Supporting Information

for

Gold(I)-catalyzed synthesis of γ-vinyl butyrolactones by intramolecular oxaallylic alkylation with alcohols

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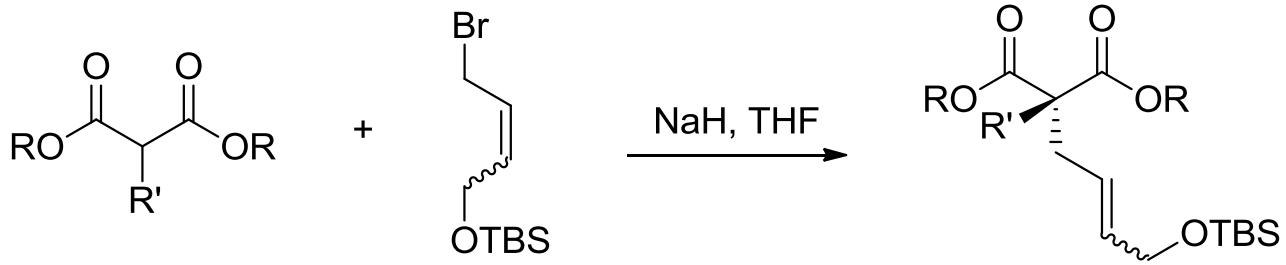
Experimental details and characterization of the synthesized compounds

General methods

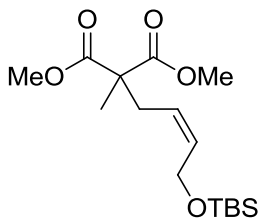
^{1}H NMR spectra were recorded on Varian 200 (200 MHz) and Varian 400 (400 MHz) spectrometers. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: δ 7.27 ppm). Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = duplet, , t = triplet, q = quartet, pq = pseudo quartet, pquint = pseuodo quintet, b = broad, m = multiplet), coupling constants (Hz). ^{13}C NMR spectra were recorded on Varian 200 (50 MHz) and Varian 400 (100 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: δ 77.0 ppm). GC–MS spectra were taken by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection. They are reported as: *m*/*z* (rel. intense). LC–electrospray ionization mass spectra were obtained with Agilent Technologies MSD1100 single-quadrupole mass spectrometer. Chromatographic purification was performed with 240–400 mesh silica gel. THF was distilled from sodium-benzophenone prior to use. Other anhydrous solvents were supplied by Fluka in Sureseal® bottles and used without any further purification. (*Z*)-allyl bromide **5a** was obtained from commercially available (*Z*)-1,4-but-2-en-ol following a known procedure [1]. The corresponding (*E*)-allyl bromide **5b** was obtained analogously starting from (*E*)-1,4-but-2-en-ol.

General procedures for the synthesis of OTBS-protected alcohols 1a–j′

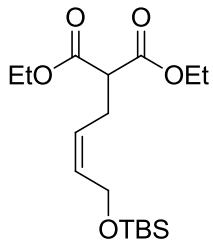


5a-b **1a-j'**

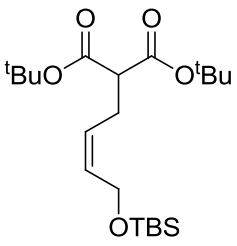
In an oven-dried Schlenk tube, under nitrogen atmosphere, 1.2 mmol (1.2 eq.) of malonate was dissolved in 10 ml of anhydrous THF and cooled to 0 °C. NaH (1.1 mmol, 1.1 eq., 60% dispersion in mineral oil) was added portionwise and the solution was stirred for 30 min at rt. The allyl bromide **5** (1 mmol, 1 eq.) was added at 0 °C and the reaction mixture was stirred overnight at rt. The reaction was quenched with water (10 mL) and extracted with ethyl acetate (3 × 10 ml). The combined organic layers were washed with brine (2 × 10 mL) and dried over Na_2SO_4. The solvent was evaporated at reduced pressure and the crude product was purified with flash chromatography on silica gel eluting with cyclohexane/ethyl acetate, to afford the pure product as a clear oil in variable yield.



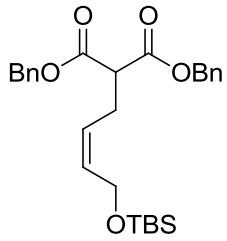
(*Z*)-Dimethyl 2-(4-(*tert*-butyldimethylsilyloxy)but-2-en-1-yl)-2-methyl-malonate (1a′): Flash chromatography (*c*-Hex:AcOEt = 90:10). Yield = 84%**.** ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.73–5.62 (m, 1H), 5.38–5.24 (m, 1H), 4.21 (d, *J* = 6.0 Hz, 2H), 3.73 (s, 6H), 2.63 (d, *J* = 7.6 Hz, 2H), 1.43 (s, 3H), 0.90 (s, 9H), 0.07 (s, 6H). GC–MS (*m*/*z*): 315 (2) $[M - CH_3]^+$, 299 (3), 241 (11), 213 (8), 203 (8), 181 (8), 165 (8), 139 (23), 127 (13), 107 (24), 89 (100), 79 (55), 59 (36).



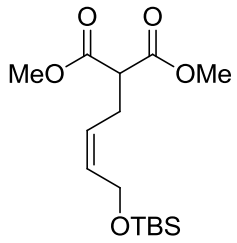
(*Z*)-Diethyl 2-(4-(*tert*-butyldimethylsilyloxy)but-2-en-1-yl)malonate (1b′): Flash chromatography (*c*-Hex:AcOEt = 90:10). Yield = 46%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.65–5.57 (m, 1H), 5.44–5.31 (m, 1H), 4.27–4.15 (m, 6H), 3.37 (t, *J* = 7.6 Hz, 1H), 2.65 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 6H), 0.90 (s, 9H), 0.08 (s, 6H). GC–MS (*m*/*z*): 329 (2) $[M - Me]^+$, 299 (10), 287 (100) $[M - t\text{-Bu}]^+$, 241 (37), 213 (12), 185 (22), 169 (24), 151 (17), 139 (40), 121 (40), 95 (43).



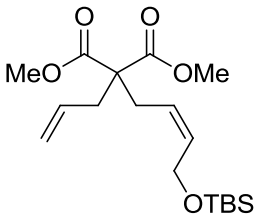
(*Z*)-Di-*tert*-butyl 2-(4-(*tert*-butyldimethylsilyloxy)but-2-en-1-yl)malonate (1c′): Flash chromatography (*c*-Hex:Et_2O = 90:10). Yield = 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.61–5.57 (m, 1H), 5.41–5.34 (m, 1H), 4.26 (d, *J* = 6.0 Hz, 2H), 3.16 (t, *J* = 7.2 Hz, 1H), 2.55 (t, *J* = 7.2 Hz, 2H), 1.46 (s, 18H), 0.90 (s, 9H), 0.07 (s, 6H). GC–MS (*m*/*z*): 287 (5), 271 (18), 231 (34), 213 (82), 185 (11), 169 (36), 139 (9), 75 (45), 57 (100).



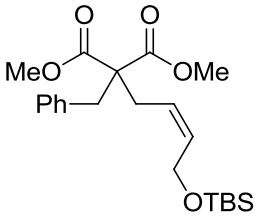
(*Z*)-Dibenzyl 2-(4-(*tert*-butyldimethylsilyloxy)but-2-en-1-yl)malonate (1d′): Flash chromatography (*c*-Hex:Et_2O = 95:5). Yield = 27%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.40–7.28 (m, 10 H), 5.71–5.59 (m, 1H), 5.47–5.34 (m, 1H), 5.18 (s, 4H), 4.25 (d, *J* = 5. Hz, 2H), 3.57 (t, *J* = 7.4 Hz, 1H), 2.73 (t, *J* = 7.4 Hz, 2H), 0.94 (s, 9H), 0.10 (s, 6H).



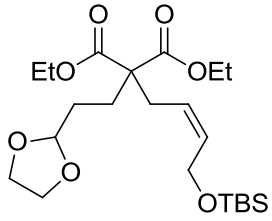
(*Z*)-Dimethyl 2-(4-(*tert*-butyldimethylsilyloxy)but-2-en-1-yl)malonate (1e′): Flash chromatography (*c*-Hex:AcOEt = 90:10). Yield = 40%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.65–5.62 (m, 1H), 5.38–5.35 (m, 1H), 4.25 (d, *J* = 6.4 Hz, 2H), 3.75 (s, H), 3.42 (t, *J* = 7.6 Hz, 1H), 2.66 (t, *J* = 7.6 Hz, 2H), 0.91 (s, 9H), 0.08 (s, 6H). ESI-MS (*m*/*z*): 339 $[M + Na]^+$.



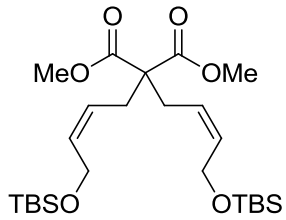
(***Z*)-Dimethyl 2-allyl-2-(4-(*tert*-butyldimethylsilyloxy)but-2-en-1-yl)-malonate (1f′):** Flash chromatography (*c*-Hex:AcOEt = 80:20). Yield = 87%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.75–5.58 (m, 2H), 5.33–5.20 (m, 1H), 5.14–5.07 (m, 2H), 4.20 (d, *J* = 6.0 Hz, 2H), 3.72 (s, 6H), 2.64 (d, *J* = 7.4 Hz, 4H), 0.90 (s, 9H), 0.07 (s, 6H). GC–MS (*m*/*z*): 341 (2) $[M - Me]^+$, 299 (100) $[M - t\text{-Bu}]^+$, 229 (11), 207 (18), 187 (23), 165 (18), 133 (23), 105 (76), 89 (86), 73 (50).



(*Z*)-Dimethyl 2-benzyl-2-(4-(*tert*-butyldimethylsilyloxy)but-2-en-1-yl)malonate (1g′): Flash chromatography (*c*-Hex:AcOEt = 80:20). Yield = 54%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.32–7.27 (m, 3H), 7.12–7.08 (m, 2H), 5.76–5.71 (m, 1H), 5.45–5.40 (m, 1H), 4.21 (d, *J* = 6.2 Hz, 2H), 3.76 (s, 6H), 3.29 (s, 2H), 2.58 (d, *J* = 7.4 Hz, 2H), 0.94 (s, 9H), 0.10 (s, 6H). GC–MS (*m*/*z*): 349 (59) $[M - t\text{-Bu}]^+$, 183 (18), 155 (27), 129 (14), 115 (14), 73 (27), 59 (18).



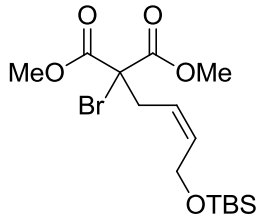
(*Z*)-Diethyl 2-(2-(1,3-dioxolan-2-yl)ethyl)-2-(4-(*tert*-butyldimethylsilyloxy)but-2-en-1-yl)malonate (1i′): Flash chromatography (*c*-Hex:AcOEt = 90:10). Yield = 57%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.70–5.58 (m, 1H), 5.36–5.22 (m, 1H), 4.86 (t, *J* = 4.4 Hz, 1H), 4.23–4.13 (m, 6H), 4.00–3.78 (m, 4H), 2.64 (d, *J* = 6.6 Hz, 2H), 2.04–1.96 (m, 2H), 1.63–1.54 (m, 2H), 1.25 (t, *J* = 7.0 Hz, 6H), 0.90 (s, 9H), 0.07 (s, 6H).



Dimethyl 2,2-bis((*Z*)-4-(*tert*-butyldimethylsilyloxy)but-2-en-1-yl)-malonate (1j′): Flash chromatography (*c*-Hex:Et_2O = 90:10). Yield = 95%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.69–5.60 (m, 2H), 5.31–5.24 (m, 2H), 4.20 (d, *J* = 5.6 Hz, 4H), 3.72 (s, 6H), 2.65 (d, *J* = 7.0 Hz, 4H), 0.90 (s, 18H), 0.06 (s, 12H). GC–MS (*m*/*z*): 485 (2) $[M - Me]^+$, 443 (100) $[M - t\text{-Bu}]^+$, 219 (5), 189 (18), 147 (18), 117 (27), 89 (64), 73 (73).

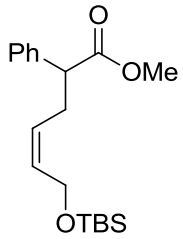
Synthesis of (*Z*)-dimethyl 2-bromo-2-(4-(*tert*-butyldimethylsilyloxy)but-2-en-1-yl) malonate (1h′) [2]: In an oven-dried Schlenk tube, under nitrogen atmosphere, 1.0 mmol (1.0 eq.) of methyl 2-bromomalonate and 1.2 mmol (1.2 eq.) of allyl bromide **5a** were dissolved in 3 mL of anhydrous DMF. K_2CO_3 (1.1 mmol, 1.1 eq.) was added and the reaction mixture was stirred overnight at rt. The solution was diluted with water (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were washed with brine (2 × 10 mL) and dried over Na_2SO_4.The solvent was evaporated at reduced pressure and the crude product was purified with flash chromatography

on silica gel eluting with cyclohexane/ethyl acetate 95:5, affording the pure product as a clear oil (Yield 73%).

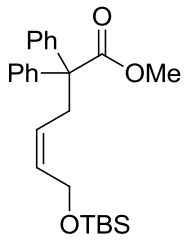


(*Z*)-Dimethyl 2-bromo-2-(4-(*tert*-butyldimethylsilyloxy)but-2-en-1-yl) malonate (1h′): ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.78–5.70 (m, 1H), 5.46–5.36 (m, 1H), 4.24 (d, *J* = 6.2 Hz, 2H), 3.83 (s, 6H), 3.09 (d, *J* = 7.2 Hz, 2H), 0.92 (s, 9H), 0.08 (s, 6H). GC–MS (*m*/*z*): 339 (45), 337 (41) [*M* – *t*-Bu]$^+$, 226 (50), 189 (18), 151 (25), 137 (23), 109 (23), 89 (100), 73 (59), 59 (64).

General procedures for the synthesis of OTBS-protected alcohols 3a–b′: In an oven-dried, three-necked round bottom flask, diisopropylamine (2.1 mmol, 1.05 eq.) was dissolved in 2 mL of anhydrous THF and cooled to 0 °C. BuLi (hexane solution 2.5 M, 2.1 mmol, 1.05 eq.) was added and the solution was stirred for 30 min at 0 °C. Then methyl 2-phenylacetate or methyl 2,2-diphenylacetate was dissolved in 1 mL of THF and added dropwise to the reaction mixture at −78 °C. The solution was stirred at this temperature for 30 min; then the bromide **5a** was added (2.2 mmol, 1.1 eq.) and the mixture was warmed to rt and stirred overnight. The reaction was quenched with saturated ammonium chloride (3 mL) and extracted with Et_2O. The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was evaporated at reduced pressure and the crude product was purified with flash chromatography on silica gel eluting with cyclohexane/ethyl acetate.

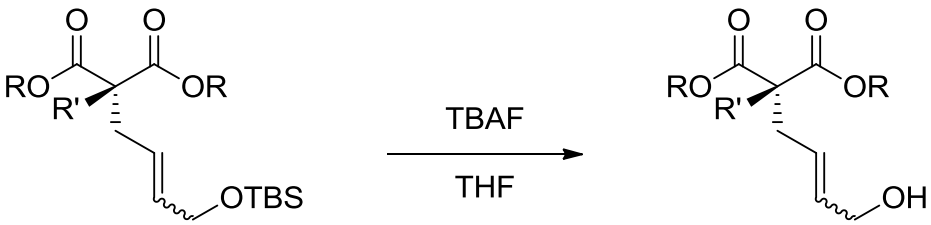


(*Z*)-Methyl 6-(*tert*-butyldimethylsilyloxy)-2-phenylhex-4-enoate (3a′): Flash chromatography (*c*-Hex:Et_2O = 95:5). Yield = 42%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.25 (m, 5H), 5.59–5.52 (m, 1H), 5.37–5.29 (m, 1H), 4.21–4.09 (m, 2H), 3.67 (s, 3H), 3.59 (t, *J* = 7.6 Hz, 1H), 2.82 (pquint, *J* = 7.6 Hz, 1H), 2.52 (pquint, *J* = 7.6 Hz, 1H), 0.90 (s, 9H), 0.06 (s, 6H).



(*Z*)-Methyl 6-(*tert*-butyldimethylsilyloxy)-2,2-diphenylhex-4-enoate (3b′): Flash chromatography (*c*-Hex:Et_2O = 90:10). Yield = 36%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.31–7.23 (m, 10H), 5.51–5.43 (m, 1H), 5.37–5.28 (m, 1H), 3.85 (d, *J* = 4.8 Hz, 2H), 3.70 (s, 3H), 3.13 (d, *J* = 7.0 Hz, 2H), 0.87 (s, 9H), 0.06 (s, 6H). GC–MS (*m*/*z*): 395 (2) [*M* – Me]$^+$, 353 (100) [*M* – *t*-Bu]$^+$, 247 (14), 19 (36), 197 (32), 165 (73), 141 (27), 105 (42), 89 (69), 73 (50), 57 (23).

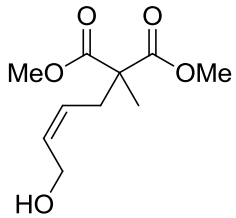
General procedure for the removal of TBS group



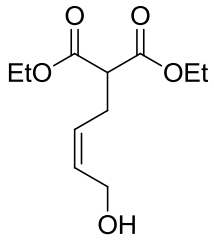
1a-j' **1a-j**

In a round bottom flask the *O*-TBS protected alcohol **1a–j′** (1 mmol, 1 eq.) was dissolved in 10 mL of THF. TBAF (1.2 mmol, 1.2 eq.) was added to the solution at 0 °C and the reaction mixture was stirred at rt until complete consumption of the starting material (TLC, 4–6 h). The solution was

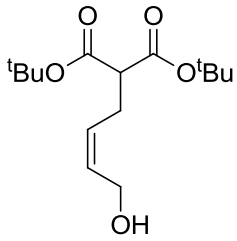
diluted with water (10 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine (2 × 10 mL) and dried over $NaSO_4$. The solvent was evaporated at reduced pressure and the crude product purified by flash chromatography on silica gel (eluent: cyclohexane/ethyl acetate), to afford the pure product as a clear oil.



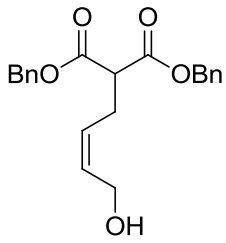
(*Z*)-Dimethyl-2-(4-hydroxybut-2-en-1-yl)-2-methylmalonate (1a): Flash chromatography (*c*-Hex:AcOEt = 70:30). Yield = 84%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82–5.76 (m, 1H), 5.51–5.44 (m, 1H), 4.20 (t, *J* = 6.0 Hz, 2H), 3.74 (s, 6H), 2.67 (d, *J* = 7.6 Hz, 2H), 1.59 (t, *J* = 6.0 Hz, 1H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3 (2C), 132.4, 126.0, 58.2, 53.7 (2C), 52.6 (2C), 33.5, 20.0. ESI–MS (*m*/*z*): 239 [*M* + Na]. Anal. calcd for ($C_{10}H_{16}O_5$: 216.10): C, 55.55; H, 7.46. Found: C, 55.50; H, 7.38.



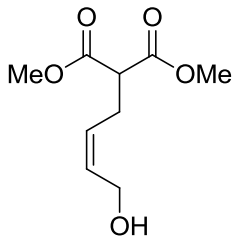
(*Z*)-Diethyl 2-(4-hydroxybut-2-en-1-yl)malonate (1b): Flash chromatography (*c*-Hex:AcOEt = 80:20). Yield = 66%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.83–5.71 (m, 1H), 5.55–5.32 (m, 1H), 4.21 (q, *J* = 7.2 Hz, 6H), 3.42 (t, *J* = 7.6 Hz, 1H), 2.71 (t, *J* = 7.6 Hz, 2H), 1.85 (bs, 1H), 1.28 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0 (2C), 131.6, 127.7, 61.6 (2C), 58.0, 51.6, 26.9, 14.0 (2C). GC–MS (*m*/*z*): 212 (2) [$M - H_2O$]$^+$, 161 (50), 139 (50), 125 (20), 111 (36), 87 (36), 67 (100), 53 (17). Anal. calcd for ($C_{11}H_{18}O_5$: 230.12): C, 57.38; H, 7.88. Found: C, 57.25; H, 7.80.



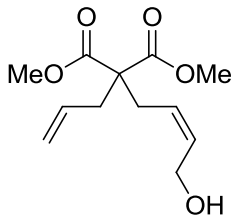
(*Z*)-Di-*tert*-butyl-2-(4-hydroxybut-2-en-1-yl)malonate (1c): Flash chromatography (*c*-Hex:AcOEt = 70:30). Yield = 52%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.78–5.72 (m, 1H), 5.51–5.45 (m, 1H), 4.09 (bd, *J* = 5.2 Hz, 2H), 3.22 (t, *J* = 7.2 Hz, 1H), 2.61 (t, *J* = 7.2 Hz, 2H), 1.41 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5 (2C), 131.1, 128.4, 81.9 (2C), 58.1, 53.4, 27.9, 26.6 (6C). ESI-MS: 309 [*M* + Na]$^+$. Anal. calcd for ($C_{15}H_{26}O_5$: 286.18): C, 62.91; H, 9.15. Found: C, 62.85; H, 9.12.



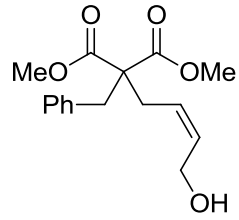
(*Z*)-Dibenzyl-2-(4-hydroxybut-2-en-1-yl)malonate (1d): Flash chromatography (*c*-Hex:AcOEt = 70:30). Yield = 22%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.26 (m, 10H), 5.75–5.69 (m, 1H), 5.49–5.42 (m, 1H), 5.15 (s, 4H), 4.15 (d, *J* = 6.8 Hz, 2H), 3.54 (t, *J* = 7.6 Hz, 1H), 2.74 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7 (2C), 135.1 (2C), 131.9, 128.6 (4C), 128.4 (4C), 128.2 (2C), 127.4, 67.3 (2C), 58.1, 51.7, 26.7. Anal. calcd for ($C_{21}H_{22}O_5$: 354.15): C, 71.17; H, 6.26. Found: C, 71.15; H, 6.18.



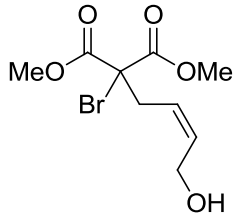
(*Z*)-Dimethyl-2-(4-hydroxybut-2-en-1-yl)malonate (1e): Flash chromatography (*c*-Hex:AcOEt = 80:20). Yield = 38%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.80–5.74 (m, 1H), 5.50–5.44 (m, 1H), 4.20 (d, *J* = 7.2 Hz, 2H), 3.75 (s, 6H), 3.47 (t, *J* = 7.6 Hz, 1H), 2.72 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3 (2C), 131.8, 127.2, 57.9, 52.9 (2C), 51.3. GC–MS (*m*/*z*): 184 (5) [$M - H_2O$]$^+$, 171 (1), 152 (9),145 (9), 133 (100), 125 (50), 109 (36), 101 (64), 93 (32), 81 (32), 69 (64), 59 (51), 53 (32). Anal. calcd for ($C_9H_{14}O_5$: 202.08): C, 53.46; H, 6.98. Found: C, 53.39; H, 6.91.



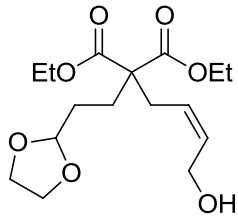
(*Z*)-Dimethyl-2-allyl-2-(4-hydroxybut-2-en-1-yl)malonate (1f): Flash chromatography (*c*-Hex:AcOEt = 70:30). Yield = 74%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.80–5.74 (m, 1H), 5.71–5.60 (m, 1H), 5.45–5.35 (m, 1H), 5.12 (d, *J* = 15.6 Hz, 1H), 5.12 (d, *J* = 115.6 Hz, 1H), 4.17 (d, *J* = 6.8 Hz, 2H), 3.73 (s, 6H), 2.67 (t, *J* = 7.2 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3 (2C), 132.4, 131.2, 125.6, 119.4, 58.3 (2C), 57.7, 52.5, 37.3, 30.6. GC–MS (*m*/*z*): 225 (3), 201 (3), 192 (3), 172 (27), 164 (32), 151 (45), 137 (41), 123 (18), 108 (100), 91 (41), 79 (54), 67 (27), 59 (56). Anal. calcd for ($C_{12}H_{18}O_5$: 242.12): C, 59.49; H, 7.49. Found: C, 59.41; H, 7.41.



