

Supporting Information

Introduction of Prenyl Fragment into Chalcones through α - Regioselective 1,2-Addition in THF

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Table of Contents

1. General Methods.....	S2
2. General Procedure for the Synthesis of 2a-r	S2
3. General Procedure for the Synthesis of 2s and 2t	S2
4. General Procedure for the Synthesis of 3a, 3h, 3j, 3l, and 3w	S3
5. Characterization of 2a-v	S3-S11
6. Characterization of 3a, 3h, 3j, 3l, and 3w	S11-S14
7. Copies of ^1H and ^{13}C NMR Spectra for Compounds 2a-v	S15-S36
8. Copy of ^1H NMR Spectrum of γ -Adduct from 4-Phenylbut-3-en-2-one 1s	S37
9. Copies of ^1H and ^{13}C NMR Spectra for Compounds 3a, 3h, 3j, 3l, and 3w	S38-S42
10. Copies of ^1H and ^{13}C NMR Spectra for Compounds 4	S43

1 General Methods

α,β -unsaturated carbonyl compounds were prepared by condensation reactions of respective aldehydes and ketones. Solvents were treated prior to use according to the standard methods. Other reagents were used as purchased without further purification.

^1H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz in CDCl_3 with chemical shift (δ) given in ppm relative to TMS as internal standard. Multiplicities are indicated, s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constant (J) are in Hertz (Hz). High resolution mass spectra (HRMS) were recorded using a TOF instrument using electrospray ionization (ESI).

2 General Procedure for the Synthesis of 2a-r

Prenyl bromide (2.0 mmol) was added into a suspension of activated zinc powder (2.5 mmol) in dry THF (10 ml); the reaction mixture was stirred for 1 h at room temperature. Filtered the solution through a Schlenk filter and kept under N_2 for the following reaction. A solution of chalcones **1** (1.0 mmol) in dry THF (5 ml) was added the solution of prenylzinc bromide prepared above. The mixture was refluxed for 10 h. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1, v/v) to afford the α -adducts **2a-r**.

3 General Procedure for the Synthesis of 2s and 2t

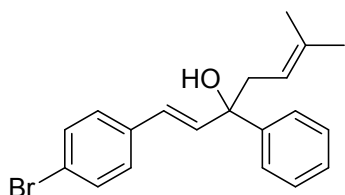
Prenyl bromide (2.0 mmol) was added into a suspension of activated zinc powder (2.5 mmol) in dry THF (10 ml); the reaction mixture was stirred for 1 h at room temperature. Filtered the solution through a Schlenk filter and kept under N_2 for the following reaction. A solution of α,β -unsaturated carbonyl compounds **1** (1.0 mmol) in dry THF (5 ml) was added the solution of prenylzinc bromide prepared above. The solution was stirred for 1 h at room temperature. Then DMI (1.5 ml) was added into the reaction mixture, followed by removal of initial reaction solvent (THF). The mixture was heated to 120 °C for 14 h. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1, v/v) to afford the α -adducts **2s** and **2t**.

4 General Procedure for the Synthesis of 3a, 3h, 3j, 3l, and 3w

Crotyl bromide (2.0 mmol) was added into a suspension of activated zinc powder (2.5 mmol) in dry THF (10 ml); the reaction mixture was stirred for 1 h at room temperature. Filtered the solution through a Schlenk filter and kept under N₂ for the following reaction. A solution of chalcones **1** (1.0 mmol) in dry THF (5 ml) was added the solution of crotylzinc bromide prepared above. The mixture was refluxed for 10 h. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1, v/v) to afford the α -adducts **3a**, **3h**, **3j**, **3l**, and **3w**.

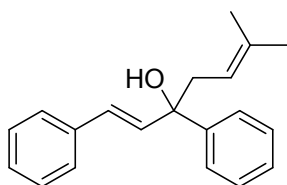
5 Characterization of 2a-r

Characterization of **2a**:



Colorless oil; ¹H NMR (CDCl₃, 400 MHz) δ : 7.50 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.36 (t, J = 8.0 Hz, 2H), 7.27-7.22 (m, 3H), 6.58 (d, J = 16.0 Hz, 1H), 6.50 (d, J = 16.0 Hz, 1H), 5.07 (t, J = 7.6 Hz, 1H), 2.80-2.70 (m, 2H), 2.30 (s, 1H), 1.71 (s, 3H), 1.66 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ : 145.5, 137.7, 136.4, 135.9, 131.6, 128.3, 128.1, 126.9, 125.4, 121.1, 117.9, 76.4, 41.2, 26.1, 18.2. HRMS (ESI): m/z calcd for C₂₀H₂₁OBrNa [M + Na]⁺: 379.0673; Found: 379.0673.

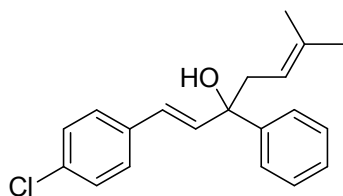
Characterization of **2b**:



Yellow oil; ¹H NMR (CDCl₃, 400 MHz) δ : 7.52 (d, J = 8.0 Hz, 2H), 7.42-7.18 (m, 8H), 6.64 (d, J = 16.0 Hz, 1H), 6.53 (d, J = 16.0 Hz, 1H), 5.09 (t, J = 7.8 Hz, 1H), 2.83-2.67 (m, 2H), 2.28 (s, 1H), 1.71 (s, 3H), 1.66 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ : 145.8, 137.6, 136.9,

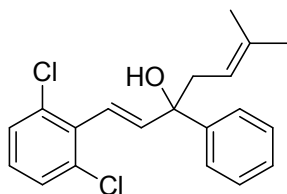
135.6, 128.6, 128.3, 128.1, 127.5, 126.9, 126.6, 125.3, 118.1, 76.4, 41.3, 26.1, 18.2. HRMS (ESI): m/z calcd for $C_{20}H_{22}ONa$ $[M + Na]^+$: 301.1568; Found: 301.1568.

Characterization of **2c**:



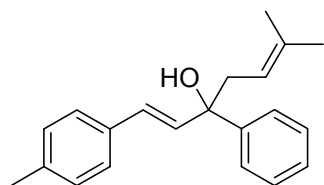
Yellow oil; 1H NMR ($CDCl_3$, 400 MHz) δ : 7.51 (d, $J = 8.0$ Hz, 2H), 7.37 (t, $J = 7.8$ Hz, 2H), 7.33-7.23 (m, 5H), 6.60 (d, $J = 16.0$ Hz, 1H), 6.49 (d, $J = 16.0$ Hz, 1H), 5.07 (t, $J = 7.0$ Hz, 1H), 2.83-2.65 (m, 2H), 2.28 (s, 1H), 1.71 (s, 3H), 1.66 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 145.5, 137.8, 136.3, 135.5, 133.0, 128.7, 128.3, 127.8, 126.9, 126.8, 125.5, 117.9, 76.4, 41.2, 26.1, 18.2. HRMS (ESI): m/z calcd for $C_{20}H_{21}ClONa$ $[M + Na]^+$: 335.1179; Found: 335.1179.

Characterization of **2d**:



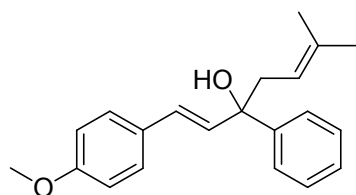
Colorless oil; 1H NMR ($CDCl_3$, 400 MHz) δ : 7.58 (d, $J = 7.6$ Hz, 2H), 7.38 (t, $J = 7.6$ Hz, 2H), 7.33-7.23 (m, 3H), 7.08 (t, $J = 8.0$ Hz, 1H), 6.67 (d, $J = 16.4$ Hz, 1H), 6.52 (d, $J = 16.4$ Hz, 1H), 5.23 (t, $J = 7.2$ Hz, 1H), 2.84-2.67 (m, 2H), 2.35 (s, 1H), 1.74 (s, 3H), 1.67 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 145.2, 143.5, 137.5, 134.8, 134.5, 128.3, 128.0, 127.0, 125.7, 122.4, 118.2, 76.6, 41.0, 26.2, 18.2. HRMS (ESI): m/z calcd for $C_{20}H_{20}Cl_2ONa$ $[M + Na]^+$: 369.0789; Found: 369.0806.

Characterization of **2e**:



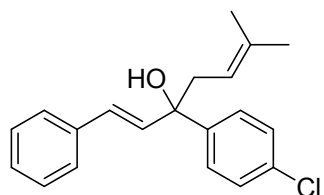
Pale yellow oil; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ : 7.52 (d, $J = 8.4$ Hz, 2H), 7.35 (t, $J = 8.0$ Hz, 2H), 7.31-7.21 (m, 3H), 7.11 (d, $J = 8.0$ Hz, 2H), 6.60 (d, $J = 16.0$ Hz, 1H), 6.47 (d, $J = 16.0$ Hz, 1H), 5.09 (t, $J = 8.0$ Hz, 1H), 2.90-2.58 (m, 2H), 2.32 (s, 3H), 2.26 (s, 1H), 1.71 (s, 3H), 1.66 (s, 3H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ : 145.9, 137.4, 137.3, 134.6, 134.1, 129.3, 128.2, 128.0, 126.8, 126.5, 125.6, 118.2, 76.7, 41.3, 26.1, 21.2, 18.3. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{24}\text{ONa}$ [$\text{M} + \text{Na}$] $^+$: 315.1725; Found: 315.1727.

Characterization of **2f**:



Colorless oil; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ : 7.52 (d, $J = 7.6$ Hz, 2H), 7.40-7.28 (m, 4H), 7.28-7.20 (m, 1H), 6.82 (d, $J = 8.0$ Hz, 2H), 6.57 (d, $J = 16.0$ Hz, 1H), 6.39 (d, $J = 16.0$ Hz, 1H), 5.09 (t, $J = 8.0$ Hz, 1H), 3.80 (s, 3H), 2.87-2.63 (m, 2H), 2.26 (s, 1H), 1.71 (s, 3H), 1.66 (s, 3H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ : 159.1, 146.0, 137.3, 133.5, 129.7, 128.2, 127.7, 127.6, 126.8, 125.6, 118.2, 114.0, 76.5, 55.3, 41.4, 26.1, 18.3. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{24}\text{O}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$: 331.1674; Found: 331.1665.

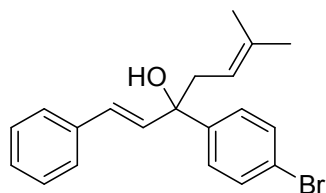
Characterization of **2g**:



Pale yellow oil; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ : 7.45 (d, $J = 8.8$ Hz, 2H), 7.38 (d, $J = 7.2$ Hz, 2H), 7.35-7.20 (m, 5H), 6.62 (d, $J = 16.0$ Hz, 1H), 6.48 (d, $J = 16.0$ Hz, 1H), 5.06 (t, $J = 8.0$

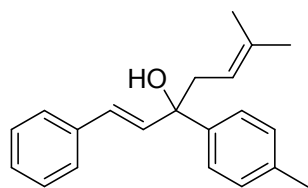
Hz, 1H), 2.80-2.61 (m, 2H), 2.28 (s, 1H), 1.71 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 144.3, 138.0, 136.7, 135.0, 132.7, 128.6, 128.5, 128.3, 127.7, 127.1, 126.6, 117.7, 76.1, 41.2, 26.2, 18.3. HRMS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{21}\text{ClONa}$ $[\text{M} + \text{Na}]^+$: 335.1179; Found: 335.1168.

Characterization of **2h**:



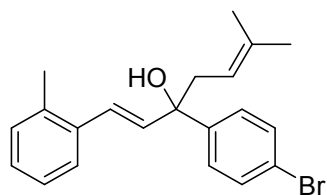
Pale yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.40 (d, $J = 8.0$ Hz, 2H), 7.33-7.25 (m, 4H), 7.23 (t, $J = 7.6$ Hz, 2H), 7.16 (t, $J = 7.6$ Hz, 1H), 6.54 (d, $J = 16.0$ Hz, 1H), 6.39 (d, $J = 16.0$ Hz, 1H), 4.98 (t, $J = 7.2$ Hz, 1H), 2.65-2.63 (m, 2H), 2.21 (s, 1H), 1.64 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 144.8, 138.1, 136.6, 135.0, 131.3, 128.6, 128.5, 127.7, 127.5, 126.6, 120.8, 117.6, 76.2, 41.2, 26.2, 18.3. HRMS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{21}\text{BrONa}$ $[\text{M} + \text{Na}]^+$: 379.0673; Found: 379.0659.

Characterization of **2i**:



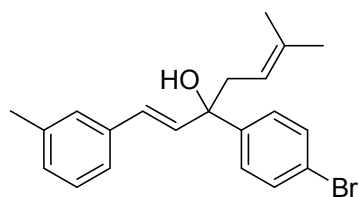
Pale yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.41 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.24-7.16 (m, 3H), 6.64 (d, $J = 16.0$ Hz, 1H), 6.52 (d, $J = 16.0$ Hz, 1H), 5.11 (t, $J = 7.2$ Hz, 1H), 2.80-2.69 (m, 2H), 2.35 (s, 3H), 2.25 (s, 1H), 1.72 (s, 3H), 1.67 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 142.8, 137.3, 137.0, 136.5, 135.8, 129.0, 128.5, 127.9, 127.4, 126.6, 125.5, 118.3, 76.4, 41.2, 26.1, 21.0, 18.2. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{24}\text{ONa}$ $[\text{M} + \text{Na}]^+$: 315.1725; Found: 315.1724.

Characterization of **2j**:



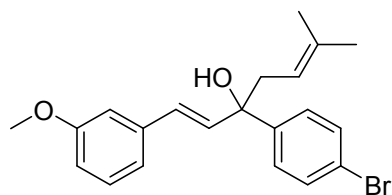
Yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.48 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.17-7.15 (m, 3H), 6.85 (d, $J = 16.0$ Hz, 1H), 6.35 (d, $J = 16.0$ Hz), 5.09 (t, $J = 7.2$ Hz, 1H), 2.76-2.66 (m, 2H), 2.33 (s, 3H), 2.29 (s, 1H), 1.73 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 145.0, 138.8, 137.8, 136.4, 136.0, 135.7, 131.3, 130.3, 127.6, 127.6, 126.5, 126.1, 125.7, 120.8, 117.8, 76.4, 41.3, 26.2, 19.9, 18.3. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{23}\text{BrONa}$ [$\text{M} + \text{Na}$] $^+$: 393.0830; Found: 393.0824.

Characterization of **2k**:



Yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.48 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.23-7.17 (m, 3H), 7.04 (d, $J = 6.4$ Hz, 1H), 6.59 (d, $J = 16.0$ Hz, 1H), 6.46 (d, $J = 16.0$ Hz, 1H), 5.07 (t, $J = 7.2$ Hz, 1H), 2.76-2.67 (m, 2H), 2.34 (s, 3H), 2.27 (s, 1H), 1.72 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 145.0, 138.3, 138.0, 136.8, 135.0, 131.4, 128.8, 128.6, 127.6, 127.4, 123.9, 121.0, 117.9, 76.4, 41.3, 26.3, 21.5, 18.4. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{23}\text{BrONa}$ [$\text{M} + \text{Na}$] $^+$: 393.0830; Found: 393.0830.

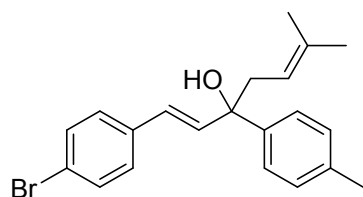
Characterization of **2l**:



Yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.48 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.25-7.23 (m, 1H), 6.98 (d, $J = 8.0$ Hz, 1H), 6.92 (s, 1H), 6.80 (d, $J = 8.0$ Hz, 1H), 6.60 (d, $J =$

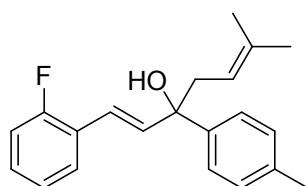
16.0 Hz, 1H), 6.47 (d, $J = 16.0$ Hz, 1H), 5.07 (t, $J = 7.2$ Hz, 1H), 3.81 (s, 3H), 2.73-2.71 (m, 2H), 2.34 (s, 1H), 1.72 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 160.0, 144.9, 138.3, 138.1, 135.5, 131.4, 129.7, 128.6, 127.6, 121.0, 119.4, 117.8, 113.5, 112.0, 76.3, 55.4, 41.3, 26.2, 18.4. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{23}\text{BrO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 409.0779; Found: 409.0780.

Characterization of **2m**:



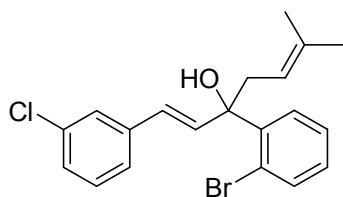
Yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.48 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.23-7.17 (m, 3H), 7.04 (d, $J = 6.4$ Hz, 1H), 6.59 (d, $J = 16.0$ Hz, 1H), 6.46 (d, $J = 16.0$ Hz, 1H), 5.07 (t, $J = 7.2$ Hz, 1H), 2.76-2.67 (m, 2H), 2.34 (s, 3H), 2.27 (s, 1H), 1.72 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 145.0, 138.3, 138.0, 136.8, 135.0, 131.4, 128.8, 128.6, 127.6, 127.4, 123.9, 121.0, 117.9, 76.4, 41.3, 26.3, 21.5, 18.4. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{23}\text{BrONa}$ $[\text{M} + \text{Na}]^+$: 393.0830; Found: 393.0826.

Characterization of **2n**:



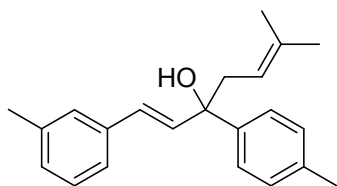
Yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.45-7.38 (m, 3H), 7.20-7.14 (m, 3H), 7.06 (d, $J = 7.6$ Hz, 1H), 7.01 (dd, $J = 8.8$ Hz, $J = 10.8$ Hz, 1H), 6.80 (d, $J = 16.0$ Hz, 1H), 6.60 (d, $J = 16.0$ Hz, 1H), 5.09 (t, $J = 6.8$ Hz, 1H), 2.81-2.68 (m, 2H), 2.34 (s, 3H), 2.27 (s, 1H), 1.71 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 160.5 ($J = 247.9$ Hz), 142.8, 138.5 ($J = 4.4$ Hz), 137.5, 136.6, 129.1, 128.7 ($J = 8.0$ Hz), 127.8 ($J = 3.7$ Hz), 125.6, 125.0, 124.9, 124.1 ($J = 3.6$ Hz), 120.5 ($J = 2.9$ Hz), 118.3, 115.9, 115.7, 76.6, 41.3, 26.2, 21.4, 18.4. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{23}\text{FONa}$ $[\text{M} + \text{Na}]^+$: 333.1631; Found: 333.1631.

Characterization of **2o**:



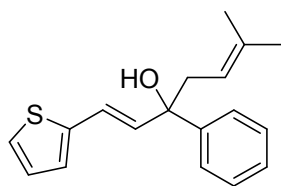
Colorless oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.80 (d, $J = 7.6$ Hz, 1H), 7.58 (d, $J = 7.6$ Hz, 1H), 7.36-7.24 (m, 5H), 7.12 (t, $J = 7.2$ Hz, 1H), 6.87 (d, $J = 16.0$ Hz, 1H), 6.52 (d, $J = 16.0$ Hz, 1H), 5.07 (t, $J = 7.6$ Hz, 1H), 3.12-2.92 (m, 2H), 2.65 (s, 1H), 1.70 (s, 3H), 1.67 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 144.1, 137.3, 135.6, 134.9, 134.8, 133.2, 128.8, 128.7, 128.5, 127.8, 127.4, 120.8, 118.0, 76.8, 38.8, 26.1, 18.2. HRMS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{20}\text{BrClONa}$ $[\text{M} + \text{Na}]^+$: 413.0284; Found: 413.0292.

