Supplementary Information

Highly Efficient and Chemoselective α-Iodination of Acrylate Esters through Morita-Baylis-Hillman-type Chemistry

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1. General Information

^{1}H, ^{13}C and ^{15}N NMR spectra were recorded on a Bruker Avance 400 spectrometer (400.23 MHz for ^{1}H, 100.65 MHz for ^{13}C, 40.56 MHz for ^{15}N) or a Bruker Avance 500 spectrometer (500.13 MHz for ^{1}H, 125.77 MHz for ^{13}C) at 25 °C. The center of the solvent signal was used as an internal standard, which was related to TMS with δ 7.26 ppm (^{1}H in $CDCl_3$) and δ 77.0 ppm (^{13}C in $CDCl_3$). Digital resolutions were 0.25 Hz/data point in the ^{1}H spectra and 0.4 Hz/data point in the ^{13}C NMR spectra. Systematic names were generated with ACD/Name according to the IUPAC recommendations. For chromatographic separations, Kieselgel 60 (70–230 mesh, Merck) was used. Acrylate esters were supplied from Sigma-Aldrich, Alfa Aesar, Acros and TCI and used as received. *N*-iodophthalimide was prepared as previously reported.[1, 2]

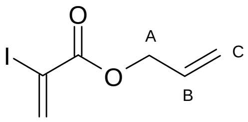
α-Iodo esters must be kept under Argon at -20°C dissolved in anhydrous benzene to avoid decomposition.

2. Procedures and Characterization Data

2.1. General Procedure for Synthesis of 2-Iodoacrylates

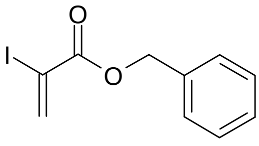
To a stirred solution of an appropriate acrylate (3.0 mmol, 1 equiv) in acetonitrile (15 mL) *N*-iodophthalimide (1.23 g, 4.5 mmol, 1.5 equiv.), 3-quinuclidinol (76 mg, 0.6 mmol, 0.2 equiv.) and KF-Celite (50% w/w) (383 mg, 3.3 mmol, 1.1 equiv.) were added successively. After stirring the reaction mixture for 24 h at room temperature, saturated aq. sodium thiosulfate solution was added, followed by the addition of ethyl acetate. The separated organic phase was dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. The crude mixture was then purified as reported below.

2.2. Physical Characterization Data



2

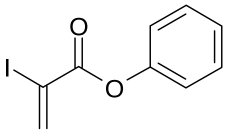
Allyl 2-iodoacrylate (2): By following the general procedure starting from **1** (336 mg, 0.36 mL, 3.0 mmol). Compound **2** was obtained as a brown liquid after column chromatography on silica gel (hexanes/AcOEt 10%) in 83% yield (593 mg). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.70 (m, J = 5.7, 1.5, 1.3 Hz, 2H, 2H_A), 5.28 (m, J = 10.5, 1.3, 1.3, 1.3 Hz, 1H, H'_{cis}), 5.38 (m, J = 17.2, 1.5, 1.5, 1.5 Hz, 1H, H'_{trans}), 5.94 (m, J = 17.2, 10.5, 5.7, 5.7 Hz, 1H, H_B), 6.60 (d, J = 1.4 Hz, 1H, H_{trans}), 7.46 (d, J = 1.4 Hz, 1H, H_{cis}). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 67.3 (C_A), 96.2 ($^{2}J(C\text{-}2,H_{trans})$ = 5.1 Hz, C-2), 118.8 (C_C), 131.3 (C_B), 139.9 ($^{1}J(C\text{-}3,H_{trans})$ = 166.9 Hz, $^{1}J(C\text{-}3,H_{cis})$ = 162.5 Hz, C-3), 162.1 ($^{3}J(CO,H_{trans})$ = 11.7 Hz, $^{3}J(CO,H_{cis})$ = 5.5 Hz, $^{3}J(CO,OCH_2)$ = 3.2 Hz, *C*O). IR (KBr) ν cm^{-1} 1713, 1254. GC-MS *m/z* 237.9.



3a

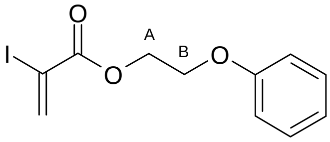
Benzyl 2-iodoacrylate (3a): By following the general procedure starting from **3** (487 mg, 0.46 mL, 3.0 mmol). Compound **3a** was obtained as a brown liquid after column chromatography on silica gel (hexanes/AcOEt 5%) in 76% yield (657 mg). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.25 (s, 2H, CH_2), 6.61 (d, J = 1.3 Hz, 1H, H_{trans}), 7.37 (m, 3H, Ph H-3,4,5), 7.39 (m, 2H, Ph H-2,6), 7.48 (d, J = 1.3 Hz, 1H, H_{cis}). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 68.5 (CH_2), 96.3 ($^{2}J(C\text{-}2,H_{trans})$ =

5.1 Hz, C-2), 128.1 (Ph C-2,6), 128.4 (Ph C-4), 128.6 (Ph C-3,5), 135.2 (Ph C-1), 140.1 (C-3), 162.2 (^3J(CO,H$_{trans}$) = 11.7 Hz, ^3J(CO,H$_{cis}$) = 5.5 Hz, *C*O). IR (KBr) ν cm^{-1} 3077, 1715, 1251. GC-MS *m/z* 287.9.



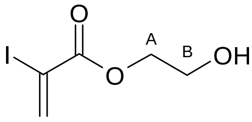
4a

Phenyl 2-iodoacrylate (4a): By following the general procedure starting from **4** (444 mg, 0.41 mL, 3.0 mmol). Compound **4a** was obtained as a yellow liquid after column chromatography on silica gel (hexanes/AcOEt 10%) in 69% yield (567 mg). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.76 (d, *J* = 1.5 Hz, 1H, H$_{trans}$), 7.15 (m, 2H, Ph H-2,6), 7.27 (m, 1H, Ph H-4), 7.41 (m, 2H, Ph H-3,5), 7.67 (d, *J* = 1.5 Hz, 1H, H$_{cis}$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 95.4 (^2J(C-2, H$_{trans}$) = 5.1 Hz, C-2), 121.2 (Ph C-2,6), 126.2 (Ph C-4), 129.5 (Ph C-3,5), 141.4 (^1J(C-3,H$_{cis}$) = 167.1 Hz, ^1J(C-3,H$_{trans}$) = 162.9 Hz, C-3), 150.9 (Ph C-1),160.9 (^3J(CO,H$_{trans}$) = 12.2 Hz, ^3J(CO,H$_{cis}$) = 5.7 Hz, *C*O). IR (KBr) ν cm^{-1} 3081, 1711, 1248. GC-MS *m/z* 273.9.



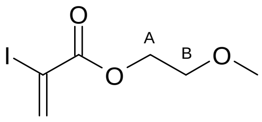
5a

2-Phenoxyethyl 2-iodoacrylate (5a): By following the general procedure starting from **5** (577 mg, 0.52 mL, 3.0 mmol). Compound **5a** was obtained as a brown thick oil after column chromatography on silica gel (hexanes/acetone 20%) in 93% yield (887 mg). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 4.23 (m, 2H, 2H$_B$), 4.56 (m, 2H, 2H$_A$), 6.62 (d, *J* = 1.5 Hz, 1H, H$_{trans}$), 6.93 (m, 2H, Ph H-2,6), 6.98 (m, 1H, Ph H-4), 7.30 (m, 2H, Ph H-3,5), 7.46 (d, *J* = 1.5 Hz, 1H, H$_{cis}$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 65.1 (C$_A$), 65.5 (C$_B$), 96.1 (^2J(C-2,H$_{trans}$) = 5.1 Hz, C-2), 114.7 (Ph C-2,6), 121.3 (Ph C-4), 129.5 (Ph C-3,5), 140.3 (^1J(C-3,H$_{trans}$) = 166.9 Hz, ^1J(C-3,H$_{cis}$) = 162.7 Hz, C-3), 158.4 (Ph C-1), 162.3 (^3J(CO,H$_{trans}$) = 11.7 Hz, ^3J(CO,H$_{cis}$) = 5.5 Hz, ^3J(CO,OCH$_2$) = 3.0 Hz, *C*O). IR (KBr) ν cm^{-1} 3079, 1717, 1247. 1224. GC-MS *m/z* 317.9.



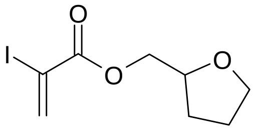
6a

2-Hydroxyethyl 2-iodoacrylate (6a): By following the general procedure starting from **6** (348 mg, 0.34 mL, 3.0 mmol). Compound **6a** was obtained as a yellow liquid after column chromatography on silica gel (dichloromethane/acetone 5%) in 66% yield (479 mg). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.27 (br s, 1H, O*H*), 3.86 (m, 2H, 2H$_B$), 4.32 (m, 2H, 2H$_A$), 6.60 (d, *J* = 1.4 Hz, 1H, H$_{trans}$), 7.47 (d, *J* = 1.4 Hz, 1H, H$_{cis}$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 60.8 (^1J(C$_B$,H$_B$) = 142.9 Hz, ^2J(C$_B$,H$_A$) = 2.0 Hz, C$_B$), 68.2 (^1J(C$_A$,H$_A$) = 148.1 Hz, ^2J(C$_A$,H$_B$) = 1.1 Hz, C$_A$), 95.7 (^2J(C-2,H$_{trans}$) = 5.1 Hz, C-2), 140.3 (^1J(C-3,H$_{trans}$) = 167.1 Hz, ^1J(C-3,H$_{cis}$) = 162.6 Hz, C-3), 162.6 (^3J(CO,H$_{trans}$) = 11.7 Hz, ^3J(CO,H$_{cis}$) = 5.5 Hz, ^3J(CO,OCH$_3$) = 3.0 Hz, *C*O). IR (KBr) ν cm^{-1} 3443, 1711, 1252. 1218. GC-MS *m/z* 241.9.



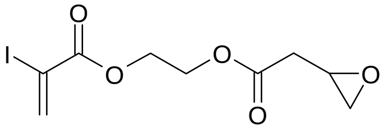
7a

2-Methoxyethyl 2-iodoacrylate (7a): By following the general procedure starting from **7** (390 mg, 0.39 mL, 3.0 mmol). Compound **7a** was obtained as a brown liquid after column chromatography on silica gel (hexanes/AcOEt 10%) in 82% yield (657 mg). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.40 (s, 3H, C*H*$_3$), 3.64 (m, 2H, 2H$_B$), 4.35 (m, 2H, 2H$_A$), 6.61 (d, *J* = 1.4 Hz, 1H, H$_{trans}$), 7.46 (d, *J* = 1.4 Hz, 1H, H$_{cis}$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 59.1 (^1J(OCH$_3$) = 141.3 Hz, ^3J(OCH$_3$,OCH$_2$) = 3.5 Hz, *C*H$_3$), 65.8 (^1J(C$_A$,H$_A$) = 148.1 Hz, ^2J(C$_A$,H$_B$) = 1.6 Hz, C$_A$), 70.1 (C$_B$), 96.3 (^2J(C-2,H$_{trans}$) = 5.1 Hz, C-2), 140.0 (^1J(C-3,H$_{trans}$) = 166.8 Hz, ^1J(C-3,H$_{cis}$) = 162.7 Hz, C-3), 162.4 (^{3}J(CO,H$_{\mathrm{trans}}$) = 11.7 Hz, ^{3}J(CO,H$_{\mathrm{cis}}$) = 5.5 Hz, ^{3}J(CO,OCH$_2$) = 2.9 Hz, *C*O). IR (KBr) ν cm^{-1} 1709, 1251, 1226. GC-MS *m/z* 255.9.



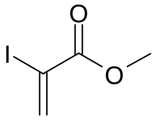
8a

Tetrahydrofuran-2-ylmethyl 2-iodoacrylate (8a): By following the general procedure starting from **8** (438 mg, 0.44 mL, 3.0 mmol). Compound **8a** was obtained as a brown liquid after column chromatography on silica gel (hexanes/AcOEt 10%) in 75% yield (635 mg). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.68 (m, 1H, Fur H-3), 1.86–1.99 (m, 2H, Fur 2H-4), 2.02 (m, 1H, Fur H-3), 3.80 (m, 1H, Fur H-5), 3.88 (m, 1H, Fur H-5), 4.16 (m, 1H, CH_{B}), 4.17 (m, 1H, Fur H-2), 4.24 (m, 1H, CH_{A}), 6.59 (d, *J* = 1.4 Hz, 1H, H$_{\mathrm{trans}}$), 7.46 (d, *J* = 1.4 Hz, 1H, H$_{\mathrm{cis}}$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 25.7 (Fur C-4), 27.9 (Fur C-3), 68.57 (Fur C-5), 68.63 (*C*H$_2$), 76.2 (Fur C-2), 96.1 (^{2}J(C-2,H$_{\mathrm{trans}}$) = 5.1 Hz, C-2), 140.0 (^{1}J(C-3,H$_{\mathrm{trans}}$) = 166.9 Hz, ^{1}J(C-3,H$_{\mathrm{cis}}$) = 162.5 Hz, C-3), 162.4 (^{3}J(CO,H$_{\mathrm{trans}}$) = 11.7 Hz, ^{3}J(CO,H$_{\mathrm{cis}}$) = 5.5 Hz, *C*O). IR (KBr) ν cm^{-1} 1711, 1252. 1216. GC-MS *m/z* 281.9.



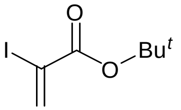
9a

2-[2-(2-oxiranyl)acetoxy]ethyl 2-iodoacrylate (9a): By following the general procedure starting from **9** (601 mg, 3.0 mmol). Compound **3a** was obtained as a brown liquid after column chromatography on silica gel (hexanes/AcOEt 5%) in 73% yield (714 mg). ^{1}H NMR (CDCl$_3$, 500 MHz) δ 2.94 (dd, *J* = 16.9, 9.5 Hz, 1H), 3.44 (dd, *J* = 16.8, 3.6 Hz, 1H), 3.79 (dd, *J* = 11.9, 9.9 Hz, 1H), 4.07 (dd, *J* = 9.9, 4.0 Hz, 1H), 4.47–4.39 (m, 4H), 4.53 (ddt, *J* = 11.9, 9.6, 3.8 Hz, 1H), 6.63 (d, *J* = 1.5 Hz, 1H), 7.49 (d, *J* = 1.5 Hz, 1H). ^{13}C NMR (CDCl3, 125 MHz,) δ 12.5, 20.9, 45.1, 62.5, 64.4, 95.9, 140.5, 140.7, 162.3, 169.9. IR (KBr) ν cm^{-1} 1716, 1709, 1240. 1220. GC-MS *m/z* 325.9.