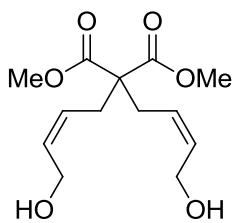
(*Z*)-Dimethyl 2-benzyl-2-(4-hydroxybut-2-en-1-yl)malonate (1g): Flash chromatography (*c*-Hex:AcOEt = 70:30). Yield = 56%.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.24 (m, 3H), 7.07 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 2H), 5.82–5.75 (m, 1H), 5.57–5.49 (m, 1H), 5.12 (t, *J* = 6.0 Hz, 2H), 3.74 (s, 6H), 3.28 (s, 2H), 2.58 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3 (2C), 135.6, 132.3, 129.8 (2C), 128.4 (2C), 127.1, 125.7, 59.0, 58.3 (2C), 52.5, 38.7, 30.3. GC–MS (*m*/*z*): 221 (9), 214 (14), 189 (18), 169 (9), 155 (27), 130 (23), 115 (18), 65 (23). Anal. calcd for ($C_{16}H_{20}O_5$: 292.13): C, 65.74; H, 6.90. Found: C, 64.71; H, 6.85.



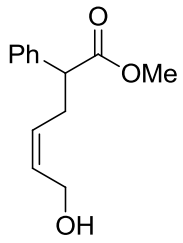
(*Z*)-Dimethyl-2-bromo-2-(4-hydroxybut-2-en-1-yl)malonate (1h): Flash chromatography (*c*-Hex:AcOEt = 70:30). Yield = 13%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.93–5.80 (m, 1H), 5.61–5.48 (m, 1H), 4.20 (d, *J* = 6.6 Hz, 2H), 3.83 (s, 6H), 3.11 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1 (2C), 133.7, 124.6, 60.9, 58.5, 54.0 (2C), 36.3. GC–MS (*m*/*z*): 212 (27), 210 (27), 180 (32), 169 (50), 151 (35), 137 (68), 109 (82), 81 (59), 59 (100). Anal. calcd for ($C_9H_{12}BrO_5$: 279.99): C, 38.45; H, 4.66. Found: C, 38.41; H, 4.61.



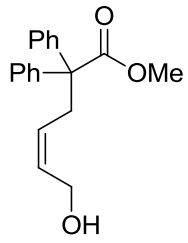
(*Z*)-Diethyl-2-(2-(1,3-dioxolan-2-yl)ethyl)-2-(4-hydroxybut-2-en-1-yl)-malonate (1i): Flash chromatography (*c*-Hex:AcOEt = 50:50). Yield = 90%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.81–5.77 (m, 1H), 5.39–5.33 (m, 1H), 4.88 (t, *J* = 4.4 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 4H), 4.15 (d, *J* = 6.4 Hz, 2H), 3.98–3.96 (m, 2H), 3.87–3.84 (m, 2H), 2.70 (d, *J* = 8.0 Hz, 2H), 2.09 (bt, *J* = 6.4 Hz, 1H), 2.03–1.99 (m, 2H), 1.62–1.57 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0 (2C), 132.7, 125.2, 103.7, 64.9 (2C), 61.3 (2C), 57.7, 56.7, 29.9, 28.3, 25.9, 14.0 (2C). GC–MS (*m*/*z*): 258 (5), 229 (5), 183 (9), 166 (5), 137 (9), 99 (20), 73 (100), 57 (9). Anal. calcd for ($C_{16}H_{26}O_7$: 330.13): C, 58.17; H, 7.93. Found: C, 58.10; H, 7.85.



Dimethyl-2,2-bis((*Z*)-4-hydroxybut-2-en-1-yl)malonate (1j): Flash chromatography (*c*-Hex:AcOEt = 80:20). Yield = 83%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.75–5.69 (m, 2H), 5.28–5.21 (m, 2H), 4.14 (d, *J* = 6.4 Hz, 4H), 3.74 (s, 6H), 3.08 (bs, 2H), 2.65 (d, *J* = 7.2 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2 (2C), 132.9 (2C), 124.7 (2C), 58.0 (2C), 57.0, 52.7 (2C), 30.3 (2C). ESI-MS (*m*/*z*): 295 $[M + Na]^+$. Anal. calcd for ($C_{13}H_{20}O_6$: 272.13): C, 57.34; H, 7.40. Found: C, 57.21; H, 7.21.



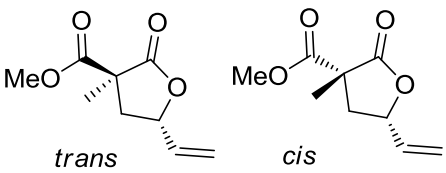
(*Z*)-Methyl 6-hydroxy-2-phenylhex-4-enoate (3a): Flash chromatography (*c*-Hex:AcOEt = 70:30). Yield = 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.28 (m, 5H), 5.73–5.66 (m, 1H), 5.51–5.45 (m, 1H), 4.20 (dd, *J* = 12.4 Hz, *J* = 6.8 Hz, 1H), 4.02 (dd, *J* = 12.4 Hz, *J* = 6.8 Hz, 1H), 3.67 (s, 3H), 3.67 (dd, *J* = 8.4 Hz, *J* = 6.8 Hz, 1H), 2.94 (dt, *J* = 14.0 Hz, *J* = 8.4 Hz, 1H), 2.48 (dt, *J* = 14.0 Hz, *J* = 6.8 Hz, 1H), 1.48 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.1, 138.4, 130.9, 129.0, 128.7 (2C), 127.9 (2C), 127.5, 58.2, 52.2, 51.4, 31.7. GC–MS (*m*/*z*): 202 (5) [M – H_2O]$^+$, 188 (5), 151 (50), 143 (100), 121 (82), 91 (64), 77 (27), 65 (14), 51 (14). Anal. calcd for ($C_{13}H_{16}O_3$: 220.11): C, 70.89; H, 7.32. Found: C, 70.78; H, 7.25.



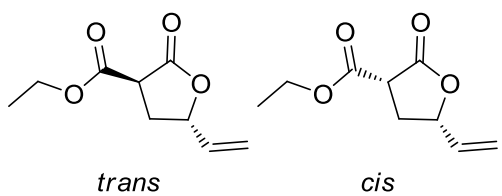
(*Z*)-Methyl 6-hydroxy-2,2-diphenylhex-4-enoate (3b): Flash chromatography (*c*-Hex:AcOEt = 70:30). Yield = 46%.^{1}H NMR (200 MHz, $CDCl_3$): δ 7.39–7.28 (m, 10H), 5.63–5.42 (m, 2H), 3.85 (d, *J* = 6.6 Hz, 2H), 3.73 (s, 3H), 3.19 (d, *J* = 7.4 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 174.4, 142.3 (2C), 131.5, 129.0 (4C), 127.8 (4C), 127.7 (2C), 127.0, 60.6, 58.2, 52.5, 36.2. ESI-MS (*m*/*z*): 279 [*M* – OH]$^+$, 335 [*M* + K]$^+$. Anal. calcd for ($C_{19}H_{20}O_3$: 296.14): C, 77.00; H, 6.80. Found: C, 76.95; H, 6.79.

General procedure for the gold(I)-catalyzed synthesis of vinyl lactones 2a–j or 4a,b

In a screw-capped vial, under air atmosphere, (NHC)AuCl (0.05 eq.), and AgOTf (0.05 eq) were dissolved in 300 µL of reagent-grade dichloroethane (DCE) and the solution was stirred for 30 min at rt in the dark. Then, 20 mg (1 eq.) of allylic alcohol **1a–j** or **3a,b** was added and the reaction mixture stirred at 80 °C until complete consumption of the starting material (TLC, 7–9 h). The crude product was purified with flash chromatography on a short pad of silica gel eluting with diethyl ether or cyclohexane/ethyl acetate mixture, to afford the analytical pure product as an oil.

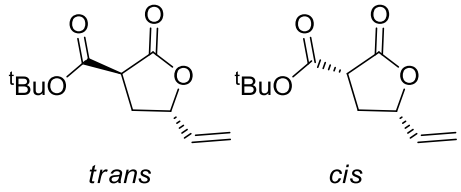


Methyl 3-methyl-2-oxo-5-vinyltetrahydrofuran-3-carboxylate (2a): Flash chromatography (*c*-Hex:AcOEt = 90:10). Yield =94%, dr (*trans*:*cis*) = 2.1:1 (Table 1, entry 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ (*trans*): 5.89–5.82 (m, 1H), 5.43 (dd, *J* = 17.2 Hz, *J* = 1.2 Hz, 1H), 5.31 (dd, *J* = 10.8 Hz, *J* = 1.2 Hz, 1H), 5.00 (m, 1H), 3.80 (s, 3H), 2.87 (dd, *J* = 12.8 Hz, *J* = 6.4 Hz, 1H), 1.92 (dd, *J* = 12.8 Hz, *J* = 10.0 Hz, 1H), 1.55 (s, 3H). δ (*cis*): 5.89–5.82 (m, 1H), 5.41 (d, *J* = 16.4 Hz, 1H), 5.30 (d, *J* = 10.8 Hz, 1H), 4.94 (pq, *J* = 7.2 Hz, 1H), 3.78 (s, 3H), 2.65 (dd, *J* = 12.8 Hz, *J* = 8.0 Hz, 1H), 2.32 (dd, *J* = 12.8 Hz, *J* = 7.2 Hz, 1H), 1.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (*trans*): 174.8, 170.8, 135.0, 118.7, 78.4, 53.2, 51.5, 41.4, 20.9. δ (*cis*): 175.1, 171.0, 135.0, 118.5, 78.1, 53.1, 50.8, 40.3, 20.1. GC–MS (*m*/*z*): 169 (2) [*M* – Me]$^+$, 156 (9), 125 (71), 97 (14), 81 (100), 69 (50).

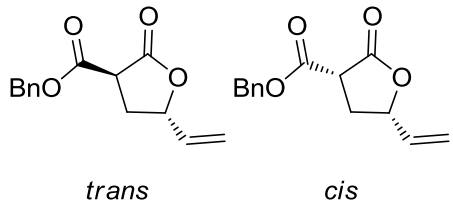


Ethyl 2-oxo-5-vinyltetrahydrofuran-3-carboxylate (2b): Flash chromatography (Et_2O). Yield = 95%, dr (*trans*:*cis*) = 1:1 (Table 2, entry 2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.97–5.84 (m, 1H$_{cis}$, 1H$_{trans}$), 5.43 (d, *J* = 17.2 Hz, 1H$_{trans}$), 5.41 (d, *J* = 16.8 Hz, 1H$_{cis}$), 5.33 (d, *J* = 10.4 Hz, 1H$_{trans}$), 5.31 (d, *J* = 10.8 Hz, 1H$_{cis}$), 5.13 (pq, *J* = 6.4 Hz, 1H$_{trans}$), 4.88 (pq, *J* = 8.0 Hz, 1H$_{cis}$), 4.27 (q, *J* = 7.2 Hz, 2H$_{cis}$, 2H$_{trans}$), 3.66–3.58 (m, 1H$_{cis}$, 1H$_{trans}$), 2.80 (ddd, *J* = 12.8 Hz, *J* = 6.4 Hz, *J* = 6.4 Hz, 1H$_{trans}$), 2.68–2.61 (m, 1H$_{cis}$), 2.52–2.44 (m,

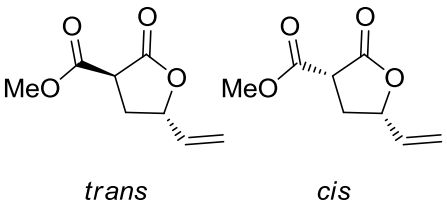
1H$_{cis}$), 2.25 (ddd, *J* = 12.8 Hz, *J* = 9.2 Hz, *J* = 6.4 Hz, 1H$_{trans}$), 1.33 (t, *J* = 7.2 Hz, 3H$_{cis}$, 3H$_{trans}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (*trans*): 171.4, 167.5, 134.9, 119.0, 79.5, 62.3, 47.1, 32.4, 14.0. δ (*cis*): 171.6, 167.6, 134.8, 118.1, 79.4, 62.3, 44.3, 32.2, 14.0. GC–MS (*m*/*z*): 184 (2) $[M]^+$, 156 (14), 138 (23), 111 (50), 97 (23), 73 (14), 63 (91), 55 (100).



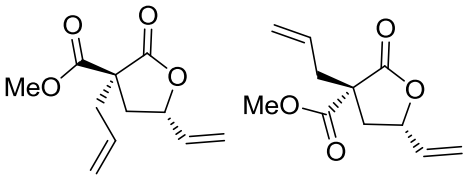
***tert*-Butyl 2-oxo-5-vinyltetrahydrofuran-3-carboxylate (2c):** Flash chromatography (Et_2O). Yield = 66%. dr (*trans*:*cis*) = 1.1:1 (Table 2, entry 3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.98–5.83 (m, 1H$_{cis}$, 1H$_{trans}$), 5.42 (d, *J* = 16.8 Hz, 1H$_{trans}$), 5.40 (d, *J* = 17.6 Hz, 1H$_{cis}$), 5.31 (d, *J* = 10.0 Hz, 1H$_{trans}$), 5.29 (d, *J* = 10.4 Hz, 1H$_{cis}$), 5.10 (pq, *J* = 6.8 Hz, 1H$_{trans}$), 4.88–4.83 (m, 1H$_{cis}$), 3.53 (dd, *J* = 10.4 Hz, *J* = 9.2 Hz, 1H$_{cis}$), 3.50 (dd, *J* = 9.2 Hz, *J* = 6.0 Hz, 1H$_{trans}$), 2.74 (ddd, *J* = 13.2 Hz, *J* = 7.2 Hz, *J* = 6.0 Hz, 1H$_{trans}$), 2.61 (ddd, *J* = 13.2 Hz, *J* = 9.2 Hz, *J* = 6.4 Hz, 1H$_{cis}$), 2.41 (ddd, *J* = 13.2 Hz, *J* = 10.4 Hz, *J* = 9.2 Hz, 1H$_{cis}$), 2.21 (ddd, *J* = 13.2 Hz, *J* = 9.2 Hz, *J* = 6.8 Hz, 1H$_{trans}$), 1.44 (s, 9H$_{cis}$, 9H$_{trans}$). ^{13}C NMR (400 MHz, $CDCl_3$): δ (*trans*): 171.8, 166.8, 135.1, 118.8, 82.9, 79.5, 48.0, 29.7, 27.9. δ (*cis*): 171.9, 166.6, 135.0, 118.0, 83.1, 79.3, 47.4, 29.7, 27.9. GC–MS (*m*/*z*): 157 (9), 139 (18), 121 (9), 95 (7), 64 (32), 57 (100).



Benzyl 2-oxo-5-vinyltetrahydrofuran-3-carboxylate (2d): Flash chromatography (*c*-Hex:AcOEt = 90:10). Yield = 67%, dr (*trans*:*cis*) = 1.4:1 (Table 2, entry 4). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.35 (m, 5H$_{cis}$, 5H$_{trans}$), 5.96–5.82 (m, 1H$_{cis}$, 1H$_{trans}$), 5.41(d, *J* = 17.2 Hz, 1H$_{trans}$), 5.40 (d, *J* = 17.2 Hz, 1H$_{cis}$), 5.31 (d, *J* = 10.4 Hz, 1H$_{trans}$), 5.30 (d, *J* = 10.4 Hz, 1H$_{cis}$), 5.25 (s, 2H$_{trans}$), 5.24 (s, 2H$_{cis}$), 5.12 (pq, *J* = 6.4 Hz, 1H$_{trans}$), 4.91–4.8 (m, 1H$_{cis}$), 3.77–3.64 (m, 1H$_{cis}$, 1H$_{trans}$), 2.83–2.77 (m, 1H$_{trans}$), 2.68–2.61 (m, 1H$_{cis}$), 2.33–2.44 (m, 1H$_{cis}$), 2.30–2.22 (m, 1H$_{trans}$). GC–MS (*m*/*z*): 178 (1), 140 (23), 122 (14), 107 (43), 91 (100), 77 (14), 65 (32), 54 (36).

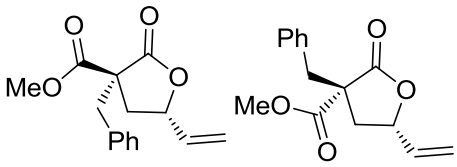


Methyl 2-oxo-5-vinyltetrahydrofuran-3-carboxylate (2e): Flash chromatography (*c*-Hex:AcOEt = 90:10). Yield = 85%. dr (*trans*:*cis*) = 1:1 (Table 2, entry 5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.98–5.83 (m, 1H$_{cis}$, 1H$_{trans}$), 5.43 (d, *J* = 17.2 Hz, 1H$_{trans}$), 5.41 (d, *J* = 17.2 Hz, 1H$_{cis}$), 5.34 (d, *J* = 10.4 Hz, 1H$_{trans}$), 5.31 (d, *J* = 10.8 Hz, 1H$_{cis}$), 5.13 (q, *J* = 6.8 Hz, 1H$_{trans}$), 4.92–4.86 (m, 1H$_{cis}$), 3.83 (s, 3H$_{trans}$), 3.82 (s, 3H$_{cis}$), 3.67 (dd, *J* = 10.8 Hz, *J* = 9.2 Hz, 1H$_{cis}$), 3.63 (dd, *J* = 9.2 Hz, *J* = 6.0 Hz, 1H$_{trans}$), 2.81 (ddd, *J* = 13.2 Hz, *J* = 6.8 Hz, *J* = 6.0 Hz, 1H$_{trans}$), 2.65 (ddd, *J* = 13.2 Hz, *J* = 9.2 Hz, *J* = 6.4 Hz, 1H$_{cis}$), 2.49 (ddd, *J* = 13.2 Hz, *J* = 10.8 Hz, *J* = 6.4 Hz, 1H$_{cis}$), 2.26 (ddd, *J* = 13.2 Hz, *J* = 9.2 Hz, *J* = 6.8 Hz, 1H$_{trans}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (*trans*): 171.2, 167.9, 134.7, 119.1, 79.6, 53.2, 47.0, 32.4. δ (*cis*): 171.4, 168.0, 134.8, 118.2, 79.5, 53.1, 46.1, 32.2. ESI-MS (*m*/*z*): 193 $[M + Na]^+$, 188 $[M + H_2O]^+$, 171 $[M + H]^+$.



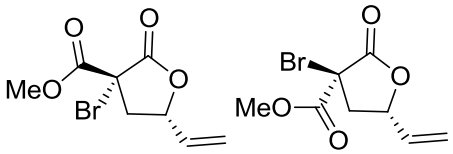
trans *cis*

Methyl 3-allyl-2-oxo-5-vinyltetrahydrofuran-3-carboxylate (2f): Flash chromatography (*c*-Hex:AcOEt = 90:10). Yield = 94%. dr (*trans*:*cis*) = 1.5:1 (Table 2, entry 6). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.95–5.81 (m, 1H$_{cis}$, 1H$_{trans}$), 5.79–5.64 (m, 1H$_{cis}$, 1H$_{trans}$), 5.42 (d, *J* = 17.2 Hz, 1H$_{trans}$), 5.38 (d, *J* = 16.8 Hz, 1H$_{cis}$), 5.31 (d, *J* = 10.4 Hz, 1H$_{trans}$), 5.28 (d, *J* = 10.4 Hz, 1H$_{cis}$), 5.25–5.16 (m, 2H$_{cis}$, 2H$_{trans}$), 5.01–4.95 (m, 1H$_{trans}$), 4.89 (q, *J* = 7.2 Hz, 1H$_{cis}$), 3.81 (s, 3H$_{trans}$), 3.79 (s, 3H$_{cis}$), 2.84–2.74 (m, 3H$_{trans}$), 2.68–2.58 (m, 3H$_{cis}$), 2.48 (dd, *J* = 13.6 Hz, *J* = 7.2 Hz, 1H$_{cis}$), 2.01 (dd, *J* = 13.6 Hz, *J* = 10.0 Hz, 1H$_{trans}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (*trans*): 173.9, 169.7, 135.1, 131.8, 120.3, 118.8, 78.9, 55.6, 53.3, 38.4, 37.4. δ (*cis*): 174.0, 170.1, 135.4, 131.5, 120.7, 118.2, 78.1, 54.7, 53.2, 38.4, 36.5. GC–MS (*m*/*z*): 178 (5), 160 (32), 133 (32), 105 (50), 79 (100), 54 (77).



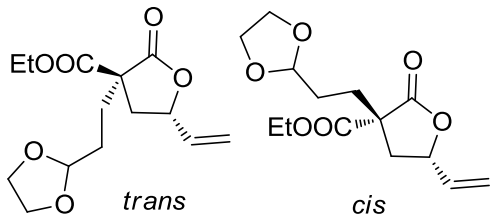
trans *cis*

Methyl 3-benzyl-2-oxo-5-vinyltetrahydrofuran-3-carboxylate (2g): Flash chromatography (*c*-Hex:AcOEt = 80:20). Yield = 63%. dr (*trans*:*cis*) = 1:1.4 (Table 2, entry 7). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.23 (m, 3H$_{cis}$, 3H$_{trans}$), 7.17 (d, *J* = 6.8 Hz, 2H$_{cis}$), 7.06 (d, *J* = 6.8 Hz, 2H$_{trans}$), 5.78 (ddd, *J* = 17.2 Hz, *J* = 10.4 Hz, *J* = 6.4 Hz, 1H$_{trans}$), 5.55 (ddd, *J* = 17.2 Hz, *J* = 10.4 Hz, *J* = 6.8 Hz, 1H$_{cis}$), 5.30 (d, *J* = 17.2 Hz, 1H$_{trans}$), 5.29 (d, *J* = 10.4 Hz, 1H$_{trans}$), 5.20 (d, *J* = 17.2 Hz, 1H$_{cis}$), 5.19 (d, *J* = 10.4 Hz, 1H$_{cis}$), 4.93–4.87 (m, 1H$_{trans}$), 4.04 (pq, *J* = 7.6 Hz, 1H$_{cis}$), 3.82 (s, 3H$_{cis}$), 3.81 (s, 3H$_{trans}$), 3.42–3.18 (m, 2H$_{cis}$, 2H$_{trans}$), 2.72 (dd, *J* = 13.2 Hz, *J* = 6.4 Hz, 1H$_{trans}$), 2.55 (dd, *J* = 13.6 Hz, *J* = 7.6 Hz, 1H$_{cis}$), 2.47 (dd, *J* = 13.6 Hz, *J* = 7.6 Hz, 1H$_{cis}$), 1.97 (dd, *J* = 13.2 Hz, *J* = 10.0 Hz, 1H$_{trans}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (*trans*): 173.6, 169.6 135.0, 130.0, 128.8, 128.7, 127.7, 118.0, 79.0, 56.4, 52.5, 39.7, 36.3. δ (*cis*): 174.5, 170.5, 134.9, 130.0, 128.8, 128.7, 127.4, 118.8, 78.1, 57.3, 53.3, 39.5, 37.0. ESI-MS (*m*/*z*): 261 [*M* + H]$^+$, 283 [*M* + Na]$^+$, 299 [*M* + K]$^+$.



cis *trans*

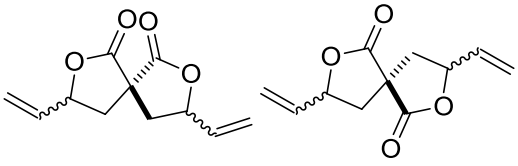
Methyl 3-bromo-2-oxo-5-vinyltetrahydrofuran-3-carboxylate (2h): Flash chromatography (*c*-Hex:AcOEt = 90:10). Yield = 54 %. dr (*cis*:*trans*) = 1:3.2 (Table 2, entry 8). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.01–5.89 (m, 1H$_{cis}$, 1H$_{trans}$), 5.52 (d, *J* = 17.2 Hz, 1H$_{cis}$), 5.47 (d, *J* = 17.6 Hz, 1H$_{trans}$), 5.41 (d, *J* = 10.4 Hz, 1H$_{cis}$), 5.39 (d, *J* = 10.4 Hz, 1H$_{trans}$), 5.14–5.08 (m, 1H$_{cis}$), 4.99 (pq, *J* = 6.8 Hz, 1H$_{trans}$), 3.92 (s, 3H$_{cis}$), 3.91 (s, 3H$_{trans}$), 3.43 (dd, *J* = 14.0 Hz, *J* = 6.4 Hz, 1H$_{trans}$), 2.91 (dd, *J* = 14.4 Hz, *J* = 9.6 Hz, 1H$_{cis}$), 2.79 (dd, *J* = 14.4 Hz, *J* = 5.2 Hz, 1H$_{cis}$), 2.62 (dd, *J* = 14.0 Hz, *J* = 8.0 Hz, 1H$_{trans}$). ^{13}C NMR (50 MHz, $CDCl_3$): δ (*trans*): 168.8, 165.4, 158.1,133.7, 120.1, 79.1, 54.7, 44.1, 29.7. δ (*cis*): 168.8, 165.4, 132.9, 120.4, 79.0, 54.6, 44.3, 29.7. GC–MS (*m*/*z*): 191 (27), 189 (18) [*M* – COOMe]$^+$,137 (45), 93 (100), 79 (28), 65 (86).