Characterization of **2p**:



Colorless oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.40 (d, $J = 8.0$ Hz, 2H), 7.21-7.14 (m, 5H), 7.03 (t, $J = 3.2$ Hz, 1H), 6.59 (d, $J = 16.0$ Hz, 1H), 6.49 (d, $J = 16.0$ Hz, 1H), 5.11 (t, $J = 7.6$ Hz, 1H), 2.78-2.68 (m, 2H), 2.34 (s, 3H), 2.32 (s, 3H), 2.23 (s, 1H), 1.71 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 143.0, 138.2, 137.4, 137.1, 136.6, 135.8, 129.1, 128.6, 128.4, 128.1, 127.4, 125.6, 123.9, 118.5, 76.5, 41.4, 26.3, 21.5, 21.2, 18.4. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{26}\text{ONa}$ $[\text{M} + \text{Na}]^+$: 329.1881; Found: 329.1876.

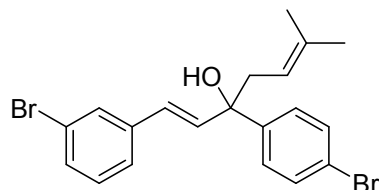
Characterization of **2q**:



Yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.50 (d, $J = 8.0$ Hz, 2H), 7.36 (t, $J = 8.0$ Hz, 2H), 7.27-7.23 (m, 1H), 7.14-7.13 (m, 1H), 6.94-6.93 (m, 2H), 6.76 (d, $J = 16.0$ Hz, 1H), 6.36 (d, J

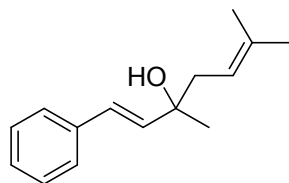
= 16.0 Hz, 1H), 5.07 (t, $J = 7.2$ Hz, 1H), 2.78-2.67 (m, 2H), 2.26 (s, 1H), 1.71 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 145.7, 142.4, 137.8, 135.4, 128.4, 127.5, 127.1, 125.9, 125.7, 124.2, 121.8, 118.1, 76.4, 41.4, 26.2, 18.4. HRMS (ESI): m/z calcd for $\text{C}_{18}\text{H}_{20}\text{OSNa}$ $[\text{M} + \text{Na}]^+$: 307.1133; Found: 307.1134.

Characterization of **2r**:



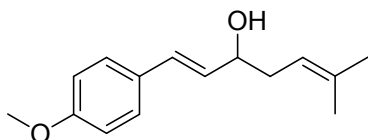
Yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.52 (s, 1H), 7.48 (d, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.8$ Hz, 1H), 7.26 (d, $J = 7.2$ Hz, 1H), 7.16 (t, $J = 8.0$ Hz, 1H), 6.56 (d, $J = 16.0$ Hz, 1H), 6.46 (d, $J = 16.0$ Hz, 1H), 5.03 (t, $J = 7.2$ Hz, 1H), 2.73-2.71 (m, 2H), 2.28 (s, 1H), 1.72 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 144.4, 138.9, 138.5, 136.5, 131.4, 130.5, 130.1, 129.3, 127.4, 127.0, 125.3, 122.8, 121.0, 117.3, 76.1, 41.1, 26.2, 18.3. HRMS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{20}\text{Br}_2\text{ONa}$ $[\text{M} + \text{Na}]^+$: 456.9779; Found: 456.9780.

Characterization of **2s**:



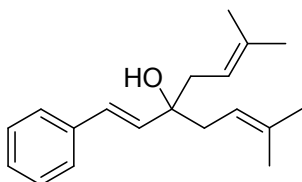
Yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.39 (d, $J = 8.0$ Hz, 2H), 7.32 (t, $J = 8.0$ Hz, 2H), 7.22 (t, $J = 8.0$ Hz, 1H), 6.59 (d, $J = 16.0$ Hz, 1H), 6.30 (d, $J = 16.0$ Hz, 1H), 5.19 (t, $J = 7.8$ Hz, 1H), 2.46-2.25 (m, 2H), 1.78 (s, 1H), 1.78 (s, 3H), 1.74 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 137.1, 136.7, 136.2, 128.6, 127.3, 127.1, 126.4, 118.8, 73.3, 41.4, 27.9, 26.1, 18.1. HRMS (ESI): m/z calcd for $\text{C}_{15}\text{H}_{20}\text{ONa}$ $[\text{M} + \text{Na}]^+$: 239.1412; Found: 239.1421.

Characterization of **2t**:



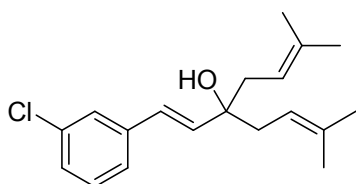
Yellow oil; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ : 7.32 (d, $J = 8.0$ Hz, 2H), 6.86 (d, $J = 8.0$ Hz, 2H), 6.54 (d, $J = 16.0$ Hz, 1H), 6.12 (dd, $J = 6.4$ Hz, $J = 16.0$ Hz, 1H), 5.20 (t, $J = 7.2$ Hz, 1H), 4.28 (s, 1H), 3.81 (s, 3H), 2.39-2.31 (m, 2H), 1.75 (s, 3H), 1.66 (s, 3H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ : 159.0, 135.3, 129.6, 129.5, 129.3, 127.4, 119.2, 113.7, 72.5, 55.1, 36.2, 25.7, 17.8. HRMS (ESI): m/z calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 255.1361; Found: 255.1353.

Characterization of **2u**:



Pale yellow oil; $^1\text{H NMR}$ (400MHz, CDCl_3) δ : 7.39-7.37 (m, 2H), 7.33-7.30 (m, 2H), 7.25-7.22 (m, 1H), 6.58 (d, $J = 16.0$ Hz, 1H), 6.25 (d, $J = 16.0$ Hz, 1H), 5.20 (s, 2H), 2.43-2.27 (m, 4H), 1.86 (s, 1H), 1.73 (s, 6H), 1.64 (s, 6H). $^{13}\text{C NMR}$ (100MHz, CDCl_3) δ : 137.3, 135.7, 135.6, 128.6, 127.9, 127.2, 126.4, 118.8, 75.6, 39.6, 26.1, 18.1. HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{26}\text{ONa}$ $[\text{M} + \text{Na}]^+$: 293.1881; Found: 293.1889.

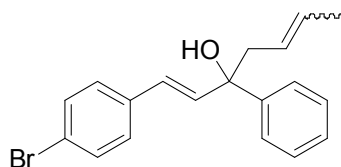
Characterization of **2v**:



Pale yellow oil; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ : 7.36 (s, 1H), 7.24-7.19 (m, 3H), 6.54 (d, $J = 16.0$ Hz, 1H), 6.26 (d, $J = 16.0$ Hz, 1H), 5.18 (t, $J = 7.2$ Hz, 1H), 2.43-2.37 (m, 2H), 2.32-2.26 (m, 2H), 1.87 (s, 1H), 1.74 (s, 6H), 1.64 (s, 6H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ : 139.2, 137.3, 136.0, 134.5, 129.8, 127.1, 126.7, 126.2, 124.7, 118.5, 75.5, 39.5, 26.1, 18.1. HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{25}\text{ClONa}$ $[\text{M} + \text{Na}]^+$: 327.1492; Found: 327.1490.

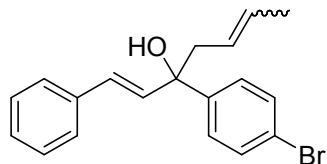
6 Characterization of 3a, 3h, 3j, 3l, and 3w:

Characterization of 3a:



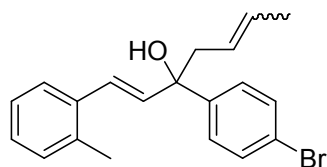
Yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.51 (t, $J = 7.6$ Hz, 2H), 7.41 (d, $J = 7.2$ Hz, 2H), 7.37 (t, $J = 8.0$ Hz, 2H), 7.30-7.22 (m, 3H), 6.61 (d, $J = 10.4$ Hz, 0.28H, isomer 1), 6.57 (d, $J = 10.8$ Hz, 0.72H, isomer 2), 6.54 (d, $J = 14.0$ Hz, 0.73H, isomer 2), 6.50 (d, $J = 16.0$ Hz, 0.27H, isomer 1), 5.75-5.62 (m, 1H), 5.38-5.26 (m, 1H), 2.83-2.69 (m, 2H), 2.36 (s, 0.48H, isomer 1), 2.26 (s, 0.52H, isomer 2), 1.66 (t, $J = 6.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 Hz): 145.4, 145.4, 136.4, 136.3, 136.0, 136.0, 132.0, 131.8, 131.8, 129.6, 128.5, 128.5, 128.2, 127.2, 127.2, 127.1, 127.1, 125.6, 125.6, 125.1, 124.2, 121.4, 121.4, 76.5, 75.7, 46.0, 40.0, 18.3, 13.4. HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{19}\text{OBrNa}$ [$\text{M} + \text{Na}$] $^+$: 365.0517; Found: 365.0517.

Characterization of 3h:



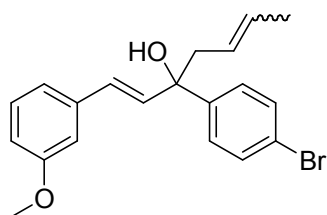
Yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.48 (d, $J = 8.4$ Hz, 2H), 7.41-7.37 (m, 4H), 7.31 (t, $J = 7.2$ Hz, 2H), 7.26-7.22 (m, 1H), 6.64 (d, $J = 9.2$ Hz, 0.38H, isomer 1), 6.60 (d, $J = 9.2$ Hz, 0.62H, isomer 2), 6.49 (d, $J = 14.8$ Hz, 0.62H, isomer 2), 6.45 (d, $J = 15.6$ Hz, 0.38H, isomer 1), 5.76-5.62 (m, 1H), 5.38-5.27 (m, 1H), 2.83-2.68 (m, 2H), 2.36 (s, 0.48H, isomer 1), 2.26 (s, 0.52H, isomer 2), 1.67 (t, $J = 8.4$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 Hz): 144.8, 144.7, 136.8, 136.7, 135.0, 134.9, 132.2, 131.5, 129.7, 128.9, 128.8, 128.8, 128.8, 127.9, 127.8, 127.6, 126.7, 124.9, 124.0, 121.1, 121.0, 76.3, 75.6, 46.1, 40.0, 18.4, 13.4. HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{19}\text{OBrNa}$ [$\text{M} + \text{Na}$] $^+$: 365.0517; Found: 365.0517.

Characterization of 3j:



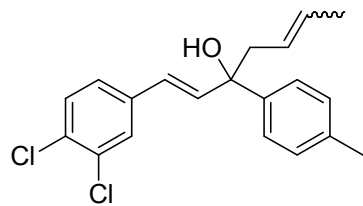
Yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.50 (d, $J = 8.4$ Hz, 2H), 7.44-7.40 (m, 3H), 7.19-7.16 (m, 3H), 6.90 (d, $J = 8.4$ Hz, 0.48H, isomer 1), 6.86 (d, $J = 8.4$ Hz, 0.52H, isomer 2), 6.38 (d, $J = 15.6$ Hz, 0.52H, isomer 2), 6.35 (d, $J = 15.2$ Hz, 0.48H, isomer 1), 5.78-5.64 (m, 1H), 5.42-5.31 (m, 1H), 2.85-2.70 (m, 2H), 2.39 (s, 0.40H, isomer 1), 2.34 (s, 3H), 2.30 (s, 0.60H, isomer 2), 1.71 (d, $J = 6.4$ Hz, 1.20H, isomer 1), 1.68 (d, $J = 6.8$ Hz, 1.80H, isomer 2). ^{13}C NMR (CDCl_3 , 100 Hz): 144.8, 144.8, 136.3, 136.2, 135.9, 135.8, 135.7, 131.8, 131.3, 130.3, 130.3, 129.4, 127.6, 127.6, 127.5, 127.4, 126.7, 126.6, 126.1, 126.1, 125.7, 125.7, 124.9, 123.9, 120.9, 120.8, 76.3, 75.6, 46.0, 40.0, 19.9, 18.2, 13.2. HRMS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{21}\text{OBrNa}$ $[\text{M} + \text{Na}]^+$: 379.0673; Found: 379.0652.

Characterization of **3l**:

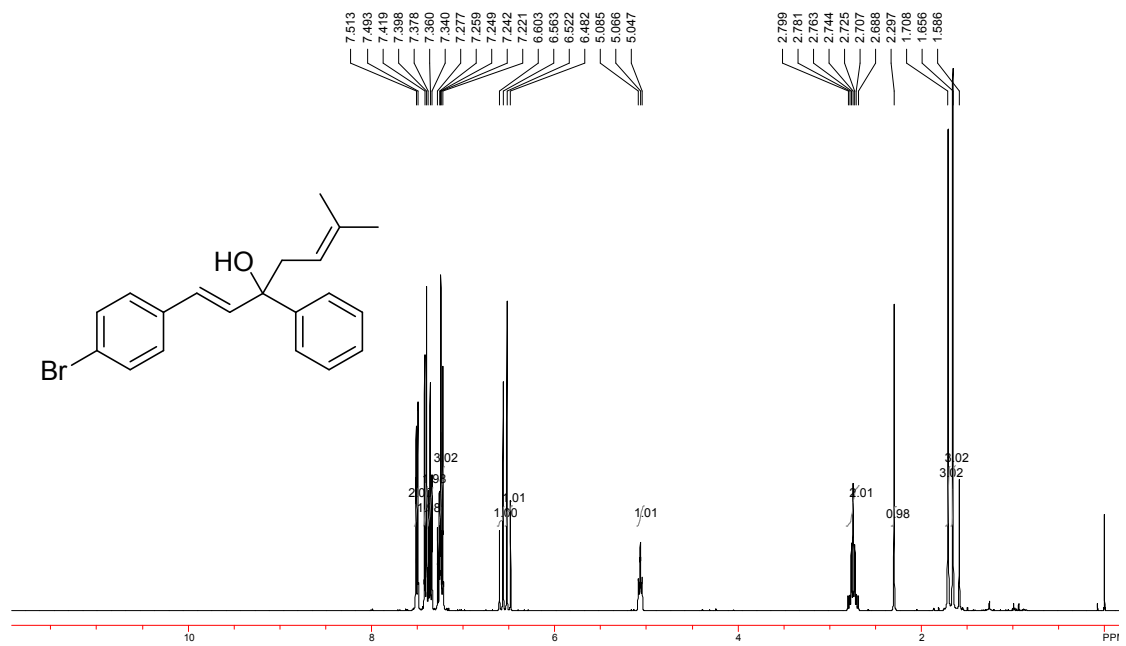


Pale yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.48 (d, $J = 8.0$ Hz, 2H), 7.39 (t, $J = 7.2$ Hz, 2H), 7.23 (t, $J = 8.4$ Hz, 1H), 6.97 (d, $J = 7.6$ Hz, 1H), 6.80 (d, $J = 8.0$ Hz, 1H), 6.61 (d, $J = 9.2$ Hz, 0.36H, isomer 1), 6.57 (d, $J = 8.8$ Hz, 0.64H, isomer 2), 6.48 (d, $J = 14.4$ Hz, 0.64H, isomer 2), 6.44 (d, $J = 16.0$ Hz, 0.36H, isomer 1), 5.76-5.62 (m, 1H), 5.37-5.26 (m, 1H), 3.81 (s, 3H), 2.83-2.68 (m, 2H), 2.38 (s, 0.60H, isomer 1), 2.27 (s, 0.40H, isomer 2), 1.67 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 Hz): 160.0, 160.0, 144.7, 138.2, 138.2, 135.2, 135.2, 132.2, 131.5, 129.7, 129.7, 128.8, 128.7, 127.6, 127.6, 124.9, 124.0, 121.1, 121.0, 119.4, 113.5, 113.5, 112.0, 76.3, 75.5, 55.4, 46.0, 40.0, 18.4, 13.4. HRMS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{21}\text{O}_2\text{BrNa}$ $[\text{M} + \text{Na}]^+$: 395.0623; Found: 395.0623.

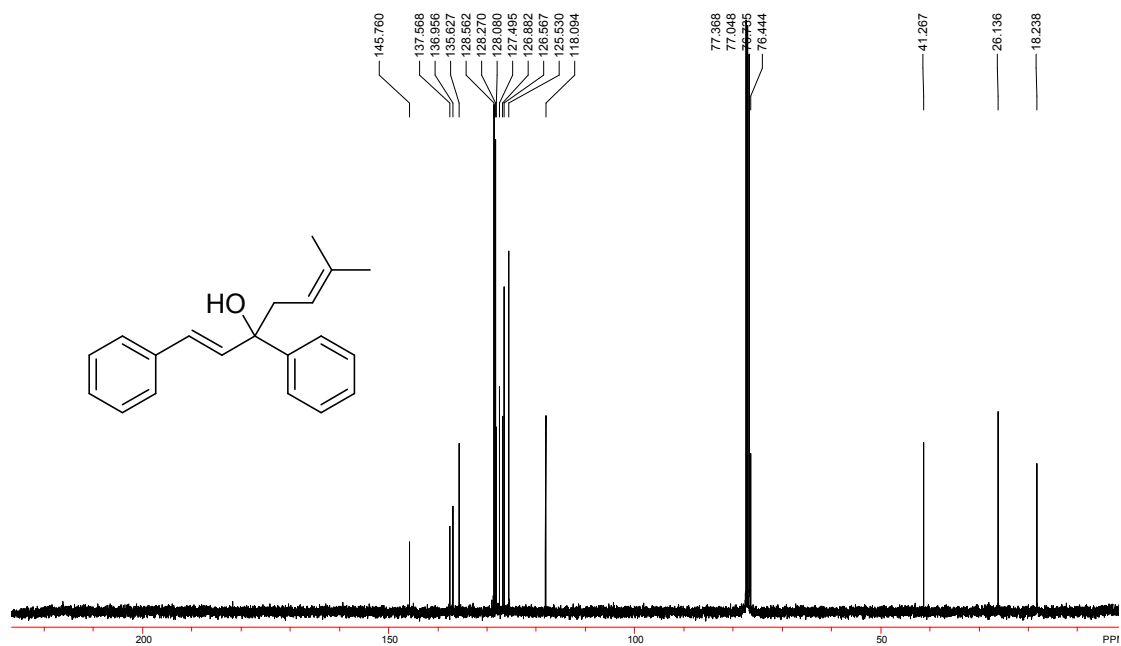
Characterization of **3w**:



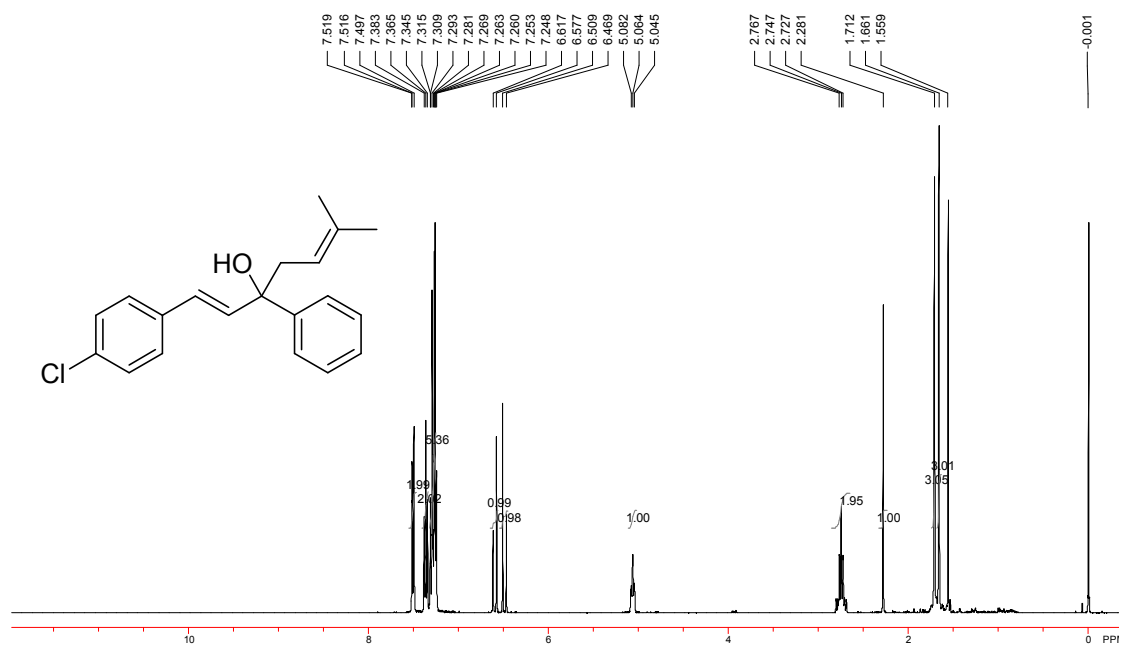
Pale yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.45-7.34 (m, 4H), 7.19-7.17 (m, 3H), 8.59-6.44 (m, 2H), 5.76-5.62 (m, 1H), 5.36-5.25 (m, 1H), 2.85-2.63 (m, 2H), 2.35 (s, 3H), 2.35 (s, 0.25H, isomer 1), 2.23 (s, 0.75H, isomer 2), 1.67 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 142.6, 138.2, 138.1, 137.7, 137.6, 137.4, 137.2, 133.1, 133.1, 132.4, 131.5, 130.9, 130.9, 130.0, 129.6, 129.6, 128.7, 128.7, 126.3, 126.2, 126.1, 125.8, 125.8, 125.4, 124.5, 76.7, 75.9, 46.2, 40.2, 21.5, 18.7, 13.7. HRMS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{20}\text{OCl}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$: 369.0789; Found: 369.0780.



