Supporting Information

XtalFluor-E® mediated proteo functionalization of olefin, access to N-acetyl N,O-acetals

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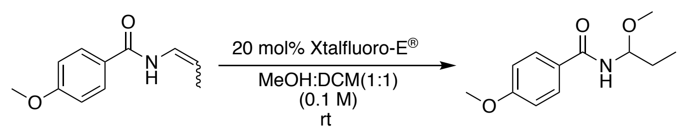
I. General Information

All reagents were purchased from commercial sources and were used without purification. XtalFluor-E® and *N*-vinylcaprolactam were purchased from Aldrich. *N*-vinyl-2-pyrrolidone was purchased from Combi-Blocks. TLC analyses were performed on silica gel plates (pre-coated on glass; 0.20 mm thickness with fluorescent indicator UV254) and were visualized by UV or charred in PMA stains. ^{1}H and ^{13}C NMR spectra were collected on 500 MHz NMR spectrometers (Agilent) using $CDCl_3$. Chemical shifts are reported in parts per million (ppm) and are referenced to residual solvent peaks. Flash silica gel (32-63 µm, Silicycle 60 Å) was used for column chromatography. All known compounds were characterized by ^{1}H and ^{13}C NMR and are in complete agreement with samples reported elsewhere. All new compounds were characterized by ^{1}H and ^{13}CNMR, HRMS, and melting point (where appropriate).

II. General Procedure A for Screening and Optimization

A 5 mL vial equipped with a magnetic stir bar was charged with the substrate (0.1 mmol, 1 equiv.) and XtalFluor-E® (20 mol%). The mixture was dissolved with freshly distilled dichloromethane (0.5 mL) and alcohol (0.5 mL). The vial was flushed with argon and sealed. The reaction was stirred at ambient temperature for 1-24 h. The reaction was then quenched with saturated Na_2SO_3 and extracted with dichloromethane. The combined organics were dried over anhydrous Na_2SO_4 and filtered. Conversions were calculated by ^{1}H NMR. Pure product was isolated by column chromatography on silica gel or aluminum oxide (activated, neutral) as stationary phase (EtOAc in Hexanes as gradient).

III. Analytical data for products:



(Z)-1b/(E)-1b **2b**

General procedure A was used with 19.1 mg (0.1 mmol) of **1b** yielding 21.8 mg (98 % for (***Z***)-**1b**) and 19 mg (85 % for (***E***) **-1b**) of **2b** respectively as a white solid.

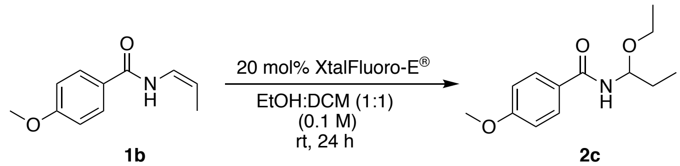
white solids; M.P.: 66 - 70 ºC

R_f : 0.23 (30% EtOAc in Hexane, UV)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 9 Hz, 2H), 6.17 (d, J = 9.5 Hz, 1H), 5.24 (tt, J = 5 Hz, 13 Hz, 1H), 3.83 (s, 3H), 3.37 (s, 3H), 1.76 (m, 1H), 1.63 (m, 1H), 0.96 (t, J = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 162.5, 128.8, 126.2, 113.8, 82.7, 56.0, 55.4, 28.8, 9.2

HRMS analysis (ESI): calculated for (M+Na): $C_{12}H_{17}NO_3Na$ 246.1106; found: 246.1113



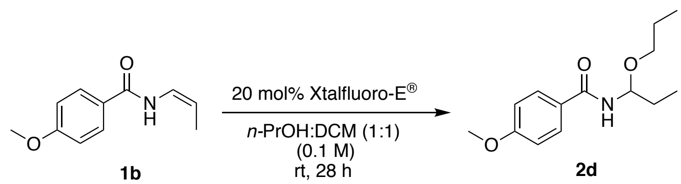
General procedure A was used with 19.1 mg (0.1 mmol) of (***Z***)-**1b** yielding 22.5 mg (95 %) of **2c** as a clear oil.

R_f : 0.33 (30% EtOAc in Hexane, UV)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 8.5 Hz, 2H), 6.94 (d, J = 9 Hz, 2H), 6.2 (d, J = 9 Hz, 1H), 5.36 (m， 1H), 3.86 (s, 3H), 3.70 (m, 1H), 3.57 (m, 1H), 1.78 (m, 1H), 1.66 (m, 1H), 1.20 (t, J = 7 Hz, 3H), 0.99 (t, J = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 162.4, 128.8, 126.2, 113.8, 81.2, 63.8, 55.4, 29.1, 15.2, 9.3

HRMS analysis (ESI): calculated for (M+Na): $C_{13}H_{19}NO_3Na$ 260.1263; found: 260.1270



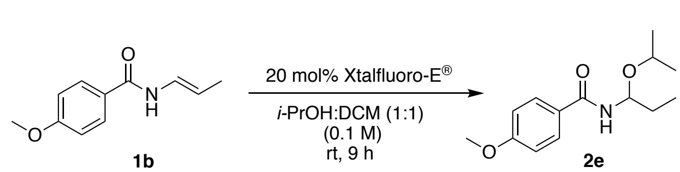
General procedure A was used with 19.1 mg (0.1 mmol) of (***Z***)-**1b** yielding 20 mg (80 %) of **2d** as a clear oil.

R_f : 0.29 (30% EtOAc in Hexane, UV)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 9 Hz, 2H), 6.92 (d, J = 9 Hz, 2H), 6.17 (d, J = 9 Hz, 1H), 5.34 (m, 1H), 3.85 (s, 3H), 3.59 (m, 1H), 3.47 (m, 1H), 1.79 (m, 1H), 1.71-1.56 (m, 3H), 0.99 (t, J = 7.5 Hz, 3H), 0.91 (t, J = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 162.4, 128.8, 126.3, 113.8, 81.4, 70.2, 55.4, 29.1, 22.9, 10.6, 9.4

HRMS analysis (ESI): calculated for (M+Na): $C_{14}H_{21}NO_3Na$ 274.1419; found: 274.1425



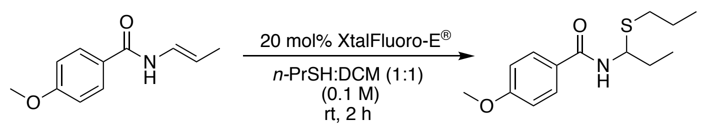
General procedure A was used with 19.1 mg (0.1 mmol) of (***E***)-**1b** yielding 20 mg (40 %) of **2e** as a clear oil.

R_f : 0.41 (30% EtOAc in Hexane, UV)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.19 (d, *J* = 9.4 Hz, 1H), 5.43 – 5.35 (m, 1H), 3.87 (dt, *J* = 12.3, 6.1 Hz, 1H), 3.83 (s, 3H), 1.75 – 1.66 (m, 1H), 1.67 – 1.58 (m, 1H), 1.19 (d, *J* = 6.0 Hz, 3H), 1.13 (d, *J* = 6.2 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.57, 162.38, 128.77, 126.36, 113.82, 79.32, 69.22, 55.45, 29.48, 23.52, 21.70, 9.45.

HRMS analysis (ESI): calculated for (M+Na): $C_{14}H_{21}NO_3Na$ 274.1419; found: 274.1420



1b 2f

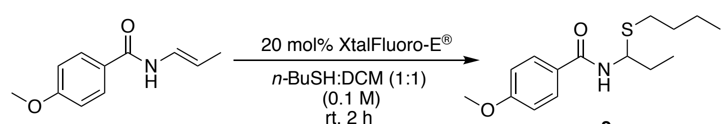
General procedure A was used with 19.1 mg (0.1 mmol) of (***E***)-**1b** yielding 29 mg (98 %) of **2f** as a wax.

R_f : 0.43 (30% EtOAc in Hexane, UV)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.12 (d, *J* = 9.8 Hz, 1H), 5.30 (ddd, *J* = 9.8, 7.3, 6.3 Hz, 1H), 3.83 (s, 3H), 2.64 (ddd, *J* = 12.7, 8.0, 6.0 Hz, 1H), 2.46 (ddd, *J* = 12.8, 8.2, 6.9 Hz, 1H), 1.86 – 1.69 (m, 2H), 1.69 – 1.52 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.20, 162.35, 128.71, 126.19, 113.82, 56.00, 55.44, 32.80, 29.59, 23.11, 13.53, 10.86.

HRMS analysis (ESI): calculated for (M+Na): $C_{14}H_{21}NO_2SNa$ 290.1191; found: 290.1197



1b 2g

General procedure A was used with 19.1 mg (0.1 mmol) of (***E***)-**1b** yielding 20 mg (85 %) of **2g** as a white solid.

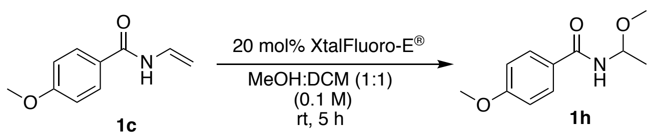
white solids; M.P.: 75 - 80 ºC

R_f : 0.52 (30% EtOAc in Hexane, UV)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.09 (d, *J* = 9.8 Hz, 1H), 5.31 (ddd, *J* = 9.8, 7.3, 6.3 Hz, 1H), 3.83 (s, 3H), 2.65 (ddd, *J* = 12.7, 8.3, 6.0 Hz, 1H), 2.49 (ddd, *J* = 12.7, 8.4, 6.7 Hz, 1H), 1.87 – 1.69 (m, 2H), 1.64 – 1.48 (m, 2H), 1.34 (ddq, *J* = 13.9, 8.8, 7.2 Hz, 2H), 1.02 (t, *J* = 7.4 Hz, 3H), 0.85 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.19, 162.35, 128.69, 128.69, 126.22, 113.82, 56.04, 55.44, 31.83, 30.49, 29.59, 21.99, 13.63, 10.86.

HRMS analysis (ESI): calculated for (M+Na): $C_{15}H_{23}NO_2SNa$ 304.1347; found: 304.1362

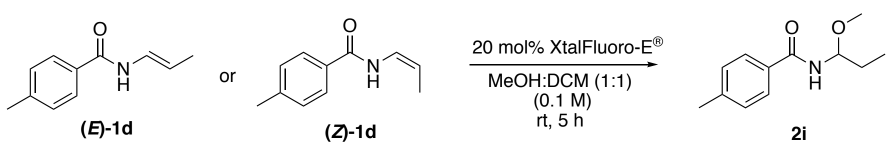


General procedure A was used with 18 mg (0.102 mmol) of **1c** yielding 21 mg (98 %) of **2h** as a clear oil.

R_f : 0.13 (30% EtOAc in Hexane, UV)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.8 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.25 (d, *J* = 9.5 Hz, 1H), 5.49 (dd, *J* = 9.5, 5.8 Hz, 1H), 3.85 (s, 4H), 3.39 (s, 3H), 1.43 (d, *J* = 5.9 Hz, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.67, 162.45, 128.83, 126.09, 113.81, 78.17, 55.78, 55.43, 21.82.
HRMS analysis (ESI): calculated for (M+Na): $C_{11}H_{15}NO_3Na$ 232.0950; found: 232.0954



General procedure A was used with 17.5 mg (0.1 mmol) of **(*E*)-1d** yielding 18.9 mg (91 % for (***Z***)**-1i**) and 14.9 mg (72% for (***E***)**-1i**) of **2i** respectively as a yellowish solid.

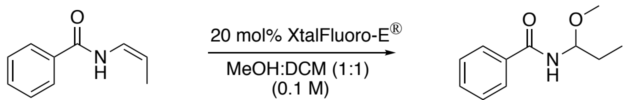
Yellowish solid, M.P.: 56 - 63 ºC

R_f : 0.35 (30% EtOAc in Hexane, UV)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 2H), 7.28 – 7.18 (m, 2H), 6.22 (d, *J* = 9.7 Hz, 1H), 5.26 (dtd, *J* = 9.8, 6.1, 1.8 Hz, 1H), 3.38 (d, *J* = 1.4 Hz, 3H), 2.38 (s, 2H), 1.77 (dddd, *J* = 13.7, 7.6, 6.1, 1.5 Hz, 1H), 1.67 – 1.57 (m, 1H), 0.97 (td, *J* = 7.5, 1.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.44, 142.35, 131.10, 129.30, 126.96, 82.73, 56.01, 28.83, 21.47, 9.22.

HRMS analysis (ESI): calculated for (M+Na): $C_{12}H_{17}NO_2Na$ 230.1157; found: 230.1154



(*Z*)-1a 2a

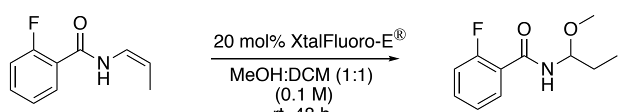
General procedure A was used with 16.1 mg (0.1 mmol) of (***Z***)**-1a** yielding 18.4 mg (95 %) of **2a** as a clear oil.

R_f : 0.71 (30% EtOAc in Hexane, UV)

^1H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.71 (m, 2H), 7.55 – 7.47 (m, 1H), 7.43 (dd, *J* = 8.2, 6.9 Hz, 2H), 6.26 (d, *J* = 9.6 Hz, 1H), 5.26 (dt, *J* = 9.6, 6.2 Hz, 1H), 3.39 (s, 3H), 1.78 (ddd, *J* = 14.0, 7.7, 6.5 Hz, 1H), 1.65 (ddd, *J* = 14.0, 7.7, 6.5 Hz, 1H), 0.98 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.56, 134.01, 131.85, 128.67, 126.97, 82.83, 56.06, 28.82, 9.21.

HRMS analysis (ESI): calculated for (M+Na): $C_{11}H_{15}NO_2Na$ 216.1000; found: 216.1004



(*Z*)-1e 2j

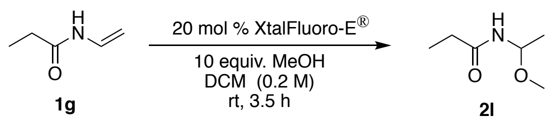
General procedure A was used with 17.9 mg (0.1 mmol) of (***Z***)**-1e** yielding 14.2 mg (67 %) of **2j** as a clear oil.

R_f : 0.53 (30% EtOAc in Hexane, UV)

^1H NMR (500 MHz, $CDCl_3$) δ 8.06 (td, *J* = 7.9, 1.9 Hz, 1H), 7.47 (dddd, *J* = 8.3, 7.2, 5.2, 1.9 Hz, 1H), 7.27 – 7.21 (m, 1H), 7.11 (ddd, *J* = 12.1, 8.2, 1.1 Hz, 1H), 6.77 (d, *J* = 12.4 Hz, 1H), 5.29 (dddd, *J* = 9.0, 6.1, 6.1, 2.7 Hz, 1H), 3.39 (s, 3H), 1.76 (dddd, *J* = 14.9, 13.5, 7.5, 7.5, 6.0 Hz, 1H), 1.73 – 1.62 (m, 1H), 0.97 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.56 (d, *J* = 2.9 Hz), 161.59, 159.62, 133.60 (d, *J* = 9.3 Hz), 132.17 (d, *J* = 2.2 Hz), 124.88 (d, *J* = 3.2 Hz), 116.11 (d, *J* = 24.8 Hz), 82.77, 56.05, 28.68, 9.01.

HRMS analysis (ESI): calculated for (M+Na): $C_{11}H_{14}NO_2FNa$ 234.0906; found: 234.0904

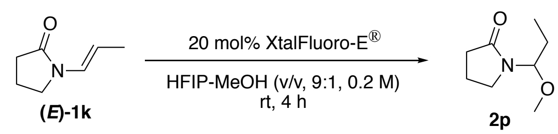


General procedure A was used with 20 mg (0.202 mmol) of **1g** yielding 18.8mg (71 %) of **2l** as a clear oil.

R_f : 0.08 (30% EtOAc in Hexane, dye with PMA)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.70 (s, 1H), 5.32 – 5.12 (m, 1H), 3.29 (d, *J* = 1.3 Hz, 2H), 2.21 (q, *J* = 7.6, 2H), 1.29 (dd, *J* = 5.9, 1.3 Hz, 3H), 1.14 (td, *J* = 7.6, 1.2 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 173.79, 77.47, 55.60, 29.77, 21.57, 9.68.

HRMS analysis (ESI): calculated for (M+Na): $C_6H_{13}NO_2Na$ 154.0844; found: 154.0843



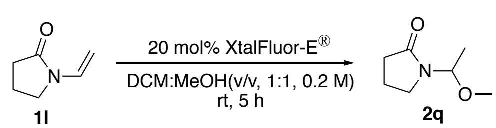
General procedure A was used with 25 mg (0.2 mmol) of **1k** yielding 31 mg (98 %) of **2p** as a clear oil.

R_f : 0.09 (30% EtOAc in Hexane, dye with PMA)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.05 (t, *J* = 6.9 Hz, 1H), 3.34 (dt, *J* = 9.9, 6.9 Hz, 1H), 3.27 (dt, *J* = 9.9, 7.2 Hz, 1H), 3.24 (s, 3H), 2.51 – 2.37 (m, 2H), 2.09 – 1.94 (m, 2H), 1.82 – 1.65 (m, 2H), 1.60 – 1.42 (m, 2H), 0.88 (t, *J* = 7.5, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.27, 83.80, 55.62, 40.83, 31.68, 25.55, 18.26, 9.25.

HRMS analysis (ESI): calculated for (M+Na): $C_8H_{15}NO_2Na$ 180.1000; found: 180.1000



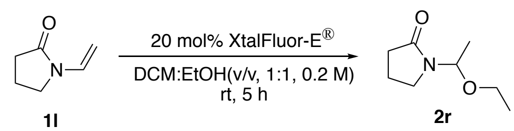
General procedure A was used with 22.2 mg (0.2 mmol) of **1l** yielding 26.8 mg (100 %) of **2q** as a clear oil.

R_f : 0.14 (30% EtOAc in Hexane, dye with PMA)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.28 (q, *J* = 6.1 Hz, 1H), 3.37 – 3.24 (m, 2H), 3.18 (d, *J* = 1.1 Hz, 3H), 2.47 – 2.34 (m, 2H), 2.08 – 1.89 (m, 2H), 1.27 (dd, *J* = 6.1, 1.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 175.74, 78.77, 55.41, 40.73, 31.68, 18.67, 18.09.

HRMS analysis (ESI): calculated for (M+Na): $C_7H_{13}NO_2Na$ 166.0844; found: 166.0844



1l 2r

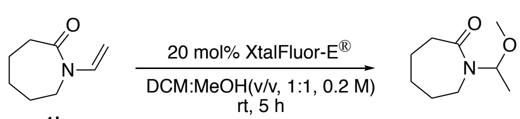
General procedure A was used with 22.2 mg (0.2 mmol) of **1l** yielding 31 mg (100 %) of **2r** as a clear oil.

R_f : 0.14 (30% EtOAc in Hexane, dye with PMA)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.40 (q, *J* = 6.1 Hz, 1H), 3.42 – 3.27 (m, 4H), 2.41 (td, *J* = 8.2, 1.7 Hz, 2H), 2.00 (p, *J* = 7.7 Hz, 2H), 1.27 (s, 2H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 175.55, 77.18, 63.14, 40.83, 31.71, 18.88, 18.07, 14.98.

HRMS analysis (ESI): calculated for (M+Na): $C_8H_{15}NO_2Na$ 180.1000; found: 180.0996



1j 2o

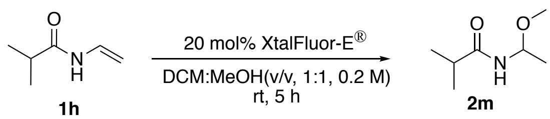
General procedure A was used with 31 mg (0.22 mmol) of **1j** yielding 37 mg (98 %) of **2o** as a clear oil.

R_f : 0.15 (30% EtOAc in Hexane, dye with PMA)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.71 (q, *J* = 6.1 Hz, 1H), 3.30 (ddd, *J* = 15.4, 7.7, 1.7 Hz, 1H), 3.23 – 3.07 (m, 4H), 2.56 (ddd, *J* = 13.8, 10.3, 1.8 Hz, 1H), 2.47 (ddd, *J* = 13.8, 9.3, 1.6 Hz, 1H), 1.78 – 1.43 (m, 6H), 1.20 (d, *J* = 6.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.66, 80.78, 55.47, 40.83, 37.73, 30.09, 29.32, 23.59, 19.13.

HRMS analysis (ESI): calculated for (M+Na): $C_9H_{17}NO_2Na$ 194.1157; found: 194.1160



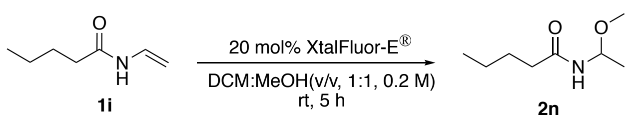
General procedure A was used with 22.6 mg (0.2 mmol) of **1h** yielding 24 mg (83 %) of **2m** as a colorless oil.

R_f : 0.30 (30% EtOAc in Hexane, dye with PMA)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 – 5.68 (m, 1H), 5.26 (dq, *J* = 9.6, 5.4 Hz, 1H), 3.29 (d, *J* = 1.1 Hz, 3H), 2.43 – 2.24 (m, 1H), 1.30 (dd, *J* = 5.9, 1.0 Hz, 3H), 1.15 (ddd, *J* = 12.8, 7.0, 1.0 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.12, 77.40, 55.49, 35.78, 21.55, 19.73, 19.35.

HRMS analysis (ESI): calculated for (M+Na): $C_7H_{15}NO_2Na$ 168.1000 found: 168.1002



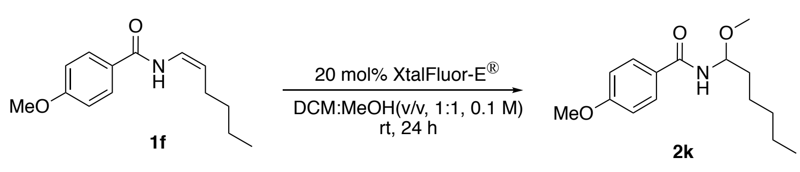
General procedure A was used with 25.4 mg (0.2 mmol) of **1i** yielding 27.4 mg (86 %) of **2n** as a clear oil.

R_f : 0.26 (30% EtOAc in Hexane, dye with PMA)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76 (d, *J* = 9.6 Hz, 1H), 5.27 (dq, *J* = 9.5, 5.9 Hz, 1H), 3.30 (d, *J* = 0.9 Hz, 3H), 2.19 (t, *J* = 7.6 Hz, 2H), 1.67 – 1.46 (m, 2H), 1.32 (dd, *J* = 19.5, 6.7 Hz, 5H), 0.90 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.18, 77.44, 55.59, 36.59, 27.64, 22.37, 21.60, 13.77.

HRMS analysis (ESI): calculated for (M+Na): $C_8H_{17}NO_2Na$ 182.1157; found: 182.1156



General procedure A was used with 23.3 mg (0.1 mmol) of ***(Z)*-1f** yielding 26.5 mg (100 %) of **2k** as a clear oil.

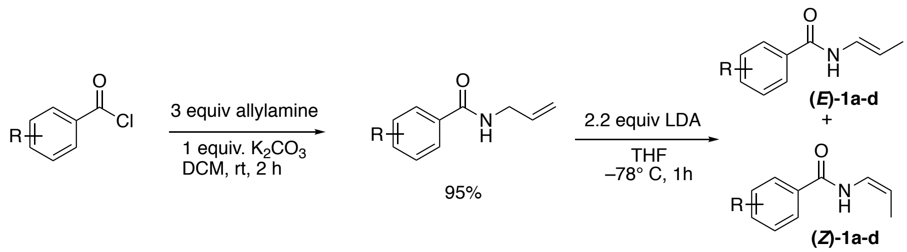
R_f : 0.39 (30% EtOAc in Hexane, UV)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.70 (m, 2H), 6.96 – 6.84 (m, 2H), 6.17 (d, *J* = 9.7 Hz, 1H), 5.31 (dt, *J* = 9.7, 6.2 Hz, 1H), 3.83 (s, 4H), 3.37 (s, 3H), 1.82 – 1.64 (m, 1H), 1.50 – 1.31 (m, 1H), 1.32 – 1.23 (m, 6H), 0.86 (q, *J* = 6.9, 5.5 Hz, 3H).

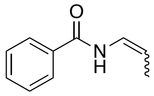
^{13}C NMR (125 MHz, $CDCl_3$) δ 166.90, 162.45, 128.82, 126.18, 113.83, 81.61, 55.96, 55.45, 35.81, 31.53, 24.60, 22.54, 14.00.

HRMS analysis (ESI): calculated for (M+Na): $C_{15}H_{23}NO_3Na$ 288.1576; found: 288.1574

IV. General procedure for synthesis of unsaturated amides 1a-l and analytical data



General procedure B: The appropriate aryl chloride (1 equiv) was dissolved in freshly distilled dichloromethane (15 mL) at room temperature. K_2CO_3 (1 equiv) was added in one portion to the solution at 0 °C. After stirring for 5 min, allylamine (3 equiv) was added in one portion. The reaction mixture was stirred for 2 h and gradually warmed to room temperature. The reaction was quenched with addition of H_2O, the organic layer was separated and washed with dichloromethane. The combined organic fraction was dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel chromatography (25% EtOAc in Hexane). The purified allyl amide product was used in the next step. Freshly distilled *i*-Pr_2NH (2.2 equiv) was dissolved in anhydrous THF (0.3 M) and the solution was cooled down to –78 °C. *n*-BuLi (2.5 M in hexane, 2.2 equiv) was added dropwise to the solution. After stirring for 15 min, allyl amide (1 equiv) in anhydrous THF was added dropwise to the LDA solution at –78 °C. The reaction mixture was warmed to room temperature gradually. After 1 h, saturated NH_4Cl solution was added to work up the reaction. The organics were separated and dried over Na_2SO_4. The organic fraction was concentrated under vacuo and the residue was purified by silica gel column chromatography (15% EtOAc in Hex).



(*E*)-1a and (*Z*)-1a

General procedure B was used with 2 g (12.5 mmol) of benzoyl chloride yielding 1.1 g (55%) of (***Z***)-**1a** and 600 mg (30%) of (***E***)-**1a** as a white solid.

For (***Z***)-**1a**:

White solid, M.P.: 68 - 73 ºC

R_f : 0.72 (30% EtOAc in Hexane, UV)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 2H), 7.59 (d, *J* = 9.6 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.47 – 7.39 (m, 2H), 6.92 (ddq, *J* = 10.8, 8.9, 1.8 Hz, 1H), 4.97 – 4.87 (m, 1H), 1.69 (dd, *J* = 7.1, 1.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.30, 133.98, 131.92, 128.75, 126.99, 122.24, 106.08, 10.99.