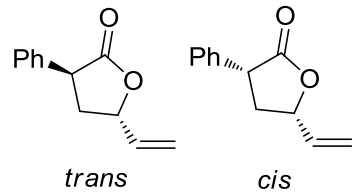
trans *cis*

Ethyl 3-(2-(1,3-dioxolan-2-yl)ethyl)-2-oxo-5-vinyltetrahydrofuran-3-carboxylate (2i): Flash chromatography (*c*-Hex:AcOEt = 80:20). Yield = 45 %. dr (*trans*:*cis*) = 1.4:1 (Table 2, entry 9). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.91 (ddd, *J* = 16.8 Hz, *J* = 10.4 Hz, *J* = 6.4 Hz, 1H$_{cis}$), 5.86 (ddd, *J* = 17.2 Hz, *J* = 10.4 Hz, *J* = 6.8 Hz, 1H$_{trans}$), 5.42 (d, *J* = 17.2 Hz, 1H$_{trans}$), 5.34 (d, *J* = 16.8 Hz,

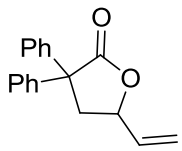
1H$_{cis}$), 5.31 (d, *J* = 10.4 Hz, 1H$_{trans}$), 5.28 (d, *J* = 10.4 Hz, 1H$_{cis}$), 4.99–4.89 (m, 2H$_{cis}$, 2H$_{trans}$), 4.27–4.21 (m, 2H$_{cis}$, 2H$_{trans}$), 3.97–4.96 (m, 2H$_{cis}$, 2H$_{trans}$), 3.89–3.84 (m, 2H$_{cis}$, 2H$_{trans}$), 2.85 (dd, *J* = 12.8 Hz, *J* = 6.4 Hz, 1H$_{trans}$), 2.64 (dd, *J* = 13.2 Hz, *J* = 6.8 Hz, 1H$_{cis}$), 2.42 (dd, *J* = 13.2 Hz, *J* = 7.2 Hz, 1H$_{cis}$), 2.27 (ddd, *J* = 13.6 Hz, *J* = 12.4 Hz, *J* = 4.4 Hz, 1H$_{trans}$), 2.16 (ddd, *J* = 13.6 Hz, *J* = 12.4 Hz, *J* = 4.8 Hz, 1H$_{cis}$), 2.05–1.77 (m, 3H$_{cis}$, 3H$_{trans}$), 1.93 (dd, *J* = 12.8 Hz, *J* = 10.0 Hz, 1H$_{trans}$), 1.32 (t, *J* = 7.2 Hz, 3H$_{trans}$), 1.29 (t, *J* = 7.2 Hz, 3H$_{cis}$). GC–MS (*m*/*z*): 256 (5), 183 (5), 99 (11), 73 (100), 55 (9).



3,8-Divinyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (2j): Flash chromatography (*c*-Hex:AcOEt = 80:20). Yield = 93%. dr: 1.1:1 (two diastereoisomers detected, Table 2, entry 10). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.05 (ddd, *J* = 17.6 Hz, *J* = 10.4 Hz, *J* = 7.2 Hz, 2H$_{major}$), 5.88 (ddd, *J* = 17.2 Hz, *J* = 10.8 Hz, *J* = 6.8 Hz, 2H$_{minor}$), 5.47 (d, *J* = 16.8, 2H$_{minor}$), 5.44 (d, *J* = 16.8, 2H$_{major}$), 5.38–5.28 (m, 2H$_{major}$, 4H$_{minor}$), 4.97 (pq, *J* = 7.2 Hz, 2H$_{major}$), 2.88 (dd, *J* = 12.8 Hz, *J* = 6.0 Hz, 2H$_{minor}$), 2.77 (dd, *J* = 13.6 Hz, *J* = 8.4 Hz, 2H$_{major}$), 2.41 (dd, *J* = 13.6 Hz, *J* = 7.2 Hz, 2H$_{major}$), 2.10 (dd, *J* = 12.8 Hz, *J* = 9.6 Hz, 2H$_{minor}$). GC–MS (*m*/*z*): 208 (2) [*M*]$^+$, 193 (2) 175 (2), 154 (27), 126 (27), 108 (18), 79 (100), 55 (45).



2-Phenyl-4-vinylbutyrolactone (4a): Flash chromatography (*c*-Hex:AcOEt = 90:10). Yield = 93%. dr (*trans*:*cis*) = 1.1:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.37 (m, 2H$_{cis}$, 2H$_{trans}$), 7.33–7.29 (m, 3H$_{cis}$, 3H$_{trans}$), 5.98 (dd, *J* = 17.2 Hz, *J* = 10.4 Hz, 1H$_{cis}$), 5.96 (dd, *J* = 16.8 Hz, *J* = 10.8 Hz, 1H$_{trans}$), 5.47 (d, *J* = 16.8 Hz, 1H$_{trans}$), 5.44 (d, *J* = 17.2 Hz, 1H$_{cis}$), 5.34 (d, *J* = 10.8 Hz, 1H$_{trans}$), 5.33 (d, *J* = 10.4 Hz, 1H$_{cis}$), 5.14–5.09 (m, 1H$_{cis}$), 4.97–4.92 (m, 1H$_{trans}$), 3.95–3.87 (m, 1H$_{cis}$, 1H$_{trans}$), 2.85 (ddd, *J* = 12.8 Hz, *J* = 8.4 Hz, *J* = 5.6 Hz, 1H$_{trans}$), 2.65–2.49 (m, 2H$_{cis}$), 2.20 (ddd, *J* = 12.8 Hz, *J* = 12.8 Hz, *J* = 10.8 Hz, 1H$_{trans}$). ^{13}C NMR (50 MHz, $CDCl_3$): δ (*trans*): 176.5, 136.3, 129.0, 128.8, 128.2, 127.9, 118.6, 78.7, 47.1, 38.3. δ (*cis*): 177.0, 136.7, 129.1, 128.2, 128.0, 127.8, 117.4, 78.1, 44.9, 36.8. GC–MS (*m*/*z*): 144 (64), 129 (100), 115 (23), 102 (23), 66 (50), 51 (23).

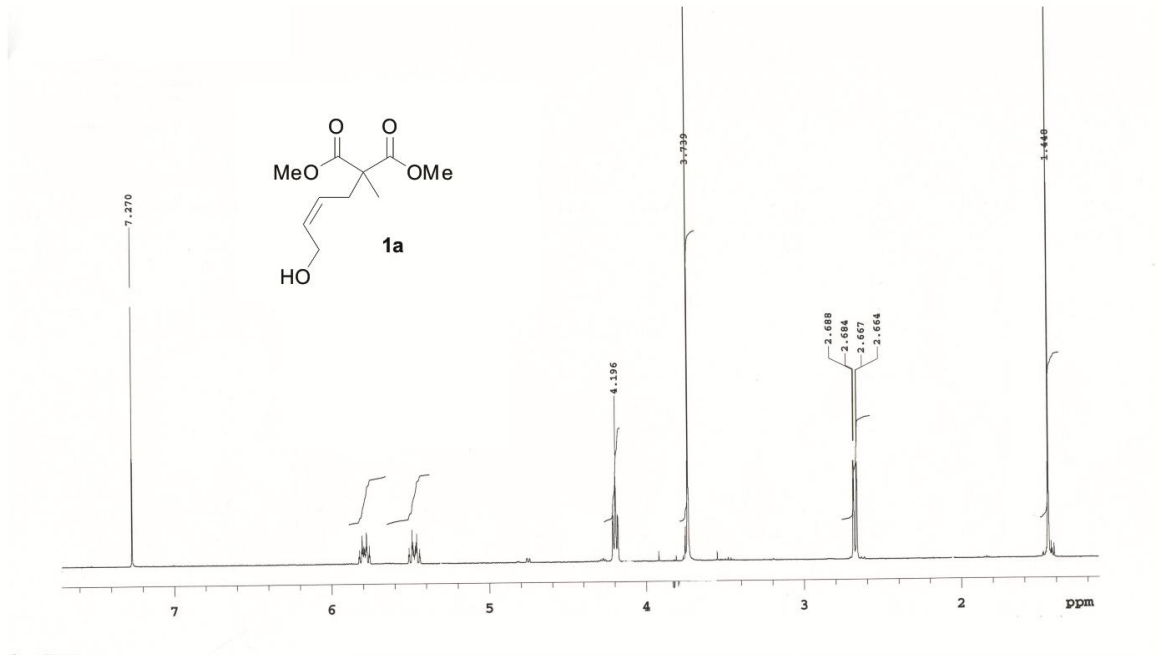


2,2-Diphenyl-4-vinylbutyrolacton (4b): Flash chromatography (*c*-Hex:AcOEt = 90:10). Yield = 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.39 (m, 4H), 7.32 (d, *J* = 4.0 Hz, 6H), 5.94 (ddd, *J* = 17.2 Hz, *J* = 10.4 Hz, *J* = 6.8 Hz, 1H), 5.42 (d, *J* = 17.2 Hz, 1H), 5.31 (d, *J* = 10.4 Hz, 1H), 4.78 (pquint, *J* = 5.2 Hz, 1H), 3.11 (dd, *J* = 13.2 Hz, *J* = 5.2 Hz, 1H), 2.77 (dd, *J* = 13.2 Hz, *J* = 10.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.8, 141.7, 139.6, 134.9, 129.0, 128.4, 127.8, 127.7, 127.3, 127.3, 118.9, 77.5, 58.1, 43.8. GC–MS (*m*/*z*): 220 (64), 205 (50), 191 (18), 165 (54), 143 (50), 129 (100), 115 (36), 91 (32), 77 (23), 51 (18). Anal. calcd for ($C_{18}H_{16}O_2$: 264.12): C, 81.79; H, 6.10. Found: C, 81.70; H, 6.05.