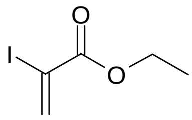
10a

Methyl 2-iodoacrylate (10a)^{3}: By following the general procedure, starting from **10** (258 mg, 0.27 mL, 3.0 mmol). Compound **10a** was obtained as a brown liquid after column chromatography on silica gel (hexanes/AcOEt 10%) in 79% yield (502 mg). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.83 (s, 3H, CH_3), 6.58 (d, *J* = 1.4 Hz, 1H, H_{trans}), 7.43 (d, *J* = 1.4 Hz, 1H, H_{cis}). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 53.7 (^{1}J(OCH$_3$) = 147.9 Hz, *C*H$_3$), 95.8 (^{2}J(C-2, H$_{\mathrm{trans}}$) = 5.1 Hz, C-2), 139.9 (^{1}J(C-3,H$_{\mathrm{trans}}$) = 166.9 Hz, ^{1}J(C-3,H$_{\mathrm{cis}}$) = 162.5 Hz, C-3), 162.9 (^{3}J(CO,H$_{\mathrm{trans}}$) = 11.6 Hz, ^{3}J(CO,H$_{\mathrm{cis}}$) = 5.4 Hz, ^{3}J(CO,OCH$_3$) = 3.8 Hz, *C*O). IR (KBr) ν cm^{-1} 1713, 1232. GC-MS *m/z* 211.9.



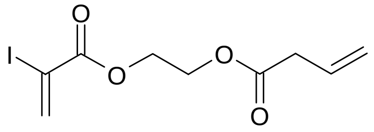
11a

2-Methyl-2-propanyl 2-iodoacrylate (11a)^{4}: By following the general procedure starting from **11** (384 mg, 0.44 mL, 3.0 mmol). Compound **11a** was obtained as a brown liquid after column chromatography on silica gel (hexanes/AcOEt 5%) in 88% yield (670 mg). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.49 (s, 9H, 3xCH_3), 6.50 (d, *J* = 1.3 Hz, 1H, H$_{\mathrm{trans}}$), 7.31 (d, *J* = 1.3 Hz, 1H, H$_{\mathrm{cis}}$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 27.8 (^{1}J(CH$_3$) = 127.1 Hz, ^{3}J($\underline{\mathrm{C}}$H$_3$,C$\underline{\mathrm{H}}_3$) = 4.1 Hz, *C*H$_3$), 83.1 (^{2}J(Cq,CH$_3$) = 4.1 Hz, Cq), 99.7 (^{2}J(C-2, H$_{\mathrm{trans}}$) = 4.9 Hz, C-2), 138.5 (^{1}J(C-3,H$_{\mathrm{trans}}$) = 166.3 Hz, ^{1}J(C-3,H$_{\mathrm{cis}}$) = 162.3 Hz, C-3), 161.3 (^{3}J(CO,H$_{\mathrm{trans}}$) = 11.2 Hz, ^{3}J(CO,H$_{\mathrm{cis}}$) = 5.3 Hz, *C*O). IR (KBr) ν cm^{-1} 1719, 1254. 1221, 987. GC-MS *m/z* 253.9.



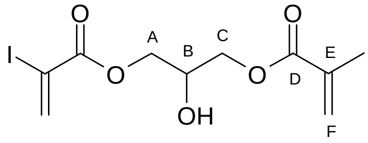
12a

Ethyl 2-iodoacrylate (12a): By following the general procedure starting from **12** (300 mg, 0.32 mL, 3.0 mmol). Compound **12a** was obtained as a brown liquid after column chromatography on silica gel (hexanes/AcOEt 15%) in 83% yield (563 mg). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.31 (t, J = 7.1 Hz, 3H, $C\mathit{H}_3$), 4.25 (q, J = 7.1 Hz, 2H, $C\mathit{H}_2$), 6.56 (d, J = 1.4 Hz, 1H, H_{trans}), 7.41 (d, J = 1.4 Hz, 1H, H_{cis}). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1 ($^1J(CH_3)$ = 127.3 Hz, $^2J(\underline{C}H_3,C\underline{H}_2)$ = 2.7 Hz, CH_3), 62.9 ($^1J(OCH_2)$ = 148.3 Hz, $^2J(OCH_2,CH_3)$ = 4.4 Hz, CH_2), 96.8 (^2J(C-2, H_{trans}) = 5.1 Hz, C-2), 139.5 (^1J(C-3,H_{cis}) = 166.7 Hz, ^1J(C-3,H_{trans}) = 162.4 Hz, C-3), 162.4 (^3J(CO,H_{trans}) = 11.5 Hz, ^3J(CO,H_{cis}) = 5.4 Hz, $^3J(CO,OCH_2)$ = 3.1 Hz, *C*O). IR (KBr) ν cm^{-1} 1719, 1237. GC-MS *m/z* 225.9.



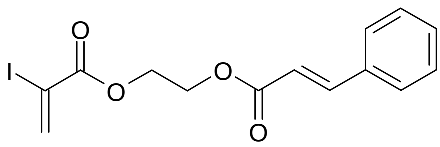
13a

2-[(2-iodoacryloyl)oxy]ethyl 3-butenoate (13a): By following the general procedure starting from **13** (553 mg, 3.0 mmol). Compound **13a** was obtained as a brown liquid after column chromatography on silica gel (hexanes/acetone 10%) in 87% yield (809 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.12 (m, J = 6.9, 1.5 Hz, 2H), 4.39–4.30 (m, 2H), 4.48–4.38 (m, 2H), 5.18 (m, J = 13.3, 3.4, 1.6 Hz, 2H), 5.98–5.83 (m, 1H), 6.62 (d, J = 1.5 Hz, 1H), 7.45 (d, J = 1.5 Hz, 1H). ^{13}C NMR (CDCl3, 125 MHz,) δ 39.0, 62.4, 64.5, 95.9, 119.0, 130.0, 140.5, 162.3, 171.4. IR (KBr) ν cm^{-1} 1719, 1711, 1252. 1221, 994. GC-MS *m/z* 309.9.



14a

2-Hydroxy-3-(methacryloyloxy)propyl 2-iodoacrylate (14a): By following the general procedure starting from **14** (643 mg, 3.0 mmol). Compound **14a** was obtained as a brown liquid after column chromatography on silica gel (dichloromethane/acetone 5%) in 72% yield (734 mg). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.94 (dd, J = 1.5, 1.0 Hz, 1H, $C\mathit{H}_3$), 2.73 (br s, 1H, O*H*), 4.19 (quint, J = 5.1 Hz, 1H, H_B), 4.23–4.35 (m, 4H, 2H_A, 2H_B), 5.61 (m, J = 1.5, 1.5, 1.5, 1.5 Hz, 1H, H'$_{trans}$), 6.13 (m, J = 1.5, 1.0, 1.0, 1.0 Hz, 1H, H'$_{cis}$), 6.61 (d, J = 1.5 Hz, 1H, H_{trans}), 7.47 (d, J = 1.5 Hz, 1H, H_{cis}). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.2 (CH_3), 65.3 (CH_2), 67.2 (CH_2), 68.0 (C_B), 95.1 (^2J(C-2,H_{trans}) = 5.0 Hz, C-2), 126.5 (^1J(C_F,H'$_{trans}$) = 161.3 Hz, ^1J(C_F,H'$_{cis}$) = 158.5 Hz, ^3J(C_F,CH_3) = 5.8 Hz, C_F), 135.6 (^2J(C_E,CH_3) = 6.6 Hz, ^3J(C_E,H'$_{trans}$) = 3.0 Hz, C_E), 140.5 (^1J(C-3,H_{trans}) = 167.2 Hz, ^1J(C-3,H_{cis}) = 162.6 Hz, C-3), 162.3 (^3J(CO,H_{trans}) = 11.9 Hz, ^{3}J(CO,Hcis) = 5.5 Hz, ^{3}J(CO,OCH2) = 2.8 Hz, CO), 167.3 (C_D). IR (KBr) ν cm^{-1} 3414, 1720, 1714, 1233. GC-MS *m/z* 339.9.

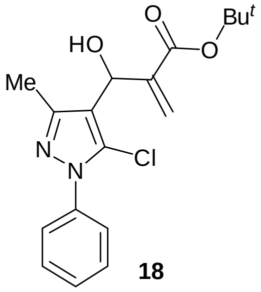


15a

2-{[(2*E*)-3-phenyl-2-propenoyl]oxy}ethyl 2-iodoprop-2-enoate (15a): By following the general procedure, starting from **15** (738 mg, 3.0 mmol). Compound **15a** was obtained as a brown liquid after column chromatography on silica gel (chloroform/acetone 5%) in 81% yield (904 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.66–4.34 (m, 4H), 6.45 (d, J = 16.1 Hz, 1H), 6.62 (d, J = 1.5 Hz, 1H), 7.41–7.34 (m, 3H), 7.47 (d, J = 1.5 Hz, 1H), 7.56–7.49 (m, 2H), 7.71 (d, J = 16.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 61.9, 64.6, 96.0, 117.4, 128.3, 129.0, 130.6, 134.3, 140.5, 145.7, 162.3, 166.7. IR (KBr) ν cm^{-1} 3078, 1721, 1713, 1246, 1212. GC-MS *m/z* 371.9.

2.3. Procedure for NKH Reaction and Physical Characterization Data

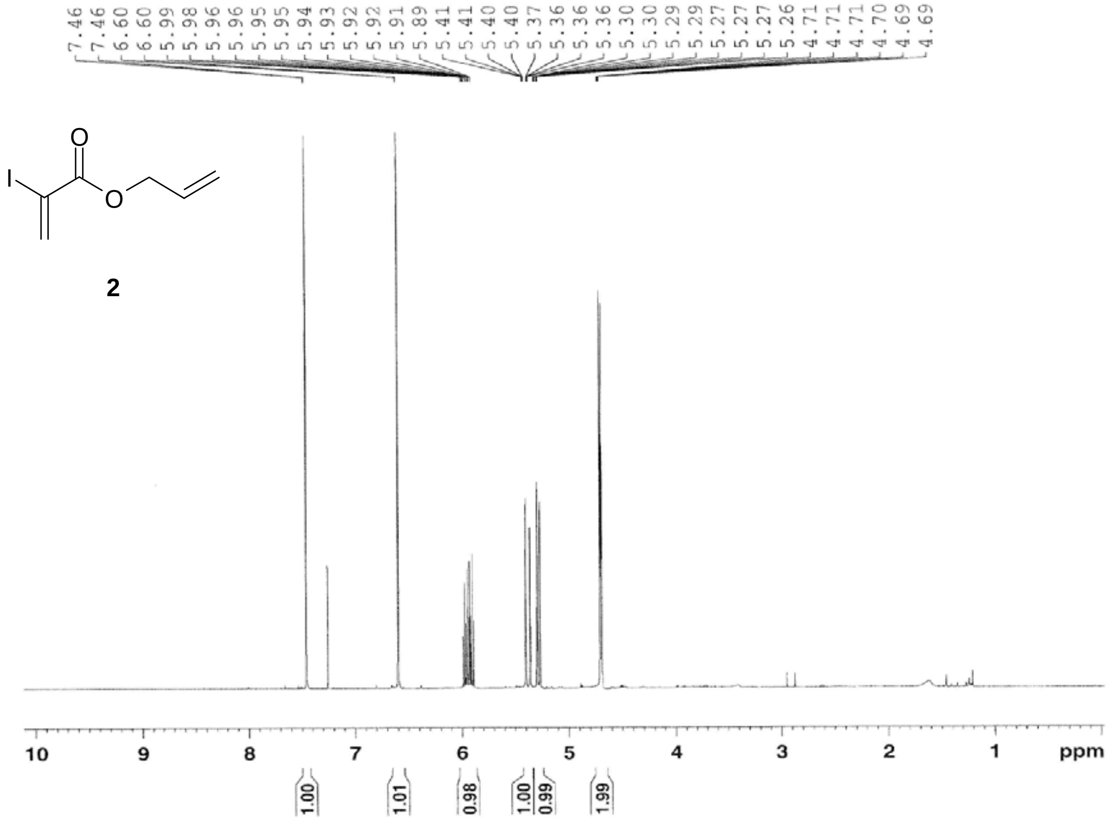
To a stirred solution of 5-chloro-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde **17** (57 mg, 0.26 mmol) in abs. DMF (3 mL) 2-methyl-2-propanyl 2-iodoacrylate **11a** (100 mg, 0.39 mmol)**,** $CrCl_2$ (129 mg, 1.05 mmol) and $NiCl_2$ (1 mg, 0.005 mmol) were added. After stirring the reaction mixture for 24 h at room temperature, the solvent was evaporated under reduced pressure, the residue was dissolved in ethyl acetate, water was added and the mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and evaporated. The residue was purified by flash chromatography with light petroleum/ethyl acetate = 1:3, v/v (R_f 0.3), affording the title compound **18** as a yellowish liquid in 89% yield (80 mg).



18

2-methyl-2-propanyl-2-[(5-chloro-3-methyl-1-phenyl-1H-pyrazol-4-yl)(hydroxyl)methyl]acrylate (18): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.48 (s, 9H, 3xC*H₃*), 2.32 (s, 3H, Me), 3.00 (br s, 1H, O*H*), 5.62 (t, *J* = 1.3 Hz, 1H, C*H*), 5.76 (dd, *J* = 1.3, 1.7 Hz, 1H, H_A), 6.28 (dd, *J* = 1.3, 1.7 Hz, 1H, H_B), 7.38 (m, 1H, Ph H-4), 7.46 (m, 2H, Ph H-3,5), 7.51 (m, 2H, Ph H-2,6). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.5 (Me), 28.0 (3 x *C*H_3), 65.3 (*C*-OH), 81.8 (*C*$(CH_3)_3$), 116.4 (C-4), 124.8 (*C*H_2), 125.0 (Ph C-2,6), 126.0 (C-5), 128.1 (Ph C-4), 129.0 (Ph C-3,5), 138.2 (Ph C-1), 141.3 (*C*=CH_2), 148.9 (C-3), 165.8 (*C*O). ^{15}N NMR ($CDCl_3$, 40 MHz) δ –173.2 (N-1), –79.2 (N-2). MS: 348.2.

