Supporting Information

Synthesis of Tetralones and Indanones Derivatives *via* Cascade Reductive Friedel−Crafts Alkylation/Cyclization of Keto Acids/Esters

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Table of contents **Pages**

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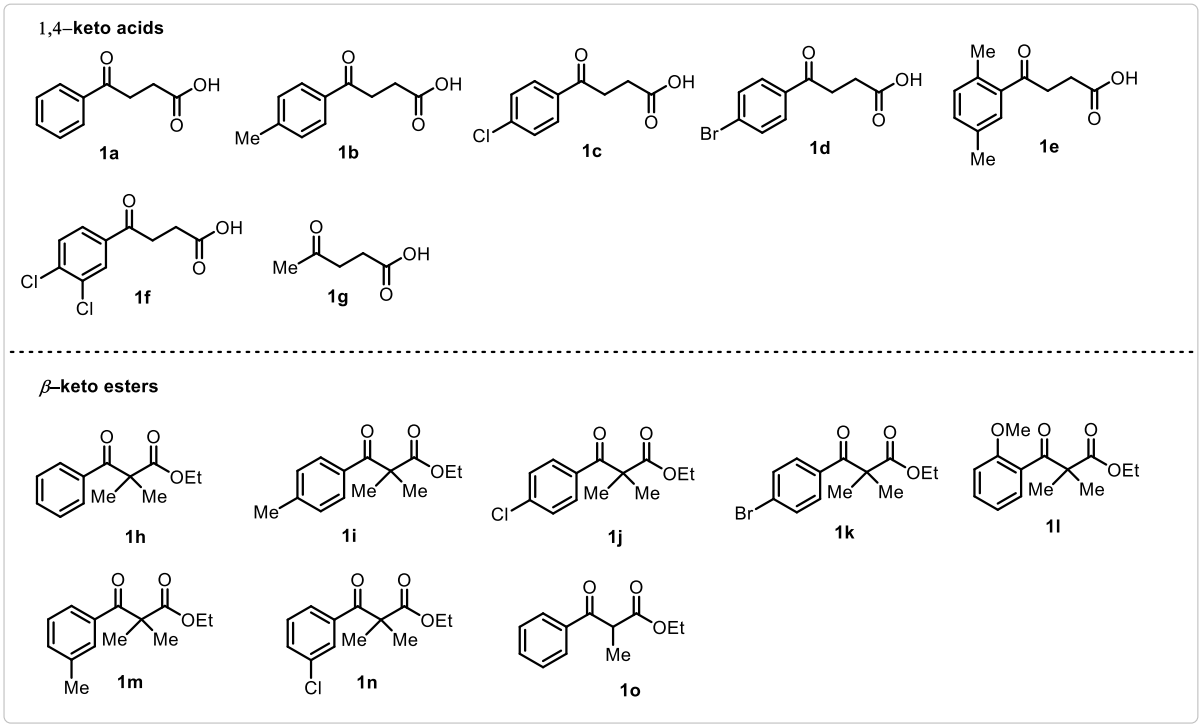
1. General Information:

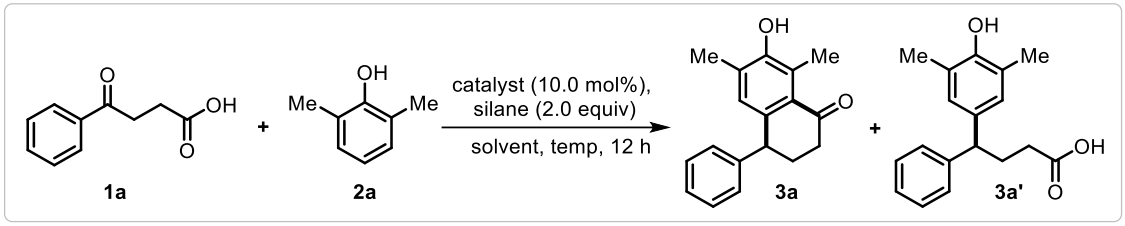
All reagents and solvents were of pure analytical grade. Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (silica gel 60, F254, EMD Chemical). High-resolution mass spectra (HRMS) were recorded on a mass spectrometer using electrospray ionization-time of-flight (ESITOF) reflectron experiments. Ethyl 3-oxo-3-phenylpropanoate, phenols and its derivatives, arenes and triflic acid were purchased from Sigma-Aldrich, TCI, or Alfa Aesar. All reactions were run in flame- or oven-dried glassware under an air atmosphere with high grade solvents unless otherwise stated. ^{1}H-NMR and ^{13}C-NMR were recorded on 400 MHz, and 500 MHz spectrometers, using $CDCl_3$ or DMSO-d_6 solution, the chemical shifts are reported as parts per million (ppm) referenced to residual protium or carbon of the solvents; $CDCl_3$ δ H (7.26 ppm) or DMSO-d_6 δ H (2.50 ppm) and $CDCl_3$ δ C (77.16 ppm) or DMSO-d_6 δ C (39.52 ppm). Coupling constants are reported in Hertz (Hz). Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to protium; s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration).

2. Experimental Section: Synthetic Procedure for the Preparation of Starting Materials:

All the phenols and arenes were commercially available. All the *β*–keto esters were prepared using known literature procedures.[1] The 1,4-ketoacids,[2] was synthesized according to reported literature.



3. Table S1. Optimization of Reaction Conditions for the Synthesis of 4-aryl tetralone

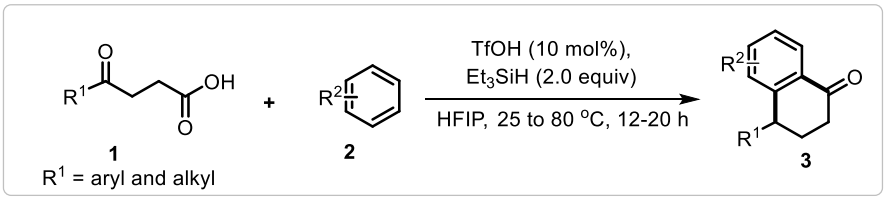


S. No.	Catalyst	Solvent	Silane	Temp (°C)	Yield of 4 (%)	Yield of 4' (%)
1	TfOH	HFIP	Et_3SiH	25	<5	80
2	TfOH	HFIP	Et_3SiH	60	72	15
3	**TfOH**	**HFIP**	**Et_3SiH**	**80**	**85**	**<5**
4	-	HFIP	Et_3SiH	80	-	<10
5	TfOH	DCE	Et_3SiH	80	40	24
6	TfOH	toluene	Et_3SiH	80	34	21
7	TfOH	CH_3CN	Et_3SiH	80	trace	<10
8	TfOH	dioxane	Et_3SiH	80	trace	<5
9	TfOH	HFIP	Ph_3SiH	80	50	<10
10	TfOH	HFIP	$PhSiH_3$	80	46	<10
11	*p*TSA•H_2O	HFIP	Et_3SiH	80	15	<10
12	CF_3COOH	HFIP	Et_3SiH	80	trace	trace
13	CH_3COOH	HFIP	Et_3SiH	80	NR	NR

[a]Reaction conditions: **1** (0.3 mmol, 1.0 equiv), **2** (0.33 mmol, 1.1 equiv), silane (0.6 mmol, 2.0 equiv), catalyst (10 mol%), solvent (0.5 mL), 12 h. TfOH = trifluoromethanesulfonic acid, DCE = 1,2-dichloroethane, DCM = dichloromethane, *p*TSA•H_2O = *p*-toluenesulfonic acid monohydrate, HFIP = 1,1,1,3,3,3-Hexafluoroisopropanol.

4. General Experimental Procedures

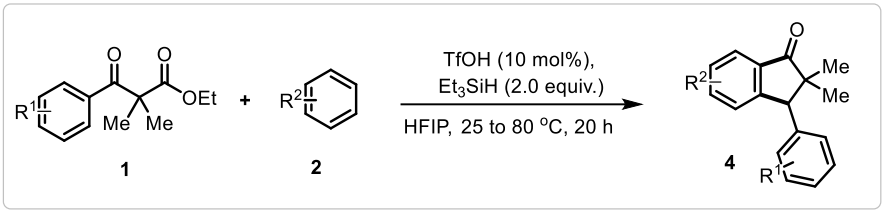
4.1 Procedure for the Synthesis of 4-aryl tetralones (GP1).



To a flame-dried Schlenk tube equipped with a magnetic stir bar, charged with 1,4-keto acid derivatives **1** (0.30 mmol, 1.0 equiv.), arene **2** (0.36 mmol, 1.2 equiv) and Et_3SiH (0.6 mmol, 2.0 equiv) in HFIP (0.5 mL) was added triflic acid (TfOH, 2.6 µL 10 mol%) at room temperature. Then the reaction was stirred at room temperature for 0.5 h. After 0.5 h, the reaction Schlenk tube kept at 80 °C and stirred for another 12-20 h. After completion of the reaction, the solvent was evaporated in vacuo, and the residue was purified by column chromatography using a hexane-ethyl acetate gradient to afford the corresponding 4-aryl tetralones products in good to excellent yields. The product was characterized and identified by analyzing spectral data (^1H, ^{13}C, ^{19}F NMR, and HRMS).

Note: For the measurement of the 2.6 µL triflic acid we have utilised Thermo Fisher Micro Laboratory Pipette (1-10 µL).

4.2 Procedure for the Synthesis of 3-aryl indanones (GP2).

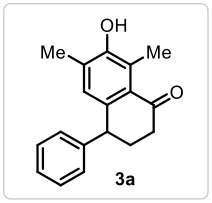


To a flame-dried Schlenk tube equipped with a magnetic stir bar, charged with 1,4-keto acid derivatives **1** (0.30 mmol, 1.0 equiv.), arene **2** (0.36 mmol, 1.2 equiv) and Et_3SiH (0.6 mmol, 2.0 equiv) in HFIP (0.5 mL) was added triflic acid (TfOH, 2.6 µL, 10 mol%) at room temperature. Then the reaction was stirred at room temperature for 0.5 h. After 0.5 h, the reaction Schlenk tube kept at 80 °C and stirred for another 12-24 h. After completion of the reaction, the solvent was evaporated in vacuo, and the residue was purified by column chromatography using a hexane-ethyl acetate gradient to afford the corresponding 3-aryl-1-indanones products in good to excellent yields. The product was characterized and identified by analyzing spectral data (^1H, ^{13}C, ^{19}F NMR, and HRMS).

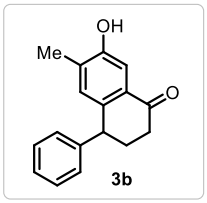
Note: For the measurement of the 2.6 µL triflic acid we have utilised Thermo Fisher Micro Laboratory Pipette (1-10 µL).

5. Analytical Data of Synthesized compound 3a-3v

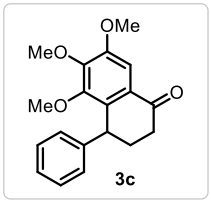
7-Hydroxy-6,8-dimethyl-4-phenyl-3,4-dihydronaphthalen-1(2*H*)-one (3a): The compound **3a** was prepared according to **GP1**, 4-oxo-4-phenylbutanoic acid **1a** (1.0 equiv, 0.3 mmol, 53.4 mg), 2,6-dimethylphenol (1.1 equiv, 0.33 mmol, 40.3 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (10.0 mol%, 2.6 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 90:10); brown solid (67.9 mg, 85% yield); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.6 Hz, 2H), 7.23 (q, *J* = 6.3 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 2H), 6.65 (s, 1H), 5.15 (s, 1H), 4.24 – 4.18 (m, 1H), 2.67 – 2.61 (m, 1H), 2.60 (s, 3H), 2.55 (ddd, *J* = 12.2, 7.6, 3.8 Hz, 1H), 2.41 (ddt, *J* = 13.7, 9.3, 4.7 Hz, 1H), 2.25 – 2.20 (m, 1H), 2.19 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 200.7, 151.8, 144.4, 139.4, 131.0, 129.7, 129.4, 128.62, 128.60, 126.6, 124.9, 45.5, 38.0, 31.5, 16.9, 13.4. **HRMS** (EI) calculated for $C_{18}H_{19}O_2$ [M + H]$^+$: 267.1385, found: 267.1388.



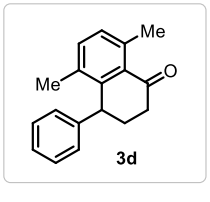
7-Hydroxy-6-methyl-4-phenyl-3,4-dihydronaphthalen-1(2*H*)-one (3b): The compound **3b** was prepared according to **GP1**, 4-oxo-4-phenylbutanoic acid **1a** (1.0 equiv, 0.3 mmol, 53.4 mg), 2-methylphenol (1.1 equiv, 0.33 mmol, 30.5 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (10.0 mol%, 2.6 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 90:10); brown solid (59 mg, 78% yield); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.26 – 7.21 (m, 2H), 7.19 – 7.15 (m, 2H), 7.05 – 7.01 (m, 2H), 6.68 (s, 1H), 4.19 – 4.07 (m, 1H), 2.62 (ddd, *J* = 17.4, 8.6, 4.4 Hz, 1H), 2.53 – 2.42 (m, 1H), 2.37 (ddt, *J* = 13.3, 8.9, 4.5 Hz, 1H), 2.21 – 2.15 (m, 1H), 2.14 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 199.8, 153.9, 144.1, 138.8, 133.0, 132.1, 131.7, 128.71, 128.68, 126.8, 112.1, 44.5, 36.5, 32.3, 16.6. **HRMS** (EI) calculated for $C_{17}H_{17}O_2$ $[M + H]^+$: 253.1229, found: 253.1234.



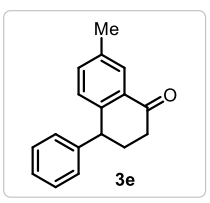
5,6,7-Trimethoxy-4-phenyl-3,4-dihydronaphthalen-1(2*H*)-one (3c): The compound **3c** was prepared according to **GP1**, 4-oxo-4-phenylbutanoic acid **1a** (1.0 equiv, 0.3 mmol, 53.4 mg), 1,2,3-trimethoxybenzene (1.1 equiv, 0.33 mmol, 55.5 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (10.0 mol%, 2.6 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 80:20); white solid (74.9 mg, 80% yield); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.22 – 7.17 (m, 1H), 7.04 (dd, *J* = 7.2, 1.7 Hz, 2H), 4.63 (t, *J* = 3.7 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H), 3.44 (s, 3H), 2.56 – 2.50 (m, 2H), 2.49 – 2.41 (m, 1H), 2.20 (dt, *J* = 9.3, 3.4 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 197.7, 152.9, 150.8, 147.8, 143.3, 133.1, 128.6, 128.5, 128.2, 126.6, 105.1, 60.9, 60.7, 56.2, 38.0, 33.6, 30.9. **HRMS** (EI) calculated for $C_{19}H_{21}O_4$ $[M + H]^+$: 313.1440, found: 313.1445.



5,8-Dimethyl-4-phenyl-3,4-dihydronaphthalen-1(2*H*)-one (3d): The compound **3d** was prepared according to modified **GP1**, 4-oxo-4-phenylbutanoic acid **1a** (1.0 equiv, 0.3 mmol, 53.4 mg), *p*-xylene (3.3 equiv, 1.0 mmol, 106.1 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (30.0 mol%, 7.8 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 95:05); white solid (52.6 mg, 70% yield); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 – 7.25 (m, 1H), 7.23 (d, *J* = 0.8 Hz, 1H), 7.22 – 7.20 (m, 1H), 7.20 – 7.17 (m, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 7.02 – 6.98 (m, 2H), 4.53 – 4.42 (m, 1H), 2.68 (s, 3H), 2.56 – 2.41 (m, 3H), 2.28 – 2.19 (m, 1H), 2.07 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 200.8, 144.4, 142.0, 139.1, 134.8, 134.6, 132.2, 131.1, 128.6, 128.3, 126.6, 41.9, 35.3, 30.4, 23.6, 19.6. **HRMS** (EI) calculated for $C_{18}H_{19}O$ $[M + H]^+$: 281.1436, found: 281.1440.

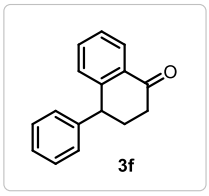


7-Methyl-4-phenyl-3,4-dihydronaphthalen-1(2*H*)-one (3e): The compound **3e** was prepared according to modified **GP1**, 4-oxo-4-phenylbutanoic acid **3e** (1.0 equiv, 0.3 mmol, 53.4 mg), toluene (3.3 equiv, 1.0 mmol, 92.1 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (30.0 mol%, 7.8 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 95:05); white solid

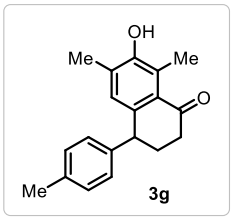


(46.1 mg, 65% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.26 – 7.20 (m, 3H), 7.12 – 7.08 (m, 2H), 7.02 – 6.95 (m, 1H), 6.86 (s, 1H), 4.26 (dd, *J* = 7.8, 4.4 Hz, 1H), 2.71 (ddd, *J* = 17.3, 7.9, 4.4 Hz, 1H), 2.66 – 2.55 (m, 1H), 2.47 – 2.42 (m, 1H), 2.37 (s, 3H), 2.29 – 2.22 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 143.6, 134.8, 129.7, 129.5, 128.8, 128.7, 127.3, 126.9, 45.1, 36.9, 32.1, 21.1. **HRMS** (EI) calculated for $C_{17}H_{17}O$ $[M + H]^+$: 237.1279, found: 237.1284.

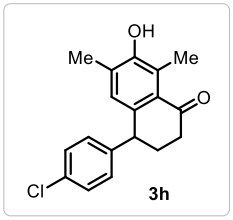
4-Phenyl-3,4-dihydronaphthalen-1(2*H*)-one (3f): The compound **3f** was prepared according to modified **GP1**, 4-oxo-4-phenylbutanoic acid **3f** (1.0 equiv, 0.3 mmol, 53.4 mg), benzene (3.3 equiv, 1.0 mmol, 78.1 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (30.0 mol%, 7.8 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 95:05); white solid (40 mg, 60% yield); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.34 (dt, *J* = 14.7, 7.5 Hz, 4H), 7.11 (d, *J* = 7.2 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 1H), 4.31 (dd, *J* = 8.0, 4.3 Hz, 1H), 2.76 – 2.61 (m, 2H), 2.48 (ddt, *J* = 12.8, 8.8, 4.5 Hz, 2H), 2.31 (dtd, *J* = 13.3, 8.7, 4.4 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 198.3, 143.8, 133.7, 133.5, 129.7, 128.8, 128.7, 127.21, 127.16, 126.9, 45.4, 36.8, 31.9. **HRMS** (EI) calculated for $C_{16}H_{15}O$ $[M + H]^+$: 223.1123, found: 223.1126.



7-Hydroxy-6,8-dimethyl-4-(*p*-tolyl)-3,4-dihydronaphthalen-1(2*H*)-one (3g): The compound **3g** was prepared according to **GP1**, 4-oxo-4-(*p*-tolyl)butanoic acid **1b** (1.0 equiv, 0.3 mmol, 57.7 mg), 2,6-dimethylphenol (1.1 equiv, 0.33 mmol, 40.3 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (10.0 mol%, 2.6 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 90:10); white solid (65.6 mg, 78% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 – 7.05 (m, 2H), 6.98 – 6.93 (m, 2H), 6.65 (s, 1H), 5.05 (s, 1H), 4.17 (dd, *J* = 7.0, 4.5 Hz, 1H), 2.67 – 2.60 (m, 1H), 2.59 (s, 3H), 2.57 – 2.49 (m, 1H), 2.43 – 2.34 (m, 1H), 2.32 (s, 3H), 2.19 (d, *J* = 0.7 Hz, 3H), 2.18 – 2.10 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 200.8, 151.7, 141.4, 139.6, 136.2, 130.9, 129.6, 129.4, 129.3, 128.5, 124.7, 45.1, 38.0, 31.6, 21.1, 16.9, 13.4. **HRMS** (EI) calculated for $C_{19}H_{21}O_2$ $[M + H]^+$: 281.1542, found: 281.1546.

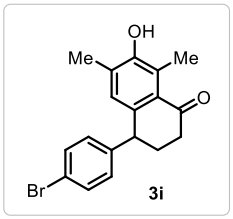


4-(4-Chlorophenyl)-7-hydroxy-6,8-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one (3h): The compound **3h** was prepared according to **GP1**, 4-(4-chlorophenyl)-4-oxobutanoic acid **1c** (1.0 equiv, 0.3 mmol, 63.7 mg), 2,6-dimethylphenol (1.1 equiv, 0.33 mmol, 40.3 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (10.0 mol%, 2.6 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 90:10); white solid (67.7 mg, 75% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 7.02 – 6.97 (m, 2H), 6.60 (s, 1H), 5.17 (s, 1H), 4.17 (dd, *J* = 7.1, 4.5 Hz, 1H), 2.58 – 2.57 (m, 3H), 2.58 – 2.51 (m, 2H), 2.38 (dddd, *J* = 13.1, 8.5, 5.4, 4.6 Hz, 1H), 2.19 (s, 3H), 2.17 – 2.11 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 200.4, 151.9,



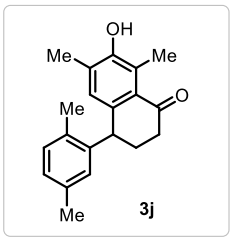
142.9, 138.8, 132.4, 130.9, 129.9, 129.8, 129.2, 128.8, 125.0, 45.0, 37.9, 31.4, 16.9, 13.4. **HRMS** (EI) calculated for $C_{18}H_{18}ClO_2$ [M + H]$^+$: 301.0995, found: 301.1003.

4-(4-Bromophenyl)-7-hydroxy-6,8-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one (3i): The



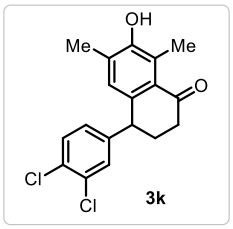
compound **3i** was prepared according to **GP1**, 4-(4-bromophenyl)-4-oxobutanoic acid **1d** (1.0 equiv, 0.3 mmol, 77.1 mg), 2,6-dimethylphenol (1.1 equiv, 0.33 mmol, 40.3 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (10.0 mol%, 2.6 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 90:10); brown solid (70 mg, 70% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H), 7.09 – 7.05 (m, 2H), 6.65 (s, 1H), 5.06 (s, 1H), 4.21 (dd, *J* = 6.9, 4.5 Hz, 1H), 2.59 (s, 3H), 2.59 – 2.55 (m, 2H), 2.44 – 2.37 (m, 1H), 2.25 – 2.20 (m, 1H), 2.19 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 200.7, 151.7, 144.4, 139.3, 131.7, 131.0, 130.3, 129.6, 129.4, 128.63, 128.61, 126.6, 124.7, 45.5, 38.0, 31.5, 16.9, 13.4. **HRMS** (EI) calculated for $C_{18}H_{18}BrO_2$ [M + H]: 345.0490, found: 345.0496.

4-(2,5-Dimethylphenyl)-7-hydroxy-6,8-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one (3j): The



compound **3j** was prepared according to **GP1**, 4-(2,5-dimethylphenyl)-4-oxobutanoic acid **1e** (1.0 equiv, 0.3 mmol, 61.8 mg), 2,6-dimethylphenol (1.1 equiv, 0.33 mmol, 40.3 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (10.0 mol%, 2.6 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 90:10); white solid (54.7 mg, 62% yield); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.13 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.63 (s, 1H), 6.58 (s, 1H), 5.00 (s, 1H), 4.44 – 4.38 (m, 1H), 2.73 (ddt, *J* = 17.8, 9.3, 4.8 Hz, 1H), 2.64 (s, 3H), 2.62 – 2.56 (m, 1H), 2.39 (s, 3H), 2.36 – 2.29 (m, 2H), 2.23 (s, 3H), 2.21 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 201.0, 151.5, 142.2, 140.0, 135.7, 132.9, 131.2, 130.7, 129.7, 129.4, 129.1, 127.3, 124.5, 41.9, 38.7, 29.7, 21.2, 19.3, 16.9, 13.4. **HRMS** (EI) calculated for $C_{20}H_{23}O_2$ [M + H]$^+$: 295.1698, found: 295.1711.

