Supplementary Information for:

Chemoselective Esterification and Amidation of Carboxylic Acids with Imidazole Carbamates and Ureas

Stephen T. Heller and Richmond Sarpong*

Department of Chemistry, University of California, Berkeley, California 94720

E-mail: rsarpong@berkeley.edu

Table of Contents:

Materials and Methods:

Unless stated otherwise, reactions were performed in oven-dried glassware sealed with rubber septa under a nitrogen atmosphere and were stirred with Teflon-coated magnetic stir bars. Liquid reagents and solvents were transferred via syringe using standard

Schlenk techniques. Tetrahydrofuran (THF), toluene, acetonitrile (MeCN), and dimethylformamide (DMF) were dried by passage over a column of activated alumina; dichloromethane was distilled over calcium hydride. All other solvents and reagents were used as received unless otherwise noted. Thin layer chromatography was performed using SiliCycle silica gel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation and anisaldehyde or potassium permanganate stain. Sorbent silica gel (particle size 40-63 μm) was used for flash chromatography. NMR experiments were performed on Bruker spectrometers operating at 300, 400 or 500 MHz for ^{1}H and 75, 100, or 125 MHz for ^{13}C experiments. ^{1}H and ^{1}3C chemical shifts (δ) are reported relative to the residual solvent signal. Data are reported as follows: chemical shift (multiplicity, coupling constants where applicable, number of hydrogens). Abbreviations are as follows: *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *dd* (doublet of doublet), *dt* (doublet of triplet), *m* (multiplet), *bs* (broad singlet). High resolution mass spectral data were obtained from the University of California, Berkeley Mass Spectral Facility. *N*-Phthaloylglycine,[1] 2-(benzoyloxy)acetic acid,[2] and *N*-tosylglycine[3] were prepared according to literature procedures.

Preparation of methyl 1-imidazolecarboxylate (MImC, S1):

Imidazole (7.50 g, 110 mmol) was dissolved in dry THF (100 mL) and the resulting solution was stirred with cooling to 0 °C. Methyl chloroformate (4.25 mL, 55 mmol) was added dropwise and the resulting white suspension was vigorously stirred at 0 °C for 1 h

[1] Pinter, A.; Haberhauer, G. *Eur. J. Org. Chem.* **2008**, *14*, 2375-2387.
[2] Barratt, B. J. W.; Easton, C. J.; Henry, D. J.; Li, I. H. W.; Radom, L.; Simpson, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 13306-13311.
[3] Li, G-L.; Zhao, G. *Org. Lett*. **2006**, *8*, 633-636.

and then at room temperature for 4 h. The mixture was filtered and the filtrate was concentrated *in vacuo* to approximately 50 mL and then hexanes (50 mL) was added. The resulting precipitate was filtered and the filtrate was concentrated to afford a white solid (5.69 g, 82%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.41 (s, 1H), 7.06 (s, 1H), 4.03 (s, 3H). Spectra were consistent with those reported previously.[4]

Preparation of Imidazole Carbamates: Representative Procedure A

Imidazole (3.75 g, 55 mmol) was dissolved in dry THF (50 mL) and the resulting solution was stirred with cooling to 0 °C. Allyl chloroformate (2.98 mL, 28 mmol) was added dropwise and the resulting white suspension was vigorously stirred at 0 °C for 1 h and then at room temperature for 4 h. The mixture was filtered and the filter cake was washed with ether (50 mL). The filtrate was concentrated *in vacuo* and the colorless concentrate obtained was dissolved in diethyl ether (100 mL), washed with water (2 x 50 mL), dried over $MgSO_4$, and concentrated *in vacuo* to afford a colorless oil (3.94 g, 94%).

Allyl 1-imidazolecarboxylate (S2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.42 (t, J = 1.3 Hz, 1H), 7.05 (s, 1H), 6.00 (ddt, J = 16.4, 10.4, 6.0 Hz, 1H), 5.40 (ddd, J = 13.8, 11.4, 1.1 Hz, 2H), 4.87 (dt, J = 6.0, 1.1 Hz, 2H). Spectra were consistent with those reported previously.[5]

---

[4] Trost, B. M.; Zhang, Y.; Zhang, T. *J. Org. Chem.* **2009**, *74*, 5115-5117.

[5] Trost, B. M.; Xu, J.; Schmidt, T. *J. Am. Chem. Soc.* **2009**, *51*, 18343-18357.

Preparation of Imidazole Carbamates: Representative Procedure B

1,1'-Carbonyldiimidazole (1.14 g, 9.00 mmol) was dissolved in DCM (20 mL) and the resulting solution was stirred with cooling to 0 °C. (±)-3-buten-2-ol (0.520 mL, 6.00 mmol) was then added dropwise. The reaction mixture was stirred at 0 °C for 1 h, and then at room temperature for 16 h. The homogeneous mixture was then diluted with DCM (20 mL), washed with water (2 x 20 mL), dried over $MgSO_4$, and concentrated *in vacuo* to afford a colorless oil (0.877 g, 90%).

(±)-But-3-en-2-yl 1-imidazolecarboxylate (S3)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.47 (t, *J* = 1.3 Hz, 1H), 7.11 (s, 1H), 5.98 (ddd, *J* = 17.0, 10.5, 6.3 Hz, 1H), 5.58 (quint, *J* = 6.5 Hz, 1H), 5.43 (d, *J* = 17.2 Hz, 1H), 5.32 (d, *J* = 10.5 Hz, 1H), 1.55 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.0, 137.0, 135.9, 130.6, 117.9, 117.1, 76.0, 19.9.

Ethyl 1-imidazolecarboxylate (S4)

Prepared using Representative Procedure A with ethyl chloroformate (2.58 mL, 27 mmol) to obtain a colorless oil (2.68 g, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.46 (t, *J* = 1.3 Hz, 1H), 7.10 (s, 1H), 4.51 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H). Spectra were consistent with those reported previously.[6]

Isopropyl 1-imidazolecarboxylate (S5)

[6] Nishiguchi, I.; Sunderrao, K. P.; Yamamato, U.; Yamamoto, Y.; Uchida, T.; Maekawa, H. *Electrochemistry*, **2006**, *74*, 680-684.

Prepared using Representative Procedure A with isopropyl chloroformate (1.0 M solution in toluene, 20 mL, 20 mmol) to obtain a colorless oil (2.19 g, 71%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.39 (s, 1H), 7.03 (s, 1H), 5.20 (hept, *J* = 6.3 Hz, 1H), 1.39 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.1, 137.0, 130.3, 117.0, 73.0, 21.6.

Benzyl 1-imidazolecarboxylate

Prepared using Representative Procedure A with benzyl chloroformate (4.27 mL, 30 mmol) to obtain a colorless oil (5.36 g, 88%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.49 – 7.33 (m, 1H), 7.04 (dd, *J* = 1.6, 0.8 Hz, 1H), 6.02 – 5.85 (m, 1H), 5.75 – 5.57 (m, 1H), 4.83 – 4.76 (m, 2H), 1.75 (ddt, *J* = 6.5, 1.8, 0.9 Hz, 3H). Spectra were consistent with those reported previously.[7]

Propargyl 1-imidazolecarboxylate (S6)

Prepared using Representative Procedure B with propargyl alcohol (0.500 mL, 8.58 mmol) to obtain a pale yellow oil (1.15 g, 89%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.43 (t, *J* = 1.4 Hz, 1H), 7.06 (d, *J* = 0.7 Hz, 1H), 4.98 (d, *J* = 2.5 Hz, 2H), 2.62 (t, *J* = 2.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.0, 137.1, 130.8, 117.1, 76.9, 75.7, 55.3.

(*R*)-1-phenylethyl 1-imidazolecarboxylate (6)

Prepared using Representative Procedure B with (*R*)-1-phenethyl alcohol (Alfa Aesar, 97% ee) (0.50 mL, 4.1 mmol) to obtain a colorless oil (0.80 g, 90%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.46 – 7.32 (m, 6H), 7.06 (s, 1H), 6.07 (q, *J* = 6.6 Hz, 1H),

[7] Werner, T.; Barrett, A. G. M. *J. Org. Chem.* **2006**, *71*, 4302-4304.

1.73 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.0, 139.6, 137.1, 130.6, 128.8, 128.8, 126.2, 117.1, 77.2, 21.9.

***trans*-crotyl 1-imidazolecarboxylate (S7)**

Prepared using Representative Procedure B with *trans*-crotyl alcohol (0.512 mL, 6.00 mmol) to obtain a colorless oil (0.913 g, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.49 – 7.33 (m, 1H), 7.04 (dd, J = 1.6, 0.8 Hz, 1H), 6.02 – 5.85 (m, 1H), 5.75 – 5.57 (m, 1H), 4.83 – 4.76 (m, 2H), 1.75 (ddt, J = 6.5, 1.8, 0.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.5, 137.1, 134.0, 130.5, 123.4, 117.0, 68.8, 17.8.