3. ^{1}H and ^{13}C NMR Spectra



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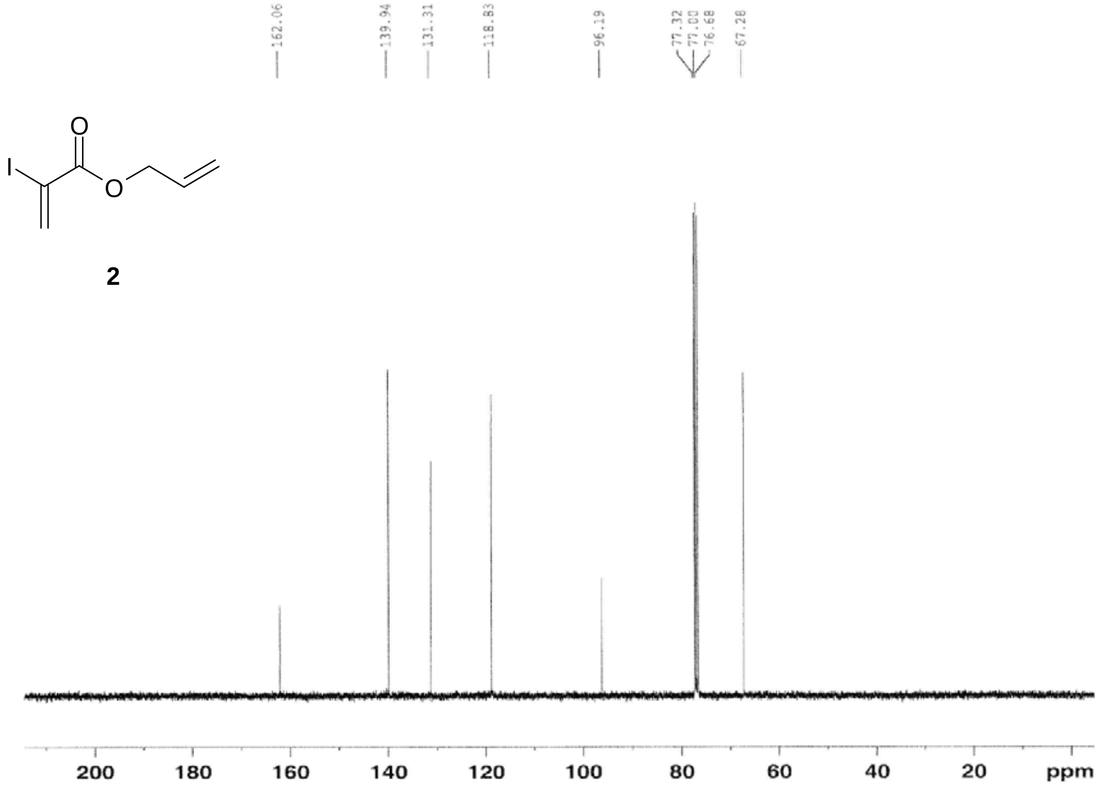

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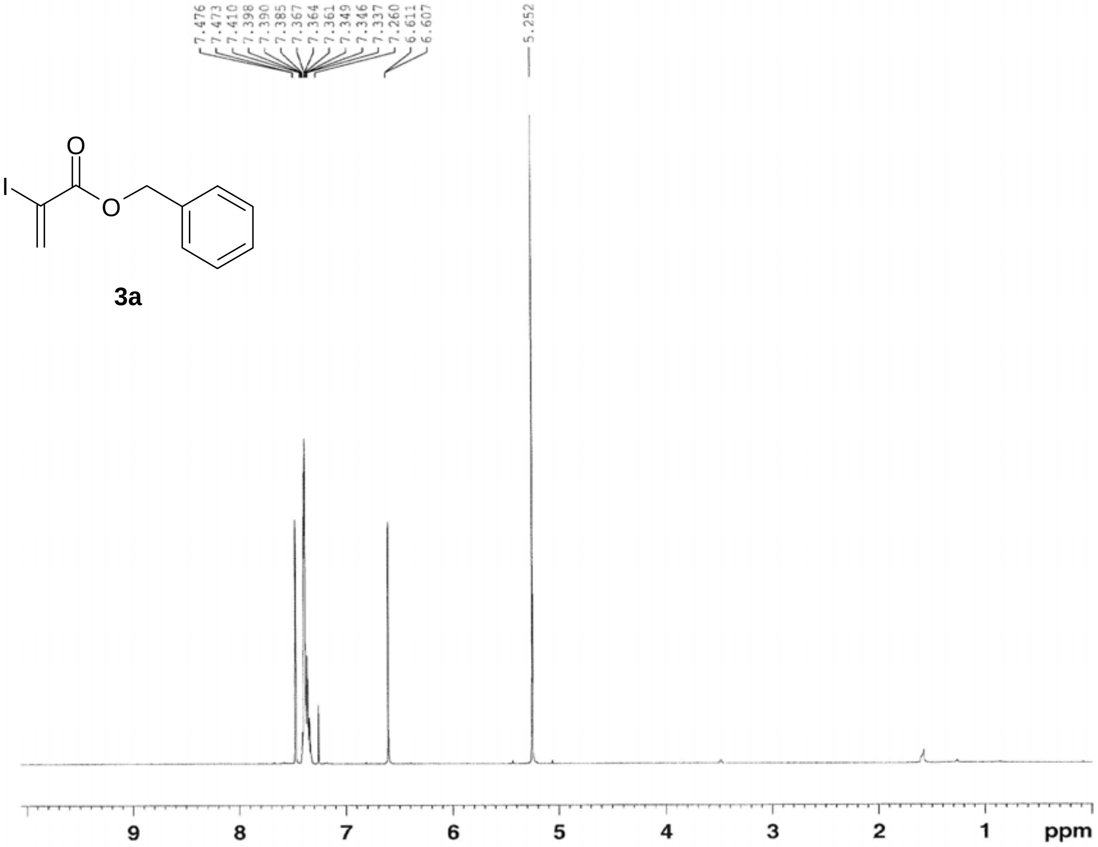

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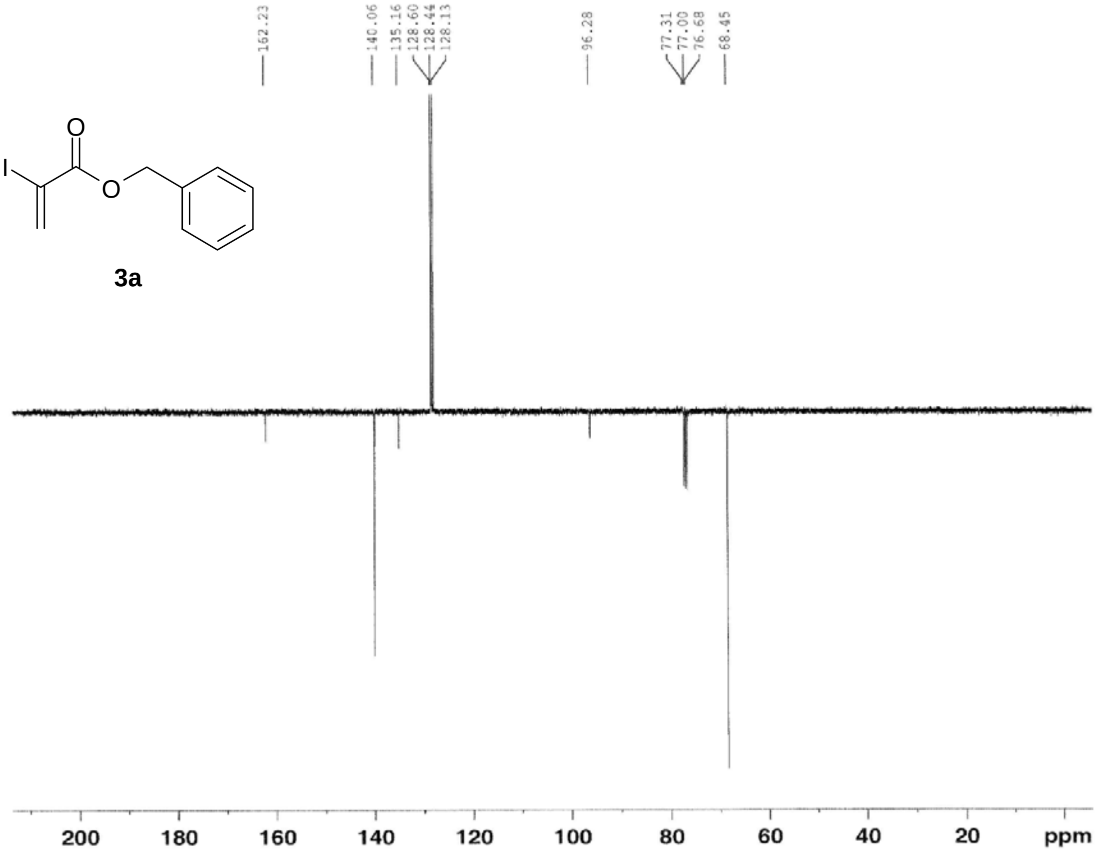

