Supporting Information

$InCl_3$-Catalyzed Alkylative Rearrangement of Propargylic Acetates Using Alkyl Chlorides, Alcohols, and Acetates: Facile Synthesis of α-Alkyl-α,β-Unsaturated Carbonyl Compounds

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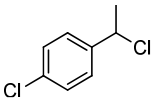
General.

New compounds were characterized by ^{1}H, ^{13}C, ^{13}C off-resonance, ^{1}H-^{1}HCOSY, NOESY, HMQC, HMBC, IR, MS, HRMS, and elemental analysis. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained with TMS as internal standard. IR spectra were recorded as thin film or as solids in KBr pellets on HORIBA FT-720 spectrophotometer. Column chromatography was performed on silica gel (MERCK silica gel 60 or Fuji Silysia FL100DX). Bulb-to-bulb distillation (Kugelrohr) was accomplished in Sibata GTO-250RS at the oven temperature and pressure indicated. Yields were determined by ^{1}H-NMR analysis of crude products using internal standard.

1. Materials.

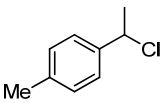
Commercial solvents and reagents were used as received with the following exception. $ClCH_2CH_2Cl$ was dried over P_2O_5 and distilled under ordinary pressure. Alkyl chlorides (**1c**[1], **1d**[1], **1j**[1]), propargylic acetates (**2a**[4], **2b**[5], **2d**[6], **2h**[7], **2i**[8]), and alkyl acetates (**5**[9], **6**[10]) were prepared by known methods[11−15] and these compounds were reported. Propargylic acetates (**2c**, **2e**, **2f**, **2j**, **2k**) were prepared and the experimental details are described below (These preparation methods were not optimized.). Other alkyl chlorides (**1a, 1b, 1e, 1f, 1g, 1h**) and propargyl acetate **2g** are commercially available.

(1c) 1-Chloro-1-(4-Chlorophenyl)ethane[1]



To a stirred solution of $BiCl_3$ (1.5 mmol) and 1-(4-chlorophenyl)ethanol (30 mmol) in CH_2Cl_2 (10 mL) was slowly added Me_3SiCl (36 mmol) at room temperature. The mixture was stirred for 23 h, and then quenched by water (50 mL). The mixture was extracted with EtOAc (30 mL x 3). The collected organic layer was washed with brine (100 mL) and then dried over $MgSO_4$. The solvent was evaporated and the residue was purified by distillation under reduced pressure to give the product (4.58 g, 89%). The analytical data for this compound matched that previously reported. ^{1}H and ^{13}C NMR charts are listed below.

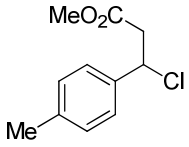
(1d) 1-Chloro-1-(4-tolyl)ethane[1]



To a stirred solution of $BiCl_3$ (1.5 mmol) and 1-(4-tolyl)ethanol (30 mmol) in CH_2Cl_2 (10 mL) was slowly added Me_3SiCl (36 mmol) at room temperature. The mixture was stirred for 12 h, and then quenched by water (50 mL). The mixture was extracted with EtOAc (30 mL x 3). The collected

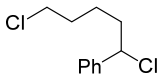
organic layer was washed with brine (100 mL) and then dried over $MgSO_4$. The solvent was evaporated and the residue was purified by distillation under reduced pressure to give the product (3.89 g, 85%). The analytical data for this compound matched that previously reported. ^1H and ^{13}C NMR charts are listed below.

(1i) Ethyl 3-chloro-3-phenylpropionate



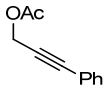
To a stirred solution of $BiCl_3$ (1 mmol, 0.33 g) and methyl 3-hydroxy-3-(4-methylphenyl)-propionate (20 mmol, 3.7 g) in CH_2Cl_2 (60 mL) was slowly added Me_3SiCl (30 mmol, 3.4 g) at room temperature. The mixture was stirred for 3 h, and then quenched by water (50 mL). The mixture was extracted with diethyl ether (30 mL x 3). The collected organic layer was washed with brine (20 mL) and then dried over $MgSO_4$. The solvent was evaporated and the residue was purified by distillation under reduced pressure to give the product (2.9 g, 71%). ^1H and ^{13}C NMR charts are listed below.; IR: (neat) 1743 (C=O) cm^{-1}; b.p. 150 ^oC (0.6 mmHg); ^1H NMR: (400 MHz, $CDCl_3$) 7.30 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 5.33 (dd, J = 8.7, 5.8 Hz, 1H, 3-H), 3.70 (s, 3H, OMe), 3.18 (dd, J = 16.4, 8.7 Hz, 1H, 2-H^A), 3.02 (dd, J = 16.4, 5.8 Hz, 1H, 2-H^B), 2.34 (s, 3H, *p*-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 170.1 (s, C-1), 138.6 (s, C-*p*), 137.3 (s, C-*i*), 129.4 (d, C-*m*), 126.8 (d, C-*o*), 57.9 (d, C-3), 52.0 (q, OMe), 44.6 (t, C-2), 21.1 (q, *p*-Me); MS: (EI, 70 eV) *m*/*z* 214 (M + 2, 9), 212 (M^+, 27), 177 (33), 139 (34), 135 (100), 117 (22); HRMS: (EI, 70 eV) Calculated ($C_{11}H_{13}ClO_2$) 212.0604 (M^+), Found: 212.0606.

(1j) 1,5-Dichloro-1-phenylpentane[1]



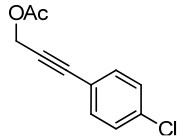
To a stirred solution of $BiCl_3$ (0.35 mmol, 0.12 g) and 5-chloro-1-phenylpentan-1-ol (5.5 mmol, 1.1 g) in CH_2Cl_2 (7 mL) was slowly added Me_3SiCl (8.5 mmol, 1.0 g) at room temperature. The mixture was stirred for 3 h, and then quenched by water (50 mL). The mixture was extracted with diethyl ether (30 mL x 3). The collected organic layer was washed with brine (20 mL) and then dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (hexane, column length 10 cm, diagram 5 cm) to give the product (0.53 g, 44%). The analytical data for this compound matched that previously reported (Ravikumar, P. C.; Yao, Lihua; Fleming, Fraser F. *J. Org. Chem.* **2009**, *74*, 7294-7299.). ^1H and ^{13}C NMR charts are listed below.

(2a) 3-Acetoxy-1-phenyl-1-propyne[4]



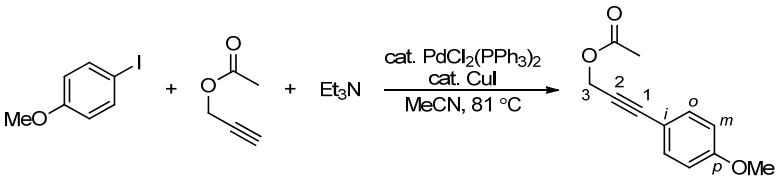
To a stirred solution of phenylacetylene (100 mmol) in THF (80 mL) at -78 °C was slowly added *n*-BuLi (1.6 M solution in hexane, 120 mmol). The reaction was stirred at -78 °C for 20 min before the addition of paraformaldehyde (120 mmol). The mixture was stirred at -78 °C for 20 min and at room temperature for additional 3 h. After addition of acetic anhydride (105 mmol) at room temperature, the resulting solution was stirred for 10 h. The mixture was quenched by saturated NH_4Cl aq. (30 mL) and then extracted with EtOAc (30 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (hexane/EtOAc = 95:5, column length 10 cm, diagram 5 cm). Further purification was performed by distillation under reduced pressure to give the product (13.0 g, 73%).

(2b) 3-Acetoxy-1-(4-chlorophenyl)-1-propyne[5]



To a stirred solution of 1-chloro-4-iodobenzene (30 mmol), 2-propynyl acetate (30 mmol), triethylamine (90 mmol), and $Pd(PPh_3)_2Cl_2$ (0.36 mmol) in MeCN (180 mL) was added CuI (0.36 mmol). The mixture was heated to reflux for 25 h and then diluted by EtOAc (30 mL). The resulting solution was filtered by silica gel column. The solvent was evaporated and the residue was purified by column chromatography (hexane/EtOAc = 95:5, column length 10 cm, diagram 5 cm). Further purification was performed by distillation under reduced pressure to give the product (4.82 g, 78%). The analytical data for this compound matched that previously reported. ^1H and ^{13}C NMR charts are listed below.

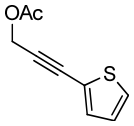
(2c) 3-Acetoxy-1-(4-methoxyphenyl)-1-propyne



To a stirred solution of 4-iodoanisole (30 mmol, 7.00 g), 2-propynyl acetate (30 mmol, 2.96 g), and triethylamine (90 mmol, 9.128 g) in MeCN (180 mL) was added $PdCl_2(PPh_3)_2$ (0.36 mmol, 0.256 g) and CuI (0.40 mmol, 0.077 g). The mixture was heated to reflux for 24 h and then diluted by EtOAc (30 mL). The solution was filtered through a pad of silica gel, and the solvent was evaporated. The

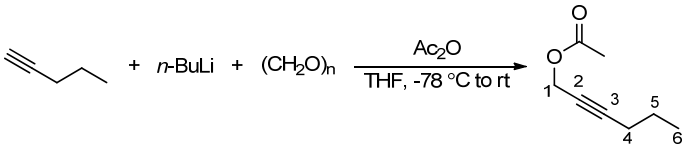
residue was purified by column chromatography (hexane/EtOAc = 95:5, column length 10 cm, diagram 5 cm). Further purification was performed by distillation under reduced pressure to give the product (1.848 g, 26%). ^{1}H and ^{13}C NMR charts are listed below.; IR: (neat) 2233 (C≡C), 1747 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.39 (d, *J* = 8.8 Hz, 2H, *o*), 6.83 (d, *J* = 8.8 Hz, 2H, *m*), 4.89 (s, 2H, 3-H_2), 3.79 (s, 3H, OMe), 2.12 (s, 3H, OCOMe); ^{13}C NMR: (100 MHz, $CDCl_3$) 170.2 (s, O*C*OMe), 159.9 (s, *p*), 133.3 (d, *o*), 114.0 (s, *i*), 113.8 (d, *m*), 86.4 (s, C-1), 81.5 (s, C-2), 55.1 (q, OMe), 52.9 (t, C-3), 20.7 (q, OCO*Me*); MS: (EI, 70 eV) *m*/*z* 204 (M^+, 29), 189 (M^+ - Me, 41), 145 (M^+ - OAc, 69), 144 (100), 133 (33); HRMS: (EI, 70 eV) Calculated ($C_{12}H_{12}O_3$) 204.0786 (M^+) Found: 204.0795

(2d) 3-Acetoxy-1-(2-thienyl)-1-propyne[6]



To a stirred solution of 2-iodothiophene (35 mmol), 2-propynyl acetate (35 mmol), triethylamine (105 mmol), and $Pd(PPh_3)_2Cl_2$ (0.42 mmol) in MeCN (210 mL) was added CuI (0.42 mmol). The mixture was stirred at room temperature for 9 h and then diluted by EtOAc (30 mL). The resulting solution was filtered by silica gel column. The solvent was evaporated and the residue was purified by column chromatography (hexane/EtOAc = 95:5, column length 10 cm, diagram 5 cm). Further purification was performed by distillation under reduced pressure to give the product (4.79 g, 73%). The analytical data for this compound matched that previously reported. ^{1}H and ^{13}C NMR charts are listed below.

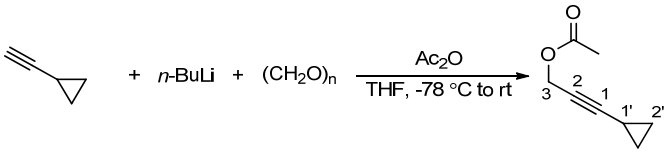
(2e) 1-Acetoxy-2-hexyne



To a stirred solution of 1-pentyne (51 mmol, 3.470 g) in THF (50 mL) at -78 °C was slowly added *n*-BuLi (1.6 M solution in hexane, 60 mmol, 37.5 mL). The reaction was stirred at -78 °C for 20 min before the addition of paraformaldehyde (62 mmol, 1.907 g). The mixture was stirred at -78 °C for 20 min and at room temperature for additional 2 h. After addition of acetic anhydride (56 mmol, 5.722 g) at room temperature, the resulting solution was stirred for 21 h. The mixture was quenched by saturated NH_4Cl aq. (30 mL) and then extracted with EtOAc (30 mL x 3). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (hexane/EtOAc = 95:5, column length 10 cm, diagram 5 cm). Further purification

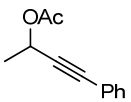
was performed by distillation under reduced pressure to give the product (2.305 g, 32%). ^{1}H and ^{13}C NMR charts are listed below.; IR: (neat) 2237 (C≡C), 1747 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 4.67 (t, J = 2.4 Hz, 2H, 1-H_2), 2.20 (tt, J = 7.2, 2.4 Hz, 2H, 4-H_2), 2.09 (s, 3H, COMe), 1.54 (qt, J = 7.6, 7.2 Hz, 2H, 5-H_2), 0.98 (t, J = 7.6 Hz, 3H, 6-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 170.3 (s, *C*OMe), 87.4 (s, C-3), 74.0 (s, C-2), 52.8 (t, C-1), 21.8 (t, C-5), 20.7 (q, CO*Me*), 20.6 (t, C-4), 13.3 (q, C-6); MS: (CI, 200 eV) *m*/*z* 141 (M + 1, 85), 99 (100), 81 (M - OAc, 45); HRMS: (CI, 200 eV) Calculated ($C_8H_{13}O_2$) 141.0916 (M + 1) Found: 141.0918

(2f) 3-Acetoxy-1-cyclopropyl-1-propyne



To a stirred solution of cyclopropylacetylene (24 mmol, 1.56 g) in THF (20 mL) at 0 °C was slowly added *n*-BuLi (1.6 M solution in hexanes, 20 mmol, 12.5 mL). The reaction was stirred at -78 °C for 20 min before the addition of paraformaldehyde (23 mmol, 0.72 g). The mixture was stirred at -78 °C for 30 min and at room temperature for additional 6 h. After addition of acetic anhydride (24 mmol, 2.49 g) at room temperature, the resulting solution was stirred for 2 h. The mixture was quenched by saturated NH_4Cl aq. (20 mL) and then extracted with EtOAc (20 mL x 3). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (hexane/EtOAc = 95:5, column length 10 cm, diagram 3 cm). Further purification was performed by distillation under reduced pressure to give the product (0.994 g, 36%). ^{1}H and ^{13}C NMR charts are listed below.; IR: (neat) 2240 (C≡C), 1739 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 4.63 (d, J = 2.0 Hz, 2H, 3-H_2), 2.09 (s, COMe), 1.31−1.23 (m, 1H, 1' -H), 0.81−0.771 (m, 2H, 2'-H^A), 0.767−0.69 (m, 2H, 2'-H^B); ^{13}C NMR: (100 MHz, $CDCl_3$) 170.3 (s, *C*OMe), 90.7 (s, C-1), 69.2 (s, C-2), 52.8 (t, C-3), 20.8 (q, CO*Me*), 8.2 (t, C-2'), -0.6 (d, C-1'); MS: (EI, 70 eV) *m*/*z* 138 (M^+, 0.6), 96 (100), 78 (50), 77 (50), 43 (COMe, 73); HRMS: (EI, 70 eV) Calculated ($C_8H_{10}O_2$) 138.0681 (M^+) Found: 138.0677; Analysis: $C_8H_{10}O_2$ (138.16) Calcd: C, 69.54; H, 7.30 Found: C, 69.26; H, 7.22

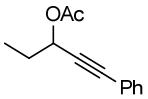
(2h) 3-Acetoxy-1-phenyl-1-butyne[7]



To a stirred solution of phenylacetylene (50 mmol) in THF (50 mL) at 0 °C was slowly added *n*-BuLi (1.6 M solution in hexane, 60 mmol). The reaction was stirred at -78 °C for 20 min before the addition of acetaldehyde (60 mmol). The mixture was stirred at -78 °C for 1 h, and

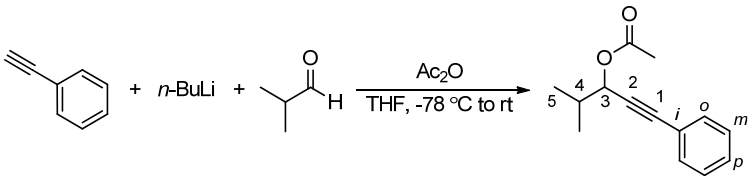
then acetic anhydride (55 mmol) was added. The resulting solution was stirred at -78 °C for 10 min and at room temperature for additional 10 h. The mixture was quenched by saturated NH_4Cl aq. (30 mL) and then extracted with EtOAc (30 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (hexane/EtOAc = 95:5, column length 10 cm, diagram 5 cm). Further purification was performed by distillation under reduced pressure to give the product (6.54 g, 69%). ^1H and ^{13}C NMR charts are listed below.

(2i) 3-Acetoxy-1-phenyl-1-pentyne[8]



To a stirred solution of phenylacetylene (120 mmol) in THF (150 mL) at -78 °C was slowly added *n*-BuLi (1.6 M solution in hexane, 120 mmol). The reaction was stirred at -78 °C for 20 min before the addition of propionaldehyde (100 mmol). The mixture was stirred at -78 °C for 1 h, and then acetic anhydride (120 mmol) was added. The resulting solution was stirred at -78 °C for 10 min and at room temperature for additional 10 h. The mixture was quenched by saturated NH_4Cl aq. (30 mL) and then extracted with EtOAc (30 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by distillation under reduced pressure to give the product (19.1 g, 54%). ^1H and ^{13}C NMR charts are listed below.

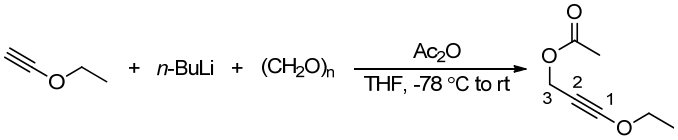
(2j) 3-Acetoxy-4-methyl-1-phenyl-1-pentyne



To a stirred solution of phenylacetylene (125 mmol, 12.8 g) in THF (210 mL) at -78 °C was slowly added *n*-BuLi (1.6 M solution in hexane, 120 mmol, 75 mL). The reaction was stirred at -78 °C for 15 min before the slow addition of isobutyraldehyde (100 mmol, 7.19 g). The mixture was stirred at -78 °C for 1 h. After addition of acetic anhydride (222 mmol, 22.7 g) at -78 °C, the resulting solution was stirred for 15 min at -78 °C and at room temperature for additional 2 h. The mixture was quenched by saturated NH_4Cl aq. (50 mL) and then extracted with EtOAc (50 mL x 3). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (hexane/EtOAc = 95:5, column length 10 cm, diagram 10 cm). Further purification was performed by distillation under reduced pressure to give the product as an yellow liquid (6.391 g, 30%). ^1H and ^{13}C NMR charts are listed below.; IR: (neat) 2229 (C≡C), 1739 (C=O)

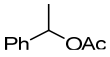
cm^{-1}: ^1H NMR: (400 MHz, $CDCl_3$) 7.46−7.43 (m, 2H, *o*), 7.32−7.25 (m, 3H, *m* and *p*), 5.46 (d, *J* = 5.2 Hz, 1H, 3-H), 2.15−2.02 (m, 4H, 4-H and COMe), 1.09 (d, *J* = 6.8 Hz, 3H, 5-H_3), 1.06 (d, *J* = 6.8 Hz, 3H, 4-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 170.1 (s, *C*OMe), 131.9 (d, C-*o*), 128.5 (d, C-*p*), 128.2 (d, C-*m*), 122.4 (s, C-*i*), 85.7 (s, C-1), 85.2 (s, C-2), 69.4 (d, C-3), 32.6 (d, C-4), 21.0 (q, CO*Me*), 18.3 (q, C-5), 17.6 (q, 4-Me); MS: (EI, 70 eV) *m*/*z* 216 (M^+, 20), 174 (50), 173 (M^+ - COMe and M^+ - *i*-Pr, 20), 156 (33), 145 (28), 141 (28), 131 (100), 43 (COMe, 47); HRMS: (EI, 70 eV) Calculated ($C_{14}H_{16}O_2$) 216.1150 (M^+) Found: 216.1143

(2k) 3-Acetoxy-1-ethoxy-1-propyne



To a stirred solution of ethoxyacetylene (40 wt% solution in hexane, 28 mmol, 4.99 g) in THF (20 mL) at 0 °C was slowly added *n*-BuLi (1.6 M solution in hexanes, 24 mmol, 15 mL). The reaction was stirred at -78 °C for 20 min before the addition of paraformaldehyde (30 mmol, 0.91 g). The mixture was stirred at -78 °C for 15 min and at room temperature for additional 5 h. After addition of acetic anhydride (30 mmol, 3.05 g) at room temperature, the resulting solution was stirred for 2 h. The mixture was quenched by saturated NH_4Cl aq. (20 mL) and then extracted with EtOAc (20 mL x 3). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (hexane/EtOAc = 95:5, column length 10 cm, diagram 3 cm). Further purification was performed by distillation under reduced pressure to give the product (0.908 g, 27%). ^1H and ^{13}C NMR charts are listed below.; IR: (neat) 2275 (C≡C), 1747 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 4.70 (s, 2H, 1-H_2), 4.13 (q, *J* = 7.2 Hz, 2H, O*C*H_2CH$_3$), 2.08 (s, 3H, COMe), 1.38 (t, *J* = 7.2 Hz, 3H, OCH$_2$CH_3); ^{13}C NMR: (100 MHz, $CDCl_3$); 170.5 (s, *C*OMe), 94.9 (s, C-3), 74.8 (t, O*C*H$_2$CH$_3$), 52.8 (t, C-1), 33.0 (s, C-2), 20.9 (q, CO*Me*), 14.3 (q, OCH$_2$*C*H$_3$); MS: (CI, 200 eV) *m*/*z* 143 (M + 1, 61), 115 (36), 101 (100), 83 (M - OAc, 51); HRMS: (CI, 200 eV) Calculated ($C_7H_{11}O_3$) 143.0708 (M + 1) Found: 141.0710

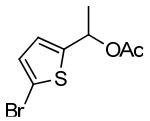
(5) 1-Phenylethyl acetate[9]



To a stirred solution of 1-phenylethanol (50 mmol) and acetic anhydride (75 mmol) in dry Et_2O (10 mL) was added dehydrated pyridine (75 mmol) at room temperature. After stirring for 6 h, resulting solution was diluted by ethyl acetate (30 mL) and quenched by 2N HCl aq (20 mL) at 0°C. The mixture was washed water (20 mL x 3) and saturated $NaHCO_3$ aq (20 mL x 1), and then the collected organic layer was dried over $MgSO_4$. The solvent was evaporated, and then the residue was purified by distillation under reduced pressure to give the product as a colorless liquid (7.96 g, 97%).

The analytical data of this compound matched that previously reported. ^{1}H and ^{13}C NMR chart are listed below.

(6) 2-(1-Acetoxyethyl)-5-bromothiophene[10]



To a stirred solution of 2-bromo-5-(1-hydroxyethyl)thiophene (20 mmol, 4.0 g) and acetic anhydride (30 mmol, 2.9 g) in dry Et_2O (5 mL) was added dehydrated pyridine (25 mmol) at room temperature. After stirring for 14 h, resulting solution was diluted by ethyl acetate (30 mL) and quenched by water. The mixture was washed water (20 mL x 3) and saturated $NaHCO_3$ aq (20 mL x 1), and then the collected organic layer was dried over $MgSO_4$. The solvent was evaporated, and then the residue was purified by distillation under reduced pressure to give the product as a colorless liquid (3.4 g, 71%). The analytical data of this compound matched that previously reported. ^{1}H and ^{13}C NMR chart are listed below.

2. Experimental Procedures.

2.1. Typical Procedure for the Reaction of Alkyl Chloride 1a with Propargylic Acetate 2a (Table 1, entry 1).

To a mixture of $InCl_3$ (0.05 mmol) and propargylic acetate **2a** (1 mmol) in CH_2Cl_2 (1 mL) was added alkyl chloride **1a** (0.5 mmol) under nitrogen. The resulting mixture was stirred for 3 h at room temperature and then quenched with water (10 mL). The solution was extracted with Et_2O (10 mL x 3). The collected organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford the crude product, which was analyzed by NMR spectroscopy. The detail of further purification was described in Product Data.

2.2. Experimental Procedure for the Reaction of Alkyl Chloride 1c with Propargylic Acetate 2a (Table 2, entry 2).

To a mixture of $InCl_3$ (0.075 mmol) and propargylic acetate **2a** (1 mmol) in CH_2Cl_2 (1 mL) was added alkyl chloride **1c** (0.5 mmol) under nitrogen. The resulting mixture was heated to reflux for 3 h and then quenched with water (10 mL). The solution was extracted with Et_2O (10 mL x 3). The collected organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford the crude product, which was analyzed by NMR spectroscopy. The detail of further purification was described in Product Data.

2.3. Experimental Procedure for Reactions of Alkyl Chloride 1 with Propargylic Acetate 2a

(Table 2, entries 5, 9, and 10).

To a mixture of $InCl_3$ (0.075 mmol) and propargylic acetate **2a** (1 mmol) in $ClCH_2CH_2Cl$ (1 mL) was added alkyl chloride **1** (0.5 mmol) under nitrogen. The resulting mixture was heated to reflux for 3 h and then quenched with water (10 mL). The solution was extracted with Et_2O (10 mL x 3). The collected organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford the crude product, which was analyzed by NMR spectroscopy. The detail of further purification was described in Product Data.

2.4. Experimental Procedure for the Reaction of Alkyl Chloride 1i with Propargylic Acetate 2a (Table 2, entry 8).

To a mixture of $InCl_3$ (0.05 mmol) and propargylic acetate **2a** (1 mmol) in 1,4-dichlorobutane (1 mL) was added alkyl chloride **1i** (0.5 mmol) under nitrogen. The resulting mixture was heated at 150 ºC for 3 h and then quenched with water (10 mL). The solution was extracted with Et_2O (10 mL x 3). The collected organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford the crude product, which was analyzed by NMR spectroscopy. The detail of further purification was described in Product Data.

2.5. Experimental Procedure for the Reaction of Alkyl Chloride 1b with Propargylic Acetate 2c (Table 3, entry 2).

To a mixture of $InCl_3$ (0.05 mmol) and propargylic acetate **2c** (1 mmol) in CH_2Cl_2 (1 mL) was added alkyl chloride **1b** (0.5 mmol) under nitrogen. The resulting mixture was stirred for 5 h at room temperature and then quenched with water (10 mL). The solution was extracted with Et_2O (10 mL x 3). The collected organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford the crude product, which was analyzed by NMR spectroscopy. The detail of further purification was described in Product Data.

