

Palladium-catalyzed Insertion of *N*-tosylhydrazones and Trapping with Carbon Nucleophiles

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1. General remarks

For product purification by flash column chromatography, silica gel (200~300 mesh). ^1H NMR spectra and ^{13}C NMR spectra were recorded on 400 MHz in CDCl_3 solution and TMS as internal standard. All products were further characterized by HRMS (high resolution mass spectra). Copies of their ^1H NMR and ^{13}C NMR spectra were provided. THF, and toluene, 1,4-dioxane were dried over Na with benzophenone-ketyl intermediate as indicator. MeCN was distilled over P_2O_5 . Commercially available reagents and solvents were used without further purification. **1a**,¹ **1b**², **1c**³ and *N*-tosylhydrazones **2**⁴ were synthesized according to the literature procedure.

2. Procedure for the preparation of sodium malonate.

A solution of dimethyl malonate (101mmol, 1.01eq) in THF (50 mL) was slowly added to a suspension of NaH (100 mmol, 1.0 eq) in THF (50 mL) at 0 °C then stirred at room temperature for 5 min. The solvents were evaporated under reduced pressure to afford sodium malonate as white solid.

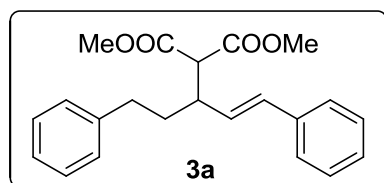
3. General procedure for the preparation of the products 3

An oven-dried Schlenk tube under a nitrogen atmosphere was charged with vinyl iodide **1a** (0.30 mmol, 1.0 eq), *N*-tosylhydrazones **2** (0.675 mmol, 2.25 eq), sodium malonate (3.6 mmol, 12.0 equiv), $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (2.5 mol %), PPh_3 (10 mol %), K_2CO_3 (0.9 mmol, 3.0 eq) and THF (2 mL). The mixture was stirred at room temperature for 15 minutes and then stirred at 46 °C for 2 h. The resulting mixture was cooled to room temperature and filtered through celite with EtOAc as eluents. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 25:1) on silica gel to afford pure **3**.

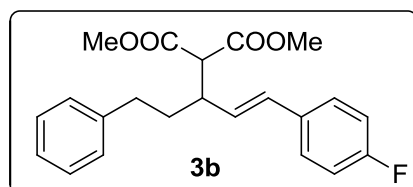
4. One-pot procedure for the preparation of the product 3a

Benzaldehyde (0.7425 mmol, 2.475 eq), tosylhydrazide (0.675 mmol, 2.25 eq) and Na_2SO_4 (0.90 mmol, 3.0 eq) were suspended in THF (1 mL) in a 10 mL Schlenk tube and heated at 70 °C for 1.5 h. After cooling to room temperature, vinyl iodide **1a** (0.30 mmol, 1.0 eq), sodium malonate (3.6 mmol, 12.0 equiv), $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (2.5 mol %), PPh_3 (10 mol %), K_2CO_3 (0.9 mmol, 3.0 eq) and THF (1 mL) were added. The Schlenk tube was evacuated to a vacuum and fitted with an Ar balloon. The mixture was stirred at room temperature for 15 minutes and then stirred at 46 °C for 2 h. The resulting mixture was cooled to room temperature and filtered through celite with EtOAc as eluents. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford pure **3a**.

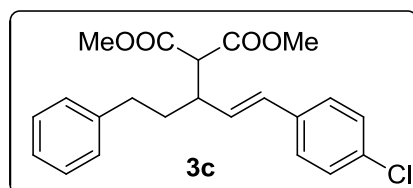
5. Spectral data of compound 3



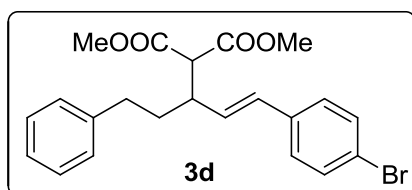
(E)-dimethyl 2-(1,5-diphenylpent-1-en-3-yl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.37-7.14(m, 10H), 6.47(d, J = 15.6 Hz, 1H), 6.11-6.05(m, 1H), 3.71(s, 3H), 3.63(s, 3H), 3.49(d, J = 8.0 Hz, 1H), 3.03-2.95(m, 1H), 2.76-2.69(m, 1H), 2.59-2.52(m, 1H), 1.94-1.86(m, 1H), 1.78-1.69(m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.5, 168.4, 141.5, 136.9, 133.1, 129.1, 128.5, 128.4, 128.3, 127.5, 126.3, 125.8, 56.9, 52.4, 52.3, 43.2, 34.4, 33.5; HRMS (ESI) m/z : calcd for $\text{C}_{22}\text{H}_{24}\text{O}_4$: $\text{M}+\text{NH}_4=370.2013$; found: 370.2020; EA: calcd for C: 74.98%, H: 6.86%; found: C: 74.94%, H: 7.08%.



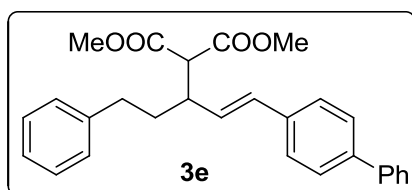
(E)-dimethyl 2-(1-(4-fluorophenyl)-5-phenylpent-1-en-3-yl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.33-7.30(m, 2H), 7.27(t, J = 7.2 Hz, 2H), 7.19-7.14(m, 3H), 7.01-6.97(m, 2H), 6.43(d, J = 15.6 Hz, 1H), 6.03-5.97(m, 1H), 3.71(s, 3H), 3.64(s, 3H), 3.49(d, J = 8.4 Hz, 1H), 3.01-2.93(m, 1H), 2.75-2.68(m, 1H), 2.59-2.52(m, 1H), 1.94-1.86(m, 1H), 1.78-1.69(m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.5, 168.4, 141.5, 133.1, 133.0, 131.9, 128.9, 128.3, 127.8, 127.7, 125.9, 115.5, 115.3, 56.9, 52.4, 52.3, 43.2, 34.4, 33.5; HRMS (ESI) m/z : calcd for $\text{C}_{22}\text{H}_{23}\text{FO}_4$: $\text{M}+\text{Na}=393.1473$; found: 393.1466.



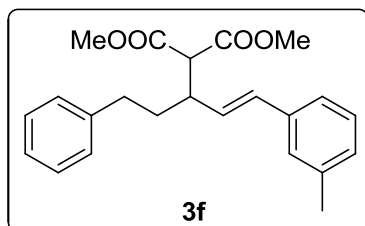
(E)-dimethyl 2-(1-(4-chlorophenyl)-5-phenylpent-1-en-3-yl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.25(d, J = 10.8 Hz, 6H), 7.15(dd, J = 13.2 Hz, 7.2 Hz, 3H), 6.41(d, J = 16.0 Hz, 1H), 6.07(dd, J = 16.0 Hz, 9.6 Hz, 1H), 3.70(s, 3H), 3.63(s, 3H), 3.49(d, J = 8.4 Hz, 1H), 3.01-2.94(m, 1H), 2.74-2.67(m, 1H), 2.59-2.51(m, 1H), 1.91-1.89(m, 1H), 1.78-1.69(m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.4, 168.3, 141.4, 135.4, 133.1, 131.8, 129.9, 128.6, 128.3, 127.5, 125.9, 56.8, 52.4, 52.2, 43.2, 34.3, 33.4; HRMS (ESI) m/z : calcd for $\text{C}_{22}\text{H}_{23}\text{ClO}_4$: $\text{M}+\text{NH}_4=404.1623$; found: 404.1628; EA: calcd for C: 68.30%, H: 5.99%; found: C: 68.22%, H: 5.98%.



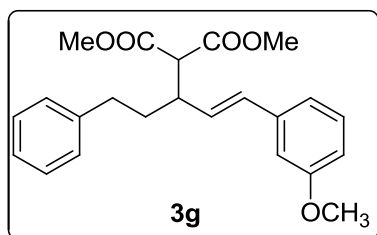
(E)-dimethyl 2-(1-(4-bromophenyl)-5-phenylpent-1-en-3-yl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.41(d, J = 8.4 Hz, 2H), 7.28-7.20(m, 4H), 7.18-7.13(m, 3H), 6.40(d, J = 15.6 Hz, 1H), 6.09(dd, J = 15.6 Hz, 9.6 Hz, 1H), 3.70(s, 3H), 3.63(s, 3H), 3.49(d, J = 8.4 Hz, 1H), 3.01-2.93(m, 1H), 2.74-2.66(m, 1H), 2.59-2.51(m, 1H), 1.94-1.86(m, 1H), 1.78-1.69(m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.4, 168.3, 141.3, 135.8, 131.9, 131.5, 130.0, 128.3, 127.8, 125.9, 121.2, 56.7, 52.4, 52.2, 43.2, 34.2, 33.4; HRMS (ESI) m/z : calcd for $\text{C}_{22}\text{H}_{23}\text{BrO}_4$: $\text{M}+\text{NH}_4=448.1118$; found: 448.1122.



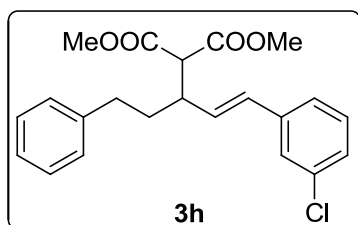
(E)-dimethyl 2-(1-([1,1'-biphenyl]-4-yl)-5-phenylpent-1-en-3-yl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.56(dd, J = 14.4 Hz, 8.0 Hz, 4H), 7.44-7.40(m, 4H), 7.34-7.30(m, 1H), 7.28-7.25(m, 2H), 7.19-7.15(m, 3H), 6.52(d, J = 15.6 Hz, 1H), 6.13(dd, J = 15.6 Hz, 9.6 Hz, 1H), 3.71(s, 3H), 3.64(s, 3H), 3.51(d, J = 8.8 Hz, 1H), 3.05-2.97(m, 1H), 2.77-2.70(m, 1H), 2.61-2.53(m, 1H), 1.96-1.87(m, 1H), 1.80-1.70(m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.5, 168.4, 141.5, 140.6, 140.3, 135.9, 132.7, 129.3, 128.7, 128.4, 128.3, 127.2, 127.1, 126.9, 126.7, 125.8, 56.9, 52.4, 52.3, 43.3, 34.4, 33.5; HRMS (ESI) m/z : calcd for $\text{C}_{28}\text{H}_{28}\text{O}_4$: $\text{M}+\text{NH}_4=446.2326$; found: 446.2336; EA: calcd for C: 78.48%, H: 6.59%; found: C: 78.45%, H: 6.57%.



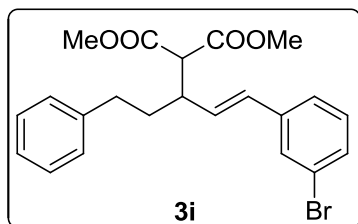
(E)-dimethyl 2-(5-phenyl-1-(m-tolyl)pent-1-en-3-yl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.28-7.24(m, 2H), 7.20-7.14(m, 6H), 7.04(d, J = 7.2 Hz, 1H), 6.44(d, J = 15.6 Hz, 1H), 6.06(dd, J = 16.0 Hz, 9.6 Hz, 1H), 3.71(s, 3H), 3.63(s, 3H), 3.48(d, J = 8.4 Hz, 1H), 3.02-2.94(m, 1H), 2.75-2.68(m, 1H), 2.59-2.51(m, 1H), 2.34(s, 3H), 1.93-1.85(m, 1H), 1.78-1.68(m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.5, 168.4, 141.6, 138.0, 136.9, 133.2, 128.9, 128.4, 128.3, 128.2, 128.2, 126.9, 125.8, 123.5, 57.0, 52.4, 52.3, 43.3, 34.4, 33.4, 21.3; HRMS (ESI) m/z : calcd for $\text{C}_{23}\text{H}_{26}\text{O}_4$: $\text{M}+\text{Na}=389.1723$; found: 389.1720.



(E)-dimethyl 2-(1-(3-methoxyphenyl)-5-phenylpent-1-en-3-yl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.28-7.22(m, 3H), 7.20-7.14(m, 3H), 6.96(d, J = 7.6 Hz, 1H), 6.90(s, 1H), 6.78(dd, J = 8.0 Hz, 2.4 Hz, 1H), 6.44(d, J = 15.6 Hz, 1H), 6.11-6.04(m, 1H), 3.81(s, 3H), 3.71(s, 3H), 3.64(s, 3H), 3.49(d, J = 8.4 Hz, 1H), 3.02-2.94(m, 1H), 2.79-2.68(m, 1H), 2.59-2.52(m, 1H), 1.94-1.86(m, 1H), 1.78-1.68(m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.5, 168.4, 159.8, 141.5, 138.4, 133.0, 129.4, 128.4, 128.3, 125.8, 118.9, 113.0, 111.7, 56.9, 55.1, 52.4, 52.3, 43.2, 34.3, 33.4; HRMS (ESI) m/z : calcd for $\text{C}_{23}\text{H}_{26}\text{O}_5$: $\text{M}+\text{NH}_4=400.2118$; found: 400.2121; EA: calcd for C: 72.23%, H: 6.85%; found: C: 72.16%, H: 6.69%.

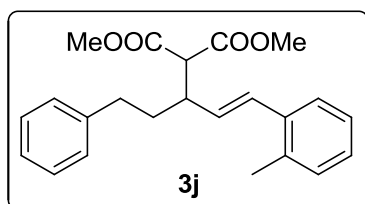


(E)-dimethyl 2-(1-(3-chlorophenyl)-5-phenylpent-1-en-3-yl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.34(s, 1H), 7.28-7.23(m, 2H), 7.21-7.14(m, 6H), 6.40(d, J = 16.0 Hz, 1H), 6.11(dd, J = 16.0 Hz, 9.6 Hz, 1H), 3.71(s, 3H), 3.64(s, 3H), 3.49(d, J = 8.4 Hz, 1H), 3.02-2.94(m, 1H), 2.74-2.67(m, 1H), 2.59-2.51(m, 1H), 1.95-1.86(m, 1H), 1.79-1.69(m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.4, 168.3, 141.3, 138.8, 134.5, 131.8, 130.8, 129.7, 128.4, 128.3, 127.4, 126.1, 125.9, 124.6, 56.8, 52.5, 52.3, 43.1, 34.2, 33.5; HRMS (ESI) m/z : calcd for $\text{C}_{22}\text{H}_{23}\text{ClO}_4$: $\text{M}+3\text{H}=389.1503$; found: 389.1520; EA: calcd for C: 68.30%, H: 5.99%; found: C: 68.33%, H: 6.19%.

