Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information
For the article entitled

Ruthenium- and Rhodium-Catalyzed Cross-Coupling Reaction of Acrylamides with Alkenes: Efficient Access to (*Z, E*)-Dienamides

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]Supporting Information

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General Methods

All commercially available reagents for the cross-coupling reaction were used as received: AR grade acetone, 1,2-dichloroethane, 1,2-dimethoxyethane and acetonitrile were obtained from Sigma-Aldrich and used as received. $[RhCp^*Cl_2]_2$ and $[RuCl_2(p\text{-cymene})]_2$ were obtained from Strem Chemicals Inc. $Cu(OAc)_2 \cdot H_2O$ was purchased from Alfa Aesar. The starting materials of acrylamides were prepared according to the reported method. All cross-coupling reactions were run in vials under sealed nitrogen atmosphere. Thin-layer chromatography (TLC) was conducted with Merck 60 F254 pre-coated silica *gel* plate (0.2 mm thickness) and visualized with UV and potassium permanganate staining, followed by heating on a hot plate. Flash chromatography was performed using Merck silica gel 60 with distilled solvents. ^1H NMR spectra were performed on a Bruker 400 NMR spectrometer and are reported in ppm downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ = 7.26 ppm, singlet). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration. Proton-decoupled ^{13}C NMR spectra were recorded on a 400 (100 MHz) or ECA-400 (100 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.23 ppm). IR spectra were recorded as thin films on NaCl plates on a Bio-Rad FTS 165 FTIR spectrometer and are reported in frequency of absorption (cm^{-1}). High resolution mass spectral analysis (HRMS) was performed on Waters Q-Tof Permies Mass Spectrometer.

General Procedure for the Synthesis of Acrylamides

Representative Procedure A: Synthesis of Acrylamides from Acid Chlorides and Anilines

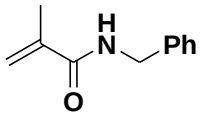
Acid chloride (5.00 mmol) was added dropwise at 0 ℃ to a solution of aniline (5.00 mmol) and NEt_3 (0.73 mL, 5.25 mmol) in dry ethyl acetate (20.0 mL). The temperature was allowed to rise to ambient temperature, and then the mixture was stirred at room temperature for 2-6 h. After dilution with ethyl acetate and washing with water, the organic phase was dried over anhydrous Na_2SO_4, filtered. After removal of the solvents in reduced pressure, the crude product was purified by column chromatography on silica gel (EtOAc/Hexane) to yield corresponding acrylamide. [2]

Representative Procedure B: Synthesis of Acrylamides from Acid Chlorides and Amines

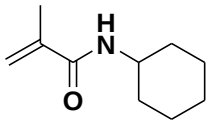
Acid chloride (5.00 mmol) was added dropwise at 0 ℃ to a solution of amine (5.00 mmol) and NEt_3 (0.73 mL, 5.25 mmol) in dry DCM (20.0 mL). The temperature was allowed to rise to ambient temperature, and then the mixture was stirred at the same temperature for 2-6 h. After dilution with DCM and washing with water, the organic phase was dried over anhydrous Na_2SO_4, filtrated. After removal of the solvents in reduced pressure, the crude product was purified by column chromatography on silica gel (EtOAc/Hexane) to yield corresponding acrylamide.

Representative Procedure C: Synthesis of Acrylamides from Acids

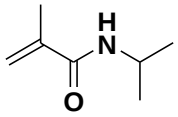
EDC·HCl (1.15 g, 6.00 mmol) was added at ambient temperature to a stirred mixture of acid (5.00 mmol), HOBt·H_2O (230 mg, 1.50 mmol) and amine (5.25 mmol) in anhydrous MeCN (6.00 mL). After 5 min, Et_3N (0.73 mL, 5.25 mmol) was added, and the reaction mixture was allowed to stir for several hours at the same temperature. Thereafter, water was added, and the mixture was extracted with EtOAc. The combined organic phase was washed with brine (30.0 mL) and dried over anhydrous Na_2SO_4. After removal of the solvents in reduced pressure, the crude product was purified by column chromatography on silica gel (EtOAc/Hexane) to yield corresponding acrylamide. [2]



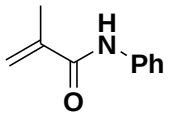
***N*-Benzyl methacrylamide[1]:** This compound was prepared by **Procedure B** and was obtained as a white solid, yield = 61 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27-7.37 (m, 5H), 6.30 (b, 1H), 5.73 (s, 1H), 5.35 (s, 1H), 4.50 (d, *J* = 5.6 Hz, 2H), 1.99(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.31, 139.96, 138.30, 128.74, 127.83, 127.53, 119.68, 43.74, 18.73.



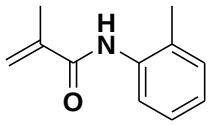
***N*-Cyclohexyl methacrylamide[2]:** This compound was prepared by **Procedure B** and was obtained as a white solid, yield = 67 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.72 (b, 1H), 5.64 (s, 1H), 5.28 (s, 1H), 3.80 (m, 1H), 1.93-2.02 (m, 5H), 1.61-1.74 (m, 3H), 1.33-1.43 (m, 2H), 1.11-1.24 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.55, 140.54, 118.87, 48.21, 33.09, 25.55, 24.87, 18.70.



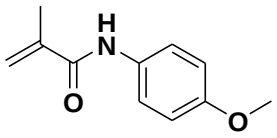
***N*-*iso*propyl methacrylamide[2]:** This compound was prepared by **Procedure B** and was obtained as a white solid, yield = 71 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.64 (b, 1H), 5.64 (s, 1H), 5.29 (s, 1H), 4.12 (m, 1H), 1.95 (s, 3H), 1.18 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.63, 140.44, 118.92, 41.42, 22.72, 18.67.



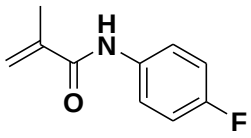
***N*-Phenyl methacrylamide[2]:** This compound was prepared by **Procedure A** and was obtained as a yellow solid, yield = 81 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (b, 1H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 1H), 5.81 (s, 1H), 5.46 (s, 1H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.72, 140.94, 137.82, 129.01, 124.43, 120.11, 119.84, 18.78.



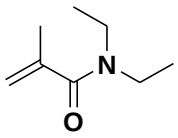
***N*-(*o*-Tolyl) methacrylamide[2]:** This compound was prepared by **Procedure A** and was obtained as a white solid, yield = 91 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.0 Hz, 1H), 7.45 (b, 1H), 7.20-7.26 (m, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 5.84 (s, 1H), 5.48 (s, 1H), 2.29 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.52, 140.86, 135.67, 130.46, 128.94, 126.83, 125.17, 122.88, 119.93, 18.79, 17.70.



***N*-(4-Methoxyl phenyl) methacrylamide[2]:** This compound was prepared by **Procedure A** and was obtained as a white solid, yield = 89 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (b, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 5.79 (s, 1H), 5.43 (s, 1H), 3.80 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.61, 156.49, 140.82, 130.92, 122.00, 119.67, 114.13, 55.48, 18.79.

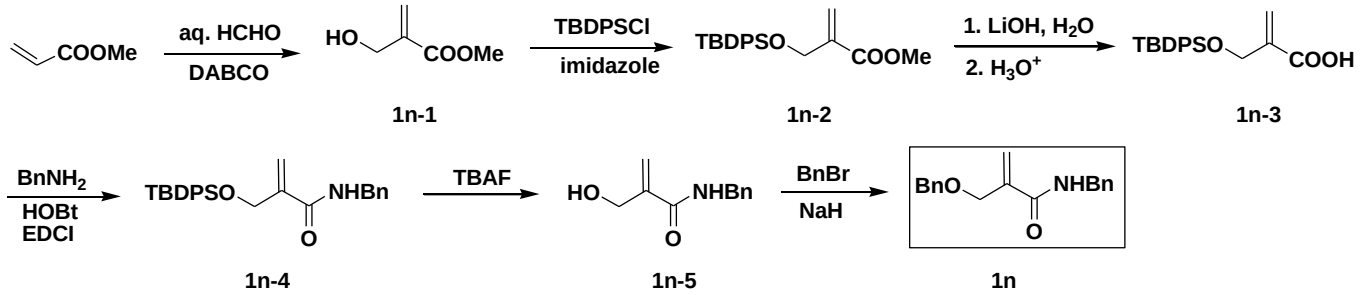


***N*-(4-Fluoro phenyl) methacrylamide[2]:** This compound was prepared by **Procedure A** and was obtained as a white solid, yield = 76 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (b, 1H), 7.52-7.55 (m, 2H), 7.03 (t, *J* = 8.4 Hz, 2H), 5.80 (s, 1H), 5.47 (s, 1H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.65, 159.44 (*J* = 243 Hz), 140.68, 133.76, 122.02 (*J* = 8 Hz), 120.02, 115.61 (*J* = 22 Hz), 18.74.



***N*,*N*-Diethyl methacrylamide[5]:** This compound was prepared by **Procedure B** and was obtained as a colourless oil, yield = 69 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.08 (s, 1H), 4.98 (s, 1H), 3.37 (b, 4H), 1.94 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 6H).

Preparation of *N*-Benzyl-2-benzyloxymethyl-propenamide



A solution of formaldehyde (10 mmol) and methyl acrylate (3 mmol) in 10 mL of 1, 4-dioxane-water (1:1, v/v) was stirred at room temperature in the presence of 1.0 equiv DABCO, and the reaction progress was monitored by TLC. Upon completion, the reaction mixture was diluted with water (80 mL) and extracted with ethyl acetate. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel, using ethyl acetate and hexane as the eluting solvents to give the **1n-1**, methyl 2-hydroxymethylpropenate [6], as a colourless liquid (0.226 g, 65 %). ^{1}H NMR ($CDCl_3$): δ = 6.21 (m, 1H), 5.81 (m, 1H), 4.27 (m, 2H), 3.73 (s, 3H), 2.82 (br, 1H). ^{13}C NMR ($CDCl_3$): δ = 166.6, 139.3, 125.5, 62.0, 51.7.

To a mixture of methyl 2-hydroxymethylpropenate (0.226 g, 1.95 mmol) and imidazole (2.14 mmol) in dry DCM (10 mL) was added TBDPSCl (2.14 mmol) in dropwise at 0 ℃. Then the mixture was allowed to warm to room temperature and stirred for additional 1 hours. After that, the reaction was quenched with water and extracted with ethyl acetate. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel, using ethyl acetate and hexane as the eluting solvents to give the **1n-2**, 2-(tert-butyl-diphenyl-silanyloxymethyl)-acrylic acid methyl ester, as a white solid (670 mg, 97%). ^{1}H NMR ($CDCl_3$): δ

= 7.69-7.71 (m, 4H), 7.39-7.48 (m, 6H), 6.36-6.38 (dd, *J* = 2.0 Hz, *J* = 3.6 Hz, 1H), 6.15 (d, *J* = 2.4 Hz, 1H), 4.46 (t, *J* = 2.0 Hz, 2H), 3.73 (s, 3H), 1.10 (s, 9H). ^{13}C NMR ($CDCl_3$): δ = 166.3, 139.4, 135.5, 133.3, 129.8, 127.8, 124.1, 62.2, 51.6, 26.8, 19.3.

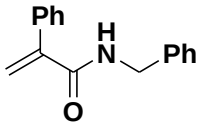
To a solution of ester obtained above (670 mg, 1.89 mmol) in THF/H_2O (v/v = 1/1, 10 mL) was treated with aq. LiOH (4.6 N, 2 mL). The mixture was stirred at room temperature for overnight. The reaction was acidified (pH = 1.0) with 1.0 N aq. HCl and extracted with diethyl ether. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford 2-(tert-butyl-diphenyl-silanyloxymethyl)-acrylic acid (**1n-3**) for further usage (610 mg, 95 %).

Compound **1n-4,** *N*-Benzyl-2-(tert-butyl-diphenyl-silanyloxymethyl)-propenamide, was prepared by **Procedure C** and was obtained as a white solid (517 mg, 67%). ^{1}H NMR ($CDCl_3$): δ = 7.62-7.64 (m, 4H), 7.27-7.48 (m, 12H), 6.08 (s, 1H), 5.40 (d, *J* = 0.8 Hz, 1H), 4.57 (d, *J* = 5.6 Hz, 2 H), 4.43 (s, 2 H), 0.98 (s, 9H).

^{13}C NMR ($CDCl_3$): δ = 166.6, 141.1, 138.1, 135.5, 132.5, 130.0, 128.8, 128.1, 127.8, 127.6, 122.7, 64.8, 43.7, 26.7, 19.1.

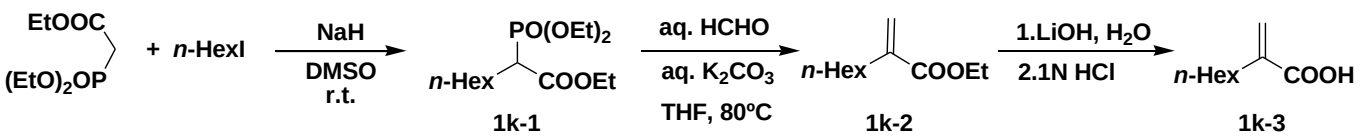
To a solution of compound **1n-4** (517 mg, 1.2 mmol) in dry THF was added TBAF (1.0 M sol. In THF, 1.3 mL) in dropwise at 0^{o}C. After 0.5 h, the reaction was quenched with water and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. Purification by flash-chromatography (eluent, ethyl acetate and hexane) afforded *N*-Benzyl-2-hydroxymethyl propenamide (**1n-5**) (209 mg, 91 %). ^{1}H NMR ($CDCl_3$): δ = 7.29-7.39 (m, 5H), 6.92 (b, 1H), 5.94 (s, 1H), 5.57 (s, 1H), 4.54 (d, *J* = 6.0 Hz, 2H), 4.40 (d, *J* = 4.8 Hz, 2H), 2.78 (b, 1H). ^{13}C NMR ($CDCl_3$): δ = 167.2, 142.2, 138.0, 128.8, 127.8, 127.6, 121.7, 63.9, 43.6.

To a suspension of NaH (60 wt% in mineral oil, 48 mg, 1.2 mmol) and TBAI (cat.) in dry THF (5 mL) was added a solution of methyl 2-hydroxymethylpropenate (209 mg, 1.09 mmol) in THF (5 mL) at 0 ℃. After 5 min., benzyl bromide (204 mg, 1.2 mmol) was added and the mixture was allowed to stir at room temperature for 2 hours. Then the reaction was quenched with water and extracted with dichloromethane. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. Purification by flash-chromatography (eluent, ethyl acetate and hexane) afforded *N*-Benzyl-2-benzyloxymethylpropenamide (**1n**) as a white solid, mp: 71-72 ℃, yield = 76 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23-7.34 (m, 10H), 6.29 (s, 1H), 5.62 (s, 1H), 4.54 (s, 2H), 4.52 (s, 2H), 4.32 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.26, 138.77, 138.23, 137.06, 128.71, 128.59, 128.06, 128.02, 127.78, 127.43, 125.40, 72.08, 70.44, 43.54. HR-MS (ESI): Calculated for $C_{18}H_{20}NO_2$: $[M+H]^+$ 282.1494. Found: *m/z* 282.1491. FTIR (NaCl, cm^{-1}): 3053, 2985, 2628, 2304, 1701, 1648, 1561, 1419, 1265, 895, 738, 704.



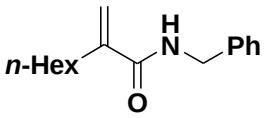
***N*-Benzyl-2-phenylpropenamide[7]:** This compound was prepared by **Procedure C** and was obtained as a white solid, yield = 67 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27-7.41 (m, 10H), 6.21 (d, *J* = 1.2 Hz, 1H), 6.08 (b, 1H), 5.67(d, *J* = 1.2 Hz, 1H), 4.56 (d, *J* = 6.0 Hz, 2H).

Preparation of 2-hexylpropenoic acid (for synthesis of *N*-Benzyl-2-hexylpropenamide)



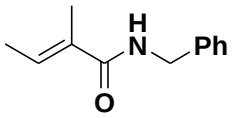
To a suspension of NaH (60 wt% in mineral oil, 5.5mmol) in dry DMSO (5mL) was added triethyl phosphonoacetate (0.99mL, 5.0mmmol). After the mixture was stirred at room temperature for 30 min., hexyl iodide (5.0 mmol) was added in dropwise. The mixture was heated to 60 ℃ and stirred for 2 hours. After cooling, the reaction was quenched with water and extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. To a solution of the residue in THF (5 mL) were added aqueous potassium carbonate (1 g dissolved in 2.5 mL of H_2O) and aqueous formaldehyde (37 wt%, 5 mL) and the mixture was heated at 80 ^oC for 2 h. The mixture was extracted with ethyl acetate, and the organic layer was dried over sodium sulfate and evaporated. The residue was chromatographed on silica gel to give ethyl 2-hexylpropenate (**1k-2**) [8] as a colourless oil (561 mg, 61 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 6.11 (s, 1H), 5.49 (s, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 2.28 (t, *J* = 7.6 Hz, 2H), 1.41-1.46 (m, 2H), 1.26-1.34 (m, 9H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.42, 141.18, 124.08, 60.50, 31.86, 31.63, 28.89, 28.37, 22.59, 14.21, 14.06.

To a solution of ester obtained above (561 mg, 3.0 mmol) in THF (9 mL) was treated with an aq. solution of LiOH (4.6 N, 5 mL). The mixture was stirred at r.t. for hours. After the reaction was complete, the aqueous solution was acidified (pH = 1.0) with 1.0 N aq. HCl and extracted with diethyl ether. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford the 2-hexylpropenoic acid (**1k-3**) for further usage (0.464 g, 99 %).

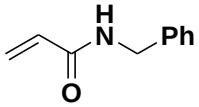


***N*-Benzyl-2-hexylpropenamide[9]:** This compound was prepared by **Procedure C** and was obtained as a white solid, yield = 81 %. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.28-7.39 (m, 5H), 6.11(b, 1H), 5.62 (s, 1H), 5.29 (s, 1H), 4.53 (d, *J* = 5.6 Hz, 2H), 2.35 (t, *J* = 7.6 Hz, 2H), 1.45-1.51 (m, 2H), 1.28-1.36 (m, 6H), 0.90 (t, *J* = 7.2 Hz, 3H).

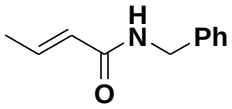
^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.85, 145.78, 138.34, 128.75, 127.80, 127.54, 117.26, 43.69, 32.44, 31.65, 28.91, 28.06, 22.58, 14.08.



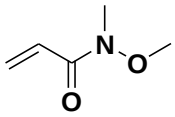
***N*-Benzyl-2,3-dimethylpropenamide[10]:** This compound was prepared by **Procedure C** and was obtained as a colourless oil, yield = 85 %. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.28-7.38 (m, 5H), 6.47-6.52 (m, 1H), 6.02 (b, 1H), 4.52 (d, *J* = 6.0 Hz, 2H), 1.88 (s, 3H), 1.77 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.22, 138.55, 131.68, 130.93, 128.72, 127.85, 127.48, 43.81, 13.93, 12.45.



***N*-Benzyl propenamide[11]:** This compound was prepared by **Procedure B** and was obtained as a white solid, yield = 89 %. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.28-7.38 (m, 5H), 6.33 (dd, *J* = 1.6 Hz, *J* = 17.2 Hz, 1H), 6.14 (dd, *J* = 10.4 Hz, *J* = 17.2 Hz, 1H), 6.01 (b, 1H), 5.68 (dd, *J* = 1.2 Hz, *J* = 10.4 Hz, 1H), 4.53 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.40, 138.05, 130.67, 128.76, 127.93, 127.62, 126.80, 43.70.

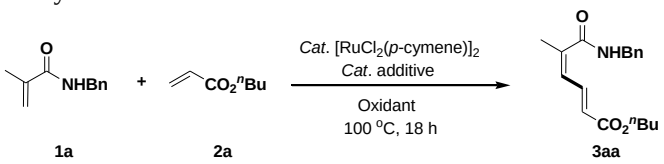


***N*-Benzyl-3-methylpropenamide[12]:** This compound was prepared by **Procedure C** and was obtained as a white solid, yield = 79 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24-7.33 (m, 5H), 6.78-6.87 (m, 1H), 6.45 (b, 1H), 5.85-5.89 (m, 1H), 4.44 (d, *J* = 5.6 Hz, 2H), 1.81 (d, *J* = 1.6 Hz, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.07, 140.03, 138.48, 128.61, 127.75, 127.34, 125.02, 43.42, 17.73.



***N*-Methyl-*N*-methoxylpropenamide[13]:** This compound was prepared by reported method [13] and was obtained as a colourless oil, yield = 79 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.73 (dd, *J* = 10.4 Hz, *J* = 17.2 Hz, 1H), 6.41 (dd, *J* = 1.8 Hz, *J* = 17.2 Hz, 1H), 5.73 (dd, *J* = 1.8 Hz, *J* = 10.4 Hz, 1H), 3.70 (s, 3H), 3.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.16, 128.98, 125.92, 61.76, 31.20.

Table S1. Optimization of the Ru-catalytic conditions [a]

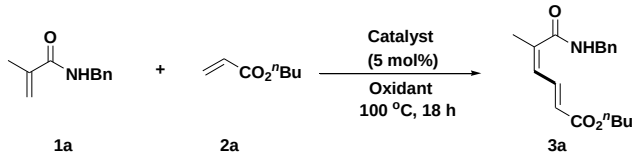


1a 2a 3aa

Entry	Catalyst	Additive	Oxidant	Solvent	Yield (%)
1	$[RuCl_2(p\text{-cymene})]_2$	-	$Cu(OAc)_2$ H_2O	*t*-AmOH	28
2	$[RuCl_2(p\text{-cymene})]_2$	KPF_6	$Cu(OAc)_2$ H_2O	Dioxane	50
3	$[RuCl_2(p\text{-cymene})]_2$	$AgSbF_6$	$Cu(OAc)_2$ H_2O	Dioxane	44
4	$[RuCl_2(p\text{-cymene})]_2$	KPF_6	$Cu(OAc)_2$ H_2O	*t*-AmOH	45
5[b]	$[RuCl_2(p\text{-cymene})]_2$	KPF_6	$Cu(OAc)_2$ H_2O	Dioxane/H_2O	55
6[c]	**$[RuCl_2(p\text{-cymene})]_2$**	**KPF_6**	**$Cu(OAc)_2$ H_2O**	**Dioxane/H_2O/AcOH**	**83**
7[d]	$[RuCl_2(p\text{-cymene})]_2$	KPF_6	$Cu(OAc)_2$ H_2O	Dioxane/H_2O	57
8[e]	$[RuCl_2(p\text{-cymene})]_2$	KPF_6	$Cu(OAc)_2$ H_2O	Dioxane/H_2O/AcOH	77
9[f]	$[RuCl_2(p\text{-cymene})]_2$	KPF_6	$Cu(OAc)_2$ H_2O	Dioxane/H_2O/AcOH	53
10	$[RuCl_2(p\text{-cymene})]_2$	KPF_6	AgOAc	Dioxane/H_2O/AcOH	21
11[g]	$[RuCl_2(p\text{-cymene})]_2$	KPF_6	$Cu(OAc)_2$ H_2O	Dioxane/H_2O/AcOH	< 5
12	$RuCl_3$	KPF_6	$Cu(OAc)_2$ H_2O	Dioxane/H_2O/AcOH	0

[a] Reaction conditions unless otherwise specified: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2.0 equiv), Ru (5 mol%), additive (20 mol%) and an oxidant (2.0 equiv) in a specific solvent (0.6 mL), at 100 °C, under nitrogen, 18 h. The yields indicated in the table are isolated yields. [b] Dioxane/H_2O/ = 2/1. [c] Dioxane/H_2O/AcOH = 8/4/1. [d] 2.0 equiv AcOH added. [e] The reaction was performed at 120 °C. [f] The reaction was performed at 80 °C. [g] The reaction was performed under air.

Table S2. Optimization of the Rh-catalytic conditions [a]



1a 2a 3a

Entry	Catalyst	Oxidant	Solvent	Yield (%)
1	$[RhCp^*Cl_2]_2$	Ag_2CO_3	MeCN	0
2[b]	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2 \cdot H_2O$	DME	63
3	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2 \cdot H_2O$	*t*-AmOH	68
4	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2 \cdot H_2O$	DCE	78
5	**$[RhCp^*Cl_2]_2$**	**$Cu(OAc)_2 \cdot H_2O$**	**Acetone**	**85**
6[c]	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2 \cdot H_2O$	Acetone	80
7[d]	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2 \cdot H_2O$	Acetone	57
8[e]	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2 \cdot H_2O$	Acetone	76
9[f]	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2 \cdot H_2O$	Acetone	75
10[g]	$RhCp^*Cl_2]_2$	$Cu(OAc)_2 \cdot H_2O$	Acetone/H_2O	83
11	$[RhCp^*Cl_2]_2$	O_2	Acetone	0
12	$RhCl_3$	$Cu(OAc)_2 \cdot H_2O$	Acetone	Trace
13	$Rh_2(OAc)_4$	$Cu(OAc)_2 \cdot H_2O$	Acetone	0
14[h]	$Pd(OAc)_2$	$Cu(OAc)_2 \cdot H_2O$	DMSO/AcOH	9

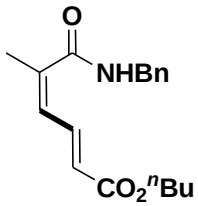
[a] Reaction conditions unless otherwise specified: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), Pd or Rh (5 mol%), and an oxidant (2.0 equiv) in a specific solvent (0.6 mL), under nitrogen, at 100 °C, 18 h. The yields indicated in the table are isolated yields. [b] 10 mol% $AgSbF_6$ added. The reaction was messy. [c] 1.0 equiv acrylate used. [d] The reaction was performed at 70 °C. [e] The reaction was performed under air. [f] 2.5 mol% Rh(III) used. [g] Acetone/H_2O = 2/1 (v/v) [h] This catalytic condition is efficient for the cross-coupling of alkenes with acrylates. The reaction was carried out under oxygen at 60 °C for 24 h, and 1.0 equiv oxidant used. DME: 1,2-dimethoxyethane; DCE: 1,2-dichloroethane; DMSO: dimethyl sulfoxide.

General Procedure for Cross-Coupling of Acrylamides with Alkenes

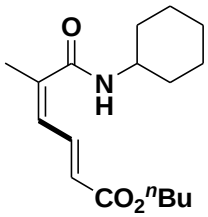
[Ru]-catalyzed conditions: A screw-cap vial was charged with $[RuCl_2(p\text{-cymene})]_2$ (2.5-5.0 mol%, 0.0025-0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv, 0.2 mmol), KPF_6 (20-40 mol%) and dioxane/H_2O/AcOH = 8/4/1(v/v/v) (0.6 ml). Then, acrylamide (1.0 equiv, 0.1 mmol) and acrylate (1.5-2.0 equiv, 0.15-0.20 mmol) were added into the solution in sequence. The vial was sealed under nitrogen and heated to 100 °C with stirring for 18 hours. After cooling down, the mixture was diluted with ethyl acetate, filtered and washed with water and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated to give the crude product which was directly applied to a flash column chromatography (EtOAc/Hexanes mixtures).

[Rh]-catalyzed conditions: An oven-dried screw-cap vial was charged with $[RhCp^*Cl_2]_2$ (2.5 mol%, 0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv, 0.4 mmol) and acetone (0.6 ml). Then, acrylamide (1.0 equiv, 0.2 mmol) and acrylate (1.5 equiv, 0.3 mmol) were added into the solution in sequence. The vial was sealed under nitrogen and heated to 100 °C with stirring for 18 hours. After cooling down, the mixture was diluted with ethyl acetate, filtered and washed with water and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated to give the crude product which was directly applied to a flash column chromatography (EtOAc/Hexanes mixtures).

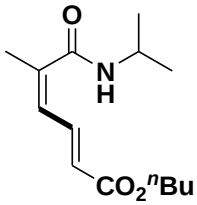
Characterization Data for the Dienamides



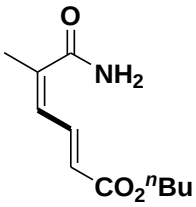
(*2E,4Z*)-*n*-Butyl 6-benzylamino-5-methyl-6-oxohexa-2,4-dienoate (3aa): This compound was prepared by the General Procedure described above and was obtained as an orange oil. Yield = 83 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (dd, *J* = 11.6 Hz, *J* = 15.2 Hz, 1H), 7.26-7.38 (m, 5H), 6.21 (d, *J* = 11.6 Hz, 1H), 5.88 (d, *J* = 15.2 Hz, 1H), 5.94 (b, 1H), 4.55 (d, *J* = 5.6 Hz, 2H), 4.14 (t, *J* = 6.8 Hz, 2H), 2.08 (s, 3H), 1.60-1.67 (m, 2H), 1.34-1.43 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =168.38, 166.63, 141.47, 139.45, 137.65, 129.06, 128.89, 127.97, 127.77, 123.78, 64.44, 43.87, 30.72, 21.47, 19.16, 13.75. HR-MS (ESI): Calculated for $C_{18}H_{23}NO_3Na$: $[M+Na]^+$ 324.1576. Found: *m/z* 324.1578. FTIR (NaCl, cm^{-1}): 3056, 2985, 2304, 1705, 1663, 1645, 1632, 1502, 1421, 1265, 1152, 895, 738, 704.



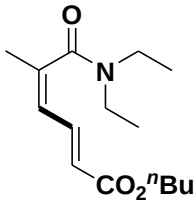
(*2E,4Z*)-*n*-Butyl 6-cyclohexylamino-5-methyl-6-oxohexa-2,4-dienoate (3ba): This compound was prepared by the General Procedure described above and was obtained as a yellow oil. Yield = 70 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (dd, *J* = 11.6 Hz, *J* = 15.2 Hz, 1H), 6.18 (d, *J* = 11.6 Hz, 1H), 5.89 (d, *J* = 15.6 Hz, 1H), 5.53 (b, 1H), 4.16 (t, *J* = 6.4 Hz, 2H), 3.91-3.93 (m, 1H), 2.07 (s, 3H), 2.01-2.05 (m, 2H), 1.74-1.79 (m, 2H), 1.62-1.69 (m, 3H), 1.41-1.48 (m, 5H), 1.16-1.39 (m, 4H), 0.96 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.70, 166.70, 142.99, 139.58, 127.83, 123.07, 64.41, 48.50, 33.14, 30.72, 25.45, 24.86, 21.33, 19.19, 13.73. HR-MS (ESI): Calculated for $C_{17}H_{28}NO_3$: $[M+H]^+$ 294.2069. Found: *m/z* 294.2068. FTIR (NaCl, cm^{-1}): 3420, 3059, 2961, 2938, 2857, 2309, 1705, 1659, 1648, 1635, 1508, 1450, 1421, 1308, 1266, 1198, 1150, 1123, 984, 890, 747, 709.



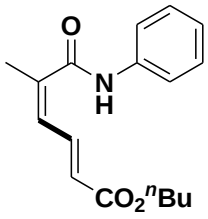
(*2E,4Z*)-*n*-Butyl 6-*iso*-propylamino-5-methyl-6-oxohexa-2,4-dienoate (3ca): This compound was prepared by the General Procedure described above and was obtained as an orange oil. Yield = 75 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (dd, *J* = 11.6 Hz, *J* = 15.2 Hz, 1H), 6.18 (d, *J* = 11.6 Hz, 1H), 5.89 (d, *J* = 15.2 Hz, 1H), 5.48 (b, 1H), 4.18-4.27 (m, 1H), 4.15 (t, *J* = 6.4 Hz, 2H), 2.06 (s, 3H), 1.61-1.68 (m, 2H), 1.36-1.45 (m, 2H), 1.25 (d, *J* = 6.4 Hz, 6H), 0.95 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.77, 166.67, 142.80, 139.53, 127.93, 123.12, 64.40, 41.71, 30.70, 22.73, 21.30, 19.17, 13.70. HR-MS (ESI): Calculated for $C_{14}H_{24}NO_3$: $[M+H]^+$ 254.1756. Found: *m/z* 254.1761. FTIR (NaCl, cm^{-1}): 3420, 3053, 2965, 2309, 2054, 1702, 1654, 1633, 1512, 1458, 1420, 1387, 1304, 1262, 1198, 1148, 983, 891, 752, 711.



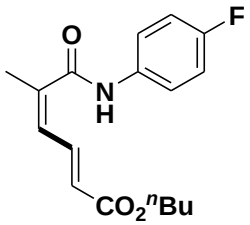
(*2E,4Z*)-*n*-Butyl 6-amino-5-methyl-6-oxohexa-2,4-dienoate (3da): This compound was prepared by the General Procedure described above and was obtained as an orange oil. Yield = 82 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (dd, *J* = 11.6 Hz, *J* = 15.2 Hz, 1H), 6.25 (d, *J* = 11.6 Hz, 1H), 6.18 (b, 1H), 5.94 (d, *J* = 15.2 Hz, 1H), 5.79 (b, 1H), 4.17 (t, *J* = 6.8 Hz, 2H), 2.10 (s, 3H), 1.63-1.70 (m, 2H), 1.37-1.46 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.47, 166.75, 140.23, 139.56, 129.82, 124.03, 64.49, 30.69, 21.40, 19.15, 13.72. HR-MS (ESI): Calculated for $C_{11}H_{18}NO_3$: $[M+H]^+$ 212.1287. Found: *m/z* 212.1288. FTIR (NaCl, cm^{-1}): 3469, 3397, 3051, 2971, 2963, 2309, 1708, 1675, 1637, 1609, 1423, 1315, 1271, 1202, 1152, 986, 895, 744, 706.



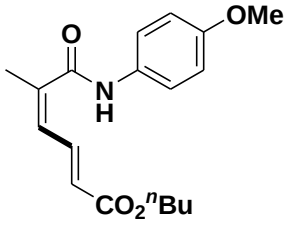
(*2E,4Z*)-*n*-Butyl 6-diethylamino-5-methyl-6-oxohexa-2,4-dienoate (3ea): This compound was prepared by the General Procedure described above and was obtained as an orange oil. Yield = 54 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 (dd, *J* = 11.6 Hz, *J* = 15.2 Hz, 1H), 6.08 (dd, *J* = 0.8 Hz, *J* = 11.6 Hz, 1H), 5.83 (d, *J* = 15.2 Hz, 1H), 4.11 (t, *J* = 6.4 Hz, 2H), 3.48-3.50 (m, 2H), 3.28-3.33 (q, *J* = 7.2 Hz, 2H), 2.05 (s, 3H), 1.58-1.60 (m, 2H), 1.32-1.42 (m, 2H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.66, 166.69, 143.33, 139.89, 125.33, 121.90, 64.27, 42.49, 38.48, 30.69, 21.31, 19.17, 14.21, 13.69, 12.79. HR-MS (ESI): Calculated for $C_{15}H_{26}NO_3$: $[M+H]^+$ 268.1913. Found: *m/z* 268.1918. FTIR (NaCl, cm^{-1}): 3439, 3053, 2985, 2304, 1705, 1653, 1638, 1625, 1474, 1435, 1421, 1306, 1269, 1206, 1161, 1142, 1101, 1036, 982, 908, 894, 744, 701.



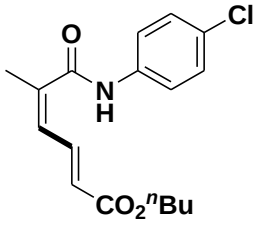
(*2E,4Z*)-*n*-Butyl 6-phenylamino-5-methyl-6-oxohexa-2,4-dienoate (3fa): This compound was prepared by the General Procedure described above and was obtained as an orange oil. Yield= 39 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (dd, *J* = 11.6 Hz, *J* = 15.2 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.35-7.41 (m, 3H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.31 (d, *J* = 11.6 Hz, 1H), 5.97 (d, *J* = 15.2 Hz, 1H), 4.15 (t, *J* = 6.4 Hz, 2H), 2.18 (s, 3H), 1.60-1.67 (m, 2H), 1.34-1.40 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.59, 166.55, 141.63, 139.11, 137.19, 129.38, 129.13, 124.98, 124.28, 120.26, 64.50, 30.66, 21.40, 19.15, 13.69. HR-MS (ESI): Calculated for $C_{17}H_{21}NO_3Na$: $[M+Na]^+$ 310.1419. Found: *m/z* 310.1414. FTIR (NaCl, cm^{-1}): 3412, 3055, 2963, 2949, 2874, 2309, 1708, 1671, 1636, 1599, 1519, 1500, 1440, 1311, 1266, 1185, 1149, 1063, 1030, 983, 907, 897, 749, 709.



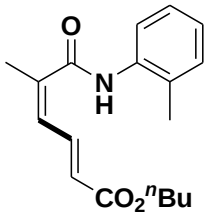
(*2E,4Z*)-*n*-Butyl 6-*p*-fluorophenylamino-5-methyl-6-oxohexa-2,4-dienoate (3ga): This compound was prepared by the General Procedure described above and was obtained as a yellow liquid. Yield = 34 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (dd, *J* = 12.0 Hz, *J* = 15.2 Hz, 1H), 7.55-7.58 (m, 2H), 7.39 (b, 1H), 7.05-7.09 (m, 2H), 6.32 (d, *J* = 11.6 Hz, 1H), 5.99 (d, *J* = 15.2 Hz, 1H), 4.16 (t, *J* = 6.4 Hz, 2H), 2.19 (s, 3H), 1.61-1.68 (m, 2H), 1.36-1.43 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.60, 166.53, 159.76 (d, *J* = 243 Hz), 141.43, 139.06, 133.18, 129.49, 124.34, 122.12 (d, *J* = 8 Hz), 115.81 (d, *J* = 23 Hz), 64.56, 30.66, 21.38, 19.16, 13.69. HR-MS (ESI): Calculated for $C_{17}H_{21}NO_3F$: $[M+H]^+$ 306.1505. Found: *m/z* 306.1509. FTIR (NaCl, cm^{-1}): 3412, 3059, 2960, 2301, 1705, 1668, 1643, 1636, 1614, 1508, 1407, 1308, 1259, 1213, 1183, 1149, 981, 897, 836, 755, 701.