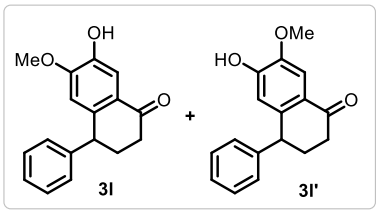
4-(3,4-Dichlorophenyl)-7-hydroxy-6,8-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one (3k): The



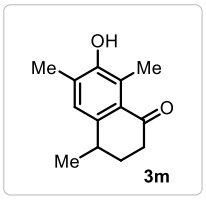
compound **3k** was prepared according to **GP1**, 4-(3,4-dichlorophenyl)-4-oxobutanoic acid **1f** (1.0 equiv, 0.3 mmol, 74.1 mg), 2,6-dimethylphenol (1.1 equiv, 0.33 mmol, 40.3 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (10.0 mol%, 2.6 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 90:10); white solid (81 mg, 80% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.3 Hz, 1H), 7.18 (d, *J* = 2.2 Hz, 1H), 6.90 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.60 (s, 1H), 5.16 (s, 1H), 4.17 (dd, *J* = 7.1, 4.5 Hz, 1H), 2.59 (s, 3H), 2.57 (d, *J* = 1.8 Hz, 1H), 2.45 – 2.35 (m, 1H), 2.22 (s, 3H), 2.16 (ddd, *J* = 13.4, 7.0, 5.6 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz,

$CDCl_3$) δ 200.1, 152.1, 144.8, 137.9, 132.7, 130.8, 130.7, 130.6, 130.5, 129.9, 129.2, 128.0, 125.2, 44.8, 37.8, 31.3, 16.9, 13.4. **HRMS** (EI) calculated for $C_{18}H_{17}Cl_2O_2$ $[M + H]^+$: 335.0606, found: 335.0610.

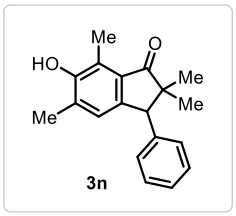
7-Hydroxy-6-methoxy-4-phenyl-3,4-dihydronaphthalen-1(2*H*)-one (3l): The compound **3l** was prepared according to **GP1**, 4-oxo-4-phenylbutanoic acid **1a** (1.0 equiv, 0.3 mmol, 53.4 mg), 2-methoxyphenol (1.1 equiv, 0.33 mmol, 40.9 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (10.0 mol%, 2.6 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 90:10); white solid (58.7 mg, 73% yield); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.61 (s, 1H), 7.32 (td, *J* = 6.7, 4.5 Hz, 3H), 7.29 – 7.24 (m, 2H), 7.11 (d, *J* = 7.5 Hz, 3H), 6.48 (s, 1H), 6.40 (s, 1H), 4.26 – 4.21 (m, 1H), 4.21 – 4.16 (m, 1H), 3.96 (s, 2H), 3.76 (s, 3H), 2.71 – 2.50 (m, 4H), 2.45 (dtt, *J* = 13.3, 8.3, 4.2 Hz, 2H), 2.25 (tdd, *J* = 13.2, 10.2, 5.8 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 197.2, 197.1, 151.3, 150.8, 145.9, 144.8, 143.8, 143.6, 142.0, 140.1, 128.6, 128.6, 128.5, 127.0, 126.8, 126.1, 114.7, 112.2, 110.6, 108.3, 56.2, 56.0, 45.0, 44.9, 36.3, 35.8, 32.2, 32.1. **HRMS** (EI) calculated for $C_{17}H_{17}O_3$ $[M + H]^+$: 269.1178, found: 269.1182.



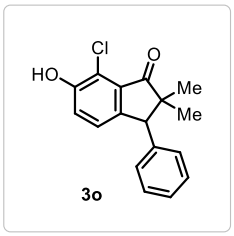
7-Hydroxy-4,6,8-trimethyl-3,4-dihydronaphthalen-1(2*H*)-one (3m): The compound **3m** was prepared according to **GP1**, 4-oxo-4-(*p*-tolyl)butanoic acid **1g** (1.0 equiv, 0.3 mmol, 57.7 mg), 2,6-dimethylphenol (1.1 equiv, 0.33 mmol, 40.3 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (30.0 mol%, 7.8 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 90:10); white solid (42.9 mg, 70% yield); **^{1}H NMR** (400 MHz, $CDCl_3$)δ 6.93 (s, 1H), 4.82 (d, *J* = 1.4 Hz, 1H), 2.95 (td, *J* = 6.9, 4.5 Hz, 1H), 2.75 (ddd, *J* = 17.4, 9.4, 5.3 Hz, 1H), 2.60 – 2.54 (m, 1H), 2.51 (s, 3H), 2.28 (s, 3H), 2.21 – 2.10 (m, 1H), 1.86 – 1.76 (m, 1H), 1.31 (d, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 200.8, 151.3, 142.5, 130.0, 129.3, 127.2, 124.6, 37.8, 33.3, 30.2, 21.4, 17.0, 13.3. **HRMS** (EI) calculated for $C_{13}H_{17}O_2$ $[M + H]^+$: 205.1229, found: 205.1232.



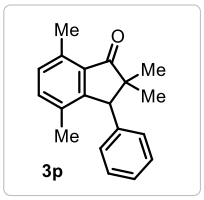
6-Hydroxy-2,2,5,7-tetramethyl-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3n)[3]: The compound **3n** was prepared according to **GP2**, ethyl 2,2-dimethyl-3-oxo-3-phenylpropanoate **1h** (1.0 equiv, 0.3 mmol, 66.1 mg), 2,6-dimethylphenol (1.1 equiv, 0.33 mmol, 40.3 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (10.0 mol%, 2.6 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 90:10); white solid (75.6 mg, 90% yield); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 3H), 7.02 (d, *J* = 7.6 Hz, 2H), 6.93 (s, 1H), 5.25 (s, 1H), 4.16 (s, 1H), 2.63 (s, 3H), 2.29 (s, 3H), 1.31 (s, 3H), 0.67 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 212.2, 152.4, 147.6, 141.1, 132.3, 131.8, 129.4, 128.3, 126.9, 126.1, 122.0, 56.4, 51.3, 26.0, 23.0, 17.4, 10.0.



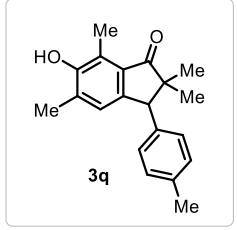
7-Chloro-6-hydroxy-2,2-dimethyl-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3o)[3]: The compound **3o** was prepared according to **GP4**, ethyl 2,2-dimethyl-3-oxo-3-phenylpropanoate **1h** (1.0 equiv, 0.3 mmol, 66.1 mg), 2-chlorophenol (1.1 equiv, 0.33 mmol, 42.4 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (10.0 mol%, 2.6 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 90:10); white solid (58.9 mg, 68% yield); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.06 – 6.94 (m, 2H), 6.84 (d, *J* = 10.1 Hz, 1H), 5.73 (s, 1H), 4.24 (s, 1H), 1.34 (s, 3H), 0.73 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.6, 154.1, 150.6, 135.5, 135.4, 133.5, 129.6, 128.4, 127.0, 124.4, 116.3, 56.7, 50.9, 25.4, 22.9.



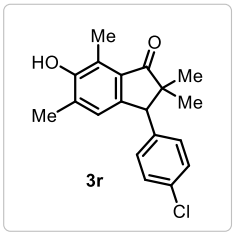
2,2,4,7-Tetramethyl-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3p)[3]: The compound **3p** was prepared according to **GP2**, ethyl 2,2-dimethyl-3-oxo-3-phenylpropanoate **1h** (1.0 equiv, 0.3 mmol, 66.1 mg), *p*-xylene (3.3 equiv, 1.0 mmol, 106.1 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (20.0 mol%, 5.2 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 90:10); white solid (57 mg, 72% yield); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 3H), 7.29 – 7.22 (m, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 4.26 (s, 1H), 2.75 (s, 3H), 2.02 (s, 3H), 1.38 (s, 3H), 0.81 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 212.5, 153.7, 141.3, 136.3, 135.9, 133.8, 132.8, 130.3, 128.4, 128.1, 126.7, 57.1, 50.7, 28.9, 21.8, 18.3, 18.2.



6-Hydroxy-2,2,5,7-tetramethyl-3-(p-tolyl)-2,3-dihydro-1*H*-inden-1-one (3q)[3]: The compound **3q** was prepared according to **GP2**, ethyl 2,2-dimethyl-3-oxo-3-(*p*-tolyl)propanoate **1i** (1.0 equiv, 0.3 mmol, 70.2 mg), 2,6-dimethylphenol (1.1 equiv, 0.33 mmol, 40.3 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (10.0 mol%, 2.6 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 90:10); white solid (71 mg, 80% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 7.8 Hz, 2H), 6.94 – 6.88 (m, 3H), 4.11 (s, 1H), 2.61 (s, 3H), 2.33 (s, 3H), 2.27 (s, 3H), 1.29 (s, 3H), 0.67 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 212.4, 152.4, 147.9, 137.9, 136.5, 132.4, 131.7, 129.7, 129.3, 129.0, 126.0, 122.1, 56.0, 51.3, 25.9, 23.0, 21.2, 19.5, 17.4, 16.2, 10.1.

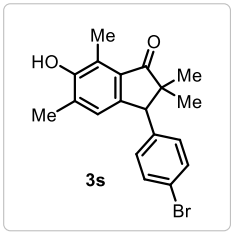


3-(4-Chlorophenyl)-6-hydroxy-2,2,5,7-tetramethyl-2,3-dihydro-1*H*-inden-1-one (3r)[3]: The compound **3r** was prepared according to **GP2**, ethyl 3-(4-chlorophenyl)-2,2-dimethyl-3-oxopropanoate **1j** (1.0 equiv, 0.3 mmol, 76.4 mg), 2,6-dimethylphenol (1.1 equiv, 0.33 mmol, 40.3 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (10.0 mol%, 2.6 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 90:10); white solid (69.8 mg,



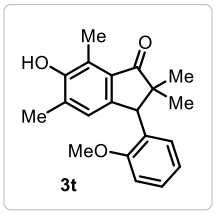
74% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.3 Hz, 2H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.89 (s, 1H), 5.49 (s, 1H), 4.13 (s, 1H), 2.62 (s, 3H), 2.29 (s, 3H), 1.29 (s, 3H), 0.67 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 211.8, 152.6, 147.1, 139.6, 132.7, 132.6, 131.7, 130.7, 128.5, 125.9, 122.3, 55.7, 51.2, 25.9, 23.0, 17.5, 10.1.

3-(4-Bromophenyl)-6-hydroxy-2,2,5,7-tetramethyl-2,3-dihydro-1*H*-inden-1-one (3s)[3]: The



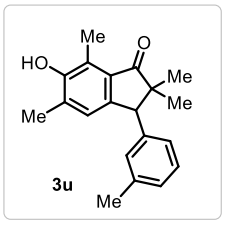
compound **3s** was prepared according to **GP2**, ethyl 3-(4-bromophenyl)-2,2-dimethyl-3-oxopropanoate **1k** (1.0 equiv, 0.3 mmol, 89.7mg), 2,6-dimethylphenol (1.1 equiv, 0.33 mmol, 40.3 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (10.0 mol%, 2.6 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 90:10); white solid (76.5 mg, 71% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 3H), 5.11 (s, 1H), 4.11 (s, 1H), 2.61 (s, 3H), 2.29 (s, 3H), 1.29 (s, 3H), 0.67 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 211.5, 152.5, 147.0, 140.2, 132.3, 131.8, 131.5, 131.1, 126.0, 122.1, 120.8, 55.8, 51.1, 26.0, 23.0, 17.4, 10.0.

6-Hydroxy-3-(2-methoxyphenyl)-2,2,5,7-tetramethyl-2,3-dihydro-1*H*-inden-1-one (3t)[3]: The



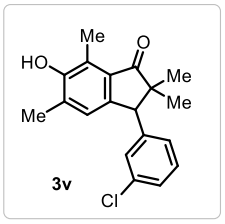
compound **3t** was prepared according to **GP2**, ethyl 3-(2-methoxyphenyl)-2,2-dimethyl-3-oxopropanoate **1l** (1.0 equiv, 0.3 mmol, 75.1 mg), 2,6-dimethylphenol (1.1 equiv, 0.33 mmol, 40.3 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (10.0 mol%, 2.6 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 90:10); white solid (70.7 mg, 76% yield); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23 – 7.17 (m, 1H), 6.92 (d, *J* = 9.6 Hz, 2H), 6.79 (t, *J* = 6.9 Hz, 1H), 6.56 (dd, *J* = 7.6, 1.8 Hz, 1H), 5.22 (s, 1H), 4.73 (s, 1H), 3.90 (s, 3H), 2.63 (s, 3H), 2.30 (s, 3H), 1.35 (s, 3H), 0.68 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 213.1, 158.1, 152.2, 148.4, 132.3, 132.2, 130.8, 129.6, 127.7, 126.4, 121.8, 120.3, 110.0, 55.4, 51.0, 48.5, 27.3, 22.0, 17.4, 10.0.

6-Hydroxy-2,2,5,7-tetramethyl-3-(m-tolyl)-2,3-dihydro-1*H*-inden-1-one (3u)[3]: The compound **3u**



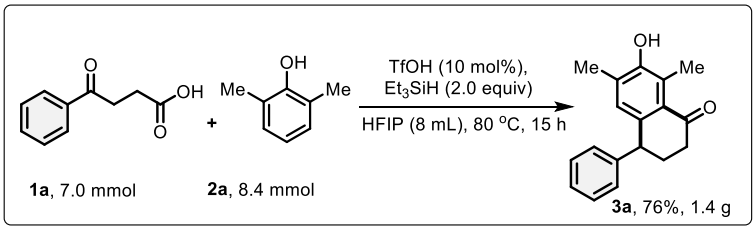
was prepared according to **GP2**, ethyl 2,2-dimethyl-3-oxo-3-(m-tolyl)propanoate **1m** (1.0 equiv, 0.3 mmol, 70.2 mg), 2,6-dimethylphenol (1.1 equiv, 0.33 mmol, 40.3 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (10.0 mol%, 2.6 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 90:10); white solid (61.8 mg, 70% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.94 (s, 1H), 6.85 – 6.75 (m, 2H), 5.07 (s, 1H), 4.12 (s, 1H), 2.63 (s, 3H), 2.32 (s, 3H), 2.29 (s, 3H), 1.30 (s, 4H), 0.69 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 212.1, 152.3, 147.8, 141.1, 137.9, 132.1, 131.8, 128.2, 127.7, 126.2, 121.8, 56.4, 51.3, 26.2, 22.9, 21.6, 17.4, 10.0.

3-(3-Chlorophenyl)-6-hydroxy-2,2,5,7-tetramethyl-2,3-dihydro-1*H*-inden-1-one (3v)[3]: The compound **3v** was prepared according to **GP2**, ethyl 2,2-dimethyl-3-oxo-3-(m-tolyl)propanoate **1n** (1.0 equiv, 0.3 mmol, 76.4 mg), 2,6-dimethylphenol (1.1 equiv, 0.33 mmol, 40.3 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (10.0 mol%, 2.6 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 90:10); white solid (67.9 mg, 72% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.18 (m, 2H), 6.99 (s, 1H), 6.89 (s, 1H), 5.07 (s, 1H), 4.11 (s, 1H), 2.60 (s, 3H), 2.28 (s, 3H), 1.28 (s, 3H), 0.67 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 211.3, 152.5, 146.8, 143.4, 134.3, 132.3, 129.6, 127.2, 126.0, 122.0, 56.1, 51.2, 26.2, 22.9, 17.4, 10.0.



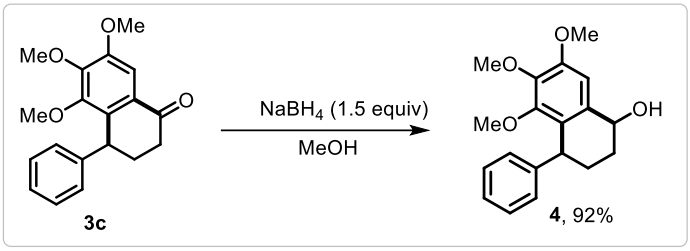
6-Hydroxy-2,5,7-trimethyl-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3w): The compound **3w** was prepared according to **GP2**, ethyl 2-methyl-3-oxo-3-phenylpropanoate **1i** (1.0 equiv, 0.3 mmol, 61.9 mg), 2,6-dimethylphenol (1.1 equiv, 0.33 mmol, 40.3 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (10.0 mol%, 2.6 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 90:10); white solid (55 mg, 68% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.28 (t, *J* = 1.5 Hz, 1H), 7.18 – 7.09 (m, 2H), 6.78 (s, 1H), 4.93 (s, 1H), 3.85 (d, *J* = 5.0 Hz, 1H), 2.60 (s, 3H), 2.57 (dd, *J* = 7.3, 5.0 Hz, 1H), 2.24 (s, 3H), 1.31 (d, *J* = 7.3 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 208.9, 152.2, 149.3, 143.7, 132.7, 128.9, 128.4, 128.1, 127.0, 125.6, 121.2, 54.4, 52.7, 17.3, 14.5, 9.9. **HRMS** (EI) calculated for $C_{18}H_{19}O_2$ $[M + H]^+$: 267.1385, found: 267.1389.

6. Gram-Scale reaction

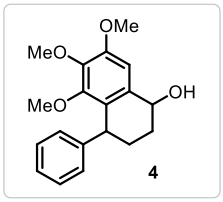


To a flame-dried Schlenk tube equipped with a magnetic stir bar, charged with 4-oxo-4-phenylbutanoic acid **1a** (1.0 equiv, 7.0 mmol, 1.2 g), 2,6-dimethyl phenol **2a** (1.2 equiv, 8.4 mmol, 1.0 g) and Et_3SiH (2.0 equiv, 14.0 mmol, 2.2 mL) in HFIP (8.0 mL) was added triflic acid (TfOH, 61.7 µL, 10 mol%) at room temperature. Then, the reaction was stirred at room temperature for 0.5 h. After 0.5 h, the reaction Schlenk tube was kept at 80 °C and stirred for another 15 h. After completion of the reaction, the solvent was evaporated in vacuo, and the residue was purified by column chromatography using a hexane-ethyl acetate gradient to afford the corresponding 4-aryl tetralone **3a** in 76% yield.

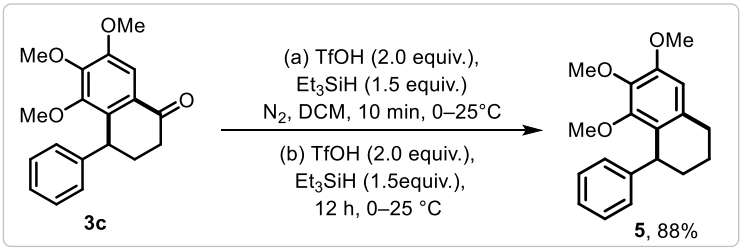
7. Experimental Procedures and Analytical Data of Synthesized Compounds (4−7)



To a solution of **3c** (62.4 mg, 0.2 mmol, 1.0 equiv.) in methanol (anhydrous, 2 mL), sodium borohydride (0.3 mmol, 1.5 equiv.) was added portion-wise and stirred at room temperature for 1 h. Reaction progress was monitored by TLC analysis and after completion of the reaction, the solvent was removed under reduced pressure and the crude was treated with ice-cold water. The aqueous layer was acidified (pH~2) and extracted using ethyl acetate (3 × 10 mL). The combined organic layers were dried over Na_2SO_4 and then concentrated. The crude reaction mixture was subjected to column chromatographic purification using hexanes/ethyl acetate (9:1, v/v) as eluent to yield the corresponding product **4** in 92%.

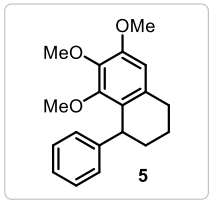


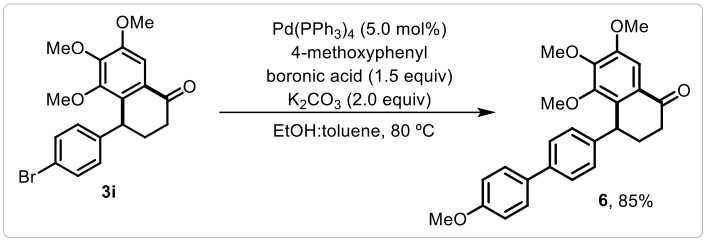
5,6,7-Trimethoxy-4-phenyl-1,2,3,4-tetrahydronaphthalen-1-ol (4): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 2H), 7.16 – 7.12 (m, 1H), 7.06 – 7.02 (m, 2H), 6.97 (s, 1H), 4.79 – 4.70 (m, 1H), 4.31 – 4.26 (m, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 3.26 (s, 3H), 2.17 – 2.07 (m, 1H), 1.96 – 1.88 (m, 2H), 1.77 – 1.71 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 152.7, 151.4, 147.6, 141.8, 135.9, 128.3, 128.1, 125.9, 125.2, 105.4, 69.6, 60.7, 60.1, 56.0, 39.3, 29.7, 28.5. **HRMS** (EI) calculated for $C_{19}H_{23}O_4$ $[M + H]^+$: 315.1596, found: 315.1590.



To a solution of **3c** (62.4 mg, 0.2 mmol) in DCM (5 mL), triflic acid (2.0 equiv.) was dropwise added in ice-cold condition under a nitrogen atmosphere. Subsequently, a solution of triethylsilane (0.3 mmol, 1.5 equiv.) is added dropwise. After 5 minutes, additional triflic acid (2.0 equiv.) is added, again followed by the addition of triethylsilane (0.3 mmol, 1.5 equiv.). When the addition was completed, the ice bath was removed and stirred at room temperature for 2 hours. The mixture was poured into a cold saturated sodium bicarbonate solution and extracted with DCM (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and then concentrated. The crude reaction mixture was subjected to column chromatographic purification using hexanes/ethyl acetate (8:2, v/v) as eluent to give the corresponding product **5** in 88% yield.

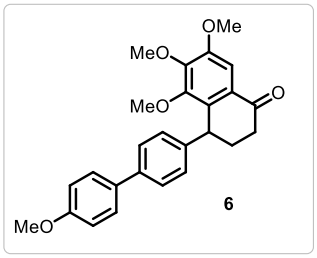
6,7,8-Trimethoxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 2H), 7.16 – 7.09 (m, 1H), 7.05 – 6.98 (m, 2H), 6.47 (s, 1H), 4.32 (dd, *J* = 5.8, 3.4 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.27 (s, 3H), 2.83 – 2.68 (m, 2H), 2.01 (dddd, *J* = 13.1, 12.1, 6.0, 3.2 Hz, 1H), 1.87 (ddtd, *J* = 13.0, 5.3, 3.0, 1.0 Hz, 1H), 1.75 – 1.58 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 152.1, 151.9, 148.4, 140.5, 133.4, 128.3, 128.0, 125.6, 125.1, 107.2, 60.7, 60.0, 56.0, 39.0, 32.1, 29.7, 18.1. **HRMS** (EI) calculated for $C_{19}H_{23}O_3$ $[M + H]^+$: 299.1647, found: 299.1651.

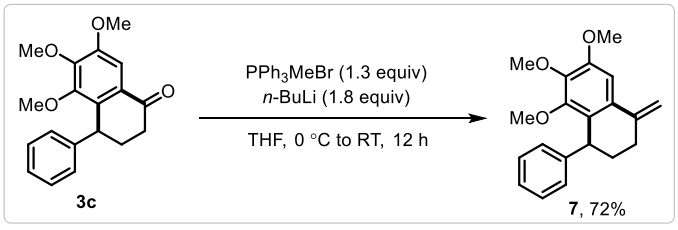




Under a nitrogen atmosphere, **3i** (0.1 mmol, 39.1 mg), 4-methoxyphenylboronic acid (0.15 mmol, 22.8 mg), Tetrakis (triphenylphosphine)palladium (0.005 mmol, 5.8 mg), and potassium carbonate (0.2 mmol, 27.6 mg) were added to a mixture solution of toluene (1 mL) and ethanol (0.3 mL) in a 10 mL Schlenk flask. After that, the reaction mixture was stirred at 80 °C for 4 h and cooled to 25 °C; plenty of ice-cold water was added to the solution and extracted with dichloromethane (3 × 10 mL). The organic layer was washed with water, dried over anhydrous MgSO4, and purified through column chromatography using hexane and ethyl acetate (90:10) to afford the desired colourless liquid product **6** in 85% yield.

5,6,7-trimethoxy-4-(4'-methoxy-[1,1'-biphenyl]-4-yl)-3,4-dihydronaphthalen-1(2*H*)-one (6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 6.8, 2.2 Hz, 3H), 7.47 – 7.44 (m, 2H), 7.11 – 7.06 (m, 2H), 6.98 – 6.93 (m, 2H), 4.66 (t, *J* = 3.9 Hz, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 3.84 (s, 3H), 3.50 (s, 3H), 2.60 – 2.48 (m, 2H), 2.35 – 2.22 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 197.8, 159.2, 152.9, 150.8, 147.8, 141.7, 139.0, 133.4, 133.1, 128.6, 128.1, 126.7, 114.3, 105.1, 60.9, 60.9, 56.2, 55.5, 37.7, 33.6, 31.0. **HRMS** (EI) calculated for $C_{26}H_{27}O_5$ $[M + H]^+$: 419.1858, found: 419.1860.