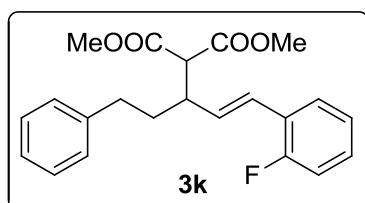


(E)-dimethyl 2-(1-(3-bromophenyl)-5-phenylpent-1-en-3-yl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.50(s, 1H), 7.34(d, J = 8.0 Hz, 1H), 7.28-7.23(m, 3H), 7.19-7.13(m, 4H), 6.39(d, J = 15.6 Hz, 1H), 6.10(dd, J = 15.6 Hz, 9.6 Hz, 1H), 3.71(s, 3H), 3.64(s, 3H), 3.49(d, J = 8.4 Hz, 1H), 3.02-2.94(m, 1H), 2.74-2.67(m, 1H), 2.59-2.51(m, 1H), 1.94-1.86(m, 1H), 1.79-1.69(m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.4, 168.3, 141.3, 139.0, 131.7, 130.8, 130.3, 130.0, 129.0, 128.4, 128.3, 125.9, 125.0, 122.7, 56.7, 52.4, 52.3, 43.1, 34.2, 33.4; HRMS (ESI) m/z : calcd for $\text{C}_{22}\text{H}_{23}\text{BrO}_4$: $\text{M}+\text{NH}_4=448.1118$; found: 448.1122; EA: calcd for C: 61.26%, H:

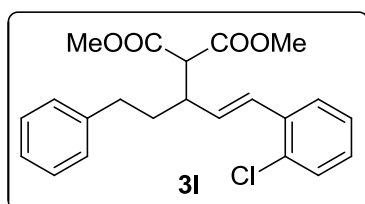
5.37%; found: C:61.39%, H: 5.44%.



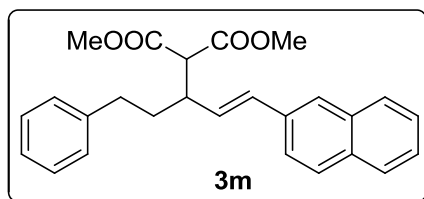
(E)-dimethyl 2-(5-phenyl-1-(o-tolyl)pent-1-en-3-yl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.40-7.38(m, 1H), 7.29-7.25(m, 2H), 7.19-7.15(m, 6H), 6.68(d, J = 15.6 Hz, 1H), 5.92(dd, J = 15.6 Hz, 9.6 Hz, 1H), 3.71(s, 3H), 3.65(s, 3H), 3.49(d, J = 8.8 Hz, 1H), 3.05-2.97(m, 1H), 2.79-2.71(m, 1H), 2.61-2.54(m, 1H), 2.33(s, 3H), 1.95-1.87(m, 1H), 1.78-1.65(m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.5, 168.4, 141.5, 136.3, 135.2, 131.4, 130.6, 130.1, 128.4, 128.3, 127.4, 126.0, 125.9, 125.8, 57.1, 52.4, 52.3, 43.5, 34.4, 33.5, 19.7; HRMS (ESI) m/z : calcd for $\text{C}_{23}\text{H}_{26}\text{O}_4$: $M+\text{Na}$ =389.1723; found: 389.1720.



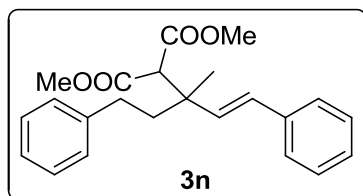
(E)-dimethyl 2-(1-(2-fluorophenyl)-5-phenylpent-1-en-3-yl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.44-7.40(m, 1H), 7.29-7.23(m, 2H), 7.21-7.15(m, 4H), 7.07(t, J = 7.6 Hz, 1H), 7.04-6.99(m, 1H), 6.62(d, J = 16.0 Hz, 1H), 6.17(dd, J = 16.0 Hz, 9.6 Hz, 1H), 3.71(s, 3H), 3.65(s, 3H), 3.50(d, J = 8.8 Hz, 1H), 3.05-2.97(m, 1H), 2.76-2.69(m, 1H), 2.61-2.53(m, 1H), 1.95-1.87(m, 1H), 1.80-1.70(m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.5, 168.3, 141.4, 132.0, 131.9, 128.8, 128.7, 128.4, 128.3, 127.5, 127.4, 125.9, 125.6, 125.5, 124.0, 123.9, 115.7, 115.5, 56.9, 52.4, 52.3, 43.5, 34.3, 33.5; HRMS (ESI) m/z : calcd for $\text{C}_{22}\text{H}_{23}\text{FO}_4$: $M+\text{Na}$ =393.1473; found: 393.1476; EA: calcd for C: 71.34%, H: 6.26%; found: C: 71.31%, H: 6.28%.



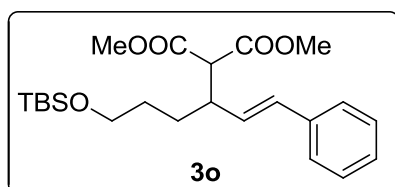
(E)-dimethyl 2-(1-(2-chlorophenyl)-5-phenylpent-1-en-3-yl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.49-7.47(m, 1H), 7.33(dd, J = 7.6 Hz, 1.6 Hz, 1H), 7.29-7.25(m, 2H), 7.23-7.15(m, 5H), 6.84(d, J = 16.0 Hz, 1H), 6.08(dd, J = 15.6 Hz, 9.6 Hz, 1H), 3.73(s, 3H), 3.68(s, 3H), 3.51(d, J = 8.4 Hz, 1H), 3.08-3.00(m, 1H), 2.78-2.71(m, 1H), 2.63-2.55(m, 1H), 1.96-1.88(m, 1H), 1.81-1.71(m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.5, 168.4, 141.4, 135.3, 132.8, 132.3, 129.6, 129.5, 128.5, 128.4, 128.3, 127.1, 126.8, 125.9, 56.9, 52.5, 52.4, 43.2, 34.3, 33.5; HRMS (ESI) m/z : calcd for $\text{C}_{22}\text{H}_{23}\text{ClO}_4$: $M+\text{H}$ =387.1358; found: 387.1362.



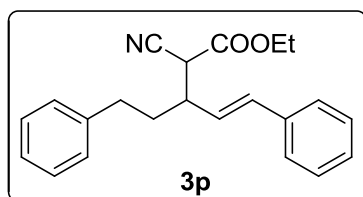
(E)-dimethyl 2-(1-(naphthalen-2-yl)-5-phenylpent-1-en-3-yl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.80-7.76(m, 3H), 7.70(s, 1H), 7.57(d, J = 8.8 Hz, 1H), 7.46-7.40(m, 2H), 7.29-7.25(m, 2H), 7.19-7.16(m, 3H), 6.63(d, J = 15.6 Hz, 1H), 6.25-6.18(m, 1H), 3.72(s, 3H), 3.63(s, 3H), 3.53(d, J = 8.8 Hz, 1H), 3.09-3.01(m, 1H), 2.79-2.72(m, 1H), 2.63-2.56(m, 1H), 1.98-1.90(m, 1H), 1.83-1.74(m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.5, 168.4, 141.5, 134.3, 133.5, 133.2, 132.9, 129.5, 128.4, 128.3, 128.1, 127.9, 127.6, 126.2, 126.0, 125.8, 125.7, 123.6, 57.0, 52.4, 52.3, 43.4, 34.4, 33.5; HRMS (ESI) m/z : calcd for $\text{C}_{26}\text{H}_{26}\text{O}_4$: $\text{M}+\text{NH}_4=420.2169$; found: 420.2173; EA: calcd for C: 77.59%, H: 6.51%; found: C: 77.45%, H: 6.67%.



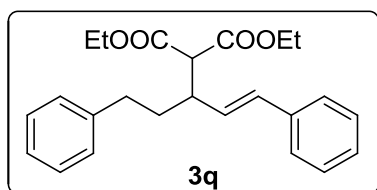
(E)-dimethyl 2-(3-methyl-1,5-diphenylpent-1-en-3-yl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.38(d, J = 8.0 Hz, 2H), 7.33-7.29(m, 2H), 7.27-7.22(m, 3H), 7.18-7.14(m, 3H), 6.43(s, 2H), 3.69(s, 3H), 3.65(s, 3H), 3.59(s, 1H), 2.65-2.53(m, 2H), 2.03-1.90(m, 2H), 1.48(s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.2, 168.0, 142.2, 137.4, 134.9, 129.2, 128.5, 128.4, 128.3, 127.3, 126.3, 125.8, 60.3, 52.1, 52.0, 42.0, 41.5, 30.6, 20.4; HRMS (ESI) m/z : calcd for $\text{C}_{23}\text{H}_{26}\text{O}_4$: $\text{M}+\text{NH}_4=384.2169$; found: 384.2173; EA: calcd for C: 75.38%, H: 7.15%; found: C: 75.29%, H: 7.21%.



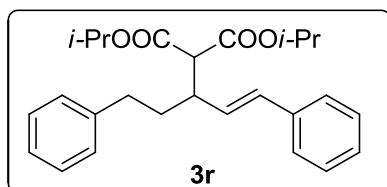
(E)-dimethyl 2-(6-((tert-butyldimethylsilyl)oxy)-1-phenylhex-1-en-3-yl)malonate: colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.33-7.25(m, 4H), 7.21-7.20(m, 1H), 6.42(d, J = 16.0 Hz, 1H), 6.00(dd, J = 15.6 Hz, 9.6 Hz, 1H), 3.72(s, 3H), 3.63(s, 3H), 3.59-3.57(m, 2H), 3.46(d, J = 8.8 Hz, 1H), 2.97-2.90(m, 1H), 1.61-1.51(m, 2H), 1.49-1.39(m, 2H), 0.87(s, 9H), 0.01(d, J = 1.6 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.6, 168.5, 137.0, 132.7, 129.5, 128.4, 127.4, 126.3, 62.8, 57.1, 52.4, 52.2, 43.5, 30.5, 29.2, 25.9, 18.3, -5.4; HRMS (ESI) m/z : calcd for $\text{C}_{23}\text{H}_{36}\text{O}_5\text{Si}$: $\text{M}+\text{H}=421.2405$; found: 421.2418.



(E)-ethyl 2-cyano-3-phenethyl-5-phenylpent-4-enoate: colorless oil; HRMS (ESI) m/z : calcd for $C_{22}H_{23}NO_2$: $M+NH_4=351.2067$; found: 351.2070.



(E)-diethyl 2-(1,5-diphenylpent-1-en-3-yl)malonate: colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ : 7.35(d, $J=7.6$ Hz, 2H), 7.32-7.18(m, 5H), 7.16-7.12(m, 3H), 6.46(d, $J=16.0$ Hz, 1H), 6.10(dd, $J=15.6$ Hz, 9.6Hz, 1H), 4.21-4.15(m, 2H), 4.14-4.06(m, 2H), 3.45(d, $J=8.4$ Hz, 1H), 3.03-2.95(m, 1H), 2.76-2.69(m, 1H), 2.61-2.53(m, 1H), 1.96-1.88(m, 1H), 1.79-1.69(m, 1H), 1.25-1.21(m, 3H), 1.18-1.14(m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 168.1, 168.0, 141.6, 136.9, 133.0, 129.3, 128.5, 128.3, 128.2, 127.4, 126.2, 125.8, 61.3, 61.2, 57.2, 43.2, 34.4, 33.5, 14.0; HRMS (ESI) m/z : calcd for $C_{24}H_{28}O_4$: $M+H=381.2060$; found: 381.2064.

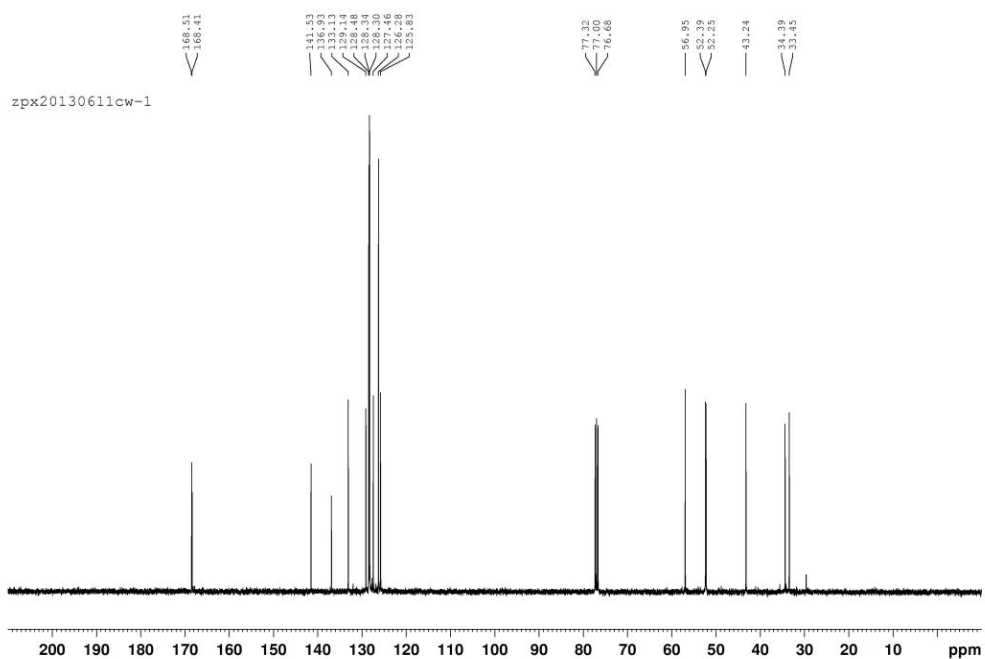
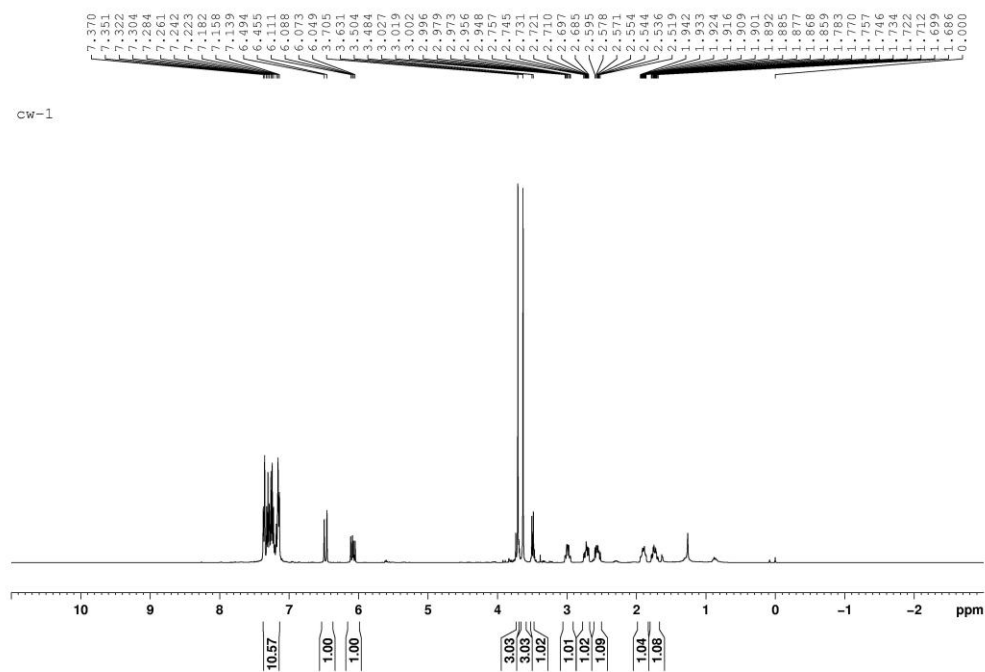
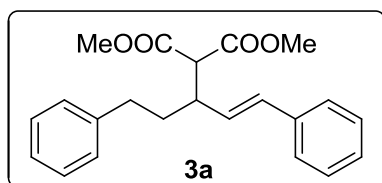


(E)-diisopropyl 2-(1,5-diphenylpent-1-en-3-yl)malonate: colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ : 7.35(d, $J=7.6$ Hz, 2H), 7.32-7.22(m, 5H), 7.16(t, $J=8.0$ Hz, 3H), 6.46(d, $J=15.6$ Hz, 1H), 6.11(dd, $J=15.6$ Hz, 9.6Hz, 1H), 5.08-5.02(m, 1H), 5.00-4.94(m, 1H), 3.38(d, $J=8.4$ Hz, 1H), 3.01-2.94(m, 1H), 2.76-2.68(m, 1H), 2.61-2.53(m, 1H), 1.97-1.89(m, 1H), 1.78-1.68(m, 1H), 1.23-1.12(m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 167.8, 167.6, 141.7, 137.0, 133.0, 129.4, 128.5, 128.4, 128.3, 127.4, 126.3, 125.8, 68.9, 68.7, 57.5, 43.1, 34.6, 33.5, 21.7, 21.6, 21.6, 21.5; HRMS (ESI) m/z : calcd for $C_{26}H_{32}O_4$: $M+H=409.2373$; found: 409.2377.

