Supporting Information

Ni-Catalyzed Reductive Coupling of α-Halocarbonyl Derivatives with Vinyl Bromides

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Table of Contents

I. Experimental Section

Part 1. General Information

1. Chemicals and Reagents

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk or glove box techniques. DMA (*N*,*N*-dimethylacetamide, 99.5%, extra dry, Acros) was purchased and used directly. Deuterated solvents were used as received ($CDCl_3$ from J&K Co., China). $NiCl_2$ (Alfa Aesar), $NiBr_2$ (Alfa Aesar), NiI_2 (Alfa Aesar), $Ni(COD)_2$ (Strem), $Ni(ClO_4)_2{\cdot}6H_2O$ (Alfa Aesar), $Ni(acac)_2$ (Aladdin Co., China) were used as received. Zinc powder (Aladdin) was activated with hydrochloric acid before use. Manganese powder (~325 mesh, 99.3%) was purchased from (Alfa Aesar) activated with hydrochloric acid before use. Anhydrous $MgCl_2$ (Alfa Aesar) was purchased, and used directly. All other reagents and starting materials were purchased from commercial sources and used without further purification.

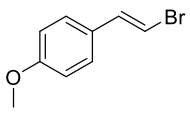
2. Physical method

Column chromatography was performed using silica gel 300-400 mesh (purchased from Qingdao-Haiyang Co., China) as the solid support. All NMR spectra were recorded on Bruker Avance 500 MHz spectrometer at STP unless otherwise indicated. ^1H NMR and ^{13}C NMR chemical shifts are reported in δ units, parts per million (ppm) relative to the chemical shift of residual solvent. Reference peaks for chloroform in ^1H NMR and ^{13}C NMR spectra were set at 7.26 ppm and 77 ppm, respectively. High-resolution mass spectra (HRMS) were obtained using a Bruker APEXIII 7.0 and IonSpec 4.7 TESLA FTMS. Low resolution mass spectra were recorded on GCMS-QP2010 SE (SHIMADZU). Melting point was recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China).

Part 2. Preparation of Vinyl Bromides

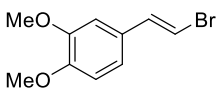
1. **General Procedure 1:** Synthesis of (*E*)-Vinyl bromide from cinnamic acid.[1, 2]

To a solution of cinnamic acid (20 mmol, 100 mol %) in CH_2Cl_2 (80 mL, technical grade) was added NEt_3 (0.5 mmol, 5 mol %). The mixture was stirred for 5 min at room temperature, and NBS (12 mmol, 120 mol %) was added in small portions. After 20 min, CO_2 evolution stopped indicating the completion of the reaction. CH_2Cl_2 was evaporated under reduced pressure and the remaining slush was purified by flash chromatography over silica gel (ethyl acetate/petroleum ether).



(*E*)-1-(2-Bromovinyl)-4-methoxybenzene[1, 2]

This compound was prepared from (*E*)-3-(4-methoxyphenyl)acrylic acid (3.56 g, 20.0 mmol) according to General Procedure 1. The crude residue was purified by silica gel chromatography (petroleum ether) to yield the vinyl bromide as a colorless crystal (3.40 g, 80%).

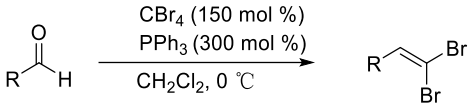


(*E*)-4-(2-Bromovinyl)-1, 2–dimethoxybenzene[3]

This compound was prepared from (*E*)-3-(3,4-dimethoxyphenyl)acrylic acid (4.16 g, 20.0 mmol) according to General Procedure 1. The crude residue was purified by silica gel chromatography (2% ethyl acetate/petroleum ether) to yield the vinyl bromide as a white solid (3.30 g, 80%).

2. **General Procedure 2:** Synthesis of (*E*)-vinyl bromide synthesis from aldehydes.

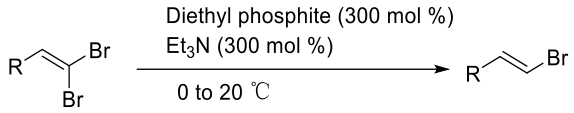
Step 1: The Ramirez protocol for the Wittig-type dibromoolefination.[4]



To a flame-dried flask was added aldehyde (20 mmol, 100 mol %), CBr_4 (30 mmol, 150 mol %), and CH_2Cl_2 (80 mL). The flask was cooled to 0 °C, at which point a solution of PPh_3 (60 mmol, 300 mol %) in CH_2Cl_2 (70 mL) was added dropwise via addition funnel over 30 min. The solution was stirred at 0 °C under N_2 for 1 h. About half of the volume of CH_2Cl_2 was removed under reduced pressure. Pentane (100 mL) was added, and triphenylphosphine oxide (TPPO) precipitated out. After filtration and evaporation of the solvent, the residue was dissolved in pentane (50 mL) which led to

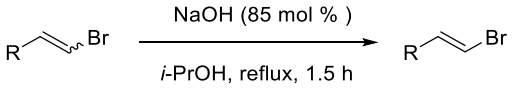
further precipitation of TPPO. Filtration and evaporation of the solvent afforded the crude dibromide which was directly used for the next step.

Step 2: Hayes protocol of the Hirao reaction.[5]

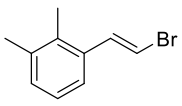


To a solution of the crude dibromide (~ 20.0 mmol, 100 mol %) and NEt_3 (60 mmol, 300 mol %) in DMF (20 mL) was added dimethylphosphonate (60.0 mmol, 300 mol %). The solution was stirred over night at room temperature. Water (60 mL) was added to the mixture, which was extracted with pentane (2 × 100 mL). The combined organic phases were washed with an aqueous solution of HCl (1 M, 55 mL) and dried over Na_2SO_4, filtered, and concentrated. The crude material was purified by flash chromatography.

Step 3: Selective destruction of the (*Z*)-isomer as reported by Dolby.[6]

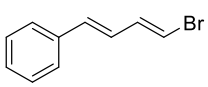


The crude product (~20.0 mmol, 100 mol %) from the previous step was dissolved in *i*-PrOH (30 mL). Solid NaOH (17.0 mmol, 85 mol %) was added and the mixture was heated to reflux for 1.5 hours. The reaction mixture was cooled to room temperature, diluted with pentane (100 mL), and partitioned with distillated H_2O (2 × 100 mL). The organic phase was collected, and washed with an aqueous solution of HCl (1M, 75 mL), dried over Na_2SO_4. The solvent was removed under reduced pressure. The crude material was purified by flash chromatography.



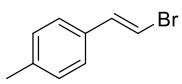
(*E*)-1-(2-Bromovinyl)-2,3-dimethylbenzene[7]

This compound was prepared from 2,3-dimethylbenzaldehyde (2.68 g, 20.0 mmol) according to General Procedure 2. The crude residue was purified by silica gel chromatography (petroleum ether) to yield the (*E*)-vinyl bromide (3.36 g, 80%) as a yellow oil.



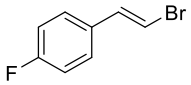
((1*E*,3*E*)-4-Bromobuta-1,3-dien-1-yl) benzene[8]

This compound was prepared from cinnamaldehyde (2.64 g, 20.0 mmol) according to General Procedure 2. The crude residue was purified by silica gel chromatography (petroleum ether) to yield the (*E*)-vinyl bromide (1.67 g, 40% yield) as a yellow oil.



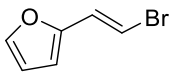
(*E*)-1-(2-Bromovinyl)-4-methylbenzene[7]

This compound was prepared from 4-methylbenzaldehyde (2.40 g, 20.0 mmol) according to General Procedure 2. The crude residue was purified by silica gel chromatography (petroleum ether) to yield the (*E*)-vinyl bromide (2.95 g, 75% yield) as a white solid.



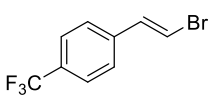
(*E*)-1-(2-Bromovinyl)-4-fluorobenzene[10]

This compound was prepared from 4-fluorobenzaldehyde (2.48 g, 20.0 mmol) according to General Procedure 2. The crude residue was purified by silica gel chromatography (petroleum ether) to yield the (*E*)-vinyl bromide (2.81 g, 70% yield) as a white solid.



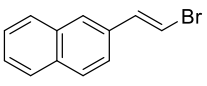
(*E*)-2-(2-Bromovinyl)furan[11]

This compound was prepared from furan-2-carbaldehyde (1.92 g, 20.0 mmol) according to General Procedure 2. The crude residue was purified by silica gel chromatography (petroleum ether) to yield the (*E*)-vinyl bromide (1.82 g, 54% yield) as a yellow oil.



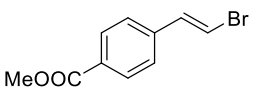
(*E*)-1-(2-Bromovinyl)-4-(trifluoromethyl)benzene[7]

This compound was prepared from 4-(trifluoromethyl)benzaldehyde (3.48 g, 20.0 mmol) according to General Procedure 2. The crude residue was purified by silica gel chromatography (petroleum ether) to yield the (*E*)-vinyl bromide (4.00 g, 80% yield) as a yellow oil.



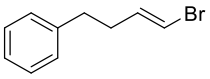
(*E*)-2-(2-Bromovinyl)naphthalene[10]

This compound was prepared from 2-naphthaldehyde (3.12 g, 20.0 mmol) according to General Procedure 2. The crude residue was purified by silica gel chromatography (petroleum ether) to yield the (*E*)-vinyl bromide (3.26 g, 70% yield) as a white solid.



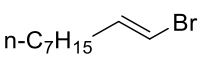
(*E*)-Methyl-4-(2-bromovinyl)benzoate[10]

This compound was prepared from 4-formylbenzoate (3.28 g, 20.0 mmol) according to General Procedure 2. The crude residue was purified by silica gel chromatography (1% ethyl acetate/petroleum ether) to yield the (*E*)-vinyl bromide (3.37 g, 70% yield) as a white solid.



(*E*)-(4-Bromobut-3-en-1-yl)benzene[12]

This compound was prepared from 3-phenylpropanal (2.68 g, 20.0 mmol) according to General Procedure 2. The crude residue was purified by silica gel chromatography (petroleum ether) to yield the (*E*)-vinyl bromide (2.11 g, 50% yield) as a colorless oil.



1-Bromo-1-nonene[13]

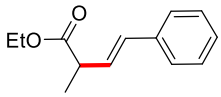
This compound was prepared from octanal (2.56 g, 20.0 mmol) according to General Procedure 2. The crude residue was purified by silica gel chromatography (petroleum ether) to yield the vinyl bromide, (*E*/*Z* = 35/65, GC-MS analysis), (1.64 g, 40% yield) as a colorless oil.

Part 3. Reductive Vinylation of α-Halo Carbonyl Derivatives with Vinyl Halides

1. *General procedures*

***General Procedure A* for the coupling of α-halocarbonyl derivatives with aryl-conjugated vinyl halides (*GP-A*):** To a flame-dried Schlenk tube was charge with vinyl bromide (0.30 mmol, 200 mol %, if solid), α-halocarbonyl compound (0.15 mmol, 100 mol %, if solid), Mn (16.5 mg, 0.30 mmol, 200 mol %), $MgCl_2$ (14.2 mg, 0.15 mmol, 100 mol %，if the reactant is α-bromocarbonyl derivatives). The tube was moved into a dry glove box, at which point $Ni(COD)_2$ (4.2 mg, 0.015 mmol, 10 mol %). The tube was capped with a rubber septum, and it was moved out of the glove box. Vinyl bromide (0.30 mmol, 200 mol %, if liquid), α-Halocarbonyl (0.15 mmol, 100 mol %, if liquid), solvent (1 mL) and pyridine (11.8 mg, 0.15 mmol, 100 mol %) werw then added via a syringe. After the reaction mixture was allowed to stir for 16 hours under N_2 atmosphere at 25 °C, it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM. Flash column chromatography provided the product as a solid or oil. The *E/Z* ratio of the product was determined by GC-MS.

***General Procedure B* for the coupling of α-halocarbonyl derivatives with alkyl-substituted vinyl halides (*GP-B*):** To a flame-dried Schlenk tube was charge with vinyl bromide (0.30 mmol, 200 mol %, if solid), α-Halocarbonyl compound (0.15 mmol, 100 mol %, if solid), 2,2'-dipyridine (70.0 mg, 0.045 mmol, 30 mol%), Mn (16.5 mg, 0.30 mmol, 200 mol %), $MgCl_2$ (14.2 mg, 0.15 mmol, 100 mol %，if the reactant is α-bromocarbonyl derivative). The tube was moved into a dry glove box, at which point $Ni(COD)_2$ (4.2 mg, 0.015 mmol, 10 mol %). The tube was capped with a rubber septum, and it was moved out of the glove box. Vinyl bromide (0.30 mmol, 200 mol %, if liquid), α-halocarbonyl (0.15 mmol, 100 mol %, if liquid), solvent (1 mL) and pyridine (11.8 mg, 0.15 mmol, 100 mol %) were then added via a syringe. After the reaction mixture was allowed to stir for 16 hours under N_2 atmosphere at 25 °C, it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM. Flash column chromatography provided the product as a solid or oil. The *E/Z* ratio of the product was determined by GC-MS.



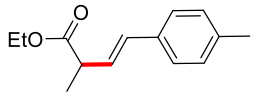
(*E*)-Ethyl 2-methyl-4-phenylbut-3-enoate (3).

This compound was prepared according to the ***GP-A***, using ethyl 2-chloropropionate (20.4 mg, 0.150 mmol, 100 mol %), (2-bromovinyl)benzene (*E/Z* = 84/16) (54.3 mg, 0.30 mmol, 200 mol %). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 88% yield (26.9 mg, 0.132 mmol, *E/Z* = 90/10, determined by GC-MS) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38-7.35 (m, 2H), 7.34-7.29 (m, 2H), 7.24-7.21 (m, 1H), 6.49-6.46 (d, *J* = 15.9 Hz, 1H), 6.31-6.26 (dd, *J* = 8.0 Hz, *J* = 15.9 Hz, 1H), 4.18-4.14 (q, *J* = 7.0 Hz, 2H), 3.33-3.27 (m, 1H), 1.37-1.36 (d, *J* = 7.1 Hz, 3H), 1.29-1.26 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.4, 136.8, 128.8, 128.4, 127.4, 126.2, 60.6, 43.2, 17.4, 14.1.

HRMS (ESI): calculated for $C_{13}H_{16}O_2$ $[M]^+$ 227.1043; found: 227.1042.



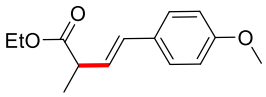
(*E*)-Ethyl 2-methyl-4-(p-tolyl)but-3-enoate (4).

This compound was prepared according to the ***GP-A***, using ethyl 2-chloropropionate (20.4 mg, 0.150 mmol, 100 mol %), (*E*)-1-(2-bromovinyl)-4-methylbenzene (59.1 mg, 0.30 mmol, 200 mol %). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 92% yield (30.1 mg, 0.138 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-7.26 (d, *J* = 8.0 Hz, 1H), 7.12-7.10 (d, *J* = 7.9 Hz, 2H), 6.46-6.43 (d, *J* = 16.1 Hz, 1H), 6.25-6.20 (dd, *J* = 8.0 Hz, *J* = 16.1 Hz, 1H), 4.18-4.13 (q, *J* = 7.0 Hz, 2H), 3.31-3.25 (m, 1H), 2.33 (s, 3H), 1.36-1.34 (d, *J* = 7.0 Hz, 3H), 1.28-1.25 (t, *J* = 7.5Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.6, 137.2, 134.0, 130.8, 129.1, 127.8, 126.1, 60.6, 43.2, 21.1, 17.4, 14.1.

HRMS (ESI): calculated for $C_{13}H_{16}O_2$ $[M]^+$ 219.1379; found: 219.1378.



(*E*)-Ethyl 4-(4-methoxyphenyl)-2-methylbut-3-enoate(5).

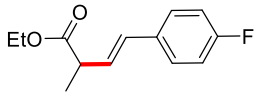
This compound was prepared according to the ***GP-A***, using ethyl 2-chloropropionate (20.4 mg, 0.150 mmol, 100 mol %), (*E*)-1-(2-bromovinyl)-4-methoxybenzene (63.3 mg, 0.30 mmol, 200 mol %). After purification by column chromatography (SiO_2: 1% ethyl acetate in

petroleum ether), the title compound was isolated in 87% yield (30.5 mg, 0.130 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.29 (d, *J* = 8.7 Hz, 2H), 6.85-6.83 (d, *J* = 8.7 Hz, 2H), 6.43-6.40 (d, *J* = 15.9 Hz, 1H), 6.15-6.12 (dd, *J* = 7.9 Hz, *J* = 15.9 Hz, 1H), 4.18-4.13 (q, *J* = 7.0 Hz, 2H), 3.79 (s, 3H), 3.30-3.24 (m, 1H), 1.36-1.34 (d, *J* = 7.0 Hz, 3H), 1.8-1.25 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.6, 159.0, 130.3, 129.6, 127.3, 126.5, 113.8, 60.5, 55.1, 43.1, 17.4, 14.1.

HRMS (ESI): calculated for $C_{14}H_{18}O_3$ $[M]^+$ 235.1329; found: 235.1327.



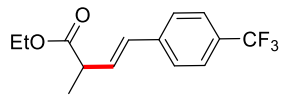
(*E*)-Ethyl 4-(4-fluorophenyl)-2-methylbut-3-enoate (6).

This compound was prepared according to the ***GP-A***, using ethyl 2-chloropropionate (20.4 mg, 0.150 mmol, 100 mol %), (*E*)-1-(2-bromovinyl)-4-fluorobenzene (60.3 mg, 0.30 mmol, 200 mol %). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 91% yield (30.3 mg, 0.137 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.31 (m, 2H), 7.00-6.97 (m, 2H), 6.45-6.41 (d, *J* = 16.0 Hz, 1H), 6.22-6.17 (dd, *J* = 8.0 Hz, *J* = 16.0 Hz, 1H), 4.18-4.14 (q, *J* = 7.0 Hz, 2H), 3.30-3.25 (m, 1H), 1.36-1.34 (d, *J* = 7.0 Hz, 3H), 1.28-1.25 (t, *J* = 7.5Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.4, 162.2 (d, *J* = 246.56 Hz), 129.8, 128.5, 127.7 (d, *J* = 8.02 Hz), 115.4, 115.2, 60.7, 43.1, 17.4, 14.1.

HRMS (ESI): calculated for $C_{14}H_{18}O_3$ $[M]^+$ 235.1329; found: 235.1327.



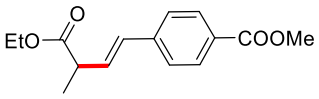
(*E*)-Ethyl 2-methyl-4-(4-(trifluoromethyl)phenyl)but-3-enoate (7).

This compound was prepared according to the ***GP-A***, using ethyl 2-chloropropionate (20.4 mg, 0.150 mmol, 100 mol %), (*E*)-1-(2-bromovinyl)-4-(trifluoromethyl)benzene (75.3 mg, 0.30 mmol, 200 mol %). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (36.8 mg, 0.135 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56-7.54 (d, *J* = 8.1 Hz, 2H), 7.46-7.44 (d, *J* = 8.1, 2H), 6.52-6.48 (d, *J* = 15.9 Hz, 1H), 6.41-6.37 (dd, *J* = 8.0 Hz, *J* = 15.9 Hz, 1H), 4.19-4.15 (q, *J* = 7.0 Hz, 2H), 3.35-3.29 (m, 1H), 1.38-1.37 (d, *J* = 7.0, 3H), 1.29-1.26 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.1, 140.4, 131.6, 129.7, 129.1 (dd, *J* = 32.59 Hz), 126.4, 125.4 (dd, *J* = 3.71 Hz), 124.1 (dd, *J* = 271.99 Hz), 60.8, 43.2, 17.2, 14.1.

HRMS (ESI): calculated for $C_{14}H_{15}F_3O_2$ $[M]^+$ 273.1099; found: 273.1096.

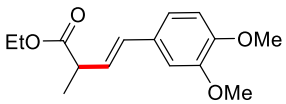


(*E*)-Methyl 4-(4-ethoxy-3-methyl-4-oxobut-1-en-1-yl)benzoate (8). This compound was prepared according to the ***GP-A***, using Ethyl 2-chloropropionate (20.4 mg, 0.150 mmol, 100 mol %), methyl (*E*)-4-(2-bromovinyl)benzoate (75.3 mg, 0.30 mmol, 200 mol %). After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (35.4 mg, 0.135 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97-7.96 (d, *J* = 8.3 Hz, 2H), 7.42-7.40 (d, *J* = 8.3, 2H), 6.51-6.48 (d, *J* = 15.9 Hz, 1H), 6.43-6.38 (dd, *J* = 8.0 Hz, *J* = 15.9 Hz, 1H), 4.18-4.14 (q, *J* = 7.0 Hz, 2H), 3.89 (s, 3H), 3.34-3.28 (m, 1H), 1.37-1.36 (d, *J* = 7.0, 3H), 1.28-1.25 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.1, 166.8, 141.3, 131.5, 130.1, 129.8, 128.8, 126.1, 60.8, 52.0, 43.2, 17.2, 14.1.

HRMS (ESI): calculated for $C_{14}H_{18}O_4$ $[M]^+$ 263.1278; found: 263.1277.

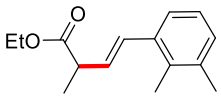


(*E*)-Ethyl 4-(3,4-dimethoxyphenyl)-2-methylbut-3-enoate (9). This compound was prepared according to the ***GP-A***, using ethyl 2-chloropropionate (20.4 mg, 0.150 mmol, 100 mol %), (*E*)-4-(2-bromovinyl)-1,2-dimethoxybenzene (72.9 mg, 0.30 mmol, 200 mol %). After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (35.6 mg, 0.135 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.92 (s, 1H), 6.89-6.87 (m, 1H), 6.82-6.78 (d, *J* = 8.2 Hz, 1H), 6.42-6.38 (d, *J* = 15.9Hz, 1H), 6.15-6.10 (dd, *J* = 8.0 Hz, *J* = 15.9Hz, 1H), 4.17-4.12 (q, *J* = 7.0 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H), 3.29-3.23 (m, 1H), 1.35-1.34 (d, *J* = 7.0Hz, 3H), 1.27-1.24 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.6, 148.8, 148.6, 130.6, 129.9, 126.8, 119.4, 110.9, 108.4, 60.6, 55.8, 55.7, 43.1, 17.5, 14.1.

HRMS (ESI): calculated for $C_{15}H_{20}O_4$ $[M]^+$ 265.1434; found: 235.1433.



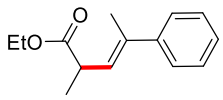
(*E*)-Ethyl 4-(2,3-dimethylphenyl)-2-methylbut-3-enoate (10).

This compound was prepared according to the ***GP-A***, using ethyl 2-chloropropanoate (29.7 mg, 0.150 mmol, 100 mol %), (*E*)-1-(2-bromovinyl)-2,3-dimethylbenzene (63.3 mg, 0.30 mmol, 200 mol %). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 60% yield (20.9 mg, 0.09 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29-7.28 (m, 1H), 7.09-7.08 (d, *J* = 4.7 Hz, 2H), 6.80-6.77 (d, *J* = 15.7 Hz, 1H), 6.13-6.08 (dd, *J* = 8.0 Hz, *J* = 15.7 Hz, 1H), 4.21-4.17 (q, *J* = 7.0 Hz, 2H), 3.37-3.32 (m, 1H), 2.3 (s, 3H), 2.2 (s, 3H), 1.41-1.39 (d, *J* = 7.1Hz, 3H), 1.31-1.29 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.5, 136.6, 136.4, 133.7, 130.5, 129.8, 129.0, 125.4, 124.0, 60.5, 43.4, 20.5, 17.4, 15.2, 14.1.

HRMS (ESI): calculated for $C_{15}H_{20}O_2$ $[M]^+$ 255.1356; found: 255.1353.



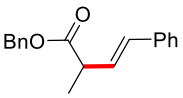
(*E*)-Ethyl 2-methyl-4-phenylpent-3-enoate (11).

This compound was prepared according to the ***GP-A***, using ethyl 2-chloropropanoate (29.7 mg, 0.150 mmol, 100 mol %), (*E*)-(1-bromoprop-1-en-2-yl)benzene (59.1 mg, 0.30 mmol, 200 mol %). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 48% yield (15.7 mg, 0.072 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.38 (d, *J* = 7.7 Hz, 2H), 7.33-7.30 (m, 2H), 7.24-7.23 (m, 1H), 5.80-5.78 (dd, *J* = 8.0 Hz, 1H), 4.17-4.13 (q, *J* = 7.0 Hz, 2H), 3.54-3.48 (m, 1H), 2.09 (s, 3H), 1.33-1.31 (d, *J* = 7.0 Hz, 3H), 1.28-1.25 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.9, 143.1, 136.5, 128.1, 127.0, 127.0, 125.8, 60.5, 39.6, 17.9, 16.1, 14.2.

HRMS (ESI): calculated for $C_{14}H_{18}O_2$ $[M]^+$ 219.1379; found: 219.1378.



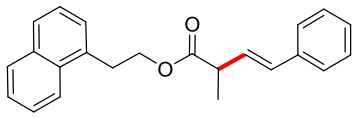
(*E*)-Benzyl 2-methyl-4-phenylbut-3-enoate (12).