References

1. Oppolzer, W.; Moretti, R.; Zhou, C. *Helv. Chim. Acta* **1994**, *77*, 2663.

2. Odabachian, Y.; Gagosz, F. *Adv. Synt. Cat.* **2009**, *351*, 379. doi: 10.1002/adsc.200900056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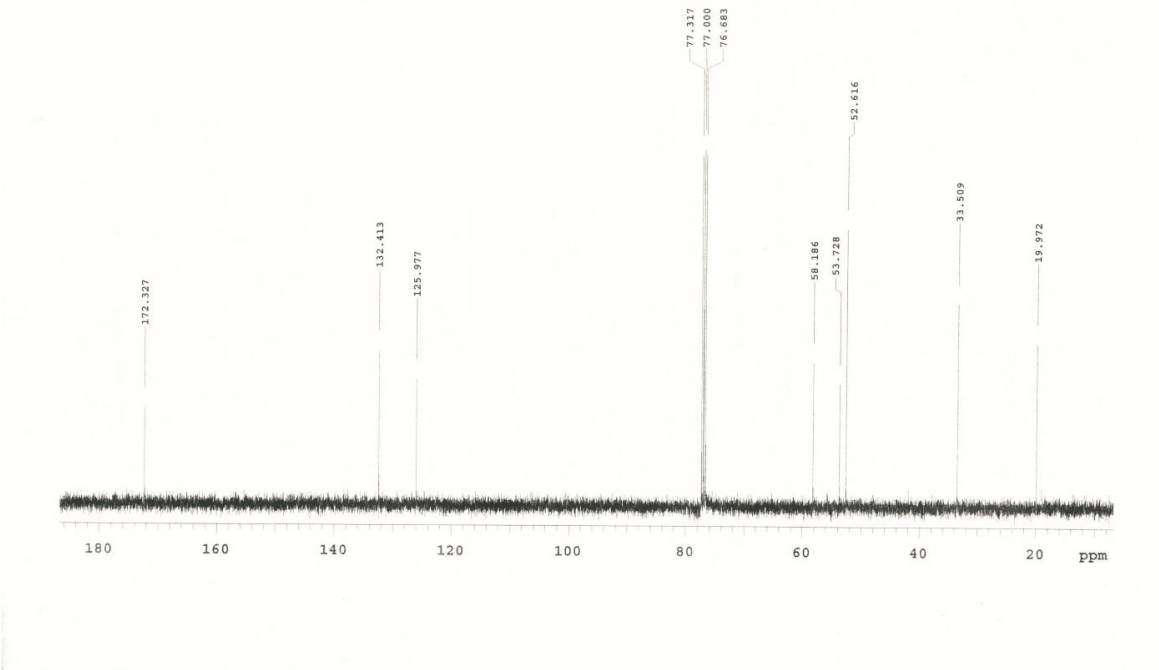
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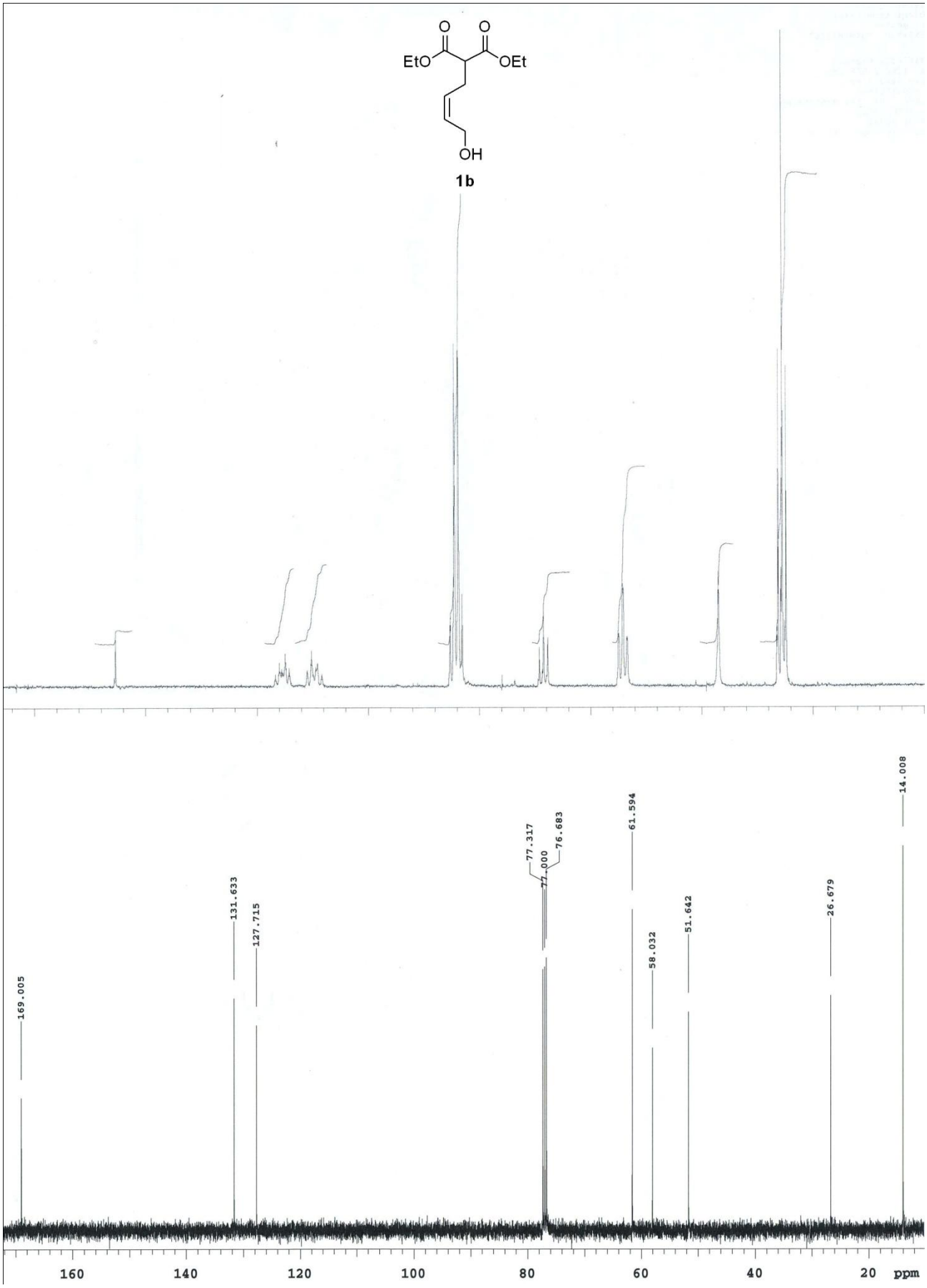
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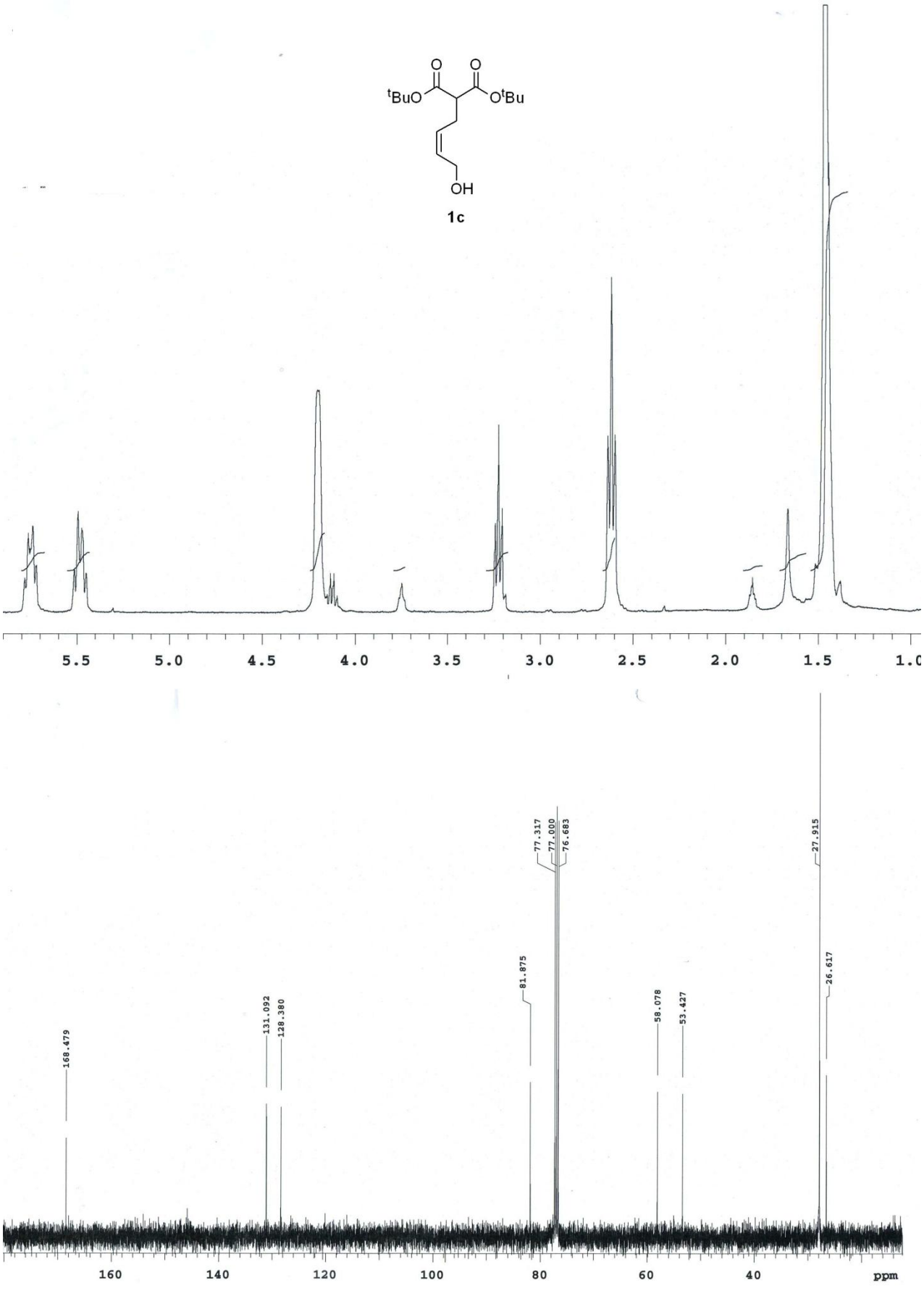
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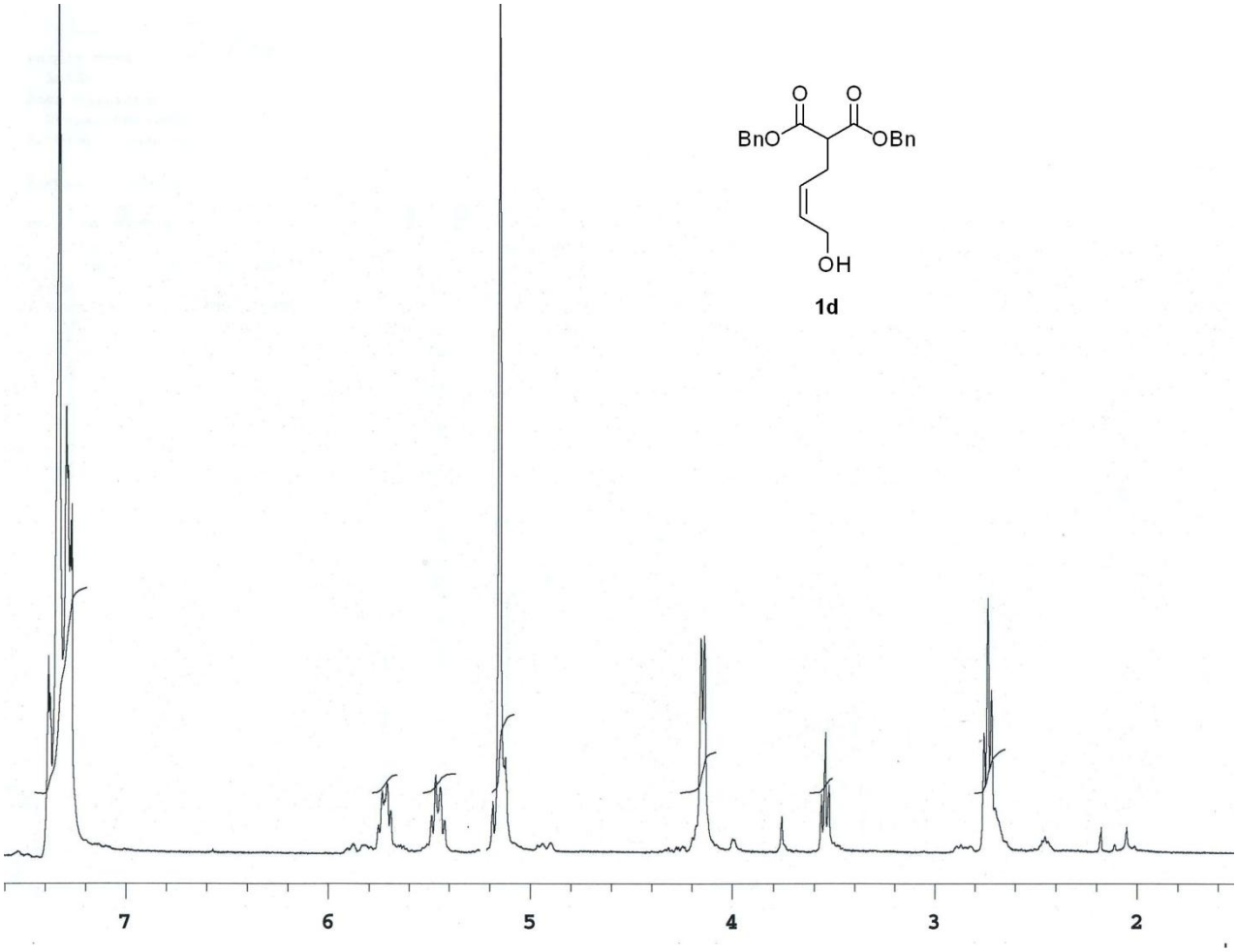
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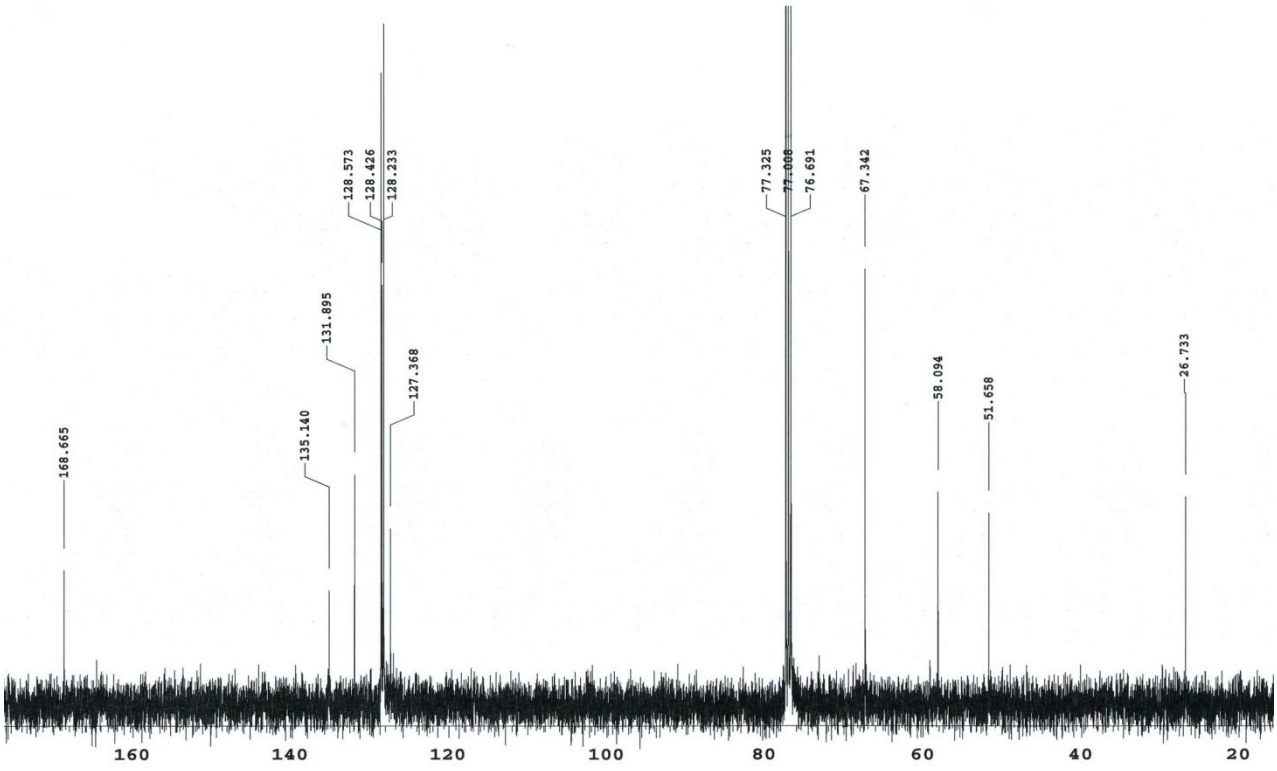
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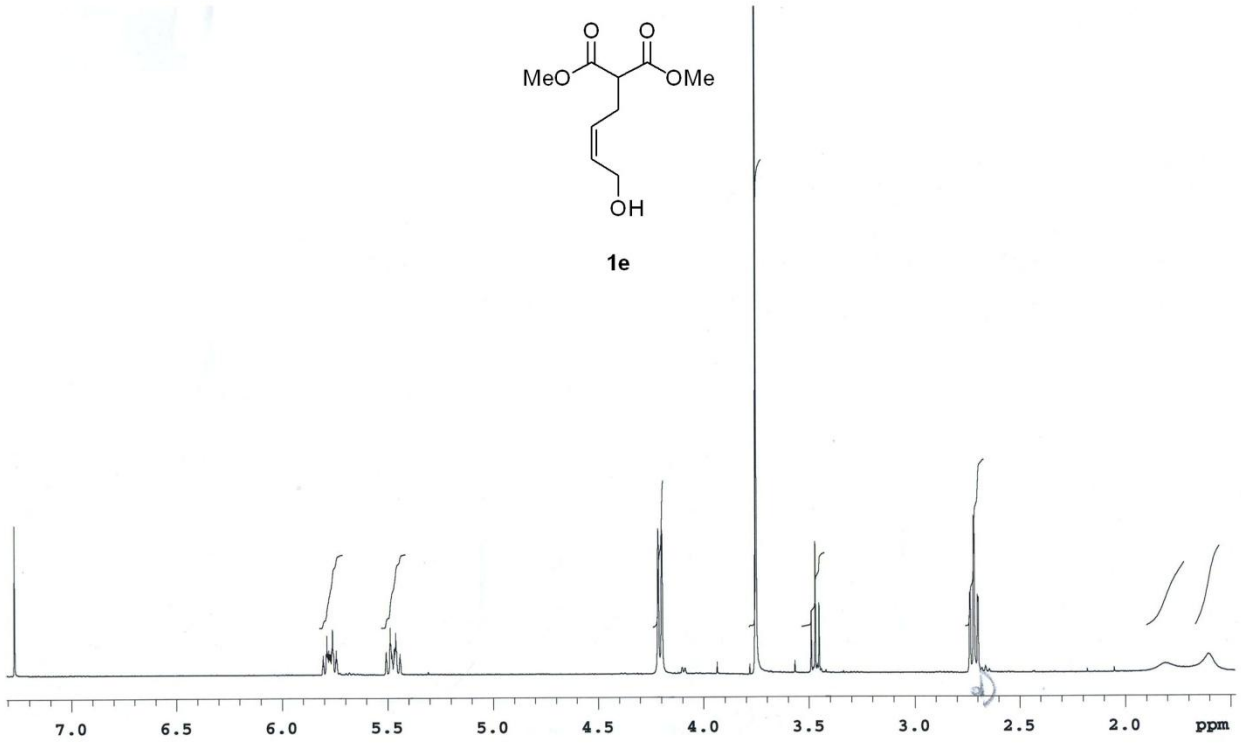
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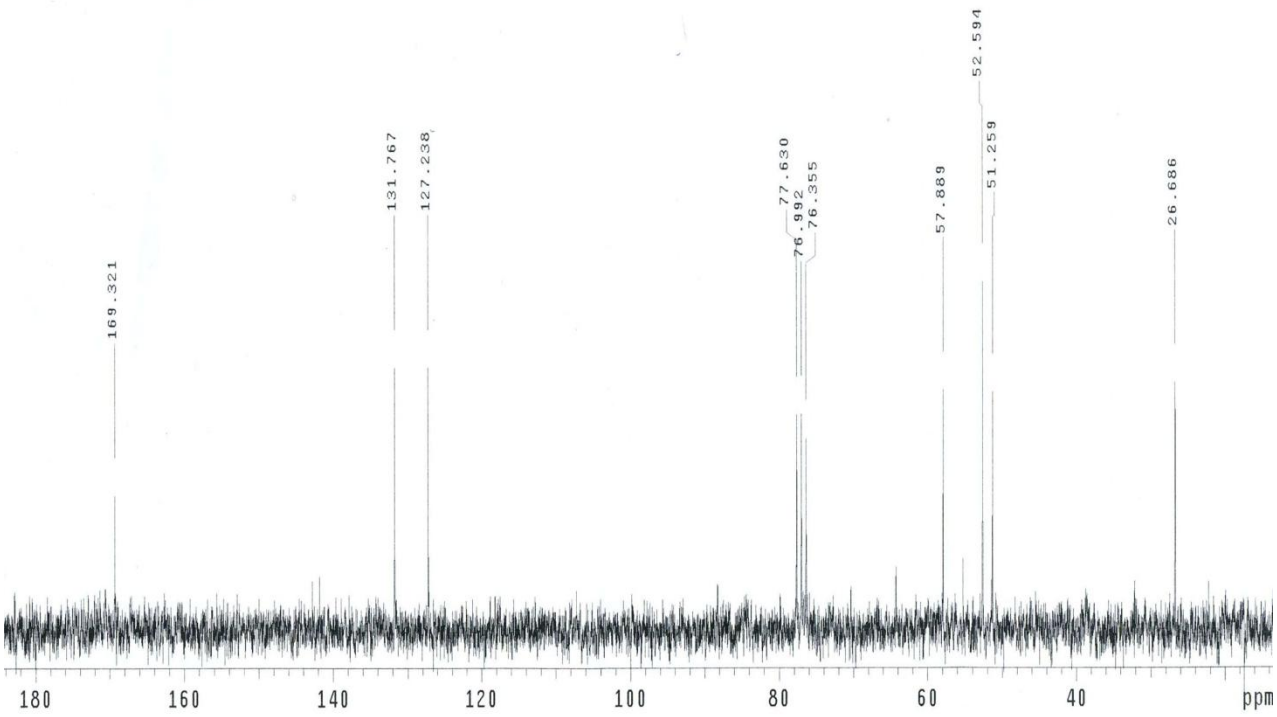