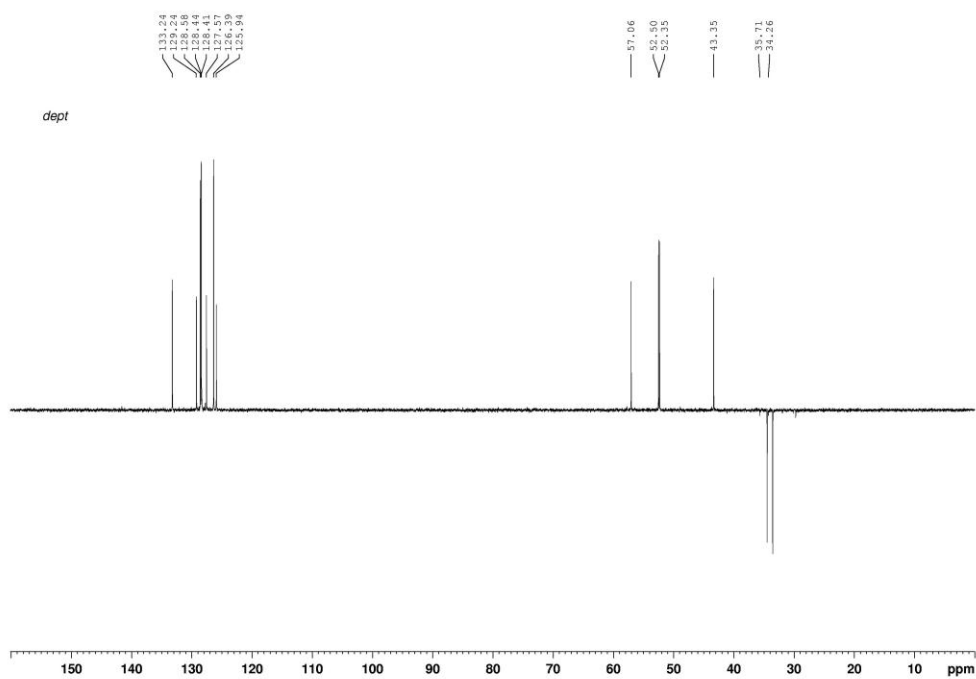
6. References

- 1) Denmark, S. E.; Wang, Z. *Org. Synth.* **2005**, *81*, 42-53.
- 2) Negishi, E.; Van Horn, D. E.; Yoshida, T. *J. Am. Chem. Soc.* **1985**, *107*, 6639-6647.
- 3) Pearson, W. H.; Kropf, J. E.; Choy, A. L.; Lee, I. L.; Kampf, J. W. *J. Org. Chem.* **2007**, *72*, 4135-4148.
- 4) Fulton, J. R.; Aggarwal, V. K.; de Vicente, J. *Eur. J. Org. Chem.* **2005**, 1479.

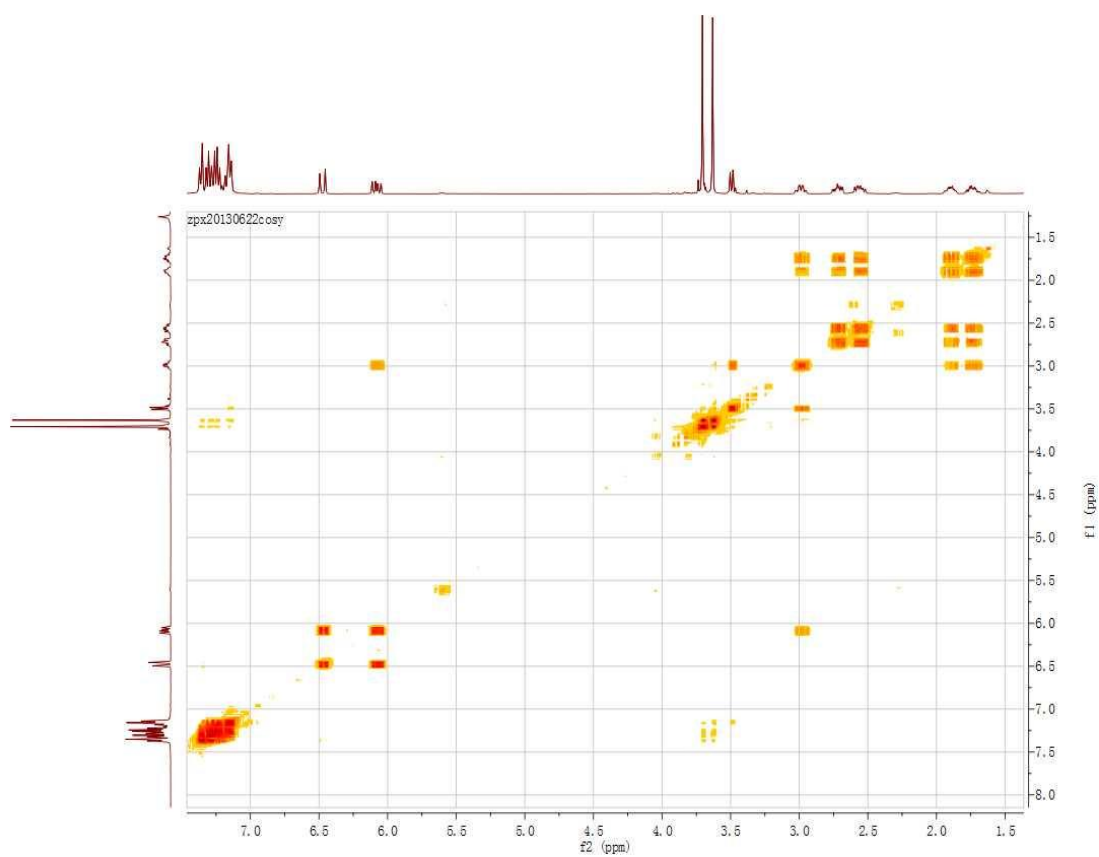
7. ^1H , ^{13}C NMR, Dept135 and 2D-NMR of product 3a



