Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Easy Access to Secondary and Tertiary Alcohols via Metal-free and Light Mediated Radical Carbonyl Allylation

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1. General Information

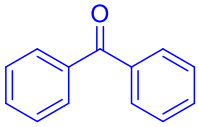
All reagents were obtained from commercial suppliers and used without further purification. Anhydrous *N,N*-Dimethylacetamide from Sigma Aldrich was degassed using 3 cycles of freeze-pump-thaw and used for all the reactions. All reactions were performed in oven-dried vials and under an Argon atmosphere. Monitoring of reactions were done on Merck TLC Silica Gel 60 F_{254} plates and visualised using UV irradiation at 254 nm and/or phosphomolybdic acid stain. Flash column chromatography purifications were conducted on silica gel purchased from Aldrich (technical grade, 60 Å pore size, 230-400 mesh, 40-63 μm). Technical grade solvents were used for chromatography and distilled before use. All NMR spectra were recorded on Bruker 400 MHz and/or 500 MHz spectrometers. Chemical shifts are given in ppm relative to the solvent residual peak (^{1}H NMR: $CDCl_3$ δ = 7.26 ppm (s), ^{13}C NMR: $CDCl_3$ δ = 77.16 ppm (t)). With multiplicity (brs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, hept = heptet, m = multiplet) All reactions were performed with 34W Blue LED H150 made by Kessil.

2. General Procedure

In an oven dried 8 mL vial with a magnetic stirrer, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (2.5 mol%), anhydrous K_2CO_3 (20 mol%) and if solid, ketone/aldehyde (0.2 mmol, 1 equiv) was added. The vial was brought into a glovebox and under Ar atmosphere, triisopropylsilanethiol (0.2 eq.), allylic substrate (5.0 equiv), DMA (2 mL) and if liquid, ketone/aldehyde (0.2 mmol, 1 equiv) was added. The vial was then brought out of the glovebox, sealed with parafilm and stirred under irradiation by blue LED at room temperature. After completion of reaction, the vial was opened and quenched with water. The resulting mixture was extracted 3 times with EtOAc and dried over Na_2SO_4. The extracted organic layer was evaporated under reduced pressure and the residue was purified by silica gel flash column chromatography using EtOAc/Hexane eluent to obtain the product.

3. List of Substrates Used in This Work

3.1. Ketones



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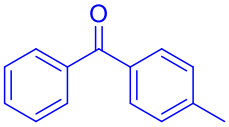

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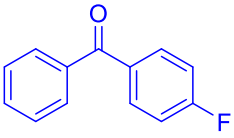

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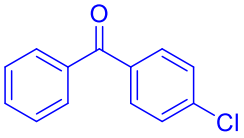

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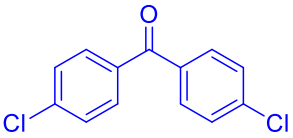

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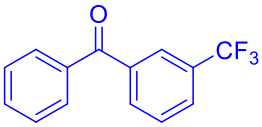

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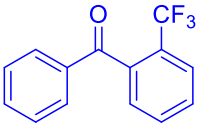

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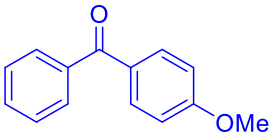

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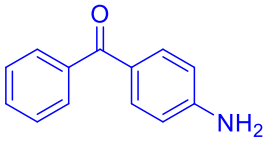

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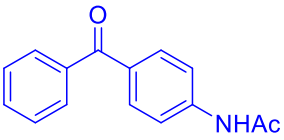

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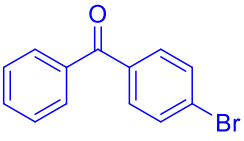

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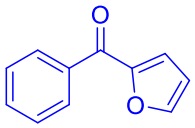

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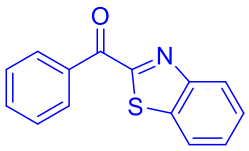

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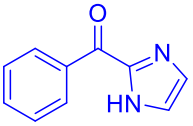

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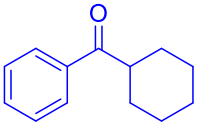

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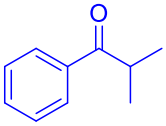

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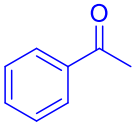

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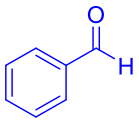
3.2. Aldehydes



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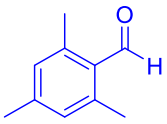

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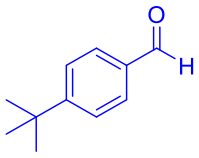

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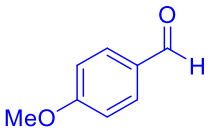

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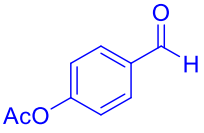

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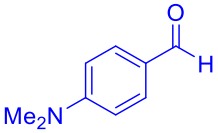

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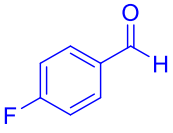

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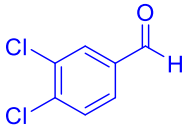

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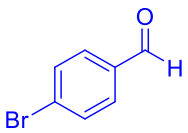

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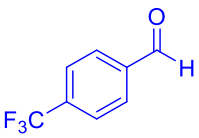

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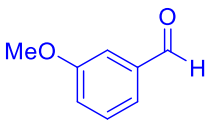

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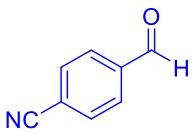

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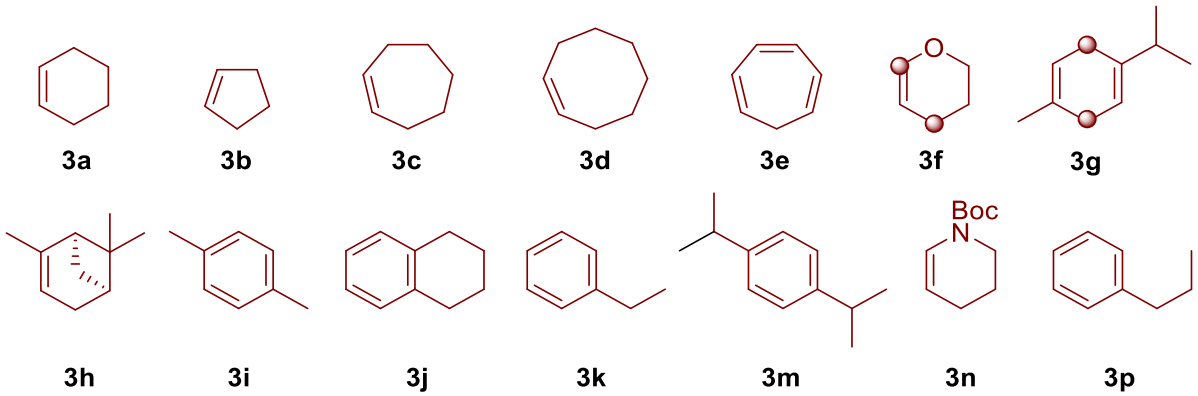
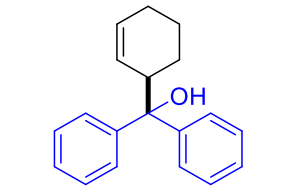
3.3. Allylic/Benzylic Substrates



4. Characterisation Information

4.1 Ketone Scope



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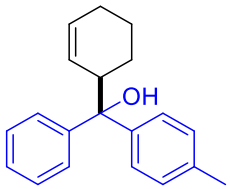

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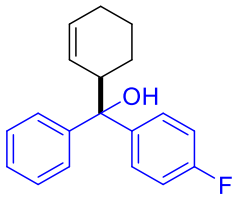

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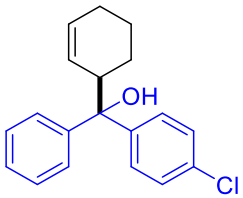

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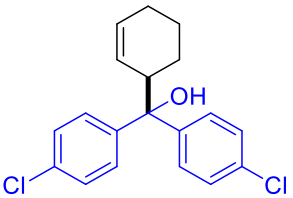

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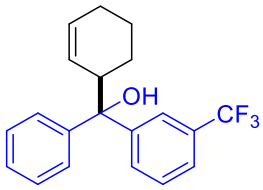

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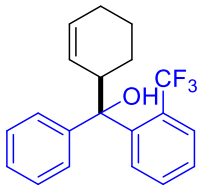

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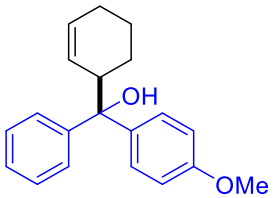

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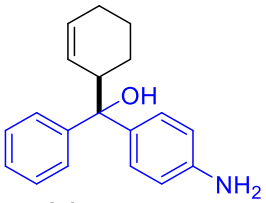

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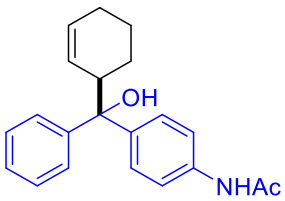

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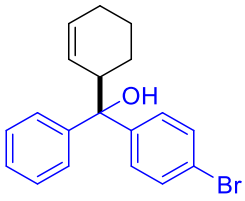

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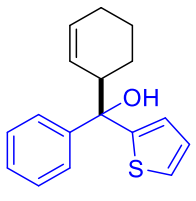

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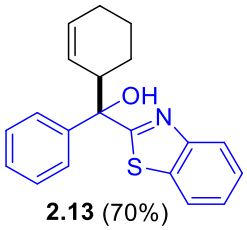

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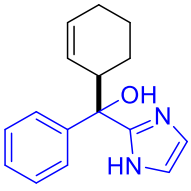

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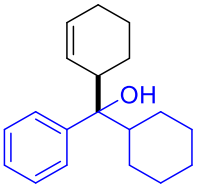

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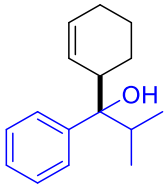

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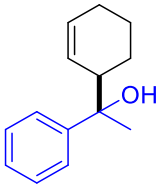
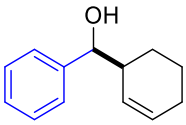


2.17 (50%)

4.2. Aldehyde Scope



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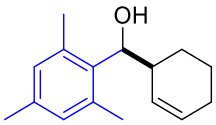

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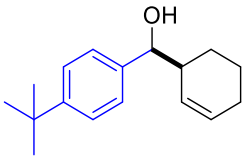

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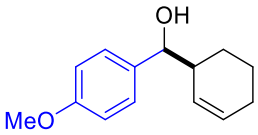
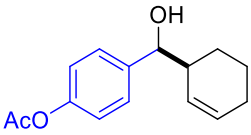
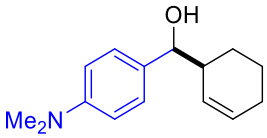


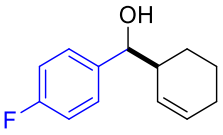
2.4 (48%)



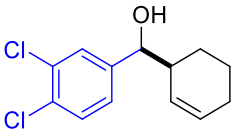
2.5 (40%)



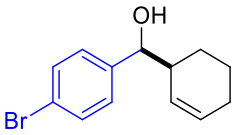
2.6 (16%)



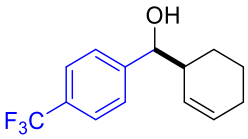
2.7 (46%)



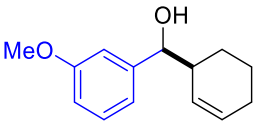
2.8 (70%)



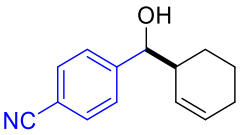
2.9 (32%)



2.10 (49%)

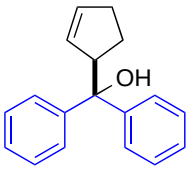


2.11 (49%)

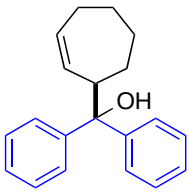


2.12 (20%)

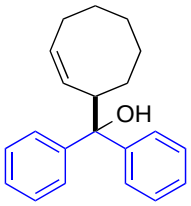
4.3. Allylic/Benzylic Scope



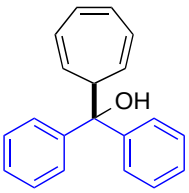
4.1 (78%)



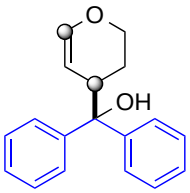
4.2 (72%)



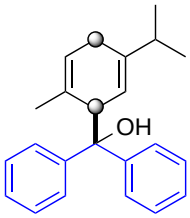
4.3 (68%)



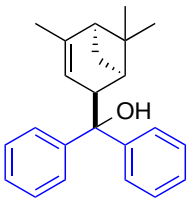
4.4 (84%)



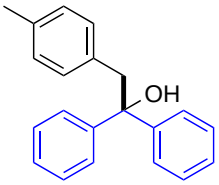
4.5 (83%, 3:1)



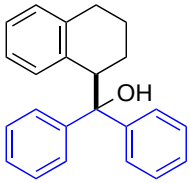
4.6 (52%, 3:1)



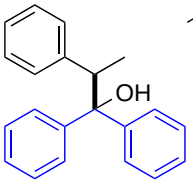
4.7 (58%)



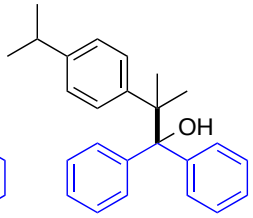
4.8 (18%)



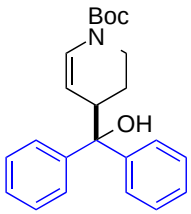
4.9 (68%)



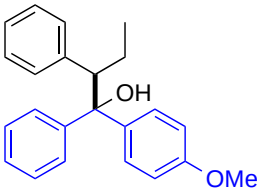
4.10 (57%)



4.11 (61%)

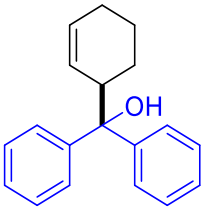


4.12 (60%)



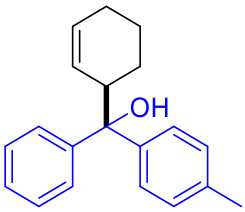
4.13 (51%)

Cyclohex-2-en-1-yldiphenylmethanol (2.1)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), benzophenone (**1a)** (36.4 mg, 0.2 mmol, 1.0 equiv), cyclohexene (**3a) (**0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (2-5% EtOAc-Hex) to obtain the product as a white solid (47.6 mg, 90%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.58 (m, 2H), 7.48-7.46 (m, 2H), 7.34-7.13 (m, 2H), 5.99-5.94 (m, 1H), 5.49 (dd, *J* = 10.4, 2.0 Hz, 1H), 3,45 (brs, 1H), 2.21 (s, 1H), 2.03-1.98 (m, 2H), 1.81-1.76 (m, 1H), 1.52-1.43 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 145.6, 133.9, 128.4, 128.1, 126.7, 126.6, 126.3, 126.2, 125.6 79.5, 43.9, 25.4, 24.0, 22.1. HRMS calcd. for $C_{19}H_{20}O+H^+$ $(M+H^+)^+$: 265.1592, found 265.1592.

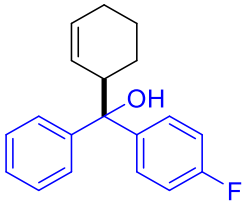
Cyclohex-2-en-1-yl(phenyl)(p-tolyl)methanol (2.2)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), ketone **1b** (39.2 mg, 0.2 mmol, 1.0 equiv), cyclohexene (**3a)** (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (2-5% EtOAc-Hex) to obtain the product as a colourless oil (45.6 mg, 82%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.57 (m, 1H), 7.48-7.45 (m, 2H), 7.36-7.24 (m, 3H), 7.20-7.07 (m, 3H), 5.97-5.94 (m, 1H), 5.52-5.46 (m, 1H), 3.44-3.41 (m, 1H), 2.30 (s, 1.5H), 2.28 (s, 1.5H), 2.17 (d, *J* = 3.6 Hz, 1H), 2.03-1.97 (m, 2H), 1.79-1.76 (m, 1H), 1.52-1-41 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 145.9, 144.1, 142.8, 136.3, 135.9, 133.7, 129.1, 128.9, 128.4,

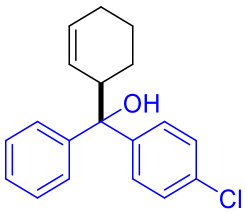
128.1, 126.7, 126.6, 126.1, 125.6, 79.4, 43.9, 25.4, 24.0, 22.2, 21.0. HRMS calcd. for $C_{20}H_{22}O+H^+$ $(M+H^+)^+$: 279.1749, found 279.1754.

Cyclohex-2-en-1-yl(4-fluorophenyl)(phenyl)methanol (2.3)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), ketone **1c** (40.0 mg, 0.2 mmol, 1.0 equiv), cyclohexene (**3a)** (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (2-5% EtOAc-Hex) to obtain the product as a colourless oil (49.6 mg, 88%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.54 (m, 2H), 7.45-7.41 (m, 2H), 7.35-7.26 (m, 2H), 7.23-7.15 (m, 1H), 7.02-6.93 (m, 2H), 6.00-5.96 (m, 1H), 5.59-5.46 (d, *J* = 10.4 Hz, 1H), 3.41 (brs, 1H), 2.21 (s, 1H), 2.03-1.98 (m, 2H), 1.81-1.74 (m, 1H), 1.55-1.41 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 162.6, 160.5, 160.2, 146.8, 145.5, 142.8, 141.5, 134.2, 128.5, 128.2, 128.0, 127.9, 127.4, 127.3, 126.9, 126.5, 126.3, 126.2, 126.1, 125.5, 115.2, 115.0, 114.9, 114.7, 79.2, 43.9, 25.4, 24.0, 23.9, 22.1. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ -116.7, -117.2. HRMS calcd. for $C_{19}H_{19}FO+H^+$ $(M+H^+)^+$: 283.1498, found 283.1500.

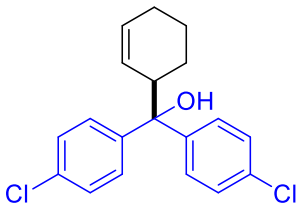
(4-Chlorophenyl)(cyclohex-2-en-1-yl)(phenyl)methanol (2.4)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), ketone **1d** (43.3 mg, 0.2 mmol, 1.0 equiv), cyclohexene (**3a)** (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (2-5% EtOAc-Hex) to obtain the product as a white solid (41.8 mg, 88%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400

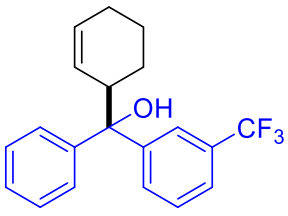
MHz, $CDCl_3$): δ 7.59-7.53 (m, 2H), 7.47-7.41 (m, 2H), 6.01-5.98 (m, 1H), 5.50-5.45 (m, 1H), 3.45-3.39 (m, 1H), 2.25 (s, 1H), 2.04-1.99 (m, 2H), 1.82-1.76 (m, 1H), 1.59-1.38 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 145.6, 145.2, 144.3, 134.3, 132.5, 132.1, 128.5, 128.2, 127.7, 127.1, 126.9, 126.6, 126.1, 125.5, 79.2, 43.8, 43.7, 25.4, 23.9, 23.8, 22.0. HRMS calcd. for $C_{19}H_{19}OCl+H^+$ $(M+H^+)^+$: 299.1203, found 299.1210.

Bis(4-chlorophenyl)(cyclohex-2-en-1-yl)methanol (2.5)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), ketone **1e** (50.2 mg, 0.2 mmol, 1.0 equiv), cyclohexene (**3a)** (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (2-5% EtOAc-Hex) to obtain the product as a white solid (41.3 mg, 62%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.30-7.23 (m, 4H), 6.02-5.99 (m, 1H), 5.42 (dd, *J* = 10.4, 1.2 Hz, 1H), 3.39-3.34 (m, 1H), 2.22 (s, 1H), 2.04-1.97 (m, 2H), 1.80-1.75 (m, 1H), 1.55-1.38 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 143.8, 132.9, 132.4, 128.7, 128.4, 127.6, 127.0, 125.7, 79.0, 43.7, 25.3, 23.8, 22.0. HRMS calcd. for $C_{19}H_{18}OCl_2+H^+$ $(M+H^+)^+$: 333.0813, found 333.0819.

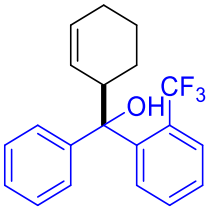
Cyclohex-2-en-1-yl(phenyl)(3-(trifluoromethyl)phenyl)methanol (2.6)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), ketone **1f** (50.0 mg, 0.2 mmol, 1.0 equiv), cyclohexene (**3a)** (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (2-5% EtOAc-Hex) to obtain the product as a colourless oil (53.2 mg, 80%). Product was obtained as a mixture of 2 diastereomers. ^1H NMR

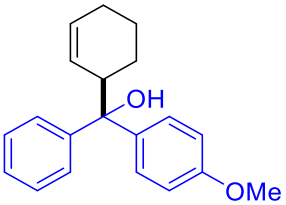
(400 MHz, $CDCl_3$): δ 7.91-7.17 (m, 9H), 6.03-6.00 (m, 1H), 5.51-5.39 (m, 1H), 3.50-3.47 (m, 1H), 2.31 (s, 1H), 2.05-1.99 (m, 2H), 1.82-1.77 (m, 1H), 1.61-1.35 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 146.7, 146.3, 144.8, 134.7, 130.7 (q, *J* = 32 Hz), 130.5 (q, *J* = 32 Hz), 129.7, 129.1, 128.8, 128.7, 128.6, 128.4, 127.1, 126.7, 126.1, 125.9, 125.8, 125.5, 123.6 (q, *J* = 4 Hz), 123.2 (q, *J* = 4 Hz), 123.0 (q, *J* = 4 Hz), 122.4 (q, *J* = 4 Hz), 79.3, 79.2, 43.9, 43.7, 25.3, 23.8, 22.0. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ -62.3, -62.4. HRMS calcd. for $C_{20}H_{19}OF_3+Na^+$ $(M+Na^+)^+$: 355.1286, found 355.1283.

Cyclohex-2-en-1-yl(phenyl)(2-(trifluoromethyl)phenyl)methanol (2.7)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), ketone **1g** (50.0 mg, 0.2 mmol, 1.0 equiv), cyclohexene (**3a)** (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (2-5% EtOAc-Hex) to obtain the product as a colourless oil (32.6 mg, 49%). Product was obtained as a mixture of 2 diastereomers. ^1H NMR (400 MHz, $CDCl_3$): δ 7.66-7.15 (m, 9H), 6.05-5.97 (m, 1H), 5.52-5.44 (m, 1H), 3.50 (brs, 0.5H), 3.39 (brs, 0.5H), 2.49-2.47 (m, 1H), 2.02-2.01 (m, 2H), 1.80-1.77 (m, 1H), 1.51-1.44 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 145.1, 144.8, 144.2, 133.8, 133.3, 131.1, 130.3, 129.8, 129.2, 129.1, 129.0, 128.6, 127.2, 126.9, 126.8, 126.6, 126.4, 126.3, 126.1, 125.9, 80.6, 80.1, 46.4, 25.5, 25.3, 24.2, 23.8, 22.2, 22.1. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ -54.8. HRMS calcd. for $C_{20}H_{19}OF_3+H^+$ $(M+H^+)^+$: 333.1466, found 333.1469.

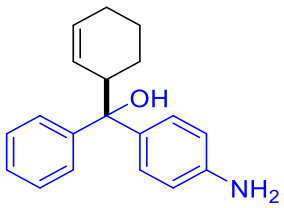
Cyclohex-2-en-1-yl(4-methoxyphenyl)(phenyl)methanol (2.8)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%),

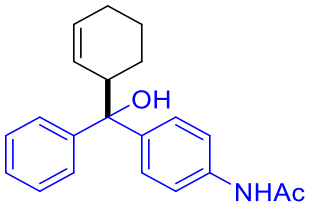
ketone **1h** (42.4 mg, 0.2 mmol, 1.0 equiv), cyclohexene (**3a)** (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (10-15% EtOAc-Hex) to obtain the product as a colourless oil (43.5 mg, 74%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (500 MHz, $CDCl_3$): 7.57 (d, *J* = 8.5 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.0 Hz, 0.5H), 7.15 (t, *J* = 7. Hz, 0.5H), 6.86 (d, *J* = 8.5 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 1H), 5.99-5.93 (m, 1H), 5.53 (d, *J* = 10.5 Hz, 0.5H), 5.48 (d, *J* = 10.0 Hz, 0.5H), 3.78 (s, 1.5H), 3.76 (s, 1.5H), 3.40 (brs, 1H), 2.19 (s, 0.5H), 2.17 (s, 0.5H), 2.01-2.00 (m, 2H), 1.79-1.77 (m, 1H), 1.55-1.41 (m, 3H). δ ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.3, 158.0, 147.2, 146.0, 139.2, 138.0, 133.7, 133.6, 128.4, 128.1, 127.4, 126.8, 126.7, 126.7, 126.6, 126.2, 126.1, 125.5, 113.7, 113.5, 79.3, 79.2, 55.3, 44.0, 43.9, 25.4, 24.0, 22.2. HRMS calcd. for $C_{20}H_{22}O_2$+H^+ $(M+H^+)^+$: 295.1698, found 295.1698.

(4-Aminophenyl)(cyclohex-2-en-1-yl)(phenyl)methanol (2.9)



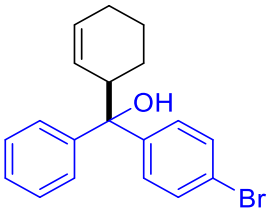
Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), ketone **1i** (39.5 mg, 0.2 mmol, 1.0 equiv), cyclohexene (**3a)** (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (40-60% EtOAc-Hex) to obtain the product as a colourless oil (23.3 mg, 47%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.11 (m, 7H), 6.65-6.59 (m, 2H), 5.97-5.91 (m, 1H), 5.57 (d, 10.4 Hz, 0.5H), 5.47 (d, 10.4 Hz, 0.5H), 3.60 (brs, 2H), 3.38-3.33 (m, 1H), 2.15-2.08 (m, 1H), 2.00-1.99 (m, 2H), 1.80-1.74 (m, 1H), 1.55-1.38 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 146.3, 145.0, 144.7, 137.2, 136.1, 133.4, 133.3, 128.3, 128.0, 127.3, 127.0, 126.8, 126.5, 126.1, 125.6, 115.1, 114.9, 79.4, 79.3, 44.1, 43.9, 25.4, 24.0, 22.2. HRMS calcd. for $C_{19}H_{21}NO$+H^+ $(M+H^+)^+$: 280.1701, found 280.1703.

N-(4-(cyclohex-2-en-1-yl(hydroxy)(phenyl)methyl)phenyl)acetamide (2.10)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), ketone **1j** (47.9mg, 0.2 mmol, 1.0 equiv), cyclohexene (**3a)** (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (40-60% EtOAc-Hex) to obtain the product as a colourless oil (53.4 mg, 83%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.12 (m, 10H), 5.97-5.95 (m, 1H), 5.50-5.45 (m, 1H), 3.41-3.40 (m, 1H), 2.21 (s, 1H), 2.14 (s, 1.5H), 2.12 (s, 1.5H), 2.00-1.99 (m, 2H), 1.78-1.75 (m, 1H), 1.53-1.41 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.4, 146.9, 145.6, 143.0, 141.8, 136.4, 136.1, 133.9, 128.4, 128.1, 126.9, 126.7, 126.5, 126.3, 126.1, 125.6, 119.9, 119.7, 79.3, 43.8, 25.4, 24.7, 23.9, 22.1. HRMS calcd. for $C_{22}H_{24}NO_2$+H^+ $(M+H^+)^+$: 322.1807, found 322.1810.

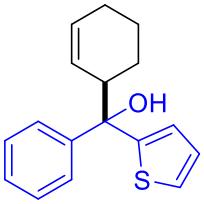
(4-Bromophenyl)(cyclohex-2-en-1-yl)(phenyl)methanol (2.11)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), ketone **1k** (52.2mg, 0.2 mmol, 1.0 equiv), cyclohexene (**3a)** (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (2-5% EtOAc-Hex) to obtain the product as a colourless oil (51.5 mg, 75%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.13 (m, 9H), 5.98 (brs, 1H), 5.51-5.43 (m, 1H), 3.41 (brs, 1H), 2.21 (s, 1H), 2.01 (brs, 2H), 1.79-1.76 (m, 1H), 1.52-1.43 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 146.4, 146.0, 145.5, 145.0, 144.7, 134.3, 133.8, 131.3, 131.1, 128.4, 128.3, 128.2, 128.0, 127.4, 126.8, 126.6, 126.5, 126.2, 126.1, 126.0, 125.5, 125.4, 120.6, 79.1, 43.7,

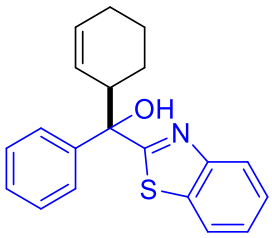
43.5, 25.3, 25.2, 23.8, 23.7, 22.0. HRMS calcd. for $C_{19}H_{19}BrO+H^+$ $(M+H^+)^+$: 343.0698, found 343.0693.

Cyclohex-2-en-1-yl(phenyl)(thiophen-2-yl)methanol (2.12)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), ketone **1m** (37.7 mg, 0.2 mmol, 1.0 equiv), allylic substrate **3a** (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (2-5% EtOAc-Hex) to obtain the product as a colourless oil (35.3 mg, 65%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.61 (m, 2H), 7.53-7.51 (m, 2H), 7.36-7.14 (m, 8H), 7.09 (dd, *J* = 3.6, 1.0 Hz, 1H), 6.96 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.93-6.90 (m, 2H), 6.05-6.00 (m, 1H), 5.93-5.89 (m, 1H), 5.63 (dd, *J* = 10.4, 2.0 Hz, 1H), 5.36 (dt, *J* = 10.4, 1.6 Hz, 1H), 3.35-3.23 (m, 2H), 2.61 (s, 1H), 2.39 (s, 1H), 2.03-1.96 (m, 4H), 1.83-1.68 (m, 2H), 1.60-1.34 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 151.2, 146.0, 144.8, 134.4, 133.4, 128.4, 128.2, 127.1, 126.9, 126.7, 126.3, 126.2, 125.7, 125.4, 124.6, 124.0, 123.3, 123.0, 79.5, 79.2, 46.5, 46.4, 25.4, 25.3, 24.2, 24.0, 22.0, 21.9. HRMS calcd. for $C_{17}H_{18}OS+H^+$ $(M+H^+)^+$: 271.1157, found 271.1158.

Benzo[*d*]thiazol-2-yl(cyclohex-2-en-1-yl)(phenyl)methanol (2.13)



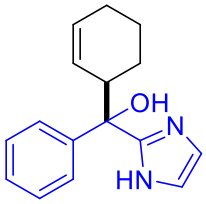
Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), ketone **1n** (47.9 mg, 0.2 mmol, 1.0 equiv), cyclohexene (**3a)** (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (2-5% EtOAc-Hex) to obtain the product as a yellow oil (Diastereomer 1) and colourless oil (Diastereomer 2) (45.0 mg, 70%).

Diastereomer 1: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.79-7.77 (m, 2H), 7.48-7.44 (m, 1H), 7.33 (t, *J* = 7.6 Hz, 3H), 7.25-7.21 (m, 1H), 6.07-6.03 (m, 1H), 5.47 (dd, *J* = 10.4, 2.0 Hz, 1H), 3.80-3.75 (m, 1H), 3.37 (s, 1H), 2.05-2.00 (m, 2H), 1.79-1.74 (m, 1H), 1.56-1.37 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.8, 153.6, 141.8, 135.7, 135.0, 128.3, 127.4, 126.0, 125.7, 125.6, 125.0, 123.3, 121.8, 80.9, 46.1, 25.4, 23.6, 21.7.

Diastereomer 2: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.85-7.82 (m, 3H), 7.45-7.24 (m, 5H), 5.96-5.93 (m, 1H), 5.32 (d, *J* = 10.0 Hz, 1H), 3.66-3.63 (m, 1H), 3.43 (s, 1H), 2.01 (brs, 2H), 1.82-1.77 (m, 1H), 1.69-1.53 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.3, 153.1, 143.5, 135.5, 133.5, 128.5, 127.6, 126.1, 125.9, 125.4, 124.8, 123.1, 121.8, 80.9, 46.2, 25.2, 23.8, 21.9.

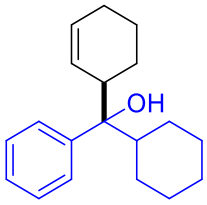
HRMS calcd. for $C_{20}H_{19}NOS+H^+$ $(M+H^+)^+$: 322.1266, found 322.1267.

Cyclohex-2-en-1-yl(1*H*-imidazol-2-yl)(phenyl)methanol (2.14)



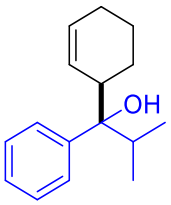
Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), ketone **1p** (34.4 mg, 0.2 mmol, 1.0 equiv), cyclohexene (**3a)** (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (20-30% EtOAc-Hex) to obtain the product as a white solid (20.3 mg, 40%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.32 (brs, 1H), 7.74-6.93 (m, 7H), 6.03-6.01 (m, 0.5H), 5.94-5.92 (m, 0.5H), 5.42 (d, *J* = 10.0 Hz, 0.5H), 5.25 (d, *J* = 10.4 Hz, 0.5H), 3.56-3.49 (m, 1H), 1.98 (brs, 2H), 1.75-1.37 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ HRMS calcd. for $C_{16}H_{18}N_2O+H^+$ $(M+H^+)^+$: 255.1497, found 255.1501.

Cyclohex-2-en-1-yl(cyclohexyl)(phenyl)methanol (2.15)



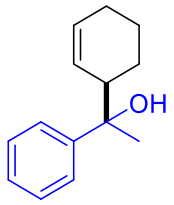
Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), ketone **1q** (37.6 mg, 0.2 mmol, 1.0 equiv), cyclohexene (**3a)** (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (2-5% EtOAc-Hex) to obtain the product as a colourless oil (36.3 mg, 67%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.28 (m, 4H), 7.25-7.20 (m, 1H), 5.92-5.81 (m, 1.5H), 5.15 (d, *J* = 10.4 Hz, 0.5H), 3.04-3.00 (m, 0.5H), 2.96-2.92 (m, 0.5H), 1.95-1.42 (m, 14H), 1.25-1.17 (m, 2H), 1.03-0.87 (m, 2H), 0.59-0.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 143.0, 132.8, 131.8, 127.5, 127.4, 127.3, 126.8, 126.6, 126.4, 126.4, 126.2, 80.4, 80.2, 46.1, 44.8, 41.8, 41.1, 27.9, 27.8, 27.3, 27.2, 27.0, 26.9, 26.8, 26.7, 26.6, 25.4, 25.3, 24.4, 23.1, 22.4, 22.1. HRMS calcd. for $C_{19}H_{25}O+H^+$ $(M+H^+)^+$: 271.2062, found 271.2066.

1-(Cyclohex-2-en-1-yl)-2-methyl-1-phenylpropan-1-ol (2.16)



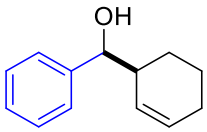
Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), ketone **1r** (30.0 µL, 0.2 mmol, 1.0 equiv), cyclohexene (**3a)** (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (2-5% EtOAc-Hex) to obtain the product as a colourless oil (28.1 mg, 61%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43-7.18 (m, 5H), 5.87-5.81 (m, 1.5H), 5.19 (d, *J* = 10.0 Hz, 0.5H), 2.98 (brs, 0.5H), 2.88 (brs, 0.5H), 2.29-2.18 (m, 1H), 1.91-1.17 (m, 7H), 0.85-0.75 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.3, 142.3, 132.5, 131.4, 127.4, 127.3, 127.2, 126.9, 126.7, 126.4, 126.3, 126.2, 80.5, 42.2,41.7, 34.8, 33.8, 25.3, 25.2, 24.4, 23.0, 22.3, 21.9, 17.6, 17.5, 16.9, 16.8. δ HRMS calcd. for $C_{16}H_{22}O+H^+$ $(M+H^+)^+$: 231.1749, found 231.1746.

1-(Cyclohex-2-en-1-yl)-1-phenylethan-1-ol (2.17)



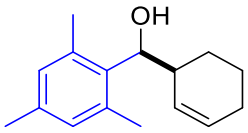
Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), ketone **1s** (23.6 µL, 0.2 mmol, 1.0 equiv), cyclohexene (**3a)** (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (2-5% EtOAc-Hex) to obtain the product as a colourless oil (20.2 mg, 50%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.22 (m, 5H) 5.93-5.89 (m, 0.5H), 5.86-5.82 (m, 0.5H), 5.78 (d, *J* = 10.4 Hz, 0.5H), 5.36 (d, *J* = 10.4 Hz, 0.5H), 2.68-2.52 (m, 1H), 1.97-1.95 (m, 2H), 1.79-1.69 (m, 3H), 1.60 (s, 1.5H), 1.49-1.38 (m, 3.5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 147.3, 131.8, 131.7, 128.2, 128.1, 127.0, 126.6, 125.3, 125.2, 76.4, 76.2, 46.7, 46.5, 28.0, 26.8, 25.3 24.5, 24.1, 22.2, 22.1. HRMS calcd. for $C_{20}H_{22}O_2$+H^+ $(M+H^+)^+$: 203.1436, found 203.1435.

Cyclohex-2-en-1-yl(phenyl)methanol (3.1)



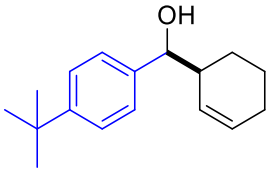
Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), aldehyde **2a** (30.0 µL, 0.2 mmol, 1.0 equiv), cyclohexene (**3a)** (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (5-10% EtOAc-Hex) to obtain the product as a colourless oil (23.7 mg, 63%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.26 (m, 5H), 5.88-5.79 (m, 1.5H), 5.39 (dd, *J* = 10.0, 2.0 Hz, 0.5H), 4.59 (d, *J* = 6.4 Hz, 0.5H), 4.47 (dd, *J* = 6.8, 3.2 Hz, 0.5H), 2.54-2.46 (m, 1H), 2.01-1.97 (m, 2H), 1.92-1.88 (m, 1H), 1.80-1.68 (m, 1.5H), 1.56-1.45 (m, 2H), 1.35-1.26 (m, 0.5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 143.0, 130.6, 130.1, 128.4, 128.3, 128.1, 127.6, 127.5, 127.1, 126.7, 126.4, 78.2, 43.2, 43.0, 26.4, 25.4, 25.3, 24.0, 21.7, 21.3. HRMS calcd. for $C_{13}H_{16}O$+H^+ $(M+H^+)^+$: 189.1279, found 189.1287.

Cyclohex-2-en-1-yl(mesityl)methanol (3.2)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), aldehyde **2b** (29.5 µL, 0.2 mmol, 1.0 equiv), cyclohexene (**3a**) (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (5-10% EtOAc-Hex) to obtain the product as a colourless oil (21.7 mg, 47%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (s, 2H), 6.10 (dd, *J* = 10.0, 1.6 Hz, 0.5H), 5.88-5.83 (m, 0.5H), 5.68-5.63 (m, 0.5H), 5.02 (dd, *J* = 10.0, 2.4 Hz, 0.5H), 4.85 (dd, *J* = 14.4, 10.0 Hz, 1H), 2.87-2.78 (m, 1H), 2.42 (s, 3H), 2.39 (s, 3H), 2.25 (s, 3H), 2.04-1.98 (m, 2H), 1.85-1.60 (m, 3H), 1.52-1.42 (m, 0.5H), 1.36-1.29 (m, 1H), 1.11-1.02 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8, 136.7, 135.8, 135.6, 130.4, 129.3, 129.0, 128.4, 127.7, 75.1, 74.7, 40.1, 39.8, 26.6, 25.8, 25.5, 25.4, 21.8, 21.2, 20.9, 20.6. HRMS calcd. for $C_{16}H_{22}O+H^+$ $(M+H^+)^+$: 231.1749, found 231.1754.

