Supporting Information

for

Efficient synthesis of β'-amino-α,β-unsaturated ketones

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1. Characterizations of β-*N*-protected aminoester 10

(*R*)-Methyl 3-(ethoxycarbonylamino)butanoate (**10a**).

Spectral data are identical with those reported [1]: $[\alpha]_D^{25}$ = −37.07 (*c* 1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.03 (br s, 1H), 4.03 (m, 3H), 3.62 (s, 3H), 2.46 (d, *J* = 6.9 Hz, 2H), 1.16 (t, *J* = 6.9 Hz, 3H), 1.15 (d, *J* = 6.6 Hz, 3H)

(*R*)-Methyl 3-(benzyloxycarbonylamino)butanoate (**10b**).

Spectral data are identical with those reported [2]: $[\alpha]_D^{25}$ = +16.9 (*c* 1.4, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.03 (br s, 1H), 4.03 (m, 3H), 3.62 (s, 3H), 2.46 (d, *J* = 6.9 Hz, 2H), 1.16 (t, *J* = 6.9 Hz, 3H), 1.15 (d, *J* = 6.6, 3H).

(*R*)-Methyl 3-(benzyloxycarbonylamino)butanoate (**10c**) and (*S*)-methyl 3-(benzyloxycarbonylamino)butanoate (**10c'**).

R enantiomer: $[\alpha]_D^{25}$ = +41.5 (*c* 1.03, $CHCl_3$), *S* enantiomer: $[\alpha]_D^{25}$ = −40.9 (*c* 1.035, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 4.98 (br s, 1H), 4.02 (m, *2*H), 3.90 (m, 1H), 3.61 (s, 3H), 2.49 (dd, *J* = 15.8, 4.8 Hz, 1H), 2.43 (dd, *J* = 15.8, 5.3 Hz, 1H), 1.48–1.22 (m, 2H), 1.16 (t, *J* = 7.0 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172,0, 156.0, 60.7, 51.6, 47.7, 38.9, 36.6, 19.3, 14.6, 13.8. HRMS-ESI (M + Na), *m/z*: calcd. for $C_{10}H_{19}NO_4Na$ 240.1212, found 240.1216.

(*R*)-Methyl 3-(ethoxycarbonylamino)undecanoate (**10d**).

$[\alpha]_D^{25}$ = +29.2 (*c* 1.05, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.07 (br s, 1H), 4.22–4.03 (m, 2H), 3.98 (m, 1H), 3.69 (s, 3H), 2.57 (dd, *J* = 15.1, 4.6 Hz, 1H), 2.51 (dd, *J* = 15.1, 5.1, Hz 1H), 1.55–1.45 (m, 2H), 1.41–1.10 (m, 15H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 156.1, 60.7, 51.5, 48.0, 38.9, 34.4, 31.8, 29.4, 29.3, 29.2, 26.1, 22.6, 14.6, 14.1; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{15}H_{29}NO_4Na$ 310.1994, found 310.1996.

(*S*)-Methyl 3-(ethoxycarbonylamino)-3-phenylpropanoate (**10e**).

$[\alpha]_D^{25}$ = −9.7 (*c* 0.99, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.25 (m, 5H), 5.75 (br s, 1H), 5.17 (m, 1H), 4.11 (q, *J* = 7.0 Hz, 2H), 3.62 (s, 3H), 2.91 (dd, *J* = 15.5, 6,0 Hz, 1H), 2.84 (dd, *J* = 15.5, 5.9 Hz, 1H), 1.23 (t, *J* = 7.0, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 155.8, 140.9, 128.6, 127.6, 126.2, 61.0, 51.8, 51.7, 40.5, 14.6; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{13}H_{17}NO_4Na$ 274.1055, found 274.1069.

(*S*)-Methyl 3-(*tert*-butoxycarbonylamino)-3-phenylpropanoate (**10f**).

Spectral data are identical with those reported [3]: $[\alpha]_D^{25}$ = −37.4 (*c* 1.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.25 (m, 5H), 5.60 (br s, 1H), 3.62 (s, 3H), 2.84 (m, 2H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 155.0, 128.6, 127.5, 126.0, 111.7, 107.3, 100.3, 79.6, 51.6, 40.6, 28.4

(*S*)-Methyl 3-(benzyloxycarbonylamino)-3-phenylpropanoate (**10g**).

Spectral data are identical with those reported [4]: $[\alpha]_D^{25}$ **=** −16.1 (*c* 0.97, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (m, 10 H), 5.73 (br s, 1H), 5.09 (m, 1H), 5.01 (d, *J* = 12.3 Hz, 1H), 4.97 (d, *J* = 12.3 Hz, 1H), 3.50 (s, 3H), 2.81 (dd, *J* = 15.3, 5.0 Hz, 1H), 2.74 (dd, *J* = 15.3, 5.7 Hz, 1H).

2. Characterizations of phosphonates 13

(*R*)-Ethyl [5-(diethoxyphosphoryl)-4-oxopentan-2-yl]carbamate (**13a**).

$[\alpha]_D^{25}$ = +33.6 (*c* 1.17, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.03 (br s, 1H), 4.16–3.94 (m, 7H), 3.08 (dd, *J* = 23.0, 14.0 Hz, 1H), 2.99 (dd, *J* = 22.6, 14.0 Hz, 1H), 2.84 (dd, *J* = 17.1, 6.0 Hz, 1H), 2.71 (dd, *J* = 17.1, 5.7 Hz, 1H), 1.33–1.21 (m, 6H), 1.15-1.20 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.6, 155.8, 62.6 (d, *J* = 6.6 Hz), 62.5 (d, *J* = 6.5 Hz), 60.5, 49.6, 43.5, 42.9 (d, *J* = 127.4 Hz), 20.7, 16.2, 16.1, 14.6; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{12}H_{24}NO_6PNa$ 332.1239, found 332.1239.

(*R*)-Benzyl [5-(diethoxyphosphoryl)-4-oxopentan-2-yl]carbamate (**13b**).

$[\alpha]_D^{25}$ **=** −26.4 (*c* 0.85, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.22 (m, 5H), 5.26 (br s, 1H), 5.00 (s, 2H), 4.03 (m, 5H), 3.05 (dd, *J* = 23.2, 13.6 Hz, 1H), 2.96 (dd, *J* = 22.7, 13.6 Hz, 1H), 2.85 (dd, *J* = 17.3, 5.8 Hz, 1H), 2.70 (dd, *J* = 17.3, 5.6 Hz, 1H), 1.26 (t, *J* = 6.2 Hz, 6H), 1.16 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.7, 155.6, 136.6, 128.5, 128.0, 66.5, 62.7 (d, *J* = 6.6 Hz), 62.6 (d, *J* = 6.8 Hz), 49.5, 43.6, 43.3 (d, *J* = 129.5 Hz), 20.4, 16.3, 16.2; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{17}H_{26}NO_6PNa$ 394.1395, found 394.1395.

(*R and S*)-Ethyl [1-(diethoxyphosphoryl)-2-oxoheptan-4-yl]carbamate (**13c** and **13c'**).

R enantiomer: $[\alpha]_D^{25}$ = +43.09 (*c* 1.03, $CHCl_3$), *S* enantiomer: $[\alpha]_D^{25}$ **=** −42.55 (*c* 1.075, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.00 (d, *J* = 9.0 Hz, 1H), 4.15–3.97 (m, 6H), 3.90 (m, 1H), 3.09 (dd, *J* = 22.9, 13.5 Hz, 1H), 2.96 (dd, *J* = 22.5, 13.5 Hz, 1H), 2.80 (dd, *J* = 17.2, 5.9 Hz, 1H), 2.74 (dd, *J* = 17.2, 5.3 Hz, 1H), 1.48–1.39 (m, 2H), 1.37–1.29 (m, 2H), 1.27 (dt, *J* = 7.2, 2.0 Hz, 6H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.84 (t, *J* = 7.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.9, 156.2, 62.7 (d, *J* = 6.5 Hz), 62.6 (d, *J* = 6.6 Hz), 60.6, 48.2, 47.5, 42.9 (d, *J* = 126.6 Hz), 36.7, 19.3, 16.3, 16.2, 14.6, 13.8; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{14}H_{28}NO_6PNa$ 360.552, found 360.1562.

(*R*)-Ethyl [1-(diethoxyphosphoryl)-2-oxododecan-4-yl]carbamate (**13d**).

$[\alpha]_D^{25}$ = +30.06 (*c* 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.02 (brs, 1H), 4.17–3.99 (m, 6H), 3.95 (m, 1H), 3.07 (dd, *J* = 23.1, 13.5 Hz, 1H), 2.98 (dd, *J* = 22.7, 13.5 Hz, 1H), 2.83 (dd, *J* = 17.4, 5.8 Hz, 1H), 2.75 (dd, *J* = 17.4, 5.2 Hz, 1H), 1.51–1.41 (m, 2H), 1.39–1.23 (m, 12H), 1.21 (t, *J* = 7.2 Hz, 6H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.8, 156.1, 62.9 (d, *J* = 6.6 Hz), 62.8

(d, *J* = 6.7 Hz), 60.7, 48.2, 48.1, 42.7 (d, *J* = 127.1 Hz), 34.4, 31.8, 29.4, 29.3, 29.2, 26.1, 22.6, 16.4, 16.3, 14.6, 14.0; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{19}H_{38}NO_6PNa$ 430.2334 found 430.2349.

(*S*)-Ethyl [4-(diethoxyphosphoryl)-3-oxo-1-phenylbutyl]carbamate (**13e**).

$[\alpha]_D^{25}$ = +1.65 (*c* 1.09, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.21 (m, 4H), 7.16 (m, 1H), 5.72 (s, 1H), 5.09 (dd, *J* = 12.7, 6.7 Hz, 1H), 4.11–3.94 (m, 6H), 3.26 (dd, *J* = 16.9, 7.3 Hz, 1H), 3.04 (dd, *J* = 23.3, 13.1 Hz, 1H), 2.97 (dd, *J* = 16.9, 12.7 Hz, 1H), 2.93 (dd, *J* = 22.9, 13.1 Hz, 1H), 1.22 (td, *J* = 7.1, 1.9 Hz, 6H), 1.13 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.9, 155.9, 141.4, 128.6, 127.4, 126.3, 62.8 (d, *J* = 6.2 Hz), 62.6 (d, *J* = 6.5 Hz), 60.8, 51.1, 49.4, 43.3 (d, *J* = 125.5 Hz), 16.2 (d, *J* = 6.1 Hz), 14.6; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{17}H_{26}NO_6PNa$ 394.1395, found 394.1414.

(*S*)-*tert*-Butyl [4-(diethoxyphosphoryl)-3-oxo-1-phenylbutyl]carbamate (**13f**).

$[\alpha]_D^{25}$ = +3.12 (*c* 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.12 (m, 4H), 7.16 (m, 1H), 5.44 (br s, 1H), 5.03 (br s, 1H), 4.04–3.95 (m, 4H), 3.20 (dd, *J* = 16.8, 7.4 Hz, 1H), 3.01 (dd, *J* = 23.1, 12.9 Hz, 1H), 2.99 (m, 1H), 2.92 (dd, *J* = 22.7, 12.9 Hz, 1H), 1.32 (s, 9H), 1.21 (td, *J* = 7.1, 1.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 155.1, 133.6, 130.9, 128.5, 126.3, 66.7, 62.8 (d, *J* = 6.3 Hz), 62.6 (d, *J* = 6.2 Hz), 50.9, 49.6, 41.0 (d, *J* = 127.6 Hz), 16.3 (d, *J* = 5.8 Hz), 16.2 (d, *J* = 5.6 Hz); HRMS-ESI (M + Na), *m/z*: calcd. for $C_{19}H_{30}NO_6PNa$ 422.1708, found 422.1722.

(*S*)-Benzyl [4-(diethoxyphosphoryl)-3-oxo-1-phenylbutyl]carbamate (**13g**).

$[\alpha]_D^{25}$ = +8.66 (*c* 1.55, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.20 (m, 8H), 7.16 (m, 2H), 5.88 (br s, 1H), 5.11 (dd, *J* = 13.1, 7.4 Hz, 1H), 5.04 (d, *J* = 12.3 Hz, 1H), 4.96 (d, *J* = 12.3 Hz, 1H), 4.02–3.89 (m, 4H), 3.27 (dd, *J* = 16.6, 7.4 Hz, 1H), 3.02 (dd, *J* = 23.3, 13.1 Hz, 1H), 2.97 (m, 1H), 2.90 (dd, *J* = 22.6, 13.1 Hz, 1H), 1.21 (t, *J* = 7.0 Hz, 3H), 1.15 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.0, 155.6, 141.3, 136.5, 128.6, 128.4, 128.0, 127.5, 126.3, 66.7, 62.9 (d, *J* = 5.3 Hz), 62.6 (d, *J* = 6.4 Hz), 51.3, 49.3, 43.5 (d, *J* = 123.8 Hz), 16.3 (d, *J* = 4.1 Hz), 16.2 (d, *J* = 3.7 Hz); HRMS-ESI (M + Na), *m/z*: calcd. for $C_{22}H_{28}NO_6PNa$ 456.1552, found 456.1559.

3. Characterizations of β-*N*-protected ketone 15

(*R*,*E*)-Ethyl [4-oxo-6-phenylhex-5-en-2-yl]carbamate (**15a**).

$[\alpha]_D^{25}$ = +9.5 (*c* 1.21, $CHCl_3$). White solid: Mp 74 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 16.7 Hz, 1H), 7.47 (dd, *J* = 7.8, 3.0 Hz, 1H, 2H), 7.33–7.30 (m, 3H), 6.65 (d, *J* = 16.7 Hz, 1H), 5.14 (s, 1H), 4.14–4.06 (m, 1H), 4.02 (q, *J* = 6.9 Hz, 2H), 2.95 (dd, *J* = 15.9, 4.2 Hz, 1H), 2.71 (dd, *J* = 15.9, 6.5 Hz, 1H), 1.19 (d, *J* = 6.8 Hz, 3H), 1.14 (t, *J* = 6.9 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 155.9, 143.4, 134.3,

130.6, 128.9, 128.4, 126.3, 60.6, 46.3, 44.1, 20.5, 14.6 ; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{15}H_{19}NO_3Na$ 284.1263, found 284.1275.

(*R*,*E*)-Ethyl [6-(2-nitrophenyl)-4-oxohex-5-en-2-yl]carbamate (**15b**).

$[\alpha]_D^{25}$ = +21.94 (*c* 1.015, $CHCl_3$). Yellow solid: Mp 90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 16.1 Hz, 1H), 7.71–7.59 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 16.1 Hz, 1H), 5.08 (br s, 1H), 4.22–4.08 (m, 3H), 3.04 (dd, *J* = 16.3, 4.7 Hz, 1H), 2.85 (dd, *J* = 16.3, 6.3 Hz, 1H), 1.28 (d, *J* = 6.7 Hz, 3H), 1.22 (t, *J* = 7.0 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3, 155.8, 148.3, 138.7, 133.7, 131.1, 130.8, 130.5, 129.1, 125.1, 60.7, 46.0, 43.9, 20.6, 14.6 ; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{15}H_{18}N_2O_5Na$ 329.1113, found 329.1117.

(*R*,*E*)-Ethyl [6-(3-nitrophenyl)-4-oxohex-5-en-2-yl]carbamate (**15c**).

$[\alpha]_D^{25}$ = +5.92 (*c* 0.995, $CHCl_3$). Yellow solid: Mp 97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.27 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 16.2 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 16.2 Hz, 1H), 5.08 (br s, 1H), 4.27–4.04 (m, 3H), 3.07 (dd, *J* = 16.1, 3.3 Hz, 1H), 2.84 (dd, *J* = 16.1, 6.6 Hz, 1H), 1.31 (d, *J* = 6.7 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3, 155.6, 148.5, 140.2, 136.0, 133.9, 130.0, 128.6, 124.8, 122.6, 60.8, 47.0, 44.0, 20.5, 14.6 ; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{15}H_{18}N_2O_5Na$ 329.1113, found 329.1125.

(*R*,*E*)-[Ethyl-6-(4-nitrophenyl)-4-oxohex-5-en-2-yl]carbamate (**15d**).

$[\alpha]_D^{25}$ = +16.42 (*c* 0.52, $CHCl_3$). Yellow solid: Mp 98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 16.2 Hz, 1H), 6.75 (d, *J* = 16.2 Hz, 1H), 4.97 (s, 1H), 4.10 (m, 1H), 4.03 (q, *J* = 7.0 Hz, 2H), 2.99 (dd, *J* = 15.6, 3.5 Hz, 1H), 2.74 (dd, *J* = 15.6, 6.5 Hz, 1H), 1.21 (d, *J* = 6.8 Hz, 1H), 1.15 (t, *J* = 7.0 Hz, 1H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 155.9, 140.5, 140.1, 128.5, 128.9, 124.8, 124.2, 60.8, 47.1, 44.0, 20.5, 14.6 ; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{15}H_{18}N_2O_5Na$ 329.1113, found 329.1119.

(*R*,*E*)-Ethyl [6-(4-methoxyphenyl)-4-oxohex-5-en-2-yl]carbamate (**15e**).

$[\alpha]_D^{25}$ = +6.1 (*c* 1.055, $CHCl_3$). White solid: Mp 108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 16.1 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 2H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.60 (d, *J* = 16.1 Hz, 1H), 5.21 (br s, 1H), 4.22–4.07 (m, 3H), 3.83 (s, 3H), 2.99 (dd, *J* = 15.8, 4.4 Hz, 1H), 2.76 (dd, *J* = 15.8, 5.8 Hz, 1H), 1.25 (d, *J* = 6.8 Hz, 1H), 1.21 (t, *J* = 7.0 Hz, 1H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 161.9, 155.9, 143.2, 130.3, 127.1, 124.3, 114.6, 60.8, 55.5, 46.2, 44.4, 20.6, 14.7 ; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{16}H_{21}NO_4Na$ 314.1368, found 314.1371.

(*R*,*E*)-Ethyl [6-(2-bromophenyl)-4-oxohex-5-en-2-yl]carbamate (**15f**).

$[\alpha]_D^{25}$ = +18.2 (*c* 1.175, $CHCl_3$). White solid : Mp 65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 16.2 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 1H), 7.17 (td, *J* = 7.8, 1.5 Hz, 1H), 6.57 (d, *J* = 16.2 Hz, 1H), 5.08 (br s, 1H),

4.15–3.88 (m, 3H), 2.96 (dd, *J* = 16.4, 4.8 Hz, 1H), 2.79 (dd, *J* = 16.3, 6.2 Hz, 1H), 1.22 (d, *J* = 6.8 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 158.1, 145.0, 141.6, 133.5, 131.5, 129.0, 127.8, 60.7, 46.5, 44.0, 20.6, 14.6 ; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{15}H_{18}BrNO_3Na$ 362.0368, found 362.0371.

(*R*,*E*)-Ethyl [6-(4-bromophenyl)-4-oxo-hex-5-en-2-yl]carbamate (**15g**).

$[\alpha]_D^{25}$ = +4.0 (*c* 1.03, $CHCl_3$). White solid : Mp 90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 16.2 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 6.70 (d, *J* = 16.2 Hz, 1H), 5.10 (s, 1H, NH), 4.14 (m, 1H), 4.09 (q, *J* = 7.1 Hz, 1H), 3.01 (dd, *J* = 15.5, 3.4 Hz, 1H), 2.77 (dd, *J* = 15.5, 6.6 Hz, 1H), 1.27 (d, *J* = 6.8 Hz, 1H), 1.23 (t, *J* = 7.1, 1H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 156.0, 141.9, 133.2, 132.2, 129.7, 126.7, 124.9, 60.7, 50.0, 46.5, 44.1, 20.5, 14.6 ; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{15}H_{18}BrNO_3Na$ 362.0368, found 362.0380.

(*R*,*E*)-Ethyl [6-(2-chloro-5-nitrophenyl)-4-oxo-hex-5-en-2-yl]carbamate (**15h**).

$[\alpha]_D^{25}$ = +15.06 (*c* 1.06, $CHCl_3$). Yellow solid : Mp 149 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.6 Hz, 1H), 7.97 (d, *J* = 16.0 Hz, 1H), 7.62 (s, 1H), 7.51 (d, *J* = 8.6, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 5.09 (br s, 1H), 4.23–4.03 (m, 3H), 3.05 (dd, *J* = 16.5, 5.2 Hz, 1H), 2.84 (dd, *J* = 16.5, 6.5 Hz, 1H), 1.28 (d, *J* = 6.9 Hz, 3H), 1.21 (t, *J* = 7.5 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 158.9, 146.5, 140.4, 137.7, 132.9, 131.9, 130.5, 129.3, 126.7, 60.9, 46.5, 44.1, 20.7, 14.7 ; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{15}H_{17}ClN_2O_5Na$ 363.0724, found 363.0717.

(*R*,*E*)-Ethyl [4-oxo-6-(pyridin-3-yl)-hex-5-en-2-yl]carbamate (**15i**).

$[\alpha]_D^{25}$ = +10.25 (*c* 0.865, $CHCl_3$). White solid: Mp 90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 1.6 Hz, 1H), 8.56 (d, *J* = 4.7 Hz, 1H), 7.82 (dt, *J* = 7.9,1.6, 1H), 7.51 (d, *J* = 16.3 Hz, 1H), 7.30 (dd, *J* = 7.9, 4.9 Hz, 1H), 6.72 (d, *J* = 16.3 Hz, 1H), 5.03 (br s, 1H), 4.20–3.70 (m, 3H), 2.98 (dd, *J* = 16.1, 4.0 Hz, 1H), 2.74 (dd, *J* = 16.1, 6.7 Hz, 1H), 1.21 (d, *J* = 6.9 Hz, 3H), 1.16 (t, *J* = 7.5 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 155.9, 151.1, 149.9, 139.4, 134.5, 130.2, 128.0, 123.8, 60.7, 46.7, 44.1, 20.5, 14.6 ; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{14}H_{18}N_2O_3Na$ 285.1215, found 285.1210.

(*R*,2*E*,4*E*)-Ethyl 8-(ethoxycarbonylamino)-6-oxo-nona-2,4-dienoate (**15j**).

$[\alpha]_D^{25}$ = +17.6 (*c* 0.695, $CHCl_3$). Viscous yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 14.9, 11.4 Hz, 1H), 7.14 (dd, *J* = 15.1, 11.4 Hz, 1H), 6.35 (d, *J* = 15.0 Hz, 1H), 6.19 (d, *J* = 15.0 Hz, 1H), 4.97 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 4.05–4.00 (m, 3H), 2.89 (d, *J* = 12.5 Hz, 1H), 2.67 (dd, *J* = 16.3, 6.5 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.18 (d, *J* = 6.8 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 165.7, 155.8, 141.1, 139.1, 135.3, 129.5, 60.9, 60.7, 46.7, 43.9, 20.4, 14.6, 14.2 ; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{14}H_{21}NO_5Na$ 306.1317, found 306.1331.

(*R*)-Ethyl 6-(ethoxycarbonylamino)-4-oxohept-2-enoate (**15k**).

Mixture of *Z* and *E* isomers (Z/E : 60/40): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (d, *J* = 16.0 Hz, 1H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.43 (d, *J* = 12.0 Hz, 1H), 5.97 (d, *J* = 12.0 Hz, 1H), 5.18 (s, 1H), 5.12 (s, 1H), 4.25–4.11 (m, 6H), 2.91 (d, *J* = 15.0 Hz, 1H), 2.81 (dd, *J* = 16.9, 5.7 Hz, 1H), 2.78–2.67 (m, 1H), 1.27–1.13 (m, 12H) ; ^{13}C NMR (101 MHz, $CDCl_3$) (mixture of Z and E) δ 201.1, 197.3, 164.4, 164.2, 155.7, 155.0, 140.6, 138.3, 130.4, 124.0, 60.5, 60.3, 59.8, 59.7, 47.3, 46.0, 42.7, 42.4, 19.6, 19.4, 13.6, 13.1, 13.0 ; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{12}H_{19}NO_5Na$ 280.1161, found 280.1163.

(*R*,*E*)-Ethyl [4-oxo-non-5-en-2-yl]carbamate (**15l**).

$[\alpha]_D^{25}$ = +12.13 (*c* 1.025, $CHCl_3$). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (dt, *J* = 15.9, 7.2 Hz, 1H), 6.07 (dd, *J* = 15.9, 1.5 Hz, 1H), 5.13 (br s, 1H), 4.11–4.02 (m, 3H), 2.87 (dd, *J* = 16.1, 4.4 Hz, 1H), 2.65 (dd, *J* = 16.1, 6.4 Hz, 1H), 2.19 (td, *J* = 7.2, 1.5 Hz, 2H), 1.49 (qd, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 3H), 0.92 (t, *J* = 7.1 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 156.0, 148.5, 130.9, 60.7, 45.5, 44.2, 34.6, 21.4, 20.6, 14.7, 13.8 ; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{12}H_{21}NO_3Na$ 250.1419, found 250.1421.

(*R*,*E*)-Ethyl [4-oxo-tetradec-5-en-2-yl]carbamate (**15m**).

$[\alpha]_D^{25}$ = +10.71 (*c* 1.025, $CHCl_3$). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (dt, *J* = 15.8, 6.9 Hz, 1H), 6.01 (d, *J* = 15.8 Hz, 1H), 5.16 (s, 1H), 4.07–4.03 (m, 1H, 3H), 2.86 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.63 (dd, *J* = 16.0, 6.4 Hz, 1H), 2.14 (q, *J* = 6.9 Hz, 2H), 1.45–1.32 (m, 2H), 1.30–1.18 (m, 15H), 1.15 (d, *J* = 7.1 Hz, 3H), 0.81 (t, *J* = 6.9 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 155.9, 148.7, 130.7, 60.7, 45.5, 44.1, 32.6, 31.9, 29.5, 29.4, 29.3, 29.2, 28.1, 22.7, 20.5, 14.7, 14.2 ; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{17}H_{31}NO_3Na$ 320.2202, found 320.2209.

(*R*,*E*)-Benzyl [4-oxo-6-phenyl-hex-5-en-2-yl]carbamate (**15n**).

$[\alpha]_D^{25}$ = +2.56 (*c* 1.95, $CHCl_3$). White solid : Mp 96 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 16.1 Hz, 1H), 7.48–7.46 (m, 2H), 7.33–7.19 (m, 8H), 6.64 (d, *J* = 16.1 Hz, 1H), 5.23 (s, 1H), 5.10–4.96 (m, 2H), 4.18–4.06 (m, 1H), 2.97 (d, *J* = 15.7 Hz, 1H), 2.73 (dd, *J* = 15.7, 5.6 Hz, 1H), 1.21 (d, *J* = 6.2 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 155.6, 143.1, 134.0, 130.7, 129.0, 128.5, 128.4, 128.1, 126.3, 66.6, 46.1, 44.3, 20.5 ; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{20}H_{21}NO_3Na$ 346.1419, found 346.1424.

(*R*,*E*)-Benzyl [4-oxo-pentadec-5-en-2-yl]carbamate (**15o**).

$[\alpha]_D^{25}$ = -9.86 (*c* 0.975, $CHCl_3$). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.30 (m, 5H), 6.87 (dt, *J* = 16.0, 6.7 Hz, 1H), 6.09 (d, *J* = 16.0 Hz, 1H), 5.29 (br s, 1H), 5.10 (br s, 2H), 4.13 (m, 1H), 2.91 (dd, *J* = 16.1, 3.1 Hz, 1H), 2.69 (dd, *J* = 16.1, 6.1 Hz, 1H), 2.22 (dt, *J* = 6.7, 7.1 Hz, 2H), 1.52–1.41 (m, 2H), 1.36–1.27 (m, 12H), 1.25 (d, *J* = 6.8 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 155.6, 148.7,

139.5, 130.5, 128.5, 128.1, 128.0, 66.5, 45.2, 44.2, 32.5, 31.8, 29.5, 29.4, 29.3, 29.2, 28.04, 22.6, 20.4, 14.1 ; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{23}H_{36}NO_3$ 374.2695, found 374.2706.

(*R*,*E*)-Benzyl [4-oxo-heptadec-5-en-2-yl]carbamate (**15p**).

$[\alpha]_D^{25}$ = -9.80 (*c* 1.015, $CHCl_3$). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.30 (m, 5H), 6.87 (dt, *J* = 15.9, 7.2 Hz, 1H), 6.06 (d, *J* = 15.9 Hz, 1H), 5.31 (br s, 1H), 5.08 (br s, 2H), 4.10 (m, 1H), 2.89 (d, *J* = 15.6 Hz, 1H), 2.66 (dd, *J* = 15.6, 5.3 Hz, 1H), 2.19 (q, *J* = 7.2 Hz, 2H), 1.47–1.40 (m, 6H), 1.33–1.21 (m, 15H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 155.7, 148.9, 136.7, 130.6, 128.6, 128.1, 66.6, 45.3, 44.3, 32.6, 32.0, 29.7, 29.6, 29.5, 29.4, 29.3, 28.1, 27.0, 22.8, 20.5, 14.2; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{25}H_{40}NO_3$ 402.3008, found 402.3015.

(*E*)-Ethyl [6-oxo-8-phenyl-oct-7-en-4-yl]carbamate (**15q** and **15q'**).

R enantiomer: $[\alpha]_D^{25}$ = +21.87 (*c* 0.97, $CHCl_3$), *S* enantiomer: $[\alpha]_D^{25}$ = −21.32 (c 0.76 $CHCl_3$). White solid: Mp 96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 16.8 Hz, 1H), 7.45–7.3 (m, 2H), 7.33–7.30 (m, 3H), 6.64 (d, *J* = 16.8 Hz, 1H), 5.06 (br s, 1H), 4.09–3.91 (m, 3H), 2.90 (dd, *J* = 17.2, 6.0 Hz, 1H), 2.78 (dd, *J* = 17.2, 5.5 Hz, 1H), 1.62–1.29 (m, 4H), 1.17 (t, *J* = 6.9 Hz, 3H), 0.85 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 156.2, 143.2, 134.3, 130.6, 128.9, 128.4, 126.3, 60.6, 48.1, 44.8, 36.5, 19.5, 14.6, 13.8; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{17}H_{23}NO_3Na$ 312.1576, found 312.1585.

(*R*,*E*)-Ethyl 8-(4-nitrophenyl)-6-oxo-oct-7-en-4-yl]carbamate (**15r**).

$[\alpha]_D^{25}$ = +13.8 (*c* 0.985, $CHCl_3$). Yellow solid : Mp 102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 16.2 Hz, 1H), 6.83 (d, *J* = 16.2 Hz, 1H), 5.01 (s, 1H), 4.14–4.01 (m, 3H), 3.01 (d, *J* = 16.2 Hz, 1H), 2.85 (dd, *J* = 16.2, 5.7 Hz, 1H), 1.64–1.49 (m, 2H), 1.47–1.30 (m, 2H), 1.22 (t, *J* = 6.8 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 156.2, 140.6, 140.0, 129.5, 128.9, 124.2, 124.2, 60.8, 48.1, 45.8, 36.6, 19.5, 14.6, 13.8; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{17}H_{22}N_2O_5Na$ 357.1426, found 357.1420.

(*R*,*E*)-Ethyl [3-oxo-1-phenyl-tridec-1-en-5-yl]carbamate (**15s**).

$[\alpha]_D^{25}$ = +17.26 (*c* 1.015, $CHCl_3$). White solid : Mp 76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 16.1 Hz, 1H), 7.57–7.52 (m, 2H), 7.44–7.36 (m, 3H), 6.74 (d, *J* = 16.1 Hz, 1H), 5.23 (d, *J* = 7.4 Hz, 1H), 4.21–3.94 (m, 3H), 3.01 (d, *J* = 15.2 Hz, 1H), 2.84 (dd, *J* = 15.2, 3.8 Hz, 1H), 1.69–1.49 (m, 2H), 1.48–1.11 (m, 15H), 0.85 (t, *J* = 6.8 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 156.2, 143.2, 134.3, 130.6, 129.6, 128.9, 128.4, 126.3, 60.6, 48.4, 44.9, 34.4, 31.8, 29.5, 29.2, 26.3, 22.6, 14.6, 14.1 ; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{22}H_{33}NO_3Na$ 382.2358, found 382.2364.

(*R*,*E*)-Ethyl [4-oxo-tetradec-2-en-6-yl]carbamate (**15t**).

