Electronic Supplementary Material (ESI) for Green Chemistry.

Visible light mediated oxidation of benzylic sp^3 C–H bonds using catalytic 1,4-hydroquinone, or its biorenewable glucoside, arbutin, as a pre-oxidant

Laura C. Finney, Lorna J. Mitchell and Christopher J. Moody*

School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, U.K.

ELECTRONIC SUPPLEMENTARY INFORMATION

CONTENTS

General Experimental Details

Commercially available reagents were used throughout, without purification unless otherwise stated. Reactions requiring anhydrous conditions were conducted under an inert atmosphere of dry argon in flame-dried apparatus. Tetrahydrofuran was distilled from sodium benzophenone ketyl radical according to standard procedures. All other solvents and reagents were used as supplied, without further purification. Light petroleum refers to the fractions with bp 40 – 60 °C. Ether refers to diethyl ether.

Thin Layer Chromatography (TLC) was performed using Merck aluminium foil backed plates, pre-coated with silica gel 60 F_{254}.Visualisation was carried out *via* U.V. fluorescence (λ_{max} = 254 nm and/or 360 nm) and/or staining with potassium permanganate and heating. Flash chromatography was carried out using Davisil silica 60 Å under medium pressure. The eluent has been specified.

For reactions that required visible light irradiation, a 400 W Trac metal halide floodlight containing a 400 W Ostram Powerstar HQI-T metal halide bulb (λ_{max} 590 nm), (illuminance; 80,000 lux) was used. All reactions that required irradiation were carried out in a sealed pyrex microwave tube and placed in front of the light source for the stated time period. Other light sources tested were a Minisun 20639 200W LED Pro2 Daylight Floodlight and LEDs comprised of 5 x Citizen CL-L233-C13N1-C LED chips (output: 1000 lumen) mounted on an in-house built aluminium block with fan cooling. Their emission spectra are shown in Figures S1-S3.

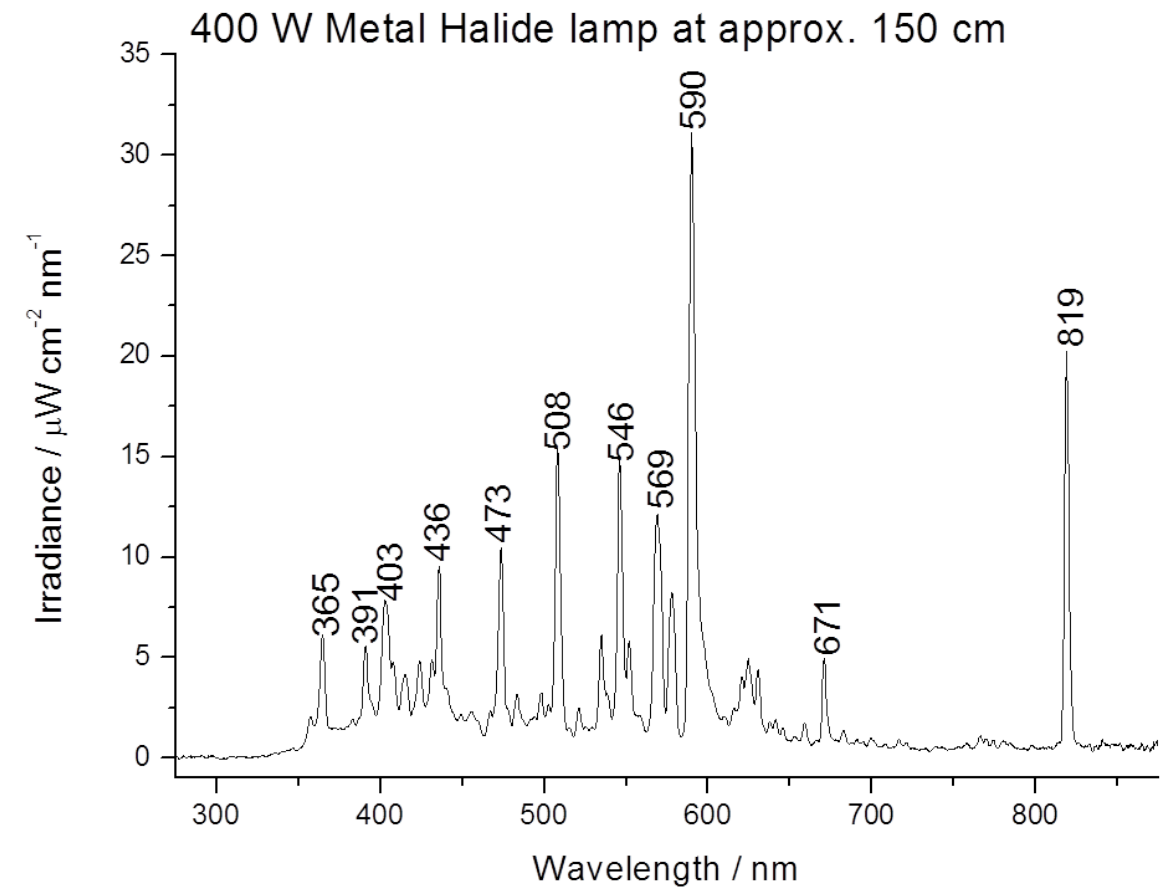
NMR experiments were performed on a Bruker DPX400 (400 MHz), Bruker AV400 (400 MHz), Bruker AV(III)400 (400 MHz), Bruker AV(III)400HD (400 MHz) or Bruker DPX300 (300 MHz) spectrometer at ambient temperature. Proton magnetic resonance shifts (δ_H) recorded in parts per million (ppm) are recorded to two decimal places and are referenced to residual H in the deuterated solvent as the internal standard. Coupling constants (*J*) are reported to the nearest 0.1 Hz. The multiplicity of each signal is designated a combination of the following abbreviations; s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Peaks were assigned using ACD software. Carbon magnetic resonance chemical

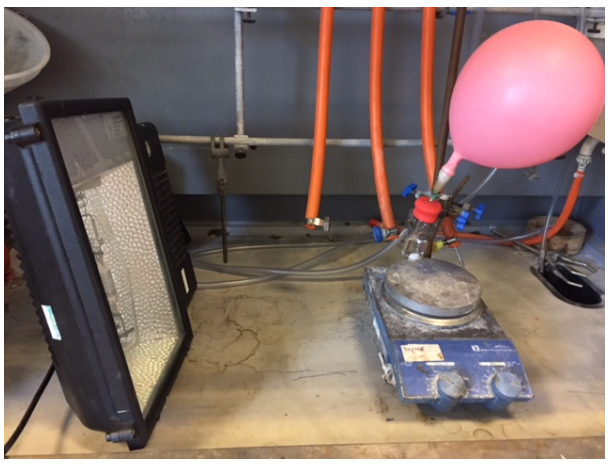
shifts (δ_C), recorded in ppm, are recorded to one decimal place. Multiplicity was determined by DEPT analysis.

Infrared spectra were obtained Nicolet Avatar 360 T instrument on the near compound using attenuated total reflection technique. Absorption maxima (λ_{max}) of major, peaks are reported in wavenumbers (cm^{-1}), quoted to the nearest integral wavenumber.

Mass spectra were recorded on a Bruker MicroTOF 61 (ESI) mass spectrometer that uses electrospray ionisation (ESI). All mass spectrometry data are high resolution. Melting points were measured on a Riechert-Kofter hot stage apparatus and are uncorrected.

Figure S1. Emission spectrum of 400 W metal halide lamp, and experimental set up





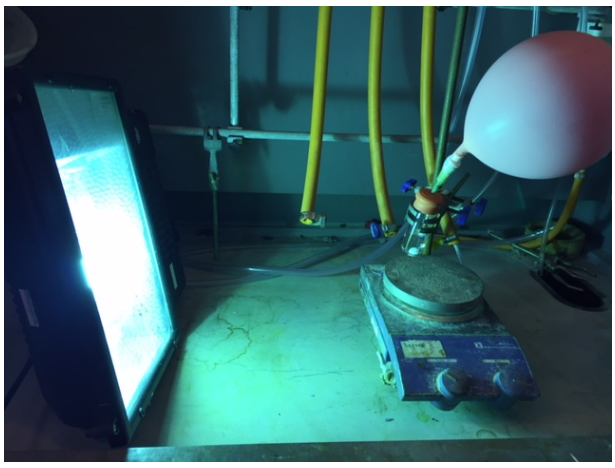


Figure S2. Emission spectrum of Minisun 20639 200W LED Pro2 Daylight Floodlight

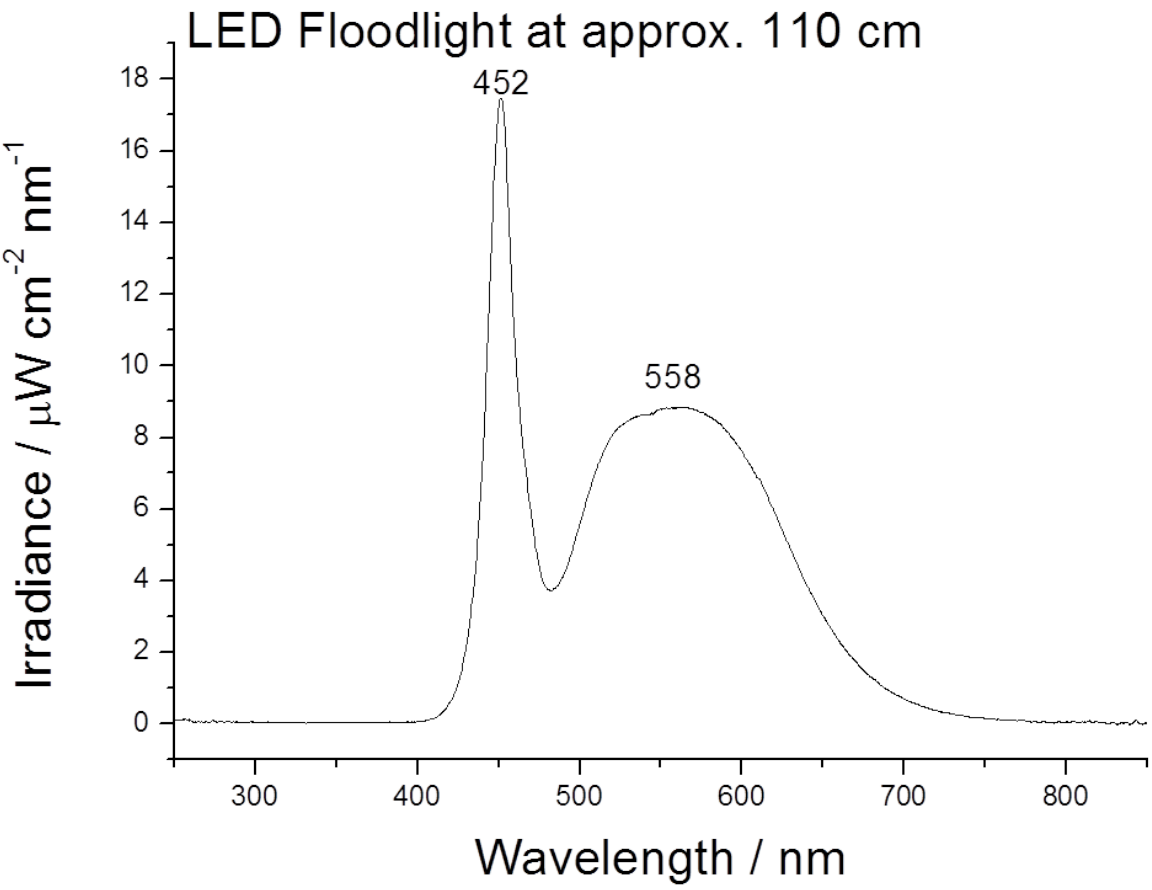
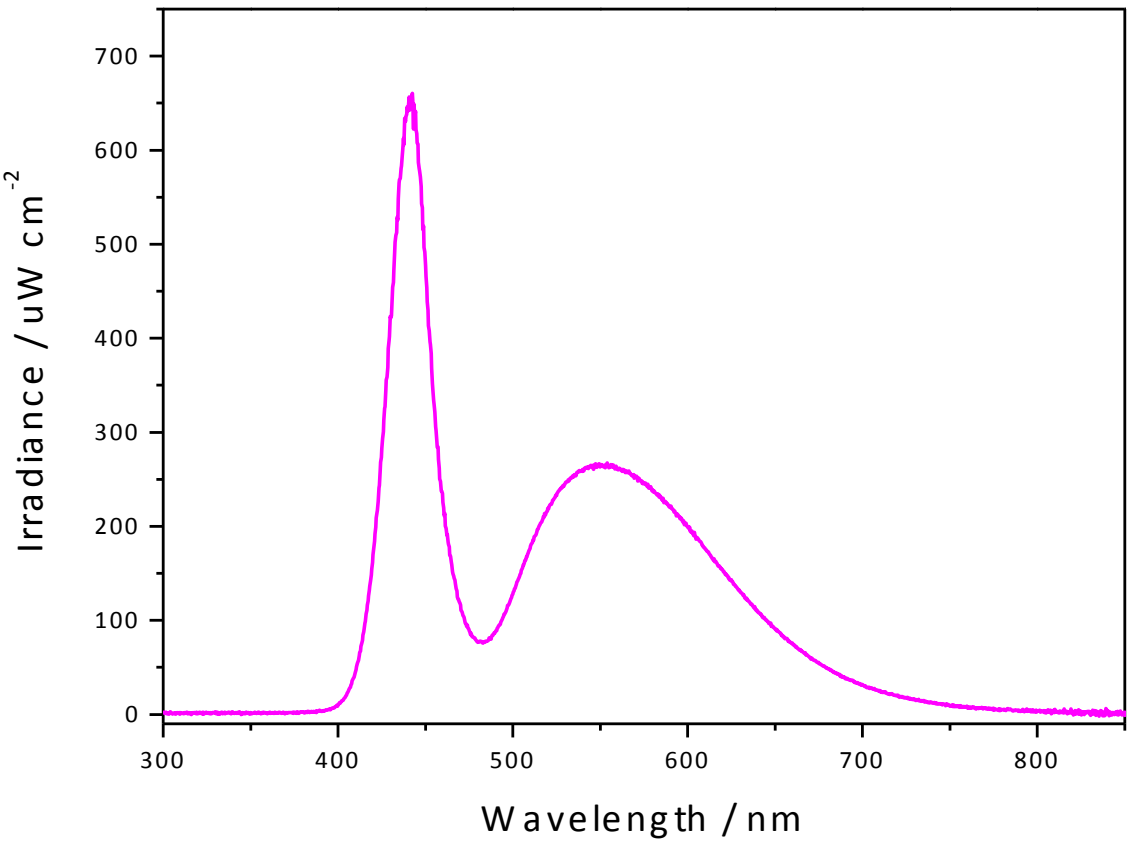


Figure S3. Emission spectrum of 5 x Citizen CL-L233-C13N1-C LED chips (output: 1000 lumen) mounted on an in-house built aluminium block



Arbutin Hydrolysis and BQH_2 Isolation

To a solution of arbutin (272 mg, 1.00 mmol) in DMC (12 mL) was added hydrochloric acid (2 mL) and the mixture stirred at reflux under an atmosphere of Ar for 2 h. The mixture was allowed to cool to rt and solvent removed *in vacuo*. Any remaining solvent was azoetroped with toluene. The residue was triturated with DMC (5 x 5 mL) and the extraction solvent removed *in vacuo* to give BQH_2 that was used without any further purification.

Arbutin Extraction from Leaves

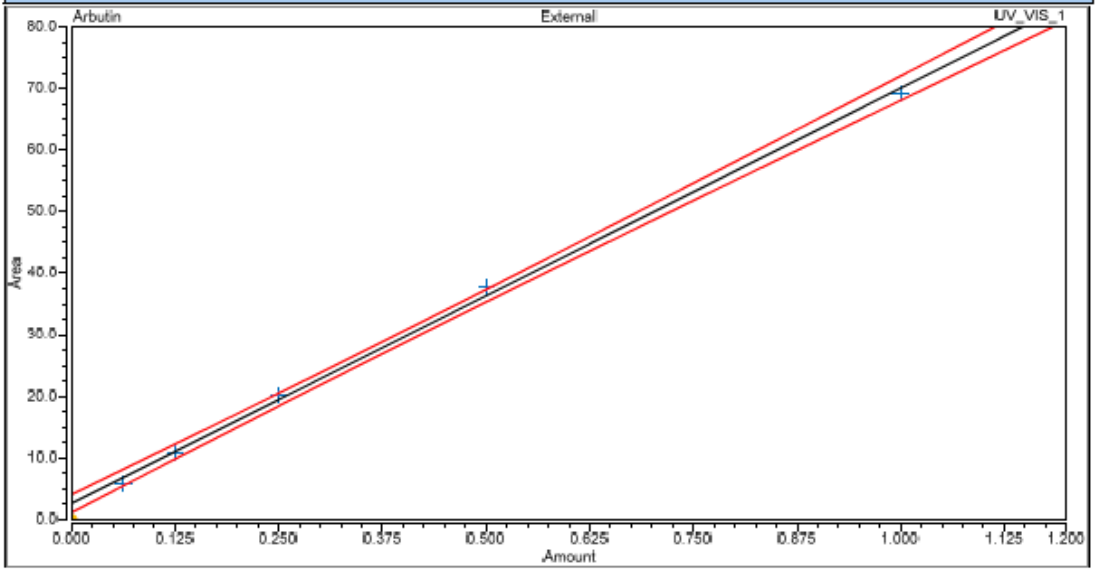
To a mixture of powered leaves (5 g) in water (238 mL) was added methanol (12 mL). The mixture was sonicated at 30 °C for 30 min. The arbutin content was established using quantitative HPLC.

A suitable portion was removed from the extraction mixture and solvent removed *in vacuo.* The residue was subjected to the above hydrolysis conditions and the product used in the oxidation reaction.

Arbutin calibration curve

Calibration			
Calibration Details	**n.a.**		
Calibration Type	Lin, WithOffset	*Offset (C0)*	n.a.
Evaluation Type	Area	*Slope (C1)*	n.a.
Number of Calibration Points	n.a.	*Curve (C2)*	n.a.
Number of disabled Calibration Points	n.a.	*R-Square*	n.a.