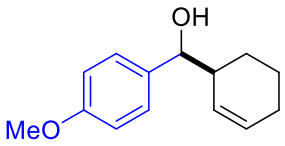
(4-(Tert-butyl)phenyl)(cyclohex-2-en-1-yl)methanol (3.3)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), aldehyde **2c** (33.7 µL, 0.2 mmol, 1.0 equiv), cyclohexene (**3a**) (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (5-10% EtOAc-Hex) to obtain the product as a colourless oil (22.0 mg, 45%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.36 (m, 2H), 7.28-7.26 (m, 2H), 5.89-5.78 (m, 1.5H), 3.38 (dd, *J* = 10.4, 2.0 Hz, 0.5H), 4.54 (d, *J* = 6.8 Hz, 0.5H), 4.44 (d, *J* = 6.8 Hz, 0.5H), 2.51-2.45 (m, 1H), 2.02-1.98 (m, 2H), 1.83-1.44 (m, 5H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 150.4, 140.7, 140.1, 130.2, 129.8, 128.3, 127.4, 126.4, 126.1, 125.3, 125.2, 78.0, 43.0, 42.9,

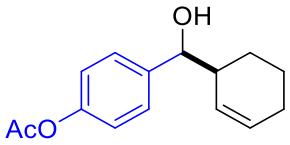
34.6, 31.5, 26.5, 25.4, 25.3, 24.2, 21.7, 21.3, 17.8. HRMS calcd. for $C_{17}H_{24}O+H^+$ $(M+H^+)^+$: 245.1905, found 189.1905.

Cyclohex-2-en-1-yl(4-methoxyphenyl)methanol (3.4)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), aldehyde **2d** (24.3 µL, 0.2 mmol, 1.0 equiv), cyclohexene (**3a**) (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (10-15% EtOAc-Hex) to obtain the product as a colourless oil (21.0 mg, 48%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.25 (m, 2H), 6.90-6.87 (d, *J* = 8.4 Hz, 2H), 5.89-5.77 (m, 1.5H), 5.36 (dd, *J* = 10.0, 2.0 Hz, 0.5H), 4.51 (dd, *J* = 6.8, 2.0 Hz, 0.5H), 4.41 (dd, *J* = 7.2, 4.0 Hz, 0.5H), 3.81 (s, 3H), 2.50-2.42 (m, 1H), 2.00-1.97 (m, 2H), 1.82-1.67 (m, 2.5H), 1.54-1.43 (m, 2H), 1.29-1.20 (m, 0.5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 159.1, 135.9, 135.3, 130.3, 129.8, 128.2, 127.9, 127.6, 127.5, 113.8, 113.7, 77.9, 77.3, 55.4, 43.2, 43.0, 26.4, 25.4, 24.4, 21.6, 21.2. HRMS calcd. for $C_{14}H_{18}O_2+H^+$ $(M+H^+)^+$: 219.1385, found 219.1386.

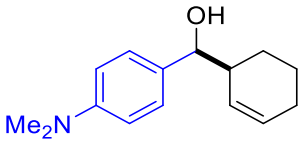
4-(Cyclohex-2-en-1-yl(hydroxy)methyl)phenyl acetate (3.5)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), aldehyde **2e** (28.1 µL, 0.2 mmol, 1.0 equiv), cyclohexene (**3a**) (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (10-15% EtOAc-Hex) to obtain the product as a colourless oil (19.7 mg, 40%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.33 (m, 2H), 7.08-7.05 (m, 2H), 5.88-5.80 (m, 1.5H), 5.39 (d, *J* = 10.0 Hz, 0.5H), 4.59 (d, *J* = 6.4 Hz, 0.5H), 4.47 (d, *J* = 6.8 Hz, 0.5H), 2.49-2.45 (m, 1H), 2.29 (s, 3H), 1.99-1.93 (m, 3H), 1.79-1.44 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 150.0,

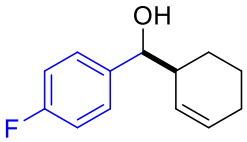
141.3, 140.6, 130.7, 130.2, 128.0, 127.7, 127.4, 126.9, 121.5, 121.4, 77.6, 77.0, 43.1, 43.0, 26.4, 25.4, 23.9, 21.6, 21.3, 21.2. HRMS calcd. for $C_{15}H_{18}O_3+H^+$ $(M+H^+)^+$: 247.1334, found 247.1341.

Cyclohex-2-en-1-yl(4-(dimethylamino)phenyl)methanol (3.6)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), aldehyde **2f** (33.7 µL, 0.2 mmol, 1.0 equiv), cyclohexene (**3a**) (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (20-30% EtOAc-Hex) to obtain the product as a green oil (7.4 mg, 16%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.19 (m, 2H), 6.73-6.71 (m, 2H), 5.93 (dd, *J* = 10.4, 1.6 Hz, 0.5H), 5.86-5.82 (m, 0.5H), 5.78-5.73 (m, 0.5H), 5.35 (dd, *J* = 10.0, 2.0 Hz, 0.5H), 4.44 (d, *J* = 7.2 Hz, 0.5H), 4.34 (d, *J* = 7.6 Hz, 0.5H), 2.94 (s, 6H), 2.50-2.43 (m, 1H), 2.00-1.96 (m, 2H), 1.86-1.67 (m, 2.5H), 1.54-1.42 (m, 2.5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 131.6, 131.1, 129.8, 129.3, 128.5, 128.1, 127.7, 127.4, 112.5, 78.3, 77.7, 43.0, 42.8, 40.8, 26.4, 25.5, 25.4, 24.8, 21.7, 21.3. HRMS calcd. for $C_{15}H_{21}NO+H^+$ $(M+H^+)^+$: 254.1521, found 254.1523.

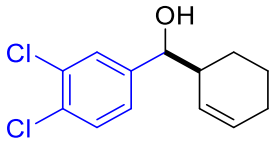
Cyclohex-2-en-1-yl(4-fluorophenyl)methanol (3.7)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), aldehyde **2g** (21.5 µL, 0.2 mmol, 1.0 equiv), cyclohexene (**3a**) (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (5-10% EtOAc-Hex) to obtain the product as a colourless oil (19.0 mg, 46%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.28 (m, 2H), 7.05-7.00 (m, 2H), 5.88-5.78 (m, 1.5H), 5.36 (d, *J* = 10.0 Hz, 0.5H), 4.57 (d, *J* = 6.4 Hz, 0.5H), 4.45 (d, *J* = 6.8 Hz, 0.5H), 2.50-2.43 (m, 1H), 1.98-

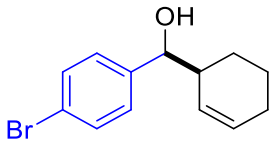
1.94 (m, 3H), 1.78-1.65 (m, 1.5H), 1.55-1.44 (m, 2H), 1.31-1.29 (m, 0.5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5, 163.4, 161.1, 161.0, 139.4, 139.3, 138.7, 138.6, 130.8, 130.3, 128.2, 128.1, 128.0, 127.9, 127.8, 126.9, 115.3, 115.2, 115.1, 115.0, 77.5, 43.2, 43.0, 26.3, 25.4, 25.3, 23.9, 21.6, 21.2. HRMS calcd. for $C_{13}H_{15}FO+H^+$ $(M+H^+)^+$: 207.1185, found 207.1179.

Cyclohex-2-en-1-yl(3,4-dichlorophenyl)methanol (3.8)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), aldehyde **2h** (35.0 mg, 0.2 mmol, 1.0 equiv), cyclohexene (**3a**) (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (5-10% EtOAc-Hex) to obtain the product as a yellow oil (35.5 mg, 70%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.39 (m, 2H), 7.17-7.15 (m, 1H), 5.89-5.86 (m, 1H), 5.69 (dd, *J* = 10.0, 1.6 Hz, 0.5H), 5.40 (10.0, 1.6 Hz, 0.5H), 4.58 (d, *J* = 5.6 Hz, 0.5H), 4.46 (d, *J* = 6.4 Hz, 0.5H), 2.48-2.42 (m, 1H), 2.01-1.96 (m, 3H), 1.76-1.70 (m, 1H), 1.61-1.45 (m, 2H), 1.36-1.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 143.2, 132.6, 132.5, 132.4, 131.6, 131.3, 131.2, 131.0, 130.3, 130.2, 128.6, 128.4, 127.4, 126.0, 125.9, 125.8, 76.1, 43.1, 43.0, 26.3, 25.3, 23.4, 21.6, 21.2. HRMS calcd. for $C_{13}H_{15}Cl_2O+H^+$ $(M+H^+)^+$: 257.0500, found 257.0500.

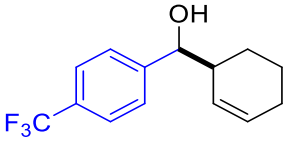
(4-Bromophenyl)(cyclohex-2-en-1-yl)methanol (3.9)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), aldehyde **2i** (37.0 mg, 0.2 mmol, 1.0 equiv), cyclohexene (**3a**) (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (5-10% EtOAc-Hex) to obtain the product as a yellow oil (17.1 mg, 32%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.34 (m, 3H), 7.30-7.27 (m, 1H), 5.88-5.80 (m, 1.5H), 5.39 (d, *J* =

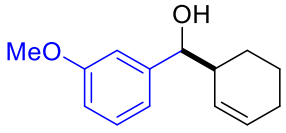
10.0, 2.0 Hz, 0.5H), 4.59 (d, *J* = 6.4 Hz, 0.5H), 4.48 (dd, *J* = 6.8, 3.6 Hz, 0.5H), 2.53-2.47 (m, 1H), 2.00-1.97 (m, 2H), 1.88-1.68 (m, 2.5H), 1.52-1.30 (m, 2.5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 143.0, 130.6, 130.1, 128.4, 128.3, 128.2, 127.6,127.5, 127.1, 126.7, 126.4, 78.2, 43.2, 43.0, 29.8, 26.5, 25.4, 24.0, 21.7, 21.3. HRMS calcd. for $C_{13}H_{15}BrO+Na^+$ $(M+Na^+)^+$: 289.0204, found 289.0208.

Cyclohex-2-en-1-yl(4-(trifluoromethyl)phenyl)methanol (3.10)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), aldehyde **2j** (27.3 µL, 0.2 mmol, 1.0 equiv), cyclohexene (**3a**) (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (5-10% EtOAc-Hex) to obtain the product as a colourless oil (25.1 mg, 49%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.60 (m, 2H), 7.47-7.45 (m, 2H), 5.90-5.87 (m, 1H), 5.72 (dd, *J* = 10.0, 1.2 Hz, 0.5H), 5.42 (dd, *J* = 10.0, 1.6 Hz, 0.5H), 4.71 (d, *J* = 4.4 Hz, 0.5H), 4.58 (t, *J* = 5.6 Hz), 2.55-2.47 (m, 1H), 2.00-1.93 (m, 3H), 1.79-1.70 (m, 1H), 1.62-1.31 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 146.9, 131.5, 131.0, 129.9, 129.8, 129.6, 129.5, 127.6, 126.9, 126.7, 126.1, 125.4-125.2 (m), 76.7, 43.2, 43.0, 26.4, 25.3, 23.3, 21.6, 21.2. HRMS calcd. for $C_{14}H_{15}F_3O+H^+$ $(M+H^+)^+$: 257.1153, found 257.1154.

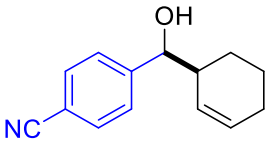
Cyclohex-2-en-1-yl(3-methoxyphenyl)methanol (3.11)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), aldehyde **2k** (24.4 µL, 0.2 mmol, 1.0 equiv), cyclohexene (**3a**) (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (10-15% EtOAc-Hex) to obtain the product as a colourless oil (21.4 mg, 49%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR

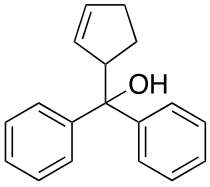
(400 MHz, $CDCl_3$): δ 7.28-7.24 (m, 1.5H), 6.92-6.81 (m, 3H), 5.88-5.80 (m, 1.5H), 5.40 (dd, *J* = 10.0, 1.6 Hz, 0.5H), 4.56 (d, *J* = 6.4 Hz, 0.5H), 4.45 (d, *J* = 6.4 Hz, 0.5H), 3.82 (s, 3H), 2.49 (brs, 1H), 1.99 (brs, 2H), 1.89-1.86 (m, 1H), 1.79-1.70 (m, 1.5H), 1.55-1.44 (m, 2H), 1.37-1.28 (m, 0.5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 159.7, 145.4, 144.8, 130.6, 130.1, 129.4, 129.3, 128.2, 127.1, 119.0, 118.8, 113.0, 112.9, 112.2, 112.0, 78.1, 55.4, 43.1, 43.0, 26.5, 25.4, 25.3, 24.0, 21.7, 21.3. HRMS calcd. for $C_{14}H_{18}O_2+H^+$ $(M+H^+)^+$: 241.1204, found 241.1200.

4-(Cyclohex-2-en-1-yl(hydroxy)methyl)benzonitrile (3.12)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), aldehyde **2m** (33.7 µL, 0.2 mmol, 1.0 equiv), cyclohexene (**3a**) (0.1 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (15-20% EtOAc-Hex) to obtain the product as a colourless oil (8.5 mg, 20%). Product was obtained as a mixture of 2 diastereomers. ^1H NMR (500 MHz, $CDCl_3$): δ 7.64 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 5.93-5.87 (m, 1H), 5.64 (dd, *J* = 10.4, 1.2 Hz, 0.5H), 5.42 (dd, *J* = 10.0, 2.0 Hz, 0.5H), 4.72 (d, 5.6 Hz, 0.5H), 4.59 (d, *J* = 6.0 Hz, 0.5H), 2.54-2.46 (m, 1H), 2.02-1.97 (m, 3H), 1.77-1.70 (m, 1H), 1.54-1.45 (m, 2H), 1.41-1.33 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 148.2, 132.8, 132.2, 132.1, 132.0, 131.4, 130.7, 127.2, 127.1, 126.1, 125.6, 119.1, 119.0, 111.3, 111.2, 76.4, 43.2, 43.1, 26.3, 25.3, 23.1, 21.5, 21.1. HRMS calcd. for $C_{14}H_{15}NO+H^+$ $(M+H^+)^+$: 214.1232, found 214.1231.

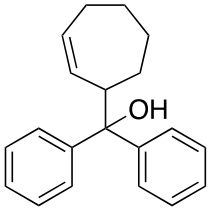
Cyclopent-2-en-1-yldiphenylmethanol (4.1)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), benzophenone (**1a)** (36.4 mg, 0.2 mmol, 1.0 equiv), allylic substrate **3b** (0.13 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up

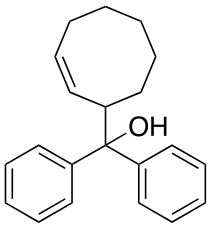
was purified by silica gel flash column chromatography (1-5% EtOAc-Hex) to obtain the product as a colourless oil (39.1 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.15 (m, 10H), 6.02-5.99 (m, 1H), 5.44-5.41 (m, 1H), 2.40-2.33 (m, 2H), 2.24 (s, 1H) 1.91-1.78 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 146.4, 136.7, 129.9, 128.3, 128.2, 126.6, 126.5, 126.0, 125.9, 79.4, 55.2, 32.9, 24.9. HRMS calcd. for $C_{18}H_{18}O+H^+$ $(M+H^+)^+$: 251.1436, found 251.1436.

Cyclohept-2-en-1-yldiphenylmethanol (4.2)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), benzophenone (**1a)** (36.4 mg, 0.2 mmol, 1.0 equiv), allylic substrate **3c** (0.18 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (1-5% EtOAc-Hex) to obtain the product as a colourless oil (40.1 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.14 (m, 10H), 5.86-5.79 (m, 1H), 5.65-5.61 (m, 1H), 3.55-3.53 (m, 1H), 2.24-2.19 (m, 3H), 1.98-1.93 (m, 1H), 1.77-1.58 (m, 3H), 1.38-1.29 (m, 2H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8, 146.7, 133.7, 132.6, 128.4, 128.3, 126.6, 126.2, 125.8, 81.2, 47.8, 30.7, 28.4, 26.4. HRMS calcd. for $C_{20}H_{22}O+H^+$ $(M+H^+)^+$: 279.1749, found 279.1750.

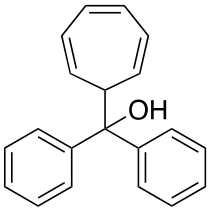
(*Z*)-Cyclooct-2-en-1-yldiphenylmethanol (4.3)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), benzophenone (**1a)** (36.4 mg, 0.2 mmol, 1.0 equiv), allylic substrate **3d** (0.13 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (1-5% EtOAc-Hex) to obtain the

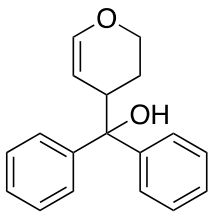
product as a colourless oil (44.2 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.14 (m, 10H), 5.72-5.65 (m, 1H), 5.52-5.47 (m, 1H), 3.73-3.67 (m, 1H), 1.76-1.66 (m, 2H), 1.55-1.32 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 147.0, 130.2, 130.1, 128.3, 128.2, 126.7, 126.5, 126.3, 125.9, 80.2, 44.2, 30.2, 29.6, 27.2, 27.1, 25.7. HRMS calcd. for $C_{21}H_{24}O+H^+$ $(M+H^+)^+$: 293.1905, found 293.1909.

Cyclohepta-2,4,6-trien-1-yldiphenylmethanol (4.4)

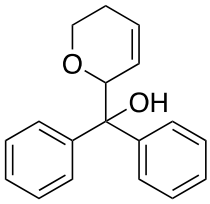


Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), benzophenone (**1a)** (36.4 mg, 0.2 mmol, 1.0 equiv), allylic substrate **3e** (0.18 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (1-5% EtOAc-Hex) to obtain the product as a colourless oil (46.1 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.20 (m, 10H), 6.76-6.70 (m, 1H), 6.26-6.22 (m, 2H), 5.40 (dd, *J* = 5.6, 9.2 Hz, 2H), 2.64 (t, *J* = 5.6 Hz, 1H), 2.52 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 130.9, 128.5, 127.1, 126.3, 125.0, 122.9, 78.9, 47.7. HRMS calcd. for $C_{20}H_{18}O+H^+$ $(M+H^+)^+$: 275.1436, found 275.1442.

(3,4-Dihydro-2*H*-pyran-4-yl)diphenylmethanol and (5,6-dihydro-2*H*-pyran-2-yl)diphenylmethanol (4.5)



Regioisomer 1



Regioisomer 2

Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), benzophenone (**1a)** (36.4 mg, 0.2 mmol, 1.0 equiv), allylic substrate **3f** (0.09 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up

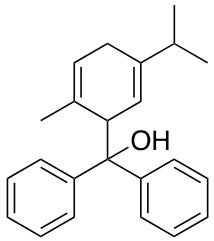
was purified by silica gel flash column chromatography (15-20% EtOAc-Hex) to obtain the product as two separate regioisomers. Product obtained in total 44.2 mg, 83%.

Regioisomer 1: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.14 (m, 10H), 6.57 (dd, *J* = 1.6, 6.4 Hz, 1H), 4.48 (dt, *J* = 2.0, 6.4 Hz, 1H), 4.12 (dt, *J* = 4.4, 10.8 Hz, 1H), 3.91 (td, *J* = 2.4, 10.8 Hz, 1H), 3.53-3.48 (m, 1H), 2.35 (s, 1H), 1.96-1.87 (m, 1H), 1.52-1.46 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 146.5, 145.0, 128.5, 128.3, 127.0, 126.6, 126.2, 125.5, 99.3, 78.6, 65.6, 38.9, 24.3.

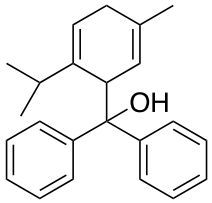
Regioisomer 2: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.18 (m, 10H), 5.99-5.95 (m, 1H), 5.42 (dt, *J* = 1.2, 10.4 Hz, 1H), 5.11-5.10 (m, 1H), 4.09 (dd, *J* = 6.0, 11.2 Hz, 1H), 3.79 (td, *J* = 3.6, 11.2 Hz, 1H), 3.19 (s, 1H), 2.44-2.35 (m, 1H), 1.94-1.87 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 143.8, 128.3, 128.2, 128.1, 127.0, 126.9, 126.7, 126.2, 126.0, 79.3, 78.2, 64.8, 25.2.

HRMS calcd. for $C_{18}H_{18}O_2+H^+$ $(M+H^+)^+$: 267.1385, found 267.1385.

(5-Isopropyl-2-methylcyclohexa-2,5-dien-1-yl)diphenylmethanol and 2-isopropyl-5-methylcyclohexa-2,5-dien-1-yl)diphenylmethanol (4.6)



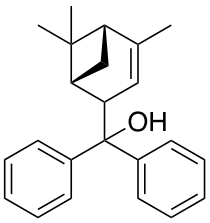
Regioisomer 1



Regioisomer 2

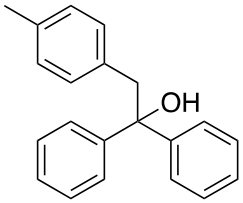
Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), benzophenone (**1a)** (36.4 mg, 0.2 mmol, 1.0 equiv), allylic substrate **3g** (0.16 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (1-5% EtOAc-Hex) to obtain the product as a colourless oil (33.1 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.16 (m, 10H), 5.76-5.30 (m, 2H), 2.74-2.51 (m, 3H), 2.22-2.16 (m, 1H), 1.69 (s, 0.5H), 1.13 (s, 2.5H), 0.92-0.66 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 146.4, 146.3, 146.0, 144.2, 138.3, 133.2, 129.1, 128.6, 128.1, 128.0, 127.9, 126.9, 126.6, 126.5, 126.4, 126.3, 126.2, 122.0, 121.3, 118.9, 81.5, 80.8, 50.6, 48.8, 34.6, 33.3, 31.9, 28.7, 24.5, 23.9, 23.1, 21.7, 21.3, 20.3. HRMS calcd. for $C_{23}H_{26}O+H^+$ $(M+H^+)^+$: 319.2062, found 319.2061.

Diphenyl((1*R*,5*S*)-4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-yl)methanol (4.7)



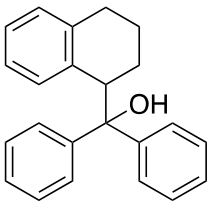
Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), benzophenone (**1a)** (36.4 mg, 0.2 mmol, 1.0 equiv), allylic substrate **3h** (0.16 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (1-5% EtOAc-Hex) to obtain the product as a colourless oil (36.9 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.14 (m, 10H), 5.12 (s, 1H), 3.47 (d, *J* = 2.0 Hz, 1H), 2.21-2.14 (m, 2H), 1.99-1.97 (m, 1H), 1.85-1.83 (m, 1H), 1.69 (s, 3H), 1.53 (d, *J* = 8.8 Hz, 1H), 1.27-1.26 (m, 1H), 1.22 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5, 147.8, 146.1, 128.3, 128.1, 126.6, 126.3, 125.8, 114.7, 80.3, 47.6, 47.2, 42.9, 42.2, 27.9, 26.4, 23.6, 20.8. HRMS calcd. for $C_{23}H_{26}O+H^+$ $(M+H^+)^+$: 319.2062, found 319.2062.

1,1-Diphenyl-2-(p-tolyl)ethan-1-ol (4.8)



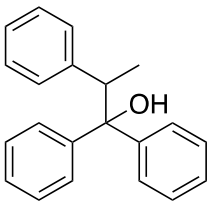
Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), benzophenone (**1a)** (36.4 mg, 0.2 mmol, 1.0 equiv), benzylic substrate **3i** (0.12 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (1-5% EtOAc-Hex) to obtain the product as a white solid (13.8 mg, 24%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45-7.43 (m, 4H), 7.32-7.29 (m, 4H), 7.24-7.21 (m, 2H), 6.97-6.96 (m, 2H), 6.79-6.78 (m, 2H), 3.62 (s, 2H), 2.33 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.8, 136.6, 132.6, 130.9, 129.0, 128.2, 127.0, 126.3, 77.9, 47.7, 21.2. HRMS calcd. for $C_{21}H_{20}O+H^+$ $(M+H^+)^+$: 289.1592, found 289.1593.

Diphenyl(1,2,3,4-tetrahydronaphthalen-1-yl)methanol (4.9)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), benzophenone (**1a)** (36.4 mg, 0.2 mmol, 1.0 equiv), benzylic substrate **3j** (0.13 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (1-5% EtOAc-Hex) to obtain the product as a colourless oil (42.8 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.60 (m, 2H), 7.55-7.53 (m, 2H), 7.33-7.28 (m, 4H), 7.21-7.16 (m, 2H), 7.12-7.05 (m, 2H), 6.76 (t, *J* = 7.6 Hz, 1H), 6.52-6.50 (m, 1H), 4.20 (t, *J* = 6.8 Hz, 1H), 2.84-2.66 (m, 2H), 2.10 (brs, 1H), 1.98 (sept, *J* = 6.0 Hz, 1H), 1.87-1.71 (m, 2H), 1.53-1.44 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 146.2, 141.2, 135.0, 130.4, 129.4, 128.3, 128.2,126.7, 126.6, 126.4, 126.2, 126.1, 125.2, 81.7, 46.0, 30.2, 26.5, 21.6. HRMS calcd. for $C_{23}H_{22}O+H^+$ $(M+H^+)^+$: 315.1749, found 315.1747.

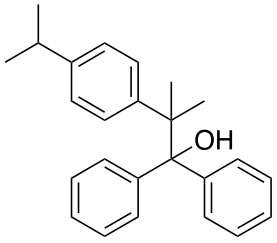
1,1,2-Triphenylpropan-1-ol (4.10)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), benzophenone (**1a)** (36.4 mg, 0.2 mmol, 1.0 equiv), benzylic substrate **3k** (0.12 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (1-5% EtOAc-Hex) to obtain the product as a colourless oil (32.9 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.61 (m, 2H), 7.38-7.33 (m, 2H), 7.29-7.22 (m, 3H), 7.16-7.02 (m, 8H), 3.99 (q, *J* = 6.8 Hz, 1H), 2.38 (brs, 1H), 1.34 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 145.9, 142.1, 129.6, 128.3,

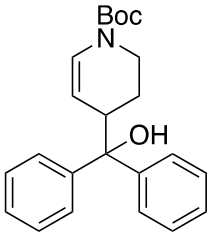
127.9, 127.8, 126.8, 126.6, 126.4, 126.3, 125.9, 80.6, 47.8, 16.7. HRMS calcd. for $C_{23}H_{26}O+H^+$ $(M+H^+)^+$: 311.1412, found 311.1418.

2-(4-Isopropylphenyl)-2-methyl-1,1-diphenylpropan-1-ol (4.11)



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), benzophenone (**1a)** (36.4 mg, 0.2 mmol, 1.0 equiv), benzylic substrate **3m** (0.16 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (1-5% EtOAc-Hex) to obtain the product as a colourless oil (42.0 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): 7.48-7.46 (m, 4H), 7.24-7.18 (m, 6H), 7.05-6.99 (m, 4H), 2.87 (sept, *J* = 6.8 Hz, 1H), 2.48 (s, 1H), 1.52 (s, 6H), 1.24 (d, *J* = 6.8 Hz, 6H). δ ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 145.3, 143.3, 129.0, 128.5, 127.3, 126.7, 125.4, 82.3, 47.5, 33.6, 26.7, 24.1. HRMS calcd. for $C_{25}H_{28}O+H^+$ $(M+H^+)^+$: 345.2218, found 345.2217.

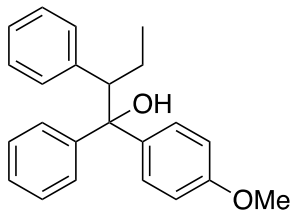
***Tert*-butyl 4-(hydroxydiphenylmethyl)-3,4-dihydropyridine-1(2H)-carboxylate (4.12)**



Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), benzophenone (**1a)** (36.4 mg, 0.2 mmol, 1.0 equiv), allylic substrate **3n** (0.19 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (15-25% EtOAc-Hex) to obtain the product as a colourless oil (43.7 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.15 (m, 10H), 7.08-6.90 (m, 1H), 4.70-4.57 (m, 1H), 3.95-3.81 (m, 1H), 3.50-3.46 (m, 1H), 3.27-3.24 (m, 1H), 2.29 (brs, 1H), 1.79-1.74 (m, 1H), 1.47 (s, 9H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8,

152.2, 146.6, 145.1, 130.1, 128.5, 128.3, 126.9, 126.6, 126.2, 125.5, 103.6, 103.3, 81.0, 79.1, 41.9, 41.0, 40.7, 40.4, 28.4, 23.2. HRMS calcd. for $C_{23}H_{27}NO_3+H^+$ $(M+H^+)^+$: 366.2069, found 366.2066.

1-(4-Methoxyphenyl)-1,2-diphenylbutan-1-ol (4.13)

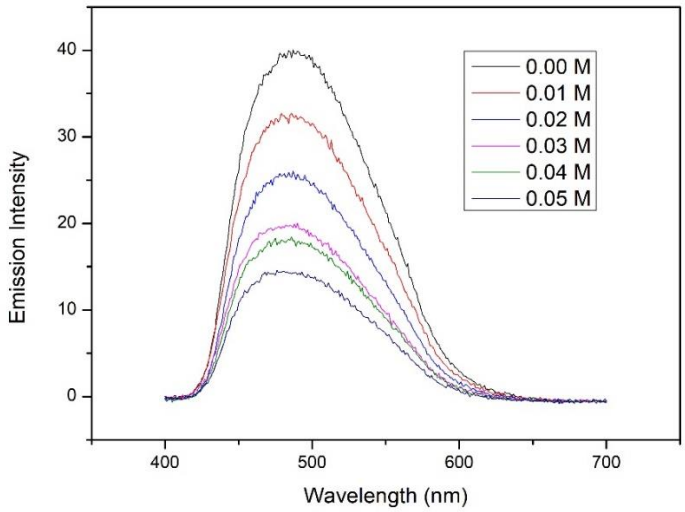


Following the general procedure, 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (3.1 mg, 2.5 mol%), anhydrous K_2CO_3 (5.6 mg, 20 mol%), Triisopropylsilanethiol (8.6 µL, 20 mol%), ketone **1h** (42.5 mg, 0.2 mmol, 1.0 equiv), benzylic substrate **3p** (0.14 mL, 5 equiv) and DMA (2 mL) was irradiated under blue LED for 24 hours. The crude mixture after work-up was purified by silica gel flash column chromatography (5-10% EtOAc-Hex) to obtain the product as a colourless oil (34.2 mg, 51%). Product was obtained as a mixture of 2 diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-6.63 (m, 14H), 3.81 (s, 1.5H), 3.69 (s, 1.5H), 3.60-3.55 (m, 1H), 2.38 (d, *J* = 2.8 Hz, 1H), 1.87-1.76 (m, 2H), 0.78-0.72 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 157.9, 146.9, 146.3, 140.0, 139.0, 138.4, 130.4, 130.3, 128.2, 127.9, 127.8, 127.7, 127.2, 126.7, 126.5, 126.4, 126.2, 125.9, 113.6, 113.1, 80.8, 56.6, 56.5, 55.4, 55.2, 23.5, 12.7. HRMS calcd. for $C_{23}H_{24}O_2+H^+$ $(M+H^+)^+$: 333.1855, found 333.1853.

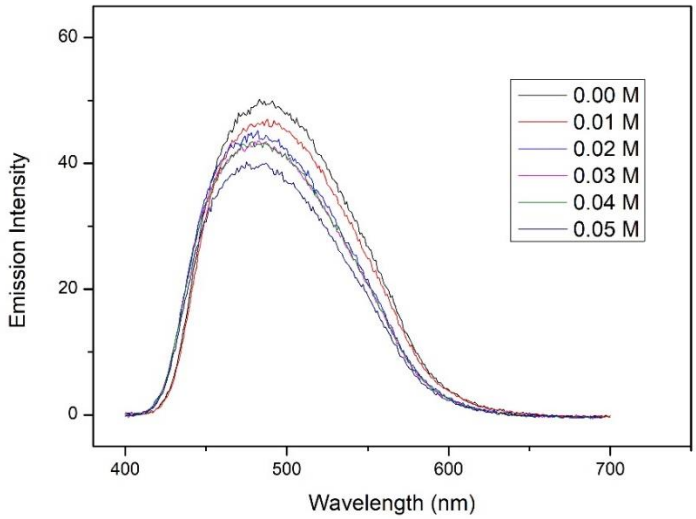
5. Fluorescence Quenching Study

Fluorescence quenching studies were performed with a RF-5301PC Spectrofluorophotometer. The experiments were carried out mixing a 5 x 10^{-4} M solution of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine in DMSO with the desired amount of quencher in quartz cuvette. All the solutions were irradiated at λ = 375 nm and the emission intensity at λ = 550 nm was observed. The samples were degassed first with nitrogen for 15 minutes then the emission spectrum of the sample was collected.

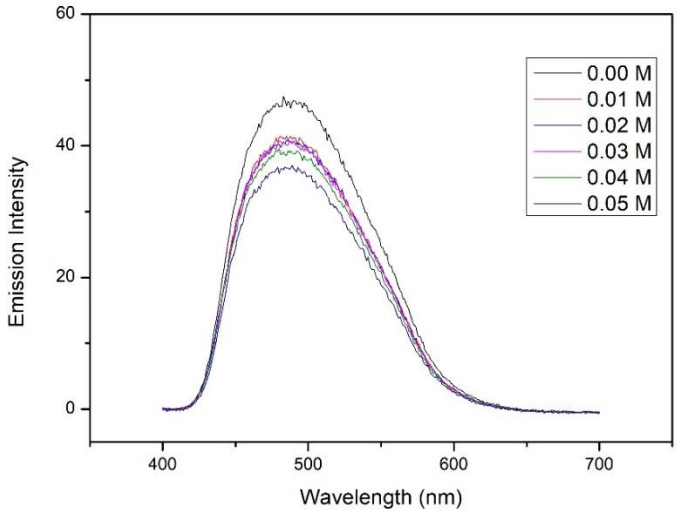
Quenching of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine with benzophenone:



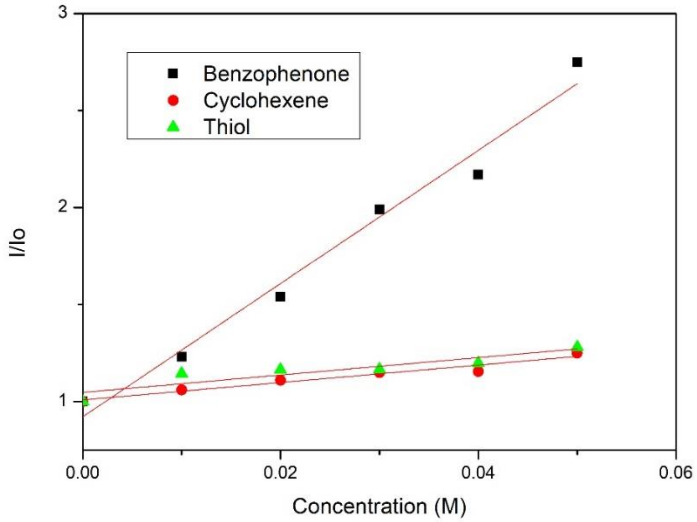
Quenching of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine with cyclohexene:



Quenching of 3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine with triisopropylsilanethiol:



Stern-Volmer Plot:



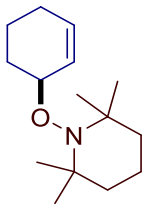
This confirms that the excited photocatalyst is quenched by the ketone not by the other two components.

6. Gram Scale Reaction

To an oven dried 100 ml round bottom flask equipped with a magnetic stirrer was added 0.1 mol% 3,7-Di(4-biphenyl)1-naphthalene-10-phenoxazine (3.36 mg, $5.49 \cdot 10^{-3}$ mmol), benzophenone (1 g, 5.48 mmol), 2 mol% triisopropylsilanethiol (23.57 µl, 0.11 mmol) and 2 mol% potassium carbonate (15.17 mg, 0.11 mmol). The flask was brought into a glove box under Ar atmosphere and dimethylacetamide (55 ml), cyclohexene (2.78 ml, 27.45 mmol) was added. The flask was sealed tightly and irradiate under 34 W Blue LED (with an USB cooling fan). After 48 hrs the reaction mixture was concentrated using vacuum and desired product was obtained after purification by flash column chromatography (Ethyl acetate/ hexane) as a white solid (1.19 g, 82%).

7. TEMPO Trapping Experiment

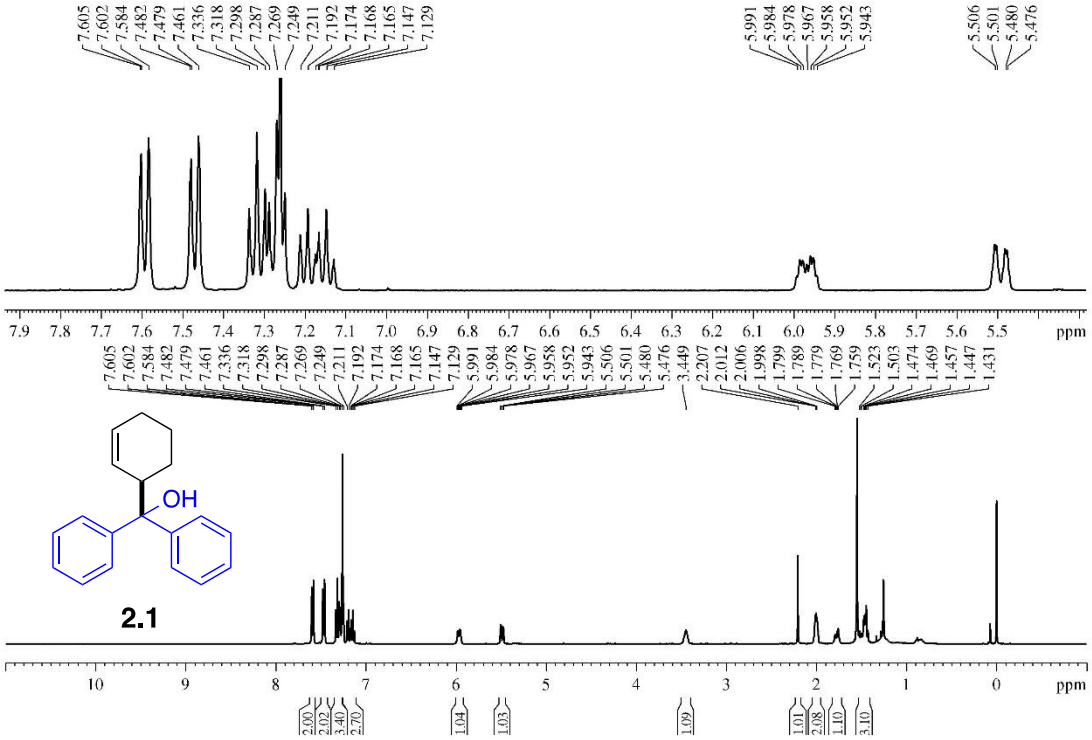
To an oven dried 4 ml vial equipped with a magnetic stirrer was added 3,7-Di(4-biphenyl)1-naphthalene-10-phenoxazine (0.05 mmol), benzophenone (0.2 mmol), 10 mol% triisopropylsilanethiol and 10 mol% potassium carbonate and TEMPO (1.2 equiv.). The vial was brought into a glove box under argon atmosphere and dimethylacetamide (2 mL), cyclohexene (5 equiv.) was added. The vial was sealed tightly and irradiate under 34 W Blue LEDs (with an USB cooling fan). After 12 hrs the reaction was stopped, and TEMPO adduct was obtained after purification by preparative thin layer chromatography (1%). NMR data is consistent with reported data* (see page S81).