$[\alpha]_D^{25}$ = +17.44 (*c* 1.12, $CHCl_3$). White solid : Mp 59 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (dt, *J* = 15.8, 6.8, 1H), 6.10 (d, *J* = 15.8, 1.6 Hz, 1H), 5.1 (br s, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 3.91 (m, 1H), 2.84 (dd, *J* = 15.8, 4.2 Hz, 1H), 2.67 (dd, *J* = 15.8, 5.5 Hz, 1H), 1.90 (d, 3H, *J* = 6.8 Hz), 1.55–1.46 (m, 2H), 1.33–1.20 (m, 15H), 0.86 (t, *J* = 6.9 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 156.3, 143.6, 132.4, 60.7, 48.5, 44.0, 34.5, 31.9, 29.6, 29.5, 29.4, 26.4, 22.8, 18.5, 14.7, 14.2 ; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{17}H_{31}NO_3Na$ 320.2202, found 320.2207.

(*R*,*E*)-Ethyl [6-oxo-hexadec-4-en-8-yl]carbamate (**15u**).

$[\alpha]_D^{25}$ = +12.1 (*c* 1.05, $CHCl_3$). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (dt, *J* = 15.9, 7.2 Hz, 1H), 6.07 (dd, *J* = 15.9, 1.4 Hz, 1H), 5.11 (br s, 1H), 4.07 (qd, *J* = 6.9, 2H), 3.91 (m, 1H), 2.85 (dd, *J* = 16.3, 4.5 Hz, 1H), 2.69 (dd, *J* = 16.3, 5.7 Hz, 1H), 2.18 (dd, *J* = 7.2, 1.4 Hz, 1H), 1.53–1.44 (m, 2H), 1.49 (qd, *J* = 7.2 Hz, 2H), 1. 29–1.19 (m, 15H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.4, 156.3, 148.3, 130.9, 60.7, 46.5, 44.1, 34.6, 34.5, 31.9, 29.6, 29.5, 29.4, 26.4, 22.8, 21.4, 14.7, 14.2, 13.8; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{19}H_{35}NO_3Na$ 348.2515, found 348.2525.

(*S*,*E*)-Ethyl [3-oxo-1,5-diphenyl-pent-4-enyl]carbamate (**15v**).

$[\alpha]_D^{25}$ = +6.6 (*c* 0.94, $CHCl_3$). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 16.2 Hz, 1H), 7.41–7.11 (m, 10H), 6.59 (d, *J* = 16.2 Hz, 1H), 5.74 (br s, 1H), 5.16 (m, 1H), 4.01 (q, *J* = 6.3 Hz, 1H), 3.26 (dd, *J* = 15.9 Hz, 1H), 3.06 (dd, *J* = 15.9, 5.0 Hz, 1H), 1.13 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 155.9, 143.6, 134.2, 130.7, 128.9, 128.6, 128.4, 127.5, 126.3, 126.0, 61.0, 51.7, 46.1, 14.6; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{20}H_{21}NO_3Na$ 346.1419, found 346.1414.

(*S*,*E*)-Ethyl [3-oxo-1-phenyl-hex-4-enyl]carbamate (15w).

$[\alpha]_D^{25}$ = −13.3 (*c* 0.715, $CHCl_3$). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.12 (m, 5H), 6.75 (dq, *J* = 15.9, 6.8 Hz, 1H), 5.96 (dd, *J* = 15.9,1.5 Hz, 1H), 5.68 (br s, 1H), 5.09 (m, 1H), 4.01 (q, *J* = 6.9 Hz, 2H), 3.12 (dd, *J* = 16.6, 5.8 Hz, 1H), 2.93 (dd, *J* = 16.6, 6.8 Hz, 1H), 1.79 (dd, *J* = 6.8, 1.5 Hz, 3H), 1.10 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 158.2, 146.2, 143.7, 134.2, 130.8, 129.6, 128.5, 63.2, 53.9, 45.5, 20.6, 16.8; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{15}H_{19}NO_3Na$ 284.1263, found 284.1275.

(*S*,*E*)-Ethyl [3-oxo-1-phenyl-oct-4-enyl]carbamate (15x).

$[\alpha]_D^{25}$ = −9.11 (*c* 1.14, $CHCl_3$). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.21 (m, 5H), 6.80 (dt, *J* = 15.9, 6.9 Hz, 1H), 6.05 (td, *J* = 15.9, 1.5, 1H), 5.75 (s, 1H), 5.15 (dd, *J* = 5.8,3.1 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.23 (dd, *J* = 16.1, 3.1 Hz, 1H), 3.04 (dd, *J* = 16.1, 5.8 Hz, 1H), 2.16 (qd, *J* = 6.9, 1.5 Hz, 2H), 1.47 (sex, *J* = 6.8 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3,

156.1, 148.8, 141.6, 130.6, 128.6, 127.4, 126.4, 61.0, 51.8, 45.3, 34.6, 21.3, 14.6, 13.7; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{17}H_{23}NO_3Na$ 312.1576, found 312.1576.

(*S*,*E*)-Ethyl [3-oxo-1-phenyl-tridec-4-enyl]carbamate (**15y**).

$[\alpha]_D^{25}$ = −1.22 (*c* 0.995, $CHCl_3$). White solid: Mp 60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.17 (m, 4H), 7.13 (m, 1H), 6.70 (dt, *J* = 15.9, 6.9 Hz, 1H), 5.93 (d, *J* = 15.9 Hz, 1H), 5.88 (br s, 1H), 5.07 (m, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 3.09 (d, *J* = 16.1 Hz, 1H), 2.89 (dd, *J* = 16.1, 5.7 Hz, 1H), 2.06 (q, *J* = 6.9 Hz, 2H), 1.39–1.29 (m, 2H), 1.27–1.13 (m, 10H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.79 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 156.0, 148.9, 141.7, 130.3, 128.5, 127.3, 126.3, 60.8, 51.6, 45.3, 32.5, 31.8, 29.4, 29.3, 29.2, 29.1, 27.9, 22.6, 14.5, 14.1; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{22}H_{33}NO_3Na$ 382.2358, found 382.2362.

(*S*,*E*)-*tert*-Butyl [3-oxo-1-phenyl-hex-4-enyl]carbamate (**15z**).

$[\alpha]_D^{25}$ = −10.68 (*c* 1.015, $CHCl_3$). White solid: Mp 94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.18 (m, 5H), 6.84 (dq, *J* = 15.9, 6.8 Hz, 1H), 6.06 (dd, *J* = 15.9, 1.6 Hz, 1H), 5.55 (br s, 1H), 5.09 (m, 1H), 3.12 (d, *J* = 16.6 Hz, 1H), 2.98 (dd, *J* = 16.6, 5.6 Hz, 1H), 1.85 (dd, *J* = 6.8, 1.6 Hz, 3H), 1.40 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 155.3, 144.0, 132.1, 128.7, 127.4, 126.4, 51.5, 45.6, 28.5, 18.5; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{17}H_{23}NO_3Na$ 312.1576, found 312.1591.

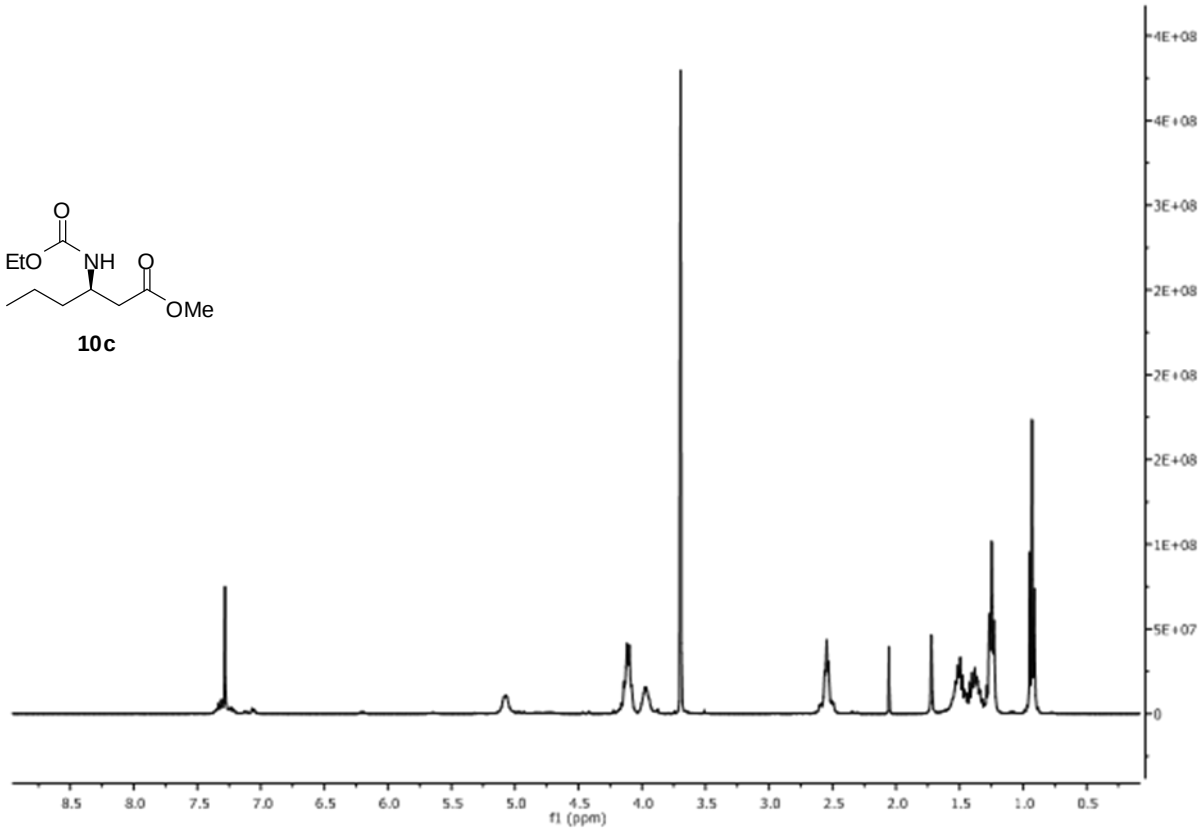
(*S*,*E*)-Benzyl [3-oxo-1-phenyl-hex-4-enyl]carbamate (**1)**.

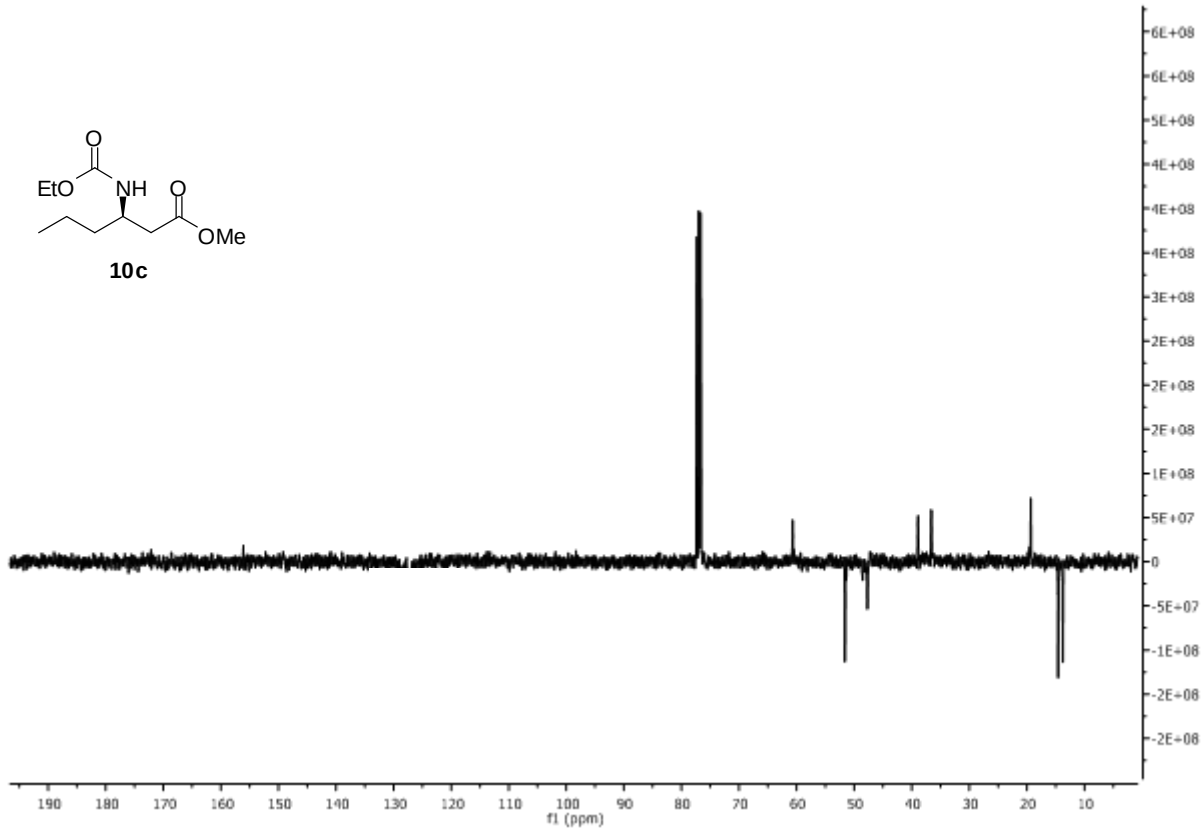
$[\alpha]_D^{25}$ = −5.34 (*c* 1.05, $CHCl_3$). White solid: Mp 60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.17 (m, 5H), 6.80 (dq, *J* = 15.8, 6.8 Hz, 1H), 6.05 (d, *J* = 15.8 Hz, 1H), 5.88 (br s, 1H), 5.18 (dd, *J* = 6.2, 5.6 Hz, 1H), 5.10 (d, *J* = 12.3 Hz, 1H), 5.05 (d, *J* = 12.3 Hz, 1H), 3.19 (dd, *J* = 16.2, 5.6 Hz, 1H), 3.00 (dd, *J* = 16.2, 6.2 Hz, 1H), 1.85 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 155.7, 144.0, 136.4, 136.2, 131.9, 128.7, 128.6, 128.5, 128.0, 126.4, 126.3, 66.8, 51.8, 45.1, 18.3; HRMS-ESI (M + Na), *m/z*: calcd. for $C_{17}H_{23}NO_3Na$ 346.1419, found 346.1426.

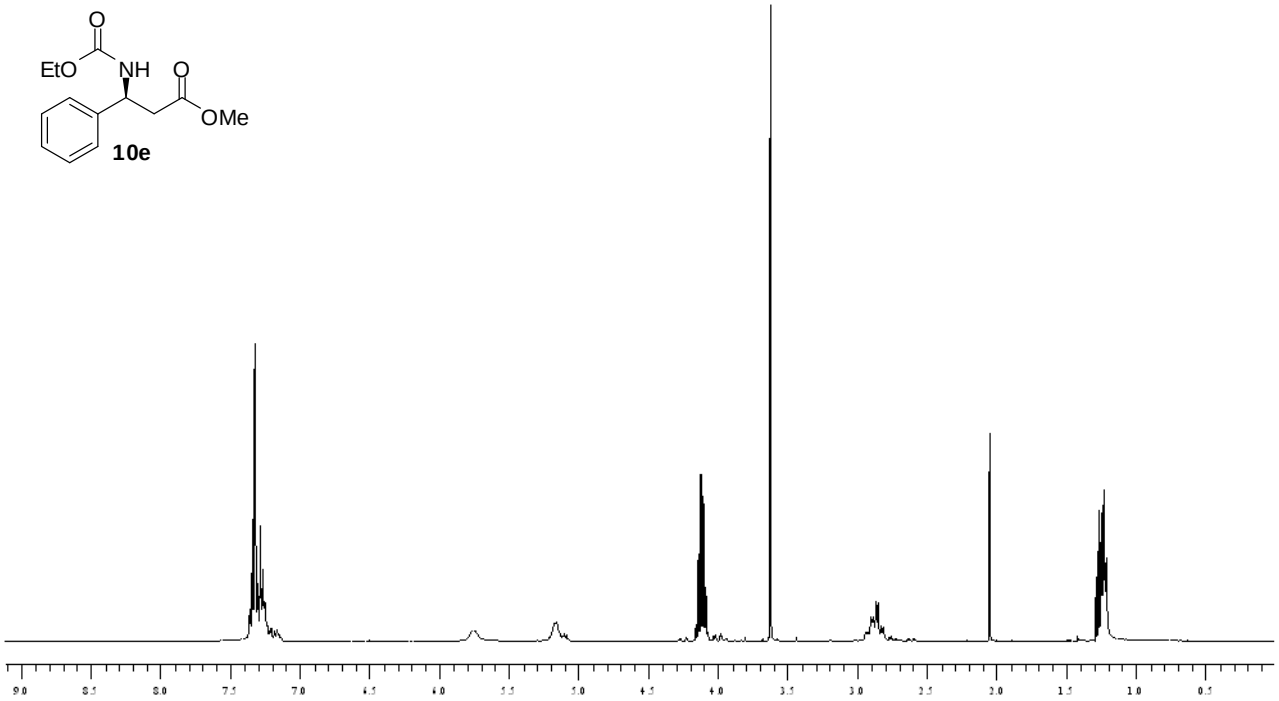
4. References

1. Cooper, J.; Knight, D.W.; Gallagher, P.T. *J. Chem. Soc.: Perkin Trans. 1* **1991**, 705-713.
2. Fleck, T. J.; McWhorter, W. W.; Dekam, R. N.; Pearlman, B. A. *J. Org. Chem.* **2003**, *68*, 9612-9617.
3. Hansen, K. B.; Rosner, T.; Kubryk, M.; Dormer, P. G.; Armstrong, J. D. III. *Org. Lett.* **2005**, *7*, 4935-4938.
4. Tillman, A. L.; Ye, J.; Dixon, D. J. *Chem. Commun.* **2006**, 1191-1193.