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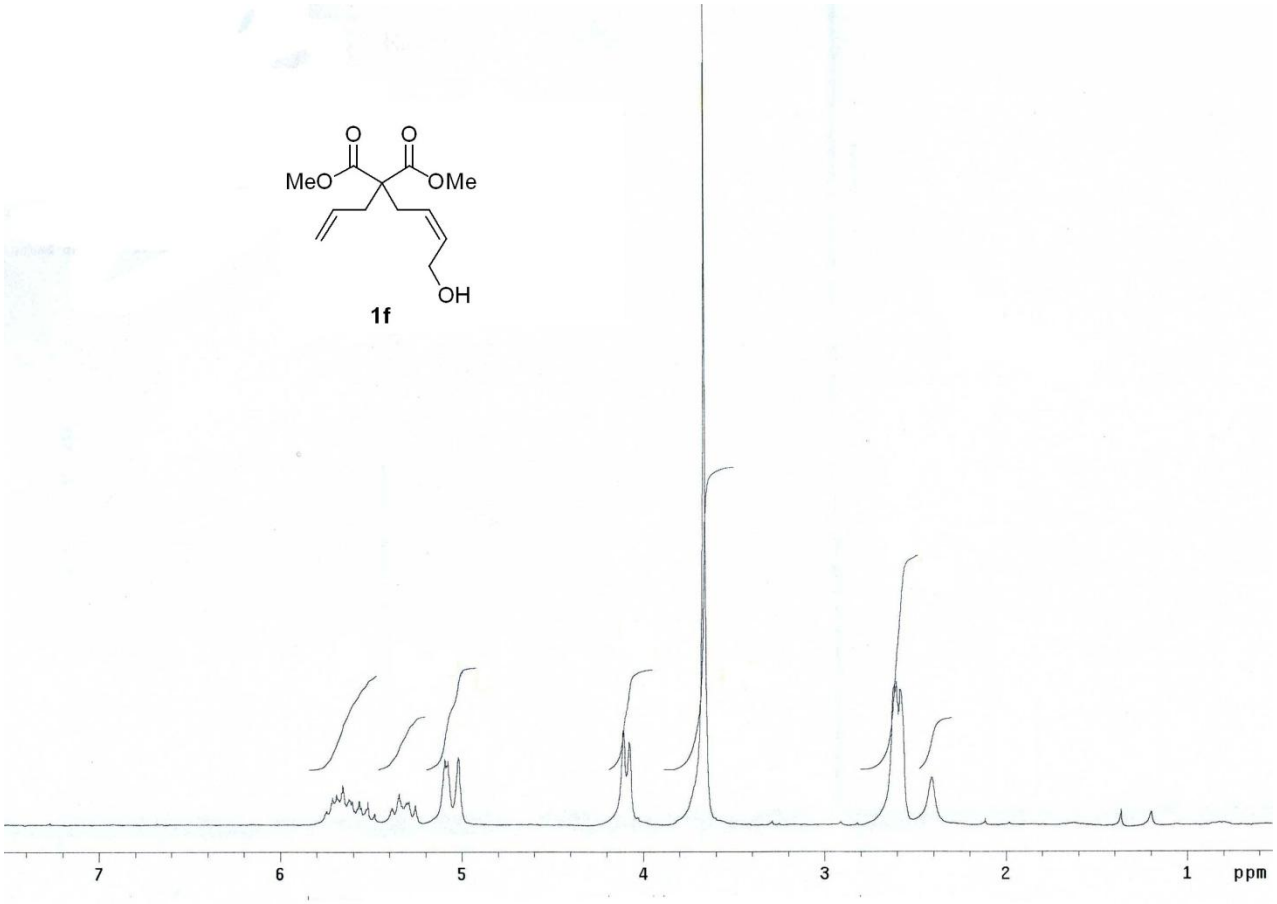
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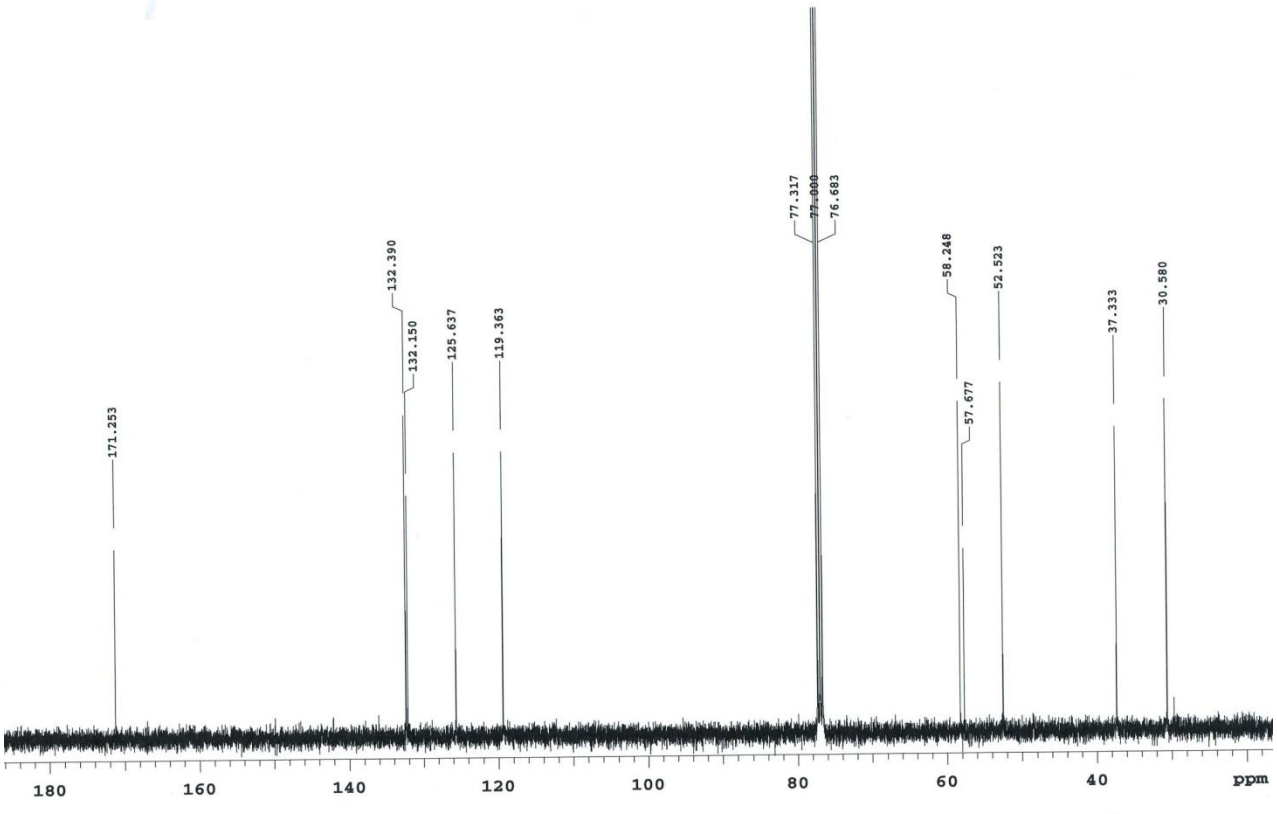
1f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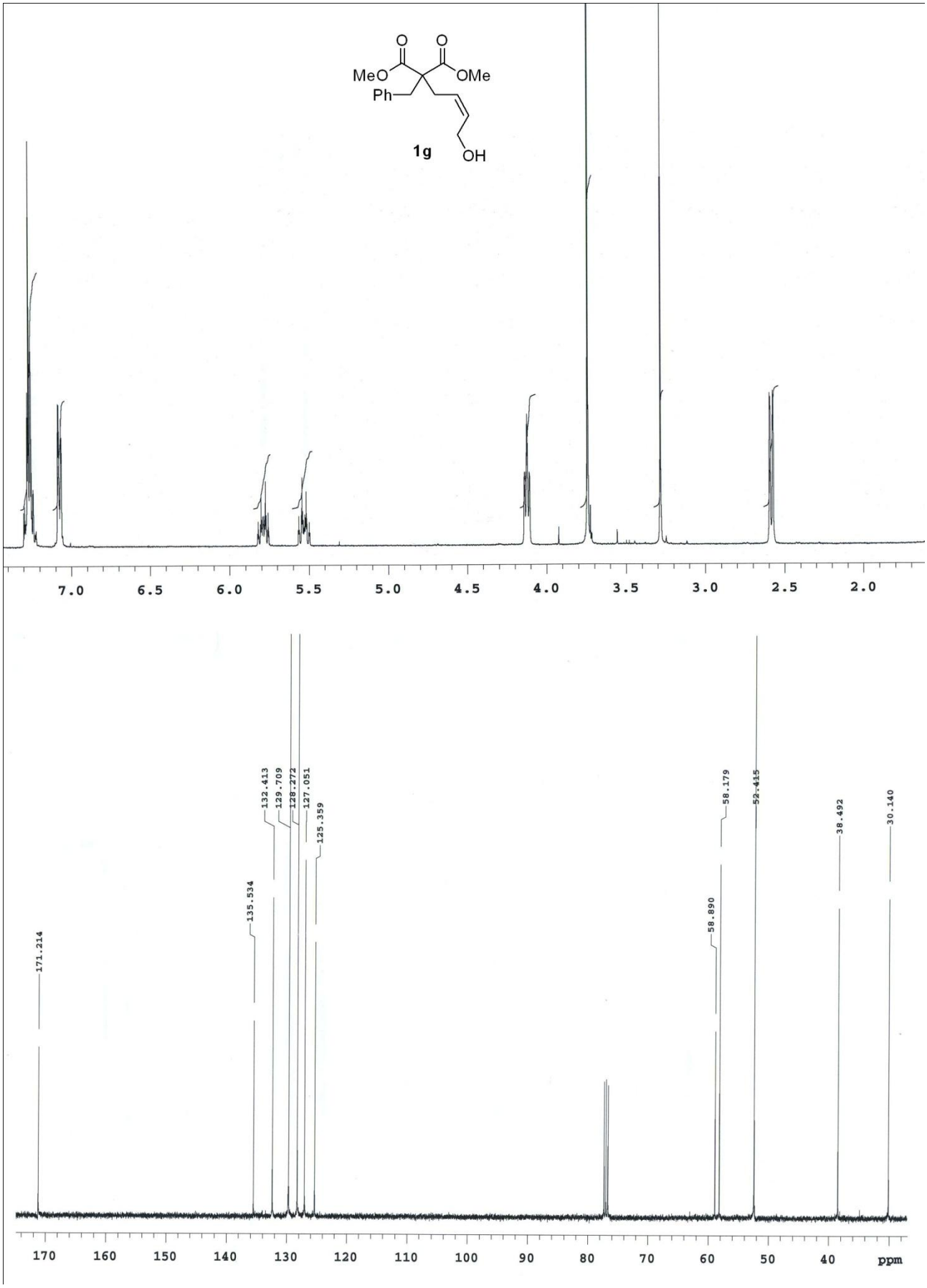
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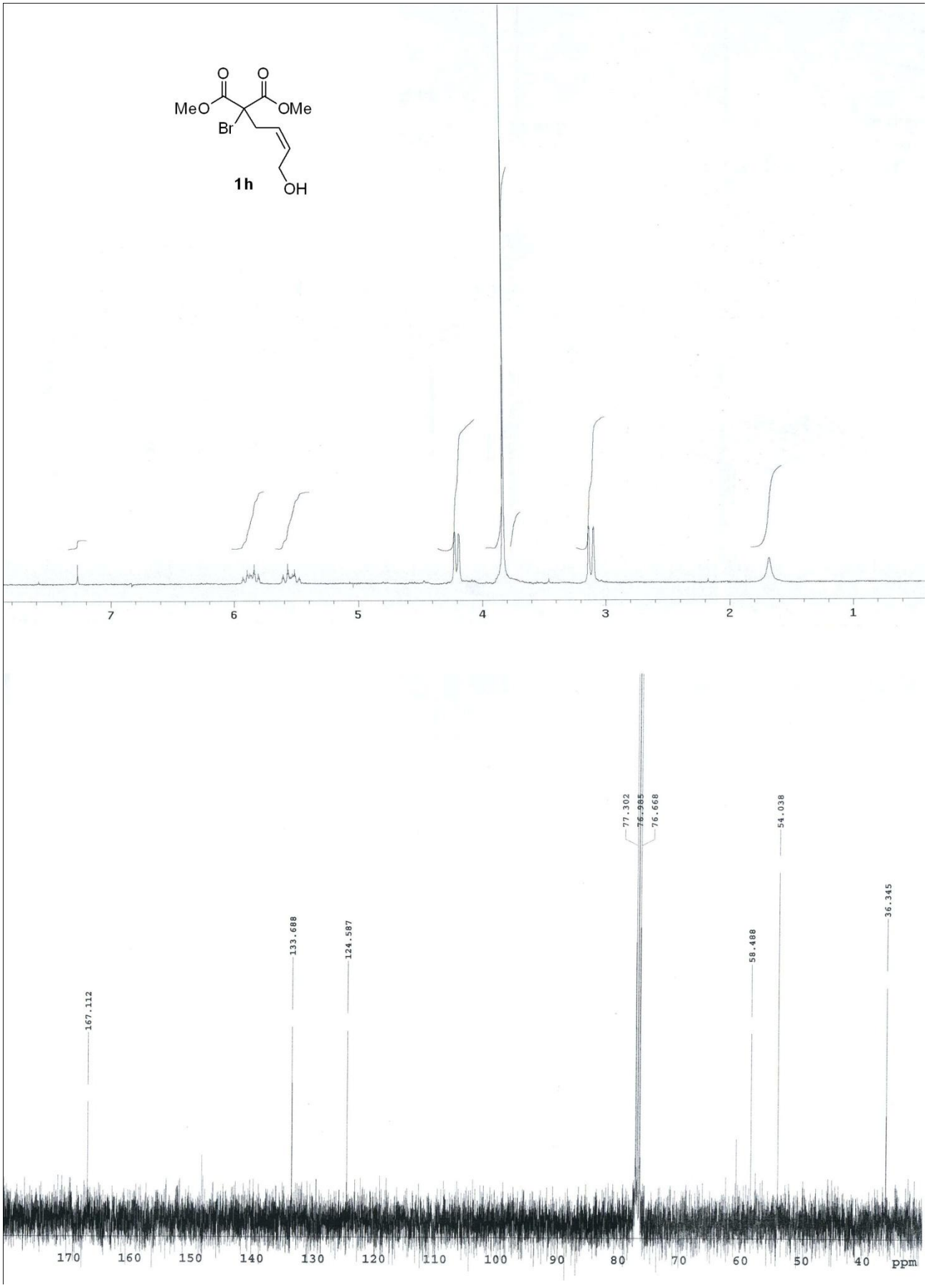
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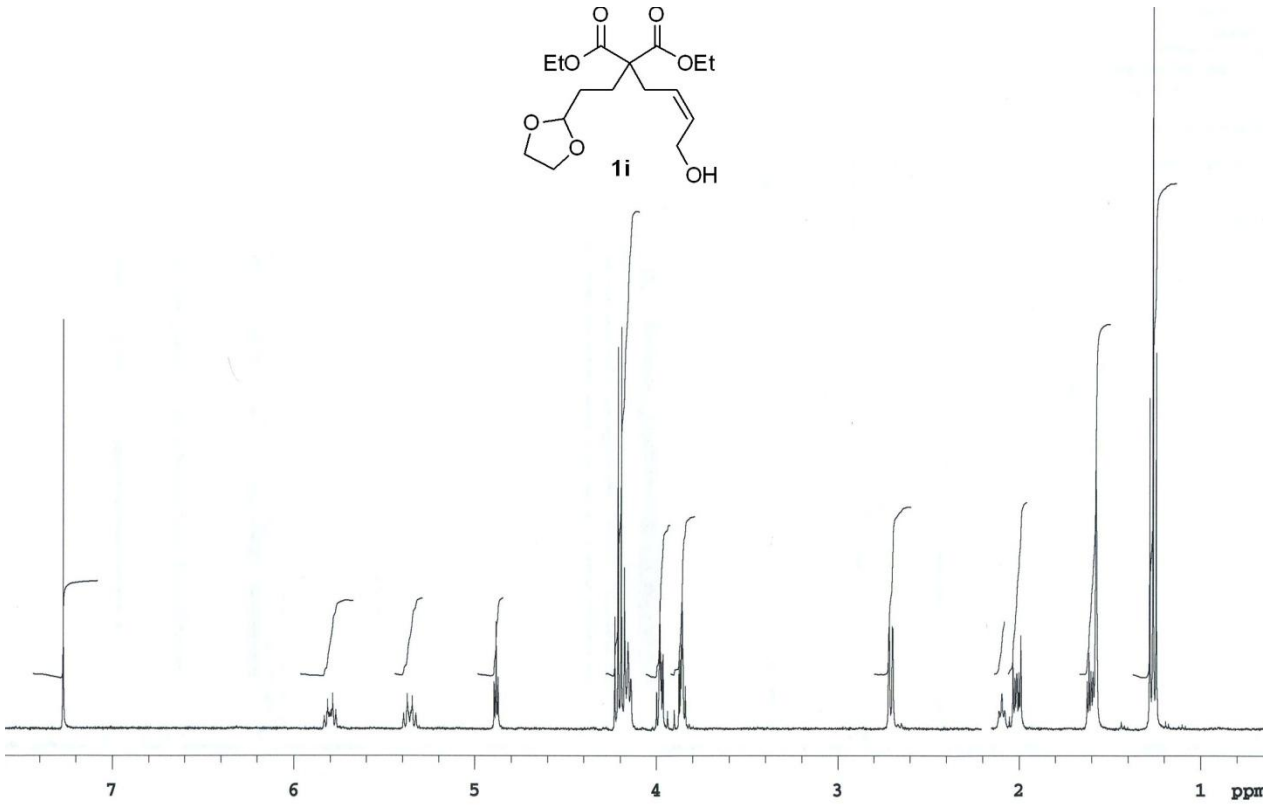
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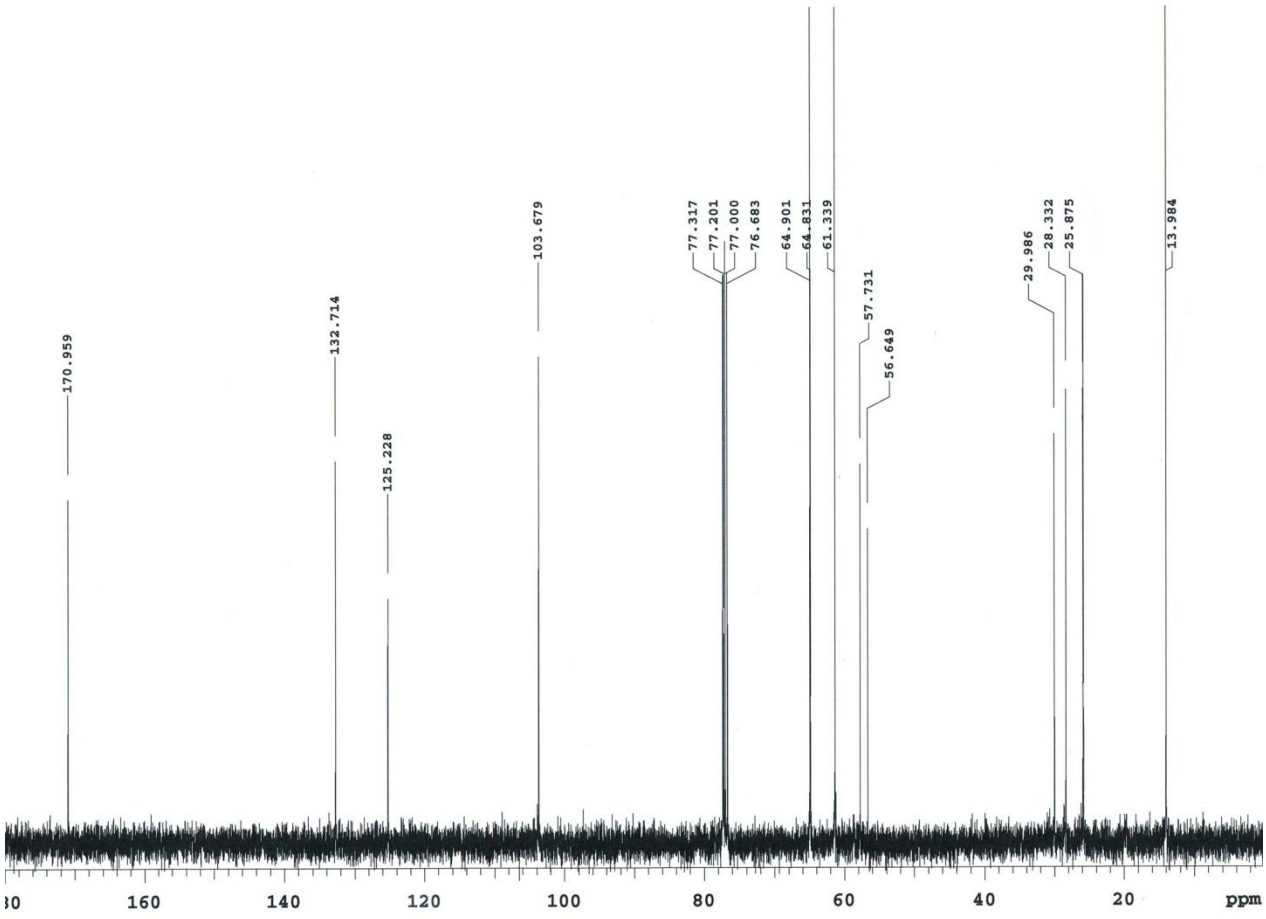
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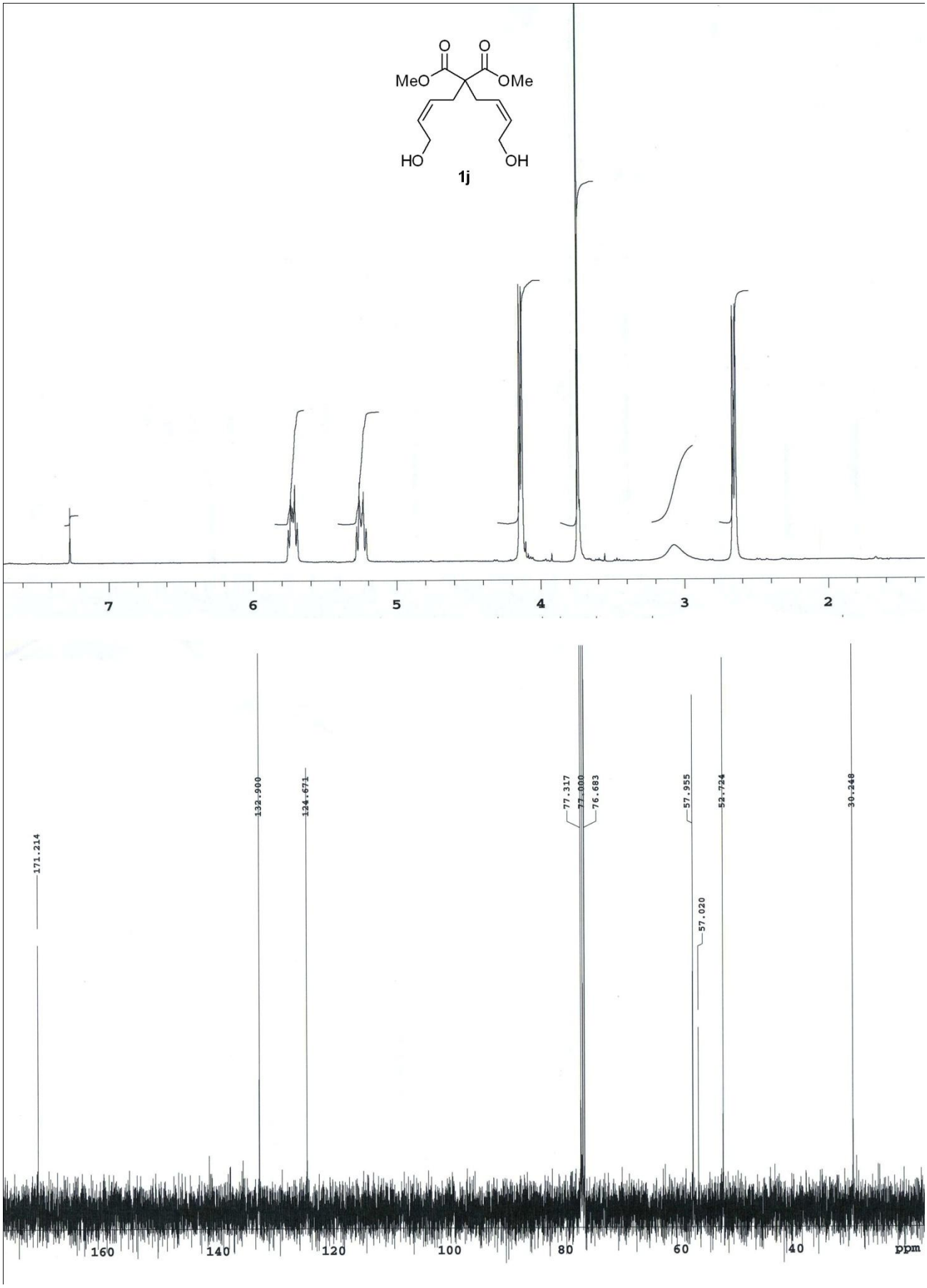
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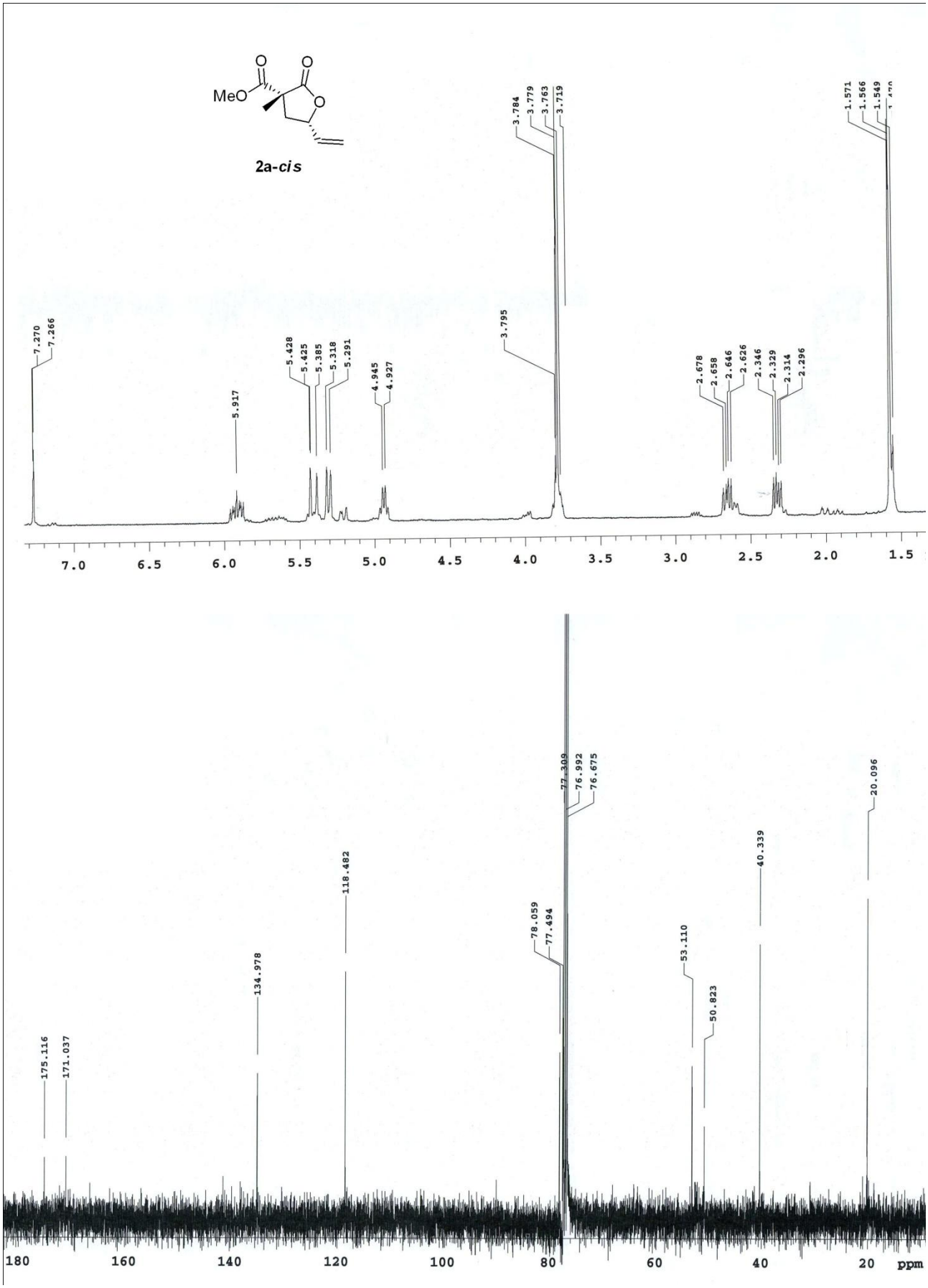
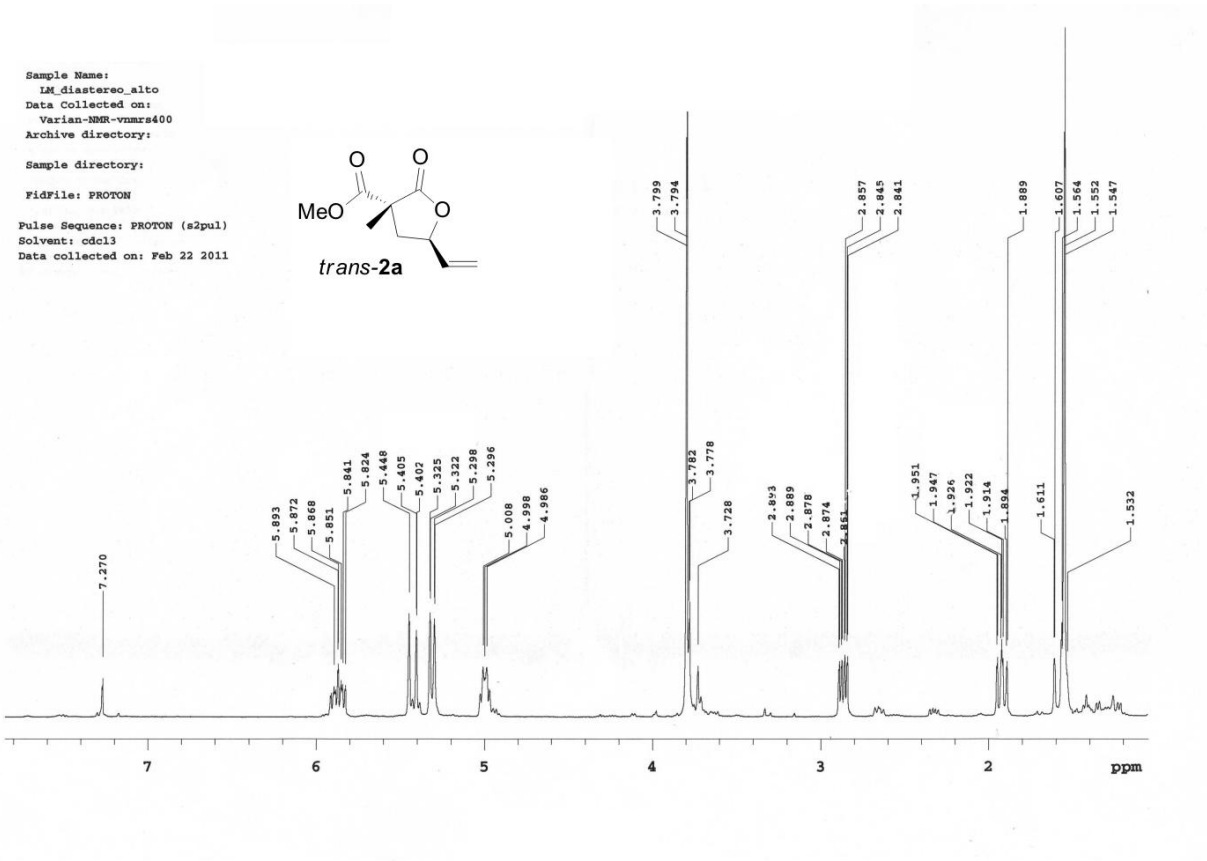
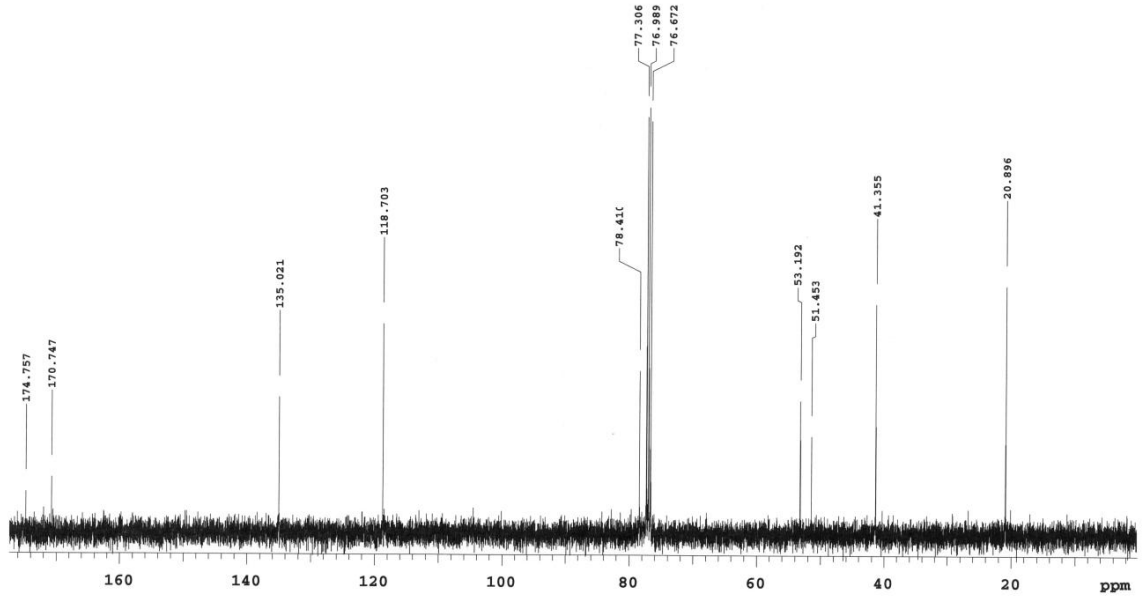
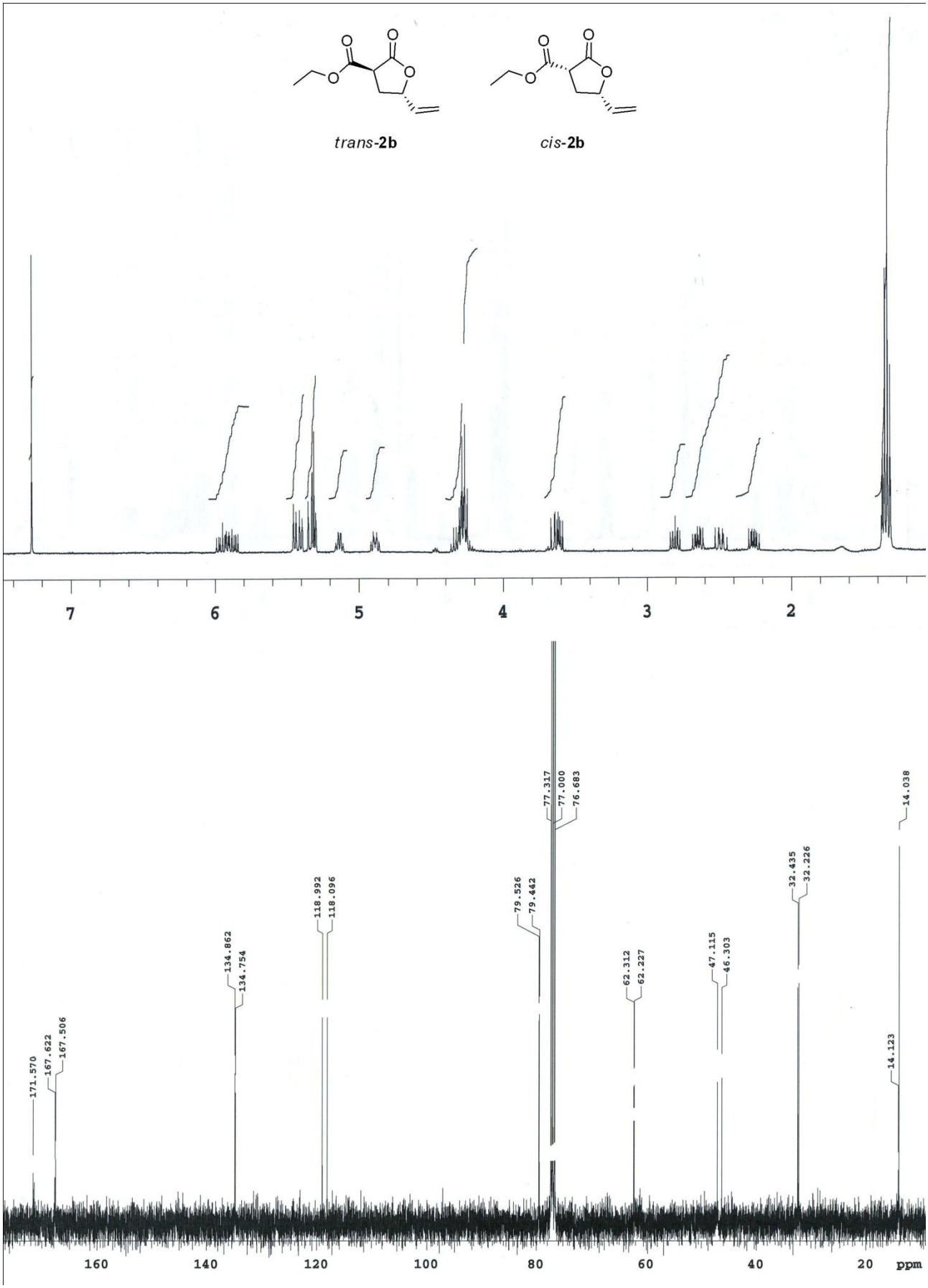
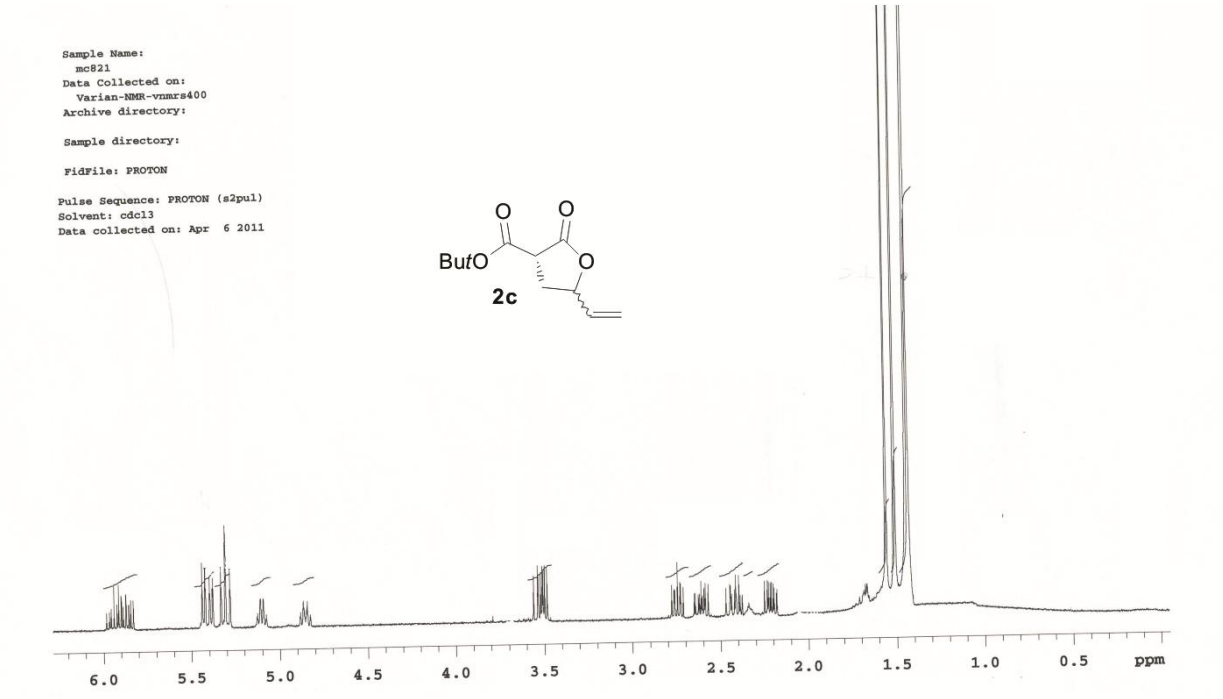
40
ppm