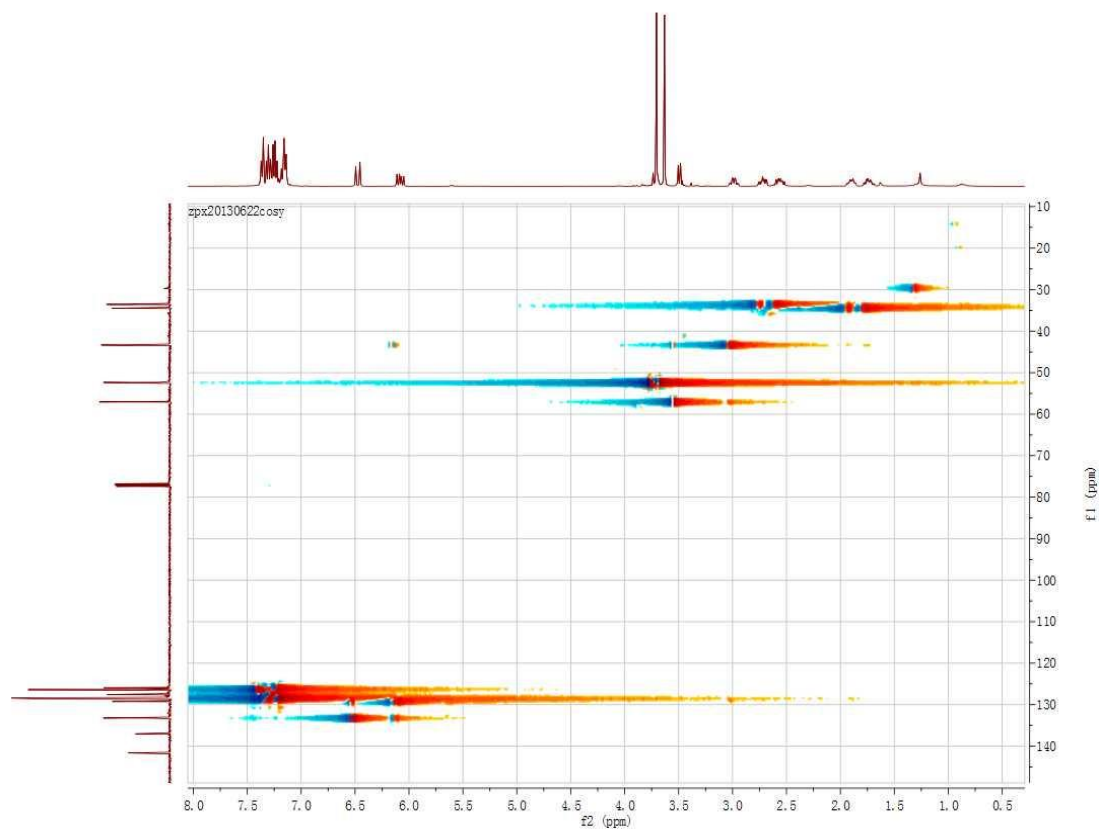
Dept135



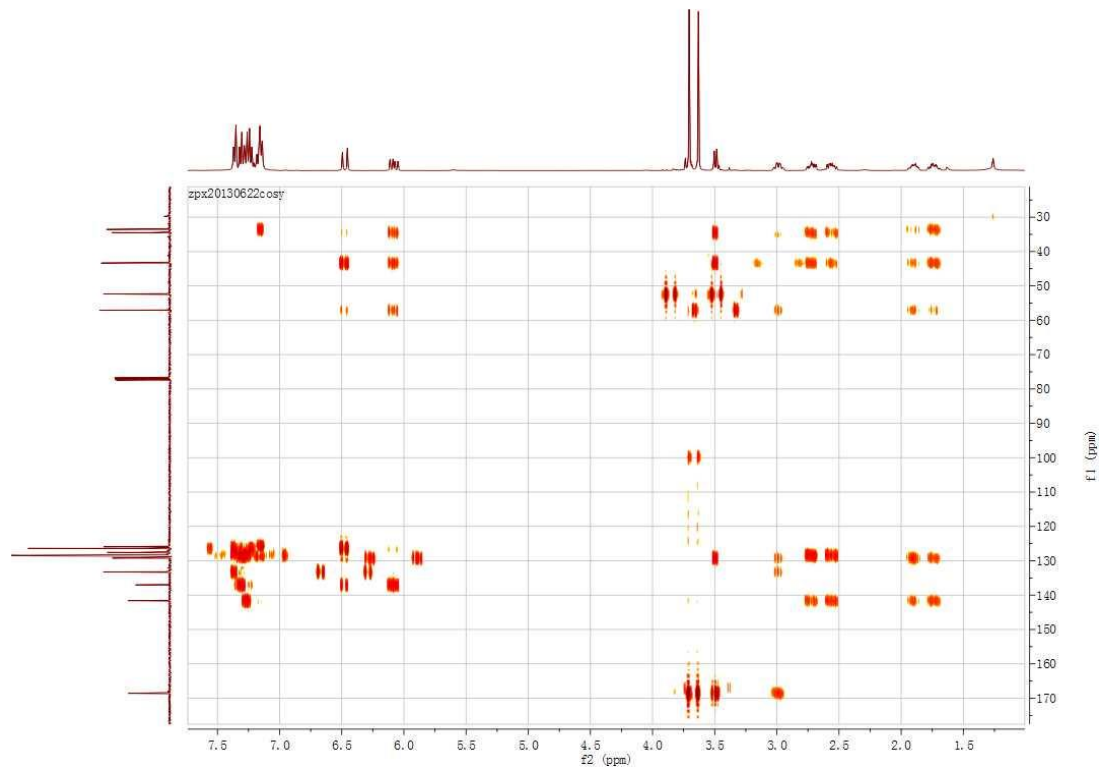
H-H COSY



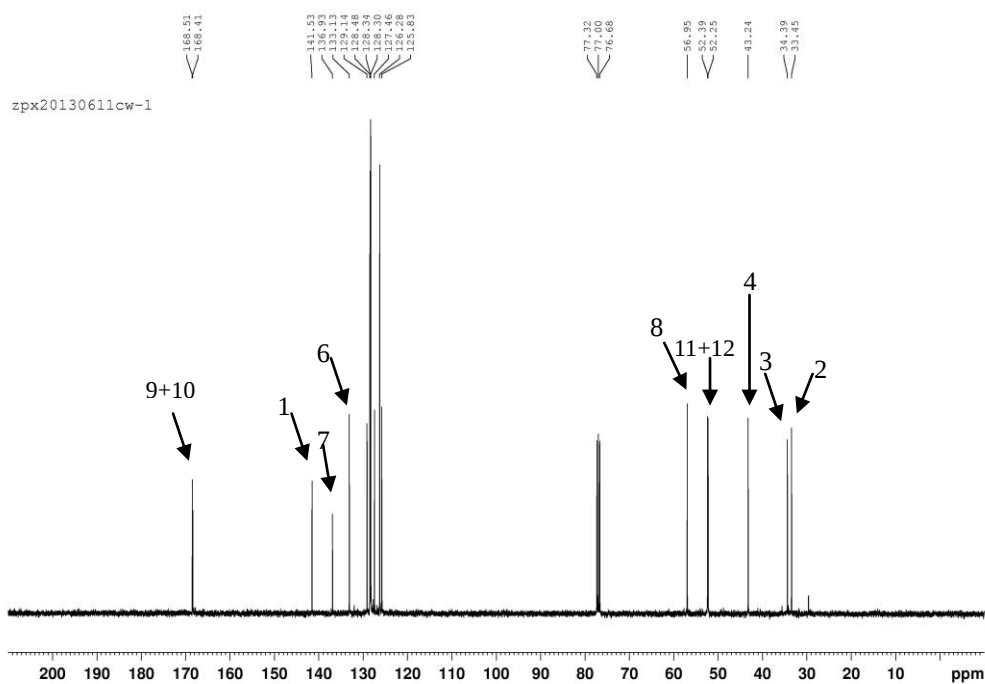
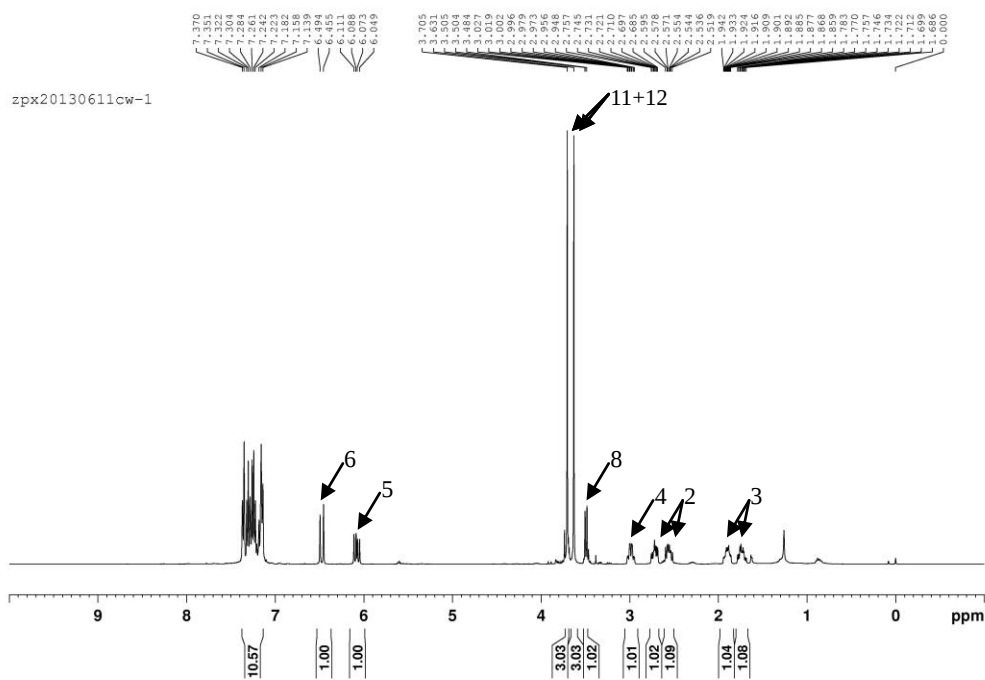
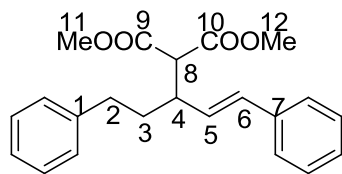
HMQC

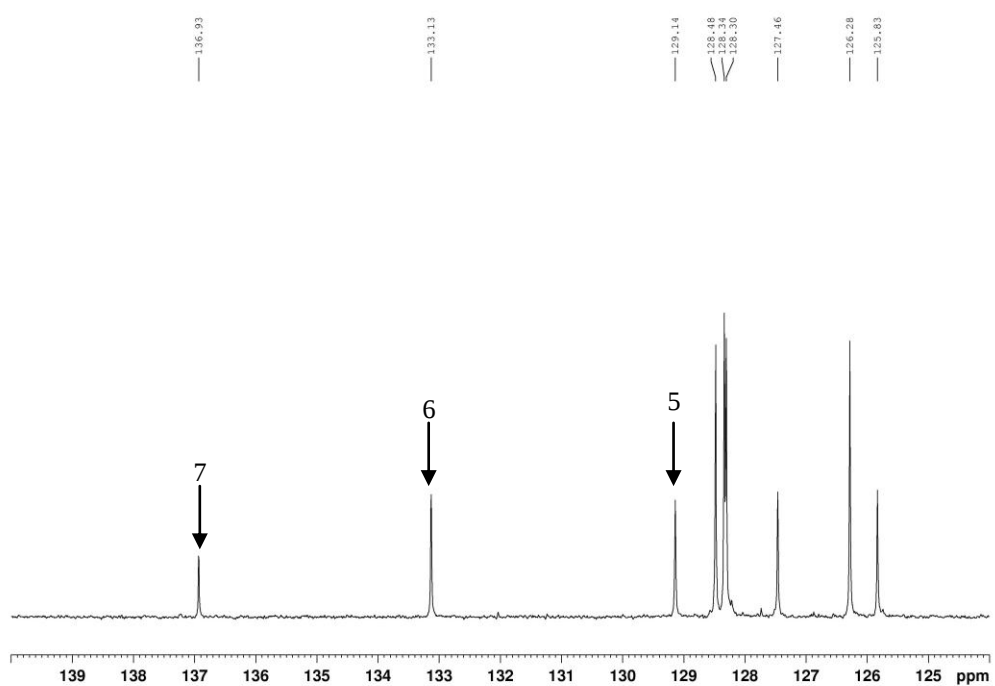


HMBC

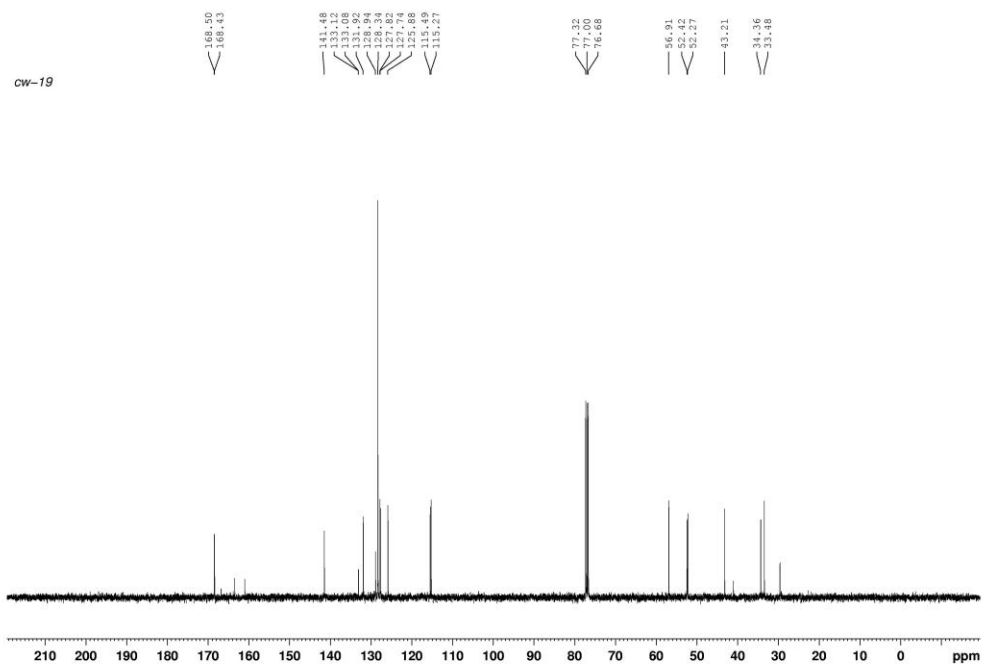
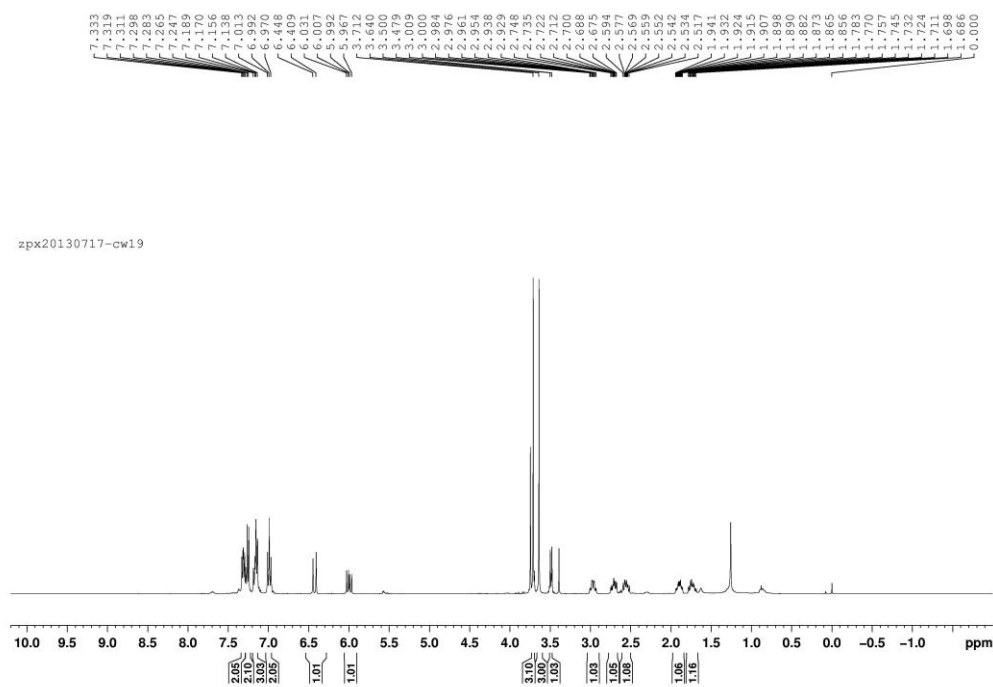
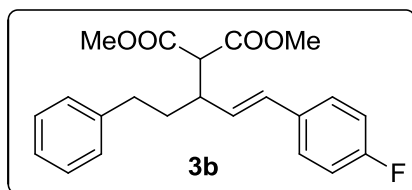


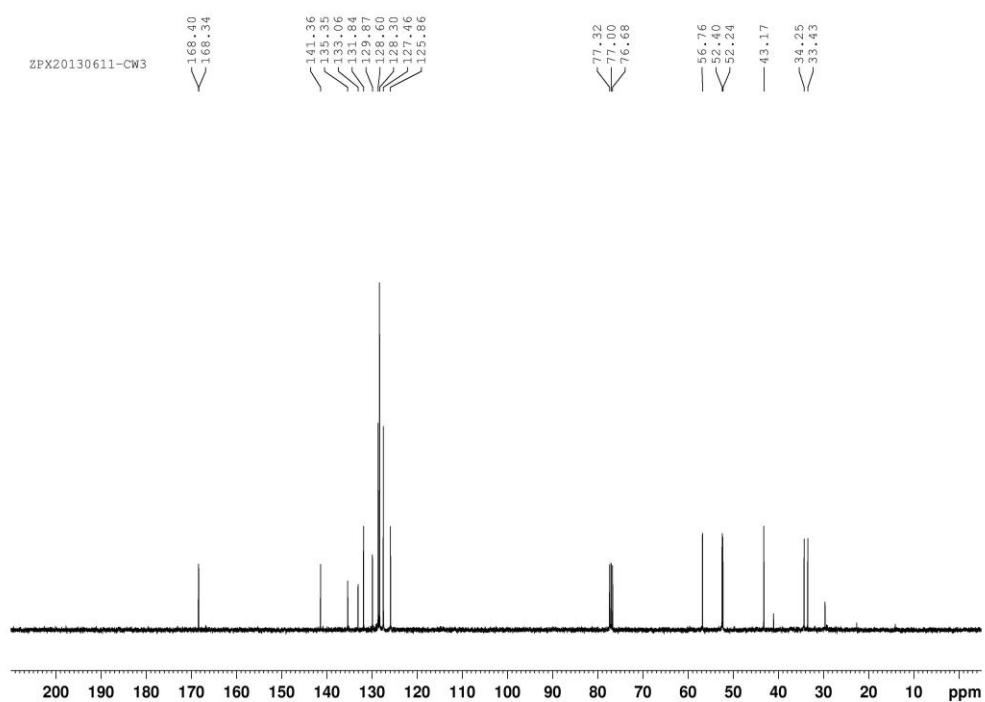
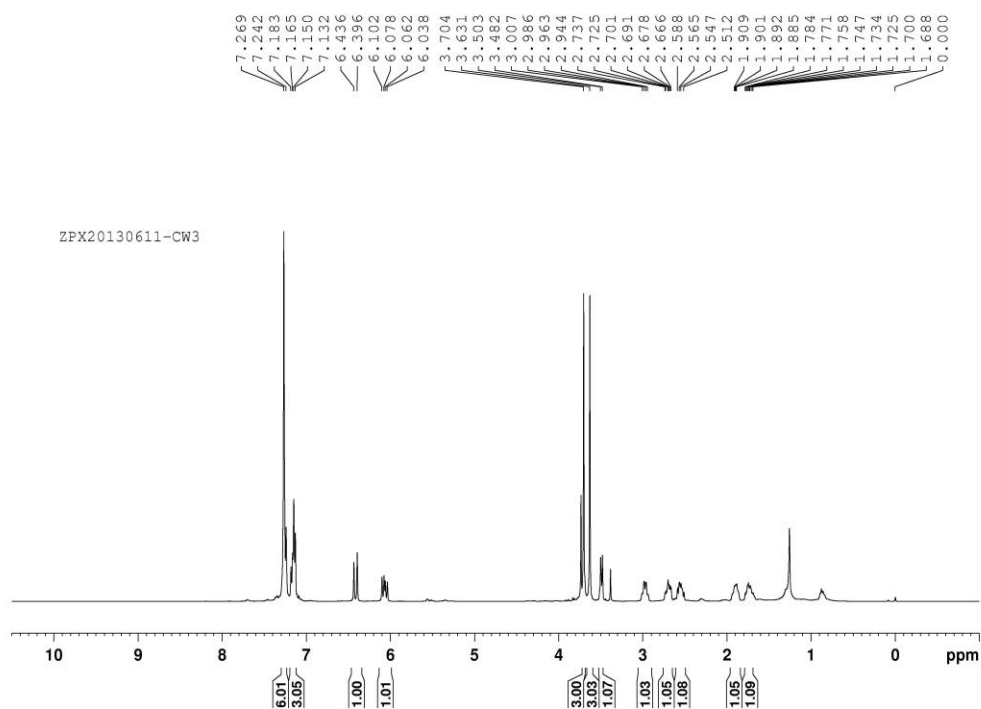
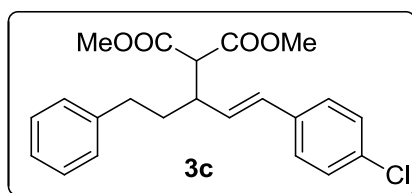
From the ^1H , ^{13}C NMR, Dept135 and 2D-NMR of product **3a**, we can identify the site of the hydrogen and carbon atom in **3a**, see below:

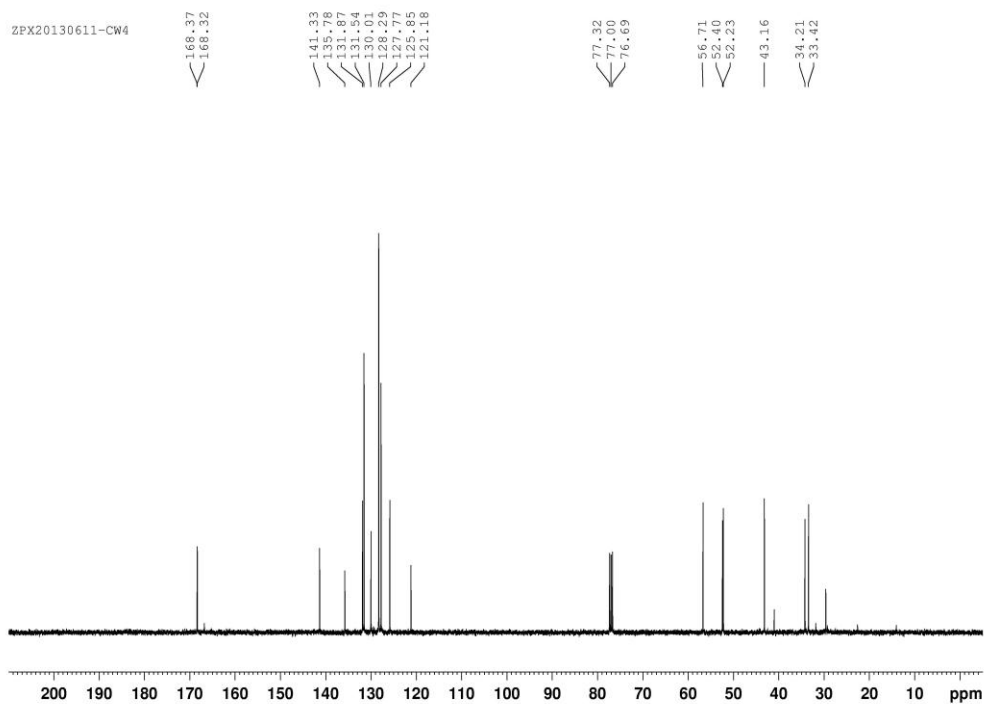
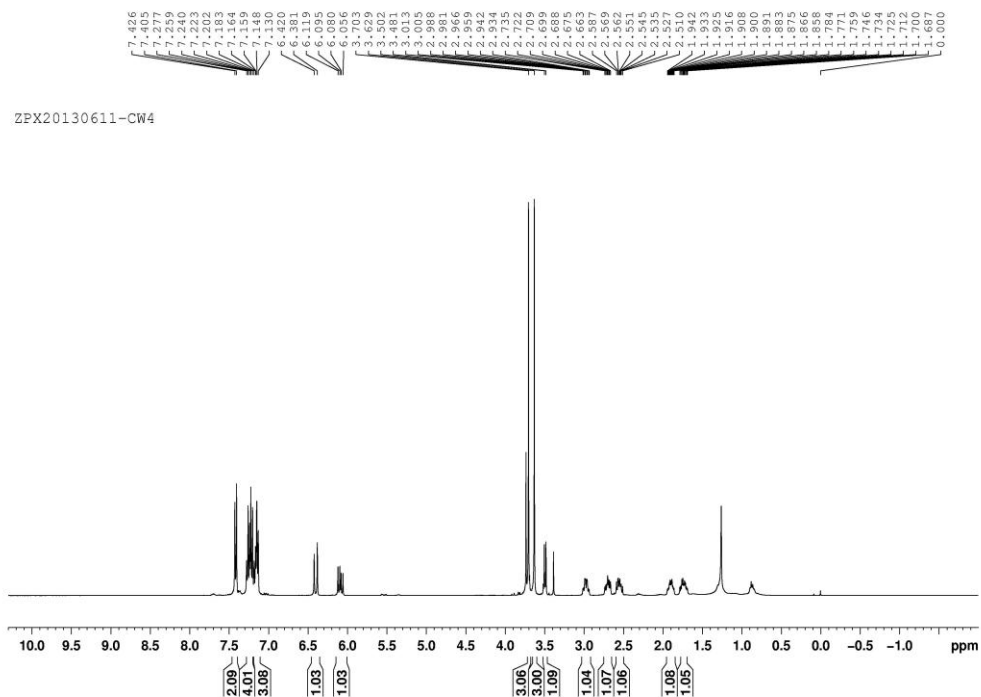
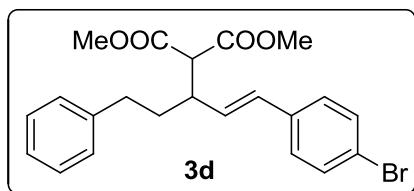


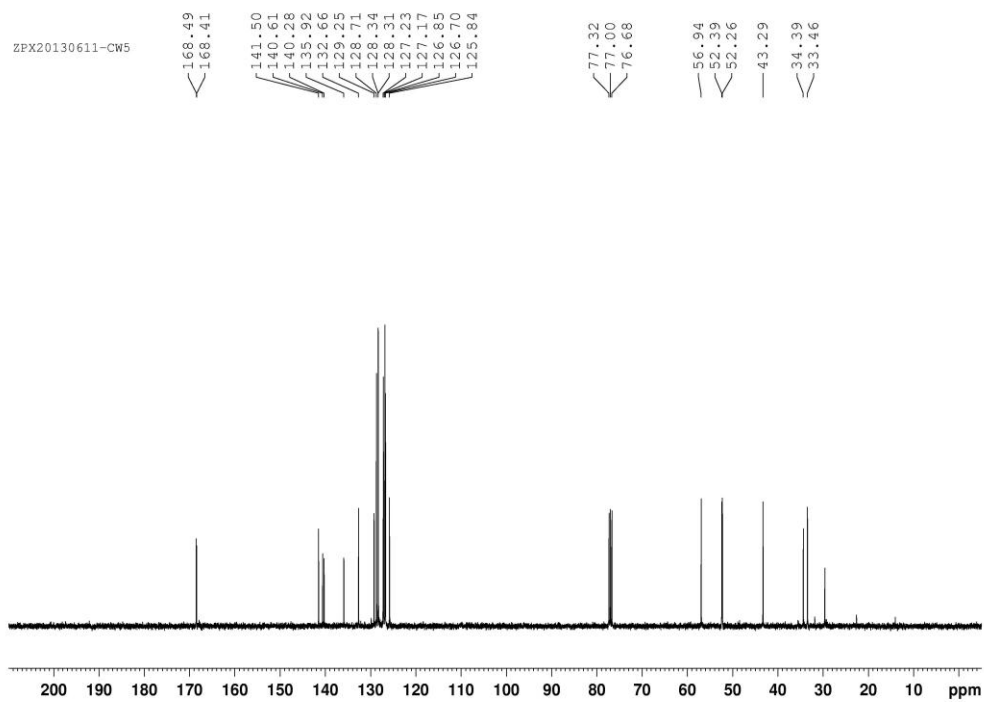
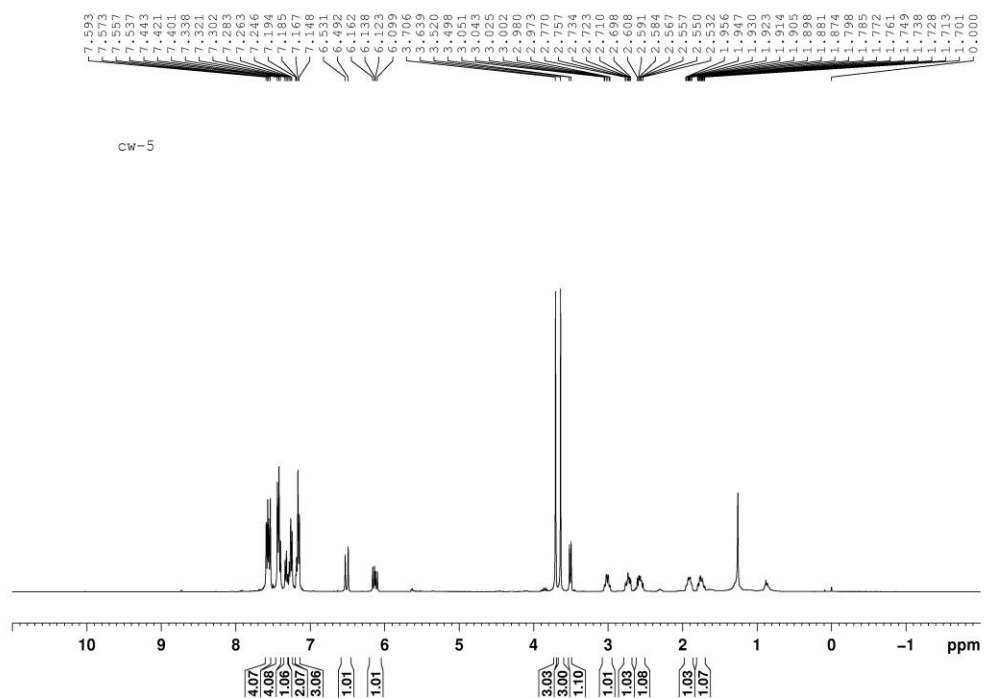
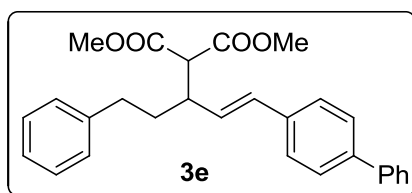


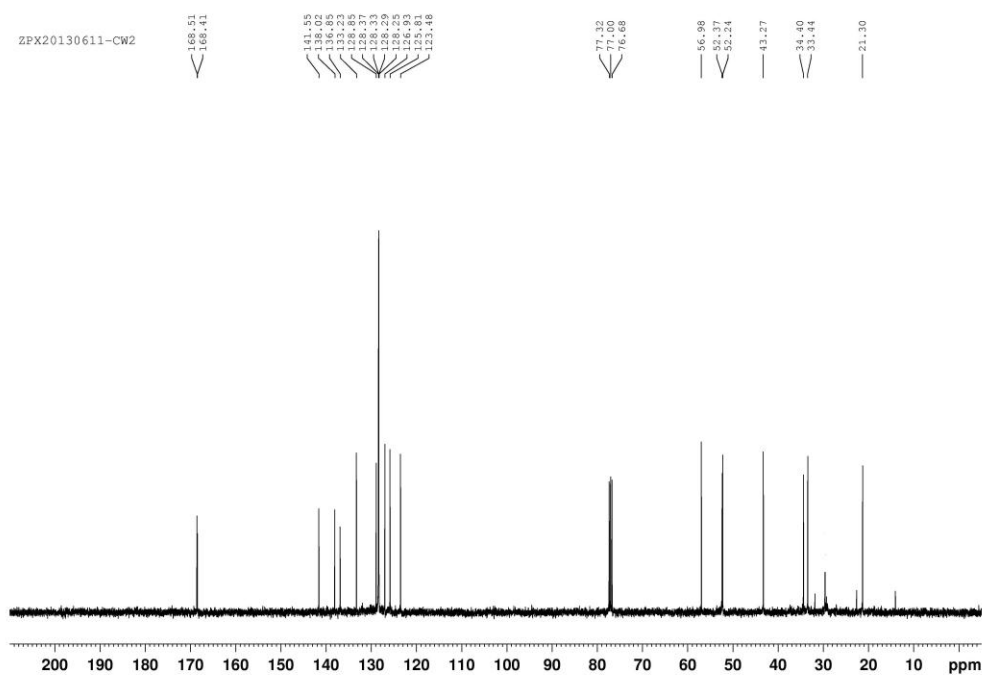
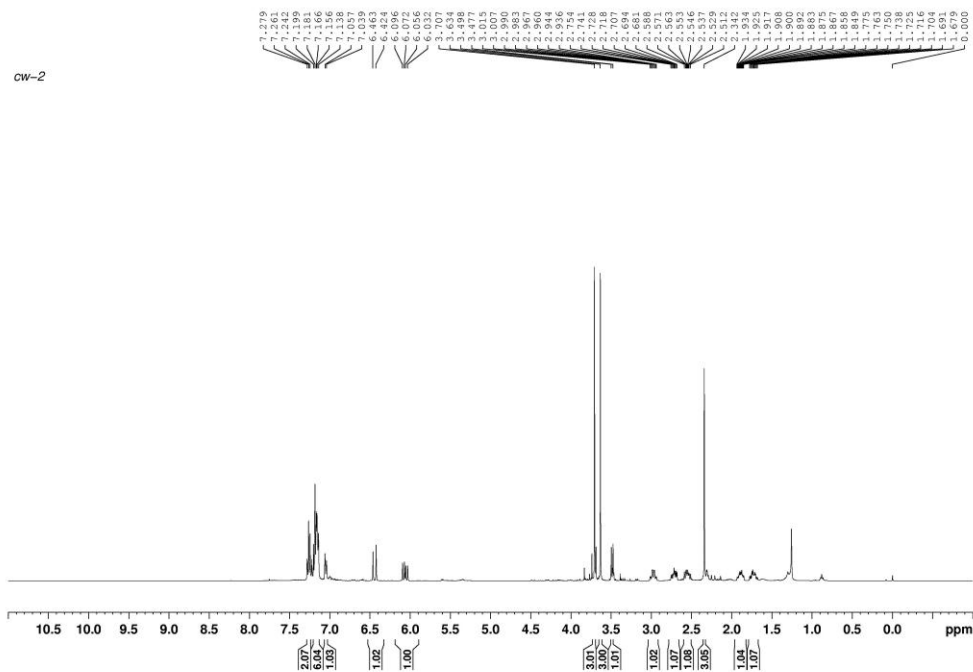
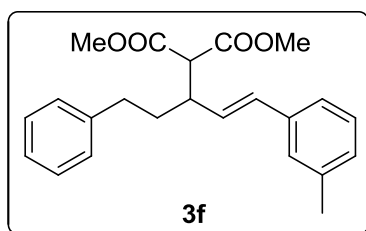
8. ^1H and ^{13}C NMR spectra for compound 3

