**Supporting Information**

**For the article entitled**

# Direct Cross-coupling Reaction of Electron-Deficient Alkenes Using an Oxidizing Directing Group

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## Supporting Information

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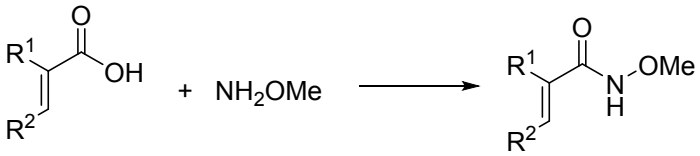
## General methods

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate. Flash column chromatography was performed using Merck aluminium oxide 90 active neutral with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. Proton nuclear magnetic resonance spectra ($^1$H NMR) were recorded on Bruker AMX 400 and 500 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for $^1$H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.26, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra ($^{13}$C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.0, triplet). Mass spectrometry was performed by Waters Q-Tof Premier Micromass instrument, using Electro Spray Ionization (ESI) mode. IR spectra were recorded as thin films on KBr plates on a Bio-Rad FTS 165 FTIR spectrometer and are reported in frequency of absorption ($cm^{-1}$). [Ru(*p*-cymene)$Cl_2$]$_2$ and KOPiv were purchased from TCI and used directly. Other reagents, unless otherwise noted below, are commercially available from Alfa Aesar (China) Chemical Co., Ltd. and used without further purification.

## General Procedure for the Preparation of *N*-Methoxy Acrylamides

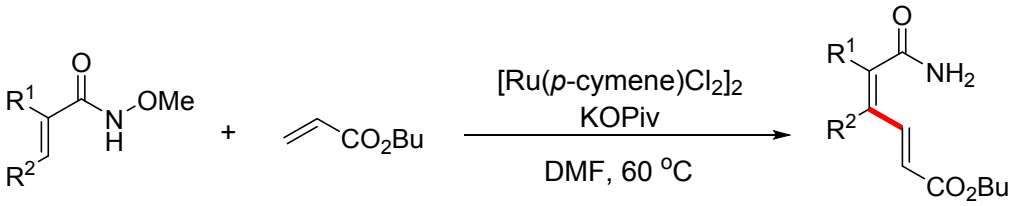



*N*-Methoxy acrylamides were prepared following the procedure reported by literatures.[1]

**Typical procedure**: To a mixture of acid (1.0 mmol, 1.0 equiv.) and methoxyamine hydrochloride (1.5 mmol, 1.5 equiv.) in dry DCM (3.0 mL) was added EDC (1.5 mmol, 1.5 equiv.). After DMAP (3.0 mmol, 3.0 equiv) was added, the reaction was allowed to stir for overnight. Then the reaction was quenched with water and extracted with

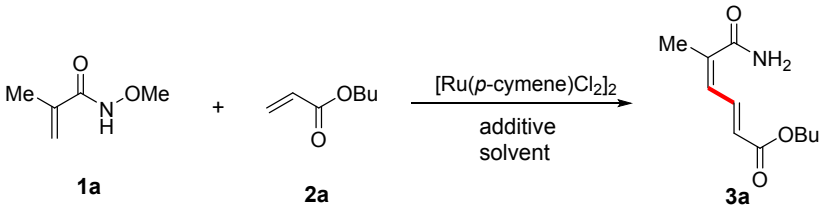
EtOAc. The organic layer was combined and dried over anhydrous sodium sulfate. After filtration and concentration, the residue was applied to a flash column chromatography (EtOAc/Petroleum ether mixtures) for separation.

## General Procedure for Ru-Catalyzed Cross-Coupling between Alkenes




An oven-dried screw-cap vial was charged with [Ru(*p*-cymene)$Cl_2$]$_2$ (5.0 mol%, 0.01 mmol), KOPiv (30.0 mol%, 0.06 mmol) and DMF (1.0 ml). Then, acrylamide (1.0 equiv, 0.20 mmol) and acrylate (1.8 equiv, 0.36 mmol) were added into the solution in sequence. The vial was sealed under nitrogen and heated to 60 ℃ with stirring for 16 hours. After cooling down, the mixture was diluted with ethyl acetate, filtered and washed with water and brine. The organic layer was dried over anhydrous $Na_2SO_4$, filtered and concentrated to give the crude product which was directly applied to a flash column chromatography (EtOAc/Petroleum ether mixtures).

## Table S1. Optimization of Catalytic Conditions[a]

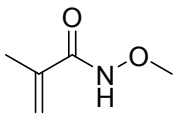



| Entry | Additive | Solvent | Yield (%) | *Z/E* |
|---|---|---|---|---|
| 1 | NaOAc | DCE | 19 | 99/1 |
| 2 | NaOAc | $H_2O$ | 26 | 96/4 |
| 3 | NaOAc | DMF | 49 | 99/1 |
| 4 | NaOAc | $CH_3CN$ | 37 | 93/7 |
| 5 | NaOAc | THF | 0 | - |
| 6 | NaOAc | EtOH | 24 | 97/3 |
| 7 | NaOAc | Acetone | 37 | 99/1 |

| | | | | |
|---|---|---|---|---|
| 8 | NaOAc | Hexane | 10 | 99/1 |
| 9 | NaOAc | EtOAc | 25 | 99/1 |
| 10 | NaOAc | DMSO | 0 | - |
| 11 | NaOAc | DME | 25 | 96/4 |
| 12 | NaOAc | *t*-AmOH | 20 | 99/1 |
| 13 | KOAc | DMF | 55 | 99/1 |
| 14 | CsOAc | DMF | 32 | 99/1 |
| 15 | $Cu(OAc)_2$ | DMF | 50 | 99/1 |
| 16 | LiOAc | DMF | 58 | 94/6 |
| 17 | $AgSbF_6$ | DMF | 0 | - |
| 18 | $KO_2CMes$ | DMF | 63 | 99/1 |
| **19** | **KOPiv** | **DMF** | **82** | **99/1** |
| 20[b] | KOPiv | DMF | 55 | 99/1 |
| 21[c] | KOPiv | DMF | 42 | 99/1 |
| 22[d] | KOPiv | DMF | 67 | 99/1 |
| 23[e] | KOPiv | DMF | 63 | 99/1 |
| 24[f] | KOPiv | DMF | - | - |

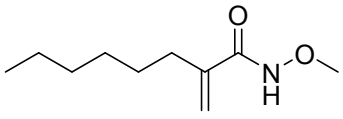
[a]Unless otherwise noted, the reactions were carried out using acrylamide (**1a**) (0.20 mmol), acrylate **2a** (0.36 mmol), [Ru(*p*-cymene)$Cl_2$]$_2$ (5.0 mol%), additive (30 mol%) in a solvent (0.2 M, 1.0 mL) at 60 °C for 16 h under an argon atmosphere (1 atm). The yields indicated in the table are $^1$H NMR yields. [b]additive (15 mol%). [c]additive (60 mol%). [d]The reaction was performed at 40 °C. [e]The reaction was performed at 80 °C. [f]The reaction was performed in the absence of [Ru(*p*-cymene)$Cl_2$]$_2$. DCE = 1,2-dichloroethane; EtOAc = ethyl acetate; DMSO = dimethyl sulphoxide; DME = 1,2-dimethoxyethane; DMF = *N*,*N*-Dimethylformamide.

## Characterization of Substrates



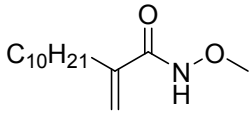
*N*-Methoxy-2-methyl-2-propenamide (**1a**)[2]

$^1$H NMR ($CDCl_3$): δ = 9.52 (brs, 1H), 5.72 (s, 1H), 5.36 (s, 1H), 3.79 (s, 3H), 1.95 (s, 3H).



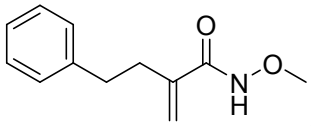
*N*-Methoxy-2-hexyl-2-propenamide (**1b**)

$^1$H NMR ($CDCl_3$): δ = 8.48 (brs, 1H), 5.55 (s, 1H), 5.30 (s, 1H), 3.81 (s, 3H), 2.30 (t, 2H, *J* = 7.5 Hz), 1.26-1.34 (m, 8H), 0.88 (t, 3H, *J* = 7.0 Hz). $^{13}$C NMR ($CDCl_3$): δ = 167.6, 143.0, 118.3, 64.3, 32.2, 31.6, 28.8, 27.8, 22.5, 14.0. HR-MS (ESI): *m/z* = 186.1484, $[M+H]^+$, calcd. for $C_{10}H_{19}NO_2$: 186.1489. FTIR (KBr, $cm^{-1}$): 3564.63, 3195.99, 2925.90, 2855.90, 1660.66, 1652.00, 1505.23, 1053.39, 935.51.



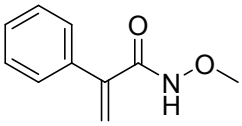
*N*-Methoxy-2-decyl-2-propenamide (**1c**)

$^1$H NMR ($CDCl_3$): δ = 8.36 (brs, 1H), 5.54 (s, 1H), 5.30 (s, 1H), 3.81 (s, 3H), 2.30 (t, 2H, *J* = 9.5 Hz), 1.26-1.28 (m,16H), 0.88 (t, 3H, *J* = 8.0 Hz). $^{13}$C NMR ($CDCl_3$): δ = 167.7, 143.2, 118.2, 64.5, 32.2, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 27.9, 22.7, 14.1. HR-MS (ESI): *m/z* = 242.2112, $[M+H]^+$, calcd. for $C_{14}H_{27}NO_2$: 242.2115. FTIR (KBr, $cm^{-1}$): 2923.94, 2853.35, 1866.22, 1789.94, 1770.20, 1651.59, 1557.17, 1494.89, 1434.81, 1035.07.



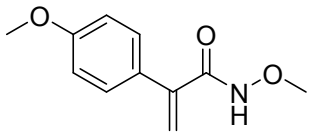
*N*-Methoxy-2-phenylethyl-2-propenamide (**1d**)

$^1$H NMR ($CDCl_3$): δ = 8.53 (s, 1H), 7.26-7.29 (m, 2H), 7.17-7.20 (m, 3H), 5.54 (s, 1H), 5.28 (s, 1H), 3.77 (s, 3H), 2.79 (t, 2H, *J* = 7.5 Hz), 2.63 (t, 2H, *J* = 8.0 Hz). $^{13}$C NMR ($CDCl_3$): δ = 167.4, 142.2, 140.9, 128.5, 128.4, 126.1, 119.1, 64.5, 34.3, 34.0. HR-MS (ESI): *m/z* = 206.1173, $[M+H]^+$, calcd. for $C_{12}H_{15}NO_2$: 206.1176. FTIR (KBr, $cm^{-1}$): 3444.48, 2923.45, 2352.77, 1651.52, 1505.02, 1494.92, 1434.75, 1053.42.



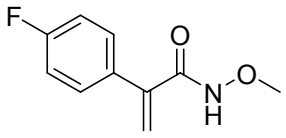
*N*-Methoxy-2-phenyl-2-propenamide (**1e**)[2]

$^1$H NMR ($CDCl_3$): δ = 8.82 (brs, 1H), 7.32-7.37 (m, 5H), 6.00 (s, 1H), 5.66 (s, 1H), 3.79 (s, 3H).



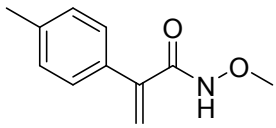
*N*-Methoxy-2-methoxyphenyl-2-propenamide (**1f**)

$^1$H NMR ($CDCl_3$): δ = 8.31 (brs, 1H), 7.33 (d, 2H, *J* = 9.0 Hz), 6.90 (d, 2H, *J* = 9.0 Hz), 5.98 (s, 1H), 5.61 (s, 1H), 3.83 (s, 3H), 3.76 (s, 3H). $^{13}$C NMR ($CDCl_3$): δ = 160.1, 141.6, 129.4, 129.1, 128.6, 128.2, 114.2, 64.6, 55.4. HR-MS (ESI): *m/z* = 208.0962, $[M+H]^+$, calcd. for $C_{11}H_{13}NO_3$: 208.0968. FTIR (KBr, $cm^{-1}$): 3564.56, 2922.52, 1866.52, 1842.12, 1694.24, 1614.74, 1514.99, 1495.08, 1434.84, 1417.02.



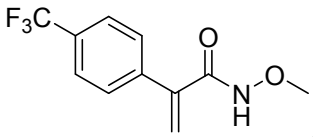
*N*-Methoxy-2-fluorophenyl-2-propenamide (**1g**)

$^1$H NMR ($CDCl_3$): δ = 8.42 (brs, 1H), 7.37-7.40 (m, 2H), 7.05-7.09 (m, 2H), 6.00 (s, 1H), 5.67 (s, 1H), 3.82 (s, 3H). $^{13}$C NMR ($CDCl_3$): δ = 163.0 (d, $J_{C\text{-}F}$ = 247.4 Hz), 141.2, 131.9 (d, $J_{C\text{-}F}$ = 2.1 Hz), 129.6 (d, $J_{C\text{-}F}$ = 7.8 Hz), 122.1, 155.8 (d, $J_{C\text{-}F}$ = 21.6 Hz), 129.9 (d, $J_{C\text{-}F}$ = 7.9 Hz), 64.6. HR-MS (ESI): *m/z* = 196.0770, $[M+H]^+$, calcd. for $C_{10}H_{10}FNO_2$: 196.0768. FTIR (KBr, $cm^{-1}$): 3564.20, 2351.97, 1644.84, 1557.19, 1514.73, 1494.94, 1434.72, 1416.83.



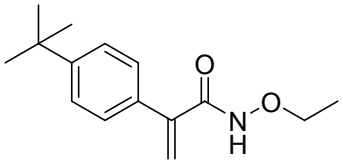
*N*-methoxy-2-methyphenyl-2-Propenamide (**1h**) [5]

$^1$H NMR ($CDCl_3$): δ = 8.28 (s, 1H), 7.28 (d, 2H, *J* = 8.0 Hz), 7.19 (d, 2H, *J* = 8.0 Hz), 6.07 (s, 1H), 5.64 (s, 1H), 3.82 (s, 3H), 2.37 (s, 3H).



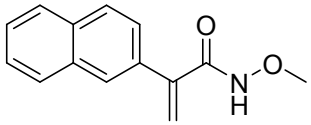
*N*-methoxy-2-(4-(trifluoromethyl)phenyl)acrylamide (**1i**) [5]

$^1$H NMR ($CDCl_3$): δ = 8.42 (s, 1H), 7.57 (d, 2H, *J* = 8.5 Hz), 7.19 (d, 2H, *J* = 8.5 Hz), 6.02 (s, 1H), 5.71 (s, 1H), 3.77 (s, 3H).



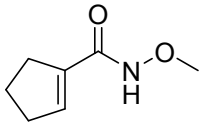
2-(4-(tert-butyl)phenyl)-N-ethoxyacrylamide (**j**) [5]

$^1$H NMR ($CDCl_3$): δ = 8.23 (s, 1H), 7.33 (d, 2H, *J* = 8.5 Hz), 7.25 (d, 2H, *J* = 8.5 Hz), 6.01 (s, 1H), 5.59 (s, 1H), 3.75 (s, 3H), 1.26(s, 9H).



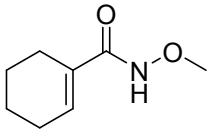
*N*-methoxy-2-naphthyl-2-propenamide (**1k**)[5]

$^1$H NMR ($CDCl_3$): δ = 8.01 (brs, 1H), 7.88-7.90 (m, 2H), 7.81-7.83 (m, 1H), 7.47-7.54 (m, 3H), 7.39-7.40 (m, 1H), 6.74 (s, 1H), 5.69 (s, 1H), 3.66 (s, 3H).



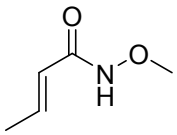
*N*-Methoxy-1-cyclopentene-1-carboxamide (**1l**)[4]

$^1$H NMR ($CDCl_3$): δ = 8.23 (brs, 1H), 6.60 (t, 1H, *J* = 2.5 Hz), 3.81 (s, 3H), 2.52-2.55 (m, 2H), 2.46-2.51 (m, 2H), 1.95-2.02 (m, 2H).



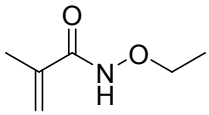
*N*-Methoxy-1-cyclohexene-1-carboxamide (**1m**) [4]

$^1$H NMR ($CDCl_3$): δ = 8.32 (brs, 1H), 6.81 (t, 1H, *J* = 3.5 Hz), 3.90 (s, 3H), 2.52-2.55 (m, 2H), 2.46-2.51 (m, 2H), 1.95-2.02 (m, 2H), 1.88-1.94(m, 2H).



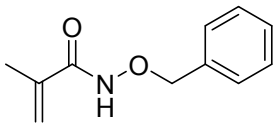
*N*-Methoxy-2-butenamide (**1n**)[3]

$^1$H NMR ($CDCl_3$): δ = 8.70 (brs, 1H), 6.94 (s, 1H), 5.88 (s, 1H), 3.77 (s, 3H), 1.87 (s, 3H).



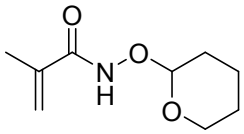
*N*-Ethoxy-2-methyl-2-propenamide (**1u**)

$^1$H NMR ($CDCl_3$): δ = 9.31 (s, 1H), 5.70 (s, 1H), 5.35 (s, 1H), 4.00 (q, 2H, *J* = 7.0 Hz), 1.95 (s, 3H), 1.27 (t, 3H, *J* = 7.0 Hz).



*N*-Benzyloxy -2-methyl-2-propenamide (**1v**)[6]

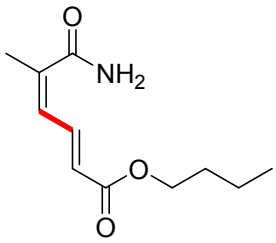
$^1$H NMR ($CDCl_3$): δ = 8.22 (s, 1H), 7.37-7.43 (m, 5H), 5.55 (s, 1H), 5.32 (s, 1H), 4.96 (s, 2H), 1.92 (s, 3H).



*N*-(Tetrahydro-2H-pyran-2-yl)oxy)methacrylamide (**1w**)

$^1$H NMR ($CDCl_3$): δ = 7.27 (s, 1H), 5.68 (s, 1H), 5.37 (s, 1H), 4.98 (t, 1H, *J* = 2.5 Hz), 3.98 (t, 1H, *J* = 3.5 Hz), 3.65 (t, 1H, *J* = 4.5 Hz), 1.97 (s, 3H), 1.59-1.70 (m, 6H). $^{13}$C NMR ($CDCl_3$): δ = 166.8, 137.9, 120.5, 102.6, 62.68, 28.0, 25.0, 18.6, 18.5. HR-MS (ESI): *m/z* = 186.1118, $[M+H]^+$, calcd. for $C_9H_{15}NO_3$: 186.1125. FTIR (KBr, $cm^{-1}$): 3444.77, 2924.64, 1866.59, 1760.18, 1621.69, 1470.82, 1455.40, 1204.54, 1113.97, 1034.76, 902.76, 872.87.

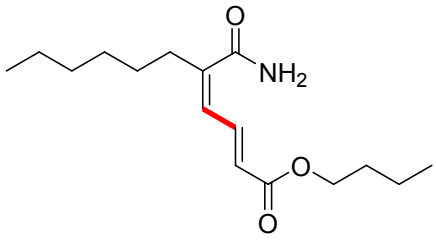
## Characterization of Butadienes



Butyl (2*E*,4*Z*)-6-amino-5-methyl-6-oxohexa-2,4-dienoate (**3a**)[7]

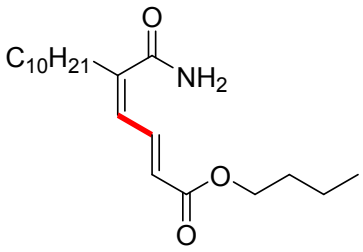
White solid, m.p.: 106.0 °C, yield = 82%. $^1$H NMR ($CDCl_3$): δ = 7.75 (dd, 1H, *J* = 11.5, 15.0 Hz ), 6.24 (d, 1H, *J* = 11.0 Hz), 6.20 (brs, 1H), 5.92 (d, 1H, *J* = 15.5 Hz), 5.84 (brs, 1H), 4.15 (t, 2H, *J* = 6.5 Hz), 2.09 (s, 3H), 1.62-1.67 (m, 2H), 1.36-1.43 (m, 2H), 0.94 (t, 3H, *J* = 7.5 Hz). $^{13}$C NMR ($CDCl_3$): δ = 170.6, 166.8, 140.3, 139.6, 129.8, 124.0,

64.5, 30.7, 21.4, 19.1, 13.7. HR-MS (ESI): *m/z* = 212.1283, $[M+H]^+$, calcd. for $C_{11}H_{17}NO_3$: 212.1281. FTIR (KBr, $cm^{-1}$): 3331.68, 3167.46, 2956.87, 2356.97, 1705.41, 1633.77, 1276.53, 984.19.



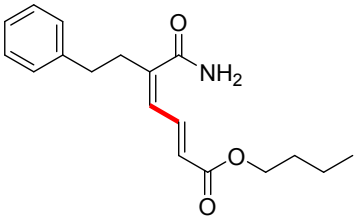

Butyl (2*E*,4*Z*)-6-amino-5-hexyl-6-oxohexa-2,4-dienoate (**3b**)

Light yellow solid, m.p.: 95.8 °C, yield = 59%. $^1H$ NMR ($CDCl_3$): δ = 7.63 (dd, 1H, *J* = 12.0, 15.5 Hz), 6.20 (brs, 1H), 6.18(d, 1H, *J* = 12.0 Hz), 5.93 (d, 1H, *J* = 15.5 Hz), 5.74 (brs, 1H), 4.15 (t, 2H, *J* = 6.5 Hz), 2.37 (t, 2H, *J* = 7.5 Hz), 1.61-1.67 (m, 2H), 1.47-1.53 (m, 2H), 1.36-1.43 (m, 2H), 1.29-1.32 (m, 6H), 0.94 (t, 3H, *J* = 7.0 Hz), 0.88 (t, 3H, *J* = 6.5 Hz). $^{13}C$ NMR ($CDCl_3$): δ = 170.7, 166.8, 146.4, 139.6, 127.4, 123.6, 64.5, 35.3, 31.5, 30.7, 28.9, 27.9, 22.5, 19.1, 14.0, 13.7. HR-MS (ESI): *m/z* = 282.2068, $[M+H]^+$, calcd. for $C_{16}H_{27}NO_3$: 282.2064. FTIR (KBr, $cm^{-1}$): 3565.03, 3383.22, 2923.89, 1713.51, 1651.60, 1557.62, 1455.66, 1416.82, 1259.60.