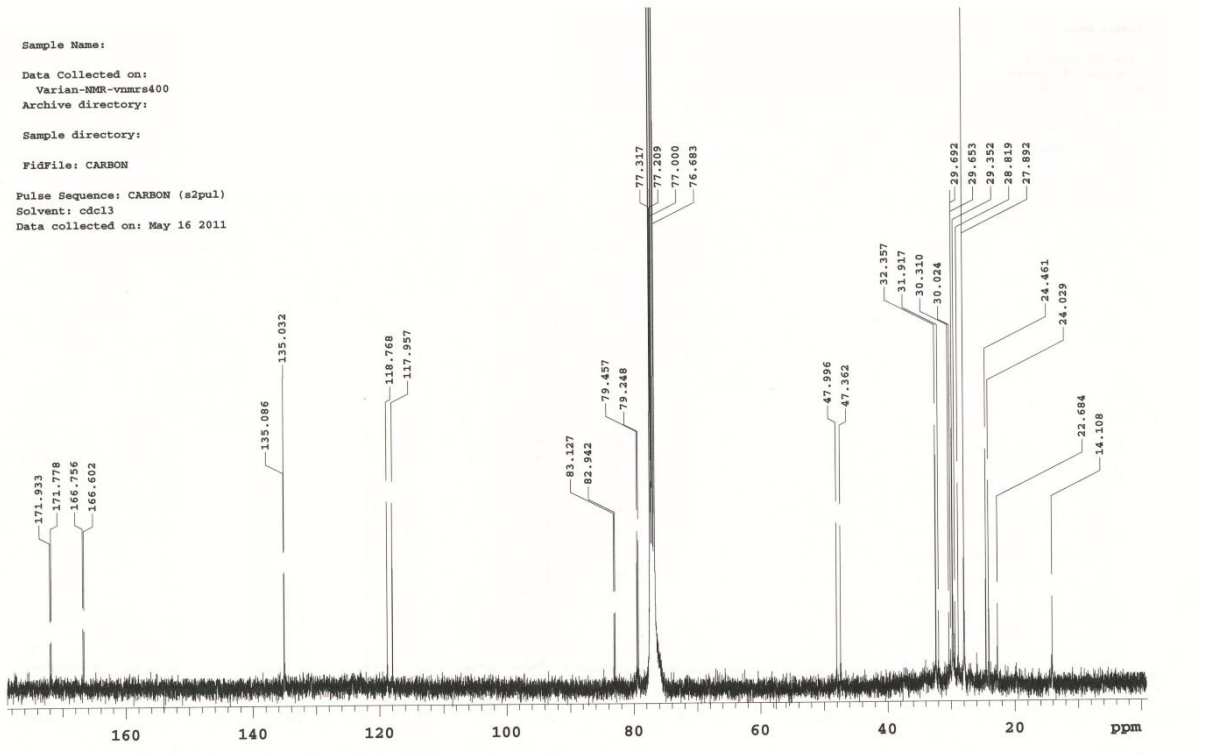

MeO
O
O
O
2a-cis
7.270
7.266
5.917
5.428
5.425
5.385
5.318
5.291
4.945
4.927
3.795
3.784
3.779
3.763
3.719
2.678
2.658
2.646
2.626
2.346
2.329
2.314
2.296
1.571
1.566
1.549
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
175.116
171.037
134.978
118.482
78.059
77.494
77.309
76.992
76.675
53.110
50.823
40.339
20.096
180
160
140
120
100
80
60
40
20
ppm

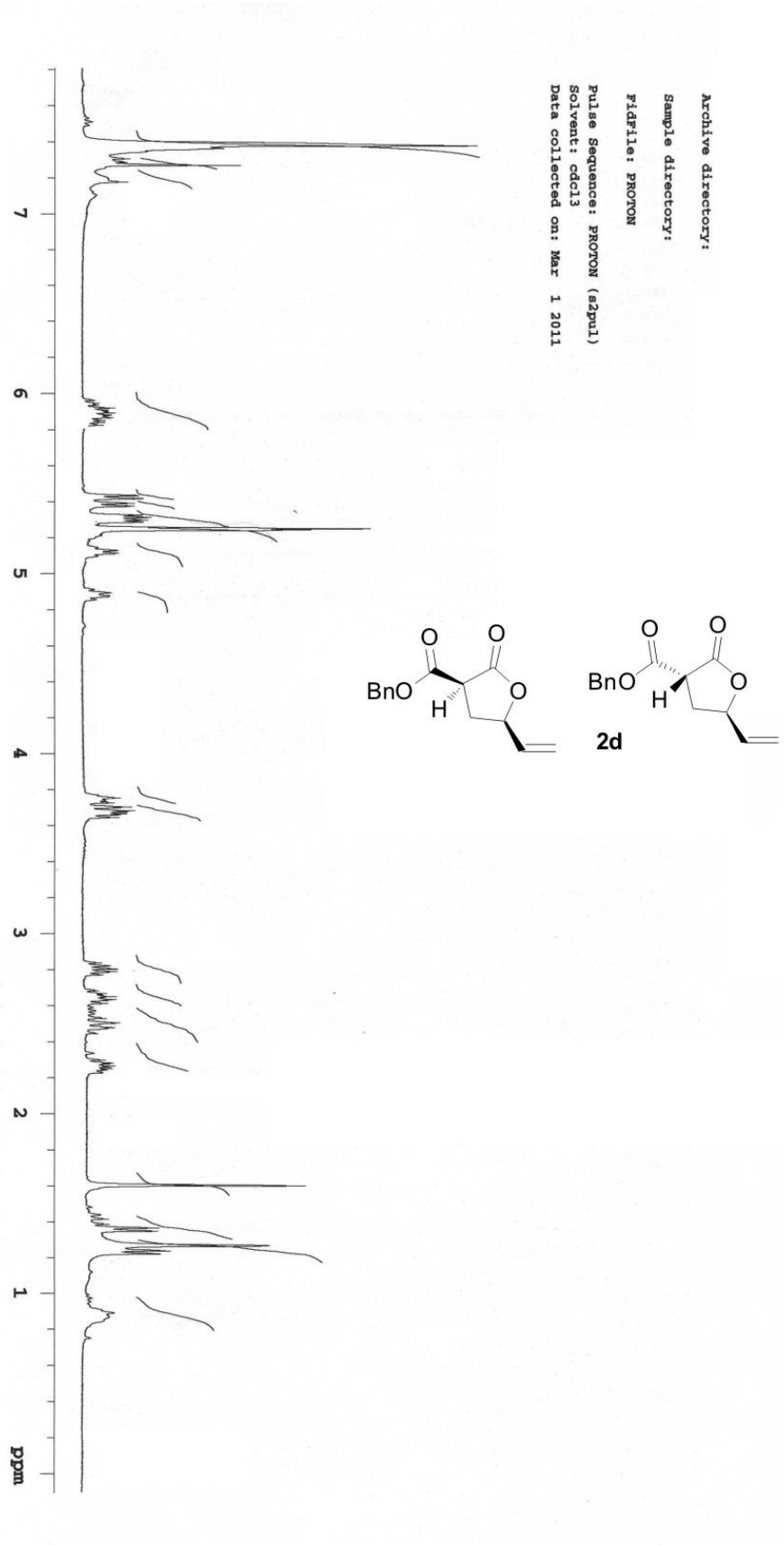

Sample Name:
LM_diastereo_alto
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 22 2011
MeO
trans-2a
7.270
5.893
5.872
5.868
5.851
5.841
5.824
5.448
5.405
5.402
5.325
5.322
5.298
5.296
5.008
4.998
4.986
3.799
3.794
3.782
3.778
3.728
2.893
2.889
2.878
2.874
2.857
2.845
2.841
1.951
1.947
1.926
1.922
1.914
1.894
1.889
1.611
1.607
1.564
1.552
1.547
1.532
7
6
5
4
3
2
ppm

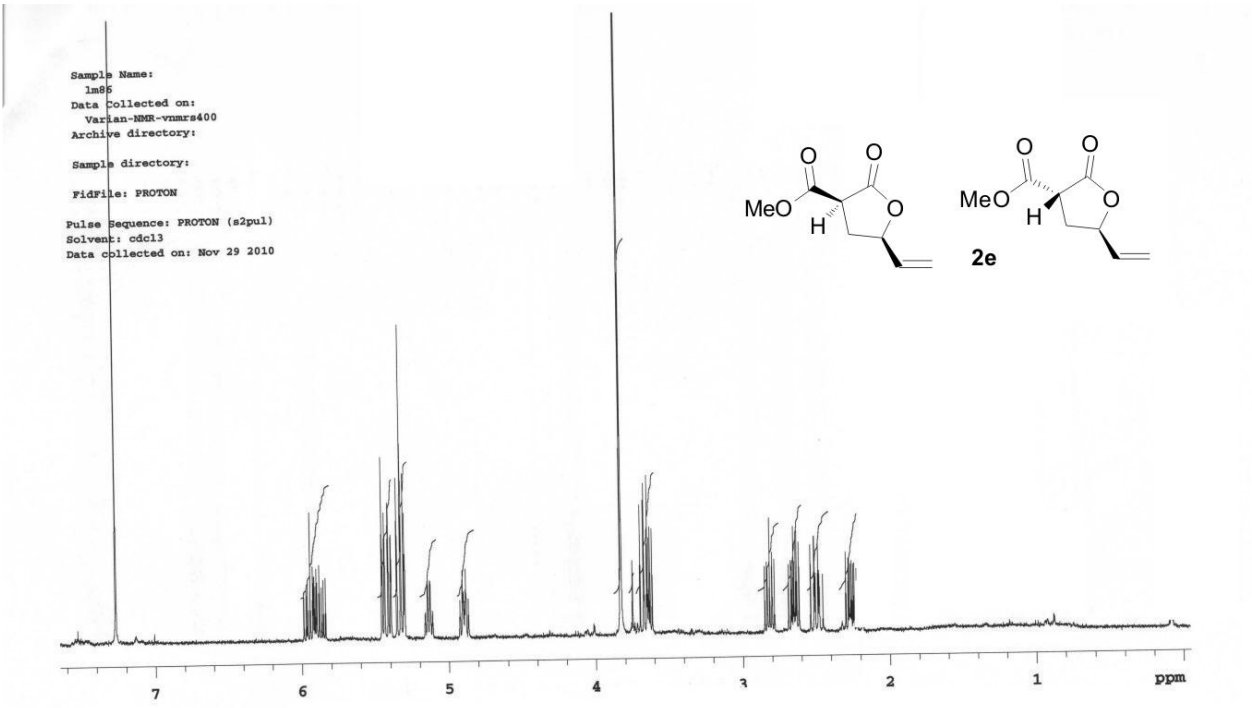

174.757
170.747
135.021
118.703
78.41
77.306
76.989
76.672
53.192
51.453
41.355
20.896
160
140
120
100
80
60
40
20
ppm

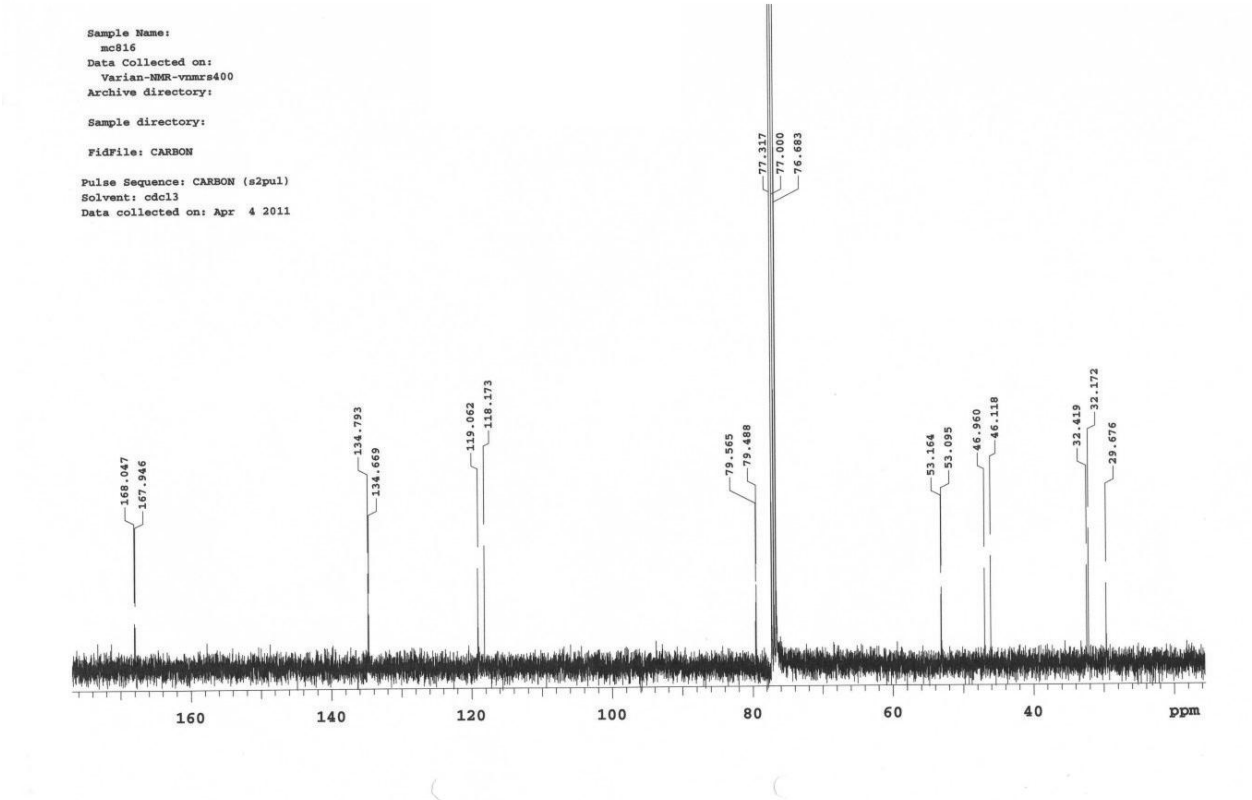

trans-2b
cis-2b
7
6
5
4
3
2
171.570
167.622
167.506
134.862
134.754
118.992
118.096
79.526
79.442
77.317
77.000
76.683
62.312
62.227
47.115
46.303
32.435
32.226
14.123
14.038
160
140
120
100
80
60
40
20
ppm

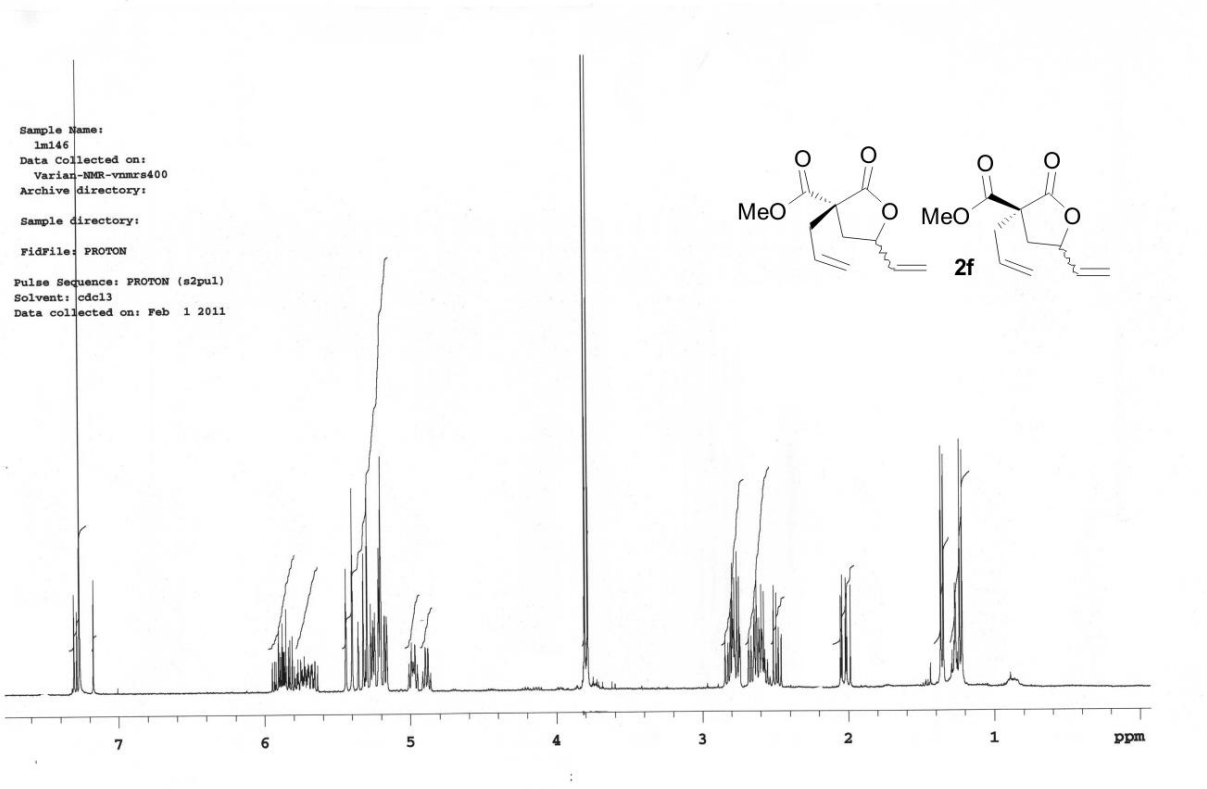

Sample Name:
mc821
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 6 2011
ButO
2c
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

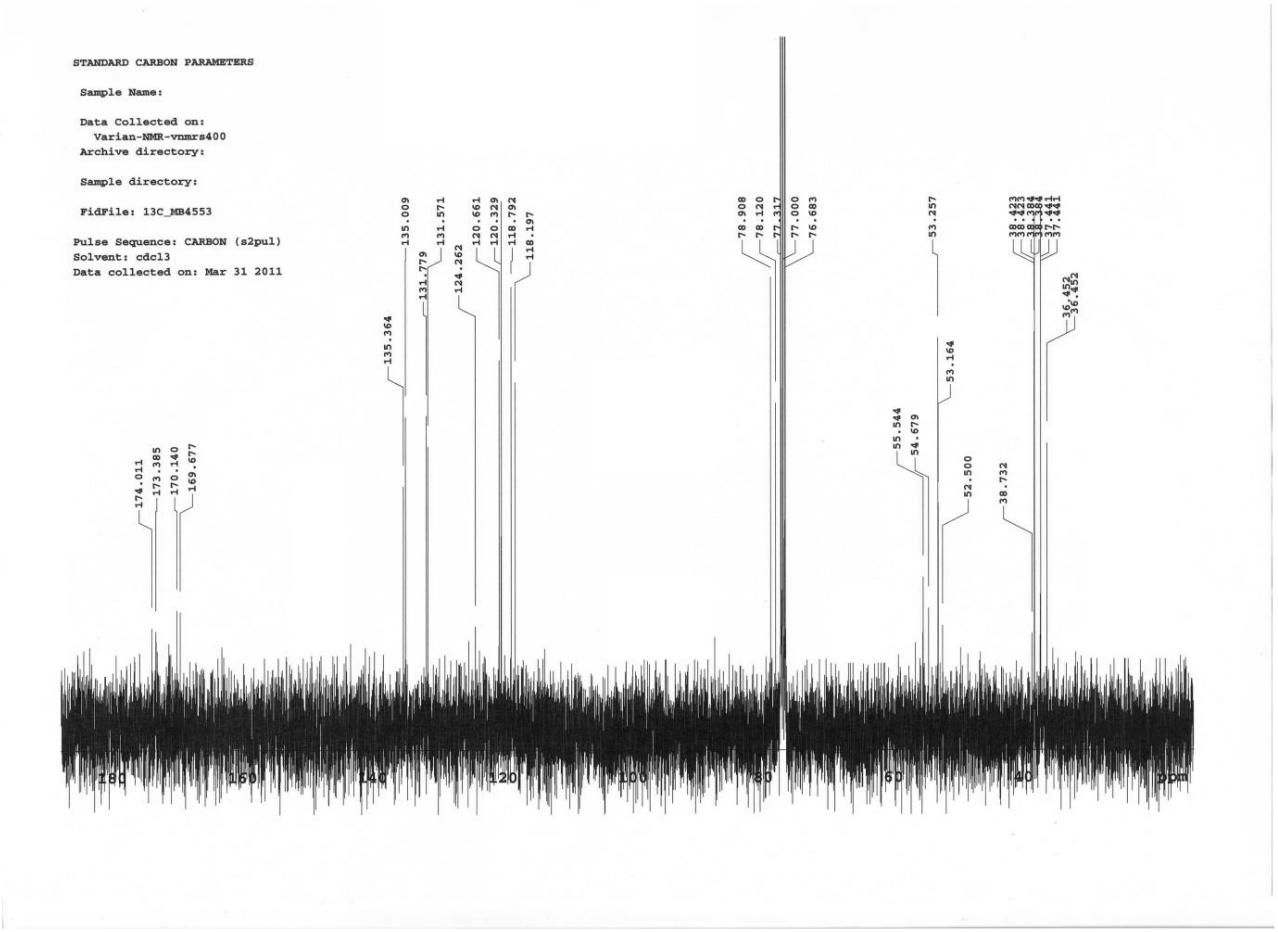

Sample Name:
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 16 2011
171.933
171.778
166.756
166.602
135.086
135.032
118.768
117.957
83.127
82.942
79.457
79.248
77.317
77.209
77.000
76.683
47.996
47.362
32.357
31.917
30.310
30.024
29.692
29.653
29.352
28.819
27.892
24.461
24.029
22.684
14.108
160
140
120
100
80
60
40
20
ppm