HRMS analysis (ESI): calculated for (M+H): $C_{10}H_{12}NO$ 162.0919; found: 162.0920

For (***E***)-**1a**:

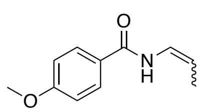
White solid, M.P.: 92 - 97 ºC

R_f : 0.51 (30% EtOAc in Hexane, UV)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.72 (m, 2H), 7.63 (s, 1H), 7.54 – 7.39 (m, 3H), 6.94 (ddq, *J* = 14.0, 10.4, 1.7 Hz, 1H), 5.29 (dq, *J* = 13.6, 6.7 Hz, 1H), 1.72 (dd, *J* = 6.7, 1.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.16, 133.84, 131.78, 128.67, 126.95, 123.55, 108.79, 14.97.

HRMS analysis (ESI): calculated for (M+H): $C_{10}H_{12}NO$ 162.0919; found: 162.0920



(*E*)-1b and (*Z*)-1b

General procedure B was used with 2 g (11.72 mmol) of *p*-methoxybenzoyl chloride yielding 560 mg (26%) of (***Z***)-**1b** and 630 mg (28%) of (***E***)-**1b** after 2 steps as a white solid.

For (***Z***)-**1b**:

white solids; M.P.: 70 - 75 ºC

R_f : 0.38 (30% EtOAc in Hexane, UV)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 2H), 7.54 (d, *J* = 10.4 Hz, 1H), 6.96 – 6.88 (m, 3H), 4.94 – 4.80 (m, 1H), 3.83 (s, 3H), 1.68 (dd, *J* = 7.1, 1.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.79, 162.49, 128.88, 126.13, 122.38, 113.91, 105.46, 55.44, 10.97.

HRMS analysis (ESI): calculated for (M+H): $C_{11}H_{14}NO_2$ 192.1025; found: 192.1025

For (***E***)-**1b**:

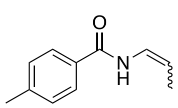
white solids; M.P.: 122 -125 ºC

R_f : 0.33 (30% EtOAc in Hexane, UV)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 2H), 7.66 (d, *J* = 10.4 Hz, 1H), 6.94 (dq, *J* = 12.5, 1.7 Hz, 1H), 6.91 – 6.86 (m, 2H), 5.26 (dq, *J* = 13.6, 6.7 Hz, 1H), 3.82 (s, 3H), 1.70 (dd, *J* = 6.7, 1.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.71, 162.37, 128.85, 126.02, 123.73, 113.82, 108.17, 55.42, 14.98.

HRMS analysis (ESI): calculated for (M+H): $C_{11}H_{14}NO_2$ 192.1025; found: 192.1028



(*E*)-1d and (*Z*)-1d

General procedure B was used with 1.5 g (11.72 mmol) of *p*-methylbenzoyl chloride yielding 937 mg (56 %) of **(*Z*)-1d** and 468 mg (28 %) of **(*E*)-1d** after 2 steps as a white solid.

For **(*Z*)-1d**:

white solid, M.P.: 54 -58 ºC

R_f : 0.58 (30% EtOAc in Hexane, UV)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.9 Hz, 3H), 7.20 (d, *J* = 7.8 Hz, 2H), 6.88 (ddd, *J* = 11.0, 8.9, 2.1 Hz, 1H), 4.92 – 4.83 (m, 1H), 2.36 (s, 3H), 1.67 (dd, *J* = 7.0, 1.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.33, 142.40, 131.06, 129.33, 127.04, 122.31, 105.89, 21.47, 10.99.

HRMS analysis (ESI): calculated for (M+H): $C_{11}H_{14}NO$ 176.1075; found: 176.1073

For **(*E*)-1d**:

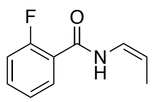
white solid, M.P.: 117 - 122 ºC

R_f : 0.47 (30% EtOAc in Hexane, UV)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 10.3 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.91 (t, *J* = 12.2 Hz, 1H), 5.29 (dq, *J* = 13.6, 6.7 Hz, 1H), 2.35 (s, 3H), 1.68 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.31, 142.18, 130.94, 129.23, 127.08, 123.71, 108.62, 21.46, 14.99.

HRMS analysis (ESI): calculated for (M+H): $C_{11}H_{14}NO$ 176.1075; found: 176.1073



(*Z*)-1e

General procedure B was used with 1 g (6.3 mmol) of *o*-fluorobenzoyl chloride yielding 332 mg (29 %) of ***(Z)*-1e** after 2 steps as a colorless crystal.

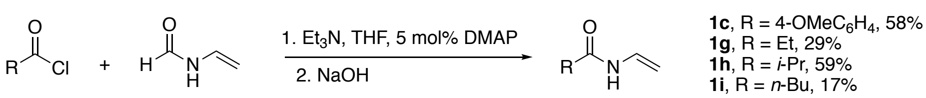
colorless crystal, M.P.: 30 - 35 ºC

R_f : 0.77 (30% EtOAc in Hexane, UV)

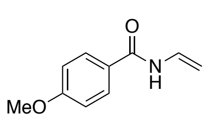
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.15 (tt, J = 8.0, 1.4 Hz, 1H), 7.53 – 7.45 (m, 1H), 7.28 (td, J = 7.6, 1.1 Hz, 1H), 7.14 (ddd, J = 12.6, 8.3, 1.2 Hz, 1H), 6.97 (m, 1H), 5.00 – 4.87 (m, 1H), 1.69 (dd, J = 7.1, 1.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.72, 160.09 (d, J = 3.7 Hz), 159.76, 133.77 (d, J = 9.7 Hz), 132.39 (d, J = 1.9 Hz), 125.06 (d, J = 3.2 Hz), 122.01, 116.06 (d, J = 25 Hz), 106.82, 11.01.

HRMS analysis (ESI): calculated for (M+H): $C_{10}H_{11}NOF$ 180.0825; found: 180.0826



General procedure C: Freshly distilled *N*-vinyl formamide (1 equiv), Et_3N (1.2 equiv), DMAP (5 mol%) and anhydrous THF (1M) were added to a round bottom flask. The resulting mixture was cooled to 0 °C. Acyl chloride (1.2 equiv) was then slowly added and the mixture was stirred at 0-5 °C for 2 h, 5N NaOH solution was added at 0 °C and the solution was stirred for another 2 h. Organic layers were separated and dried over Na_2SO_4 and concentrated under vacuo. The residue was isolated by silica gel column chromatography.



1c

General procedure C was used with 543 mg (7.64 mmol) of *N*-vinylformamide yielding 788 mg (58 %) of **1c** as a white solid.

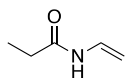
White solid, M.P.: 76 - 83 ºC

R_f : 0.32 (30% EtOAc in Hexane, UV)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 10.5 Hz, 1H), 7.83 – 7.70 (m, 2H), 7.21 – 7.06 (m, 1H), 6.88 – 6.78 (m, 2H), 4.76 (d, *J* = 15.8 Hz, 1H), 4.43 (d, *J* = 8.7 Hz, 1H), 3.78 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.47, 162.54, 129.29, 129.19, 125.62, 113.80, 95.88, 55.40.

HRMS analysis (ESI): calculated for (M+Na): $C_{10}H_{11}NO_2Na$ 200.0687; found: 200.0679



1g

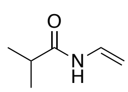
General procedure C was used with 668 mg (9.4 mmol) of *N*-vinylformamide and propanoyl chloride 1 g (10.8 mmol) yielding 120 mg (29 %) of **1g** as a purplish liquid.

R_f : 0.30 (30% EtOAc in Hexane, UV)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.23 (s, 1H), 6.50 (ddd, *J* = 15.9, 8.8, 0.6 Hz, 1H), 5.42 (dd, *J* = 15.9, 0.7 Hz, 1H), 5.35 – 5.24 (m, 1H), 2.66 (q, *J* = 7.2 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.90, 128.72, 95.17, 29.42, 9.50.

HRMS analysis (ESI): calculated for (M+H): $C_5H_{10}NO$ 100.0762; found: 100.0754



1h

General procedure C was used with 600 mg (8.44 mmol) of *N*-vinylformamide and *iso*-butyryl chloride 1.03 g (9.7 mmol) yielding 563 mg (59 %) of **1h** as a white solid.

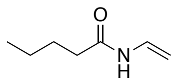
White solid, M.P.: 40 – 45 ºC

R_f : 0.47 (30% EtOAc in Hexane, UV)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 47.1 Hz, 1H), 6.97 (ddd, *J* = 15.8, 10.8, 8.7 Hz, 1H), 4.58 (d, *J* = 15.8 Hz, 1H), 4.37 (d, *J* = 8.7 Hz, 1H), 2.37 (p, *J* = 6.9 Hz, 1H), 1.16 (d, *J* = 7.0 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.39, 128.78, 94.90, 35.56, 19.35.

HRMS analysis (ESI): calculated for (M+H): $C_6H_{12}NO$ 114.0919; found: 114.0918



1i

General procedure C was used with 1 g (14.1 mmol) of *N*-vinylformamide and valeroyl chloride 1.95 g (16.2 mmol) yielding 310 mg (17 %) of **1i** as a white solid.

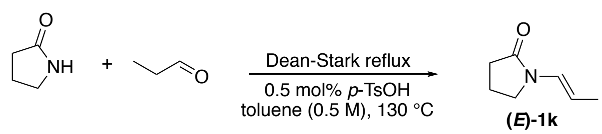
White solid, M.P.: 41 – 45 ºC

R_f : 0.44 (30% EtOAc in Hexane, UV)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 – 6.89 (m, 3H), 4.56 (dd, *J* = 15.8, 0.8 Hz, 1H), 4.36 (dd, *J* = 8.2, 0.8 Hz, 1H), 2.25 – 2.14 (m, 2H), 1.68 – 1.55 (m, 2H), 1.34 (h, *J* = 7.4 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.98, 128.64, 94.66, 36.38, 27.42, 22.36, 13.77.

HRMS analysis (ESI): calculated for (M+H): $C_7H_{14}NO$ 128.1075; found: 128.1063



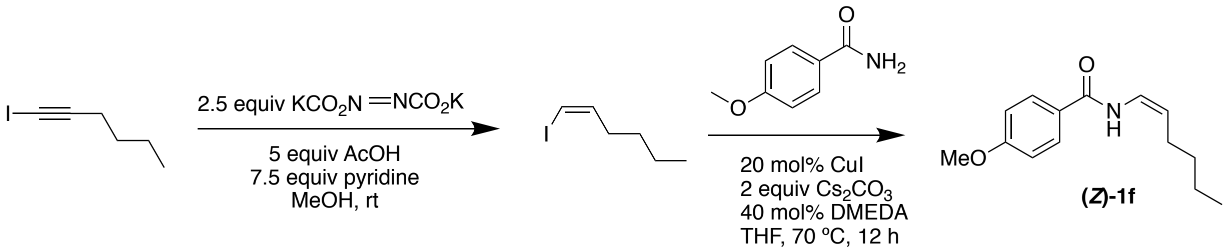
(*E*)-1-(prop-1-en-1-yl)pyrrolidin-2-one **1k** was synthesized according to the reported literature.[1]

R_f : 0.20 (30% EtOAc in Hexane, UV)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 (dq, *J* = 14.3, 1.9 Hz, 1H), 4.97 – 4.84 (m, 1H), 3.45 (dd, *J* = 8.6, 5.9 Hz, 2H), 2.44 (td, *J* = 8.1, 3.3 Hz, 2H), 2.11 – 1.98 (m, 2H), 1.69 (dt, *J* = 6.5, 1.6 Hz, 3H).

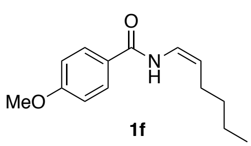
^{13}C NMR (126 MHz, $CDCl_3$) δ 172.61, 124.31, 106.83, 45.22, 31.23, 17.40, 15.19.

HRMS analysis (ESI): calculated for (M+H): $C_7H_{12}NO$ 126.0919; found: 126.0921



1-iodohexyne was synthesized according to reported literature procedure in quantitative yield.[2] 1-iodohexyne (1.15g, 5.53 mmol) was dissolved in methanol (10 mL) and pyridine (1.65 mL), followed by adding potassium diazodiimide (2.7g, 13.8 mmol) with vigorous stiring. Acetic acid (1.66 g) was added via syringe to the reaction mixture dropwise at room temperature. The reaction was followed by GC. After 8 h 15% of the hexyne was observed via GC. To the reaction 0.5 equiv of potassium diazodiimide and 1 equiv of AcOH were added. Aq. HCl (5%, 20 mL) was added and the mixture was extracted with Et_2O. The organics were washed with brine, dried over Na_2SO_4 and the solvents were removed in vacuo. The residue was purified through a flash column of SiO_2 (100% hexane). A pale yellow liquid was isolated as product (52% yield).

The enamide substrate **1f** was synthesized accord to reported literature.[3] An oven-dried 25 mL screw-cap sealed tube equipped with a Teflon-coated magnetic stir bar was charged with vinyl halide (1 equiv), amide (1.2 equiv), CuI (20 mol%), and Cs_2CO_3 (2 equiv). The tube was then evacuated and backfilled with argon. 1,2-Dimethylethylenediamine(DMEDA) (40 mol%) was added into the tube followed by anhydrous THF via a syringe. The sealed tube was placed in a preheated oil bath (70 °C). After stirring at the same temperature for 12 h, the reaction mixture was allowed to cool to room temperature. The reaction mixture was filtered through a thin layer of celite and washed by EtOAc. The filtrate was concentrated in vacuo. The crude residue was purified by flash chromatography, **(*Z*)-1f** was given as oil in 67% yield.



1f

R_f : 0.46 (30% EtOAc in Hexane, UV)

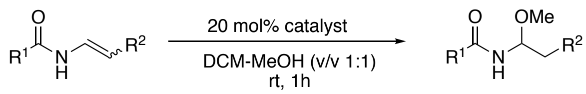
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.71 (m, 2H), 7.71 – 7.17 (m, 1H), 7.01 – 6.81 (m, 3H), 4.89 – 4.73 (m, 1H), 3.83 (s, 3H), 2.08 (qd, J = 7.2, 1.7 Hz, 2H), 1.53 – 1.28 (m, 4H), 0.91 (t, J = 7.1 Hz, 3H).

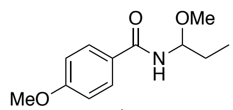
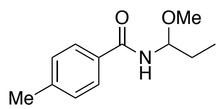
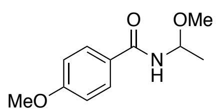
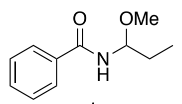
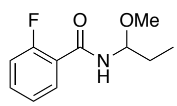
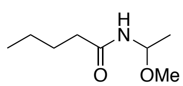
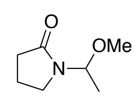
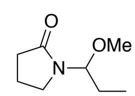
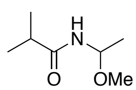
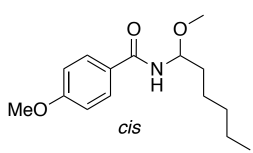
^{13}C NMR (126 MHz, $CDCl_3$) δ 163.80, 162.46, 128.87, 126.14, 121.27, 113.89, 111.74, 55.42, 31.49, 25.55, 22.33, 13.94.

HRMS analysis (ESI): calculated for (M+H): $C_{14}H_{20}NO_2$ 234.1494; found: 234.1497

V. HBF_4 Catalyzed Proton-functionalization

Based on our proposed mechanism, we believe that HBF_4, putatively generated from XtalFluor-E® and alcohol, is the species that catalyzes the reaction. To verify this, HBF_4•OEt_2 (20 mol%) was used as the catalyst instead of XtalFluor-E® with different substrates. We observed comparable results to those obtained with XtalFluor-E®. Most reactions proceeded much faster than XtalFluor-E® catalyzed reactions. However, for some substrates yields are a bit lower than with XtalFluor-E® as catalysts since products are prone to decomposition under strong acidic condition.



entry	substrate	catalyst = Xtal-FluorE® [a]	$HBF_4 \cdot OEt_2$ [a]
1	 *cis*	98	98
2	 *cis*	91	98
3		98	70
4	 *cis*	95	98
5	 *cis*	60	99
6		86	75
7		94	98
8	 *trans*	98	83
9		83	83
10	 *cis*	98	64

[a] isolated yield of N,O-acetal products

Table S1. Comparison of yields between XtalFluor-E® and $HBF_4 \cdot OEt_2$ as catalyst

VI. ^{19}F NMR Study of XtalFluor-E® with addition of MeOH

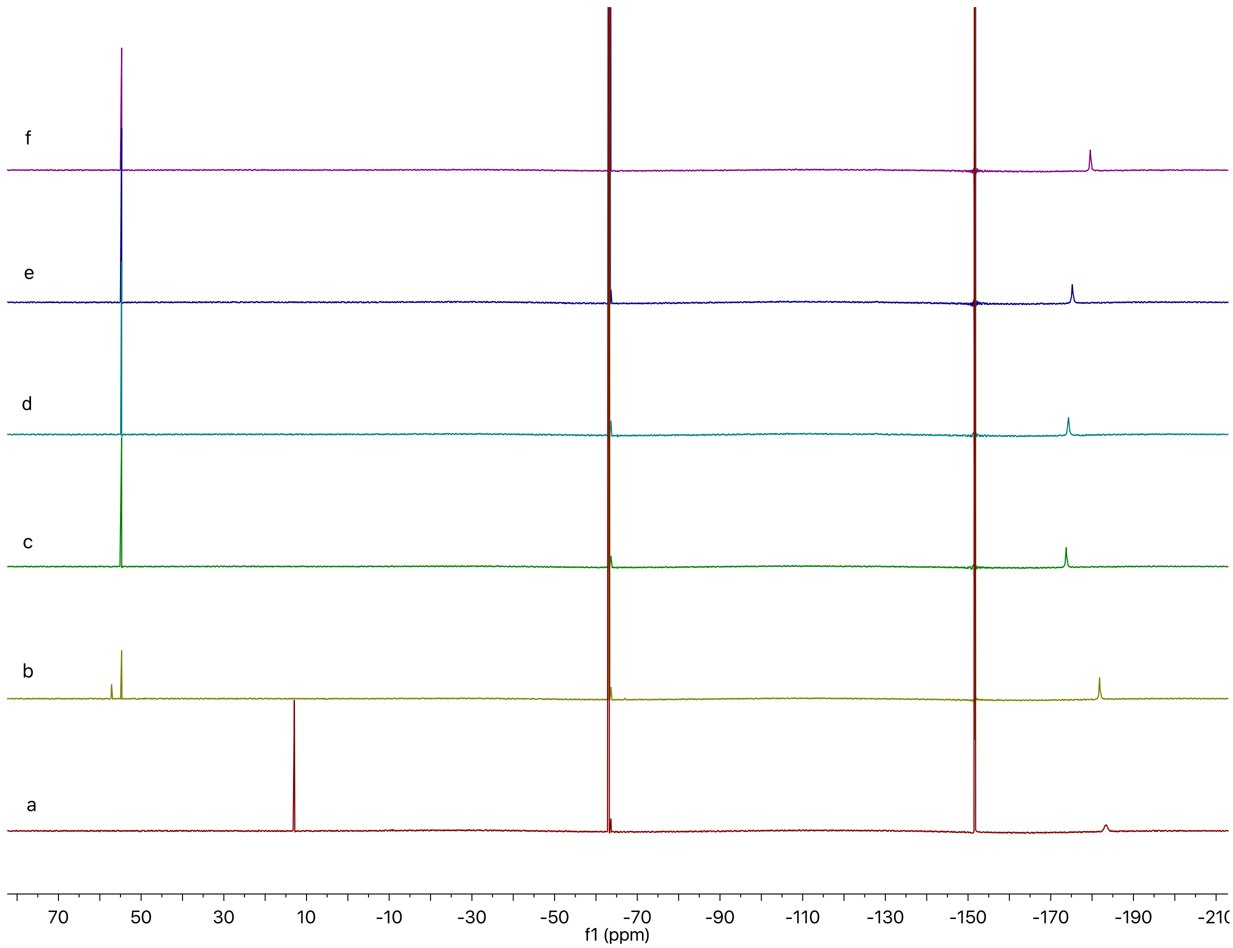
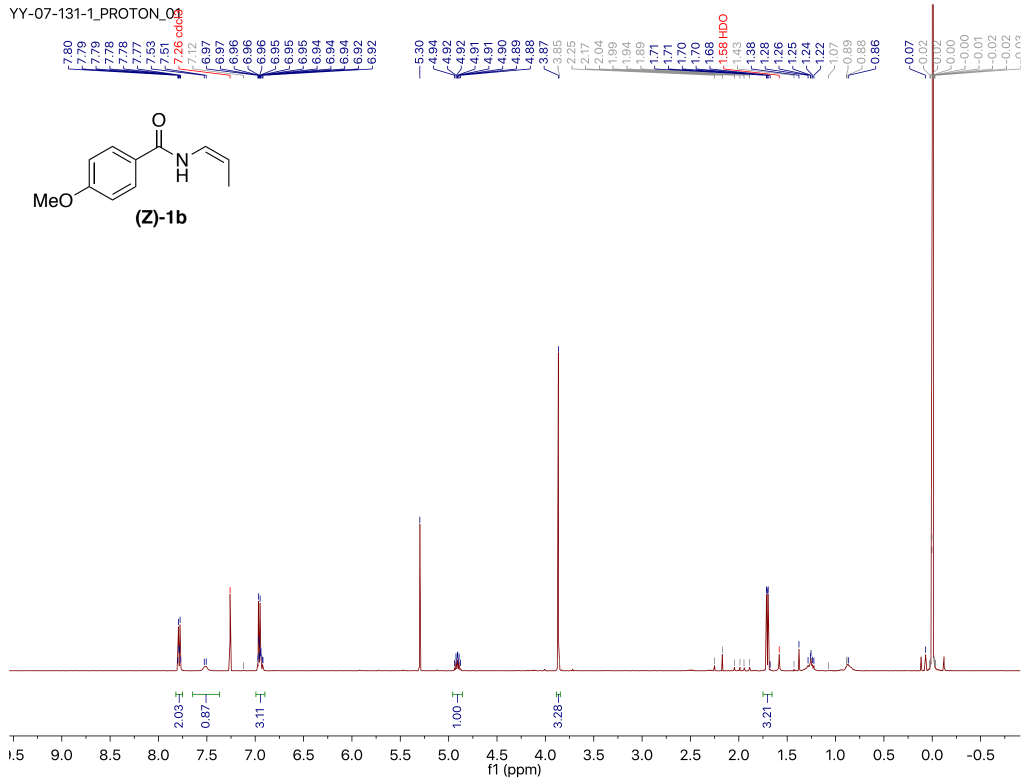


Figure S1. ^{19}F NMR spectrum of a) XtalFluor-E®; b) XtalFluor-E® + 1 equiv MeOH; c) XtalFluor-E® + 2 equiv MeOH; d) XtalFluor-E® + 4 equiv MeOH; e) XtalFluor-E® + 5 equiv MeOH; f) XtalFluor-E® + 10 equiv MeOH