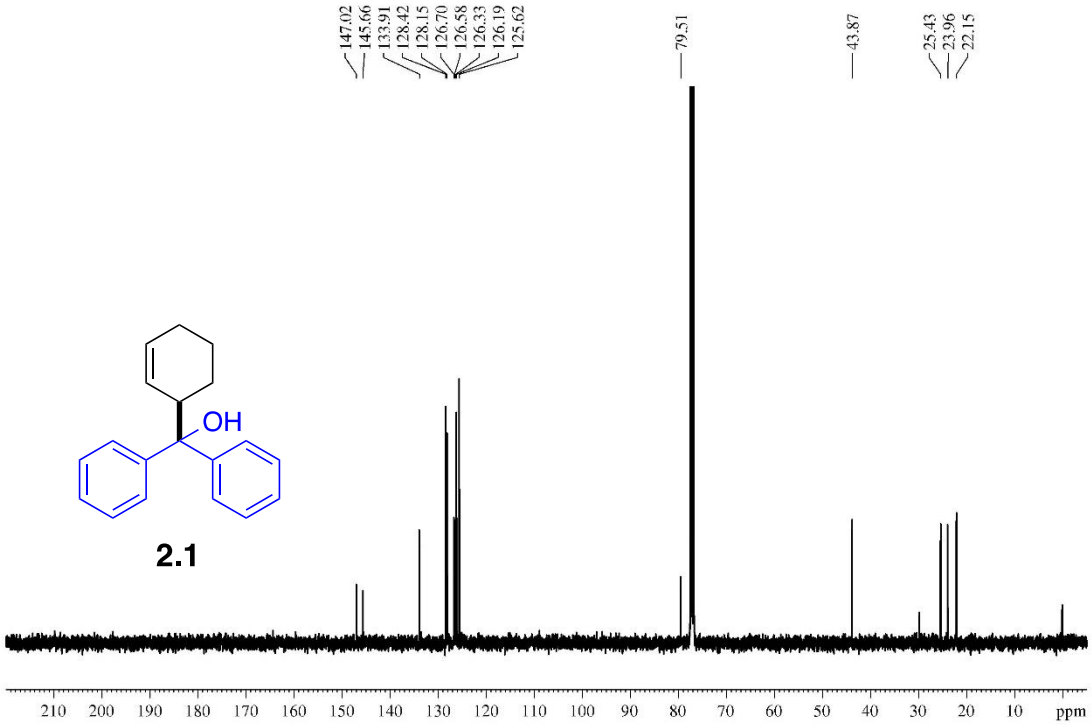
*L. Li, Z. Yu, Z. Shen, *Adv. Synth. Cat.*, 2015, **357**, 3495-3500.

Copy of NMR Spectra

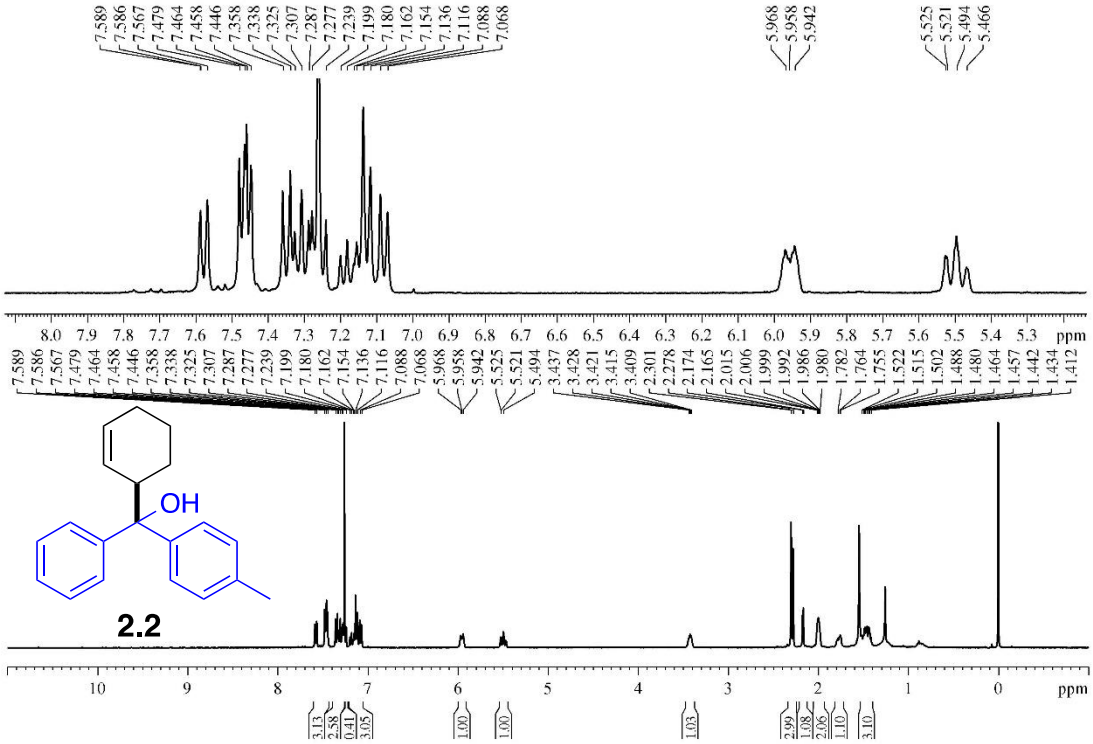
^{1}H NMR of **2.1**, $CDCl_3$, 400 MHz



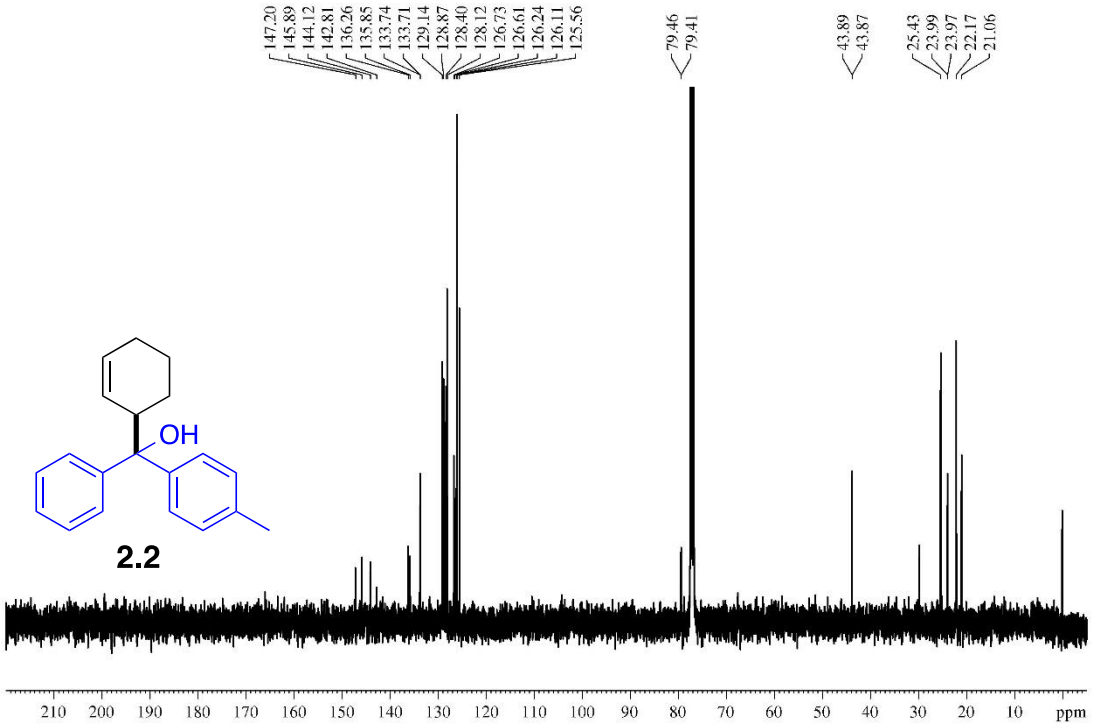
^{13}C NMR of **2.1**, $CDCl_3$, 100 MHz



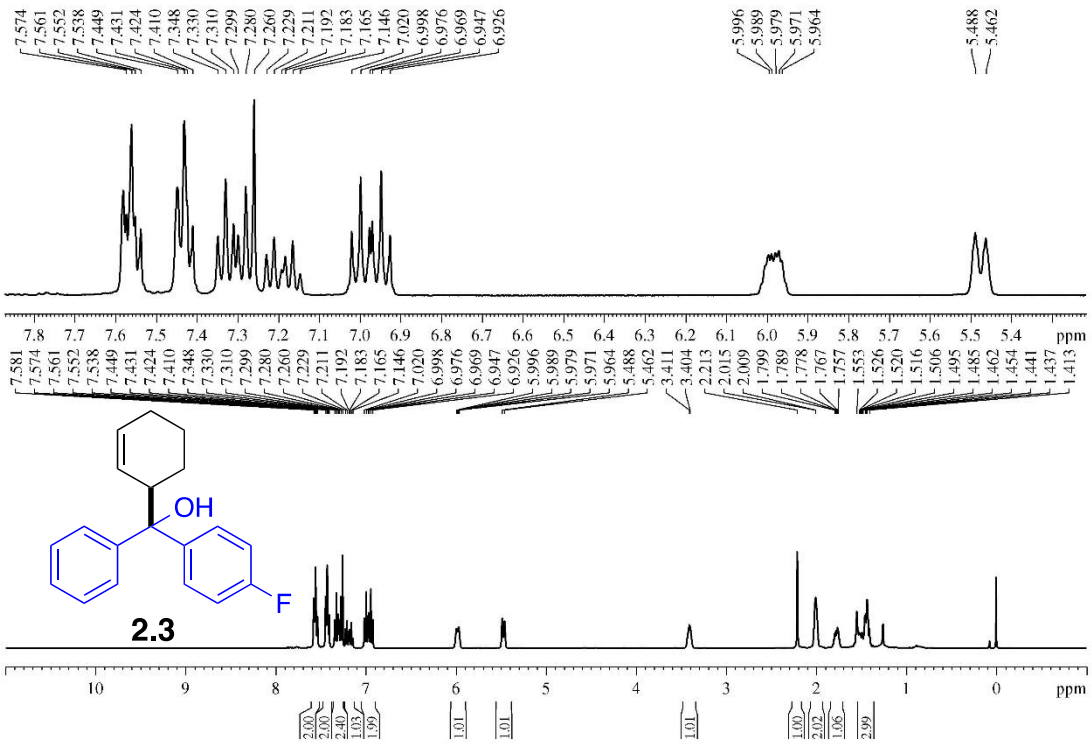
^{1}H NMR of **2.2**, $CDCl_3$, 400 MHz



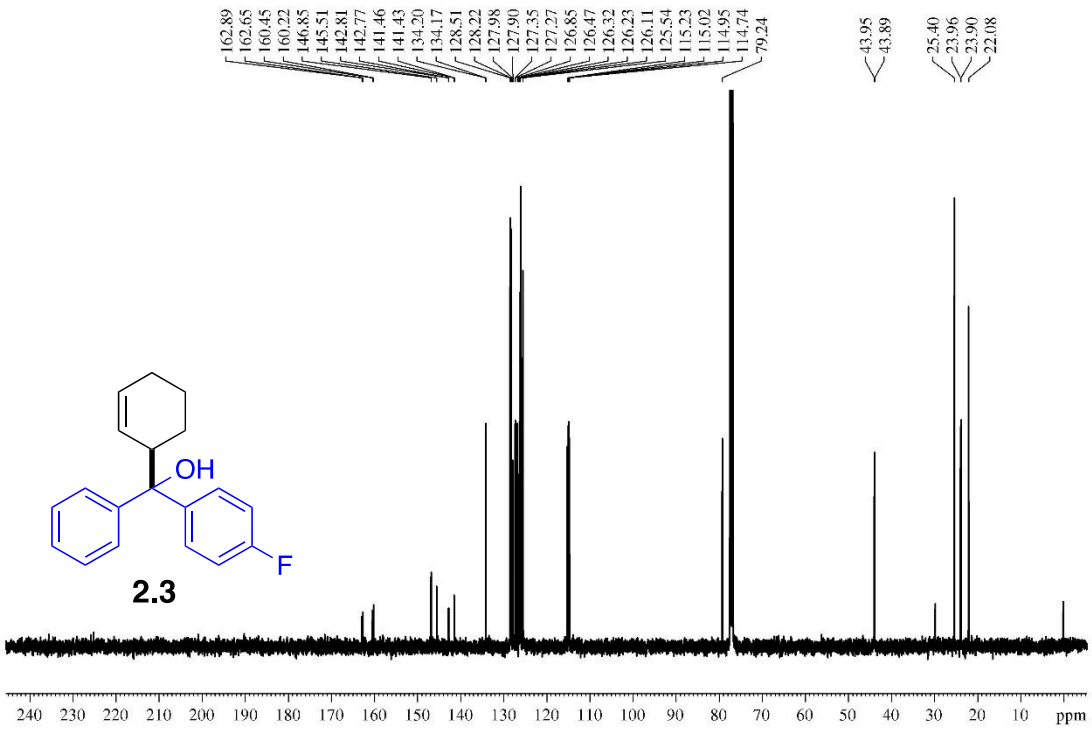
^{13}C NMR of **2.2**, $CDCl_3$, 100 MHz



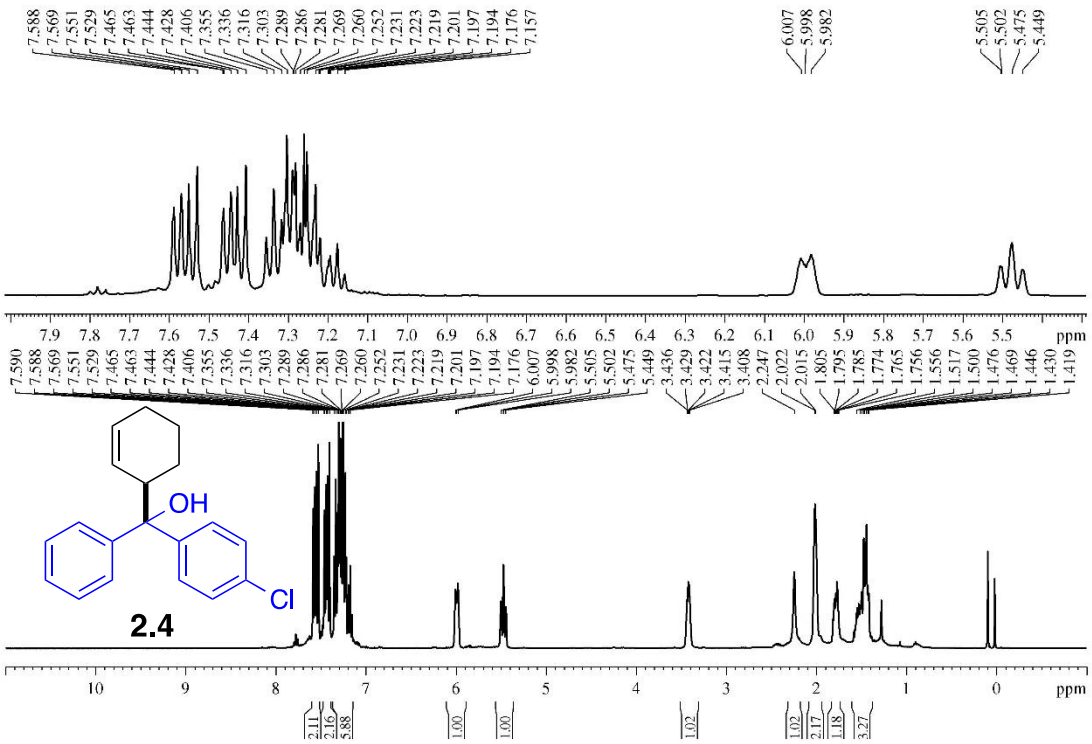
^{1}H NMR of **2.3**, $CDCl_3$, 400 MHz



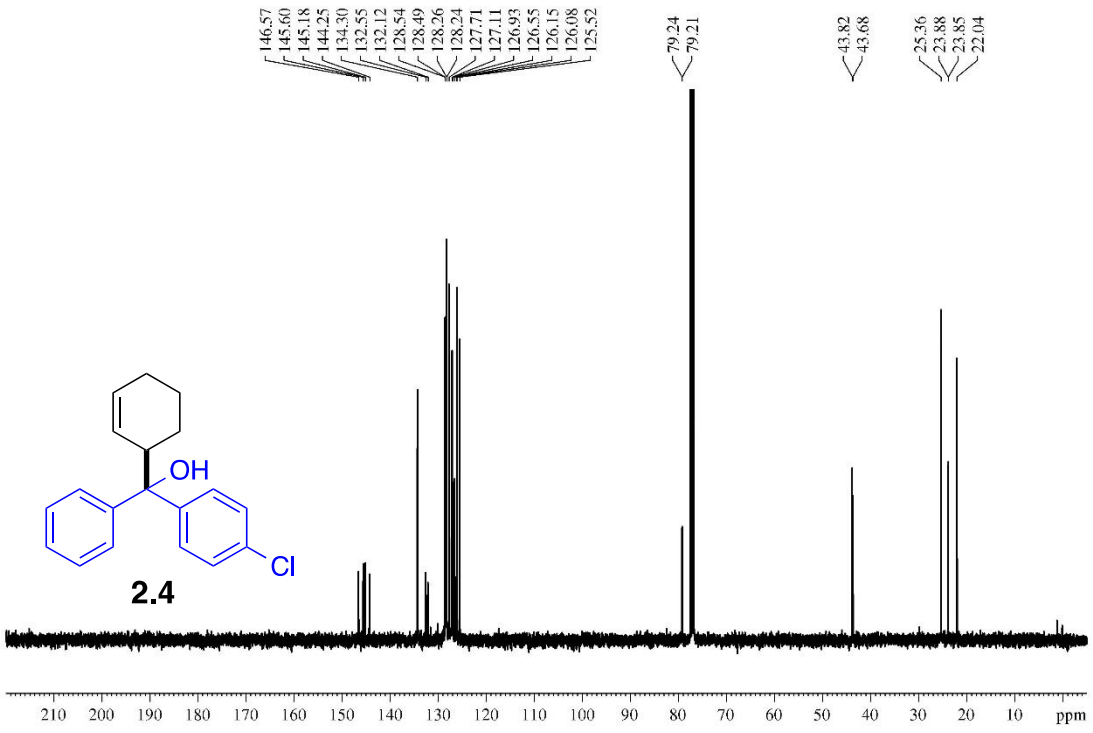
^{13}C NMR of **2.3**, $CDCl_3$, 100 MHz



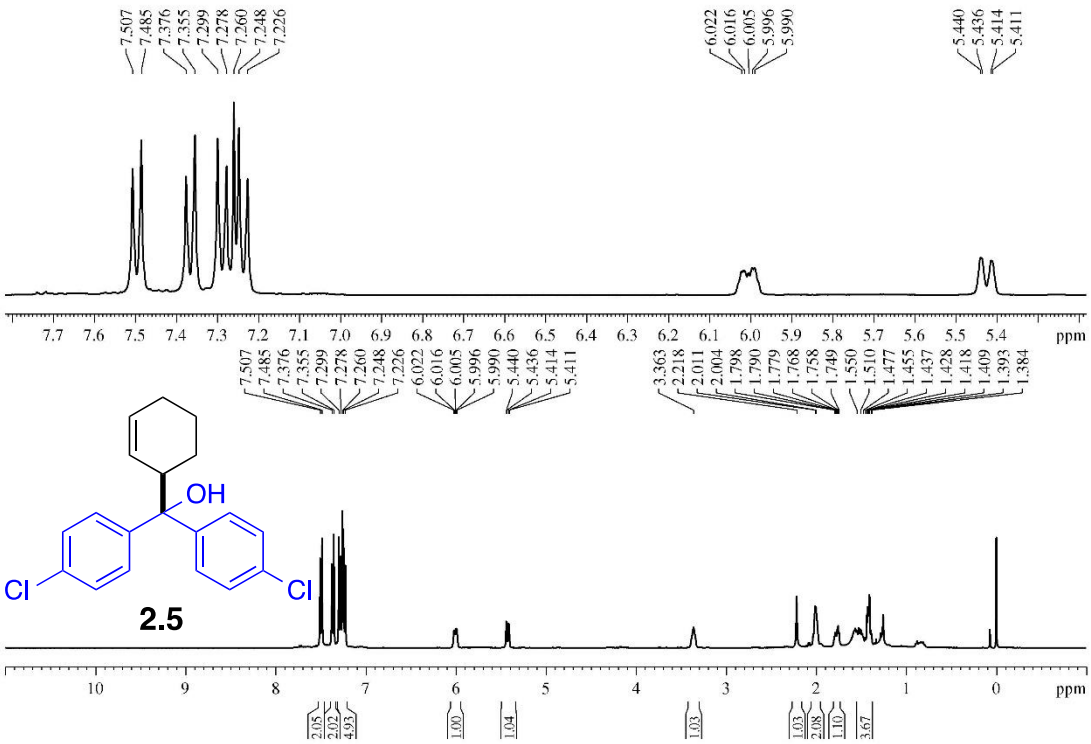
^{1}H NMR of **2.4**, $CDCl_3$, 400 MHz



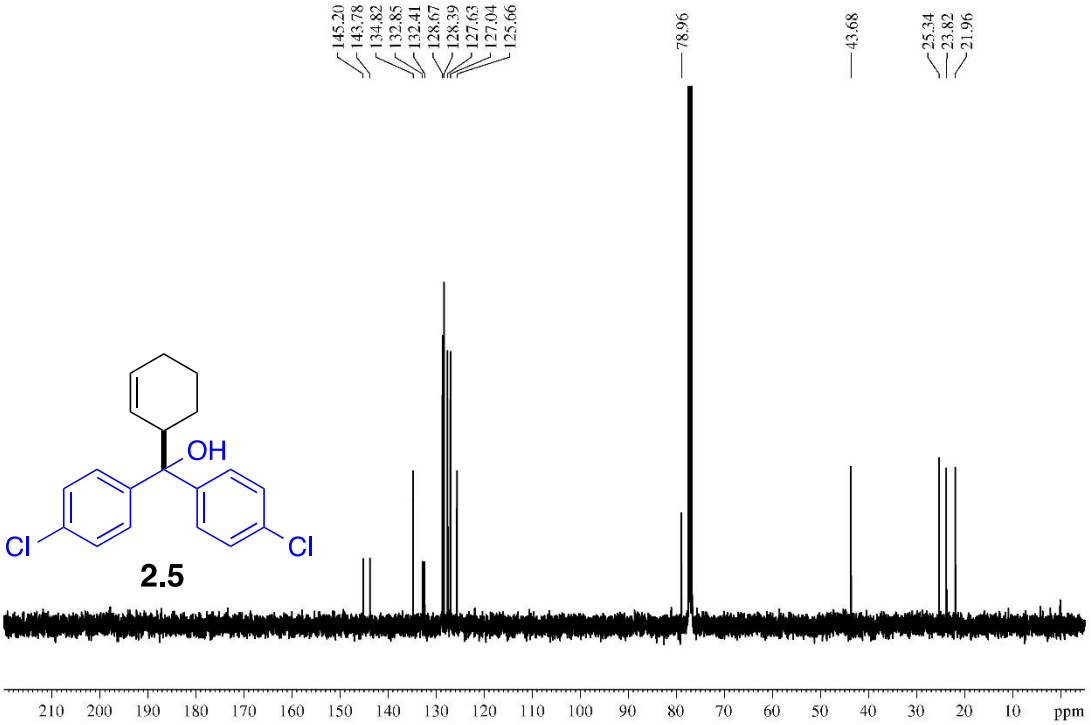
^{13}C NMR of **2.4**, $CDCl_3$, 100 MHz



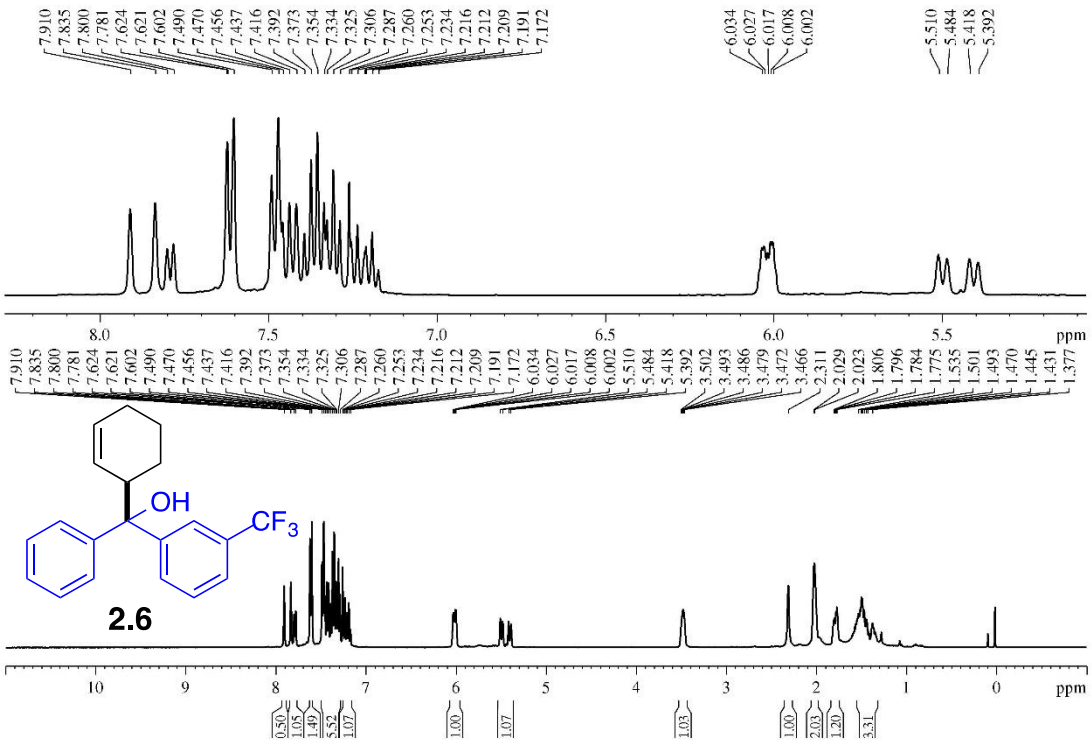
^{1}H NMR of **2.5**, $CDCl_3$, 400 MHz



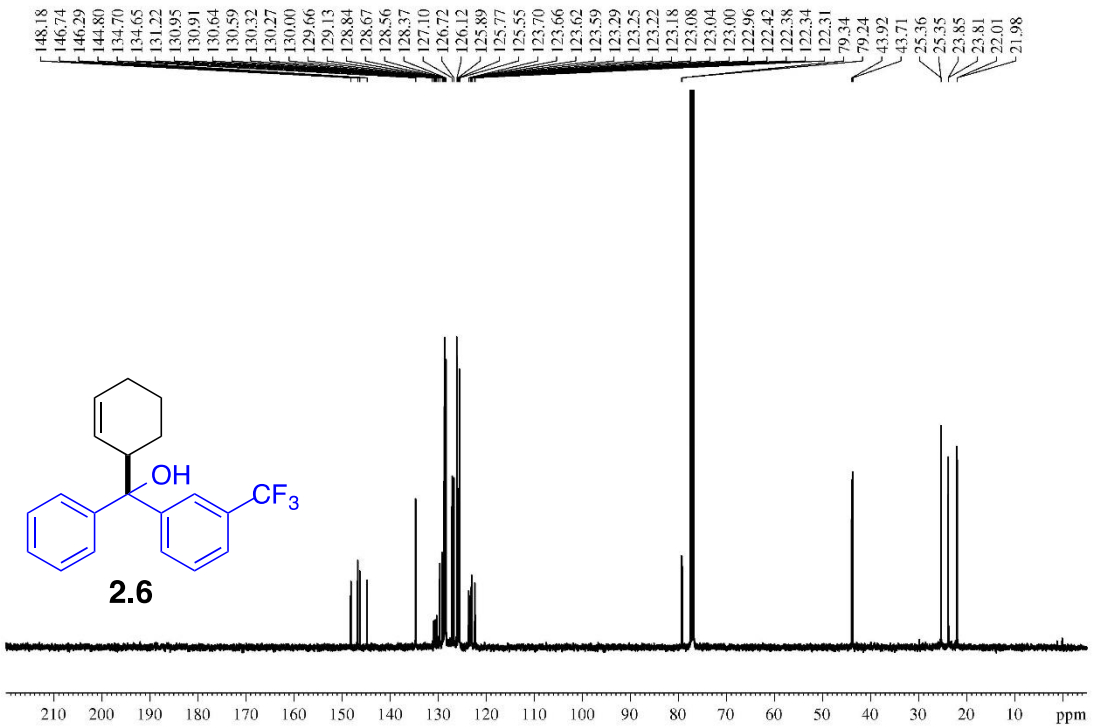
^{13}C NMR of **2.5**, $CDCl_3$, 100 MHz



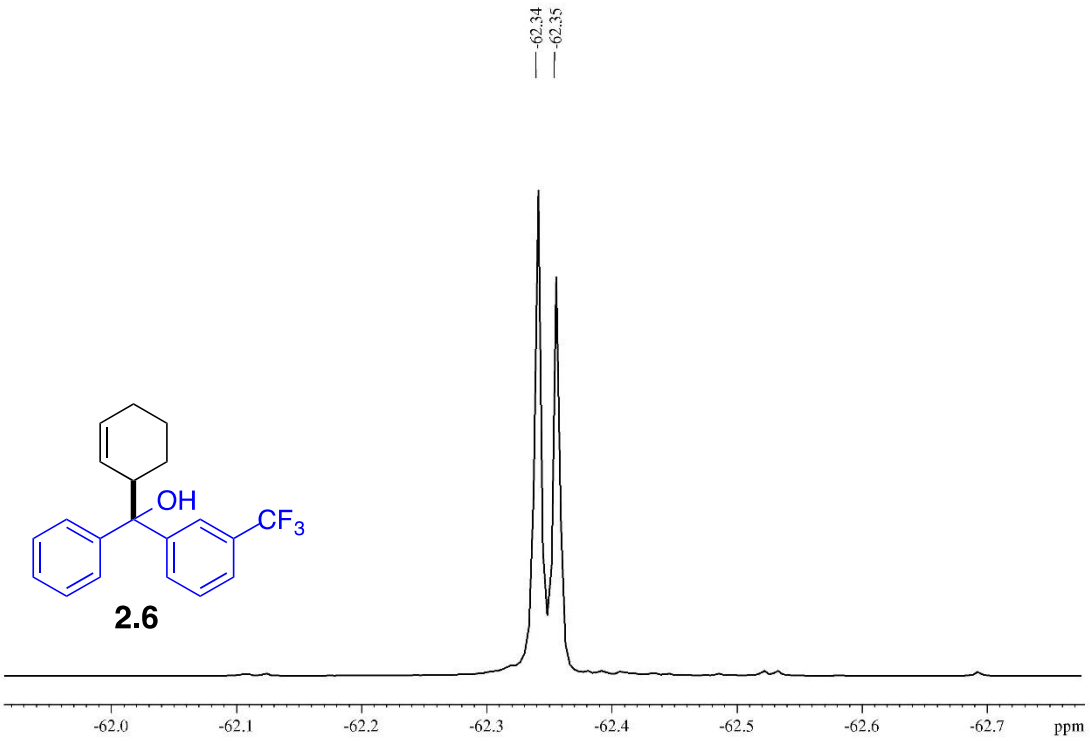
^{1}H NMR of **2.6**, $CDCl_3$, 400 MHz



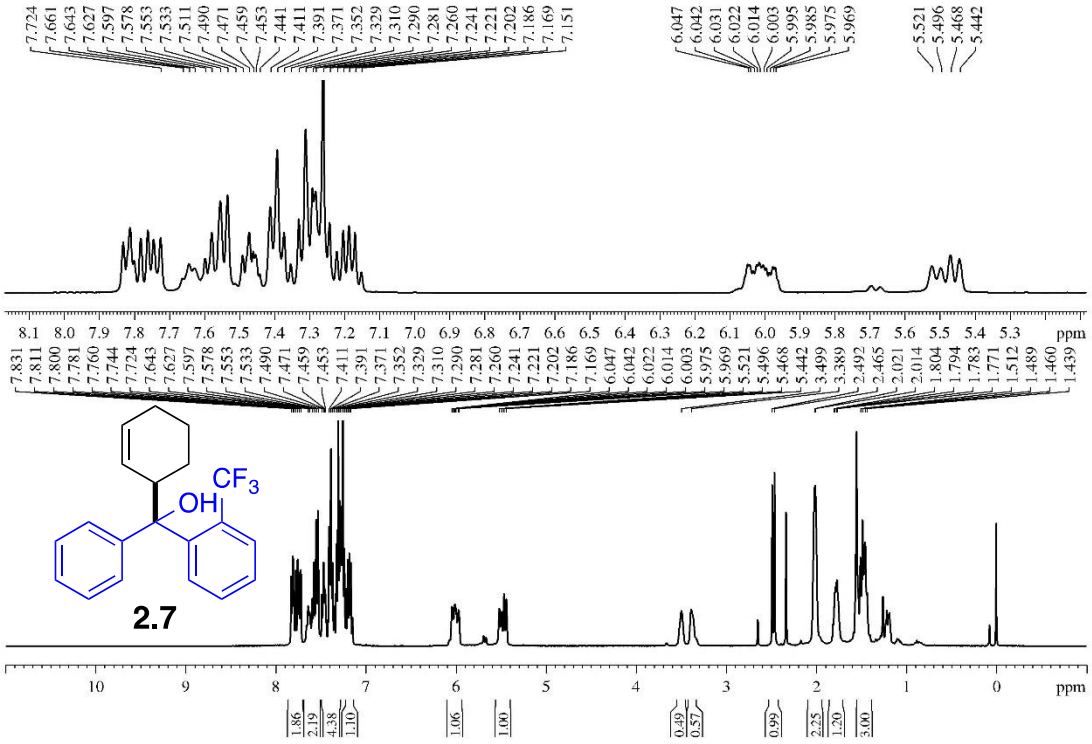
^{13}C NMR of **2.6**, $CDCl_3$, 100 MHz



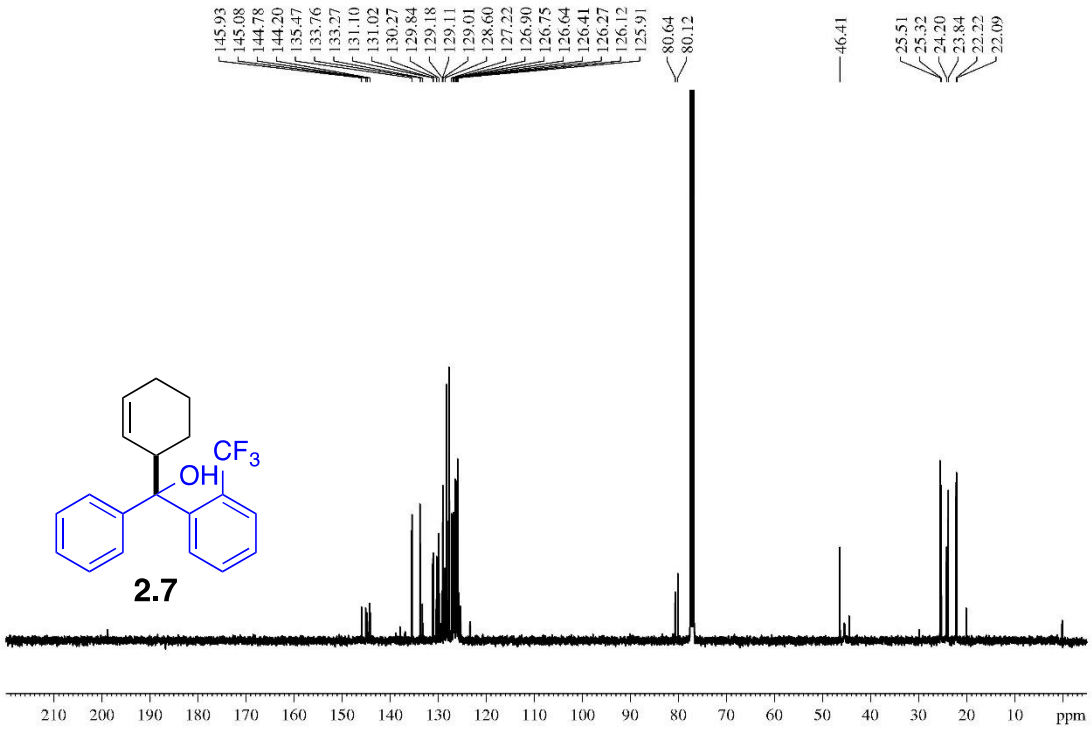
^{19}F NMR of **2.6**, $CDCl_3$, 376 MHz