This compound was prepared according to the ***GP-A***, using benzyl 2-chloropropanoate (29.7 mg, 0.150 mmol, 100 mol %), (2-bromovinyl)benzene (*E/Z* = 84/16) (54.3 mg, 0.30 mmol, 200 mol %). After purification by column chromatography (SiO_2: 3% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (35.9 mg, 0.135 mmol, *E/Z* = 90/10, determined by GC-MS) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.32 (m, 9H), 7.27-7.24 (m, 1H), 6.53-6.50 (d, *J* = 16.1 Hz, 1H), 6.36-6.31 (dd, *J* = 8.0 Hz, *J* = 16.1 Hz, 1H), 5.19 (s, 2H), 3.43-3.38 (m, 1H), 1.43-1.42 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.2, 136.7, 135.9, 131.2, 128.5, 128.4, 128.4, 128.1, 127.9, 127.4, 126.2, 66.3, 43.1, 17.3.

HRMS (ESI): calculated for $C_{18}H_{18}O_2$ $[M]^+$ 267.1379; found: 267.1379.



(*E*)-2-(Naphthalen-1-yl)ethyl 2-methyl-4-phenylbut-3-enoate (13).

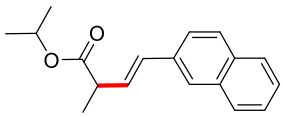
This compound was prepared according to the ***GP-A***, using 2-(naphthalen-1-yl)ethyl-2-chloropropanoate (39.3 mg, 0.150 mmol, 100 mol %), (2-bromovinyl)benzene (*E/Z* = 84/16) (54.3 mg, 0.30 mmol, 200 mol %). After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 85% yield (42.1 mg, 0.128 mmol, *E/Z* = 90/10, determined by GC-MS) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13-8.12 (d, *J* = 8.3 Hz, 1H), 7.88-7.87 (d, *J* = 8.3, 1H), 7.77-7.75 (m, 1H), 7.57-7.55 (m, 1H), 7.51-7.48 (m, 1H), 7.38-7.31 (m, 6H), 7.27-7.24 (m, 1H), 6.49-6.46 (d, *J* = 15.8 Hz, 1H), 6.28-6.23 (m, 1H), 4.48-4.45 (m, 2H), 3.46-3.43 (m, 2H), 3.33-3.30 (m, 1H), 1.37-1.35 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.4, 136.8, 133.8, 133.6, 132.0, 131.1, 128.7, 128.6, 128.4, 127.4, 127.4, 127.1, 126.3, 126.1, 125.6, 125.4, 123.5, 64.6, 43.2, 32.1, 17.2.

HRMS (ESI): calculated for $C_{23}H_{22}O_2$ $[M]^+$ 331.1693; found: 331.1693.

M.p. 35-36 °C.



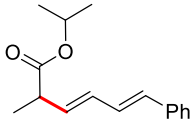
(*E*)-*iso*-Propyl 2-methyl-4-(naphthalen-2-yl)but-3-enoate (14).

This compound was prepared according to the ***GP-A***, using *iso*-propyl-2-chloropropanoate (22.5 mg, 0.150 mmol, 100 mol %), (*E*)-2-(2-bromovinyl)naphthalene (66.9 mg, 0.30 mmol, 200 mol %). After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 75% yield (30.2 mg, 0.113 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81-7.78 (m, 3H), 7.73 (s, 1H), 7.62-7.60 (m, 1H), 7.49-7.43 (m, 2H), 6.67-6.64 (d, *J* = 15.9Hz, 1H), 6.46-6.42 (m, 1H), 5.10-5.05 (m, 1H), 3.37-3.31 (m, 1H), 1.42-1.41 (d, *J* = 7.1 Hz, 3H), 1.30-1.27 (d, *J* = 6.5 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.0, 134.4, 133.5, 132.8, 130.9, 129.3, 128.0, 127.8, 127.5, 126.1, 126.0, 125.7, 123.4, 67.9, 43.4, 21.7, 21.7, 17.4.

HRMS (ESI): calculated for $C_{18}H_{20}O_2$ $[M]^+$ 269.1536; found: 269.1538.



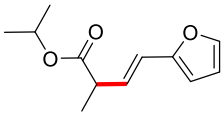
(*E*)-*iso*-Propyl-2-methyl-6-phenylhexa-3,5-dienoate (15).

This compound was prepared according to the ***GP-A***, using *iso*-propyl-2-chloropropanoate (22.5 mg, 0.150 mmol, 100 mol %), ((1*E*,3*E*)-4-bromobuta-1,3-dien-1-yl)benzene (62.7 mg, 0.30 mmol, 200 mol %). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 85% yield (31.1 mg, 0.128 mmol) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.38 (m, 2H), 7.32-7.29 (m, 2H), 7.23-7.20 (m, 1H), 7.79-7.74 (dd, *J* = 10.39 Hz, J = 15.6 Hz, 1H), 6.53-6.50 (d, *J* = 15.6 Hz, 1H), 6.31-6.26 (dd, *J* = 10.5 Hz, *J* = 15.2 Hz, 1H), 5.91-5.86 (dd, *J* = 7.7 Hz, *J* = 15.2 Hz, 1H), 6.04-4.99 (m, 1H), 3.22-3.16 (m, 1H), 1.32-1.30 (d, *J* = 7.1Hz, 3H), 1.26-1.23 (d, *J* = 6.5 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 173.9, 137.2, 133.0, 131.9, 131.3, 128.5, 127.4, 126.2, 67.8, 43.1, 21.7, 21.7, 17.2.

HRMS (ESI): calculated for $C_{16}H_{20}O_2$ $[M]^+$ 245.1513; found: 245.1513.



(*E*)-*iso*-Propyl-4-(furan-2-yl)-2-methylbut-3-enoate (16).

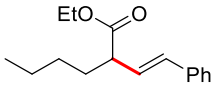
This compound was prepared according to the ***GP-A***, using

iso-propyl-2-chloropropanoate (22.5 mg, 0.150 mmol, 100 mol %), (*E*)-2-(2-bromovinyl)furan (51.9 mg, 0.30 mmol, 200 mol %). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 70% yield (21.8 mg, 0.105 mmol) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (m, 1H), 6.35-6.34 (m, 1H), 6.30-6.27 (d, *J* = 15.8 Hz, 1H), 6.24-6.19 (dd, *J* = 7.4 Hz, *J* = 18.1 Hz, 1H), 5.03-4.98 (m, 1H), 3.23-3.18 (m, 1H), 1.32-1.31 (d, *J* = 7.1 Hz, 3H), 1.24-1.22 (d, *J* = 5.9 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.6, 174.0, 152.3, 142.0, 141.8, 135.9, 128.4, 128.4, 128.1, 128.0, 127.9, 127.8, 127.1, 119.6, 118.1, 111.1, 111.0, 110.1, 107.6, 66.4, 66.2, 42.8, 39.6, 18.3, 17.1.

HRMS (ESI): calculated for $C_{12}H_{16}O_3$ $[M]^+$ 209.1120; found: 209.1120.



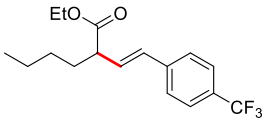
(*E*)-Ethyl-2-styrylhexanoate (17).

This compound was prepared according to the ***GP-A***, using ethyl 2-bromohexanoate (33.5 mg, 0.150 mmol, 100 mol %), (2-bromovinyl)benzene (*E/Z* = 84/16) (54.9 mg, 0.30 mmol, 200 mol %), and $MgCl_2$ (14.3 mg, 0.15 mmol, 100 mol %). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 75% yield (27.7 mg, 0.113 mmol, *E/Z* = 92/8, determined by GC-MS) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38-7.37 (m, 2H), 7.32-7.29 (m, 2H), 7.24-7.21 (m, 1H), 6.48-6.45 (d, *J* = 15.8 Hz, 1H), 6.23-6.18 (m, 1H), 4.19-4.14 (m, 2H), 3.16-3.12 (m, 1H), 1.88-1.81 (m, 1H), 1.67-1.60 (m, 1H), 1.36-1.26 (m, 7H), 0.92-0.89 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.2, 136.8, 131.9, 128.4, 127.9, 127.4, 126.2, 60.5, 49.7, 32.4, 29.2, 22.4, 14.2, 13.8.

HRMS (ESI): calculated for $C_{16}H_{22}O_2$ $[M]^+$ 247.1693; found: 247.1692.



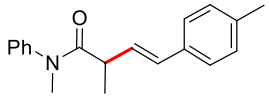
(*E*)-Ethyl-2-(4-(trifluoromethyl)styryl)hexanoate (18).

This compound was prepared according to the ***GP-A***, using ethyl 2-bromohexanoate (33.5 mg, 0.150 mmol, 100 mol %), (*E*)-1-(2-bromovinyl)-4-(trifluoromethyl)benzene (75.3 mg, 0.30 mmol, 200 mol %), and $MgCl_2$ (14.3 mg, 0.15 mmol, 100 mol %). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 85% yield (40.1 mg, 0.128 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55-7.54 (d, *J* = 7.9 Hz, 2H), 7.46-7.44 (d, *J* = 7.9 Hz, 2H), 6.50-6.47 (d, *J* = 15.9 Hz, 1H), 6.34-6.29 (m, 1H), 4.19-4.15 (m, 2H), 3.18-3.14 (m, 1H), 1.87-1.84 (m, 1H), 1.67-1.61 (m, 1H), 1.35-1.26 (m, 7H), 0.91-0.88 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 173.8, 140.3, 140.3, 130.7, 130.6, 129.3, 126.4, 125.4，125.4，125.4, 125.4, 125.3, 125.2, 60.6, 49.6, 32.3, 29.2, 22.3, 14.1, 13.8.

HRMS (ESI): calculated for $C_{17}H_{21}F_3O_2$ $[M]^+$ 315.1566; found: 315.1568.



(*E*)-*N*-2-Dimethyl-*N*-phenyl-4-(*p*-tolyl)but-3-enamide (19)

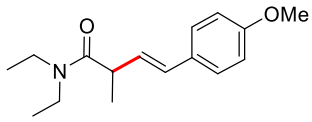
This compound was prepared according to the ***GP-A***, using 2-bromo-*N*-methyl-*N*-phenylpropanamide (36.3 mg, 0.150 mmol, 100 mol %), (*E*)-1-(2-bromovinyl)-4-methoxybenzene (59.1 mg, 0.30 mmol, 200 mol %), and $MgCl_2$ (14.3 mg, 0.15 mmol, 100 mol %). After purification by column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 73% yield (30.5 mg, 0.110 mmol) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-7.41 (m, 2H), 7.38-7.35 (m, 1H), 7.21-7.17 (m, 4H), 7.09-7.07 (d, *J* = 7.8 Hz, 2H), 6.17-6.13 (m, 1H), 6.01-5.99 (d, *J* = 15.8Hz, 1H), 3.27-3.20 (m, 4H), 2.31 (s, 3H), 1.23-1.22 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.3, 143.8, 137.0, 134.1, 130.2, 129.5, 129.4, 129.1, 127.8, 127.6, 126.0, 40.9, 37.5, 21.0, 18.6.

HRMS (ESI): calculated for $C_{19}H_{21}NO$ $[M]^+$ 280.1700; found: 280.1699.

M.p. 66 -67 °C.



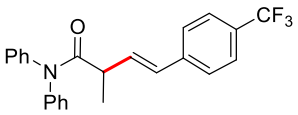
(*E*)-*N*,*N*-Diethyl-4-(4-methoxyphenyl)-2-methylbut-3-enamide (20).

This compound was prepared according to the ***GP-A***, using 2-bromo-*N*,*N*-diethylpropanamide (31.2 mg, 0.150 mmol, 100 mol %), (*E*)-1-(2-bromovinyl)-4-methoxybenzene (63.9 mg, 0.30 mmol, 200 mol %), and $MgCl_2$ (14.3 mg, 0.15 mmol, 100 mol %). After purification by column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 73% yield (28.6 mg, 0.110 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29-7.27 (d, *J* = 8.7 Hz, 2H), 6.83-6.82 (d, *J* = 8.6 Hz, 2H), 6.36-6.33 (d, *J* = 16.0 Hz, 1H), 6.18-6.13 (m, 1H), 3.79 (s, 3H), 3.46-3.41 (m, 3H), 3.33-3.24 (m, 2H), 1.31-1.29 (d, *J* = 7.0 Hz, 3H), 1.20-1.17 (t, *J* = 7.0 Hz, 3H), 1.13-1.10 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 158.9, 129.7, 129.5, 128.6, 127.2, 113.8, 55.2, 41.7, 40.3, 18.9, 14.8, 13.0.

HRMS (ESI): calculated for $C_{16}H_{23}NO_2$ $[M]^+$ 262.1802; found: 262.1798.



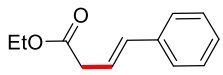
(*E*)-2-Methyl-*N*,*N*-diphenyl-4-(4-(trifluoromethyl)phenyl)but-3-ena mide (21)

This compound was prepared according to the ***GP-A*** using 2-bromo-*N*,*N*-diphenylpropanamide (45.6 mg, 0.30 mmol, 100 mol %), (*E*)-1-(2-bromovinyl)-4-(trifluoromethyl)benzene (75.3 mg, 0.30 mmol, 100 mol %), and $MgCl_2$ (14.3 mg, 0.15 mmol, 100 mol %). After purification by column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 75% yield (44.4 mg, 0.113 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56-7.54 (d, *J* = 8.3 Hz, 2H), 7.42-7.25 (m, 12H), 6.44-6.39 (m, 1H), 6.21-6.18 (m, 1H), 3.51-3.45 (m, 1H), 1.37-1.36 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 173.9, 142.6, 140.4, 133.0, 129.5, 129.3, 129.0, 126.3, 125.4, 125.4, 125.4, 41.9, 18.6.

HRMS (ESI): calculated for $C_{24}H_{20}F_3NO$ $[M]^+$ 396.1570; found: 396.1569.

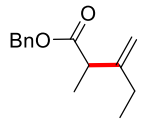


(*E*)-ethyl-4-phenylbut-3-enoate (22).

This compound was prepared according to the ***GP-A***, using ethyl 2-chloroacetate (18.3 mg, 0.150 mmol, 100 mol %), (*E*)-(2-bromovinyl)benzene (54.6 mg, 0.30 mmol, 200 mol %). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 86% yield (24.5 mg, 0.129 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.37 (d, *J* = 7.3 Hz, 2H), 7.33-7.30 (m, 2H), 7.25-7.23 (t, *J* = 7.3 Hz, 1H), 6.51-6.48 (d, *J* = 15.8 Hz, 1H), 6.34-6.28 (m, 1H), 4.20-4.16 (q, *J* = 7.1 Hz, 2H), 3.25-3.24 (m, 2H), 1.30-1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.5, 136.8, 133.2, 128.4, 127.4, 126.2, 121.8, 60.7, 38.4, 14.1.



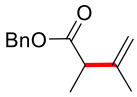
Benzyl-2-methyl-3-methylenepentanoate (23)

This compound was prepared according to the ***GP-B*** using benzyl 2-chloropropanoate (29.7 mg, 0.15 mmol, 100 mol %), 2-bromobut-1-ene (40.5 mg, 0.30 mmol, 200 mol %). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 82% yield (26.8 mg, 0.123 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.33 (m, 5H), 5.13 (s, 2H), 4.94 (s, 1H), 4.90 (s, 1H), 3.23-3.19 (m, 1H), 2.13-2.01 (m, 2H), 1.32-1.30 (d, *J* = 7.3Hz, 3H), 1.05-1.02 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, CDCl3): δ 174.3, 149.5, 136.0, 128.4, 128.0, 127.9, 109.9, 66.2, 45.8, 27.2, 16.2, 12.0.

HRMS (ESI): calculated for $C_{14}H_{18}O_2$ $[M]^+$ 219.1380; found: 219.1378.



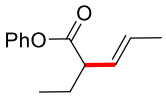
Benzyl-2,3-dimethylbut-3-enoate (24)

This compound was prepared according to the ***GP-B*** using benzyl-2-chloropropanoate (29.7 mg, 0.15 mmol, 100 mol %), 2-bromoprop-1-ene (36.0 mg, 0.30 mmol, 200 mol %). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 80% yield (24.5 mg, 0.120 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.31 (m, 5H), 5.13 (s, 2H), 4.87 (s, 2H), 3.23-3.19 (m, 1H), 1.74 (s, 1H), 1.30-1.29 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.1, 143.7, 136.0, 128.4, 127.9, 112.6, 66.2, 46.8, 20.4, 15.7.

HRMS (ESI): calculated for $C_{14}H_{16}O_2$ $[M]^+$ 227.1043; found: 227.1043.



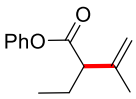
(*E*)-Phenyl-2-ethylpent-3-enoate (25)

This compound was prepared according to the ***GP-B*** using phenyl-2-bromobutanoate (36.5 mg, 0.15 mmol, 100 mol %), 1-bromoprop-1-ene (*E/Z* = 40/60) (36.0 mg, 0.30 mmol, 200 mol %), and $MgCl_2$ (14.3 mg, 0.15 mmol, 100 mol %). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound as a mixture of isomer was isolated in 70% yield (21.4 mg, 0.105 mmol, *E/Z* = 77/23, determined by GC-MS) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.35 (m, 2H), 7.23-7.20 (m, 1H), 7.08-7.06 (m, 2H), 5.76-5.65 (m, 1H), 5.57-5.48 (m, 1H), 3.13-3.08 (m, 1H), 1.98-1.86 (m, 1H), 1.75-1.74 (m, 3H), 1.70-1.73 (m, 1H), 1.01-0.98 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 173.0, 150.8, 129.3, 128.0, 127.5, 125.6, 121.5, 50.8, 25.9, 17.9, 11.6.

HRMS (ESI): calculated for $C_{13}H_{16}O_2$ $[M]^+$ 205.1223; found: 205.1220.



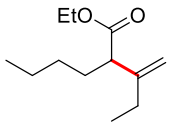
(*E*)-Benzyl-2-methylpent-3-enoate (26)

This compound was prepared according to the ***GP-B*** using phenyl-2-bromobutanoate (36.5 mg, 0.15 mmol, 100 mol %), 2-bromoprop-1-ene (36.0 mg, 0.30 mmol, 200 mol %), and $MgCl_2$ (14.3 mg, 0.15 mmol, 100 mol %). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 70% yield (21.4 mg, 0.105 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.36 (m, 2H), 7.23-7.22 (m, 1H), 7.07-7.06 (m, 2H), 5.01 (s, 2H), 3.19-3.16 (m, 1H), 2.00-1.94 (m, 1H),1.86 (s, 3H), 1.80-1.70 (m, 1H), 1.01-0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.2, 150.7, 141.8, 129.3, 125.6, 121.4, 114.2, 54.8, 23.3, 20.2, 11.9.

HRMS (ESI): calculated for $C_{13}H_{16}O_2$ $[M]^+$ 205.1217; found: 205.1213.



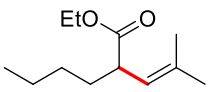
Ethyl 2-(but-1-en-2-yl)hexanoate (27)

This compound was prepared according to the ***GP-B*** using ethyl 2-bromohexanoate (33.5 mg, 0.15 mmol, 100 mol %), 2-bromobut-1-ene (40.5 mg, 0.30 mmol, 200 mol %), and $MgCl_2$ (14.3 mg, 0.15 mmol, 100 mol %). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 74% yield (22.2 mg, 0.111 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.93 (s, 1H), 4.88 (s, 1H), 4.14-4.10 (m, 2H), 2.98-2.94 (m, 1H), 2.07-2.03 (m, 2H), 1.82-1.78 (m, 1H), 1.61-1.54 (m, 1H), 1.32-1.20 (m, 7H), 1.05-1.02 (m, 3H), 0.89-0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.1, 148.5, 110.3, 60.3, 52.2, 30.6, 29.8, 27.2, 22.5, 14.1, 13.9, 12.0.

HRMS (ESI): calculated for $C_{12}H_{22}O_2$ $[M]^+$ 221.1512; found: 221.1510.



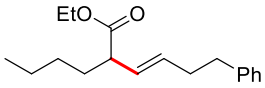
Ethyl 2-(2-methylprop-1-en-1-yl)hexanoate (28)

This compound was prepared according to the ***GP-B*** using ethyl 2-bromohexanoate (33.5 mg, 0.15 mmol, 100 mol %), 1-bromo-2-methylprop-1-ene (40.5 mg, 0.30 mmol, 200 mol %), and $MgCl_2$ (14.3 mg, 0.15 mmol, 100 mol %). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 71% yield (21.2 mg, 0.107 mmol) as a colorless oil.

1H NMR (500 MHz, $CDCl_3$): δ 5.10 (d, *J* = 9.5 Hz, 1H), 4.12-4.08 (m, 2H), 3.18-3.13 (m, 1H), 1.70-1.64 (m, 7H), 1.47-1.40 (m, 1H), 1.31- 1.21 (m, 7H), 0.88-0.85 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 175.0, 134.4, 122.9, 60.1, 44.9, 32.7, 29.2，25.7，22.5, 18.1, 14.2, 13.9.

HRMS (ESI): calculated for $C_{12}H_{22}O_2$ $[M]^+$ 199.1693; found: 199.1691.



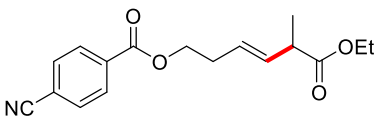
(*E*)-Ethyl-2-butyl-6-phenylhex-3-enoate (29)

This compound was prepared according to the ***GP-B*** using ethyl 2-bromohexanoate (33.5 mg, 0.15 mmol, 100 mol %), (*E*)-(4-bromobut-3-en-1-yl)benzene (63.3 mg, 0.30 mmol, 200 mol %), and $MgCl_2$ (14.3 mg, 0.15 mmol, 100 mol %). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 86% yield (35.3 mg, 0.129 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29-7.26 (m, 2H), 7.19-7.16 (m, 3H), 5.59-5.54 (m, 1H), 5.46-5.41 (m, 1H), 4.15-4.11 (t, *J* = 7.1 Hz, 2H), 2.94-2.89 (dd, *J* = 7.6 Hz, *J* = 15.5 Hz, 1H), 2.71-2.68 (m, 2H), 2.37-2.33 (m, 2H), 1.74-1.67 (m, 1H), 1.51-1.44 (m, 1H), 1.32-1.21 (m, 7H), 0.90-0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.6, 141.6, 132.0, 128.6, 128.4, 128.2, 125.7, 60.2, 49.2, 35.6, 34.1, 32.2, 29.1, 22.3, 14.1, 13.8.

HRMS (ESI): calculated for $C_{18}H_{26}O_2$ $[M]^+$ 275.1935; found: 275.1931.



(*E*)-6-Ethoxy-5-methyl-6-oxohex-3-en-1-yl 4-cyanobenzoate (30).

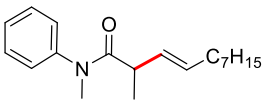
This compound was prepared according to the ***GP-B***, using ethyl 2-chloropropionate (20.4 mg, 0.150 mmol, 100 mol %), (*E*)-4-bromobut-3-en-1-yl 4-cyanobenzoate (84.0 mg, 0.30 mmol, 200 mol %). After purification by column chromatography (SiO_2: 7% ethyl

acetate in petroleum ether), the title compound was isolated in 81% yield (36.7 mg, 0.122 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12-8.11 (d, *J* = 8.6 Hz, 2H), 7.74-7.72 (d, *J* = 8.6 Hz, 2H), 5.70-5.66 (m, 1H), 5.59-5.53 (m, 1H), 4.38-4.35 (m, 2H), 4.10-4.07 (m, 2H), 3.13-3.07 (m, 1H), 2.52-2.48 (q, *J* = 6.6 Hz, 2H), 1.24-1.20 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.5, 164.7, 134.0, 132.3, 132.1, 130.0, 126.5, 117.9, 116.3, 64.7, 60.5, 42.8, 31.8, 17.3, 14.1.

HRMS (ESI): calculated for $C_{13}H_{16}O_2$ $[M]^+$ 302.1392; found: 302.1392.



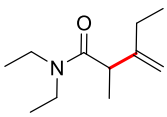
(*E*)-*N*,2-Dimethyl-*N*-phenylundec-3-enamide (31)

This compound was prepared according to the ***GP-B*** using 2-bromo-*N*-methyl-*N*-phenylpropanamide (36.3 mg, 0.15 mmol, 100 mol %), 1-bromonon-1-ene (*E*/*Z* = 35/65) (61.5 mg, 0.30 mmol, 200 mol %), and $MgCl_2$ (14.3 mg, 0.15 mmol, 100 mol %). After purification by column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound as a mixture of isomer was isolated in 78% yield (33.5 mg, 0.117 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41-7.31 (m, 2H), 7.34-7.31 (m, 1H), 7.17-7.15 (m, 2H), 5.46-5.38 (m, 1H), 5.14-5.09 (m, 1H), 3.23 (s, 1H), 3.03-3.01 (m, 1H), 1.91-1.90 (m, 2H), 1.28-1.23 (m, 10H), 1.10-1.09 (d, *J* = 6.4 Hz, 3H), 0.87-0.85 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.9, 144.0, 131.4, 130.2, 129.4, 127.6, 127.5, 40.4, 32.3, 31.7, 29.1, 29.0, 29.0, 22.6, 18.6, 14.0.