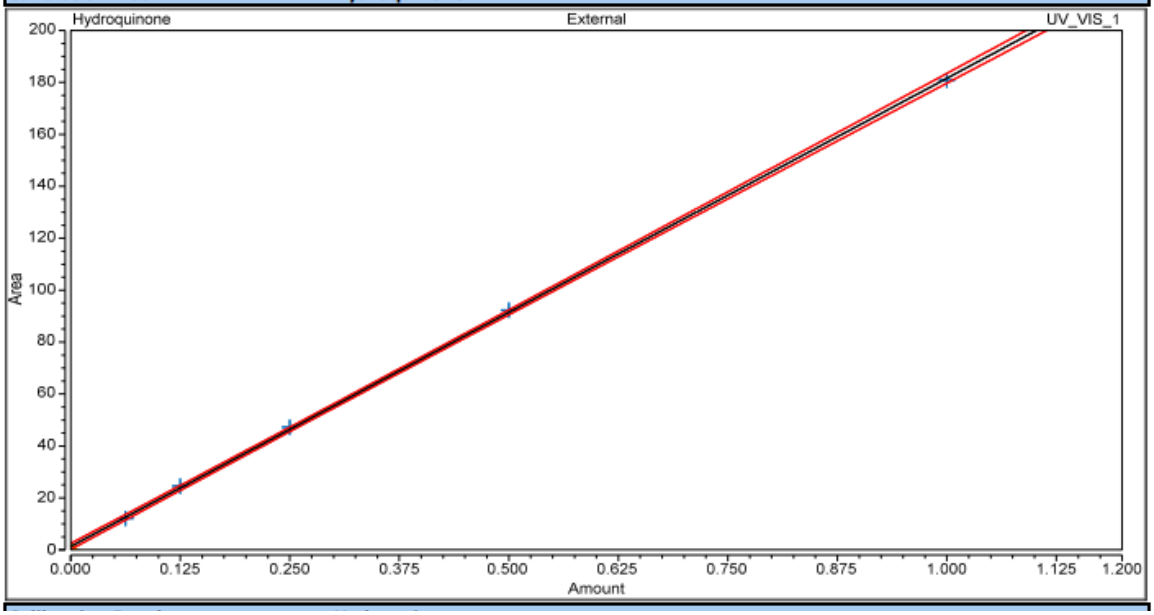
Calibration Plot **n.a.**



Hydroquinone Calibration Curve

Calibration			
Calibration Details	**Hydroquinone**		
Calibration Type	Lin, WithOffset	*Offset (C0)*	1.2959
Evaluation Type	Area	*Slope (C1)*	180.2869
Number of Calibration Points	12	*Curve (C2)*	0.0000
Number of disabled Calibration Points	0	*R-Square*	0.9998

Calibration Plot **Hydroquinone**



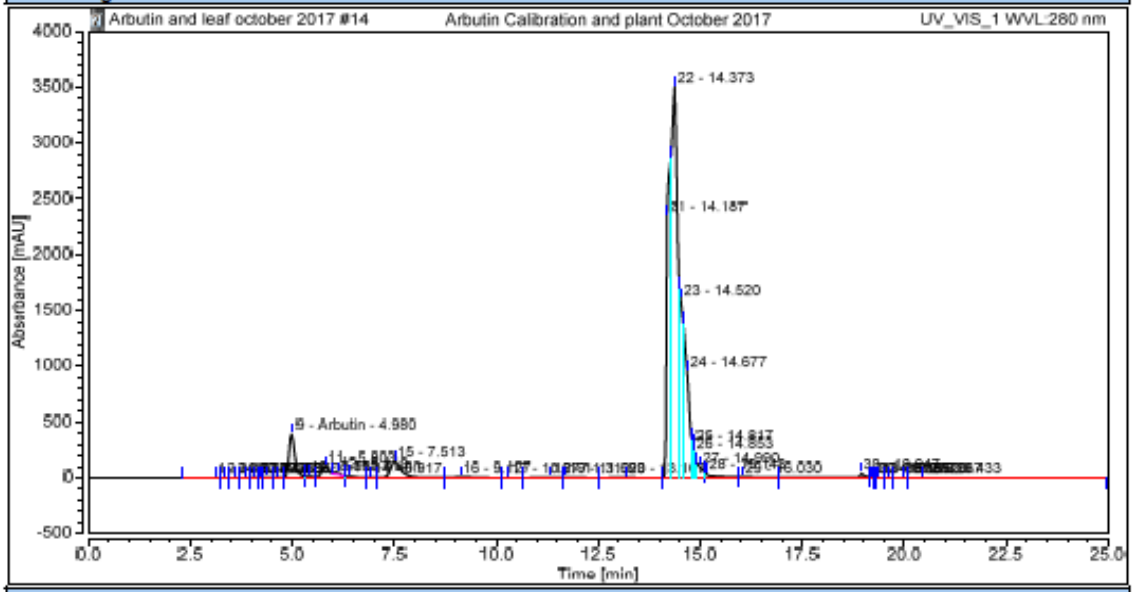
Quantitative HPLC of Arbutin in Bearberry leaves

Chromatogram and Results

Injection Details

Injection Name:	**Arbutin Calibration and plant October 2017**	*Run Time (min):*	**25.00**
Vial Number:	**RD7**	*Injection Volume:*	**10.00**
Injection Type:	**Unknown**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**280**
Instrument Method:	**Sample Method**	*Bandwidth:*	**2**
Processing Method:	**Arbutin in leaves Octover 2017**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**17/Oct/17 19:06**	*Sample Weight:*	**1.0000**

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		3.107	0.297	0.900	0.02	0.01	n.a.
2		3.323	0.281	1.506	0.02	0.02	n.a.
3		3.577	0.439	1.792	0.03	0.02	n.a.
4		3.833	0.444	1.938	0.03	0.02	n.a.
5		4.087	0.572	3.624	0.04	0.04	n.a.
6		4.230	0.528	4.105	0.04	0.04	n.a.
7		4.380	0.949	4.963	0.06	0.05	n.a.
8		4.650	0.844	3.409	0.06	0.03	n.a.
9	Arbutin	4.980	68.058	392.953	4.60	3.99	0.9704
10		5.383	3.095	14.489	0.21	0.15	n.a.

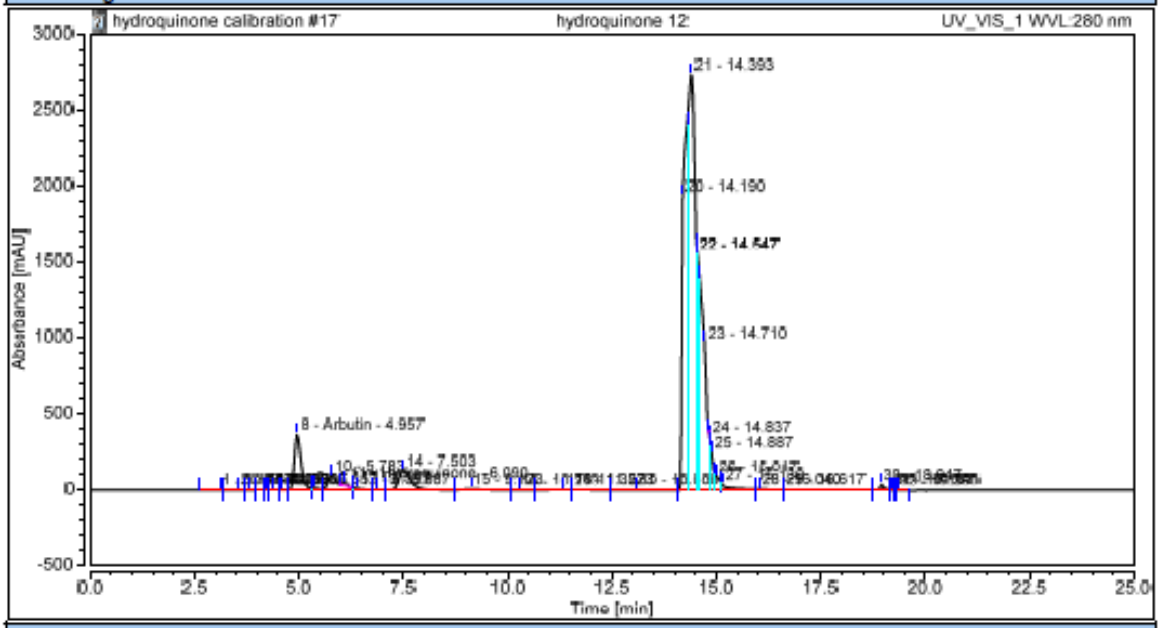
Quantitative HPLC of Hydroquinone in Bearberry leaves

Chromatogram and Results

Injection Details

Injection Name:	hydroquinone 12	*Run Time (min):*	25.00
Vial Number:	RD1	*Injection Volume:*	10.00
Injection Type:	Unknown	*Channel:*	UV_VIS_1
Calibration Level:		*Wavelength:*	280
Instrument Method:	Sample Method	*Bandwidth:*	2
Processing Method:	Hydroquinone processing method	*Dilution Factor:*	1.0000
Injection Date/Time:	17/Oct/17 15:28	*Sample Weight:*	1.0000

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		3.103	0.114	0.483	0.01	0.01	n.a.
2		3.563	0.603	1.504	0.04	0.02	n.a.
3		3.823	0.336	1.555	0.02	0.02	n.a.
4		4.150	0.496	3.075	0.04	0.04	n.a.
5		4.217	0.398	3.562	0.03	0.04	n.a.
6		4.360	0.878	4.256	0.06	0.05	n.a.
7		4.607	0.641	2.813	0.05	0.03	n.a.
8	Arbutin	4.957	67.827	365.368	4.86	4.40	n.a.
9		5.357	2.620	13.138	0.19	0.16	n.a.
10		5.783	29.807	90.482	2.14	1.09	n.a.
11	Hydroquinone	6.090	2.392	16.291	0.17	0.20	0.0061
12		6.397	3.595	12.183	0.26	0.15	n.a.
13		6.887	0.779	2.737	0.06	0.03	n.a.

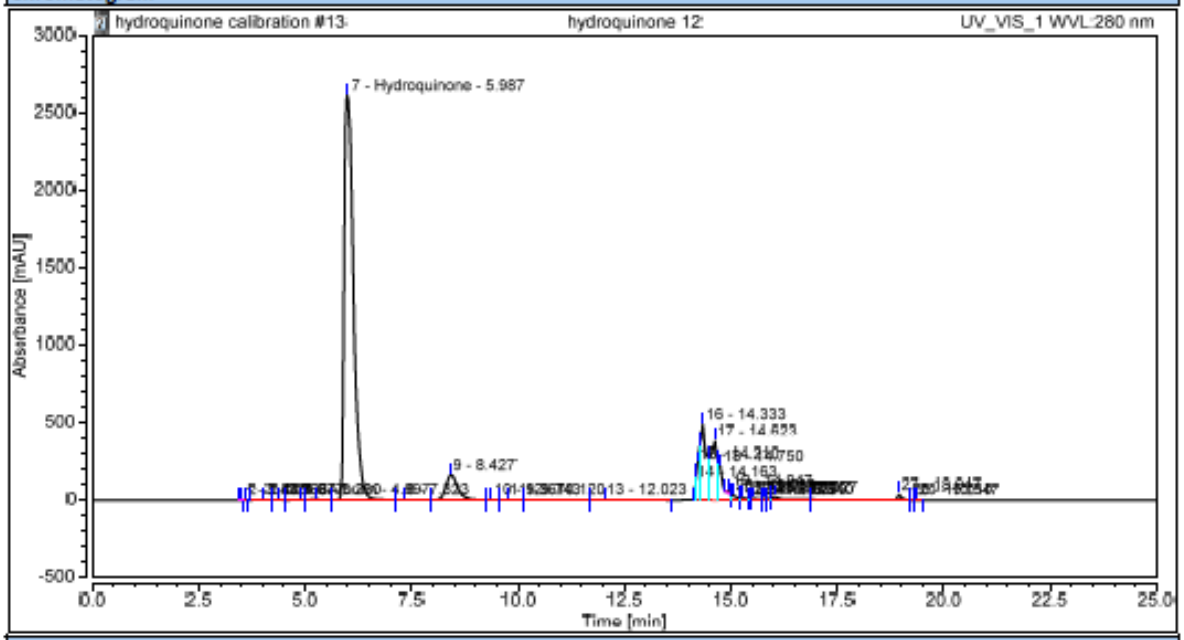
Quantity of Hydroquinone and Arbutin after 1 h hydrolysis

Chromatogram and Results

Injection Details

Injection Name:	**hydroquinone 12**	*Run Time (min):*	**25.00**
Vial Number:	**RB7**	*Injection Volume:*	**10.00**
Injection Type:	**Unknown**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**280**
Instrument Method:	**Sample Method**	*Bandwidth:*	**2**
Processing Method:	**Hydroquinone processing method**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**17/Oct/17 13:34**	*Sample Weight:*	**1.0000**

Chromatogram

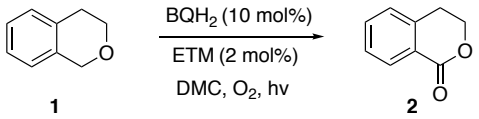


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		3.503	0.002	0.032	0.00	0.00	n.a.
2		3.587	0.022	0.568	0.00	0.01	n.a.
3		3.983	0.511	2.007	0.05	0.05	n.a.
4		4.377	0.292	1.514	0.03	0.03	n.a.
5	Arbutin	4.897	0.451	1.620	0.05	0.04	n.a.
6		5.230	1.578	5.322	0.17	0.12	n.a.
7	Hydroquinone	5.987	659.318	2613.995	69.10	59.34	3.6499
8		7.323	1.473	3.054	0.15	0.07	n.a.

Optimization experiments

Table S1. Benzylic oxidation of isochroman **1** to isochroman-1-one **2** in presence of copper-based ETMs.



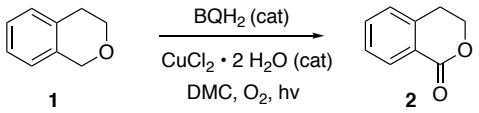
Entry	ETM	Yield /%
[1]	Cu_{NP}	33[a]
2	Cu_{NP}	30
3	CuBr	27
4	$CuBr•SMe_2$	51
5	CuCl	25
6	CuI	16
7	CuOAc	27
8	$CuBr_2$	55
9	$CuCl_2•2H_2O$	66
10	$Cu(OAc)_2$	42
11	$Cu(OTf)_2$	76
12	$CuSO_4$	11
13	$Cu(acac)_2$	43
14	$Cu(hfacac)_2$	34
15	$Cu(tfa)_2$	3
16	Cu powder	6

Experimental conditions: BQH_2 (10 mol%), ETM (2 mol%), DMC, O_2 atmosphere. All reactions were carried out on 1 mmol scale at a 0.08 M concentration in sealed 25 mL Pyrex tubes, using a 400 W HQI-T metal halide lamp.

[a] in acetone; hfacac = hexafluoroacetylacetonate; tfa = trifluoroacetate

Optimization experiments

Table S2. Benzylic oxidation of isochroman **1** to isochroman-1-one **2** in presence of copper(II) chloride.



Entry	BQH_2 /(mol%)	$CuCl_2 \bullet 2H_2O$ /(mol%)	Yield /%
1	10	2	66
2	5	4	60
3	5	2	70 72[a]
4	5	1	39
5	2.5	4	51
6	2.5	2	51
7	2.5	1	40

Experimental conditions: All reactions were carried out on 1 mmol scale at a 0.08 M concentration in sealed 25 mL Pyrex tubes, using a 400 W HQI-T metal halide lamp.

[a] Using BQH_2 derived from arbutin.

Substrates

The following substrates were obtained commercially and used as supplied; Isochroman, phthalan, diphenylmethane, 4-methoxydiphenylmethane, 4,4'-dimethoxydiphenylmethane, 9H-fluorene, xanthene and benzyl methyl ether.

General Procedures

General Procedure A

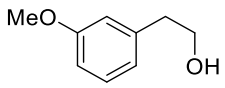
To a suspension of sodium hydride (60% in mineral oil, 1.2 equiv.) in dry THF at 0 °C and under an atmosphere of Ar was added alcohol (1.0 equiv.) and the mixture was stirred for 15 min. Iodomethane (3.0 equiv.) was added and the mixture was allowed to warm to rt and stirred for a further 2-18 h. A saturated solution of sodium hydroxide was added and the mixture was extracted into ethyl acetate. The organic extracts were combined and washed with water and brine. The extracts were then dried over Na_2SO_4, filtered and solvent removed *in vacuo* to give the ether product. When necessary, purification was carried out by column chromatography.

General Procedure B

To a solution of sodium methoxide (1.0 equiv.) in methanol, under an atmosphere of Ar was added benzyl halide (1 equiv.) and the mixture was stirred at reflux for 2 h. A saturated solution of sodium hydroxide was added and the mixture was extracted into ethyl acetate. The organic extracts were combined and washed with water and brine, dried over Na_2SO_4, filtered and concentrated *in vacuo* to give the product.

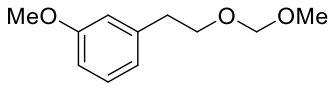
Experimental Data

2-(3-Methoxyphenyl)ethan-1-ol



To a solution of 3-methoxyphenylacetic acid (3.32 g, 20.0 mmol) in THF (150 mL) at 0 °C was added lithium aluminium hydride (40 mL; 1 M in THF) and the reaction mixture was stirred at rt for 16 h. Aqueous saturated potassium sodium tartrate solution (50 mL) was added and the reaction mixture was stirred for a further 1 h. The phases were separated and the organic layer was washed with brine (50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the *title compound* as a colorless oil (2.11 g, 70%) which did not require further purification; υ_{max} ($CHCl_3$)/cm^{-1} 3618, 2952, 1601, 1489, 1260, 1045; δ_H (400 MHz; $CDCl_3$) 7.26 (1 H, t, *J* 7.9, Ar<u>H</u>), 6.90-6.75 (3 H, m, Ar<u>H</u>), 3.84-3.79 (5 H, m, C<u>H</u>$_2$, C<u>H</u>$_3$), 2.85 (2 H, t, *J* 6.8, C<u>H</u>$_2$), OH not observed; δ_C (100 MHz; $CDCl_3$) 159.2 (C), 140.0 (C), 129.0 (CH), 121.0 (CH), 114.4 (CH), 111.2 (CH), 62.9 (CH_2), 54.6 (CH_3), 38.8 (CH_2). Data are consistent with those reported in the literature.[1]

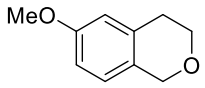
1-Methoxy-3-(2-(methoxymethoxy)ethyl)benzene



To a solution of 2-(3-methoxyphenyl)ethan-1-ol (1.52 g, 10.0 mmol) and diisopropylethylamine (3.49 mL, 20.0 mmol) in dichloromethane (100 mL) was added chloromethyl methyl ether (caution) (1.21 mL, 15.0 mmol), and the reaction mixture was stirred at rt for 16 h. Saturated ammonium chloride solution (100 mL) was added and the phases were separated. The organic layer was washed with further aqueous saturated ammonium chloride solution (100 mL), dried over $MgSO_4$, filtered and the solvent removed *in vacuo* to give the *title compound* as an orange oil (1.96 g, 100%) which did not require further purification; (Found: M^+, 196.1096. $C_{11}H_{16}O_3^+$, requires 196.1099); υ_{max} ($CHCl_3$)/cm^{-1} 3062, 3004, 1602, 1491, 1259, 1030; δ_H (400 MHz; $CDCl_3$) 7.21 (1 H, t, *J* 7.6, Ar<u>H</u>), 6.83 (1 H, br. d, *J* 7.6, Ar<u>H</u>), 6.80-8.75 (2 H, m, Ar<u>H</u>), 4.62 (2 H, s, C<u>H</u>$_2$), 3.80 (3

H, s, C<u>H</u>$_3$), 3.77 (2 H, t, *J* 7.0, C<u>H</u>$_2$), 3.31 (3 H, s, C<u>H</u>$_3$), 2.89 (2 H, t, *J* 7.0, C<u>H</u>$_2$); δ_C (100 MHz; $CDCl_3$) 159.6 (C), 140.5 (C), 129.3 (CH), 121.2 (CH), 114.6 (CH), 111.5 (CH), 96.3 (CH_2), 68.3 (CH_2), 55.1 (2 × CH_3), 36.3 (CH_2).