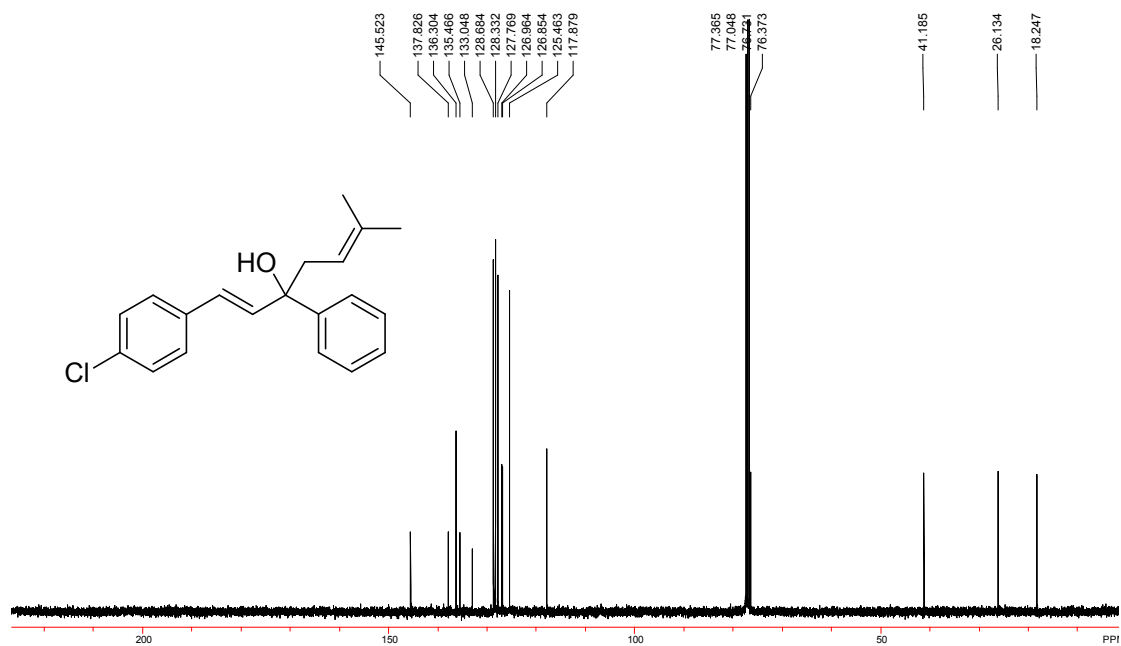
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound 2a



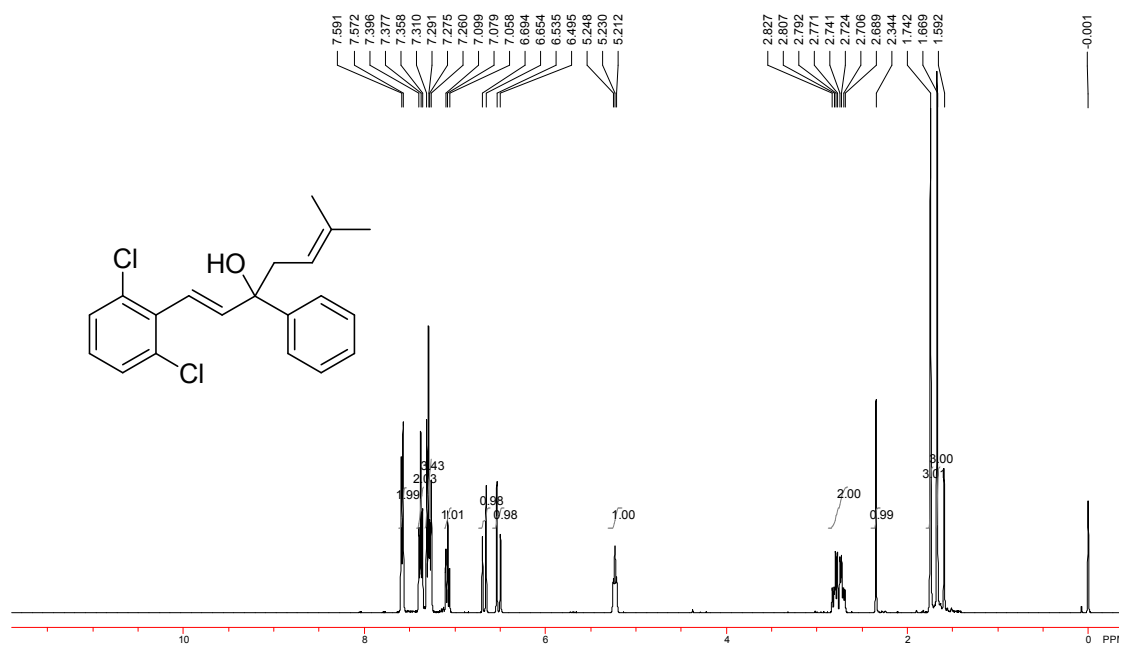
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound **2b**



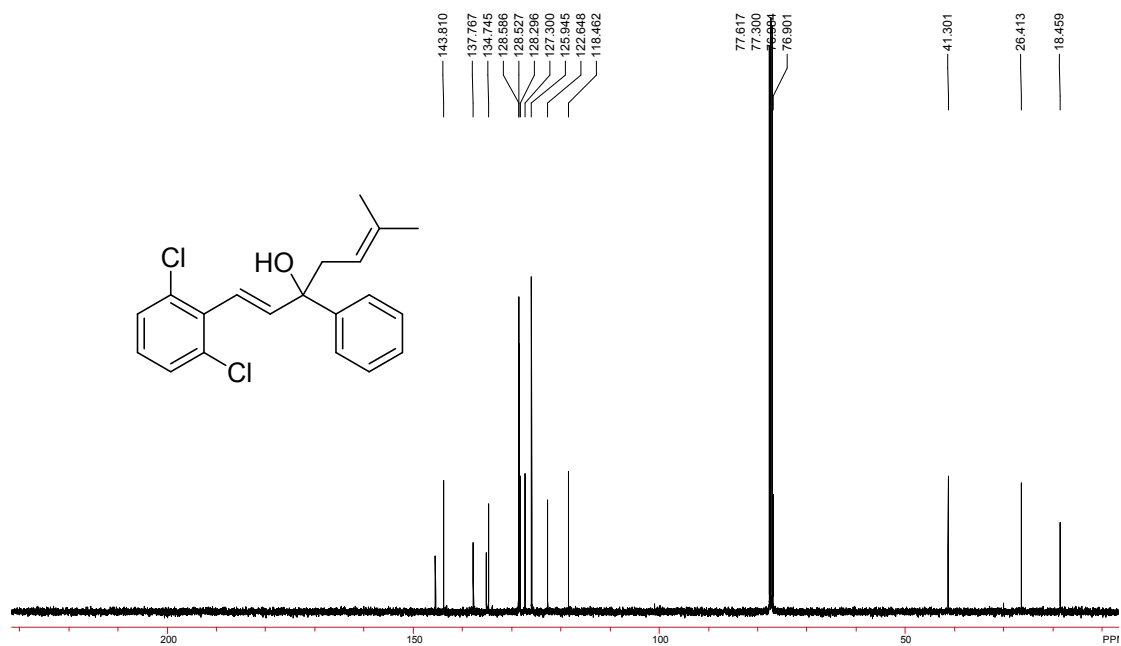
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound **2c**



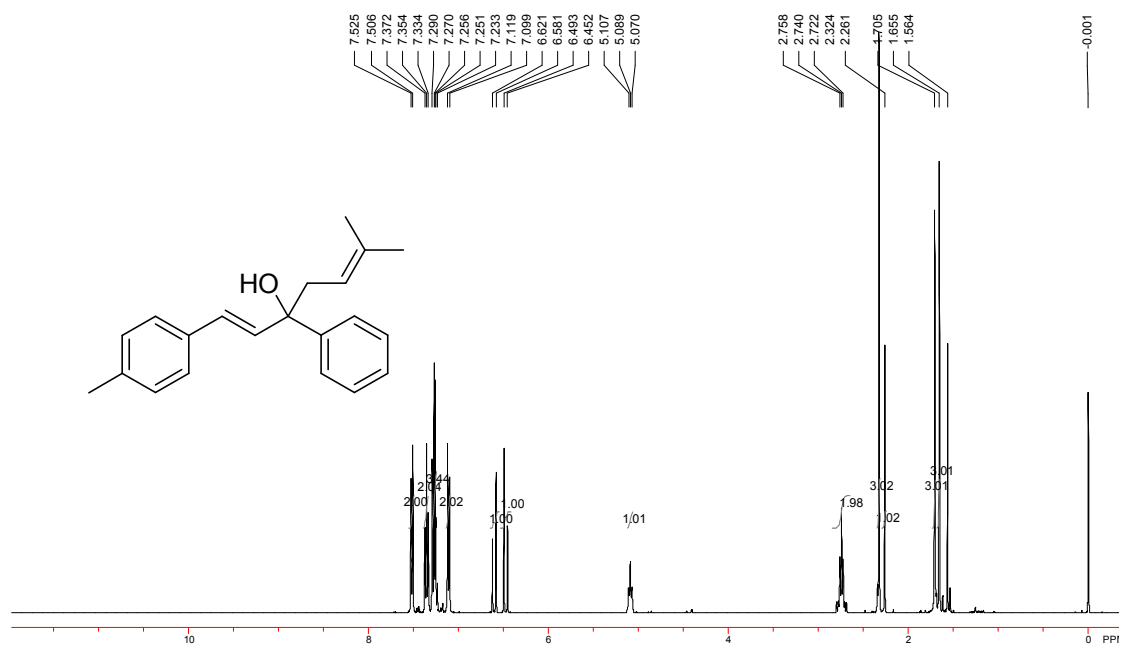
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound **2c**



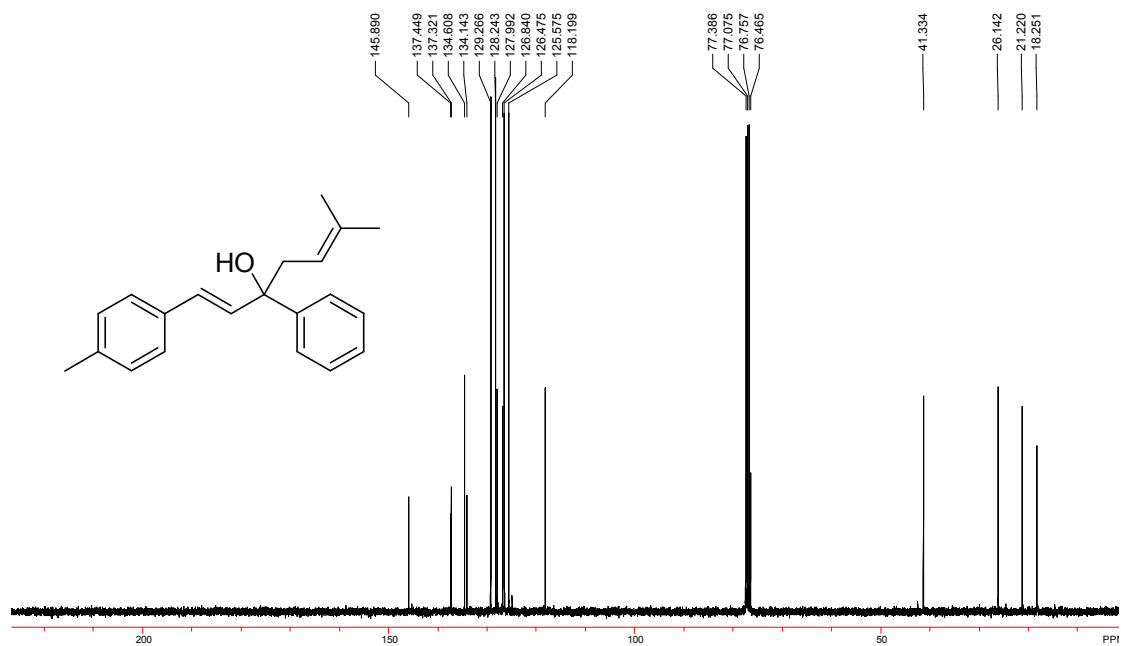
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound **2d**



¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound **2d**



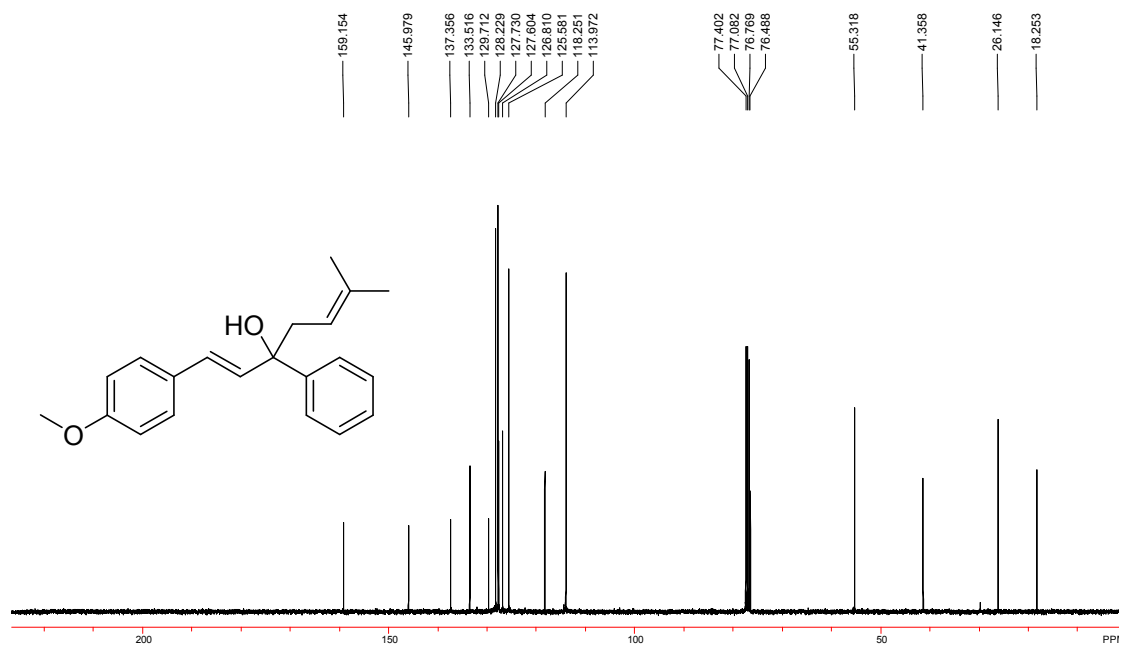
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound **2e**



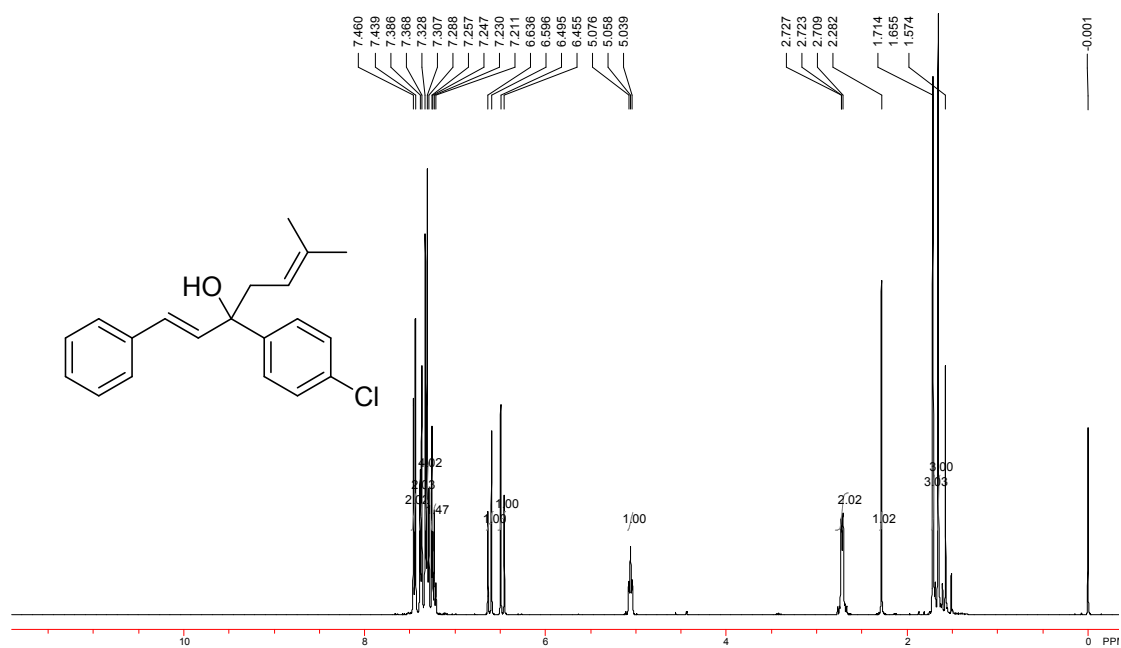
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound 2e