HRMS (ESI): calculated for $C_{19}H_{29}NO$ $[M]^+$ 288.2218; found: 288.2215.



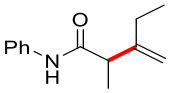
***N*,*N*-Diethyl-2-methyl-3-methylenepentanamide (32)**

This compound was prepared according to the ***GP-B*** using 2-bromo-*N*,*N*-diethylpropanamide (31.2 mg, 0.15 mmol, 100 mol %), 2-bromobut-1-ene (40.5 mg, 0.30 mmol, 200 mol %), and $MgCl_2$ (14.3 mg, 0.15 mmol, 100 mol %). After purification by column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 83% yield (22.8 mg, 0.125 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.85 (s, 1H), 4.83 (s, 1H), 3.58-3.52 (m, 1H), 3.41-3.34 (m, 1H), 3.27-3.22 (m, 1H), 3.18-3.11 (m, 2H), 2.10-2.00 (m, 2H), 1.25-1.23 (d, *J* = 6.9 Hz, 3H), 1.14-1.12 (t, *J* = 7.2 Hz, 3H), 1.10-1.07 (t, *J* = 7.2 Hz, 3H), 1.25-1.23 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.8, 151.0, 109.2, 43.5, 41.5, 40.1, 26.3, 17.4, 14.3, 12.7, 12.1.

HRMS (ESI): calculated for $C_{14}H_{18}O_3$ $[M]^+$ 184.1629; found: 184.1627.



2-Methyl-3-methylene-*N*-phenylpentanamide (33)

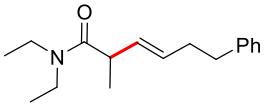
This compound was prepared according to the ***GP-B*** using 2-bromo-*N*-phenylpropanamide (34.2 mg, 0.15 mmol, 100 mol %), 2-bromobut-1-ene (40.5 mg, 0.30 mmol, 200 mol %), and $MgCl_2$ (14.3 mg, 0.15 mmol, 100 mol %). After purification by column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 83% yield (25.3 mg, 0.124 mmol) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50-7.48(m, 3H), 7.31-7.28 (m, 2H), 7.10-7.07 (m, 1H), 5.11 (s, 1H), 5.06 (s, 1H), 3.23-3.18 (m, 1H), 2.18-2.04 (m, 2H), 1.38-1.37 (d, *J* = 7.0 Hz, 3H), 1.34-1.31 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.6, 137.9, 130.8, 130.3, 128.8, 128.7, 124.0, 119.6, 119.6, 45.4, 39.9, 17.9, 17.4, 17.1.

HRMS (ESI): calculated for $C_{13}H_{17}NO$ $[M]^+$ 204.1318; found: 204.1316.

M.p. 67 -68 °C.



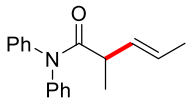
(*E*)-*N*,*N*-Diethyl-2-methyl-6-phenylhex-3-enamide (34)

This compound was prepared according to the ***GP-B*** using 2-bromo-*N*,*N*-diethylpropanamide (31.2 mg, 0.15 mmol, 100 mol %), (*E*)-(4-bromobut-3-en-1-yl)benzene (63.3 mg, 0.30 mmol, 200 mol %), and $MgCl_2$ (14.3 mg, 0.15 mmol, 100 mol %). After purification by column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 85% yield (33.0 mg, 0.128mmol) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21-7.24 (m, 2H), 7.18-7.14 (m, 3H), 5.56-5.45 (m, 2H), 3.38-3.15 (m, 5H), 2.68-2.65 (d, *J* = 7.8 Hz, 2H), 2.35-2.30 (m, 2H), 1.19-1.17 (d, *J* = 6.9 Hz, 3H), 1.15-1.12 (t, *J* = 7.0 Hz, 3H), 1.10-1.07 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 173.6, 141.7, 131.4, 130.0, 128.4, 128.1, 125.7, 41.5, 40.1, 39.7, 35.6, 34.0, 18.6, 14.7, 12.9.

HRMS (ESI): calculated for $C_{17}H_{25}NO$ $[M]^+$ 260.1922; found: 260.1918.



(*E*)-2-Methyl-*N*,*N*-diphenylpent-3-enamide (35)

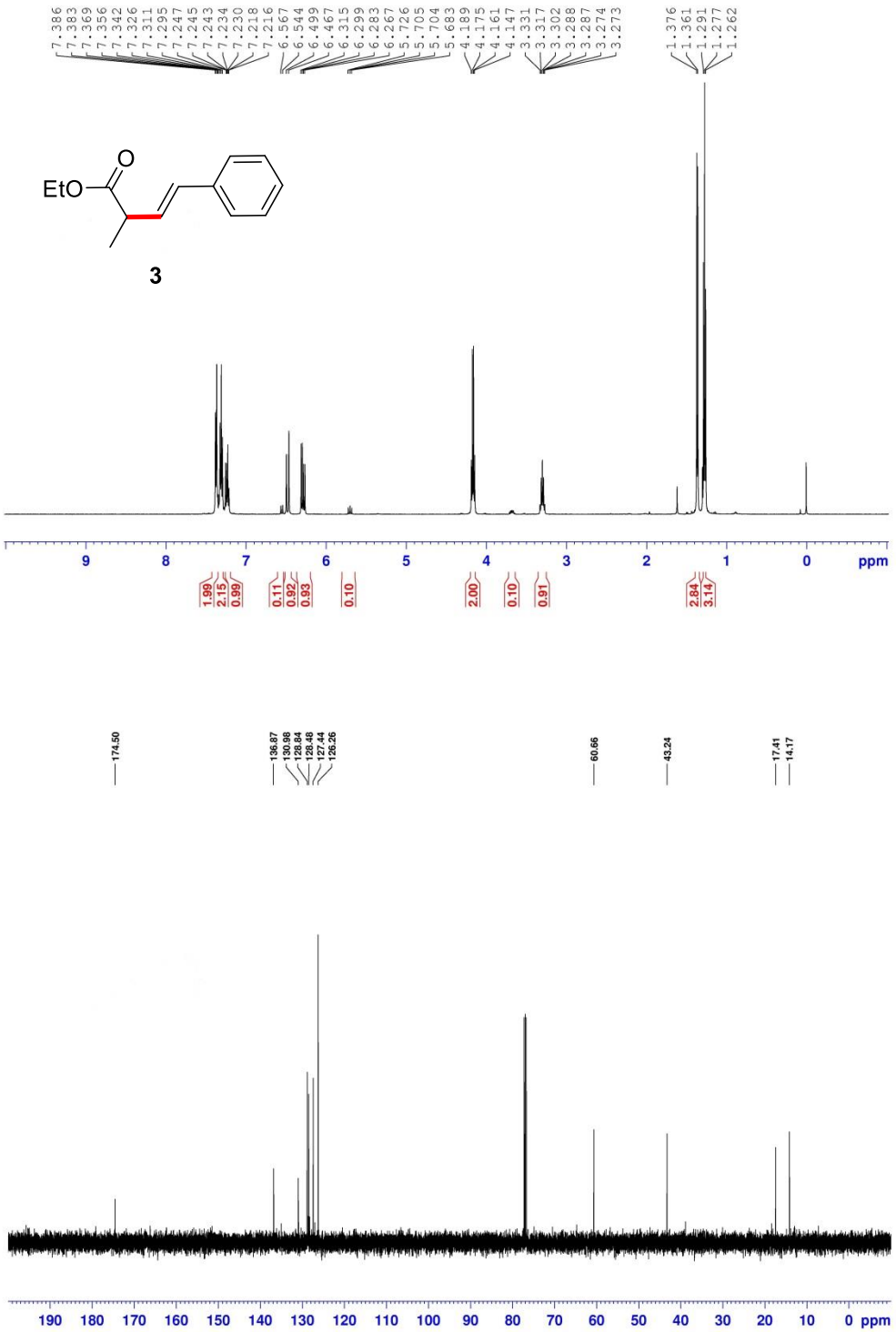
This compound was prepared according to the ***GP-B*** using 2-bromo-*N*,*N*-diphenylpropanamide (45.6 mg, 0.15 mmol, 100 mol %), 1-bromoprop-1-ene (*E/Z* = 40/60) (36.0 mg, 0.30 mmol, 200 mol %), and $MgCl_2$ (14.3 mg, 0.15 mmol, 100 mol %). After purification by column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound as a mixture of isomer was isolated in 75% yield (29.8 mg, 0.113 mmol, *E/Z* = 85/15, determined by GC-MS) as a colorless oil.

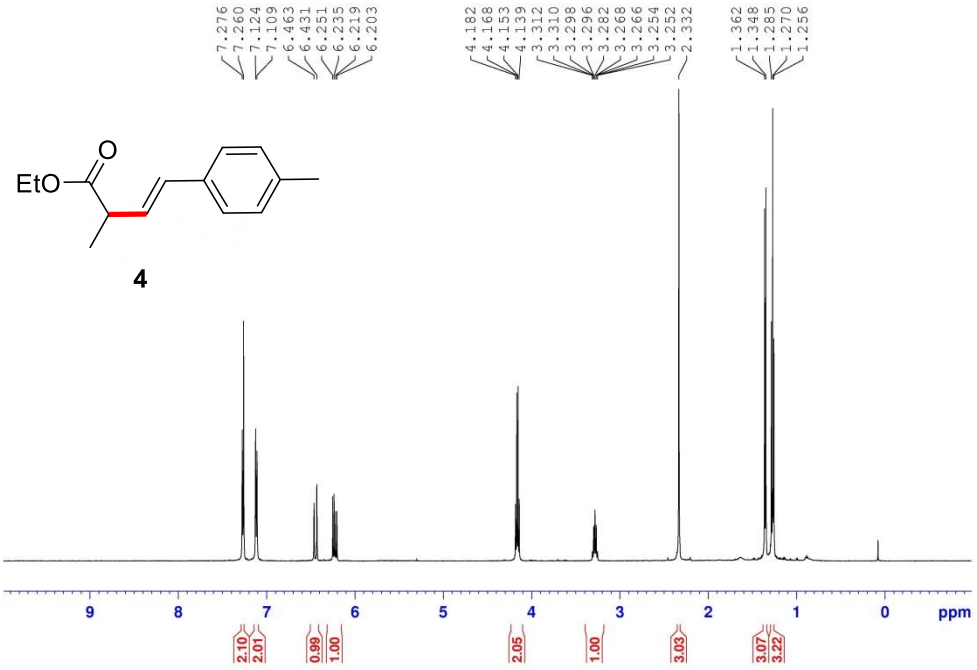
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.16 (m, 10H), 5.57-5.50 (m, 1H), 5.29-5.22 (m, 1H), 3.26-3.20 (m, 1H), 1.65-1.63 (dd, *J* = 6.4 Hz, 3H), 1.22-1.21 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 175.0, 142.8, 131.2, 130.9, 128.8, 128.3, 128.3, 127.7，127.6，126.3, 126.0, 126.0, 124.7, 41.3, 18.4, 17.8.

HRMS (ESI): calculated for $C_{18}H_{19}NO$ $[M]^+$ 266.1539; found: 266.1537.

II. NMR Data for New Compounds

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6.235
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6.203
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4.153
4.139
3.312
3.310
3.298
3.296
3.282
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3.266
3.254
3.252
2.332
1.362
1.348
1.285
1.270
1.256
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EtO
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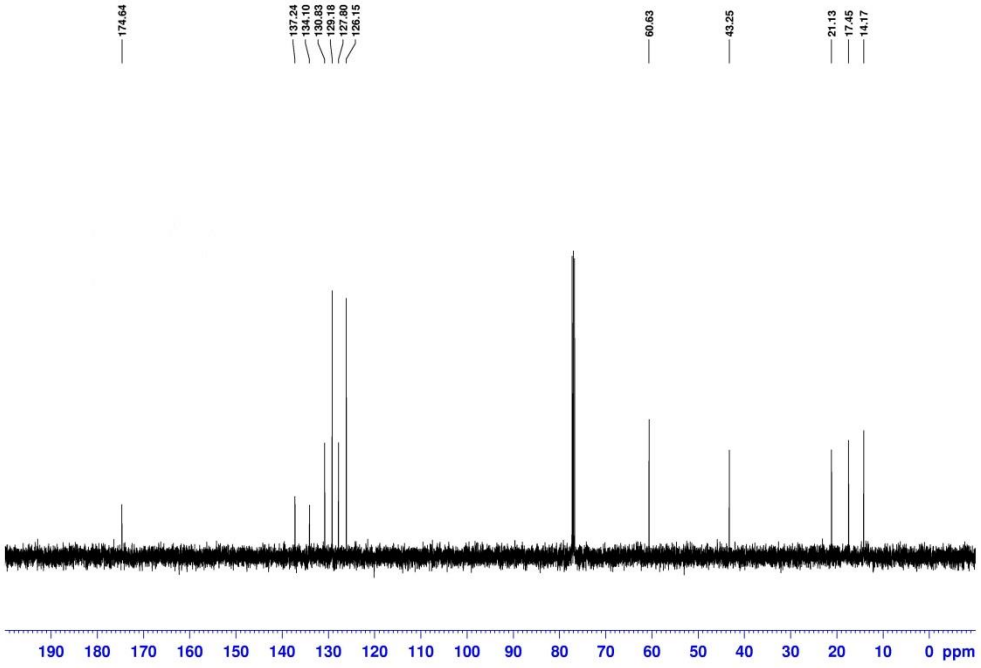
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60.63
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21.13
17.45
14.17
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130
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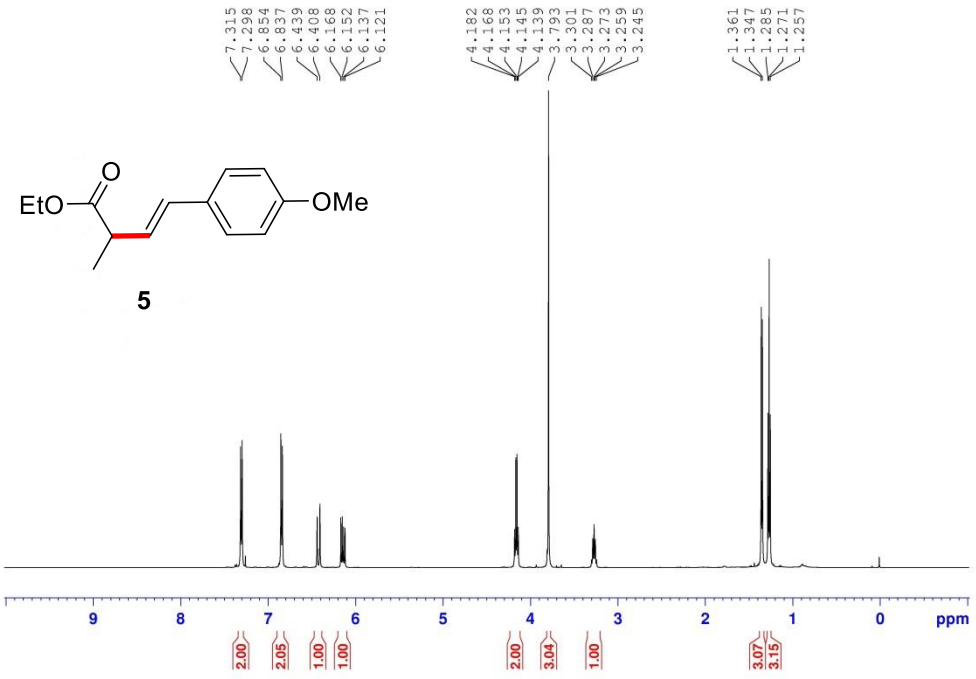
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4.139
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3.301
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1.347
1.285
1.271
1.257
EtO
O
OMe
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8
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6
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4
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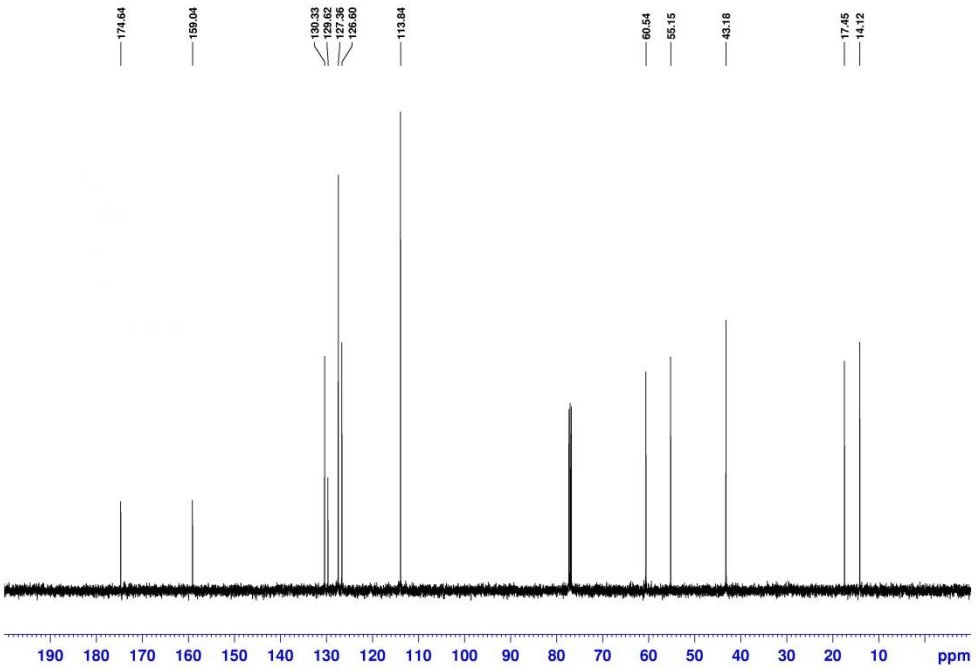
3.15