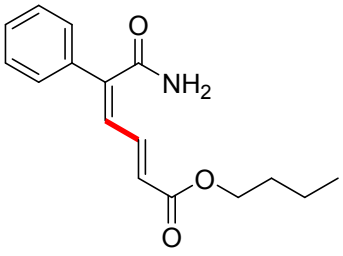

Butyl (2*E*,4*Z*)-6-amino-5-decyl-6-oxohexa-2,4-dienoate (**3c**)

Light yellow solid, m.p.: 91.5 °C, yield = 48%. $^1H$ NMR ($CDCl_3$): δ = 7.63 (dd, 1H, *J* = 14.5, 19.0 Hz), 6.29 (brs, 1H), 6.17 (d, 1H, *J* = 14.5 Hz), 5.92 (d, 1H, *J* = 19.5 Hz), 5.79 (brs, 1H), 4.14 (t, 2H, *J* = 8.0 Hz), 2.37 (t, 2H, *J* = 9.5 Hz), 1.61-1.68 (m, 2H), 1.36-1.44 (m, 2H), 1.21-1.33 (m, 16H), 0.94 (t, 3H, *J* = 9.0 Hz), 0.88 (t, 3H, *J* = 8.5 Hz). $^{13}C$ NMR ($CDCl_3$): δ = 170.7, 166.7, 146.4, 139.6, 127.4, 123.6, 64.4, 35.3, 31.9, 30.7, 29.6, 29.5, 29.3, 29.3, 29.2, 28.0, 22.7, 19.1, 14.1, 13.7. HR-MS (ESI): *m/z* = 338.2685, $[M+H]^+$, calcd. for $C_{20}H_{35}NO_3$: 338.2690. FTIR (KBr, $cm^{-1}$): 3374.05, 3182.44, 2955.64, 2923.50, 2851.59, 2353.35, 1713.52, 1645.36, 1567.91, 1267.87, 432.94.



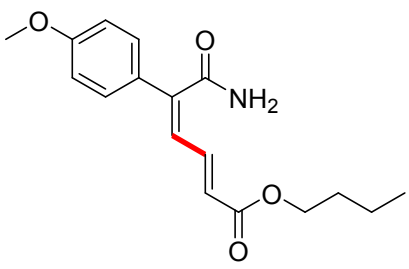
Butyl (2*E*,4*Z*)-5-carbamoyl-7-phenylhepta-2,4-dienoate (**3d**)

White solid, m.p.: 100.0 °C, yield = 67%. $^{1}$H NMR ($CDCl_3$): δ = 7.61 (dd, 1H, *J* = 11.5, 15.0 Hz), 7.26-7.29 (m, 2H), 7.17-7.21 (m, 3H), 6.29 (brs, 1H), 6.14 (d, 1H, *J* = 12.0 Hz), 5.90 (d, 1H, *J* = 15.0 Hz), 5.73 (brs, 1H), 4.13 (t, 2H, *J* = 7.0 Hz), 2.84 (t, 2H, *J* = 7.5 Hz), 2.69 (t, 2H, *J* = 8.5 Hz), 1.60-1.66 (m, 2H), 1.34-1.42 (m, 2H), 0.93 (t, 3H, *J* = 7.5 Hz). $^{13}$C NMR ($CDCl_3$): δ = 170.5, 166.7, 145.1, 140.5, 139.4, 128.5, 128.5, 128.3, 126.3, 124.0, 64.5, 36.9, 34.3, 30.7, 19.1, 13.7. HR-MS (ESI): *m/z* = 302.1747, $[M+H]^+$, calcd. for $C_{18}H_{23}NO_3$: 302.1751. FTIR (KBr, $cm^{-1}$): 3564.35, 2353.35, 1714.04, 1694.18, 1682.33, 1651.45, 1644.88, 1538.31, 1505.09, 1470.59, 1455.16.



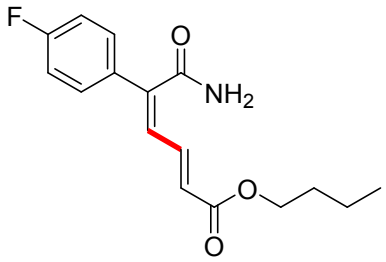
Butyl (2*E*,4*Z*)-6-amino-6-oxo-5-phenylhexa-2,4-dienoate (**3e**)

Brown solid, m.p.: 125.0 °C, yield = 38%. $^{1}$H NMR ($CDCl_3$): δ = 7.76 (dd, 1H, *J* = 12.0, 15.0 Hz), 7.51 (d, 2H, *J* = 8.0 Hz), 7.38 (d, 3H, *J* = 7.0 Hz), 6.67 (d, 1H, *J* = 11.5 Hz), 6.34 (brs, 1H), 6.08 (d, 1H, *J* = 15.5 Hz), 5.90 (brs, 1H), 4.15 (t, 2H, *J* = 6.5 Hz), 1.63-1.68 (m, 2H), 1.36-1.44 (m, 2H), 0.95 (t, 3H, *J* = 7.5 Hz). $^{13}$C NMR ($CDCl_3$): δ = 169.6, 166.6, 144.0, 139.8, 135.5, 129.4, 129.0, 127.5, 127.0, 125.4, 64.6, 30.7, 19.2, 13.7. HR-MS (ESI): *m/z* = 274.1435, $[M+H]^+$, calcd. for $C_{16}H_{19}NO_3$: 274.1438. FTIR (KBr, $cm^{-1}$): 3564.80, 3444.91, 2957.99, 2924.83, 2358.53, 2340.16, 1682.43, 1651.85, 1470.77, 1317.52, 1272.85, 1187.06, 1140.11, 979.35, 768.36.



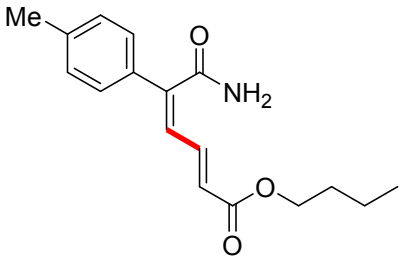
Butyl (2*E*,4*Z*)-6-amino-5-(4-methoxyphenyl)-6-oxohexa-2,4-dienoate (**3f**)

Yellow solid, m.p.: 141.2 °C, yield = 49%. $^1$H NMR ($CDCl_3$): δ = 7.73 (dd, 1H, *J* = 11.5, 15.0 Hz), 7.46 (d, 2H, *J* = 8.5 Hz), 6.91 (d, 2H, *J* = 9.0 Hz), 6.61 (d, 1H, *J* = 12.0 Hz), 6.11 (brs, 1H), 6.05 (d, 1H, *J* = 15.0 Hz), 5.79 (brs, 1H), 4.16 (t, 2H, *J* = 6.5 Hz), 3.83 (s, 3H), 1.63-1.68 (m, 2H), 1.37-1.44 (m, 2H), 0.95 (t, 3H, *J* = 7.0 Hz). $^{13}$C NMR ($CDCl_3$): δ = 169.9, 166.7, 160.7, 143.7, 140.0, 128.4, 127.8, 125.2, 124.3, 114.4, 64.5, 55.4, 30.7, 19.2, 13.8. HR-MS (ESI): *m/z* = 304.1546, $[M+H]^+$, calcd. for $C_{17}H_{21}NO_4$: 304.1543. FTIR (KBr, $cm^{-1}$): 3564.67, 2358.01, 1694.36, 1682.45, 1600.37, 1538.61, 1505.47, 1455.50, 1253.13.




Butyl (2*E*,4*Z*)-6-amino-5-(4-fluorophenyl)-6-oxohexa-2,4-dienoate (**3g**)

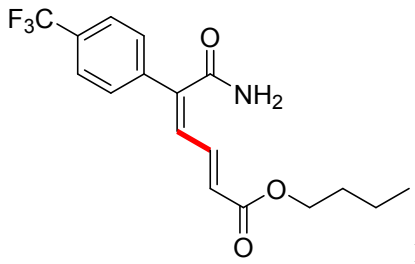
White solid, m.p.: 142.6 °C, yield = 26%. $^1$H NMR ($CDCl_3$): δ = 7.74 (dd, 1H, *J* = 11.5, 15.0 Hz), 7.49-7.52 (m, 2H), 7.07-7.10 (m, 2H), 6.64 (d, 1H, *J* = 11.5 Hz), 6.09 (d, 1H, *J* = 15.0 Hz), 6.08 (brs, 1H), 5.77 (brs, 1H), 4.17 (t, 2H, *J* = 7.0 Hz), 1.63-1.69 (m, 2H), 1.37-1.44 (m, 2H), 0.95 (t, 3H, *J* = 7.5 Hz). $^{13}$C NMR ($CDCl_3$): δ = 169.3, 166.5, 164.4 (d, $J_{C-F}$ = 250.5 Hz), 142.8, 139.5, 131.6 (d, $J_{C-F}$ = 3.5 Hz), 128.9 (d, $J_{C-F}$ = 8.3 Hz), 127.3 (d, $J_{C-F}$ = 1.6 Hz), 125.6, 116.1 (d, $J_{C-F}$ = 21.8 Hz), 64.6, 30.7, 19.2, 13.7. HR-MS (ESI): *m/z* = 292.1348, $[M+H]^+$, calcd. for $C_{16}H_{18}FNO_3$: 292.1343. FTIR (KBr, $cm^{-1}$): 3564.75, 2358.22, 1732.28, 1714.29, 1651.68, 1557.46, 1505.44, 1470.89, 1455.47.




Butyl (2*E*,4*Z*)-6-amino-5-(4-methylphenyl)-6-oxohexa-2,4-dienoate (**3h**)

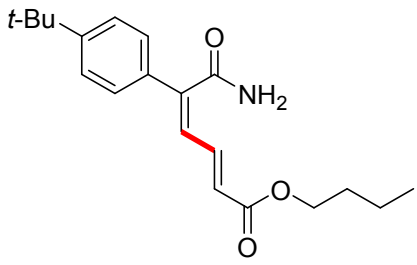
White solid, mp: 166.7 °C, yield = 49%. $^1$H NMR ($CDCl_3$): δ = 7.74 (dd, 1H, *J* = 12.0, 15.0 Hz), 7.40 (d, 2H, *J* = 8.0 Hz), 7.19 (d, 2H, *J* = 8.0 Hz), 6.64 (d, 1H, *J* = 11.5 Hz), 6.25 (brs, 1H), 6.05 (d, 1H, *J* = 15.0 Hz), 5.85 (brs, 1H), 4.15 (t, 2H, *J* = 7.0 Hz), 2.36 (s, 3H), 1.62-1.68 (m, 2H), 1.36-1.44 (m, 2H), 0.94 (t, 3H, *J* = 7.5 Hz). $^{13}$C NMR ($CDCl_3$): δ = 169.8, 166.6, 144.0, 139.9, 139.7, 132.6, 129.7, 126.9, 126.4, 124.8, 64.5, 30.7, 21.3, 19.2, 13.7. HR-

MS (ESI): *m/z* = 288.1597, [M+H$^+$], calcd. for $C_{17}H_{21}NO_3$: 288.1594. FTIR (KBr, cm$^{-1}$): 3867.97, 3585.36, 3241.17, 3195.79, 2357.18, 2337.32, 1273.78, 1020.08, 988.46, 819.53, 667.39, 500.33.



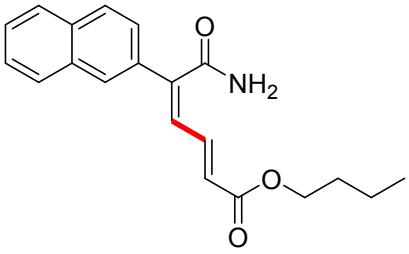

Butyl (2*E*,4*Z*)-6-amino-5-(4-trifluoromethylphenyl)-6-oxohexa-2,4-dienoate (**3i**)

White solid, mp: 164.9 °C, yield = 22%. $^1$H NMR ($CDCl_3$): δ = 7.68 (dd, 1H, *J* = 12.0, 15.5 Hz), 7.55-7.59 (m, 4H), 6.67 (d, 1H, *J* = 12.0 Hz), 6.18 (brs, 1H), 6.08 (d, 1H, *J* = 15.5 Hz), 5.77 (brs, 1H), 4.10 (t, 2H, *J* = 7.0 Hz), 1.56-1.62 (m, 2H), 1.30-1.37 (m, 2H), 0.88 (t, 3H, *J* = 7.5 Hz). $^{13}$C NMR ($CDCl_3$): δ = 167.8, 165.3, 141.4, 138.0, 137.9 (q, $J_{C\text{-}F}$ = 1.3 Hz), 130.1 (q, $J_{C\text{-}F}$ = 32.6 Hz), 128.1, 126.2, 125.7, 124.9 (d, $J_{C\text{-}F}$ = 3.8 Hz), 121.8 (d, $J_{C\text{-}F}$ = 270.6 Hz), 63.7, 29.7, 18.1, 12.7. HR-MS (ESI): *m/z* = 342.1310, [M+H$^+$], calcd. for $C_{17}H_{18}F_3NO_3$: 342.1312. FTIR (KBr, cm$^{-1}$): 3878.01, 3799.09, 3472.77, 3262.89, 1915.90, 1866.45, 1614.76, 989.51, 881.02, 842.46, 717.57, 666.51.



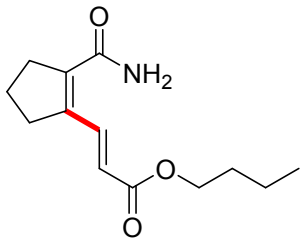

Butyl (2*E*,4*Z*)-6-amino-5-(4-*tert*-butylphenyl)-6-oxohexa-2,4-dienoate (**3j**)

Yellow liquid, yield = 48%. $^1$H NMR ($CDCl_3$): δ = 7.67 (dd, 1H, *J* = 11.5, 15.0 Hz), 7.37 (d, 2H, *J* = 8.5 Hz), 7.33 (d, 2H, *J* = 8.5 Hz), 6.58 (d, 1H, *J* = 12.0 Hz), 6.27 (brs, 1H), 5.99 (d, 1H, *J* = 15.5 Hz), 5.80 (brs, 1H), 4.08 (t, 2H, *J* = 6.5 Hz), 1.55-1.60 (m, 2H), 1.29-1.36 (m, 2H), 1.25(s, 9H), 0.87 (t, 3H, *J* = 7 Hz). $^{13}$C NMR ($CDCl_3$): δ = 168.8, 165.6, 151.9, 142.9, 139.0, 131.6, 125.7, 125.6, 124.9, 123.8, 63.5, 33.8, 30.1, 29.7, 18.1, 12.7. HR-MS (ESI): *m/z* = 330.2063, [M+H$^+$], calcd. for $C_{20}H_{27}NO_3$: 330.2064. FTIR (KBr, cm$^{-1}$): 3878.20, 3799.34, 3263.71, 2958.17, 2933.22, 1866.59, 1269.33, 1187.35, 1025.81, 981.42, 835.23, 717.57, 666.51.



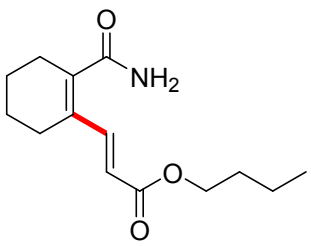
Butyl (2*E*,4*Z*)-6-amino-5-(naphthalen-2-yl)-6-oxohexa-2,4-dienoate (**3k**)

Yellow oil, yield = 42%. $^{1}$H NMR ($CDCl_3$): δ = 8.43 (dd, 1H, *J* = 11.5 Hz, *J* =15.5 Hz), 7.88-7.95 (m, 3H), 7.46-7.55 (m, 4H), 6.63 (d, 1H, *J* = 11.5 Hz), 6.09 (d, 1H, *J* = 15.5 Hz), 5.64 (brs, 1H), 5.33 (brs, 1H), 4.20 (t, 2H, *J* = 6.5 Hz), 1.64-1.71 (m, 2H), 1.39-1.47 (m, 2H), 0.96 (t, 3H, *J* = 7.5 Hz). $^{13}$C NMR ($CDCl_3$): δ = 164.4, 162.6, 136.3, 135.8, 133.4, 132.0, 129.7, 127.6, 125.7, 124.6, 123.7, 123.4, 123.2, 122.7, 121.5, 121.2, 60.7, 26.8, 15.2, 9.8. HR-MS (ESI): *m/z* = 324.1596, $[M+H]^+$, calcd. for $C_{20}H_{21}NO_3$: 324.1594. FTIR (KBr, $cm^{-1}$): 3444.79, 2957.60, 2923.91, 2353.35, 1747.35, 1651.83, 1505.56, 1316.23, 1259.86, 1190.87, 1139.59, 777.10.



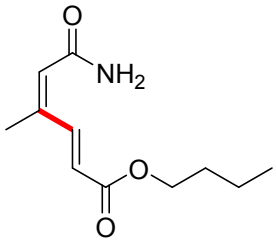
Butyl (*E*)-3-(2-carbamoylcyclopent-1-en-1-yl)acrylate (**3l**)

White solid, m.p.: 116.7 °C, yield = 20%. $^{1}$H NMR ($CDCl_3$): δ = 8.24 (d, 1H, *J* = 16.0 Hz), 5.96 (d, 1H, *J* = 15.5 Hz), 5.74 (brs, 1H), 5.60 (brs, 1H), 4.17 (t, 2H, *J* = 7.0 Hz), 2.76 (t, 2H, *J* = 7.5 Hz), 2.67 (t, 2H, *J* = 7.5 Hz), 1.96-2.02 (m, 2H), 1.63-1.69 (m, 2H), 1.37-1.45 (m, 2H), 0.95 (t, 3H, *J* = 7.0 Hz). $^{13}$C NMR ($CDCl_3$): δ = 163.5, 163.0, 141.4, 135.1, 133.7, 119.4, 60.6, 31.4, 29.5, 26.8, 17.6, 15.2, 9.8. HR-MS (ESI): *m/z* = 238.1435, $[M+H]^+$, calcd. for $C_{13}H_{19}NO_3$: 238.1438. FTIR (KBr, $cm^{-1}$): 3381.97, 2957.46, 2354.82, 1715.35, 1651.69, 1634.26.



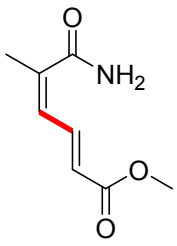
Butyl (*E*)-3-(2-carbamoylcyclohex-1-en-1-yl)acrylate (**3m**)

Brown oil, yield = 33%. $^{1}$H NMR ($CDCl_3$): δ = 7.73 (d, 1H, *J* = 15.5 Hz), 5.94 (d, 1H, *J* = 16.0 Hz), 5.64 (brs, 1H), 5.53 (brs, 1H), 4.15 (t, 2H, *J* = 6.5 Hz), 2.45 (brs, 2H), 2.24 (brs, 2H), 1.67-1.72 (m, 4H), 1.62-1.67 (m, 2H), 1.36-1.43 (m, 2H), 0.94 (t, 3H, *J* = 7.5 Hz ). $^{13}$C NMR ($CDCl_3$): δ = 172.0, 167.1, 142.0, 141.0, 132.4, 118.7, 64.4, 30.7, 28.2, 24.8, 21.7, 21.6, 19.2, 13.7. HR-MS (ESI): *m/z* = 252.1599, $[M+H]^+$, calcd. for $C_{14}H_{21}NO_3$: 252.1594. FTIR (KBr, $cm^{-1}$): 3382.92, 2923.59, 2351.97, 1738.21, 1494.95, 1434.76, 1393.06, 1293.31, 1172.22.



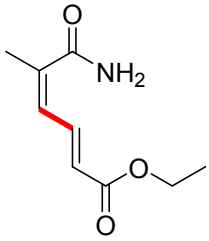

Butyl (2*E*,4*Z*)-6-amino-4-methyl-6-oxohexa-2,4-dienoate (**3n**) [3]

White solid, m.p.: 123.6 °C, yield = 15%. $^{1}$H NMR ($CDCl_3$): δ = 8.56 (d, 1H, *J* = 20.0 Hz ), 6.12 (d, 1H, *J* = 20.0 Hz), 5.94 (s, 1H), 5.76 (brs, 1H), 5.60 (brs, 1H), 4.18 (t, 2H, *J* = 8.5 Hz ), 2.01 (s, 3H), 1.63-1.70 (m, 2H), 1.37-1.46 (m, 2H), 0.95 (t, 3H, *J* = 9.0 Hz ). $^{13}$C NMR ($CDCl_3$): δ = 167.3, 166.7, 144.2, 140.5, 125.6, 123.6, 64.6, 30.7, 20.34, 19.1, 13.7. HR-MS (ESI): *m/z* = 212.1276, $[M+H]^+$, calcd. for $C_{11}H_{17}NO_3$: 212.1281. FTIR (KBr, $cm^{-1}$): 3564.40, 2352.46, 1841.97, 1651.57, 1567.71, 1455.17, 1416.75.



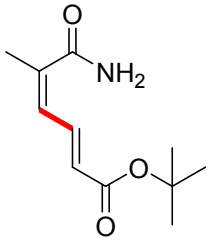

Methyl (2*E*,4*Z*)-6-amino-5-methyl-6-oxohexa-2,4-dienoate (**3o**)

White solid, m.p.: 133.6 °C, yield = 66%. $^{1}$H NMR ($CDCl_3$): δ = 7.76 (dd, 1H, *J* = 14.5, 19.0 Hz ), 6.36 (brs, 1H), 6.25 (d, 1H, *J* = 14.5 Hz), 5.92 (d, 1H, *J* = 19.5 Hz), 5.90 (brs, 1H), 3.75 (s, 3H), 2.09 (s, 3H). $^{13}$C NMR ($CDCl_3$): δ = 170.6, 167.1, 140.5, 134.0, 129.8, 123.4, 51.7, 21.4. HR-MS (ESI): *m/z* = 170.0806, $[M+H]^+$, calcd. for $C_8H_{11}NO_3$: 170.0812. FTIR (KBr, $cm^{-1}$): 3564.65, 3417.68, 2922.86, 2352.39, 1667.50, 1322.83, 1270.96.



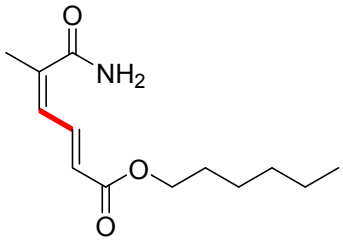
Ethyl (2*E*,4*Z*)-6-amino-5-methyl-6-oxohexa-2,4-dienoate (**3p**)

White solid, m.p.: 117.4 °C, yield = 74 %. $^{1}$H NMR ($CDCl_3$): δ = 7.75 (dd, 1H, *J* = 15.0, 19.5 Hz), 6.33 (brs, 1H), 6.24 (d, 1H, *J* = 14.5 Hz), 5.92 (d, 1H, *J* = 19.5 Hz), 5.87 (brs, 1H), 4.20 (q, 2H, *J* = 9.0 Hz), 2.09 (s, 3H), 5.92 (t, 3H, *J* = 9.0 Hz). $^{13}$C NMR ($CDCl_3$): δ = 170.3, 166.6, 140.2, 139.5, 129.9, 124.1, 60.6, 21.4, 14.3. HR-MS (ESI): *m/z* = 184.0971, $[M+H]^+$, calcd. for $C_9H_{13}NO_3$: 184.0968. FTIR (KBr, $cm^{-1}$): 3417.84, 2923.68, 2853.06, 2353.97, 1651.70, 1557.51, 1270.23.