3a

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20
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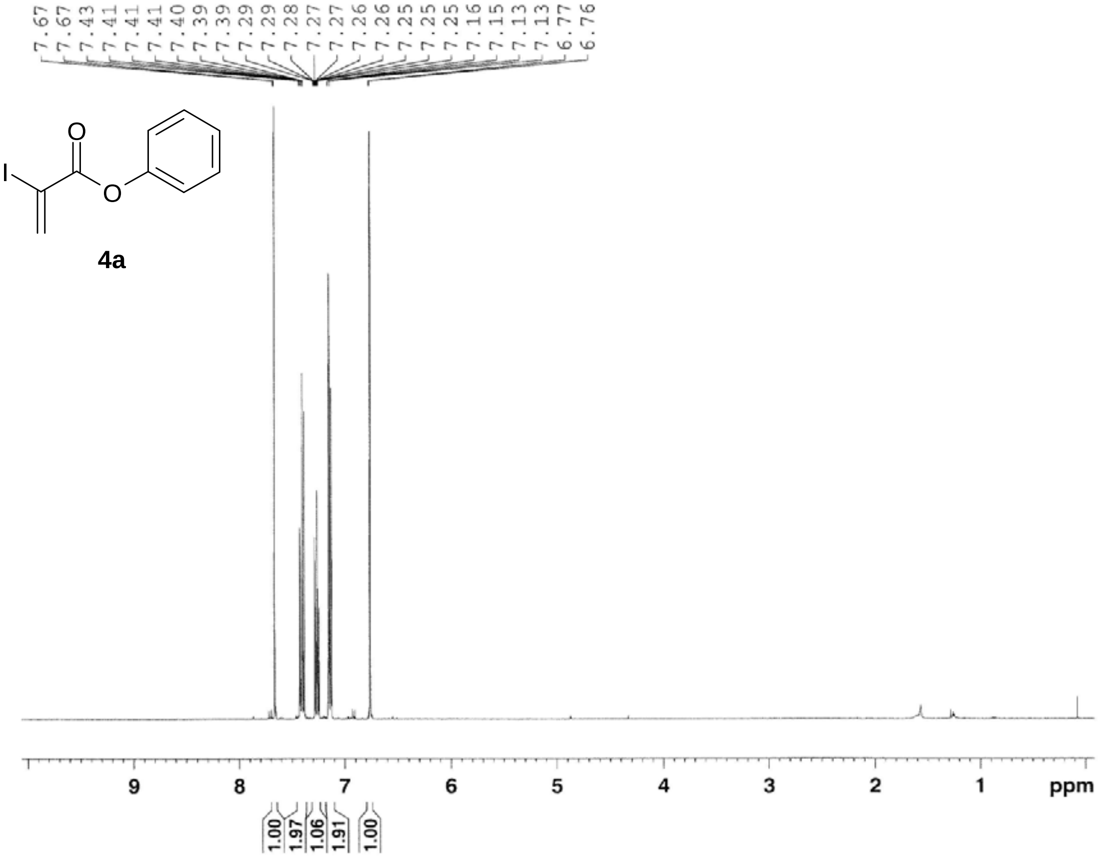
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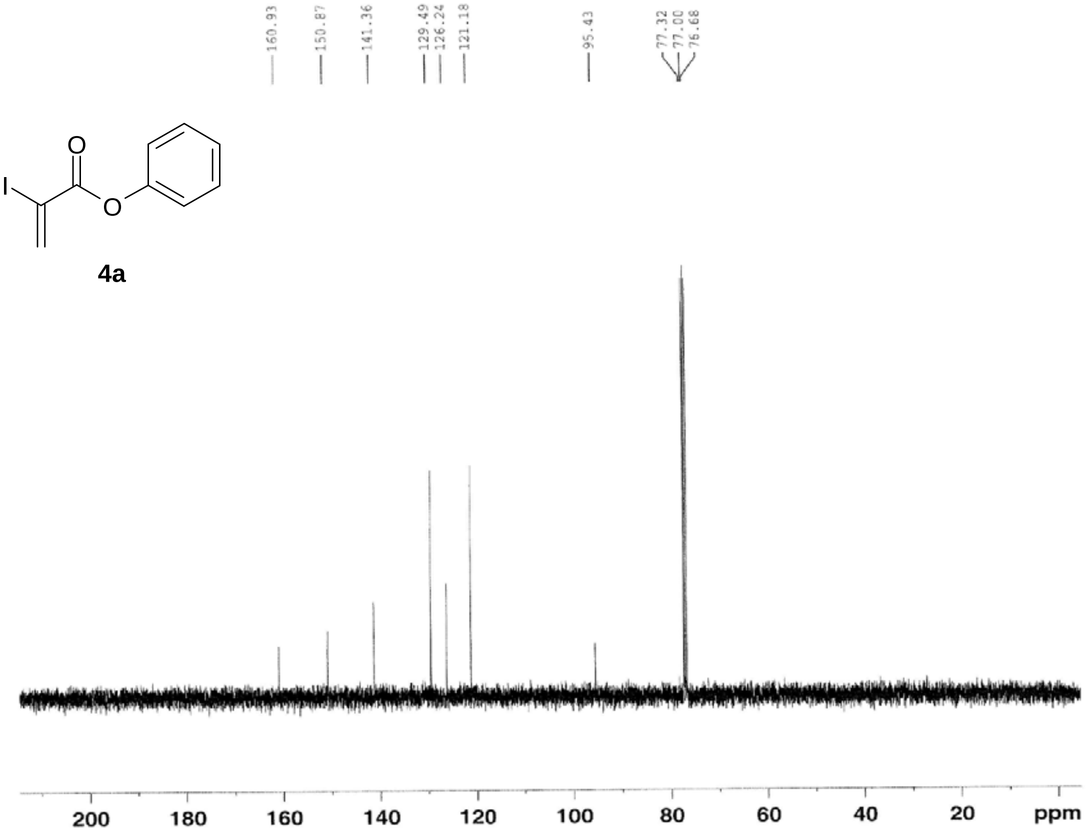
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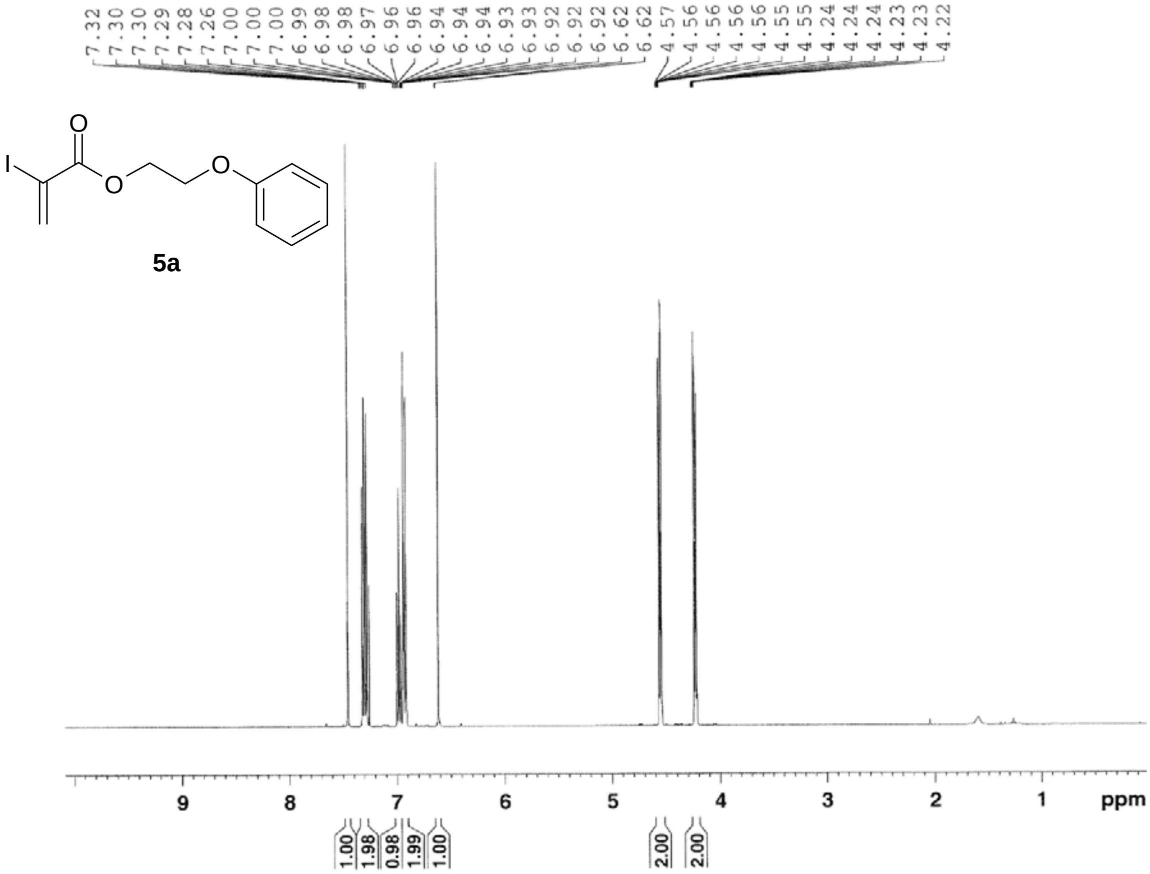
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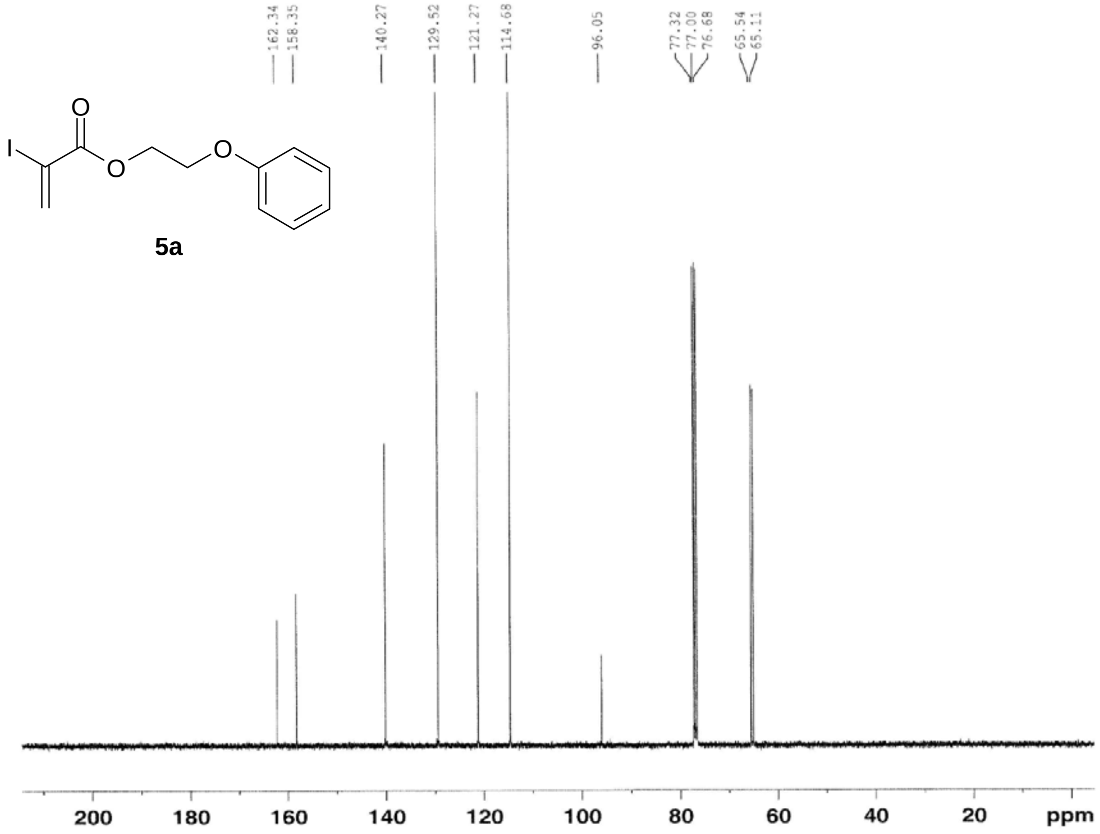
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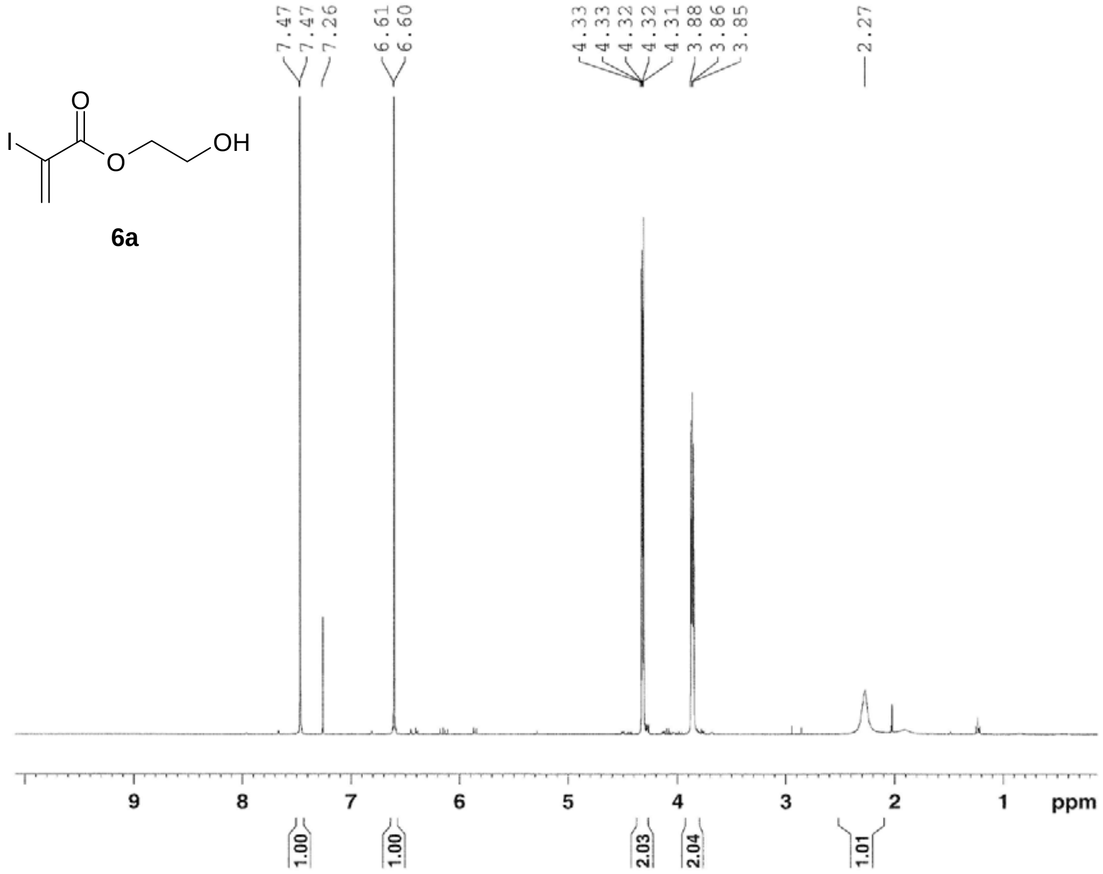

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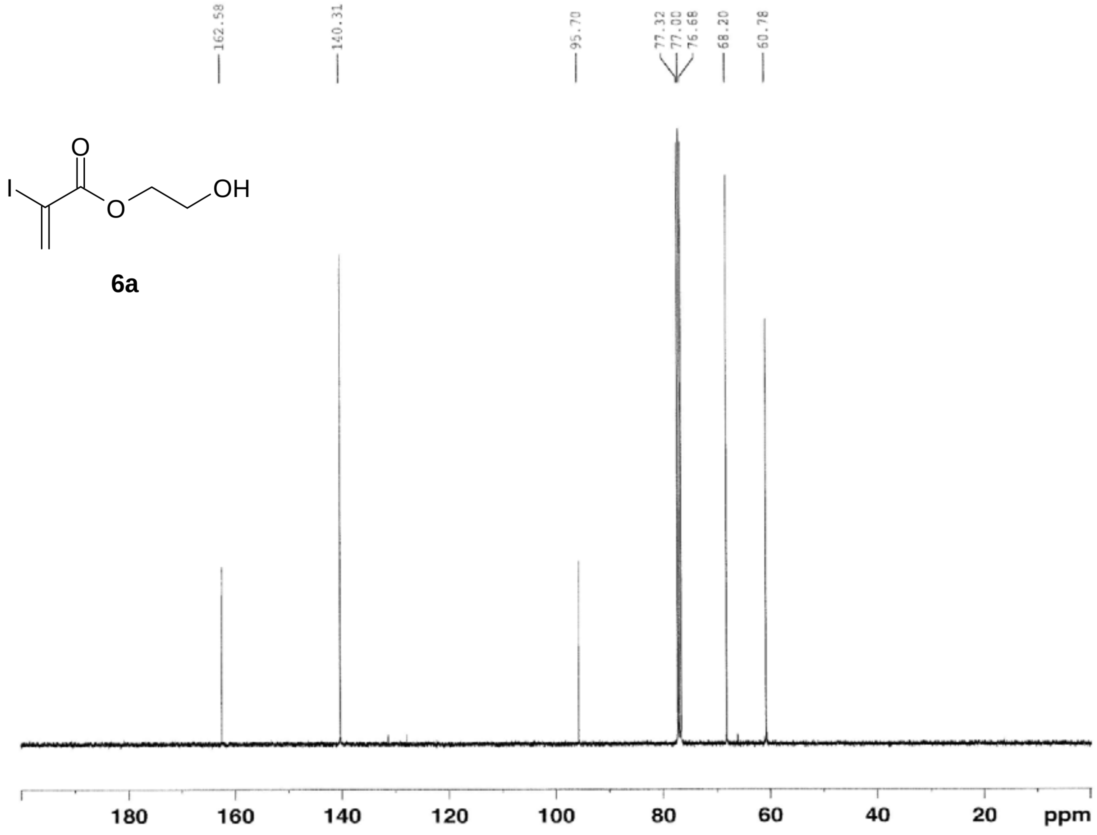