5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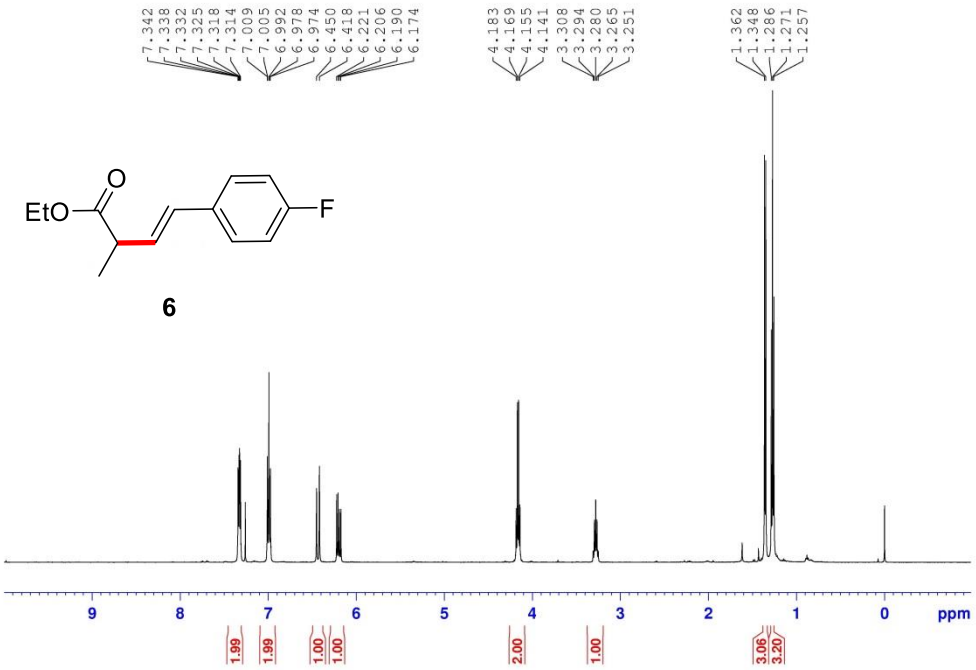
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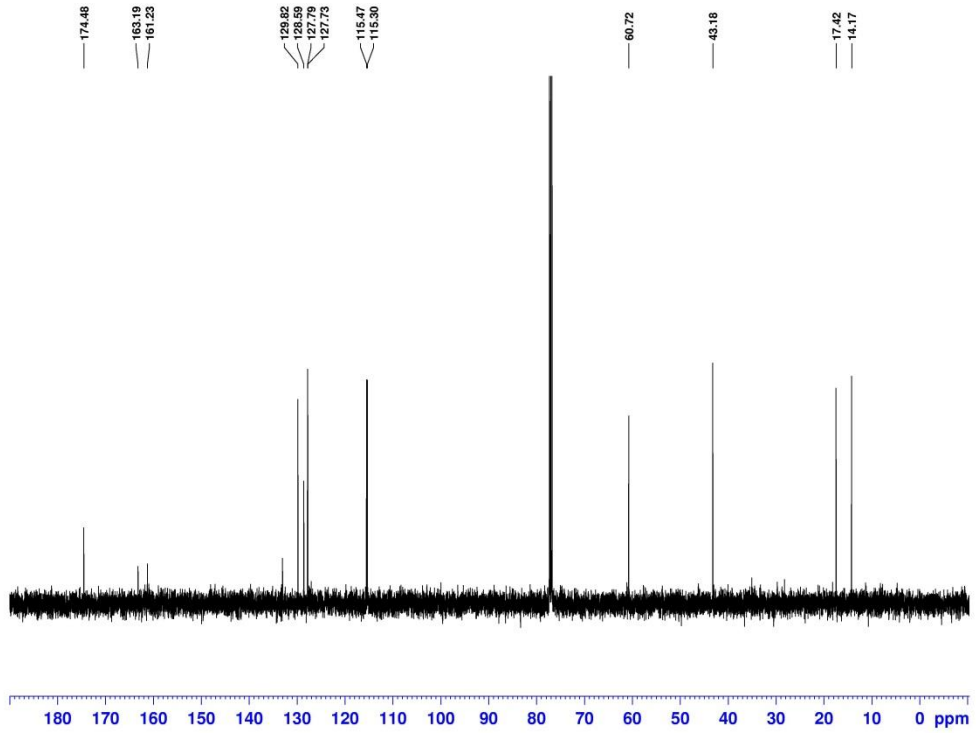
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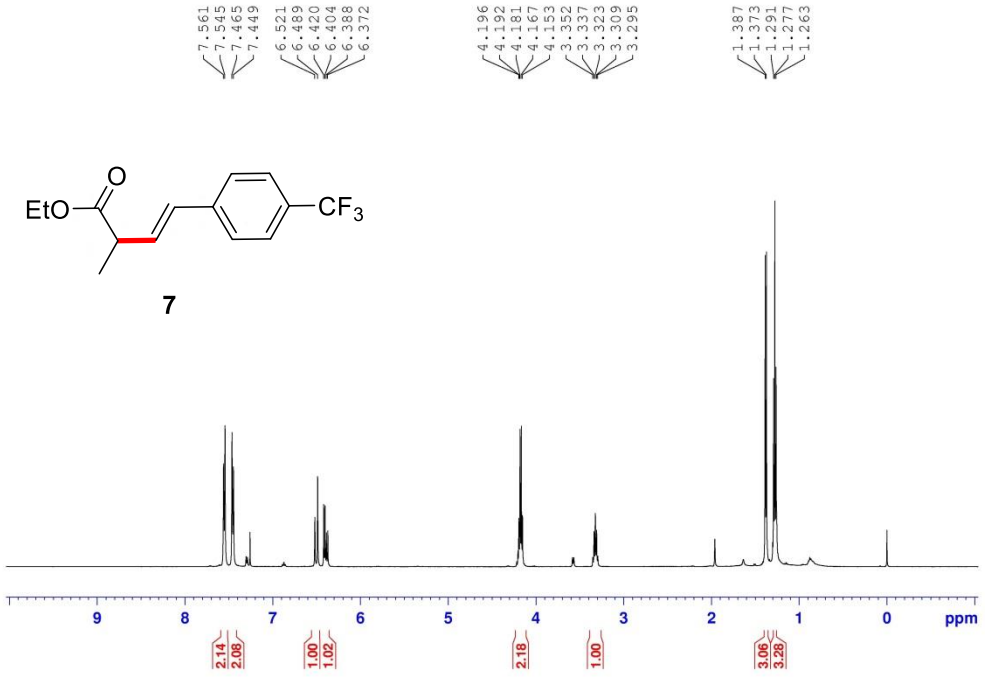
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4.167
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3.337
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3.295
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1.277
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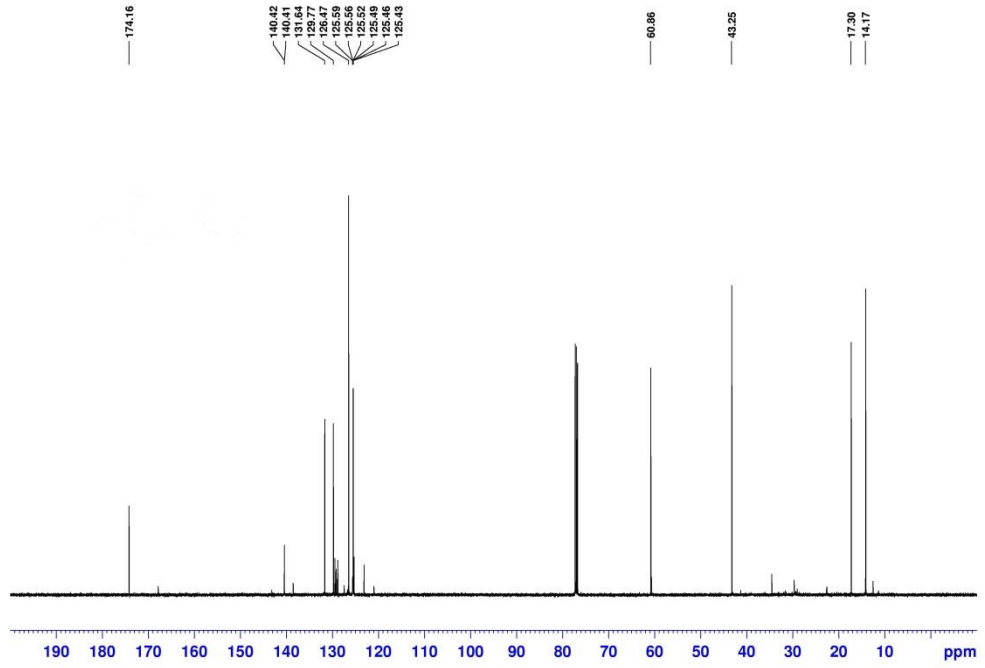
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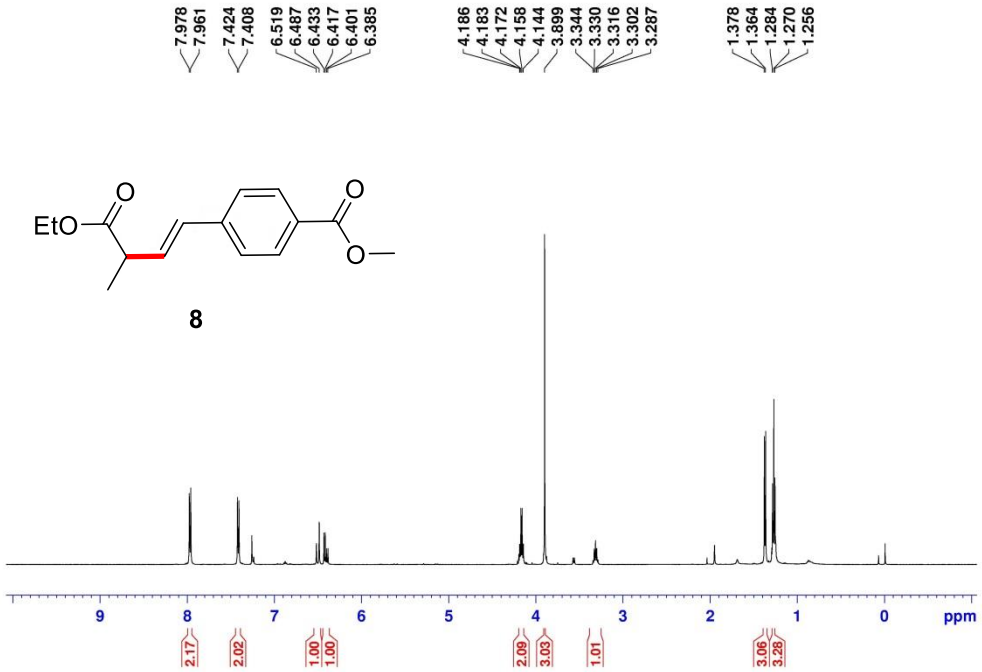
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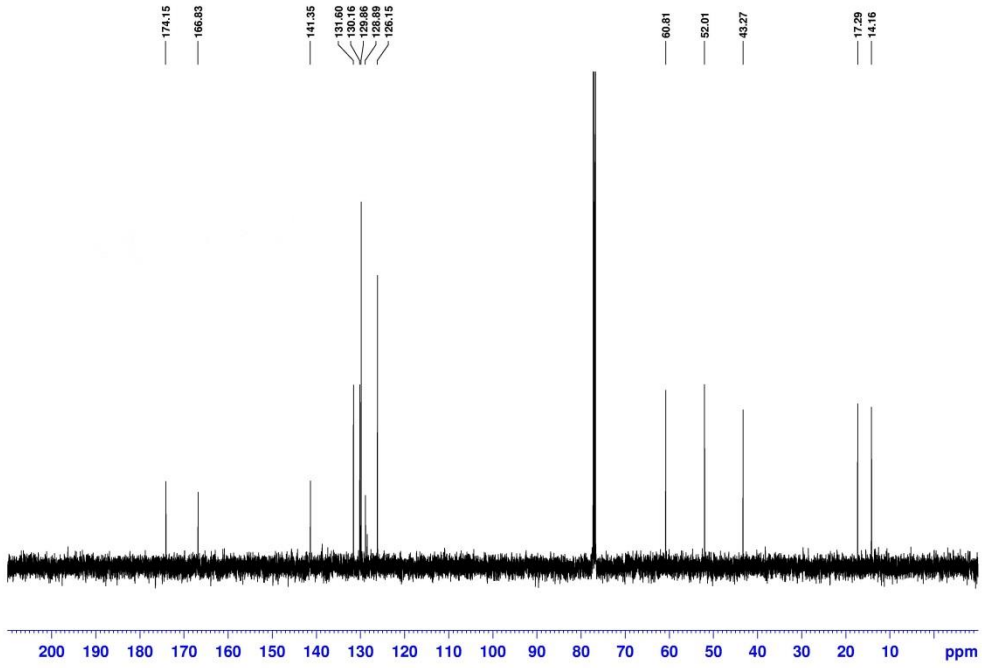
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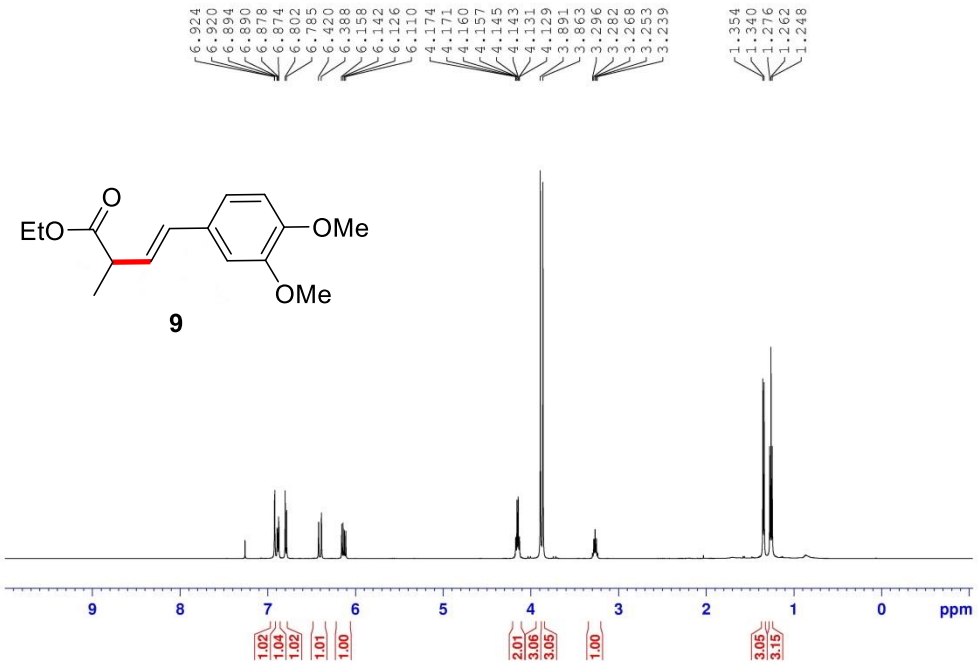
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OMe
OMe
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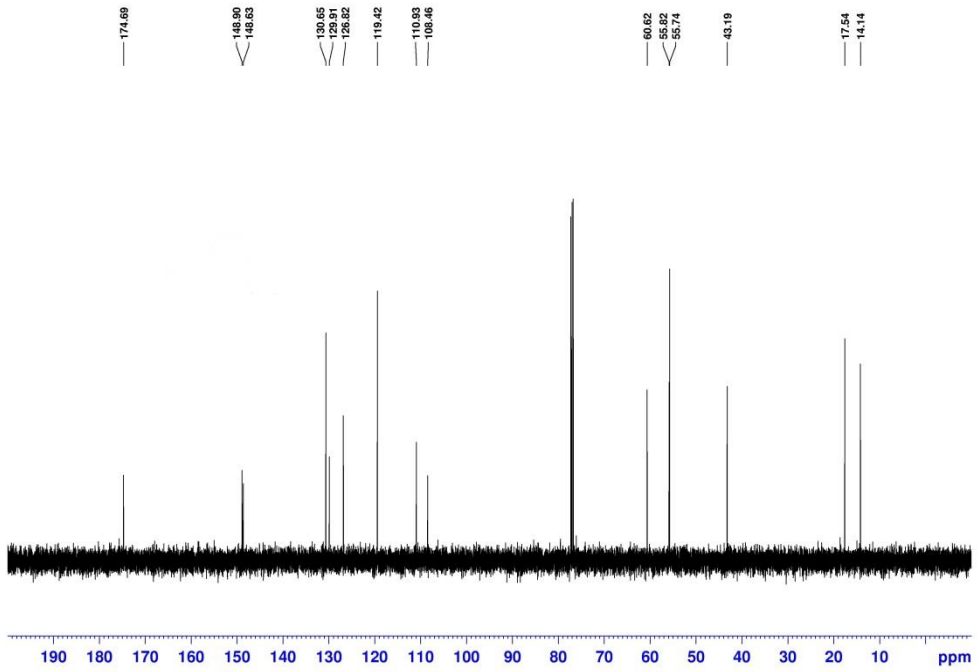
3.15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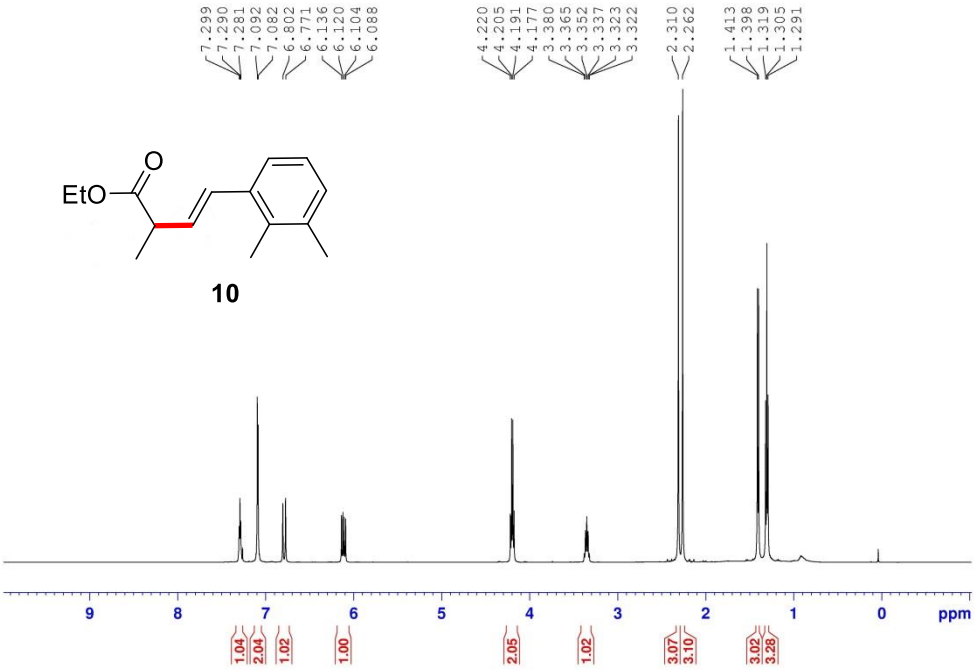
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6
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3
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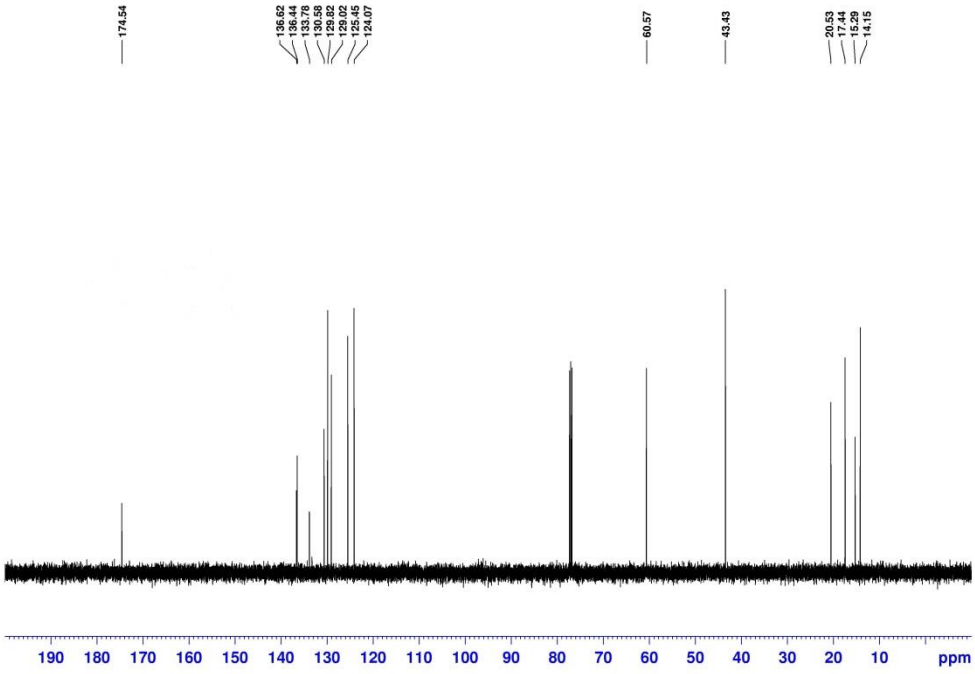
10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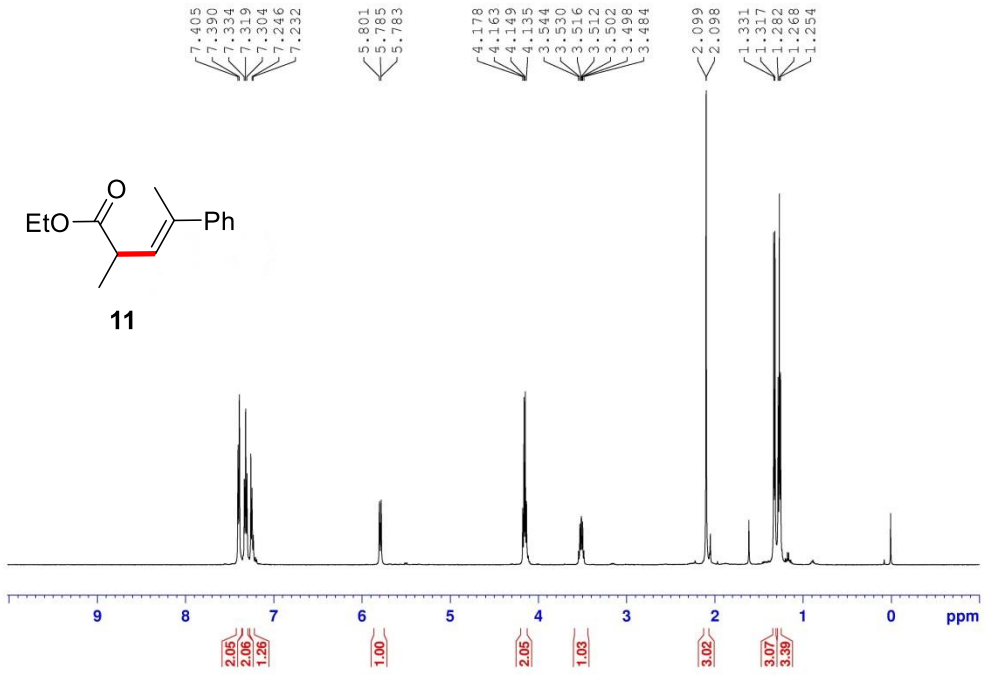
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Ph
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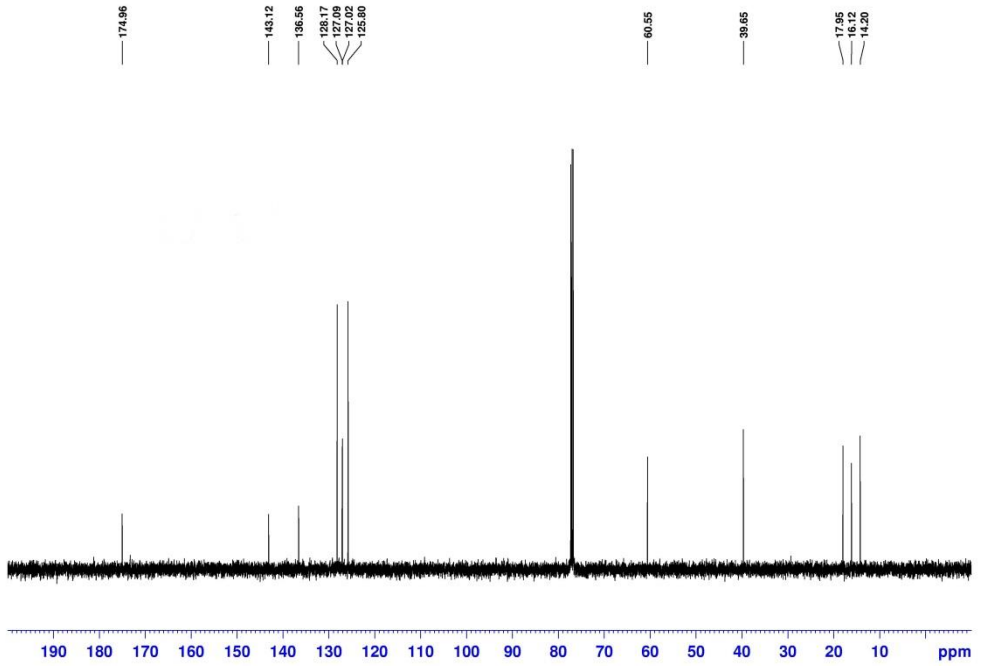
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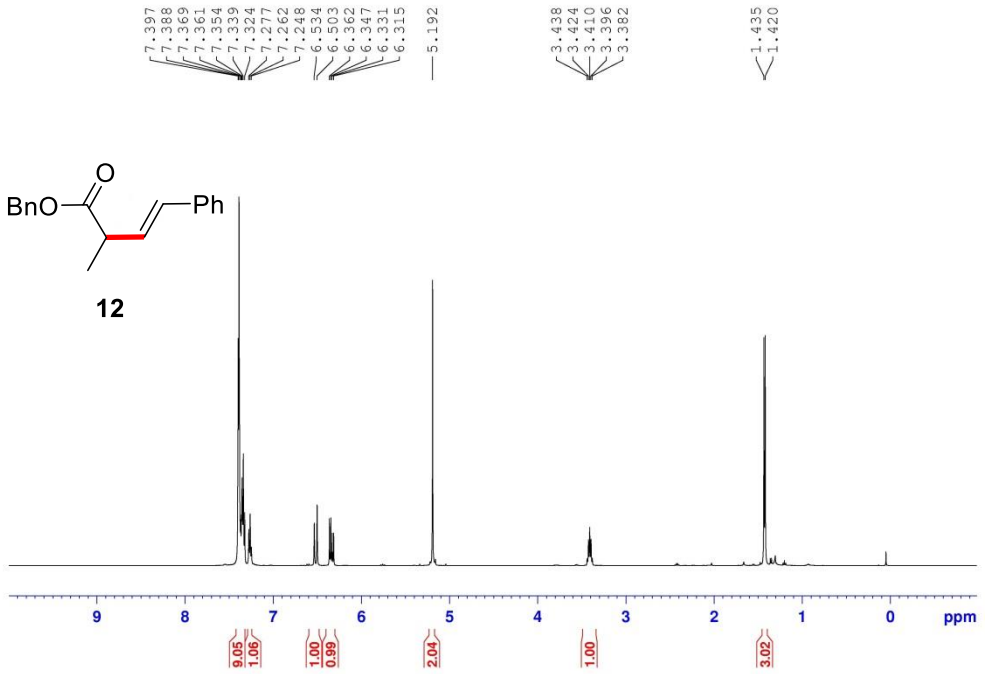
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Ph
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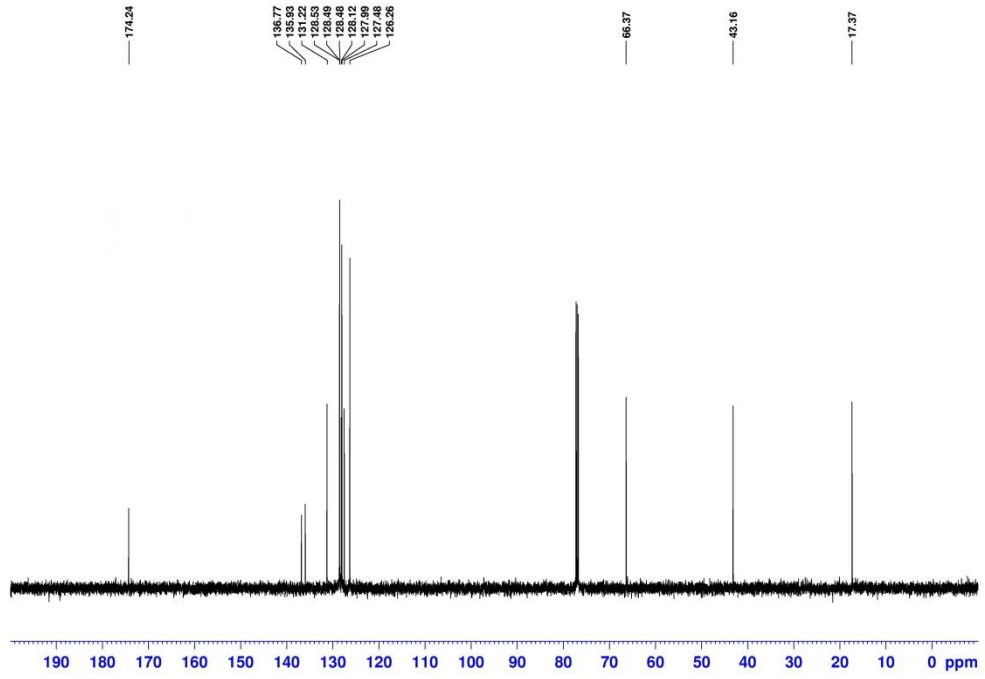
3.02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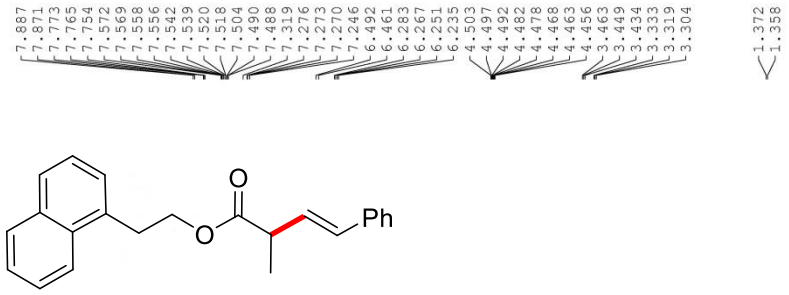
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Ph

