Rhodium(III)-Catalyzed C–H/C–C Activation Sequence: Vinylcyclopropanes as Versatile Synthons in Direct C–H Allylation Reactions

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Supporting Information

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1. General Considerations

Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen in flame-dried glassware. If reaction was not carried out at room temperature, reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The dry solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under argon: THF (Na-benzophenone), 1,2-dichloroethane (CaH_2), dichloromethane (CaH_2). Anhydrous CF_3CH_2OH, DMF and MeOH were purchased from Acros Organics and stored under argon. Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Strem Chemicals, Alfa Aesar, ABCR and TCI Europe and used as received unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} plates. Visualization was accomplished with short wave UV light, or $KMnO_4$ staining solutions followed by heating. Flash chromatography was performed on silica gel (200-300 mesh) by standard technique.

^1H were recorded on a Bruker AV 400 in solvents as indicate. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; d_6-DMSO: δ_H = 2.50 ppm, δ_C = 39.52 ppm; d_4-MeOD: δ_H = 3.31 ppm, δ_C = 49.00 ppm). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR spectra were recorded on 101 MHz spectrometers. Chemical shifts were reported in parts per million relative to tetramethylsilane (δ = 0). High-resolution

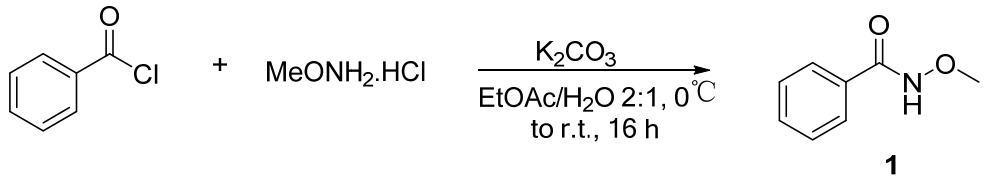
mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

No attempts were made to optimize yields for substrate synthesis.

2. Synthesis of Starting Materials 1, 2 and 4

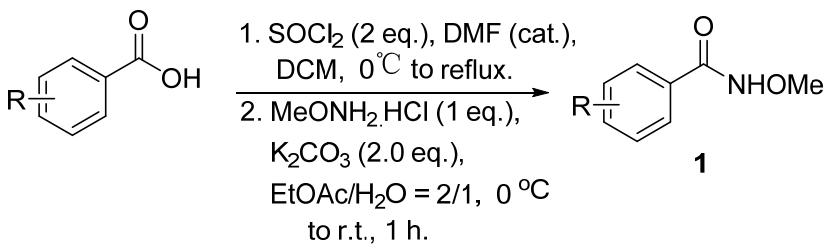
I) Synthesis of *N*-methoxybenzamide 1 and *N*-methoxymethacrylamide 4:

General Procedure A:



Following a modified procedure by Fagnou et al.[1] in a 100 mL round-bottom flask, *O*- methylhydroxylamine (835 mg, 10.00 mmol, 1.00 eq.) and K_2CO_3 (2.76 g, 20.00 mmol, 2.00 eq.) were combined in a 2:1 mixture of EtOAc (50 mL) and H_2O (25 mL). The flask was capped and the mixture was cooled in an ice bath. No special precautions were taken to exclude moisture or oxygen. The acid chloride (10.0 mmol, 1.0 eq.) was added dropwise and the mixture was stirred to r.t. over 16 h. The reaction mixture was then diluted with EtOAc (30 mL) and washed twice with sat. $NaHCO_3$ and brine. The organic layers were dried over Na_2SO_4, filtered and concentrated. The purification was made by flash column chromatography using an appropriate solvent mixture (petroleum ether/ethyl acetate = 2/1) to obtain the pure product.

General procedure B:

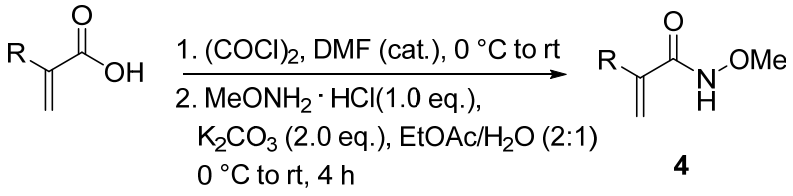


Following a procedure by Fagnou et. al.[1]

1) To a solution of the carboxylic acid (10.0 mmol, 1.0 eq.) in dry CH_2Cl_2 (60 mL) at 0 °C under an atmosphere of N_2 was added dropwise $SOCl_2$ (1.5 mL, 20 mmol, 2 eq.) followed by a catalytic amount of dry DMF (3 drops). The reaction was allowed to stir at r.t. until completion (typically 3 h). The solvent was then removed under reduce pressure to afford the corresponding crude acid chloride.

2) Methoxyamine hydrochloride (835.2 mg, 10.0 mmol, 1.0 eq.) was added to a biphasic mixture of K_2CO_3 (2.76 g, 6.0 mmol, 2.0 eq.) in a 2:1 mixture of EtOAc (50 mL) and H_2O (25 mL). The resulting solution was cooled to 0 °C followed by dropwise addition of the unpurified acid chloride dissolved in a minimum amount of EtOAc. The flask containing the acid chloride was then rinsed with additional EtOAc. The reaction was allowed to stir for 30 min at rt. Afterwards, the phases were separated and the aqueous phase was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The pure products were purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as eluent.

General Procedure C:



Following a modified procedure by Singh et al.[2]

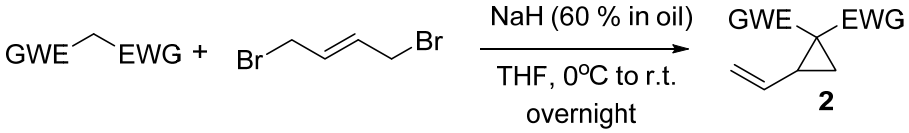
1) To a solution of the carboxylic acid (10.0 mmol, 1.0 eq.) in dry CH_2Cl_2 (60 mL) at 0 °C under N_2 was added dropwise $(COCl)_2$ (0.64 mL, 10 mmol, 1 eq.) followed by a catalytic amount of dry DMF (2 drops). The reaction was allowed to stir at r.t.

until completion (typically 3 h). The solvent was then removed under reduce pressure to afford the corresponding crude acid chloride.

2) Methoxyamine hydrochloride (920 mg, 11.0 mmol, 1.1 eq.) was added to a biphasic mixture of Et_3N (1.9 mL, 15.0 mmol, 1.5 eq.) in dry CH_2Cl_2 (30 mL). The resulting solution was cooled to 0 °C followed by dropwise addition of the unpurified acid chloride dissolved in a minimum amount of dry CH_2Cl_2. The reaction was allowed to stirred overnight at rt. Afterwards, the phases were separated and the aqueous phase was extracted twice with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The pure products were purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as eluent.

II) Synthesis of Vinylcyclopropanes (VCPs) 2

General Procedure D:



Following a modified procedure by Johnson et al,[3,4] and Plietker et al.[5]

A flame-dried flask (250 mL in volume) was charged with NaH (60 % in oil, 3.06 g, 44 mmol, 2.2 equiv) and dry THF (60 mL) with a stir bar under an atmosphere of nitrogen. The suspension was cooled to 0 °C (ice bath) and the corresponding activated methylene compound (20 mmol, 1 equiv) was added dropwise via syringe (caution: gas evolution). The reaction mixture was allowed to warm to r.t. and stirred for 1 h. 1,4-Dibromobut-2-ene (4.278 g, 20 mmol, 1 equiv) in 8 mL dry THF was added slowly via syringe (caution: gas evolution) at 0°C (ice bath). After the suspension mixture was allowed to stir under N_2 atmosphere overnight, sat. NH_4Cl

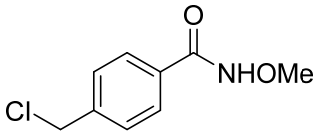
was added to quench the reaction. The aqueous layer was extracted with EtOAc (2 x 100 mL), washed with brine (100 mL) and water (100 mL), dried over Na_2SO_4, and concentrated by vacuum to afford the crude products. The crude products was purified by column chromatography to give the corresponding product.

2. Characterization of Starting Materials 1, 2 and 4

Preparation and Characterization of *N*-methoxybenzamides 1 and *N*-methoxymethacryl amides 4

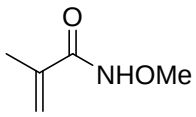
N-methoxybenzamides **1a-1k**, **1m-1s**, **1u** were prepared by following the procedure reported by Fagnou. [1] All the characteristic datas are consistent with the data reported before.[6-8]

4-(chloromethyl)-*N*-methoxybenzamide (1l)



Following general procedure B, using 4-(hydroxymethyl)benzoic acid as starting material, **1l** was obtained as a white solid (1.23 g, 6.5 mmol, 65 %). $\mathbf{R_F}$ (Petroleum ether/EtOAc 2:1): 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 4.60 (s, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, MeOD) δ 167.9, 143.9, 130.3, 130.2, 128.3, 64.5, 21.6.

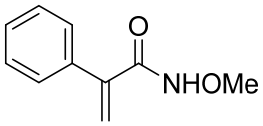
***N*-methoxymethacrylamide (4a)**



Following general procedure C, **4a** was obtained as a yellow oil (368 mg, 3.2 mmol, 32 %). $\mathbf{R_F}$ (Petroleum ether /EtOAc 2:1): 0.21; **1** H

NMR (400 MHz, CDCl3) δ 8.93 (bs, 1H), 5.73 – 5.59 (m, 1H), 5.42 – 5.26 (m, 1H), 3.79 (s, 3H), 1.93 (s, 3H). The spectral characteristics of **4a** were agreement with the preciously published data. [9]

***N*-methoxy-2-phenylacrylamide (4b)**

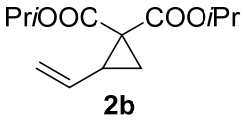


Following general procedure C, **4b** was obtained as a white solid (437 mg, 2.4 mmol, 80%). $\mathbf{R_F}$ (Petroleum ether/EtOAc 2:1): 0.32. The characteristics data is consistent with the one reported before. [10]

Preparation and Characterization of VCPs

The following VCPs were prepared by following the same procedure by Johnson et al. and Plietker et al. **2a**[11], **2e**[12], **2h-2i**[13].

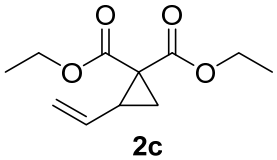
Diisopropyl 2-vinylcyclopropane-1,1-dicarboxylate (2b)



2b

Following general procedure D, **2b** was obtained as a colorless oil (3.94 g, 16.2 mmol, 81%). $\mathbf{R_F}$ (petroleum ether/EtOAc = 32:1): 0.33. The characteristics data is consistent with the one reported before.[14]

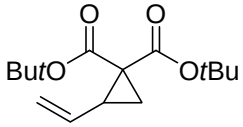
Diethyl 2-vinylcyclopropane-1,1-dicarboxylate (2c)



2c

Following general procedure D, **2c** was obtained as a colorless oil (3.68 g, 17.4 mmol, 87%). $\mathbf{R_F}$ (petroleum ether/EtOAc = 32:1): 0.42. The characteristics data is consistent with the one reported before.[15]

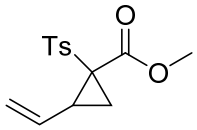
Di-*tert*-butyl 2-vinylcyclopropane-1,1-dicarboxylate (2d)



2d

Following general procedure D, **2d** was obtained as a white solid (3.32 g, 10.4 mmol, 52%). $\mathbf{R_F}$ (petroleum ether/EtOAc = 32:1): 0.22. The characteristics data is consistent with the one reported before.[16]

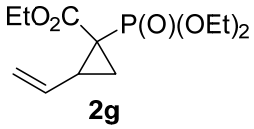
Methyl 1-tosyl-2-vinylcyclopropane-1-carboxylate (2f)[17]



2f

Following general procedure D, **2f** was obtained as a white solid (2.59 g, 10.8 mmol, 54%). $\mathbf{R_F}$ (petroleum ether/EtOAc = 16:1): 0.22; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 5.54 (ddd, *J* = 17.2, 10.1, 8.4 Hz, 1H), 5.38 (d, *J* =17.5 Hz, 1H), 5.19 (d, *J* = 10.1 Hz, 1H), 3.64 (s, 3H), 2.88 (dd, *J* = 18.0, 8.4 Hz, 1H), 2.45 (s, 3H), 2.25 (dd, *J* = 9.9, 5.5 Hz, 1H), 1.96 (dd, *J* = 8.2, 5.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 144.7, 136.9, 131.1, 129.5, 128.9, 120.4, 52.7, 51.2, 32.0, 21.6, 19.7.

Diethoxyphosphoryl-2-vinylcyclopropane-1-carboxylic acid ethyl ester (2g)



2g

Following general procedure D, **2g** was obtained as a white solid (279 mg, 1.0 mmol, 35%). $\mathbf{R_F}$ (petroleum ether/EtOAc = 4:1): 0.32. The characteristics data is consistent with the one reported before.[18]

Preparation and Characterization of 1-(*p*-tolyl)ethan-1-one oxime (2v) and 2-pyrimidylindoles (2w and 2x)

1-(*p*-tolyl)ethan-1-one oxime **(2v)** were prepared readily from the corresponding N-H indoles and 2-chloropyrimidine according to the literature.[19]

Both of the 2-pyrimidylindoles (**2w**, **2x**) were prepared readily from the corresponding *N*-H indoles and 2-chloropyrimidine according to the literature.[20]

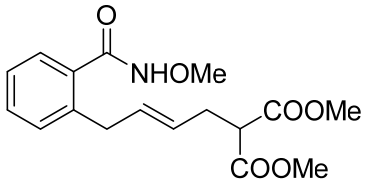
4. General Procedure for the Rh(III)-Catalyzed C-H/C-C activation with vinylcyclopropanes

General Procedure E:

A 15 mL-schlenk tube charged with a stirring bar, was added *N*-methoxybenzamide **1** (0.5 mmol, 1 equiv) and vinylcyclopropane **2** (0.6 mmol, 1.2 equiv). $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (20.8 mg, 0.025 mmol, 5 mol%) and CsOAc (96.0 mg, 0.5 mmol, 1.0 equiv), CF_3CH_2OH (3 mL) were added subsequently into the reaction vessel. The reaction was allowed to stir at 30°C until the complete consumption of **1** as monitored by TLC analysis (typically 24 hours). The reaction mixture was then diluted with EtOAc (20 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **3**.

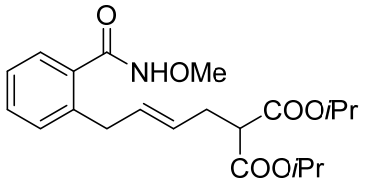
5. Characterization of Products 3

Dimethyl (*E*)-2-(4-(2-(methoxycarbamoyl)phenyl)but-2-en-1-yl)malonate (3aa)



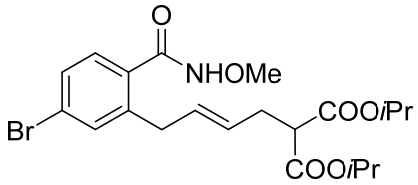
Following general procedure E, the reaction was ran for 18 h, **3aa** was obtained as a colorless oil (52.3 mg, 0.156 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.72 (s, 1H), 7.37 (ddd, *J* = 7.2, 5.7, 1.4 Hz, 2H), 7.37 (ddd, *J* = 7.2, 5.7, 1.4 Hz, 3H), 7.27 – 7.15 (m, 3H), 7.26 – 7.17 (m, 2H), 5.74 – 5.63 (m, 1H), 5.43 – 5.30 (m, 1H), 3.90 (s, 3H), 3.63 (s, 6H), 3.48 (d, *J* = 6.4 Hz, 2H), 3.41 (t, *J* = 7.5 Hz, 1H), 2.58 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 168.0, 138.6, 133.0, 132.7, 130.5, 130.2, 127.8, 126.9, 126.2, 64.4, 52.4, 51.7, 35.9, 31.6. **ESI-MS:** calculated $[C_{17}H_{21}NO_6Na]^+$: 358.1267, found: 358.1262.

Diisopropyl (*E*)-2-(4-(2-(methoxycarbamoyl)phenyl)but-2-en-1-yl)malonate (3ab)



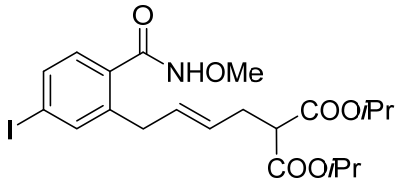
Following general procedure E, **3ab** was obtained as a colorless oil (61.8 mg, 0.158 mmol, 79%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.9 Hz, 1H), 7,95 (s, 1H), 7.33 (s, 1H), 7.16 (dd, *J* = 7.9, 0.9 Hz, 1H), 5.90 (d, *J* = 9.4 Hz, 1H), 4.27 (t, *J* = 2.0 Hz, 2H), 2.41 (d, *J* = 15.8 Hz, 3H), 2.31 (ddd, *J* = 14.1, 9.1, 3.0 Hz, 1H), 1.82-1.61 (m, 5H), 1.39-1.10 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 142.8, 138.0, 134.3, 128.7, 128.0, 126.2, 124.4, 123.4, 41.7, 37.3, 33.0, 25.9, 25.8, 21.9. **ESI-MS:** calculated $[C_{21}H_{29}NO_6H]^+$: 392.2067, found: 392.2064.

Diisopropyl (*E*)-2-(4-(5-bromo-2-(methoxycarbamoyl)phenyl)but-2-en-1-yl)malonate (3bb)



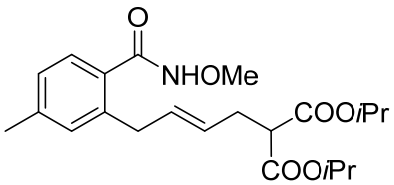
Following general procedure E, **3bb** was obtained as a yellow oil (75 mg, 0.160 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 7.47 – 7.30 (m, 2H), 7.28 – 7.15 (m, 1H), 5.71 – 5.55 (m, 1H), 5.43 – 5.28 (m, 1H), 5.05 – 4.83 (m, 2H), 3.87 (s, 3H), 3.41 (d, *J* = 6.3 Hz, 2H), 3.28 (t, *J* = 7.5 Hz, 1H), 2.54 (t, *J* = 7.0 Hz, 2H), 1.15 (dd, *J* = 13.1, 6.3 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 167.2, 140.9, 133.2, 132.1, 131.6, 129.4, 129.3, 127.9, 124.7, 69.1, 64.4, 52.3, 35.7, 31.4, 21.5, 21.4. **ESI-MS:** calculated $[C_{21}H_{28}NBrO_6H]^+$: 470.1173, found: 470.1171.

Diisopropyl (*E*)-2-(4-(5-iodo-2-(methoxycarbamoyl)phenyl)but-2-en-1-yl)malonate (3cb)



Following general procedure E, **3cb** was obtained as a yellow oil (77.6 mg, 0.150 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 1H), 5.74 – 5.51 (m, 1H), 5.45 – 5.24 (m, 1H), 5.02 – 4.82 (m, 2H), 3.85 (s, 3H), 3.37 (d, *J* = 6.4 Hz, 2H), 3.28 (t, *J* = 7.5 Hz, 1H), 2.53 (t, *J* = 7.2 Hz, 2H), 1.16 (dd, *J* = 13.1, 6.3 Hz, 12H).^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 167.2, 140.8, 139.0, 135.3, 132.7, 131.6, 129.4, 127.8, 96.9, 69.1, 64.3, 52.3, 35.5, 31.4, 21.6, 21.5. **ESI-MS:** calculated $[C_{21}H_{28}INO_6H]^+$: 518.1034, found: 518.1036.

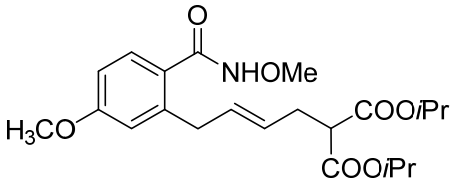
Diisopropyl (*E*)-2-(4-(2-(methoxycarbamoyl)-5-methylphenyl)but-2-en-1-yl)malonate (3db)



Following general procedure E, **3db** was obtained as a colorless oil (59.9 mg, 0.148 mmol, 74%). ^{1}H

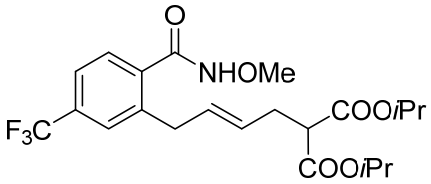
NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.28 (s, 1H), 7.03 (d, *J* = 8.6 Hz, 2H), 5.74 – 5.62 (m, 1H), 5.41 – 5.30 (m, 1H), 5.00 – 4.87 (m, 2H), 3.90 (s, 3H), 3.45 (d, *J* = 6.3 Hz, 2H), 3.30 (t, *J* = 7.6 Hz, 1H), 2.56 (t, *J* = 7.0 Hz, 2H), 2.34 (s, 3H), 1.17 (dd, *J* = 13.9, 6.3 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 168.2, 140.6, 138.5, 132.6, 131.0, 130.2, 127.9, 127.0, 126.8, 68.9, 64.3, 52.4, 35.9, 31.5, 21.5, 21.5, 21.2. **ESI-MS:** calculated $[C_{22}H_{31}NO_6H]^+$: 406.2224, found: 406.2228.

Diisopropyl (*E*)-2-(4-(5-methoxy-2-(methoxycarbamoyl)phenyl)but-2-en-1-yl)malonate (3eb)



Following general procedure E, the reaction was ran for 28 h, **3eb** was obtained as yellow oil (64.8 mg, 0.154 mmol, 77%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 7.32 (d, *J* = 9.1 Hz, 1H), 6.71 (m, 2H), 5.74 – 5.60 (m, 1H), 5.44 – 5.31 (m, 1H), 4.94 (m, 2H), 3.86 (s, 3H), 3.80 (s, 3H), 3.46 (d, *J* = 6.3 Hz, 2H), 3.29 (t, *J* = 7.5 Hz, 1H), 2.55 (t, *J* = 7.1 Hz, 2H), 1.17 (dd, *J* = 11.7, 6.3 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 168.2, 161.2, 140.9, 132.2, 129.6, 127.3, 125.4, 115.9, 111.2, 68.9, 64.3, 55.3, 52.4, 36.1, 31.5, 21.5, 21.4. **ESI-MS:** calculated $[C_{22}H_{31}NO_7H]^+$: 422.2173, found: 422.2174.

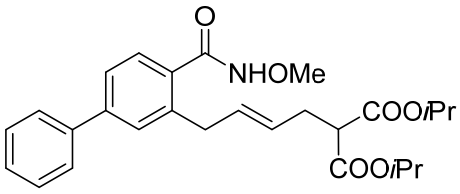
Diisopropyl (*E*)-2-(4-(2-(methoxycarbamoyl)-5-(trifluoromethyl)phenyl)but-2-en-1-yl)malonate (3fb)



Following general procedure E, **3fb** was obtained as yellow oil (70.7 mg, 0.154 mmol, 77%). ^1H NMR (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 7.48 (d, *J* = 2.0 Hz, 2H), 7.45 (s, 1H), 5.70 – 5.56 (m, 1H), 5.43 – 5.27 (m, 1H), 4.88 (dt, *J* = 12.2, 6.0 Hz, 2H), 3.91 (s,

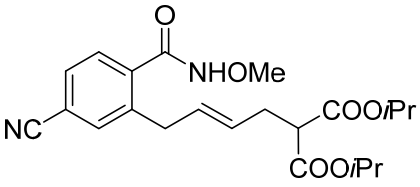
3H), 3.51 (d, *J* = 6.3 Hz, 2H), 3.28 (t, *J* = 7.5 Hz, 1H), 2.54 (t, *J* = 7.1 Hz, 2H), 1.13 (dd, *J* = 20.8, 6.2 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 166.8, 139.6., 136.8, 132.5, 132.2, 131.7, 128.5, 128.0, 126.9, 125.0, 123.2, 122.2, 69.1, 64.4, 52.3, 35.8, 31.4, 21.5, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.01, **ESI-MS:** calculated $[C_{22}H_{28}F_3NO_6H]^+$: 460.1942, found: 460.1942.

Diisopropyl (*E*)-2-(4-(4-(methoxycarbamoyl)-[1,1'-biphenyl]-3-yl)but-2-en-1-yl)malonate (3gb)



Following general procedure E, **3gb** was obtained as yellow oil (71.9 mg, 0.154 mmol, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.61 – 7.52 (m, 2H), 7.50 – 7.40 (m, 5H), 7.40 – 7.33 (m, 1H), 5.74 – 5.67 (m, 1H), 5.43 – 5.36 (m, 1H), 4.90 (dt, *J* = 12.5, 6.3 Hz, 2H), 3.90 (s, 3H), 3.53 (d, *J* = 6.3 Hz, 2H), 3.29 (t, *J* = 7.6 Hz, 1H), 2.55 (t, *J* = 7.2 Hz, 2H), 1.12 (dd, *J* = 13.9, 6.3 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 168.0, 143.4, 140.1, 139.1, 132.4, 131.9, 129.0, 128.8, 128.5, 127.8, 127.3, 127.1, 124.9, 69.0, 64.4, 52.4, 36.1, 31.5, 21.5, 21.4. **ESI-MS:** calculated $[C_{27}H_{33}NO_6H]^+$: 468.2381, found: 468.2385.

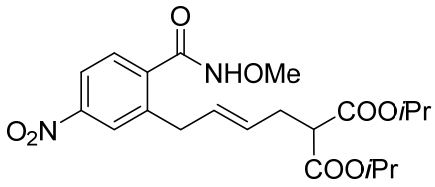
Diisopropyl (*E*)-2-(4-(5-cyano-2-(methoxycarbamoyl)phenyl)but-2-en-1-yl)malonate (3hb)



Following general procedure E, 50°C was used, **3hb** was obtained as a white solid (55.7 mg, 0.134 mmol, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.61 – 7.42 (m, 3H),5.66 – 5.59 (m, 1H), 5.38– 5.33 (m, 1H), 4.94-4.88 (m, 2H), 3.92 (s, 3H), 3.49 (d, *J* = 6.0 Hz, 2H), 3.29 (t, *J* = 7.4 Hz, 1H), 2.55 (t, *J* = 7.0 Hz, 2H),

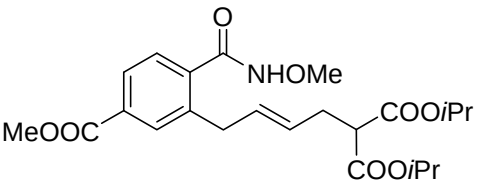
1.20 (dd, 13.2, 4.2 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 166.0, 140.3, 137.4, 133.4, 132.3, 130.7, 129.8, 128.7, 117.9, 114.1, 69.1, 64.3, 52.1, 35.4, 21.5, 21.4. **ESI-MS:** calculated $[C_{27}H_{28}N_2O_6H]^+$: 417.2020, found: 417.2023.

Diisopropyl (*E*)-2-(4-(2-(methoxycarbamoyl)-5-nitrophenyl)but-2-en-1-yl)malonate (3ib)



Following general procedure E, 50°C was used, **3ib** was obtained as yellow oil (69.8 mg, 0.160 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (s, 1H), 8.18 – 7.96 (m, 2H), 7.54 (d, *J* = 8.2 Hz, 1H), 5.75 – 5.58 (m, 1H), 5.48 – 5.29 (m, 1H), 4.92 (m, 2H), 3.92 (s, 3H), 3.56 (d, *J* = 6.1 Hz, 2H), 3.30 (t, *J* = 7.4 Hz, 1H), 2.56 (t, *J* = 7.1 Hz, 2H), 1.16 (dd, *J* = 15.0, 6.2 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 165.0, 147.8, 140.0, 138.2, 129.8, 128.1, 127.7, 123.9, 120.3, 68.2, 63.4, 51.2, 34.8, 30.4, 20.5, 20.4. **ESI-MS:** calculated $[C_{21}H_{28}N_2O_8H]^+$: 437.19184, found: 437.1917.

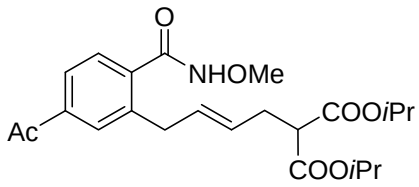
Diisopropyl (*E*)-2-(4-(2-(methoxycarbamoyl)-5-(methoxycarbonyl)phenyl)but-2-en-1-yl)malonate (3jb)



Following general procedure E, **3jb** was obtained as yellow oil (74.5 mg, 0.166 mmol, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 7.93 – 7.80 (m, 2H), 7.42 (d, *J* = 7.8 Hz, 1H), 5.73 – 5.58 (m, 1H), 5.36 – 5.25 (m, 1H), 4.88 (dt, *J* = 12.3, 6.1 Hz, 2H), 3.91 (s, 6H), 3.49 (d, *J* = 6.2 Hz, 2H), 3.27 (t, *J* = 7.5 Hz, 1H), 2.53 (t, *J* = 7.2 Hz, 2H), 1.13 (dd, *J* = 16.4, 6.2 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 166.9, 166.2, 139.0, 137.2, 131.7, 131.6, 131.0,

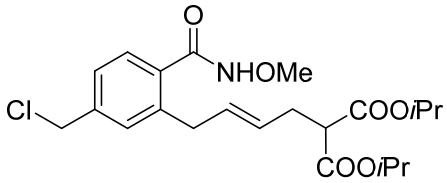
127.9, 127.7, 127.2, 68.9, 64.2, 52.2, 35.7, 31.4, 21.4, 21.4. **ESI-MS:** calculated $[C_{23}H_{31}NO_8H]^+$: 450.2122, found: 450.2127.

Diisopropyl (*E*)-2-(4-(5-acetyl-2-(methoxycarbamoyl)phenyl)but-2-en-1-yl)malonate (3kb)



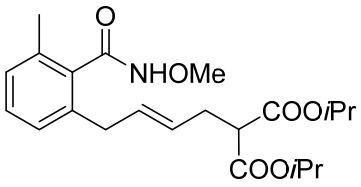
Following general procedure E, **3kb** was obtained as yellow oil (69.3 mg, 0.160 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 7.86 – 7.70 (m, 2H), 7.45 (d, *J* = 7.8 Hz, 1H), 5.73 – 5.61 (m, 1H), 5.41 – 5.27 (m, 1H), 4.90 (dt, *J* = 12.3, 6.1 Hz, 2H), 3.91 (s, 3H), 3.51 (d, *J* = 6.3 Hz, 2H), 3.28 (t, *J* = 7.5 Hz, 1H), 2.60 (s, 3H), 2.54 (t, *J* = 7.2 Hz, 2H), 1.14 (dd, *J* = 16.5, 6.2 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 168.7, 167.1, 139.1, 138.5, 137.6, 132.0, 130.0, 128.4, 127.7, 126.2, 69.1, 64.4, 52.3, 35.9, 31.4, 21.5, 21.4. **ESI-MS:** calculated $[C_{23}H_{31}NO_7H]^+$: 434.2173, found: 434.2176.

Diisopropyl (*E*)-2-(4-(5-(chloromethyl)-2-(methoxycarbamoyl)phenyl)but-2-en-1-yl)malonate (3lb)



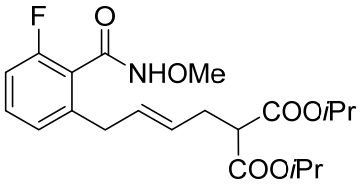
Following general procedure E, **3lb** was obtained as colorless oil (65.9 mg, 0.150 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.7 Hz, 1H), 7.20 (m, 2H), 5.65 – 5.56 (m, 1H), 5.38 – 5.28 (m, 1H), 4.89 (dt, *J* = 12.5, 6.2 Hz, 2H), 4.51 (s, 2H), 3.83 (s, 3H), 3.41 (d, *J* = 6.4 Hz, 2H), 3.25 (t, *J* = 7.5 Hz, 1H), 2.51 (t, *J* = 7.2 Hz, 2H), 1.12 (dd, *J* = 15.1, 6.3 Hz, 14H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 167.5, 139.8, 139.2, 133.1, 131.9, 130.2, 128.3, 127.5, 126.3, 69.0, 64.3, 52.3, 45.4, 35.8, 31.4, 21.5, 21.5. **ESI-MS:** calculated $[C_{22}H_{30}ClNO_6H]^+$: 440.1834, found: 440.1836.

Diisopropyl (E)-2-(4-(2-(methoxycarbamoyl)-3-methylphenyl)but-2-en-1-yl)malonate (3mb)



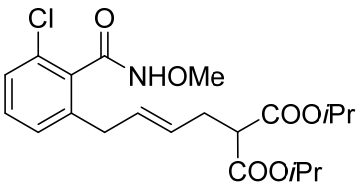
Following general procedure E, 50ºC was ised, **3mb** was obtained as a colorless oil (52.3 mg, 0.134 mmol, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 5.70 – 5.58 (m, 1H), 5.41 – 5.26 (m, 1H), 4.97 – 4.85 (m, 2H), 3.91 (s, 3H), 3.38 – 3.18 (m, 3H), 2.54 (t, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 1.15 (dd, *J* = 13.1, 6.3 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 167.0, 137.2, 135.9, 133.5, 132.7, 129.5, 128.0, 127.0, 127.0, 69.0, 64.2, 52.4, 36.1, 31.4, 21.5, 21.5, 19.0. **ESI-MS:** calculated $[C_{22}H_{31}NO_6H]^+$: 406.2224, found: 406.2224.

Diisopropyl (*E*)-2-(4-(3-fluoro-2-(methoxycarbamoyl)phenyl)but-2-en-1-yl)malonate (3nb)



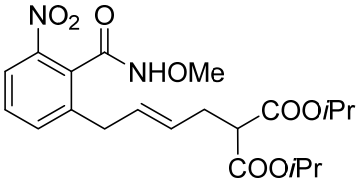
Following general procedure E, 50oC was used, 3nb was obtained as a yellow oil (75.3 mg, 0.184 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.92 (t, *J* = 8.5 Hz, 1H), 5.69 – 5.55 (m, 1H), 5.45 – 5.31 (m, 1H), 4.94 (td, *J* = 12.5, 6.3 Hz, 2H), 3.88 (s, 3H), 3.37 (d, *J* = 6.0 Hz, 2H), 3.29 (t, *J* = 7.3 Hz, 1H), 2.54 (t, *J* = 7.0 Hz, 2H), 1.17 (dd, *J* = 12.0, 6.2 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 162.4, 159.6 (d, *J* = 242.4 Hz), 141.0, 131.5, 131.1 (d, *J* = 10.1 Hz), 127.6, 125.3, 121.6 (d, *J* = 20.2 Hz), 113.4(d, *J* = 30.3 Hz), 69.0, 64.3, 52.3, 35.7, 31.4, 21.5, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.62. ESI-MS: calculated $[C_{21}H_{28}FNO_6H]^+$: 410.1973, found: 410.1977.

Diisopropyl (*E*)-2-(4-(3-chloro-2-(methoxycarbamoyl)phenyl)but-2-en-1-yl)malonate (3ob)



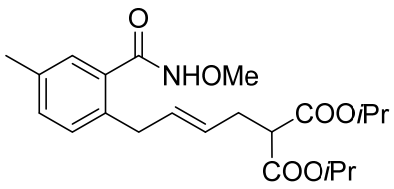
Following general procedure E, 50°C was used, **3ob** was obtained as a yellow oil (60.4 mg, 0.142 mmol, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 7.29 – 7.19 (m, 2H), 7.07 (d, *J* = 6.3 Hz, 1H), 5.66 – 5.55 (m, 1H), 5.40 – 5.29 (m, 1H), 4.99 – 4.85 (m, 2H), 3.92 (s, 3H), 3.33 (d, *J* = 6.3 Hz, 2H), 3.28 (t, *J* = 7.4 Hz, 1H), 2.53 (t, *J* = 7.1 Hz, 2H), 1.15 (dd, *J* = 13.3, 6.2 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 163.9, 140.1, 132.9, 132.0, 131.6, 130.6, 128.0, 127.7, 127.3, 69.1, 64.3, 52.3, 36.2, 31.4, 21.5, 21.5. **ESI-MS:** calculated $[C_{21}H_{28}ClNO_6H]^+$: 426.1678, found: 426.1675.

Diisopropyl (*E*)-2-(4-(2-(methoxycarbamoyl)-3-nitrophenyl)but-2-en-1-yl)malonate (3pb)



Following general procedure E, 50°C was ued, **3pb** was obtained as a yellow oil (58.4 mg, 0.134 mmol, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.96 (d, *J* = 7.4 Hz, 1H), 7.65 – 7.36 (m, 2H), 5.65 – 5.52 (m, 1H), 5.43 – 5.26 (m, 1H), 5.02 – 4.80 (m, 2H), 3.87 (s, 3H), 3.39 (d, *J* = 6.2 Hz, 2H), 3.26 (t, *J* = 7.4 Hz, 1H), 2.51 (t, *J* = 6.6 Hz, 2H), 1.13 (dd, *J* = 13.7, 6.0 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 163.4, 146.7, 140.9, 135.5, 130.9, 130.1, 128.9, 128.6, 122.5, 69.1, 63.7, 52.2, 35.6, 31.4, 21.5, 21.5. **ESI-MS:** calculated $[C_{21}H_{29}N_2O_8]^+$: 437.1918, found: 437.1917.

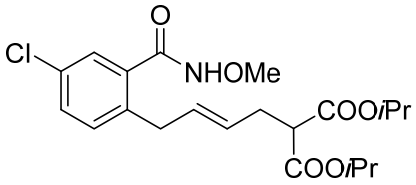
Diisopropyl (*E*)-2-(4-(2-(methoxycarbamoyl)-4-methylphenyl)but-2-en-1-yl)malonate (3pb)



Following general procedure E, **3qb** was obtained as a white solid (56.7 mg, 0.140 mmol, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.15 (d, *J* = 9.4 Hz,

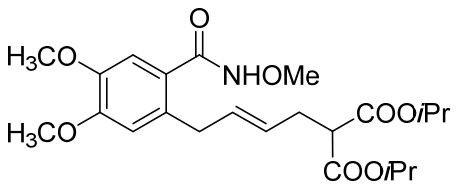
2H), 7.06 (d, *J* = 7.6 Hz, 1H), 5.75 – 5.59 (m, 1H), 5.41 – 5.25 (m, 1H), 4.93 (m, 2H), 3.88 (s, 3H), 3.41 (d, *J* = 6.2 Hz, 2H), 3.28 (t, *J* = 7.5 Hz, 1H), 2.54 (t, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 1.16 (dd, *J* = 12.6, 6.3 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 168.1, 135.9, 135.2, 133.0, 132.7, 131.1, 130.2, 128.4, 126.9, 69.0, 64.3, 52.4, 35.5, 31.4, 21.53, 21.45, 20.7. **ESI-MS:** calculated $[C_{22}H_{32}NO_6]^+$: 406.2224, found: 406.2223.

Diisopropyl (*E*)-2-(4-(4-chloro-2-(methoxycarbamoyl)phenyl)but-2-en-1-yl)malonate (3rb)



Following general procedure E, **3rb** was obtained as a white solid (40.0 mg, 0.094 mmol, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 7.34 – 7.16 (m, 2H), 7.05 (d, *J* = 8.1 Hz, 1H), 5.62 – 5.47 (m, 1H), 5.32 – 5.19 (m, 1H), 4.86 (dt, *J* = 12.5, 6.3 Hz, 2H), 3.79 (s, 3H), 3.33 (d, *J* = 6.3 Hz, 2H), 3.21 (t, *J* = 7.5 Hz, 1H), 2.46 (t, *J* = 7.1 Hz, 2H), 1.09 (dd, *J* = 12.4, 6.3 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 166.4, 137.1, 134.7, 131.9, 131.8, 131.6, 130.3, 127.8, 127.6, 69.0, 64.3, 52.3, 35.3, 31.4, 21.5, 21.4. **ESI-MS:** calculated $[C_{21}H_{28}ClNO_6H]^+$: 426.1678, found: 426.1680.

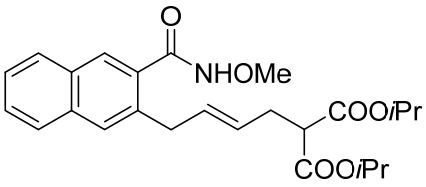
Diisopropyl (*E*)-2-(4-(4,5-dimethoxy-2-(methoxycarbamoyl)phenyl)but-2-en-1-yl)malonate (3sb)



Following general procedure E, **3sb** was obtained as a white solid (72.2 mg, 0.160 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 6.93 (s, 1H), 6.66 (s, 1H), 5.70 (m, 1H), 5.40 – 5.28 (m, 1H), 5.03 – 4.87 (m, 2H), 4.03 – 3.78 (m, 9H), 3.41 (d, *J* = 5.8 Hz, 2H), 3.30 (t, *J* = 7.5 Hz, 1H), 2.56 (t, *J* = 6.9

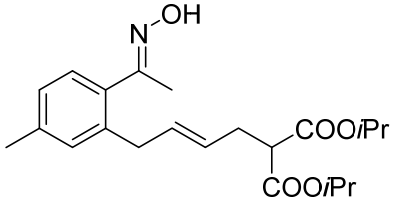
Hz, 2H), 1.17 (dd, J = 10.5, 6.3 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 150.6, 147.2, 132.9, 131.2, 127.2, 125.0, 113.1, 111.2, 69.0, 64.4, 56.1, 56.0, 52.3, 35.9, 31.5, 21.5, 21.5. **ESI-MS:** calculated $[C_{23}H_{33}NO_8H]^+$: 452.2279, found: 452.2279.

Diisopropyl (*E*)-2-(4-(3-(methoxycarbamoyl)naphthalen-2-yl)but-2-en-1-yl)malonate (3tb)



Following general procedure D, **3ub** was obtained as a white solid (64.4 mg, 0.146 mmol, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.74 – 7.46 (m, 3H), 7.49 – 7.24 (m, 3H), 5.52 (m, 1H), 5.25 – 5.12 (m, 1H), 4.76 (dt, J = 12.4, 6.2 Hz, 2H), 3.73 (s, 3H), 3.39 (d, J = 5.9 Hz, 2H), 3.15 (t, J = 7.5 Hz, 1H), 2.41 (t, J = 7.0 Hz, 2H), 0.98 (dd, J = 14.8, 6.2 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 168.3, 135.5, 134.2, 132.4, 131.6, 131.1, 128.7, 128.0, 127.4, 127.3, 126.1, 69.0, 64.3, 52.4, 35.8, 31.5, 21.5, 21.4. **ESI-MS:** calculated $[C_{25}H_{31}NO_6H]^+$: 442.2224, found: 442.2228.

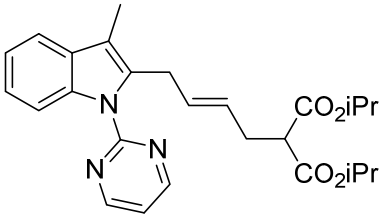
Diisopropyl 2-((*E*)-4-(2-((*E*)-1-(hydroxyimino)ethyl)-5-methylphenyl)but-2-en-1-yl)malonate (3ub)



Following general procedure E, except MeOH was used, **3vb** was obtained as a colourless oil (45.9 mg, 0.118 mmol, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) major δ 8.35 (s, 1H), 7.10 (m, 1H), 7.06 – 6.95 (m, 2H), 5.71 – 5.58 (m, 1H), 5.44 – 5.37 (m, 1H), 5.11 – 4.94 (m, 2H), 3.34 (m, 3H), 2.58 (t, J = 7.2 Hz, 2H), 2.32 (s, 3H), 2.16 (s, 3H), 1.25 – 1.17 (m, 12H); minor δ 8.52 (s, 1H), 7.10 (m, 1H), 7.06 – 6.95 (m, 2H), 5.58 – 5.53 (m, 1H), 5.54 – 5.37 (m, 1H), 5.11 – 4.94 (m, 2H), 3.47 (d, J = 7.1

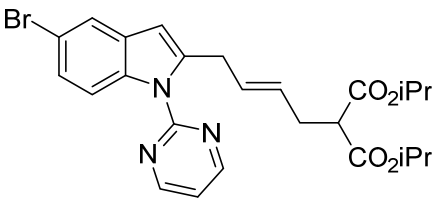
Hz, 2H), 3.34 (m, 1H), 2.73 (t, *J* = 7.2 Hz, 2H), 2.32 (s, 3H), 2.20 (s, 3H), 1.25 – 1.17 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) major δ 168.6, 157.5, 138.3, 137.8, 134.5, 132.1, 130.6, 128.3, 127.1, 126.9, 68.8, 52.5, 36.2, 31.6, 21.6, 21.6, 21.1, 16.2; minor δ 168.9, 157.3, 138.4,138.3, 134.4, 131.4, 130.5, 128.4, 126.8, 125.5, 69.0, 52.3, 31.3, 29.7, 26.7, 21.7, 21.1, 16.1. **ESI-MS:** calculated $[C_{22}H_{31}NO_5H]^+$: 390.2275, found: 390.2277.

Diisopropyl (*E*)-2-(4-(3-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)but-2-en-1-yl)malonate (3vb)



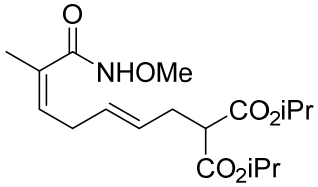
Following general procedure E, DCE was used as solvent and the reaction time was 13 h, **3wb** was obtained as a yellow oil (82.6 mg, 0.184 mmol, 92%).^{1}H NMR (400 MHz, $CDCl_3$) major δ 8.64 (d, *J* = 4.8 Hz, 2H), 8.23 – 8.05 (m, 1H), 7.50 – 7.32 (m, 1H), 7.20 – 7.04 (m, 2H), 6.98 (t, *J* = 4.8 Hz, 1H), 5.57-5.50 (m, 1H), 5.28 – 5.11 (m, 1H), 4.88 (dt, *J* = 12.5, 6.3 Hz, 2H), 3.80 (d, *J* = 6.0 Hz, 2H), 3.06 (t, *J* = 7.6 Hz, 1H), 2.34 (t, *J* = 7.2 Hz, 2H), 2.18 (s, 3H), 1.12 – 1.02 (m, 12H); minor δ 8.64 (d, *J* = 4.8 Hz, 2H), 8.23 – 8.05 (m, 1H), 7.50 – 7.32 (m, 1H), 7.20 – 7.04 (m, 2H), 6.98 (t, *J* = 4.8 Hz, 1H), 5.41 - 5.31 (m, 1H), 5.28 – 5.11 (m, 1H), 5.02-4.93 (dt, *J* = 12.5, 6.3 Hz, 2H), 3.92 (d, *J* = 6.0 Hz, 2H), 3.18 (t, *J* = 7.6 Hz, 1H), 2.61 (t, *J* = 7.2 Hz, 2H), 2.23 (s, 3H), 1.16 (d, *J* = 6.3, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) major δ 168.4, 158.0, 136.2, 134.4, 130.7, 130.4, 126.4, 122.8, 121.4, 118.0, 116.8, 113.6, 113.5, 68.7, 52.5, 31.6, 29.4, 21.6, 21.5, 8.8; minor δ 168.6, 158.2, 158.1, 136.3, 135.0, 130.4,130.2, 125.1, 122.9, 121.5, 118.0, 116.7, 113.6, 113.3, 68.9, 52.2, 26.9, 25.0, 21.7, 21.5, 8.9. **ESI-MS:** calculated $[C_{26}H_{31}N_3O_4H]^+$: 450.2387, found: 450.2384

Diisopropyl (*E*)-2-(4-(5-bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl)but-2-en-1-yl)malonate (3wb)



Following general procedure E, DCE was used as solvent and the reaction temperature was ran at 50°C, **3xb** was obtained as a yellow oil (60.5 mg, 0.118 mmol, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) major δ 8.76 – 8.58 (m, 2H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.52 (s, 1H), 7.18 (d, *J* = 8.6 Hz, 1H), 7.05 (m, 1H), 6.27 (s, 1H), 5.69 – 5.53 (m, 1H), 5.47 – 5.30 (m, 1H), 4.93 (m, 2H), 3.77 (d, *J* = 6.4 Hz, 2H), 3.18 (t, *J* = 7.5 Hz, 1H), 2.47 (t, *J* = 7.1 Hz, 2H), 1.12 (d, *J* = 6.3 Hz, 12H); minor δ 8.76 – 8.58 (m, 2H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.56 (s, 1H), 6.91 (d, *J* = 8.6 Hz, 1H), 6.60 (s, 1H), 6.30 (s, 1H), 6.09-6.01 (m, 1H), 5.47 – 5.30 (m, 1H), 4.93 (m, 2H), 3.88 (d, *J* = 6.4 Hz, 2H), 3.18 (t, *J* = 7.5 Hz, 1H), 2.62 (t, *J* = 7.1 Hz, 2H), 1.12 (d, *J* = 6.3 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) major δ 168.4, 158.1, 141.6, 135.7, 131.0, 129.7, 128.3, 125.3, 122.2, 117.4, 115.6, 114.9, 105.5, 68.8, 52.3, 33.0, 31.6, 21.6, 21.6. minor δ 168.5, 158.2, 141.5, 135.8, 131.1, 128.8, 127.0, 125.9, 122.6, 117.5, 115.7, 115.0, 104.3, 68.9, 68.7, 52.2, 39.5, 28.1, 26.7, 20.0. **ESI-MS:** calculated $[C_{25}H_{28}BrN_3O_4H]^+$: 514.1336, found: 514.1338.

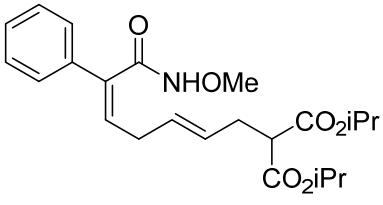
Diisopropyl 2-((2*E*,5*Z*)-7-(methoxyamino)-6-methyl-7-oxohepta-2,5-dien-1-yl)malonate (5a)



Following general procedure E, the reaction was ran at 0 °C for 4 h, **5a** was obtained as a colorless oil (40.0 mg, 0.112 mmol, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 5.63 – 5.46 (m, 2H), 5.46 – 5.34 (m, 1H), 5.10 – 4.96 (m, 2H), 3.80 (s, 3H), 3.31 (t, *J* = 7.4 Hz, 1H), 2.83 (t, *J* = 6.8 Hz, 2H), 2.55 (t, *J* = 6.9 Hz, 2H), 1.89 (s, 3H), 1.22 (dd, *J* = 6.3, 1.8 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 130.0, 129.8, 129.7, 125.8, 68.0, 63.4, 51.4, 31.4,

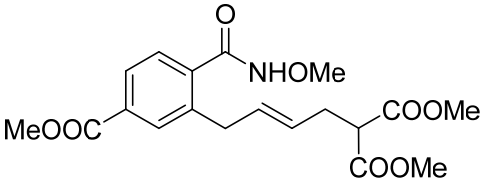
30.5, 20.6, 20.6, 19.4. **ESI-MS:** calculated $[C_{18}H_{29}NO_6H]^+$: 356.2068, found: 356.2067.

Diisopropyl 2-((2*E*,5*Z*)-7-(methoxyamino)-7-oxo-6-phenylhepta-2,5-dien-1-yl)malonate (5b)



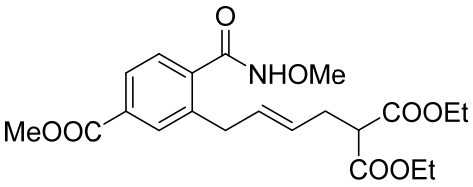
Following general procedure E, the reaction was ran at 0 °C for 28 h, **5b** was obtained as a white solid (75.9 mg, 0.182 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.32 (m, 3H), 6.09 (t, *J* = 8.0 Hz, 1H), 5.65 – 5.55 (m, 1H), 5.56 – 5.43 (m, 1H), 5.02 (m, 2H), 3.86 (s, 3H), 3.33 (t, *J* = 7.4 Hz, 1H), 3.02 (t, *J* = 6.7 Hz, 2H), 2.58 (t, *J* = 7.1 Hz, 2H), 1.22 (d, *J* = 6.2 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 166.0, 136.4, 135.7, 131.6, 130.4, 128.6, 128.1, 127.4, 126.1, 69.0, 64.4, 52.4, 32.8, 31.6, 21.6, 21.5. **ESI-MS:** calculated $[C_{23}H_{31}NO_6H]^+$: 418.2224, found: 418.2228.

