

Supplementary Material (ESI) for Chemical Communications
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Supporting Information

Iron-Catalyzed Addition of Grignard Reagents to Activated Vinyl Cyclopropanes

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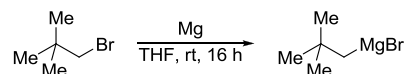
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General Information: All reactions were carried out in flame-dried glassware under an Ar atmosphere. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were purified by distillation from Mg-anthracene. Methylene chloride (CH₂Cl₂) was purified by distillation from P₄O₁₀. Acetonitrile (MeCN) and triethyl amine (Et₃N) were purified by distillation from CaH₂. Toluene (PhMe) was purified by distillation from Na/K. Flash chromatography was performed with Merck silica gel 60 (230-400 mesh). NMR spectra were recorded on Bruker DPX-300, AV-400, and DMX-600 spectrometers in the solvent indicated. Chemical shifts (δ) are given in ppm relative to the residual protio solvent signal. Peak multiplicities are designated by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad and coupling constants are provided in (*J*) Hz. Infrared spectra were recorded on a Nicolet FT-7199 spectrometer, and peaks are given in wavenumbers (ν) cm⁻¹. High resolution mass spectral data was obtained on a Finnigan MAT 95 or Bruker APEX III FT-ICR-MS (7 T magnet). Commercial Grignard reagents were titrated according to the procedure of Knochel.¹ All commercial reagents were used as received unless otherwise noted. Fe(acac)₃ (99.9+) purchased from Aldrich was used as precatalyst throughout this study.

Experimental Procedures for Grignard Reagent Preparation:

Phenylmagnesium chloride: A 50 mL 3-neck round-bottom flask equipped with a reflux condenser and dropping funnel was charged with magnesium turnings (1.00 g, 42.0 mmol). The system was evacuated, flame dried, cooled and backfilled with Ar. The magnesium turnings were stirred vigorously at room temperature for 20 min, a small crystal of I₂ was added, and the turnings were suspended in THF (2 mL). The dropping funnel was charged with a solution of PhCl (3.60 mL, 35.0 mmol) in THF (15 mL), and the solution was added to the magnesium turnings dropwise over 40 min. The funnel was washed with THF (2 x, 2.5 mL) and the washings were added to the reaction mixture. The reaction mixture was maintained at room temperature for an additional 40 min, heated to reflux and maintained for 6 h. The reaction mixture was cooled to room temperature, transferred *via* cannula to a Schlenk frit, and filtered into a flame dried Schlenk flask. Concentration = 2.00 M.

Neopentylmagnesium bromide: A 100 mL 3-neck round-bottom flask equipped with a reflux condenser and dropping funnel was charged with magnesium turnings (0.994 g, 40.9 mmol). The system was evacuated, flame dried, cooled, and backfilled with Ar. The magnesium turnings were stirred vigorously at room temperature

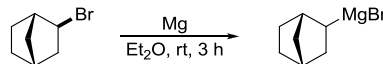


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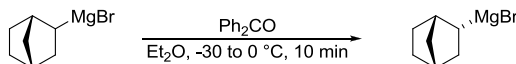
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for 1 h, suspended in THF (10 mL), and a small crystal of I₂ was added. The dropping funnel was charged with a solution of 1-bromo-2,2-dimethylpropane (4.30 mL, 34.1 mmol) in THF (20 mL), and the solution was added dropwise to the magnesium turnings over 1 h. The funnel was washed with THF (2 x, 2mL) and the washings were added to the reaction mixture. The resulting mixture was allowed to stir at room temperature for 16 h, transferred *via* cannula to a Schlenk frit, and filtered into a flame dried Schlenk flask. Concentration = 0.63 M.

2-Norbornylmagnesium bromide: A 100 mL 3-neck round-bottom flask equipped with a dropping funnel was charged with magnesium turnings (0.790 g, 32.5 mmol). The system was evacuated, flame dried, cooled, and backfilled with Ar. The magnesium turnings were stirred vigorously at room temperature overnight, suspended in Et₂O (5 mL), and a small crystal of I₂ was added. The dropping funnel was charged with a solution of *exo*-2-bromonorbornane (3.2 mL, 25 mmol) in Et₂O (10 mL), and the solution was added dropwise to the magnesium turnings over 1 h. The funnel was washed with Et₂O (5 mL) and the washing was added to the reaction mixture. The resulting mixture was maintained at room temperature for 2 h, transferred *via* cannula to a Schlenk frit, and filtered into a flame dried Schlenk flask. Concentration = 0.96 M. The diastereomeric ratio was based on previously reported literature values.²

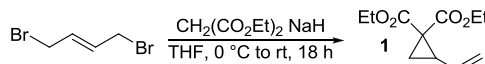


***endo*-2-Norbornylmagnesium bromide:** The Grignard reagent was prepared according to the Johnson-modified procedure of Jensen.² A 25 mL Schlenk tube was charged with benzophenone (0.189 g, 1.04 mmol), the solid was dissolved in Et₂O (2 mL) and the resulting solution was cooled to -30 °C. A second 25 mL Schlenk tube was charged with an ethereal solution 2-norbornylmagnesium bromide (2.00 mL, 1.92 mmol, 0.96 M in Et₂O) and cooled to -30 °C. The benzophenone solution was added rapidly *via* cannula to the Grignard solution resulting in immediate generation of a red color and formation of a white precipitate. The reaction mixture was warmed to 0 °C and maintained for 10 min during which time the color gradually faded to light pink. The mixture was returned to -30 °C and allowed to stand undisturbed for 3 min, after which the diastereomerically enriched Grignard reagent was used immediately in the iron-catalyzed reaction. The diastereomeric ratio was based on previously reported literature values.²

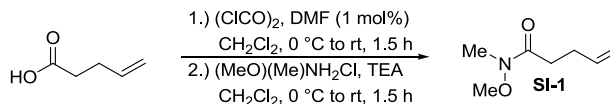


Experimental Procedures and Characterization Data for Vinyl Cyclopropane Starting Materials:

Compound 1: Modified from a procedure by Weedon and coworkers.³ A 3-neck 500 mL round bottom flask equipped with vacuum adapter, dropping funnel, and stir bar was evacuated, flame dried, cooled, and backfilled with Ar. The flask was charged with NaH (2.08 g, 86.9 mmol) and the white solid was suspended in THF (110 mL). The suspension was cooled to 0 °C (external temperature, ice bath) and a solution of diethyl malonate (6.0 mL, 40 mmol) in THF (6 mL) was added dropwise over 1 h. The resulting mixture was maintained at 0 °C for 1 h, and a solution of *trans*-1,4-dibromobut-2-ene (8.45 g, 39.5 mmol) in THF (110 mL) was added dropwise over 1 h. The reaction mixture was warmed to room temperature, maintained for 18 h, and quenched by the addition of H₂O (100 mL). The aqueous phase was extracted with methyl *tert*-butyl ether (3 x, 50 mL), and the combined organic extracts were washed with brine (100 mL), dried over Na₂SO₄, filtered, and concentrated. The crude material was purified by flash chromatography (hexanes/EtOAc 40:1) to afford **1** as a colorless oil (7.20 g, 86% yield). R_f = 0.28 (hexanes/EtOAc 9:1); ¹H NMR (400 MHz, CDCl₃): δ = 5.43 (ddd, *J* = 17.0, 10.0, 8.3 Hz, 1H), 5.28 (dd, *J* = 16.9, 1.2 Hz, 1H), 5.13 (dd, *J* = 10.1, 1.2 Hz, 1H), 4.27-4.11 (m, 4H), 2.56 (q, *J* = 8.3 Hz, 1H), 1.68 (dd, *J* = 7.4, 4.9 Hz, 1H), 1.54 (dd, *J* = 8.8, 4.9 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.26 ppm (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 169.8, 167.5, 133.3, 118.6, 61.7, 61.6, 36.1, 31.2, 20.5, 14.3, 14.2 ppm; IR (film): ν = 2983, 1719, 1369, 1317, 1267, 1195, 1128, 1024, 991, 915, 863 cm⁻¹; HRMS (EI): *m/z*: calcd for C₁₁H₁₆O₄ [M⁺]: 212.1049, found 212.1046.



Compound SI-1: A 2-neck 100 mL round bottom flask equipped with a dropping funnel and bubbler was charged with 4-pentenoic acid (3.00 mL, 30.0mmol). The white solid was dissolved in CH₂Cl₂ (30 mL), and

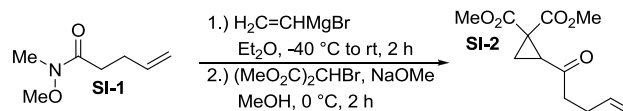


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DMF (0.02 mL, 0.30 mmol) was added. The apparatus was fitted with a vent to a 2 M NaOH solution and the reaction mixture was cooled to 0 °C. The dropping funnel was charged with oxalyl chloride (3.8 mL, 45 mmol) which was added to the stirred solution over 50 min. The reaction mixture was warmed to room temperature, allowed to stir until gas evolution had ceased (1.5 h), and concentrated to afford the crude acid chloride as an orange oil which was used directly without purification.⁴ A 200 mL Schlenk tube was charged with *N,O*-dimethylhydroxylamine hydrochloride (3.80 g, 39.0 mmol) and the white solid was suspended in CH₂Cl₂ (50 mL). Triethylamine (12.5 mL, 90.0 mmol) was added affording a voluminous white precipitate and the reaction mixture was cooled to 0 °C. A solution of the crude 4-pentenoyl chloride in CH₂Cl₂ (20 mL) was added, the flask was washed with CH₂Cl₂ (3 x, 10 mL) and the washings were added to the reaction mixture. The resulting suspension was warmed to room temperature, maintained for 1.5 h, and quenched with H₂O (100 mL). The aqueous phase was extracted with CH₂Cl₂ (3 x, 50 mL), and the combined organic extracts were washed with H₂O (100 mL), saturated aqueous NaHCO₃ (100 mL), and brine (100 mL), dried over Na₂SO₄, filtered, and concentrated. The crude material was purified by Kugelrohr distillation (120 °C, 7 mbar) to afford **SI-1** as a colorless oil (3.32 g, 77%). R_f = 0.15 (hexanes/EtOAc 4:1); ¹H NMR (400 MHz, CDCl₃): δ = 5.91-5.81 (m, 1H), 5.06 (dq, *J* = 17.1, 1.6 Hz, 1H), 4.99 (d, *J* = 10.2 Hz, 1H), 3.68 (s, 3H), 3.17 (s, 3H), 2.52 (t, *J* = 7.5 Hz, 2H), 2.38 ppm (q, *J* = 7.1 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 137.6, 115.3, 61.4, 32.3, 31.4, 28.7 ppm; IR (film): ν = 3077, 2939, 1660, 1463, 1440, 1416, 1383, 1177, 1117, 994, 912 cm⁻¹; HRMS (EI): *m/z*: calcd for C₇H₁₃O₂ [M⁺]: 143.0946, found 143.0947.

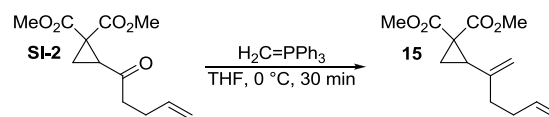
Compound SI-2: A 100 mL Schlenk tube was charged with Weinreb amide **SI-1** (2.14 g, 14.9 mmol). The colorless oil was dissolved in Et₂O (45 mL) and the resulting solution was cooled to -40 °C.



The Schlenk tube was equipped with a dropping

funnel, and the latter was charged with vinylmagnesium bromide (22.3 mL, 22.3 mmol, 1 M THF solution). The Grignard solution was added dropwise over 30 min and the reaction mixture was maintained at -40 °C for an additional 15 min. The reaction mixture was warmed to room temperature and allowed to stir for 2 h, at which point TLC analysis indicated consumption of the Weinreb amide. The reaction mixture was cooled to -15 °C and quenched with saturated aqueous NH₄Cl (100 mL, added dropwise initially). The aqueous phase was extracted with Et₂O (3 x, 40 mL), and the combined organic extracts were washed with brine (100 mL), dried over Na₂SO₄, filtered, and concentrated to afford a yellow oil (1.63 g). Analysis of the crude reaction mixture by ¹H NMR showed a 3.3:1.0 mixture of the desired enone and the amine conjugate addition product.⁵ This material was not purified, but rather used as a mixture in the subsequent step. A 25 mL Schlenk tube was charged with dimethyl 2-bromomalonate⁶ (0.281 g, 1.33 mmol) and the oil was dissolved in MeOH (1.3 mL). The crude enone mixture was added (0.168 g, 1.53 mmol) and the resulting solution was cooled to 0 °C. A solution of NaOMe (0.074 g, 1.40 mmol) in MeOH (1.4 mL) was added dropwise over 1 h, and the resulting mixture maintained at 0 °C for an additional 1 h. The reaction was quenched with H₂O (10 mL) and the aqueous phase was extracted with methyl *tert*-butyl ether (3 x, 5 mL). The combined organic extracts were washed with brine (10 mL), dried over Na₂SO₄, filtered, and concentrated. The crude material was purified by flash chromatography (hexanes/EtOAc 18:1) to afford **SI-2** as a colorless oil (0.0846 g, 26% yield). R_f = 0.32 (hexanes/EtOAc 4:1); ¹H NMR (400 MHz, CDCl₃): δ = 5.84-5.74 (m, 1H), 5.03 (dq, *J* = 17.1, 1.6 Hz, 1H), 4.98 (dq, *J* = 10.2, 1.4 Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 2.83 (dd, *J* = 8.5, 6.8 Hz, 1H), 2.77-2.69 (m, 2H), 2.34 (app. q, *J* = 7.0 Hz, 2H), 1.98 (dd, *J* = 6.8, 4.3 Hz, 1H), 1.62 ppm (dd, *J* = 8.5, 4.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 204.6, 169.5, 166.5, 136.8, 115.6, 53.3, 53.0, 43.7, 38.8, 33.8, 27.5, 20.8 ppm; IR (film): ν = 2955, 1733, 1707, 1436, 1389, 1330, 1271, 1210, 1180, 1129, 1095, 991, 914, 880 cm⁻¹; HRMS (ESI): *m/z*: calcd for C₁₂H₁₆O₅Na [M⁺ + Na]: 263.0890, found 263.0892.

Compound 15: A 25 mL Schlenk tube was charged with Ph₃P=CH₂ (0.123 g, 0.444 mmol). The solid was dissolved in THF (1.5 mL) and the resulting yellow solution was cooled to 0 °C. A solution of **SI-2** (0.089 g, 0.370 mmol) in THF (1.0 mL) was added affording an orange suspension. The reaction mixture was maintained at 0 °C for 30 min, adsorbed



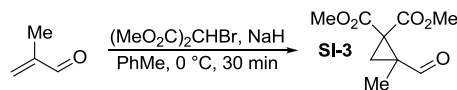
onto silica gel, filtered through a short silica gel plug (hexanes/EtOAc 10:1), and concentrated. The crude material was purified by flash chromatography (hexanes/EtOAc 50:1) to afford **15** as a colorless oil (0.040 g, 45% yield). R_f = 0.57 (hexanes/EtOAc 4:1); ¹H NMR (400 MHz, CDCl₃): δ = 5.84-5.77 (m, 1H), 5.04 (app dt, *J* = 17.2, 1.6 Hz,

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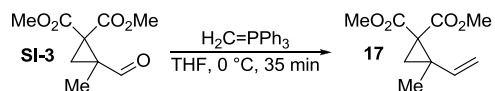
1H), 4.97 (d, $J = 10.6, 1.2$ Hz, 1H), 4.97 (app dt, $J = 10.2, 1.4$ Hz, 1H), 4.88 (s, 1H), 4.75 (s, 1H), 3.75 (s, 3H), 3.66 (s, 3H), 2.53 (t, $J = 8.5$ Hz, 1H), 2.26-2.18 (m, 4H), 1.89 (dd, $J = 8.2, 5.0$ Hz, 1H), 1.48 ppm (dd, $J = 9.0, 5.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 170.6, 167.4, 142.5, 138.1, 115.0, 111.9, 52.9, 52.6, 36.8, 35.9, 33.0, 31.9, 18.5$ ppm; IR (film): $\nu = 2953, 1724, 1642, 1436, 1328, 1277, 1209, 1128, 998, 898$ cm^{-1} ; HRMS (ESI): m/z : calcd for $\text{C}_{13}\text{H}_{18}\text{O}_4\text{Na}$ [$\text{M}^+ + \text{Na}$]: 261.1097, found 261.1098.

Compound SI-3: A 10 mL Schlenk tube was charged with NaH (0.063 g, 2.61 mmol), PhMe (3 mL) was added and the resulting suspension was cooled to 0 °C. A second 10 mL Schlenk tube was charged with dimethyl 2-bromomalonate⁶ (0.500 g, 2.37 mmol).



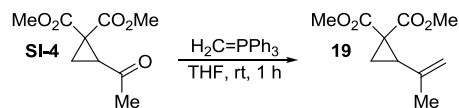
PhMe (1 mL) and methacrolein (0.39 mL, 4.74 mL) were added and the resulting colorless solution was cooled to 0 °C. The latter solution was added *via* canula to the NaH suspension. The second Schlenk tube was washed with PhMe (1 mL), and the washing was added to the reaction mixture. The resulting pale blue suspension was maintained at 0 °C for 30 min and quenched with saturated aqueous NH_4Cl (5 mL, added dropwise initially). The aqueous phase was extracted with methyl *tert*-butyl ether (3 x, 5 mL), and the combined organic extracts were washed with brine (10 mL), dried over Na_2SO_4 , filtered, and concentrated. The crude material was purified by flash chromatography (hexanes/EtOAc 20:1 then 10:1) to afford **SI-3** as a colorless oil (0.0886 g, 19% yield). $R_f = 0.30$ (hexanes/EtOAc 4:1); ^1H NMR (400 MHz, CDCl_3): $\delta = 9.25$ (s, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 2.10 (d, $J = 5.6$ Hz, 1H), 1.89 (d, $J = 5.6$ Hz, 1H), 1.35 ppm (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 198.3, 167.8, 166.9, 53.3, 53.3, 42.0, 38.5, 24.5, 12.8$ ppm; IR (film): $\nu = 2957, 2850, 1727, 1436, 1336, 1319, 1231, 1195, 1111, 1082, 983, 947, 908, 891, 708$ cm^{-1} ; HRMS (ESI): m/z : calcd for $\text{C}_9\text{H}_{12}\text{O}_5\text{Na}$ [$\text{M}^+ + \text{Na}$]: 223.0577, found 223.0576.

Compound 17: A 10 mL Schlenk tube was charged with $\text{Ph}_3\text{P}=\text{CH}_2$ (0.074 g, 0.267 mmol), the yellow solid was dissolved in THF (0.5 mL) and the resulting solution was cooled to 0 °C. A second 10 mL Schlenk tube was charged with **SI-3** and the colorless oil was dissolved in THF (0.25 mL). The latter solution was added dropwise to the cooled ylide solution,



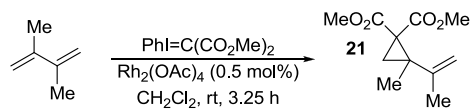
the Schlenk tube was washed with THF (0.25 mL) and the washing was added to the reaction mixture. The resulting yellow-orange suspension was maintained at 0 °C for 35 min, diluted with CH_2Cl_2 (5 mL), adsorbed onto silica gel, and filtered through a short silica gel plug (hexanes/EtOAc 4:1, 25 mL). The filtrate was concentrated and the crude material purified by flash chromatography (hexanes/EtOAc 40:1) to afford **17** as a colorless oil (0.0298 g, 42% yield). $R_f = 0.49$ (hexanes/EtOAc 4:1); ^1H NMR (400 MHz, CDCl_3): $\delta = 5.80$ (dd, $J = 17.2, 10.6$ Hz, 1H), 5.17 (dd, $J = 17.1, 1.0$ Hz, 1H), 5.13 (dd, $J = 10.6, 1.0$ Hz, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 1.80 (d, $J = 5.3$ Hz, 1H), 1.63 (d, $J = 5.3$ Hz, 1H), 1.34 ppm (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 168.6, 168.5, 138.4, 115.8, 52.7, 40.9, 34.1, 26.3, 18.0$ ppm; IR (film): $\nu = 3093, 2954, 2845, 1724, 1636, 1435, 1385, 1298, 1232, 1193, 1109, 1075, 990, 914, 894, 872, 784$ cm^{-1} ; HRMS (EI): m/z : calcd for $\text{C}_{10}\text{H}_{14}\text{O}_4$ [M^+]: 198.0892, found 198.0890.

Compound 19: A 25 mL Schlenk tube was charged with $\text{Ph}_3\text{P}=\text{CH}_2$ (0.464 g, 1.68 mmol) and the yellow solid was dissolved in THF (3.0 mL). A solution of ketone **SI-4**⁷ (0.258 g, 1.29 mmol) in THF (1.0 mL) was added dropwise affording an orange suspension. The reaction mixture was maintained at room temperature for 1 h, adsorbed onto silica gel, and purified by flash chromatography



(hexanes/EtOAc 40:1) to afford **19** as a colorless oil (0.134 g, 52% yield). $R_f = 0.45$ (hexanes/EtOAc 4:1); ^1H NMR (400 MHz, CDCl_3): $\delta = 4.86$ (br s, 1H), 4.71 (s, 1H), 3.75 (s, 3H), 3.68 (s, 3H), 2.49 (t, $J = 8.5$ Hz, 1H), 1.86 (dd, $J = 8.0, 5.0$ Hz, 1H), 1.79 (s, 3H), 1.47 ppm (dd, $J = 8.8, 5.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 170.7, 167.5, 139.2, 112.9, 52.9, 52.6, 36.4, 34.0, 22.8, 18.6$ ppm; IR (film): $\nu = 2954, 1724, 1436, 1328, 1277, 1207, 1127, 895$ cm^{-1} ; HRMS (ESI): m/z : calcd for $\text{C}_{10}\text{H}_{14}\text{O}_4\text{Na}$ [$\text{M}^+ + \text{Na}$]: 221.0784, found 221.0783.

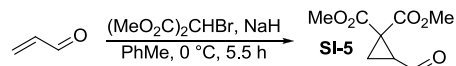
Compound 21: Modified from a procedure by Hadjirapoglou and coworkers.⁸ A 25 mL Schlenk tube was charged with 2,3-dimethyl-1,3-butadiene (1.30 mL, 11.2 mmol) and the colorless oil dissolved in CH_2Cl_2 (7.5 mL). Rhodium(II) acetate dimer (3.3 mg, 7.5 μmol) was added affording a pale green suspension. Bis(methoxy)(phenyliodinio)methanide⁹ (0.501 g, 1.50 mmol) was added



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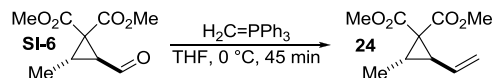
in small portions over 45 min and the resulting suspension was maintained at room temperature for an additional 2.5 h. The reaction mixture was filtered through a silica gel plug (CH₂Cl₂) and the filtrate was concentrated. The crude material was purified by flash chromatography (hexanes/EtOAc 40:1) to afford **21** as a colorless oil (0.205 g, 64% yield). *R*_f = 0.29 (hexanes/EtOAc 9:1); ¹H NMR (400 MHz, CDCl₃): δ = 4.87 (quintet, *J* = 1.4 Hz, 1H), 4.84 (br s, 1H), 3.75 (s, 3H), 3.65 (s, 3H), 1.91 (d, *J* = 5.2 Hz, 1H), 1.76 (s, 3H), 1.49 (d, *J* = 5.1 Hz, 1H), 1.31 ppm (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 169.0, 168.5, 144.4, 113.4, 52.6, 52.5, 40.2, 39.0, 25.5, 20.9, 20.5 ppm; IR (film): ν = 2953, 1724, 1434, 1266, 1230, 1109, 895 cm⁻¹; HRMS (ESI): *m/z*: calcd for C₁₁H₁₆O₄Na [M⁺ + Na]: 235.0941, found 235.0940.