*tert*-Butyl (2*E*,4*Z*)-6-amino-5-methyl-6-oxohexa-2,4-dienoate(**3q**)[7]

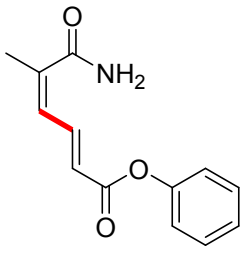
Yellow solid, m.p.: 114.6 °C, yield = 52%. $^{1}$H NMR ($CDCl_3$): δ = 7.58 (dd, 1H, *J* = 14.5, 19.0 Hz), 6.43 (brs, 1H), 6.13 (d, 1H, *J* = 14.5 Hz), 5.97 (brs, 1H), 5.77 (d, 1H, *J* = 19.5 Hz), 2.0 (s, 3H), 1.41 (s, 9H). $^{13}$C NMR ($CDCl_3$): δ = 170.9, 166.1, 139.9, 138.9, 129.7, 125.6, 80.7, 28.1, 21.4. HR-MS (ESI): *m/z* = 212.1276, $[M+H]^+$, calcd. for $C_{11}H_{17}NO_3$: 212.1281. FTIR (KBr, $cm^{-1}$): 3564.75, 1651.73, 1633.94, 1505.35, 1455.42, 1323.02, 1142.93.



Hexyl (2*E*,4*Z*)-6-amino-5-methyl-6-oxohexa-2,4-dienoate (**3r**)

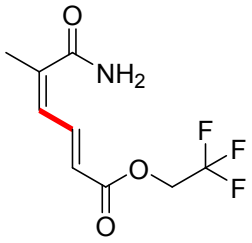
White solid, m.p.: 93.5 °C, yield = 60%. $^{1}$H NMR ($CDCl_3$): δ = 7.74 (dd, 1H, *J* = 12.0, 15.5 Hz), 6.25 (d, 1H, *J* = 12.0 Hz), 6.01 (brs, 1H), 5.93 (d, 1H, *J* = 15.5 Hz), 5.70 (brs, 1H), 4.14 (t, 2H, *J* = 7.0 Hz), 2.09 (s, 3H), 1.63-1.68 (m, 2H), 1.26-1.37 (m, 6H), 0.89 (t, 3H, *J* = 7.0 Hz). $^{13}$C NMR ($CDCl_3$): δ = 170.4, 166.7, 140.2, 139.5, 129.8, 124.1,

64.8, 31.4, 28.6, 25.6, 22.5, 21.4, 14.0. HR-MS (ESI): *m/z* = 240.1602, $[M+H]^+$, calcd. for $C_{13}H_{21}NO_3$: 240.1594. FTIR (KBr, $cm^{-1}$): 3331.70, 2923.96, 2350.93, 2284.48, 1866.34, 1704.62, 1633.64, 1335.24, 1277.11, 1152.37, 983.76.



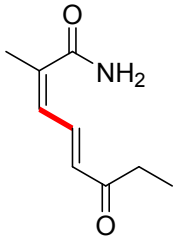
Phenyl (2*E*,4*Z*)-6-amino-5-methyl-6-oxohexa-2,4-dienoate (**3s**)

Brown solid, m.p.: 124.1 °C, yield = 70%. $^1$H NMR ($CDCl_3$): δ = 7.90 (dd, 1H, *J* = 12.0, 15.5 Hz ), 7.38 (t, 2H, *J* = 8.0 Hz), 7.23 (t, 1H, *J* = 7.5 Hz), 7.11 (d, 2H, *J* = 8.5 Hz), 6.37 (brs, 1H), 6.29 (d, 1H, *J* = 12.0 Hz), 6.09 (d, 1H, *J* = 15.0 Hz), 5.90 (brs, 1H), 2.09 (s, 3H). $^{13}$C NMR ($CDCl_3$): δ = 170.5, 165.1, 150.7, 141.6, 141.5, 129.7, 129.4, 125.8, 122.8, 121.6, 21.5. HR-MS (ESI): *m/z* = 232.0976, $[M+H]^+$, calcd. for $C_{13}H_{13}NO_3$: 232.0968. FTIR (KBr, $cm^{-1}$): 3627.19, 3565.13, 2352.39, 1732.24, 1651.79, 1634.02, 1505.55, 1455.58.



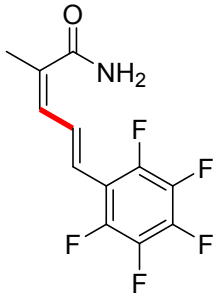
2,2,2-Trifluoroethyl (2*E*,4*Z*)-6-amino-5-methyl-6-oxohexa-2,4-dienoate (**3t**)

White solid, m.p.: 127.7 °C, yield = 45%. $^1$H NMR ($CDCl_3$): δ = 7.88 (dd, 1H, *J* =12.5, 14.5 Hz), 6.28 (d, 1H, *J* = 11.5 Hz), 6.09 (brs, 1H), 5.98 (d, 1H, *J* = 15.5 Hz), 5.69 (brs, 1H), 4.51-4.56 (m, 2H), 2.11(s, 3H). $^{13}$C NMR ($CDCl_3$): δ = 170.1, 164.8, 142.0, 141.8, 129.5, 123.0 (q, $J_{C\text{-}F}$ = 275.5 Hz), 121.5, 60.5 (q, $J_{C\text{-}F}$ = 36.5 Hz ), 21.5. HR-MS (ESI): *m/z* = 238.0689, $[M+H]^+$, calcd. for $C_9H_{10}F_3NO_3$: 238.0686. FTIR (KBr, $cm^{-1}$): 3332.11, 2352.90, 1651.71, 1574.50, 1455.50, 1417.08, 1337.39, 1267.19, 1169.39.



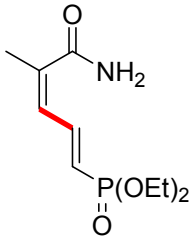
(2*Z*,4*E*)-2-Methyl-6-oxoocta-2,4-dienamide (**3u**)

White solid, m.p.: 118.4°C, yield = 49%. $^{1}$H NMR ($CDCl_3$): δ = 7.73 (dd, 1H, *J* =11.5, 15.5 Hz), 6.28 (d, 1H, *J* =11.5Hz), 6.17 (d, 1H, *J* =15.5Hz), 6.04 (brs, 1H), 5.76 (brs, 1H), 2.62 (q, 2H, *J* = 7.5 Hz), 2.10 (s, 3H), 1.11 (t, 3H, *J* = 7.5 Hz). $^{13}$C NMR ($CDCl_3$): δ = 201.5, 170.3, 140.0, 137.5, 132.1, 131.3, 33.5, 21.6, 8.1. HR-MS (ESI): *m/z* = 168.1013, $[M+H]^+$, calcd. for $C_9H_{13}NO_2$: 168.1019. FTIR (KBr, $cm^{-1}$): 3383.42, 2923.81, 2352.39, 1651.86, 1557.61, 1538.63, 1505.34, 1455.46.



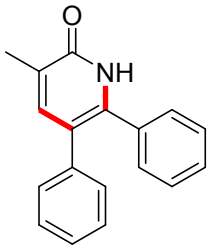
(2*Z*,4*E*)-2-Methyl-5-(perfluorophenyl)penta-2,4-dienamide (**3v**)

White solid, yield = 41%. $^{1}$H NMR (DMSO-$D_6$): δ = 7.60 (dd, 1H, *J* = 11.0, 16.0 Hz), 7.40 (brs, 1H), 6.51 (d, 2H, *J* = 16.5 Hz), 6.34 (d, 2H, *J* = 11.0 Hz), 3.33 (brs, 1H), 1.99 (s, 3H). $^{13}$C NMR (DMSO-D6): δ = 170.4-170.5 (m), 145.5, 143.4, 138.5-138.7 (m), 136.7, 135.1-135.2 (m), 131.4-131.5 (m), 116.8, 112.5-112.7 (m), 21.5. HR-MS (ESI): *m/z* = 278.0600, $[M+H]^+$, calcd. for $C_{12}H_8F_5NO$: 278.0599. FTIR (KBr, $cm^{-1}$): 3382.88, 2351.89, 1827.98, 1651.39, 1531.64, 1504.85, 1434.86, 1024.11, 984.46, 962.77.



Diethyl ((1*E*,3*Z*)-5-amino-4-methyl-5-oxopenta-1,3-dien-1-yl)phosphonate (**3w**)

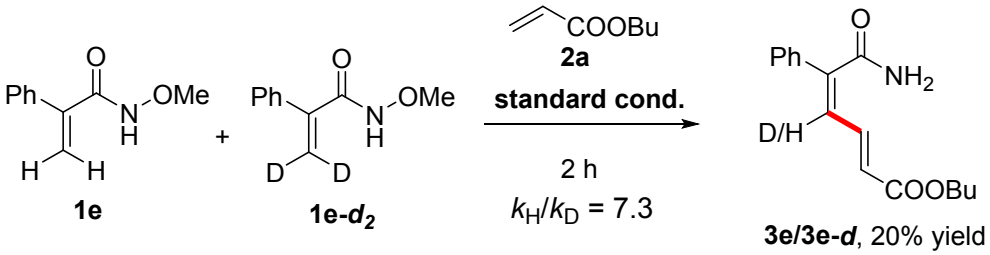
Brown oil, yield = 60%. $^1$H NMR ($CDCl_3$): δ = 7.49-7.61 (m, 1H), 6.51 (brs, 1H), 6.40 (brs, 1H), 6.19 (d, 1H, $J$ = 14.0 Hz), 5.70-5.79 (m, 1H), 4.04-4.11 (m, 4H), 2.07 (s, 3H), 1.32 (t, 6H, $J$ = 9.0 Hz). $^{13}$C NMR ($CDCl_3$): δ = 170.8, 144.0 (d, $J_{C-P}$ = 5.6 Hz), 140.4, 130.3 (d, $J_{C-P}$ = 21.1 Hz), 119.3 (d, $J_{C-P}$ = 126.3 Hz), 62.0, 21.3, 16.3. HR-MS (ESI): $m/z$ = 248.1040, $[M+H]^+$, calcd. for $C_{10}H_{18}NO_4P$: 248.1046. FTIR (KBr, $cm^{-1}$): 3354.30, 3194.82, 2984.66, 2924.05, 2356.96, 1667.46, 1393.17, 1244.05, 1162.99, 1097.11, 1024.18, 965.86, 856.26, 789.13.




3-Methyl-5,6-diphenylpyridin-2(1H)-one (**5**)

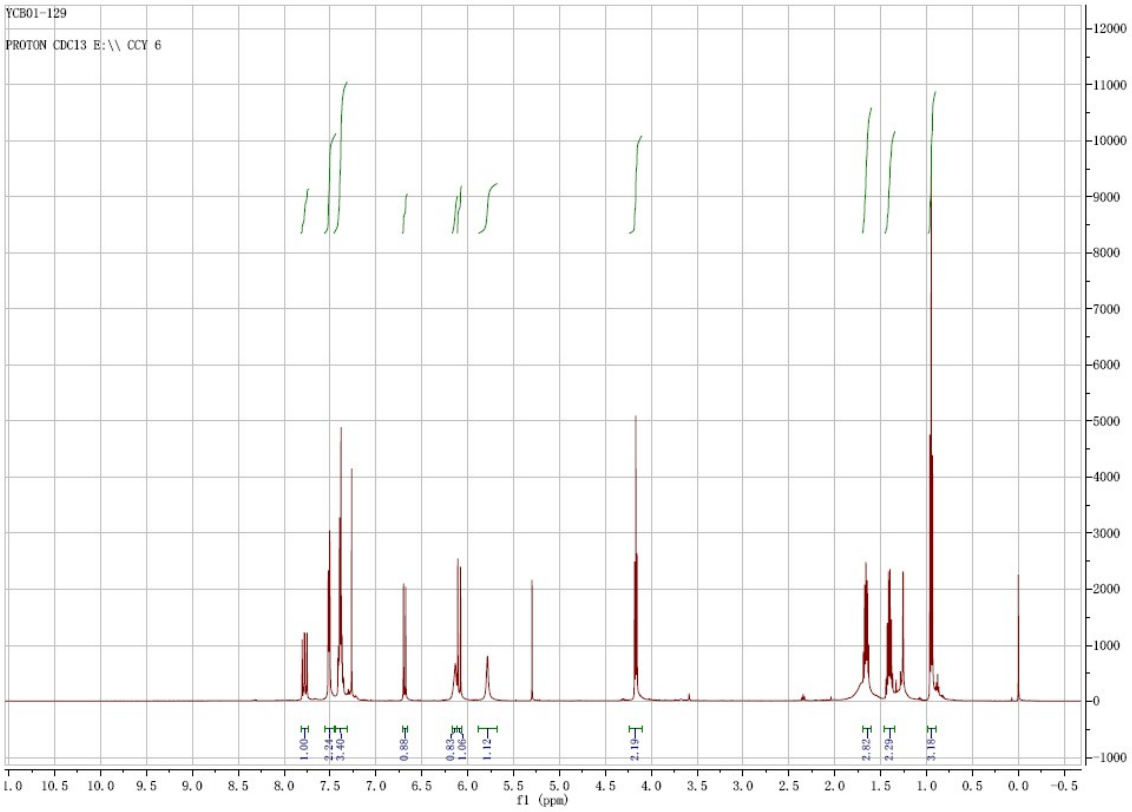
White solid, m.p.: 182.5 °C, yield = 21%. 1H NMR ($CDCl_3$): δ = 9.82 (brs, 1H), 7.42 (s, 1H), 7.27-7.32 (m, 4H), 7.21-7.23 (m, 4H), 7.06-7.08 (m, 2H), 2.21 (s, 3H). 13C NMR (CDCl3): δ = 163.4, 141.9, 140.5, 137.8, 134.1, 129.6, 129.2, 129.1, 128.7, 128.4, 126.9, 118.8, 16.3. HR-MS (ESI): m/z = 262.1233, $[M+H]^+$, calcd. for $C_{18}H_{15}NO$: 262.1226. FTIR (KBr, $cm^{-1}$): 3626.67, 3564.63, 1682.45, 1651.55, 1557.42, 1538.56, 1505.25, 461.37.

## KIE Study




An oven-dried screw-cap vial was charged with [Ru(*p*-cymene)$Cl_2$]$_2$ (5.0 mol%, 0.01 mmol), KOPiv (30.0 mol%, 0.06 mmol) and DMF (1.0 ml). Then, acrylamide **1e** (0.10 mmol), **1e-*d*$_2$** (0.10 mmol) and acrylate (0.36 mmol) were added into the solution in sequence. The vial was sealed under nitrogen and heated to 60 ℃ with stirring for 2 hours. After cooling down, the mixture was diluted with ethyl acetate, filtered and washed with water and brine. The organic layer was dried over anhydrous $Na_2SO_4$, filtered and concentrated to give the crude product which was

directly applied to a flash column chromatography (EtOAc/Petroleum ether mixtures). The ratio of **3e**/**3e-*d*** was determined by $^1$H NMR (500 MHz, $CDCl_3$) to be 7.3.




## References:


1. (a) Guimond, N.; Gorelsky, S. I.; Fagnou, K. *J. Am. Chem. Soc*. **2011**, *133*, 6449-6457. (b) Rana, N. K.; Singh, V. K. *Org. Lett*. **2011**, *13*, 6520-6523.

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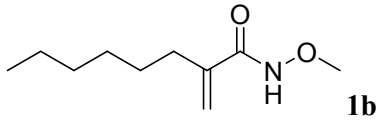
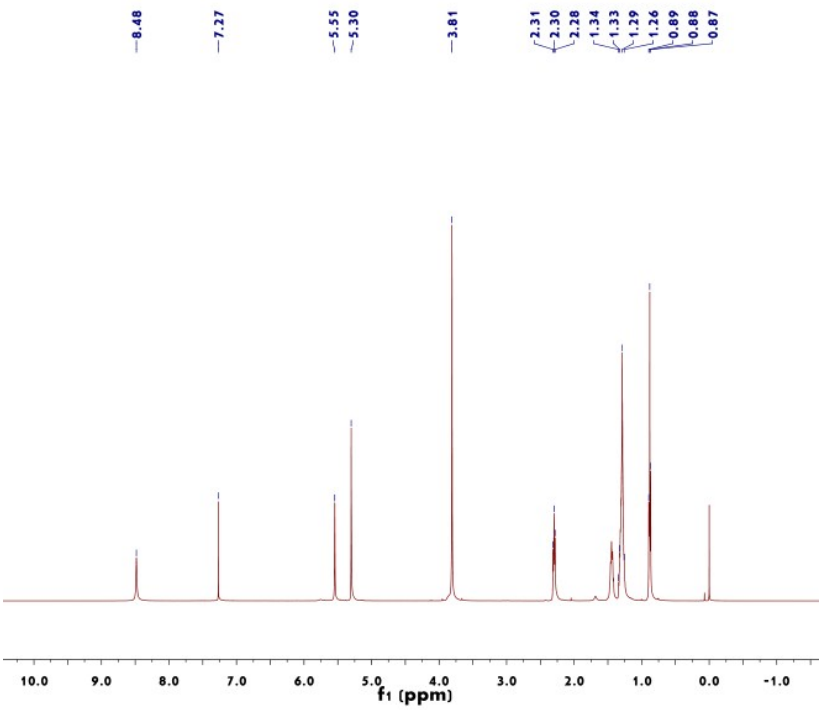
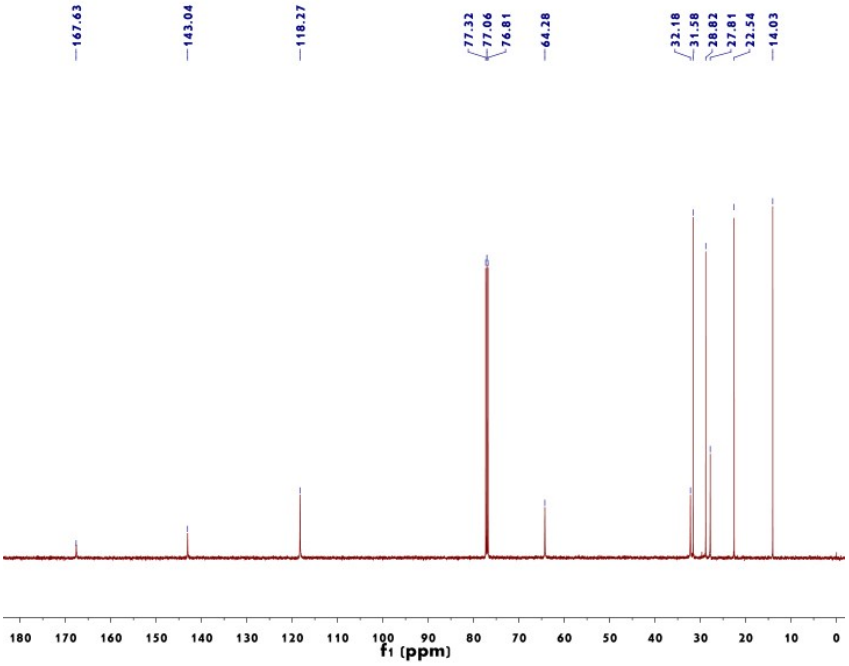
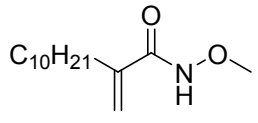
## NMR Spectra



**1b**

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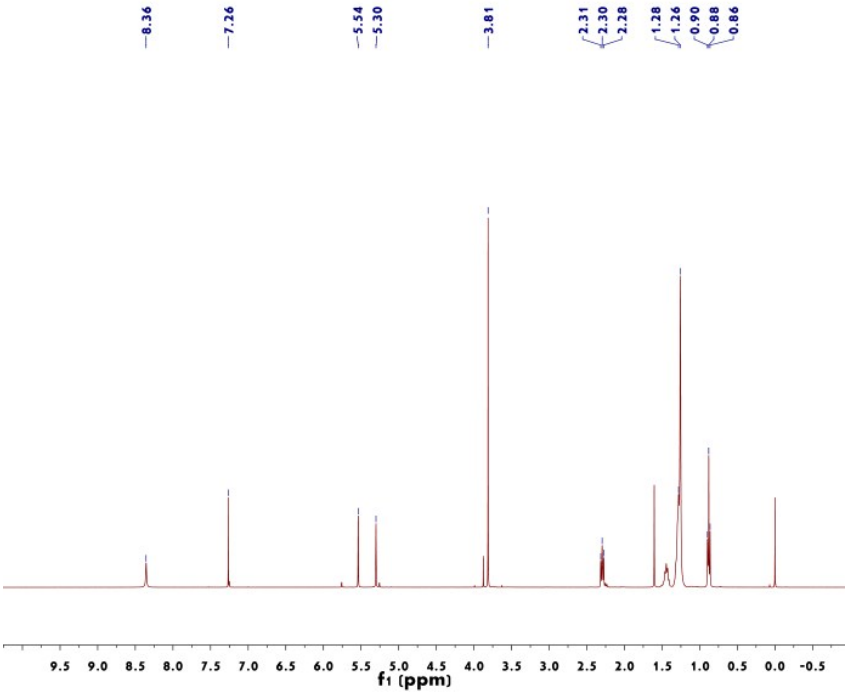
N
O
H

**1c**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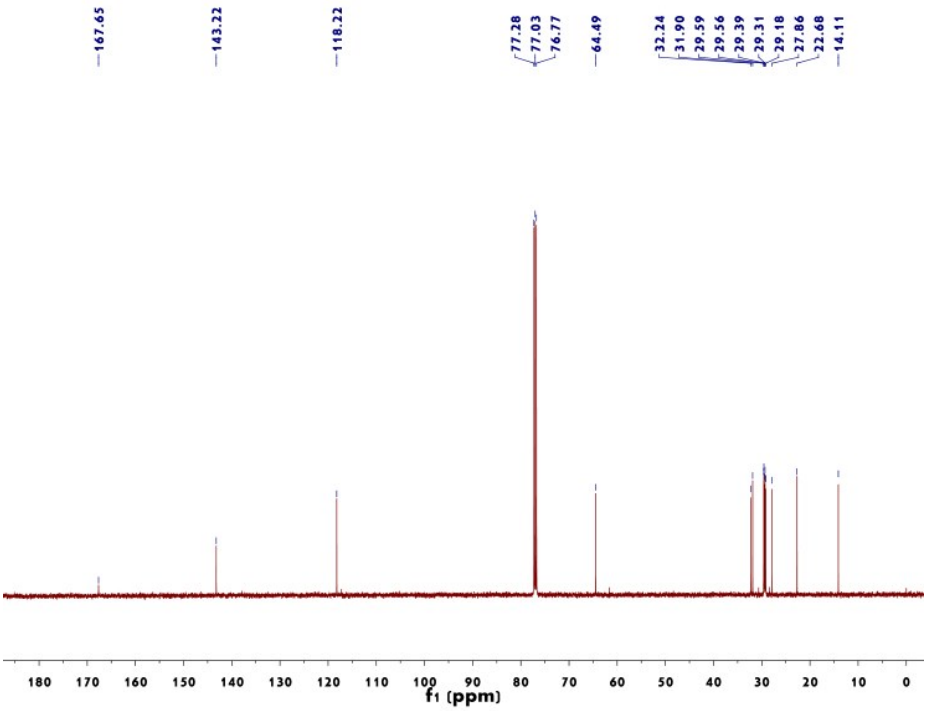
5.30
3.81
2.31
2.30
2.28
1.28
1.26
0.90
0.88
0.86
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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29.18
27.86
22.68
14.11
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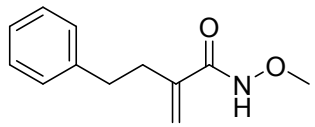