VII. Reference

1. Tamai, T.; Yoshikawa, M.; Higashimae, S.; Nomoto, A.; Ogawa, A., *J. Org. Chem.* **2016**, *81*, 324-329.
2. Hoye, R. C.; Anderson, G. L.; Brown, S. G.; Schultz, E. E., *J. Org. Chem.* **2010**, *75*, 7400-7403.
3. Cheung, C.; Buchwald, S. L. *J. Org. Chem.* **2012**, *77*, 7526-7537.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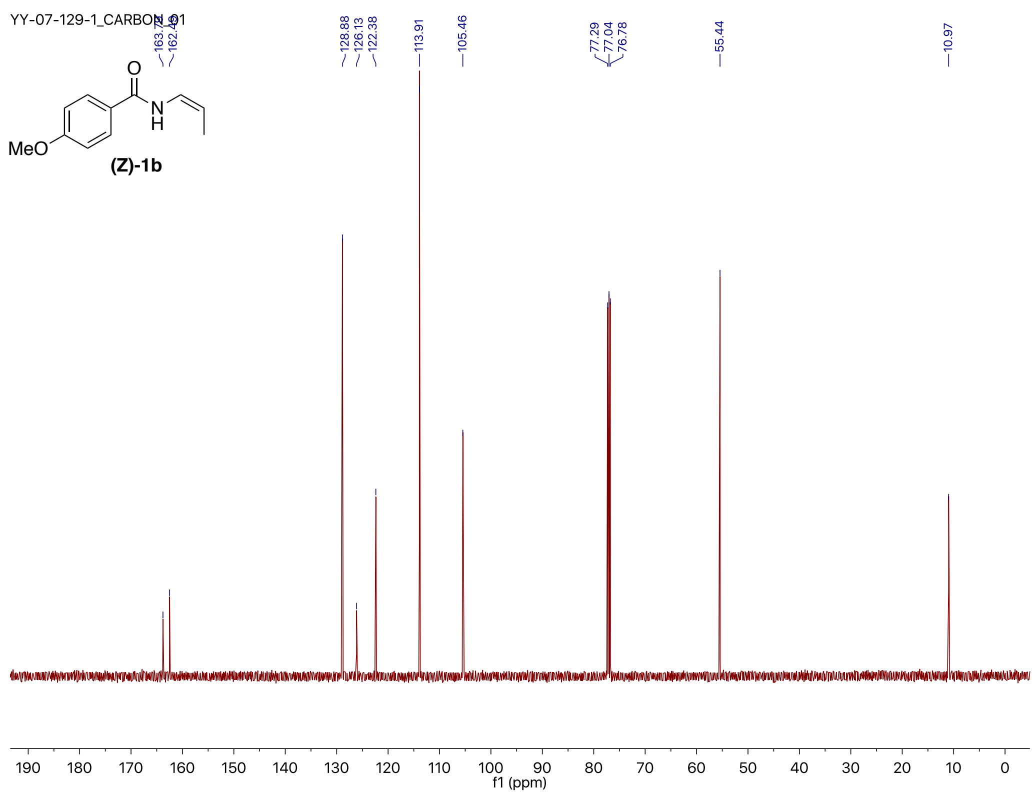
7.80 7.79 7.79 7.78 7.78 7.77 7.53 7.51 7.26 cdcl3 7.12 6.97 6.97 6.96 6.96 6.96 6.95 6.95 6.95 6.94 6.94 6.94 6.92 6.92
5.30 4.94 4.92 4.92 4.91 4.91 4.90 4.89 4.88 3.87 3.85 2.25 2.17 2.04 1.99 1.94 1.89 1.71 1.71 1.70 1.70 1.68 1.58 HDO 1.43 1.38 1.28 1.26 1.25 1.24 1.22 1.07 0.89 0.88 0.86
0.07 0.02 0.00 -0.00 -0.01 -0.02 -0.02
O
N
H
MeO
(Z)-1b
2.03 0.87 3.11 1.00 3.28 3.21
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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162.40
128.88 126.13 122.38
113.91
105.46
77.29 77.04 76.78
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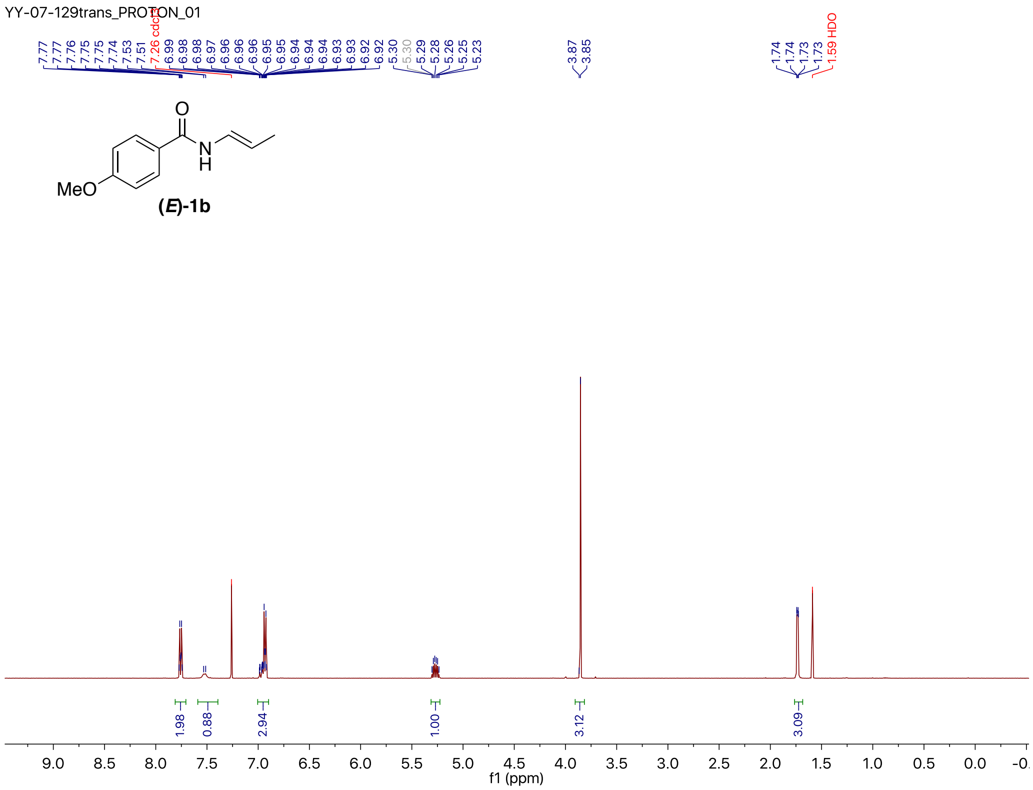
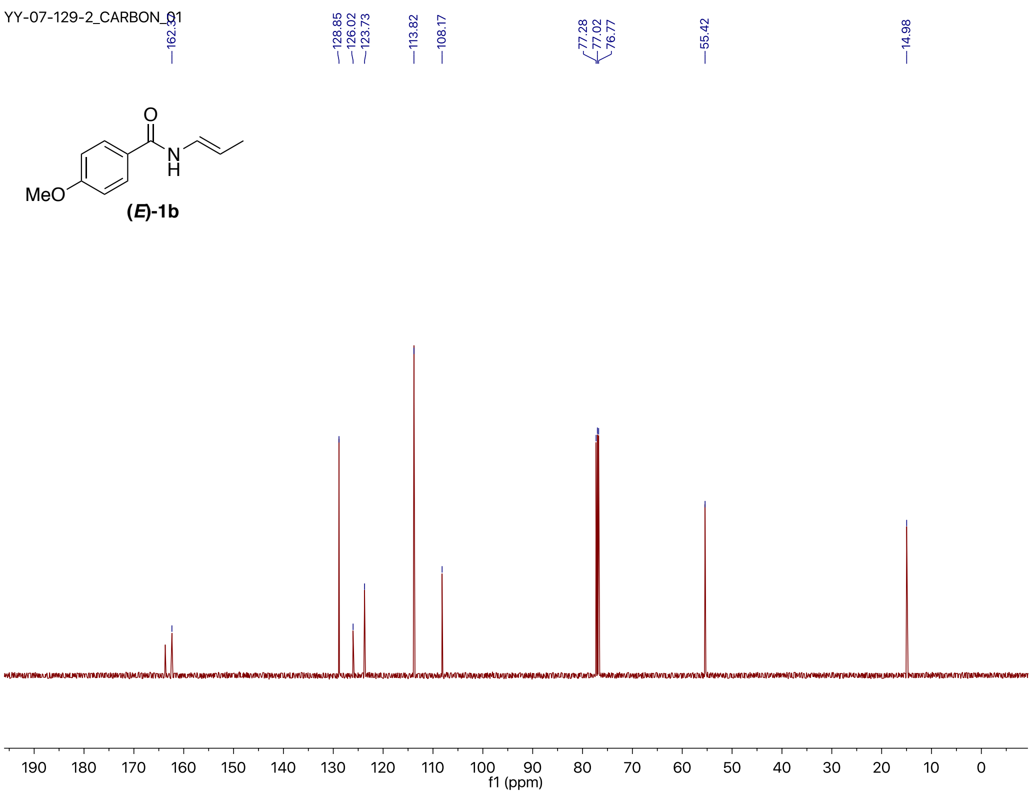
O
N
H
MeO
(Z)-1b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


YY-07-129trans_PROTON_01
7.77 7.77 7.76 7.75 7.75 7.74 7.53 7.51 7.26 cdcl3 6.99 6.98 6.98 6.97 6.96 6.96 6.96 6.95 6.95 6.94 6.94 6.94 6.93 6.93 6.93 6.92 6.92 6.92 5.30 5.30 5.29 5.28 5.26 5.25 5.23
3.87 3.85
1.74 1.74 1.73 1.73 1.59 HDO
MeO
O
N
H
(E)-1b
1.98 0.88 2.94 1.00 3.12 3.09
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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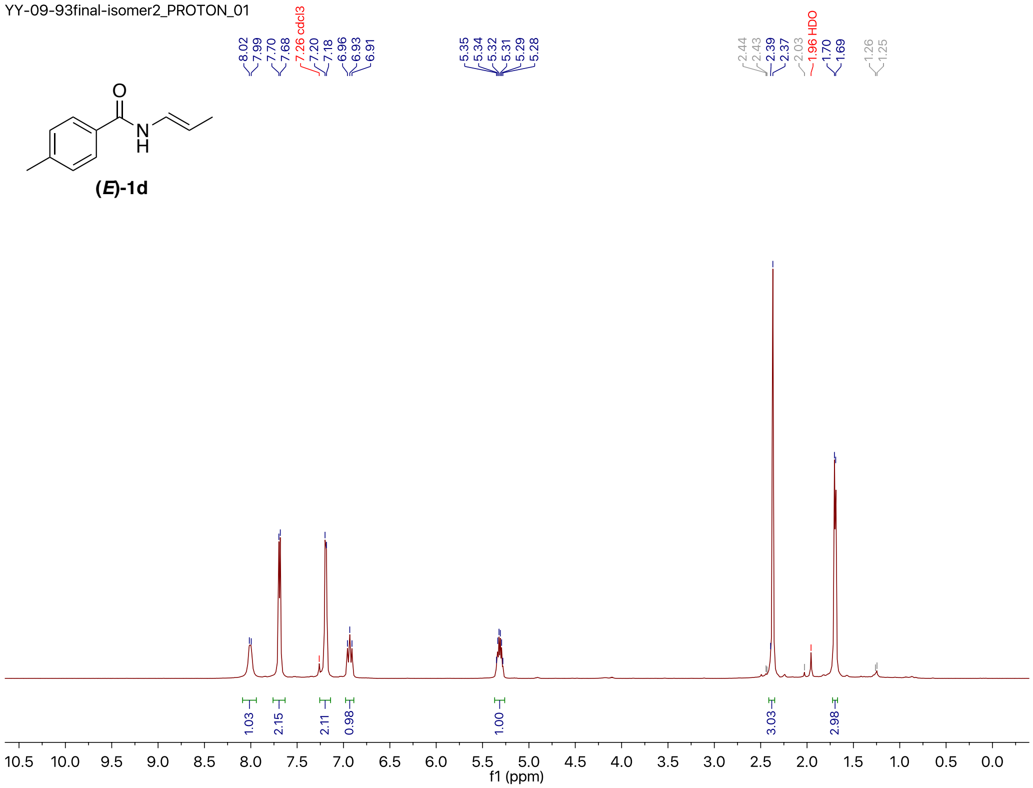
128.85 126.02 123.73
113.82
108.17
77.28 77.02 76.77
55.42
14.98
MeO
O
N
H
(E)-1b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

YY-09-93final-isomer2_PROTON_01



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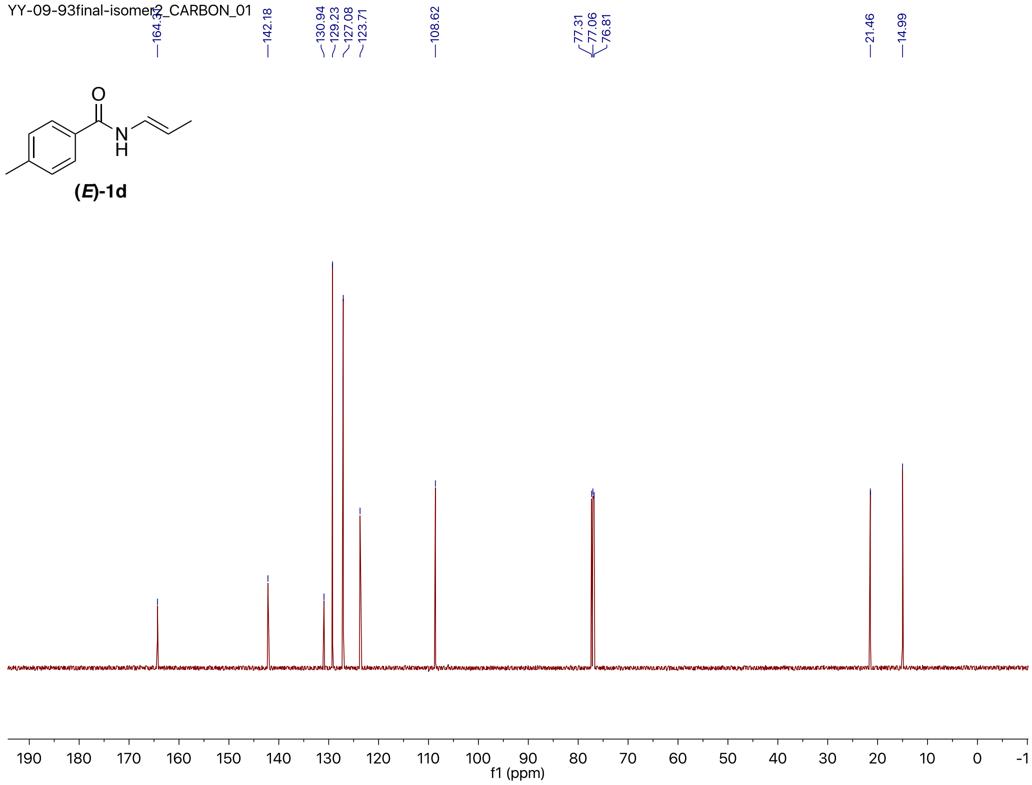

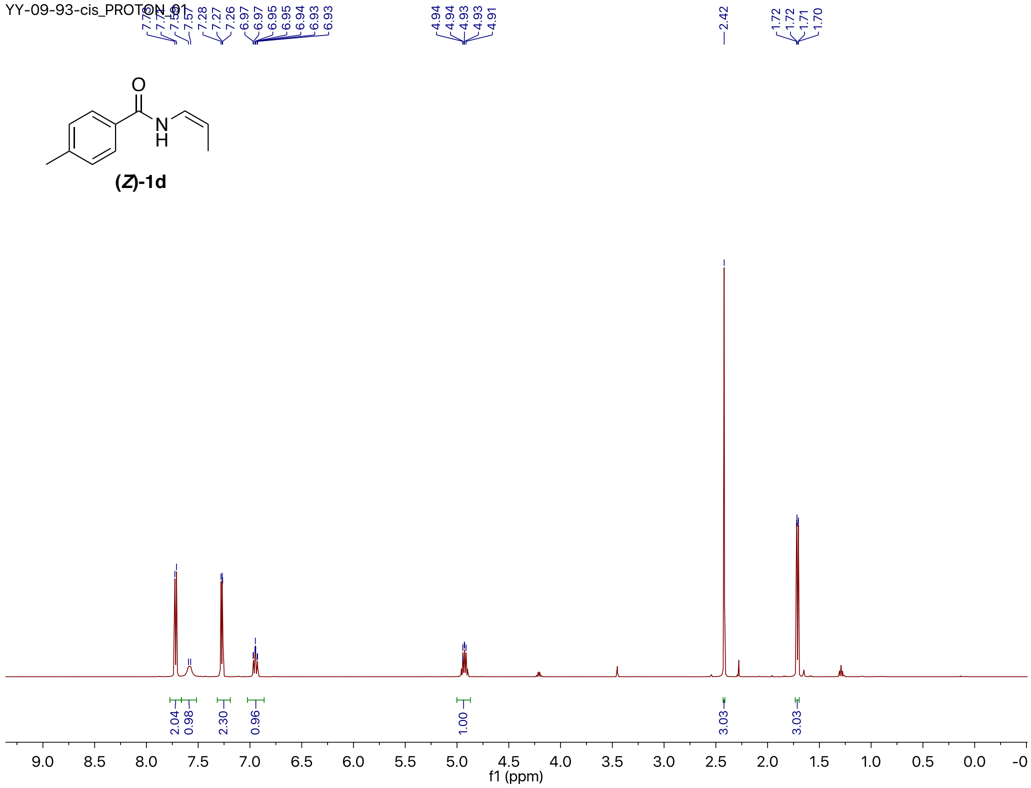

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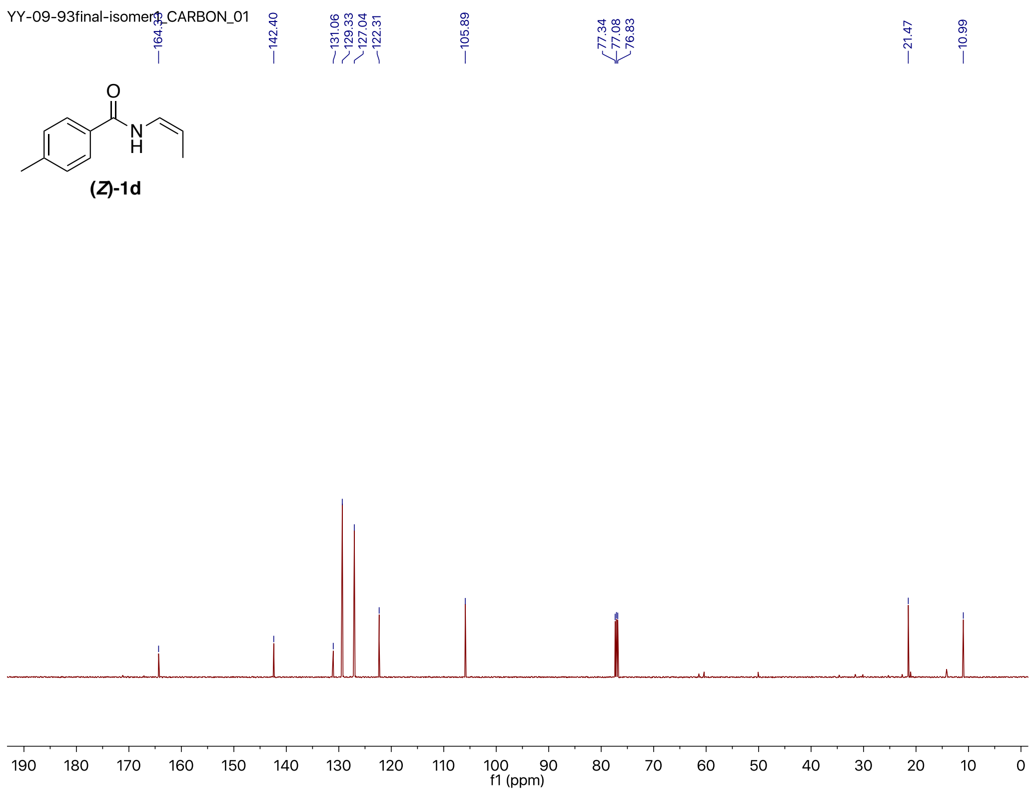
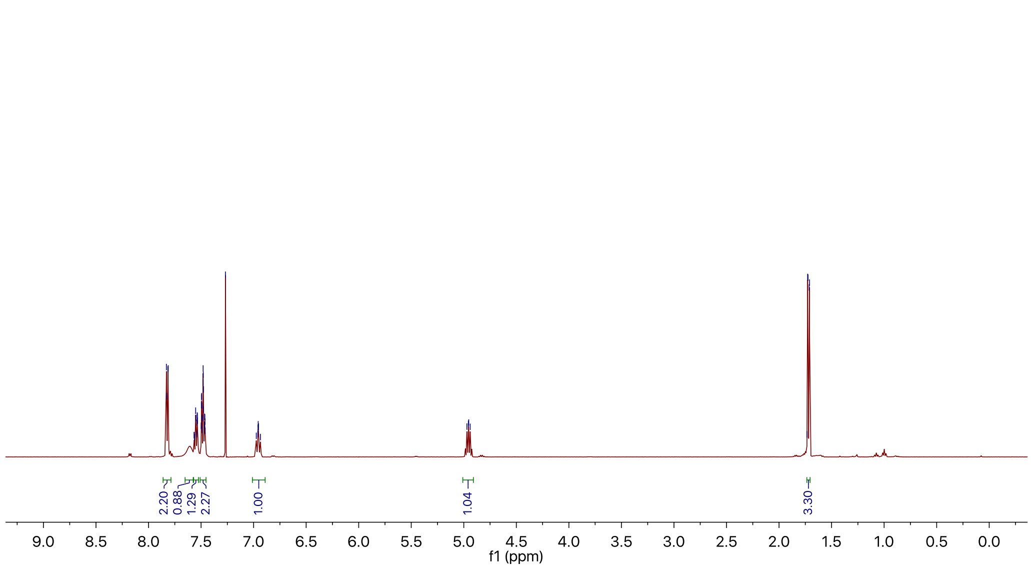
7.27
7.26
6.97
6.97
6.95
6.95
6.94
6.93
6.93
4.94
4.94
4.93
4.93
4.91
2.42
1.72
1.72
1.71
1.70
(Z)-1d
2.04
0.98
2.30
0.96
1.00
3.03
3.03
f1 (ppm)



YY-09-93final-isomer1_CARBON_01
142.40
131.06
129.33
127.04
122.31
105.89
77.34
77.08
76.83
21.47
10.99
(Z)-1d
f1 (ppm)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7.50
7.50
7.50
7.49
7.49
7.49
7.49
7.48
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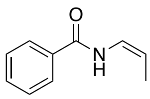
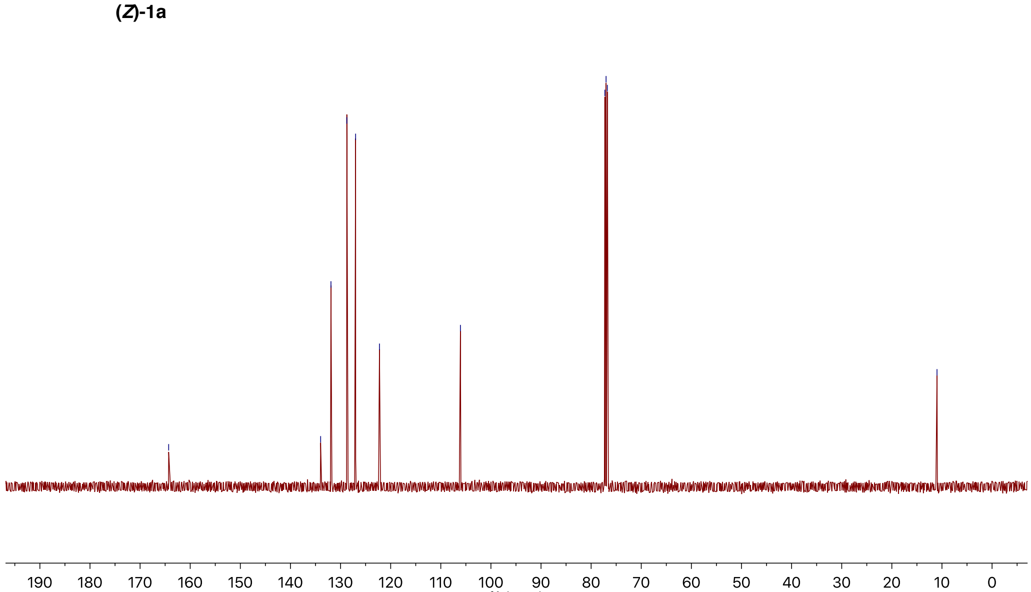
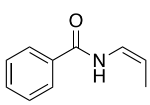
7.48
7.48
7.48
7.48
7.47
7.47
7.46
7.46
7.46
7.27
6.97
6.96
6.96
6.96
6.95
6.94
4.97
4.96
4.95
4.94
1.73
1.73
1.72
1.71
1.71
2.20
0.88
1.29
2.27
1.00
1.04
3.30
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

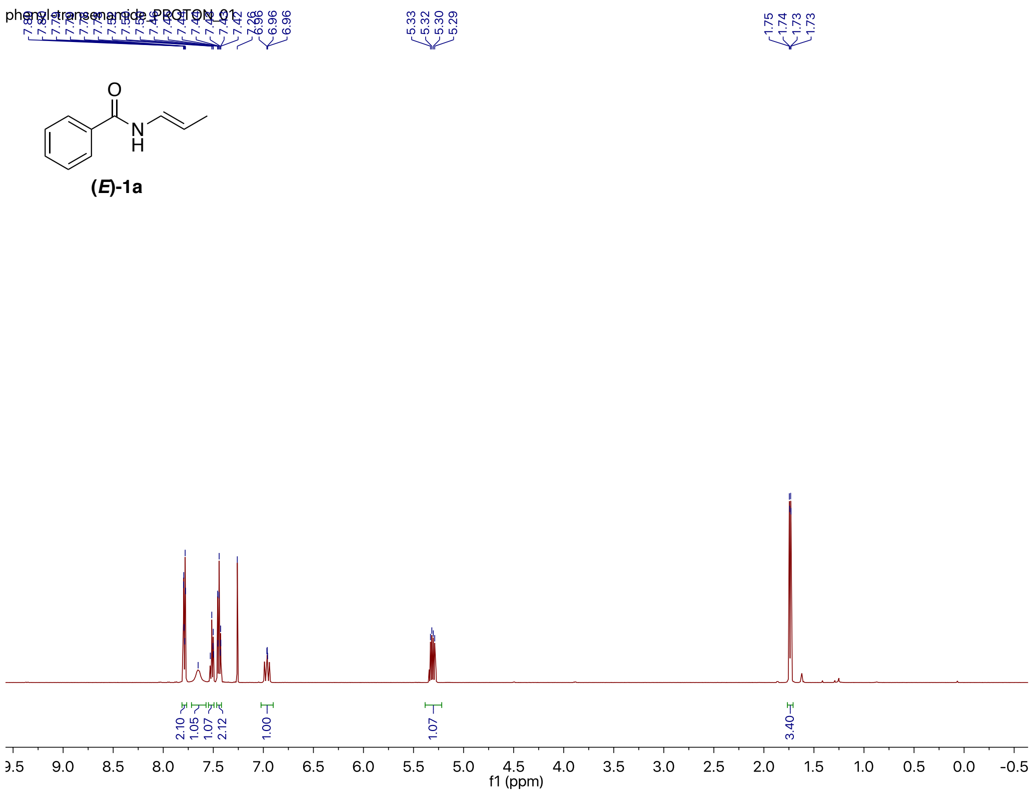


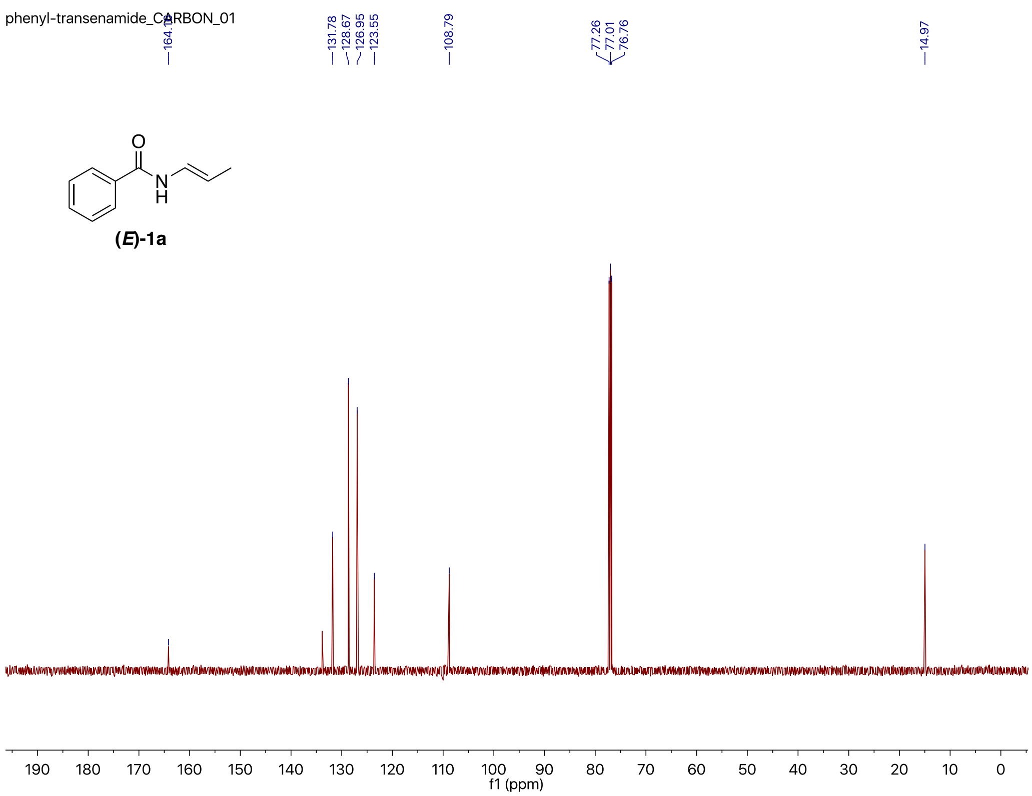
(Z)-1a


phenyl-substrate_CARBON_01
164.30
133.98
131.92
128.75
126.99
122.24
106.08
77.27
77.02
76.76
10.99
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