General Esterification Procedure:

Carboxylic acid (0.5 mmol) and MImC (1.0 mmol) were placed in a dry 20 mL vial with a Teflon tape-coated thread. A magnetic stirbar was added, followed by dry MeCN (1.0 mL), and the vial was quickly sealed with a plastic cap (***gas is evolved during the course of the reaction! All experiments should be performed behind a blast shield if a sealed container is used!)***. The reaction mixture was then stirred at 23 °C for 15 minutes and then heated to 80 °C using a heating block for 24 h. The mixture was cooled to room temperature and then the vial was carefully opened (***CAUTION: vial under pressure****!*). The volatiles were removed *in vacuo*, the resulting residue was dissolved in diethyl ether (20 mL), and then washed with 1 M HCl (10 mL). The aqueous layer was back-extracted with diethyl ether (20 mL) and the organic fractions were combined, washed with a saturated solution of $NaHCO_3$ and then brine, dried over $MgSO_4$, and concentrated *in vacuo* to afford the desired ester.

Methyl 2-(4-bromophenyl)acetate (2)

Prepared using the general esterification procedure with 4-bromophenylacetic acid (0.108 g, 0.500 mmol) and MImC (0.126 g, 1.00 mmol) to obtain a white solid (0.106 g, 93%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 3.69 (s, 2H), 3.68 (s, 3H). Spectra were consistent with those reported previously.[8]

Ethyl 2-(4-bromophenyl)acetate

Prepared using the general esterification Procedure with 4-bromophenylacetic acid (0.108 g, 0.500 mmol) and ethyl 1-imidazolecarboxylate (0.140 g, 1.00 mmol) to obtain a white solid (0.109 g, 89%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.56 (s, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

Spectra were consistent with those reported previously.[9]

Isopropyl 2-(4-bromophenyl)acetate

Prepared using the general esterification procedure with 4-bromophenylacetic acid (0.108 g, 0.500 mmol) and isopropyl 1-imidazolecarboxylate (0.154 g, 1.00 mmol) to obtain a colorless oil (0.090 g, 70%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 5.00 (hept, *J* = 6.3 Hz, 1H), 3.53 (s, 1H), 1.22 (d, *J* = 6.3 Hz, 6H). Spectra were consistent with those reported previously.[10]

Allyl 2-(4-bromophenyl)acetate (S8)

---

[8] Damm, M.; Kappe, O. C. *J. Comb. Chem.* **2009**, *11*, 460-468.
[9] Katz, C. E.; Aube, J. *J. Am. Chem. Soc.* **2003**, *125*, 13948-13949.
[10] Ginisty, M.; Roy, M.-N.; Charette, A. B. *J. Org. Chem.* **2008**, *73*, 2542-2547.

Prepared using the general esterification procedure with 4-bromophenylacetic acid (0.108 g, 0.500 mmol) to obtain a colorless oil (0.117 g, 91%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 5.93 (ddt, *J* = 17.1, 10.5, 5.7 Hz, 1H), 5.29 (dddd, *J* = 20.8, 10.4, 2.7, 1.3 Hz, 2H), 4.63 (dt, *J* = 5.7, 1.3 Hz, 2H), 3.64 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.7, 132.9, 131.9, 131.7, 131.0, 121.2, 118.51, 77.3, 77.0, 76.8, 65.7, 40.7. **HRMS-EI** (70 eV) *m/z*: M^+ calcd for $C_{11}H_{11}O_2Br$, 253.9942; found, 253.9937.

Benzyl 2-(4-bromophenyl)acetate

Prepared using the general esterification procedure with 4-bromophenylacetic acid (0.108 g, 0.5 mmol) to obtain a white solid (0.124 g, 81%) after column chromatography (5 : 95 ethyl acetate : hexanes). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.28 (m, 5H), 7.16 (d, *J* = 8.4 Hz, 2H), 5.13 (s, 2H), 3.62 (s, 2H). Spectra were consistent with those reported previously.[11]

Propargyl 2-(4-bromophenyl)acetate (S9)

Prepared using the general esterification procedure with 4-bromophenylacetic acid (0.108 g, 0.500 mmol) to obtain a colorless oil (0.111 g, 87%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 4.74 (d, *J* = 0.7 Hz, 1H), 3.67 (s, 2H), 2.52 (t, *J* = 2.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.2, 132.3, 131.8, 131.0, 121.4, 75.2, 52.5, 40.3. **HRMS-EI** (70 eV) *m/z*: M^+ calcd for $C_{11}H_9O_2Br$, 251.9786; found, 251.9785.

[11] Tilley, J. W.; Danho, W.; Lovey, K.; Wagner, R.; Swistok, J.; Makofske, R.; Michalewsky, J.; Triscari, J.; Nelson, D.; Weatherford, S. *J. Med. Chem.* **1991**, *34*, 1125-1136.

(E)-But-2-en-1-yl 2-(4-bromophenyl)acetate (S10)

Prepared using the general esterification procedure with 4-bromophenylacetic acid (0.108 g, 0.500 mmol) to obtain a colorless oil (0.112 g, 84%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 5.78 (dq, *J* = 14.0, 6.5 Hz, 1H), 5.61 – 5.52 (m, 1H), 4.52 (d, *J* = 6.6 Hz, 2H), 3.57 (s, 2H), 1.72 (dd, *J* = 6.5, 1.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.9, 132.9, 131.8, 131.6, 131.0, 124.7, 121.1, 65.8, 40.7, 17.8. **HRMS-EI** (70 eV) *m/z*: M^+ calcd for $C_{12}H_{13}O_2Br$, 268.0099; found, 268.0091.

(±)-But-3-en-2-yl 2-(4-bromophenyl)acetate (S11)

Prepared using the general esterification procedure with 4-bromophenylacetic acid (0.108 g, 0.500 mmol) to obtain a colorless oil (0.114 g, 85%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 5.81 (ddd, *J* = 16.6, 10.6, 5.9 Hz, 1H), 5.35 (p, *J* = 6.4 Hz, 1H), 5.15 (dd, *J* = 34.6, 13.9 Hz, 2H), 3.57 (s, 2H), 1.30 (d, *J* = 6.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.3, 137.3, 133.0, 131.6, 131.0, 121.1, 116.0, 71.7, 40.9, 19.8. **HRMS-EI** (70 eV) *m/z*: M^+ calcd for $C_{12}H_{13}O_2Br$, 268.0099; found, 268.0097.

Z-Gly-OMe

Prepared using the general esterification procedure with Z-Gly-OH (0.105 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid (0.104 g, 93%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 5.26 (bs, 1H), 5.13 (s, 2H),

4.00 (d, J = 5.5 Hz, 2H), 3.76 (s, 3H). Spectra were consistent with those reported previously.[12]

Boc-Gly-OMe

Prepared using the general esterification procedure with Boc-Gly-OH (0.088 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid (0.088 g, 93%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.00 (bs, 1H), 3.92 (d, J = 5.5 Hz, 2H), 3.75 (s, 3H), 1.45 (s, 10H). Spectra were consistent with those reported previously.[13]

***N*-Tosylglycine methyl ester**

Prepared using the general esterification procedure with *N*-tosylglycine (0.115 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid (0.109 g, 90%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 5.00 (bs, 1H), 3.78 (d, J = 5.4 Hz, 2H), 3.64 (s, 3H), 2.43 (s, 3H). Spectra were consistent with those reported previously.[14]

***N*-Acetylglycine methyl ester**

Prepared using the general esterification procedure with *N*-acetylglycine (0.059 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid

[12] Simunek, P.; Svete, J.; Stanovnik, B. *Heterocycles*, **2008**, *75*, 2477-2491.
[13] Morandeau, L.; Remaud-Le Saec, P.; Ouadi, A.; Bultel-Riviere, K.; Mougin-Degraef, M.; de France-Robert, A.; Faivre-Chauvet, A.; Gestin, J.-F. *J. Labelled Comp. Rad.* **2006**, *49*, 109-123.
[14] Lash, T. D.; Hoehner, M. C. *J. Heterocycl. Chem.* **1991**, *28*, 1671-1676.