4. ^{1}H NMR and ^{13}C NMR of products



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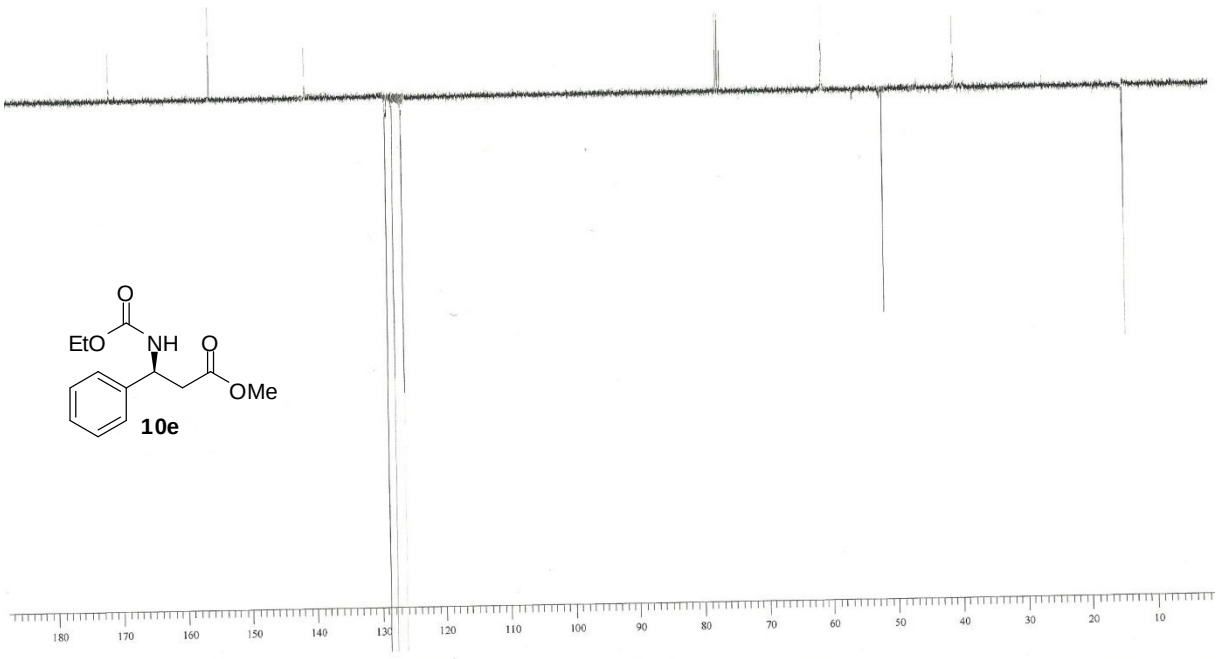
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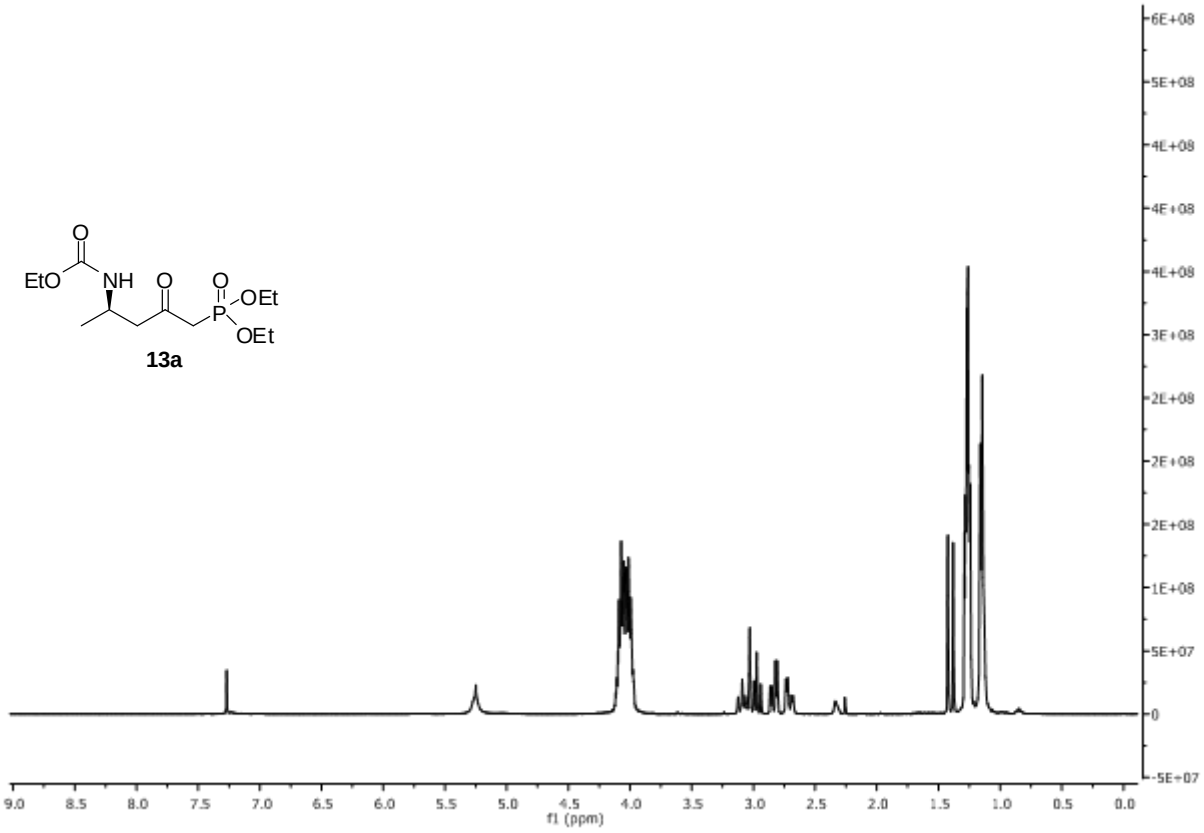
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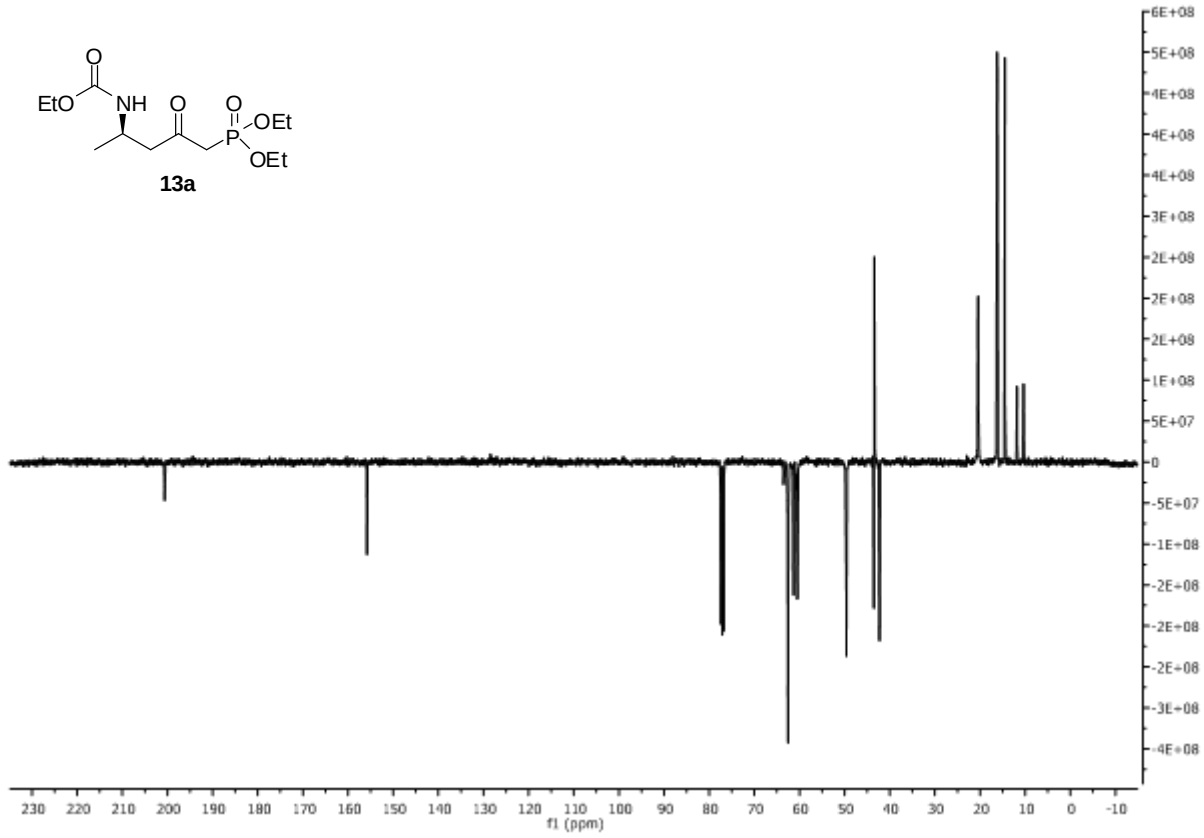
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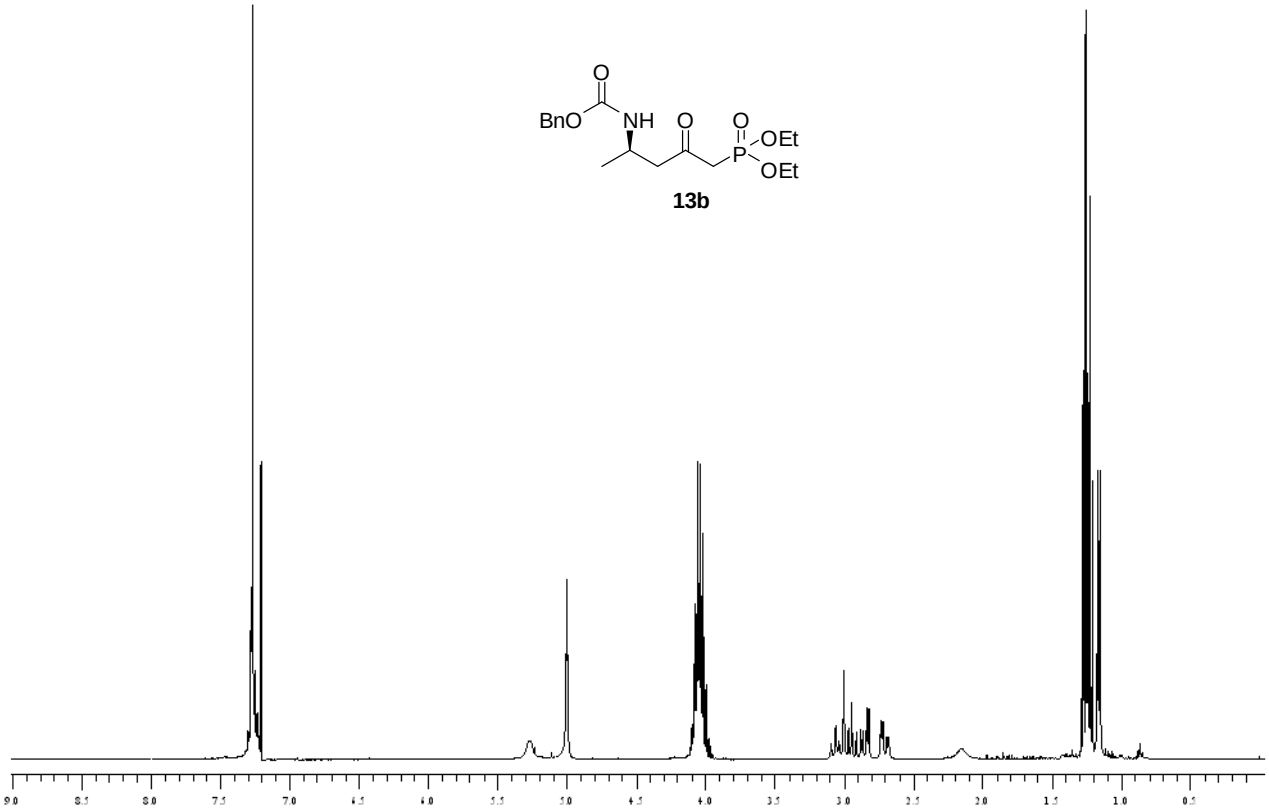
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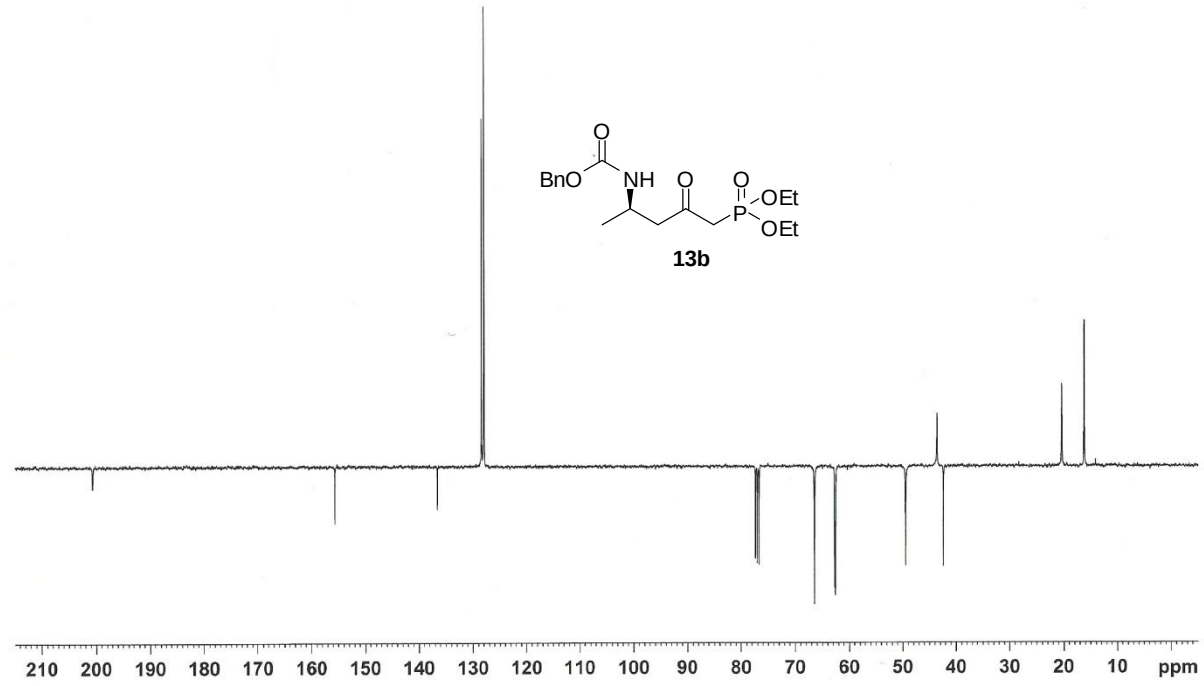
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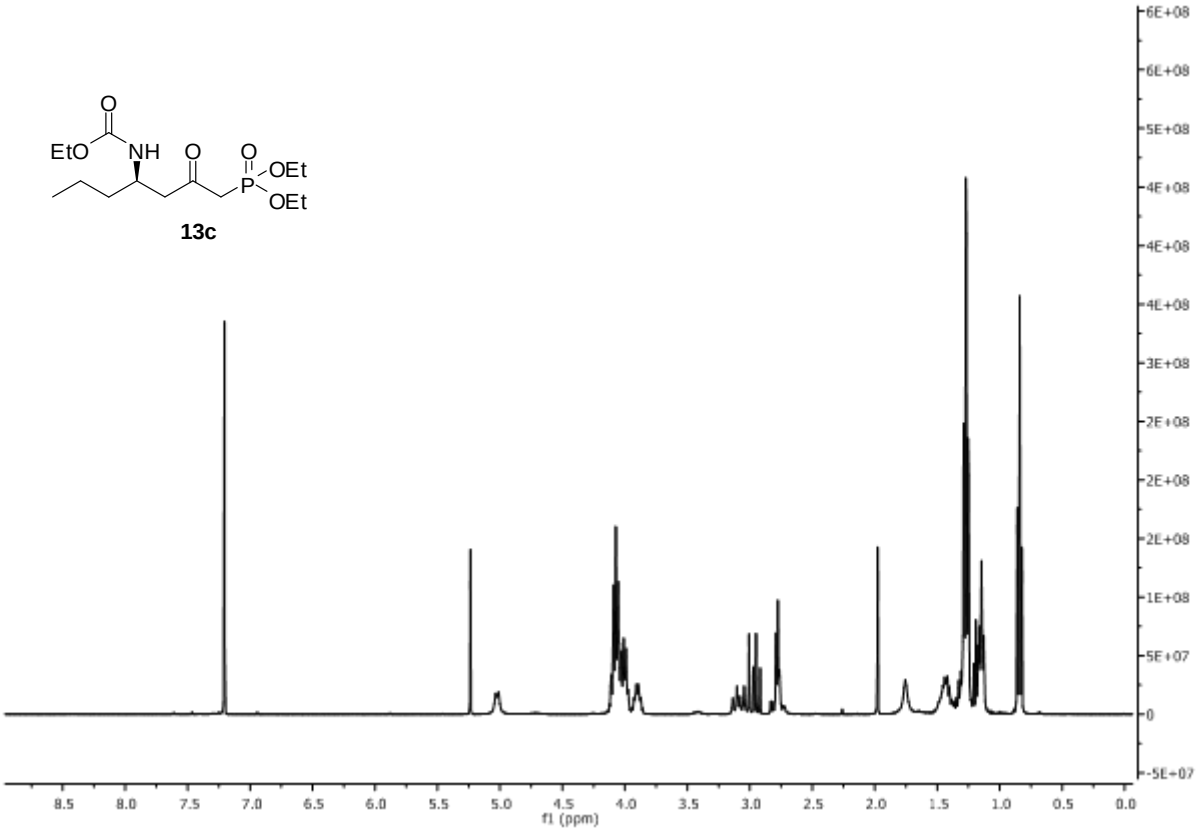
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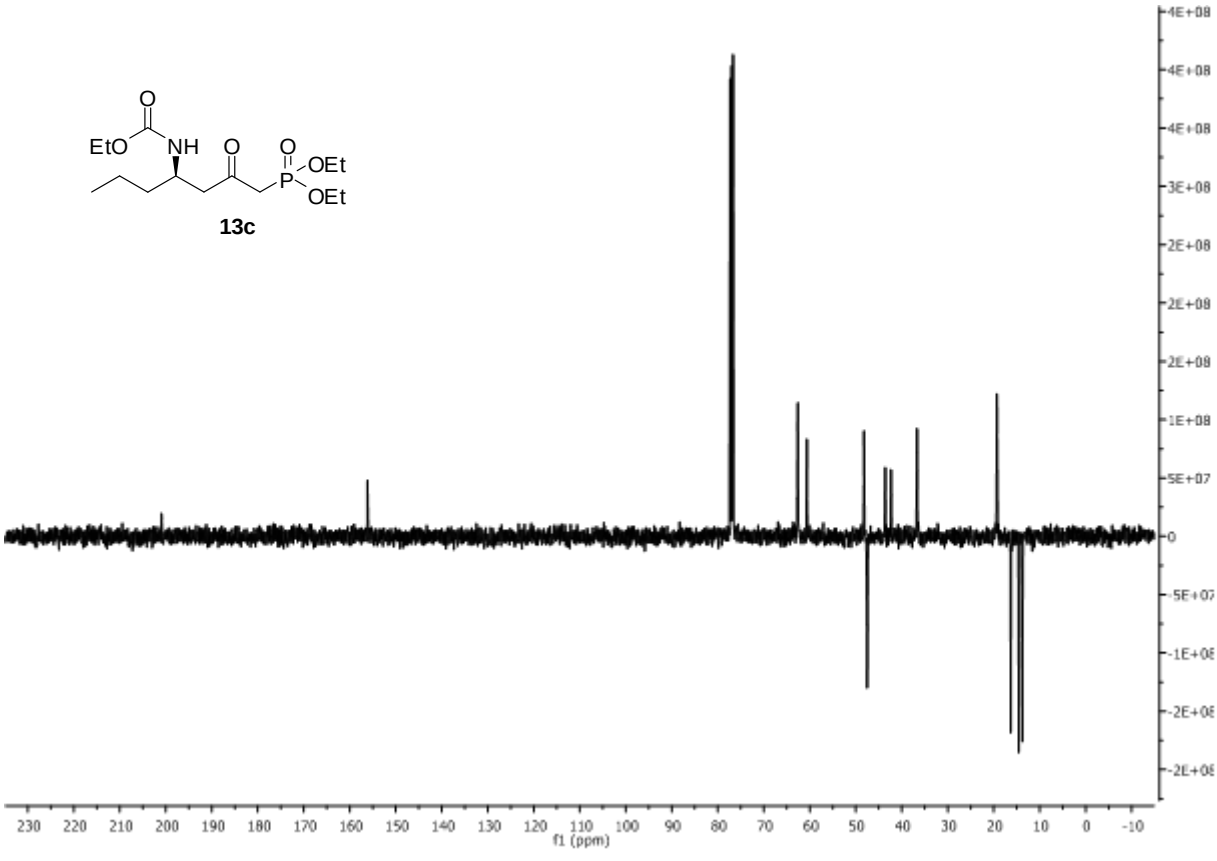
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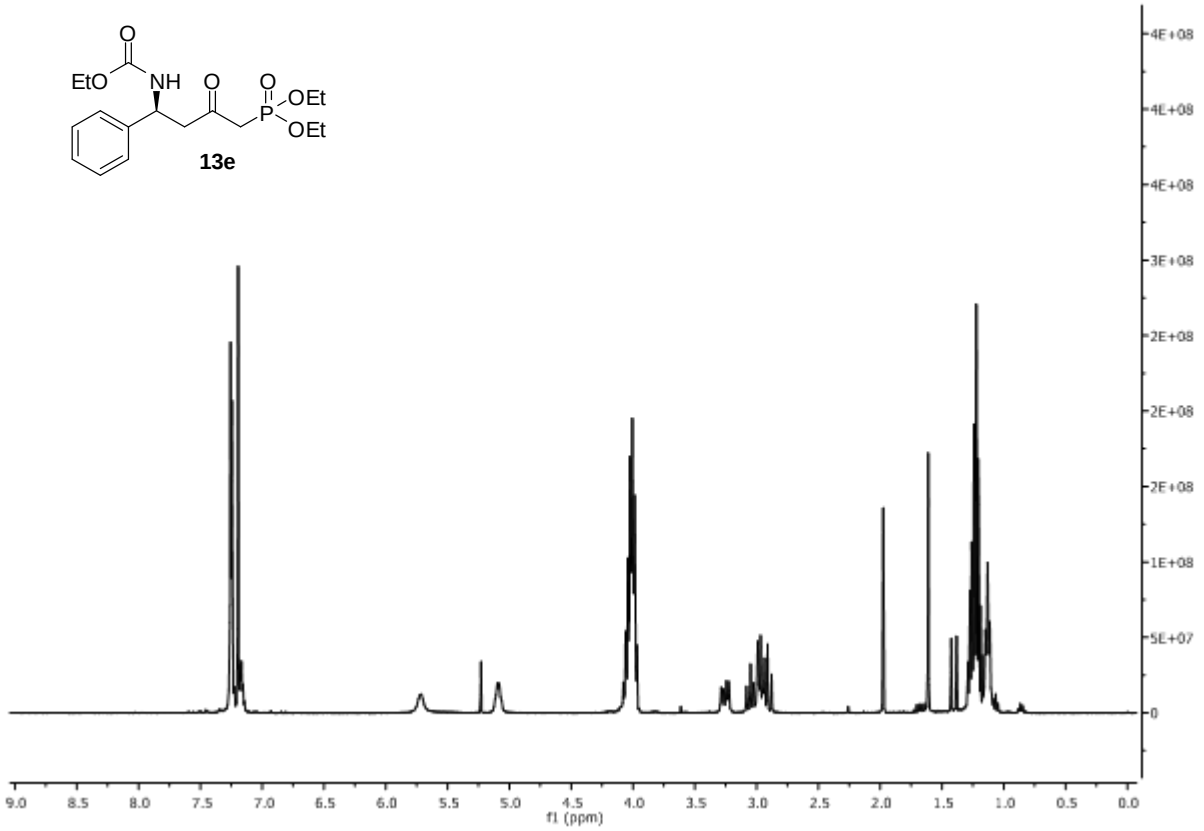
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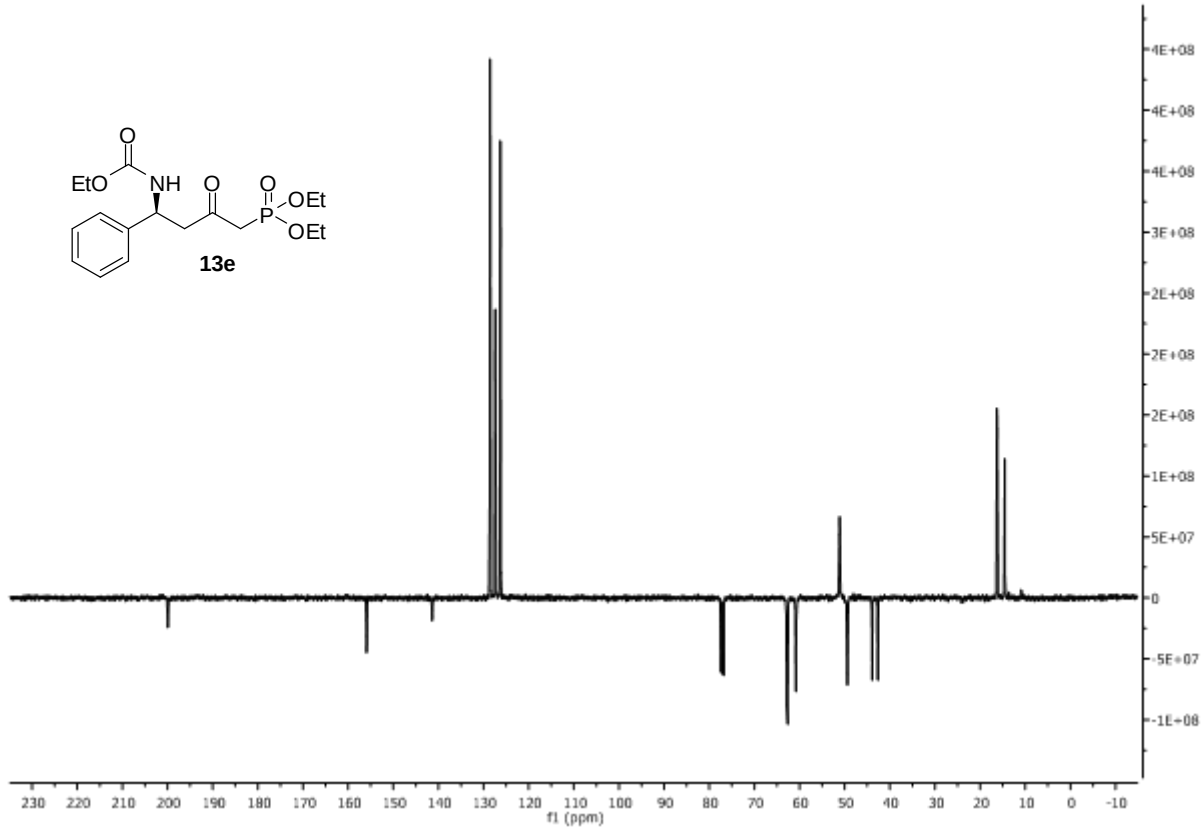
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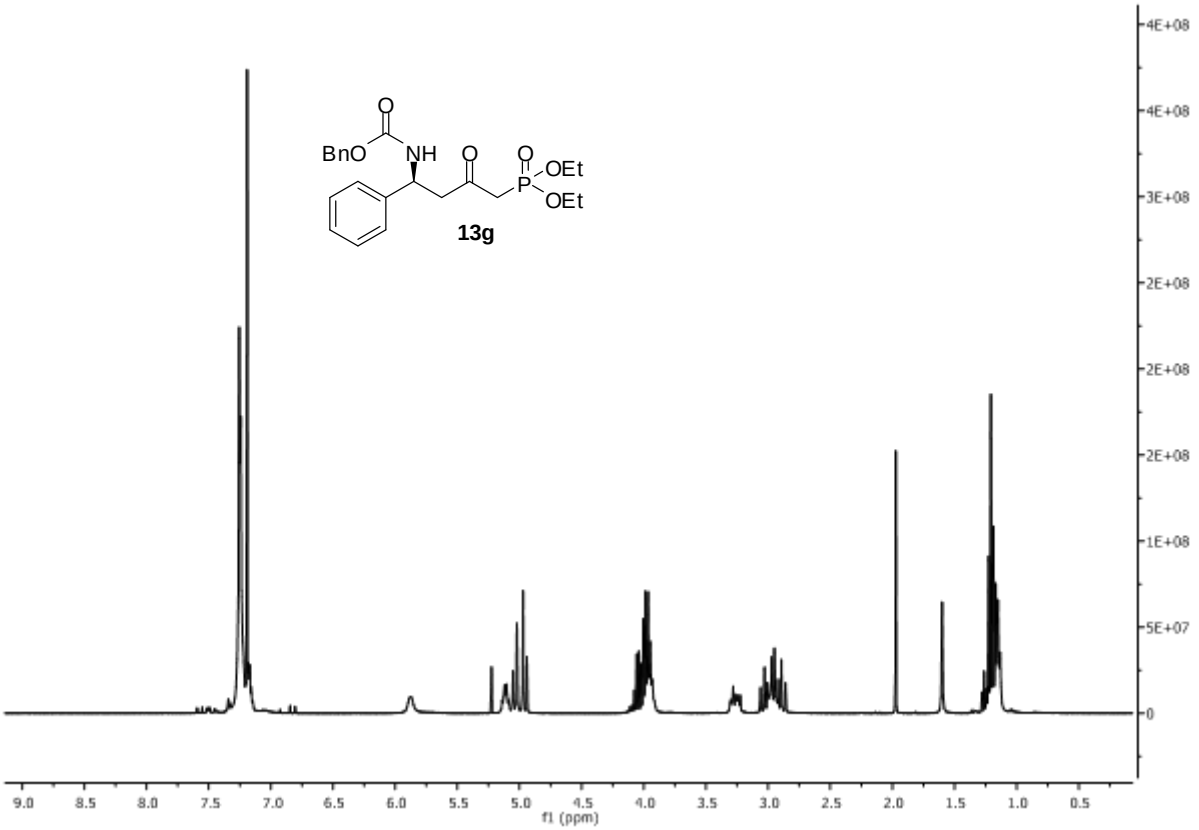
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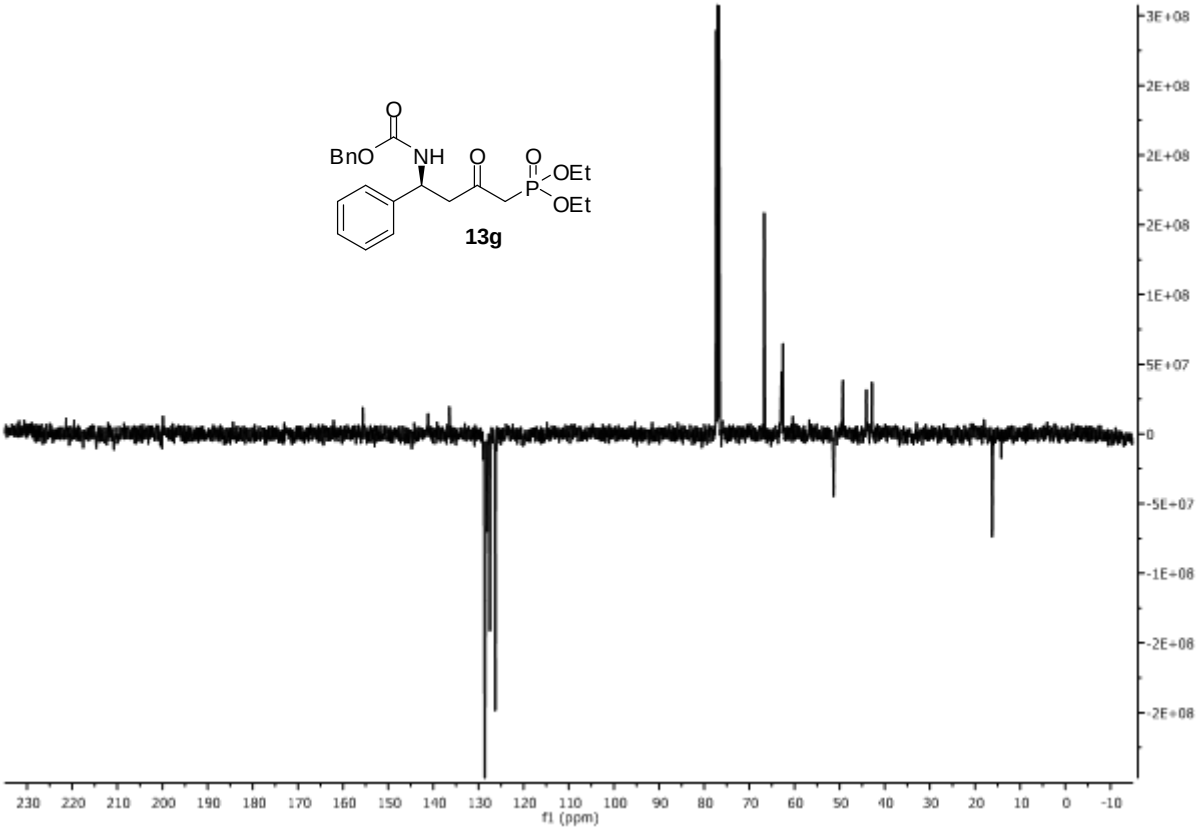