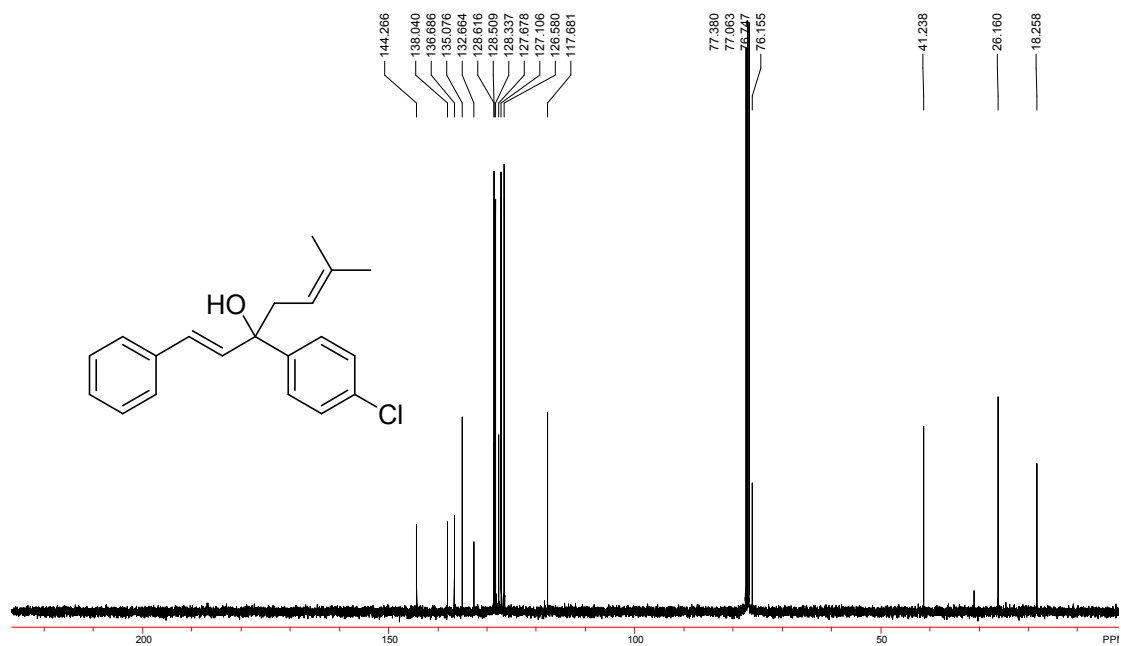
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound 2f



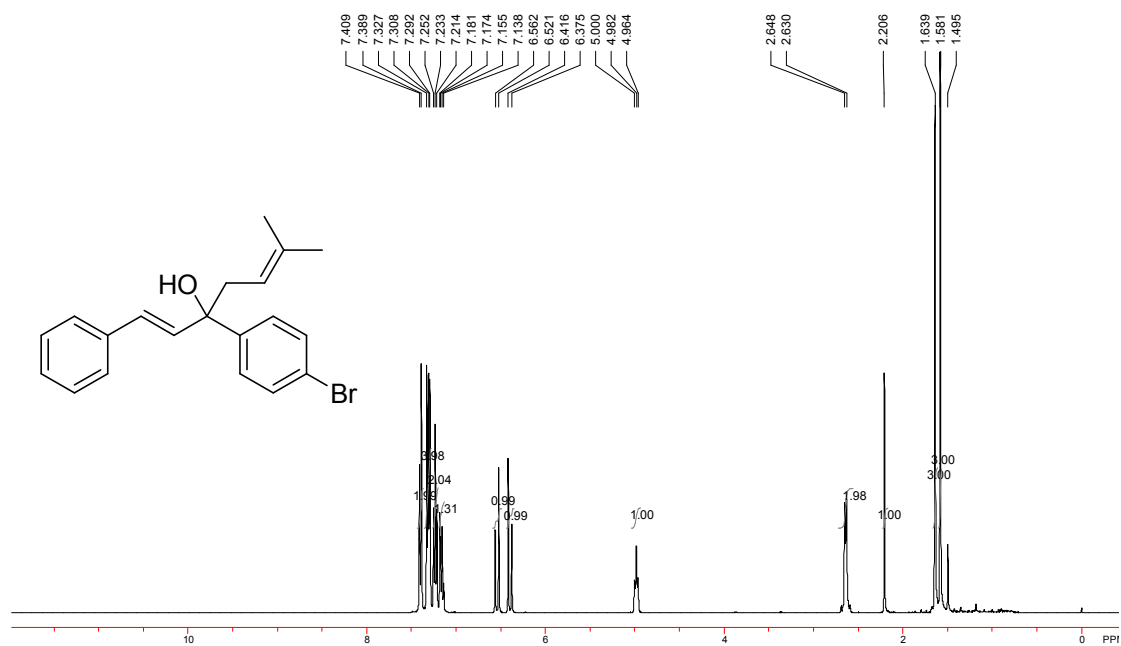
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound **2f**



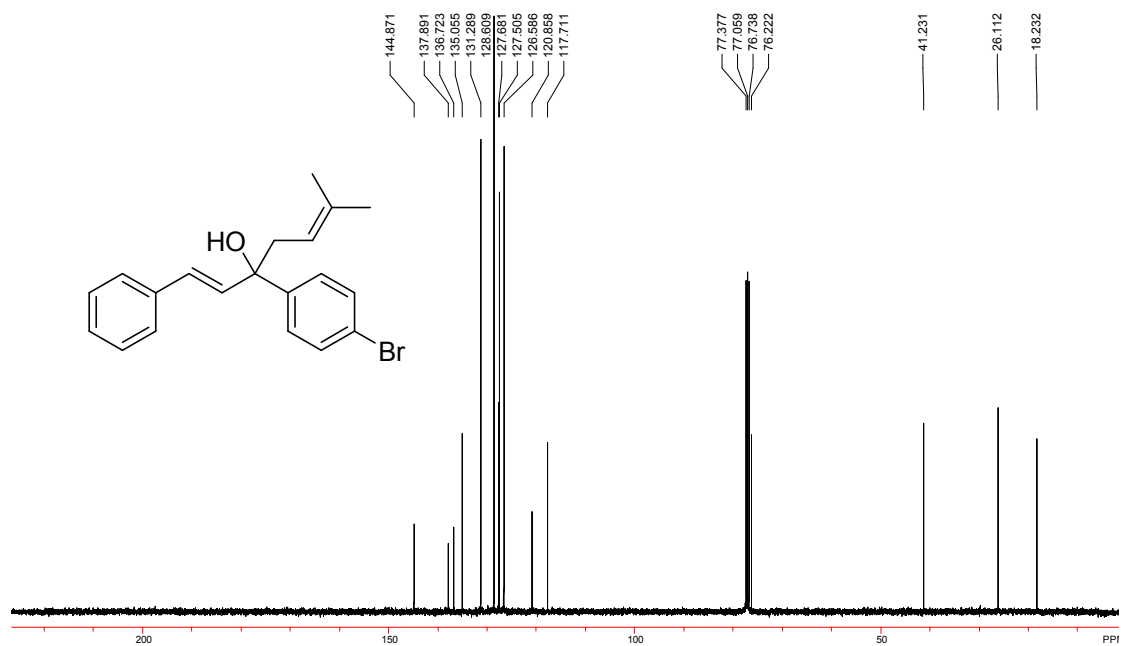
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound **2g**



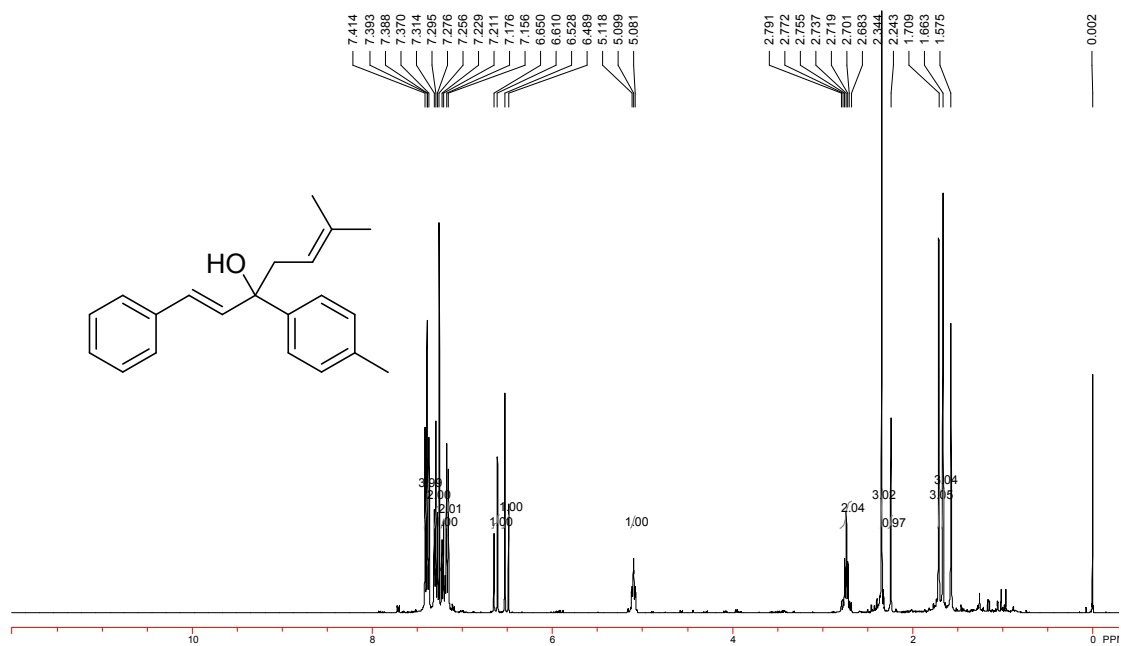
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound **2g**



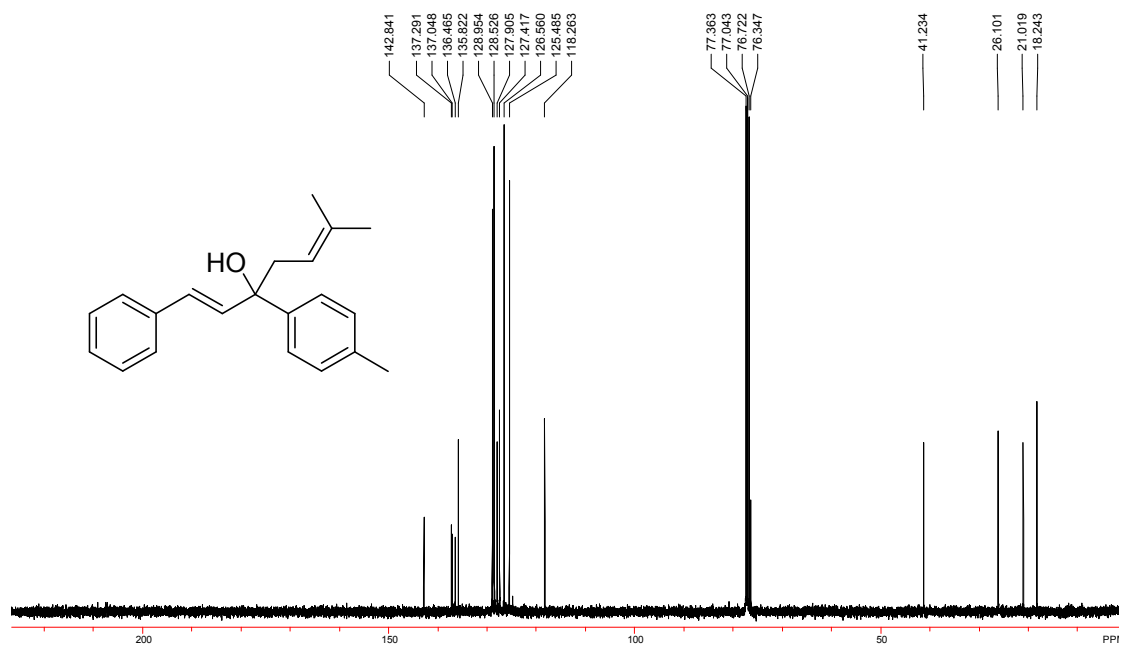
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound **2h**



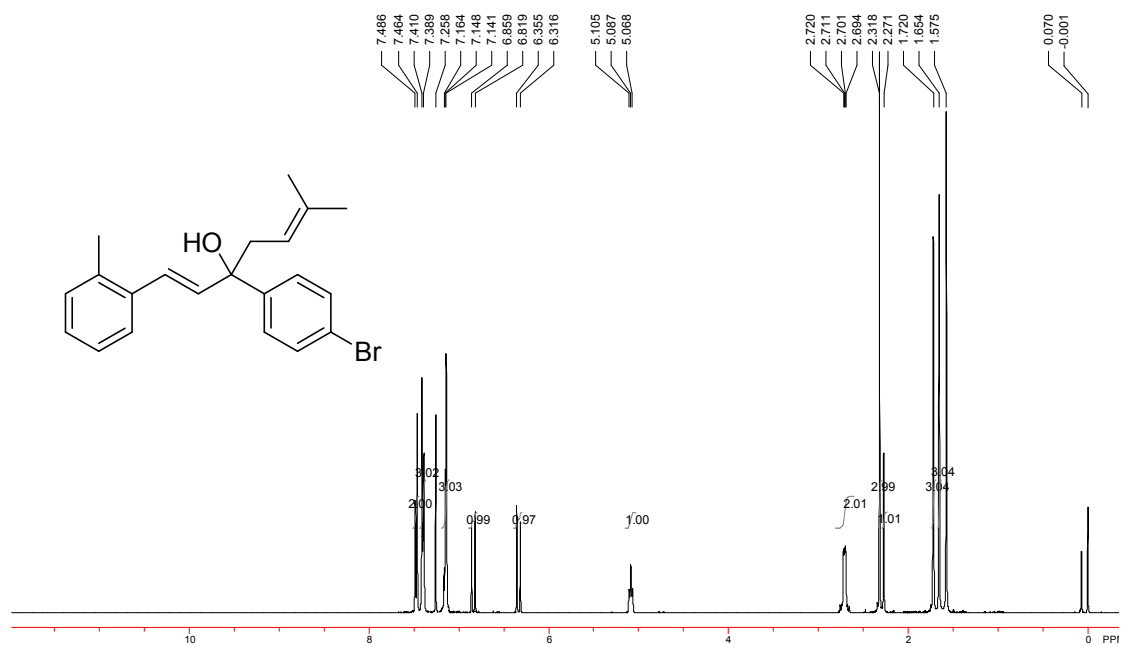
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound 2h



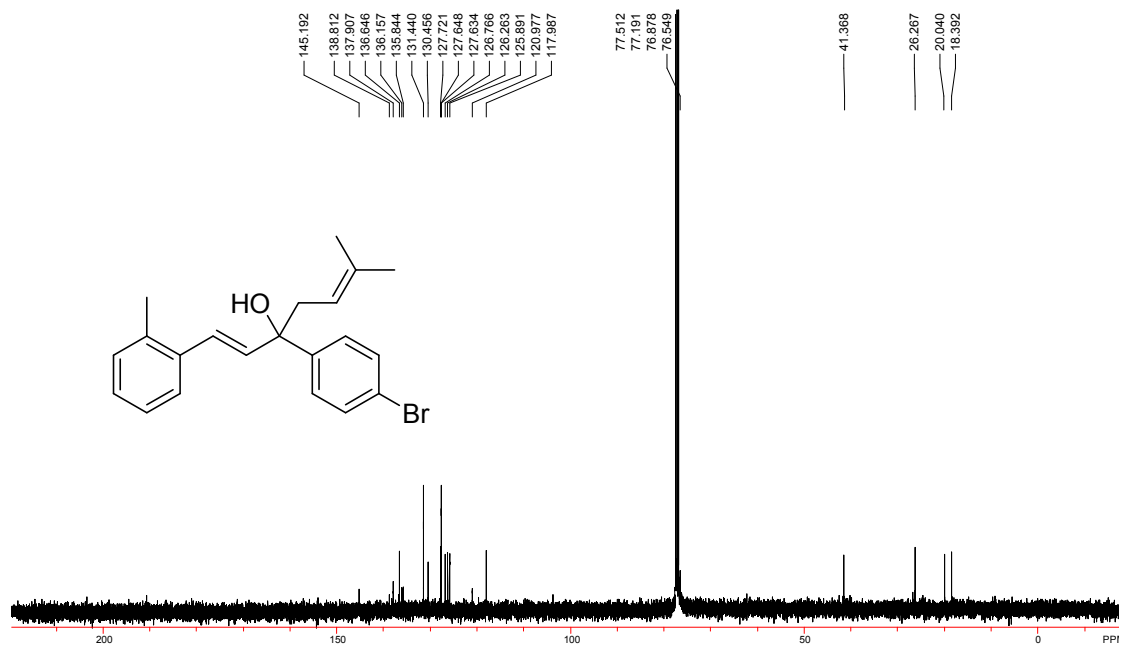
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound 2i



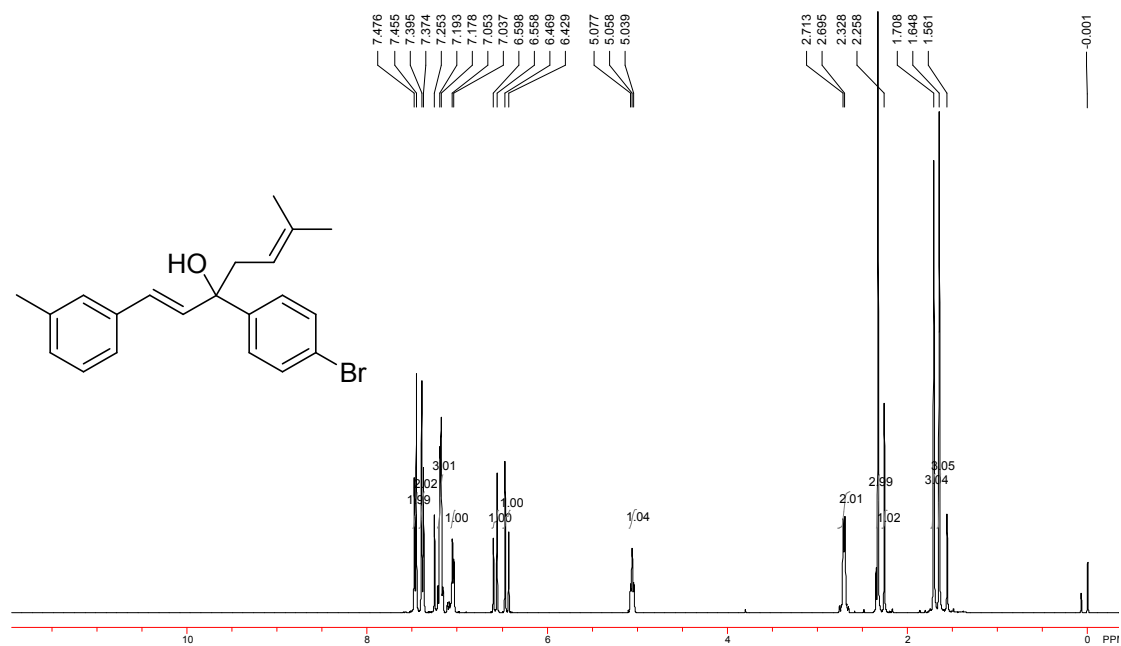
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound **2i**