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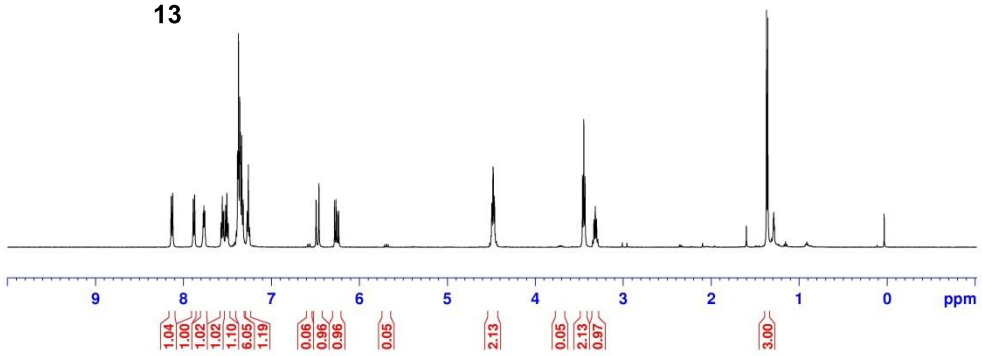
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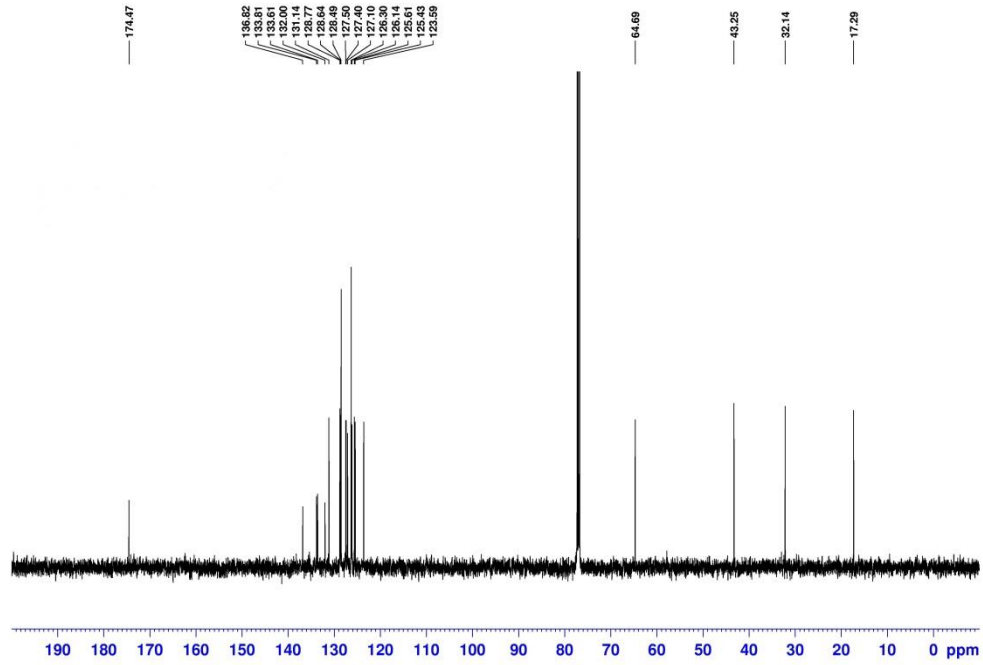
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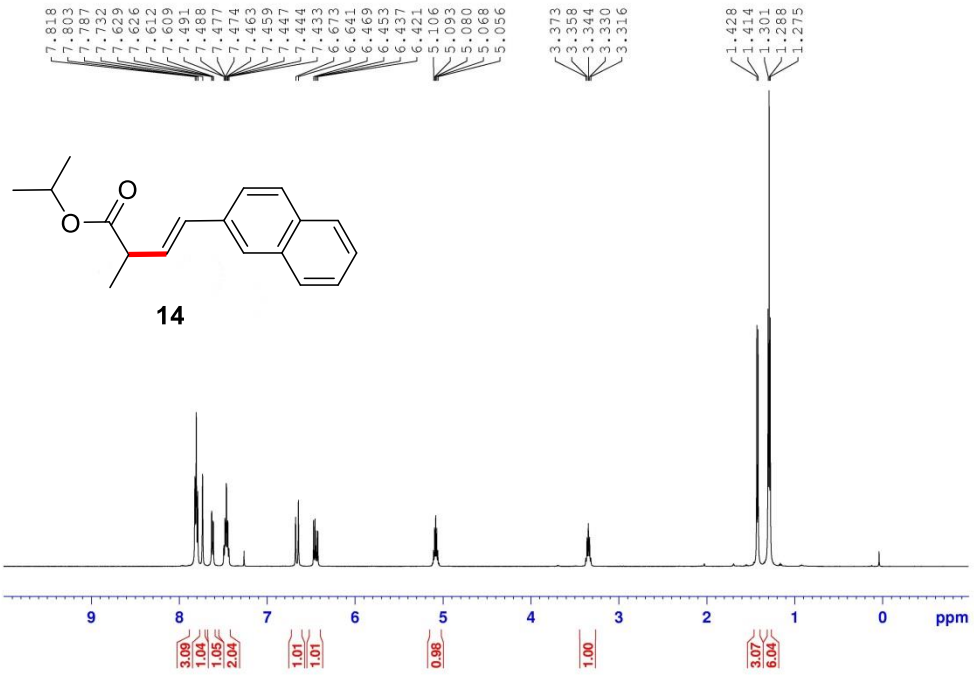
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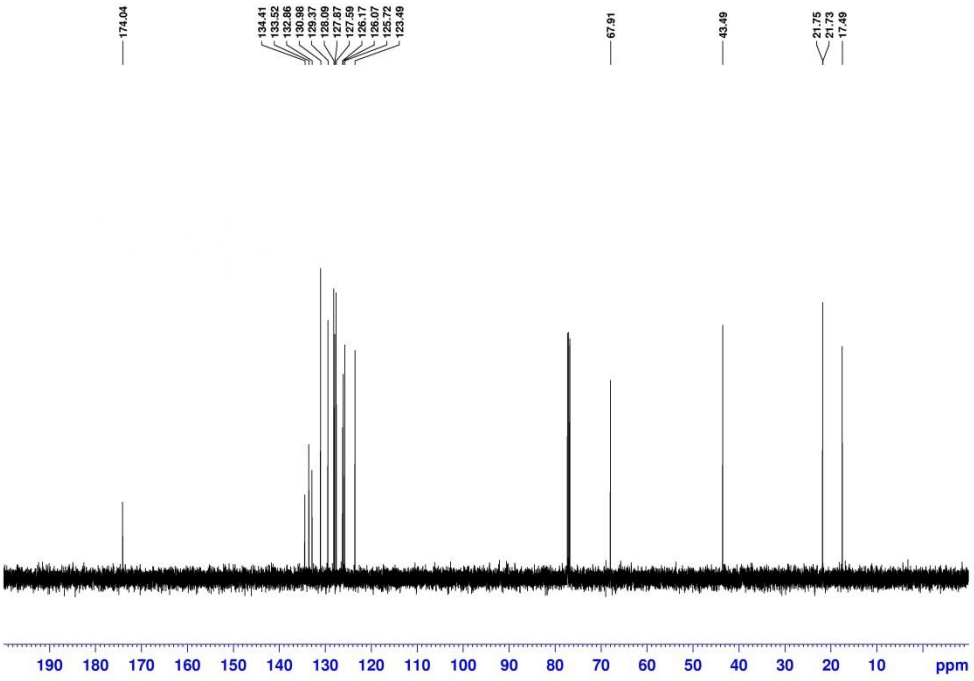
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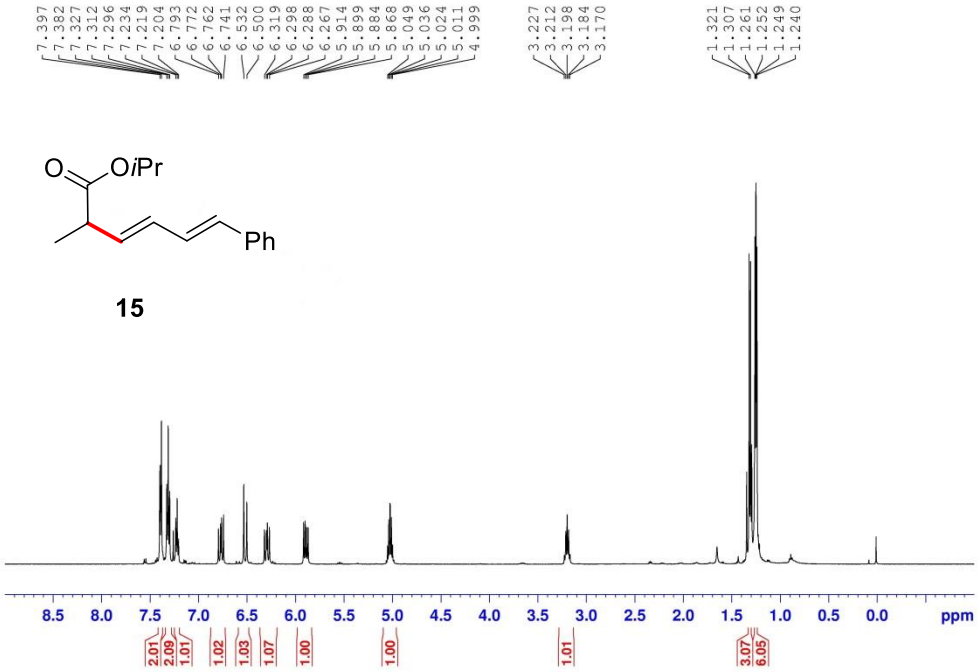
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Ph
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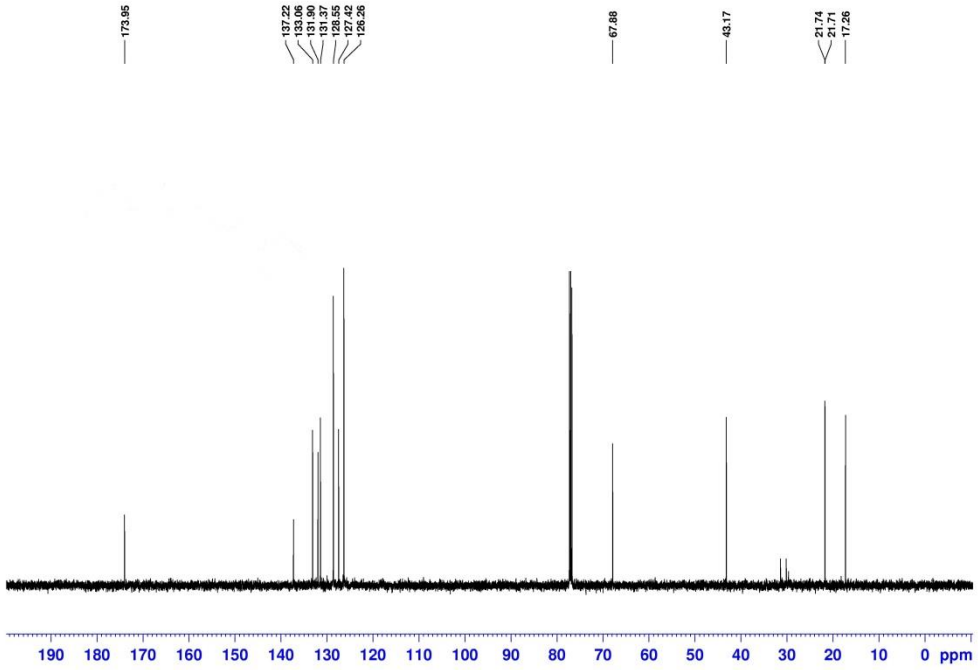
3.07
6.05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137.06
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21.74
21.71
17.26
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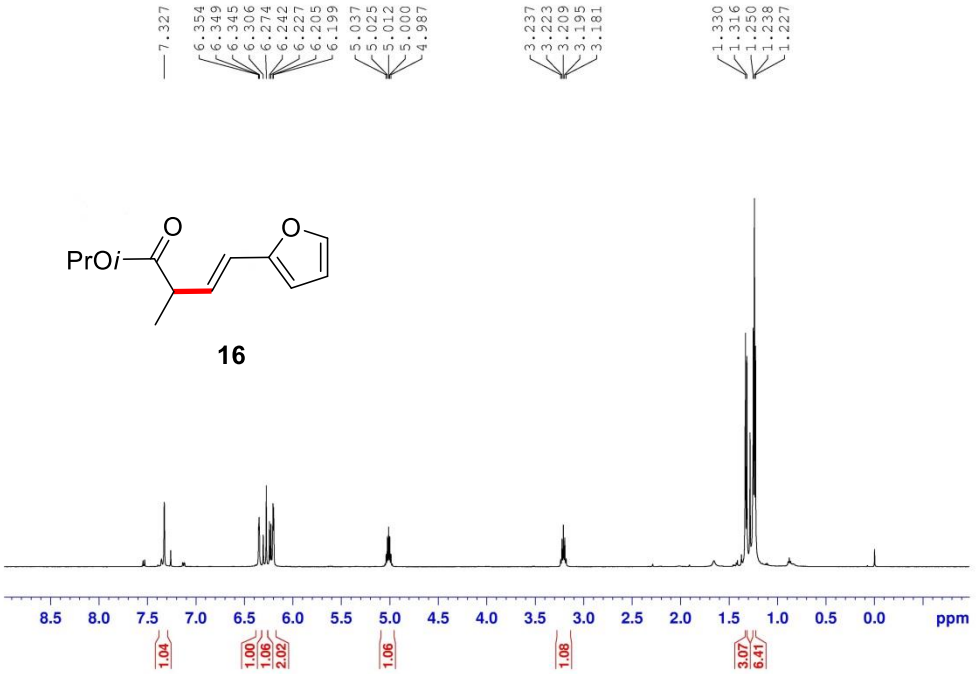
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6.227
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6.199
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5.025
5.012
5.000
4.987
3.237
3.223
3.209
3.195
3.181
1.330
1.316
1.250
1.238
1.227
PrOi
O
O
16
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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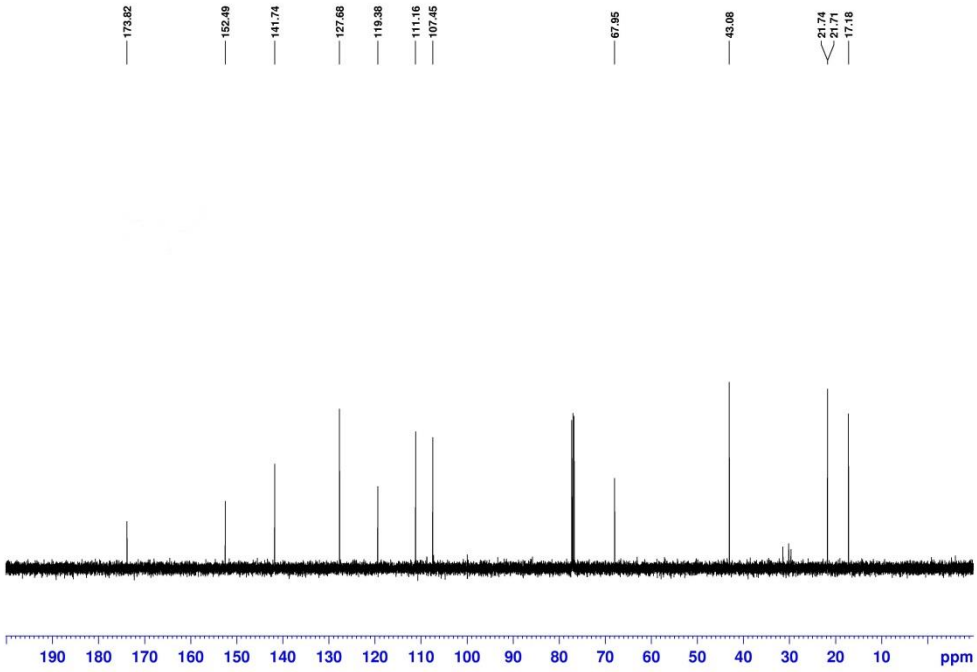
1.00
1.06
2.02
1.06
1.08
3.07
6.41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67.95
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21.74
21.71
17.18
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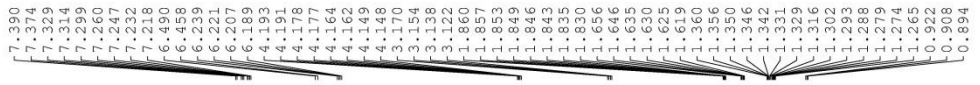
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7.232
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6.458
6.239
6.221
6.207
6.189
4.193
4.191
4.178
4.177
4.164
4.162
4.149
4.148
3.170
3.154
3.138
3.122
1.860
1.857
1.853
1.849
1.846
1.843
1.835
1.830
1.656
1.646
1.635
1.630
1.625
1.619
1.360
1.356
1.350
1.346
1.342
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1.302
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1.274
1.265
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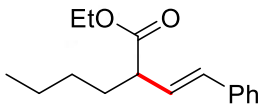
0.894


EtO
O
Ph

17

9
8
7
6
5
4
3
2
1
0
ppm
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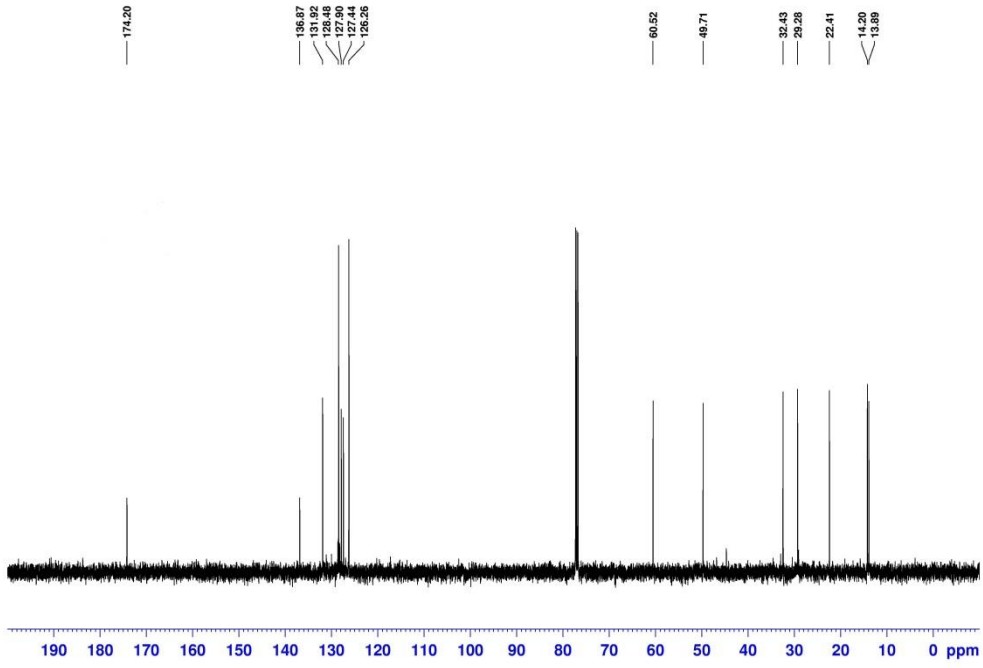
2.01
1.05
0.08
0.92
0.93
0.08
2.04
0.08
0.94
1.01
1.05
3.29
4.10
3.00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49.71
32.43
29.28
22.41
14.20
13.89
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150
140
130
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110
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80
70
60
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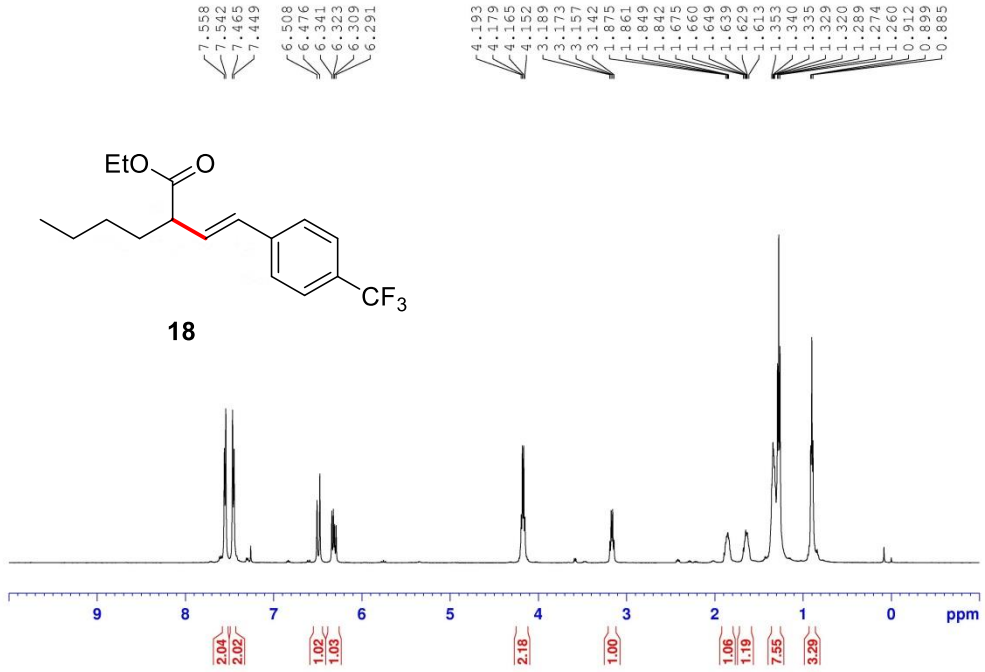
30
20
10
0 ppm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6.476
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6.323
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6.291
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4.179
4.165
4.152
3.189
3.173
3.157
3.142
1.875
1.861
1.849
1.842
1.675
1.660
1.649
1.639
1.629
1.613
1.353
1.340
1.335
1.329
1.320
1.289
1.274
1.260
0.912
0.899
0.885
EtO
O
CF3
18
9
8
7
6
5
4
3
2
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0
ppm
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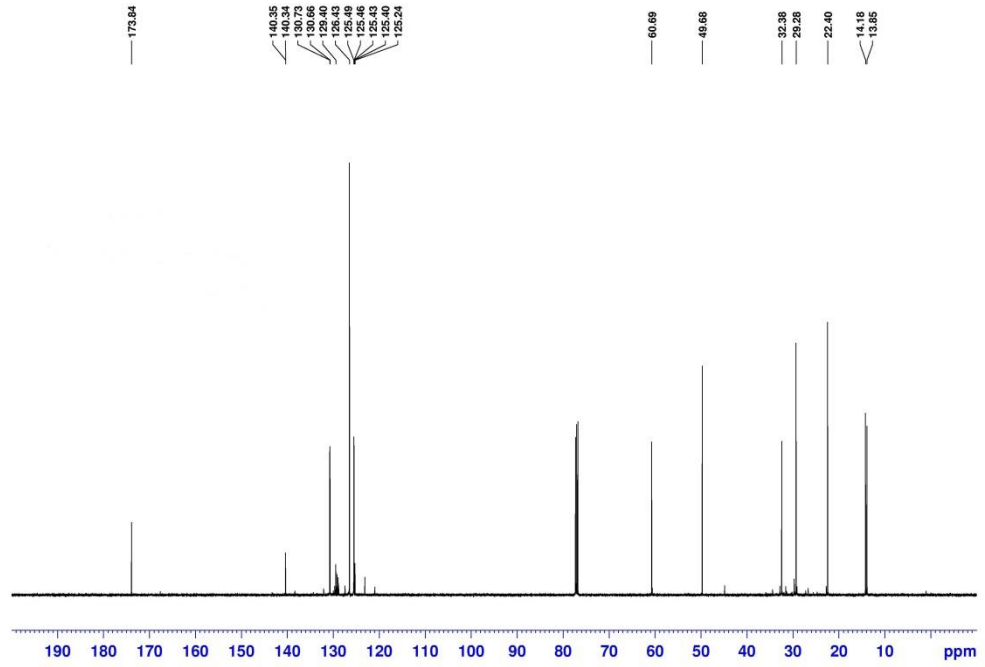
2.02
1.02
1.03
2.18
1.00
1.06
1.19
7.55
3.29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140.34
130.73
130.66
129.40
126.43
125.49
125.46
125.43
125.40
125.24
60.69
49.68
32.38
29.28
22.40
14.18
13.85
190
180
170
160
150
140
130
120
110
100
90
80
70
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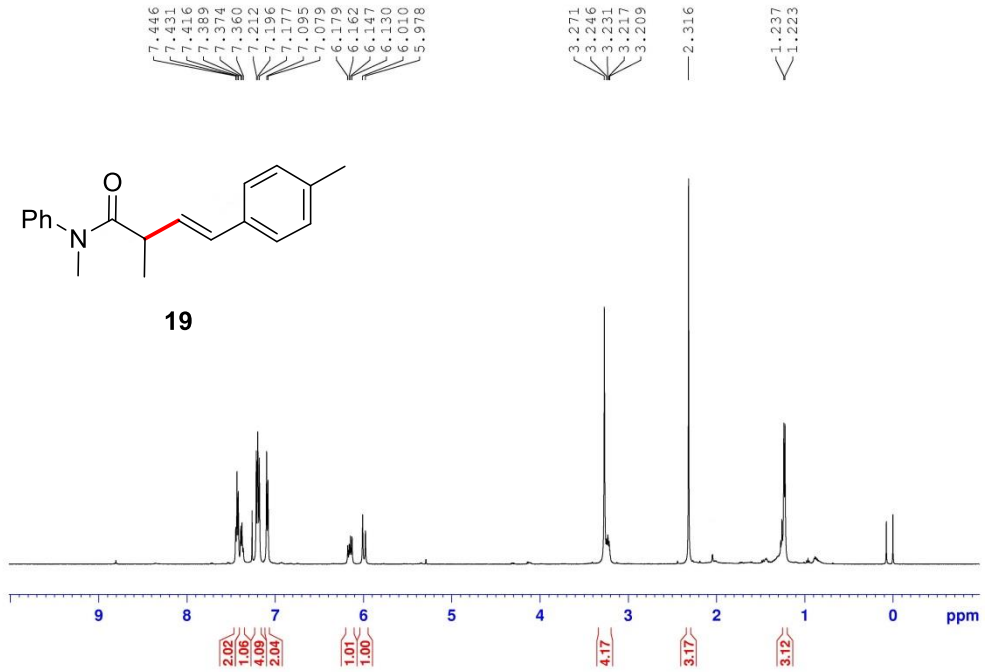
30
20
10
ppm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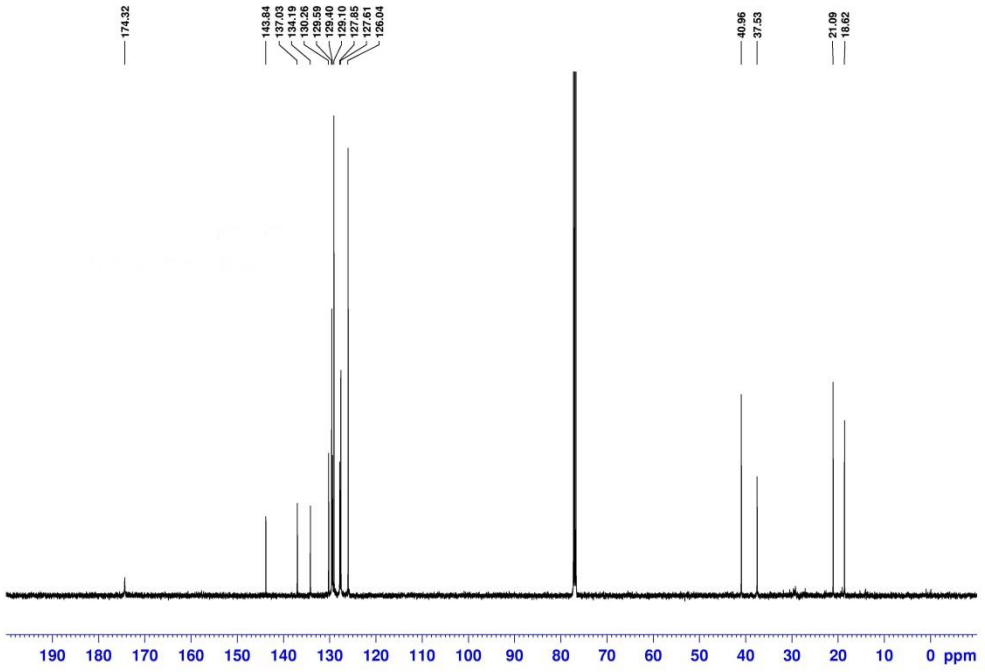
7.416
7.389
7.374
7.360
7.212
7.196
7.177
7.095
7.079
6.179
6.162
6.147
6.130
6.010
5.978
3.271
3.246
3.231
3.217
3.209
2.316
1.237
1.223
O
Ph
N
9
8
7
6
5
4
3
2
1
0
ppm
2.02
1.06
4.09
2.04
1.01
1.00
4.17
3.17
3.12