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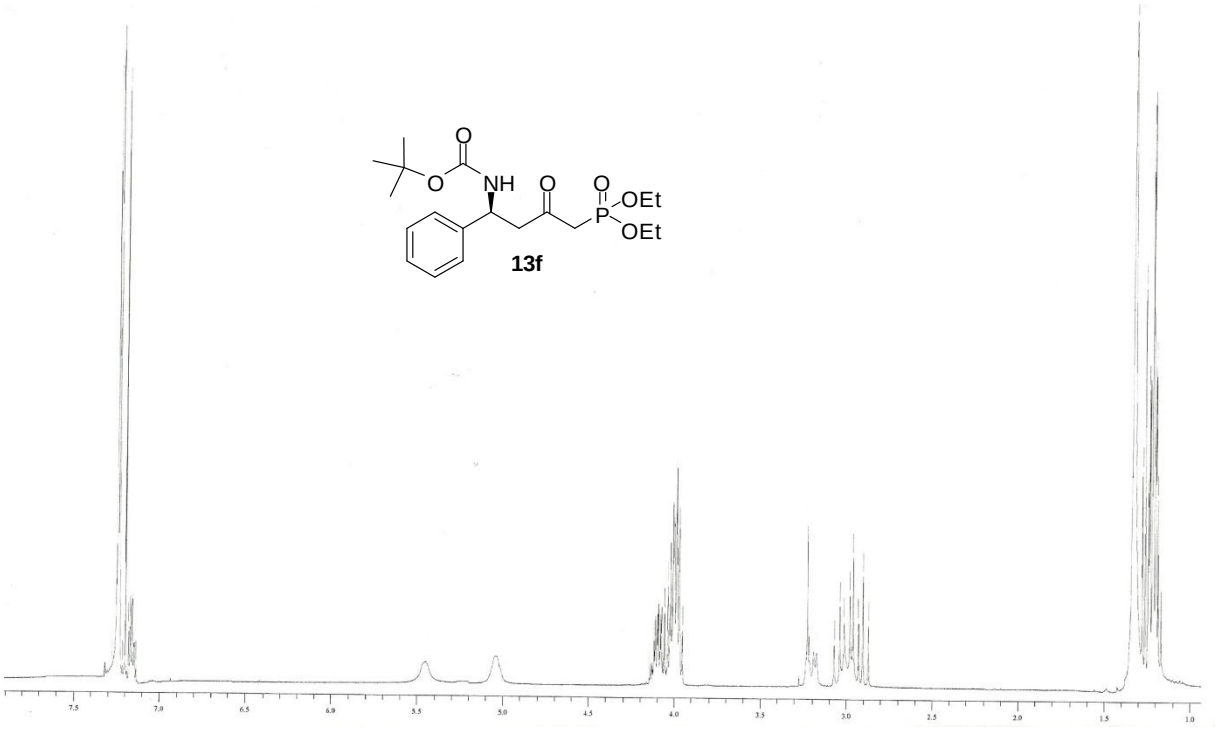
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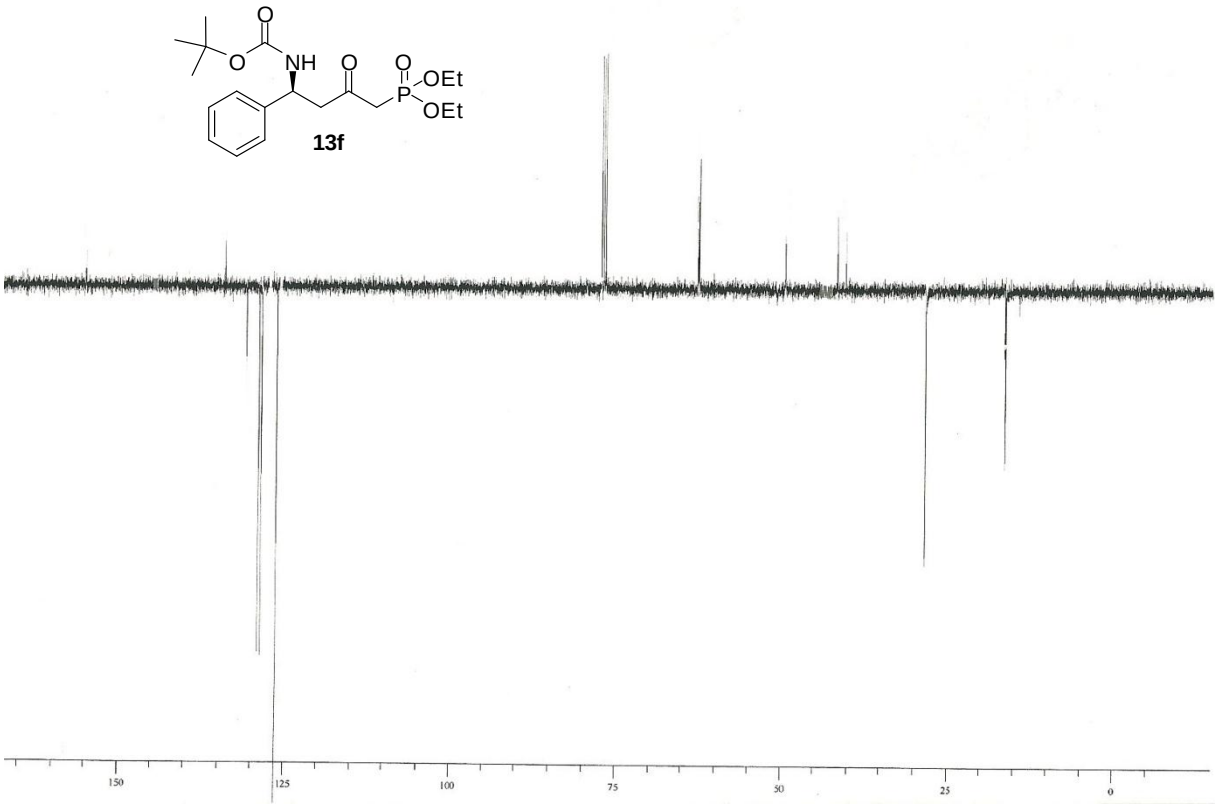
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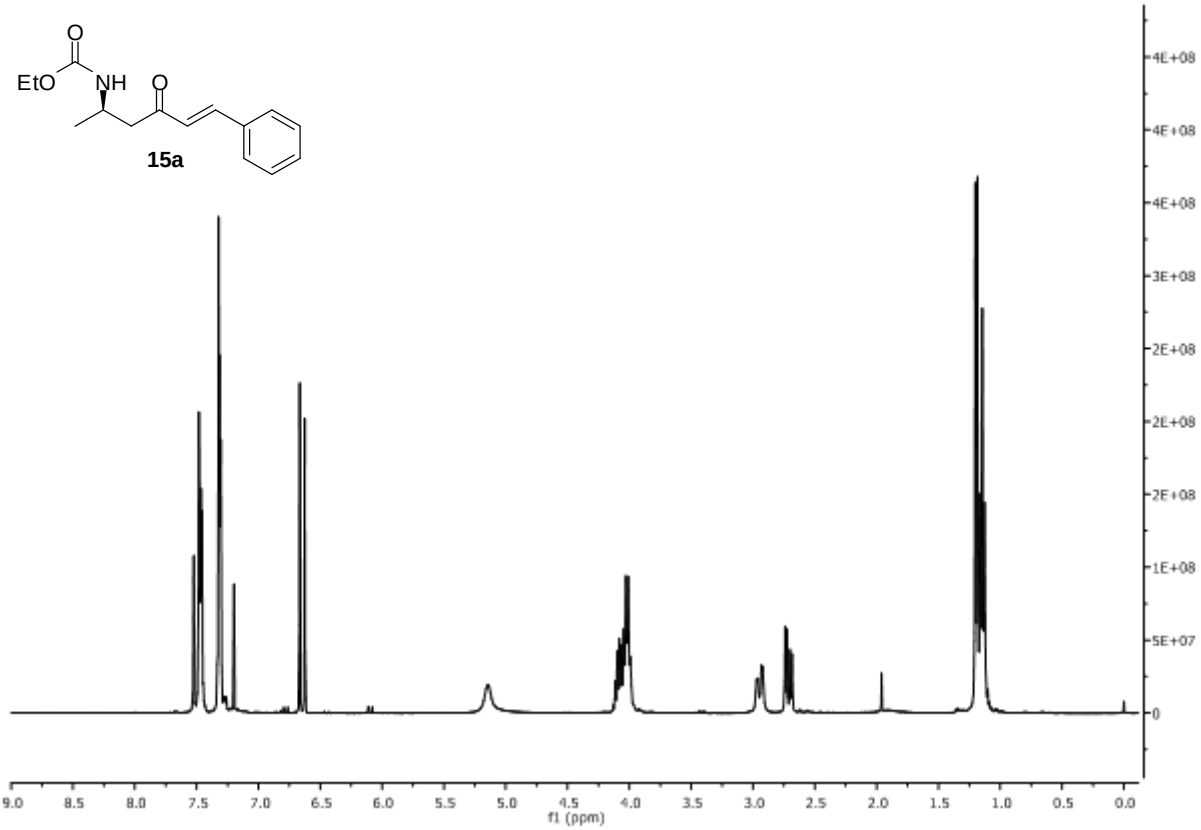
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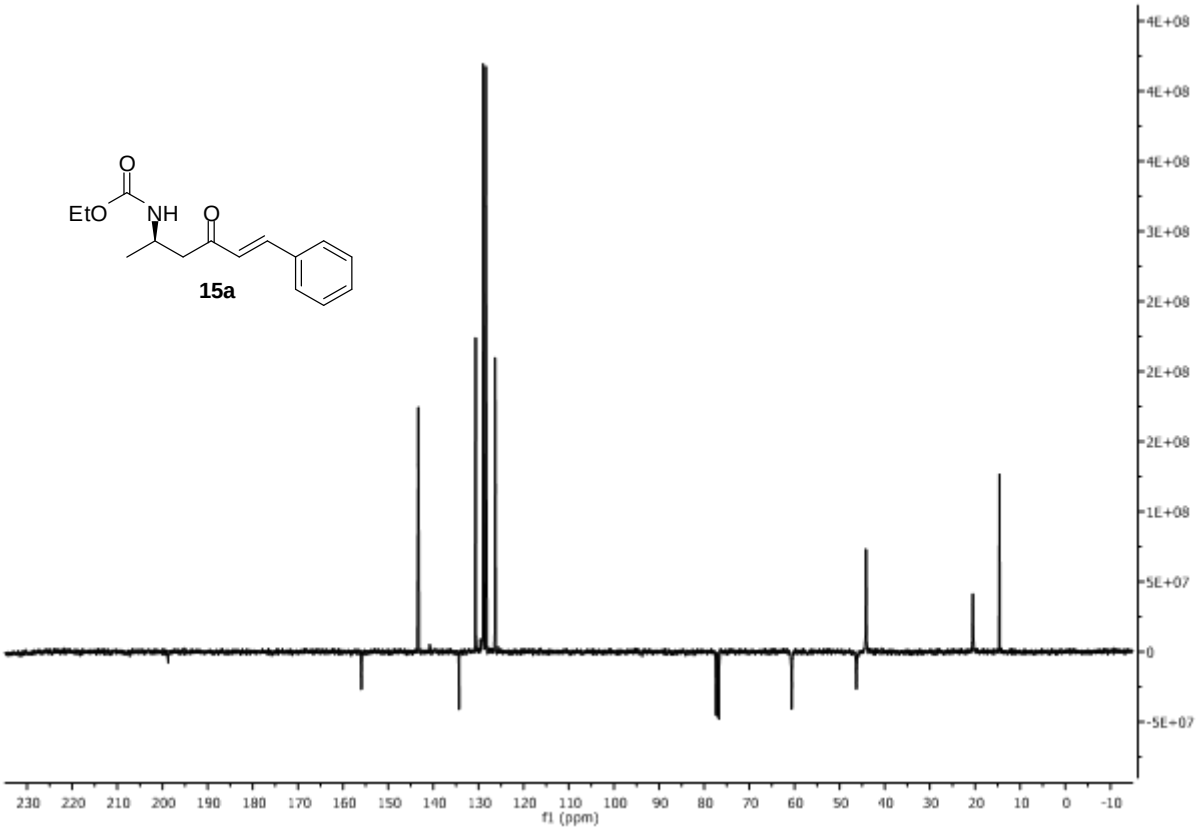
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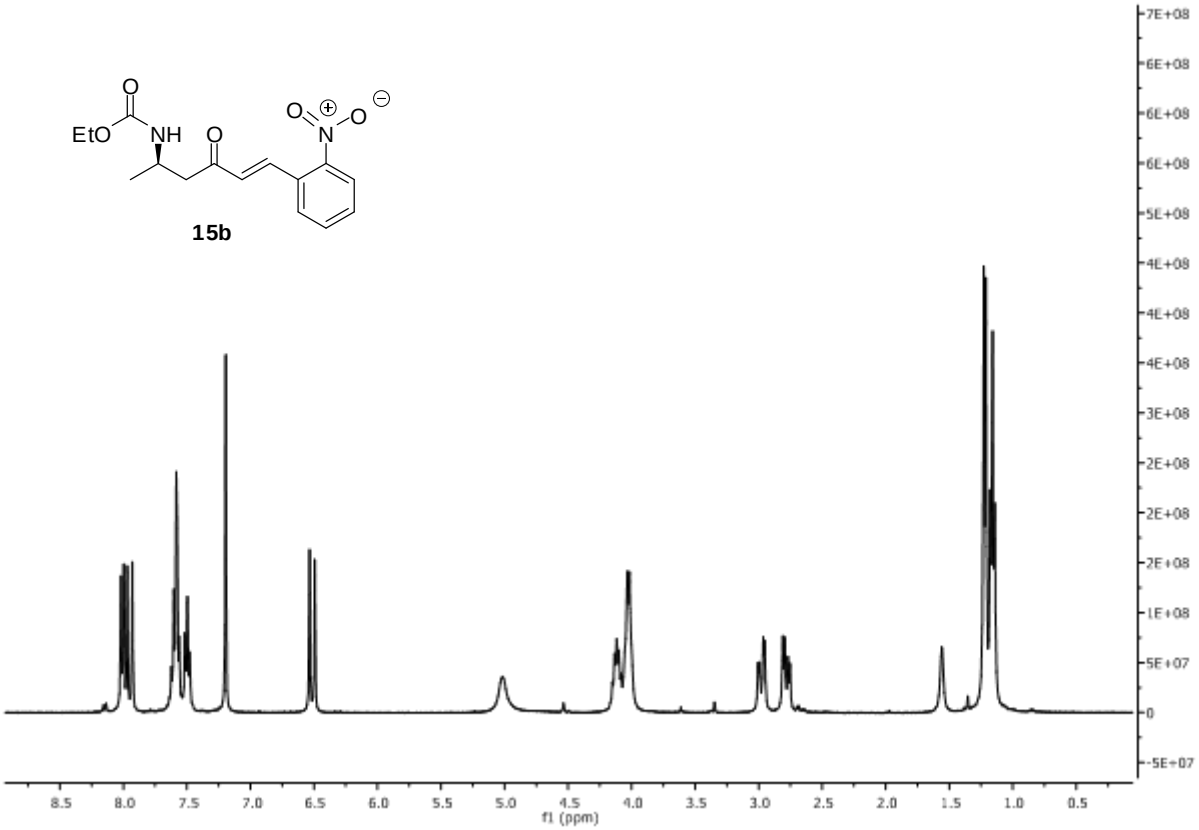
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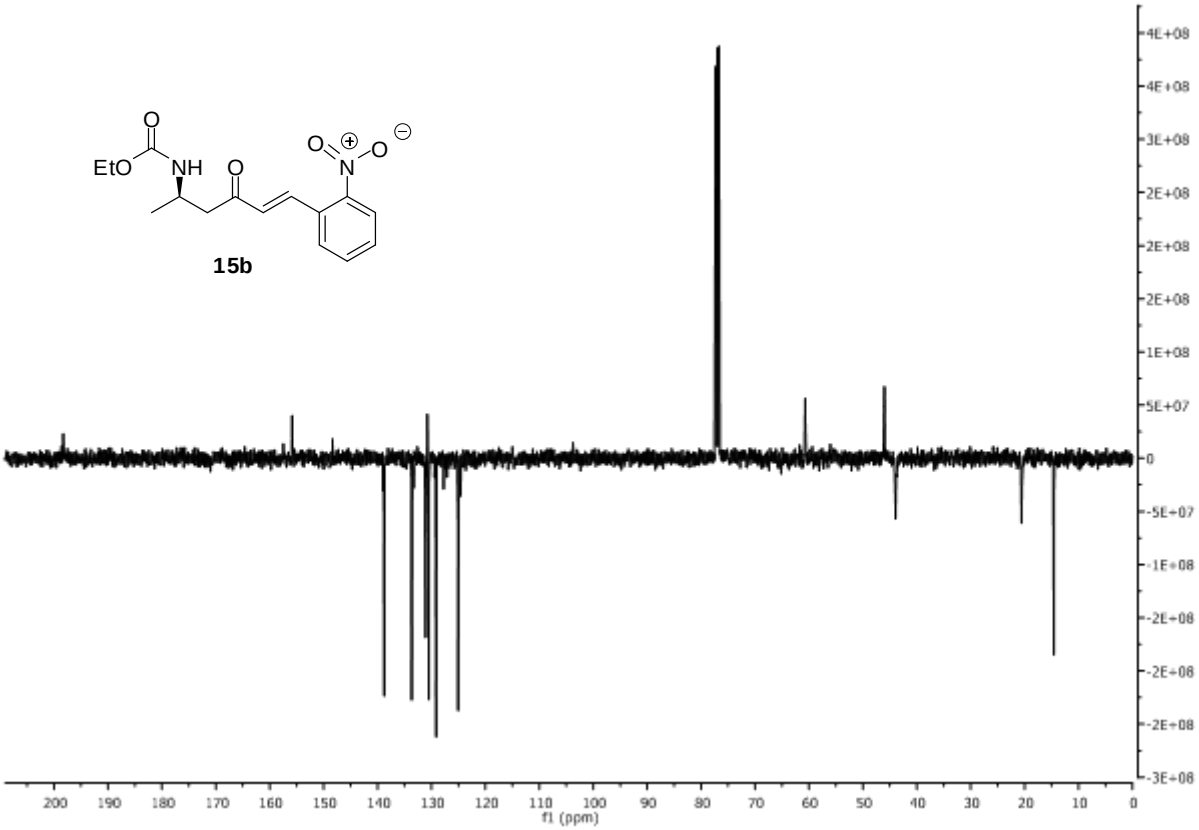
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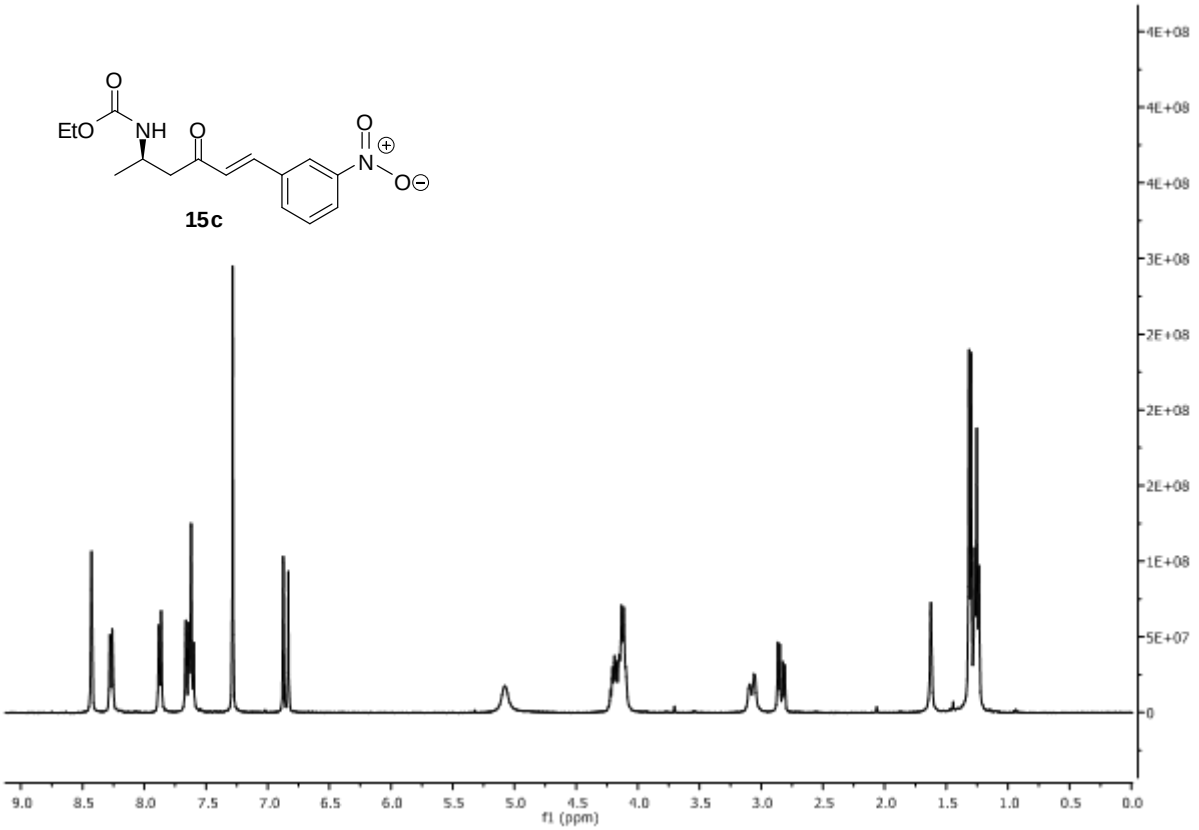
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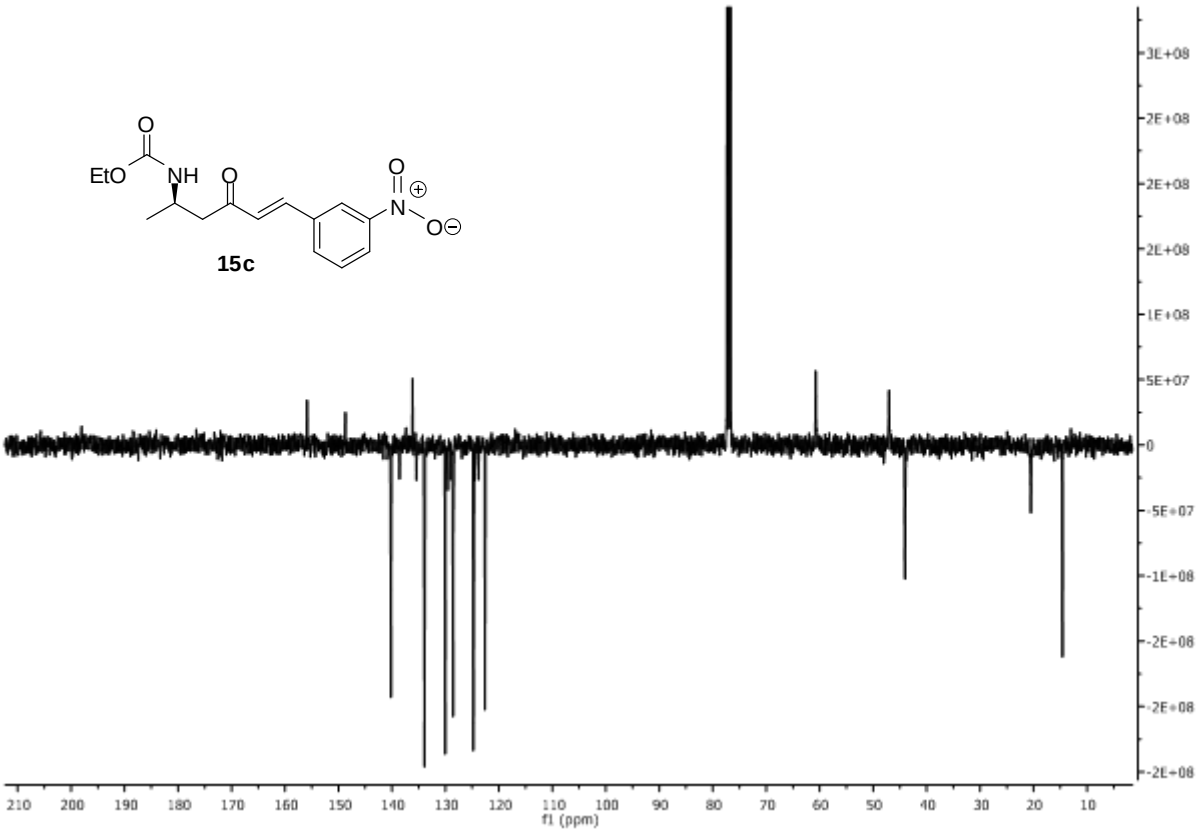
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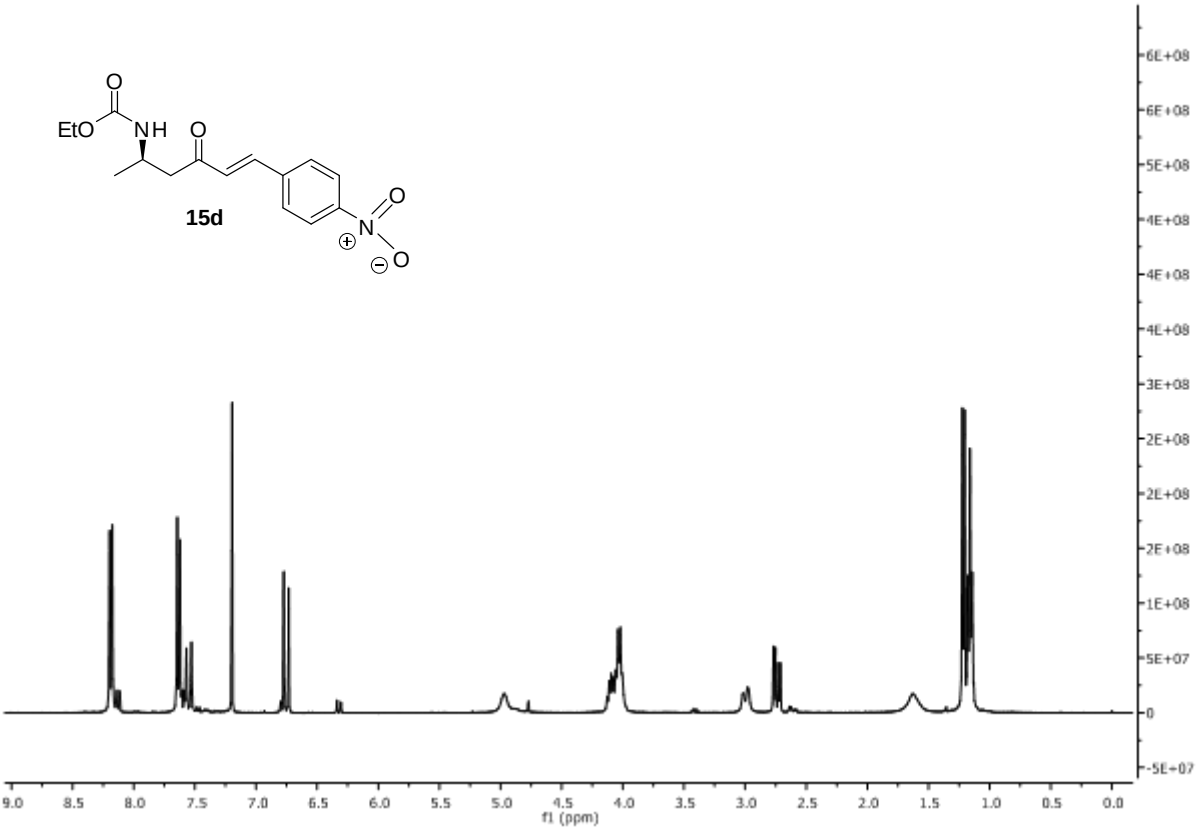
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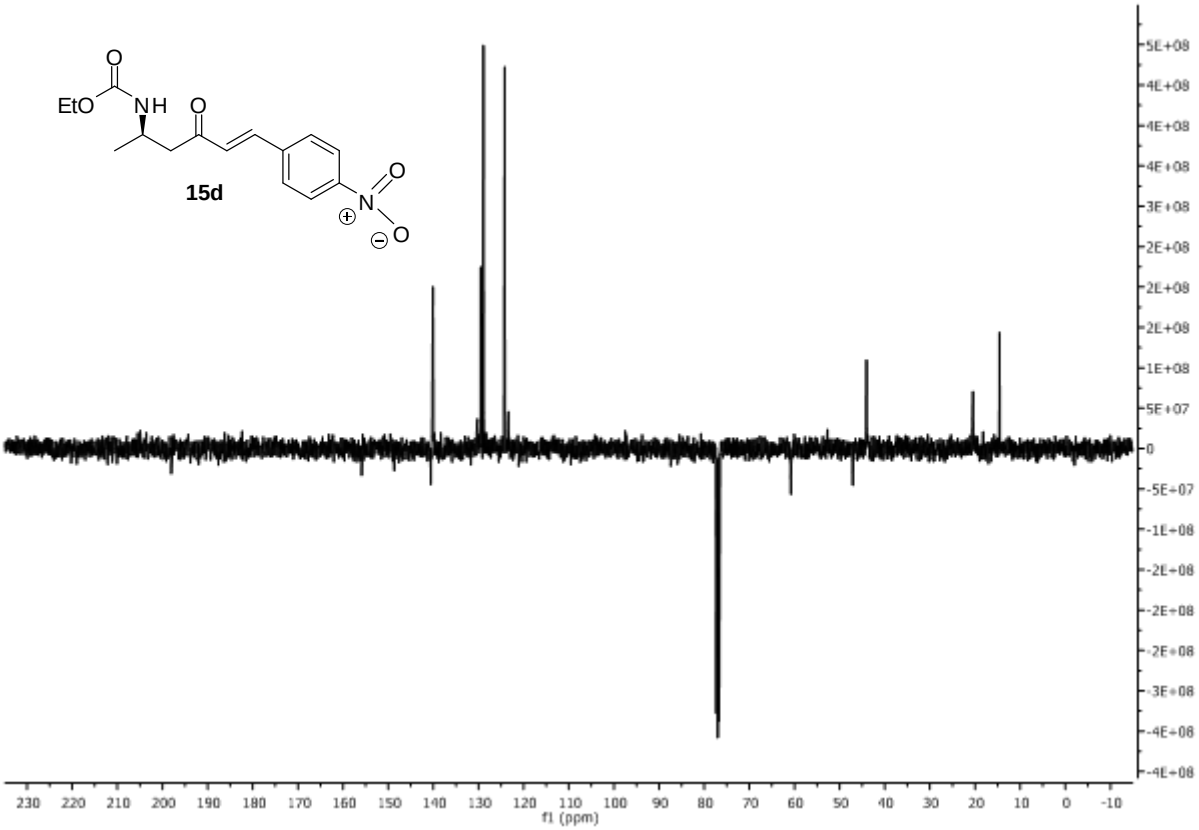
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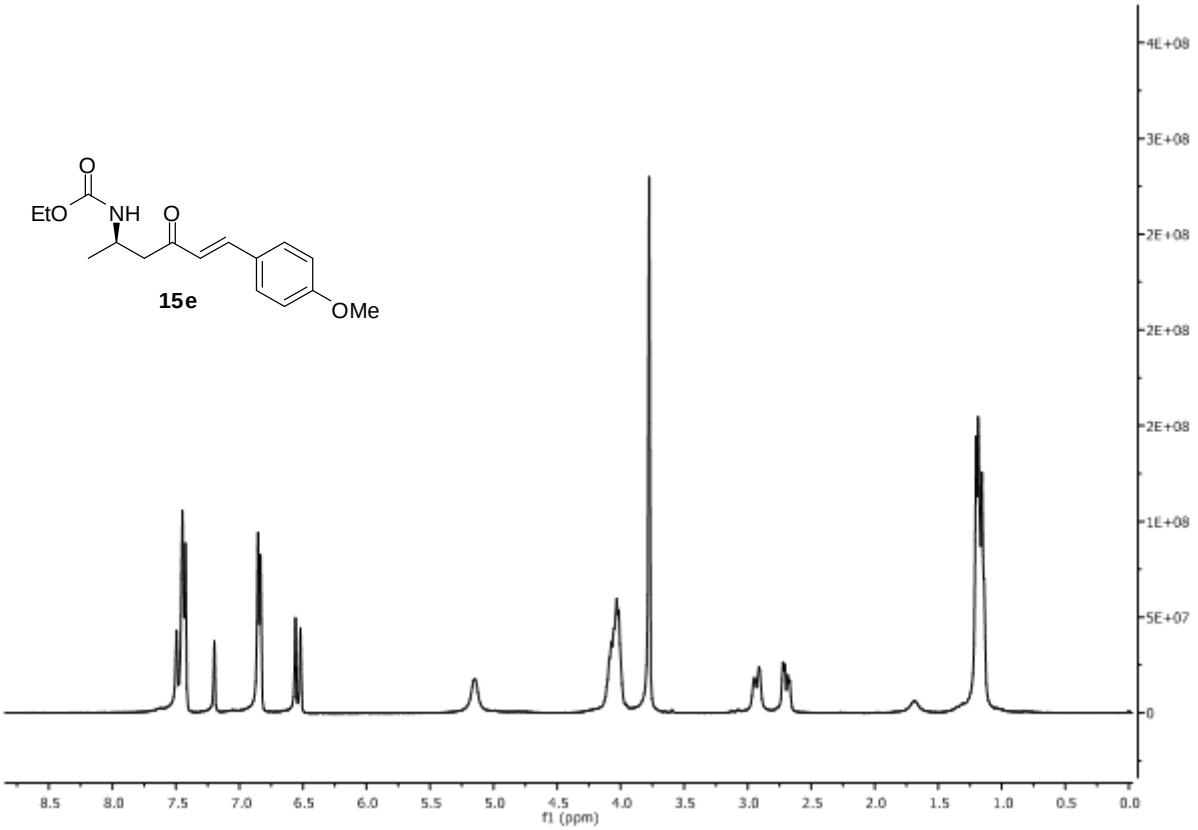
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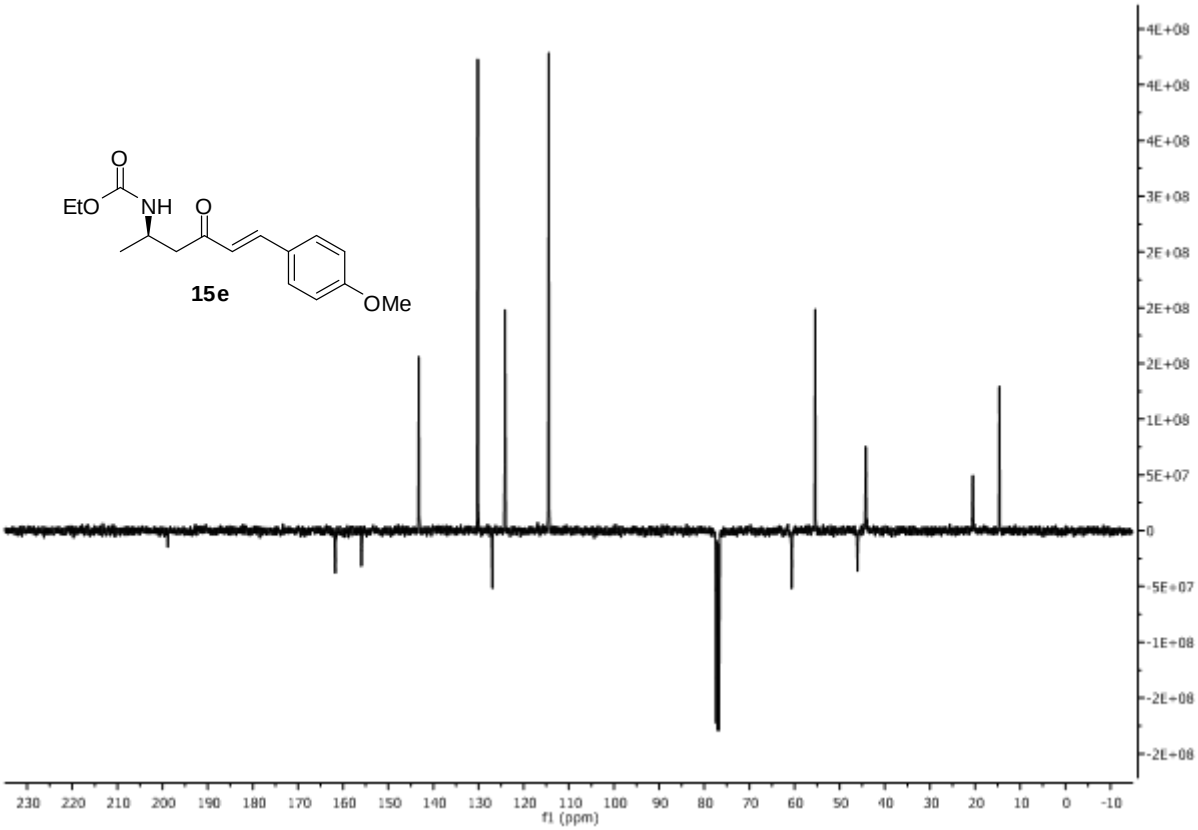
