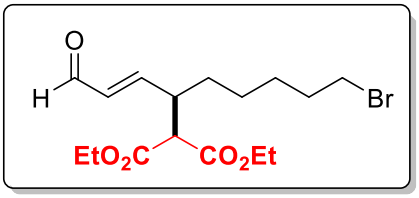
**Major diastereomer:**

**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.53 (d, 7.7 Hz, 1H), 6.92 (dd, 15.9 and 7.2 Hz, 1H), 6.17 (dd, 15.9 and 7.9 Hz, 1H), 4.20 (q, 7.2 Hz, 2H), 4.17 (q, 7.2 Hz, 2H), 3.62 (d, 6.4 Hz, 1H), 3.38-3.25 (m, 1H), 2.94-2.87 (m, 1H), 2.79-2.72 (m, 1H), 2.49-2.42 (m, 1H), 1.98-1.88 (m, 1H), 1.76-1.64 (m, 1H), 1.26 (t, 6.9 Hz, 3H), 1.24 (t, 6.9 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.5, 167.5, 167.4, 155.6, 134.5, 62.0, 61.8, 55.3, 49.9, 47.3, 40.3, 35.0, 14.1.

**EI-HRMS (positive ion) $C_{14}H_{20}O_6Na$ $[M+Na]^+$:** requires 307.1158; found 307.1172.

**Diethyl (*E*)-2-(9-bromo-1-oxonon-2-en-4-yl)malonate 6i**



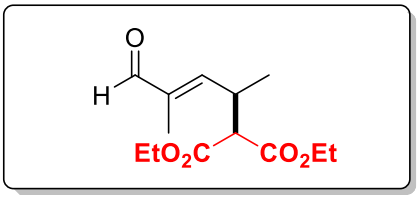

Synthesized according to GP D. m = 43 mg, 55% yield, colourless oil.

**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.52 (d, 7.9 Hz, 1H), 6.79 (dd, 15.9 and 9.5 Hz, 1H), 6.13 (dd, 15.9 and 7.9 Hz, 1H), 4.21 (q, 7.2 Hz, 2H), 4.17 (q, 7.2 Hz, 2H), 3.48 (d, 7.4 Hz, 1H), 3.38 (d, 6.7 Hz, 2H), 3.11-3.01 (m, 1H), 1.83 (quint, 7.2 Hz, 2H), 1.56-1.38 (m, 6H), 1.25 (t, 6.9 Hz, 3H), 1.22 (t, 6.9 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.6, 167.9, 167.6, 156.6, 135.3, 134.1, 124.0, 61.8, 61.6, 54.8, 42.5, 29.5, 20.7, 14.1.

**EI-HRMS (positive ion) $C_{16}H_{26}O_5Br$ $[M+H]^+$:** requires 377.0964; found 377.0952.

**Diethyl (*E*)-2-(4-methyl-5-oxopent-3-en-2-yl)malonate 6j**



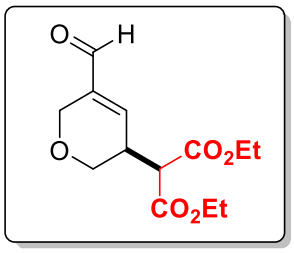

Synthesized according to GP D. m = 21.5 mg, 42% yield, colourless oil.

**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.39 (s, 1H), 6.39 (d, 10.0 Hz, 1H), 4.22 (q, 7.2 Hz, 2H), 4.15 (q, 7.2 Hz, 2H), 3.53-3.42 (m, 1H), 3.39 (d, 8.7 Hz, 1H), 1.80 (s, 3H), 1.28 (t, 6.9 Hz, 3H), 1.22 (t, 6.9 Hz, 3H), 1.17 (d, 6.4 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 195.2, 167.8, 154.0, 139.5, 61.7, 61.6, 57.0, 33.5, 17.7, 14.1, 14.1, 9.3.

**EI-HRMS (positive ion) $C_{13}H_{20}O_5Na$ $[M+Na]^+$:** requires 279.1208; found 279.1198.

**Diethyl 2-(5-formyl-3,6-dihydro-2H-pyran-3-yl)malonate 6k**



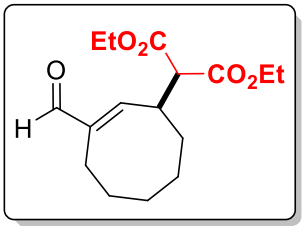

Synthesized according to GP D. m = 21.5 mg, 40% yield, colourless oil.

**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.43 (s, 1H), 6.92-6.88 (m, 1H), 4.34-4.30 (m, 2H), 4.24 (q, 7.2 Hz, 2H), 4.23 (q, 7.2 Hz, 2H), 3.82 (dd, 11.8 and 4.4 Hz, 1H), 3.72 (dd, 11.8 and 4.4 Hz, 1H), 3.54 (d, 8.4 Hz, 1H), 3.24-3.15 (m, 1H), 1.28 (t, 6.9 Hz, 6H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 191.7, 167.6, 146.4, 141.3, 66.4, 63.7, 62.0, 61.9, 53.3, 31.5, 14.1.

**EI-HRMS (positive ion) $C_{13}H_{19}O_6$ $[M+H]^+$:** requires 271.1182; found 271.1193.

**Diethyl (*E*)-2-(3-formylcyclooct-2-en-1-yl)malonate 6l**



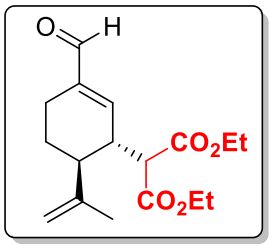

Synthesized according to GP D. m = 32 mg, 54% yield, colourless oil.

**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.35 (s, 1H), 6.47 (m, 8.2 Hz, 1H), 4.16 (q, 7.2 Hz, 2H), 4.13 (q, 7.2 Hz, 2H), 3.48-3.38 (m, 2H), 2.71 (dt, 9.7 and 4.1 Hz, 1H), 2.05 (td, 13.2 and 2.8 Hz, 1H), 1.79-1.67 (m, 2H), 1.79-1.67 (m, 2H), 1.62-1.53 (m, 2H), 1.43-1.29 (m, 2H), 1.21 (t, 7.2 Hz, 3H), 1.18 (t, 7.2 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 191.7, 167.6, 146.4, 141.3, 66.4, 63.7, 62.0, 61.9, 53.3, 31.5, 14.1.

**EI-HRMS (positive ion) $C_{13}H_{19}O_6$ $[M+H]^+$:** requires 271.1182; found 271.1193.

**Diethyl 2-(3-formyl-6-(prop-1-en-2-yl)cyclohex-2-en-1-yl)malonate 6m**



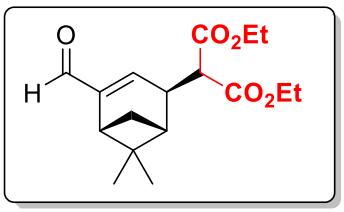

Synthesized according to GP D. m = 29.5 mg, 48% yield, colourless oil. dr > 95:5.

**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.46 (s, 1H), 6.89 (s, 1H), 4.91 (s, 1H), 4.83 (s, 1H), 4.24 (qd, 7.2 and 2.8 Hz, 2H), 4.17 (q, 7.2 Hz, 2H), 3.72 (d, 3.6 Hz, 1H), 3.15-3.04 (m, 1H), 2.51-2.40 (m, 1H), 2.24 (td, 11.4 and 2.6 Hz, 1H), 2.14-2.00 (m, 1H), 1.90-1.81 (m, 1H), 1.71 (s, 3H), 2.24 (td, 12.4 and 5.1 Hz, 1H), 1.29 (t, 7.2 Hz, 3H), 1.23 (t, 7.2 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 194.1, 169.8, 167.8, 150.5, 145.7, 141.2, 113.4, 61.9, 61.4, 52.2, 45.2, 39.9, 27.4, 21.4, 19.0, 14.2, 14.1.

**EI-HRMS (positive ion) $C_{17}H_{25}O_5$ $[M+H]^+$:** requires 309.1702; found 309.1705.

**Diethyl 2-(4-formyl-6,6-dimethylbicyclo[3.1.1]hept-3-en-2-yl)malonate 6n**



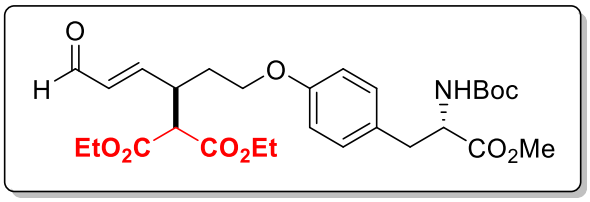

Synthesized according to GP D. m = 36 mg, 58% yield, colourless oil. dr > 95:5.

**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.44 (s, 1H), 6.62 (s, 1H), 4.25 (q, 7.2 Hz, 2H), 4.21 (q, 7.2 Hz, 2H), 3.43-3.32 (m, 2H), 2.88 (t, 5.4 Hz, 1H), 2.39 (dt, 10.0 and 5.6 Hz, 1H), 2.02 (t, 5.6 Hz, 1H), 1.35 (s, 3H), 1.29 (t, 7.2 Hz, 3H), 1.27 (t, 7.2 Hz, 3H), 1.01 (d, 9.7 Hz, 1H), 0.79 (s, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 191.3, 168.0, 167.8, 152.4, 146.3, 61.8, 61.8, 54.3, 44.1, 41.1, 40.8, 38.5, 27.9, 25.9, 20.6, 14.1.

**EI-HRMS (positive ion) $C_{17}H_{25}O_5$ $[M+H]^+$:** requires 309.1702; found 309.1696.

**Diethyl 2-((*E*)-1-(4-((S)-2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)phenoxy)-6-oxohex-4-en-3-yl)malonate 6o**



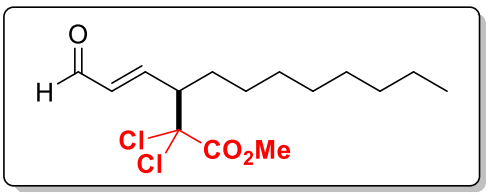

Synthesized according to GP D. m = 67 mg, 61% yield, white gum.

**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.52 (d, 7.9 Hz, 1H), 7.01 (d, 8.2 Hz, 1H), 6.92 (dd, 15.9 and 9.2 Hz, 1H), 6.77 (d, 8.2 Hz, 2H), 6.14 (dd, 15.9 and 7.9 Hz, 1H), 4.96 (d, 7.7 Hz, 1H), 4.59-4.45 (m, 1H), 4.34-4.13 (m, 5H), 4.02-3.86 (m, 2H), 3.70 (s, 3H), 3.62 (d, 6.9 Hz, 1H), 3.42-3.32 (m, 1H), 3.07-2.94 (m, 2H), 2.20-2.07 (m, 1H), 2.06-1.94 (m, 1H), 1.41 (s, 9H), 1.26 (t, 7.2 Hz, 3H), 1.25 (t, 7.2 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.5, 172.4, 167.6, 167.6, 157.5, 156.0, 155.1, 134.5, 130.4, 128.4, 114.5, 80.0, 64.9, 61.9, 61.8, 55.4, 54.6, 52.2, 39.6, 37.5, 31.4, 28.3, 14.1, 13.9.

**EI-HRMS (positive ion) $C_{28}H_{39}NO_{10}Na$ $[M+Na]^+$:** requires 572.2472; found 572.2484.

**Methyl (*E*)-2,2-dichloro-3-(3-oxoprop-1-en-1-yl)undecanoate 6p**



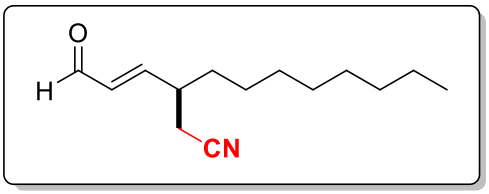

Synthesized according to GP D. m = 34 mg, 53% yield, colourless oil.

**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.58 (d, 7.7 Hz, 1H), 6.68 (dd, 15.6 and 9.5 Hz, 1H), 6.22 (dd, 15.6 and 7.7 Hz, 1H), 3.89 (s, 3H), 3.29 (td, 10.0 and 2.6 Hz, 1H), 1.80-1.55 (m, 2H), 1.34-1.19 (m, 12H), 0.87 (t, 6.4 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.1, 165.7, 152.1, 137.0, 86.5, 54.7, 54.6, 31.8, 30.0, 29.3, 29.2, 29.2, 27.0, 22.7, 14.1.

**EI-HRMS (positive ion) $C_{15}H_{23}O_3Cl_2$ $[M-H_2+H]^+$:** requires 321.1024; found 321.1018.

**(*E*)-3-(3-Oxoprop-1-en-1-yl)undecanenitrile 6q**



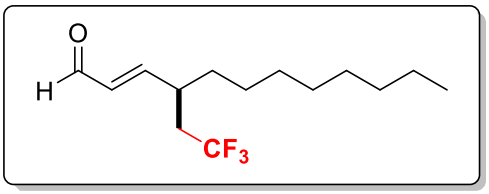

Synthesized according to GP D. m = 36 mg, 81% yield, colourless oil.

**$^{1}$H NMR (300 MHz, d6-Acetone) δ (ppm):** 9.59 (d, 7.7 Hz, 1H), 6.88 (dd, 15.6 and 7.9 Hz, 1H), 6.21 (dd, 15.6 and 7.7 Hz, 1H), 2.85-2.78 (m, 1H), 2.77-2.70 (m, 2H), 1.70-1.55 (m, 2H), 1.40-1.25 (m, 12H), 0.87 (t, 6.4 Hz, 3H).

**$^{13}$C NMR (75 MHz, d6-Acetone) δ (ppm):** 194.1, 158.4, 134.5, 118.9, 39.8, 34.0, 32.6, 29.9, 29.9, 29.8, 27.5, 23.3, 22.1, 14.3.

**EI-HRMS (positive ion) $C_{14}H_{24}ON$ $[M+H]^+$:** requires 222.1858; found 222.1855.

**(*E*)-4-(2,2,2-Trifluoroethyl)dodec-2-enal 6r**



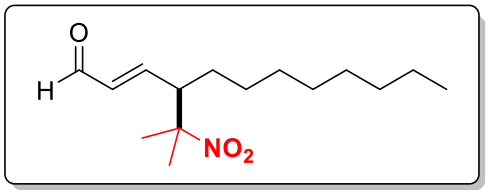

Synthesized according to GP D. m = 37.5 mg, 71% yield, colourless oil.

**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.59 (d, 7.7 Hz, 1H), 6.88 (dd, 15.6 and 7.9 Hz, 1H), 6.21 (dd, 15.6 and 7.7 Hz, 1H), 2.85-2.78 (m, 1H), 2.77-2.70 (m, 2H), 1.70-1.55 (m, 2H), 1.40-1.25 (m, 12H), 0.87 (t, 6.4 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 193.6, 158.5, 133.4, 126.3 (q, 277 Hz), 38.4 (q, 28 Hz), 37.1 (br. s), 34.2, 31.8, 29.4, 29.4, 29.2, 26.7, 22.7, 14.1.

**EI-HRMS (negative ion) $C_{14}H_{22}OF_3$ $[M-H]^-$:** requires 263.1623; found 263.1629.

**(*E*)-4-(2-nitropropan-2-yl)dodec-2-enal 6s**



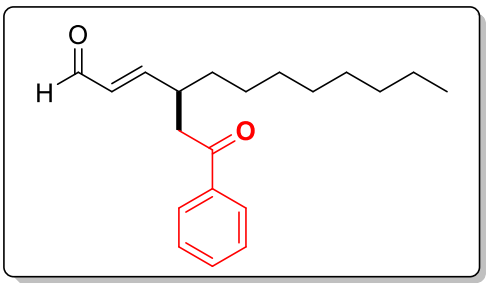

Synthesized according to GP D. m =  mg, 53% yield, colourless oil.

**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.55 (d, *J* = 7.6 Hz, 1H), 6.54 (dd, *J* = 15.6, 9.9 Hz, 1H), 6.17 (dd, *J* = 15.6, 7.6 Hz, 1H), 2.90 (td, *J* = 9.9, 3.1 Hz, 1H), 1.58 (s, 3H), 1.55 (s, 3H) 1.28-1.17 (m, 14H), 0.86 (t, *J* = 6.4 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 192.9, 153.7, 136.6, 90.5, 51.6, 31.8, 29.3, 29.2, 29.2, 28.8, 27.6, 24.6, 23.1, 22.6, 14.1.

**EI-HRMS (positive ion) $C_{15}H_{28}NO_3$ $[M+H]^+$:** requires 270.2076; found 270.2069.

**(*E*)-4-(2-Oxo-2-phenylethyl)dodec-2-enal 6t**



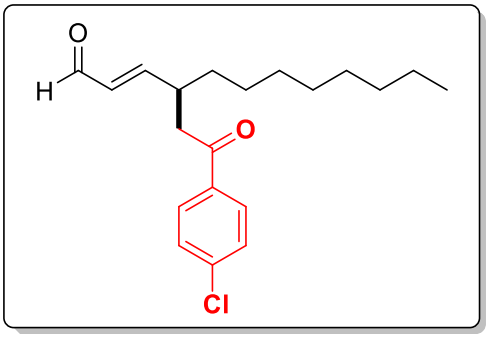

Synthesized according to GP D. m = 40 mg, 67% yield, colourless oil.

**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.49 (d, 7.7 Hz, 1H), 7.93 (d, 7.4 Hz, 2H), 7.58 (t, 7.4 Hz, 1H), 7.47 (t, 7.4 Hz, 2H), 6.80 (dd, 15.6 and 7.2 Hz, 1H), 6.11 (dd, 15.6 and 7.7 Hz, 1H), 3.19-3.05 (m, 3H), 1.62-1.48 (m, 2H), 1.33-1.17 (m, 12H), 0.87 (t, 6.5 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 197.9, 194.1, 161.2, 136.8, 133.4, 132.6, 128.8, 128.1, 42.8, 38.0, 34.0, 31.9, 29.6, 29.5, 29.3, 27.2, 22.7, 14.1.

**EI-HRMS (positive ion) $C_{20}H_{29}O_2$ $[M+H]^+$:** requires 301.2168; found 301.2170.

**(*E*)-4-(2-(4-Chlorophenyl)-2-oxoethyl)dodec-2-enal 6u**



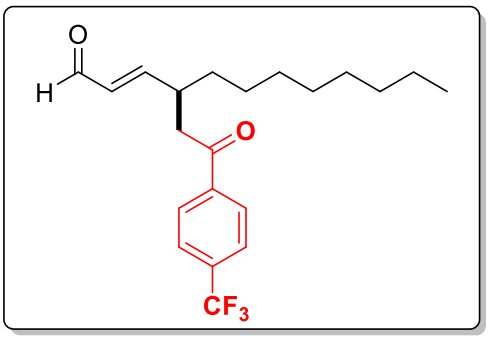

Synthesized according to GP D. m = 40.0 mg, 60% yield, colourless oil.

**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.48 (d, 7.7 Hz, 1H), 7.86 (d, 7.7 Hz, 2H), 7.44 (d, 7.7 Hz, 2H), 6.78 (dd, 15.6 and 6.1 Hz, 1H), 6.10 (dd, 15.6 and 7.7 Hz, 1H), 3.15-3.01 (m, 3H), 1.60-1.45 (m, 2H), 1.33-1.19 (m, 12H), 0.87 (t, 6.2 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 196.7, 194.0, 160.8, 139.9, 135.1, 132.6, 129.5, 129.1, 42.8, 37.9, 34.0, 31.9, 29.6, 29.5, 29.3, 27.2, 22.7, 14.1.

**EI-HRMS (positive ion) $C_{20}H_{28}ClO_2$ $[M+H]^+$:** requires 335.1778; found 335.1765.

**(*E*)-4-(2-Oxo-2-(4-(trifluoromethyl)phenyl)ethyl)dodec-2-enal 6v**




Synthesized according to GP D. m = 44.0 mg, 60% yield, colourless oil.

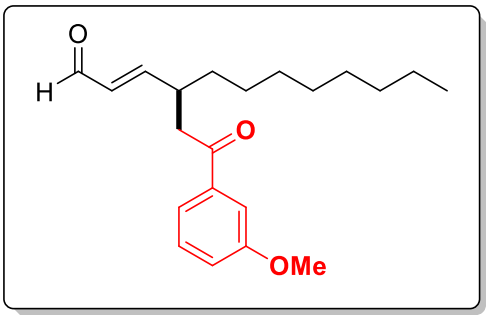
**$^{1}$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.49 (d, 7.7 Hz, 1H), 8.03 (d, 7.9 Hz, 2H), 7.74 (d, 7.9 Hz, 2H), 6.78 (dd, 15.6 and 6.9 Hz, 1H), 6.11 (dd, 15.6 and 7.7 Hz, 1H), 3.20-3.06 (m, 3H), 1.62-1.49 (m, 2H), 1.36-1.20 (m, 12H), 0.87 (t, 6.1 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 196.9, 193.8, 160.5, 139.4, 134.7 (q, 32.8 Hz), 132.8, 128.3, 125.8 (q, 3.8 Hz), 123.5 (q, 272.3 Hz), 43.1, 37.8, 34.0, 31.9, 29.5, 29.4, 29.3, 27.2, 22.7, 14.1.

**$^{19}$F NMR (188 MHz, $CDCl_3$) δ (ppm):** -63.65

**EI-HRMS (positive ion) $C_{21}H_{28}F_3O_2$ $[M+H]^+$:** requires 369.4477; found 369.4470.

**(*E*)-4-(2-(3-methoxyphenyl)-2-oxoethyl)dodec-2-enal 6w**




Synthesized according to GP D. m = 42.0 mg, 64% yield, colourless oil.

**$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.48 (d, 7.9 Hz, 1H), 7.50 (d, 7.7 Hz, 1H), 7.45 (s, 1H), 7.37 (t, 7.7 Hz, 1H), 7.12 (d, 7.7 Hz, 1H), 6.78 (dd, 15.6 and 6.4 Hz, 1H), 6.11 (dd, 15.6 and 7.7 Hz, 1H), 3.85 (s, 3H), 3.16-3.05 (m, 3H), 1.60-1.44 (m, 2H), 1.36-1.18 (m, 12H), 0.87 (t, 6.2 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm):** 197.8, 194.1, 161.2, 159.9, 138.1, 132.6, 129.7, 120.6, 119.8, 112.3, 55.5, 42.9, 38.1, 34.0, 31.9, 29.6, 29.5, 29.3, 27.2, 22.7, 14.2.

**EI-HRMS (positive ion) $C_{21}H_{31}O_3$ $[M+H]^+$:** requires 331.2273; found 331.2260.

## IX. References

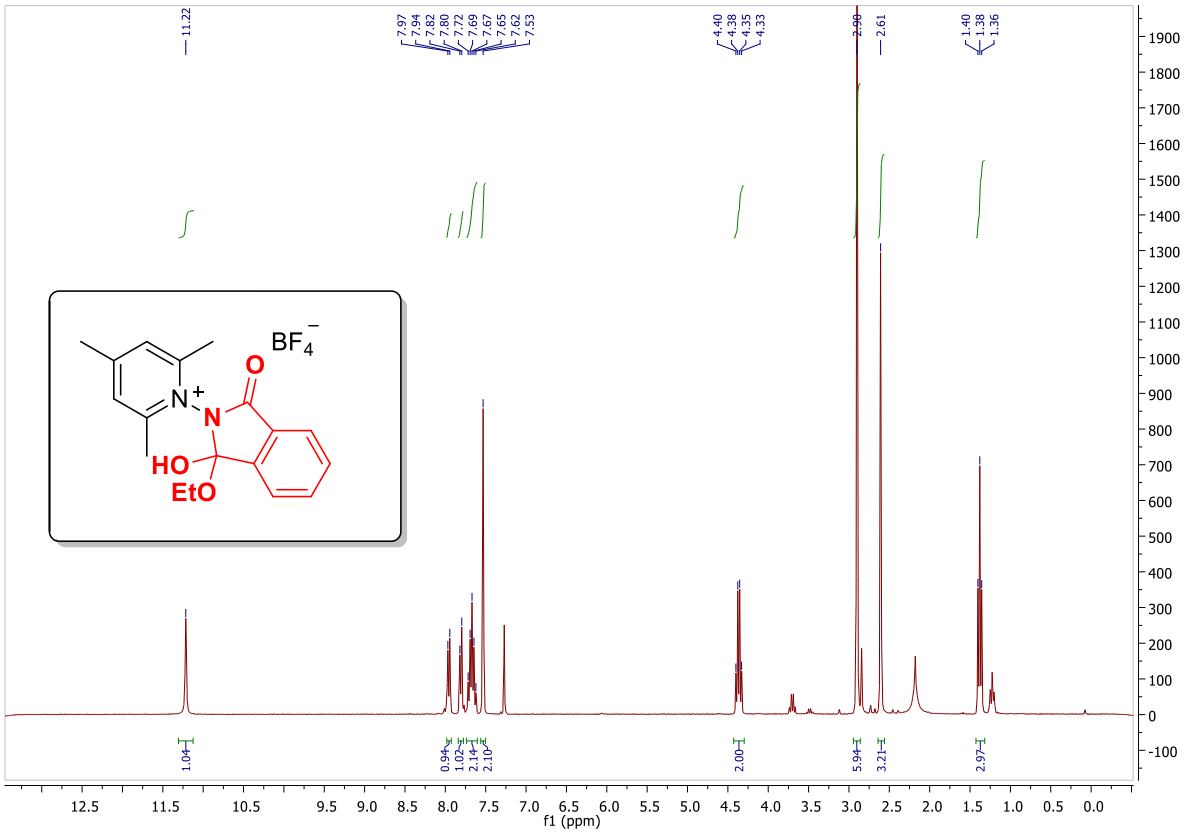
1. (a) Miyazawa, K.; Koike, T.; Akita, M. *Chem. Eur. J.* 2015, **21**, 11677; (b) Greulich, T. W.; Daniliuc, C. G.; Studer, A. *Org. Lett.* 2015, **17**, 254; (c) Barthelemy, A.; Tuccio, B.; Magnier, E.; Dagousset, G. *Angew. Chem. Int. Ed.* 2018, **57**, 13790.

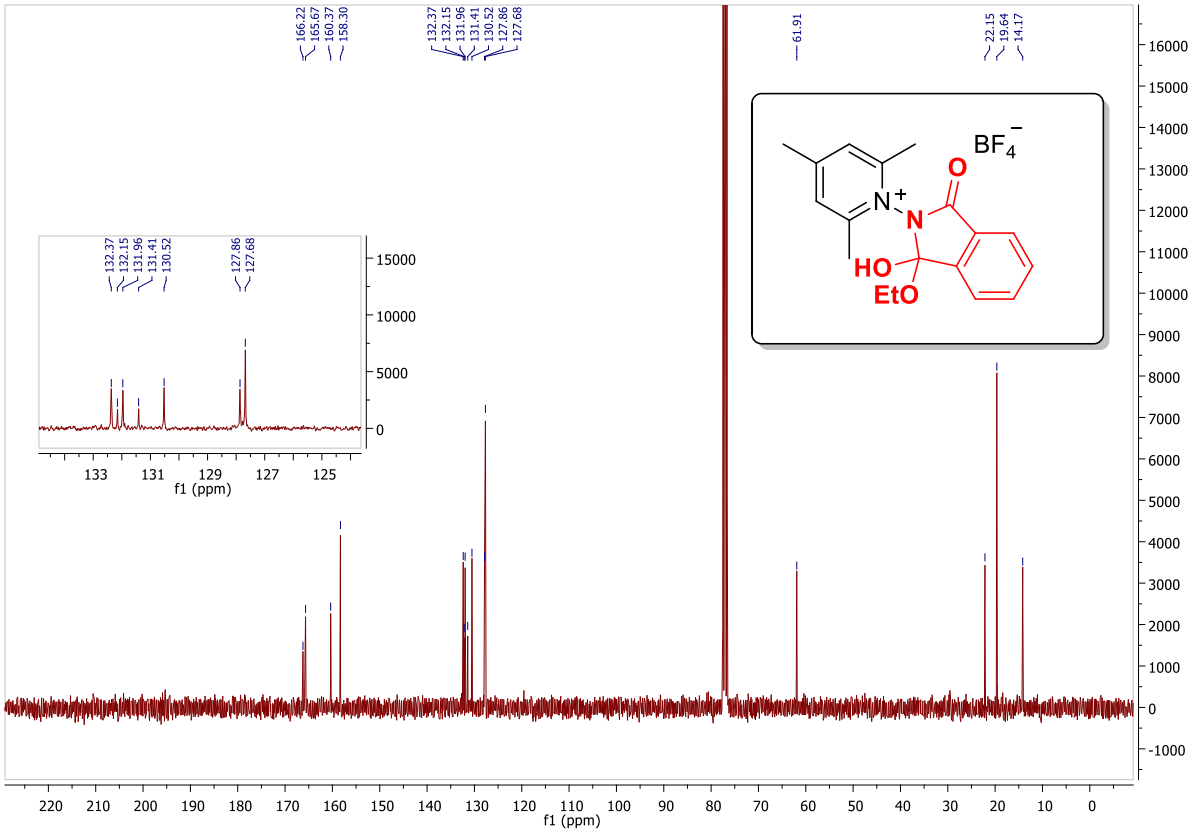
2. (a) H. G. Yayla, F. Peng, I. K. Mangion, M. McLaughlin, L.-C. Campeau, I. W. Davies, D. A. DiRocco, R. R. *Knowles, Chem. Sci*. 2016, **7**, 2066; (b) Y. Ji, D. A. DiRocco, C. M. Hong, M. K. Wismer, M. Reibarkh, *Org. Lett.* 2018, **20**, 2156.