(0.061 g, 92%). **^{1}H-NMR** (500 MHz, CD_3OD) 2.04 (3H, s), 3.72, (3H, s), 3.97 (2H, s). Spectra were consistent with those reported previously.[15]

_N_-Phthaloylglycine methyl ester

Prepared using the general esterification procedure with *N*-phthloylglycine (0.103 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid (0.101 g, 92%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 – 7.84 (m, 2H), 7.79 – 7.71 (m, 2H), 4.45 (s, 2H), 3.77 (s, 3H). Spectra were consistent with those reported previously.[16]

Methyl benzoylglycolate

Prepared using the general esterification procedure with *O*-benzoylglycolic acid (0.090 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid (0.085 g, 90%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10 (dd, J = 8.2, 1.2 Hz, 2H), 7.59 (dd, J = 10.6, 4.3 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 4.87 (s, 2H), 3.80 (s, 3H). Spectra were consistent with those reported previously.[17]

Methyl 2-(4-methoxyphenoxy)acetate

Prepared using the general esterification procedure with methyl 2-(4-methoxyphenoxy)acetic acid (0.091 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid (0.092 g, 94%). **^{1}H NMR** (500 MHz,

---

[15] Davies, S. G.; Rodriguez-Solla, H.; Tamayo, J. A.; Cowley, A. R.; Concellon, C.; Garner, A. C.; Parkes, A. L.; Smith, A. D. *Org. Biomol. Chem.* **2005**, *3*, 1435-1447.
[16] Enzmann, A.; Eckert, M.; Ponikwar, W.; Polborn, K.; Schneiderbauer, S.; Beller, M.; Beck, W. *Eur. J. Inorg. Chem.* **2004**, *6*, 1330-1340.
[17] Barratt, B. J. W.; Easton, C. J.; Henry, D. J.; Li, I. H. W.; Radom, L.; Simpson, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 13306-13311.

$CDCl_3$) δ 7.40 – 7.29 (m, 5H), 5.26 (s, 1H), 5.13 (s, 2H), 4.00 (d, *J* = 5.5 Hz, 2H), 3.76 (s, 3H). Spectra were consistent with those reported previously.[18]

Methyl 4-bromobenzoate

Prepared using the general esterification procedure with 4-bromobenzoic acid (0.101 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid (0.102 g, 94%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 3.91 (s, 3H). Spectra were consistent with those reported previously.[19]

Methyl 4-methoxybenzoate

Prepared using the general esterification procedure with 4-methoxybenzoic acid (0.076 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid (0.078 g, 94%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H). Spectra were consistent with those reported previously.[20]

Methyl 4-nitrobenzoate

Prepared using the general esterification procedure with 4-nitrobenzoic acid (0.084 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a pale yellow

[18] Jimenez, F.; Cruz, M. C.; Zuniga, C.; Martinez, M. A.; Chamorro, G.; Diaz, F.; Tamariz, J. *Med. Chem. Res.* **2010**, *19*, 33-57.
[19] Lerebours, R.; Wolf, C. *J. Am. Chem. Soc.* **2006**, *128*, 13052-13053.
[20] Gao, H-Y.; Ha, C-Y. *Synth. Comm.* **2006**, *36*, 3283-3286.

solid (0.083 g, 91%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.9 Hz, 2H), 8.22 (d, *J* = 8.9 Hz, 2H), 3.98 (s, 3H). Spectra were consistent with those reported previously.[21]

Methyl 4-acetylbenzoate

Prepared using the general esterification procedure with 4-acetylbenzoic acid (0.082 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid (0.073 g, 82%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 9.4, 7.6 Hz, 2H), 8.00 (dd, *J* = 9.1, 7.4 Hz, 2H), 3.95 (s, 3H), 2.65 (s, 3H). Spectra were consistent with those reported previously.[22]

Methyl 4-acetamidobenzoate

Prepared using the general esterification procedure with 4-acetamidobenzoic acid (0.090 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid (0.080 g, 83%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.45 (bs, 1H), 3.90 (s, 3H), 2.21 (s, 3H). Spectra were consistent with those reported previously.[23]

Methyl 2-methylbenzoate

Prepared using the general esterification procedure with 2-methylbenzoic acid (0.068 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid (0.068 g, 90%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.87 (m, 1H), 7.40 (td, *J* = 7.5, 1.4

[21] Yu, M.; Wen, W.; Wang, Z. *Synth. Comm*. **2006**, *36*, 2851-2857.
[22] Mo, J.; Xu, L.; Xiao, J. *J. Am. Chem. Soc.*, **2005**, *127*, 751-760.
[23] Stuart, D. R.; Bertrand-Laperle, M.; Burgess, K. M. N.; Fagnou, K. *J. Am. Chem. Soc.* **2008**, *130*, 16474-16475.

Hz, 1H), 7.28 – 7.20 (m, 2H), 3.89 (s, 3H), 2.60 (s, 3H). Spectra were consistent with those reported previously.[24]

Methyl 2-iodobenzoate

Prepared using the general esterification procedure with 2-iodobenzoic acid (0.124 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid (0.110 g, 84%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.80 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.40 (td, *J* = 7.6, 1.2 Hz, 1H), 7.19 – 7.12 (m, 1H), 3.93 (s, 3H). Spectra were consistent with those reported previously.[25]

Methyl diphenylacetate

Prepared using the general esterification procedure with diphenylacetic acid (0.106 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid (0.107 g, 95%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 8H), 7.28 – 7.24 (m, 2H), 5.03 (s, 1H), 3.74 (s, 3H). Spectra were consistent with those reported previously.[26]

Methyl indole-3-acetate

Prepared using the general esterification procedure with indole-3-acetic acid (0.088 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid (0.0762 g, 81%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (bs, 1H), 7.62-7.69 (m, 1H), 7.33-

[24] Yu, X-F.; Darcel, C. *Eur. J. Org. Chem.* **2009**, *8*, 1144-1147.
[25] Crawford, L. A.; McNab, H.; Mount, A. R.; Wharton, S. I. *J. Org. Chem.* **2008**, *73*, 6642-6646.
[26] Peng, C.; Zhang, W.; Yan, G.; Wang, J. *Org. Lett.* **2009**, *11*, 1667-1670.

7.38 (m, 1H), 7.12-7.19 (m, 1H), 3.82 (s, 3H), 3.73 (s, 3H). Spectra were consistent with those reported previously.[27]

Methyl pivalate

Prepared using the general esterification procedure with pivalic acid (0.051 g, 0.50 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a colorless oil (92%). Yield calculated by ^{1}H-NMR using piperonylonitrile as an internal standard. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.66 (s, 3H), 1.21 (s, 9H). Spectra were consistent with those reported previously.[28]

Methyl 1-methyl-1-cyclohexanecarboxylate

Prepared using the general esterification procedure with 1-methyl-1-cyclohexanecarboxylic acid (0.071 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a colorless oil (0.073, 93%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.67 (s, 3H), 2.06 – 1.96 (m, 2H), 1.59 – 1.46 (m, 2H), 1.39 – 1.17 (m, 6H), 1.14 (s, 3H). Spectra were consistent with those reported previously.[29]

Methyl cinnamate

Prepared using the general esterification procedure with *trans*-cinnamic acid (0.074 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a glassy solid (0.057 g, 70%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70 (d, J = 16.1 Hz, 1H), 7.53-7.50 (m,

[27] Selva, M.; Tundo, P.; Brunelli, D.; Perosa, A. *Green Chem.* **2007**, *9*, 463-468.
[28] Rivas, J. C. M.; Salvagni, E.; Prabaharan, R.; Martin de Rosales, R. T.; Parsons, S. *Dalton Trans*. **2004**, *1*, 172-177.
[29] Crane, L.; Anastassiadou, M.; El Hage, S.; Stigliani, J. L.; Baziard-Mouyesset, G.; Payard, M.; Leger, J. M.; Bizot-Espiard, J-G.; Ktorza, A.; Caignard, D-H.; Renard, P. *Bioorg. Med. Chem.* **2006**, *14*, 7419-7433.

2H), 7.41-7.34 (m, 3H), 6.41 (d, J = 16.1 Hz, 1H), 3.79 (s, 3H). Spectra were consistent with those reported previously.[30]

_N_-Boc-Cys(Trt)-OMe

Prepared using the general esterification procedure with *N*-Boc-Cys(Trt)-OH (0.231 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid (0.203 g, 85%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (d, J = 7.6 Hz, 6H), 7.29 (t, J = 7.6 Hz, 6H), 7.22 (t, J = 7.3 Hz, 3H), 5.01 (d, J = 7.9 Hz, 1H), 4.35 – 4.24 (m, 1H), 3.70 (s, 3H), 2.59 (d, J = 5.2 Hz, 2H), 1.40 (s, 9H). Spectra were consistent with those reported previously.[31]

Methyl 2-quinolinecarboxylate

Prepared using the general esterification procedure with quinaldic acid (0.087 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid (0.084 g, 89%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 – 8.29 (m, 2H), 8.21 (d, J = 8.5 Hz, 1H), 7.89 (dd, J = 8.2, 1.2 Hz, 1H), 7.80 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.66 (ddd, J = 8.1, 6.9, 1.1 Hz, 1H), 4.09 (s, 3H). Spectra were consistent with those reported previously.[32]

Methyl 2-naphthoate

---

[30] Zhang, Z.; Zha, Z.; Gan, C.; Pan, C.; Zhou, Y.; Wang, Z.; Zhou, M-M. *J. Org. Chem.* **2006**, *71*, 4339-4342.
[31] Zhu, Y.; Gieselman, M. D.; Zhou, H.; Averin, O.; van der Donk, W. A. *Org. Biomol. Chem.* **2003**. *1*, 3304-3315.
[32] Weitgenant, J. A.; Mortison, J. D.; Helquist, P. *Org. Lett.* **2005**, *7*, 3609-3612.