Dimethyl (*E*)-2-(4-(2-(methoxycarbamoyl)-5-(methoxycarbonyl)phenyl)but-2-en-1-yl)malonate (3ja)



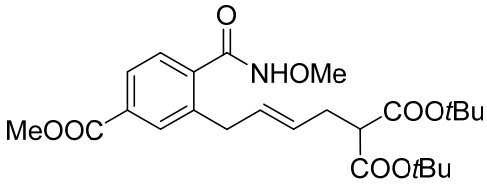
Following general procedure E, **3ja** was obtained as a colorless oil (70.7 mg, 0.180 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 1H), 5.73 – 5.58 (m, 1H), 5.33 (dt, *J* = 20.1, 6.4 Hz, 1H), 3.91 (s, 6H), 3.61 (s, 6H), 3.48 (d, *J* = 6.3 Hz, 2H), 3.39 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 167.1, 166.3, 139.0, 137.2, 132.2, 131.9, 131.2, 128.0, 127.4, 64.4, 52.5, 52.3, 51.6, 35.8, 31.6. **ESI-MS:** calculated $[C_{19}H_{23}NO_8H]^+$: 394.1496, found: 394.1496.

Diethyl (*E*)-2-(4-(2-(methoxycarbamoyl)-5-(methoxycarbonyl)phenyl)but-2-en-1-yl)malonate (3jc)



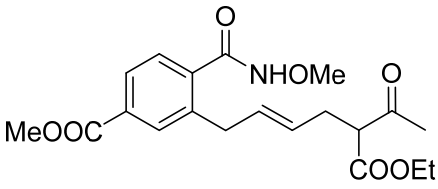
Following general procedure E, **3jc** was obtained as a white solid (69.0 mg, 0.164 mmol, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 7.88 (d, *J* = 10.5 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 1H), 5.74 – 5.58 (m, 1H), 5.41 – 5.28 (m, 1H), 4.17 – 4.00 (q, *J* = 13 Hz, 4H), 3.93 (s, 3H), 3.90 (s, 3H), 3.50 (d, *J* = 6.3 Hz, 2H), 3.36 (t, *J* = 7.4 Hz, 1H), 2.57 (t, *J* = 7.2 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 166.8, 166.2, 139.0, 137.1, 131.7, 131.0, 127.9, 127.6, 127.2, 64.2, 61.4, 52.3, 51.8, 35.7, 31.4, 13.9. **ESI-MS:** calculated $[C_{21}H_{27}NO_8H]^+$: 422.1809, found: 422.1806.

Di-*tert*-butyl (E)-2-(4-(2-(methoxycarbamoyl)-5-(methoxycarbonyl)phenyl)but-2-en-1-yl)malonate (3jd)



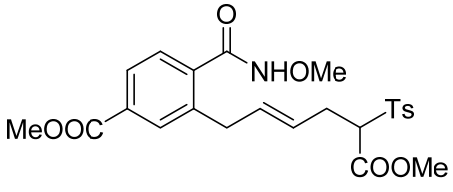
Following general procedure E, except stirred for 48 h with 10% $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$, **3jd** was obtained as a colorless oil (72.5 mg, 0.152 mmol, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 7.85 (d, *J* = 6.8 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 5.70 – 5.55 (m, 1H), 5.36 – 5.22 (m, 1H), 3.91 (s, 6H), 3.48 (d, *J* = 6.3 Hz, 2H), 3.11 (t, *J* = 7.6 Hz, 1H), 2.45 (t, *J* = 7.3 Hz, 2H), 1.31 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 167.1, 166.3, 138.9, 137.5, 131.6, 131.6, 131.2, 128.1, 127.9, 127.3, 81.7, 64.2, 53.9, 52.2, 35.8, 31.5, 27.7. **ESI-MS:** calculated $[C_{25}H_{35}NO_8H]^+$: 478.2435, found: 478.2438.

Methyl (*E*)-3-(5-(tert-butoxycarbonyl)-6-oxohept-2-en-1-yl)-4-(methoxycarbamoyl)benzoate (3je)



Following general procedure E, **3je** was obtained as a colourless oil (58.7 mg, 0.150 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) major δ 9.43 (s, 1H), 8.02 – 7.77 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 5.75 – 5.55 (m, 1H), 5.47 – 5.22 (m, 1H), 4.15 – 4.04 (m, 2H), 3.92 (s, 3H), 3.87 (s, 3H), 3.46 – 3.38 (m, 3H), 2.52 (t, *J* = 7.0 Hz, 2H), 2.19 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); minor δ 9.55 (s, 1H), 8.02 – 7.77 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 5.75 – 5.55 (m, 1H), 5.47 – 5.37 (m, 1H), 4.15 – 4.04 (m, 2H), 3.92 (s, 3H), 3.87 (s, 3H), 3.46 – 3.38 (m, 1H), 3.29 (d, *J* = 6.3, 2H), 2.61 (t, *J* = 7.0 Hz, 2H), 2.18 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) major δ 202.8, 169.5, 166.9, 166.2, 139.1, 137.1, 131.8, 131.5, 131.1, 127.9, 127.3, 64.3, 61.4, 59.4, 52.3, 35.8, 30.8, 28.9, 13.9. minor δ 202.8, 169.3, 166.7, 166.3, 138.4, 131.4, 130.7, 129.7, 128.5, 127.2, 127.0, 64.2, 61.4, 59.1, 52.3, 35.9, 30.5, 29.2, 14.0. **ESI-MS:** calculated $[C_{20}H_{25}NO_7H]^+$: 392.1704, found: 392.1707.

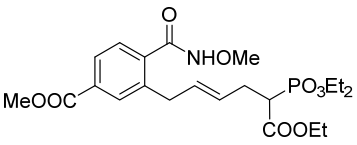
Methyl (*E*)-3-(6-methoxy-6-oxo-5-tosylhex-2-en-1-yl)-4-(methoxycarbamoyl)benzoate (3jf)



Following general procedure E, with 10% $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ and stirred for 48 h, **3jf** was obtained as a white solid (52.8 mg, 0.108 mmol, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.83 (s, 1H), 7.67 (t, *J* = 6.9 Hz, 3H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 5.80 – 5.61 (m, 1H), 5.37 – 5.17 (m, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 3.62 – 3.52

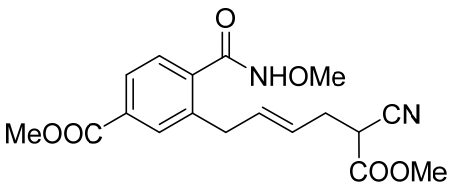
(m, 4H), 3.49 (d, J = 6.2 Hz, 2H), 2.65 (m, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 166.2, 166.1, 145.7, 138.8, 137.0, 133.9, 133.2, 131.9, 131.2, 129.8, 129.2, 127.9, 127.5, 125.4, 70.2, 64.4, 52.9, 52.4, 35.7, 30.0, 21.7. **ESI-MS:** calculated $[C_{24}H_{27}NO_8SH]^+$: 490.1530, found: 490.1533.

Methyl (*E*)-3-(5-((diethyl-l3-oxidanyl)(λ1-oxidanyl)phosphoryl)-6-ethoxy-6-oxohex-2-en-1-yl)-4-(methoxycarbamoyl)benzoate (3jg)



Following general procedure E, with 10% $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ and stirred for 48 h, **3jg** was obtained as a white solid (52.4 mg, 0.108 mmol, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.78 (dd, J = 6.5, 1.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 1H), 5.72 – 5.56 (m, 1H), 5.29 – 5.13 (m, 1H), 4.14 – 3.88 (m, 6H), 3.84 (s, 3H), 3.79 (s, 3H), 3.56 – 3.23 (m, 2H), 2.88 (dt, J = 22.1, 7.2 Hz, 1H), 2.49 (dd, J = 14.8, 7.2 Hz, 2H), 1.31 – 0.89 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 166.1, 165.4, 137.7, 137.0, 130.8, 130.7 (d, J = 15.3 Hz), 130.2, 127.1, 126.8 (d, J = 10.3 Hz), 126.3, 63.1, 61.9, 61.8 (dd, J = 15.9, 6.7 Hz), 60.5, 51.3, 45.2, 43.9, 34.7, 29.1, 15.2, 13.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.85. **ESI-MS:** calculated $[C_{22}H_{32}NO_9PH]^+$: 486.1887, found: 486.1883.

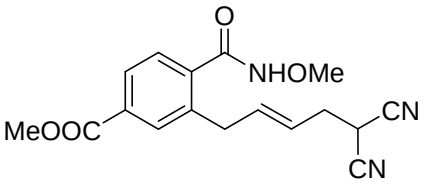
Methyl (*E*)-3-(5-cyano-6-methoxy-6-oxohex-2-en-1-yl)-4-(methoxycarbamoyl)benzoate (3jh)



Following general procedure E, **3jh** was obtained as a white solid (13.7 mg, 0.124 mmol, 62%). ^{1}H NMR (400 MHz, MeOD) major δ 7.83 (d, J = 1.3 Hz, 1H), 7.79 (dd, J = 7.9, 1.6 Hz, 1H), 7.34 (d, J = 7.9 Hz, 1H), 5.77 – 5.67 (m,

1H), 5.52 – 5.39 (m, 1H), 3.80 (s, 3H), 3.73 (s, 3H), 3.65 (s, 3H), 3.46 (d, *J* = 6.7 Hz, 2H), 2.60 – 2.44 (m, 2H); minor δ 7.83 (d, *J* = 1.3 Hz, 1H), 7.79 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 5.77 – 5.67 (m, 1H), 5.52 – 5.39 (m, 1H), 3.80 (s, 3H), 3.70 (s, 3H), 3.65 (s, 3H), 2.71 (d, *J* = 6.7 Hz, 2H), 2.60 – 2.44 (m, 2H). ^{13}C NMR (101 MHz, MeOD) major δ 166.9, 166.5, 166.2, 139.0, 137.0, 132.9, 131.8, 130.7, 127.6, 127.0, 125.7, 116.2, 63.1, 52.3, 51.4, 35.2, 32.2. minor δ166.9, 166.5, 166.2, 139.3, 137.0, 132.9, 131.4, 130.4, 127.6, 127.0, 124.3, 116.2, 63.1, 52.4, 30.2, 27.0. **ESI-MS:** calculated $[C_{18}H_{20}N_2O_6H]^+$: 361.1394, found: 361.1392.

Methyl (*E*)-3-(5,5-dicyanopent-2-en-1-yl)-4-(methoxycarbamoyl)benzoate (3ji)



Following general procedure E, with 10% $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ and stirred for 48 h, **3ji** was obtained as a white solid (13.7 mg, 0.042 mmol, 21%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 1H), 5.94 – 5.83 (m, 1H), 5.52 – 5.41 (m, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.71 (t, *J* = 6.8 Hz, 1H), 3.58 (d, *J* = 6.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 135.3, 131.4, 130.5, 126.9, 126.7, 122.2, 111.3, 63.8, 51.4, 35.0, 32.8, 22.1. **ESI-MS:** calculated $[C_{17}H_{17}N_3O_4H]^+$: 328.1292, found: 328.1291.

6. Large Scale Reaction

Without any particular precautions to exclude air and moisture, to a round flask (50 mL in volume) equipped with a stirring bar, was added $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (83.2 mg, 0.10 mmol, 2 mol%) , CsOAc (0.96 g, 5 mmol, 1.0 equiv), and *N*-methoxybenzamide (760 mg, 5.0 mmol, 1.0 equiv) subsequently, CF_3CH_2OH (20 mL)

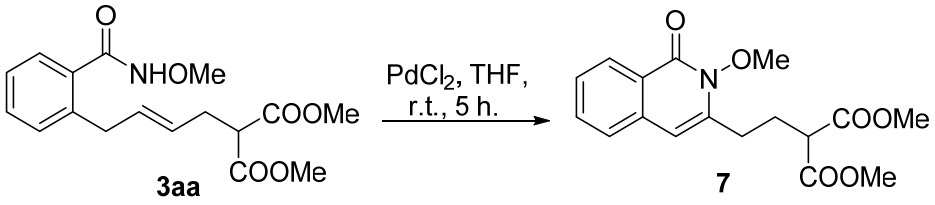
was then added followed by dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (1.11 g, 6.0 mmol, 1.2 equiv). The reaction was allowed to stir at room temperature for 24 h. The reaction mixture was then diluted with EtOAc (100 mL) and washed with water. The aqueous phase was extracted with EtOAc again. Afterwards, the organic layer was combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with petroleum:EtOAc (2:1) to afford the pure product **3aa** (1.31 g, 78%). The ratio of *E* to *Z* was found to be 14:1 as detected by ^{1}H NMR.

7. Derivatization of 3aa and 3ab

7.1 Synthesis of methyl (E)-6-(2-(methoxycarbamoyl)phenyl)hex-4-enoate (6)

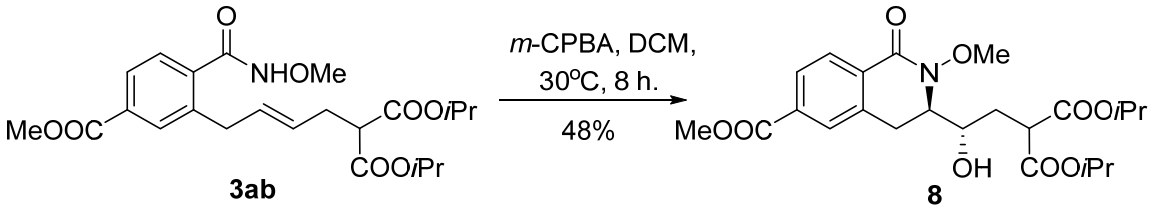
A 5 mL round bottomed flask was charged with dimethyl (*E*)-2-(4-(2-(methoxycarbamoyl)phenyl)but-2-en-1-yl)malonate **3aa** (33.5 mg, 0.1 mmol, 1.0 equiv.), NaCN (24.5 mg, 0.5 mmol, 5.0 equiv.), DMSO (0.8 mL), and H_2O (9 mg, 0.5 mmol, 5.0 equiv.). The flask was fitted with a reflux condenser and the reaction was heated to 110°C for 3 hours under a nitrogen atmosphere. The cooled reaction mixture was diluted with water (10 mL), treated with ethyl acetate (20 mL) and the separated aqueous phase was extracted with ethyl acetate (3 x 20 mL), washed with brine (10 mL). The combined organic phases were dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether:EtOAc = 2:1) to afford **6** (19.5 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.47 – 7.28 (m, 2H), 7.28 – 7.03 (m, 2H), 5.70 – 5.45 (m, 1H), 5.45 – 5.05 (m, 1H), 3.86 (s, 3H), 3.63 (s, 0.2H), 3.56 (s, 2.8H), 3.46 (d, *J* = 6.3 Hz, 2H), 2.46 – 1.38 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 168.0, 138.9, 132.9, 130.6, 130.4, 130.3, 129.9, 127.7, 126.2, 64.4, 51.5, 36.0, 33.9, 27.8. **ESI-MS:** calculated $[C_{15}H_{19}NO_4H]^+$: 278.1387, found: 278.1385.

7.2 Synthesis of dimethyl 2-(2-(2-methoxy-1-oxo-1,2-dihydroisoquinolin-3-yl)ethyl)malonate (7)



To a solution of dimethyl (*E*)-2-(4-(2-(methoxycarbamoyl)phenyl)but-2-en-1-yl)malonate **3aa** (33.5 mg, 0.1 mmol, 1.0 equiv.) in dry THF (2 mL) was added $PdCl_2$ (1 mg, 5 mol %) at room temperature. The reaction was stirred at room temperature until the complete consumption of **3a** as monitored by TLC analysis (5 h). The reaction mixture was then diluted with EtOAc (20 mL) and washed with water. The aqueous phase was extracted with EtOAc again. The organic layer was combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica (Petroleum: EtOAc = 2:1) to afford the pure product **7** (27.9 mg, 84 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.6 Hz, 1H), 7.61 (ddd, *J* = 8.4, 7.6, 1.3 Hz, 1H), 7.43 (td, *J* = 8.5, 1.4 Hz, 2H), 6.27 (s, 1H), 4.09 (s, 3H), 3.74 (s, 6H), 3.48 (t, *J* = 7.3 Hz, 1H), 2.83 – 2.77 (m, 2H), 2.34 (dd, *J* = 15.1, 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 157.9, 140.1, 134.7, 131.4, 126.6, 125.2, 124.6, 103.2, 63.0, 51.6, 49.6, 27.4, 26.4. **ESI-MS:** calculated $[C_{17}H_{19}NO_6H]^+$: 334.1286, found: 334.1283.

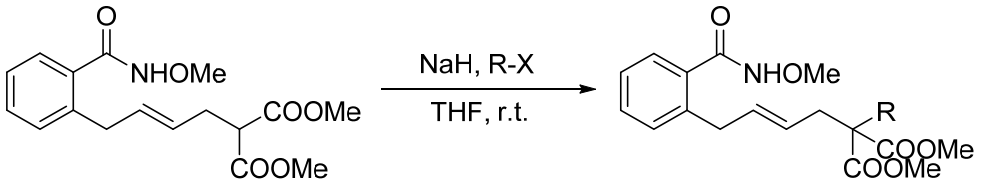
7.3 Synthesis of diisopropyl 2-((3-(2-(methoxycarbamoyl)-5-(methoxycarbonyl)benzyl)oxiran-2-yl)methyl)malonate (8)



To a solution of diisopropyl (E)-2-(4-(2-(methoxycarbamoyl)-5-(methoxycarbonyl)phenyl)but-2-en-1-yl)malonate **3ab** (58.2 mg, 0.13 mmol, 1 equiv.) in DCM (20 mL) was added *m*-CPBA (56 mg, 0.33 mmol, 2.5 equiv.) at 0ºC. After stirred for 10 min, the reaction mixture was allowed to warm to room temperature until the complete consumption of **3b** as monitored by TLC analysis. The reaction mixture was then diluted with EtOAc (20 mL) and washed with water. The aqueous phase was extracted with EtOAc again. The organic layer was combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica (Petroleum: EtOAc = 4:1) to afford the pure product **8** (29.1 mg, 48%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 2H), 5.09 – 5.00 (m, 1H), 4.18 – 4.13 (m, 1H), 4.04 – 4.00 (m, 1H), 3.63 (dd, *J* = 8.6, 5.5 Hz, 1H), 3.15 (dd, *J* = 16.2, 10.3 Hz, 1H), 2.93 (dd, *J* = 16.3, 2.8 Hz, 1H), 2.21 (ddd, *J* = 14.2, 8.7, 2.8 Hz, 1H), 2.06 (ddd, *J* = 14.3, 10.4, 5.5 Hz, 1H), 1.23 (ddd, *J* = 5.9, 4.5, 1.2 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 167.9, 165.4, 148.7, 133.2, 130.3, 128.5, 127.0, 124.2, 78.5, 68.8, 68.2, 61.7, 51.3, 48.4, 30.1, 26.9, 20.6, 20.6, 20.5. **ESI-MS:** calculated $[C_{23}H_{31}NO_9H]^+$: 466.2072, found: 466.2076.

7.4 Synthesis of substituent of methyl (*E*)-6-(2-(methoxycarbamoyl) phenyl)hex-4-enoate 9

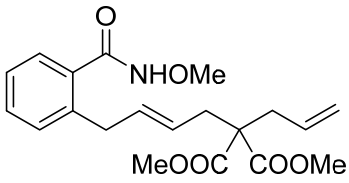
General procedure F:



To a solution of 60% NaH (8.8 mg, 0.22 mmol, 1.2 equiv.) in dry THF (2 mL) was added dimethyl (*E*)-2-(4-(2-(methoxycarbamoyl)phenyl)but-2-en-1-yl)malonate **3aa** (67 mg, 0.2 mmol, 1.0 equiv) at 0 ºC (ice bath). After stirred for 20 minutes, organo

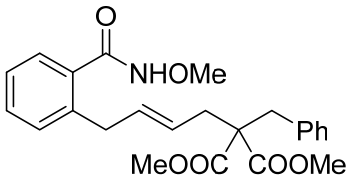
halide (0.2 mmol,1.0 equiv) was added to above solution. The mixture was stirred for 3 hours under a nitrogen atmosphere at room temperature and quenched with sat. NH_4Cl (1 mL), then diluted with EtOAc (20 mL) and washed with water. The aqueous phase was extracted with EtOAc again. Afterwards, the organic layer was combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with petroleum ether:EtOAc (2:1) to afford the corresponding product.

Dimethyl (*E*)-2-allyl-2-(4-(2-(methoxycarbamoyl)phenyl)but-2-en-1-yl)malonate (9a)



Following general procedure F, allyl bromide was used. **9a** was obtained as a colourless coil (41.3 mg, 0.116 mmol, 56%). ^{1}H NMR (400 MHz, MeOD) δ 7.47 – 7.40 (m, 1H), 7.35 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 2H), 5.73 – 5.60 (m, 2H), 5.40 (dt, *J* = 21.3, 7.5 Hz, 1H), 5.13 – 5.04 (m, 2H), 3.84 (s, 3H), 3.65 (s, 6H), 3.50 (d, *J* = 6.8 Hz, 2H), 2.60 (dd, *J* = 14.7, 7.4 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 167.9, 138.5, 134.5, 133.0, 132.1, 130.4, 130.2, 127.8, 126.1, 124.9, 119.3, 64.3, 58.1, 52.3, 36.9, 35.9, 35.5. **ESI-MS:** calculated $[C_{20}H_{25}NO_6H]^+$: 376.1755, found: 376.1758.

Dimethyl (*E*)-2-benzyl-2-(4-(2-(methoxycarbamoyl)phenyl)but-2-en-1-yl)malonate (9b)



Following general procedure, benzyl bromide was used. **9b** was obtained as a colorless coil (69.7 mg, 0.164 mmol, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 7.32 – 7.24 (m, 2H), 7.23 – 7.09 (m, 5H), 7.05 – 6.92 (m, 2H), 5.57 (dt, *J* = 15.1, 6.7 Hz, 1H), 5.31 (dt, *J* = 15.1, 7.4 Hz, 1H), 3.80 (s, 3H), 3.43 (s, 6H), 3.40 (d, *J* = 6.6 Hz, 2H), 3.11 (s, 2H), 2.37 (d, *J* = 7.4 Hz, 2H). ^{13}C NMR

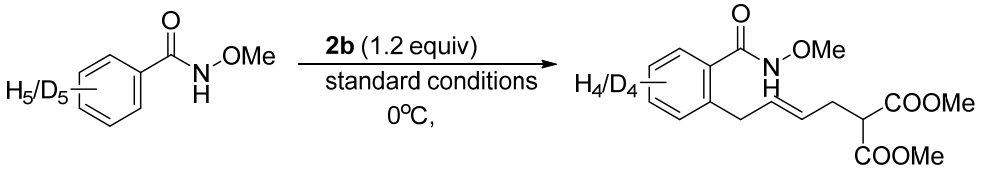
(101 MHz, $CDCl_3$) δ 170.4, 166.9, 137.5, 134.7, 133.6, 132.1, 129.4, 129.1, 128.8, 127.3, 126.8, 126.0, 125.1, 124.1, 63.3, 58.6, 51.2, 37.1, 35.0, 34.2. **ESI-MS:** calculated $[C_{24}H_{27}NO_6H]^+$: 426.1911, found: 426.1915.

8. Mechanistic Studies

8.1 Reaction of 1a with 2a in the presence of TEMPO

A 15 mL-schlenk tube charged with a stirring bar, was added *N*-methoxybenzamide **1a** (30.2 mg, 0.2 mmol, 1 equiv), vinylcyclopropane **2a** (44.2 mg, 0.24 mmol, 1.2 equiv). $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (8.3 mg, 5 mol%), CsOAc (38.4 mg, 0.2 mmol, 1.0 equiv), TEMPO (62.5 mg, 0.4 mmol, 2.0 equiv), and CF_3CH_2OH (1 mL) were added subsequently into the reaction vessel. The reaction was allowed to stir at 30°C for 24 h. The reaction mixture was then diluted with EtOAc (20 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica gel to afford the pure product **3aa,** 77% yield. The E/Z ratio was tested by ^1H NMR to be 14/1.

8.2 Kinetic isotope effect



To a flask (25 mL in volume) was added a solution of $[Cp^*Rh(CH_3CN)_3](SbF_6)$ (8.3 mg, 0.01 mmol, 2.5 mol%) in 1.0 mL CF_3CH_2OH and a solution of CsOAc (76.8 mg, 0.4 mmol, 1.0 equiv) in CF_3CH_2OH (1.0 mL). The above mixture was stirred for 2 min, then the solution of *N*-methoxybenzamide **1a** (60.4 mg, 0.4 mmol, 1.0 equiv) or

d$_5$-*N*-methoxybenzamide (62.4 mg, 0.4 mmol, 1.0 equiv) in CF_3CH_2OH (1.0 mL) and **2b** (88.4 mg, 0.48 mmol, 1.2 equiv) in CF_3CH_2OH (1.0 mL) was added at 0°C. The reaction was maintained to stir at 0°C. To another flask (10 mL in volume) was added Dimethyl terephthalate (38.8 mg, 0.2 mmol, 0.5 equiv) and 4 mL CF_3CH_2OH as internal standard solution. Aliquots (100 μL) were taken at the corresponding times from the reaction flask and internal standard solution, respectively. Combined the solution, and filtered with EtOAc in a short silica gel. The filtrate was evaporated under reduced pressure, and the the yield was determined by NMR by integration of the product peaks relative to the dimethyl terephthalate. Yields are reported as the average of three runs, with error bars representing standard deviation.

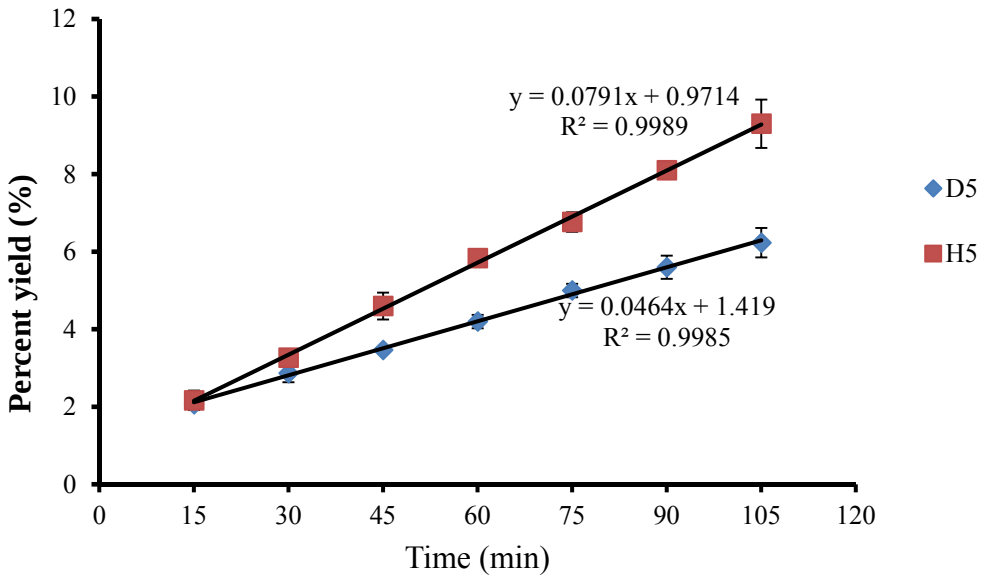


Figure S1 Kinetic isotope effect study

8.3 **Computational Details**

All species in this study were optimized, using DFT, at the M06 level.[21] Frequency calculations at the same level of theory were also performed to identify all the

stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency), and to provide the free energies at 298.15 K. Transition states were located using the Berny algorithm. Intrinsic reaction coordinates (IRC)[22] were calculated for the transition states to confirm that the saddle point connected the correct reactant and product on the potential energy surface. Rh atom was described using the LANL2DZ basis set, including a double-valence basis set with the Hay and Wadt effective core potential.[23] Polarization functions were added for Rh (ζ_f = 1.350).[24] The 6-31G basis set was used for the other atoms**.** To test the solvent effect, we performed single-point energy calculations using the polarizable continuum model (PCM)[25] for all gas phase optimized species. In the polarizable continuum model (PCM) calculations, the larger basis set are performed, the LanL2TZ(f) basis set[26] on the metal atoms and 6-311++G** for the other atoms. The non-electrostatic terms (cavity–dispersion–solvent–structure terms) of the solvation energy were calculated using the SMD model[27] to give the final fully corrected free energies (ΔG_{sol}) in 2,2,2-trifluoroethanol. All calculations were performed using Gaussian 09 packages.[28]

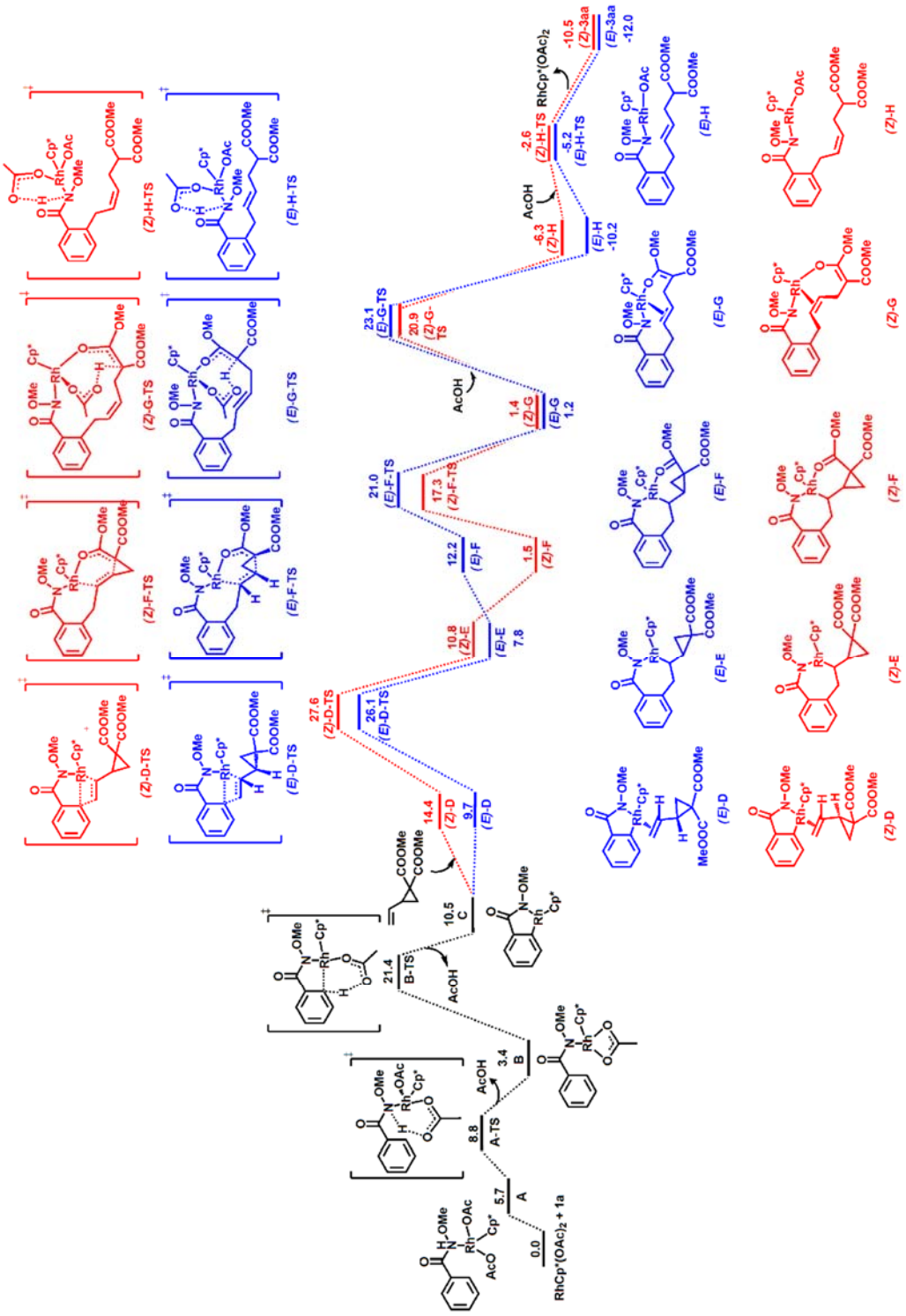


Figure S2. Calculated energy profiles for Rh^{III}-catalyzed sequential C–H/C–C activation reaction. Solvent-corrected free energies are given in kcal/mol.

Cartesian coordinates for all the species calculated in this study:

AcOH

E=-228.9540758au

C	−0.092877	0.124748	0.000216
O	−0.654537	1.191915	−0.000088
O	−0.761099	−1.047705	−0.000081
H	−1.706331	−0.814984	−0.000249
C	1.387410	−0.098141	0.000045
H	1.679614	−0.680655	0.881357
H	1.679421	−0.680812	−0.881229
H	1.905180	0.863130	−0.000098

1a

E=-515.0590565au

C	-3.391073	-0.340425	0.039210
C	-2.500123	-1.402619	0.160845
C	-1.130353	-1.166582	0.144227
C	-0.645368	0.136610	0.005231
C	-1.544404	1.199860	-0.095885
C	-2.911647	0.961289	-0.086180
H	-4.463712	-0.526895	0.051390
H	-2.873941	-2.418080	0.279614
H	-0.437830	-1.996691	0.279284
H	-1.141776	2.207503	-0.180043
H	-3.608887	1.792757	-0.172731
C	0.807960	0.471582	-0.024877
O	1.247224	1.568353	0.255969
N	1.628743	-0.601958	-0.347212
H	1.280350	-1.278155	-1.019374
O	2.941154	-0.286675	-0.655827
C	3.730219	-0.329297	0.520175
H	3.680168	-1.320318	0.993303
H	4.752983	-0.125416	0.189206
H	3.413155	0.443072	1.232215

2a

E=-650.6372565au

C	0.735182	-1.505130	0.285101
C	-0.141396	-0.239791	0.363785
C	0.391284	-0.917100	1.604126
H	0.156933	-2.381075	-0.012042
H	1.167529	-0.383437	2.147100
H	-0.345132	-1.438257	2.211488
C	2.102365	-1.423224	-0.257052
H	2.703326	-0.566167	0.057994
C	2.622621	-2.337505	-1.072842
H	2.046886	-3.204438	-1.397066
H	3.641207	-2.258946	-1.445536
C	-1.590491	-0.489341	0.106754
O	-2.114084	-1.574668	0.224826
O	-2.256540	0.627172	-0.194681
C	0.466083	1.020396	-0.161157
O	0.231148	1.495412	-1.243838
O	1.369483	1.539164	0.693559
C	-3.650485	0.452219	-0.425672
H	-4.145597	0.073974	0.475389
H	-4.034482	1.438912	-0.690696
H	-3.818644	-0.256982	-1.242858
C	2.070541	2.673744	0.194463
H	2.763459	2.970349	0.984451
H	2.615974	2.415773	-0.720678
H	1.374264	3.488045	-0.031508

$RhCp^*(OAc)_2$

E=-956.0633907au

Rh	-0.061807	0.181558	-0.120131
C	2.432309	-1.299498	-0.040746
O	2.040816	-1.790491	1.016170
O	1.757163	-0.515606	-0.822976
C	3.830979	-1.569481	-0.558379
H	3.806524	-1.840564	-1.619822
H	4.428002	-0.652925	-0.474682
H	4.306657	-2.362755	0.025300
C	1.306872	2.311671	0.023488
O	0.631977	2.059669	-1.019381

O 1.191817 1.562038 1.037880
C 2.264637 3.461764 0.039632
H 2.385686 3.850321 1.055274
H 3.242491 3.105765 -0.308201
H 1.929842 4.251919 -0.639150
C -1.674017 -0.820164 -1.075336
C -1.157800 -1.685249 -0.050208
C -1.268318 -1.001542 1.202337
C -2.177313 0.381061 -0.431628
C -1.919549 0.276132 0.964969
C -0.568772 -3.034775 -0.250328
H 0.216326 -3.223478 0.488409
H -1.347434 -3.806001 -0.159043
H -0.115723 -3.128387 -1.244451
C -0.776996 -1.511165 2.509375
H -1.319386 -2.421543 2.801828
H 0.292265 -1.749771 2.425143
H -0.905757 -0.767895 3.303712
C -2.190733 1.296426 2.013312
H -3.047826 1.005359 2.636899
H -1.319494 1.418920 2.668539
H -2.409691 2.275670 1.573416
C -2.760121 1.543733 -1.152319
H -3.779267 1.319414 -1.497632
H -2.804064 2.432712 -0.513931
H -2.153060 1.803455 -2.028687
C -1.733714 -1.117903 -2.531257
H -2.651539 -1.666888 -2.788161
H -1.715178 -0.197385 -3.126454
H -0.877043 -1.726981 -2.843411

A

E=-1471.1478467au

N -0.471829 0.648813 1.579529
C -2.850463 0.174563 0.958735
C -3.863495 -0.791908 1.022543
H -3.746225 -1.618726 1.720952
C -4.993580 -0.680399 0.226497
H -5.772918 -1.438634 0.279343
C -5.134901 0.414681 -0.625171
H -6.024023 0.508762 -1.246802
C -4.149075 1.394557 -0.666320
H -4.268764 2.262669 -1.311839
C -3.005250 1.279984 0.118267
H -2.253585 2.065985 0.093561
C 1.896969 -1.543566 -1.392171
C 1.368958 -2.218033 -0.234428
C -0.065568 -2.260671 -0.372862
C -0.430112 -1.575767 -1.571849
C 0.793608 -1.145779 -2.214593
O -0.424559 3.076737 0.293651
O -0.044894 1.604591 -1.361821
C -0.041300 2.785190 -0.850793
C 0.485946 3.869092 -1.758667
H 1.582621 3.838706 -1.700541
H 0.204285 3.688576 -2.801740
H 0.144626 4.854994 -1.430214
Rh 0.626135 -0.161650 -0.310944
C -1.692618 -0.034328 1.872775
O -1.751397 -0.809162 2.805398
O 0.309872 0.838977 2.722470
H -0.561707 1.614323 1.169658
C -0.977151 -2.956991 0.570667
H -2.029016 -2.747504 0.348888
H -0.824435 -4.042889 0.489192
H -0.791861 -2.674825 1.615772
C -1.791637 -1.373169 -2.135516
H -1.979421 -2.080902 -2.956657
H -2.573019 -1.517481 -1.380242
H -1.901248 -0.357054 -2.535308
C 0.852276 -0.391197 -3.491919
H 0.247584 -0.890001 -4.261398
H 0.449827 0.621700 -3.338319
H 1.878014 -0.303861 -3.865368
C 3.334943 -1.325901 -1.695412
H 3.718655 -2.153845 -2.310020

H	3.486092	-0.393205	-2.251719
H	3.917612	-1.258366	-0.771375
C	2.169060	-2.921816	0.802538
H	2.540706	-3.878711	0.405597
H	3.024725	-2.308336	1.106968
H	1.567736	-3.144551	1.692103
O	3.598705	-0.137607	1.178636
O	2.035609	1.238924	0.309343
C	3.134811	0.977061	0.935572
C	3.823369	2.231695	1.431357
H	3.773870	3.031894	0.685288
H	3.284638	2.585949	2.320350
H	4.861554	2.019161	1.702726
C	1.061314	-0.301184	3.108345
H	1.612382	-0.708700	2.251876
H	1.788032	0.083264	3.831766
H	0.426658	-1.062190	3.576284

A-TS

E=-1471.1402722au

N	-0.379083	0.979343	1.330220
C	-2.761917	0.450626	0.893466
C	-3.790521	-0.441352	1.220964
H	-3.677372	-1.051145	2.115673
C	-4.932968	-0.526630	0.437250
H	-5.721161	-1.230404	0.700118
C	-5.078353	0.305261	-0.671850
H	-5.977683	0.249623	-1.283379
C	-4.081582	1.224913	-0.978963
H	-4.203041	1.900783	-1.823911
C	-2.927594	1.297780	-0.204007
H	-2.175237	2.043616	-0.437151
C	1.751212	-1.908966	-1.085913
C	1.192684	-2.271986	0.196292
C	-0.245804	-2.261932	0.071009
C	-0.575863	-1.814779	-1.241039
C	0.668952	-1.613300	-1.963552
O	-0.157635	3.001523	-0.107452
O	0.034312	1.412163	-1.672775
C	0.129749	2.602850	-1.285385
C	0.621862	3.644243	-2.242726
H	1.716068	3.673407	-2.149943
H	0.375050	3.378626	-3.274681
H	0.230397	4.632813	-1.986873
Rh	0.597168	-0.251010	-0.289139
C	-1.596018	0.495644	1.836423
O	-1.736046	0.106248	2.984753
O	0.489563	1.372656	2.359057
H	-0.341619	2.065169	0.582707
C	-1.178253	-2.706243	1.141091
H	-2.224057	-2.624560	0.828573
H	-0.978996	-3.759835	1.383185
H	-1.061305	-2.129750	2.070054
C	-1.923226	-1.637993	-1.845441
H	-2.128312	-2.441999	-2.567928
H	-2.720679	-1.642833	-1.093285
H	-1.985408	-0.681884	-2.381546
C	0.749950	-1.143629	-3.370986
H	0.132425	-1.776872	-4.022916
H	0.379100	-0.111767	-3.446902
H	1.778008	-1.165412	-3.747134
C	3.198946	-1.854380	-1.415352
H	3.546379	-2.838708	-1.762523
H	3.399151	-1.124146	-2.208041
H	3.779547	-1.557763	-0.535971
C	1.961932	-2.784051	1.360462
H	2.322989	-3.802969	1.152558
H	2.824182	-2.136783	1.558711
H	1.341447	-2.827123	2.263425
O	3.590718	-0.074932	1.190096
O	2.139076	1.131863	-0.047474
C	3.191011	0.974755	0.688001
C	3.913962	2.283610	0.929175
H	4.045177	2.837011	-0.007794
H	3.287507	2.903427	1.584458
H	4.883025	2.109267	1.405542

C 1.086813 0.312170 3.085239

H 1.500522 -0.437216 2.398396

H 1.922386 0.774662 3.622036

H 0.382791 -0.143051 3.789696

B

E=-1242.1706609au

Rh -0.810163 -0.064348 0.127681

N 0.426989 1.486247 -0.549686

C -0.118519 -2.050361 -0.320629

C -1.348163 -2.161366 0.453473

C -2.384332 -1.522656 -0.267054

C -1.807560 -0.993018 -1.497243

C -0.430754 -1.390396 -1.554609

O -2.034883 1.573453 0.947243

O -0.503997 0.652341 2.215087

C -1.371451 1.557115 2.025163

C -1.577716 2.632274 3.046950

H -1.268534 2.290871 4.039207

H -0.960051 3.497799 2.773549

H -2.622589 2.957586 3.059439

O -0.371227 2.131661 -1.517741

C 1.691748 1.279399 -1.052607

C 2.624193 0.528238 -0.147372

C 2.466398 0.446672 1.238313

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C 3.383742 -0.267595 2.003875

H 1.626158 0.941932 1.719593

C 4.635605 -0.810970 0.018610

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H 3.256157 -0.318928 3.084498

H 5.486569 -1.293971 -0.460196

H 5.176704 -1.465094 2.001045

O 2.083589 1.687715 -2.142301

C 0.486768 -1.115365 -2.692704

H 0.477708 -0.056951 -2.985947

H 1.523225 -1.372309 -2.448477

H 0.186108 -1.714620 -3.564175

C -2.520562 -0.222153 -2.548802

H -1.893133 0.607748 -2.895383

H -2.763828 -0.861138 -3.410423

H -3.455102 0.205414 -2.167765

C -3.795294 -1.322580 0.158193

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H -4.473633 -1.969929 -0.415593

H -3.930574 -1.545706 1.222136

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H -2.407516 -2.635951 2.263567

H -1.233618 -3.863200 1.745537

H -0.674741 -2.345439 2.475495

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H 1.358798 -2.511139 1.158684

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H 2.027919 -2.167796 -0.435468

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H -0.774107 3.713032 -0.239774

B-TS

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C 0.659928 -1.662974 1.482543

O 1.673807 1.200637 -1.199552

O -0.111135 2.250713 -2.048575

C 1.129769 2.125752 -1.866720

C 2.035281 3.173603 -2.455264

H 1.569806 3.645859 -3.324727

H 2.201508 3.947713 -1.694315

H 3.007210 2.745929 -2.718146

O 0.788957 1.670087 2.161459

C	-1.391789	1.402391	1.489802
C	-2.231843	0.870175	0.367245
C	-1.604297	0.463321	-0.826373
C	-3.597159	0.695684	0.562006
C	-2.396306	-0.130008	-1.819938
H	-0.729583	1.285353	-1.379901
C	-4.362414	0.108076	-0.440856
H	-4.030257	1.011286	1.510564
C	-3.764731	-0.303714	-1.633687
H	-1.934757	-0.421693	-2.766084
H	-5.433186	-0.031005	-0.296292
H	-4.373259	-0.748619	-2.420479
O	-1.852214	1.750519	2.566364
C	0.373871	-1.369172	2.911899
H	0.771507	-0.385747	3.193668
H	-0.701535	-1.357879	3.120791
H	0.837629	-2.128704	3.557675
C	3.140453	-0.878224	1.461000
H	2.878755	-0.135156	2.226636
H	3.736913	-1.666352	1.944523
H	3.777634	-0.381829	0.718361
C	2.868189	-1.787466	-1.558632
H	3.203966	-0.747138	-1.668425
H	3.733614	-2.392327	-1.253567
H	2.539610	-2.140881	-2.541948
C	-0.106541	-2.918441	-2.000607
H	0.332991	-2.460333	-2.895186
H	0.083609	-4.000731	-2.050288
H	-1.191039	-2.771662	-2.058579
C	-1.669342	-2.575439	0.765565
H	-2.299223	-2.465814	-0.125033
H	-1.709838	-3.627693	1.082685
H	-2.123660	-1.966443	1.556050
C	1.725378	2.654454	1.774467
H	1.213815	3.588848	1.501998
H	2.363889	2.823893	2.648652
H	2.333221	2.312438	0.922969

C

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N	0.688840	1.632714	0.162213
C	2.596733	0.275838	0.101255
C	3.960160	0.021433	0.081326
H	4.654395	0.852874	0.203253
C	4.403916	-1.287538	-0.096466
H	5.470074	-1.508702	-0.112730
C	3.475370	-2.310118	-0.259397
H	3.819349	-3.334133	-0.407719
C	2.102794	-2.038700	-0.236180
H	1.402256	-2.864905	-0.371876
C	1.642559	-0.738265	-0.047614
C	-2.382863	0.109785	-0.788135
C	-1.784221	-1.200519	-1.067074
C	-1.566414	-1.861769	0.170530
C	-1.876966	-0.915333	1.204533
C	-2.468378	0.270470	0.601192
Rh	-0.303711	-0.040900	0.021652
C	2.079773	1.662239	0.256830
O	2.752089	2.664637	0.413461
C	-2.943782	1.487685	1.320084
H	-3.981731	1.728053	1.052034
H	-2.908513	1.351578	2.406658
H	-2.314361	2.355844	1.077121
C	-2.781779	1.111667	-1.812279
H	-2.086257	1.115968	-2.661128
H	-3.785375	0.899055	-2.210288
H	-2.795001	2.122102	-1.385361
C	-1.554486	-1.754516	-2.428206
H	-2.470521	-2.212275	-2.830924
H	-1.240827	-0.969933	-3.127516
H	-0.767203	-2.517558	-2.422937
C	-1.105447	-3.260977	0.388910
H	-1.942378	-3.901010	0.704169
H	-0.688935	-3.697545	-0.526447
H	-0.331566	-3.321014	1.164912
C	-1.733568	-1.153048	2.664485

H -2.675400 -1.530244 3.091717

H -0.950427 -1.890978 2.872187

H -1.470593 -0.230162 3.195265

O 0.056227 2.851793 0.355502

C 0.116938 3.632382 -0.824206

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E=-1663.8545966au

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C -4.352485 2.743223 -1.685182

H -5.156801 3.425593 -1.955785

C -3.881348 1.817585 -2.614487

H -4.316123 1.781231 -3.613621

C -2.858539 0.927834 -2.277490

H -2.515605 0.198013 -3.015068

C -2.303761 0.967154 -1.001067

C -0.931513 -2.226676 1.291956

C -2.263651 -1.652840 1.209073

C -2.778267 -1.888697 -0.105110

C -1.721613 -2.454986 -0.878654

C -0.600962 -2.712770 0.013638

Rh -1.037992 -0.416450 -0.177133

C -2.127330 1.931448 1.261280

O -2.541216 2.573534 2.220372

C 0.249258 0.078439 -1.901533

C 0.947273 0.401420 -0.741470

C 0.612505 -3.485900 -0.376271

H 0.401830 -4.565207 -0.334629

H 0.925651 -3.268883 -1.405993

H 1.471968 -3.293499 0.277467

C -0.123324 -2.294979 2.541524

H -0.654038 -2.865395 3.317922

H 0.841328 -2.788333 2.374652

H 0.064880 -1.287916 2.939011

C -3.010130 -1.083831 2.366654

H -3.388244 -1.892397 3.010461

H -2.369565 -0.433949 2.976477

H -3.872209 -0.488203 2.043969

C -4.163552 -1.594680 -0.565749

H -4.835406 -2.427509 -0.311804

H -4.565480 -0.685372 -0.101472

H -4.209380 -1.444061 -1.650261

C -1.822574 -2.940109 -2.284893

H -2.126111 -3.997577 -2.318448

H -2.562941 -2.369231 -2.858282

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O -0.389940 0.930163 2.450231

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H 0.488896 -0.843080 -2.438477

H -0.248627 0.849515 -2.483799

C 2.025090 -0.464285 -0.217917

C 3.397331 0.139701 0.128259

C 2.474874 -0.397815 1.192159

H 2.131140 -1.427521 -0.716165

H 2.793415 -1.321541 1.672525

H 1.992241 0.335402 1.835748

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H	4.745833	3.822173	-0.750197
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E=-1663.8288751au

N	1.476222	1.322501	-1.165597
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C	3.211161	2.530737	1.777083
H	3.915692	3.231365	1.329307
C	3.220802	2.241683	3.138959
H	3.931594	2.735368	3.799380
C	2.316003	1.315280	3.652842
H	2.315193	1.085027	4.717915
C	1.399860	0.684091	2.813277
H	0.679054	-0.023782	3.228610
C	1.382419	0.969832	1.445667
C	1.524999	-2.046250	-1.529278
C	2.758059	-1.566102	-0.916794
C	2.709619	-1.856957	0.465247
C	1.434721	-2.479222	0.738287
C	0.752529	-2.672080	-0.503908
Rh	0.998970	-0.435173	-0.139890
C	2.373920	2.140363	-0.542535
O	3.114582	2.965730	-1.066441
C	-0.459801	1.018541	0.849878
C	-0.953373	0.313961	-0.314334
C	-0.487431	-3.475194	-0.681269
H	-0.239702	-4.547327	-0.679166
H	-1.216602	-3.312132	0.123165
H	-0.986811	-3.255992	-1.631531
C	1.219032	-1.976264	-2.985596
H	1.854422	-2.660973	-3.566968
H	0.172190	-2.237381	-3.186247
H	1.382597	-0.956705	-3.359455
C	3.858821	-0.889720	-1.657996
H	4.523649	-1.630066	-2.126999
H	3.463360	-0.238686	-2.446851
H	4.468783	-0.261772	-0.997147
C	3.751153	-1.552001	1.483693
H	4.260386	-2.468833	1.814668
H	4.513704	-0.871461	1.087775
H	3.316161	-1.073584	2.372225
C	1.000545	-3.016717	2.059094
H	1.290754	-4.072727	2.171834
H	1.459623	-2.463270	2.887524
H	-0.089501	-2.966021	2.181711
O	1.560412	1.303332	-2.556666
C	0.864685	2.405555	-3.108832
H	0.907207	2.274326	-4.195456
H	-0.187615	2.415951	-2.782050
H	1.353476	3.347693	-2.829358
H	-1.010608	0.888196	-1.242334
H	-0.921154	0.734226	1.798590
H	-0.356666	2.098011	0.727770
C	-2.040300	-0.675448	-0.134624
C	-3.497581	-0.196446	-0.338317
C	-2.833459	-1.170264	-1.279727
H	-1.956013	-1.337888	0.730803
H	-3.215598	-2.188587	-1.248891
H	-2.603954	-0.770058	-2.267377
C	-3.620204	1.221545	-0.794705
O	-3.563086	1.590536	-1.943952
O	-3.681709	2.057026	0.252036
C	-4.479366	-0.794865	0.600058
O	-4.330926	-1.874870	1.129486
O	-5.567092	-0.032372	0.762475
C	-6.549806	-0.568968	1.642385
H	-7.345058	0.177015	1.693256
H	-6.937030	-1.517909	1.255685
H	-6.121811	-0.742717	2.635427
C	-3.680418	3.439194	-0.088883
H	-4.545576	3.686719	-0.713192
H	-3.723039	3.982141	0.857255
H	-2.766134	3.695474	-0.638101