2.6. Experimental Procedure for Reactions of Alkyl Chloride 1b with Propargylic Acetate 2 (Table 3, entries 4 and 6).

To a mixture of $InCl_3$ (0.05 mmol) and propargylic acetate **2** (1 mmol) in CH_2Cl_2 (1 mL) was added alkyl chloride **1b** (0.5 mmol) under nitrogen. The resulting mixture was heated to reflux for 3 h and then quenched with water (10 mL). The solution was extracted with Et_2O (10 mL x 3). The collected organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford the crude product, which was analyzed by NMR spectroscopy. The detail of further purification was described in Product Data.

2.7. Experimental Procedure for the Reaction of Alkyl Chloride 1b with Propargylic Acetate 2h (Table 3, entry 7).

To a mixture of $InCl_3$ (0.05 mmol) and propargylic acetate **2h** (1 mmol) in CH_2Cl_2 (1 mL) was added alkyl chloride **1b** (0.5 mmol) under nitrogen. The resulting mixture was stirred for 30 min at room temperature and then quenched with water (10 mL). The solution was extracted with Et_2O (10 mL x 3). The collected organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford the crude product, which was analyzed by NMR spectroscopy. The detail of further purification was described in Product Data.

2.8. Experimental Procedure for Reactions of Alchol 4 or Alkyl Acetate 5 with Propargylic Acetate 2a (Eqs 1 and 2).

To a mixture of $InCl_3$ (0.025 mmol) and propargylic acetate **2a** (1 mmol) in $ClCH_2CH_2Cl$ (1 mL) was added alcohol **4** (or alkyl acetate **5**) (0.5 mmol) under nitrogen. The resulting mixture was heated to reflux for 1 h at room temperature and then quenched with water (10 mL). The solution was extracted with Et_2O (10 mL x 3). The collected organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford the crude product, which was analyzed by NMR spectroscopy. The detail of further purification was described in Product Data.

2.9. Experimental Procedure for the Reaction of Alkyl Acetate 6 with Propargylic Acetate 2a (Eq. 3).

To a mixture of $InCl_3$ (0.05 mmol) and propargylic acetate **2a** (1 mmol) in $ClCH_2CH_2Cl$ (1 mL) was added alkyl acetate **6** (0.5 mmol) under nitrogen. The resulting mixture was heated to reflux for 1 h and then quenched with water (10 mL). The solution was extracted with Et_2O (10 mL x 3). The collected organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford the crude product, which was analyzed by NMR spectroscopy. The detail of further purification was described in Product Data.

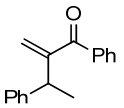
2.10. Experimental Procedure of Eq. 4.

A mixture of $InCl_3$ (0.5 mmol) and propargylic acetate **2** (0.5 mmol) in CD_2Cl_2 (1 mL) was stirred at room temperature for 2 h. And then, it was observed by ^1H NMR in situ that the rearrangement of **2** to the corresponding allenyl acetate **8** did not occur, and **2** was recovered in 91% yield.

3. Product Data.

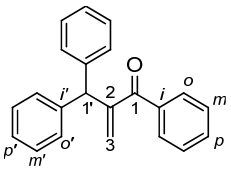
The spectral data of **3aa**[16], **3ea**[17], **3bk**[18] was in excellent agreements with the reported data. The detailed procedure and spectral data for other products are shown below.

(3aa) 1-Phenyl-2-(1-phenylethyl)-2-propen-1-one[16]



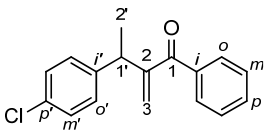
According to a typical procedure, $InCl_3$ (0.05 mmol, 0.010 g), 1-chloro-1-phenylethane (0.5 mmol, 0.075 g), and 1-phenyl-3-acetoxy-2-propyne (1 mmol, 0.185 g) gave the crude product. Purification was performed by flash column chromatography (hexane/EtOAc = 95:5, column length 10.5 cm, diagram 2.8 cm) to give the product **3aa** (0.088 g, 70%). ^1H and ^{13}C NMR chart are listed below.

(3ba) 2-Benzhydryl-1-phenylpropen-1-one



According to a typical procedure, $InCl_3$ (0.06 mmol, 0.013 g), benzhydryl chloride (0.36 mmol, 0.074 g), and 3-phenyl-2-propynyl acetate (1.02 mmol, 0.177 g) gave the crude product. Purification was performed by flash column chromatography (hexane/EtOAc = 95:5, column length 10.5 cm, diagram 2.8 cm) to give the product as a white solid (0.101 g, 93%). ^1H and ^{13}C NMR chart are listed below.; mp: 114−116 ºC; IR: (KBr) 1650 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.79 (d, *J* = 8.0 Hz, 2H, *o*), 7.51 (q, *J* = 8.0 Hz, 1H, *p*), 7.42 (t, *J* = 8.0 Hz, 2H, *m*), 7.32−7.18 (m, 10H, 1'-Ph_2), 5.92 (s, 1H, 3-H^A), 5.71 (s, 1H, 1'-H), 5.53 (s, 1H, 3-H^B); ^{13}C NMR: (100 MHz, $CDCl_3$) 196.8 (s, C-1), 151.0 (s, C-2), 141.5 (s, C-*i'*), 137.5 (s, C-*i*), 132.3 (d, C-*p*), 129.6 (d, C-*o*), 129.2 (d, C-*o'*), 128.6 (t, C-3), 128.5 (d, C-*m'*), 128.2 (d, C-*m*), 126.6 (d, C-*p'*), 52.2 (d, C-1'); MS: (EI, 70 eV) *m*/*z* 298 (M^+, 100), 297 (58), 192 (28), 115 (20), 105 (PhCO, 51), 77 (C_6H_5, 31); HRMS: (EI, 70 eV) Calculated ($C_{22}H_{18}O$) 298.1358 (M^+) Found: 298.1357; Analysis: $C_{22}H_{18}O$ (298.38) Calcd: C, 88.56; H, 6.08 Found: C, 88.26; H, 5.99

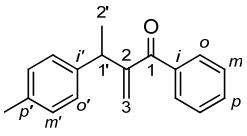
(3ca) 2-(4-Chlorophenylethyl)-1-phenylpropen-1-one



According to an experimental procedure in section 2.2., $InCl_3$ (0.058 mmol, 0.013 g),

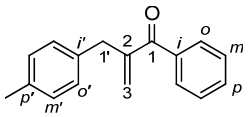
1-chloro-1-(4-chlorophenyl)ethane (0.51 mmol, 0.090 g), and 3-phenyl-2-propynyl acetate (1.03 mmol, 0.181 g) gave the crude product. Purification was performed by flash column chromatography (hexane/EtOAc = 95:5, column length 10.5 cm, diagram 2.8 cm). Further purification was performed by recrystallization from hexane/EtOAc to give the product as a white solid (0.04 g, 29%). ^{1}H and ^{13}C NMR chart are listed below.; mp: 88−90 ºC; IR: (KBr) 1650 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.67 (d, *J* = 7.6 Hz, 2H, *o*), 7.49 (t, *J* = 7.6 Hz, 1H, *p*), 7.38 (t, *J* = 7.6 Hz, 2H, *m*), 7.25−7.20 (m, 4H, *o'* and *m'*), 5.77 (s, 1H, 3-H^{A}), 5.66 (s, 1H, 3-H^{B}), 4.28 (q, *J* = 6.8 Hz, 1H, 1'-H), 1.45 (d, *J* = 6.8 Hz, 3H, 2'-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 197.6 (s, C-1), 151.8 (s, C-2), 142.4 (s, C-*i'*), 137.6 (s, C-*i*), 132.2 (d, C-*p*), 132.0 (s, C-*p'*), 129.4 (d, C-*o*), 128.9 (d), 128.5 (d), 128.1 (d), 123.9 (t, C-3), 39.9 (d, C-1'), 19.9 (q, C-2'); MS: (EI, 70 eV) *m*/*z* 272 (M^+ + 2, 24), 271 (35), 270 (M^+, 74), 269 (73), 255 (M^+ - Me, 35), 235 (M^+ - Cl, 86), 105 (PhCO, 100), 77 (C_6H_5, 49); HRMS: (EI, 70 eV) Calculated ($C_{17}H_{15}ClO$) 270.0811 (M^+) Found: 270.0809

(3da) 1-Phenyl-2-{1-(4-tolyl)ethyl}-propen-1-one



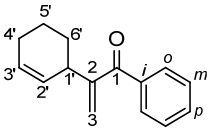
According to a typical procedure, $InCl_3$ (0.06 mmol, 0.013 g), 1-(4-tolyl)-1-chloroethane (0.48 mmol, 0.074 g), and 3-phenyl-2-propynyl acetate (0.99 mmol, 0.172 g) gave the crude product. Purification was performed by flash column chromatography (hexane/EtOAc = 95:5, column length 10.5 cm, diagram 2.8 cm). Further purification was performed by distillation under reduced pressure to give the product as a pale yellow liquid (0.092 g, 76%). ^{1}H and ^{13}C NMR chart are listed below.; IR: (neat) 1658 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.69 (d, *J* = 7.6 Hz, 2H, *o*), 7.48 (t, *J* = 7.6 Hz, 1H, *p*), 7.37 (t, *J* = 7.6 Hz, 2H, *m*), 7.17 (d, *J* = 8.0 Hz, 2H, *o'*), 7.10 (d, *J* = 8.0 Hz, 2H, *m'*), 5.76 (s, 1H, 3-H^{A}), 5.63 (s, 1H, 3-H^{B}), 4.28 (q, *J* = 7.2 Hz, 1H, 1'-H_3), 2.29 (s, 1H, *p'*-Me), 1.48 (d, *J* = 7.2 Hz, 3H, 2'-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 198.0 (s, C-1), 152.5 (s, C-2), 140.7 (s, C-*i'*), 137.8 (s, C-*i*), 135.8 (s, C-*p'*), 132.2 (d, C-*p*), 129.5 (d, C-*m*), 129.1 (d, C-*o'*), 128.0 (d, C-*o*), 127.5 (d, C-*m'*), 123.3 (t, C-3), 40.1 (d, C-1'), 20.9 (q, Me), 20.1 (q, C-2'); MS: (EI, 70 eV) *m*/*z* 250 (M^+, 42), 235 (M^+ - Me, 100), 105 (PhCO, 71), 77 (C_6H_5, 37); HRMS: (EI, 70 eV) Calculated ($C_{18}H_{18}O$) 250.1358 (M^+) Found: 250.1357; Analysis: $C_{18}H_{18}O$ (250.33) Calcd: C, 86.36; H, 7.25 Found: C, 86.16; H, 7.36

(3fa) 1-Phenyl-2-(4-tolyl)methylpropen-1-one



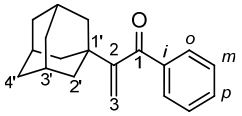
According to an experimental procedure in section 2.3., $InCl_3$ (0.08 mmol, 0.018 g), 4-methylbenzyl chloride (0.46 mmol, 0.064 g), and 3-phenyl-2-propynyl acetate (2.52 mmol, 0.439 g) gave the crude product. Purification was performed by flash column chromatography (hexane/EtOAc = 95:5, column length 10.5 cm, diagram 2.8 cm). Further purification was performed by distillation under reduced pressure to give the product (0.055 g, 51%). ^{1}H and ^{13}C NMR chart are listed below.; IR: (neat) 1658 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.71 (d, *J* = 7.6 Hz, 2H, *o*), 7.51 (d, *J* = 7.6 Hz, 1H, *p*), 7.40 (d, *J* = 7.6 Hz, 2H, *m*), 7.14 (d, *J* = 8.0 Hz, 2H, *o'*), 7.10 (d, *J* = 8.0 Hz, 2H, *m'*), 7.10 (d, 2H, *m'*), 5.75 (s, 1H, 3-H^A), 5.66 (s, 1H, 3-H^B), 3.76 (s, 2H, 1'-H_2), 2.31 (s, 3H, *p'*-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 197.7 (s, C-1), 147.8 (s, C-2), 137.7 (s, C-*i*), 135.8 (s, C-*p'*), 135.5 (s, C-*i'*), 132.1 (d, C-*p*), 129.5 (d, C-*o*), 129.2 (d, C-*m'*), 129.0 (d, C-*o'*), 128.1 (d, C-*m*), 126.8 (t, C-3), 37.9 (t, C-1'), 21.0 (q, Me); MS: (EI, 70 eV) *m*/*z* 236 (M^+, 100), 235 (65), 221 (M^+ - Me, 98), 115 (25), 105 (PhCO and $MeC_6CH_4CH_2$, 84), 77 (C_6H_5, 66); HRMS: (EI, 70 eV) Calculated ($C_{17}H_{16}O$) 236.1201 (M^+) Found: 236.1202; Analysis: $C_{17}H_{16}O$ (236.31) Calcd: C, 86.40; H, 6.82 Found: C, 86.23; H, 6.75

(3ga) 2-(2-Cyclohexenyl)-1-phenylpropen-1-one



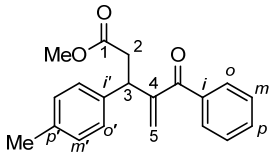
According to a typical procedure, $InCl_3$ (0.06 mmol, 0.013 g), 3-chlorocyclohexene (0.57 mmol, 0.066 g), and 3-phenyl-2-propynyl acetate (0.93 mmol, 0.162 g) gave the crude product. Purification was performed by flash column chromatography (hexane/EtOAc = 95:5, column length 10.5 cm, diagram 2.8 cm). Further purification was performed by distillation under reduced pressure to give the product (0.033 g, 45%). ^{1}H and ^{13}C NMR chart are listed below.; IR: (neat) 1658 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.76 (d, *J* = 7.6 Hz, 2H, *o*), 7.54 (t, *J* = 7.6 Hz, 1H, *p*), 7.44 (t, *J* = 7.6 Hz, 2H, *m*), 5.93−5.89 (m, 1H, 3'-H), 5.79 (s, 1H, 3-H^A), 5.63−5.61 (m, 2H, 3-H^B and 2'-H), 3.69 (m, 1H, 1'-H), 2.07−2.03 (m, 2H, 4'-H_2), 1.95−1.87 (m, 1H, 6'-H^A), 1.73−1.58 (m, 2H, 5'-H_2), 1.52−1.44 (m, 1H, 6'-H^B); ^{13}C NMR: (100 MHz, $CDCl_3$) 198.5 (s, C-1), 151.5 (s, C-2), 138.1 (s, C-*i*), 132.2 (d, C-*p*), 129.5 (d, C-*o*), 129.3 (d, C-3'), 128.3 (d, C-2'), 128.2 (d, C-*m*), 125.1 (t, C-3), 36.5 (d, C-1'), 28.1 (t, C-6'), 25.1 (t, C-4'), 19.9 (t, C-5'); MS: (EI, 70 eV) *m*/*z* 212 (M^+, 100), 211 (88), 105 (PhCO, 55), 77 (C_6H_5, 45); HRMS: (EI, 70 eV) Calculated ($C_{15}H_{16}O$) 212.1201 (M^+) Found: 212.1199

(3ha) 2-Adamantyl-1-phenylpropen-1-one



According to an experimental procedure in section 2.4., $InCl_3$ (0.1 mmol, 0.021 g), adamantyl chloride (1 mmol, 0.166 g), and 3-phenyl-2-propynyl acetate (2 mmol, 0.350 g) gave the crude product. Purification was performed by flash column chromatography (hexane/EtOAc = 95:5, column length 10.5 cm, diagram 2.8 cm) to give the product as a white solid (0.15 g, 58%). ^{1}H and ^{13}C NMR chart are listed below.; mp: 56−58 ºC; IR: (KBr) 1658 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.91 (d, *J* = 7.6 Hz, 2H, *o*), 7.55 (t, *J* = 7.6 Hz, 1H, *p*), 7.43 (t, *J* = 7.6 Hz, 2H, *m*), 5.52 (s, 1H, 3-H^A), 5.10 (s, 1H, 3-H^B), 2.05−1.97 (m, 3H, 3'-H x 3), 1.91−1.81 (m, 6H, 2'-H_2 x 3), 1.76−1.65 (m, 6H, 4'-H_2 x 3); ^{13}C NMR: (100 MHz, $CDCl_3$) 200.0 (s, C-1), 157.3 (s, C-2), 138.0 (s, C-*i*), 132.8 (d, C-*p*), 130.0 (d, C-*o*), 128.2 (d, C-*m*), 115.6 (t, C-3), 41.2 (t, C-2'), 37.6 (s, C-1'), 36.6 (t, C-4'), 28.5 (d, C-3'); MS: (EI, 70 eV) *m*/*z* 267 (21), 266 (M$^+$, 100), 209 (24), 105 (PhCO, 48), 77 (C_6H_5, 30); HRMS: (EI, 70 eV) Calculated ($C_{19}H_{22}O$) 266.1671 (M$^+$) Found: 266.1669; Analysis: $C_{19}H_{22}O$ (266.38) Calcd: C, 85.67; H, 8.32 Found: C, 85.77; H, 8.36

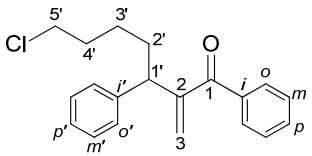
(3ia) Methyl 4-benzoyl-3-(4-methylphenyl)-4-pentenoate



The mixture of $InCl_3$ (0.05 mmol, 0.012 g), methyl 3-chloro-3-(4-methylphenyl)-propionate (0.5 mmol, 0.105 g), and 3-phenyl-2-propynyl acetate (2.0 mmol, 0.353 g), 1,2-dichloroethane (1 mL) was heated at 83 ^{o}C for 1 h and then quenched with water (10 mL). The solution was extracted with Et_2O (10 mL x 3). The collected organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford the crude product, which was analyzed by NMR spectroscopy. Purification was performed by flash column chromatography (hexane/EtOAc = 90:10, column length 10.5 cm, diagram 2.8 cm) to give the product (0.071 g, 47%). ^{1}H and ^{13}C NMR chart are listed below. IR: (neat) 1736 (C=O), 1658 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.66 (d, *J* = 7.6 Hz, 2H, *o*), 7.50 (t, *J* = 7.6 Hz, 1H, *p*), 7.38 (t, *J* = 7.6 Hz, 2H, *m*), 7.18 (d, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 7.7 Hz, 2H), 5.83 (s, 1H, 5-H^A), 5.67 (s, 1H, 5-H^B), 4.63 (t, 1H, *J* = 8.2 Hz, 3-H), 3.61 (s, 3H, OMe), 3.01 (dd, *J* = 15.7, 8.2 Hz, 1H, 2-H^A), 2.88 (dd, *J* = 15.7, 8.2 Hz, 1H, 2-H^B), 2.28 (s, 3H, *p*-Me); ^{13}C NMR: (100 MHz, $CDCl_3$), 197.3 (s, *C*OPh), 172.0 (s, C-1), 149.9 (s), 137.9 (s), 137.6 (s), 136.4 (s), 132.3 (t), 129.6 (t), 129.3 (t), 128.1 (t), 127.7 (t), 124.4 (d, C-5), 51.7 (q, OMe), 42.6 (t, C-2), 39.1 (d, C-3), 21.0 (q, *p*-Me); MS: (EI, 70 eV) *m*/*z* 308 (M$^+$, 45), 248 (22), 235 (40), 105 (100);

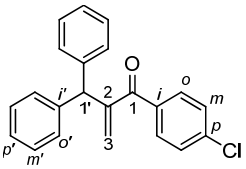
HRMS: (EI, 70 eV) Calculated ($C_{20}H_{20}O_3$) 308.1412 (M^+) Found: 308.1413.

(3ja) 2-(5-Chloro-1-phenylpentyl)-1-phenylpropen-1-one



According to an experimental procedure in section 2.1., $InCl_3$ (0.075 mmol, 0.018 g), 1,5-dichloro-1-phenylpentane (0.75 mmol, 0.157 g), and 3-phenyl-2-propynyl acetate (1.5 mmol, 0.266 g) gave the crude product. Purification was performed by flash column chromatography (hexane/EtOAc = 96:4, column length 10.5 cm, diagram 2.8 cm) to give the product (0.101 g, 45%). ^1H and ^{13}C NMR chart are listed below. IR: (neat) 1658 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.56 (d, J = 7.2 Hz, 2H, *o*), 7.38 (t, J = 7.2 Hz, 1H, *p*), 7.28 (t, J = 7.6 Hz, 2H, *m*), 7.20−7.06 (m, 5H, *o'*, *m'*, and *p'*), 5.69 (s, 1H, 3-H^A), 5.54 (s, 1H, 3-H^B), 4.02 (dd, J = 9.2, 6.3 Hz, 1H, 1'-H), 3.38 (t, J = 6.8 Hz, 2H, 5'-H_2), 1.89−1.63 (m, 4H, 2'-H_2 and 4'-H_2), 1.42−1.22 (m, 4H, 3'-H_2); ^{13}C NMR: (100 MHz, $CDCl_3$) 197.9 (s, C-1), 151.2 (s, C-2), 141.8 (s), 137.7 (s), 132.2 (d), 129.5 (d), 128.5 (d), 128.1 (d), 128.0 (d), 126.5 (d), 123.7 (t), 46.2 (d, C-1'), 44.7 (t, C-5'), 33.0 (t), 32.4 (t), 24.9 (t, C-3'); MS: (EI, 70 eV) *m*/*z* 314 (M + 2, 24), 313 (29), 312 (M^+, 73), 311 (45), 221 (99), 105 (100), 91 (22), 77 (39); HRMS: (EI, 70 eV) Calculated ($C_{20}H_{21}ClO$) 312.1281 (M^+) Found: 312.1280.

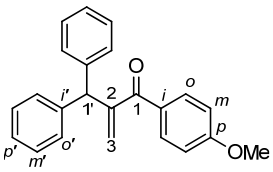
(3bb) 2-Benzhydryl-1-(4-chlorophenyl)-propen-1-one



According to a typical procedure, $InCl_3$ (0.1 mmol, 0.023 g), benzhydryl chloride (1 mmol, 0.191 g), and 3-(4-chlorophenyl)-2-propynyl acetate (2 mmol, 0.421 g) gave the crude product. Purification was performed by flash column chromatography (hexane/EtOAc = 95:5, column length 10.5 cm, diagram 2.8 cm). Further purification was performed by recrystallization from hexane/Et_2O to give the product as a white solid (0.276 g, 89%). ^1H and ^{13}C NMR chart are listed below.; mp: 116−118 ºC; IR: (KBr) 1650 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.74 (d, J = 8.0 Hz, 2H, *o*), 7.40 (d, 1H, J = 8.0 Hz, 2H, *m*), 7.32−7.19 (m, 10H), 5.87 (s, 1H, 3-H^A), 5.67 (s, 1H, 1'-H), 5.52 (s, 1H, 3-H^B); ^{13}C NMR: (100 MHz, $CDCl_3$) 195.6 (s, C-1), 150.8 (s, C-2), 141.2 (s, C-*i'*), 138.8 (s, C-*i*), 135.7 (d, C-*p*), 131.0 (d, C-*o*), 129.1 (d, C-*o'*), 128.6 (d, C-*m*), 128.5 (d, C-*m'*), 128.4 (t, C-3), 126.7 (d, C-*p'*), 52.2 (d, C-1'); MS: (EI, 70 eV) *m*/*z* 334 (M^+ + 2, 34), 333 (40), 332 (M^+, 100), 331 (60), 297 (M^+ - Cl, 35), 193 (M^+ - ArCO, 35), 192 (28), 167 (Ph_2CH, 20), 165 (M^+ - Ph_2CH, 33), 141 (36),

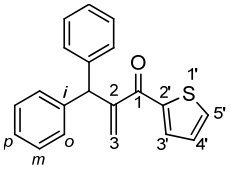
139 (ArCO, 72), 115 (34), 111 (C_6H_4Cl, 28); HRMS: (EI, 70 eV) Calculated ($C_{22}H_{17}ClO$) 332.0968 (M^+) Found: 332.0966

(3bc) 2-Benzhydryl-1-(4-methoxyphenyl)-propen-1-one



According to an experimental procedure in section 2.5., $InCl_3$ (0.06 mmol, 0.012 g), benzhydryl chloride (0.44 mmol, 0.090 g), and 3-(4-methoxyphenyl)-2-propynyl acetate (1.00 mmol, 0.204 g) gave the crude product. Purification was performed by flash column chromatography (hexane/EtOAc = 90:10, column length 10.5 cm, diagram 2.8 cm). Further purification was performed by distillation under reduced pressure to give the product (0.083 g, 57%). ^1H and ^{13}C NMR chart are listed below.; IR: (KBr) 1639 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.85 (d, J = 9.2 Hz, 2H, *o*), 7.31−7.18 (m, Ph x 2), 6.91 (d, J = 9.2 Hz, 2H, *m*), 5.84 (s, 1H, 3-H^A), 5.70 (s, 1H, 1'-H), 5.43 (s, 1H, 3-H^B), 3.84 (s, OMe); ^{13}C NMR: (100 MHz, $CDCl_3$) 195.5 (s, C-1), 163.1 (s, C-*p*), 151.0 (s, C-2), 141.5 (s, C-*i'*), 132.0 (d, C-*o*), 129.9 (d, C-*i*), 129.2 (d, C-*o'*), 128.4 (d, C-*m'*), 126.7 (t, C-3), 126.5 (d, C-1'), 113.4 (d, C-*m*), .55.4 (q, OMe), 52.5 (d, C-1'); MS: (EI, 70 eV) *m*/*z* 328 (M^+, 100), 297 (M^+ - OMe, 64), 165 (24), 135 (ArCO, 94); HRMS: (EI, 70 eV) Calculated ($C_{23}H_{20}O_2$) 328.1463 (M^+) Found: 328.1465; Analysis: $C_{23}H_{20}O_2$ (328.40) Calcd: C, 84.12; H, 6.14 Found: C, 83.90; H, 6.05

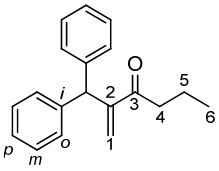
(3bd) 2-Benzhydryl-1-(2-thienyl)-propen-1-one



According to a typical procedure, $InCl_3$ (0.05 mmol, 0.011 g), benzhydryl chloride (0.46 mmol, 0.094 g), and 3-(2-thienyl)-2-propynyl acetate (1.02 mmol, 0.184 g) gave the crude product. Purification was performed by flash column chromatography (hexane/EtOAc = 95:5, column length 10.5 cm, diagram 2.8 cm). Further purification was performed by recrystallization from hexane/Et_2O to give the product as a white solid (0.061 g, 43%). ^1H and ^{13}C NMR chart are listed below.; mp: 130−132 ºC; IR: (KBr) 1635 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.76−7.74 (m, 1H, 3'-H), 7.64−7.63 (m, 1H, 5'-H), 7.31−7.19 (m, 10H, Ph rings), 7.13−7.11 (m, 1H, 4'), 6.11 (s, 1H, 3-H^A), 5.67 (s, 1H, Ph_2CH), 5.39 (s, 1H, 3-H^B); ^{13}C NMR: (100 MHz, $CDCl_3$) 188.5 (s, C-1), 151.3 (s, C-2), 143.5 (s, C-2'), 141.2 (C-*i*), 134.0 (d, C-5'), 133.7 (d, C-3'), 129.2 (d, C-*o*), 128.5 (d, C-*m*), 127.8 (d,