3. C. G. Hatchard, C. A. Parker, *Proc. R. Soc. London, Ser. A* 1956, **235**, 518.

## X. NMR spectra of new compounds

### 1-(1-Ethoxy-1-hydroxy-3-oxoisoindolin-2-yl)-2,4,6-trimethylpyridin-1-ium tetrafluoroborate 2i

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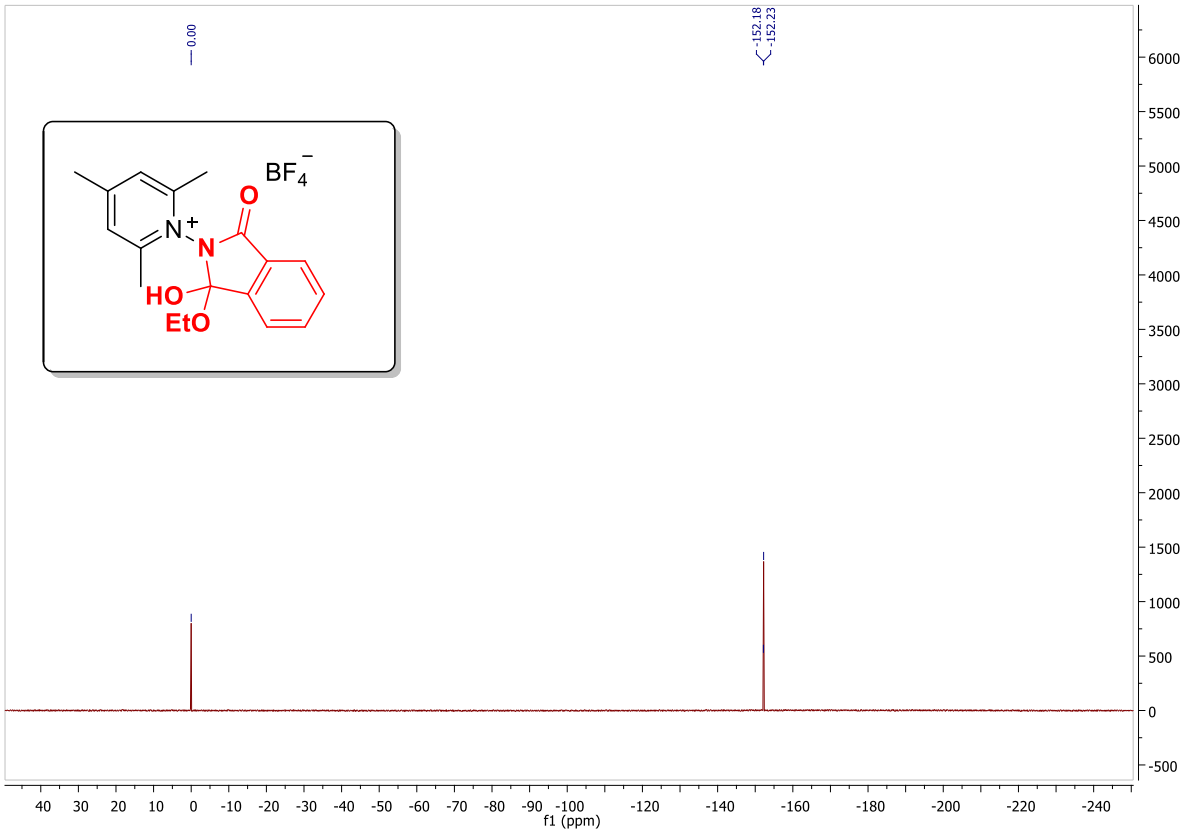
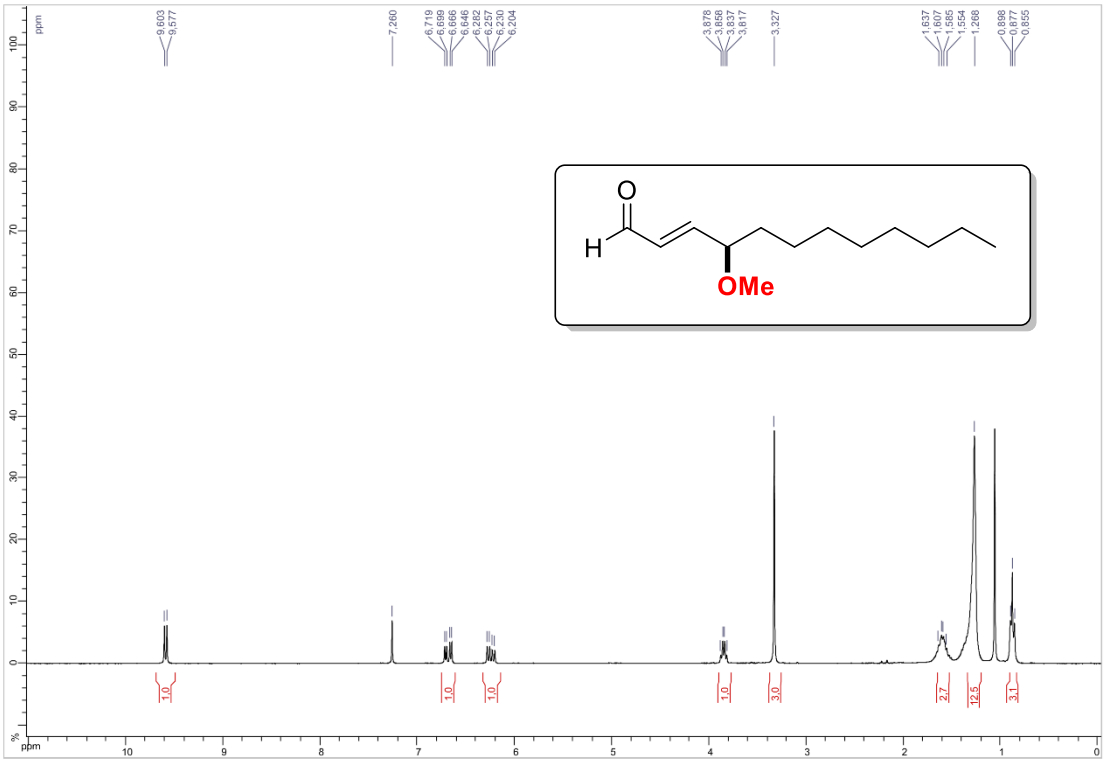
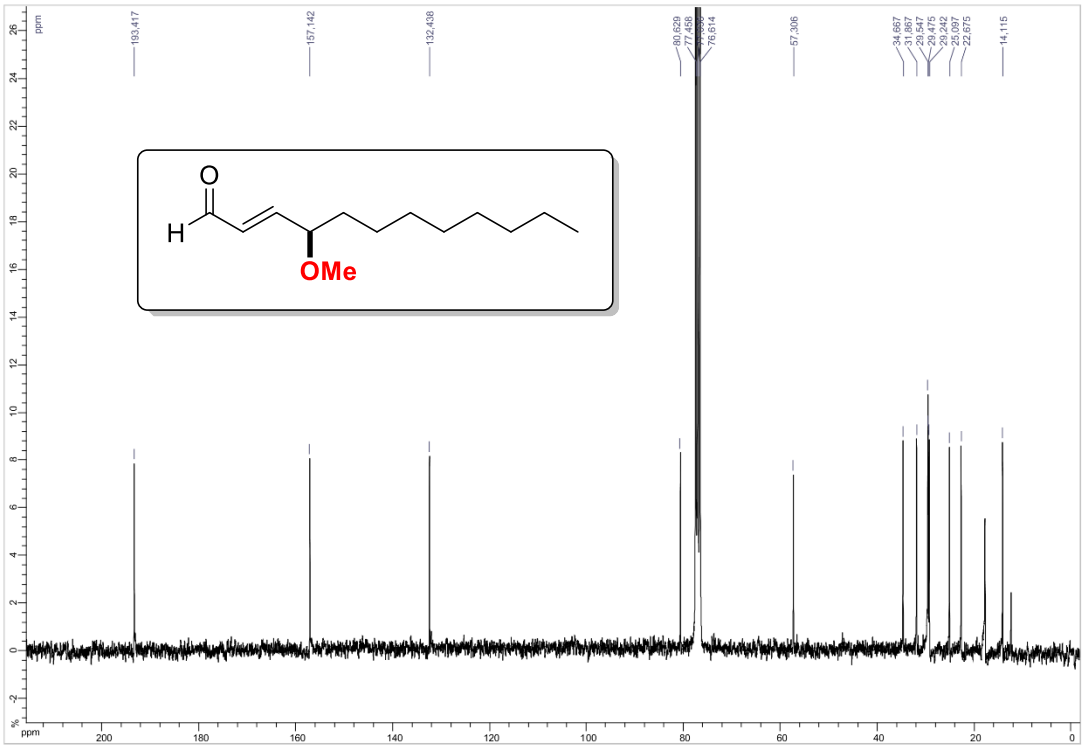
165.67
160.37
158.30
132.37
132.15
131.96
131.41
130.52
127.86
127.68
61.91
22.15
19.64
14.17
BF4−
O
N+
N
HO
EtO
f1 (ppm)

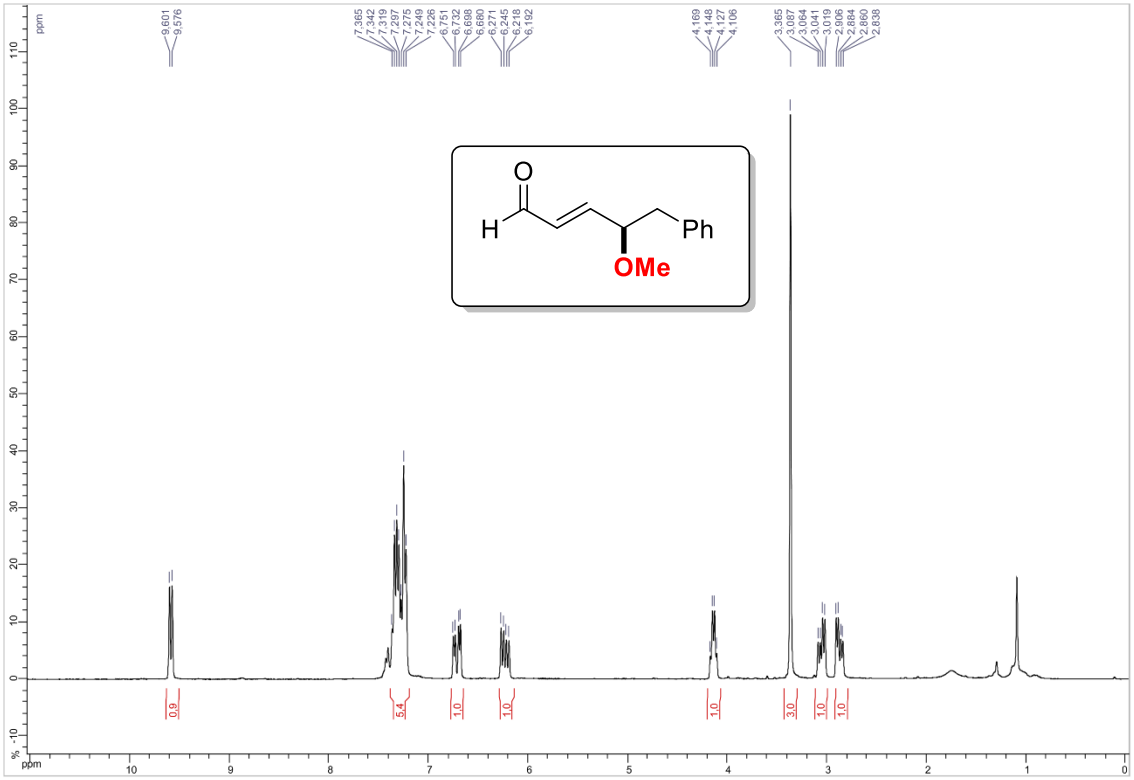

0.00
-152.18
-152.23
BF4−
O
N+
N
HO
EtO
f1 (ppm)

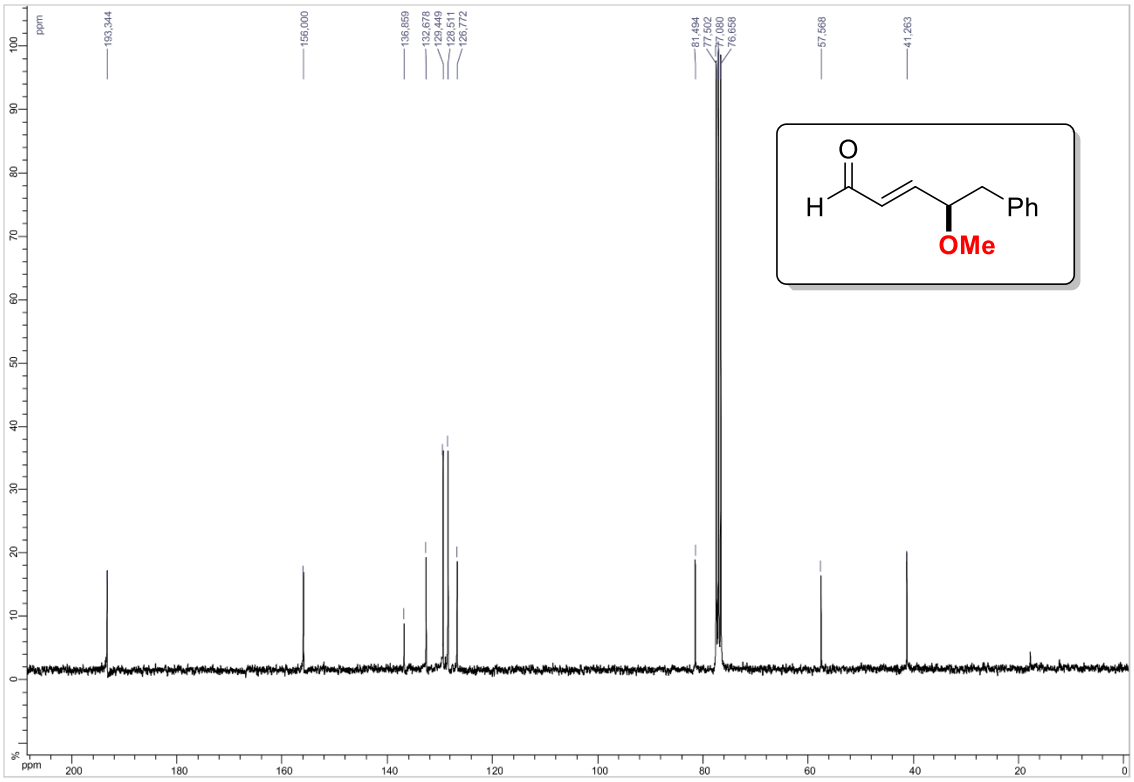
**(*E*)-4-methoxydodec-2-enal 3a**



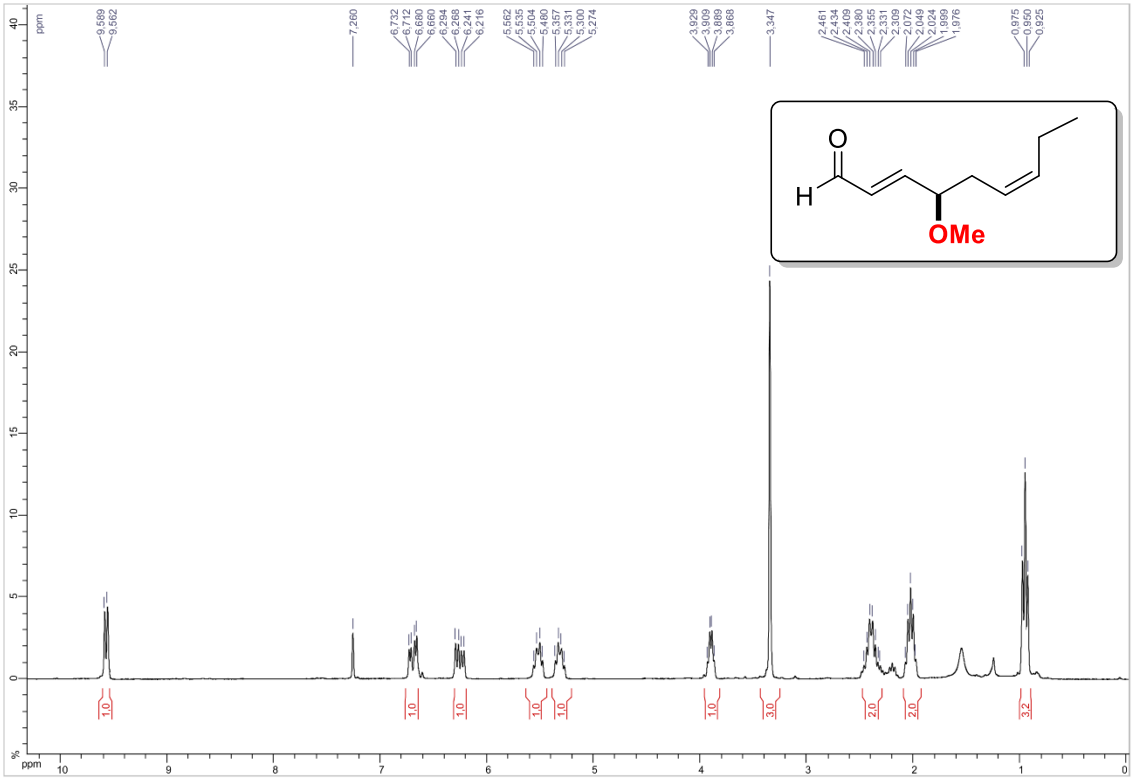



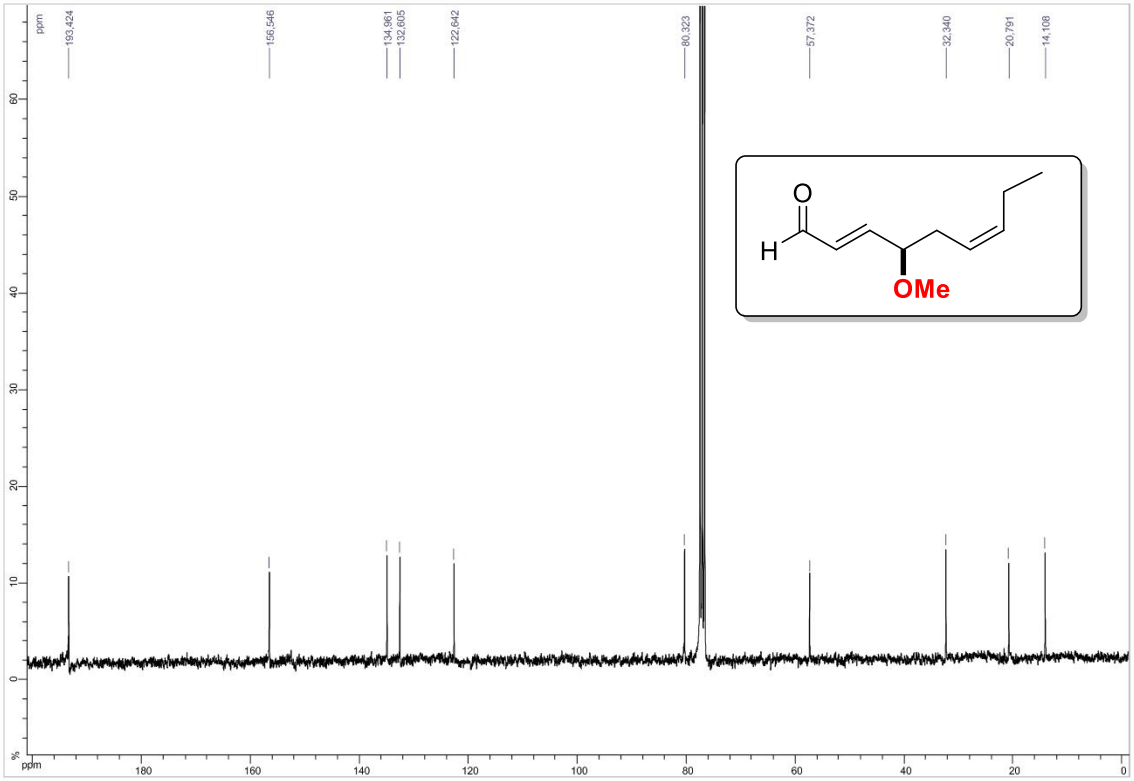
**(*E*)-4-methoxy-5-phenylpent-2-enal 3b**



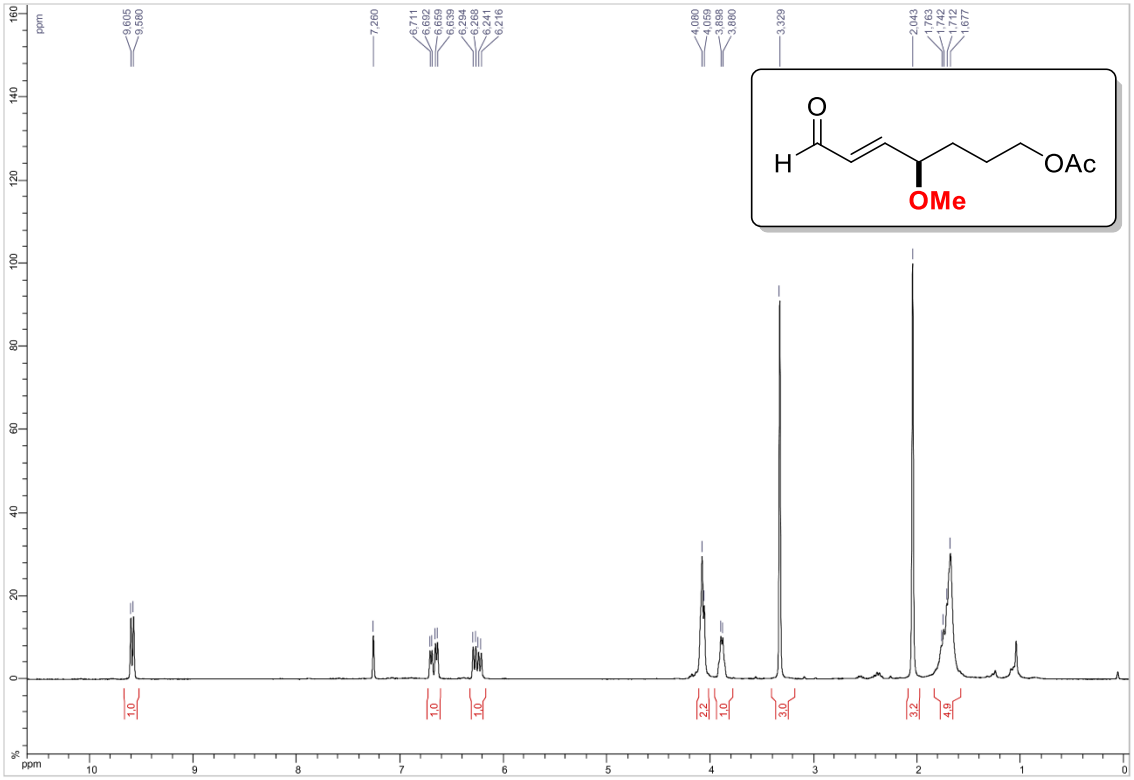



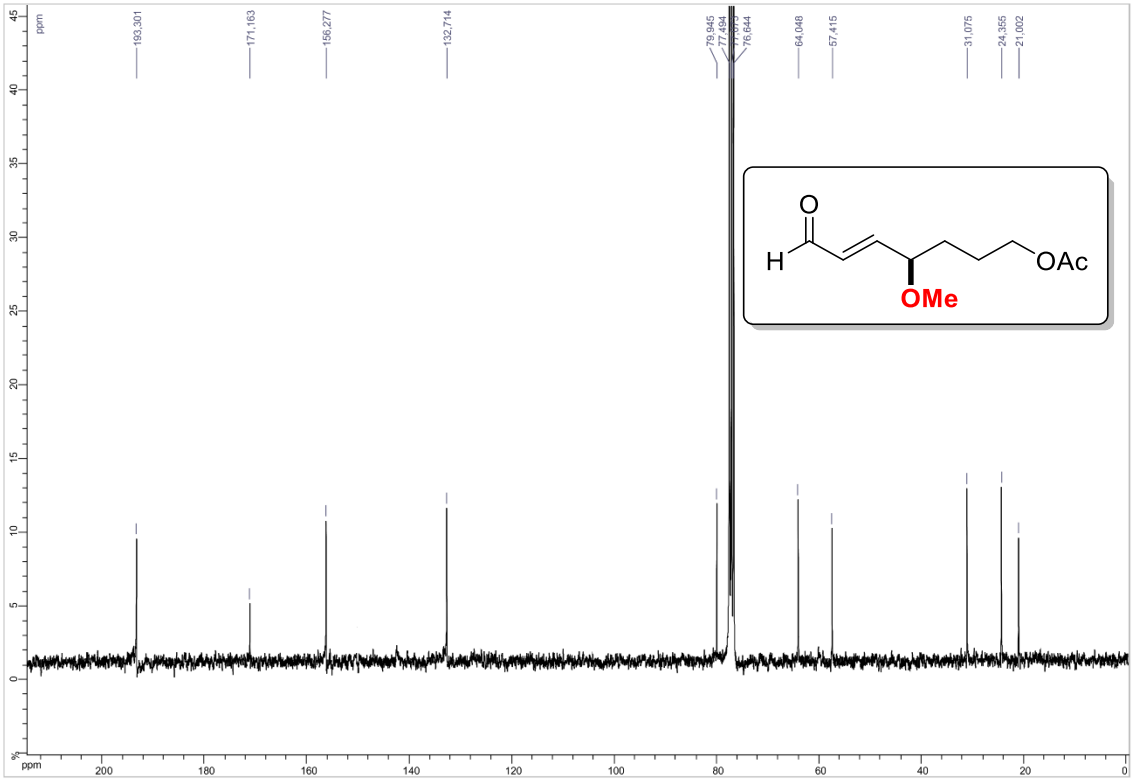
**(2*E*,6*Z*)-4-Methoxynona-2,6-dienal 3c**



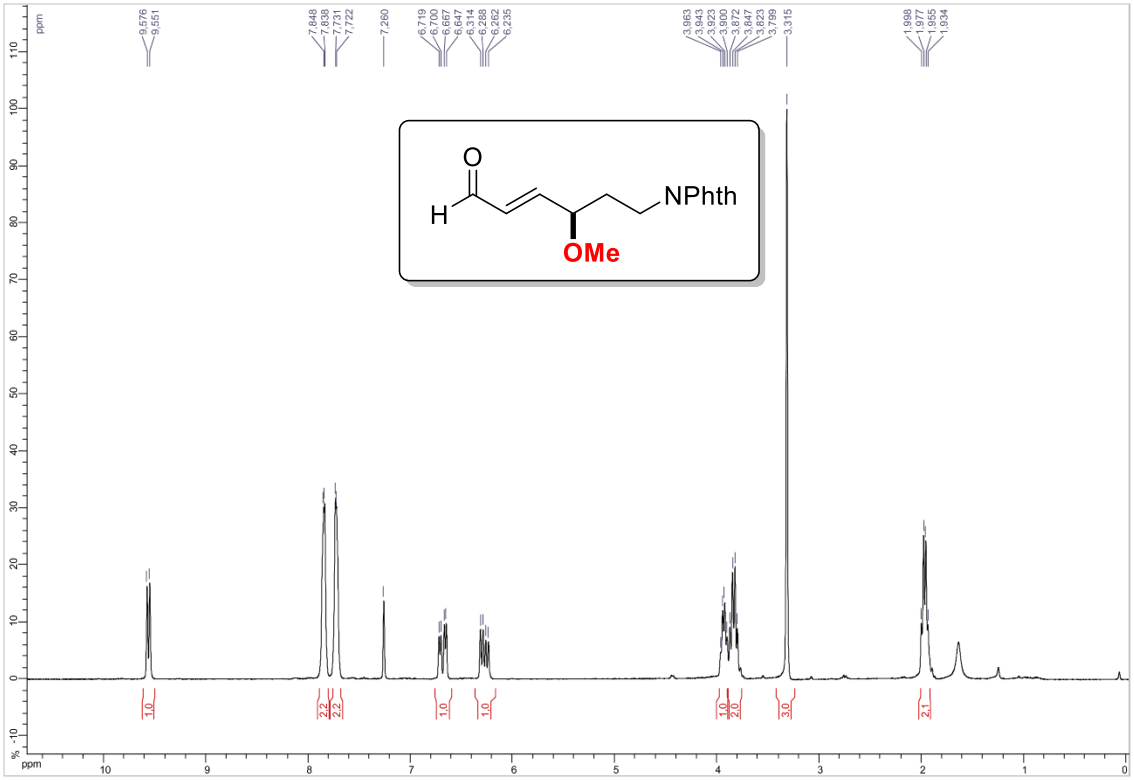



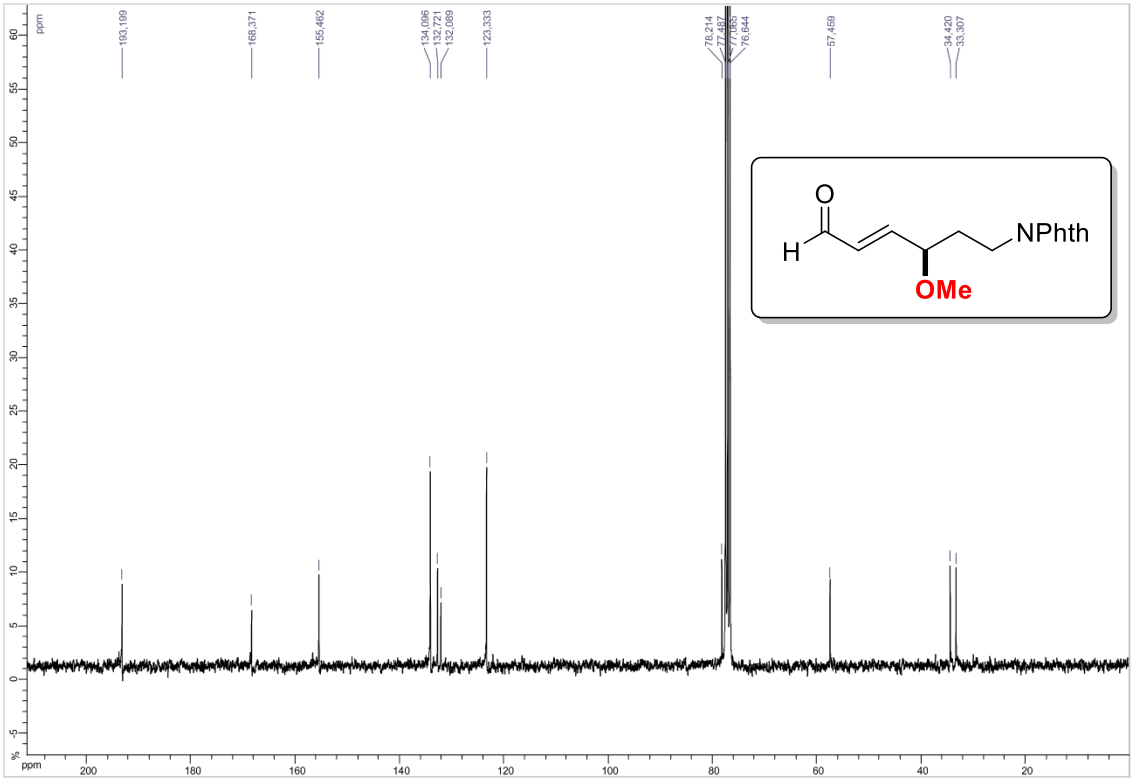
**(*E*)-4-Methoxy-7-oxohept-5-en-1-yl acetate 3d**



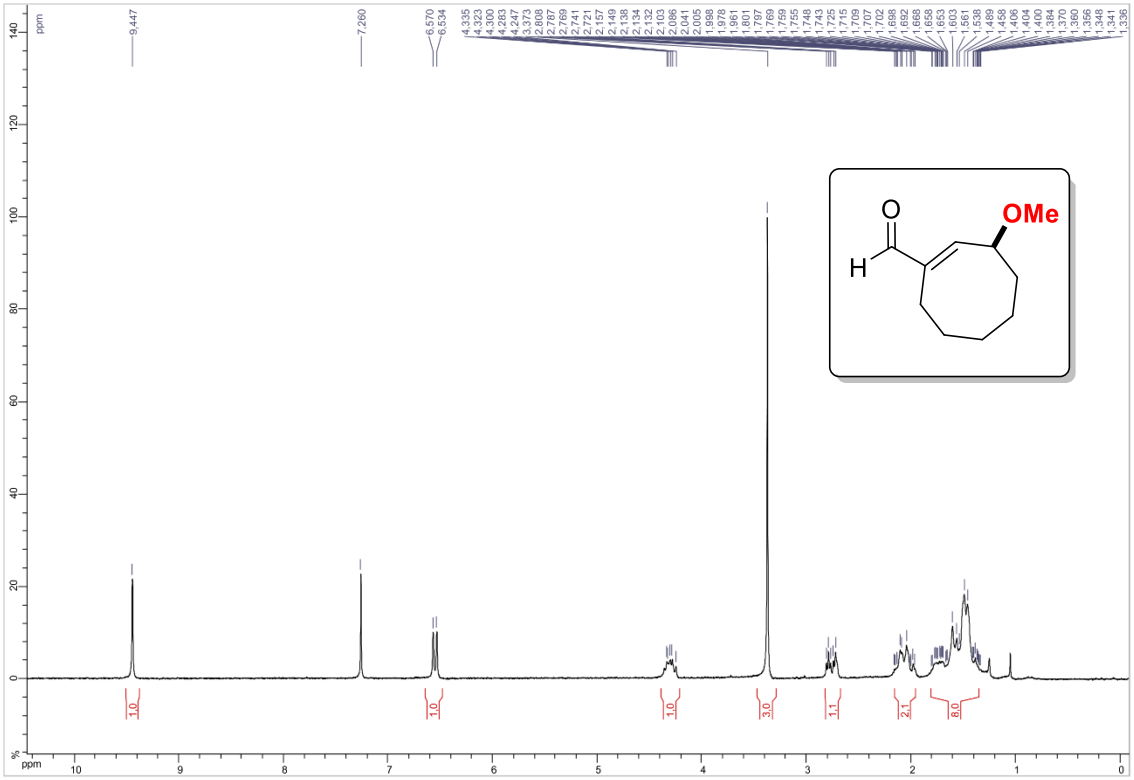



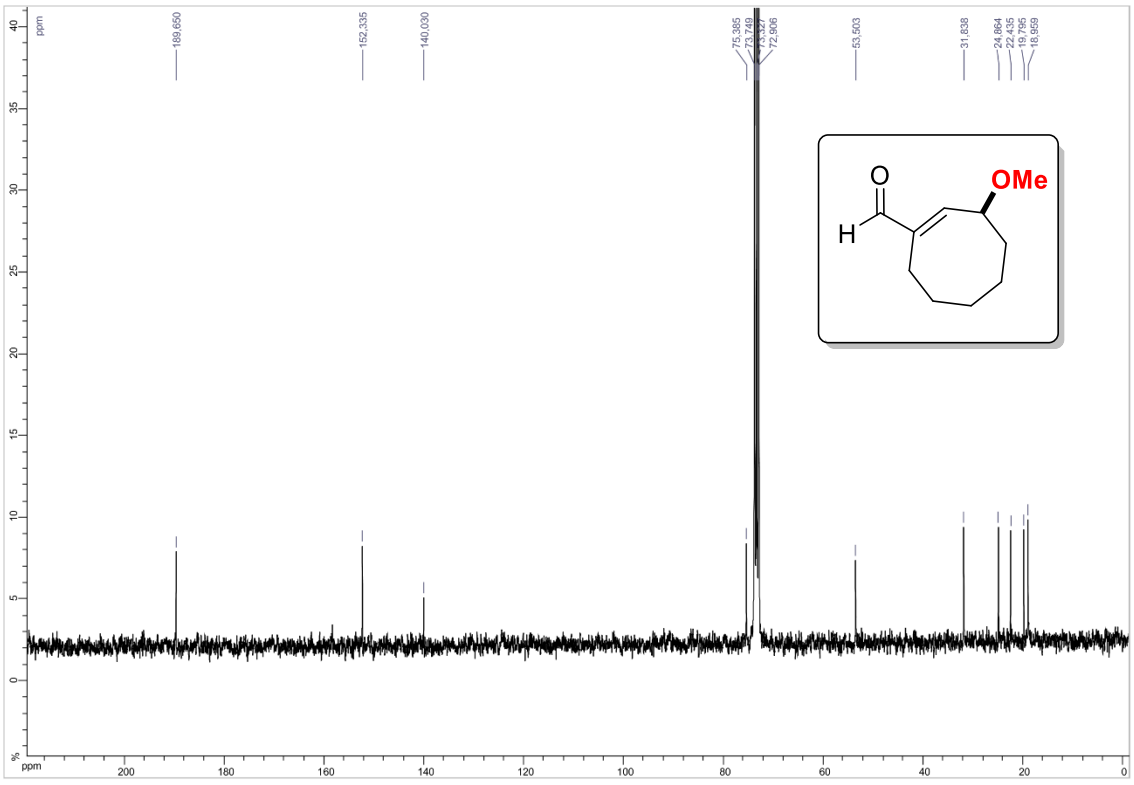
**(*E*)-6-(1,3-Dioxoisoindolin-2-yl)-4-methoxyhex-2-enal 3e**