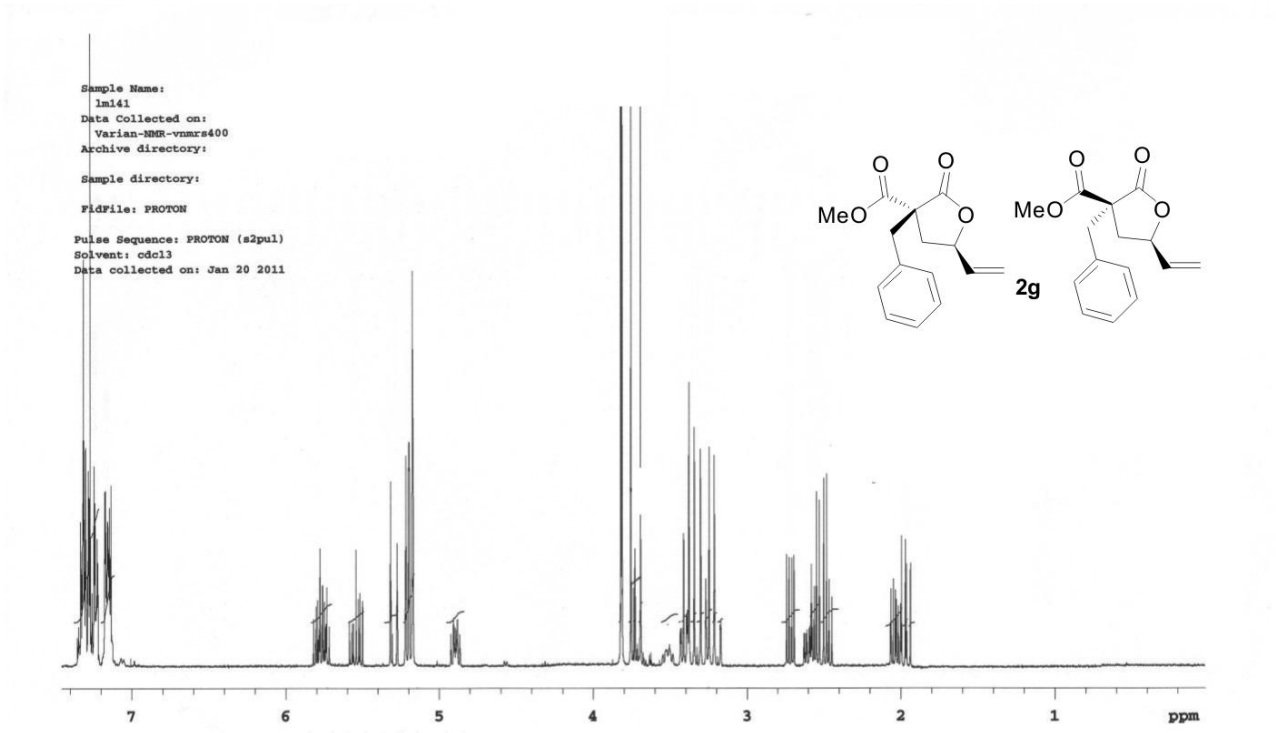

Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 1 2011
BnO
H
O
O
O
2d
7
6
5
4
3
2
1
ppm

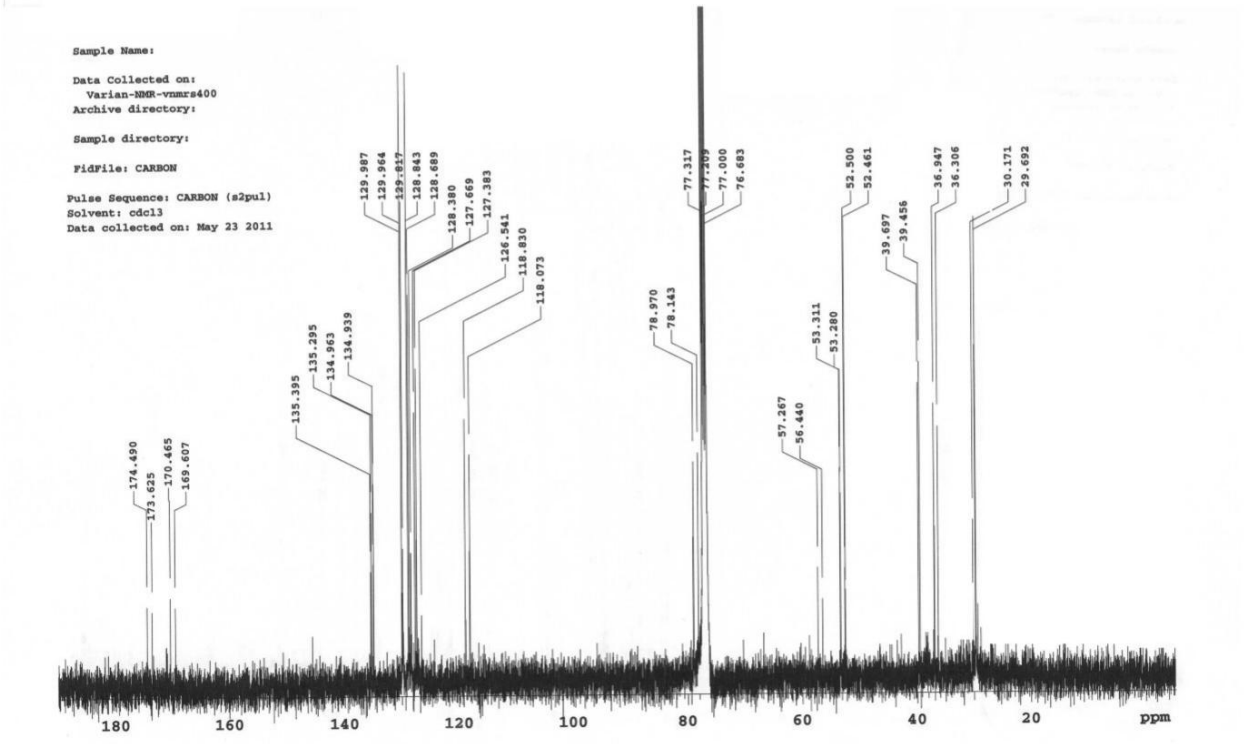

Sample Name:
lm86
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 29 2010
MeO
H
O
O
O
MeO
H
O
O
2e
7
6
5
4
3
2
1
ppm

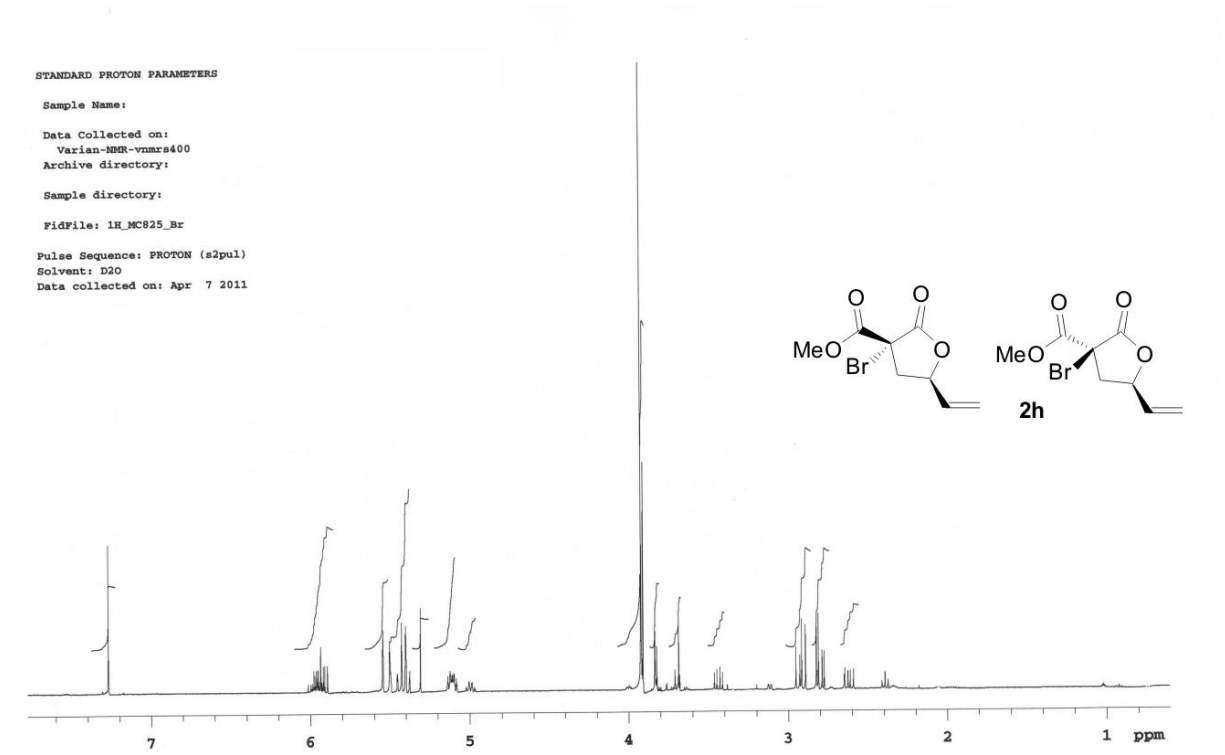

Sample Name:
mc816
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 4 2011
168.047
167.946
134.793
134.669
119.062
118.173
79.565
79.488
77.317
77.000
76.683
53.164
53.095
46.960
46.118
32.419
32.172
29.676
160
140
120
100
80
60
40
ppm

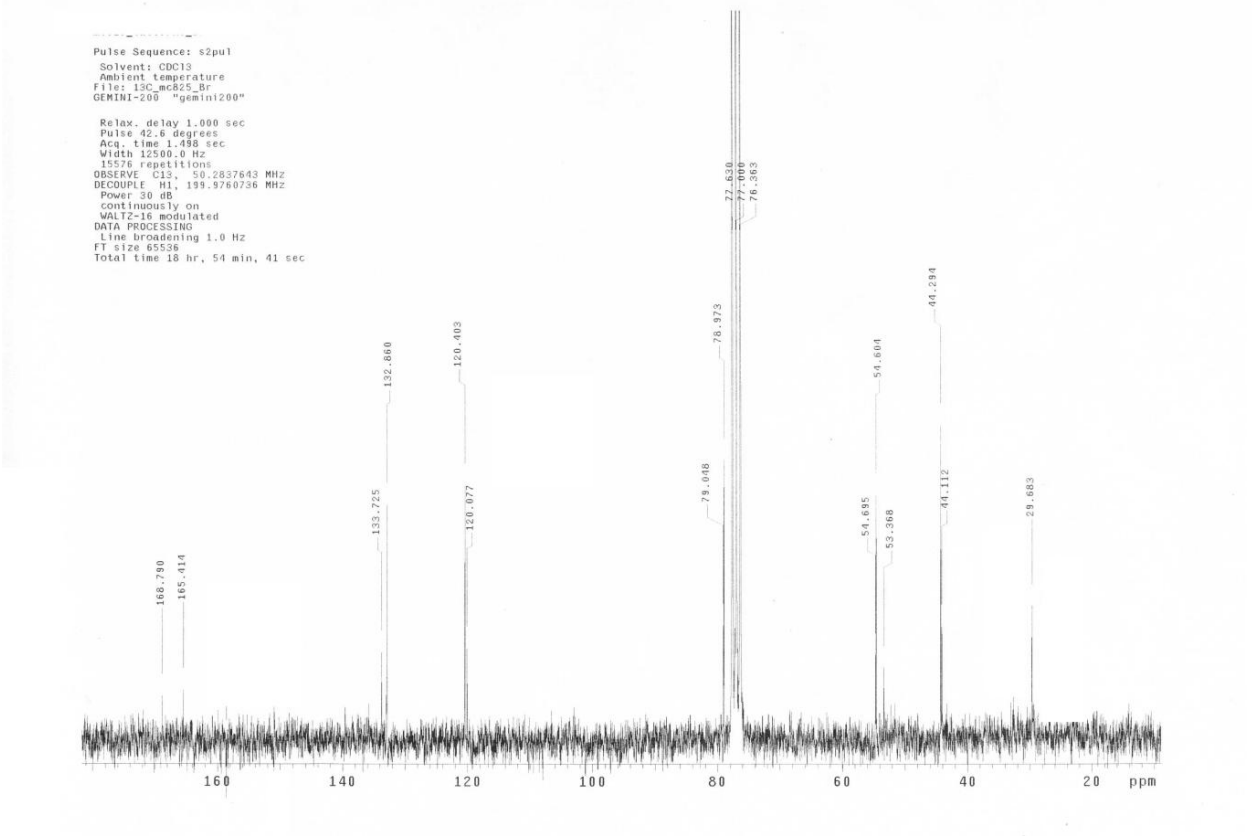

Sample Name:
lm146
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 1 2011
MeO
MeO
2f
7
6
5
4
3
2
1
ppm

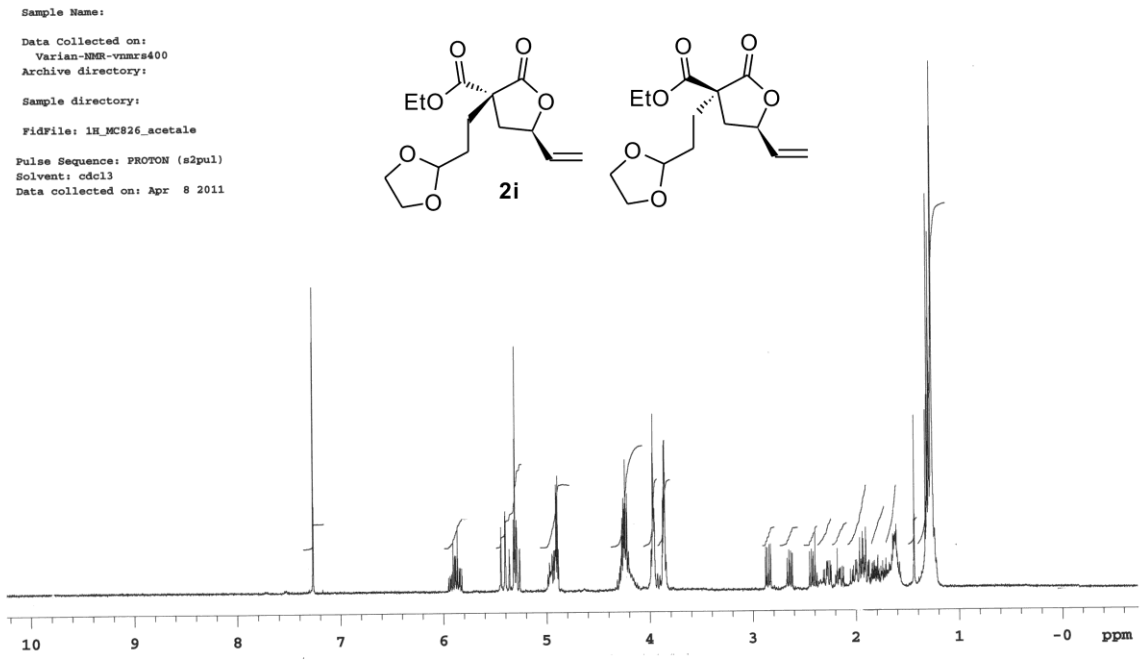

STANDARD CARBON PARAMETERS
Sample Name:
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: 13C_MB4553
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 31 2011
174.011
173.385
170.140
169.677
135.364
135.009
131.779
131.571
124.262
120.661
120.329
118.792
118.197
78.908
78.120
77.317
77.000
76.683
55.544
54.679
53.257
53.164
52.500
38.732
38.423
38.384
38.344
37.441
36.452
36.432
160
140
120
100
80
60
40
ppm

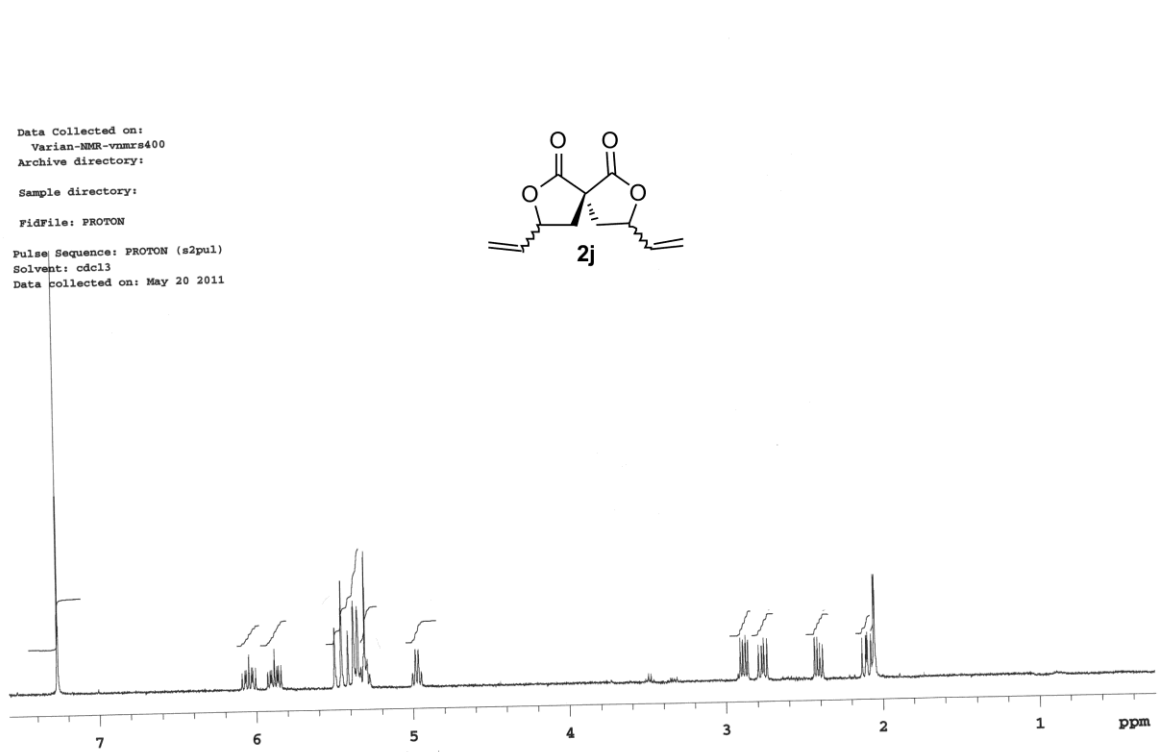

Sample Name:
lm141
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jan 20 2011
MeO
MeO
2g
7
6
5
4
3
2
1
ppm

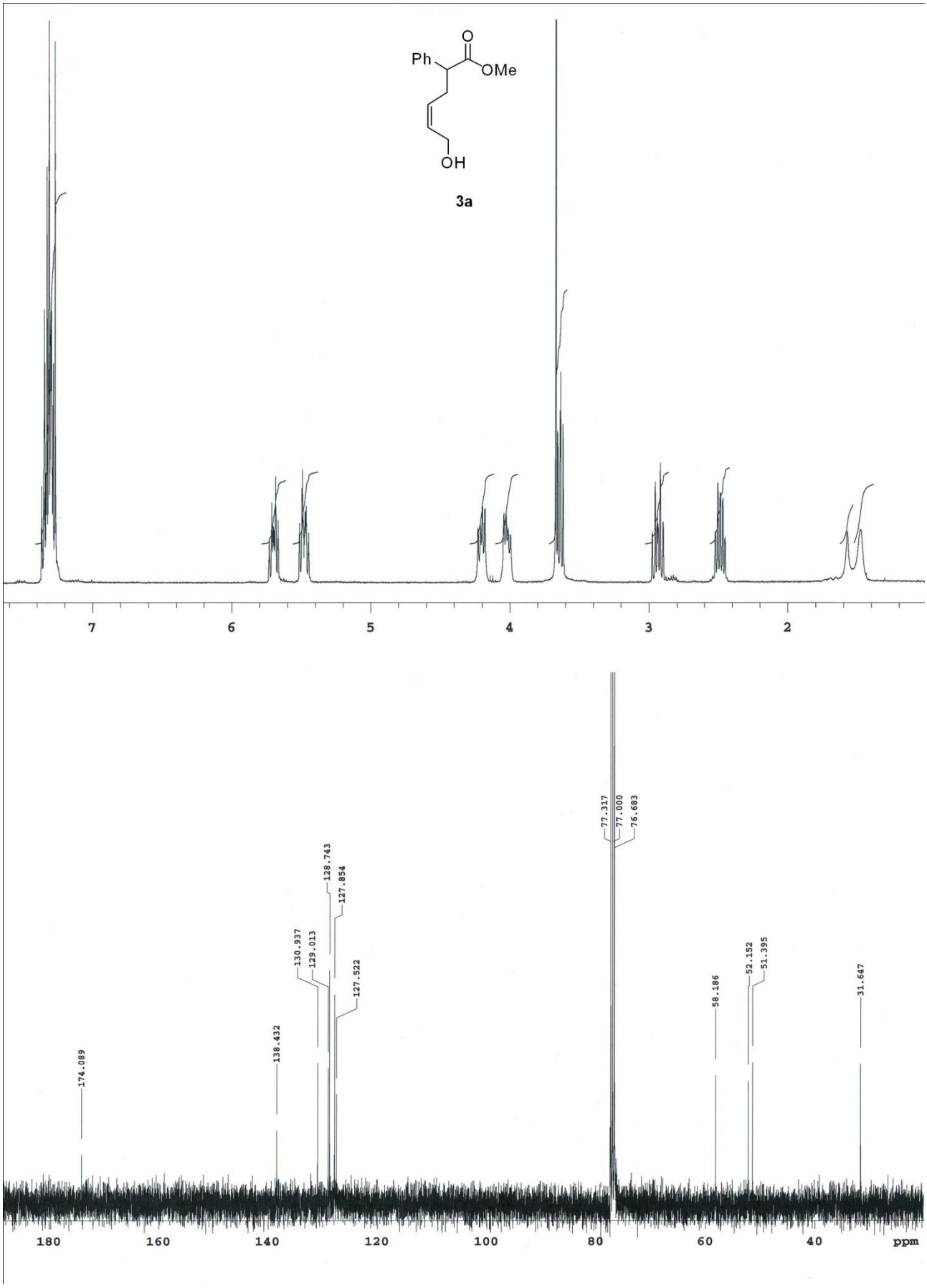

Sample Name:
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 23 2011
174.490
173.625
170.465
169.607
135.395
135.395
134.963
134.939
129.987
129.964
129.817
128.843
128.689
128.380
127.669
127.383
126.541
118.830
118.073
78.970
78.143
77.317
77.209
77.000
76.683
57.267
56.440
53.311
53.280
52.500
52.461
39.697
39.458
36.947
36.306
30.171
29.692
180
160
140
120
100
80
60
40
20
ppm