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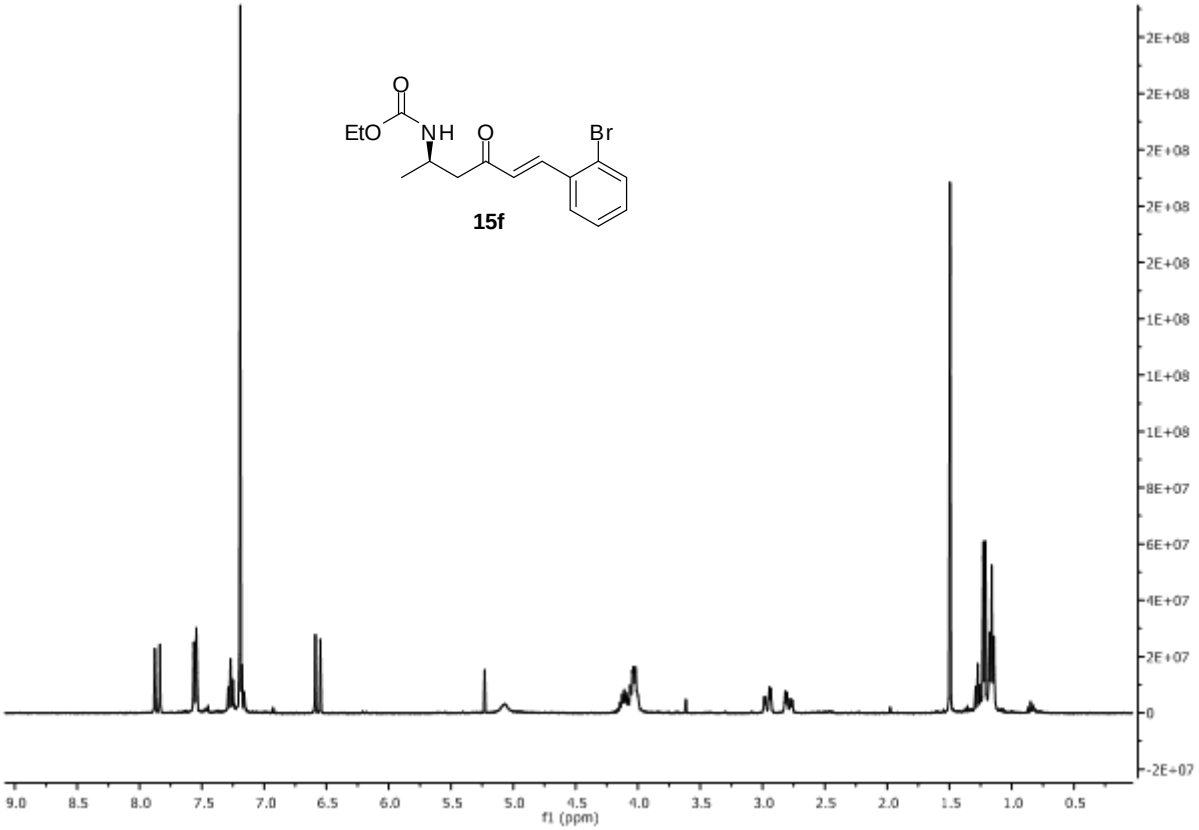
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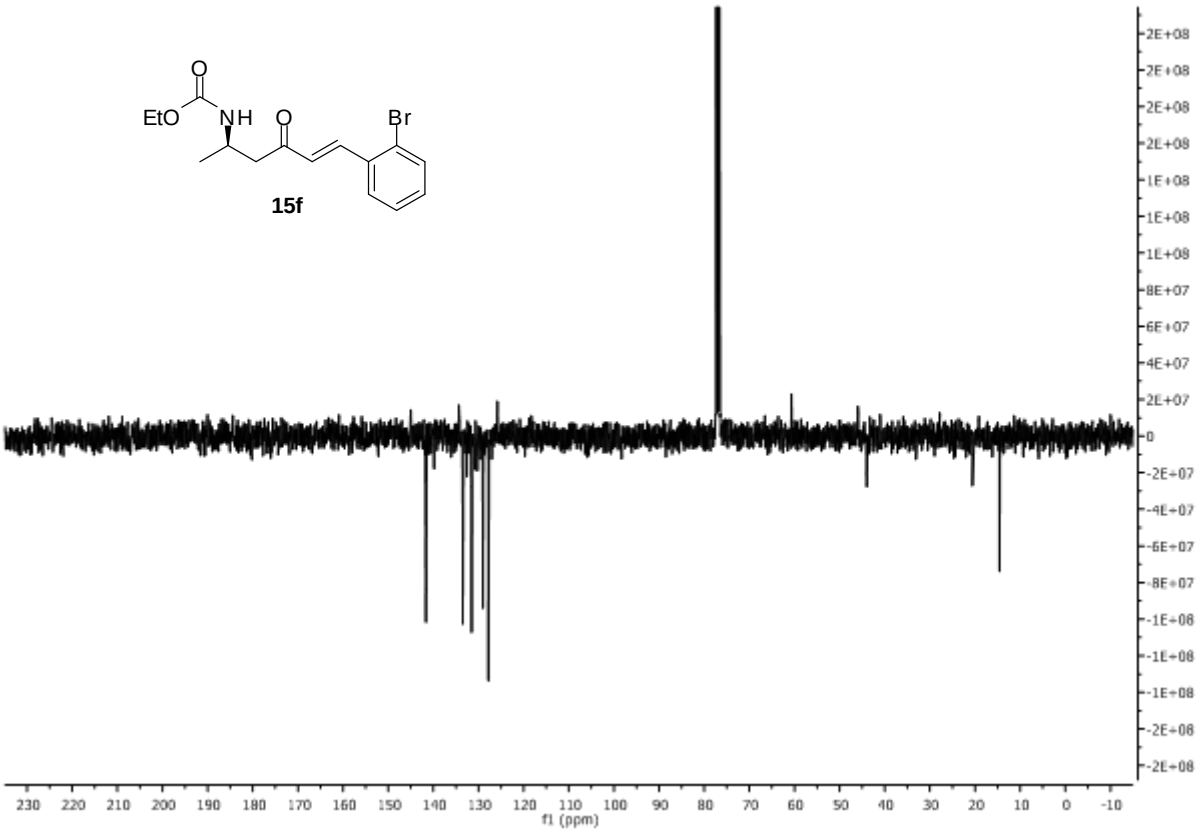
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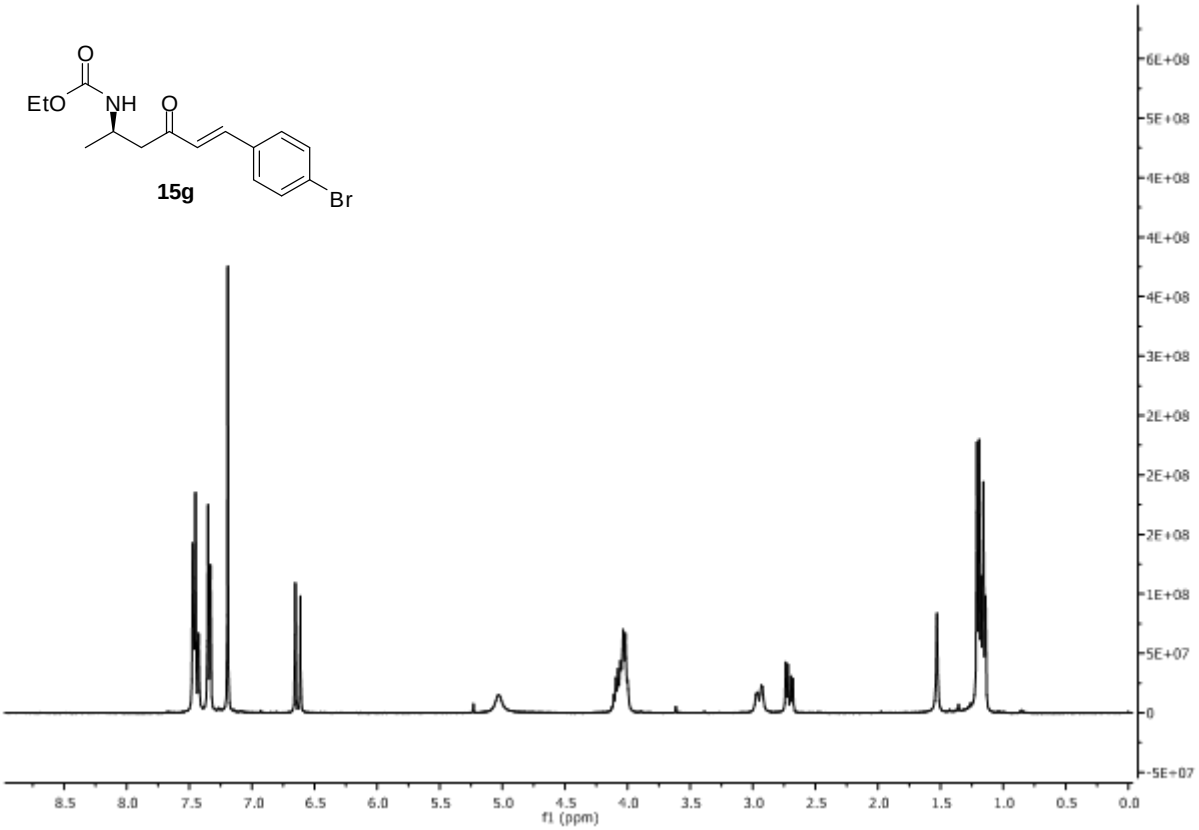
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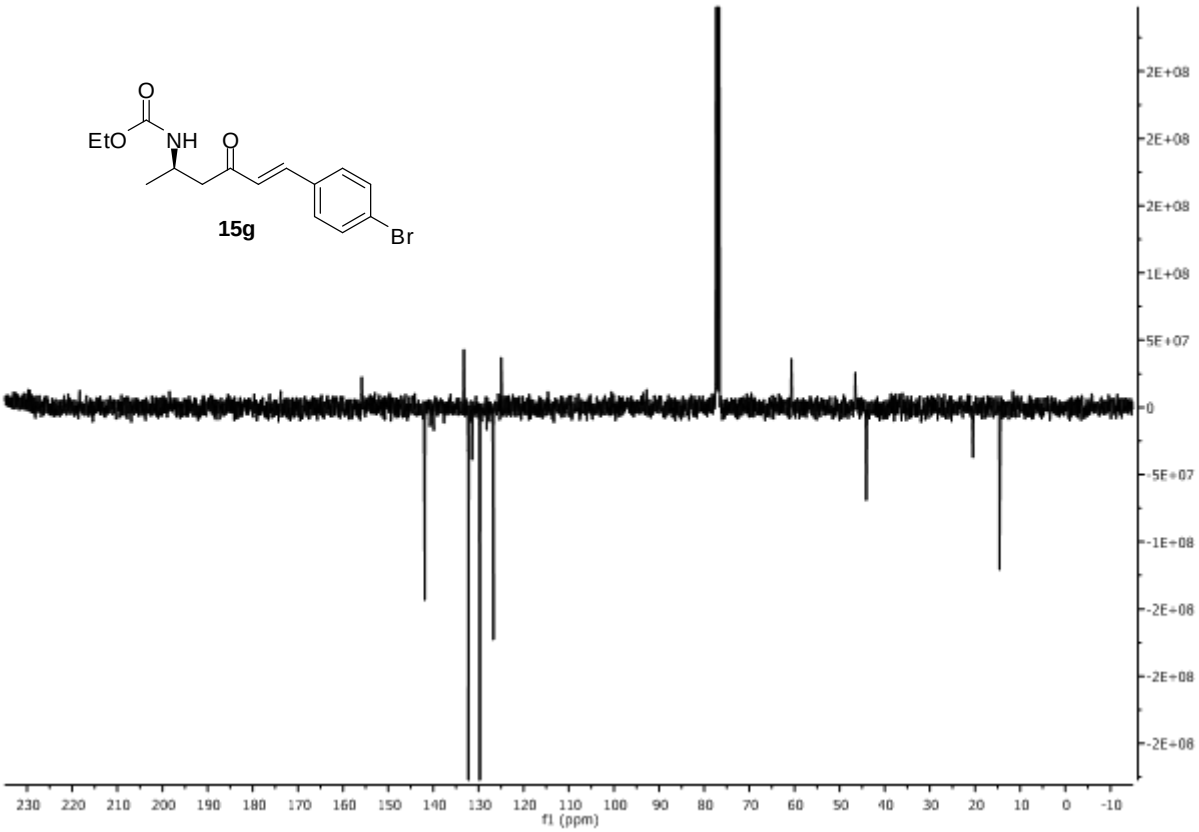
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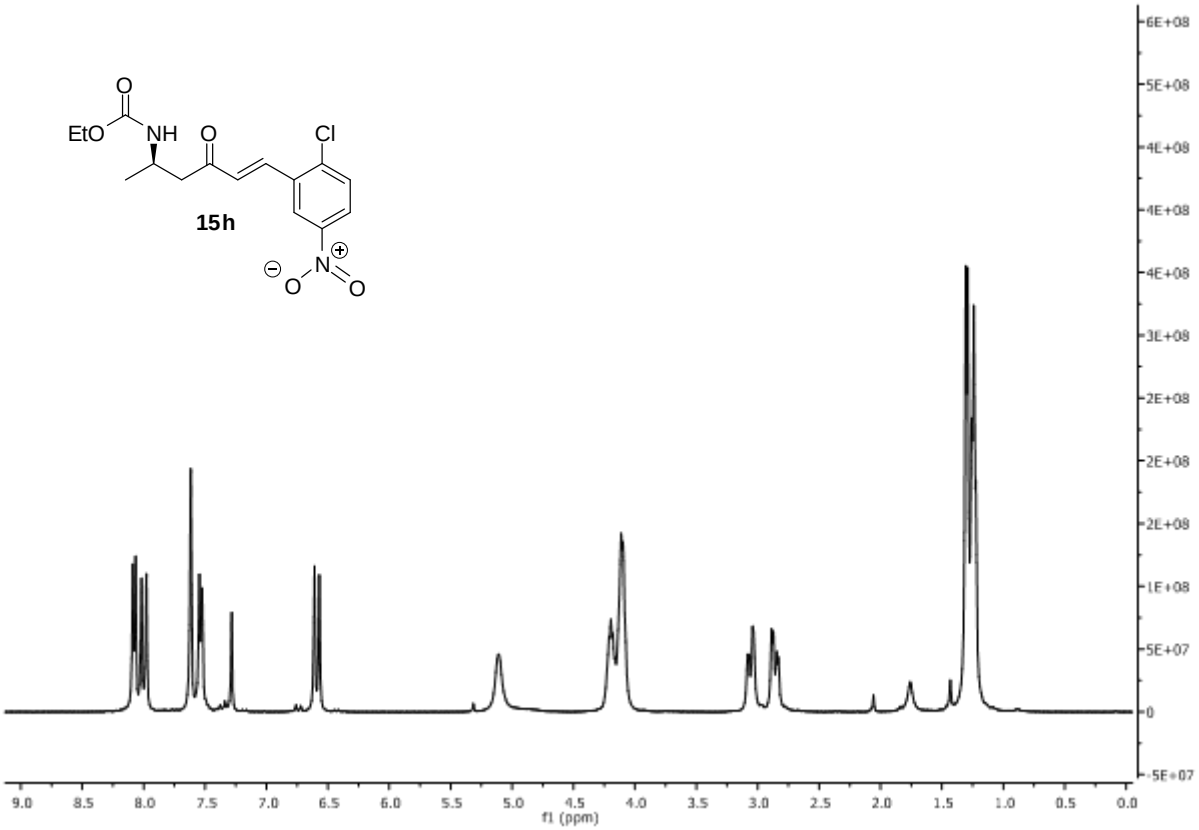
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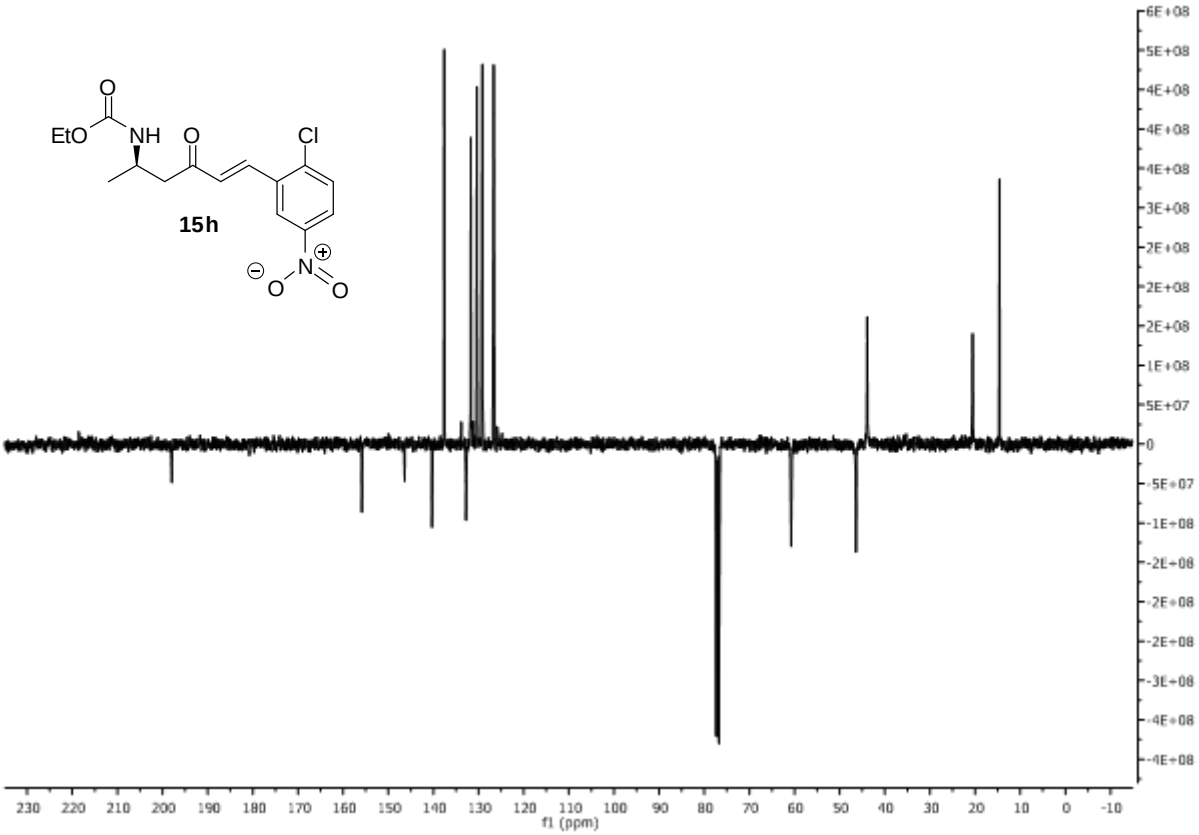
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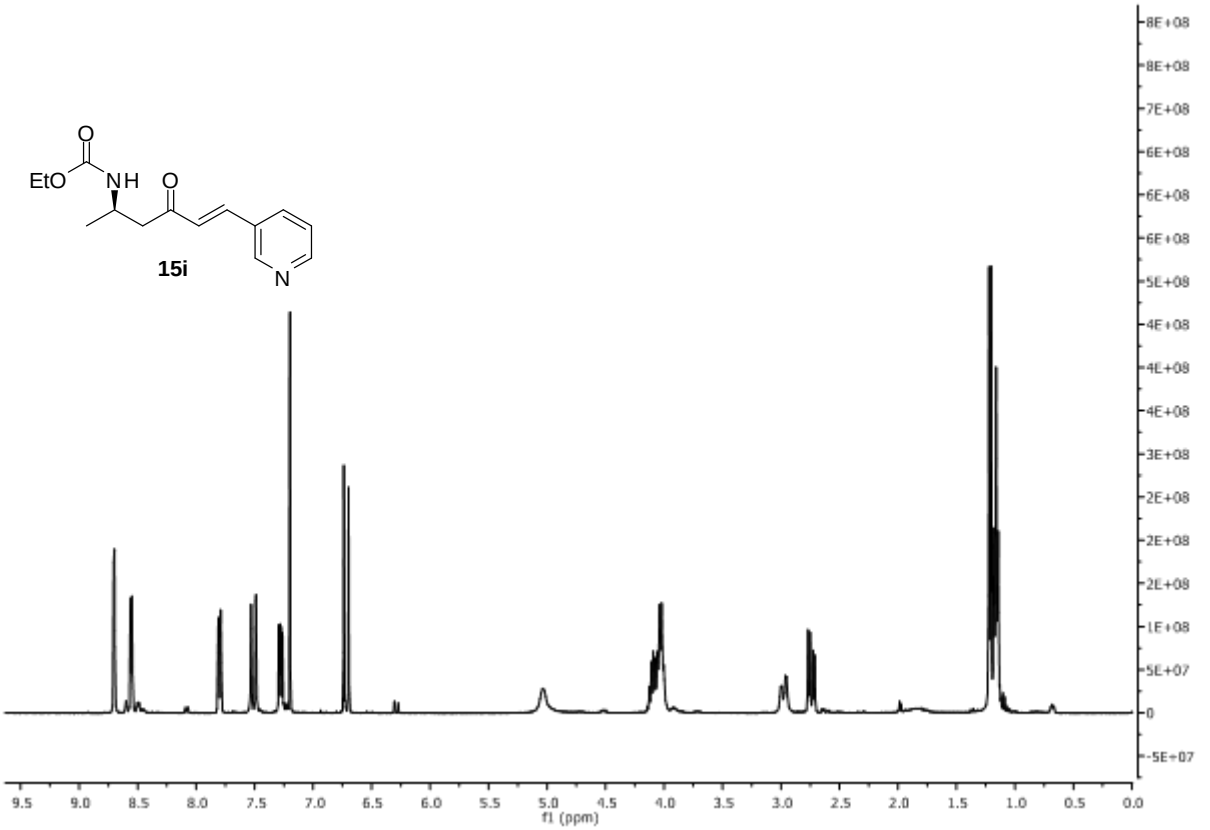
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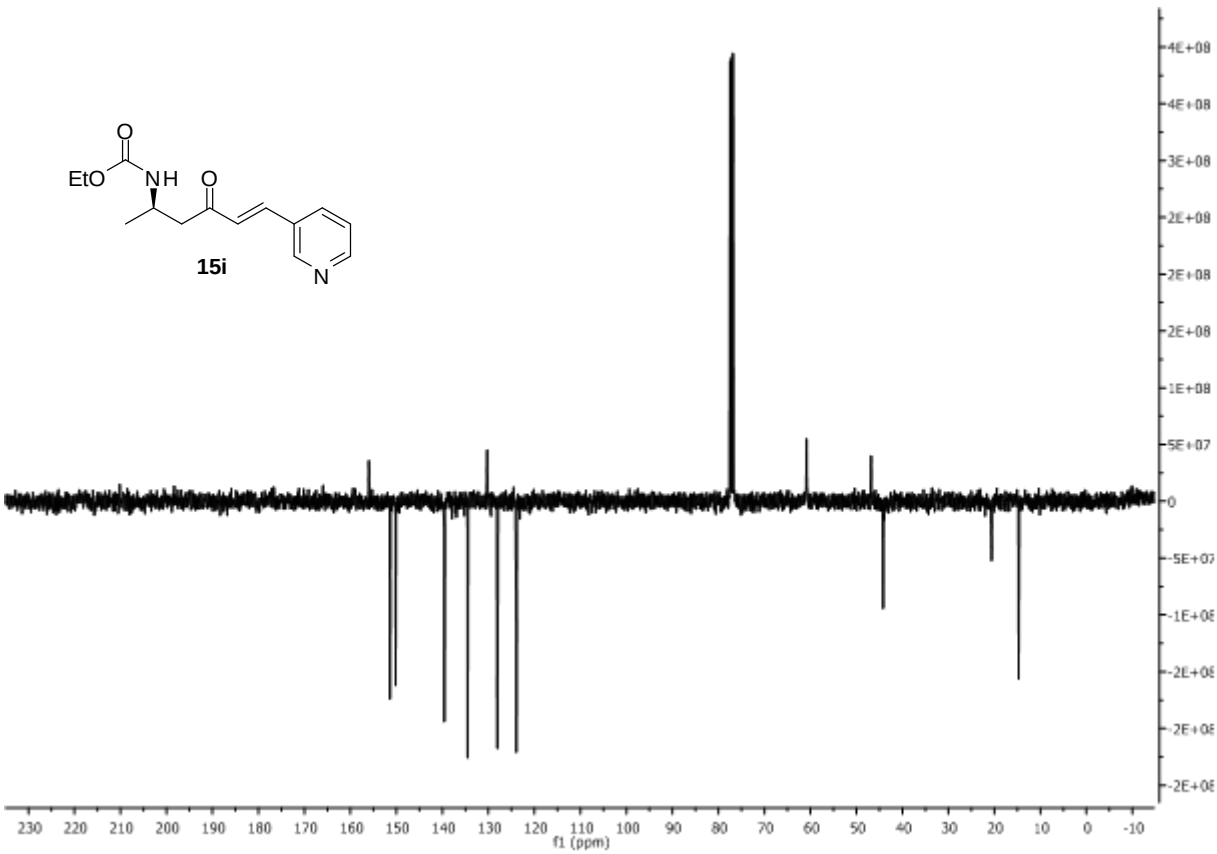
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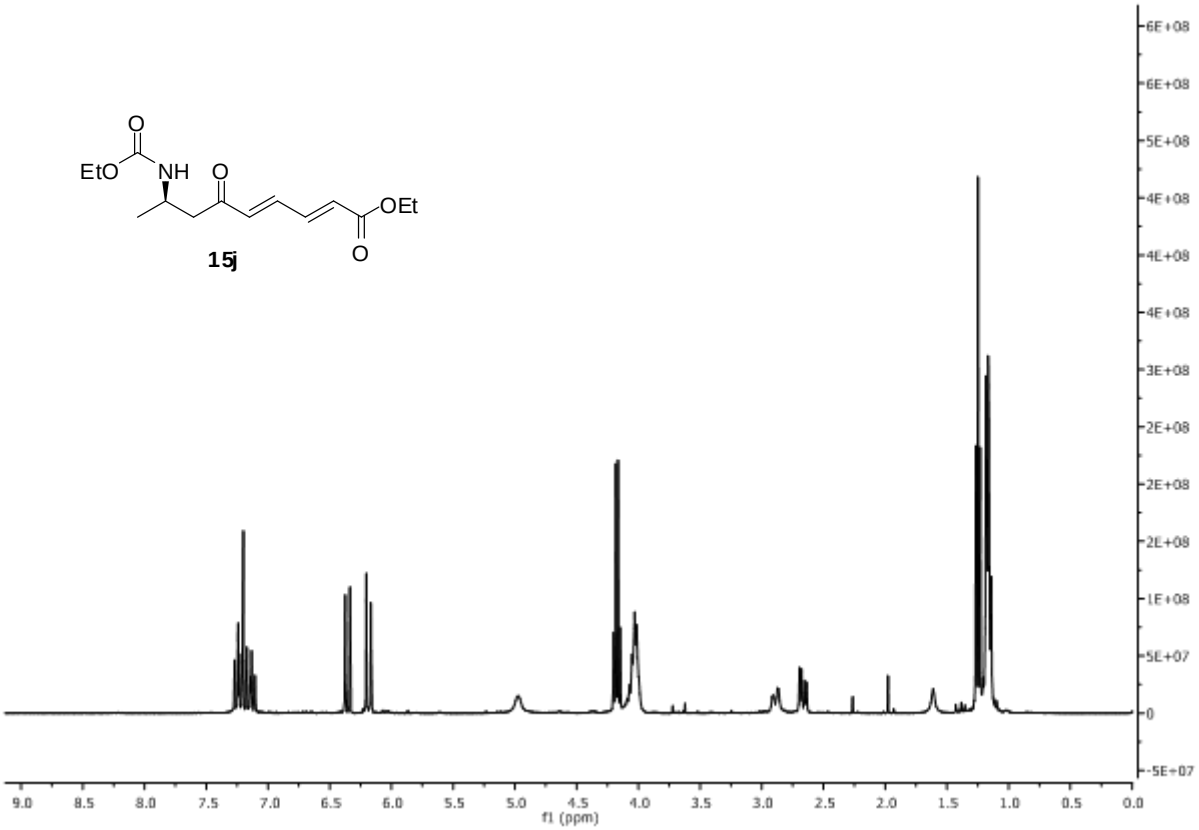
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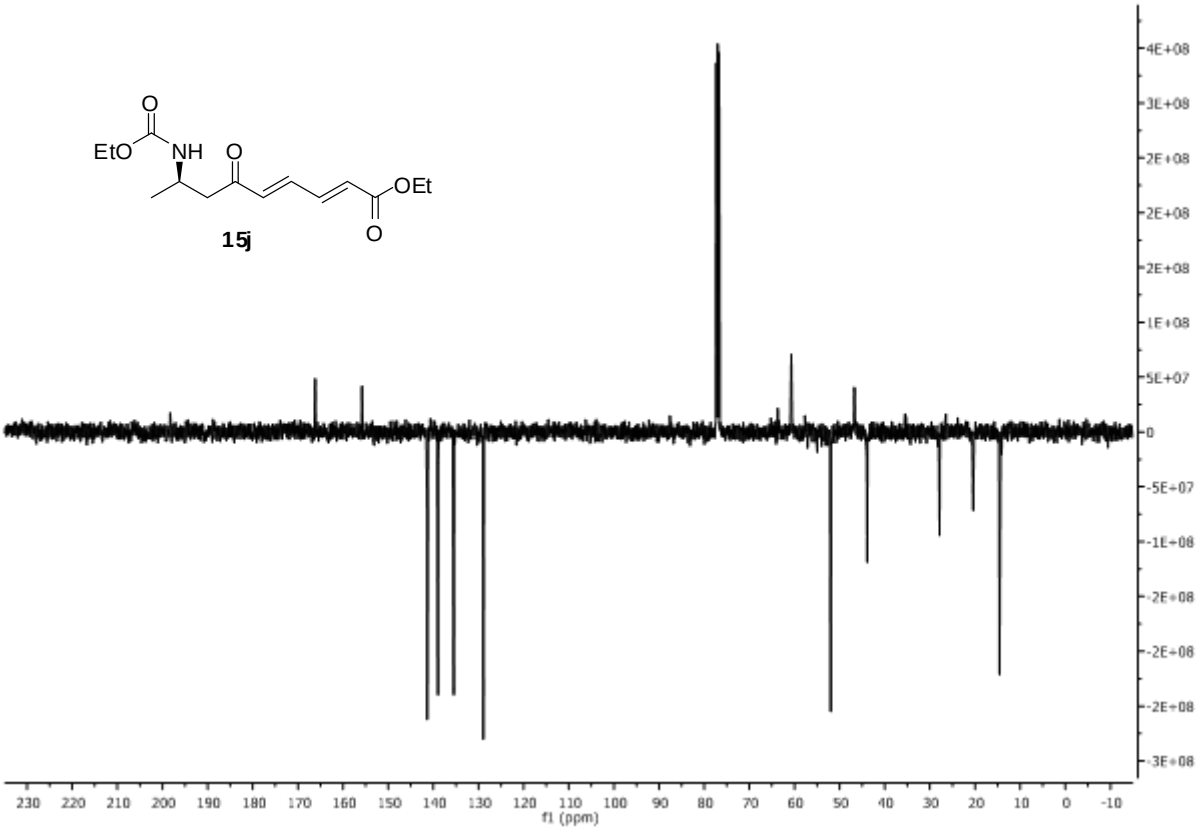
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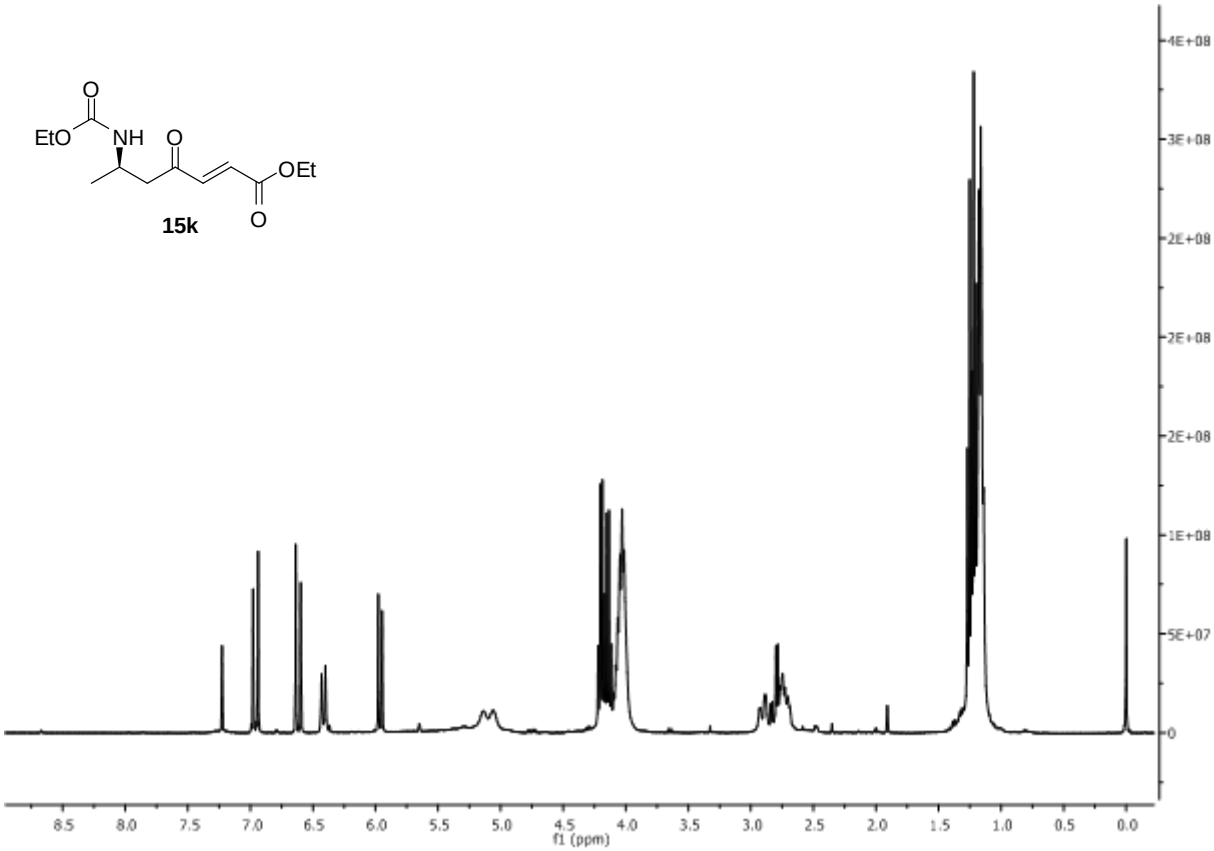
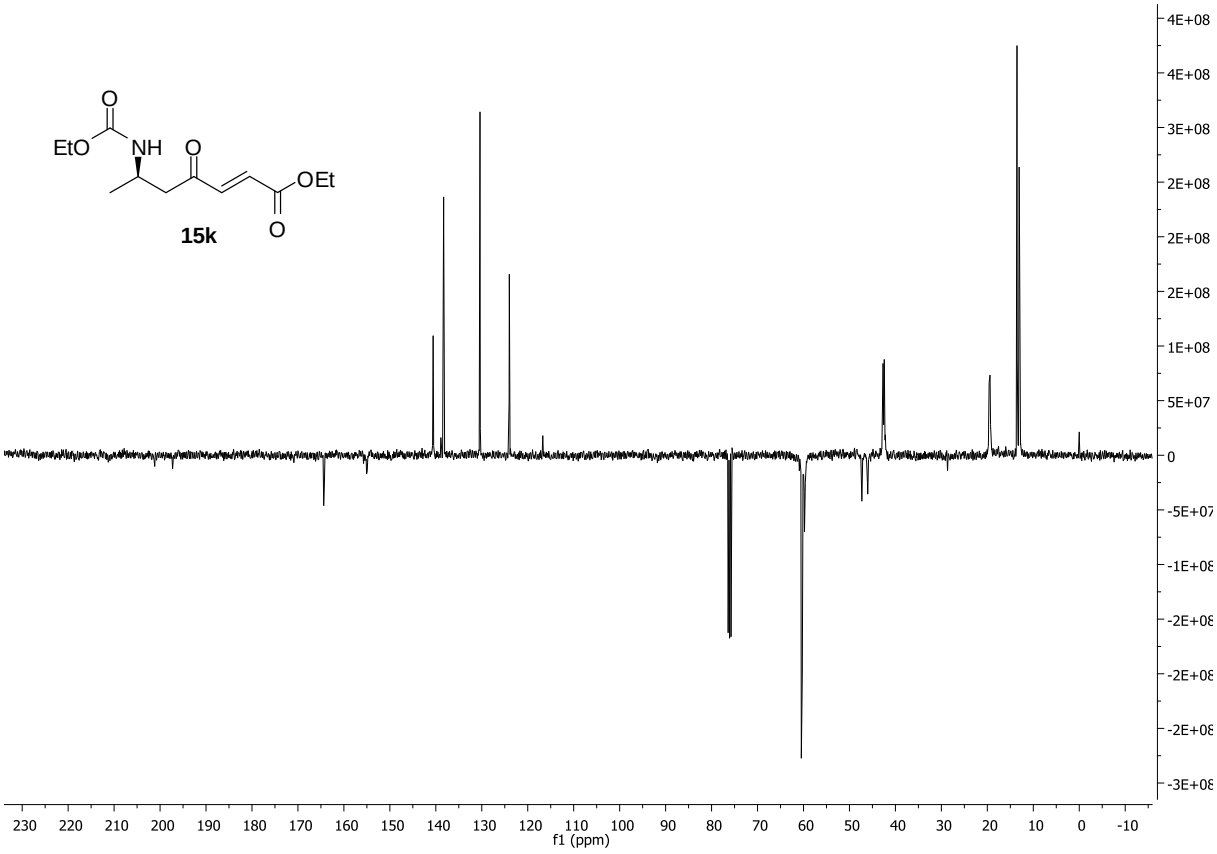
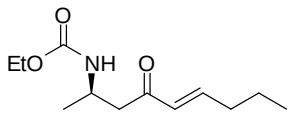
f1 (ppm)