19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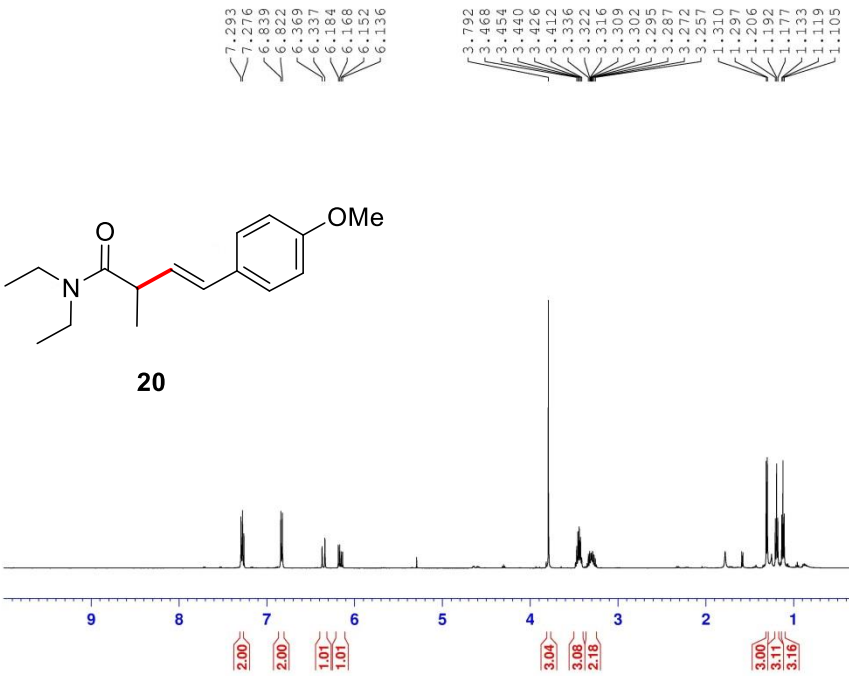
137.03
134.19
130.26
129.59
129.40
128.10
127.85
127.61
126.04
40.96
37.53
21.09
18.62
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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7.276
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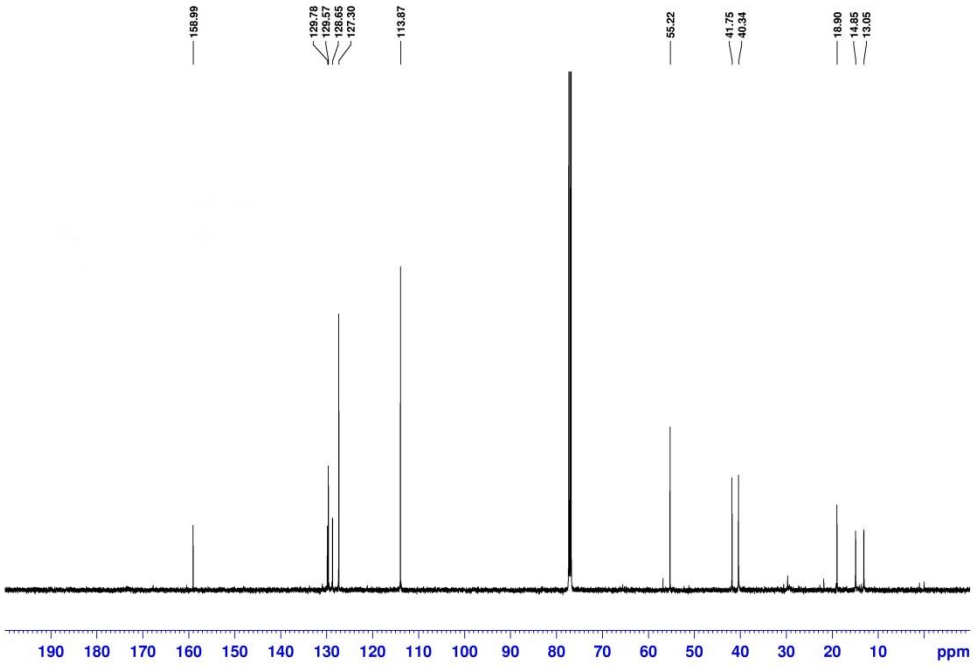
6.822
6.369
6.337
6.184
6.168
6.152
6.136
3.792
3.468
3.454
3.440
3.426
3.412
3.336
3.322
3.316
3.309
3.302
3.295
3.287
3.272
3.257
1.310
1.297
1.206
1.192
1.177
1.133
1.119
1.105
O
N
OMe
20
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.00
1.01
1.01
3.04
3.08
2.18
3.00
3.11
3.16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113.87
55.22
41.75
40.34
18.90
14.65
13.05
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180
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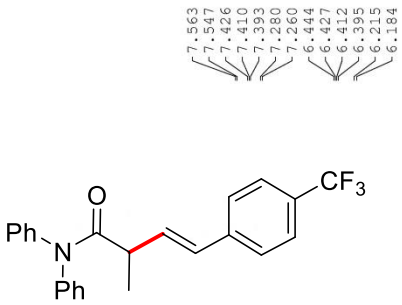
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


O
Ph
N
Ph
CF3

21

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7.410
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7.280
7.260
6.444
6.427
6.412
6.395
6.215
6.184
3.510
3.496
3.481
3.466
3.453
1.374
1.361
9
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7
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4
3
2
1
0
ppm
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12.49
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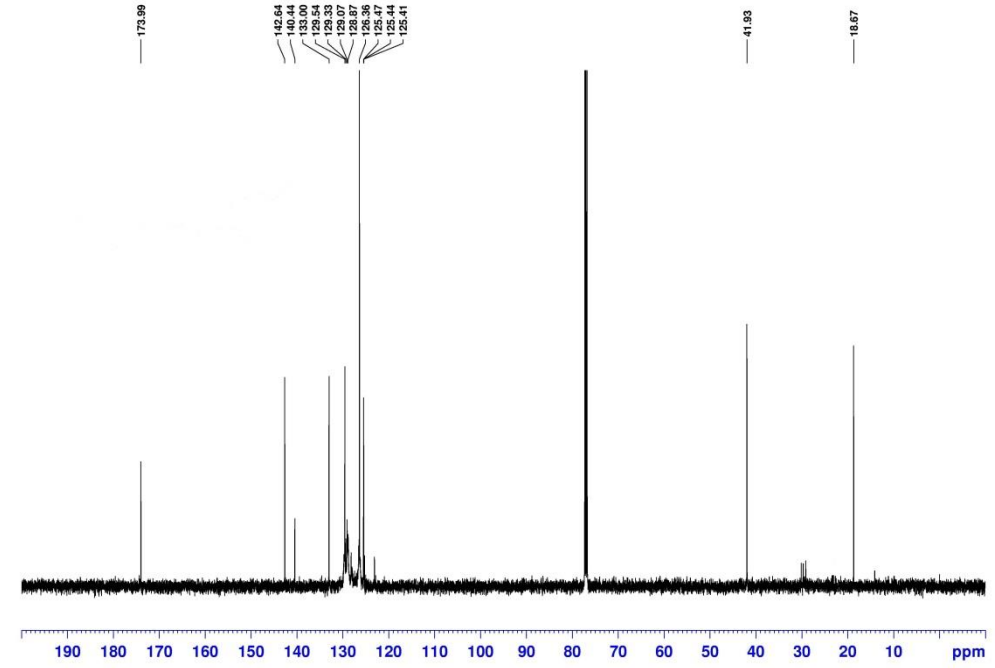
1.01
1.01
3.25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125.47
125.44
125.41
41.93
18.67
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150
140
130
120
110
100
90
80
70
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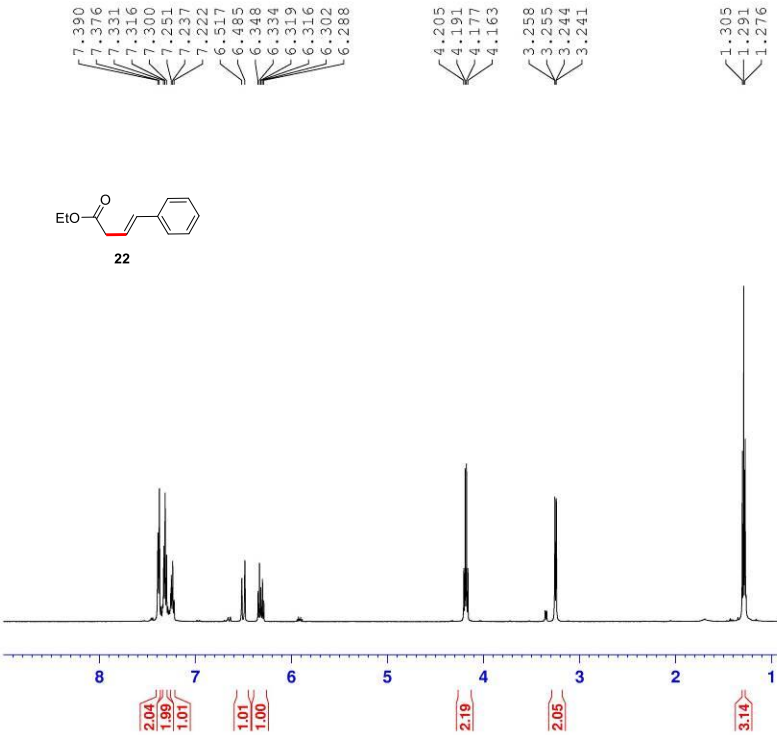
50
40
30
20
10
ppm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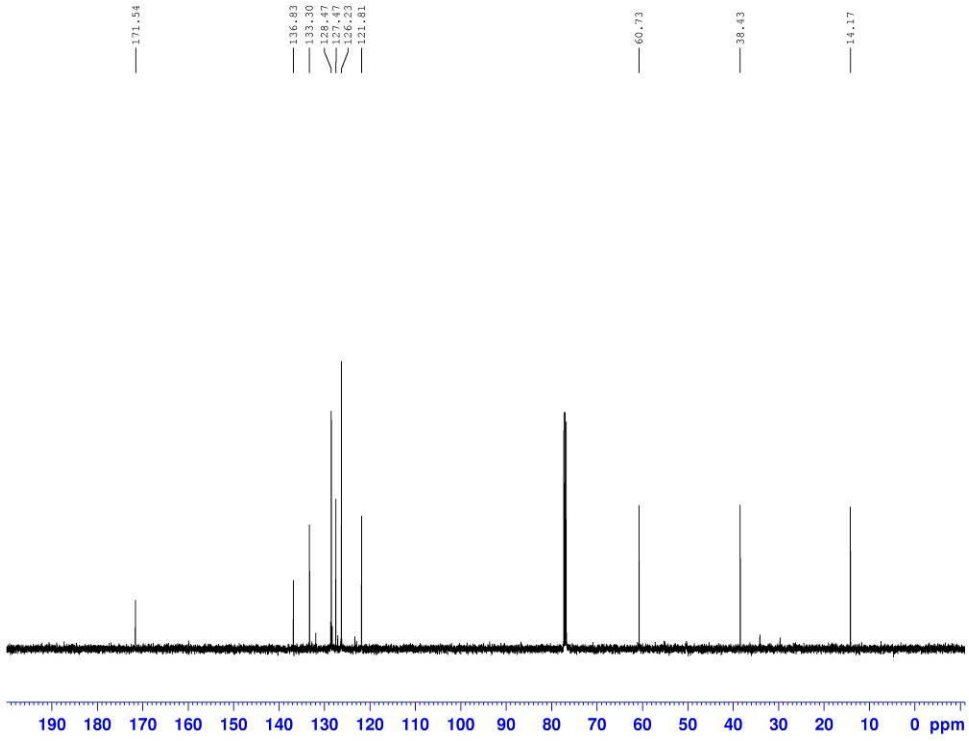
7.300
7.251
7.237
7.222
6.517
6.485
6.348
6.334
6.319
6.316
6.302
6.288
4.205
4.191
4.177
4.163
3.258
3.255
3.244
3.241
1.305
1.291
1.276
EtO
O
22
8
7
6
5
4
3
2
1
0
ppm
2.04
1.99
1.01
1.01
1.00
2.19
2.05
3.14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126.33
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60.73
38.43
14.17
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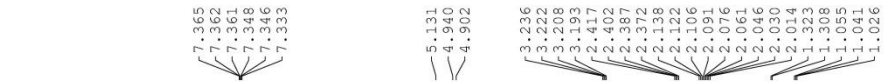
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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7.361
7.348
7.346
7.333
5.131
4.940
4.902
3.236
3.222
3.208
3.193
2.417
2.402
2.387
2.372
2.138
2.122
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2.076
2.061
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2.030
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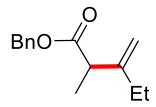
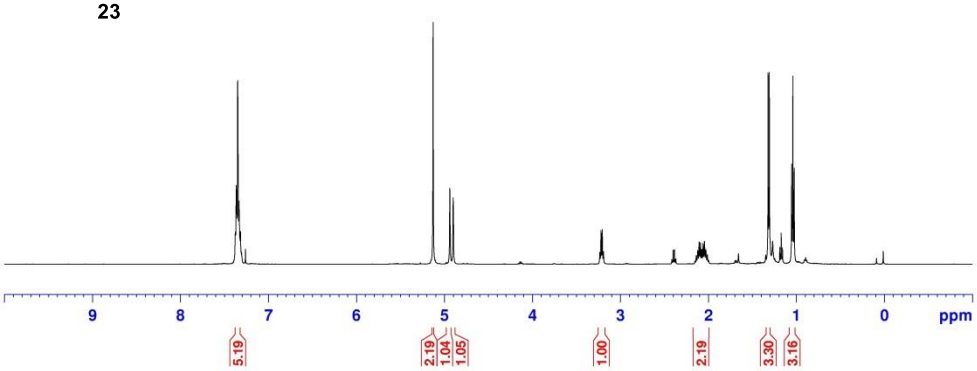
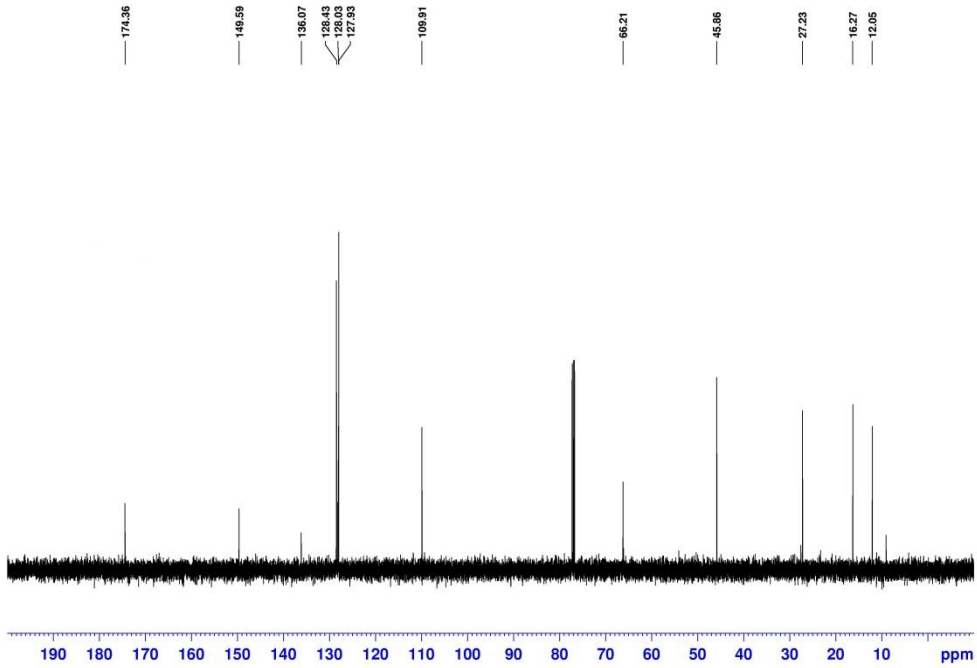
1.041
1.026


BnO
O
Et

23


9
8
7
6
5
4
3
2
1
0
ppm
5.19
2.19
1.04
1.05
1.00
2.19
3.30
3.16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128.43
128.03
127.93
109.91
66.21
45.86
27.23
16.27
12.05
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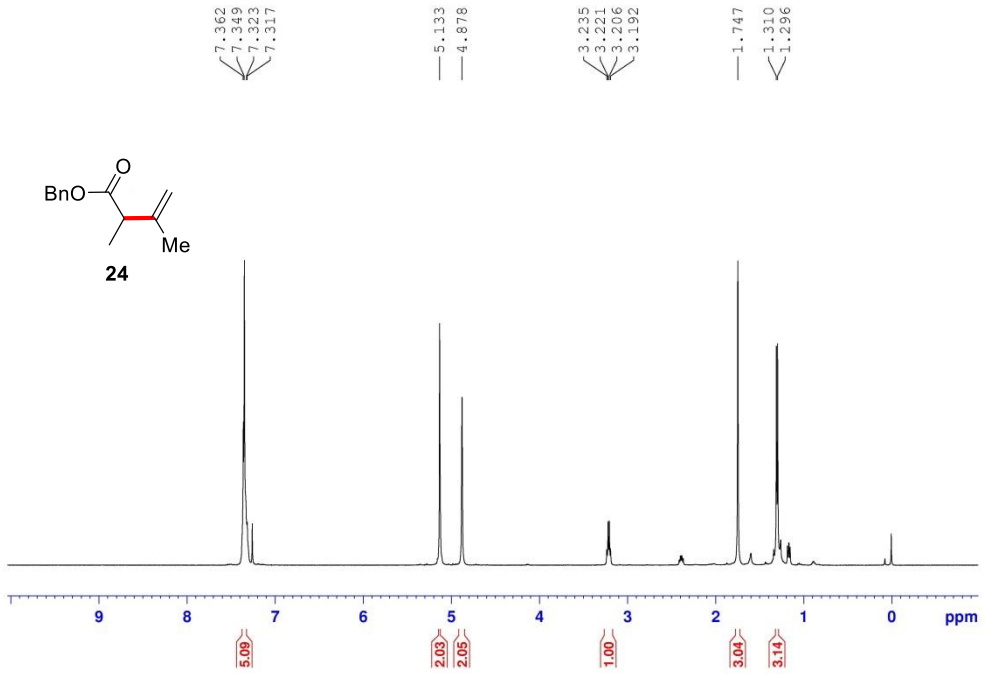
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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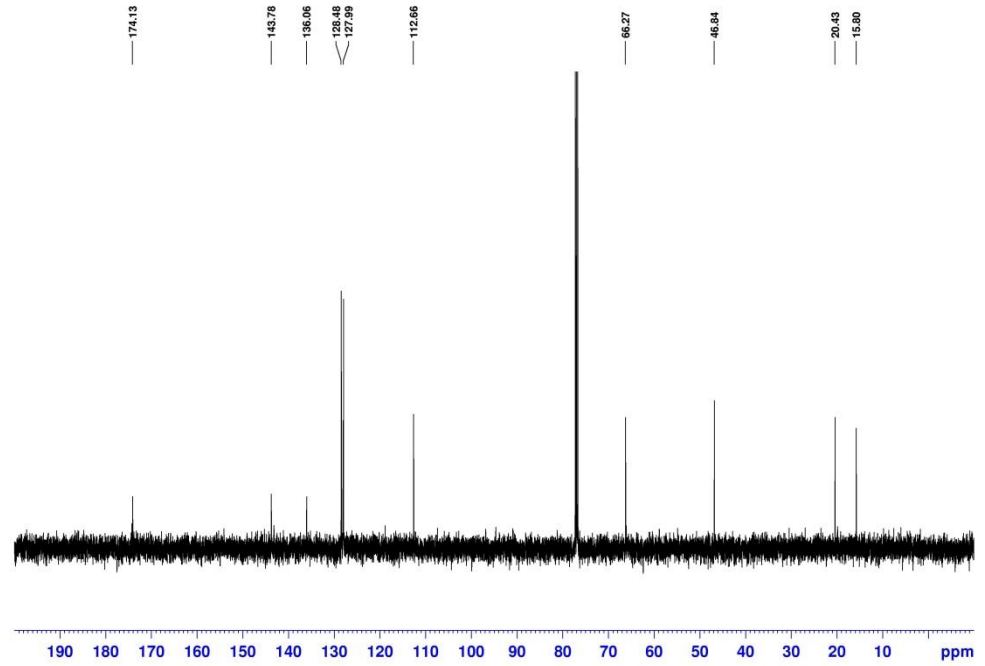
3.206
3.192
1.747
1.310
1.296
O
BnO
Me
24
9
8
7
6
5
4
3
2
1
0
ppm
5.09
2.03
2.05
1.00
3.04
3.14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112.66
66.27
46.84
20.43
15.80
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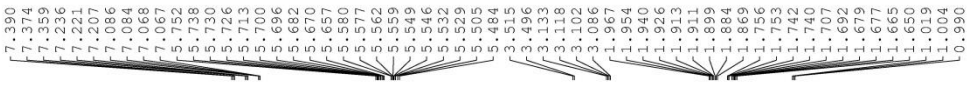
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.084
7.068
7.067
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5.738
5.730
5.726
5.713
5.700
5.696
5.682
5.670
5.657
5.580
5.577
5.562
5.559
5.549
5.546
5.532
5.529
5.505
5.484
3.515
3.496
3.133
3.118
3.102
3.086
1.967
1.954
1.940
1.926
1.913
1.911
1.899
1.884
1.869
1.756
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1.692
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1.677
1.665
1.650
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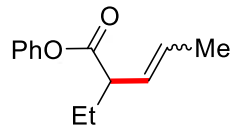
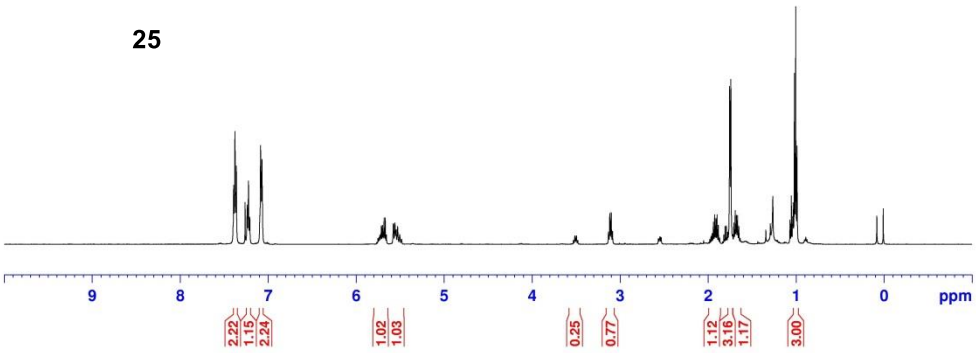
1.004
0.990