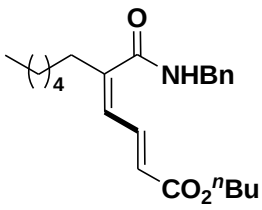
(*2E,4Z*)-*n*-Butyl 6-(*p*-methoxylphenylamino)-5-methyl-6-oxohexa-2,4-dienoate (3ha): This compound was prepared by the General Procedure described above and was obtained as a yellow oil. Yield = 38 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (dd, *J* = 12.0 Hz, *J* = 15.6 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.29 (b, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.31 (d, *J* = 11.6 Hz, 1H), 5.97 (d, *J* = 15.6 Hz, 1H), 4.16 (t, *J* = 6.8 Hz, 2H), 3.84 (s, 3H), 2.18 (s, 3H), 1.61-1.68 (m, 2H), 1.36-1.43 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.60, 166.45, 156.93, 141.79, 139.25, 130.21, 129.24, 124.10, 122.19, 114.27, 64.49, 55.52, 30.68, 21.43, 19.17, 13.71. HR-MS (ESI): Calculated for $C_{18}H_{24}NO_4$: $[M+H]^+$ 318.1705. Found: *m/z* 318.1707. FTIR (NaCl, cm^{-1}): 3306, 3057, 2960, 2933, 1714, 1697, 1659, 1634, 1605, 1510, 1466, 1414, 1302, 1273, 1246, 1180, 1147, 1036, 983, 908, 829, 735, 705.



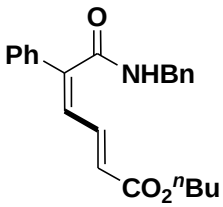
(*2E,4Z*)-*n*-Butyl 6-*p*-chlorophenylamino-5-methyl-6-oxohexa-2,4-dienoate (3ia): This compound was prepared by the General Procedure described above and was obtained as an orange oil. Yield = 31 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (dd, *J* = 15.2 Hz, *J* = 12.0 Hz 1H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.44 (b, 1H), 7.33 (d, *J* = 8.8 Hz, 2H), 6.33 (d, *J* = 12.0 Hz, 1H), 5.99 (d, *J* = 15.2 Hz, 1H), 4.16 (t, *J* = 6.4 Hz, 2H), 2.18 (s, 3H), 1.61-1.66 (m, 2H), 1.36-1.43 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =166.59, 141.27, 139.01, 135.79, 129.99, 129.64, 129.15, 124.44, 121.40, 64.59, 30.66, 21.36, 19.16, 13.69. HR-MS (ESI): Calculated for $C_{17}H_{21}NO_3Cl$: $[M+H]^+$ 322.1210. Found: *m/z* 322.1209. FTIR (NaCl, cm^{-1}): 3412, 3061, 2978, 2305, 1701, 1670, 1659, 1635, 1595, 1508, 1493, 1420, 1398, 1306, 1267, 1184, 1146, 1092, 982, 897, 828, 719, 706.



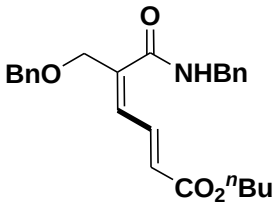
(*2E,4Z*)-*n*-Butyl 6-*o*-tolylamino-5-methyl-6-oxohexa-2,4-dienoate (3ja): This compound was prepared by the General Procedure described above and was obtained as a yellow oil. Yield = 37 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.0 Hz, 1H), 7.82 (dd, *J* = 11.6 Hz, *J* = 15.2 Hz, 1H), 7.14-7.29 (m, 4H), 6.36 (d, *J* = 11.6 Hz, 1H), 6.00 (d, *J* = 15.2 Hz, 1H), 4.17 (t, *J* = 6.8 Hz, 2H), 2.33 (s, 3H), 2.22 (s, 3H), 1.62-1.69 (m, 2H), 1.37-1.43 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.59, 166.50, 141.76, 139.12, 135.03, 130.67, 129.32, 126.92, 125.80, 124.26, 123.26, 64.51, 30.70, 21.54, 19.15, 17.88, 13.70. HR-MS (ESI): Calculated for $C_{18}H_{24}NO_3$: $[M+H]^+$ 302.1756. Found: *m/z* 302.1754. FTIR (NaCl, cm^{-1}): 3409, 3056, 2963, 1705, 1659, 1643, 1636, 1516, 1454, 1265, 1182, 1145, 984, 908, 895, 717, 704.



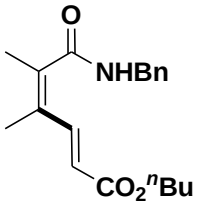
(*2E,4Z*)-*n*-Butyl 6-benzylamino-5-hexyl-6-oxohexa-2,4-dienoate (3ka): This compound was prepared by the General Procedure described above and was obtained as an orange oil. Yield = 91 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (dd, *J* = 11.6 Hz, *J* = 15.2 Hz, 1H), 7.28-7.40 (m, 5H), 6.17 (d, *J* = 12.0 Hz, 1H), 5.97 (b, 1H), 5.91 (d, *J* = 15.2 Hz, 1H), 4.58 (d, *J* = 5.6 Hz, 2H), 4.16 (t, *J* = 6.4 Hz, 2H), 2.40 (t, *J* = 7.2 Hz, 2H), 1.61-1.67 (m, 2H), 1.29-1.50 (m, 10H), 0.98 (t, *J* = 7.6 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.52, 166.63, 147.56, 139.54, 137.73, 128.85, 127.97, 127.72, 126.90, 123.42, 64.40, 43.84, 35.38, 31.55, 30.72, 28.90, 27.92, 22.51, 19.16, 14.05, 13.75. HR-MS (ESI): Calculated for $C_{21}H_{30}NO_3$: $[M+H]^+$ 344.2226. Found: *m/z* 344.2224. FTIR (NaCl, cm^{-1}): 3420, 3055, 2959, 2930, 2872, 2867, 1705, 1651, 1647, 1634, 1518, 1454, 1423, 1308, 1263, 1204, 1148, 1028, 984, 908, 741, 702.



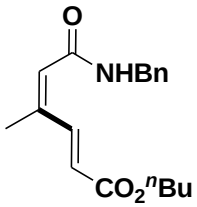
(*2E,4Z*)-*n*-Butyl 6-benzylamino-5-phenyl-6-oxohexa-2,4-dienoate (3la): This compound was prepared by the General Procedure described above and was obtained as an orange oil. Yield = 90 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (dd, *J* = 12.0 Hz, *J* = 15.2 Hz, 1H), 7.46-7.49 (m, 2H), 7.23-7.40 (m, 8H), 6.68 (d, *J* = 11.6 Hz, 1H), 6.07 (d, *J* =15.2 Hz, 1H), 5.98 (b, 1H), 4.63 (d, *J* = 6.0 Hz, 2H), 4.18 (t, *J* = 6.8 Hz, 2H), 1.64-1.68 (m, 2H), 1.38-1.44 (m, 2H), 0.95 (t, *J* = 7.6 Hz).^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.45, 166.46, 144.61, 139.77, 137.61, 135.66, 129.38, 128.93, 128.85, 128.26, 128.02, 127.85, 127.74, 127.29, 127.24, 126.89, 125.22, 64.51, 43.96, 30.75, 19.19, 13.78. HR-MS (ESI): Calculated for $C_{23}H_{25}NO_3Na$: $[M+Na]^+$ 386.1732. Found: *m/z* 386.1733. FTIR (NaCl, cm^{-1}): 3424, 3051, 2986, 2303, 1701, 1661, 1647, 1626, 1514, 1423, 1309, 1264, 1141, 983, 891, 738, 706.



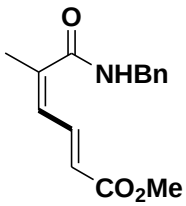
(*2E,4Z*)-*n*-Butyl 6-benzylamino-5-benzyloxymethyl-6-oxohexa-2,4-dienoate (3ma): This compound was prepared by the General Procedure described above and was obtained as an orange oil. Yield = 41 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (dd, *J* = 11.6 Hz, *J* = 15.6 Hz, 1H), 7.22-7.36 (m, 10H), 6.98 (b, 1H), 6.45 (d, *J* = 11.2 Hz, 1H), 6.05 (d, *J* = 15.6 Hz, 1H), 4.55 (d, *J* = 6.0 Hz, 2H), 4.54 (s, 2H), 4.26 (s, 2H), 4.19 (t, *J* = 6.8 Hz, 2H), 1.68-1.72 (m, 2H), 1.40-1.45 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.35, 166.31, 139.10, 137.87, 136.91, 134.63, 128.78, 128.62, 128.14, 128.01, 127.79, 127.55, 127.21, 72.59, 72.29, 64.59, 43.54, 30.71, 19.16, 13.75. HR-MS (ESI): Calculated for $C_{25}H_{30}NO_4$: $[M+H]^+$ 408.2175. Found: *m/z* 408.2177. FTIR (NaCl, cm^{-1}): 3412, 3056, 2959, 1708, 1678, 1669, 1638, 1522, 1454, 1419, 1308, 1266, 1196, 1153, 1126, 1063, 988, 908, 734, 702.



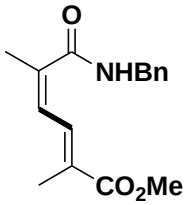
(*2E,4Z*)-*n*-Butyl 6-benzylamino-4,5-dimethyl-6-oxohexa-2,4-dienoate (3na): This compound was prepared by the General Procedure described above and was obtained as an orange oil. Yield = 39 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 15.6 Hz, 1H), 7.28-7.36 (m, 5H), 5.92 (d, *J* = 15.6 Hz, 1H), 5.73 (b, 1H), 4.56 (d, *J* = 5.6 Hz, 2H), 4.16 (t, *J* = 6.8 Hz, 2H), 2.06 (s, 3H), 1.90 (d, *J* = 0.8 Hz, 3H), 1.61-1.68 (m, 2H), 1.38-1.45 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.60, 166.94, 142.81, 139.75, 137.64, 130.90, 128.87, 128.01, 127.73, 119.39, 64.37, 43.95, 30.77, 19.19, 17.66, 13.76, 13.74. HR-MS (ESI): Calculated for $C_{19}H_{26}NO_3$: $[M+H]^+$ 316.1913. Found: *m/z* 316.1915. FTIR (NaCl, cm^{-1}): 3429, 3054, 2986, 2978, 2300, 1700, 1654, 1647, 1624, 1509, 1454, 1425, 1289, 1269, 1176, 1144, 979, 896, 748, 701.



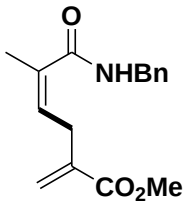
(*2E,4Z*)-*n*-Butyl 6-benzylamino-4-methyl-6-oxohexa-2,4-dienoate (3oa): This compound was prepared by the General Procedure described above and was obtained as an orange oil. Yield = 23 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, *J* = 16.0 Hz, 1H), 7.28-7.39 (m, 5H), 6.12 (d, *J* = 16.0 Hz, 1H), 5.90 (s, 1H), 5.83 (b, 1H), 4.55 (d, *J* = 5.6 Hz, 2H), 4.22 (t, *J* = 6.8 Hz, 2H), 2.02 (d, *J* = 1.2 Hz, 3H), 1.67-1.74 (m, 2H), 1.42-1.47 (m, 2H), 0.98 (t, *J* = 3.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.72, 165.11, 143.39, 140.61, 137.98, 128.80, 127.96, 127.66, 126.41, 123.54, 64.58, 43.71, 30.74, 20.41, 19.16, 13.76. HR-MS (ESI): Calculated for $C_{18}H_{24}NO_3$: $[M+H]^+$ 302.1756. Found: *m/z* 302.1755. FTIR (NaCl, cm^{-1}): 3435, 3090, 3055, 1707, 1647, 1637, 1631, 1604, 1508, 1454, 1421, 1306, 1262, 1170, 895, 748, 704.



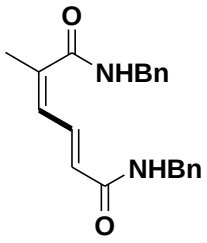
(*2E,4Z*)-Methyl 6-benzylamino-5-methyl-6-oxohexa-2,4-dienoate (3ab): This compound was prepared by the General Procedure described above and was obtained as a white solid, mp: 67-68 ℃. Yield = 71 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (dd, *J* = 11.6 Hz, *J* = 15.6 Hz, 1H), 7.29-7.41 (m, 5H), 6.24 (dd, *J* = 11.6 Hz, *J* = 0.8 Hz, 1H), 6.00 (b, 1H), 5.90 (d, *J* = 15.6 Hz, 1H), 4.58 (d, *J* = 5.6 Hz, 2H), 3.76 (s, 3H), 2.11 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.34, 166.97, 141.61, 139.82, 137.72, 129.11, 128.87, 127.97, 127.75, 123.22, 51.68, 43.81, 21.46. HR-MS (ESI): Calculated for $C_{15}H_{18}NO_3$: $[M+H]^+$ 260.1287. Found: *m/z* 260.1282. FTIR (NaCl, cm^{-1}): 3439, 3053, 2986, 2304, 1705, 1662, 1645, 1615, 1510, 1436, 1421, 1265, 1149, 895, 733, 709.



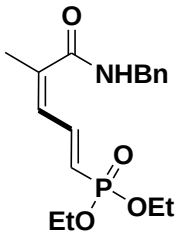
(*2E,4Z*)-Methyl 6-benzylamino-2,5-dimethyl-6-oxohexa-2,4-dienoate (3ac): This compound was prepared by the General Procedure described above and was obtained as a white solid, mp: 71-73 ℃. Yield = 21 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (dd, *J* = 12.0 Hz, *J* = 0.8 Hz, 1H), 7.26-7.36 (m, 5H), 6.42 (dd, *J* = 1.6 Hz, *J* = 11.6 Hz, 1H), 5.88 (b, 1H), 4.57 (d, *J* = 6.0 Hz, 2H), 3.73 (s, 3H), 2.11 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.80, 168.53, 140.13, 137.81, 133.13, 129.29, 128.82, 127.98, 127.69, 126.21, 51.97, 43.83, 21.72, 12.59. HR-MS (ESI): Calculated for $C_{16}H_{20}NO_3$: $[M+H]^+$ 274.1443. Found: *m/z* 274.1443. FTIR (NaCl, cm^{-1}): 3439, 3053, 2980, 2301, 1705, 1662, 1632, 1627, 1510, 1421, 1265, 895, 754, 733, 723, 706.



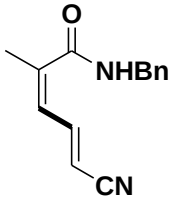
Methyl 6-benzylamino-6-oxo-2-methylene-5-methyl-hexa-(*Z*)-4-enoate (3ac′): This compound was prepared by the General Procedure described above and was obtained as an colourless oil. Yield = 22 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (b, 1H), 7.28-7.38 (m, 5H), 6.20 (d, *J* = 0.4 Hz, 1H), 5.68 (d, *J* = 0.8 Hz, 1H), 5.41-5.45 (m, 1H), 4.56 (d, *J* = 6.0 Hz, 2H), 3.74 (s, 3H), 3.19 (d, *J* = 8.0 Hz, 2H), 1.97 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =169.51, 167.67, 138.51, 138.20, 134.61, 128.60, 128.09, 127.94, 127.30, 127.02, 52.12, 43.39, 33.08, 21.16. HR-MS (ESI): Calculated for $C_{16}H_{20}NO_3$: $[M+H]^+$ 274.1443. Found: *m/z* 274.1443. FTIR (NaCl, cm^{-1}): 3429, 3053, 2981, 2300, 1707, 1667, 1638, 1619, 1541, 1512, 1440, 1422, 1339, 1247, 1222, 1166, 1134, 955, 893, 722, 701.



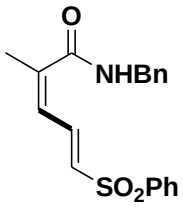
***N,N'-bis*-Benzyl-2-methyl-hexa-2*Z*,4*E*-diendiamide (3ad):** This compound was prepared by the General Procedure described above and was obtained as a yellow oil. Yield = 87 %. ^{1}H NMR (400 MHz, MeOD): δ = 7.53 (dd, *J* = 11.6 Hz, *J* = 14.8 Hz, 1H), 7.24-7.37 (m ,10H), 6.28 (dd, *J* = 0.8 Hz, *J* = 11.6 Hz, 1H), 6.11 (d, *J* = 14.8 Hz, 1H), 4.50 (s, 2H), 4.44 (s, 2H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, MeOD): δ = 170.43, 166.92, 140.78, 138.46, 138.32, 136.31, 128.25, 128.23, 128.19, 128.17, 127.28, 127.26, 126.88, 125.26, 42.86, 42.83, 19.98. HR-MS (ESI): Calculated for $C_{21}H_{23}N_2O_2$: $[M+H]^+$ 335.1760. Found: *m/z* 335.1761. FTIR (NaCl, cm^{-1}): 3419, 3053, 2985, 2301, 1701, 1635, 1611, 1603, 1512, 1421, 1265, 1163, 1143, 895, 736, 706.



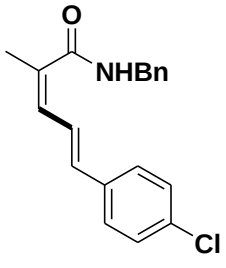
Diethyl (5-benzylamino-4-methyl-5-oxopenta-1,3-dienyl) phosphonate (3ae): This compound was prepared by the General Procedure described above and was obtained as a colourless oil. Yield = 65 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (ddd, *J* = 11.2 Hz, *J* = 16.8 Hz, *J* = 20.8 Hz, 1H), 7.28-7.38 (m, 5H), 6.17 (d, *J* = 11.6 Hz, 1H), 6.16 (b, 1H), 5.74 (dd, *J* = 16.8 Hz, *J* = 18.8 Hz, 1H), 4.55 (d, *J* = 6.0 Hz, 2H), 4.01-4.09 (m, 4H), 2.08 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.31, 143.30 (d, *J* = 7 Hz), 140.86, 137.76, 130.04 (d, *J* = 27 Hz), 128.83, 127.80 (d, *J* = 27 Hz), 120.77, 118.87, 61.92 (d, *J* = 6 Hz), 43.76, 21.35, 16.37 (d, *J* = 7 Hz). HR-MS (ESI): Calculated for $C_{17}H_{25}NO_4P$: $[M+H]^+$ 338.1521. Found: *m/z* 338.1521. FTIR (NaCl, cm^{-1}): 3439, 3053, 2985, 2304, 1658, 1631, 1614, 1513, 1421, 1265, 1157, 1051, 1026, 966, 895, 750, 729, 704.



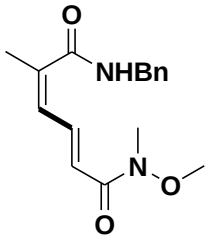
(*2Z,4E*)-*N*-benzyl-2-methyl-5-cyano-2,4-dienamide (3af): This compound was prepared by the General Procedure described above and was obtained as a white solid, mp: 106-108 ℃. Yield = 59 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (dd, *J* = 11.2 Hz, *J* = 16.0 Hz, 1H), 7.30-7.40 (m, 5H), 6.19 (d, *J* = 10.8 Hz, 1H), 5.91 (b, 1H), 5.37 (d, *J* = 16.0 Hz, 1H), 4.54 (d, *J* = 5.6 Hz, 2H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.41, 146.09, 141.53, 137.50, 129.59, 128.99, 127.97, 127.93, 117.72, 101.13, 43.84, 21.41. HR-MS (ESI): Calculated for $C_{14}H_{14}N_2ONa$: $[M+Na]^+$ 249.1004. Found: *m/z* 249.1005. FTIR (NaCl, cm^{-1}): 3421, 3053, 2966, 2689, 2301, 2218, 1660, 1651, 1627, 1611, 1509, 1439, 1421, 1265, 895, 750, 729, 704.



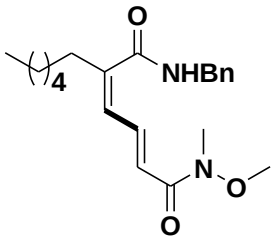
(*2Z,4E*)-*N*-benzyl-2-methyl-5-(phenylsulfonyl)-2,4-dienamide (3ag): This compound was prepared by the General Procedure described above and was obtained as a colourless oil. Yield = 50 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (m, 2H), 7.68 (dd, *J* = 11.6 Hz, *J* = 14.8 Hz, 1H), 7.48-7.61 (m, 3H), 7.27-7.40 (m, 5H), 6.34 (d, *J* = 14.8 Hz, 1H), 6.11 (dd, *J* = 11.6 Hz, J = 0.8 Hz, 1H), 6.25 (b, 1H), 4.54 (d, *J* = 5.6 Hz, 2H), 2.07 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.81, 144.57, 140.44, 137.68, 137.45, 133.44, 131.92, 129.33, 129.01, 128.06, 127.87, 127.70, 126.38, 43.96, 21.56. HR-MS (ESI): Calculated for $C_{19}H_{20}NO_3S$: $[M+H]^+$ 342.1164. Found: *m/z* 342.1166. FTIR (NaCl, cm^{-1}): 3439, 3052, 2984, 2701, 2304, 2126, 1662, 1655, 1641, 1631, 1511, 1433, 1421, 1265.3, 1147, 1086, 895, 754, 732, 704.



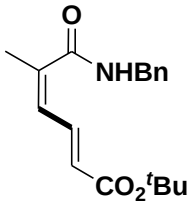
(*2Z,4E*)-*N*-benzyl-2-methyl-5-(4-chloro-phenyl)-penta-2,4-dienamide (3ah): This compound was prepared by the General Procedure described above and was obtained as a yellow solid, mp: 95-97 ℃. Yield = 60 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18-7.40 (m, 10H), 6.51 (d, *J* = 15.6 Hz, 1H), 6.32 (d, *J* = 11.2 Hz, 1H), 6.04 (b, 1H), 4.59 (d, *J* = 5.6 Hz, 2H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.88, 138.43, 135.37, 133.90, 133.57, 133.45, 132.56, 128.91, 128.76, 128.06, 127.88, 127.67, 125.68, 43.57, 21.09. HR-MS (ESI): Calculated for $C_{19}H_{19}NOCl$: $[M+H]^+$ 312.1155. Found: *m/z* 312.1161. FTIR (NaCl, cm^{-1}): 3445, 3053, 2985, 2304, 1658, 1511, 1491, 1421, 1265, 1157, 1095, 895, 738, 706.



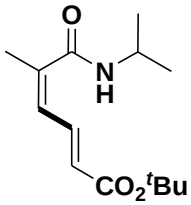
***N*-Methoxyl-*N*-methyl-*N'*-benzyl-5-methyl-hexa-2*E*,4*Z*-diendiamide (3ai):** This compound was prepared by the General Procedure described above and was obtained as a colourless oil. Yield = 80 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (dd, *J* = 12.0 Hz, *J* = 15.6 Hz, 1H), 7.29-7.40 (m, 5H), 6.52 (d, *J* = 15.2 Hz, 1H), 6.30 (dd, *J* = 11.6 Hz, *J* = 0.4 Hz, 1H), 6.04 (b, 1H), 4.58 (d, *J* = 5.6 Hz, 2H), 3.71 (s, 3H), 3.26 (s, 3H), 2.10 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.67, 166.68, 141.32, 138.32, 137.74, 129.08, 128.86, 127.99, 127.68, 121.37, 61.87, 43.83, 32.48, 21.52. HR-MS (ESI): Calculated for $C_{16}H_{21}N_2O_3$: $[M+H]^+$ 289.1552. Found: *m/z* 289.1553. FTIR (NaCl, cm^{-1}): 3439, 3419, 3050, 2987, 2304, 1666, 1653, 1648, 1637, 1513, 1447, 1421, 1265, 895, 736, 704.



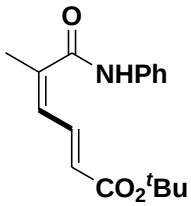
***N*-Methoxyl-*N*-methyl-*N'*-benzyl-5-hexyl-hexa-2*E*,4*Z*-diendiamide (3ki):** This compound was prepared by the General Procedure described above and was obtained as a colourless oil. Yield = 71 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (dd, *J* = 12.0 Hz, *J* = 15.2 Hz, 1H), 7.28-7.40 (m, 5H), 6.53 (d, *J* = 15.2 Hz, 1H), 6.25 (d, *J* = 11.6 Hz, 1H), 5.92 (b, 1H), 4.60 (d, *J* = 6.0 Hz, 2H), 3.72 (s, 3H), 3.27 (s, 3H), 2.42 (t, *J* = 7.6 Hz, 2H), 1.47-1.51 (m, 2H), 1.29-1.34 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.59, 166.66, 147.02, 138.33, 137.84, 128.82, 128.00, 127.65, 127.23, 121.24, 61.85, 43.82, 35.42, 32.46, 31.57, 28.92, 27.96, 22.51, 14.06. HR-MS (ESI): Calculated for $C_{19}H_{27}N_2O_3$: $[M+H]^+$ 331.2022. Found: *m/z* 331.2018. FTIR (NaCl, cm^{-1}): 3421, 3053, 2985, 2675, 2304, 1653, 1645, 1633, 1617, 1438, 1421, 1265, 895, 752, 744, 706.



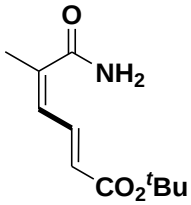
(*2E,4Z*)-*tert*-Butyl 6-benzylamino-5-methyl-6-oxohexa-2,4-dienoate (3aj): This compound was prepared by the General Procedure described above and was obtained as a yellow oil. Yield = 90 %. δ = 7.55 (dd, *J* = 12.0 Hz, *J* = 15.2 Hz, 1H), 7.26-7.36 (m, 5H), 6.15 (d, *J* = 12.0 Hz, 1H), 6.07 (b, 1H), 5.80 (d, *J* = 15.2 Hz, 1H), 4.52 (d, *J* = 5.6 Hz, 2H), 2.05 (s, 3H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.56, 165.89, 141.05, 138.57, 137.76, 128.94, 128.84, 127.93, 127.67, 125.58, 80.53, 43.79, 28.13, 21.44. HR-MS (ESI): Calculated for $C_{18}H_{24}NO_3$: $[M+H]^+$ 302.1756. Found: *m/z* 302.1756. FTIR (NaCl, cm^{-1}): 3439, 3050, 2988, 2304, 1700, 1662, 1641, 1617, 1510, 1421, 1266, 1143, 895, 733, 711, 703.



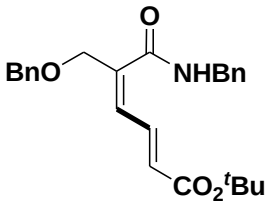
(*2E,4Z*)-*tert*-Butyl 6-*iso*-propylamino-5-methyl-6-oxohexa-2,4-dienoate (3cj): This compound was prepared by the General Procedure described above and was obtained as an orange oil. Yield = 91 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (dd, *J* = 11.6 Hz, *J* = 15.2 Hz, 1H), 6.16 (dd, *J* = 11.6 Hz, *J* = 0.8 Hz, 1H), 5.82 (d, *J* = 15.2 Hz, 1H), 5.44 (b, 1H), 4.19-4.27 (m, 1H), 2.06 (d, *J* = 0.8 Hz, 3H), 1.47 (s, 9H), 1.26 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.94, 165.83, 142.26, 138.53, 127.84, 125.07, 80.46, 41.64, 28.11, 22.73, 21.24. HR-MS (ESI): Calculated for $C_{14}H_{23}NO_3Na$: $[M+Na]^+$ 276.1576. Found: *m/z* 276.1574. FTIR (NaCl, cm^{-1}): 3440, 3050, 2987, 2304, 1696, 1662, 1645, 1632, 1510, 1421, 1379, 1265, 1176, 1143, 895, 733, 711.



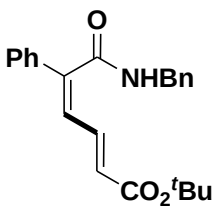
(*2E,4Z*)-*tert*-Butyl 6-phenylamino-5-methyl-6-oxohexa-2,4-dienoate (3fj): This compound was prepared by the General Procedure described above and was obtained as a white solid, mp: 109-111 ℃. Yield = 66 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (m, 3H), 7.33-7.37 (m, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.28 (d, *J* = 11.6 Hz, 1H), 5.89 (d, *J* = 15.2 Hz, 1H), 2.15 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.79, 165.86, 141.29, 138.30, 137.27, 129.21, 129.07, 126.00, 124.88, 120.29, 80.73, 28.10, 21.38. HR-MS (ESI): Calculated for $C_{17}H_{21}NO_3Na$: $[M+Na]^+$ 310.1419. Found: *m/z* 310.1414. FTIR (NaCl, cm^{-1}): 3439, 3051, 2985, 2304, 1706, 1662, 1650, 1643, 1421, 1265, 1142, 895, 754, 739, 704.



(*2E,4Z*)-*tert*-Butyl 6-amino-5-methyl-6-oxohexa-2,4-dienoate (3dj): This compound was prepared by the General Procedure described above and was obtained as an orange oil. Yield = 67 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (dd, *J* = 11.6 Hz, *J* = 15.2 Hz, 1H), 6.22 (d, *J* = 11.6 Hz, 1H), 6.22 (b, 1H), 5.85 (d, *J* = 15.6 Hz, 1H), 5.80 (b, 1H), 2.07 (s, 3H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.64, 166.01, 139.70, 138.62, 129.80, 125.91, 80.66, 28.10, 21.36. HR-MS (ESI): Calculated for $C_{11}H_{18}NO_3$: $[M+H]^+$ 212.1287. Found: *m/z* 212.1293. FTIR (NaCl, cm^{-1}): 3427, 3044, 2980, 2669, 2304, 1701, 1687, 1662, 1639, 1441, 1421, 1265, 1149, 895, 740, 732, 704.

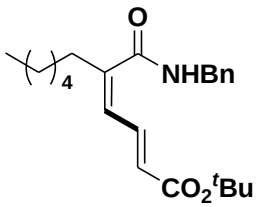


(*2E,4Z*)-*tert*-Butyl 6-benzylamino-5-benzyloxymethyl-6-oxohexa-2,4-dienoate (3mj): This compound was prepared by the General Procedure described above and was obtained as an orange oil. Yield = 57 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (dd, *J* = 11.6 Hz, *J* = 15.2 Hz, 1H), 7.19-7.33 (m, 10H), 6.93 (b, 1H), 6.40 (d, *J* = 11.6 Hz, 1H), 5.94 (d, *J* = 15.6 Hz, 1H), 4.51 (d, *J* = 6.0 Hz, 2H), 4.50 (s, 2H), 4.23 (s, 2H), 1.49 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.46, 165.55, 138.14, 137.91, 137.56, 136.99, 134.55, 129.13, 128.76, 128.60, 128.10, 127.99, 127.79, 127.51, 80.81, 72.50, 72.28, 43.53, 28.13. HR-MS (ESI): Calculated for $C_{25}H_{30}NO_4$: $[M+H]^+$ 408.2175. Found: *m/z* 408.2172. FTIR (NaCl, cm^{-1}): 3053, 2985, 2300, 1719, 1705, 1662, 1641, 1511, 1449, 1421, 1265, 1144, 895, 740, 706.

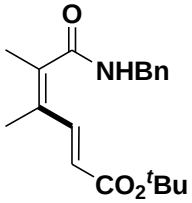


(*2E,4Z*)-*tert*-Butyl 6-benzylamino-5-phenyl-6-oxohexa-2,4-dienoate (3lj): This compound was prepared by the General Procedure described above and was obtained as an orange oil. Yield = 90 %. ^{1}H NMR (400 MHz,

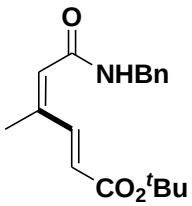
$CDCl_3$): δ = 7.64 (dd, *J* = 11.6 Hz, *J* = 15.2 Hz, 1H), 7.45-7.47 (m, 2H), 7.28-7.39 (m, 8H), 6.64 (d, *J* = 12.0 Hz, 1H), 6.20 (b, 1H), 6.00 (d, *J* = 15.2 Hz, 1H), 4.62 (d, *J* = 5.6 Hz, 2H), 1.53 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.56, 165.72, 144.16, 138.85, 137.64, 135.74, 129.25, 128.89, 128.83, 128.03, 127.71, 127.20, 127.15, 126.82, 80.67, 43.93, 28.17. HR-MS (ESI): Calculated for $C_{23}H_{26}NO_3$: $[M+H]^+$ 364.1913. Found: *m/z* 364.1910. FTIR (NaCl, cm^{-1}): 3427, 3058, 2989, 2302, 1692, 1662, 1620, 1611, 1510, 1465, 1422, 1265, 1178, 1159, 1143, 981, 895, 746, 711.



(*2E,4Z*)-*tert*-Butyl 6-benzylamino-5-hexyl-6-oxohexa-2,4-dienoate (3kj): This compound was prepared by the General Procedure described above and was obtained as an orange oil. Yield = 80 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (dd, *J* = 15.2 Hz, *J* = 11.6 Hz, 1H), 7.27-7.37 (m, 5H), 6.12 (d, *J* = 11.6 Hz, 1H), 5.98 (brs, 1H), 5.82 (d, *J* = 15.2 Hz, 1H), 4.56 (d, *J* = 5.6 Hz, 2H), 2.37 (t, *J* = 7.6 Hz, 2H), 1.42-1.50 (m, 11H), 1.26-1.31 (m, 6H), 0.87 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.58, 165.86, 146.95, 138.57, 137.74, 128.80, 127.94, 127.65, 126.90, 125.31, 80.48, 43.80, 35.33, 31.52, 28.84, 28.10, 27.91, 22.48, 14.03. HR-MS (ESI): Calculated for $C_{23}H_{33}NO_3Na$: $[M+Na]^+$ 394.2358. Found: *m/z* 394.2359. FTIR (NaCl, cm^{-1}): 3431, 3042, 2980, 2307, 1700, 1662, 1655, 1620, 1587, 1515, 1421, 1265, 1187, 1143, 981, 895, 740, 730, 707.

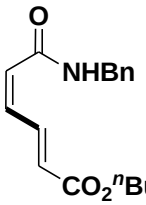


(*2E,4Z*)-*tert*-Butyl 6-benzylamino-4,5-dimethyl-6-oxohexa-2,4-dienoate (3nj): This compound was prepared by the General Procedure described above and was obtained as an orange oil. Yield = 81 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 15.6 Hz, 1H), 7.28-7.36 (m, 5H), 5.89 (b, 1H), 5.86 (d, *J* = 15.6 Hz, 1H), 4.56 (d, *J* = 5.6 Hz, 2H), 2.05 (s, 3H), 1.84 (s, 3H), 1.51(s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.72, 166.20, 141.97, 139.20, 137.68, 130.89, 128.84, 127.99, 127.66, 121.13, 80.38, 43.88, 28.17, 17.59, 13.77. HR-MS (ESI): Calculated for $C_{19}H_{26}NO_3$: $[M+H]^+$ 316.1913. Found: *m/z* 316.1916. FTIR (NaCl, cm^{-1}): 3431, 3048, 2978, 2300, 1700, 1658, 1648, 1629, 1510, 1418, 1265, 1156, 981, 899, 740, 737, 704.

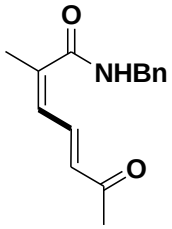


(*2E,4Z*)-*tert*-Butyl 6-benzylamino-4-methyl-6-oxohexa-2,4-dienoate (3oj): This compound was prepared by the General Procedure described above and was obtained as a white soild, mp: 124-126 ℃. Yield = 27 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 16.0 Hz, 1H), 7.29-7.39 (m, 5H), 6.05 (d, *J* = 16.0 Hz, 1H), 5.89 (s, 1H), 5.87 (b, 1H), 4.54 (d, *J* = 5.2 Hz, 2H), 2.00 (d, *J* = 1.2 Hz, 3H), 1.54 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.94, 165.24, 143.35, 139.73, 138.04, 128.78, 127.97, 127.62, 126.16, 125.37, 80.72, 43.70, 28.14, 20.44. HR-MS (ESI): Calculated for $C_{18}H_{23}NO_3Na$:

$[M+Na]^+$ 324.1576. Found: *m/z* 324.1580. FTIR (NaCl, cm^{-1}): 3439, 3050, 2989, 2307, 1696, 1662, 1645, 1633, 1510, 1421, 1265, 1158, 895, 748, 731, 706.

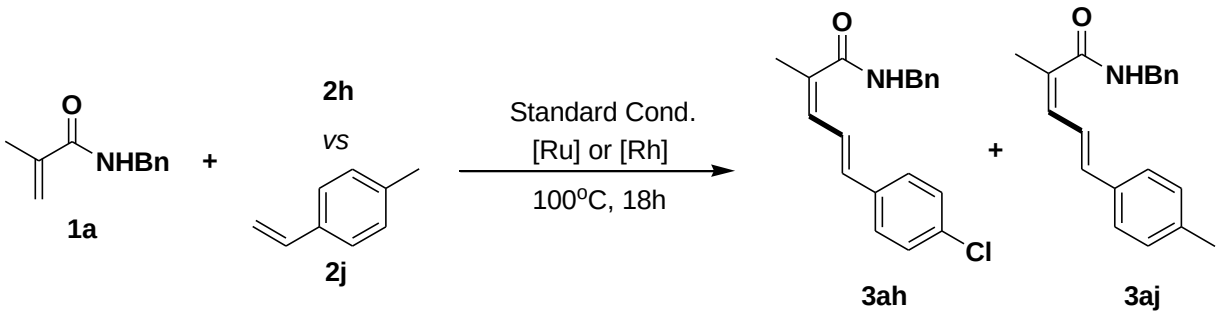


(*2E,4Z*)-Butyl 6-benzylamino-6-oxohexa-2,4-dienoate and (*2E,4E*)-Butyl 6-benzylamino-6-oxohexa-2,4-dienoate mixture (ratio: 50/50) (3pa): This compound was prepared by the General Procedure described above and was obtained as an orange oil. Yield = 31 %. ^{1}H NMR (400 MHz, MeOD): δ = 8.55 (ddd, *J* = 1.2 Hz, *J* =11.6 Hz, *J* = 15.6 Hz, 1H), 7.26-7.41 (m, 12H), 6.63 (t, *J* = 11.6 Hz, 1H), 6.44 (d, *J* = 14.0 Hz, 1H), 6.27 (d, *J* = 15.2 Hz, 1H), 6.14 (d, *J* = 11.6 Hz, 1H), 6.13 (d, *J* = 15.2 Hz, 1H), 4.49 (s, 2H), 4.46 (s, 2H), 4.18-4.22 (m, 4H), 1.66-1.73 (m, 4H), 1.42-1.48 (m, 4H), 0.99 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, MeOD): δ = 166.70, 166.41, 166.14, 165.86, 141.43, 139.55, 138.29, 138.22, 137.00, 136.84, 131.12, 128.21, 127.34, 127.32, 127.25, 126.97, 126.93, 126.79, 126.77, 64.27, 64.17, 42.97, 42.69, 30.46, 30.43, 18.78, 12.64, 12.61. HR-MS (ESI): Calculated for $C_{17}H_{22}NO_3$: $[M+H]^+$ 288.1600. Found: *m/z* 288.1606. FTIR (NaCl, cm^{-1}): 3439.1, 3053.3, 2985.8, 2304.9, 1705.1, 1662.6, 1610.0, 1510.3, 1421.5, 1265.3, 1160.1, 895.0, 738.7, 704.0.