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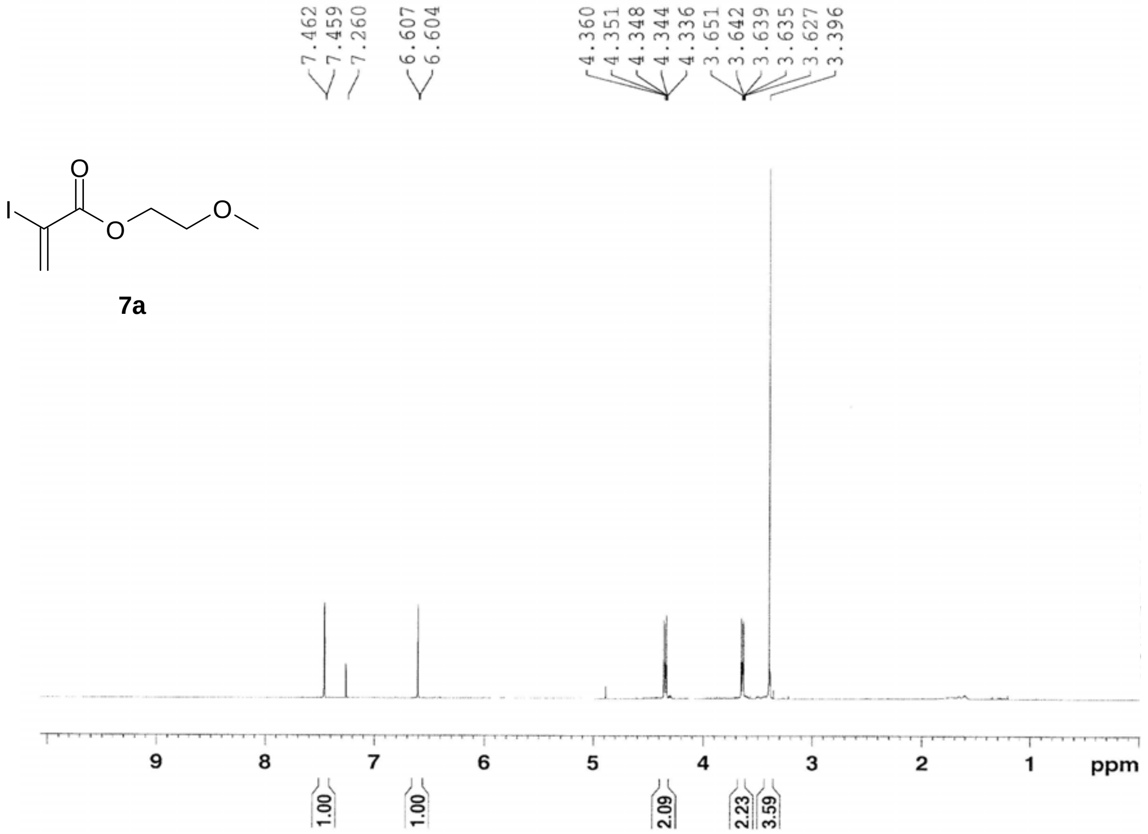
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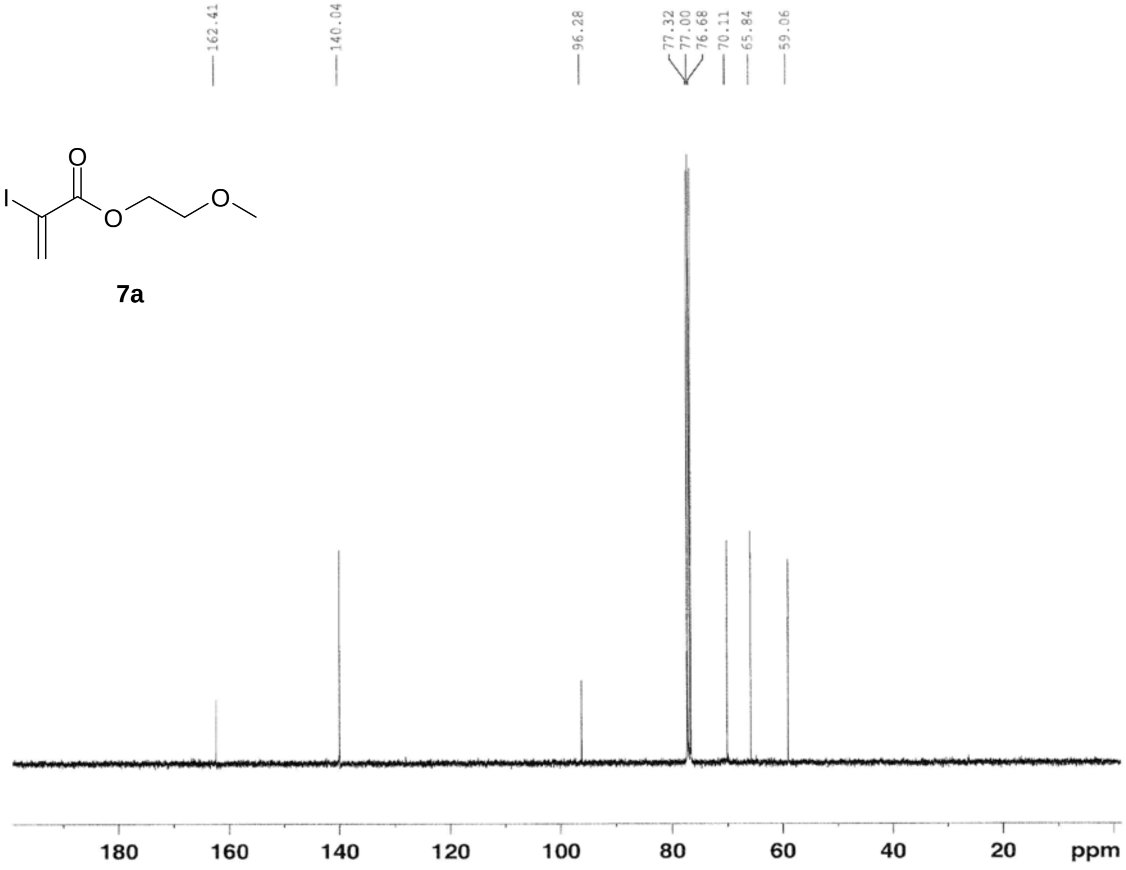
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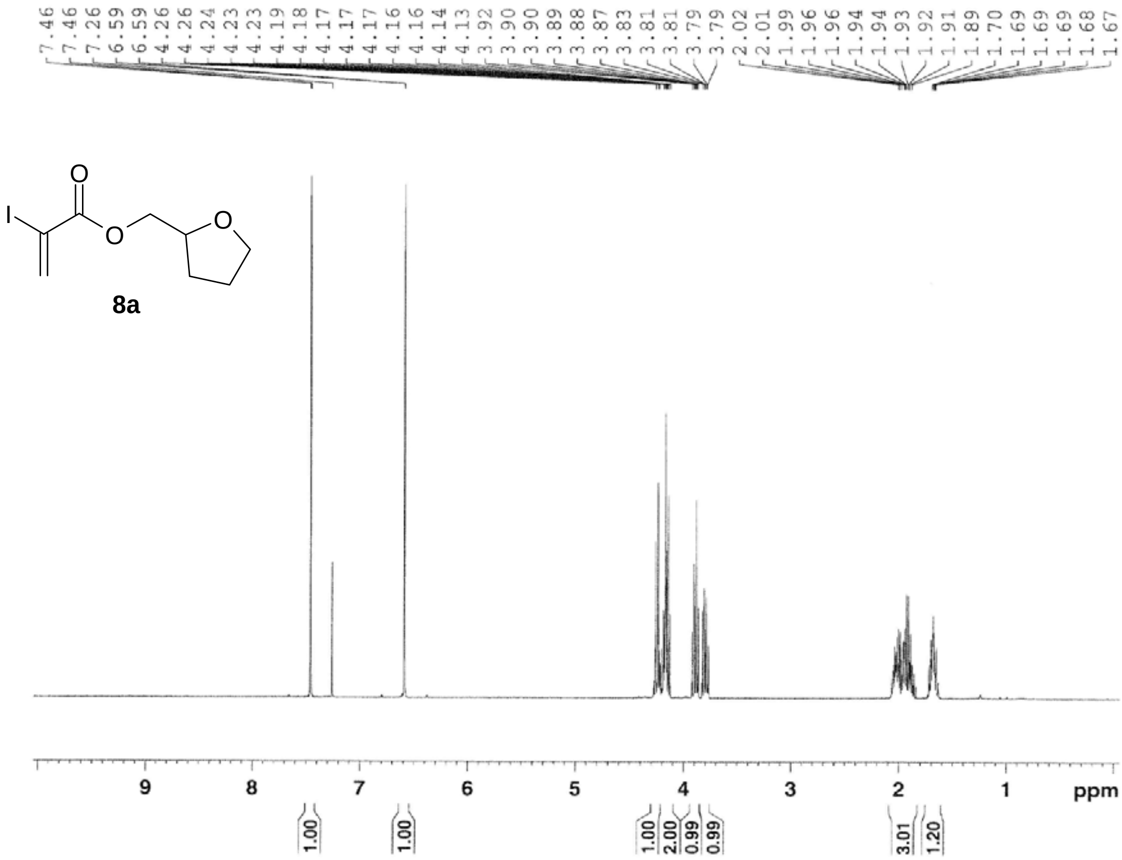
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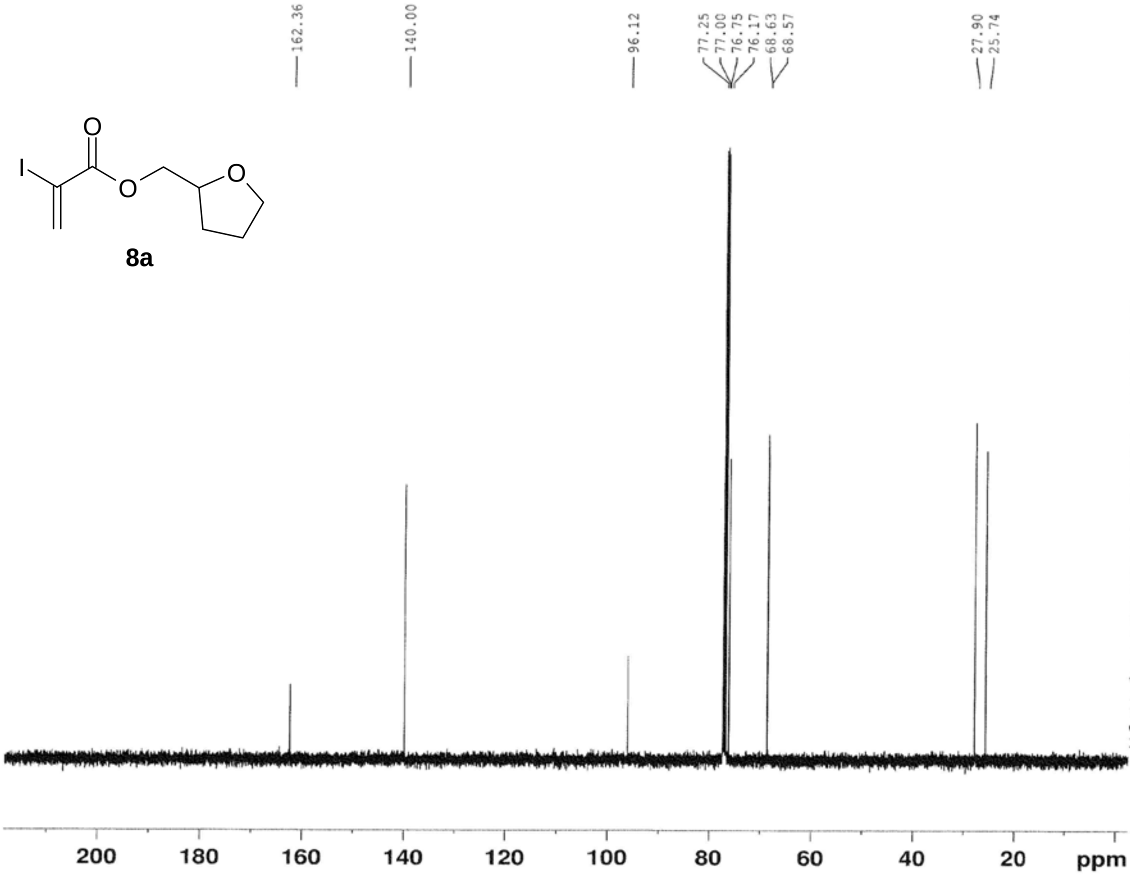
8a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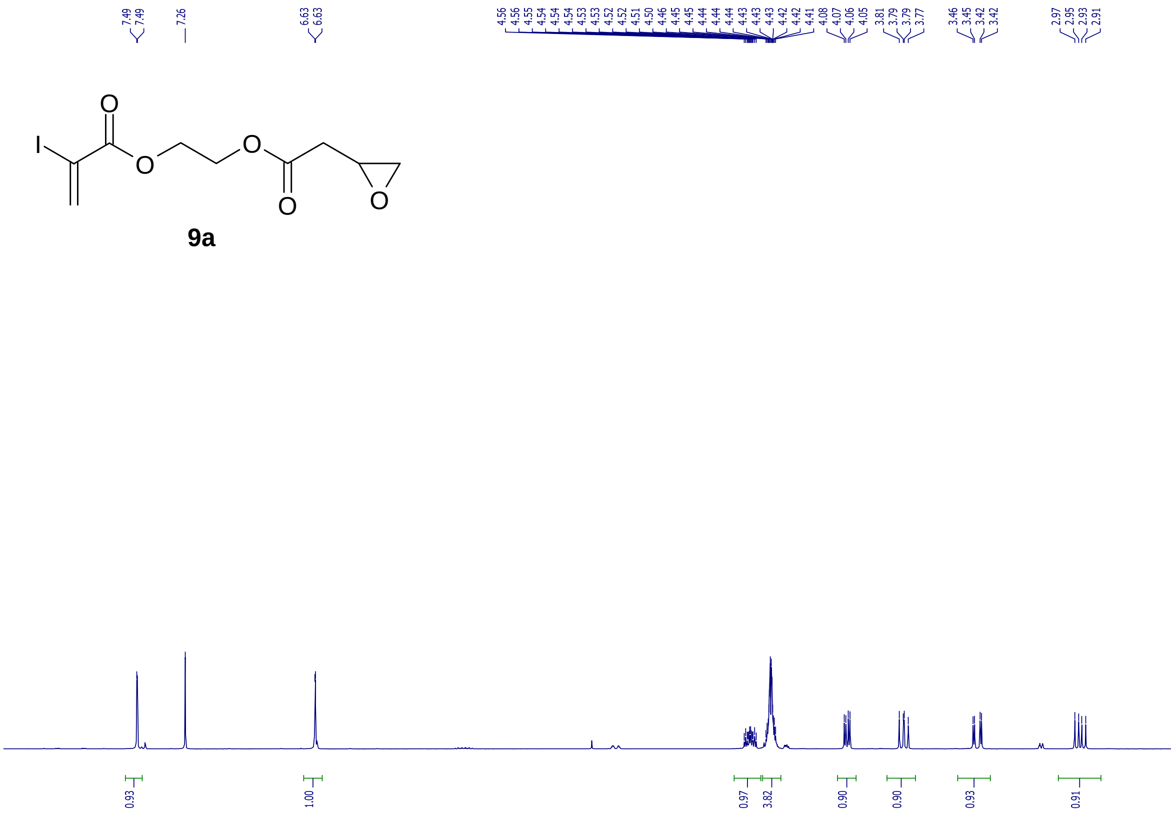
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2.91
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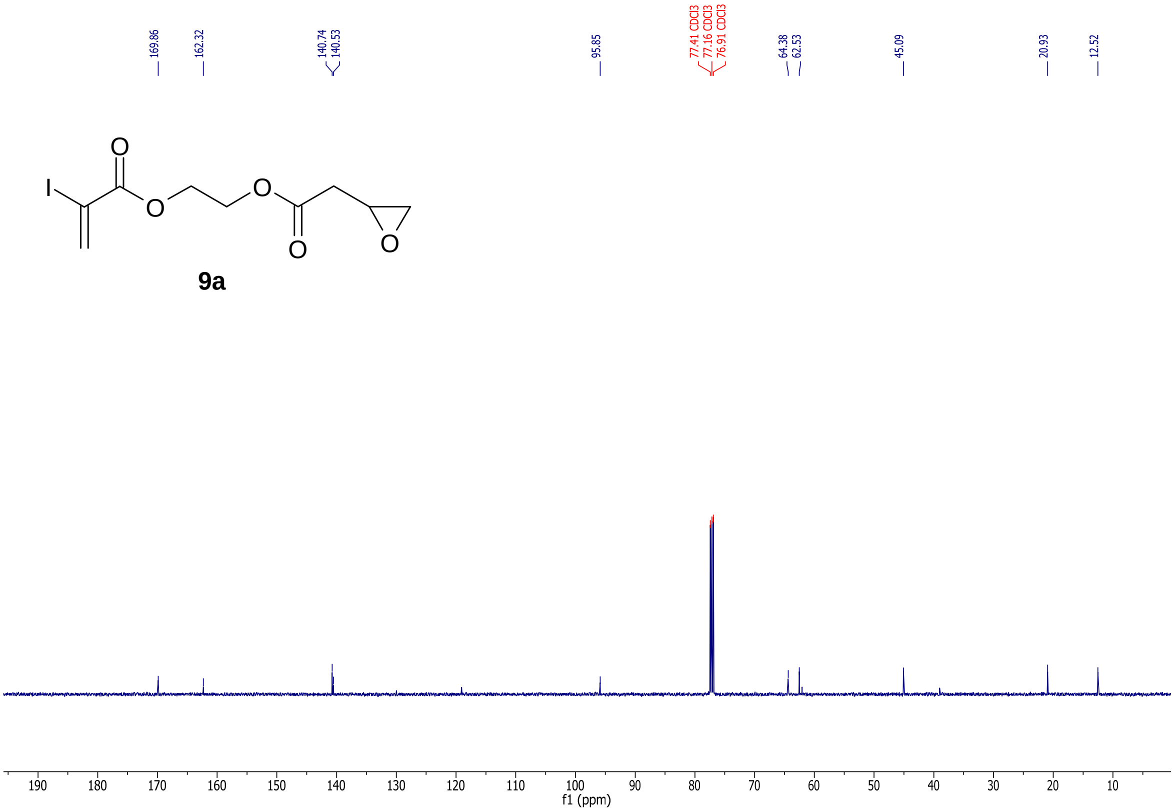
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O
O
9a
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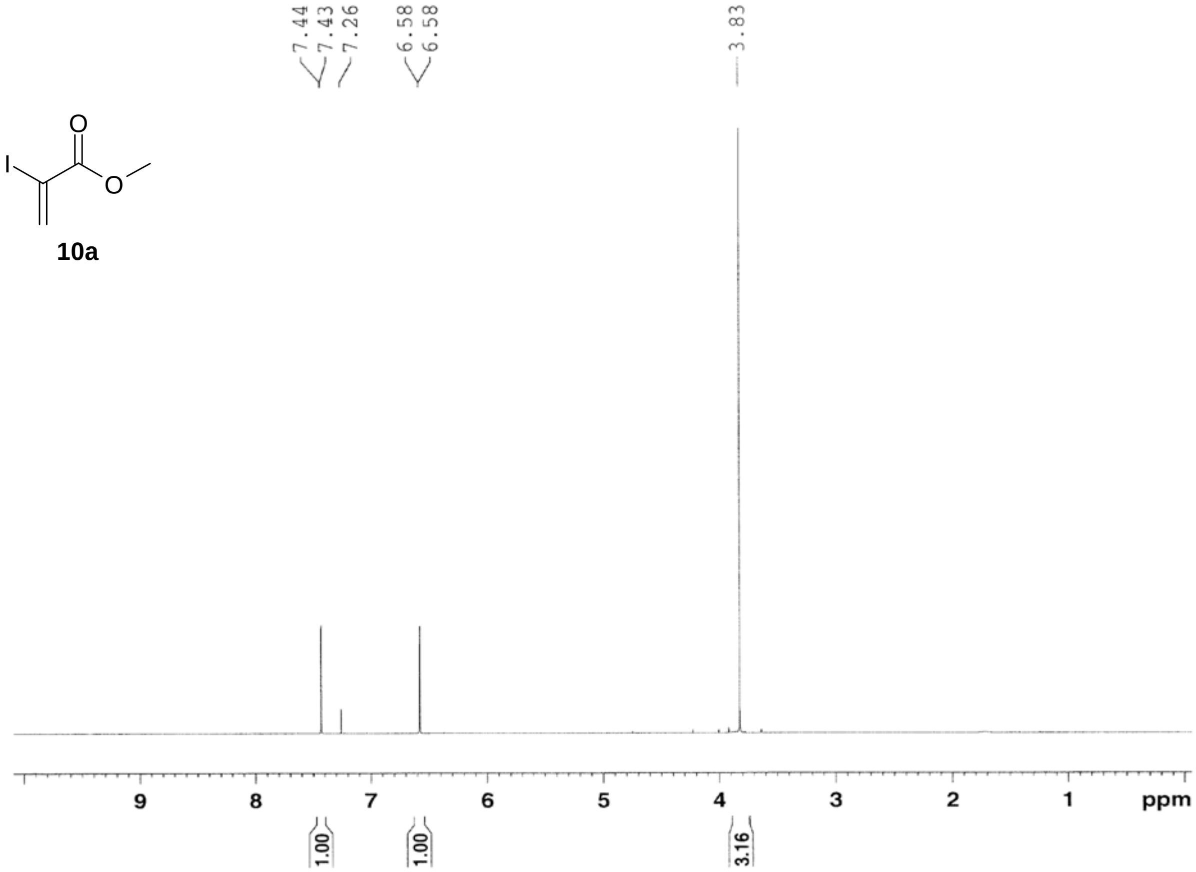