Prepared using the general esterification procedure with 2-naphthoic acid (0.086 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid (0.090 g, 97%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.06 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.7 Hz, 2H), 7.65 – 7.49 (m, 2H), 3.99 (s, 3H). Spectra were consistent with those reported previously.[33]

Methyl 1-methyl-2-pyrrolecarboxylate

Prepared using the general esterification procedure with 1-methyl-2-pyrrolecarboxylic acid (0.063 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid (0.057 g, 82%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.99 – 6.89 (m, 1H), 6.78 (s, 1H), 6.11 (dd, *J* = 3.9, 2.6 Hz, 1H), 3.93 (s, 3H), 3.81 (s, 3H). Spectra were consistent with those reported previously.[34]

Methyl hydrocinnamate

Prepared using the general esterification procedure with hydrocinnamic acid (0.075 g, 0.50 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a colorless oil (0.079 g, 96%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.24 – 7.18 (m, 3H), 3.69 (s, 3H), 2.96 (t, *J* = 7.5 Hz, 2H), 2.64 (t, *J* = 7.5 Hz, 2H). Spectra were consistent with those reported previously.[35]

Methyl 5-bromo-2-thiophenecarboxylate

---

[33] Lerebours, R.; Wolf, C. *J. Am. Chem. Soc.* **2006**, *128*, 13052-13053.
[34] Laurila, M. L.; Magnus, N. A.; Staszak, M. A. *Org. Proc. Res. Dev.* **2009**, *13*, 1199-1201.
[35] Black, P. J.; Edwards, M. G.; Williams, J. M. J. *Eur. J. Org. Chem.* **2006**, *19*, 4367-4378.

Prepared using the general esterification procedure with 5-bromo-2-thiophenecarboxylic acid (0.104 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid (0.094 g, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 4.0 Hz, 1H), 7.07 (d, *J* = 4.0 Hz, 1H), 3.87 (s, 3H). Spectra were consistent with those reported previously.[36]

Methyl 3-quinolinecarboxylate

Prepared using the general esterification procedure with 3-quinolinecarboxylic acid (0.087 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a white solid (0.086 g, 91%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.45 (d, *J* = 2.1 Hz, 1H), 8.86 (d, *J* = 2.0 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.84 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.63 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 4.02 (s, 3H). Spectra were consistent with those reported previously.[37]

(*R*)-1-phenylethyl benzoate (7)

Prepared using the general esterification procedure with benzoic acid (0.024 g, 0.195 mmol) and (*R*)-1-phenylethyl 1-imidazolecarboxylate (0.084 g, 0.39 mmol) to obtain a colorless oil (0.039 g, 89%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (dd, *J* = 11.9, 5.2 Hz, 4H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 6.14 (q, *J* = 6.6 Hz, 1H), 1.68 (d, *J* = 6.6 Hz, 3H). **$[\alpha]^{20}_D$** -25.6 (*c* 0.99, EtOH). **HPLC** Chiracel OD column (99.5 : 0.5 hexanes : isopropanol, 1.0 mL/min) t_R;

[36] Kranich, R.; Busemann, A. S.; Bock, D.; Schroeter-Maas, S.; Beyer, D.; Heinemann, B.; Meyer, M.; Schierhorn, K.; Zahlten, R.; Wolff, G.; Aydt, E. M. *J. Med. Chem.* **2007**, *50*, 1101-1115.
[37] Han, E-G.; Kim, H, J.; Lee, K-J. *Tetrahedron*, **2009**, *65*, 9616-9625.

15.97 min (major); 17.52 min (minor): 96% ee. Characterization data was consistent with those reported previously.[38]

Methyl 4-hydroxy-3-nitrobenzoate

Prepared using the general esterification procedure with 4-hydroxy-3-nitrobenzoic acid (0.092 g, 0.5 mmol) and methyl 1-imidazolecarboxylate (0.126 g, 1.0 mmol) to obtain a pale yellow solid (0.065 g, 65%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.90 (s, 1H), 8.82 (d, *J* = 2.1 Hz, 1H), 8.23 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 3.94 (d, *J* = 5.9 Hz, 3H). Spectra were consistent with those reported previously.[39]

Ethyl 4-hydroxy-3-nitrobenzoate

Prepared using the general esterification procedure with 4-hydroxy-3-nitrobenzoic acid (0.092 g, 0.5 mmol) and ethyl 1-imidazolecarboxylate (0.140 g, 1.0 mmol) to obtain a pale yellow solid (0.073 g, 69%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.89 (s, 1H), 8.82 (d, *J* = 2.1 Hz, 1H), 8.24 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). Spectra were consistent with those reported previously.[40]

Allyl 4-hydroxy-3-nitrobenzoate (S12)

4-Hydroxy-3-nitrobenzoic acid (0.092 g, 0.50 mmol) and allyl imidazole carbamate (0.15 g, 1.0 mmol) were placed in a dry 20 mL vial with a Teflon tape-coated thread. A magnetic stirbar was added, DMF (1.0 mL) was added, and the vial was quickly sealed

[38] Chenevert, R.; Pelchat, N.; Morin, P. *Tet. Asymm.* **2009**, *20*, 1191-1196.
[39] Sun, H-B.; Hua, R.; Yin, Y. *J. Org. Chem.* **2005**, *70*, 9071-9073.
[40] Le Gal, J.; Michaud, S.; Gressier, M.; Coulais, Y.; Benoist, E. *Bioorg. Med. Chem*. **2006**, *14*, 2904-2909.

with a plastic cap (***gas is evolved during the course of the reaction! All experiments should be performed behind a blast shield if a sealed container is used!)***. The reaction mixture was then heated to 80 °C in a heating block with stirring and held at this temperature for 24 h. The mixture was cooled to room temperature and then the vial was carefully opened (***CAUTION: vial under pressure!***). The resulting mixture was dissolved in ethyl acetate (20 mL), and then washed with 1 M HCl (10 mL). The aqueous layer was back-extracted with ethyl acetate (20 mL) and the organic fractions were combined, washed with water (2 x 10 mL) and then brine, dried over $MgSO_4$, and concentrated *in vacuo* to afford a yellow solid. Chromatography (3 : 7 EtOAc : hexanes) afforded the title compound as a yellow solid (79.6 mg, 71%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.90 (s, 1H), 8.83 (d, *J* = 2.1 Hz, 1H), 8.25 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 6.03 (ddt, *J* = 16.3, 10.6, 5.8 Hz, 1H), 5.42 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.32 (dd, *J* = 10.4, 1.1 Hz, 1H), 4.84 (d, *J* = 5.8 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.9, 158.1, 138.0, 133.2, 131.7, 127.4, 122.7, 120.3, 119.0, 66.2. **mp** 75-76 °C.

N-methoxy-N-methyl-1H-imidazole-1-carboxamide (WImC, 8)

1,1'-Carbonyldiimidazole (2.00 g, 12.3 mmol) was dissolved in DCM (15 mL) and then *N*,*O*-dimethylhydroxylamine hydrochloride (1.09 g, 11.2 mmol) was added. The resulting suspension was stirred with cooling to 0 °C. Triethylamine (1.56 mL, 11.2 mmol) was then added dropwise. The reaction mixture was stirred at 0 °C for 1 h, and then at room temperature for 16 h. The heterogeneous mixture was then diluted with DCM (40 mL), washed with water (2 x 20 mL), dried over $MgSO_4$, and concentrated *in vacuo* to afford a colorless oil (1.48 g, 85%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.25 (s,

1H), 7.56 (s, 1H), 7.05 (s, 1H), 3.67 (s, 3H), 3.39 (s, 3H). Spectra were consistent with those reported previously.[41]

General Amidation Procedure:

Carboxylic acid (0.5 mmol) and WImC (1.0 mmol) were placed in a dry 20 mL vial with a Teflon tape-coated thread. A magnetic stirbar was added, and then MeCN (1.0 mL) was added, and the vial was quickly sealed with a plastic cap (***gas is evolved during the course of the reaction! All experiments should be performed behind a blast shield if a sealed container is used!)***. The reaction mixture was then heated with stirring to 80 °C and held at this temperature in a heating block for 24 h. The mixture was cooled to room temperature and then the vial was carefully opened (***CAUTION: vial under pressure!***). The volatiles were removed *in vacuo*, the resulting residue was dissolved in diethyl ether (20 mL), and then washed with 1 M HCl (10 mL). The aqueous layer was back-extracted with diethyl ether (20 mL) and the organic fractions were combined, washed with a saturated solution of $NaHCO_3$ and then brine, dried over $MgSO_4$, and concentrated *in vacuo* to afford the desired ester. Minor amounts of 1,3-dimethoxy-1,3-dimethylurea were removed by heating the crude product mixture at 50 °C under high vacuum for several hours. (*NOTE: 1,3-dimethoxy-1,3-dimethylurea can also be removed by column chromatography if the product amide is also volatile*).