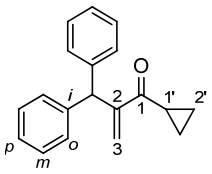
C-4'), 126.6 (d, C-*p*), 126.1 (t, C-3), 52.6 (d, Ph_2CH); MS: (EI, 70 eV) *m*/*z* 305 (23), 304 (M^+, 100), 192 (22), 111 (C_4H_4SCO, 40); HRMS: (EI, 70 eV) Calculated ($C_{20}H_{16}OS$) 304.0922 (M^+) Found: 304.0921

(3be) 2-Benzhydryl-1-hexen-3-one



According to an experimental procedure in section 2.6., $InCl_3$ (0.05 mmol, 0.011 g), benzhydryl chloride (0.58 mmol, 0.117 g), and 1-acetoxy-2-hexyne (1.12 mmol, 0.157 g) gave the crude product. Purification was performed by flash column chromatography (hexane/EtOAc = 95:5, column length 10.5 cm, diagram 2.8 cm) to give the product (0.033 g, 24%). ^1H and ^{13}C NMR chart are listed below.; IR: (neat) 1681 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.28 (t, *J* = 7.2 Hz, 4H, *m*), 7.20 (t, *J* = 7.2 Hz, 2H, *p*), 7.11 (d, *J* = 7.2 Hz, 4H, *o*), 6.28 (s, 1H, 1-H^A), 5.54 (s, 1H, Ph_2CH), 5.39 (s, 1H, 1-H^B), 2.68 (t, *J* = 7.2 Hz, 2H, 4-H_2), 1.59 (sext, *J* = 7.2 Hz, 2H, 5-H_2), 0.86 (t, *J* = 7.2 Hz, 3H, 6-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 201.1 (s, C-3), 151.9 (s, C-2), 142.0 (s, C-*i*), 129.0 (d, C-*o*), 128.4 (d, C-*m*), 126.5 (t, C-1), 126.4 (d, C-*p*), 51.0 (d, Ph_2CH), 40.2 (t, C-4), 17.8 (t, C-5), 13.7 (q, C-6); MS: (EI, 70 eV) *m*/*z* 264 (M^+, 100), 263 (64), 221 (M^+ - C_3H_7, 76), 193 (M^+ - C_3H_7CO, 21), 192 (27), 167 (Ph_2CH, 23), 165 (27), 115 (35); HRMS: (EI, 70 eV) Calculated ($C_{19}H_{20}O$) 264.1514 (M^+) Found: 264.1515

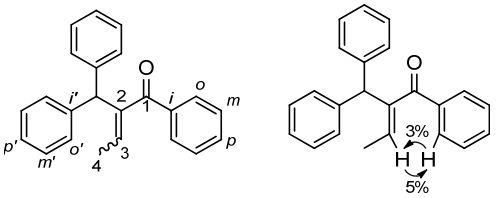
(3bf) 2-Benzhydryl-1-cyclopropylpropen-1-one



According to a typical procedure, $InCl_3$ (0.05 mmol, 0.010 g), benzhydryl chloride (0.41 mmol, 0.082 g), and 3-cyclopropyl-2-propynyl acetate (0.93 mmol, 0.129 g) gave the crude product. Purification was performed by flash column chromatography (hexane/EtOAc = 95:5, column length 10.5 cm, diagram 2.8 cm). Further purification was performed by distillation under reduced pressure to give the product as a white solid (0.085 g, 80%). ^1H and ^{13}C NMR chart are listed below.; mp: 75−77 ºC; IR: (KBr) 1654 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.30−7.25 (m, 4H, *m*), 7.22−7.18 (m, 2H, *p*), 7.14−7.12 (m, 4H, *o*), 6.41 (s, 1H, 3-H^A), 5.54 (s, 1H, Ph_2CH), 2.41 (tt, *J* = 8.0, 4.8 Hz, 1H, 1'-H), 0.99 (ddd, *J* = 8.0, 4.8, 3.2 Hz, 2H, 2'-H^A), 0.86 (dt, *J* = 8.0, 3.2 Hz, 2H, 2'-H^B); ^{13}C NMR: (100 MHz, $CDCl_3$) 201.1 (s, C-1), 152.6 (s, C-2), 142.0 (s, C-*i*), 129.0 (d, C-*m*), 128.3 (d,

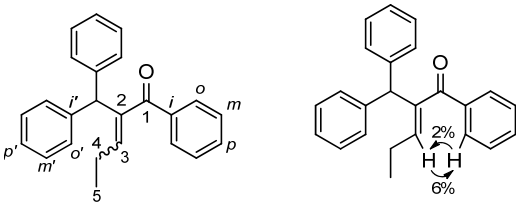
C-*o*), 126.4 (s, C-*p*), 126.2 (t, C-3), 51.4 (d, Ph_2CH), 17.2 (d, C-1'), 11.2 (t, C-2'); MS: (EI, 70 eV) *m*/*z* 262 (M^+, 100), 261 (59), 219 (22), 192 (31), 191 (24), 167 (Ph_2CH, 32), 165 (46), 152 (20), 115 (48), 91 (32), 69 (*c*-PrCO, 31); HRMS: (EI, 70 eV) Calculated ($C_{19}H_{18}O$) 262.1358 (M^+) Found: 262.1357

(3bh) 2-Benzhydryl-1-phenyl-2-buten-1-one (*E*/*Z* mixture)



According to an experimental procedure in section 2.7., $InCl_3$ (0.1 mmol, 0.023 g), benzhydryl chloride (1 mmol, 0.201 g), and 1-methyl-3-phenyl-2-propynyl acetate (2 mmol, 0.376 g) gave the crude product. Purification was performed by flash column chromatography (hexane/EtOAc = 95:5, column length 10.5 cm, diagram 2.8 cm) and GPC to give the product (0.124 g, 40%, *E*/*Z* = 78:22). ^1H and ^{13}C NMR chart are listed below.; IR: (neat) 1650 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) *Z*-isomer: 7.84 (d, *J* = 8.0 Hz, 2H, *o*), 7.53−7.36 (m, 3H, *m* and *p*), 7.31−7.17 (m, 10H, *o'*, *m'*, and *p'*), 5.57 (q, *J* = 7.2 Hz, 1H, 3-H), 5.26 (s, 1H, Ph_2CH), 1.57 (d, *J* = 7.2 Hz, 3H, 4-H_3); *E*-isomer: 7.53 (d, *J* = 8.0 Hz, 2H, *o*), 7.53−7.36 (m, 3H, *m* and *p*), 7.31−7.17 (m, 10H, *o'*, *m'*, and *p'*), 6.48 (q, *J* = 7.2 Hz, 1H, 3-H), 5.74 (s, 1H, Ph_2CH), 1.67 (d, *J* = 7.2 Hz, 3H, 4-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 199.2 (s), 198.0 (s), 143.8 (s), 143.4 (s), 142.0 (s), 141.9 (s), 141.4 (d), 138.9 (s), 137.4 (s), 132.9 (d), 131.6 (d), 130.9 (d), 129.5 (d), 129.4 (d), 129.2 (d), 129.1 (d), 128.5 (d), 128.3 (d), 128.2 (d), 128.0 (d), 126.6 (d), 126.2 (d), 55.2 (d), 49.7 (d), 15.9 (q), 15.2 (q); *E*-isomer MS: (EI, 70 eV) *m*/*z* 313 (24), 312 (M^+, 100), 311 (44), 206 (27), 165 (21), 105 (PhCO, 49), 77 (C_6H_5, 49); HRMS: (EI, 70 eV) Calculated ($C_{23}H_{20}O$) 312.1514 (M^+) Found: 312.1502; *Z*-isomer MS: (EI, 70 eV) *m*/*z* 313 (26), 312 (M^+, 100), 311 (47), 206 (26), 105 (PhCO, 55), 77 (C_6H_5, 26); HRMS: (EI, 70 eV) Calculated ($C_{23}H_{20}O$) 312.1514 (M^+) Found: 312.1513

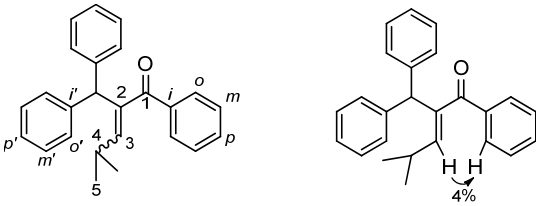
(3bi) 2-Benzhydryl-1-phenyl-2-penten-1-one (*E*/*Z* mixture)



According to an experimental procedure in section 2.8., $InCl_3$ (0.05 mmol, 0.011 g), benzhydryl chloride (0.43 mmol, 0.0873 g), and 1-ethyl-3-phenyl-2-propynyl acetate (2.36 mmol, 0.4733 g)

gave the crude product. Purification was performed by flash column chromatography (hexane/EtOAc = 95:5, column length 10.5 cm, diagram 2.8 cm). Further purification was performed by distillation under reduced pressure to give the product (0.059 g, 43%, *E*/*Z* = 89:11). ^{1}H and ^{13}C NMR chart are listed below.; IR: (neat) 1650 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) *Z*-isomer: 7.83 (d, *J* = 8.0 Hz, 2H, *o*), 7.52−7.46 (m, 1H, *p*), 7.43−7.36 (m, 2H, *m*), 7.30−7.17 (m, 10H, *o'*, *m'*, and *p'*), 5.47 (t, *J* = 7.6 Hz, 1H, 3-H), 5.23 (s, 1H, Ph_2CH), 1.93 (quint, *J* = 7.6 Hz, 2H, 4-H_2), 0.87 (t, *J* = 7.6 Hz, 3H, 5-H_3); *E*-isomer: 7.68 (d, *J* = 7.6 Hz, 2H, *o*), 6.32 (t, *J* = 7.6 Hz, 1H, 3-H), 5.73 (s, 1H, Ph_2CH), 2.10 (quint, *J* = 7.6 Hz, 2H, 4-H_2), 0.83 (t, *J* = 7.6 Hz, 3H, 5-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 199.2 (s), 198.2 (s), 148.6 (s), 142.1 (s), 141.9 (s), 138.9 (s), 137.8 (d), 137.5 (s), 132.9 (d), 131.7 (d), 129.6 (d), 129.5 (d), 129.4 (d), 129.13 (d), 129.07 (d), 128.5 (d), 128.3 (d), 128.2 (d), 128.0 (d), 126.6 (d), 126.2 (d), 55.0 (d), 49.9 (d), 23.4 (t), 22.8 (t), 13.4 (q), 12.8 (q); *E*-isomer MS: (EI, 70 eV) *m*/*z* 327 (24), 326 (M^+, 100), 325 (36), 297 (M^+ - Et, 52), 219 (18), 167 (Ph_2CH, 29), 105 (PhCO, 58), 77 (C_6H_5, 20); HRMS: (EI, 70 eV) Calculated ($C_{24}H_{22}O$) 326.1671 (M^+) Found: 326.1670; *Z*-isomer MS: (EI, 70 eV) *m*/*z* 327 (25), 326 (M^+, 100), 297 (53), 219 (21), 167 (Ph_2CH, 21), 105 (PhCO, 60), 77 (C_6H_5, 22); HRMS: (EI, 70 eV) Calculated ($C_{24}H_{22}O$) 326.1671 (M^+) Found: 326.1676

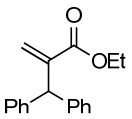
(3bj) 2-Benzhydryl-4-methyl-1-phenyl-2-penten-1-one (*E*/*Z* mixture)



According to an experimental procedure in section 2.8., $InCl_3$ (0.05 mmol, 0.012 g), benzhydryl chloride (0.47 mmol, 0.0953 g), and 1-isopropyl-3-phenyl-2-propynyl acetate (2.50 mmol, 0.5402 g) gave the crude product. Purification was performed by flash column chromatography (hexane/EtOAc = 95:5, column length 10.5 cm, diagram 2.8 cm). Further purification was performed by distillation under reduced pressure to give the product (0.019 g, 12%, *E*/*Z* = 74:26). ^{1}H and ^{13}C NMR chart are listed below.; IR: (neat) 1654 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) *Z*-isomer: 7.84 (d, *J* = 8.0 Hz, 2H, *o*), 7.55−7.38 (m, 3H, *m* and *p*), 7.30−7.10 (m, 10H, *o'*, *m'*, and *p'*), 5.28 (d, *J* = 10.4 Hz, 3-H), 5.19 (s, 1H, Ph_2CH), 2.37−2.28 (m, 1H, 4-H), 0.88 (d, *J* = 6.8 Hz, 6H, 5-H_3 and 4-Me); *E*-isomer: 7.79 (d, *J* = 7.6 Hz, 2H, *o*), 7.55−7.38 (m, 3H, *m* and *p*), 7.30−7.10 (m, 10H, *o'*, *m'*, and *p'*), 6.10 (d, *J* = 10.8 Hz, 3-H), 5.74 (s, 1H, Ph_2CH), 2.73−2.64 (m, 1H, 4-H), 0.84 (d, *J* = 6.8 Hz, 6H, 5-H_3 and 4-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 199.3 (s), 198.3 (s), 153.2 (d), 142.7 (d), 142.3 (s), 141.3 (s), 140.1 (s), 139.5 (s), 138.8 (s), 137.4 (s), 132.9 (d), 131.7 (d), 129.7 (d), 129.4 (d), 129.1 (d), 128.6 (d), 128.4 (d), 128.3 (d), 128.2 (d), 128.0 (d), 126.5 (d), 126.2 (d), 54.9 (d), 50.1 (d),

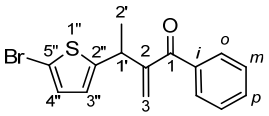
29.0 (d), 28.4 (d), 22.6 (q), 21.6 (q); *Z*-isomer MS: (EI, 70 eV) *m*/*z* 341 (28), 340 (M^+, 100), 298 (21), 297 (M^+ - *i*-Pr, 70), 167 (Ph_2CH, 51), 165 (23), 105 (PhCO, 78), 77 (C_6H_5, 24); HRMS: (EI, 70 eV) Calculated ($C_{25}H_{24}O$) 340.1827 (M^+) Found: 340.1819; *E*-isomer MS: (EI, 70 eV) *m*/*z* 341 (28), 340 (M^+, 100), 297 (M^+ - *i*-Pr, 75), 167 (Ph_2CH, 28), 105 (PhCO, 82), 77 (C_6H_5, 24); HRMS: (EI, 70 eV) Calculated ($C_{25}H_{24}O$) 340.1827 (M^+) Found: 340.1827

(3bk) Ethyl 2-(1,1-diphenylethyl)-2-propenate[18]



According to a typical procedure, $InCl_3$ (0.05 mmol, 0.011 g), benzhydryl chloride (0.5 mmol, 0.100 g), and 3-acetoxy-1-ethoxy-1-propyne (1 mmol, 0.142 g) gave the crude product. Purification was performed by flash column chromatography (hexane/EtOAc = 95:5, column length 10.5 cm, diagram 2.8 cm). Further purification was performed by distillation under reduced pressure to give the product (0.068 g, 51%). ^{1}H and ^{13}C NMR chart are listed below.

(7) 2-{1-(5-Bromo-2-thienyl)ethyl}-1-phenylpropen-1-one



According to an experimental procedure in section 2.9., $InCl_3$ (0.06 mmol, 0.013 g), 1-acetoxyethyl-5-bromothiophene (0.50 mmol, 0.124 g), and 3-phenyl-2-propynyl acetate (1.02 mmol, 0.177 g) gave the crude product. Purification was performed by flash column chromatography (hexane/EtOAc = 95:5, column length 10.5 cm, diagram 2.8 cm). Further purification was performed by distillation under reduced pressure to give the product as a white solid (0.045 g, 28%). ^{1}H and ^{13}C NMR chart are listed below.; mp: 130−132 ºC; IR: (KBr) 1658 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.73 (d, *J* = 7.6 Hz, 2H, *o*), 7.54 (t, *J* = 7.6 Hz, 1H, *p*), 7.43 (t, *J* = 7.6 Hz, 2H, *m*), 6.85 (d, *J* = 3.6 Hz, 1H, 4''-H), 6.61 (d, *J* = 3.6 Hz, 1H, 3''-H), 5.86 (s, 1H, 3-H^A), 5.70 (s, 1H, 3-H^B), 4.51 (q, *J* = 7.6 Hz, 1H, 1'-H), 1.54 (d, *J* = 7.6 Hz, 3H, 2'-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 197.2 (s, C-1), 151.0 (s, C-2), 149.5 (s, C-5''), 137.5 (s, C-*i*), 132.3 (d, C-*p*), 129.6 (d, C-*o*), 129.5 (d, C-4''), 128.2 (d, C-*m*), 124.8 (t, C-3), 124.7 (d, C-3''), 109.8 (s, C-2''), 36.3 (d, C-1'), 20.9 (q, C-2'); MS: (EI, 70 eV) *m*/*z* 322 (21), 321 (M^+, 13), 320 (20), 241 (100), 105 (PhCO, 77), 77 (C_6H_5, 53); HRMS: (EI, 70 eV) Calculated ($C_{15}H_{13}BrOS$) 319.9870 (M^+) Found: 319.9861; Analysis: $C_{15}H_{13}BrOS$ (321.23) Calcd: C, 56.08; H, 4.08; Br, 24.87 Found: C, 56.28; H, 4.10; Br, 24.67.

4. References.

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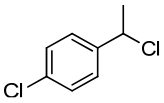
5. NMR Spectra.

1c



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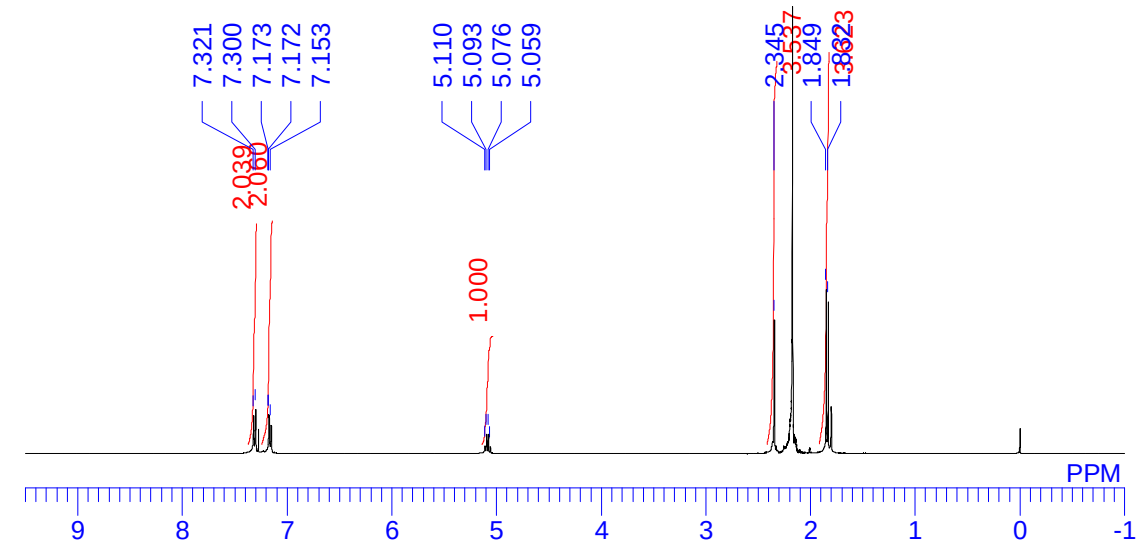

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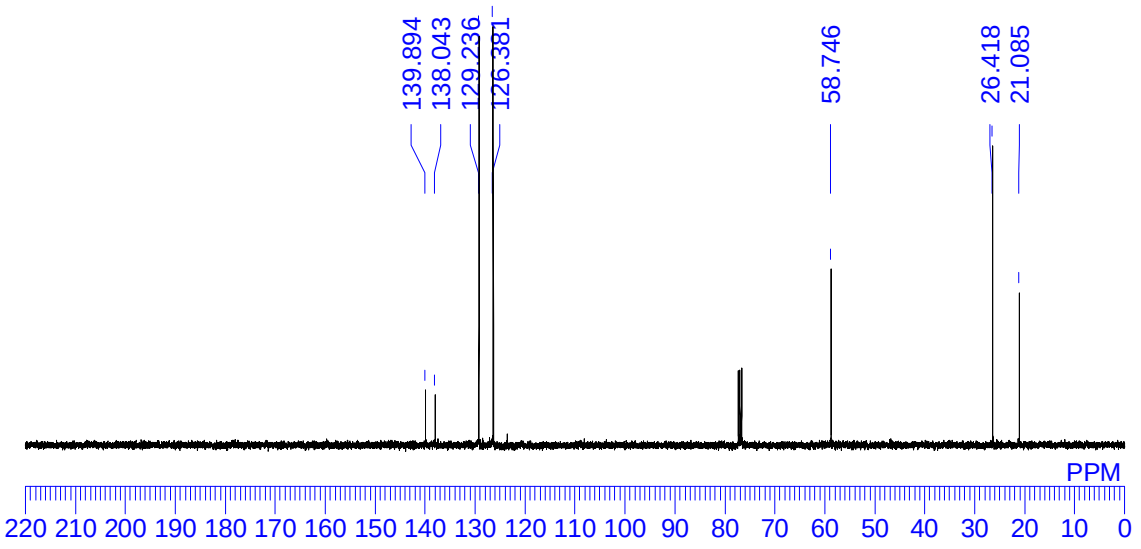

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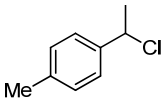

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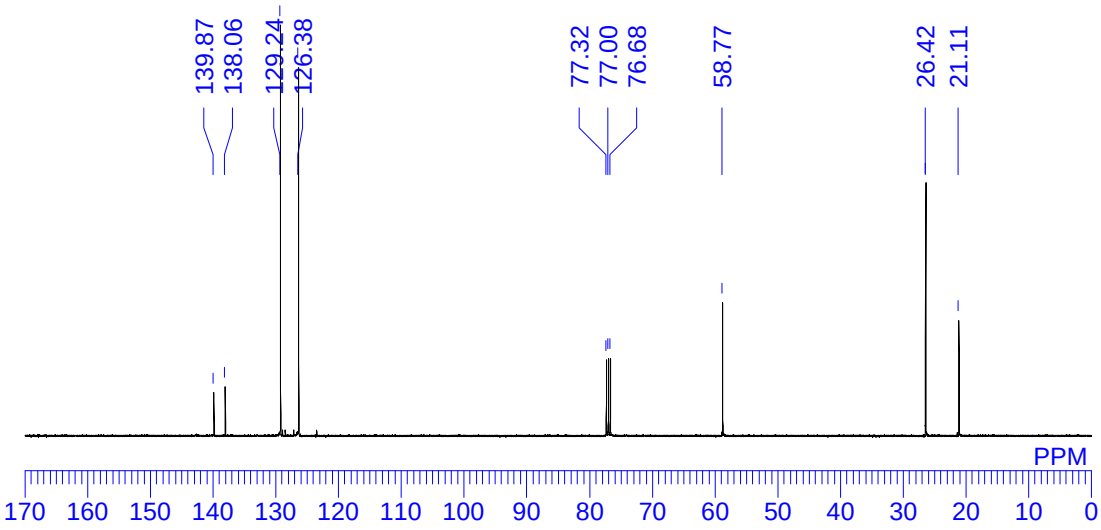

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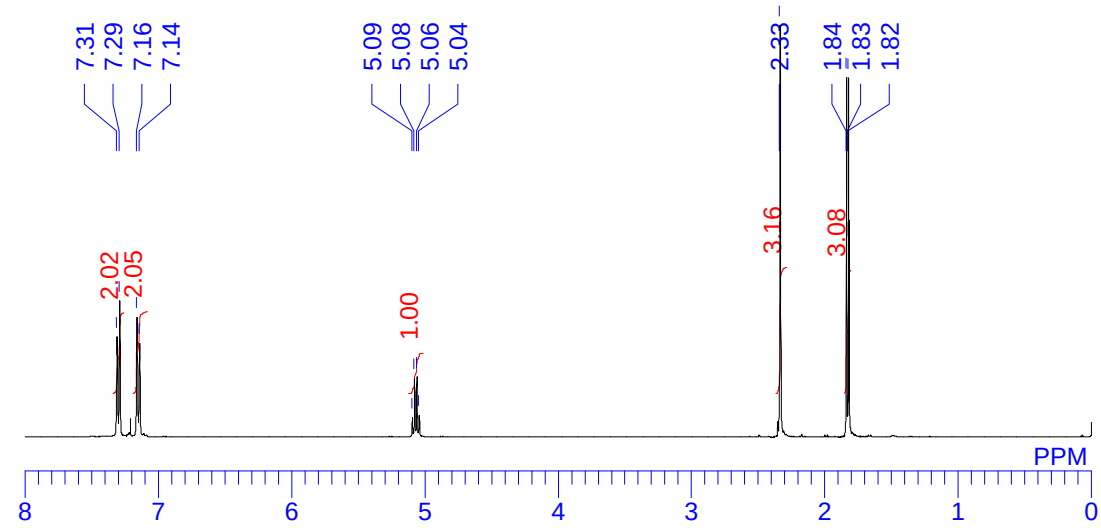

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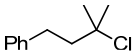

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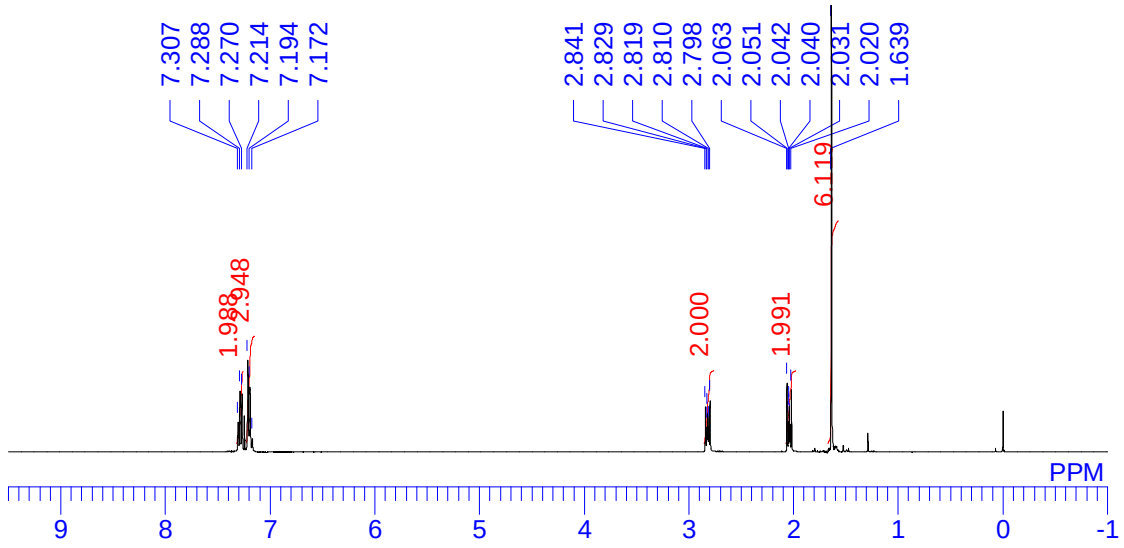