Compound SI-5: A 25 mL Schlenk tube was charged with NaH (0.0607 g, 2.53 mmol) and the white solid was suspended in PhMe (6.3 mL). Acrolein (0.28 mL, 4.22 mmol) was added and the resulting



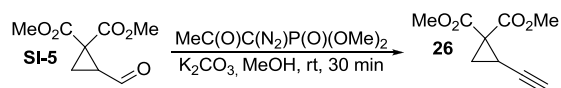
suspension was cooled to 0 °C. A second 25 mL Schlenk tube was charged with dimethyl 2-bromomalonate⁶ (0.445 g, 2.11 mmol) and the oil was dissolved in PhMe (5.0 mL). The malonate solution was transferred to the cooled NaH suspension, the Schlenk flask was washed with PhMe (1.3 mL) and the washing was added to the reaction mixture. The resulting mixture was warmed to room temperature and left to stir. Additional acrolein was added after 3 h (4 equiv.) and again after 5 h (4 equiv.). After 5.5 h the reaction was quenched with saturated aqueous NH₄Cl (15 mL) and the aqueous phase was extracted with methyl *tert*-butyl ether (3 x, 5 mL). The combined organic extracts were washed with brine (20 mL), dried over Na₂SO₄, filtered, and concentrated. The crude material was purified by flash chromatography (hexanes/EtOAc 10:1) to afford **SI-5** as a colorless oil (0.188 g, 48% yield). *R*_f = 0.19 (hexanes/EtOAc 4:1); ¹H NMR (400 MHz, CDCl₃): δ = 9.35 (d, *J* = 4.3 Hz, 1H), 3.77 (s, 6H), 2.76 (ddd, *J* = 8.9, 6.9, 4.2 Hz, 1H), 2.08 (dd, *J* = 6.9, 5.0 Hz, 1H), 1.82 ppm (dd, *J* = 8.7, 5.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 196.4, 168.5, 166.5, 53.5, 53.3, 37.6, 34.9, 19.7 ppm; IR (film): ν = 2958, 2851, 1729, 1711, 1437, 1327, 1264, 1208, 1180, 1160, 1127, 1015, 988, 944, 897, 879 cm⁻¹; HRMS (CI): *m/z*: calcd for C₈H₁₁O₅ [M⁺ + H]: 187.0607, found 187.0606.

Compound 24: A 25 mL Schlenk tube was charged with Ph₃P=CH₂ (0.683 g, 2.47 mmol). The solid was dissolved in THF (7.0 mL) and the resulting yellow solution was cooled to 0 °C. A solution of aldehyde **SI-6**⁷ (0.430 g, 2.15 mmol) in THF (1.0 mL) was added



dropwise affording an orange suspension. The reaction mixture was maintained at 0 °C for 45 min, adsorbed onto silica gel, and purified by flash chromatography (hexanes/EtOAc 40:1) to afford **24** as a colorless oil (0.314 g, 74% yield). *R*_f = 0.39 (hexanes/EtOAc 9:1); ¹H NMR (400 MHz, CDCl₃): δ = 5.45 (ddd, *J* = 17.1, 10.1, 8.6 Hz, 1H), 5.27 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.09 (dd, *J* = 10.1, 1.5 Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 2.40 (t, *J* = 8.1 Hz, 1H), 2.09 (quintet, *J* = 6.7 Hz, 1H), 1.13 ppm (d, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 168.5, 168.3, 133.2, 118.3, 52.7, 42.0, 37.1, 27.2, 12.4 ppm; IR (film): ν = 2955, 1721, 1436, 1290, 1208, 1139, 1065, 915, 788 cm⁻¹; HRMS (ESI): *m/z*: calcd for C₁₀H₁₄O₄ [M⁺]: 198.0892, found 198.0890.

Compound 26: Prepared by the method of Christie and coworkers.¹⁰ A 25 mL Schlenk tube was charged with aldehyde **SI-5** (0.174 g, 0.935 mmol). The oil was dissolved in MeOH (2.7 mL) and K₂CO₃ (0.258 g, 1.87 mmol) was

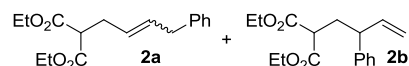


added. To the resulting mixture was added the Bestmann-Ohira reagent¹¹ (0.18 mL, 1.22 mmol) affording a bright yellow suspension. The reaction mixture was maintained at room temperature for 30 min, quenched with saturated aqueous NaHCO₃ (5 mL) and diluted with H₂O (5 mL). The aqueous phase was extracted with methyl *tert*-butyl ether (3 x, 5 mL) and the combined organic extracts were washed with brine (15 mL), dried over Na₂SO₄, filtered, and concentrated. The crude material was purified by flash chromatography (hexanes/EtOAc 20:1) to afford **26** as a colorless oil (0.0591 g, 35% yield). *R*_f = 0.41 (hexanes/EtOAc 4:1); ¹H NMR (400 MHz, CDCl₃): δ = 3.81 (s, 3H), 3.75 (s, 3H), 2.46 (ddd, *J* = 9.3, 7.2, 2.1 Hz, 1H), 1.97 (d, *J* = 2.3 Hz, 1H), 1.86 (dd, *J* = 7.1, 4.8 Hz, 1H), 1.58 ppm (dd, *J* = 9.1, 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 169.0, 166.8, 79.8, 68.8, 53.2, 53.0, 36.0, 22.1, 16.5 ppm; IR (film): ν = 3286, 3007, 2956, 1725, 1437, 1361, 1330, 1275, 1209, 1182, 1127, 994, 957, 941, 898, 880, 777, 704 cm⁻¹; HRMS (EI): *m/z*: calcd for C₉H₁₀O₄ [M⁺]: 182.0579, found 182.0577.

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Experimental Procedures for Iron-Catalyzed Addition and Product Characterization Data:

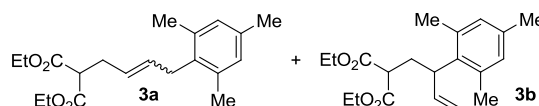
General Procedure for Iron-Catalyzed Addition Reaction: A 10 mL Schlenk tube was charged with the vinyl cyclopropane substrate (1 equiv.) and the oil was dissolved in PhMe (0.1 M). Iron(III) acetylacetonate (10 mol%) was added and the homogeneous red solution was cooled to -30 °C. A solution of the Grignard reagent (1.5 equiv) was added dropwise affording a dark brown / black solution. The reaction mixture was maintained at -30 °C for 30 min (unless indicated otherwise), at which point the starting material was completely consumed by GC or TLC analysis. The reaction mixture was diluted with methyl *tert*-butyl ether (5 mL), adsorbed onto silica gel, and the resulting slurry concentrated to dryness. The silica gel was transferred to a small column, washed (hexanes/EtOAc 5:1, 60 mL), and the washing concentrated. The regio- and stereoselectivity of the reaction was determined by ¹H NMR analysis of the crude reaction product. Alkene stereochemistry was assigned based on the alkene C-H coupling constant where appropriate, and a comparison of the ¹³C chemical shifts for the allylic carbon atoms of the two isomers. The material was purified by flash chromatography as indicated below.

Compound 2a,b: Prepared according to the general procedure. The crude material was purified by flash chromatography (hexanes/EtOAc 60:1) to afford **2a,b** as a colorless oil (0.0569 g, 75% combined yield, 1.5:1.0 **2a:2b**, 5.7:1.0 *E:Z*). R_f = 0.34 (hexanes/EtOAc 9:1); ¹H NMR (400 MHz, CDCl₃, signals for (*Z*)-**2a** where distinguishable are marked*, signals for **2b** where distinguishable are marked*): δ = 7.33-7.13 (m, 5H), 5.93** (ddd, *J* = 17.5, 9.7, 7.8 Hz, 1H), 5.69 (dt, *J* = 15.0, 6.8 Hz, 1H), 5.48 (dt, *J* = 15.1, 7.0 Hz, 1H), 5.09** (d, *J* = 11.4 Hz, 1H), 5.08** (d, *J* = 16.1 Hz, 1H), 4.22-4.11 (m, 4H), 3.43 (t, *J* = 7.6 Hz, 1H), 3.31 (t, *J* = 6.2 Hz, 2H), 3.33-3.28** (m, 2H), 2.77* (t, *J* = 7.1 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.31** (td, *J* = 7.6, 2.5 Hz, 2H), 1.29-1.22 ppm (m, 6H); ¹³C NMR (100 MHz, CDCl₃, signals for (*Z*)-**2a** are not included, signals for **2b** where distinguishable are marked*): δ = 169.6*, 169.5*, 169.1, 142.8*, 140.7, 140.4*, 132.5, 128.8, 128.6, 128.5*, 127.7, 127.0*, 126.8, 126.1*, 115.5*, 61.5, 52.3, 50.2*, 47.7*, 39.0, 34.3*, 31.9, 14.2 ppm; IR (film) ν = 2981, 1729, 1369, 1226, 1148, 1095, 1029, 970, 699 cm⁻¹; HRMS (ESI): *m/z*: calcd for C₁₇H₂₂O₄Na [M⁺ + Na]: 313.1410, found 313.1414.

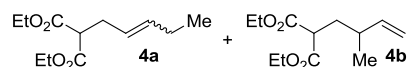


Compound 3a,b: Prepared according to the general procedure.

The crude material was purified by flash chromatography (hexanes/EtOAc 70:1) to afford **3a** and **3b** as colorless oils (**3a**: 0.0244 g, 30%; **3b**: 0.0291 g, 36%) and a mixed sample (0.0138 g, 17%). Characterization data for **3b**. R_f = 0.39 (hexanes/EtOAc 9:1); ¹H NMR (400 MHz, CDCl₃): δ = 6.80 (s, 2H), 6.06 (ddd, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.06 (dt, *J* = 10.3, 1.8 Hz, 1H), 4.97 (dt, *J* = 17.3, 1.7 Hz, 1H), 4.24-4.13 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.90-3.84 (m, 1H), 3.23 (dd, *J* = 7.9, 6.7 Hz, 1H), 2.54-2.38 (m, 2H), 2.28 (s, 6H), 2.23 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.22 ppm (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 169.7, 169.6, 139.4, 136.9, 135.9, 135.2, 130.2 (br), 115.0, 61.5, 50.6, 41.8, 31.6, 21.4, 20.8, 14.2, 14.1 ppm; IR (film): ν = 2979, 1748, 1729, 1633, 1611, 1447, 1369, 1148, 1027, 914, 851 cm⁻¹; HRMS (ESI): *m/z*: calcd for C₂₀H₂₈O₄Na [M⁺ + Na]: 355.1880, found 355.1883. Characterization data for **3a**. R_f = 0.35 (hexanes/EtOAc 9:1); ¹H NMR (400 MHz, CDCl₃, signals for (*Z*)-**3a** where distinguishable are marked*): δ = 6.84* (s, 2H), 6.83 (s, 2H), 5.60 (dt, *J* = 15.2, 5.8 Hz, 1H), 5.40-5.31* (m, 2H), 5.24 (dt, *J* = 14.8, 7.2 Hz, 1H), 4.23* (q, *J* = 7.2 Hz, 4H), 4.19-4.08 (m, 4H), 3.43* (t, *J* = 7.6 Hz, 1H), 3.38* (d, *J* = 4.2 Hz, 2H), 3.32 (t, *J* = 7.6 Hz, 1H), 3.28 (d, *J* = 5.6 Hz, 2H), 2.82* (t, *J* = 6.3 Hz, 2H), 2.82 (t, *J* = 6.3 Hz, 2H), 2.26* (s, 9H), 2.25 (s, 3H), 2.23 (s, 6H), 1.29 (t, *J* = 7.1 Hz, 6H), 1.23 ppm (t, *J* = 7.1 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃, signals for (*Z*)-**3a** where distinguishable are marked*): δ = 169.2*, 169.1, 136.5, 136.3*, 135.5*, 135.4, 134.4*, 133.4, 130.8*, 130.7, 129.0*, 128.9, 125.8, 125.2*, 61.6*, 61.4, 52.4, 52.0*, 32.2, 31.9, 27.8*, 27.1*, 20.9, 20.1*, 19.8, 14.2*, 14.2 ppm; IR (film): ν = 2979, 1732, 1613, 1578, 1445, 1224, 1148, 1032, 970, 851 cm⁻¹; HRMS (ESI): *m/z*: calcd for C₁₅H₂₆O₄Na [M⁺ + Na]: 355.1880, found 355.1880.



Compound 4a,b: Prepared according to the general procedure. The crude material was purified by flash chromatography (hexanes/EtOAc 70:1) to afford **4a,b** as a colorless oil (0.0517 g, 79% combined yield, 4.6:1.0 **4a:4b**, 4.4:1.0 *E:Z*). R_f = 0.38 (hexanes/EtOAc 9:1); ¹H NMR (400 MHz, CDCl₃, signals for (*Z*)-**4a** where distinguishable are marked*, signals for **4b** where distinguishable are marked*): δ = 5.54 (dt, *J* = 14.6, 6.8 Hz, 1H), 5.48-5.41* (m,

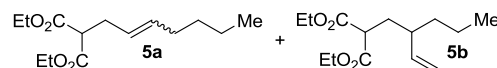


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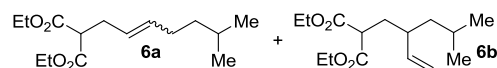
1H), 5.33 (dt, $J = 15.2, 6.9$ Hz, 1H), 5.28-5.22* (m, 1H), 4.96** (d, $J = 17.4$ Hz, 1H), 4.95** (d, $J = 10.3$ Hz, 1H), 4.17 (q, $J = 7.1$ Hz, 4H), 3.34 (t, $J = 7.6$ Hz, 1H), 2.62* (t, $J = 7.5$ Hz, 2H), 2.55 (t, $J = 7.2$ Hz, 2H), 2.14-2.08** (m, 1H), 2.05* (q, $J = 7.3$ Hz, 2H), 1.96 (q, $J = 7.4$ Hz, 2H), 1.80** (ddd, $J = 13.9, 9.2, 5.9$ Hz, 1H), 1.24 (t, $J = 7.1$ Hz, 6H), 1.01** (d, $J = 6.6$ Hz, 3H), 0.93* (t, $J = 7.3$ Hz, 3H), 0.92 ppm (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3 , signals for (*Z*)-**4a** where distinguishable are marked*, signals for **4b** where distinguishable are marked**): $\delta = 169.8^*$, 169.7^* , 169.2^* , 169.2^* , 142.8^* , 135.5^* , 134.8^* , 124.4^* , 124.1^* , 114.5^* , 61.3^* , 52.4^* , 52.2^* , 50.3^* , 36.4^* , 35.3^* , 31.9^* , 26.7^* , 25.6^* , 20.6^* , 20.6^* , 14.2^* , 13.7 ppm; IR (film) $\nu = 2965, 1731, 1463, 1446, 1369, 1224, 1149, 1033, 968, 858$ cm^{-1} ; HRMS (ESI): m/z : calcd for $\text{C}_{12}\text{H}_{20}\text{O}_4\text{Na}$ [$\text{M}^+ + \text{Na}$]: 251.1254, found 251.1256.

Compound 5a,b: Prepared according to the general procedure. The crude material was purified by flash chromatography (hexanes/EtOAc 75:1) to afford **5a,b** as a colorless oil (0.0334 g, 48% combined yield, 9.2:1.0 **5a:5b**, 5.9:1.0 *E:Z*). $R_f = 0.41$

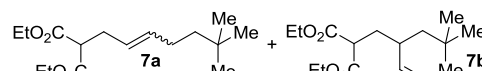


(hexanes/EtOAc 9:1); ^1H NMR (400 MHz, CDCl_3 , only signals for (*E*)-**5a** are provided): $\delta = 5.51$ (dt, $J = 15.0, 6.8$ Hz, 1H), 5.34 (dt, $J = 15.2, 6.9$ Hz, 1H), 4.17 (q, $J = 7.1$ Hz, 2H), 4.17 (q, $J = 7.1$ Hz, 2H), 3.35 (t, $J = 7.7$ Hz, 1H), 2.55 (t, $J = 7.2$ Hz, 2H), 1.95 (q, $J = 6.6$ Hz, 2H), 1.33-1.22 (m, 4H), 1.25 (t, $J = 7.1$ Hz, 6H), 0.86 ppm (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3 , signals for (*Z*)-**5a** where distinguishable are marked*, signals for **5b** where distinguishable are marked**), signals which were not conclusively assigned to either minor component are marked***): $\delta = 170.0^*$, 169.7^* , 169.3^* , 169.2^* , 141.5^* , 134.1^* , 133.3^* , 125.4^* , 124.7^* , 116.2^* , 61.5^* , 61.4^* , 61.3^* , 52.5^* , 52.2^* , 50.3^* , 42.3^* , 37.5^* , 33.8^* , 32.3^* , 32.0^* , 31.8^* , 31.6^* , 27.1^* , 26.8^* , 22.5^* , 22.2^* , 20.2^* , 14.2^* , 14.1^* , 14.0 ppm; IR (film): $\nu = 2959, 2929, 2874, 1729, 1465, 1446, 1369, 1333, 1262, 1226, 1173, 1150, 1096, 1034, 970, 859$ cm^{-1} ; HRMS (ESI): m/z : calcd for $\text{C}_{14}\text{H}_{24}\text{O}_4\text{Na}$ [$\text{M}^+ + \text{Na}$]: 279.1567, found 279.1564.

Compound 6a,b: Prepared according to the general procedure. The crude material was purified by flash chromatography (hexanes/EtOAc 70:1) to afford **6a,b** as a colorless oil (0.0457 g, 82% combined yield, 13:1 **6a:6b**, 8:1 *E:Z*). $R_f = 0.48$ (hexanes/EtOAc 9:1); ^1H NMR (400 MHz, CDCl_3 , only signals for the (*E*)-**6a** are included): $\delta = 5.50$ (dt, $J = 14.9, 6.8$ Hz, 1H), 5.34 (dt, $J = 15.1, 6.9$ Hz), 4.17 (q, $J = 7.2$ Hz, 2H), 4.17 (q, $J = 7.1$ Hz, 2H), 3.35 (t, $J = 7.6$ Hz, 1H), 2.55 (t, $J = 7.2$ Hz, 2H), 1.96 (q, $J = 7.4$ Hz, 2H), 1.50 (septet, $J = 6.7$ Hz, 1H), 1.25 (t, $J = 7.1$ Hz, 6H), 1.19 (app. q, $J = 7.5$ Hz, 2H), 0.84 ppm (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3 , signals for the (*Z*)-**6a** where distinguishable are marked*, signals for **6b** where distinguishable are marked**), signals which were not assigned to either minor component are marked***): $\delta = 169.9^*$, 169.6^* , 169.2^* , 169.2^* , 141.6^* , 134.2^* , 133.4^* , 125.2^* , 124.6^* , 116.0^* , 61.5^* , 61.4^* , 61.3^* , 52.5^* , 52.3^* , 50.2^* , 44.8^* , 40.4^* , 38.9^* , 38.6^* , 34.0^* , 32.0^* , 30.4^* , 27.8^* , 27.5^* , 26.8^* , 25.4^* , 25.3^* , 23.4^* , 22.6^* , 22.6^* , 21.9^* , 14.2 ppm; IR (film): $\nu = 2962, 1732, 1465, 1368, 1227, 1150, 1032, 971, 859$ cm^{-1} ; HRMS (ESI): m/z : calcd for $\text{C}_{15}\text{H}_{26}\text{O}_4\text{Na}$ [$\text{M}^+ + \text{Na}$]: 293.1723, found 293.1723.

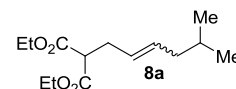


Compound 7a,b: Prepared according to the general procedure. The crude material was purified by flash chromatography (hexanes/EtOAc 75:1) to afford **7a,b** as a colorless oil (0.0532 g, 83% combined yield, 8.6:1.0 **7a:7b**, 8.7:1.0 *E:Z*). $R_f = 0.45$



(hexanes/EtOAc 9:1); ^1H NMR (400 MHz, CDCl_3 , only signals for (*E*)-**7a** are included): $\delta = 5.51$ (dt, $J = 14.6, 6.8$ Hz, 1H), 5.34 (dt, $J = 15.0, 7.0$ Hz), 4.17 (q, $J = 7.1$ Hz, 4H), 3.34 (t, $J = 7.6$ Hz, 1H), 2.55 (t, $J = 7.2$ Hz, 2H), 1.95-1.88 (m, 2H), 1.25 (t, $J = 7.1$ Hz, 6H), 1.21-1.16 (m, 2H), 0.85 ppm (s, 9H); ^{13}C NMR (100 MHz, CDCl_3 , signals for (*Z*)-**7a** where distinguishable are marked*, signals for **7b** where distinguishable are marked**), signals which were not conclusively assigned to either minor component are marked***): $\delta = 169.9^*$, 169.6^* , 169.2^* , 169.2^* , 143.5^* , 134.8^* , 133.9^* , 124.9^* , 124.3^* , 115.4^* , 61.4^* , 61.4^* , 61.3^* , 52.4^* , 52.3^* , 50.1^* , 49.5^* , 44.0^* , 43.9^* , 39.3^* , 35.7^* , 32.0^* , 31.4^* , 30.5^* , 30.4^* , 30.2^* , 29.4^* , 27.9^* , 26.7^* , 22.8^* , 14.3^* , 14.2^* ppm; IR (film): $\nu = 2954, 2909, 2868, 1732, 1467, 1446, 1393, 1366, 1261, 1225, 1175, 1144, 1096, 1035, 970, 858$ cm^{-1} ; HRMS (ESI): m/z : calcd for $\text{C}_{16}\text{H}_{28}\text{O}_4\text{Na}$ [$\text{M}^+ + \text{Na}$]: 307.1880, found 307.1879.

Compound 8a: Prepared according to the general procedure. The crude material was purified by flash chromatography (hexanes/EtOAc 70:1) to afford **8a** as a colorless oil

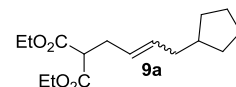


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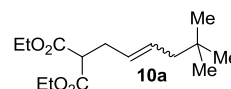
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(0.0359 g, 79% combined yield, 5.9:1.0 *E:Z*). $R_f = 0.39$ (hexanes/EtOAc 9:1); $^1\text{H NMR}$ (400 MHz, CDCl_3 , only signals for (*E*)-**8a** are included): $\delta = 5.50$ (dt, $J = 15.0, 7.0$ Hz, 1H), 5.34 (dt, $J = 15.0, 6.9$ Hz, 1H), 4.18 (q, $J = 7.1$ Hz, 2H), 4.17 (q, $J = 7.1$ Hz, 2H), 3.36 (t, $J = 7.6$ Hz, 1H), 2.57 (t, $J = 7.2$ Hz, 2H), 1.84 (t, $J = 7.0$ Hz, 2H), 1.55 (nonet, $J = 6.9$ Hz, 1H), 1.25 (t, $J = 7.1$ Hz, 6H), 0.84 ppm (d, $J = 6.8$ Hz, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , signals for (*Z*)-**8a** where distinguishable are marked*): $\delta = 169.3^*$, 169.2, 132.8, 132.0*, 126.5, 125.4*, 61.5*, 61.4, 52.5, 52.2*, 41.9, 36.4*, 32.0, 28.7*, 28.4, 26.9*, 22.4*, 22.3, 14.2 ppm; IR (film): $\nu = 2957, 1729, 1466, 1368, 1220, 1151, 1035, 970, 858$ cm^{-1} ; HRMS (ESI): m/z : calcd for $\text{C}_{14}\text{H}_{24}\text{O}_4\text{Na}$ [$\text{M}^+ + \text{Na}$]: 279.1567, found 279.1565.

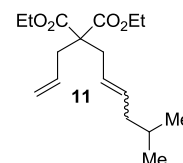
Compound 9a: Prepared according to the general procedure. The crude material was purified by flash chromatography (hexanes/EtOAc 70:1) to afford **9a** as a colorless oil (0.0330 g, 61% combined yield, 6.4:1.0 *E:Z*). $R_f = 0.43$ (hexanes/EtOAc 9:1); $^1\text{H NMR}$ (400 MHz, CDCl_3 , only signals for (*E*)-**9a** are included): $\delta = 5.52$ (dt, $J = 15.1, 7.0$ Hz, 1H), 5.34 (dt, $J = 15.1, 6.9$ Hz, 1H), 4.18 (q, $J = 7.2$ Hz, 2H), 4.17 (q, $J = 7.1$ Hz, 2H), 3.36 (t, $J = 7.6$ Hz, 1H), 2.56 (t, $J = 6.9$ Hz, 2H), 1.96 (t, $J = 7.0$ Hz, 2H), 1.78 (septet, $J = 7.4$ Hz, 1H), 1.71-1.61 (m, 2H), 1.61-1.44 (m, 4H), 1.25 (t, $J = 7.1$ Hz, 6H), 1.12-1.04 ppm (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , signals for (*Z*)-**9a** where distinguishable are marked*): $\delta = 169.3^*$, 169.2, 133.4, 132.6*, 125.8, 124.8*, 61.5*, 61.4, 52.5, 52.3*, 40.3*, 39.9, 39.0, 33.4*, 32.4*, 32.3, 32.0, 26.9*, 25.2, 14.2 ppm; IR (film): $\nu = 2929, 2868, 1729, 1446, 1368, 1226, 1150, 1096, 1032, 970, 858$ cm^{-1} ; HRMS (ESI): m/z : calcd for $\text{C}_{16}\text{H}_{26}\text{O}_4\text{Na}$ [$\text{M}^+ + \text{Na}$]: 305.1723, found 305.1724.



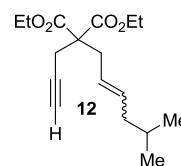
Compound 10a: Prepared according to the general procedure. The crude material was purified by flash chromatography (hexanes/EtOAc 50:1) to **10a** as a colorless oil (0.0452 g, 78% combined yield, 8.2:1.0 *E:Z*). $R_f = 0.42$ (hexanes/EtOAc 9:1); $^1\text{H NMR}$ (400 MHz, CDCl_3 , only signals for (*E*)-**10a** are included): $\delta = 5.54$ (dtt, $J = 15.0, 7.4, 1.1$ Hz, 1H), 5.33 (dt, $J = 15.0, 6.9$ Hz, 1H), 4.17 (q, $J = 7.1$ Hz, 2H), 4.17 (q, $J = 7.1$ Hz, 2H), 3.37 (t, $J = 7.6$ Hz, 1H), 2.59 (t, $J = 7.3$ Hz, 2H), 1.83 (d, $J = 7.3$ Hz, 2H), 1.25 (t, $J = 7.1$ Hz, 6H), 0.83 ppm (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , signals for (*Z*)-**10a** where distinguishable are marked*): $\delta = 169.2^*$, 169.2, 131.0, 130.1*, 127.6, 126.2*, 61.5*, 61.4, 52.5, 52.2*, 47.1, 41.2*, 32.1, 30.9, 29.3*, 29.3, 26.8*, 14.2 ppm; IR (film): $\nu = 2955, 2905, 1732, 1446, 1366, 1225, 1176, 1144, 1096, 1033, 971, 858$ cm^{-1} ; HRMS (ESI): m/z : calcd for $\text{C}_{15}\text{H}_{26}\text{O}_4\text{Na}$ [$\text{M}^+ + \text{Na}$]: 293.1723, found 293.1721.



Compound 11: The iron-catalyzed reaction was carried out as described in the general procedure; upon consumption of the starting vinyl cyclopropane (30 min), DMPU (16.4 equiv.) and allyl bromide (3 equiv.) were added and the reaction mixture was warmed to room temperature. The resulting mixture was maintained at room temperature for 23 h and quenched with aqueous HCl (5 mL, 0.5 M). The aqueous phase was extracted with methyl *tert*-butyl ether (3 x, 5 mL), washed with H_2O (2 x, 10 mL) and brine (10 mL), dried over Na_2SO_4 , filtered, and concentrated. The crude material was purified by flash chromatography (hexanes/EtOAc 70:1) to afford **11** as a colorless oil (0.0437 g, 72%, 6.0:1.0 *E:Z*). $R_f = 0.48$ (hexanes/EtOAc 9:1); $^1\text{H NMR}$ (400 MHz, CDCl_3 , only signals for the (*E*)-**11** are provided): $\delta = 5.70$ -5.60 (m, 1H), 5.48 (dt, $J = 15.0, 7.2$ Hz, 1H), 5.21 (dt, $J = 15.0, 7.5$ Hz, 1H), 5.11-5.06 (m, 2H), 4.15 (q, $J = 7.1$ Hz, 4H), 2.62 (d, $J = 7.4$ Hz, 2H), 2.58 (d, $J = 7.4$ Hz, 2H), 1.85 (t, $J = 6.9$ Hz, 2H), 1.56 (sep., $J = 6.7$ Hz, 1H), 1.23 (t, $J = 7.1$ Hz, 6H), 0.85 ppm (d, $J = 6.7$ Hz, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , signals for (*Z*)-**11** where distinguishable are marked*): $\delta = 171.1^*$, 171.0, 134.3, 132.8*, 132.7, 124.6, 123.3*, 119.1*, 119.0, 61.3*, 61.2, 57.7, 57.5*, 42.1, 36.9*, 36.8, 36.6*, 35.7, 30.2*, 28.7*, 28.5, 22.5*, 22.4, 14.3, 14.2* ppm; IR (film): $\nu = 2956, 1729, 1465, 144, 1282, 1205, 1185, 1141, 971, 919, 858$ cm^{-1} ; HRMS (ESI): m/z : calcd for $\text{C}_{17}\text{H}_{28}\text{O}_4\text{Na}$ [$\text{M}^+ + \text{Na}$]: 319.1880, found 319.1876.



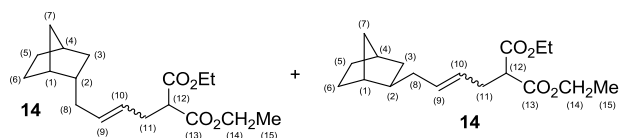
Compound 12: The iron-catalyzed reaction was carried out as described in the general procedure; upon consumption of the starting vinyl cyclopropane (30 min), DMPU (16.4 equiv.) and propargyl bromide (3 equiv.) were added and the reaction mixture was warmed to room temperature. The resulting mixture was maintained at room temperature for 23 h and quenched with aqueous HCl (5 mL, 0.5 M). The aqueous phase was extracted with methyl *tert*-butyl ether (3 x, 5 mL), washed with H_2O (2 x, 10 mL) and brine (10 mL), dried over Na_2SO_4 , filtered, and



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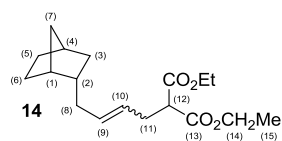
concentrated. The crude material was purified by flash chromatography (hexanes/EtOAc 70:1) to afford **12** as a colorless oil (0.0437 g, 78%, 5.4:1.0 *E:Z*). $R_f = 0.45$ (hexanes/EtOAc 9:1); $^1\text{H NMR}$ (400 MHz, CDCl_3 , only signals for (*E*)-**12** are provided): $\delta = 5.56$ (dt, $J = 14.7, 7.4$ Hz, 1H), 5.19 (dt, $J = 15.1, 7.5$ Hz, 1H), 4.19 (q, $J = 7.1$ Hz, 4H), 2.77 (d, $J = 2.6$ Hz, 2H), 2.74 (d, $J = 7.5$ Hz, 2H), 1.99 (t, $J = 2.7$ Hz, 1H), 1.86 (t, $J = 6.9$ Hz, 2H), 1.57 (sep., $J = 6.7$ Hz, 1H), 1.24 (t, $J = 7.1$ Hz, 6H), 0.85 ppm (d, $J = 6.7$ Hz, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , signals for the (*Z*)-**12** where distinguishable are marked *): $\delta = 170.1^*$, 170.0, 135.0, 133.9*, 124.0, 122.7*, 79.4*, 79.2, 71.4*, 71.3, 61.7*, 61.6, 57.0, 56.9*, 42.1, 36.5*, 35.3, 29.9*, 28.7*, 28.4, 22.6, 22.4*, 22.3, 14.2 ppm; IR (film): $\nu = 3283, 2957, 1732, 1465, 1367, 1283, 1201, 1183, 1067, 1052, 972, 857$ cm^{-1} ; HRMS (ESI): m/z : calcd for $\text{C}_{17}\text{H}_{26}\text{O}_4\text{Na}$ [$\text{M}^+ + \text{Na}$]: 317.1723, found 317.1721.

Compound 14: Prepared according to the general procedure. The crude material was purified by flash chromatography (hexanes/EtOAc 75:1) to afford **14** as a colorless oil (0.0772 g, 79% combined yield, 1.3:1.0 *endo-exo*-, 6.2:1.0 *E:Z* for both diastereomers).



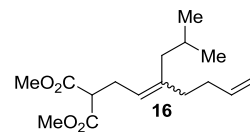
Structural and stereochemical assignment based on the COSY, HSQC, and HMBC spectra. Due to overlap in the $^1\text{H NMR}$ spectrum the *endo-exo*-ratio was determined by GC analysis. $^1\text{H NMR}$ (400 MHz, CDCl_3 , signals for *exo*-(*E*)-**14** where distinguishable are marked *, signals for *endo*-(*Z*)-**14** and *exo*-(*Z*)-**14** are not included): $\delta = 5.47$ (dt, $J = 15.2, 6.8$ Hz, 1H; *H*-9), 5.33 (dt, $J = 15.2, 6.8$ Hz, 1H; *H*-10), 4.17 (dq, $J = 10.8, 7.1$ Hz, 2H; *H*-14), 4.14 (dq, $J = 10.8, 7.1$ Hz, 2H; *H*-14), 3.33 (t, $J = 7.6$ Hz, 1H; *H*-12), 2.54 (dd, $J = 7.6, 6.8$ Hz, 2H; *H*-11), 2.14* (t, $J = 1.0$ Hz, 1H; *H*-4), 2.10 (t, $J = 4.0$ Hz, 1H; *H*-4), 2.04 (t, $J = 3.2$ Hz, 1H; *H*-1), 1.94 (t, $J = 7.0$ Hz, 2H; *H*-8), 1.90* (m, 1H; *H*-2), 1.87* (t, $J = 7.2$ Hz, 2H; *H*-8), 1.74 (m, 1H; *H*-2), 1.65 (tdd, $J = 11.6, 4.6, 2.8$ Hz, 1H; *H*-3), 1.45 (m, 1H; *H*-6), 1.44 (m, 1H; *H*-5), 1.43* (m, 1H; *H*-6), 1.34* (m, 1H; *H*-1), 1.31* (m, 1H; *H*-3), 1.27 (m, 1H; *H*-6), 1.24 (m, 2H; *H*-7), 1.23 (t, $J = 7.2$ Hz, 6H; *H*-15), 1.23* (m, 1H; *H*-7), 1.07* (m, 1H; *H*-6), 1.04 (m, 1H; *H*-5), 1.00* (m, 1H; *H*-7), 0.96* (m, 1H; *H*-3), 0.55 ppm (ddd, $J = 11.6, 4.6, 2.2$ Hz, 1H; *H*-3); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , signals for *exo*-(*E*)-**14** where distinguishable are marked *, signals for *endo*-(*Z*)-**14** where distinguishable are marked **, signals for *exo*-(*Z*)-**14** where distinguishable are marked ***): $\delta = 169.1^{**}$ (C-13), 169.0 (C-13), 133.5 (C-9), 132.9* (C-9), 132.5** (C-9), 132.2*** (C-9), 125.8* (C-10), 125.3 (C-10), 124.9*** (C-10), 124.4* (C-10), 61.3** (C-14), 61.2 (C-14), 52.3 (C-12), 52.1** (C-12), 42.2*** (C-1), 41.8* (C-1), 40.6*** (C-2), 40.5* (C-2), 40.3** (C-2), 40.0 (C-2), 39.9 (C-7), 39.8 (C-1), 39.6* (C-8), 37.8*** (C-3), 37.7* (C-3), 37.1 (C-4), 36.7** (C-3), 36.7*** (C-4), 36.6 (C-3), 36.6* (C-4), 35.7 (C-8), 35.1* (C-7), 34.2*** (C-8), 31.9* (C-11), 31.9 (C-11), 30.3* (C-8), 30.2** (C-5), 30.1 (C-5), 30.0* (C-5), 28.8* (C-6), 26.8** (C-11), 22.4* (C-6), 22.4 (C-6), 14.1 ppm (C-15); IR (film): $\nu = 2946, 2868, 1732, 1446, 1368, 1332, 1299, 1263, 1226, 1151, 1096, 1033, 970, 858, 696$ cm^{-1} ; HRMS (ESI): m/z : calcd for $\text{C}_{18}\text{H}_{28}\text{O}_4\text{Na}$ [$\text{M}^+ + \text{Na}$]: 331.1880, found 331.1878.

Compound 14: Prepared according to the general procedure. The crude material was purified by flash chromatography (hexanes/EtOAc 75:1) to afford **14** as a colorless oil (0.0545 g, 80% combined yield, >20:1 *endo-exo*-, 6.2:1.0 *E:Z*). Structural and stereochemical assignment based on the COSY, HSQC, and HMBC spectra. Due to overlap in the $^1\text{H NMR}$ spectrum the *endo-exo*-ratio was determined by GC analysis. $R_f = 0.41$ (hexanes/EtOAc 9:1); $^1\text{H NMR}$ (400 MHz, CDCl_3 , signals for *endo*-(*Z*)-**14** are not included): $\delta = 5.47$ (dt, $J = 15.2, 9.8$ Hz, 1H; *H*-9), 5.33 (dt, $J = 15.2, 6.8$ Hz, 1H; *H*-10), 4.17 (dq, $J = 10.8, 7.1$ Hz, 2H; *H*-14), 4.14 (dq, $J = 10.8, 7.1$ Hz, 2H; *H*-14), 3.33 (t, $J = 7.6$ Hz, 1H; *H*-12), 2.54 (dd, $J = 7.6, 6.8$ Hz, 2H; *H*-11), 2.10 (app t, $J = 4.0$ Hz, 1H; *H*-4), 2.04 (app t, $J = 3.2$ Hz, 1H; *H*-1), 1.94 (t, $J = 7.0$ Hz, 2H; *H*-8), 1.74 (m, 1H; *H*-2), 1.65 (tdd, $J = 11.6, 4.6, 2.2$ Hz, 1H; *H*-3), 1.45 (m, 1H; *H*-6), 1.44 (m, 1H; *H*-5), 1.27 (m, 1H; *H*-6), 1.24 (m, 2H; *H*-7), 1.23 (t, $J = 7.2$ Hz, 6H; *H*-15), 1.04 (m, 1H; *H*-5), 0.55 ppm (ddd, $J = 11.6, 4.6, 2.2$ Hz, 1H; *H*-3); $^{13}\text{C NMR}$ (400 MHz, CDCl_3 , signals for *endo*-(*Z*)-**14** where distinguishable are marked *): $\delta = 169.1^*$ (C-13), 169.1 (C-13), 133.5 (C-9), 132.5* (C-9), 125.3 (C-10), 124.4* (C-10), 61.3* (C-14), 61.2 (C-14), 52.4 (C-12), 52.1* (C-12), 40.3* (C-2), 40.0 (C-2), 39.9 (C-7), 39.8 (C-1), 37.1 (C-4), 36.7* (C-3), 36.5 (C-3), 35.7 (C-8), 31.9 (C-11), 30.3* (C-8), 30.2* (C-5), 30.1 (C-5), 26.8* (C-11), 22.4* (C-6), 22.4 (C-6), 14.1 ppm (C-15); IR (film): $\nu = 2946, 2868, 1749, 1729, 1447, 1391, 1368, 1333, 1301, 1263, 1227, 1151, 1096, 1033, 970, 858, 806, 699$ cm^{-1} ; HRMS (ESI): m/z : calcd for $\text{C}_{18}\text{H}_{28}\text{O}_4\text{Na}$ [$\text{M}^+ + \text{Na}$]: 331.1880, found 331.1877.

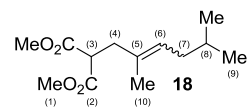


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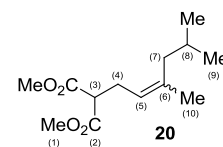
Compound 16: Prepared according to the general procedure. The crude material was purified by flash chromatography (hexanes/EtOAc 60:1) to afford **16** as a colorless oil (0.023 g, 61% combined yield, 1.0:4.9 *E:Z*). $R_f = 0.36$ (hexanes/EtOAc 9:1); $^1\text{H NMR}$ (400 MHz, CDCl_3 , only signals for (*Z*)-**16** are provided): $\delta = 5.81\text{--}5.71$ (m, 1H), 5.12 (t, $J = 7.2$ Hz, 1H), 4.98 (dq, $J = 17.0, 1.7$ Hz, 1H), 4.92 (ddt, $J = 10.1, 2.2, 1.1$ Hz, 1H), 3.72 (s, 6H), 3.36 (t, $J = 7.7$ Hz, 1H), 2.62 (t, $J = 7.5$ Hz, 2H), 2.13–2.08 (m, 2H), 2.05–2.01 (m, 2H), 1.92 (d, $J = 7.3$ Hz, 2H), 1.73 (septet, $J = 6.8$ Hz, 1H), 0.87 ppm (d, $J = 6.6$ Hz, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , signals for (*E*)-**16** where distinguishable are marked*): $\delta = 169.7, 141.5, 138.6, 138.5^*, 121.5^*, 121.0, 114.7^*, 114.5, 52.6, 52.2, 46.6^*, 39.1, 36.3, 32.6, 29.4^*, 27.6, 27.5^*, 26.9, 26.2^*, 22.7, 22.5^*$ ppm; IR (film): $\nu = 2954, 1737, 1640, 1435, 1231, 1148, 1027, 910\text{ cm}^{-1}$; HRMS (ESI): m/z : calcd for $\text{C}_{16}\text{H}_{26}\text{O}_4\text{Na}$ [$\text{M}^+ + \text{Na}$]: 305.1723, found 305.1725.



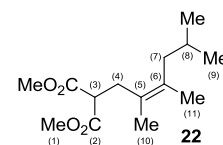
Compound 18: Prepared according to the general procedure. The crude material was purified by flash chromatography (hexanes/EtOAc 40:1) to afford **18** as a colorless oil (0.0260 g, 74% combined yield, 2.3:1.0 *E:Z*, contains *ca.* 5% of an unassigned byproduct). Structural and stereochemical assignment based on the COSY, NOESY, HMQC, and HSQC spectra. $R_f = 0.38$ (hexanes/EtOAc 9:1); $^1\text{H NMR}$ (400 MHz, CDCl_3 , signals for (*Z*)-**18** where distinguishable are marked*): $\delta = 5.24^*$ (t, $J = 7.4$ Hz, 1H; *H*-6), 5.21 (tq, $J = 7.3, 0.9$ Hz, 1H; *H*-6), 3.70^{*} (s, 6H; *H*-1), 3.69 (s, 6H; *H*-1), 3.57 (t, $J = 8.0$ Hz, 1H; *H*-3), 3.53^{*} (t, $J = 8.0$ Hz, 1H; *H*-3), 2.63^{*} (d, $J = 8.0$ Hz, 2H; *H*-4), 2.58 (d, $J = 8.0$ Hz, 2H; *H*-4), 1.85^{*} (dd, $J = 7.4, 6.6$ Hz, 2H; *H*-7), 1.82 (dd, $J = 7.4, 6.6$ Hz, 2H; *H*-7), 1.67^{*} (s, 3H; *H*-10), 1.58 (s, 3H; *H*-10), 1.54 (nonet, $J = 6.6$ Hz, 1H; *H*-8), 1.53^{*} (nonet, $J = 6.6$ Hz, 1H; *H*-8), 0.85^{*} (d, $J = 6.6$ Hz, 6H; *H*-9), 0.82 ppm (d, $J = 6.6$ Hz, 6H; *H*-9); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , signals for (*Z*)-**18** where distinguishable are marked*): $\delta = 169.7^*$ (C-2), 169.6 (C-2), 131.1 (C-5), 130.6^{*} (C-5), 128.1^{*} (C-6), 126.8 (C-6), 52.4^{*} (C-1), 52.4 (C-1), 50.7 (C-3), 50.1^{*} (C-3), 38.8 (C-4), 37.1 (C-7), 36.8^{*} (C-7), 31.1^{*} (C-4), 28.8^{*} (C-8), 28.7 (C-8), 22.8^{*} (C-10), 22.4^{*} (C-9), 22.2 (C-9), 15.8 ppm (C-10); IR (film): $\nu = 2954, 2870, 1734, 1435, 1337, 1273, 1231, 1198, 1148, 1081, 1051, 1018, 870, 695\text{ cm}^{-1}$; HRMS (ESI): m/z : calcd for $\text{C}_{13}\text{H}_{22}\text{O}_4\text{Na}$ [$\text{M}^+ + \text{Na}$]: 265.1410, found 265.1411.



Compound 20: Prepared according to the general procedure. The crude material was purified by flash chromatography (hexanes/EtOAc 50:1) to afford **20** as a colorless oil (0.0317 g, 66% combined yield, 1.0:3.8 *E:Z*). Structural and stereochemical assignment based on the COSY, NOESY, HMQC, and HMBC spectra. $R_f = 0.38$ (hexanes/EtOAc 9:1); $^1\text{H NMR}$ (400 MHz, CDCl_3 , signals for (*E*)-**20** where distinguishable are marked*): $\delta = 5.07$ (t, $J = 7.2$ Hz, 1H; *H*-5), 5.00^{*} (t, $J = 7.2$ Hz, 1H; *H*-5), 3.70 (s, 6H; *H*-1), 3.69^{*} (s, 6H; *H*-1), 3.36^{*} (t, $J = 7.6$ Hz, 1H; *H*-3), 3.32 (t, $J = 7.6$ Hz, 1H; *H*-3), 2.59^{*} (dd, $J = 7.6, 7.2$ Hz, 2H; *H*-4), 2.58 (dd, $J = 7.6, 7.2$ Hz, 2H; *H*-4), 1.89 (d, $J = 7.4$ Hz, 2H; *H*-7), 1.80^{*} (d, $J = 7.4$ Hz, 2H; *H*-7), 1.73 (t of septets, $J = 7.4, 6.6$ Hz, 1H; *H*-8), 1.69^{*} (t of septets, $J = 7.4, 6.6$ Hz, 1H; *H*-8), 1.62 (s, 3H; *H*-10), 1.57^{*} (s, 3H; *H*-10), 0.84 (d, $J = 6.6$ Hz, 6H; *H*-9), 0.78^{*} ppm (d, $J = 6.6$ Hz, 6H; *H*-9); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , signals for (*E*)-**20** where distinguishable are marked*): $\delta = 169.6$ (C-2), 138.1 (C-6), 138.0^{*} (C-6), 120.9 (C-5), 120.6^{*} (C-5), 52.4 (C-1), 52.4^{*} (C-1), 52.1 (C-3), 51.9^{*} (C-3), 49.5^{*} (C-7), 40.9 (C-7), 27.6^{*} (C-4), 27.4 (C-4), 26.5 (C-8), 25.9^{*} (C-8), 23.7 (C-10), 22.4 (C-9), 22.2^{*} (C-9), 15.9^{*} ppm (C-10); IR (film) $\nu = 2954, 2869, 1737, 1332, 1435, 1270, 1234, 1196, 1148, 1029, 962, 694\text{ cm}^{-1}$; HRMS (ESI): m/z : calcd for $\text{C}_{13}\text{H}_{22}\text{O}_4\text{Na}$ [$\text{M}^+ + \text{Na}$]: 265.1410, found 265.1409.

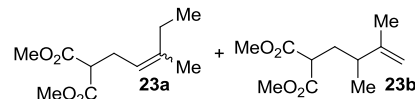


Compound 22: Prepared according to the general procedure. The crude material was purified by flash chromatography (hexanes/EtOAc 50:1) to afford **22** as a colorless oil (0.0306 g, 65% yield, contains *ca.* 3% of an unassigned byproduct). Structural and stereochemical assignment based on the COSY, NOESY, HSQC, HMQC, and INEPT spectra. $R_f = 0.33$ (hexanes/EtOAc 9:1); $^1\text{H NMR}$ (600 MHz, CDCl_3): $\delta = 3.68$ (s, 6H; *H*-1), 3.49 (t, $J = 7.8$ Hz, 1H; *H*-3), 2.66 (dq, $J = 7.8, 0.5$ Hz, 2H; *H*-4), 1.89 (dq, $J = 7.4, 0.5$ Hz, 2H; *H*-7), 1.69 (tsep, $J = 7.4, 6.6$ Hz, 1H; *H*-8), 1.59 (s, 3H; *H*-10), 1.56 (s, 3H; *H*-11), 0.81 ppm (d, $J = 6.6$ Hz, 6H; *H*-9); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): $\delta = 169.9$ (C-2), 131.6 (C-6), 124.0 (C-5), 52.4 (C-1), 50.6 (C-3), 42.9 (C-7), 33.3 (C-4), 27.0 (C-8), 22.4 (C-9), 18.9 (C-11), 17.9 ppm (C-10); IR (film): $\nu = 2954, 1734, 1435, 1229, 1150, 1050\text{ cm}^{-1}$; HRMS (ESI): m/z : calcd for $\text{C}_{14}\text{H}_{24}\text{O}_4\text{Na}$ [$\text{M}^+ + \text{Na}$]: 279.1567, found 279.1565.