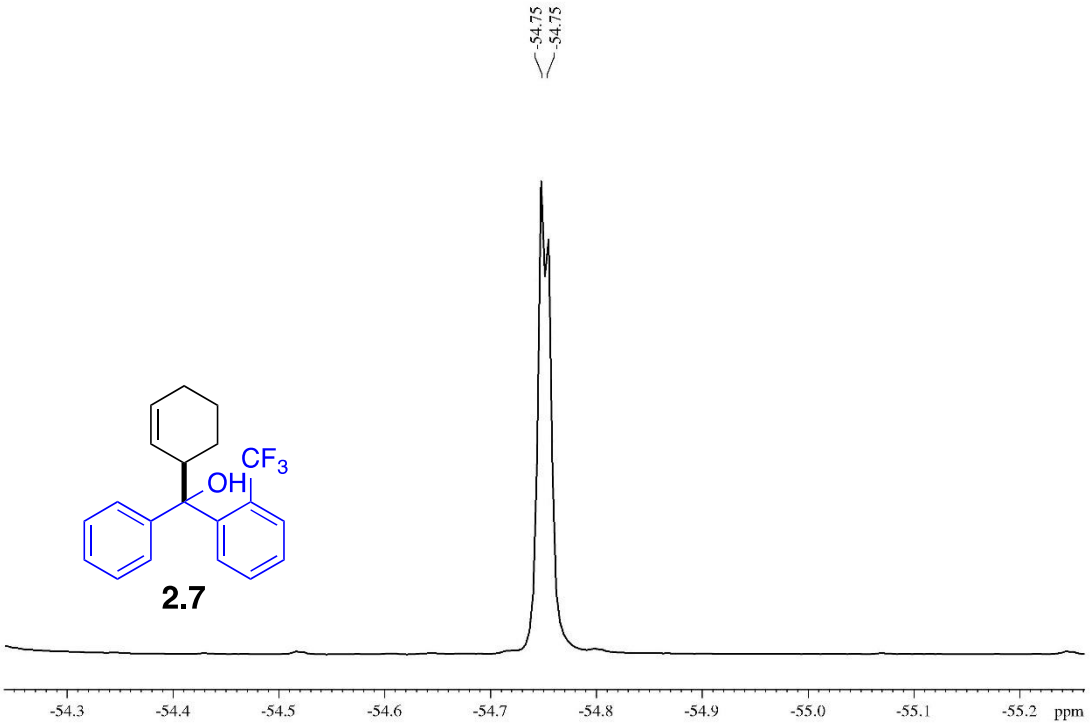
^{1}H NMR of **2.7**, $CDCl_3$, 400 MHz



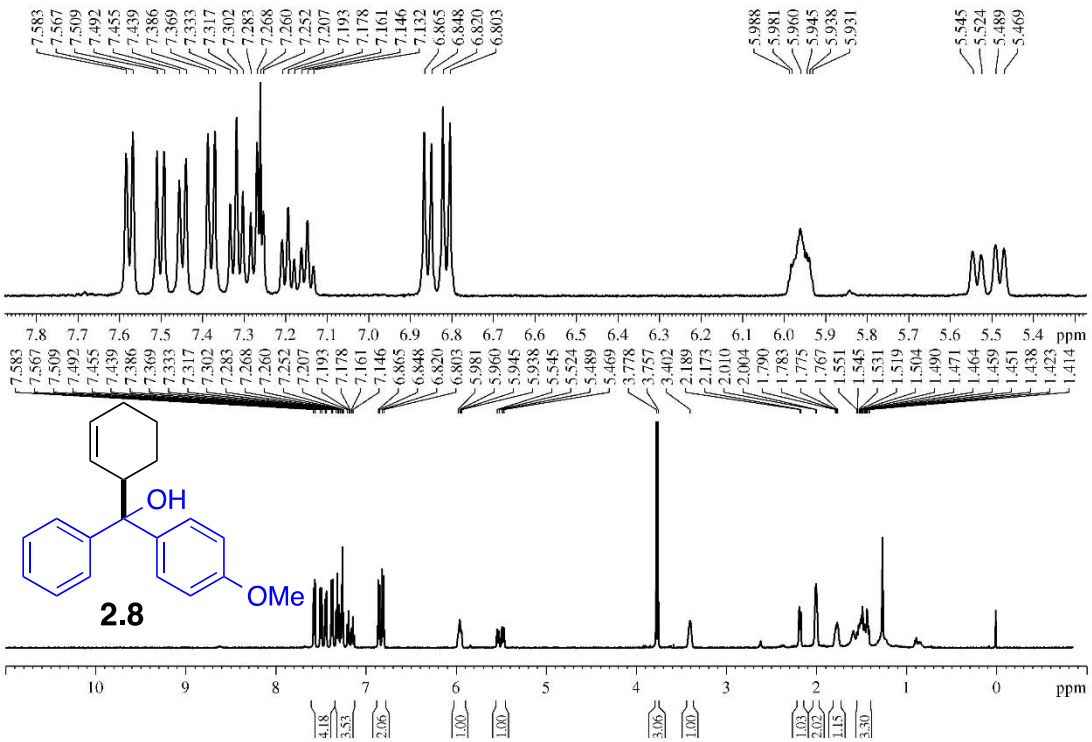
^{13}C NMR of **2.7**, $CDCl_3$, 100 MHz



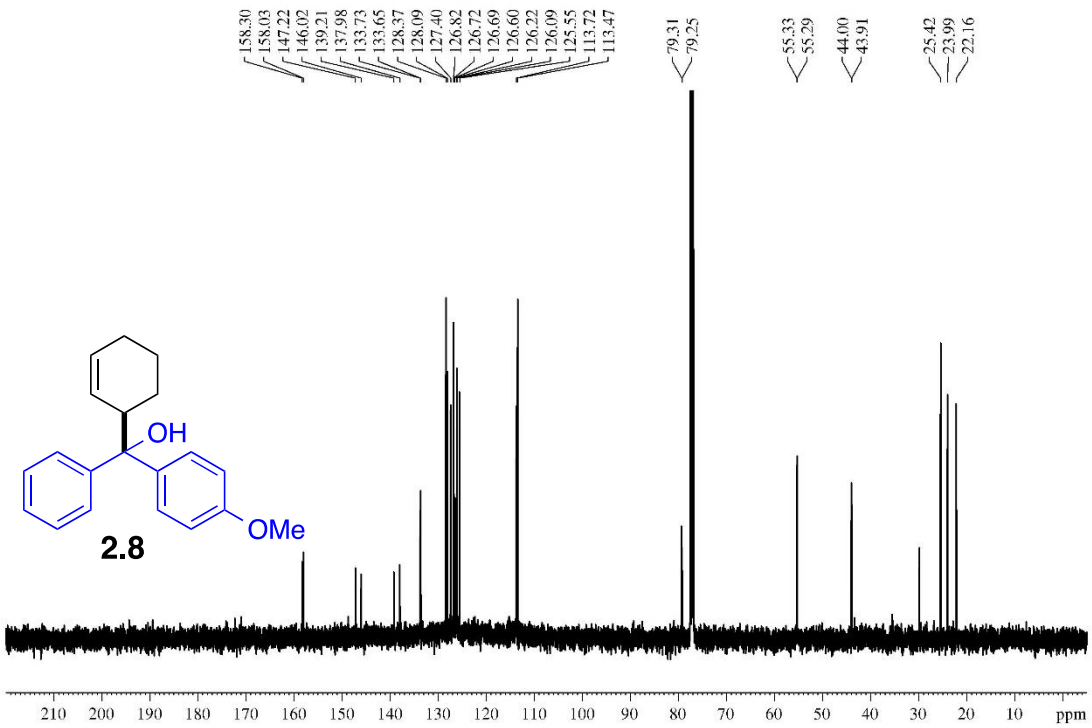
^{19}F NMR of **2.7**, $CDCl_3$, 376 MHz



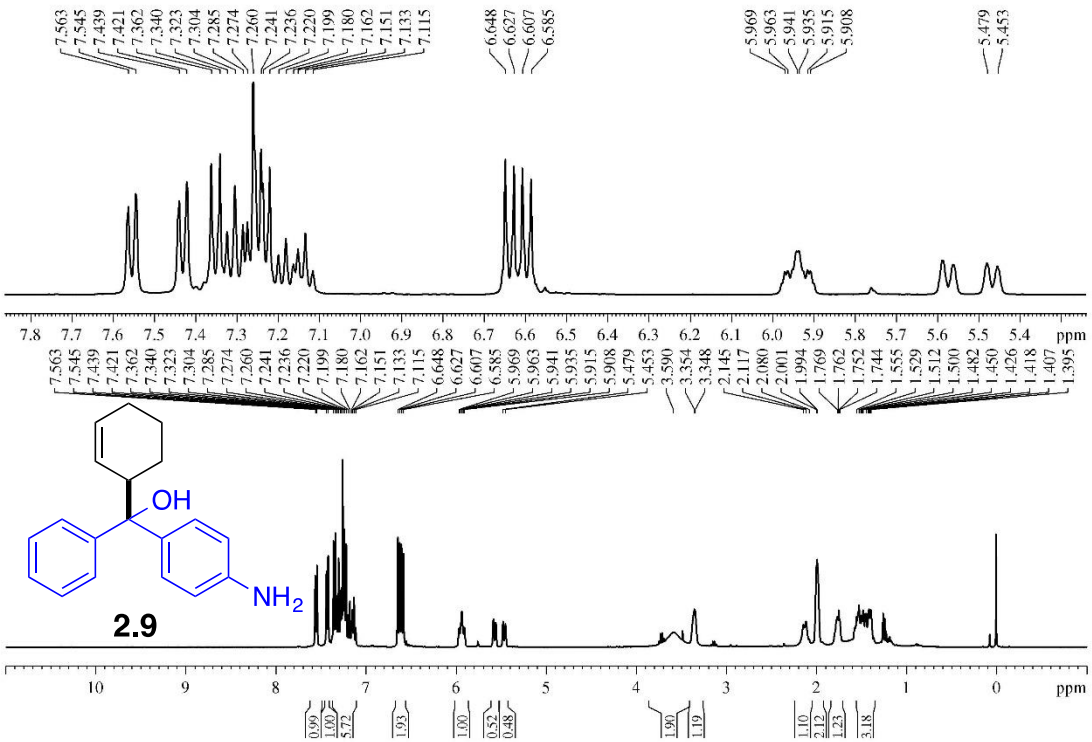
^{1}H NMR of **2.8**, $CDCl_3$, 500 MHz



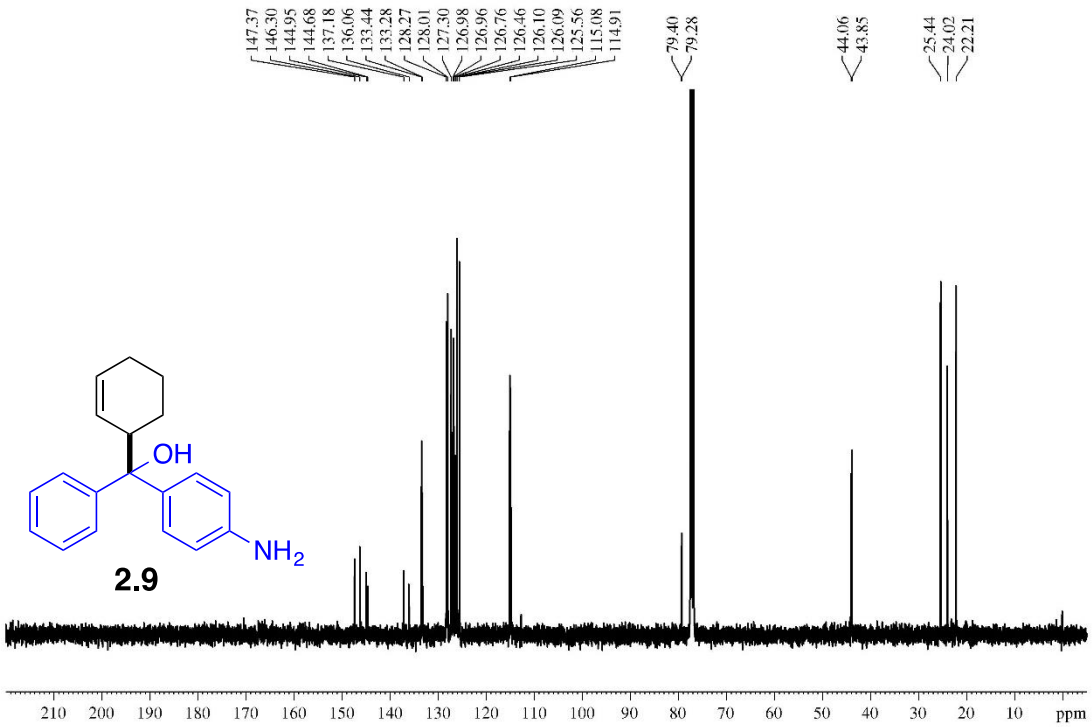
^{13}C NMR of **2.8**, $CDCl_3$, 125 MHz



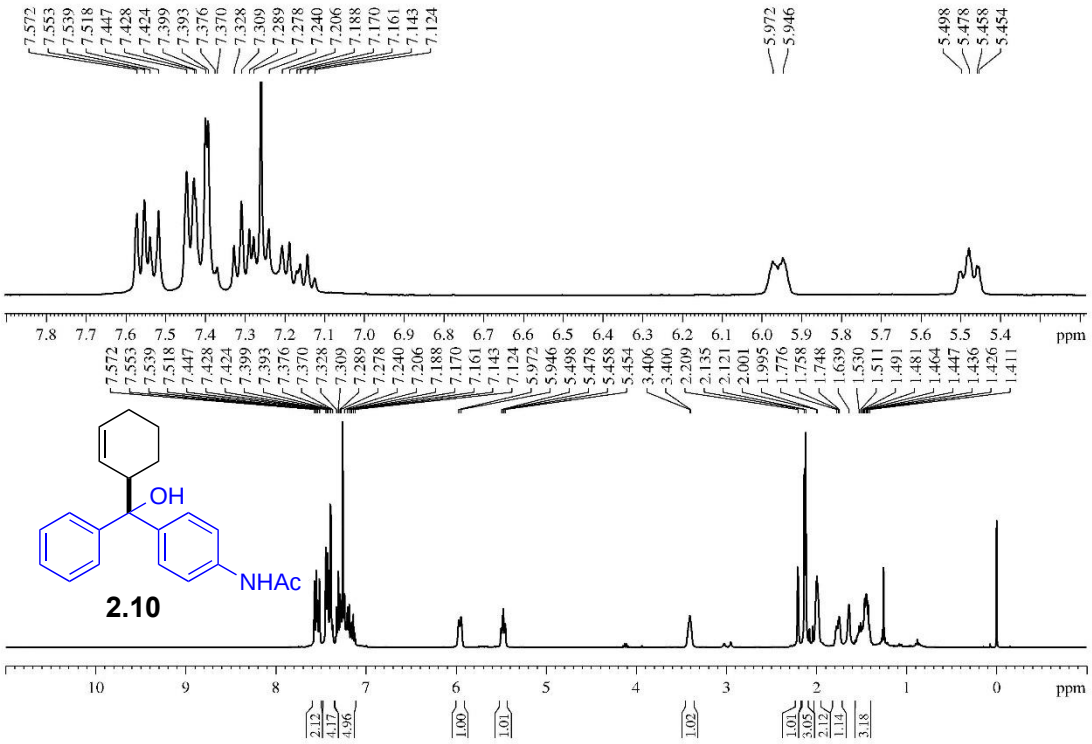
^{1}H NMR of **2.9**, $CDCl_3$, 400 MHz



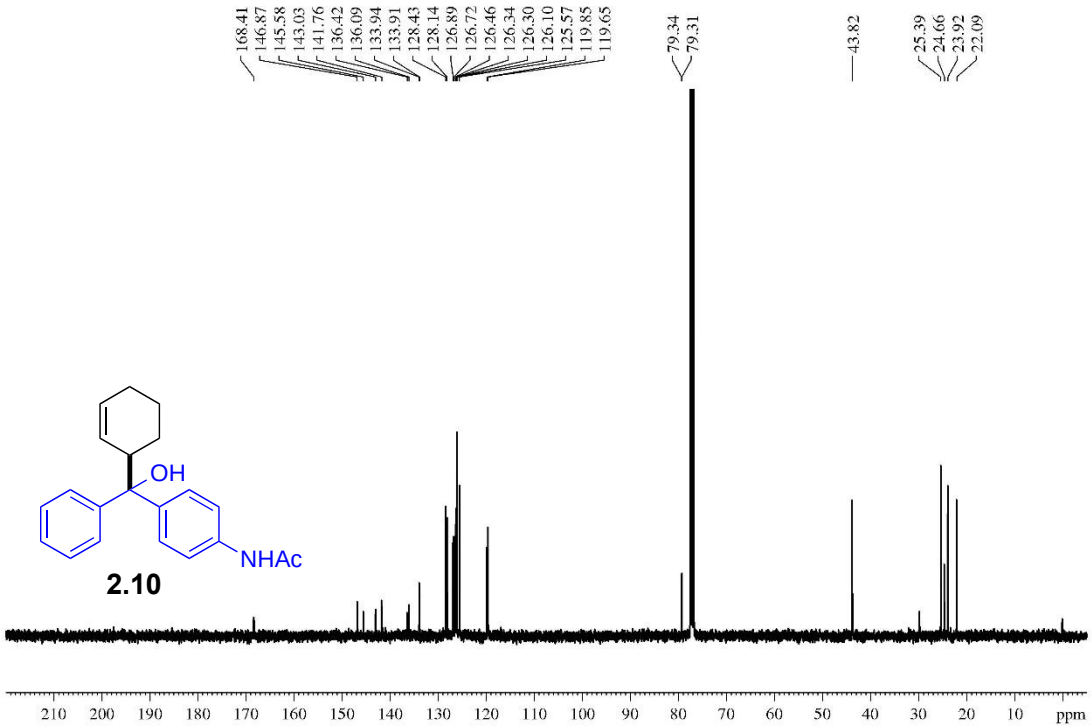
^{13}C NMR of **2.9**, $CDCl_3$, 100 MHz



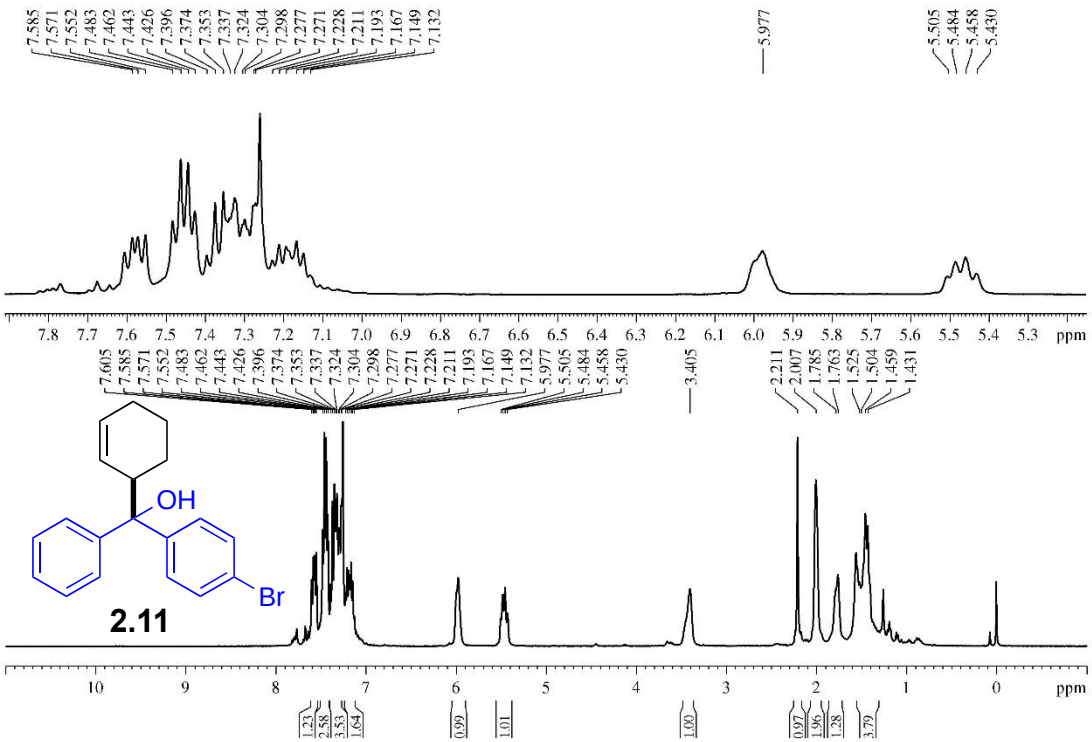
^{1}H NMR of **2.10**, $CDCl_3$, 400 MHz



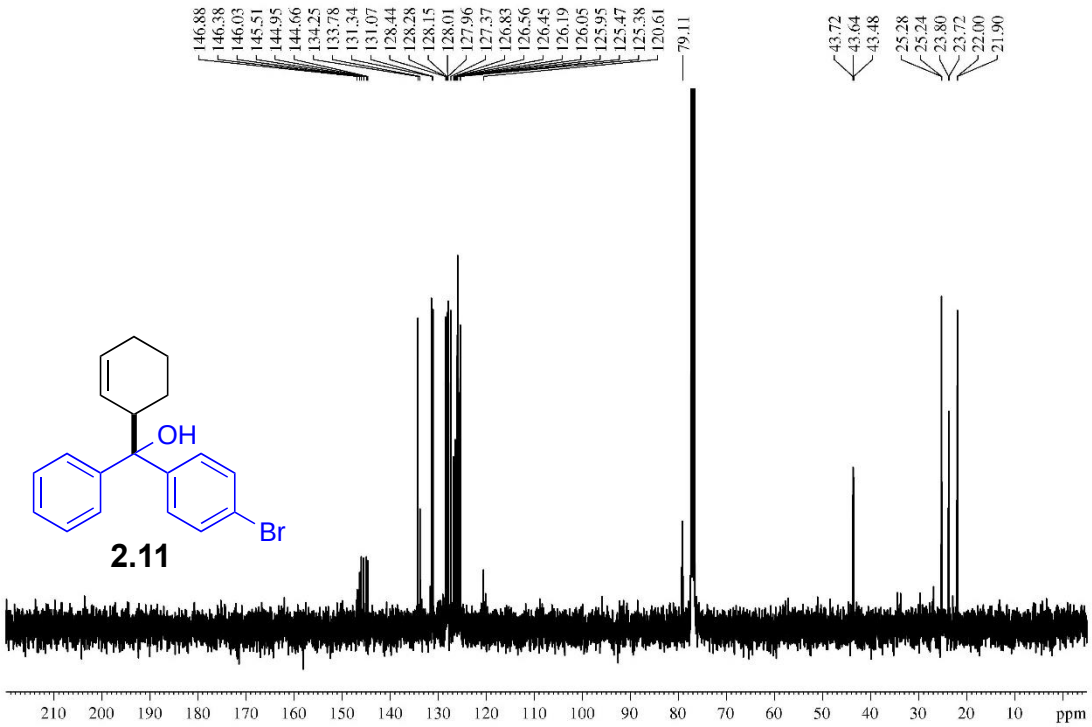
^{13}C NMR of **2.10**, $CDCl_3$, 100 MHz



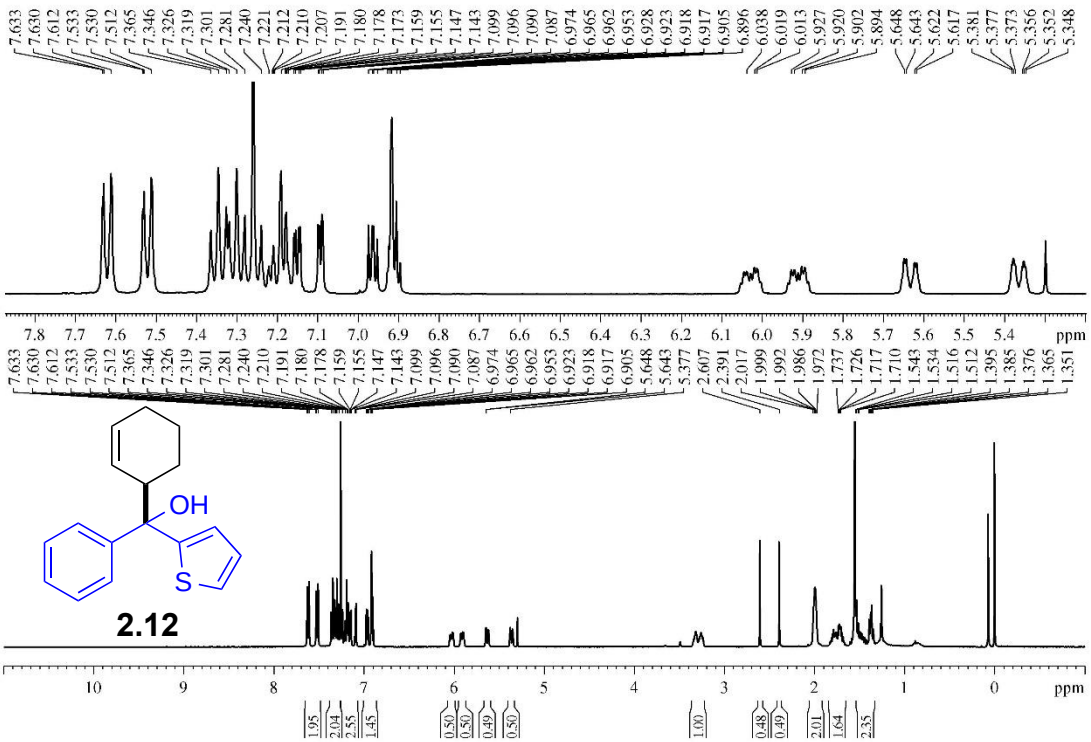
^{1}H NMR of **2.11**, $CDCl_3$, 400 MHz



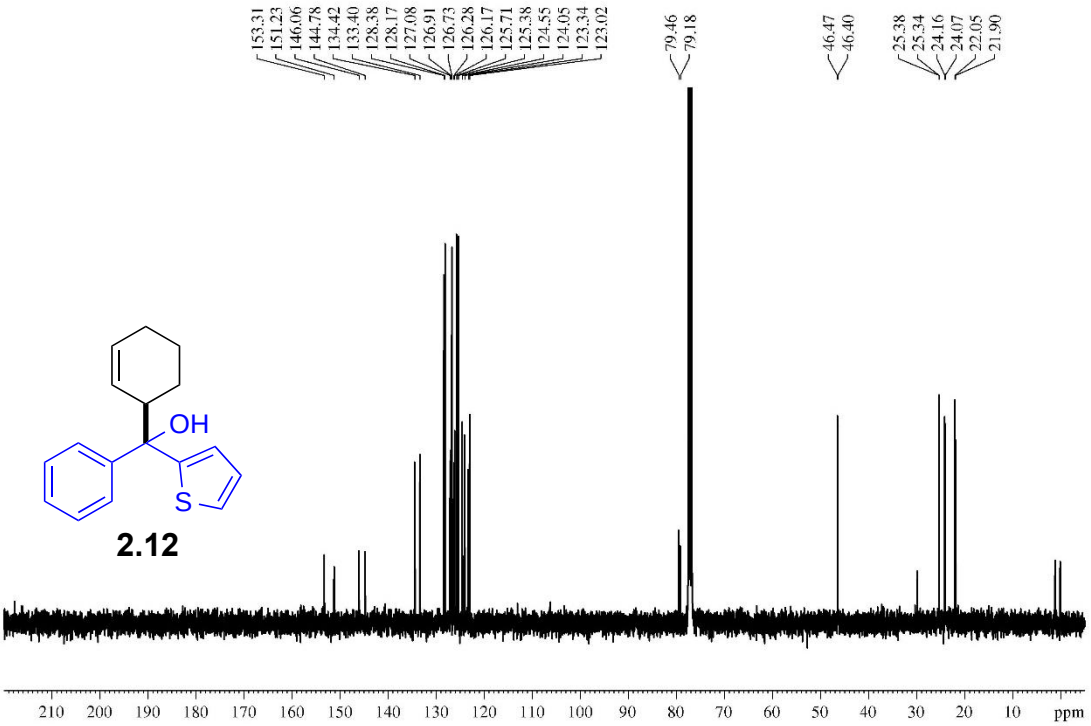
^{13}C NMR of **2.11**, $CDCl_3$, 100 MHz



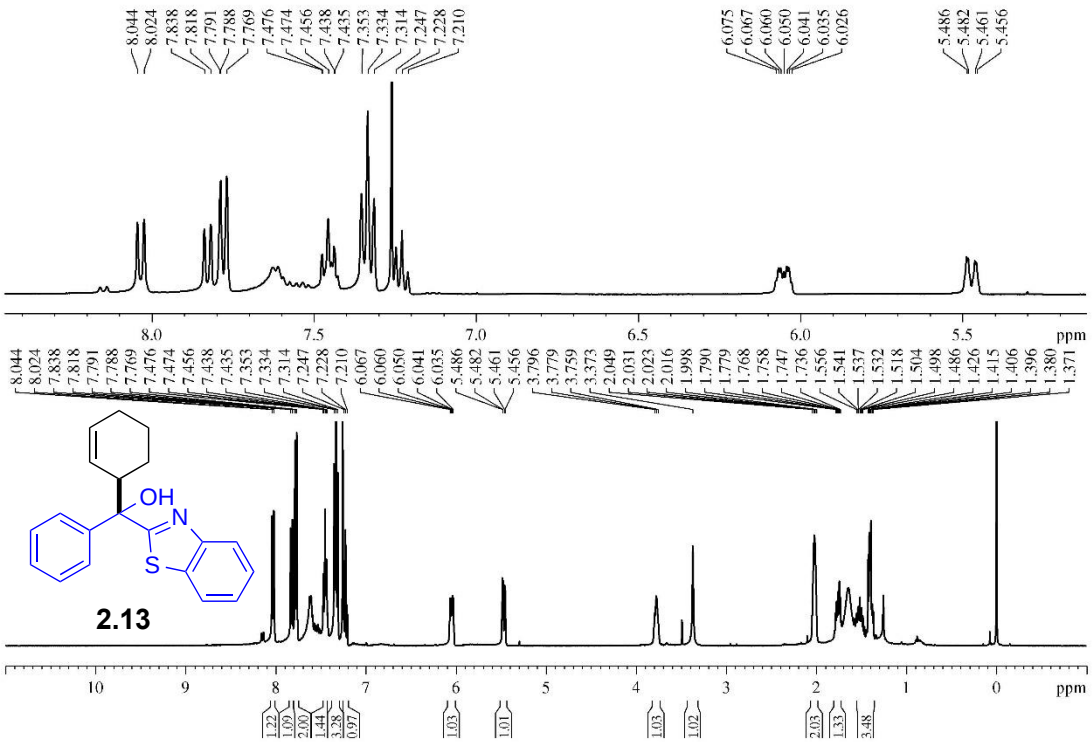
^{1}H NMR of **2.12**, $CDCl_3$, 400 MHz



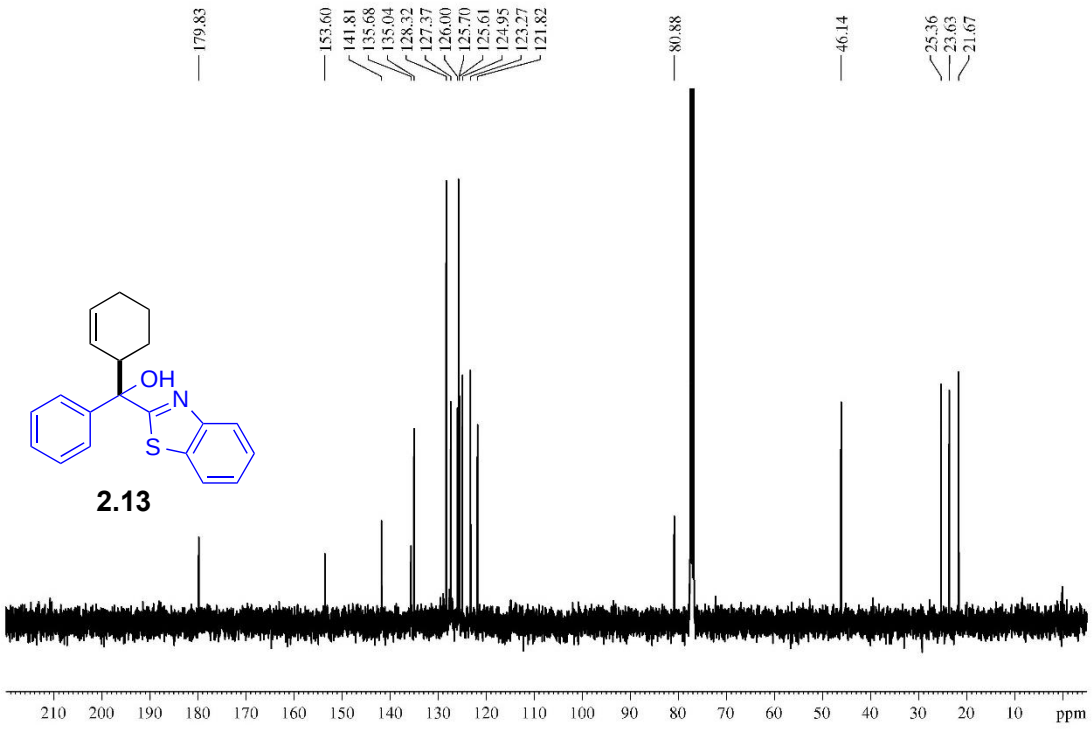
^{13}C NMR of **2.12**, $CDCl_3$, 100 MHz



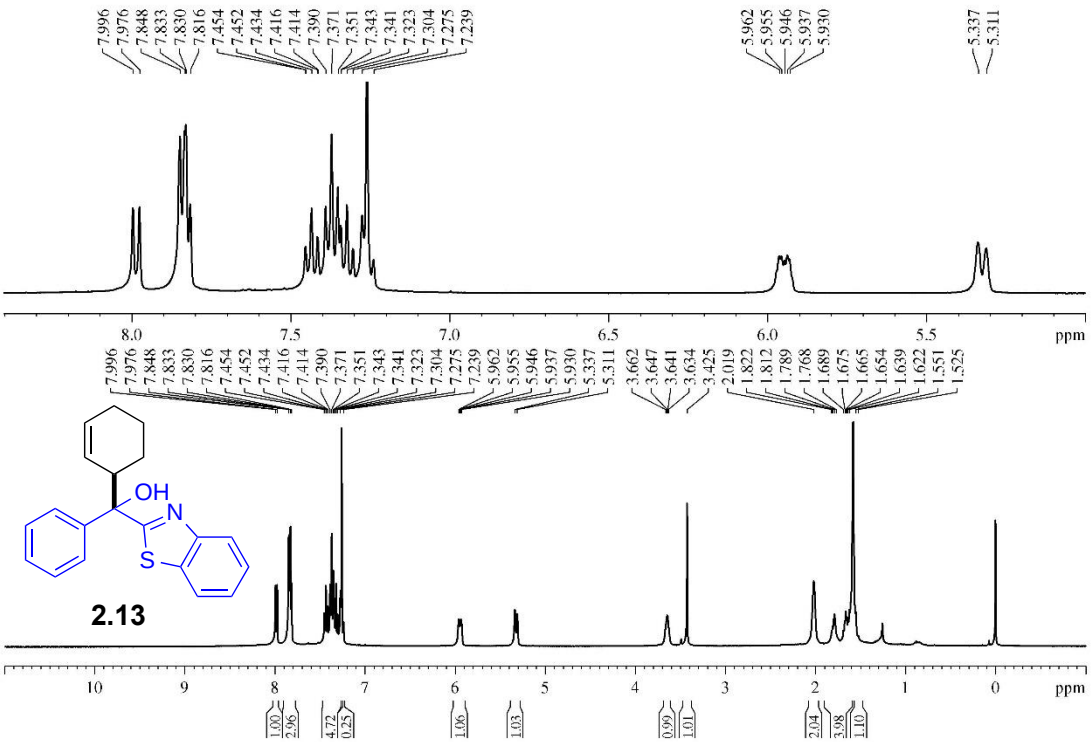
^{1}H NMR of **2.13** Diastereomer 1, $CDCl_3$, 400 MHz



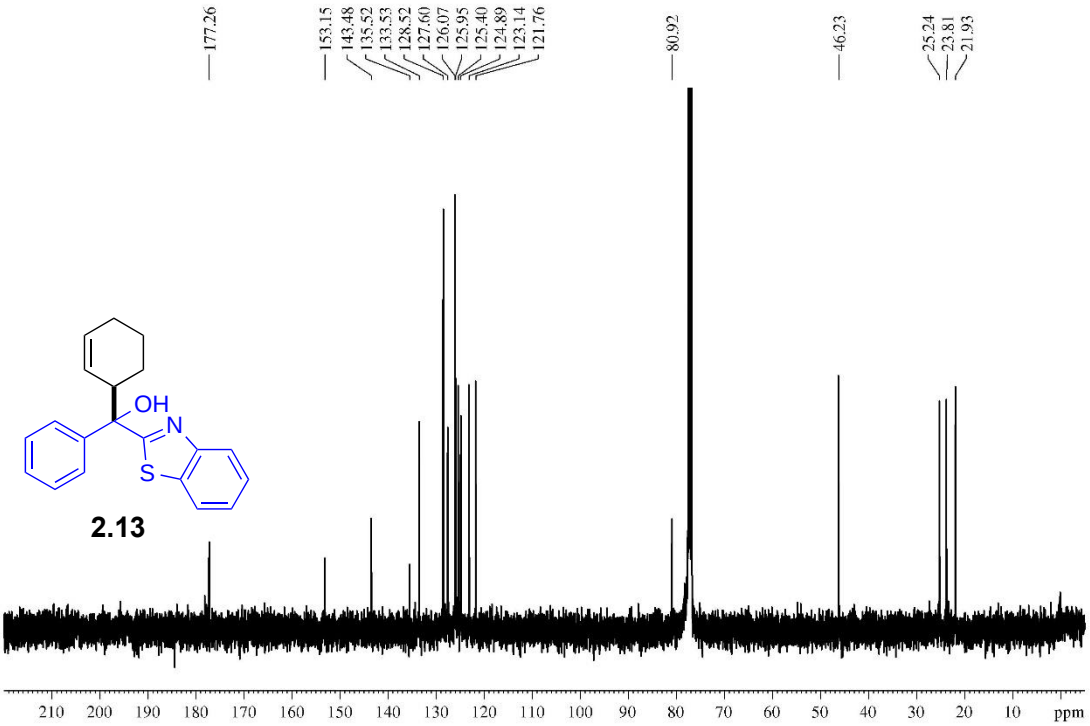
^{13}C NMR of **2.13** Diastereomer 1, $CDCl_3$, 100 MHz



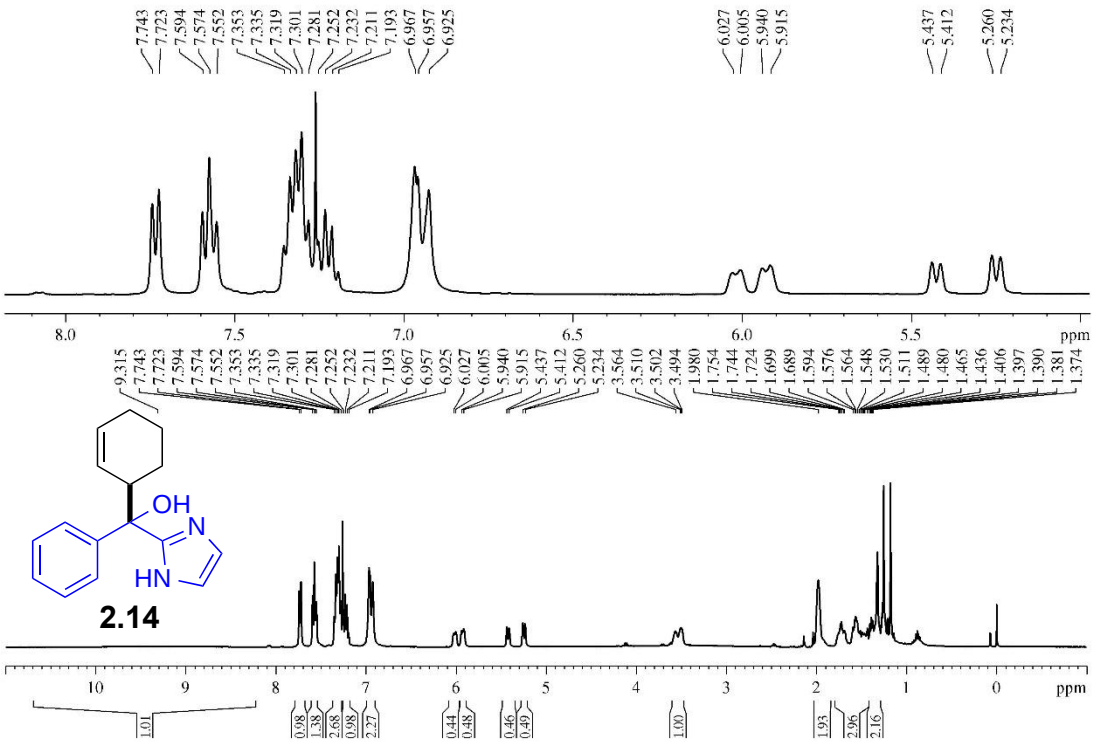
^{1}H NMR of **2.13** Diastereomer 2, $CDCl_3$, 400 MHz