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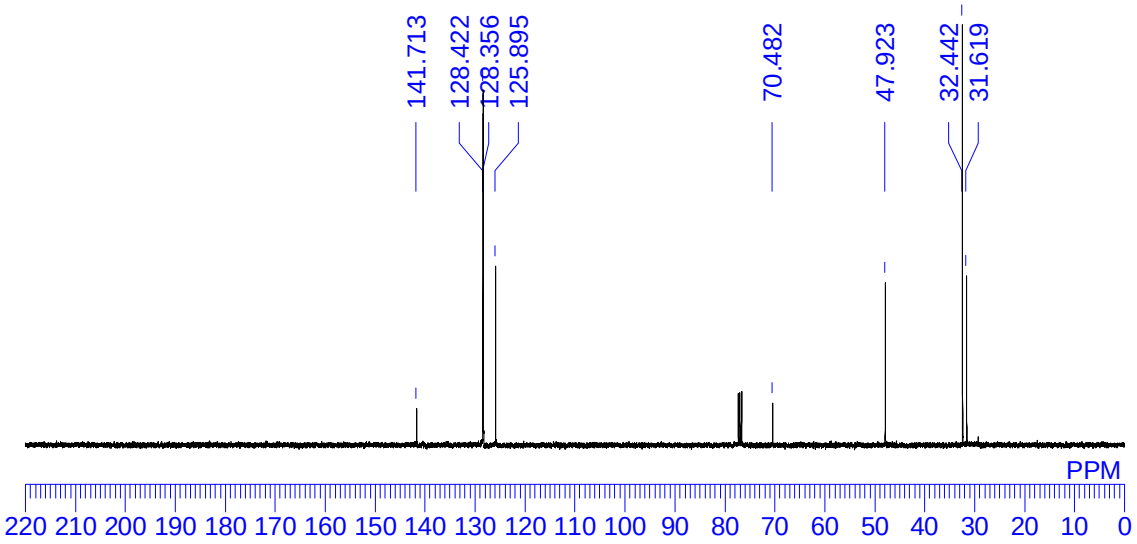

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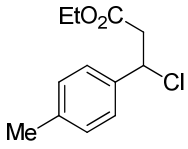

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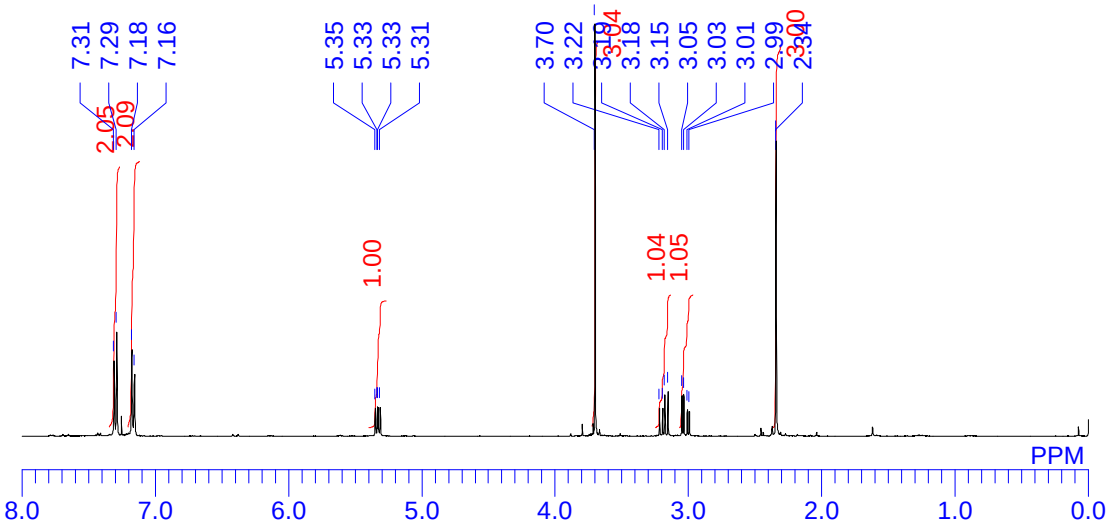

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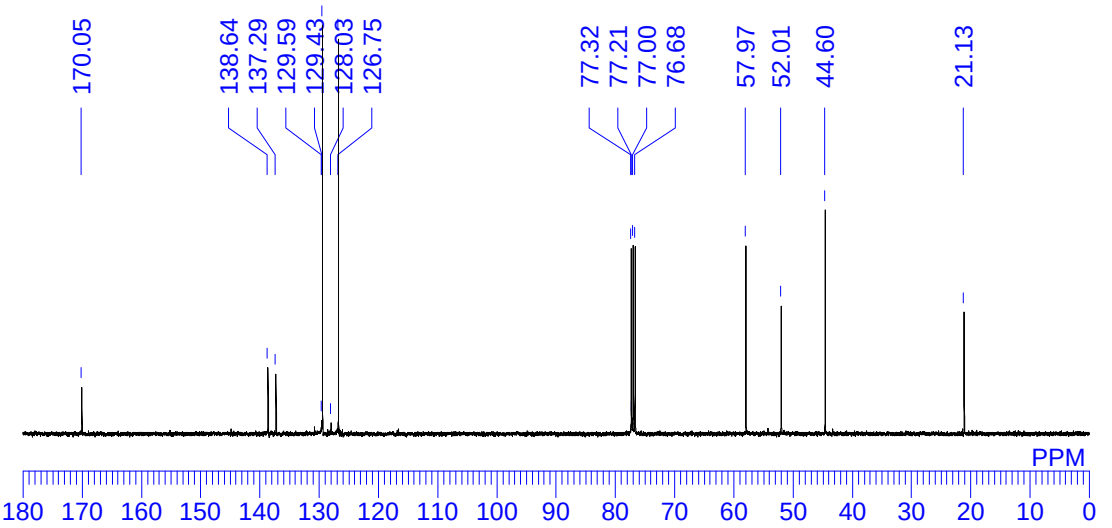

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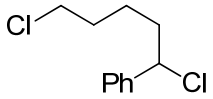

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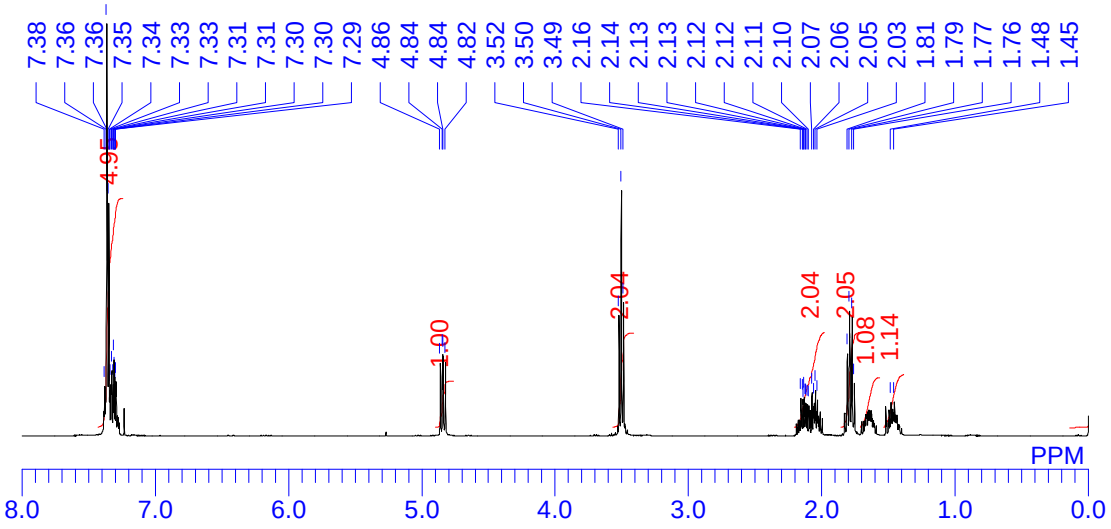

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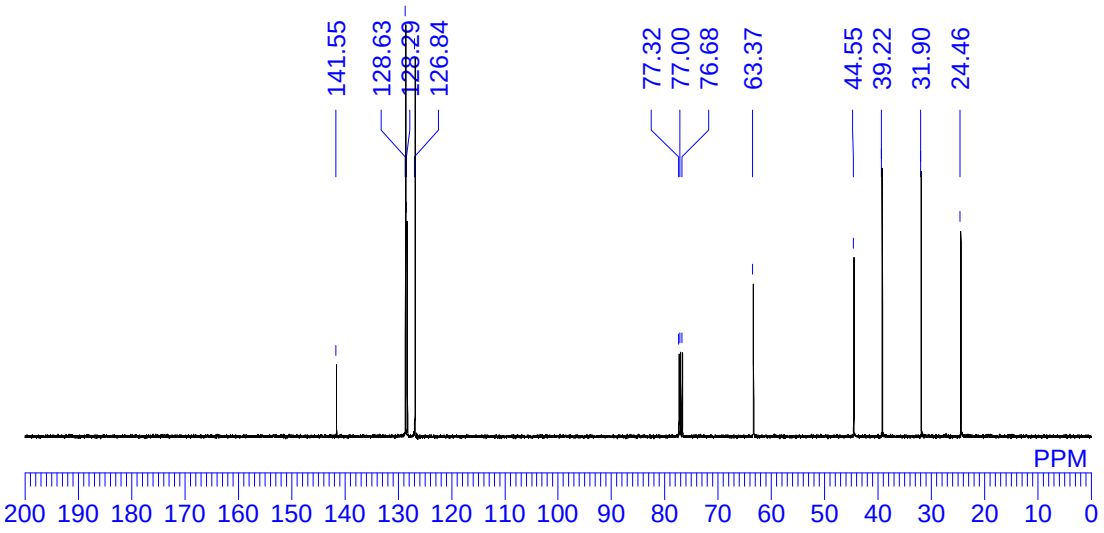

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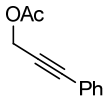

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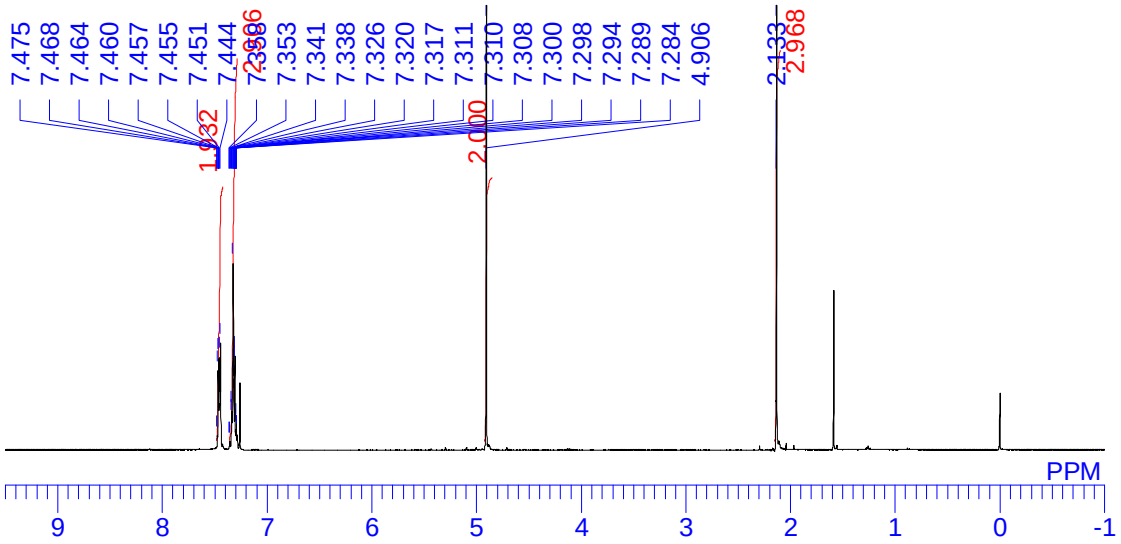

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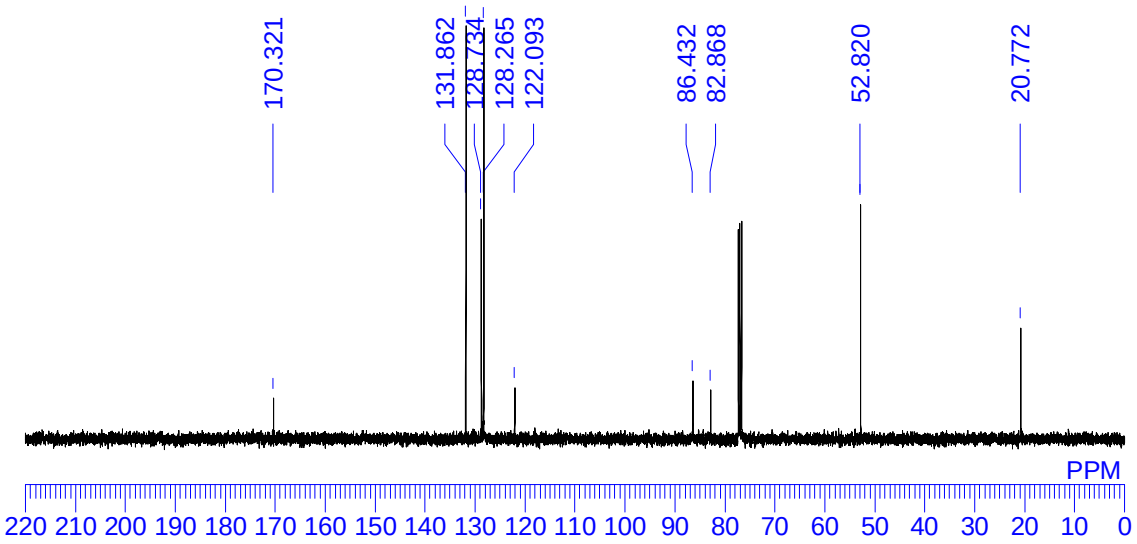

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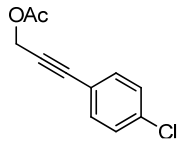

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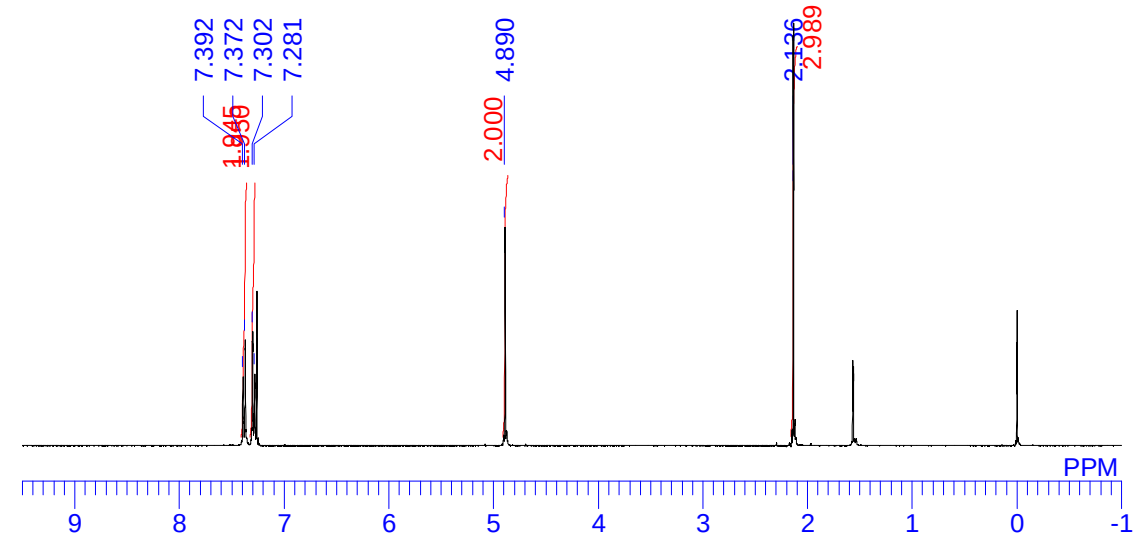

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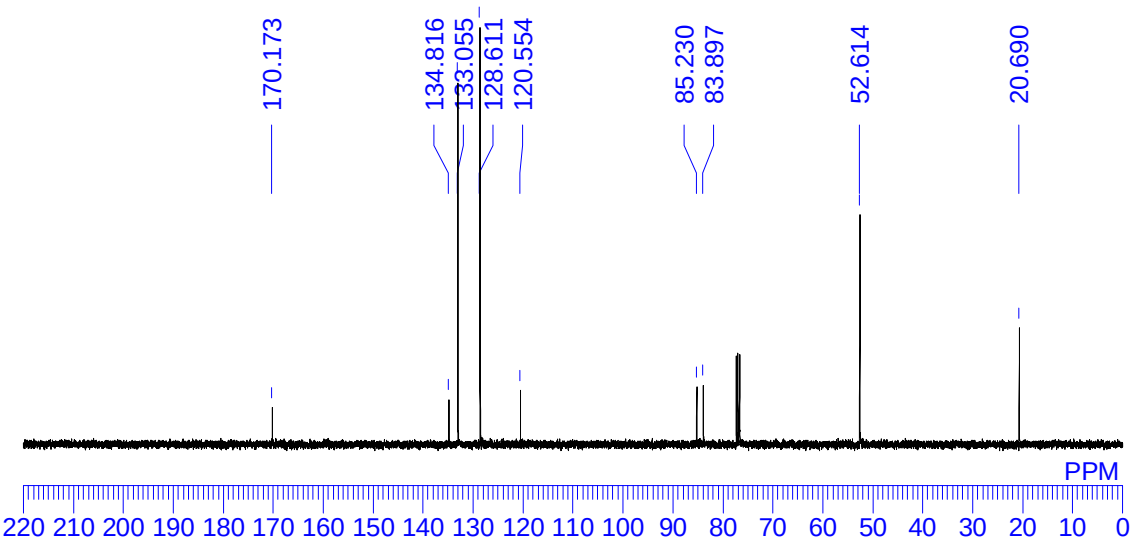

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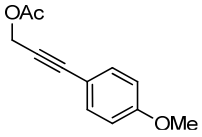

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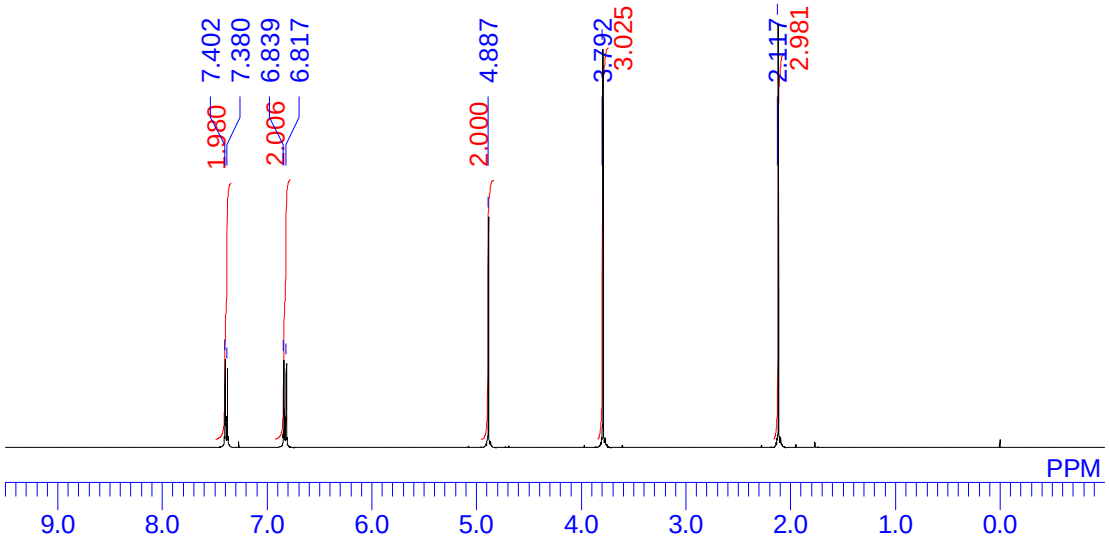

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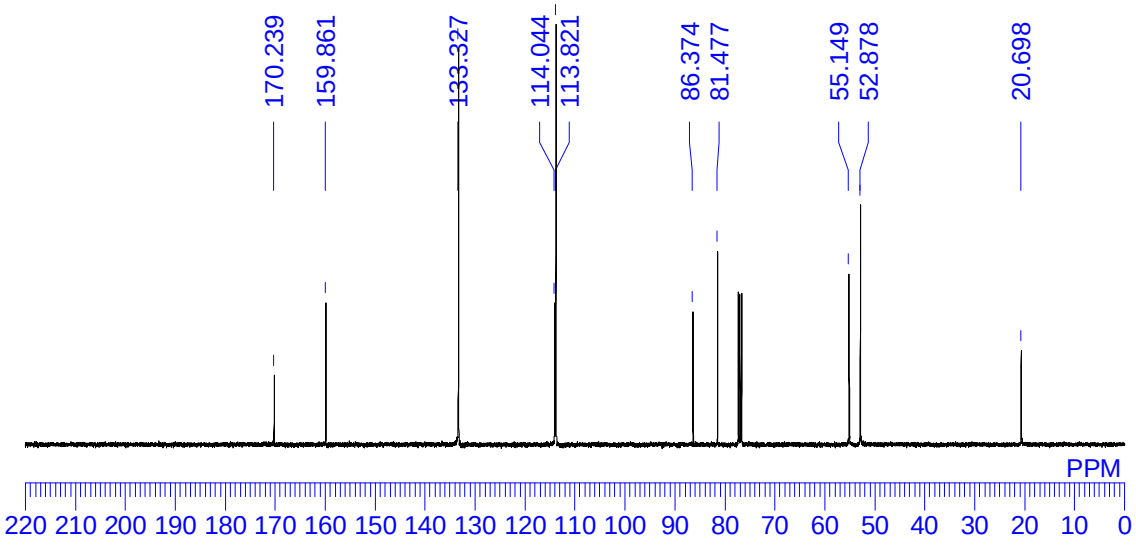

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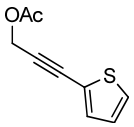

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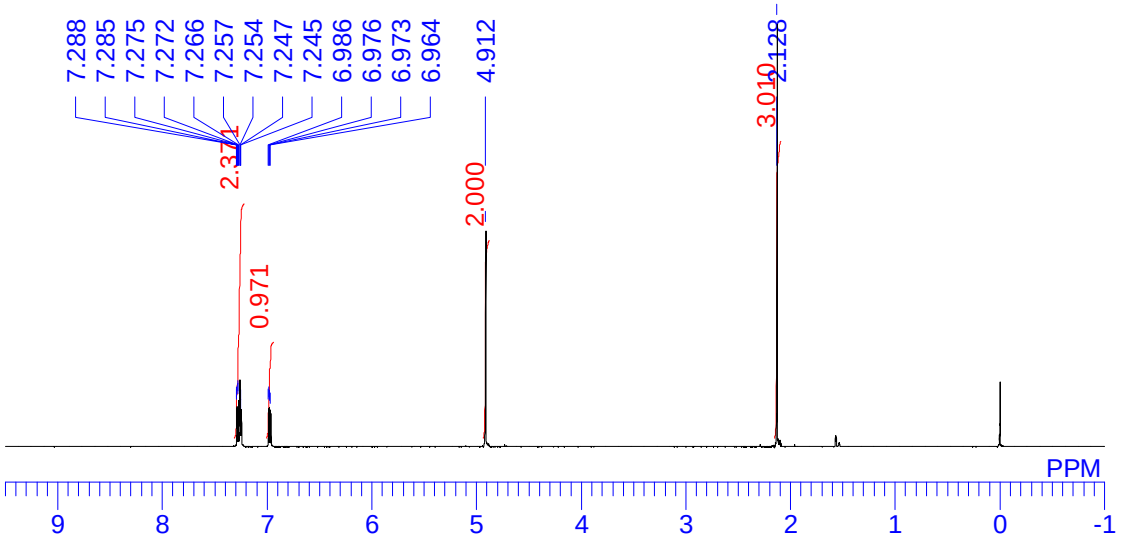

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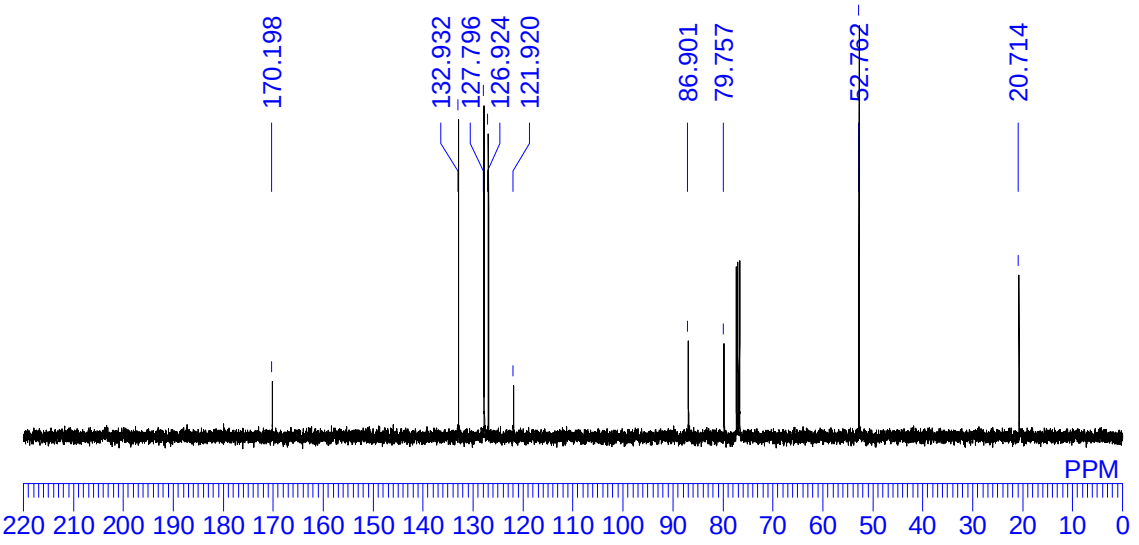

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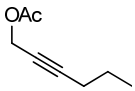