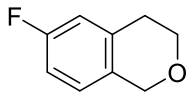
6-Methoxyisochromane



To a solution of 1-methoxy-3-(2-(methoxymethoxy)ethyl)benzene (467 mg, 2.40 mmol) in acetonitrile (25 mL) was added trimethylsilyl triflate (90.5 µL, 0.500 mmol) dropwise at 0 °C. The reaction mixture was stirred whilst being warmed to rt for 16 h. Saturated sodium hydrogen carbonate solution (50 mL) was added and the phases were separated. The organic layer was washed with further saturated ammonium carbonate solution (50 mL), dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The residue was purified by column chromatography eluting with ethyl acetate (1%) in light petroleum to give the *title compound* as a colorless oil (183 mg, 41%); υ_{max} ($CHCl_3$)/cm^{-1} 3008, 1609, 1505, 1326, 1101; δ_H (400 MHz; $CDCl_3$) 6.91 (1 H, d, *J* 8.4, Ar<u>H</u>), 6.75 (1 H, dd, *J* 8.4, 2.6, Ar<u>H</u>), 6.67 (1 H, d, *J* 2.6, Ar<u>H</u>), 4.74 (2 H, s, C<u>H</u>$_2$), 3.97 (2 H, t, *J* 5.8, C<u>H</u>$_2$), 3.80 (3 H, s, C<u>H</u>$_3$), 2.84 (2 H, t, *J* 5.8, C<u>H</u>$_2$); δ_C (100 MHz; $CDCl_3$) 158.0 (C), 134.3 (C), 127.0 (C), 125.4 (CH), 113.5 (CH), 112.3 (CH), 67.7 (CH_2), 65.2 (CH_2), 55.2 (CH_3), 28.6 (CH_2). Data are consistent with those reported in the literature.[2]

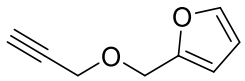
Also isolated was 8-methoxyisochromane as a colorless oil (44 mg, 11%); υ_{max} ($CHCl_3$)/cm^{-1} 3008, 1609, 1505, 1326, 1101; δ_H (400 MHz; $CDCl_3$) 7.15 (1 H, t, *J* 7.9, Ar<u>H</u>), 6.75 (1 H, d, *J* 7.9, Ar<u>H</u>), 6.69 (1 H, d, *J* 7.9, Ar<u>H</u>), 4.75 (2 H, s, C<u>H</u>$_2$), 3.94 (2 H, t, *J* 5.7, C<u>H</u>$_2$), 3.81 (3 H, s, C<u>H</u>$_3$), 2.84 (2 H, t, *J* 5.7, C<u>H</u>$_2$); δ_C (100 MHz; $CDCl_3$) 155.4 (C), 134.7 (C), 126.8 (CH), 123.7 (C), 121.0 (CH), 107.2 (CH), 64.8 (CH_2), 64.4 (CH_2), 55.1 (CH_3), 28.3 (CH_2). Data are consistent with those reported in the literature.[3]

6-Fluoroisochromane



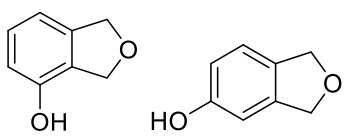
The *title compound* was synthesized according to a literature procedure using 3-fluorophenethyl alcohol (0.31 mL, 2.5 mmol) and paraformaldehyde (90 mg, 3.0 mmol) in TFA (0.6 mL).[4] The product was isolated as a colorless oil (103 mg, 27%); δ_H (400 MHz; $CDCl_3$) 6.95 (1 H, dd, J 8.5, 5.6, ArH), 6.91-6.80 (2 H, m, ArH), 4.75 (2 H, s, CH_2O), 3.97 (2 H, t, *J* 5.8, CH_2CH_2O), 2.87 (2 H, t, *J* 5.8, CH_2CH_2O); δ_c (100 MHz; $CDCl_3$) 161.3 (C, d, *J* 243.9), 135.3 (C, d, *J* 7.3), 130.5 (C, d, *J* 3.0), 125.9 (CH, d, *J* 8.4), 115.2 (CH, d, *J* 20.7), 113.7 (CH, d, *J* 21.3), 67.8 (CH_2), 64.9 (CH_2), 28.4 (CH_2); δ_F (376 MHz; $CDCl_3$) -116.6. Data are consistent with those reported in the literature.[5]

2-((Prop-2-yn-1-yloxy)methyl)furan



The *title compound* was synthesized according to a literature procedure using furfuryl alcohol (2.80 mL, 32.6 mmol),propargyl bromide (6.60 mL, 35.8 mmol) and sodium hydride (60% in mineral oil, 1.44 g, 35.8 mmol) in DMF (40 mL).[6] The product was isolated as a clear, colorless oil (2.63g, 59%); υ_{max} (ATR)/cm^{-1} 3291, 3119, 2907, 2856, 2116, 1607, 1502, 1442; δ_H (400 MHz; $CDCl_3$) 7.43 (1 H, dd, *J* 1.9, 0.9, ArH), 6.40-6.31 (2 H, m, ArH), 4.57 (2 H, s, CCH_2CO), 4.15 (2 H, d, *J* 2.5, $COCH_2CCH$), 2.49 (1 H, t, *J* 2.5, $COCH_2CCH$); δ_C (100 MHz; $CDCl_3$) 150.8 (C), 143.1 (CH), 110.3 (CH), 110.1 (CH), 79.4 (CH), 74.9 (C), 63.0 (CH_2), 56.7 (CH_2). Data are consistent with those reported in the literature.[6]

1,3-Dihydroisobenzofuran-4-ol and 1,3-dihydroisobenzofuran-5-ol



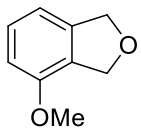
The *title compounds* were synthesized according to a literature procedure using 2-((prop-2-yn-1-yloxy)methyl)furan (2.5 g, 18 mmol) and $PtCl_2$ (239 mg, 0.900 mmol) in acetone (150 mL).[6] Both 1,3-dihydroisobenzofuran-4-ol and 1,3-dihydroisobenzofuran-5-ol were isolated.

1,3-Dihydroisobenzofuran-4-ol was isolated as a pale yellow solid (323 mg, 12%) followed by 1,3-dihydroisobenzofuran-5-ol as a pale yellow solid (821 mg, 33%).

1,3-Dihydroisobenzofuran-4-ol mp 125-127 °C (lit.,[7] mp 130-135 °C); (Found ($M-H^+$) 135.0444, $C_8H_7O_2^-$ requires 135.0452); δ_H (400 MHz; $CDCl_3$) 7.17 (1 H, t, *J* 7.8, Ar<u>H</u>), 6.83 (1 H, d, *J* 7.4, Ar<u>H</u>), 6.68 (1 H, dd, *J* 7.8, 0.8, Ar<u>H</u>), 5.96 (1 H, s, OH), 5.20 (2 H, d, *J* 2.3, C<u>H</u>$_2$O), 5.17 (2 H, d, *J* 2.3, C<u>H</u>$_2$O); δ_C (100 MHz; $CDCl_3$) 150.4 (C), 141.3 (C), 129.2 (CH), 125.1 (C), 113.8 (CH), 113.1 (CH), 74.1 (CH_2), 71.8 (CH_2). Data are consistent with those reported in the literature.[7]

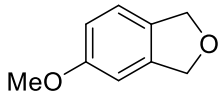
1,3-dihydroisobenzofuran-5-ol mp 122-123 °C (lit., [7] mp 120 °C); (Found ($M-H^+$) 135.0443, $C_8H_7O_2^-$ requires 135.0452**);** δ_H (400 MHz; $CDCl_3$) 7.10 (1 H, d, *J* 8.0, Ar<u>H</u>), 6.80-6.68 (2 H, m, Ar<u>H</u>), 5.08 (4 H, s, C<u>H</u>$_2$OC<u>H</u>$_2$), 5.06 (1 H, br s, OH); δ_C (100 MHz; $CDCl_3$) 155.3 (C), 141.0 (C), 131.1 (C), 121.8 (CH), 114.6 (CH), 107.9 (CH), 73.4 (CH_2) 73.2 (CH_2). Data are consistent with those reported in the literature.[7]

4-Methoxy-1,3-dihydroisobenzofuran



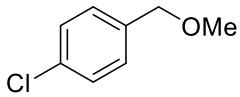
The *title compound* was synthesized according to General Procedure A using 1,3-dihydroisobenzofuran-4-ol (47 mg, 0.35 mmol), sodium hydride (60% in mineral oil, 17 mg, 0.42 mmol) and iodomethane (0.070 mL, 1.1 mmol) in THF (6 mL). The product was isolated as a pale yellow oil which did not require further purification (37 mg, 71%); υ_{max} (ATR)/cm^{-1} 3001, 2897, 2848, 2116, 1996, 1736, 1613, 1597, 1484; δ_H (400 MHz; $CDCl_3$) 7.27 (1 H,d, *J* 8.2, Ar<u>H</u>), 6.86 (1 H, dd, *J* 8.2, 2.4, Ar<u>H</u>), 6.77 (1 H, d, *J* 2.4, Ar<u>H</u>), 5.10 (2 H, d, *J* 1.8, C<u>H</u>$_2$O), 5.08 (2 H, d, *J* 2.0, C<u>H</u>$_2$O), 3.86 (3 H, s, C<u>H</u>$_3$); δ_C (100 MHz; $CDCl_3$) 154.2 (C), 141.1 (C), 129.2 (CH), 126.9 (C), 113.1 (CH), 108.8 (CH), 74.1 (CH_2), 72.2 (CH_2), 55.5 (CH_3). Data are consistent with those reported in the literature.[8]

5-Methoxy-1,3-dihydroisobenzofuran



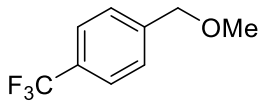
The *title compound* was synthesized according to General Procedure A using 1,3-dihydroisobenzofuran-4-ol (77 mg, 0.60 mmol), sodium hydride (60% in mineral oil, 28 mg, 0.70 mmol) and iodomethane (0.12 mL, 1.8 mmol) in THF (6 mL). The product was isolated as a pale yellow oil which did not require further purification (70 mg, 78%); υ_{max} (ATR)/cm^{-1} 2998, 2904, 2847, 1613, 1590, 1491; δ_H (400 MHz; $CDCl_3$) 7.15 (1 H, d, *J* 8.2, Ar<u>H</u>), 6.84 (1 H,dd, *J* 8.2, 2.4, Ar<u>H</u>), 6.79 (1 H, d, *J* 2.4, Ar<u>H</u>), 5.10 (2 H, d, *J* 2.1, C<u>H</u>$_2$O), 5.08 (2 H, d, *J* 2.1, C<u>H</u>$_2$O), 3.83 (3 H, s, C<u>H</u>$_3$); δ_C (100 MHz; $CDCl_3$) 159.5 (C), 140.8 (C), 131.0 (C), 121.6 (CH), 113.5 (CH), 106.3 (CH), 73.6 (CH_2), 73.2 (CH_2), 55.5 (CH_3). Data are consistent with those reported in the literature.[9]

1-Chloro-4-methoxymethylbenzene



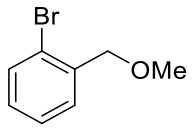
The *title compound* was synthesized according to General Procedure A using 4-chlorobenzyl alcohol (1.98 mL, 15.0 mmol), sodium hydride (60 % in mineral oil, 720 mg, 18.0 mmol) and iodomethane (2.8 mL, 45 mmol) in THF (150 mL). The *title compound* was isolated as a yellow oil which did not require further purification (2.13 g, 91%); υ_{max} (ATR)/cm^{-1} 2924, 2853, 2820, 1598, 1490, 1454, 1405, 1376, 1282, 1193, 1087; δ_H (400 MHz; $CDCl_3$) 7.36-7.32 (2 H, m, Ar<u>H</u>), 7.31-7.27 (2 H, m, Ar<u>H</u>), 4.44 (2 H, s, C<u>H</u>$_2$), 3.41 (3 H, s, C<u>H</u>$_3$); δ_C (100 MHz; $CDCl_3$) 136.7 (C), 133.4 (C), 129.0 (CH), 128.52 (CH), 73.9 (CH_2), 58.2 (CH_3); Data are consistent with those reported in the literature.[10]

1-Methoxymethyl-4-trifluoromethylbenzene



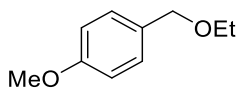
The *title compound* was synthesized according to General Procedure A using 4-trifluromethylbenzyl alcohol (4.9 mL, 15 mmol), sodium hydride (60% in mineral oil, 720 mg, 18.0 mmol) and iodomethane (2.8 mL, 45 mmol) in THF (150 mL). The *title compound* was isolated as a yellow oil (2.85 g, 100%) which did not require further purification; υ_{max} (ATR)/cm^{-1} 3060, 2984, 2922, 2854, 2821, 1593, 1568, 1465, 1441, 1378, 1273; δ_H (400 MHz; $CDCl_3$) 7.64 (2 H,d, *J* 7.8, Ar<u>H</u>), 7.48 (2 H, d, *J* 7.8, Ar<u>H</u>), 4.54 (2 H, s, C<u>H</u>$_2$), 3.44 (3 H, s, C<u>H</u>$_3$); δ_C (100 MHz; $CDCl_3$) 142.4 (C), 129.6 (C, q, *J* 32, <u>C</u>F_3), 127.5 (CH), 125.3 (CH, q, *J* 272, <u>C</u>HCF_3), 122.9 (C), 73.8 (CH_2), 58.4 (CH_3). Data are consistent with those reported in the literature.[11]

1-Bromo-2-methoxymethylbenzene



The *title compound* was synthesized according to General Procedure A using 2-bromobenzyl alcohol (2.8 g, 15 mmol), sodium hydride (60 % in mineral oil, 720 mg, 18.0 mmol) and iodomethane (2.8 mL, 45 mmol) in THF (150 mL). The *title compound* was isolated as a yellow oil which did not require further purification (2.60 g, 86%); υ_{max} (ATR)/cm^{-1} 2928, 2855, 2826, 1620, 1454, 1418, 1380, 1243; δ_H (400 MHz; $CDCl_3$) 7.56 (1 H, dd, *J* 7.9, 1.3, Ar<u>H</u>), 7.42 (1 H, dd, *J* 7.6 1.7, Ar<u>H</u>), 7.34 (1 H, app. td, *J* 7.6, 1.3, Ar<u>H</u>), 7.17 (1 H, ddd, *J* 7.9, 7.6, 1.7, Ar<u>H</u>), 4.56 (2 H, s, C<u>H</u>$_2$), 3.50 (3 H, s, C<u>H</u>$_3$); δ_C (100 MHz; $CDCl_3$); 137.6 (C), 132.5 (CH), 129.0 (CH), 128.9 (CH), 127.4 (CH), 122.7 (C), 73.9 (CH_2), 58.6 (CH_3); Data are consistent with those reported in the literature.[12]

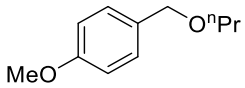
1-Ethoxymethyl-4-methoxybenzene



The *title compound* was synthesized according to General Procedure A using 4-methoxybenzyl alcohol (1.38 g, 10.0 mmol), sodium hydride (60% dispersion in mineral oil; 480 mg, 12.0 mmol) and iodoethane (1.2 mL, 15 mmol) in THF (100 mL). The residue was purified by column chromatography, eluting with ethyl acetate

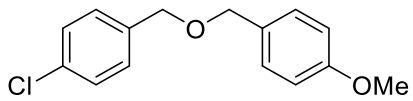
in light petroleum (5%) to give the *title compound* as a colorless oil (814 mg, 49%); υ_{max} ($CHCl_3$)/cm^{-1} 3005, 1613, 1513, 1249, 1090; δ_H (400 MHz; $CDCl_3$) 7.31 (2 H, d, *J* 8.8, ArH), 6.91 (2 H, d, *J* 8.8, ArH), 4.47 (2 H, s, CH_2), 3.82 (3 H, s, CH_3), 3.55 (2 H, q, *J* 7.2, CH_2), 1.27 (3 H, t, *J* 7.2, CH_3); δ_C (100 MHz; $CDCl_3$) 159.2 (C), 130.7 (C), 129.3 (CH), 113.8 (CH), 72.4 (CH_2), 65.4 (CH_2), 55.2 (CH_3), 15.3 (CH_3). Data are consistent with those reported in the literature.[13]

1-Methoxy-4-propoxymethylbenzene



The *title compound* was synthesized according to General Procedure A using 4-methoxybenzyl alcohol (1.38 g, 10.0 mmol), sodium hydride (60% dispersion in mineral oil; 480 mg, 12.0 mmol) and iodopropane (1.5 mL, 15 mmol) in THF (100 mL). The residue was purified by column chromatography, eluting with ethyl acetate in light petroleum (5%) to give the *title compound* as a colorless oil (424 mg, 23%); υ_{max} ($CHCl_3$)/cm^{-1} 2977, 1613, 1512, 1465, 1302, 1248, 1093; δ_H (400 MHz; $CDCl_3$) 7.29 (2 H, d, *J* 8.0, ArH), 6.90 (2 H, d, *J* 8.0, ArH), 4.46 (2 H, s, CH_2), 3.83 (3 H, s, CH_3), 3.43 (2 H, t, *J* 6.7, CH_2), 1.65 (2 H, pent, *J* 6.7, CH_2), 0.96 (3 H, t, *J* 6.7, CH_3); δ_C (100 MHz; $CDCl_3$) 159.1 (C), 130.8 (C), 129.2 (CH), 113.8 (CH), 72.5 (CH_2), 71.9 (CH_2), 55.3 (CH_3), 23.0 (CH_2), 10.6 (CH_3). Data are consistent with those reported in the literature.[14]