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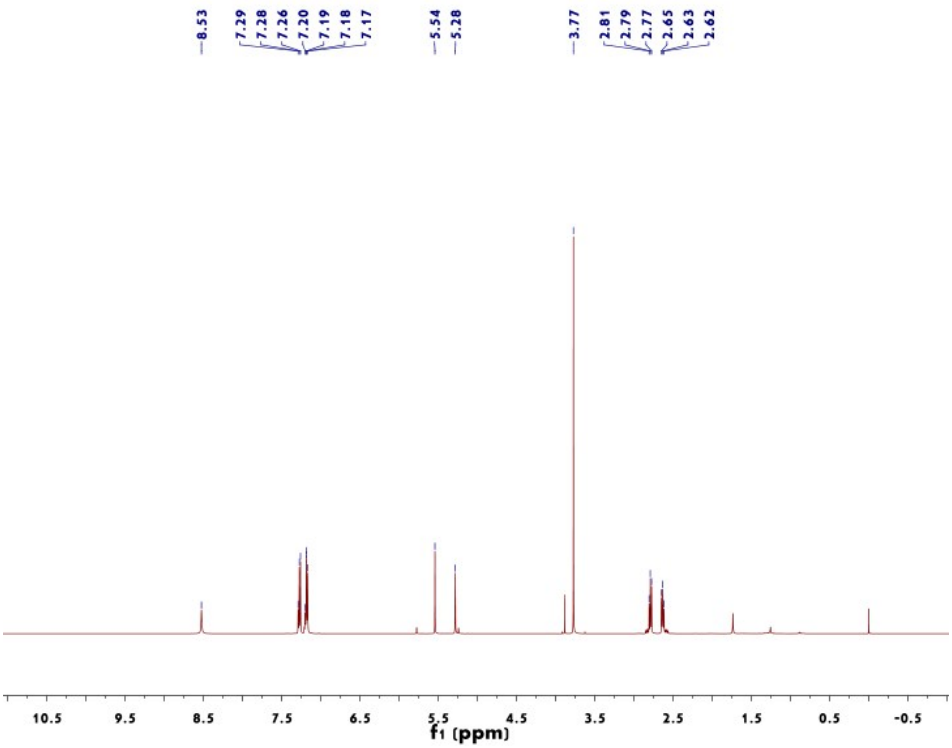
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7.19
7.18
7.17
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5.28
3.77
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2.65
2.63
2.62
10.5
9.5
8.5
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6.5
5.5
4.5
3.5
2.5
1.5
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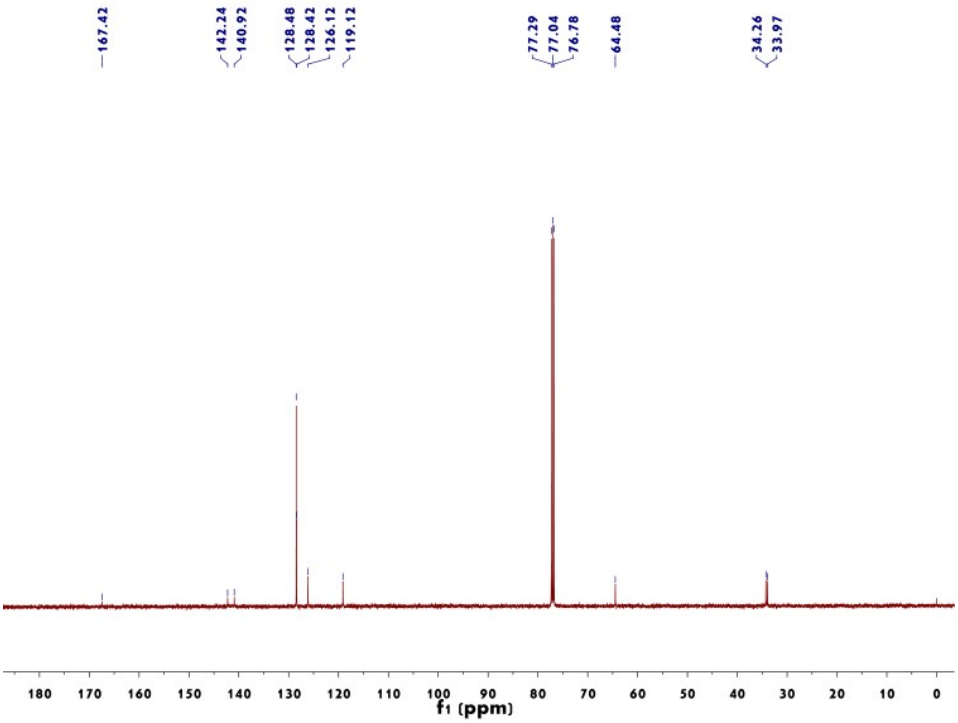
f1 (ppm)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119.12
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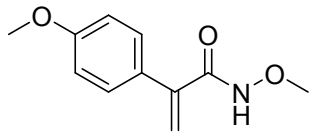
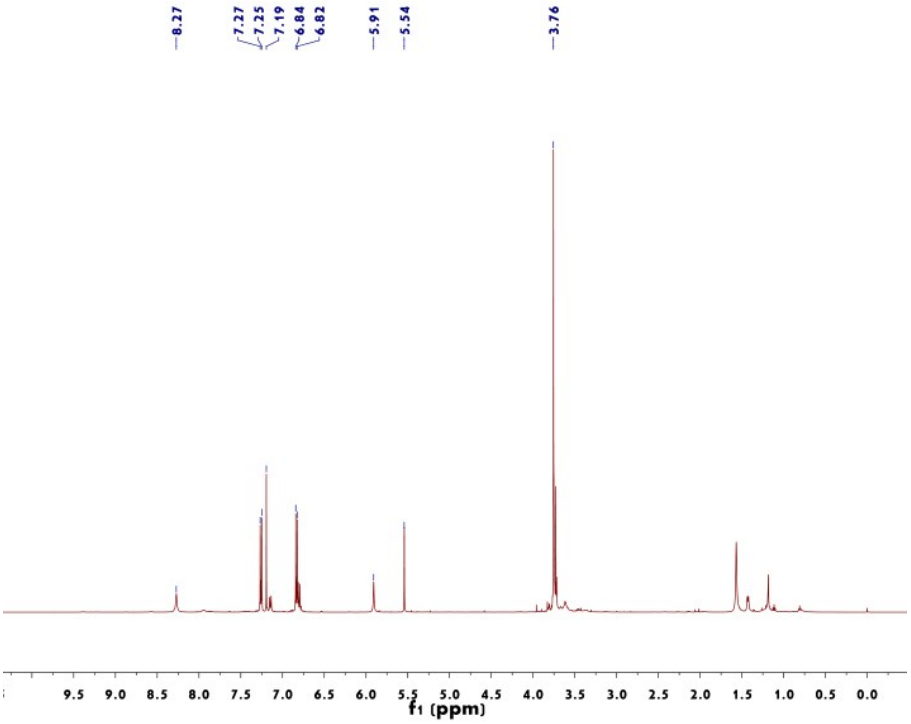
77.04
76.78
64.48
34.26
33.97
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



**1f**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7.19
6.84
6.82
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5.54
3.76
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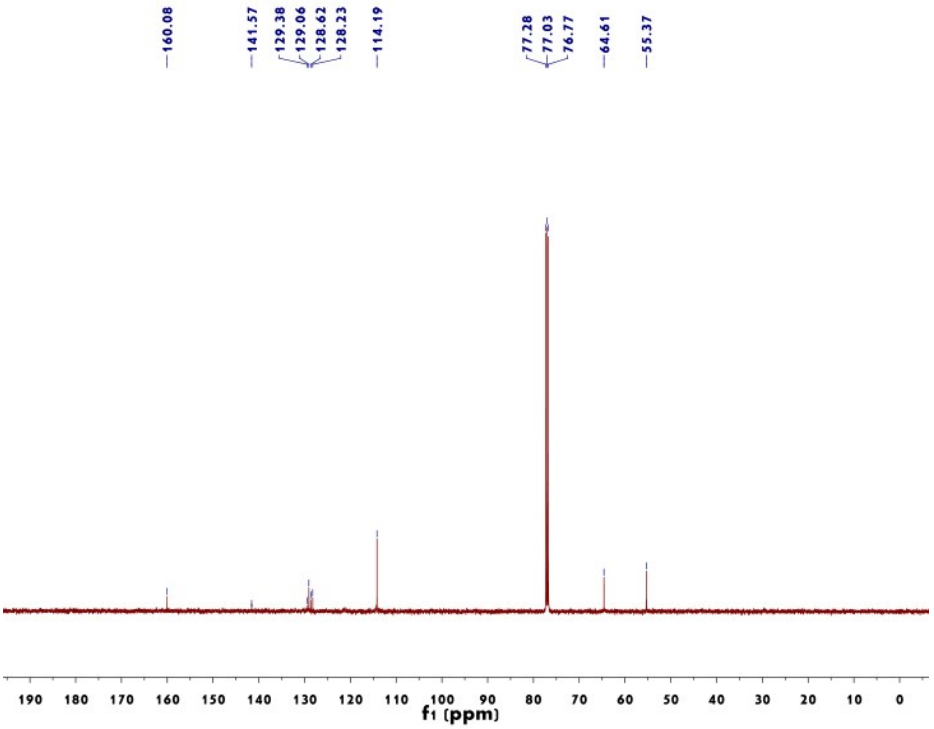
f1 (ppm)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128.62
128.23
114.19
77.28
77.03
76.77
64.61
55.37
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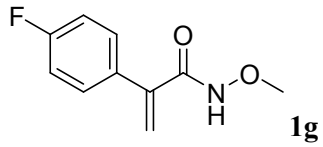
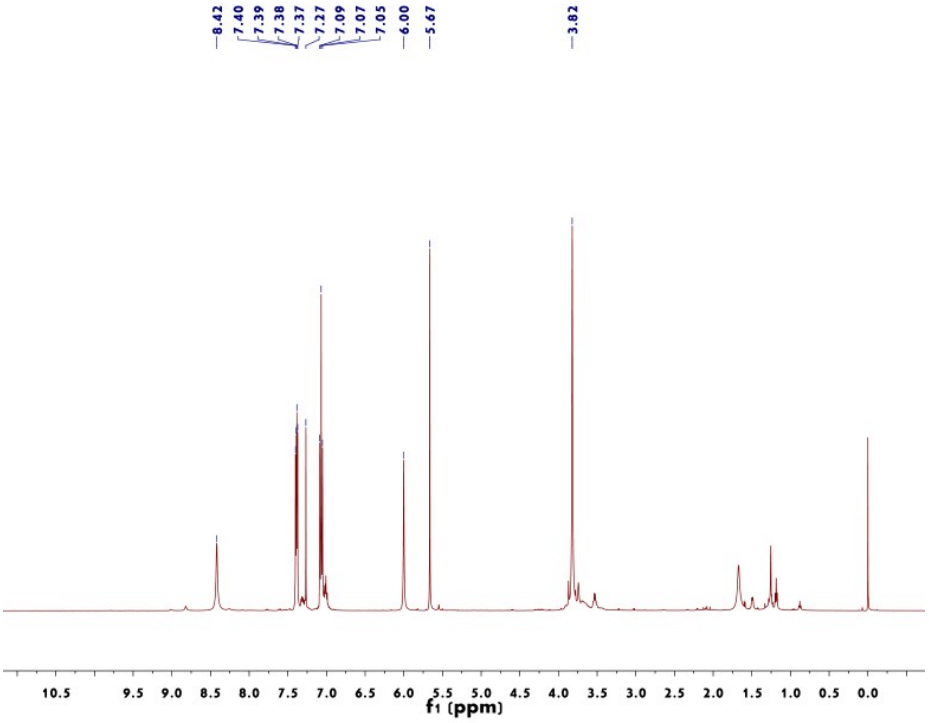
f1 (ppm)


F
O
N
H
O

**1g**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7.37
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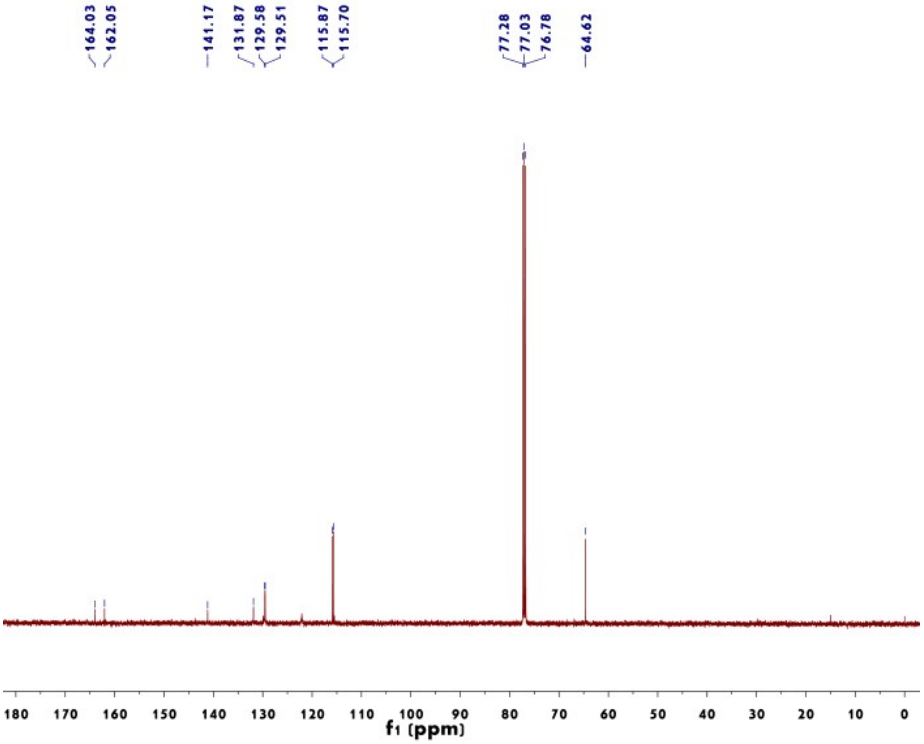
6.00
5.67
3.82
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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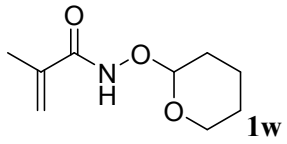
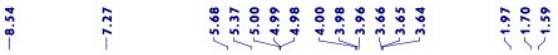
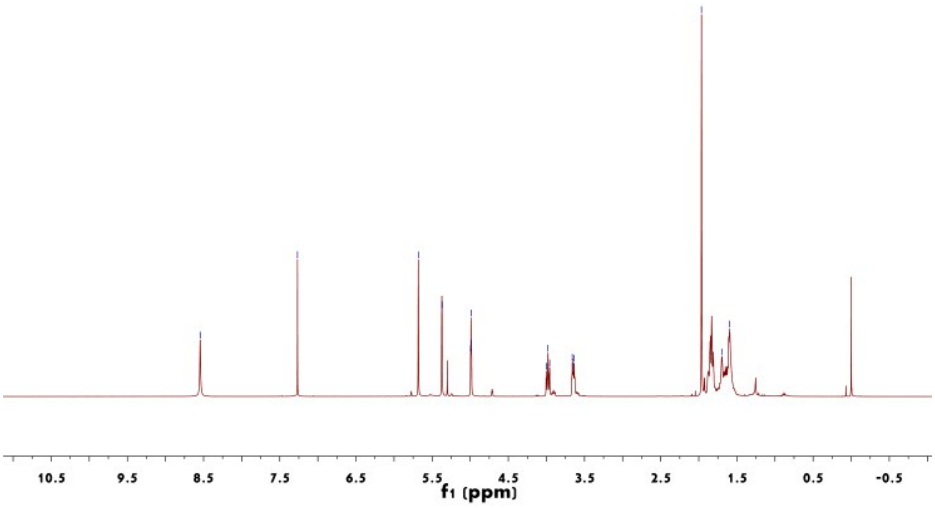
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

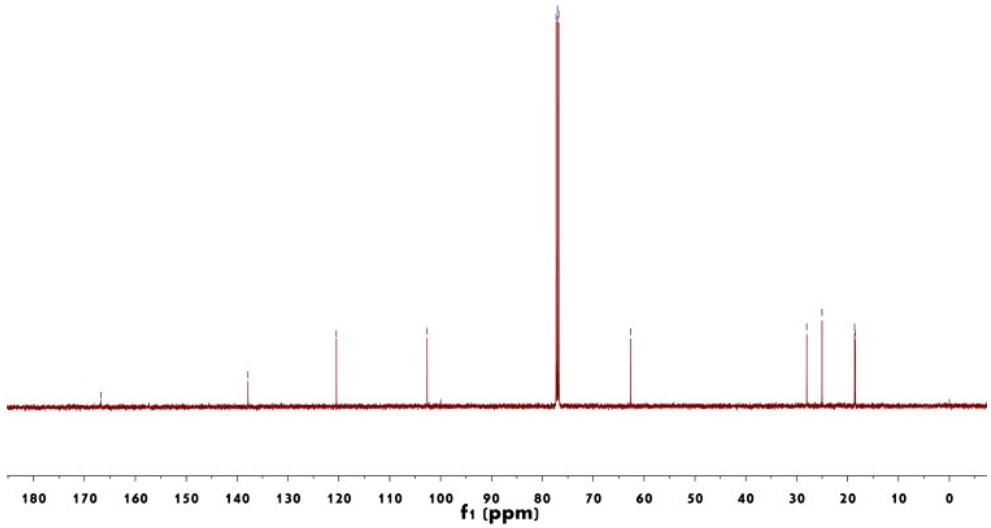


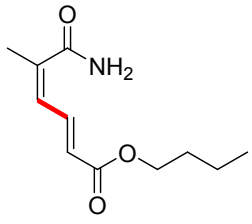
**1w**


8.54
7.27
5.68
5.37
5.00
4.99
4.98
4.00
3.98
3.96
3.66
3.65
3.64
1.97
1.70
1.59


10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

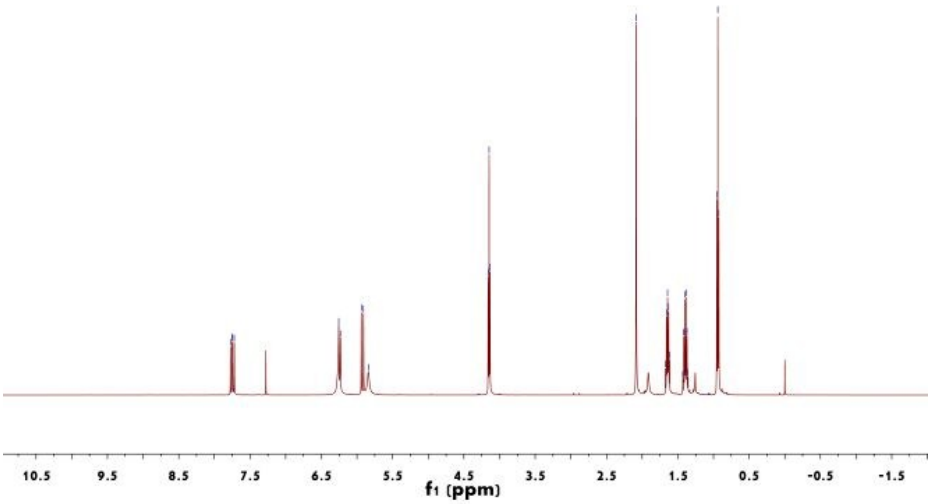

166.76
137.85
120.48
102.64
77.28
77.03
76.77
62.68
28.04
25.03
18.63
18.49


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

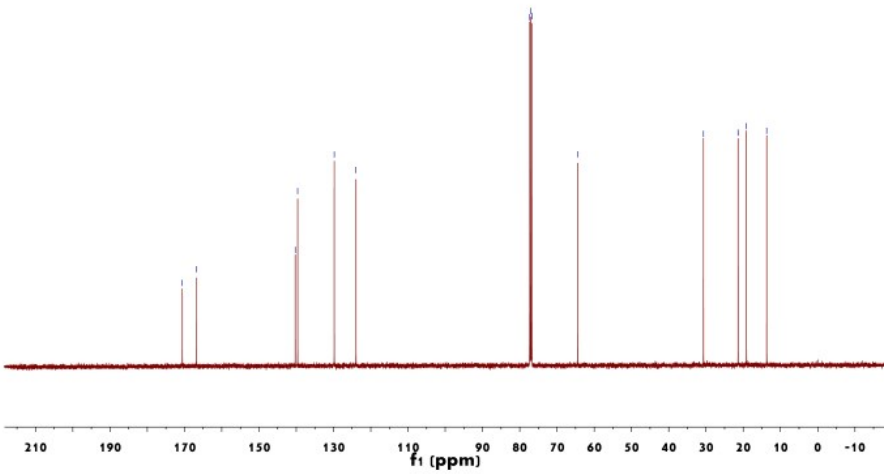


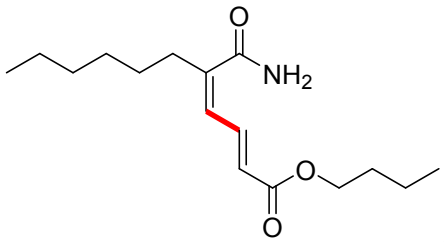
**3a**


7.77
7.75
7.74
7.72
6.26
6.23
5.94
5.91
5.84
4.16
4.15
4.13
2.09
1.67
1.66
1.64
1.63
1.62
1.43
1.42
1.40
1.39
1.37
1.36
0.95
0.94
0.93