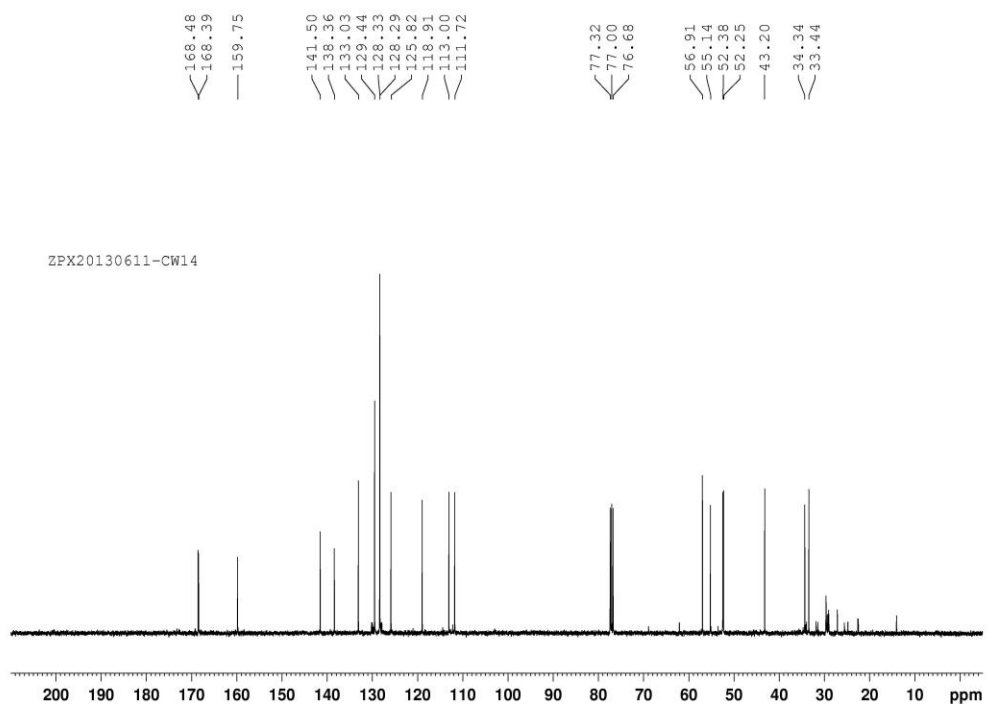
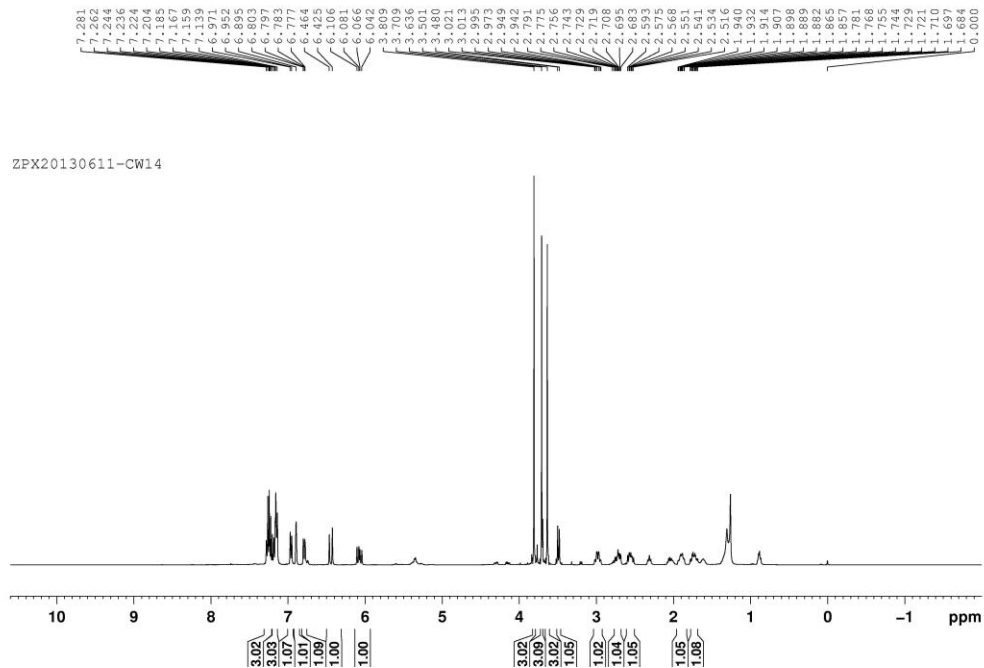
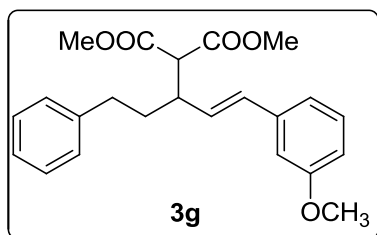


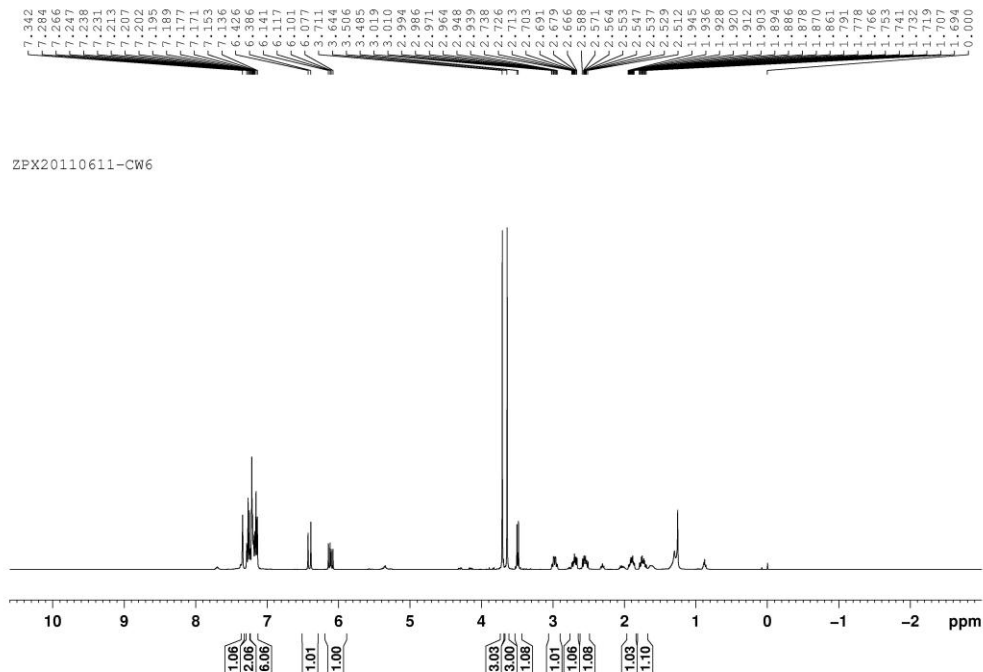
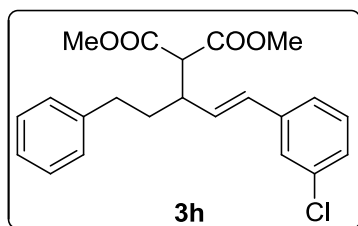




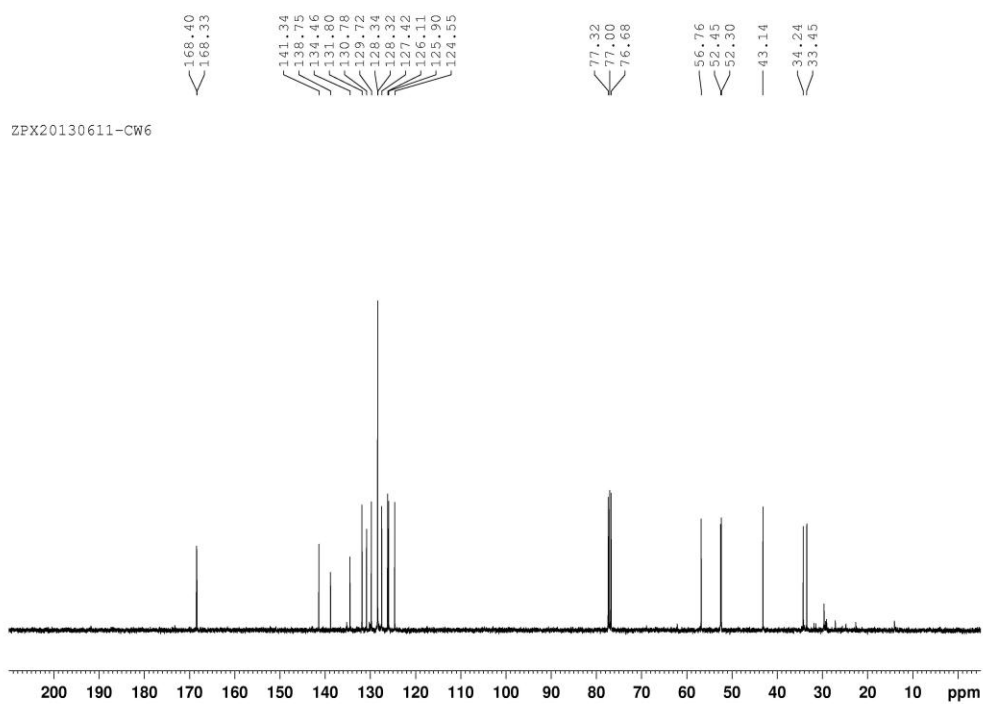




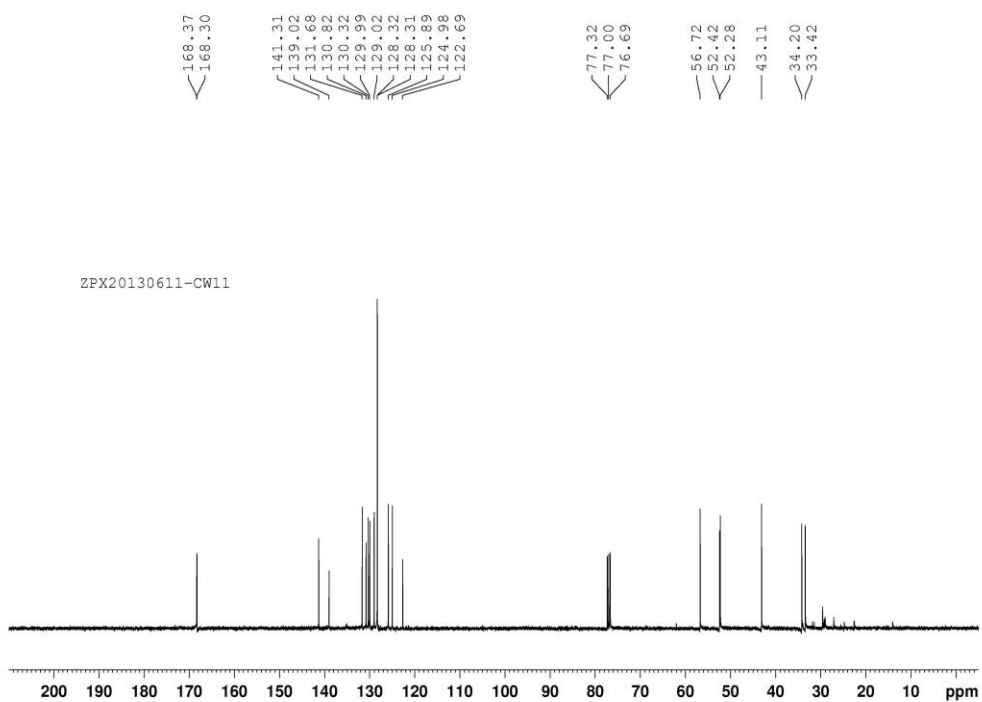
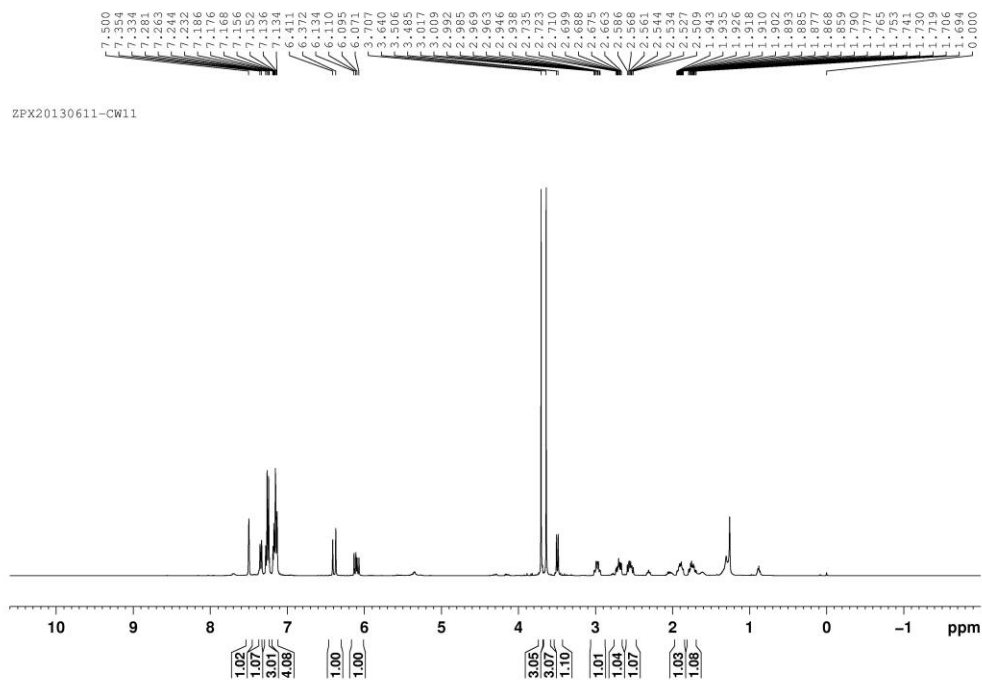
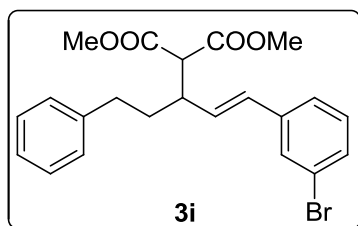