(Z)-1a


phenyl-transenamide_PROTON_01
5.33
5.32
5.30
5.29
1.75
1.74
1.73
1.73
(E)-1a
2.10
1.05
1.07
2.12
1.00
1.07
3.40
f1 (ppm)


phenyl-transenamide_CARBON_01
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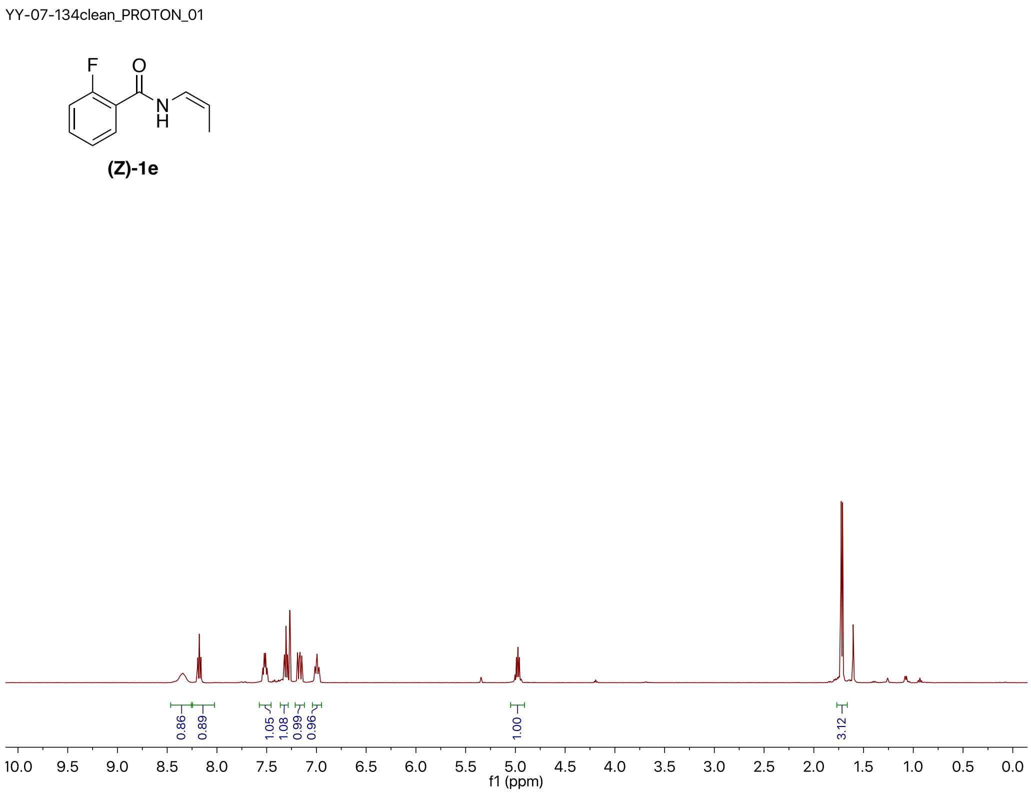
123.55
108.79
77.26
77.01
76.76
14.97
(E)-1a
f1 (ppm)


YY-07-134clean_PROTON_01
F
O
N
H
(Z)-1e
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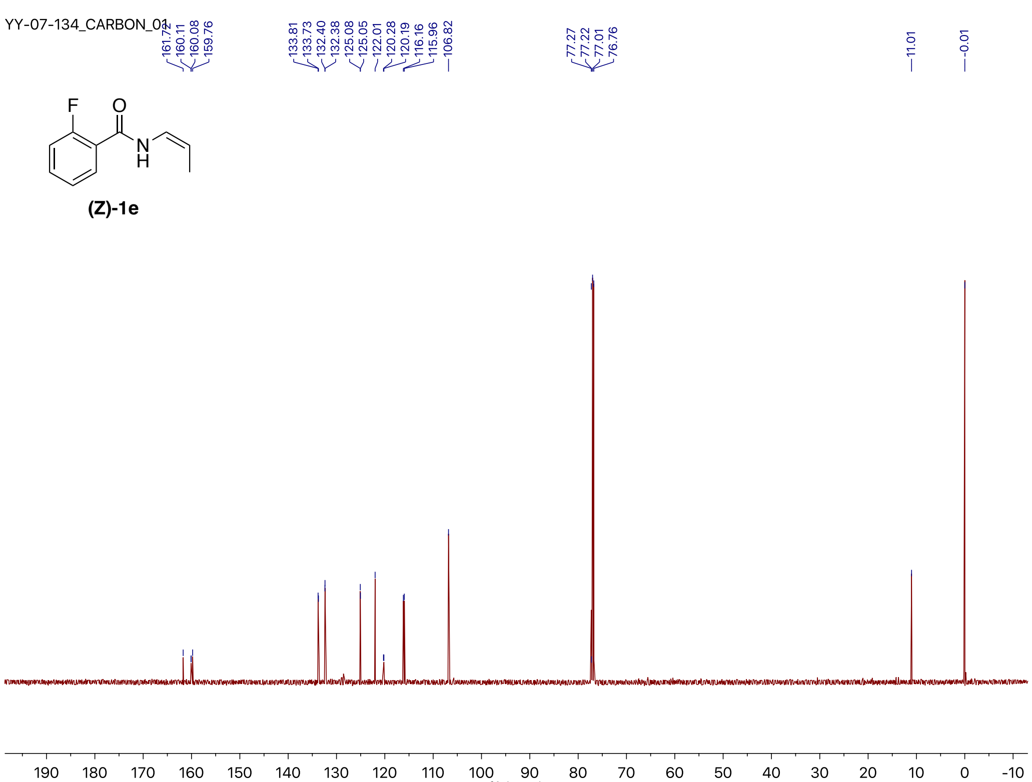
0.89
1.05
1.08
0.99
0.96
1.00
3.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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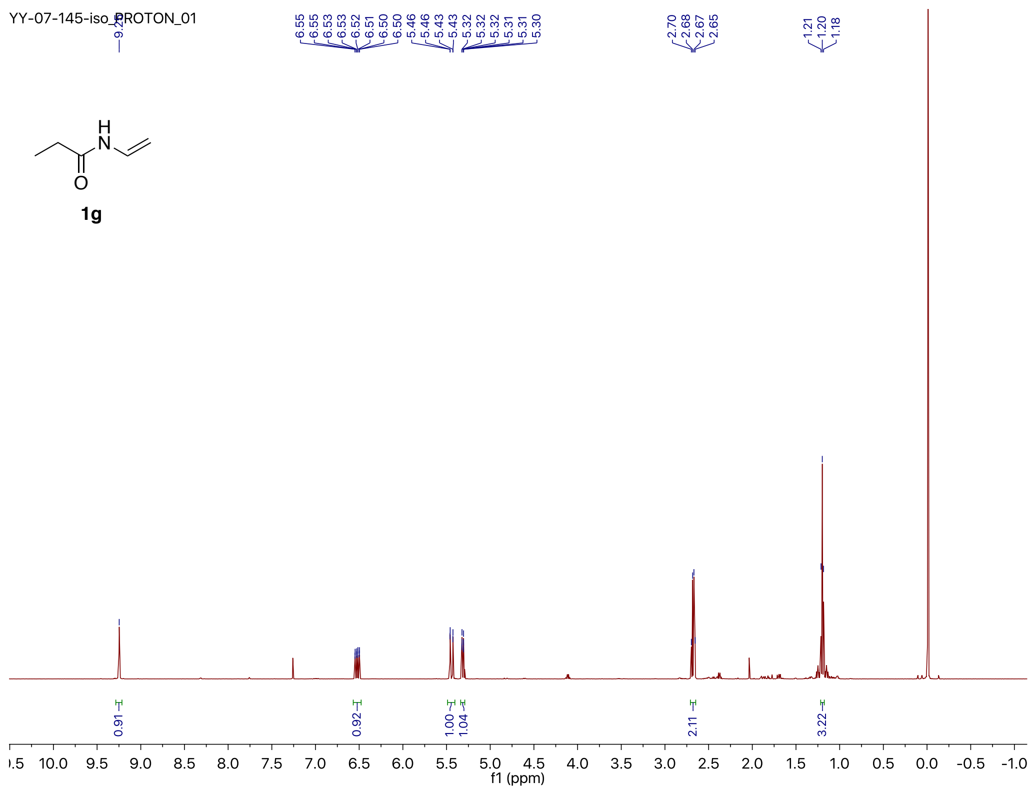
161.72
160.11
160.08
159.76
133.81
133.73
132.40
132.38
125.08
125.05
122.01
120.28
120.19
116.16
115.96
106.82
77.27
77.22
77.01
76.76
11.01
-0.01
F
O
N
H
(Z)-1e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


YY-07-145-iso_PROTON_01
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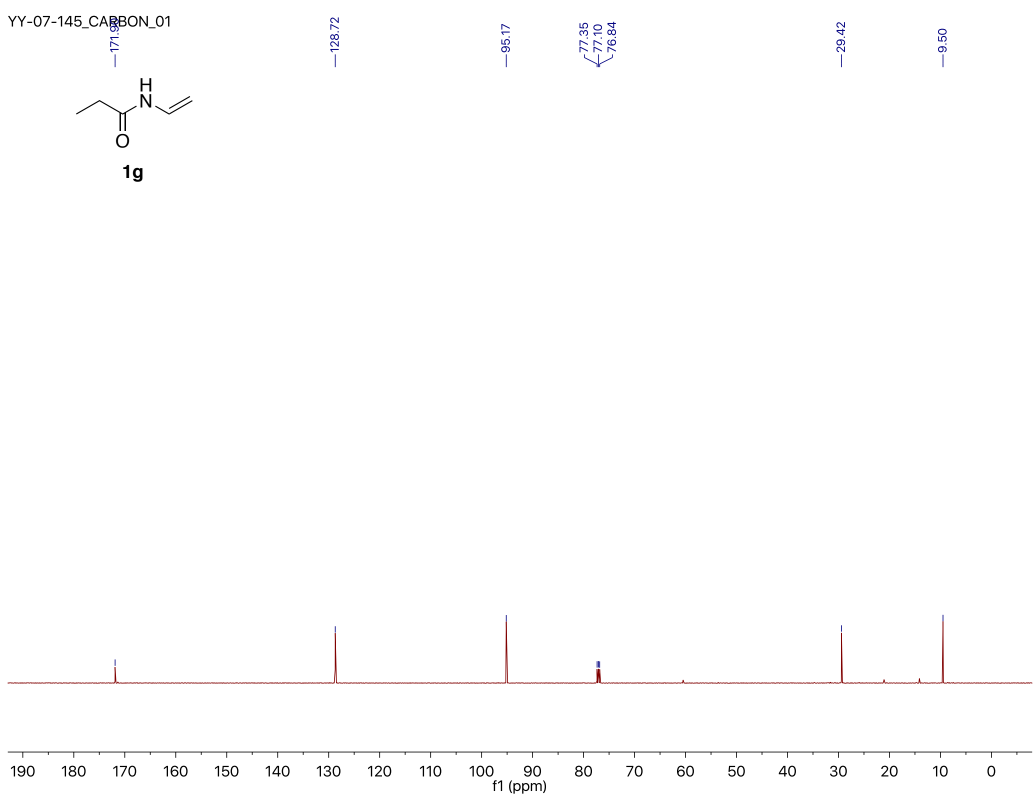
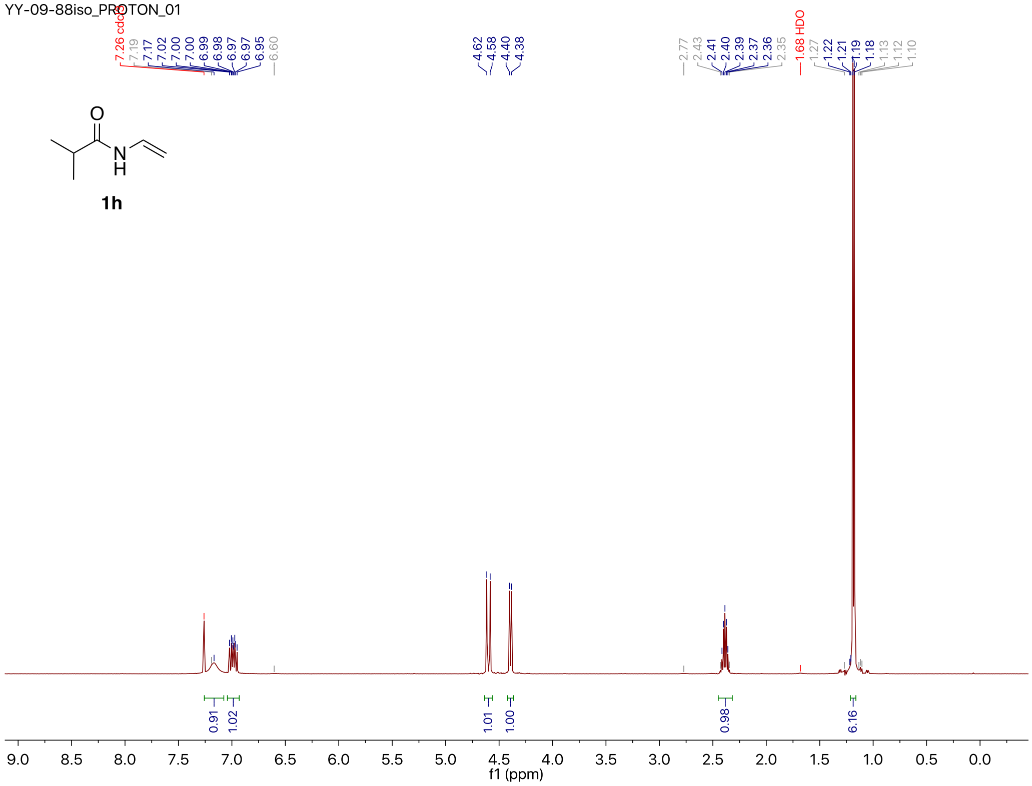
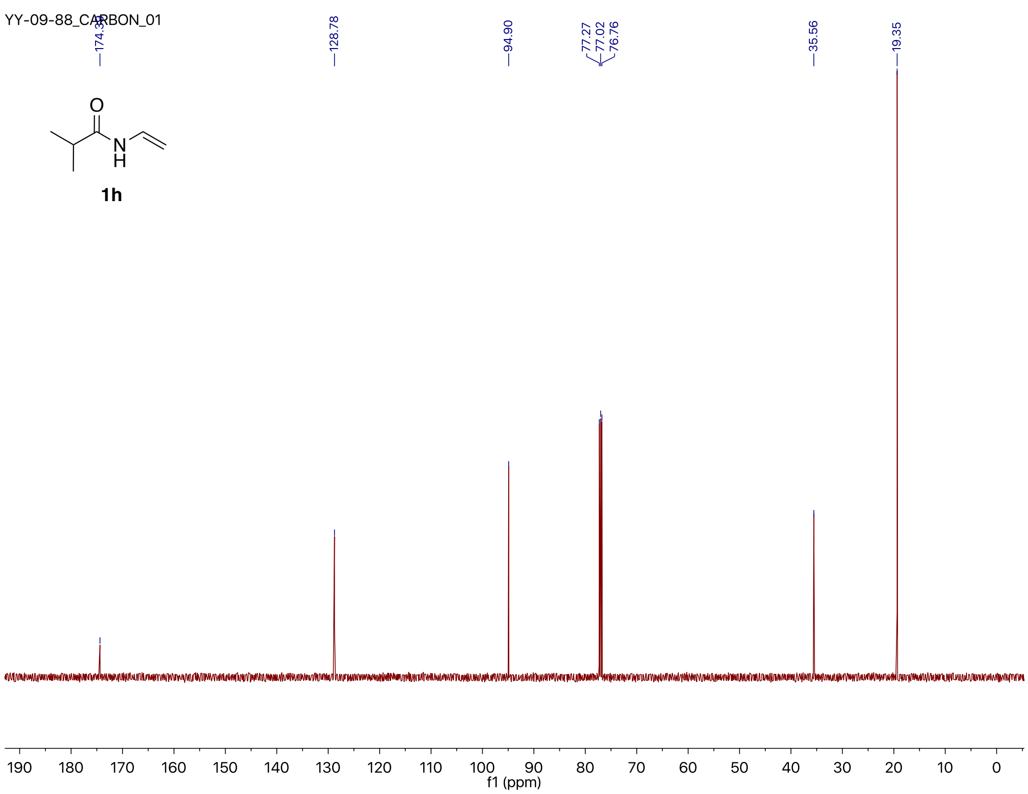
6.55 6.55 6.53 6.53 6.52 6.51 6.50 6.50 5.46 5.46 5.43 5.43 5.32 5.32 5.32 5.31 5.31 5.30
2.70 2.68 2.67 2.65
1.21 1.20 1.18
H
N
O
1g
0.91
0.92
1.00
1.04
2.11
3.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


YY-07-145_CARBON_01
171.96
128.72
95.17
77.35 77.10 76.84
29.42
9.50
H
N
O
1g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


YY-09-88iso_PROTON_01
7.26 cdcl3
7.19
7.17
7.02
7.00
7.00
6.99
6.98
6.97
6.97
6.95
6.60
4.62
4.58
4.40
4.38
2.77
2.43
2.41
2.40
2.39
2.37
2.36
2.35
1.68 HDO
1.27
1.22
1.21
1.19
1.18
1.13
1.12
1.10
O
N
H
1h
0.91
1.02
1.01
1.00
0.98
6.16
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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174.36
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94.90
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76.76
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19.35
O
N
H
1h
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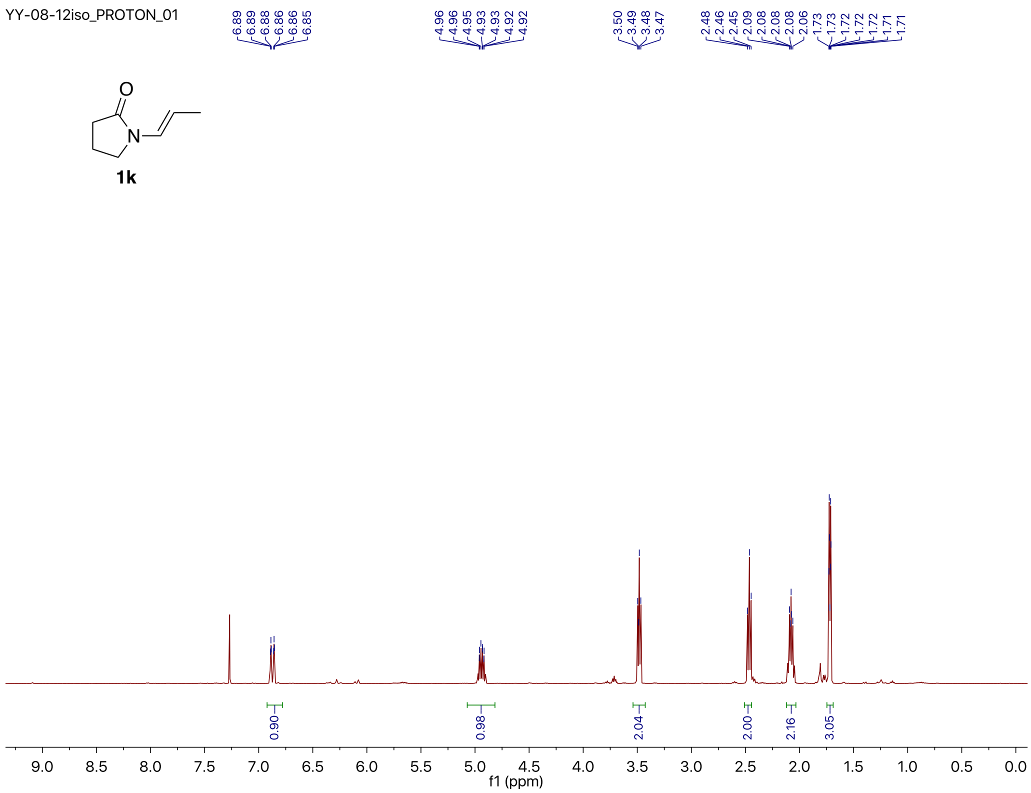
f1 (ppm)



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4.96 4.96 4.95 4.93 4.93 4.92 4.92
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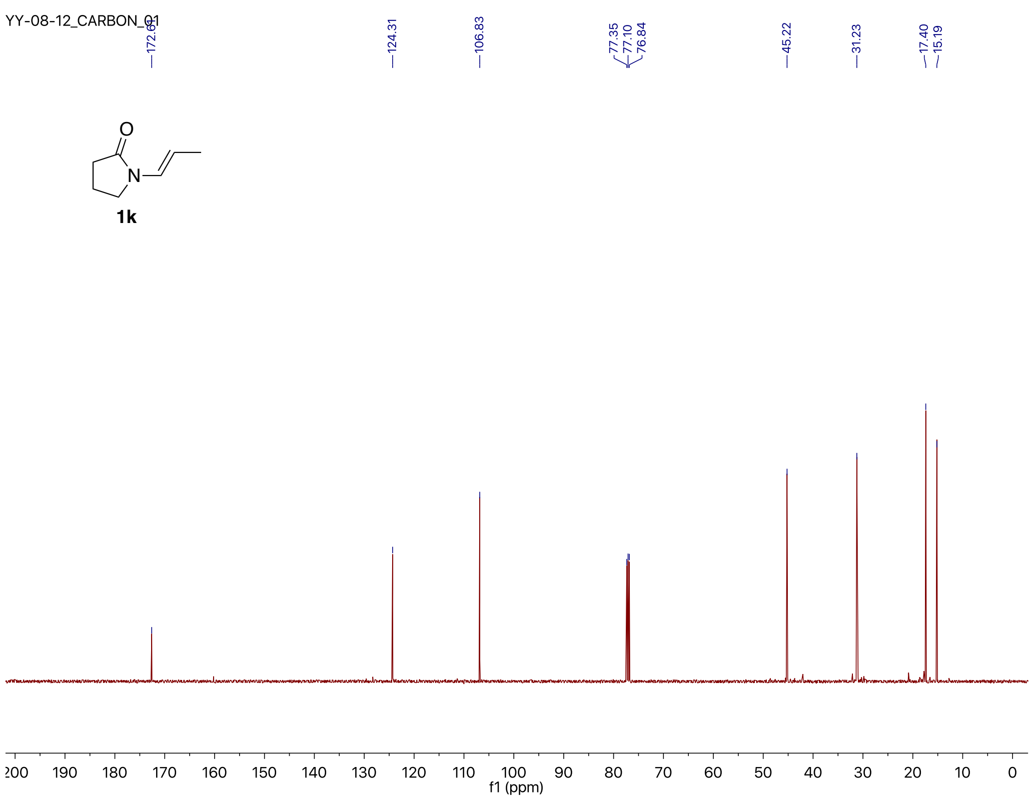
2.48 2.46 2.45 2.09 2.08 2.08 2.08 2.06 1.73 1.73 1.72 1.72 1.72 1.71 1.71
O
N
1k
0.90
0.98
2.04
2.00
2.16
3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