O
PhO
Me
Et

25


9
8
7
6
5
4
3
2
1
0
ppm
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1.15
2.24
1.02
1.03
0.25
0.77
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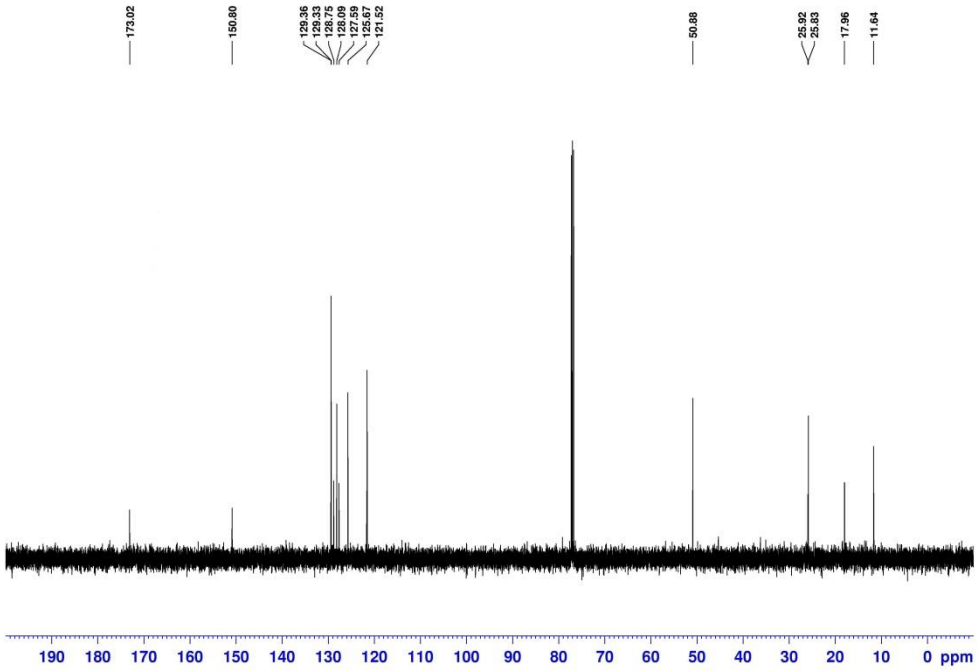
3.16
1.17
3.00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128.09
127.59
125.67
121.52
50.88
25.92
25.83
17.96
11.64
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


7.392
7.376
7.360
7.239
7.223
7.077
7.061
7.060
5.015
3.198
3.183
3.167
1.861
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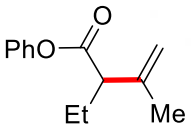
1.778
1.764
1.750
1.736
1.722
1.708
1.015
1.001
0.986


O
PhO
Et
Me

26

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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
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ppm
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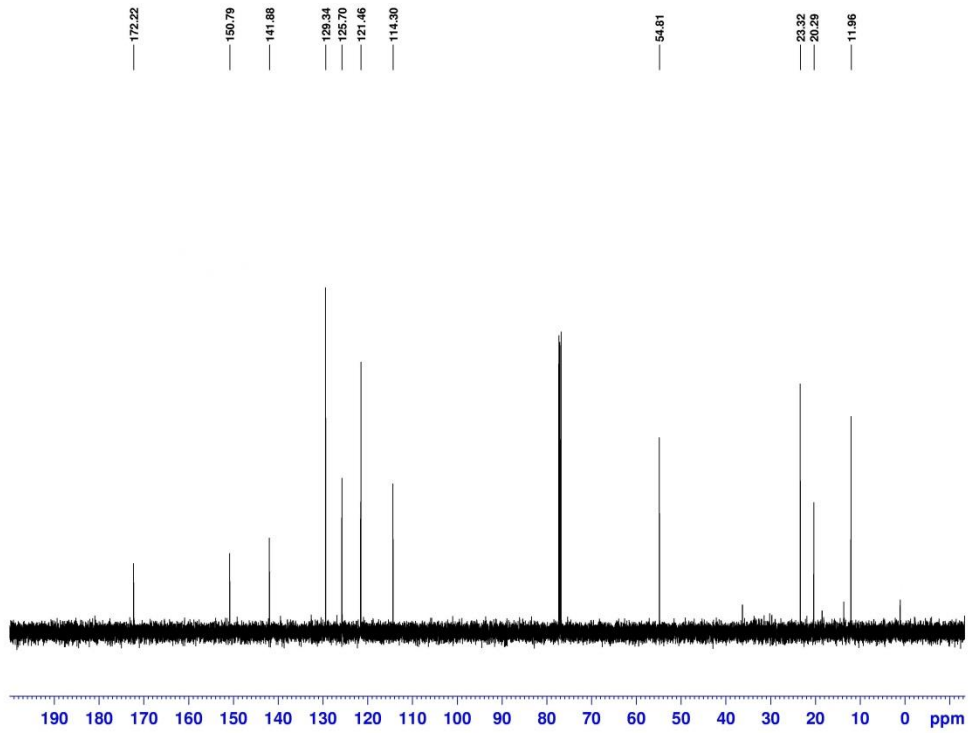
2.15
2.11
1.00
1.16
3.06
1.15
3.13


172.22
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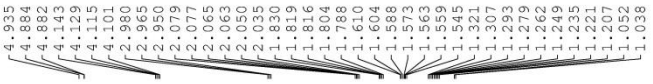
129.34
125.70
121.46
114.30
54.61
23.32
20.29
11.96
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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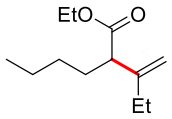
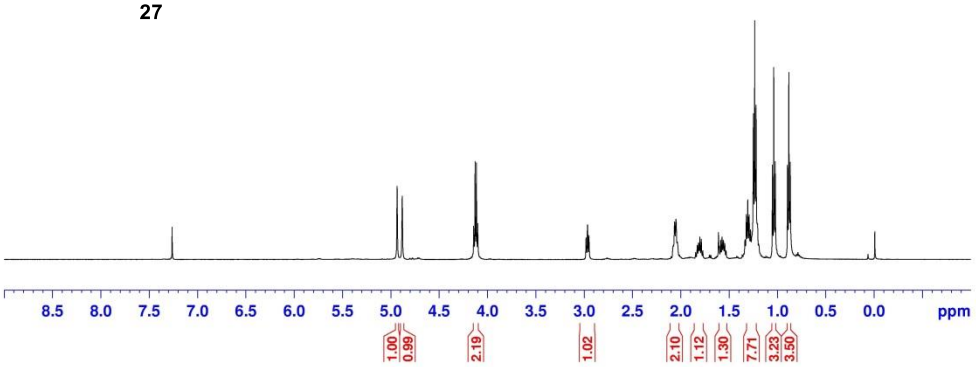
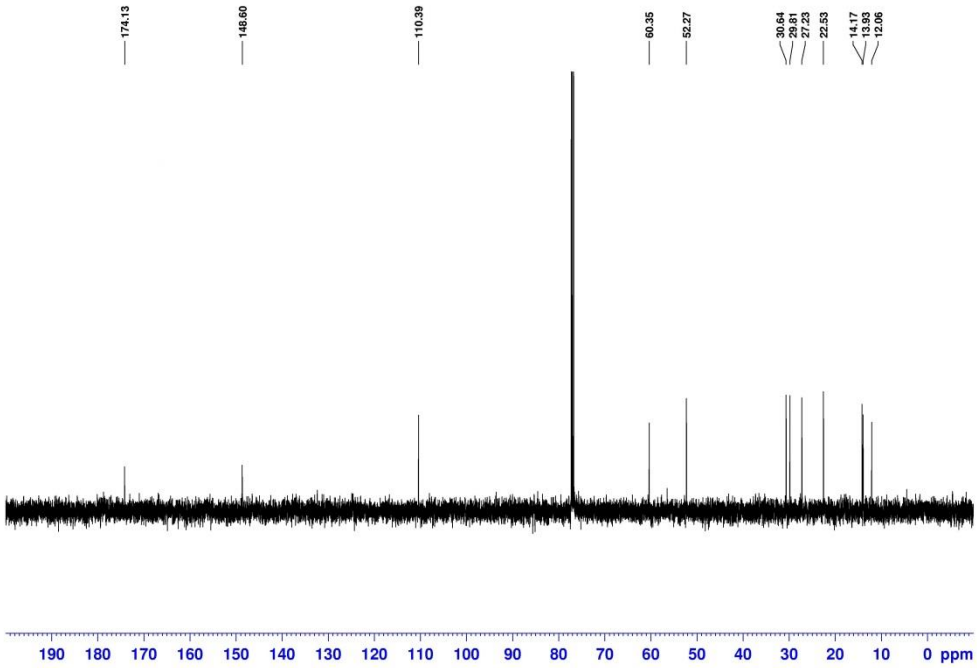
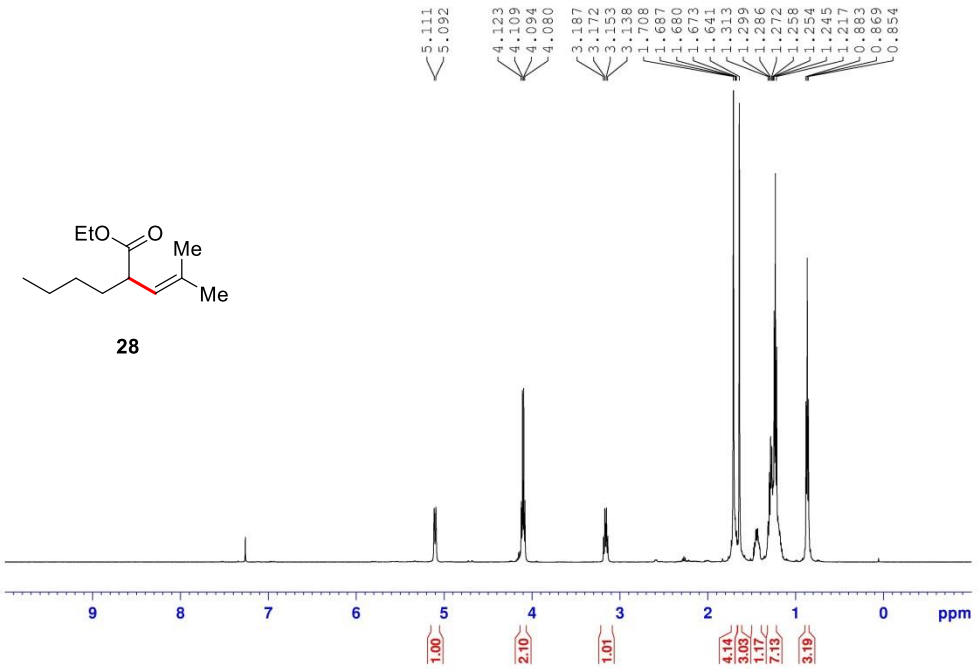
4.882
4.143
4.129
4.115
4.101
2.980
2.965
2.950
2.079
2.077
2.065
2.063
2.050
2.035
1.830
1.819
1.816
1.804
1.788
1.610
1.604
1.588
1.573
1.563
1.559
1.545
1.321
1.307
1.293
1.279
1.262
1.249
1.235
1.221
1.207
1.052
1.038


EtO
O
Et

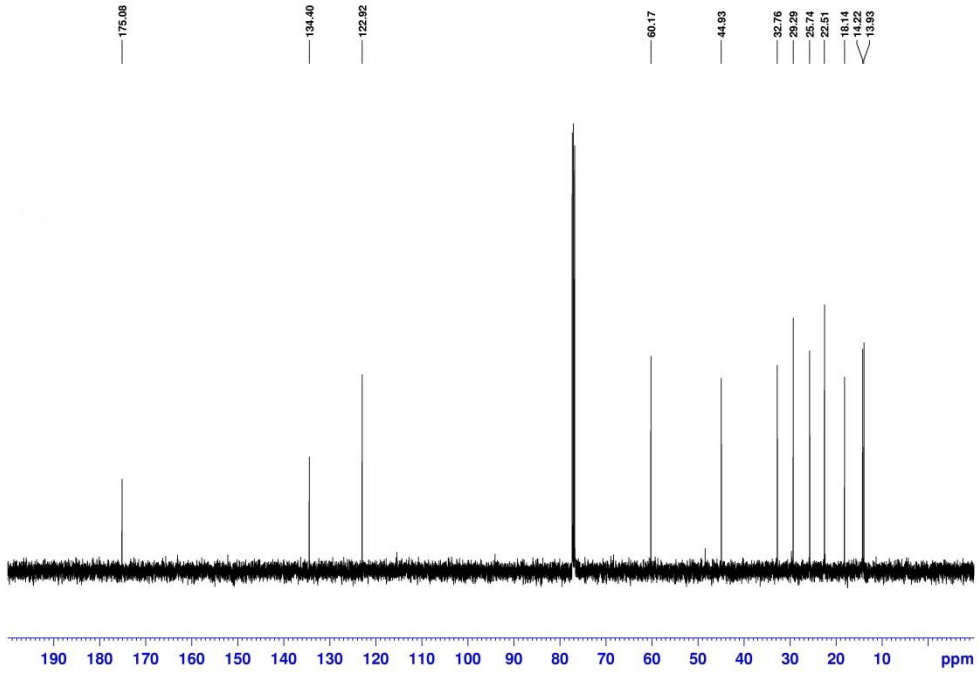
27


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 ppm
1.00
0.99
2.19
1.02
2.10
1.12
1.30
7.71
3.23
3.50


174.13
148.60
110.39
60.35
52.27
30.64
29.81
27.23
22.53
14.17
13.93
12.06
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


5.111
5.092
4.123
4.109
4.094
4.080
3.187
3.172
3.153
3.138
1.708
1.687
1.680
1.673
1.641
1.313
1.299
1.286
1.272
1.258
1.254
1.245
1.217
0.883
0.869
0.854
EtO
O
Me
Me
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.10
1.01
4.14
3.03
1.17
7.13
3.19

28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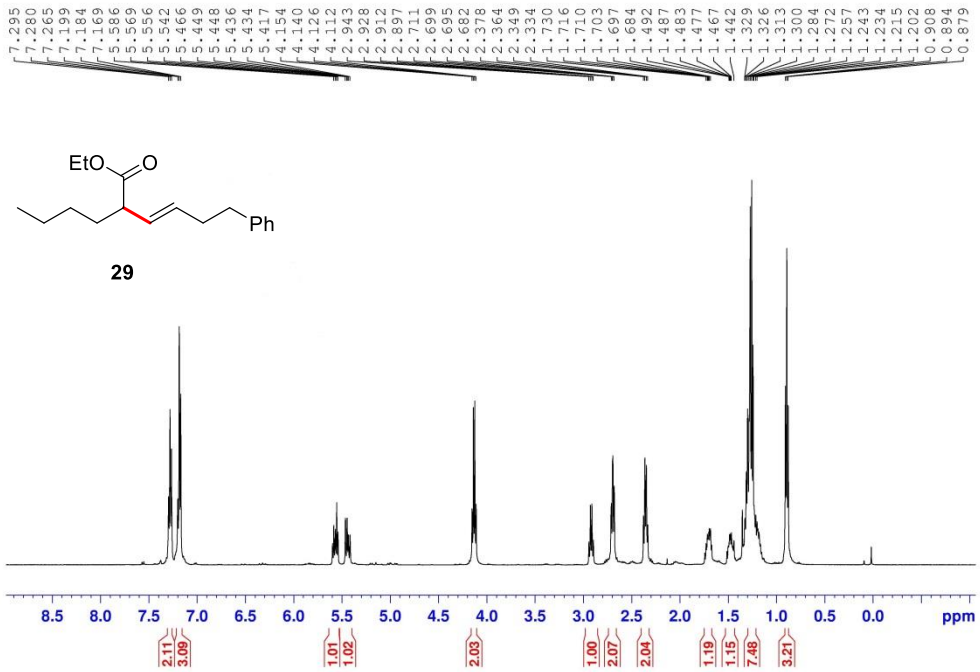
134.40
122.92
60.17
44.93
32.76
29.29
25.74
22.51
18.14
14.22
13.93
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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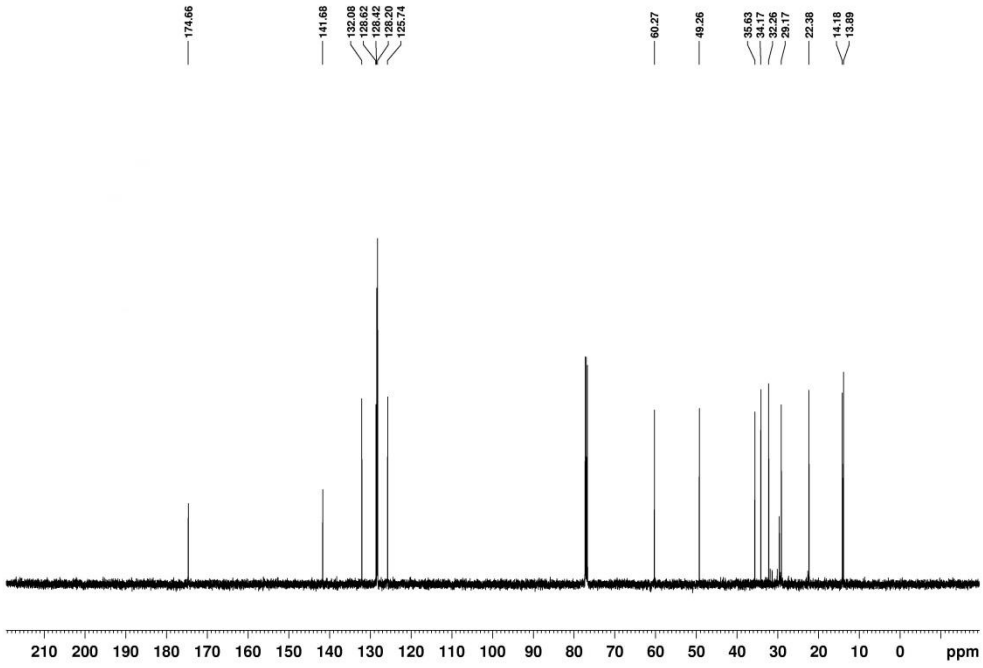
7.280
7.265
7.199
7.184
7.169
5.586
5.569
5.556
5.542
5.466
5.449
5.448
5.436
5.434
5.417
4.154
4.140
4.126
4.112
2.943
2.928
2.912
2.897
2.711
2.699
2.695
2.682
2.378
2.364
2.349
2.334
1.730
1.716
1.710
1.703
1.697
1.684
1.492
1.487
1.483
1.477
1.467
1.442
1.329
1.326
1.313
1.300
1.284
1.272
1.257
1.243
1.234
1.215
1.202
0.908
0.894
0.879
EtO
O
Ph
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 ppm
2.11
3.09
1.01
1.02
2.03
1.00
2.07
2.04
1.19
1.15
7.48
3.21

29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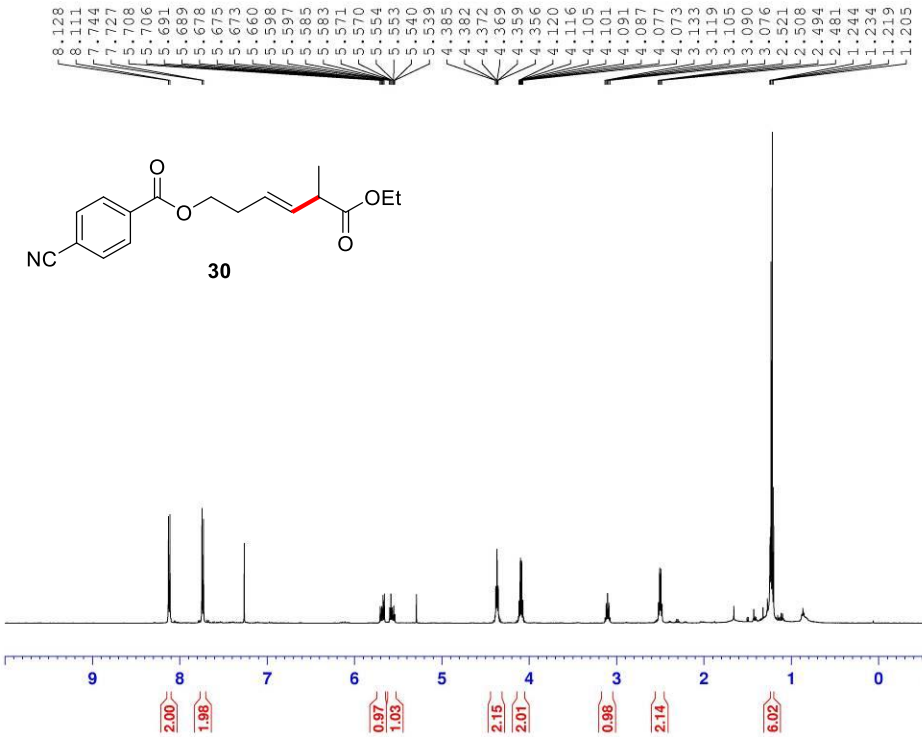
141.68
132.08
128.62
128.42
128.20
125.74
60.27
49.26
35.63
34.17
32.26
29.17
22.38
14.18
13.89
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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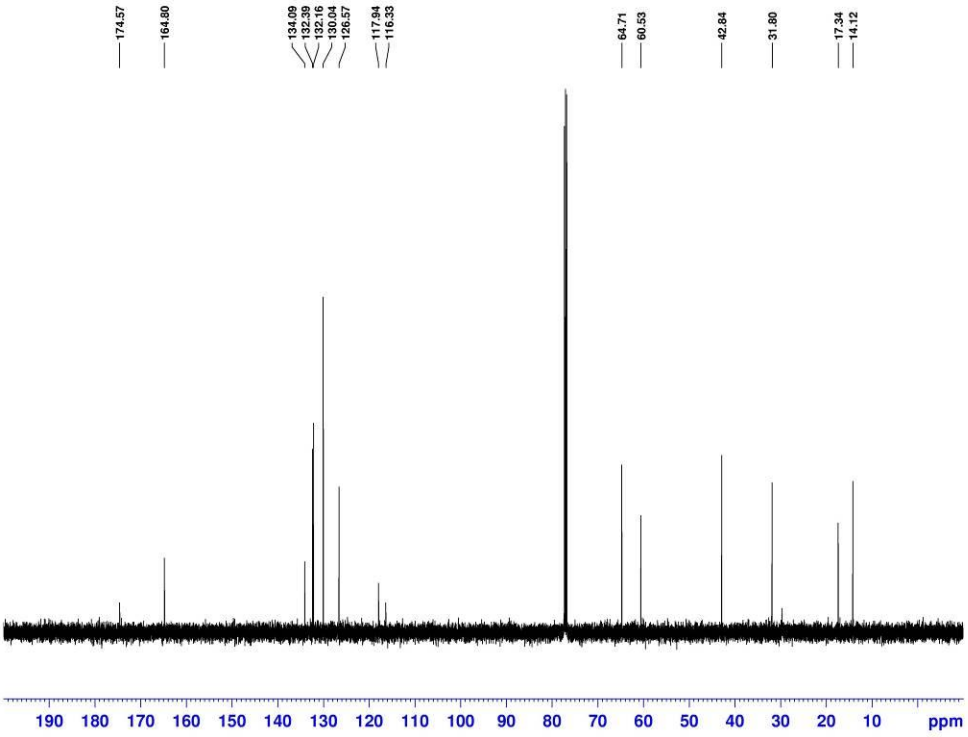
8.111
7.744
7.727
5.708
5.706
5.691
5.689
5.678
5.675
5.673
5.660
5.598
5.597
5.585
5.583
5.571
5.570
5.554
5.553
5.540
5.539
4.385
4.382
4.372
4.369
4.359
4.356
4.120
4.116
4.105
4.101
4.091
4.087
4.077
4.073
3.133
3.119
3.105
3.090
3.076
2.521
2.508
2.494
2.481
1.244
1.234
1.219
1.205
O
O
OEt
O
NC
30
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.98
0.97
1.03
2.15
2.01
0.98
2.14
6.02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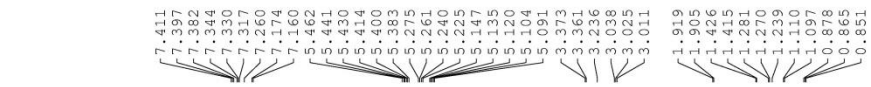
134.09
132.39
132.16
130.04
126.57
117.84
116.33
64.71
60.53
42.84
31.80
17.34
14.12
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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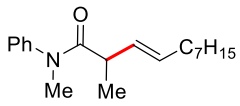
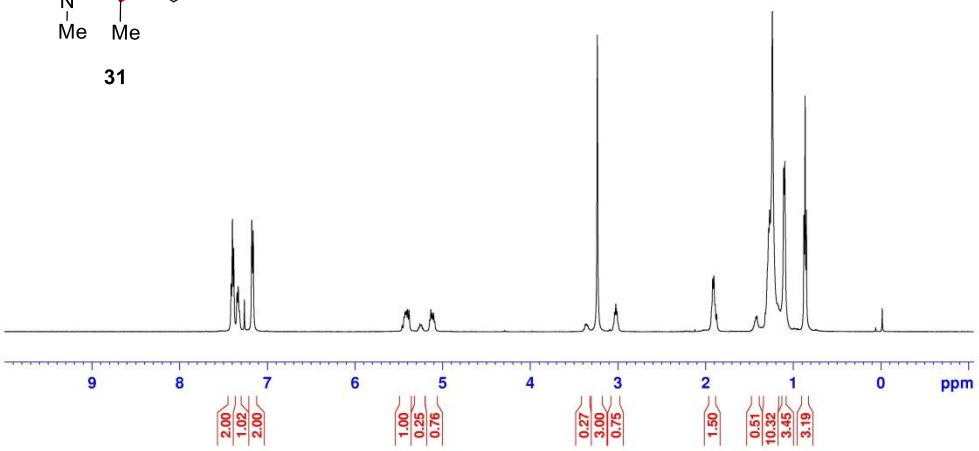
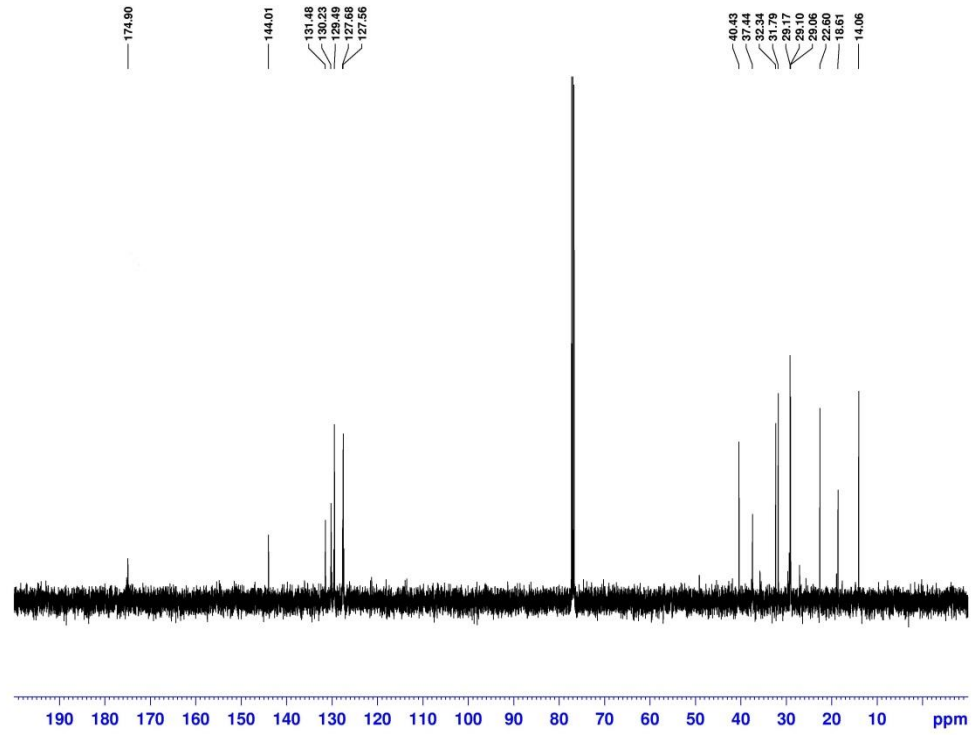
7.397
7.382
7.344
7.330
7.317
7.260
7.174
7.160
5.462
5.441
5.430
5.414
5.400
5.383
5.275
5.261
5.240
5.225
5.147
5.135
5.120
5.104
5.091
3.373
3.361
3.236
3.038
3.025
3.011
1.919
1.905
1.426
1.415
1.281
1.270
1.239
1.110
1.097
0.878
0.865
0.851