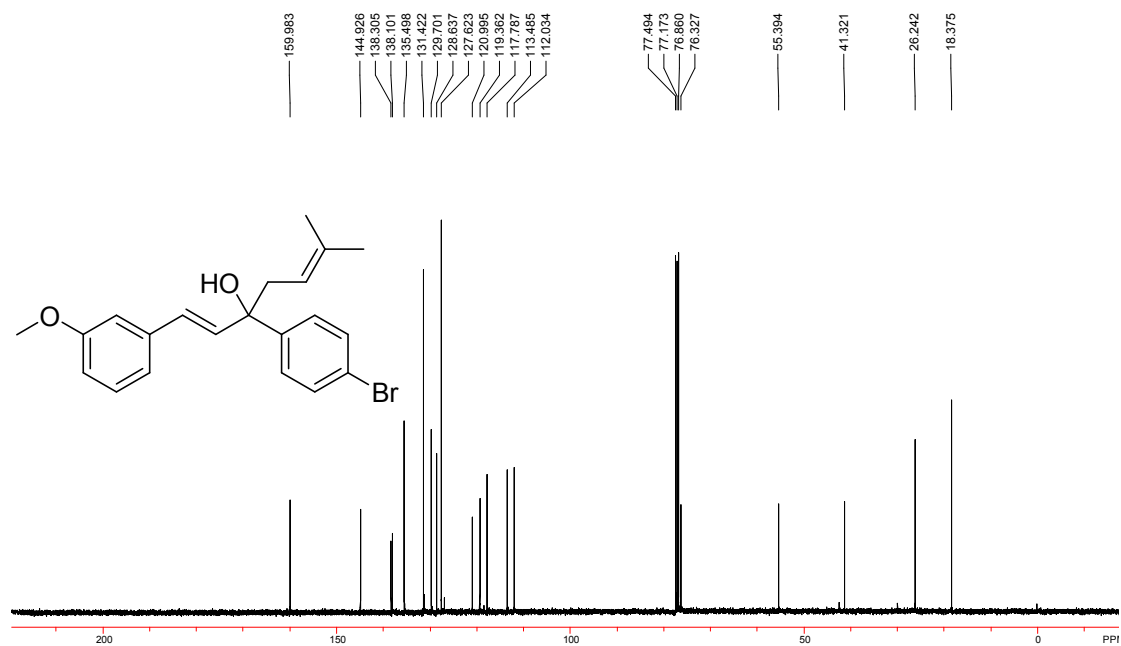
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound **2j**



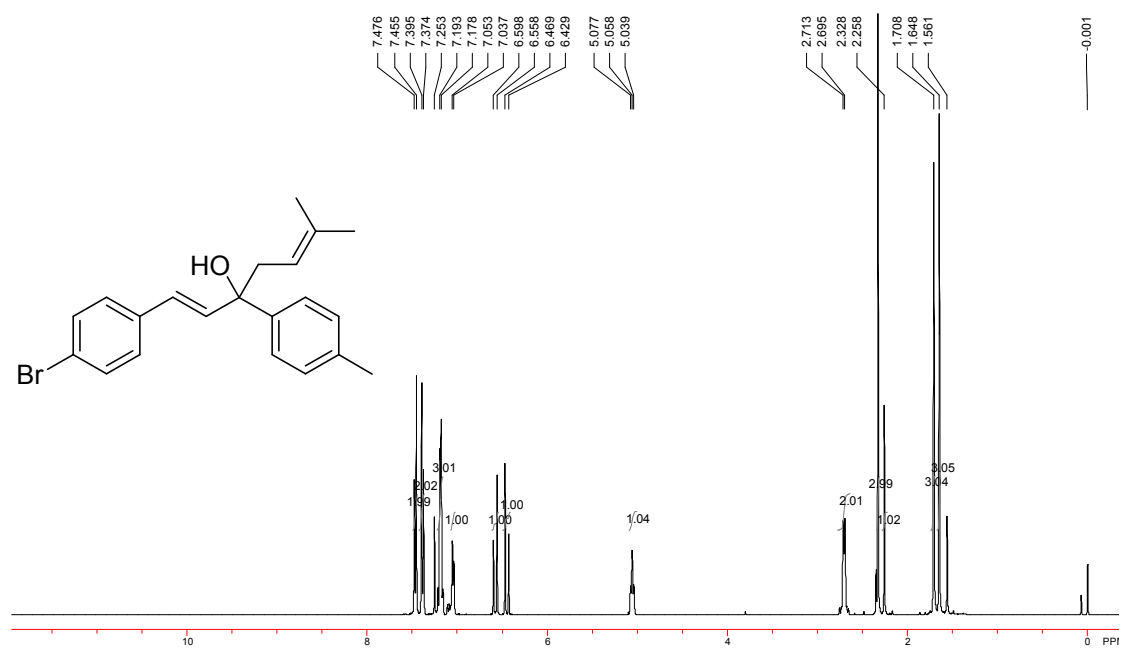
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound 2j



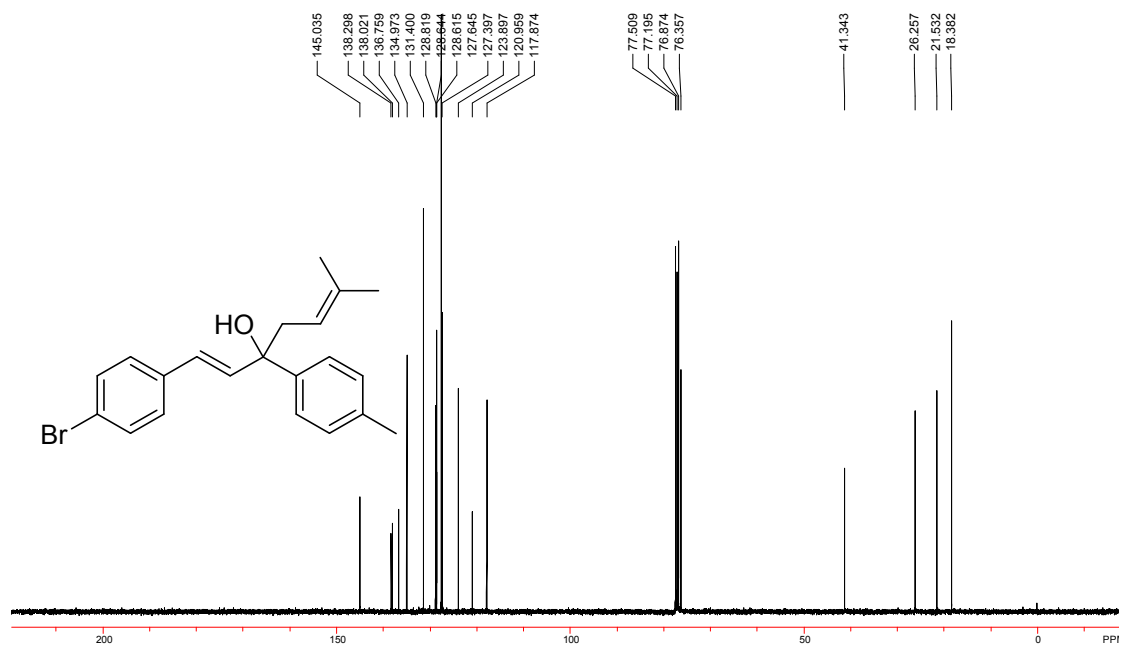
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound 2k



¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound 2l



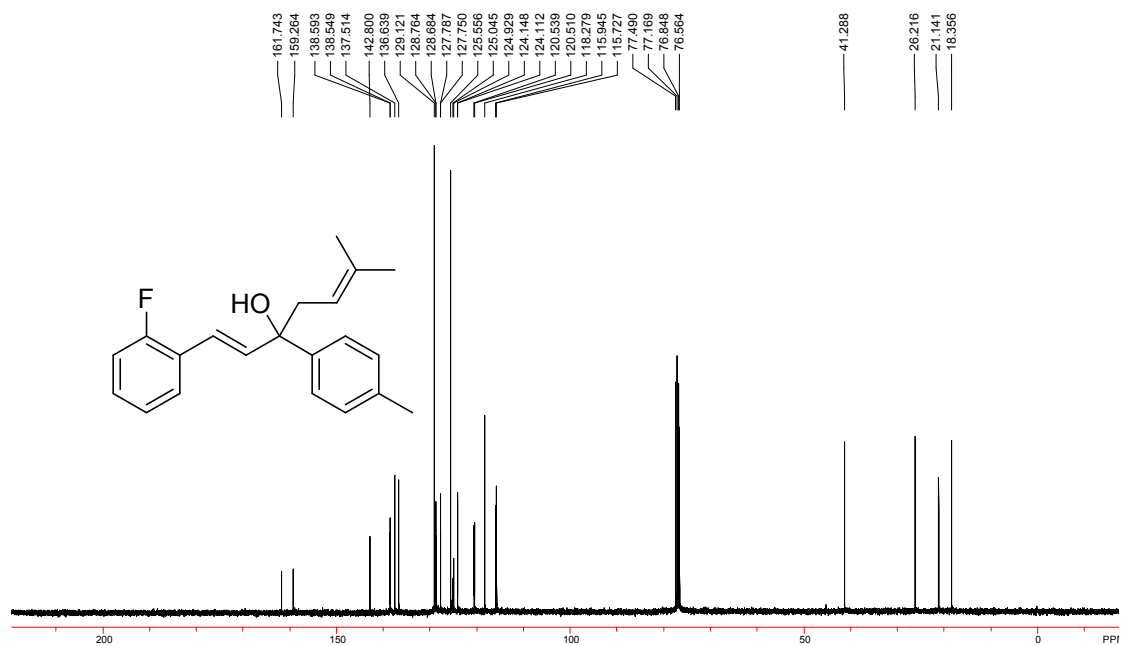
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound 2m



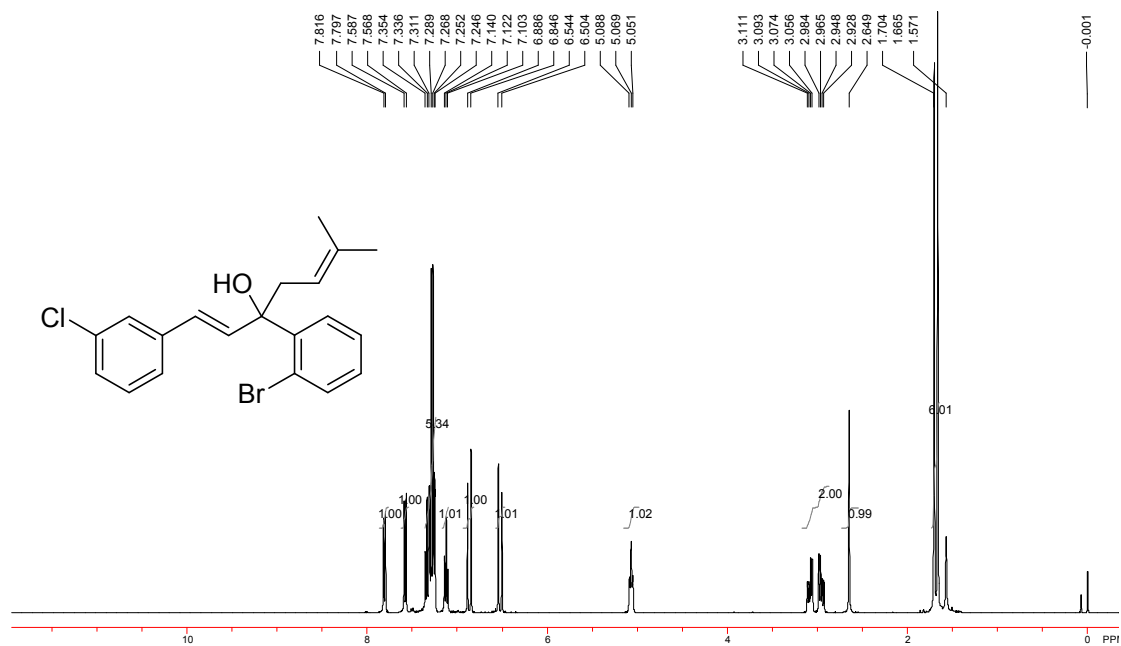
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound **2m**



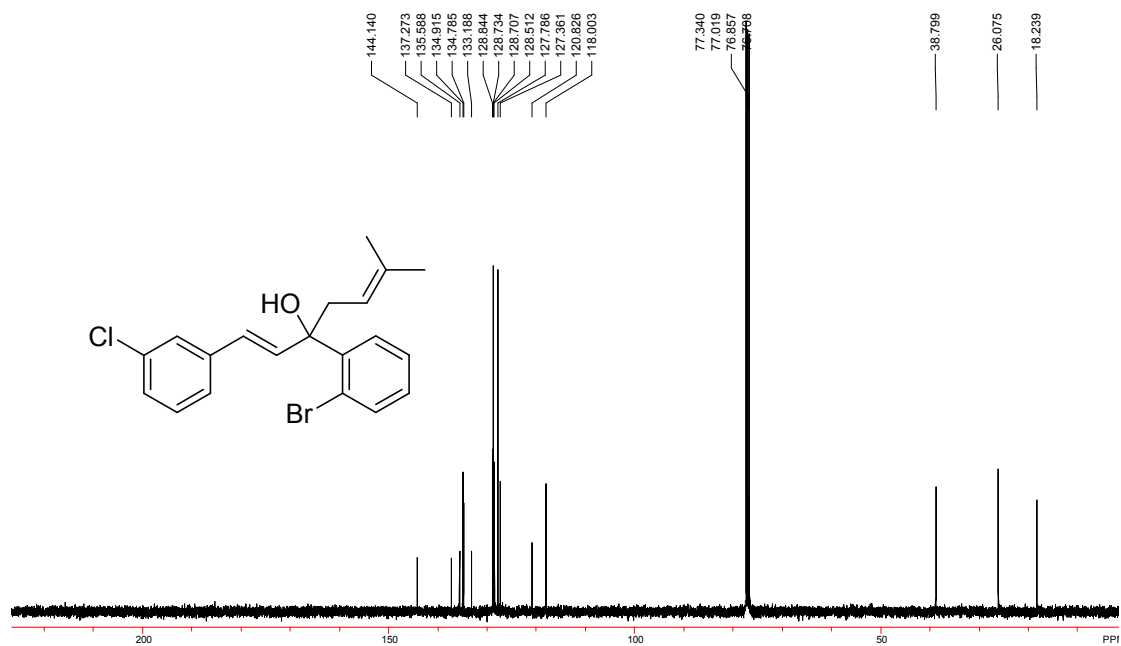
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound **2n**



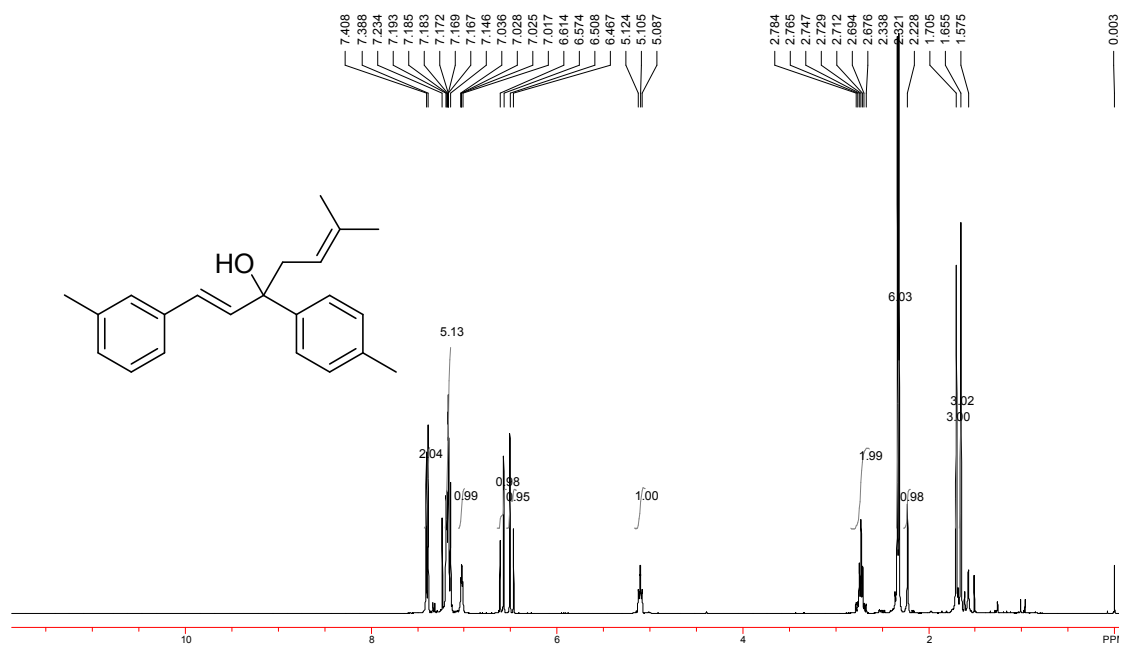
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound **2n**



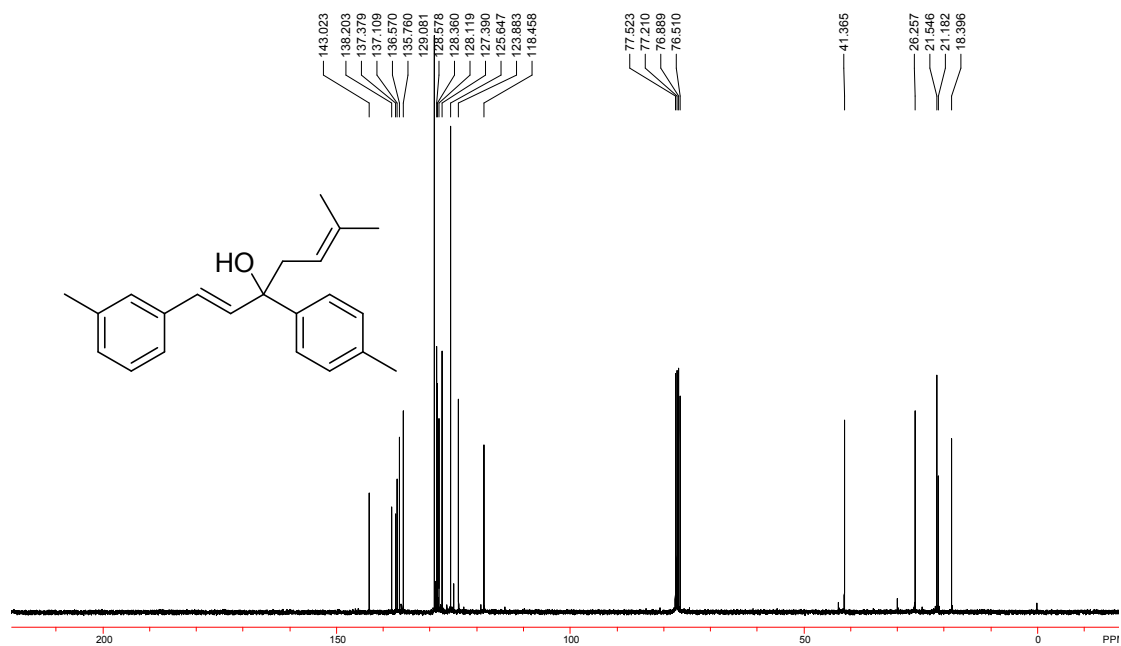
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound **2o**