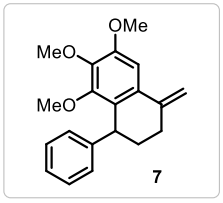




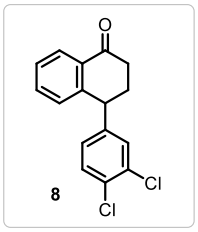
A suspension of triphenylphosphonium salt (1.3 equiv) in dry THF was added in a dried round bottom flask. The solution was cooled to 0 °C and kept under argon. Then *n*-BuLi (1.8 equiv) was added in one

portion. After stirring at 0 °C for 0.5 h the starting material **3c** (1.0 equiv) was added. The reaction mixture was gradually warmed to room temperature. After stirring for 12 h the reaction mixture was quenched by slow addition of saturated NH_4Cl. The phases were separated, and the aqueous layer was extracted twice with Et_2O. The combined organic layers were dried over Na_2SO_4 and then concentrated. The crude reaction mixture was subjected to column chromatographic purification using hexanes/ethyl acetate (9:1, v/v) as eluent to give the corresponding product **7** in 72% yield.

5,6,7-Trimethoxy-1-methylene-4-phenyl-1,2,3,4-tetrahydronaphthalene (7): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 2H), 7.17 – 7.12 (m, 1H), 7.06 – 7.02 (m, 3H), 5.46 (s, 1H), 4.97 (s, 1H), 4.46 (dd, *J* = 5.8, 3.1 Hz, 1H), 3.92 (s, 3H), 3.82 (s, 3H), 3.32 (s, 3H), 2.54 – 2.42 (m, 1H), 2.31 (dt, *J* = 14.6, 3.9 Hz, 1H), 2.13 (tdd, *J* = 13.3, 5.7, 3.5 Hz, 1H), 1.96 (dq, *J* = 12.9, 3.8 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 152.3, 151.5, 146.8, 143.2, 142.6, 131.0, 128.3, 128.1, 126.0, 125.8, 107.9, 102.4, 60.7, 60.2, 56.0, 39.3, 32.0, 27.8. **HRMS** (EI) calculated for $C_{20}H_{23}O_3$ $[M + H]^+$: 311.1647, found: 311.1650.

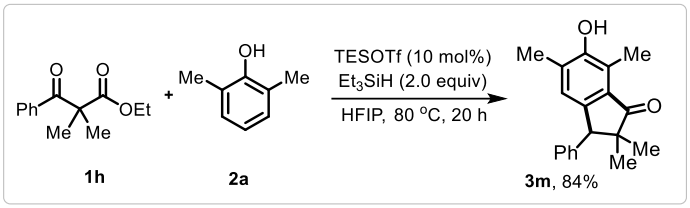


4-(3,4-Dichlorophenyl)-3,4-dihydronaphthalen-1(2*H*)-one (8)[4]: The compound **8** was prepared according to GP2, 4-(3,4-dichlorophenyl)-4-oxobutanoic acid **1af** (1.0 equiv, 0.3 mmol, 74.1 mg), benzene (3.3 equiv, 1.0 mmol, 78.1 mg), Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) and triflic acid (30.0 mol%, 7.8 µL) in HFIP (0.5 mL) and was purified by column chromatography (hexane/ethyl acetate = 95:05); white solid (62.9 mg, 72% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.47 (td, *J* = 7.4, 1.6 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.22 (d, *J* = 2.1 Hz, 1H), 6.95 (dddd, *J* = 8.2, 3.7, 1.8, 0.6 Hz, 2H), 4.27 (dd, *J* = 8.2, 4.5 Hz, 1H), 2.78 – 2.55 (m, 2H), 2.47 (ddt, *J* = 13.5, 7.9, 4.6 Hz, 1H), 2.29 – 2.17 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 197.6, 145.0, 144.1, 134.0, 132.9, 132.8, 131.1, 130.8, 130.7, 129.4, 128.1, 127.7, 127.5, 44.7, 36.7, 31.8.



8. Control Experiments

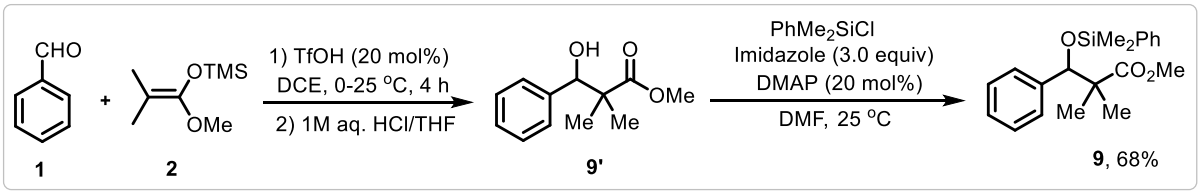
8.1 Reaction with TESOTf



To a flame dried Schlenk tube equipped with a magnetic stir bar, charged with ethyl 2,2-dimethyl-3-oxo-3-phenylpropanoate **1h** (1.0 equiv, 0.3 mmol, 66.0 mg), 2,6-dimethylphenol (1.1 equiv, 0.33 mmol, 40.3 mg) and Et_3SiH (2.0 equiv, 0.6 mmol, 96 µL) in HFIP (0.5 mL) was added triethylsilyl trifluoromethanesulfonate (TESOTf, 7.9 µL, 10 mol%) at room temperature for 0.5 h. After 0.5 h, the reaction Schlenk tube kept at 80 °C and stirred for another 20 h. After completion of the reaction, the

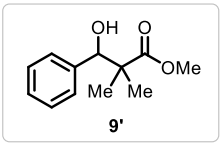
solvent was evaporated in vacuo, and the residue was purified by column chromatography using a gradient of hexane−ethyl acetate to afford the corresponding indanone products **3m** 84% yield.

Synthesis of methyl 3-((dimethyl(phenyl)silyl)oxy)-2,2-dimethyl-3-phenylpropanoate (9):

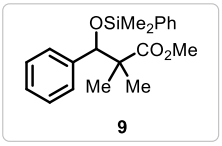


Benzaldehyde (**1**, 106 mg, 1.0 equiv, 1mmol), **2** (1.2 ml, 2.5 mmol, 2.5 equiv.) were taken in DCE at 0 °C and stirred for 4 h. The reaction was monitored through TLC. The reaction was then quenched by slow addition of 1M aq. HCl/THF (1:1, 2 mL). the reaction mixture was neutralized by saturated aq. solution of $NaHCO_3$ (2 mL) The aqueous phase was extracted three times with CH_2Cl_2. The combined organic phase was dried over Na_2SO_4, and solvent was removed in vacuo. Purification by column chromatography on silica gel (10% EtOAc / Hexane) afforded the product (9′) in 90% yield. In nitrogen atmosphere, **10′** (104 mg, 1.0 equiv., 0.5 mmol), Imidazole (1.5 mmol, 3 equiv.) and 4-(dimethylamino) pyridine (DMAP, 20 mol%) were taken in DMF (2 mL) and dimethylphenylsilyl chloride (0.6 mmol, 1.2 equiv.) was added dropwise to it and stirred overnight at 25 °C. Titled Product (**9**) was isolated with 68% yield through column chromatography.

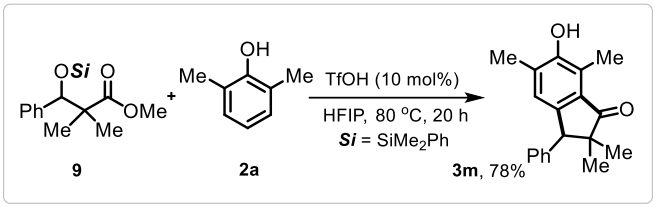
Methyl 3-hydroxy-2,2-dimethyl-3-phenylpropanoate (9')[3]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 4.8 Hz, 5H), 5.02 (s, 1H), 3.84 (s, 3H), 3.19 (s, 1H), 1.27 (s, 3H), 1.23 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 178.2, 140.1, 127.8, 127.8, 127.7, 78.6, 52.1, 47.8, 23.0, 19.1.



Methyl 3-((dimethyl(phenyl)silyl)oxy)-2,2-dimethyl-3-phenylpropanoate (9)[3]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.9 Hz, 2H), 7.43 (dt, *J* = 13.7, 6.8 Hz, 4H), 7.36 (d, *J* = 4.1 Hz, 2H), 7.35 – 7.32 (m, 2H), 5.12 (s, 1H), 3.65 (s, 3H), 1.26 (s, 3H), 1.09 (s, 3H), 0.32 (s, 3H), 0.25 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 177.4, 140.5, 138.0, 133.6, 129.6, 128.1, 127.7, 127.6, 127.5, 79.7, 51.8, 49.2, 22.1, 19.1, -1.5.



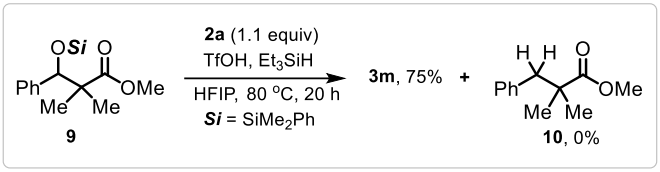
8.2. Reaction with intermediate



To a flame dried Schlenk tube equipped with a magnetic stir bar, charged with methyl 3-((dimethyl(phenyl)silyl)oxy)-2,2-dimethyl-3-phenylpropanoate **9** (1.0 equiv, 0.2 mmol, 68.5 mg and

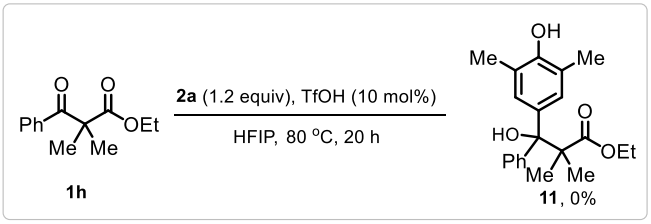
2,6-dimethylphenol (1.1 equiv, 0.33 mmol, 26.8 mg) in HFIP (0.5 mL) was added triflic acid (TfOH, 1.9 µL, 10 mol%) at room temperature. Then the reaction was kept at 80 °C and stirred for 20 h. After completion of the reaction, the solvent was evaporated in vacuo, and the residue was purified by column chromatography using a gradient of hexane−ethyl acetate to afford the product **3m** in 78% yield.

8.3 Competitive experiment



To a flame dried Schlenk tube equipped with a magnetic stir bar, charged with methyl 3-((dimethyl(phenyl)silyl)oxy)-2,2-dimethyl-3-phenylpropanoate **9** (1.0 equiv, 0.2 mmol, 68.5 mg, *p*-cresol (1.1 equiv, 0.22 mmol, 26.8 mg), Et_3SiH (1.1 equiv, 0.22 mmol, 35.1 µL) in HFIP (0.5 mL) was added triflic acid (TfOH, 1.9 µL, 10 mol%) at room temperature. Then the reaction was kept at 80 °C and stirred for 20 h. After completion of the reaction, the solvent was evaporated in vacuo, and the residue was purified by column chromatography using a gradient of hexane−ethyl acetate to afford the **3m** in 75% yield and a trace amount of reduced product ethyl 3-phenylpropanoate **10**.

8.4. Reaction without silane



To a flame-dried Schlenk tube equipped with a magnetic stir bar, charged with ethyl 2,2-dimethyl-3-oxo-3-phenylpropanoate **1h** (1.0 equiv, 0.3 mmol, 66.0 mg) and 2,6-dimethylphenol (1.1 equiv, 0.33 mmol, 40.3 mg) in HFIP (0.5 mL) was added triflic acid (TfOH, 2.6 µL, 10 mol%) at room temperature. Then the reaction was kept at 80 °C and stirred for 20 h. After the reaction time, no product formation was observed, which was confirmed by a ^{1}H NMR analysis.

9. ^{1}H and ^{13}C NMR study

9.1. ^{1}H NMR study

Experimental procedure: In a NMR tube, ethyl 2,2-dimethyl-3-oxo-3-phenylpropanoate (**1h**) (0.2 mmol., 44.1 mg) was added in 0.4 ml $CDCl_3$ and **NMR -1** was recorded. (δ of the carbonyl carbon of ketone = 197.9 ppm and δ of carbonyl carbon of ester 175.1 ppm).

In 2nd NMR tube HFIP (0.3 mmol, 31.5 µL) was added in 0.4 ml of $CDCl_3$ was added and **NMR 2** was recorded.

In 3rd NMR tube having ethyl 2,2-dimethyl-3-oxo-3-phenylpropanoate (**1h**) (0.2 mmol., 44.1 mg), HFIP (0.5 mmol, 53 µL) and 0.4 ml of $CDCl_3$ was added and **NMR 3** was recorded.

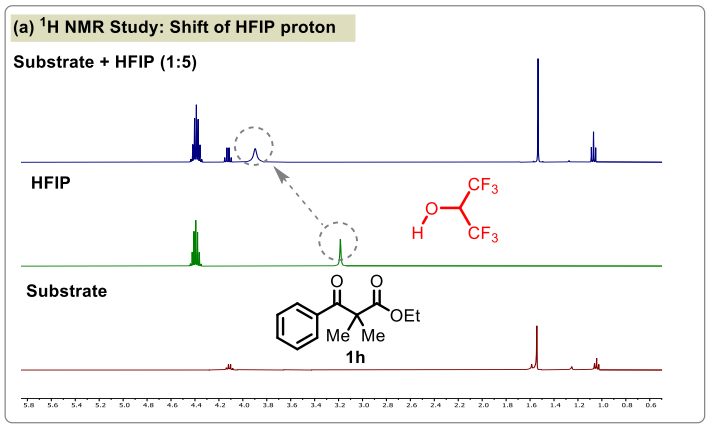


Figure S-01: ^{1}H NMR study for the shift of HFIP proton.

9.2. ^{13}C NMR study for the effect of different solvent

Experimental procedure: In an NMR tube, ethyl 2,2-dimethyl-3-oxo-3-phenylpropanoate (**1h**) (0.2 mmol., 44.1 mg) was added in 0.4 ml $CDCl_3$ and **NMR -1** was recorded. (δ of the carbonyl carbon of ketone = 197.9 ppm and δ of carbonyl carbon of ester 175.1 ppm)

In 2nd NMR tube having ethyl 2,2-dimethyl-3-oxo-3-phenylpropanoate (**1h**) (0.2 mmol., 44.1 mg), 1,2-dichloroethane (1.0 mmol, 98.9 mg), 0.4 ml of $CDCl_3$ was added and **NMR 2** was recorded. (δ of the carbonyl carbon of ketone 197.9 ppm and δ of carbonyl carbon of ester 175.1 ppm)

In 3rd NMR tube having ethyl 2,2-dimethyl-3-oxo-3-phenylpropanoate (**1h**) (0.2 mmol., 44.1 mg), Trifluoro toluene (1.0 mmol, 146.0 mg), 0.4 ml of $CDCl_3$ was added and **NMR 3** was recorded. (δ of the carbonyl carbon of ketone 197.9 ppm and δ of carbonyl carbon of ester 175.1 ppm)

In 4th NMR tube having ethyl 2,2-dimethyl-3-oxo-3-phenylpropanoate (**1h**) (0.2 mmol., 44.1 mg), 2,2,2-trifluoroethanol (TFE) (1.0 mmol, 100.0 mg), 0.4 ml of $CDCl_3$ was added and **NMR 4** was recorded. (δ of carbonyl carbon of ketone 199.1 ppm and δ of carbonyl carbon of ester 175.6 ppm)

In 5 th NMR tube having ethyl 2,2-dimethyl-3-oxo-3-phenylpropanoate (**1h**) (0.2 mmol., 44.1 mg), 1,1,1,3,3,3-Hexafluoroisopropanol. (1.0 mmol, 168.0 mg), 0.4 ml of $CDCl_3$ was added and **NMR 5** was recorded. (δ of carbonyl carbon of ketone 200.0 ppm and δ of carbonyl carbon of ester 176.1 ppm).

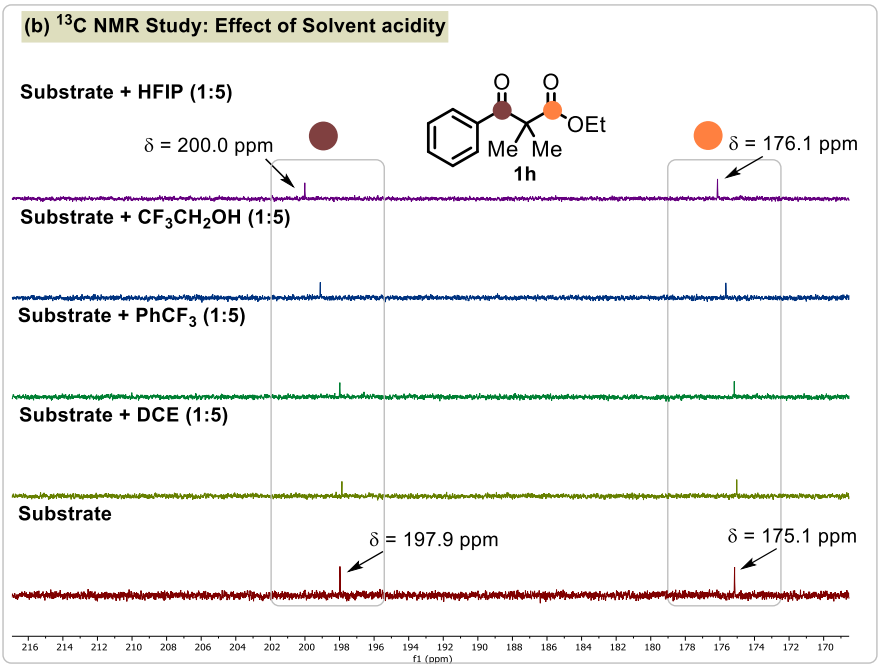


Figure S-02: ^{13}C NMR study for the effect of different solvents.

9.2. ^{13}C NMR study for the effect of HFIP concentration

Experimental procedure: In an NMR tube, ethyl 2,2-dimethyl-3-oxo-3-phenylpropanoate (**1h**) (0.2 mmol., 44.1 mg) was added in 0.4 ml $CDCl_3$ and **NMR -1** was recorded. (δ of the carbonyl carbon of ketone = 197.9 ppm and δ of carbonyl carbon of ester 175.1 ppm).

In 2nd NMR tube having ethyl 2,2-dimethyl-3-oxo-3-phenylpropanoate (**1h**) (0.2 mmol., 44.1 mg), triethylsilyl trifluoromethanesulfonate (0.04 mmol, 9µL) was added in 0.4 ml $CDCl_3$ and **NMR 2** was recorded. (δ of the carbonyl carbon of ketone = 198.3 ppm and δ of carbonyl carbon of ester 175.3 ppm).

In 3rd NMR tube having ethyl 2,2-dimethyl-3-oxo-3-phenylpropanoate (**1h**) (0.2 mmol., 44.1 mg), triethylsilyl trifluoromethanesulfonate (0.04 mmol, 9µL), Hexafluoroisopropanol. (0.2 mmol, 33.6 mg) 0.4 ml of $CDCl_3$ was added and **NMR 3** was recorded. (δ of carbonyl carbon of ketone 199.3 ppm and δ of carbonyl carbon of ester 175.7 ppm).

In the 4th NMR tube having ethyl 2,2-dimethyl-3-oxo-3-phenylpropanoate (**1h**) (0.2 mmol., 44.1 mg), triethylsilyl trifluoromethanesulfonate (0.04 mmol, 9µL), Hexafluoroisopropanol. (0.6 mmol, 100.83 mg) 0.4 ml of $CDCl_3$ was added and **NMR 4** was recorded. (δ of carbonyl carbon of ketone 199.8 ppm and δ of carbonyl carbon of ester 175.9 ppm).

In 5th NMR tube having ethyl 2,2-dimethyl-3-oxo-3-phenylpropanoate (**1h**) (0.2 mmol., 44.1 mg), triethylsilyl trifluoromethanesulfonate (0.04 mmol, 9µL), Hexafluoroisopropanol. (1.0 mmol, 168.0 mg) 0.4 ml of $CDCl_3$ was added and **NMR 5** was recorded. (δ of carbonyl carbon of ketone 200.7 ppm and δ of carbonyl carbon of ester 176.4 ppm).

In the 6th NMR tube having ethyl 2,2-dimethyl-3-oxo-3-phenylpropanoate (**1h**) (0.2 mmol., 44.1 mg), triethylsilyl trifluoromethanesulfonate (0.04 mmol, 9µL), Hexafluoroisopropanol. (3.0 mmol, 336.1mg) 0.4 ml of $CDCl_3$ was added and **NMR 6** was recorded. (δ of the carbonyl carbon of ketone 202.6 ppm and δ of carbonyl carbon of ester 177.3 ppm).

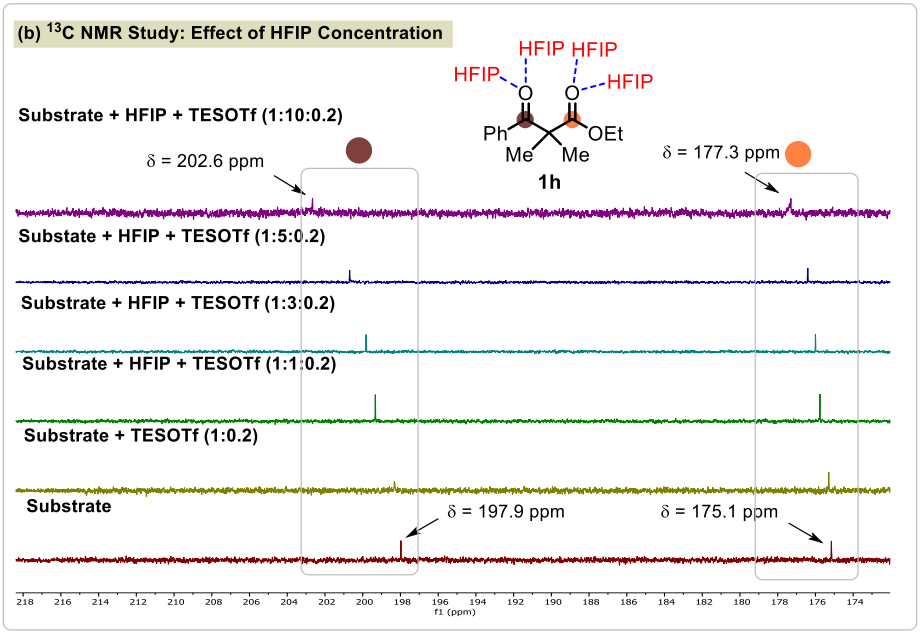


Figure S-03: ^{13}C NMR study for the effect of HFIP concentration.

The crucial role of HFIP was justified by the H-bonding interaction between ethyl 2,2-dimethyl-3-oxo-3-phenylpropanoate (**1h**) and the OH group of HFIP. Such a hypothesis was supported through a series of NMR titration studies. A clear downfield shift of the HFIP O−H proton was observed when mixed with the substrate in a 1:5 ratio (Figure S01). Further, the ^{13}C NMR spectrum was recorded with ethyl 2,2-dimethyl-3-oxo-3-phenylpropanoate (**1h**) in various solvents. Clear downfield shifts were observed (^{13}C NMR spectrum) in the carbonyl peaks of both the ketone (from 197.9 ppm to 200.0 ppm) and the ester (from 175.1 ppm to 176.1 ppm), indicating H-bond interactions between the carbonyl groups and HFIP O−H proton (Figure S02). These shifts highlighted the activation of *β*-keto ester **1h** through hydrogen bonding interactions with HFIP which is crucial for the desired product formation. Upon gradually varying the substrate vs. HFIP ratio, a significant shift of the carbonyl peaks of the ketone (from 197.9 ppm to 202.6 ppm) and the ester (from 175.1 ppm to 177.3 ppm) was noticed in the ^{13}C NMR experiments (Figure S03). This experimental finding further clarified our hypothesis of hydrogen bonding interactions between the carbonyl groups and HFIP O−H proton.

10. Reference

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(2) K. Wadhwa, C. Yang, P. R. West, K. C. Deming, S. R. Chemburkar and R. E. Reddy, *Synth. Commun.*, 2008, **38**, 4434; (b) L. Long, J. Wang, L. Gu, S. Yang, L. Qiao, G. Luo and Z. Chen, *J. Org. Chem*., 2021, **86**, 12084.

(3) P. Sharma, N. Taneja, S. Singh, and C. K. Hazra, *Chem. Eur. J*., 2023, **29**, e202202956.