(*2Z,4E*)-*N*-benzyl-2-methyl-6-oxohepta-2,4-dienamide (3ak): This compound was prepared by the General Procedure described above and was obtained as a white solid, mp: 66-68 ℃. Yield = 79 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (dd, *J* = 11.6 Hz, *J* = 16.0 Hz, 1H), 7.29-7.40 (m, 5H), 6.25 (d, *J* = 11.6 Hz, 1H), 6.14 (b, 1H), 6.08 (d, *J* = 16.0 Hz, 1H), 4.57 (d, *J* = 6.0 Hz, 2H), 2.18 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.98, 168.13, 141.42, 138.91, 137.87, 132.93, 130.49, 128.94, 127.98, 127.84, 43.74, 26.67, 21.50. HR-MS (ESI): Calculated for $C_{15}H_{18}NO_2$: $[M+H]^+$ 244.1338. Found: *m/z* 244.1335. FTIR (NaCl, cm^{-1}): 3439, 3053, 2985, 2304, 1705, 1662, 1643, 1601, 1510, 1436, 1421, 1351, 1265, 981, 895, 746, 734, 704.

Competition Experiments with alkenes 2h and 2j.



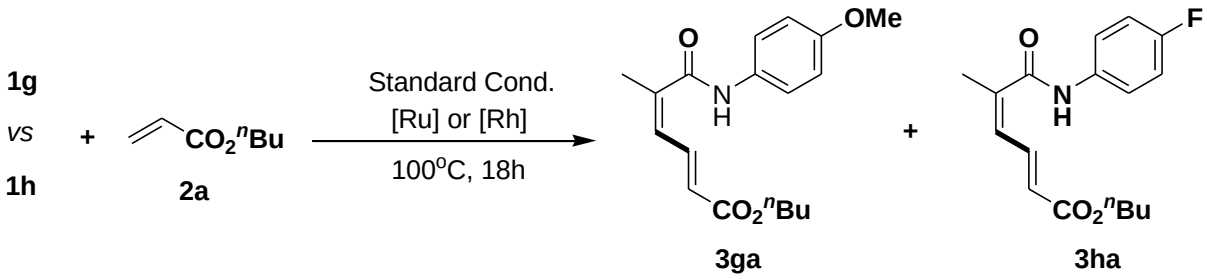
[Ru] Cond.: **3ah**/**3aj** = 71/29

[Rh] Cond.: **3ah**/**3aj** = 56/44

[Ru] Cond.: A screw-cap vial was charged with $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%, 0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv, 0.2 mmol), KPF_6 (20 mol%) and dioxane/H_2O/AcOH = 8/4/1(v/v/v) (0.6 ml). Then, acrylamide **1a** (1.0 equiv, 0.1 mmol), alkenes **2h** (1.0 equiv, 0.1 mmol), and **2j** (1.0 equiv, 0.1 mmol) were added into the solution in sequence. The vial was sealed under nitrogen and heated to 100 °C with stirring for 18 hours. After cooling down, the mixture was diluted with ethyl acetate, filtered and washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to give the crude product which was purified by flash column chromatography on silica gel to give dienamide **3ah** (8 mg, 26%) and **3aj** (3 mg, 11%). The ratio of **3ah/3aj** thus was determinted to be 71/29.

[Rh] Cond.:An oven-dried screw-cap vial was charged with $[RhCp^*Cl_2]_2$ (2.5 mol%, 0.0025 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv, 0.4 mmol) and acetone (0.6 ml). Then, acrylamides (0.2 mmol), styrene **2h** (0.1 mmol) and **2j** (0.1 mmol) were added into the solution in sequence. The vial was sealed under nitrogen and heated to 100 °C with stirring for 18 hours. After cooling down, the mixture was diluted with ethyl acetate, filtered and washed with water and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated to give the crude product which was directly applied to a flash column chromatography, affording corresponding product **3ah** (9 mg, 29%) and **3aj** (6 mg, 23%).

Competition Experiments with acrylamides 1g and 1h.



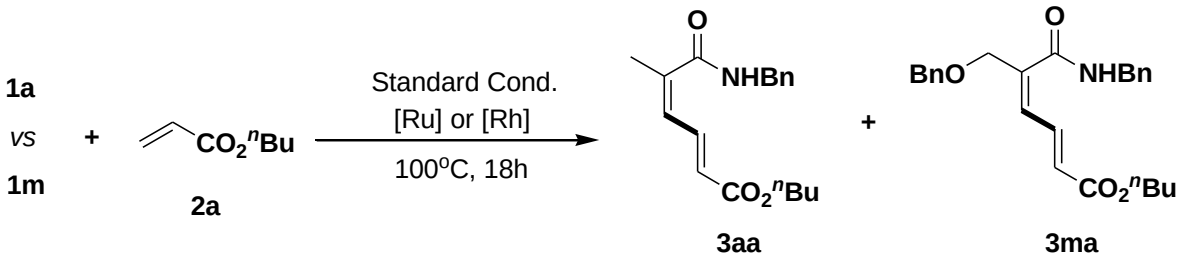
[Ru] Cond.: **3ga/3ha** = 79/21

[Rh] Cond.: **3ga/3ha** = 59/41

[Ru] Cond.: A screw-cap vial was charged with $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%, 0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv, 0.1 mmol), KPF_6 (20 mol%) and dioxane/H_2O/AcOH = 8/4/1(v/v/v) (0.6 ml). Then, acrylamide **1g** (2.0 equiv, 0.1 mmol), acrylamide **1h** (2.0 equiv, 0.1 mmol), and acrylate **2a** (1.0 equiv, 0.05 mmol) were added into the solution in sequence. The vial was sealed under nitrogen and heated to 100 °C with stirring for 18 hours. After cooling down, the mixture was diluted with ethyl acetate, filtered and washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to give the crude product which was purified by flash column chromatography on silica gel to give dienamide **3ga** (6.5 mg, 41%) and **3ha** (1.7 mg, 11%). The ratio of **3ga/3ha** thus was determinted to be 79/21.

[Rh] Cond.:An oven-dried screw-cap vial was charged with $[RhCp^*Cl_2]_2$ (2.5 mol%, 0.0025 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv, 0.4 mmol) and acetone (0.6 ml). Then, acrylamides (0.2 mmol) and acrylate (0.1 mmol) were added into the solution in sequence. The vial was sealed under nitrogen and heated to 100 °C with stirring for 18 hours. After cooling down, the mixture was diluted with ethyl acetate, filtered and washed with water and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated to give the crude product which was directly applied to a flash column chromatography, affording corresponding product **3i** (7 mg, 23%) and **3j** (5 mg, 16%).

Competition Experiments with acrylamides 1a and 1m.



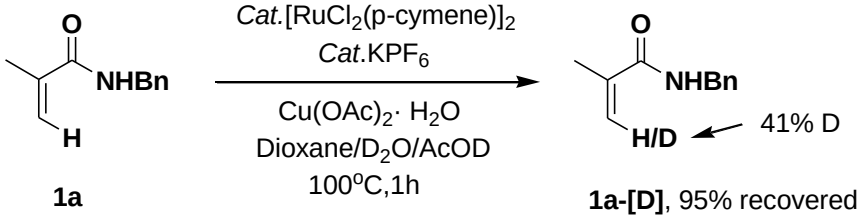
[Ru] Cond.: **3aa/3ma** = 82/18

[Rh] Cond.: **3aa/3ma** = 76/24

[Ru] Cond.: A screw-cap vial was charged with $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%, 0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv, 0.1 mmol), KPF_6 (20 mol%) and dioxane/H_2O/AcOH = 8/4/1(v/v/v) (0.6 ml). Then, acrylamide **1a** (2.0 equiv, 0.1 mmol), acrylamide **1m** (2.0 equiv, 0.1 mmol), and acrylate **2a** (1.0 equiv, 0.05 mmol) were added into the solution in sequence. The vial was sealed under nitrogen and heated to 100 °C with stirring for 18 hours. After cooling down, the mixture was diluted with ethyl acetate, filtered and washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to give the crude product. The ratio of **3aa/3ma** in the crude mixture of product was determinted to be 82/18 by ^{1}H NMR.

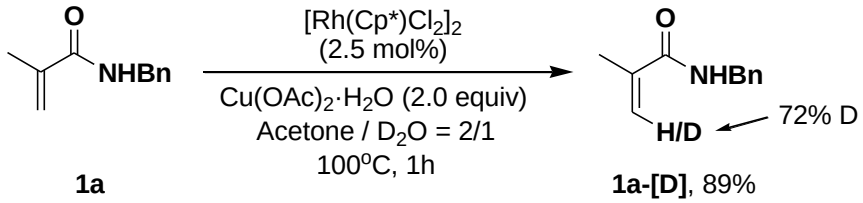
[Rh] Cond.: An oven-dried screw-cap vial was charged with $[RhCp^*Cl_2]_2$ (2.5 mol%, 0.0025 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv, 0.4 mmol) and acetone (0.6 ml). Then, acrylamides (0.2 mmol) and acrylate (0.1 mmol) were added into the solution in sequence. The vial was sealed under nitrogen and heated to 100 °C with stirring for 18 hours. After cooling down, the mixture was diluted with ethyl acetate, filtered and washed with water and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated to give the crude product, the ratio of product **3aa** and **3ma** was calculated as **3aa**/**3ma** = 76/24 by HNMR.

Ru-Catalyzed H/D Exchange in 1a.



A screw-cap vial was charged with $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%, 0.0025 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv, 0.2 mmol), KPF_6 (20 mol%) and dioxane/D_2O/AcOD = 8/4/1(v/v/v) (0.6 ml). Then, acrylamide (1.0 equiv, 0.1 mmol) were added into the solution. The vial was sealed under nitrogen and heated to 100 °C with stirring for 1 hour. After cooling down, the mixture was diluted with ethyl acetate, filtered and washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to give the crude product which was purified by flash column chromatography on silica gel (17 mg, 95 % recovered). The D % of **1a-[D]** was estimated by ^{1}H NMR.

Rh-Catalyzed H/D Exchange in 1a.



1a **1a-[D]**, 89%

An oven-dried screw-cap vial was charged with $[RhCp^*Cl_2]_2$ (2.5 mol%, 0.0025 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv, 0.4 mmol) and acetone/D_2O (V/V = 2/1) (0.6 ml). Then, acrylamides (0.2 mmol) was added into the solution. The vial was sealed under nitrogen and heated to 100 °C with stirring for 1 hour. After cooling down, the mixture was diluted with ethyl acetate, filtered and washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to give the crude product which was purified by flash column chromatography on silica gel (34 mg, 89 % recovered). The D % of **1a-[D]** was estimated by ^1H NMR.

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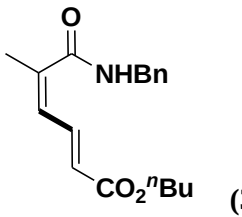
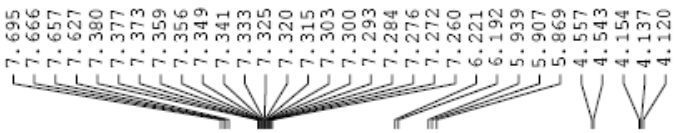

O
NHBn
CO2nBu

(3aa) (*Z*/*E* = 96/4)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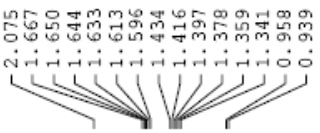
7.666
7.657
7.627
7.380
7.377
7.373
7.359
7.356
7.349
7.341
7.333
7.325
7.320
7.315
7.303
7.300
7.293
7.284
7.276
7.272
7.260
6.221
6.192
5.939
5.907
5.869
4.557
4.543
4.154
4.137
4.120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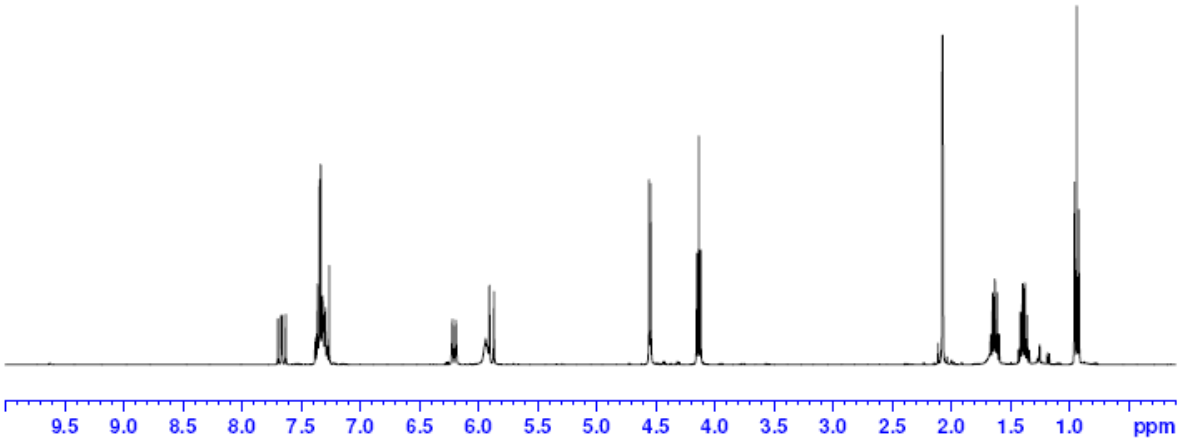
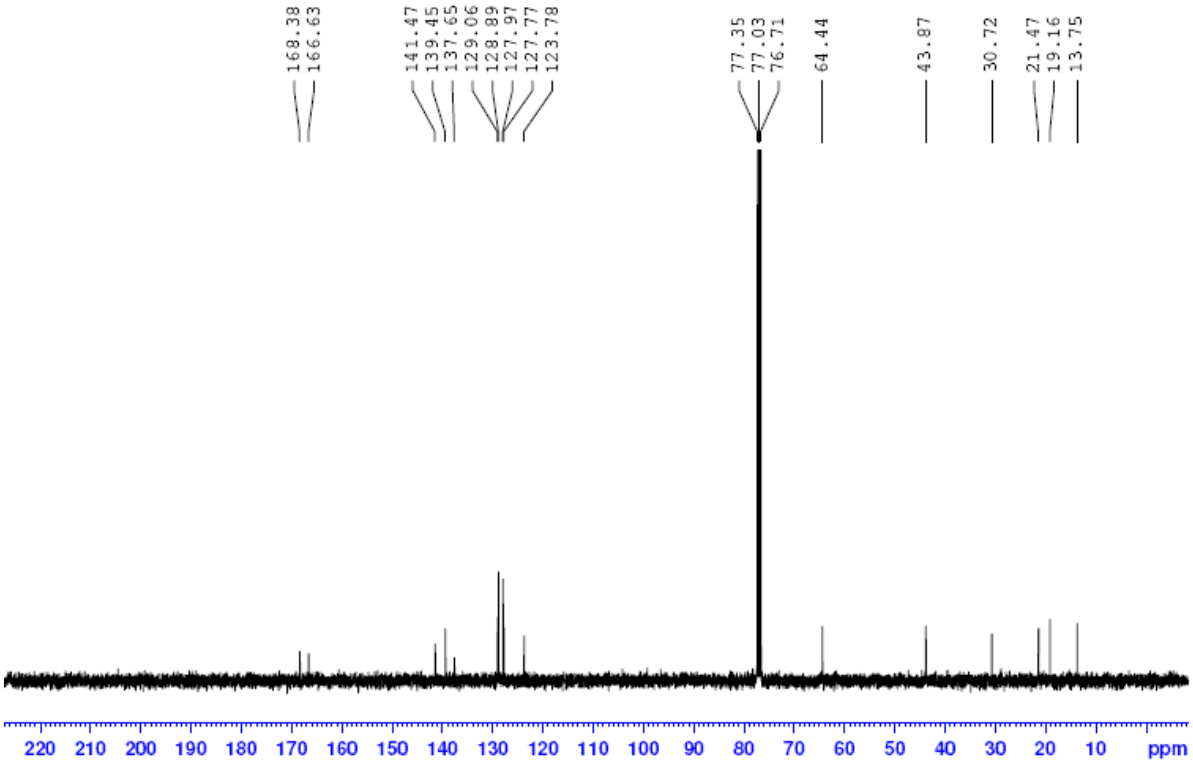
1.667
1.650
1.644
1.633
1.613
1.596
1.434
1.416
1.397
1.378
1.359
1.341
0.958
0.939


9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm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166.63
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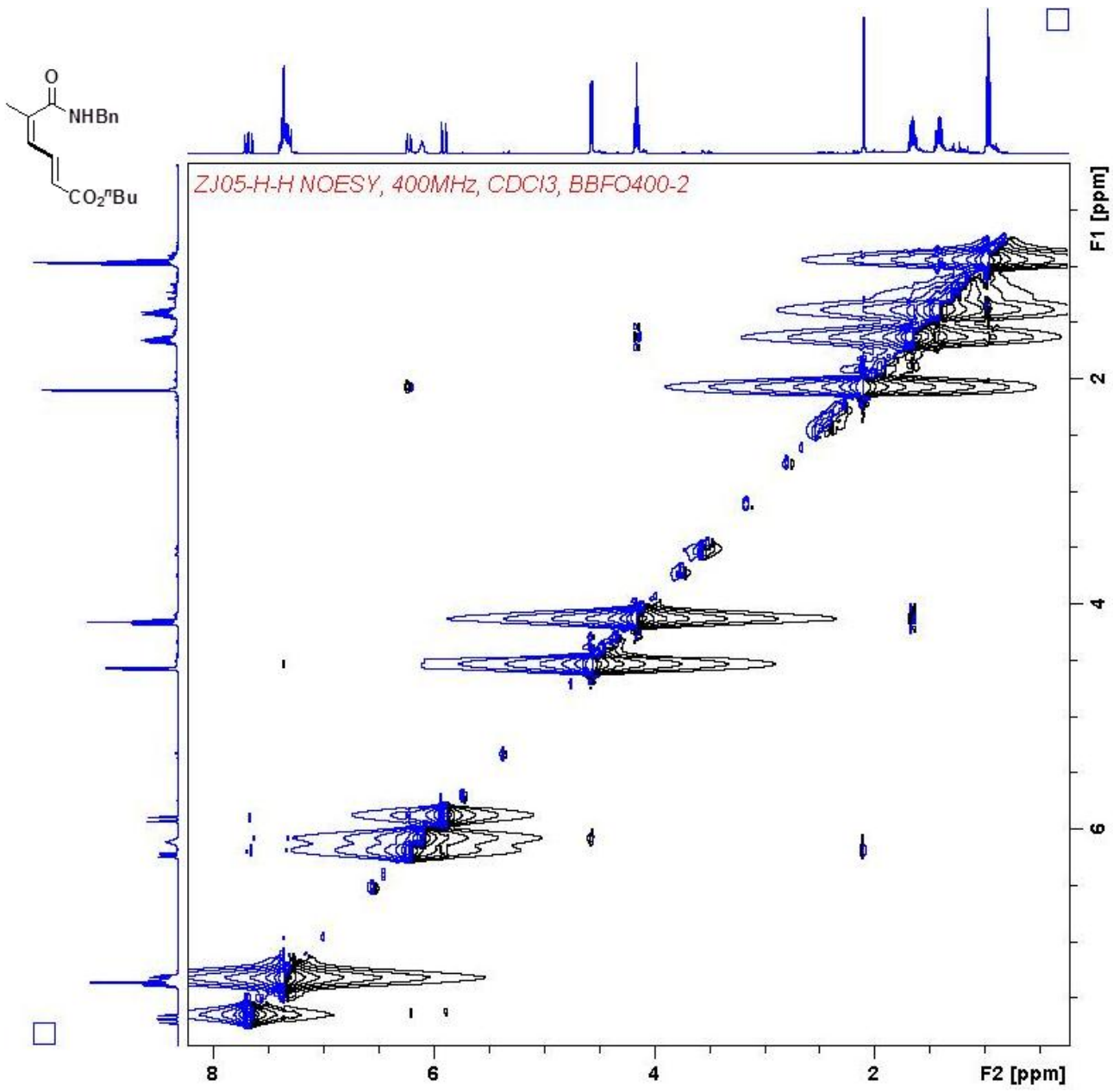
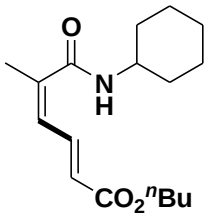
137.65
129.06
128.89
127.97
127.77
123.78
77.35
77.03
76.71
64.44
43.87
30.72
21.47
19.16
13.75
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


O
NHBn
CO2nBu
ZJ05-H-H NOESY, 400MHz, CDCl3, BBFO400-2
F1 [ppm]
F2 [ppm]
8
6
4
2


O
N
H
CO2nBu

(3ba) (*Z*/*E* > 99/1)


7.641
7.612
7.603
7.574
7.293
6.202
6.201
6.173
6.172
5.917
5.878
5.539
5.519
4.177
4.160
4.144
3.933
3.922
3.912
3.906
2.074
2.050
2.042
2.031
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1.370
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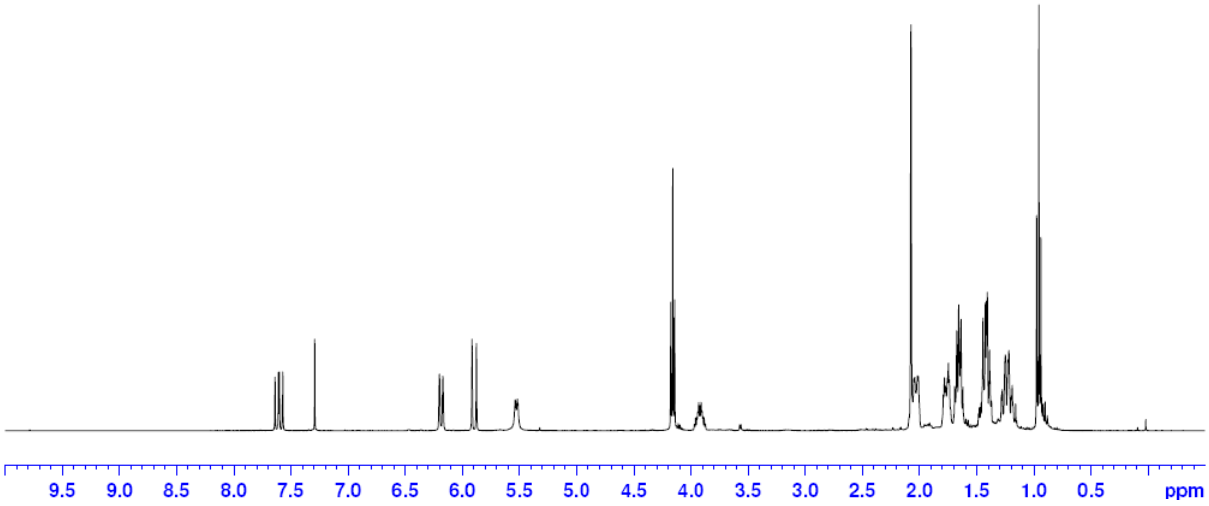
0.956
0.938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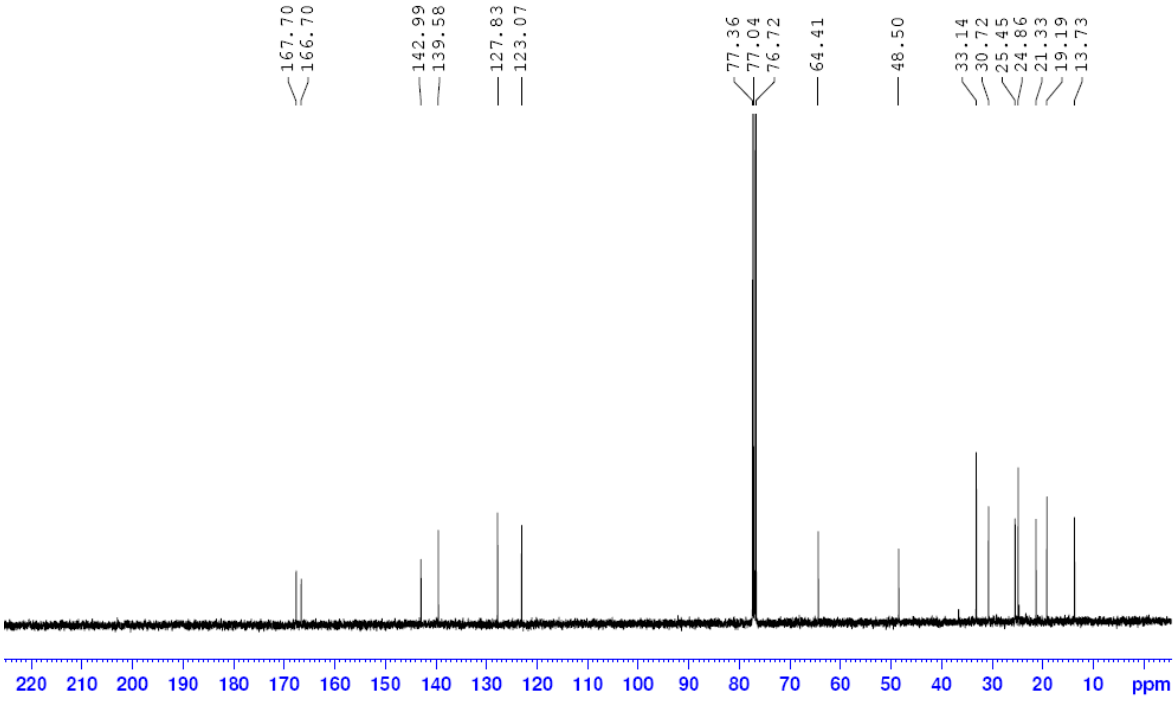
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166.70
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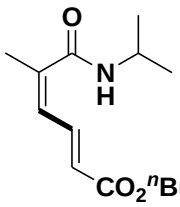
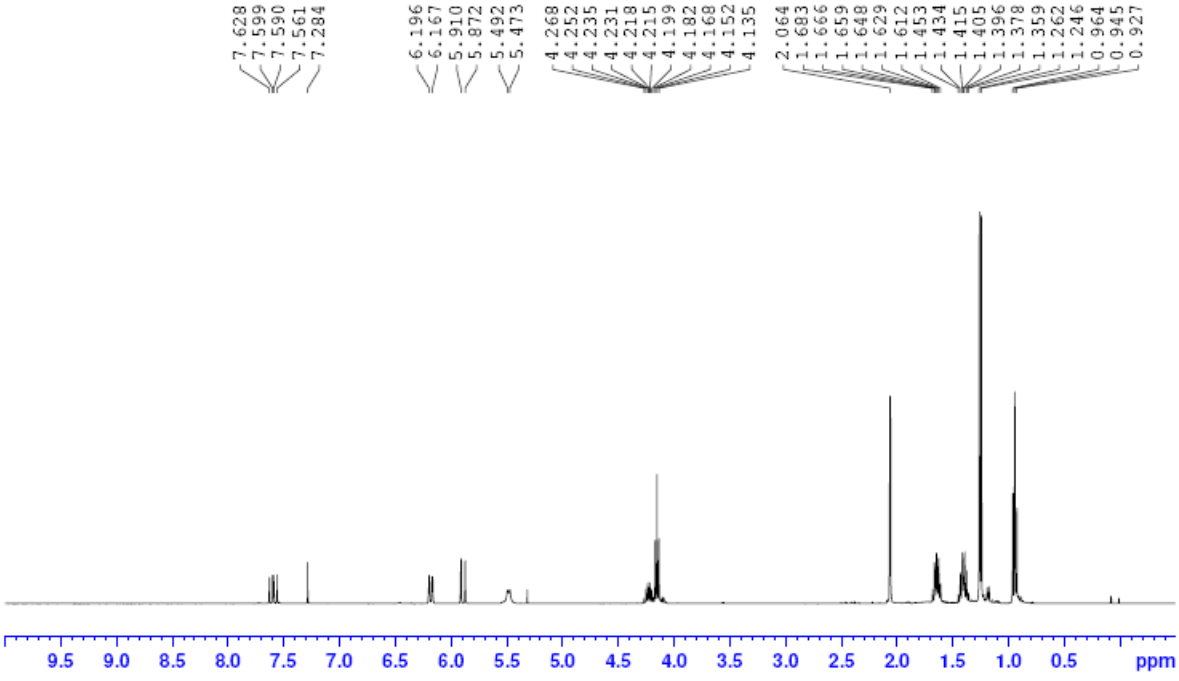
139.58
127.83
123.07
77.36
77.04
76.72
64.41
48.50
33.14
30.72
25.45
24.86
21.33
19.19
13.73
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
N
H
CO2nBu

(3ca) (*Z*/*E* = 98/2)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7.561
7.284
6.196
6.167
5.910
5.872
5.492
5.473
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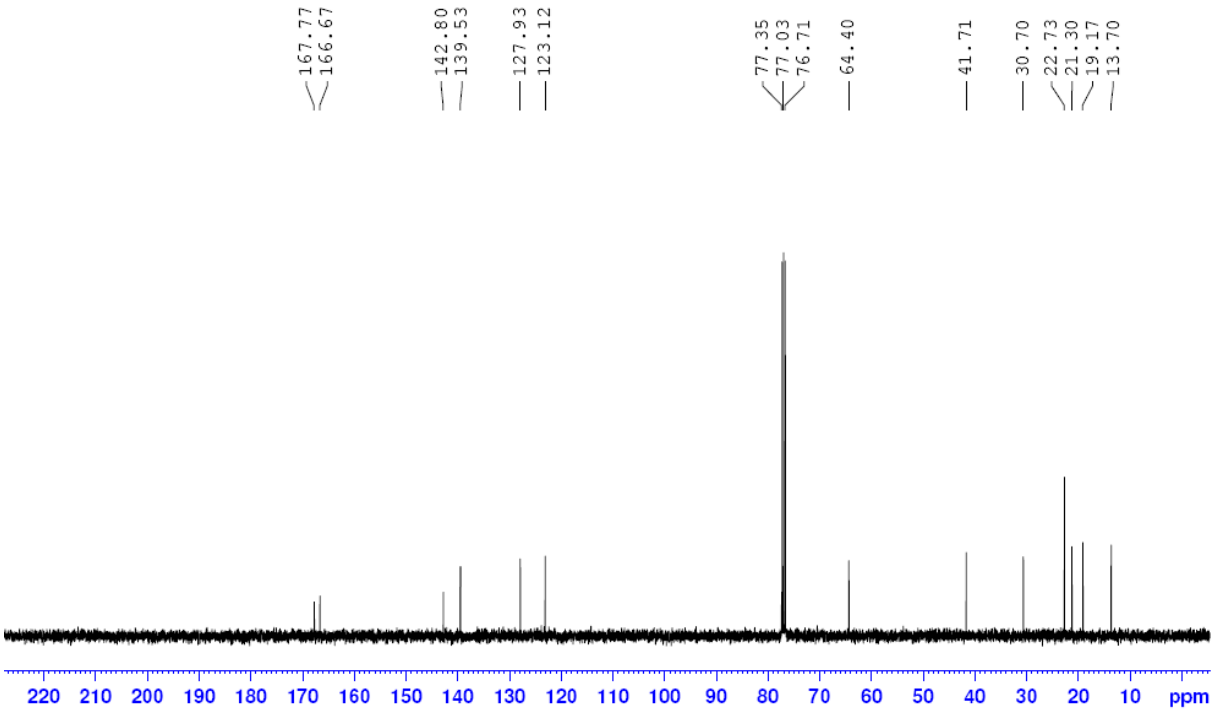
4.252
4.235
4.231
4.218
4.215
4.199
4.182
4.168
4.152
4.135
2.064
1.683
1.666
1.659
1.648
1.629
1.612
1.453
1.434
1.415
1.405
1.396
1.378
1.359
1.262
1.246
0.964
0.945
0.927
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm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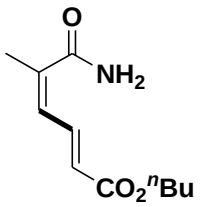
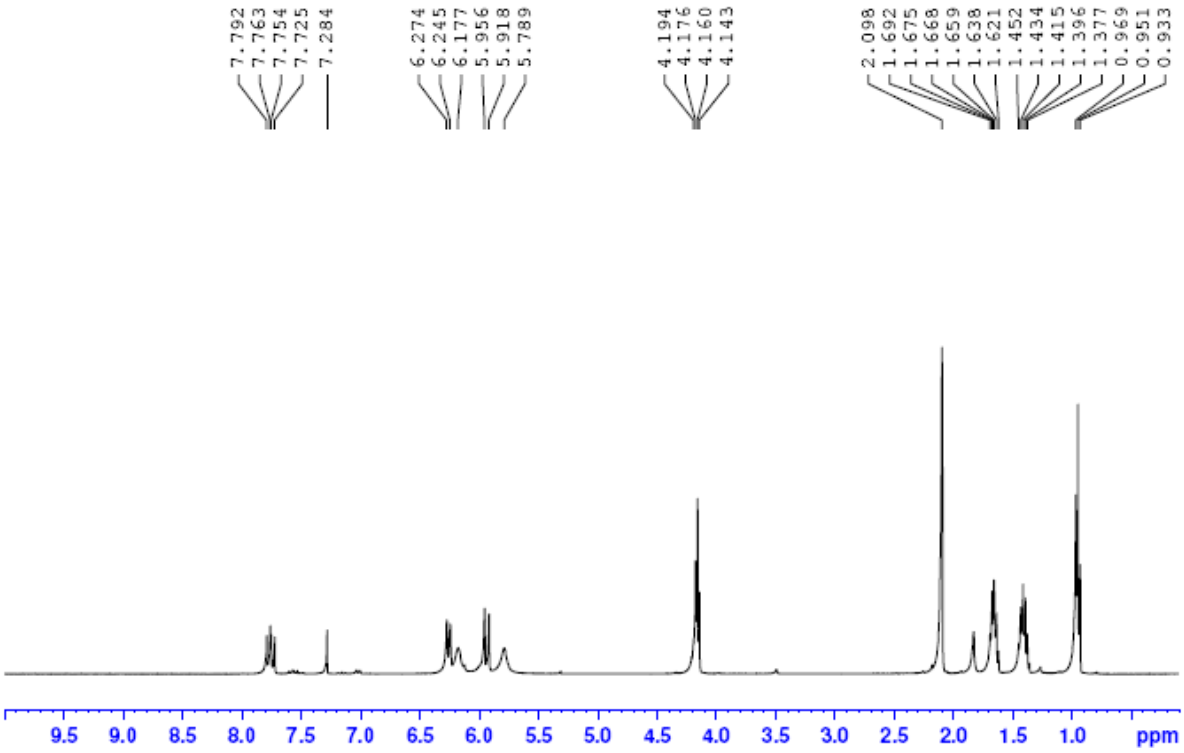
139.53
127.93
123.12
77.35
77.03
76.71
64.40
41.71
30.70
22.73
21.30
19.17
13.70
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
NH2
CO2nBu