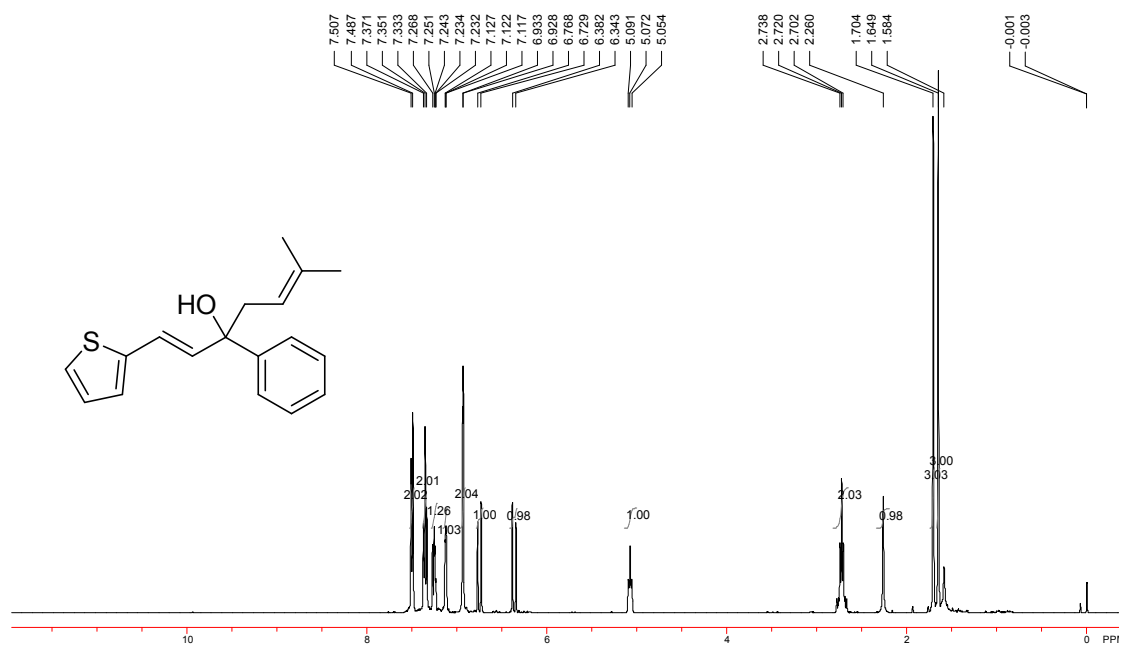
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound 2o



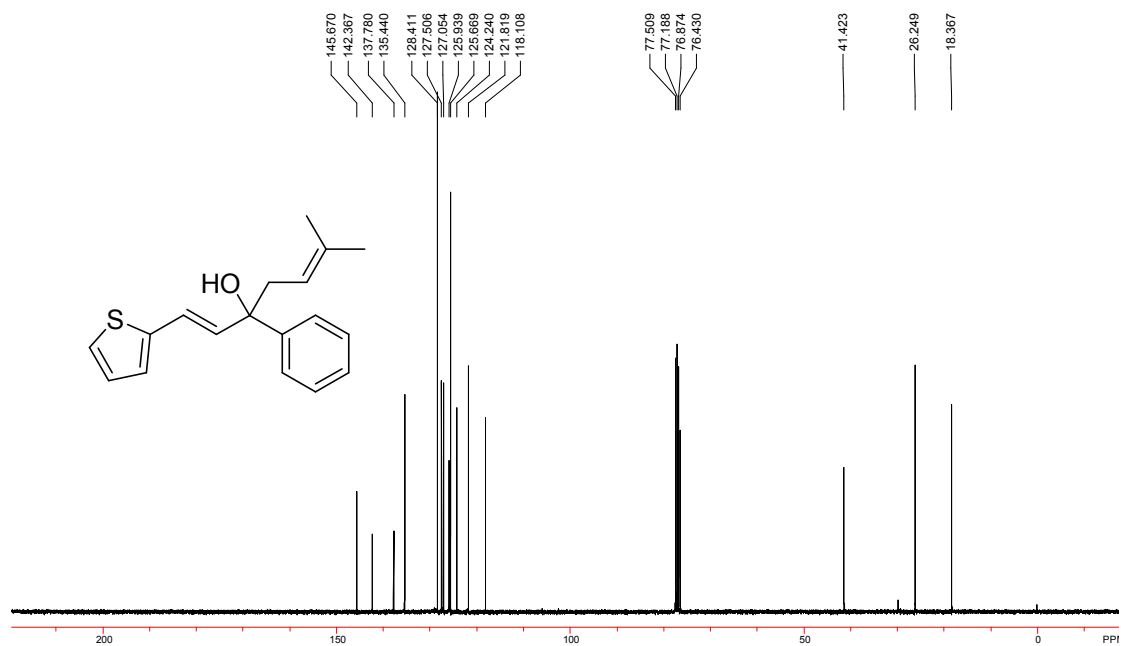
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound 2p



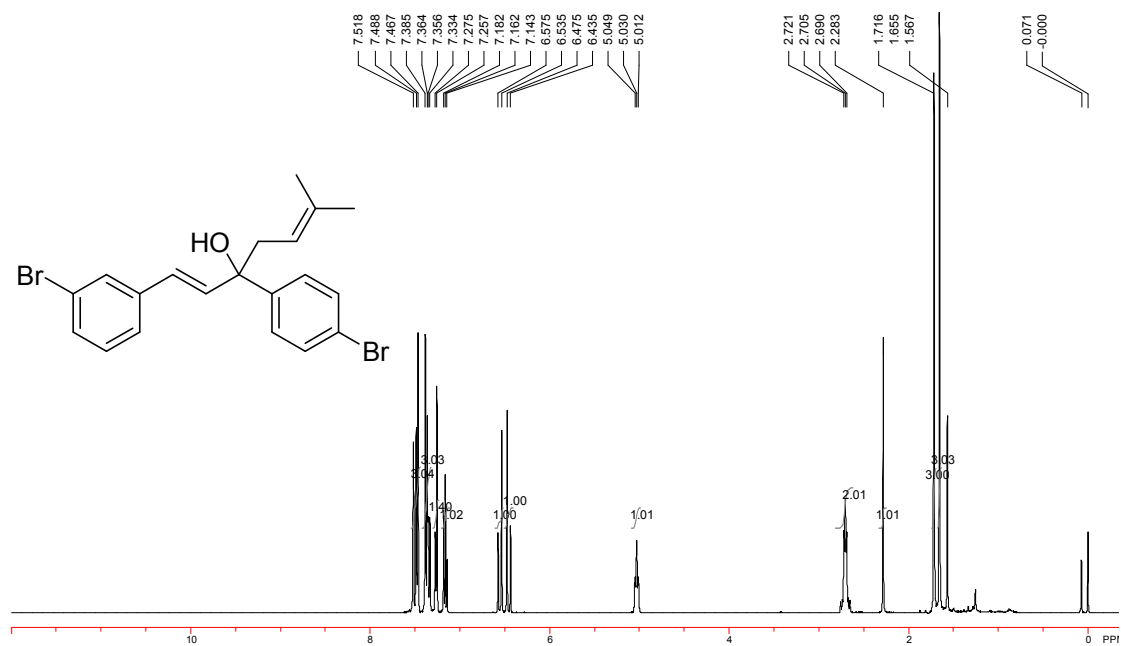
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound **2p**



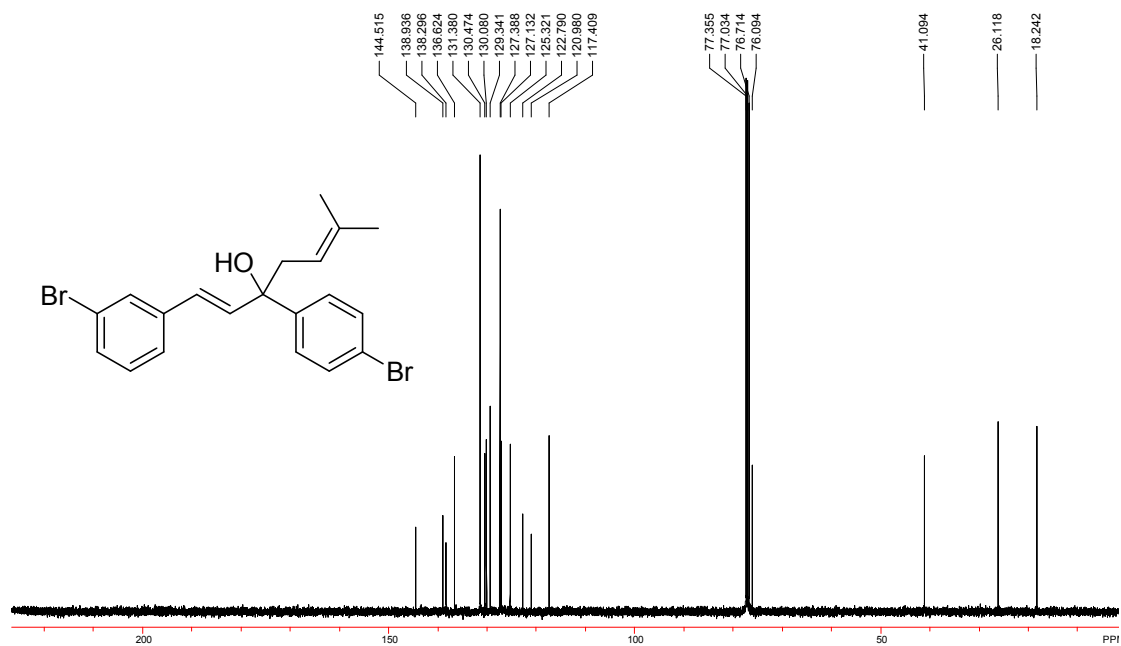
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound **2q**



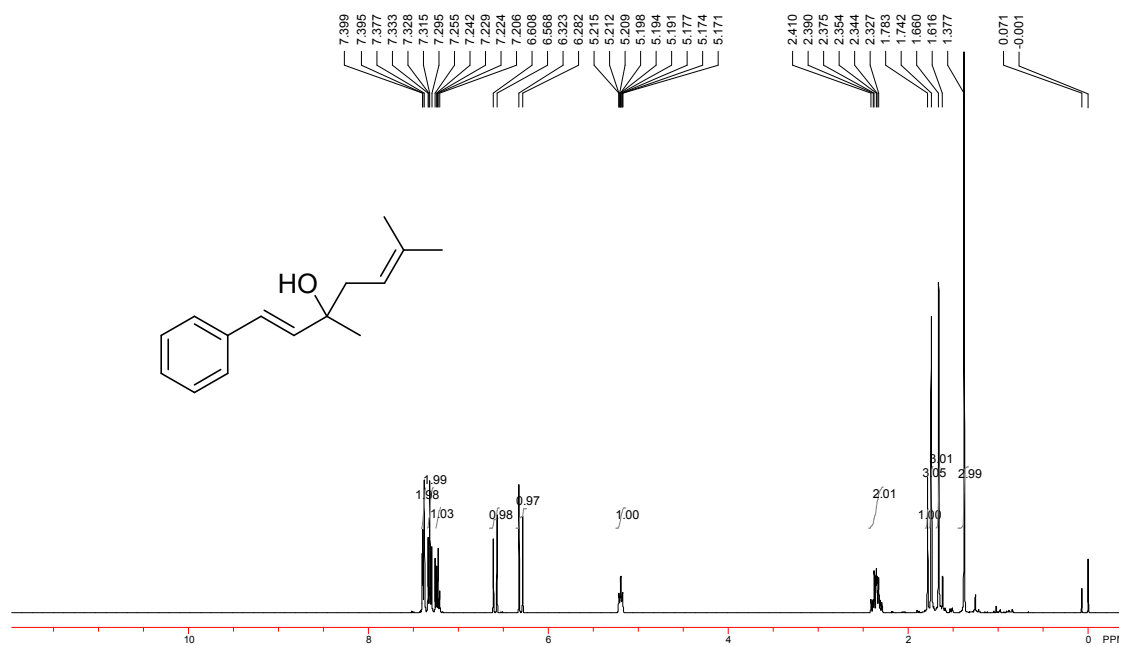
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound **2q**



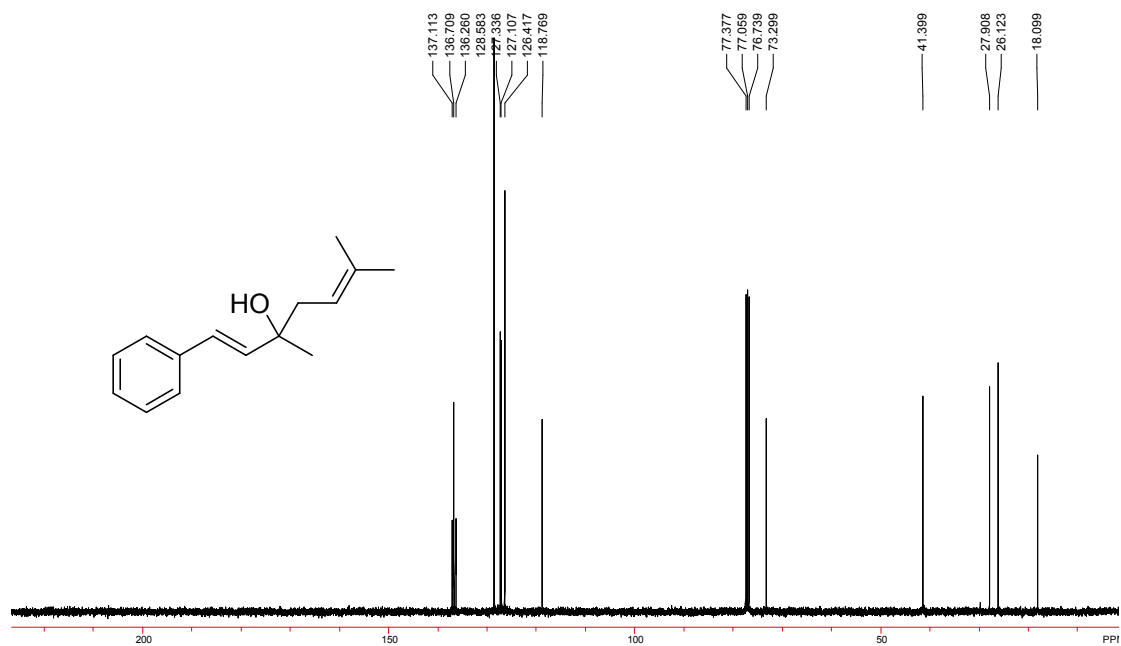
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound **2r**



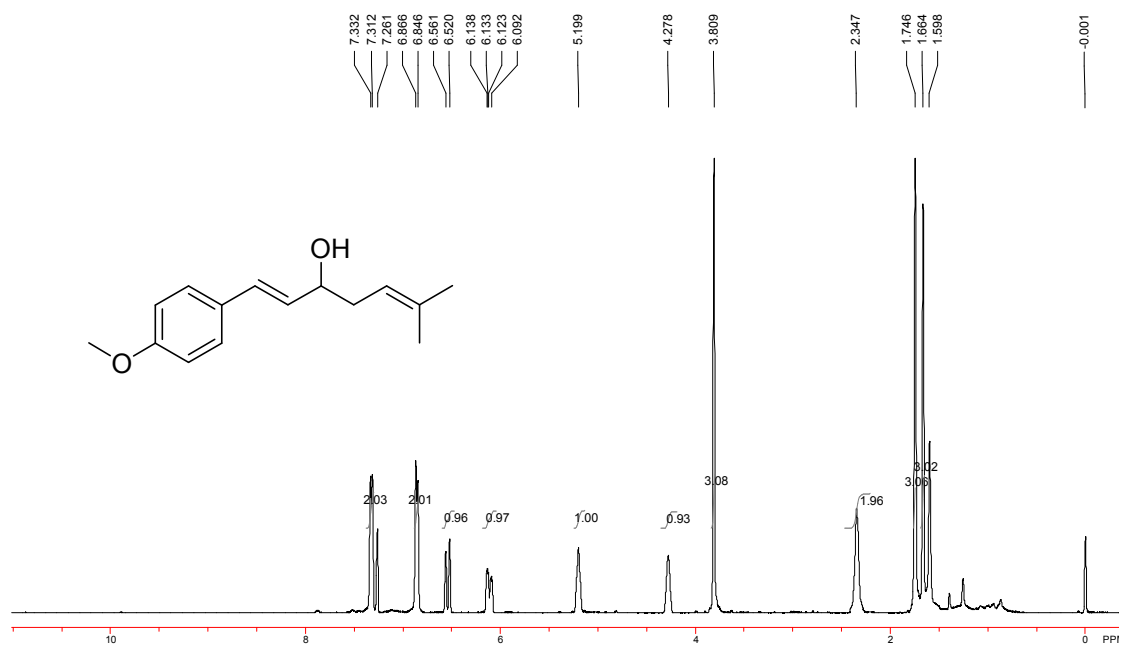
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound 2r



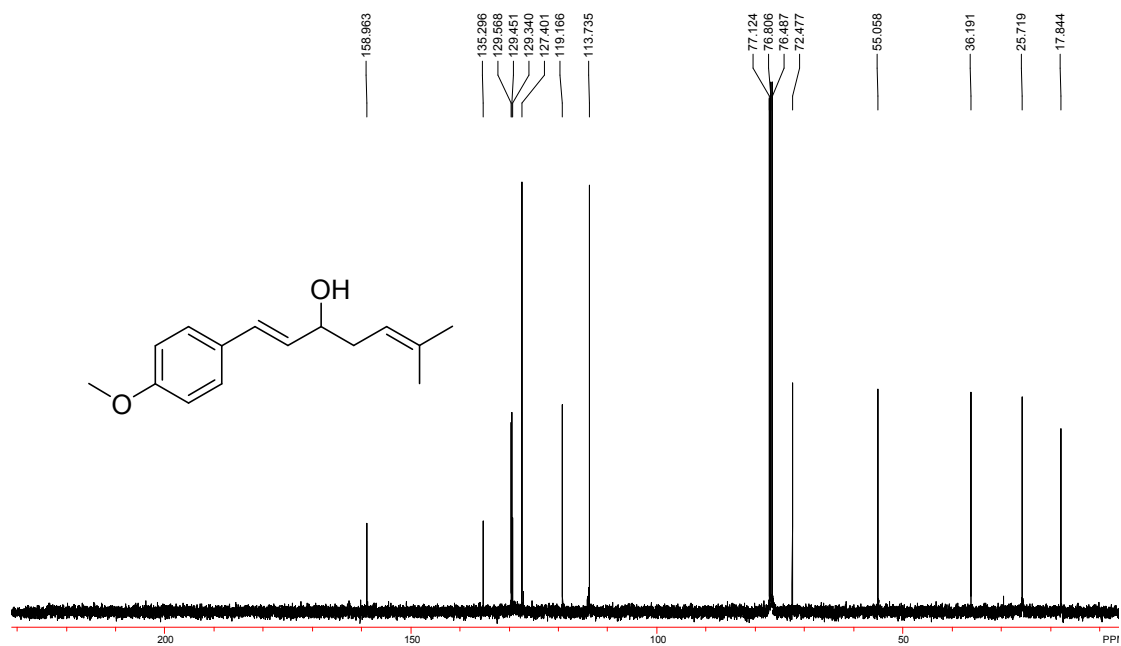
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound 2s