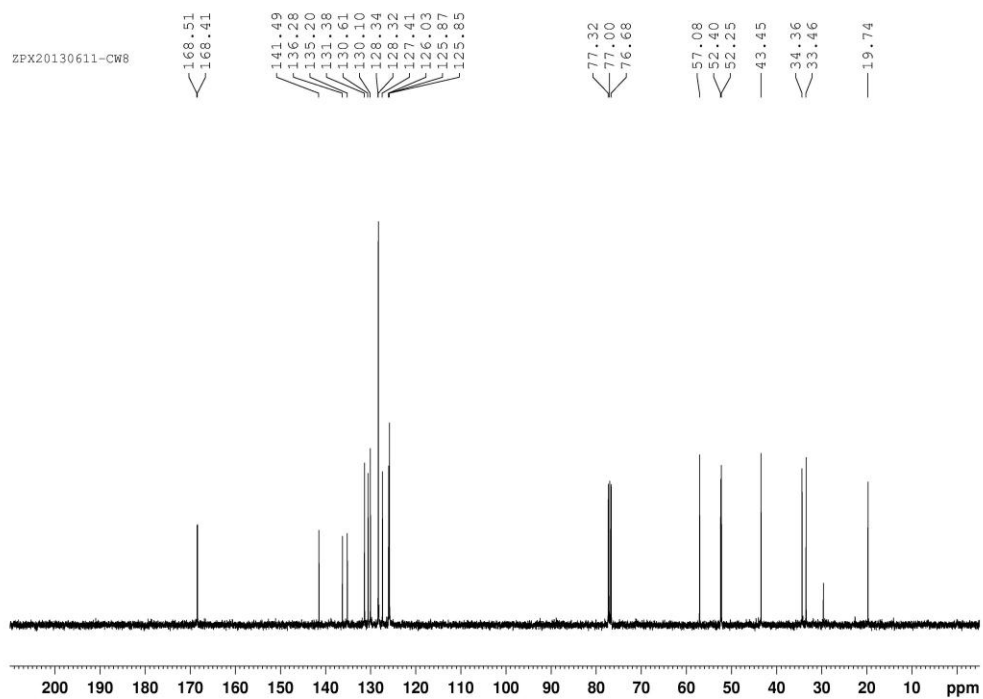
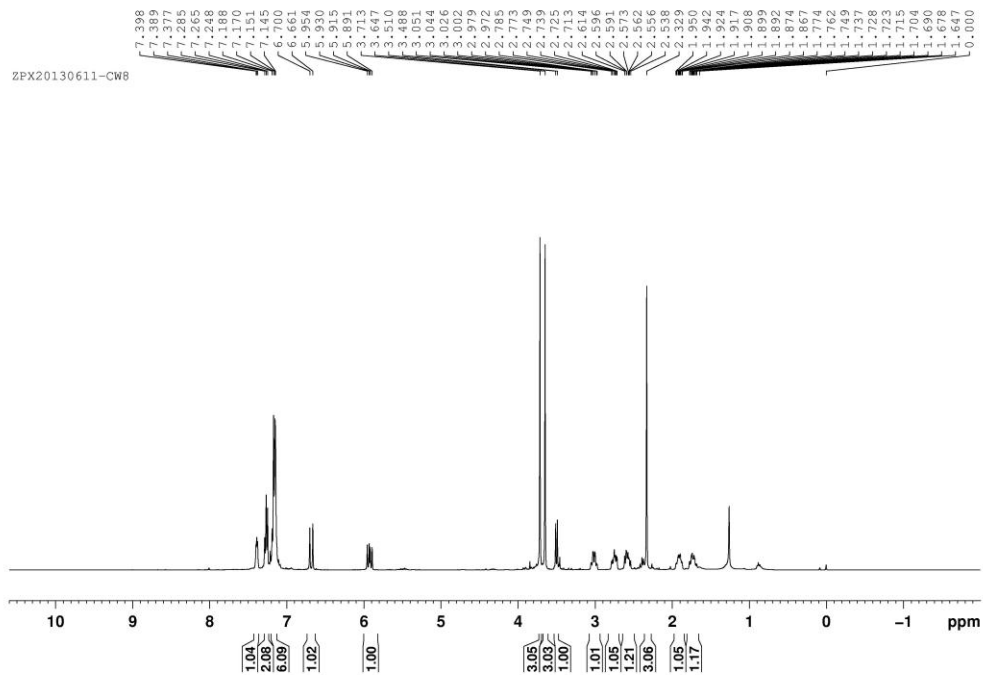
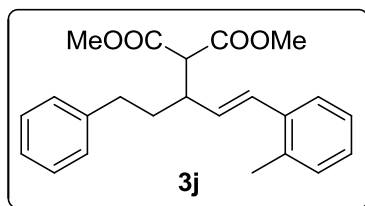


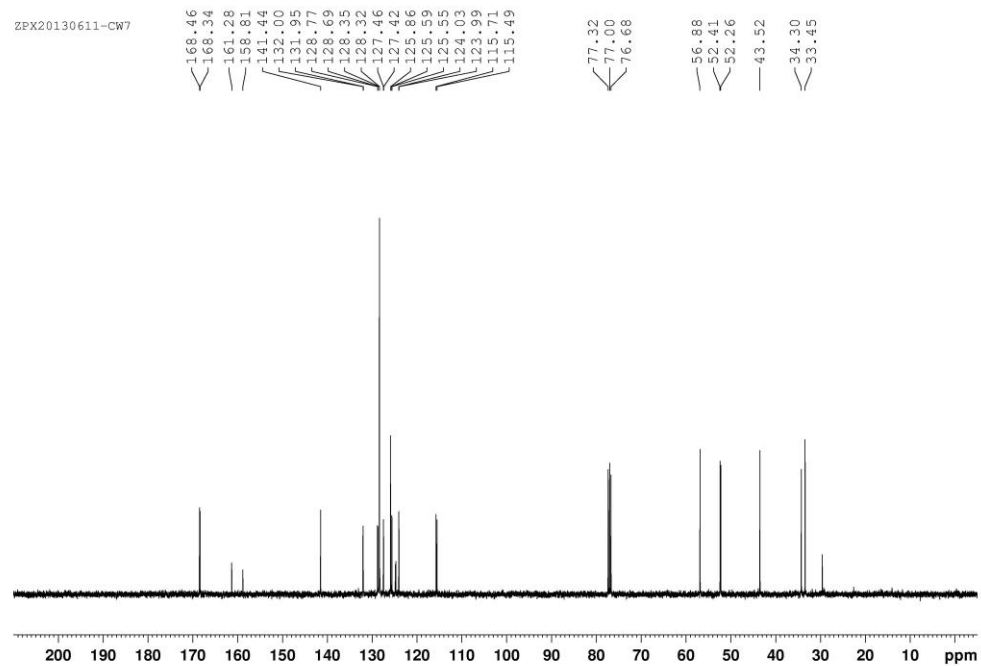
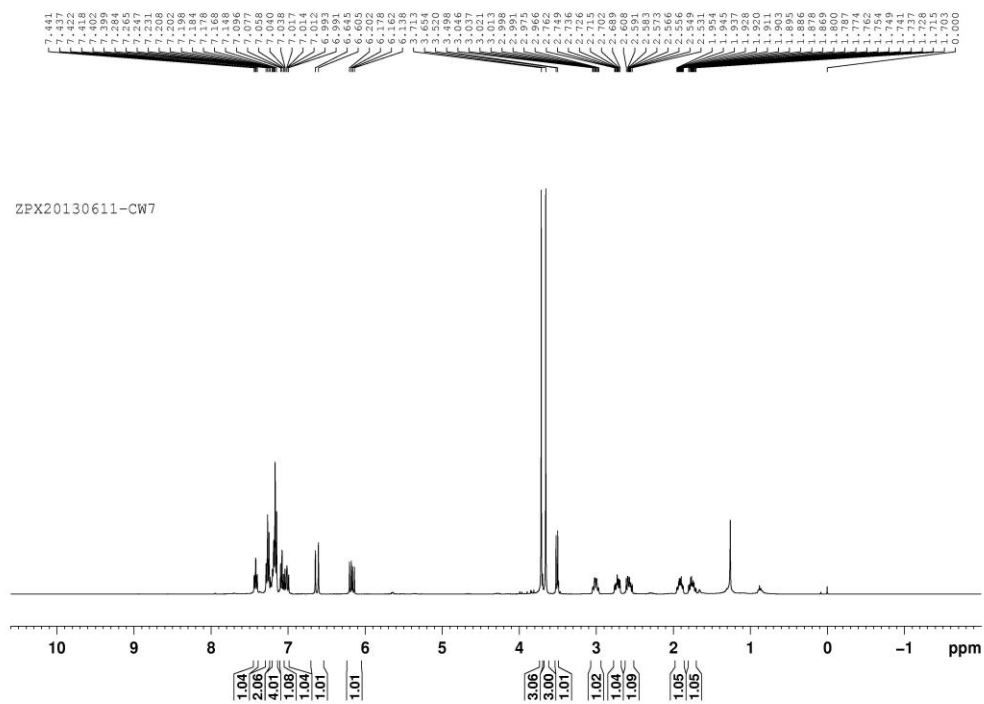
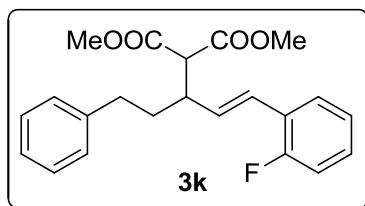
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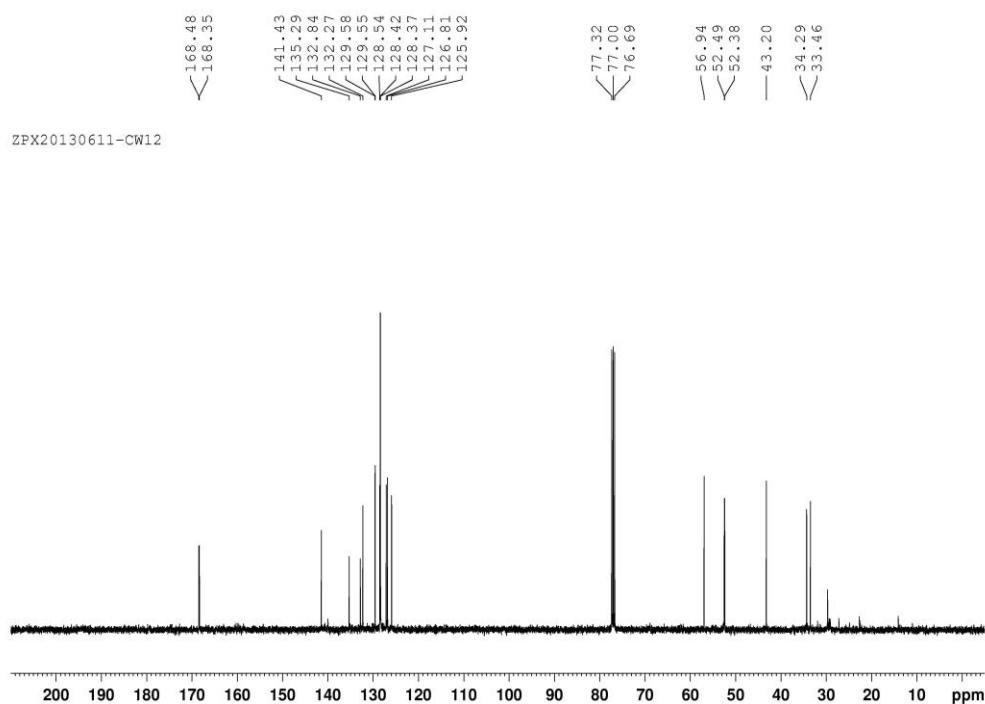
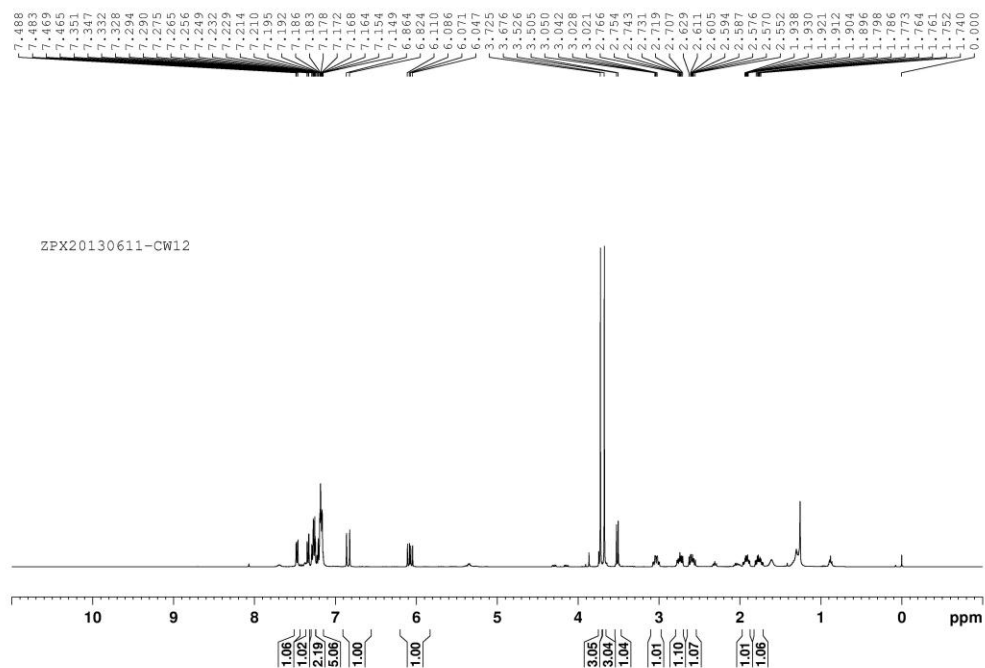
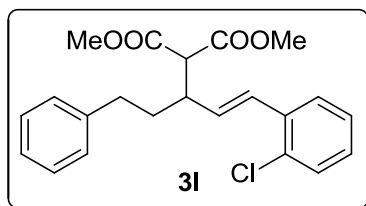