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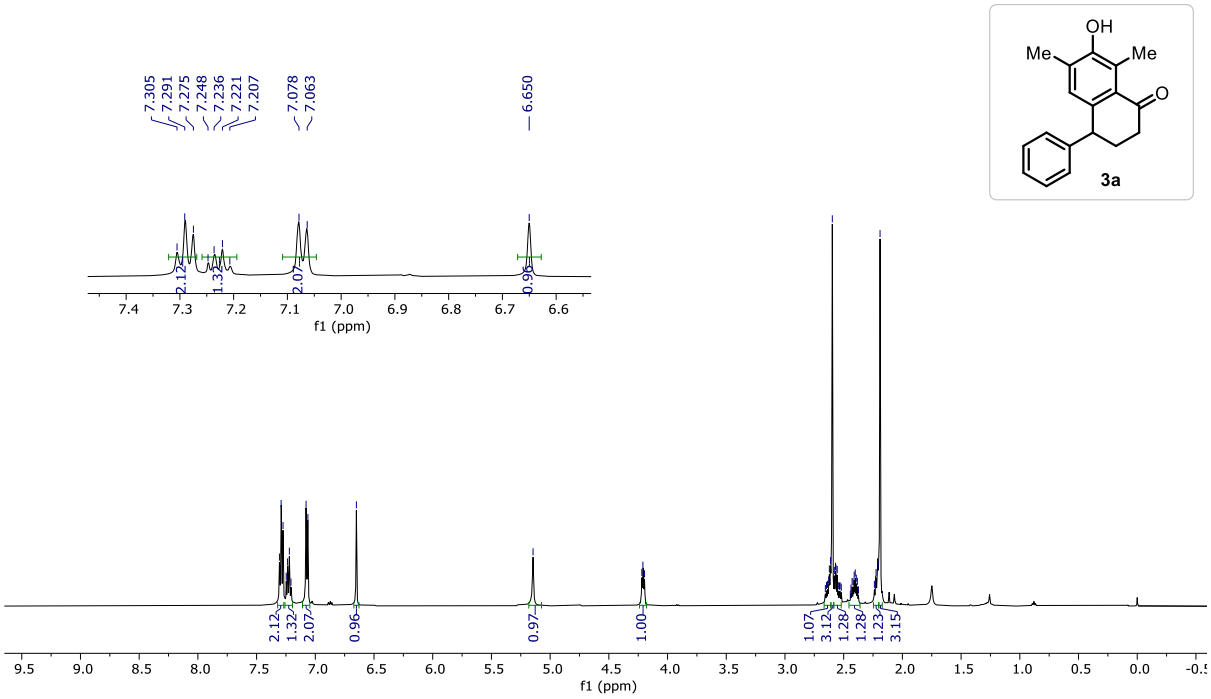
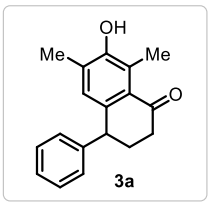
11. Copies of ^{1}H and ^{13}C Spectra of Products

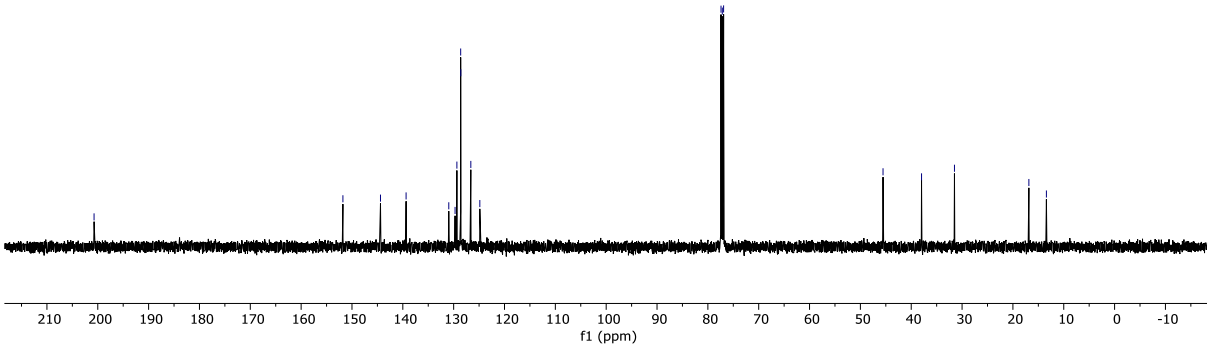
7-Hydroxy-6,8-dimethyl-4-phenyl-3,4-dihydronaphthalen-1(2*H*)-one (3a)

^{1}H NMR (500 MHz, $CDCl_3$)



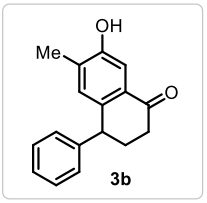
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

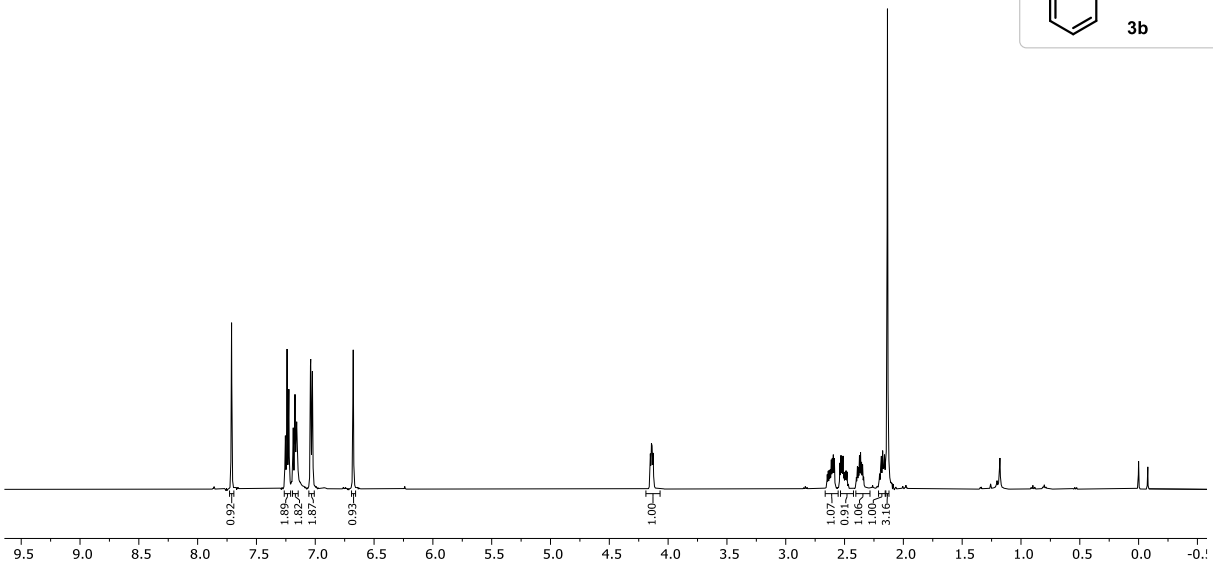




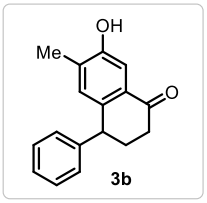
7-Hydroxy-6-methyl-4-phenyl-3,4-dihydronaphthalen-1(2*H*)-one (3b)

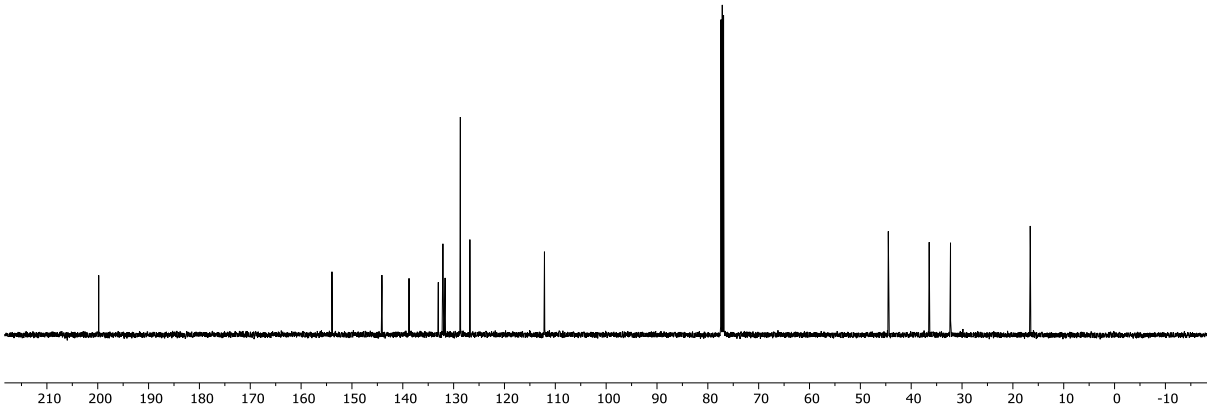
^{1}H NMR (500 MHz, $CDCl_3$)





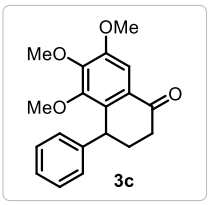
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



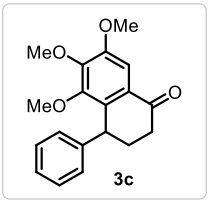


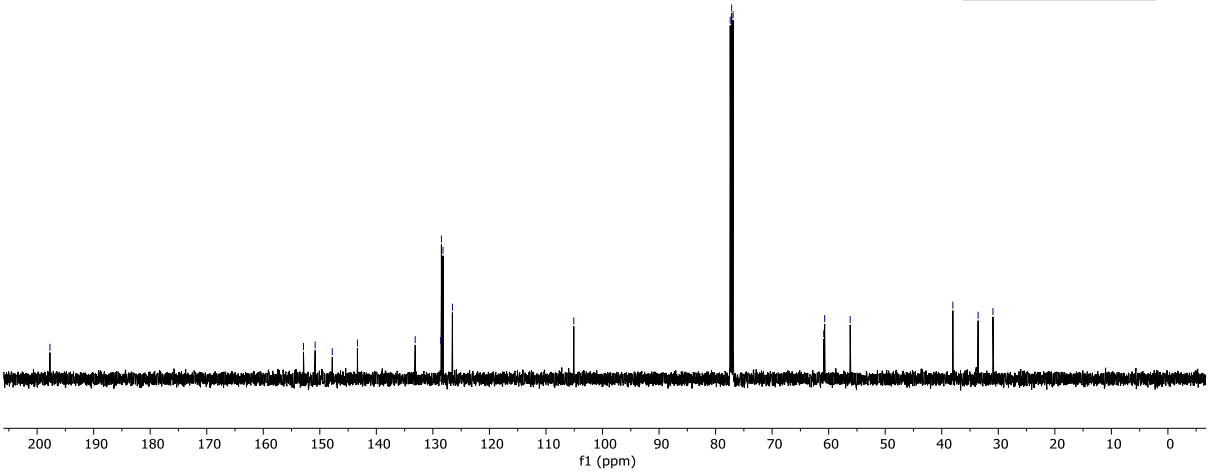
5,6,7-Trimethoxy-4-phenyl-3,4-dihydronaphthalen-1(2*H*)-one (3c)

^{1}H NMR (500 MHz, $CDCl_3$)



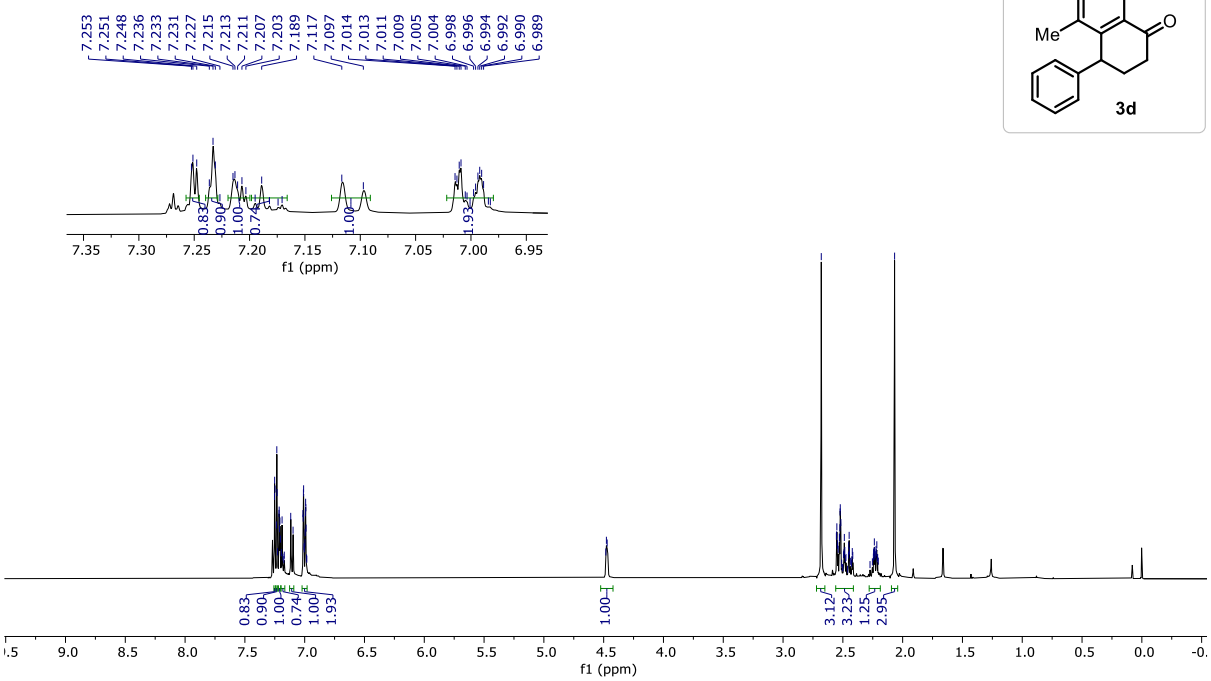
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



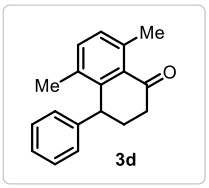


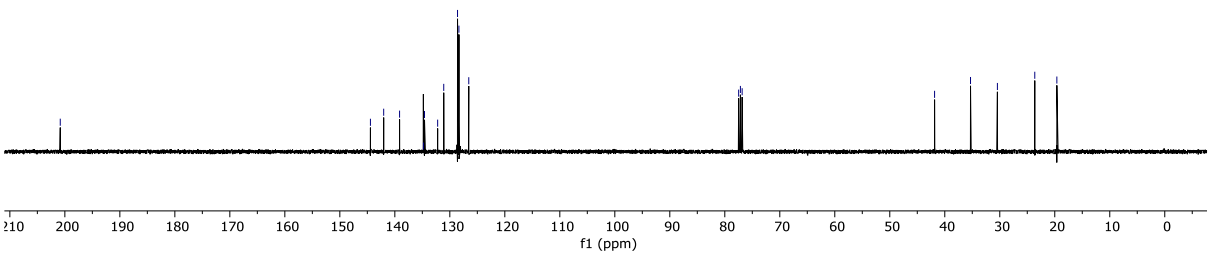
5,8-Dimethyl-4-phenyl-3,4-dihydronaphthalen-1(2*H*)-one (3d)

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



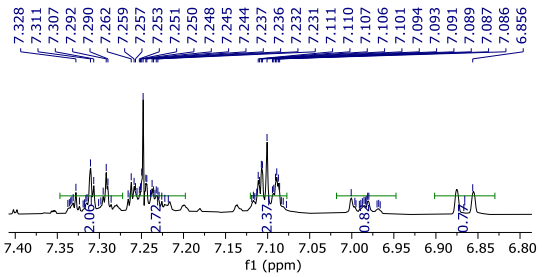
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

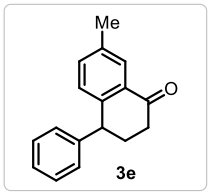


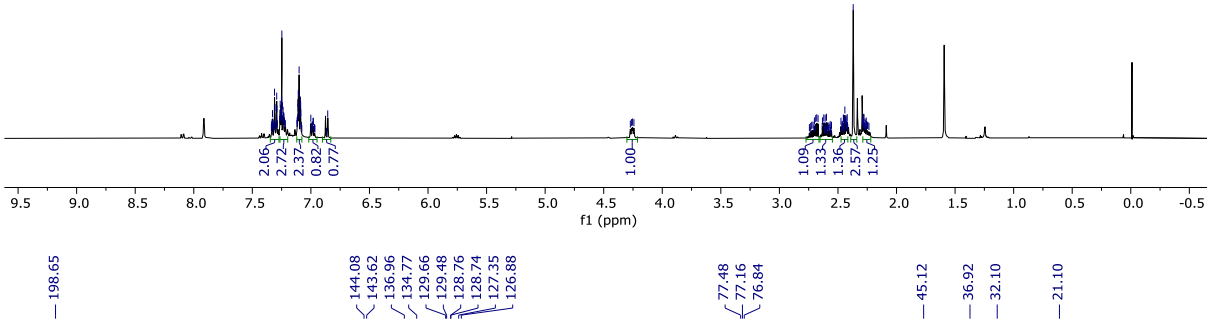


7-Methyl-4-phenyl-3,4-dihydronaphthalen-1(2*H*)-one (3e)

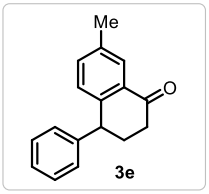
^{1}H NMR (400 MHz, $CDCl_3$)

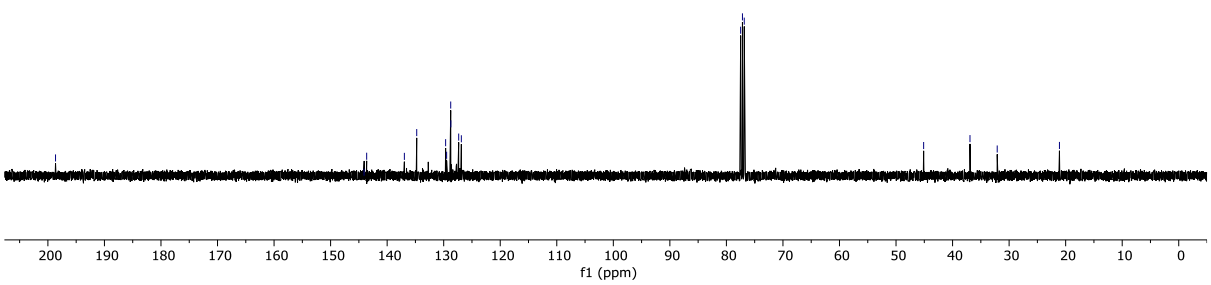






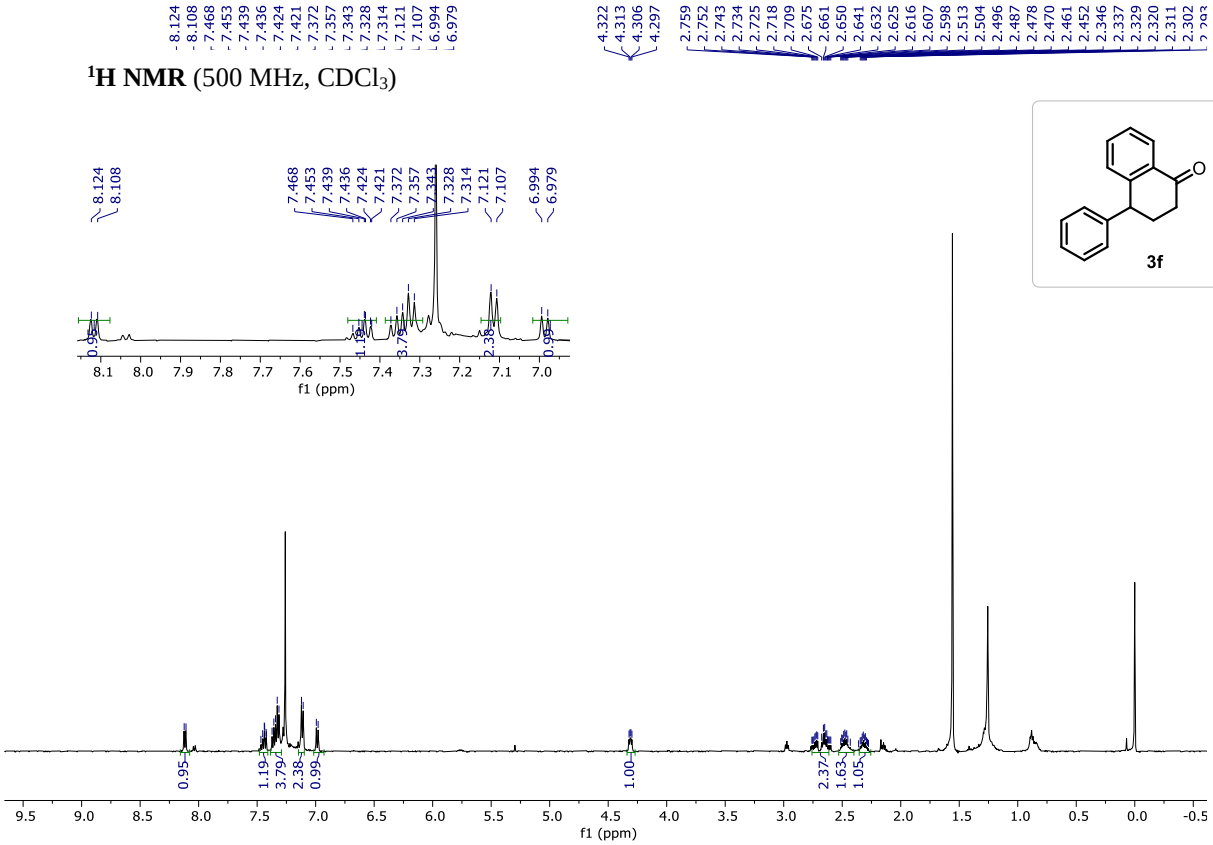
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



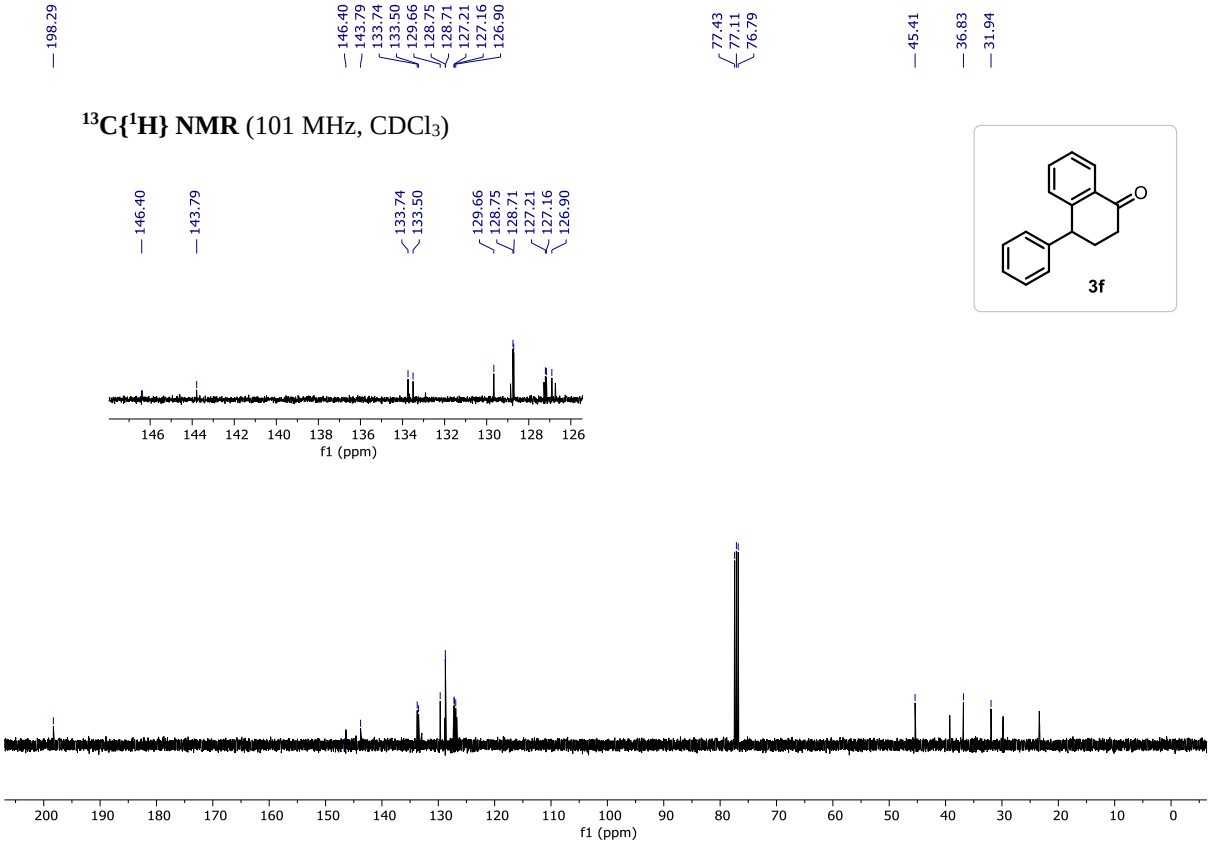


4-Phenyl-3,4-dihydronaphthalen-1(2*H*)-one (3f)