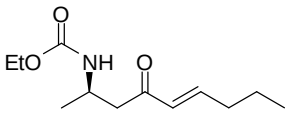

EtO
NH
O
OEt
O
15k
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


EtO
NH
O
OEt
O
15k
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
-1E+08
-2E+08
-2E+08
-2E+08
-3E+08
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
EtO
NH
O

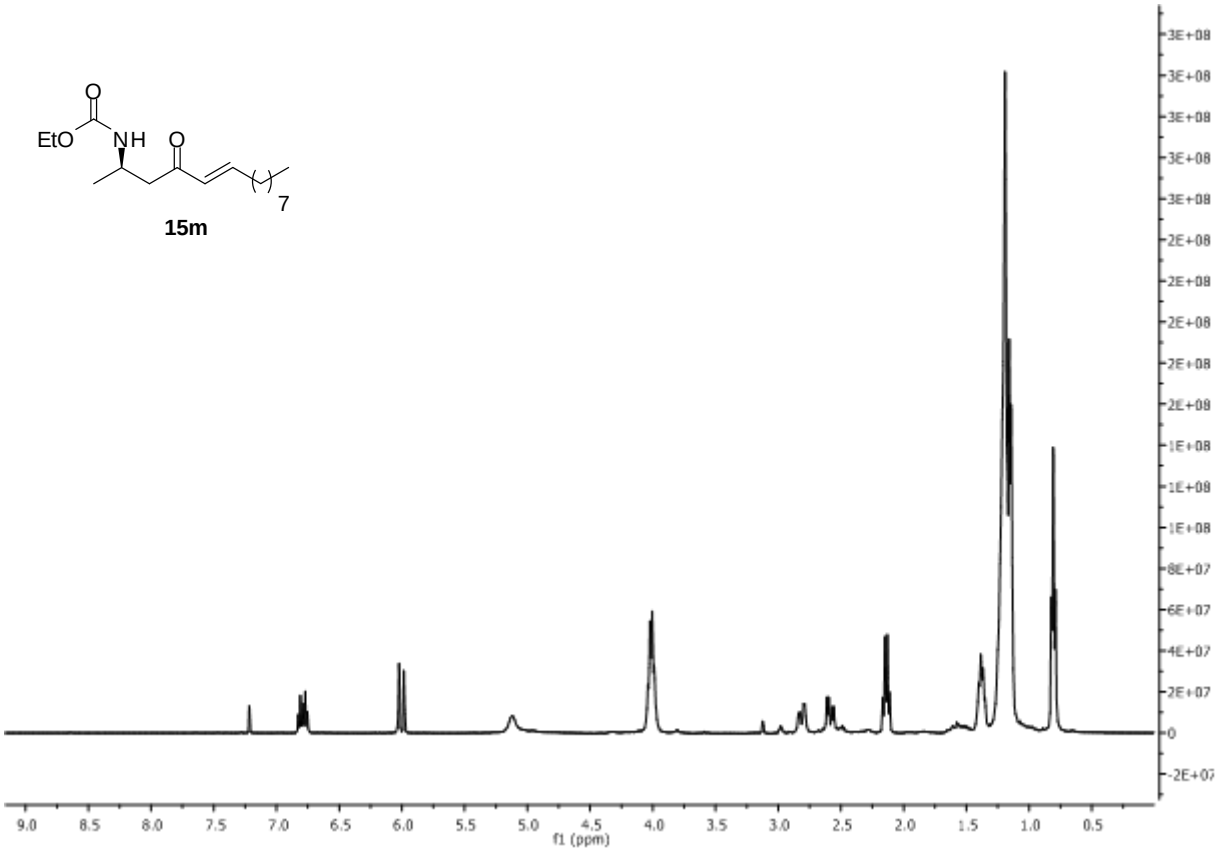
15l

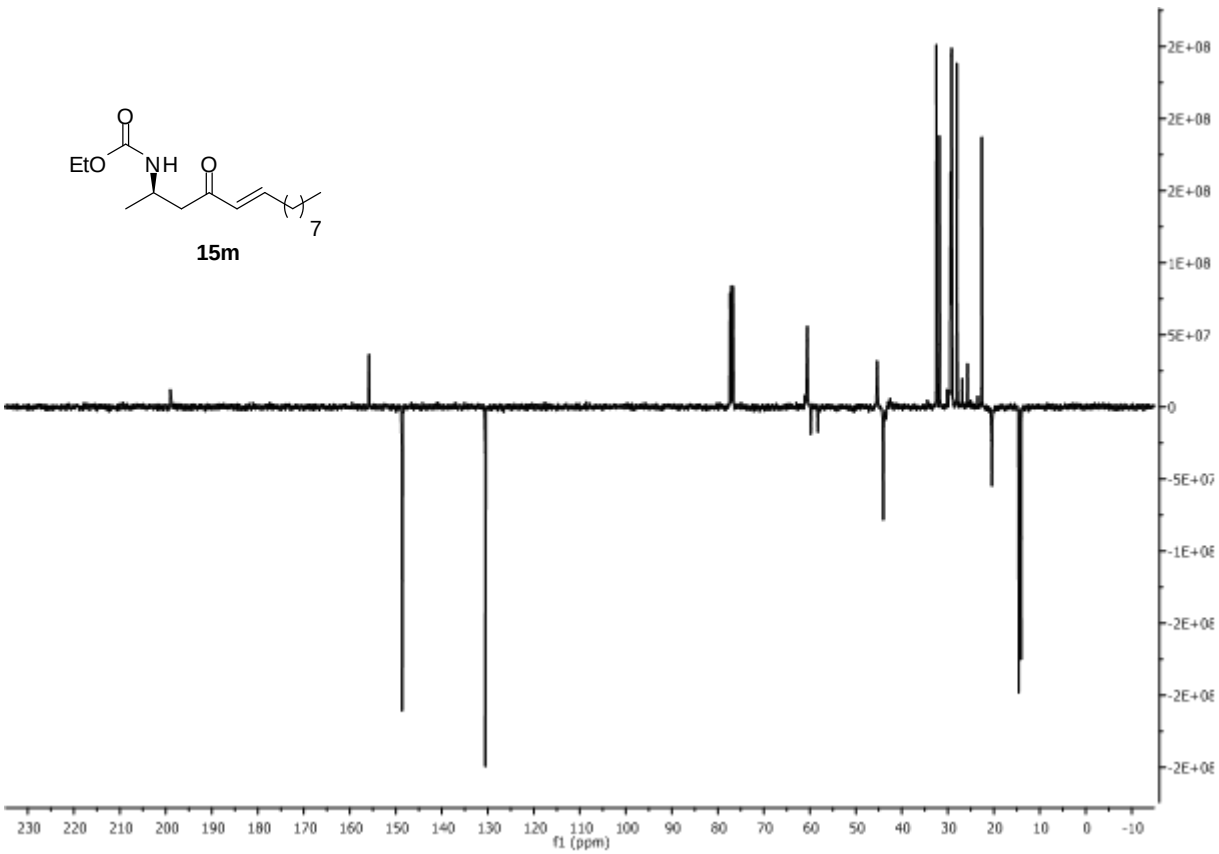
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

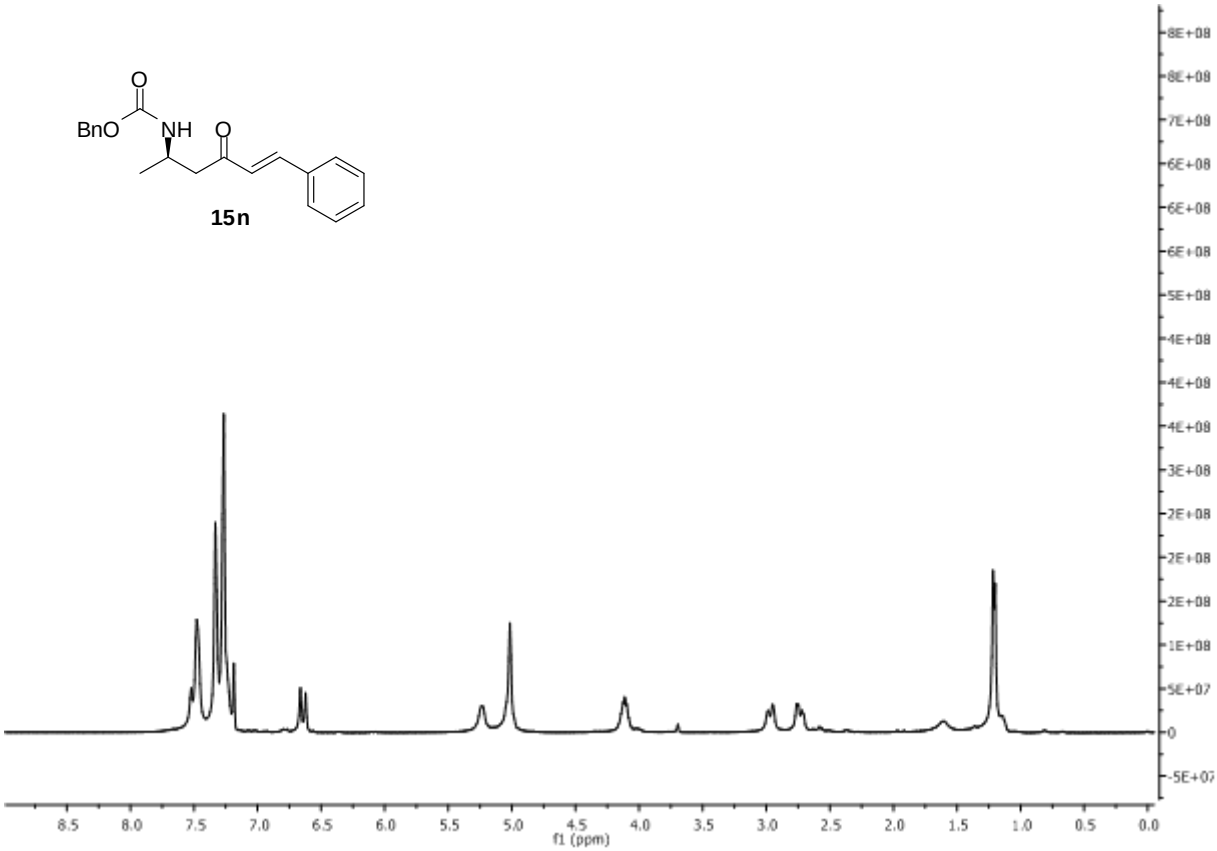

O
EtO
NH
O

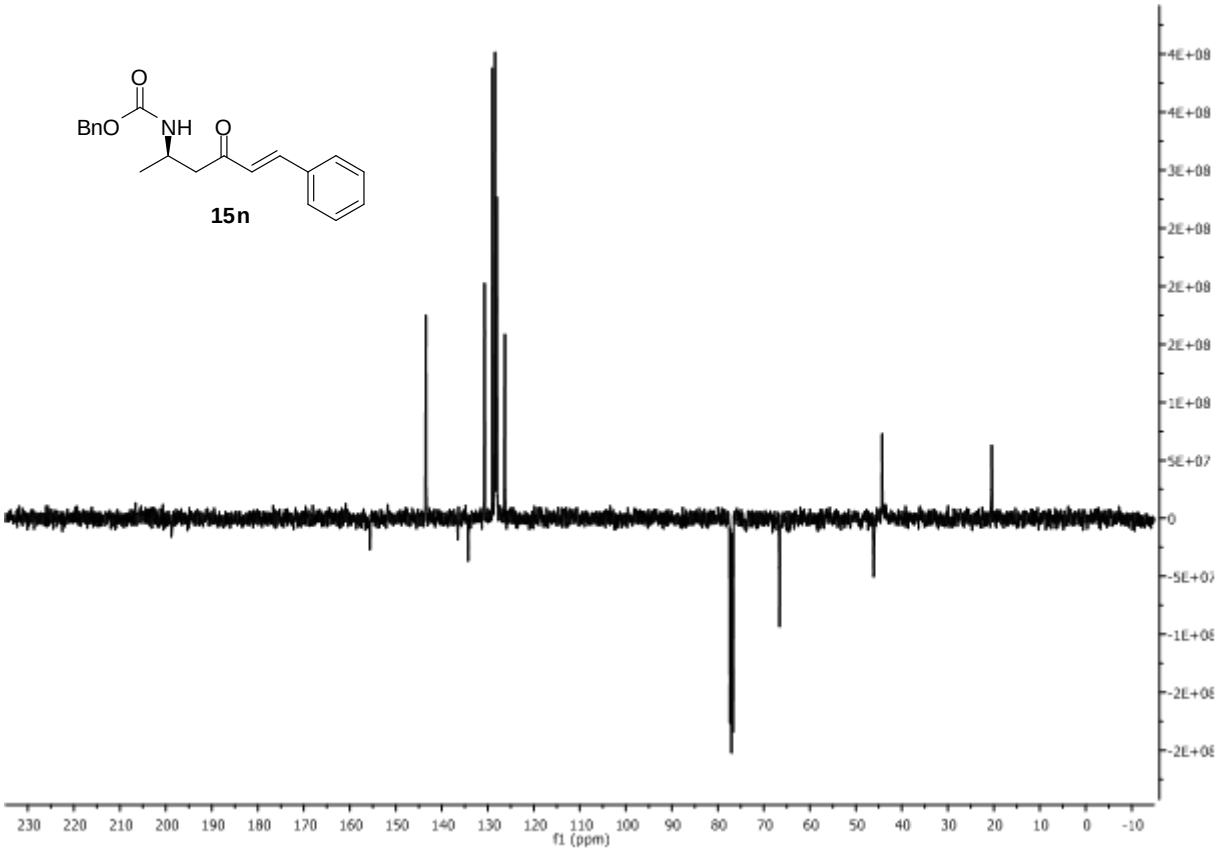
15l

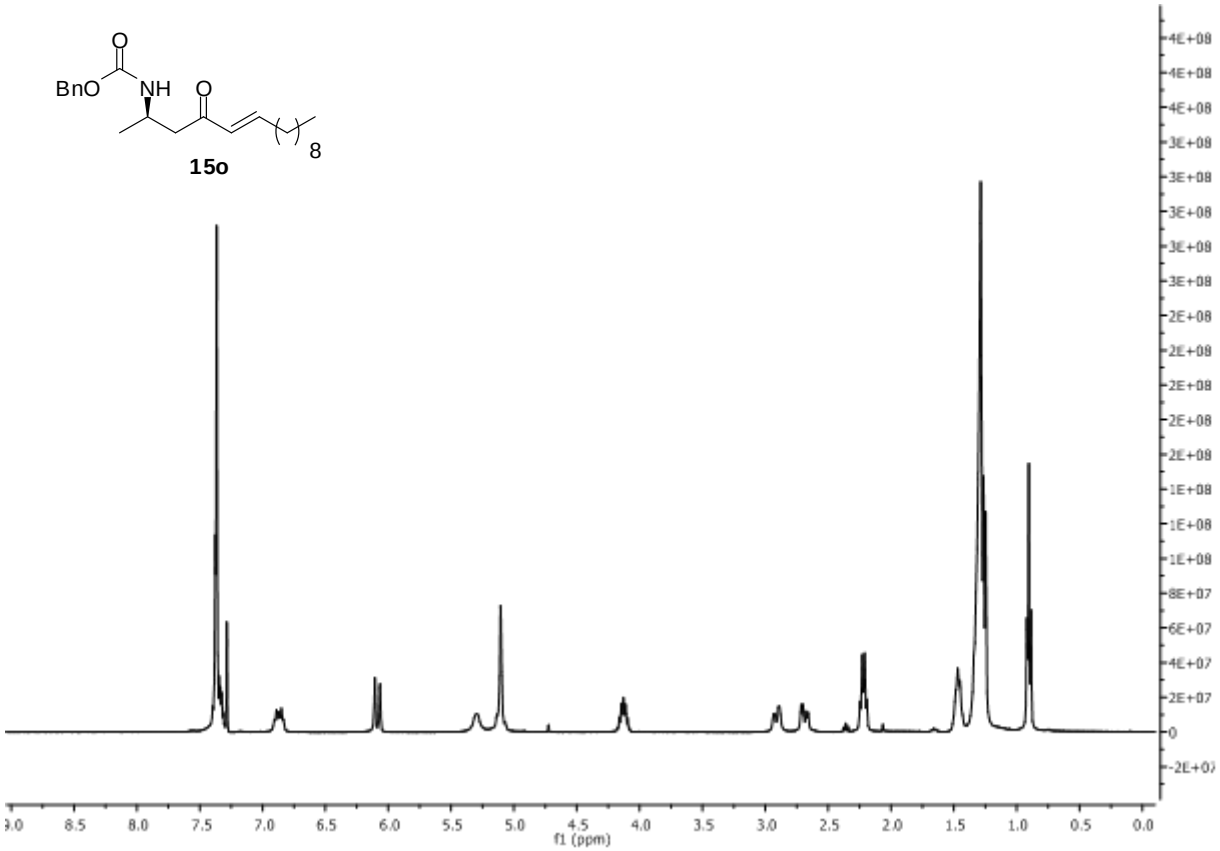
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
-1E+08
-2E+08
-2E+08
-2E+08
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

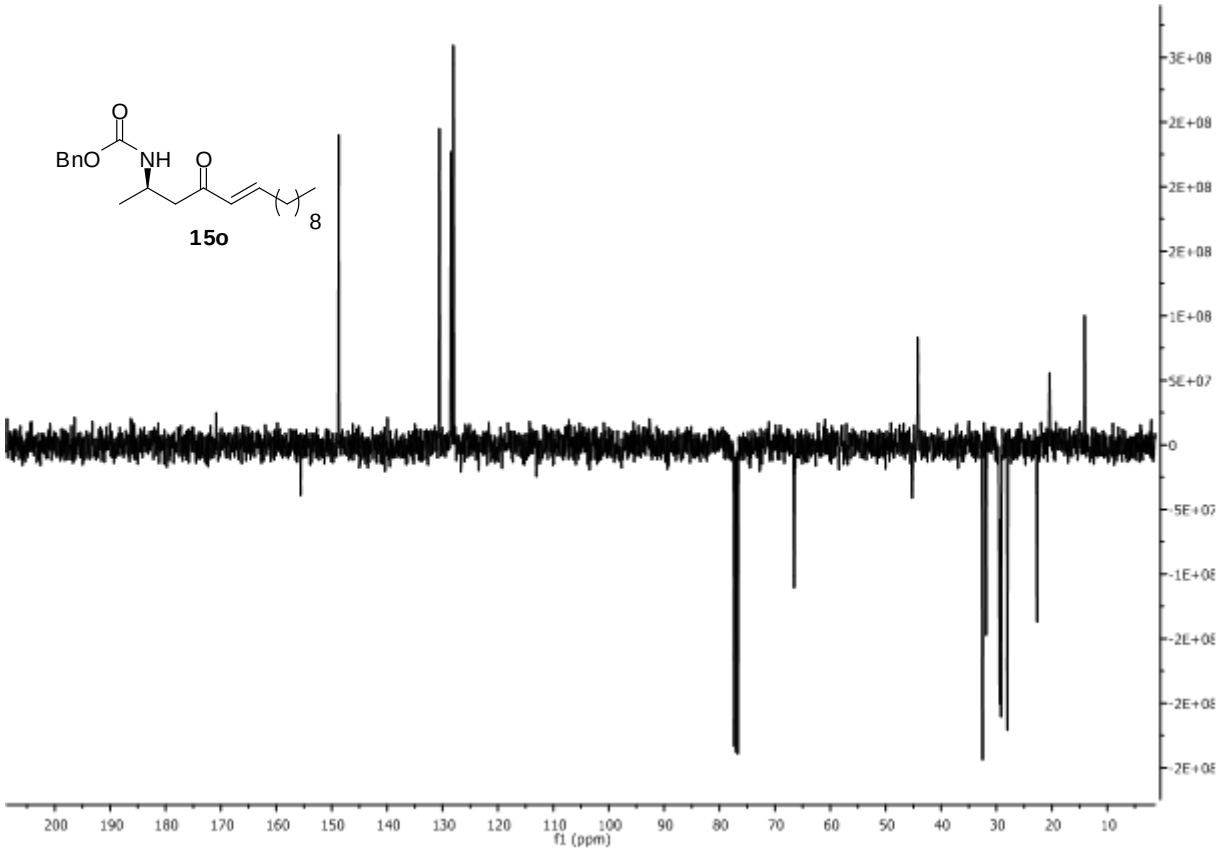

EtO
NH
O
O
7
15m
f1 (ppm)

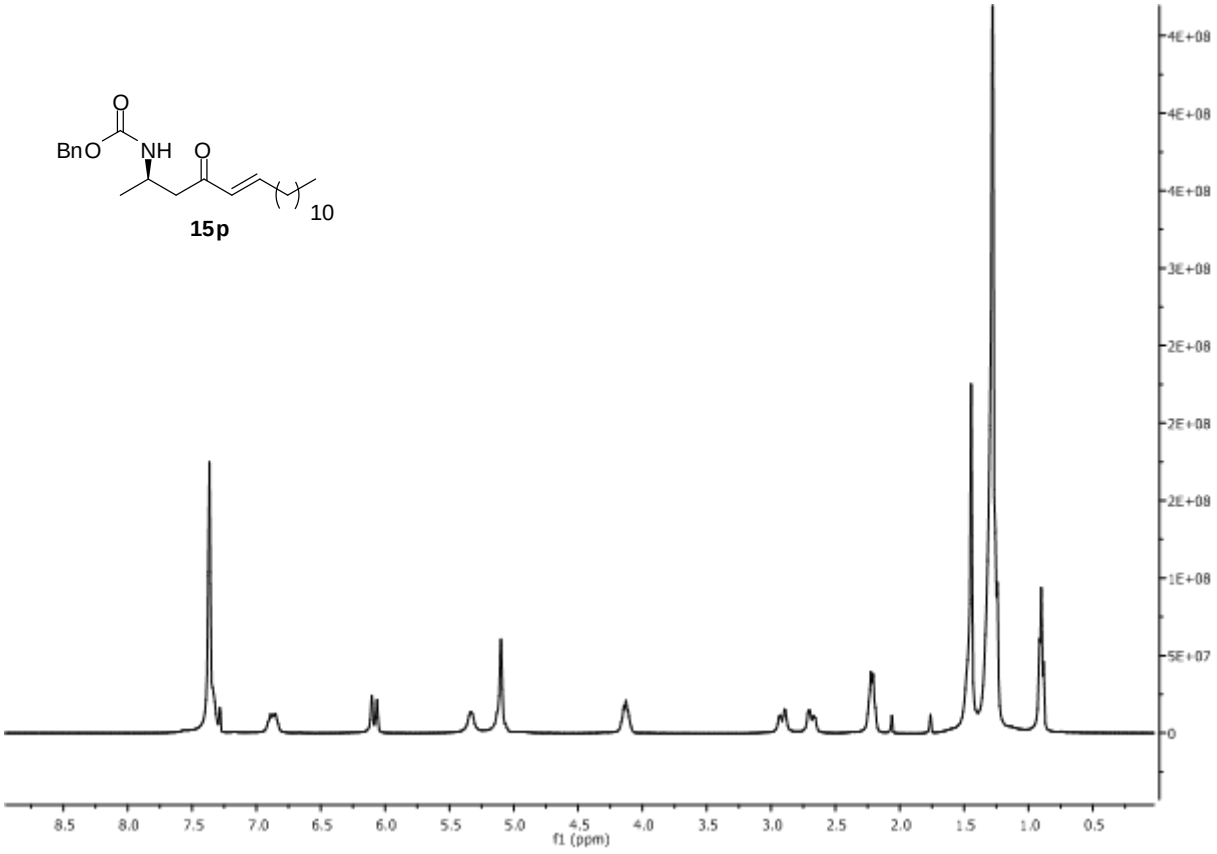

EtO
NH
O
O
7
15m
f1 (ppm)

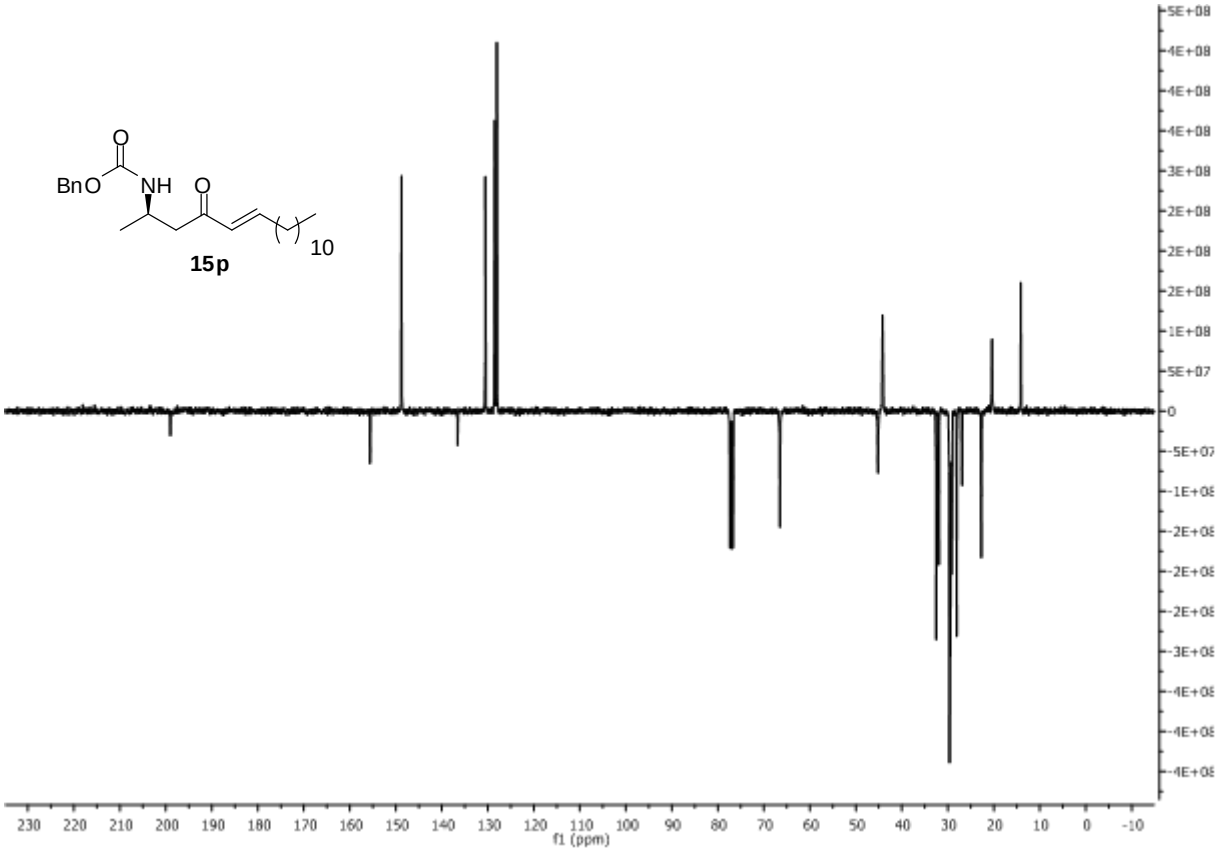

O
BnO
NH
O
15n
f1 (ppm)

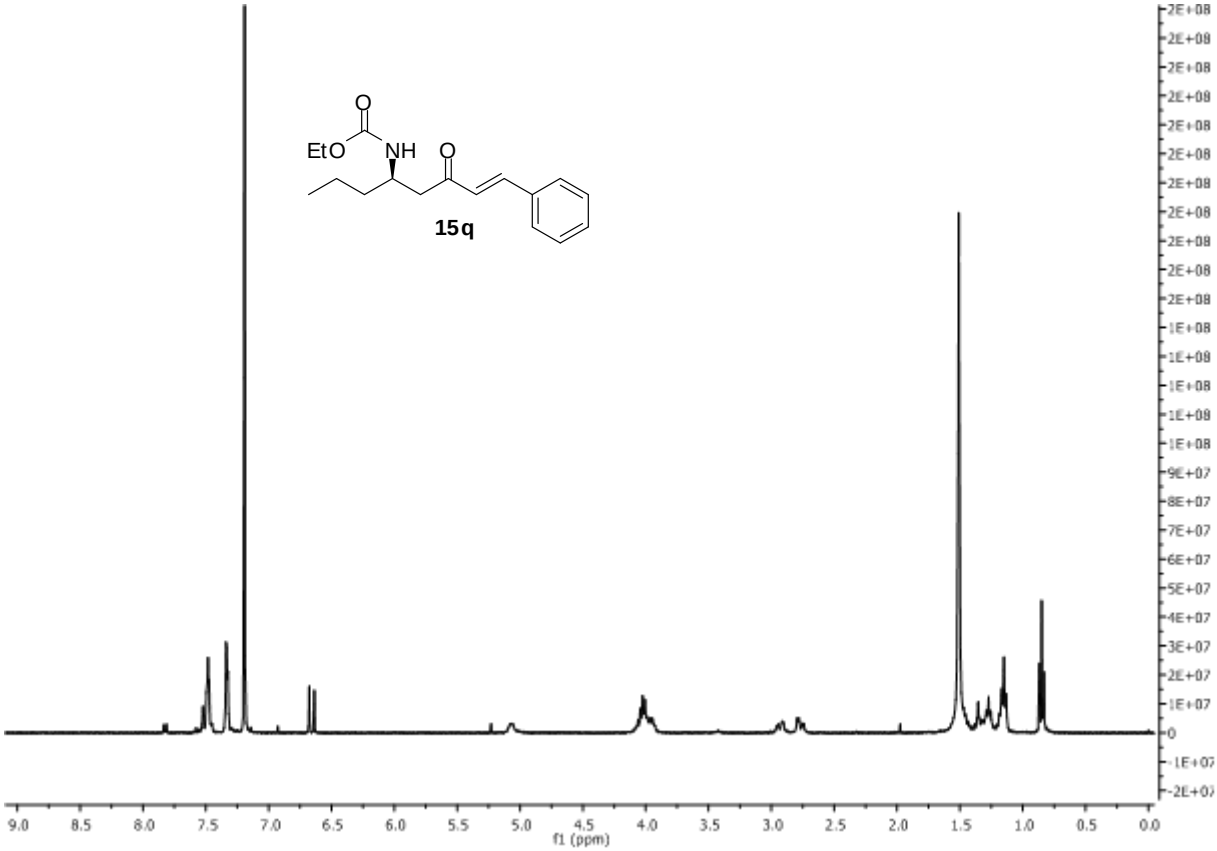

O
BnO
NH
O
15n
f1 (ppm)

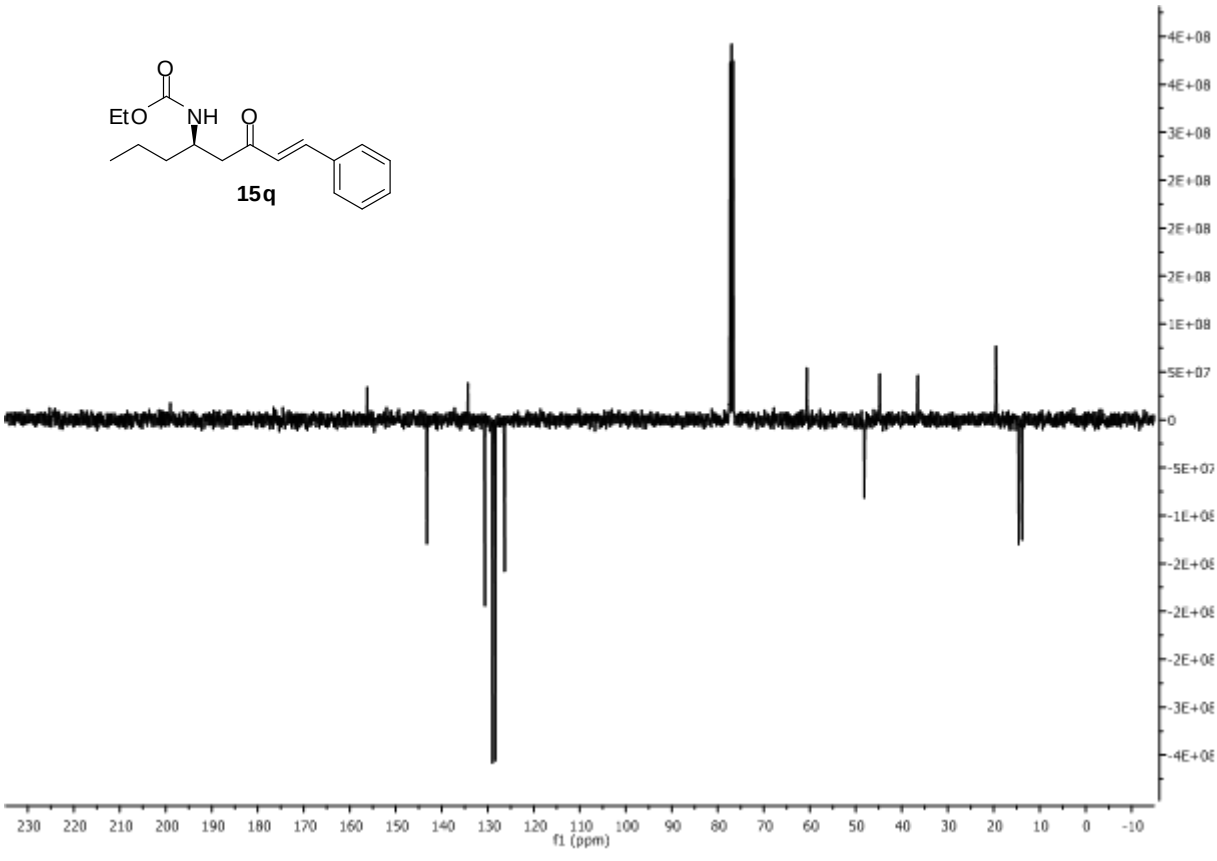

BnO
NH
O
O
8
15o
f1 (ppm)