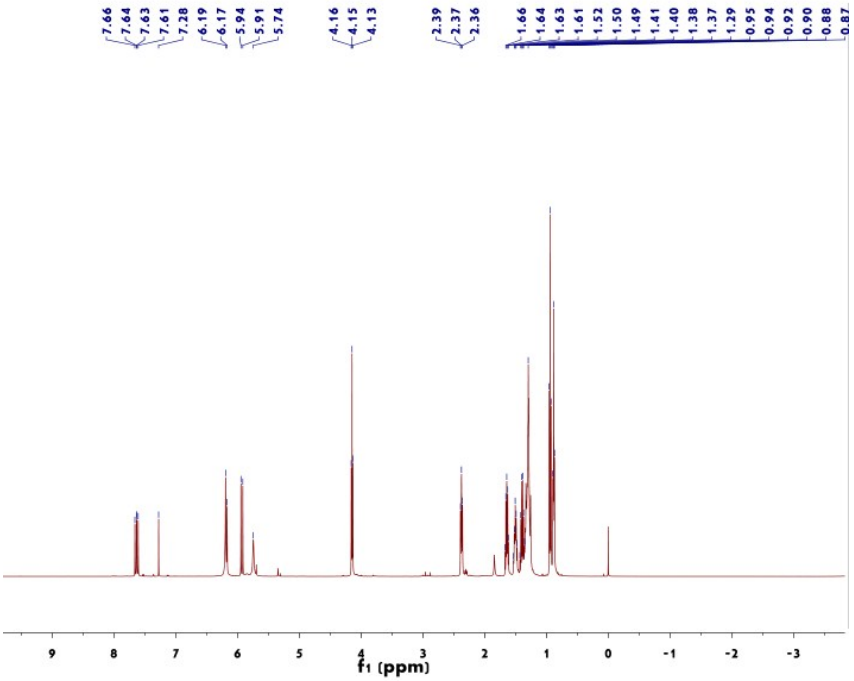

10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

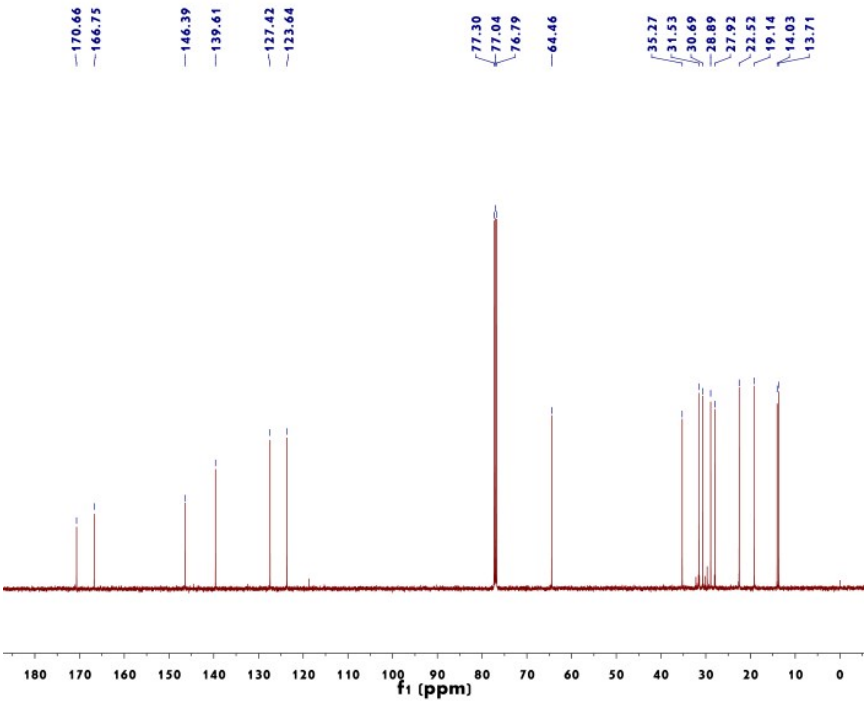

170.58
166.79
140.28
139.62
129.80
123.95
77.30
77.04
76.79
64.49
30.68
21.40
19.14
13.71

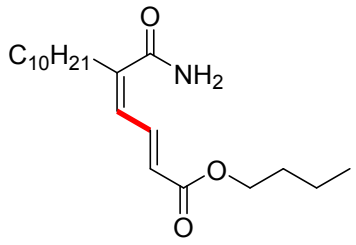

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
NH2
O
O

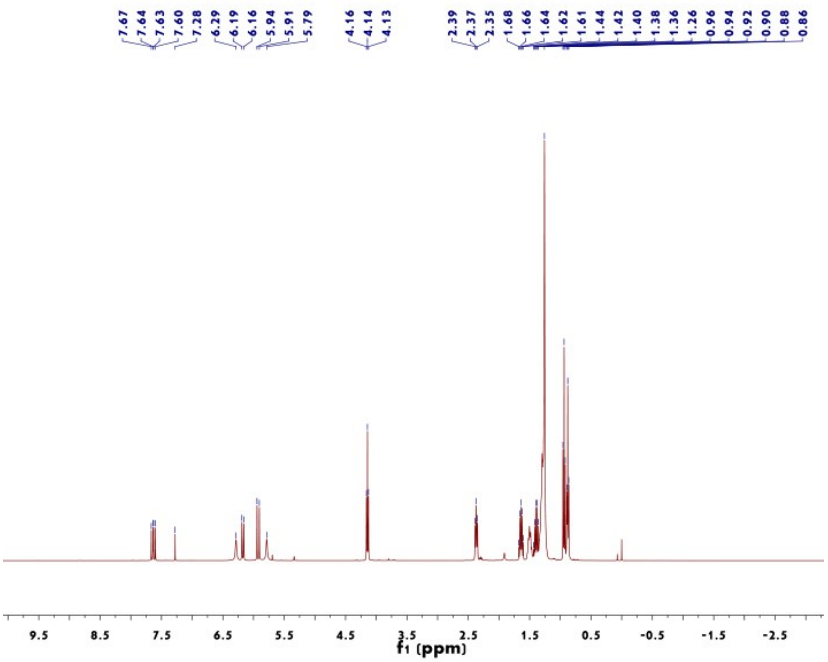
**3b**

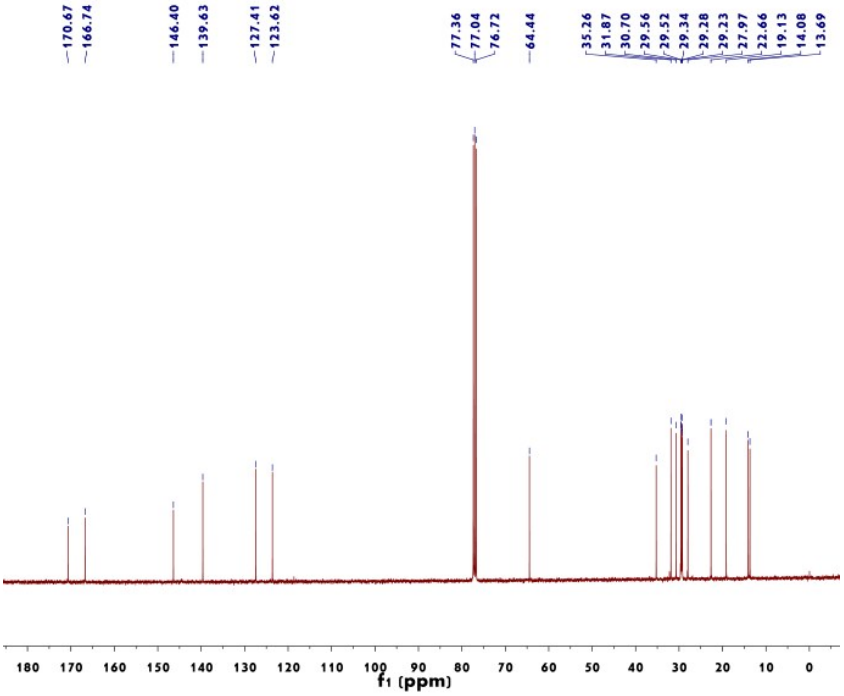

7.66
7.64
7.63
7.61
7.28
6.19
6.17
5.94
5.91
5.74
4.16
4.15
4.13
2.39
2.37
2.36
1.66
1.64
1.63
1.61
1.52
1.50
1.49
1.41
1.40
1.38
1.37
1.29
0.95
0.94
0.92
0.90
0.88
0.87
9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

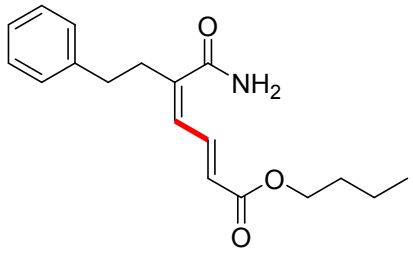

170.66
166.75
146.39
139.61
127.42
123.64
77.30
77.04
76.79
64.46
35.27
31.53
30.69
28.89
27.92
22.52
19.14
14.03
13.71
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
$C_{10}H_{21}$
$NH_2$
O
O

**3c**

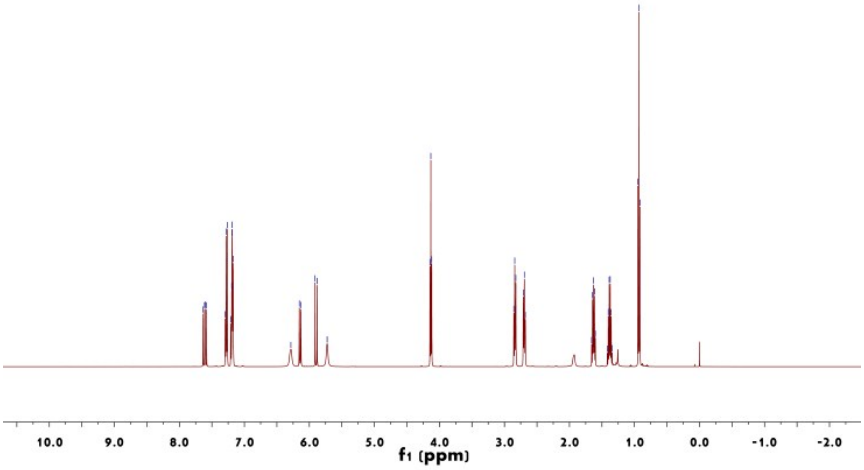

7.67
7.64
7.63
7.60
7.28
6.29
6.19
6.16
5.94
5.91
5.79
4.16
4.14
4.13
2.39
2.37
2.35
1.68
1.66
1.64
1.62
1.61
1.44
1.42
1.40
1.38
1.36
1.26
0.96
0.94
0.92
0.90
0.88
0.86
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
-2.5
f1 (ppm)


170.67
166.74
146.40
139.63
127.41
123.62
77.36
77.04
76.72
64.44
35.26
31.87
30.70
29.56
29.52
29.34
29.28
29.23
27.97
22.66
19.13
14.08
13.69
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

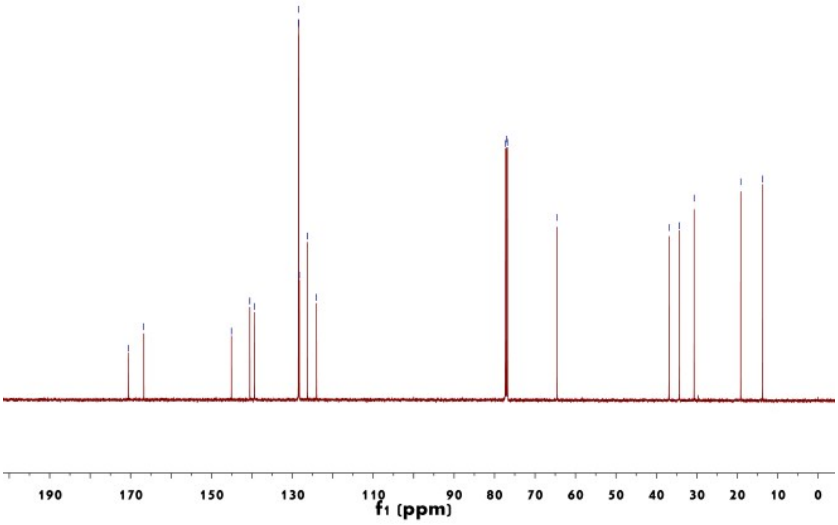

O
NH2
O
O

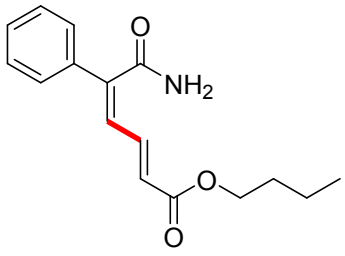
**3d**


7.64
7.61
7.61
7.58
7.29
7.28
7.26
7.21
7.19
7.19
7.19
7.17
6.29
6.16
6.13
5.91
5.88
5.73
4.15
4.13
4.12
2.86
2.84
2.82
2.71
1.65
1.63
1.62
1.60
1.42
1.40
1.39
1.37
1.36
1.34
0.95
0.93
0.92


10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
f1 (ppm)

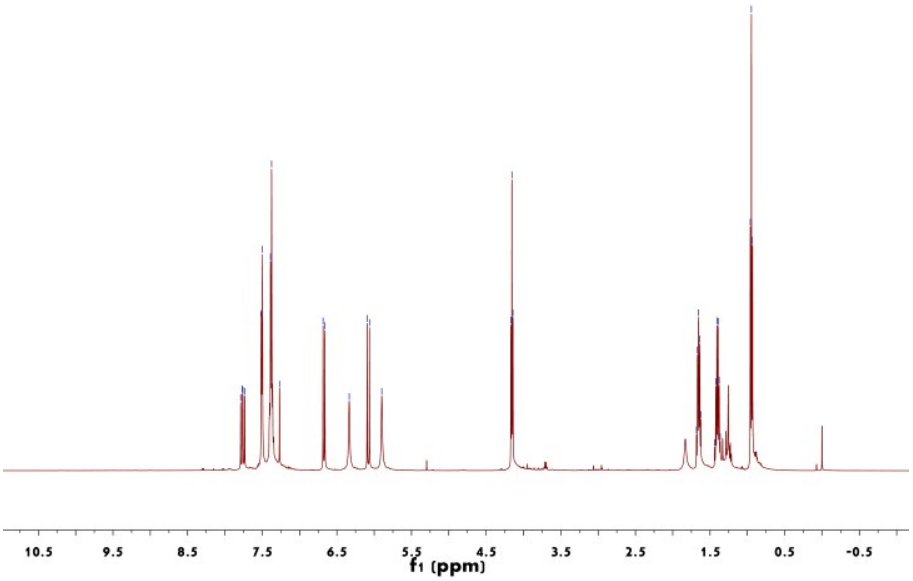

170.49
166.72
145.06
140.52
139.38
128.51
128.45
128.29
126.29
124.03
77.33
77.08
76.83
64.53
36.87
34.31
30.68
19.14
13.73


190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

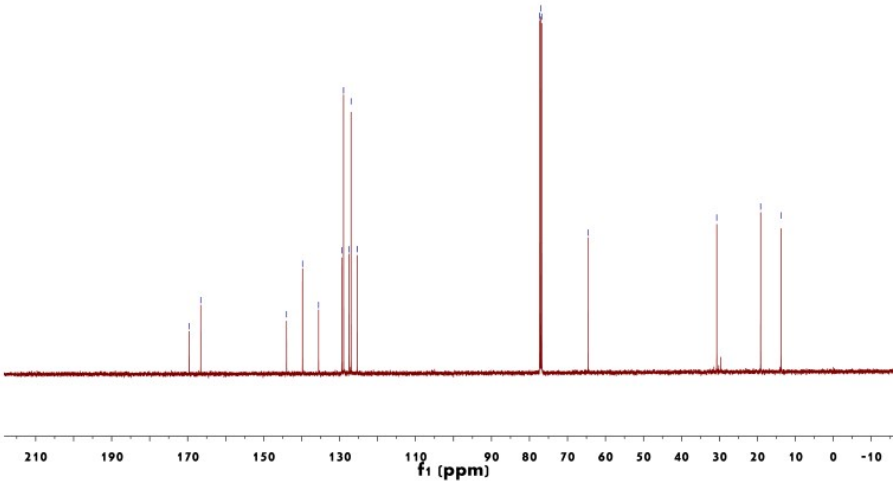


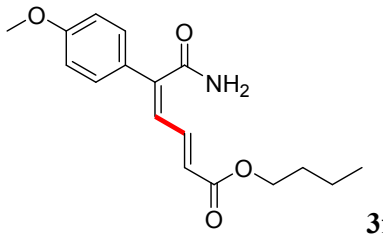
**3e**


7.79
7.77
7.76
7.73
7.51
7.50
7.39
7.38
7.27
6.69
6.66
6.34
6.09
6.06
5.90
4.17
4.15
4.14
1.68
1.67
1.65
1.64
1.63
1.44
1.42
1.41
1.39
1.38
1.36
0.96
0.95
0.93

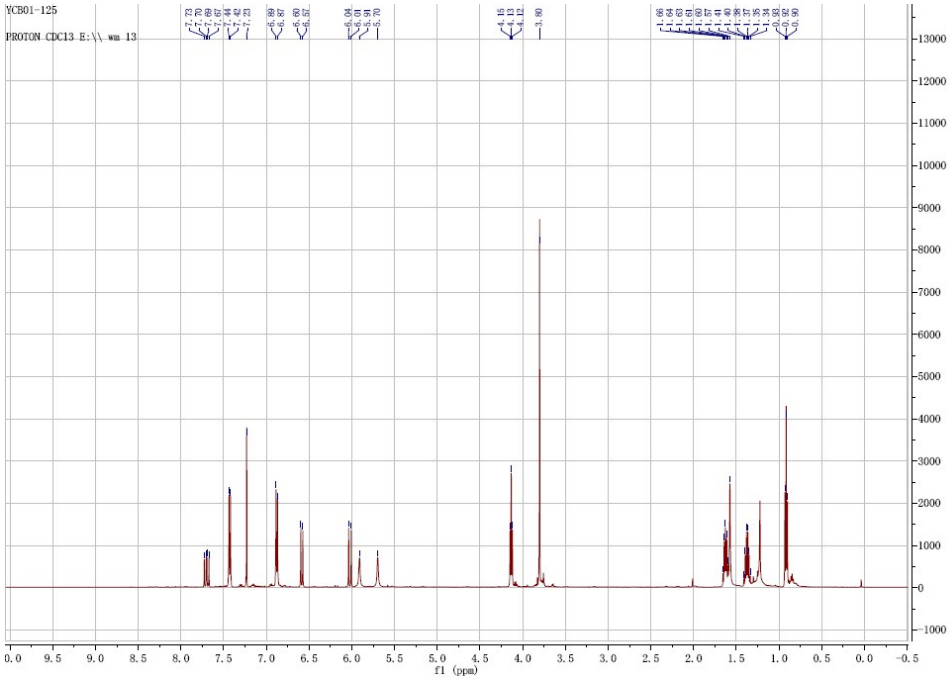

10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


169.62
166.57
143.96
139.76
135.53
129.44
128.95
127.48
126.99
125.39
77.30
77.05
76.79
64.57
30.70
19.16
13.74

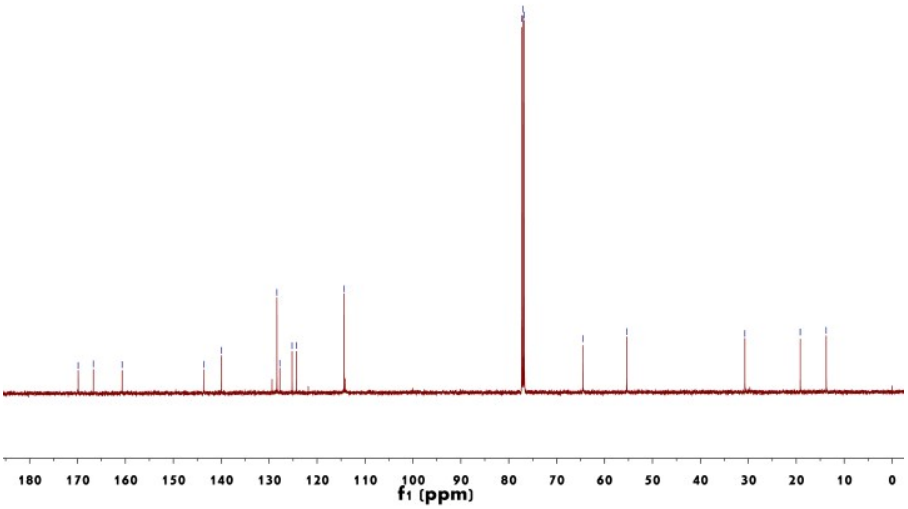

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

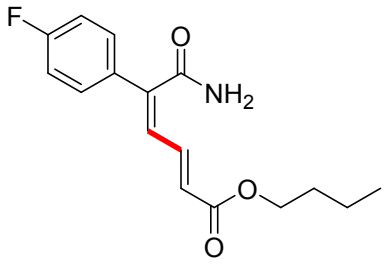


**3f**


YCB01-125
PROTON CDCl3 E:\\ wm 13
f1 (ppm)

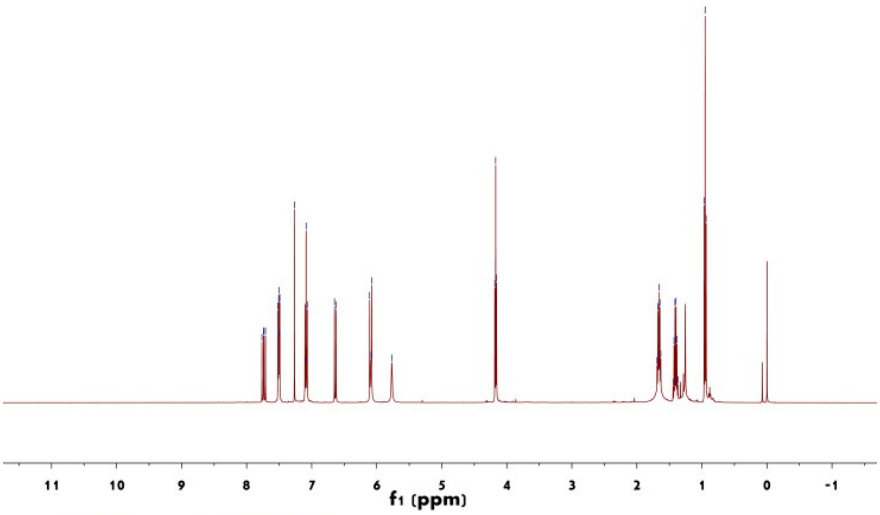

169.85
166.70
160.69
143.69
140.01
128.39
127.79
125.22
124.32
114.39
77.29
77.03
76.78
64.50
55.41
30.72
19.17
13.75


f1 (ppm)