(3da) (*Z*/*E* = 92/8)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7.725
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6.177
5.956
5.918
5.789
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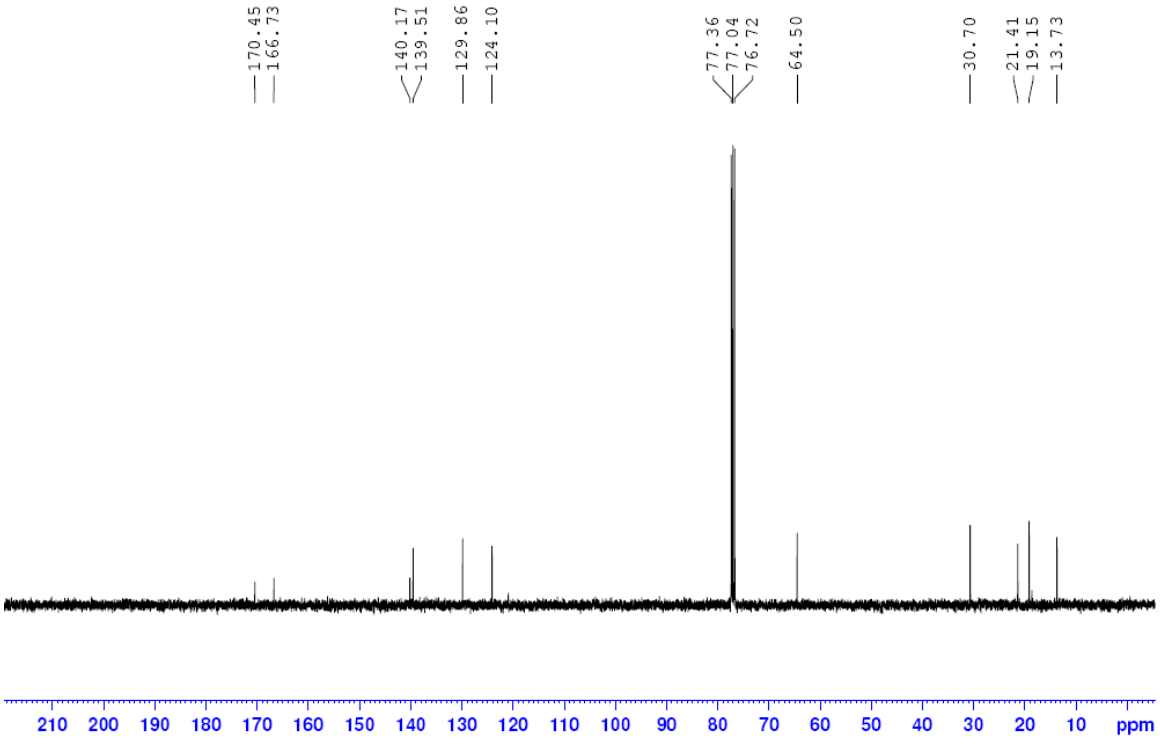
4.160
4.143
2.098
1.692
1.675
1.668
1.659
1.638
1.621
1.452
1.434
1.415
1.396
1.377
0.969
0.951
0.933
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm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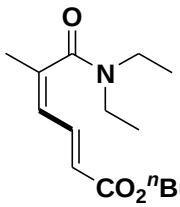
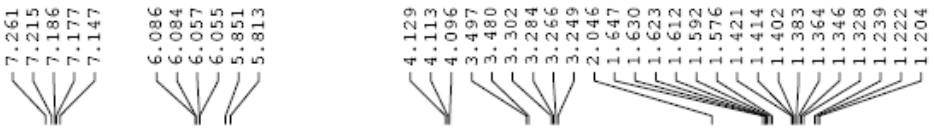
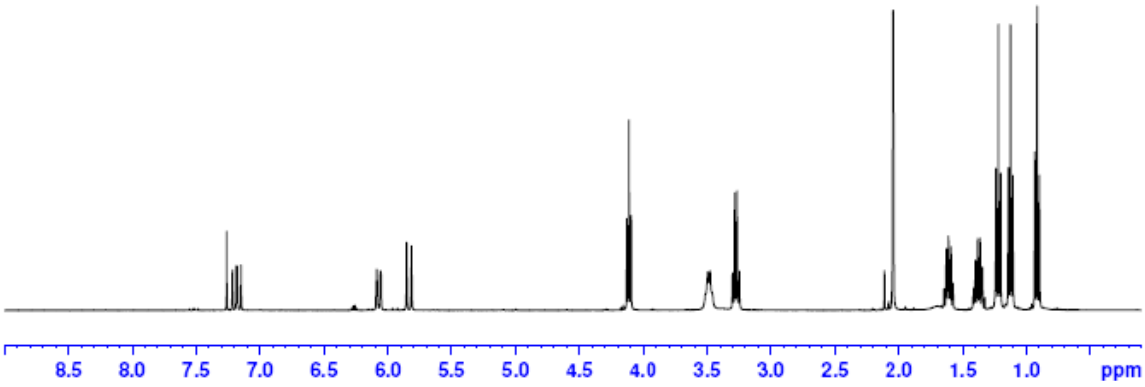
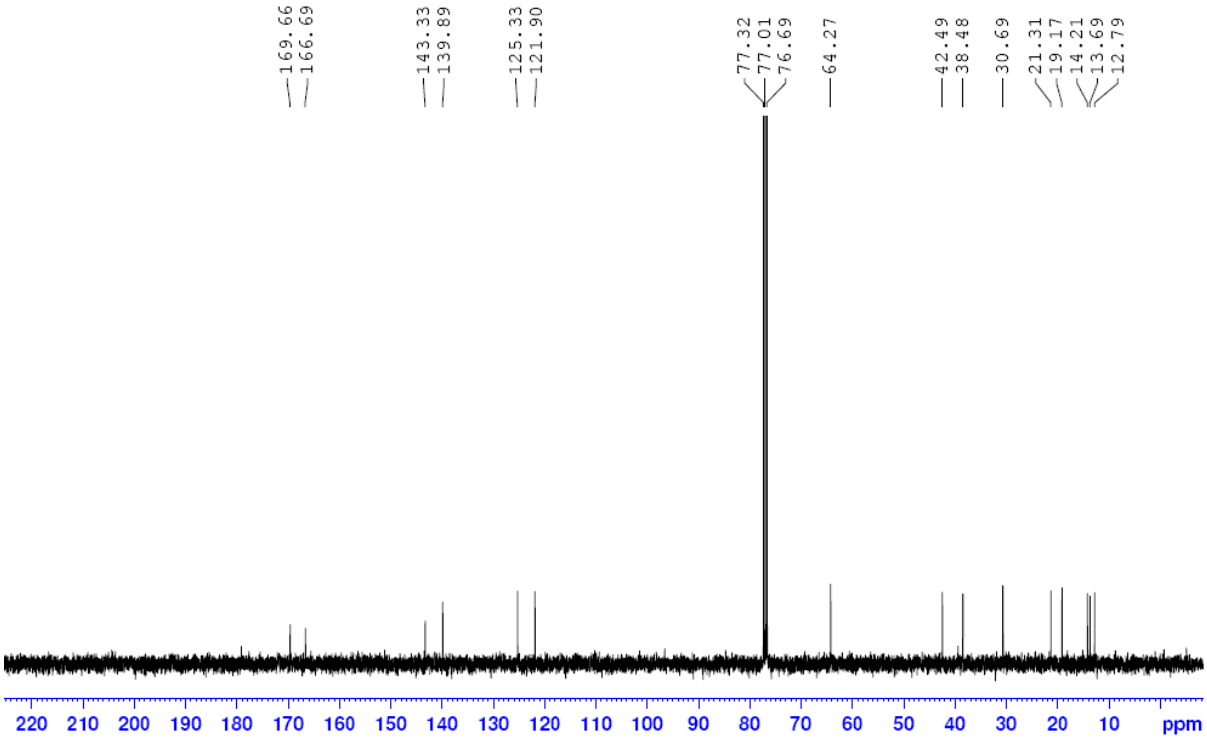
124.10
77.36
77.04
76.72
64.50
30.70
21.41
19.15
13.73
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

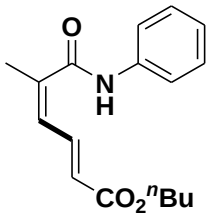

O
N
CO2nBu

(3ea) (*Z*/*E* > 99/1)

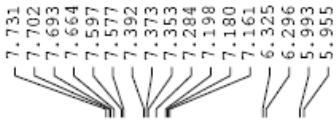

7.261
7.215
7.186
7.177
7.147
6.086
6.084
6.057
6.055
5.851
5.813
4.129
4.113
4.096
3.497
3.480
3.302
3.284
3.266
3.249
2.046
1.647
1.630
1.623
1.612
1.592
1.576
1.421
1.414
1.402
1.383
1.364
1.346
1.328
1.239
1.222
1.204

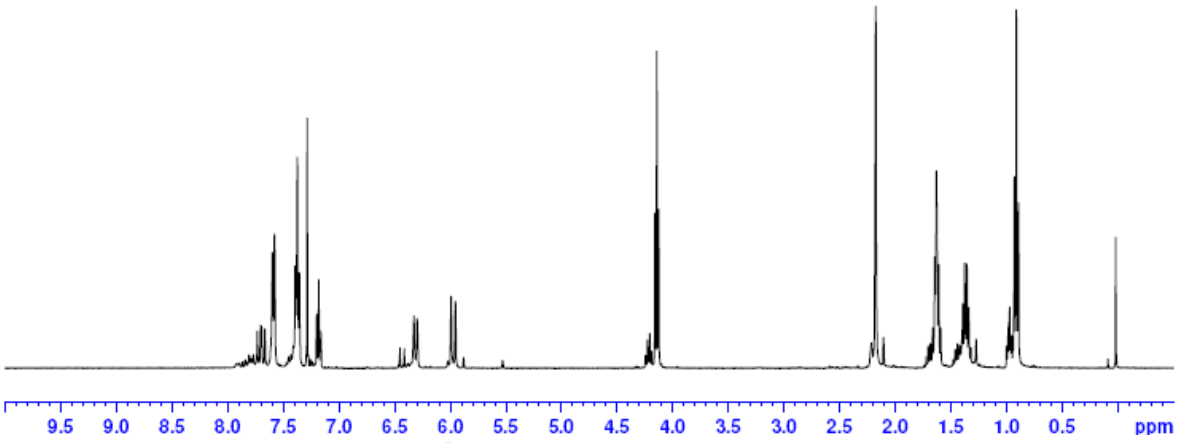

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

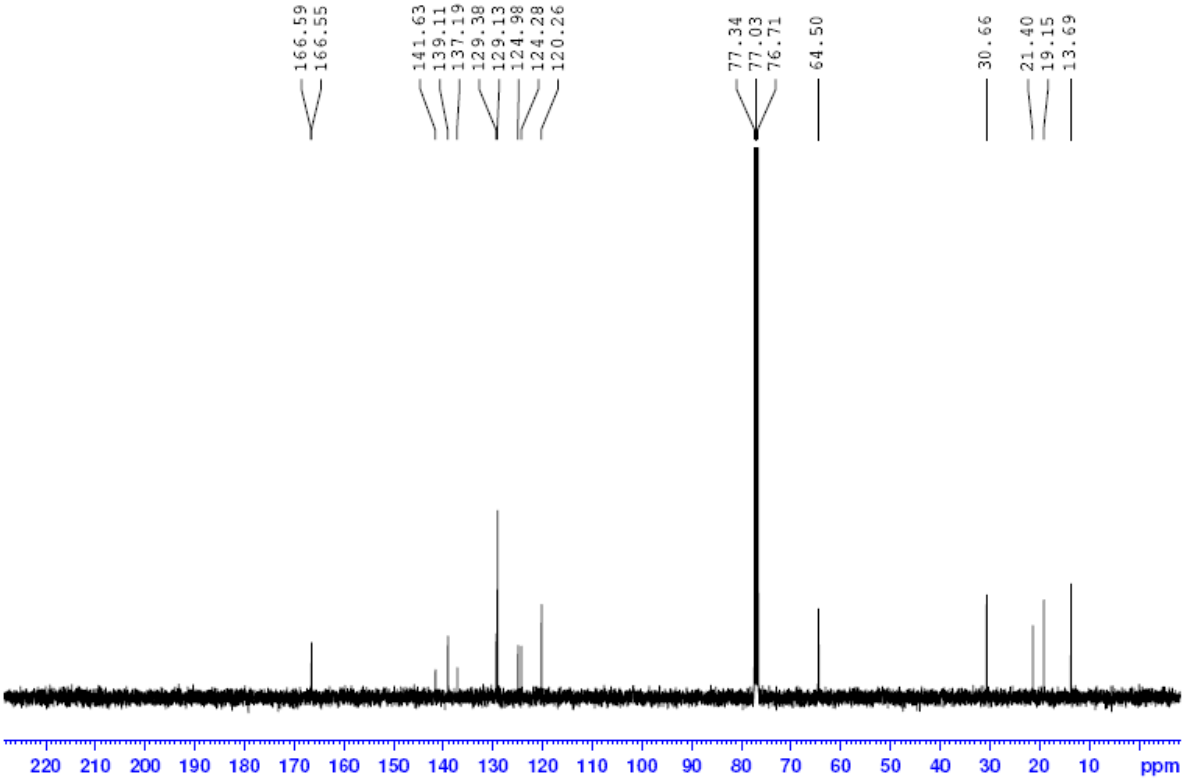

169.66
166.69
143.33
139.89
125.33
121.90
77.32
77.01
76.69
64.27
42.49
38.48
30.69
21.31
19.17
14.21
13.69
12.79
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

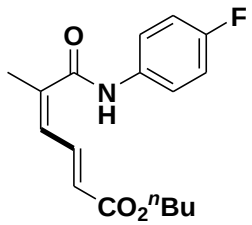

O
N
H
CO2nBu

(3fa) (*Z*/*E* = 82/18)


7.731
7.702
7.693
7.664
7.597
7.577
7.392
7.373
7.353
7.284
7.198
7.180
7.161
6.325
6.296
5.993
5.955
4.162
4.146
4.129
2.180
1.666
1.649
1.633
1.612
1.595
1.398
1.379
1.361
1.342
0.933
0.915
0.896

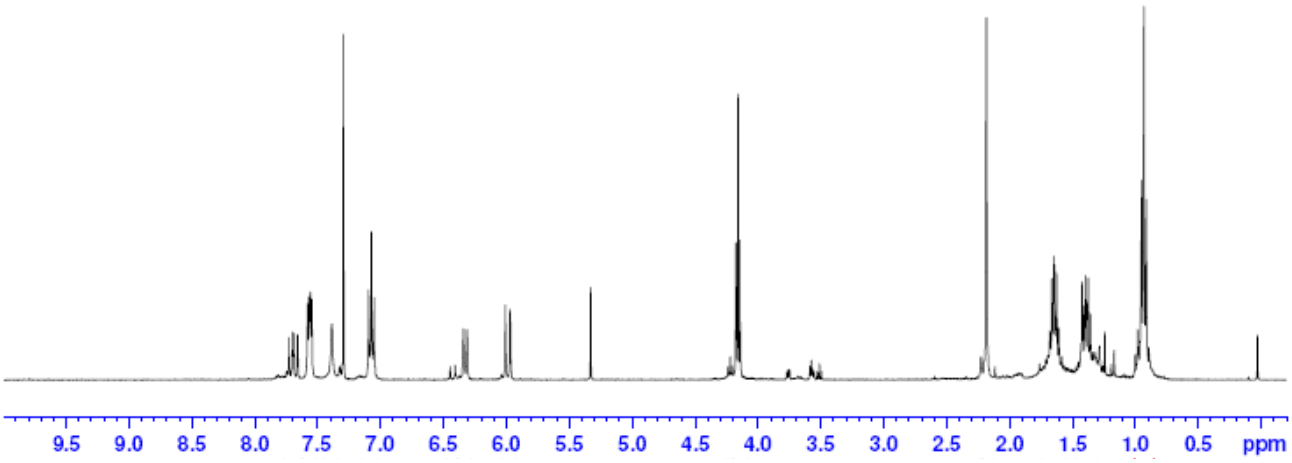

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

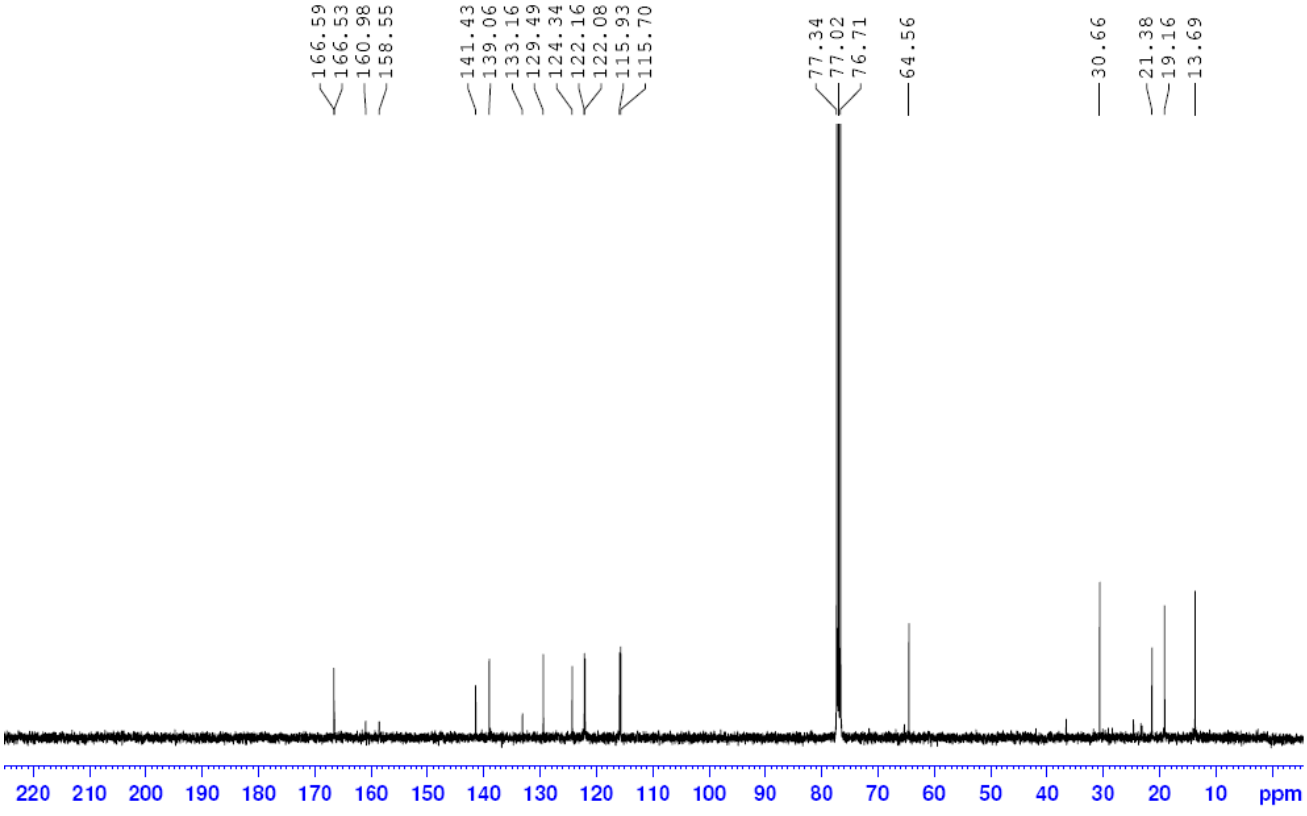

166.59
166.55
141.63
139.11
137.19
129.38
129.13
124.98
124.28
120.26
77.34
77.03
76.71
64.50
30.66
21.40
19.15
13.69
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

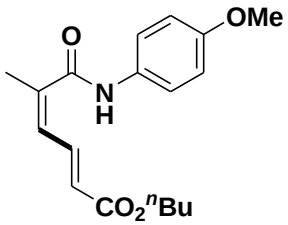

O
N
H
F
CO2nBu

(3ga) (*Z*/*E* = 84/16)

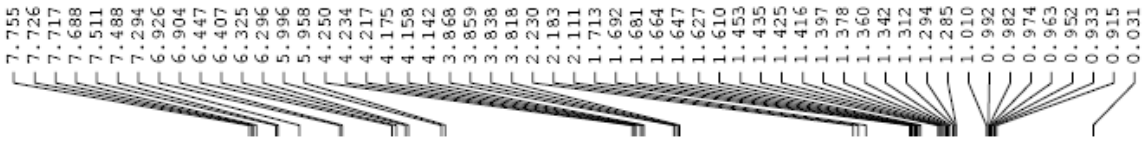

7.726
7.696
7.688
7.658
7.580
7.568
7.563
7.557
7.546
7.386
7.294
7.093
7.088
7.072
7.050
6.449
6.409
6.343
6.314
6.009
5.971
4.177
4.160
4.144
2.186
1.682
1.665
1.647
1.628
1.611
1.434
1.426
1.415
1.396
1.377
1.359
0.952
0.933
0.915

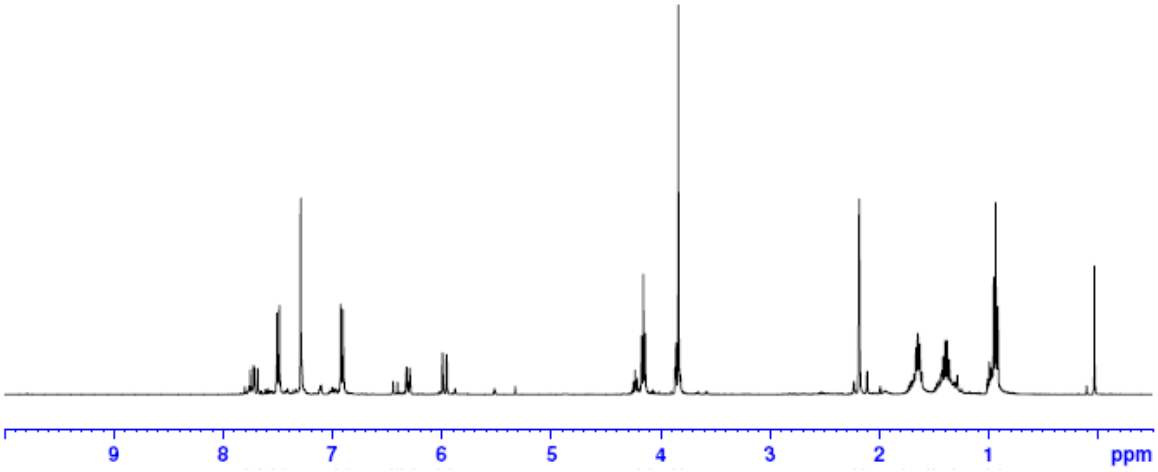

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

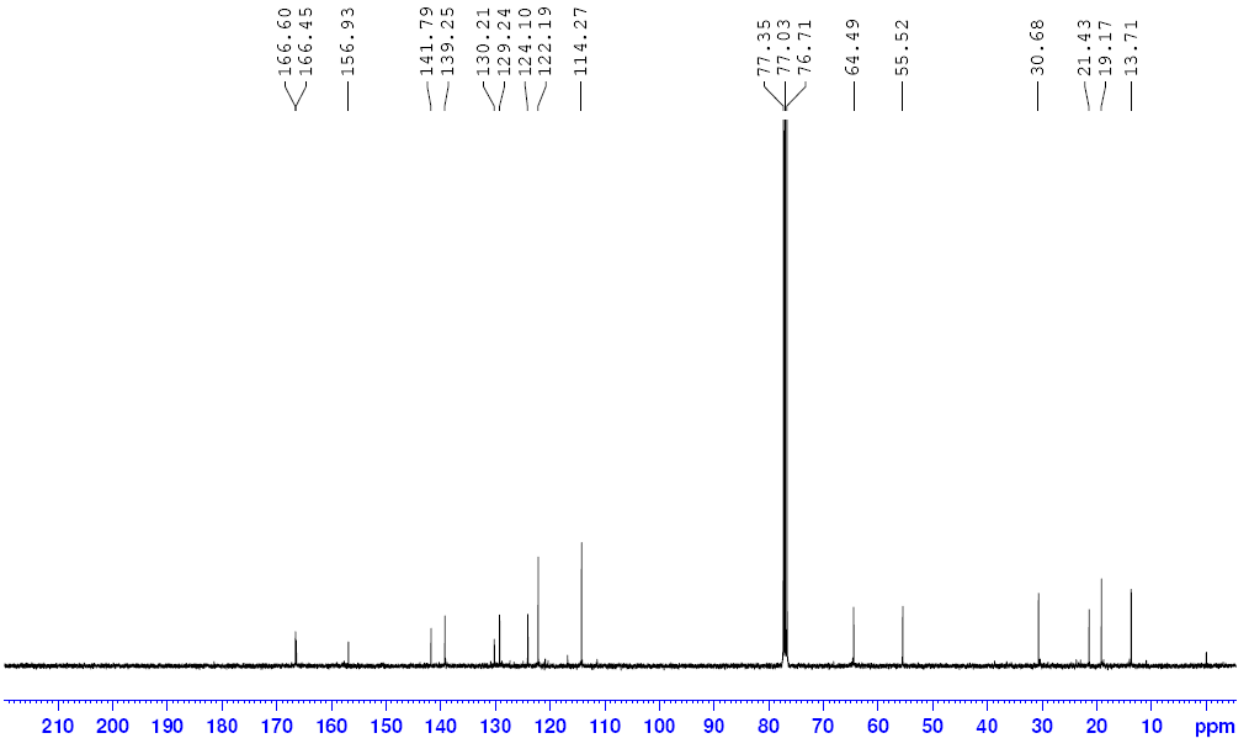

166.59
166.53
160.98
158.55
141.43
139.06
133.16
129.49
124.34
122.16
122.08
115.93
115.70
77.34
77.02
76.71
64.56
30.66
21.38
19.16
13.69
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

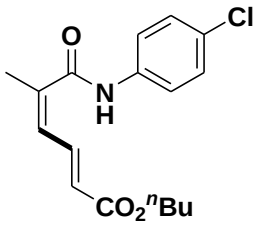

OMe
O
N
H
CO2nBu

(3ha) (*Z*/*E* =80/20)

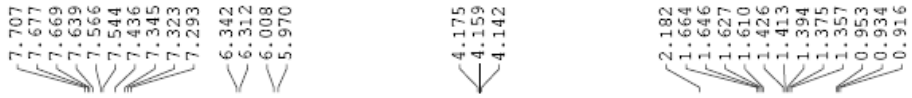

7.755
7.726
7.717
7.688
7.511
7.488
7.294
6.926
6.904
6.447
6.407
6.325
6.296
5.996
5.958
4.250
4.234
4.217
4.175
4.158
4.142
3.868
3.859
3.838
3.818
2.230
2.183
2.111
1.713
1.692
1.681
1.664
1.647
1.627
1.610
1.453
1.435
1.425
1.416
1.397
1.378
1.360
1.342
1.312
1.294
1.285
1.010
0.992
0.982
0.974
0.963
0.952
0.933
0.915
0.031

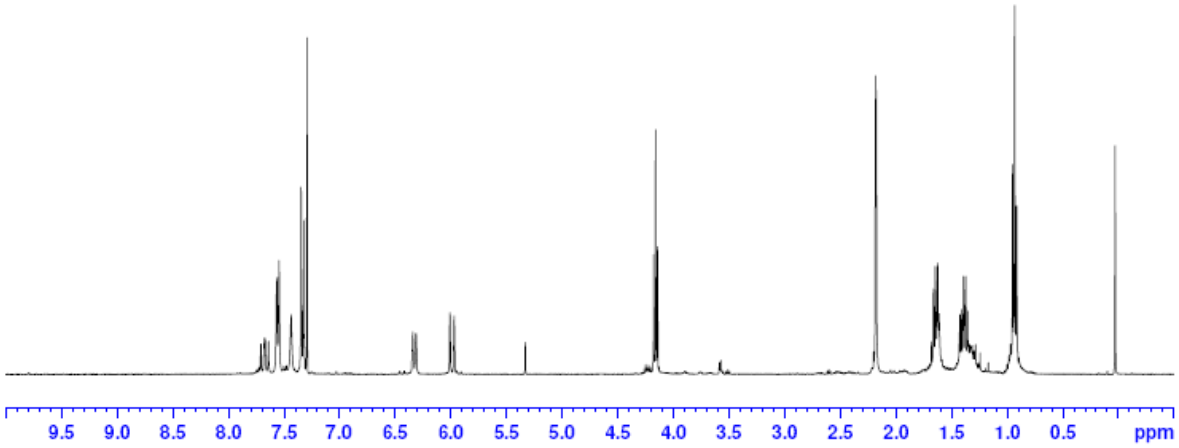

9
8
7
6
5
4
3
2
1
ppm

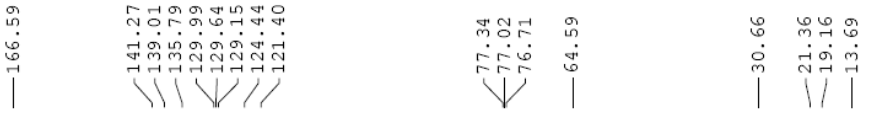

166.60
166.45
156.93
141.79
139.25
130.21
129.24
124.10
122.19
114.27
77.35
77.03
76.71
64.49
55.52
30.68
21.43
19.17
13.71
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

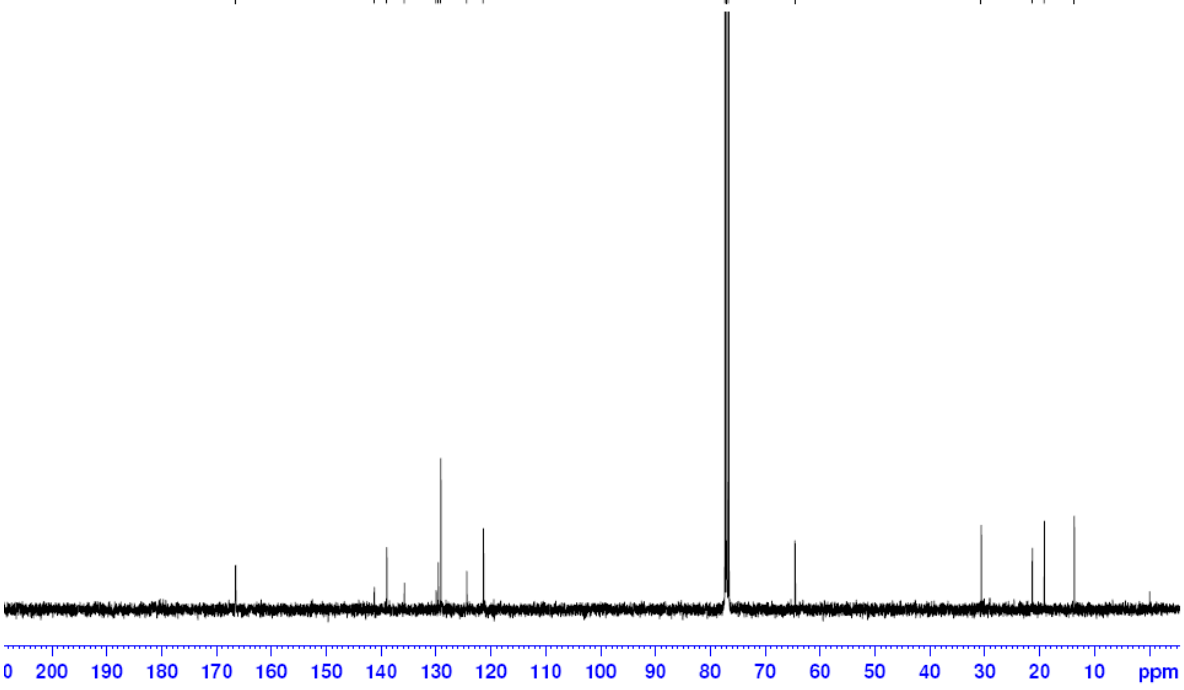

O
N
H
Cl
CO2nBu

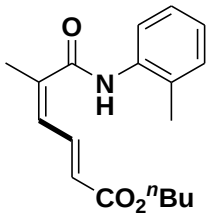
(3ia) (*Z*/*E* = 92/8)


7.707
7.677
7.669
7.639
7.566
7.544
7.436
7.345
7.323
7.293
6.342
6.312
6.008
5.970
4.175
4.159
4.142
2.182
1.664
1.646
1.627
1.610
1.426
1.413
1.394
1.375
1.357
0.953
0.934
0.916

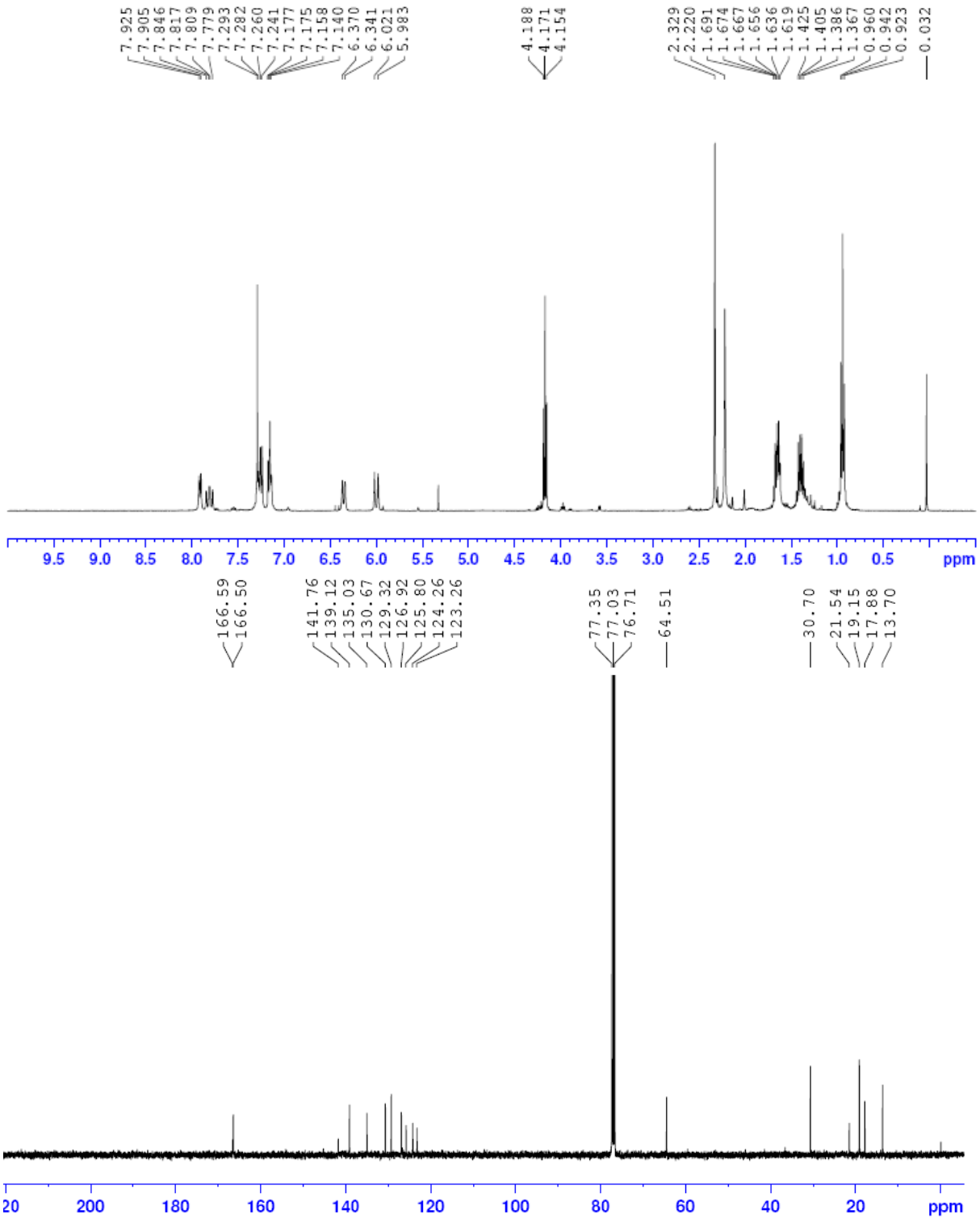

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

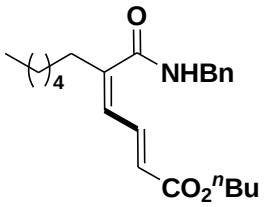

166.59
141.27
139.01
135.79
129.99
129.64
129.15
124.44
121.40
77.34
77.02
76.71
64.59
30.66
21.36
19.16
13.69


0 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
N
H
CO2nBu

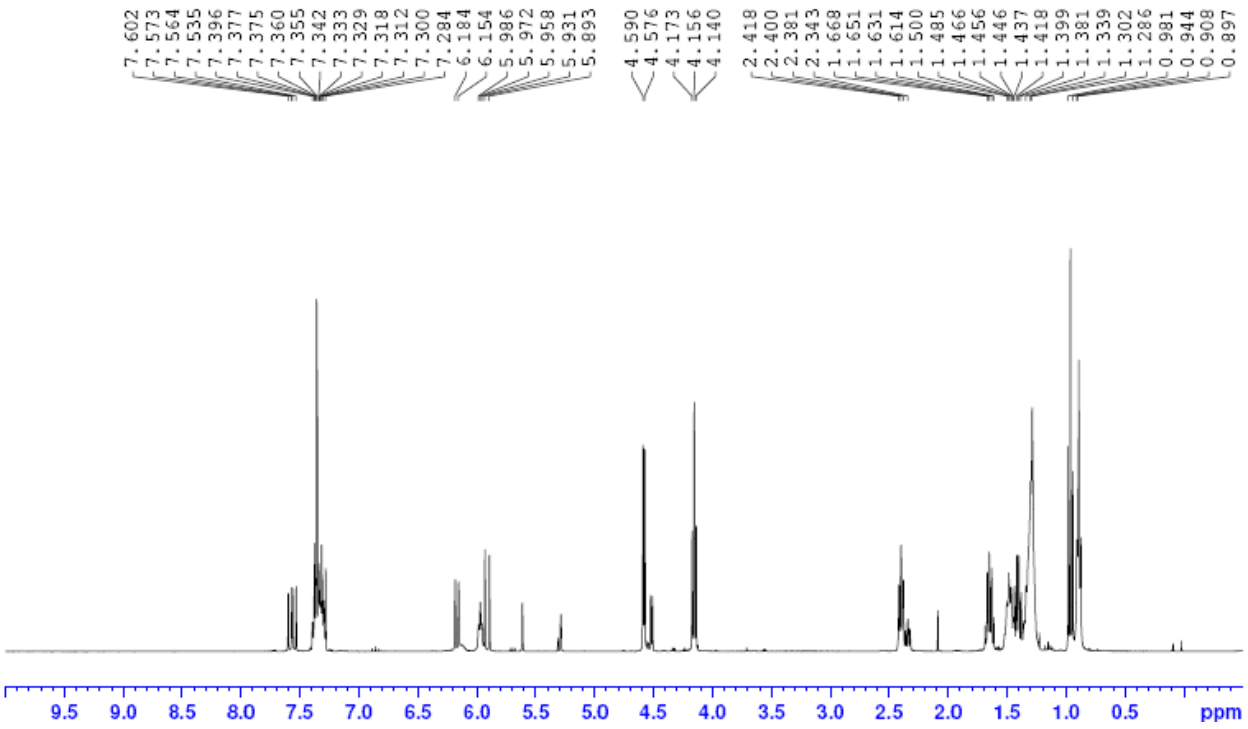
(3ja) (*Z*/*E* = 91/9)


7.925
7.905
7.846
7.817
7.809
7.779
7.293
7.282
7.260
7.241
7.177
7.175
7.158
7.140
6.370
6.341
6.021
5.983
4.188
4.171
4.154
2.329
2.220
1.691
1.674
1.667
1.656
1.636
1.619
1.425
1.405
1.386
1.367
0.960
0.942
0.923
0.032
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
166.59
166.50
141.76
139.12
135.03
130.67
129.32
126.92
125.80
124.26
123.26
77.35
77.03
76.71
64.51
30.70
21.54
19.15
17.88
13.70
220 200 180 160 140 120 100 80 60 40 20 ppm

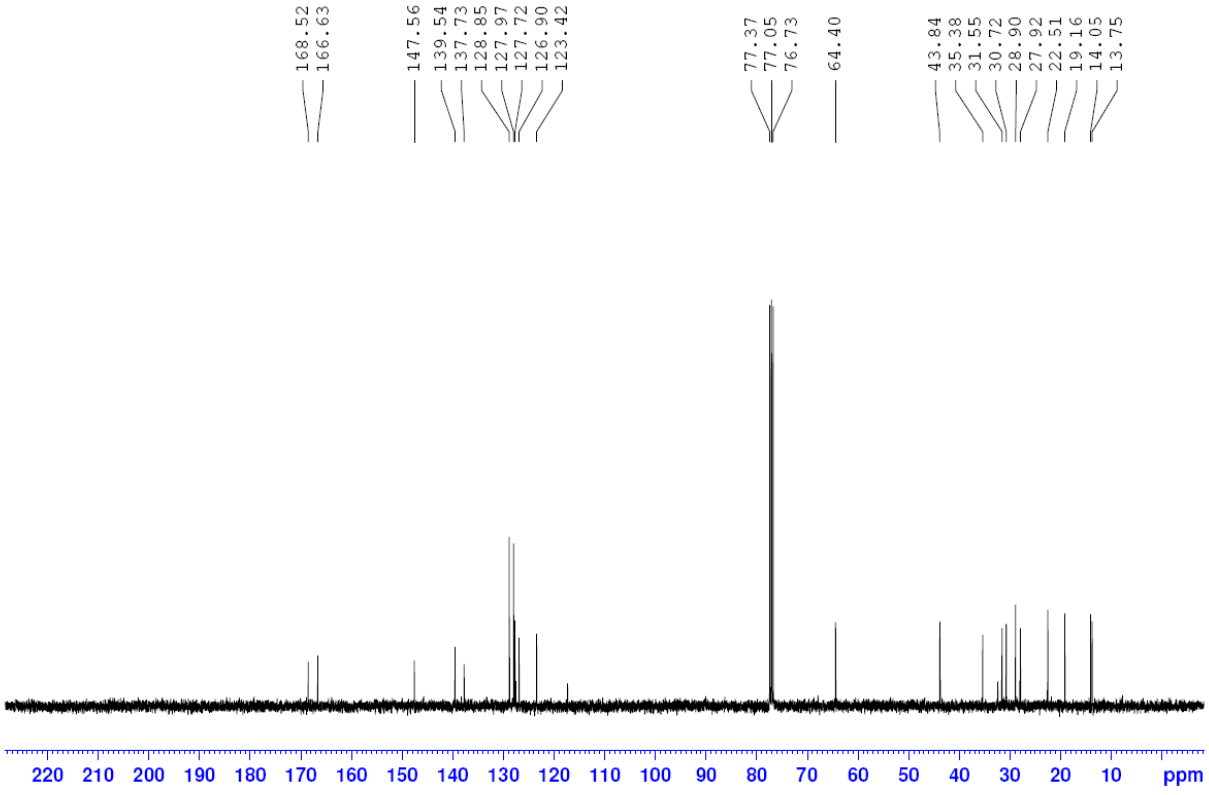


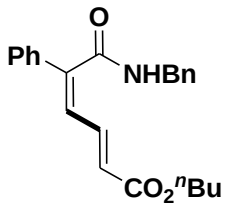
(3ka) (Z/E = 96/4) *(acrylamide included and it couldn't be seperated from product)*

Yield of product was calculated from NMR by deducting acrylamide.