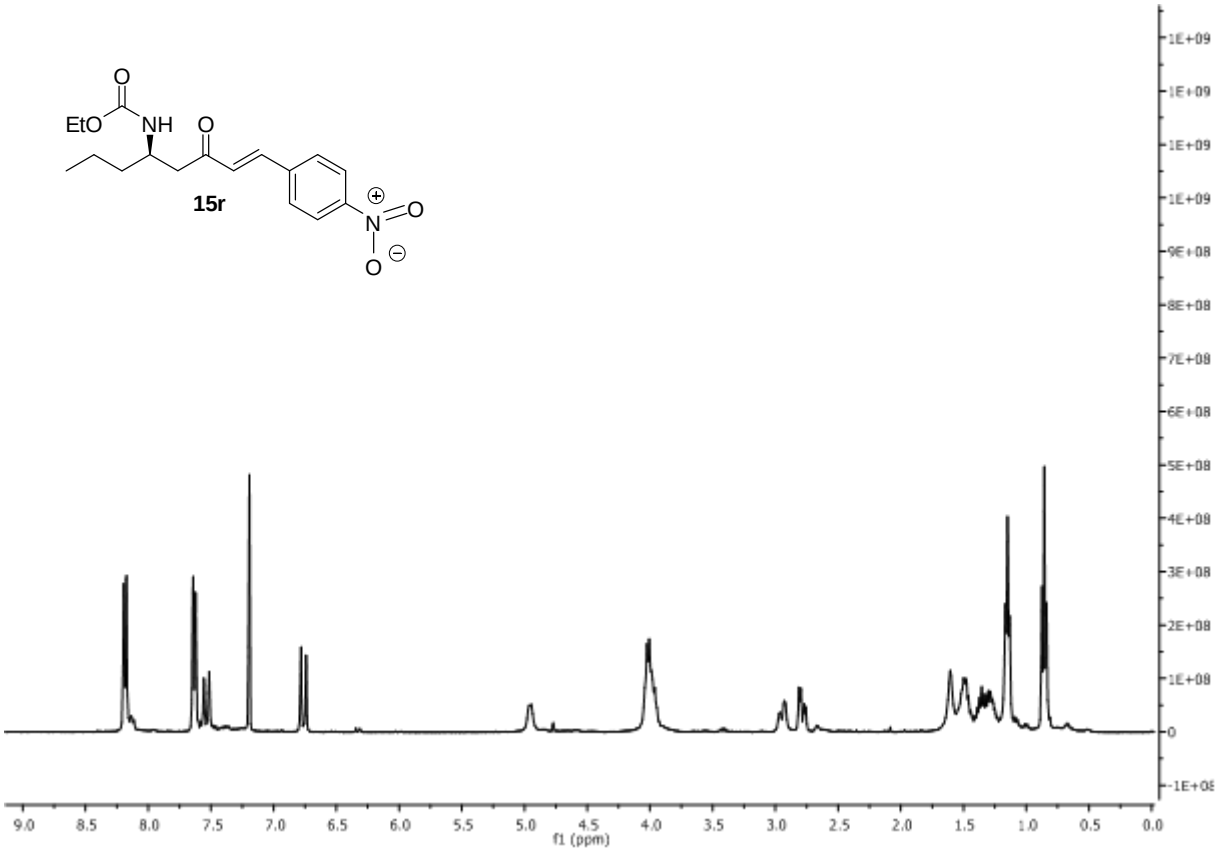

BnO
NH
O
O
8
15o
f1 (ppm)

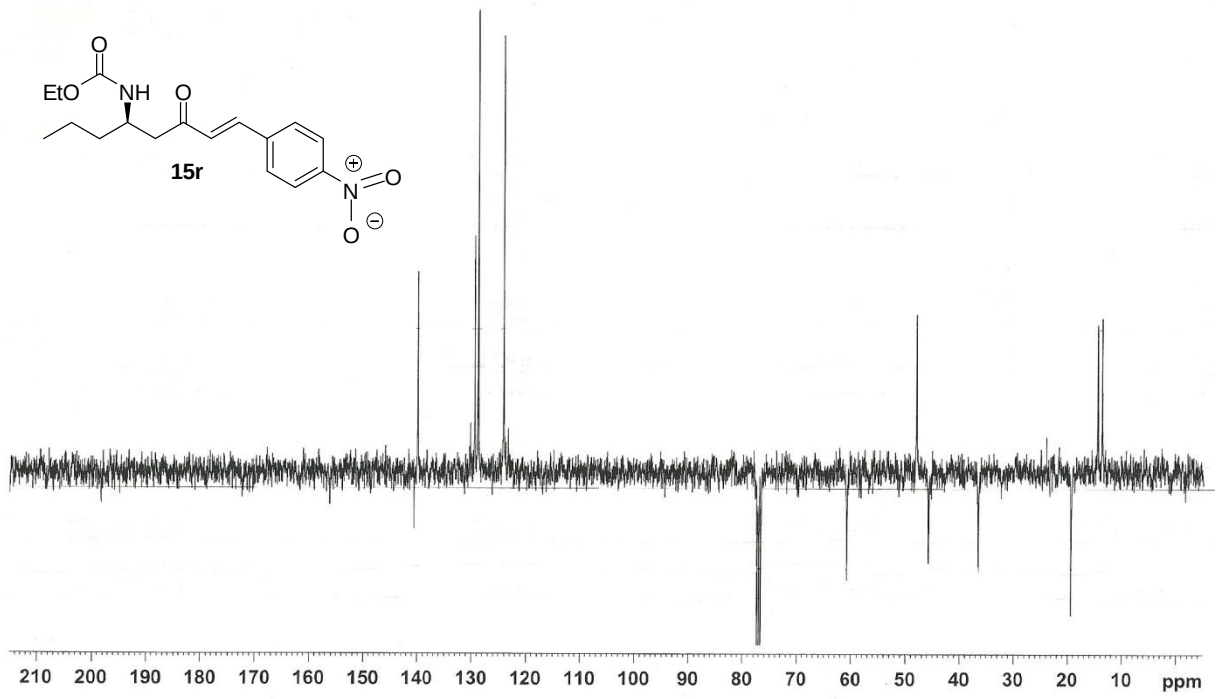

BnO
NH
O
O
10
15p
f1 (ppm)

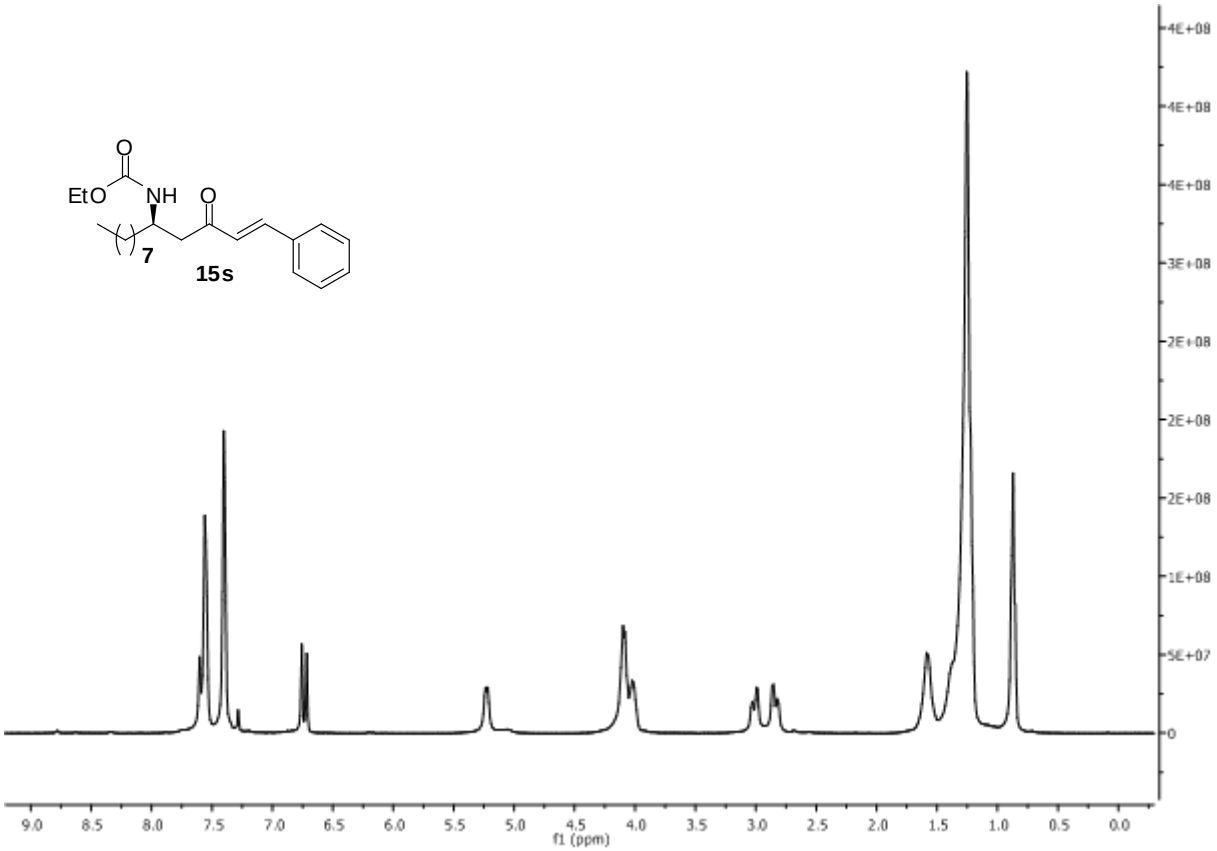

BnO
NH
O
O
10
15p
f1 (ppm)

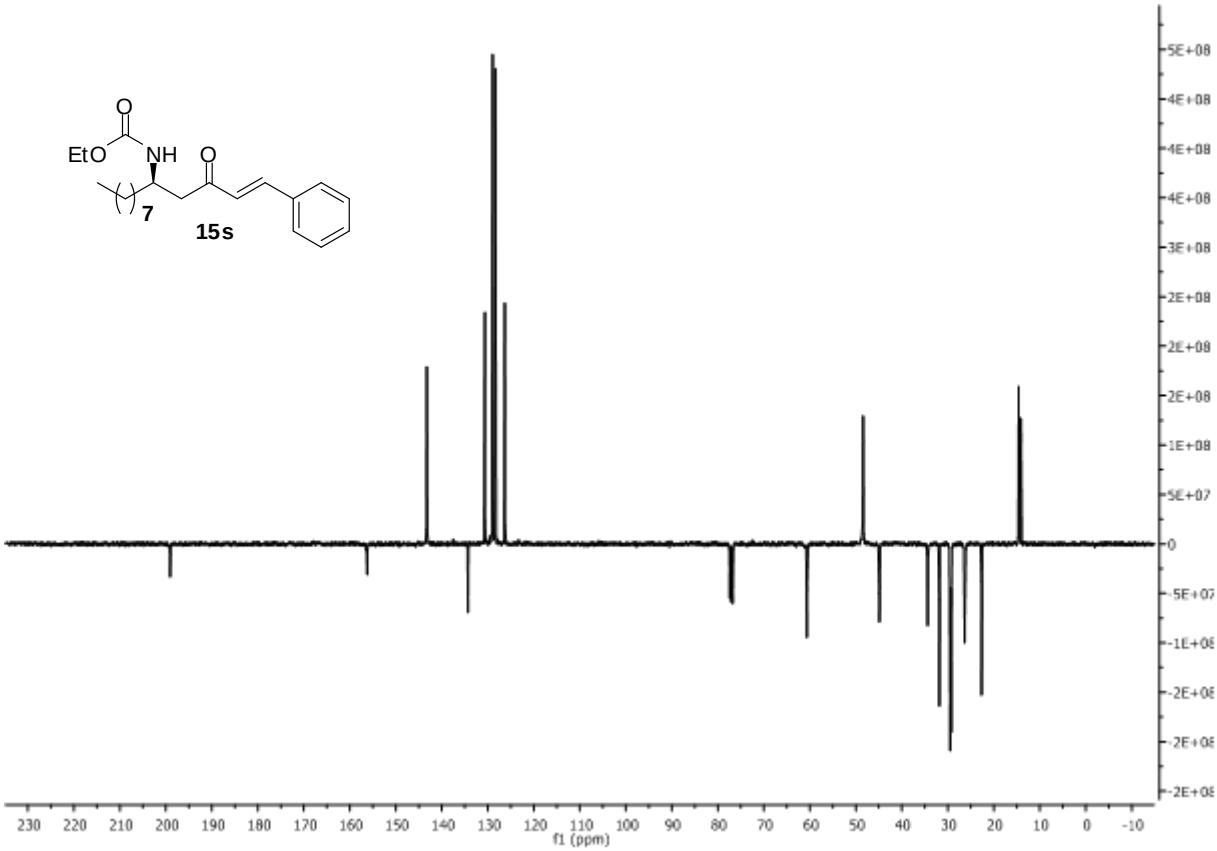

EtO
NH
O
O
15q
f1 (ppm)

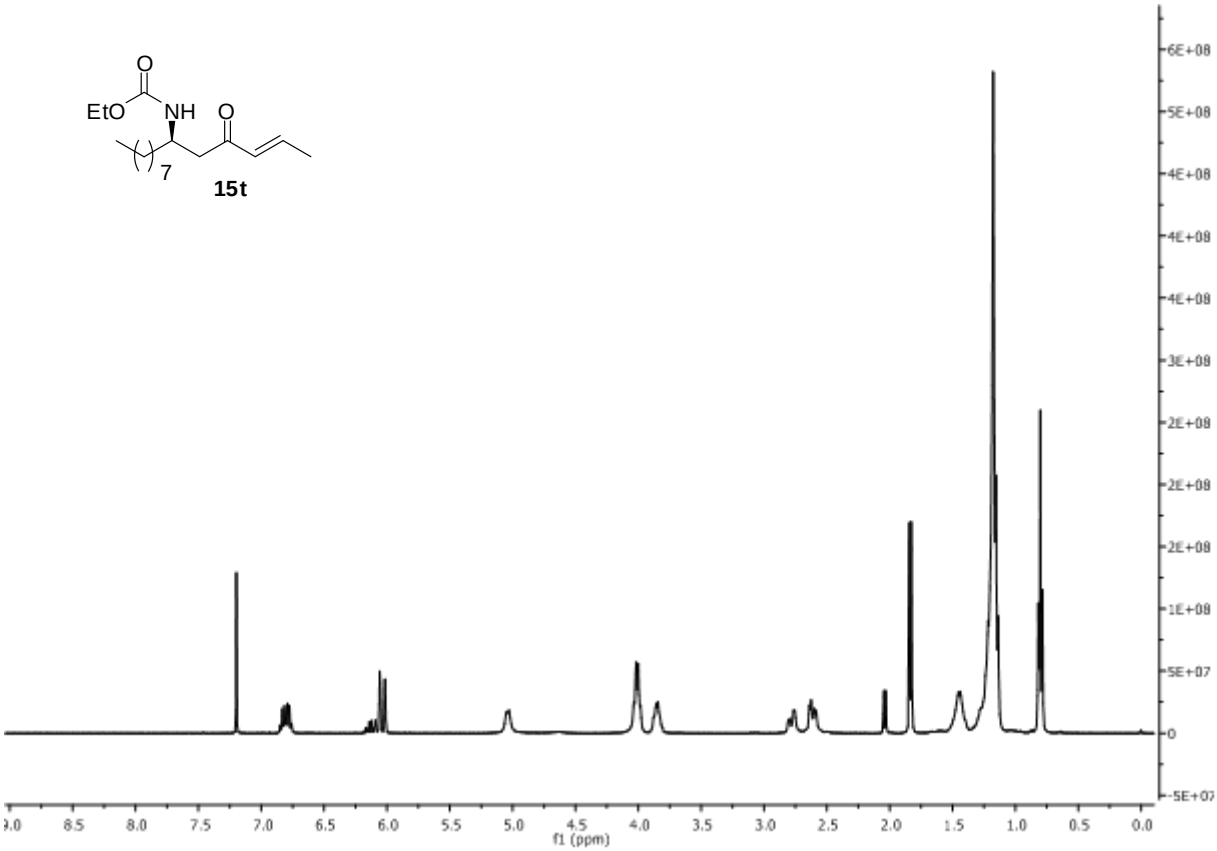

EtO
NH
O
O
15q
f1 (ppm)

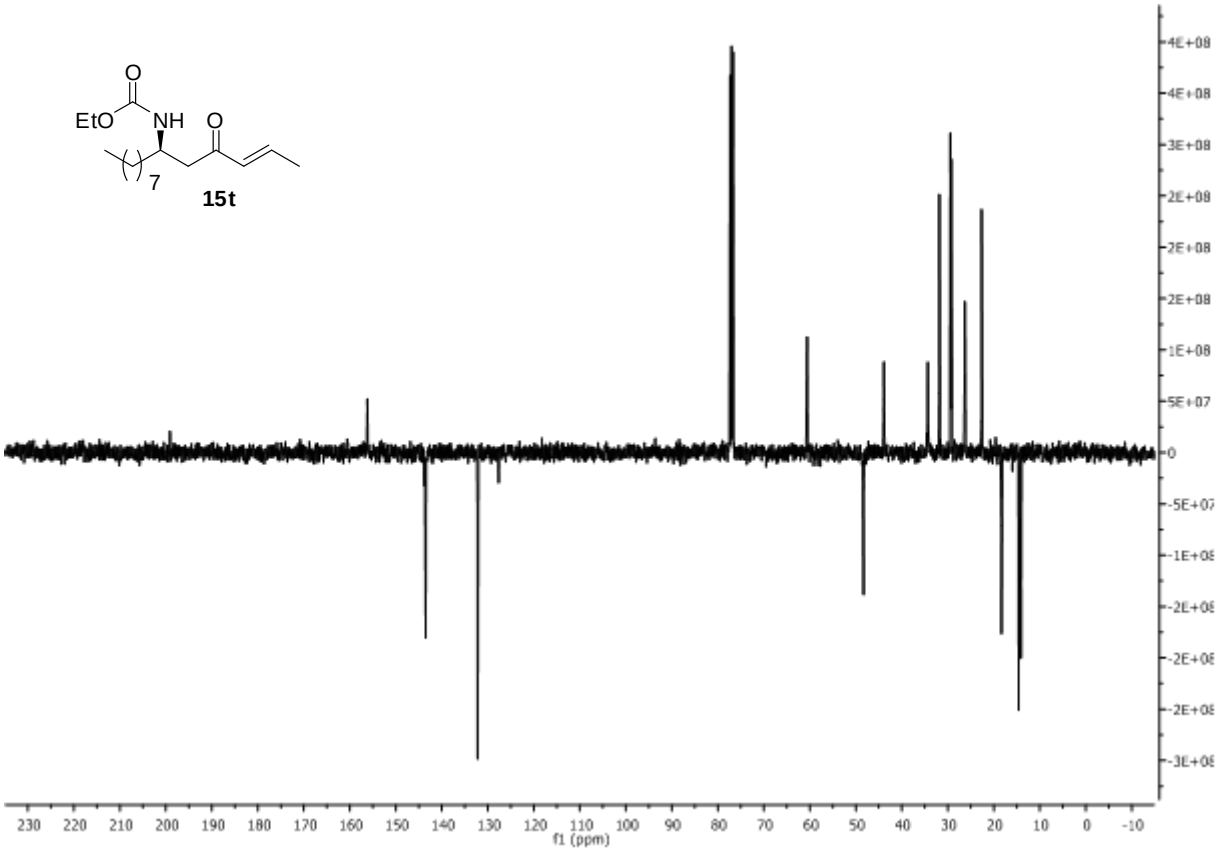

EtO
NH
O
O
15r
O
N
O
O
f1 (ppm)

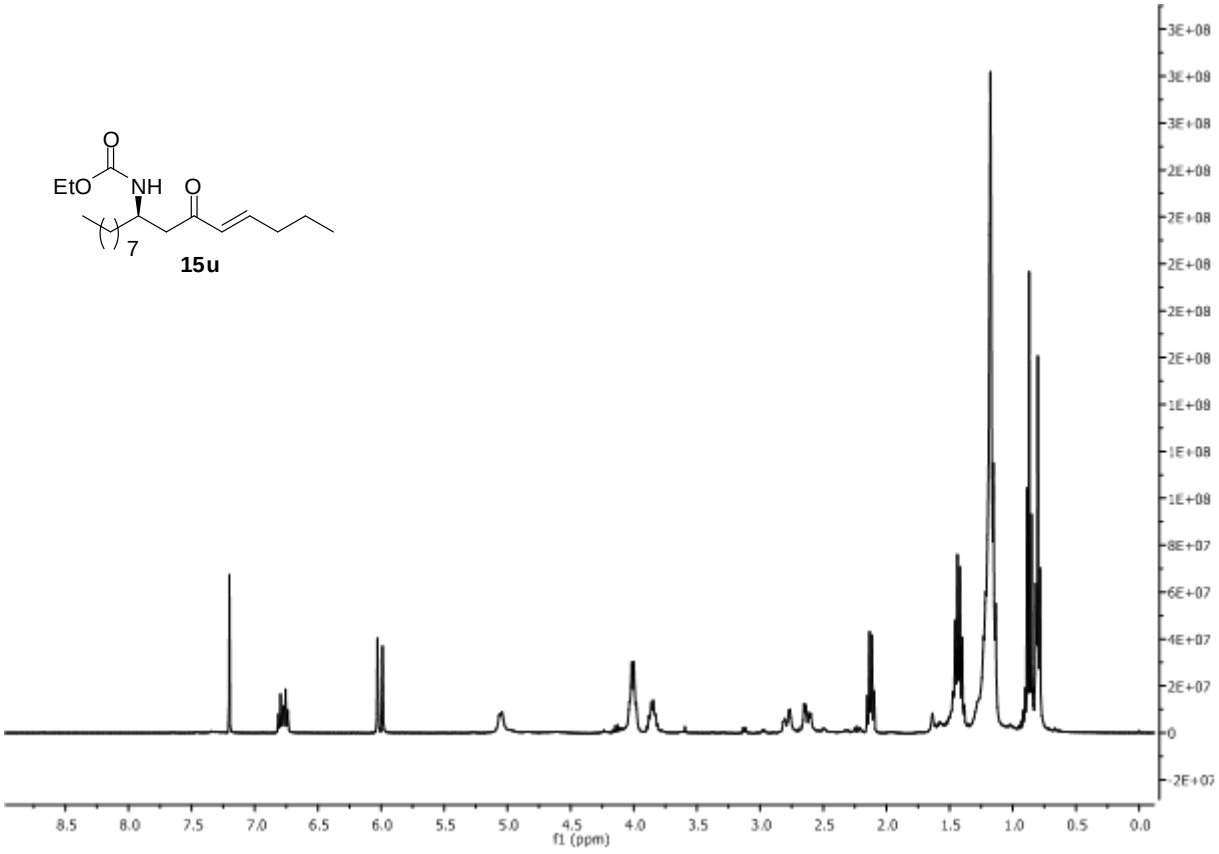

EtO
NH
O
O
15r
O
N
O
O
ppm

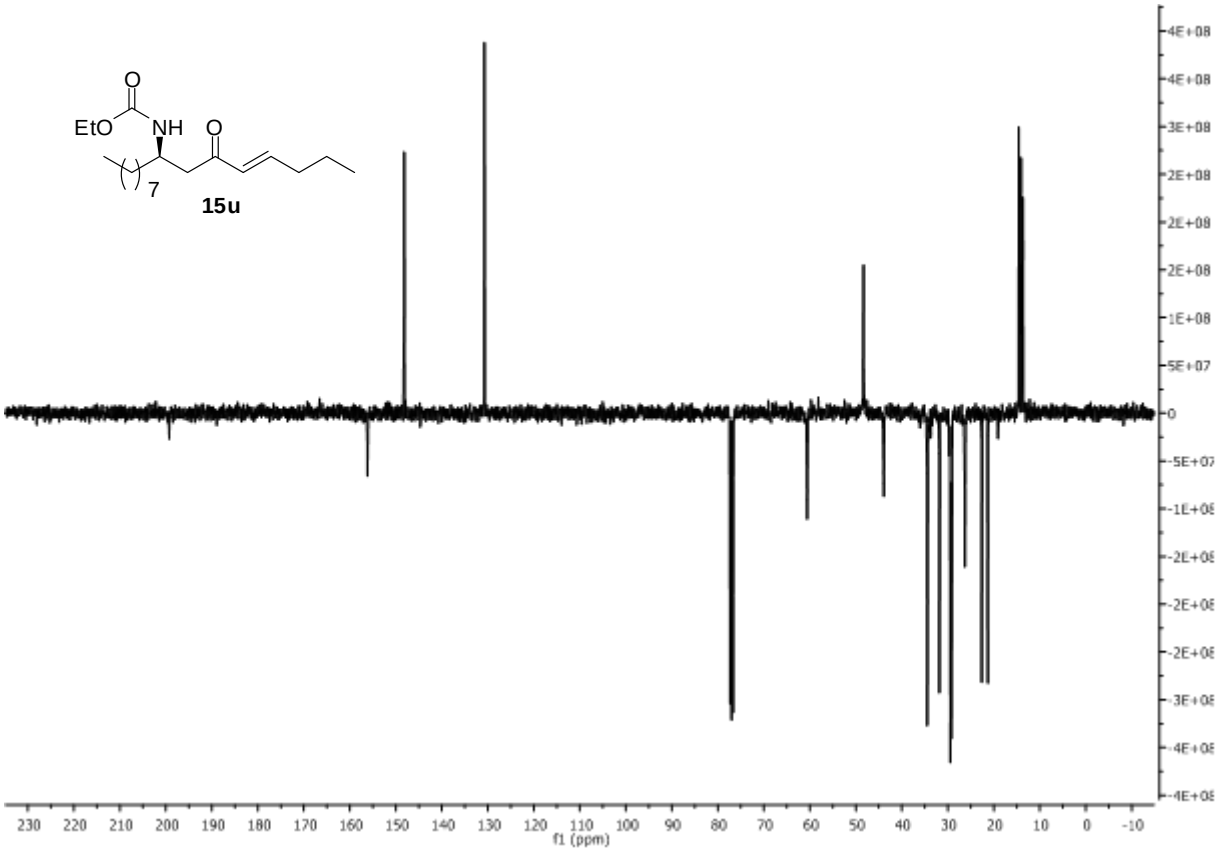

EtO
NH
O
O
7
15s
f1 (ppm)

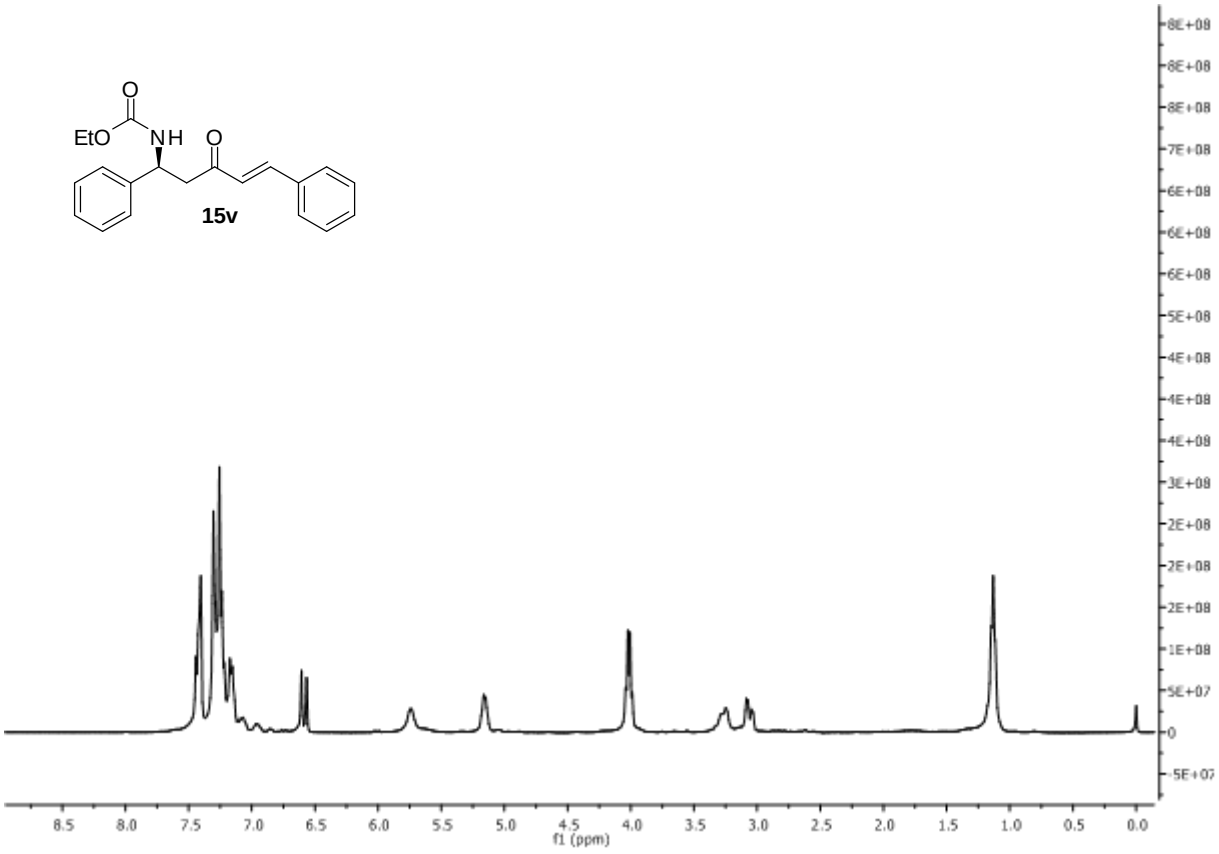

EtO
NH
O
O
7
15s
f1 (ppm)

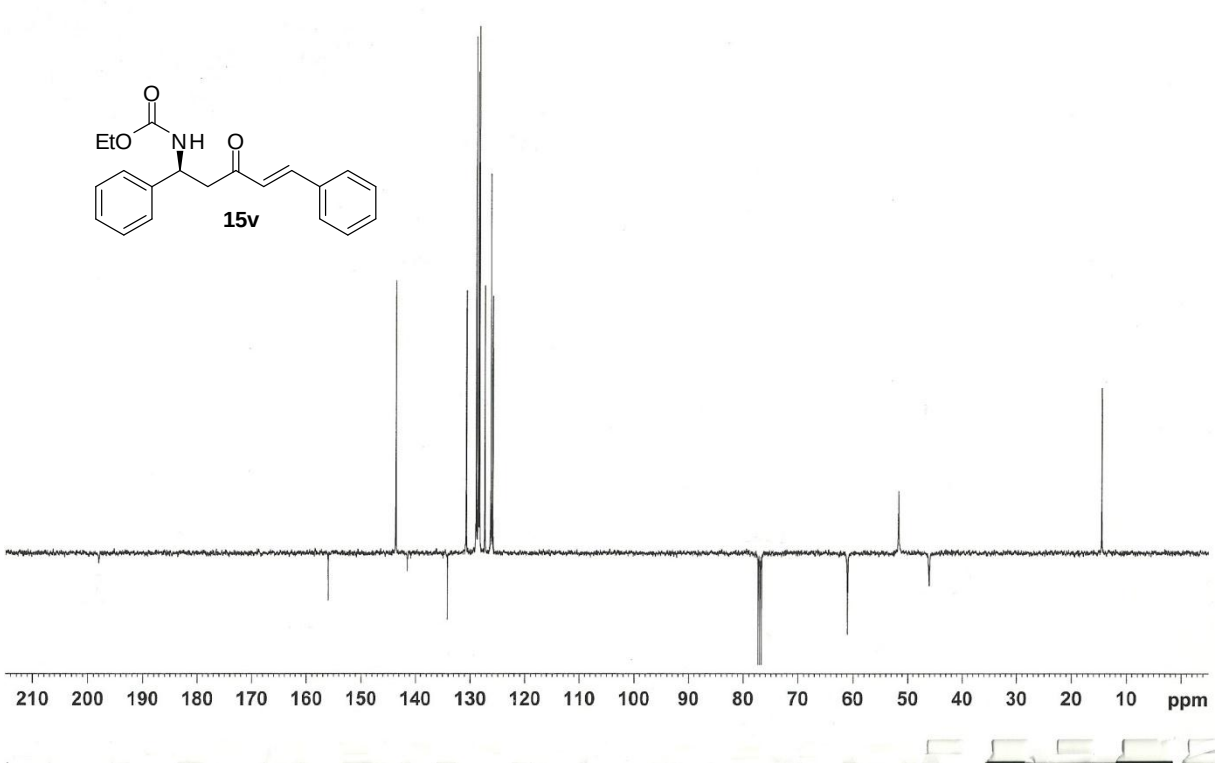

EtO
NH
O
O
7
15t
f1 (ppm)