(E)-**E**

E=-1663.8556019au

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C	1.679202	0.290440	2.185339
C	2.644391	-0.468131	2.862039
H	3.625043	-0.015813	3.006592
C	2.351888	-1.735660	3.331281
H	3.112550	-2.312057	3.856457
C	1.075482	-2.275572	3.132398
H	0.838135	-3.272042	3.501951
C	0.100267	-1.519740	2.505667
H	-0.913165	-1.912780	2.406599
C	0.360153	-0.218191	2.030623
C	1.941390	-0.051712	-2.305732
C	3.098699	-0.362543	-1.466669
C	2.846513	-1.592787	-0.850900
C	1.544267	-2.083516	-1.302288
C	1.050395	-1.190453	-2.285007
Rh	1.133730	-0.107601	-0.346037
C	2.147614	1.619425	1.629991
O	2.990498	2.312733	2.184533
C	-0.802051	0.611651	1.503236
C	-0.843901	0.545839	-0.023760
C	-0.104511	-1.397084	-3.197625
H	0.247198	-1.791226	-4.162932
H	-0.828953	-2.113405	-2.794267
H	-0.636710	-0.460199	-3.397731
C	1.828608	1.146560	-3.179078
H	2.489190	1.065569	-4.055610
H	0.801125	1.282763	-3.539231
H	2.108450	2.047629	-2.618816
C	4.255089	0.550071	-1.245419
H	4.987251	0.478301	-2.063136
H	3.921984	1.593528	-1.177547
H	4.774064	0.319399	-0.306181
C	3.695298	-2.318386	0.128712
H	4.088002	-3.247596	-0.310625
H	4.547660	-1.713830	0.459657
H	3.120976	-2.597745	1.024088
C	0.965276	-3.392616	-0.888754
H	1.517109	-4.232129	-1.338639
H	1.011560	-3.520208	0.202176
H	-0.085328	-3.488986	-1.187001
O	2.037129	2.850314	-0.330327
C	1.343955	4.040105	-0.022502
H	1.723107	4.803803	-0.710880
H	0.258858	3.912146	-0.169427
H	1.541451	4.348611	1.013552
H	-0.935669	1.539336	-0.482291
H	-1.737134	0.235178	1.946103
H	-0.688543	1.650712	1.835625
C	-1.875407	-0.395580	-0.552110
C	-3.383052	-0.019475	-0.432392
C	-2.667700	-0.109359	-1.763136
H	-1.738165	-1.455442	-0.317942
H	-2.975649	-0.937056	-2.399506
H	-2.502127	0.841121	-2.269074
C	-4.274562	-1.171309	-0.134945
O	-3.998106	-2.321722	-0.401958
O	-5.438405	-0.799637	0.407149
C	-3.674950	1.295405	0.205806
O	-3.966822	1.439276	1.369419
O	-3.505608	2.326249	-0.642102
C	-6.335918	-1.864489	0.696768
H	-7.217016	-1.398681	1.142192
H	-6.606136	-2.403808	-0.217869
H	-5.882026	-2.572204	1.398931
C	-3.592947	3.609713	-0.033993
H	-3.433479	4.335063	-0.834495
H	-4.575361	3.754123	0.427703
H	-2.823434	3.719322	0.740473

(E)-**F**

E=-1663.8503356au

Rh	0.348476	0.742955	-0.052212
C	2.022872	2.238272	-0.004686

C	2.051488	1.402382	-1.201169
C	0.899564	1.740313	-2.006679
C	0.829060	2.972804	-0.017825
C	0.115508	2.640099	-1.246907
C	4.424693	-2.998793	-1.099360
C	4.860911	-2.636357	0.171746
C	3.957967	-2.074958	1.057212
C	2.617535	-1.815267	0.715806
C	2.177162	-2.171849	-0.573143
C	3.103489	-2.772685	-1.441911
H	5.106600	-3.455625	-1.815268
H	5.892721	-2.804857	0.476215
H	4.261876	-1.828237	2.072272
H	2.753847	-3.065413	-2.434754
N	1.022735	-0.188824	1.631763
C	-0.264634	-1.226153	-0.475861
C	0.792154	-2.047208	-1.173975
C	1.874063	-1.202930	1.893700
O	2.157997	-1.587738	3.030475
O	0.535189	0.473469	2.762658
C	-0.411806	-0.306012	3.467051
H	-0.815580	0.352309	4.245749
H	-1.229004	-0.628968	2.803398
H	0.070002	-1.178899	3.923879
H	0.409527	-3.079561	-1.313699
H	0.913900	-1.667913	-2.205537
C	-1.566520	-1.334059	-1.230589
C	-2.857924	-0.692621	-0.693112
C	-2.227207	-0.276734	-2.017359
H	-1.777250	-2.344783	-1.602660
H	-2.815854	-0.549404	-2.890947
H	-1.761119	0.705754	-2.020718
C	-4.039804	-1.599730	-0.799118
O	-4.486381	-2.007028	-1.846758
O	-4.478126	-2.001251	0.399647
C	-2.765848	0.293623	0.403520
O	-1.744783	0.853604	0.787884
O	-3.944006	0.608192	0.926621
C	-5.560483	-2.926659	0.362553
H	-5.793027	-3.156260	1.404069
H	-6.428439	-2.482304	-0.136343
H	-5.272523	-3.835304	-0.176879
C	-3.921982	1.574440	1.977588
H	-4.955245	1.663283	2.316280
H	-3.272502	1.238772	2.792979
H	-3.555375	2.537611	1.604196
C	-1.180881	3.272953	-1.621378
H	-1.578883	2.889066	-2.568232
H	-1.942273	3.112610	-0.843506
H	-1.061534	4.360540	-1.733075
C	0.297520	3.875400	1.041828
H	0.224647	4.916292	0.692457
H	-0.706791	3.561589	1.361940
H	0.937121	3.865223	1.931190
C	0.662439	1.255842	-3.396064
H	-0.313108	1.572455	-3.784109
H	1.428128	1.650010	-4.080484
H	0.703844	0.159810	-3.462645
C	3.243381	0.654533	-1.688502
H	2.971592	-0.115075	-2.421390
H	3.945918	1.347651	-2.178021
H	3.778616	0.151069	-0.874219
C	3.059519	2.215278	1.063035
H	3.499743	1.215316	1.161263
H	3.871716	2.921531	0.837211
H	2.635239	2.473381	2.040100
H	-0.439644	-1.650418	0.523879

***(E)*-F-TS**

E=-1663.8340568au

Rh	0.430457	0.719631	-0.189998
C	2.141633	1.860930	0.603560
C	2.419119	1.407656	-0.739445
C	1.480941	2.065534	-1.636259
C	0.989142	2.690766	0.549030
C	0.602657	2.838480	-0.850722

C 4.383766 -2.909402 -0.988561
C 4.738660 -2.520391 0.299304
C 3.759505 -2.039702 1.158790
C 2.427525 -1.914768 0.751383
C 2.056240 -2.341009 -0.536663
C 3.053719 -2.829679 -1.386106
H 5.133984 -3.300019 -1.674727
H 5.769978 -2.606296 0.638047
H 3.997700 -1.767171 2.186347
H 2.765441 -3.182628 -2.378099
N 0.409091 -0.691384 1.331314
C -0.005285 -1.094719 -1.499130
C 0.628737 -2.387843 -1.001707
C 1.484838 -1.390952 1.802213
O 1.700075 -1.625140 2.989151
O -0.388864 -0.211054 2.379659
C -1.386658 -1.171494 2.662871
H -2.027883 -0.733089 3.436787
H -1.991106 -1.391633 1.766082
H -0.937457 -2.097670 3.047557
H 0.532908 -0.558411 -2.296243
H -0.001087 -2.755764 -0.179084
H 0.563072 -3.144130 -1.803018
C -1.374056 -1.218881 -1.772183
C -3.123963 -0.254835 -0.937216
C -2.320146 -0.199281 -2.222065
H -1.847863 -2.189501 -1.591561
H -2.948528 -0.517690 -3.060028
H -1.860762 0.778100 -2.409210
C -4.163739 -1.264470 -0.937573
O -4.351200 -2.021385 -1.881364
O -4.889013 -1.353657 0.198168
C -2.767778 0.606395 0.125175
O -1.696581 1.254606 0.189416
O -3.671078 0.782319 1.099476
C -5.870177 -2.375713 0.191952
H -6.363737 -2.320527 1.165582
H -6.599756 -2.220268 -0.611535
H -5.413042 -3.362832 0.053484
C -3.298893 1.657453 2.153087
H -4.065422 1.533272 2.922219
H -2.306846 1.408987 2.548134
H -3.292340 2.700697 1.807455
C -0.527931 3.685342 -1.313001
H -0.708121 3.579999 -2.388640
H -1.451068 3.418728 -0.782519
H -0.315754 4.745095 -1.110012
C 0.290317 3.328386 1.694803
H 0.470555 4.413463 1.720266
H -0.792016 3.162488 1.614903
H 0.622253 2.900687 2.647599
C 1.494936 1.951306 -3.121035
H 0.491397 2.062035 -3.550122
H 2.135499 2.725895 -3.567604
H 1.890830 0.981833 -3.448525
C 3.618359 0.659855 -1.198977
H 3.370375 -0.080358 -1.969546
H 4.349021 1.359831 -1.632518
H 4.107380 0.121642 -0.381255
C 2.876207 1.492957 1.845782
H 3.637159 0.728521 1.654065
H 3.380094 2.374934 2.265261
H 2.198180 1.091069 2.611292

***(E)*-G**

E=-1663.8632025au

Rh -0.149232 0.069003 0.181262
C -1.189242 0.498561 2.111901
C -1.162634 -0.917241 1.874004
C 0.226854 -1.345510 1.902689
C 0.160423 0.957496 2.150502
C 1.037302 -0.201105 2.080644
C -5.201746 -2.160524 -0.693524
C -5.596220 -0.981442 -0.068130
C -4.776771 0.136593 -0.138136
C -3.542862 0.099986 -0.799275

C	-3.157199	-1.081240	-1.452740
C	-3.999297	-2.194786	-1.387960
H	-5.837455	-3.043976	-0.659807
H	-6.547917	-0.927789	0.458097
H	-5.081976	1.084097	0.302846
H	-3.702747	-3.104372	-1.913510
N	-1.413845	1.355138	-0.896860
C	-0.673040	-1.543276	-1.419254
C	-1.882808	-1.187217	-2.236904
C	-2.787400	1.404741	-0.781204
O	-3.419087	2.451856	-0.678403
O	-0.885306	2.632534	-0.677836
C	-0.525544	3.218039	-1.908254
H	-0.030359	4.163340	-1.657069
H	0.171965	2.571929	-2.459200
H	-1.418054	3.425302	-2.517139
H	-0.748585	-2.447532	-0.805489
H	-1.679537	-0.253349	-2.775797
H	-2.005483	-1.976519	-2.997912
C	0.569168	-1.048869	-1.734517
C	2.952315	-0.638678	-0.988123
C	1.882961	-1.633550	-1.362091
H	0.594123	-0.246014	-2.476325
H	2.243563	-2.192352	-2.245290
H	1.748093	-2.415478	-0.594409
C	4.245634	-1.258159	-0.813799
O	4.444420	-2.451322	-1.005263
O	5.233615	-0.448755	-0.353271
C	2.629733	0.698017	-0.787775
O	1.448447	1.191656	-0.745153
O	3.634208	1.589435	-0.616736
C	6.478478	-1.093813	-0.169142
H	7.166763	-0.323018	0.188764
H	6.405031	-1.904426	0.566711
H	6.848622	-1.522710	-1.108188
C	3.269364	2.955480	-0.574251
H	4.186506	3.497993	-0.329924
H	2.888732	3.295485	-1.547063
H	2.496379	3.153997	0.178748
C	2.514111	-0.164398	2.237580
H	2.993252	-1.070932	1.853248
H	2.970306	0.685106	1.713951
H	2.766742	-0.068249	3.304340
C	0.576846	2.371754	2.347459
H	0.297924	2.726530	3.350527
H	1.661089	2.486554	2.239501
H	0.090556	3.019932	1.606257
C	-2.380058	1.368147	2.299980
H	-2.397151	1.743581	3.333729
H	-2.370802	2.238593	1.629750
H	-3.314270	0.824482	2.124556
C	-2.333159	-1.836446	1.890824
H	-2.526885	-2.177099	2.919390
H	-3.244450	-1.354750	1.517787
H	-2.158417	-2.730235	1.280487
C	0.681625	-2.761593	1.862929
H	0.518418	-3.237408	2.841521
H	0.128269	-3.355301	1.124268
H	1.748735	-2.845558	1.626582

(E)-G-TS

E=-1892.8073356au

Rh	0.381805	-0.948899	0.151882
C	1.205174	-2.964463	0.525699
C	1.415054	-2.068654	1.633010
C	0.110597	-1.718005	2.179895
C	-0.202861	-3.016480	0.284889
C	-0.882753	-2.289462	1.355613
C	4.006933	3.463285	0.782119
C	4.538886	2.246762	1.201755
C	4.160818	1.085243	0.547012
C	3.223206	1.090427	-0.493024
C	2.707926	2.319923	-0.941270
C	3.120288	3.485818	-0.285123
H	4.302409	4.393446	1.266339
H	5.262321	2.207732	2.014758

H 4.608024 0.131295 0.819967
H 2.735860 4.442629 -0.644973
N 1.648607 -0.491119 -1.511844
C 0.361088 2.807957 -1.628717
C 1.752073 2.500838 -2.100273
C 2.954320 -0.260485 -1.100361
O 3.879569 -1.064111 -1.206356
O 1.633935 -1.678639 -2.276500
C 0.832748 -1.470275 -3.418745
H 0.855992 -2.416904 -3.971796
H -0.201418 -1.221191 -3.144668
H 1.247837 -0.672059 -4.053610
H 2.128085 3.340458 -2.709461
C -0.722490 2.112178 -1.964862
C -2.741633 1.231364 -0.657979
C -2.094146 2.383590 -1.439742
H -0.602424 1.270868 -2.649550
H -2.767568 2.665160 -2.269455
H -2.067164 3.265676 -0.781315
C -3.981045 1.617999 -0.000775
O -4.543380 2.691755 -0.093983
O -4.422803 0.660634 0.878920
C -2.488849 -0.115092 -1.071511
O -1.356266 -0.595267 -1.279692
O -3.483686 -1.016696 -1.286665
C -5.631228 0.993588 1.539506
H -5.874020 0.142516 2.181777
H -5.515428 1.902777 2.140095
H -6.441534 1.163796 0.817865
C -4.785468 -0.618736 -1.680033
H -5.486036 -0.729150 -0.845422
H -4.799915 0.421804 -2.027789
H -5.084491 -1.278340 -2.501486
C -0.068503 1.846521 1.520487
O 0.677073 1.061213 0.921313
O -1.363179 1.812040 1.526677
C 0.528855 2.939927 2.353340
H 0.165769 3.910250 1.993518
H 0.187765 2.835679 3.391317
H 1.621519 2.908440 2.302542
H 0.261935 3.652341 -0.934291
H 1.728954 1.613003 -2.741045
H -1.830677 1.348835 0.662354
C -2.355515 -2.185477 1.530065
H -2.883021 -2.332588 0.581422
H -2.711044 -2.947797 2.239618
H -2.660054 -1.203611 1.916226
C -0.902943 -3.731789 -0.812738
H -1.535441 -4.536179 -0.410897
H -1.547442 -3.031416 -1.362379
H -0.194445 -4.170629 -1.523171
C 2.284638 -3.660529 -0.215857
H 2.801876 -4.348629 0.469353
H 1.889276 -4.240492 -1.055119
H 3.023294 -2.952415 -0.622507
C 2.736267 -1.722109 2.217842
H 2.984688 -2.398705 3.049417
H 3.525482 -1.810173 1.460474
H 2.750348 -0.693989 2.602713
C -0.120231 -0.880375 3.385880
H -0.201263 -1.518361 4.277999
H 0.710032 -0.184914 3.557629
H -1.046895 -0.299208 3.305478

***(E)*-H**

E=-1892.8547165au

Rh -1.624404 -0.613244 -0.191352
C -3.317144 -1.750895 0.504173
C -3.489252 -1.369046 -0.873667
C -2.451729 -1.995984 -1.664280
C -2.133437 -2.559892 0.579805
C -1.605683 -2.703343 -0.765967
C -1.367789 4.754874 -1.303579
C -2.439439 3.932512 -0.980314
C -2.278709 2.957858 -0.002674
C -1.065056 2.801313 0.664184

C	0.014202	3.654228	0.370209
C	-0.156745	4.611073	-0.630691
H	-1.474349	5.520437	-2.071231
H	-3.395461	4.045040	-1.489722
H	-3.106080	2.295825	0.258049
H	0.678303	5.270010	-0.875343
N	-1.321863	0.540952	1.498650
C	2.031751	2.246507	0.945417
C	1.331613	3.564245	1.107009
C	-0.971268	1.828129	1.797358
O	-0.637688	2.213530	2.915684
O	-1.358555	-0.270327	2.642403
C	-0.047592	-0.640662	3.032293
H	-0.163998	-1.402650	3.812872
H	0.506890	-1.065196	2.177790
H	0.489275	0.226041	3.437587
H	1.981985	4.375021	0.739495
C	2.484623	1.515838	1.964995
C	3.211220	-0.417574	0.490128
C	3.155086	0.178790	1.895518
H	2.330779	1.904840	2.976121
H	2.618498	-0.521812	2.551093
H	4.180468	0.243590	2.292304
C	4.386586	0.122608	-0.291451
O	5.477740	0.367085	0.160369
O	4.059758	0.314324	-1.583178
C	3.171705	-1.925715	0.510908
O	2.357956	-2.574687	1.131772
O	4.098238	-2.479719	-0.282374
C	5.117117	0.799261	-2.402429
H	4.688369	0.933920	-3.398423
H	5.500409	1.750774	-2.018003
H	5.940685	0.077454	-2.434804
C	4.067423	-3.900278	-0.358124
H	4.902228	-4.184694	-1.001351
H	4.182090	-4.342276	0.637257
H	3.119327	-4.243191	-0.788998
C	-0.011045	0.736679	-1.732878
O	-1.259344	0.929334	-1.780400
O	0.460933	-0.126828	-0.933173
C	0.897730	1.544233	-2.609279
H	1.932405	1.194335	-2.530479
H	0.555513	1.492343	-3.649434
H	0.833807	2.596434	-2.300053
H	2.150303	1.889832	-0.083448
H	1.155589	3.744459	2.176412
C	-0.337193	-3.406584	-1.086138
H	0.433079	-3.166504	-0.339928
H	-0.485906	-4.496201	-1.078394
H	0.049024	-3.115239	-2.069024
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H	-1.990319	-4.276205	1.835786
H	-0.507179	-3.301245	1.771243
H	-1.904731	-2.720373	2.695474
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H	-4.863491	-2.165743	1.923715
H	-3.553048	-1.110972	2.521447
H	-4.771407	-0.465685	1.415703
C	-4.536382	-0.472254	-1.428286
H	-5.289942	-1.053735	-1.979557
H	-5.051382	0.085278	-0.638212
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H	-3.065238	-2.363828	-3.685850
H	-2.329819	-0.766574	-3.411058
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C	-3.949412	-0.954409	-1.272439
C	-3.474063	-2.442549	0.459198
C	-3.386218	-2.241648	-0.980395

C	-0.956875	4.510131	-1.742331
C	-2.267395	4.166401	-1.418322
C	-2.499859	3.308067	-0.356500
C	-1.446870	2.741836	0.372627
C	-0.130009	3.110460	0.069123
C	0.088089	3.994145	-0.992216
H	-0.752503	5.191092	-2.567331
H	-3.103287	4.580029	-1.980139
H	-3.517452	3.059271	-0.067267
H	1.118020	4.267769	-1.227809
N	-1.252363	0.564748	1.558306
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C	-1.876156	1.821815	1.475563
O	-2.790550	2.135221	2.225636
O	-1.590033	-0.105102	2.755917
C	-0.836841	0.412914	3.836689
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H	0.242506	0.294770	3.660049
H	-1.080757	1.468301	4.022756
H	1.675227	3.494680	1.157076
C	3.264527	1.891046	-0.204072
C	4.700861	-0.152887	-0.041679
C	4.079995	0.900745	-0.974917
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H	4.889120	1.385056	-1.539614
H	3.434941	0.367469	-1.690573
C	5.256040	-1.286991	-0.873873
O	4.644634	-2.281573	-1.182975
O	6.494804	-1.009639	-1.305463
C	5.767305	0.442022	0.851468
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O	6.175849	-0.466344	1.751831
C	7.069044	-1.985424	-2.170764
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H	-3.620259	-0.747485	4.259293
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H	-3.121502	0.698395	3.313016
C	-2.518324	1.865662	-1.660645
H	-2.900127	0.970171	-2.169019
H	-2.983871	1.912248	-0.666561
H	-2.864951	2.743415	-2.227284
C	-0.864707	3.744966	0.232900
H	-1.388594	4.551445	-0.302143
H	-1.592650	3.265945	0.903480
H	-0.095488	4.201923	0.864948
C	-0.467514	0.140013	-3.440991
H	-1.519617	-0.171992	-3.413601
H	-0.292059	0.618701	-4.415780
H	0.149670	-0.768081	-3.416277
C	2.460356	0.827528	-2.426240
H	2.334192	-0.203892	-2.779547
H	2.782243	1.437348	-3.284429
H	3.279496	0.814536	-1.697087
C	2.239360	3.113887	-0.188363
H	3.171196	2.558809	-0.344542
H	2.395769	4.138166	-0.555991
H	2.074407	3.148992	0.895496
H	-1.396103	-3.389720	1.037448
H	-2.568691	-3.801254	-0.324510

(Z)-F-TS

E=-1663.841592au

Rh	0.142603	-0.374636	0.218314
C	1.069511	-1.607526	1.771284
C	0.756302	-0.275751	2.244962
C	-0.689520	-0.142869	2.264165
C	-0.148736	-2.259269	1.435480
C	-1.230980	-1.346016	1.742518
C	4.546831	3.015964	0.299005
C	5.231398	1.814281	0.457586
C	4.663618	0.642000	-0.018679
C	3.402459	0.632565	-0.628087
C	2.713034	1.845804	-0.802890
C	3.309474	3.020346	-0.331352
H	4.979196	3.949907	0.655649
H	6.209048	1.793714	0.936614
H	5.190304	-0.308471	0.052013
H	2.778007	3.963941	-0.469483
N	1.586611	-0.874002	-1.201800
C	0.311862	1.773176	-0.262401
C	1.330437	1.955984	-1.386576
C	2.941375	-0.720549	-1.094574
O	3.764992	-1.589072	-1.374498
O	1.261062	-2.192459	-1.571215
C	1.114176	-2.267011	-2.972820
H	0.765219	-3.285194	-3.184422
H	0.371768	-1.536913	-3.323441
H	2.079402	-2.103854	-3.473299
H	0.708220	2.106121	0.705636
H	1.164648	1.219285	-2.181959
H	1.218719	2.960776	-1.828802
C	-1.006756	2.265830	-0.435083
C	-2.678766	1.266355	-1.182981
C	-1.756765	2.363590	-1.679378
H	-1.189359	2.091420	-2.573203
H	-2.319697	3.291842	-1.807366
C	-3.827122	1.727946	-0.437268
O	-4.041223	2.904171	-0.183978
O	-4.629032	0.742156	0.044346
C	-2.300979	-0.077973	-1.465397

O	-1.125240	-0.417498	-1.701660
O	-3.275679	-0.997477	-1.494863
C	-5.729727	1.202134	0.810910
H	-6.286471	0.307918	1.102536
H	-5.393227	1.748378	1.701162
H	-6.368201	1.869431	0.221333
C	-2.857194	-2.317168	-1.822297
H	-3.718109	-2.959370	-1.620042
H	-2.580829	-2.381899	-2.881425
H	-1.988883	-2.623435	-1.224348
C	-2.683844	-1.635874	1.611940
H	-3.240352	-0.810486	1.149082
H	-2.870232	-2.533940	1.012827
H	-3.117353	-1.806006	2.608796
C	-0.251741	-3.652509	0.921686
H	0.358049	-3.769209	0.016476
H	0.108700	-4.374479	1.669147
H	-1.285739	-3.922261	0.675826
C	-1.484217	1.003751	2.789456
H	-2.406888	1.154064	2.210986
H	-1.776978	0.832402	3.836283
H	-0.917399	1.942591	2.763120
C	1.747389	0.688632	2.799469
H	1.335416	1.701829	2.875455
H	2.055836	0.381863	3.809765
H	2.649873	0.744446	2.175626
C	2.425597	-2.212807	1.674801
H	3.216641	-1.461669	1.781717
H	2.557927	-2.953844	2.477366
H	2.584285	-2.720491	0.715290
H	-1.536695	2.651441	0.437597

(Z)-G

E=-1663.8613242au

Rh	0.194517	0.374068	-0.314763
C	1.555223	2.125770	-0.794516
C	1.649673	1.095482	-1.792795
C	0.350933	0.981785	-2.436329
C	0.197967	2.548512	-0.730148
C	-0.549330	1.849881	-1.769091
C	5.046367	-2.555564	-0.473935
C	5.514723	-1.404994	0.153622
C	4.632918	-0.616575	0.879176
C	3.271741	-0.933927	0.969371
C	2.804147	-2.107783	0.358512
C	3.705825	-2.900590	-0.356749
H	5.724947	-3.191839	-1.040073
H	6.566828	-1.131919	0.091492
H	4.976624	0.265112	1.417448
H	3.338956	-3.816518	-0.823508
N	1.099714	0.076838	1.581359
C	0.607897	-1.833662	-0.721183
C	1.359327	-2.513040	0.387069
C	2.460981	0.019858	1.807422
O	3.032321	0.677856	2.671488
O	0.550509	1.080068	2.386531
C	-0.158670	0.486215	3.450647
H	-0.613428	1.314061	4.007003
H	-0.946017	-0.181984	3.073148
H	0.526996	-0.064470	4.111846
H	1.164495	-1.779364	-1.662633
H	0.900439	-2.288884	1.356405
H	1.283192	-3.602164	0.228437
C	-0.761729	-1.652507	-0.773322
C	-2.973804	-1.191899	0.316822
C	-1.737791	-2.043015	0.286846
H	-2.064367	-3.073680	0.071425
C	-4.221879	-1.866954	0.046204
O	-4.318552	-3.062968	-0.196817
O	-5.318478	-1.066746	0.054644
C	-2.777044	0.132459	0.672838
O	-1.627606	0.670999	0.842078
O	-3.848084	0.926057	0.908694
C	-6.535501	-1.738392	-0.200116
H	-7.318223	-0.977433	-0.131946
H	-6.540665	-2.196051	-1.197302

H	-6.715927	-2.530396	0.536852
C	-3.607552	2.183760	1.498077
H	-4.588882	2.563041	1.796570
H	-2.954720	2.106488	2.377037
H	-3.148406	2.893736	0.794356
C	-1.995349	2.026747	-2.066907
H	-2.445173	1.095111	-2.433042
H	-2.552774	2.310773	-1.167928
H	-2.153234	2.804226	-2.828109
C	-0.343085	3.555423	0.222180
H	0.386968	4.353930	0.404622
H	-1.262412	4.013793	-0.161232
H	-0.570290	3.076956	1.185668
C	2.657488	2.652907	0.052853
H	2.832608	3.712225	-0.185394
H	2.429036	2.584121	1.124863
H	3.596110	2.115287	-0.120014
C	2.903148	0.449256	-2.270631
H	3.393156	1.083914	-3.024227
H	3.617414	0.278326	-1.455176
H	2.707808	-0.522026	-2.741344
C	0.059099	0.141685	-3.629666
H	0.495067	0.600234	-4.528920
H	0.488273	-0.865660	-3.546681
H	-1.017882	0.036510	-3.801435
H	-1.214270	-1.439544	-1.747627
H	-1.228738	-2.063995	1.263810

(Z)-G-TS

E=-1892.8081499au

Rh	0.552958	-0.995414	0.189914
C	2.018591	-2.578949	0.439667
C	1.936342	-1.754467	1.618648
C	0.599842	-1.901581	2.181903
C	0.712591	-3.123281	0.208079
C	-0.147369	-2.734187	1.323734
C	3.644363	3.504689	0.980998
C	4.386867	2.329167	0.913737
C	4.004127	1.343839	0.015601
C	2.859837	1.478589	-0.775080
C	2.118333	2.669662	-0.726958
C	2.543288	3.671601	0.151324
H	3.939607	4.304662	1.659104
H	5.271987	2.195267	1.534221
H	4.604031	0.440360	-0.101748
H	1.998367	4.616100	0.178954
N	1.359975	-0.259372	-1.602147
C	-0.272685	3.486225	-0.940544
C	0.941331	2.942237	-1.640775
C	2.601625	0.329955	-1.713370
O	3.467006	-0.009694	-2.511244
O	1.274529	-1.354597	-2.486969
C	0.516512	-0.981795	-3.613726
H	0.468284	-1.871608	-4.252518
H	-0.499552	-0.679125	-3.321072
H	1.009240	-0.165860	-4.164990
H	1.267137	3.688080	-2.387044
C	-1.498454	2.956209	-0.902153
C	-2.748865	0.754686	-0.625823
C	-1.950986	1.681550	-1.546745
H	-2.594193	1.944916	-2.405218
C	-4.047168	1.286893	-0.212174
O	-4.552666	2.320193	-0.605905
O	-4.617430	0.545728	0.779221
C	-2.512731	-0.646852	-0.820267
O	-1.374447	-1.136594	-0.967671
O	-3.492745	-1.577291	-0.844410
C	-5.883064	1.016651	1.209386
H	-6.222390	0.318750	1.979265
H	-5.806141	2.028985	1.621063
H	-6.597748	1.038809	0.375731
C	-4.784539	-1.309072	-1.362750
H	-5.522639	-1.309190	-0.554615
H	-4.822048	-0.346869	-1.888830
H	-5.014110	-2.111902	-2.071665
C	-0.421000	1.560591	1.711787

O	0.462445	1.006356	1.034221
O	-1.673206	1.258389	1.710814
C	-0.031940	2.677471	2.632722
H	-0.394904	3.619267	2.200177
H	-0.520802	2.553708	3.606055
H	1.055569	2.728498	2.741754
H	-0.131806	4.448160	-0.437700
H	0.694070	2.036220	-2.203417
H	-2.064603	0.889252	0.709720
C	-1.581699	-3.095424	1.457171
H	-2.056819	-3.186029	0.473671
H	-1.694258	-4.051913	1.988306
H	-2.135581	-2.328959	2.015009
C	0.284538	-3.995077	-0.917061
H	1.098181	-4.157973	-1.630226
H	-0.056256	-4.971228	-0.543470
H	-0.548237	-3.523399	-1.456406
C	3.206135	-2.775071	-0.434190
H	3.564902	-3.811214	-0.355844
H	2.963113	-2.567273	-1.484018
H	4.031805	-2.110810	-0.154775
C	3.026283	-0.977994	2.267034
H	3.241329	-1.380558	3.267537
H	3.949661	-1.010673	1.680407
H	2.746117	0.079703	2.373858
C	0.117499	-1.244096	3.426660
H	0.159733	-1.942895	4.274444
H	0.737246	-0.377083	3.684863
H	-0.919101	-0.899554	3.326587
H	-1.093236	1.122908	-1.938450
H	-2.282408	3.506743	-0.375311

(Z)-H

E=-1892.8454507au

Rh	2.037927	-0.704474	0.154037
C	3.454753	-1.554504	-1.264918
C	4.139252	-0.792484	-0.260823
C	3.908629	-1.421099	1.031897
C	2.718916	-2.585412	-0.593493
C	3.040103	-2.518721	0.827065
C	2.386361	4.607775	-0.043773
C	3.049356	3.590258	-0.718324
C	2.323846	2.503678	-1.193917
C	0.945013	2.415744	-1.007327
C	0.264234	3.465018	-0.368665
C	1.006143	4.538959	0.120083
H	2.937509	5.465374	0.339755
H	4.125133	3.648225	-0.885216
H	2.824349	1.700762	-1.735157
H	0.482531	5.346942	0.633702
N	0.748749	0.039981	-1.285716
C	-1.591254	2.467638	0.946828
C	-1.227911	3.421837	-0.151579
C	0.204594	1.249024	-1.590019
O	-0.770322	1.408103	-2.325377
O	0.208263	-1.016743	-2.025920
C	-1.037758	-1.448511	-1.507878
H	-1.223687	-2.436256	-1.949266
H	-0.988046	-1.531738	-0.410982
H	-1.836709	-0.755454	-1.805073
H	-1.569538	4.433104	0.123634
C	-2.523057	1.513656	0.897176
C	-4.093931	-0.154593	-0.100415
C	-3.411376	1.200119	-0.270252
H	-2.839199	1.206714	-1.208757
H	-4.203056	1.958298	-0.381871
C	-5.042056	-0.117862	1.079112
O	-5.980971	0.635737	1.166814
O	-4.701354	-1.002635	2.028628
C	-4.872447	-0.549461	-1.339105
O	-4.815115	-0.008350	-2.412843
O	-5.633109	-1.629637	-1.084577
C	-5.553119	-1.005707	3.169626
H	-5.138062	-1.748302	3.854080
H	-5.571522	-0.016582	3.639901
H	-6.575740	-1.276026	2.884957

C	-6.411076	-2.085786	-2.185920
H	-6.986125	-2.937595	-1.817270
H	-7.080662	-1.293537	-2.537257
H	-5.763861	-2.390563	-3.015735
C	0.700048	0.236600	2.133016
O	1.658725	0.897313	1.637024
O	0.341262	-0.854629	1.596703
C	0.040230	0.697209	3.398327
H	-1.047430	0.588147	3.327398
H	0.378264	0.059770	4.225739
H	0.307113	1.734281	3.622265
H	-1.025616	2.596328	1.874505
H	-1.731283	3.147442	-1.085816
C	2.450332	-3.414069	1.855245
H	1.368531	-3.517285	1.703346
H	2.897341	-4.416838	1.799229
H	2.603401	-3.024994	2.867625
C	1.860298	-3.611693	-1.239714
H	2.440733	-4.514062	-1.482688
H	1.034931	-3.911110	-0.580869
H	1.419615	-3.217747	-2.161940
C	3.425958	-1.303339	-2.730515
H	3.994872	-2.078891	-3.262411
H	2.394224	-1.316321	-3.101664
H	3.861309	-0.331286	-2.986415
C	5.018559	0.390988	-0.454279
H	6.061585	0.133290	-0.218906
H	4.988775	0.762064	-1.484691
H	4.721401	1.216714	0.206870
C	4.433753	-0.899520	2.322787
H	5.520371	-1.047651	2.400494
H	4.227989	0.174664	2.418288
H	3.963881	-1.398728	3.177908
H	-3.344349	-0.940441	0.081425
H	-2.674326	0.903036	1.794138

(Z)-H-TS

E=-2121.8270016au

Rh	2.085688	-0.776192	0.167143
C	3.338704	-1.864940	-1.274318
C	4.057023	-0.745001	-0.702164
C	4.164547	-0.960882	0.719672
C	2.954370	-2.723144	-0.211968
C	3.467286	-2.167964	1.035351
C	1.589579	4.936967	0.212699
C	2.703599	4.254327	-0.265215
C	2.521189	3.063459	-0.948054
C	1.252165	2.504188	-1.119210
C	0.120022	3.198832	-0.662180
C	0.321249	4.419668	-0.009351
H	1.705042	5.886902	0.732723
H	3.704331	4.659946	-0.125546
H	3.376700	2.537666	-1.364993
H	-0.545748	4.996104	0.313182
N	0.608892	0.144545	-1.208999
C	1.213094	1.208622	-1.879620
O	1.715639	1.119736	-2.993472
O	0.351894	-0.946060	-2.081705
C	-0.841316	-0.718538	-2.800158
H	-1.015365	-1.625887	-3.388028
H	-1.694602	-0.572261	-2.119380
H	-0.744310	0.141541	-3.480038
C	1.537034	0.911098	2.536656
O	1.586382	0.923123	1.241937
O	1.982350	0.041061	3.281411
C	0.829994	2.142039	3.067126
H	-0.170291	2.199174	2.615904
H	0.756247	2.110588	4.158012
H	1.368858	3.044592	2.751432
C	4.719658	0.307392	-1.513462
H	4.050527	0.674739	-2.304369
H	5.042893	1.155151	-0.899321
H	5.613304	-0.106713	-2.004808
C	3.072902	-2.020713	-2.727449
H	4.017038	-2.220472	-3.256125
H	2.385702	-2.848422	-2.929113

H	2.625145	-1.107520	-3.142510
C	4.811537	-0.045535	1.696354
H	4.297434	-0.091808	2.663249
H	5.869775	-0.310971	1.834622
H	4.762551	0.994037	1.347456
C	3.298783	-2.746722	2.394388
H	2.614984	-3.602126	2.380159
H	4.264417	-3.088350	2.793906
H	2.882190	-1.986471	3.068876
C	2.119999	-3.948069	-0.319822
H	2.741087	-4.854094	-0.278437
H	1.392923	-3.991854	0.499691
H	1.555924	-3.956087	-1.259394
C	-0.822328	-1.273302	1.130647
O	0.329248	-1.740130	1.111658
O	-1.179137	-0.192439	0.520721
H	-0.384448	0.117580	-0.175567
C	-1.912288	-1.978154	1.876672
H	-2.417647	-1.276193	2.550645
H	-2.656972	-2.336985	1.152314
H	-1.509261	-2.817316	2.448167
C	-2.282022	2.954967	0.147969
C	-1.295542	2.767120	-0.973878
H	-1.632975	3.361093	-1.842665
C	-3.488908	2.394726	0.244363
C	-4.316994	0.059873	-0.002996
C	-4.086892	1.405423	-0.705743
H	-3.428474	1.248168	-1.572897
H	-5.050786	1.766584	-1.092606
C	-5.495650	0.108320	0.944964
O	-6.228334	1.048076	1.127231
O	-5.614128	-1.068183	1.584960
C	-4.499475	-1.075224	-0.983153
O	-3.744525	-2.009093	-1.123382
O	-5.612740	-0.903472	-1.711493
C	-6.695094	-1.144284	2.510280
H	-6.655152	-2.148048	2.937333
H	-6.581681	-0.388341	3.294782
H	-7.650663	-0.979612	2.000825
C	-5.867304	-1.916839	-2.679981
H	-6.790340	-1.625506	-3.184544
H	-5.041510	-1.980032	-3.396693
H	-5.985185	-2.891200	-2.193605
H	-1.981298	3.629768	0.951244
H	-1.306503	1.726283	-1.320318
H	-3.421104	-0.196320	0.575353
H	-4.107668	2.642275	1.109207

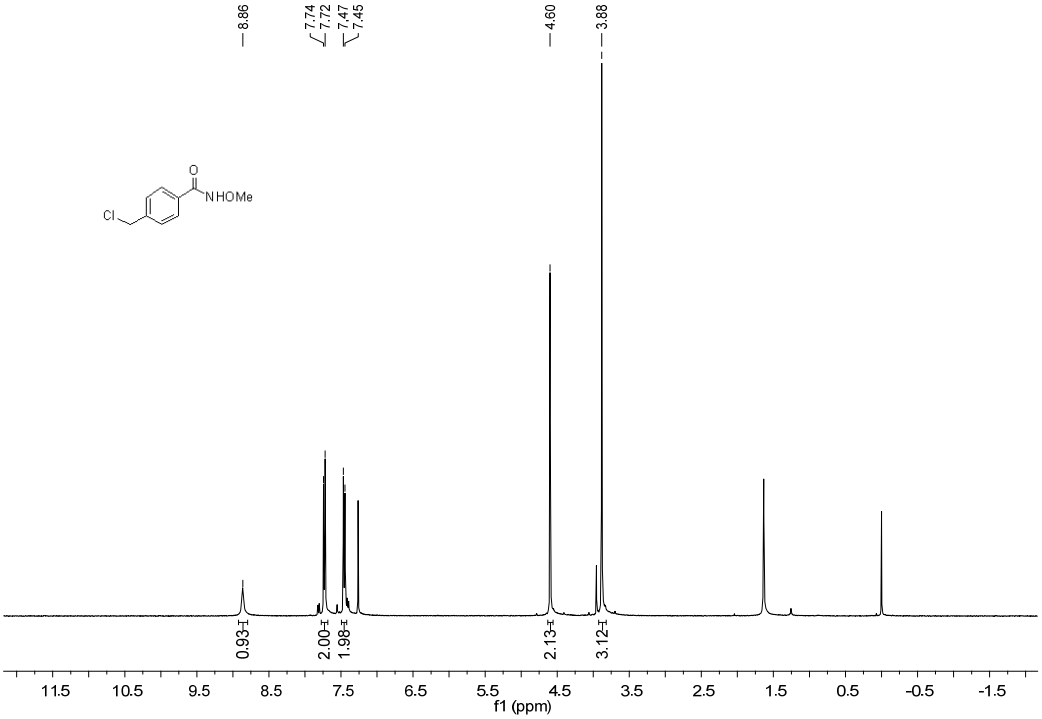
(Z)-3aa

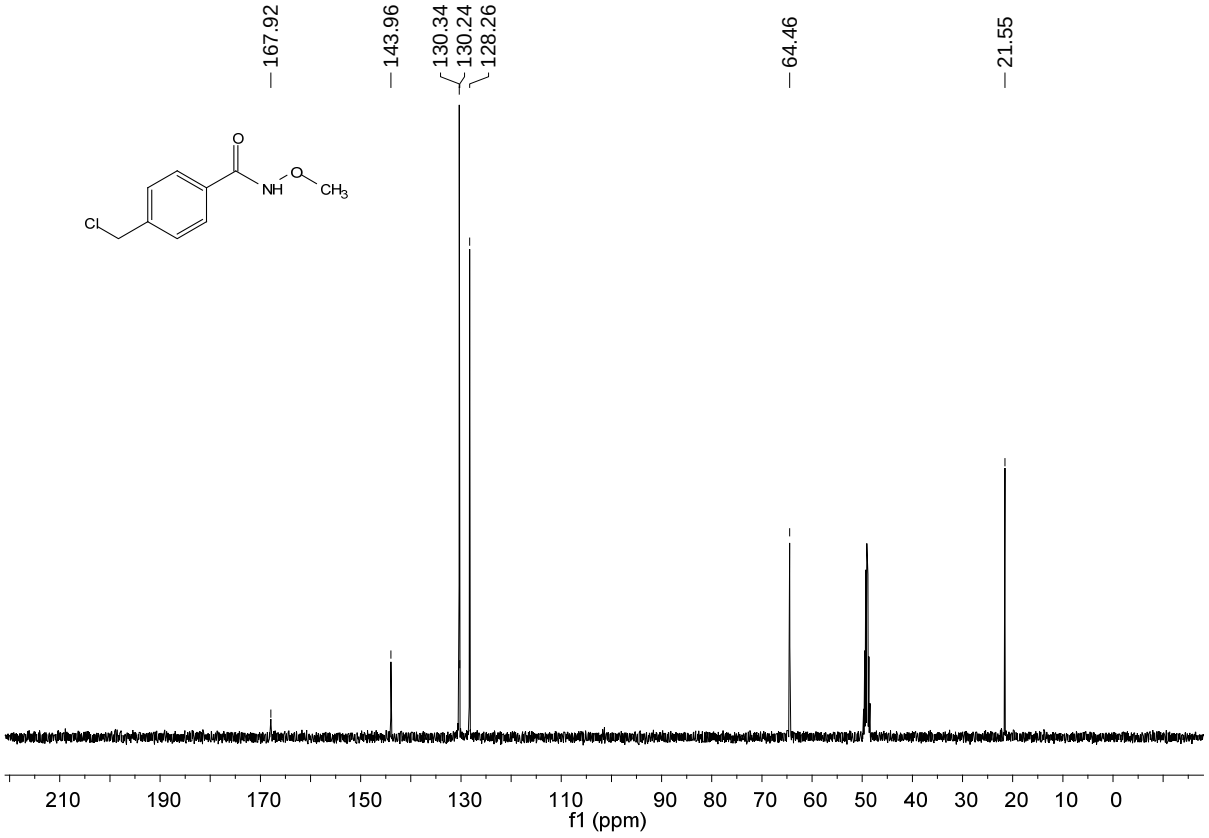
E=-1165.7423583au

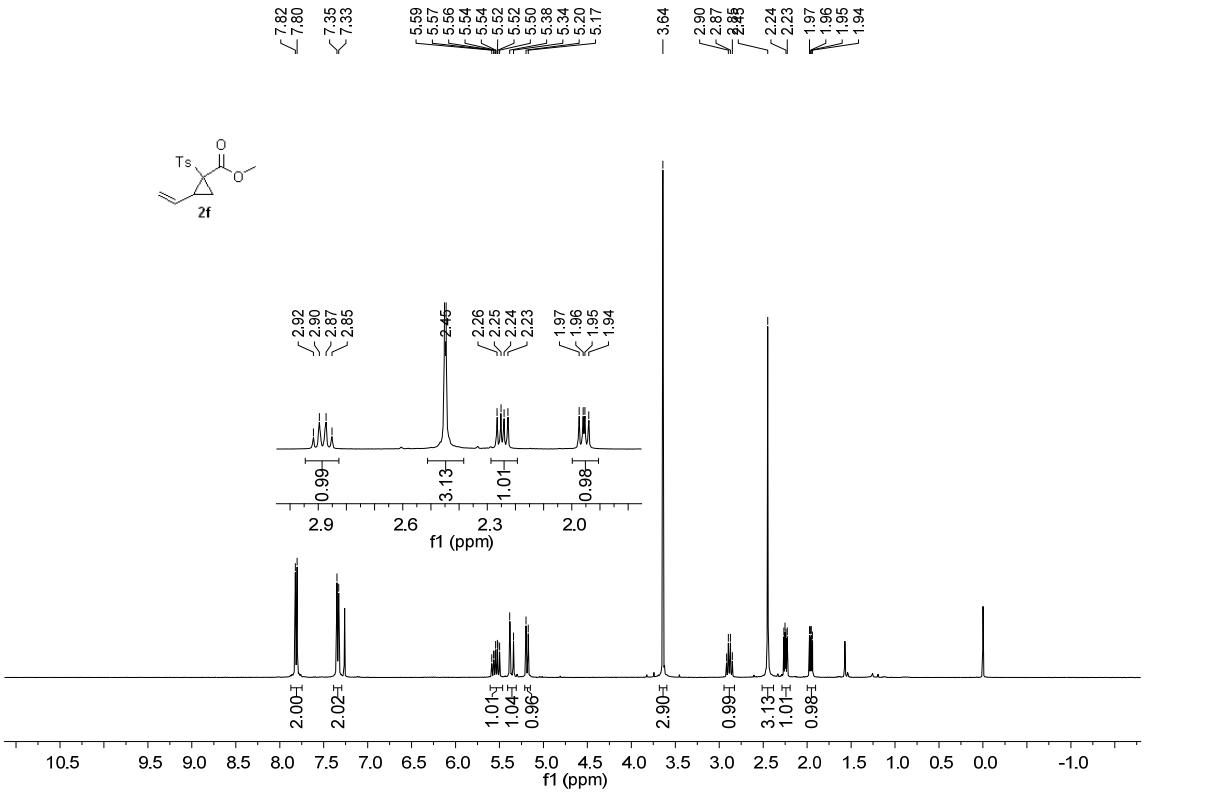
C	-4.732644	-2.261227	-0.347848
C	-5.449099	-1.068782	-0.358546
C	-4.762939	0.134475	-0.321922
C	-3.365911	0.175978	-0.250449
C	-2.633238	-1.026297	-0.265807
C	-3.345510	-2.228551	-0.314270
H	-5.252586	-3.217378	-0.383445
H	-6.536448	-1.077024	-0.402918
H	-5.294277	1.083639	-0.350303
H	-2.782844	-3.163437	-0.341199
N	-1.608347	1.690124	0.489513
C	-2.808029	1.570010	-0.183899
O	-3.367698	2.522208	-0.691789
O	-1.235510	2.965493	0.872960
C	-0.406962	3.554541	-0.119154
H	-0.195586	4.562163	0.251580
H	0.537955	3.003907	-0.240234
H	-0.935786	3.622623	-1.077741
H	-1.382519	1.017550	1.220015
C	-0.580785	-1.291639	1.137656
C	-1.121967	-1.113297	-0.254153
H	-0.822610	-1.987980	-0.853693
C	0.437824	-0.638110	1.709943
C	2.698260	-0.120338	0.757450
C	1.295283	0.406828	1.067172
H	1.386404	1.293305	1.712190

H	0.862466	0.755473	0.121722
C	2.562658	-1.355861	-0.107441
O	2.073611	-1.347700	-1.212034
O	2.992163	-2.453527	0.521834
C	3.505445	0.927723	0.016892
O	3.155021	2.062686	-0.190931
O	4.681599	0.419914	-0.372714
C	2.803894	-3.667323	-0.200902
H	3.220893	-4.458107	0.425128
H	1.736208	-3.841223	-0.378600
H	3.318930	-3.624541	-1.166116
C	5.512609	1.312631	-1.111925
H	6.407987	0.744342	-1.369838
H	4.997440	1.650815	-2.016936
H	5.772888	2.186397	-0.505002
H	-1.101335	-2.047502	1.733348
H	-0.672629	-0.246454	-0.748539
H	3.239734	-0.392853	1.674802
H	0.707314	-0.911745	2.733807