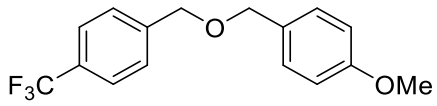
1-Chloro-4-((4-methoxybenzyloxymethyl)benzene



To a solution of 4-chlorobenzyl alcohol (4.27 g, 30.0 mmol) in THF (300 mL) at 0 °C was added sodium hydride (60 % in mineral oil, 1.44g, 36.0 mmol) and stirred at 0 °C for 1h. TBAI (1.11 g, 3.00 mmol) and 4-methoxybenzyl chloride (4.0 mL, 36 mmol) were added and reaction stirred at rt for 18 h. The reaction was quenched with a saturated solution of ammonium chloride (200 mL) and the mixture was extracted into ethyl acetate (3 x 200 mL). The organic extracts were combined and dried over $MgSO_4$, filtered and solvent removed *in vacuo.* The residue was purified by column chromatography, eluting with ethyl acetate in light

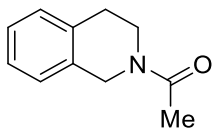
petroleum (0-1% step gradient) to give the product as a pale yellow oil (5.91 g, 75%); (Found: M+Na^+ 285.0648, $C_{15}H_{15}ClO_2Na^+$ requires 285.0653); δ_H (400 MHz; $CDCl_3$) 7.385-7.28 (6 H, m, ArH), 7.93 (2H, ddd, *J* 8.56, 3.1, 2.1, ArH), 4.52 (2 H, s, CH_2) 4.52 (2 H, s, CH_2), 3.85 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 159.3 (C),136.9 (C), 133.1 (C), 130.1 (C), 129.4 (CH), 129.1 (CH), 128.5 (CH), 113.9 (CH), 71.9 (CH_2), 71.0 (CH_2), 53.3 (CH_3). Data are consistent with those reported in the literature.[15]

1-Methoxy-4-(((4-(trifluoromethyl)benzyl)oxy)methyl)benzene



To a solution of 4-(trifluoromethyl)phenyl)methanol (1.76 g, 10.0 mmol) in THF (100 mL) was added sodium hydride (60% dispersion in mineral oil; 480 mg, 12.0 mmol) at 0 °C and stirred for 1h. 4-Methoxybenzyl bromide (1.7 mL, 15 mmol) was added and the mixture stirred at rt for 3 days. The reaction mixture was added to saturated ammonium chloride solution (100 mL) and extracted into ethyl acetate (100 mL). The organic layer was dried over $MgSO_4$, filtered and solvent removed *in vacuo*. The residue was purified by column chromatography, eluting with ethyl acetate in light petroleum (5%) to give the *title compound* as a colorless oil (2.38 g, 80%); (Found: M^+, 296.1026. $C_{16}H_{15}O_2F_3^+$, requires 296.1024); υ_{max} ($CHCl_3$)/cm^{-1} 3008, 2911, 1612, 1513, 1461, 1251; δ_H (400 MHz; $CDCl_3$) 7.62 (2 H, d, *J* 7.9, ArH), 7.49 (2 H, d, *J* 7.9, ArH), 7.31 (2 H, dt, *J* 8.7, 2.9, ArH), 6.92 (2 H, dt, *J* 8.7, 2.9, ArH), 4.59 (2 H, s, CH_2), 4.54 (2 H, s, CH_2), 3.83 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 159.4 (C), 142.6 (C), 129.9 (C), 129.5 (CH), 127.7 (CH), 125.6 (C, q, *J* 278) 125.3 (CH, q, *J* 3.4), 113.9 (CH), 72.2 (CH_2), 71.0 (CH_2), 55.3 (CH_3), one C not observed; *m/z* (ESI) 296 (M^+, 100%).

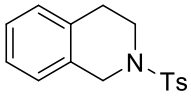
1-(3,4-Dihydroisoquinolin-2(1H)-yl)ethan-1-one



The *title compound* was synthesized according to a literature procedure using 1,2,3,4-tetrahydroquinoline (666 mg, 5.00 mmol), triethylamine (0.84 mL, 6.0 mmol), acetyl chloride (0.43 mL, 6.0 mmol) and

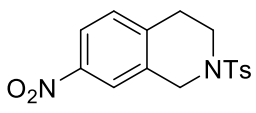
dichloromethane (14 mL).[16] The product was isolated as a colorless solid which did not require further purification (921 mg, 100%); mp 47-49 °C (lit.,[17] mp 45-46 °C); (Found M+Na 198.0886, $C_{11}H_{13}NONa$ requires 198.0889); δ_H (400 MHz; $CDCl_3$) (two rotamers) 7.23-7.06 (8 H, m, ArH), 4.70 (2 H, app. d, *J* 3.1, CH_2N), 4.69 (2 H, app. d, *J* 3.1, CH_2N), 3.82-3.77 (2 H, m, CH_2CH_2N), 3.68-3.62 (2 H, m, CH_2CH_2N), 2.88 (2 H, app. q, *J* 5.2, CH_2CH_2N), 2.82 (2 H, app. q, *J* 5.2, CH_2CH_2N), 2.16 (6 H, br s, 2 x CH_3); δ_C (100 MHz; $CDCl_3$) (two rotamers) 169.6 (C), 169.5 (C), 135.0 (C), 134.0 (C), 133.5 (C), 132.5 (C), 128.9 (CH), 128.3 (CH), 126.9 (CH), 126.6(CH), 126.6 (CH), 126.5 (CH), 126.3 (CH), 126.0 (CH), 48.1 (CH_2), 44.1 (CH_2), 44.0 (CH_2), 39.5 (CH_2), 29.4 (CH_2), 28.5 (CH_2), 22.0 (CH_3), 21.7 (CH_3). Data are consistent with those reported in the literature.[18]

2-Tosyl-1,2,3,4-tetrahydroisoquinoline



The *title compound* was synthesized according to a literature procedure using 1,2,3,4-tetrahydroisoquinoline (1 mL, 8 mmol), tosyl chloride (1.84 g, 9.6 mmol) and pyridine (2 mL) in dichloromethane (20 mL).[19] The product was obtained as a colorless solid (1.5 g, 66%); mp 142-143 °C (lit.,[19] mp 147 °C); (Found ($M+H^+$) 288.1056, $C_{16}H_{18}NO_2S^+$ requires 288.1053); δ_H (400 MHz; $CDCl_3$) 7.75 (2 H, d, *J* 8.3, ArH), 7.35 (2 H, d, *J* 8.3, ArH), 7.20-7.12 (2 H, m, ArH), 7.12-7.07 (1 H, m, ArH), 7.07-7.01 (1 H, m, ArH), 4.33 (2H, s, CCH_2N), 3.38 (2 H, t, *J* 5.9, CH_2CH_2N), 2.95 (2 H, t, *J* 5.9, CH_2CH_2N), 2.44 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 143.7 (C), 133.3 (C), 133.1 (C), 131.7 (C), 129.7 (CH), 128.8 (CH), 127.8 (CH), 126.7 (CH), 126.4 (CH), 126.3 (CH), 47.6 (CH_2), 43.8 (CH_2), 28.9 (CH_2), 21.5 (CH_3). Data recorded matched those in the literature.[19]

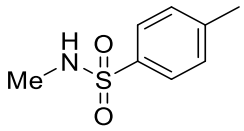
7-Nitro-2-tosyl-1,2,3,4-tetrahydroisoquinoline



To a solution of 7-nitro-1,2,3,4-tetrahydroisoquinoline hydrochloride (132 mg, 1.00 mmol) and tosyl chloride (420 mg, 2.2 mmol) in dichloromethane (3 mL) under an atmosphere of argon, was added DIPEA

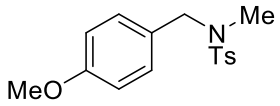
(0.42 mL, 2.4 mmol) over 1 min. The mixture was stirred at rt for 2 h. Hydrochloric acid (1 N, 5 mL) was added and the solution was extracted using ethyl acetate (3 x 5 mL). The organic extracts were combined and washed with water (3 x 3 mL) and brine (3 x 3 mL) before it was dried over Na_2SO_4, filtered and solvent removed *in vacuo*. Purification by column chromatography, eluting with ethyl acetate in light petroleum (5%) gave the product as a pale yellow solid (120 mg, 36%); mp 170-173 °C; %); υ_{max} (ATR)/cm^{-1} 3071, 2922, 2823, 1735, 1612, 1595, 1520, 1491; (Found $M+H^+$ 333.0911, $C_{16}H_{17}N_2O_4S^+$ requires 333.0911); δ_H (400 MHz; $CDCl_3$) 8.03 (1 H, dd, *J* 8.4,2.4, ArH), 7.97 (1 H, d, *J* 2.4, ArH), 7.76 (1 H, dt, *J* 8.4, 1.9, ArH), 7.37 (2 H, d, *J* 8.3, SO_2CH), 7.28 (2 H, d, *J* 8.3, ArH), 4.34 (2 H, s, CCH_2NTs), 3.43 (2 H, t, *J* 5.9, CH_2CH_2NTs), 3.06 (2 H, t, *J* 5.9, CH_2CH_2NTs), 2.46 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 146.5 (C), 144.1 (C), 140.8 (C), 133.3 (C), 132.3 (C), 129.9 (CH), 127.7 (CH), 121.8 (CH), 121.7 (CH), 47.4 (CH_2), 43.1 (CH_2), 21.6 (CH_3).

N,4-Dimethylbenzenesulfonamide



To a solution of methylamine hydrochloride (878 mg, 1.30 mmol) and tosyl chloride (953 mg, 5.00 mmol) in THF (50 mL) under an atmosphere of Ar at 0 °C, was added triethylamine (4.2 mL, 10 mmol). The mixture was stirred for 3 days and allowed to warm to rt. Water (30 mL) was added, and the mixture extracted into ethyl acetate (3 x 20 mL). The organic extracts were combined and washed with water (3 x 10 mL) and brine (3 x 10 mL), dried over Na_2SO_4, filtered and solvent removed *in vacuo* to give the product as a colorless solid which did not require further purification (821 mg, 87%); mp 74 °C (lit.,[20] 75-76 °C); δ_H (400 MHz; $CDCl_3$) 7.77 (2 H, app dt, *J* 8.2, 1.8, SO_2CH), 7.33 (2 H, d, *J* 8.2, $CHCH_3$), 2.64 (3 H, s, NCH_3), 2.44 (2 H, s, CCH_3); δ_C (100 MHz; $CDCl_3$) 143.5 (C), 135.8 (C), 129.7 (CH), 127.3 (CH), 29.3 (CH_3), 21.52 (CH_3). Data recorded matched those in the literature.[21]

N-(4-Methoxybenzyl)-N,4-dimethylbenzenesulfonamide



To a solution of N,4-dimethylbenzenesulfonamide (400 mg, 1.10 mmol) and potassium carbonate (228 mg, 1.70 mmol) in acetonitrile (10 mL) was added 4-methoxybenzyl chloride (0.18 mL, 1.3 mmol) and stirred at reflux for 18 h. The mixture was then cooled to rt before water (5 mL) was added and the mixture extracted with ethyl acetate (3 x 5 mL). The organic extracts were combined and washed with water (3 x 5 mL) and brine (3 x 5 mL), dried over Na_2SO_4, filtered and solvent removed *in vacuo* to give the product as a beige solid (331 mg, 99%); mp 71-73 °C; δ_H (400 MHz; $CDCl_3$) 7.74 (2 H, ddd, *J* 8.3, 2.2, 1.7, Ar<u>H</u>), 7.37 (2 H, d, *J* 8.0, Ar<u>H</u>), 7.23 (2 H, ddd, *J* 8.8, 2.9, 2.2, Ar<u>H</u>), 6.88 (ddd, *J* 8.8, 2.9, 2.0, Ar<u>H</u>), 4.08 (2 H, s, C<u>H</u>$_2$), 3.82 (3 H, s, OC<u>H</u>$_3$), 2.58 (3 H, NC<u>H</u>$_3$), 2.47 (3 H, C<u>H</u>$_3$); δ_C (100 MHz; $CDCl_3$) 159.3 (C), 143.4 (C), 134.4 (C), 129.7 (CH), 129.7 (CH), 127.6 (C), 127.5 (CH), 114.0 (CH), 55.3 (CH_3), 53.6 (CH_2), 34.1 (CH_3), 21.5 (CH_3). Data are consistent with those reported in the literature.[22]

Oxidation Products

General Procedure C

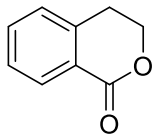
To a solution of substrate (1 mmol) and $CuCl_2$•$2H_2O$ (2 mol%) in dimethyl carbonate (12 mL) was added BQH_2 (5 mol%). The mixture was stirred under an atmosphere of O_2 with light irradiation for 18 h. The solvent was removed *in vacuo* and the residue purified by column chromatography.

General Procedure D

To a solution of arbutin-derived BQH_2 (5 mol%) and $CuCl_2$•$2H_2O$ (5 mol%) in DMC (12 mL) was added the substrate (1 mmol) . The mixture was stirred under an atmosphere of O_2 and visible light irradiation at rt for 18 h. The solvent was removed *in vacuo* and the residue purified by column chromatography.

Experimental Data

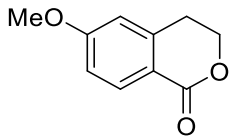
Isochromanone (2)



The *title compound* was synthesized according to General Procedure C using isochroman (0.13 mL, 1.0 mmol), $CuCl_2$•$2H_2O$ (3 mg, 2 mol%) and BQH_2 (6 mg, 5 mol%) in dimethyl carbonate (12 mL). Purification by column chromatography, eluting with ethyl acetate in light petroleum (5%) gave the *title compound* as a clear, colorless oil (142 mg, 95%); (Found: M+Na^+, 171.0420. $C_9H_8O_2Na^+$ requires 171.0417); (Found: M+H^+, 149.0597. $C_9H_9O_2^+$ requires 149.0597); δ_H (400 MHz; $CDCl_3$) 8.05 (1 H, d, *J* 7.8, Ar<u>H</u>), 7.52 (1 H, app. td, *J* 7.8, 1.4, Ar<u>H</u>), 7.39-7.34 (1, m, H, Ar<u>H</u>), 7.26 (1 H, d, *J* 7.7, Ar<u>H</u>), 4.51 (2 H, t, *J* 6.0, $CH_2C\underline{H_2}O$), 3.04 (2 H, t, *J* 6.0, $C\underline{H_2}CH_2O$); δ_C (100 MHz; $CDCl_3$) 165.0 (C), 139.4 (C), 133.5 (CH), 130.1 (CH), 127.5 (CH), 127.1 (CH), 125.1 (C), 67.2 (CH_2), 27.6 (CH_2). Data are consistent with those reported in the literature.[23]

The ^{18}O isomer of isochroman-1-one was isolated as a colourless oil (79 mg, 53%) by conducting the reaction under an atmosphere of $^{18}O_2$. Data are consistent with that of ^{16}O isochroman-1-one with the exception of the following which signify the presence of ^{18}O: (Found: M+H^+, 151.0653. $C_9H_9{}^{16}O{}^{18}O^+$ requires 151.0640); ν_{max} ($CHCl_3$)/cm^{-1} 2254, 1690, 1460, 1393, 1295, 1123, 901; *m/z* 151 (M+H^+, 100%).

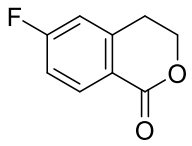
6-Methoxyisochroman-1-one (3)



The *title compound* was synthesized according to General Procedure C using 6-methoxyisochroman (164 mg, 1.00 mmol), $CuCl_2.2H_2O$ (3 mg, 2 mol%) and BQH_2 (6 mg, 5 mol%) in dimethyl carbonate (12 mL). Purification by column chromatography, eluting with ethyl acetate in light petroleum (1%) gave the *title compound* as a yellow oil (95 mg, 53%); υ_{max} ($CHCl_3$)/cm^{-1} 2254, 1712, 1606, 1499, 1393, 1261, 1094, 917; δ_H

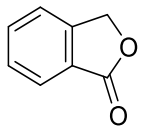
(400 MHz; $CDCl_3$) 8.06 (1 H, d, *J* 8.6, ArH), 6.90 (1 H, dd, *J* 8.6, 2.5, ArH), 6.73 (1 H, d, *J* 2.5, ArH), 4.51 (2 H, t, *J* 5.9, CH_2CH_2O), 3.88 (3 H, s, CH_3), 3.03 (2 H, t, *J* 5.9, CH_2CH_2O); δ_C (100 MHz; $CDCl_3$) 165. 1 (C), 163.7 (C), 141.8 (C), 132.8 (CH), 117.9 (C), 113.6 (CH), 111.9 (CH), 67.0 (CH_2), 55.5 (CH_3), 28.2 (CH_2). Data are consistent with those reported in the literature.[24]

6-Fluoroisochroman-1-one (4)



The *title compound* was synthesized according to General Procedure C using 6-fluoroisochromane (76 mg, 0.5 mmol), BQH_2 (3 mg, 2.5 mol%) and $CuCl_2 \cdot 2H_2O$ (2 mg, 1 mol%) in DMC (6 mL). The product was purified *via* column chromatography eluting with ethyl acetate in light petroleum (10%) to give a colorless oil (42 mg, 51%); υ_{max} (ATR)/cm^{-1} 3097, 3065, 2960, 2925, 1708, 1613, 1588, 1514, 1491, 1466, 1436, 1390, 1336, 1310, 1282; δ_H (300 MHz; $CDCl_3$) 8.14 (1 H, dd, *J* 8.6, 5.7, ArH), 7.10 (1 H, app. td, *J* 8.6, 2.6, ArH), 6.98 (1 H, dd, *J* 8.6, 1.8, ArH), 4.56 (2 H, t, *J* 6.1, CH_2CH_2O), 3.08 (2 H, t, *J* 6.1, CH_2CH_2O); δ_C (125 MHz; $CDCl_3$) 166.8 (C), 164.5 (C, d, *J* 67.2), 142.5 (C, d, *J* 9.1), 133.5 (CH, d, *J* 10.0), 121.7 (C, d, *J* 2.7), 115.4 (CH, d, *J* 22.5), 114.1 (CH, d, *J* 22.4), 67.1(CH_2), 28.0 (CH_2). Data are consistent with those reported in the literature.[5]

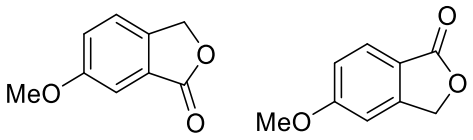
Isobenzofuran-1(3H)-one (5)



The *title compound* was synthesized according to General Procedure D using crude arbutin-derived BQH_2 (6 mg, 5 mol%), phthalan (0.10 mL, 1.0 mmol), $CuCl_2 \cdot 2H_2O$ (9.0 mg, 5.0 mol%) and dimethyl carbonate (12 mL). Purification by column chromatography, eluting with ethyl acetate in light petroleum (30 %) gave the *title compound* as a clear, colorless oil (59 mg, 44%); υ_{max} (ATR)/cm^{-1} 2946, 1850, 1758, 1617, 1596, 1466, 1450, 1363, 1313; δ_H (400 MHz; $CDCl_3$) 7.95 (1 H, d, *J* 7.5, ArH), 7.70 (1 H, t, *J* 14.2, 5.7, ArH), 7.60-7.48 (2 H,

m, ArH), 5.35 (2 H, s, CH_2O); δ_C (100 MHz; $CDCl_3$) 171.2 (C), 146.6 (C), 136.1 (C), 134.1 (CH), 129.1 (CH), 125.8 (CH), 122.1 (CH), 69.7 (CH_2); Data are consistent with those reported in the literature.[25]

6-Methoxyisobenzofuran-1(3H)-one (6) and 5-Methoxyisobenzofuran-1(3H)-one (7)

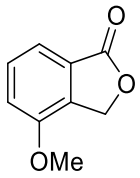


The *title compounds* were synthesized according to General Procedure C using 5-methoxy-1,3-dihydroisobenzofuran (60 mg, 0.4 mmol), $CuCl_2 \bullet 2H_2O$ (1 mg, 2 mol%) and BQH2 (2mg, 5 mol%) in DMC (5 mL). The residue was purified by column chromatography, eluting with ethyl acetate in light petroleum (25%) to give 5-methoxyisobenzofuran-1(3H)-one **7** as a colorless oil (20 mg, 30%) followed by 6-methoxyisobenzofuran-1(3H)-one **6** as a colorless oil (18 mg, 21%).