^{1}H NMR (500 MHz, $CDCl_3$)

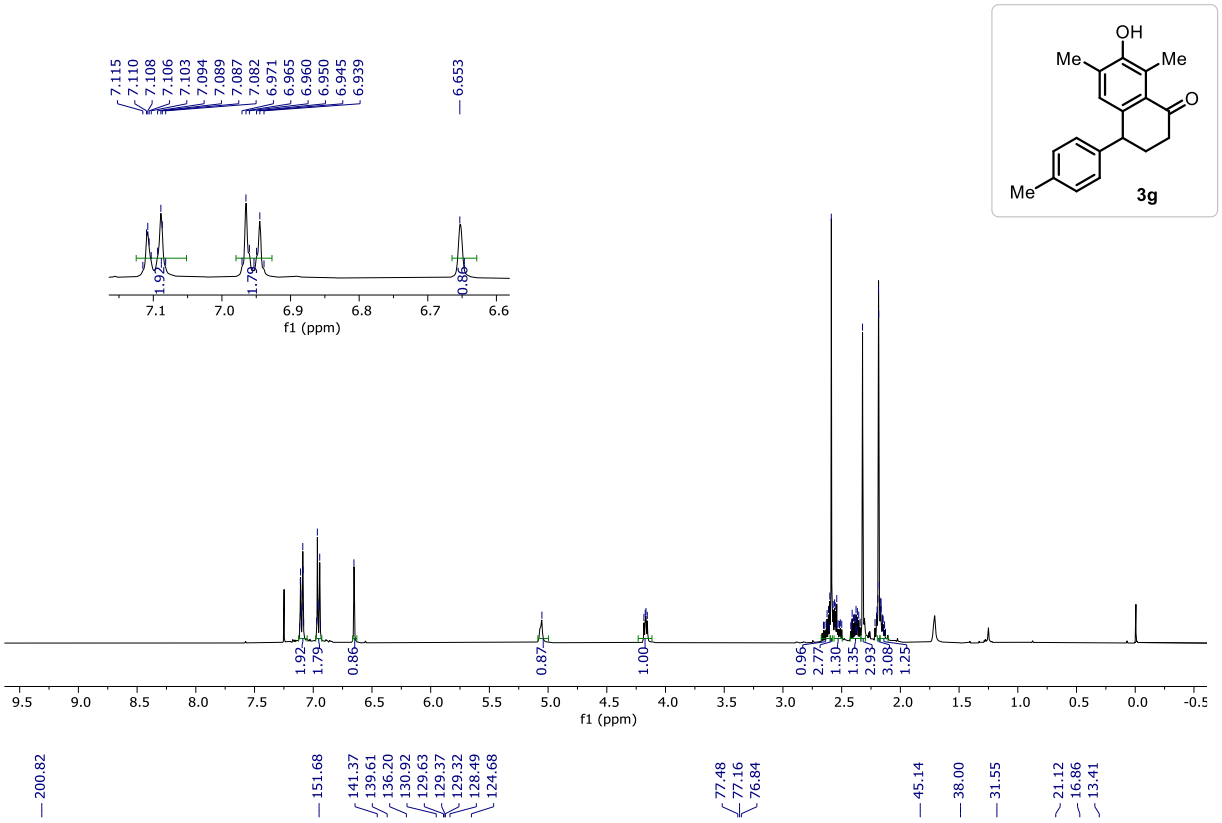


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

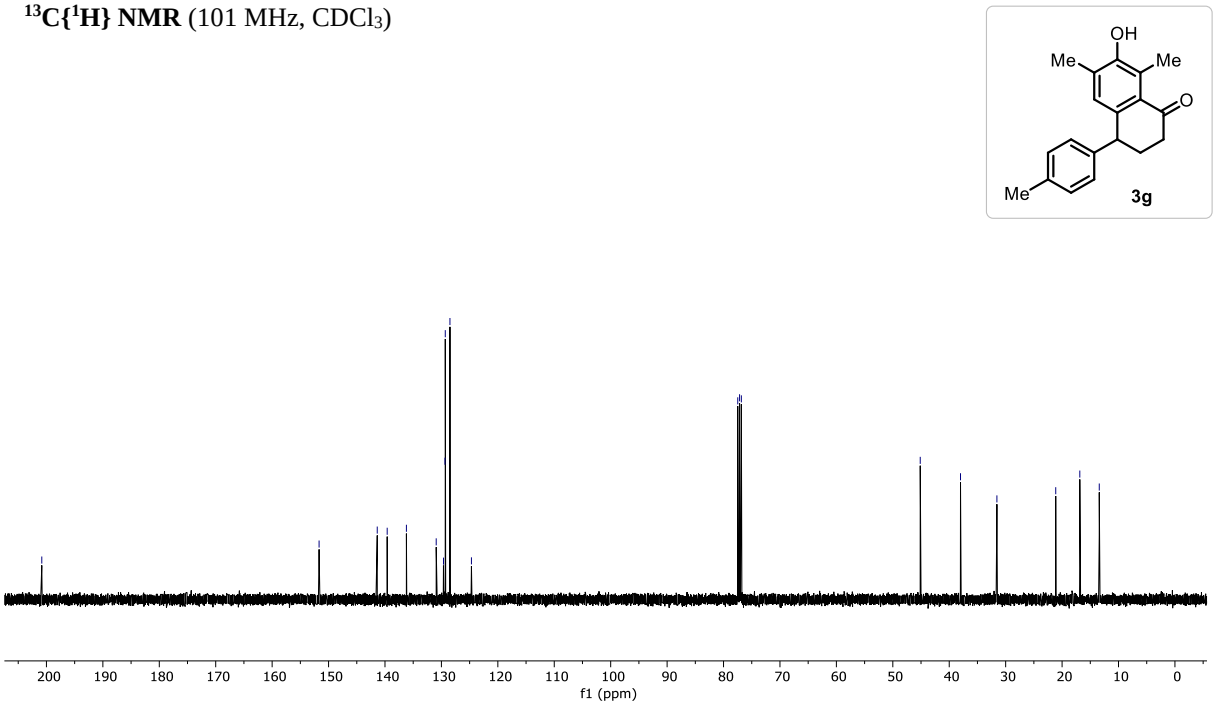


7-Hydroxy-6,8-dimethyl-4-(*p*-tolyl)-3,4-dihydronaphthalen-1(2*H*)-one (3g)

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

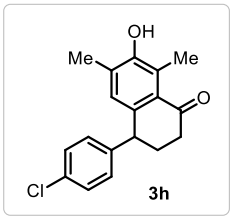


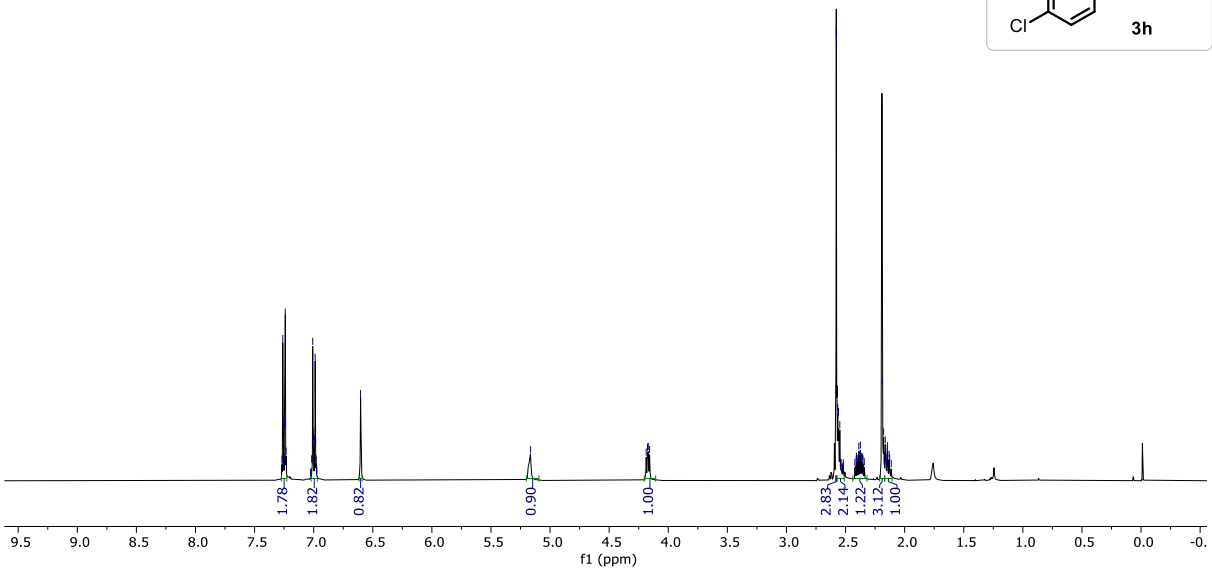
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



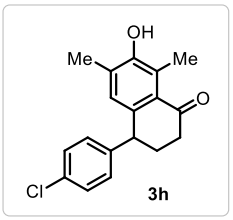
4-(4-Chlorophenyl)-7-hydroxy-6,8-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one (3h)

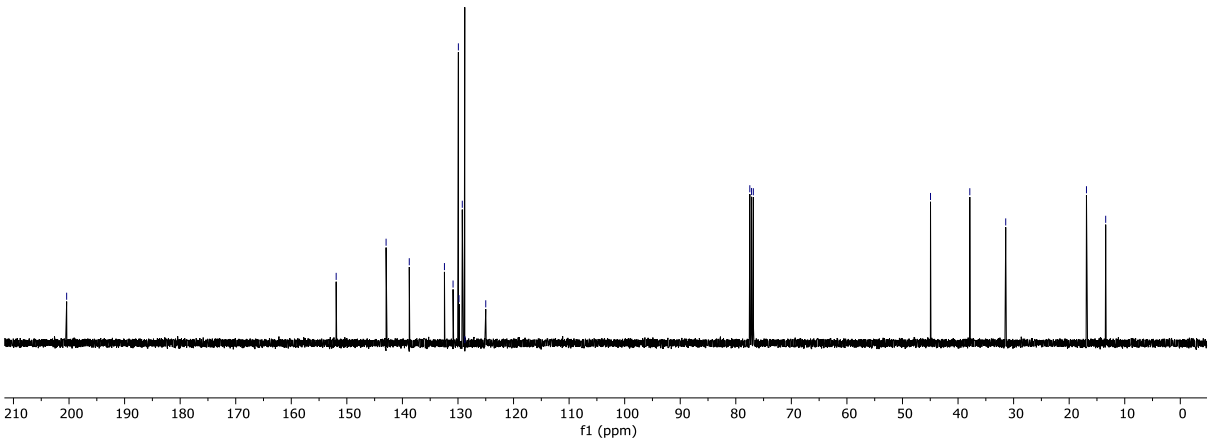
^{1}H NMR (400 MHz, $CDCl_3$)





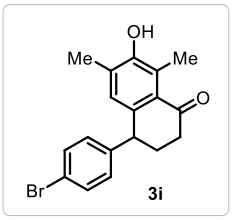
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

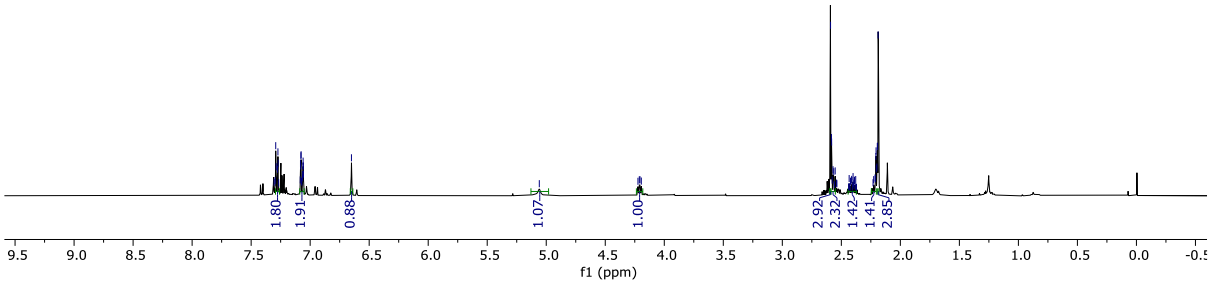




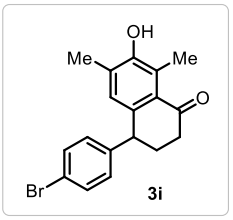
4-(4-Bromophenyl)-7-hydroxy-6,8-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one (3i)

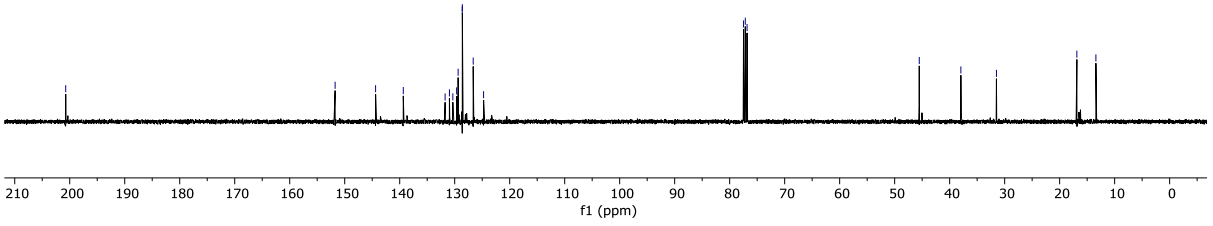
^{1}H NMR (400 MHz, $CDCl_3$)





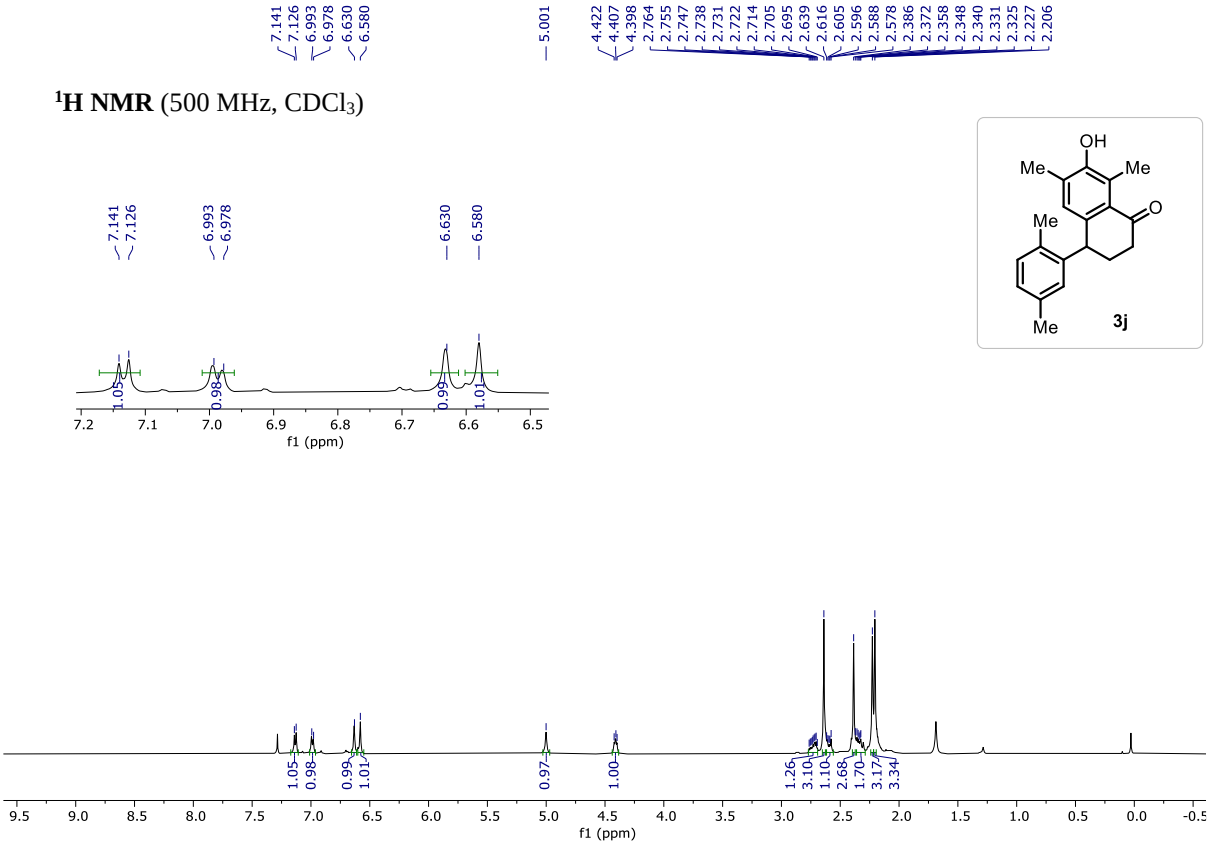
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



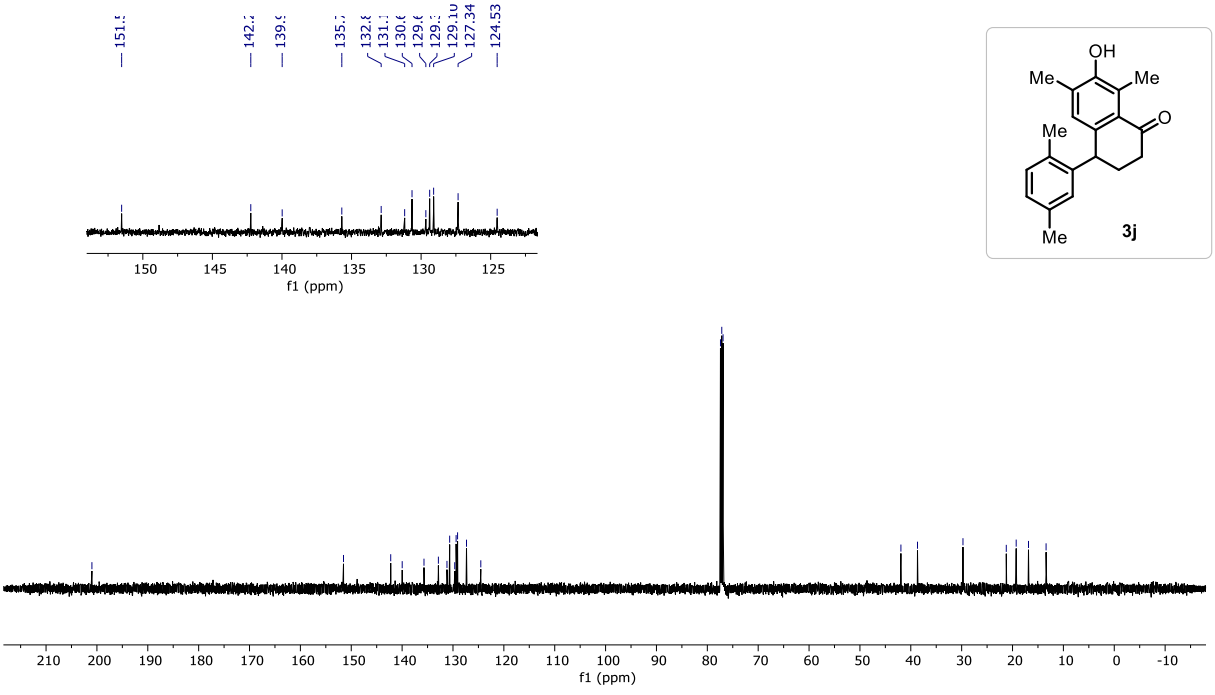


4-(2,5-Dimethylphenyl)-7-hydroxy-6,8-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one (3j)

^{1}H NMR (500 MHz, $CDCl_3$)

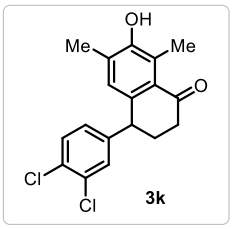


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

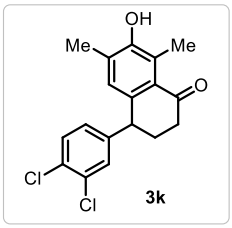


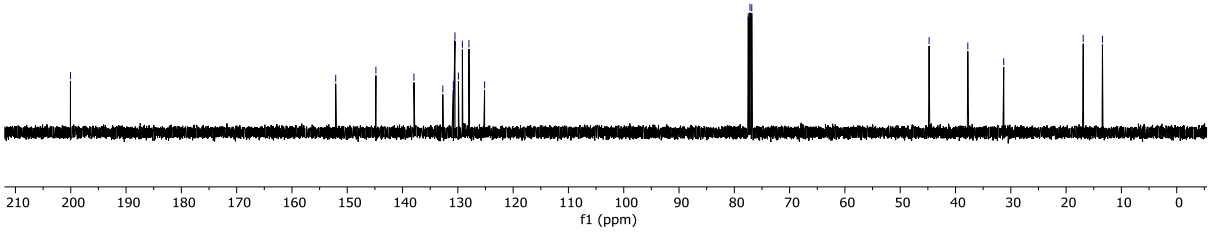
4-(3,4-Dichlorophenyl)-7-hydroxy-6,8-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one (3k)

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



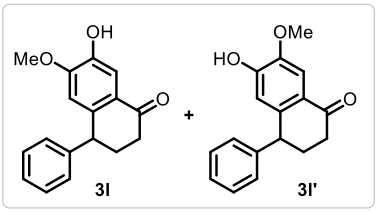
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

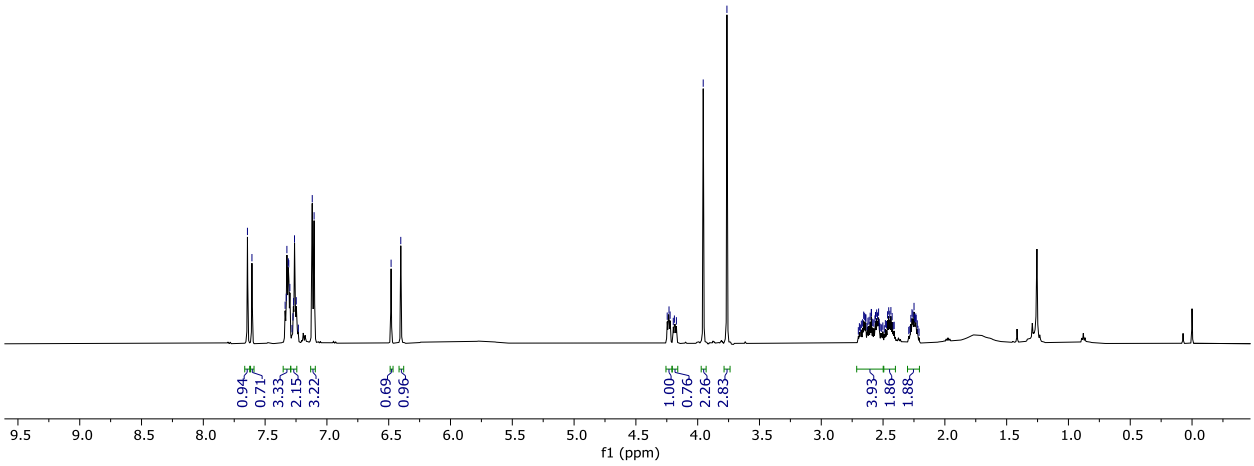




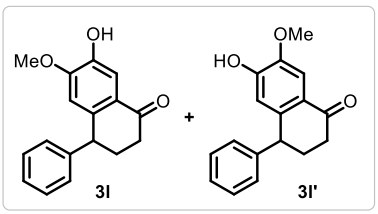
7-Hydroxy-6-methoxy-4-phenyl-3,4-dihydronaphthalen-1(2H)-one (3l)

^{1}H NMR (500 MHz, $CDCl_3$)



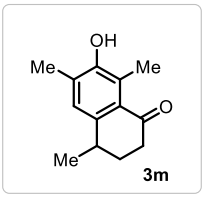


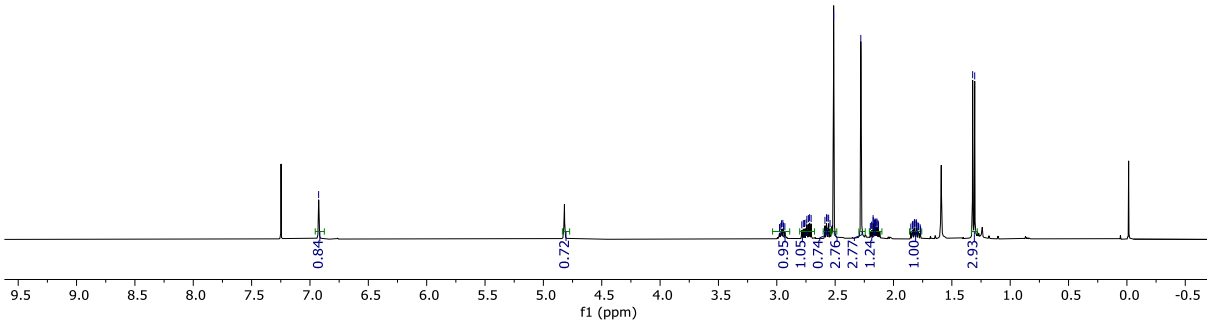
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