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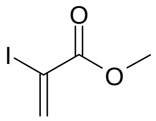

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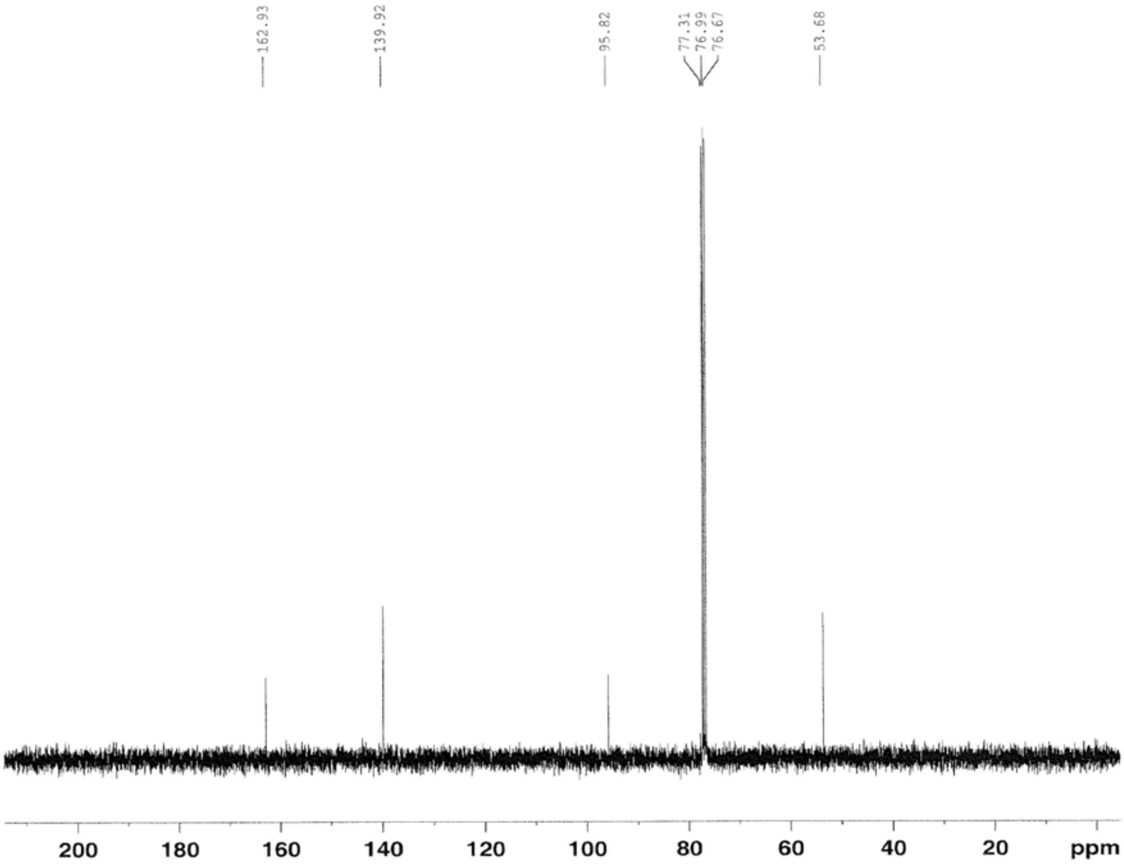
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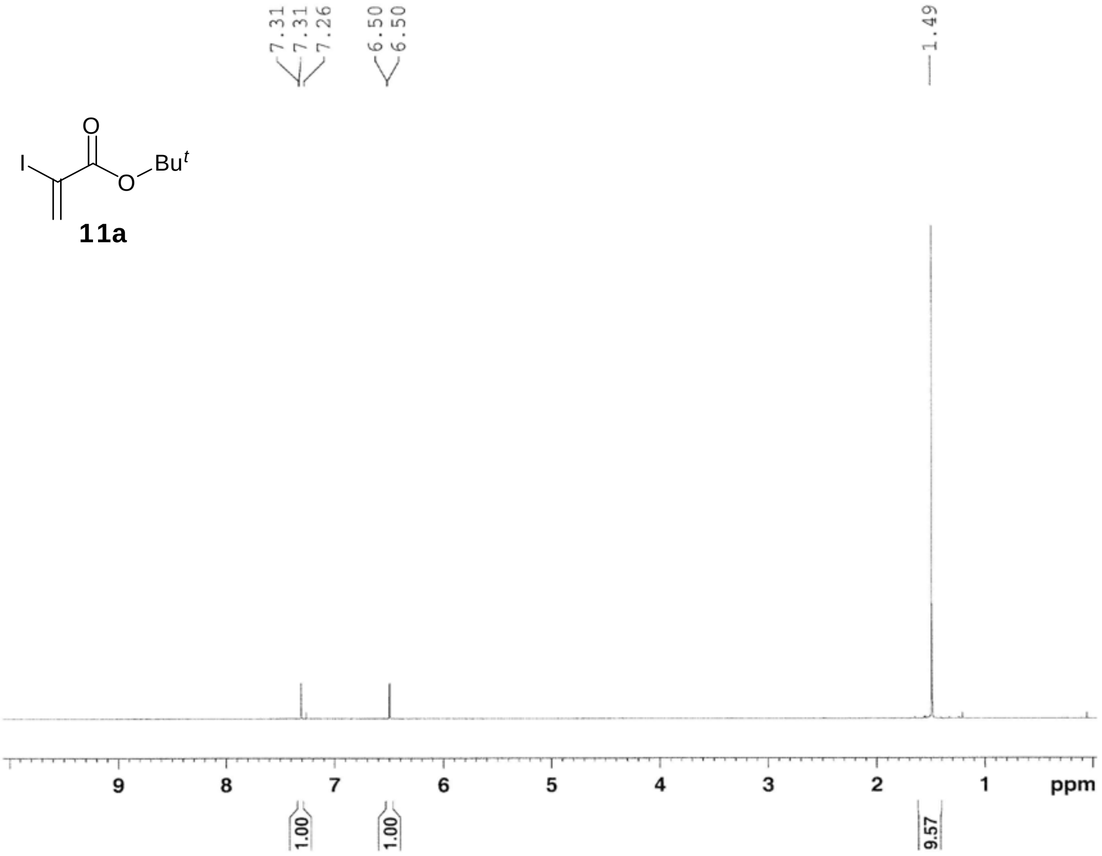
20
ppm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ppm
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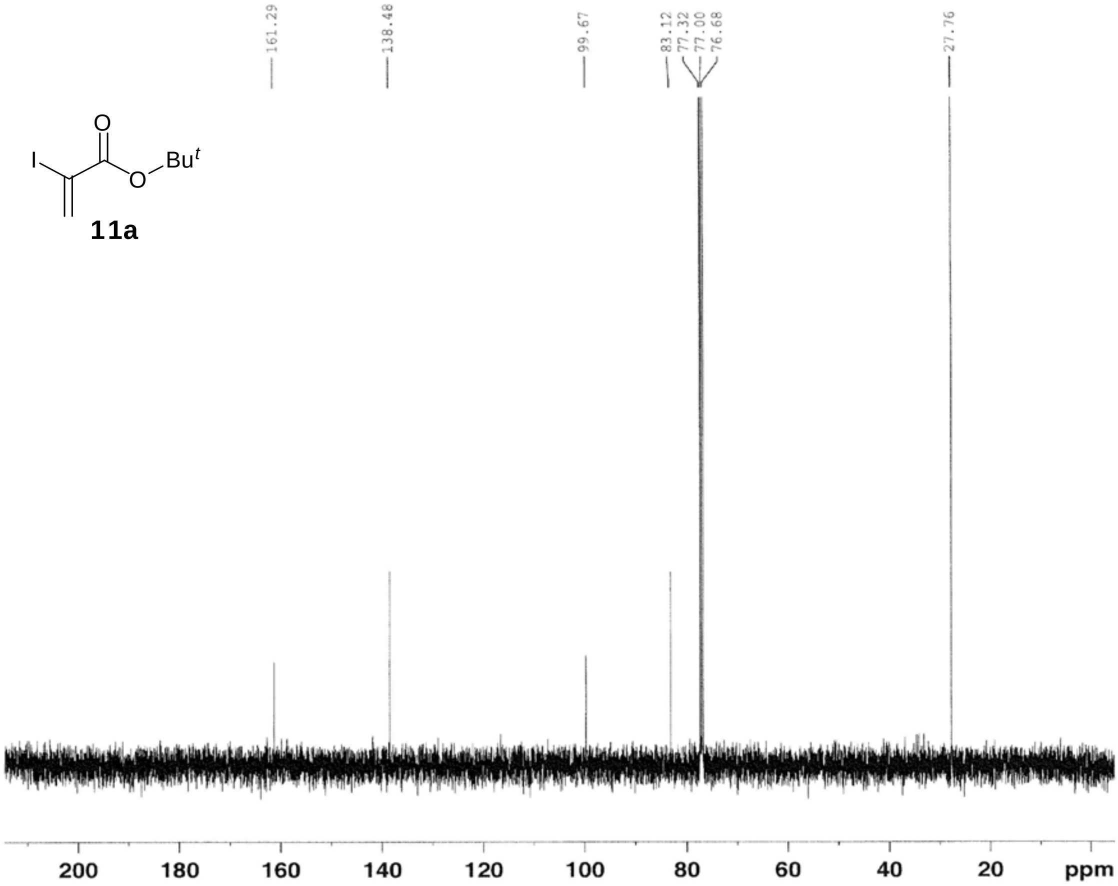
11a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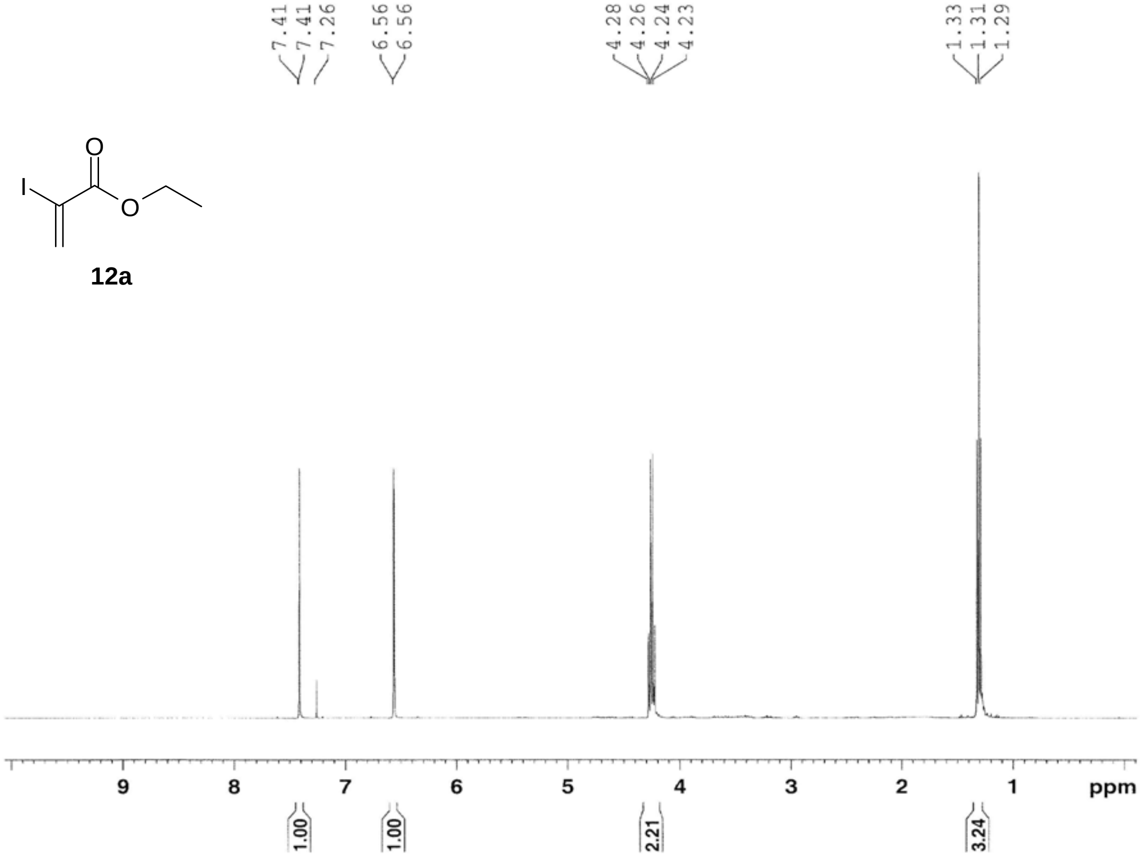
ppm