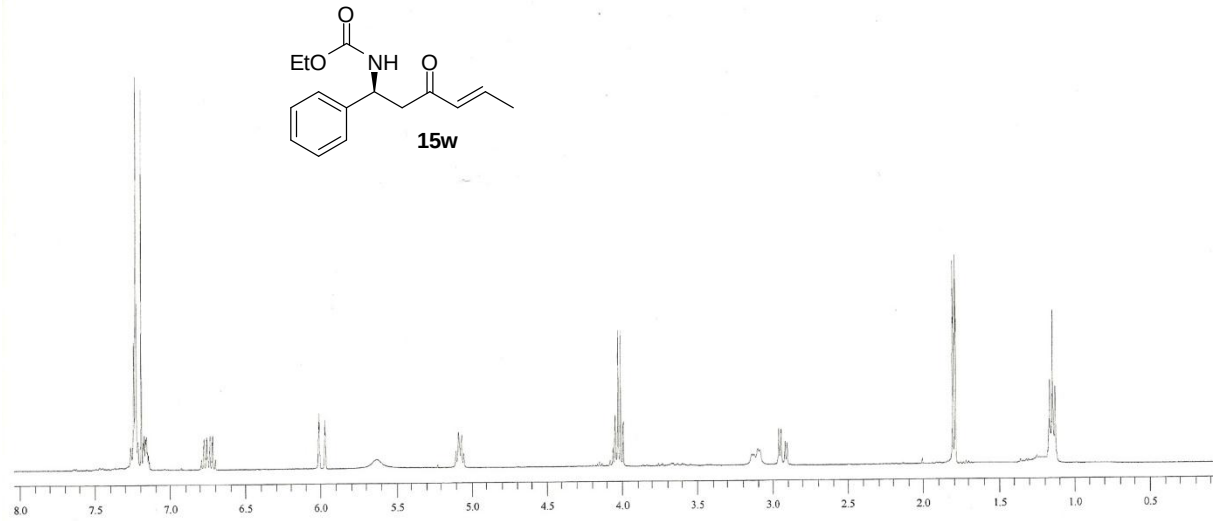

EtO
NH
O
O
7
15t
f1 (ppm)

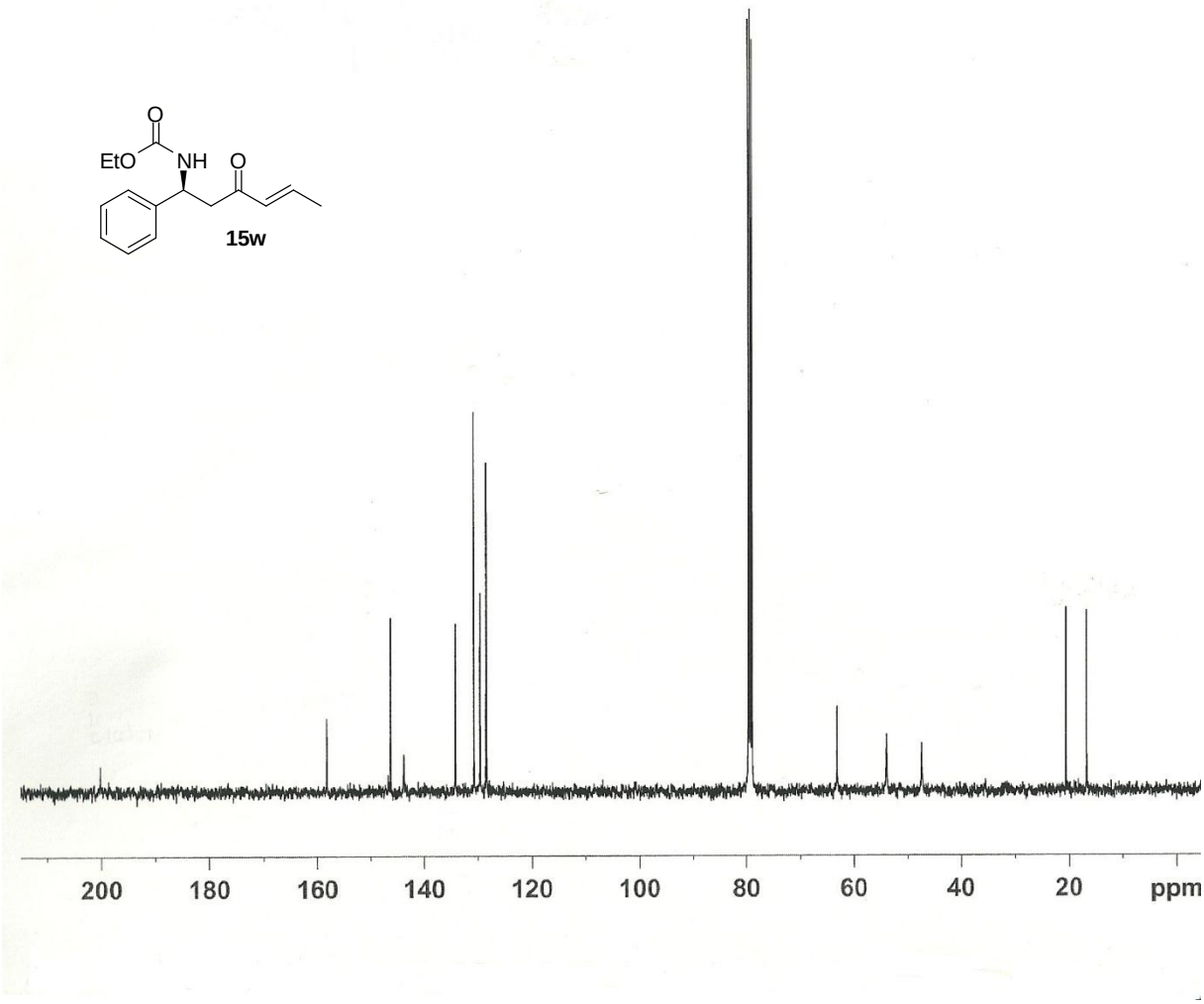

EtO
NH
O
O
7
15u
f1 (ppm)

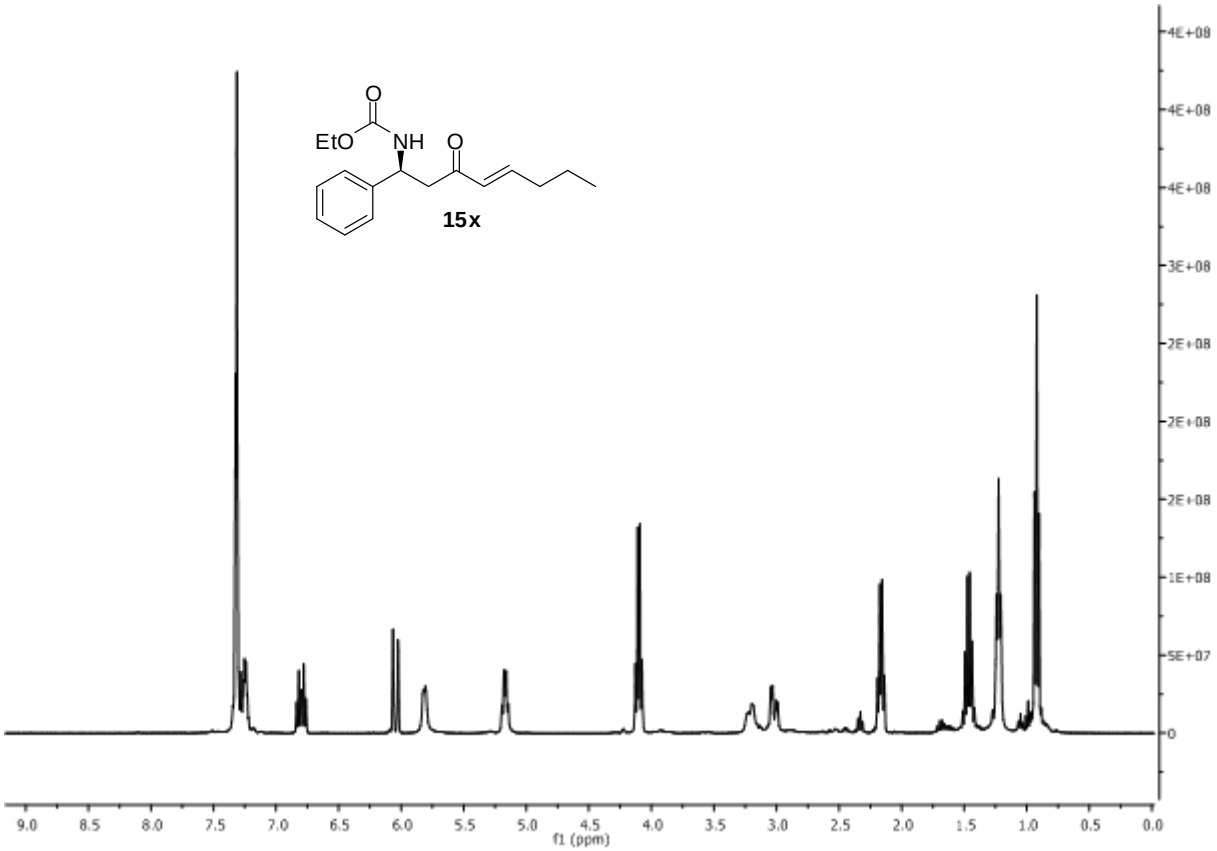

EtO
NH
O
O
7
15u
f1 (ppm)

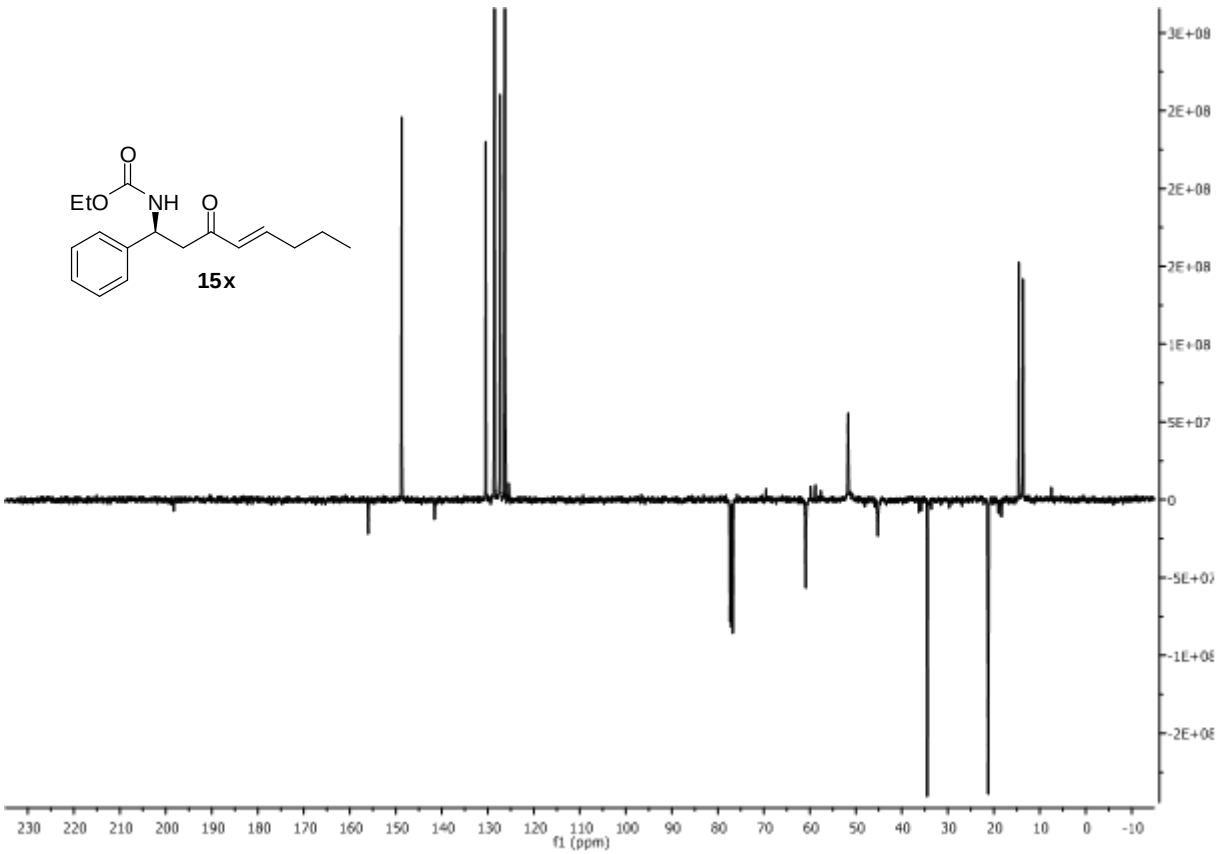

EtO
NH
O
O
15v
f1 (ppm)

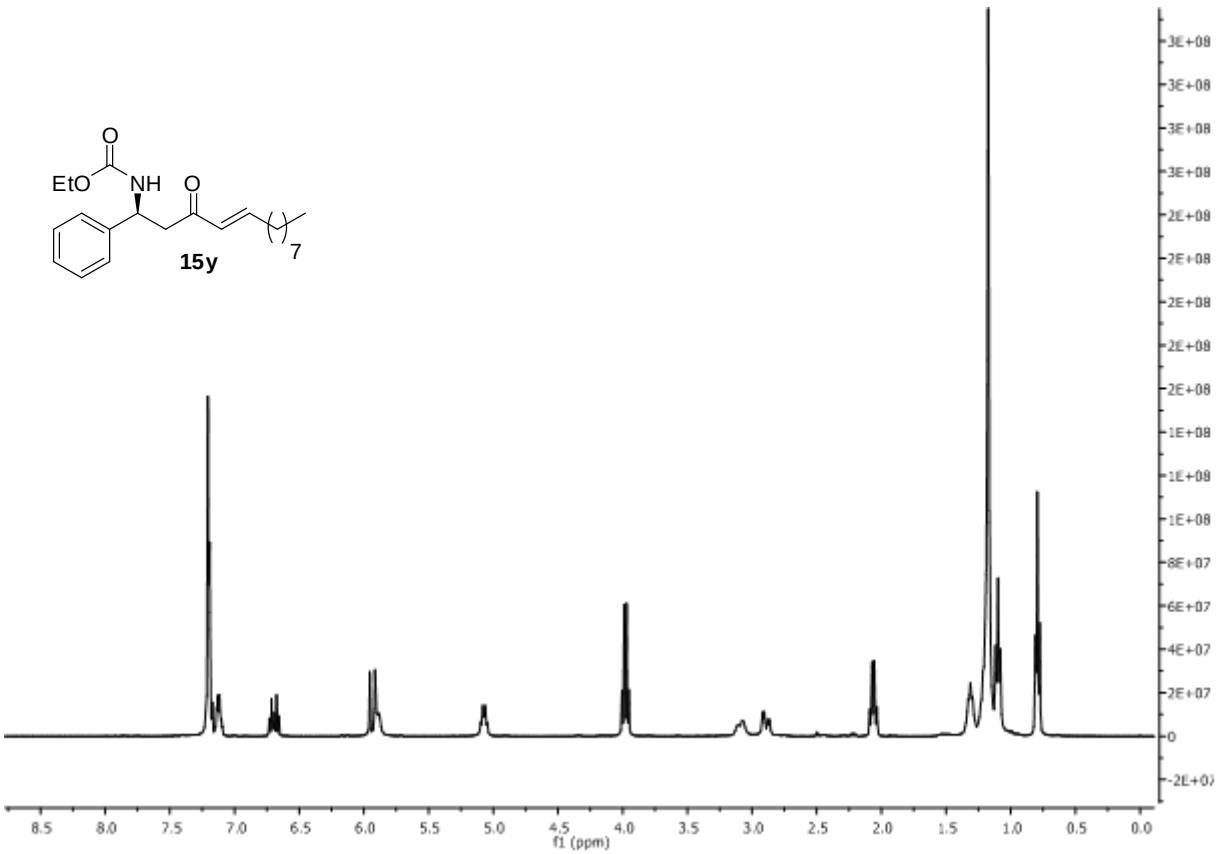

EtO
NH
O
O
15v
ppm

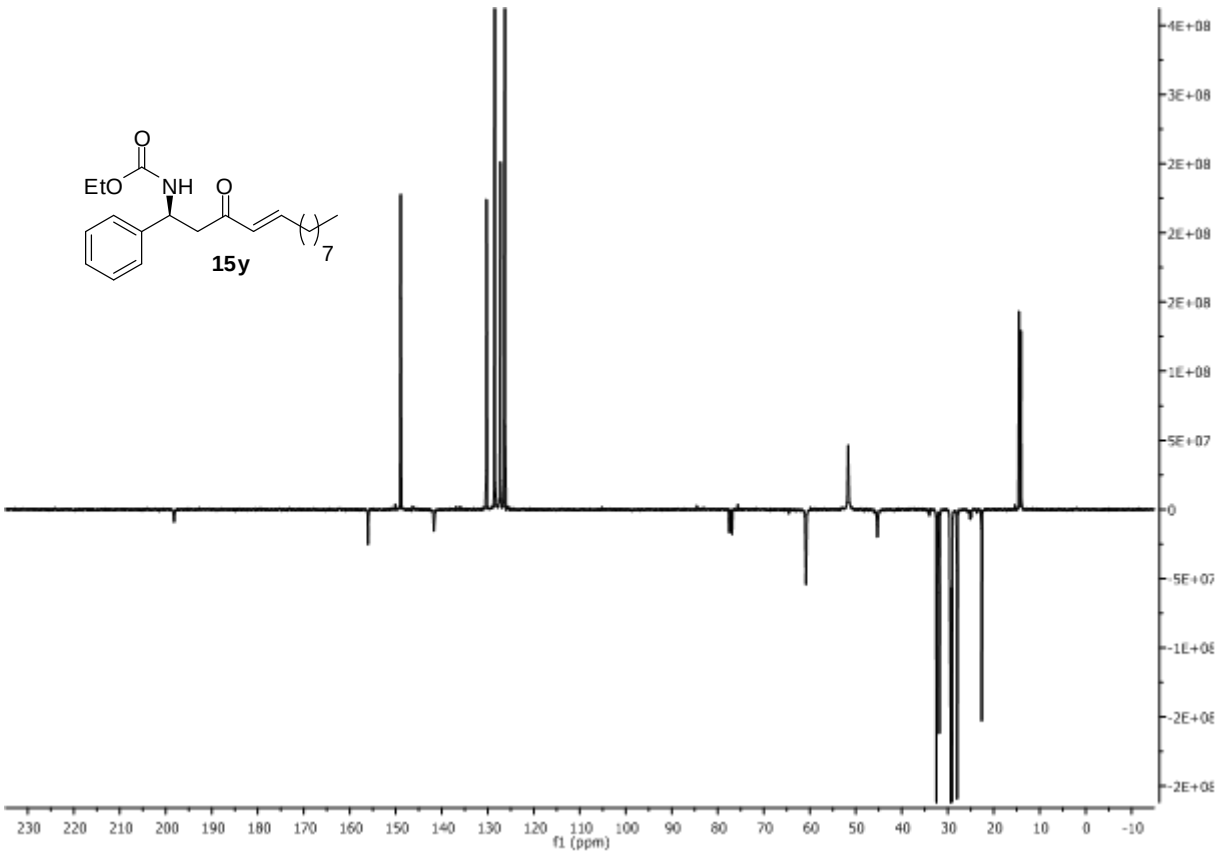

O
EtO
NH
O
15w
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

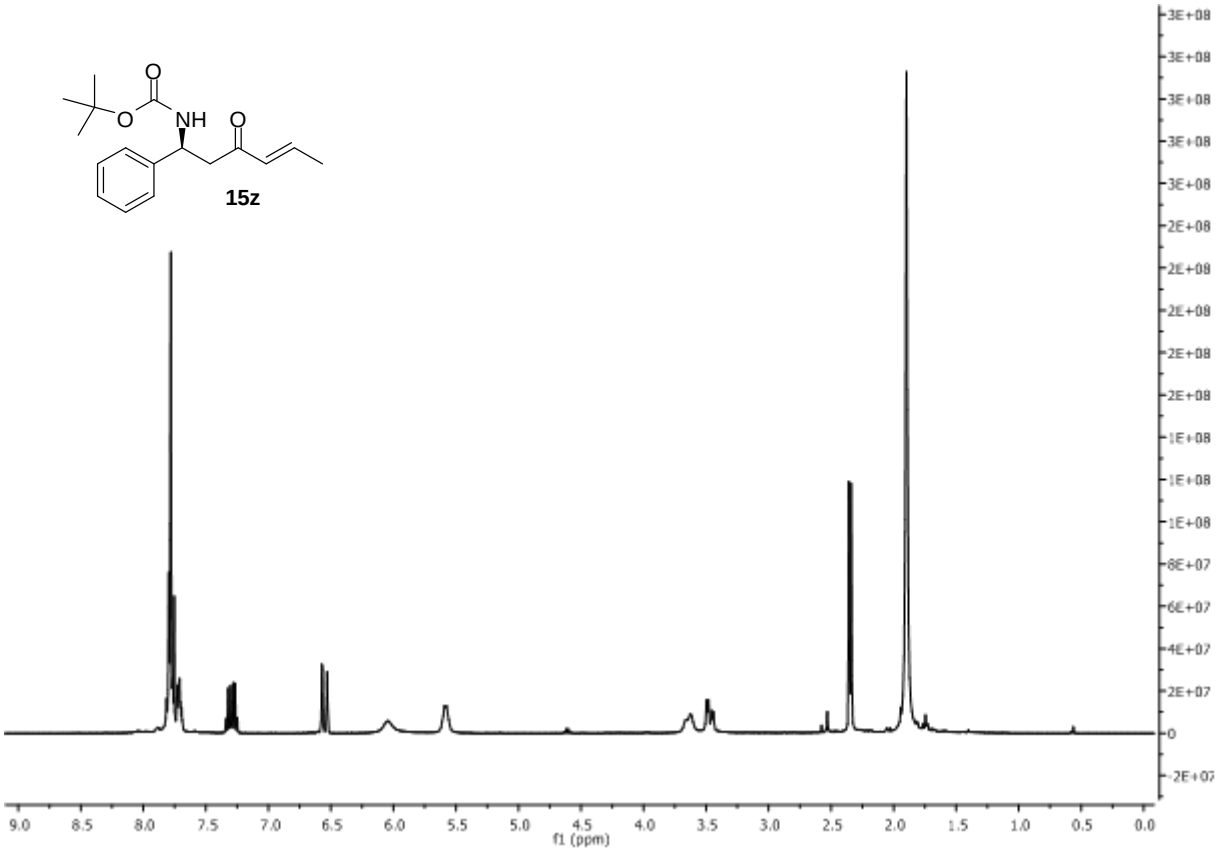

O
EtO
NH
O
15w
200
180
160
140
120
100
80
60
40
20
ppm

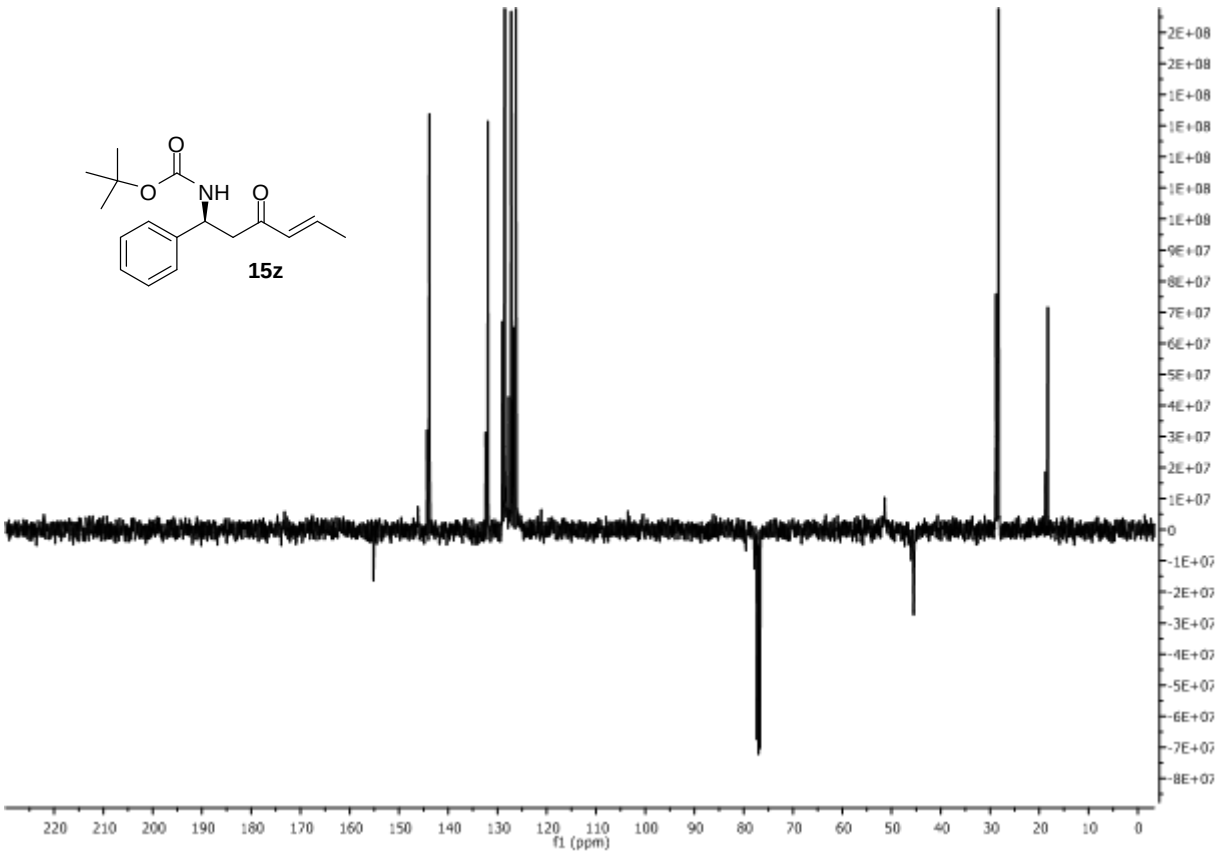

O
EtO
NH
O
15x
4E+08
3E+08
2E+08
1E+08
5E+07
0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

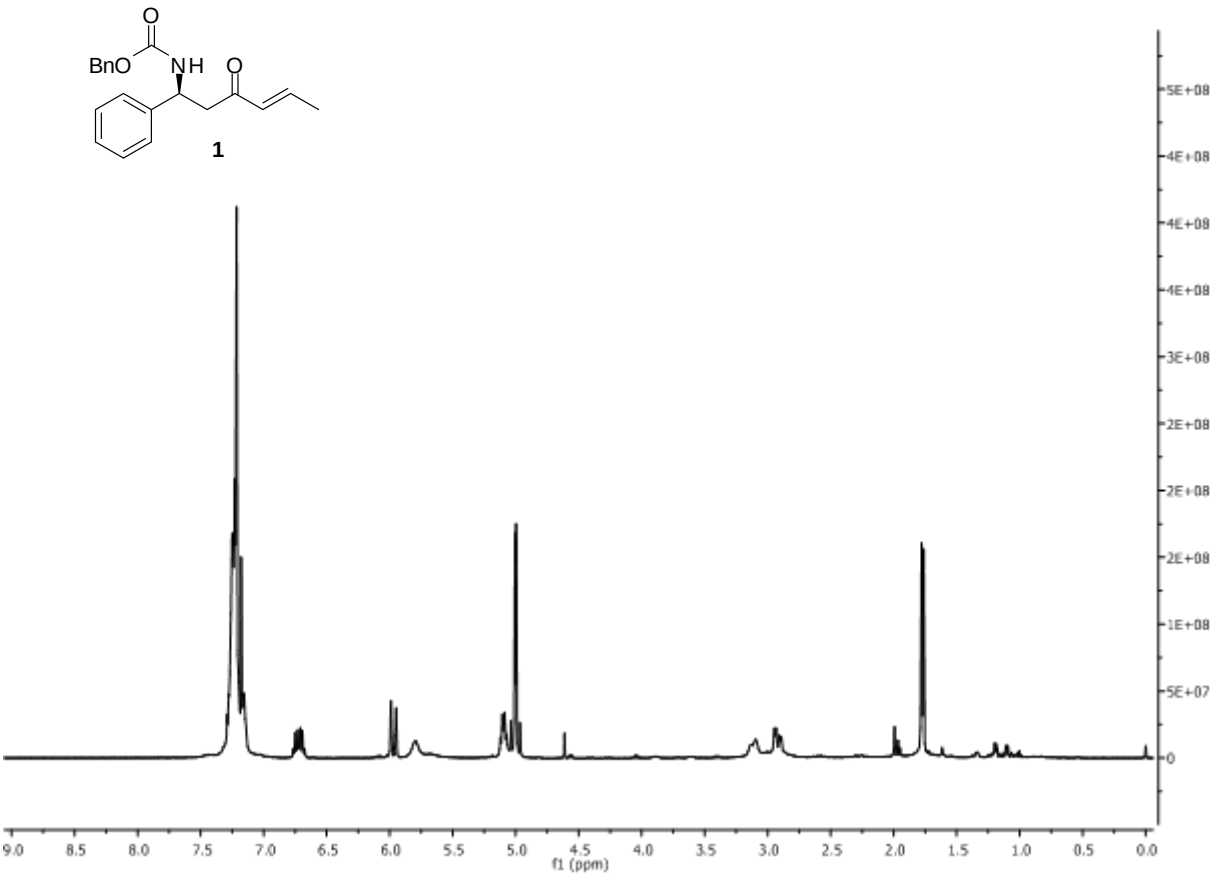

O
EtO
NH
O
15x
3E+08
2E+08
1E+08
5E+07
0
-5E+07
-1E+08
-2E+08
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

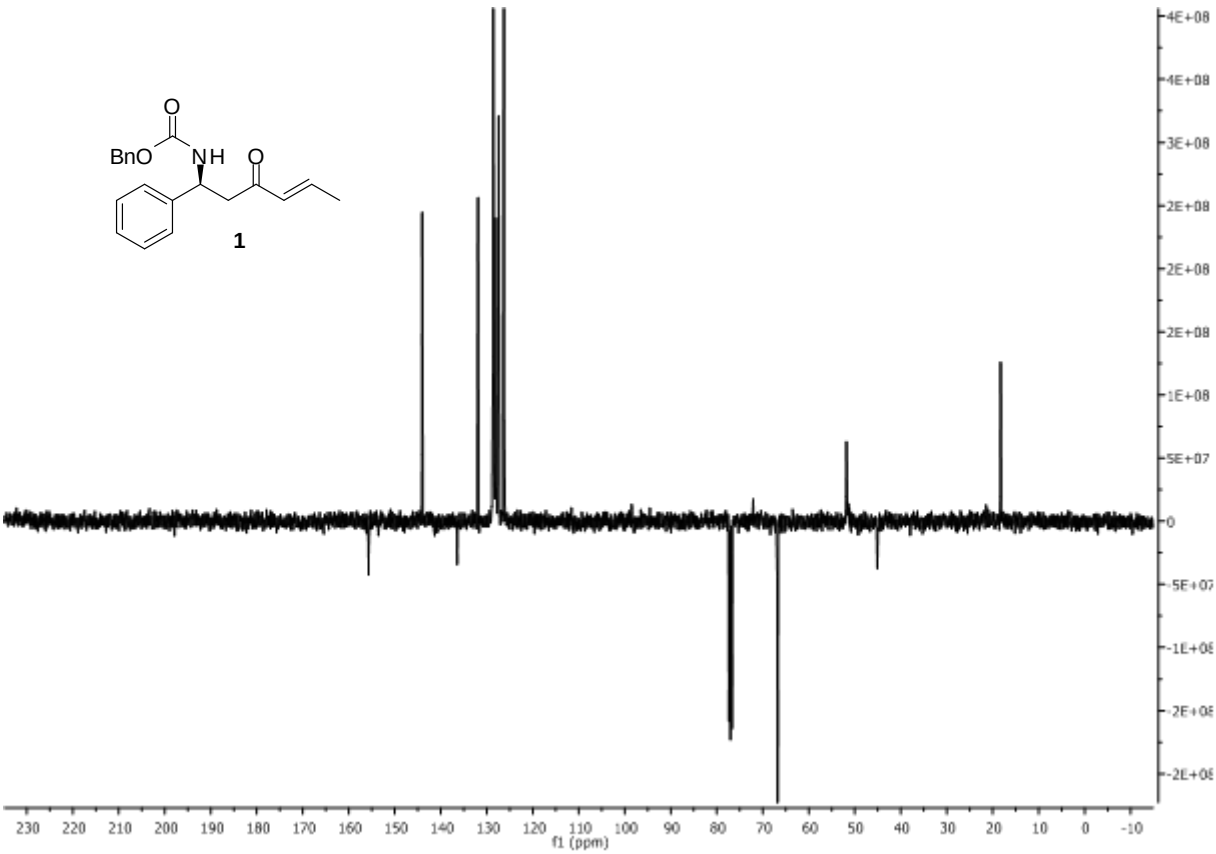

O
EtO
NH
O
7
15y
f1 (ppm)


O
EtO
NH
O
7
15y
f1 (ppm)


O
O
NH
O
15z
f1 (ppm)


O
O
NH
O
15z
f1 (ppm)


BnO
NH
O
O
1
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
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)


BnO
NH
O
O
1
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
-1E+08
-2E+08
-2E+08
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)