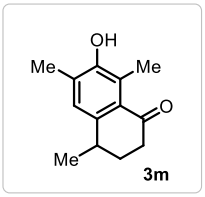
7-Hydroxy-4,6,8-trimethyl-3,4-dihydronaphthalen-1(2*H*)-one (3m)

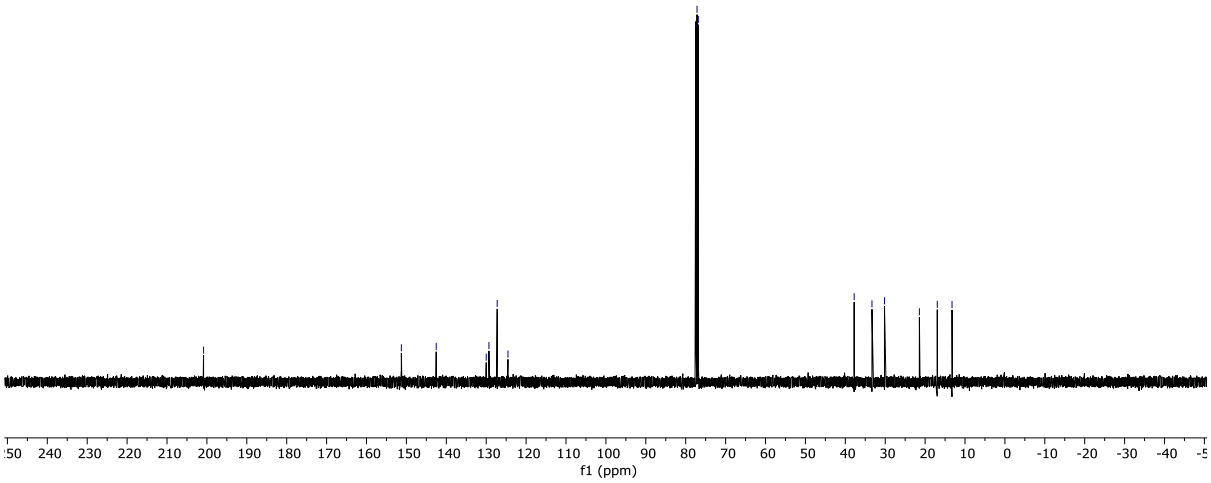
^{1}H NMR (400 MHz, $CDCl_3$)





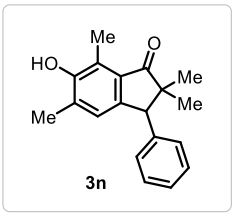
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

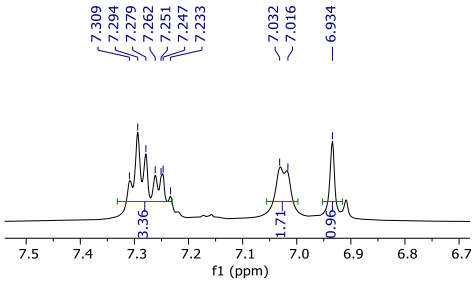


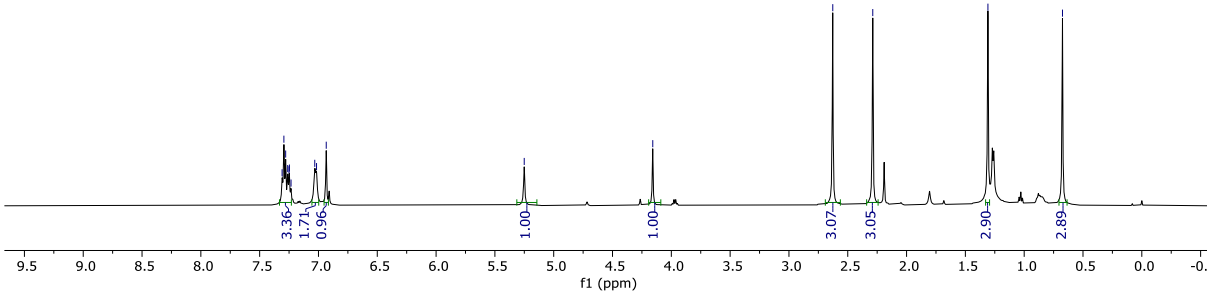


6-Hydroxy-2,2,5,7-tetramethyl-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3n)

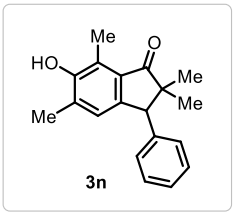
^{1}H NMR (500 MHz, $CDCl_3$)

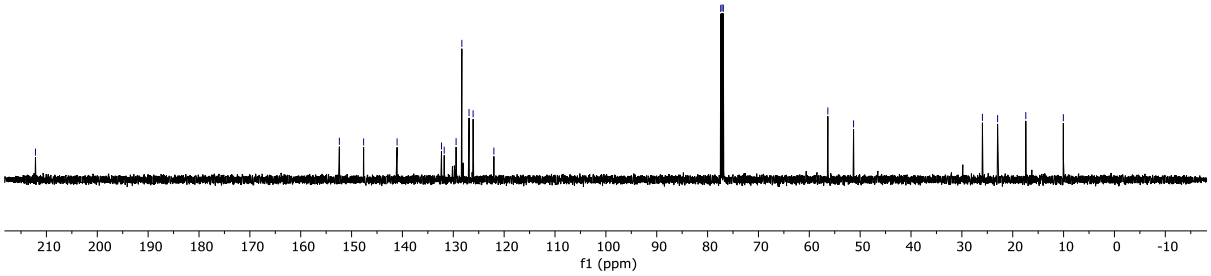






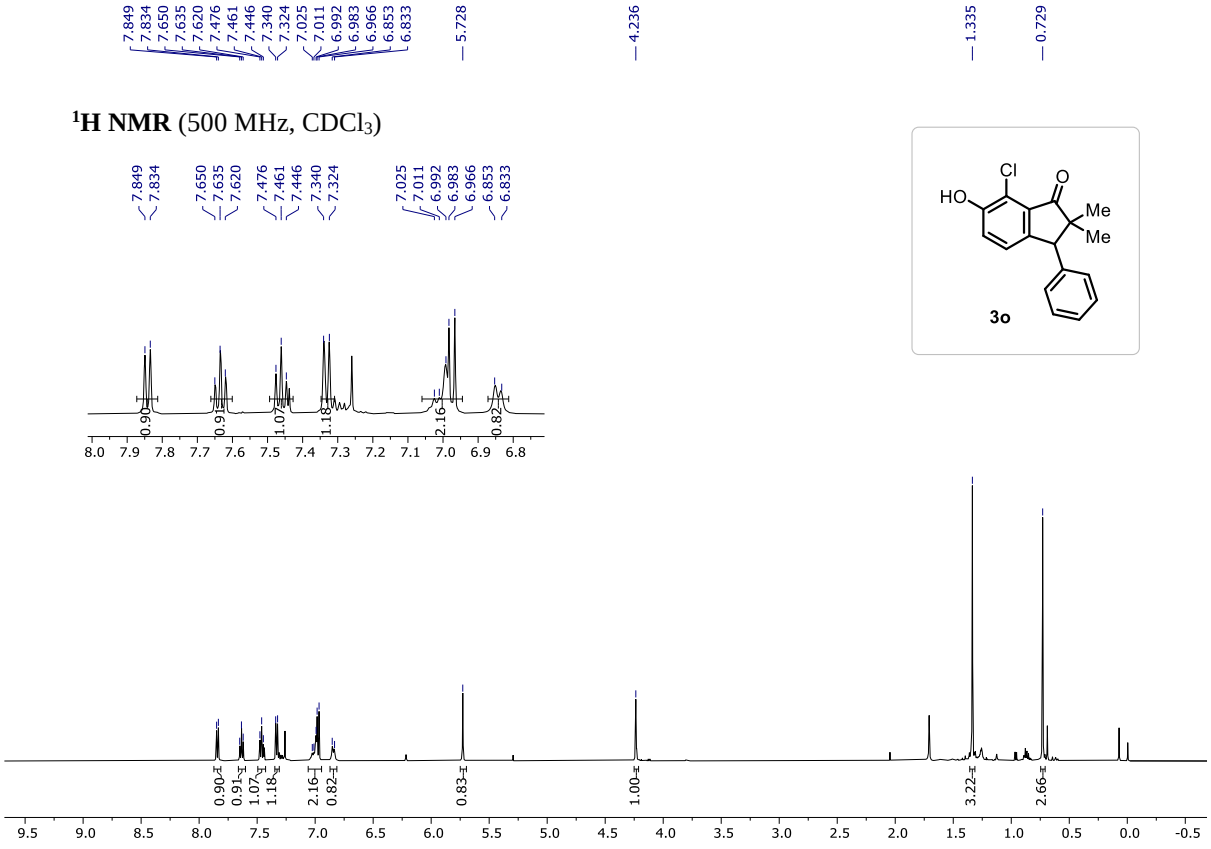
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



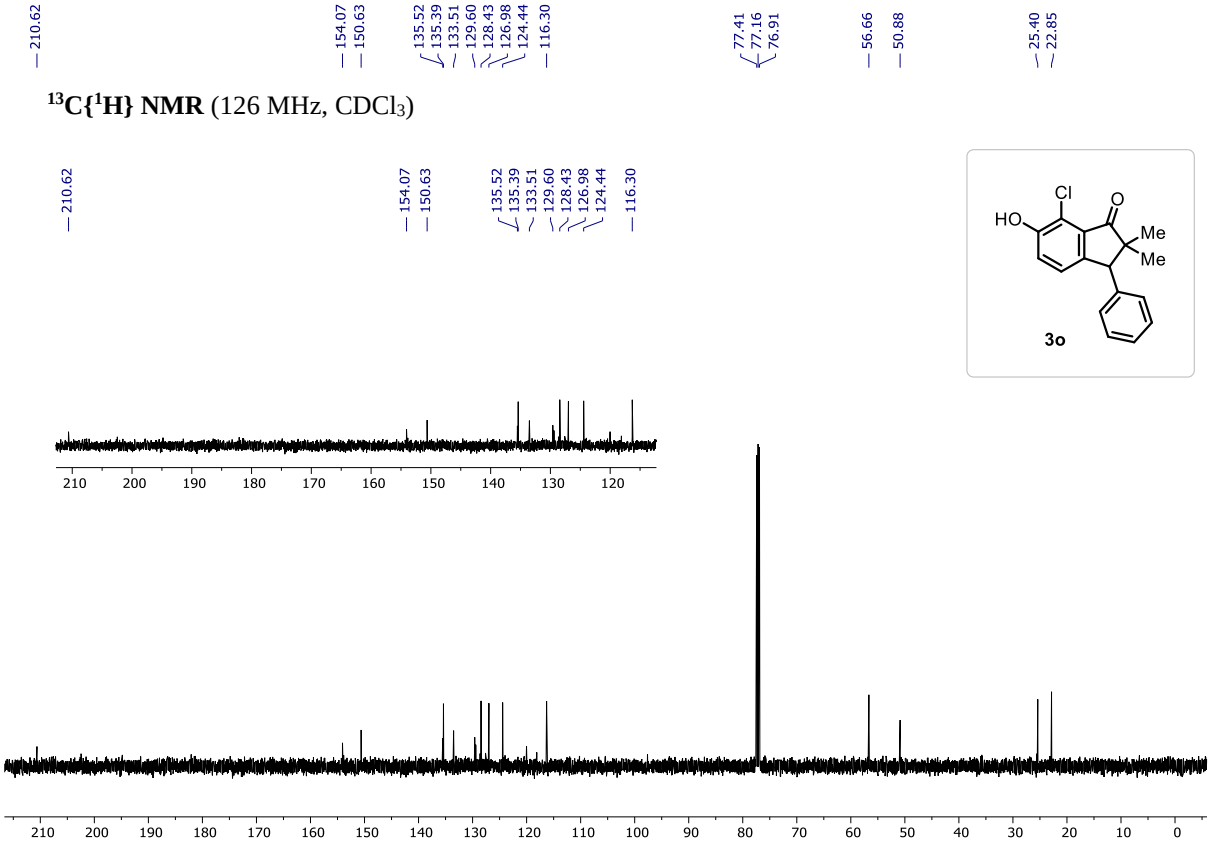


7-Chloro-6-hydroxy-2,2-dimethyl-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3o)

^{1}H NMR (500 MHz, $CDCl_3$)

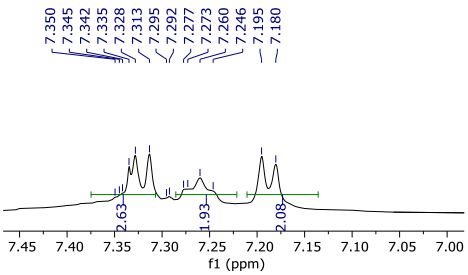


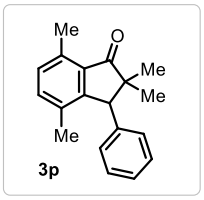
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

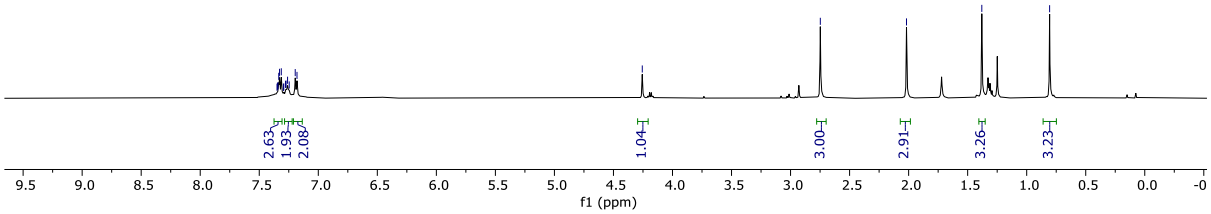


2,2,4,7-Tetramethyl-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3p)

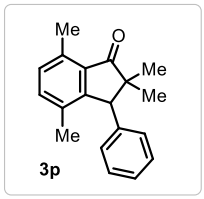
^{1}H NMR (500 MHz, $CDCl_3$)

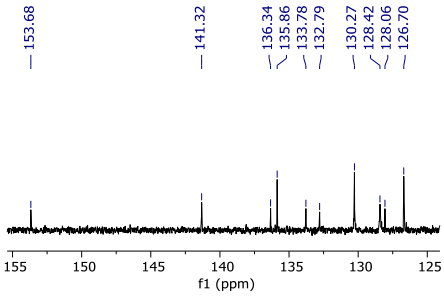


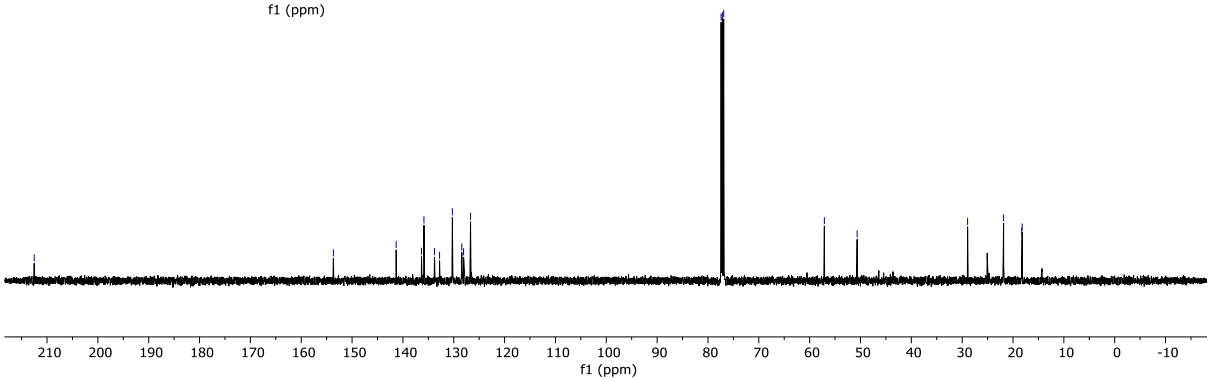




^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

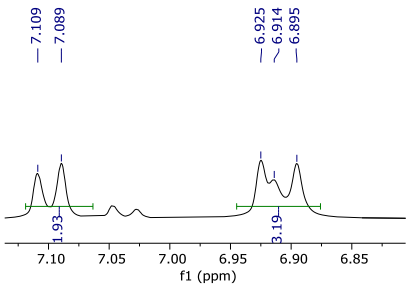


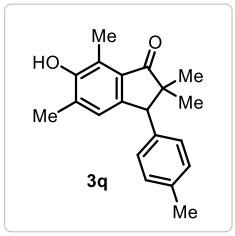


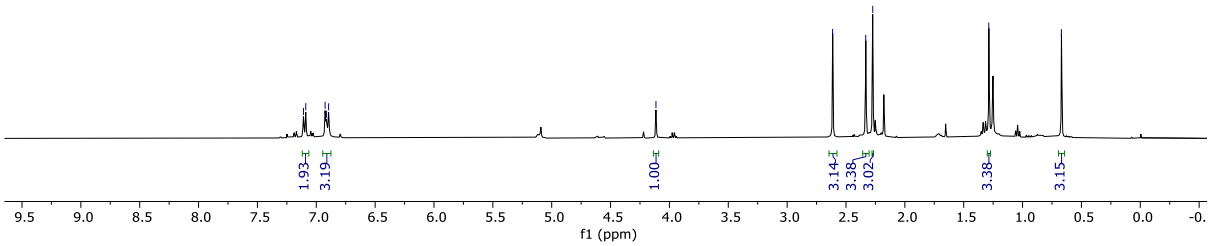


6-Hydroxy-2,2,5,7-tetramethyl-3-(*p*-tolyl)-2,3-dihydro-1*H*-inden-1-one (3q)

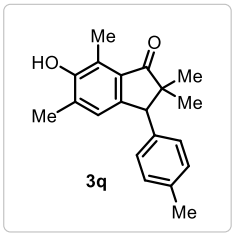
^{1}H NMR (500 MHz, $CDCl_3$)

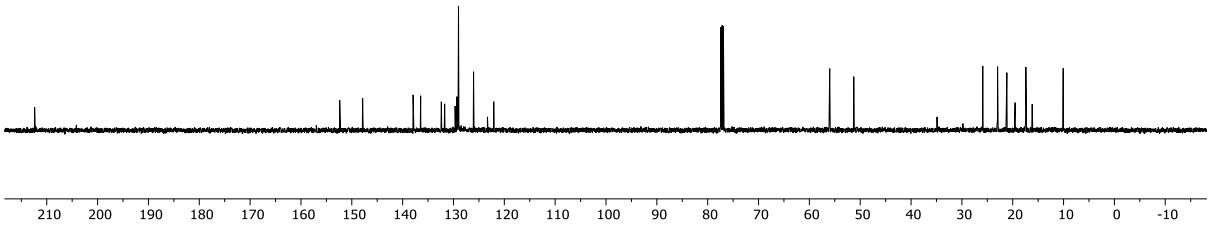






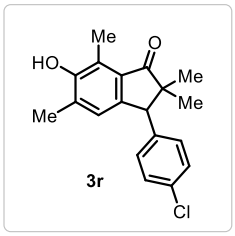
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

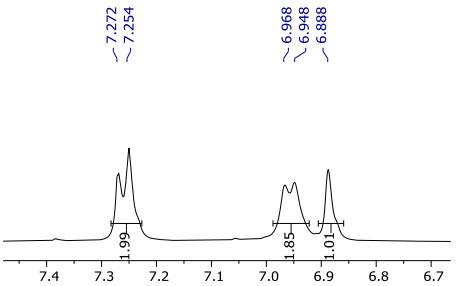


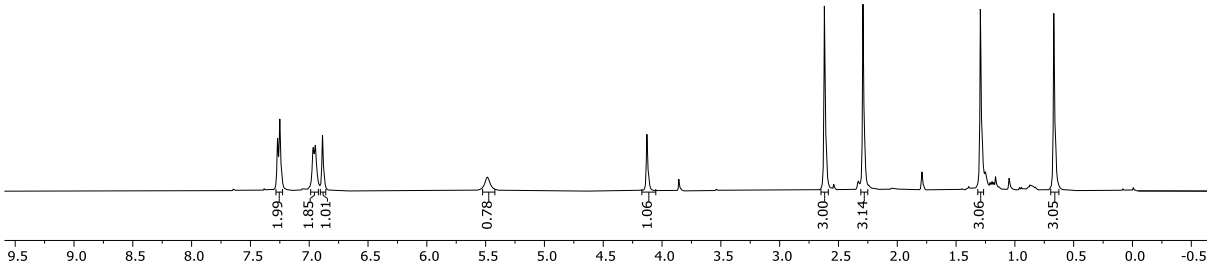


3-(4-Chlorophenyl)-6-hydroxy-2,2,5,7-tetramethyl-2,3-dihydro-1*H*-inden-1-one (3r)

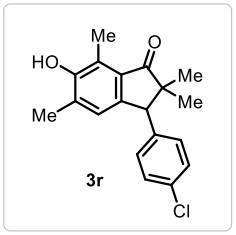
^{1}H NMR (500 MHz, $CDCl_3$)

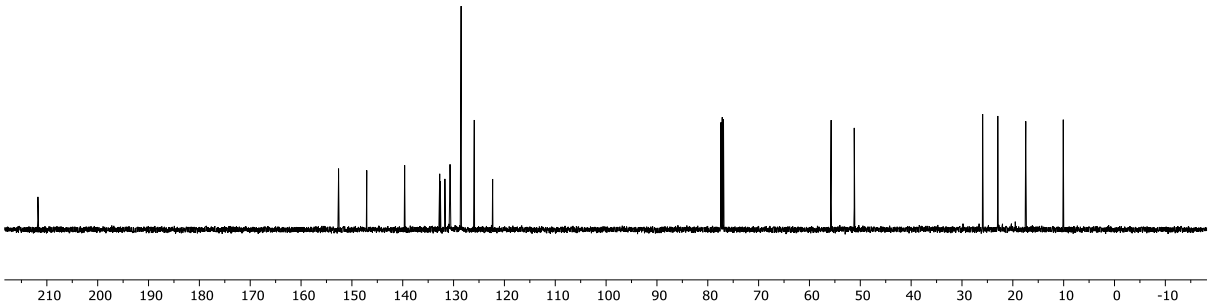






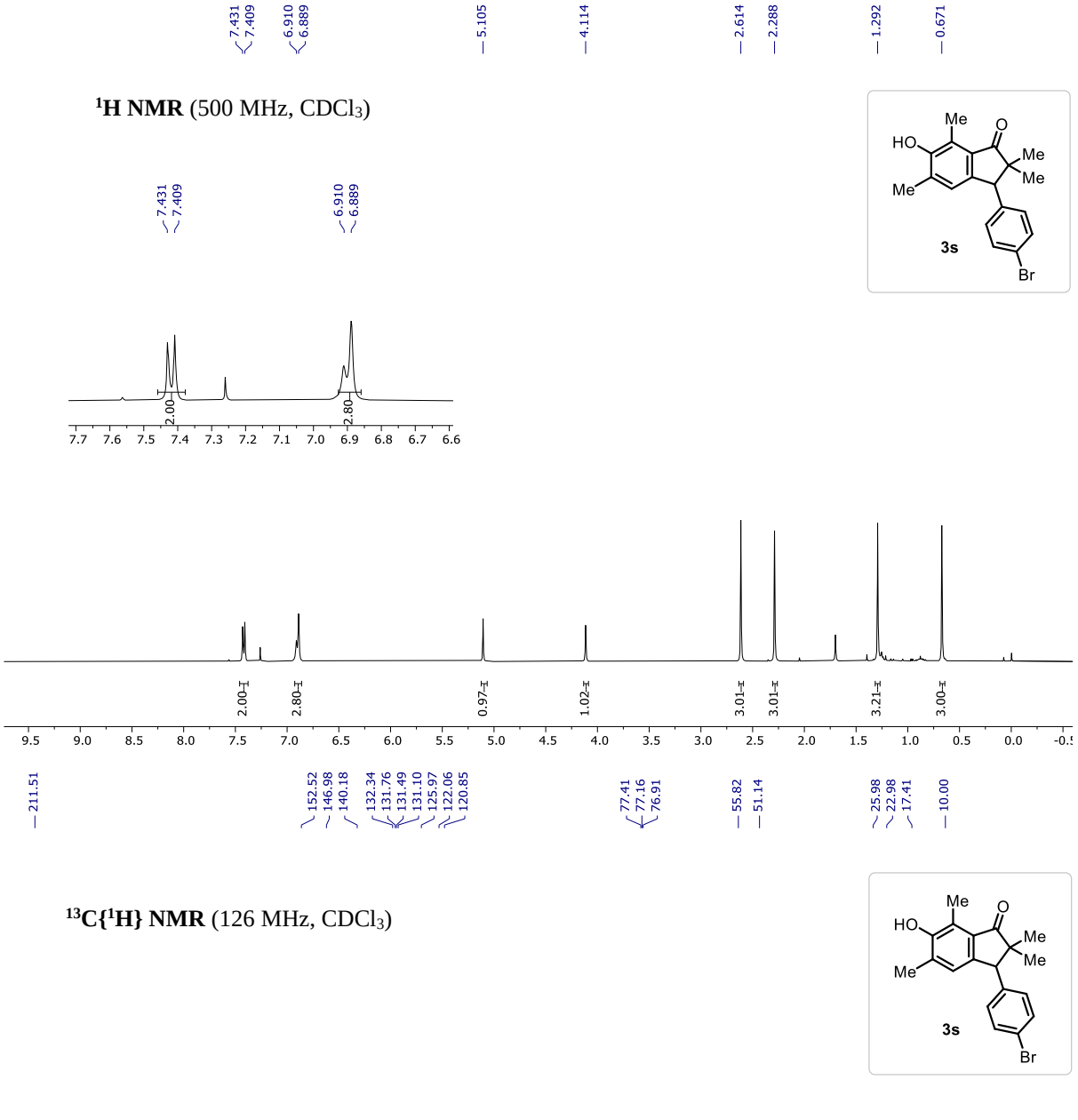
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