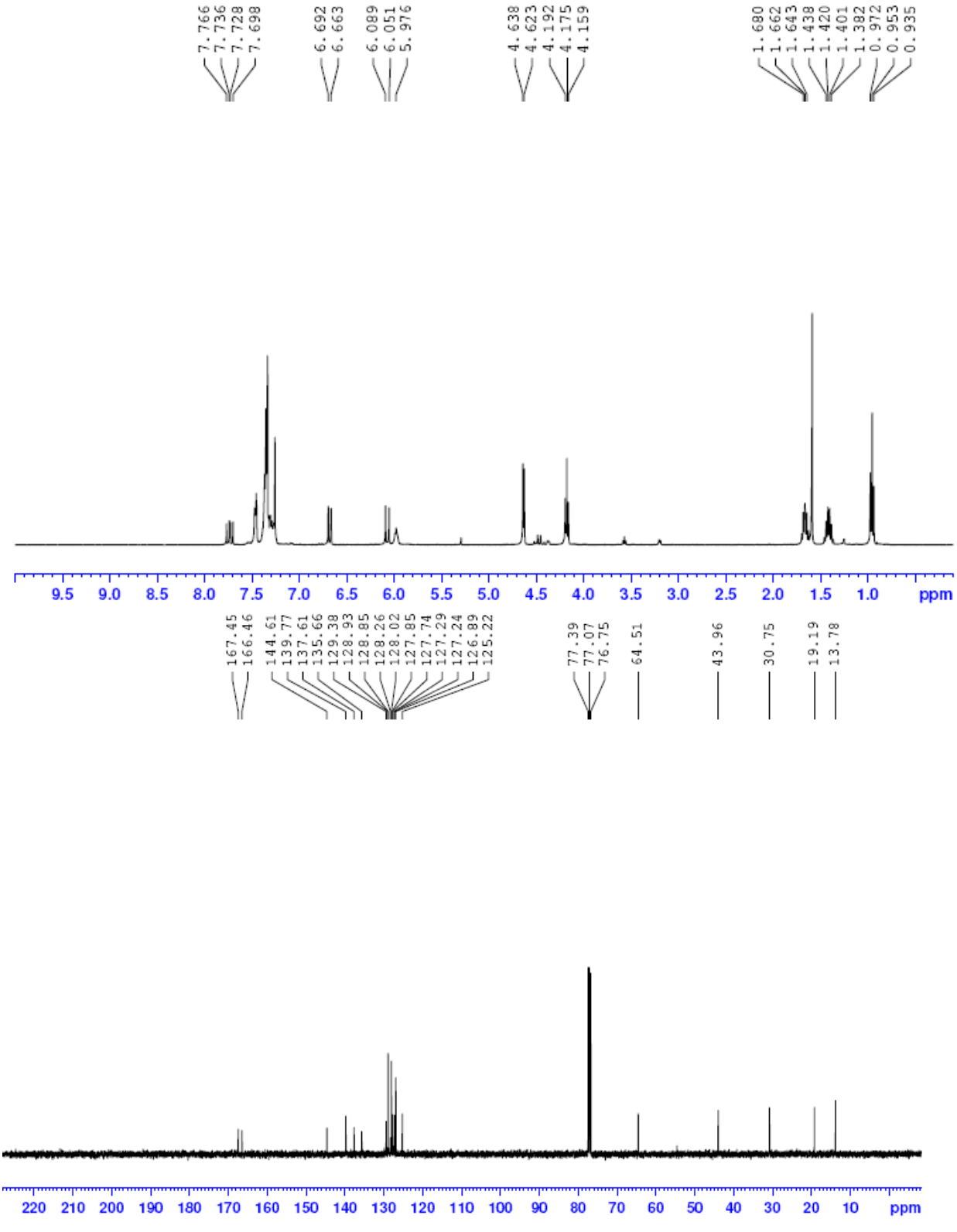


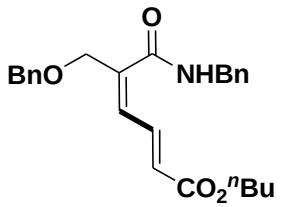
ZJ05-137-6-13C,CDCl3, 1H NMR, AV400



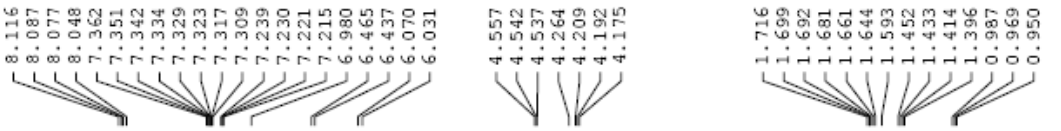

O
Ph
NHBn
CO2nBu

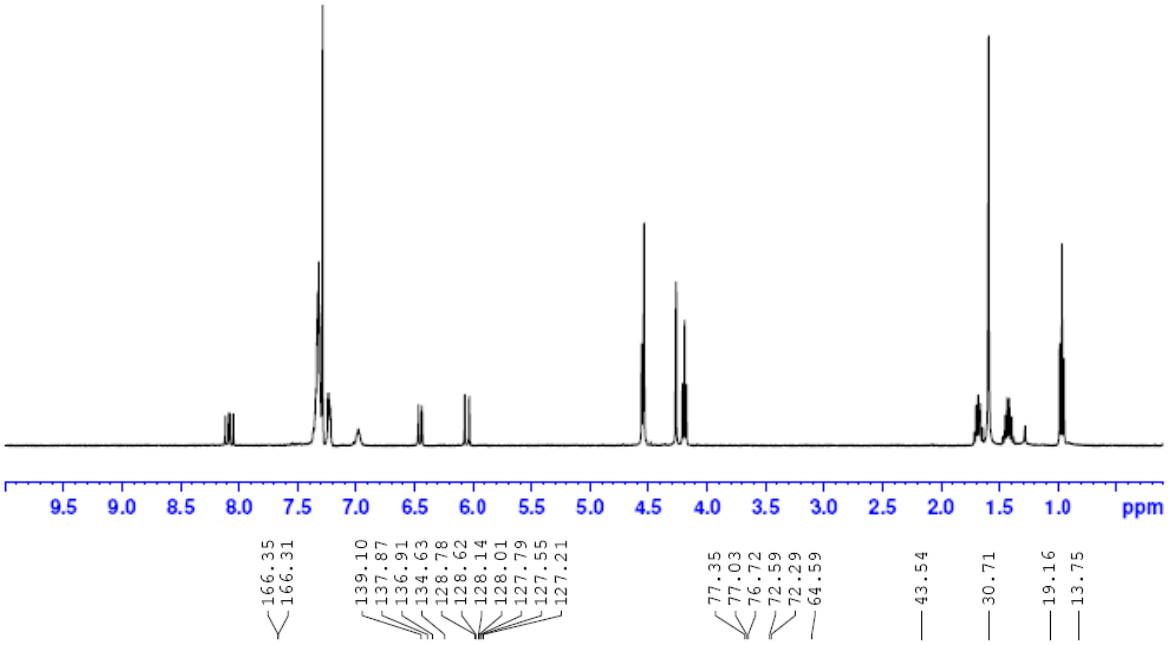
(3la) (*Z*/*E* = 97/3)


7.766
7.736
7.728
7.698
6.692
6.663
6.089
6.051
5.976
4.638
4.623
4.192
4.175
4.159
1.680
1.662
1.643
1.438
1.420
1.401
1.382
0.972
0.953
0.935
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
167.45
166.46
144.61
139.77
137.61
135.66
129.38
128.93
128.85
128.26
128.02
127.85
127.74
127.29
127.24
126.89
125.22
77.39
77.07
76.75
64.51
43.96
30.75
19.19
13.78
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

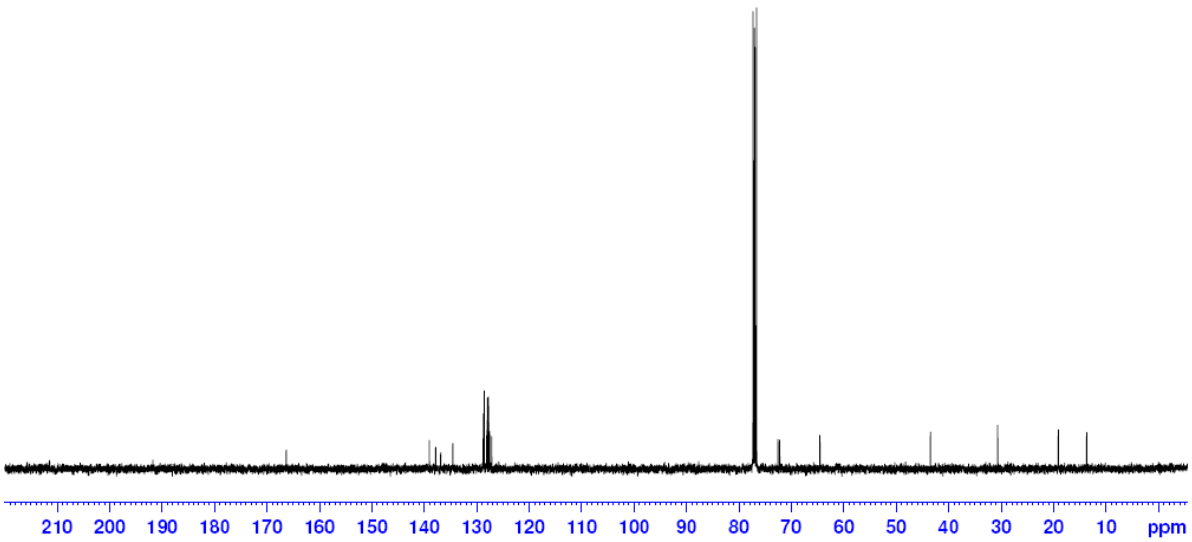

O
BnO
NHBn
CO2nBu

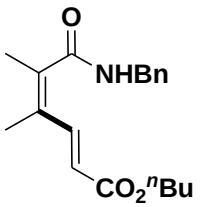
(3ma) (*Z*/*E* = 96/4)


8.116
8.087
8.077
8.048
7.362
7.351
7.342
7.334
7.329
7.323
7.317
7.309
7.239
7.230
7.221
7.215
6.980
6.465
6.437
6.070
6.031
4.557
4.542
4.537
4.264
4.209
4.192
4.175
1.716
1.699
1.692
1.681
1.661
1.644
1.593
1.452
1.433
1.414
1.396
0.987
0.969
0.950

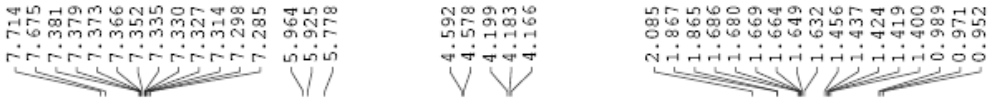

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

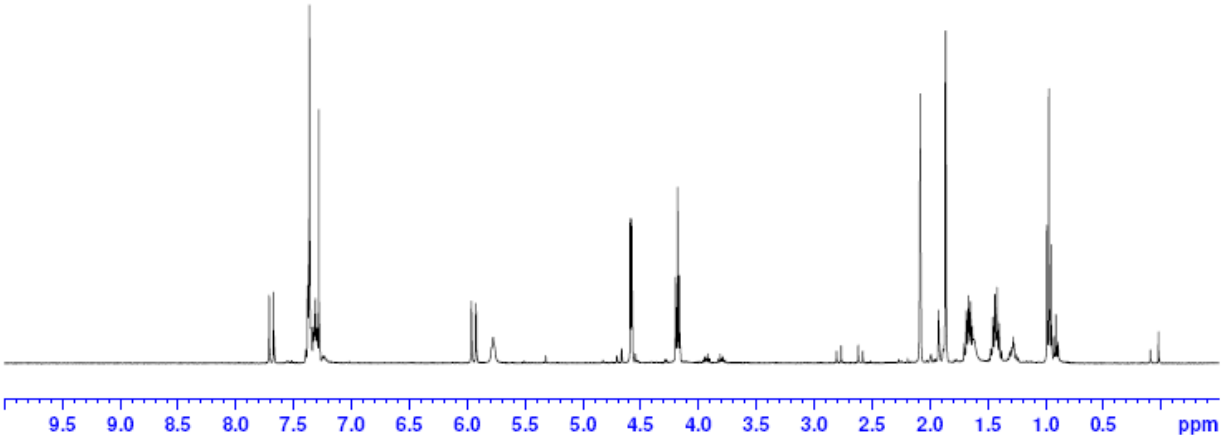
166.35
166.31
139.10
137.87
136.91
134.63
128.78
128.62
128.14
128.01
127.79
127.55
127.21
77.35
77.03
76.72
72.59
72.29
64.59
43.54
30.71
19.16
13.75

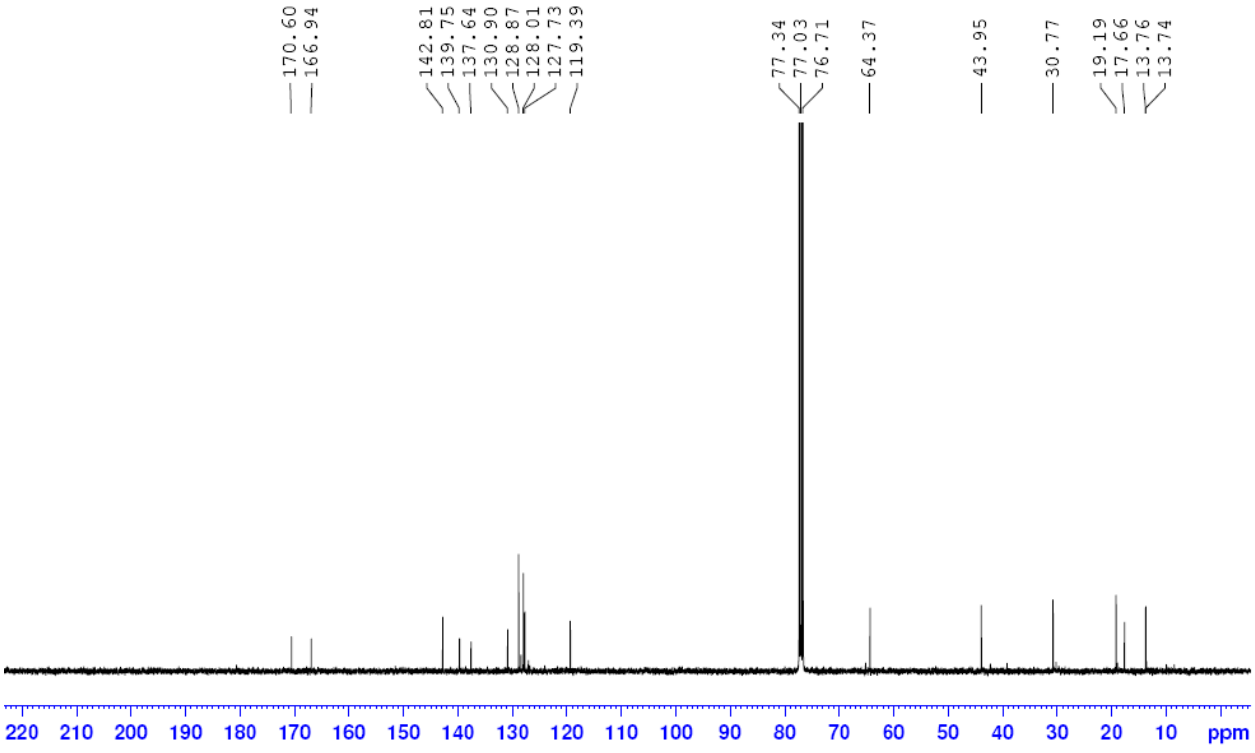

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

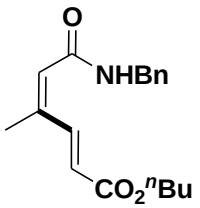

O
NHBn
CO2nBu

(3na) (*Z*/*E* > 99/1)

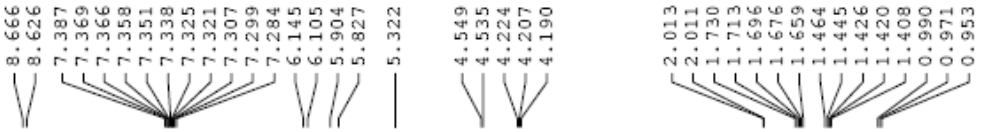

7.714
7.675
7.381
7.379
7.373
7.366
7.352
7.335
7.330
7.327
7.314
7.298
7.285
5.964
5.925
5.778
4.592
4.578
4.199
4.183
4.166
2.085
1.867
1.865
1.686
1.680
1.669
1.664
1.649
1.632
1.456
1.437
1.424
1.419
1.400
0.989
0.971
0.952

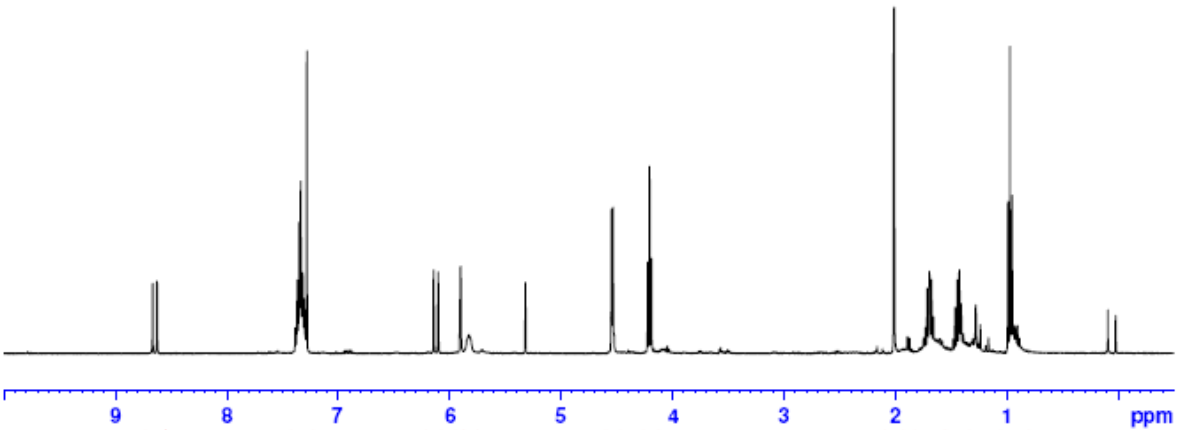

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

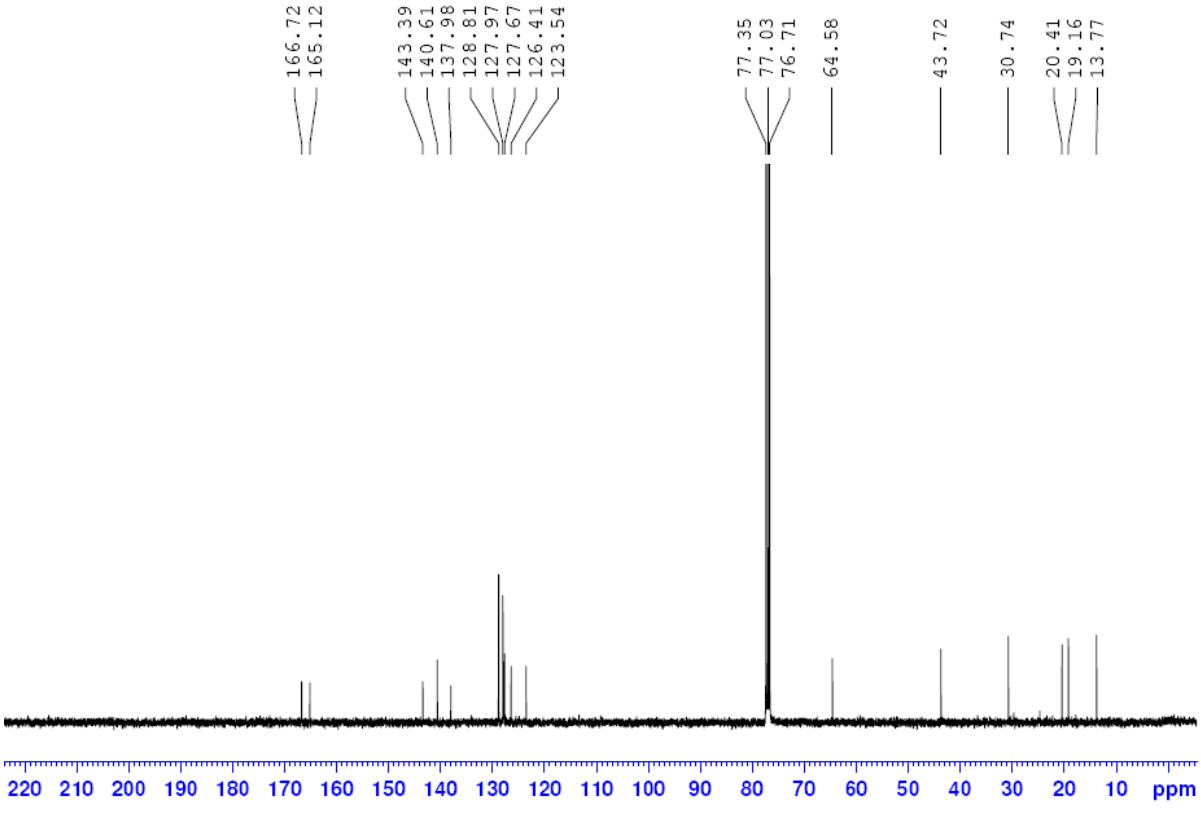

170.60
166.94
142.81
139.75
137.64
130.90
128.87
128.01
127.73
119.39
77.34
77.03
76.71
64.37
43.95
30.77
19.19
17.66
13.76
13.74
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

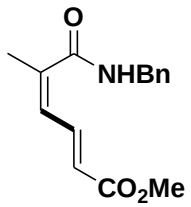

O
NHBn
CO2nBu

(3oa) (*Z*/*E* > 99/1)

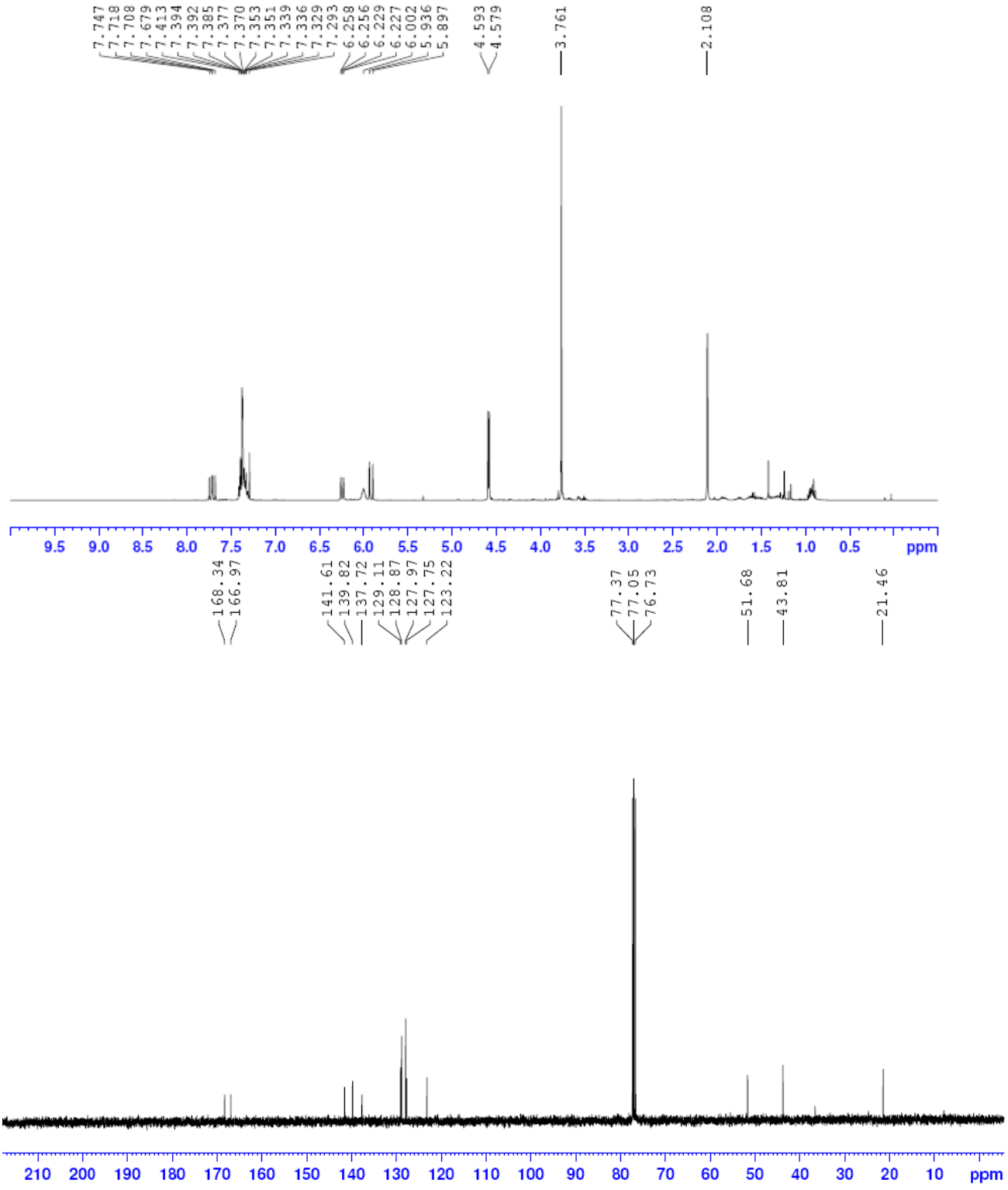

8.666
8.626
7.387
7.369
7.366
7.358
7.351
7.338
7.325
7.321
7.307
7.299
7.284
6.145
6.105
5.904
5.827
5.322
4.549
4.535
4.224
4.207
4.190
2.013
2.011
1.730
1.713
1.696
1.676
1.659
1.464
1.445
1.426
1.420
1.408
0.990
0.971
0.953

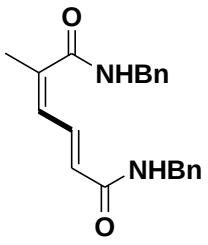

9
8
7
6
5
4
3
2
1
ppm


166.72
165.12
143.39
140.61
137.98
128.81
127.97
127.67
126.41
123.54
77.35
77.03
76.71
64.58
43.72
30.74
20.41
19.16
13.77
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

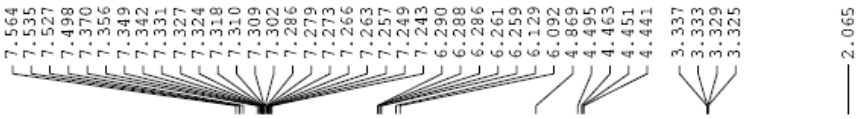

O
NHBn
CO2Me

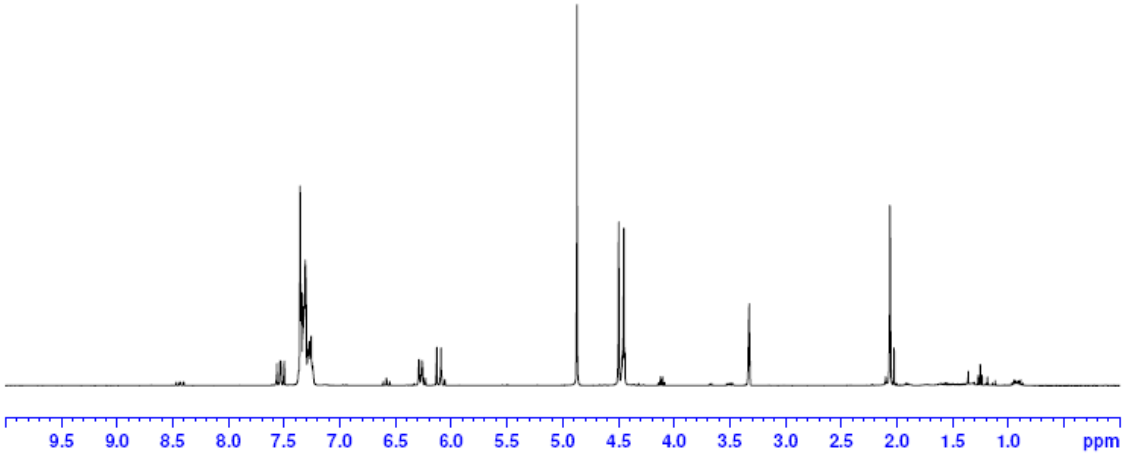
(3ab) (*Z*/*E* > 99/1)

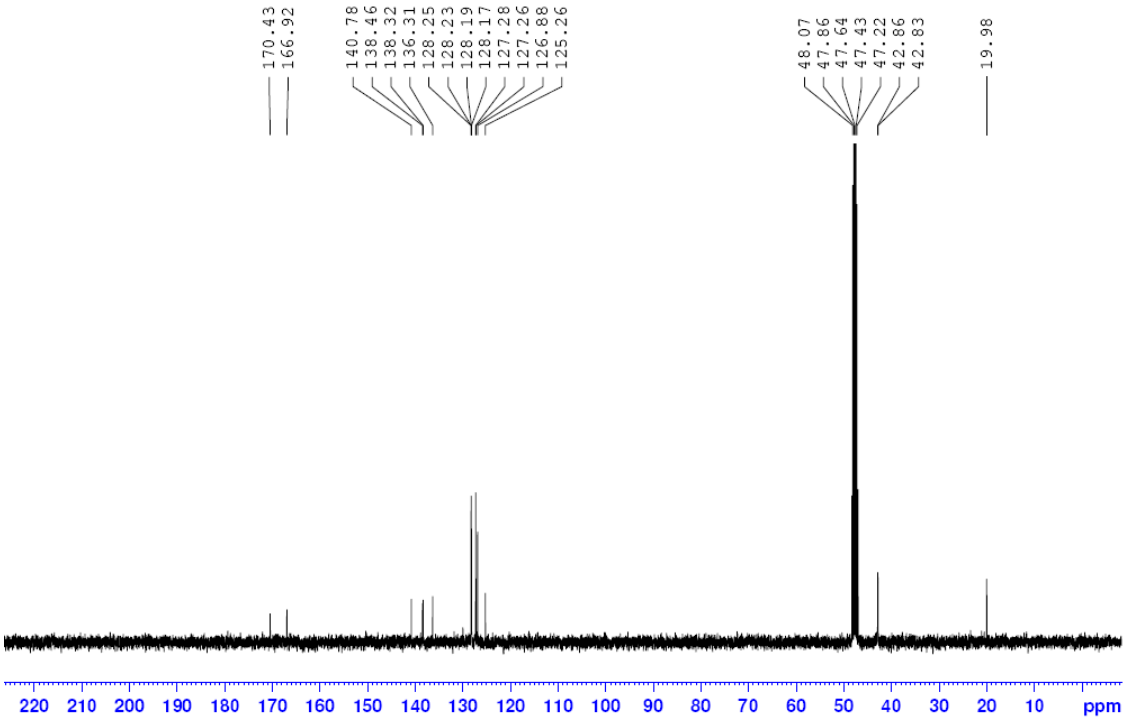

7.747
7.718
7.708
7.679
7.413
7.394
7.392
7.385
7.377
7.370
7.353
7.351
7.339
7.336
7.329
7.293
6.258
6.256
6.229
6.227
6.002
5.936
5.897
4.593
4.579
3.761
2.108
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
168.34
166.97
141.61
139.82
137.72
129.11
128.87
127.97
127.75
123.22
77.37
77.05
76.73
51.68
43.81
21.46
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

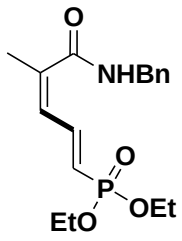


(MeOD) (3ad) (*Z*/*E* = 87/13)

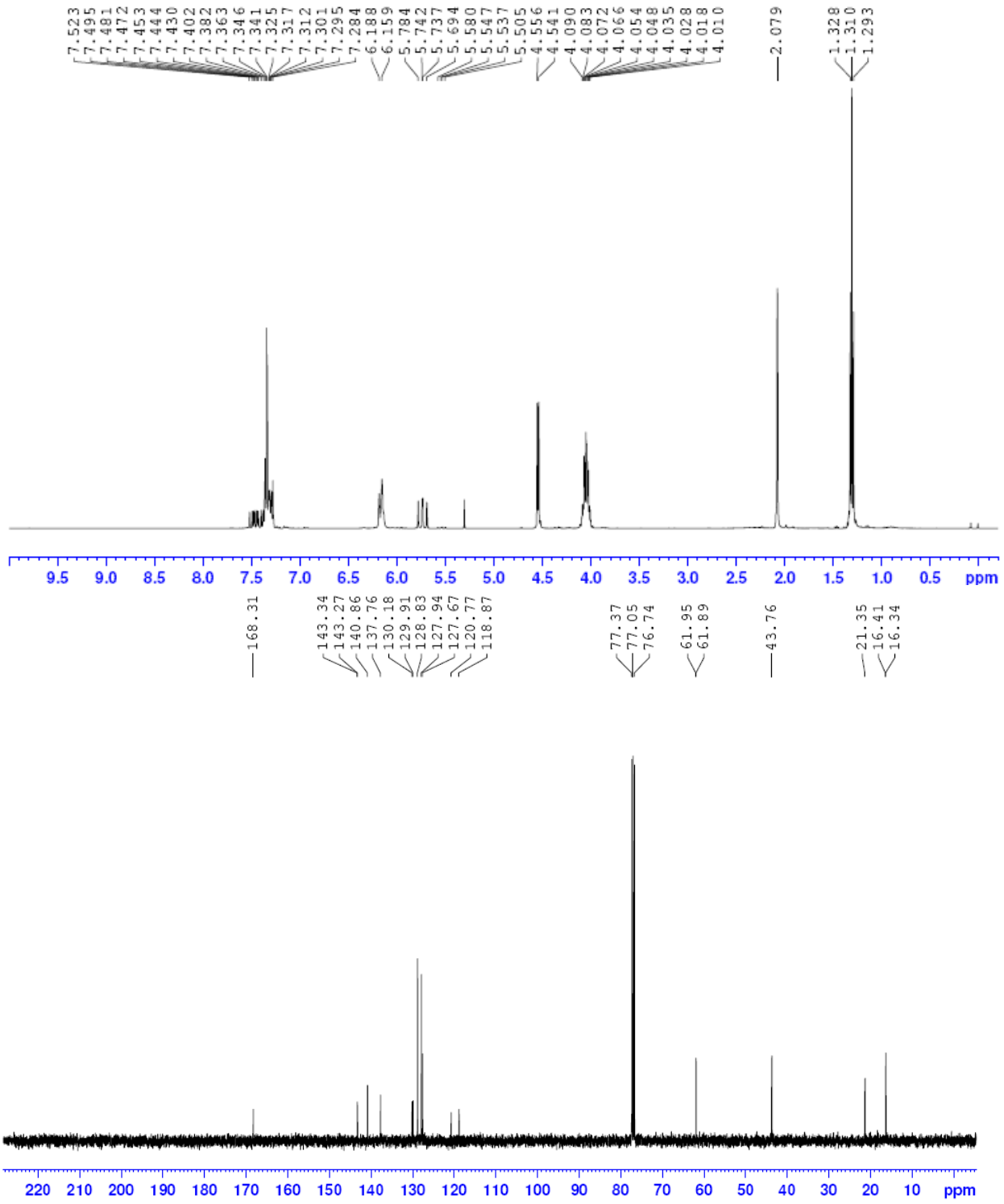


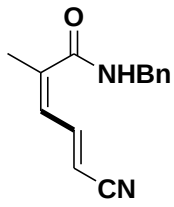





O
NHBn
O
P
EtO
OEt

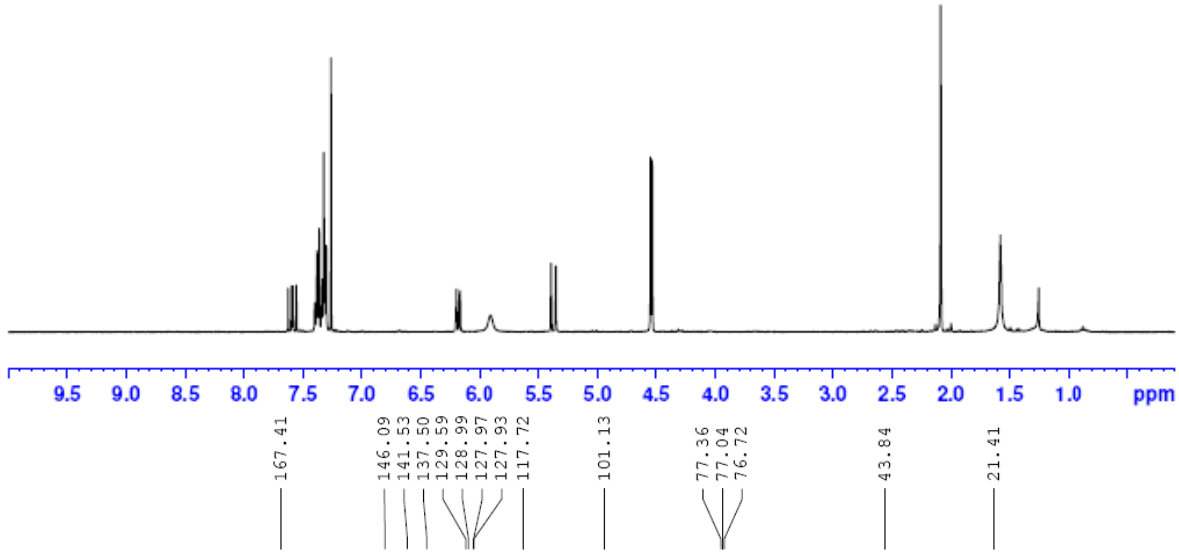
(3ae) (*Z*/*E* = 95/5)