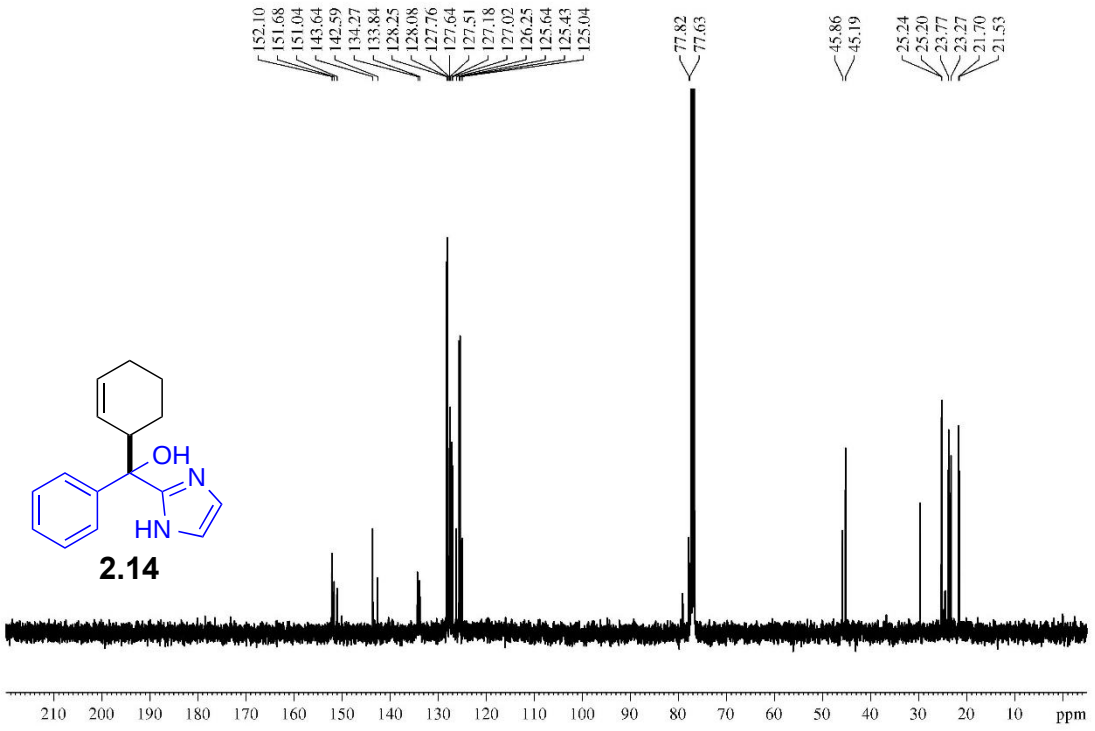
^{13}C NMR of **2.13** Diastereomer 2, $CDCl_3$, 100 MHz



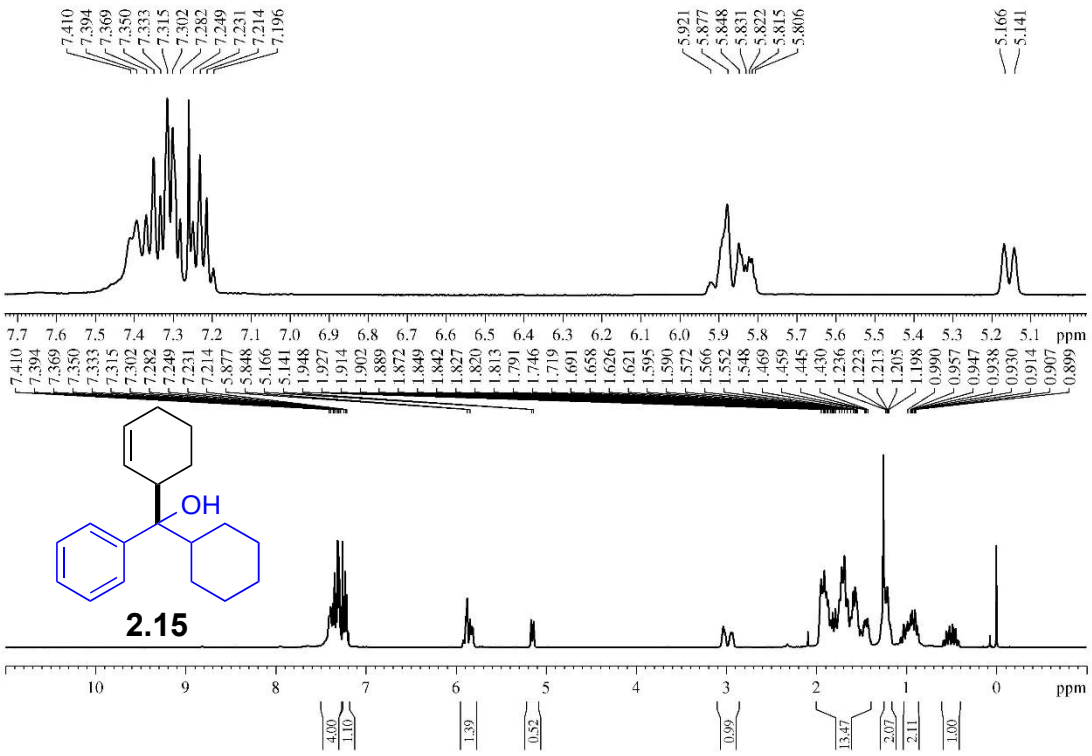
^{1}H NMR of **2.14**, $CDCl_3$, 400 MHz



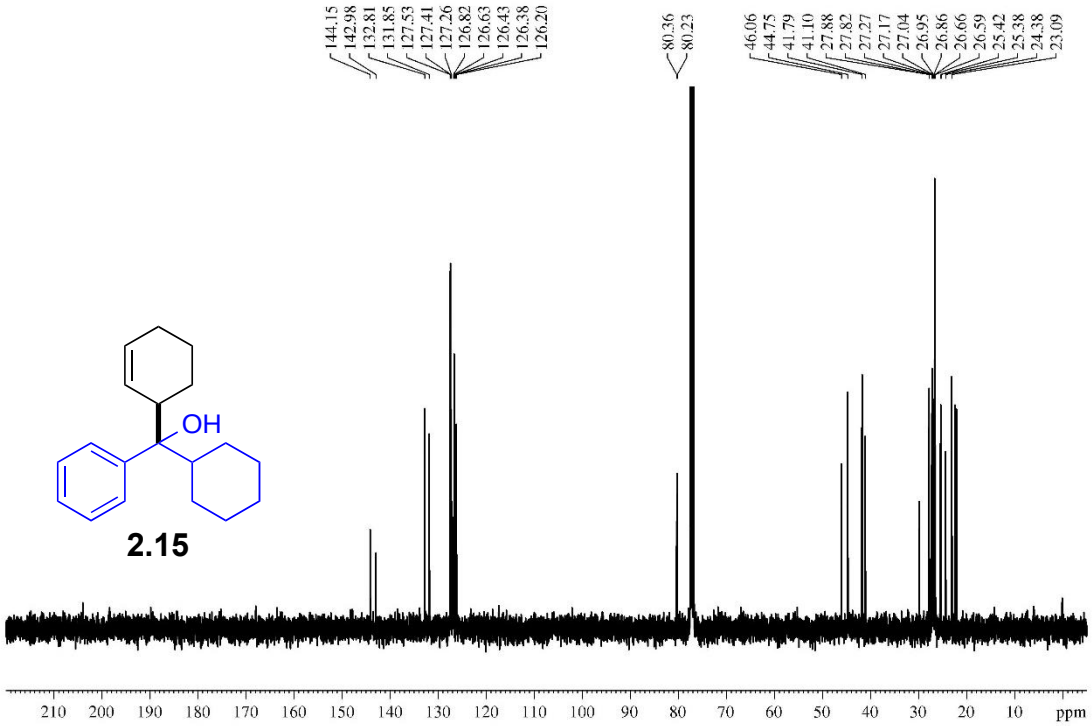
^{13}C NMR of **2.14**, $CDCl_3$, 100 MHz



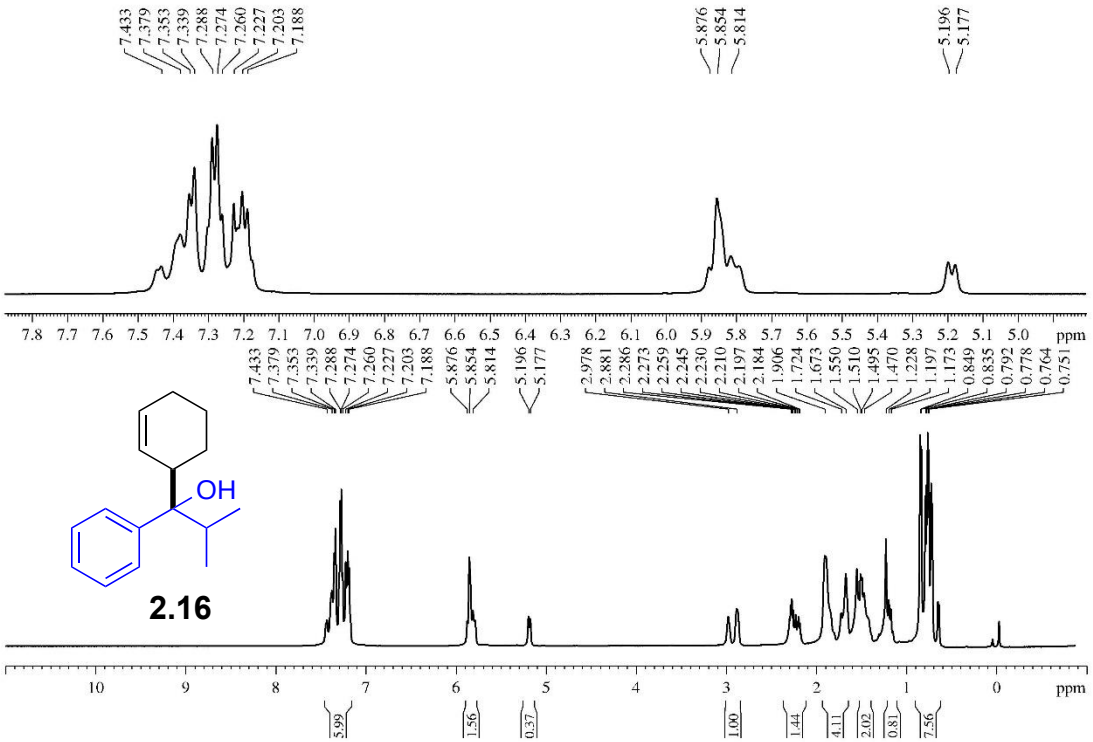
^{1}H NMR of **2.15**, $CDCl_3$, 400 MHz



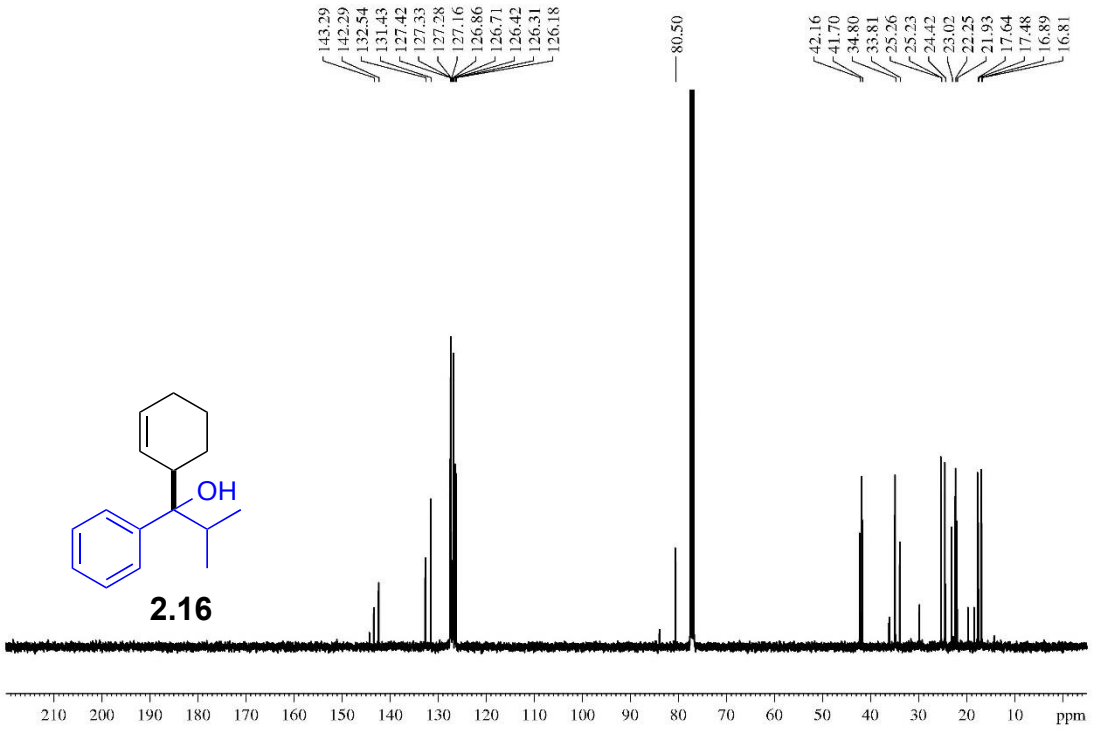
^{13}C NMR of **2.15**, $CDCl_3$, 100 MHz



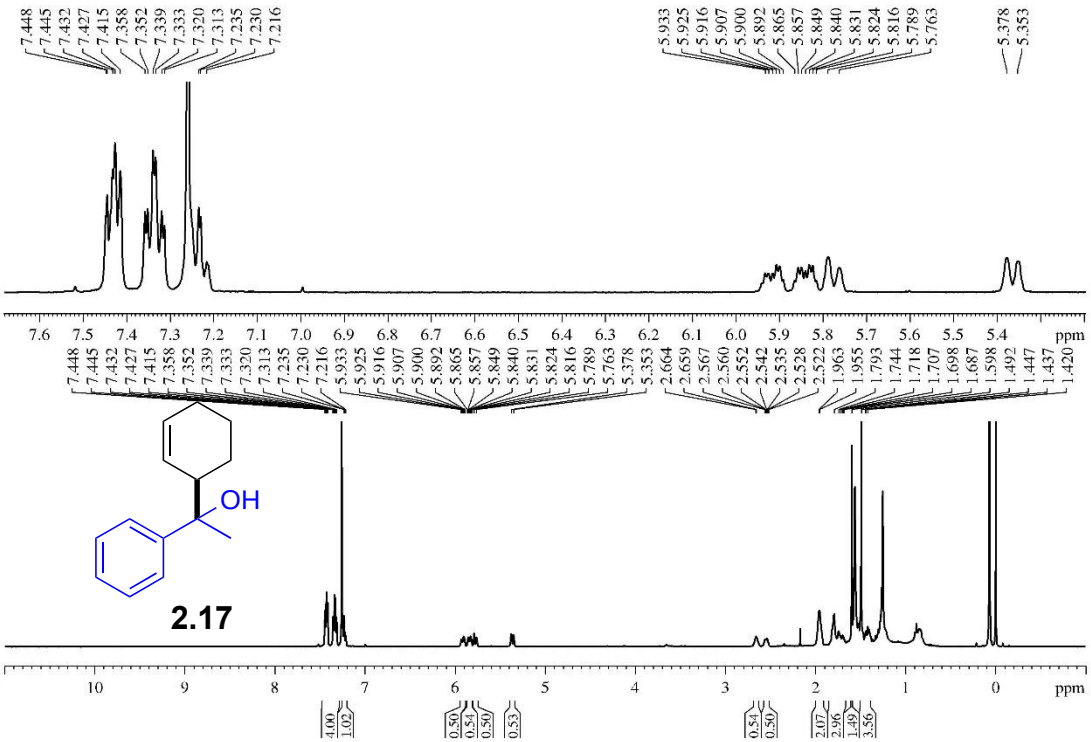
^{1}H NMR of **2.16**, $CDCl_3$, 400 MHz



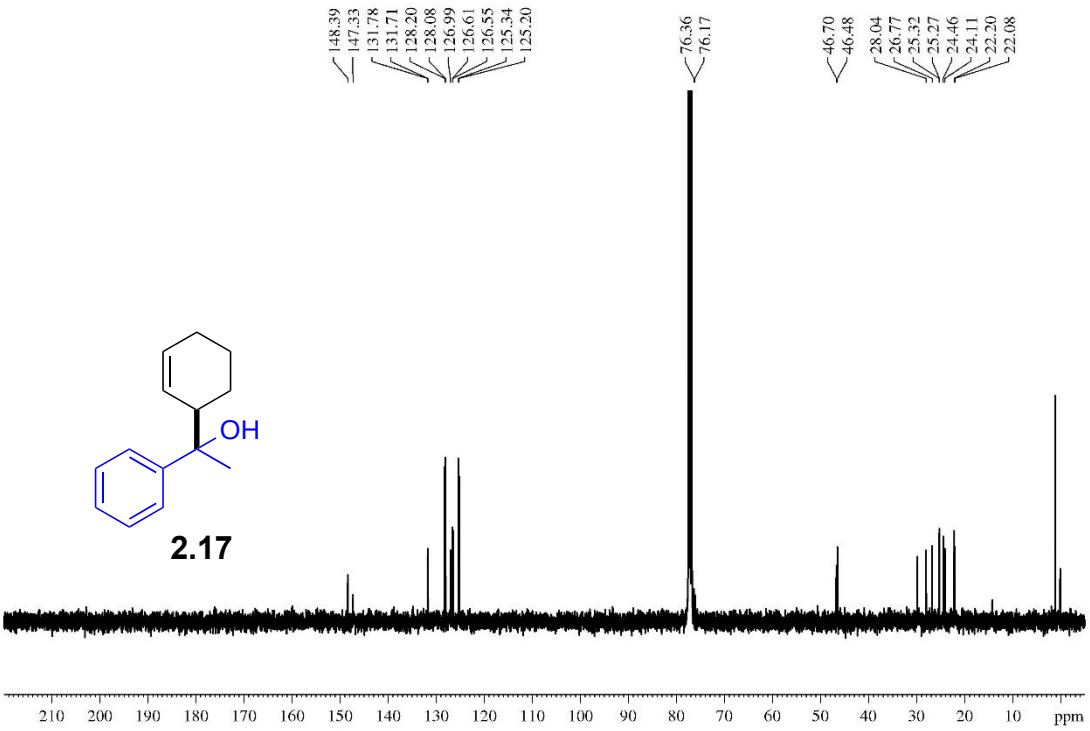
^{13}C NMR of **2.16**, $CDCl_3$, 100 MHz



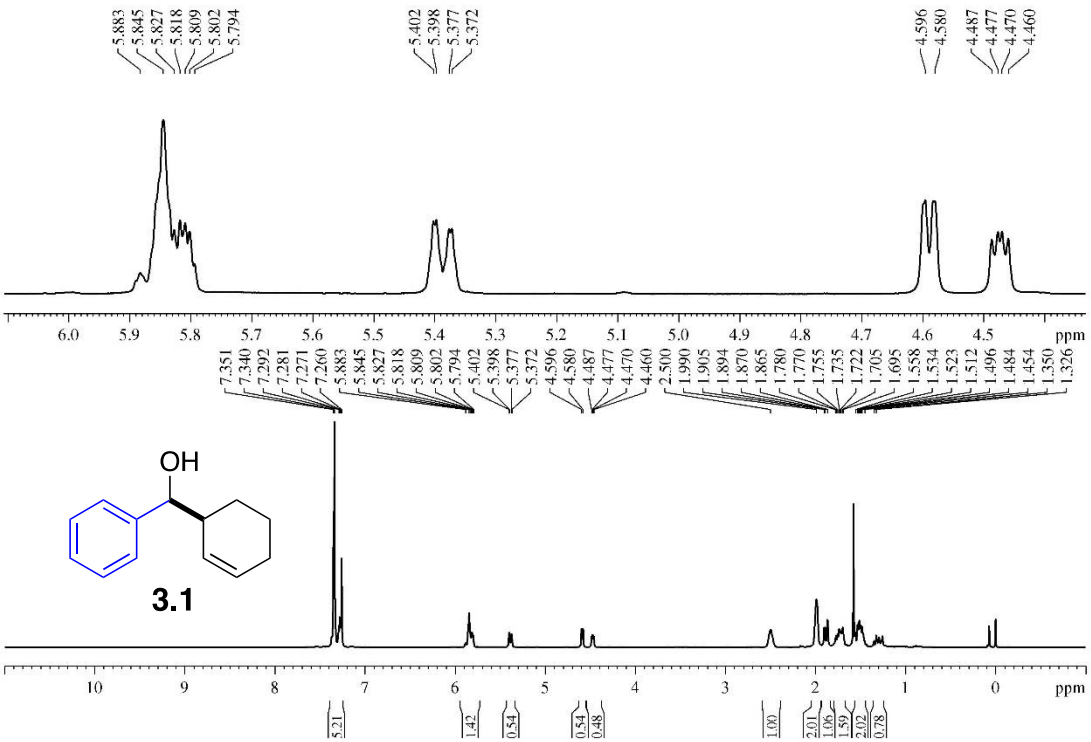
^{1}H NMR of **2.17**, $CDCl_3$, 400 MHz



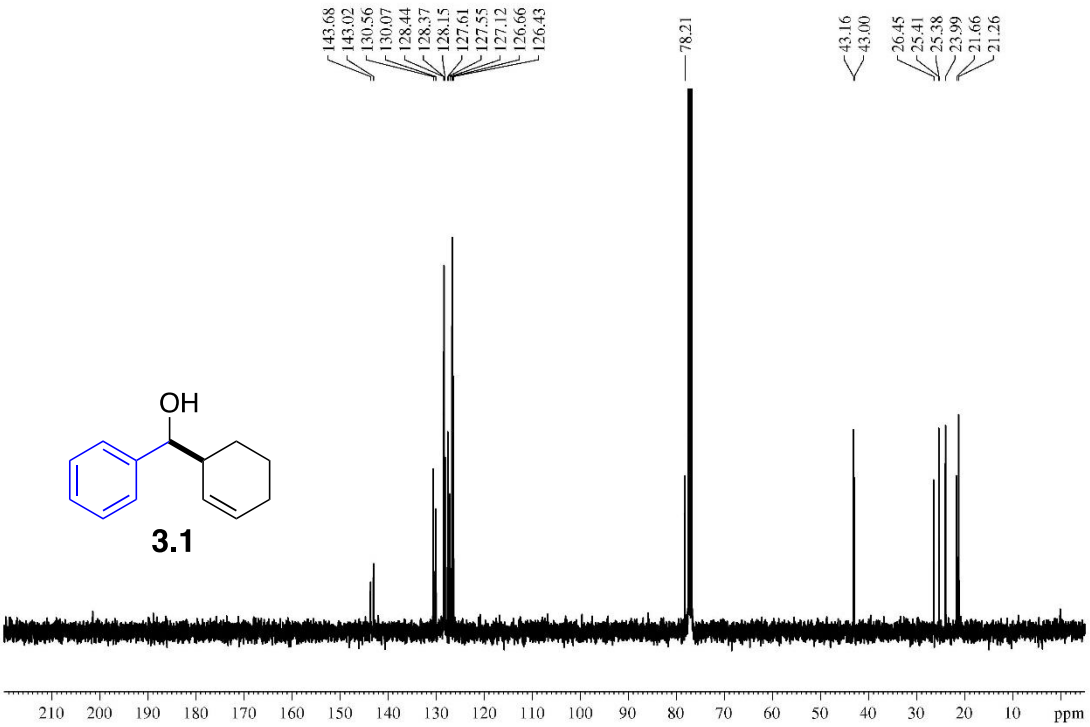
^{13}C NMR of **2.17**, $CDCl_3$, 100 MHz



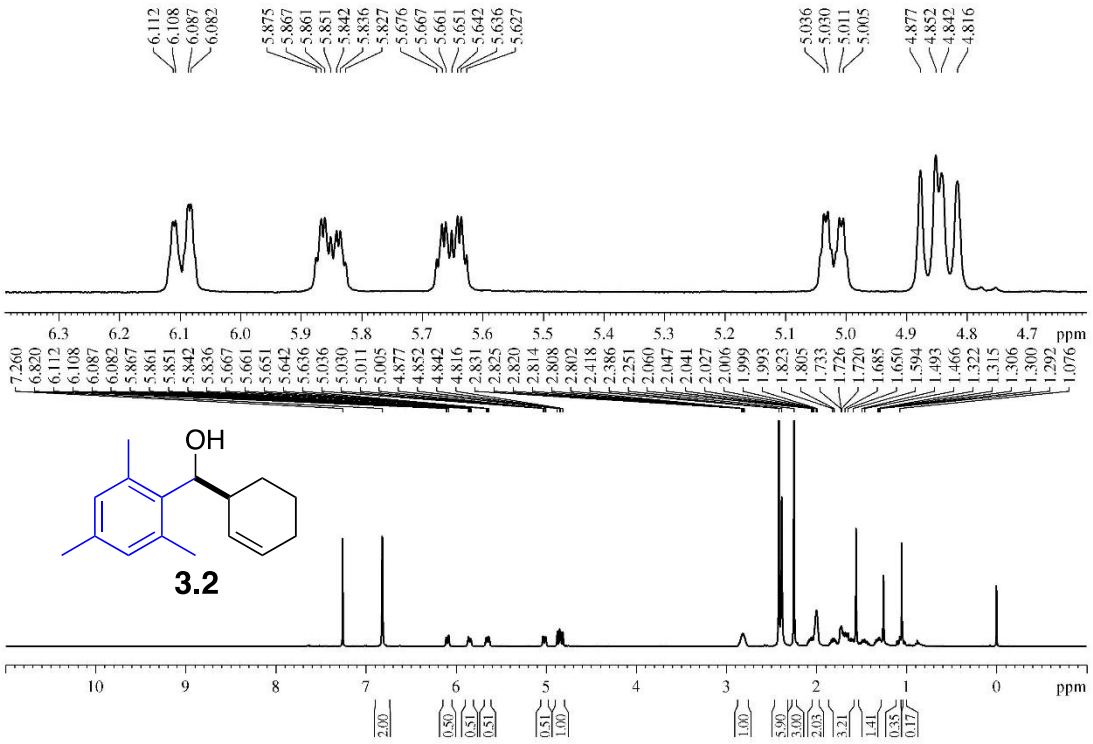
^{1}H NMR of **3.1**, $CDCl_3$, 400 MHz



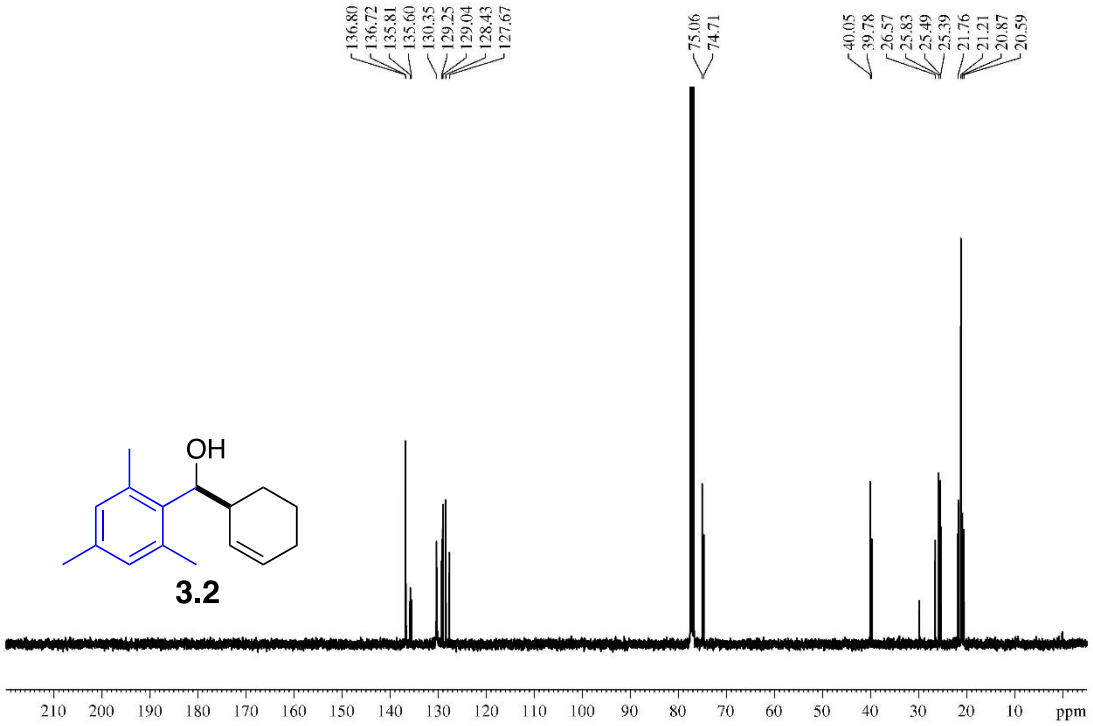
^{13}C NMR of **3.1**, $CDCl_3$, 100 MHz



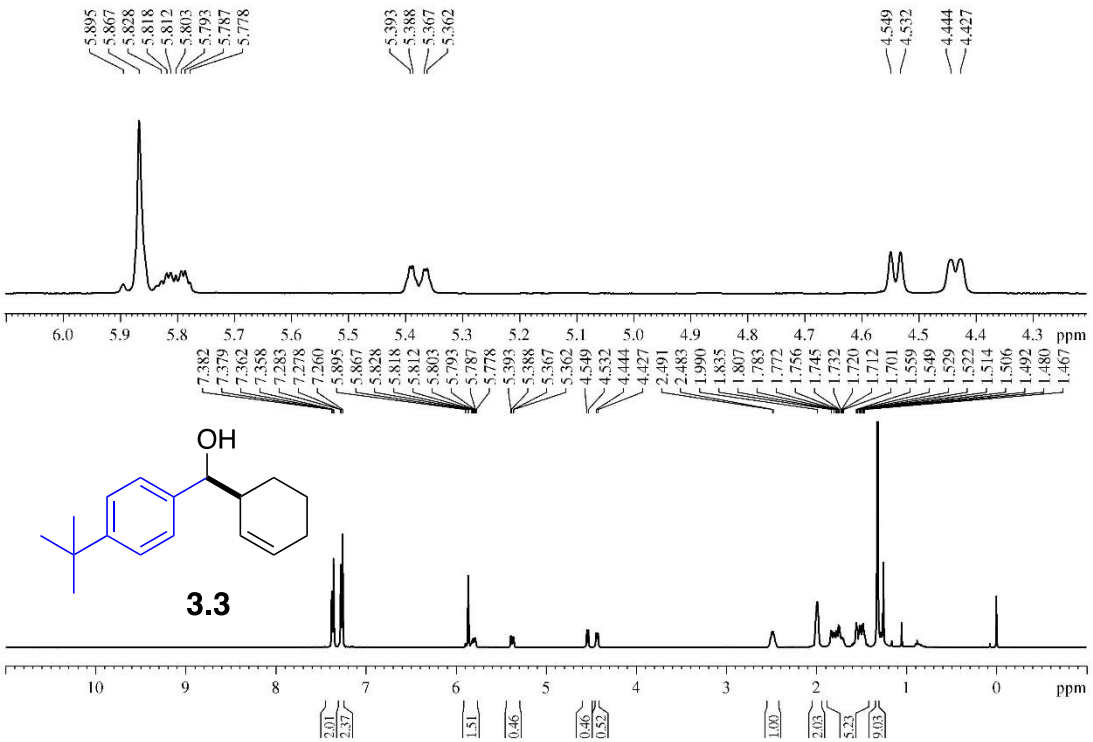
^{1}H NMR of **3.2**, $CDCl_3$, 400 MHz



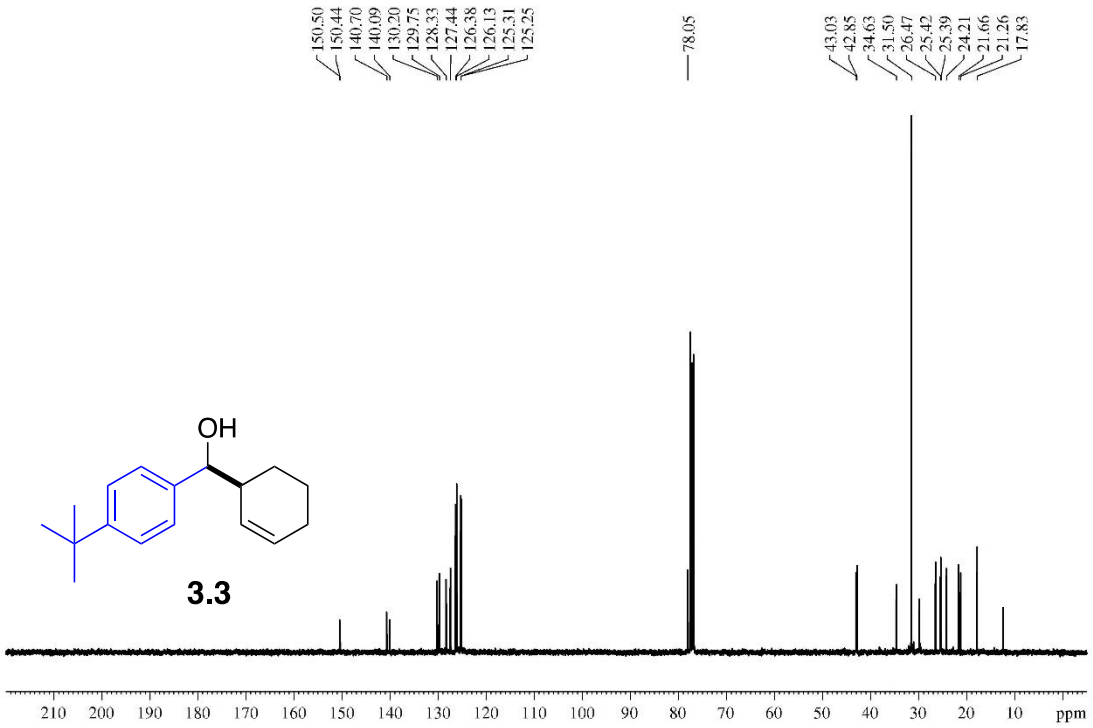
^{13}C NMR of **3.2**, $CDCl_3$, 100 MHz



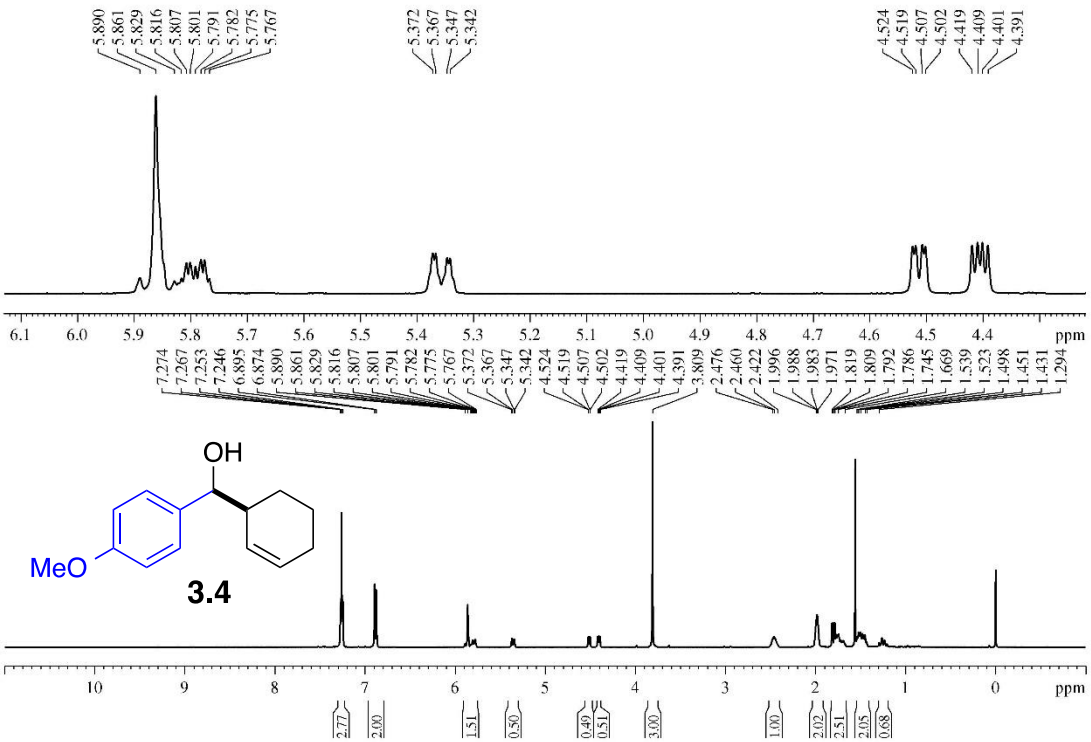
^{1}H NMR of **3.3**, $CDCl_3$, 400 MHz



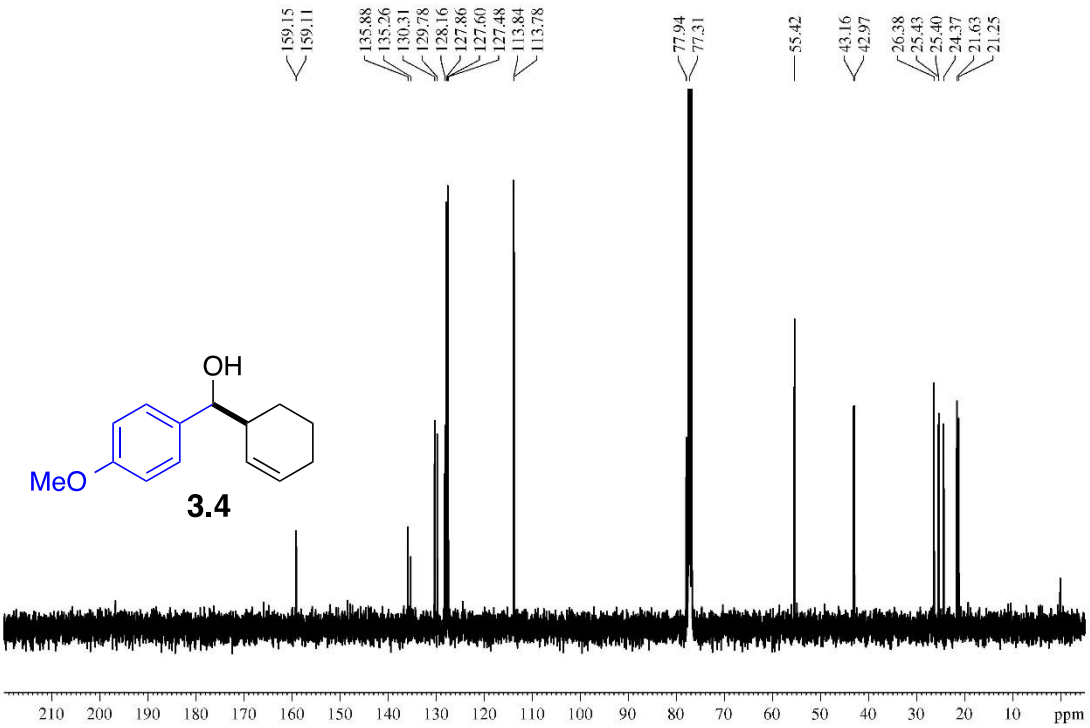
^{13}C NMR of **3.3**, $CDCl_3$, 100 MHz