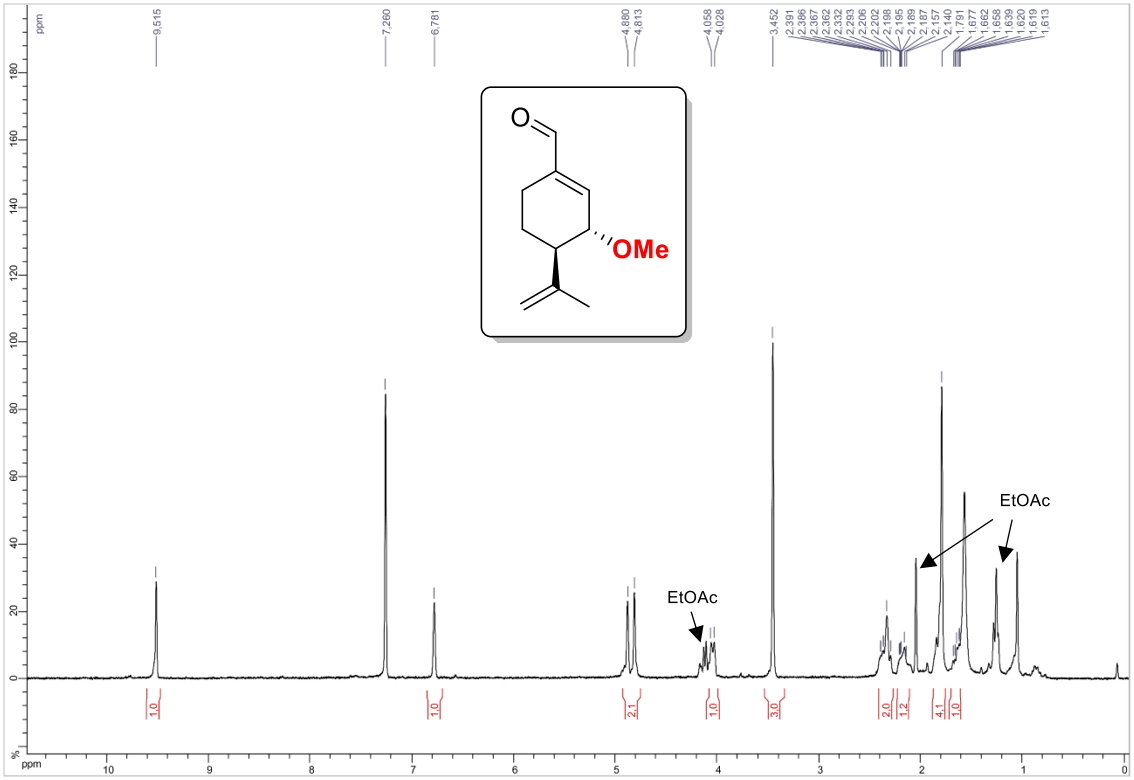



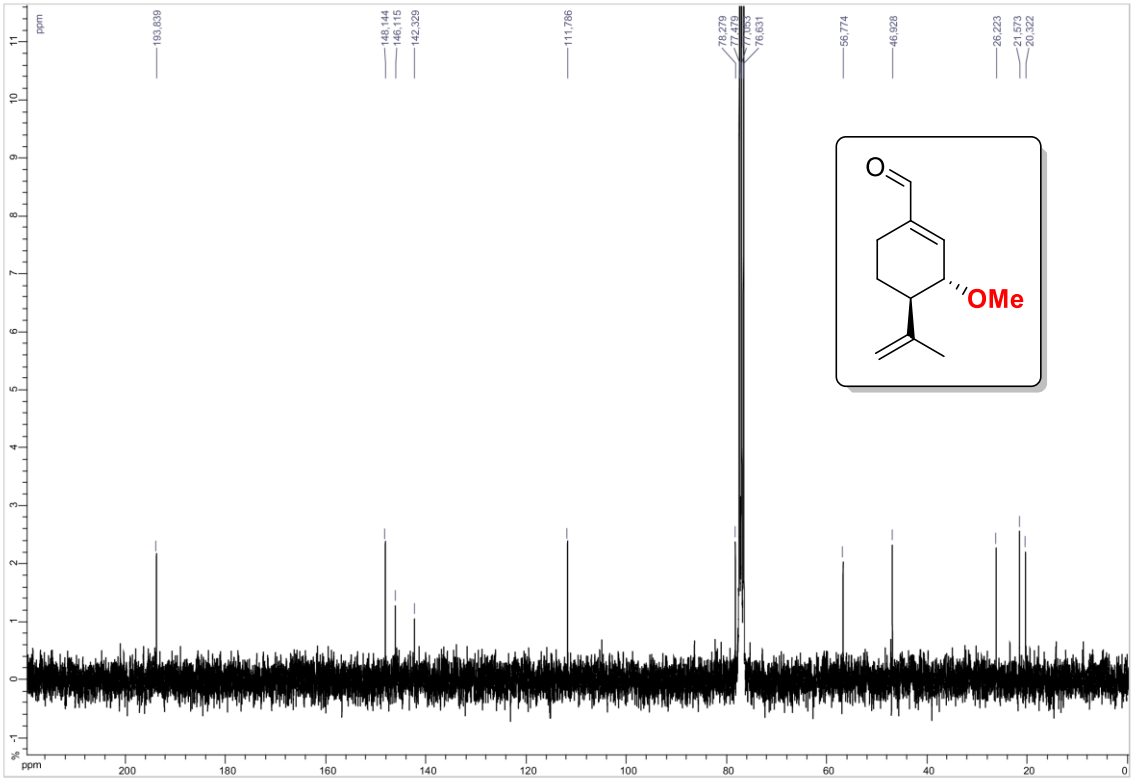
## (*E*)-3-Methoxycyclooct-1-ene-1-carbaldehyde 3f



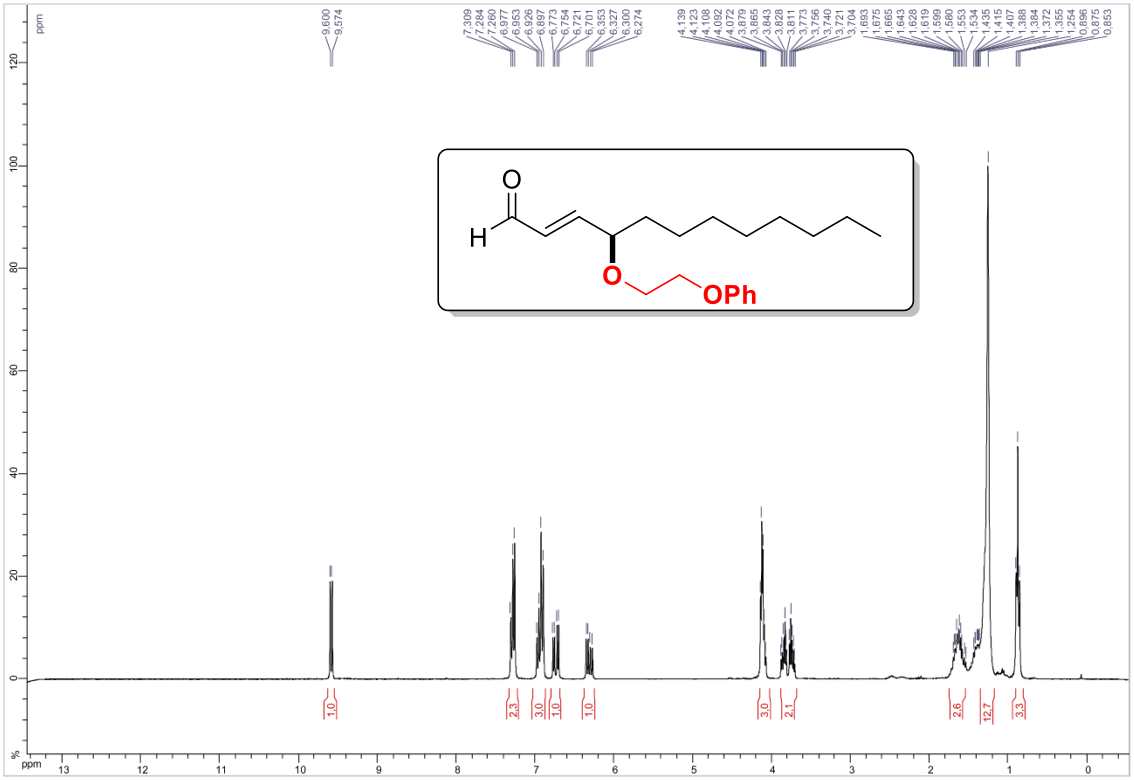



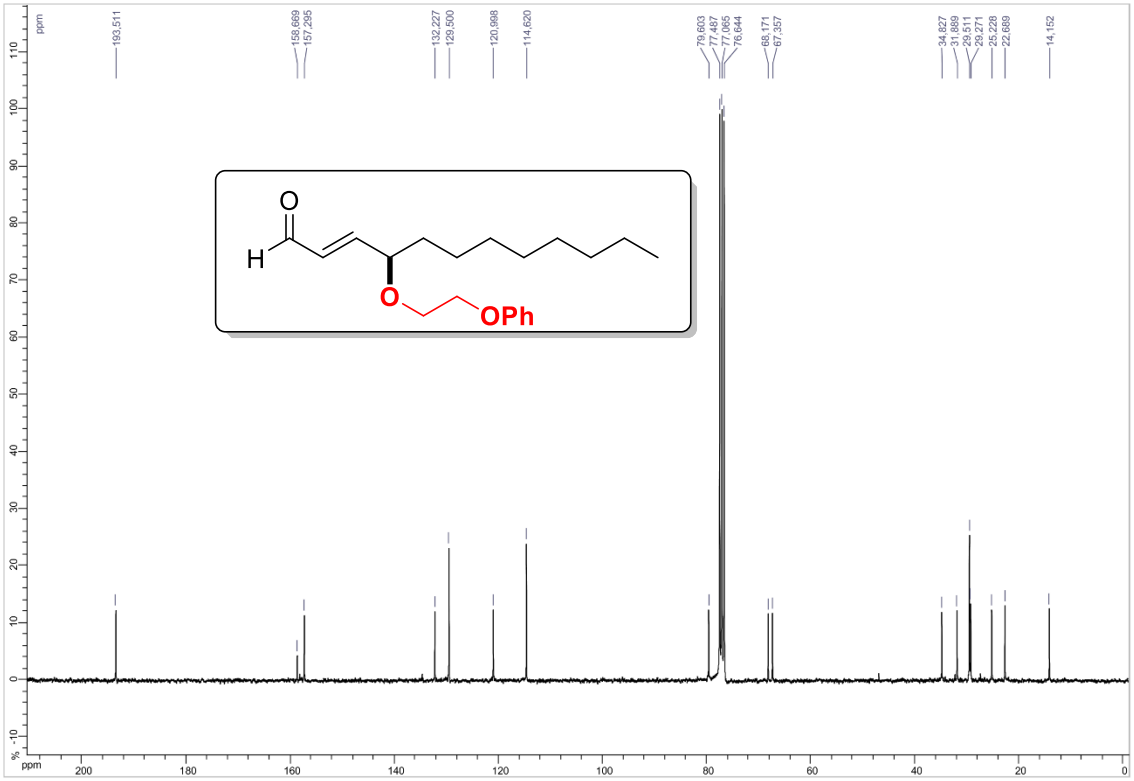
**3-Methoxy-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carbaldehyde 3g**



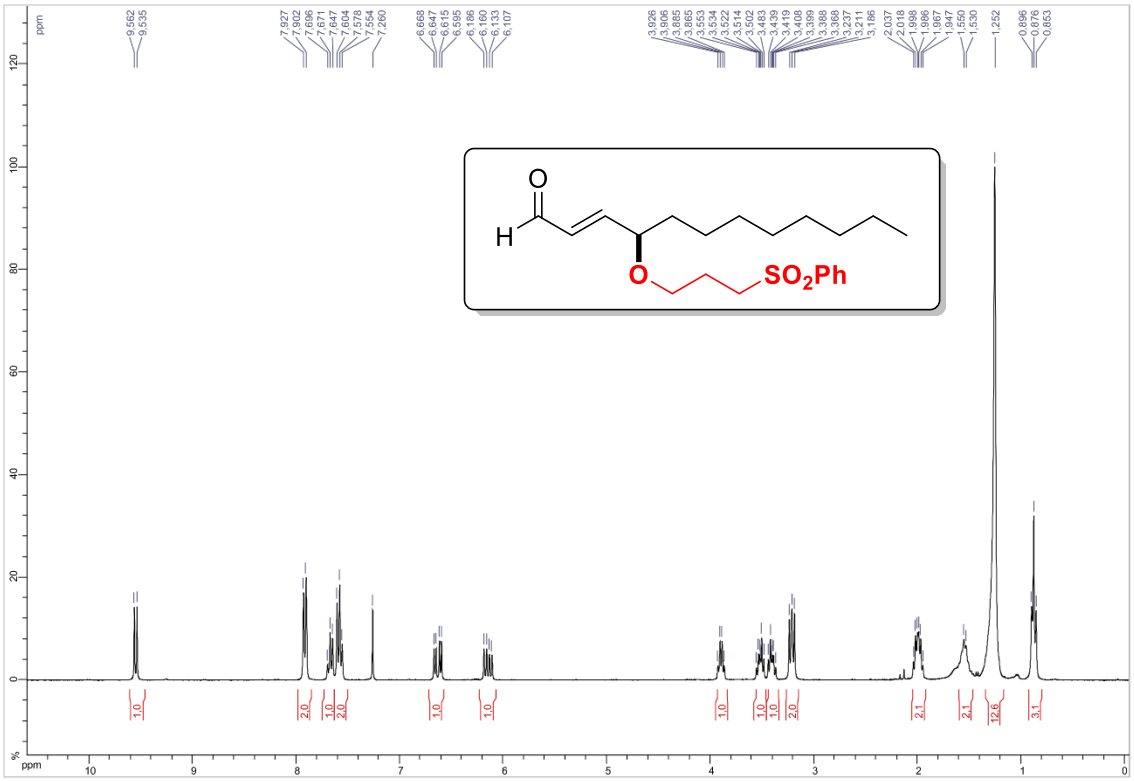



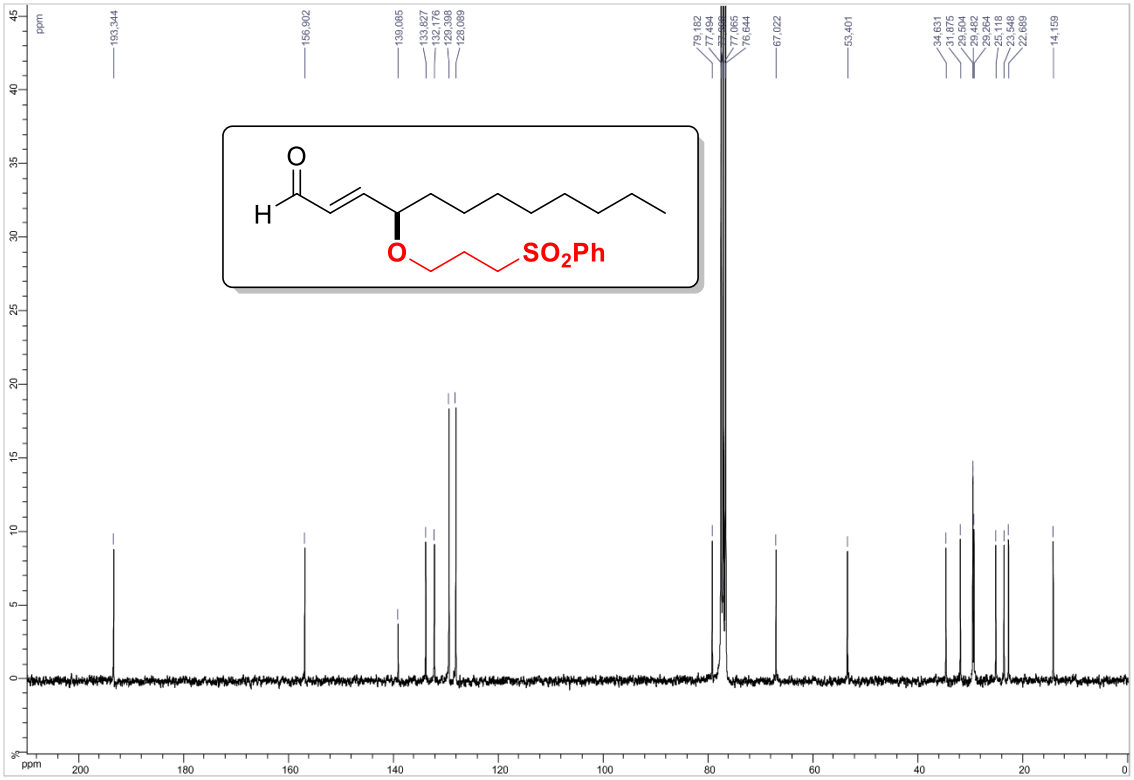
**(*E*)-4-(2-Phenoxyethoxy)dodec-2-enal 3h**



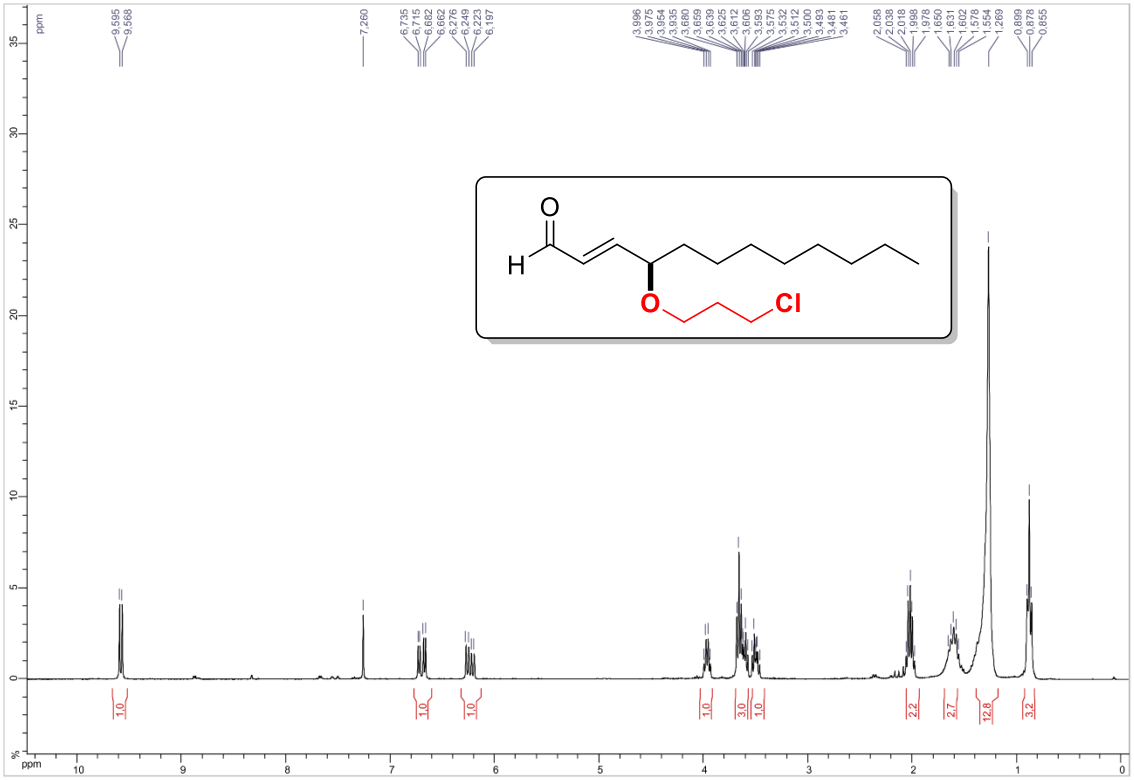



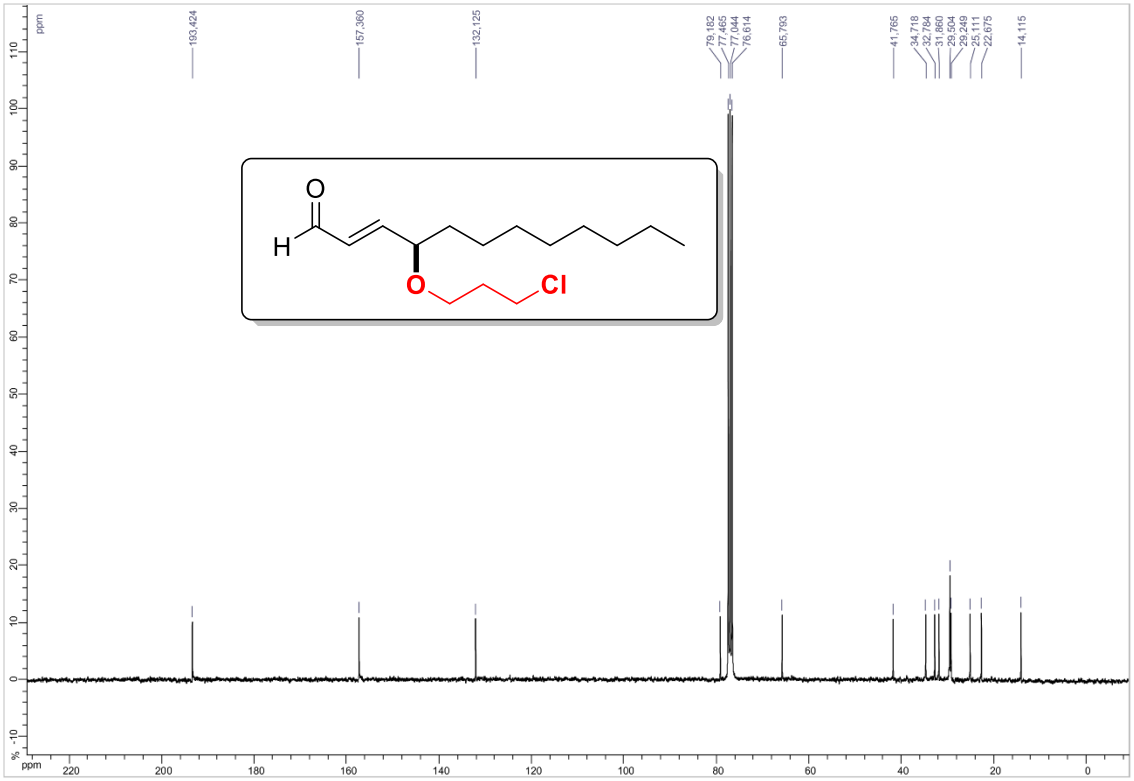
**(*E*)-4-(3-((λ1-oxidanyl)(oxo)(phenyl)-l5-sulfanyl)propoxy)dodec-2-enal 3i**



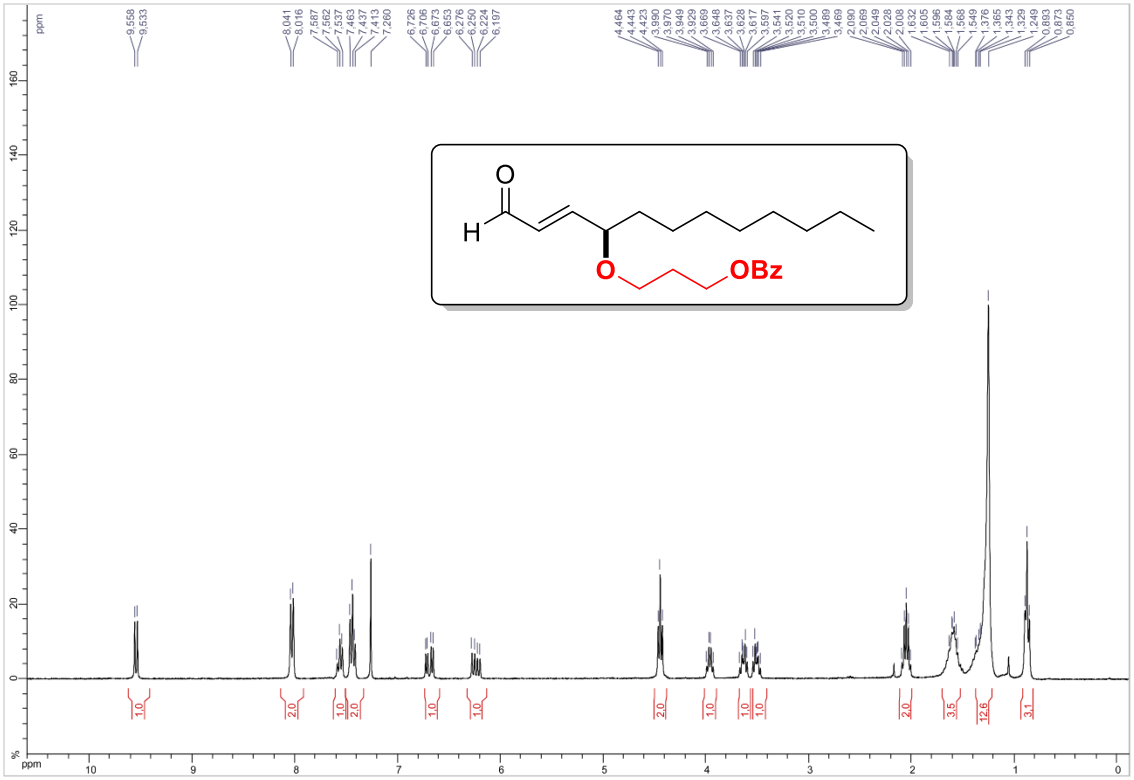



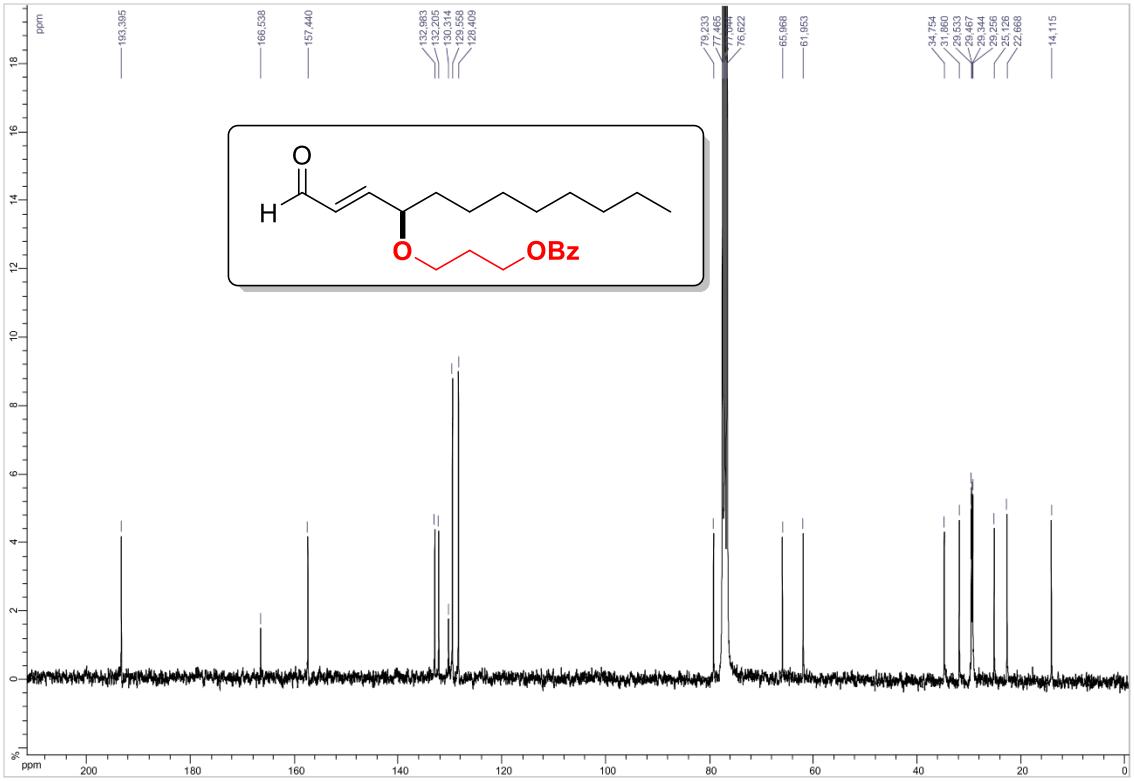
**(*E*)-4-(3-Chloropropoxy)dodec-2-enal 3j**



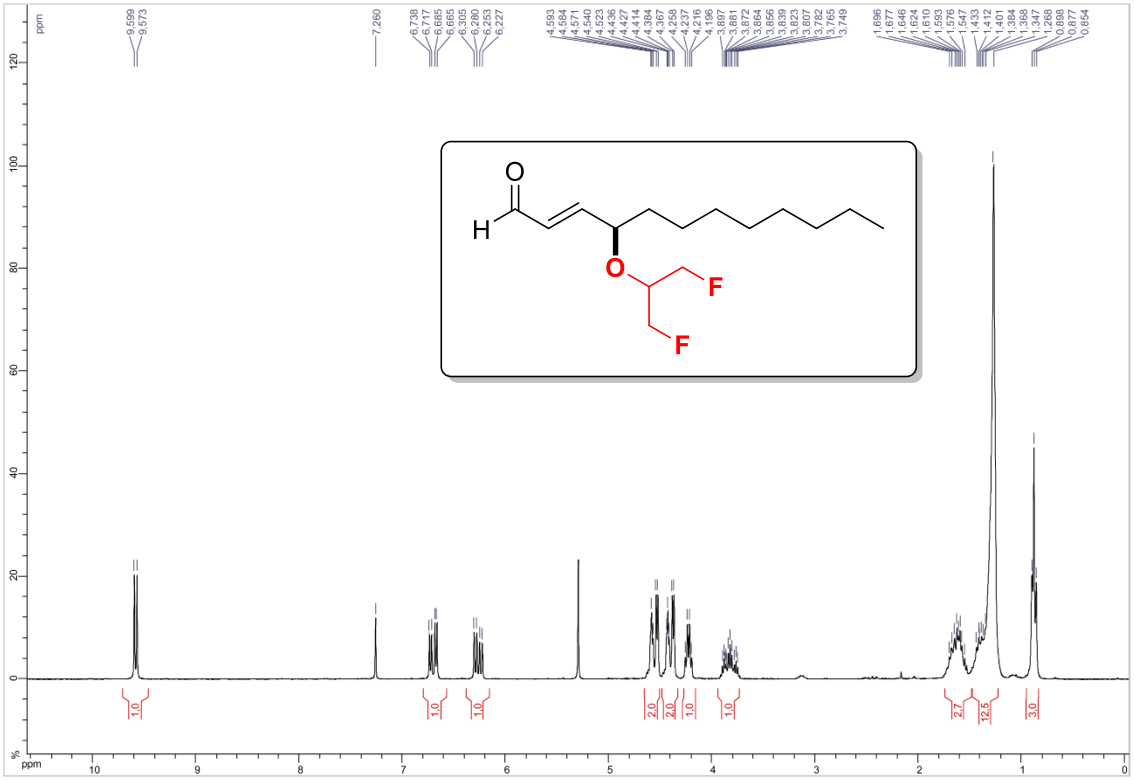



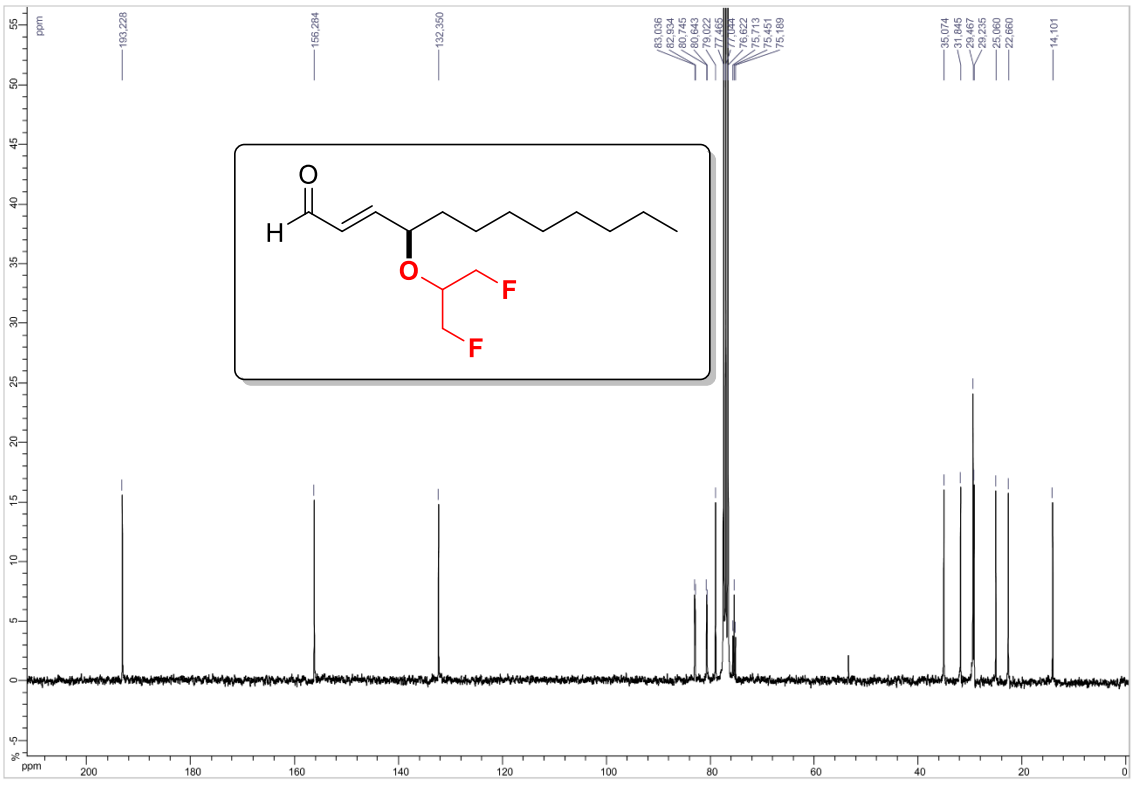
**(*E*)-3-((1-Oxododec-2-en-4-yl)oxy)propyl benzoate 3k**