11a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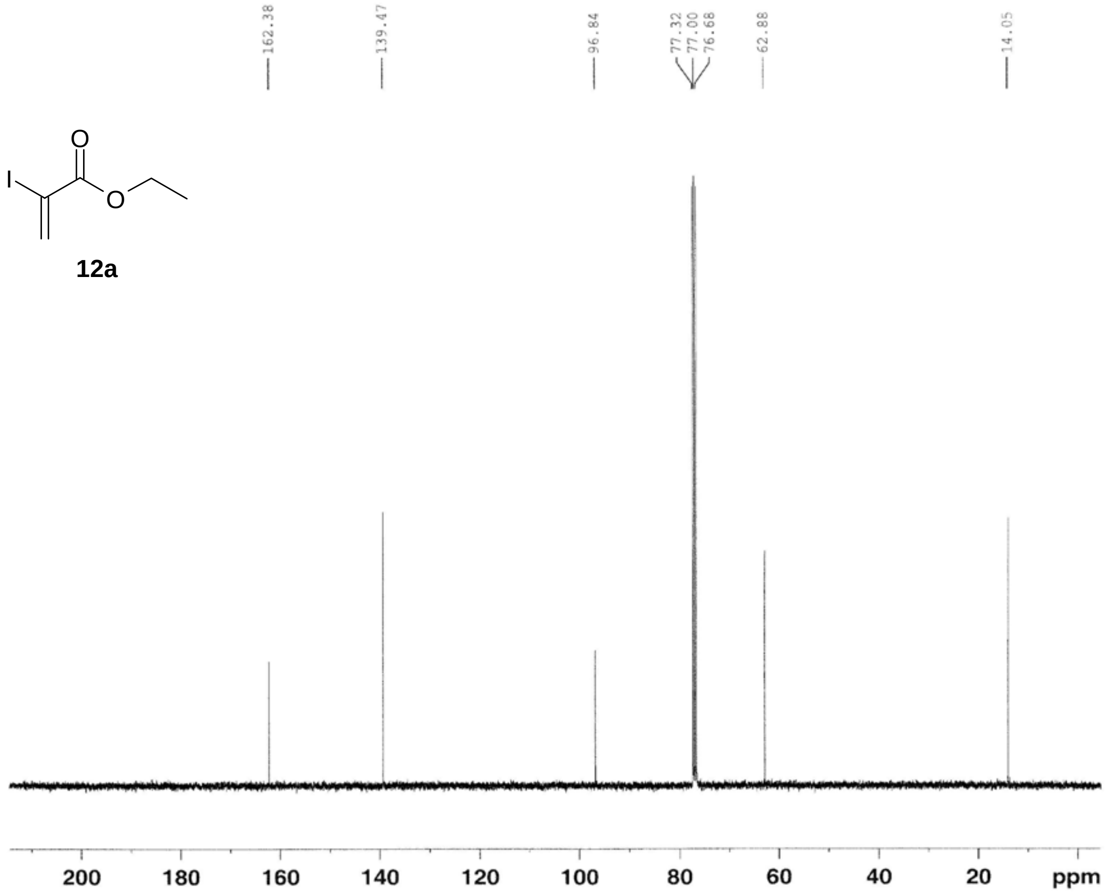
12a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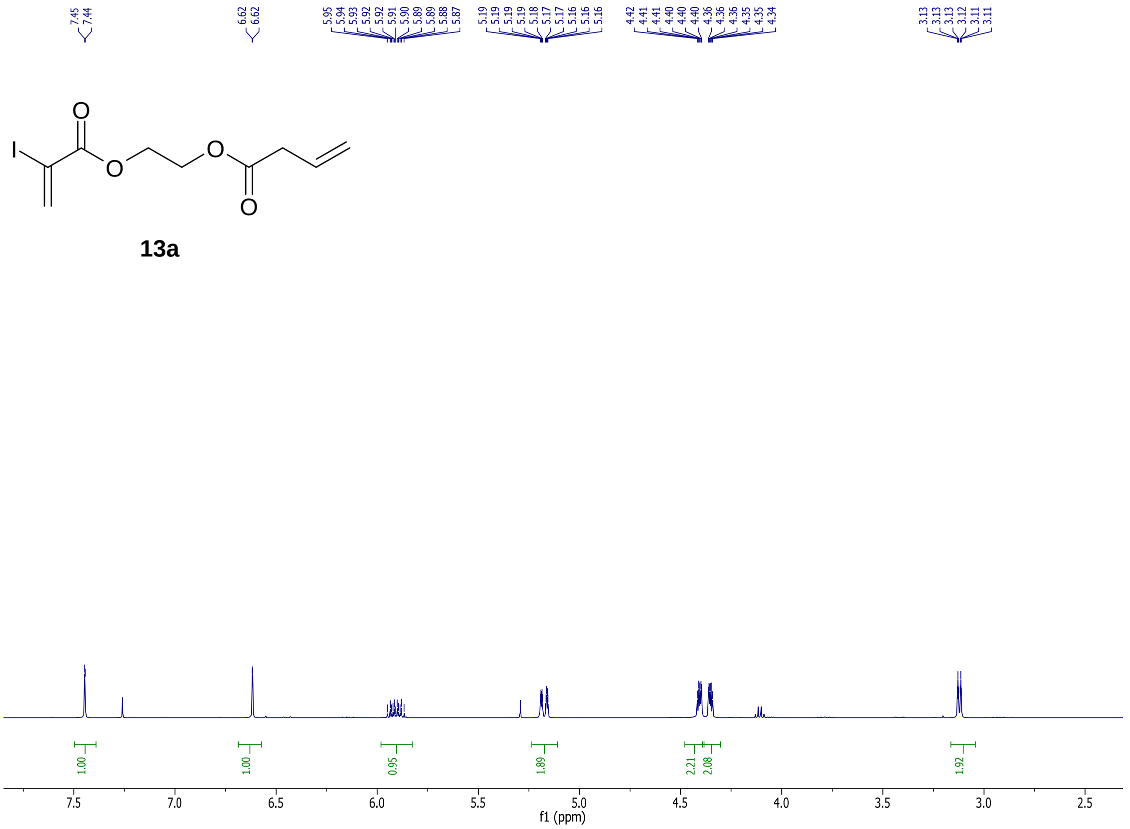
12a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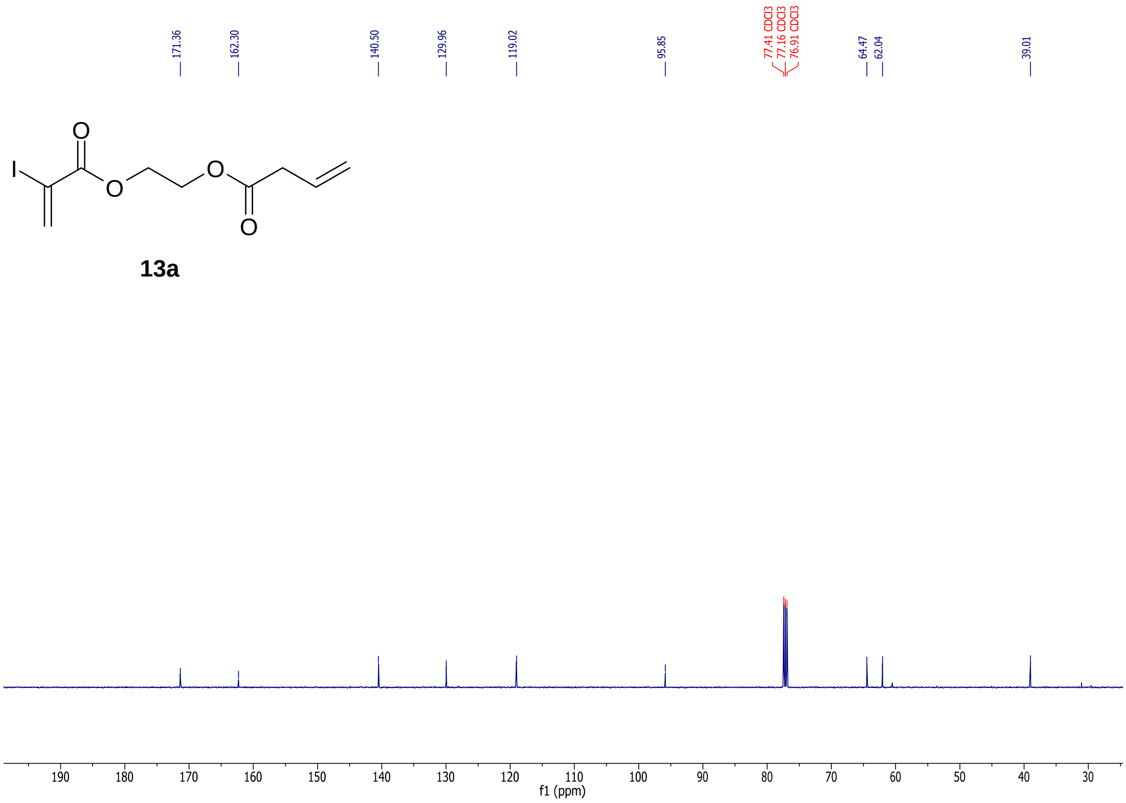
13a