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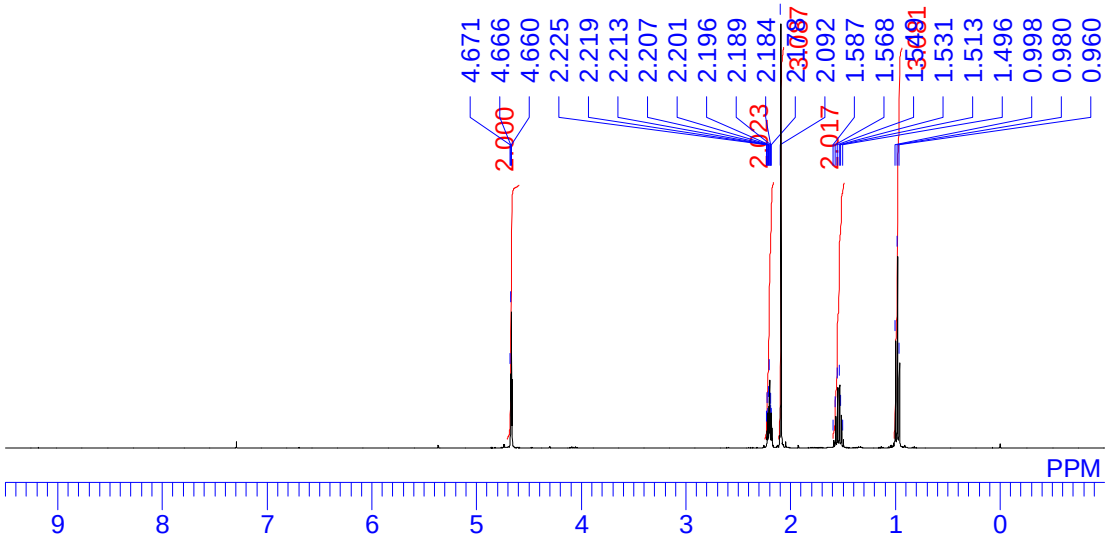

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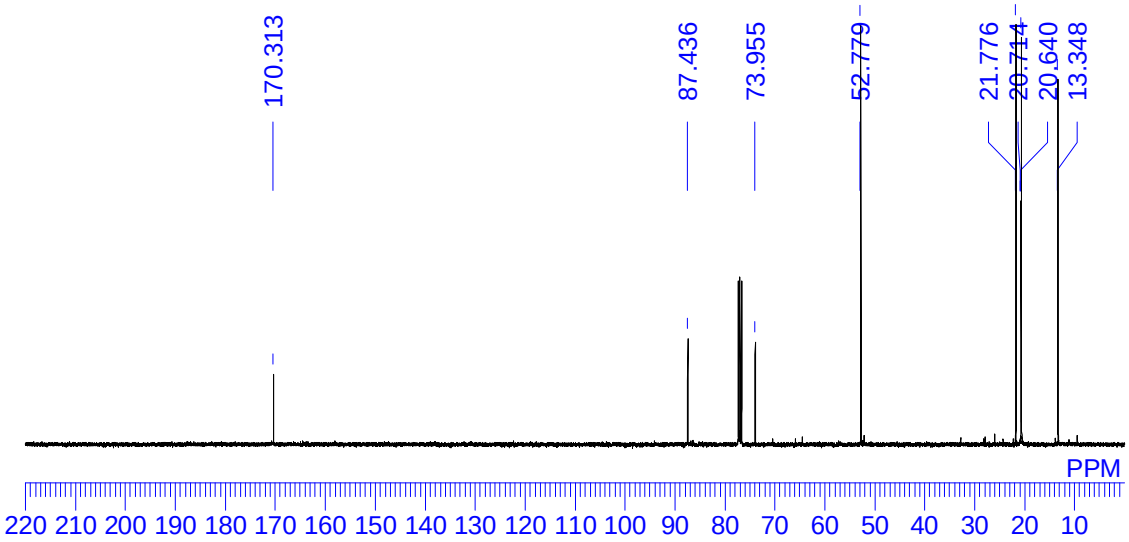

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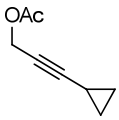

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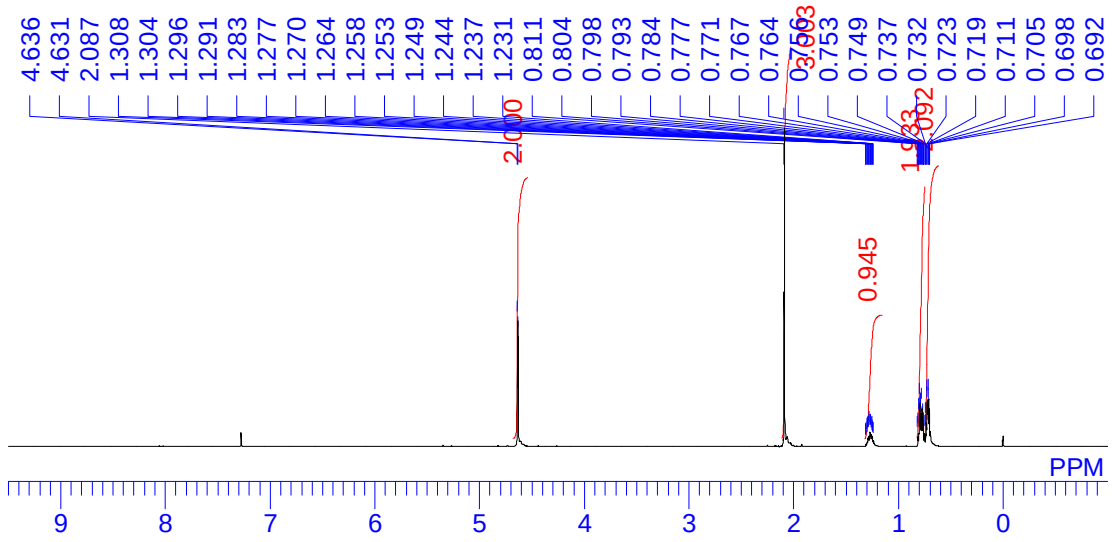

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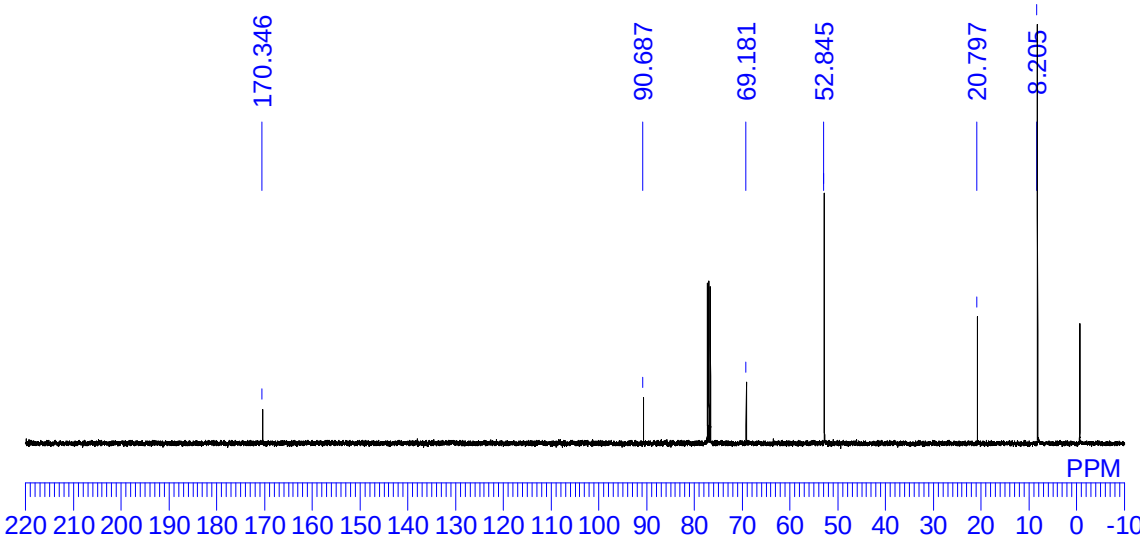

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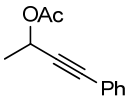

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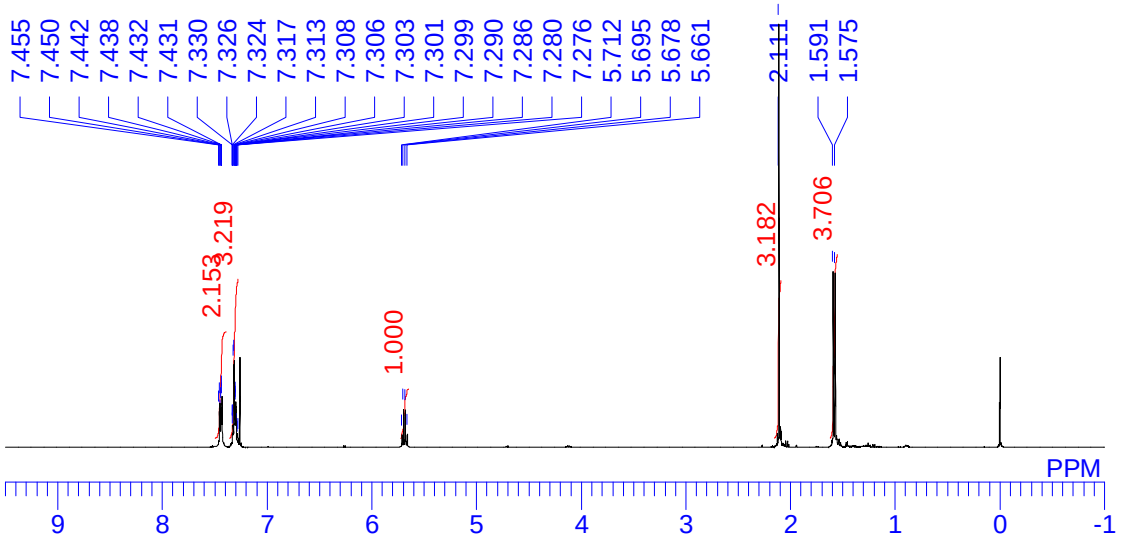

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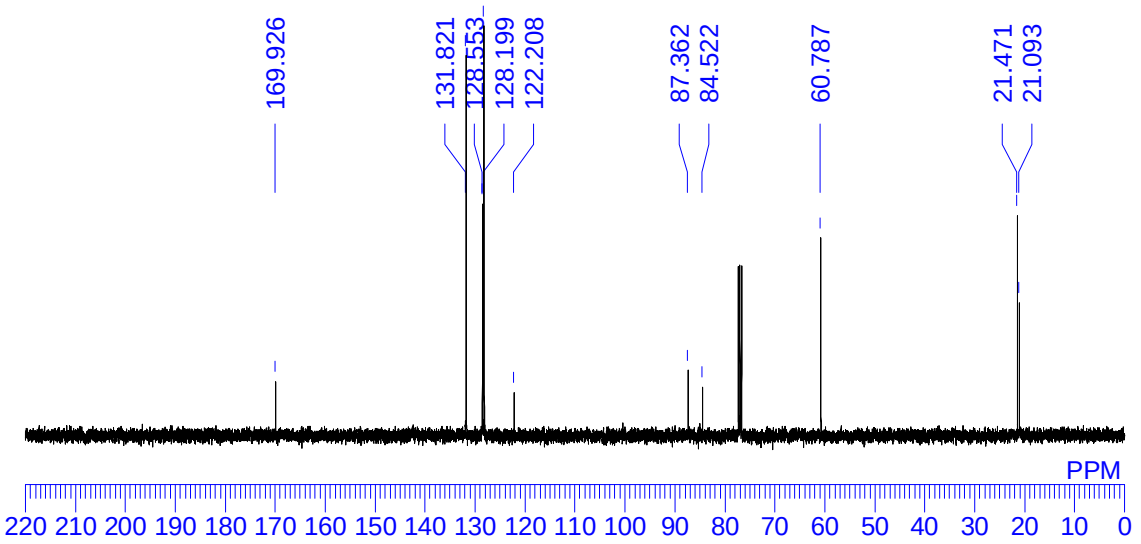

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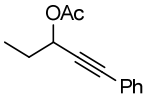

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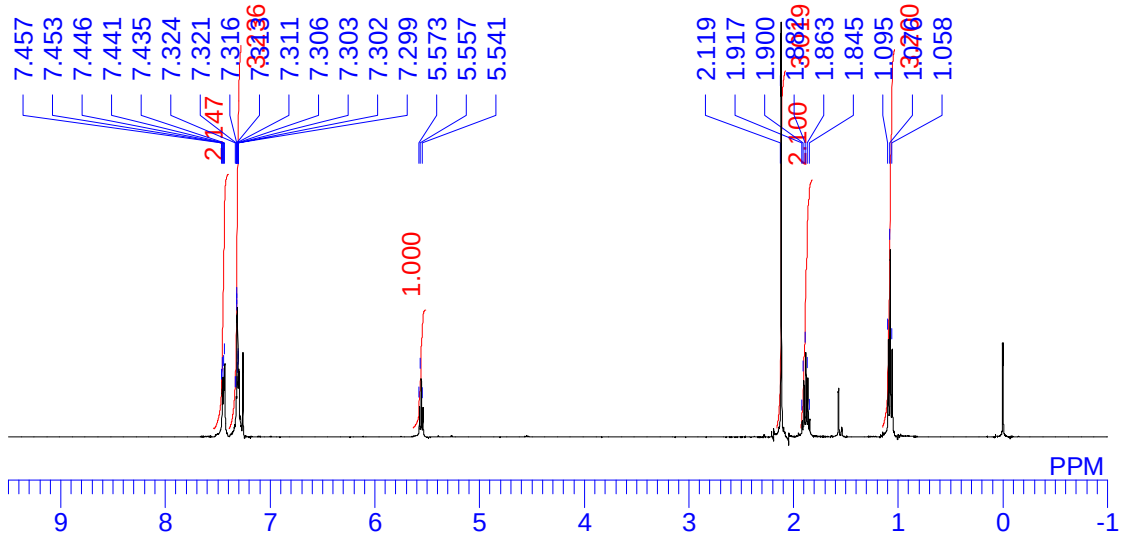

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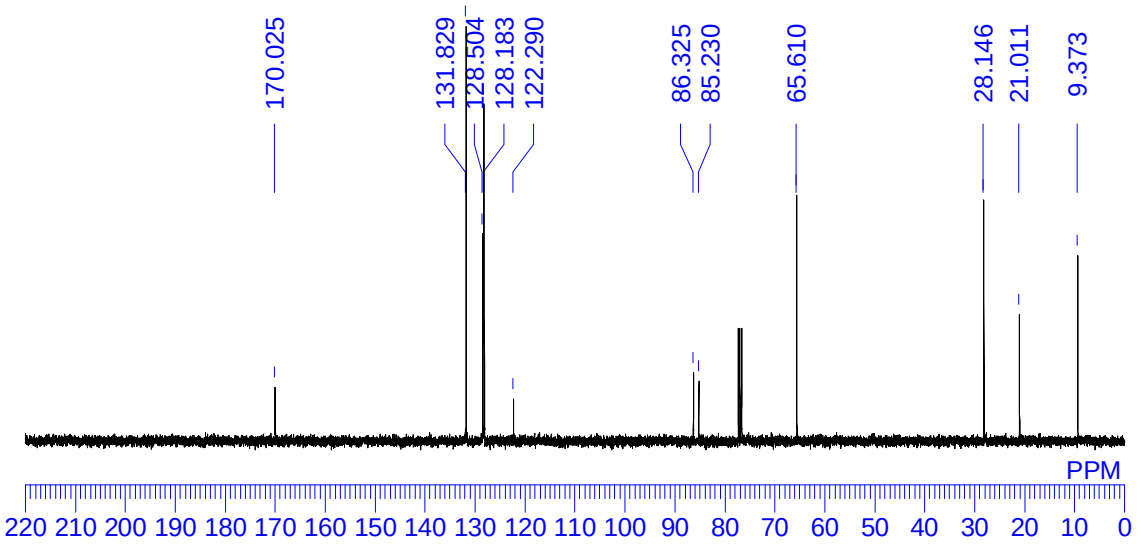

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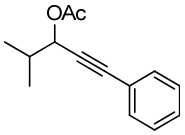

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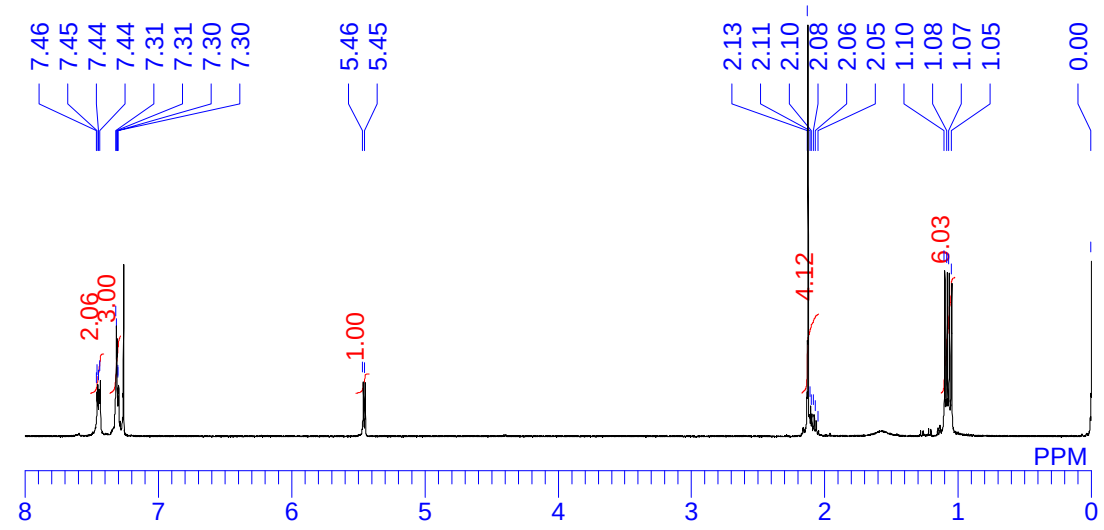

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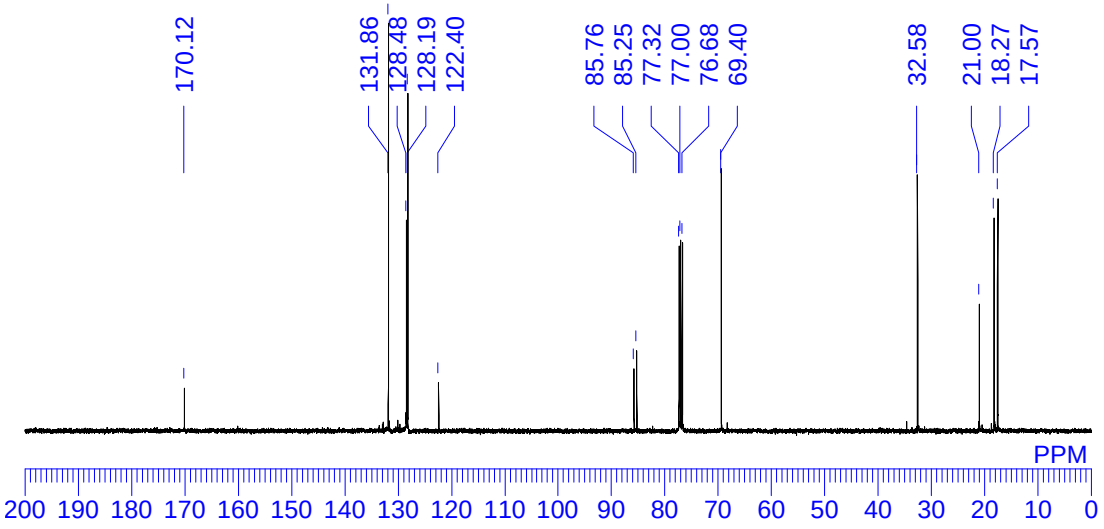

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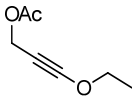

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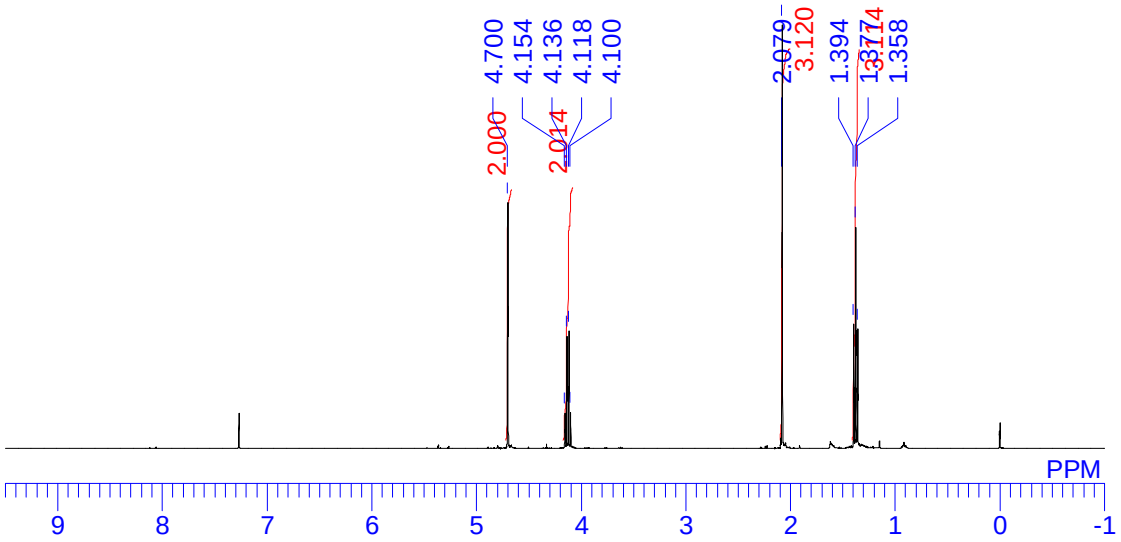
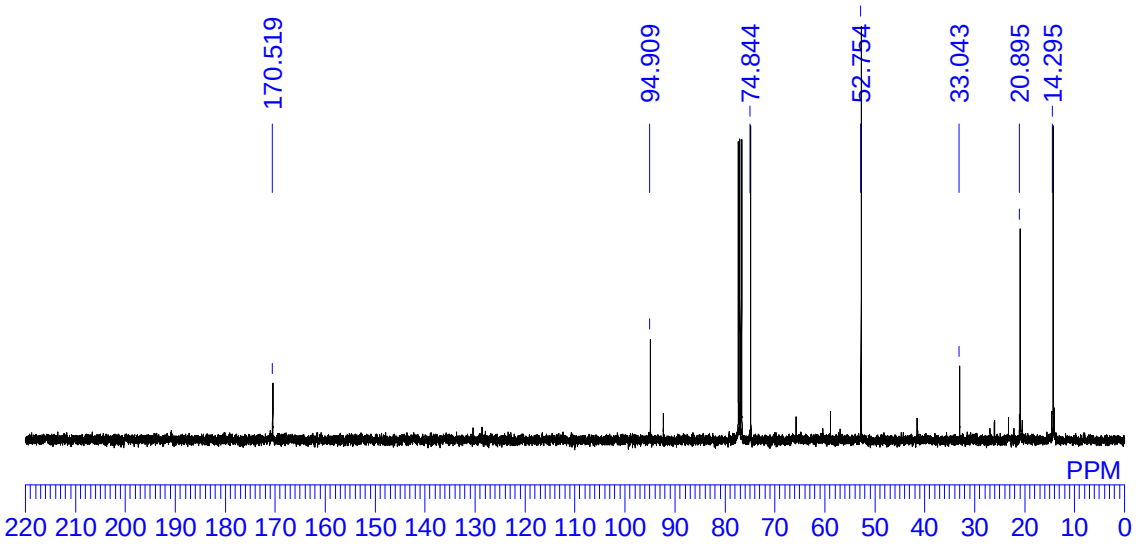


^{13}C NMR (100 MHz, $CDCl_3$)



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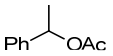
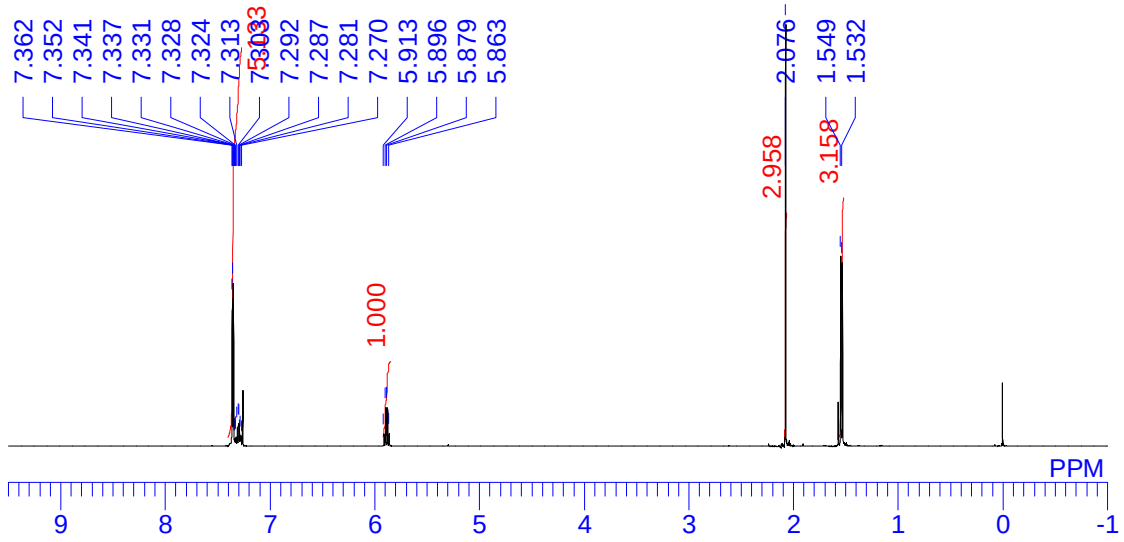
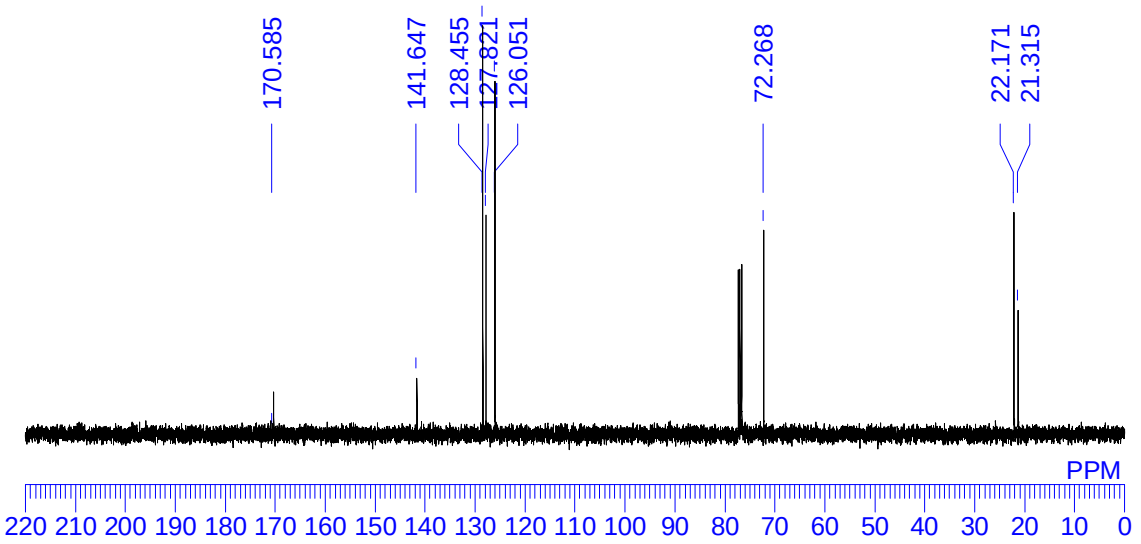