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172.6
124.31
106.83
77.35 77.10 76.84
45.22
31.23
17.40 15.19
O
N
1k
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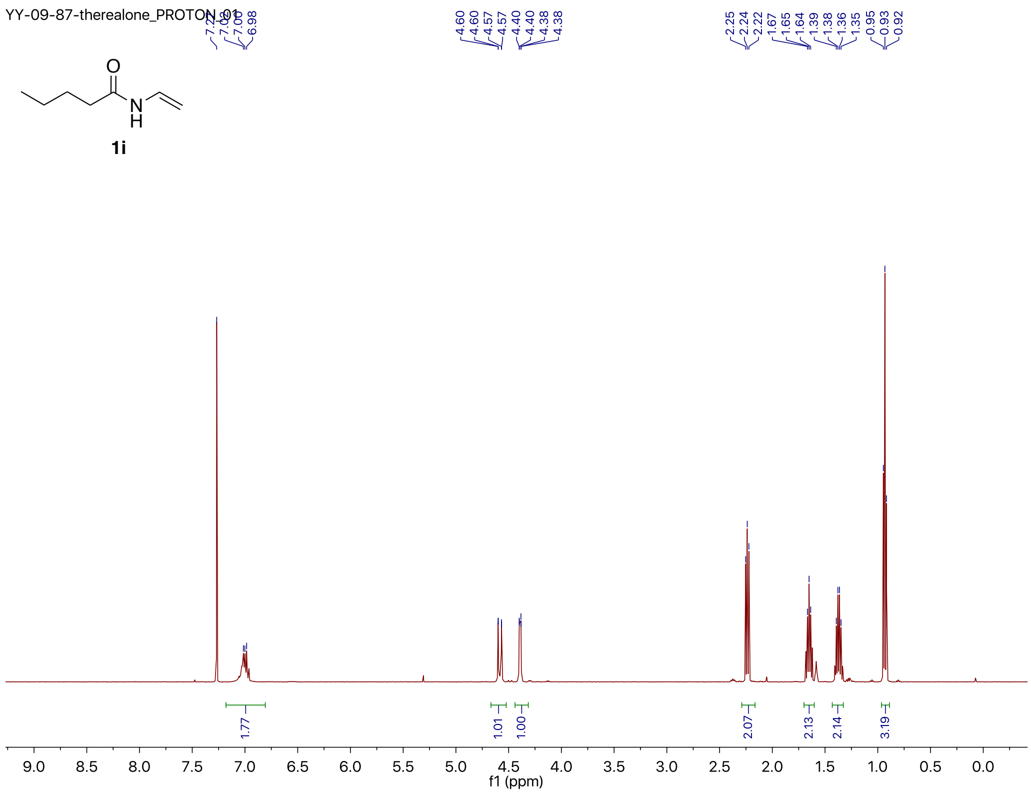
f1 (ppm)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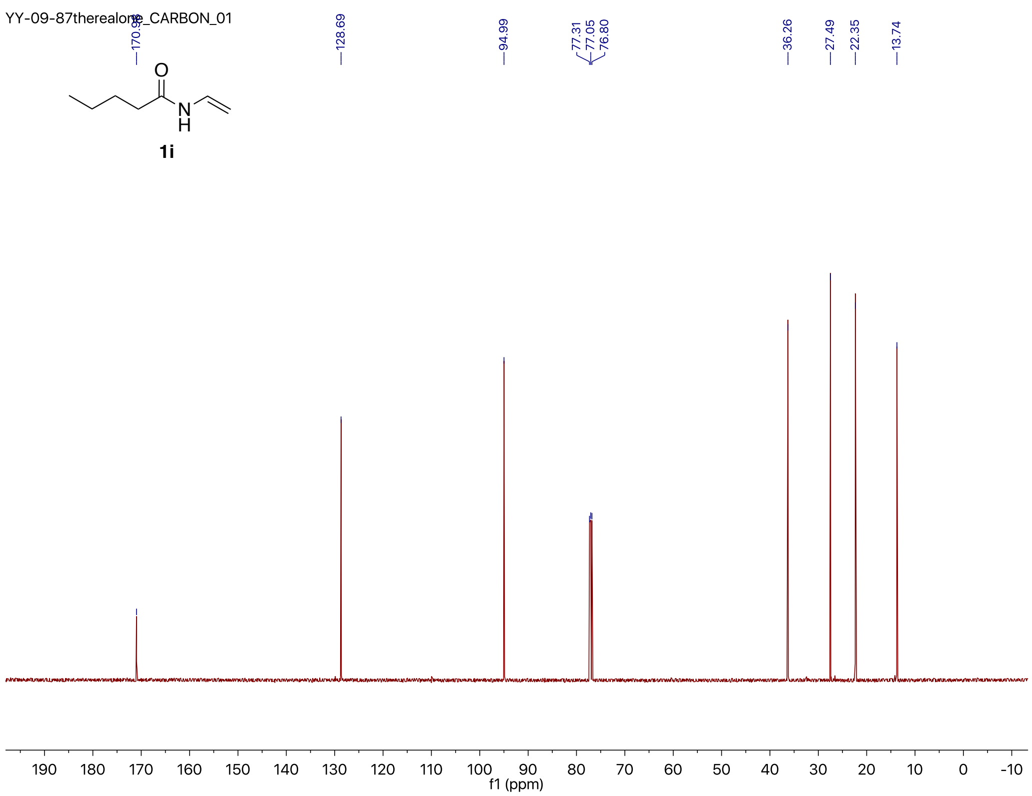
4.60
4.57
4.57
4.40
4.40
4.38
4.38
2.25
2.24
2.22
1.67
1.65
1.64
1.39
1.38
1.36
1.35
0.95
0.93
0.92
O
N
H
1i
1.77
1.01
1.00
2.07
2.13
2.14
3.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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94.99
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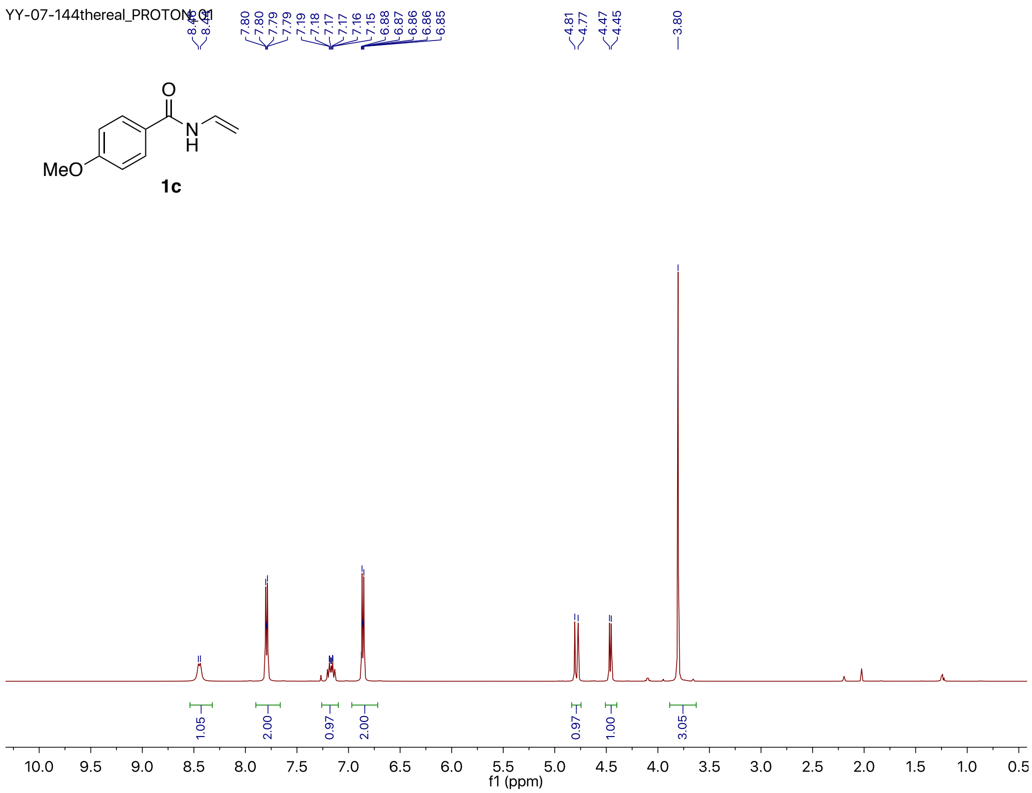
77.05
76.80
36.26
27.49
22.35
13.74
O
N
H
1i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.80
7.79
7.79
7.19
7.18
7.17
7.17
7.16
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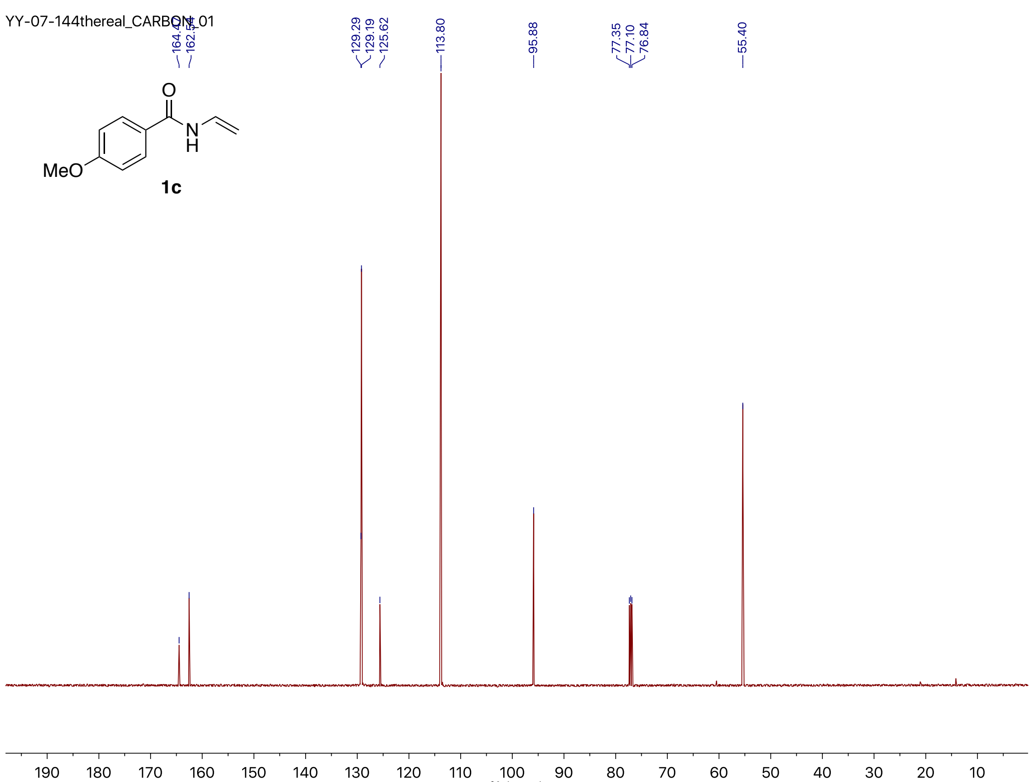
6.87
6.86
6.86
6.85
4.81
4.77
4.47
4.45
3.80
MeO
1c
1.05
2.00
0.97
2.00
0.97
1.00
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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129.19
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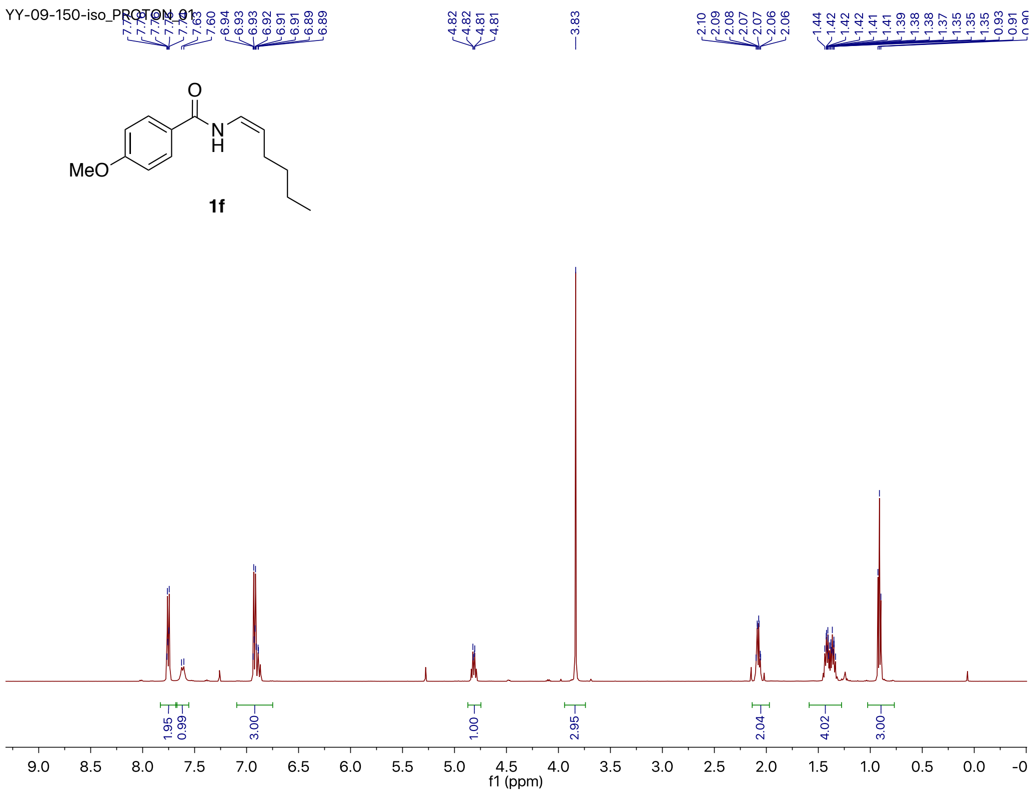
113.80
95.88
77.35
77.10
76.84
55.40
MeO
1c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


YY-09-150-iso_PROTON_01
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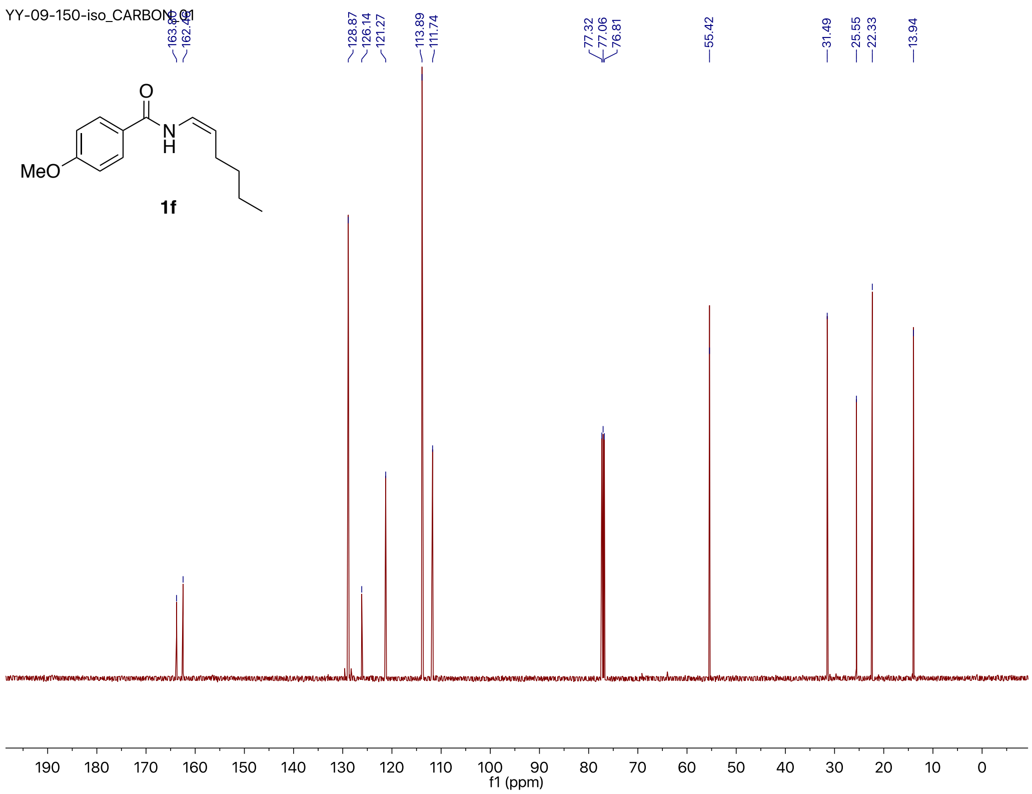
4.82
4.81
4.81
3.83
2.10
2.09
2.08
2.07
2.07
2.06
2.06
1.44
1.42
1.42
1.42
1.41
1.41
1.39
1.38
1.38
1.37
1.35
1.35
1.35
0.93
0.91
1.95
0.99
3.00
1.00
2.95
2.04
4.02
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
MeO
O
N
H

1f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77.32
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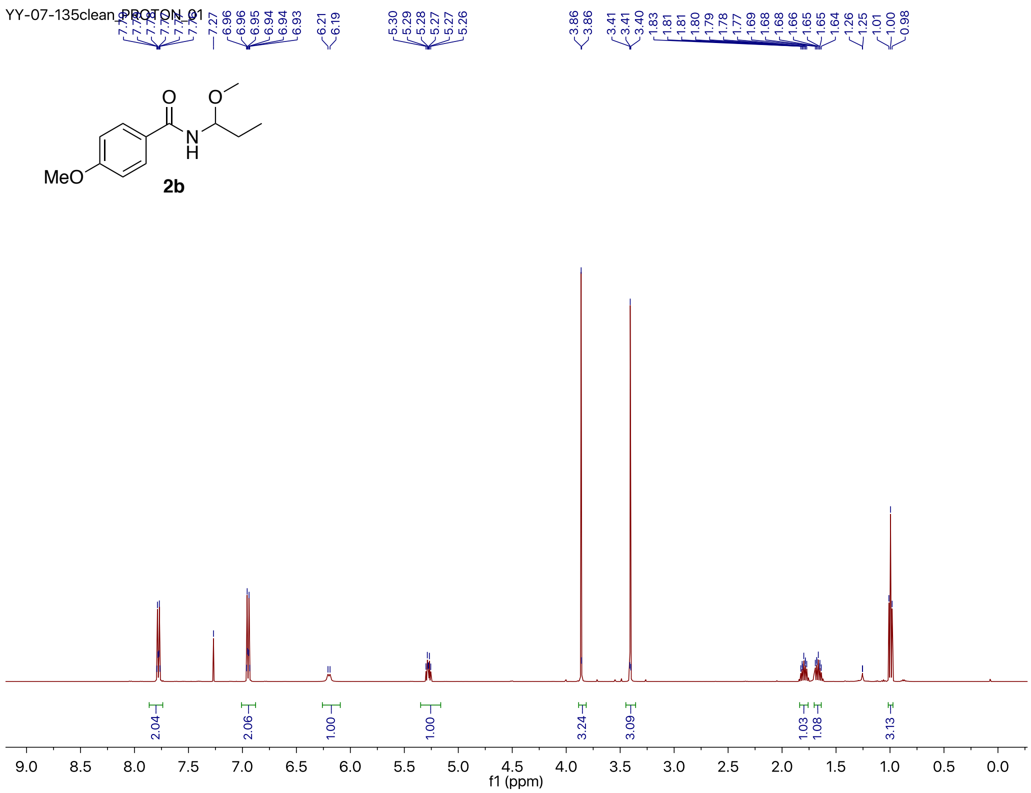
76.81
55.42
31.49
25.55
22.33
13.94
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
MeO
O
N
H

1f


YY-07-135clean_PROTON_01
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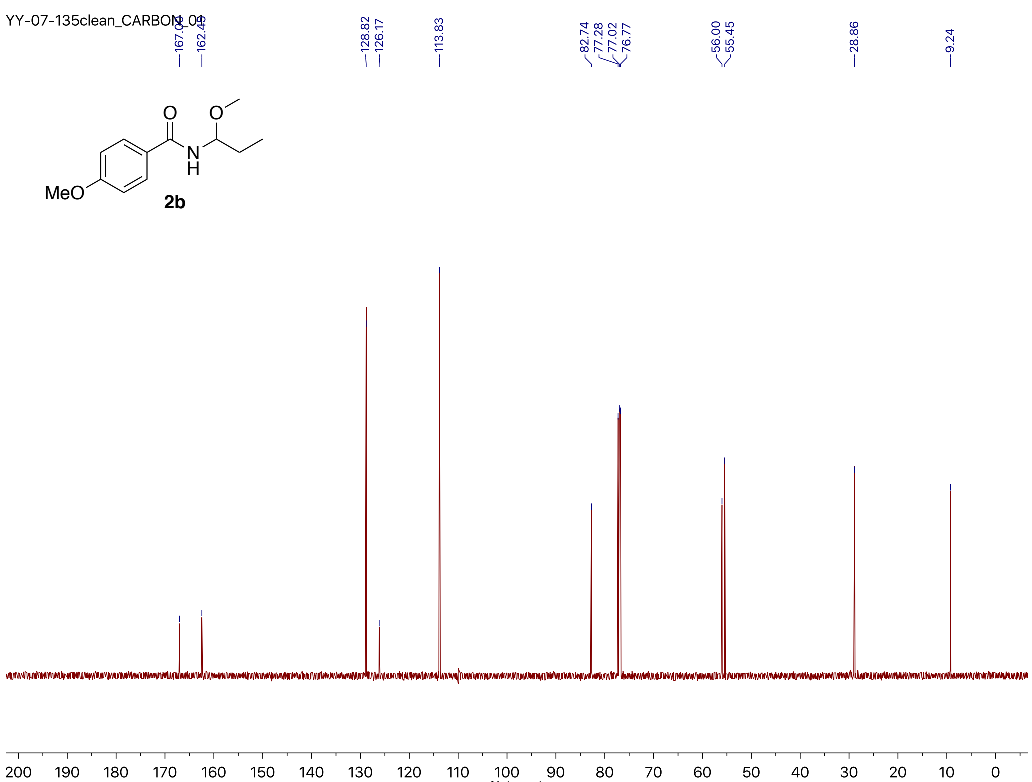
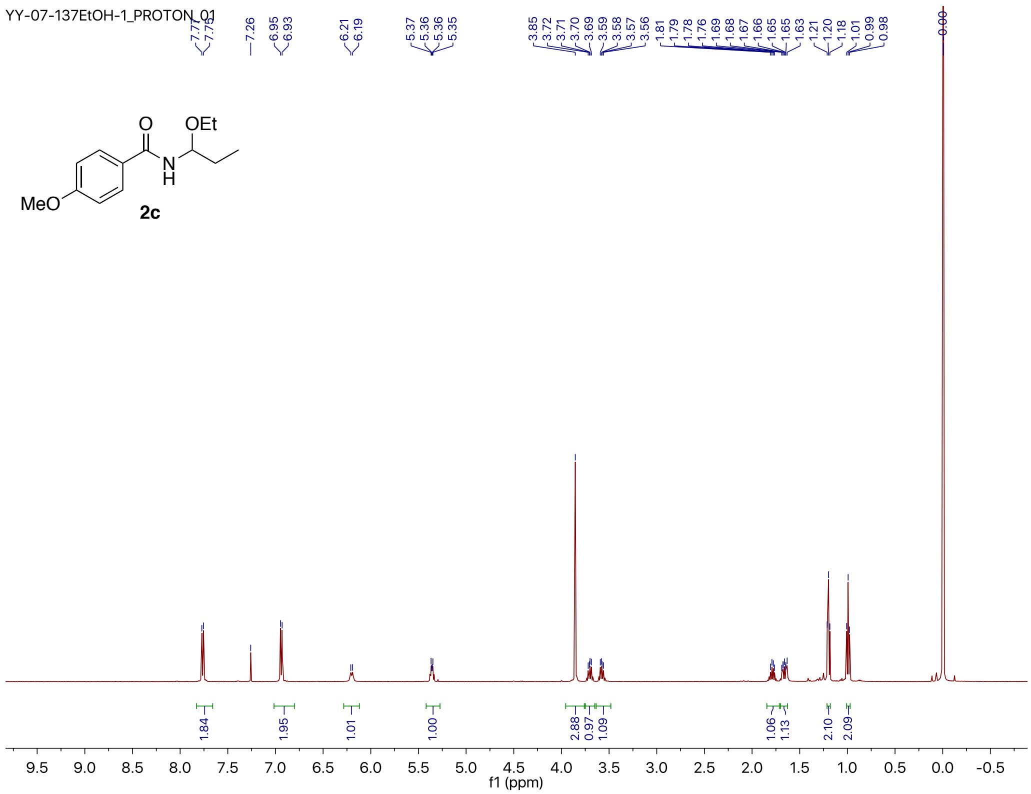
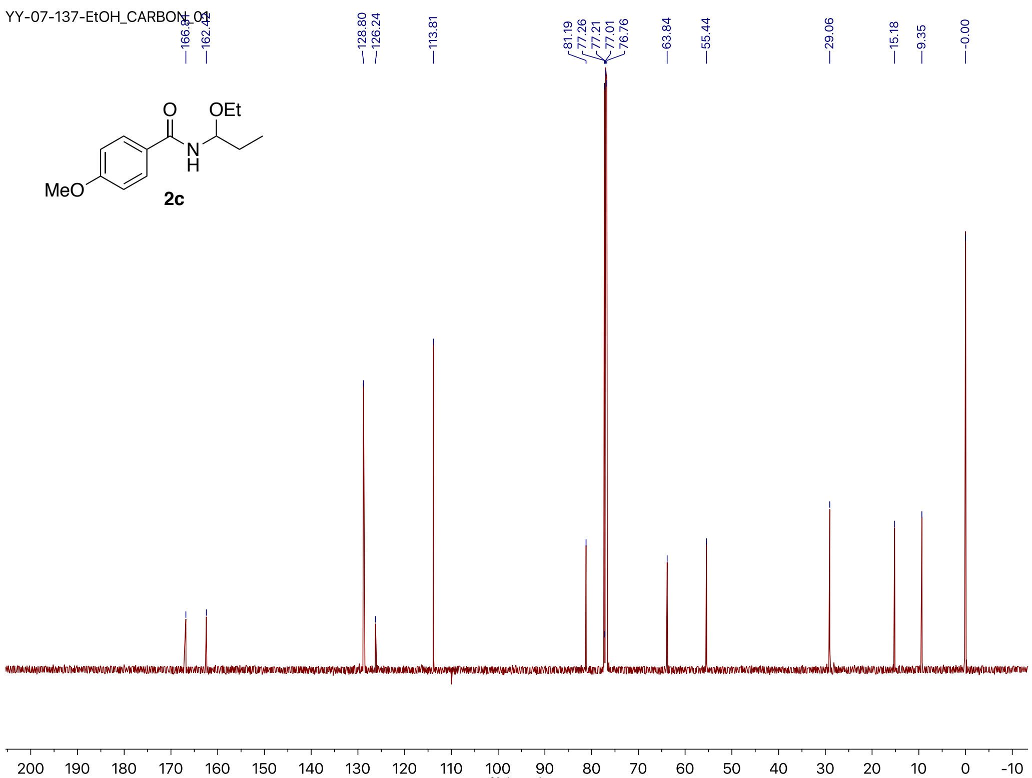
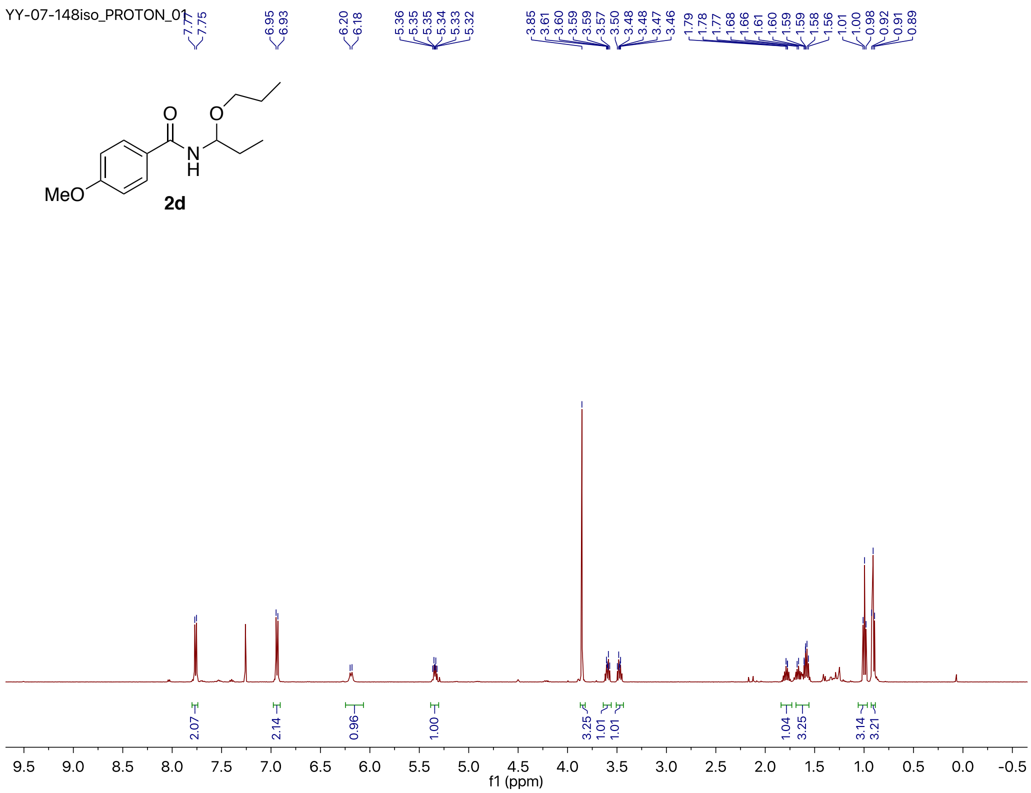
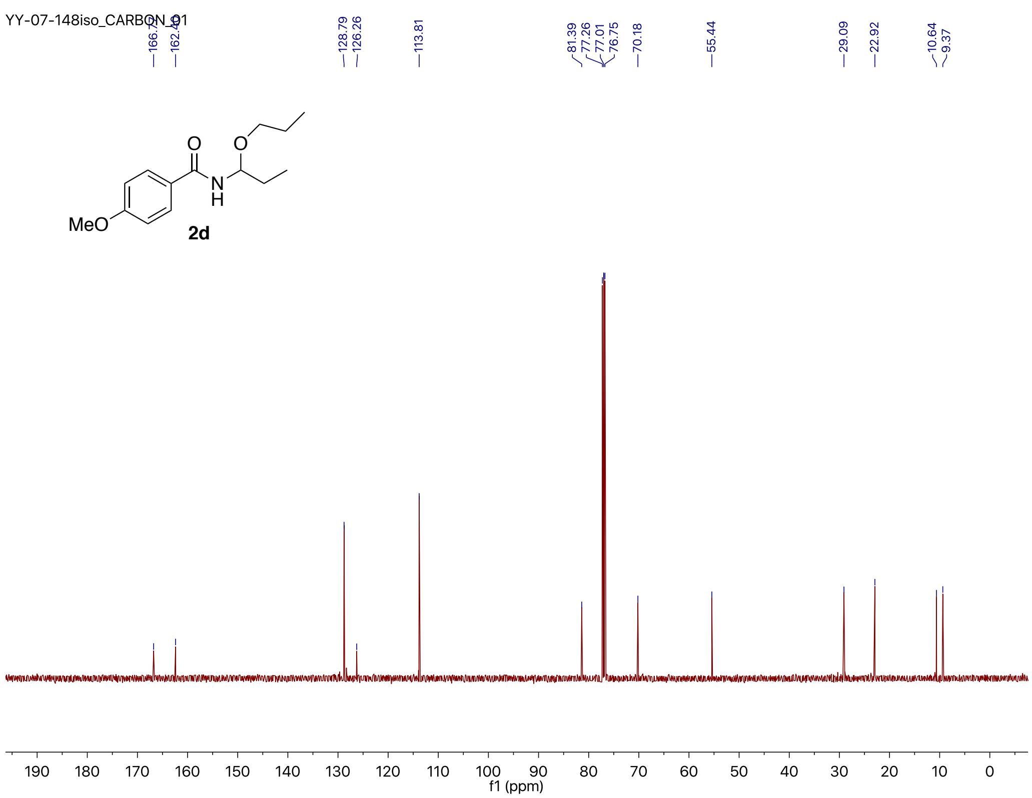
6.96
6.95
6.94
6.94
6.93
6.21
6.19
5.30
5.29
5.28
5.27
5.27
5.26
3.86
3.86
3.41
3.41
3.40
1.83
1.81
1.81
1.80
1.79
1.78
1.77
1.69
1.68
1.68
1.66
1.65
1.65
1.64
1.26
1.25
1.01
1.00
0.98
O
O
N
H
MeO
2b
2.04
2.06
1.00
1.00
3.24
3.09
1.03
1.08
3.13
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