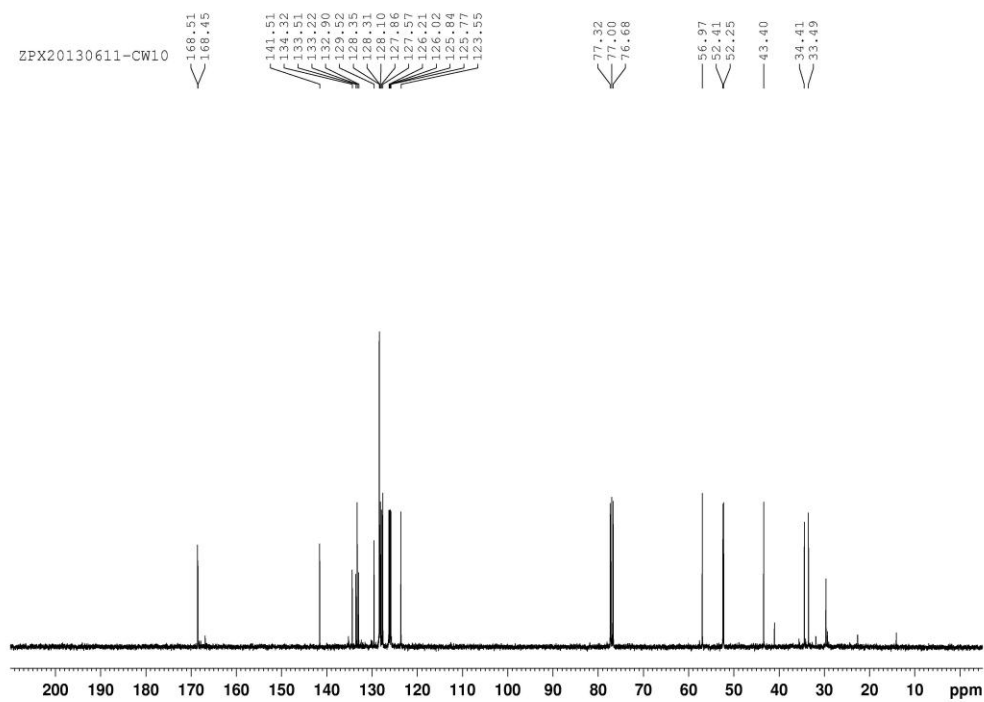
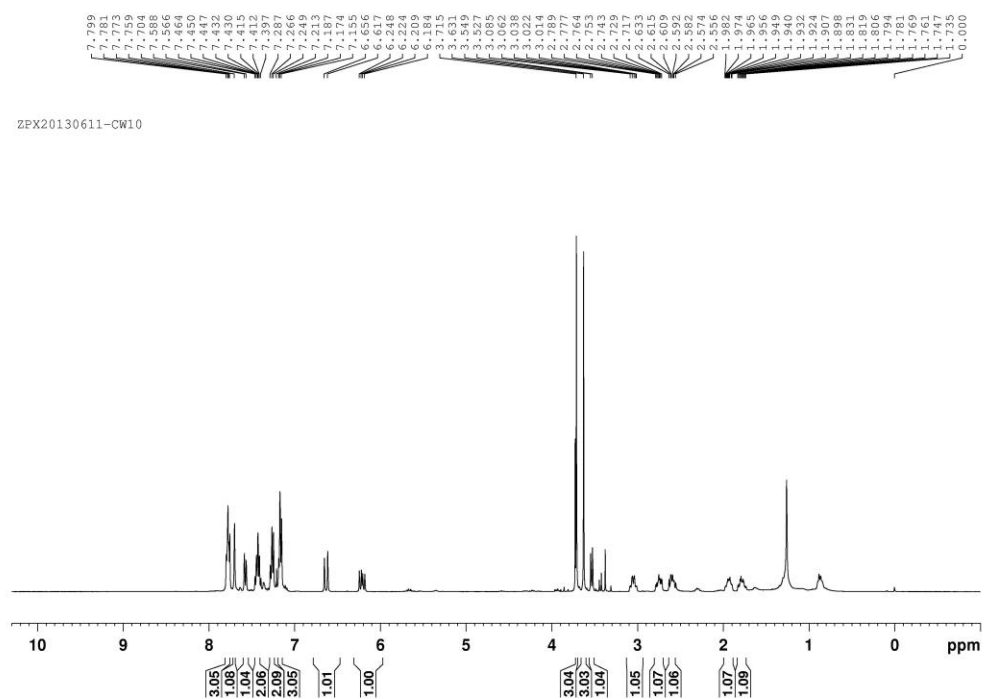
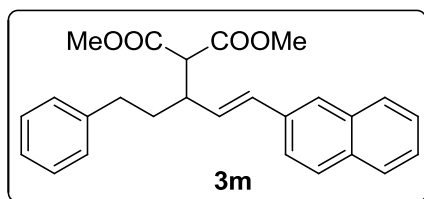
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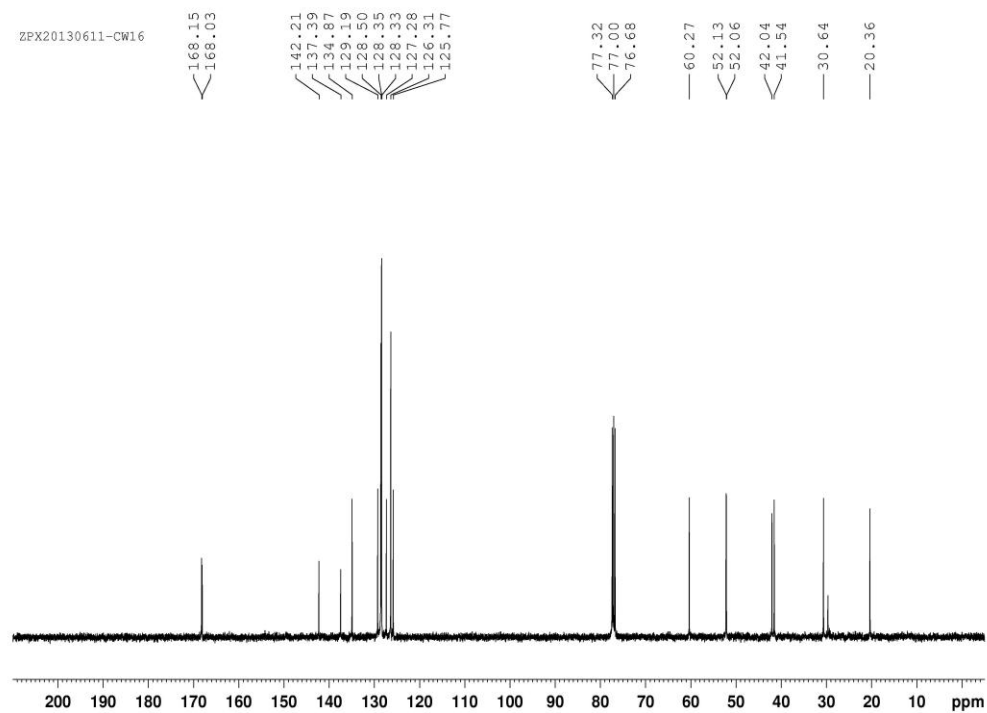
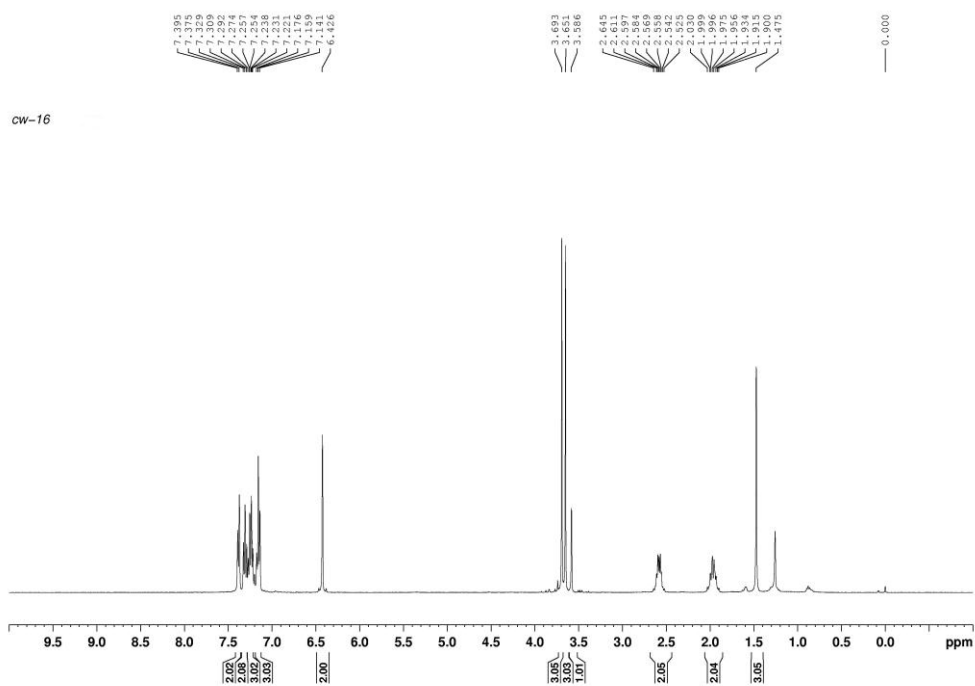
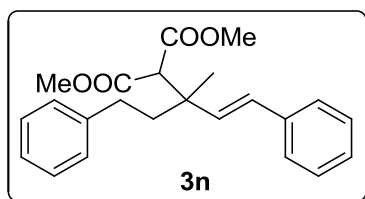


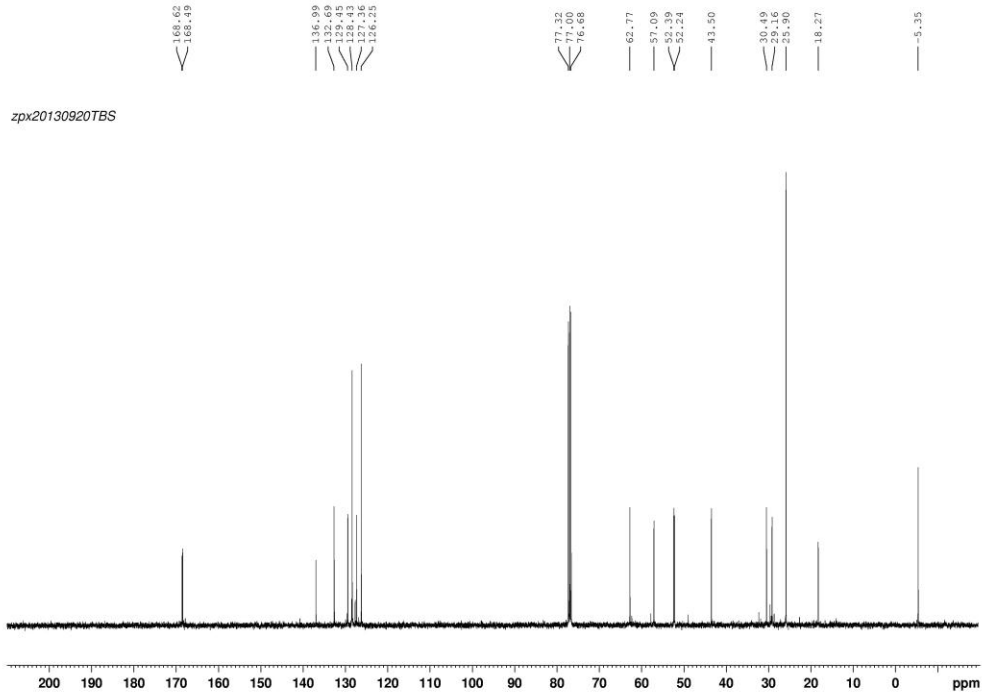
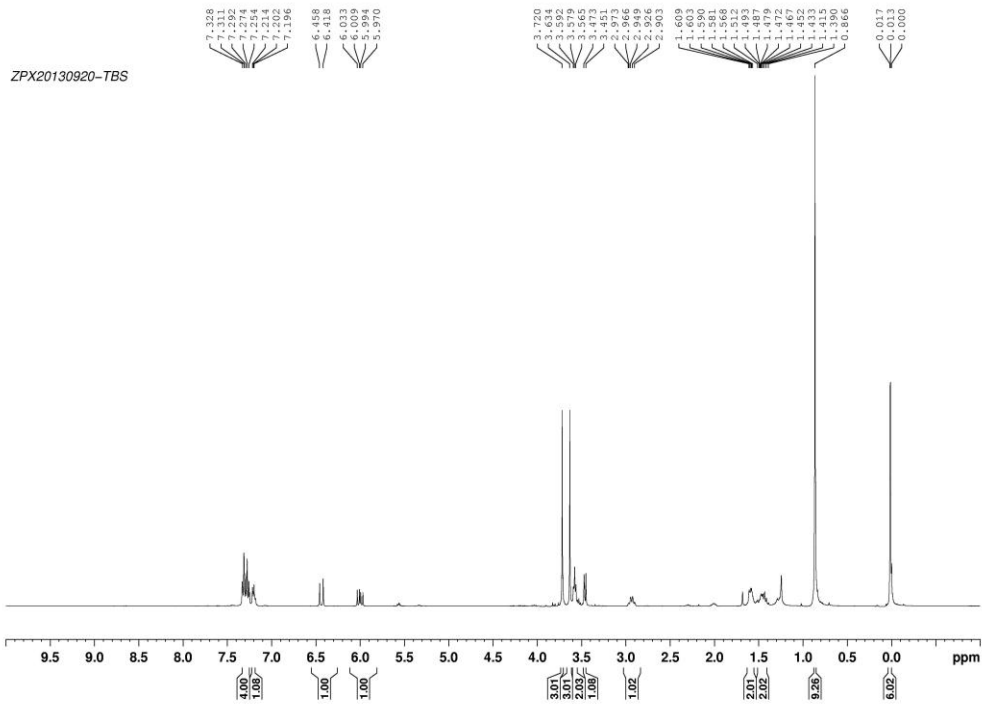
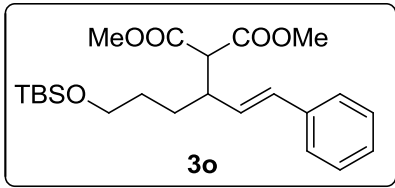


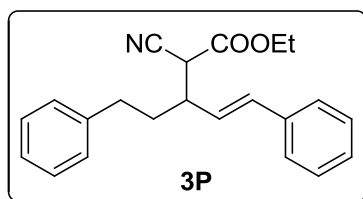




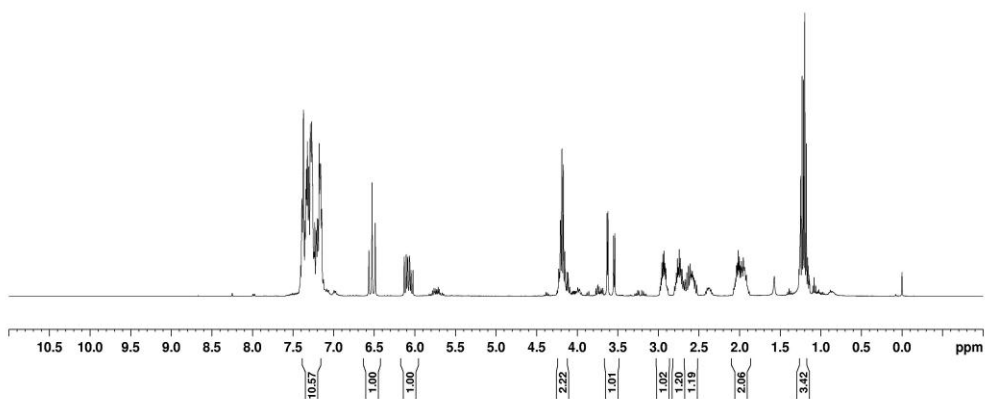








CW-17



CW-17