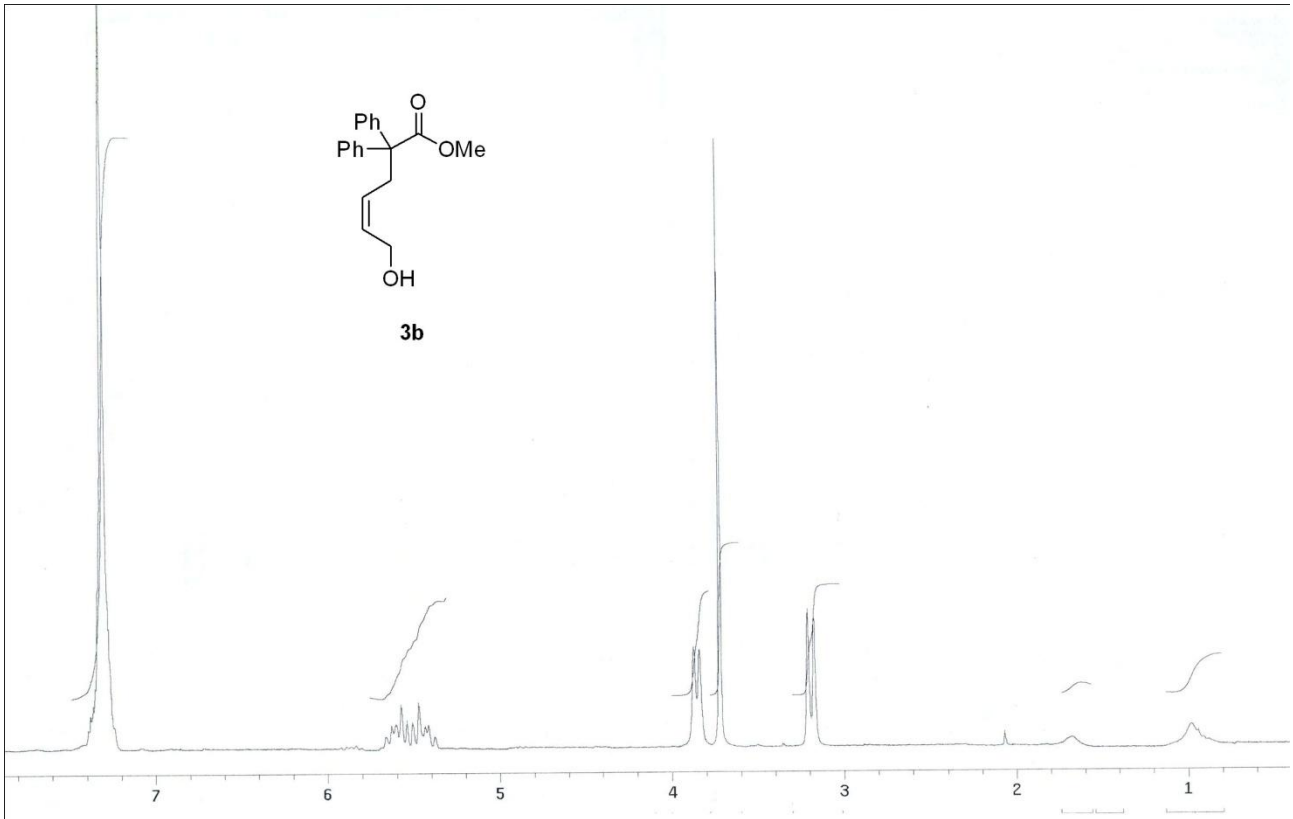

STANDARD PROTON PARAMETERS
Sample Name:
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: 1H_MC825_Br
Pulse Sequence: PROTON (s2pul)
Solvent: D2O
Data collected on: Apr 7 2011
MeO
Br
O
O
O
2h
7
6
5
4
3
2
1
ppm


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: 13C_mc825_Br
GEMINI-200 "gemini200"
Relax. delay 1.000 sec
Pulse 42.6 degrees
Acq. time 1.498 sec
Width 12500.0 Hz
15576 repetitions
OBSERVE C13, 50.2837643 MHz
DECOUPLE H1, 199.9760736 MHz
Power 30 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 18 hr, 54 min, 41 sec
168.790
165.414
133.725
132.660
120.403
120.077
79.048
76.973
77.630
77.000
76.363
54.695
54.604
53.368
44.294
44.112
29.683
160
140
120
100
80
60
40
20
ppm

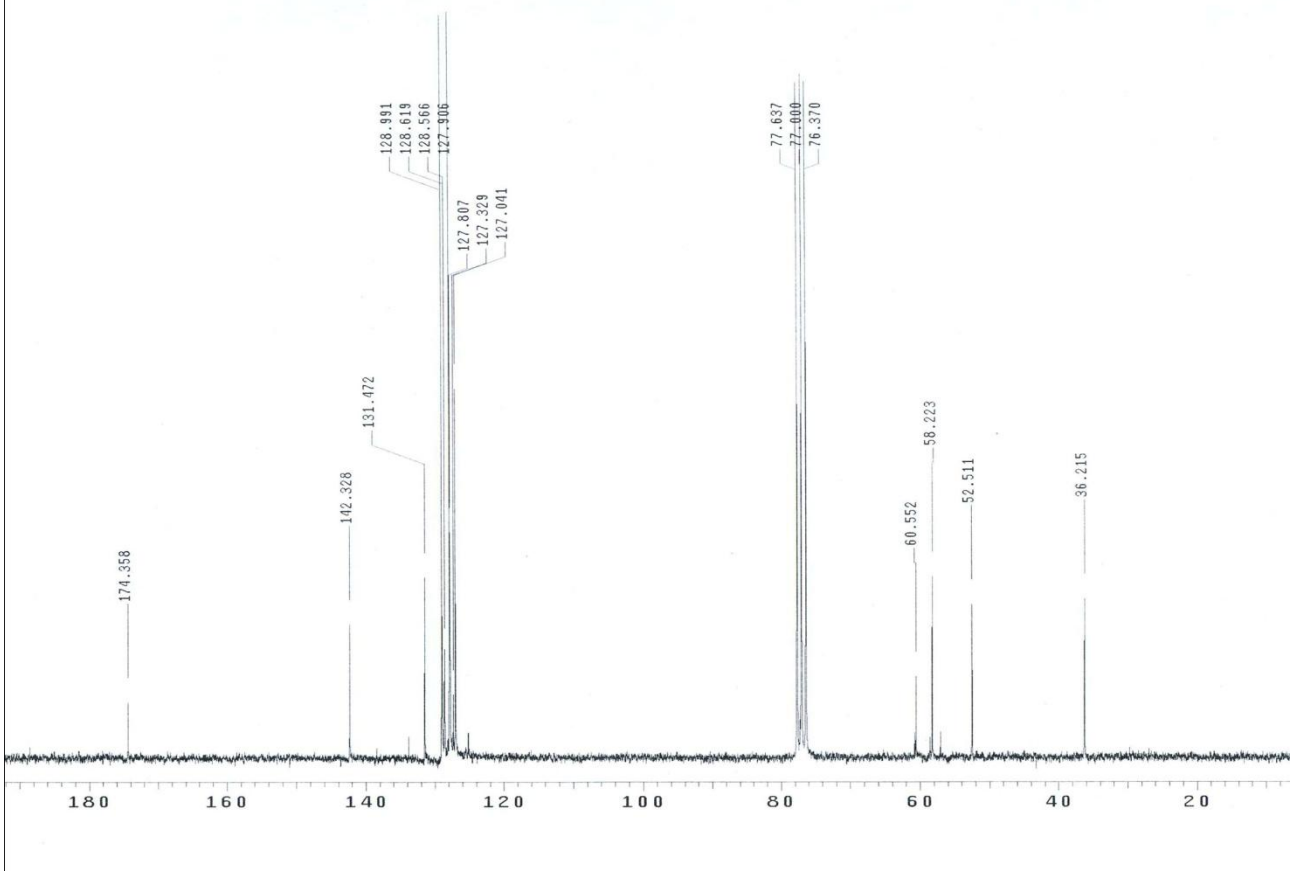

Sample Name:
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: 1H_MC826_acetale
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 8 2011
EtO
EtO
2i
10
9
8
7
6
5
4
3
2
1
-0
ppm

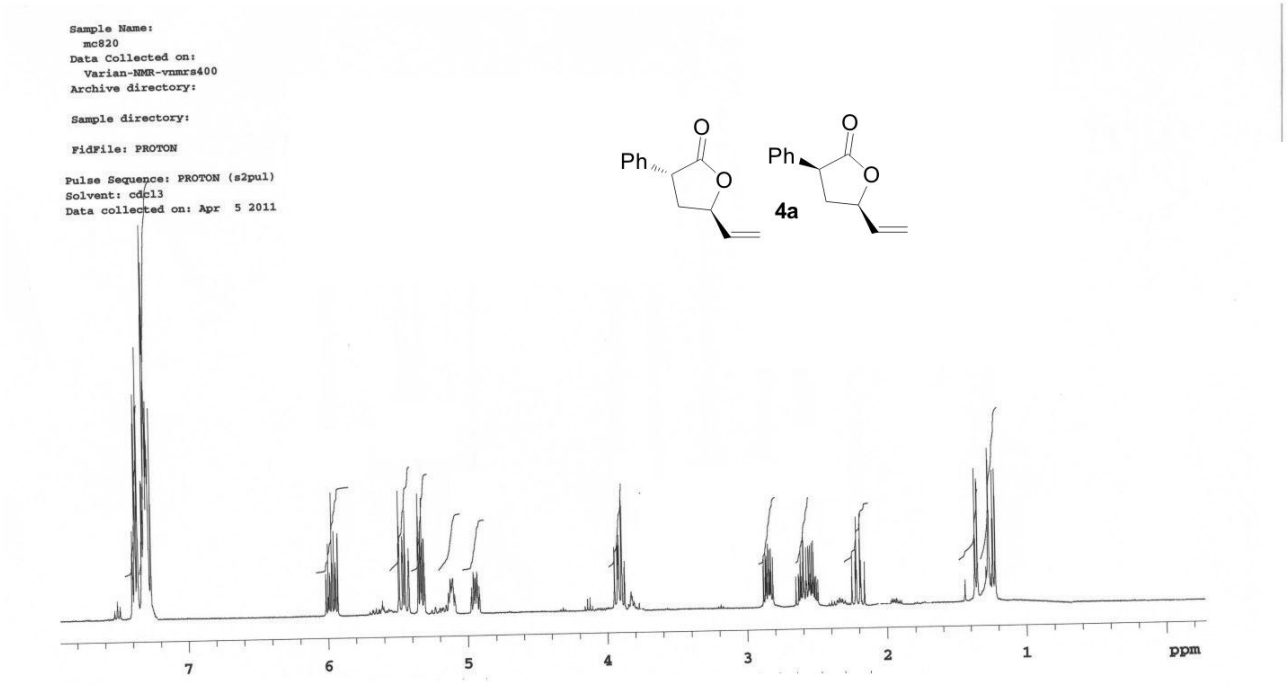

Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 20 2011
2j
7
6
5
4
3
2
1
ppm

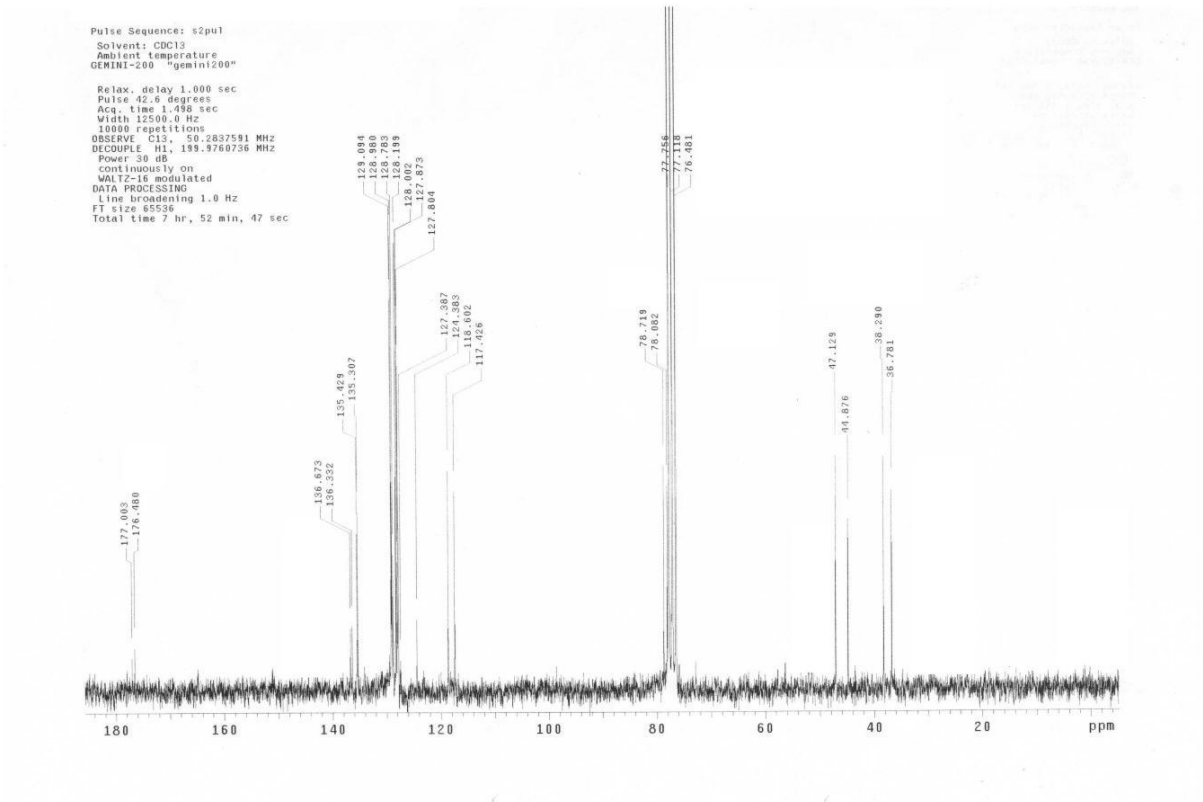

Ph
O
OMe
OH
3a
7
6
5
4
3
2
174.089
138.432
130.937
129.013
128.743
127.854
127.522
77.317
77.000
76.683
58.186
52.152
51.395
31.647
180
160
140
120
100
80
60
40
ppm

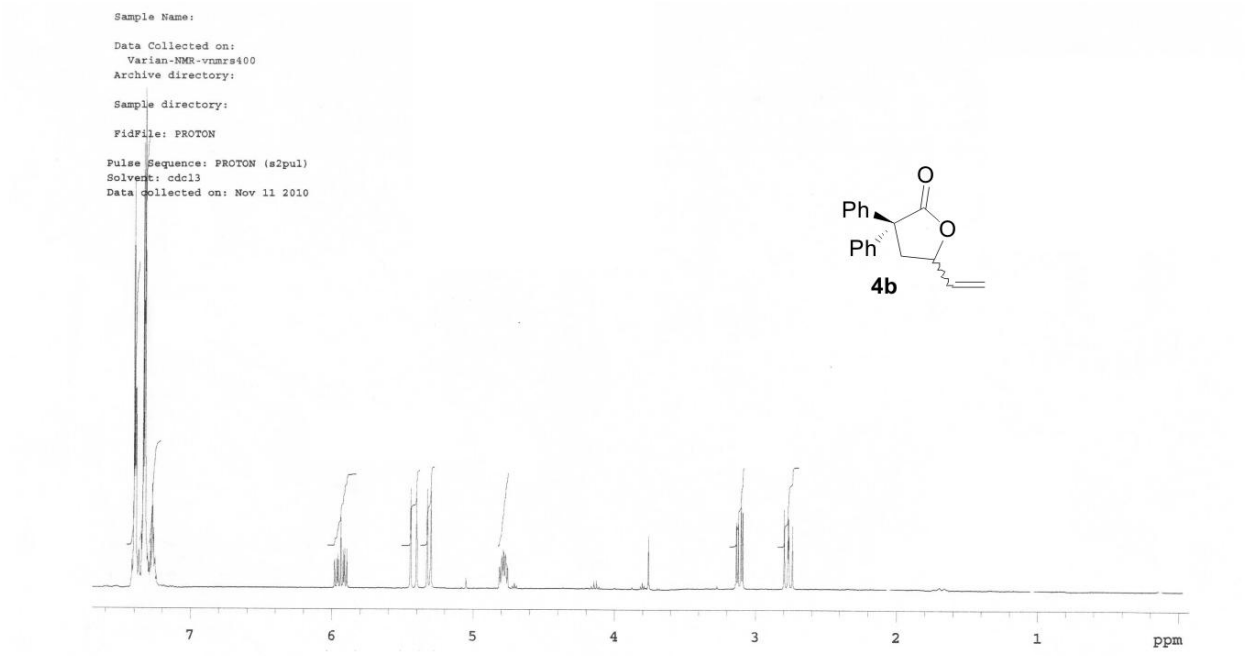

Ph
Ph
O
OMe
OH
7
6
5
4
3
2
1

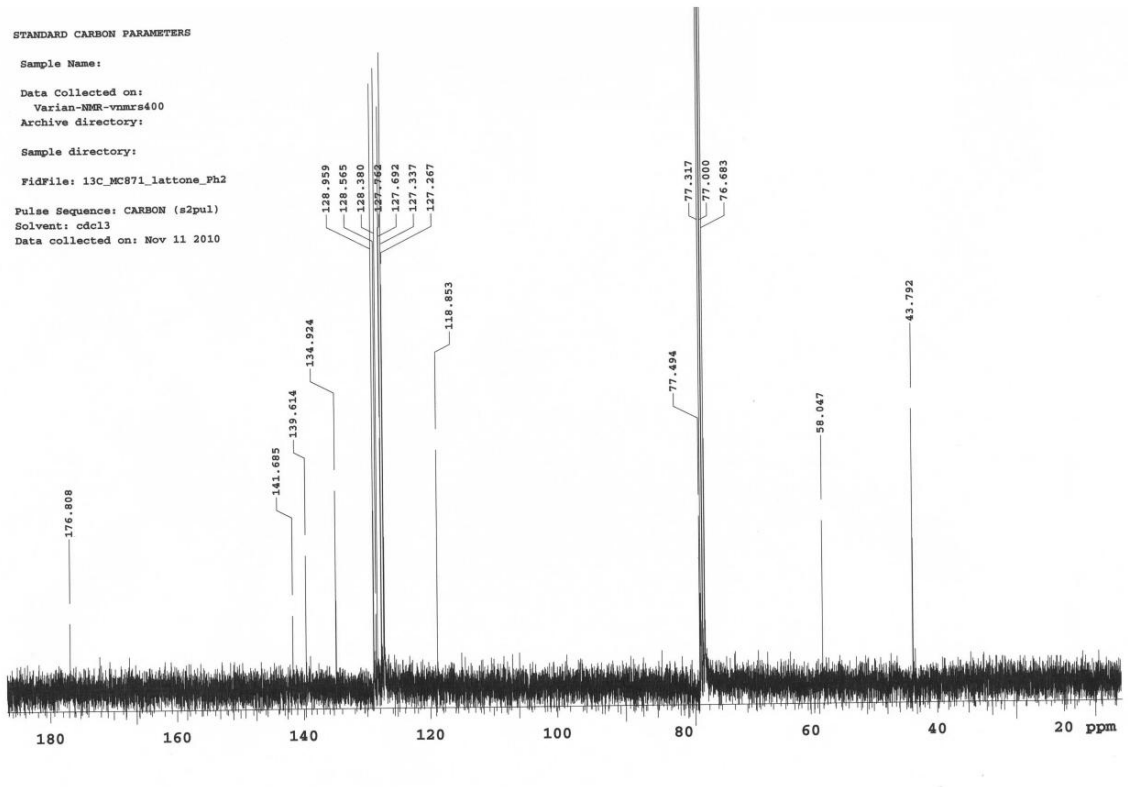
3b

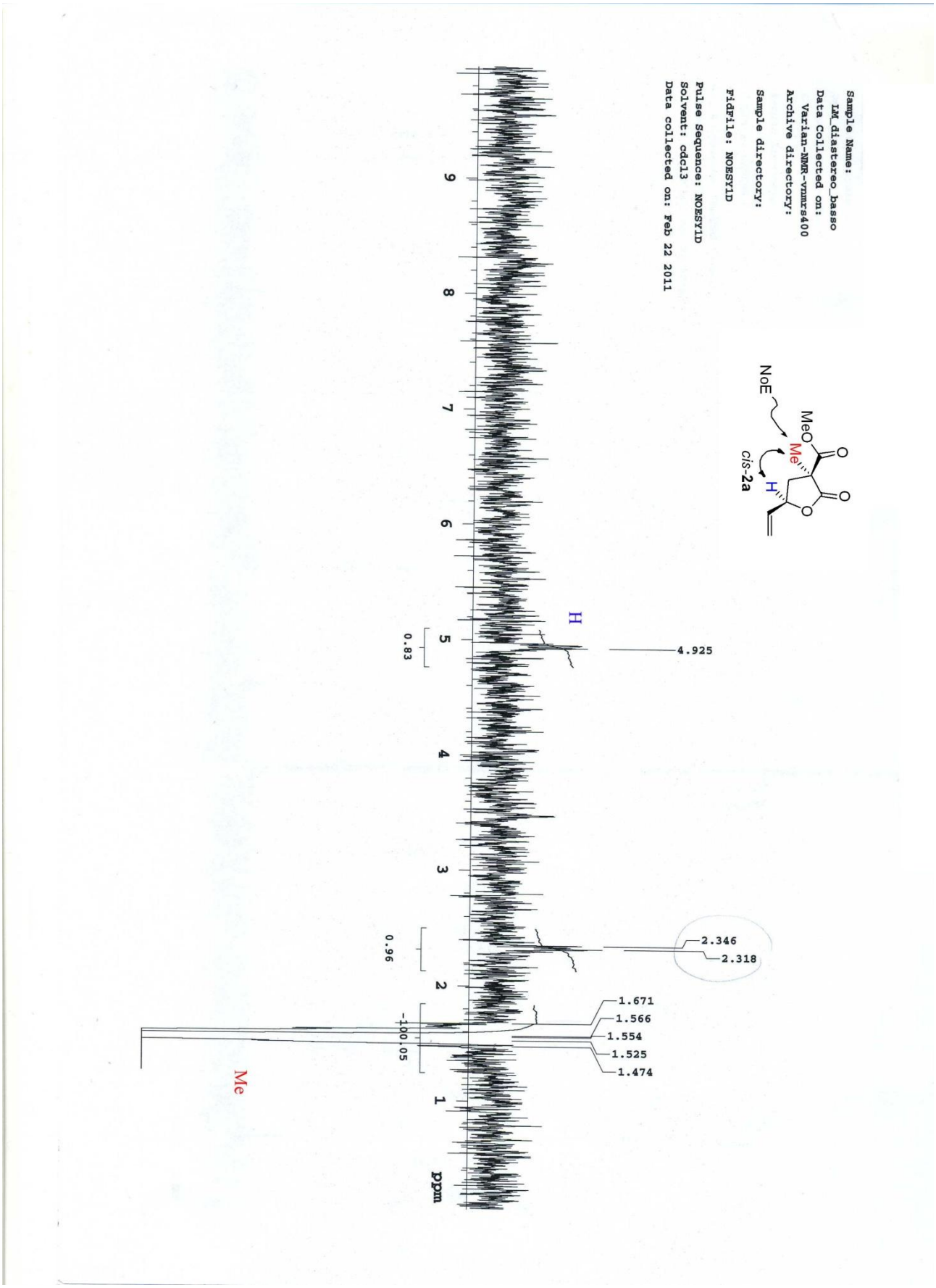

128.991
128.619
128.566
127.306
127.807
127.329
127.041
131.472
142.328
174.358
77.637
77.000
76.370
60.552
58.223
52.511
36.215
180
160
140
120
100
80
60
40
20


Sample Name:
mc820
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 5 2011
Ph
O
O
4a
7
6
5
4
3
2
1
ppm


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-200 "gemini200"
Relax. delay 1.000 sec
Pulse 42.6 degrees
Acq. time 1.498 sec
Width 12500.0 Hz
10000 repetitions
OBSERVE C13, 50.2837591 MHz
DECOUPLE H1, 199.9768736 MHz
Power 30 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 7 hr, 52 min, 47 sec
177.003
176.480
136.673
136.332
135.429
135.307
129.094
128.980
128.783
128.199
128.002
127.873
127.804
127.387
124.383
118.602
117.426
78.719
78.082
77.256
77.118
76.481
47.129
44.876
38.290
36.781
180
160
140
120
100
80
60
40
20
ppm


Sample Name:
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 11 2010
O
Ph
Ph
O
4b
7
6
5
4
3
2
1
ppm


STANDARD CARBON PARAMETERS
Sample Name:
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: 13C_MC871_lattone_Ph2
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Nov 11 2010
176.808
141.685
139.614
134.924
128.959
128.565
128.380
127.963
127.692
127.337
127.267
118.853
77.494
77.317
77.000
76.683
58.047
43.792
180
160
140
120
100
80
60
40
20
ppm


Sample Name:
LM_diastereo_basso
Data Collected on:
Varian-NMR-vnmrs400
Archive directory:
Sample directory:
FidFile: NOESY1D
Pulse Sequence: NOESY1D
Solvent: cdcl3
Data collected on: Feb 22 2011
NoE
MeO
Me
H
cis-2a
H
Me
4.925
2.346
2.318
1.671
1.566
1.554
1.525
1.474
0.83
0.96
1.00
1.05
ppm