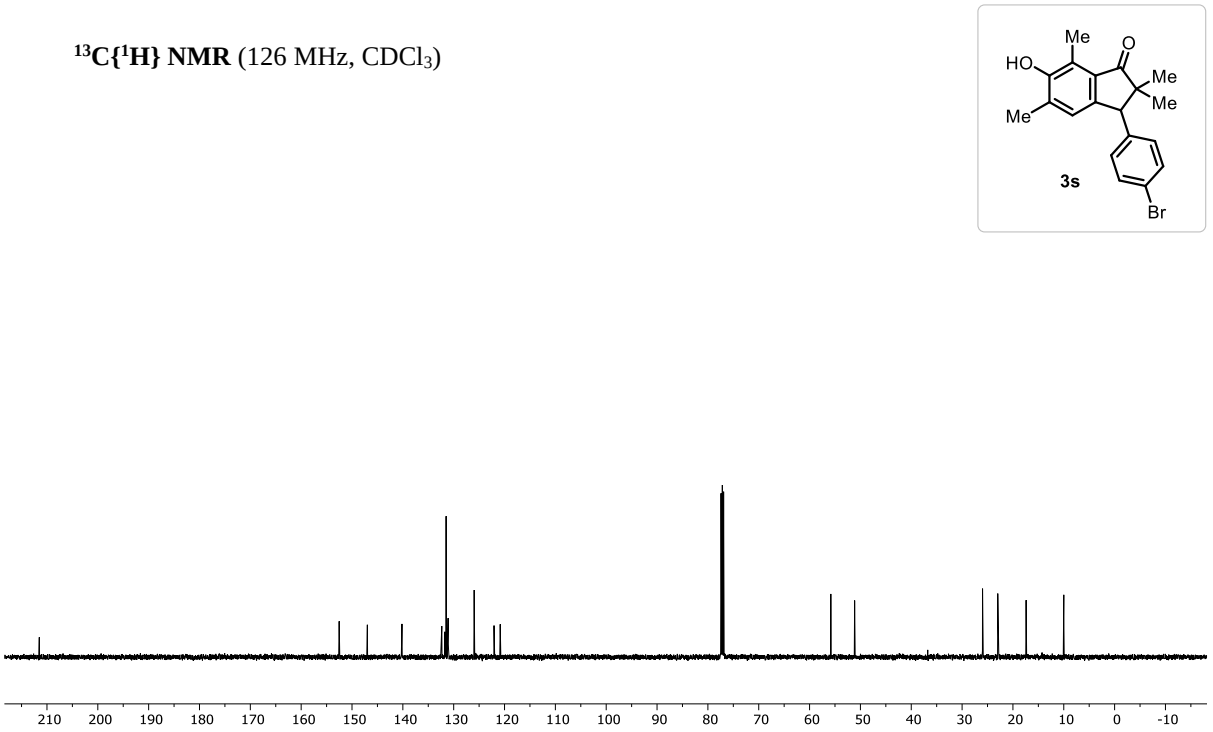


3-(4-Bromophenyl)-6-hydroxy-2,2,5,7-tetramethyl-2,3-dihydro-1*H*-inden-1-one (3s)

^{1}H NMR (500 MHz, $CDCl_3$)

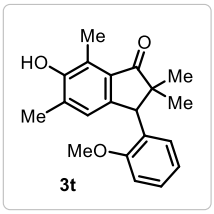


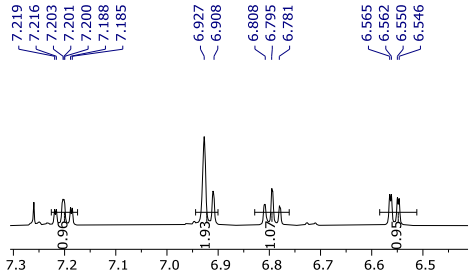
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

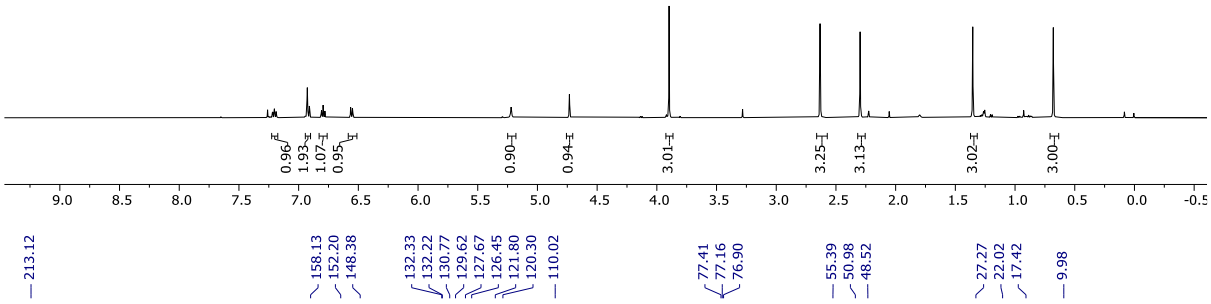


6-Hydroxy-3-(2-methoxyphenyl)-2,2,5,7-tetramethyl-2,3-dihydro-1*H*-inden-1-one (3t)

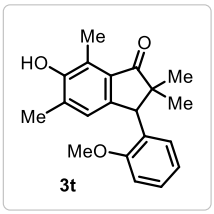
^{1}H NMR (500 MHz, $CDCl_3$)

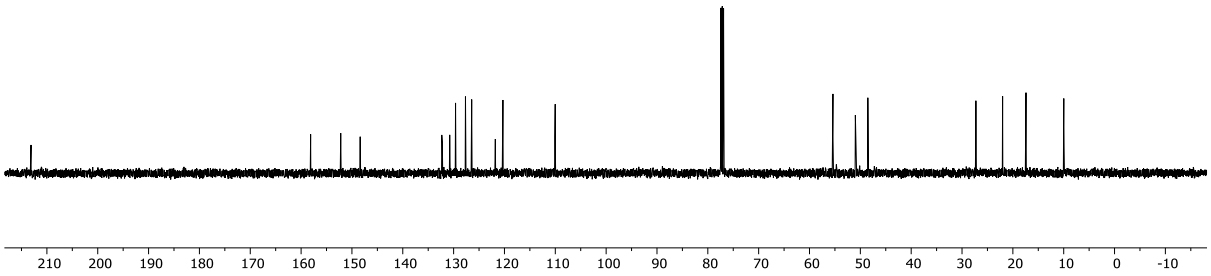






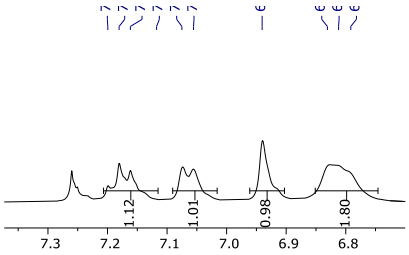
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

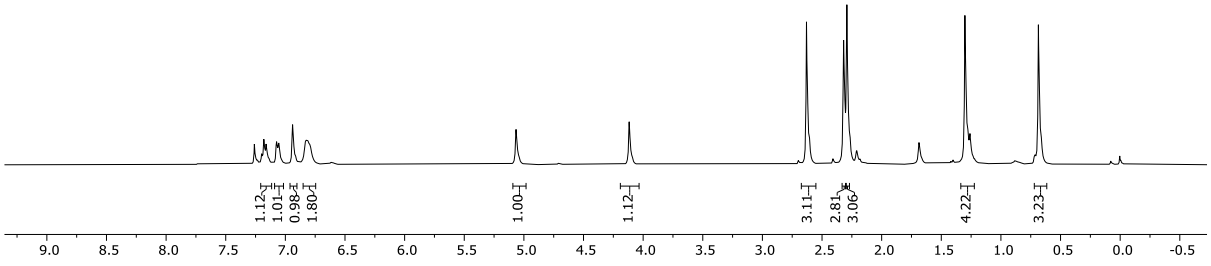




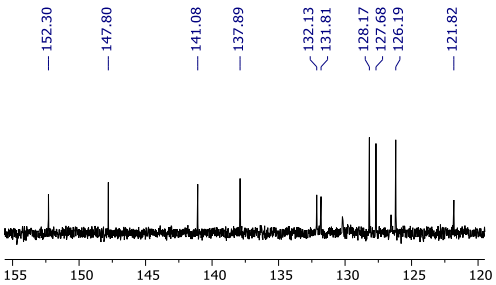
6-Hydroxy-2,2,5,7-tetramethyl-3-(*m*-tolyl)-2,3-dihydro-1*H*-inden-1-one (3u)

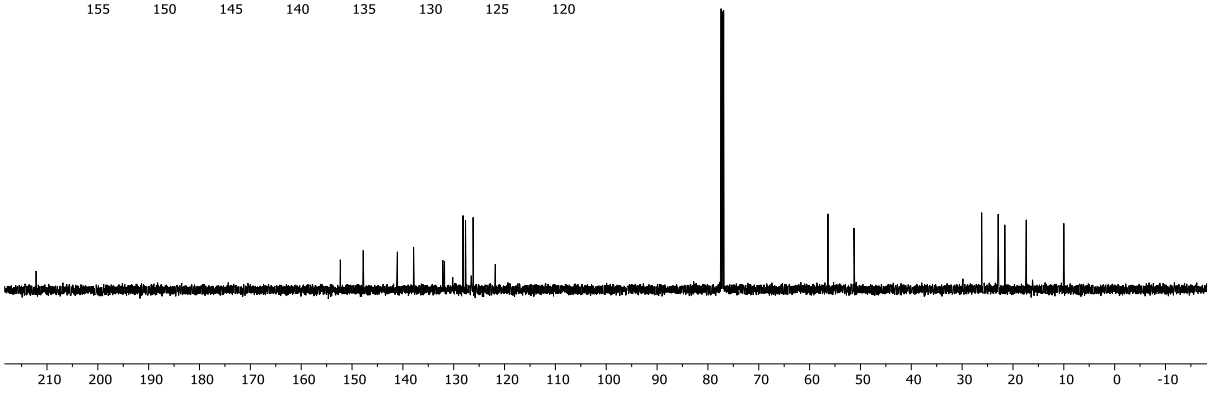
^{1}H NMR (500 MHz, $CDCl_3$)





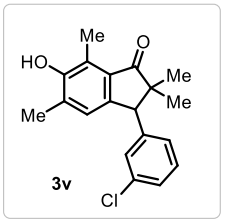
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

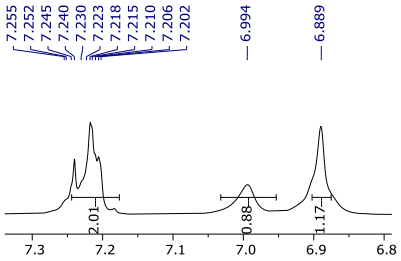


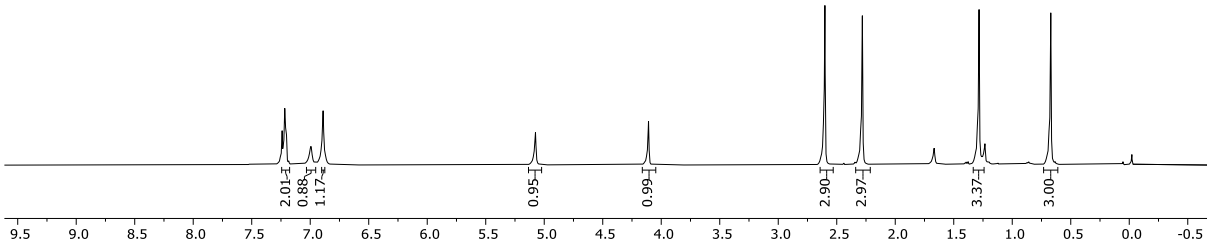


3-(3-Chlorophenyl)-6-hydroxy-2,2,5,7-tetramethyl-2,3-dihydro-1*H*-inden-1-one (3v)

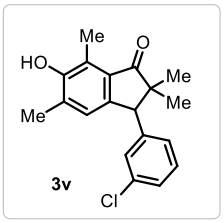
^{1}H NMR (500 MHz, $CDCl_3$)

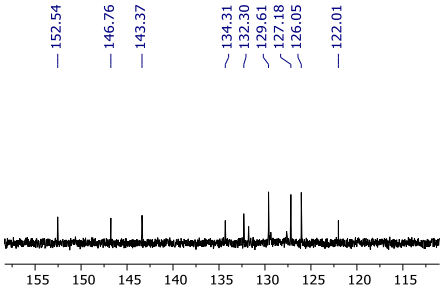


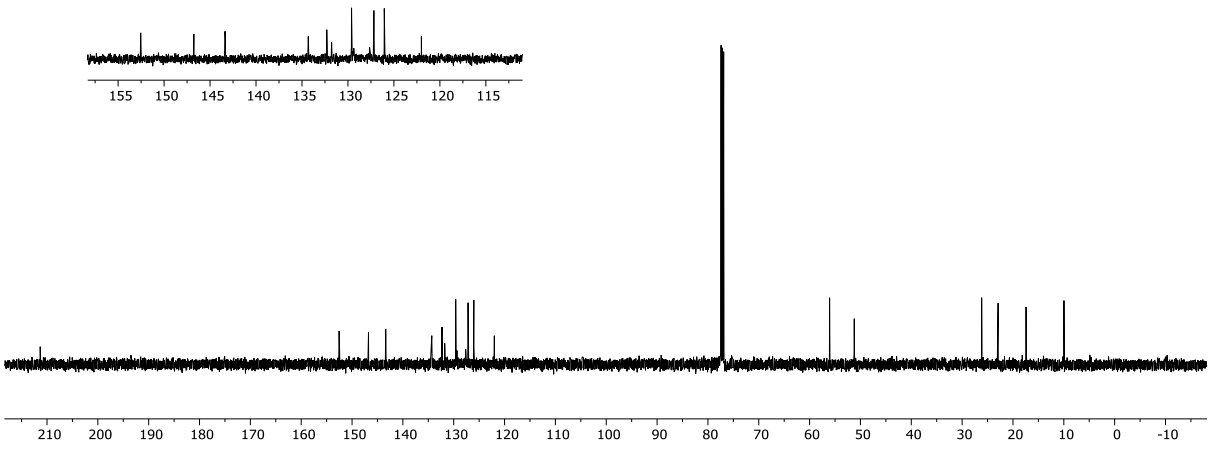




^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

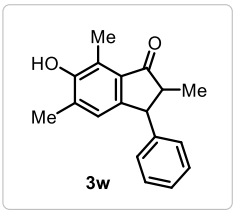


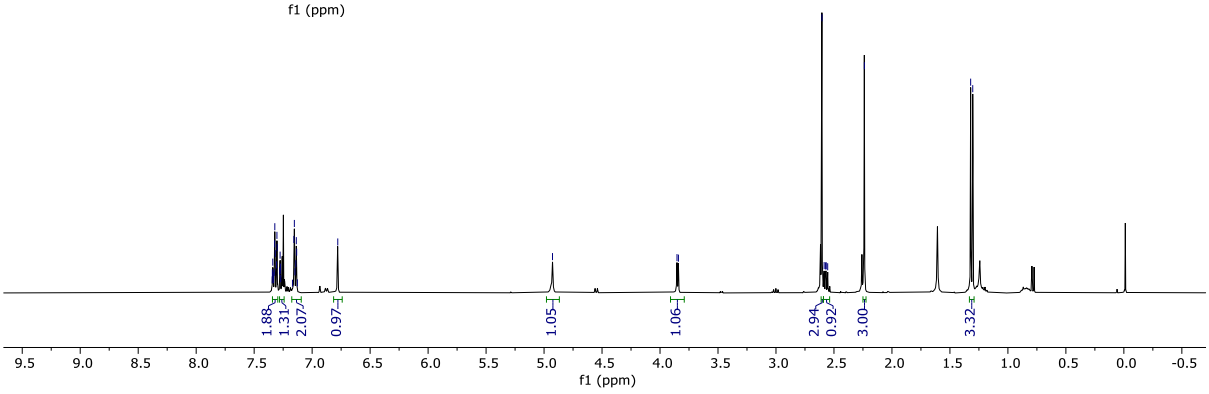




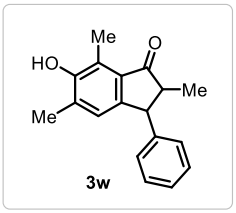
6-Hydroxy-2,5,7-trimethyl-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3w)

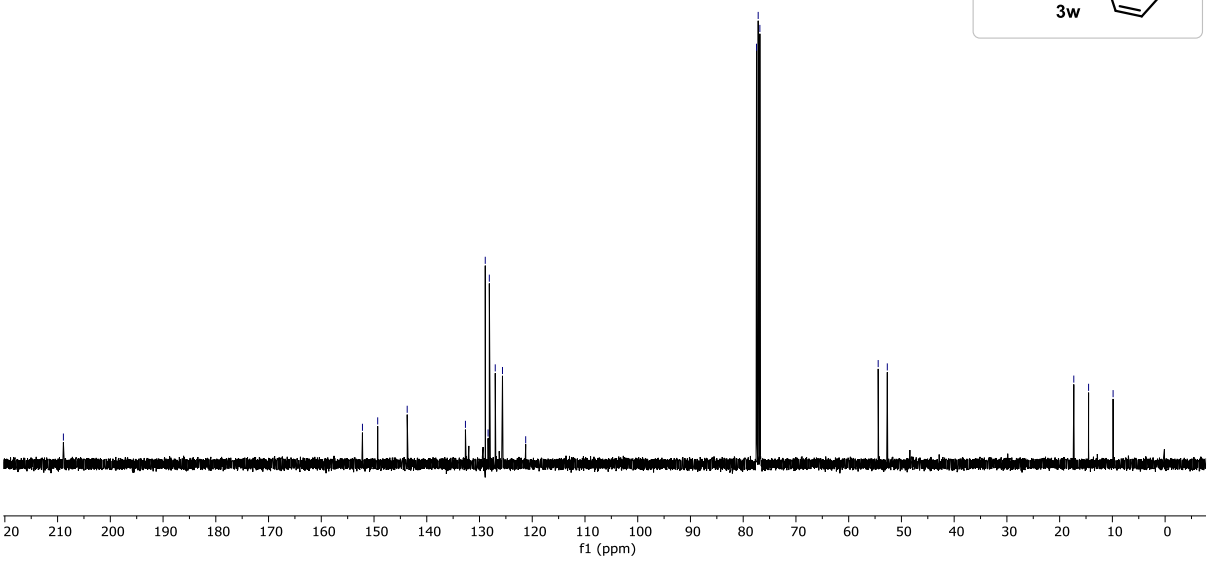
^{1}H NMR (400 MHz, $CDCl_3$)





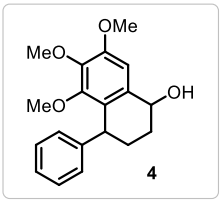
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



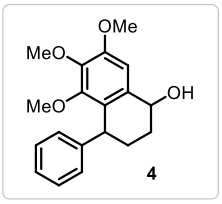


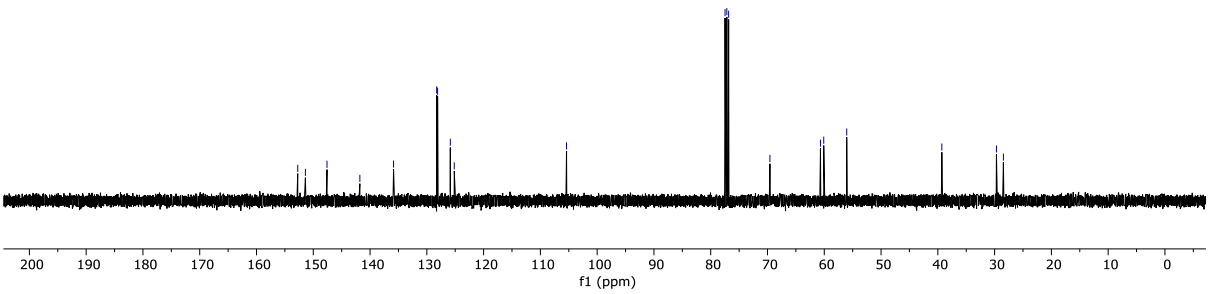
5,6,7-Trimethoxy-4-phenyl-1,2,3,4-tetrahydronaphthalen-1-ol (4)

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



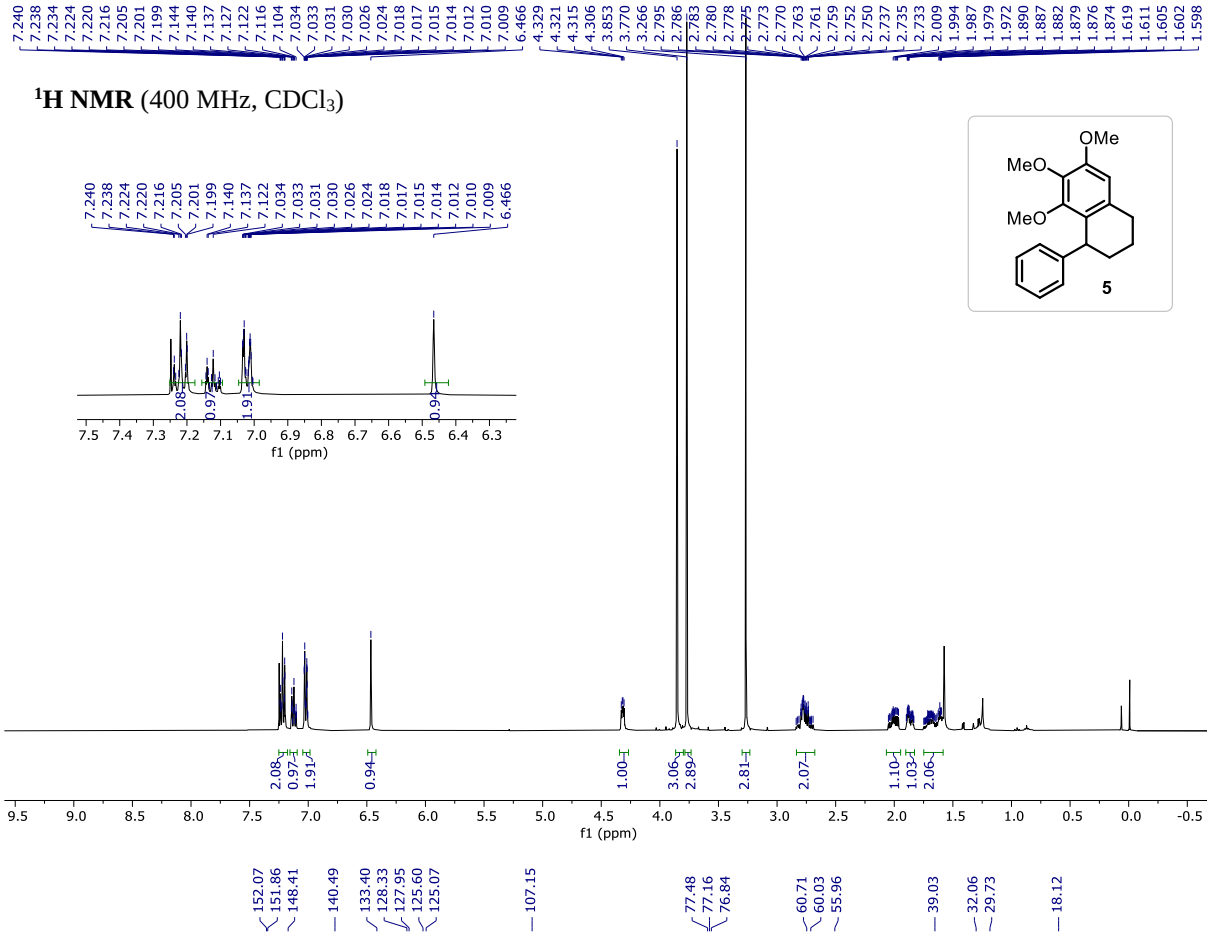
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