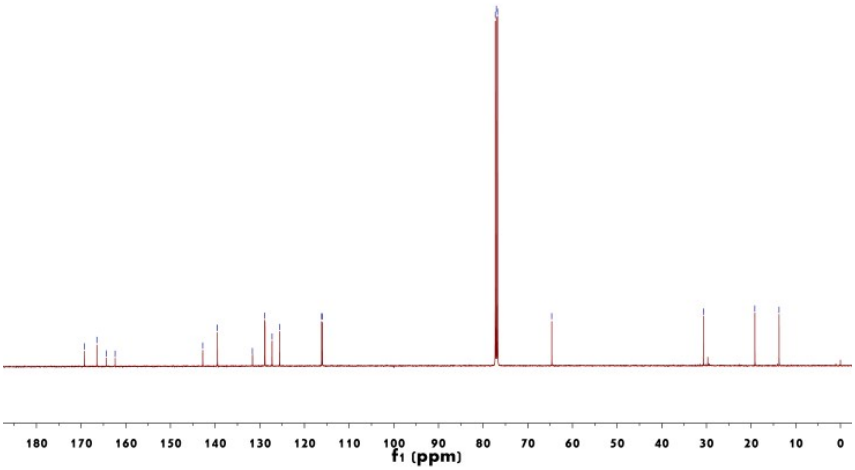

F
O
NH2
O
O

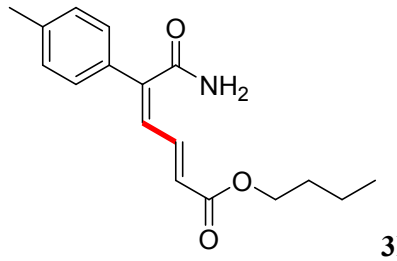
**3g**


7.76
7.74
7.73
7.71
7.52
7.51
7.50
7.50
7.49
7.26
7.10
7.09
7.07
6.65
6.63
6.11
6.09
6.08
5.77
4.18
4.17
4.16
1.69
1.68
1.66
1.65
1.63
1.44
1.43
1.41
1.40
1.38
1.37
0.97
0.95
0.94


11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

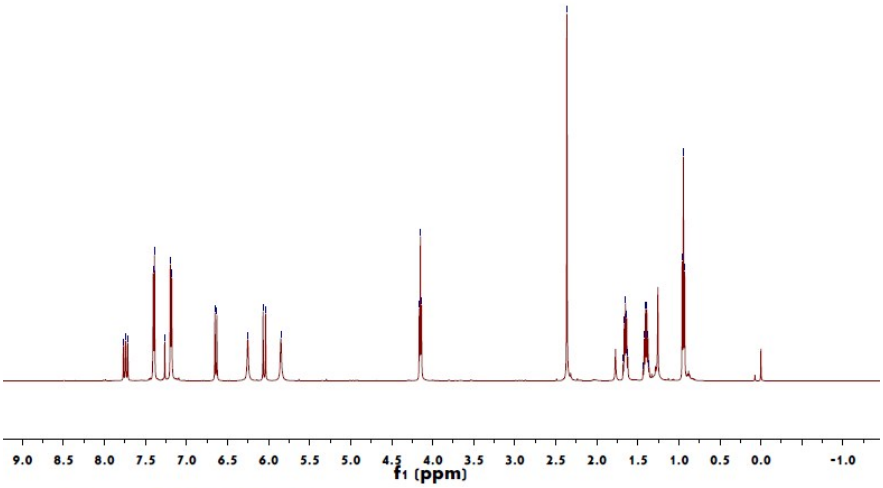

169.25
166.48
164.39
162.39
142.77
139.47
131.65
128.91
127.25
125.57
116.16
115.98
77.28
77.03
76.78
64.63
30.70
19.16
13.74


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

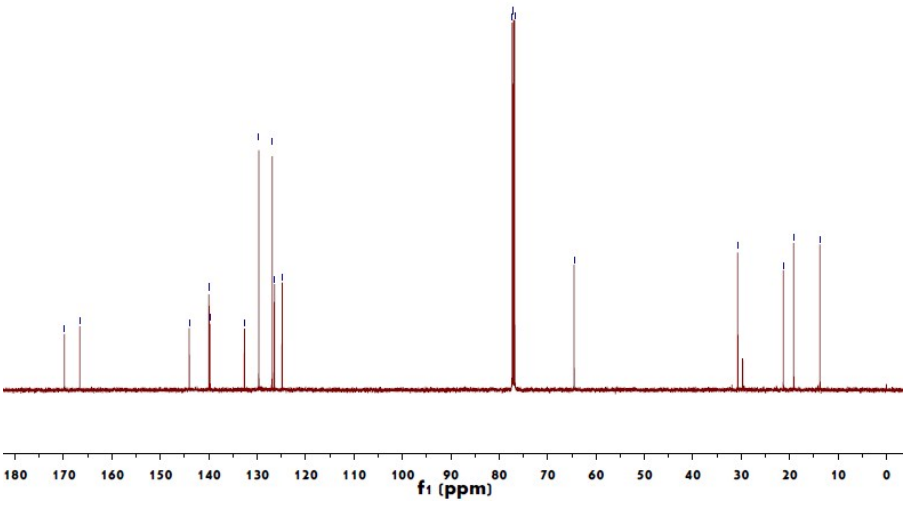

O
NH2
O
O

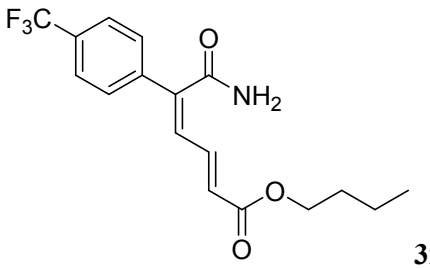
**3h**


7.77
7.75
7.74
7.72
7.41
7.39
7.27
7.20
7.18
6.65
6.63
6.25
6.07
6.04
5.85
4.16
4.15
4.14
2.36
1.68
1.66
1.65
1.64
1.62
1.44
1.42
1.41
1.39
1.38
1.36
0.96
0.94
0.93

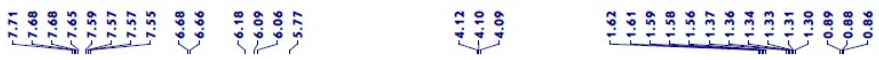

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
f1 (ppm)

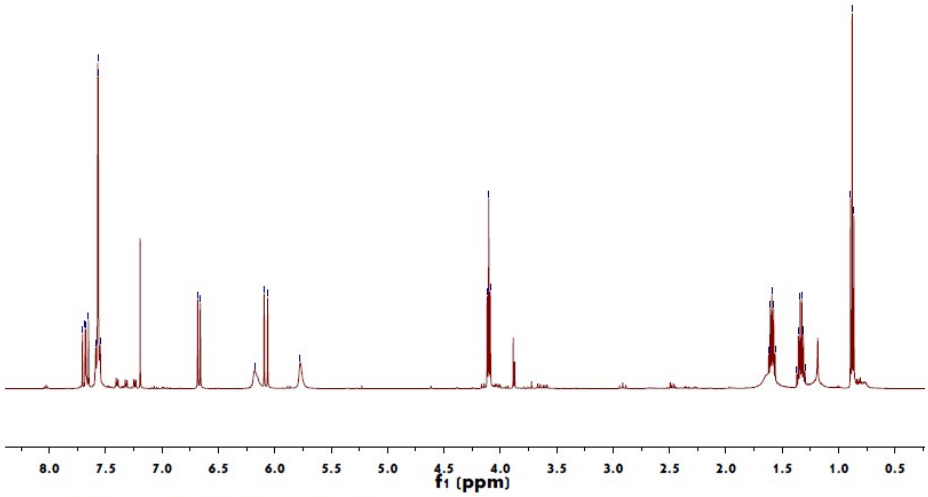

169.82
166.64
144.02
139.95
139.73
132.63
129.65
126.88
126.43
124.83
77.30
77.05
76.80
64.52
30.71
21.30
19.16
13.74


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

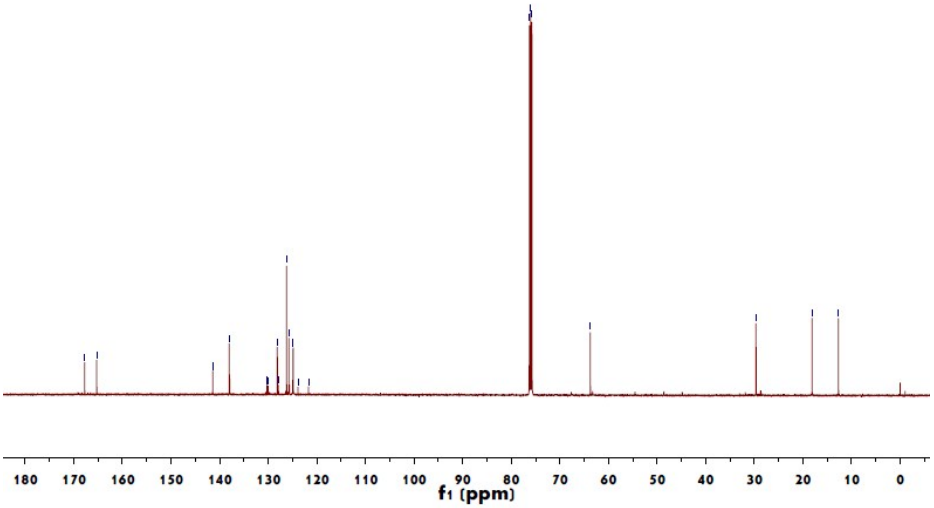

F3C
O
NH2
O
O

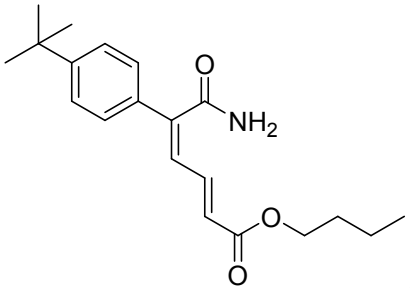
**3i**


7.71
7.68
7.68
7.65
7.59
7.57
7.57
7.57
7.55
6.68
6.66
6.18
6.09
6.06
5.77
4.12
4.10
4.09
1.62
1.61
1.59
1.58
1.56
1.37
1.36
1.34
1.33
1.31
1.30
0.89
0.88
0.86


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

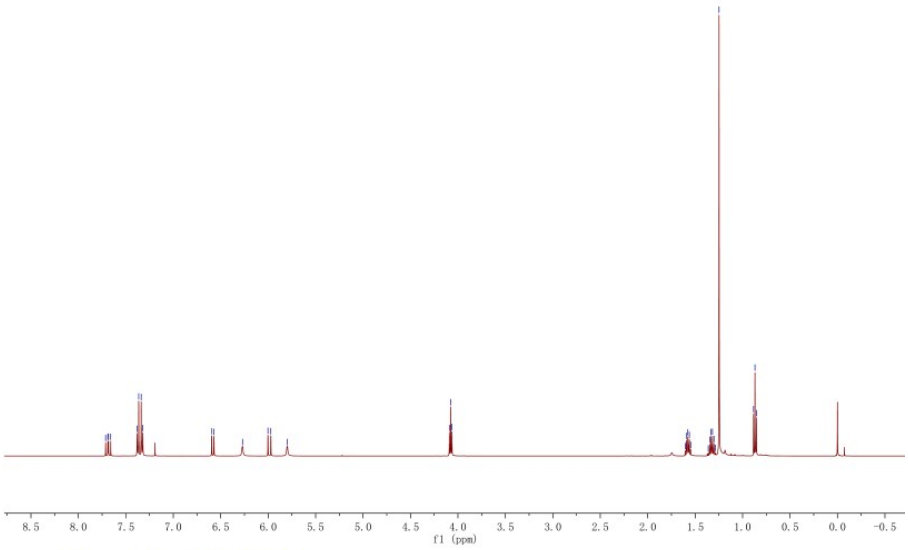

167.75
165.28
141.41
138.01
130.27
130.01
128.13
127.94
127.90
126.22
125.74
124.90
124.87
123.87
121.71
76.26
76.01
75.75
63.73
29.65
18.12
12.70


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

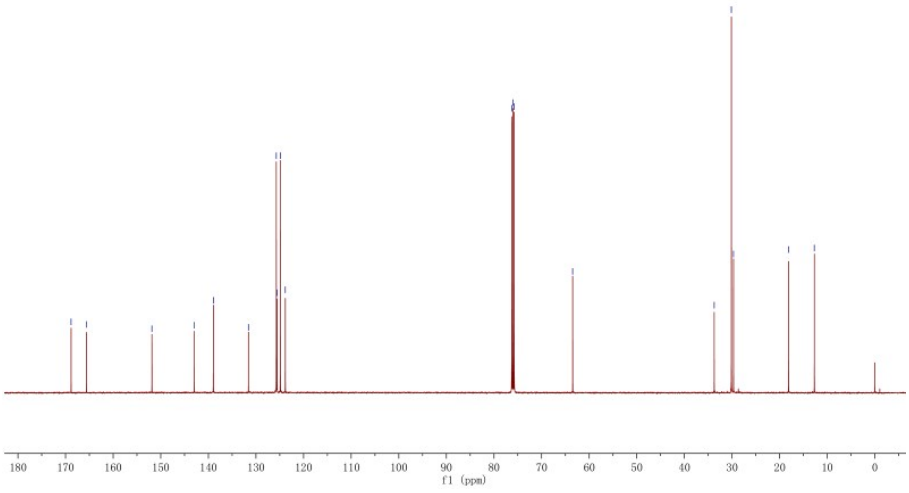

O
NH2
O
O

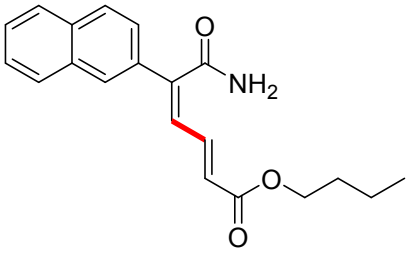
**3j**


7.71
7.69
7.68
7.66
7.38
7.36
7.34
7.32
6.60
6.57
6.27
6.00
5.97
5.80
4.09
4.08
4.06
1.60
1.59
1.58
1.56
1.55
1.36
1.35
1.33
1.32
1.30
1.29
1.25
0.88
0.87
0.85


f1 (ppm)

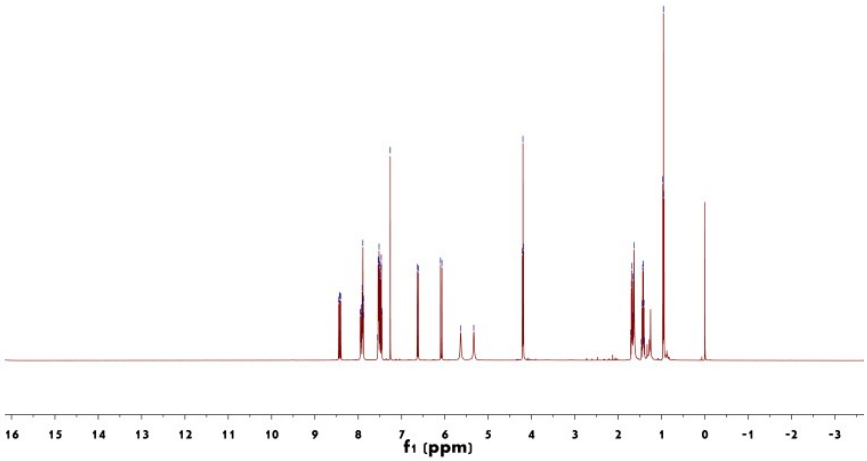

168.83
165.62
151.86
142.95
138.96
131.58
125.73
125.58
124.89
123.84
76.28
76.03
75.77
63.48
33.75
30.14
29.69
18.13
12.72


f1 (ppm)

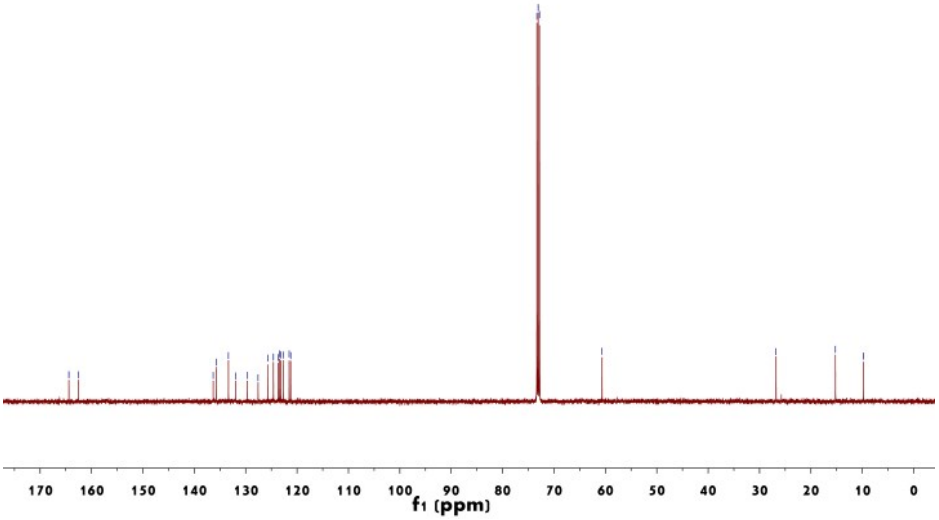

O
NH2
O
O

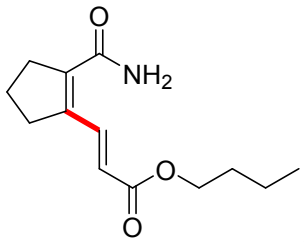
**3k**


8.46
8.43
8.42
8.40
7.95
7.94
7.93
7.91
7.90
7.89
7.89
7.88
7.54
7.53
7.52
7.51
7.49
7.47
7.47
7.46
7.26
6.64
6.62
6.10
6.07
5.33
4.21
4.20
4.19
1.71
1.70
1.68
1.67
1.65
1.64
1.47
1.45
1.44
1.42
1.41
1.39
0.97
0.96
0.94


16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

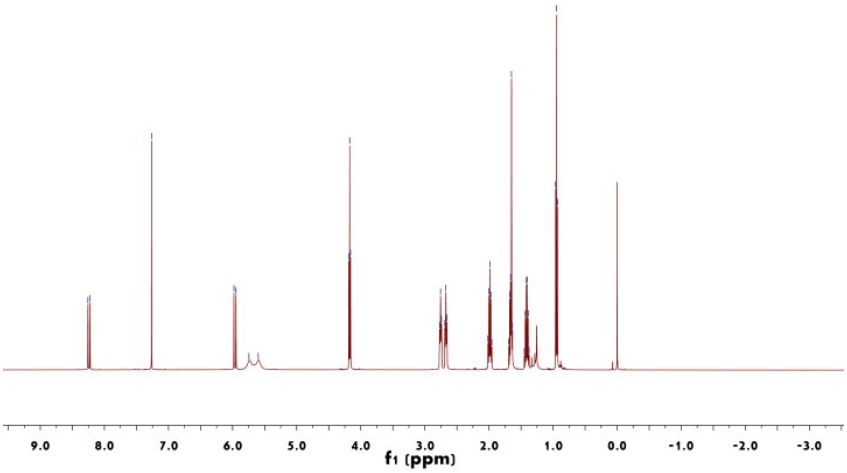

164.41
162.57
136.32
135.75
133.35
131.95
129.73
127.58
125.71
124.60
123.70
123.41
123.19
122.67
121.53
121.24
73.34
73.09
72.83
60.66
26.79
15.24
9.82

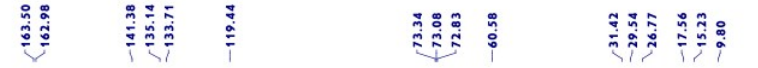

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

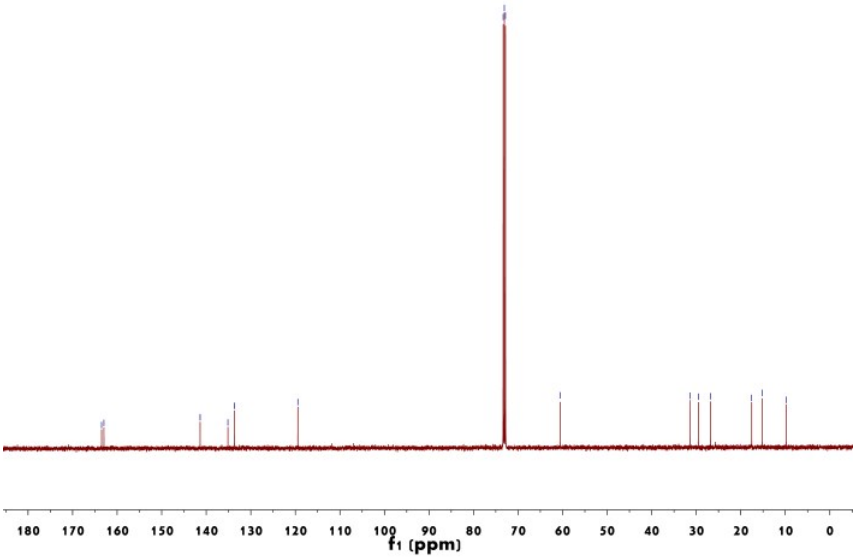


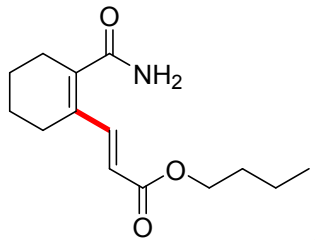
**3l**


8.26
8.23
7.26
5.98
5.95
5.74
5.60
4.19
4.17
4.16
2.76
2.74
2.67
2.66
2.01
2.00
1.99
1.97
1.96
1.69
1.68
1.66
1.65
1.63
1.45
1.43
1.42
1.40
1.39
1.37
0.96
0.95
0.93

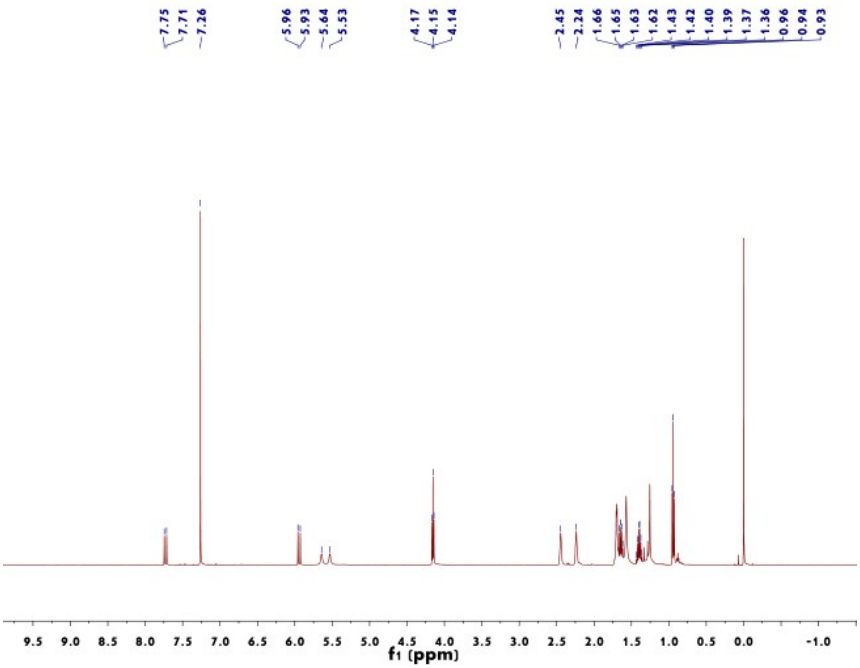

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
f1 (ppm)