9. ^{1}H NMR and ^{13}C NMR spectra of Substrates and Products



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7.35
7.33
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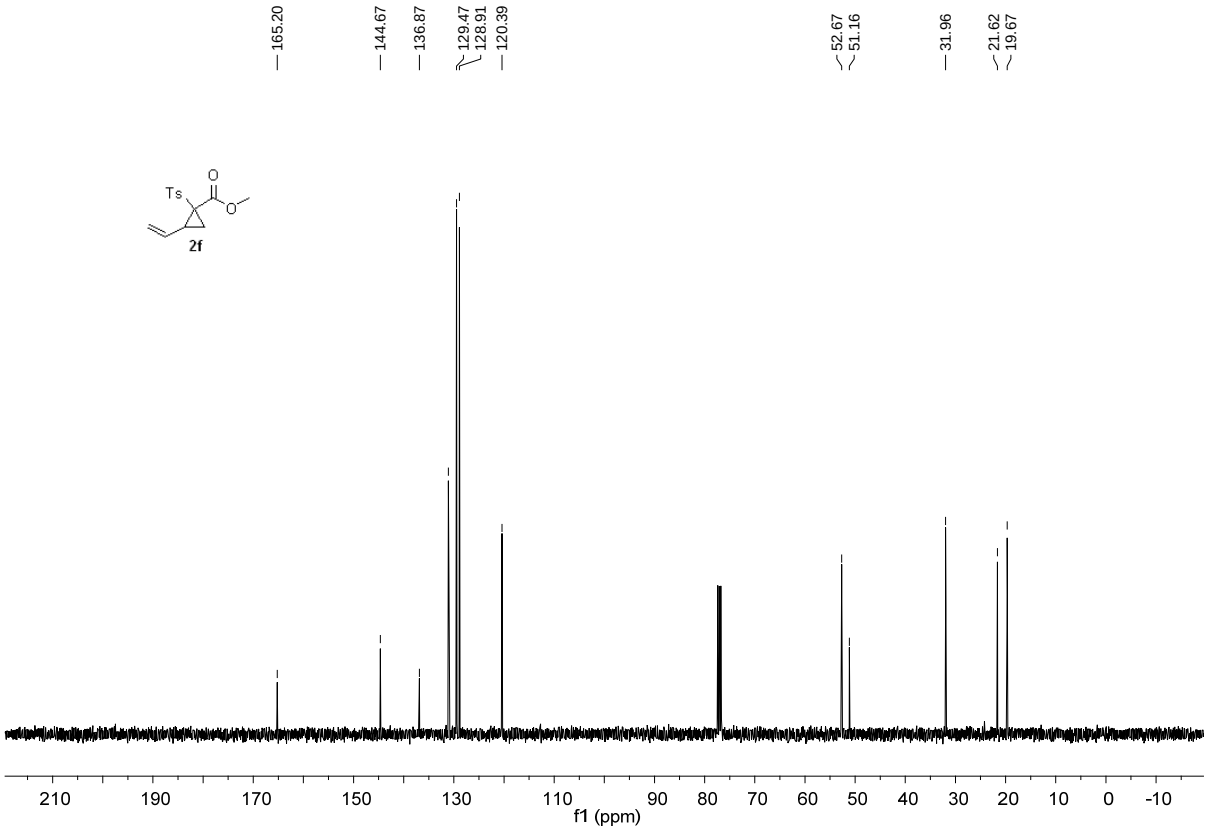
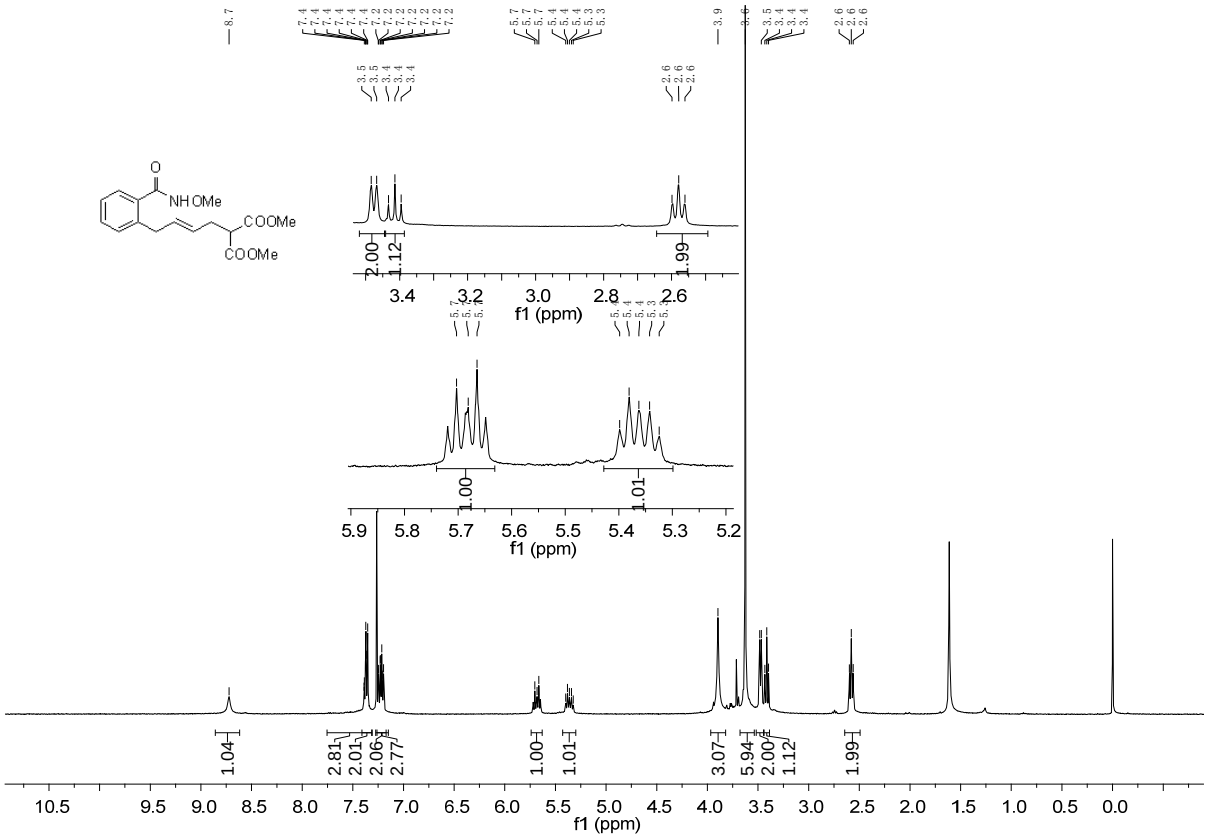
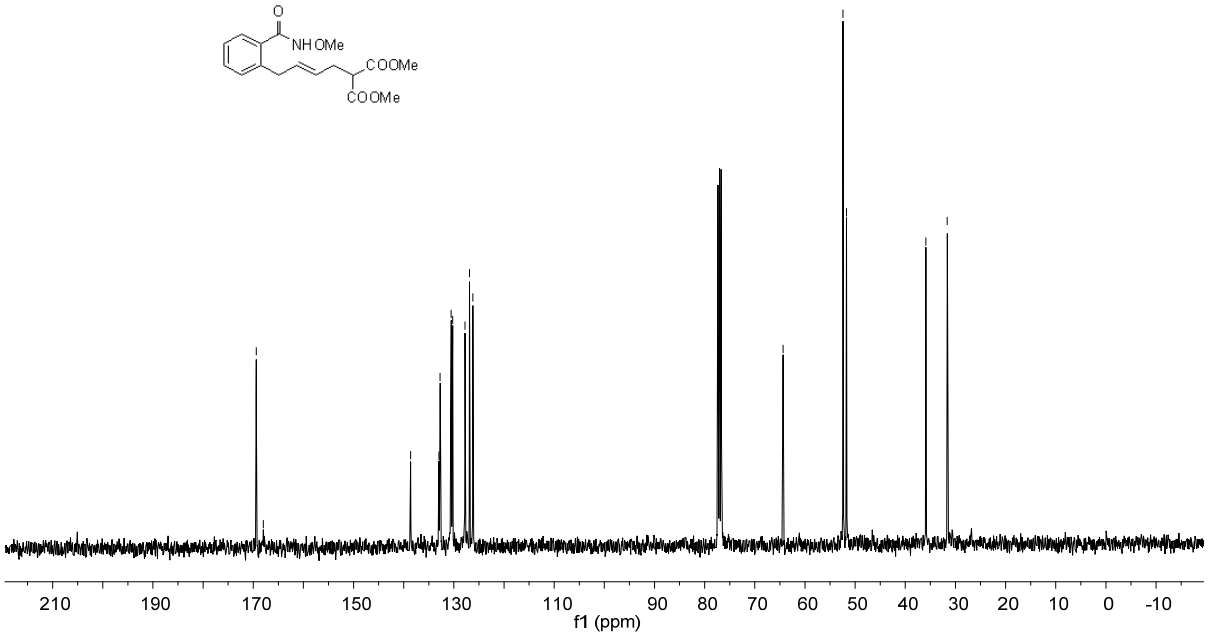
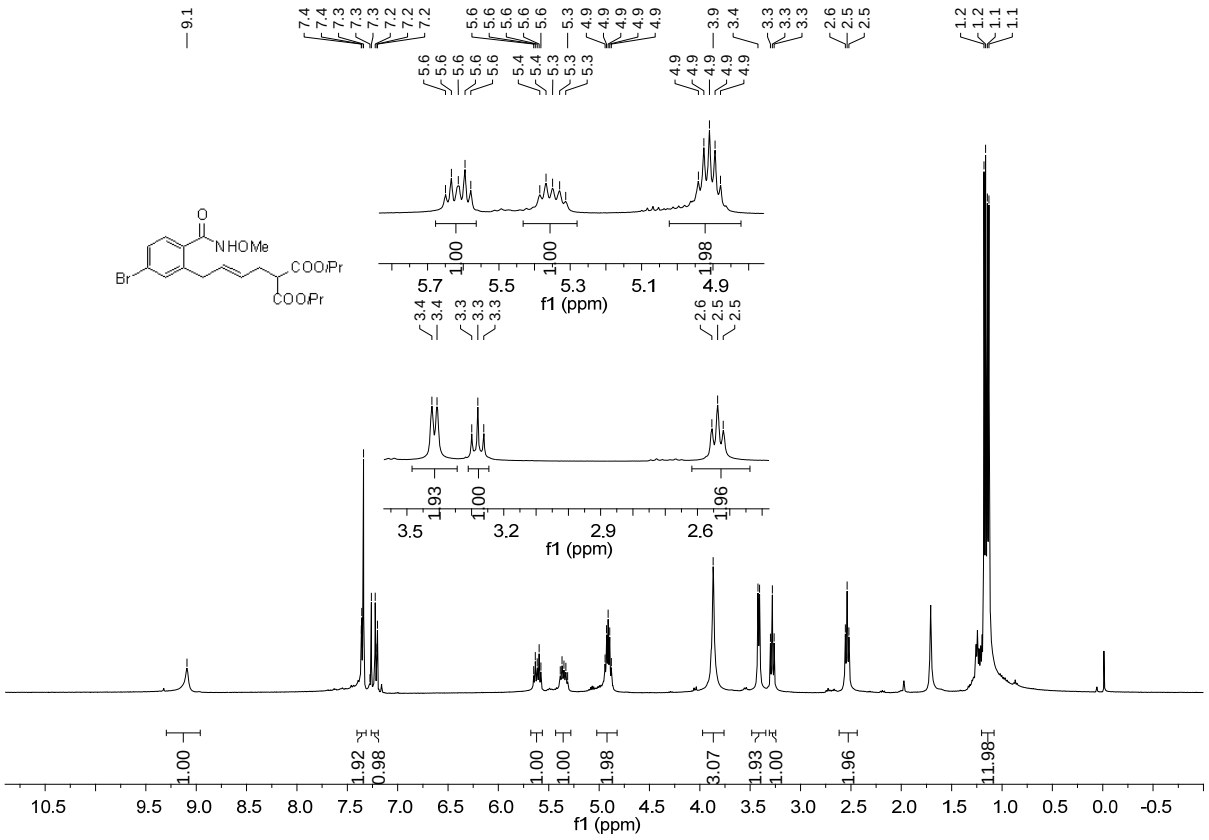
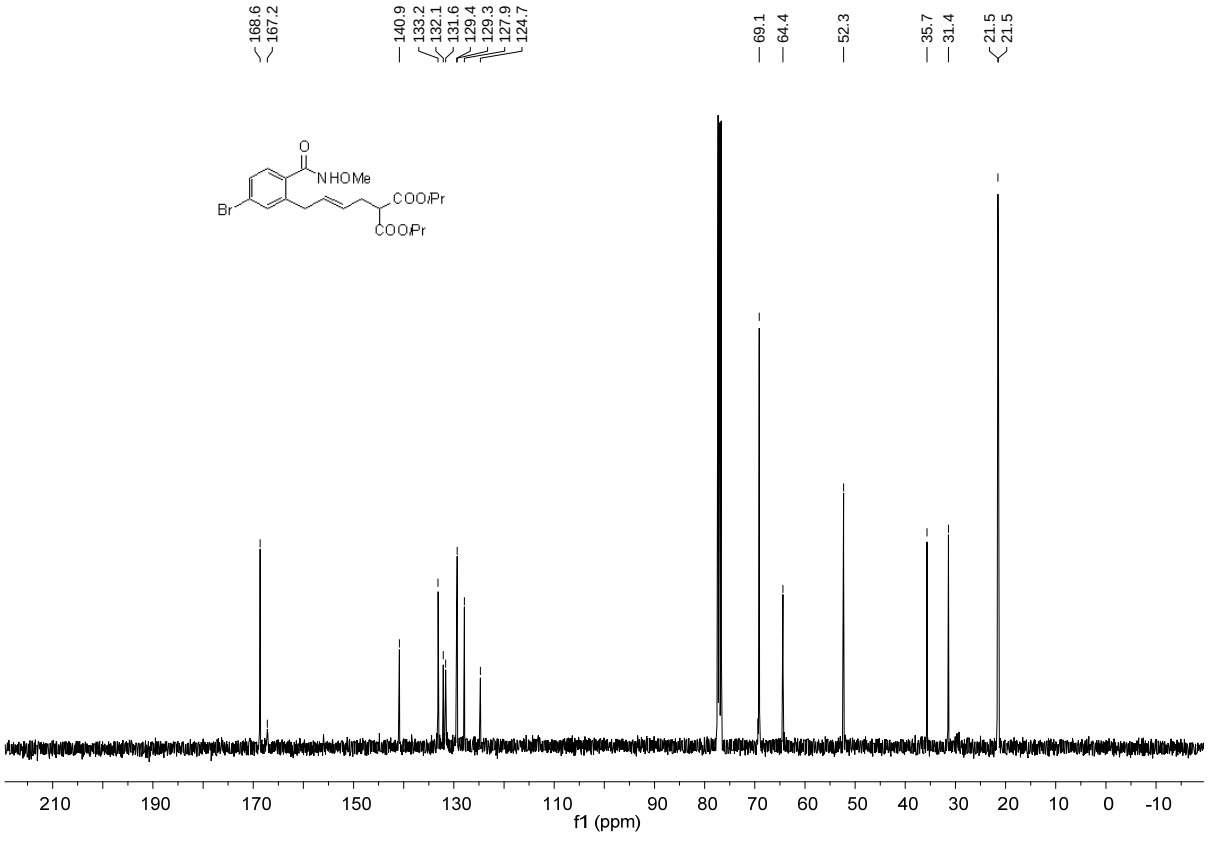
5.57
5.56
5.54
5.54
5.52
5.52
5.50
5.38
5.34
5.20
5.17
3.64
2.90
2.87
2.24
2.23
1.97
1.96
1.95
1.94
Ts
O
O
2f
2.92
2.90
2.87
2.85
2.45
2.26
2.25
2.24
2.23
1.97
1.96
1.95
1.94
0.99
3.13
1.01
0.98
2.9
2.6
2.3
2.0
f1 (ppm)
2.00
2.02
1.01
1.04
0.96
2.90
0.99
3.13
1.01
0.98
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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
-1.0
f1 (ppm)

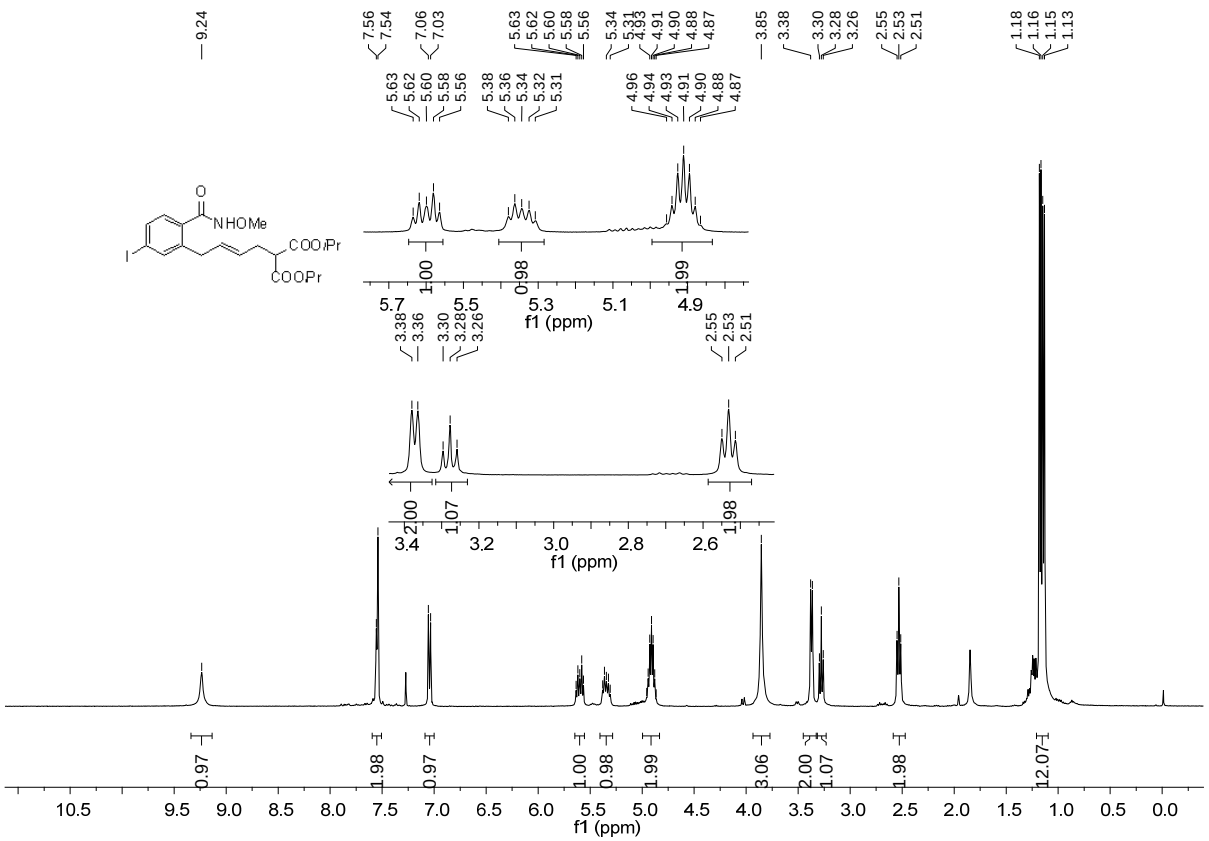

165.20
144.67
136.87
129.47
128.91
120.39
52.67
51.16
31.96
21.62
19.67
Ts
O
O
2f
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


NH OMe
COOMe
COOMe
f1 (ppm)


NH OMe
COOMe
COOMe
f1 (ppm)


O
NHOMe
Br
COOiPr
COOiPr
f1 (ppm)
f1 (ppm)
f1 (ppm)


O
NHOMe
Br
COOiPr
COOiPr
f1 (ppm)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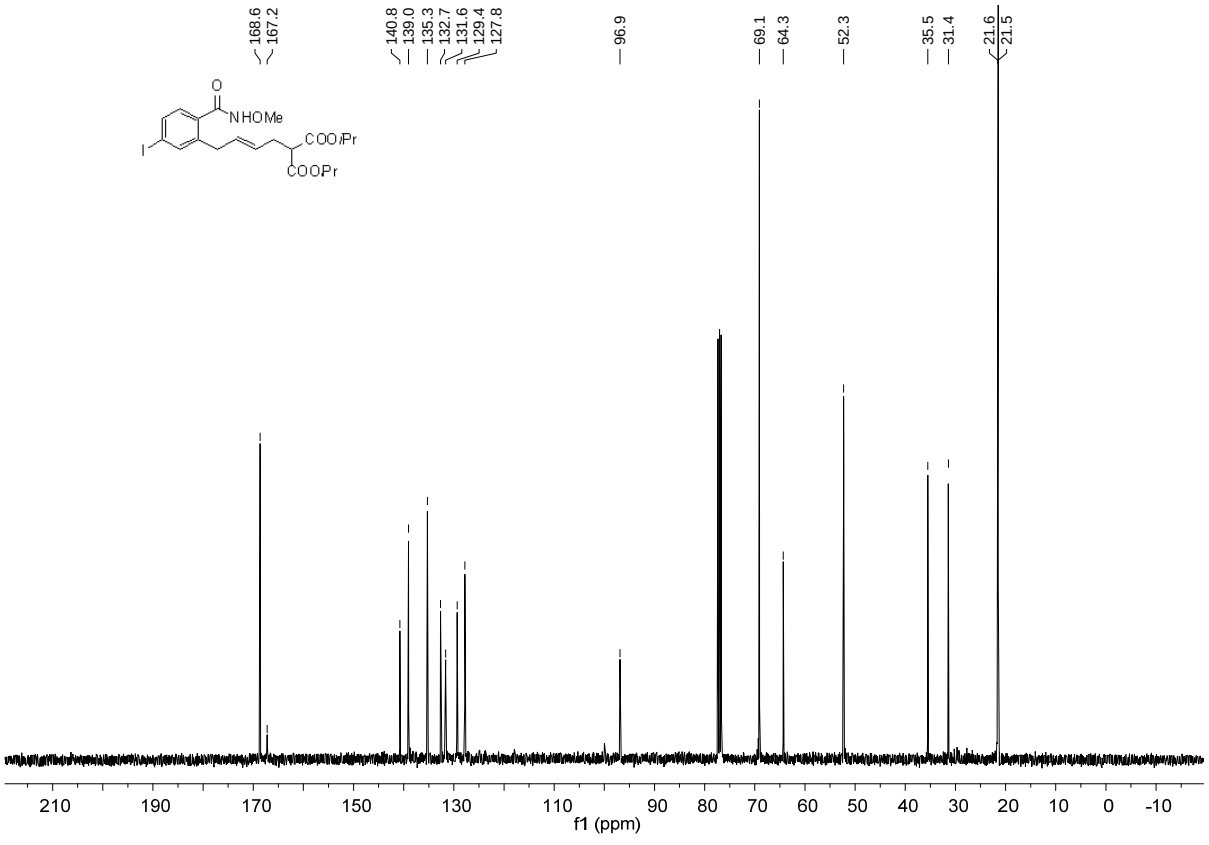
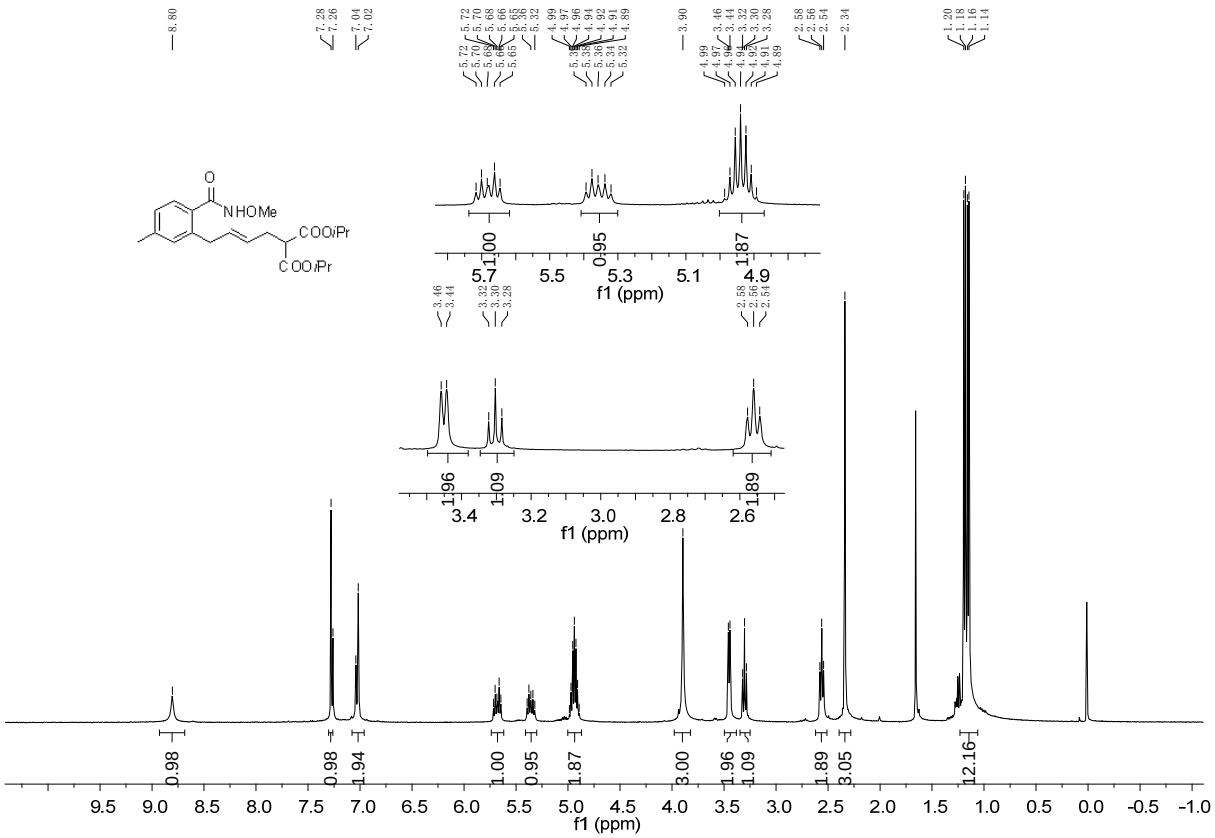
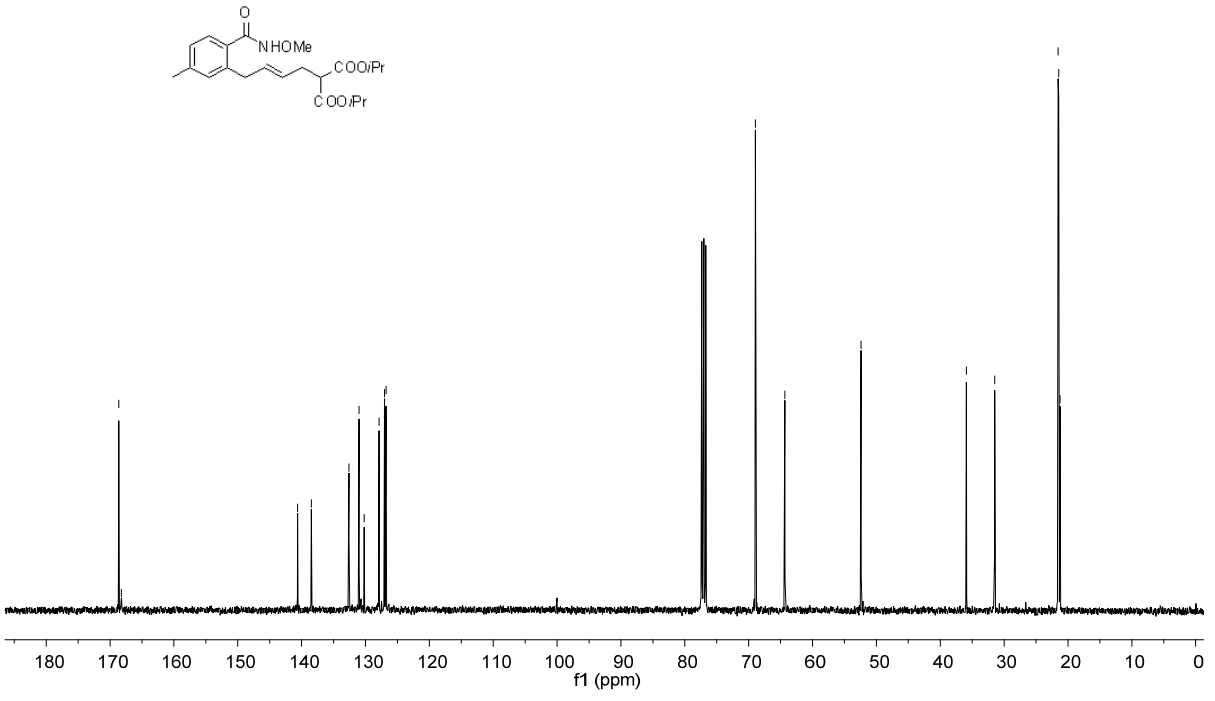
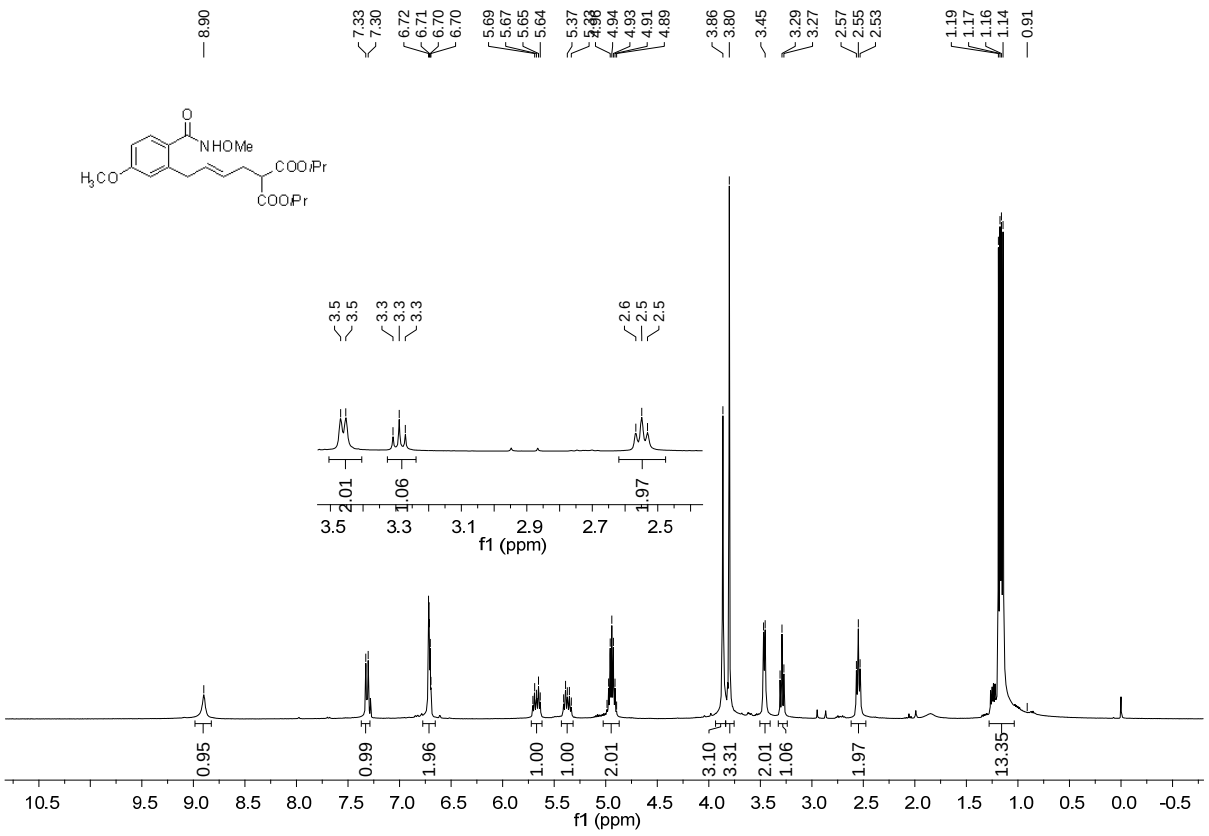
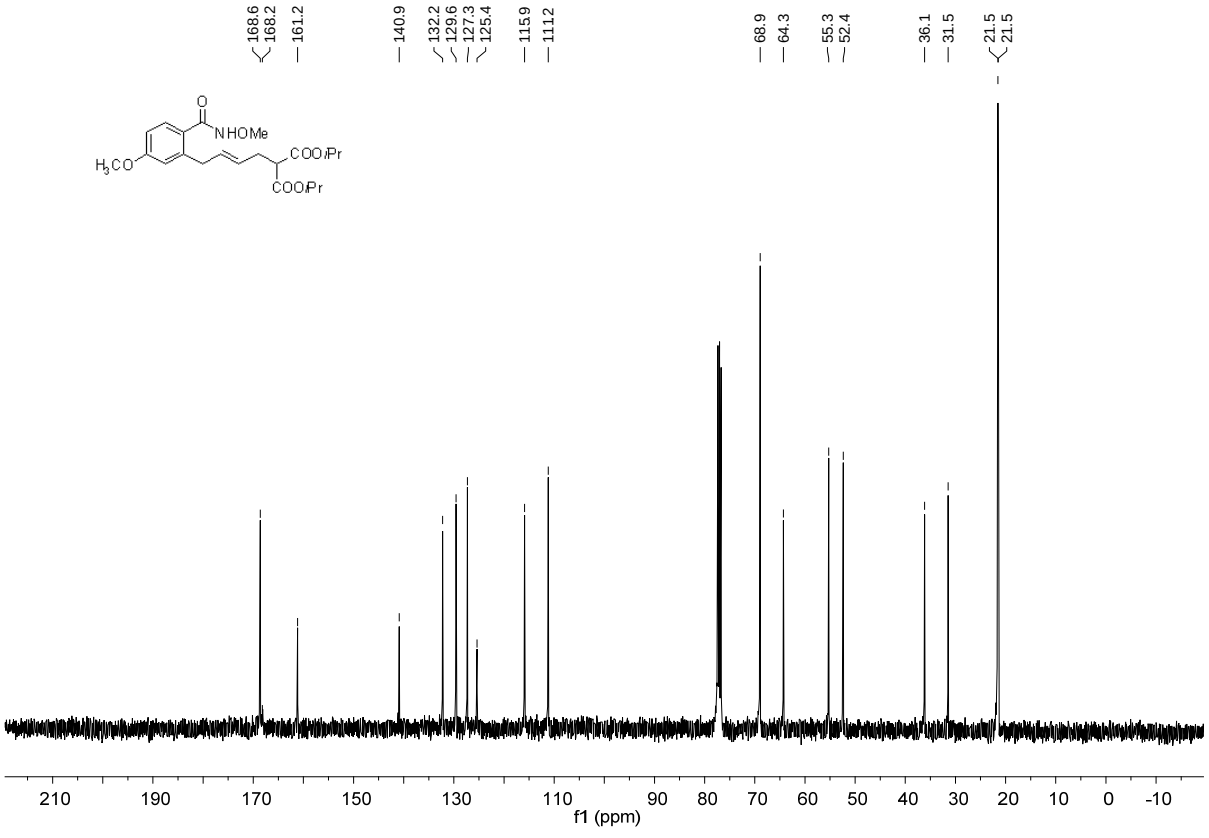
7.56
7.54
7.06
7.03
5.63
5.62
5.60
5.58
5.56
5.38
5.36
5.34
5.32
5.31
5.34
5.31
4.96
4.94
4.93
4.91
4.90
4.88
4.87
3.85
3.38
3.30
3.28
3.26
2.55
2.53
2.51
1.18
1.16
1.15
1.13
O
NHOMe
I
COOiPr
COOPr
1.00
0.98
1.99
5.7
5.5
5.3
5.1
4.9
f1 (ppm)
2.00
1.07
1.98
3.4
3.2
3.0
2.8
2.6
f1 (ppm)
0.97
1.98
0.97
1.00
0.98
1.99
3.06
2.00
1.07
1.98
12.07
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

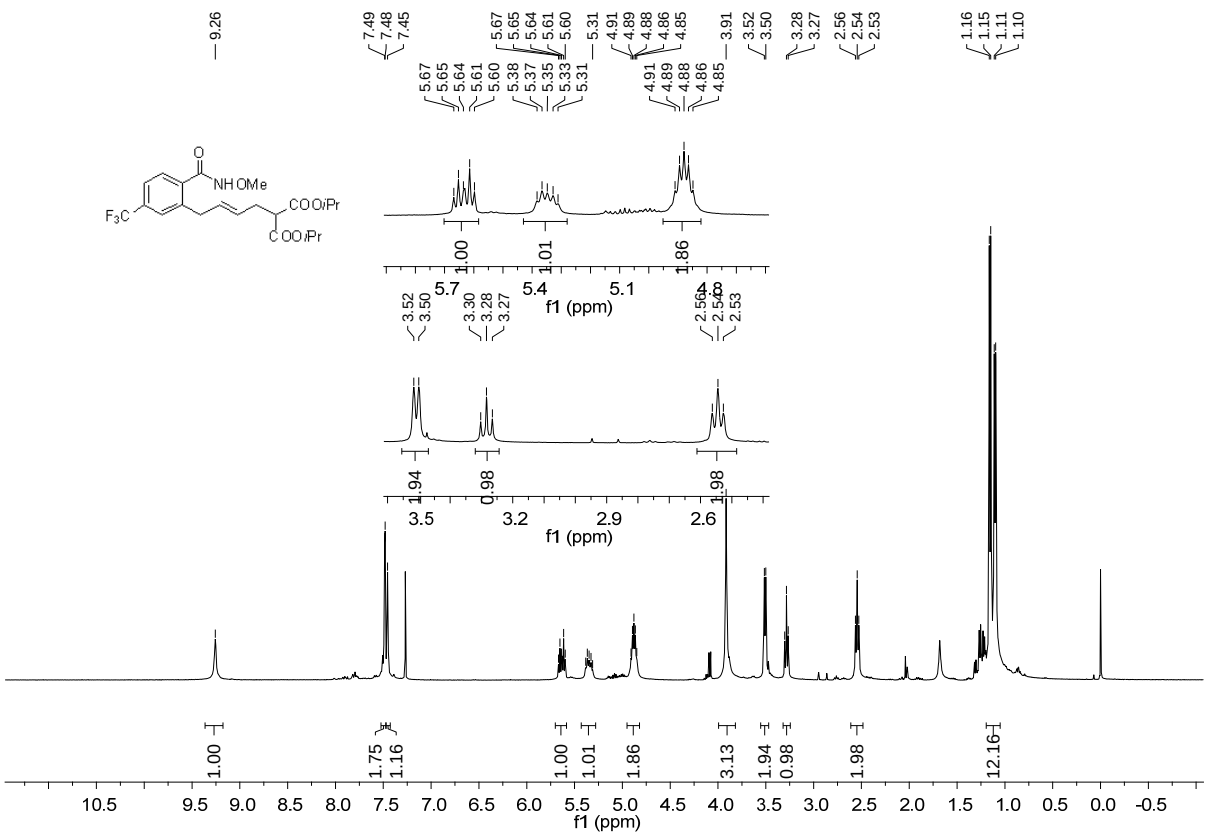

168.6
167.2
140.8
139.0
135.3
132.7
131.6
129.4
127.8
96.9
69.1
64.3
52.3
35.5
31.4
21.6
21.5
O
NHOMe
I
COOiPr
COOPr
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


NHOMe
COOiPr
COOiPr
f1 (ppm)


NHOMe
COOiPr
COOiPr
f1 (ppm)


8.90
7.33
7.30
6.72
6.71
6.70
6.70
5.69
5.67
5.65
5.64
5.37
4.94
4.93
4.91
4.89
3.86
3.80
3.45
3.29
3.27
2.57
2.55
2.53
1.19
1.17
1.16
1.14
0.91
O
NHOMe
H3CO
COOiPr
COOiPr
3.5
3.5
3.3
3.3
3.3
2.6
2.5
2.5
2.01
1.06
1.97
3.5
3.3
3.1
2.9
2.7
2.5
f1 (ppm)
0.95
0.99
1.96
1.00
1.00
2.01
3.10
3.31
2.01
1.06
1.97
13.35
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


168.6
168.2
161.2
140.9
132.2
129.6
127.3
125.4
115.9
111.2
68.9
64.3
55.3
52.4
36.1
31.5
21.5
21.5
O
NHOMe
H3CO
COOiPr
COOiPr
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


9.26
7.49
7.48
7.45
5.67
5.65
5.64
5.61
5.60
5.38
5.37
5.35
5.33
5.31
4.91
4.89
4.88
4.86
4.85
3.91
3.52
3.50
3.30
3.28
3.27
2.56
2.54
2.53
1.16
1.15
1.11
1.10
NHOMe
COOiPr
COOiPr
F3C
1.00
1.01
1.86
1.94
0.98
1.98
f1 (ppm)
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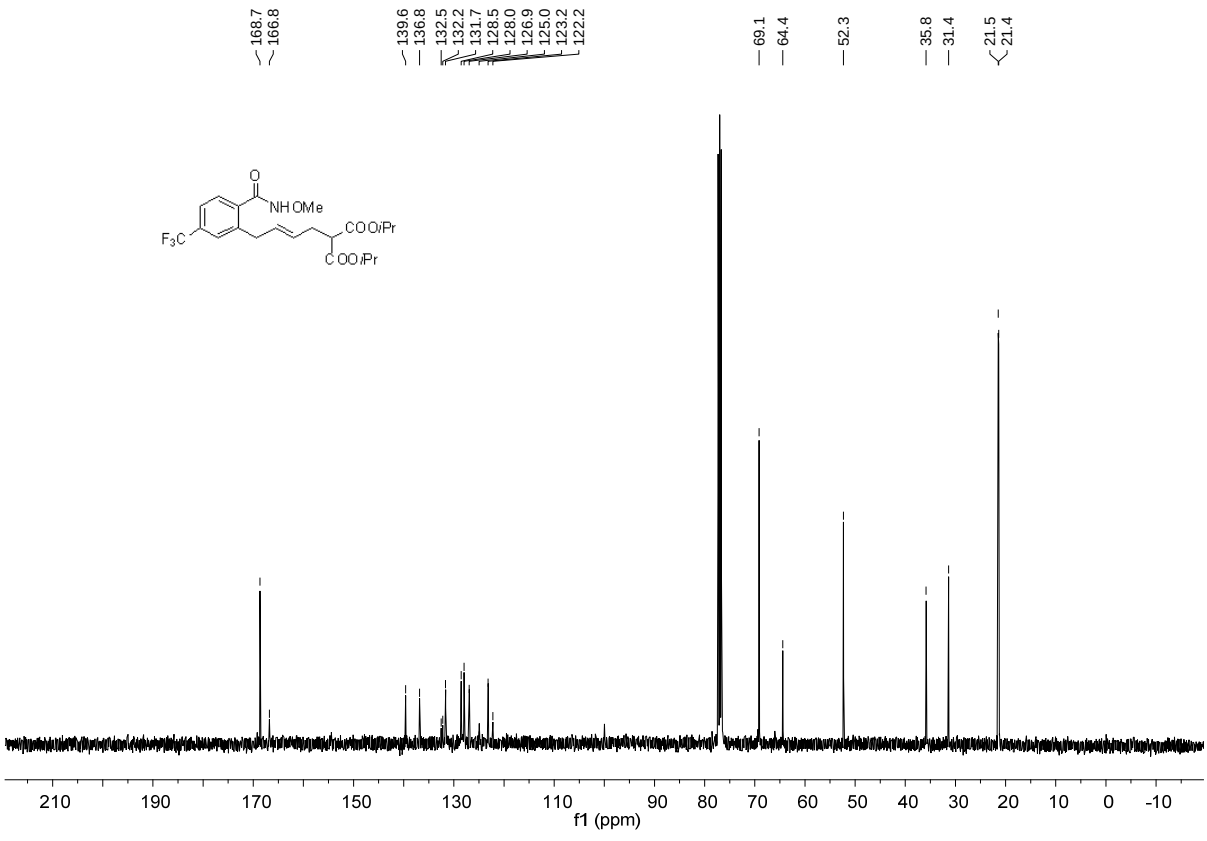
1.75
1.16
1.00
1.01
1.86
3.13
1.94
0.98
1.98
12.16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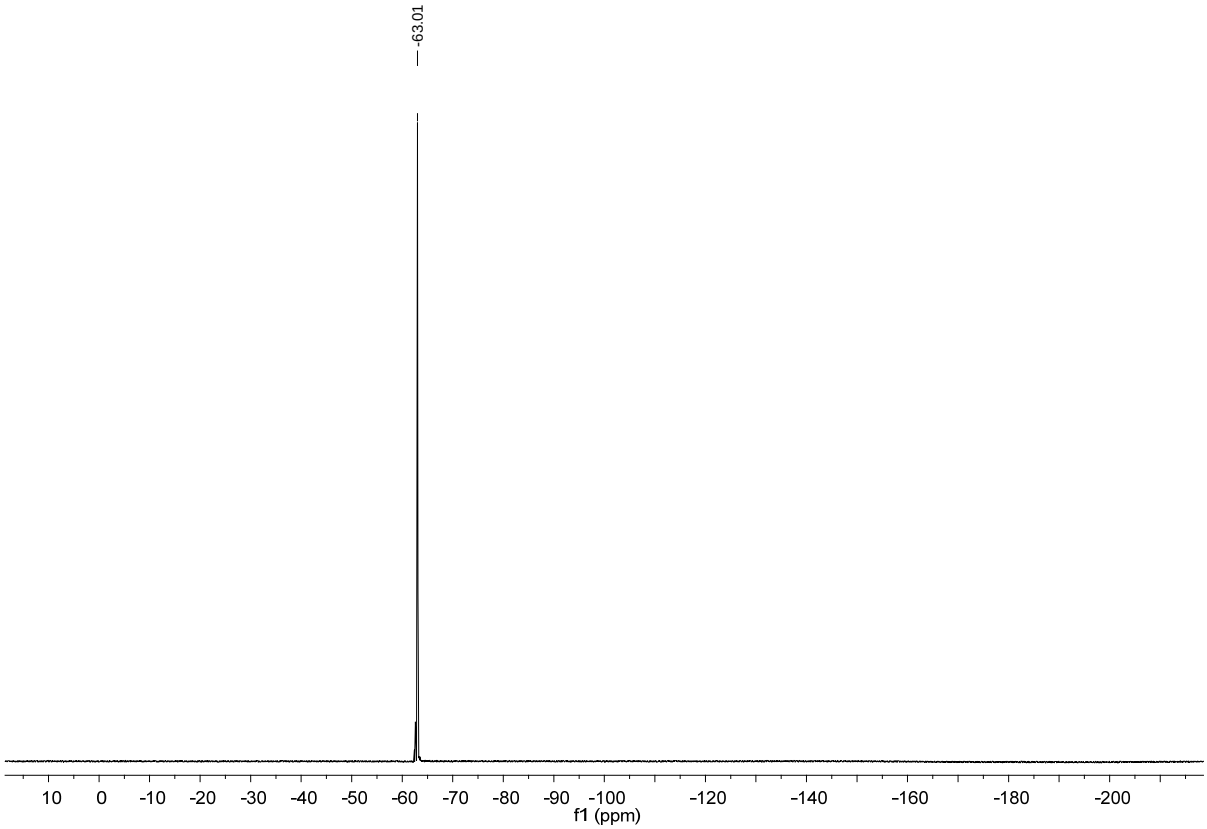
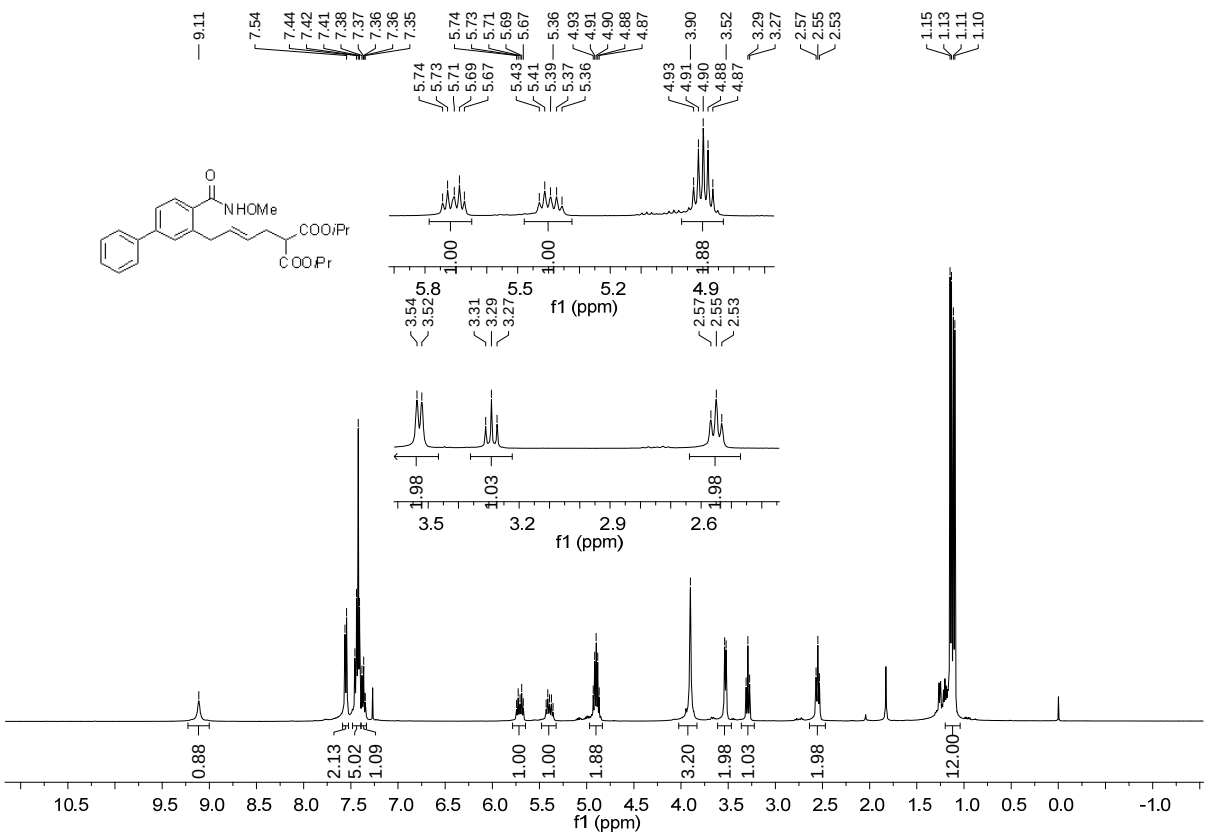
166.8
139.6
136.8
132.5
132.2
131.7
128.5
128.0
126.9
125.0
123.2
122.2
69.1
64.4
52.3
35.8
31.4
21.5
21.4
NHOMe
COOiPr
COOiPr
F3C
f1 (ppm)