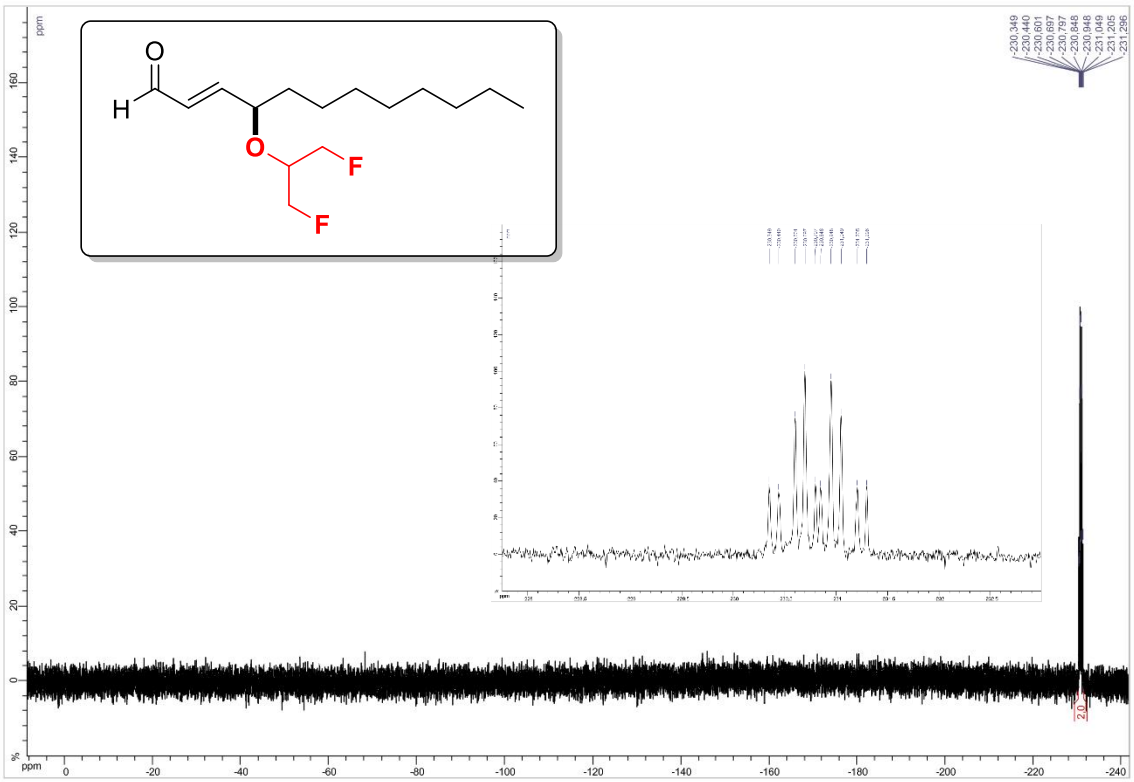


**(*E*)-4-((1,3-Difluoropropan-2-yl)oxy)dodec-2-enal 3l**




O
H
O
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F
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ppm
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-100
-120
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-220
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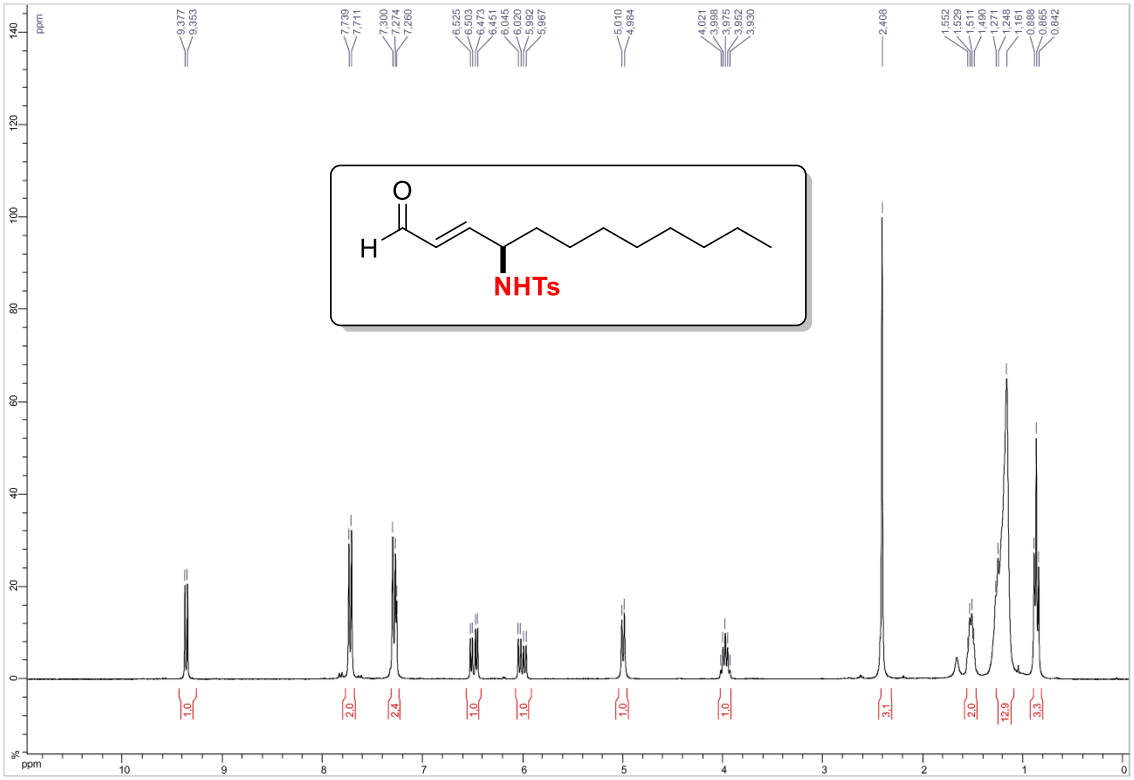
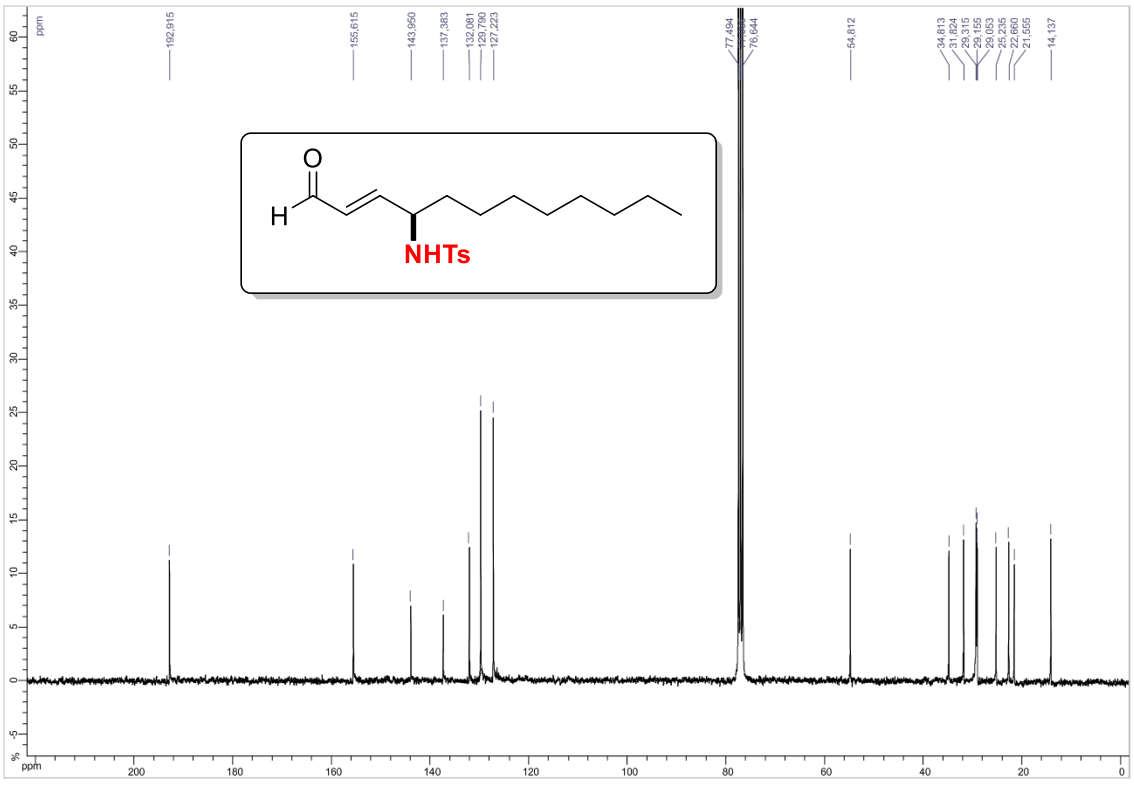
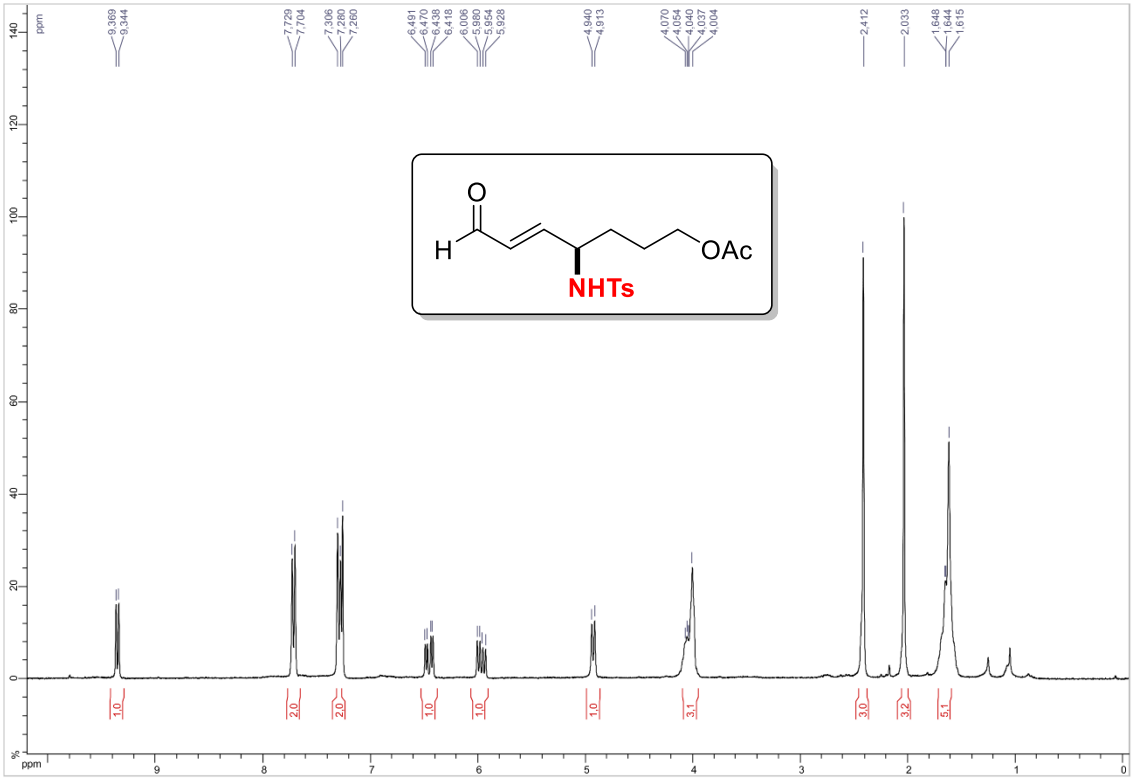
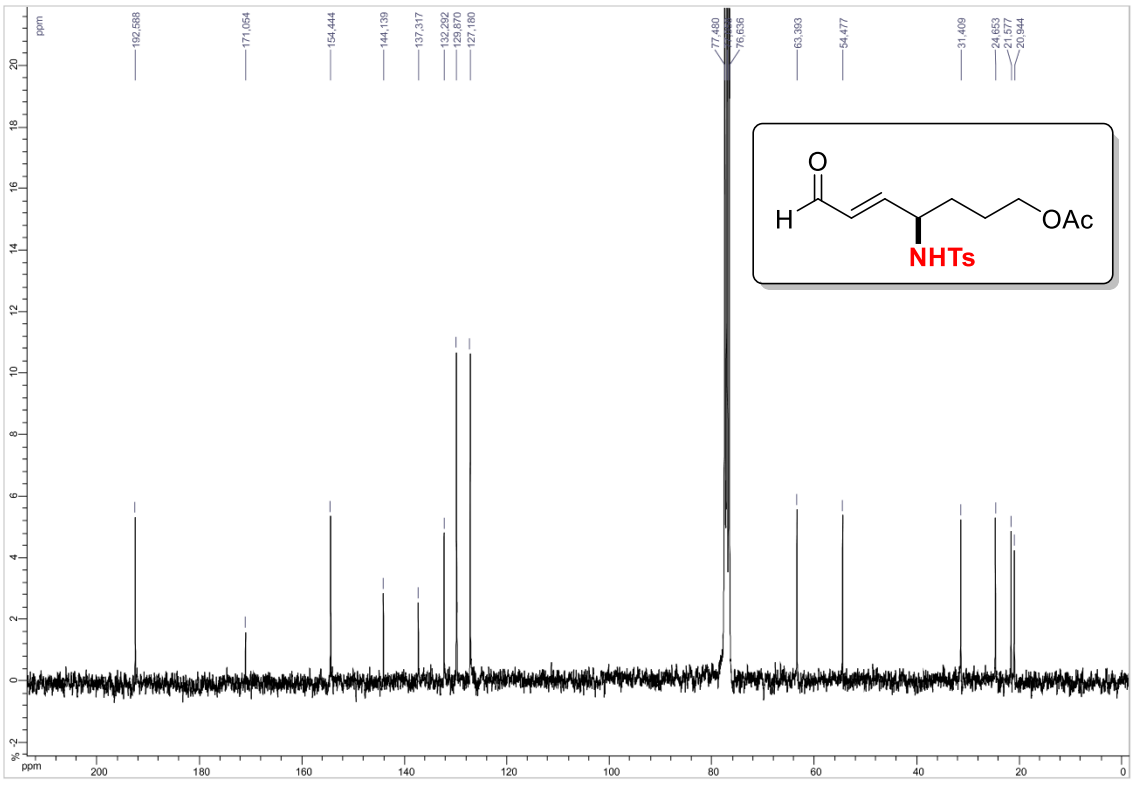
**(*E*)-4-Methyl-*N*-(1-oxododec-2-en-4-yl)benzenesulfonamide 4a**



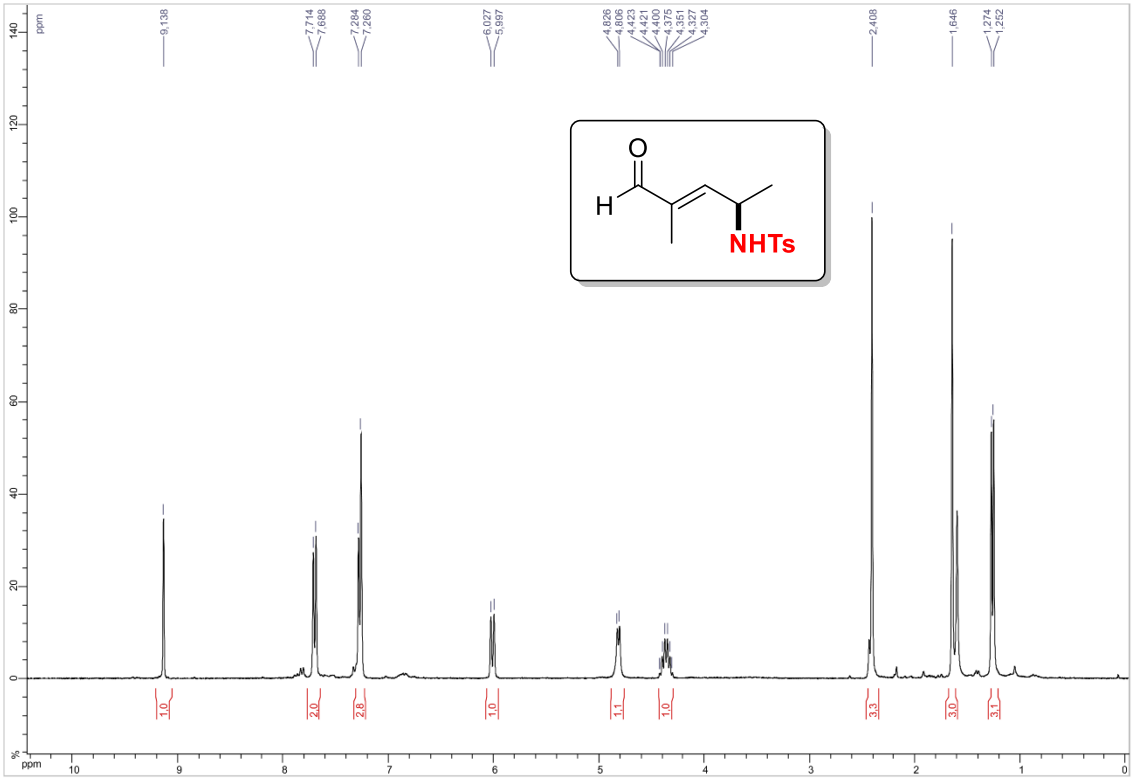



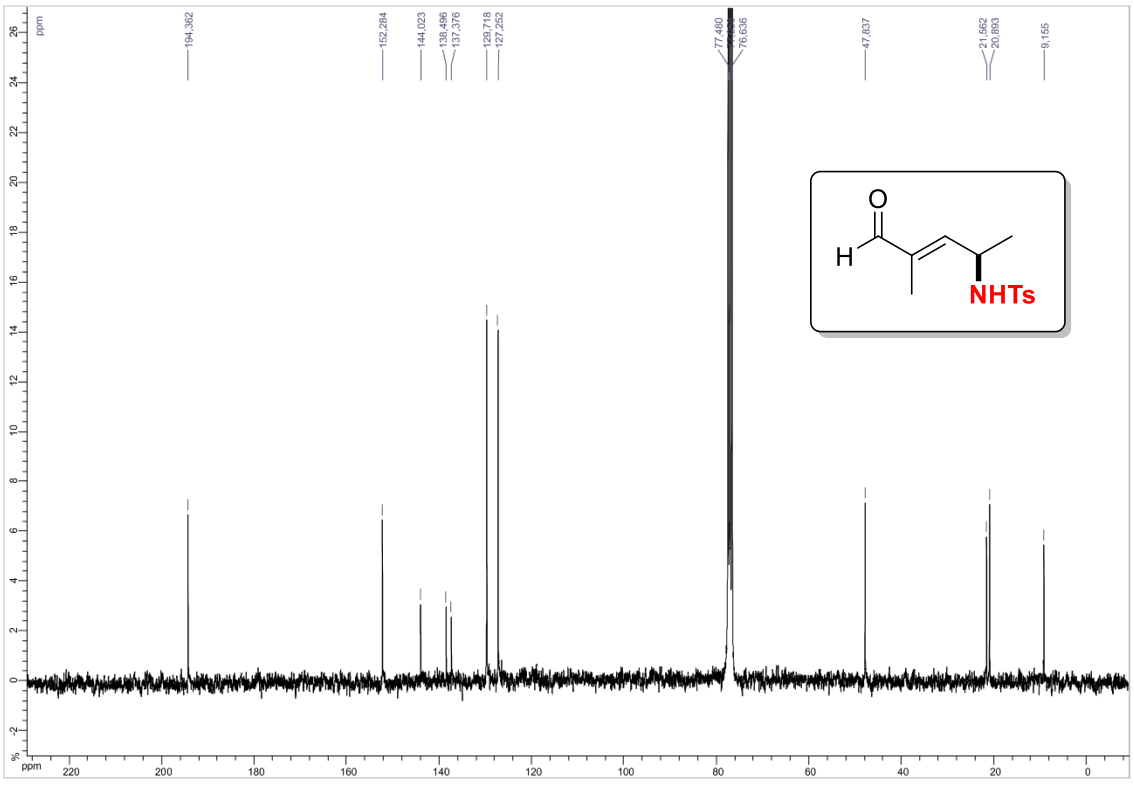
**(*E*)-4-((4-Methylphenyl)sulfonamido)-7-oxohept-5-en-1-yl acetate 4b**



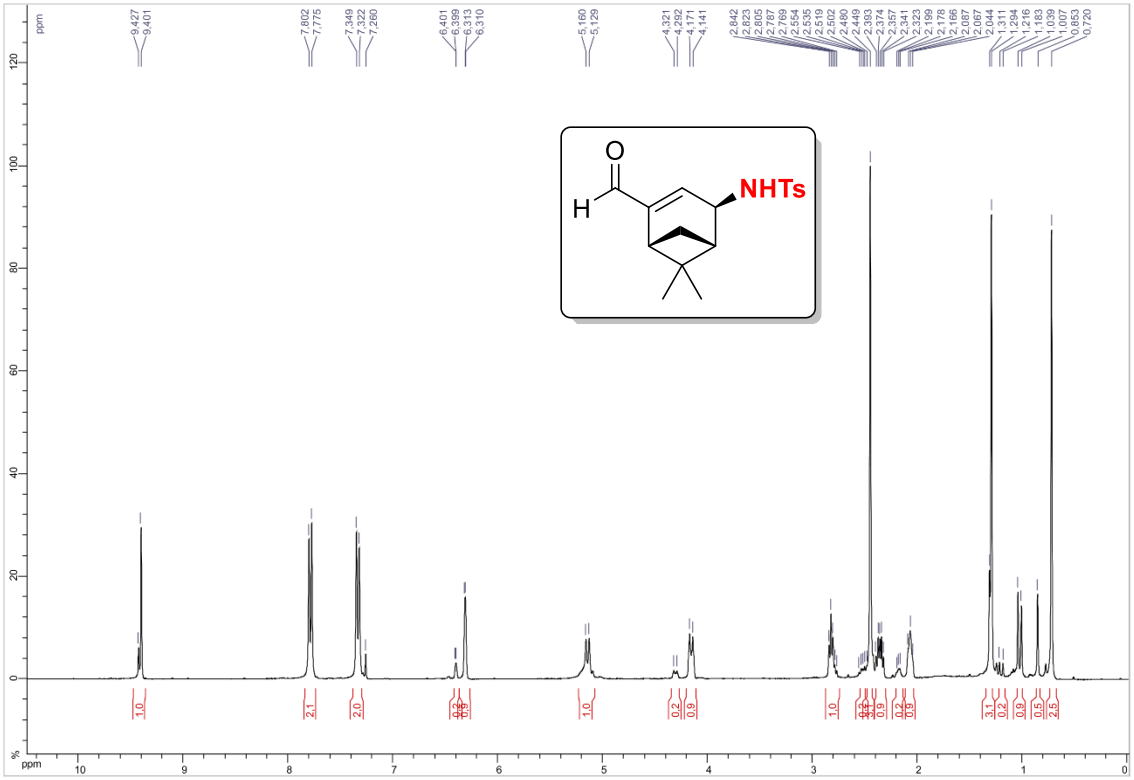



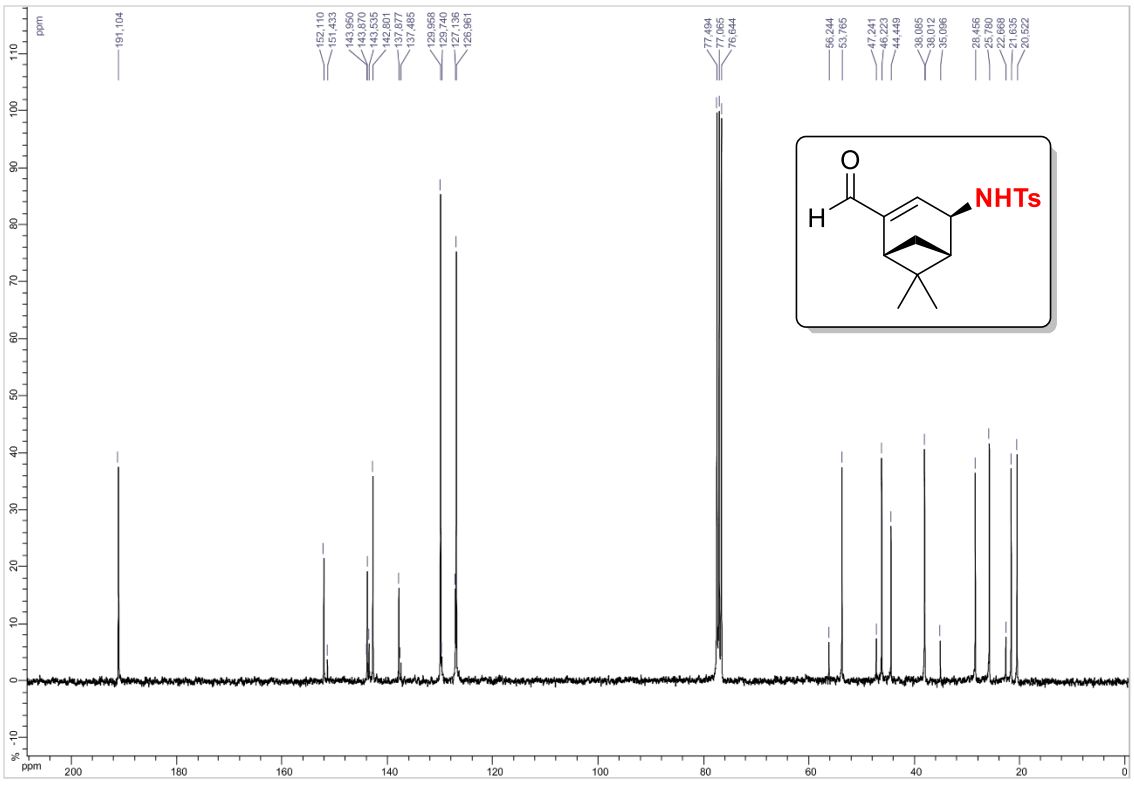
**(*E*)-4-Methyl-*N*-(4-methyl-5-oxopent-3-en-2-yl)benzenesulfonamide 4c**



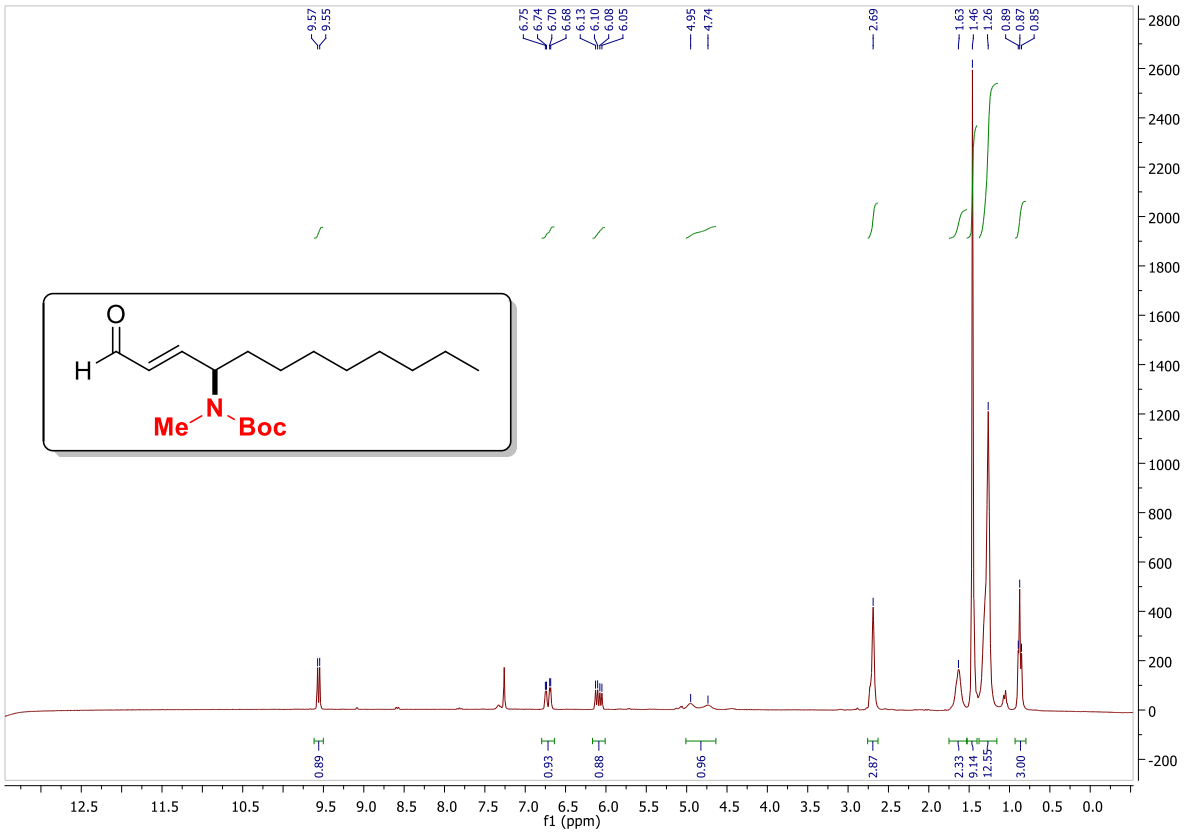



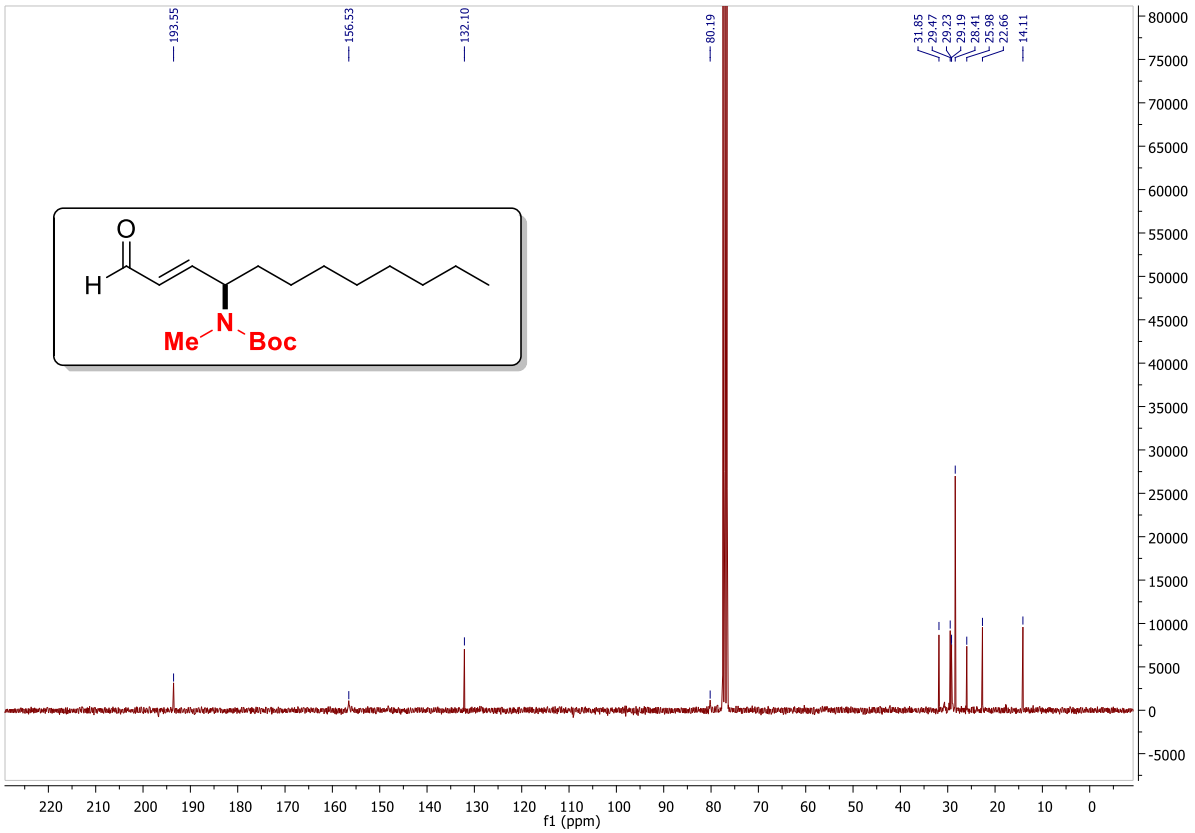
***N*-(4-formyl-6,6-dimethylbicyclo[3.1.1]hept-3-en-2-yl)-4-methylbenzenesulfonamide 4d**



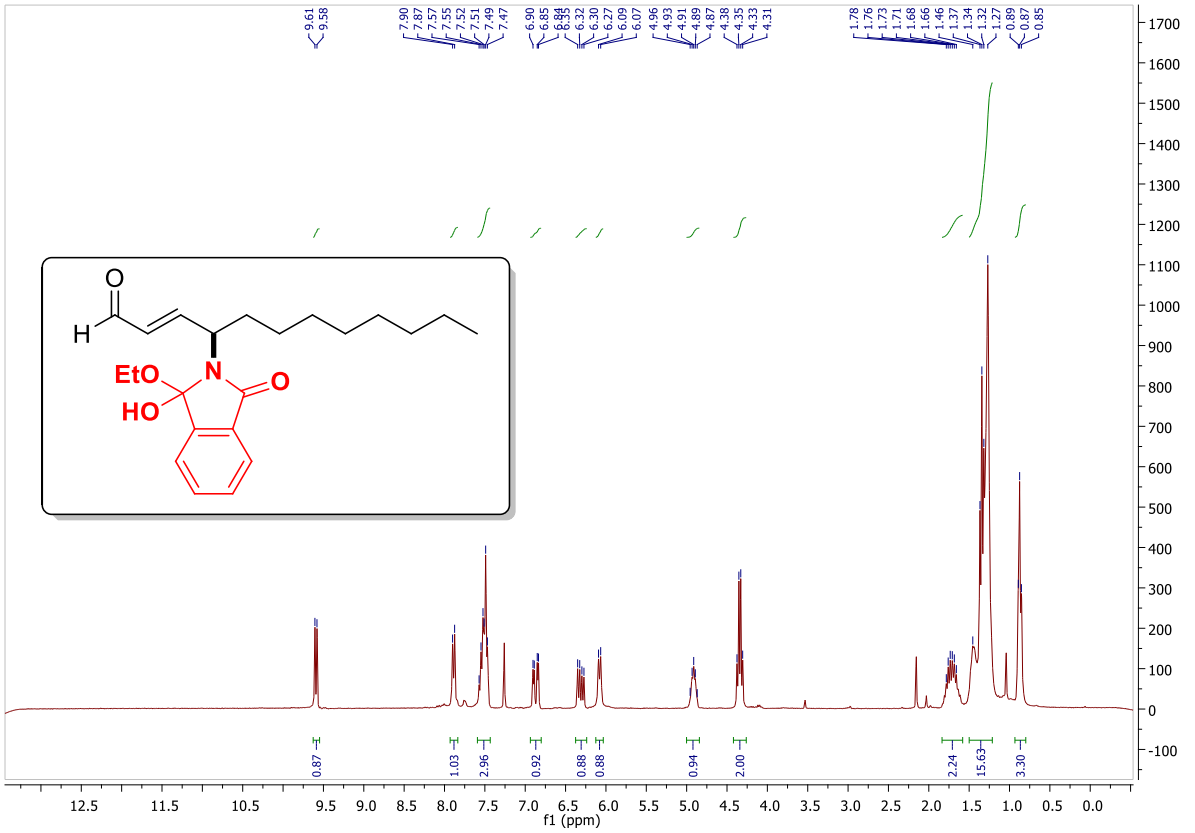



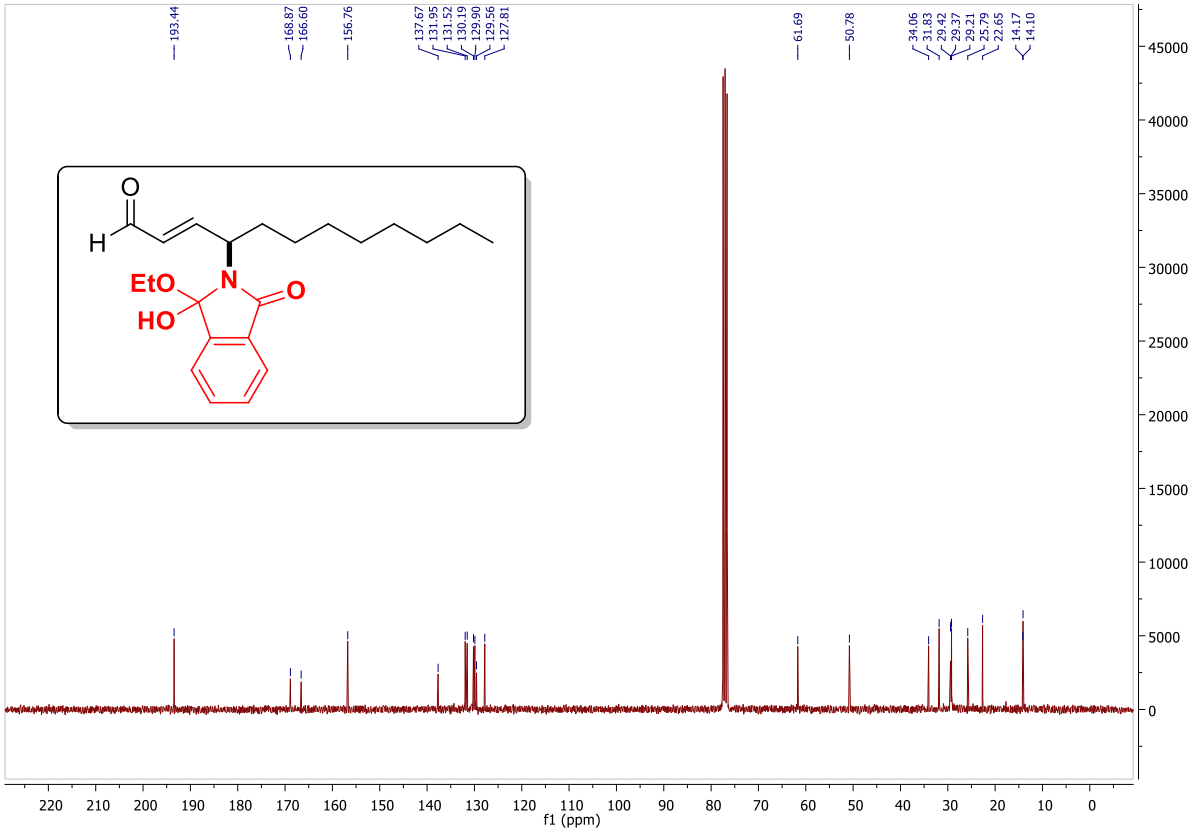
## (E)-tert-butyl methyl(1-oxododec-2-en-4-yl)carbamate 4e