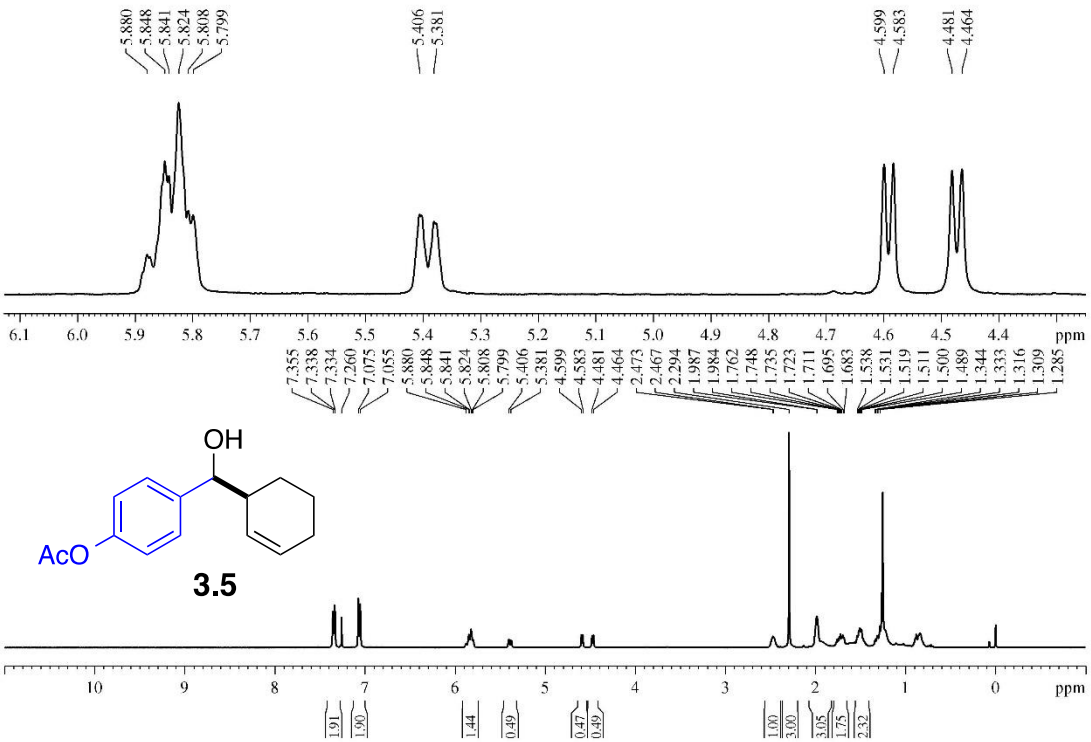
^{1}H NMR of **3.4**, $CDCl_3$, 400 MHz



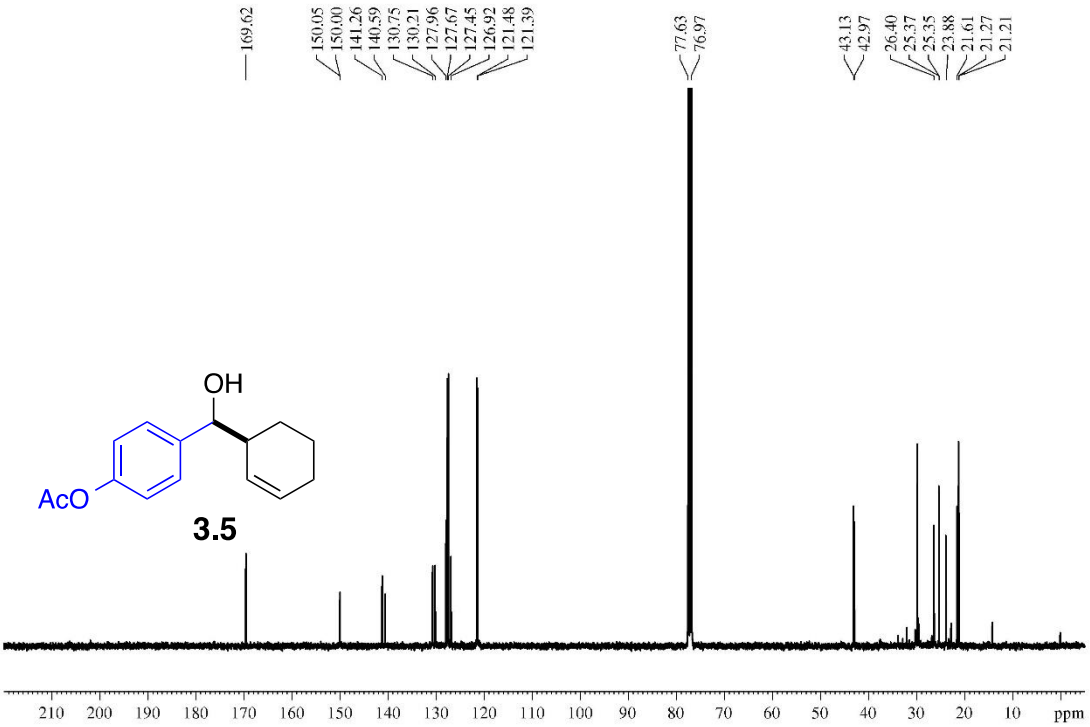
^{13}C NMR of **3.4**, $CDCl_3$, 100 MHz



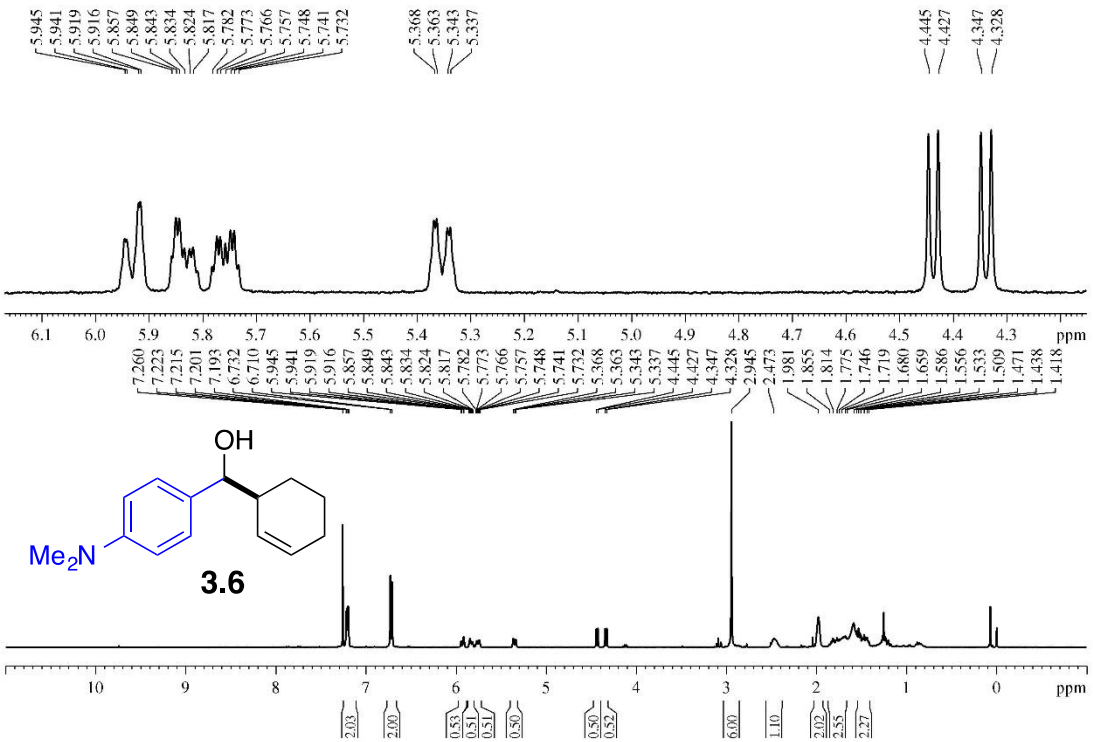
^{1}H NMR of **3.5**, $CDCl_3$, 400 MHz



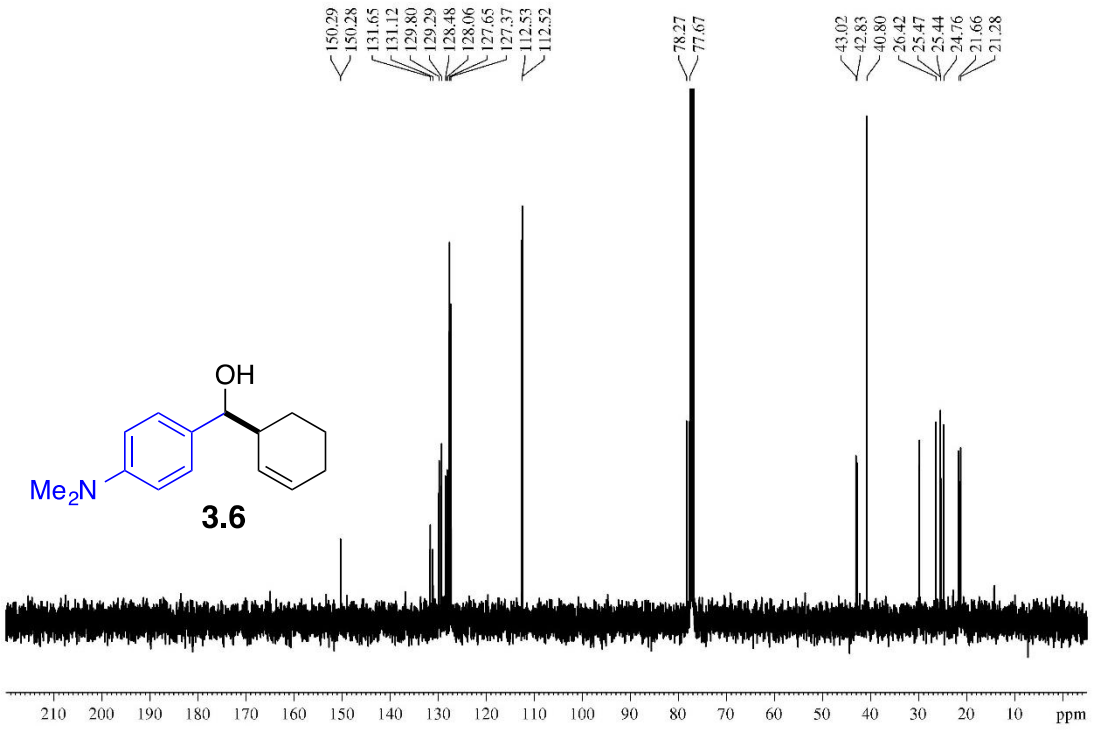
^{13}C NMR of **3.5**, $CDCl_3$, 100 MHz



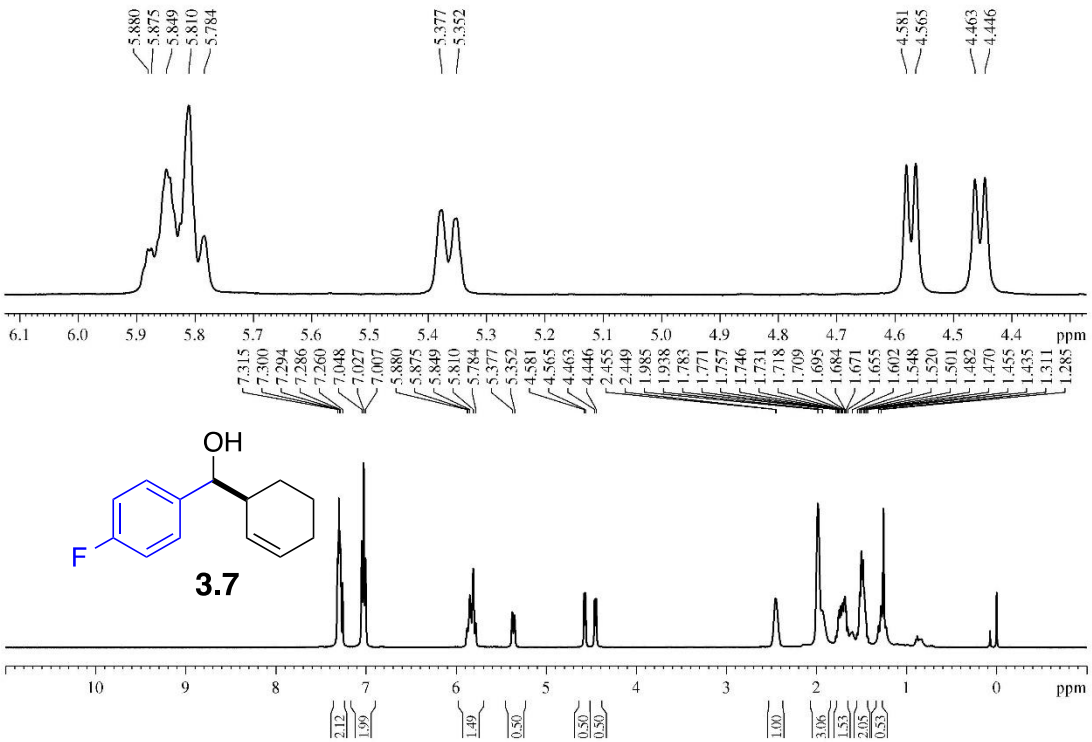
^{1}H NMR of **3.6**, $CDCl_3$, 400 MHz



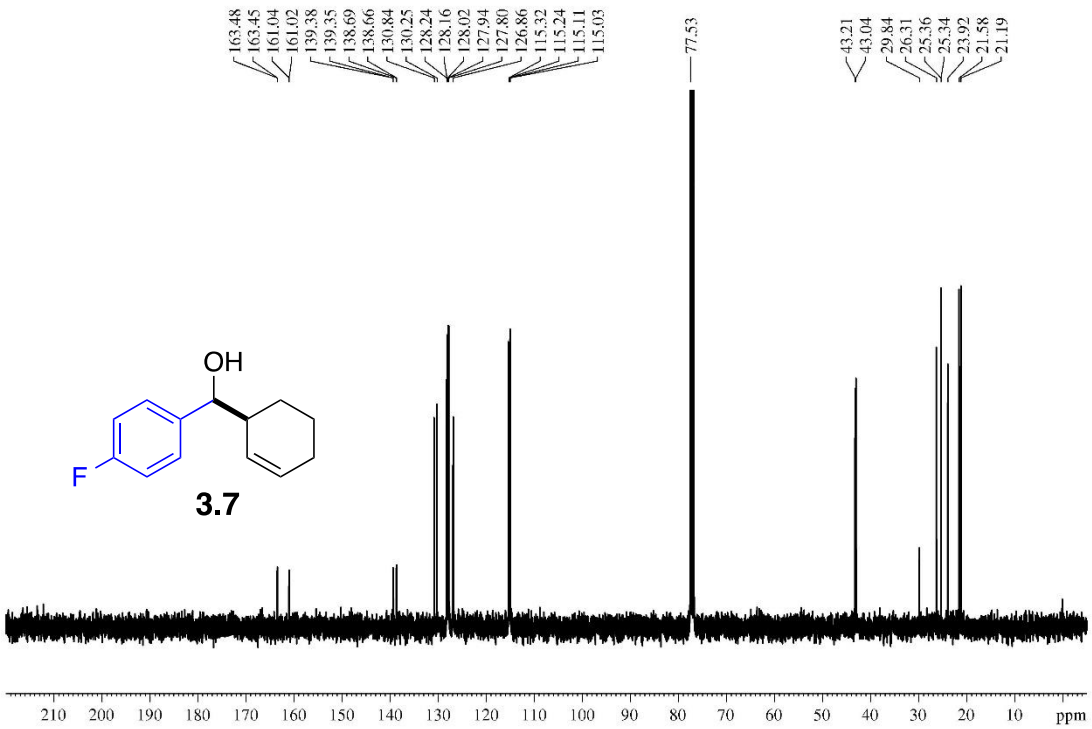
^{13}C NMR of **3.6**, $CDCl_3$, 100 MHz



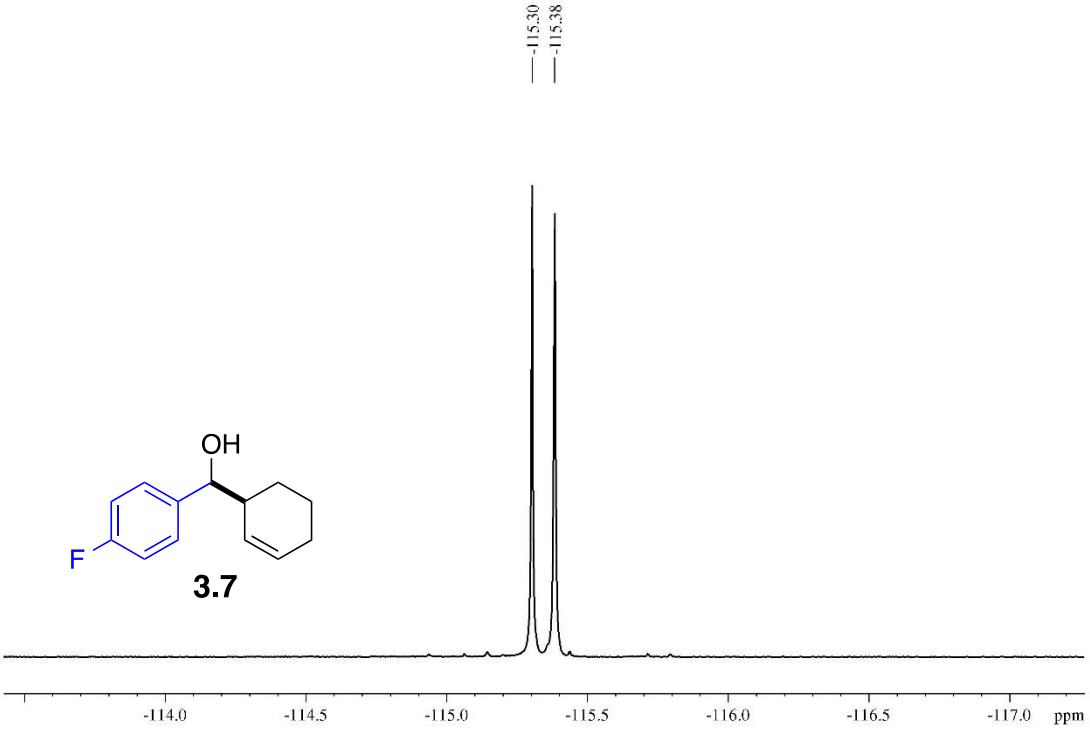
^{1}H NMR of **3.7**, $CDCl_3$, 400 MHz



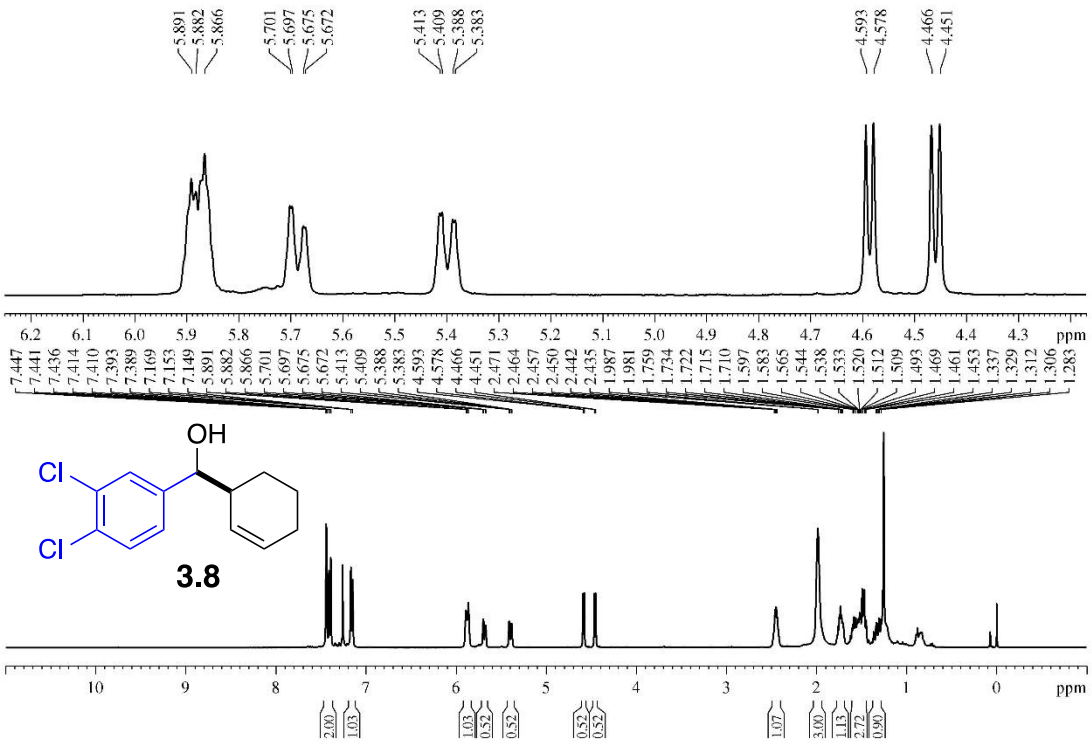
^{13}C NMR of **3.7**, $CDCl_3$, 100 MHz



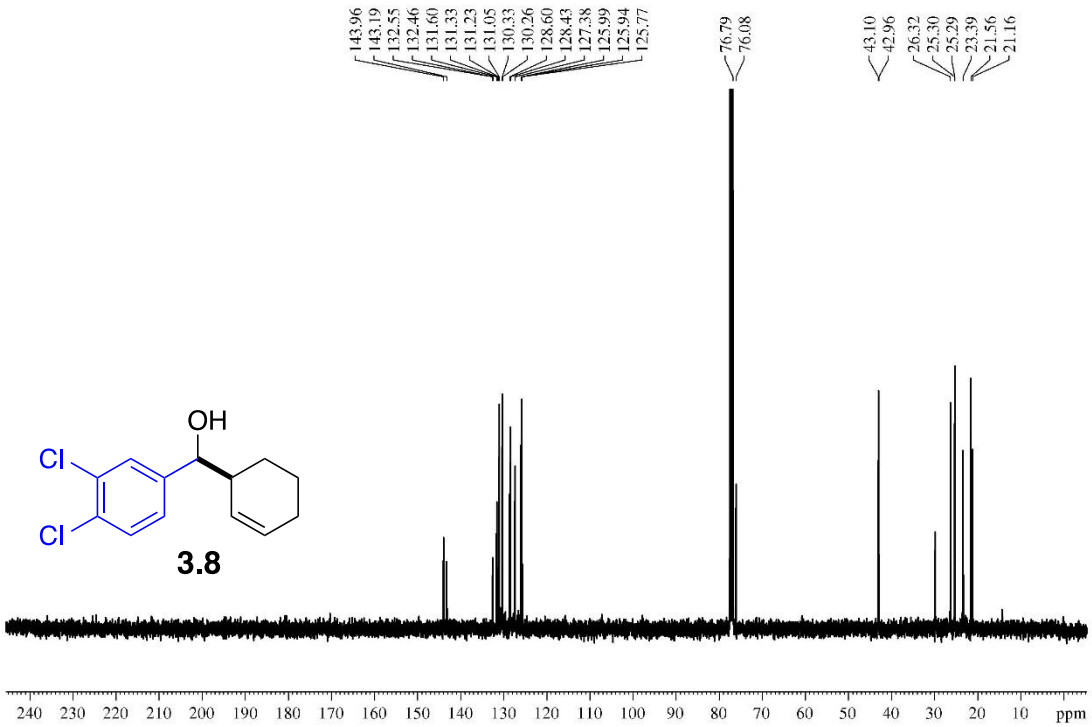
^{19}F NMR of **3.7**, $CDCl_3$, 376 MHz



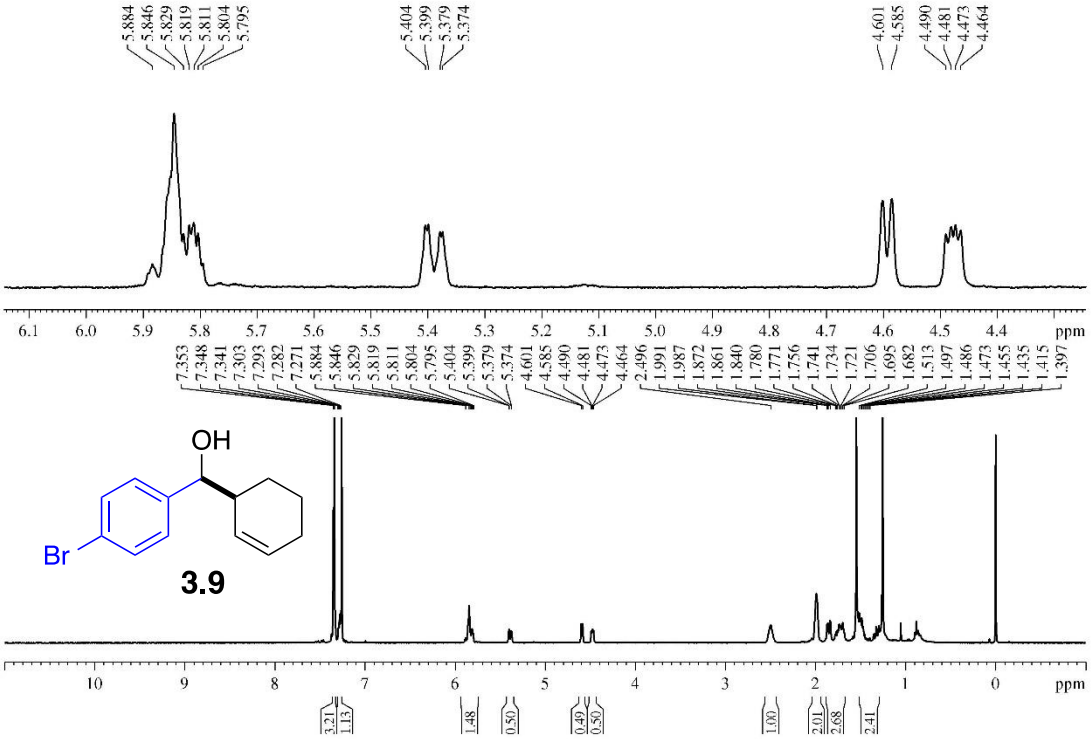
^{1}H NMR of **3.8**, $CDCl_3$, 400 MHz



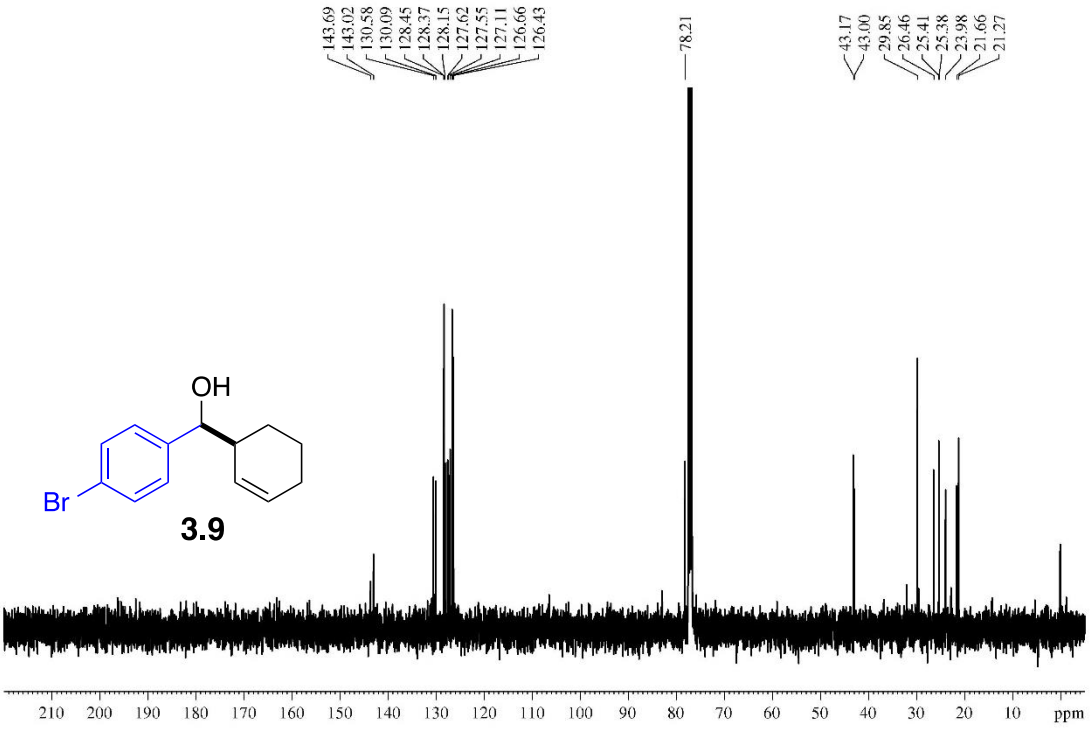
^{13}C NMR of **3.8**, $CDCl_3$, 100 MHz



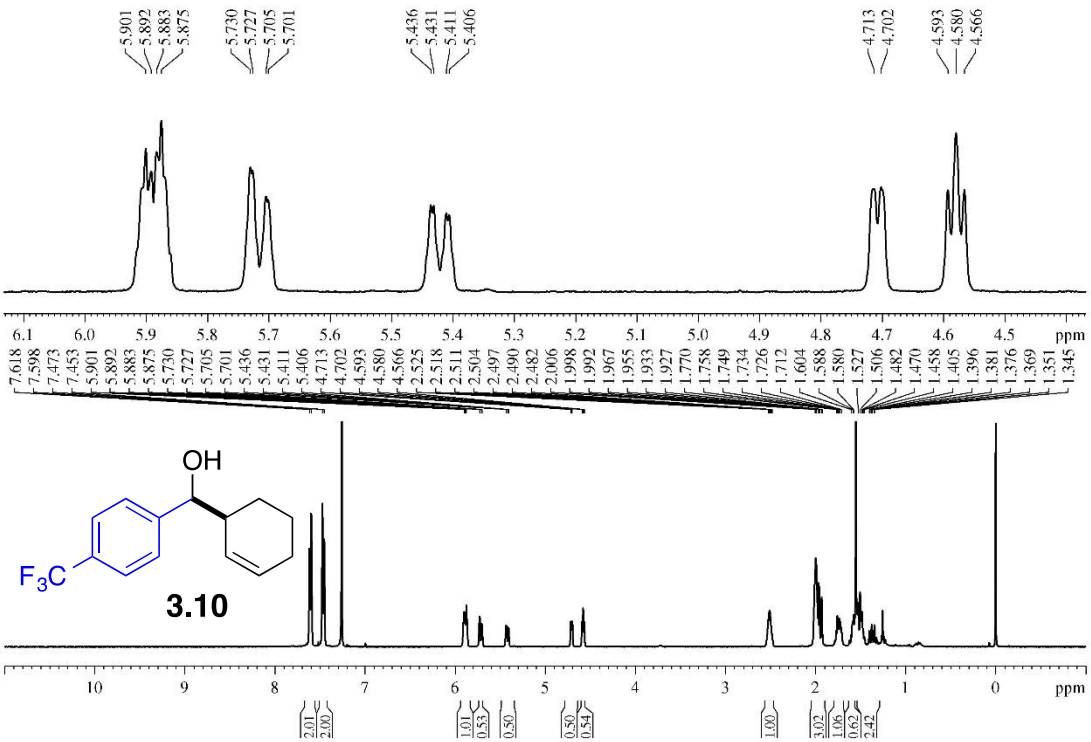
^{1}H NMR of **3.9**, $CDCl_3$, 400 MHz



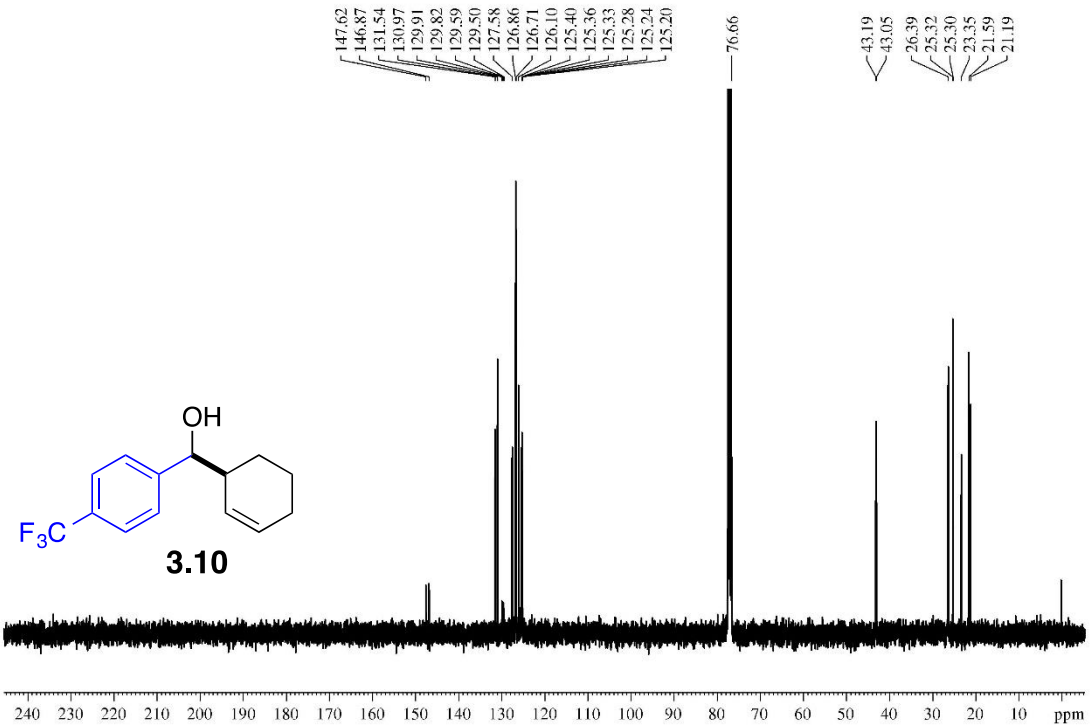
^{13}C NMR of **3.9**, $CDCl_3$, 100 MHz



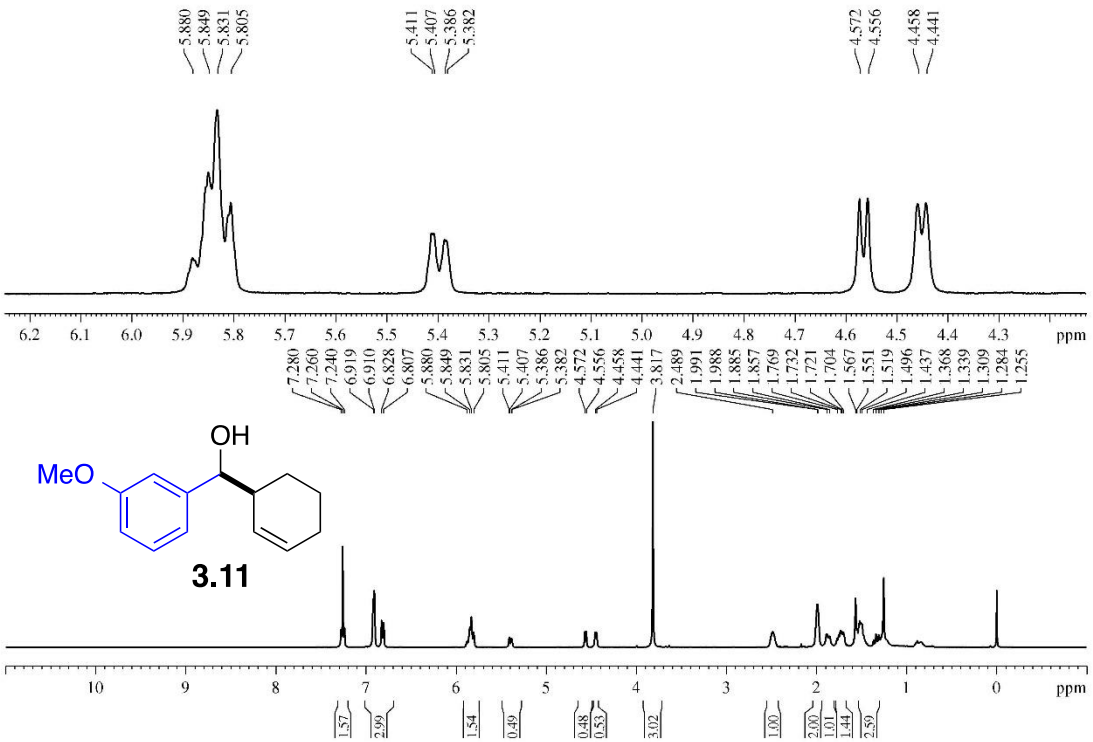
^{1}H NMR of **3.10**, $CDCl_3$, 400 MHz



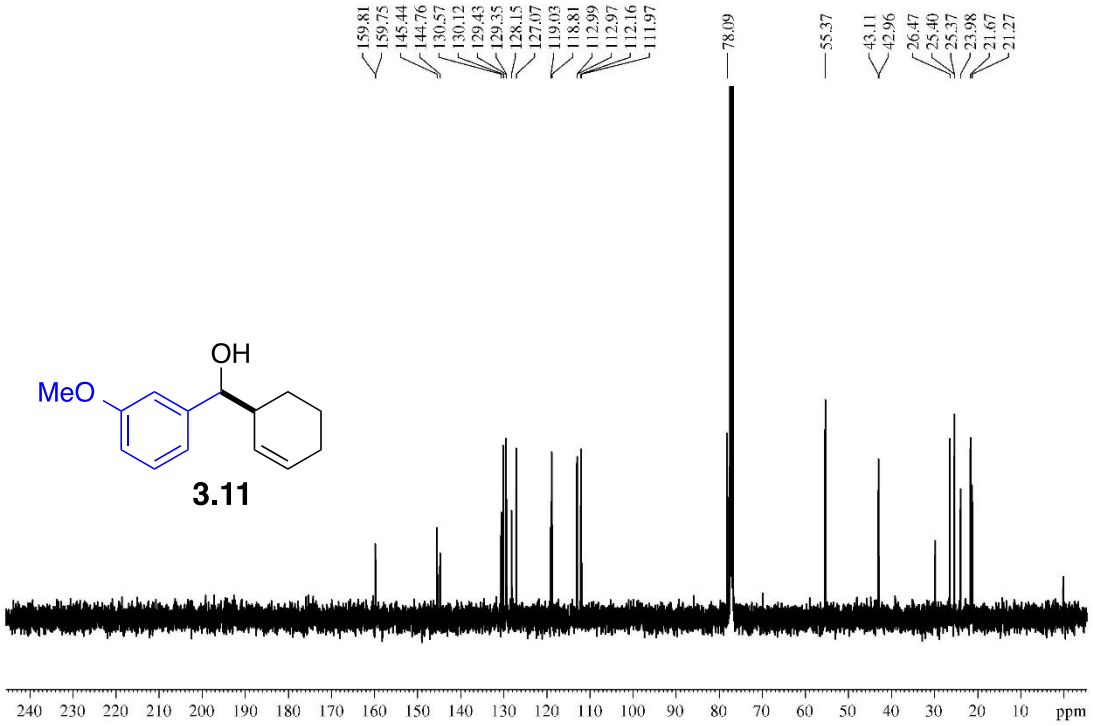
^{13}C NMR of **3.10**, $CDCl_3$, 100 MHz



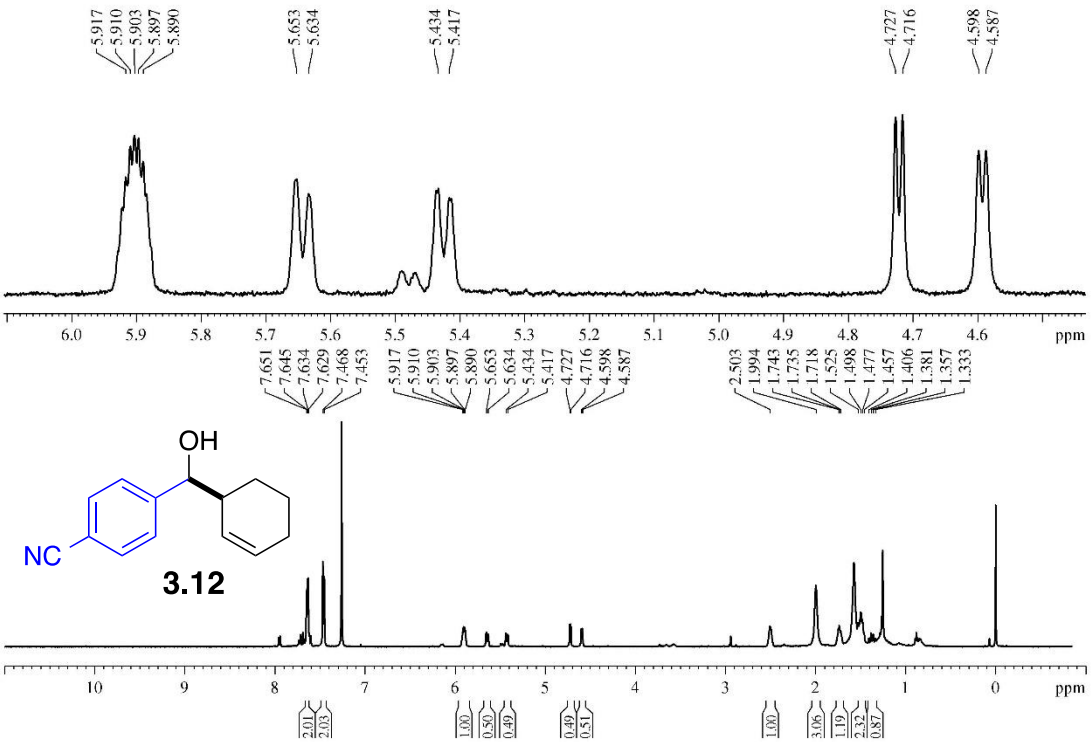
^{1}H NMR of **3.11**, $CDCl_3$, 400 MHz