-63.01
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)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7.38
7.37
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7.35
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5.73
5.71
5.69
5.67
5.43
5.41
5.39
5.37
5.36
4.93
4.91
4.90
4.88
4.87
3.90
3.52
3.29
3.27
2.57
2.55
2.53
1.15
1.13
1.11
1.10
NHOMe
COOiPr
COOiPr
1.00
1.00
1.88
5.8
5.5
5.2
4.9
f1 (ppm)
3.54
3.52
3.31
3.29
3.27
2.57
2.55
2.53
1.98
1.03
1.98
3.5
3.2
2.9
2.6
f1 (ppm)
0.88
2.13
5.02
1.09
1.00
1.00
1.88
3.20
1.98
1.03
1.98
12.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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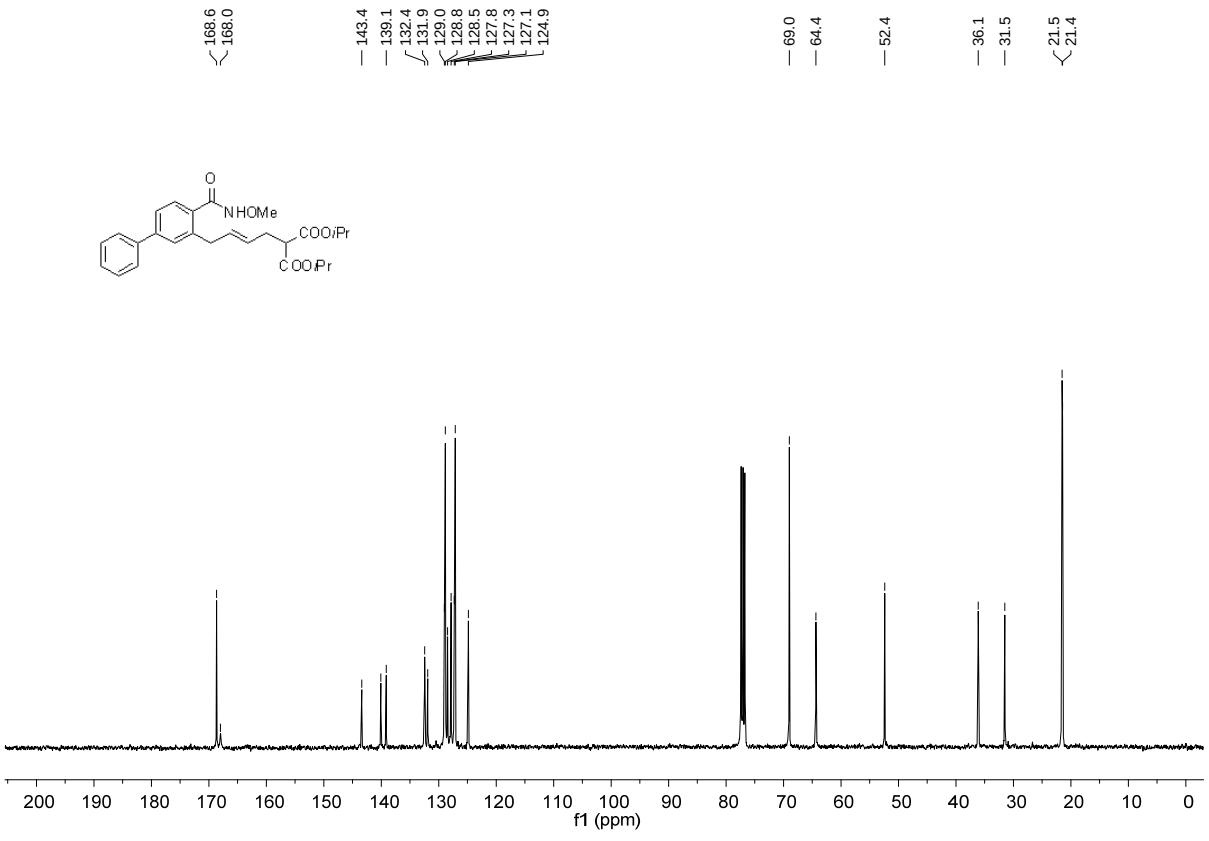
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)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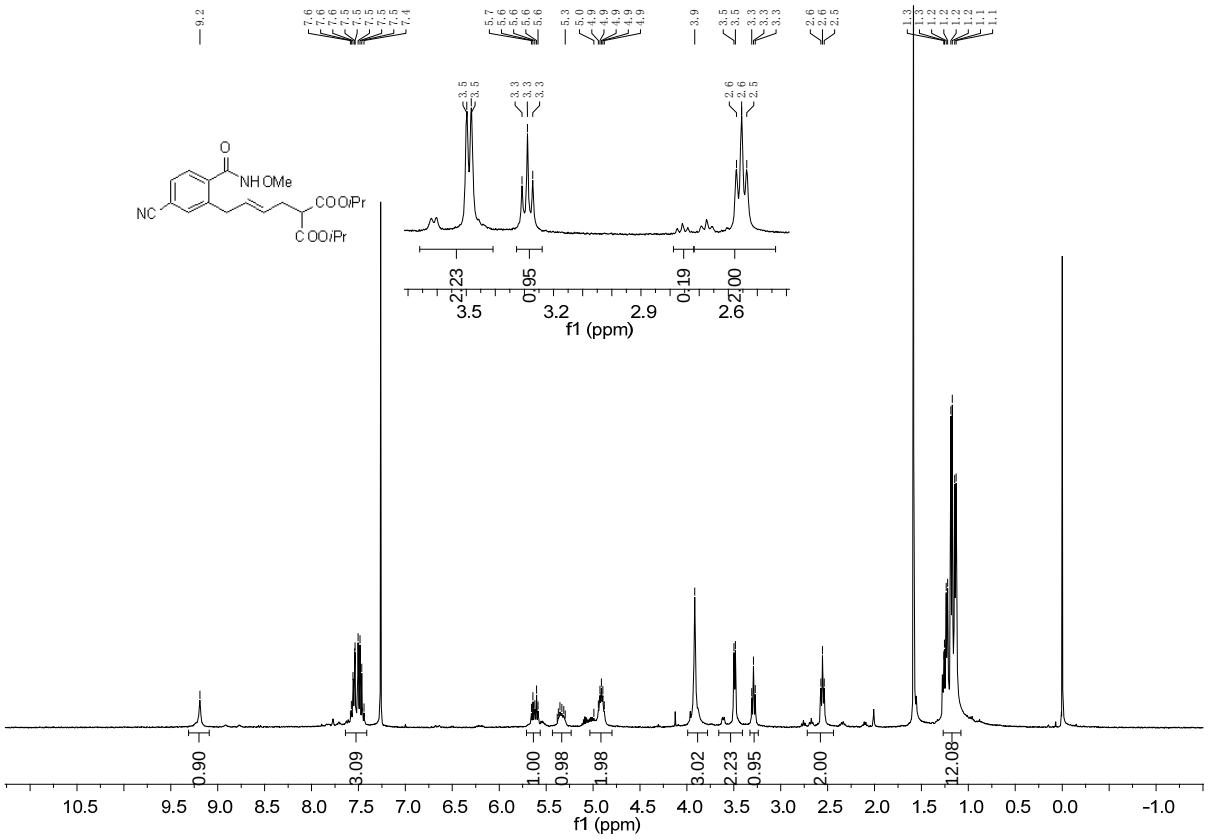
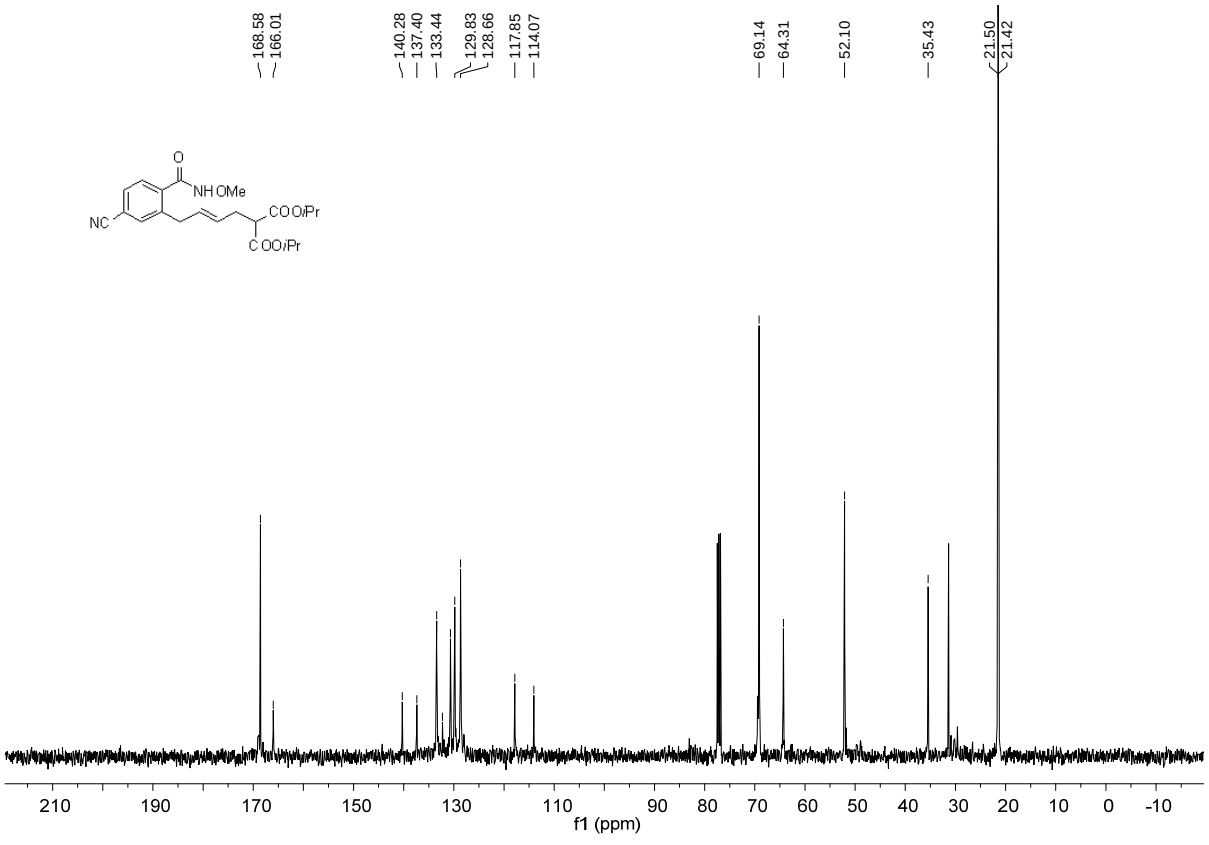
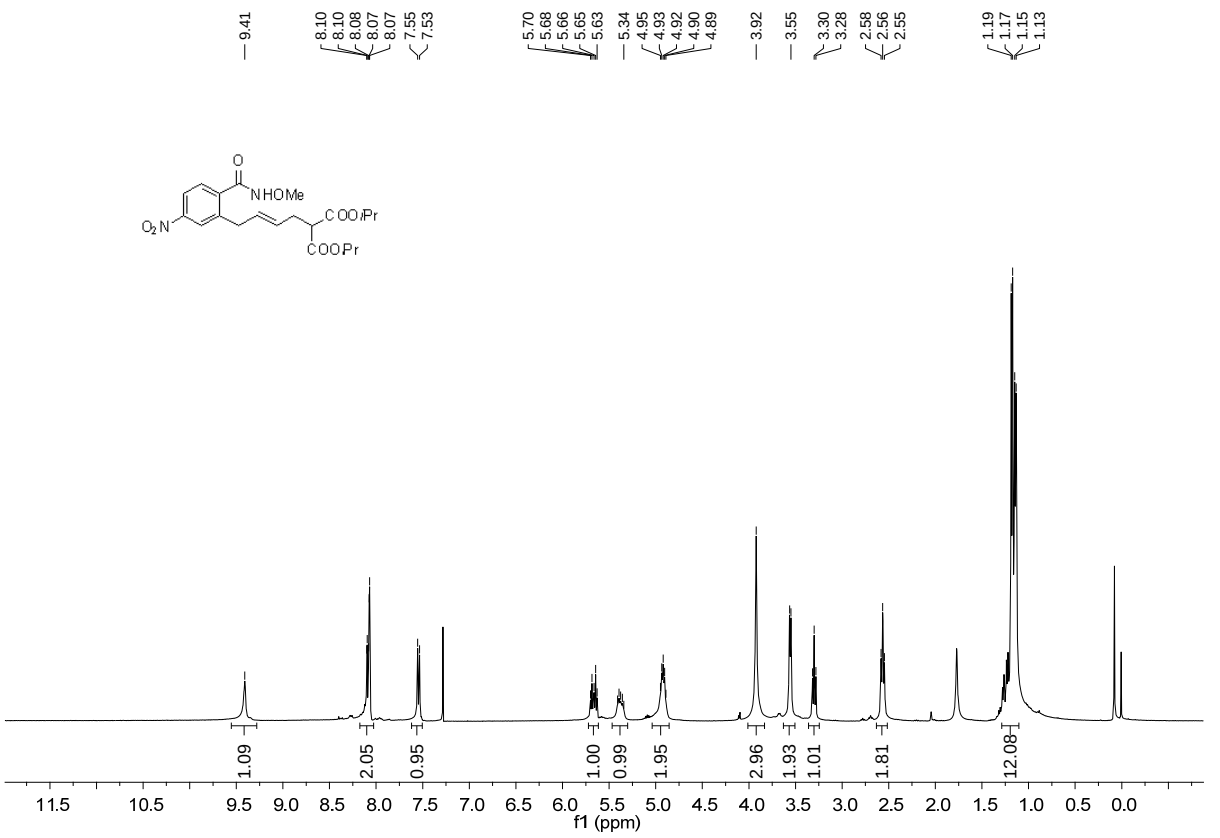
139.1
132.4
131.9
129.0
128.8
128.5
127.8
127.3
127.1
124.9
69.0
64.4
52.4
36.1
31.5
21.5
21.4
NHOMe
COOiPr
COOiPr
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
NH OMe
NC
CO OiPr
CO OiPr
f1 (ppm)
f1 (ppm)


O
NH OMe
NC
CO OiPr
CO OiPr
f1 (ppm)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8.07
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5.66
5.65
5.63
5.34
4.95
4.93
4.92
4.90
4.89
3.92
3.55
3.30
3.28
2.58
2.56
2.55
1.19
1.17
1.15
1.13
O
NHOMe
O2N
COOiPr
COOPr
1.09
2.05
0.95
1.00
0.99
1.95
2.96
1.93
1.01
1.81
12.08
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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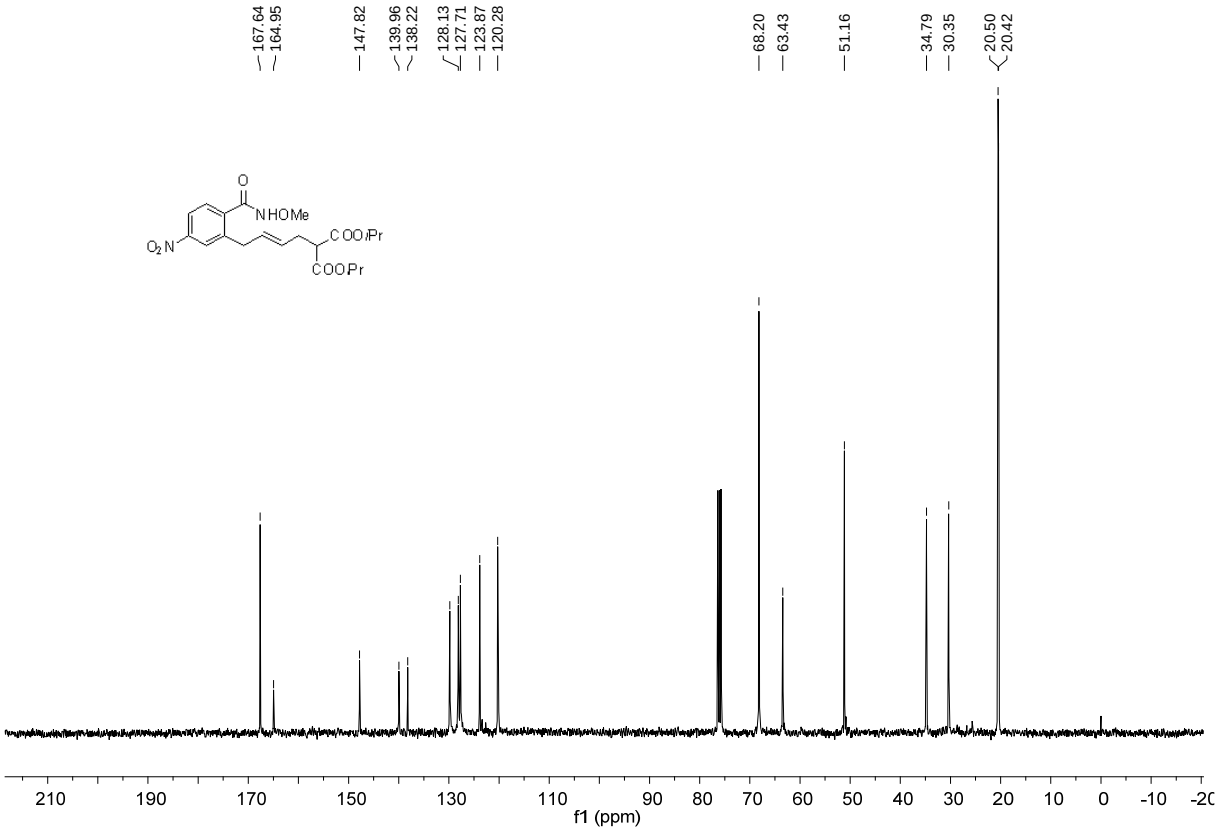
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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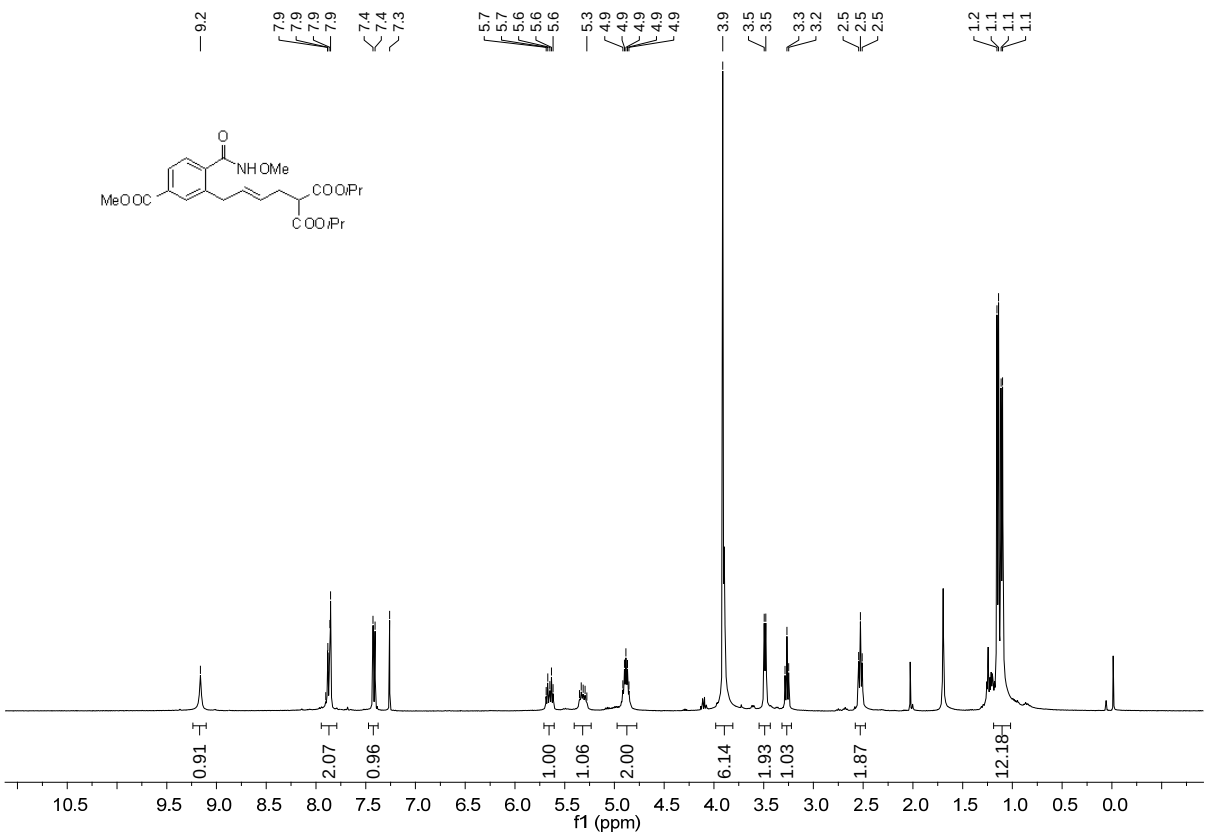
147.82
139.96
138.22
128.13
127.71
123.87
120.28
68.20
63.43
51.16
34.79
30.35
20.50
20.42
O
NHOMe
O2N
COOiPr
COOPr
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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7.9
7.9
7.9
7.4
7.4
7.3
5.7
5.7
5.6
5.6
5.6
5.3
4.9
4.9
4.9
4.9
4.9
3.9
3.5
3.5
3.3
3.2
2.5
2.5
2.5
1.2
1.1
1.1
1.1
O
NH OMe
MeOOC
COOiPr
COOiPr
0.91
2.07
0.96
1.00
1.06
2.00
6.14
1.93
1.03
1.87
12.18
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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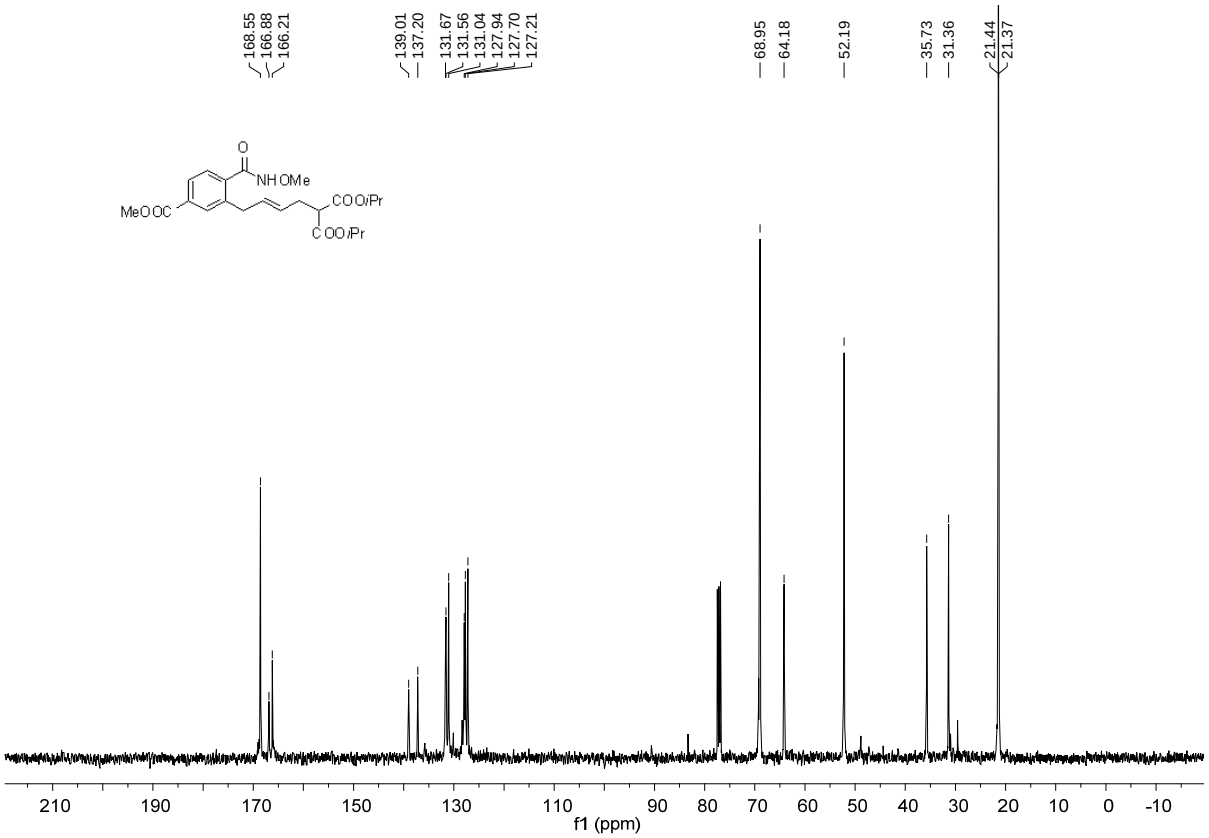
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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131.67
131.56
131.04
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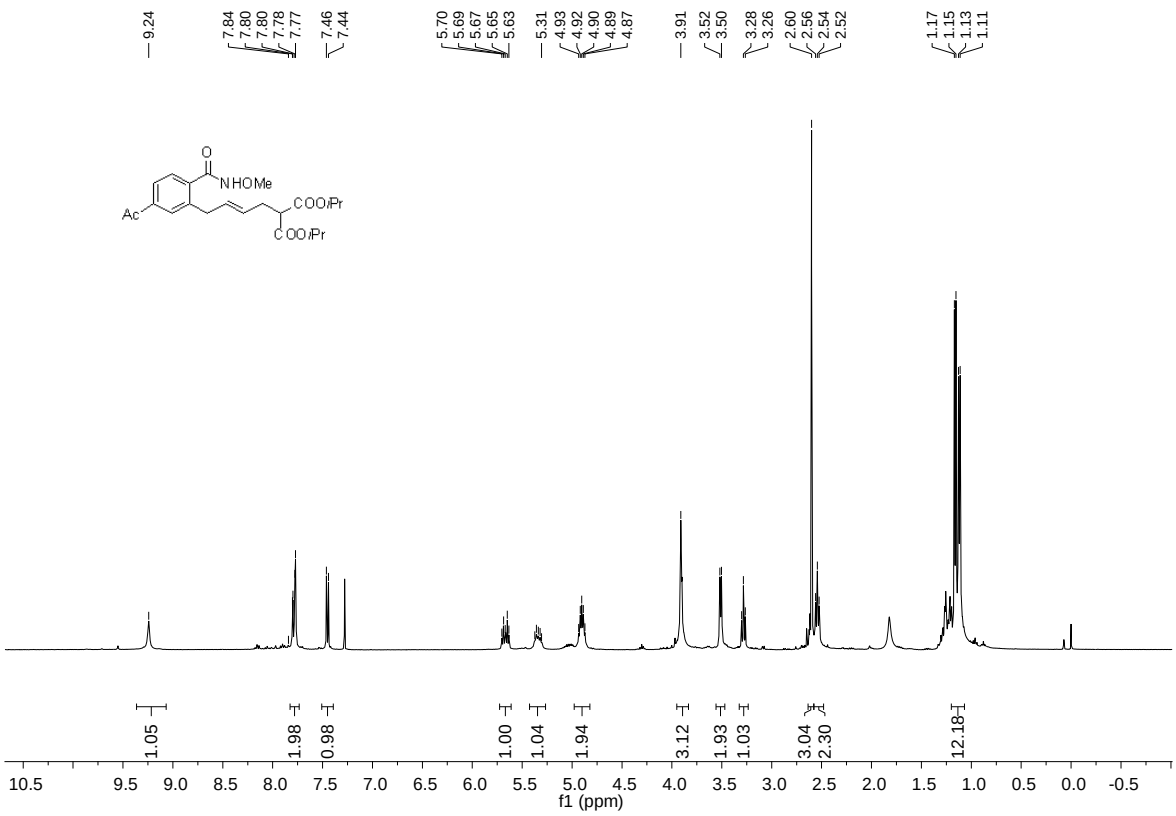
127.70
127.21
68.95
64.18
52.19
35.73
31.36
21.44
21.37
O
NH OMe
MeOOC
COOiPr
COOiPr
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.80
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5.69
5.67
5.65
5.63
5.31
4.93
4.92
4.90
4.89
4.87
3.91
3.52
3.50
3.28
3.26
2.60
2.56
2.54
2.52
1.17
1.15
1.13
1.11
O
NHOMe
Ac
COOiPr
COOiPr
1.05
1.98
0.98
1.00
1.04
1.94
3.12
1.93
1.03
3.04
2.30
12.18
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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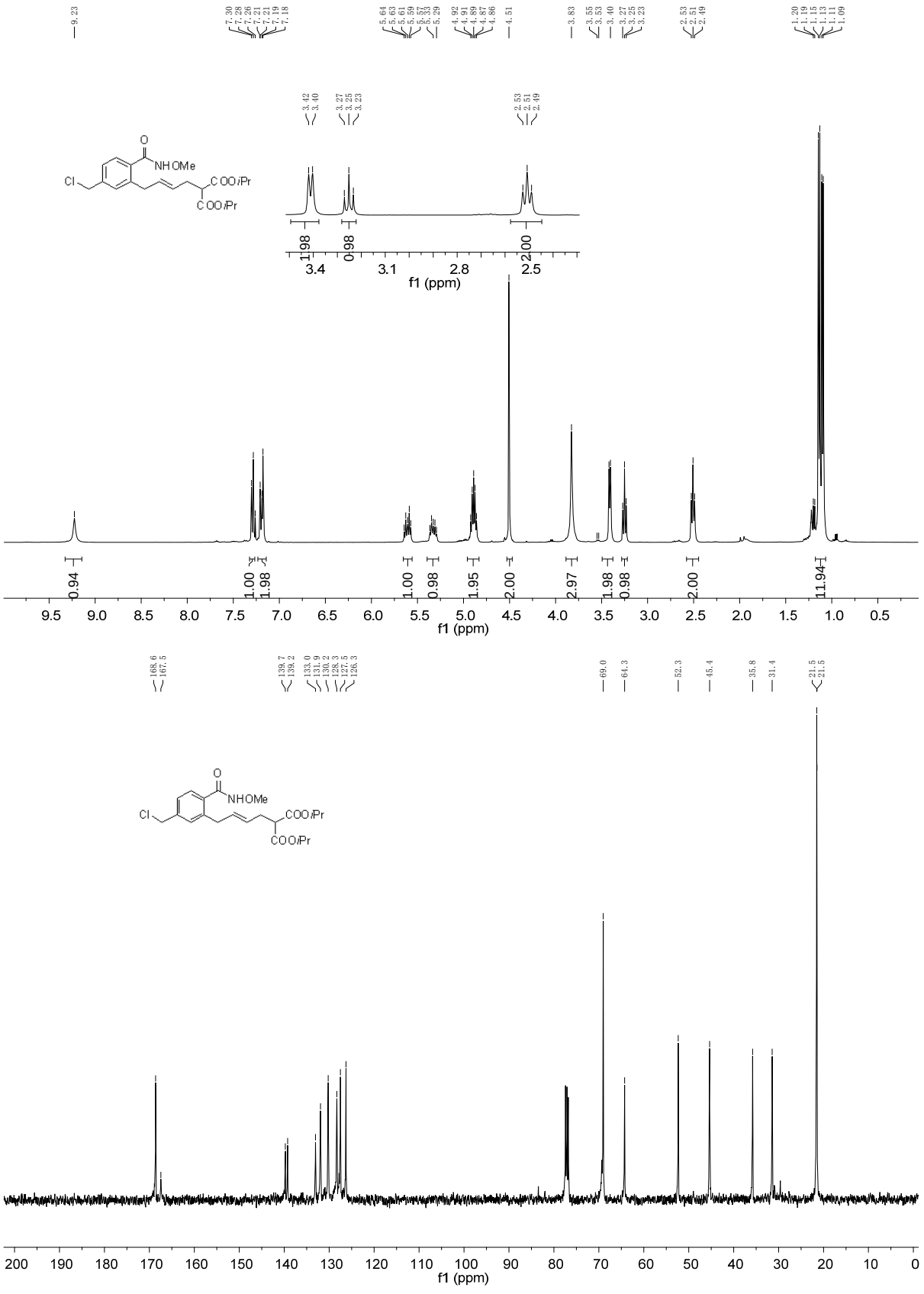
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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7.18
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5.57
5.53
5.29
4.92
4.91
4.89
4.87
4.86
4.51
3.83
3.55
3.53
3.40
3.27
3.25
3.23
2.53
2.51
2.49
1.20
1.19
1.15
1.13
1.11
1.09
NHOMe
Cl
COOiPr
COOiPr
0.94
1.00
1.98
1.00
0.98
1.95
2.00
2.97
1.98
0.98
2.00
11.94
f1 (ppm)
168.6
167.5
139.7
139.2
133.0
131.9
130.2
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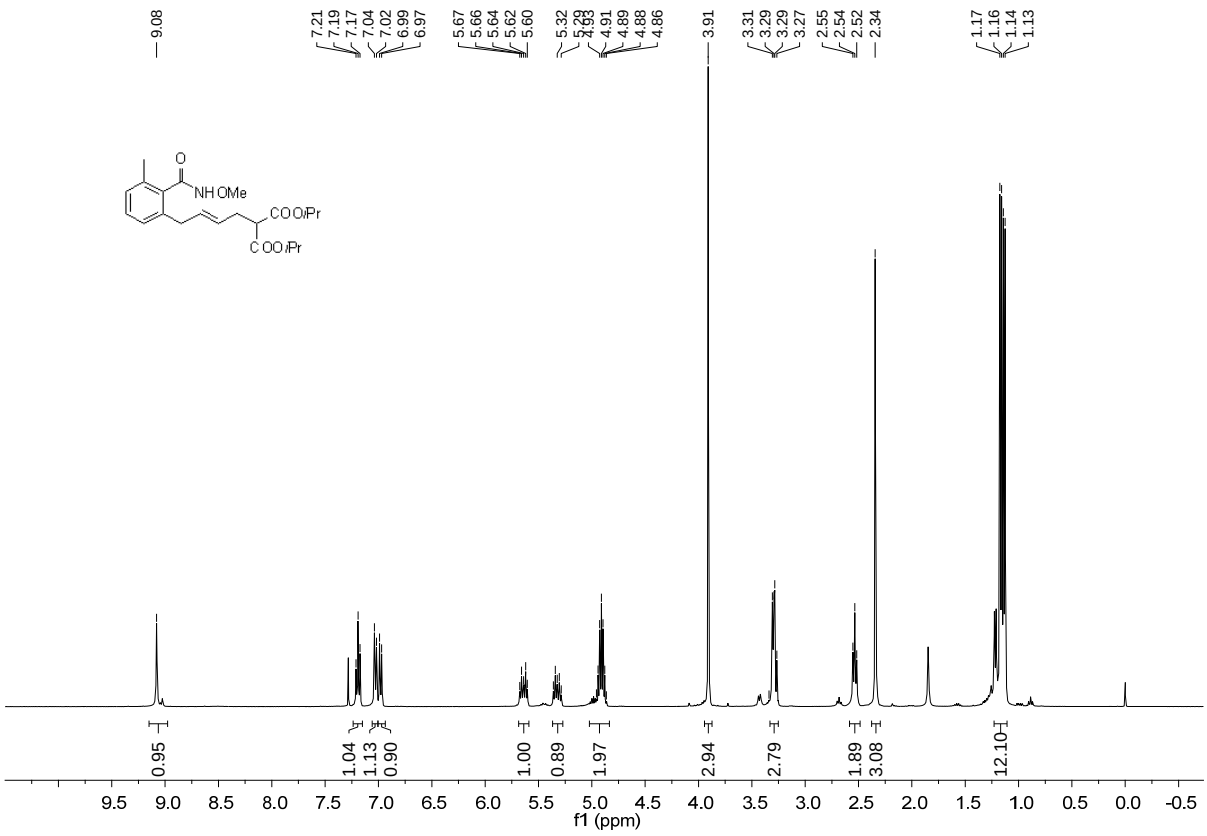
127.5
126.3
69.0
64.3
52.3
45.4
35.8
31.4
21.5
21.5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7.21
7.19
7.17
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7.02
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6.97
5.67
5.66
5.64
5.62
5.60
5.32
4.91
4.89
4.88
4.86
3.91
3.31
3.29
3.29
3.27
2.55
2.54
2.52
2.34
1.17
1.16
1.14
1.13
NH OMe
COOiPr
COOiPr
0.95
1.04
1.13
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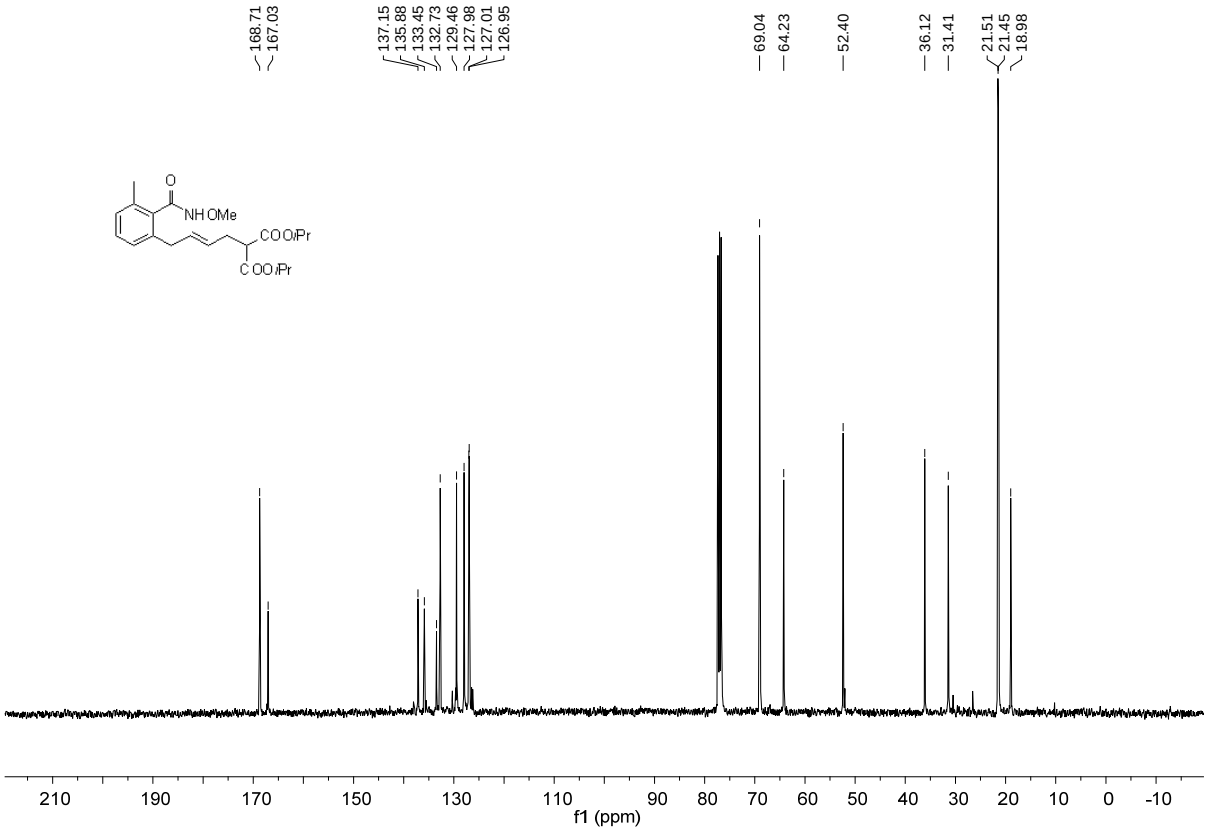
1.00
0.89
1.97
2.94
2.79
1.89
3.08
12.10
f1 (ppm)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167.03
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135.88
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132.73
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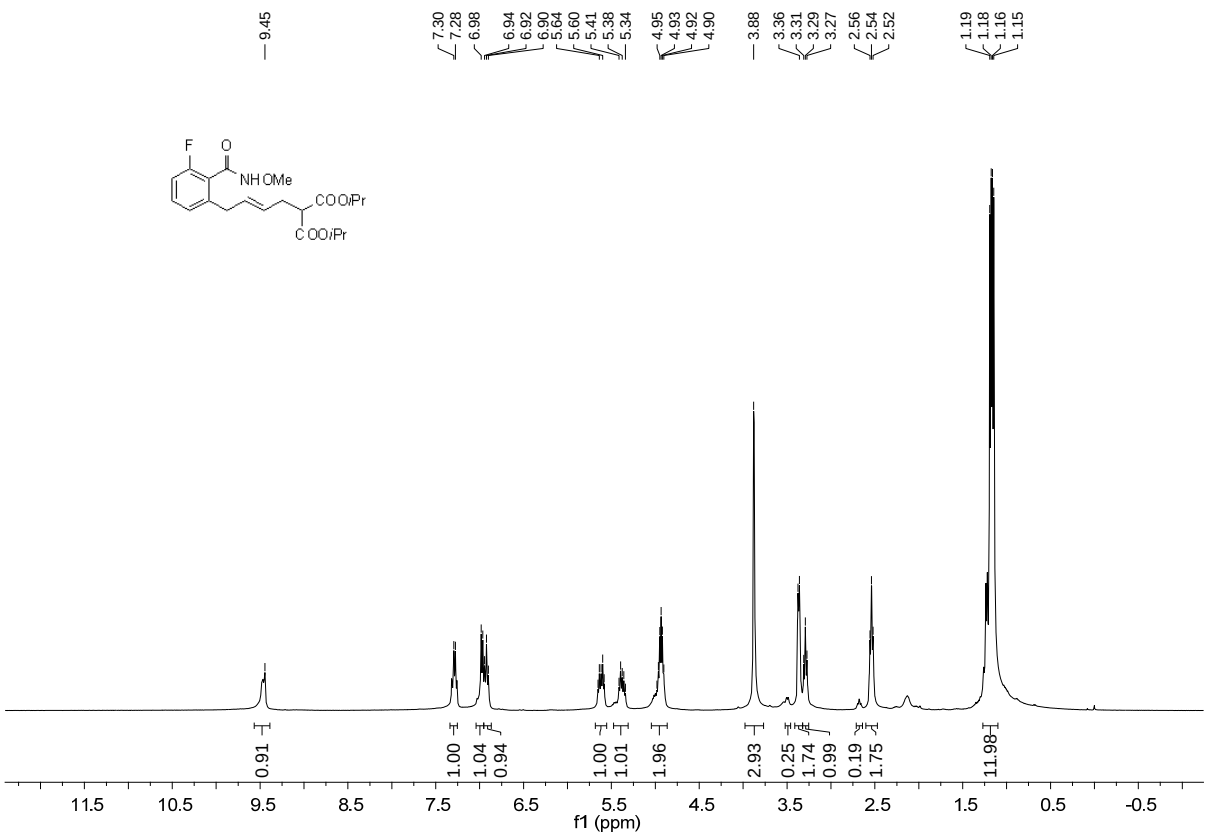
127.98
127.01
126.95
69.04
64.23
52.40
36.12
31.41
21.51
21.45
18.98
NH OMe
COOiPr
COOiPr
f1 (ppm)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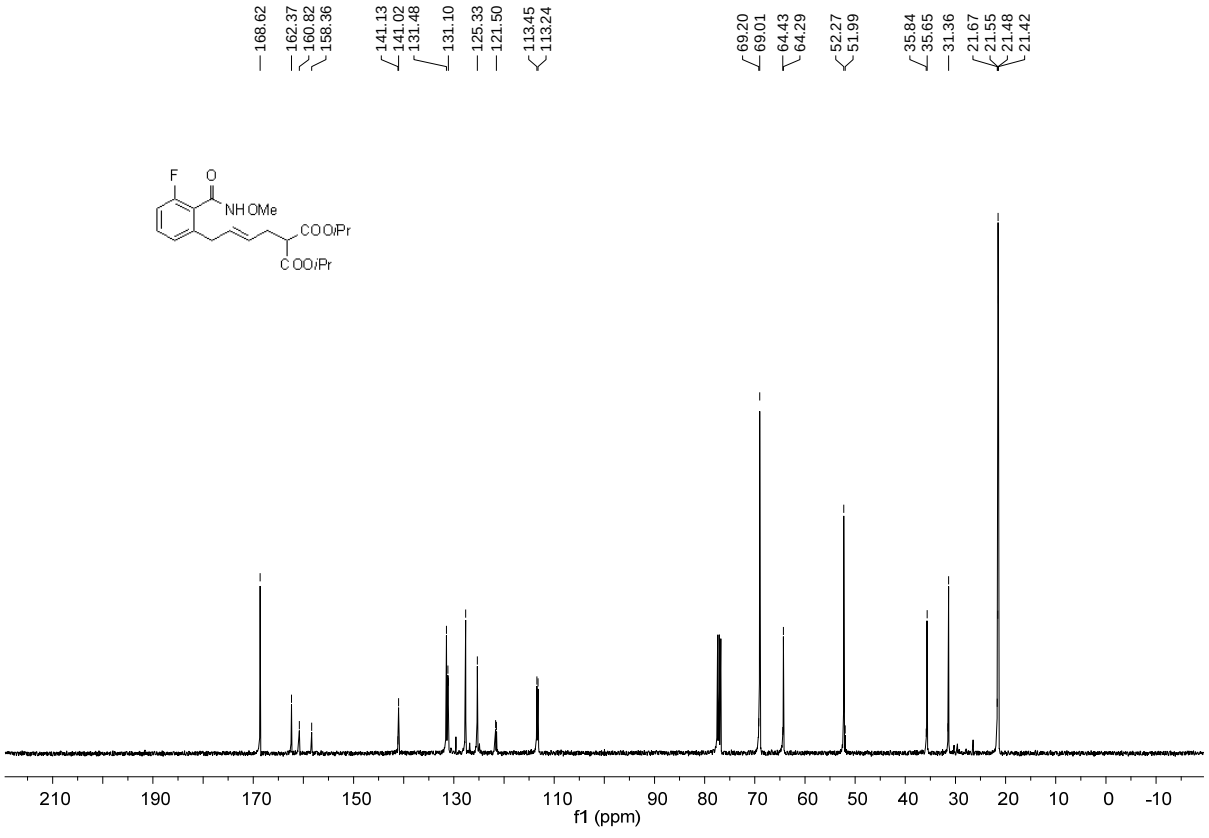
6.92
6.90
5.64
5.60
5.41
5.38
5.34
4.95
4.93
4.92
4.90
3.88
3.36
3.31
3.29
3.27
2.56
2.54
2.52
1.19
1.18
1.16
1.15
F
O
NH OMe
COOiPr
COOiPr
0.91
1.00
1.04
0.94
1.00
1.01
1.96
2.93
0.25
1.74
0.99
0.19
1.75
11.98
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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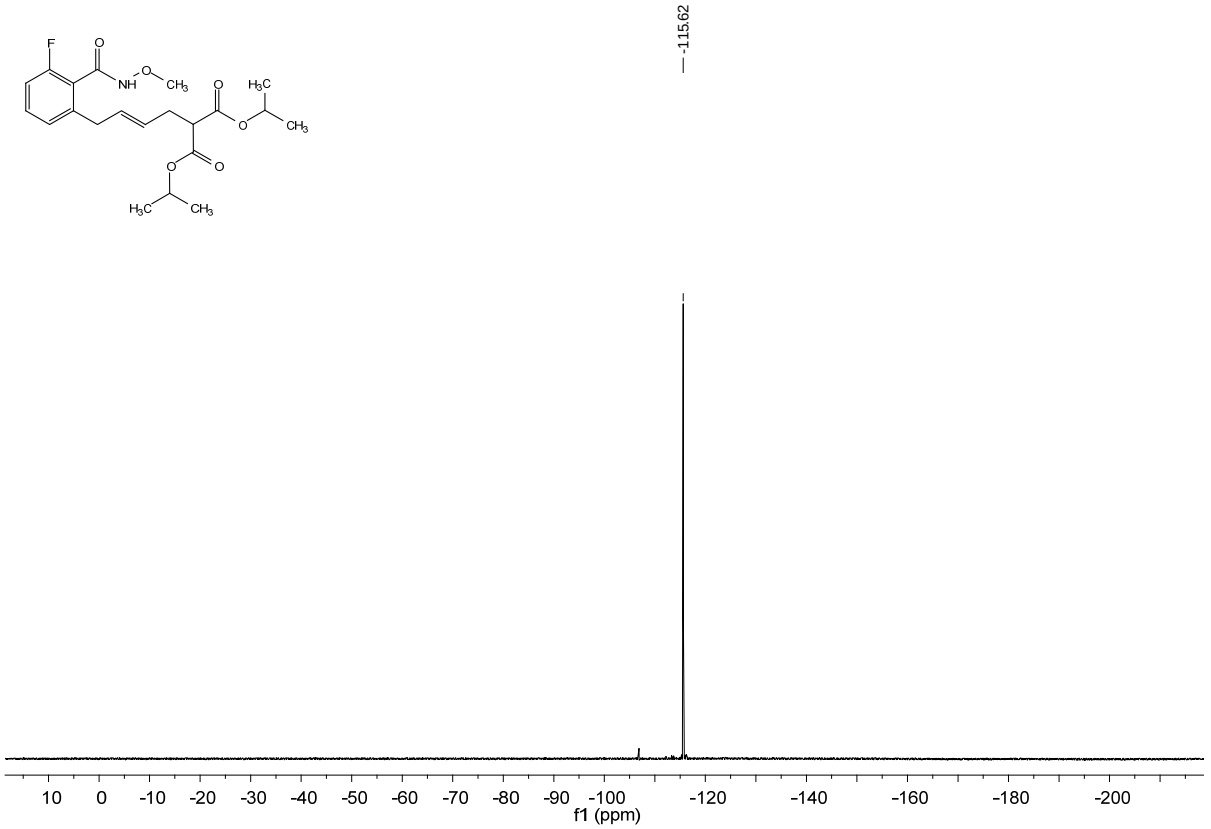
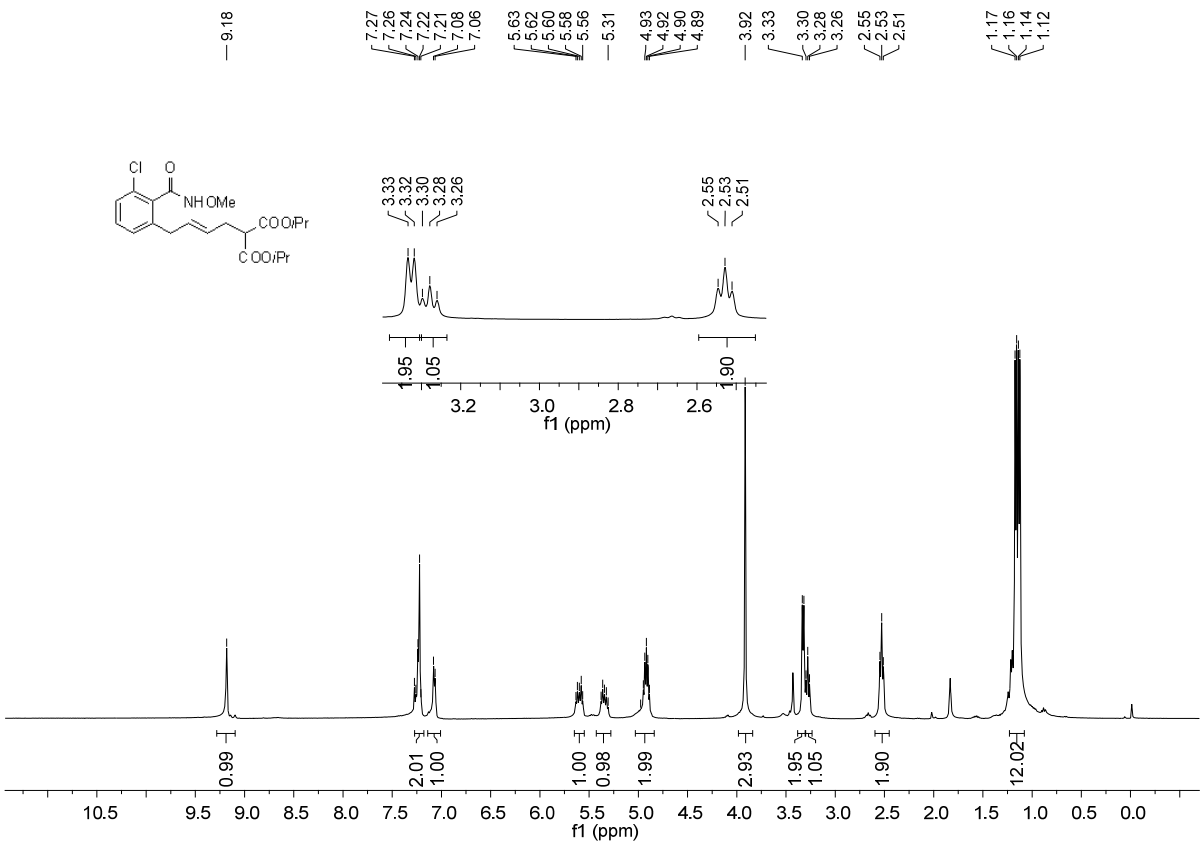
162.37
160.82
158.36
141.13
141.02
131.48
131.10
125.33
121.50
113.45
113.24
69.20
69.01
64.43
64.29
52.27
51.99
35.84
35.65
31.36
21.67
21.55
21.48
21.42
F
O
NH OMe
COOiPr
COOiPr
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