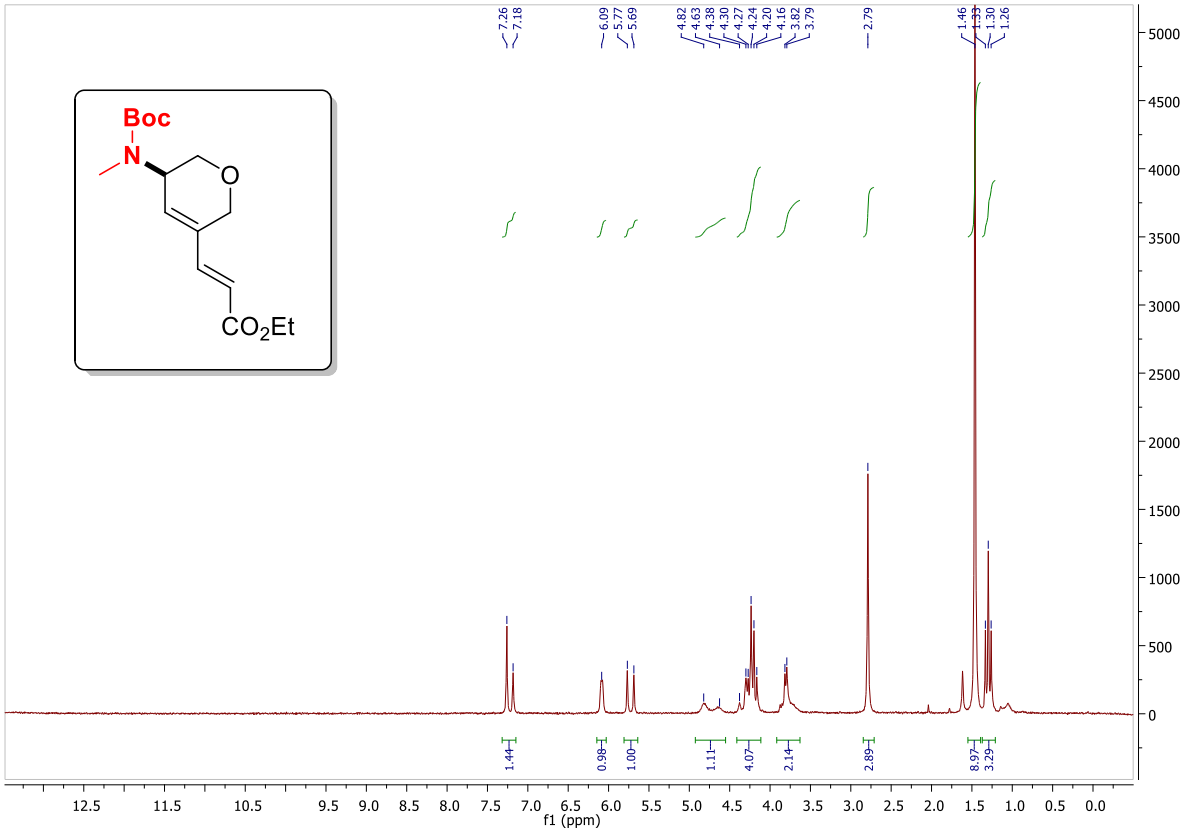



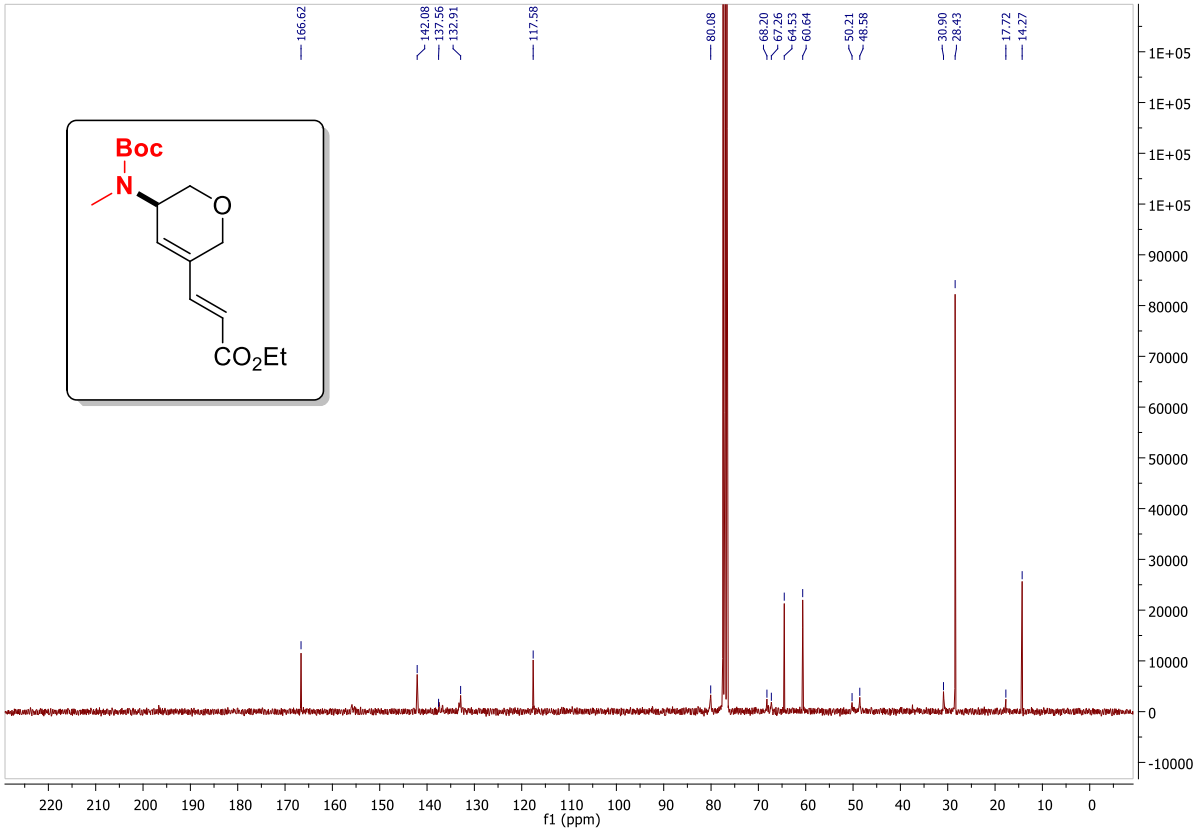
## (E)-4-(1-ethoxy-1-hydroxy-3-oxoisoindolin-2-yl)dodec-2-enal 4f



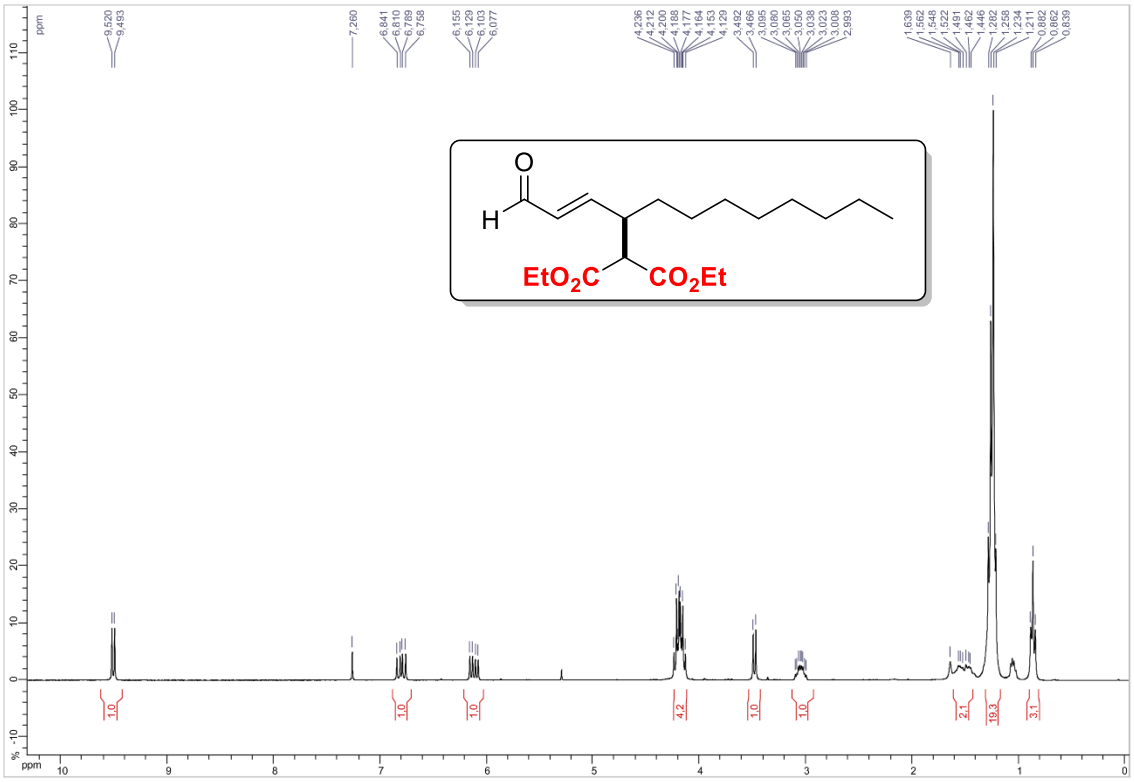



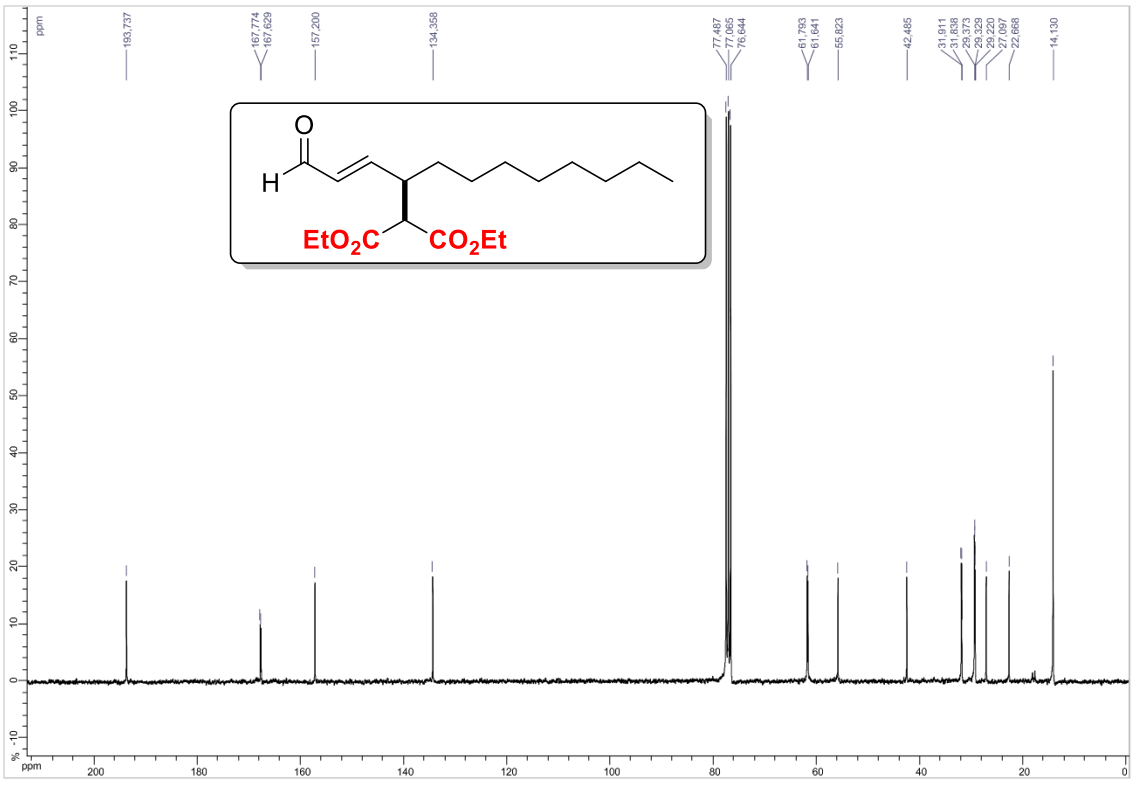
**Ethyl (E)-3-(5-((tert-butoxycarbonyl)(methyl)amino)-5,6-dihydro-2H-pyran-3-yl)acrylate 4g'**



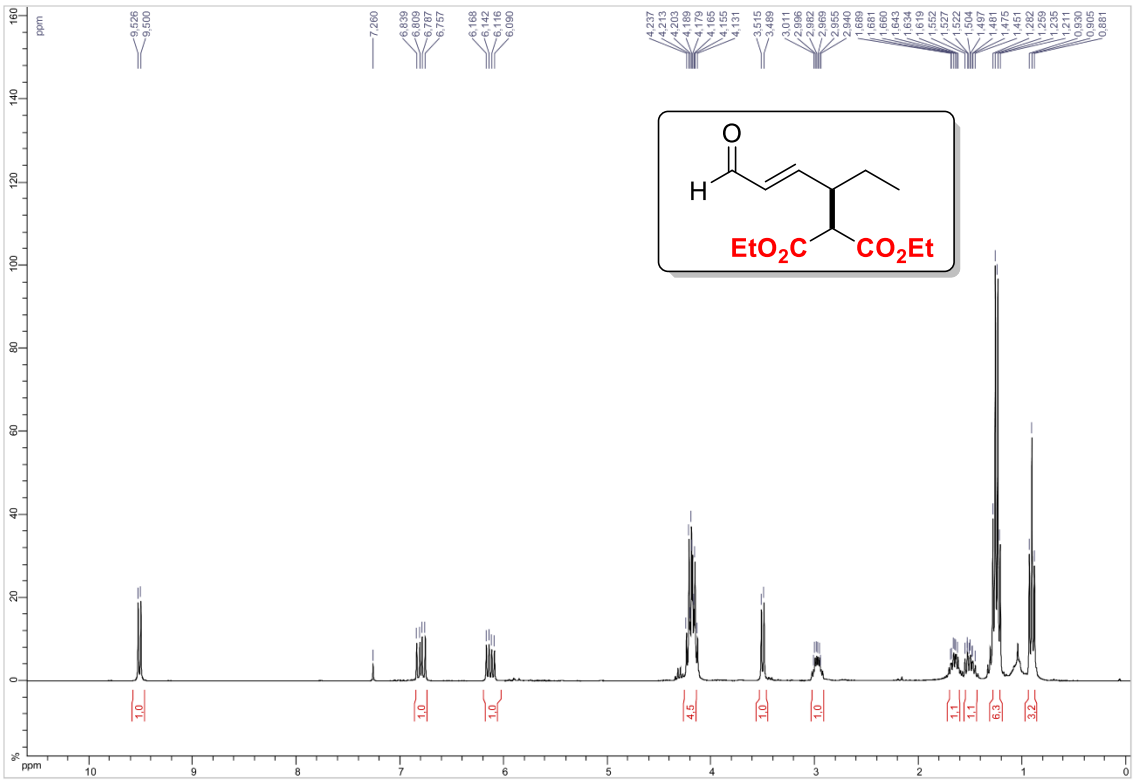



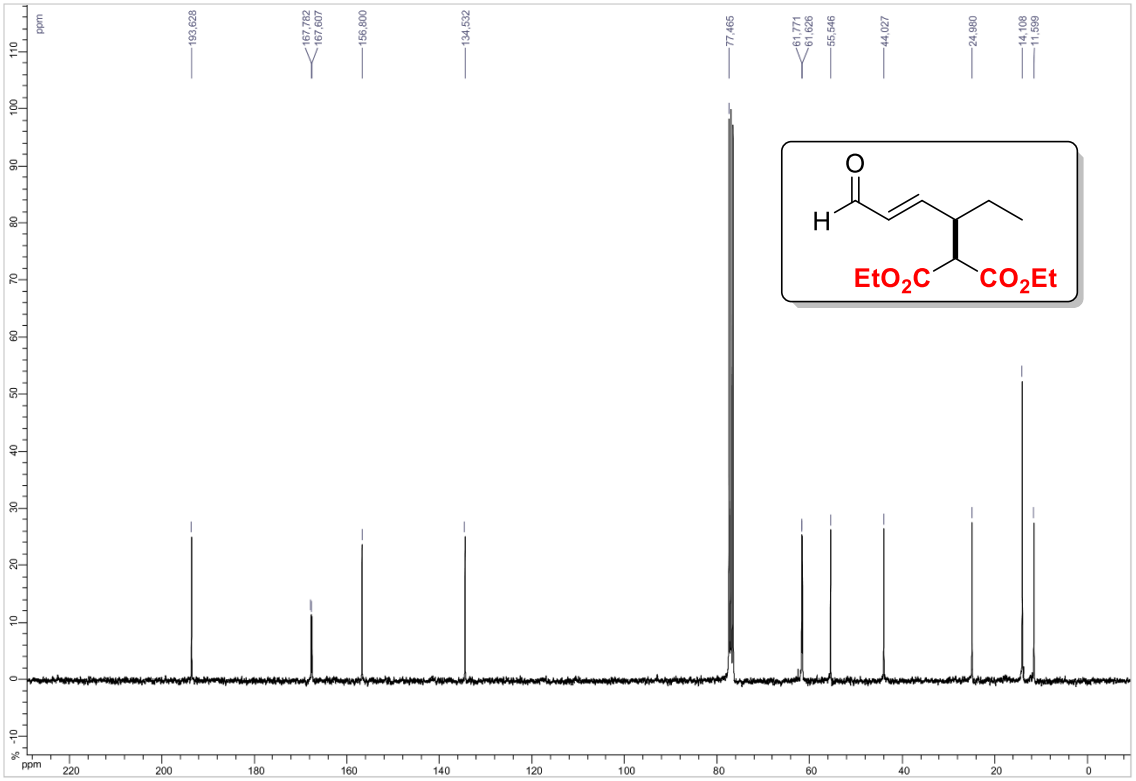
**Diethyl (*E*)-2-(1-oxododec-2-en-4-yl)malonate 6a**



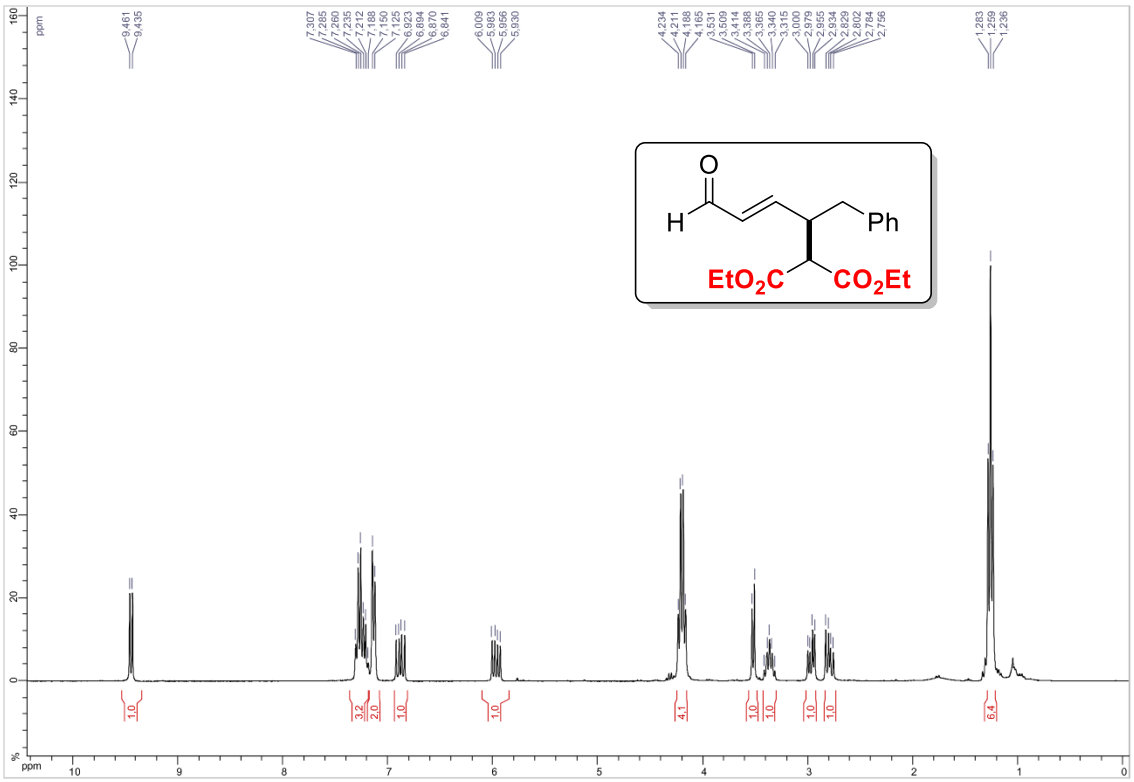



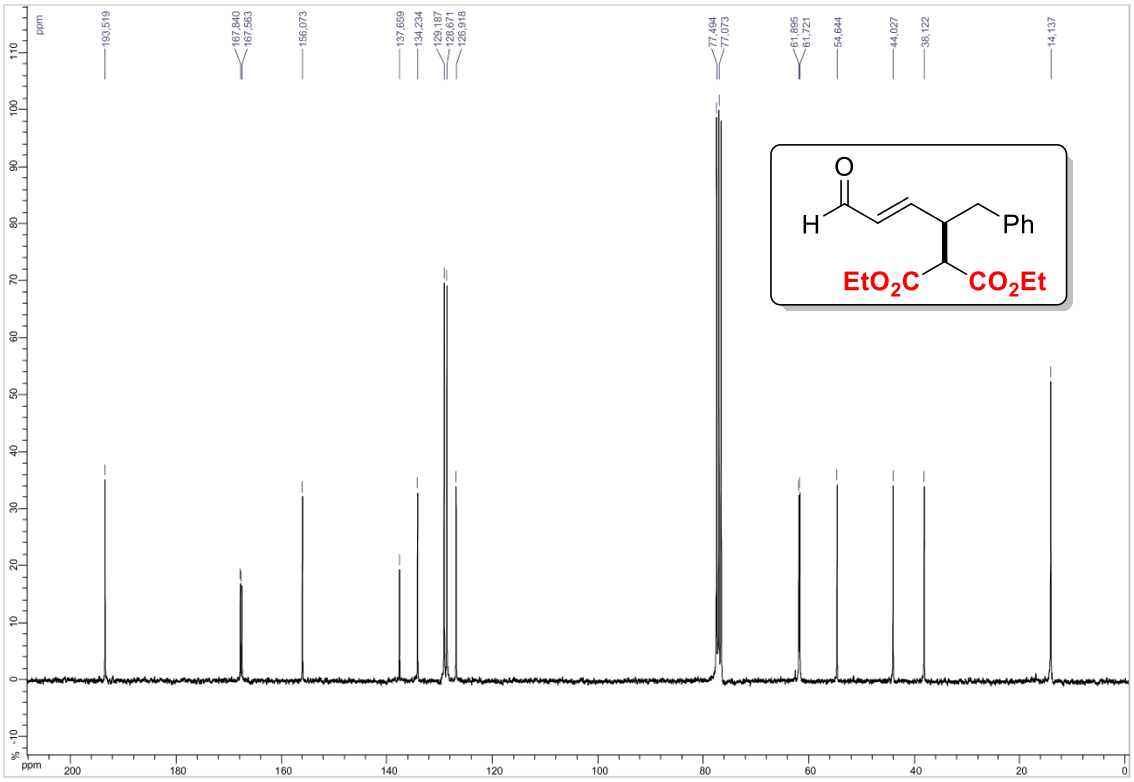
**Diethyl (*E*)-2-(6-oxohex-4-en-3-yl)malonate 6b**



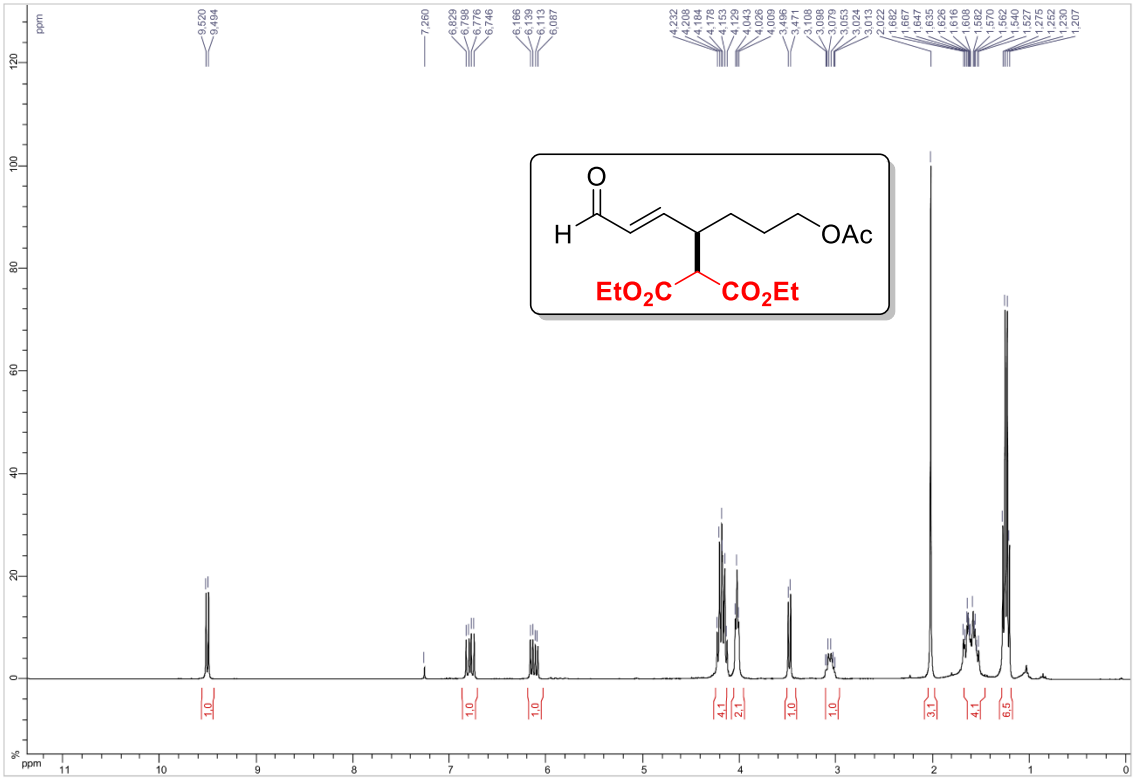



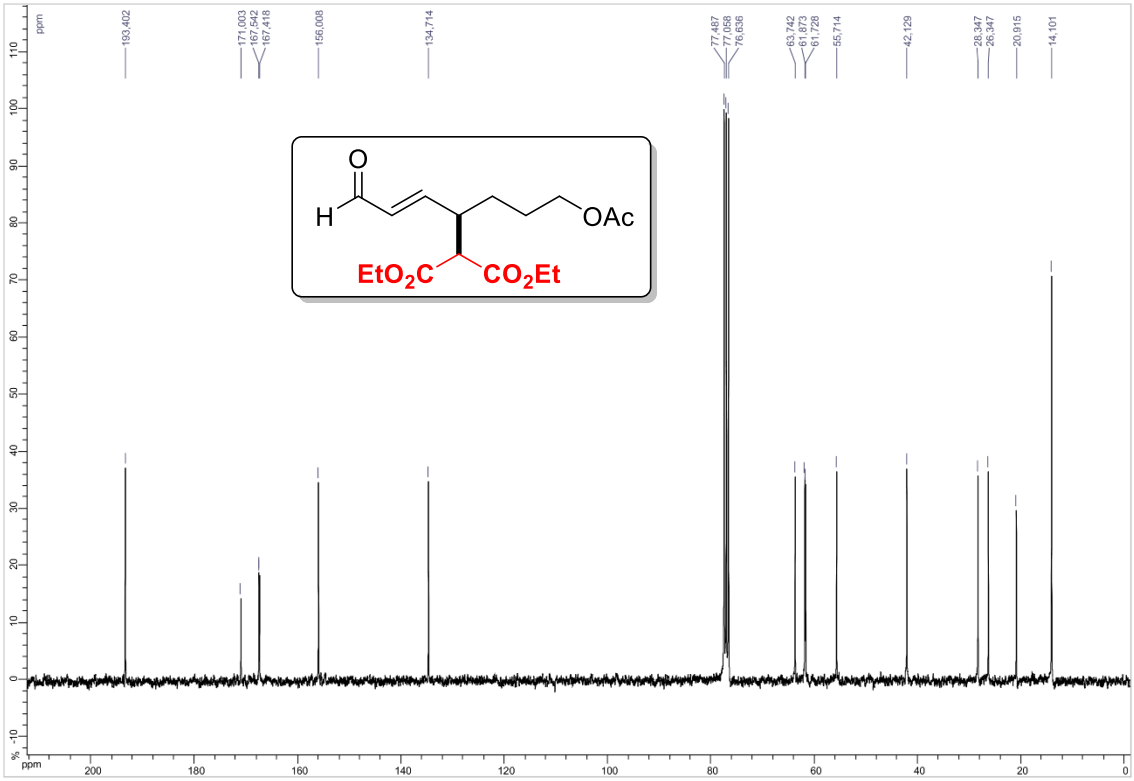
**Diethyl (*E*)-2-(5-oxo-1-phenylpent-3-en-2-yl)malonate 6c**



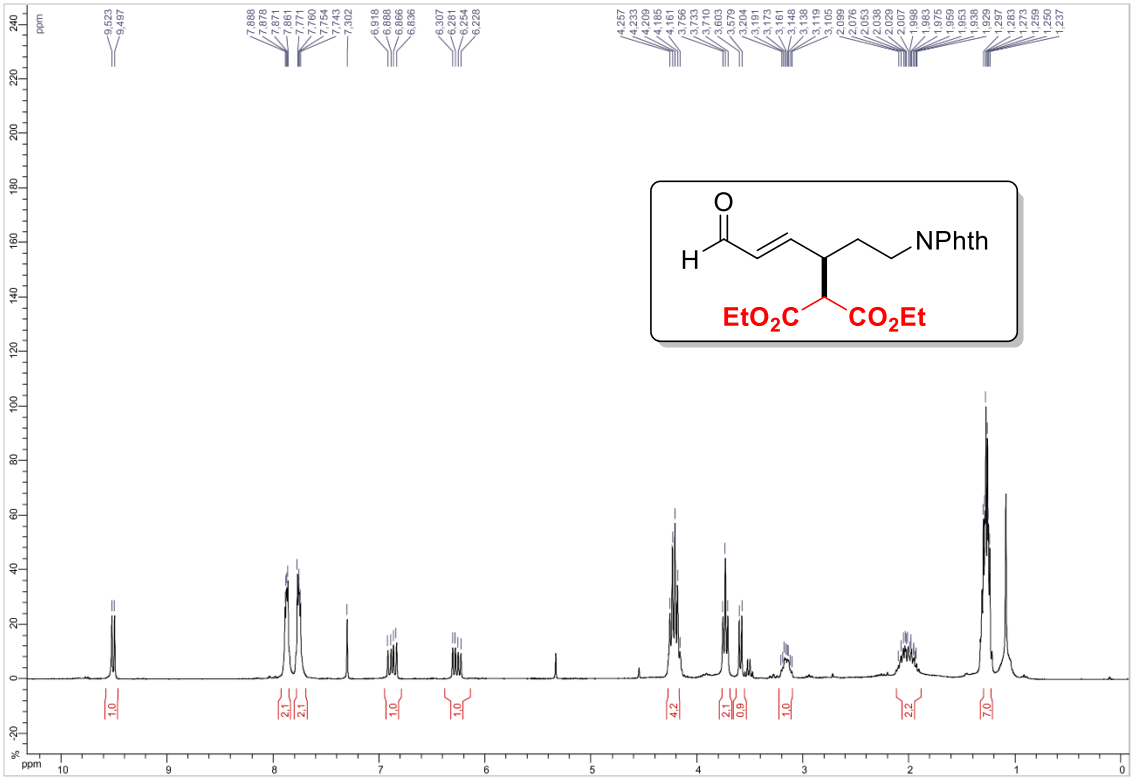



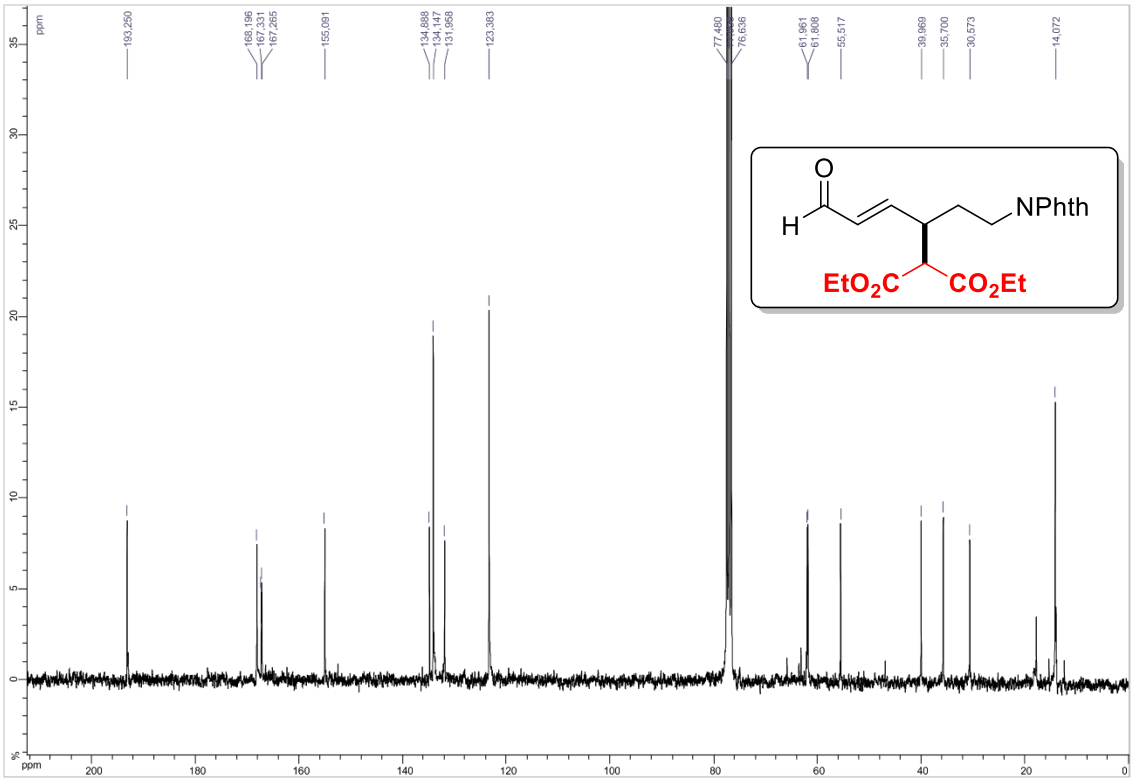
**Diethyl (*E*)-2-(7-acetoxy-1-oxohept-2-en-4-yl)malonate 6d**



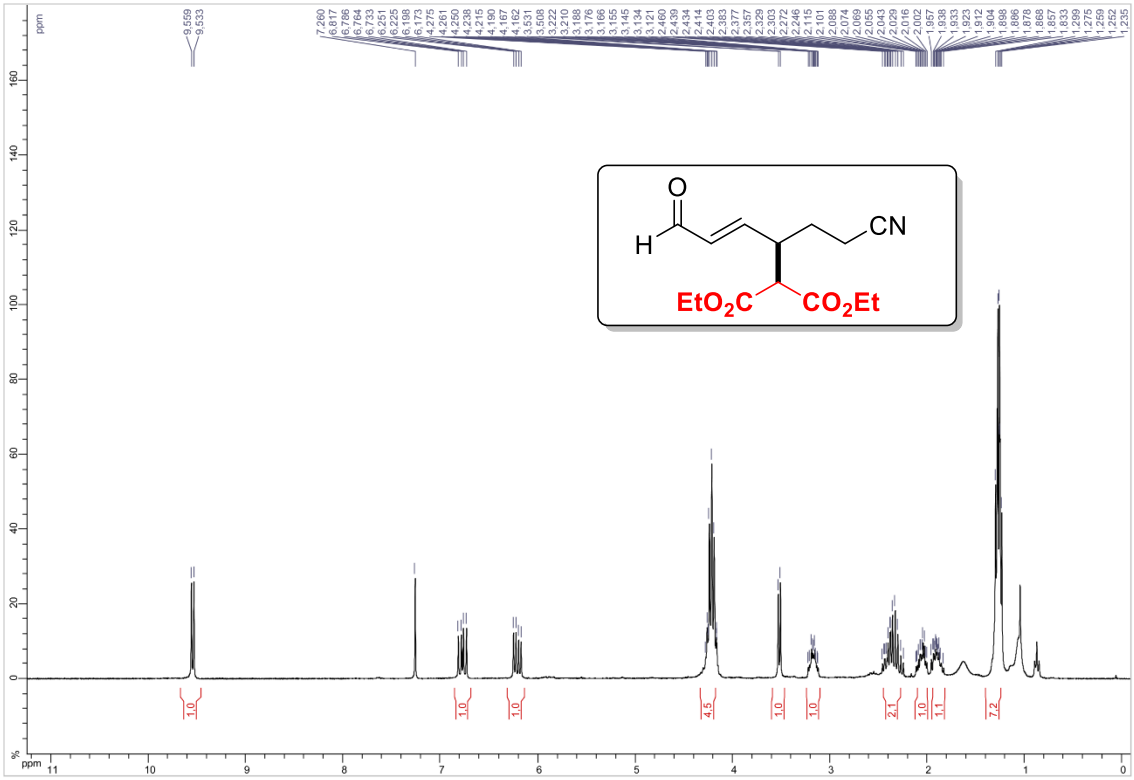



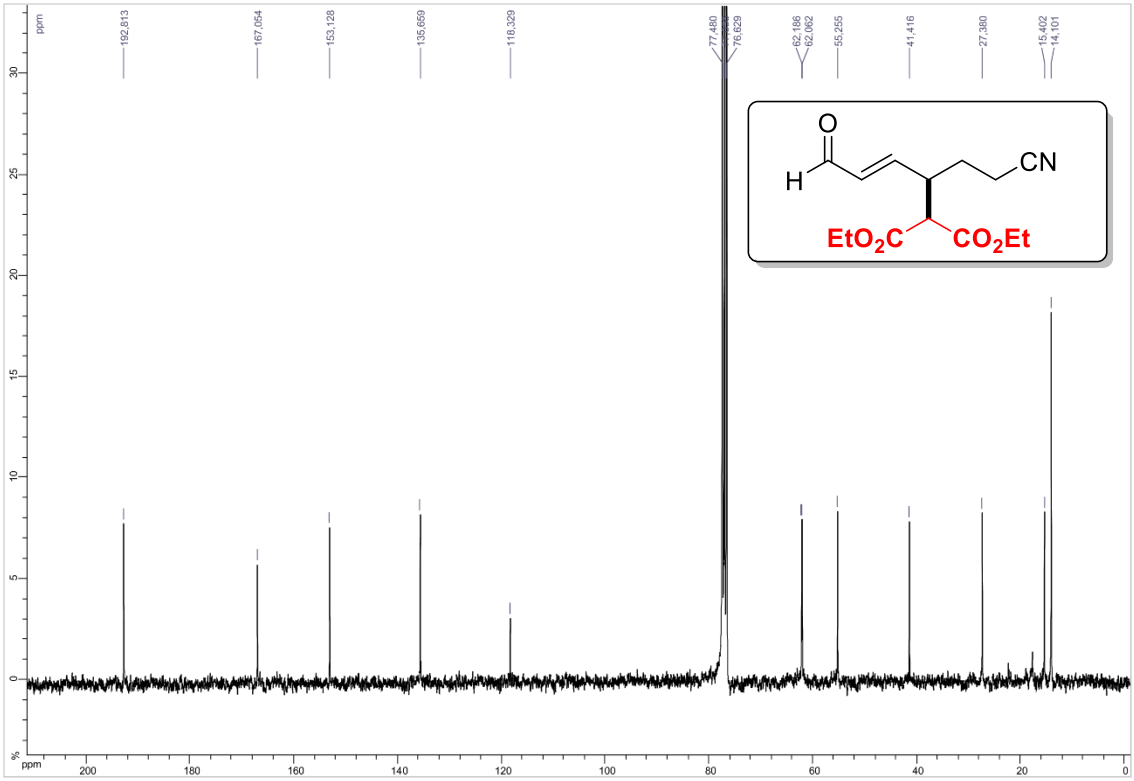
**Diethyl (*E*)-2-(1-(1,3-dioxoisoindolin-2-yl)-6-oxohex-4-en-3-yl)malonate 6e**



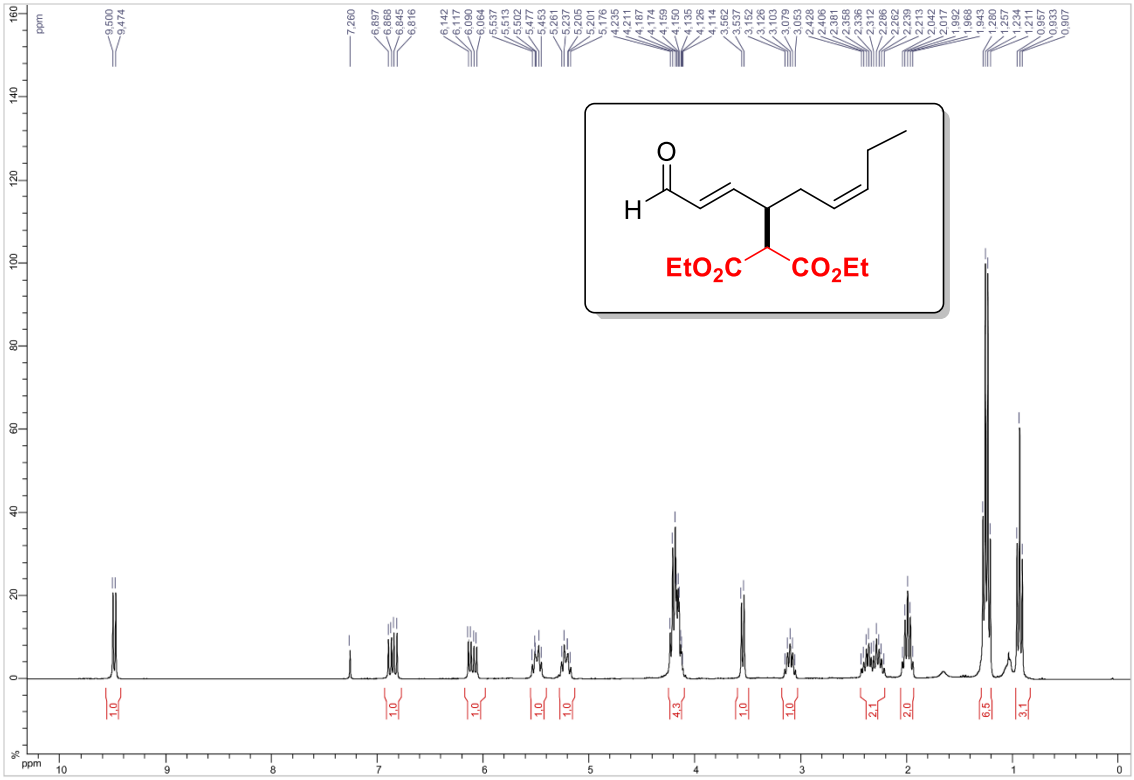



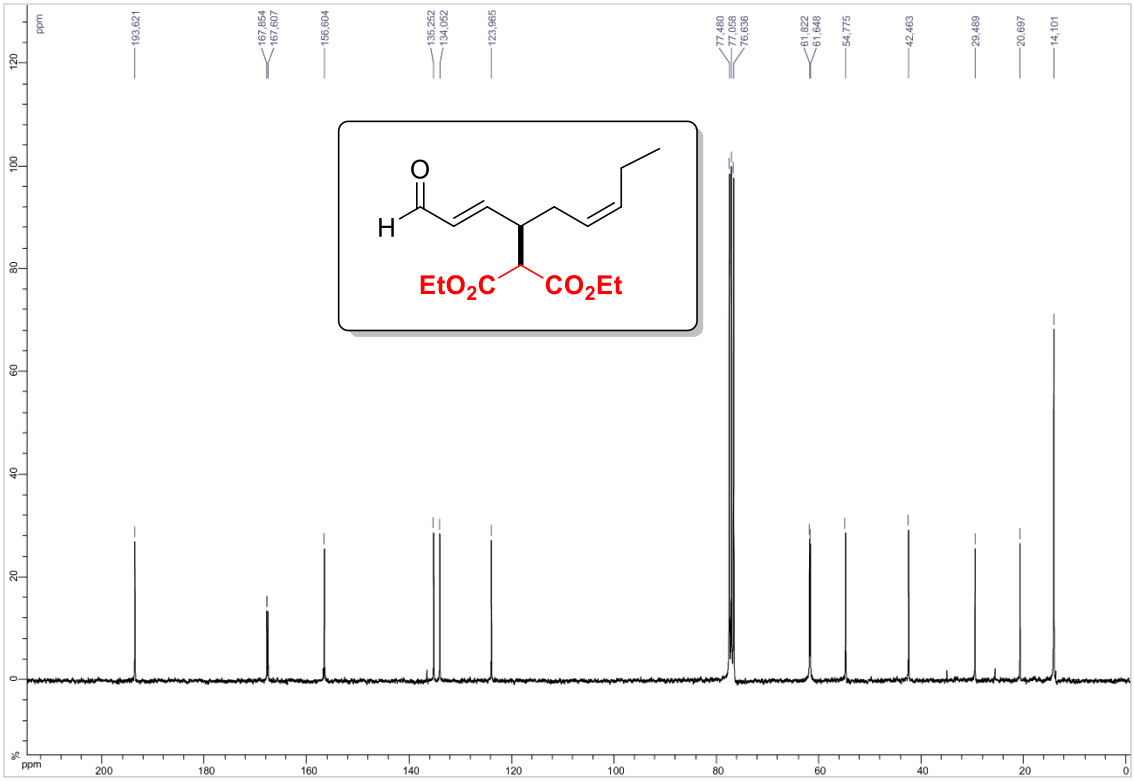
**Diethyl (*E*)-2-(1-cyano-6-oxohex-4-en-3-yl)malonate 6f**



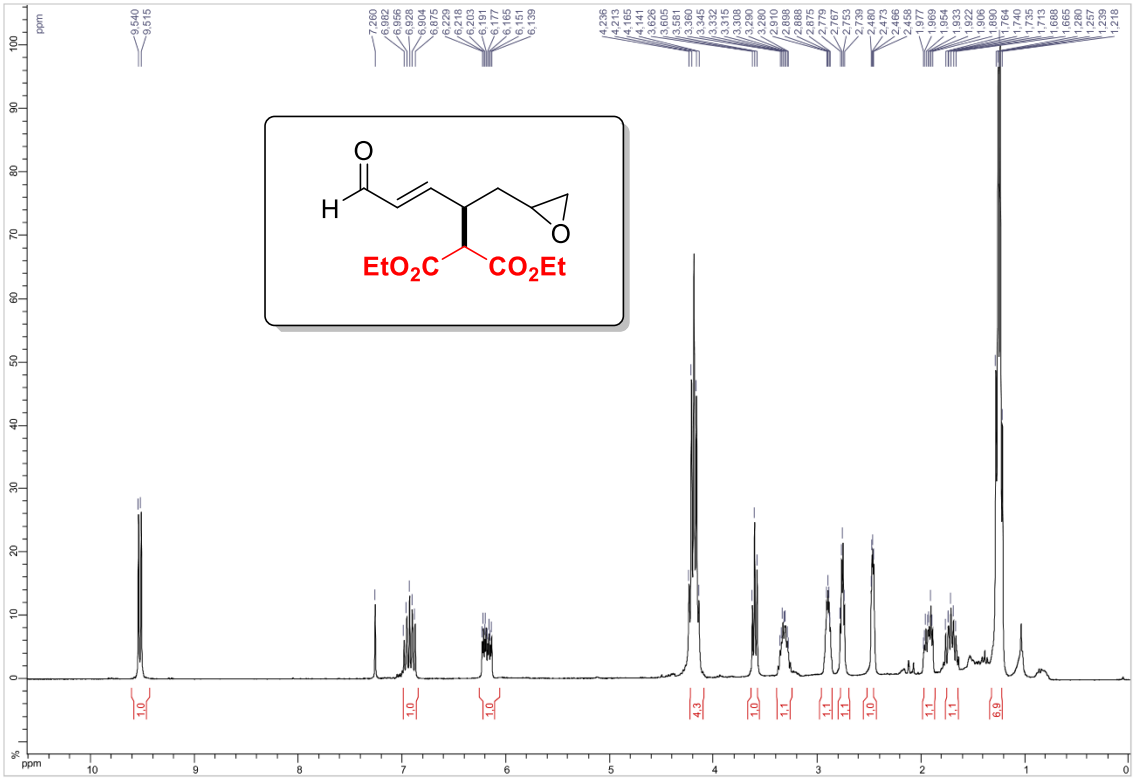



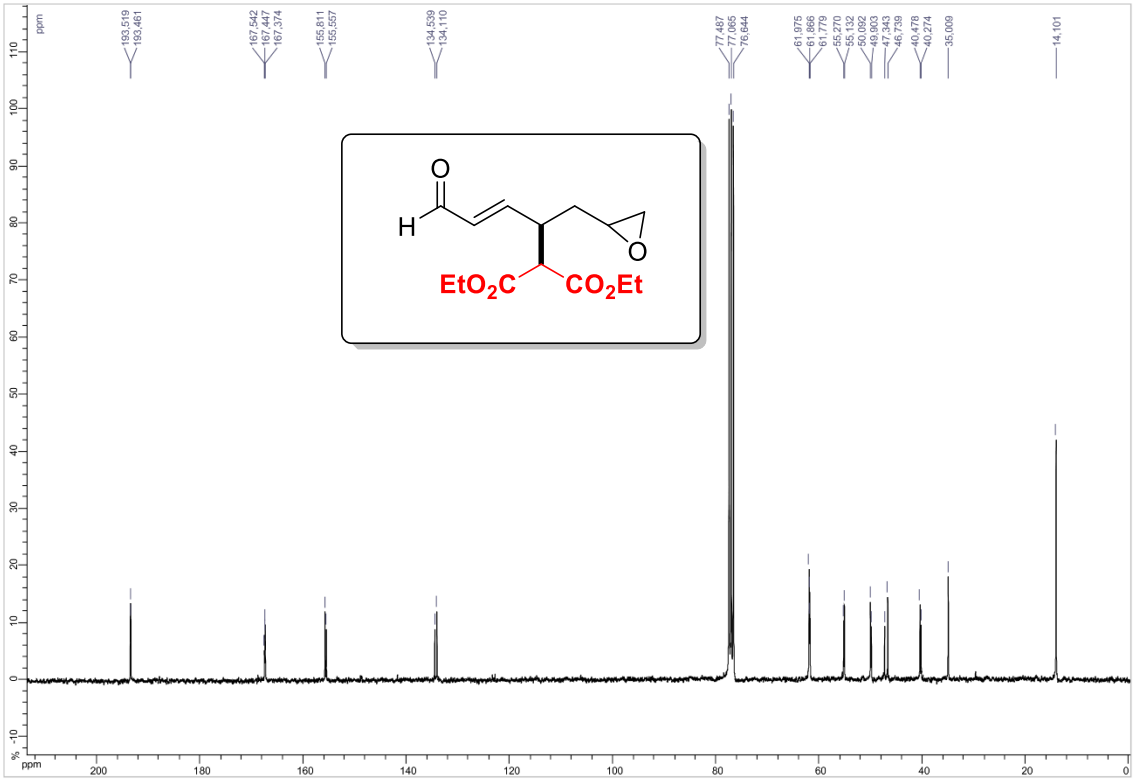
**Diethyl 2-(2*E*,6*Z*)-1-oxonona-2,6-dien-4-yl)malonate 6f**



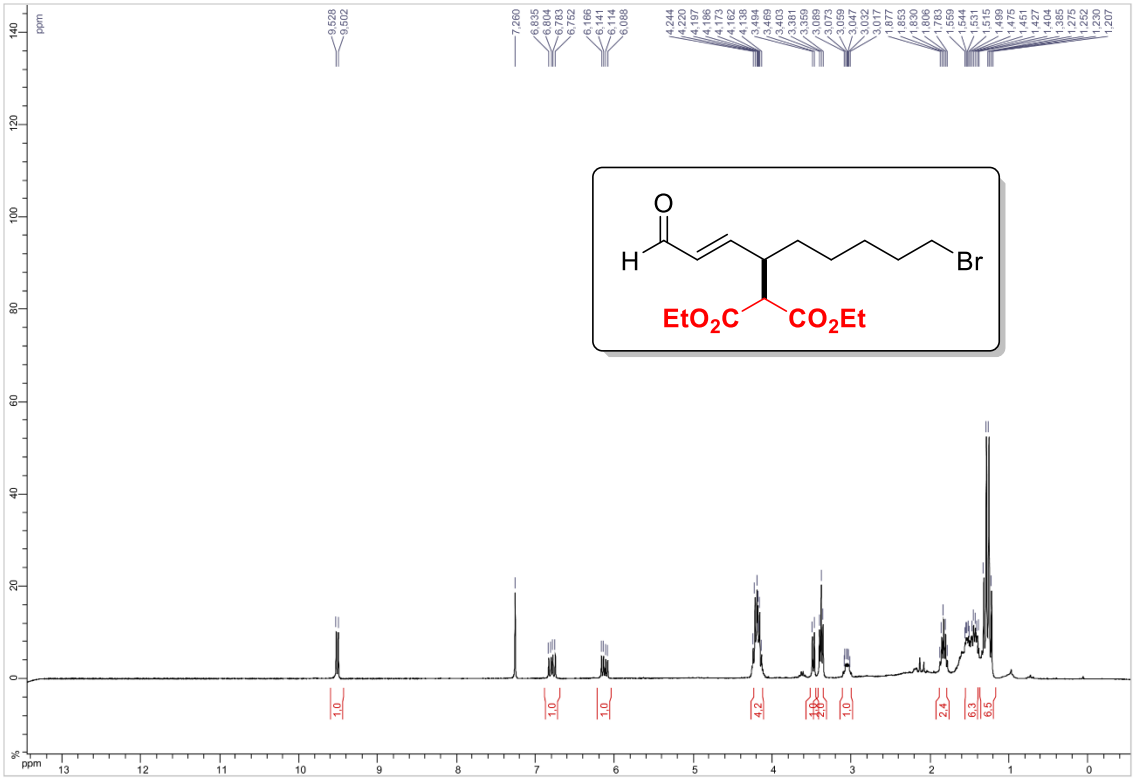



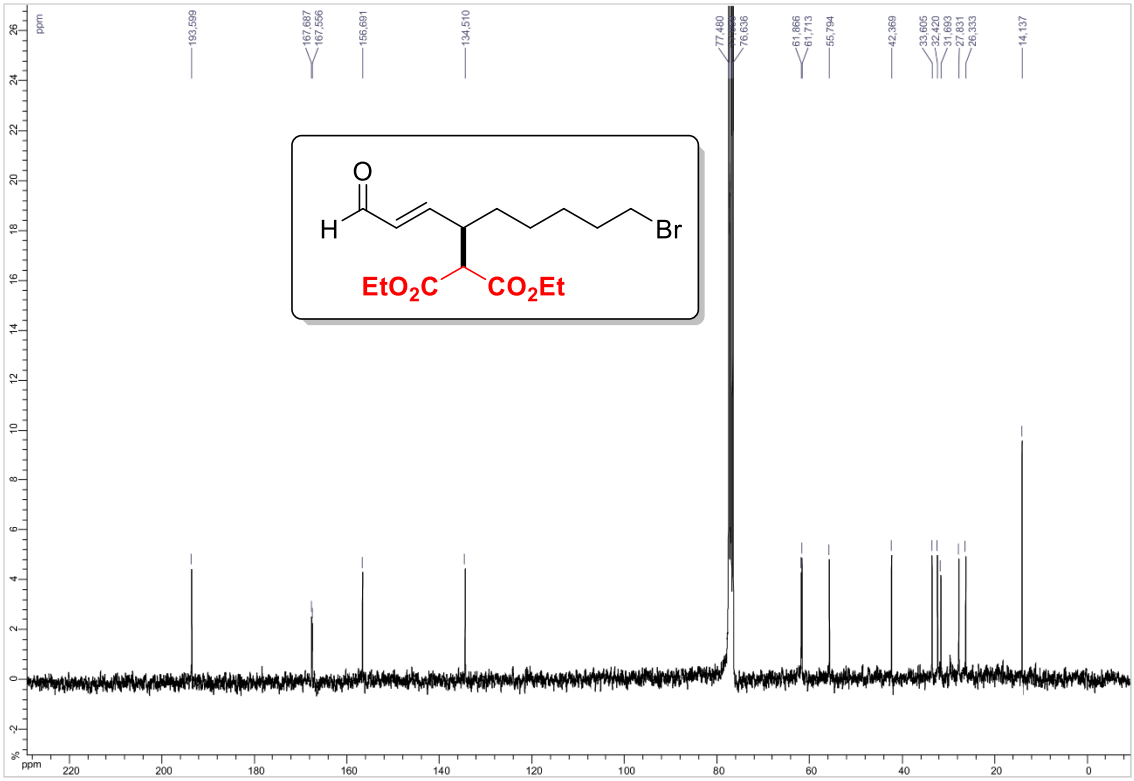
**Diethyl 2-((*E*)-1-(oxiran-2-yl)-5-oxopent-3-en-2-yl)malonate 6h**



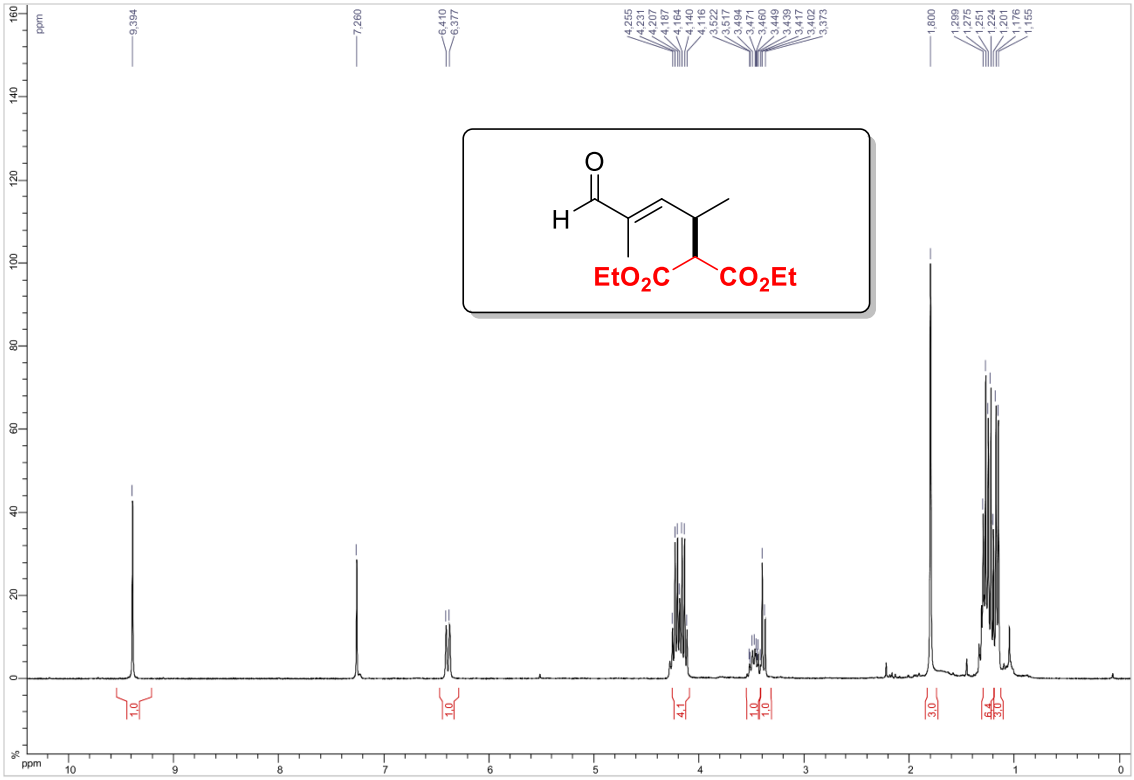



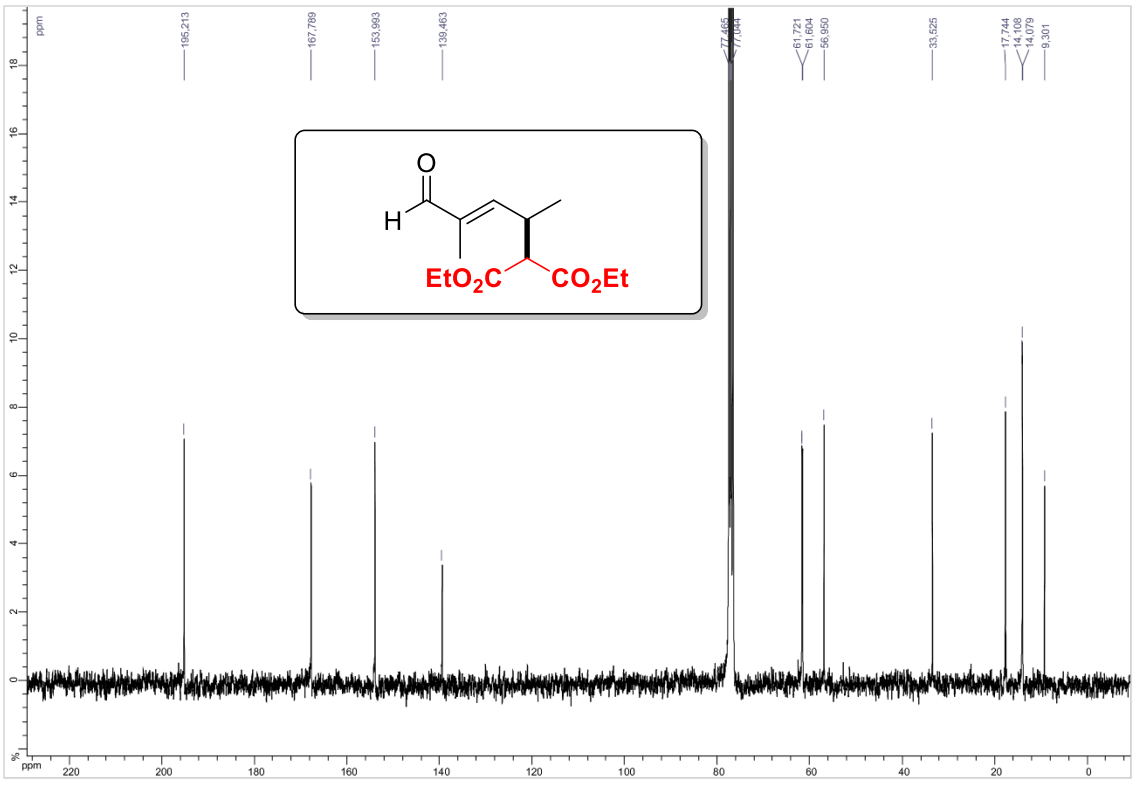
**Diethyl (*E*)-2-(9-bromo-1-oxonon-2-en-4-yl)malonate 6i**



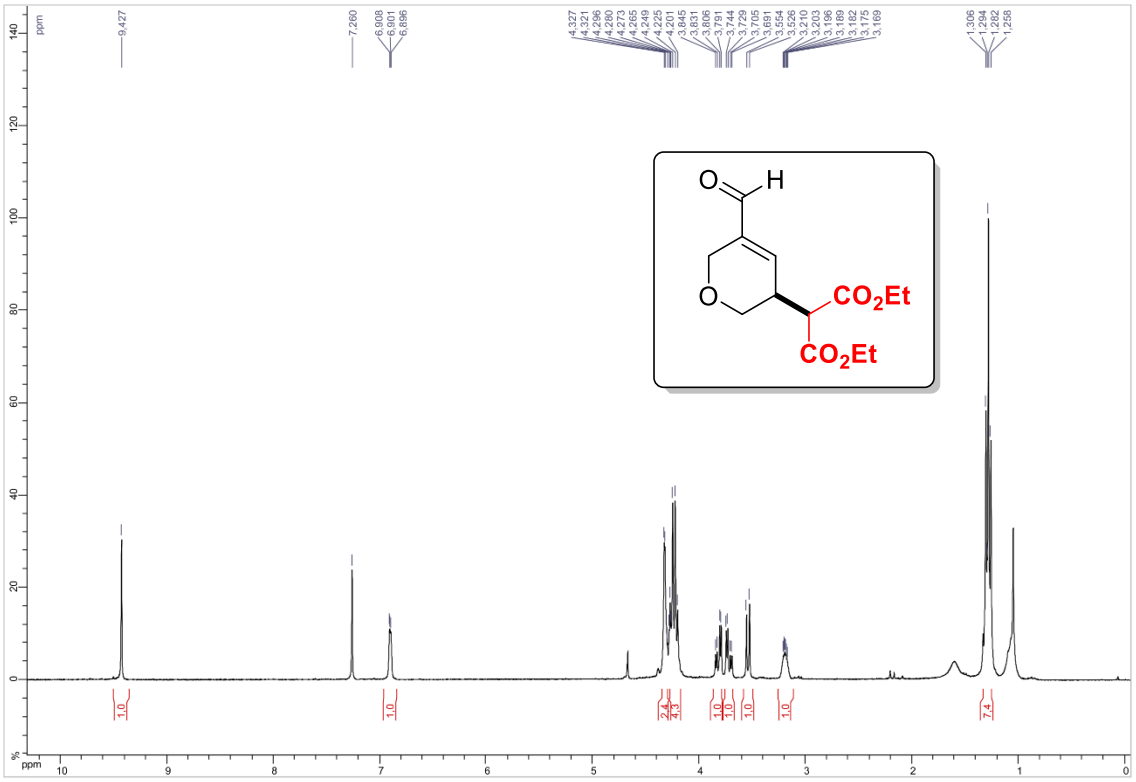



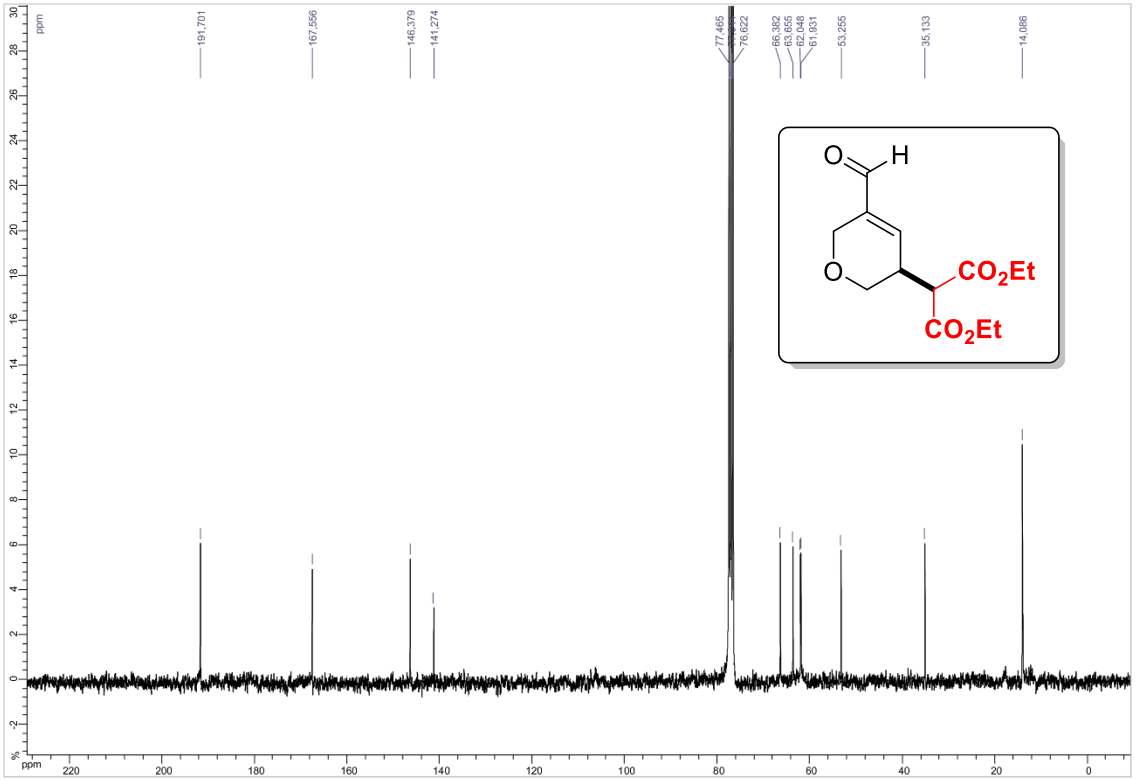
**Diethyl (*E*)-2-(4-methyl-5-oxopent-3-en-2-yl)malonate 6j**