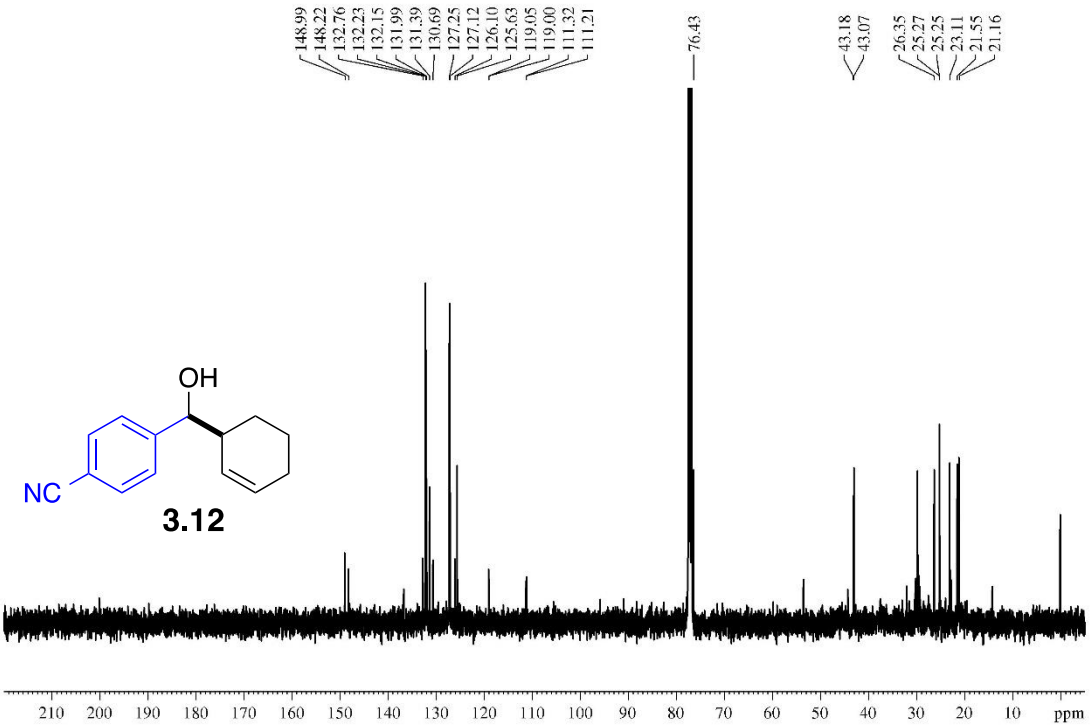
^{13}C NMR of **3.11**, $CDCl_3$, 100 MHz



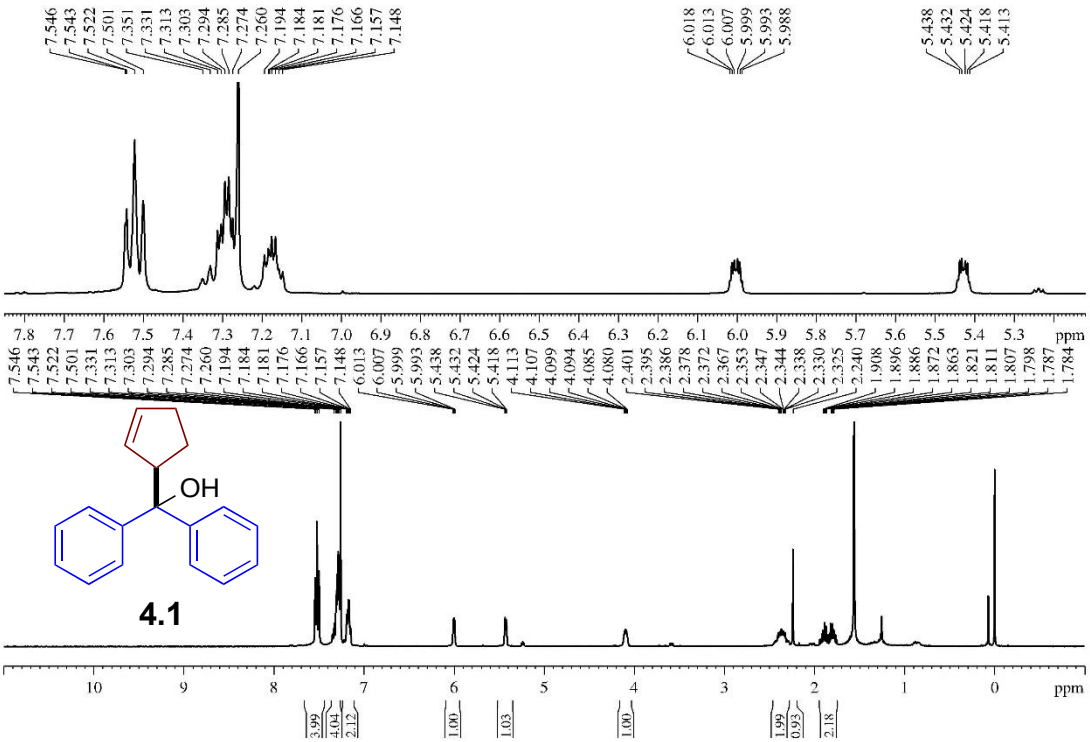
^{1}H NMR of **3.12**, $CDCl_3$, 500 MHz



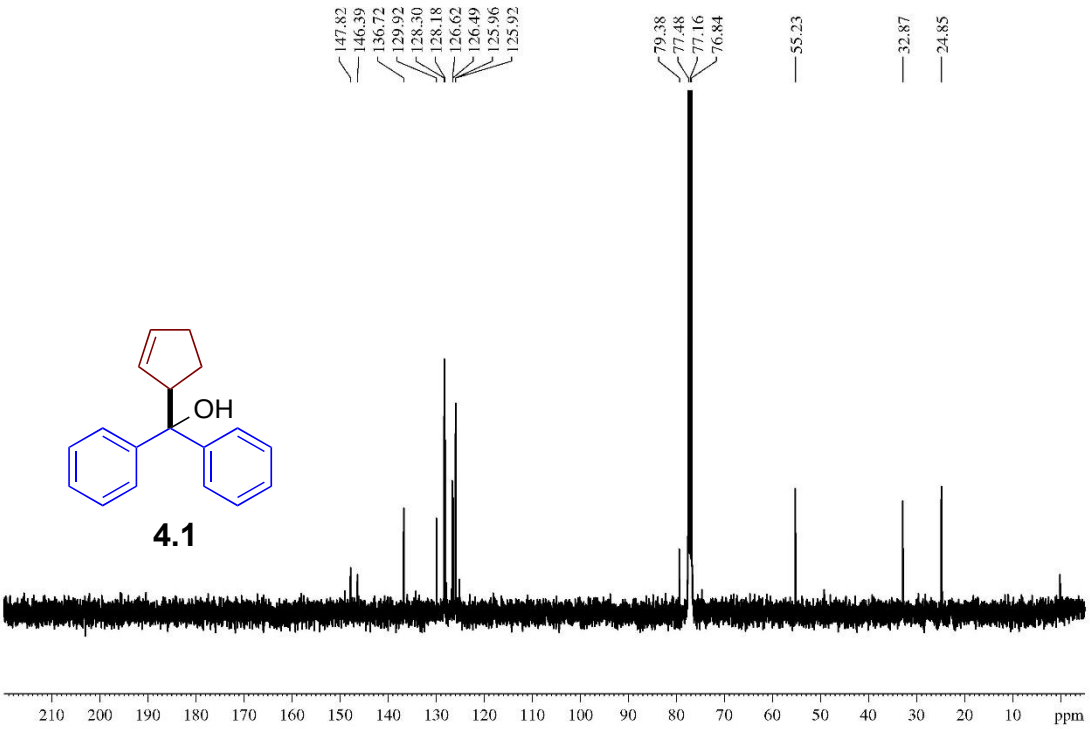
^{13}C NMR of **3.12**, $CDCl_3$, 100 MHz



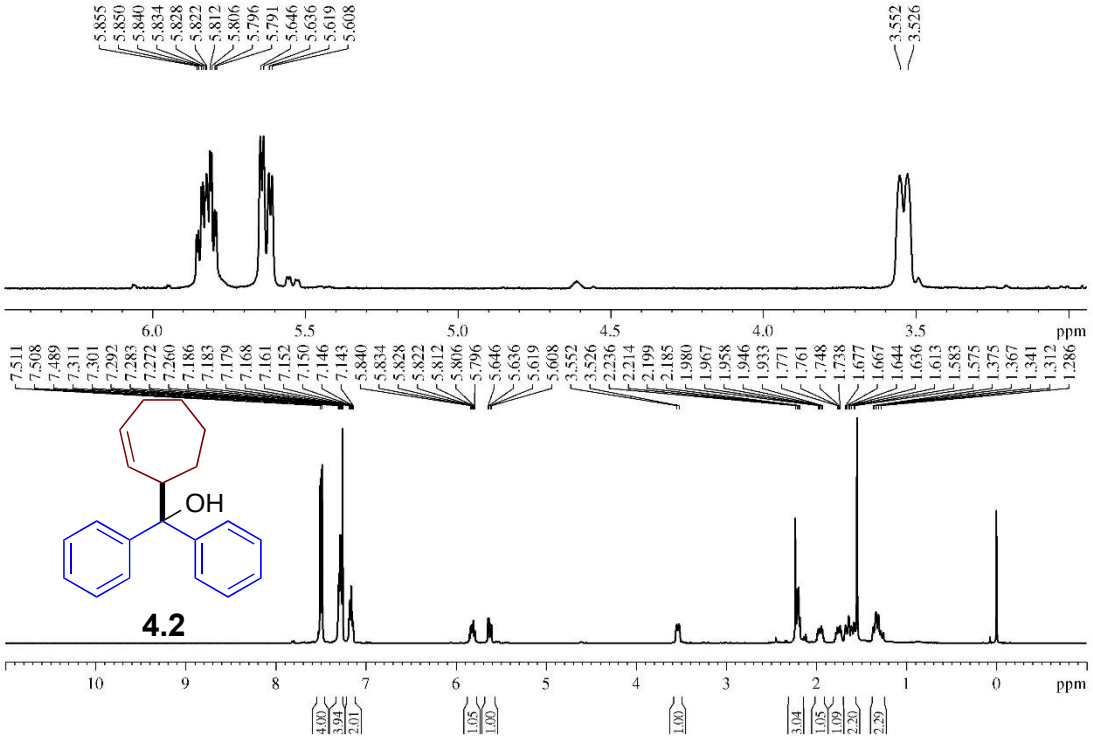
^{1}H NMR of **4.1**, $CDCl_3$, 400 MHz



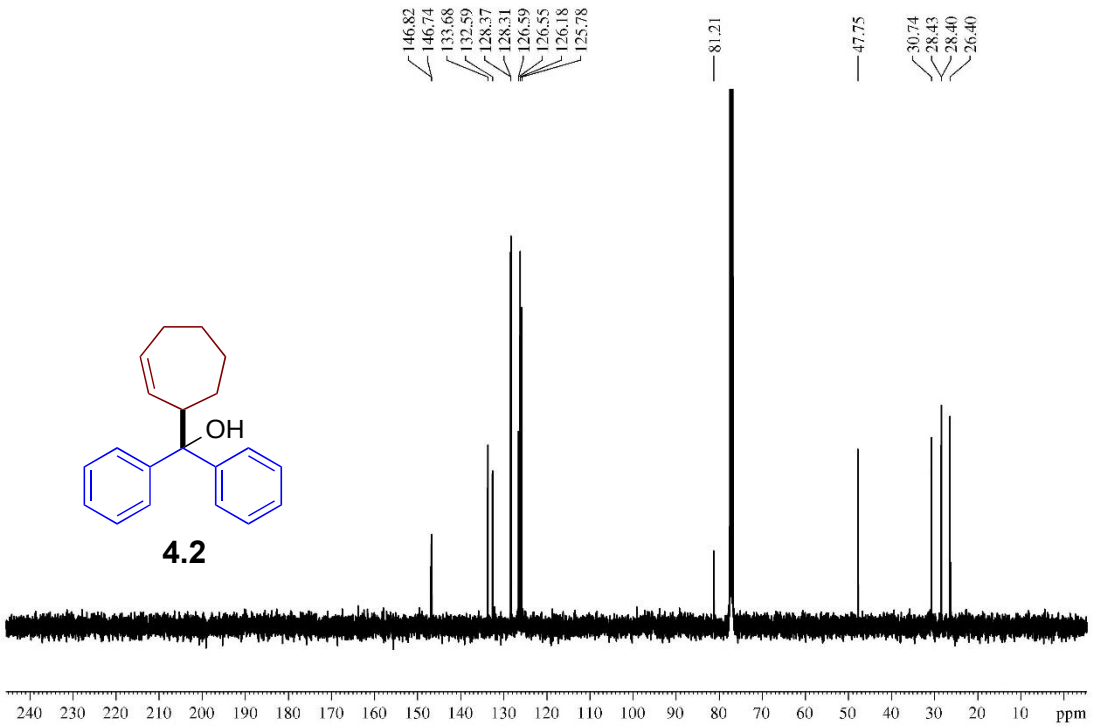
^{13}C NMR of **4.1**, $CDCl_3$, 100 MHz



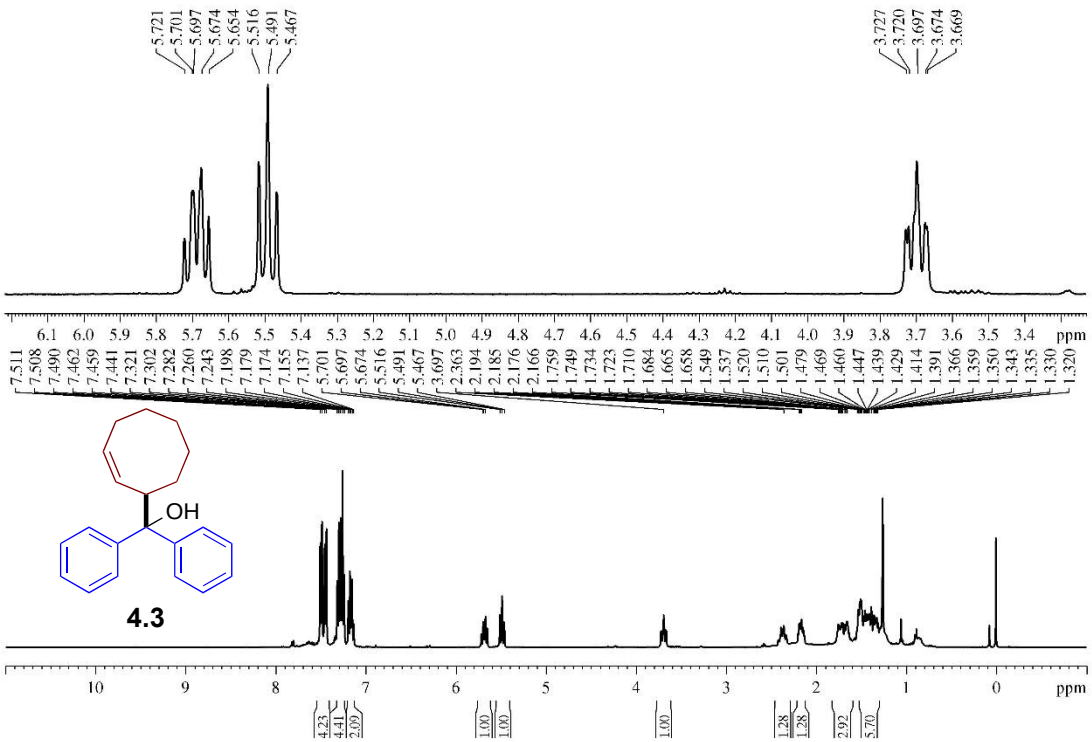
^{1}H NMR of **4.2**, $CDCl_3$, 400 MHz



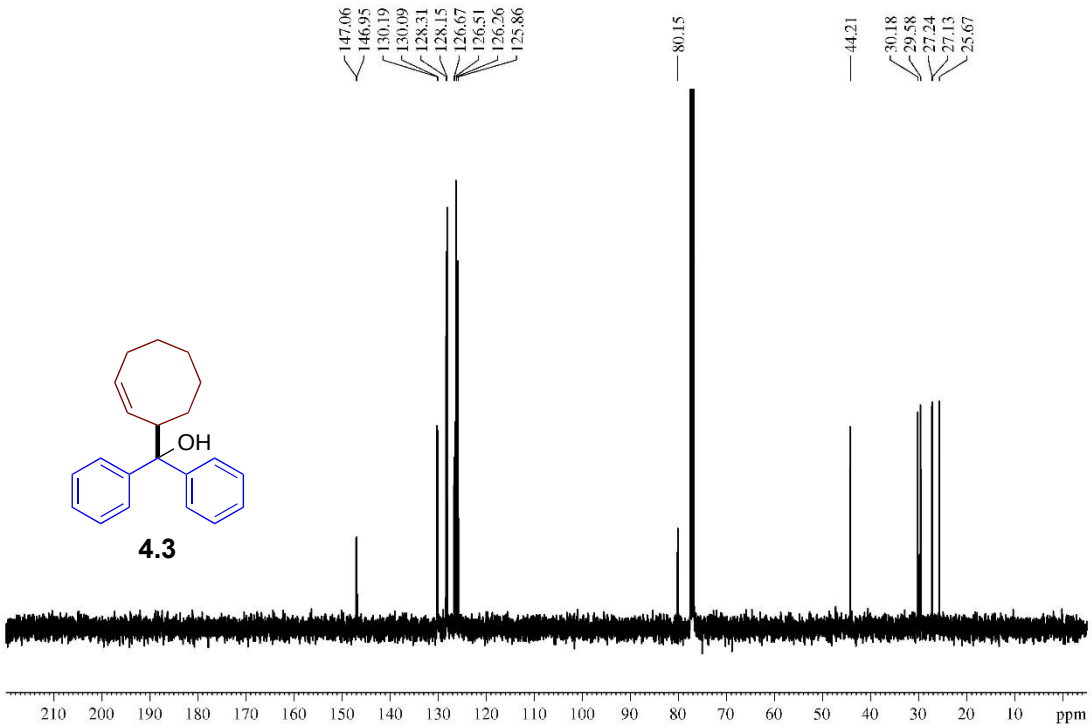
^{13}C NMR of **4.2**, $CDCl_3$, 100 MHz



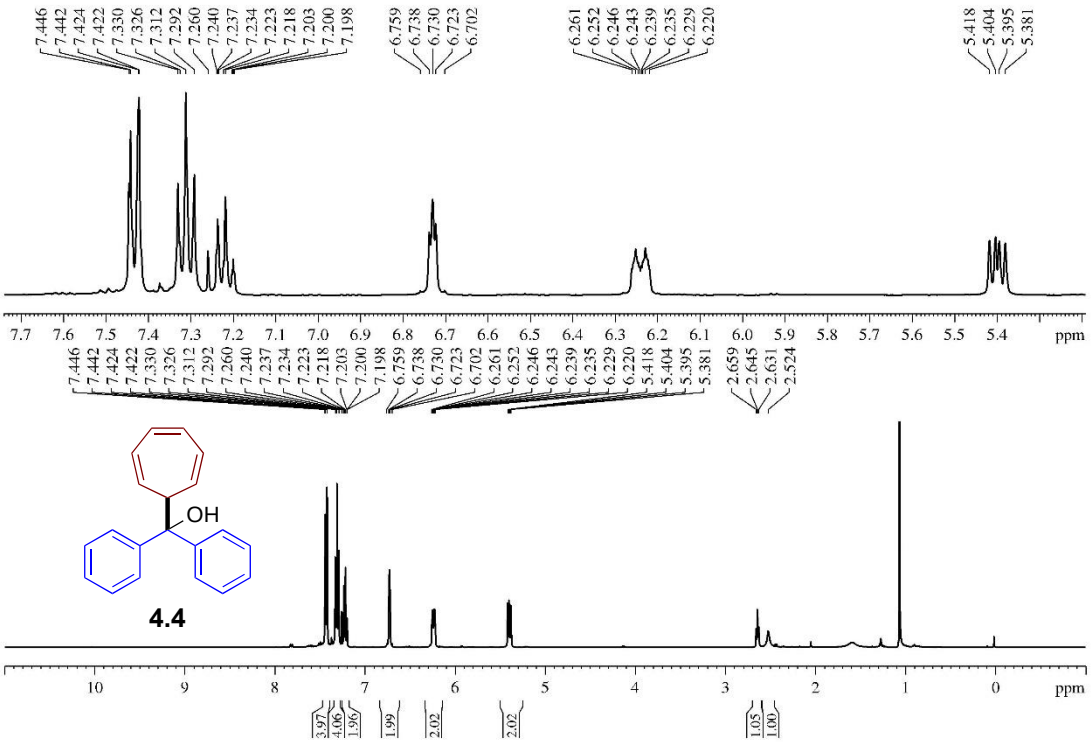
^{1}H NMR of **4.3**, $CDCl_3$, 400 MHz



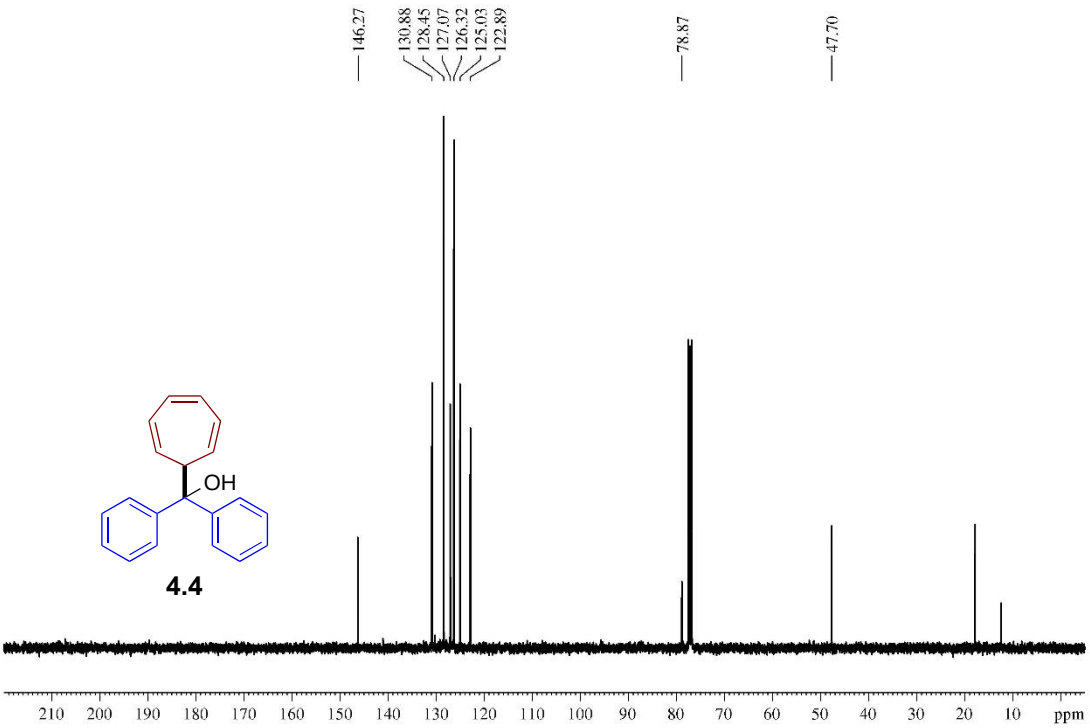
^{13}C NMR of **4.3**, $CDCl_3$, 100 MHz



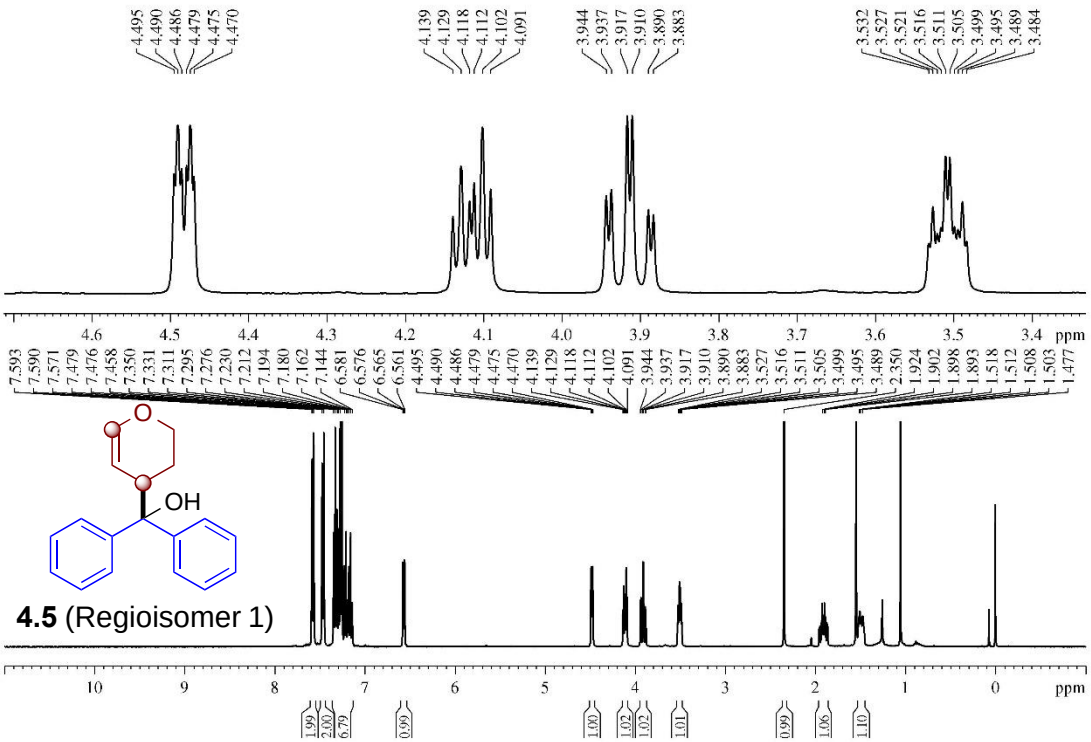
^{1}H NMR of **4.4**, $CDCl_3$, 400 MHz



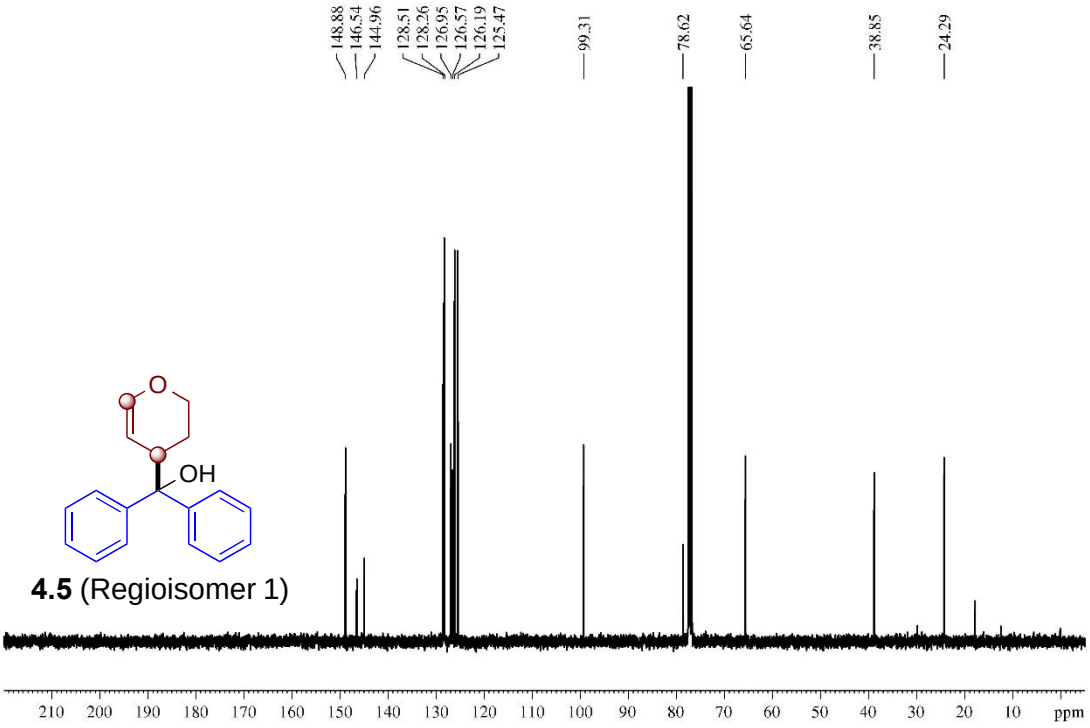
^{13}C NMR of **4.4**, $CDCl_3$, 100 MHz



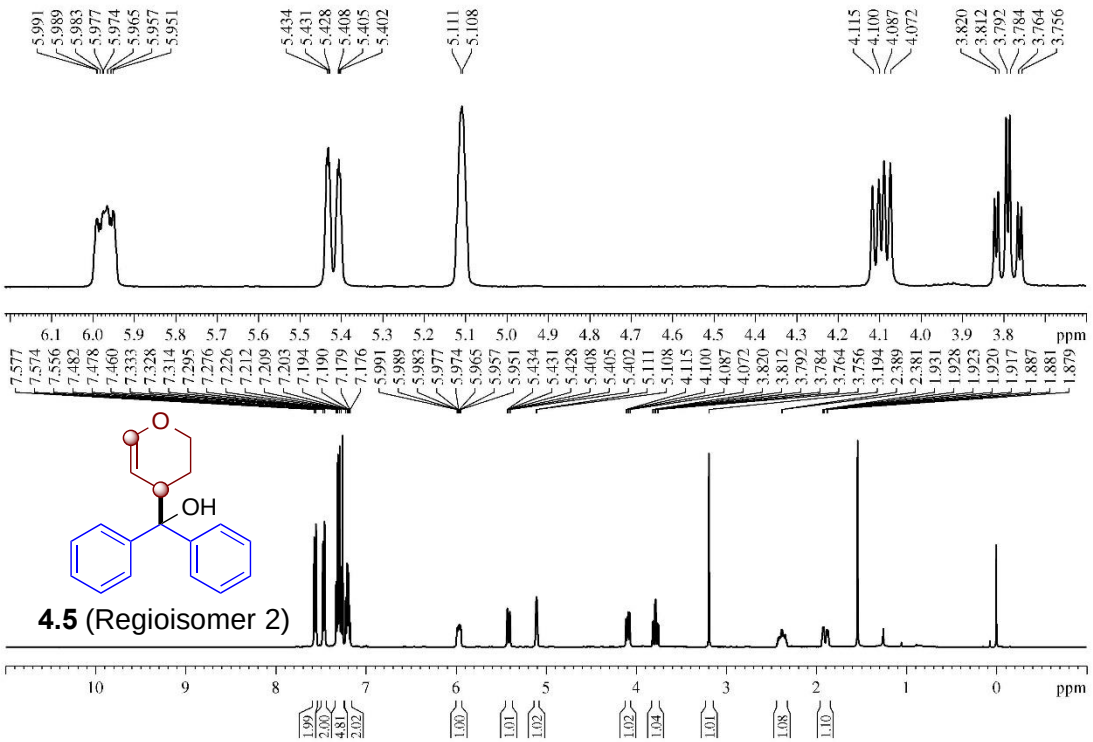
^{1}H NMR of **4.5** Regioisomer 1, $CDCl_3$, 400 MHz



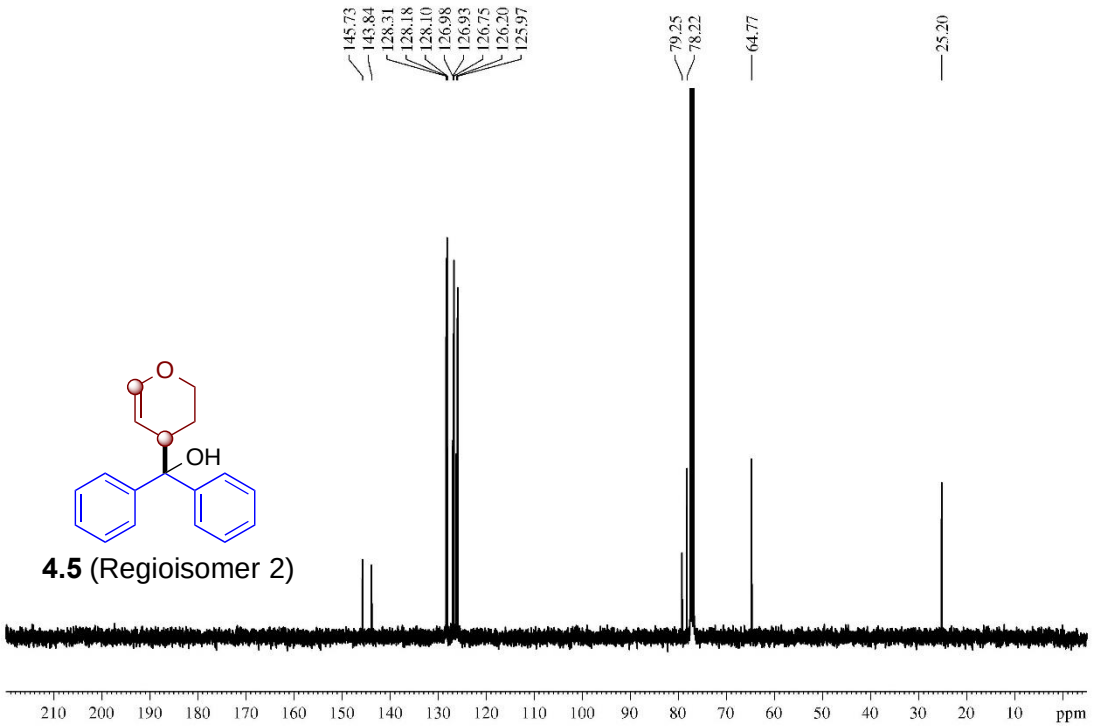
^{13}C NMR of **4.5** Regioisomer 1, $CDCl_3$, 100 MHz



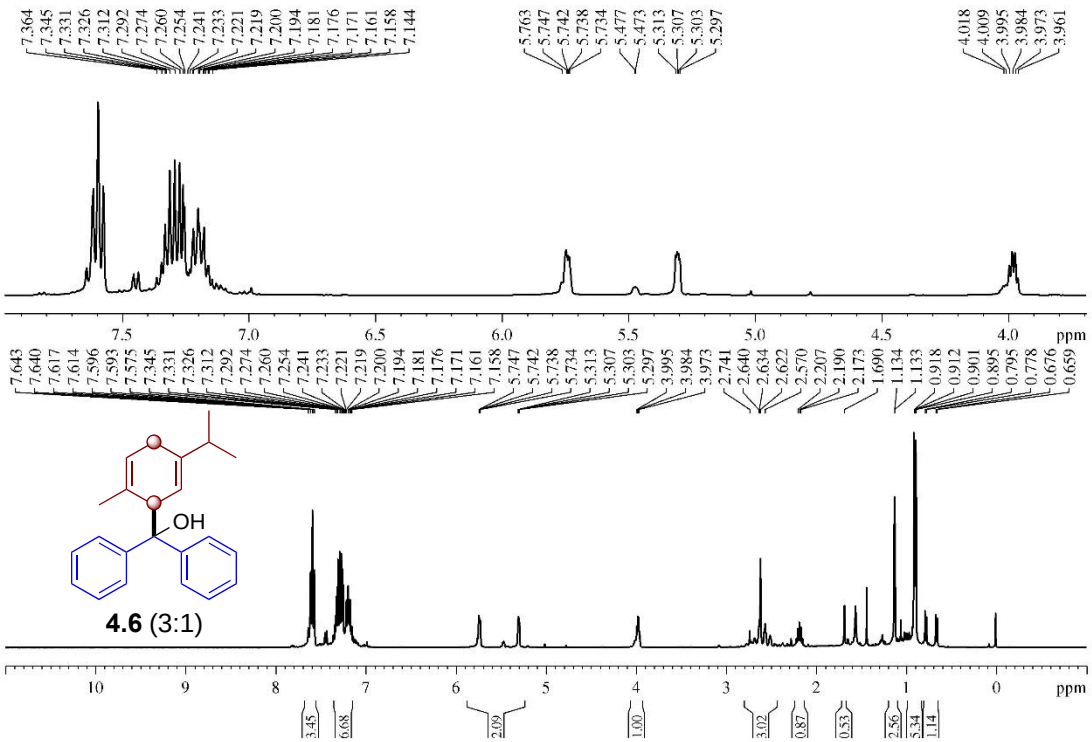
^{1}H NMR of **4.5** Regioisomer 2, $CDCl_3$, 400 MHz



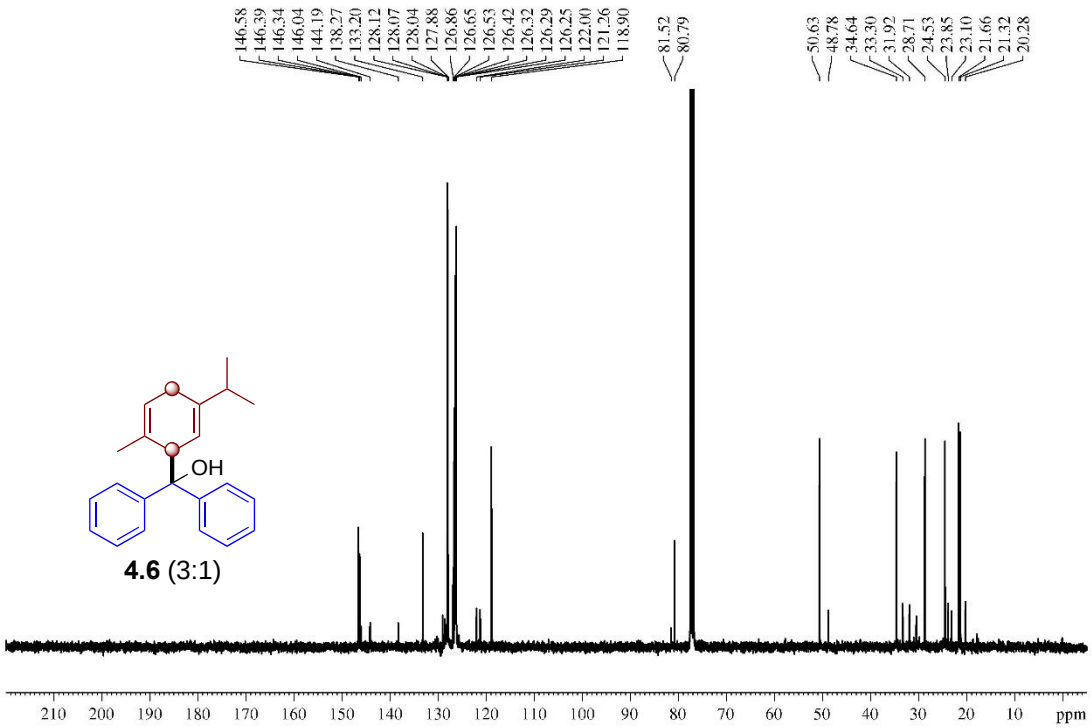
^{13}C NMR of **4.5** Regioisomer 2, $CDCl_3$, 100 MHz



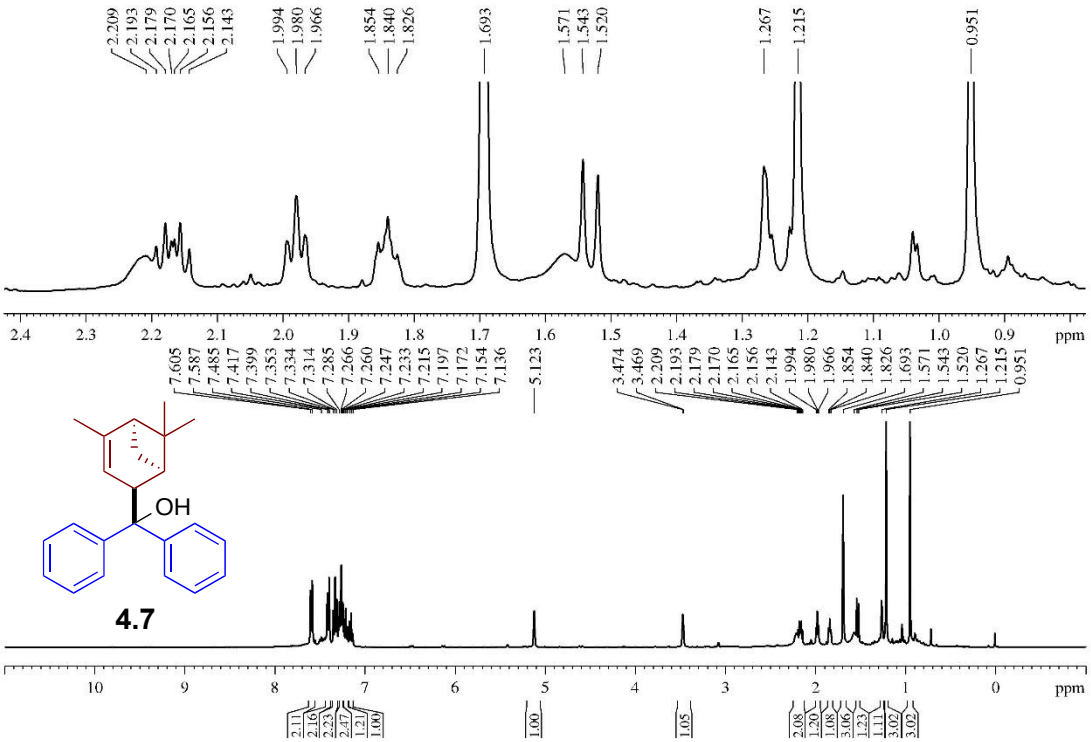
^{1}H NMR of **4.6** (Mixture of Regioisomers), $CDCl_3$, 400 MHz



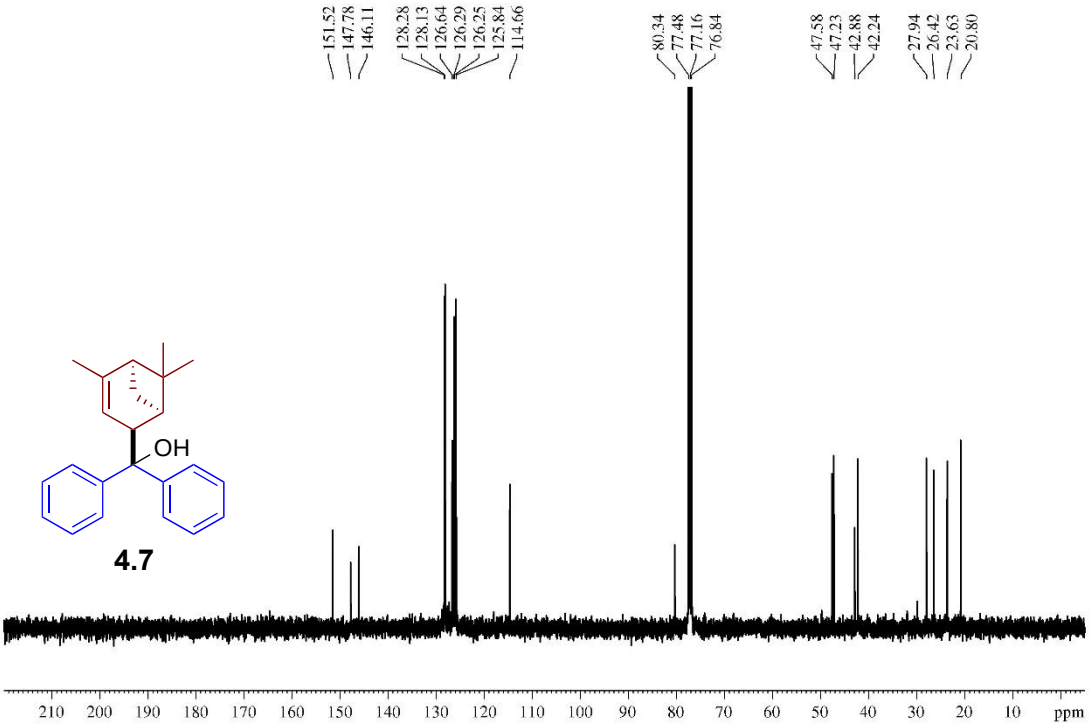
^{13}C NMR of **4.6** (Mixture of Regioisomers), $CDCl_3$, 100 MHz



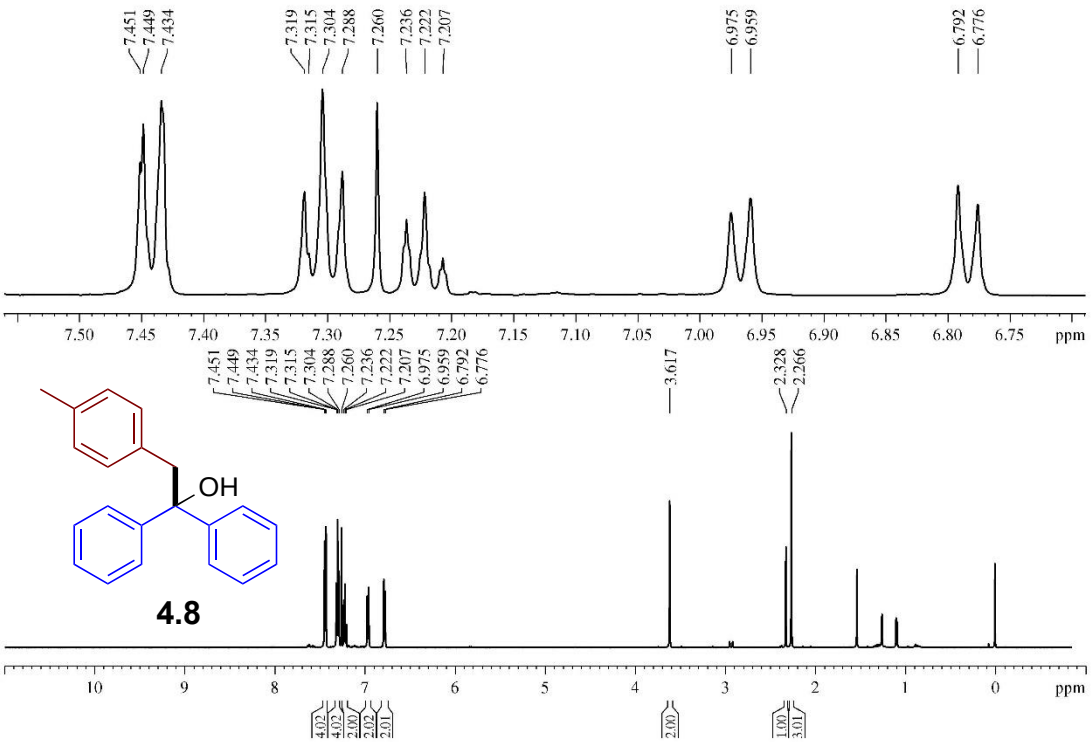
^{1}H NMR of **4.7**, $CDCl_3$, 400 MHz



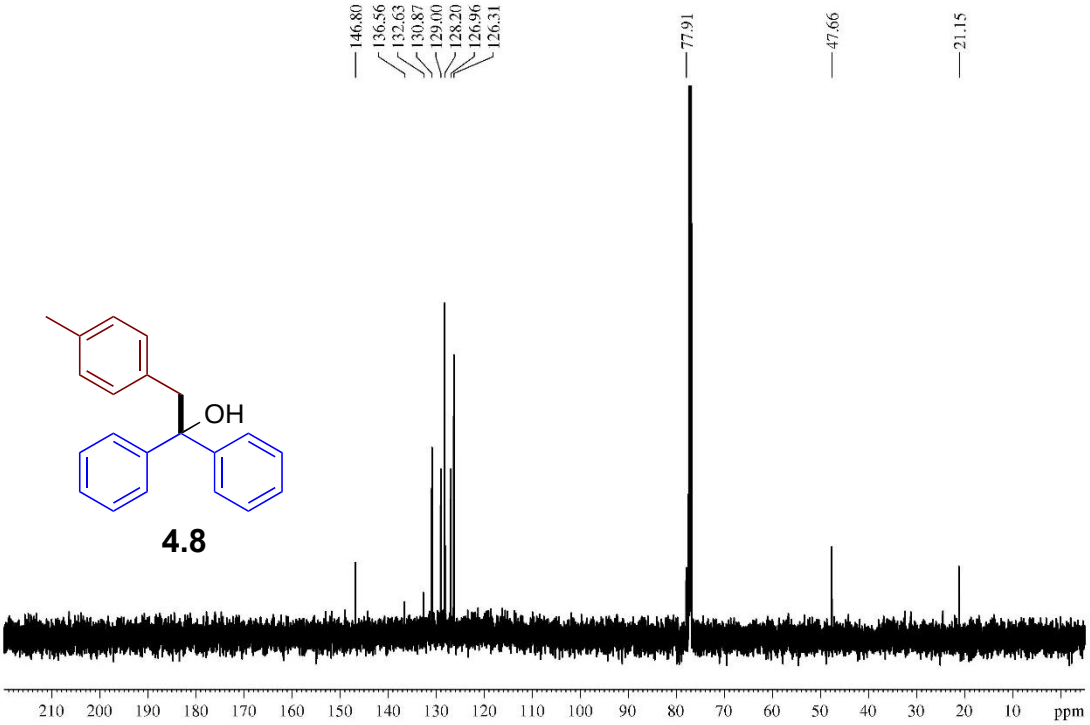
^{13}C NMR of **4.7**, $CDCl_3$, 100 MHz



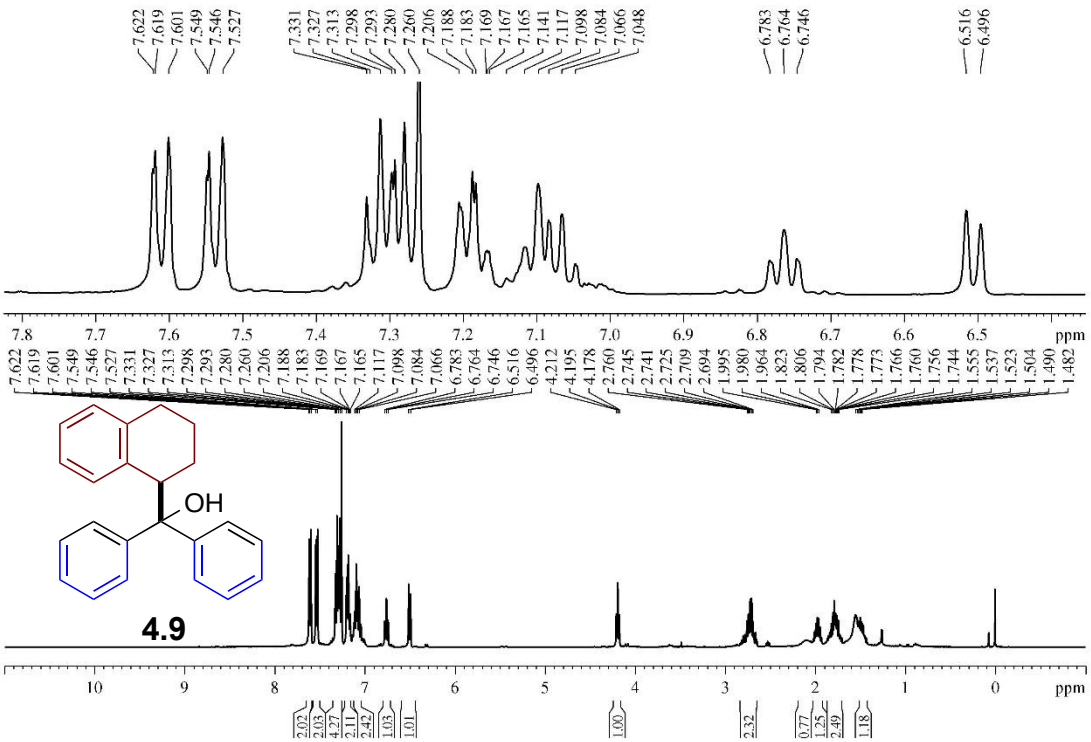
^{1}H NMR of **4.8**, $CDCl_3$, 500 MHz



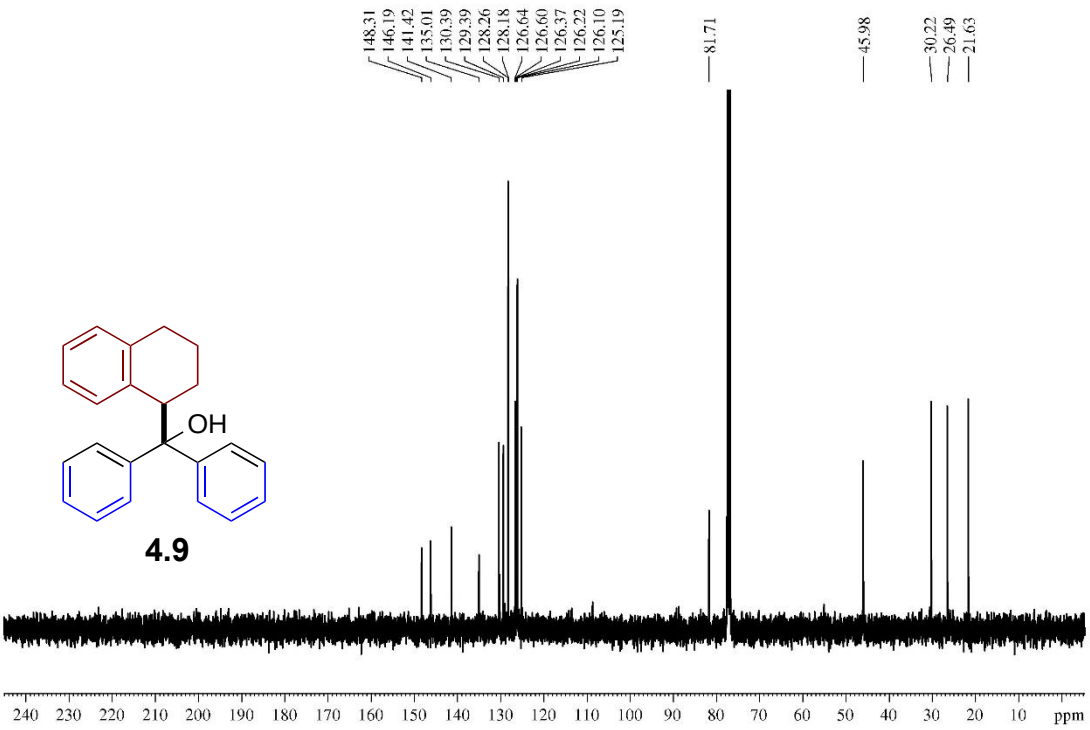
^{13}C NMR of **4.8**, $CDCl_3$, 125 MHz



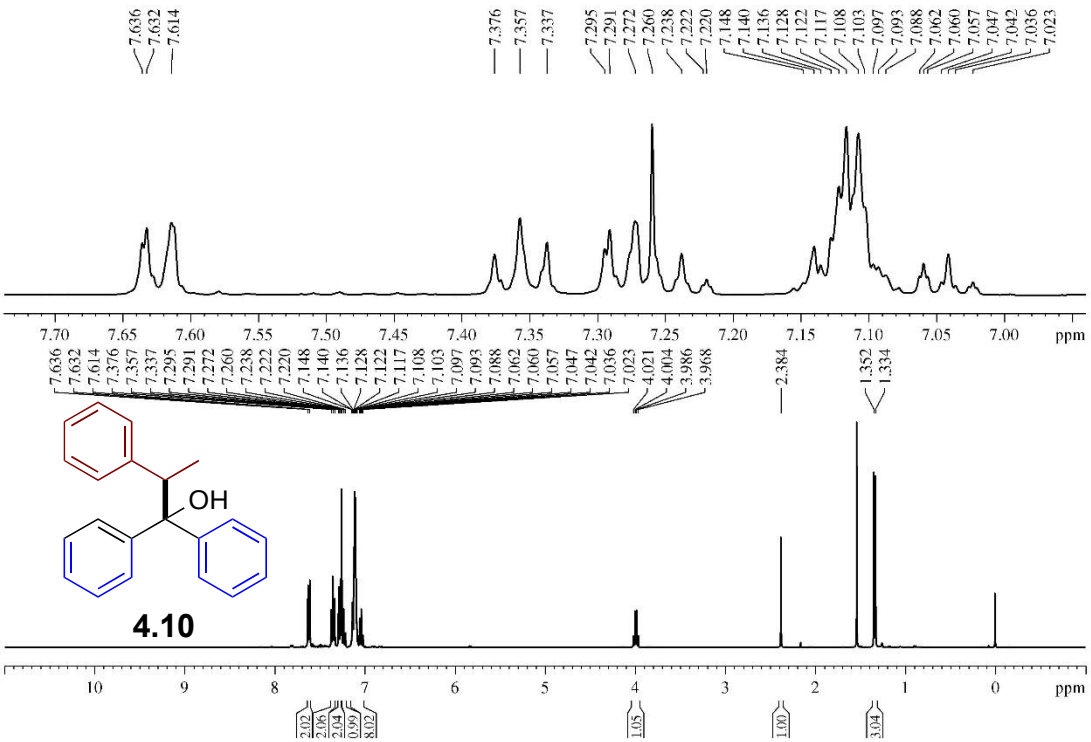
^{1}H NMR of **4.9**, $CDCl_3$, 400 MHz



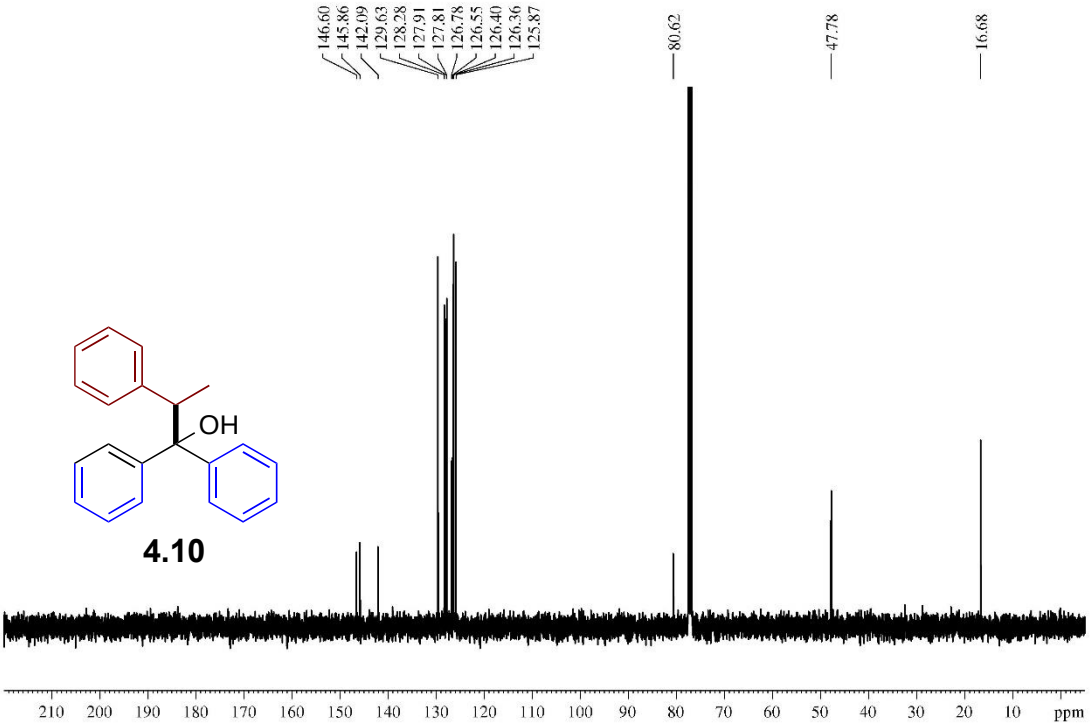
^{13}C NMR of **4.9**, $CDCl_3$, 100 MHz



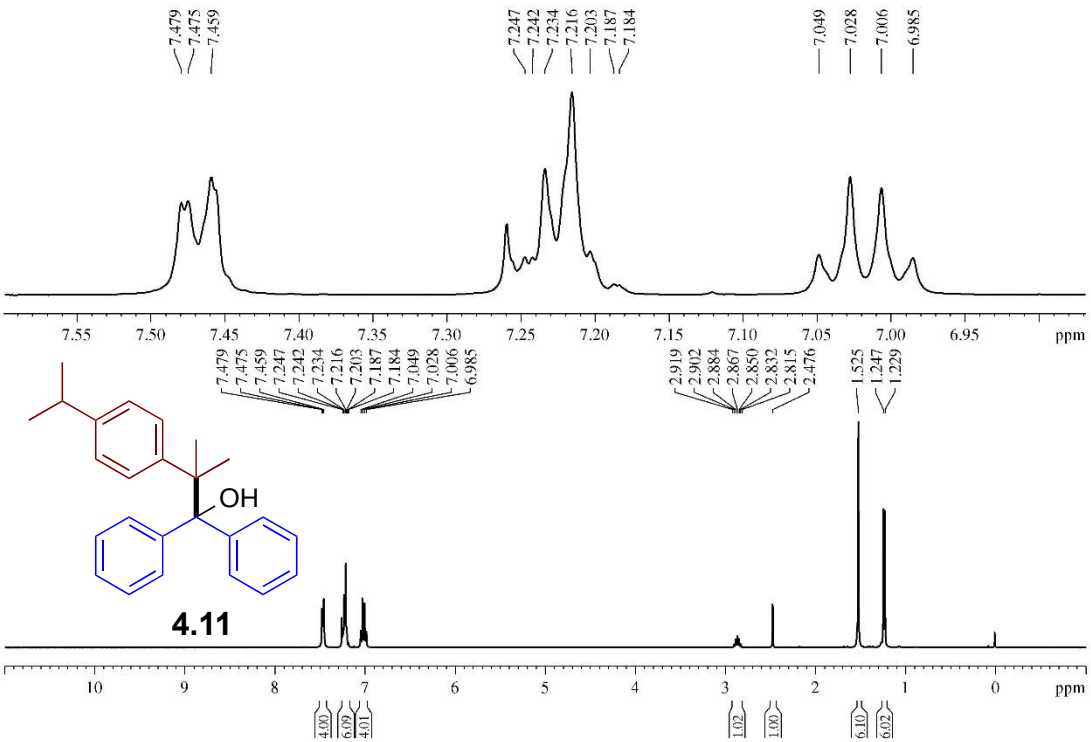
^{1}H NMR of **4.10**, $CDCl_3$, 400 MHz



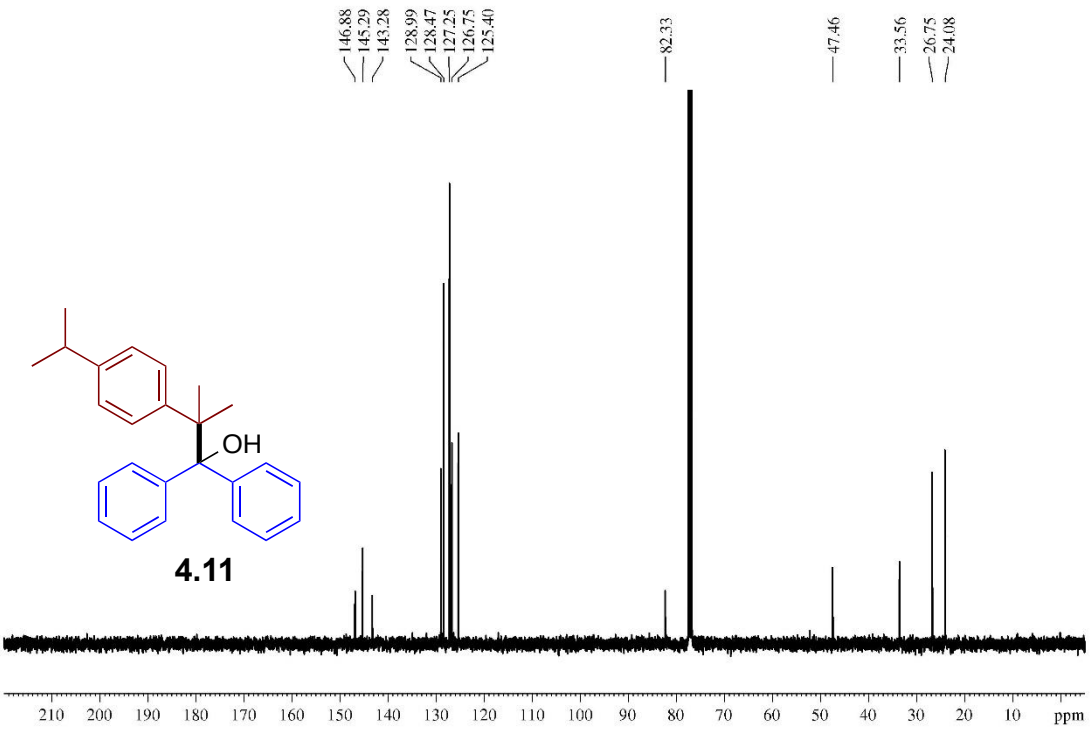
^{13}C NMR of **4.10**, $CDCl_3$, 100 MHz



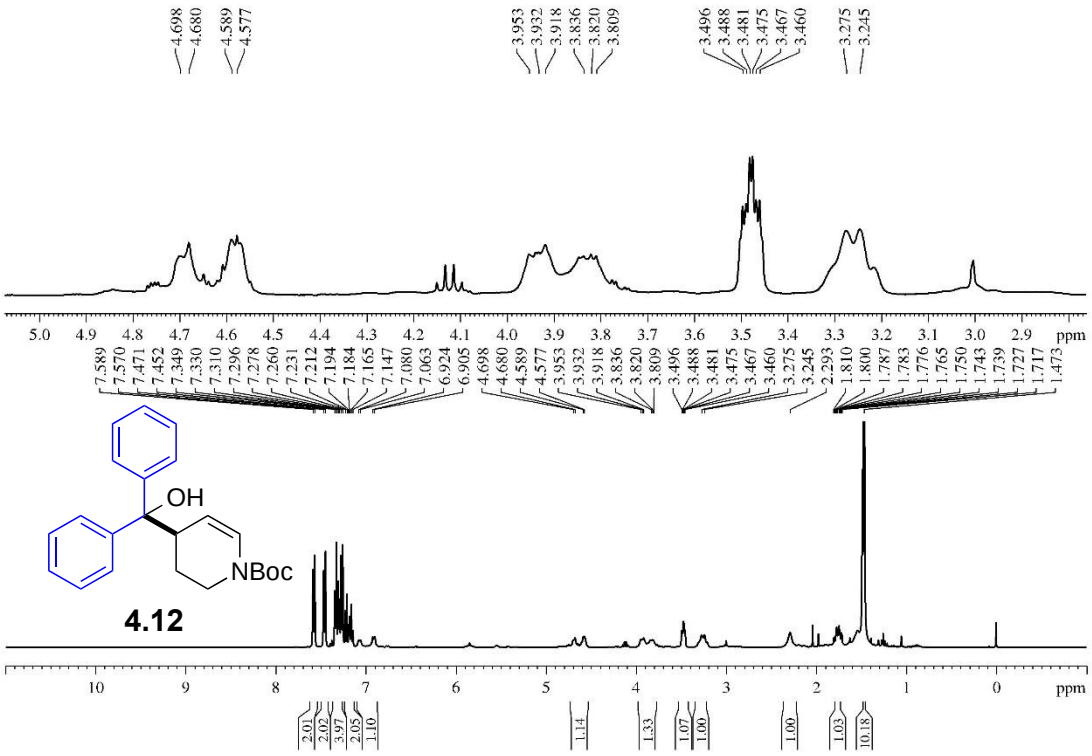
^{1}H NMR of **4.11**, $CDCl_3$, 400 MHz



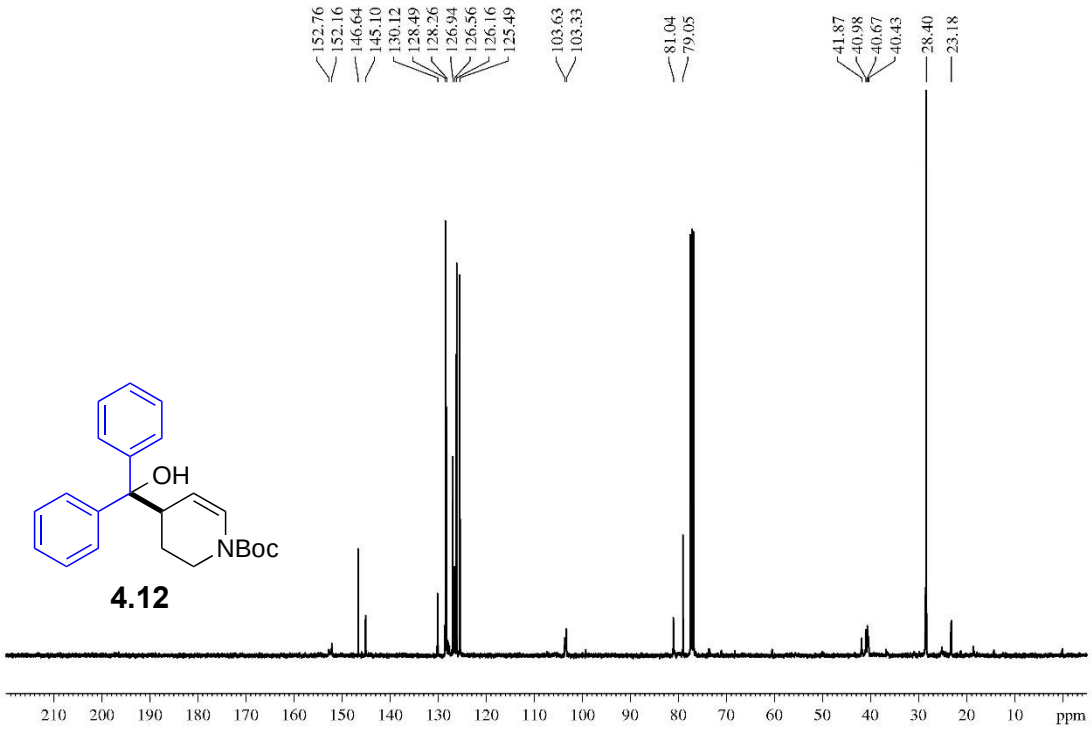
^{13}C NMR of **4.11**, $CDCl_3$, 100 MHz



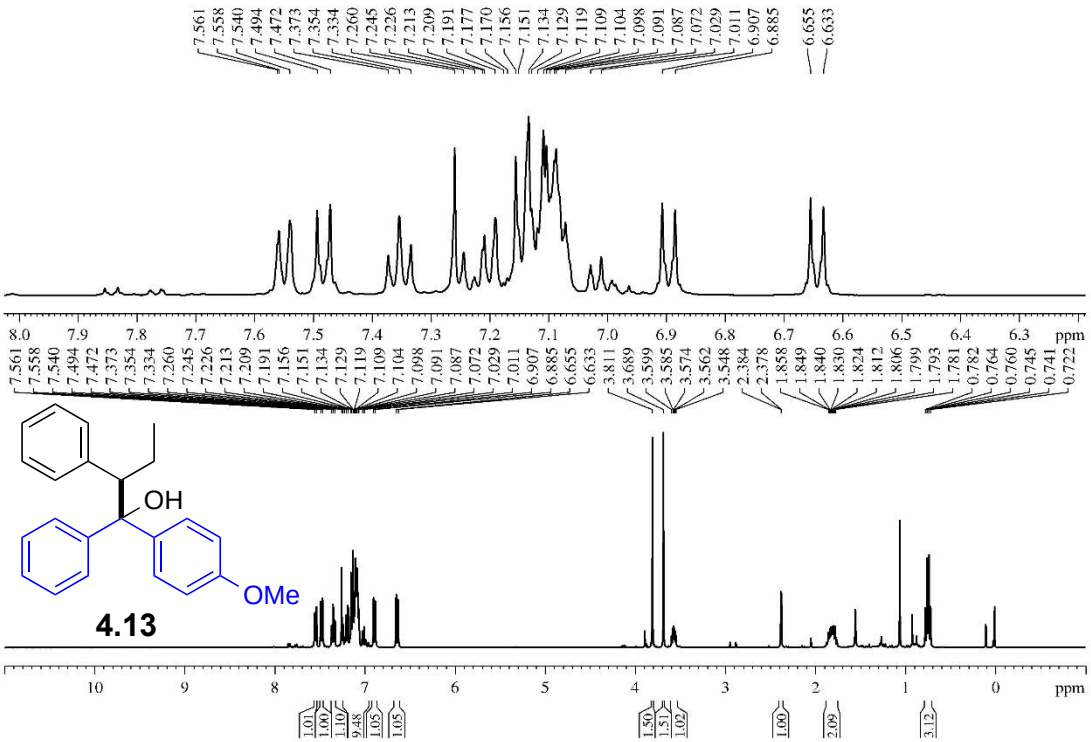
^{1}H NMR of **4.12**, $CDCl_3$, 400 MHz



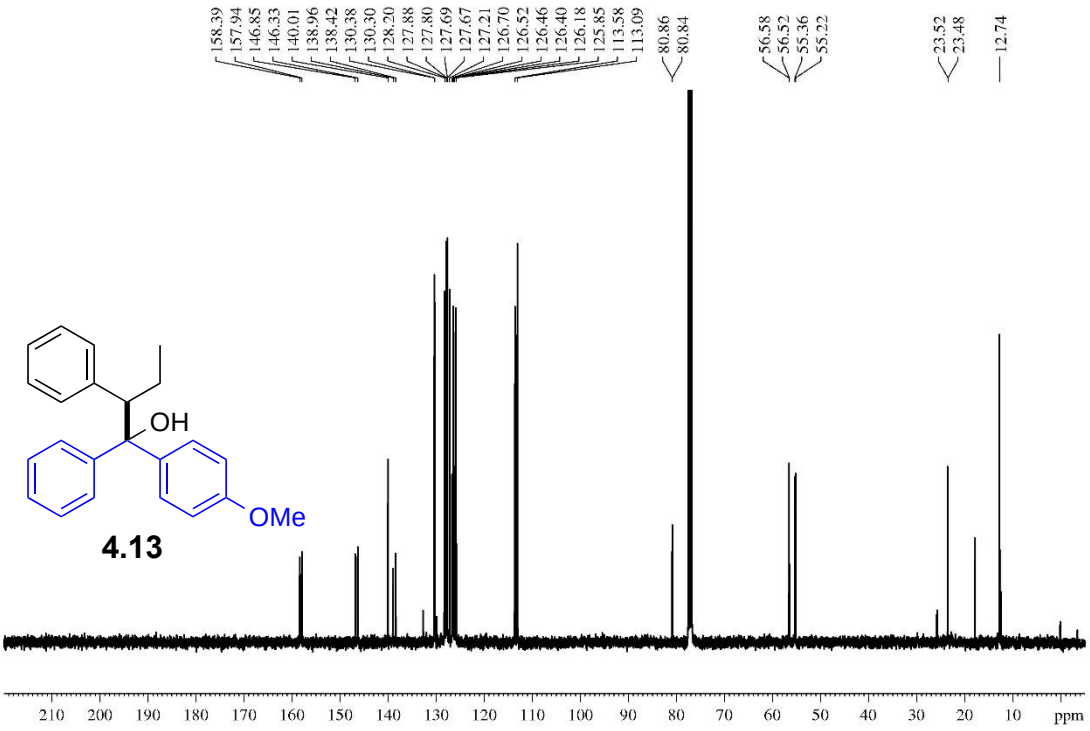
^{13}C NMR of **4.12**, $CDCl_3$, 100 MHz



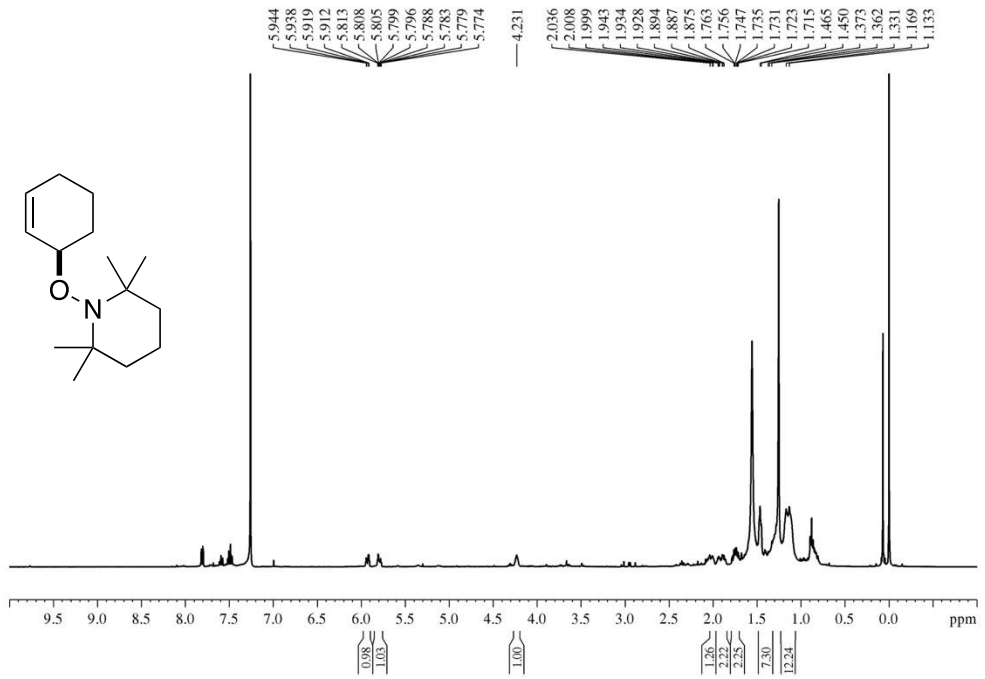
^{1}H NMR of **4.13**, $CDCl_3$, 400 MHz



^{13}C NMR of **4.13**, $CDCl_3$, 100 MHz



^{1}H NMR of **TEMPO Adduct**, $CDCl_3$, 400 MHz



^{13}C NMR of **TEMPO Adduct** $CDCl_3$, 100 MHz