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I
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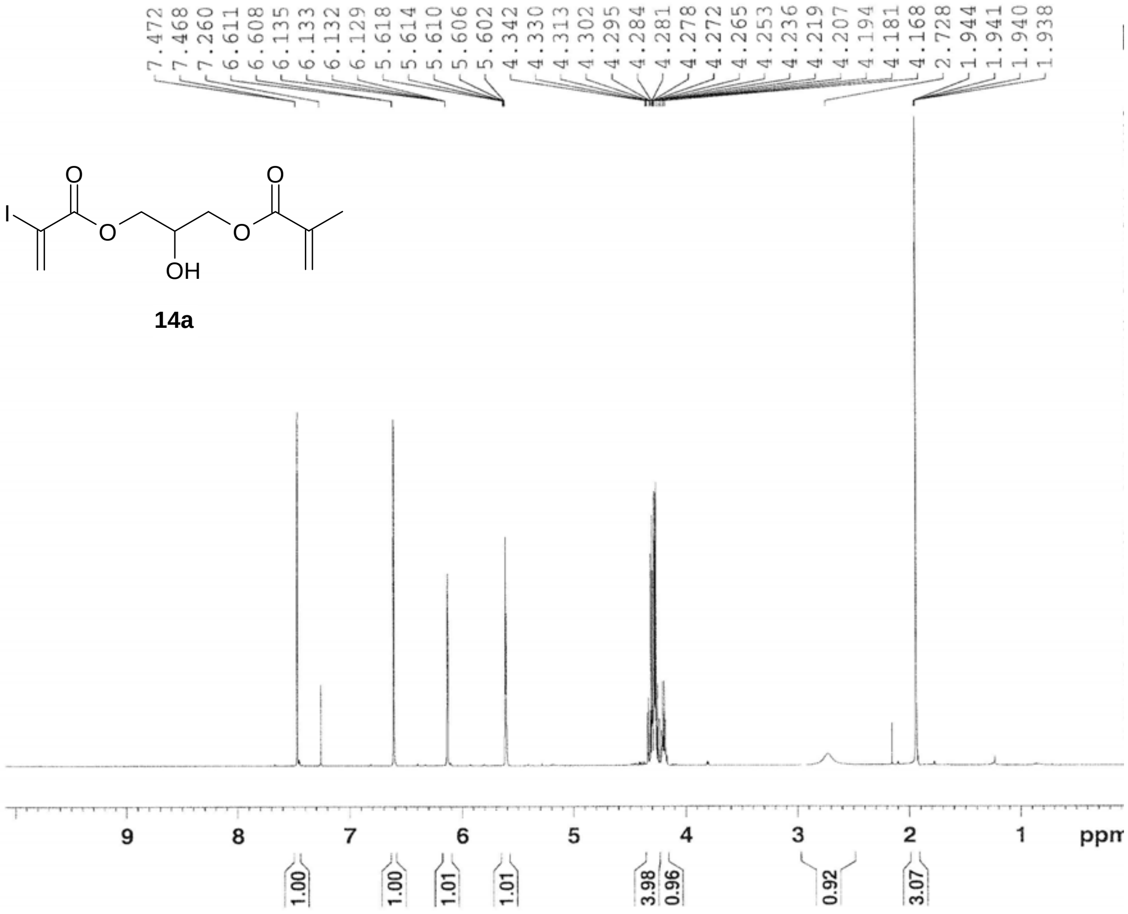
13a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4.181
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O
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OH
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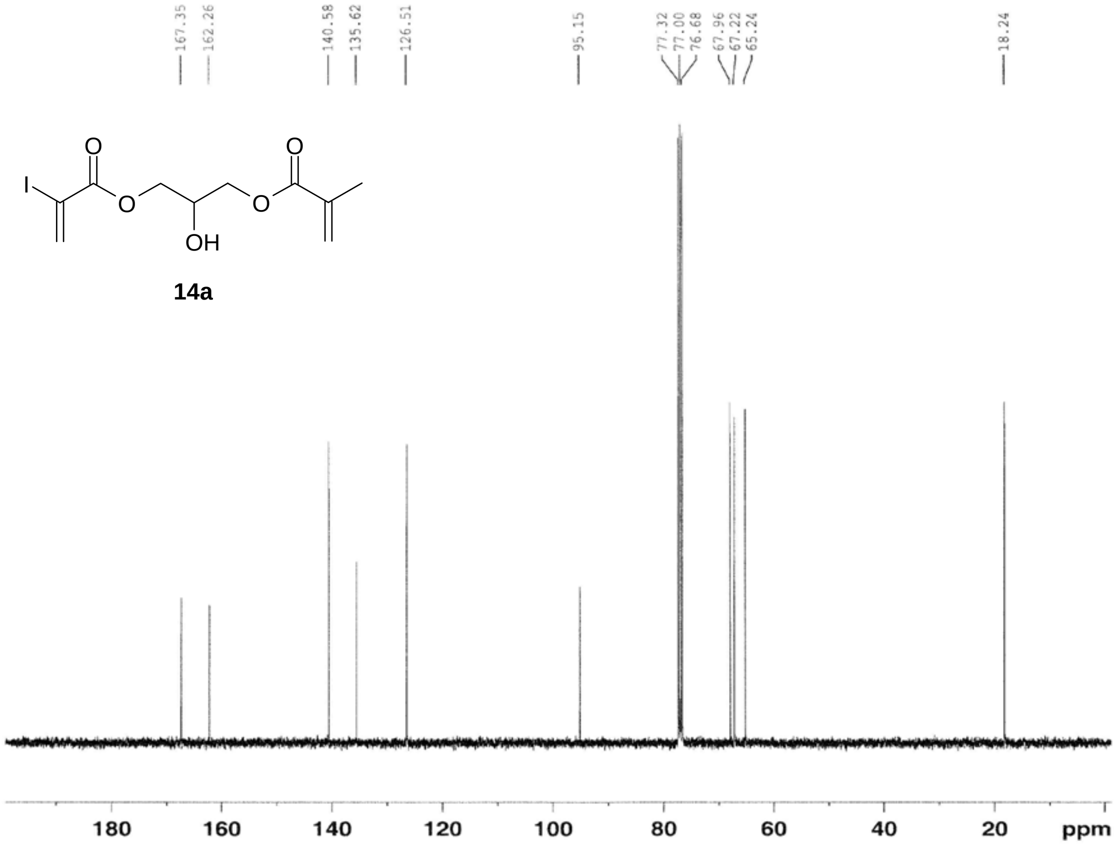
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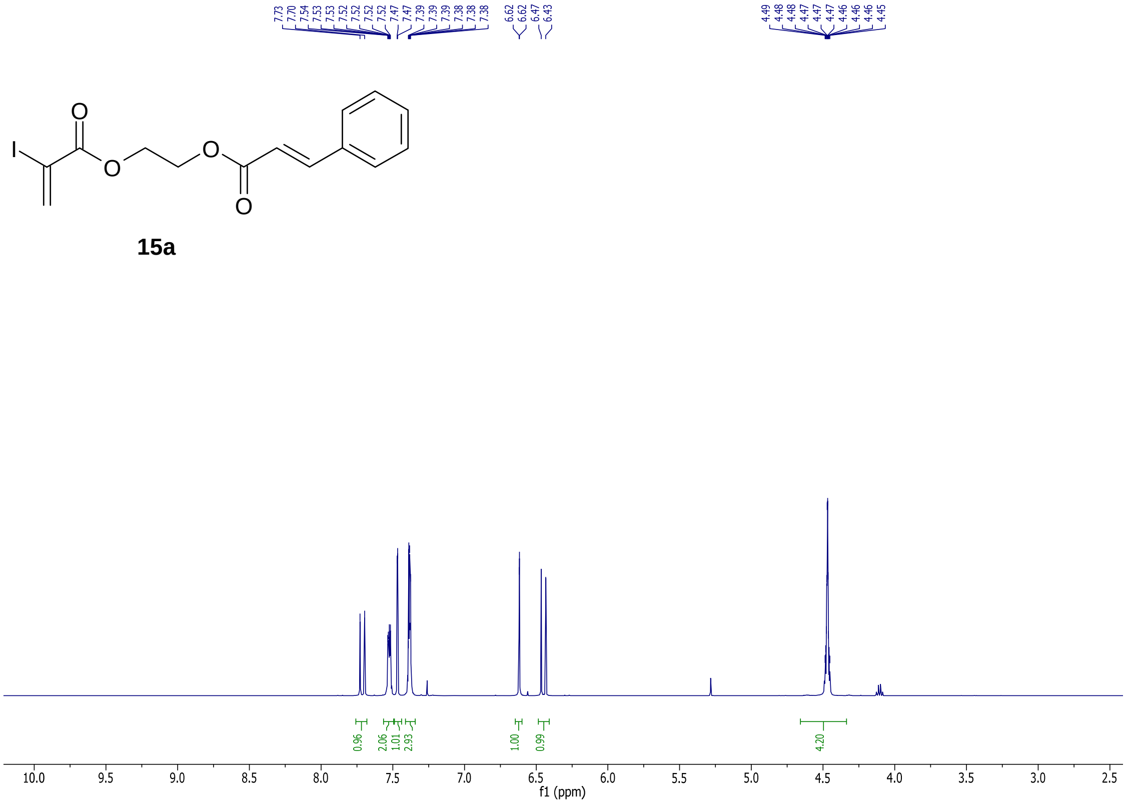
20
ppm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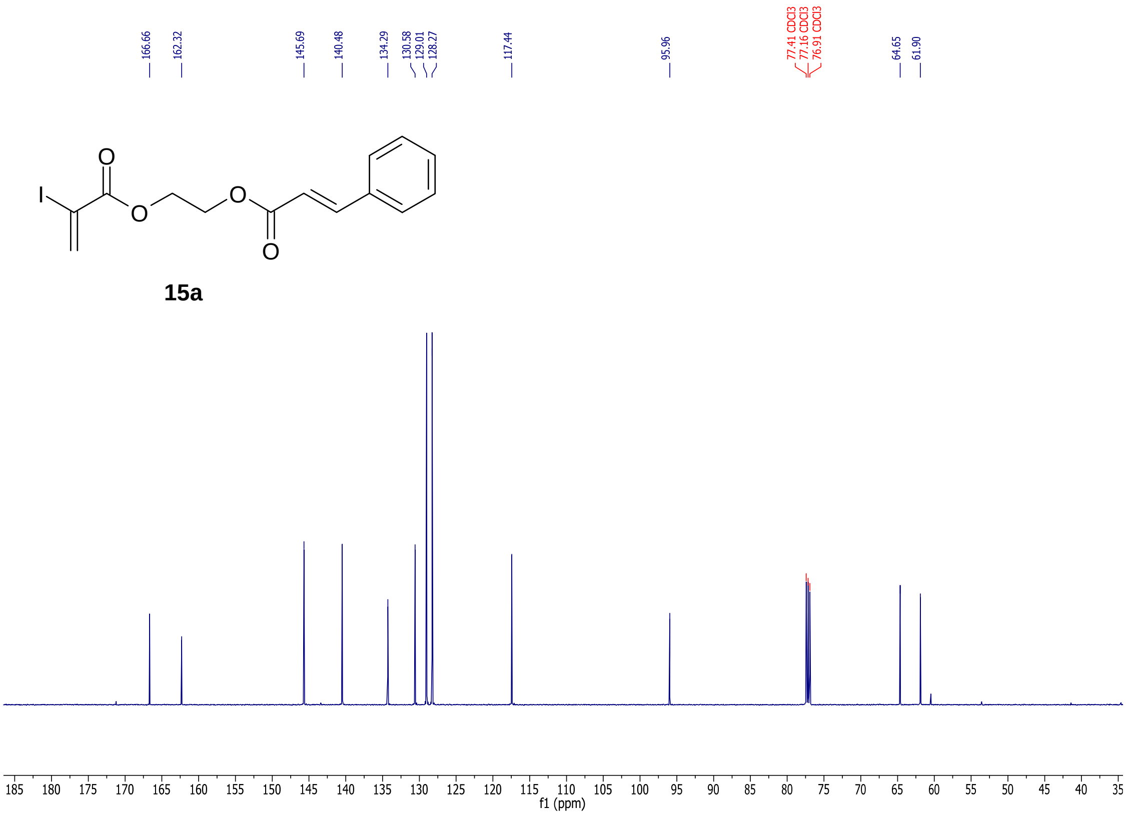
2.5
f1 (ppm)

15a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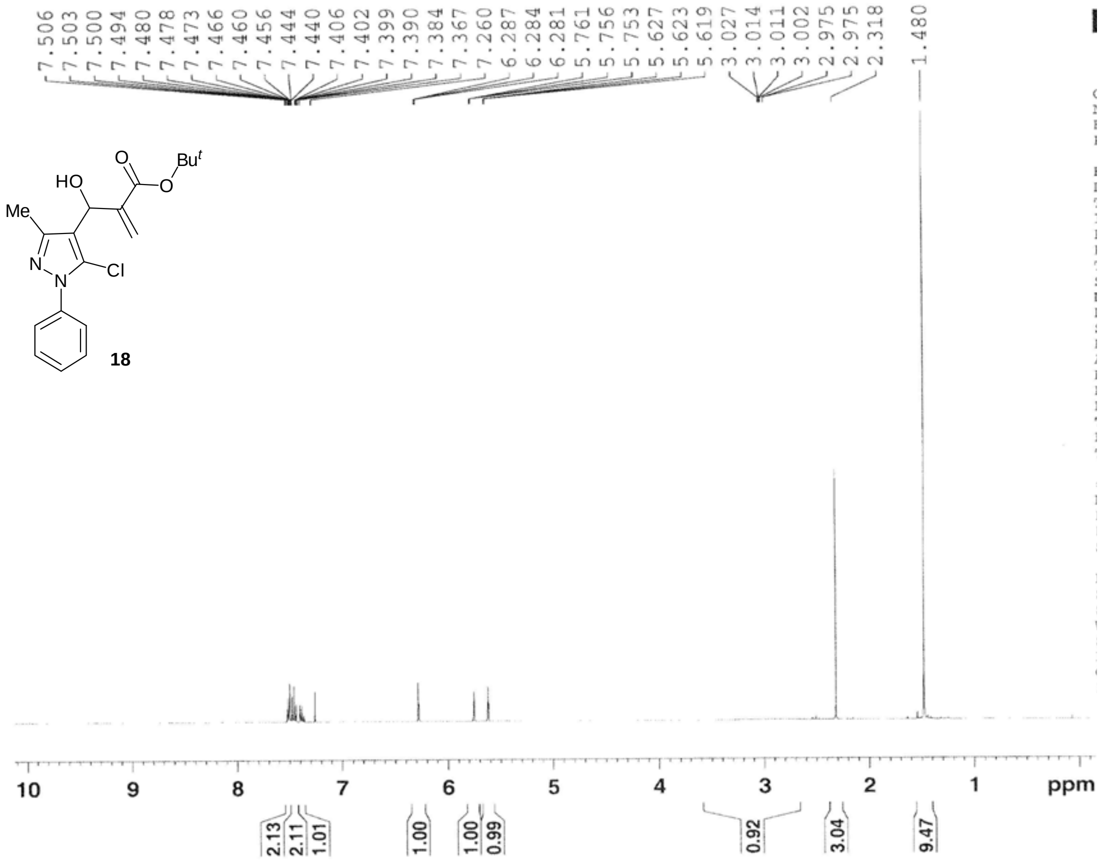
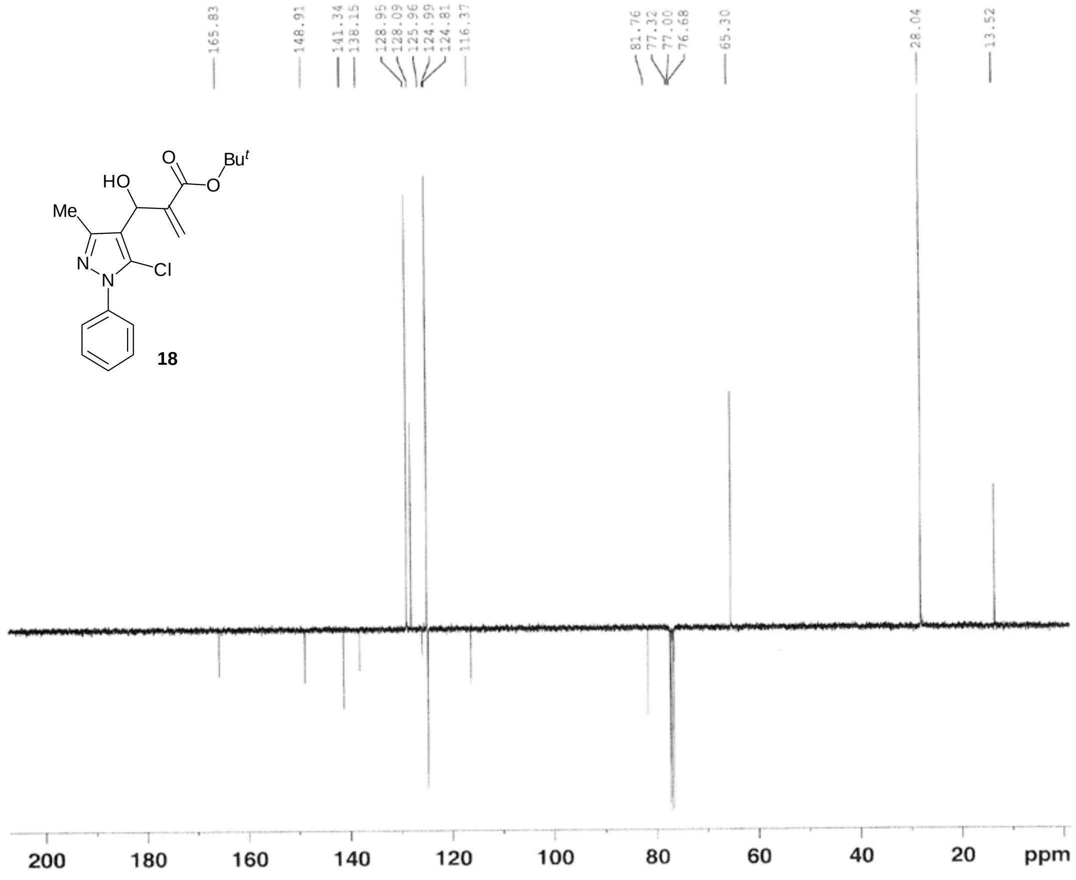
70
65
60
55
50
45
40
35
f1 (ppm)

15a


7.506
7.503
7.500
7.494
7.480
7.478
7.473
7.466
7.460
7.456
7.444
7.440
7.406
7.402
7.399
7.390
7.384
7.367
7.260
6.287
6.284
6.281
5.761
5.756
5.753
5.627
5.623
5.619
3.027
3.014
3.011
3.002
2.975
2.975
2.318
1.480
HO
O
Bu^t
O
Me
N
N
Cl
10
9
8
7
6
5
4
3
2
1
ppm
2.13
2.11
1.01
1.00
1.00
0.99
0.92
3.04
9.47

18


165.83
148.91
141.34
138.15
128.95
128.09
125.96
124.99
124.81
116.37
81.76
77.32
77.00
76.68
65.30
28.04
13.52
HO
O
Bu^t
O
Me
N
N
Cl
200
180
160
140
120
100
80
60
40
20
ppm

18

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