***N*-Methoxy-N-methyl-2,2-diphenylacetamide**

[41] Grzyb, J. A.; Shen, M.; Yoshina-Ishii, C.; Chi, W.; Brown, R. S.; Batey, R. A. *Tetrahedron*, **2005**, *61*, 7153-7175.

Prepared using the general amidation procedure with diphenylacetic acid (0.106 g, 0.5 mmol) to obtain a white solid (0.113 g, 88%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.21 (m, 10H), 5.55 (s, 1H), 3.49 (s, 3H), 3.24 (s, 3H). Spectra were consistent with those reported previously.[42]

2-(Methoxy(methyl)amino)-2-oxoethyl benzoate

Prepared using the general amidation procedure with *O*-benzoylglycolic acid (0.090 g, 0.5 mmol) to obtain a white solid (0.103 g, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (dd, J = 8.4, 1.3 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 1H), 5.07 (s, 1H), 3.79 (s, 2H), 3.23 (s, 2H). Spectra were consistent with those reported previously.[43]

2-(4-Bromophenyl)-N-methoxy-N-methylacetamide (S13)

Prepared using the general amidation procedure with 4-bromophenylacetic acid (0.108 g, 0.5 mmol) to obtain a white solid (0.118 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 3.72 (s, 2H), 3.63 (s, 3H), 3.19 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.7, 133.8, 131.5, 131.0, 20.7, 76.9, 61.3, 38.6, 32.2. **HRMS-ESI** (*m/z*): $[M+Na]^+$ calcd for $C_{10}H_{13}BrNNaO_2$, 279.9944; found, 279.9939. **mp** 59-60 °C.

***N*-Methoxy-N-methyl-3-phenylpropanamide**

Prepared using the general amidation procedure with hydrocinnamic acid (0.075 g, 0.5 mmol) to obtain a colorless oil (0.088 g, 91%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 –

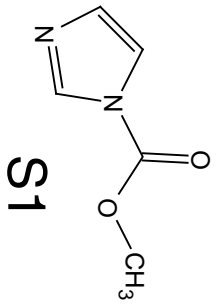
[42] Woo, J. C. S.; Fenster, E.; Dake, G. R. *J. Org. Chem.* **2004**, *69*, 8984-8986.
[43] Tius, M. A.; Busch-Petersen, J. *Synlett*, **1997**, *5*, 531.

7.12 (m, 5H), 3.60 (s, 3H), 3.18 (s, 3H), 3.00 – 2.92 (m, 2H), 2.79 – 2.70 (m, 2H). Spectra were consistent with those reported previously.[44]

2-(1,3-Dioxoisoindolin-2-yl)-N-methoxy-N-methylacetamide (S14)

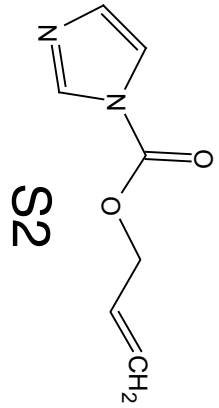
Prepared using the general amidation procedure with *N*-phthaloylglycine (0.103 g, 0.500 mmol) to obtain a white solid (0.114 g, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 2H), 7.76 – 7.68 (m, 2H), 4.62 (s, 2H), 3.82 (s, 3H), 3.21 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.9, 167.0, 134.0, 132.2, 123.4, 61.5, 38.6, 32.5. **HRMS-ESI** (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{13}N_2O_4$, 249.0870; found, 249.0869. **mp** 147-148 °C.

[44] Trost, B. M.; Machacek, M. R.; Faulk, B. D. *J. Am. Chem. Soc*. **2006**, *128*, 6745-6754.

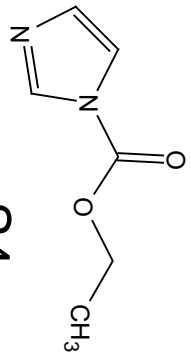


S1

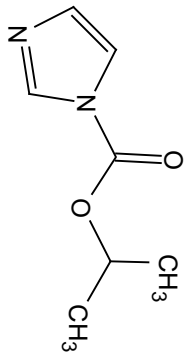
1.00
0.99
1.00
3.07
f1 (ppm)
0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5



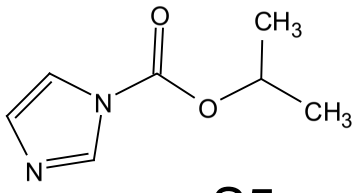
S2



S4

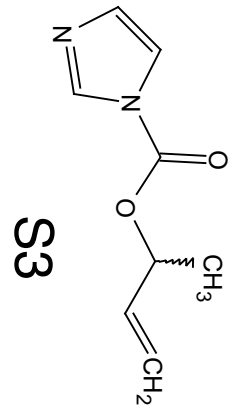


S5

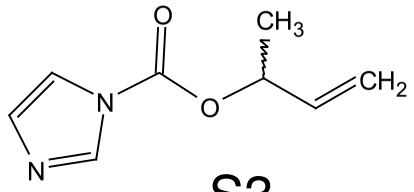


S5

Heller and Sarpong - 28

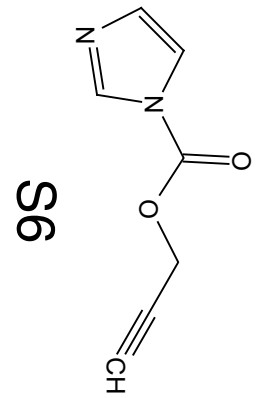


S3



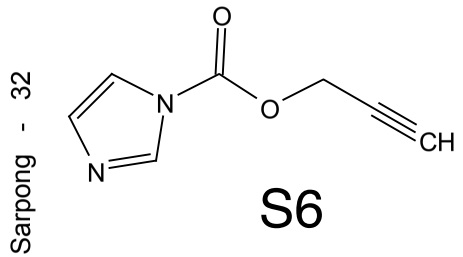
S3

Heller and Sarpong - 30


N
N
O
O
CH

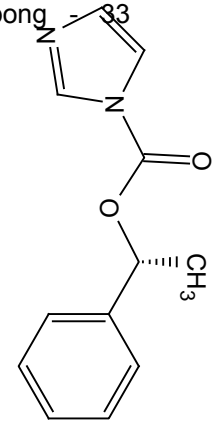
S6

1.00
1.01
1.01
2.08
0.98
f1 (ppm)
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3