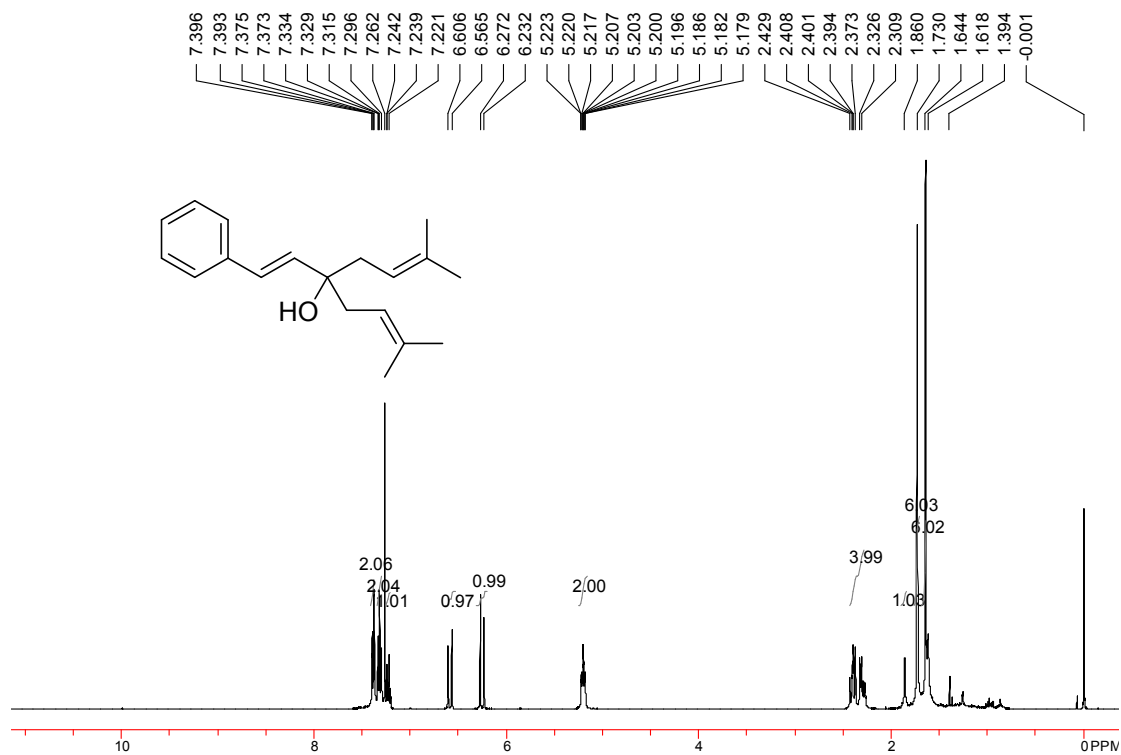
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound **2s**



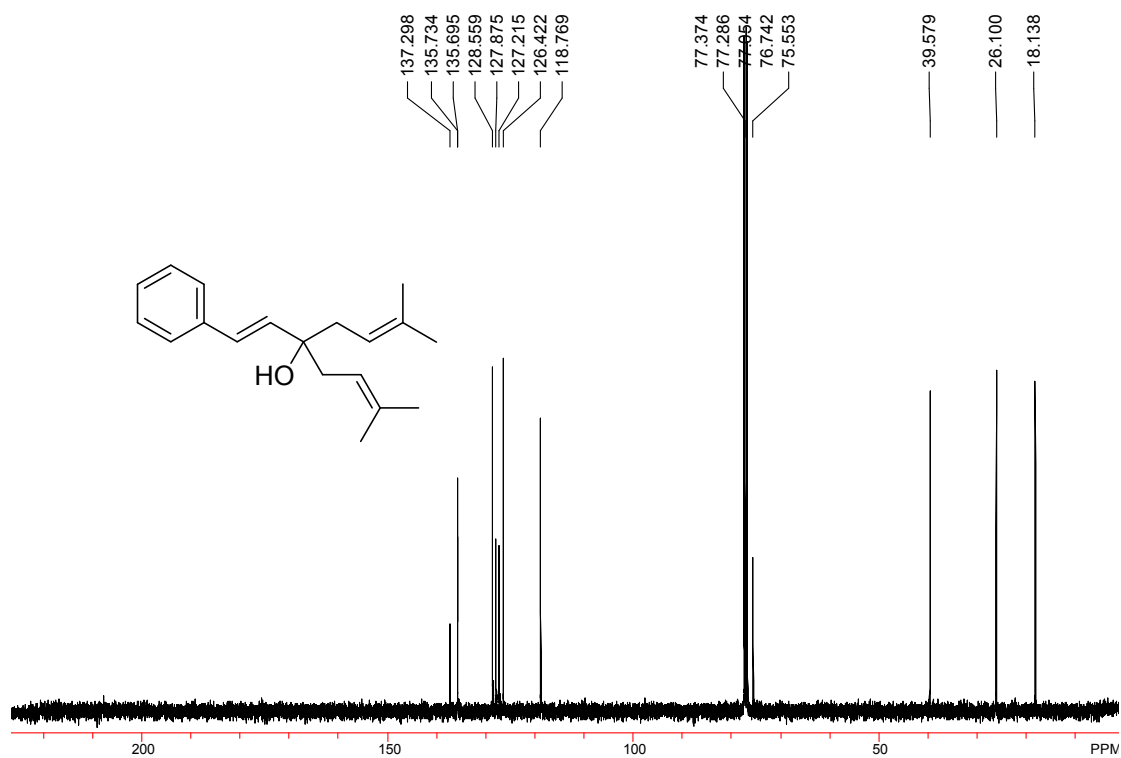
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound **2t**



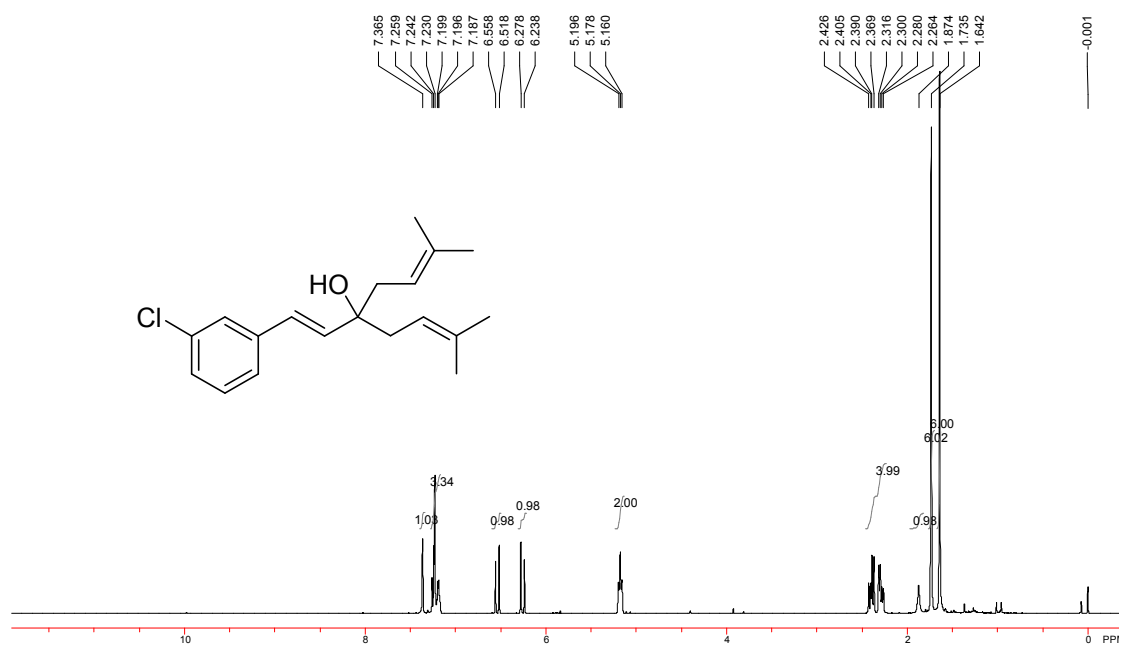
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound **2t**



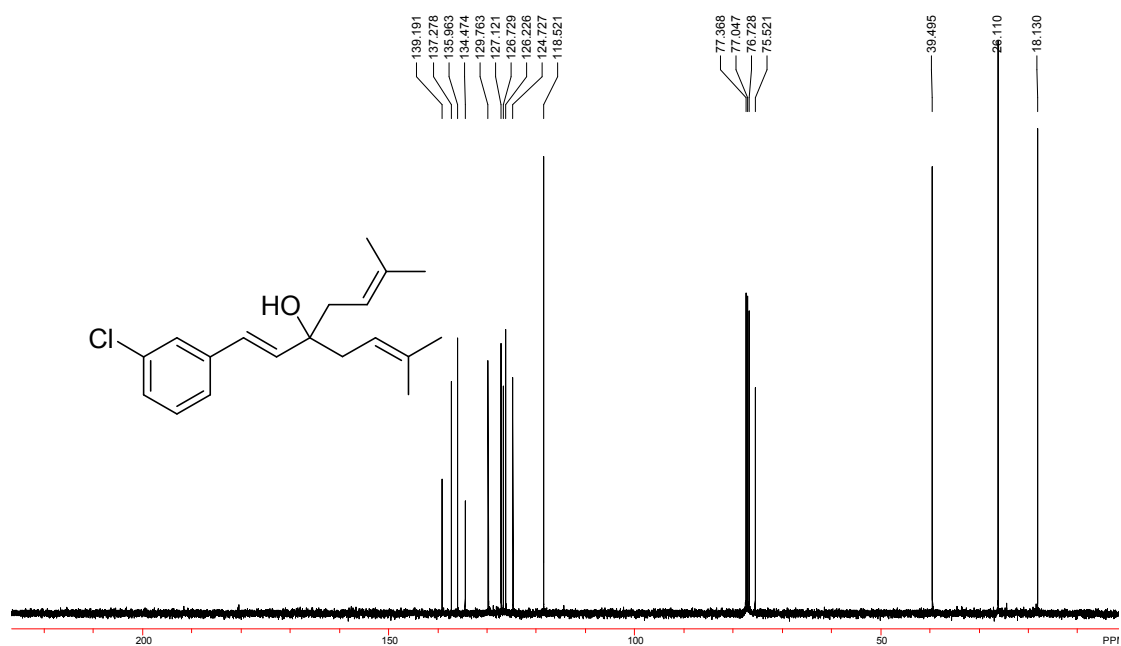
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound **2u**



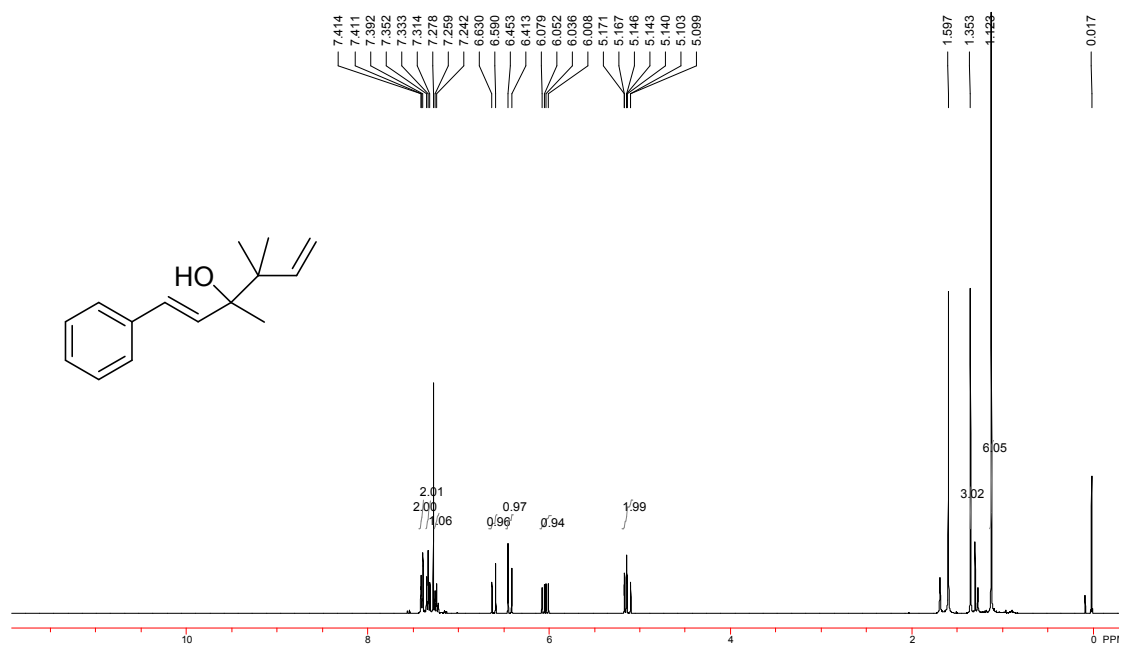
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound **2u**



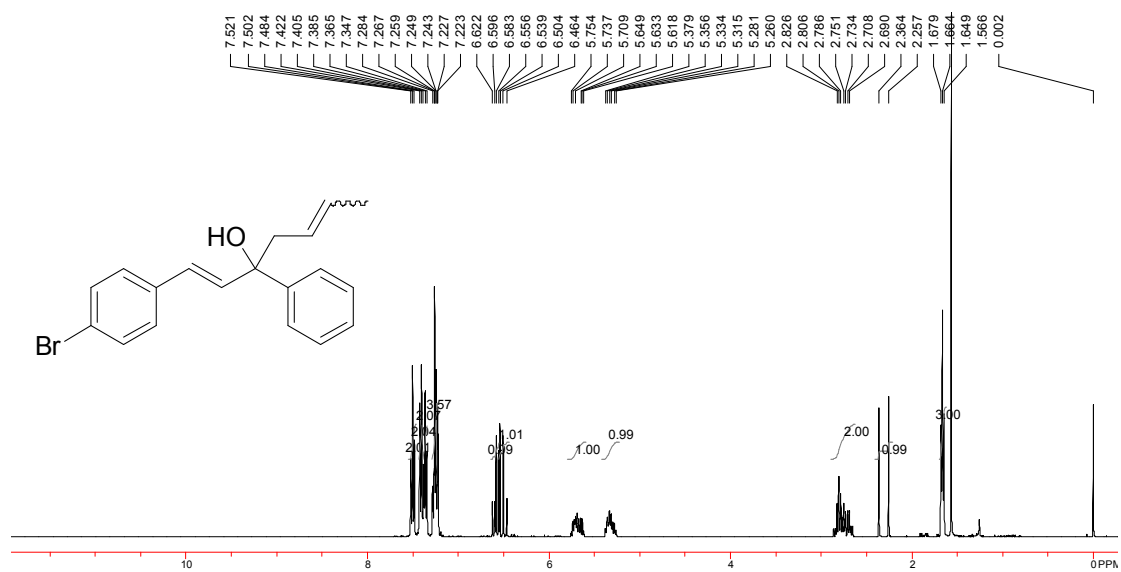
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound **2v**



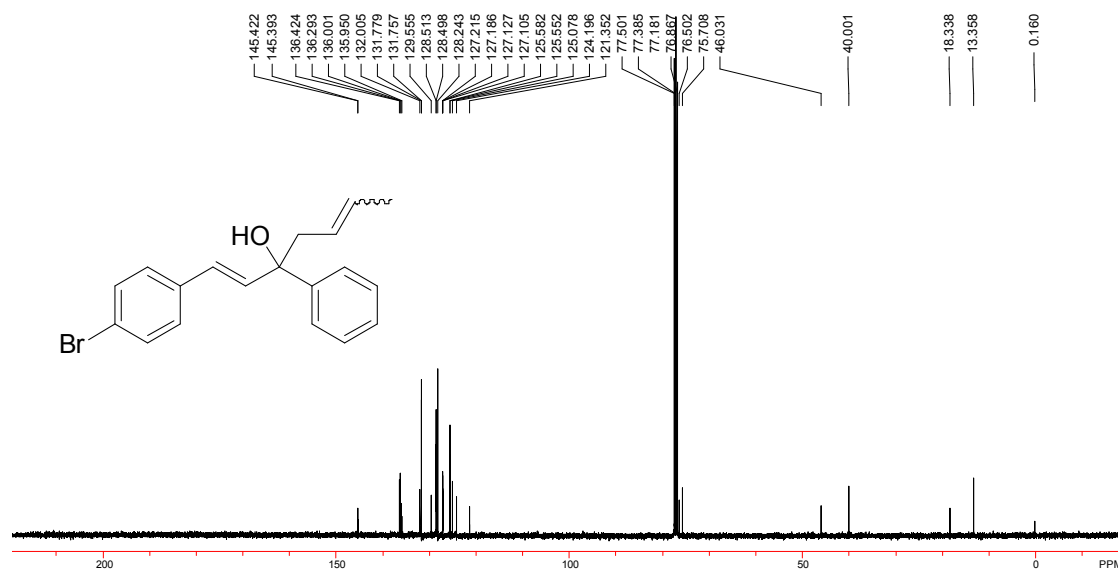
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound **2v**



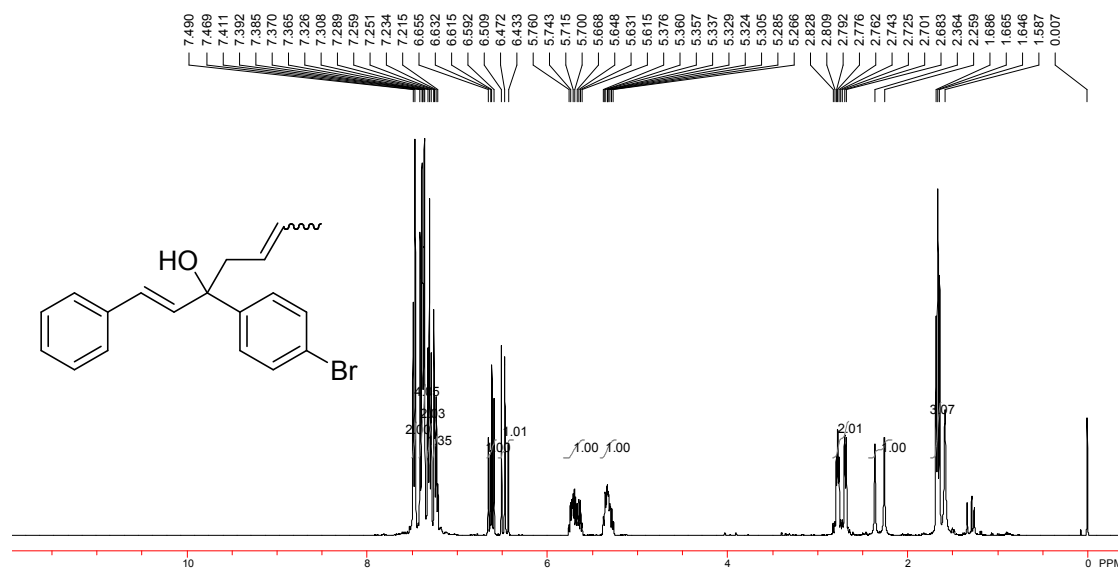
¹H NMR Spectrum (400 MHz, CDCl₃) of γ -Adduct from 4-Phenylbut-3-en-2-one **1s**