(6) (Found M+Na 187.0365, $C_9H_8O_3Na$ requires 187.0366); δ_H (400 MHz; $CDCl_3$) 7.40 (1 H, s, COCCH), 7.28 (1 H, d, *J* 2.4, ArH), 7.26 (1 H, d, *J* 2.4, ArH) , 5.28 (2 H, s, CH_2), 3.89 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 171.2 (C), 160.3 (C), 138.9 (C), 127.1 (C), 123.1 (CH), 122.9 (CH), 107.5 (CH), 69.5 (CH_2), 55.8 (CH_3). Data are consistent with those reported in the literature.[26]

(7) (Found M+Na^+ 187.0372, $C_9H_8O_3Na^+$ requires 187.0366); δ_H (400 MHz; $CDCl_3$) 7.82 (1H, d, *J* 8.5, ArH), 7.04 (1 H, dd, *J* 8.5, 2.2, ArH), 6.93 (1 H, d, *J* 2.2, ArH), 5.26 (2 H, s, CH_2), 3.91 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 170.9 (C), 164.8 (C), 149.4 (C), 127.2 (CH), 118.0 (C), 116.5 (CH), 106.0 (CH), 69.1 (CH_2), 55.9 (CH_3). Data are consistent with those reported in the literature.[27]

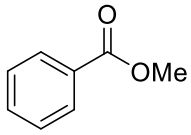
4-Methoxyisobenzofuran-1(3H)-one (8)



The *title compound* was synthesized according to General Procedure C using 4-methoxy-1,3-dihydroisobenzofuran (150 mg, 1 mmol), $CuCl_2.2H_2O$ (3 mg, 2 mol%) and BQH_2 (6 mg, 5 mol%) in dimethyl

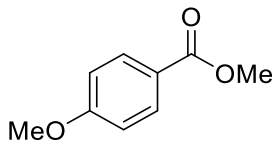
carbonate (12 mL). Purification by column chromatography, eluting with ethyl acetate in light petroleum (25%) gave the product as a colorless solid (35 mg, 21%); mp 114-116 °C (lit.,[28] mp 117-120 °C); δ_H (400 MHz; $CDCl_3$) 7.53-7.48 (2 H, m, Ar<u>H</u>), 7.15-7.09 (1 H, m, Ar<u>H</u>), 5.28 (2 H, s, C<u>H</u>$_2$), 3.94 (3 H, s, C<u>H</u>$_3$). δc (100 MHz; $CDCl_3$) 171.2 (C), 154.3 (C), 134.9 (C), 130.85 (CH), 127.4 (C), 117.3 (CH), 114.7 (CH), 68.1 (CH_2), 55.6 (CH_3). Data are consistent with those reported in the literature.[28]

Methyl benzoate (9)



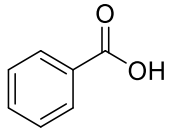
The *title compound* was synthesized according to General Procedure C using benzyl methyl ether (166 mg, 1.20 mmol), BQH_2 (7 mg, 5 mol%), $CuCl_2$•$2H_2O$ (4 mg, 2 mol%) in DMC (14 mL). The *title compound* (63 mg, 38%) was isolated as a colorless oil; υ_{max} ($CHCl_3$)/cm^{-1} 3011, 2414, 2245, 1884, 1522, 1424, 1239; δ_H (400 MHz; $CDCl_3$) 8.07-8.03 (2 H, m, ArH), 7.57 (1 H, tt, *J* 7.4, 1.9, ArH), 7.47-7.40 (2 H, m, ArH), 3.93 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 167.1 (C), 132.9 (CH), 130.2 (C), 129.6 (CH), 128.3 (CH), 52.1 (CH_3). Data are consistent with those reported in the literature.[336]

Methyl 4-methoxybenzoate (10)



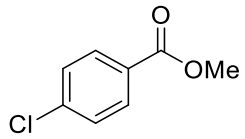
The *title compound* was synthesized according to General Procedure D using arbutin-derived BQH_2 (6 mg, 5 mol%), 1-methoxy-4-(methoxymethyl)benzene (152 mg, 1.00 mmol) and $CuCl_2$•$2H_2O$ (9.0 mg, 5 mol%) in dimethyl carbonate (12 mL). Purification by column chromatography, eluting with ethyl acetate in light petroleum (5-10 % step gradient) gave the *title compound* as a clear, colorless oil (63 mg, 38%); υ_{max} (ATR)/cm^{-1} 2952, 2840, 1711, 1604, 1579, 1510, 1459, 1433, 1380, 1316; δ_H (400 MHz; $CDCl_3$) 8.03-7.99 (2 H, m, Ar<u>H</u>), 6.96-6.92 (2 H, m, Ar<u>H</u>), 3.90 (3 H, s, C<u>H</u>$_3$), 3.88 (3 H, s, C<u>H</u>$_3$); δ_C (100 MHz; $CDCl_3$) 166.9 (C), 163.3

(C), 131.6 (CH), 122.6 (C), 114.0 (CH), 54.4 (CH_3), 51.9 (CH_3). Data are consistent with those reported in the literature.[29]



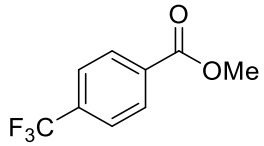
Also isolated was benzoic acid as a colorless solid (53 mg, 43%); mp 121 °C (lit.,[30] mp 122 °C) υ_{max} (ATR)/cm^{-1} 3070, 2825, 2663, 2604, 2553, 1679, 1600, 1581, 1496, 1453, 1419, 1323, 1288; δ_H (400 MHz; $CDCl_3$) 8.18-8.14 (2 H, m, Ar<u>H</u>), 7.70 (1 H, tt, *J* 7.5, 1.3, Ar<u>H</u>), 7.54-7.48 (2 H, m, Ar<u>H</u>); δ_C (100 MHz; $CDCl_3$) 172.3 (C), 138.8 (CH), 130.2 (CH), 129.3 (C), 128.5 (CH); Data are consistent with those reported in the literature.[31]

Methyl 4-chlorobenzoate (11)



The *title compound* was synthesized according to General Procedure D using arbutin-derived BQH_2 (6 mg, 5 mol%), 1-chloro-4-(methoxymethyl)benzene (156 mg, 1.00 mmol) and $CuCl_2$•$2H_2O$ (9 mg, 5 mol%) in dimethyl carbonate (12 mL). Purification by column chromatography, eluting with ethyl acetate in light petroleum (2-5 % step gradient) gave the *title compound* as a clear, colorless oil (65 mg, 38%); υ_{max} (ATR)/cm^{-1} 2997, 2952, 2843, 1720, 1595, 1488, 1433, 1400, 1272; δ_H (400 MHz; $CDCl_3$) 8.00-7.95 (2 H, m, Ar<u>H</u>), 7.43-7.39 (2 H, m, Ar<u>H</u>), 3.92 (3 H, s, C<u>H</u>$_3$); δ_C (100 MHz; $CDCl_3$) 171.3 (C), 166.2 (C), 139.4 (C), 131.0 (CH), 128.7 (CH), 52.2 (CH_3); Data are consistent with those reported in the literature.[32]

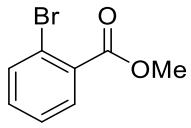
Methyl 4-trifluoromethylbenzoate (12)



The *title compound* was synthesized according to General Procedure C using 1-(methoxymethyl)-4-(trifluoromethyl)benzene (190 mg, 1.00 mmol), BQH_2 (6 mg, 5 mol%) and $CuCl_2$•$2H_2O$ (3 mg, 2 mol%) in

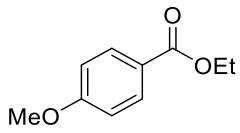
DMC (12 mL). Purification by column chromatography, eluting with ethyl acetate in light petroleum (1%) gave the *title compound* as a colorless oil (12 mg, 6%); υ_{max} (ATR)/cm^{-1} 2924, 2852, 1730, 1694, 1622, 1583, 1514, 1424, 1337; δ_H (400 MHz; $CDCl_3$); 8.01 (2 H, d, *J* 8.2, ArH), 7.73 (2 H, d, *J* 8.2, ArH), 3.98 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$); 165.9 (C), 134.2 (q, J 32.3, C), 133.1 (C), 129.9 (CH), 125.4 (q, *J* 3.7, CH), 123.6 (q, *J* 271.0, C), 52.5 (CH_3); Data are consistent with those reported in the literature.[33]

Methyl 2-bromobenzoate (13)



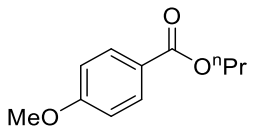
The *title compound* was synthesized according to General Procedure C using 1-bromo-2-(methoxymethyl)benzene (213 mg, 1.00 mmol), BQH_2 (6 mg, 5 mol%) and $CuCl_2$•$2H_2O$ (3 mg, 2 mol%) in DMC (12 mL). Purification by column chromatography eluting with ethyl acetate in light petroleum (1%) gave the *title compound* as a colorless oil (28 mg, 41%); υ_{max} (ATR)/cm^{-1} 3071, 2997, 2951, 2840, 1728, 1589, 1566, 1469, 1431; δ_H (400 MHz; $CDCl_3$); 7.81 (1 H, dd, *J* 7.5, 1.9, ArH), 7.68 (1 H, dd, *J* 7.5,1.9, ArH), 7.41-7.32 (2 H, m, ArH), 3.96 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 166.6 (C), 134.3 (CH), 132.6 (CH), 132.1 (C), 131.3 (CH), 127.3 (CH), 121.6 (C), 52.2 (CH_3); Data are consistent with those reported in the literature.[34]

Ethyl 4-methoxybenzoate (14)



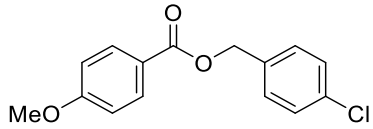
The *title compound* was synthesized according to General Procedure C. The *title compound* (40% yield by ^1H NMR integration using 1,1,2,2-tetrachloroethane as an internal standard) was isolated as a colorless oil (95:5 light petroleum: ethyl acetate); δ_H (400 MHz; $CDCl_3$) 8.01 (2 H, d, *J* 9.0, ArH), 6.93 (2 H, d, *J* 9.0, ArH), 4.35 (2 H, q, *J* 7.2, CH_2), 3.87 (3 H, s, CH_3), 3.43 (3 H, t, *J* 7.2, CH_3); δ_C (100 MHz; $CDCl_3$) 166.4 (C), 163.3 (C), 131.6 (CH), 129.3 (C), 113.6 (CH), 60.7 (CH_2), 55.4 (CH_3), 14.4 (CH_3). Data are consistent with those reported in the literature.[35]

Propyl 4-methoxybenzoate (15)



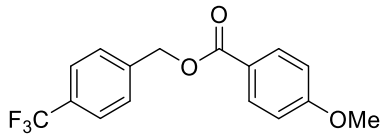
The *title compound* was synthesized according to General Procedure C. The *title compound* (40% yield by ^{1}H NMR integration using 1,1,2,2-tetrachloroethane as an internal standard) was isolated as a colorless oil (95:5 light petroleum: ethyl acetate); υ_{max} ($CHCl_3$)/cm^{-1} 2970, 1709, 1608, 1582, 1512, 1463, 1270, 1168, 1105; δ_H (400 MHz; $CDCl_3$) 8.01 (2 H, d, *J* 9.0, ArH), 6.93 (2 H, d, *J* 9.0, ArH), 4.26 (2 H, t, *J* 6.6, CH_2), 3.87 (3 H, s, CH_3), 1.79 (2 H, sex, *J* 6.6, CH_2), 1.03 (3 H, t, *J* 6.6, CH_3); δ_C (100 MHz; $CDCl_3$) 166.5 (C), 163.2 (C), 131.5 (CH), 123.0 (C), 113.5 (CH), 66.2 (CH_2), 55.4 (CH_3), 22.2 (CH_2), 10.5 (CH_3). Data are consistent with those reported in the literature.[36]

4-Chlorobenzyl 4-methoxybenzoate (16)



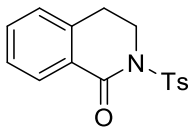
The *title compound* was synthesized according to General Procedure C using 1-chloro-4-(((4-methoxybenzyl)oxy)methyl)benzene (263 mg, 1.00 mmol), BQH_2 (6 mg, 5 mol%) and $CuCl_2$•$2H_2O$ (3 mg, 2 mol%) in DMC (12 mL). Purification by column chromatography, eluting with ethyl acetate in light petroleum (10%) gave the *title compound* (66 mg, 24%); mp 68-72 °C (lit.,[37] mp 78-79 °C); (Found: M+Na$^+$, 276.0552. $C_{15}H_{13}{}^{35}ClO_3{}^+$, requires 276.0553); υ_{max} ($CHCl_3$)/cm^{-1} 1710, 1606, 1512, 1316, 1257, 1099; δ_H (400 MHz; $CDCl_3$) 8.03 (2 H, d, *J* 8.8, ArH), 7.40-7.34 (4 H, m, ArH), 6.93 (2 H, d, *J* 8.8, ArH), 5.31 (2 H, s, CH_2), 3.86 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 166.0 (C) 163.5 (C), 134.8 (C), 134.0 (C), 131.7 (CH), 129.5 (CH), 128.7 (CH), 122.3 (C), 113.6 (CH), 65.5 (CH_2), 55.4 (CH_3); *m/z* 299 (M+Na$^+$, 100%). Data are consistent with those reported in the literature.[37]

4-(Trifluoromethyl)benzyl 4-methoxybenzoate (17)



The *title compound* was synthesized according General Procedure C using 1-methoxy-4-(((4-(trifluoromethyl)benzyl)oxy)methyl)benzene (296 mg, 1.00 mmol), BQH_2 (6 mg, 5 mol%) and $CuCl_2•2H_2O$ (3 mg, 2 mol%) in DMC (12 mL). The residue was purified by column chromatography, eluting with ethyl acetate in light petroleum (10%) and gave the product as a yellow oil (62 mg, 20%); (Found: $M+Na^+$, 310.0815. $C_{16}H_{13}F_3O_3^+$, requires 310.0817); υ_{max} ($CHCl_3$)/cm^{-1} 3006, 2842, 1709, 1607, 1511, 1461, 1321; δ_H (400 MHz; $CDCl_3$) 8.06 (2 H, d, *J* 9.0, CH), 7.67 (2 H, d, *J* 8.2, ArH), 7.57 (2 H, d, *J* 8.2, ArH), 6.96 (2 H, d, *J* 9.0, ArH), 5.41 (2 H, s, CH_2), 3.89 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 166.0 (C), 163.6 (C), 140.4 (C), 131.8 (CH), 130.3 (C, q, *J* 32.5), 128.0 (CH), 127.3 (C, q, *J* 272.5), 125.0 (CH, q, *J* 3.9, CH), 122.1 (C), 113.8 (CH), 65.4 (CH_2), 55.4 (CH_3), one C not observed; *m/z* 310 ($M+Na^+$, 100%). Data are consistent with those reported in the literature.[38]

2-Tosyl-3,4-dihydroisoquinolin-1(2H)-one (18)

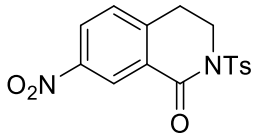


The *title compound* was synthesized according General Procedure C using 2-tosyl-1,2,3,4-tetrahydroisoquinoline (287 mg, 1.00 mmol), BQH_2 (6 mg, 5 mol%) and $CuCl_2•2H_2O$ (3 mg, 2 mol%) in DMC (12 mL). The residue was purified by column chromatography, eluting with ethyl acetate in light petroleum (5% – 10% step gradient) to give a colorless solid (71 mg, 23%).