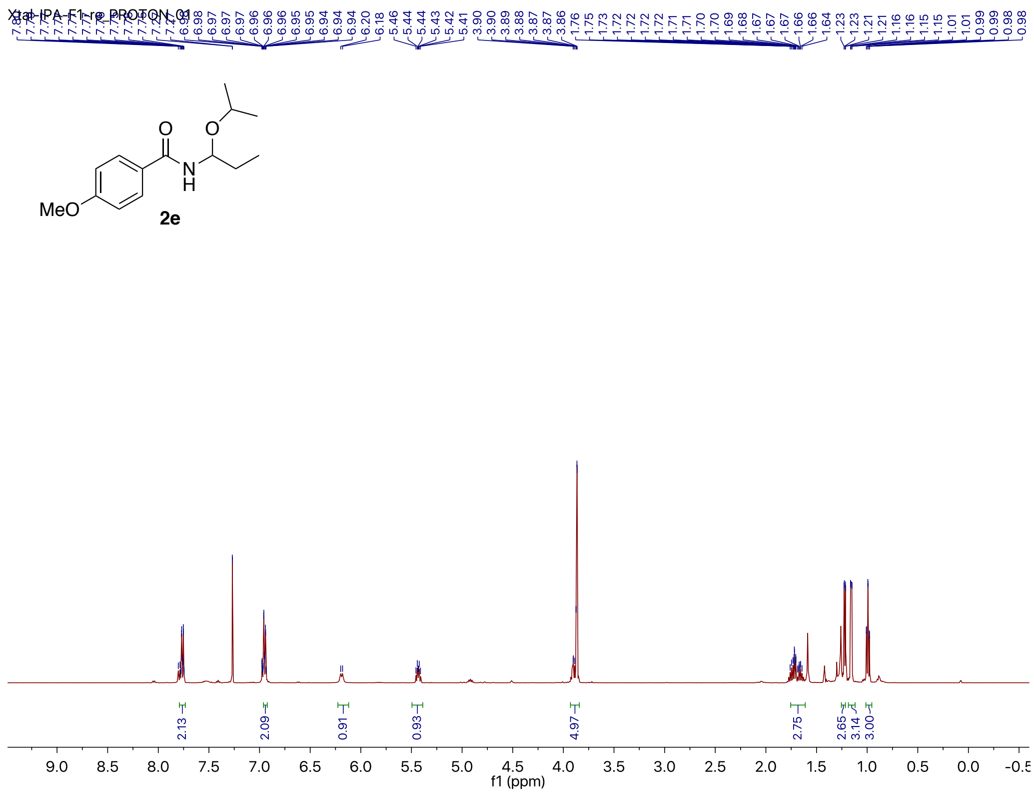

YY-07-135clean_CARBON_01
128.82
126.17
113.83
82.74
77.28
77.02
76.77
56.00
55.45
28.86
9.24
O
O
N
H
MeO
2b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

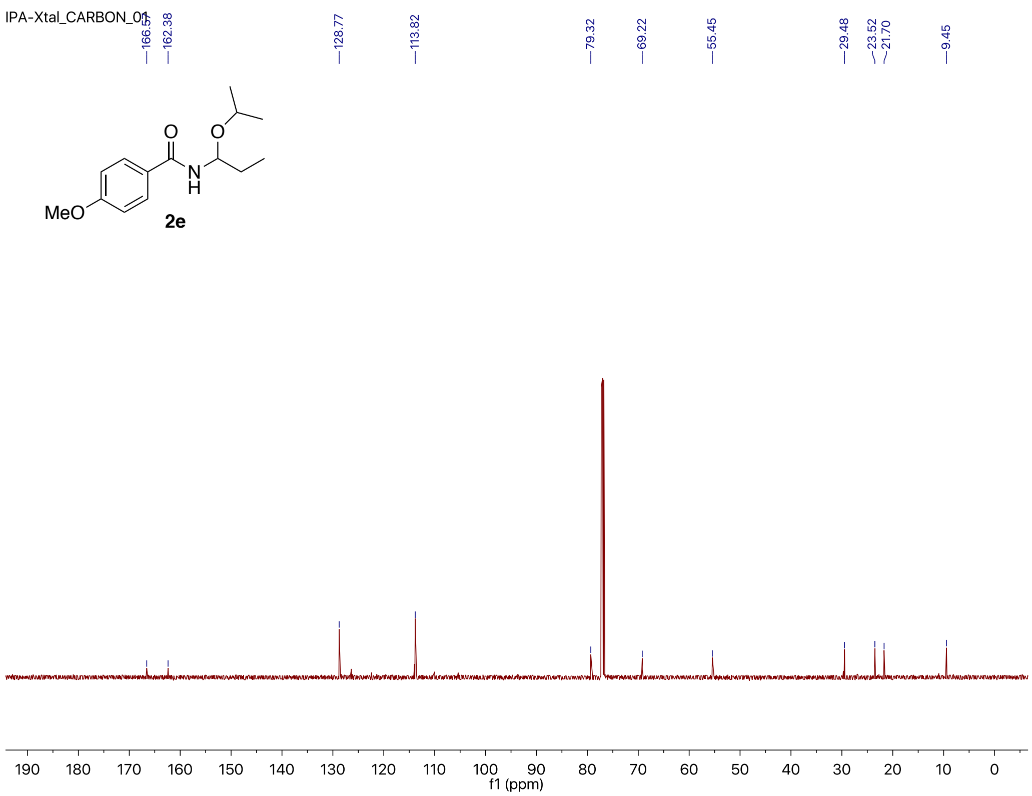

YY-07-137EtOH-1_PROTON_01
7.77
7.75
7.26
6.95
6.93
6.21
6.19
5.37
5.36
5.36
5.35
3.85
3.72
3.71
3.70
3.69
3.59
3.58
3.57
3.56
1.81
1.79
1.78
1.76
1.69
1.68
1.67
1.66
1.65
1.65
1.63
1.21
1.20
1.18
1.01
0.99
0.98
0.00
O
OEt
N
H
MeO
2c
1.84
1.95
1.01
1.00
2.88
0.97
1.09
1.06
1.13
2.10
2.09
9.5 9.0 8.5 8.0 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)

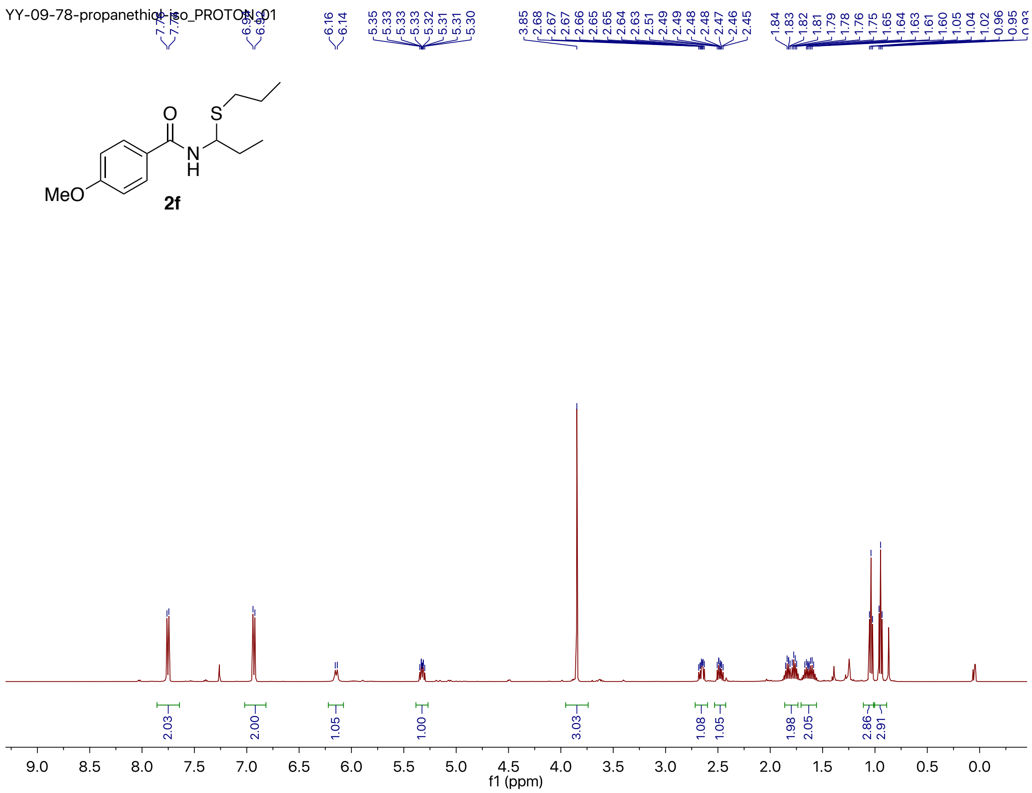

YY-07-137-EtOH_CARBON_01
166.81
162.42
128.80
126.24
113.81
81.19
77.26
77.21
77.01
76.76
63.84
55.44
29.06
15.18
9.35
0.00
O
OEt
N
H
MeO
2c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

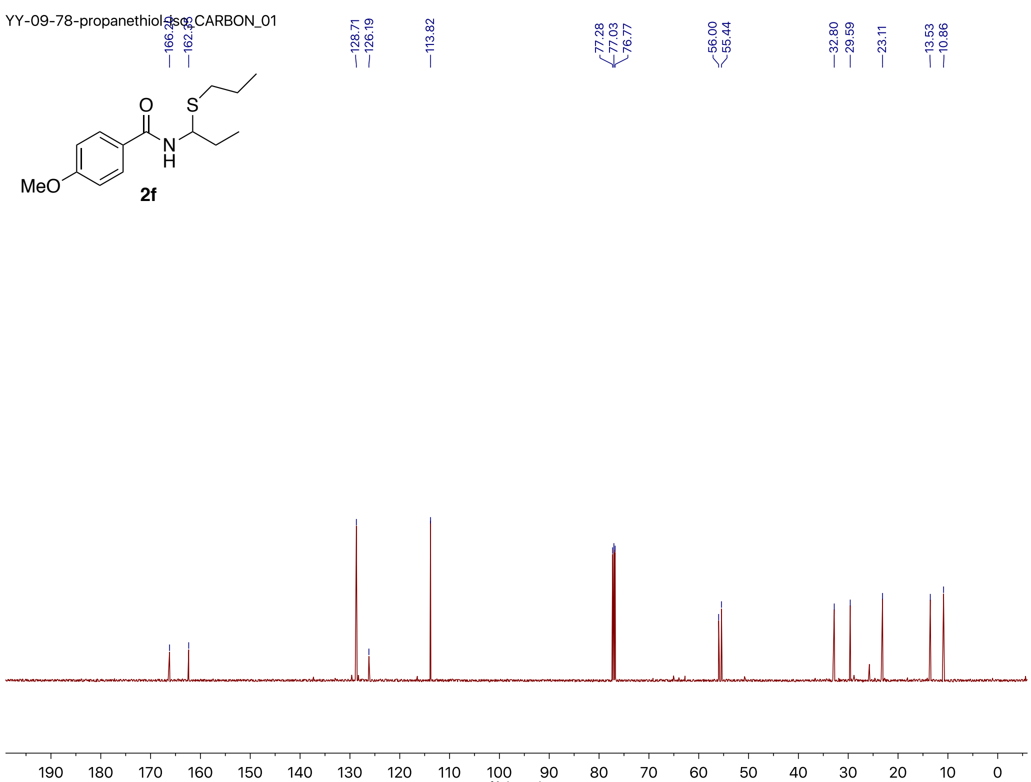

YY-07-148iso_PROTON_01
7.77
7.75
6.95
6.93
6.20
6.18
5.36
5.35
5.35
5.34
5.33
5.32
3.85
3.61
3.60
3.59
3.59
3.57
3.50
3.48
3.48
3.47
3.46
1.79
1.78
1.77
1.68
1.66
1.61
1.60
1.59
1.59
1.58
1.56
1.01
1.00
0.98
0.92
0.91
0.89
MeO
O
O
N
H
2d
2.07
2.14
0.96
1.00
3.25
1.01
1.01
1.04
3.25
3.14
3.21
9.5 9.0 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)

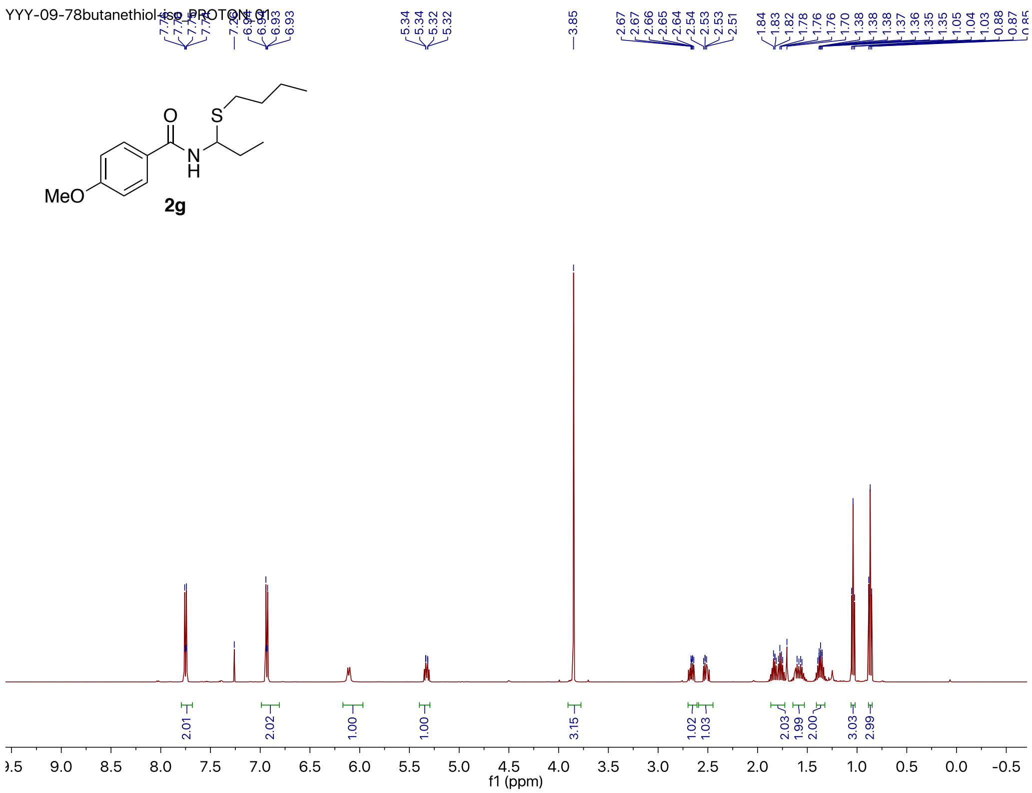

YY-07-148iso_CARBON_01
166.72
162.40
128.79
126.26
113.81
81.39
77.26
77.01
76.75
70.18
55.44
29.09
22.92
10.64
9.37
MeO
O
O
N
H
2d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

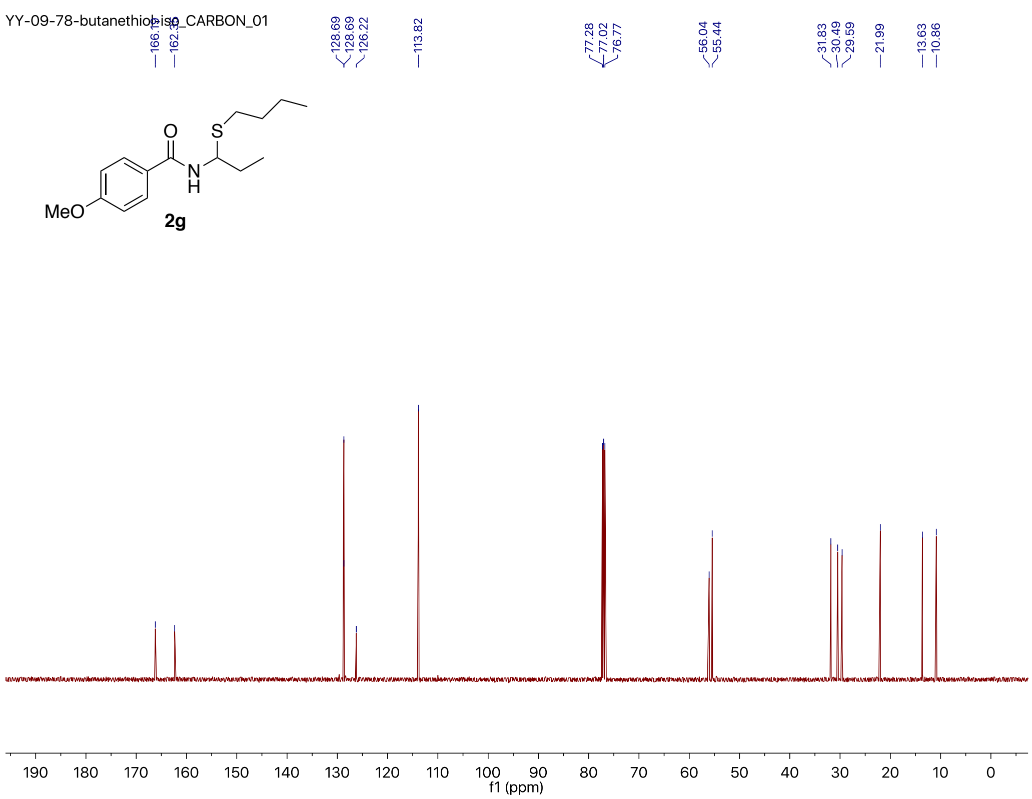

Xtal-IPA-F1-re PROTON_01
MeO
2e
f1 (ppm)

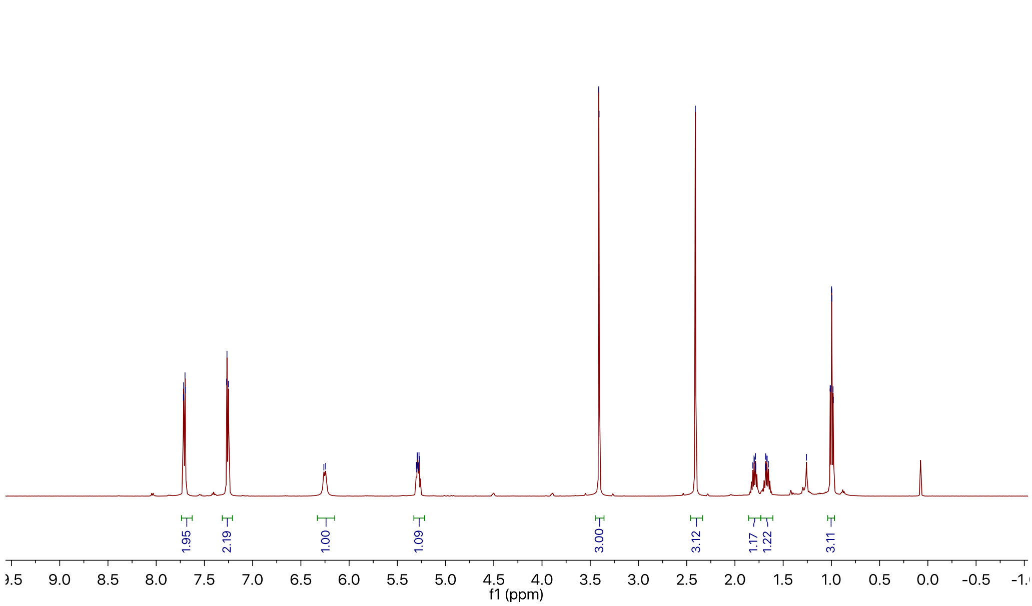

IPA-Xtal_CARBON_01
MeO
2e
f1 (ppm)

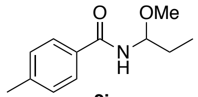

YY-09-78-propanethiol-iso_PROTON_01
MeO
O
S
N
H
2f
f1 (ppm)


YY-09-78-propanethiol-iso_CARBON_01
MeO
O
S
N
H
2f
f1 (ppm)

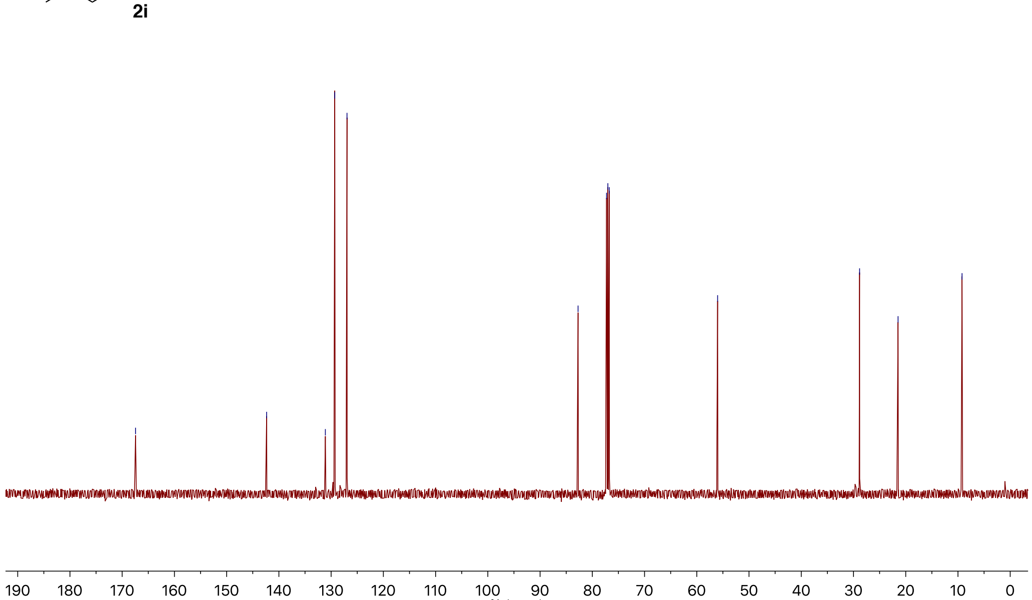

YYY-09-78butanethiol-iso_PROTON_01
5.34
5.34
5.32
5.32
3.85
2.67
2.67
2.66
2.65
2.64
2.54
2.53
2.53
2.51
1.84
1.83
1.82
1.78
1.76
1.76
1.70
1.38
1.38
1.38
1.37
1.36
1.35
1.05
1.04
1.03
0.88
0.87
O
S
N
H
MeO
2g
2.01
2.02
1.00
1.00
3.15
1.02
1.03
2.03
1.99
2.00
3.03
2.99
f1 (ppm)

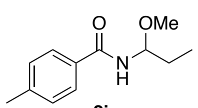

YY-09-78-butanethiol-iso_CARBON_01
128.69
128.69
126.22
113.82
77.28
77.02
76.77
56.04
55.44
31.83
30.49
29.59
21.99
13.63
10.86
O
S
N
H
MeO
2g
f1 (ppm)


YY-09-94iso_PROTON_01
7.72
7.70
7.70
7.27
7.27
7.25
6.26
6.24
5.30
5.30
5.29
5.29
5.29
5.28
5.28
5.27
3.41
3.41
2.41
1.81
1.80
1.80
1.79
1.79
1.78
1.68
1.68
1.68
1.67
1.67
1.65
1.26
1.01
1.01
1.00
0.98
0.98
1.95
2.19
1.00
1.09
3.00
3.12
1.17
1.22
3.11
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 -0.5 -1.0
f1 (ppm)