F
O
NH
O
CH3
O
H3C
O
CH3
O
O
O
H3C
CH3
-115.62
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)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7.27
7.26
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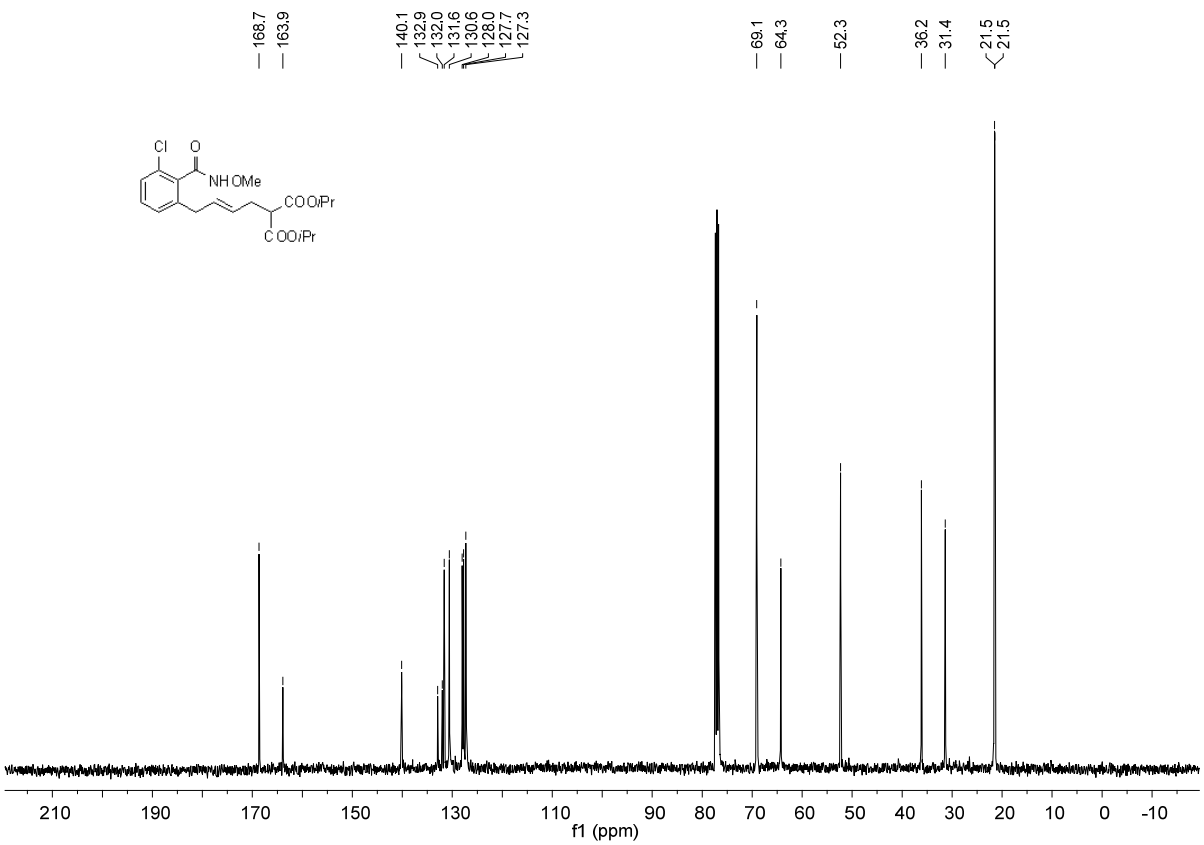
7.22
7.21
7.08
7.06
5.63
5.62
5.60
5.58
5.56
5.31
4.93
4.92
4.90
4.89
3.92
3.33
3.30
3.28
3.26
2.55
2.53
2.51
1.17
1.16
1.14
1.12
Cl
O
NH OMe
COOiPr
COOiPr
1.95
1.05
1.90
f1 (ppm)
0.99
2.01
1.00
1.00
0.98
1.99
2.93
1.95
1.05
1.90
12.02
f1 (ppm)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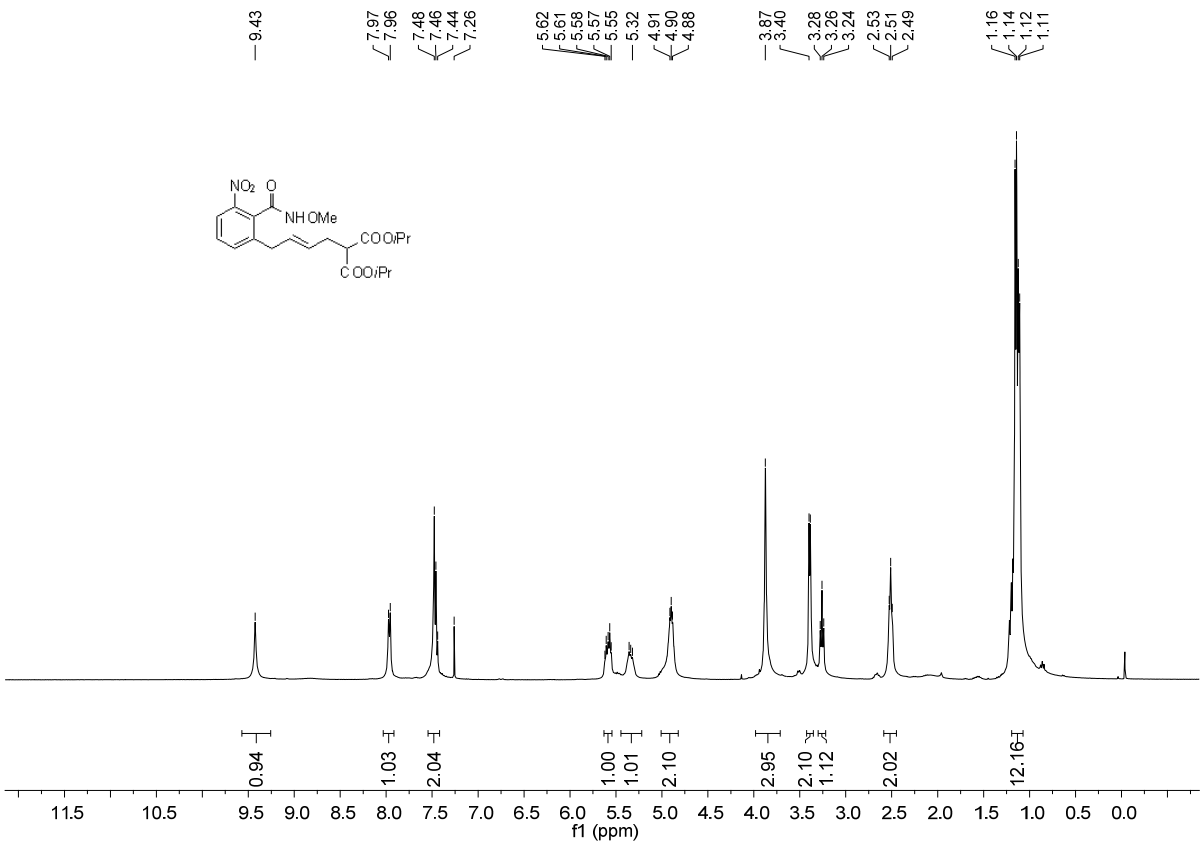
131.6
130.6
128.0
127.7
127.3
69.1
64.3
52.3
36.2
31.4
21.5
21.5
Cl
O
NH OMe
COOiPr
COOiPr
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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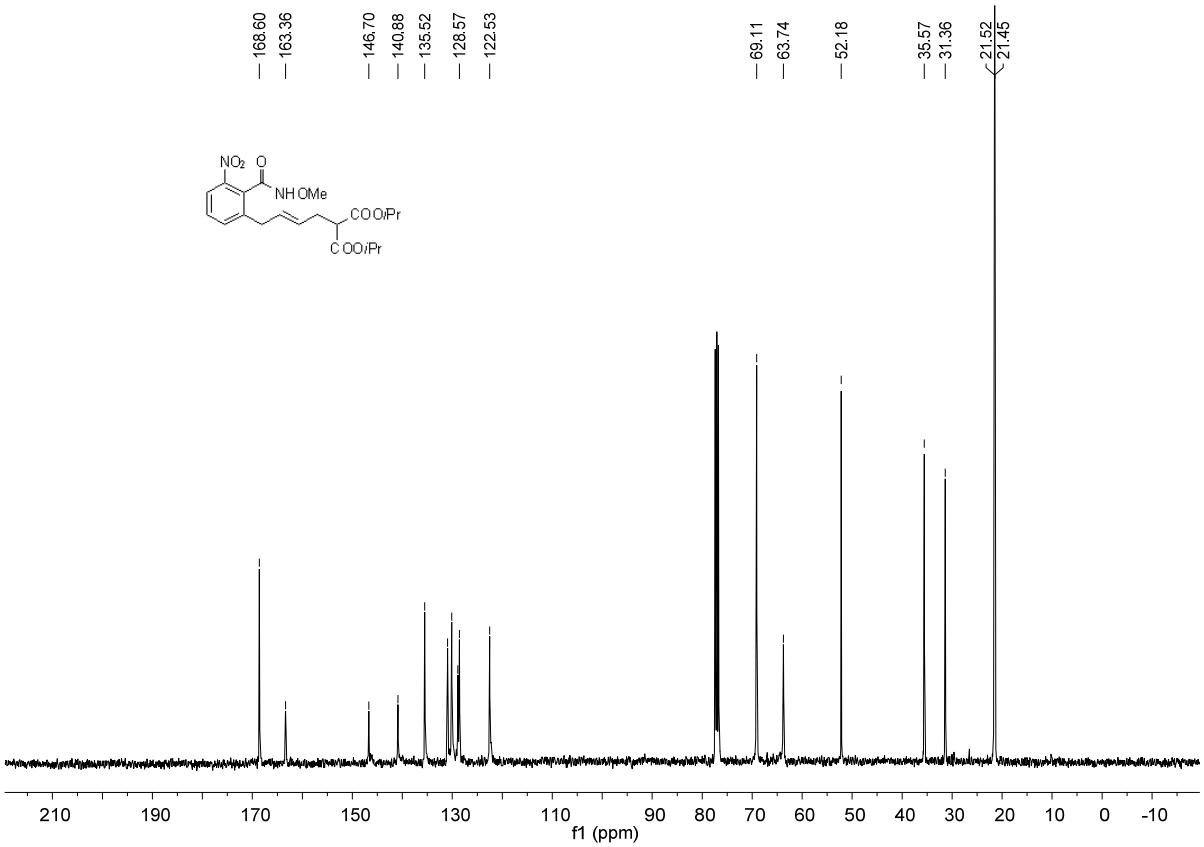
5.62
5.61
5.58
5.57
5.55
5.32
4.91
4.90
4.88
3.87
3.40
3.28
3.26
3.24
2.53
2.51
2.49
1.16
1.14
1.12
1.11
NO2
O
NH OMe
COOiPr
COOiPr
0.94
1.03
2.04
1.00
1.01
2.10
2.95
2.10
1.12
2.02
12.16
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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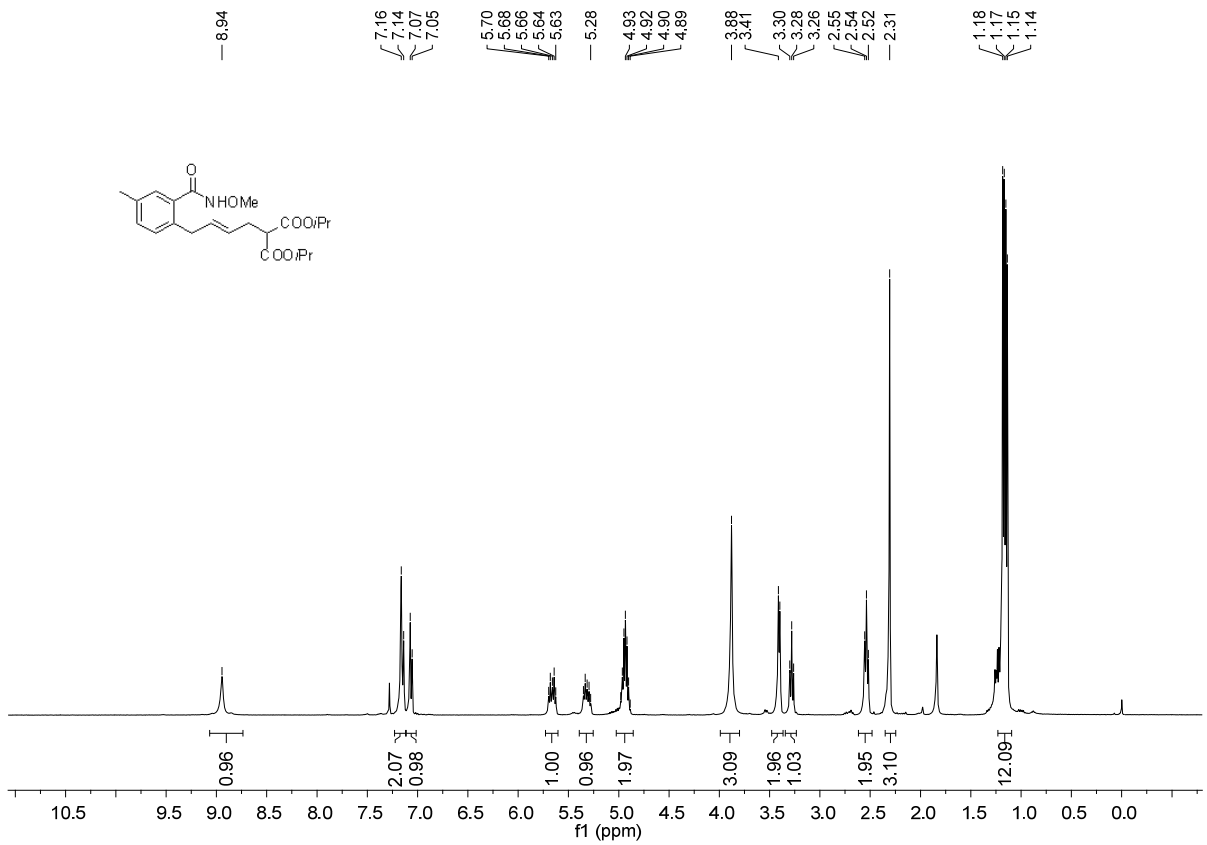
122.53
69.11
63.74
52.18
35.57
31.36
21.52
21.45
NO2
O
NH OMe
COOiPr
COOiPr
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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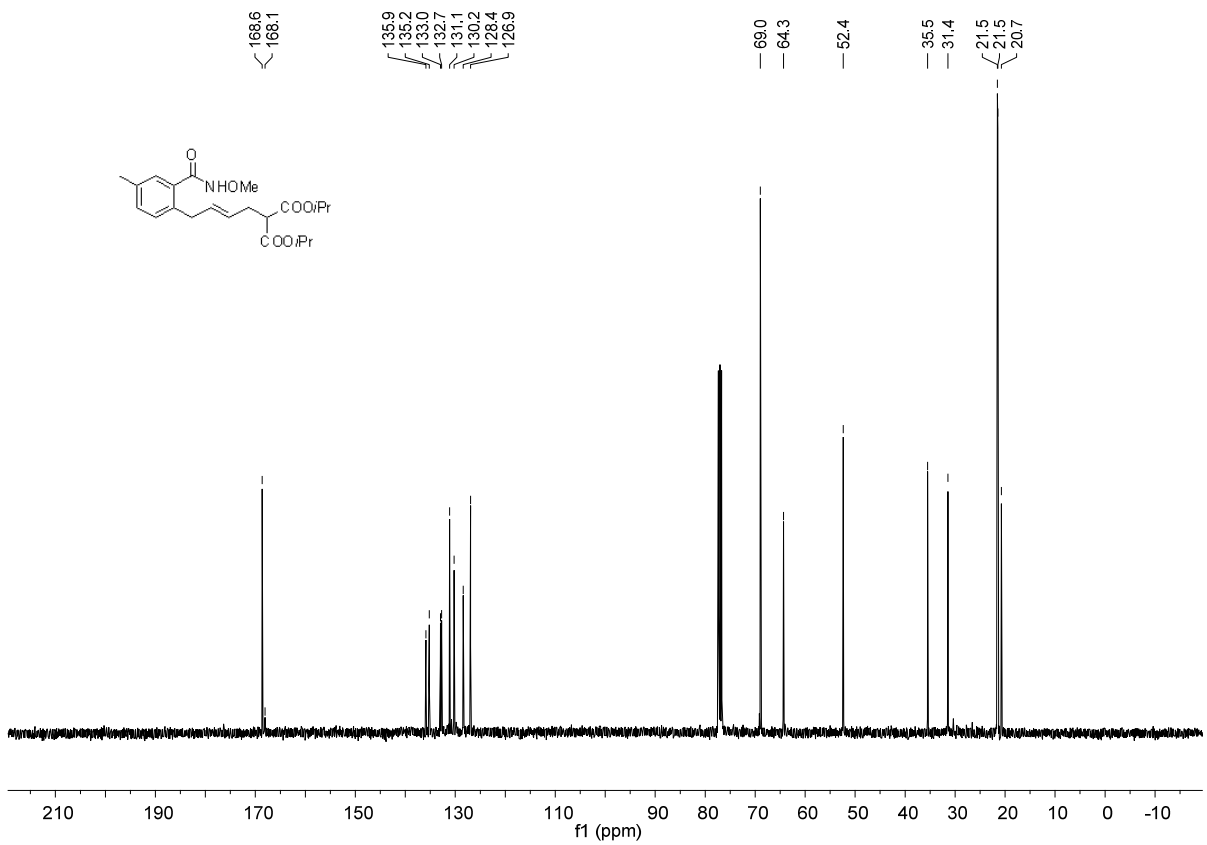
5.64
5.63
5.28
4.93
4.92
4.90
4.89
3.88
3.41
3.30
3.28
3.26
2.55
2.54
2.52
2.31
1.18
1.17
1.15
1.14
O
NHOMe
COOiPr
COOiPr
0.96
2.07
0.98
1.00
0.96
1.97
3.09
1.96
1.03
1.95
3.10
12.09
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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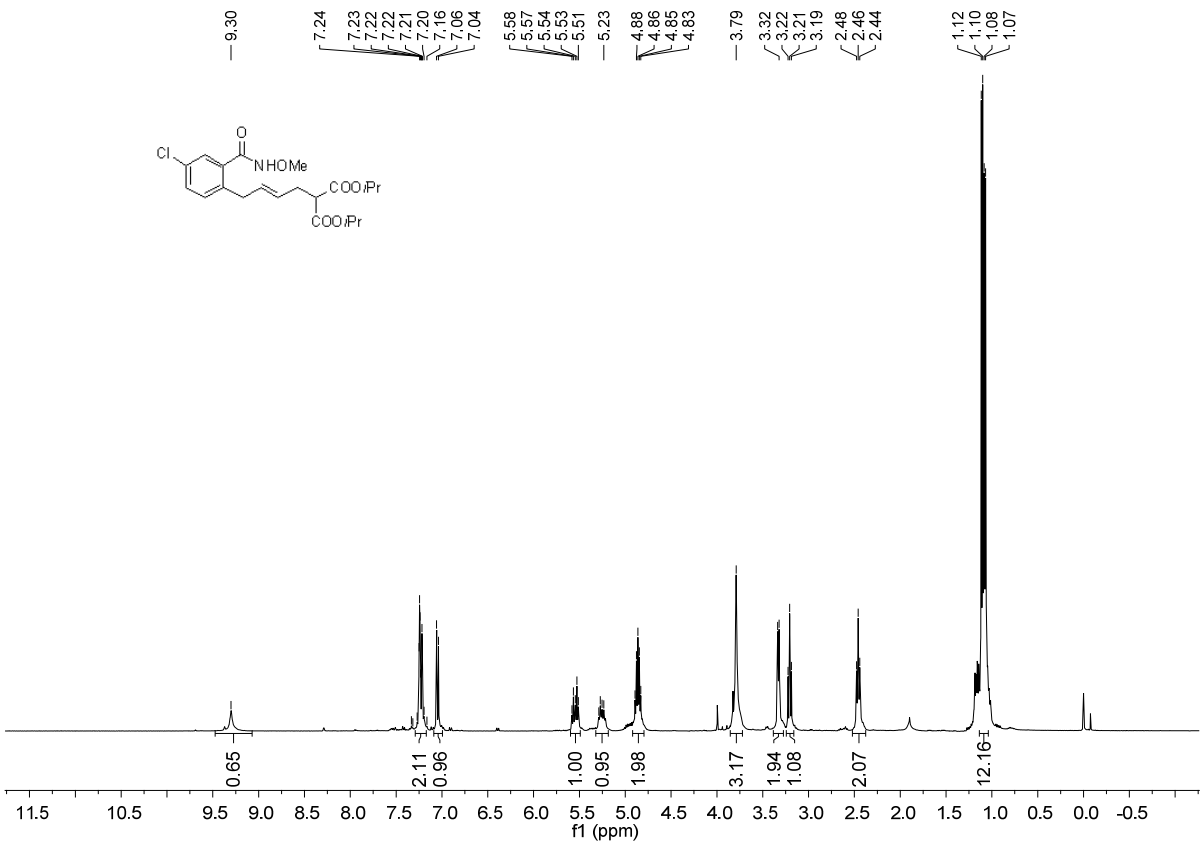
69.0
64.3
52.4
35.5
31.4
21.5
21.5
20.7
O
NHOMe
COOiPr
COOiPr
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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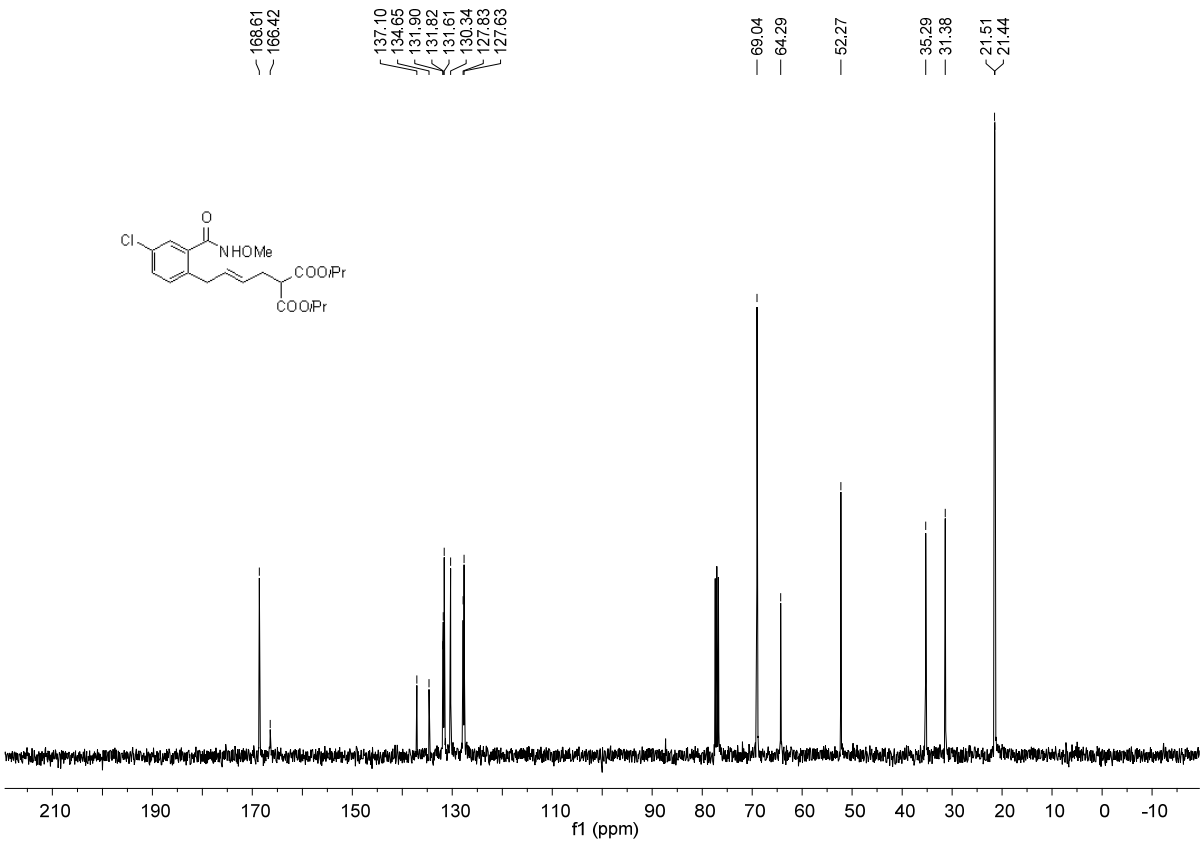
7.24
7.23
7.22
7.22
7.21
7.20
7.16
7.06
7.04
5.58
5.57
5.54
5.53
5.51
5.23
4.88
4.86
4.85
4.83
3.79
3.32
3.22
3.21
3.19
2.48
2.46
2.44
1.12
1.10
1.08
1.07
Cl
O
NHOMe
COOiPr
COOiPr
0.65
2.11
0.96
1.00
0.95
1.98
3.17
1.94
1.08
2.07
12.16
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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130.34
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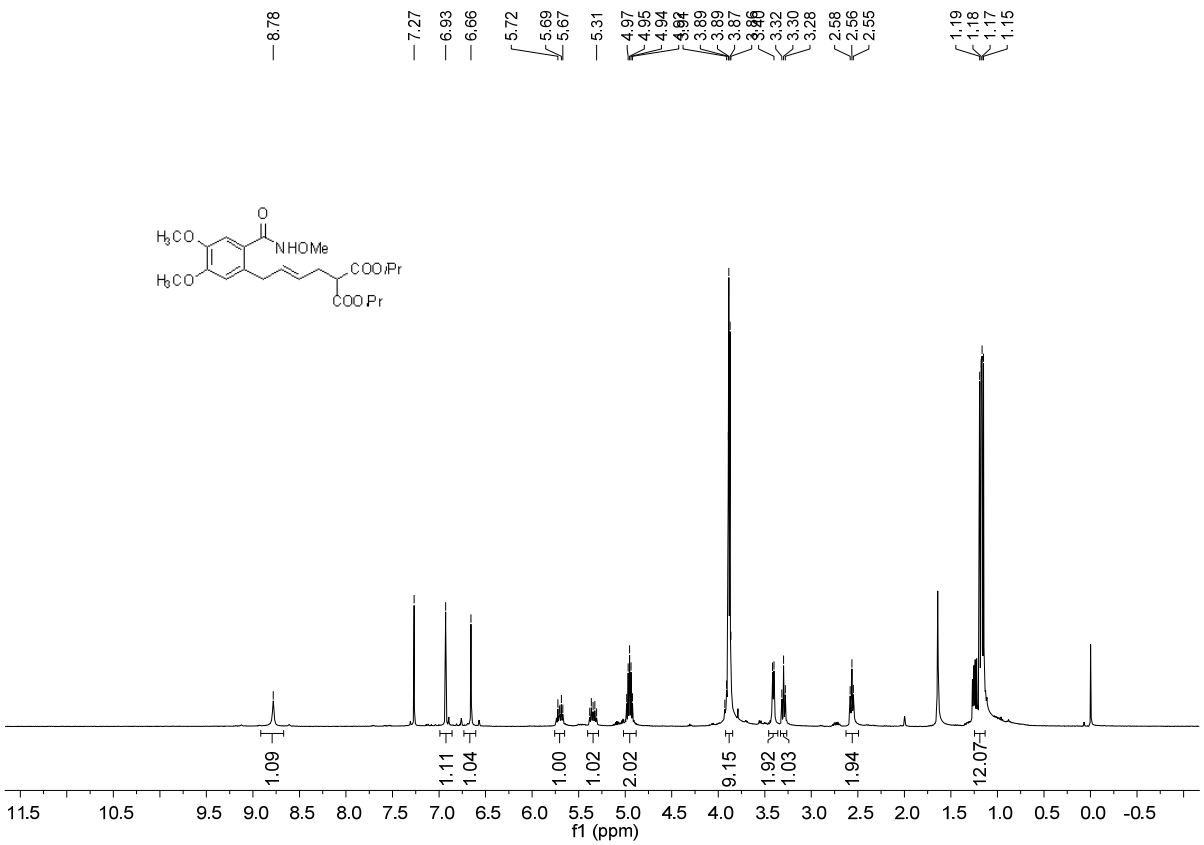
127.63
69.04
64.29
52.27
35.29
31.38
21.51
21.44
Cl
O
NHOMe
COOiPr
COOiPr
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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4.94
3.89
3.89
3.87
3.32
3.30
3.28
2.58
2.56
2.55
1.19
1.18
1.17
1.15
O
H3CO
H3CO
NHOMe
COOiPr
COOiPr
1.09
1.11
1.04
1.00
1.02
2.02
9.15
1.92
1.03
1.94
12.07
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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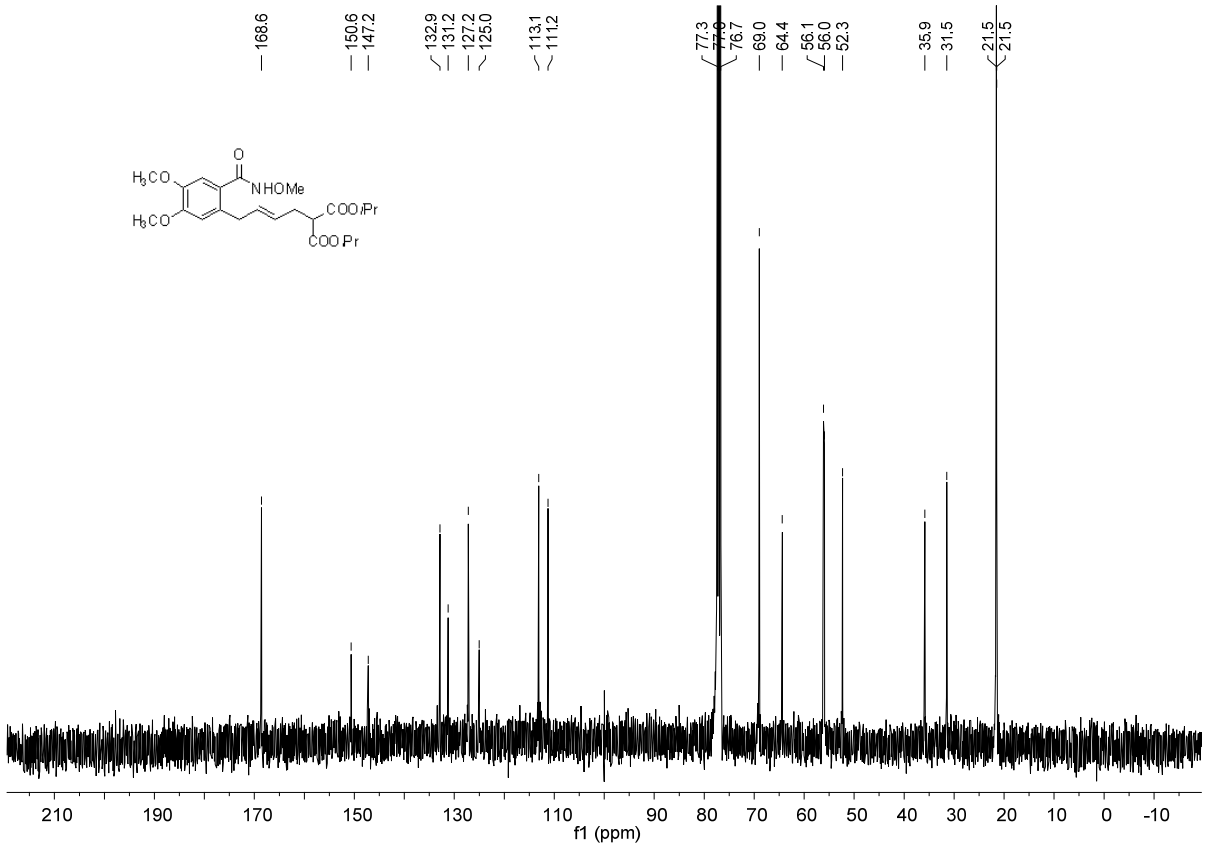
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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76.7
69.0
64.4
56.1
56.0
52.3
35.9
31.5
21.5
21.5
H3CO
H3CO
O
NHOMe
COOiPr
COOiPr
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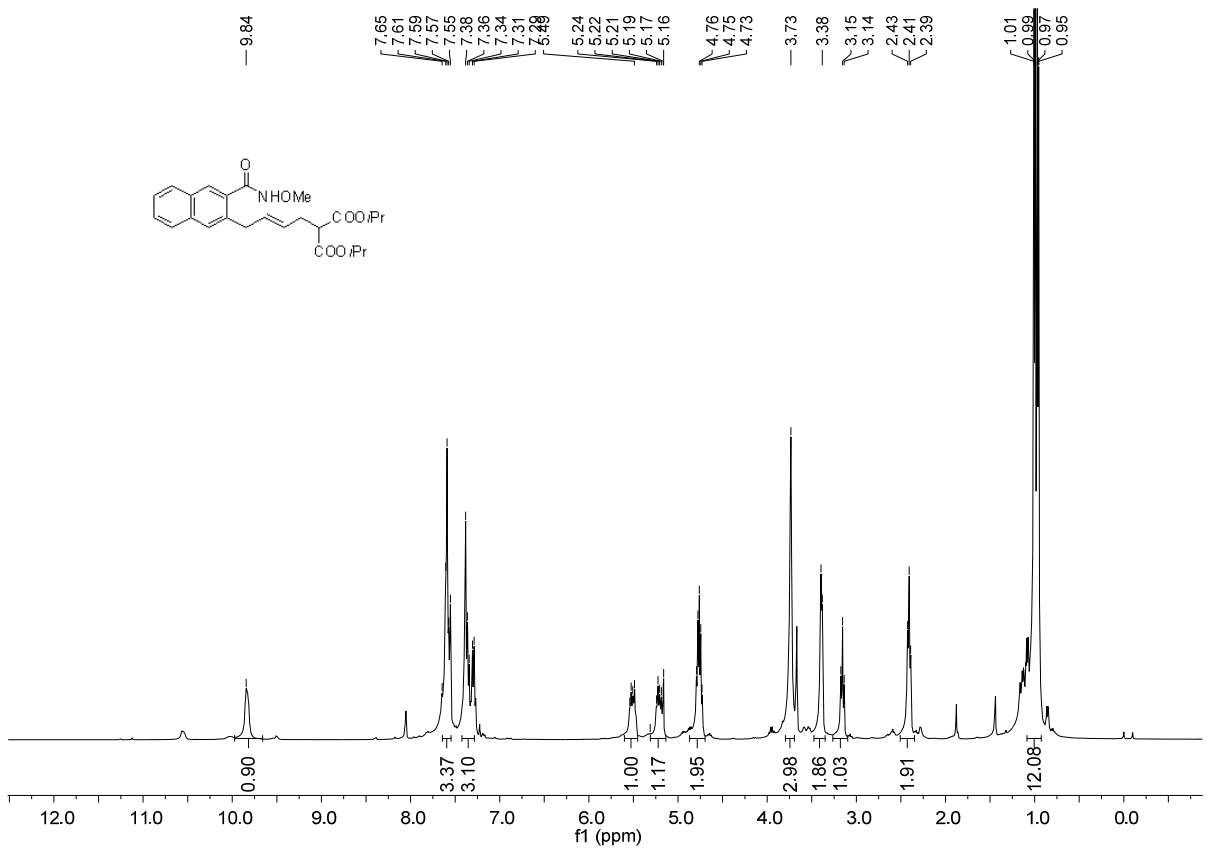
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.31
5.24
5.22
5.21
5.19
5.17
5.16
4.76
4.75
4.73
3.73
3.38
3.15
3.14
2.43
2.41
2.39
1.01
0.99
0.97
0.95
O
NHOMe
COOiPr
COOiPr
0.90
3.37
3.10
1.00
1.17
1.95
2.98
1.86
1.03
1.91
12.08
12.0
11.0
10.0
9.0
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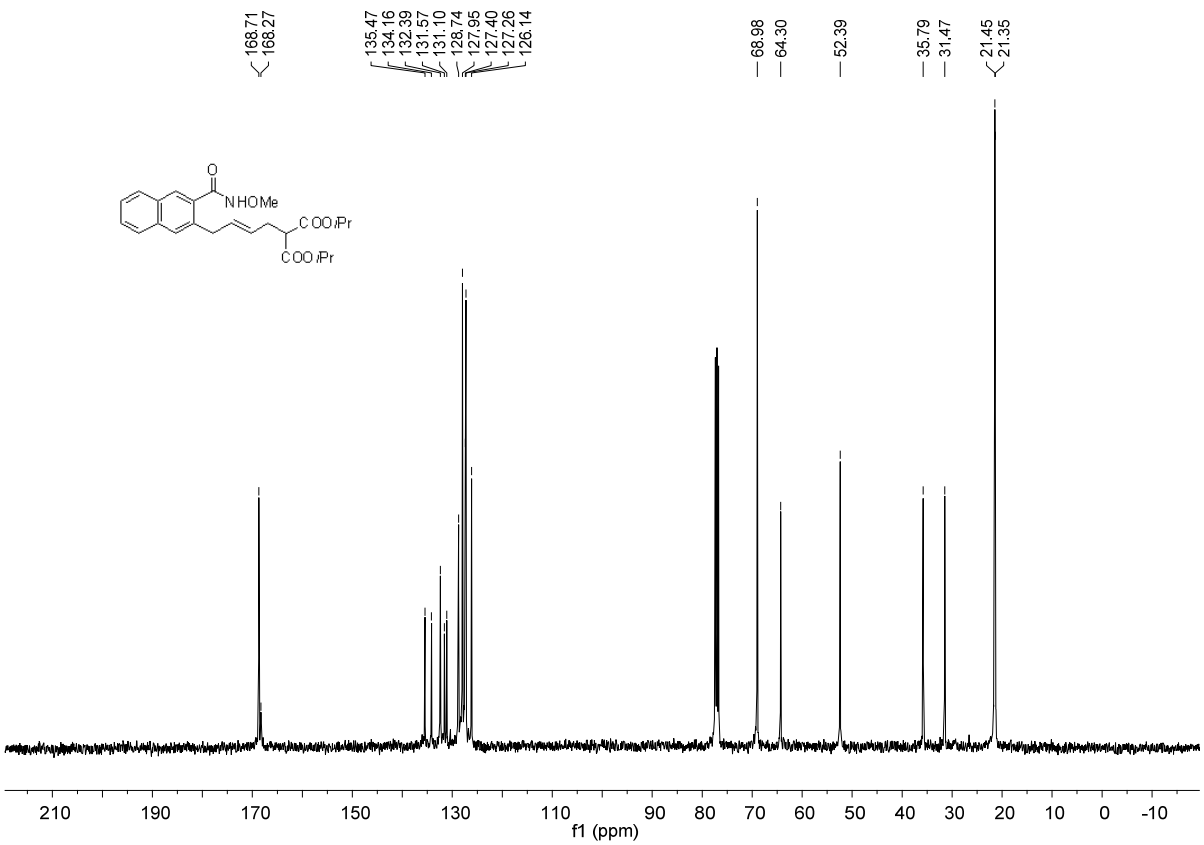
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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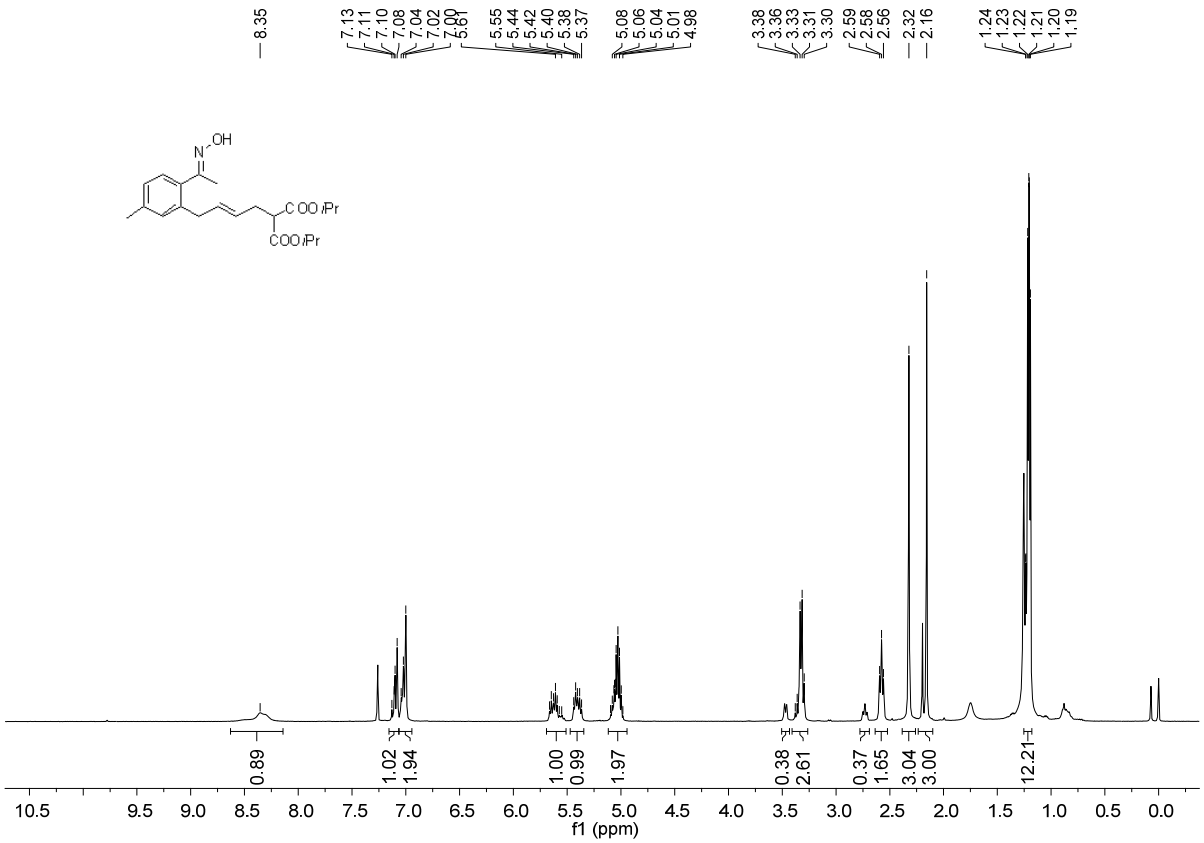
134.16
132.39
131.57
131.10
128.74
127.95
127.40
127.26
126.14
68.98
64.30
52.39
35.79
31.47
21.45
21.35
O
NHOMe
COOiPr
COOiPr
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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5.40
5.38
5.37
5.08
5.06
5.04
5.01
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3.38
3.36
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3.30
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2.58
2.56
2.32
2.16
1.24
1.23
1.22
1.21
1.20
1.19
N
OH
COOiPr
COOiPr
0.89
1.02
1.94
1.00
0.99
1.97
0.38
2.61
0.37
1.65
3.04
3.00
12.21
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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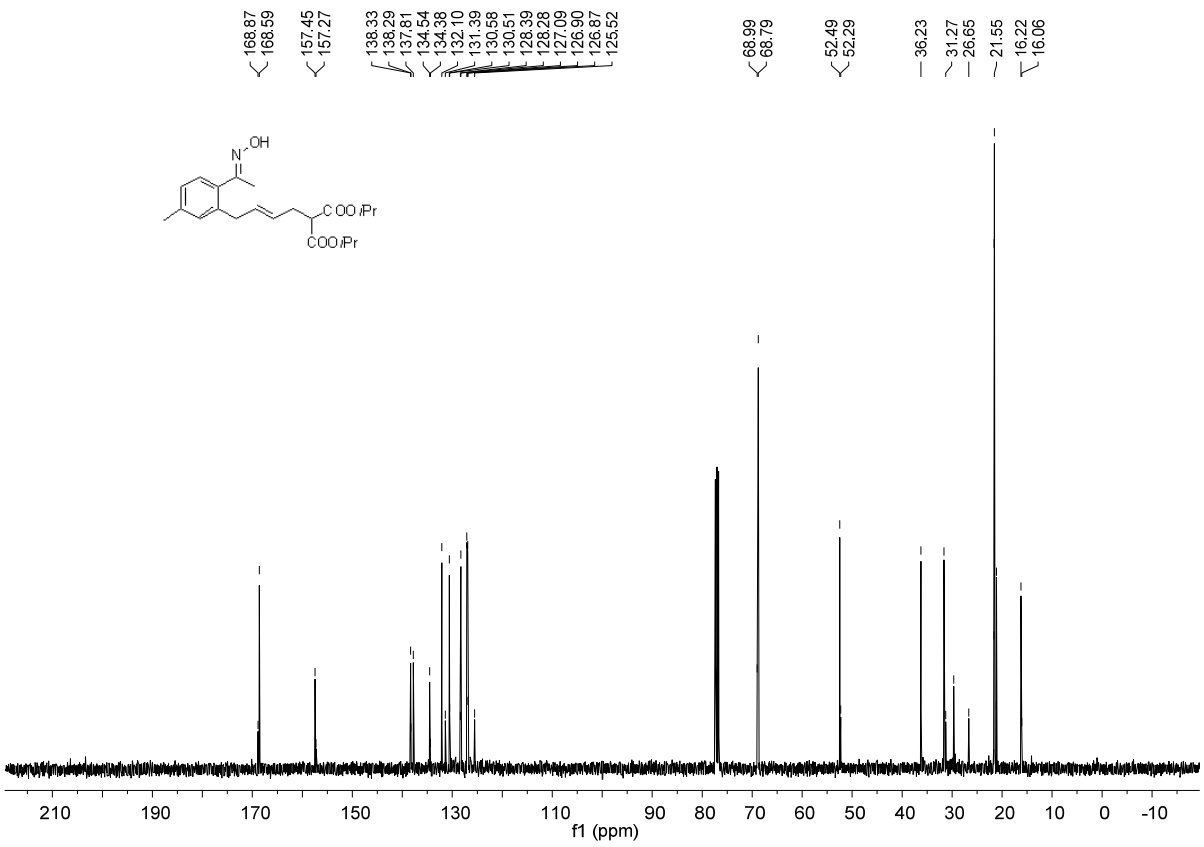
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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157.45
157.27
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138.29
137.81
134.54
134.38
132.10
131.39
130.58
130.51
128.39
128.28
127.09
126.90
126.87
125.52
68.99
68.79
52.49
52.29
36.23
31.27
26.65
21.55
16.22
16.06
N
OH
COO/Pr
COO/Pr
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190
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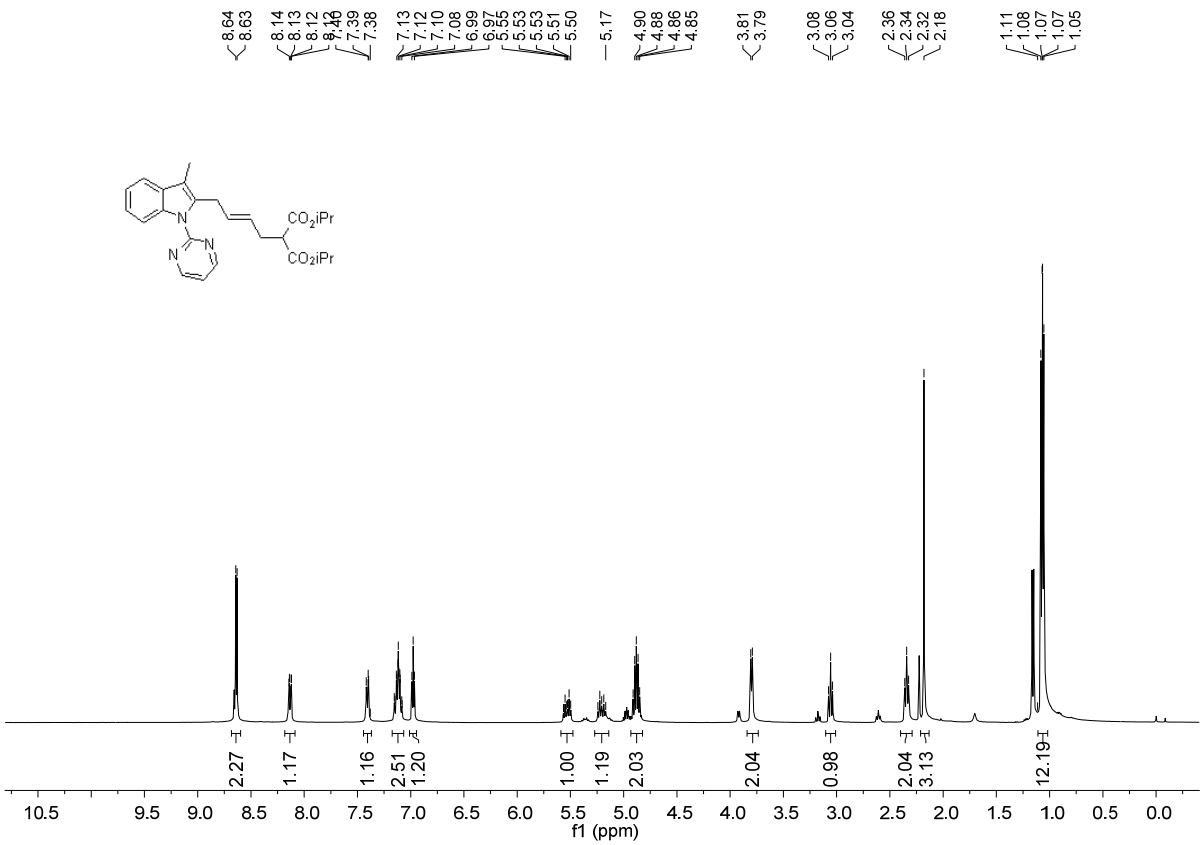
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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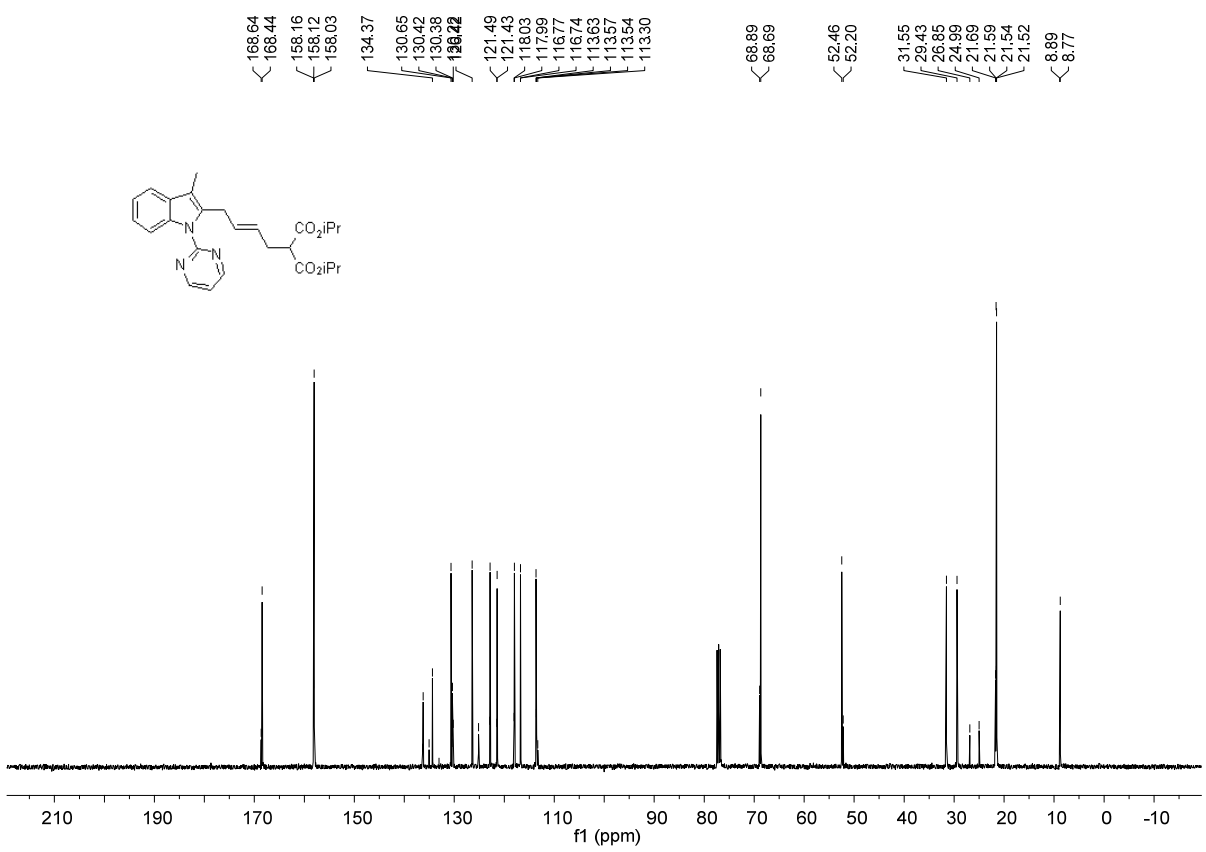
8.12
7.40
7.39
7.38
7.13
7.12
7.10
7.08
6.99
6.97
5.55
5.53
5.53
5.51
5.50
5.17
4.90
4.88
4.86
4.85
3.81
3.79
3.08
3.06
3.04
2.36
2.34
2.32
2.18
1.11
1.08
1.07
1.07
1.05
CO2iPr
CO2iPr
N
N
2.27
1.17
1.16
2.51
1.20
1.00
1.19
2.03
2.04
0.98
2.04
3.13
12.19
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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130.42
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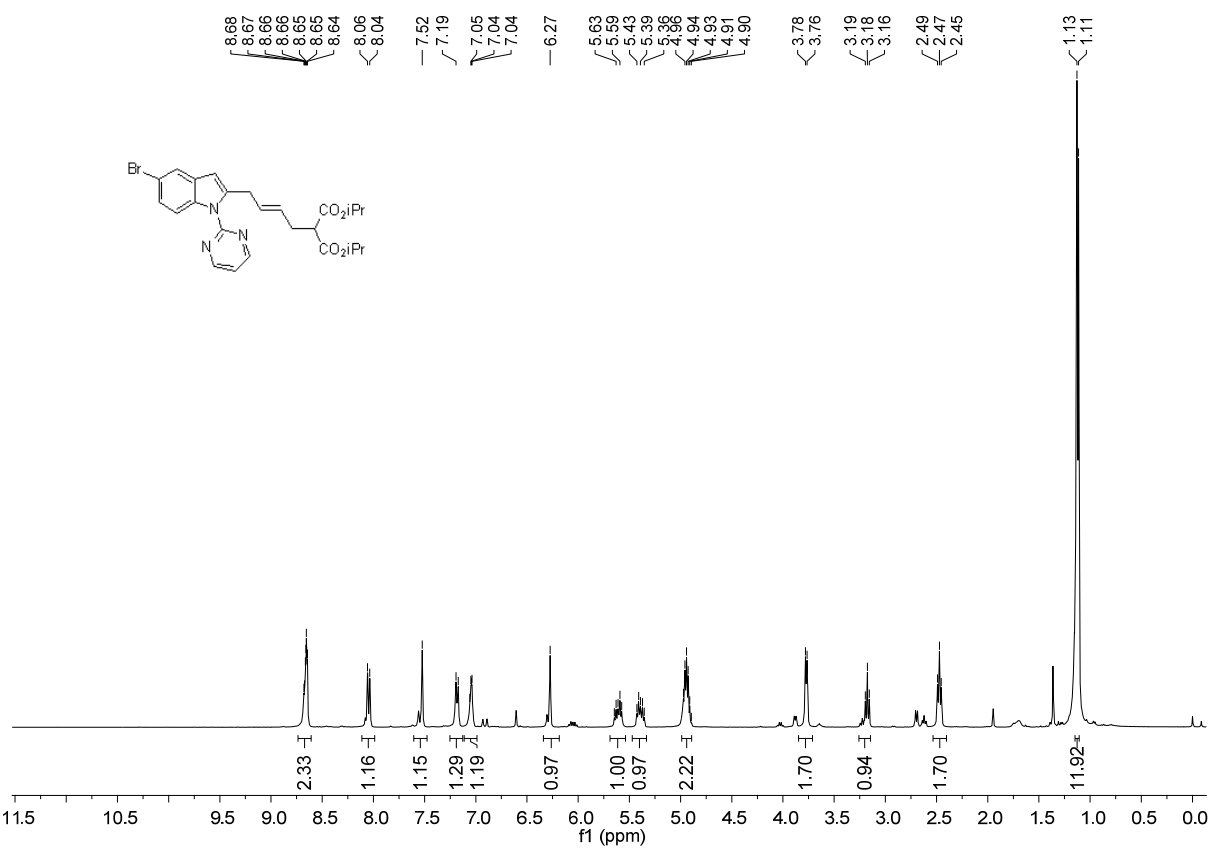
121.43
118.03
117.99
116.77
116.74
113.63
113.57
113.54
113.30
68.89
68.69
52.46
52.20
31.55
29.43
26.85
24.99
21.69
21.59
21.54
21.52
8.89
8.77
CO2iPr
CO2iPr
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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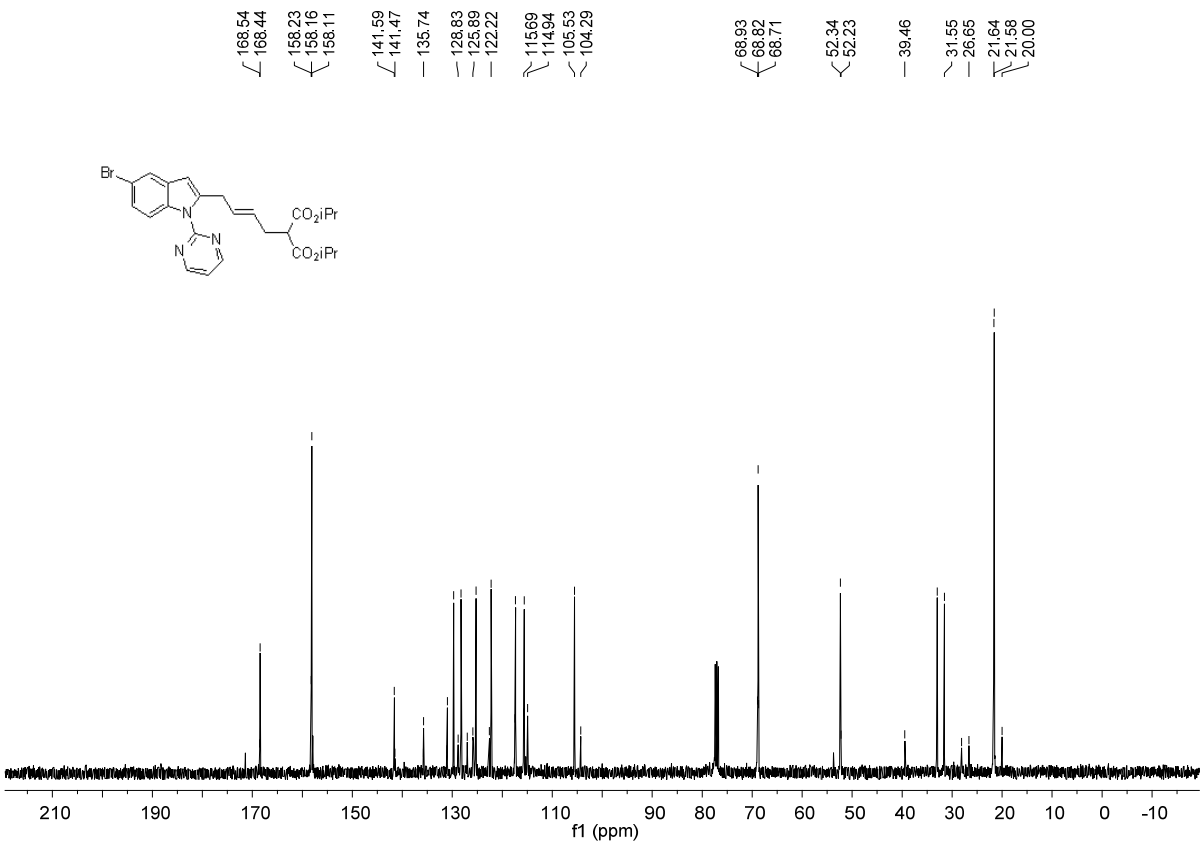
8.67
8.66
8.66
8.65
8.65
8.64
8.06
8.04
7.52
7.19
7.05
7.04
7.04
6.27
5.63
5.59
5.43
5.39
5.36
4.96
4.94
4.93
4.91
4.90
3.78
3.76
3.19
3.18
3.16
2.49
2.47
2.45
1.13
1.11
Br
CO2iPr
CO2iPr
N
N
2.33
1.16
1.15
1.29
1.19
0.97
1.00
0.97
2.22
1.70
0.94
1.70
11.92
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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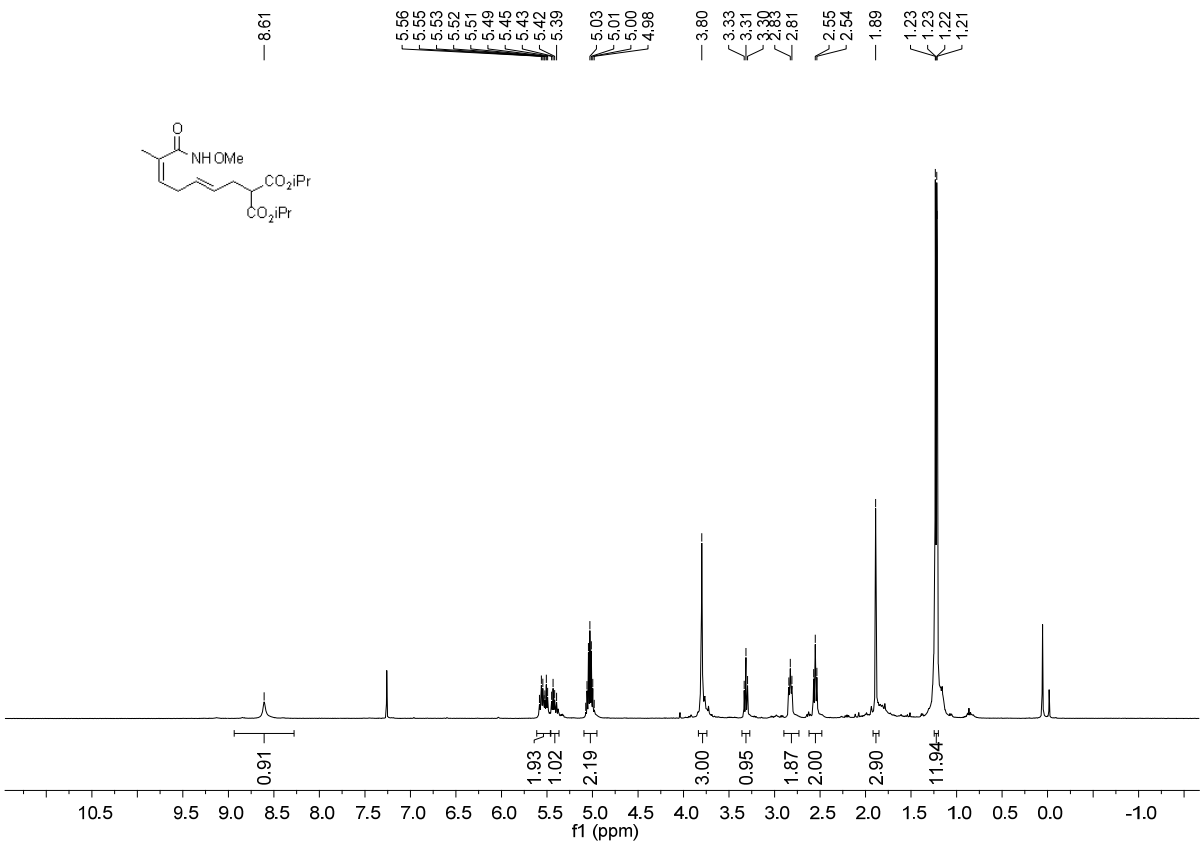
168.44
158.23
158.16
158.11
141.59
141.47
135.74
128.83
125.89
122.22
115.69
114.94
105.53
104.29
68.93
68.82
68.71
52.34
52.23
39.46
31.55
26.65
21.64
21.58
20.00
Br
N
N
CO2iPr
CO2iPr
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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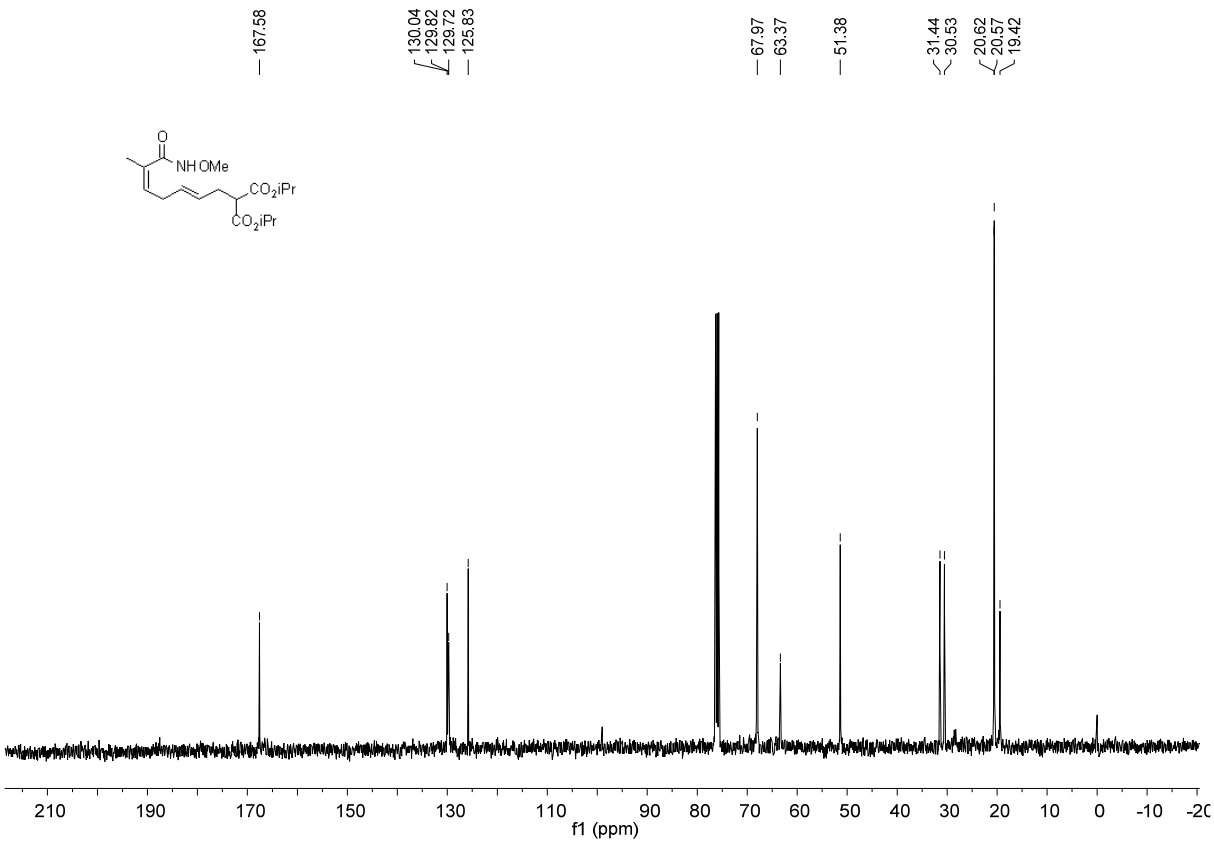
5.56
5.55
5.53
5.52
5.51
5.49
5.45
5.43
5.42
5.39
5.03
5.01
5.00
4.98
3.80
3.33
3.31
2.83
2.81
2.55
2.54
1.89
1.23
1.23
1.22
1.21
O
NH OMe
CO2iPr
CO2iPr
0.91
1.93
1.02
2.19
3.00
0.95
1.87
2.00
2.90
11.94
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)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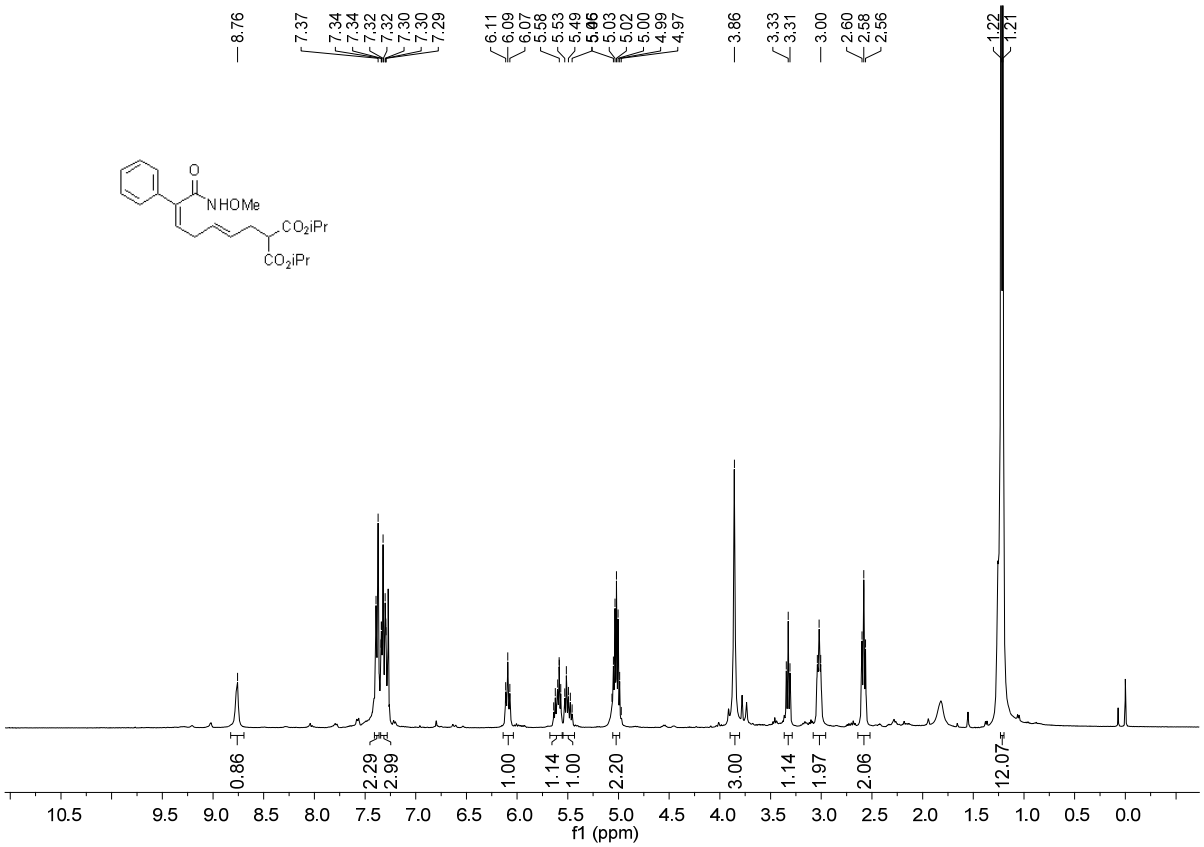
130.04
129.82
129.72
125.83
67.97
63.37
51.38
31.44
30.53
20.62
20.57
19.42
O
NH OMe
CO2iPr
CO2iPr
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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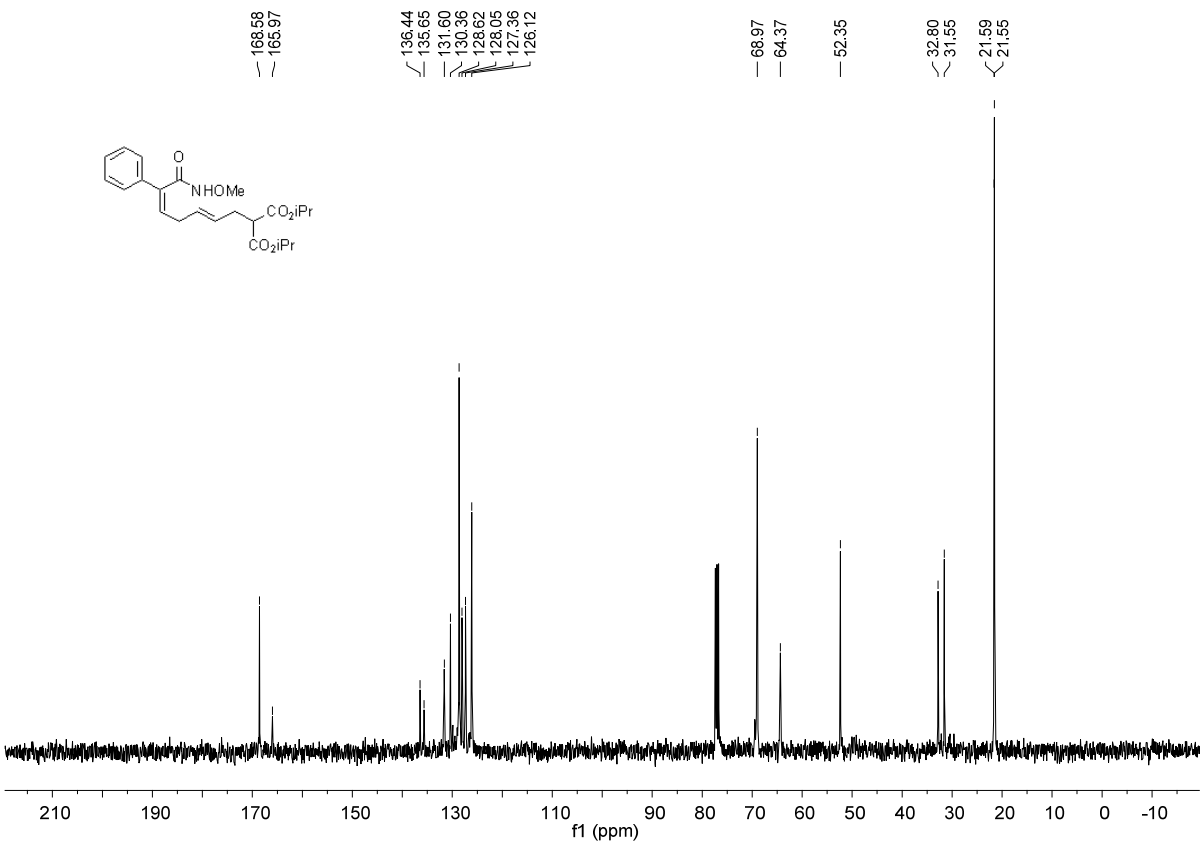
7.34
7.34
7.32
7.32
7.30
7.30
7.29
6.11
6.09
6.07
5.58
5.53
5.49
5.03
5.02
5.00
4.99
4.97
3.86
3.33
3.31
3.00
2.60
2.58
2.56
1.22
1.21
O
NHOMe
CO2iPr
CO2iPr
0.86
2.29
2.99
1.00
1.14
1.00
2.20
3.00
1.14
1.97
2.06
12.07
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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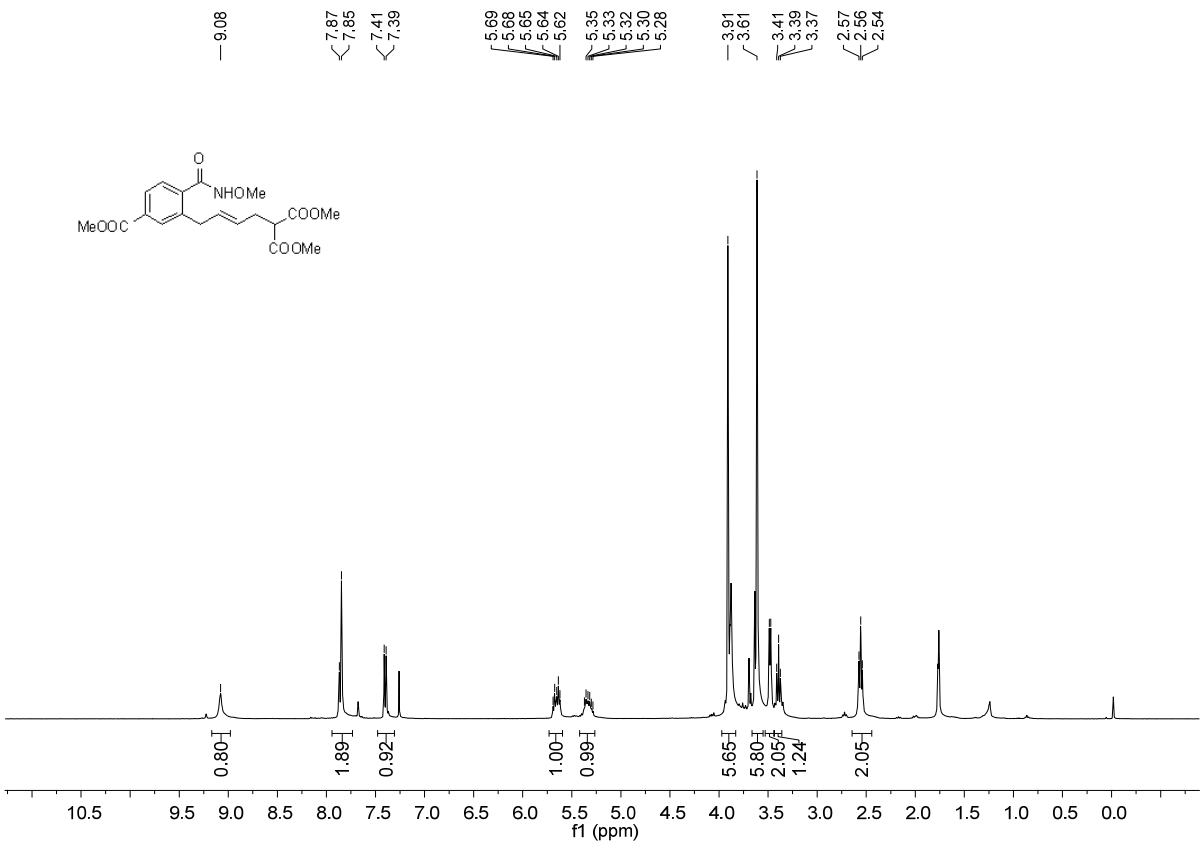
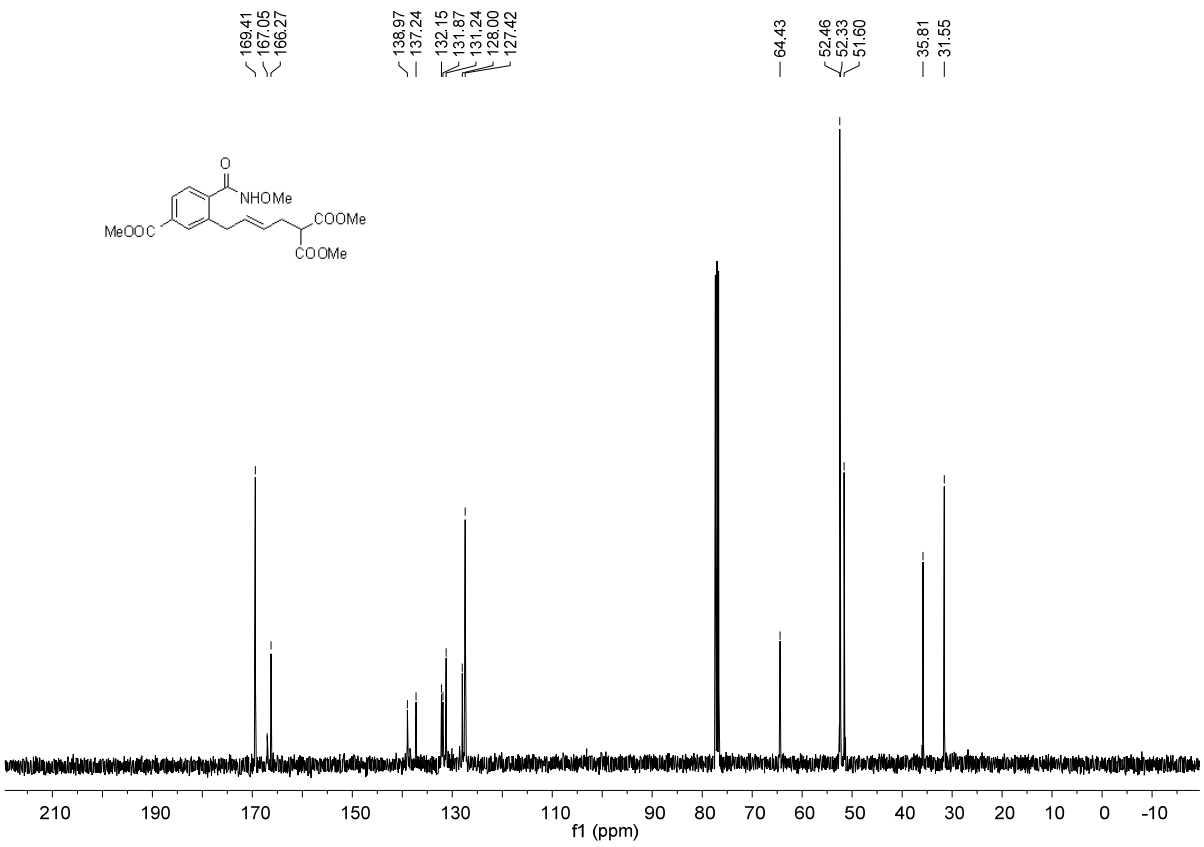
165.97
136.44
135.65
131.60
130.36
128.62
128.05
127.36
126.12
68.97
64.37
52.35
32.80
31.55
21.59
21.55
O
NHOMe
CO2iPr
CO2iPr
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


9.08
7.87
7.85
7.41
7.39
5.69
5.68
5.65
5.64
5.62
5.35
5.33
5.32
5.30
5.28
3.91
3.61
3.41
3.39
3.37
2.57
2.56
2.54
O
NHOMe
MeOOC
COOMe
COOMe
0.80
1.89
0.92
1.00
0.99
5.65
5.80
2.05
1.24
2.05
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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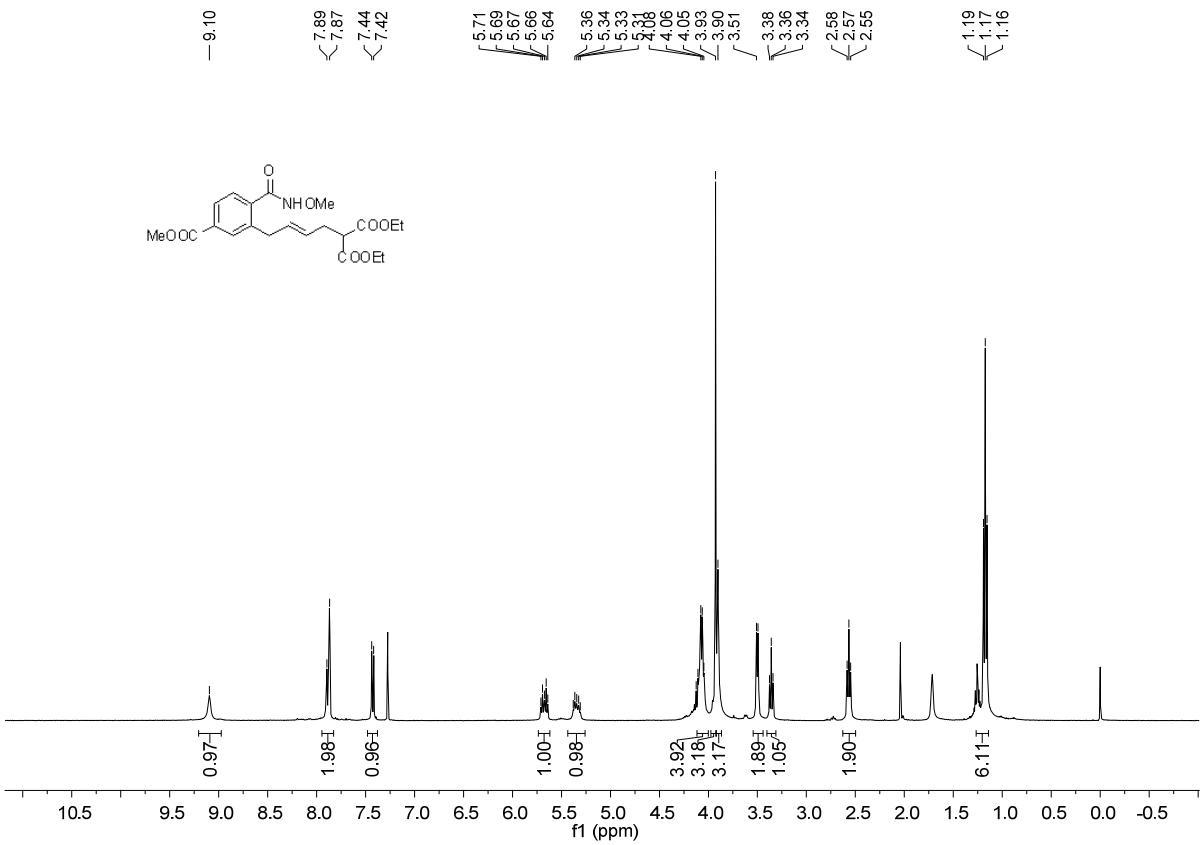
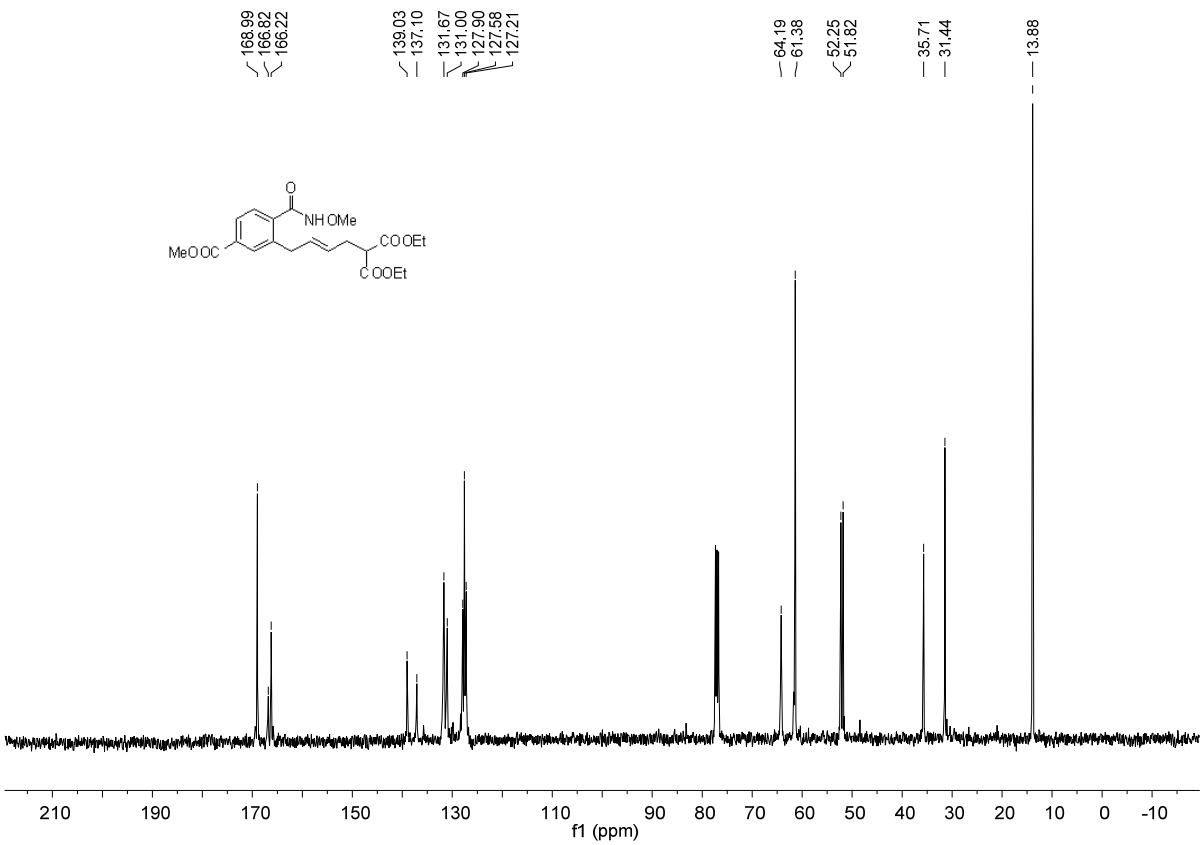
138.97
137.24
132.15
131.87
131.24
128.00
127.42
64.43
52.46
52.33
51.60
35.81
31.55
O
NHOMe
MeOOC
COOMe
COOMe
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


9.10
7.89
7.87
7.44
7.42
5.71
5.69
5.67
5.66
5.64
5.36
5.34
5.33
5.31
4.08
4.06
4.05
3.93
3.90
3.51
3.38
3.36
3.34
2.58
2.57
2.55
1.19
1.17
1.16
O
NHOMe
MeOOC
COOEt
COOEt
0.97
1.98
0.96
1.00
0.98
3.92
3.18
3.17
1.89
1.05
1.90
6.11
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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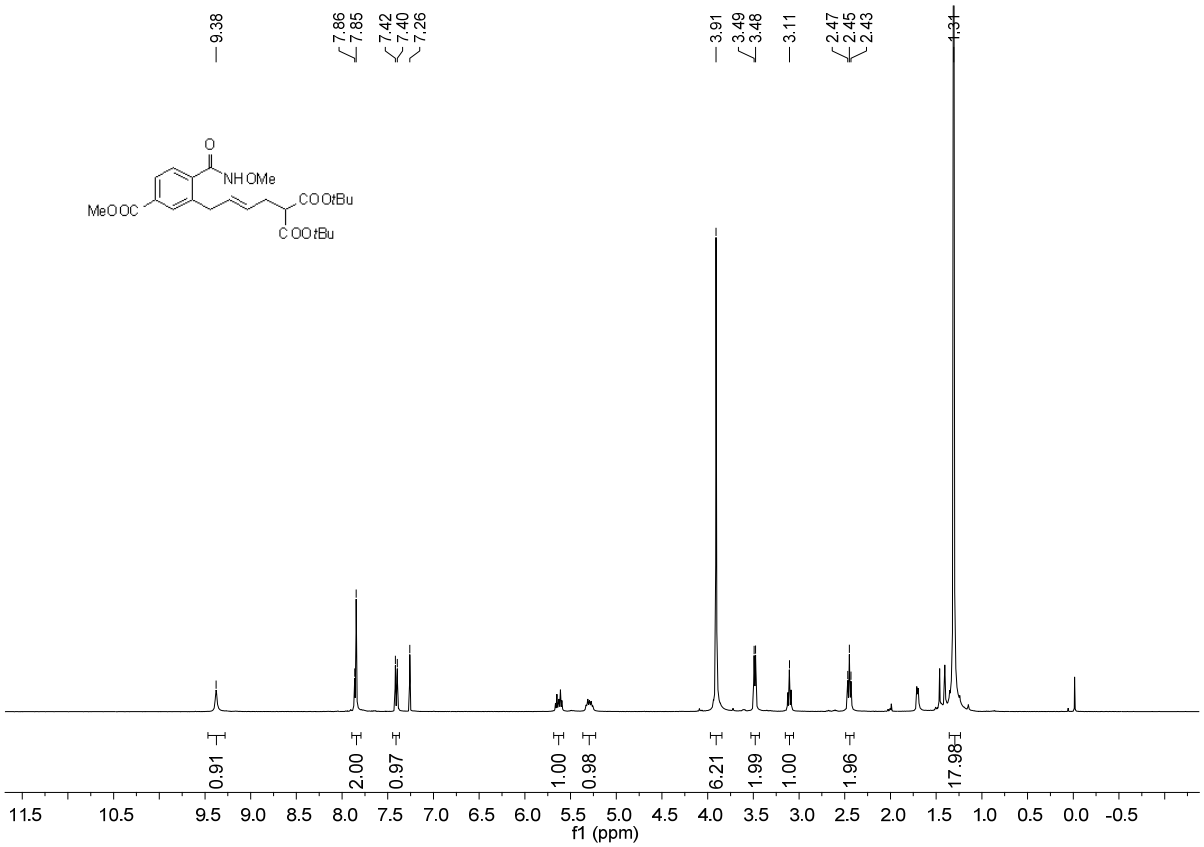
166.82
166.22
139.03
137.10
131.67
131.00
127.90
127.58
127.21
64.19
61.38
52.25
51.82
35.71
31.44
13.88
O
NH OMe
MeO OC
COOEt
COOEt
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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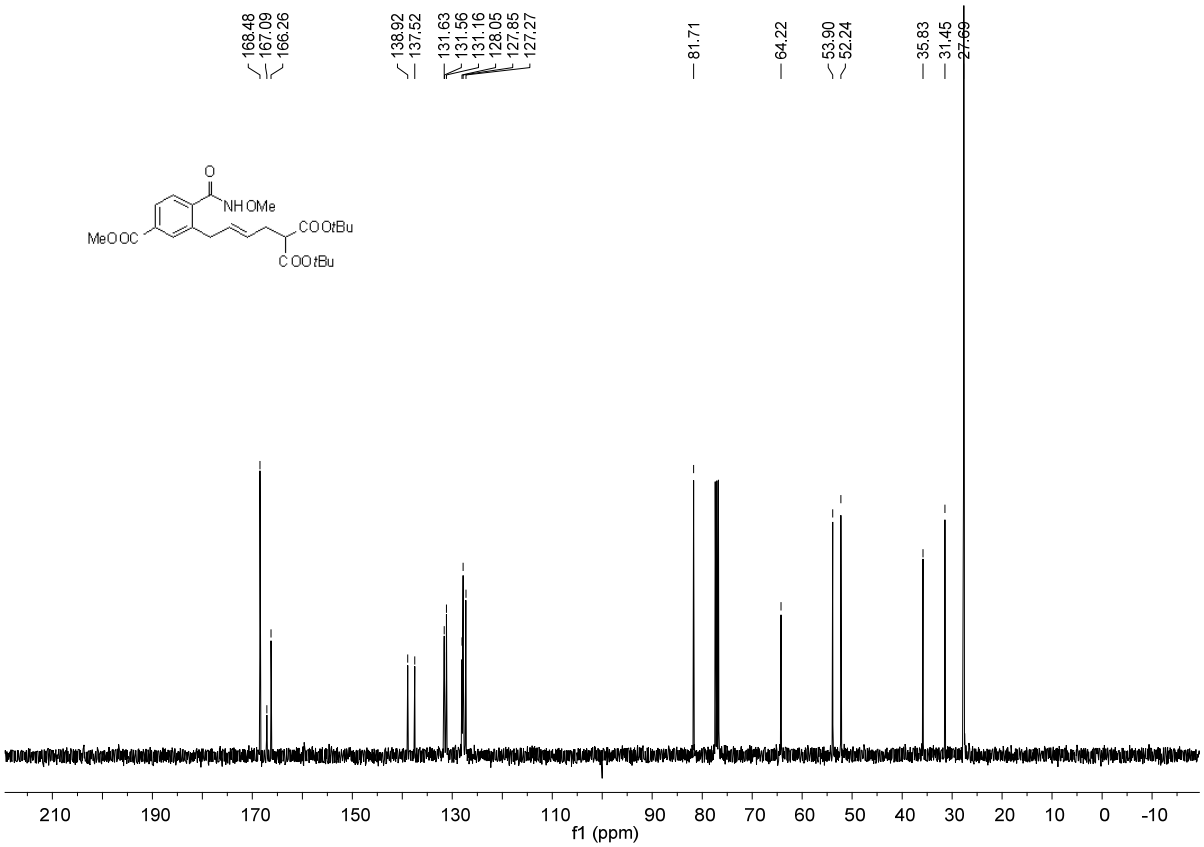
7.42
7.40
7.26
3.91
3.49
3.48
3.11
2.47
2.45
2.43
1.31
O
NH OMe
MeOOC
COOtBu
COOtBu
0.91
2.00
0.97
1.00
0.98
6.21
1.99
1.00
1.96
17.98
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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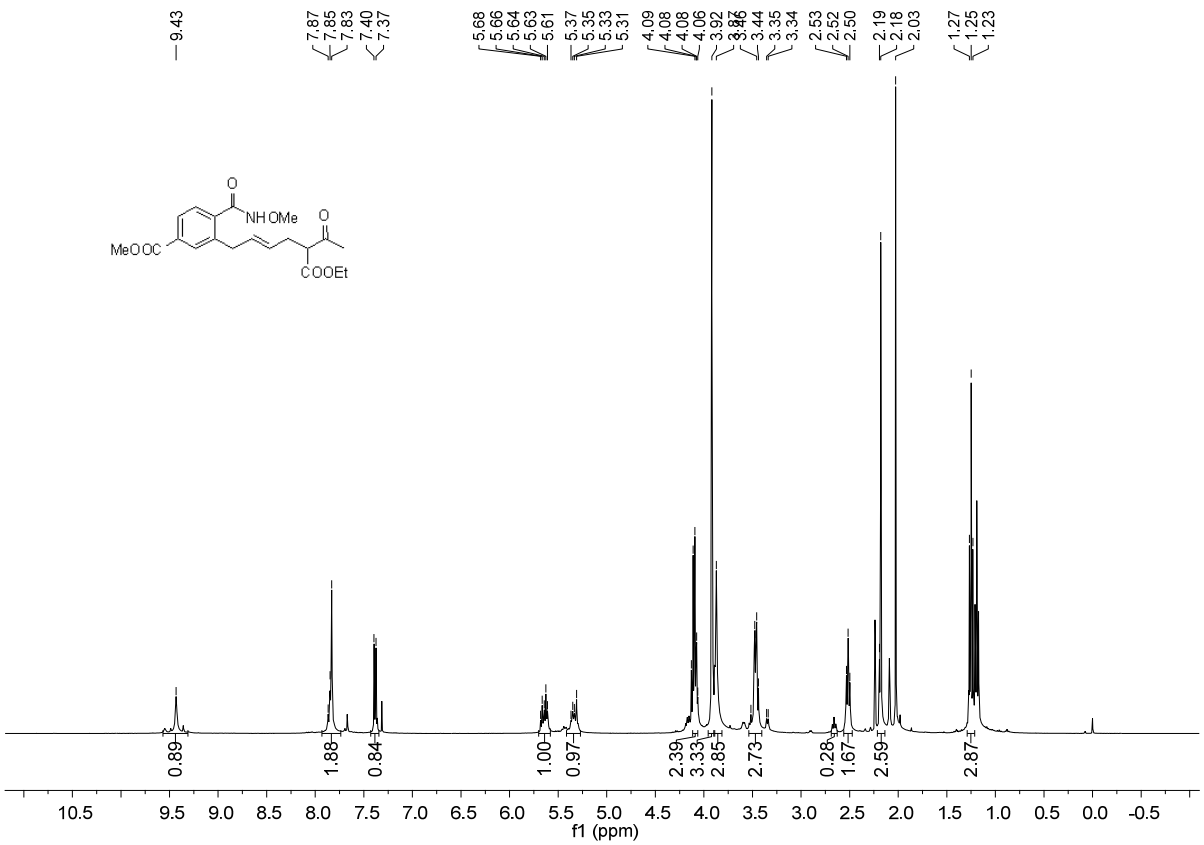
166.26
138.92
137.52
131.63
131.56
131.16
128.05
127.85
127.27
81.71
64.22
53.90
52.24
35.83
31.45
27.69
O
NH OMe
MeOOC
COOtBu
COOtBu
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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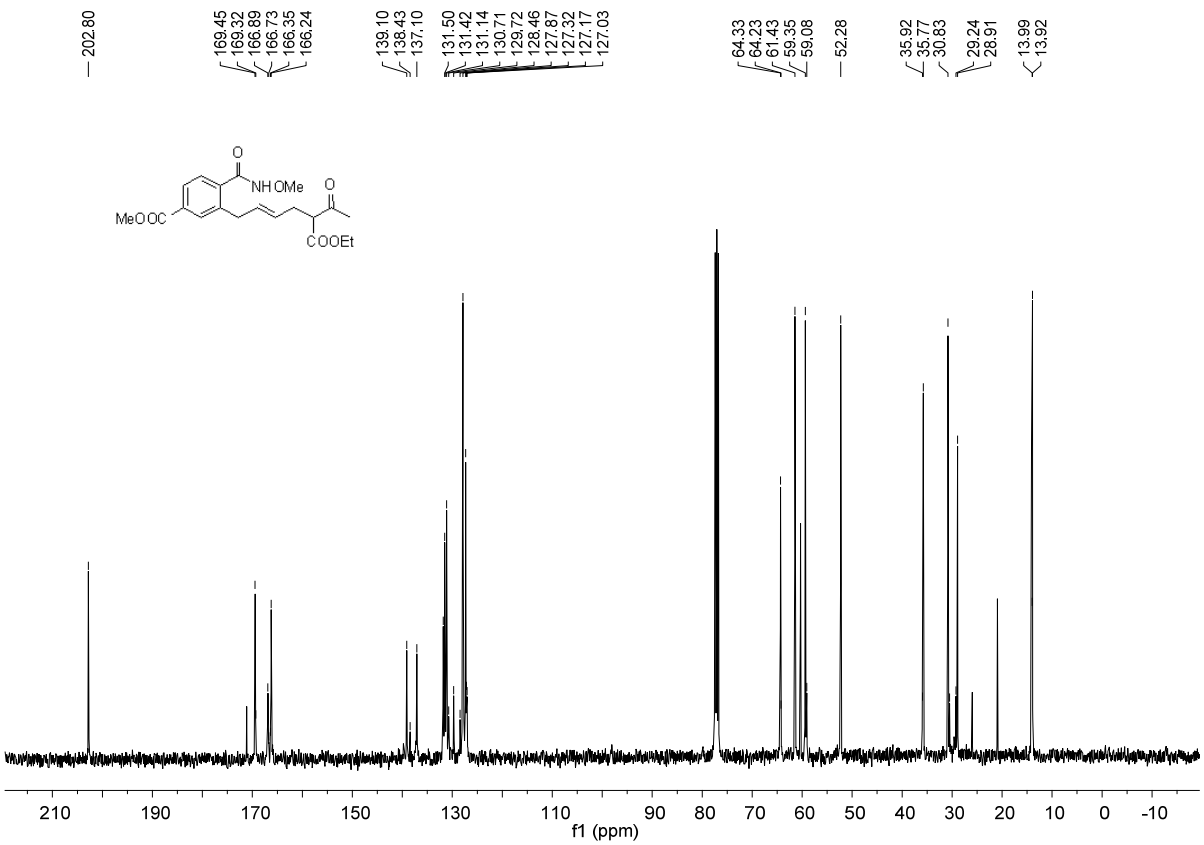
7.85
7.83
7.40
7.37
5.68
5.66
5.64
5.63
5.61
5.37
5.35
5.33
5.31
4.09
4.08
4.06
3.92
3.44
3.35
3.34
2.53
2.52
2.50
2.19
2.18
2.03
1.27
1.25
1.23
O
NH OMe
O
MeO OC
COOEt
0.89
1.88
0.84
1.00
0.97
2.39
3.33
2.85
2.73
0.28
1.67
2.59
2.87
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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166.35
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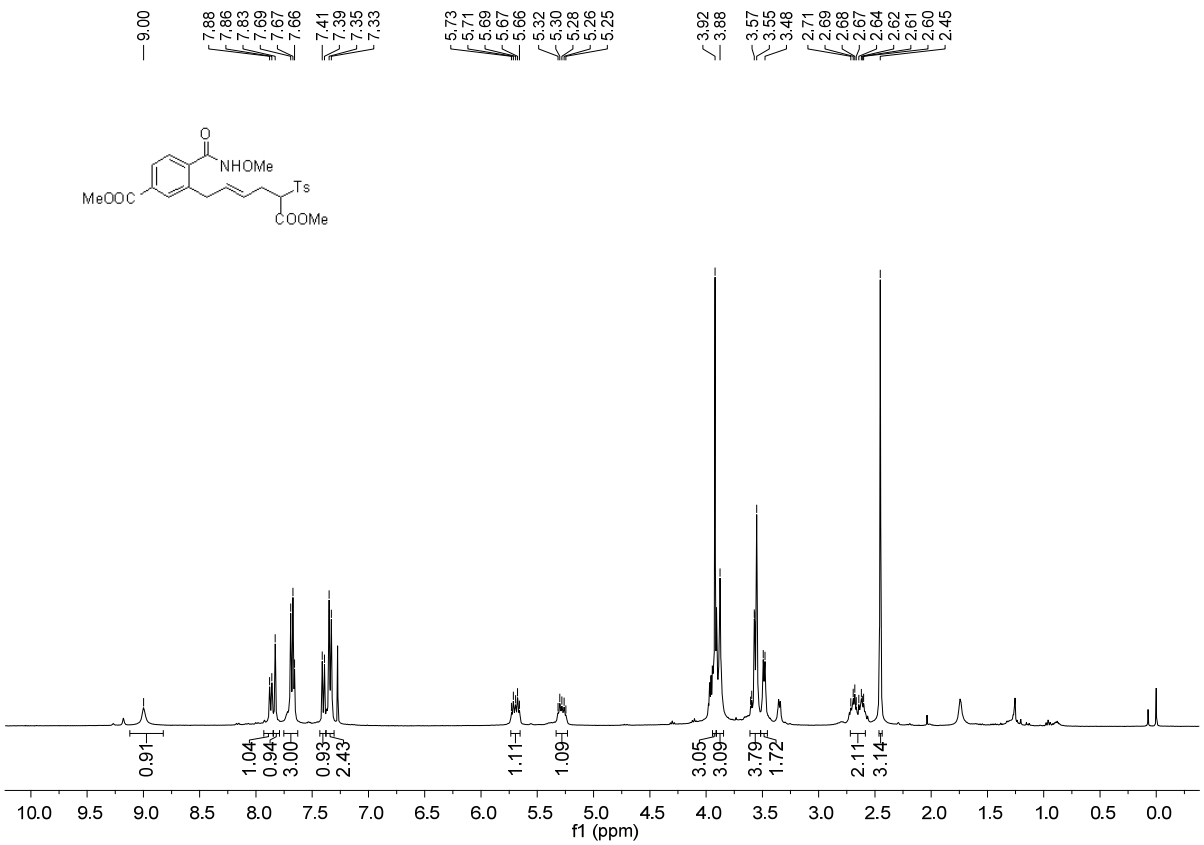
139.10
138.43
137.10
131.50
131.42
131.14
130.71
129.72
128.46
127.87
127.32
127.17
127.03
64.33
64.23
61.43
59.35
59.08
52.28
35.92
35.77
30.83
29.24
28.91
13.99
13.92
O
NHOMe
O
MeOOC
COOEt
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.67
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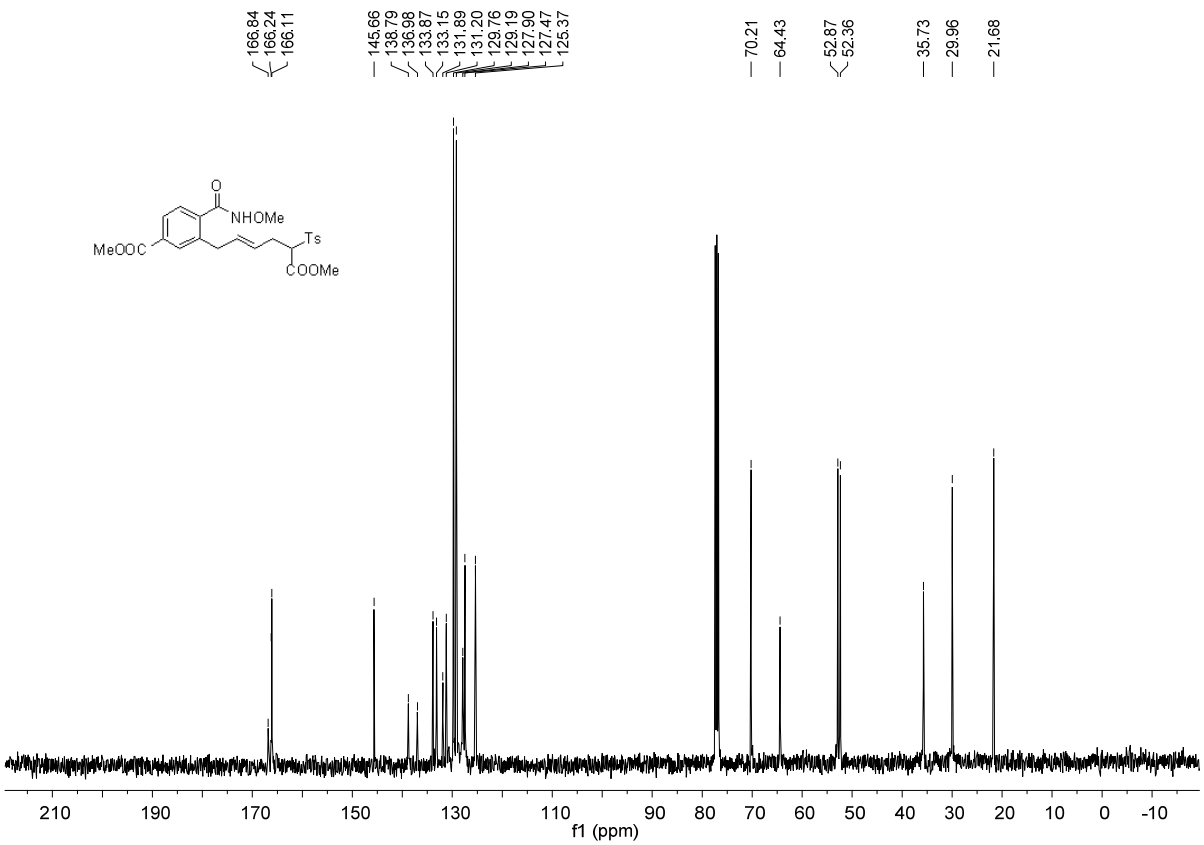
7.41
7.39
7.35
7.33
5.73
5.71
5.69
5.67
5.66
5.32
5.30
5.28
5.26
5.25
3.92
3.88
3.57
3.55
3.48
2.71
2.69
2.68
2.67
2.64
2.62
2.61
2.60
2.45
O
NHOMe
MeOOC
Ts
COOMe
0.91
1.04
0.94
3.00
0.93
2.43
1.11
1.09
3.05
3.09
3.79
1.72
2.11
3.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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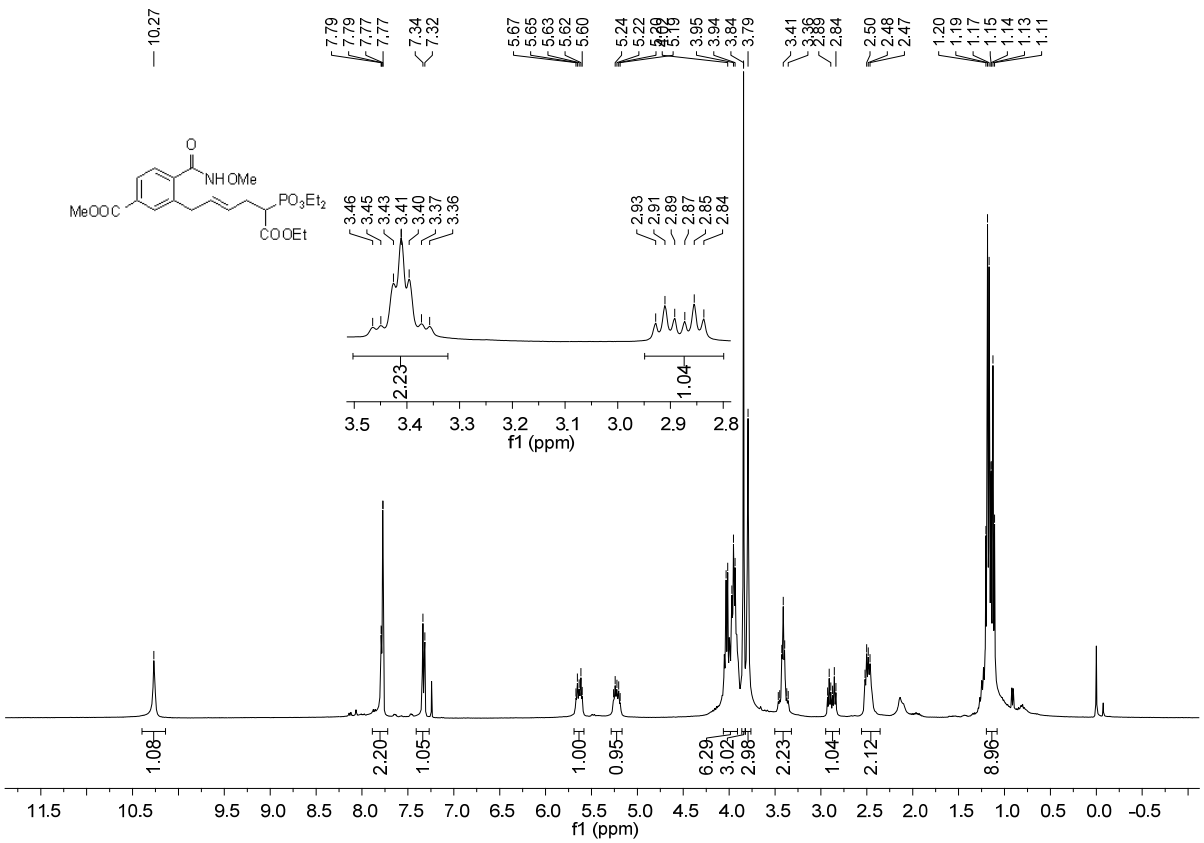
166.24
166.11
145.66
138.79
136.98
133.87
133.15
131.89
131.20
129.76
129.19
127.90
127.47
125.37
70.21
64.43
52.87
52.36
35.73
29.96
21.68
O
NHOMe
MeOOC
Ts
COOMe
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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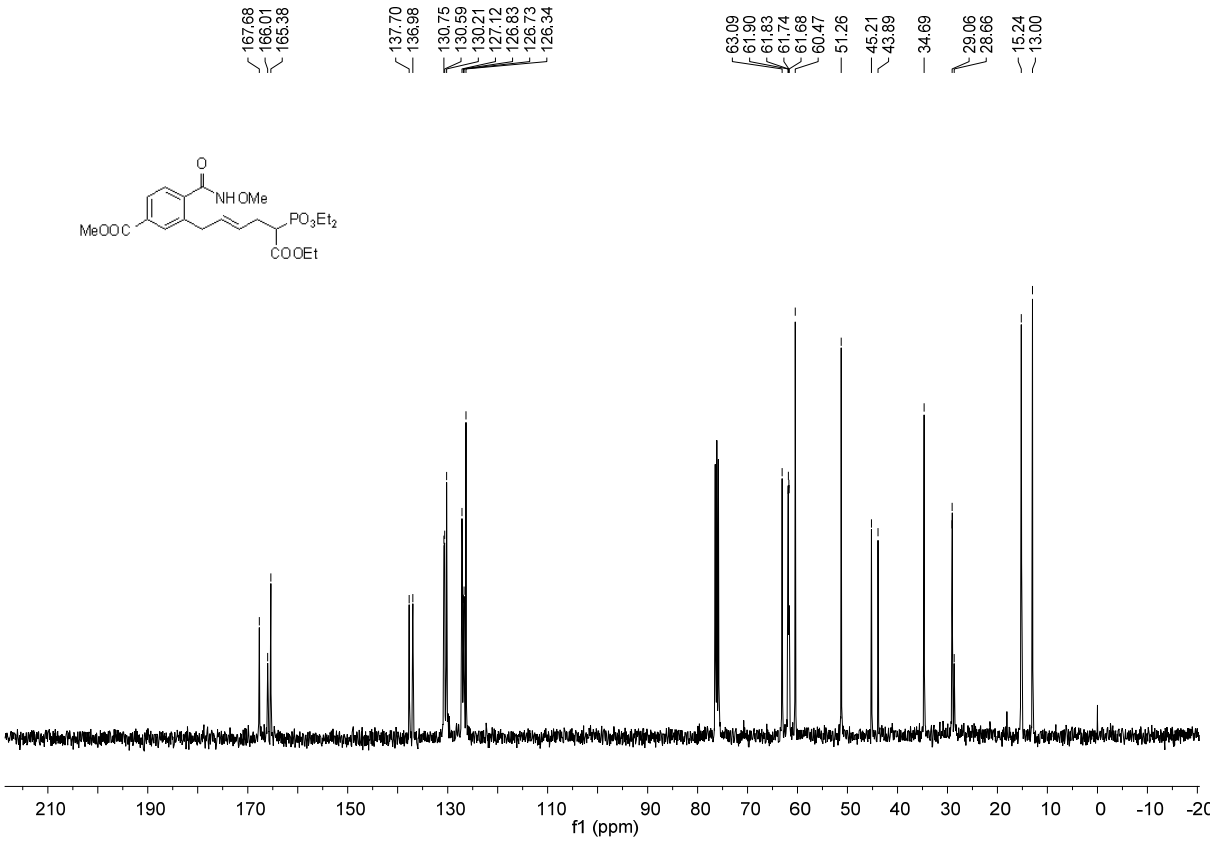
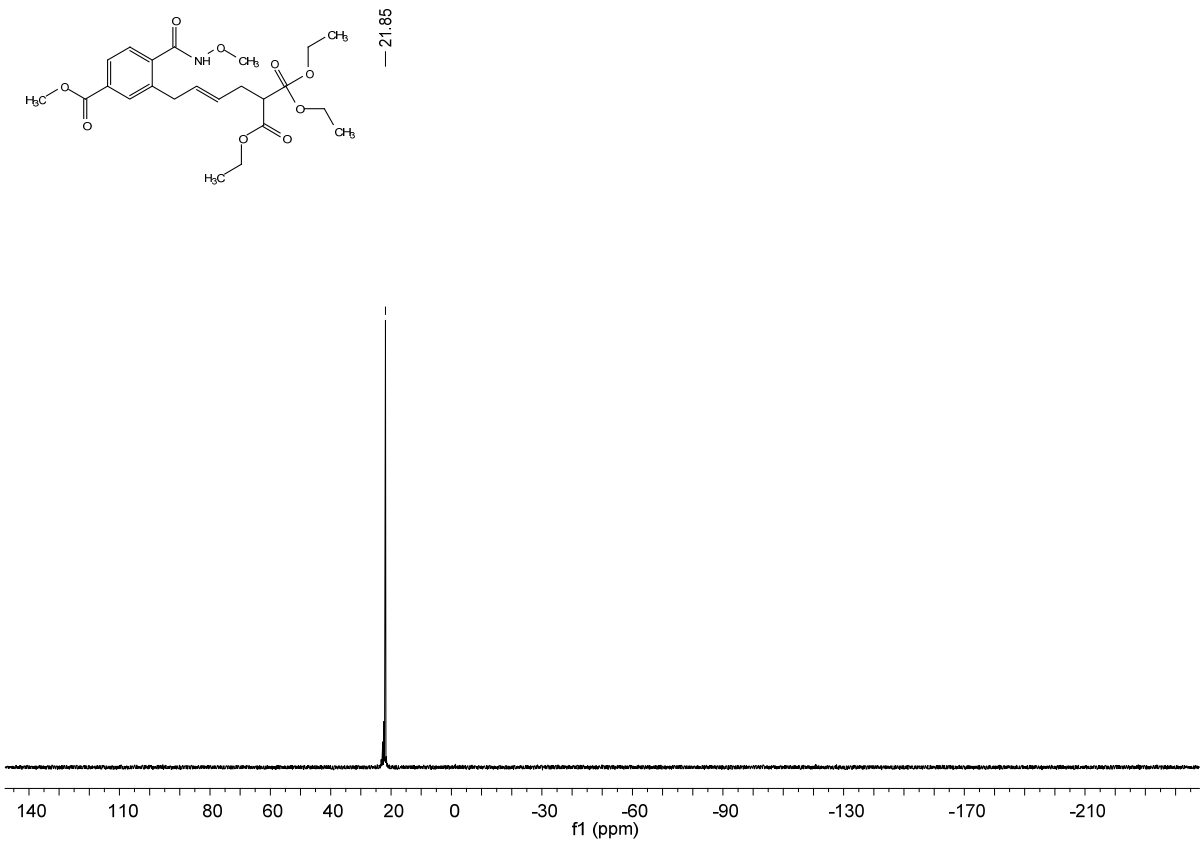
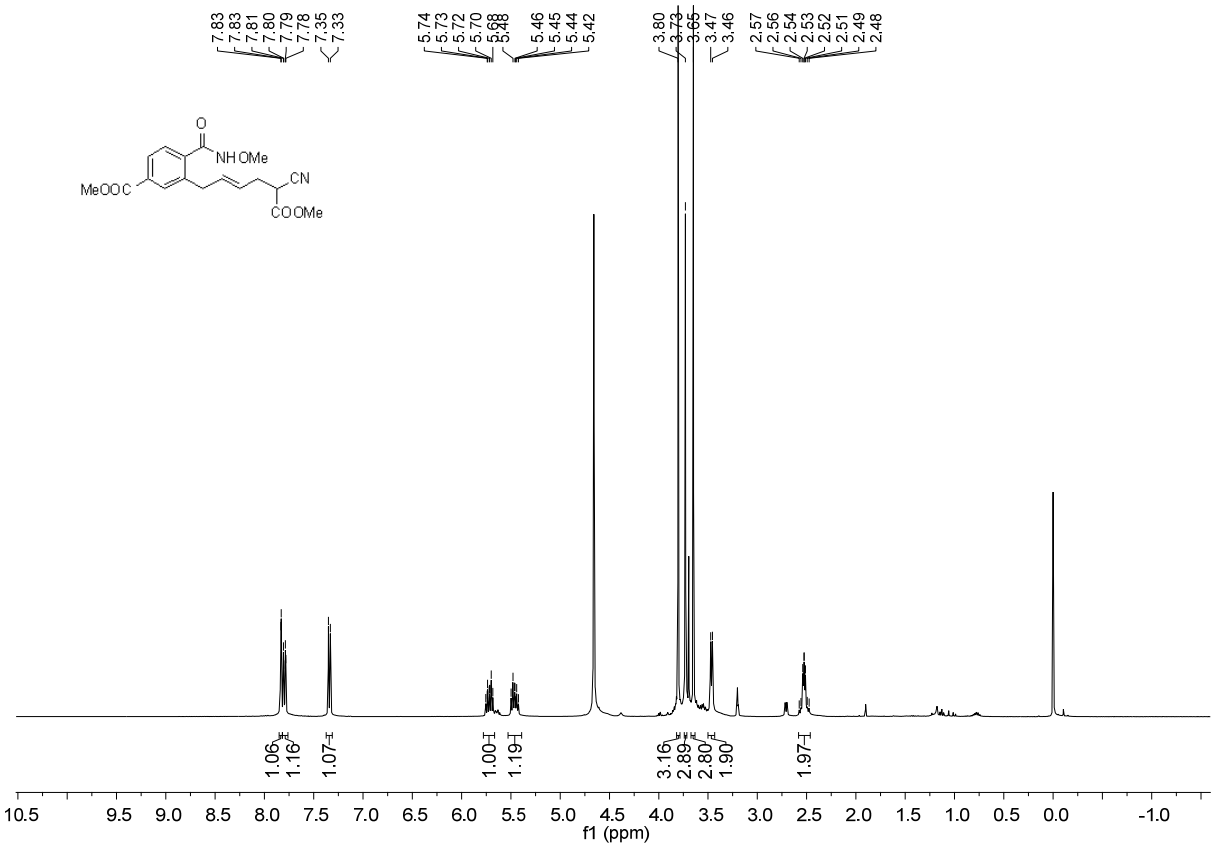
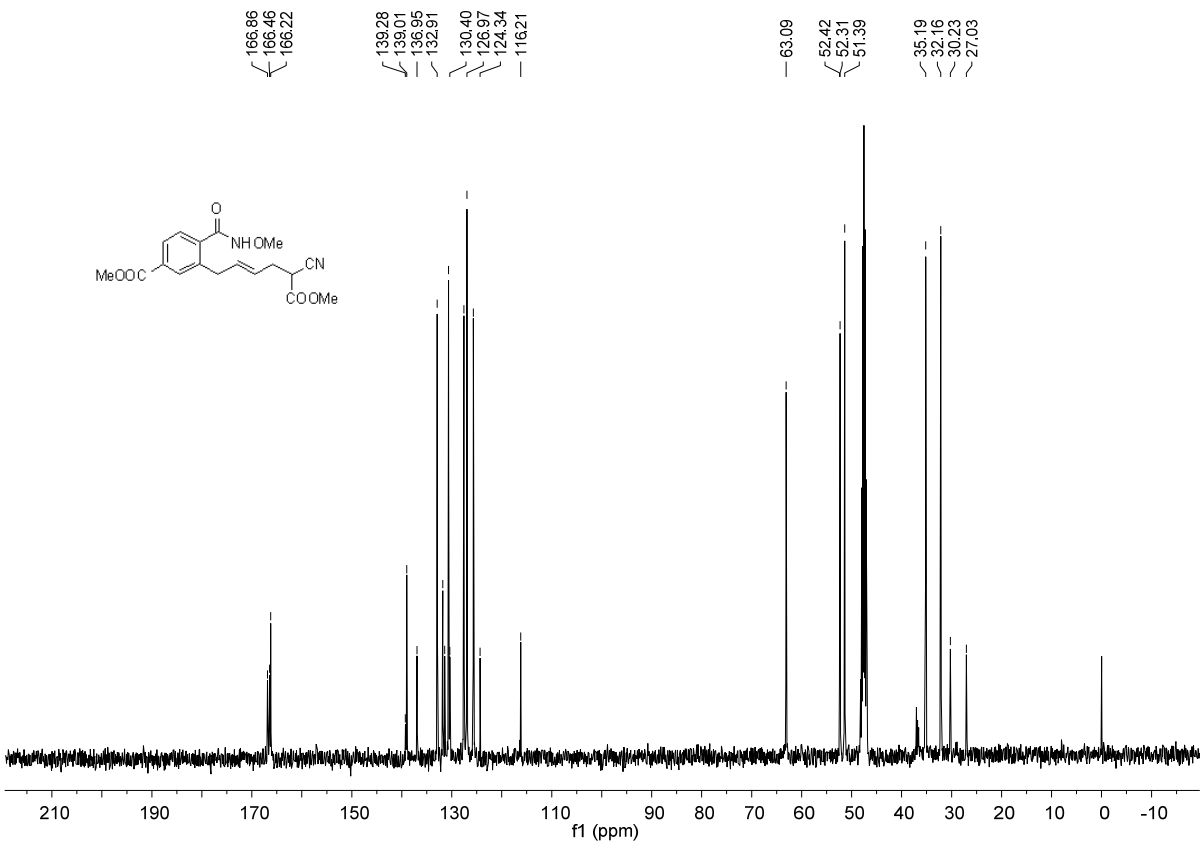
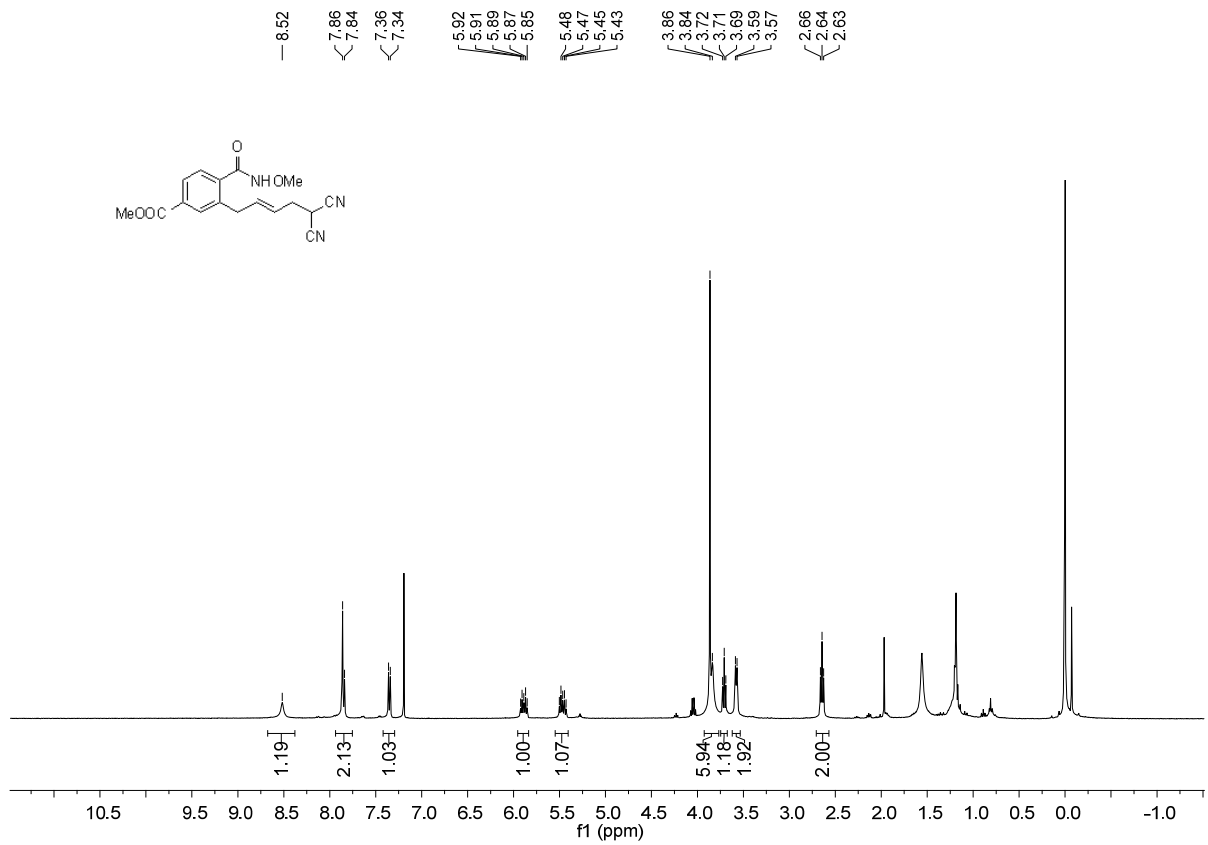
5.63
5.62
5.60
5.24
5.22
3.95
3.94
3.84
3.79
3.41
2.84
2.50
2.48
2.47
1.20
1.19
1.17
1.15
1.14
1.13
1.11
O
NH OMe
MeOOC
PO3Et2
COOEt
3.46
3.45
3.43
3.41
3.40
3.37
3.36
2.93
2.91
2.89
2.87
2.85
2.84
2.23
1.04
3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8
f1 (ppm)
1.08
2.20
1.05
1.00
0.95
6.29
3.02
2.98
2.23
1.04
2.12
8.96
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

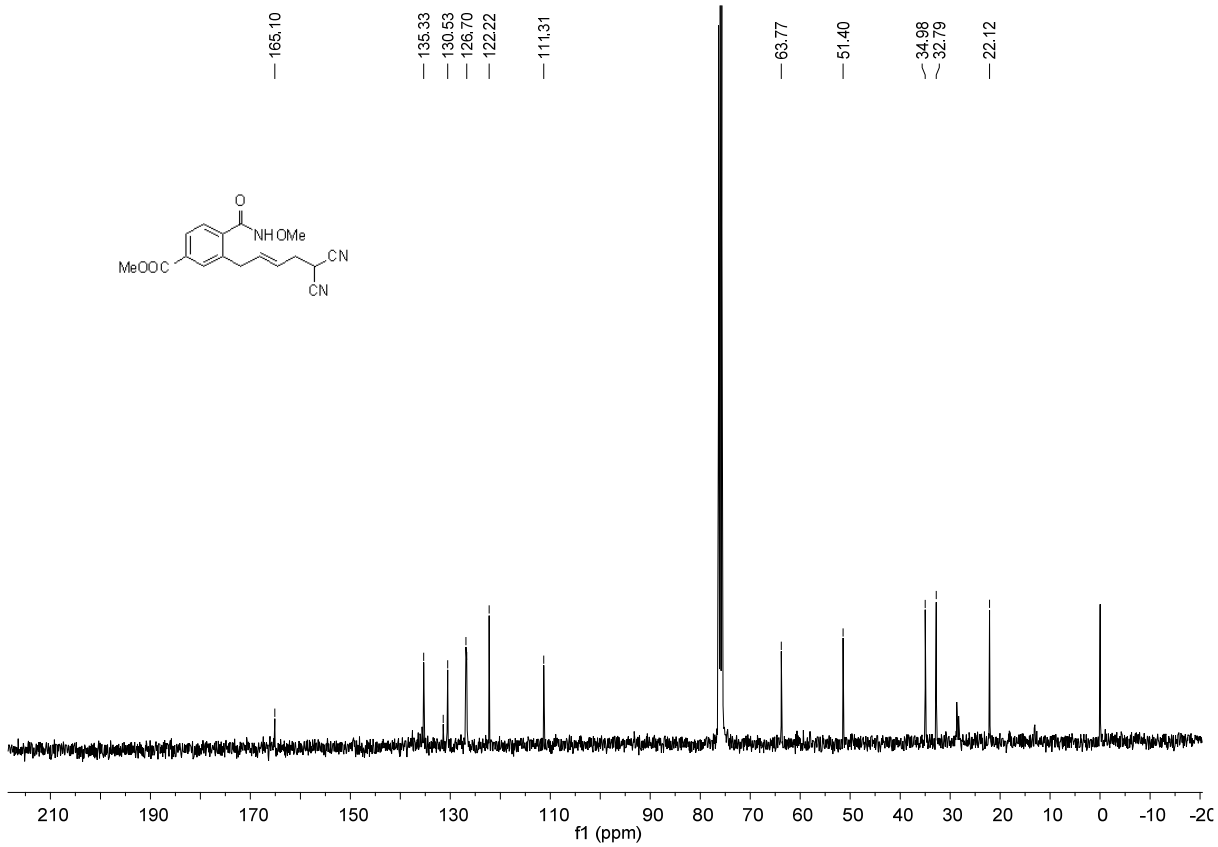

167.68
166.01
165.38
137.70
136.98
130.75
130.59
130.21
127.12
126.83
126.73
126.34
63.09
61.90
61.83
61.74
61.68
60.47
51.26
45.21
43.89
34.69
29.06
28.66
15.24
13.00
O
NH OMe
MeOOC
PO3Et2
COOEt
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

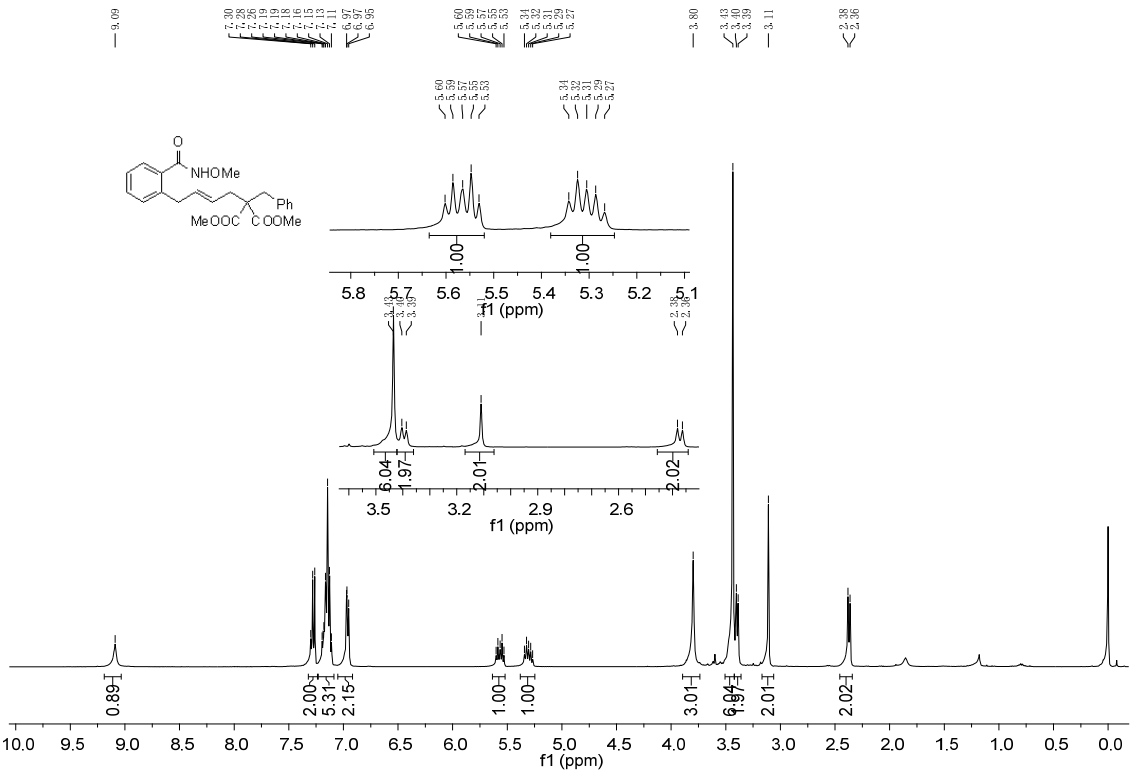

21.85
140
110
80
60
40
20
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

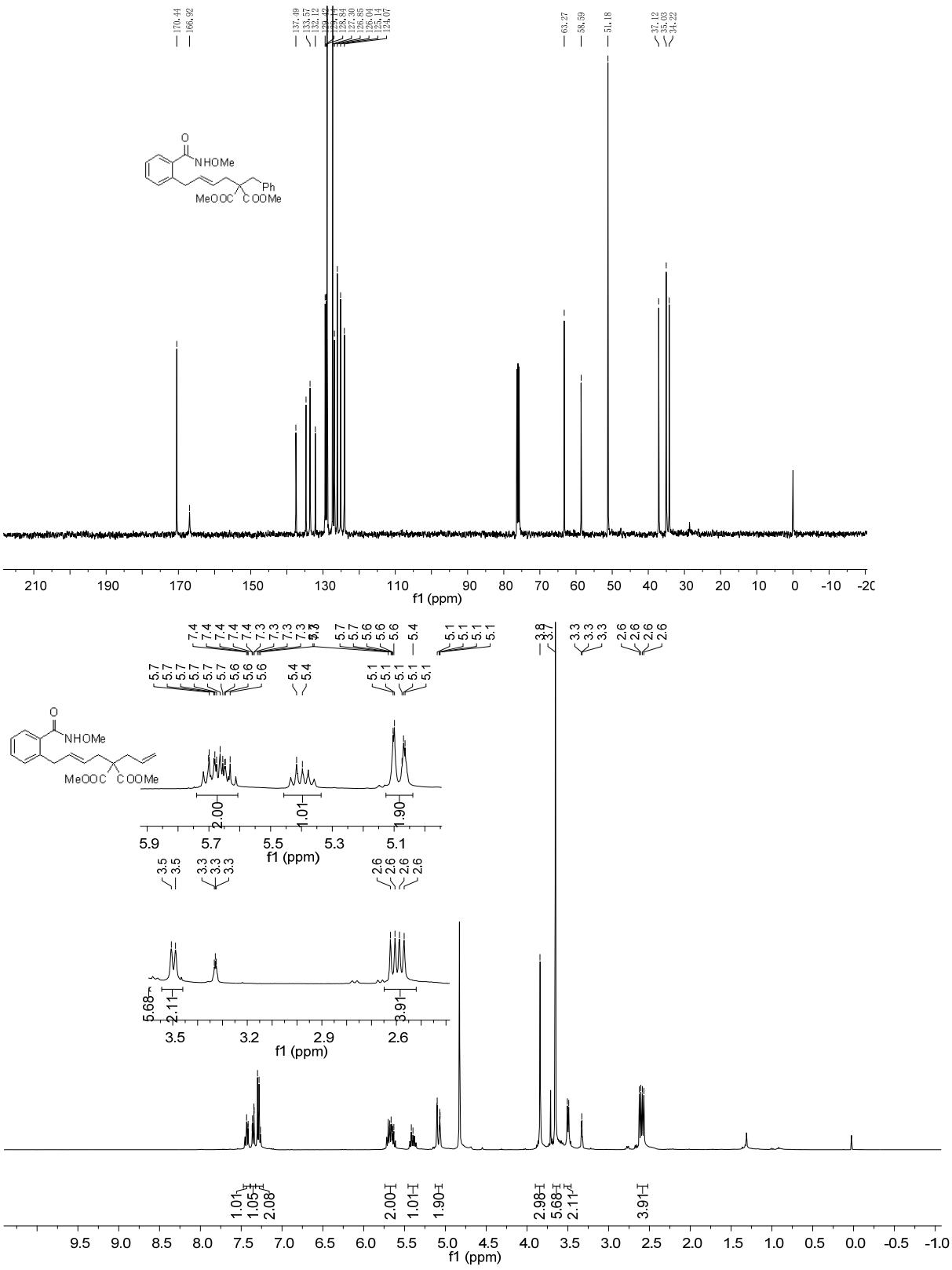

7.83
7.83
7.81
7.80
7.79
7.78
7.35
7.33
5.74
5.73
5.72
5.70
5.68
5.46
5.45
5.44
5.42
3.80
3.73
3.65
3.47
3.46
2.57
2.56
2.54
2.53
2.52
2.51
2.49
2.48
O
NH OMe
CN
MeOOC
COOMe
1.06
1.16
1.07
1.00
1.19
3.16
2.89
2.80
1.90
1.97
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

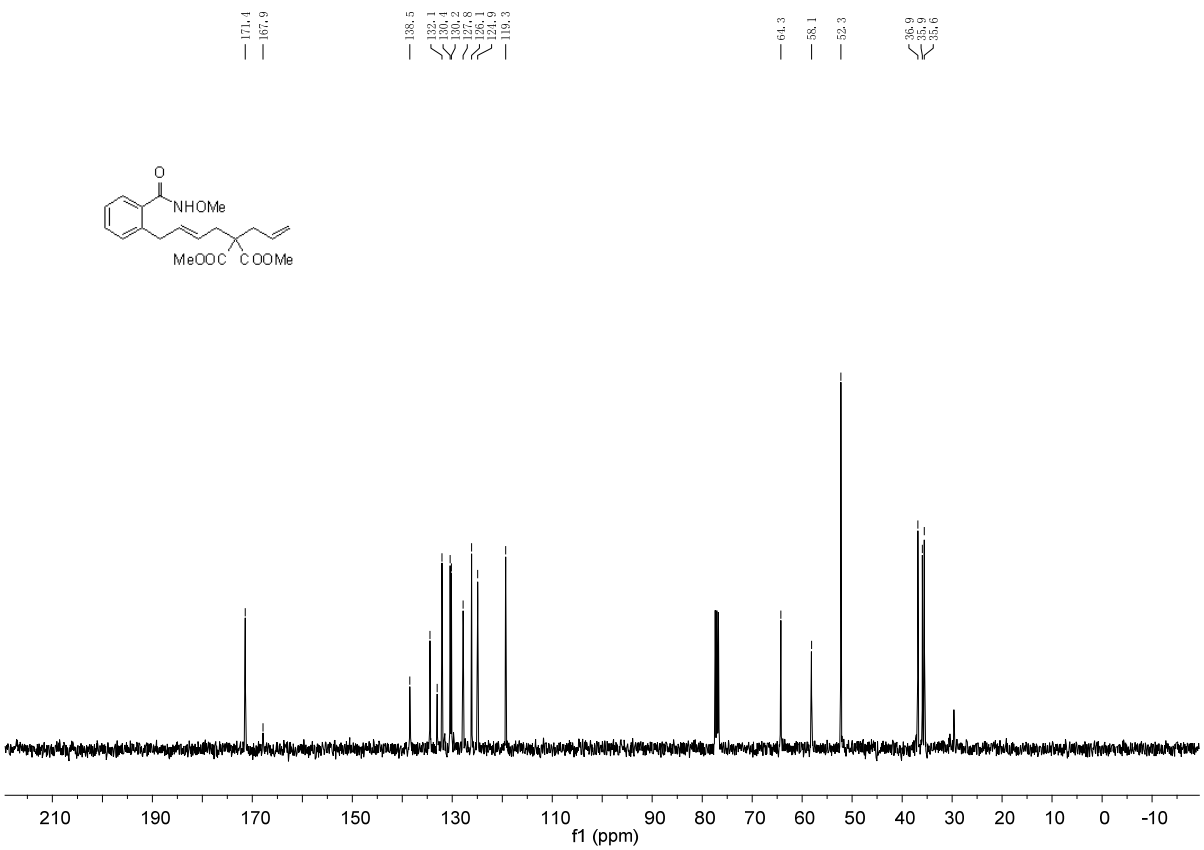

166.86
166.46
166.22
139.28
139.01
136.95
132.91
130.40
126.97
124.34
116.21
63.09
52.42
52.31
51.39
35.19
32.16
30.23
27.03
O
NH OMe
CN
MeOOC
COOMe
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

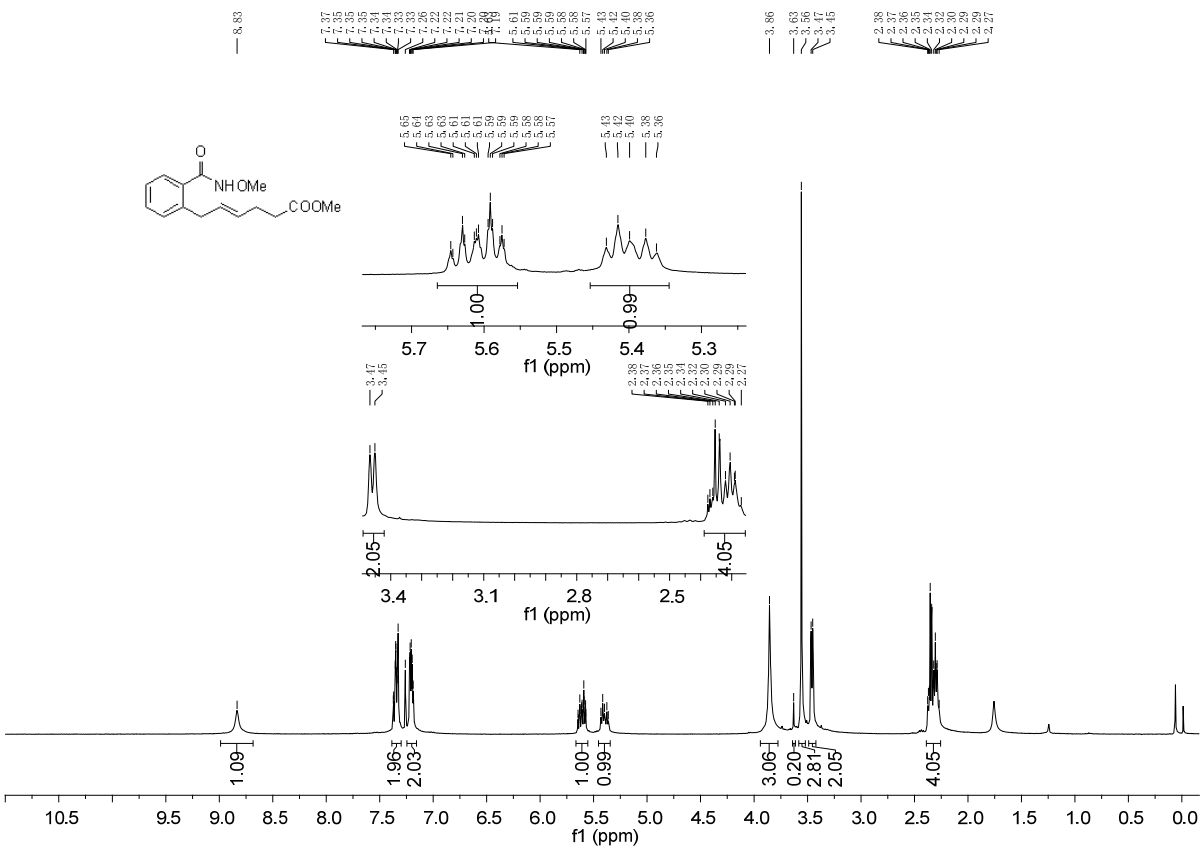

8.52
7.86
7.84
7.36
7.34
5.92
5.91
5.89
5.87
5.85
5.48
5.47
5.45
5.43
3.86
3.84
3.72
3.71
3.69
3.59
3.57
2.66
2.64
2.63
O
NH OMe
MeOOC
CN
CN
1.19
2.13
1.03
1.00
1.07
5.94
1.18
1.92
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

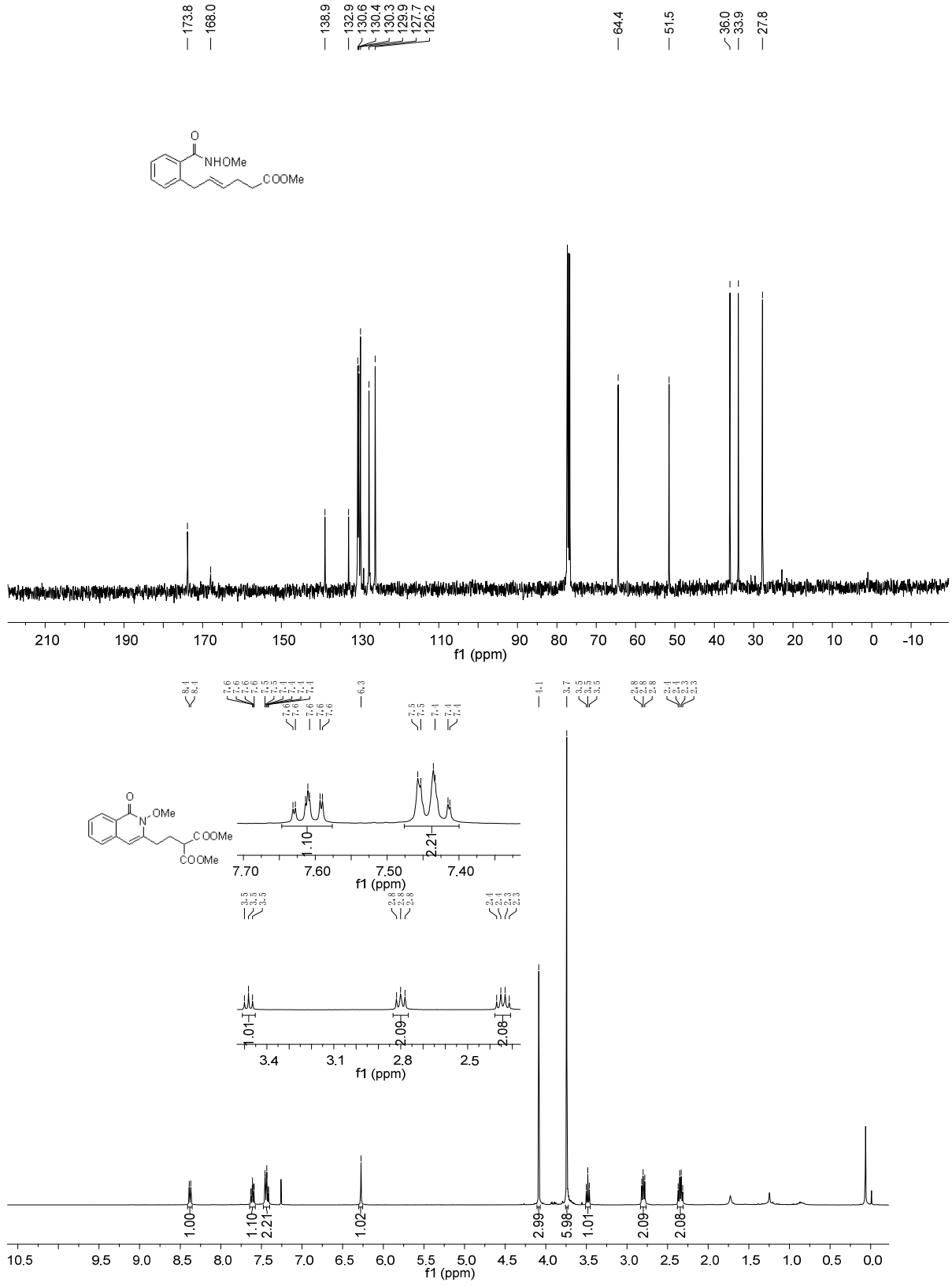

165.10
135.33
130.53
126.70
122.22
111.31
63.77
51.40
34.98
32.79
22.12
O
NHOMe
MeOOC
CN
CN
f1 (ppm)

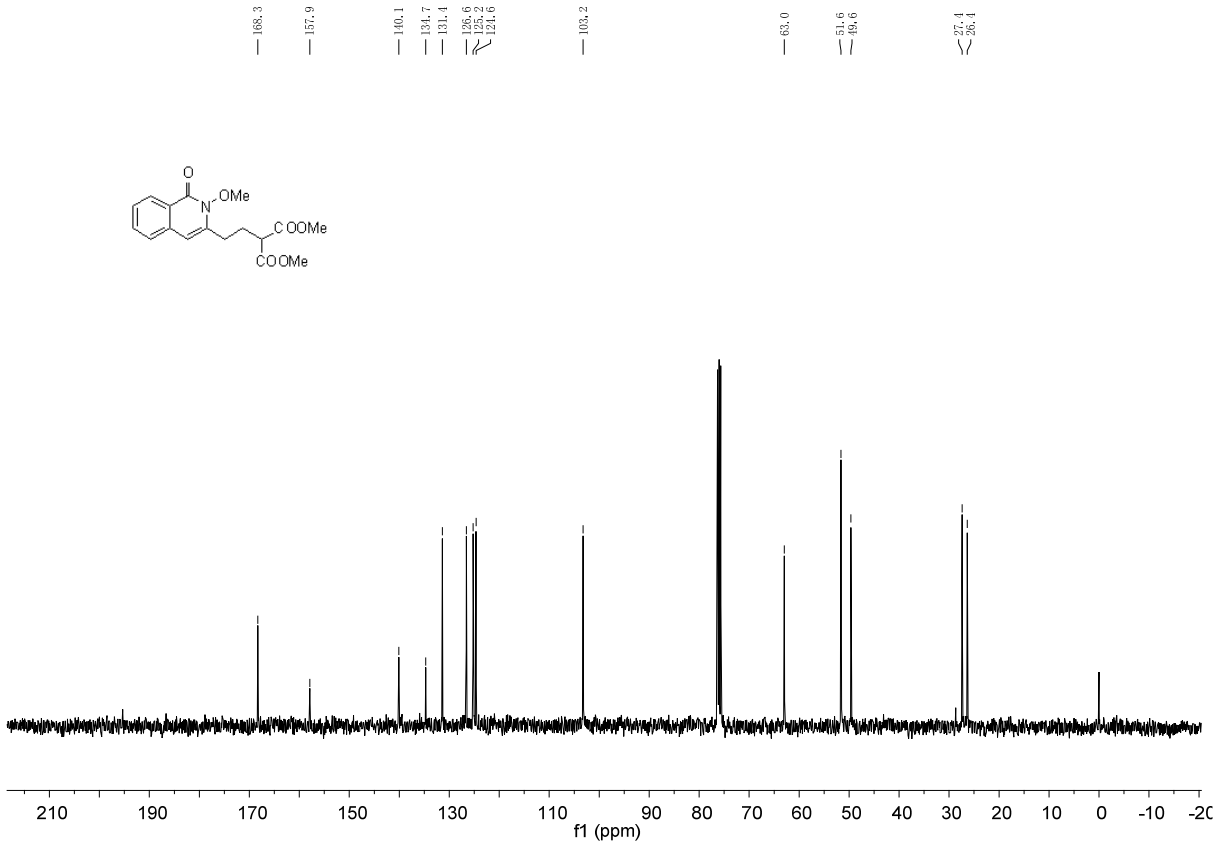

9.09
7.30
7.28
7.26
7.19
7.19
7.18
7.16
7.15
7.13
7.11
7.07
6.97
6.95
5.60
5.59
5.57
5.55
5.53
5.34
5.32
5.31
5.29
5.27
3.80
3.43
3.40
3.39
3.11
2.38
2.36
O
NHOMe
Ph
MeOOC
COOMe
1.00
1.00
f1 (ppm)
6.04
1.97
2.01
2.02
f1 (ppm)
0.89
2.00
5.31
2.15
1.00
1.00
3.01
6.04
1.97
2.01
2.02
f1 (ppm)

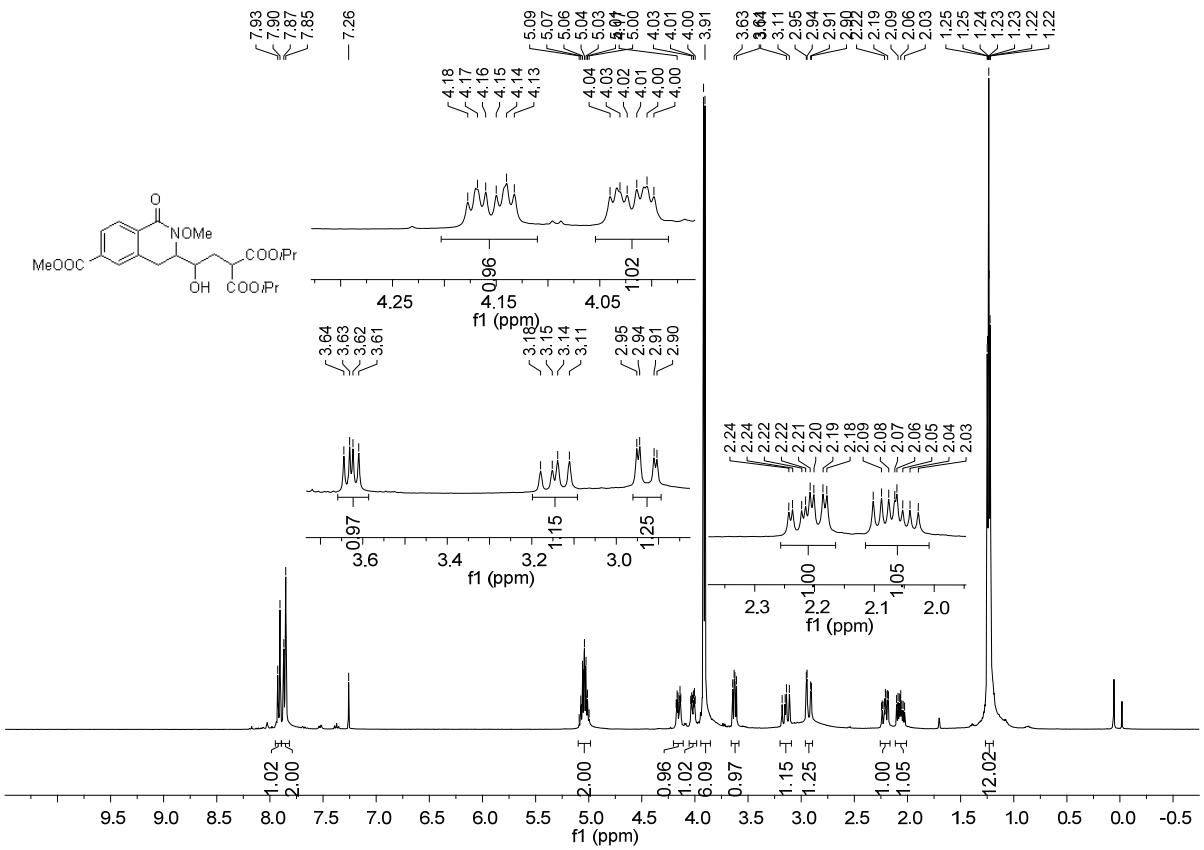

NHOMe
Ph
MeOOC
COOMe
f1 (ppm)

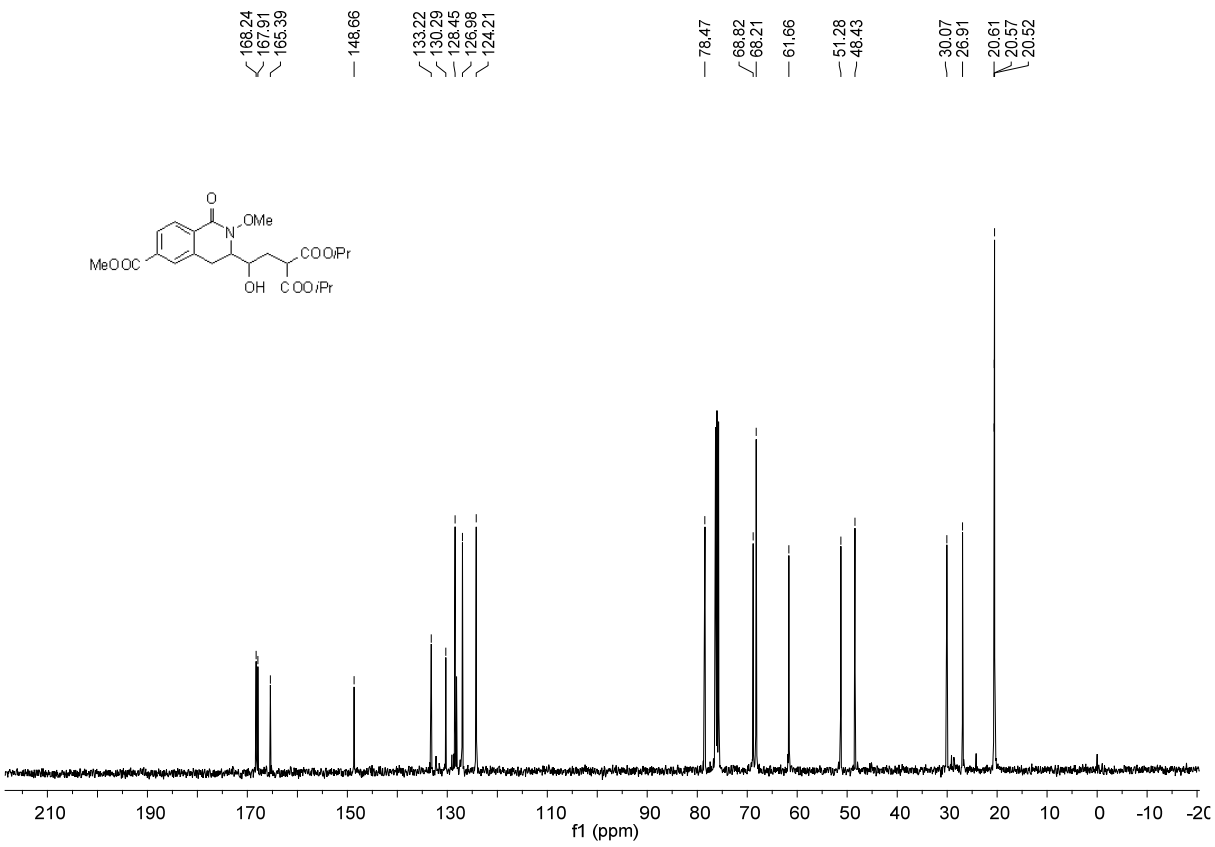

171.4
167.9
138.5
132.1
130.4
130.2
127.8
126.1
124.9
119.3
64.3
58.1
52.3
36.9
35.9
35.6
O
NHOMe
MeOOC
COOMe
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
NHOMe
COOMe
1.00
0.99
5.7
5.6
5.5
5.4
5.3
f1 (ppm)
2.05
4.05
3.4
3.1
2.8
2.5
f1 (ppm)
1.09
1.96
2.03
1.00
0.99
3.06
0.20
2.81
2.05
4.05
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


173.8
168.0
138.9
132.9
130.6
130.4
130.3
129.9
127.7
126.2
64.4
51.5
36.0
33.9
27.8
O
NHOMe
COOMe
f1 (ppm)
OMe
COOMe
COOMe
1.10
2.21
1.01
2.09
2.08
1.00
1.10
2.21
1.02
2.99
5.98
1.01
2.09
2.08


168.3
157.9
140.1
134.7
131.4
126.6
125.2
124.6
103.2
63.0
51.6
49.6
27.4
26.1
O
N
OMe
COOMe
COOMe
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


MeOOC
O
NOMe
COOiPr
OH
COOiPr
f1 (ppm)
f1 (ppm)
f1 (ppm)
f1 (ppm)


168.24
167.91
165.39
148.66
133.22
130.29
128.45
126.98
124.21
78.47
68.82
68.21
61.66
51.28
48.43
30.07
26.91
20.61
20.57
20.52
O
N
OMe
MeOOC
COOiPr
OH
COOiPr
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

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