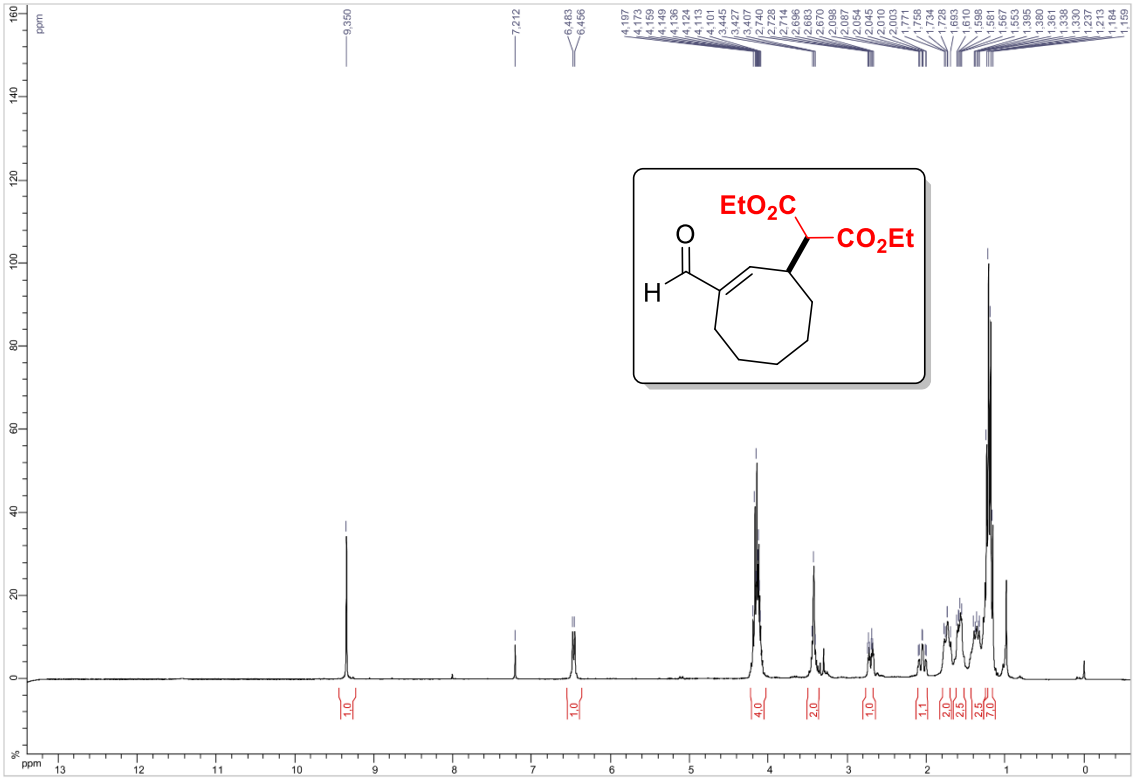



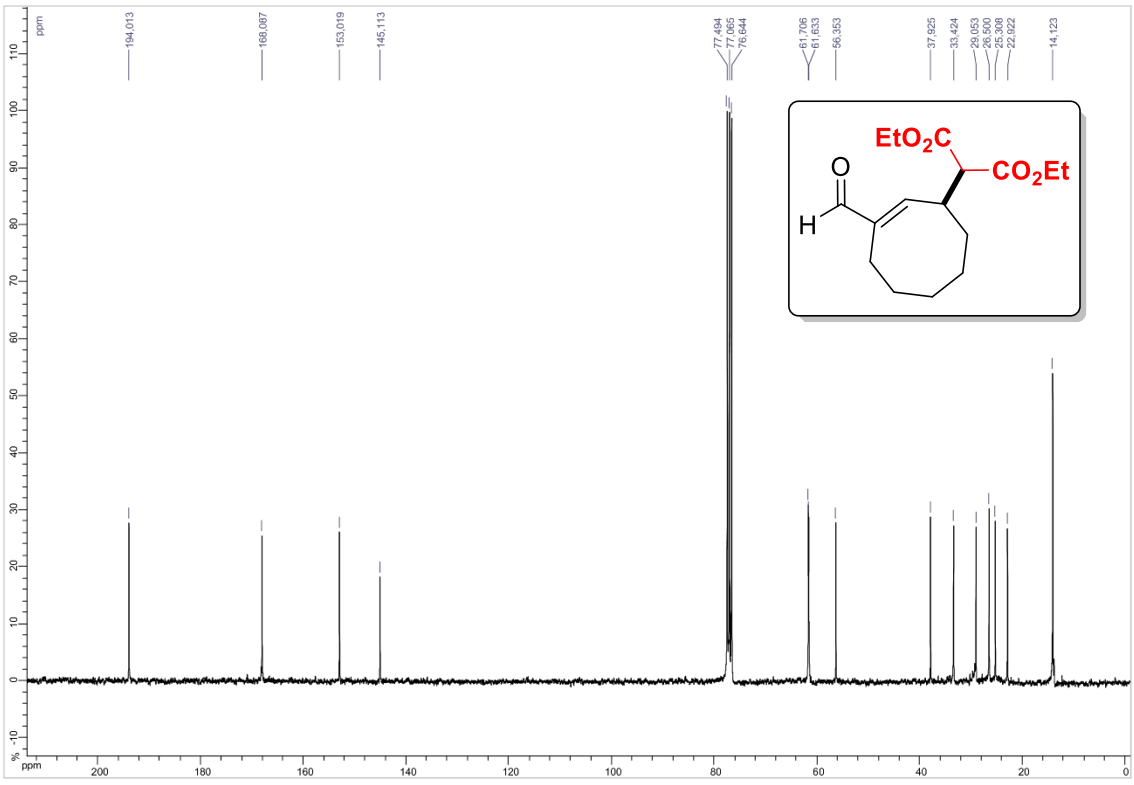
**Diethyl 2-(5-formyl-3,6-dihydro-2H-pyran-3-yl)malonate 6k**



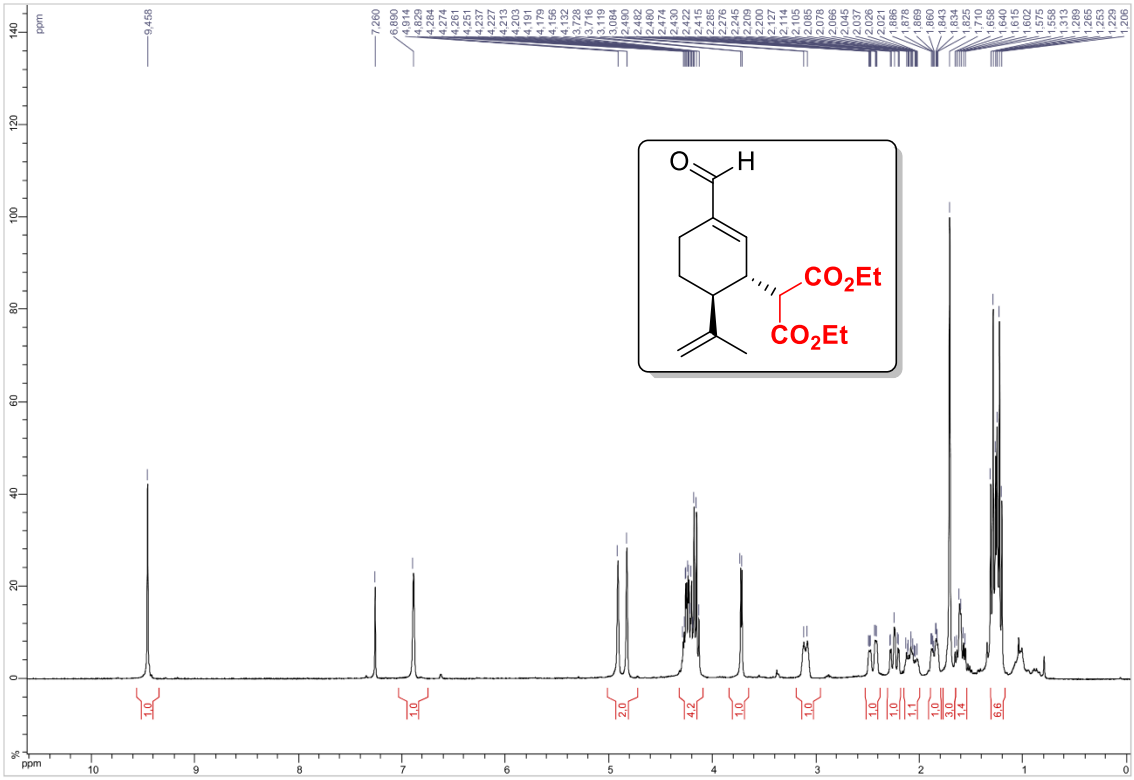



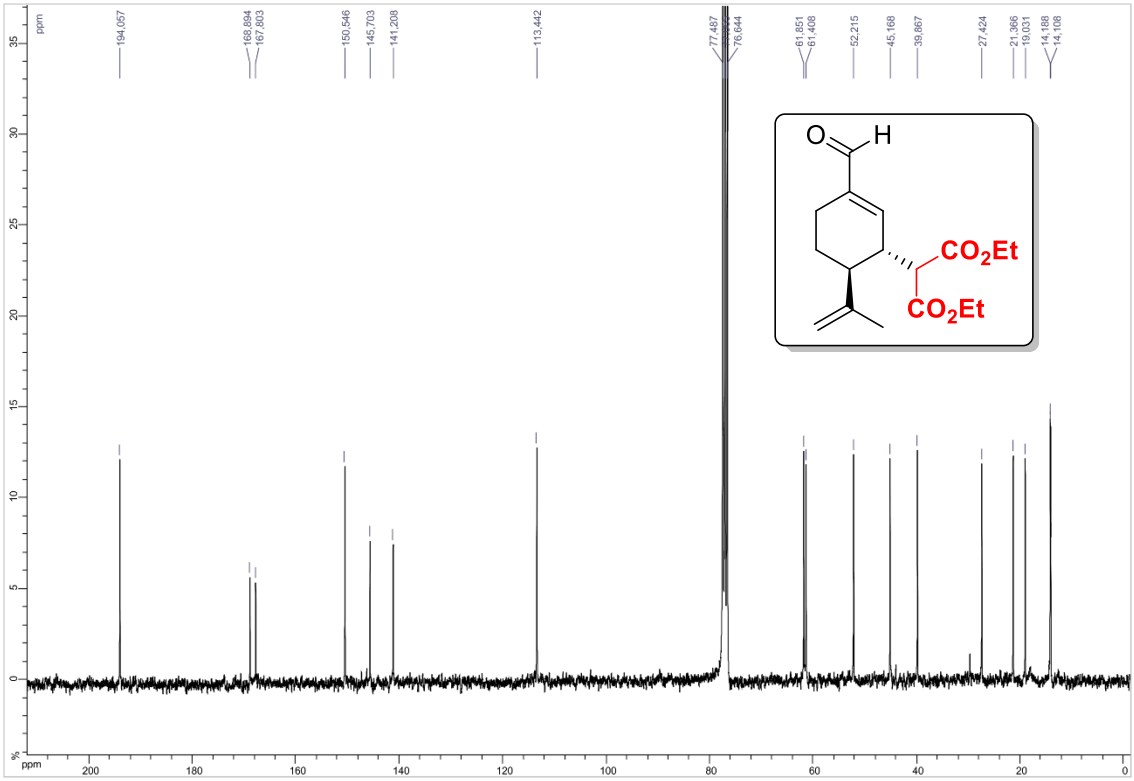
**Diethyl (*E*)-2-(3-formylcyclooct-2-en-1-yl)malonate 6l**



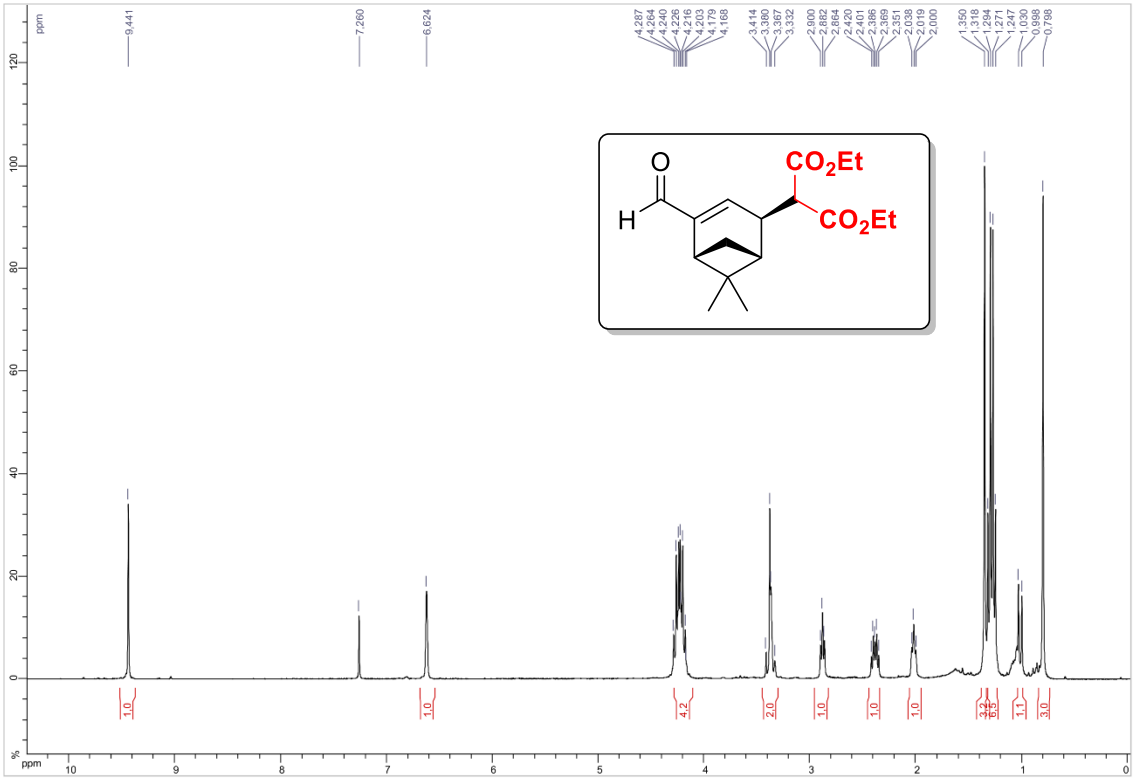



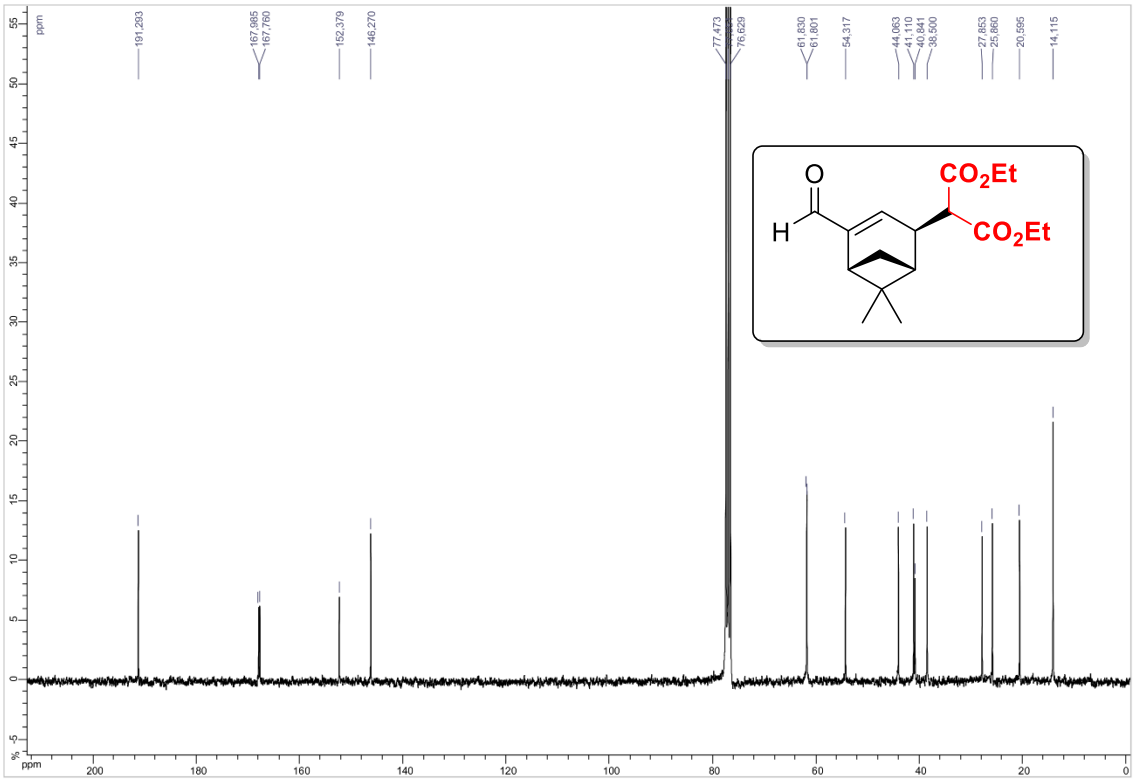
**Diethyl 2-(3-formyl-6-(prop-1-en-2-yl)cyclohex-2-en-1-yl)malonate 6m**



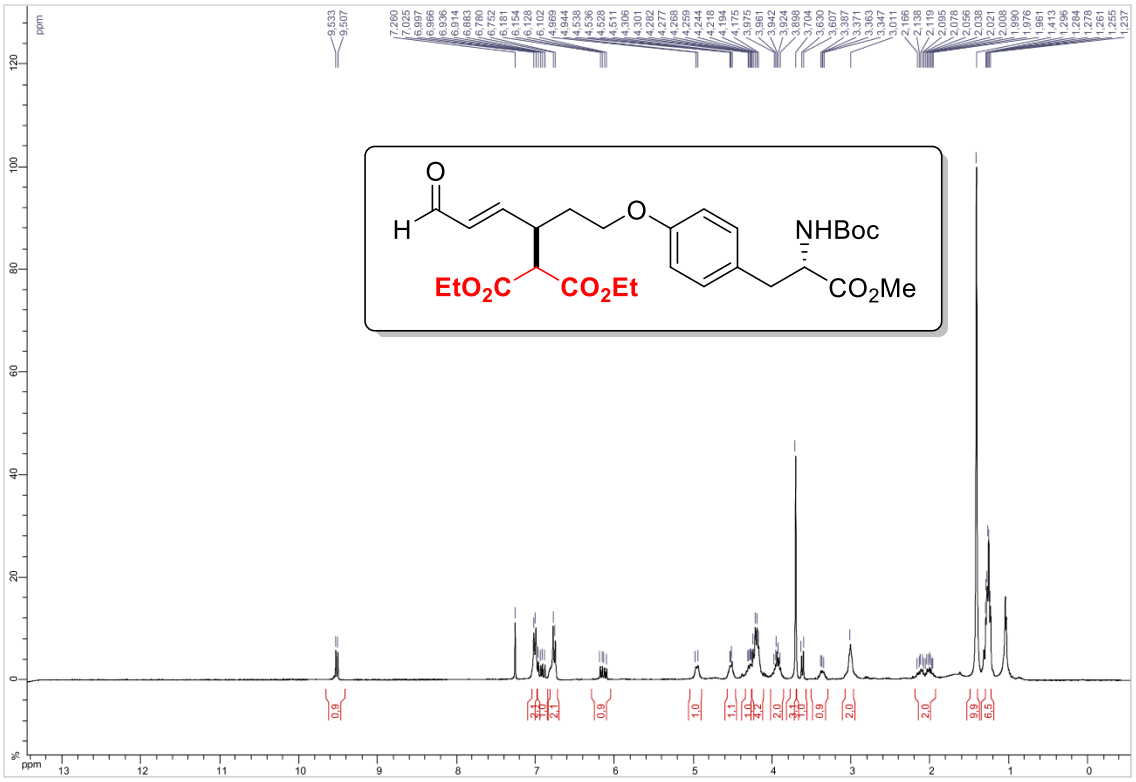



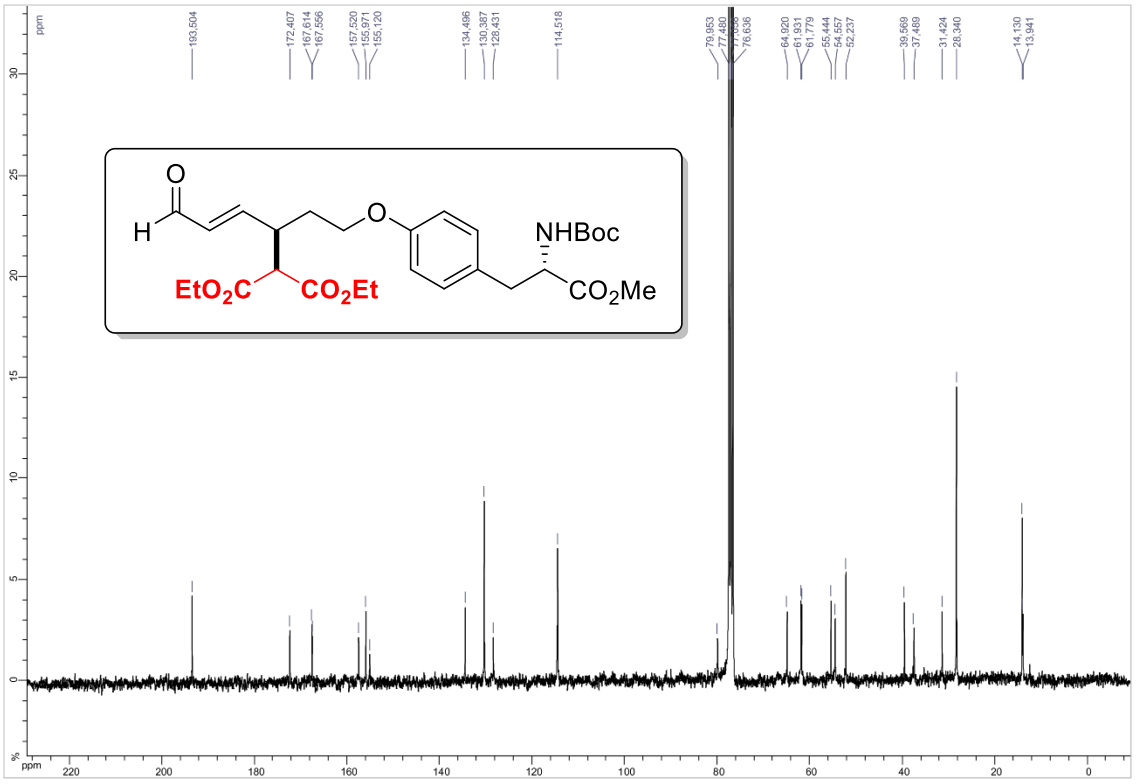
**Diethyl 2-(4-formyl-6,6-dimethylbicyclo[3.1.1]hept-3-en-2-yl)malonate 6n**



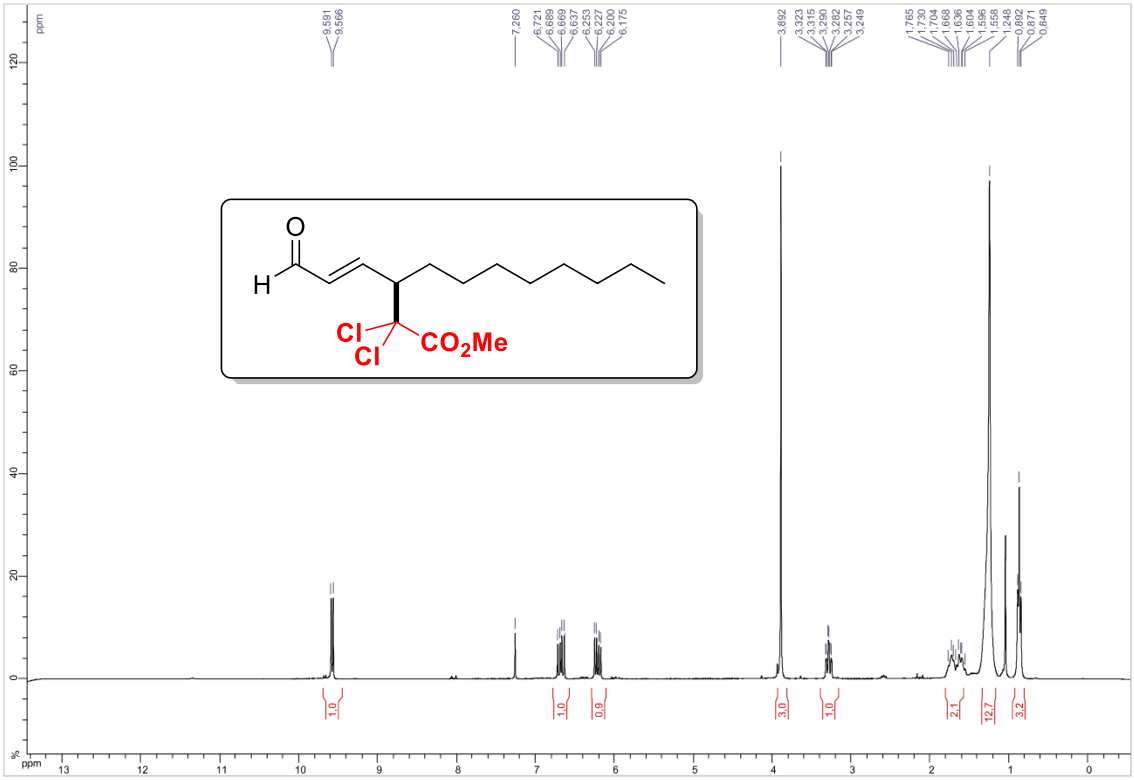



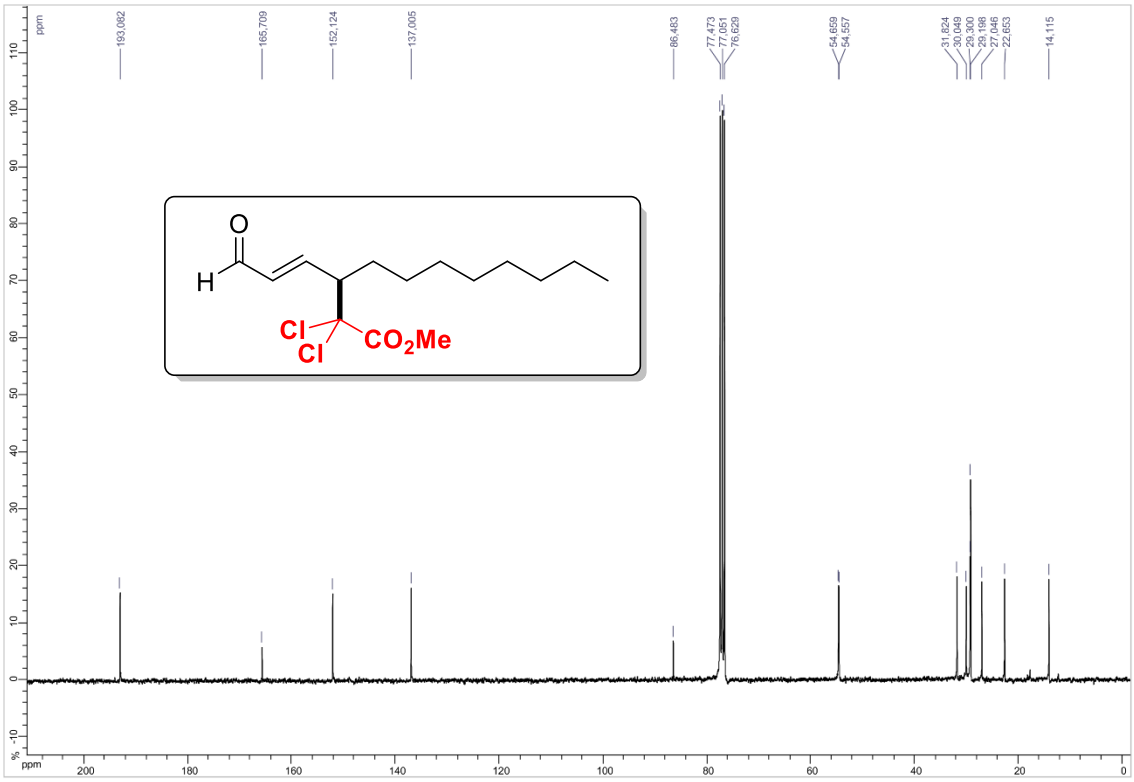
**Diethyl 2-((*E*)-1-(4-((S)-2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)phenoxy)-6-oxohex-4-en-3-yl)malonate 6o**



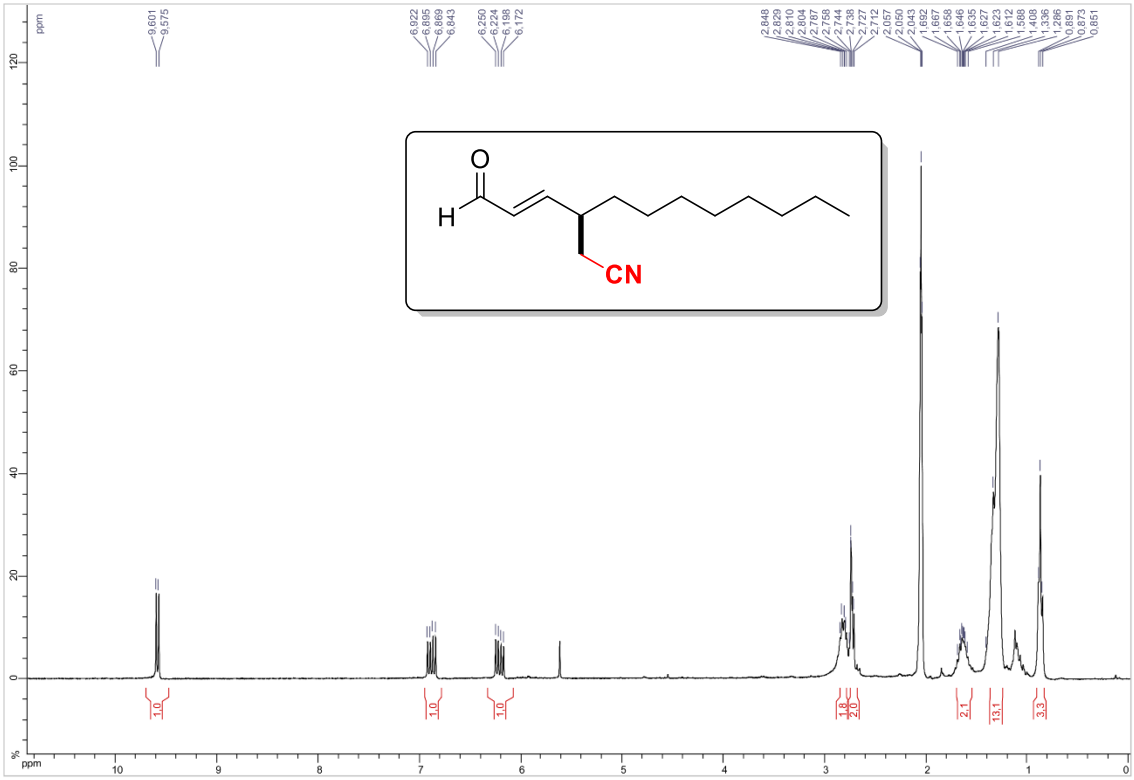



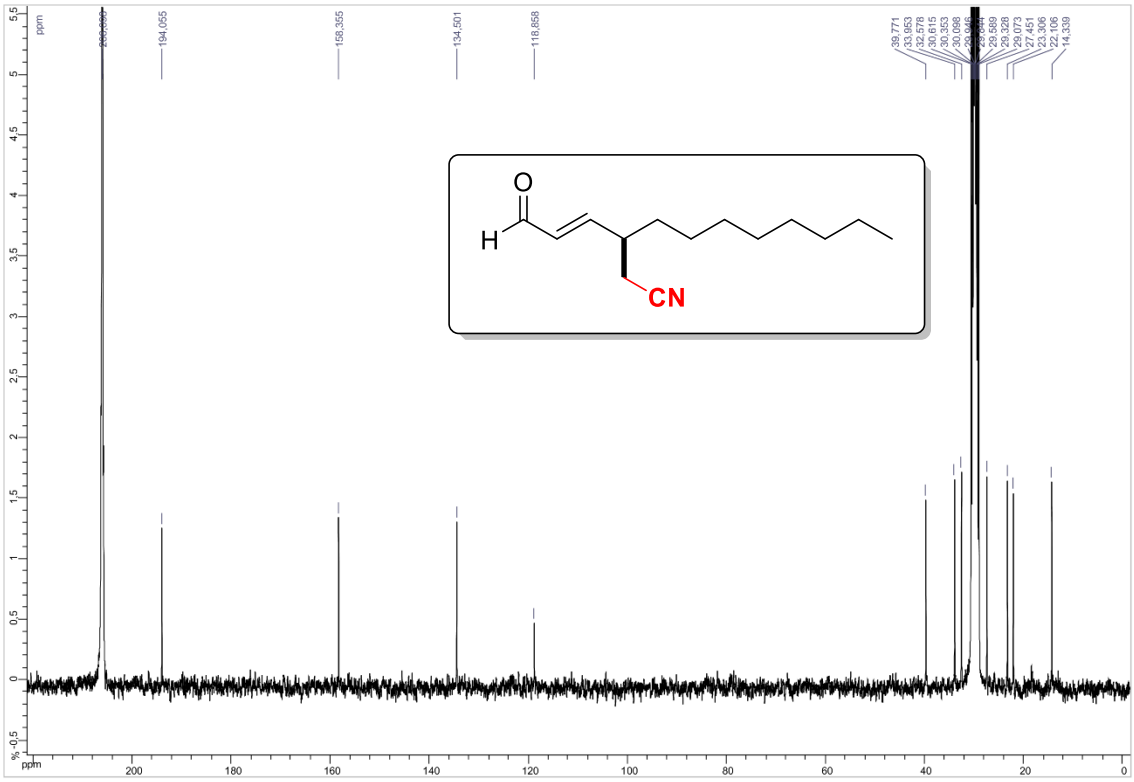
**Methyl (*E*)-2,2-dichloro-3-(3-oxoprop-1-en-1-yl)undecanoate 6p**