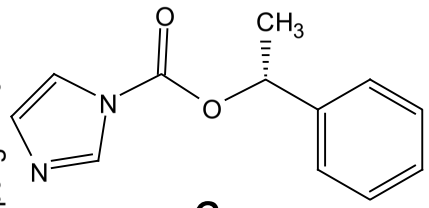
S6

Heller and Sarpong - 32

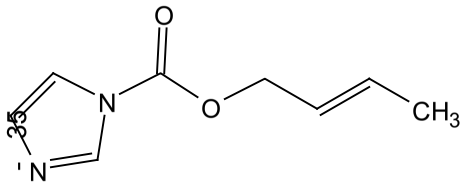


6

Heller and Sarpong - 34

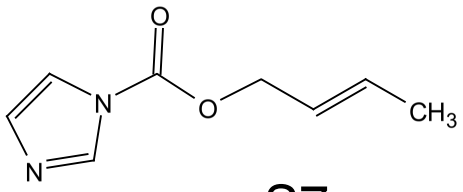


6



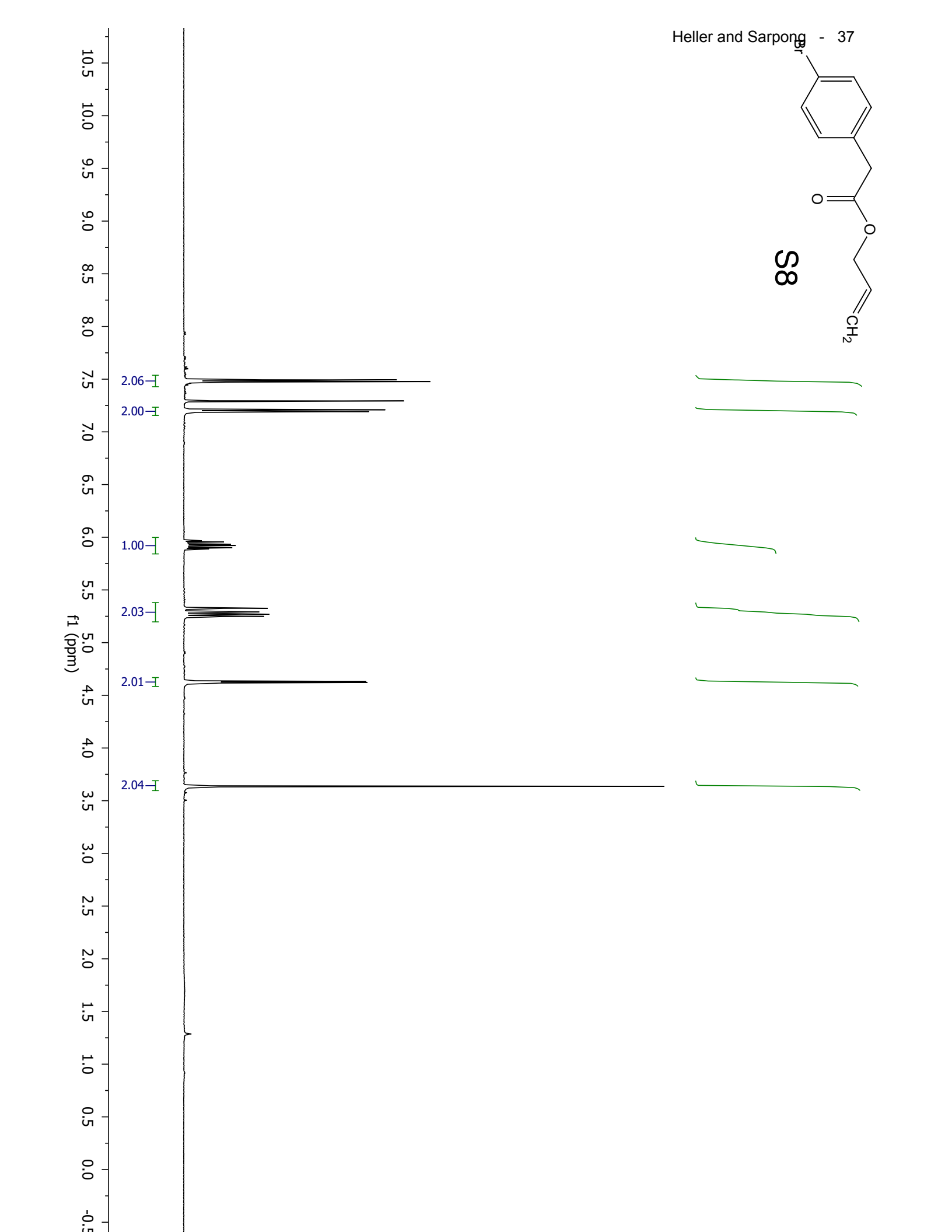
S7

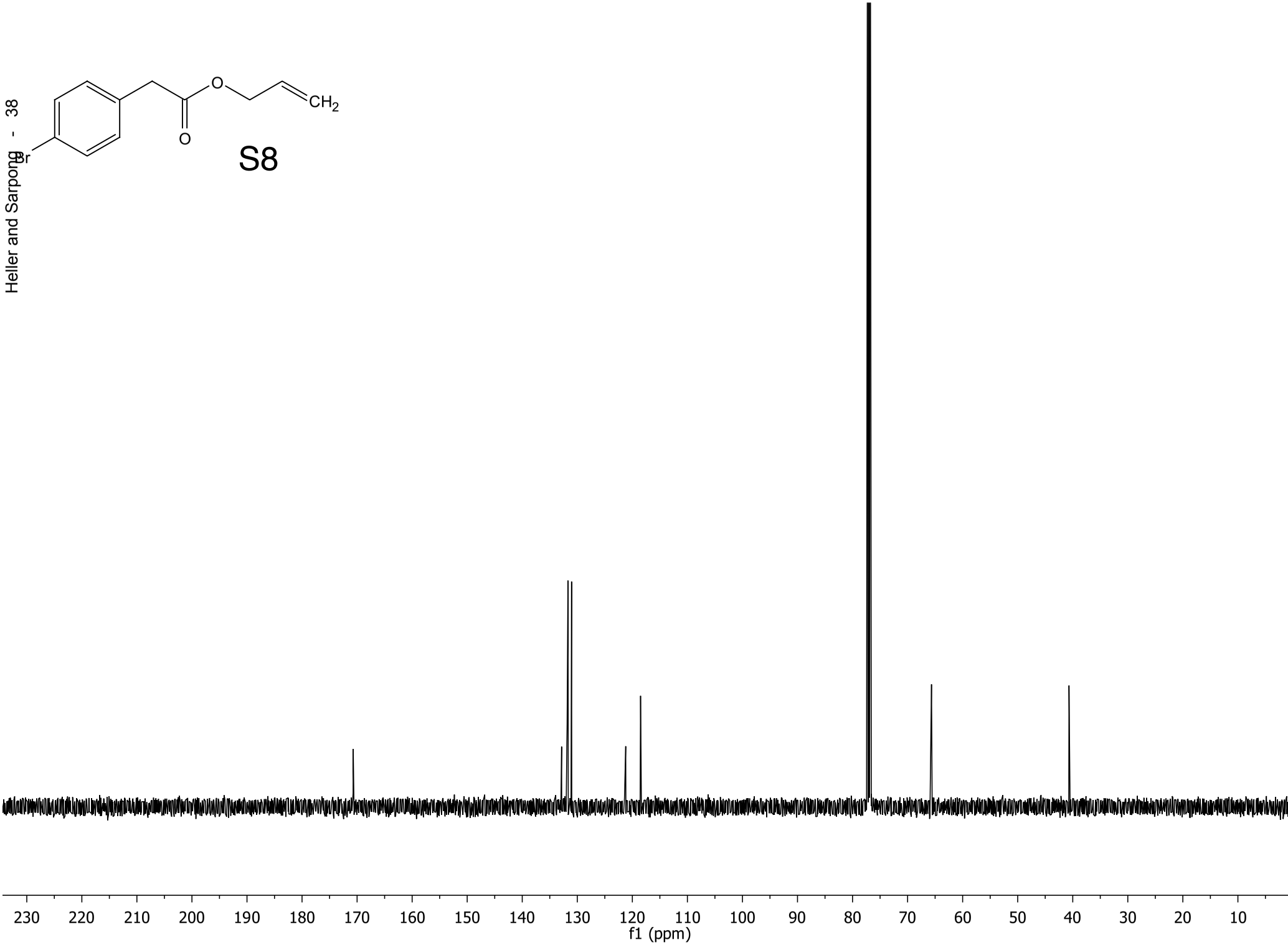
Heller and Sarpong 35

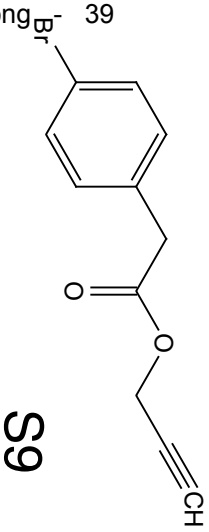


S7

Heller and Sarpong - 36

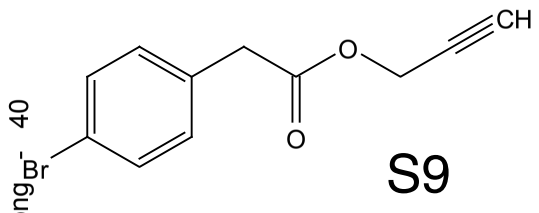

Br
O
O
CH2
S8
2.06
2.00
1.00
2.03
2.01
2.04
f1 (ppm)
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


Heller and Sarpong - 38
Br
O
O
CH2
S8
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Br
O
O
CH