Also synthesized according to General Procedure D using arbutin-derived BQH_2 (6 mg, 5 mol%), 2-tosyl-1,2,3,4-tetrahydroisoquinoline (287 mg, 1.00 mmol) and $CuCl_2•2H_2O$ (9.0 mg, 5.0 mol%) in dimethyl carbonate (12 mL). The residue was purified by column chromatography, eluting with ethyl acetate in light petroleum (5-10% step gradient) gave the product as a colorless solid (164 mg, 54%); mp 134-135 °C (lit.,[39]

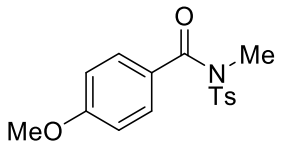
mp 132-133 °C); (Found ($M+H^+$) 302.0853, $C_{16}H_{16}NO_3S^+$ requires 302.0845); (Found ($M+Na^+$) 324.0663, $C_{16}H_{15}NO_3SNa^+$ requires 324.0665); δ_H (400 MHz; $CDCl_3$) 8.04-7.95 (3 H, m, ArH), 7.49 (1 H, app. td, *J* 7.5, 1.4, ArH), 7.35 (3 H, m, ArH), 7.24 (1 H, d, *J* 7.5, ArH), 4.26 (2 H, t, *J* 6.2, CH_2CH_2N), 3.15 (2H, t, *J* 6.2, CH_2CH_2N), 2.44 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 163.5 (C), 144.8 (C), 139.3 (C), 136.2 (C), 133.5 (CH), 129.4 (CH), 129.2 (CH), 128.6 (CH), 128.2 (C), 127.5 (CH), 127.4 (CH), 44.7 (CH_2), 29.0 (CH_2), 21.7 (CH_3). Data matched those in the literature.[39]

7-Nitro-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one (18)



The *title compound* was synthesized according to General Procedure C using 7-nitro-2-tosyl-1,2,3,4-tetrahydroisoquinoline (110 mg, 0.300 mmol) BQH_2 (2 mg, 5 mol%) and $CuCl_2$•$2H_2O$ (1 mg, 2 mol%) in DMC (4 mL). Purification by column chromatography, eluting with ethyl acetate in light petroleum (30%) gave the *title compound* as a colorless solid (73 mg, 63%); mp 160 °C (dec); (Found M+Na 369.0513, $C_{16}H_{14}N_2O_5Na$ requires 369.0515); υ_{max} (ATR)/cm^{-1} 3116, 2924, 1693, 1614, 1593, 1520, 1473, 1431; δ_H (400 MHz; $CDCl_3$) 8.87 (1 H, d, *J* 2.4, NO_2CCHC), 8.34 (1 H, dd, *J* 8.4, 2.4, NO_2CCHCH), 8.02 (2 H, app. dt, *J* 8.4, 1.9), 7.46 (1 H, d, *J* 8.0), 7.38 (2 H, d, *J* 8.4, SO_2CHCH), 4.30 (2 H, t, *J* 6.2, CH_2CH_2N), 3.27 (2 H, t, *J* 6.2, CH_2CH_2N), 2.47 (3 H, s, CH_3); δ_C (00 MHz; $CDCl_3$) 161.4 (C), 147.6 (C), 145.6 (C), 145.4 (C), 135.4 (C), 129.7(C), 129.6 (CH), 128.8 (CH), 128.7 (CH), 127.6 (CH), 124.6 (CH),

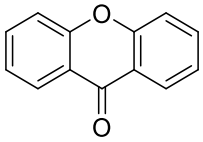
4-Methoxy-N-methyl-N-tosylbenzamide (20)



The *title compound* was synthesized according to General Procedure C using N-(4-methoxybenzyl)-N,4-dimethylbenzenesulfonamide (305 mg, 1.00 mmol), BQH_2 (6 mg, 5 mol%) and $CuCl_2$•$2H_2O$ (2 mg, 2 mol%) in

DMC (4 mL). Purification by column chromatography, eluting with ethyl acetate in light petroleum (20%) gave the *title compound* as a colorless solid (30 mg, 9%); mp 89-90 °C (lit.,[40] mp 39-41 °C); δ_H (400 MHz; $CDCl_3$) 7.82 (2 H, app dt, *J* 8.3, 1.8, ArH), 7.62 (2 H, ddd, *J* 8.9, 2.9, 2.0, ArH), 7.33 (2 H, d, *J* 8.3, ArH), 6.91 (2 H, ddd, *J* 8.9, 2.9, 2.0, ArH), 3.86 (3 H, s, CH_3O), 3.23 (3 H, s, NCH_3), 2.44 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 171.3 (C), 162.9 (C), 144.7 (C), 135.1 (C), 131.4 (CH), 129.6 (CH), 128.4 (CH), 126.4 (CH), 113.6 (CH), 55.5 (CH_3), 35.8 (CH_3), 21.7 (CH_3). Data are consistent with those reported in the literature.[40]

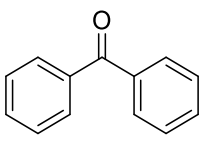
9H-Xanthen-9-one (21)



The *title compound* was synthesized according to General Procedure C using xanthene (182 mg, 1.00 mmol), BQH_2 (6 mg, 5 mol%) and $CuCl_2•2H_2O$ (6 mg, 4 mol%) in DMC (12 mL). The product was purified *via* column chromatography eluting with ethyl acetate in light petroleum (1%) to give the product as a colorless solid (65 mg, 33%).

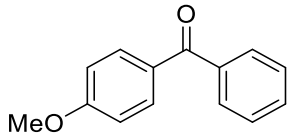
Also synthesized according to General Procedure D using arbutin derived BQH_2 (6 mg, 5 mol%), xanthene (182 mg, 1 mmol) and $CuCl_2•2H_2O$ (9 mg, 5 mol%) in DMC (12 mL). Purification by column chromatography gave the product as a colorless solid (171 mg, 87%); mp 173-174 °C (lit.,[41] mp 174 °C); δ_H (300 MHz; $CDCl_3$) 8.37 (2 H, dd, *J* 8.0, 1.8, ArH), 7.76 (2 H, ddd, *J* 8.5, 7.1, 1.8, ArH), 7.53 (2 H, dd, *J* 8.5, 1.0, ArH), 7.41 (2 H, ddd, *J* 8.0, 7.1, 1.0, ArH); δ_C (75 MHz; $CDCl_3$) 177.5 (C), 156.1 (C), 134.0 (CH), 126.8 (CH), 123.9 (CH), 121.9 (C), 118.0 (CH). Data are consistent with those reported in the literature.[42]

Benzophenone (22)



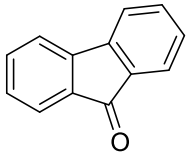
The *title compound* was synthesized according to General Procedure C using diphenylmethane (168 mg, 1.00 mmol), BQH_2 (6 mg, 5 mol%) and $CuCl_2•2H_2O$ (3 mg, 2 mol%) in DMC (12 mL). The product was purified *via* column chromatography eluting with ethyl acetate in light petroleum (1%) to give the product as a colorless solid (60 mg, 33%); mp 47-48 °C (lit.,[43] mp 47-49 °C); δ_H (300 MHz; $CDCl_3$) 7.87-7.79 (4 H, m, Ar<u>H</u>), 7.65-7.57 (1 H, m, Ar<u>H</u>), 7.55-7.46 (4 H, m, Ar<u>H</u>); δ_C (75 MHz; $CDCl_3$) 196.7 (C), 137.6 (C), 132.4 (CH), 130.1 (CH), 128.3 (CH). Data are consistent with those reported in the literature.[44]

(4-Methoxyphenyl)(phenyl)methanone (23)



The *title compound* was synthesized according to General Procedure C using 4-methoxydiphenylmethane (198 mg, 1.00 mmol), BQH_2 (6 mg, 5 mol%) and $CuCl_2•2H_2O$ (3 mg, 2 mol%) in DMC (12 mL). The product was purified *via* column chromatography eluting with light petroleum (100%) to give the product as a colorless solid (74 mg, 35%); mp 60 °C (lit.,[45] mp 60-62 °C); (Found ($M+Na^+$) 235.0725, $C_{14}H_{12}O_2Na^+$ requires 235.0730); δ_H (300 MHz; $CDCl_3$) 7.85 (2 H, d, *J* 8.1, Ar<u>H</u>), 7.78 (2 H, d, *J* 8.1, Ar<u>H</u>), 7.63-7.54 (1 H, m, Ar<u>H</u>), 7.53-7.45 (2 H, m, Ar<u>H</u>), 6.99 (2 H, d, *J* 8.1, Ar<u>H</u>), 3.91 (3 H, s, OC<u>H</u>$_3$); δ_C (75 MHz; $CDCl_3$) 195.7 (C), 163.3 (C), 138.3 (C), 132.6 (CH), 131.9 (CH), 130.2 (C), 129.7 (CH), 128.2 (CH), 113.6 (CH), 55.5 (CH_3). Data are consistent with those reported in the literature.[46]

9H-Fluoren-9-one (24)



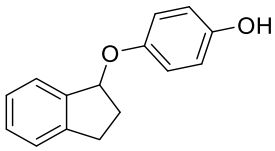
The *title compound* was synthesized according to General Procedure C using 9H-fluorene (166 mg, 1.00 mmol), BQH_2 (6 mg, 5 mol%) and $CuCl_2•2H_2O$ (3 mg, 2 mol%) in DMC (12 mL). The product was purified *via* column chromatography eluting with ethyl acetate in light petroleum (1%) to give the product as a yellow

solid (33 mg, 19%); mp 80 °C (lit.,[47] mp 84 °C); δ_H (300 MHz; $CDCl_3$) 7.68 (2 H, app. dt, *J* 7.5, 0.9, ArH), 7.58-7.46 (4 H, m, ArH), 7.31 (2 H, app. td, *J* 7.5, 1.6, ArH); δ_C (75 MHz; $CDCl_3$) 194.0 (C), 144.3 (C), 134.6 (CH), 134.2 (C), 129.1 (CH), 124.3 (CH), 120.3 (CH). Data are consistent with those reported in the literature.[48]

General Procedure E

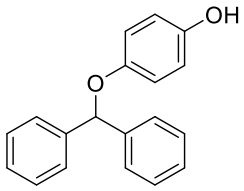
To a solution of benzoquinone (36 mg, 0.33 mmol) in acetic acid (4 mL) was added the aromatic hydrocarbon (1.65 mmol, 5 equiv) and the reaction mixture was purged with argon, stirred and irradiated for the specified time. The reaction mixture was then concentrated *in vacuo* and purified by flash chromatography on silica gel (95:5 light petroleum: ethyl acetate) to afford the product.

4-((2,3-Dihydro-1H-inden-1-yl)oxy)phenol (25)



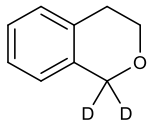
The reaction was carried out according to General Procedure E, and was irradiated for 16 h. The residue was purified by column chromatography, eluting with ethyl acetate in light petroleum (10%) to give the *title compound* as a yellow oil (74 mg, 99%); υ_{max} ($CHCl_3$)/cm^{-1} 3600, 3010, 1481, 1290, 1239, 910; (Found: M+Na^+, 249.0880. $C_{15}H_{14}O_2Na^+$, requires 249.0886); δ_H (400 MHz; $CDCl_3$) 7.43 (1 H, d, *J* 7.5, ArH), 7.34-7.31 (2 H, m, ArH), 7.26-7.23 (1 H, m, ArH), 6.91 (2 H, d, *J* 8.8, ArH), 6.79 (2 H, d *J* 8.8, ArH), 5.68 (1 H, dd, *J* 6.6, 4.3, CH), 4.97 (1 H, s, OH), 3.20-3.10 (1 H, m, CH), 2.96-2.88 (1 H, m, CH), 2.57-2.48 (1 H, m, CH), 2.28-2.20 (1 H, m, CH); δ_C (100 MHz; $CDCl_3$) 152.4 (C), 149.7 (C), 144.0 (C), 141.9 (C), 128.8 (CH), 126.6 (CH), 125.2 (CH), 124.9 (CH), 117.4 (CH), 116.1 (CH), 82.5 (CH), 32.3 (CH_2), 30.1 (CH_2); *m/*z 249 (M+Na^+, 100%).

4-(Benzhydryloxy)phenol (26)



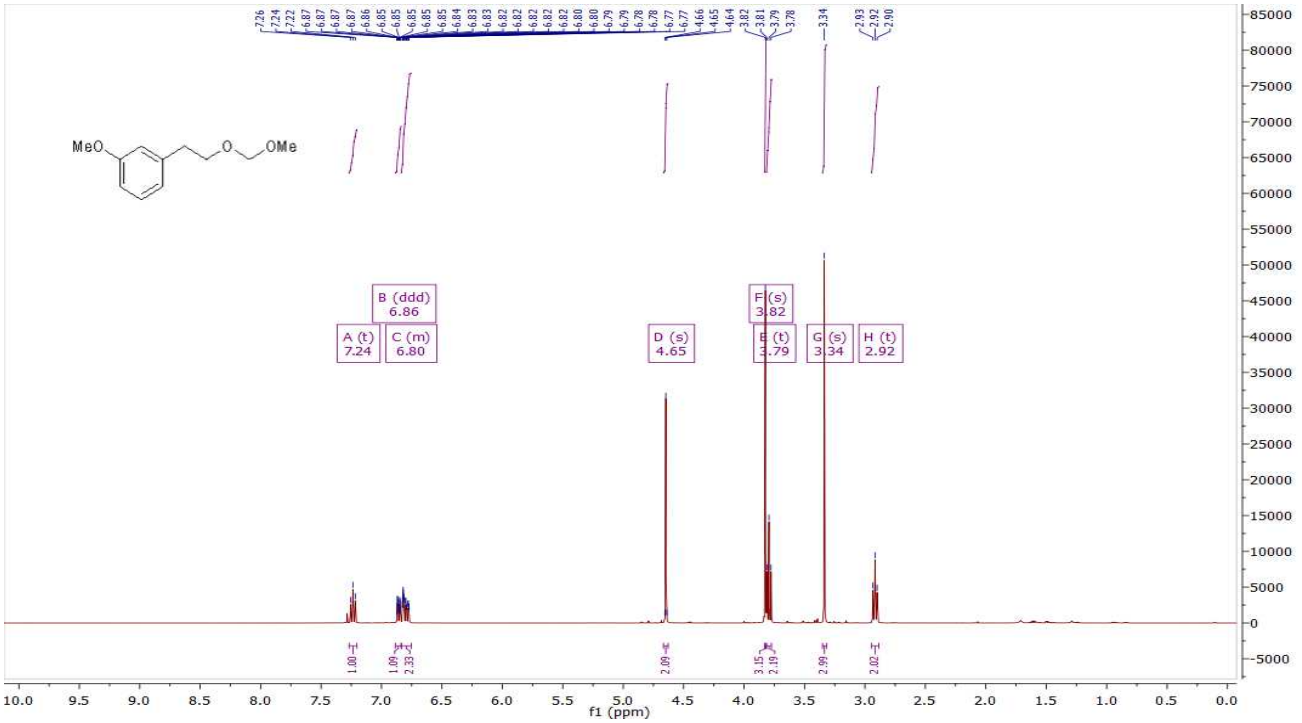
The reaction was carried out according to General Procedure E, and was irradiated for 40 h. The residue was purified by column chromatography, eluting with ethyl acetate in light petroleum (5%) to give the *title compound* as a yellow oil (37 mg, 41%); υ_{max} ($CHCl_3$)/cm^{-1} 3691, 3089, 1507, 1239, 917; (Found: M-H^+, 275.1062. $C_{19}H_{15}O_2^-$, requires 275.1062); δ_H (400 MHz; $CDCl_3$) 7.48-7.42 (4 H, m, ArH), 7.41-7.34 (4 H, m, ArH), 7.31 (2 H, tt, *J* 7.3, 1.4, ArH), 6.87 (2 H, d, *J* 9.0, ArH), 6.71 (2 H, d, *J* 9.0, ArH), 6.14 (1 H, s, CH); δ_C (100 MHz; $CDCl_3$) 152.4 (C), 149.2 (C), 141.5 (C), 128.6 (CH), 127.7 (CH), 127.0 (CH), 117.5 (CH), 116.0 (CH), 82.7 (CH); *m/*z 275 (M-H^+, 100%). Data are consistent with those reported in the literature.[49]

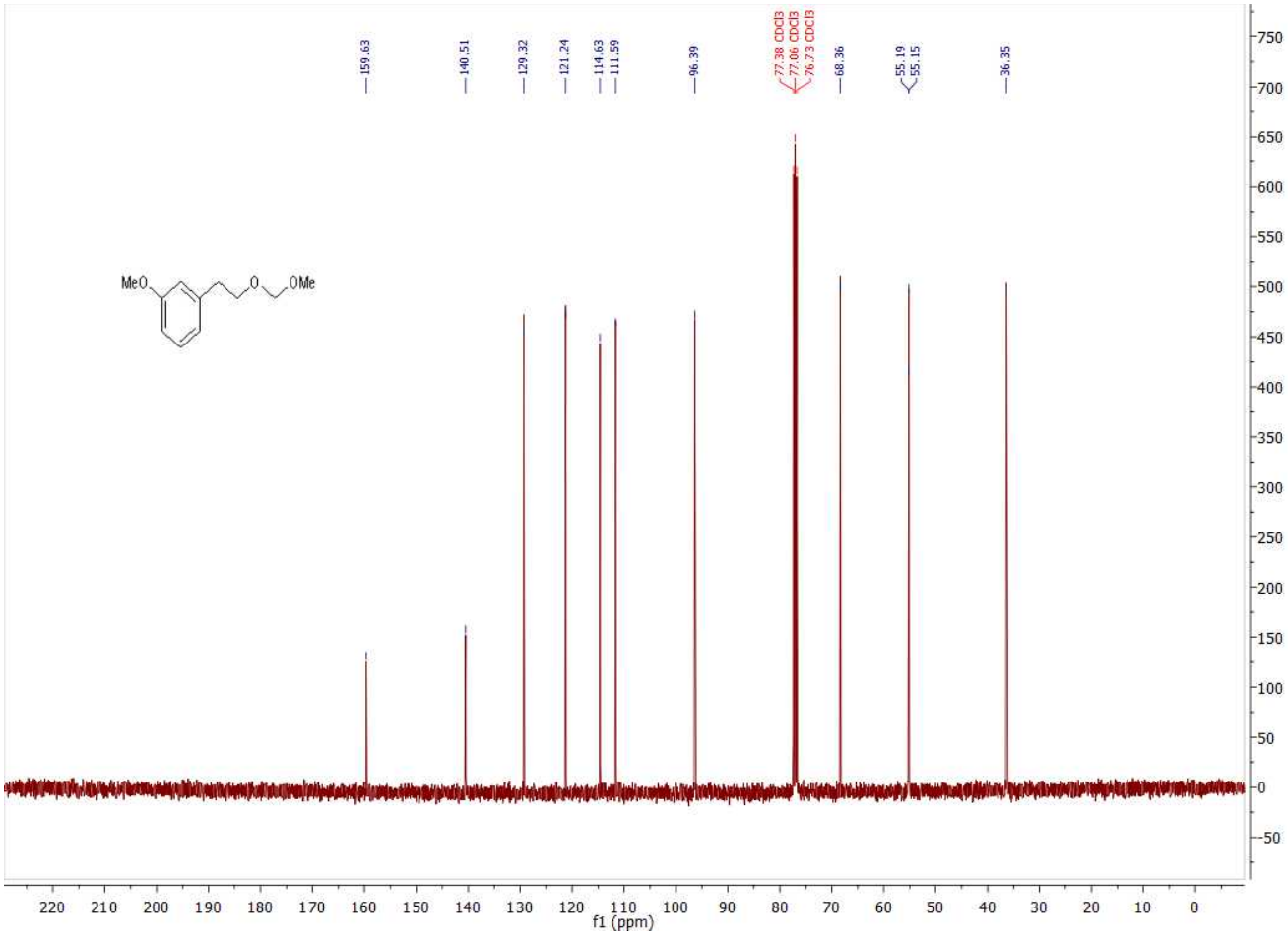
Isochromane-1,1-d_2



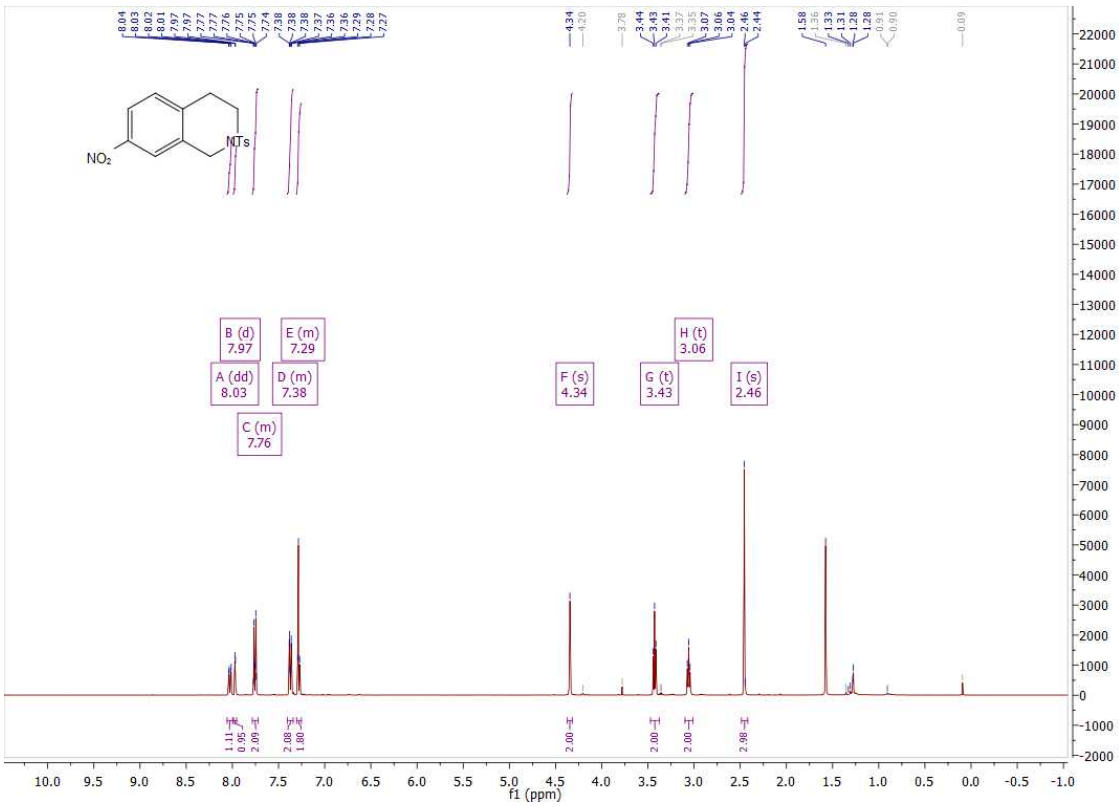
To a solution of *d*-formaldehyde (4.8 g, 20% solution in D_2O) was added H_2SO_4 (100 µL, 2.00 mmol) and phenethyl alcohol (1.83 g, 15.0 mmol) and the reaction mixture was heated at 65 °C for 3 d. The reaction mixture was cooled and ethyl acetate (50 mL) and water (50 mL) were added and the phases were separated. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by column chromatography, eluting with ethyl acetate in light petroleum (5%) to give the title compound as a colorless oil; (Found: M^+, 136.0851. $C_9H_8D_2^+$, requires 136.0852); υ_{max} ($CHCl_3$)/cm^{-1} 3066, 3008, 1731, 1494, 1465, 1252, 1109; δ_H (400 MHz; $CDCl_3$) 7.20-7.10 (3 H, m, ArH), 7.05-6.95 (1 H, m, ArH), 4.00 (2 H, t, J 5.7, 3-C$\underline{H}_2$), 2.88 (2 H, t, J 5.7, 4-C$\underline{H}_2$); δ_C (100 MHz; $CDCl_3$) 134.7 (C), 133.2 (C), 128.8 (CH), 126.3 (CH), 125.9 (CH), 124.3 (CH), 67.4 67.0 (pent, *J* 22.0, CD_2), 65.3 (3-CH_2), 28.3 (4-CH_2). Data are consistent with those previously reported.[50]

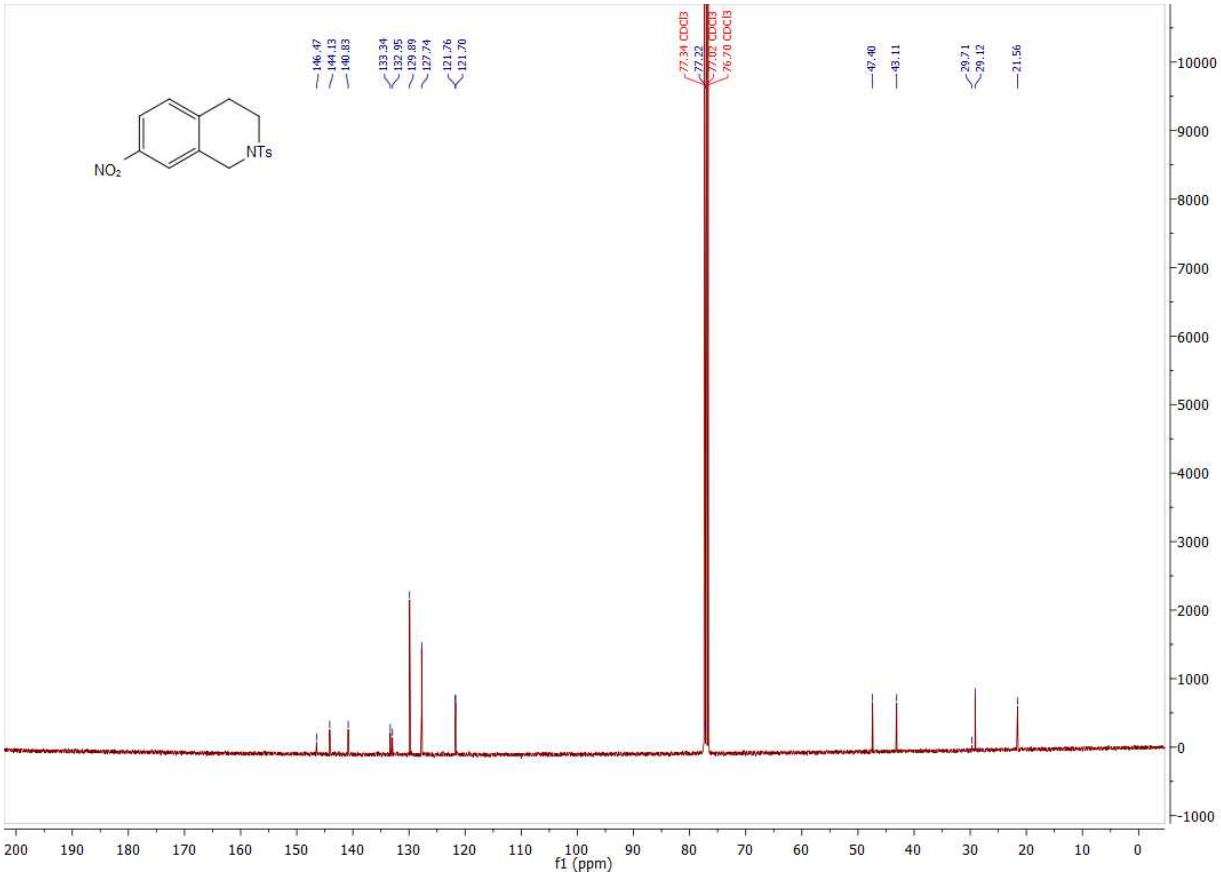
1-Methoxy-3-(2-(methoxymethoxy)ethyl)benzene



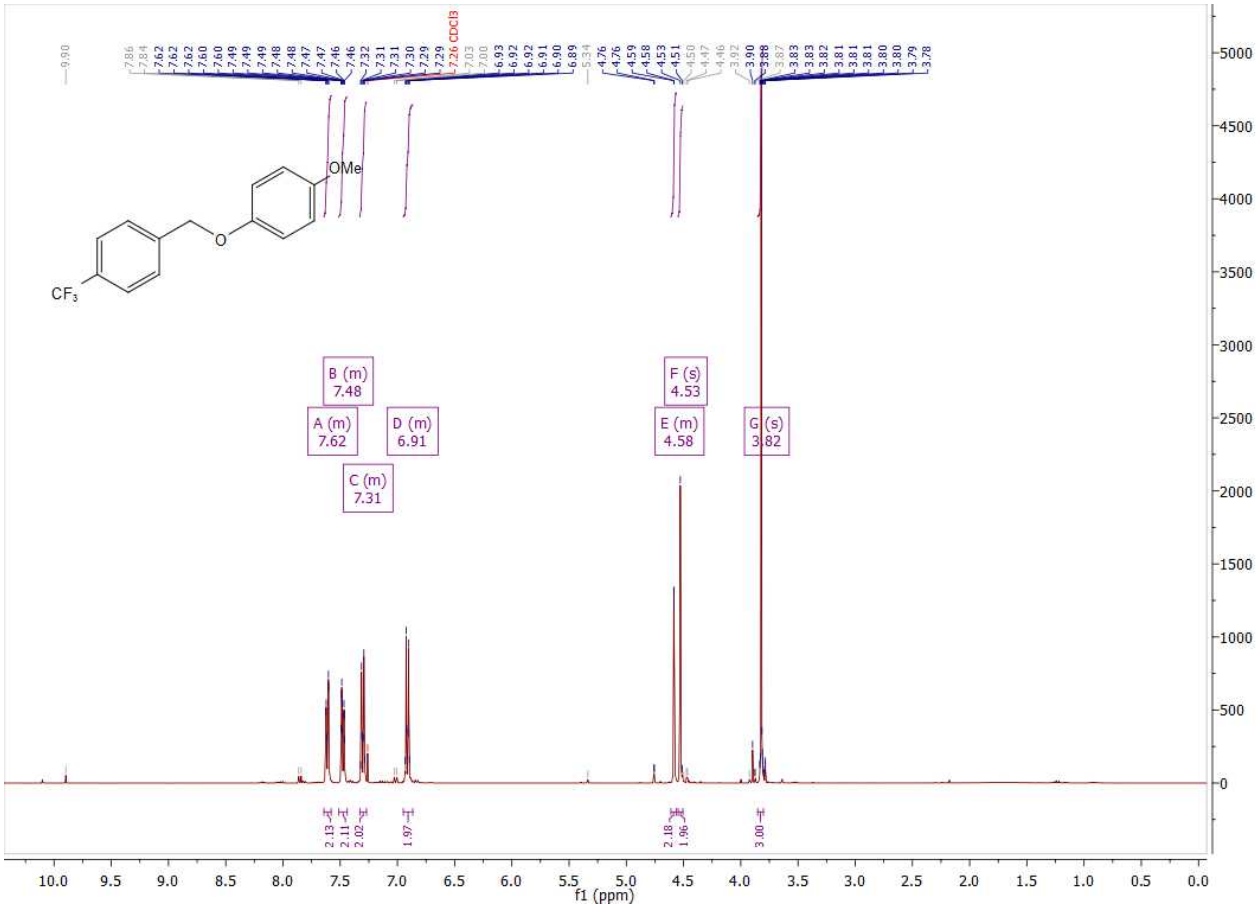


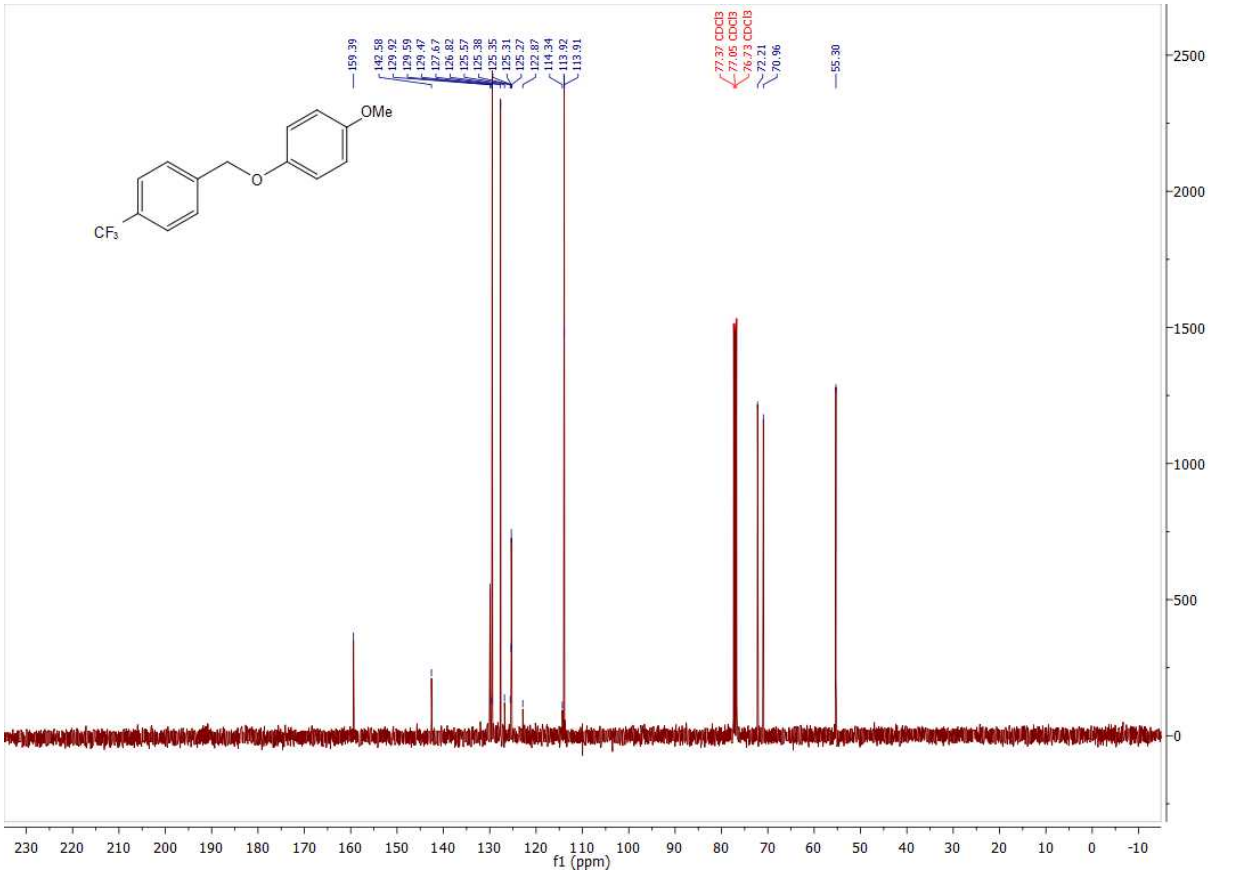
7-Nitro-2-tosyl-1,2,3,4-tetrahydroisoquinoline