O
Ph
N
Me
Me
C7H15

31


9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.02
2.00
1.00
0.25
0.76
0.27
3.00
0.75
1.50
0.51
10.32
3.45
3.19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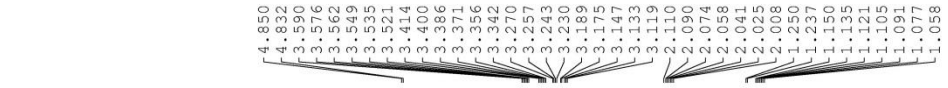
144.01
131.48
130.23
129.49
127.68
127.56
40.43
37.44
32.34
31.79
29.17
29.10
29.06
22.60
18.61
14.06
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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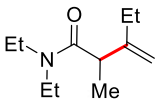
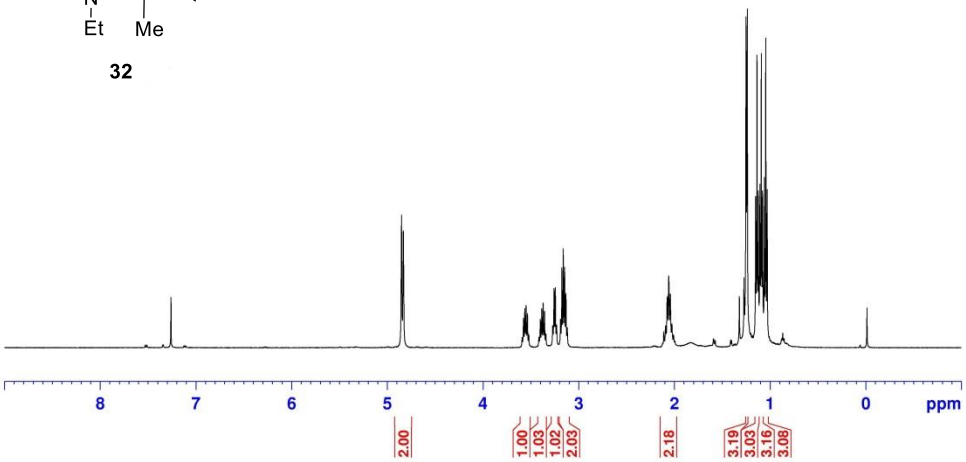
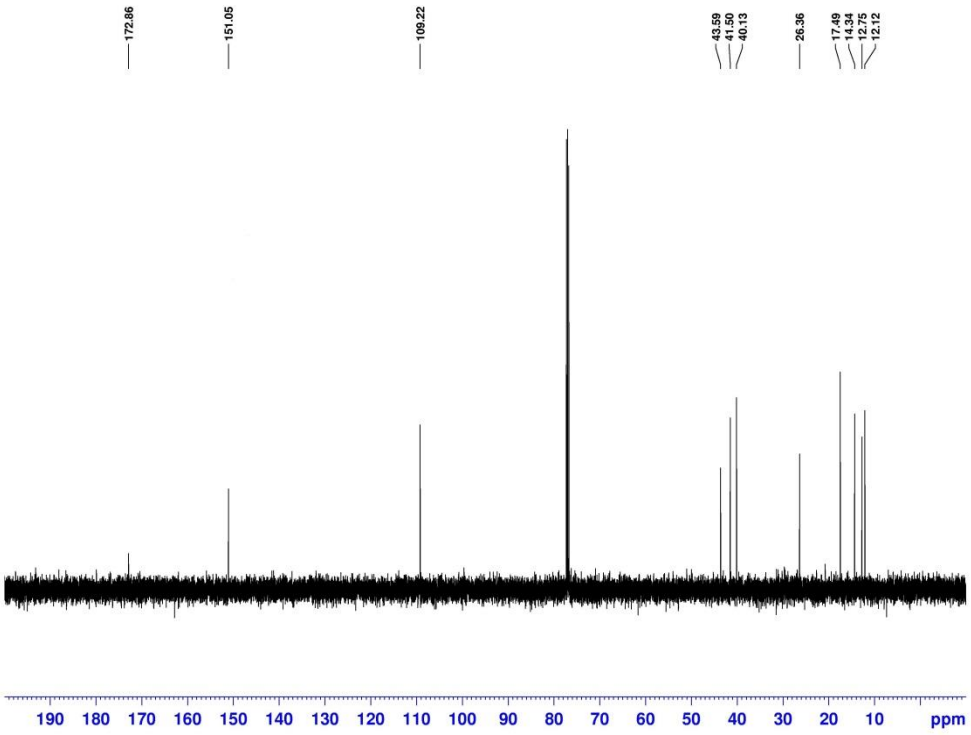
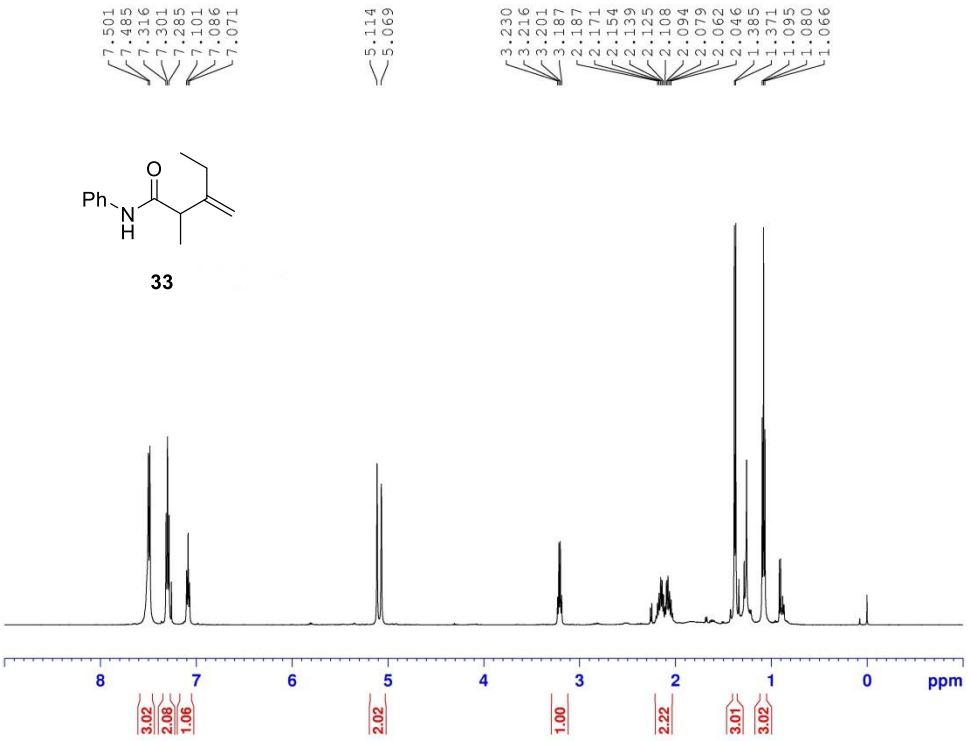
4.832
3.590
3.576
3.562
3.549
3.535
3.521
3.414
3.400
3.386
3.371
3.356
3.342
3.270
3.257
3.243
3.230
3.189
3.175
3.147
3.133
3.119
2.110
2.090
2.074
2.058
2.041
2.025
2.008
1.250
1.237
1.150
1.135
1.121
1.105
1.091
1.077
1.058


O
Et
Et
N
Et
Me

32


8
7
6
5
4
3
2
1
0
ppm
2.00
1.00
1.03
1.02
2.03
2.18
3.19
3.03
3.16
3.08


172.86
151.05
109.22
43.59
41.50
40.13
26.36
17.49
14.34
12.75
12.12
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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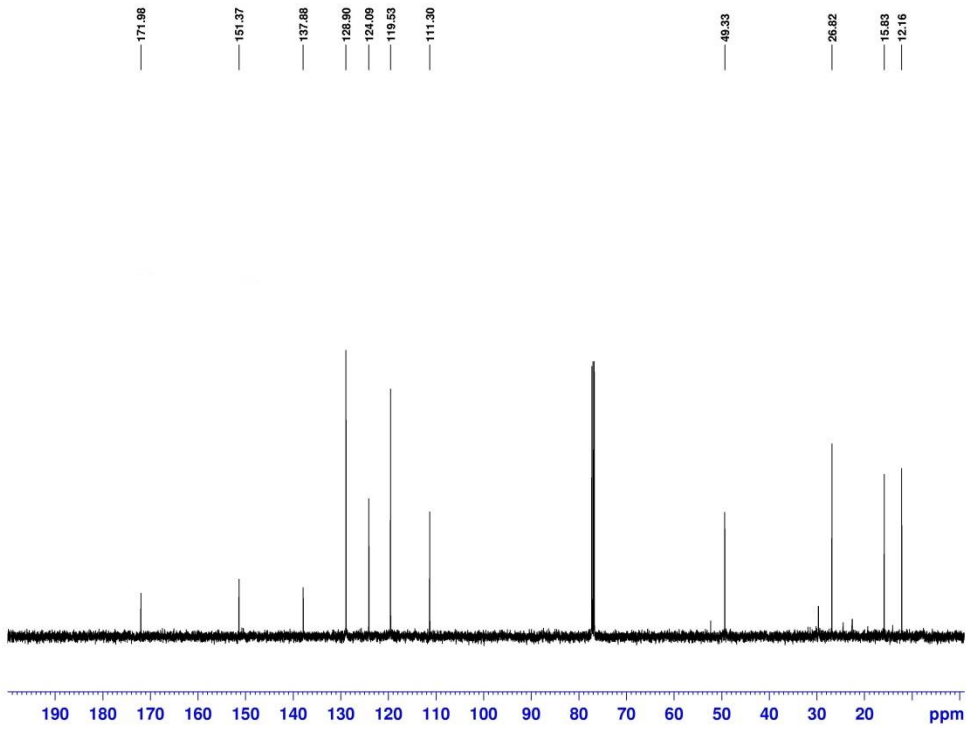
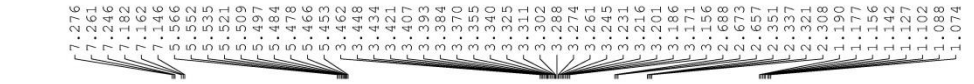
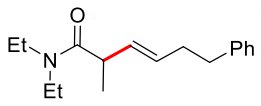
7.485
7.316
7.301
7.285
7.101
7.086
7.071
5.114
5.069
3.230
3.216
3.201
3.187
2.187
2.171
2.154
2.139
2.125
2.108
2.094
2.079
2.062
2.046
1.385
1.371
1.095
1.080
1.066
Ph
N
H
O
33
8
7
6
5
4
3
2
1
0
ppm
3.02
2.08
1.06
2.02
1.00
2.22
3.01
3.02

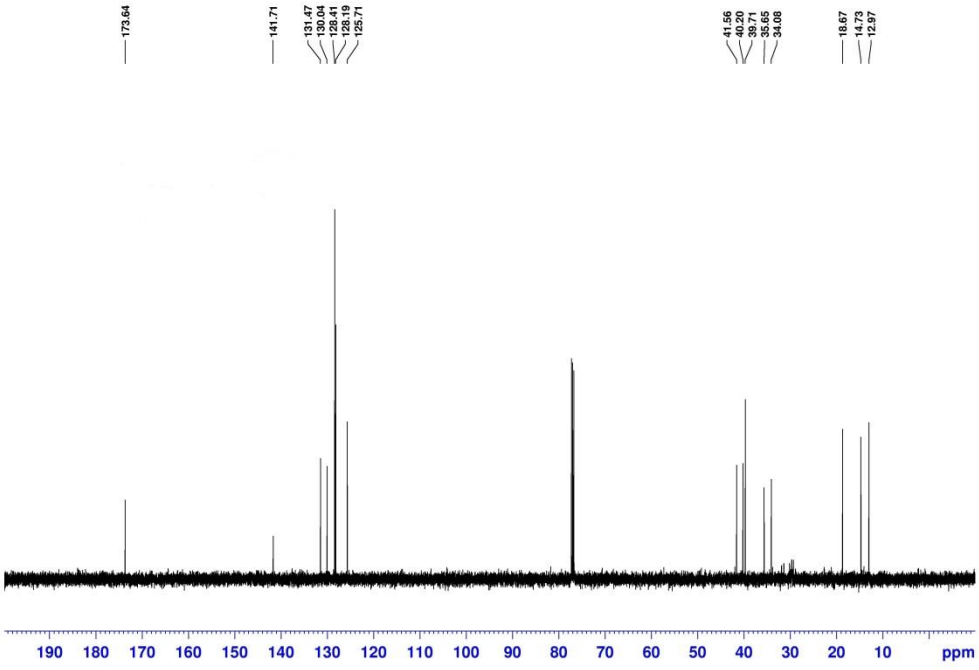

171.98
151.37
137.88
128.90
124.09
119.53
111.30
49.33
26.82
15.83
12.16
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

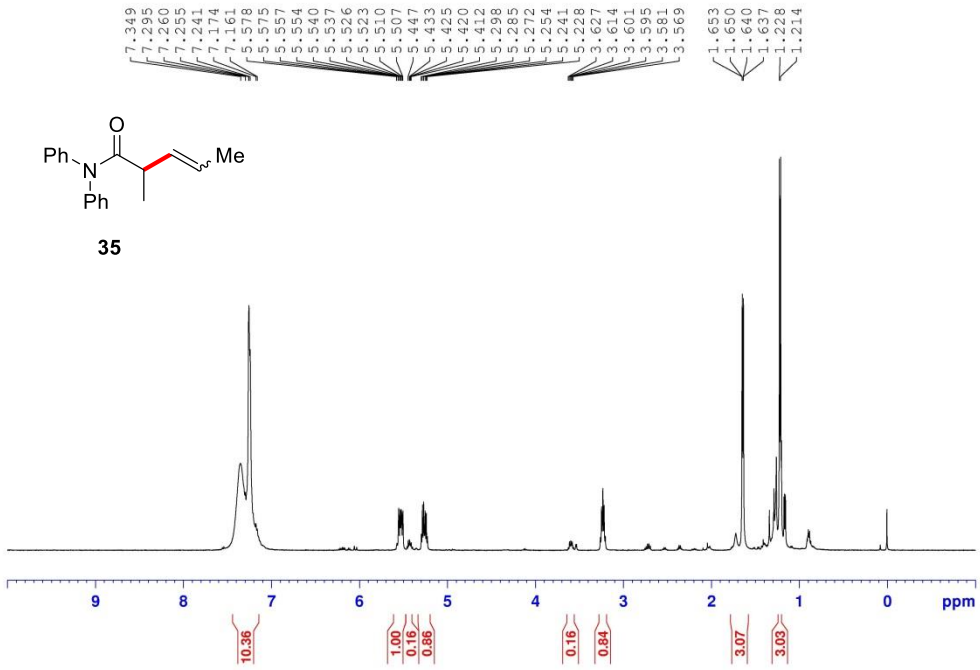

7.276
7.261
7.246
7.182
7.162
7.146
5.566
5.552
5.535
5.521
5.509
5.497
5.484
5.478
5.466
5.453
3.462
3.448
3.434
3.421
3.407
3.393
3.384
3.370
3.355
3.340
3.325
3.311
3.302
3.288
3.274
3.261
3.245
3.231
3.216
3.201
3.186
3.171
3.156
2.688
2.673
2.657
2.351
2.337
2.321
2.308
1.190
1.177
1.156
1.142
1.127
1.102
1.088
1.074


O
Et
N
Et
Ph

34

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
ppm
2.06
3.02
2.00
5.37
2.12
2.08
3.02
3.26
3.16


173.64
141.71
131.47
130.04
128.41
128.19
125.71
41.56
40.20
39.71
35.65
34.08
18.67
14.73
12.97
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.260
7.255
7.241
7.174
7.161
5.578
5.575
5.557
5.554
5.540
5.537
5.526
5.523
5.510
5.507
5.447
5.433
5.425
5.420
5.412
5.298
5.285
5.272
5.254
5.241
5.228
3.627
3.614
3.601
3.595
3.581
3.569
1.653
1.650
1.640
1.637
1.228
1.214
O
Ph
N
Ph
Me
35
9
8
7
6
5
4
3
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1
0
ppm
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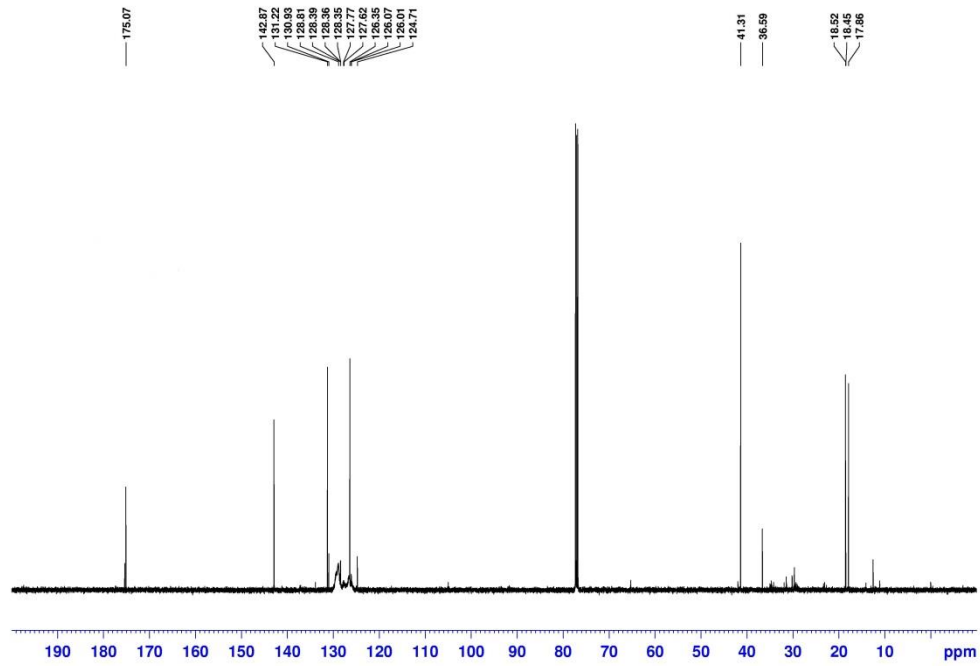
1.00
0.16
0.86
0.16
0.84
3.07
3.03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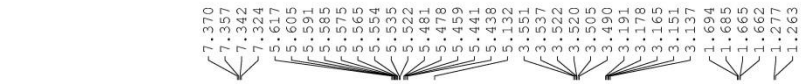
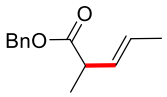
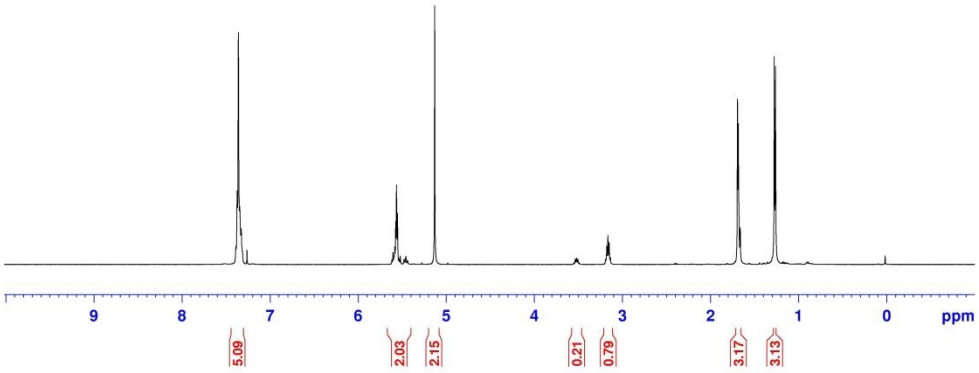
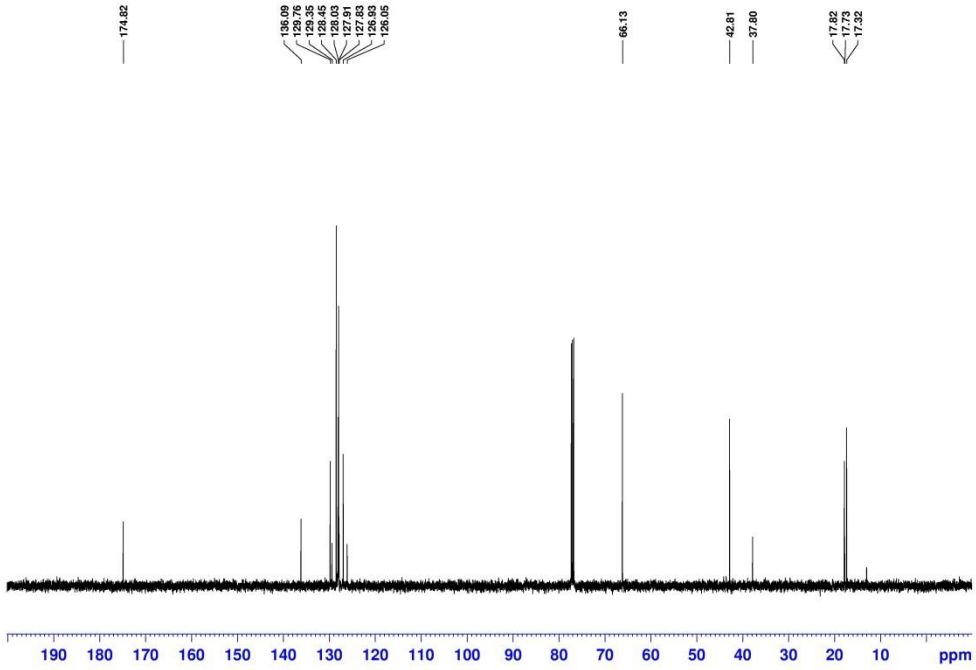
142.87
141.22
130.68
128.81
128.39
128.36
128.35
127.77
127.62
126.35
126.07
126.01
124.71
41.31
36.59
18.52
18.45
17.66
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.370
7.357
7.342
7.324
5.617
5.605
5.591
5.585
5.575
5.565
5.554
5.535
5.522
5.481
5.478
5.459
5.441
5.438
5.132
3.551
3.537
3.522
3.520
3.505
3.490
3.191
3.178
3.165
3.151
3.137
1.694
1.685
1.665
1.662
1.277
1.263


O
BnO

36


9
8
7
6
5
4
3
2
1
0
ppm
5.09
2.03
2.15
0.21
0.79
3.17
3.13


174.82
136.09
129.76
128.85
128.45
128.03
127.91
127.83
126.93
126.05
66.13
42.61
37.80
17.82
17.73
17.32
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

III. Reference

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