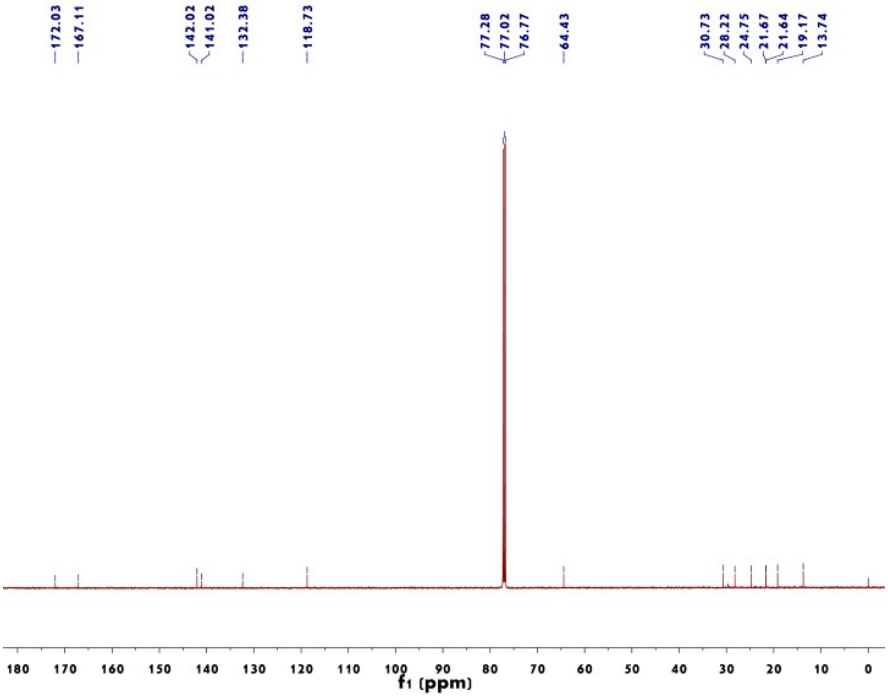

163.50
162.98
141.38
135.14
133.71
119.44
73.34
73.08
72.83
60.58
31.42
29.54
26.77
17.56
15.23
9.80

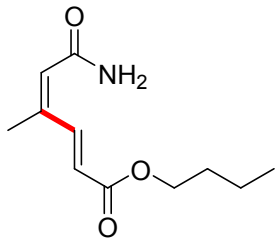

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
NH2
O
O

**3m**

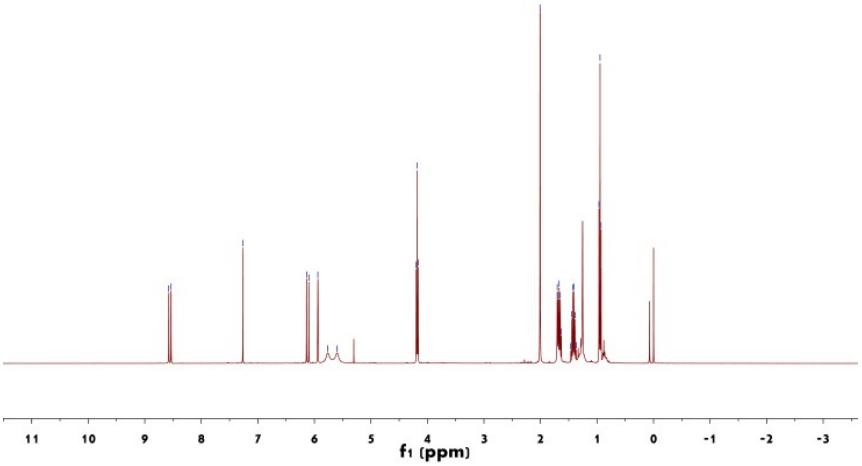

7.75
7.71
7.26
5.96
5.93
5.64
5.53
4.17
4.15
4.14
2.45
2.24
1.66
1.65
1.63
1.62
1.43
1.42
1.40
1.39
1.37
1.36
0.96
0.94
0.93
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
f1 (ppm)


172.03
167.11
142.02
141.02
132.38
118.73
77.28
77.02
76.77
64.43
30.73
28.22
24.75
21.67
21.64
19.17
13.74
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

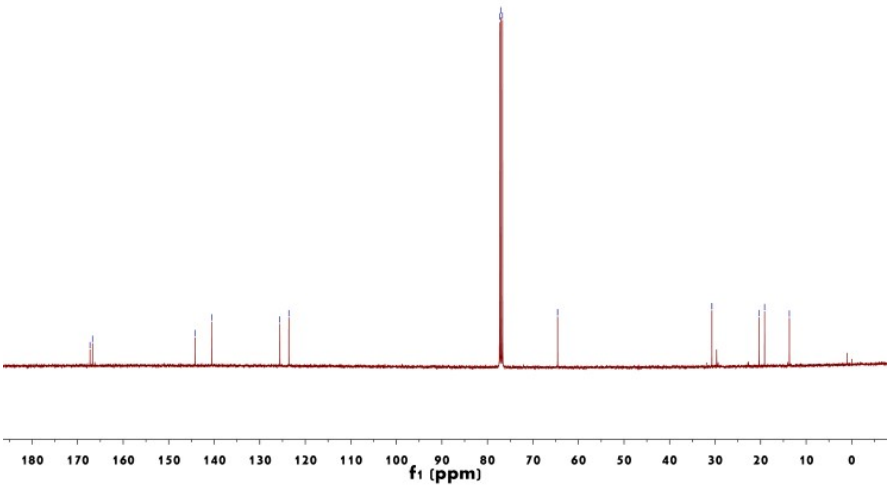


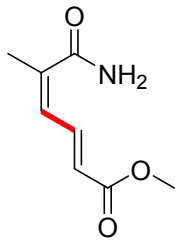
**3n**


8.58
8.54
7.27
6.14
6.10
5.94
5.76
5.60
4.20
4.18
4.16
2.01
1.70
1.69
1.67
1.65
1.63
1.46
1.44
1.43
1.41
1.39
1.37
0.97
0.95
0.93

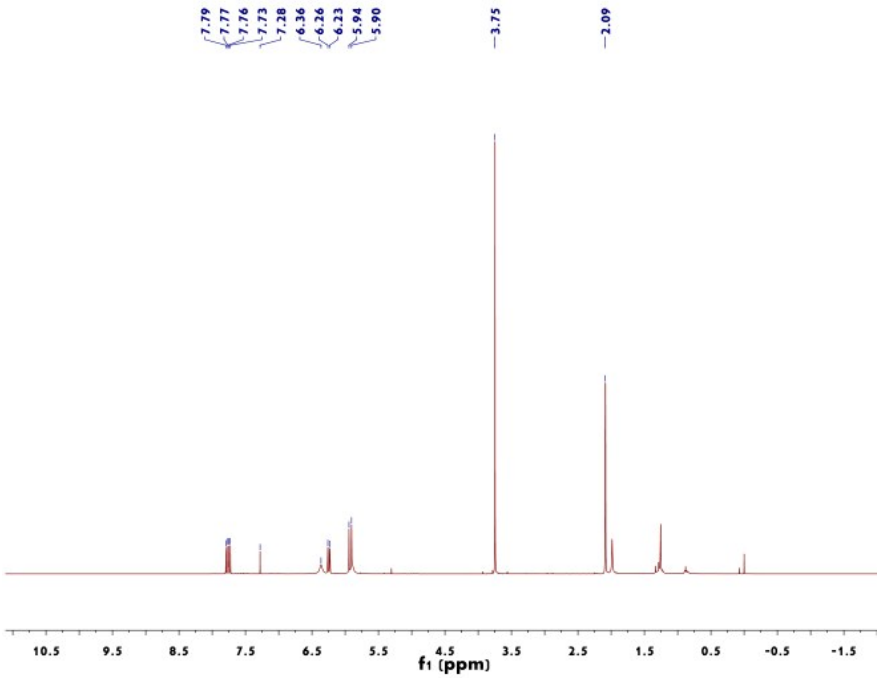

11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

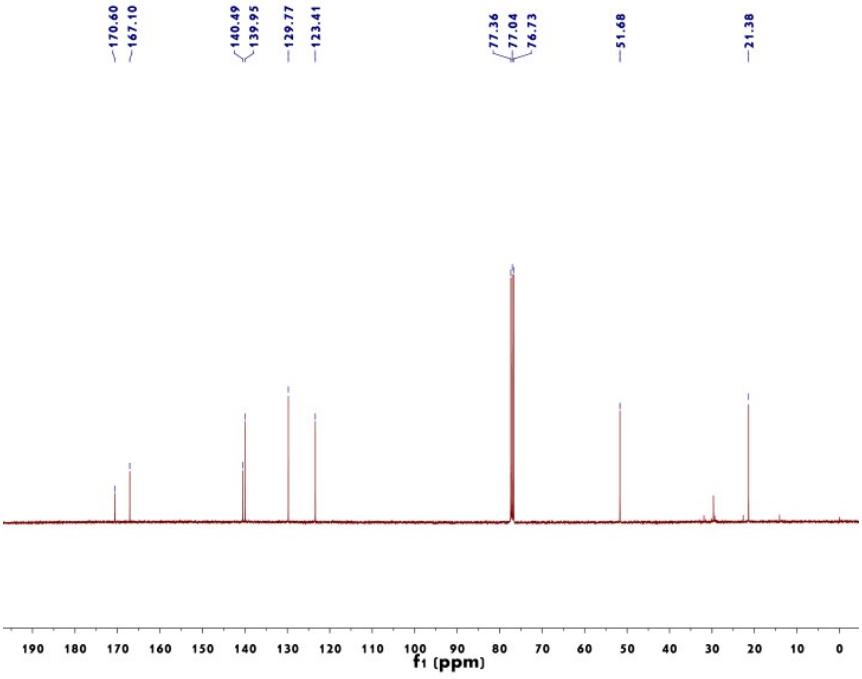

167.28
166.73
144.19
140.49
125.58
123.62
77.33
77.01
76.69
64.59
30.70
20.34
19.13
13.69

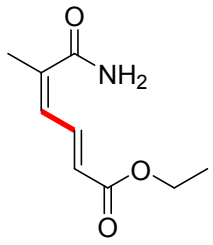

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



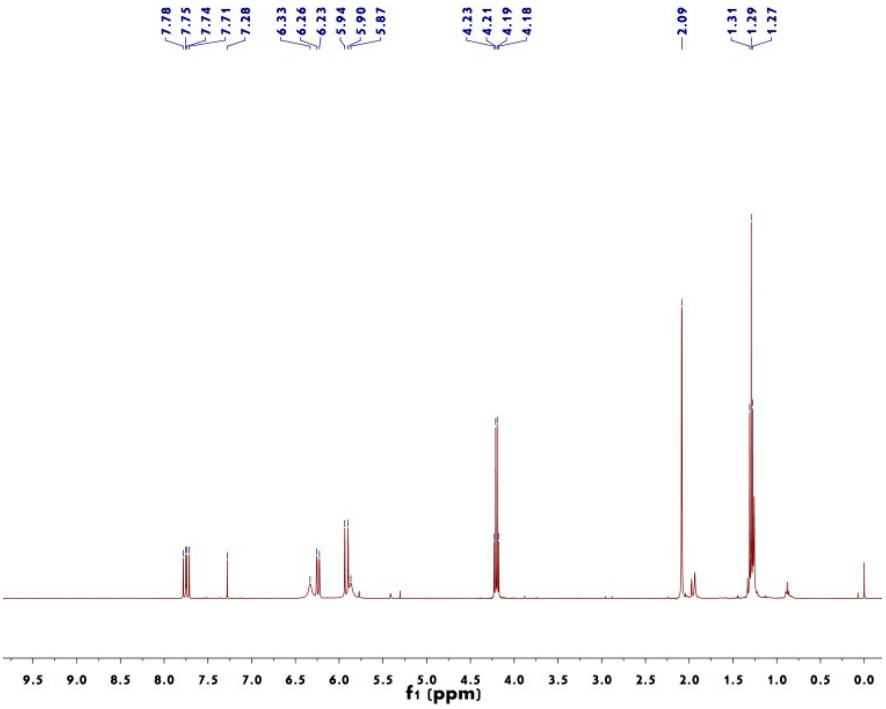
**3o**

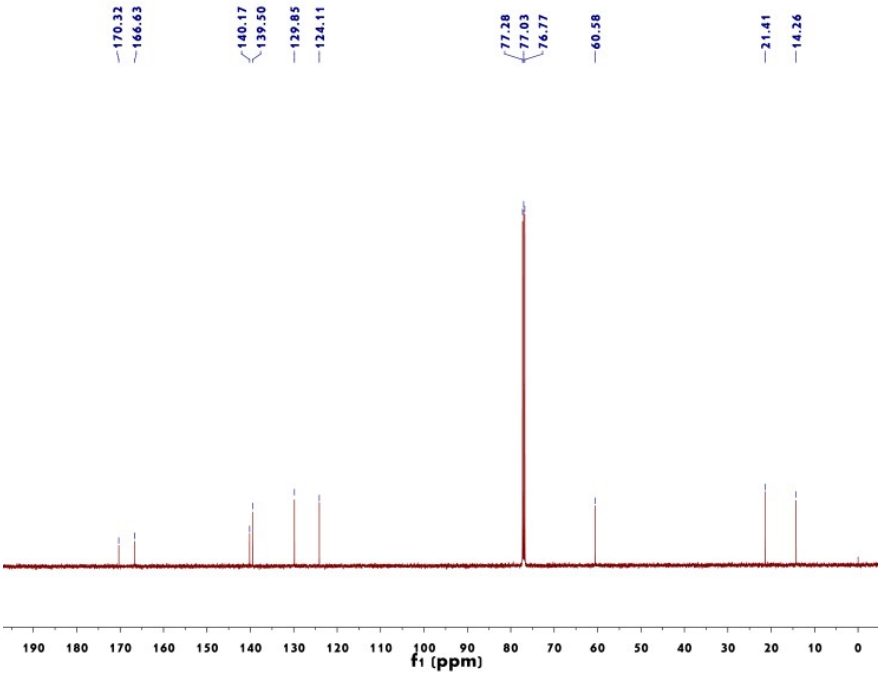

7.79
7.77
7.76
7.73
7.28
6.36
6.26
6.23
5.94
5.90
3.75
2.09
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

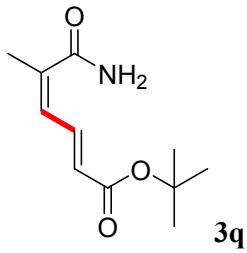

170.60
167.10
140.49
139.95
129.77
123.41
77.36
77.04
76.73
51.68
21.38
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
NH2
O
O

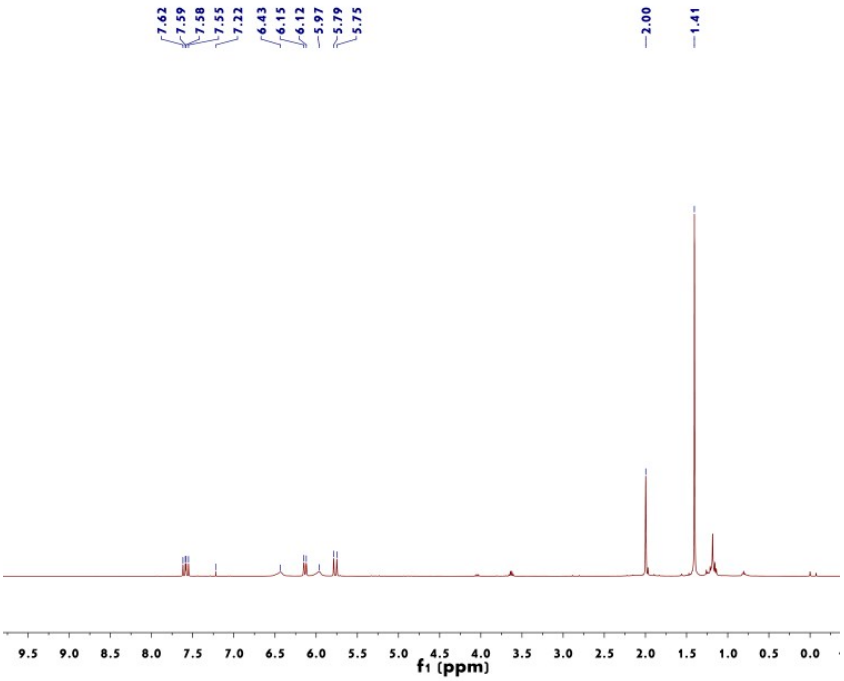
**3p**

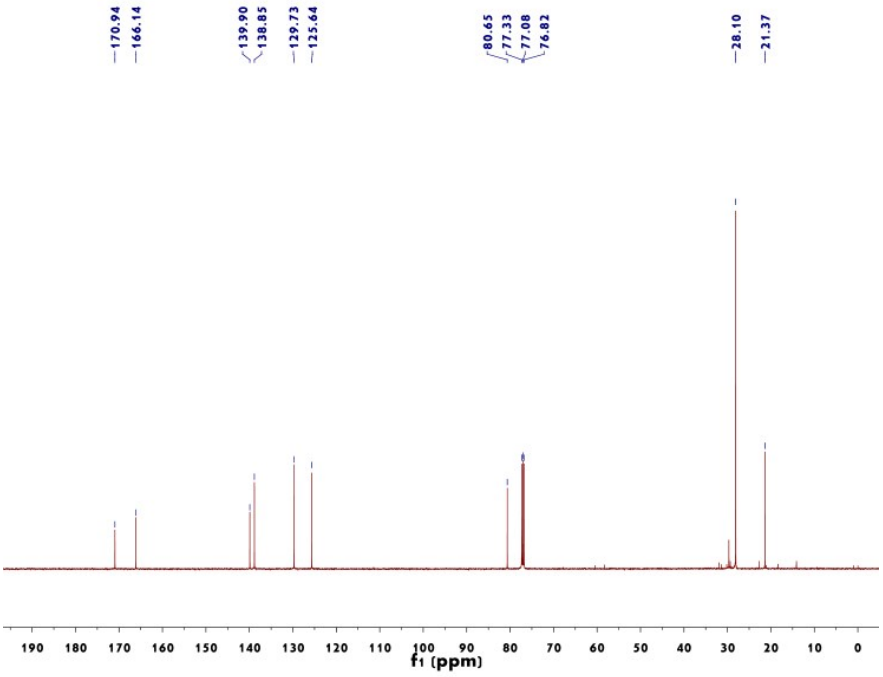

7.78
7.75
7.74
7.71
7.28
6.33
6.26
6.23
5.94
5.90
5.87
4.23
4.21
4.19
4.18
2.09
1.31
1.29
1.27
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

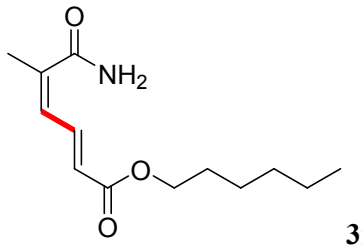

170.32
166.63
140.17
139.50
129.85
124.11
77.28
77.03
76.77
60.58
21.41
14.26
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
NH2
O
O

**3q**

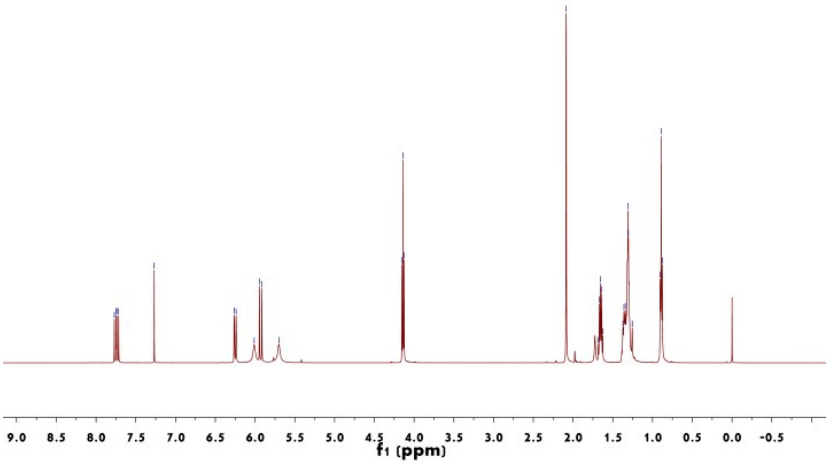

7.62
7.59
7.58
7.55
7.22
6.43
6.15
6.12
5.97
5.79
5.75
2.00
1.41
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


170.94
166.14
139.90
138.85
129.73
125.64
80.65
77.33
77.08
76.82
28.10
21.37
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

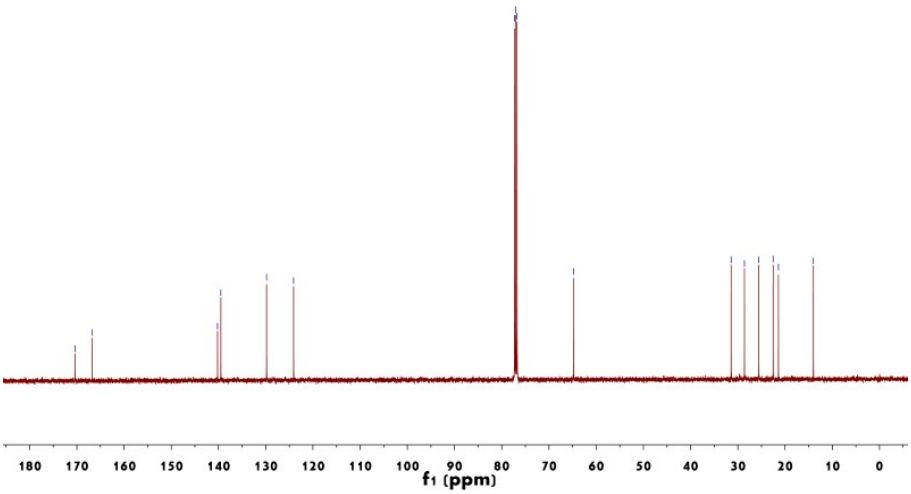


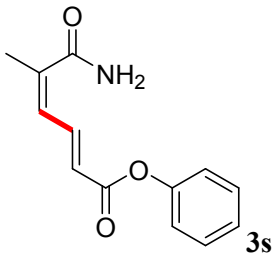
**3r**

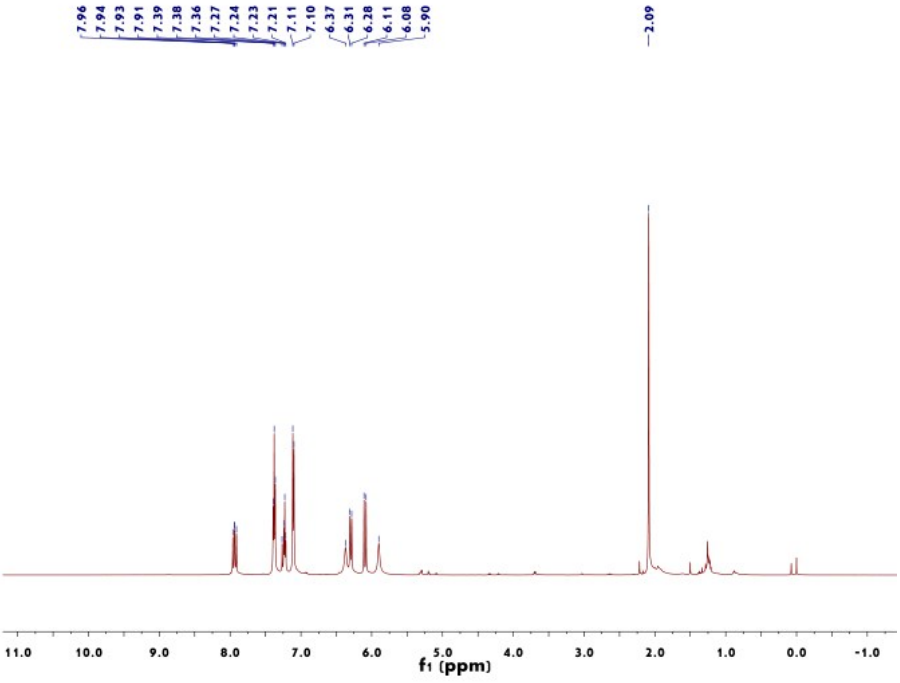

7.77
7.75
7.74
7.72
7.27
6.26
6.24
6.01
5.95
5.91
5.70
4.15
4.14
4.13
2.09
1.68
1.67
1.66
1.64
1.63
1.37
1.36
1.34
1.31
1.30
1.26
0.90
0.89
0.88