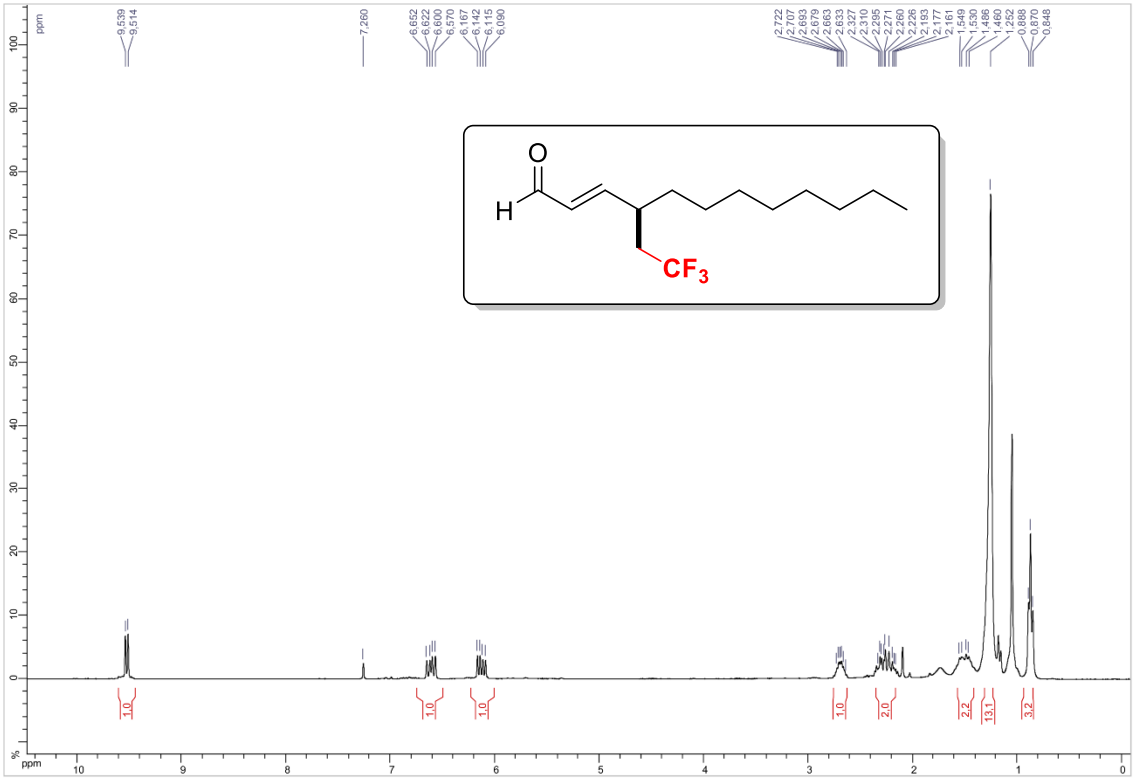



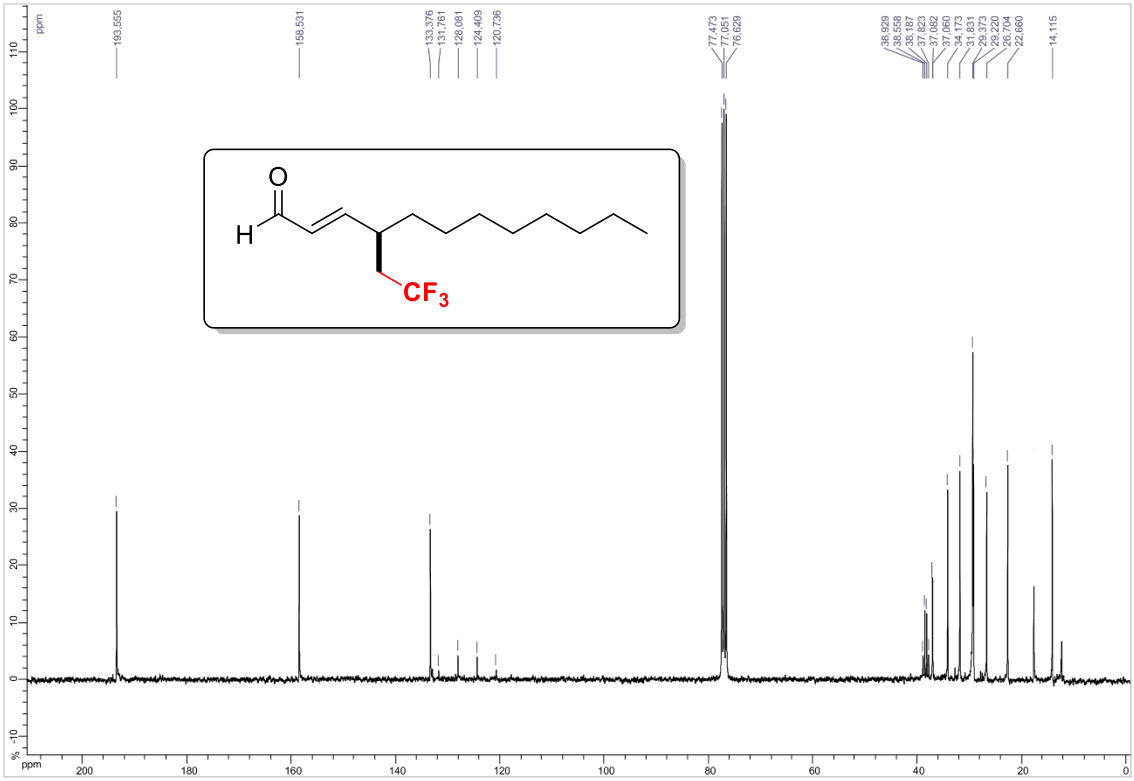
## (*E*)-3-(3-Oxoprop-1-en-1-yl)undecanenitrile 6q



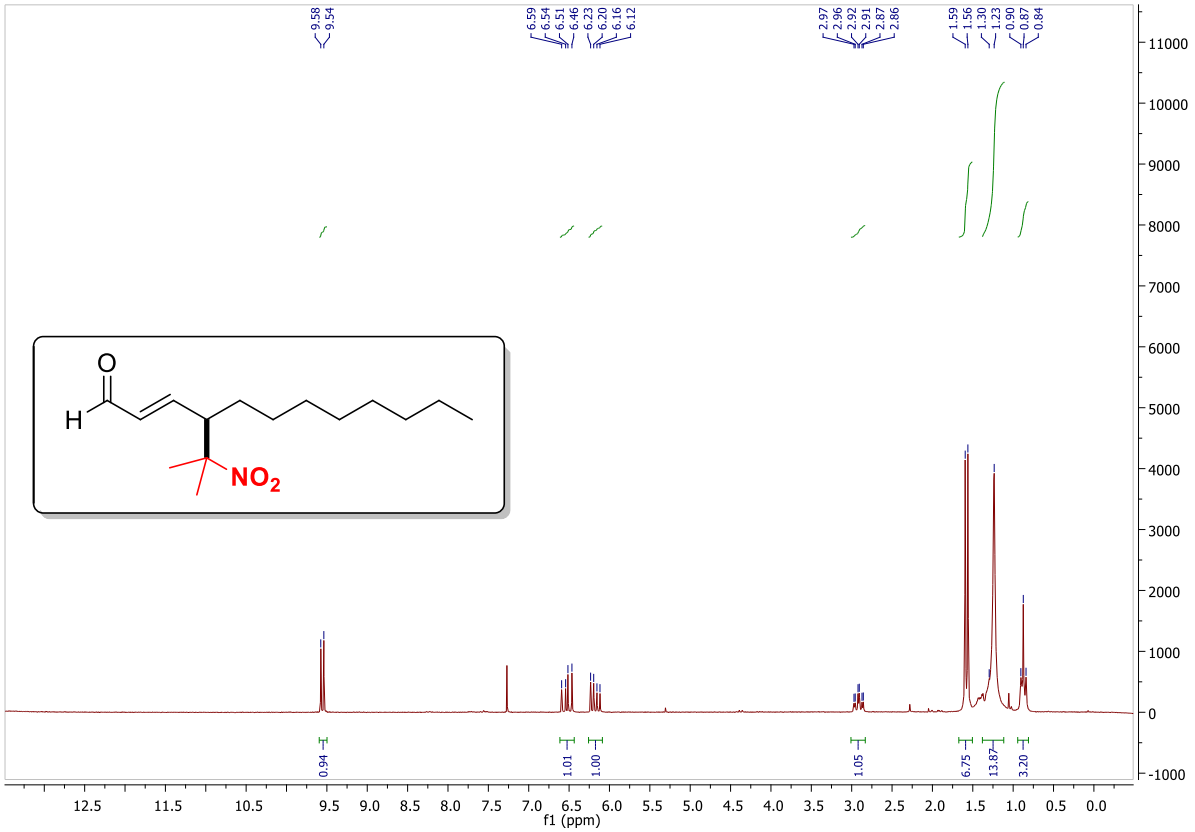



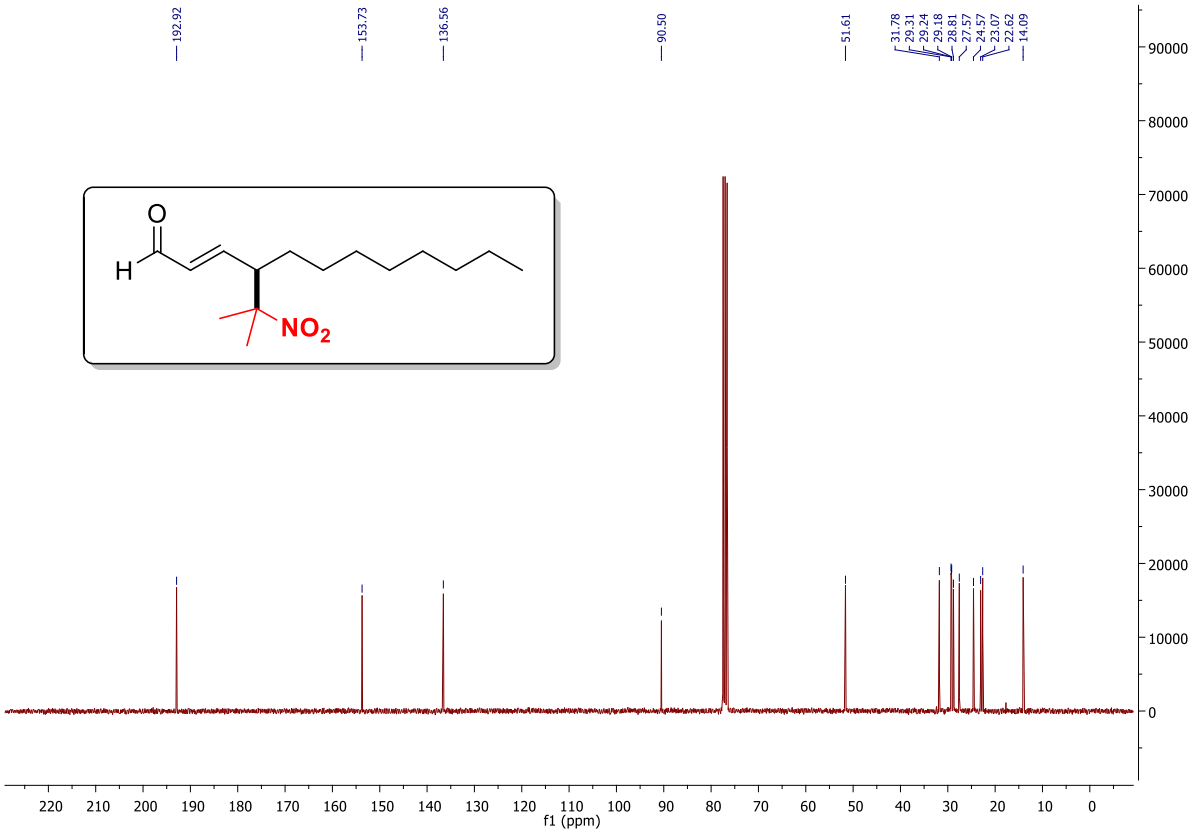
**(*E*)-4-(2,2,2-Trifluoroethyl)dodec-2-enal 6r**



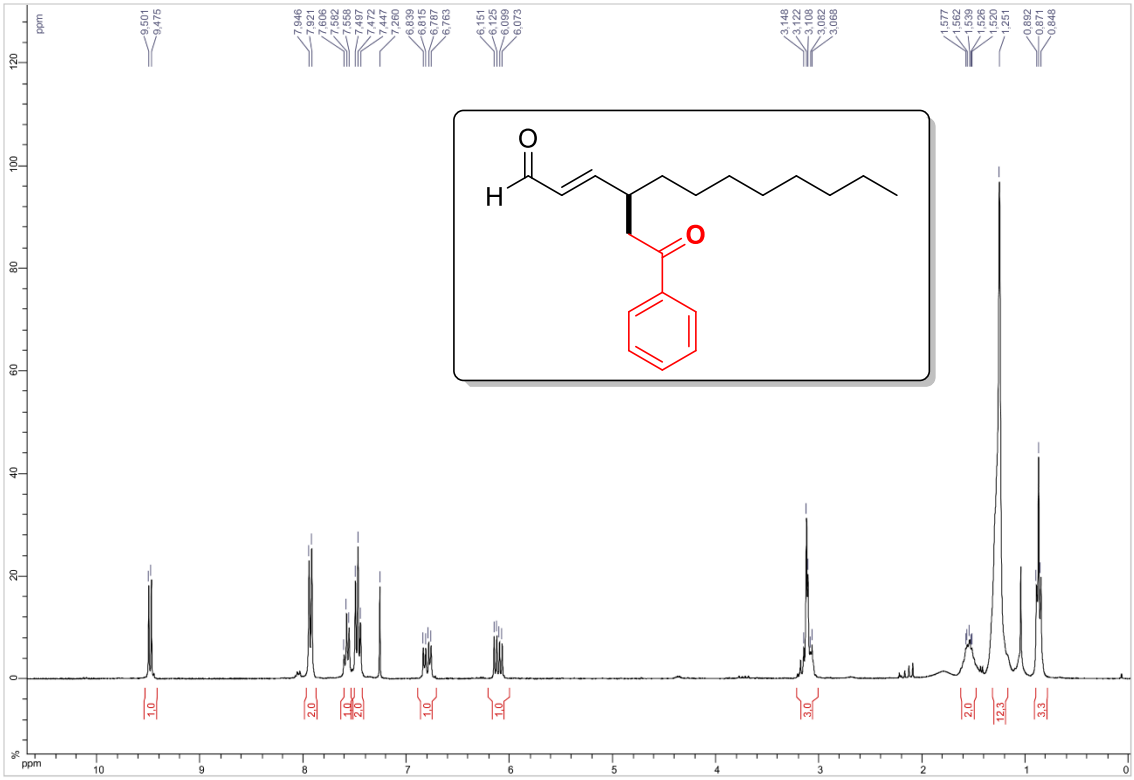



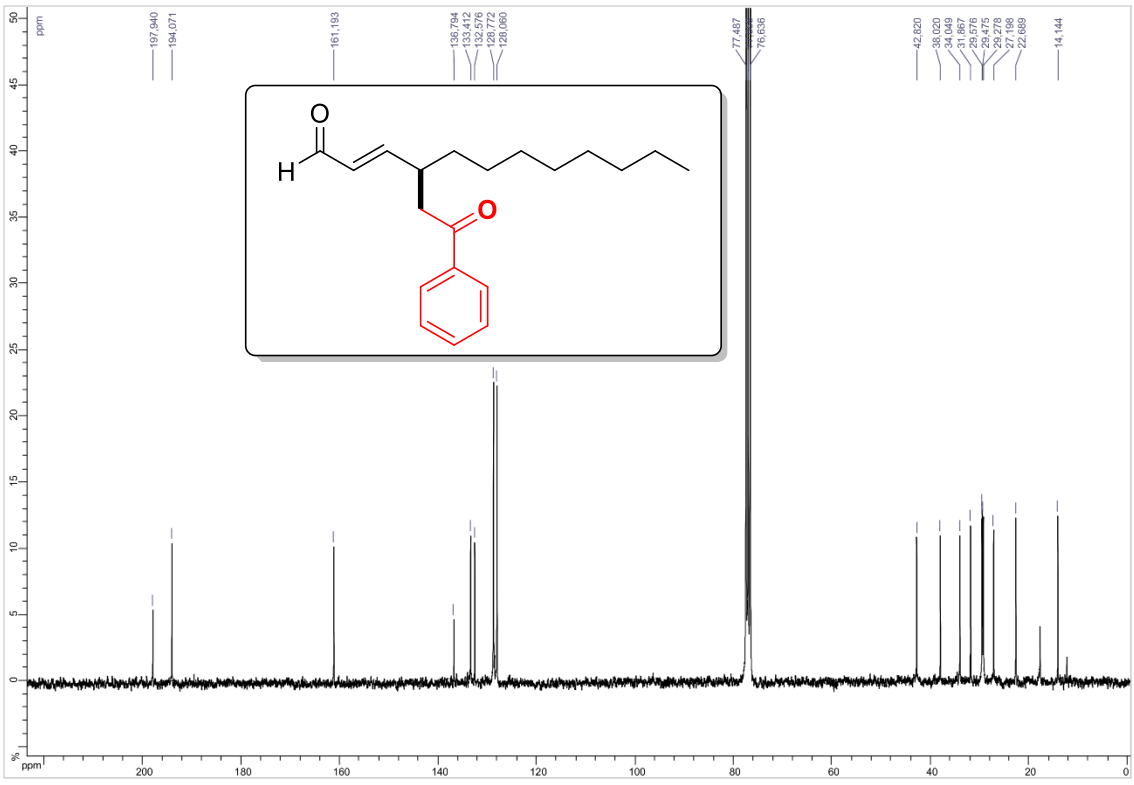
## (*E*)-4-(2-nitropropan-2-yl)dodec-2-enal 6s



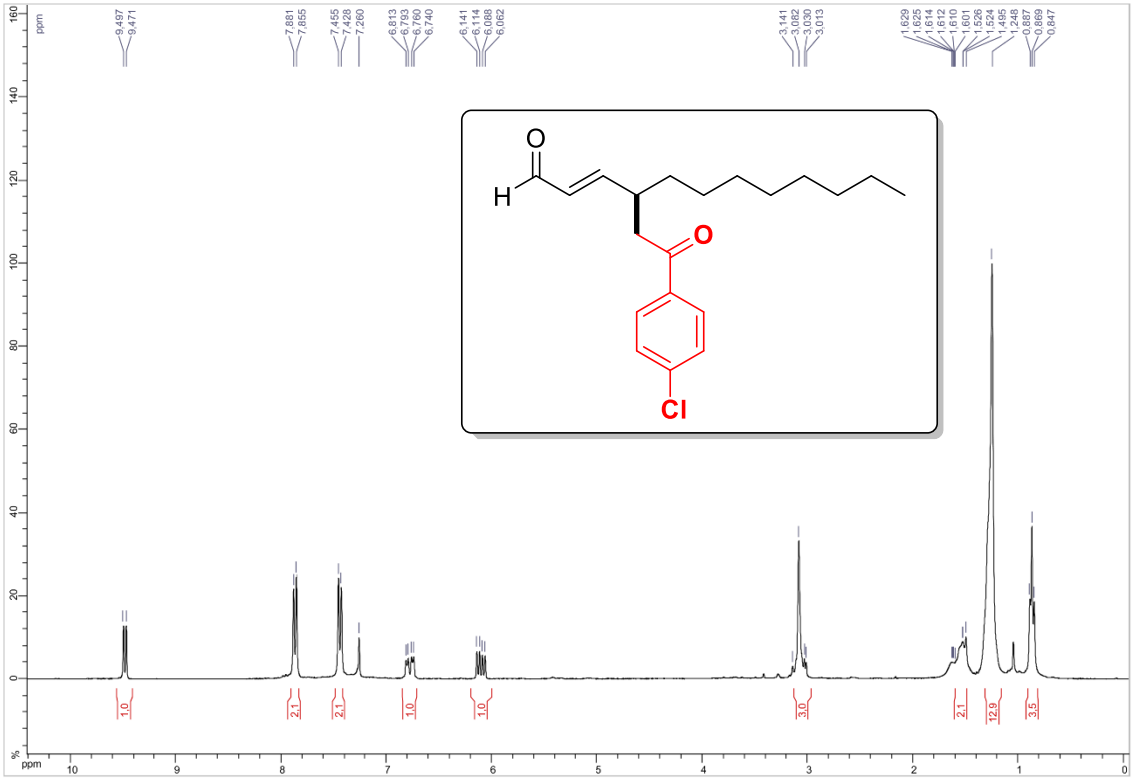



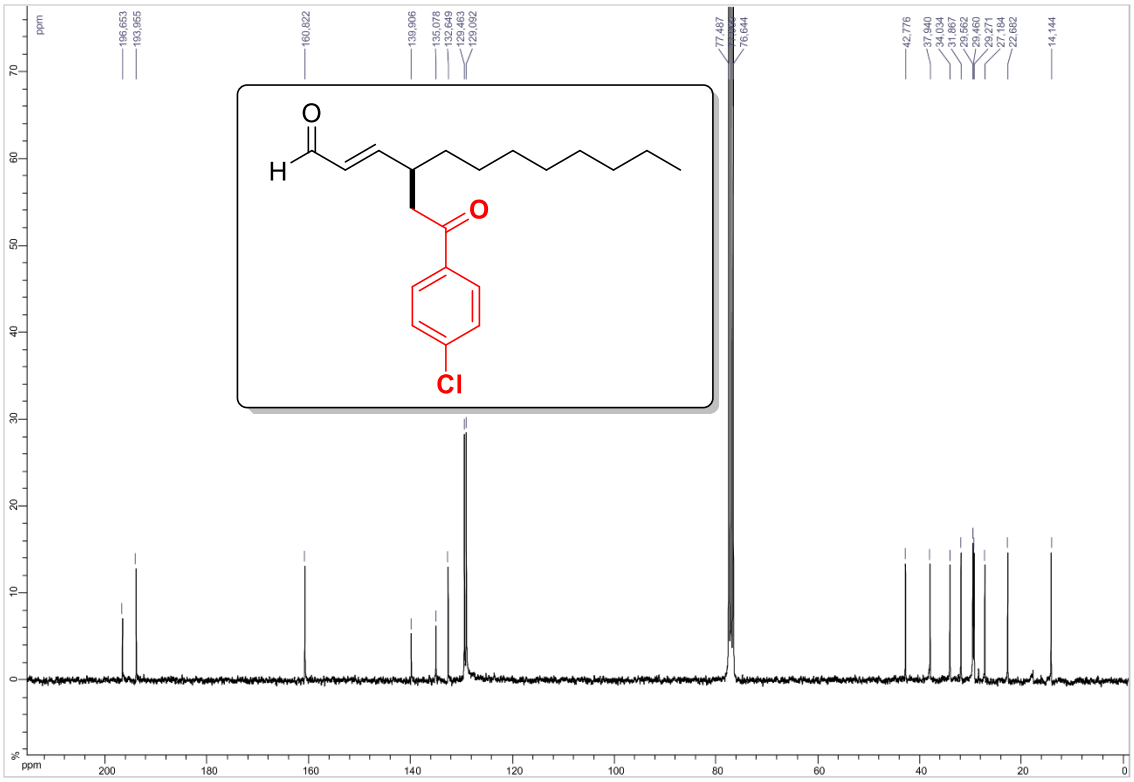
**(*E*)-4-(2-Oxo-2-phenylethyl)dodec-2-enal 6t**



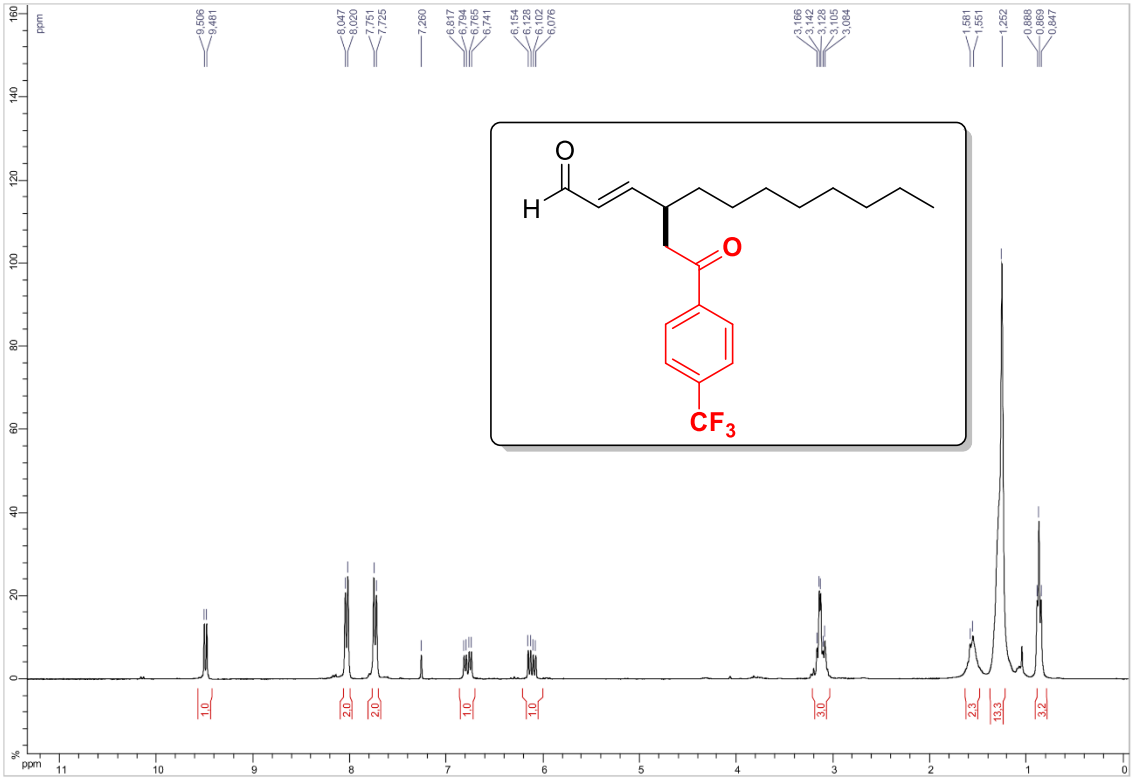



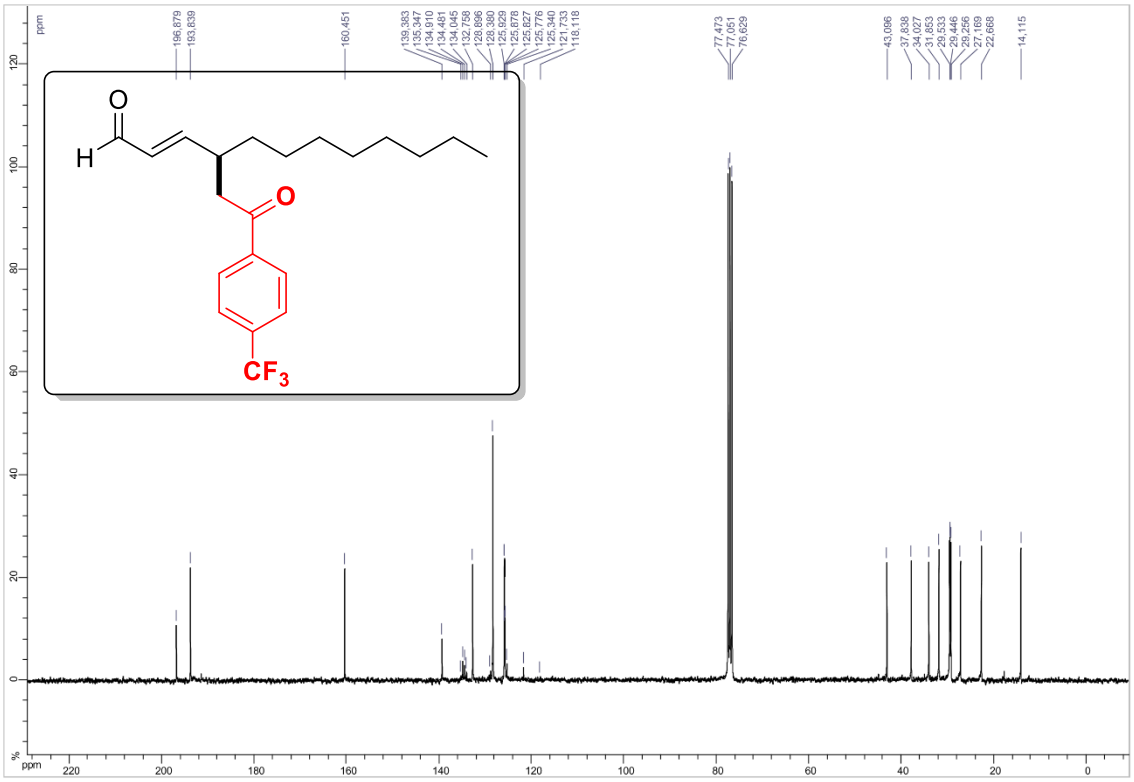
**(*E*)-4-(2-(4-Chlorophenyl)-2-oxoethyl)dodec-2-enal 6u**

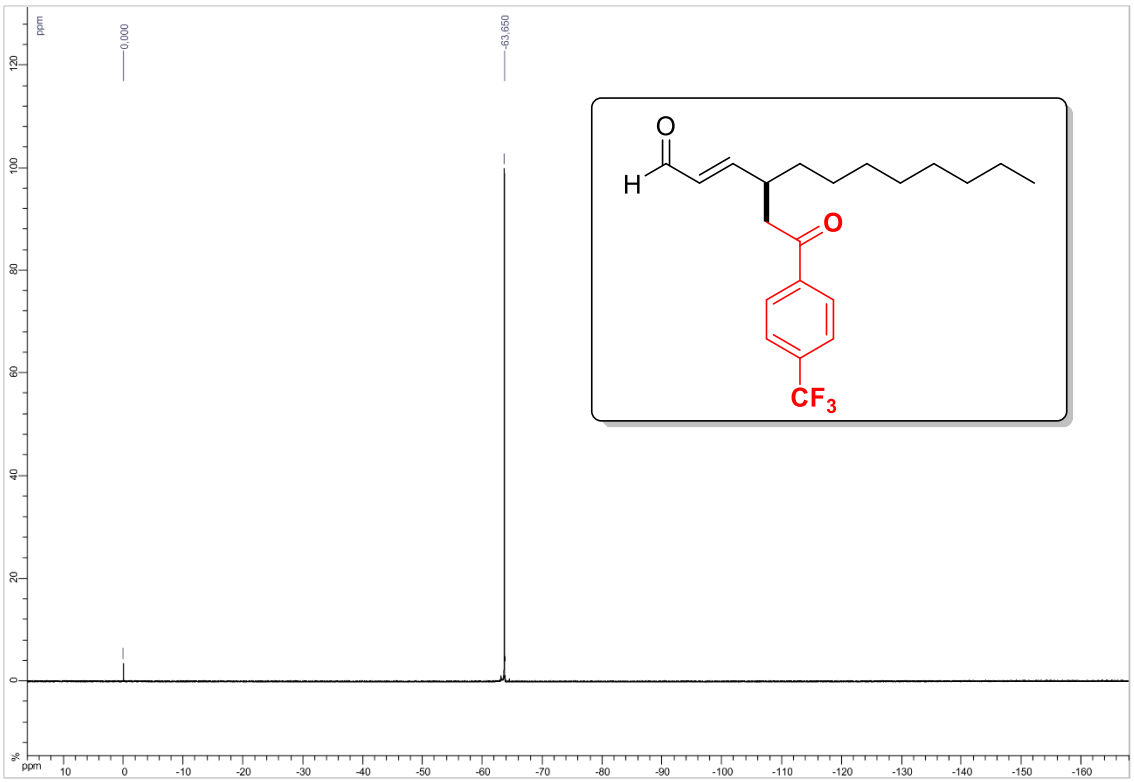


**(*E*)-4-(2-Oxo-2-(4-(trifluoromethyl)phenyl)ethyl)dodec-2-enal 6v**

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O
H
O
CF3

**(*E*)-4-(2-(3-methoxyphenyl)-2-oxoethyl)dodec-2-enal 6w**