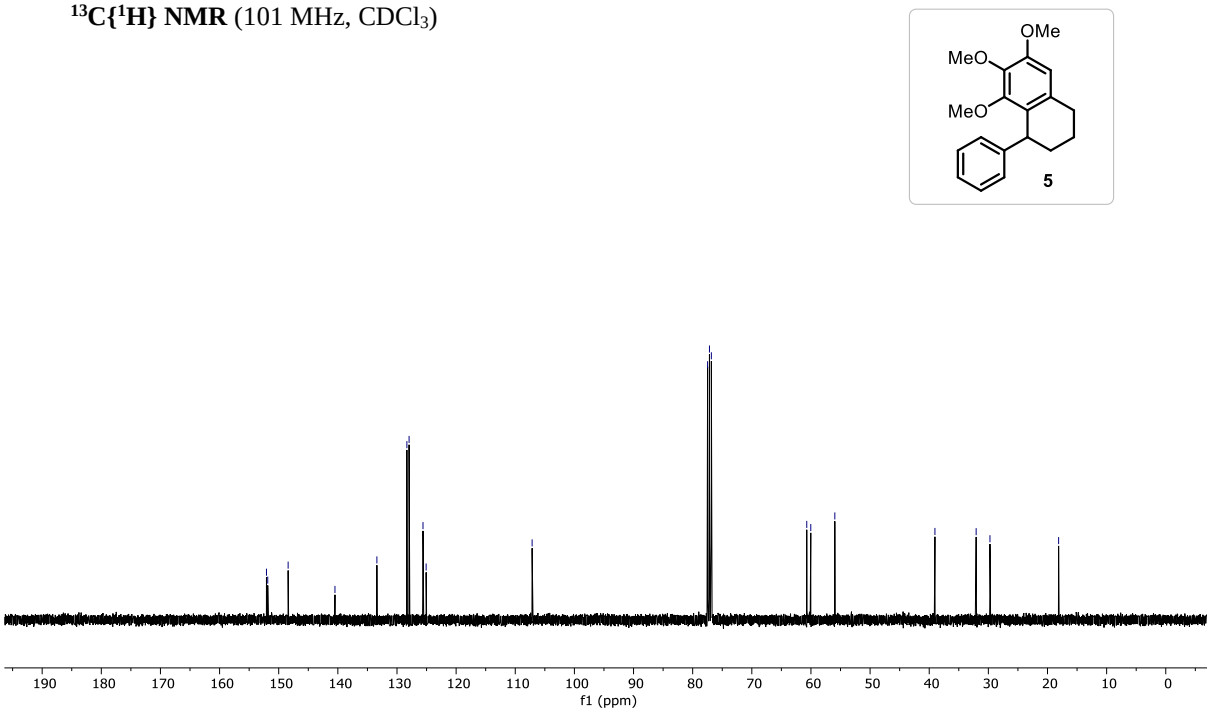


6,7,8-Trimethoxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (5)

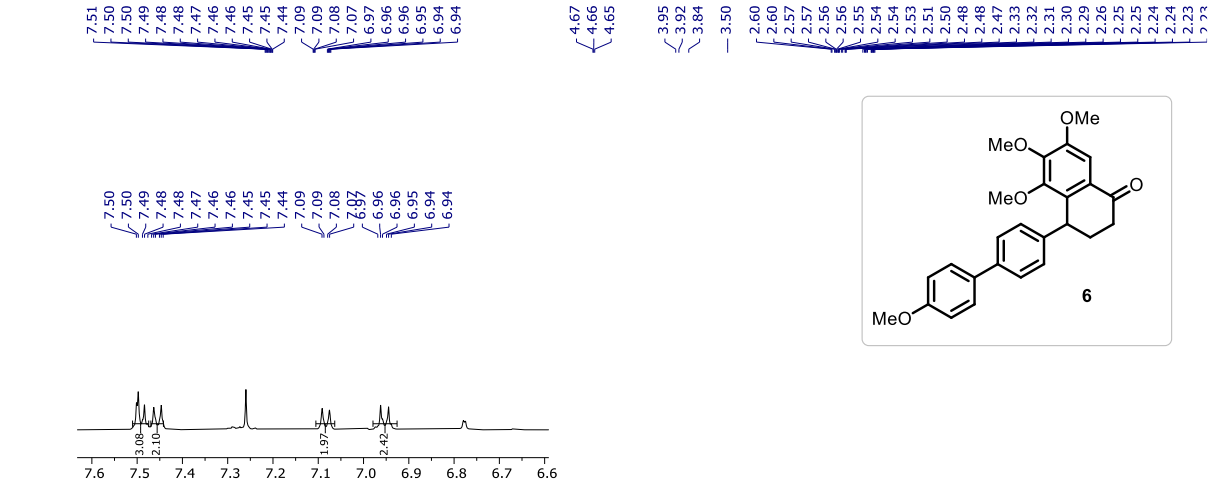
^{1}H NMR (400 MHz, $CDCl_3$)

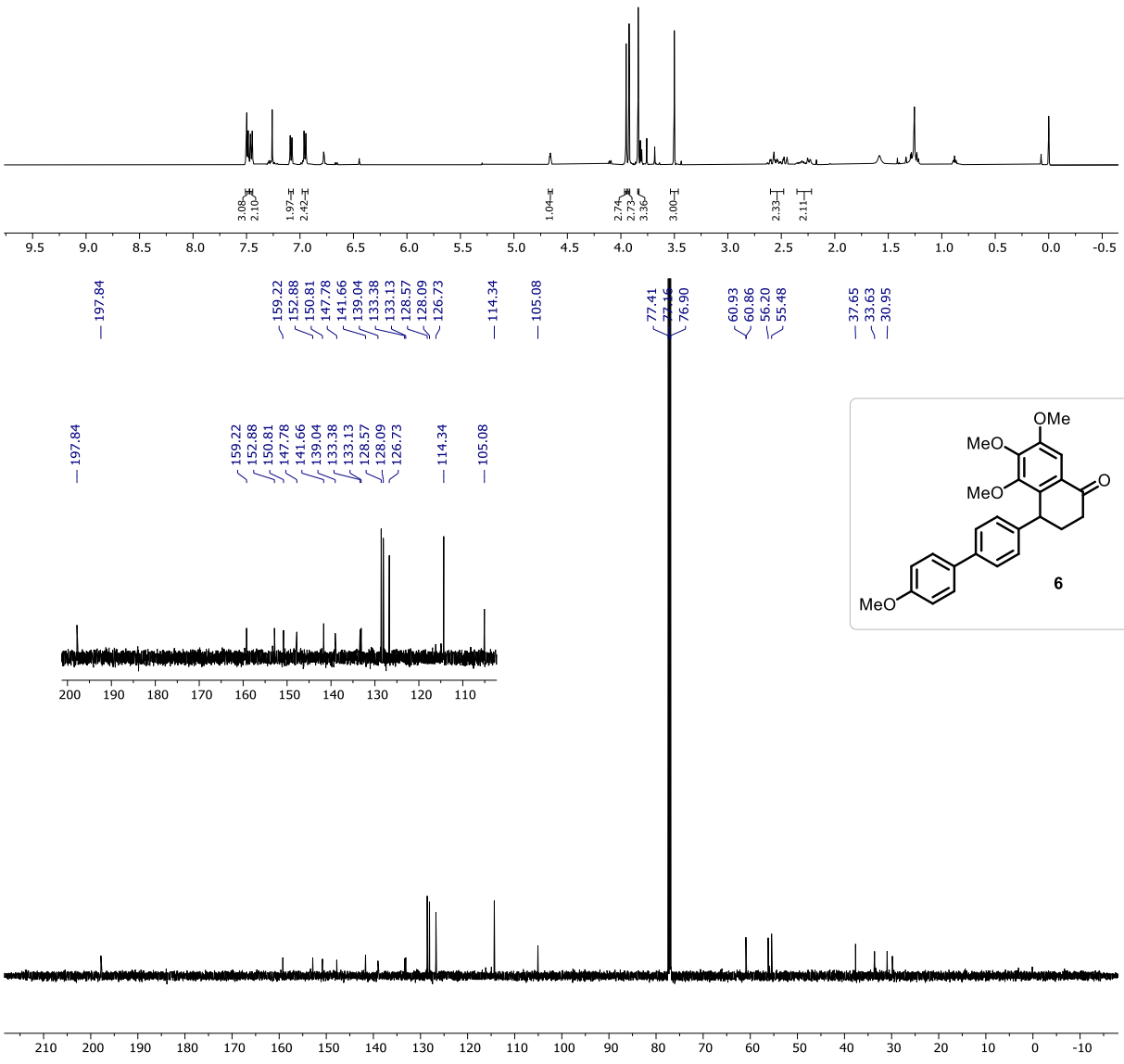


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



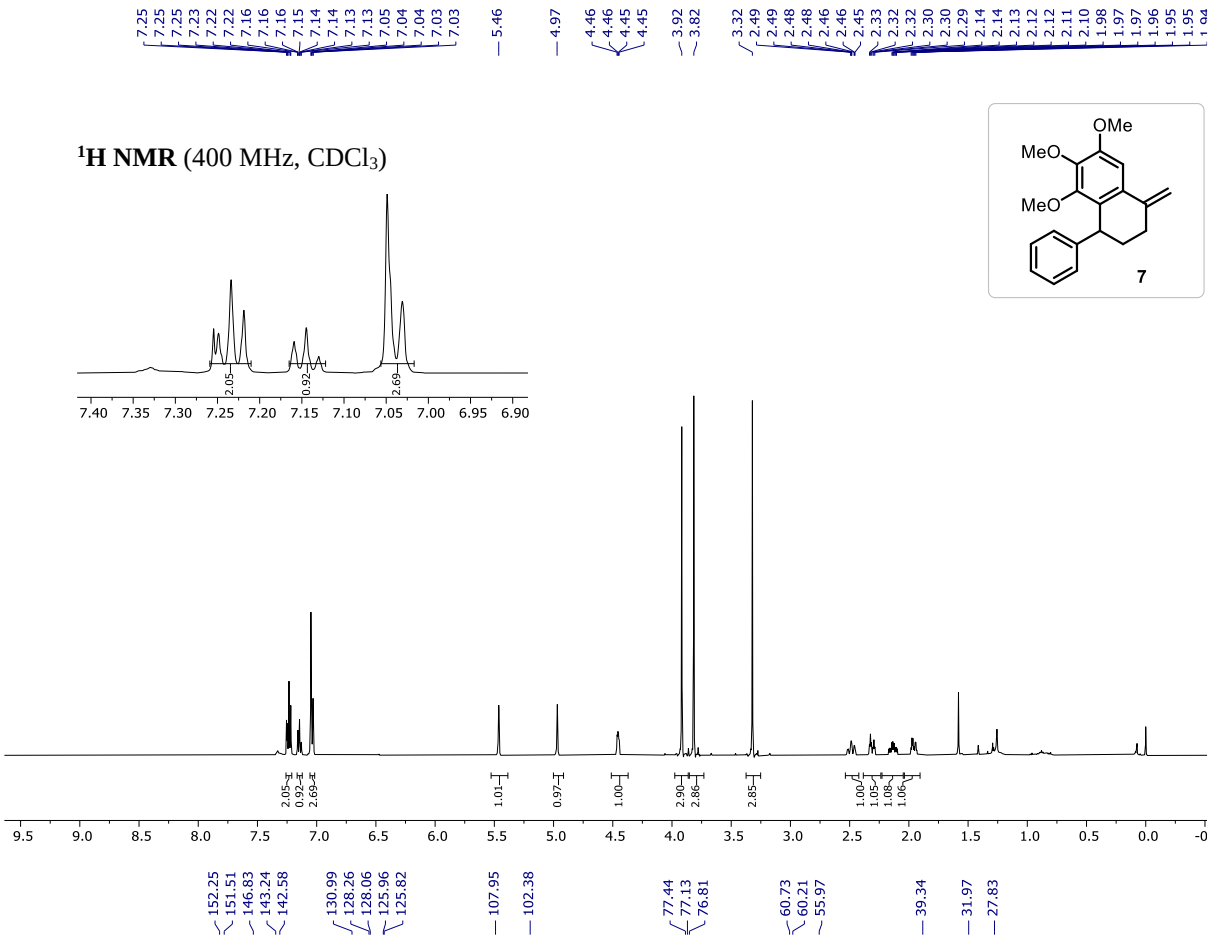
5,6,7-trimethoxy-4-(4'-methoxy-[1,1'-biphenyl]-4-yl)-3,4-dihydronaphthalen-1(2H)-one (6)



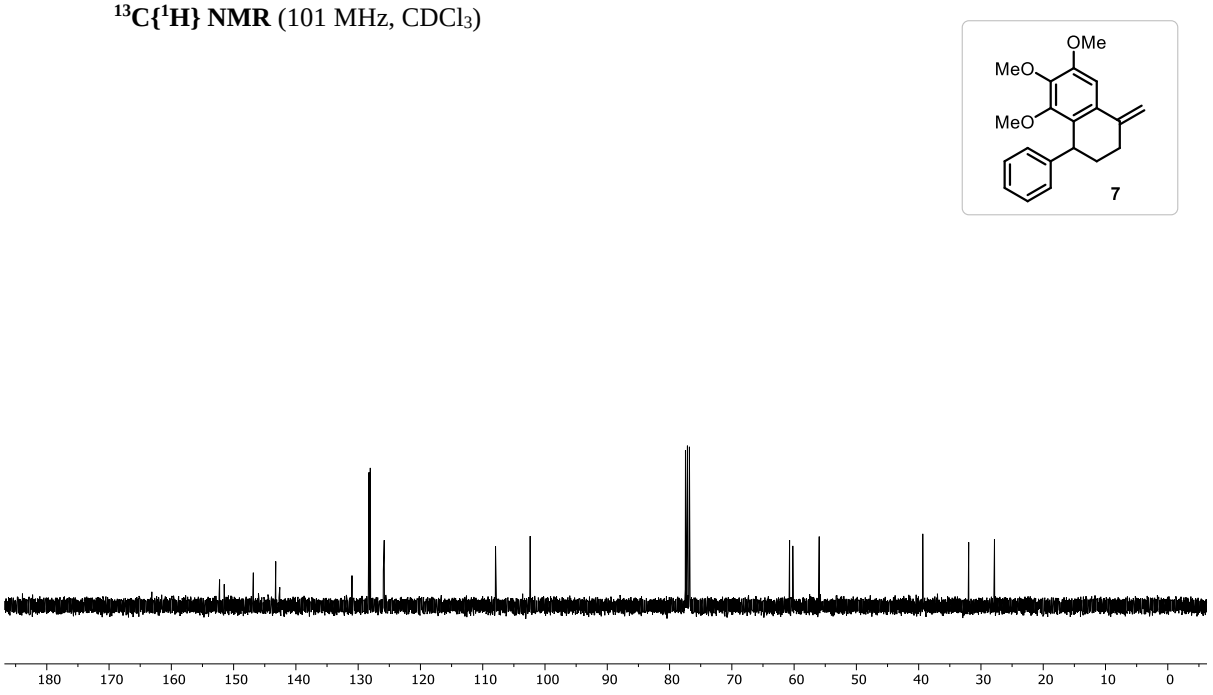


5,6,7-Trimethoxy-1-methylene-4-phenyl-1,2,3,4-tetrahydronaphthalene (7)

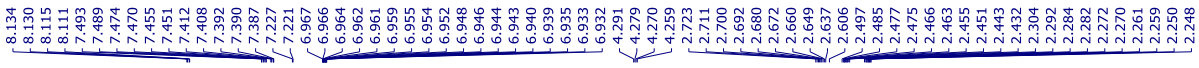
^{1}H NMR (400 MHz, $CDCl_3$)



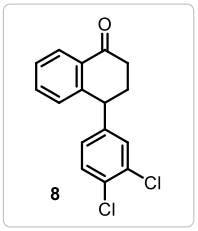
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

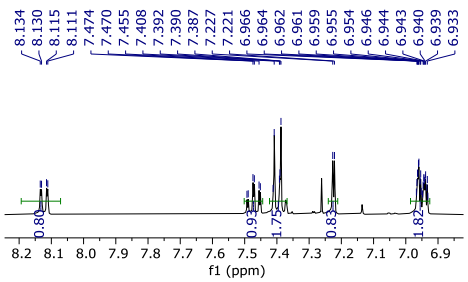


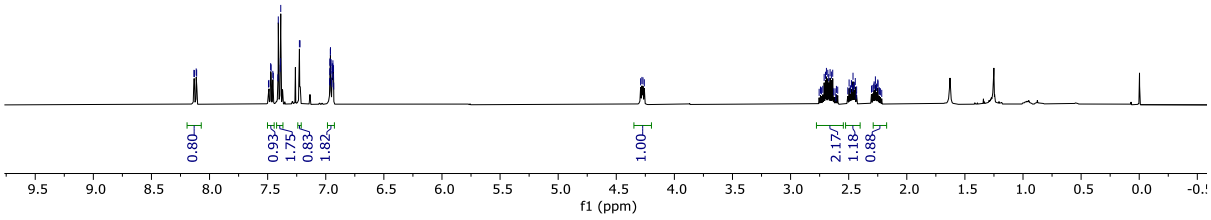
4-(3,4-Dichlorophenyl)-3,4-dihydronaphthalen-1(2*H*)-one (8)



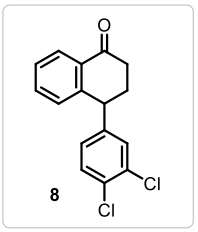
^{1}H NMR (400 MHz, $CDCl_3$)

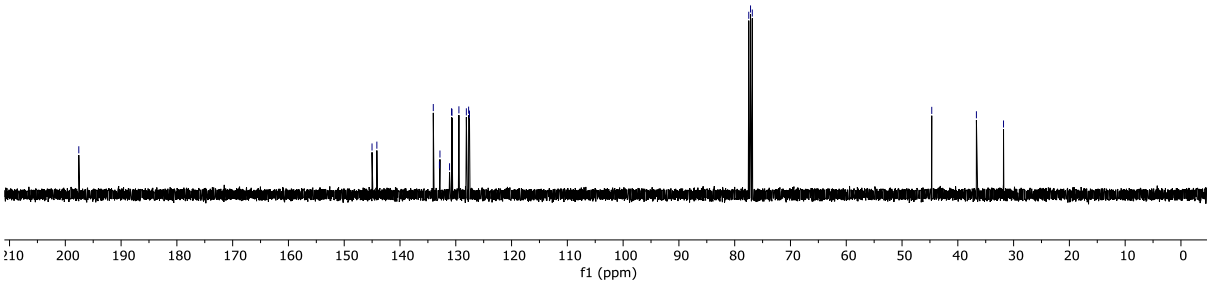






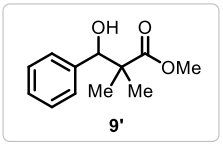
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

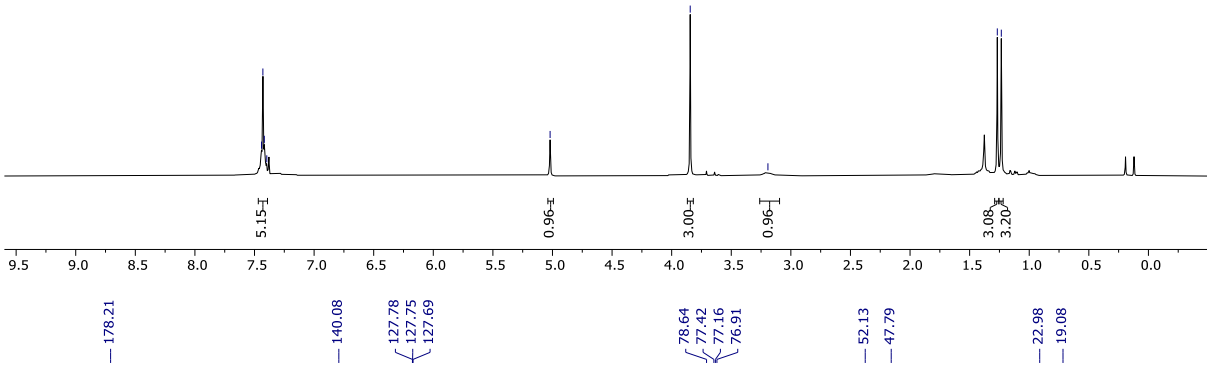




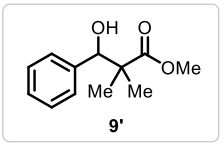
Methyl 3-hydroxy-2,2-dimethyl-3-phenylpropanoate (9')

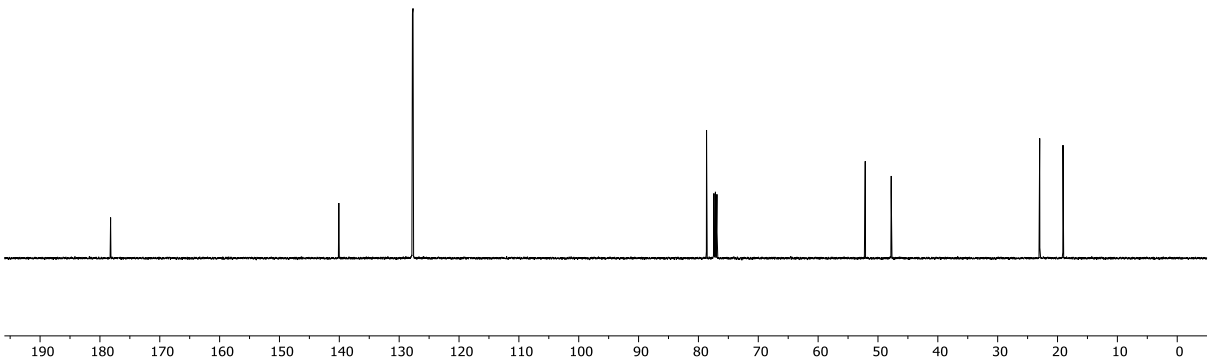
^{1}H NMR (400 MHz, $CDCl_3$)





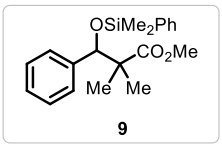
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

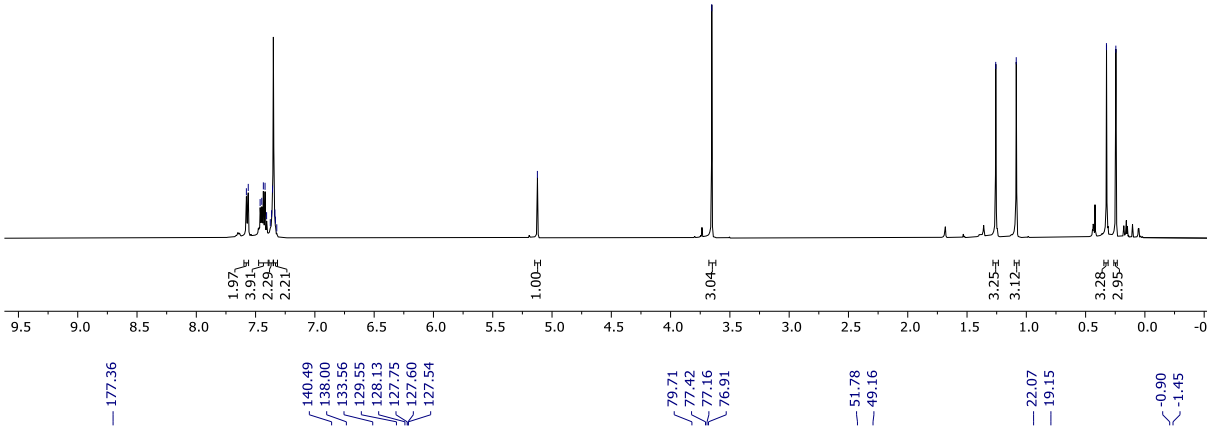




Methyl 3-((dimethyl(phenyl)silyl)oxy)-2,2-dimethyl-3-phenylpropanoate (9)

^{1}H NMR (500 MHz, $CDCl_3$)





^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)