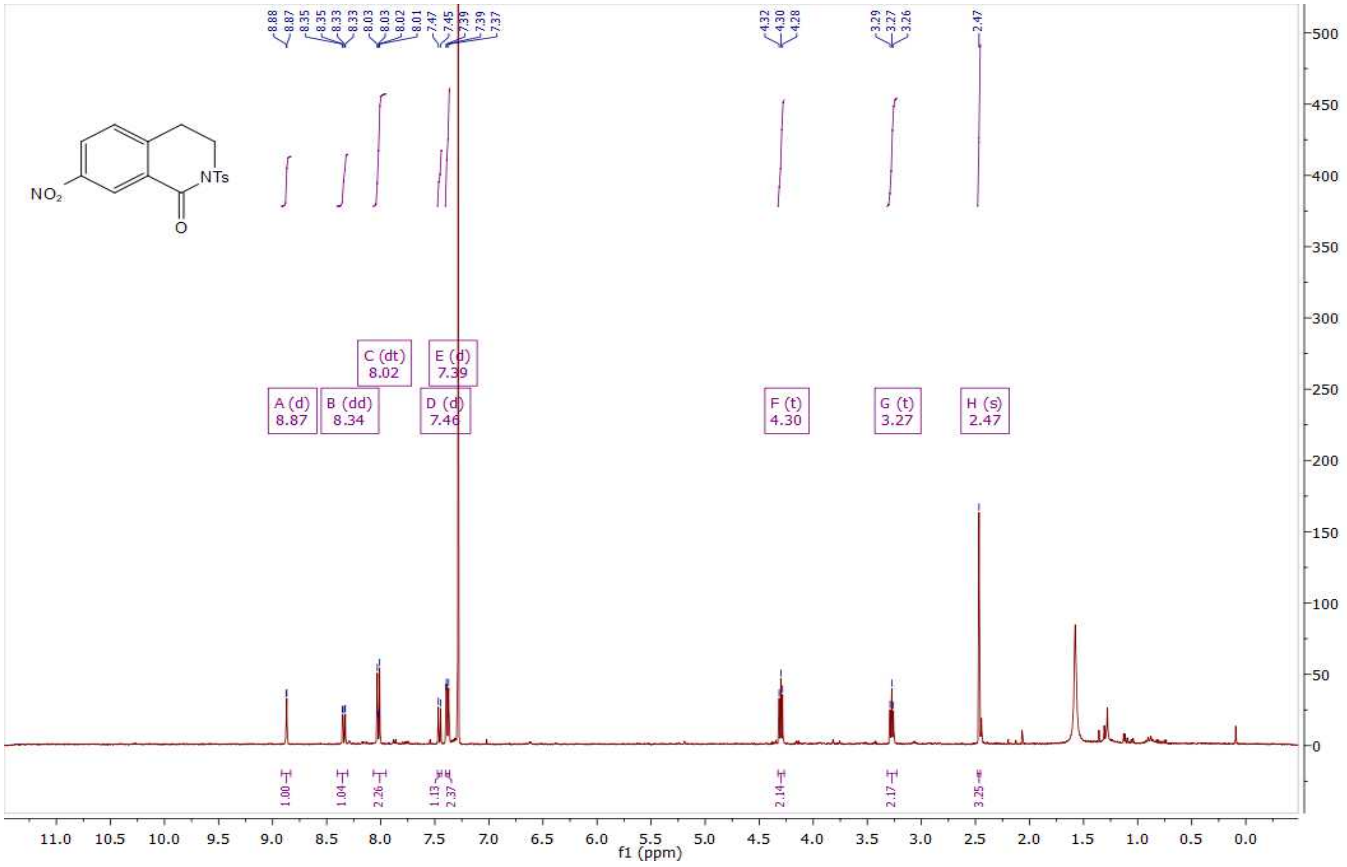


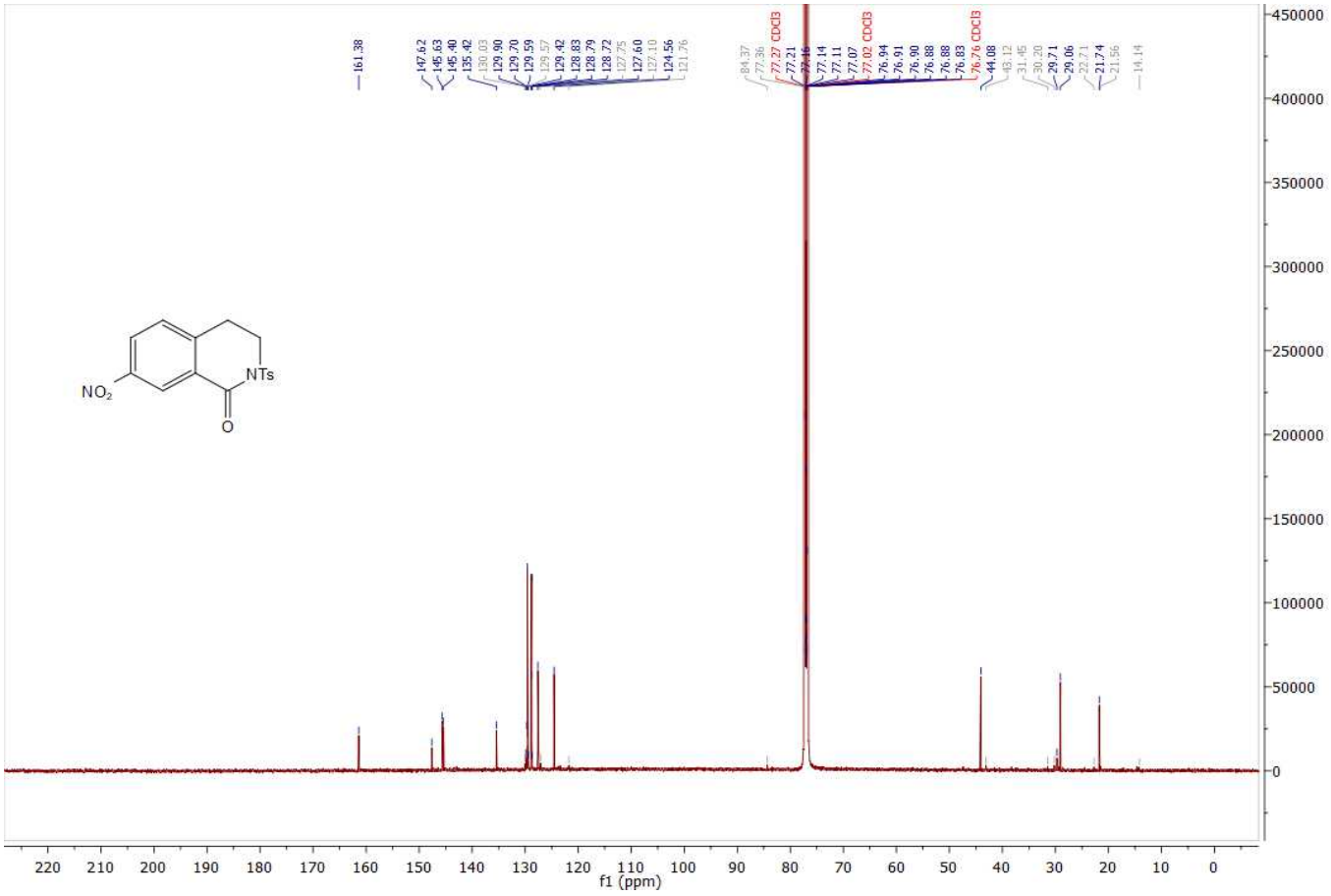
1-Methoxy-4-(((4-(trifluoromethyl)benzyl)oxy)methyl)benzene



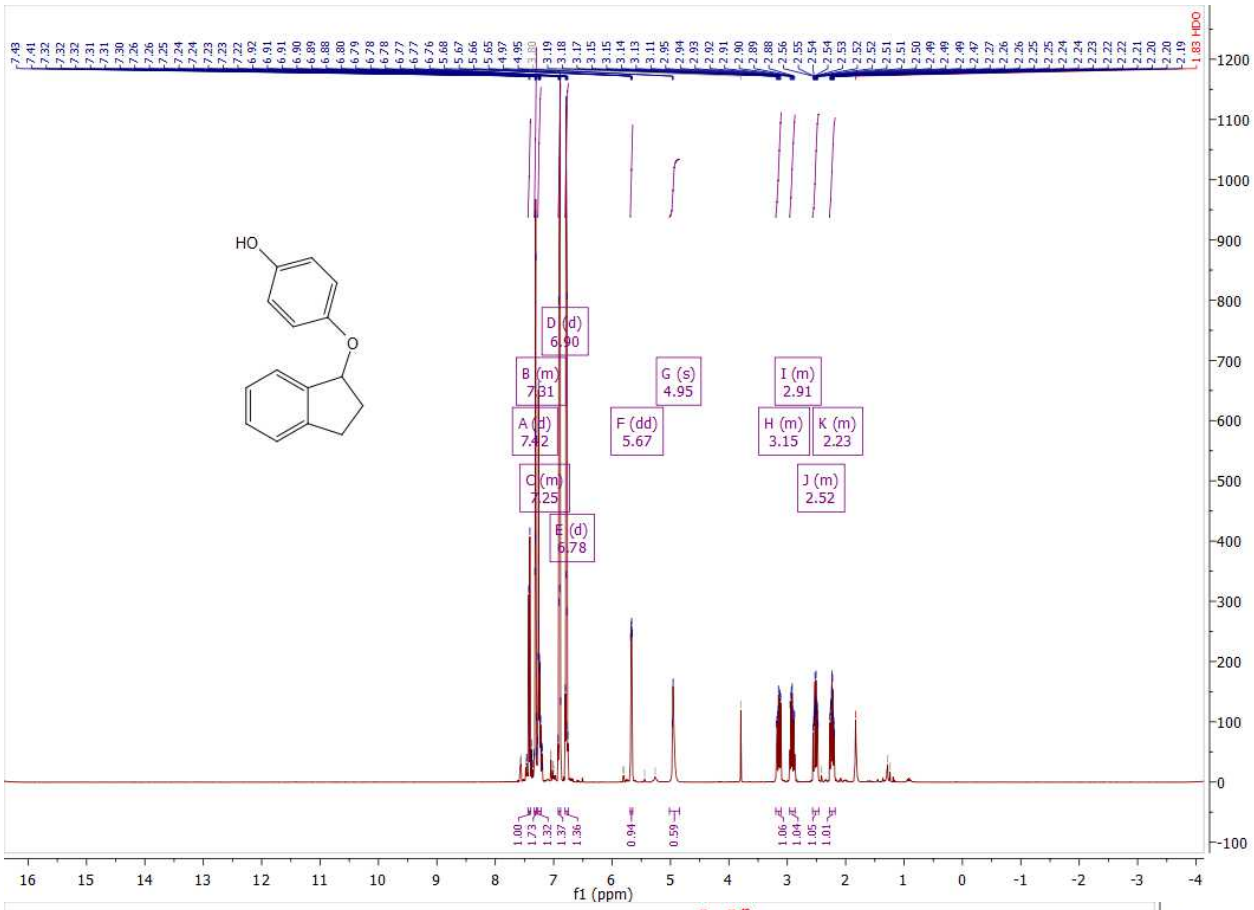


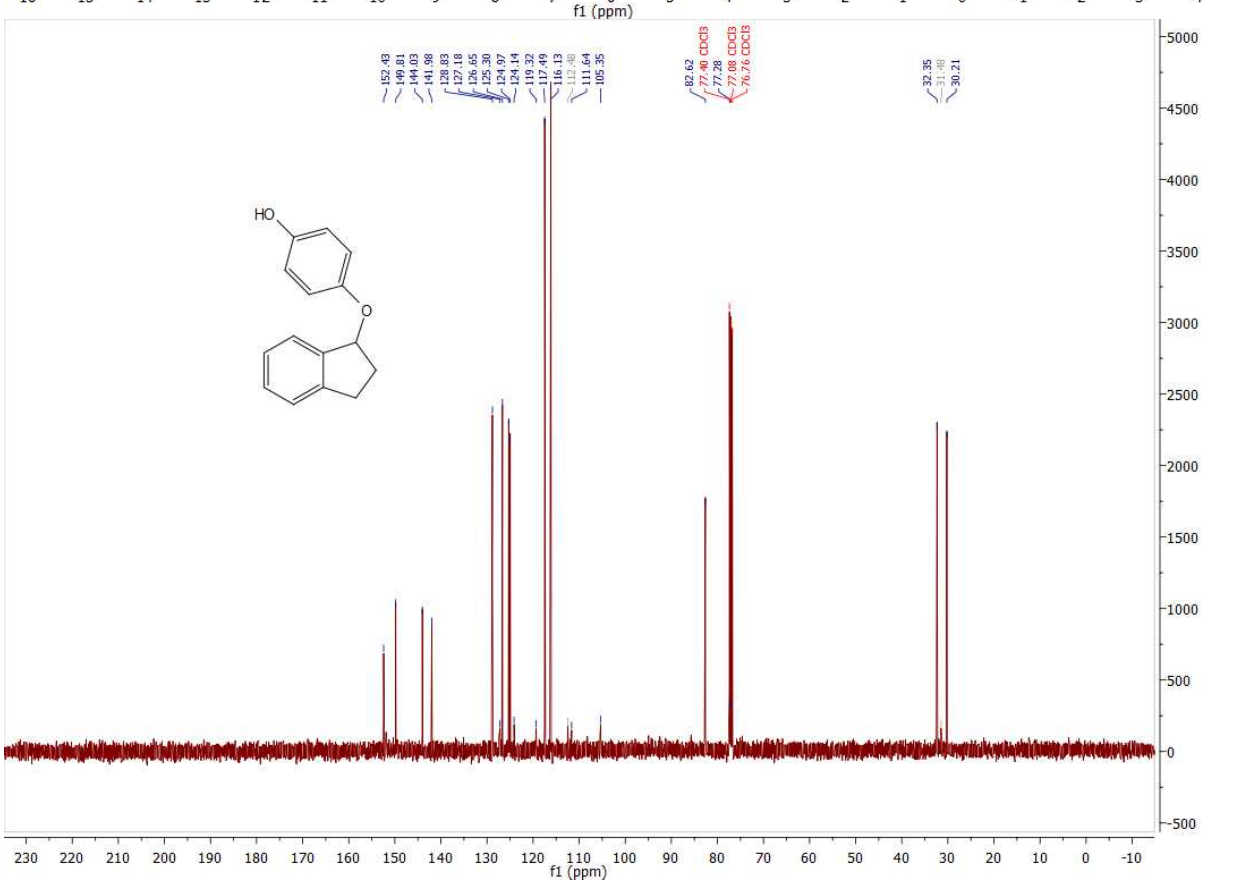
7-Nitro-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one (18)





4-((2,3-Dihydro-1H-inden-1-yl)oxy)phenol (25)





References

1 C. Raviola, D. Ravelli, S. Protti and M. Fagnoni, *J. Am. Chem. Soc.*, 2014, **136**, 13874–13881.

2 S. J. Park, J. R. Price and M. H. Todd, *J. Org. Chem.*, 2012, **77**, 949–955.

3 A. L. Meyer and R. B. Turner, *Tetrahedron*, 1971, **27**, 2609–2615.

4 R. Yang, Z. F. Gao, J. Y. Zhao, W. B. Li, L. Zhou and F. Miao, *J. Agric. Food Chem.*, 2015, **63**, 1906–1914.

5 S. E. Reisman, A. G. Doyle and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2008, **130**, 7198–7199.

6 B. Martin-Matute, C. Nevado, D. J. Cardenas and A. M. Echavarren, *J. Am. Chem. Soc.*, 2003, **125**, 5757–5766.

7 A. K. Ganai, R. Bhardwaj, S. Hotha, S. Sen Gupta and B. L. V. Prasad, *New J. Chem.*, 2010, **34**, 2662.

8 N. M. Weldy, A. G. Schafer, C. P. Owens, C. J. Herting, A. Varela-Alvarez, S. Chen, Z. Niemeyer, D. G. Musaev, M. S. Sigman, H. M. L. Davies and S. B. Blakey, *Chem. Sci.*, 2016, **7**, 3142–3146.

9 D. García, F. Foubelo and M. Yus, *Tetrahedron*, 2008, **64**, 4275–4286.

10 G. Argouarch, G. Grelaud, T. Roisnel, M. G. Humphrey and F. Paul, *Tetrahedron Lett.*, 2012, **53**, 5015–5018.

11 W. Hilborn and E. Macknight, *J. Am. Chem. Soc.*, 1994, **116**, 3337–3346.

12 H. J. Reich, W. S. Goldenberg, A. W. Sanders, K. L. Jantzi and C. C. Tzschucke, *J. Am. Chem. Soc.*, 2003, 3509–3521.

13 S. P. Chavan and K. R. Harale, *Tetrahedron Lett.*, 2012, **53**, 4683–4686.

14 G. Bhaskar, M. Solomon, G. Babu, D. Muralidharan and P. T. Perumal, *Indian J. Chem. - Sect. B Org. Med. Chem.*, 2010, **49**, 795–801.

15 Z. Shen, M. Chen, T. Fang, M. Li, W. Mo, B. Hu, N. Sun and X. Hu, *Tetrahedron Lett.*, 2015, **56**, 2768–2772.

16 D. van der Waals, A. Pettman and J. M. J. Williams, *RSC Adv.*, 2014, **4**, 51845–51849.

17 A. Venkov and L. Lukanov, *Synthesis (Stuttg).*, 1989, **12**, 59–61.

18 C. Aubert, C. Huard-perrio and M. Lasne, *J. Chem. Soc. Perkin Trans. 1*, 1997, **1**, 2837–2842.

19 S. O. Sullivan, E. Doni, T. Tuttle and J. A. Murphy, *Angew. Chemie Int. Ed.*, 2014, **53**, 474–478.

20 J. M. Mellor and N. M. Smith, *J. Chem. Soc. Perkin Trans. 1*, 1984, 2927.

21 A. Bruneau-Voisine, D. Wang, V. Dorcet, T. Roisnel, C. Darcel and J. B. Sortais, *J. Catal.*, 2017, **347**, 57–62.

22 X. Tang, L. Huang, C. Qi, X. Wu, W. Wu and H. Jiang, *Chem. Commun.*, 2013, **49**, 6102.

23 C. Enzensperger and J. Lehmann, *J. Med. Chem.*, 2006, **49**, 6408–6411.

24 G. Pandey, S. Pal and R. Laha, *Angew. Chemie Int. Ed.*, 2013, **52**, 5146–5149.

25 Y. Z. Li, B. J. Li, X. Y. Lu, S. Lin and Z. J. Shi, *Angew. Chemie Int. Ed.*, 2009, **48**, 3817–3820.

26 K. I. Fujita, W. Ito and R. Yamaguchi, *ChemCatChem*, 2014, **6**, 109–112.

27 S. Sueki, Z. Wang and Y. Kuninobu, *Org. Lett.*, 2016, **18**, 304–307.

28 B. A. Egan, M. Paradowski, L. H. Thomas and R. Marquez, *Org. Lett.*, 2011, **13**, 2086–2089.

29 J. B. Stothers and K. S. Dhami, *Can. J. Chem.*, 1967, **45**, 233–238.

30 W. von E. Doering and R. M. Haines, *J. Am. Chem. Soc.*, 1954, **76**, 482–486.

31 A. Monrose, H. Salembier, T. Bousquet, S. Pellegrini and L. Pélinski, *Adv. Synth. Catal.*, 2017, **359**, 2699–2704.

32 X. Liu, Q. Xia, Y. Zhang, C. Chen and W. Chen, *J. Org. Chem.*, 2013, **78**, 8531–6.

33 T. Miyazaki, S. Kasai, Y. Ogiwara and N. Sakai, *European J. Org. Chem.*, 2016, **2016**, 1043–1049.

34 B. N. Hemric, K. Shen and Q. Wang, *J. Am. Chem. Soc.*, 2016, **138**, 5813–5816.

35 R. H. Munday, J. R. Martinelli and S. L. Buchwald, *J. Am. Chem. Soc.*, 2008, **130**, 2754–2755.

36 X. F. Wu and K. Natte, *Adv. Synth. Catal.*, 2016, **358**, 336–352.

37 C. C. Zeng, N. T. Zhang, C. M. Lam and R. D. Little, *Org. Lett.*, 2012, **14**, 1314–1317.

38 C. Liu, S. Tang, L. Zheng, D. Liu, H. Zhang and A. Lei, *Angew. Chemie Int. Ed.*, 2012, **51**, 5662–5666.

39 T. Morimoto, Ã. M. Fujioka, K. Fuji, K. Tsutsumi and K. K. Ã, *Chem. Lett.*, 2003, **32**, 1–2.

40 Y. Inamoto, Y. Kaga, Y. Nishimoto, M. Yasuda and A. Baba, *Org. Lett.*, 2013, **15**, 3452–3455.

41 A. L. G. Wade, Jr.,* K. J. Acker, R. A. Earl and R. A. Osteryoung, *J. Org. Chem*, 1979, **44**, 3724–3725.

42 J. Zhao and R. C. Larock, *Org. Lett.*, 2005, **7**, 4273–4275.

43 A. Shaabani, K. Soleimani and A. Bazgir, *Synth. Commun.*, 2004, **34**, 3303–3315.

44 Y. Yuan, X. Shi and W. Liu, *Synlett*, 2011, 559–564.

45 K. O. Jeon, J. H. Jun, J. S. Yu, C. K. Lee, K. O. Jeon, J. H. Jun, J. S. Yu and C. K. Lee, *J. Heterocycl. Chem.*, 2003, **40**, 763–771.

46 J. Karthikeyan, K. Parthasarathy and C.-H. Cheng, *Chem. Commun.*, 2011, **47**, 10461–10463.

47 S. K. Masahiro Miura, Masatomo Nojima, *J. Chem. Soc. Perkin Trans. 2*, 1950, 1950–1954.

48 V. S. Thirunavukkarasu, K. Parthasarathy and C. H. Cheng, *Angew. Chemie Int. Ed.*, 2008, **47**, 9462–9465.

49 K. C. Nicolaou, G. Liu, K. Beabout, M. D. McCurry and Y. Shamoo, *J. Am. Chem. Soc.*, 2017, **139**, 3736–3746.

50 M. Wan, Z. Meng, H. Lou, L. Liu, *Angew. Chem. Int. Ed.* **2014**, *53*, 13845-13849.