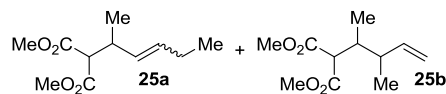
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Compound 23a,b: Prepared according to the general procedure. The crude material was purified by flash chromatography (hexanes/EtOAc 50:1) to afford **23a,b** as a colorless oil (0.0431 g, 85% combined yield, 1.0:1.9 **23a**:**23b**, 1.0:1.9 *E*:*Z*). $R_f = 0.38$ (hexanes/EtOAc 9:1); $^1\text{H NMR}$



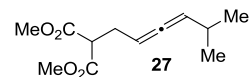
(400 MHz, CDCl_3 , signals for (*Z*)-**23a** where distinguishable are marked*, signals for the (*E*)-**23a** where distinguishable are marked**, signals which were not conclusively assigned to either minor component or where the two overlap are marked***): $\delta = 5.03^{**}$ (tq, $J = 7.4, 1.0$ Hz, 1H), 4.99^* (t, $J = 7.7$ Hz, 1H), 4.73 (quintet, $J = 1.5$ Hz, 1H), 4.67 (s, 1H), 3.72 (s, 3H), 3.71^* (s, 6H), 3.71^{**} (s, 6H), 3.68 (s, 3H), 3.36^{***} (t, $J = 7.7$ Hz, 1H), 3.35 (t, $J = 7.5$ Hz, 1H), 3.34^{***} (t, $J = 7.7$ Hz, 1H), 2.58^{***} (t, $J = 7.5$ Hz, 2H), 2.17 (sextet, $J = 7.1$ Hz, 1H), 2.03^{***} (q, $J = 7.6$ Hz, 2H), 1.93 (t, $J = 7.4$ Hz, 2H), 1.65^* (q, $J = 1.3$ Hz, 3H), 1.63 (s, 3H), 1.61^{**} (s, 3H), 1.02 (d, $J = 6.8$ Hz, 3H), 0.94^{***} ppm (t, $J = 7.6$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , signals for (*Z*)-**23a** where distinguishable are marked*, signals for (*E*)-**23a** where distinguishable are marked**, signals which were not conclusively assigned to either minor component or where the two overlap are marked***): $\delta = 170.2, 170.1, 169.8^*, 169.7^*, 148.0, 140.8^*, 140.8^{**}, 119.1^*, 118.1^{**}, 111.4, 52.6, 52.6^{***}, 52.5, 52.2^*, 52.0^{**}, 50.0, 39.4, 33.7, 32.5^{**}, 27.6^{**}, 27.4^*, 24.8^*, 23.0^*, 19.8, 18.5, 16.0^*, 12.8^{***}$ ppm; IR (film): $\nu = 2958, 1734, 1435, 1268, 1234, 1197, 1149, 1045, 1014, 971, 893, 844$ cm^{-1} ; HRMS (ESI): m/z : calcd for $\text{C}_{11}\text{H}_{18}\text{O}_4\text{Na}$ [$\text{M}^+ + \text{Na}$]: 237.1097, found 237.1097.

Compound 25a,b: Prepared according to the general procedure. The crude material was purified by flash chromatography (hexanes/EtOAc 50:1) to afford **25a,b** as a colorless oil (0.0554 g, 85% combined yield, 12.2:1.0 **25a**:**25b**, 16.6:1.0 *E*:*Z*). $R_f = 0.35$ (hexanes/EtOAc



9:1); $^1\text{H NMR}$ (400 MHz, CDCl_3 , only signals for the (*E*)-**25a** are provided): $\delta = 5.51$ (dt, $J = 15.0, 6.5$ Hz, 1H), 5.28 (ddt, $J = 15.2, 8.4, 1.4$ Hz, 1H), 3.70 (s, 3H), 3.66 (s, 3H), 3.24 (d, $J = 9.1$ Hz, 1H), 2.86 (sextet, $J = 7.5$ Hz, 1H), 1.95 (quintet, $J = 7.5$ Hz, 2H), 1.04 (d, $J = 6.6$ Hz, 3H), 0.91 ppm (t, $J = 7.5$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , signals for (*Z*)-**25a** where distinguishable are marked*, signals for **25b** where distinguishable are marked**, signals which were not conclusively assigned to either minor component are marked***): $\delta = 169.8^{***}, 169.3^{***}, 168.9, 168.9, 142.6^{**}, 133.6, 133.0^*, 130.2, 114.6^{**}, 58.2, 58.0^{***}, 55.4^{***}, 52.5^{***}, 52.4^{***}, 52.4, 52.3^{***}, 52.2, 40.1^{***}, 40.0^{***}, 37.6, 32.6^{***}, 25.6, 20.7^*, 19.3^{***}, 18.7, 15.0^{***}, 14.4^{***}, 13.9, 12.9^{***}$ ppm; IR (film): $\nu = 2961, 1732, 1434, 1237, 1193, 1144, 1019, 970$ cm^{-1} ; HRMS (ESI): m/z : calcd for $\text{C}_{11}\text{H}_{18}\text{O}_4\text{Na}$ [$\text{M}^+ + \text{Na}$]: 237.1097, found 237.1097.

Compound 27: Prepared according to the general procedure. The crude material was purified by flash chromatography (hexanes/EtOAc 20:1) to afford **27** as a colorless oil (0.0363 g, 60% yield). $R_f = 0.31$ (hexanes/EtOAc 9:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta =$



5.15 (q, $J = 4.5$ Hz, 2H), 3.73 (s, 3H), 3.73 (s, 3H), 3.49 (t, $J = 7.5$ Hz, 1H), 2.58 (dt, $J = 7.4, 4.7$ Hz, 2H), 2.30 - 2.18 (m, 1H), 0.97 ppm (d, $J = 6.8$ Hz, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 202.6, 169.6, 169.5, 100.5, 88.8, 52.6, 51.4, 28.3, 28.0, 22.5, 22.4$ ppm; IR (film): $\nu = 2957, 2869, 1961, 1734, 1435, 1340, 1230, 1150, 1040, 875, 731$ cm^{-1} ; HRMS (ESI): m/z : calcd for $\text{C}_{12}\text{H}_{18}\text{O}_4\text{Na}$ [$\text{M}^+ + \text{Na}$]: 249.1097, found 249.1093.

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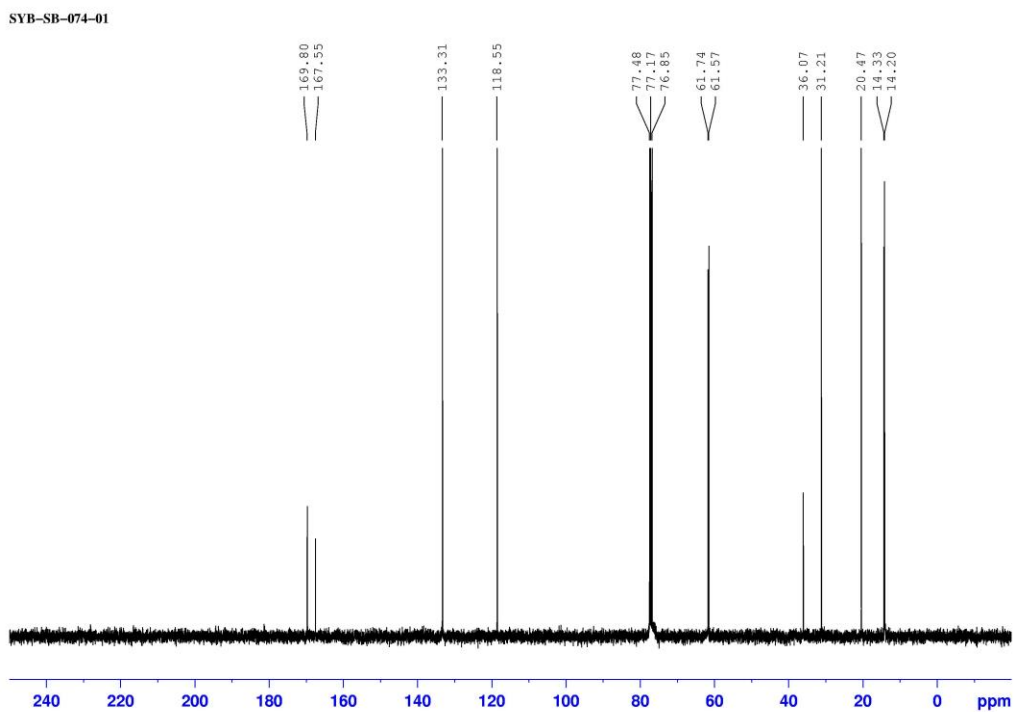
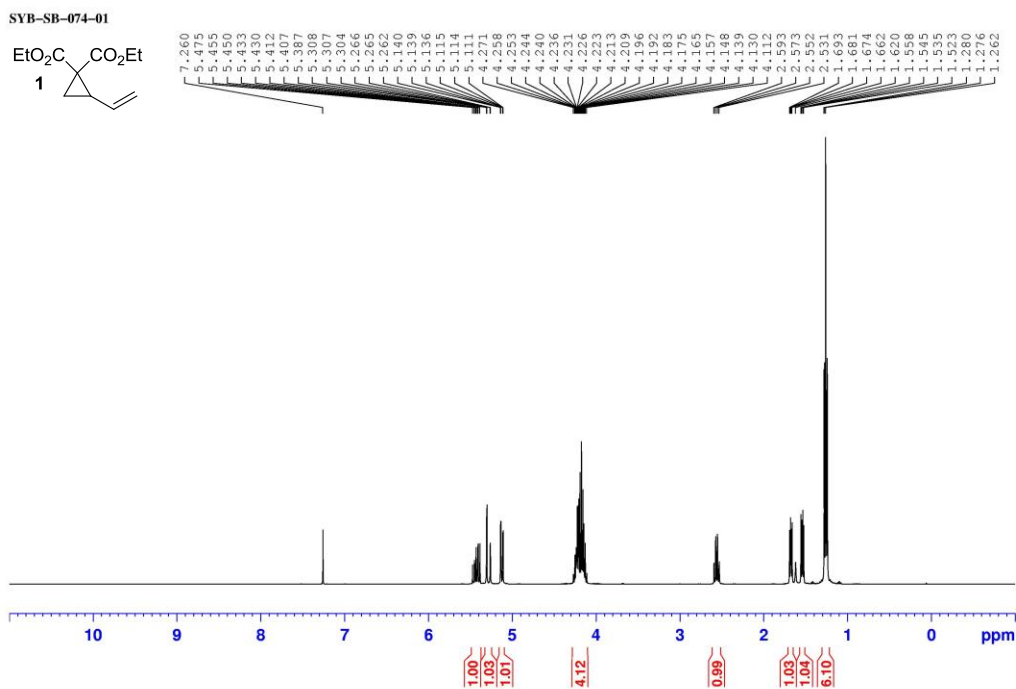
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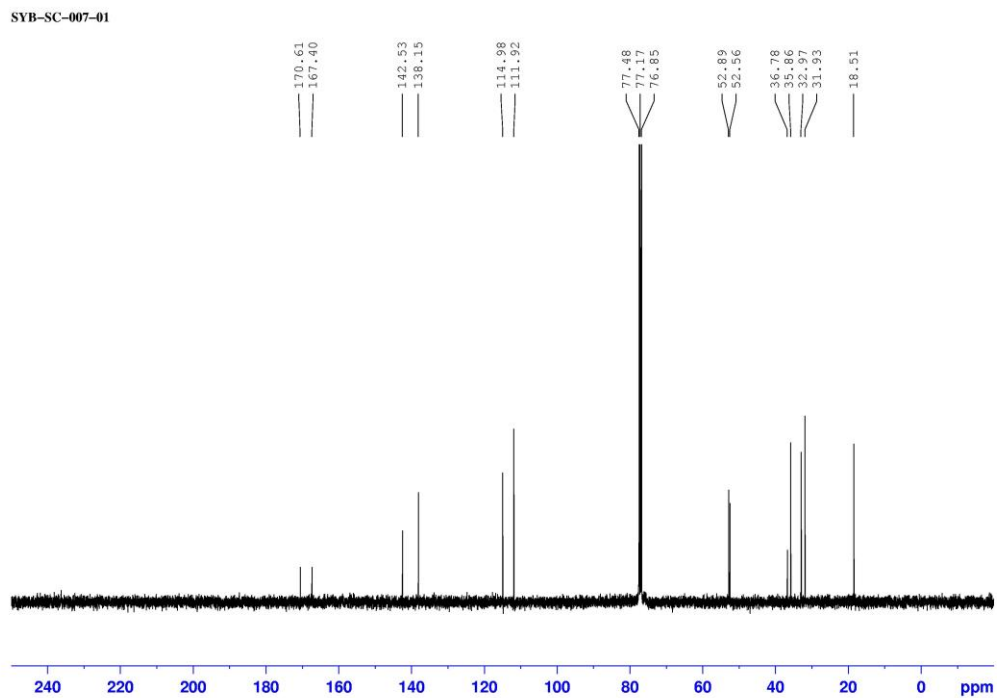
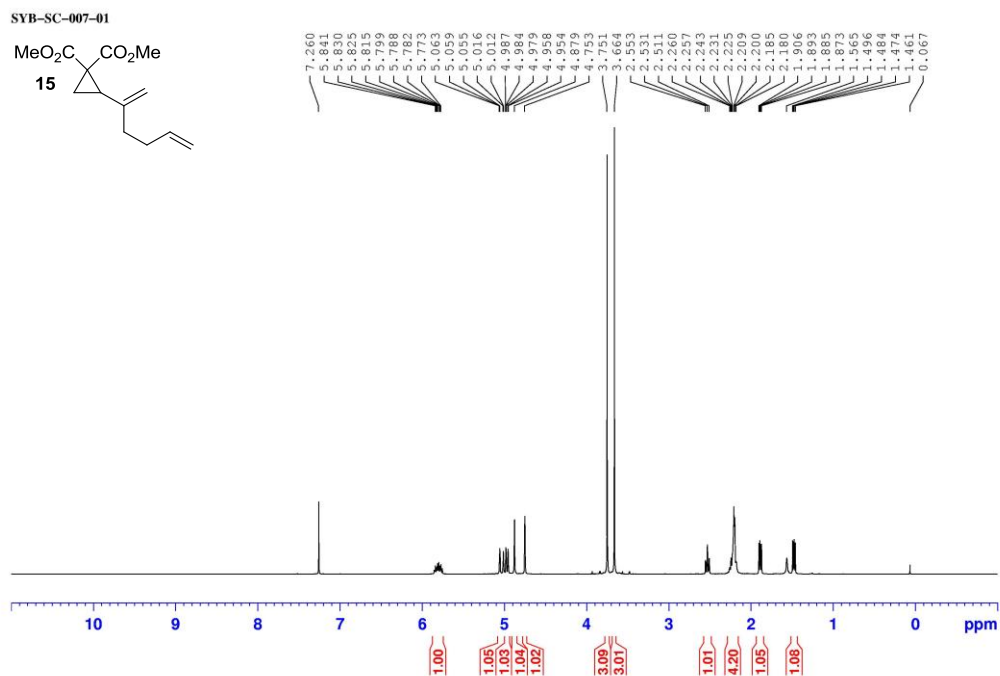
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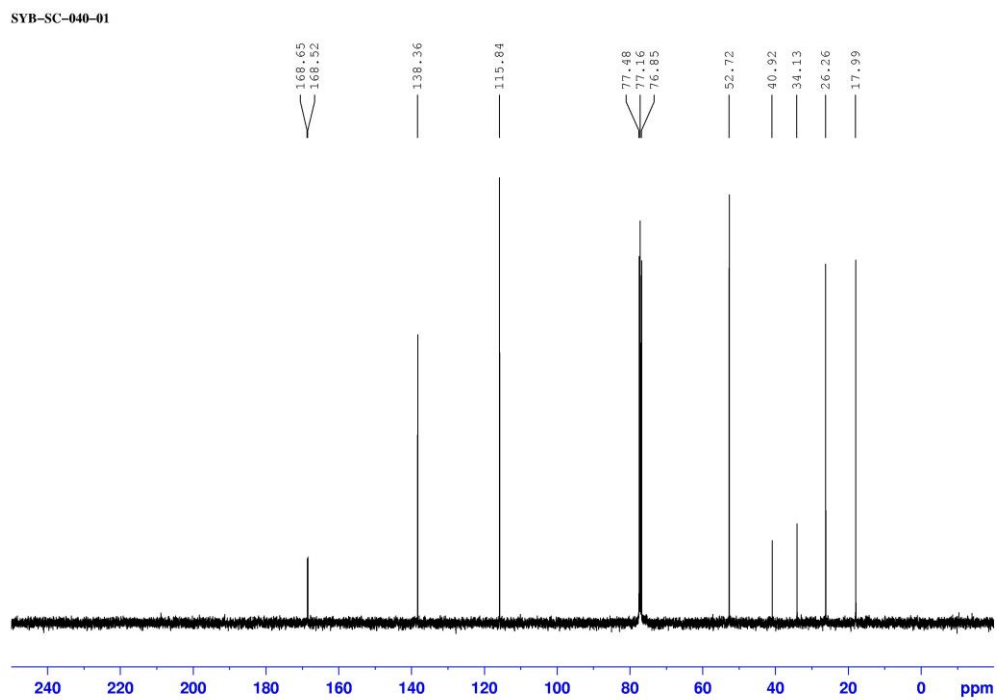
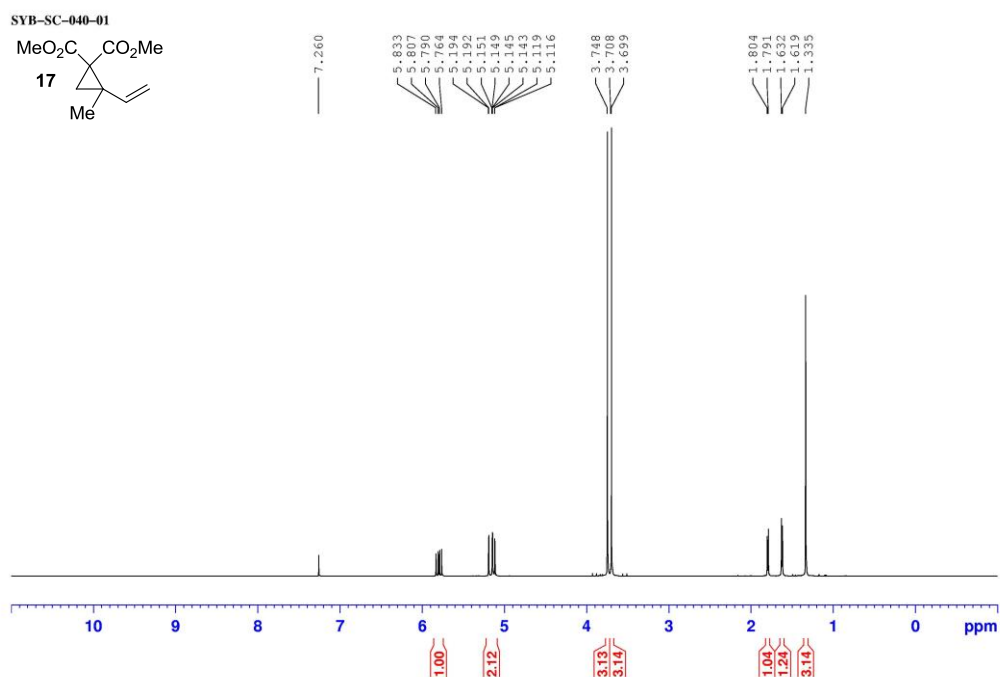
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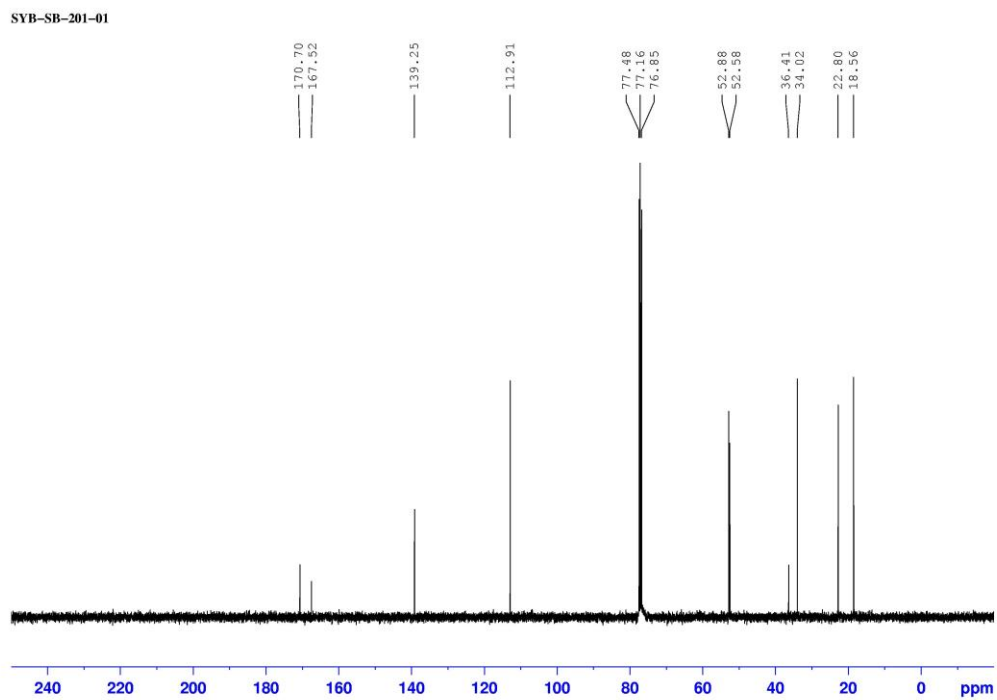
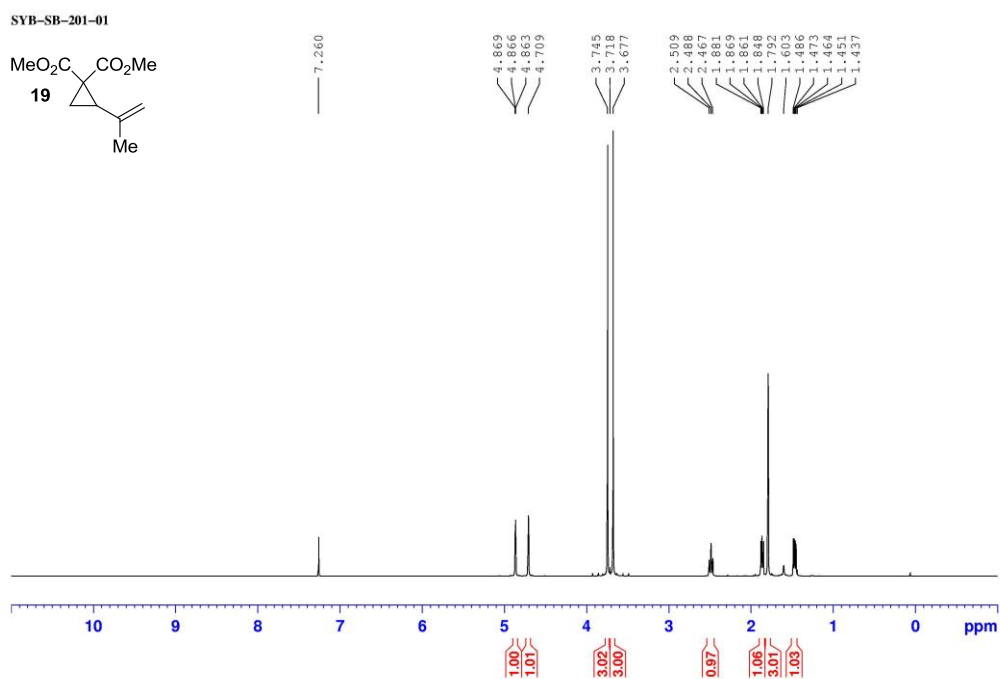
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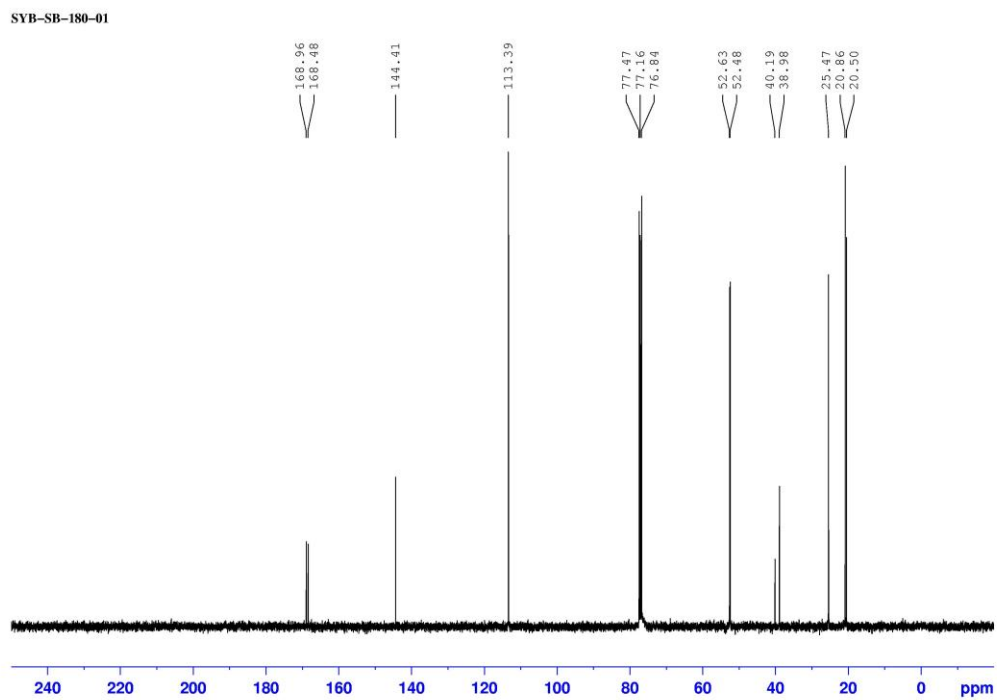
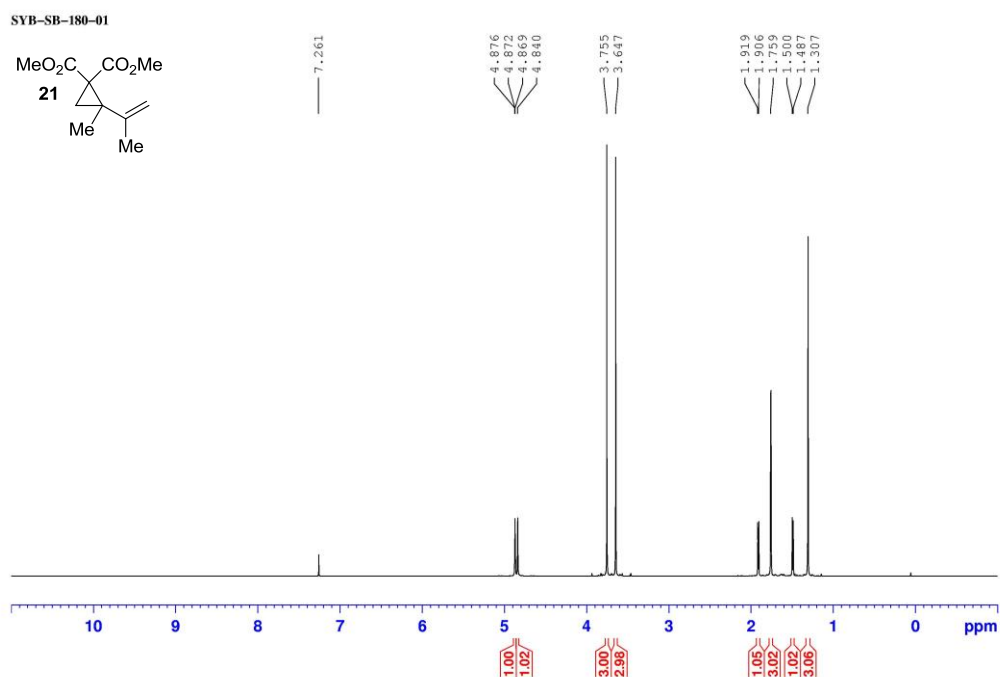
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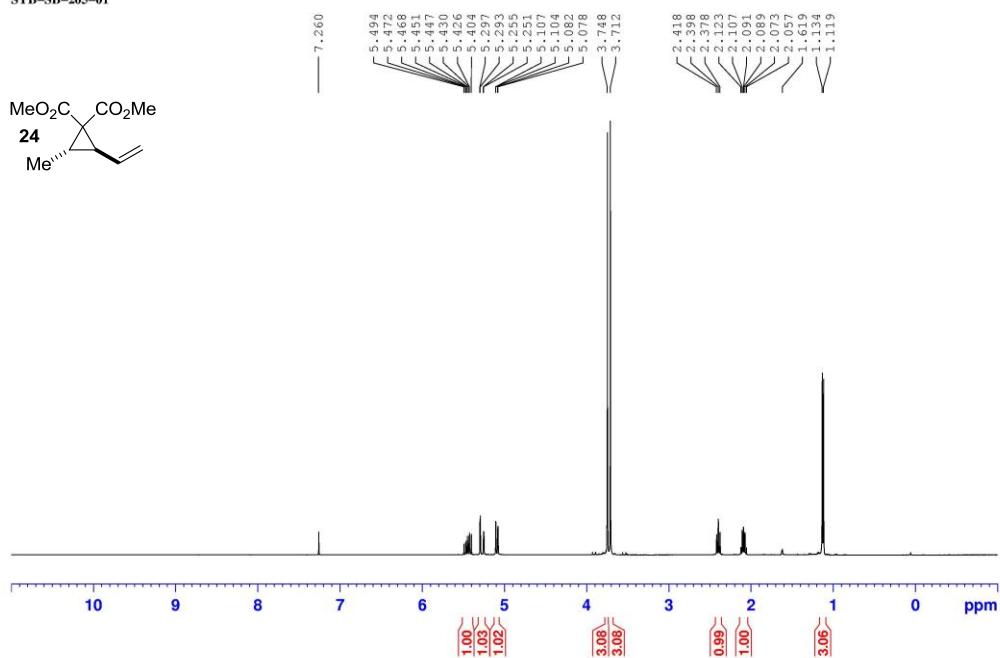


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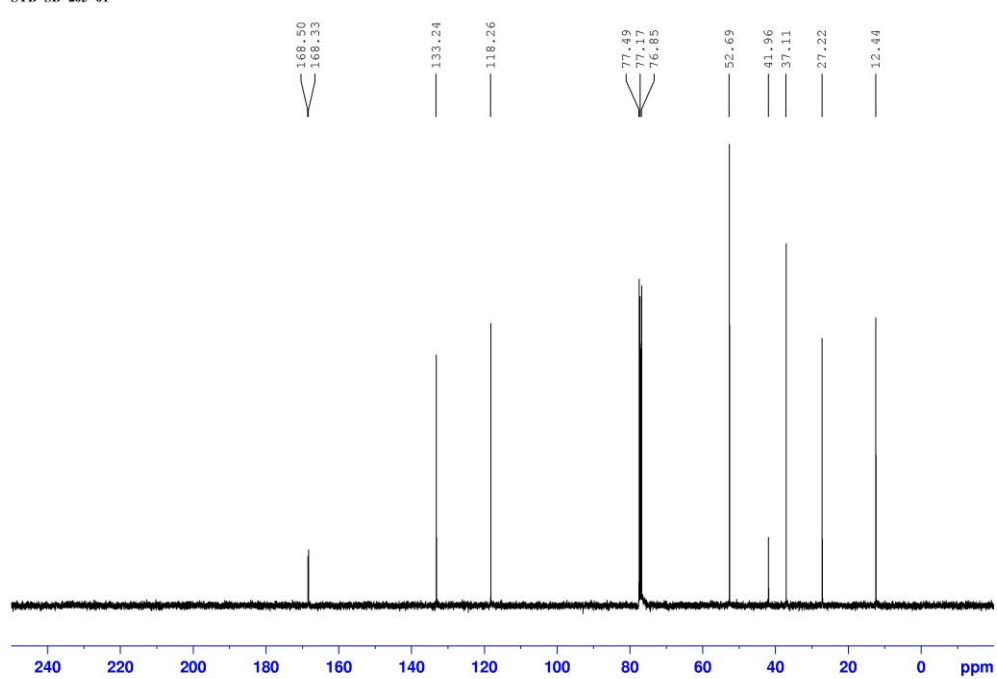


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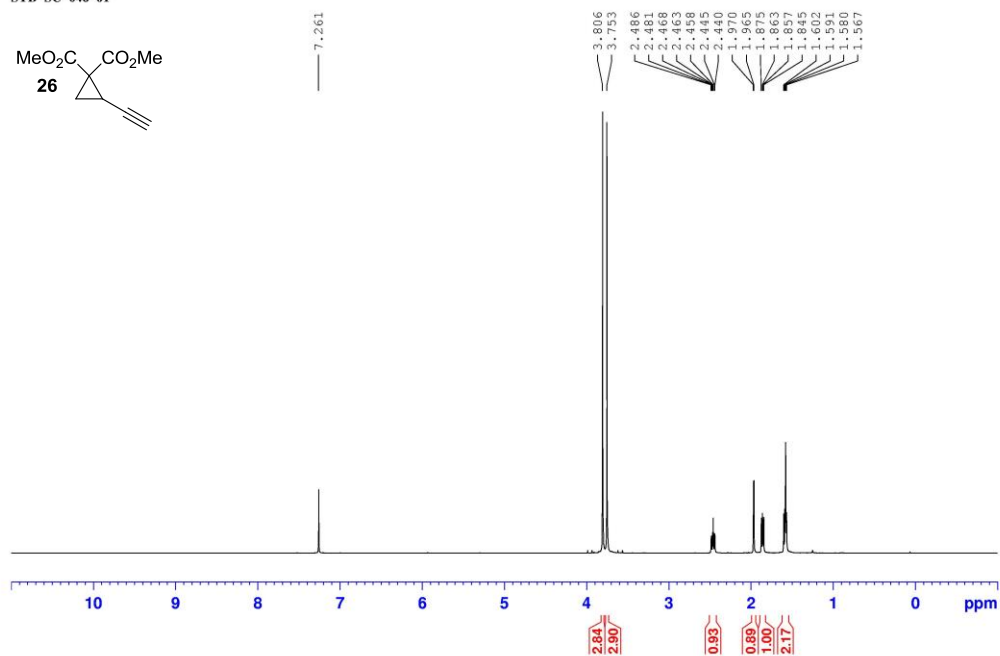
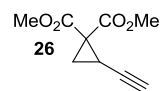


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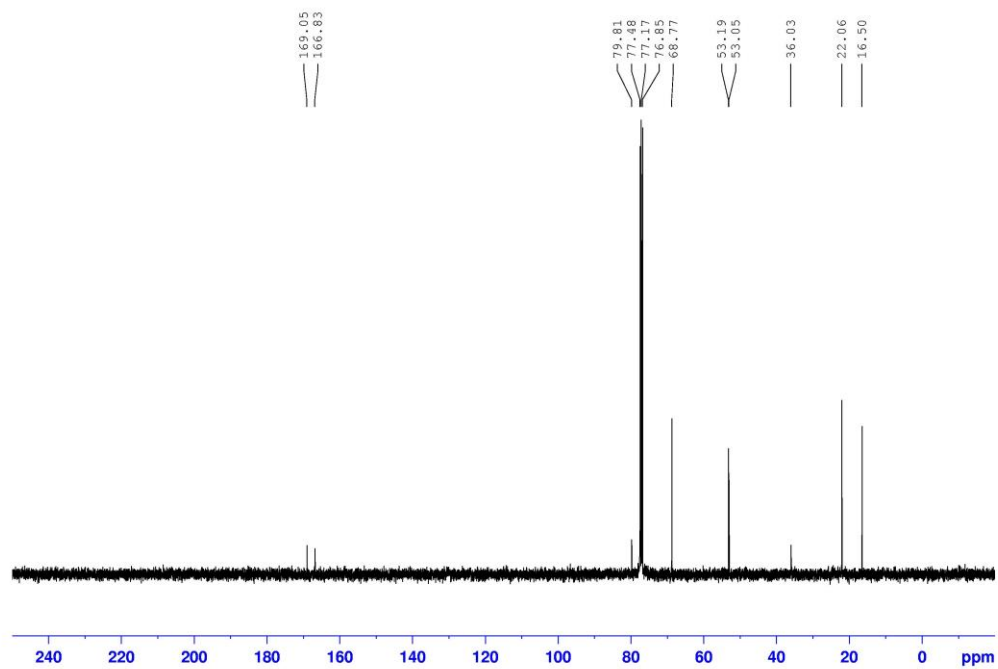


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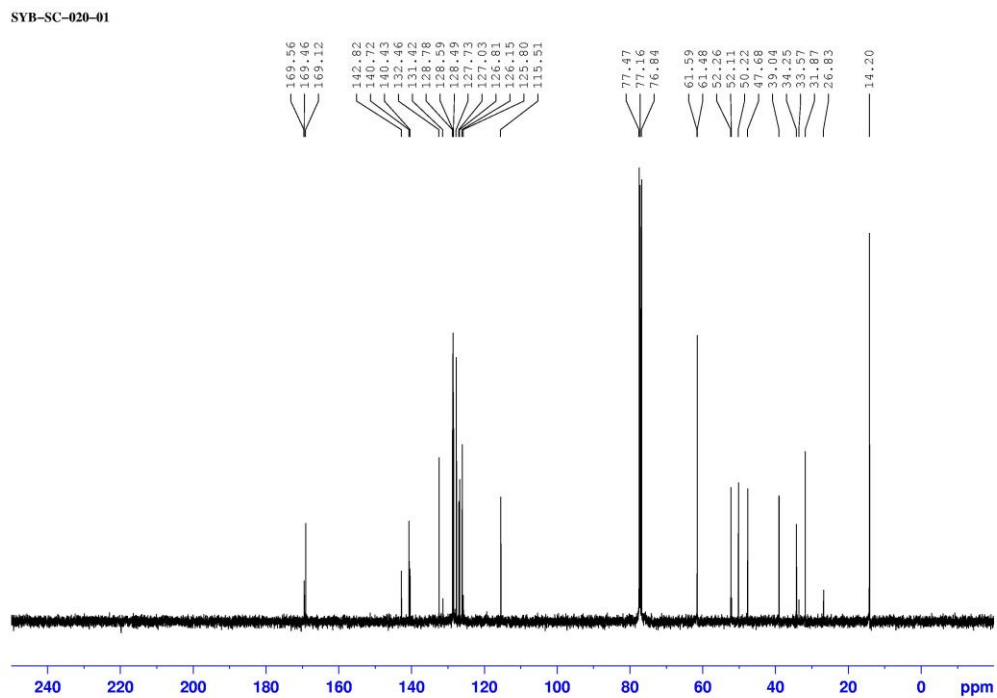
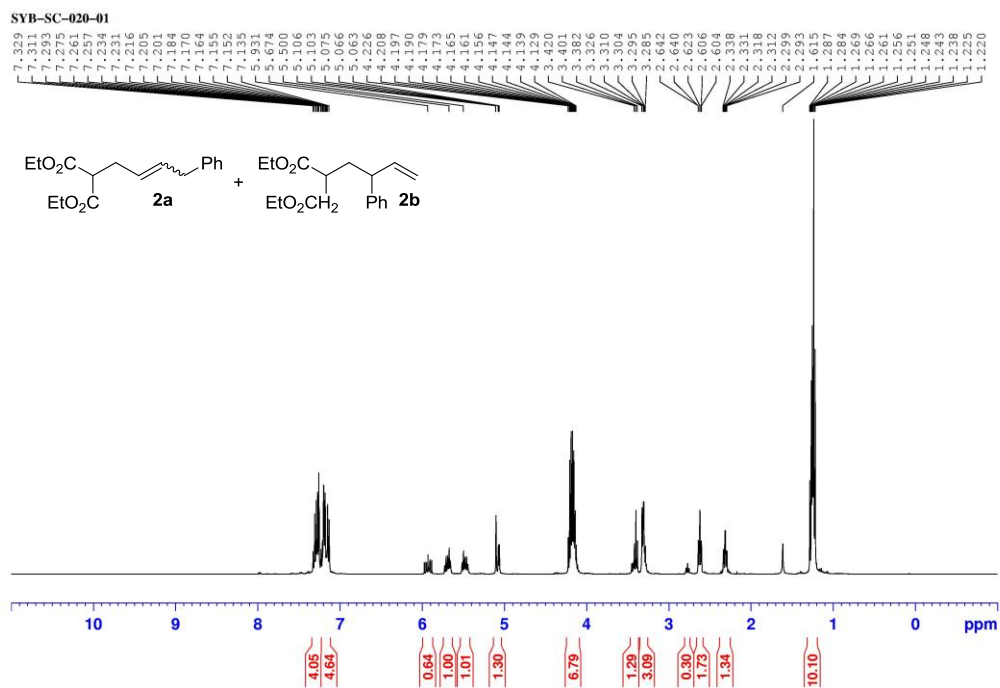
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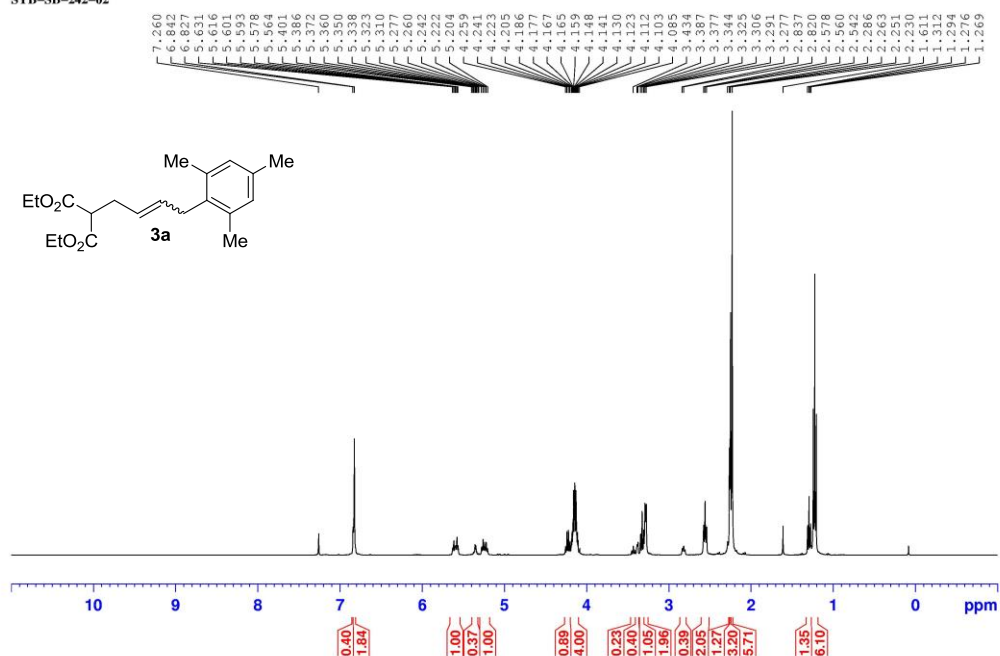


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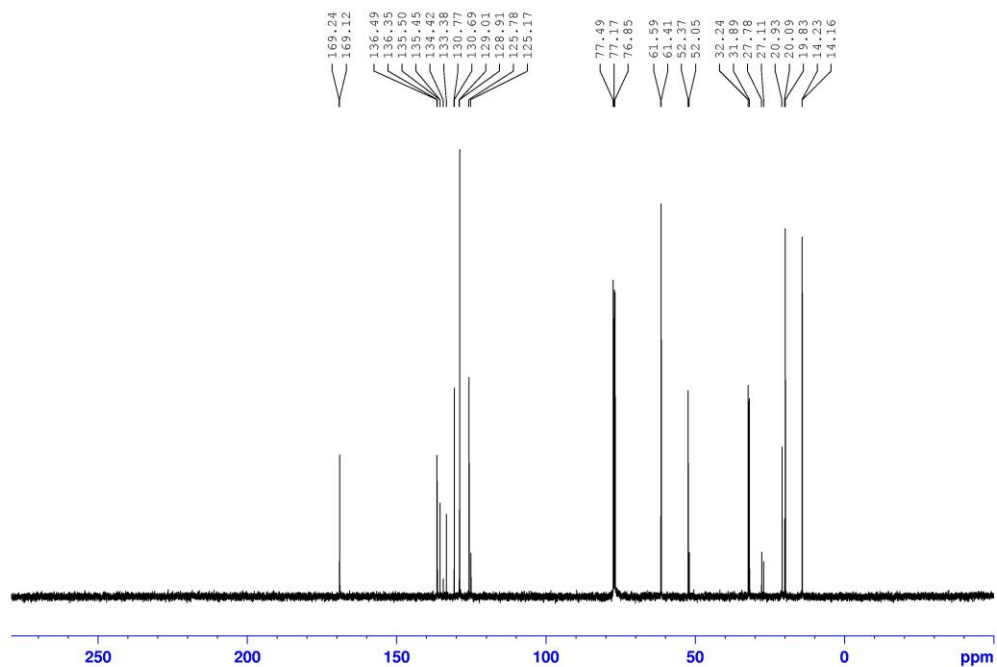