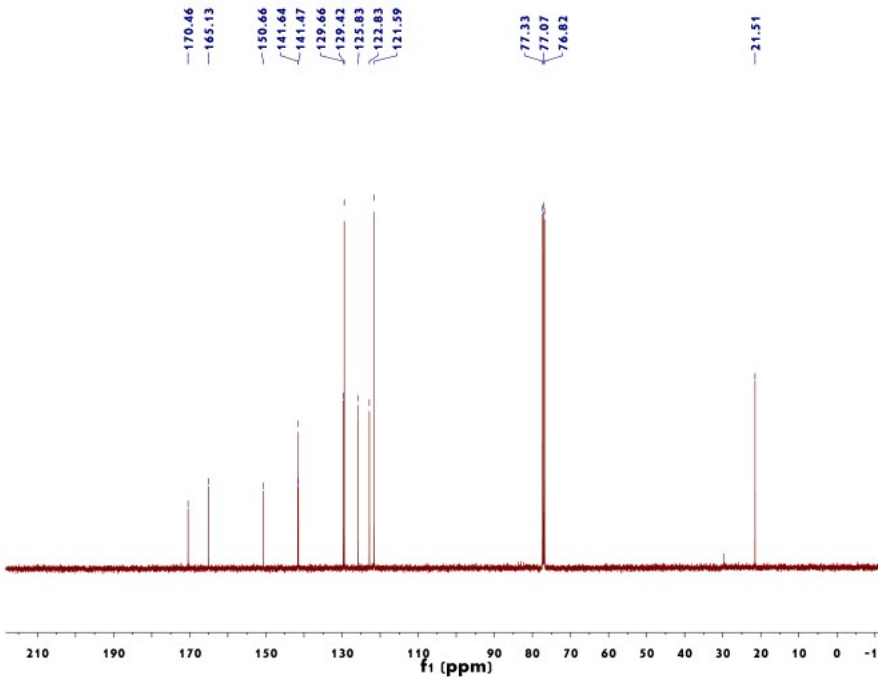

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

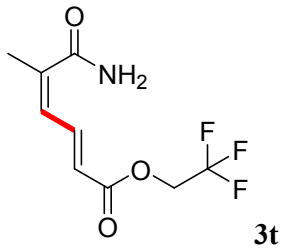

170.36
166.72
140.20
139.50
129.81
124.09
77.29
77.03
76.78
64.79
31.42
28.61
25.57
22.53
21.41
14.00


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
NH2
O
O
3s

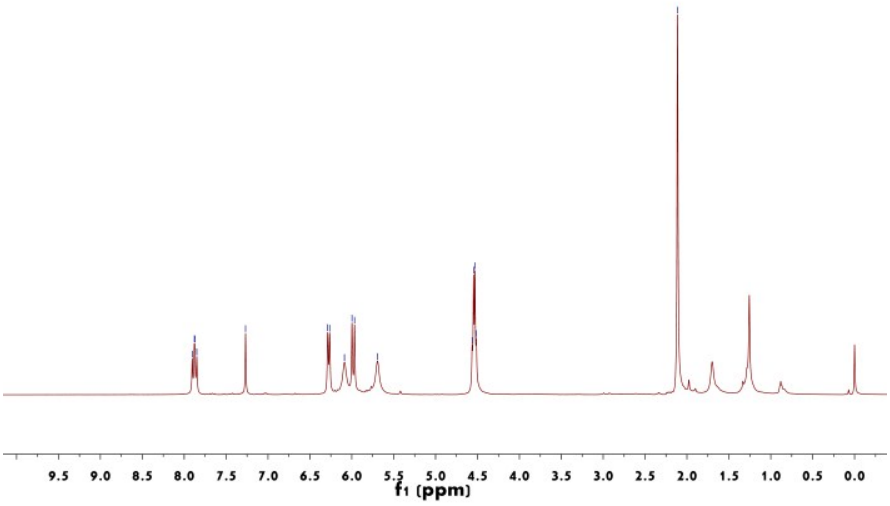

7.96
7.94
7.93
7.91
7.39
7.38
7.36
7.27
7.24
7.23
7.21
7.11
7.10
6.37
6.31
6.28
6.11
6.08
5.90
2.09
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


170.46
165.13
150.66
141.64
141.47
129.66
129.42
125.83
122.83
121.59
77.33
77.07
76.82
21.51
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

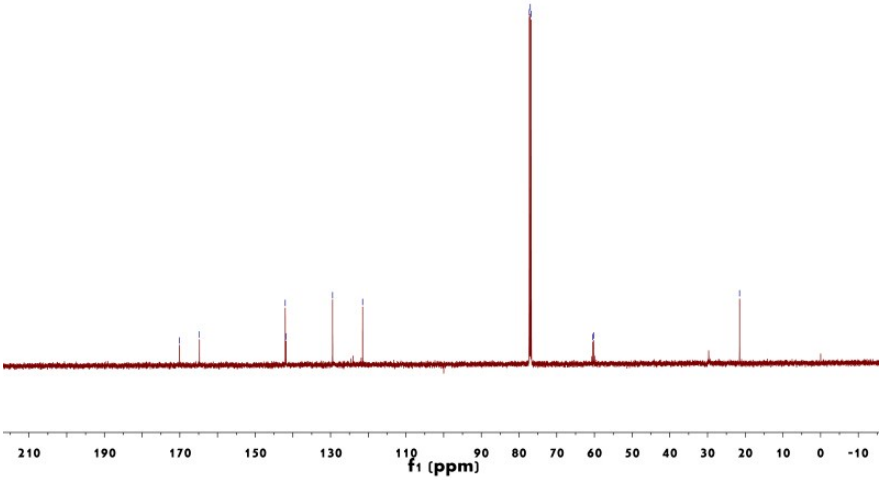


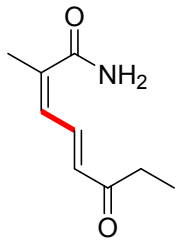
**3t**


7.90
7.88
7.88
7.85
7.27
6.29
6.26
6.09
6.00
5.97
5.69
4.56
4.55
4.53
4.51
2.11


9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

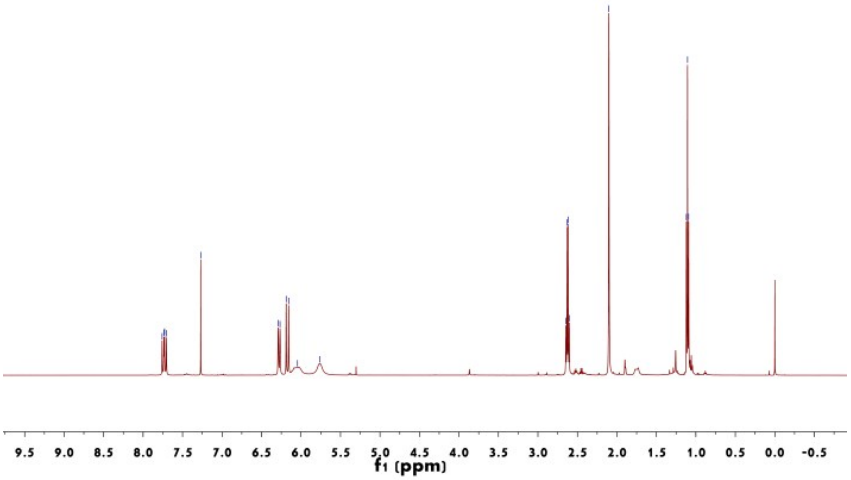

170.08
164.80
142.03
141.82
129.47
121.50
77.28
77.03
76.77
60.47
60.18
21.50


210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

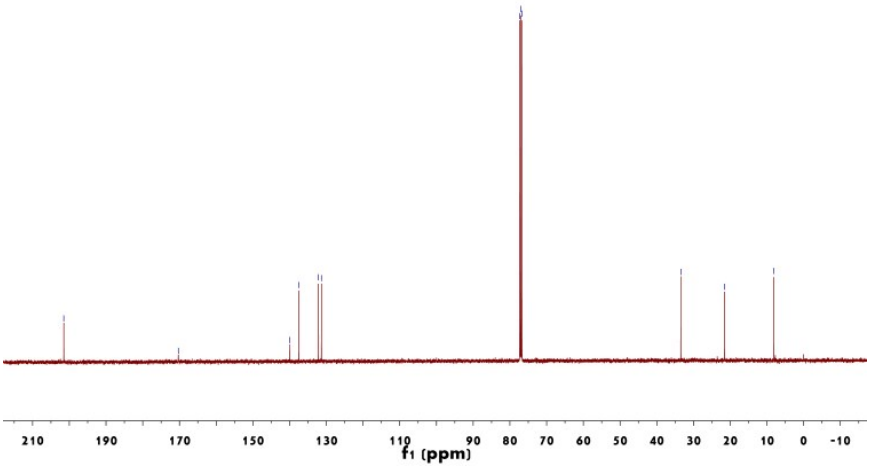


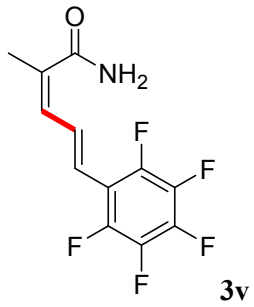
**3u**


7.76
7.74
7.73
7.70
7.27
6.29
6.27
6.19
6.16
6.04
5.76
2.65
2.63
2.62
2.60
2.10
1.12
1.11
1.09


9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

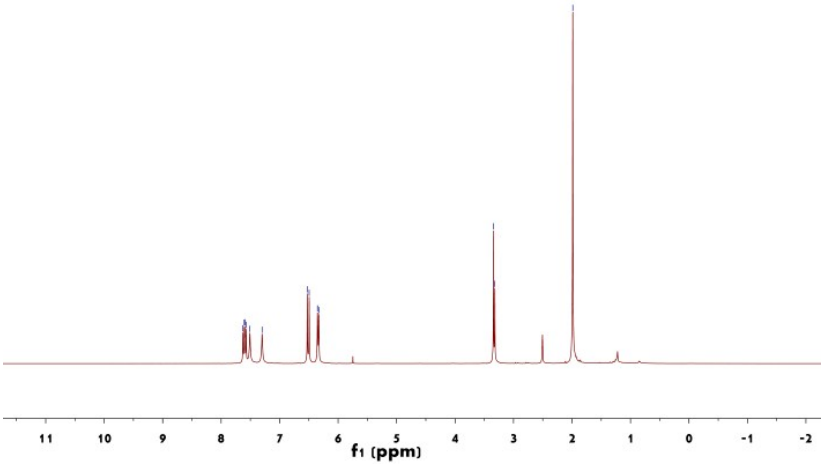

201.50
170.30
140.02
137.52
132.14
131.34
77.29
77.04
76.78
33.46
21.57
8.11


210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

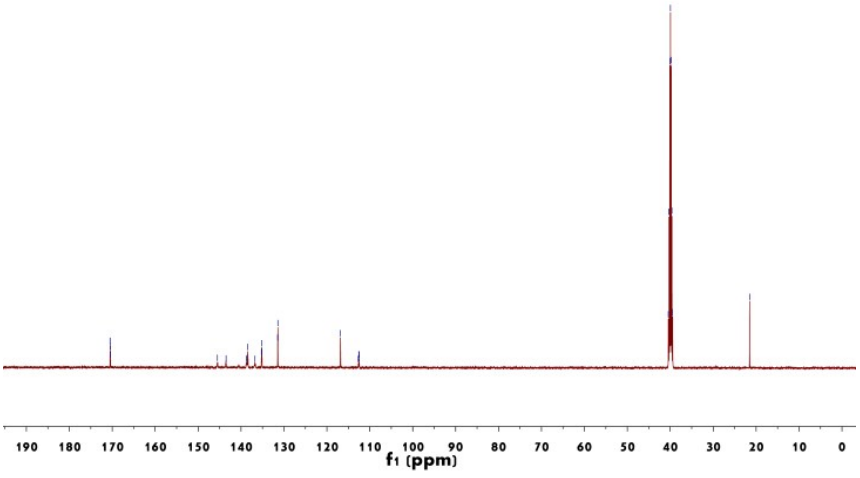

O
NH2
F
F
F
F
F

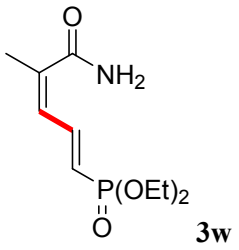
**3v**


7.63
7.60
7.60
7.57
7.51
7.30
6.53
6.49
6.35
6.33
3.34
3.32
1.99

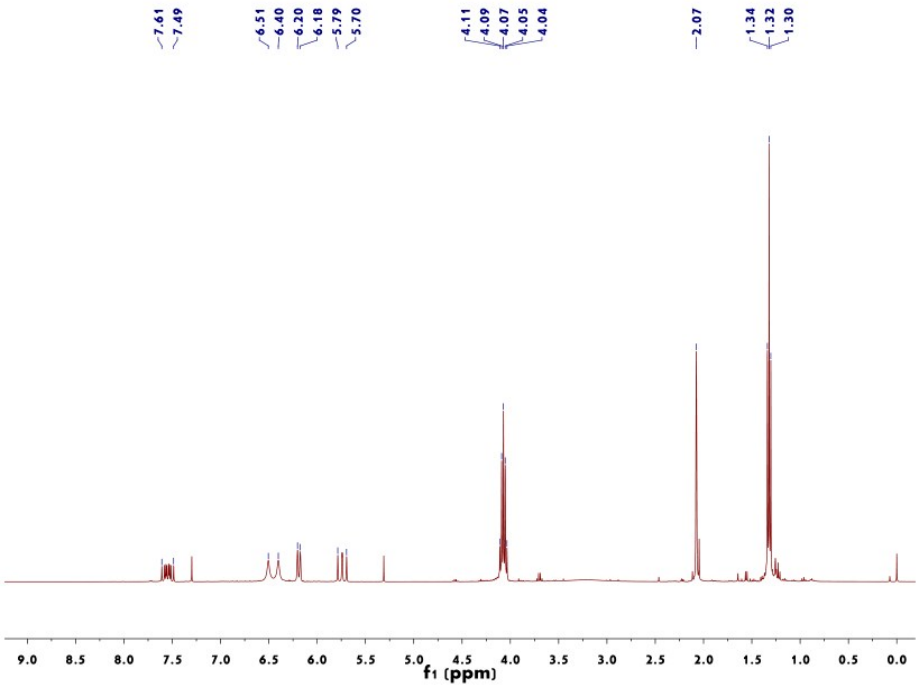

11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

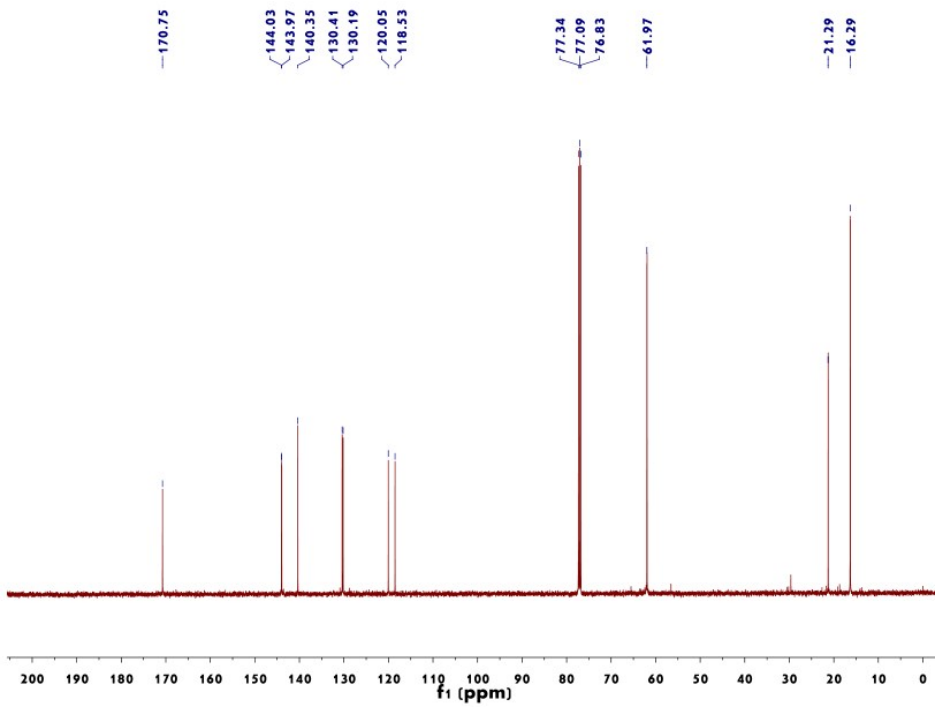

170.50
170.45
170.38
145.49
143.48
138.57
138.45
135.24
135.19
135.13
131.47
131.43
116.83
112.68
112.57
112.54
112.46
40.45
40.28
40.12
39.95
39.78
39.62
39.45
21.53

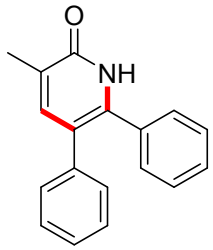

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
NH2
P(OEt)2
O

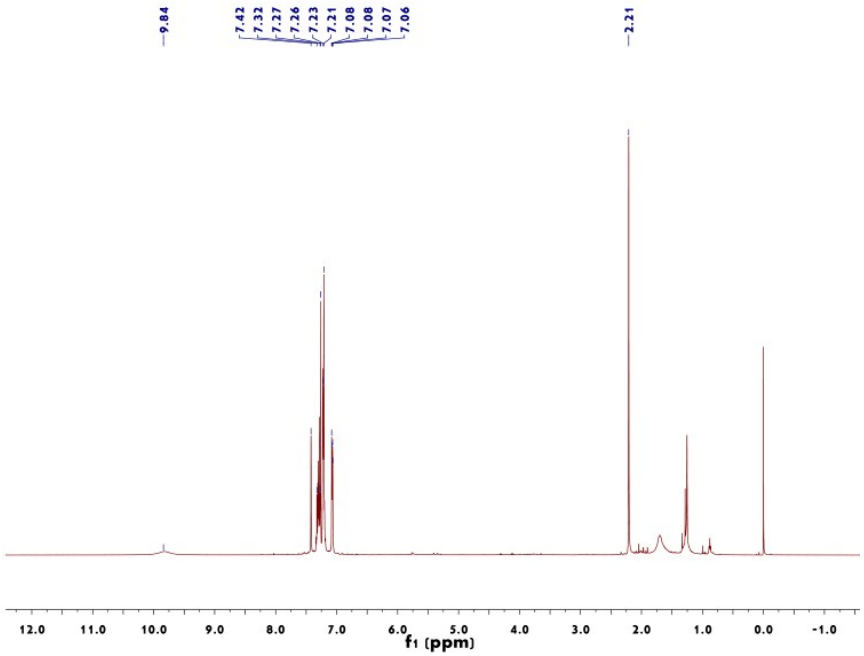
**3w**

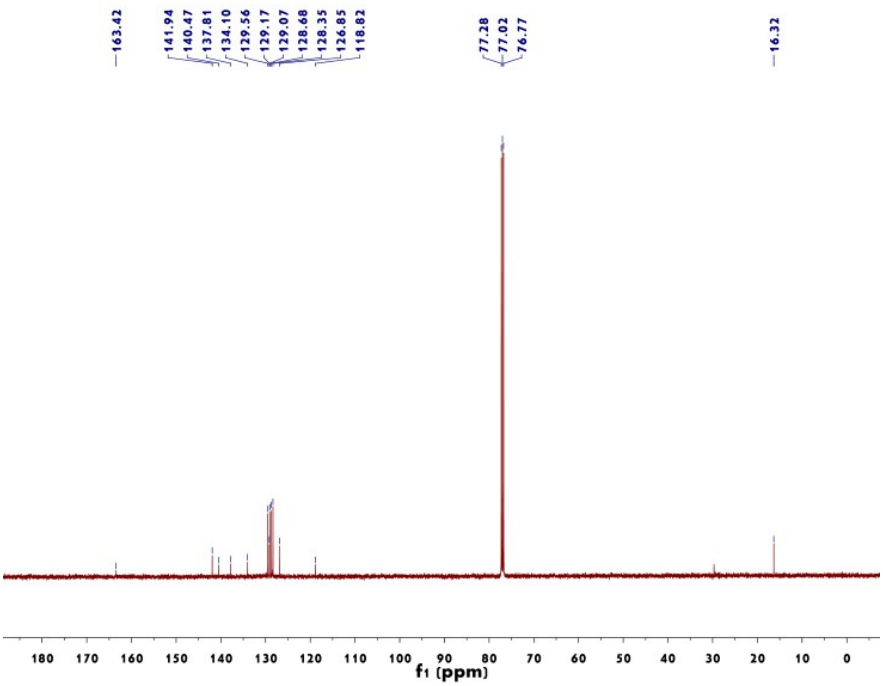

7.61
7.49
6.51
6.40
6.20
6.18
5.79
5.70
4.11
4.09
4.07
4.05
4.04
2.07
1.34
1.32
1.30
f1 (ppm)

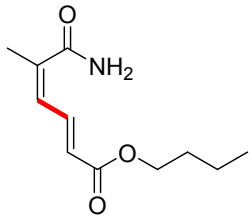

170.75
144.03
143.97
140.35
130.41
130.19
120.05
118.53
77.34
77.09
76.83
61.97
21.29
16.29
f1 (ppm)


O
NH

**5**


9.84
7.42
7.32
7.27
7.26
7.23
7.21
7.08
7.08
7.07
7.06
2.21
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


163.42
141.94
140.47
137.81
134.10
129.56
129.17
129.07
128.68
128.35
126.85
118.82
77.28
77.02
76.77
16.32
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)




**NOESY**