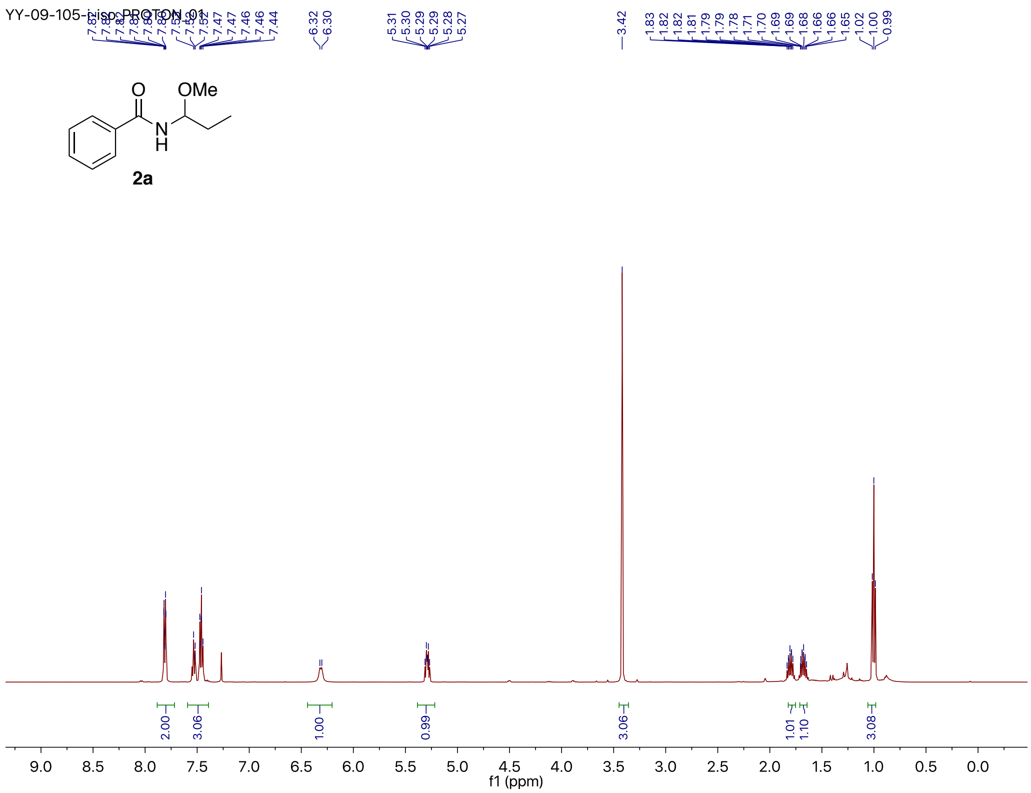

OMe
N
H

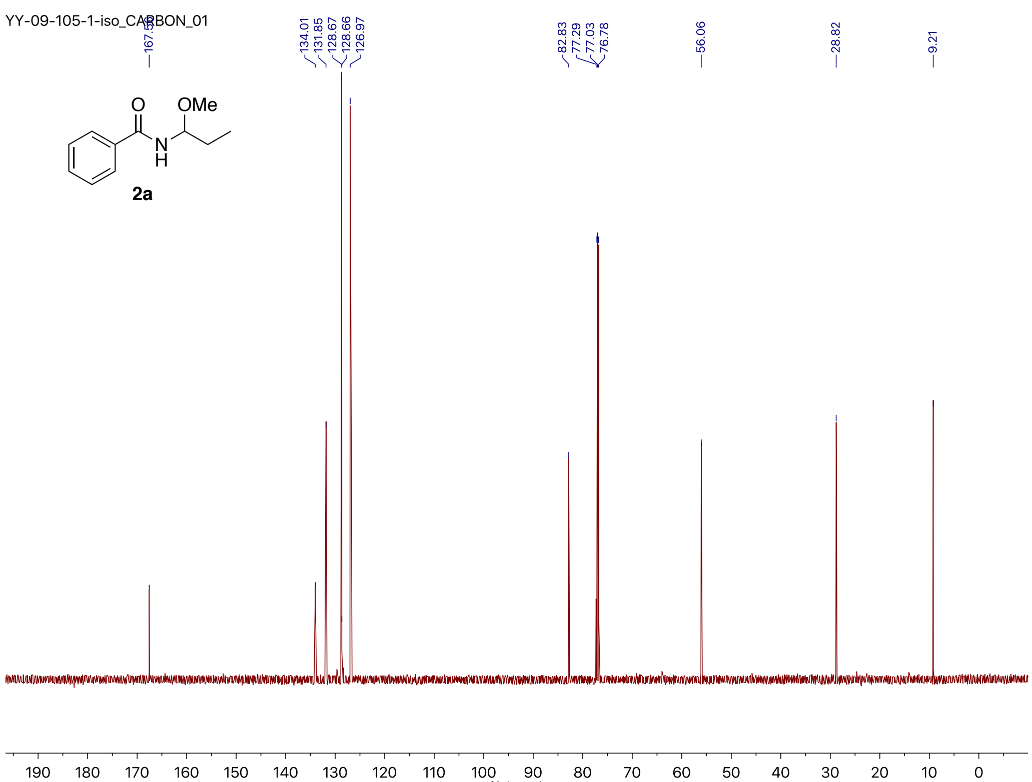
2i

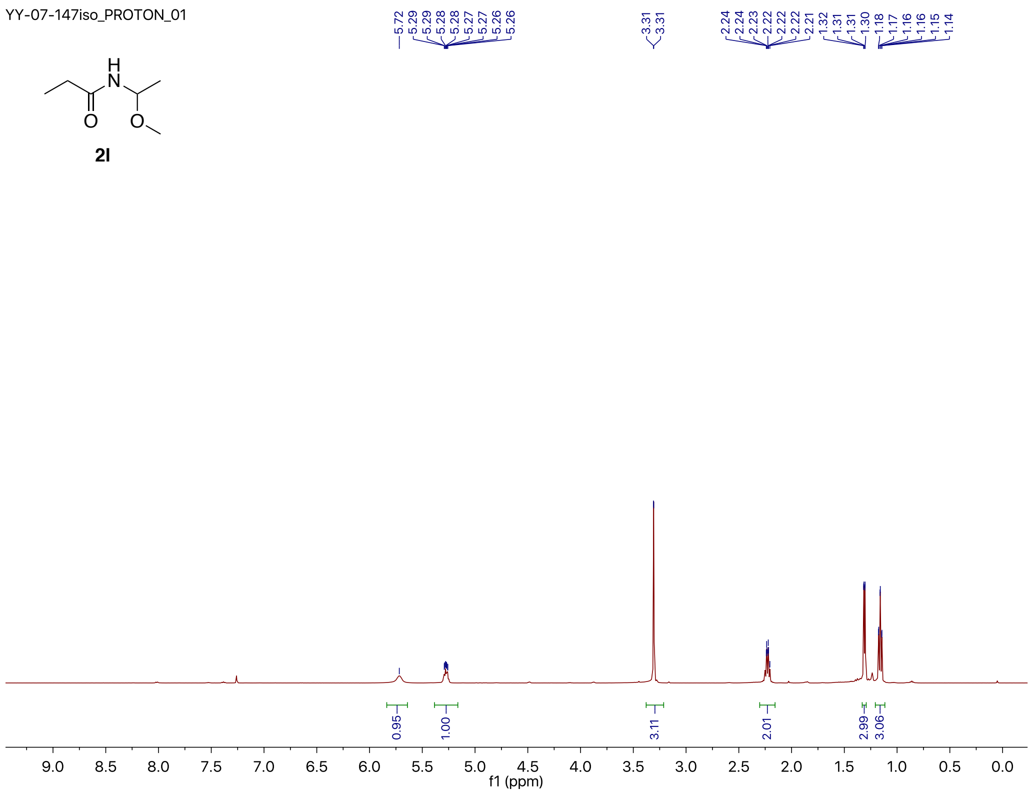

YY-09-94cis-iso_CARBON_01
167.4
142.35
131.10
129.30
126.96
82.73
77.27
77.02
76.77
56.01
28.83
21.47
9.22
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

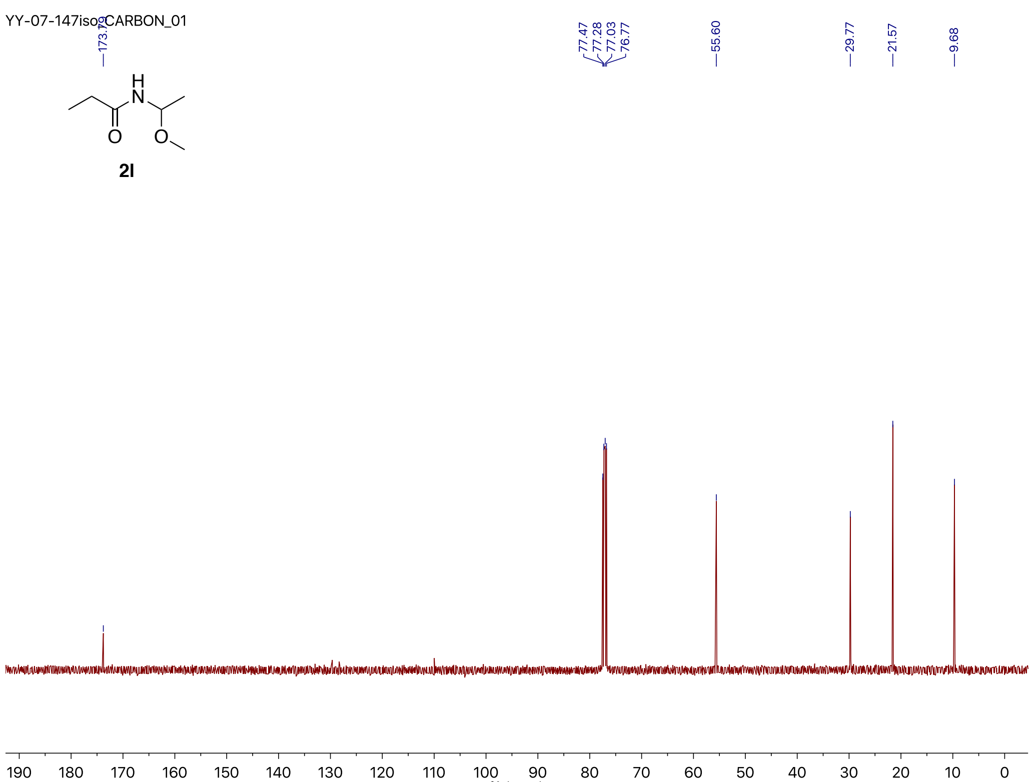

OMe
N
H

2i

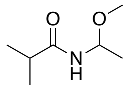

YY-09-105-1-iso_PROTON_01
OMe
N
H
2a
f1 (ppm)


YY-09-105-1-iso_CARBON_01
OMe
N
H
2a
f1 (ppm)

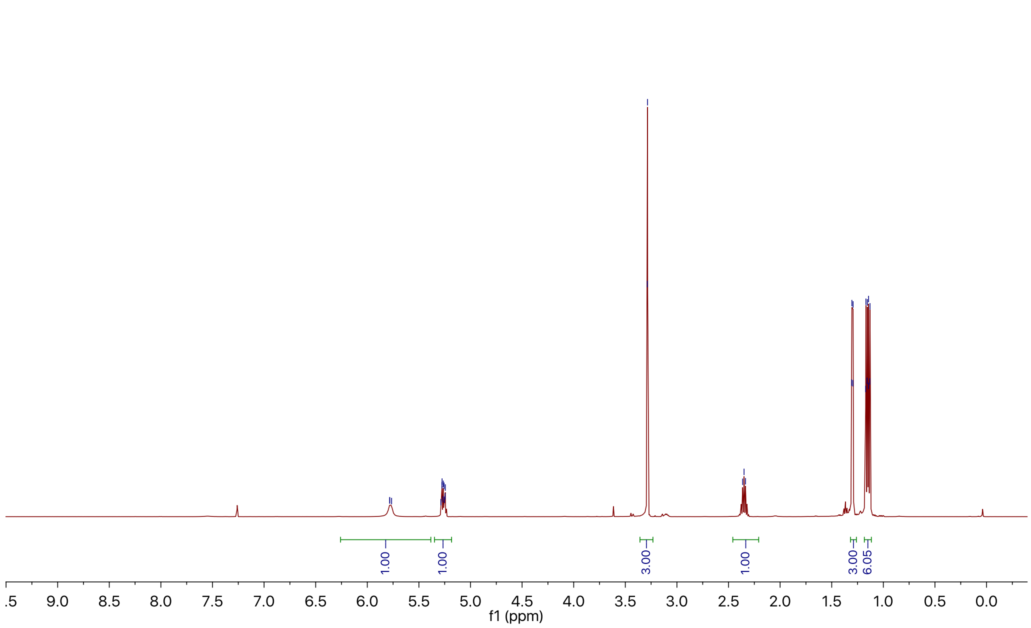

YY-07-147iso_PROTON_01
2l
5.72
5.29
5.29
5.28
5.28
5.27
5.27
5.26
5.26
3.31
3.31
2.24
2.24
2.23
2.22
2.22
2.22
2.21
1.32
1.31
1.31
1.30
1.18
1.17
1.16
1.16
1.15
1.14
0.95
1.00
3.11
2.01
2.99
3.06
f1 (ppm)


YY-07-147iso_CARBON_01
173.79
2l
77.47
77.28
77.03
76.77
55.60
29.77
21.57
9.68
f1 (ppm)

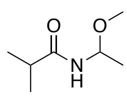
YY-09-90workup-Na2S2O3_PROTON_01



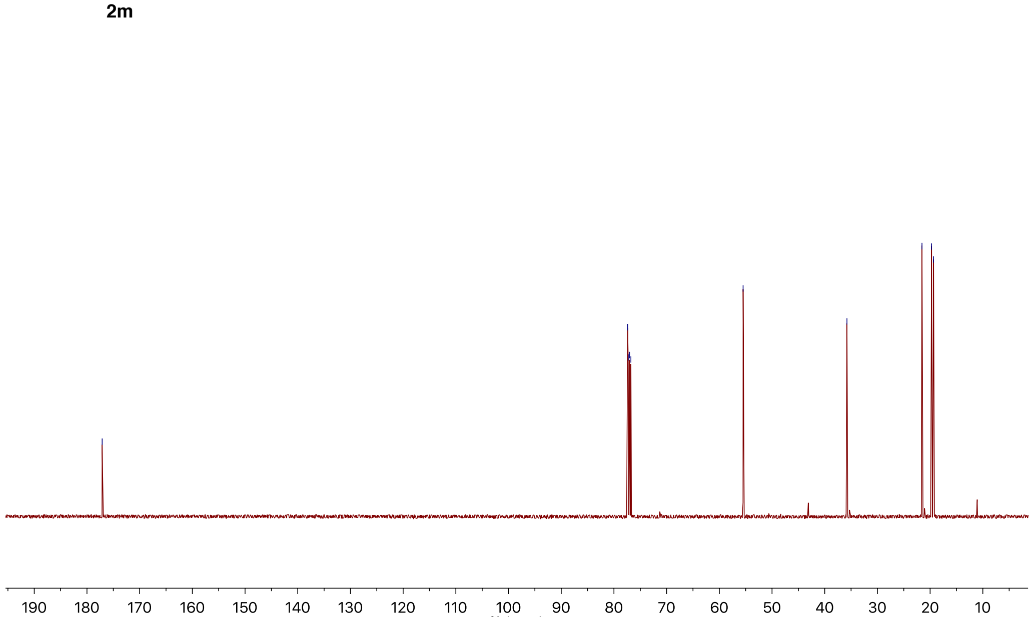
2m

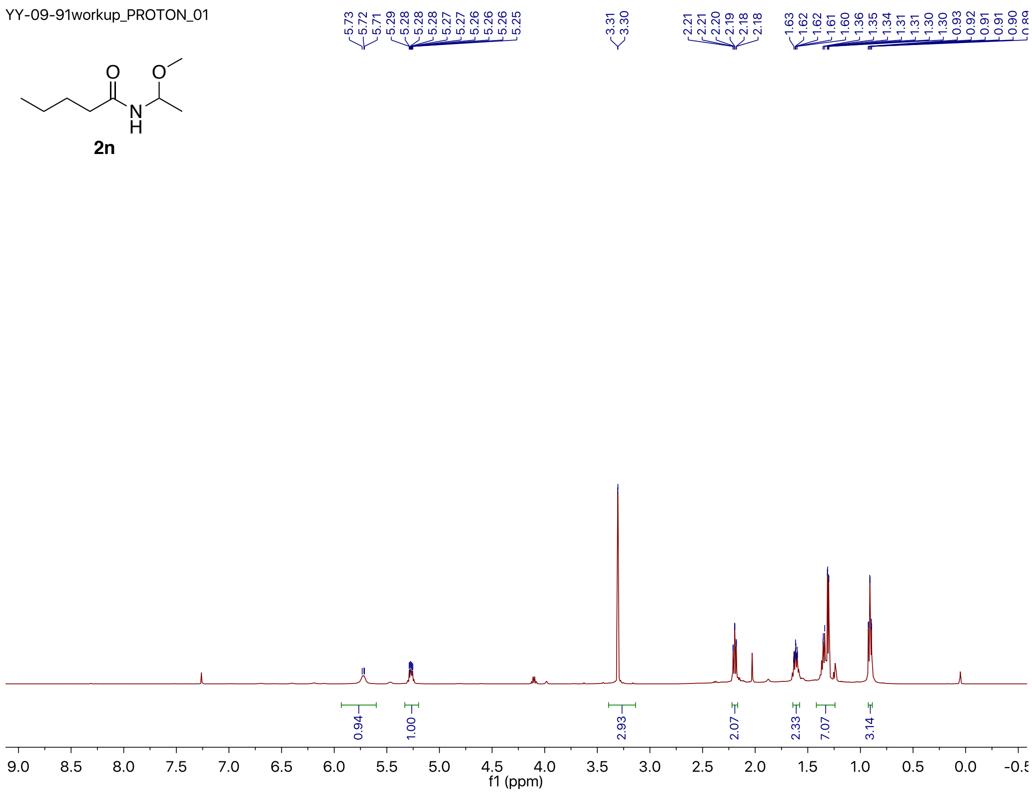


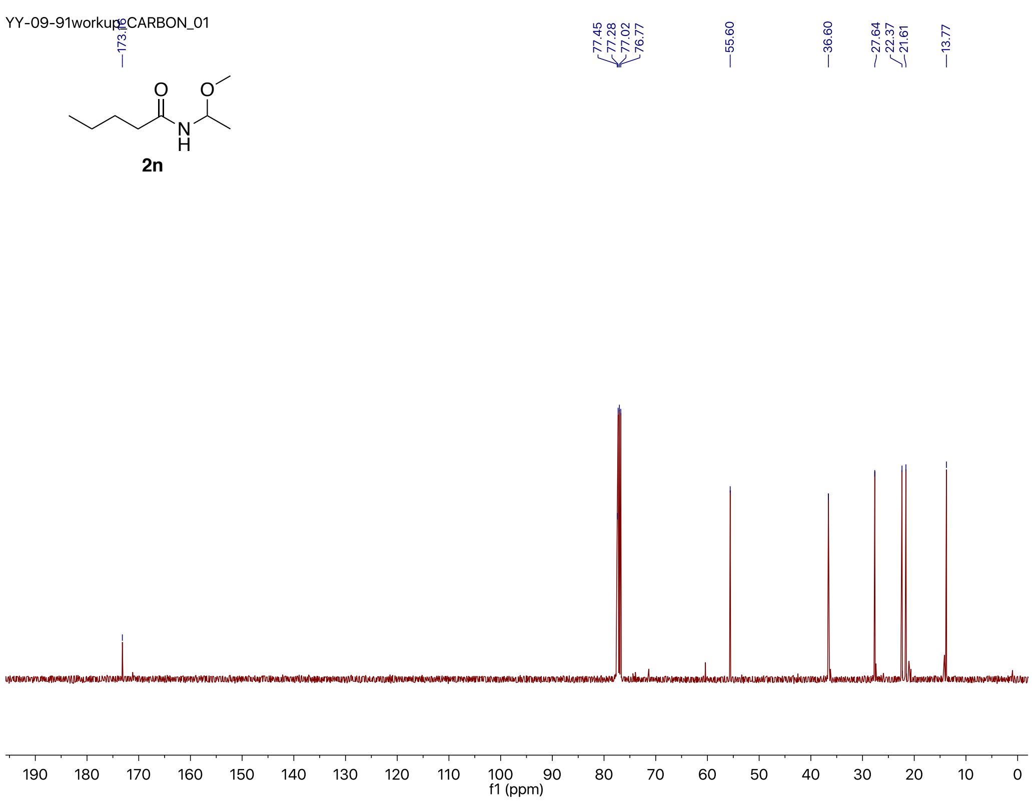
YY-09-90workup-Na2S2O3_CARBON_01

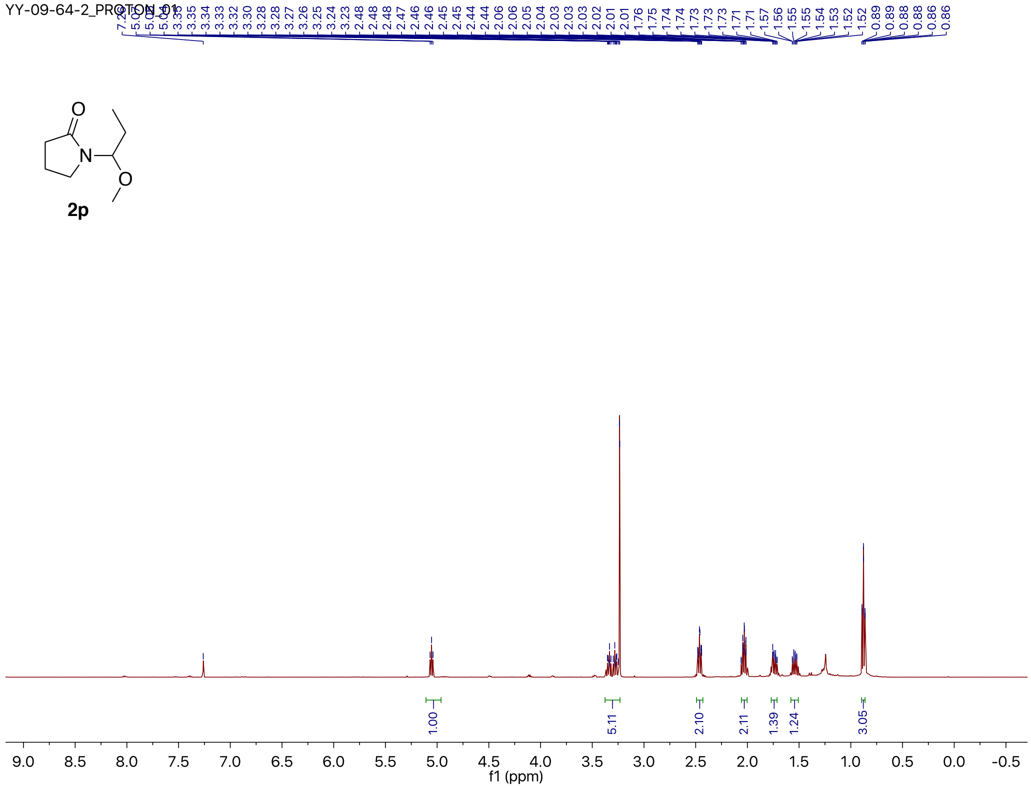


2m

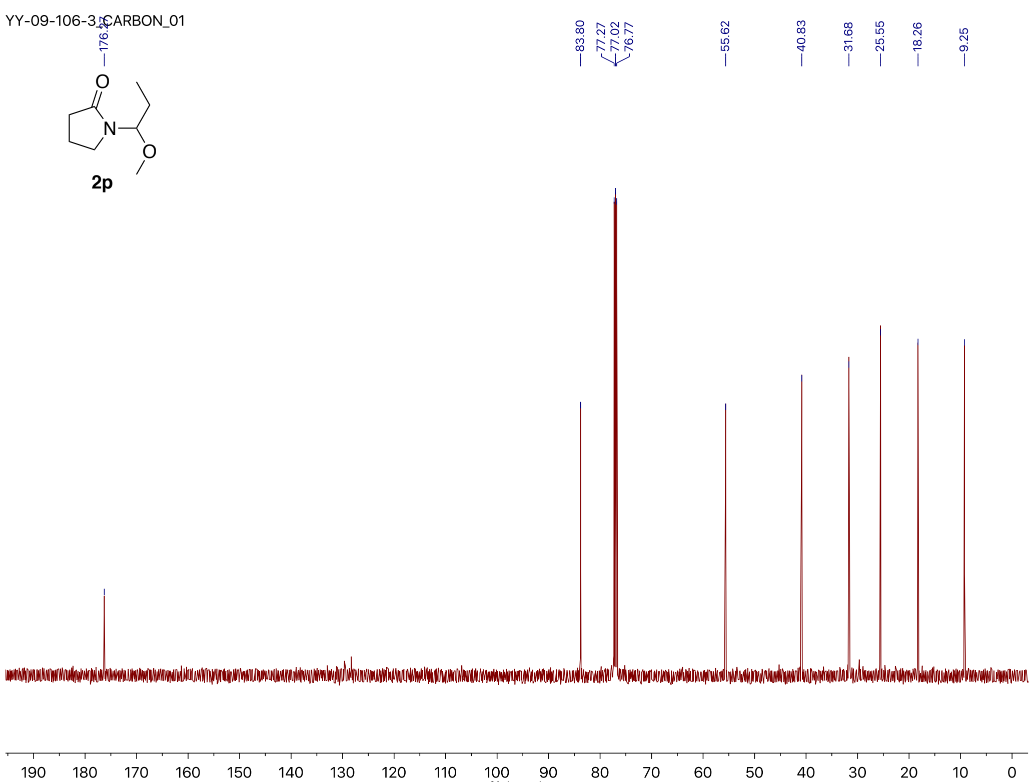



YY-09-91workup_PROTON_01
O
O
N
H
2n
5.73
5.72
5.71
5.29
5.28
5.28
5.27
5.27
5.26
5.26
5.25
3.31
3.30
2.21
2.21
2.20
2.19
2.18
2.18
1.63
1.62
1.62
1.61
1.60
1.36
1.35
1.34
1.31
1.31
1.30
1.30
0.93
0.92
0.91
0.91
0.90
0.94
1.00
2.93
2.07
2.33
7.07
3.14
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

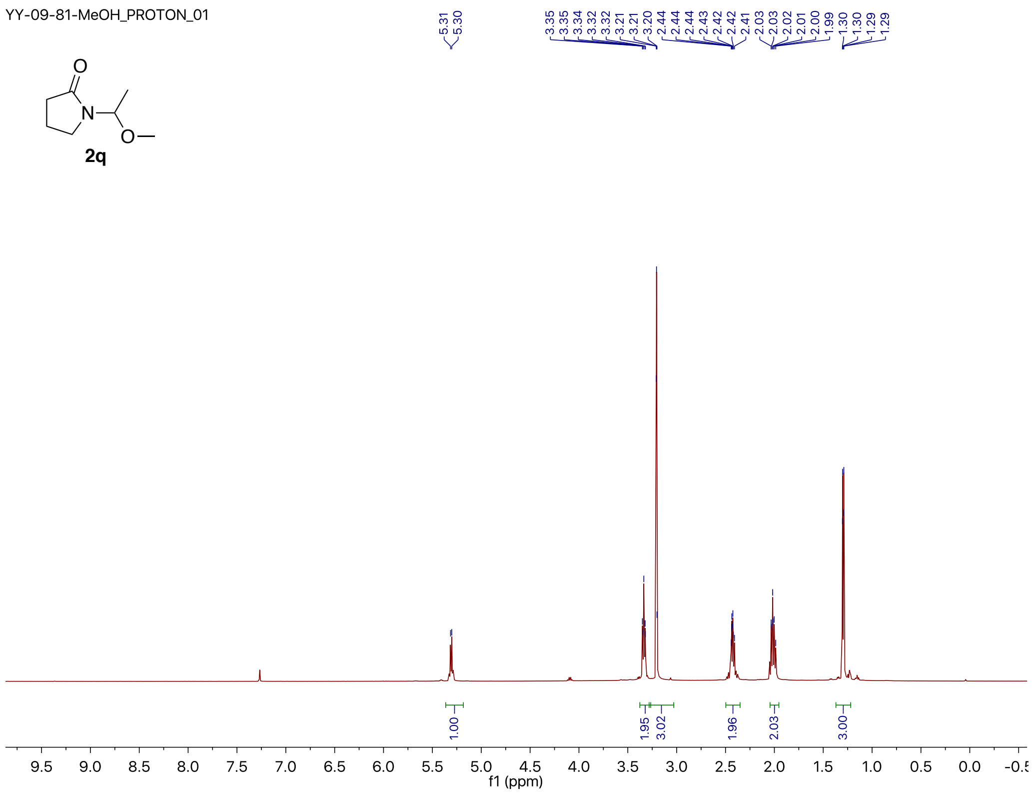

YY-09-91workup_CARBON_01
O
O
N
H
2n
77.45
77.28
77.02
76.77
55.60
36.60
27.64
22.37
21.61
13.77
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