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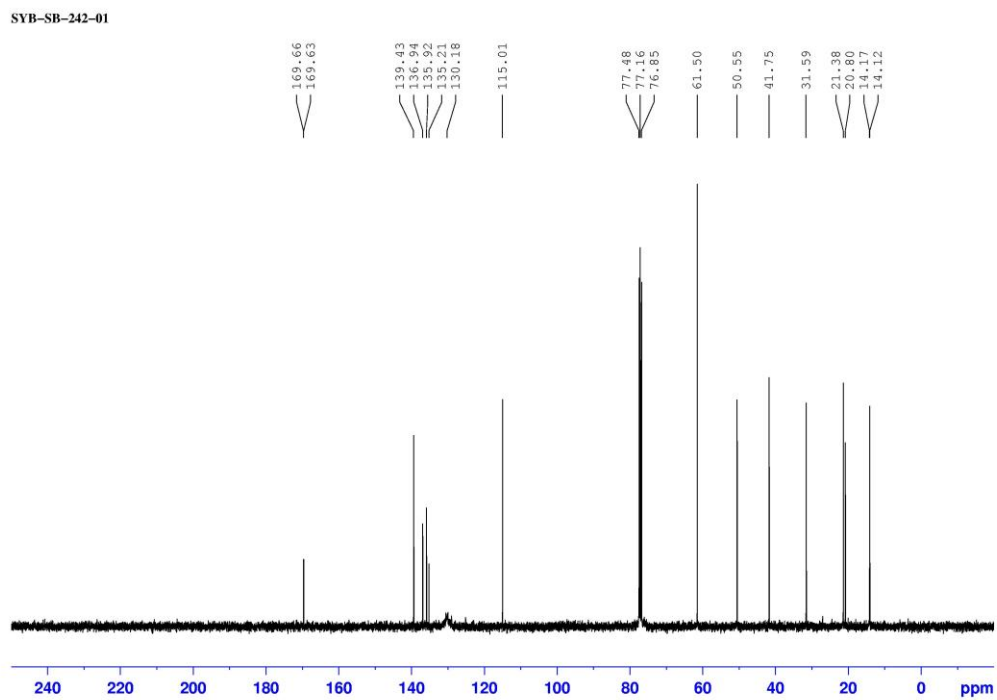
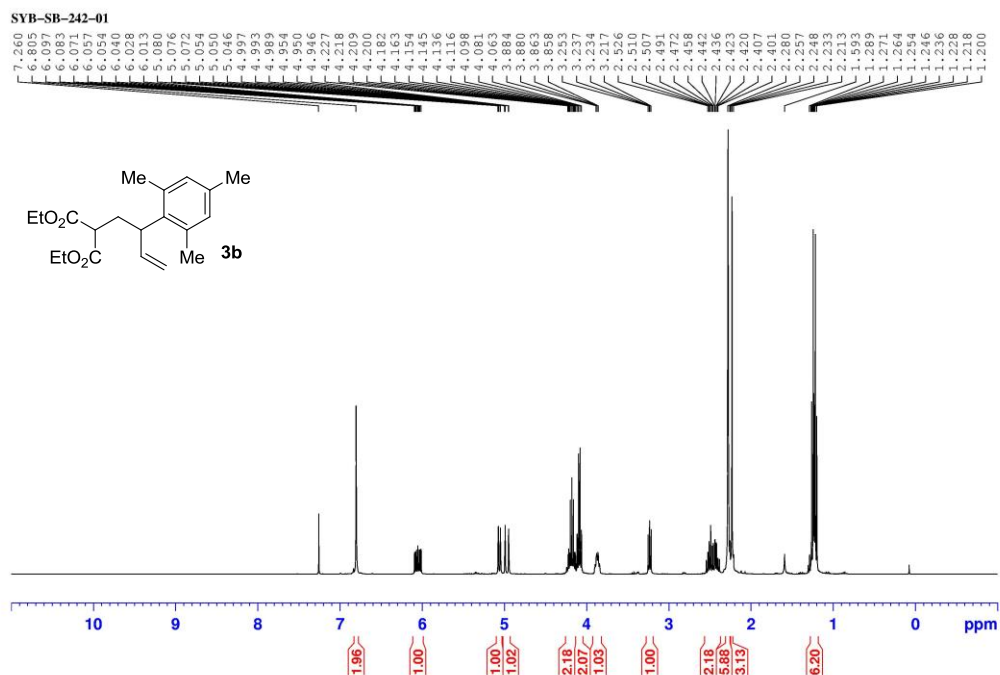
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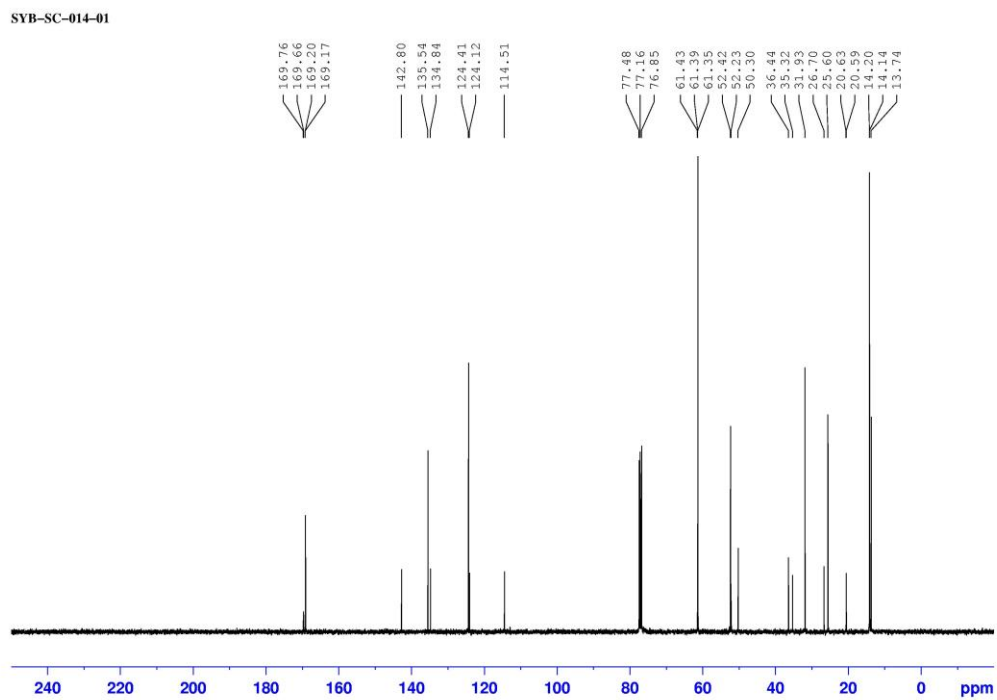
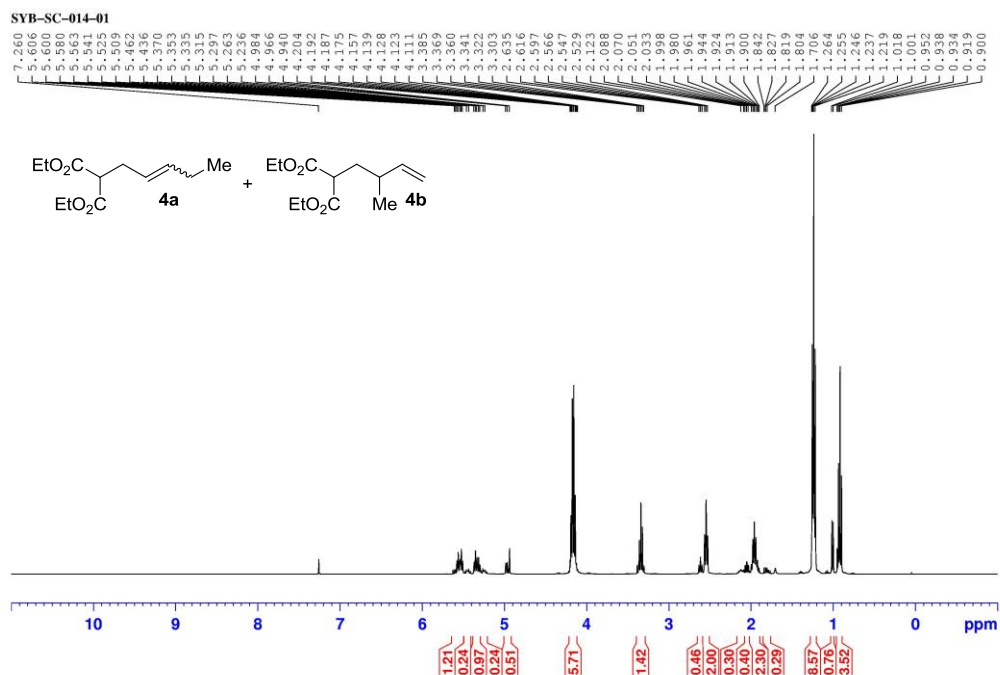
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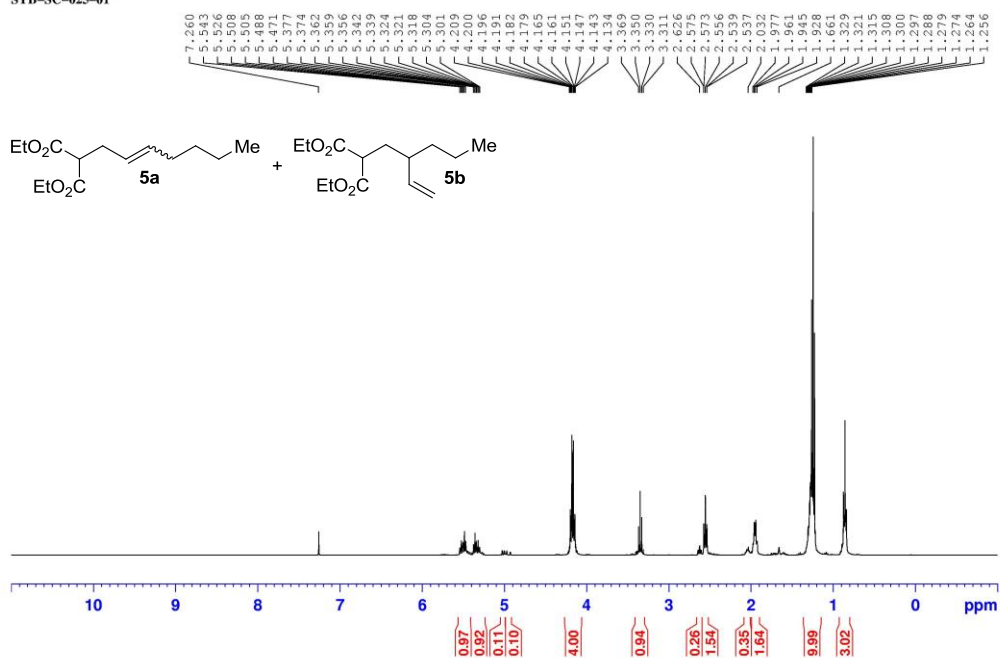


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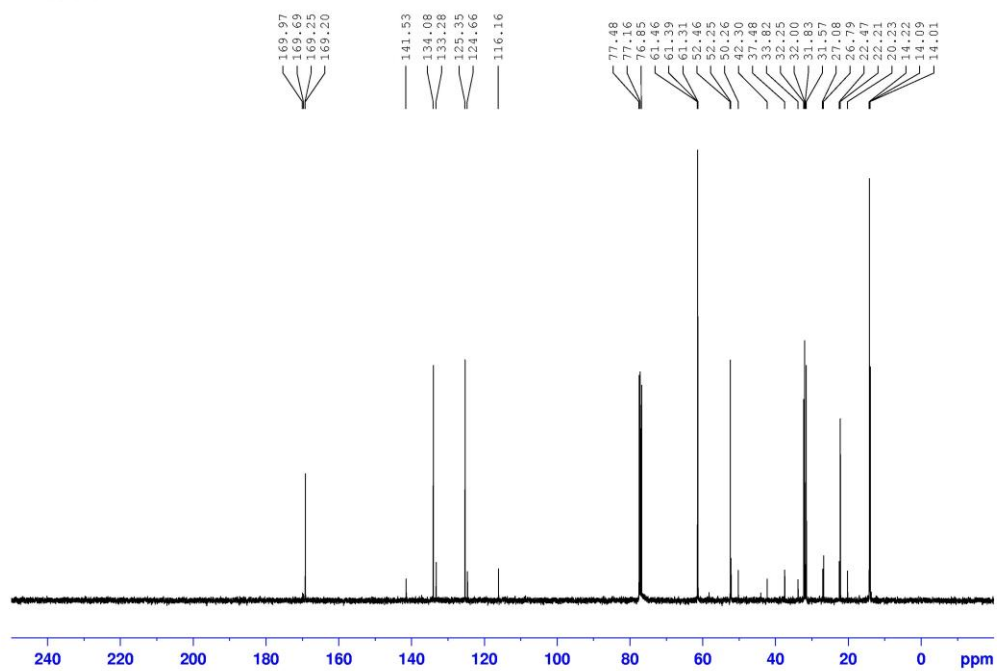


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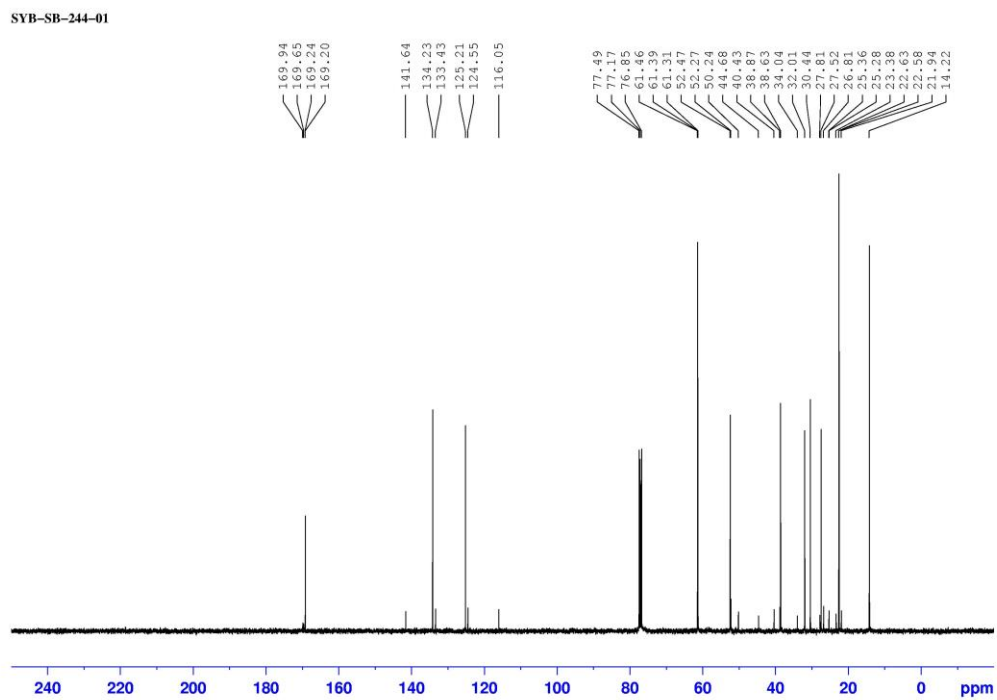
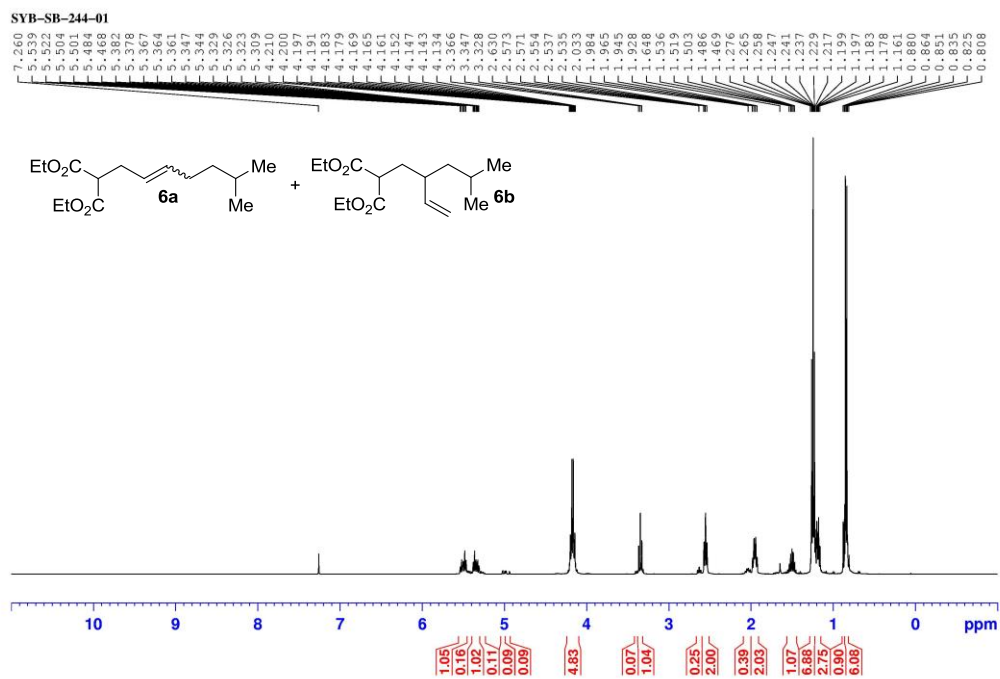
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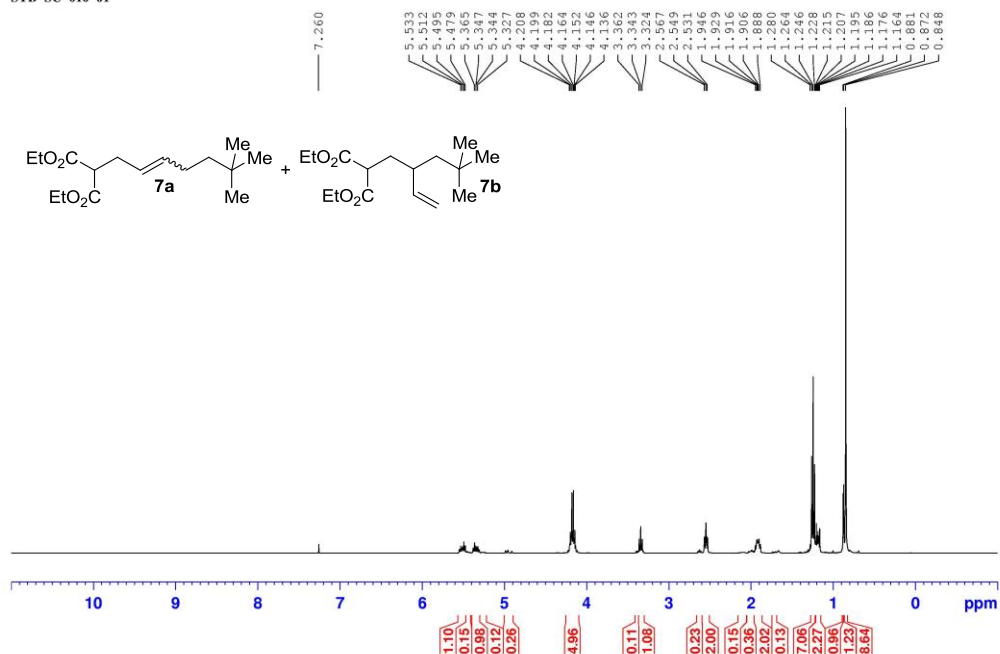


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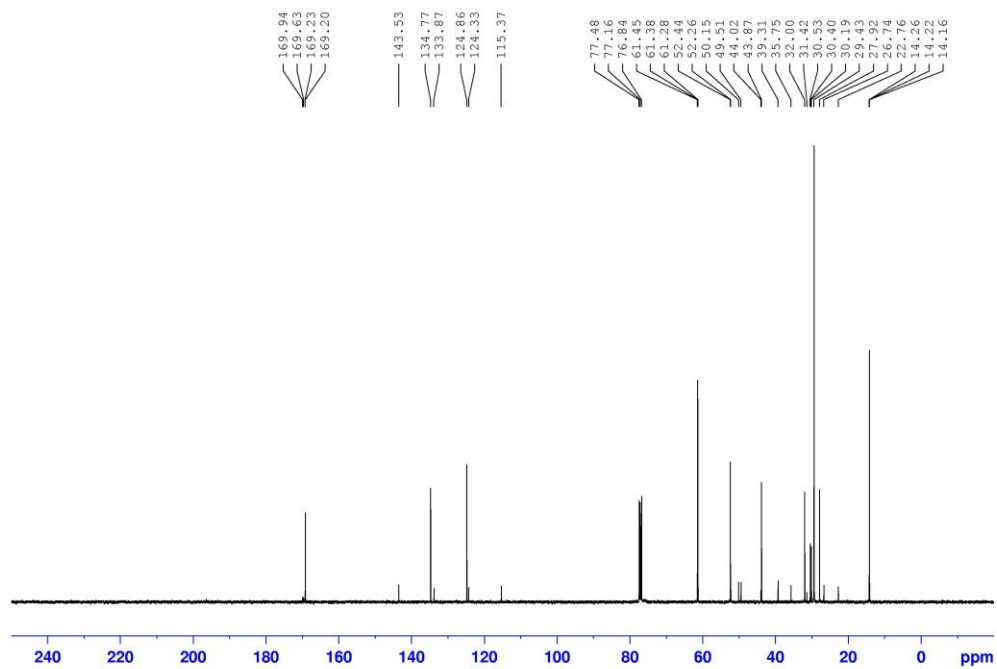


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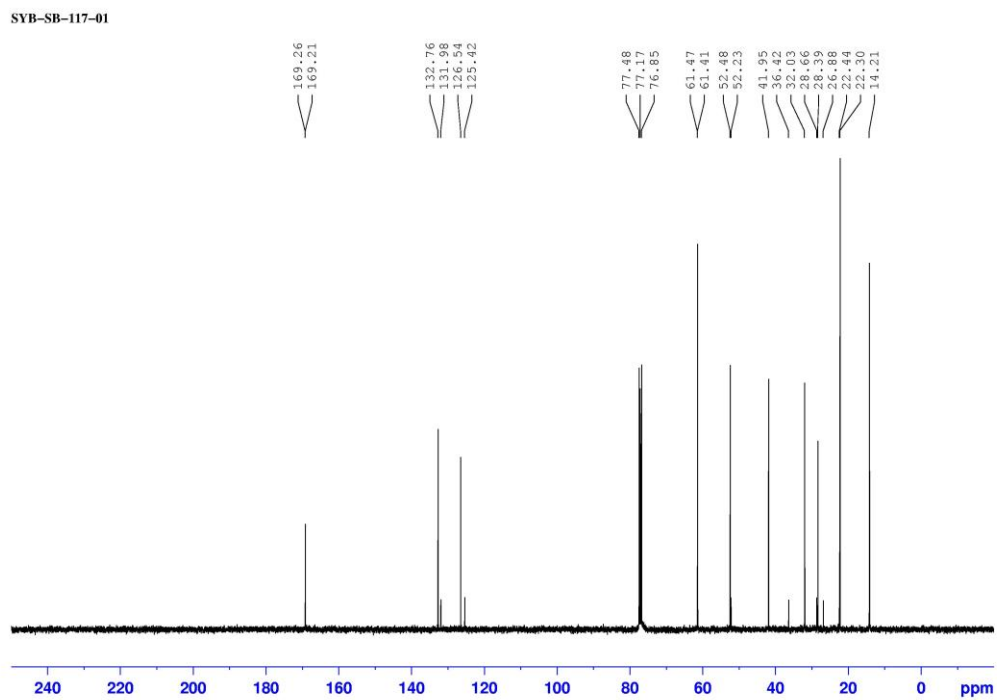
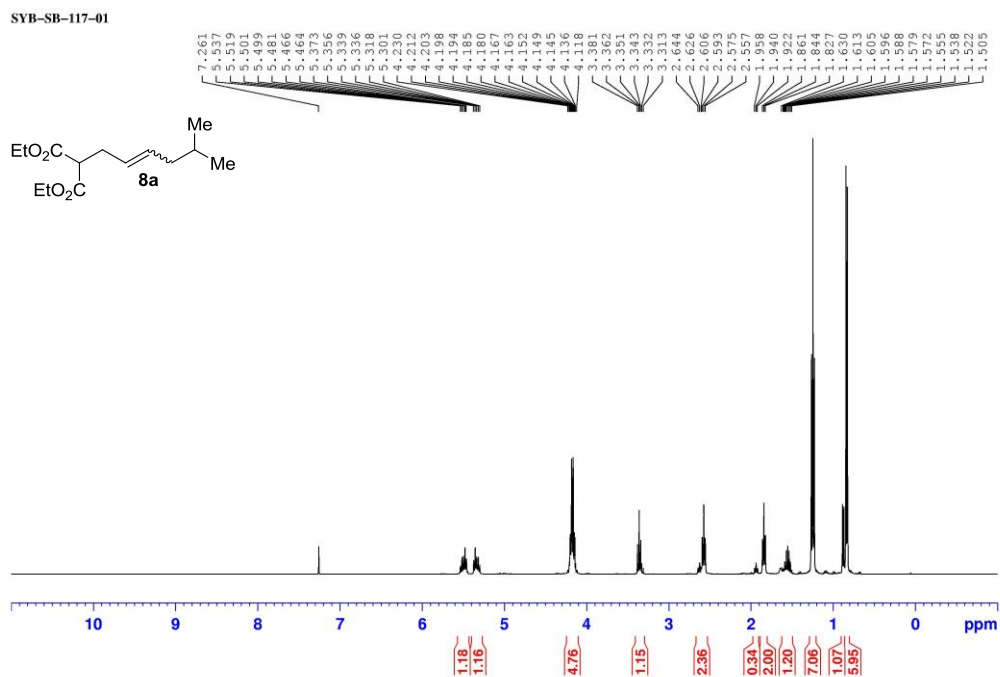
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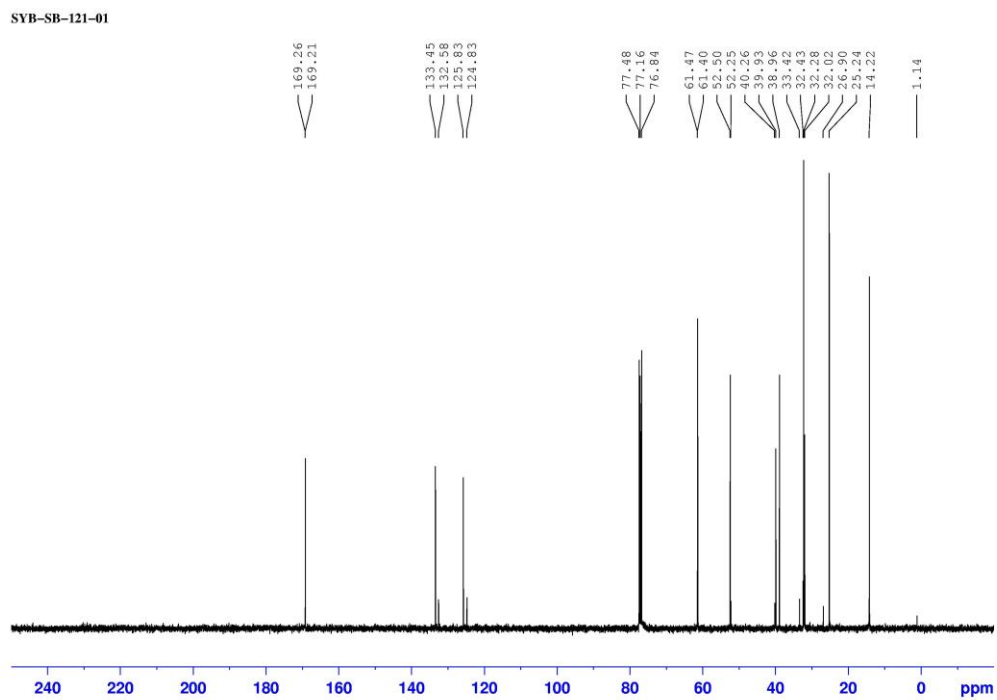
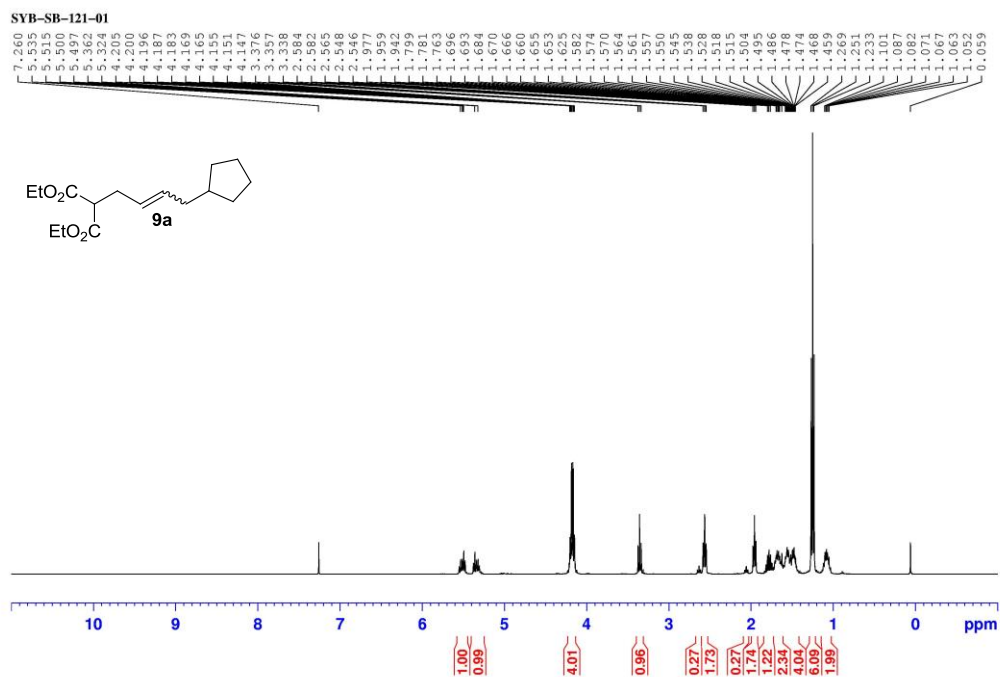
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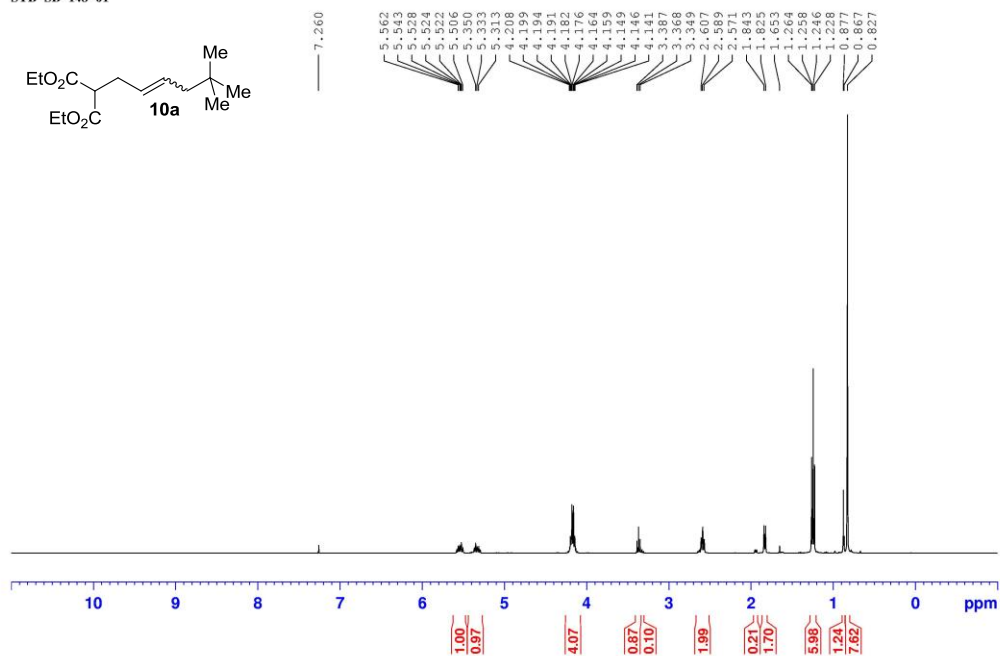


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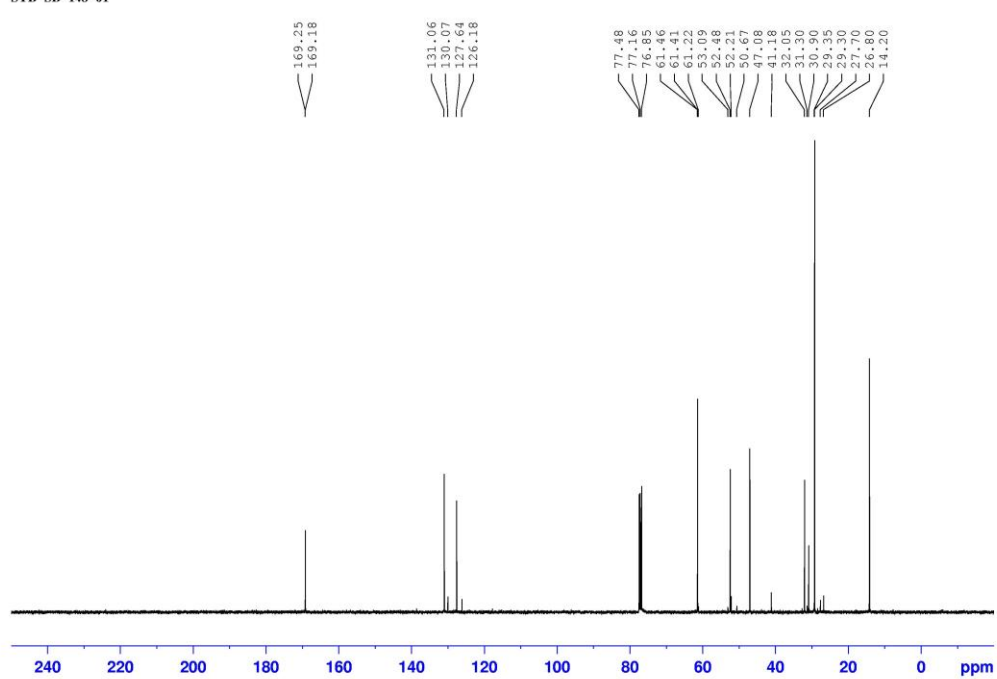


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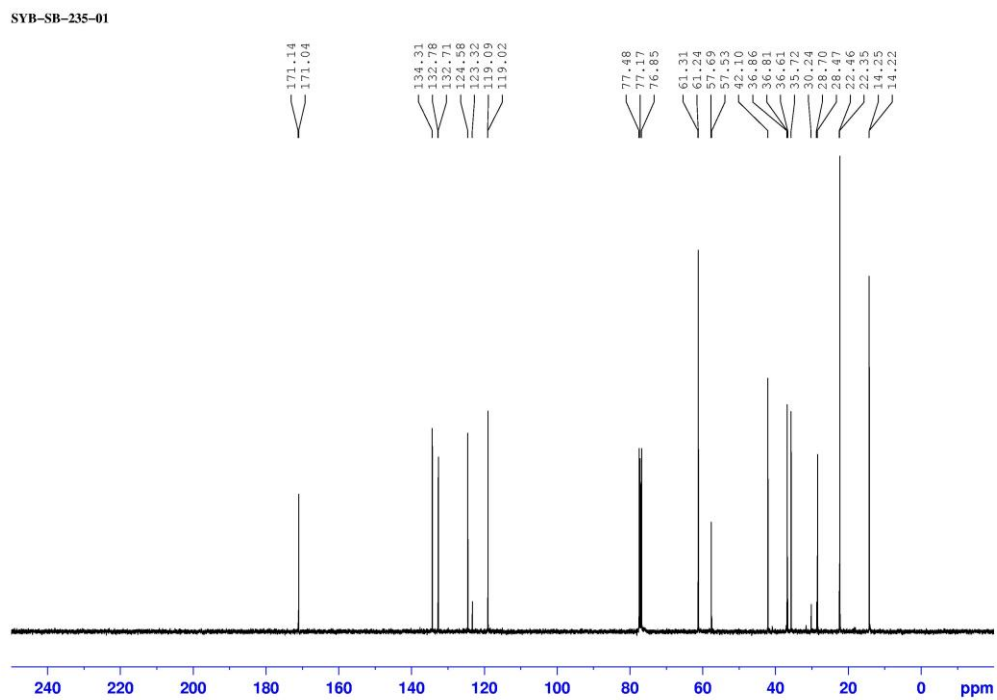
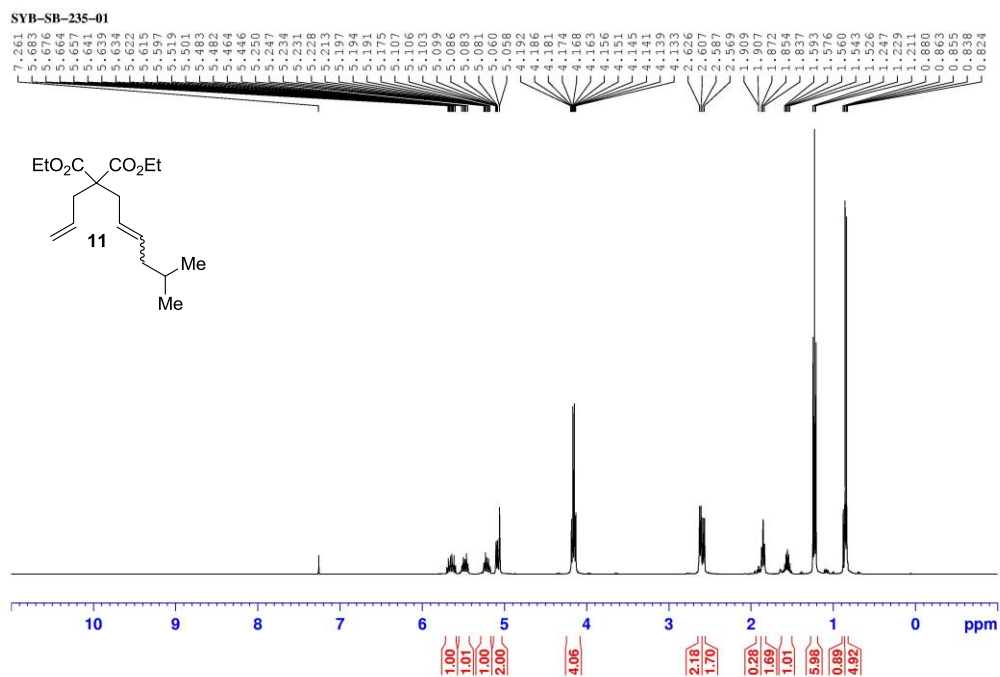
SYB-SB-148-01



SYB-SB-148-01

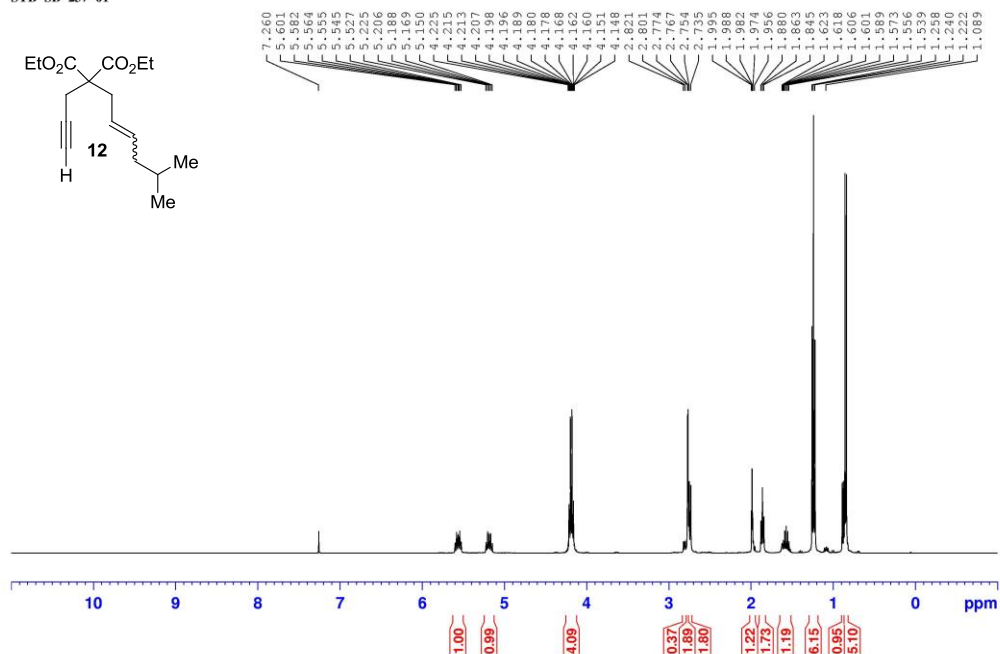


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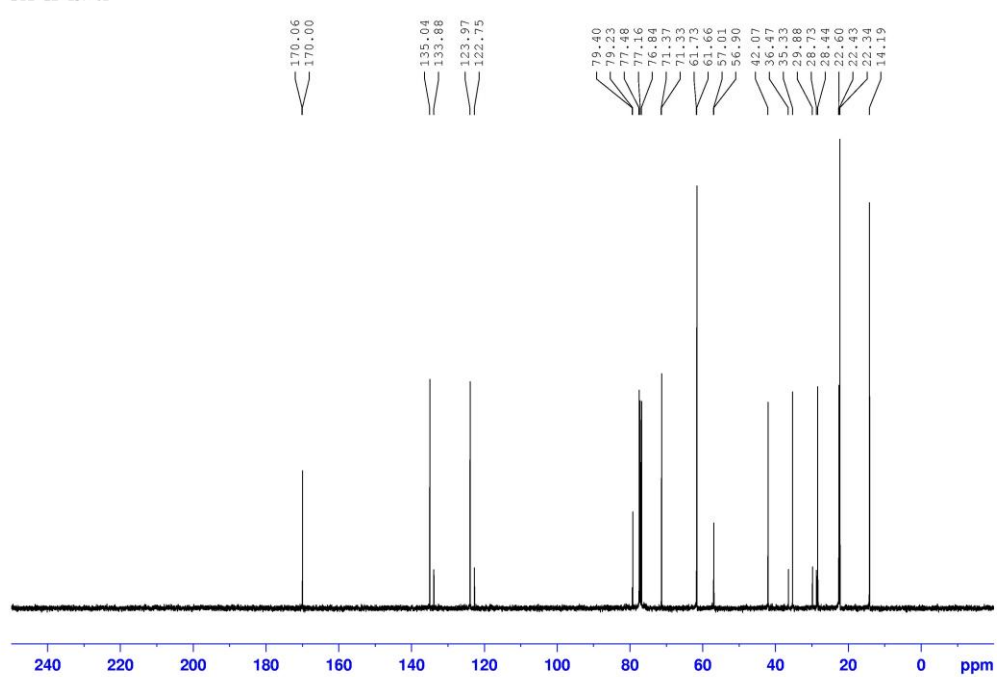


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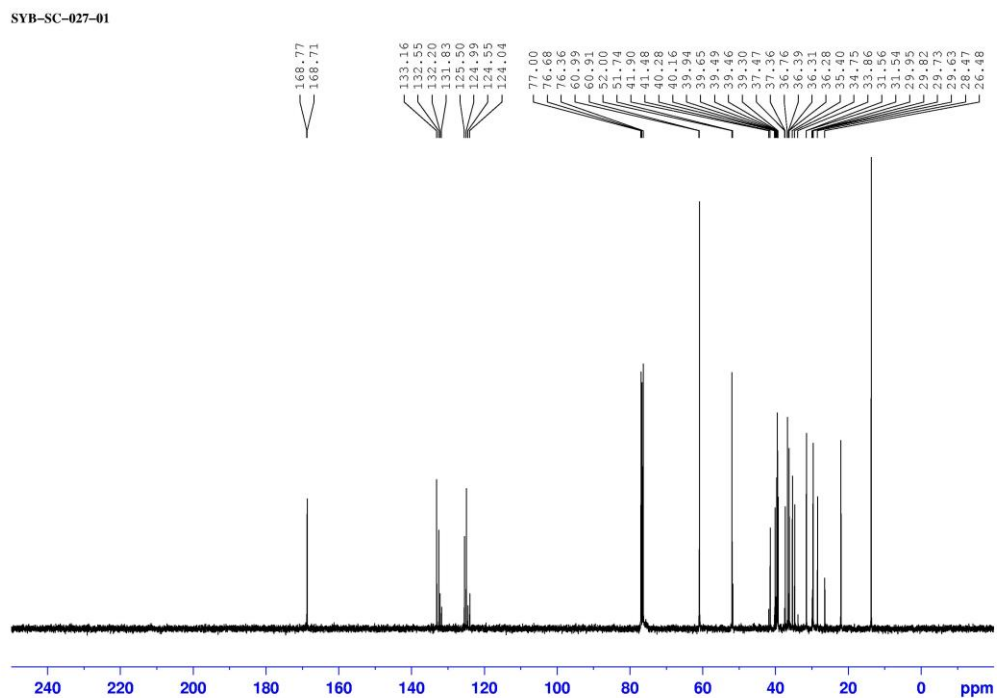
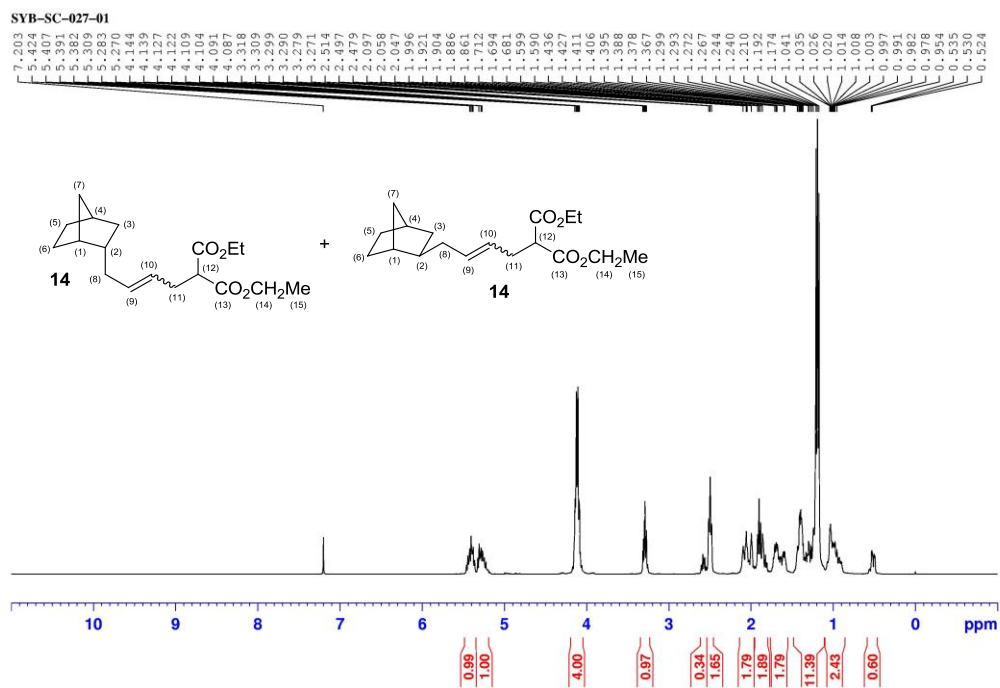
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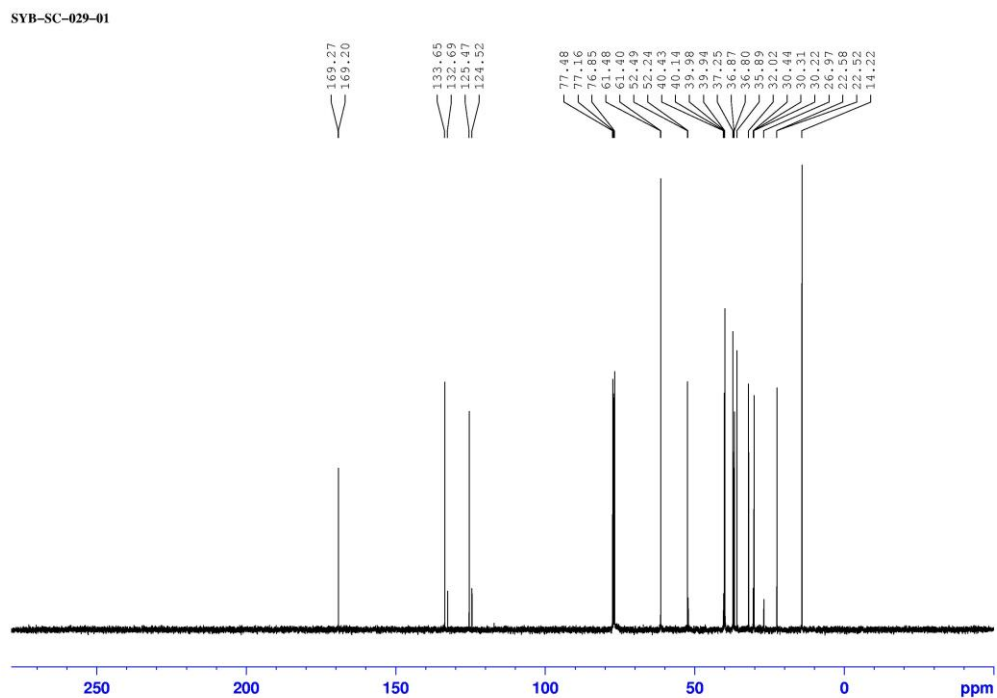
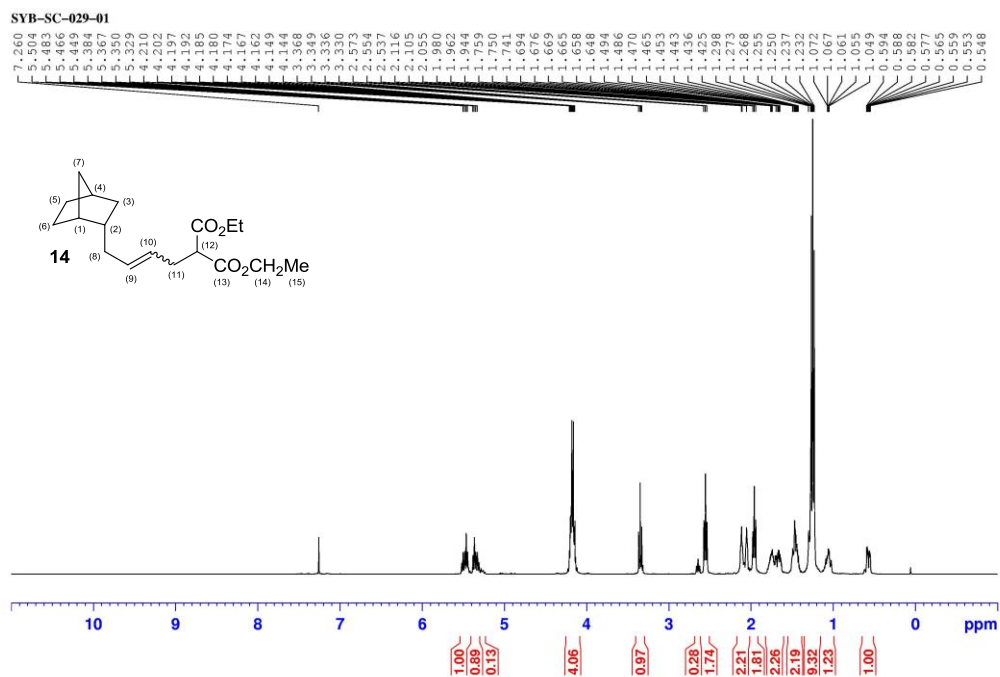
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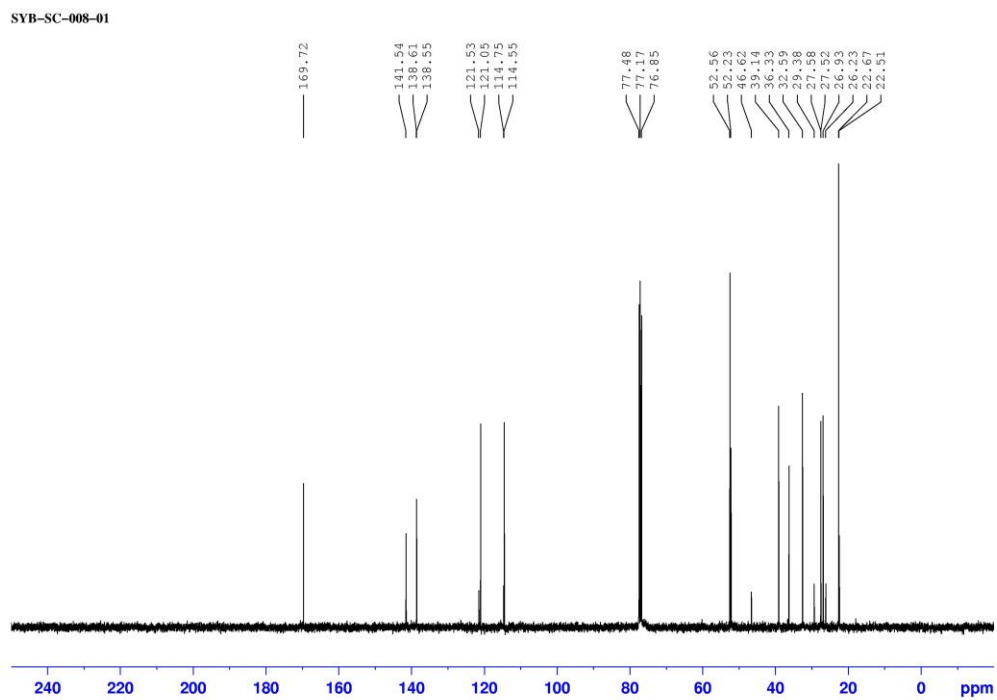
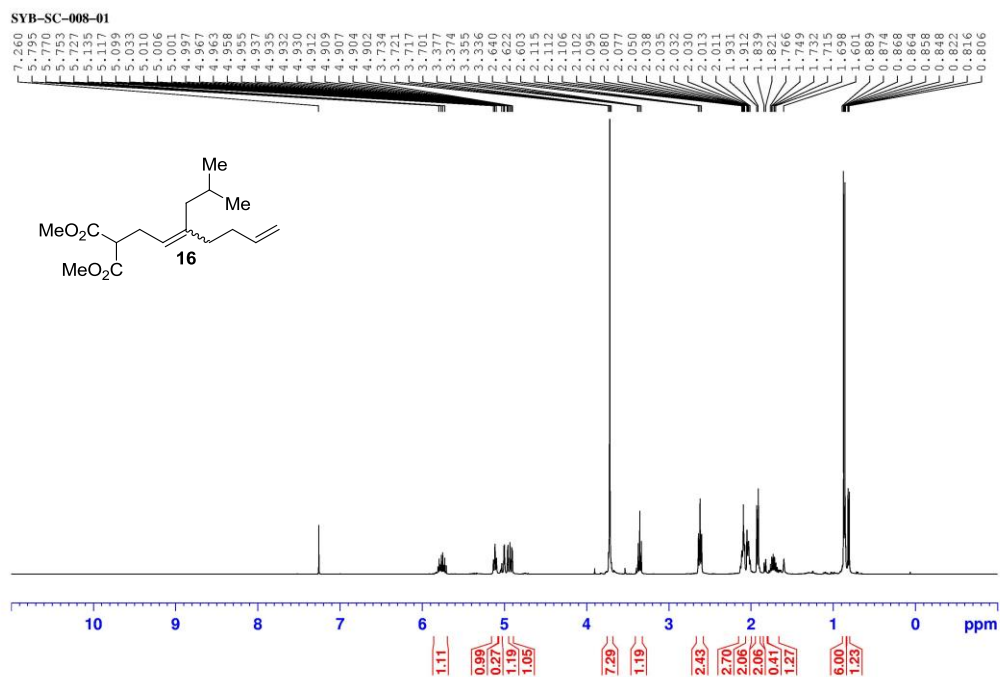
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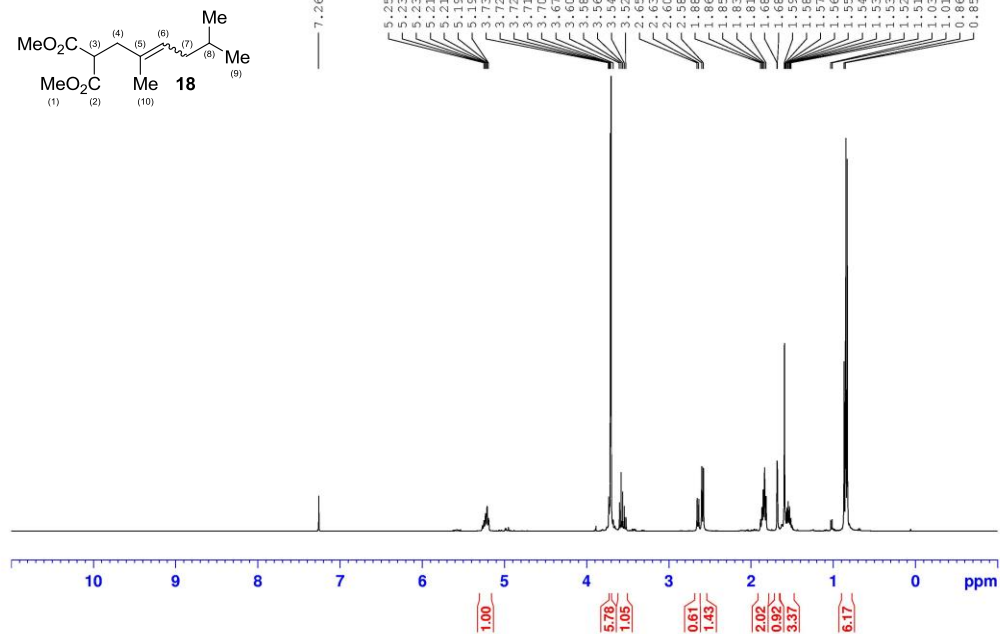