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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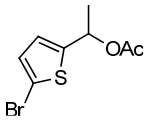
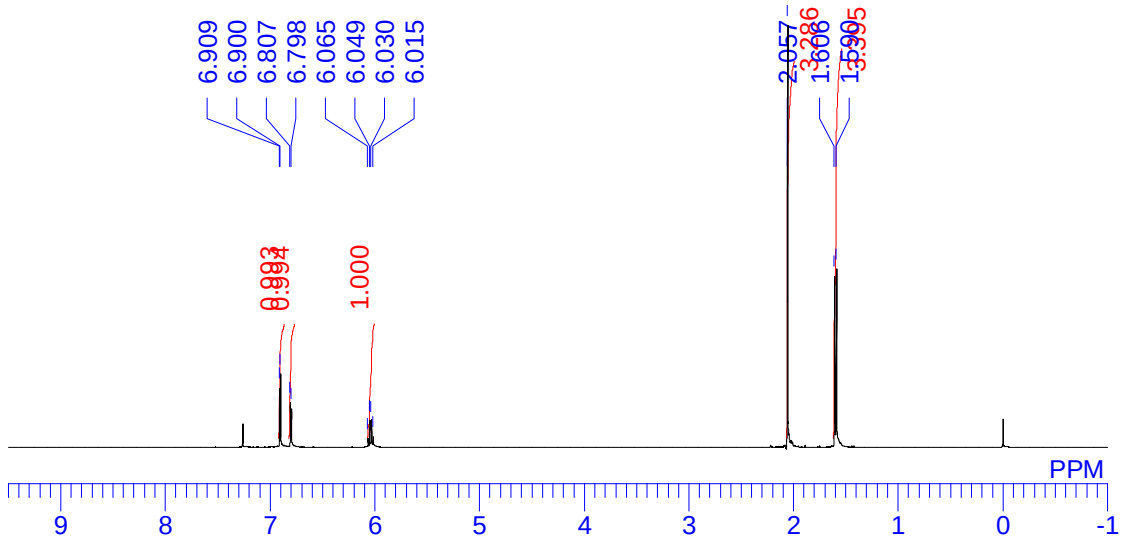
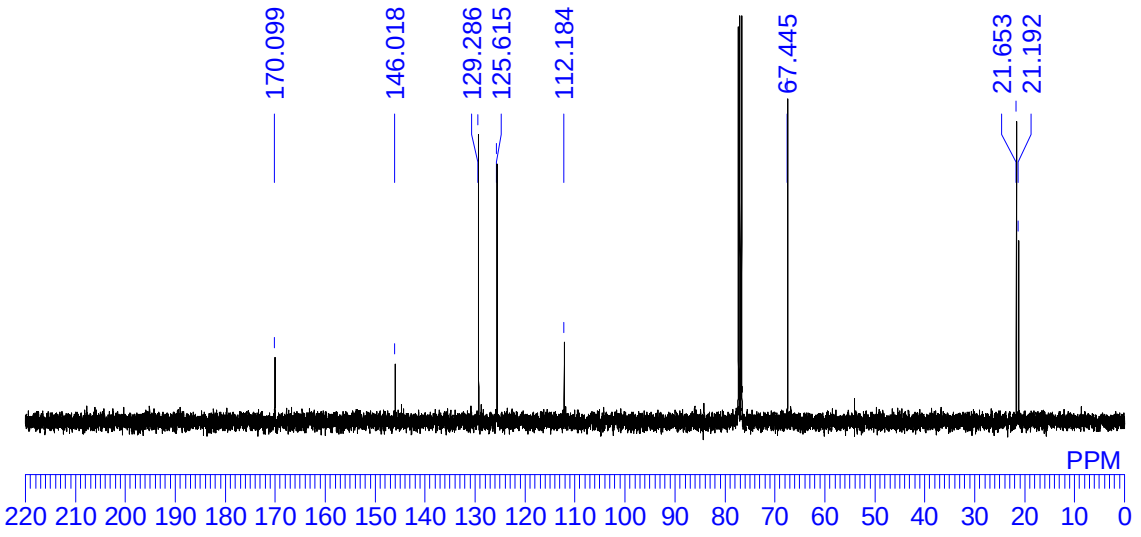


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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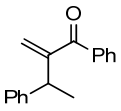
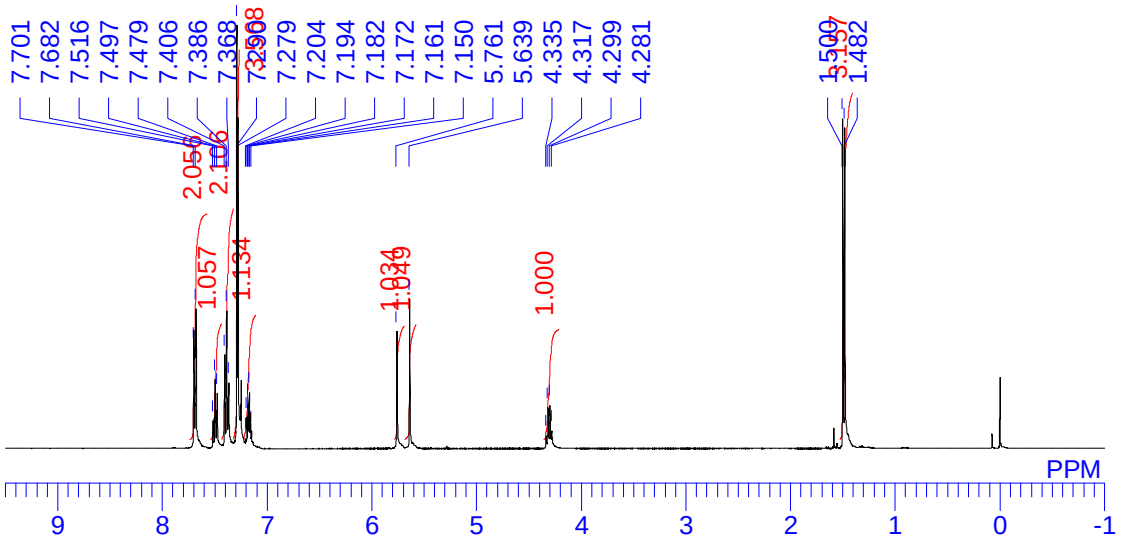
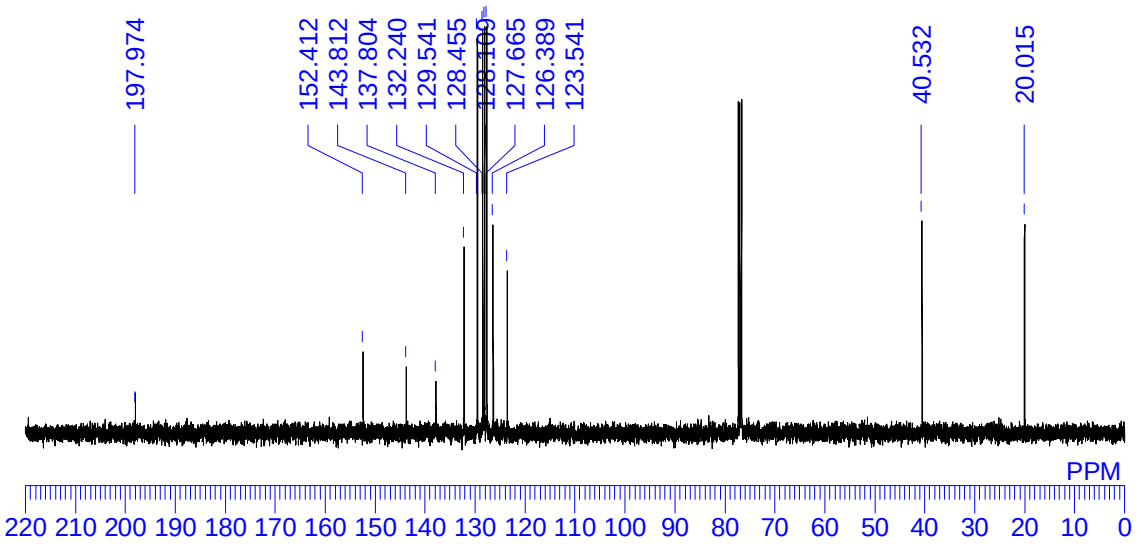


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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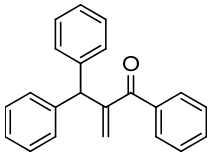
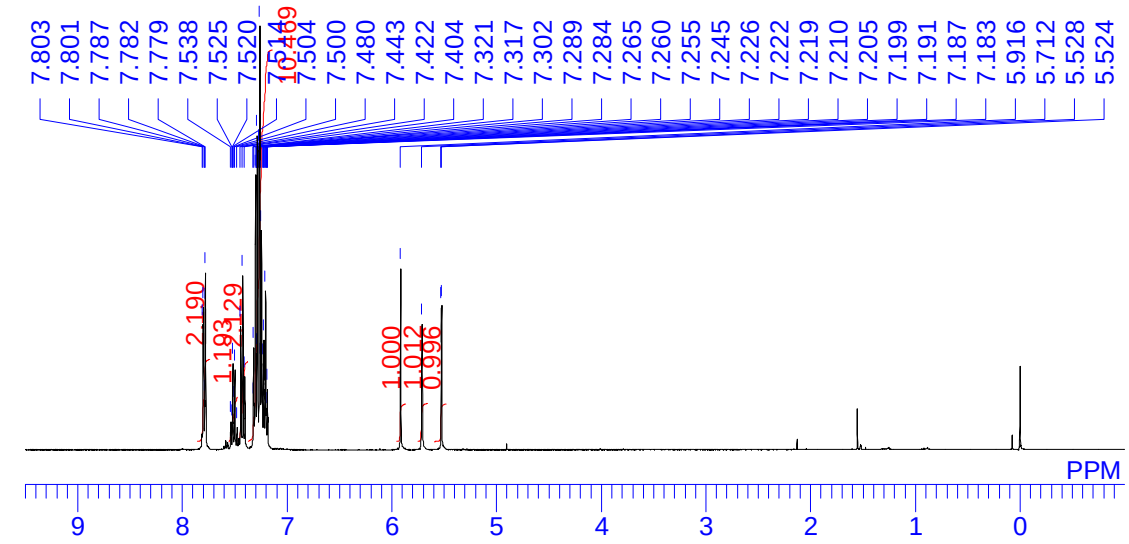
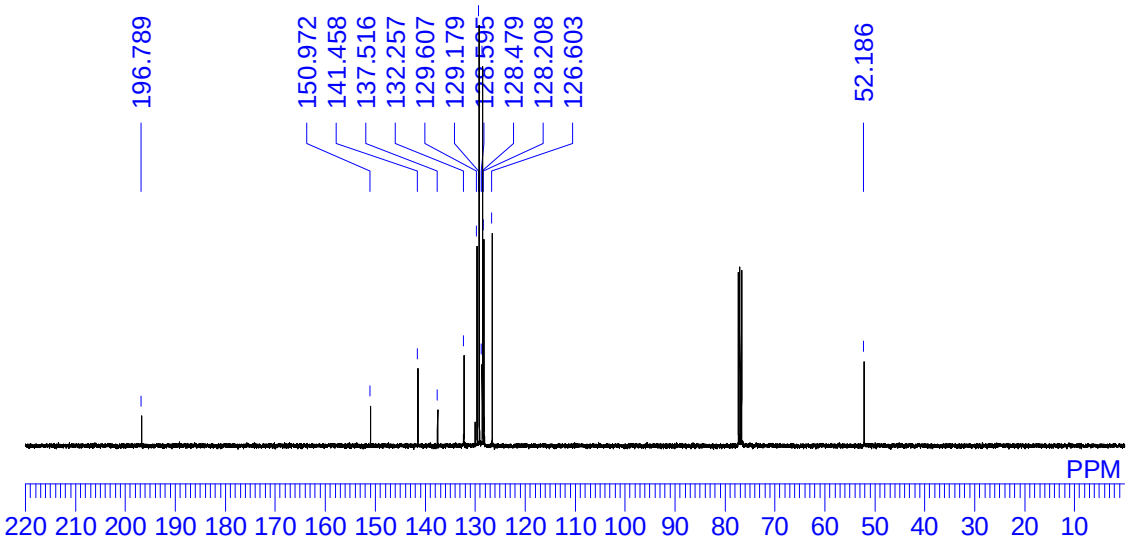


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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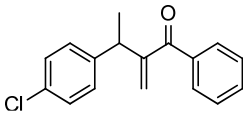
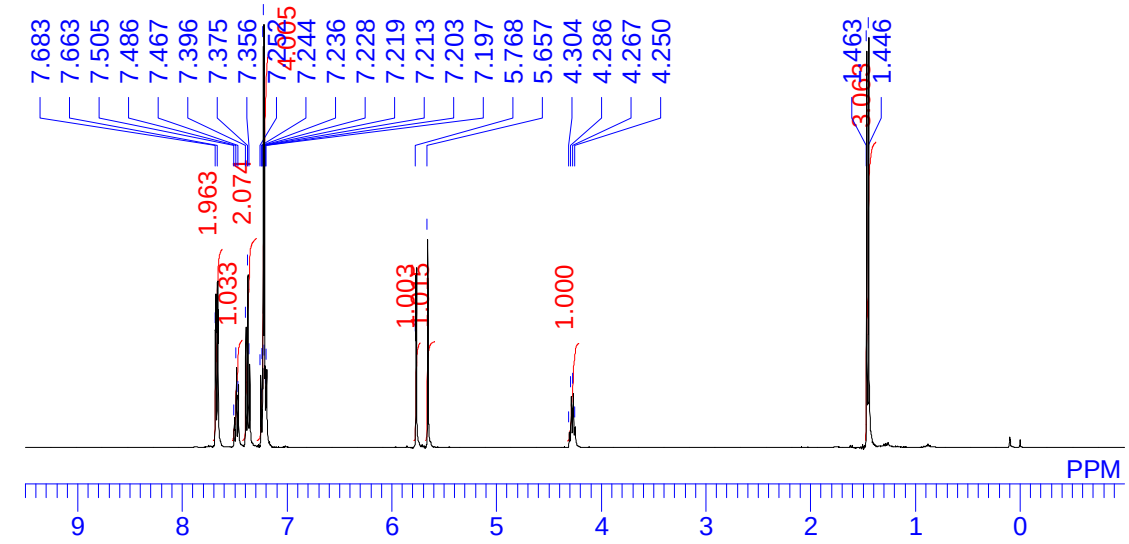
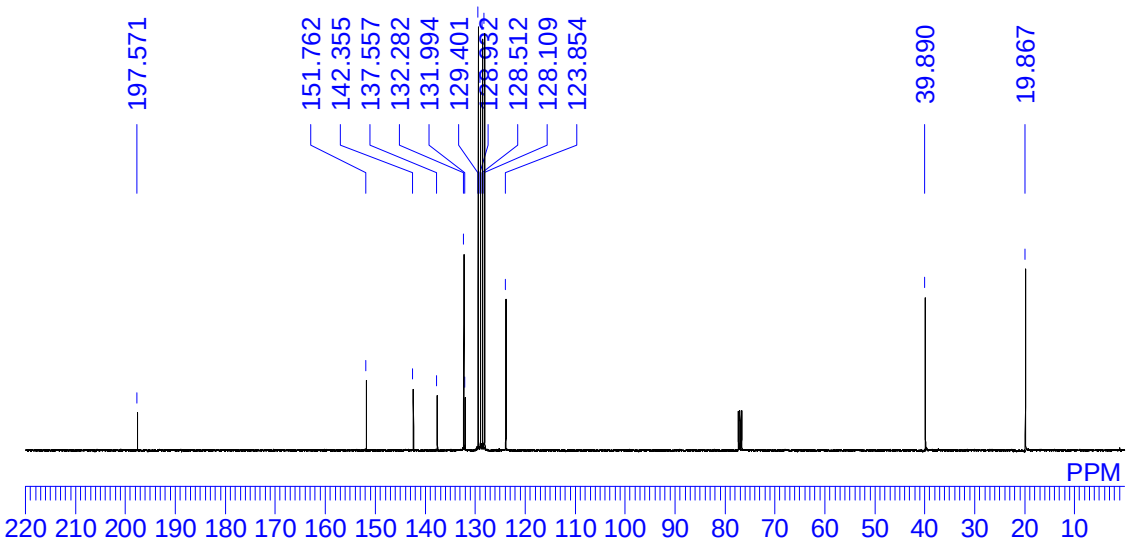


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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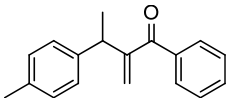
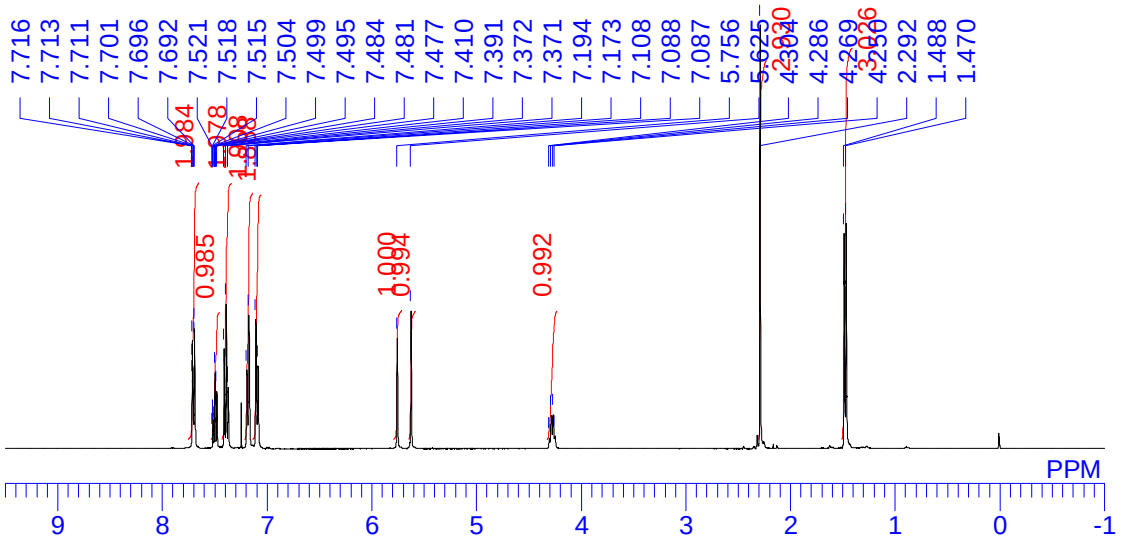
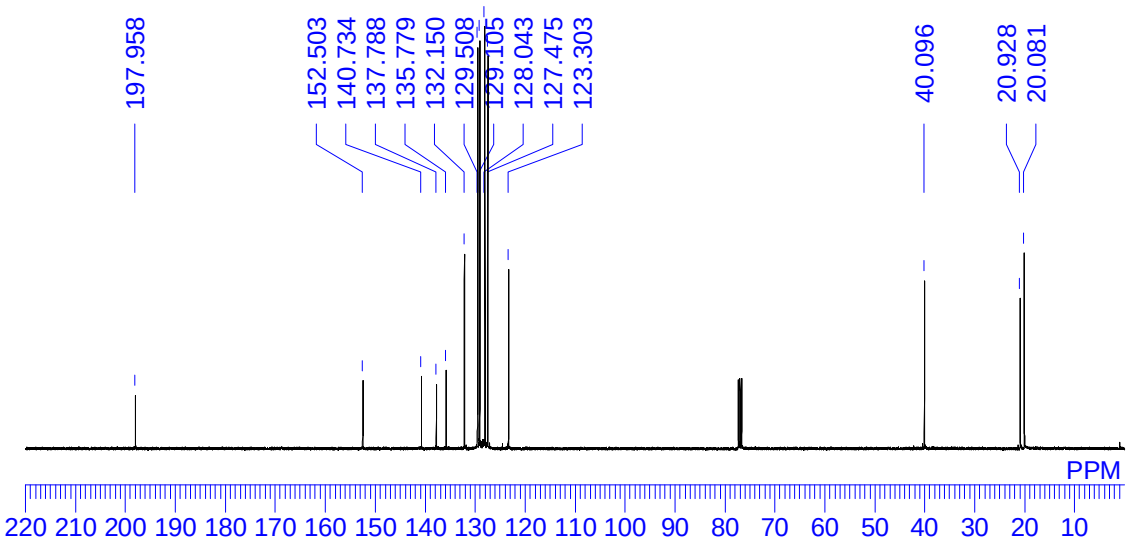


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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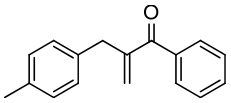
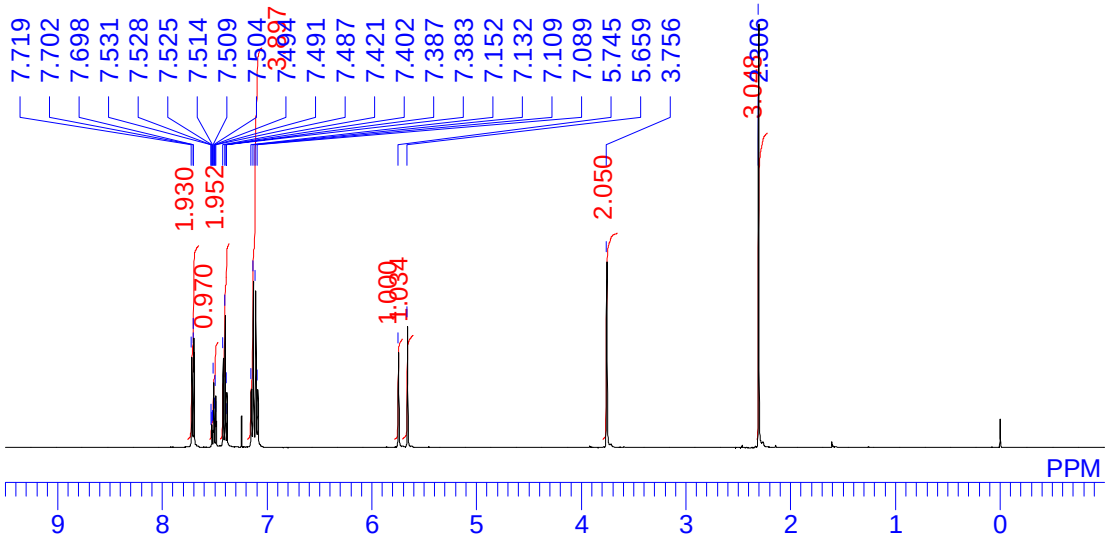
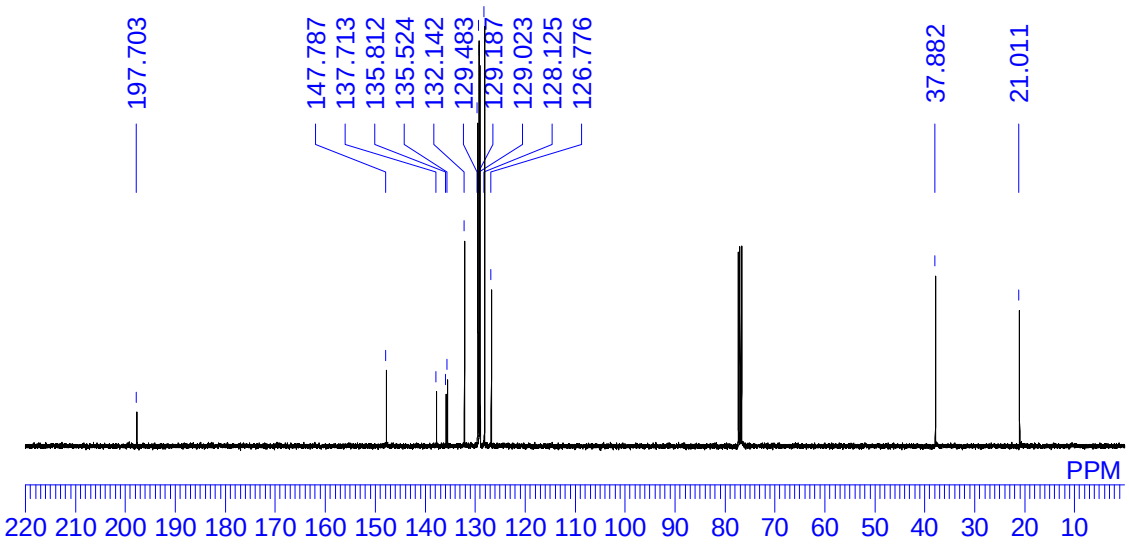