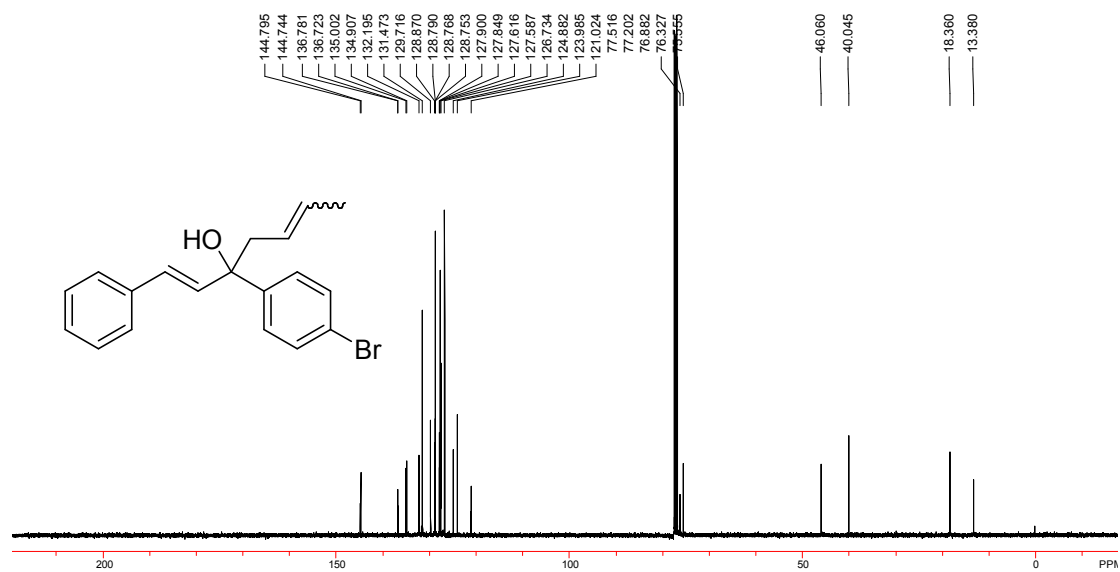
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound 3a



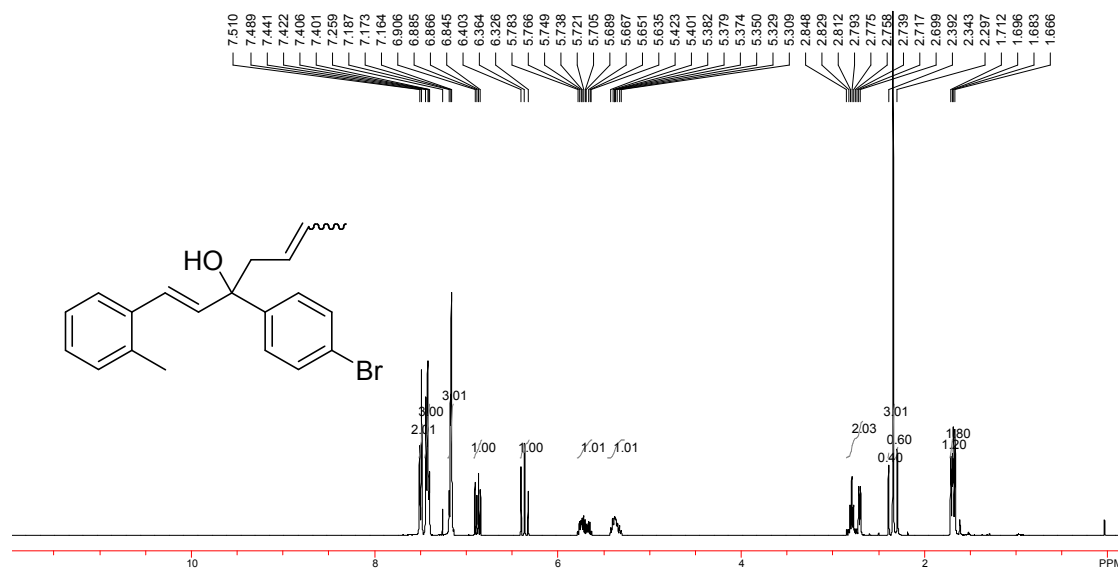
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound 3a



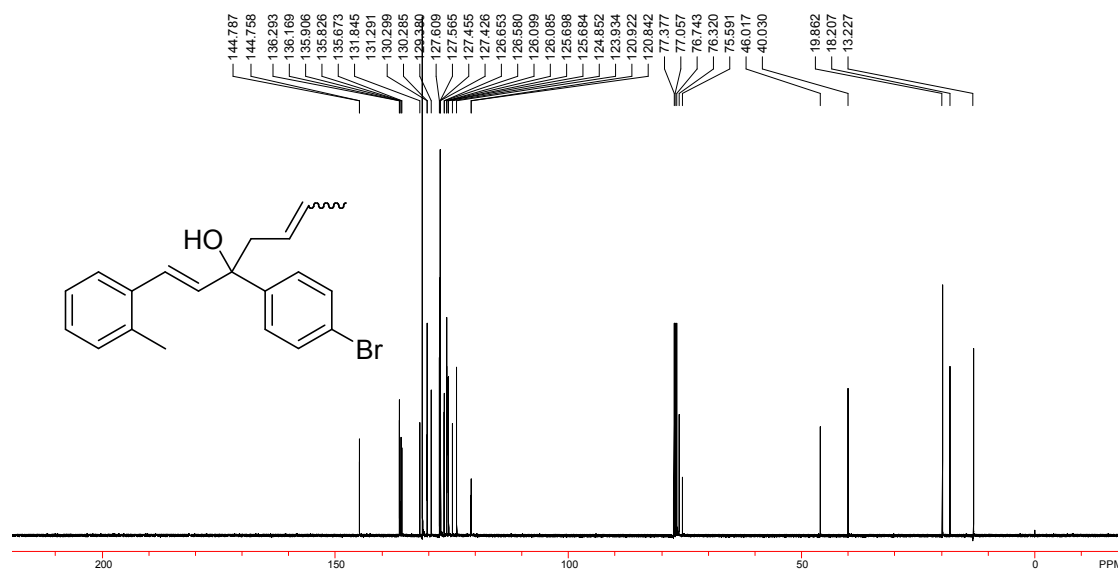
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound 3h



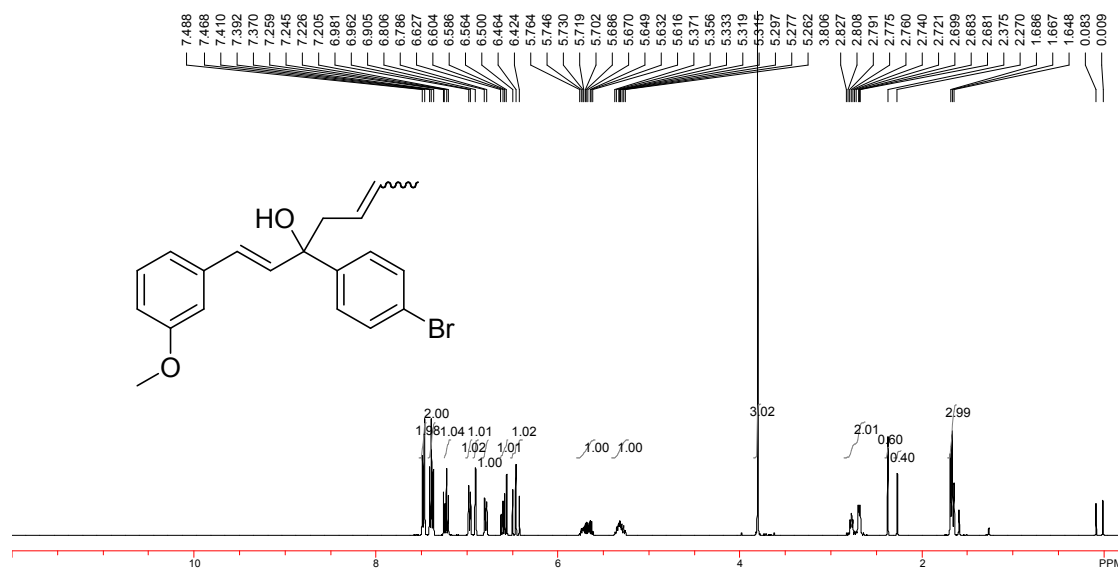
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound **3h**



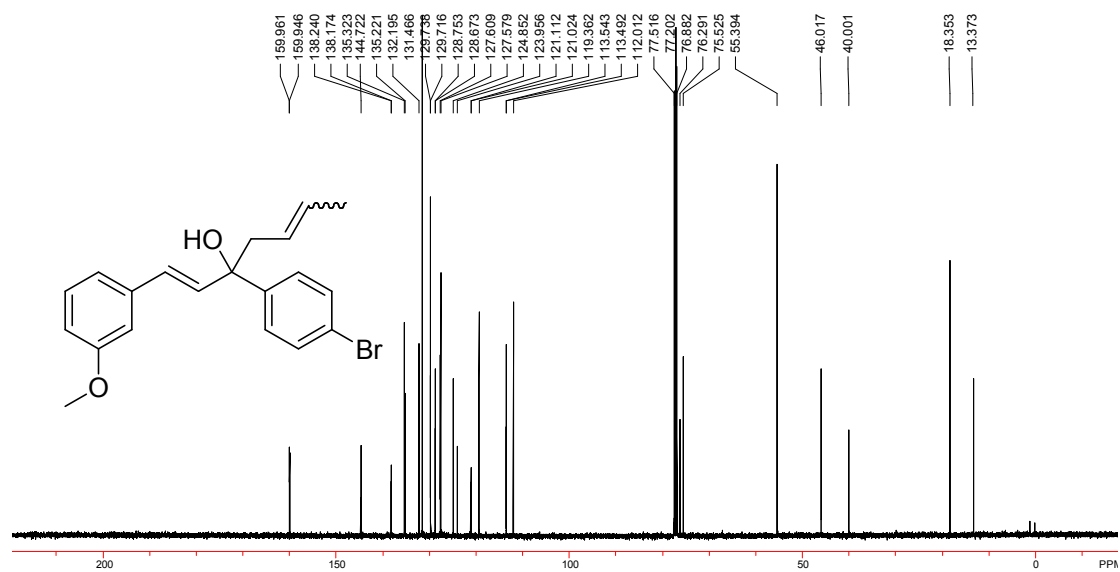
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound **3j**



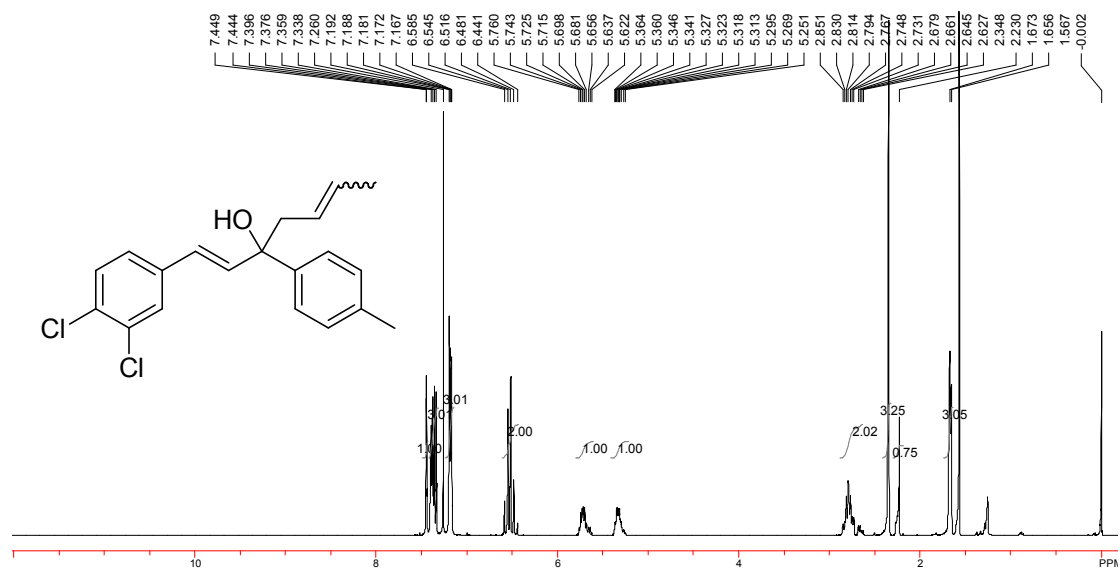
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound 3j



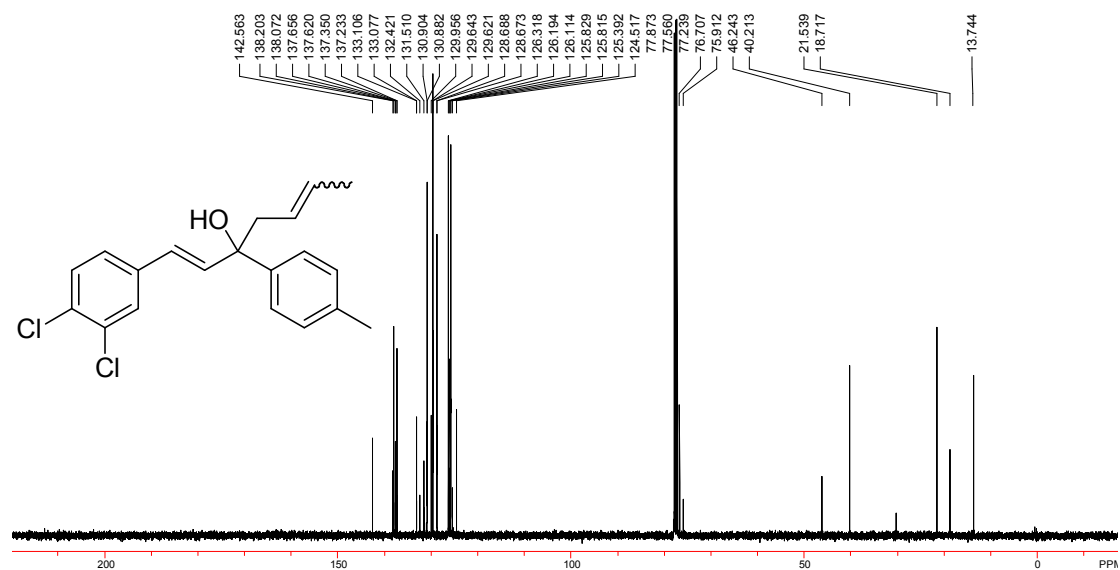
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound 3l



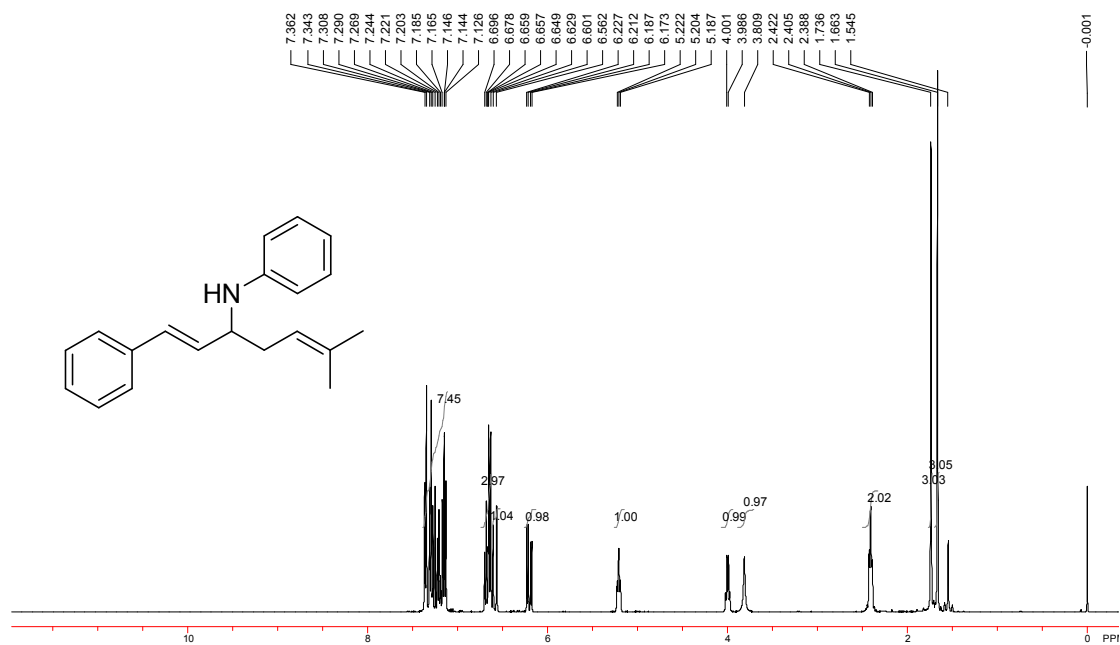
¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound **3l**



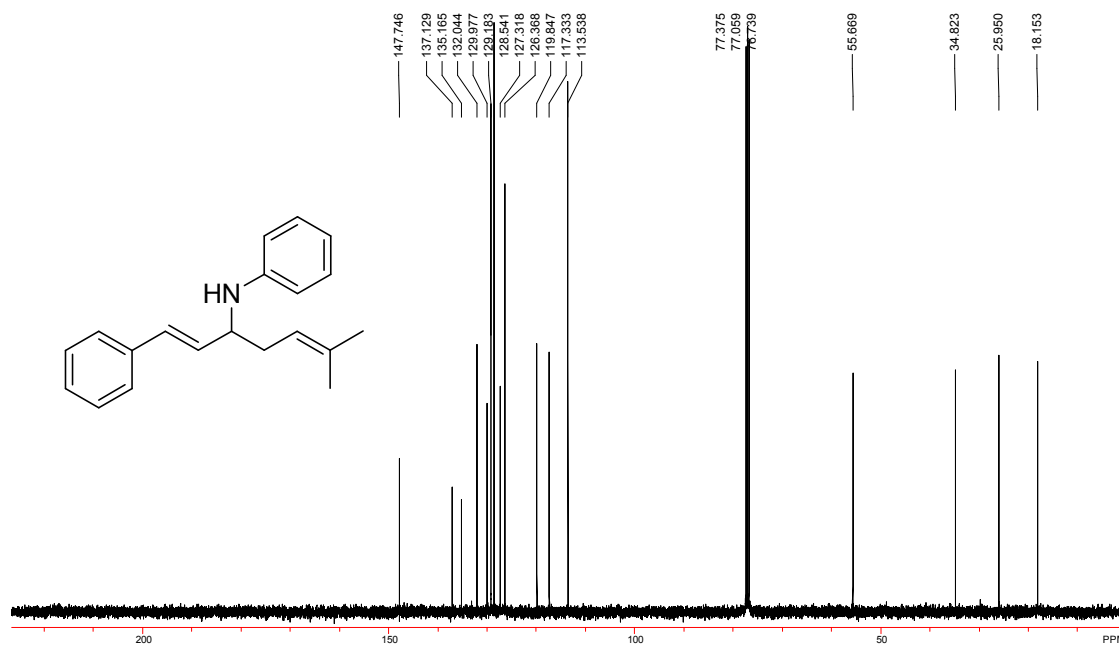
¹H NMR Spectrum (400 MHz, CDCl₃) of Compound **3w**



¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound 3w



¹H NMR Spectrum (400 MHz, CDCl₃) of Compound 4



¹³C NMR Spectrum (100 MHz, CDCl₃) of Compound 4