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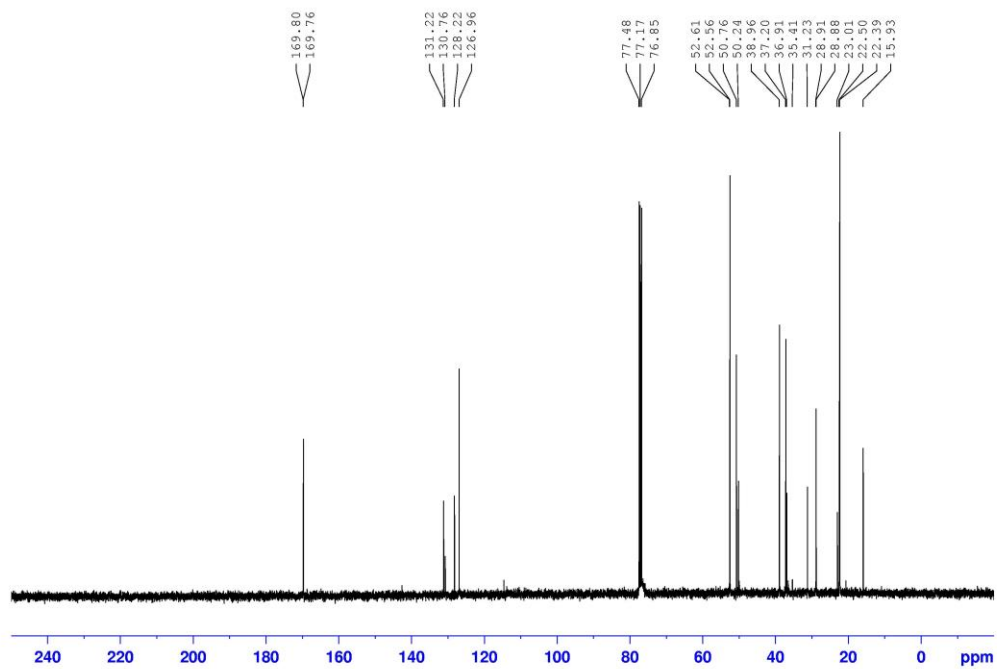


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SYB-SB-196-01

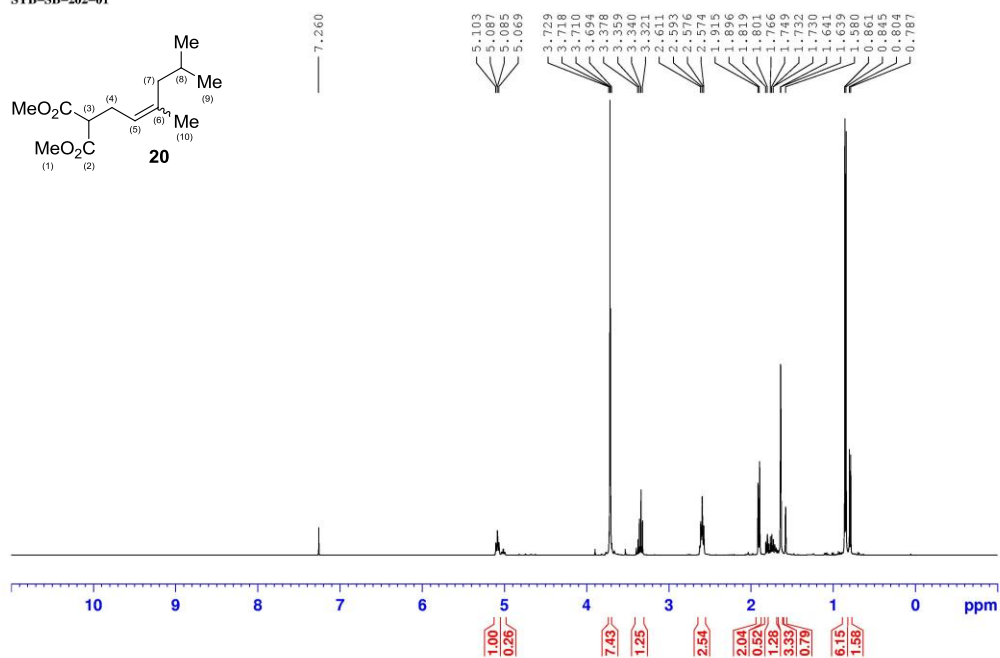


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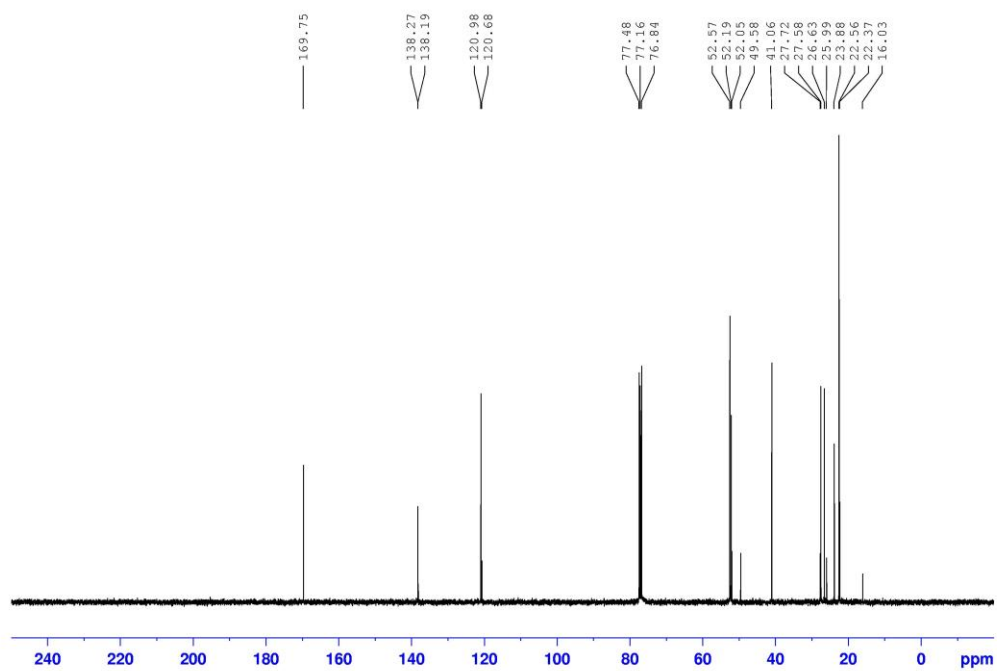


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SYB-SB-202-01

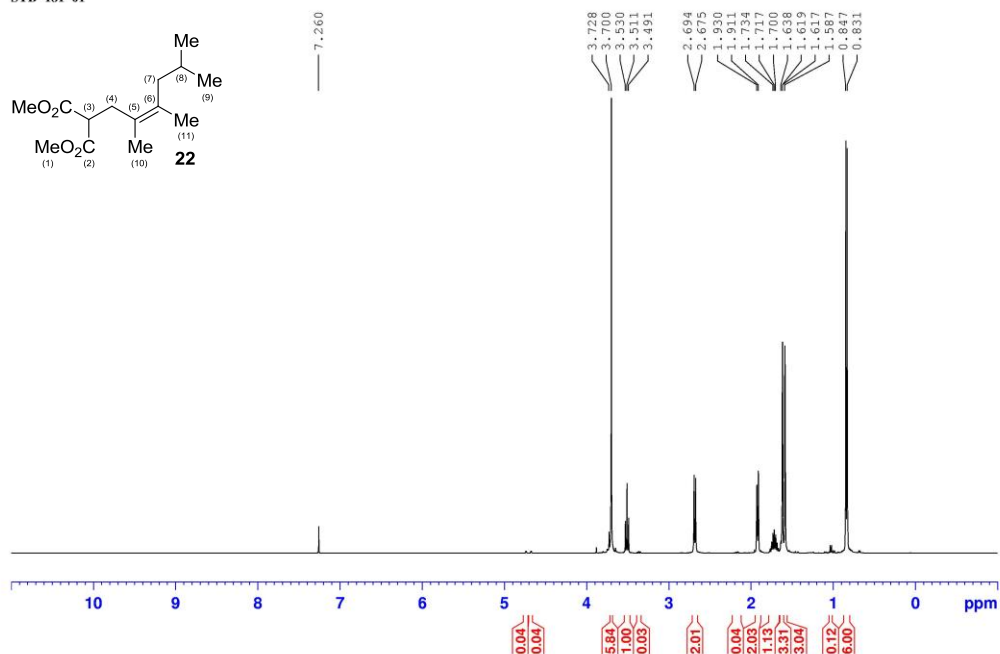


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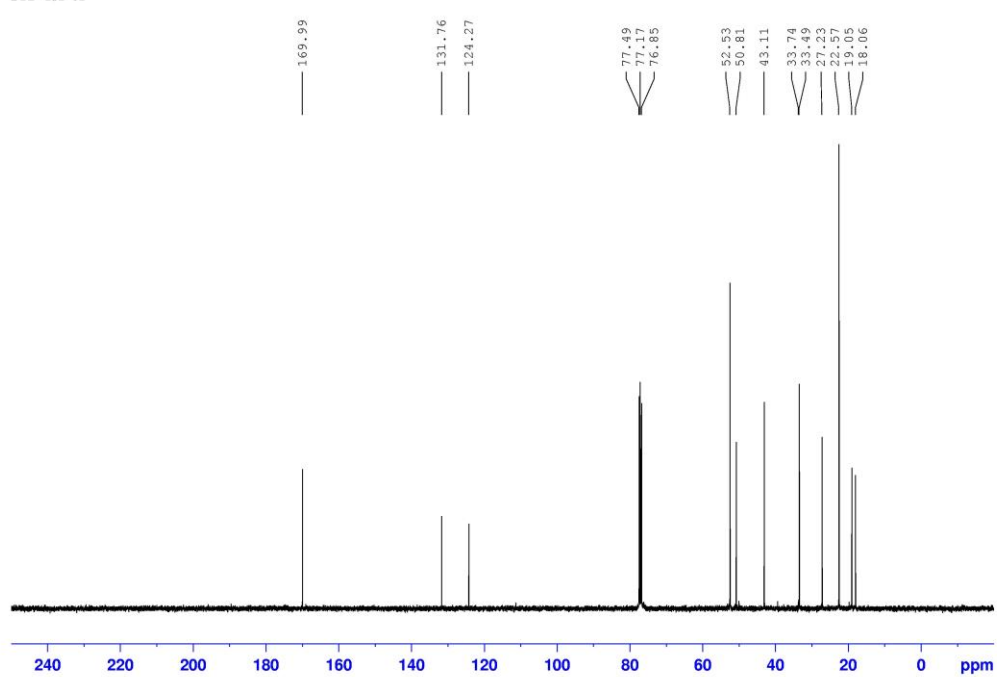


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SYB-181-01

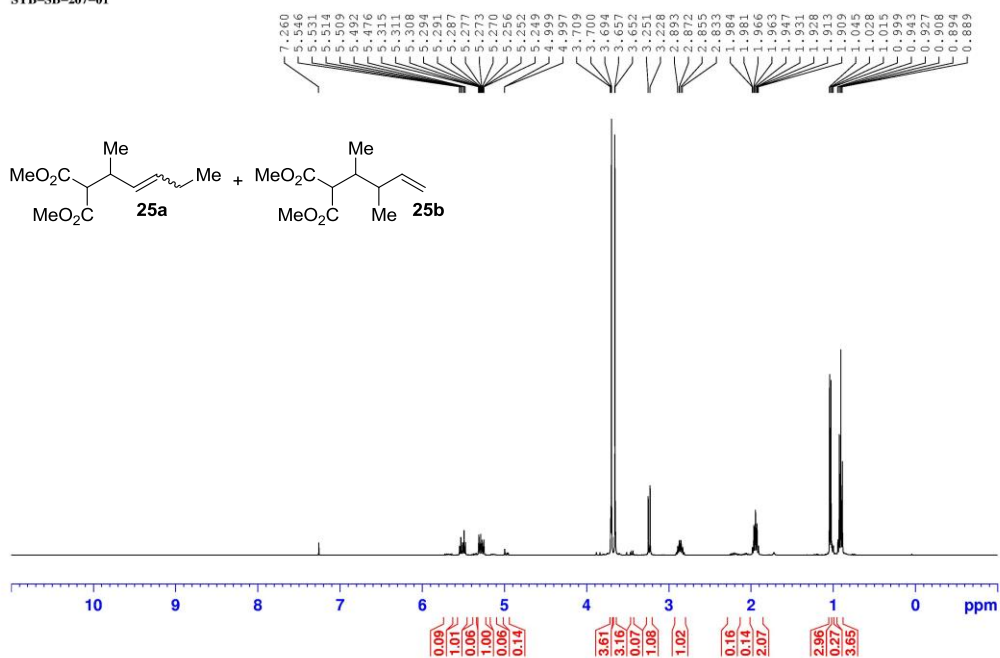


SYB-181-01

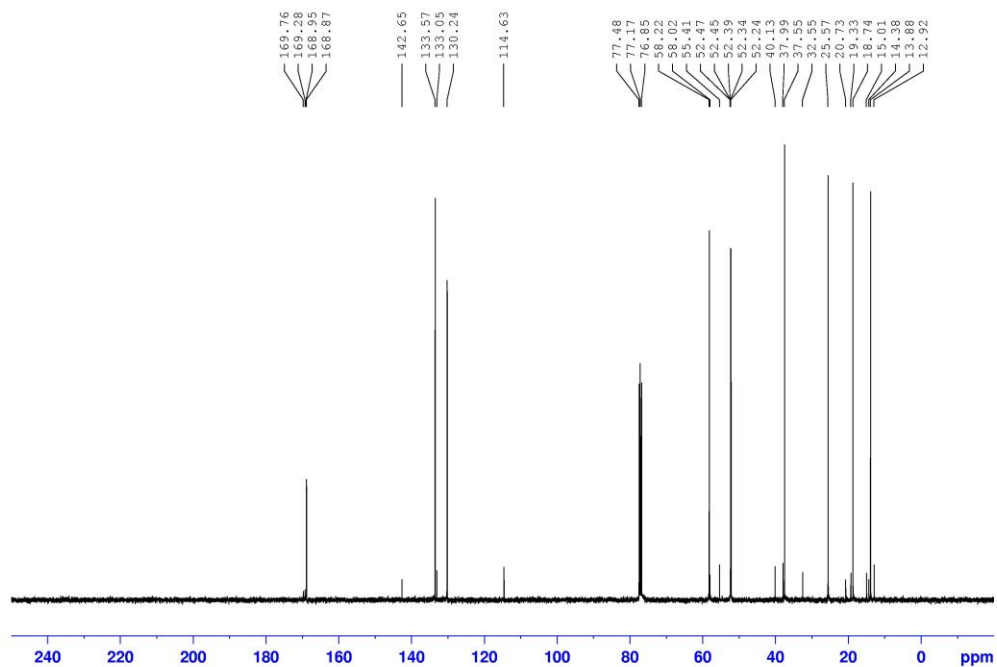


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SYB-SB-207-01

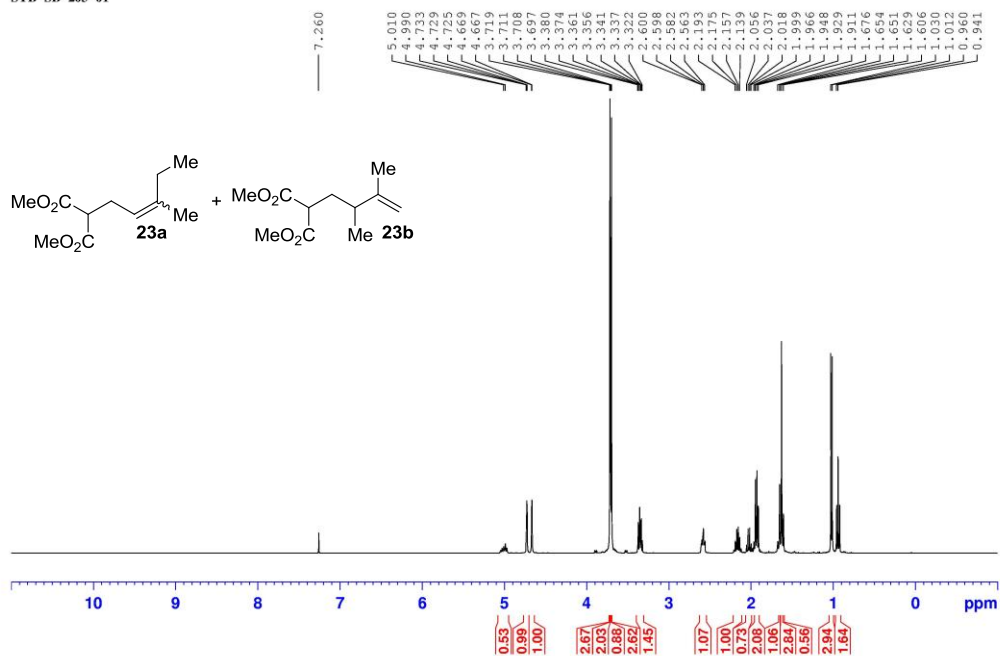


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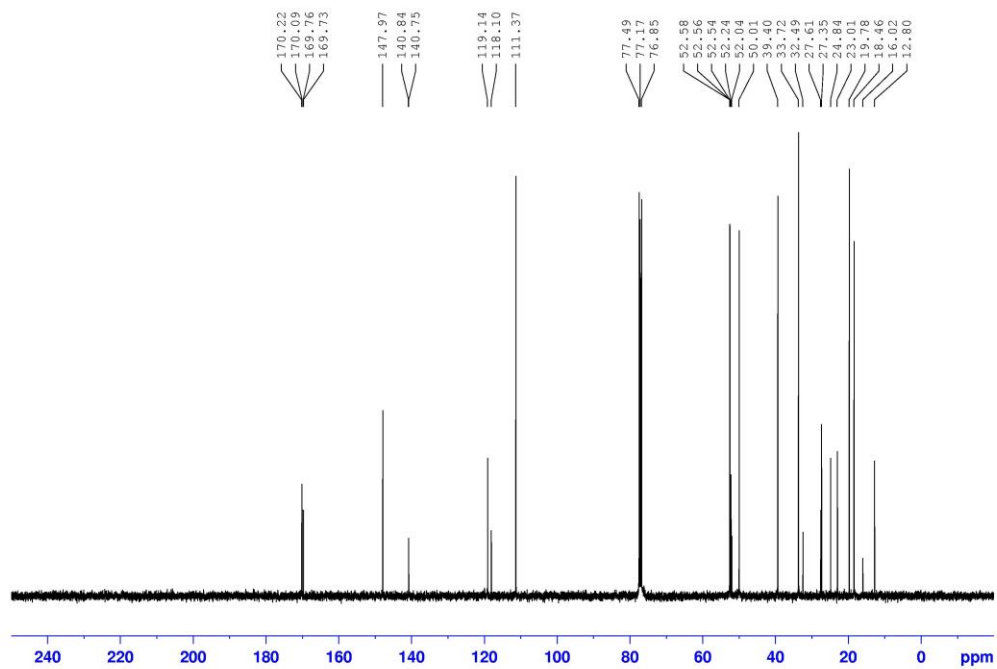


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SYB-SB-203-01

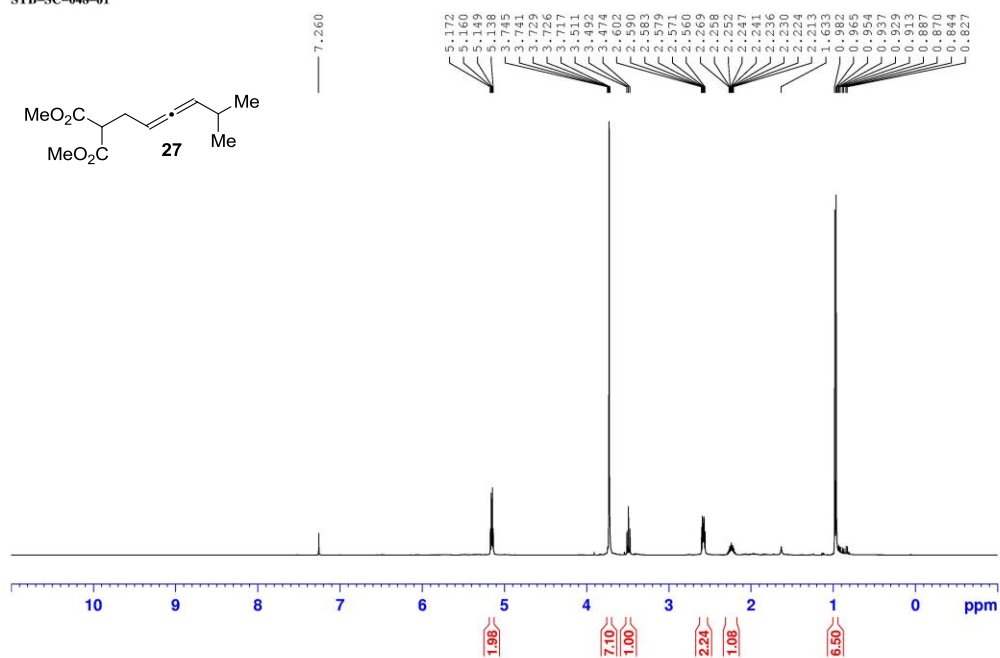


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SYB-SC-048-01