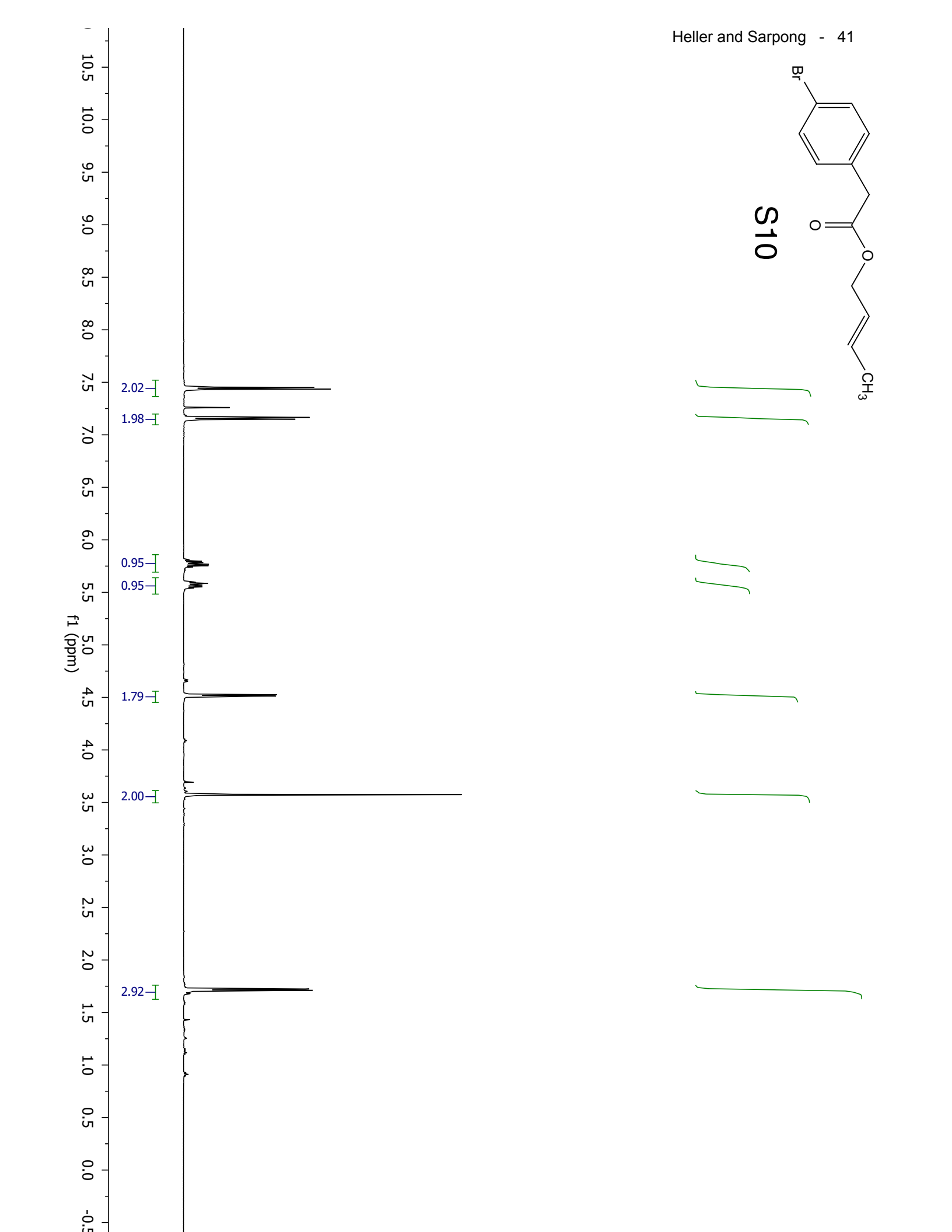
S9

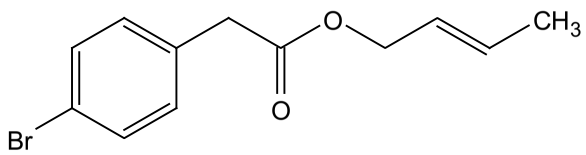
2.03
2.00
2.01
2.05
0.96
f1 (ppm)
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5



S9

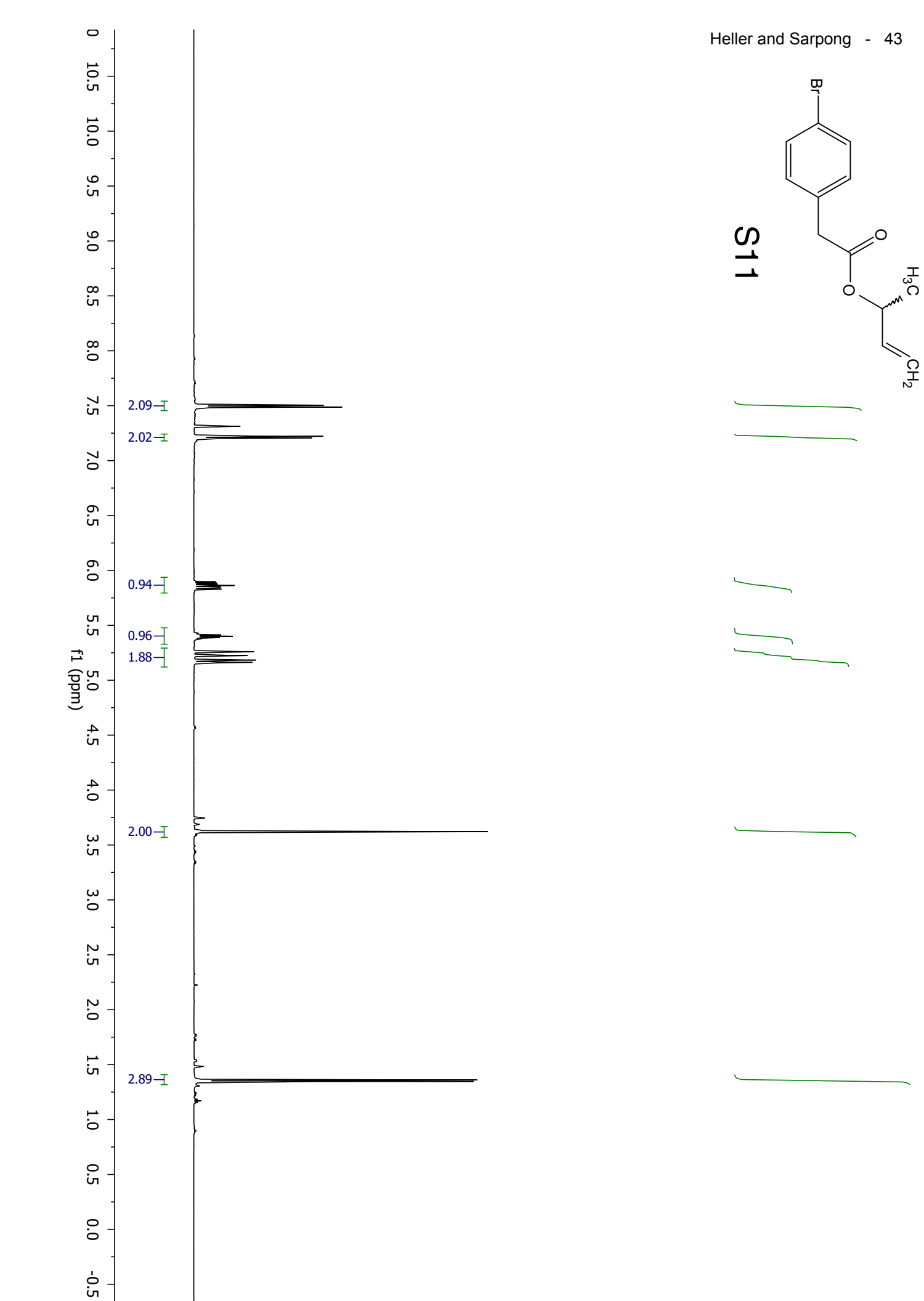
Heller and Sarpong 40

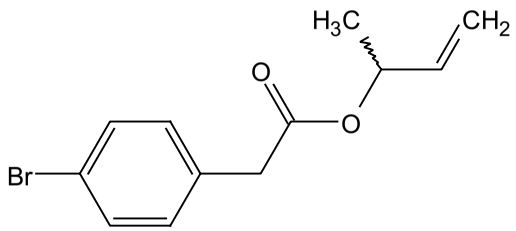

S10
Br
O
O
CH3
2.02
1.98
0.95
0.95
1.79
2.00
2.92
f1 (ppm)
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5