7.523
7.495
7.481
7.472
7.453
7.444
7.430
7.402
7.382
7.363
7.346
7.341
7.325
7.317
7.312
7.301
7.295
7.284
6.188
6.159
5.784
5.742
5.737
5.694
5.580
5.547
5.537
5.505
4.556
4.541
4.090
4.083
4.072
4.066
4.054
4.048
4.035
4.028
4.018
4.010
2.079
1.328
1.310
1.293
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
168.31
143.34
143.27
140.86
137.76
130.18
129.91
128.83
127.94
127.67
120.77
118.87
77.37
77.05
76.74
61.95
61.89
43.76
21.35
16.41
16.34
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

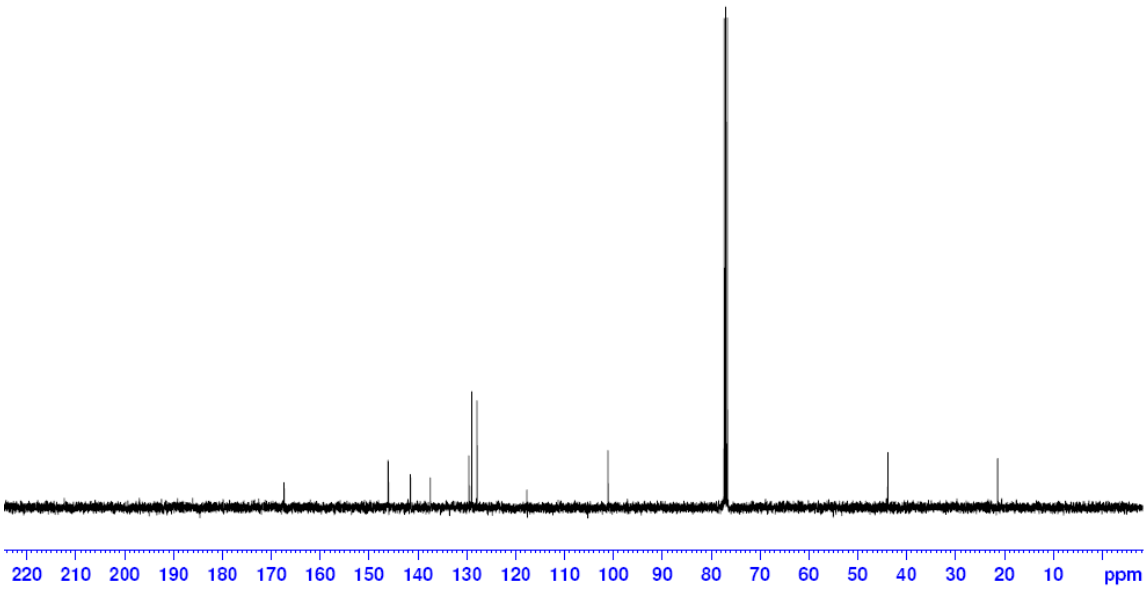

O
NHBn
CN

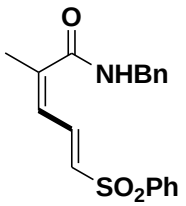
(3af) (Z/*E* = 95/5)


7.623
7.595
7.583
7.555
7.401
7.398
7.383
7.380
7.368
7.362
7.335
7.322
7.303
6.196
6.169
5.908
5.393
5.353
4.548
4.534
2.086

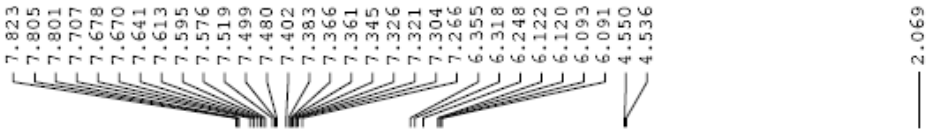

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

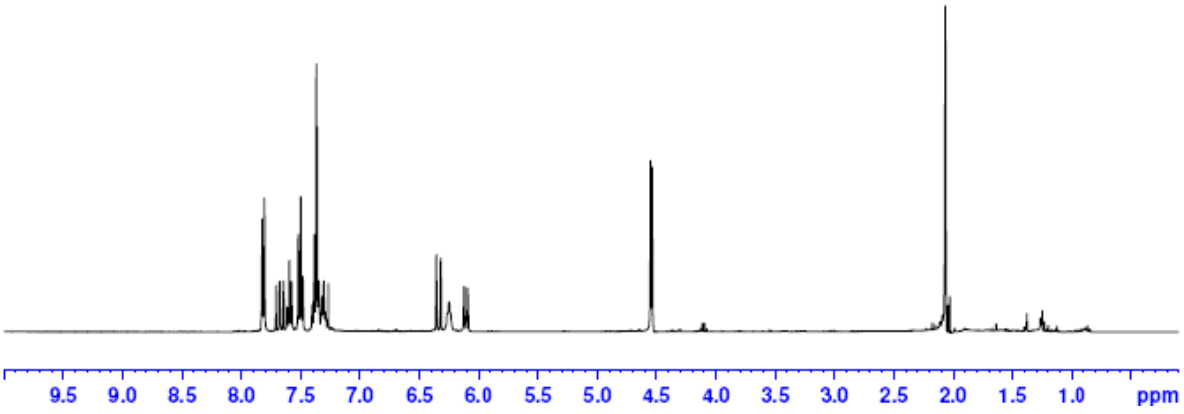
167.41
146.09
141.53
137.50
129.59
128.99
127.97
127.93
117.72
101.13
77.36
77.04
76.72
43.84
21.41

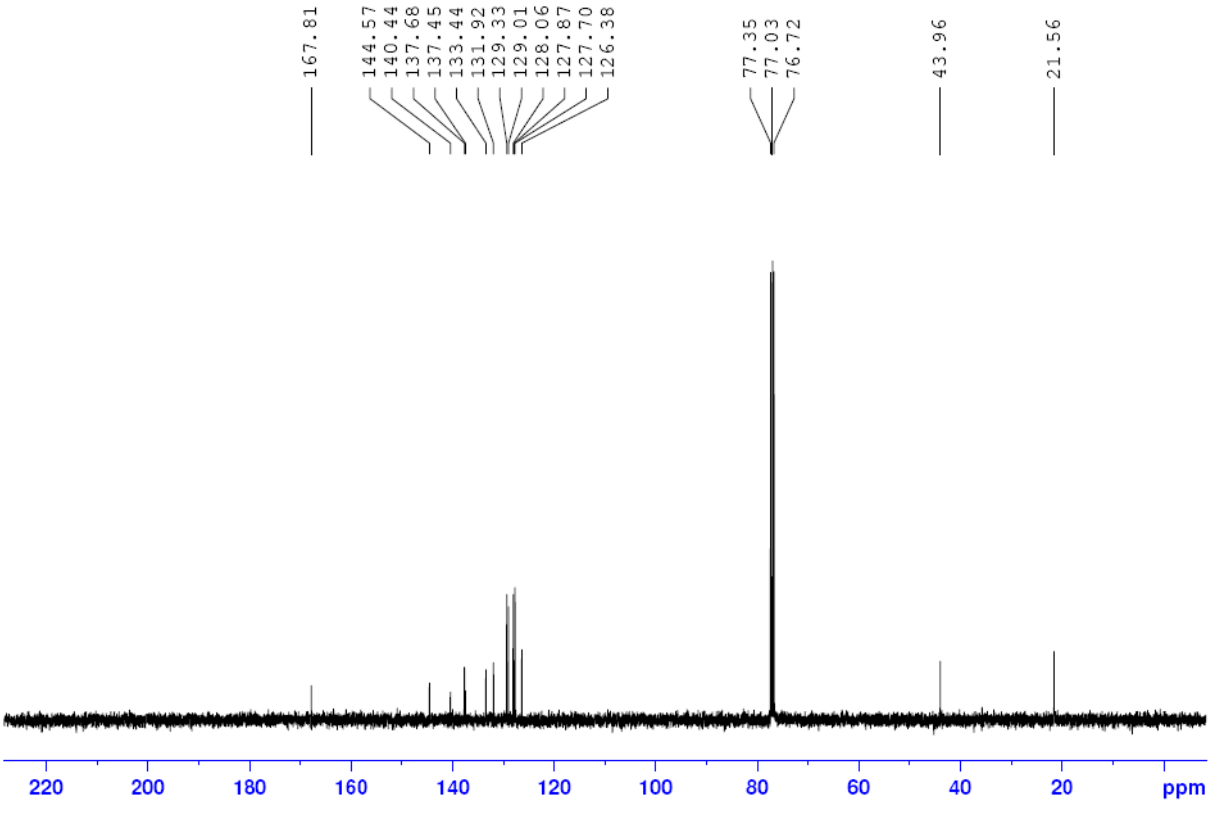

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

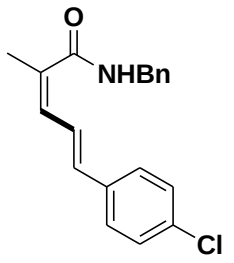

O
NHBn
SO2Ph

(3ag) (*Z*/*E* > 99/1)

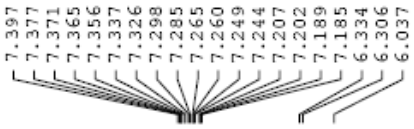

7.823
7.805
7.801
7.707
7.678
7.670
7.641
7.613
7.595
7.576
7.519
7.499
7.480
7.402
7.383
7.366
7.361
7.345
7.326
7.321
7.304
7.266
6.355
6.318
6.248
6.122
6.120
6.093
6.091
4.550
4.536
2.069

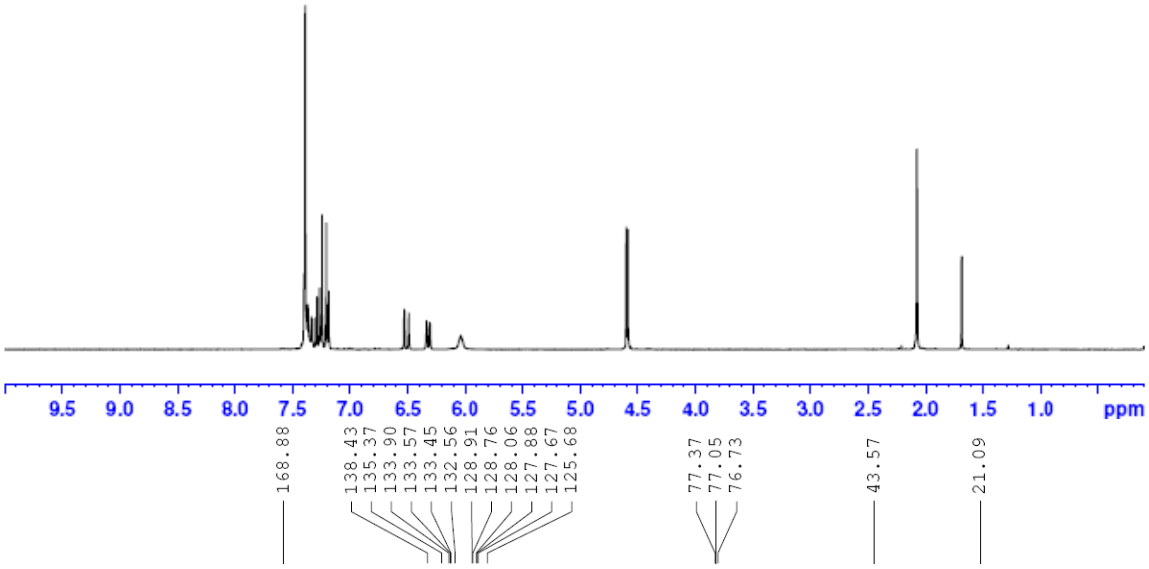

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


167.81
144.57
140.44
137.68
137.45
133.44
131.92
129.33
129.01
128.06
127.87
127.70
126.38
77.35
77.03
76.72
43.96
21.56
220
200
180
160
140
120
100
80
60
40
20
ppm

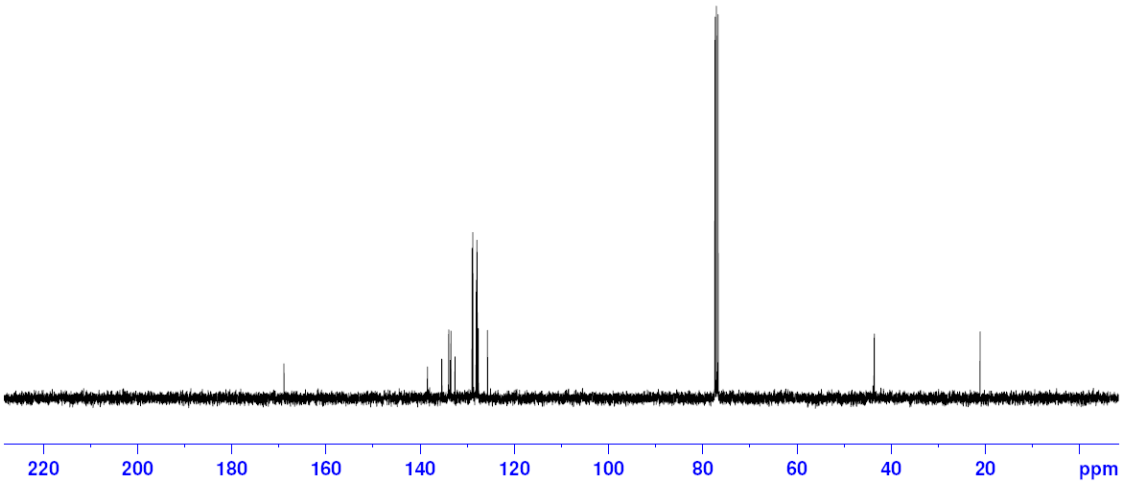

O
NHBn
Cl

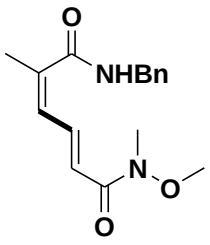
(3ah) (*Z*/*E* = 96/4)


7.397
7.377
7.371
7.365
7.356
7.337
7.326
7.298
7.285
7.265
7.260
7.249
7.244
7.207
7.202
7.189
7.185
6.334
6.306
6.037
4.600
4.586
2.075
1.685

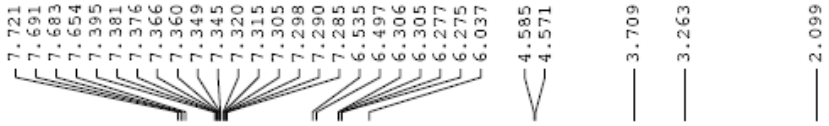

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

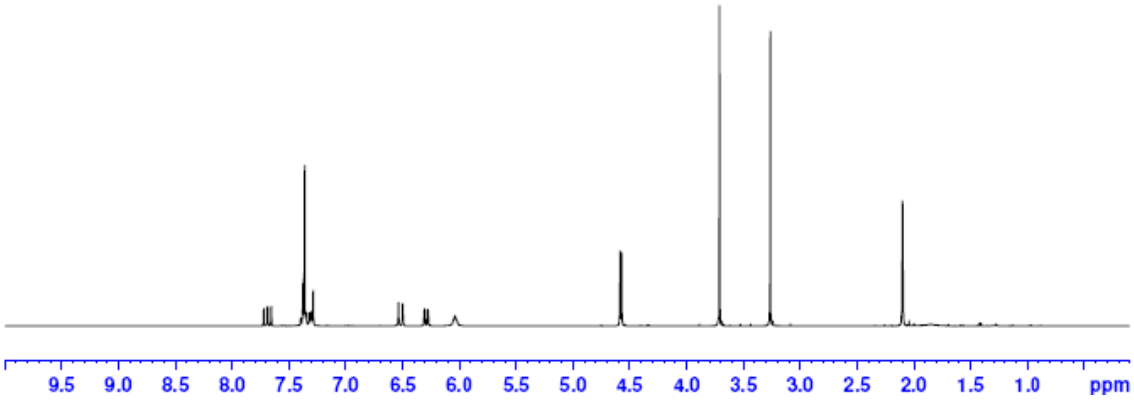
168.88
138.43
135.37
133.90
133.57
133.45
132.56
128.91
128.76
128.06
127.88
127.67
125.68
77.37
77.05
76.73
43.57
21.09

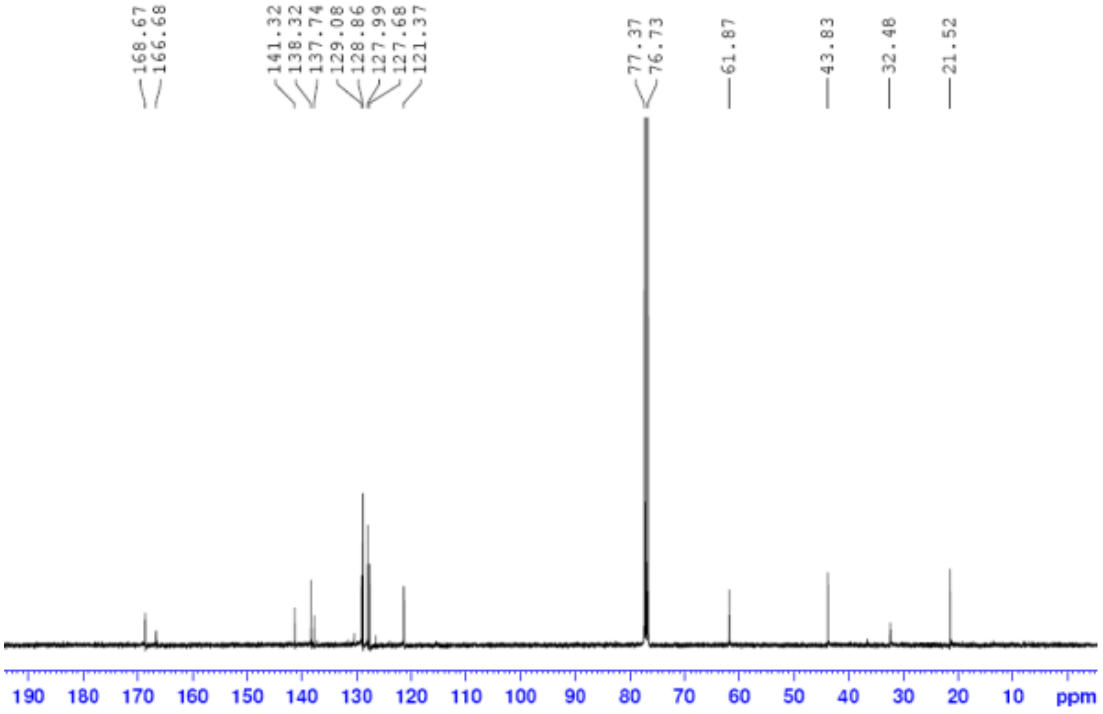

220
200
180
160
140
120
100
80
60
40
20
ppm

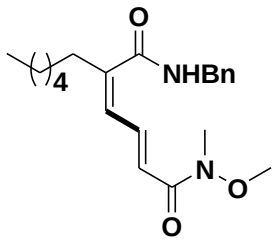

O
NHBn
N
O
O

(3ai) (*Z*/*E* =95/5)


7.721
7.691
7.683
7.654
7.395
7.381
7.376
7.366
7.360
7.349
7.345
7.320
7.315
7.305
7.298
7.290
7.285
6.535
6.497
6.306
6.305
6.277
6.275
6.037
4.585
4.571
3.709
3.263
2.099

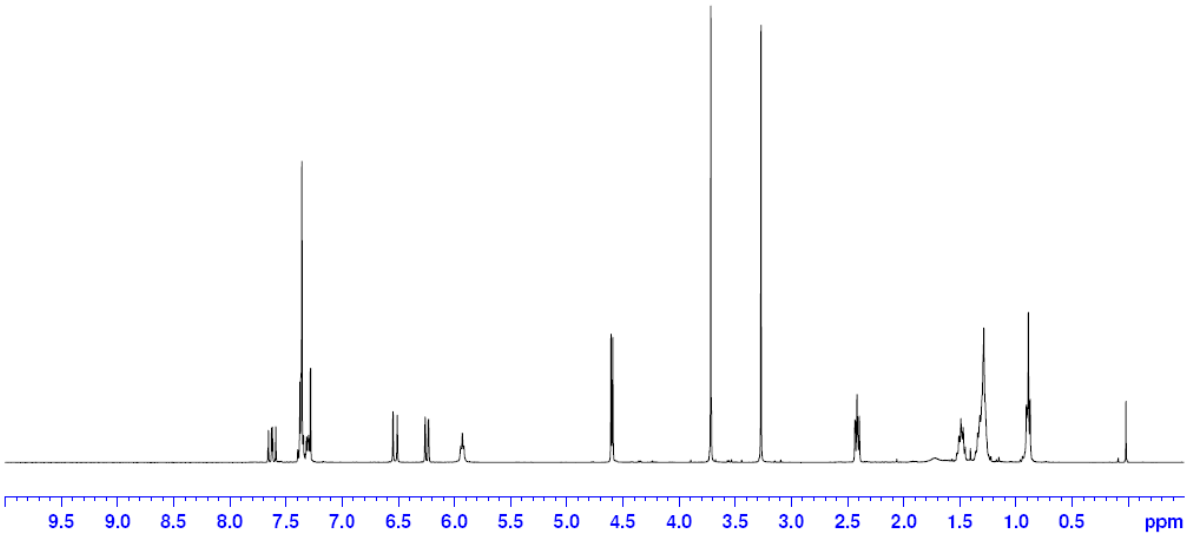

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

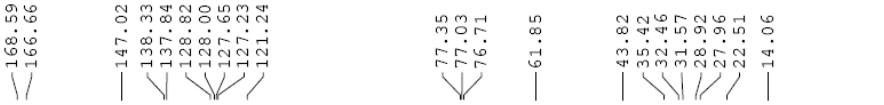

168.67
166.68
141.32
138.32
137.74
129.08
128.86
127.99
127.68
121.37
77.37
76.73
61.87
43.83
32.48
21.52
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

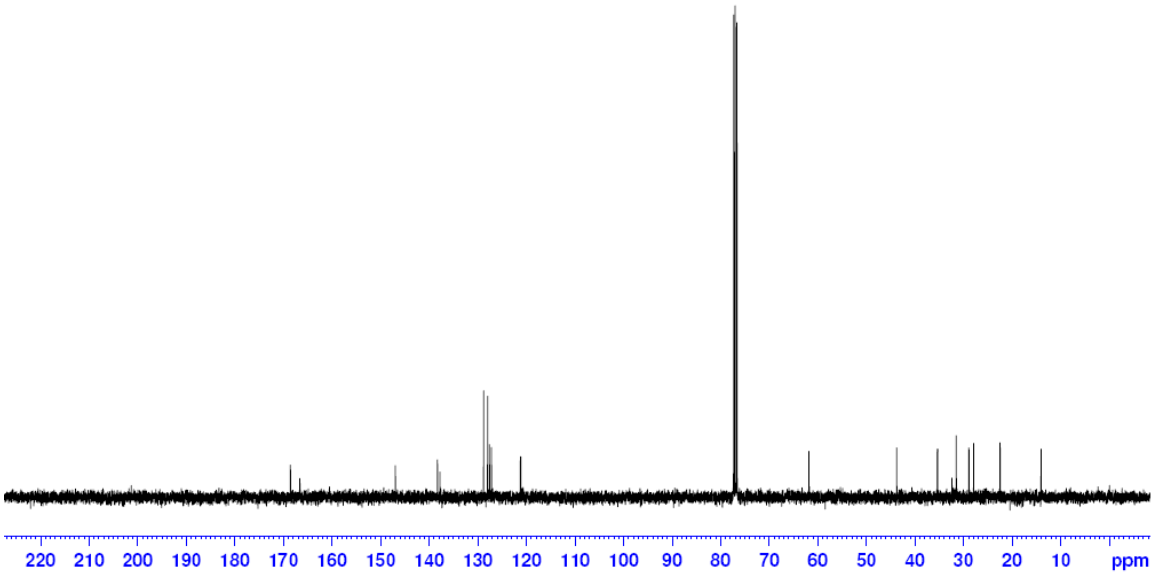

O
NHBn
4
N
O
O

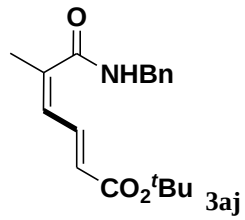
(3ki) (*Z*/*E* > 99/1)


7.660
7.630
7.622
7.593
7.397
7.377
7.362
7.347
7.323
7.317
7.308
7.301
7.293
7.284
6.549
6.511
6.263
6.234
5.946
5.932
5.918
4.607
4.592
3.718
3.271
2.435
2.416
2.397
1.509
1.490
1.471
1.342
1.321
1.287
0.907
0.891
0.874

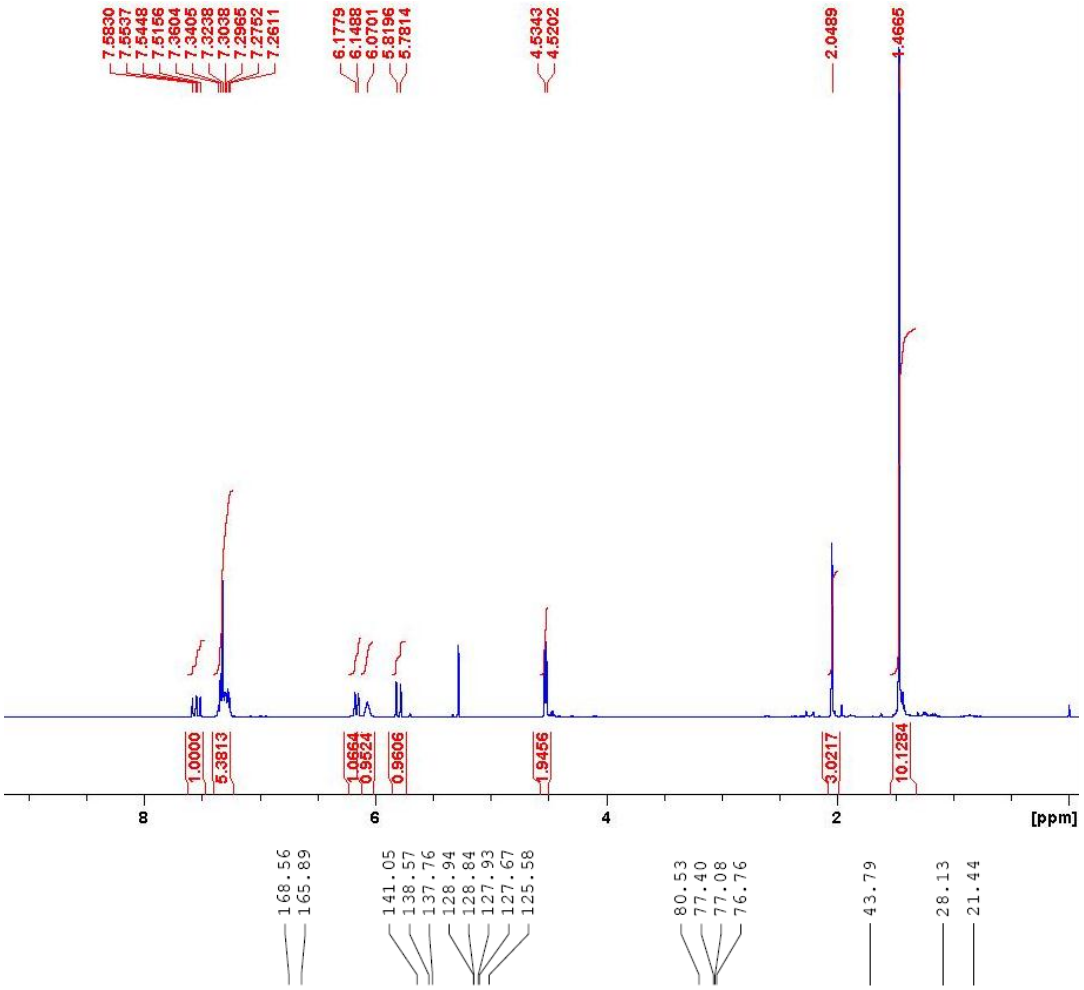

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

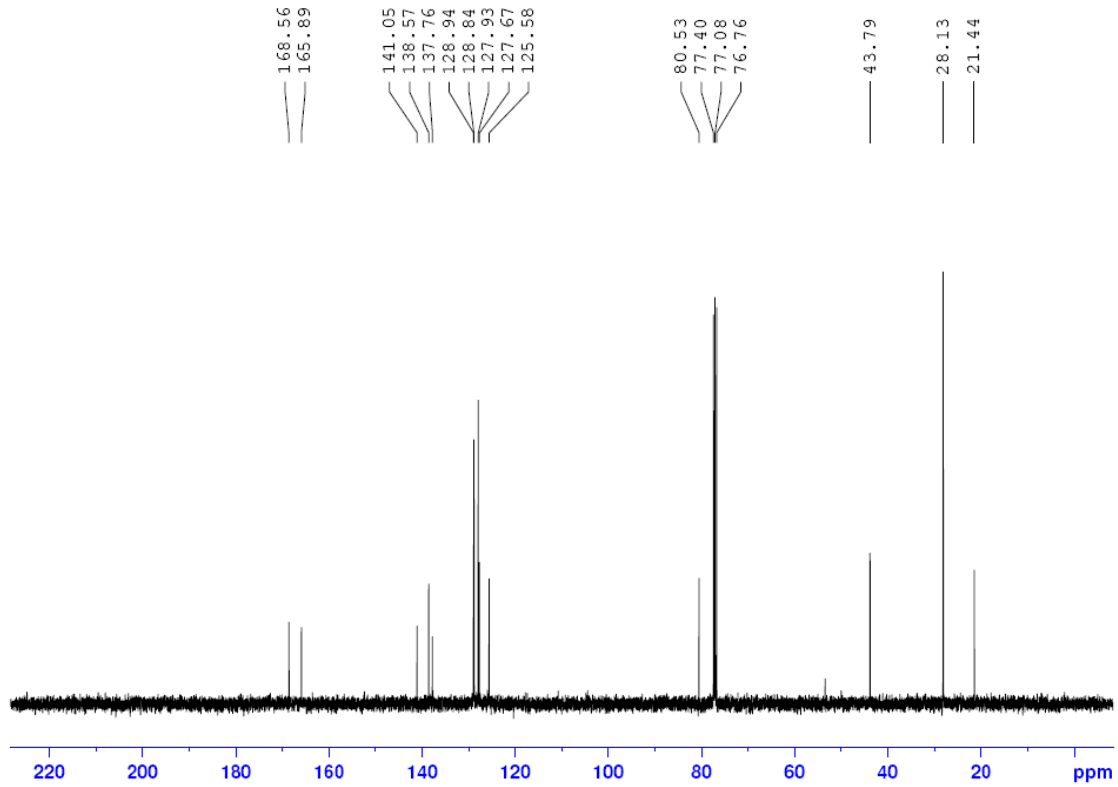

168.59
166.66
147.02
138.33
137.84
128.82
128.00
127.65
127.23
121.24
77.35
77.03
76.71
61.85
43.82
35.42
32.46
31.57
28.92
27.96
22.51
14.06

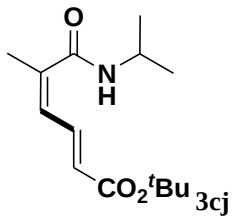

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


O
NHBn
CO2tBu

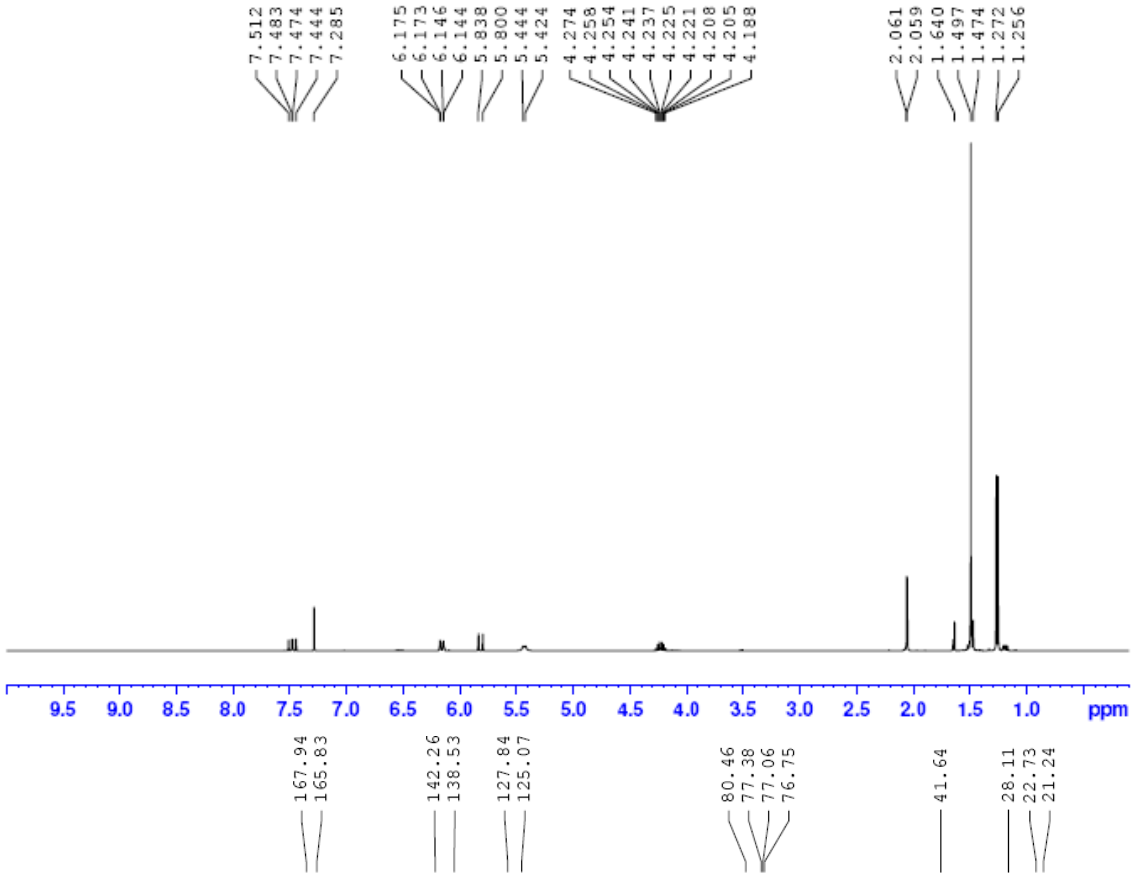
3aj

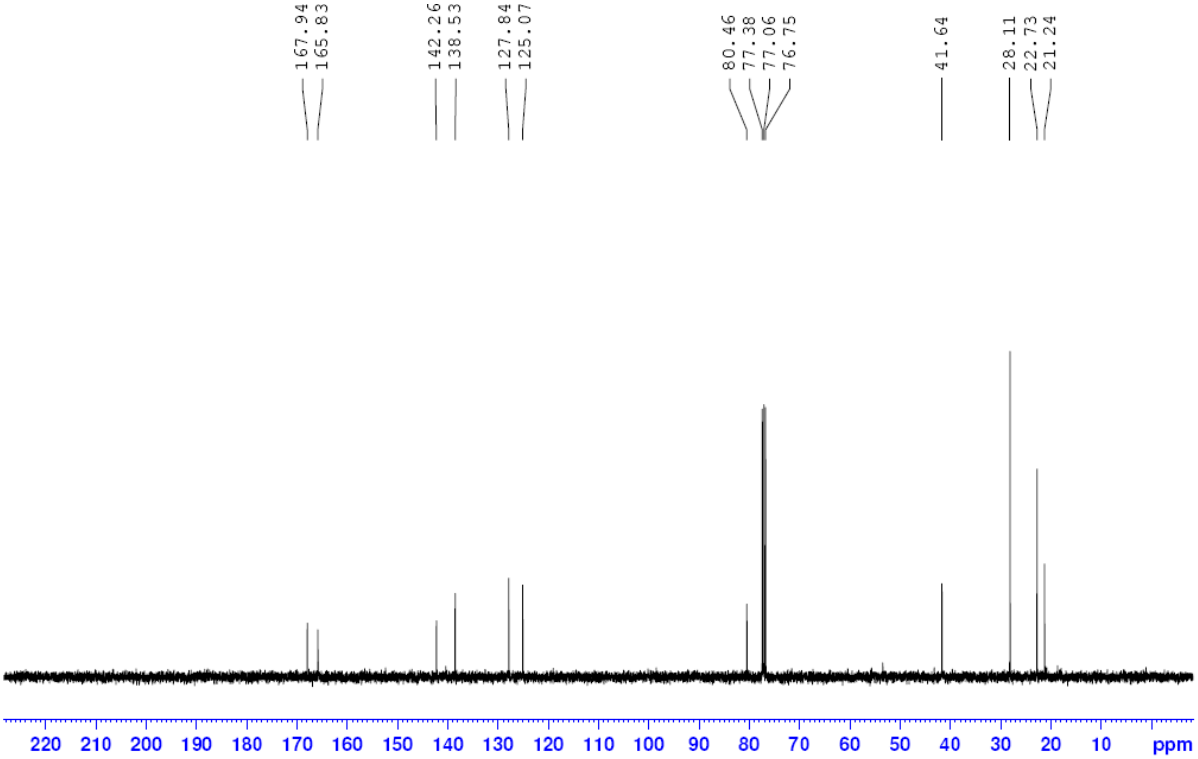

7.5830
7.5537
7.5448
7.5156
7.3604
7.3405
7.3238
7.3038
7.2965
7.2752
7.2611
6.1779
6.1488
6.0701
5.8196
5.7814
4.5343
4.5202
2.0489
1.4665
1.0000
5.3813
1.0664
0.9524
0.9606
1.9456
3.0217
10.1284
8
6
4
2
[ppm]