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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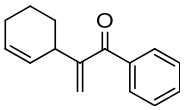
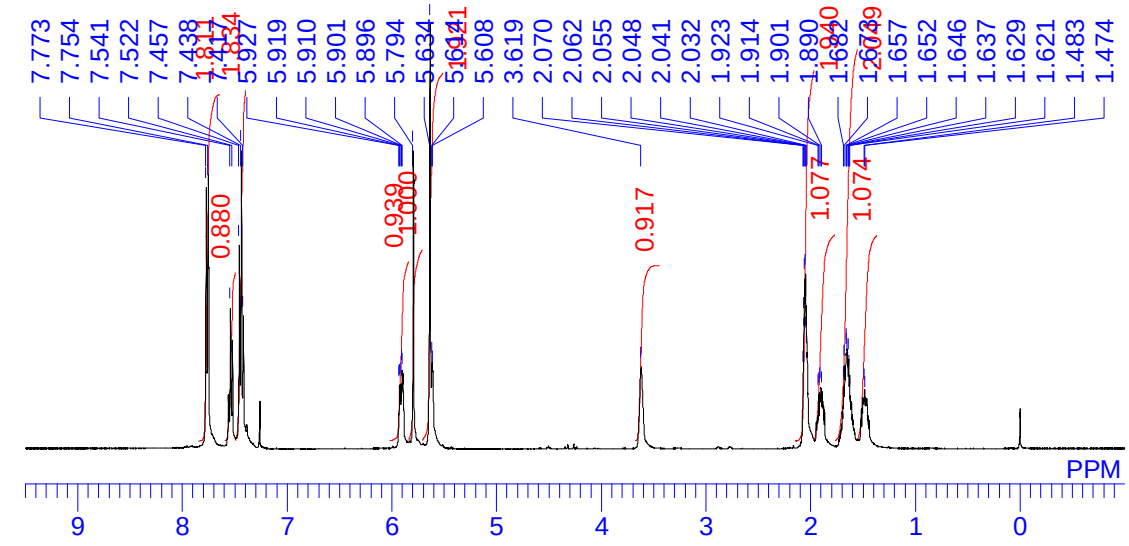
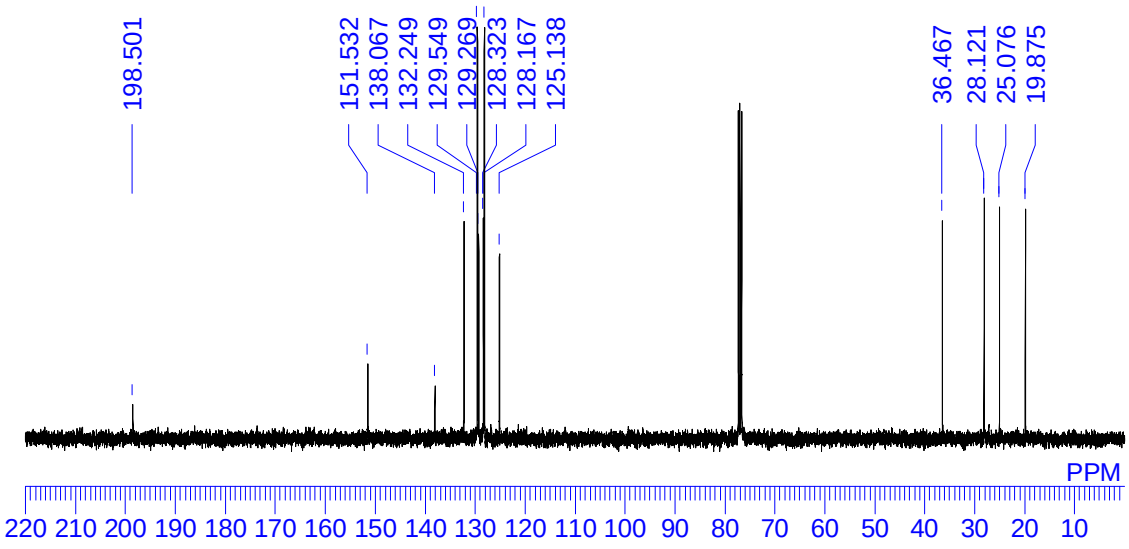


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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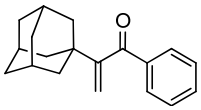
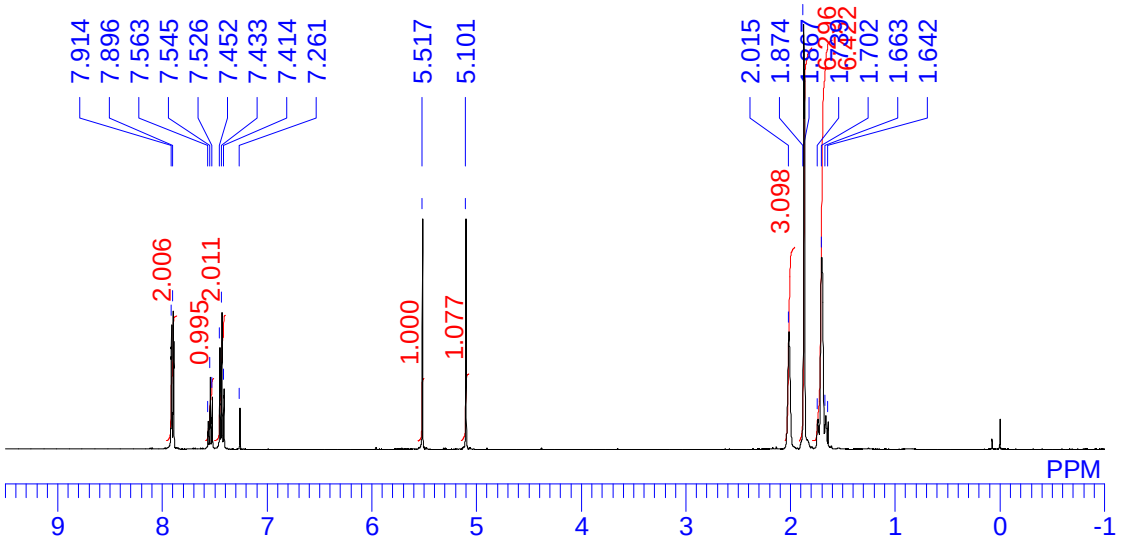
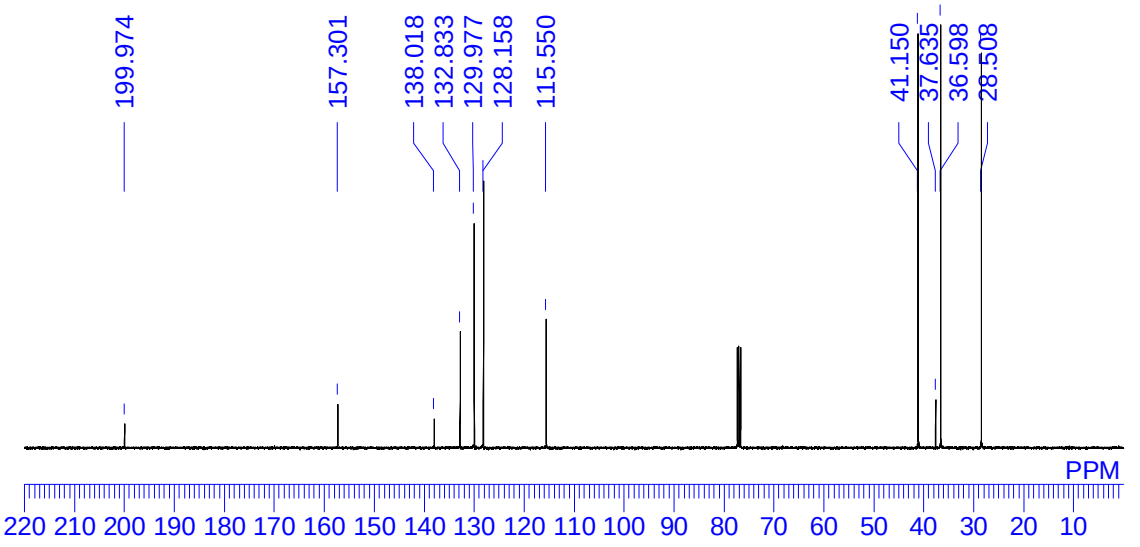


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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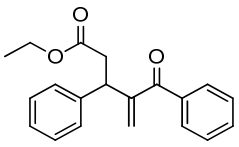
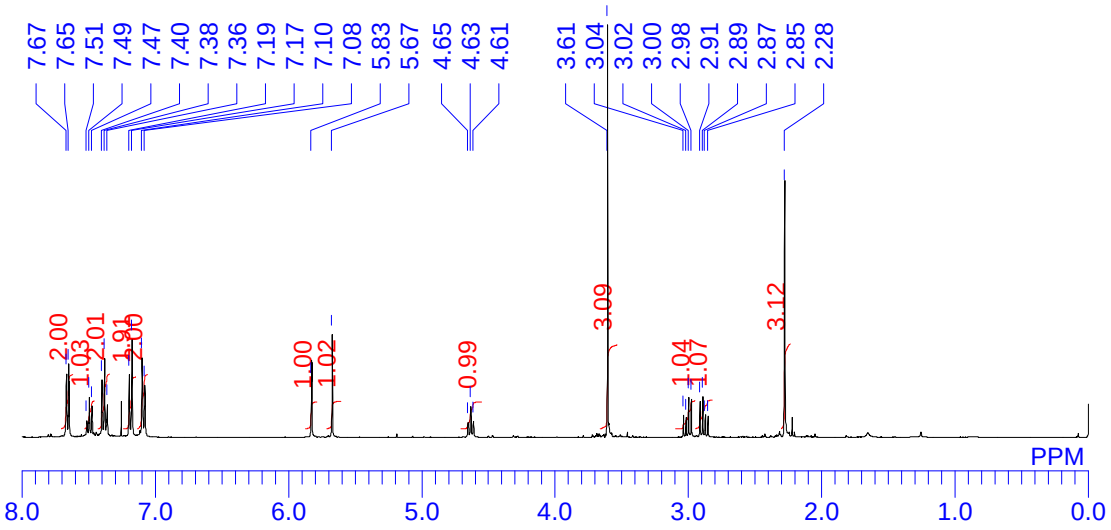
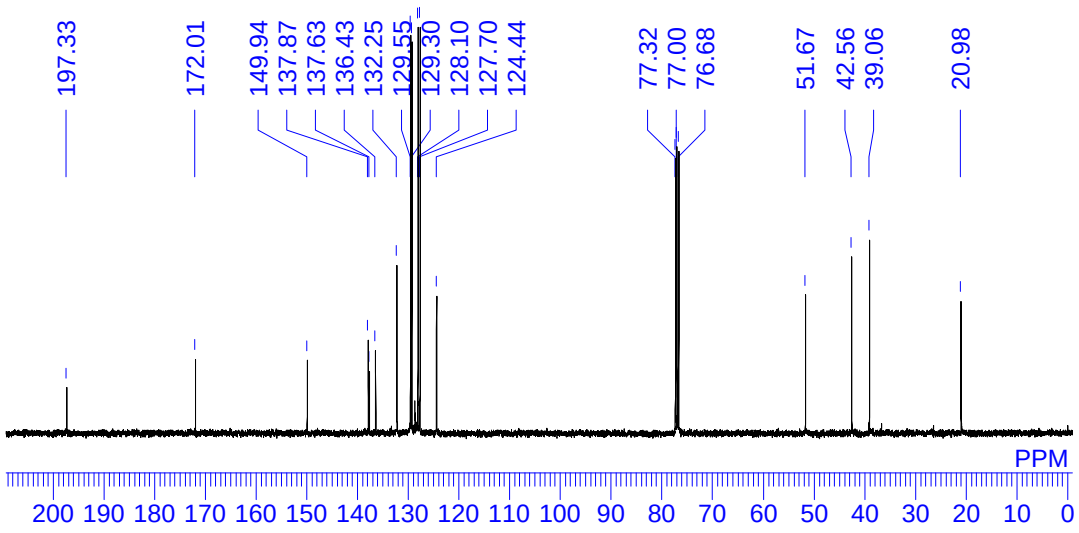


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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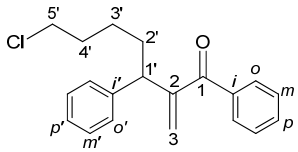
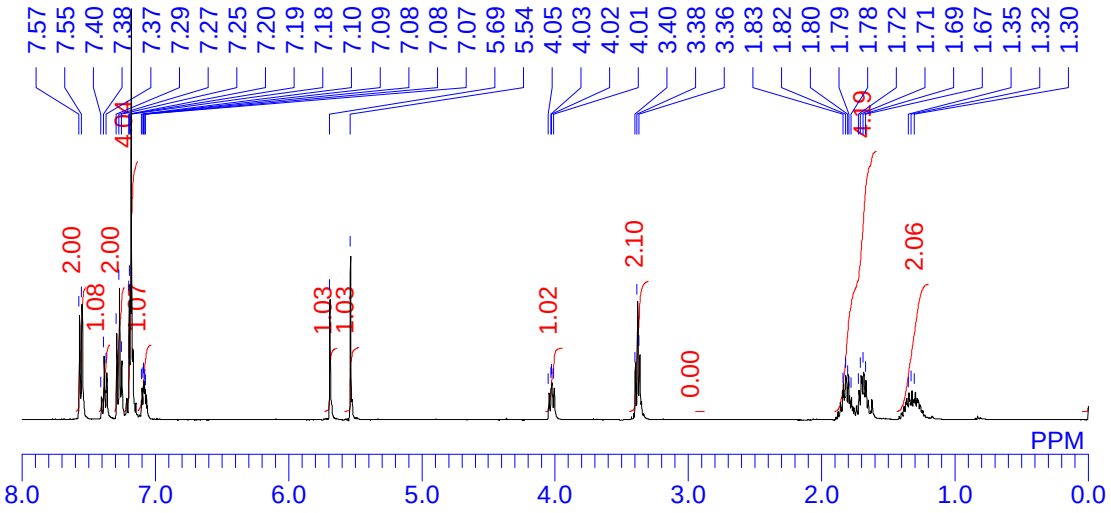
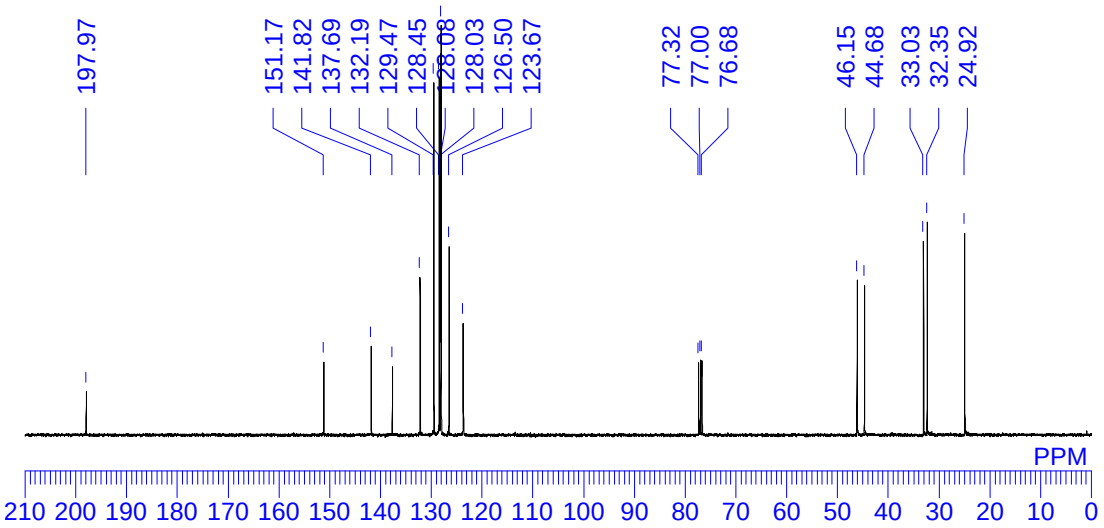


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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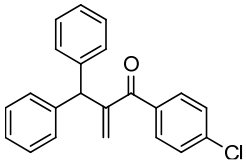
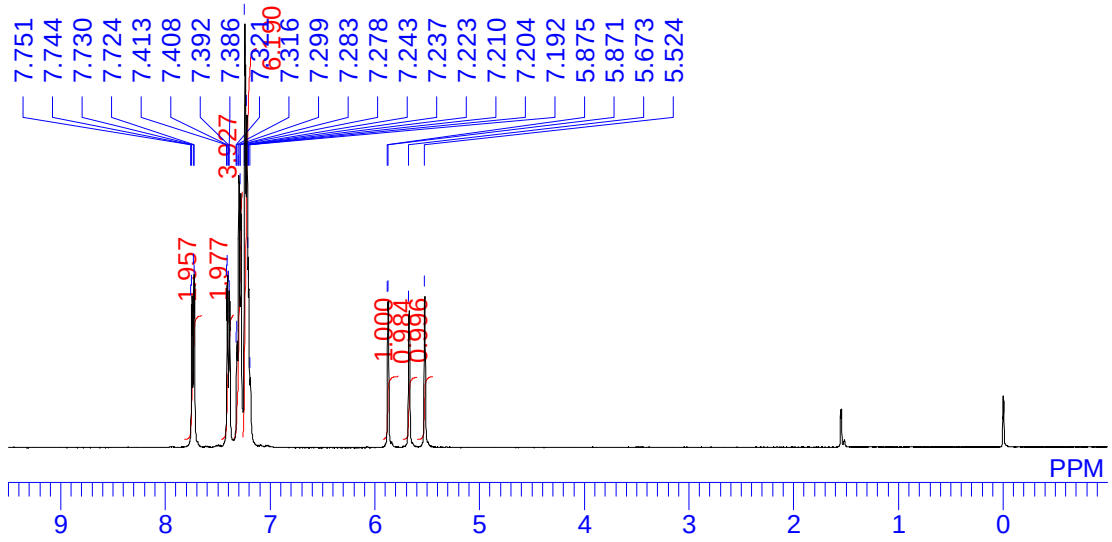
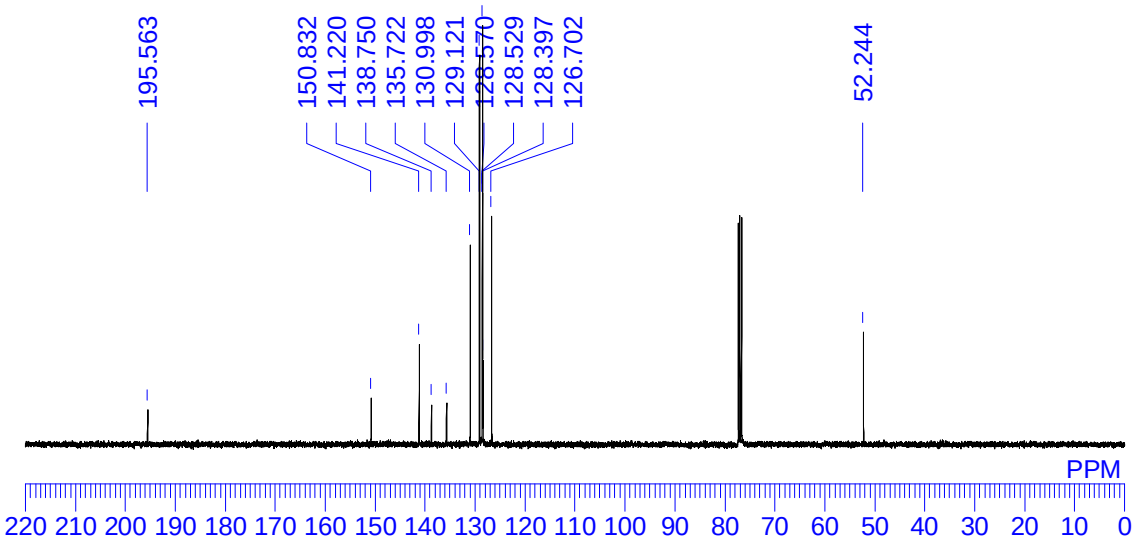


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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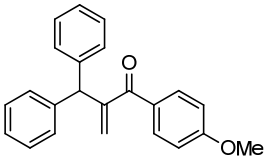
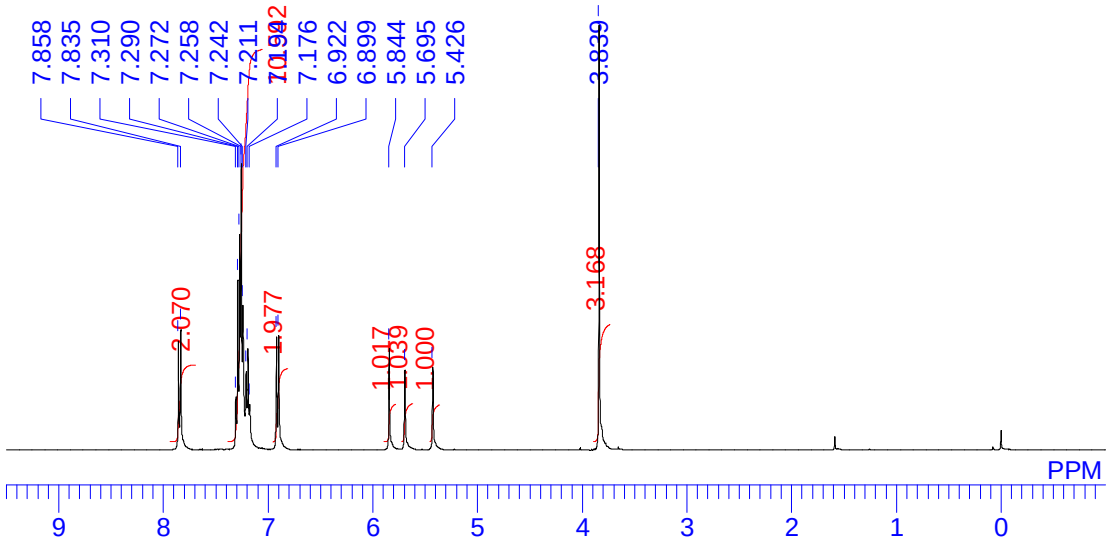
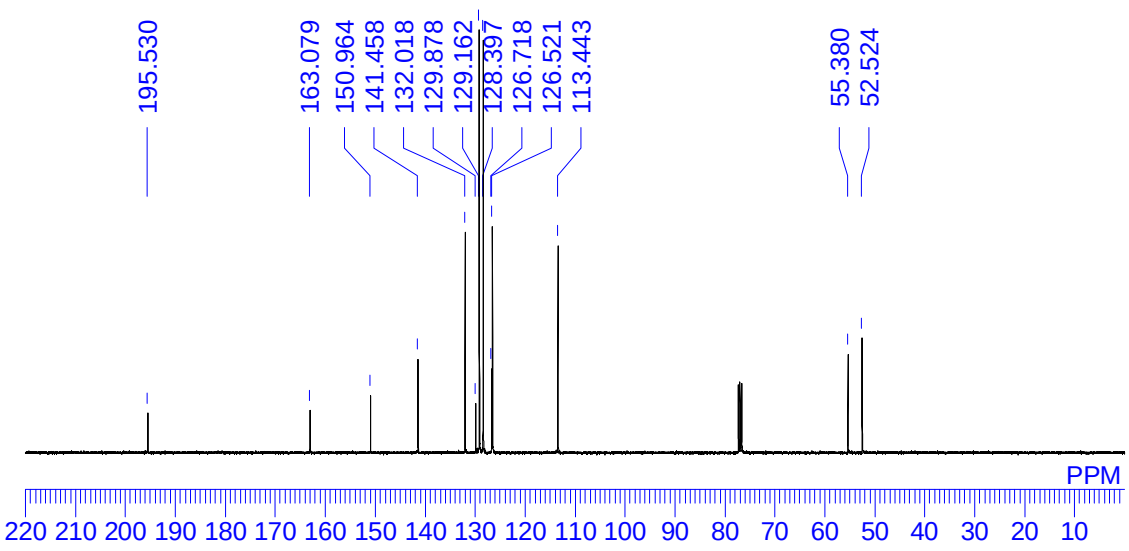


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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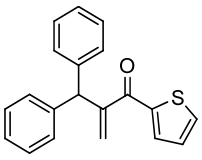
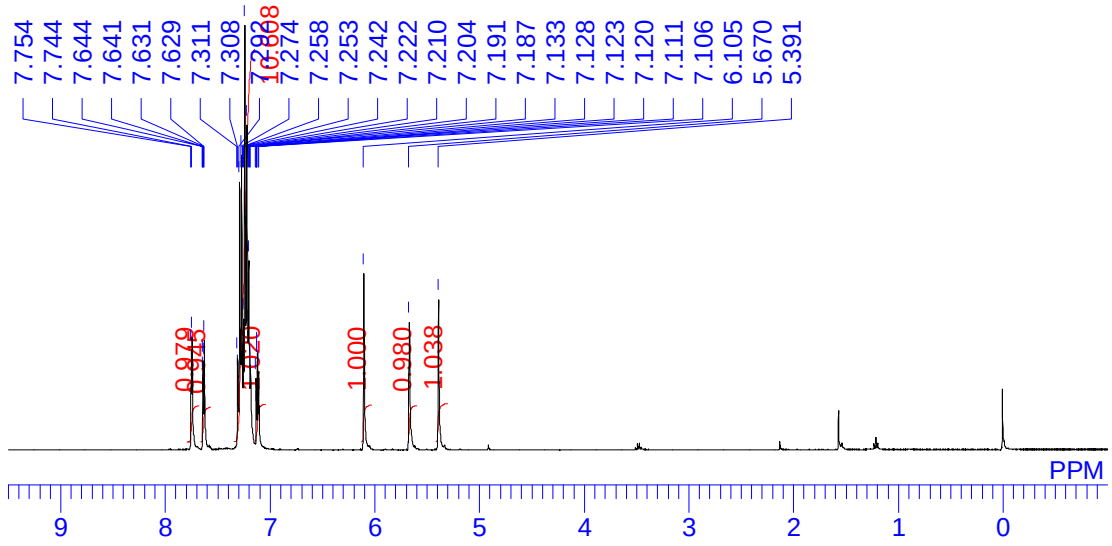
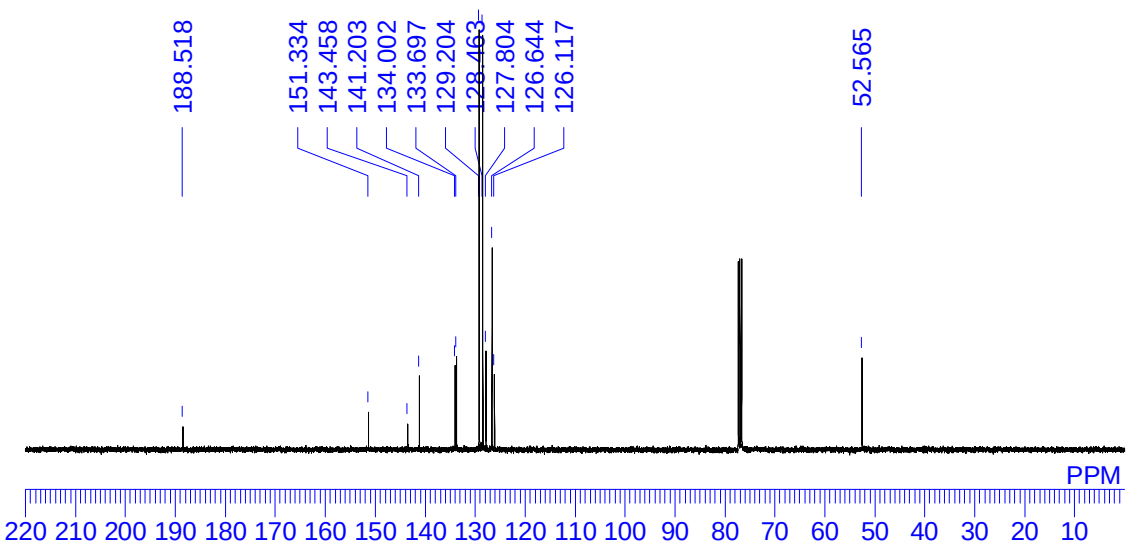


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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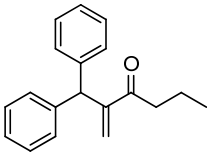
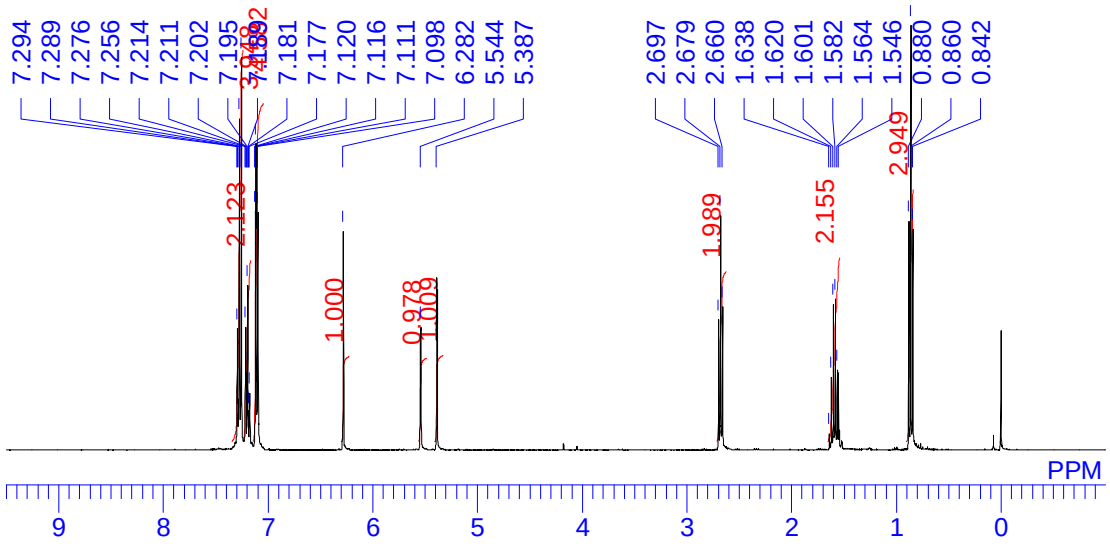
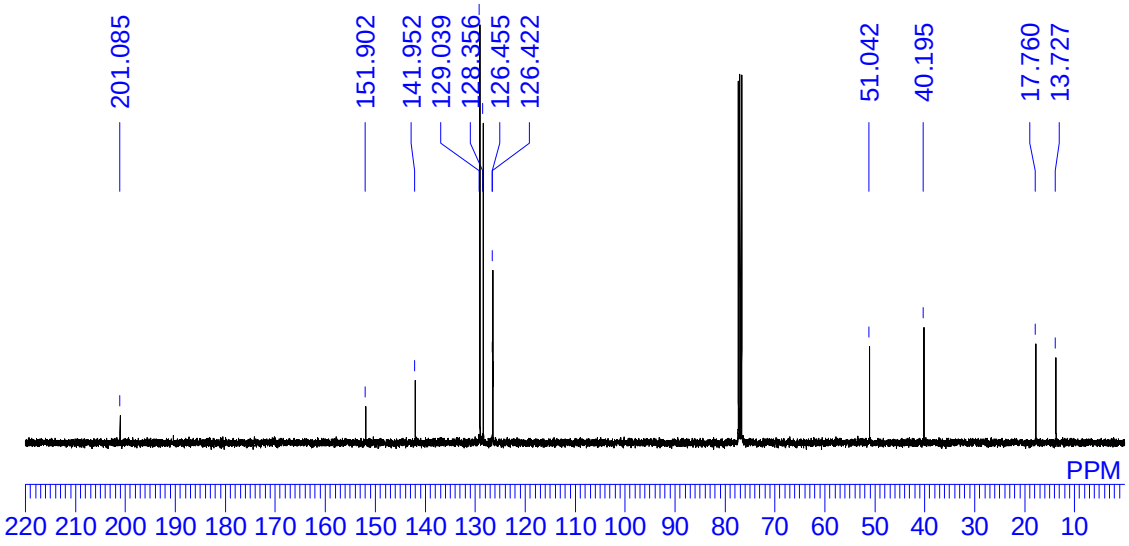


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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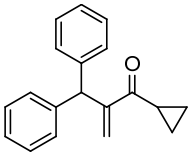
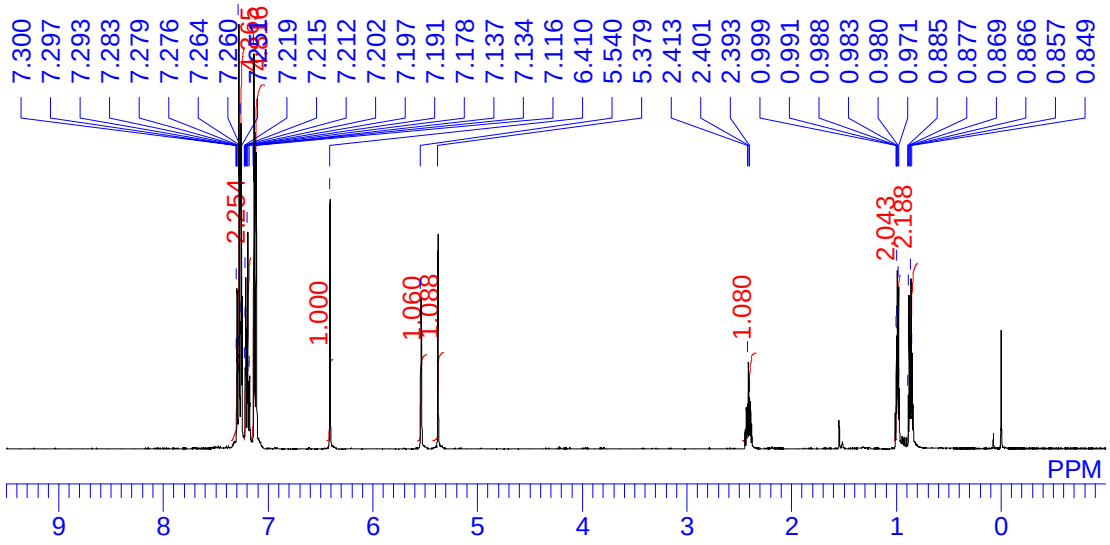
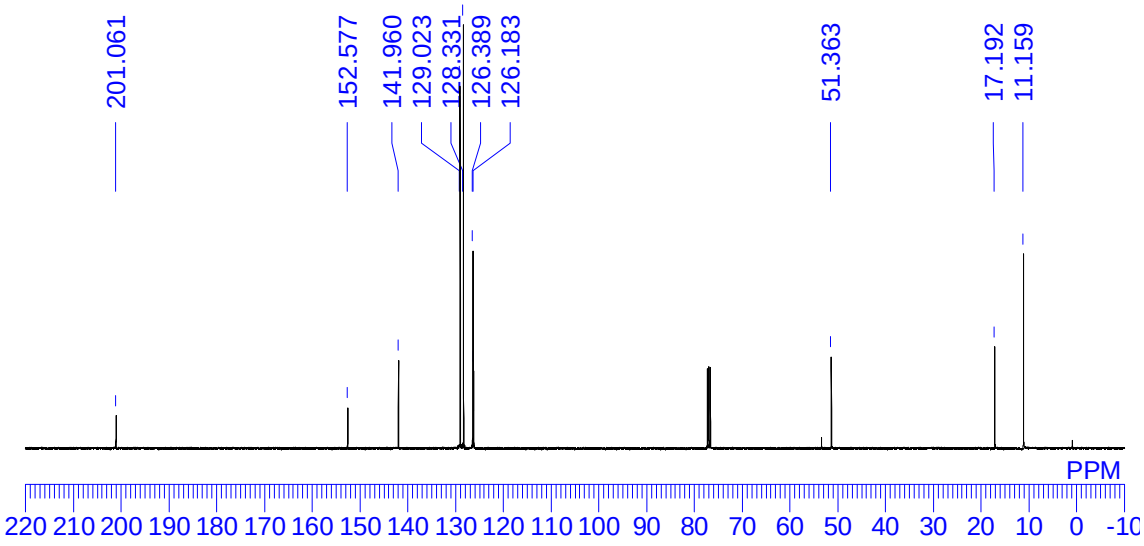


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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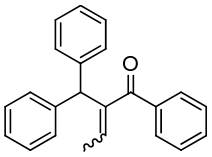
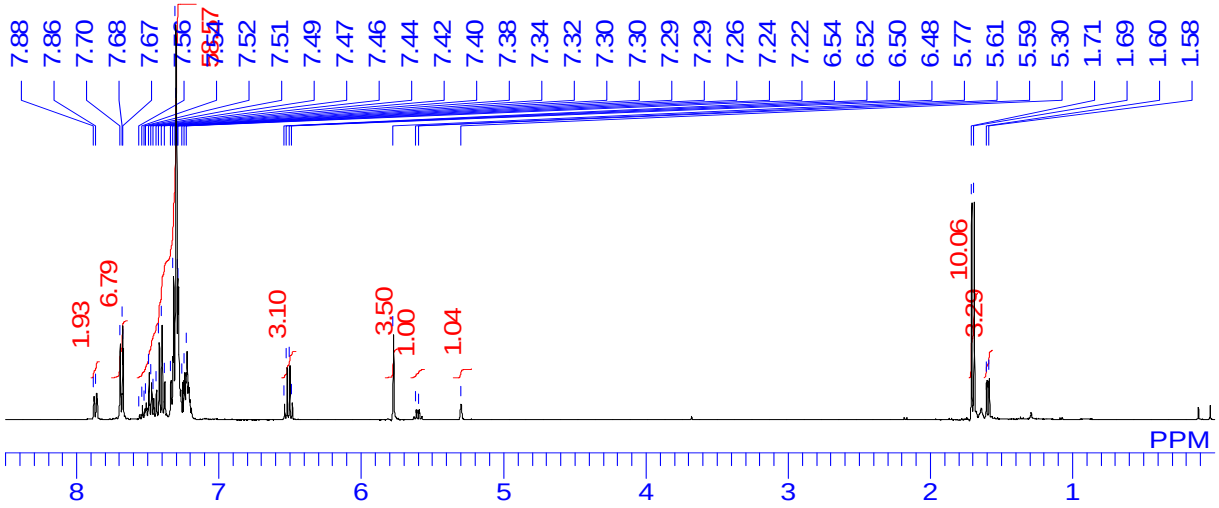
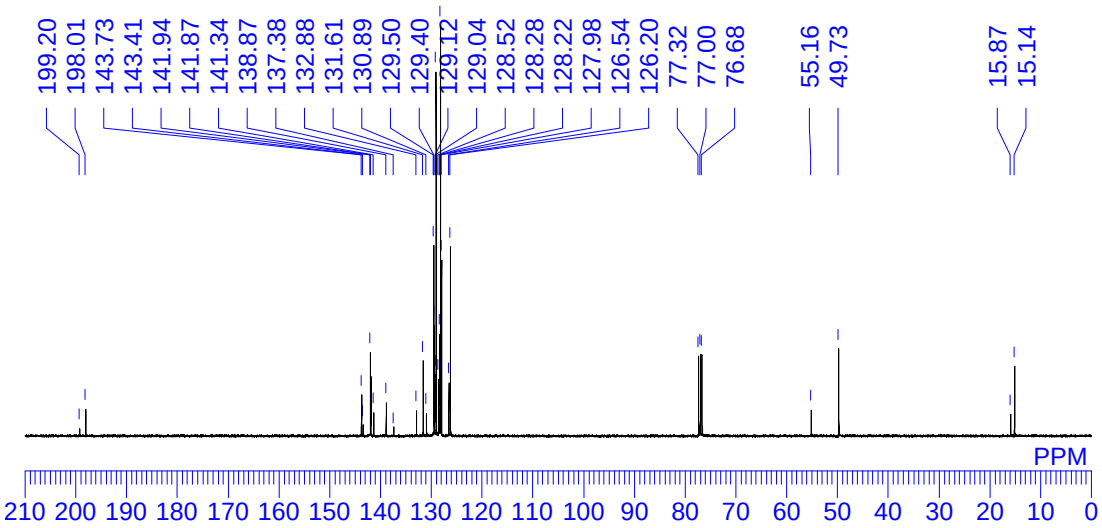


(mixture of *E*- and *Z*-isomer, *E*/*Z* = 78:22)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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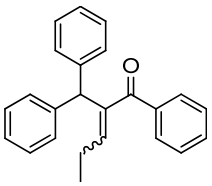
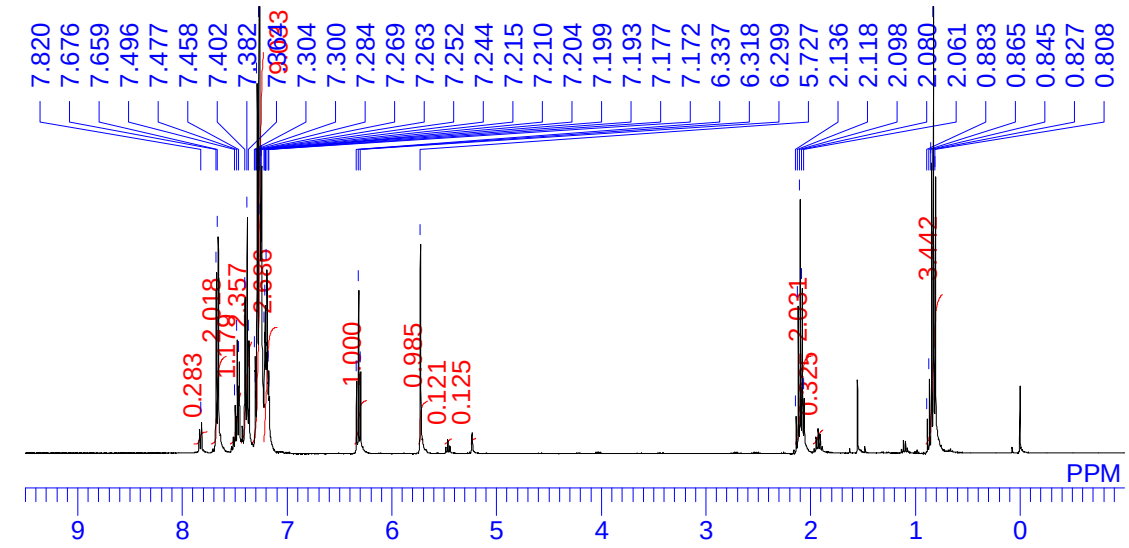
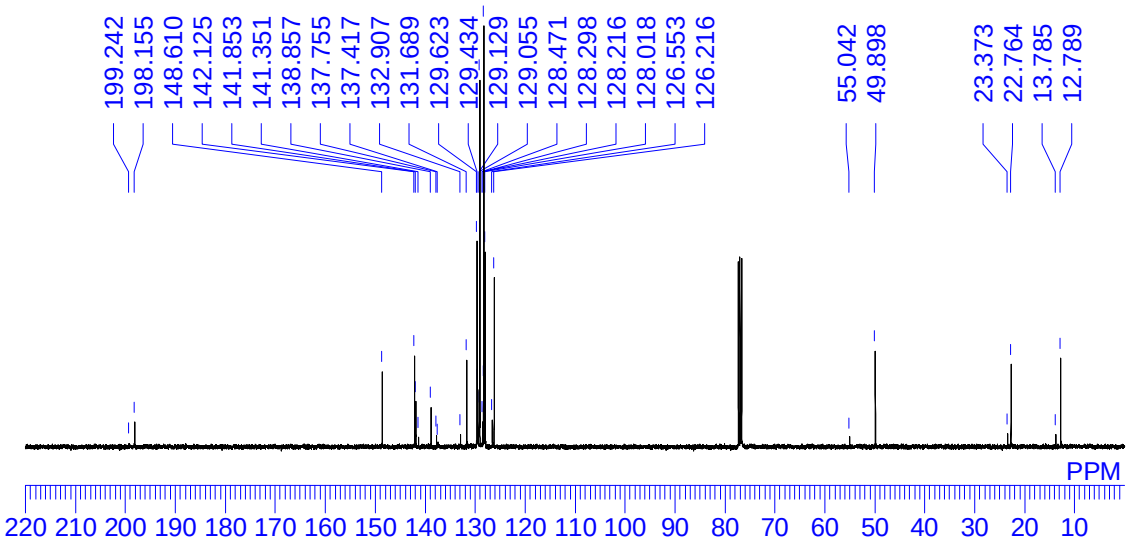


(mixture of *E*- and *Z*-isomer, *E*/*Z* = 89:11)

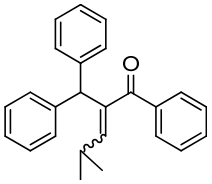
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

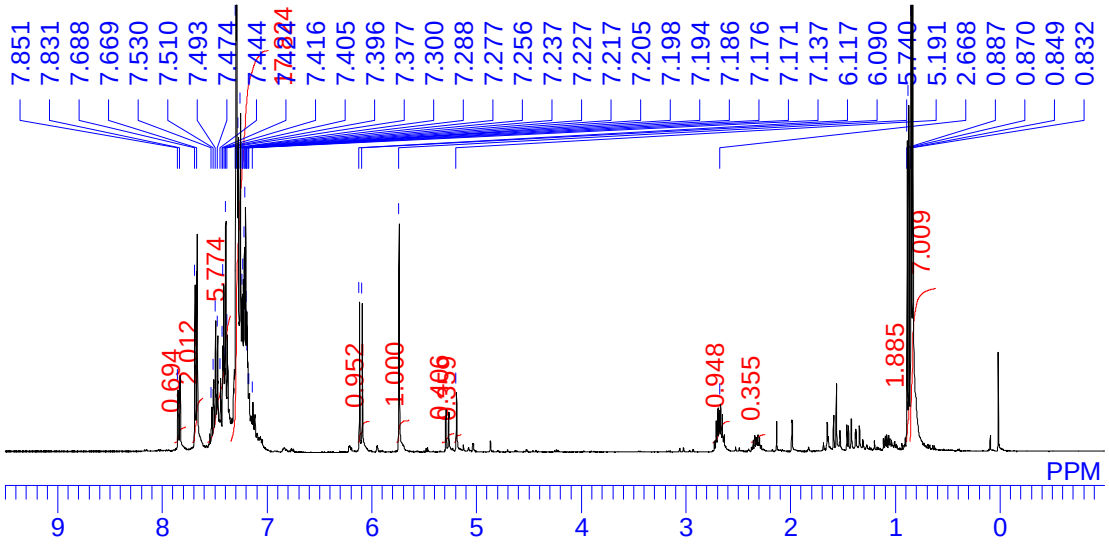


3bj

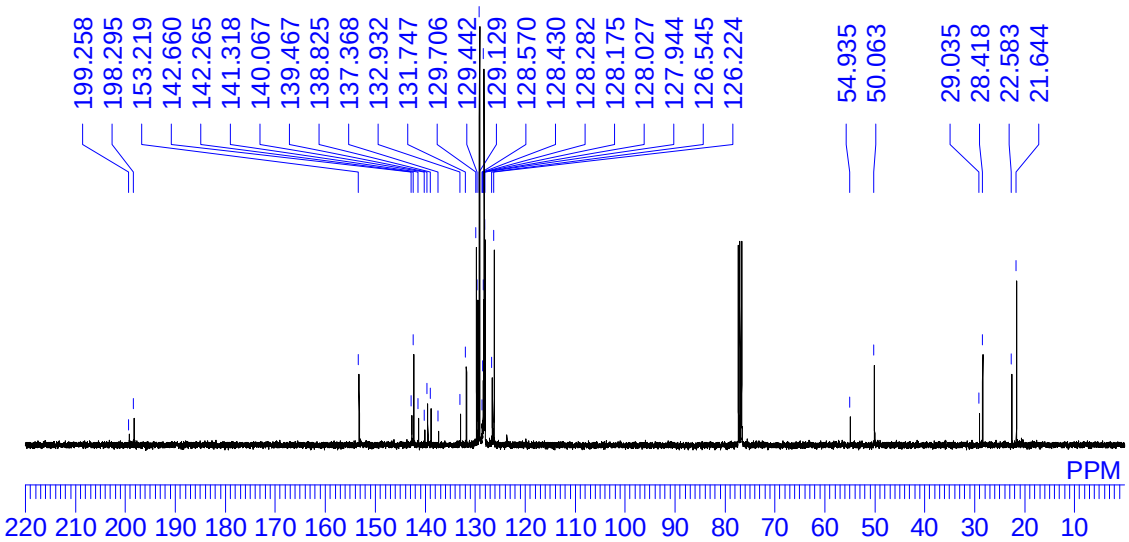


^{1}H NMR (400 MHz, $CDCl_3$)

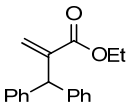
(mixture of *E*- and *Z*-isomer, *E*/*Z* = 74:26)



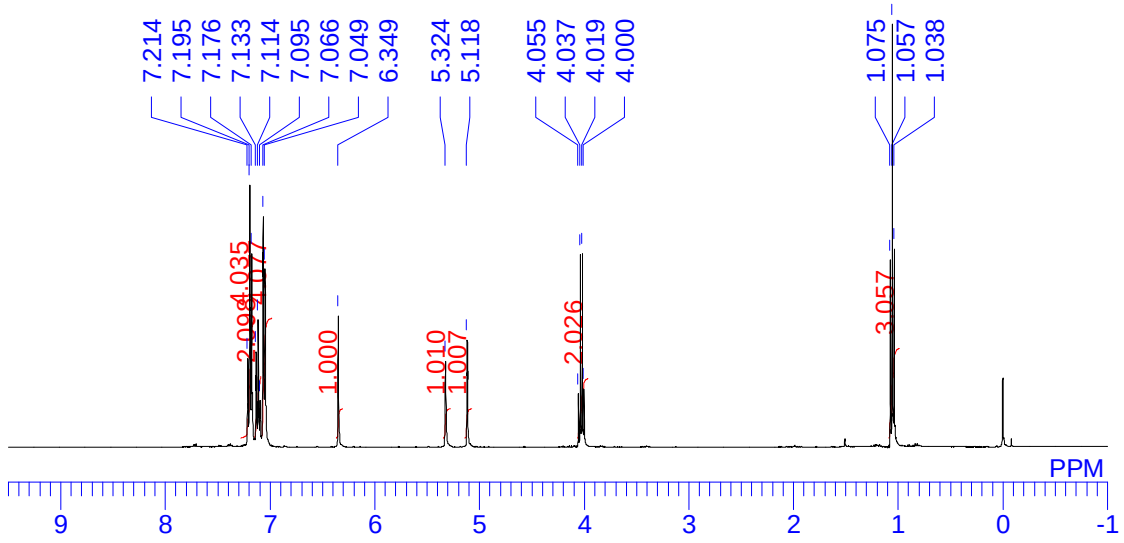
^{13}C NMR (100 MHz, $CDCl_3$)



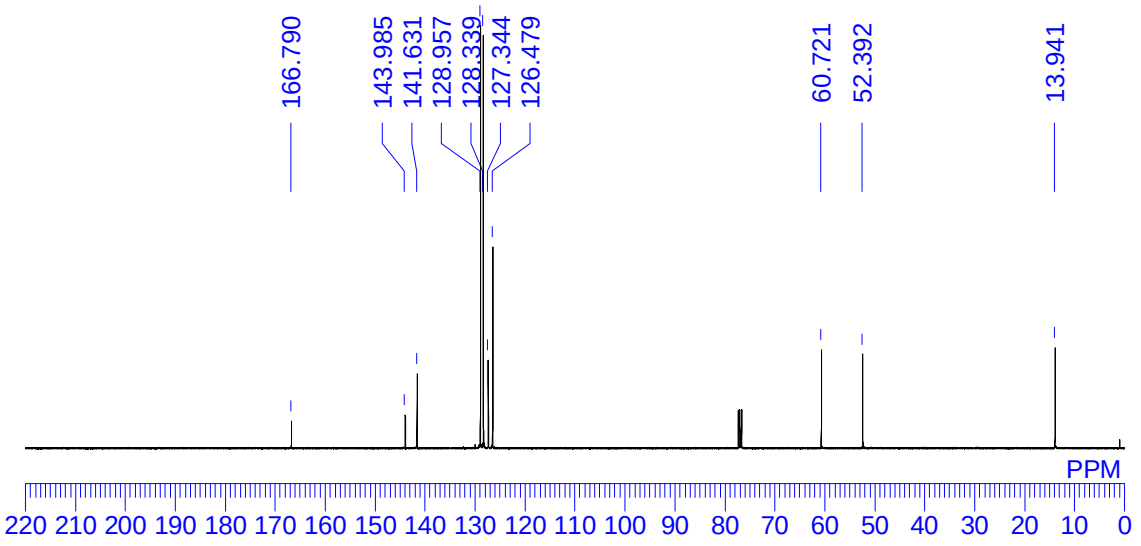
3bk



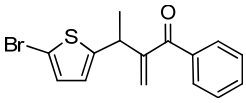
^{1}H NMR (400 MHz, $CDCl_3$)



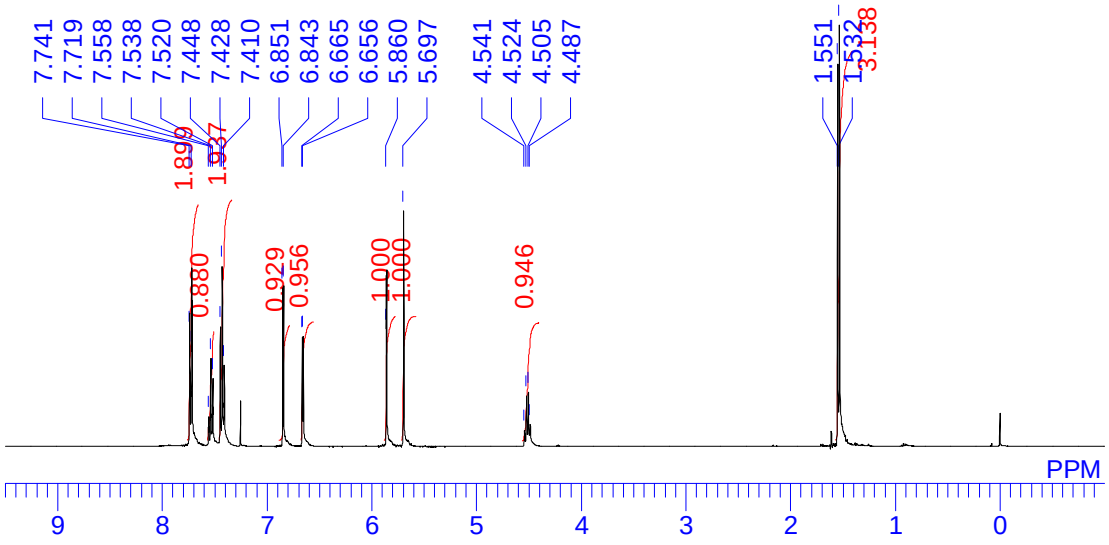
^{13}C NMR (100 MHz, $CDCl_3$)



7



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)