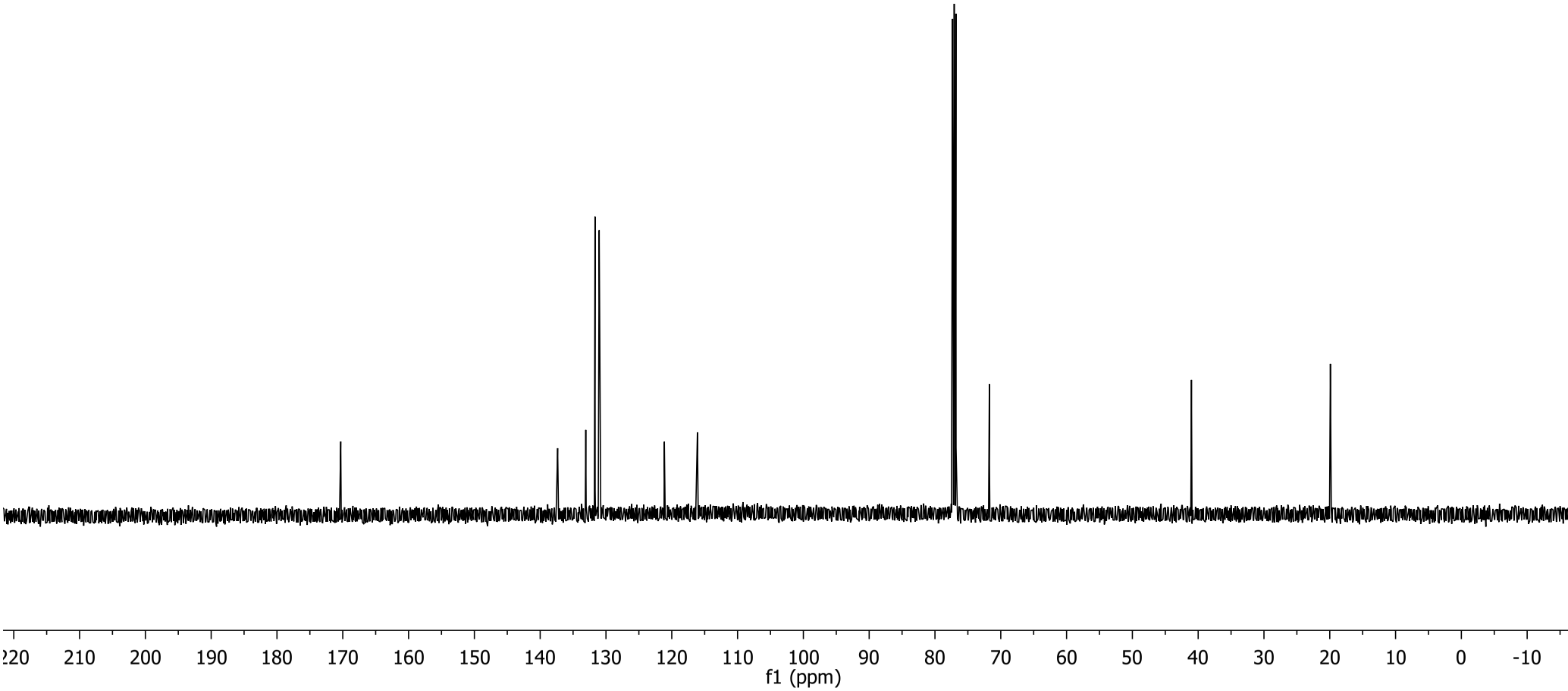
S10

Heller and Sarpong - 42

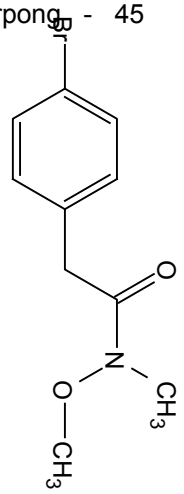

S11
Br
O
O
H3C
CH2
2.09
2.02
0.94
0.96
1.88
2.00
2.89
f1 (ppm)


H3C
CH2
O
O
Br

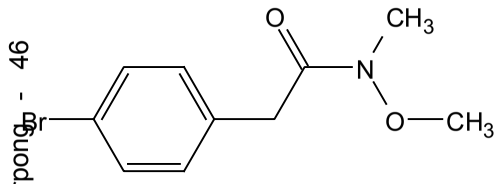
S11


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)

S13


Br
O
N
CH3
O
CH3

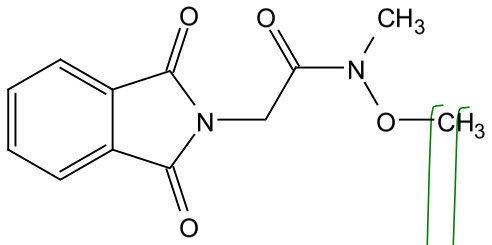
2.03
2.01
2.04
2.95
3.00
f1 (ppm)
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5



S13

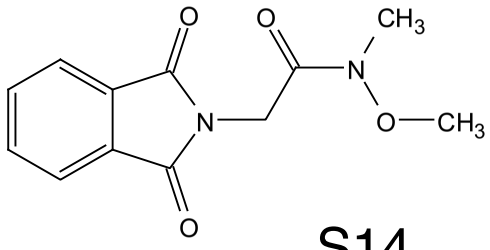
Heller and Sarpong - 46

Heller and Sarpong - 47



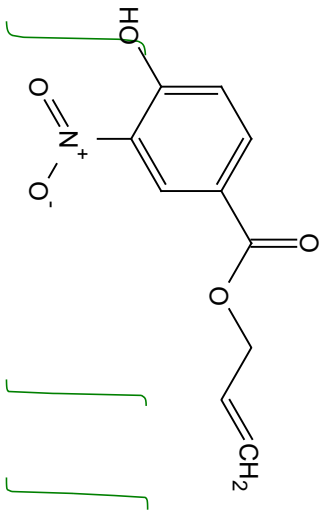
S14

Heller and Sarpong - 48

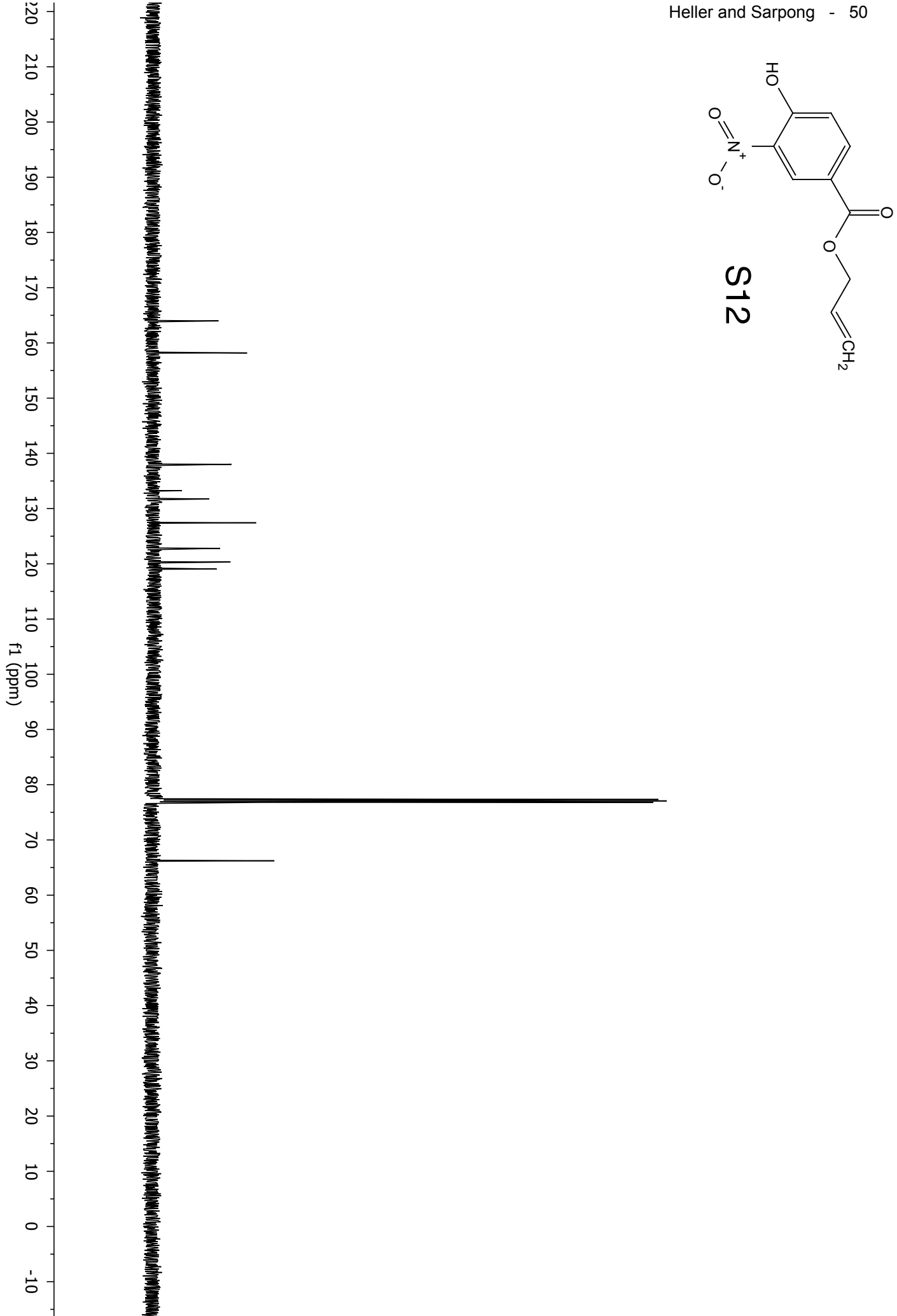


S14

S12


HO
O
N+
O-
O
O
CH2

1.00
1.01
1.02
1.00
1.01
2.05
2.05
f1 (ppm)
11.5
11.0
10.5
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


HO
O
N+
O-
O
O
CH2
S12
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10