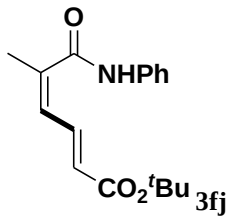

168.56
165.89
141.05
138.57
137.76
128.94
128.84
127.93
127.67
125.58
80.53
77.40
77.08
76.76
43.79
28.13
21.44
220
200
180
160
140
120
100
80
60
40
20
ppm


O
N
H
CO2tBu

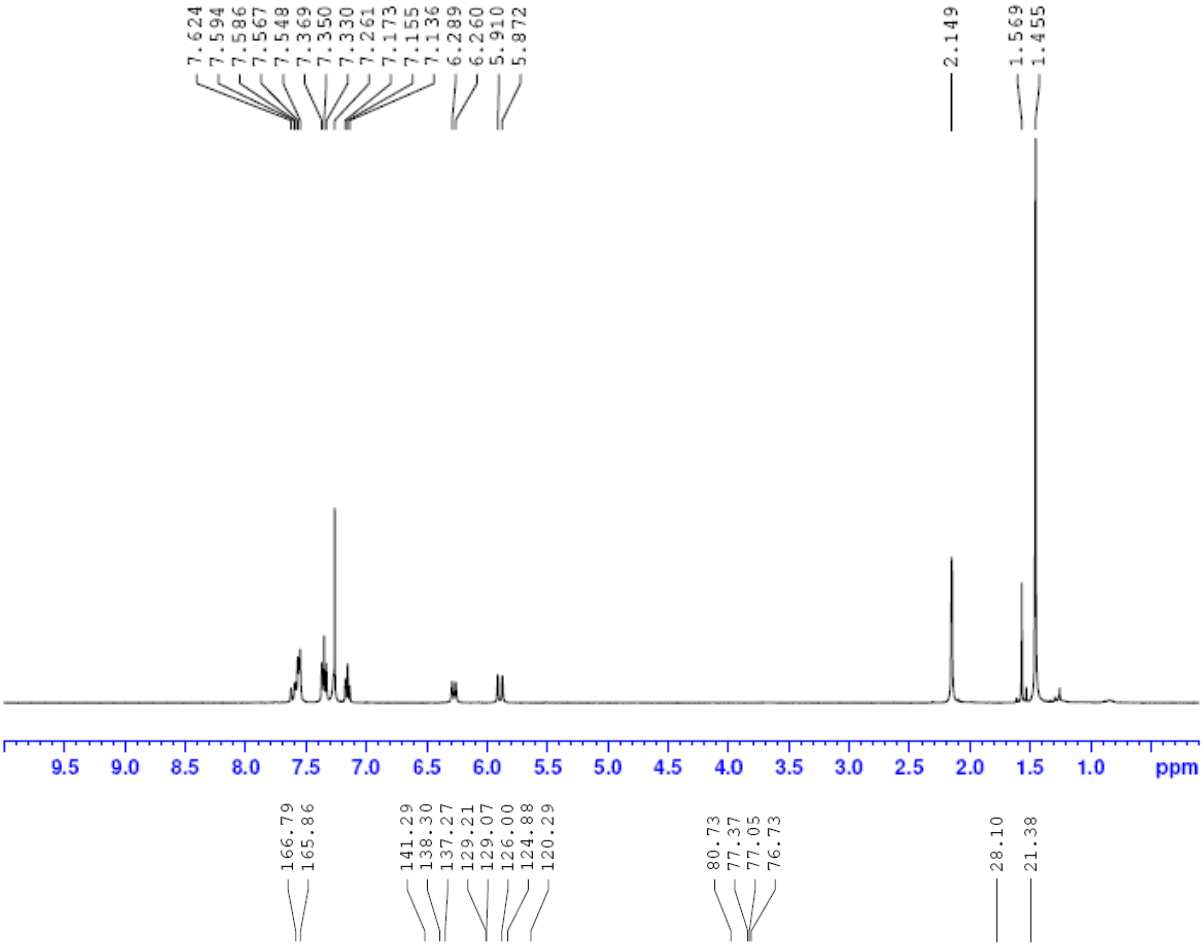
3cj

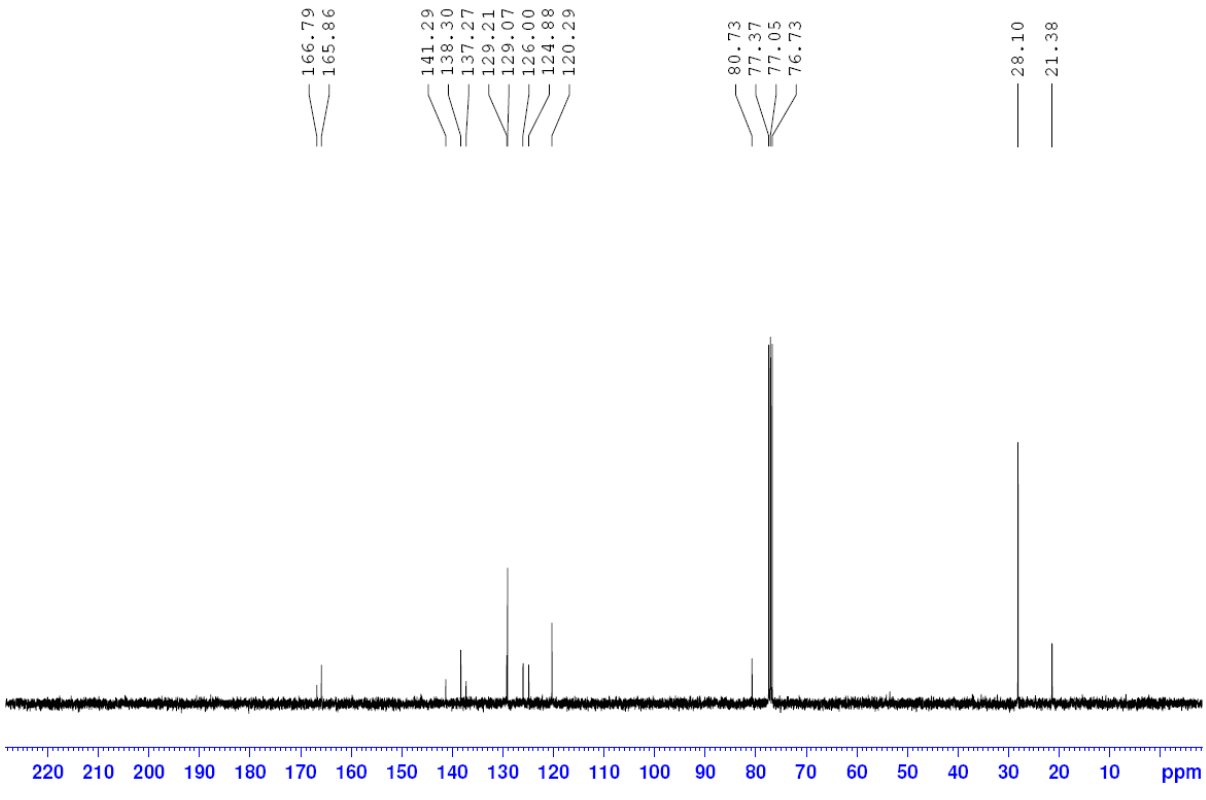

7.512
7.483
7.474
7.444
7.285
6.175
6.173
6.146
6.144
5.838
5.800
5.444
5.424
4.274
4.258
4.254
4.241
4.237
4.225
4.221
4.208
4.205
4.188
2.061
2.059
1.640
1.497
1.474
1.272
1.256
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

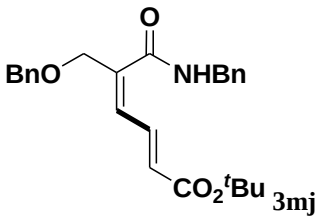

167.94
165.83
142.26
138.53
127.84
125.07
80.46
77.38
77.06
76.75
41.64
28.11
22.73
21.24
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
NHPh
CO2tBu

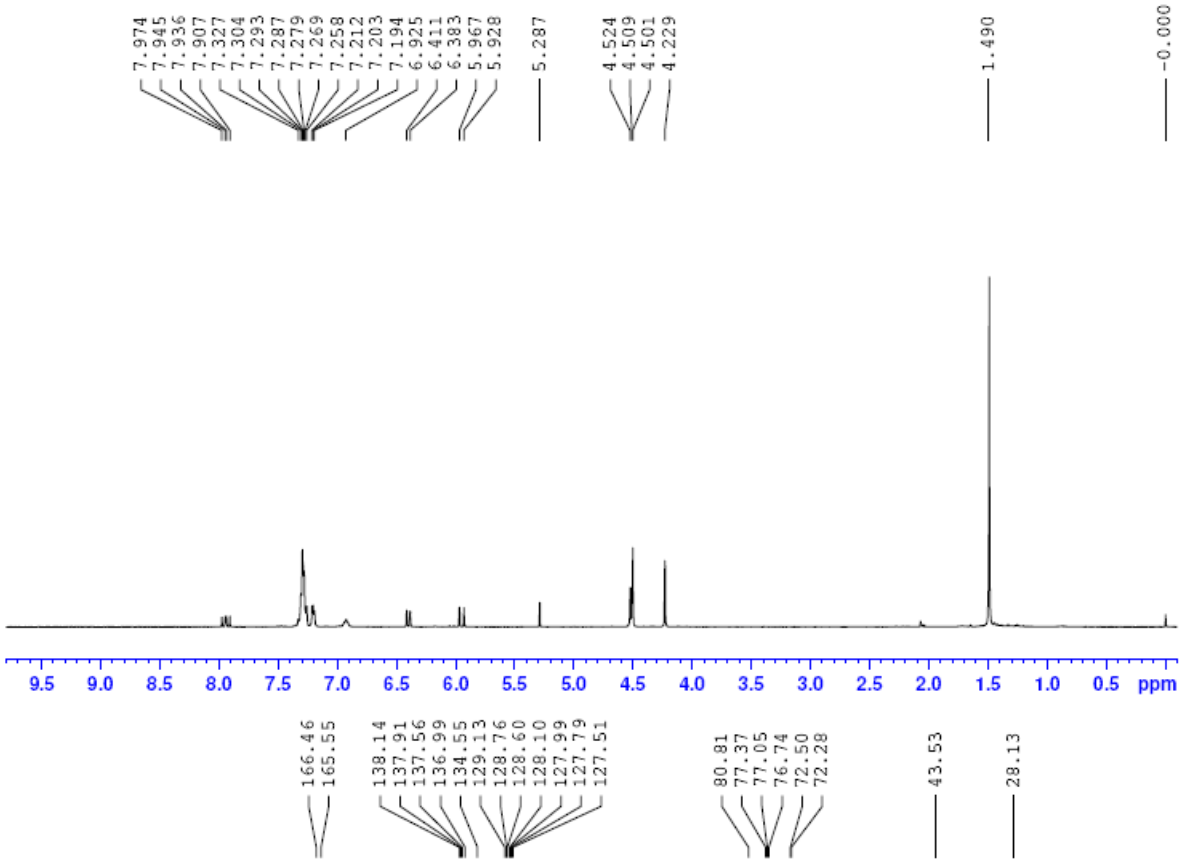
3fj

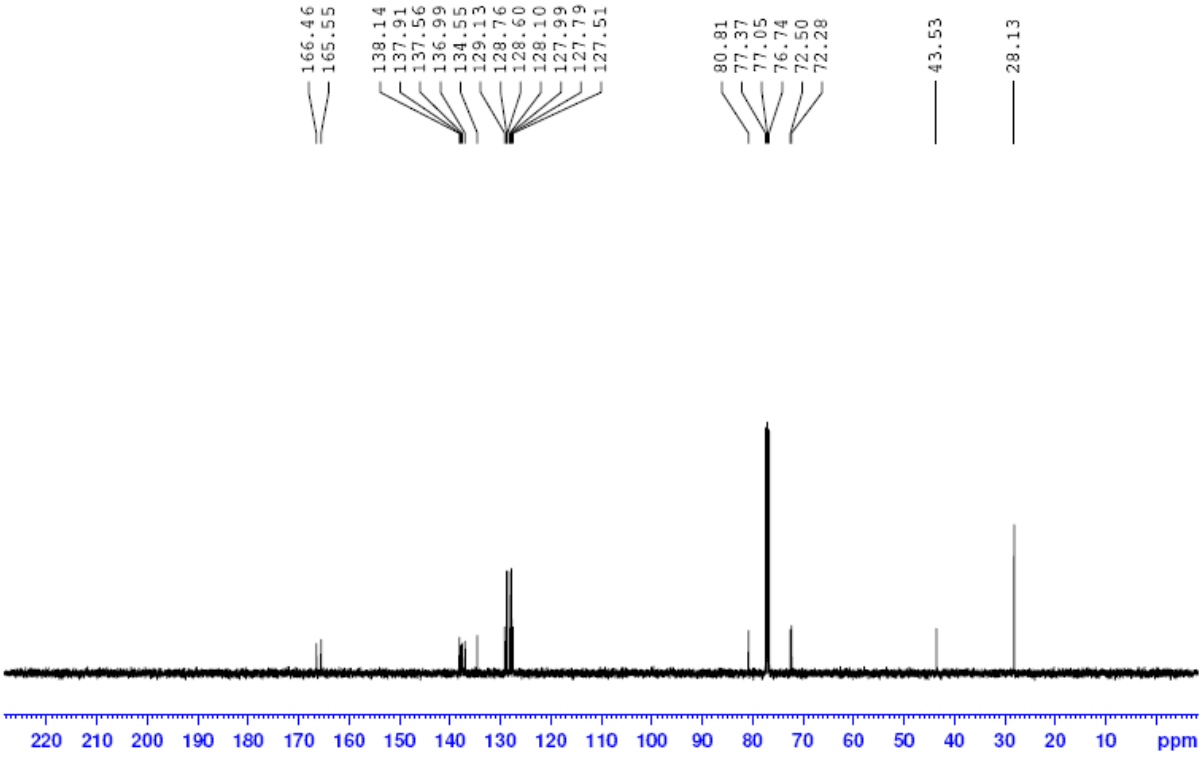

7.624
7.594
7.586
7.567
7.548
7.369
7.350
7.330
7.261
7.173
7.155
7.136
6.289
6.260
5.910
5.872
2.149
1.569
1.455
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

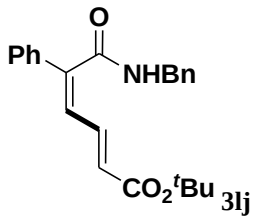

166.79
165.86
141.29
138.30
137.27
129.21
129.07
126.00
124.88
120.29
80.73
77.37
77.05
76.73
28.10
21.38
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
BnO
NHBn
CO2tBu

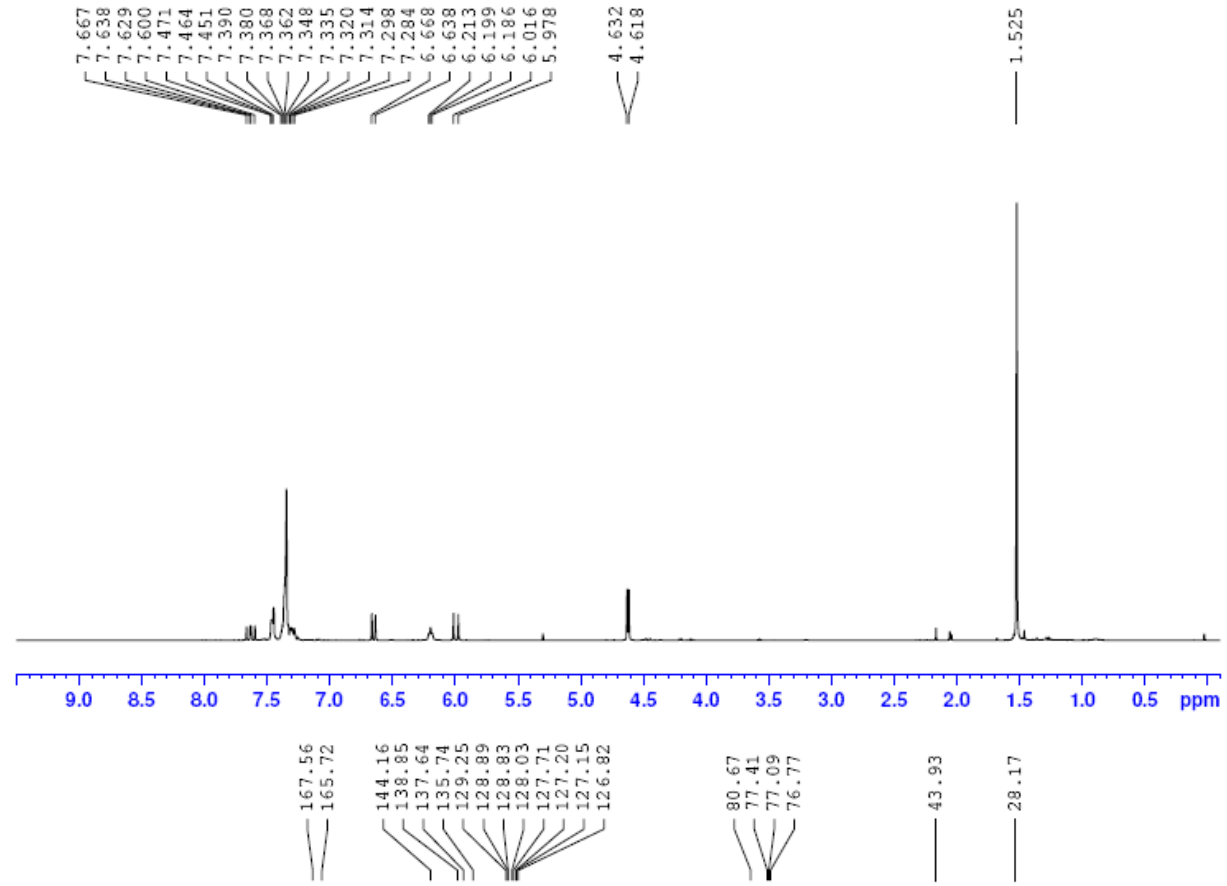
3mj

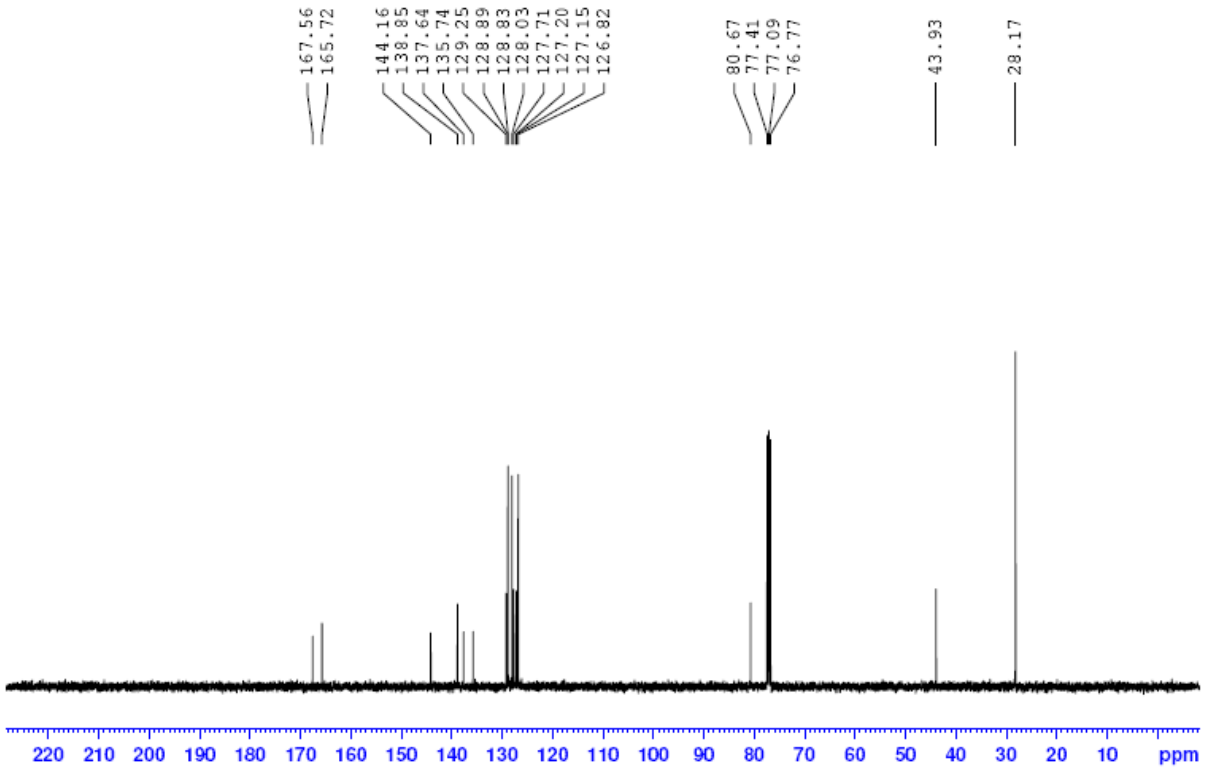

7.974
7.945
7.936
7.907
7.327
7.304
7.293
7.287
7.279
7.269
7.258
7.212
7.203
7.194
6.925
6.411
6.383
5.967
5.928
5.287
4.524
4.509
4.501
4.229
1.490
-0.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

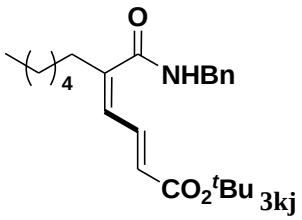

166.46
165.55
138.14
137.91
137.56
136.99
134.55
129.13
128.76
128.60
128.10
127.99
127.79
127.51
80.81
77.37
77.05
76.74
72.50
72.28
43.53
28.13
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
Ph
NHBn
CO2tBu

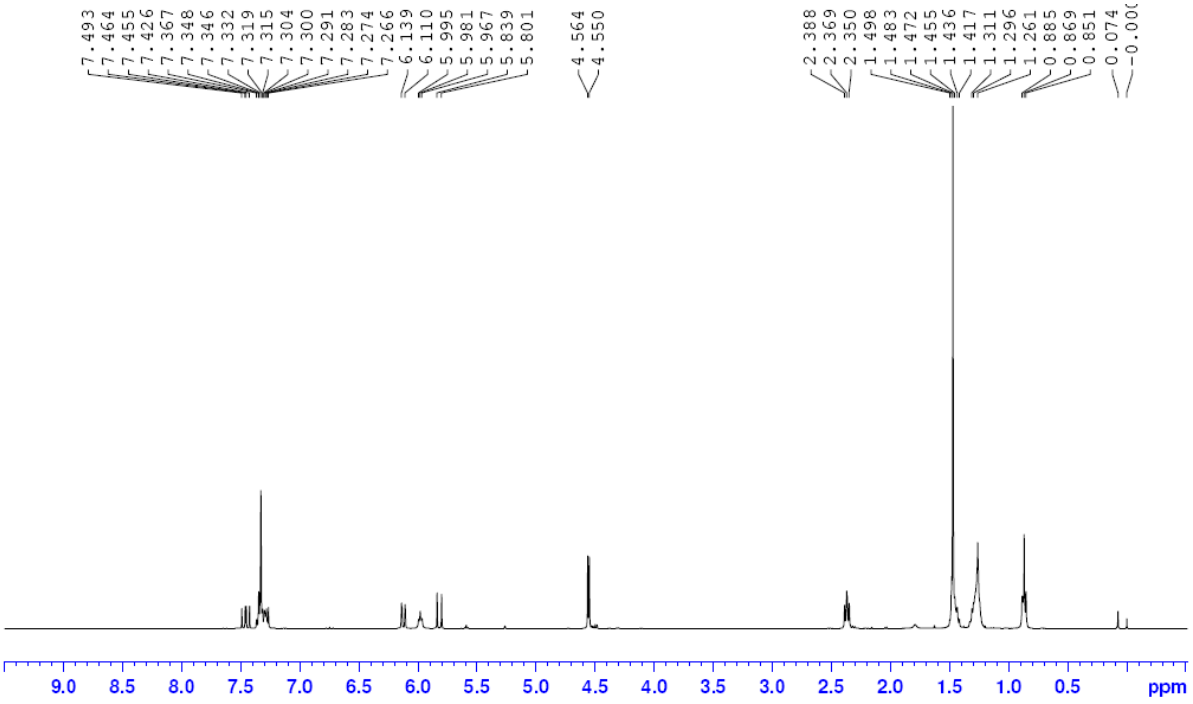
3lj

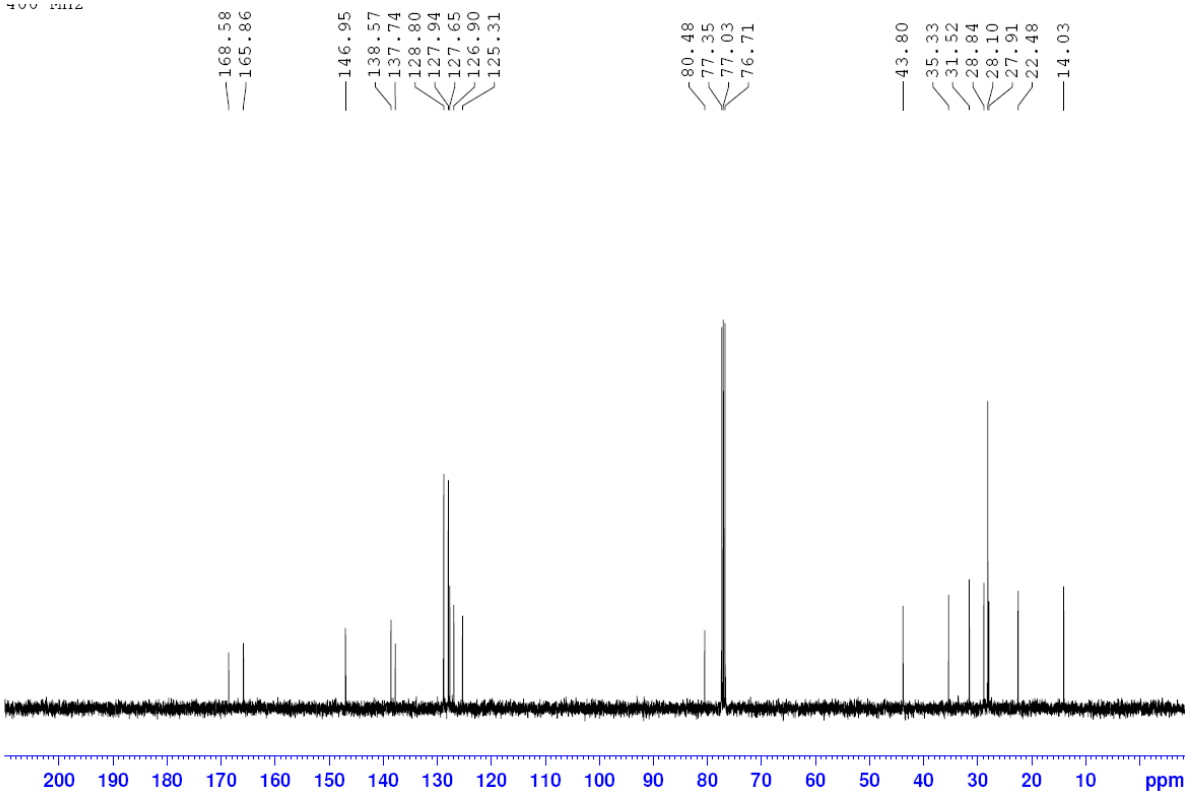

7.667
7.638
7.629
7.600
7.471
7.464
7.451
7.390
7.380
7.368
7.362
7.348
7.335
7.320
7.314
7.298
7.284
6.668
6.638
6.213
6.199
6.186
6.016
5.978
4.632
4.618
1.525
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

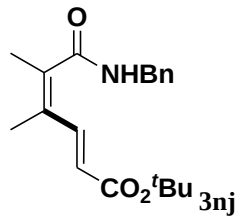

167.56
165.72
144.16
138.85
137.64
135.74
129.25
128.89
128.83
128.03
127.71
127.20
127.15
126.82
80.67
77.41
77.09
76.77
43.93
28.17
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


O
NHBn
4
CO2tBu

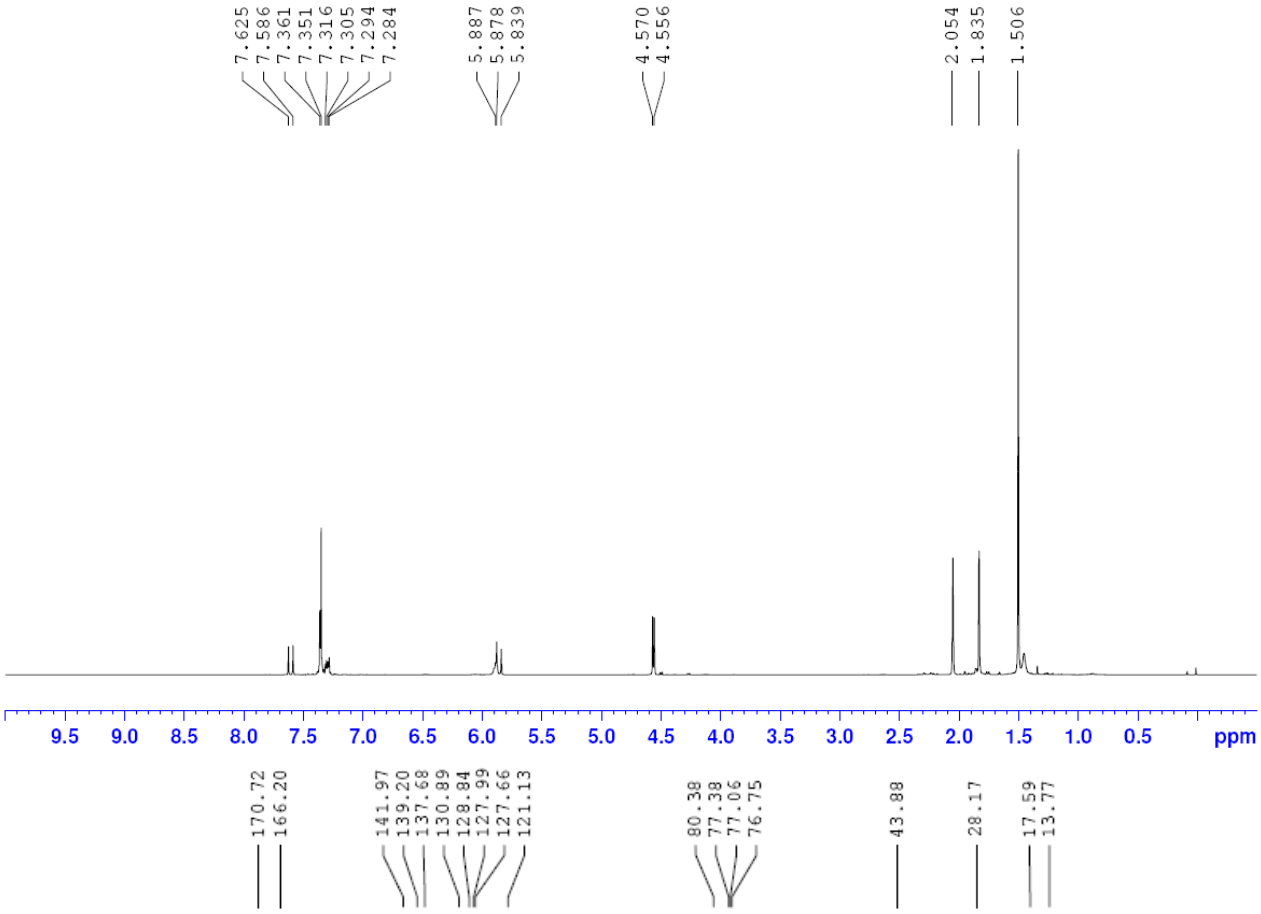
3kj

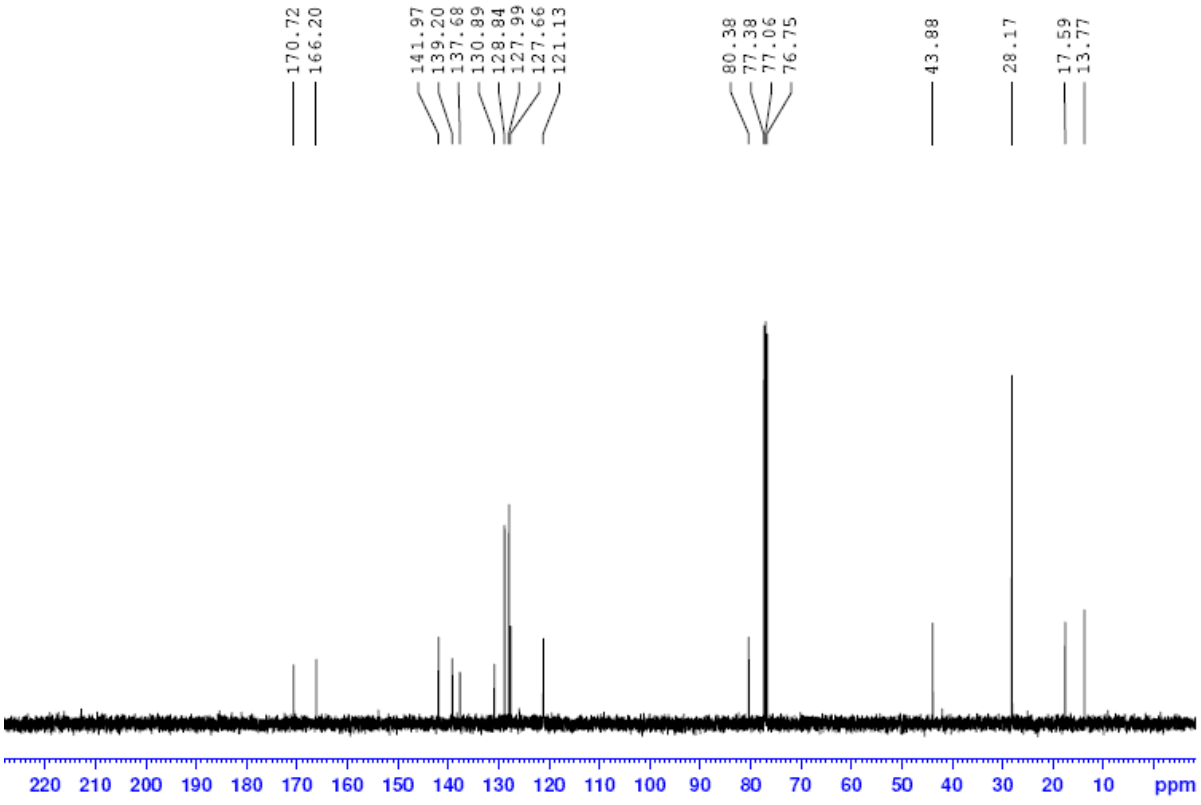

7.493
7.464
7.455
7.426
7.367
7.348
7.346
7.332
7.319
7.315
7.304
7.300
7.291
7.283
7.274
7.266
6.139
6.110
5.995
5.981
5.967
5.839
5.801
4.564
4.550
2.388
2.369
2.350
1.498
1.483
1.472
1.455
1.436
1.417
1.311
1.296
1.261
0.885
0.869
0.851
0.074
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

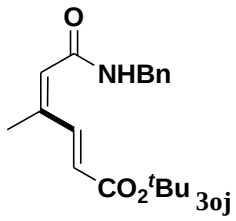

168.58
165.86
146.95
138.57
137.74
128.80
127.94
127.65
126.90
125.31
80.48
77.35
77.03
76.71
43.80
35.33
31.52
28.84
28.10
27.91
22.48
14.03
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
NHBn
CO2tBu