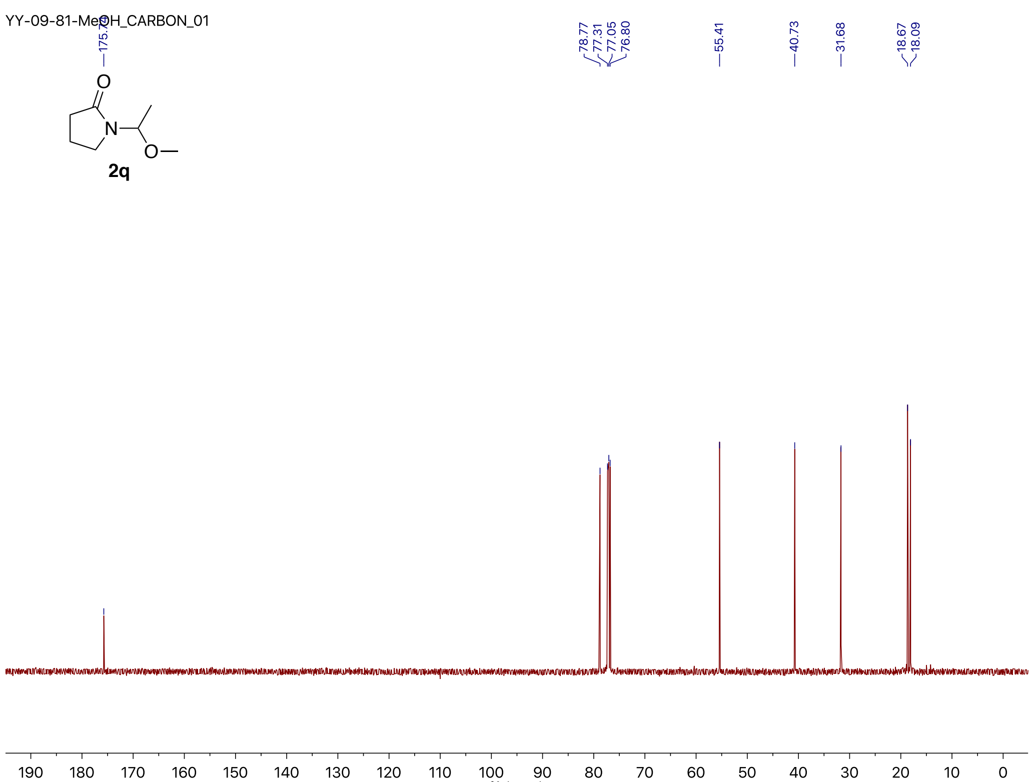


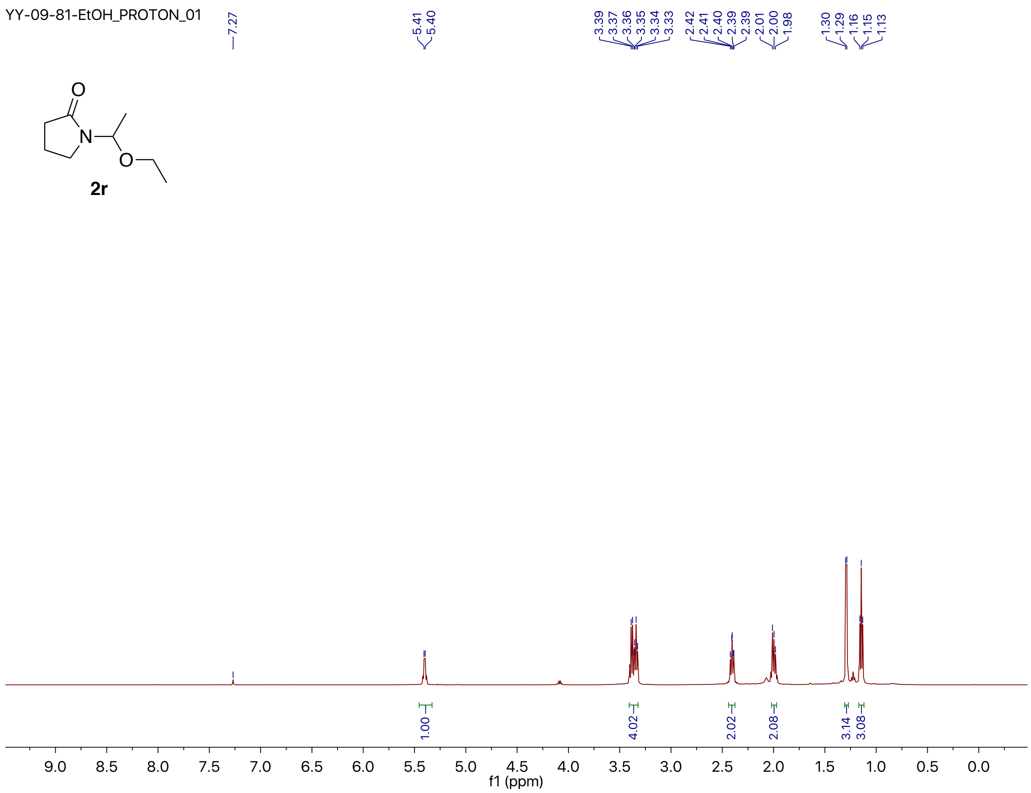
YY-09-64-2_PROTON_01
3.35 3.34 3.33 3.32 3.30 3.28 3.28 3.27 3.26 3.25 3.24 3.23 2.48 2.48 2.48 2.47 2.46 2.46 2.45 2.45 2.44 2.44 2.06 2.06 2.05 2.04 2.03 2.03 2.03 2.02 2.01 2.01 1.76 1.75 1.74 1.74 1.73 1.73 1.73 1.71 1.71 1.57 1.56 1.55 1.55 1.54 1.53 1.52 1.52 0.89 0.89 0.88 0.86 0.86
O
N
O
2p
1.00
5.11
2.10
2.11
1.39
1.24
3.05
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)

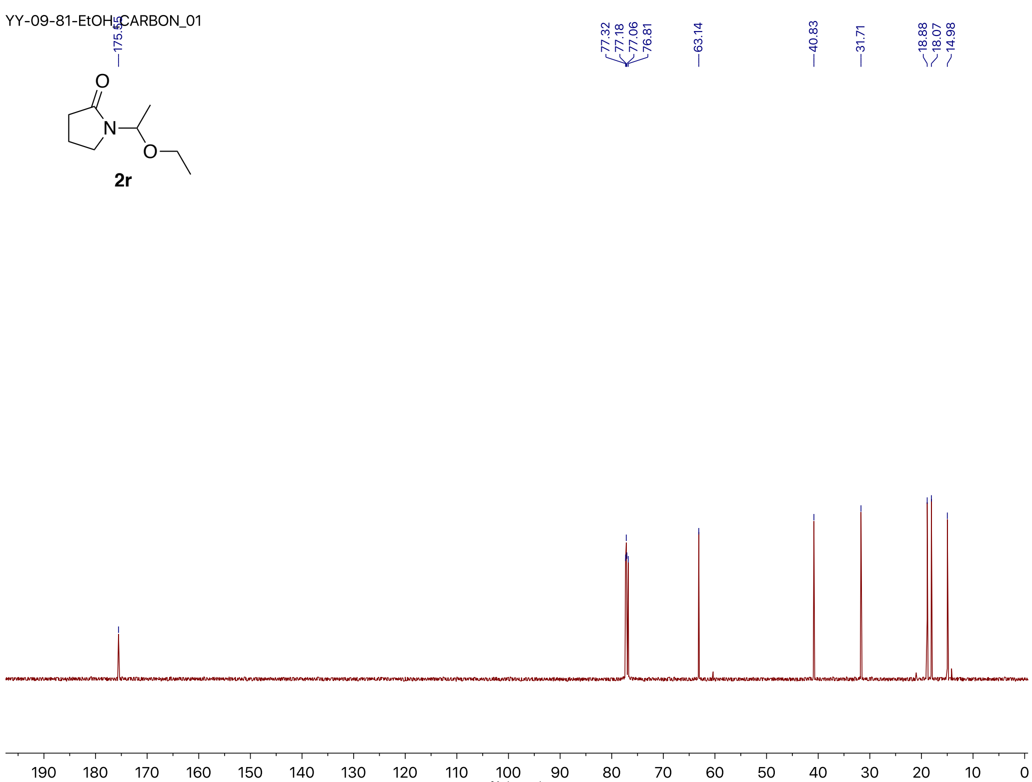


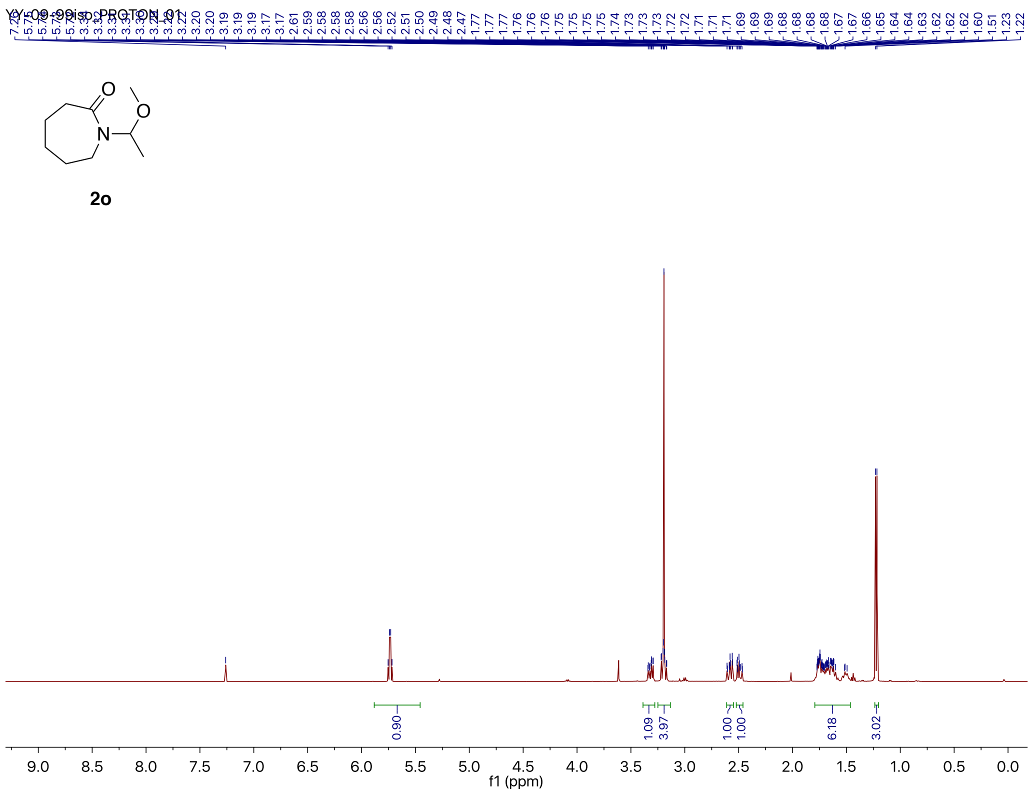
YY-09-106-3_CARBON_01
176.2
83.80
77.27
77.02
76.77
55.62
40.83
31.68
25.55
18.26
9.25
O
N
O
2p
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


YY-09-81-MeOH_PROTON_01
2q
5.31
5.30
3.35
3.35
3.34
3.32
3.32
3.21
3.21
3.20
2.44
2.44
2.43
2.42
2.42
2.41
2.03
2.03
2.02
2.01
2.00
1.99
1.30
1.30
1.29
1.29
1.00
1.95
3.02
1.96
2.03
3.00
f1 (ppm)

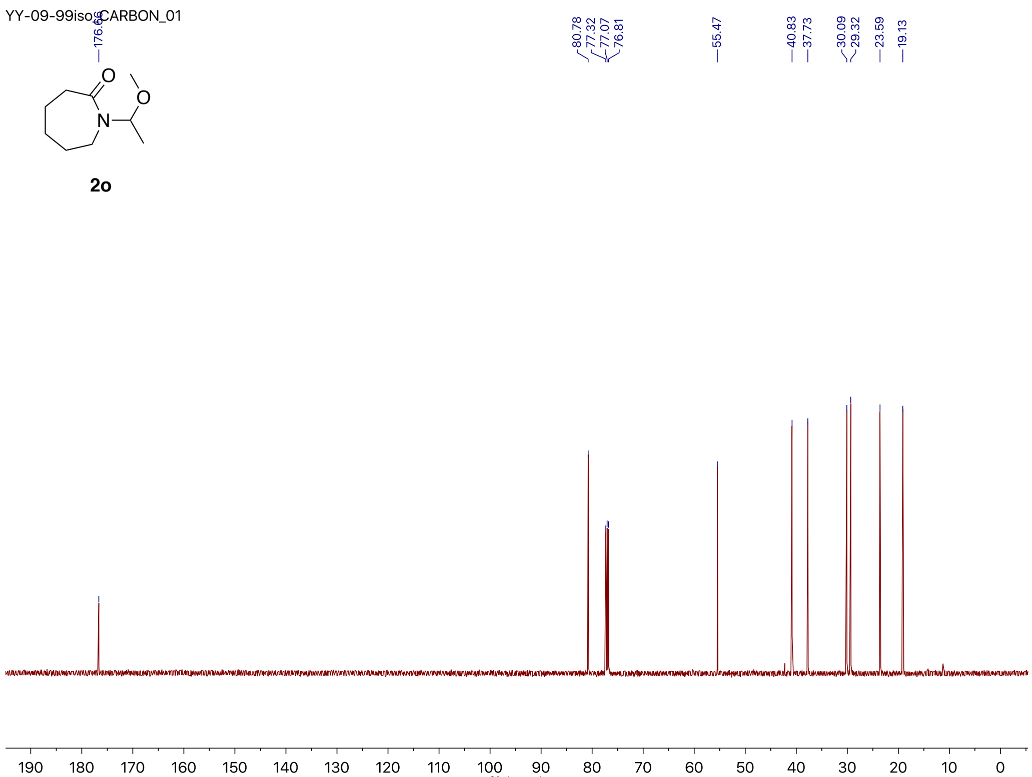

YY-09-81-MeOH_CARBON_01
2q
78.77
77.31
77.05
76.80
55.41
40.73
31.68
18.67
18.09
f1 (ppm)


YY-09-81-EtOH_PROTON_01
7.27
5.41
5.40
3.39
3.37
3.36
3.35
3.34
3.33
2.42
2.41
2.40
2.39
2.39
2.01
2.00
1.98
1.30
1.29
1.16
1.15
1.13
O
N
O
2r
1.00
4.02
2.02
2.08
3.14
3.08
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)

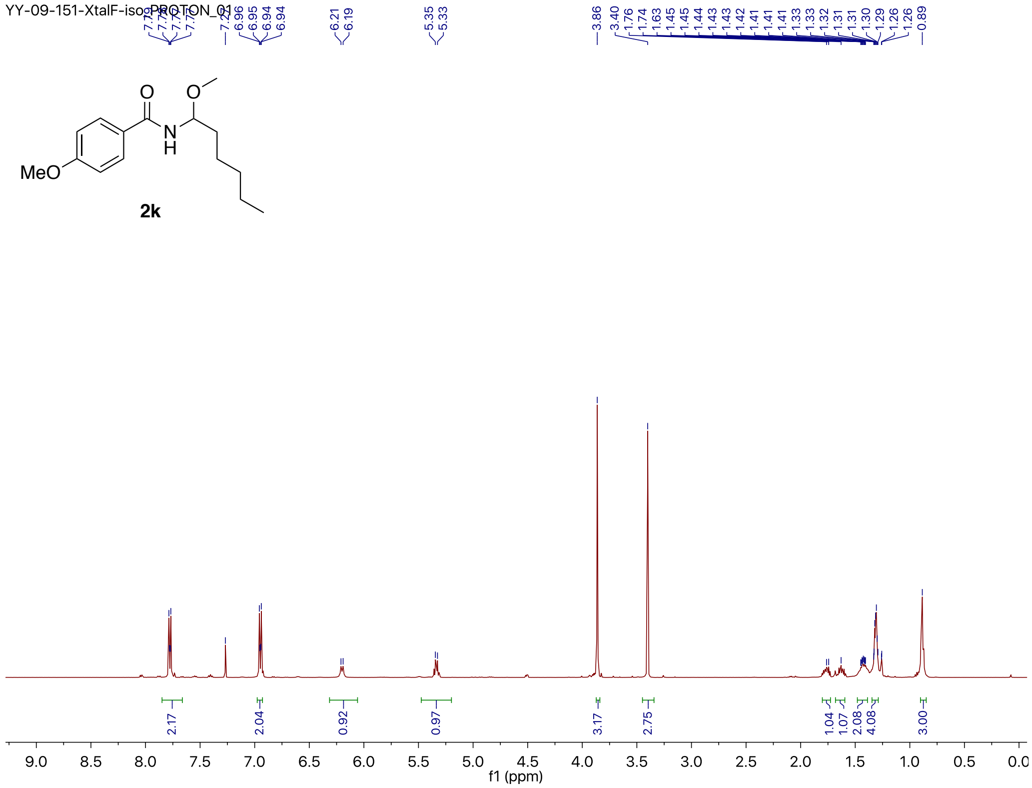

YY-09-81-EtOH_CARBON_01
175.55
77.32
77.18
77.06
76.81
63.14
40.83
31.71
18.88
18.07
14.98
O
N
O
2r
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

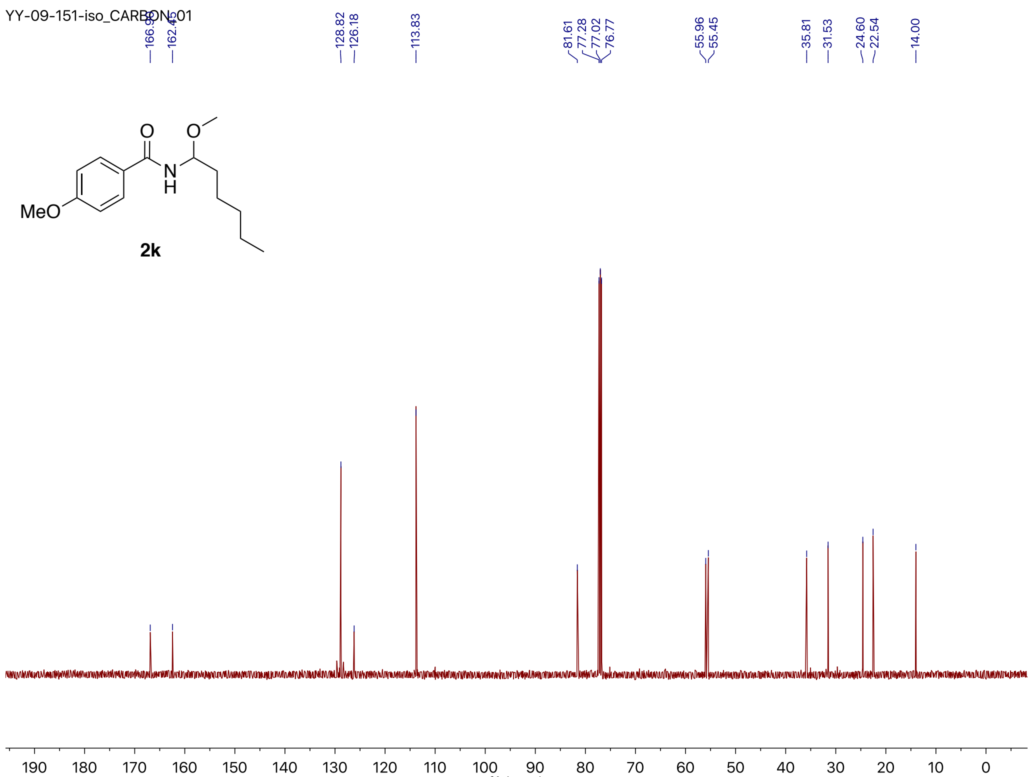


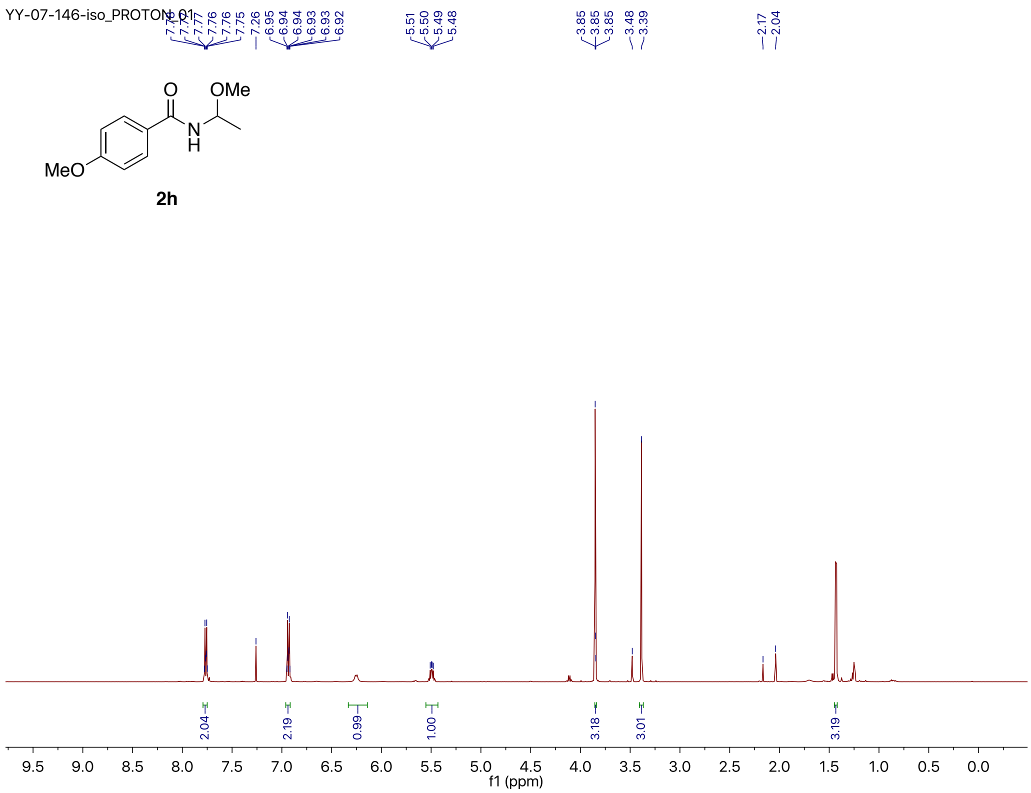
YY-09-99iso_PROTON_01
3.22
3.20
3.20
3.19
3.19
3.19
3.17
3.17
2.61
2.59
2.58
2.58
2.56
2.52
2.51
2.50
2.49
2.48
2.47
1.77
1.77
1.77
1.76
1.76
1.76
1.75
1.75
1.75
1.75
1.74
1.73
1.73
1.73
1.72
1.72
1.71
1.71
1.71
1.69
1.69
1.69
1.68
1.68
1.68
1.68
1.67
1.67
1.66
1.65
1.64
1.63
1.62
1.62
1.62
1.60
1.51
1.23
1.22
O
O
N
2o
0.90
1.09
3.97
1.00
1.00
6.18
3.02
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)



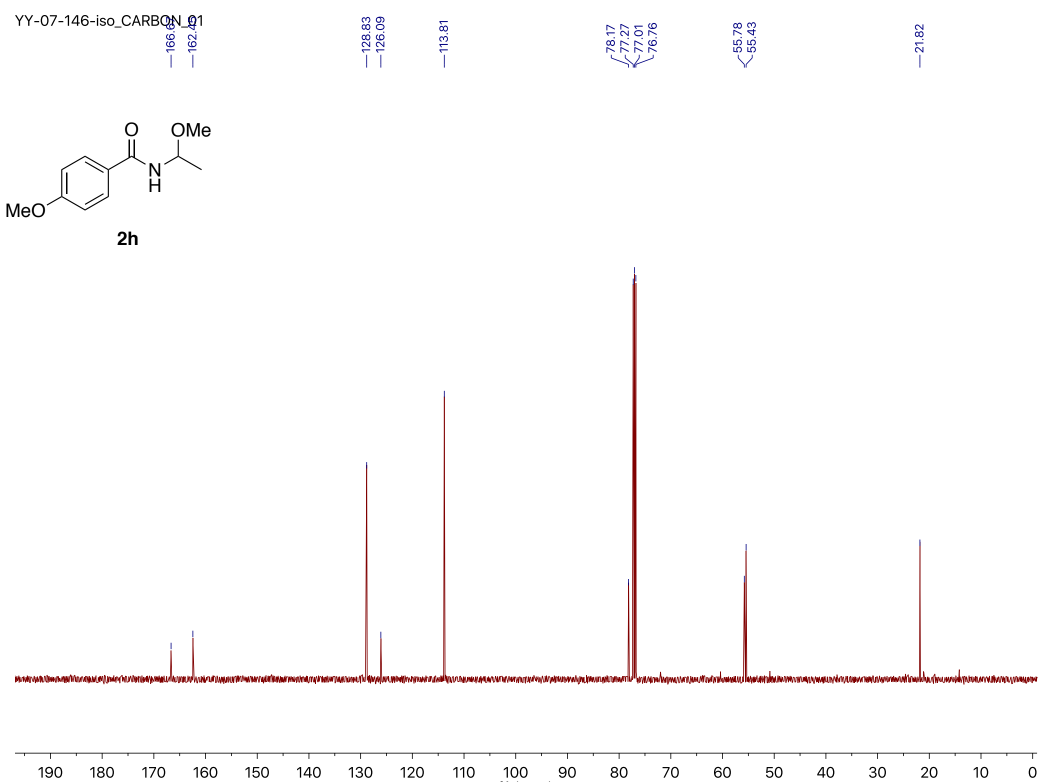
YY-09-99iso_CARBON_01
176.66
80.78
77.32
77.07
76.81
55.47
40.83
37.73
30.09
29.32
23.59
19.13
O
O
N
2o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


YY-09-151-XtalF-iso_PROTON_01
7.79 7.78 7.77 7.77 7.26 6.96 6.95 6.94 6.94 6.21 6.19 5.35 5.33 3.86 3.40 1.76 1.74 1.63 1.45 1.45 1.44 1.43 1.43 1.42 1.41 1.41 1.41 1.33 1.33 1.32 1.31 1.31 1.30 1.29 1.26 0.89
MeO
O
N
H
O
2k
2.17 2.04 0.92 0.97 3.17 2.75 1.04 1.07 2.08 4.08 3.00
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)


YY-09-151-iso_CARBON_01
166.9 162.45 128.82 126.18 113.83 81.61 77.28 77.02 76.77 55.96 55.45 35.81 31.53 24.60 22.54 14.00
MeO
O
N
H
O
2k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


YY-07-146-iso_PROTON_01
7.77
7.77
7.76
7.76
7.75
7.26
6.95
6.94
6.94
6.93
6.93
6.92
5.51
5.50
5.49
5.48
3.85
3.85
3.85
3.48
3.39
2.17
2.04
O
OMe
N
H
MeO
2.04
2.19
0.99
1.00
3.18
3.01
3.19
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)

2h


YY-07-146-iso_CARBON_01
128.83
126.09
113.81
78.17
77.27
77.01
76.76
55.78
55.43
21.82
O
OMe
N
H
MeO
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2h