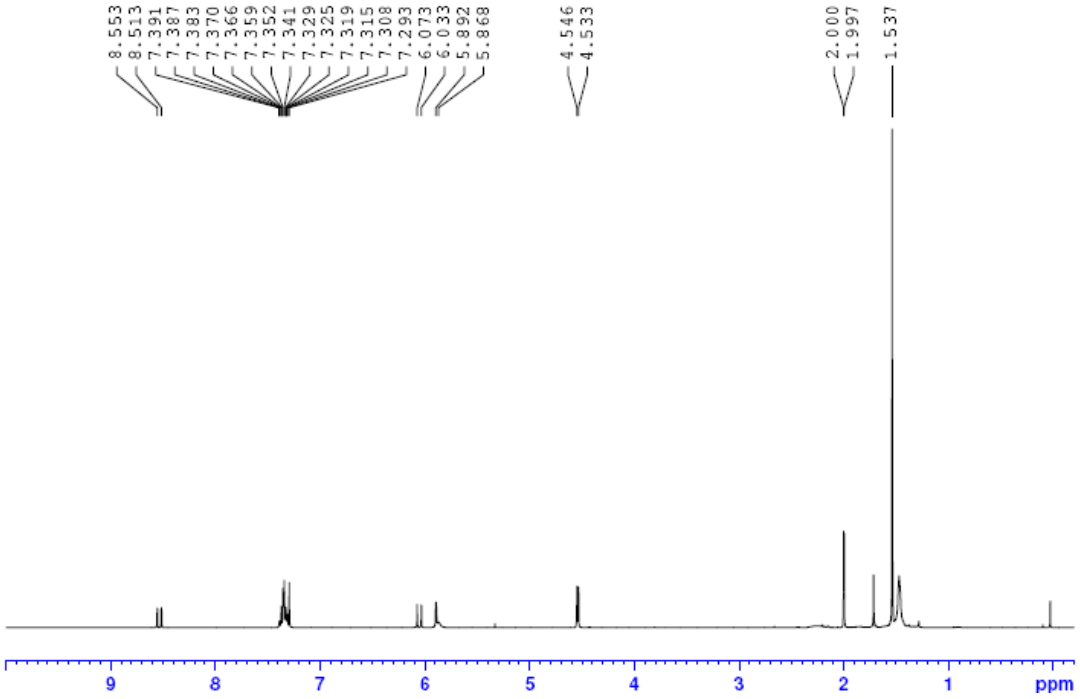
3nj

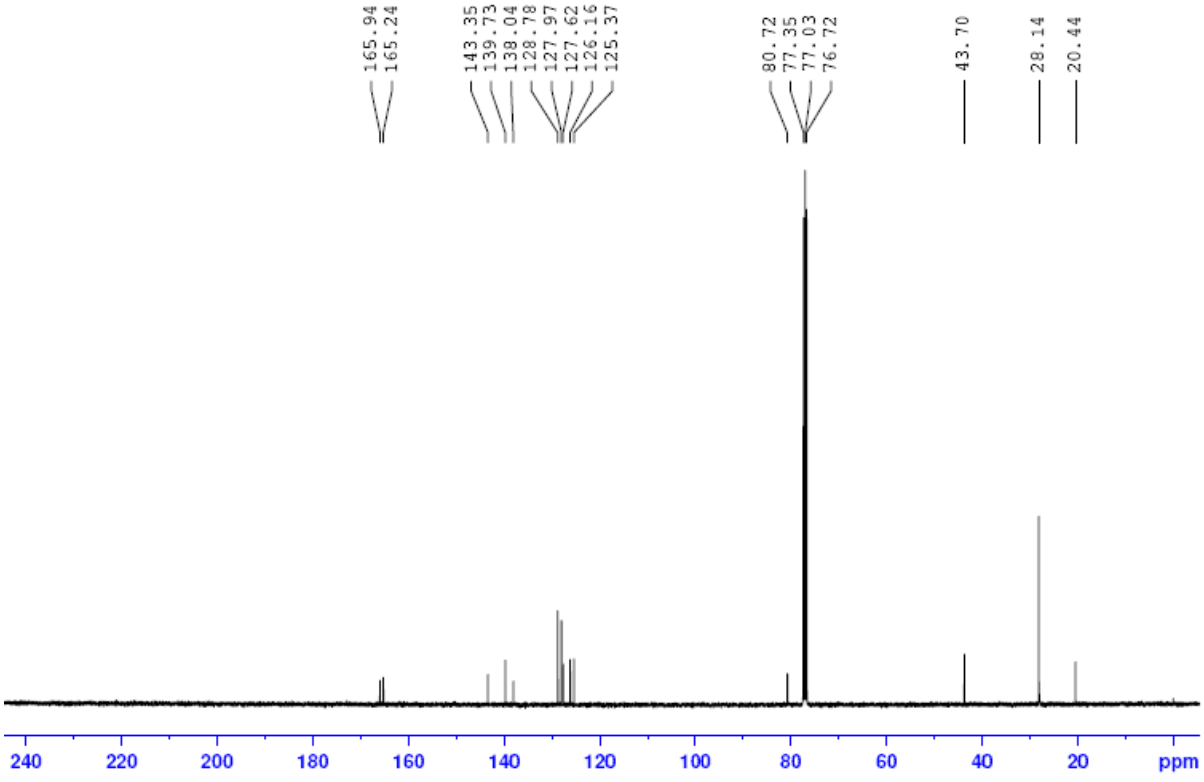

7.625
7.586
7.361
7.351
7.316
7.305
7.294
7.284
5.887
5.878
5.839
4.570
4.556
2.054
1.835
1.506
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

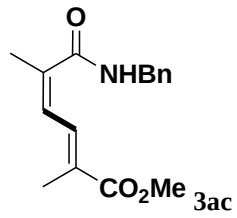

170.72
166.20
141.97
139.20
137.68
130.89
128.84
127.99
127.66
121.13
80.38
77.38
77.06
76.75
43.88
28.17
17.59
13.77
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
NHBn
CO2tBu

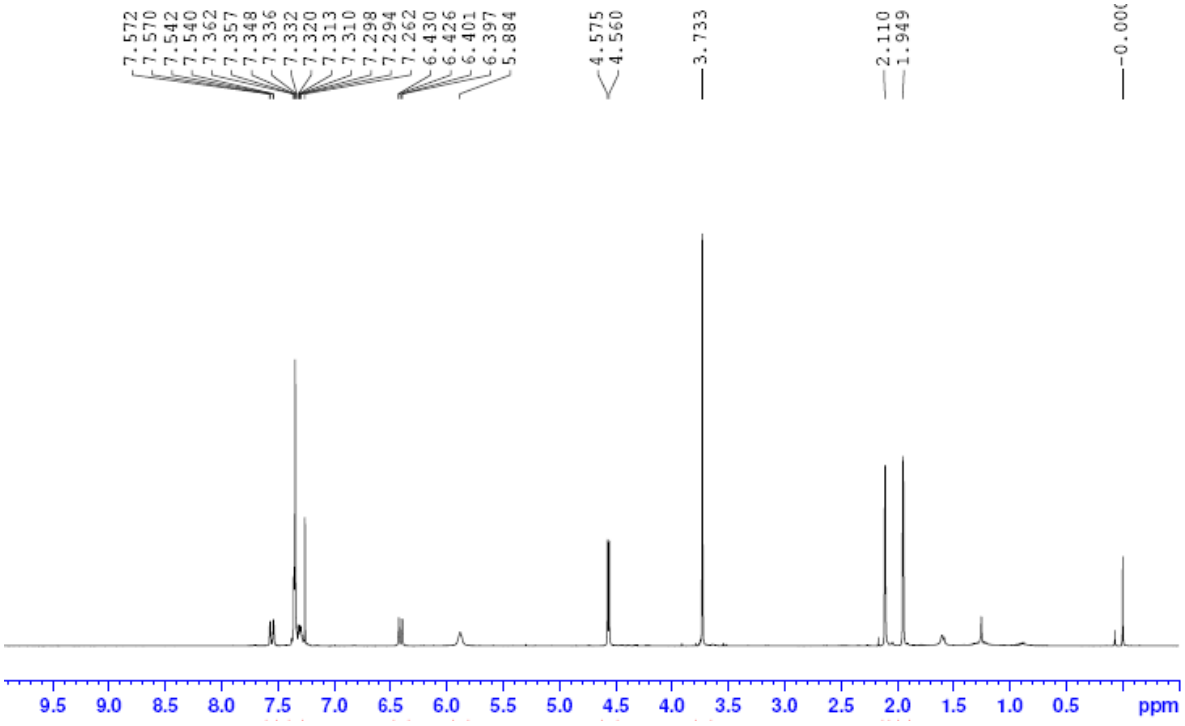
3oj

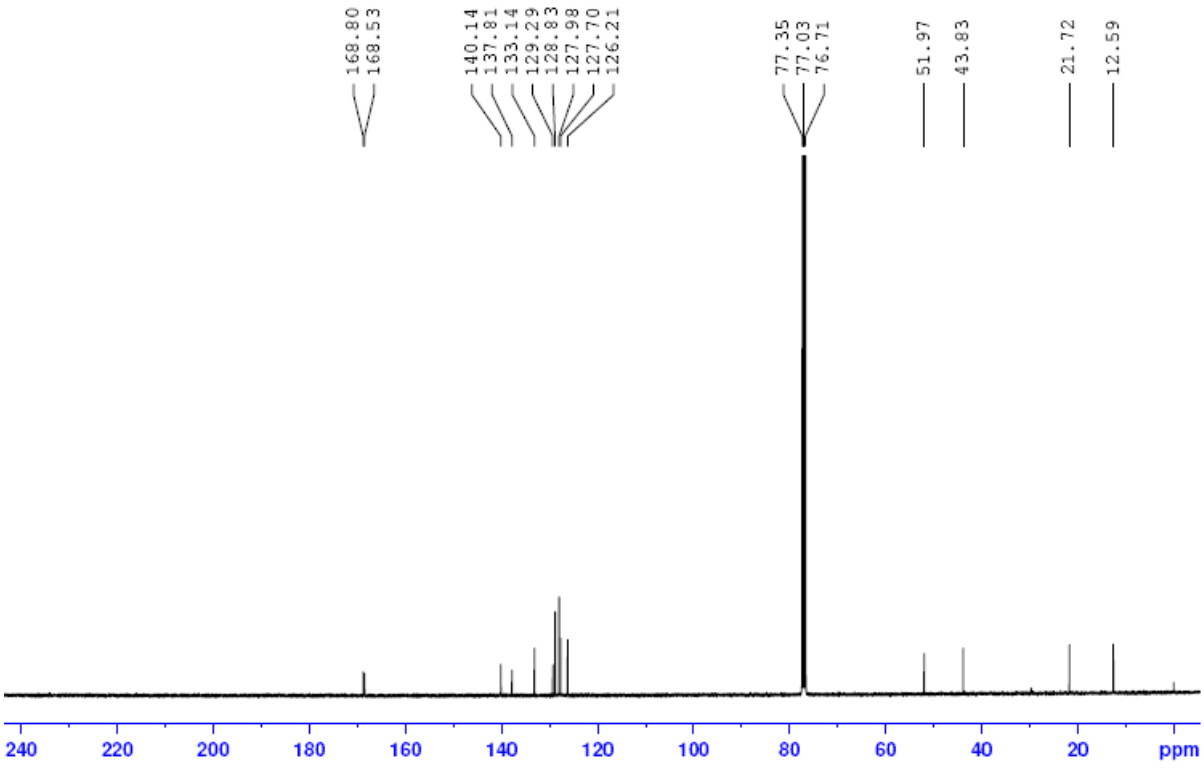

8.553
8.513
7.391
7.387
7.383
7.370
7.366
7.359
7.352
7.341
7.329
7.325
7.319
7.315
7.308
7.293
6.073
6.033
5.892
5.868
4.546
4.533
2.000
1.997
1.537
9
8
7
6
5
4
3
2
1
ppm

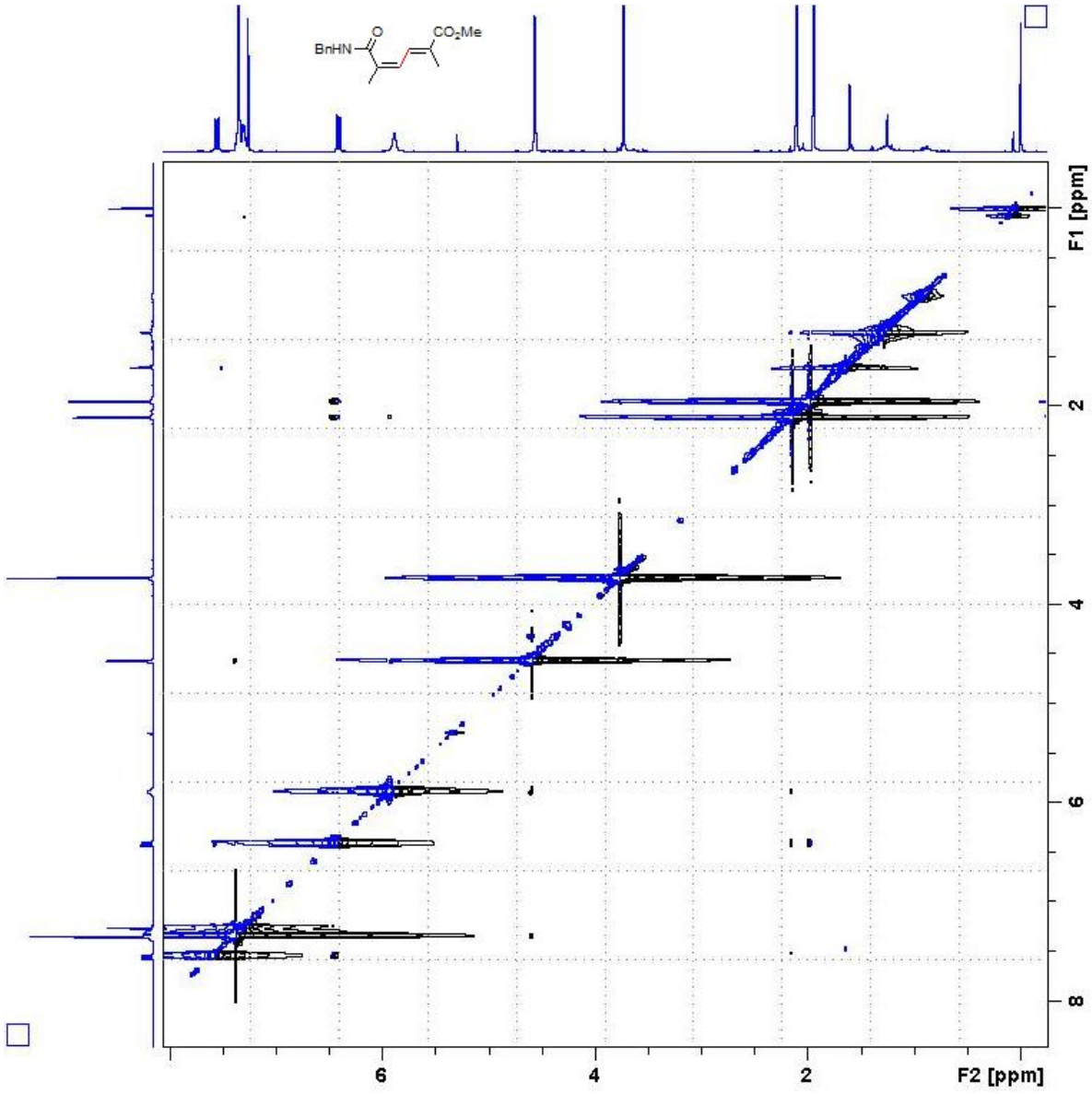

165.94
165.24
143.35
139.73
138.04
128.78
127.97
127.62
126.16
125.37
80.72
77.35
77.03
76.72
43.70
28.14
20.44
240
220
200
180
160
140
120
100
80
60
40
20
ppm

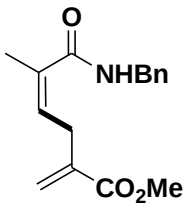

O
NHBn
CO2Me

3ac

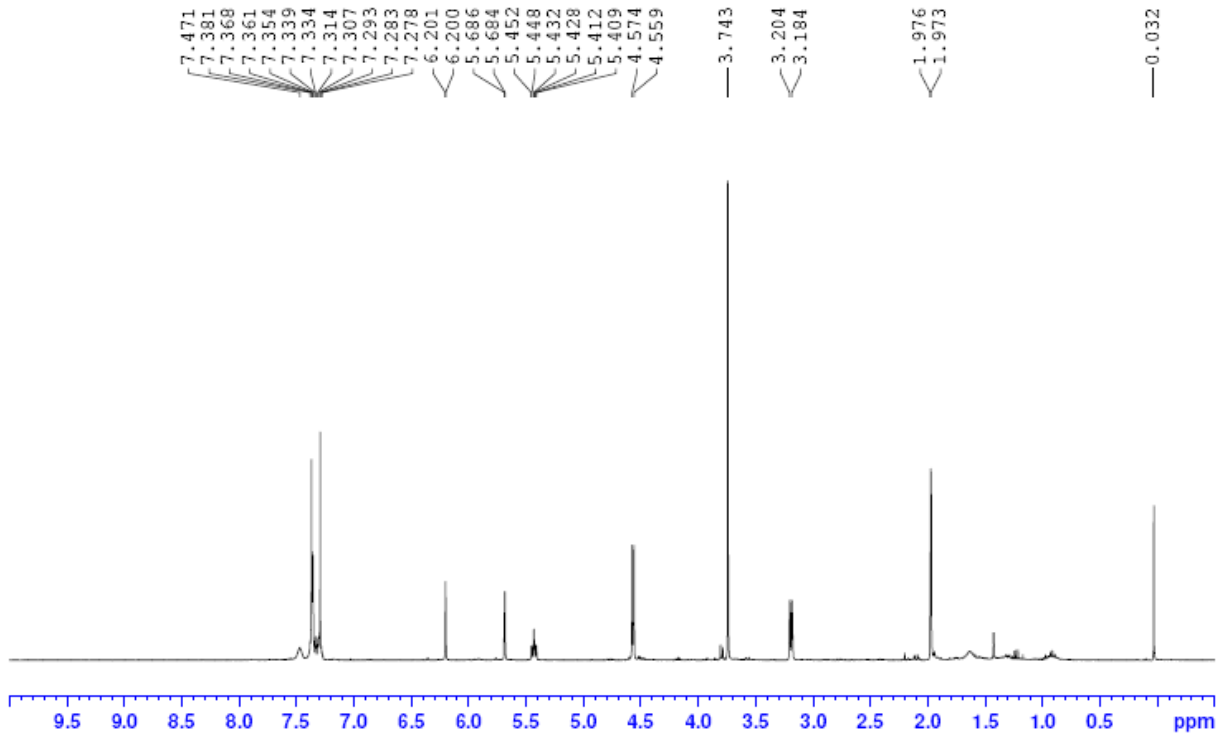

7.572
7.570
7.542
7.540
7.362
7.357
7.348
7.336
7.332
7.320
7.313
7.310
7.298
7.294
7.262
6.430
6.426
6.401
6.397
5.884
4.575
4.560
3.733
2.110
1.949
0.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

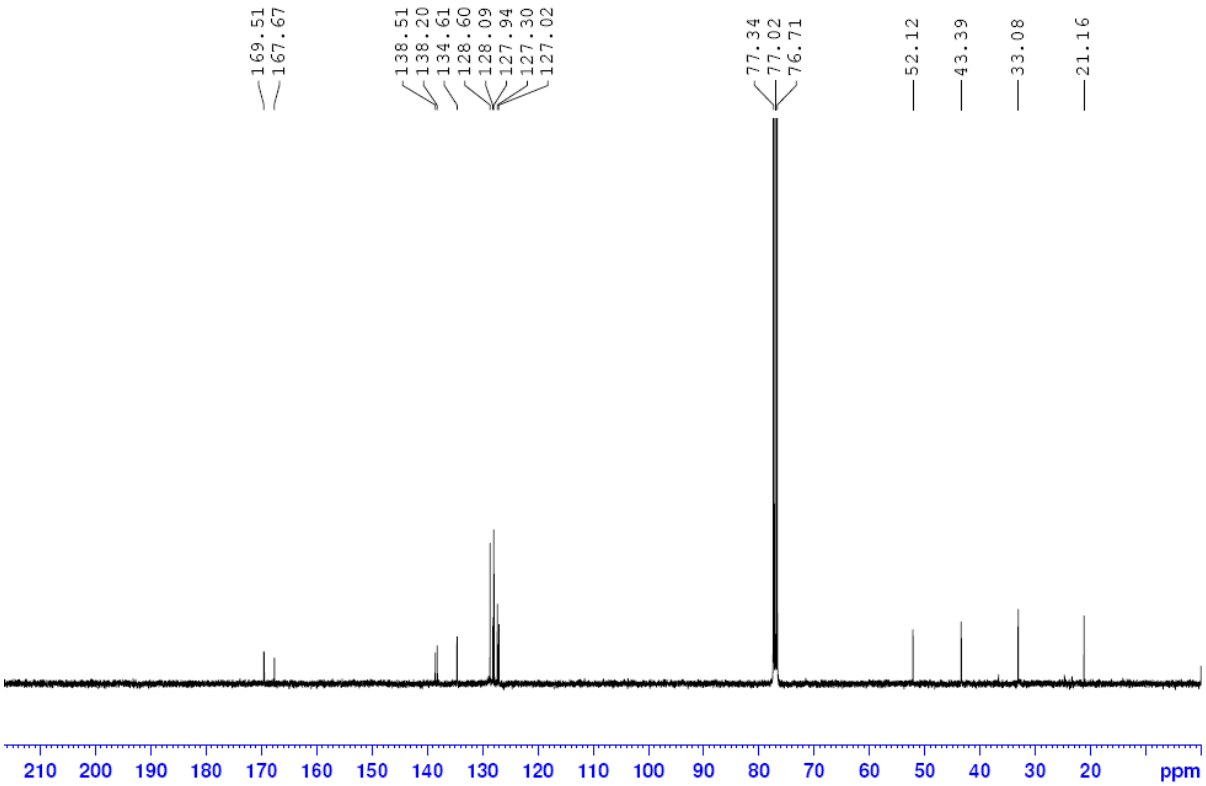

168.80
168.53
140.14
137.81
133.14
129.29
128.83
127.98
127.70
126.21
77.35
77.03
76.71
51.97
43.83
21.72
12.59
240 220 200 180 160 140 120 100 80 60 40 20 ppm

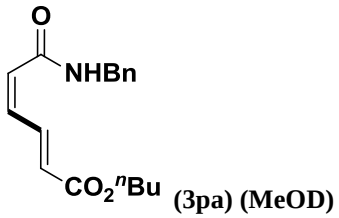

BnHN
O
CO2Me
F1 [ppm]
2
4
6
8
6
4
2
F2 [ppm]


O
NHBn
CO2Me

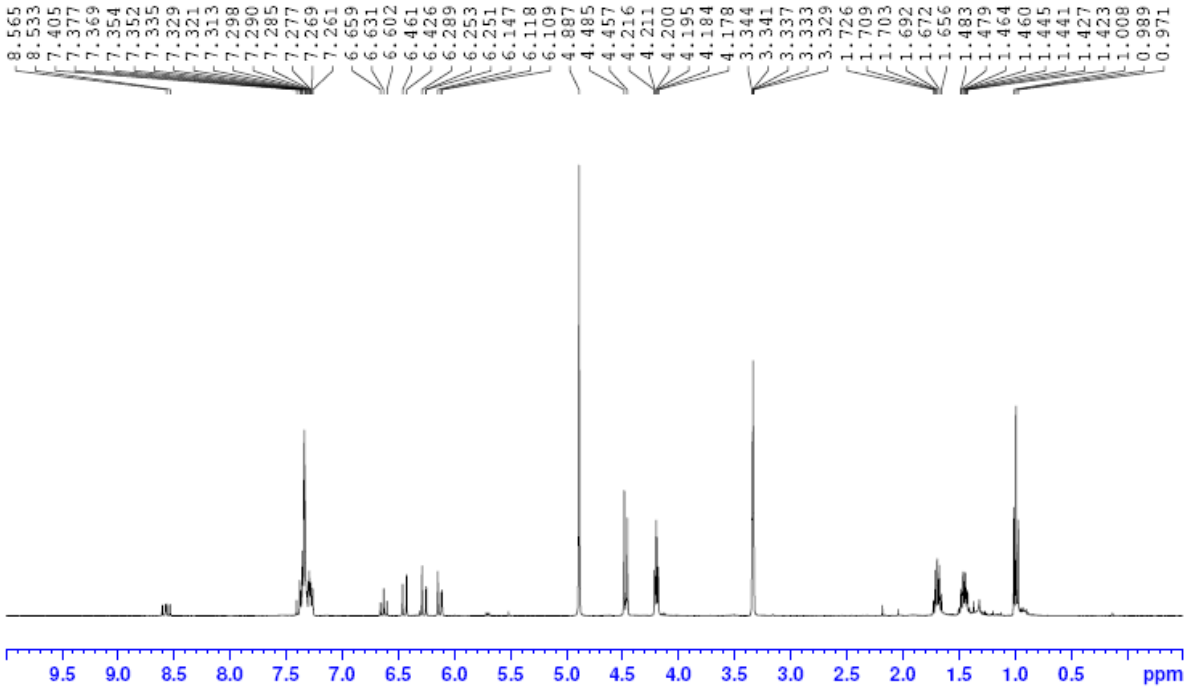
(3ac′)

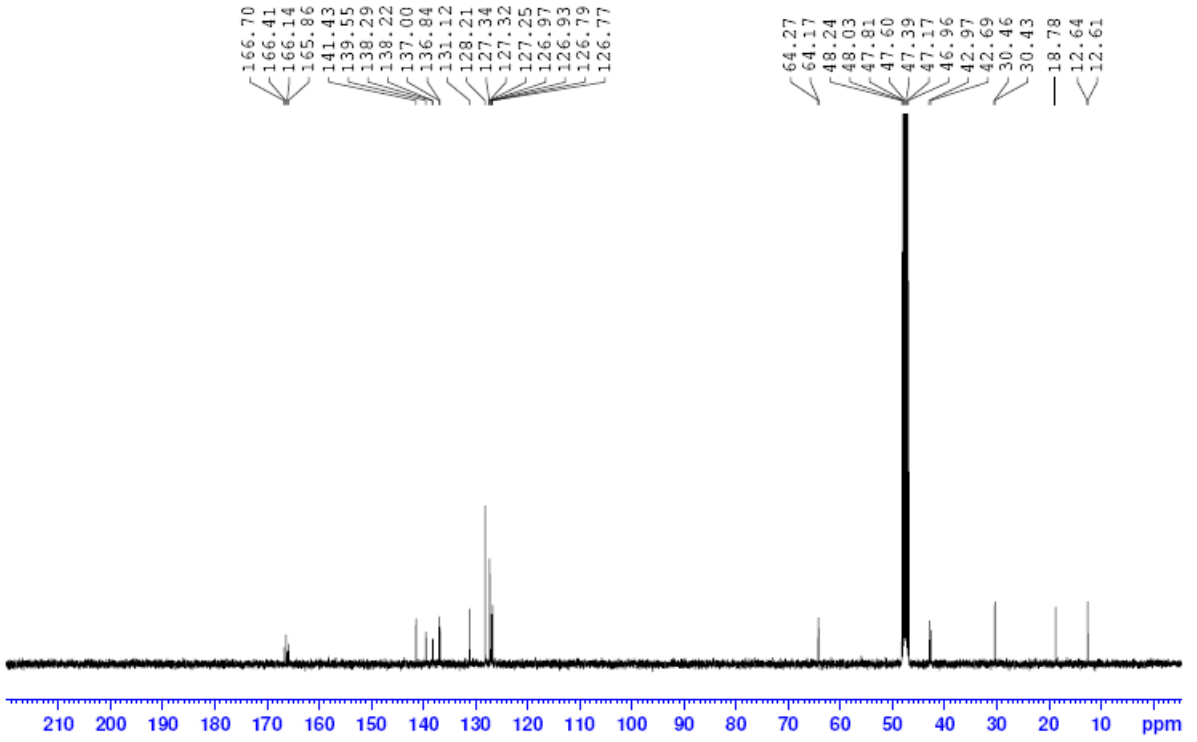

7.471
7.381
7.368
7.361
7.354
7.339
7.334
7.314
7.307
7.293
7.283
7.278
6.201
6.200
5.686
5.684
5.452
5.448
5.432
5.428
5.412
5.409
4.574
4.559
3.743
3.204
3.184
1.976
1.973
0.032
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

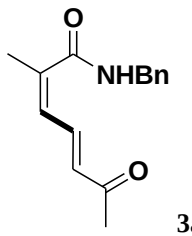

169.51
167.67
138.51
138.20
134.61
128.60
128.09
127.94
127.30
127.02
77.34
77.02
76.71
52.12
43.39
33.08
21.16
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


O
NHBn
CO2nBu

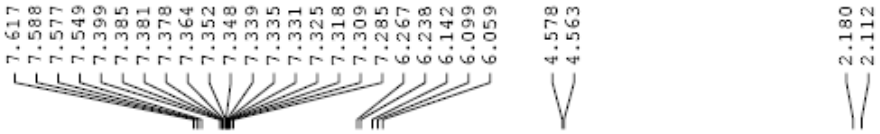
(3pa) (MeOD)


8.565
8.533
7.405
7.377
7.369
7.354
7.352
7.335
7.329
7.321
7.313
7.298
7.290
7.285
7.277
7.269
7.261
6.659
6.631
6.602
6.461
6.426
6.289
6.253
6.251
6.147
6.118
6.109
4.887
4.485
4.457
4.216
4.211
4.200
4.195
4.184
4.178
3.344
3.341
3.337
3.333
3.329
1.726
1.709
1.703
1.692
1.672
1.656
1.483
1.479
1.464
1.460
1.445
1.441
1.427
1.423
1.008
0.989
0.971
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


166.70
166.41
166.14
165.86
141.43
139.55
138.29
138.22
137.00
136.84
131.12
128.21
127.34
127.32
127.25
126.97
126.93
126.79
126.77
64.27
64.17
48.24
48.03
47.81
47.60
47.39
47.17
46.96
42.97
42.69
30.46
30.43
18.78
12.64
12.61
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
NHBn
O

3ak


7.617
7.588
7.577
7.549
7.399
7.385
7.381
7.378
7.364
7.352
7.348
7.339
7.335
7.331
7.325
7.318
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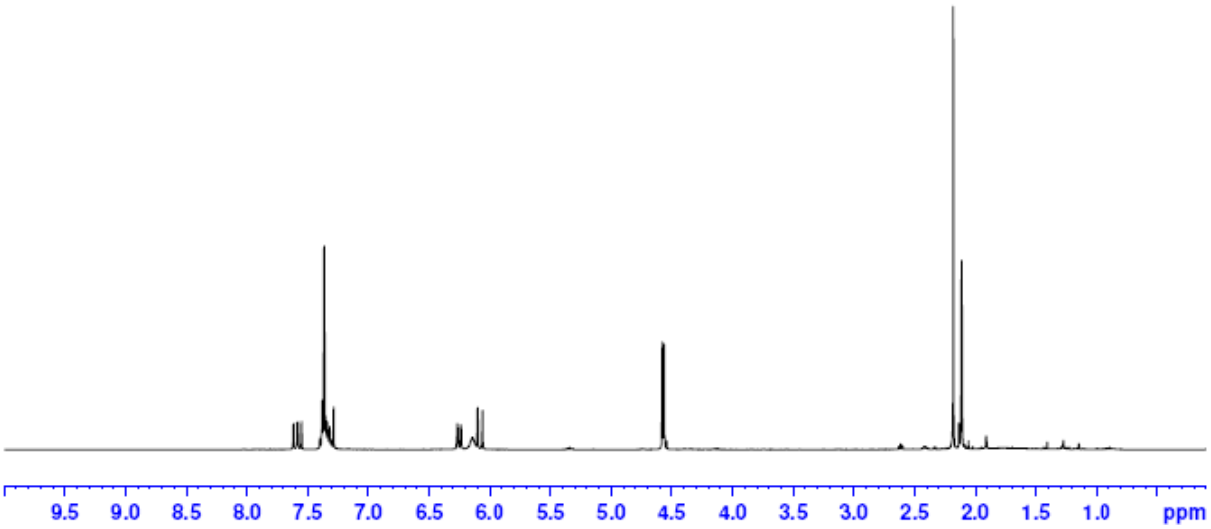
7.285
6.267
6.238
6.142
6.099
6.059
4.578
4.563
2.180
2.112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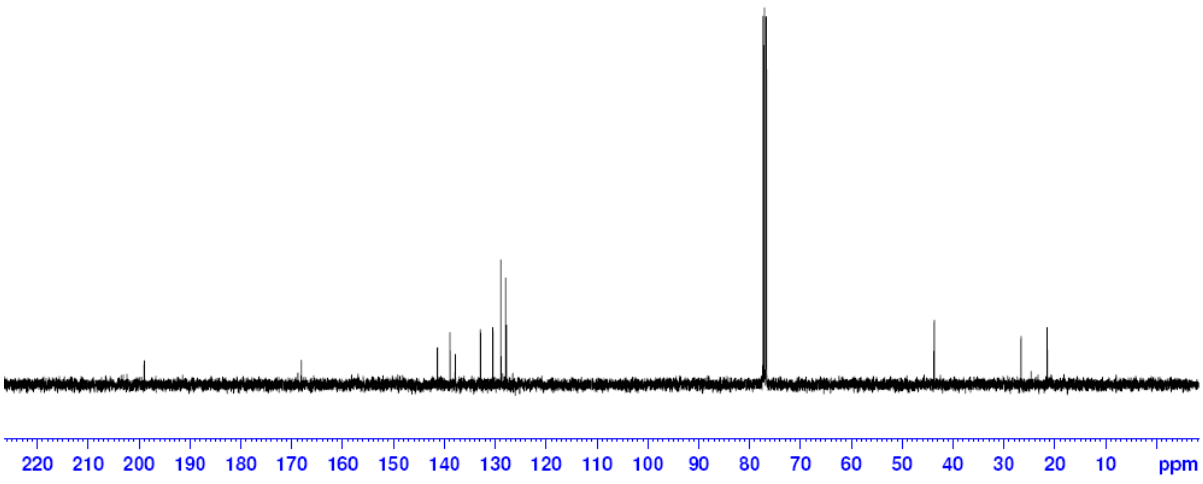
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


199.01
168.12
141.39
138.91
137.84
132.91
130.48
128.93
127.97
127.82
77.35
77.03
76.71
43.72
26.65
21.49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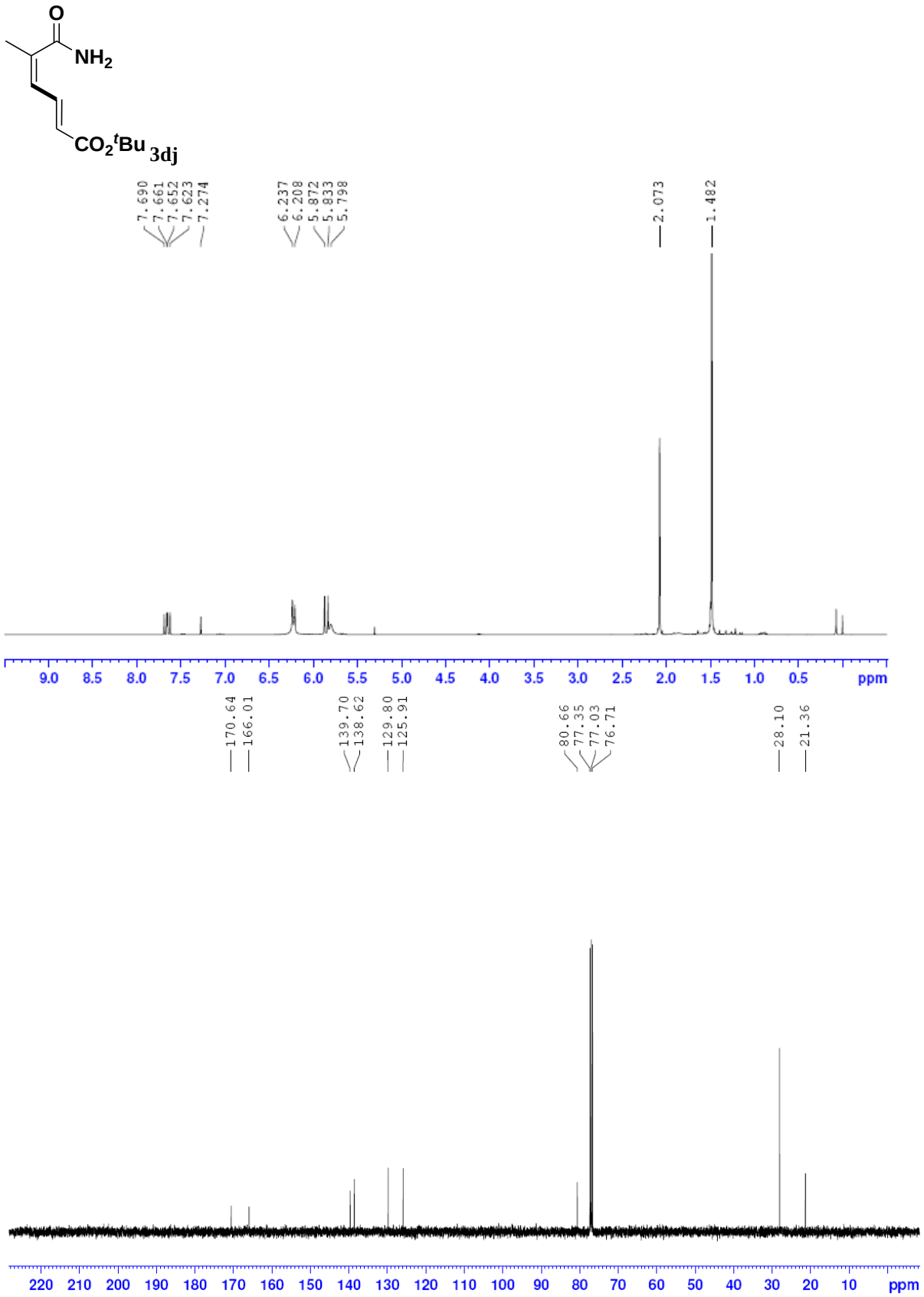
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


O
NH2
CO2tBu
3dj
7.690
7.661
7.652
7.623
7.274
6.237
6.208
5.872
5.833
5.798
2.073
1.482
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
170.64
166.01
139.70
138.62
129.80
125.91
80.66
77.35
77.03
76.71
28.10
21.36
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm