Supporting information for:

Photo-induced proton-coupled electron transfer from an acetylphenyl 'antenna' to an isoindoline nitroxide

Jason C. Morris[a,b,†] Liam Walsh, [a,†] Brunell A. Gomes,[a] Didier Gigmes,[b] Kathryn E. Fairfull-Smith,[a] Steven E. Bottle[a] and James P. Blinco[a,*]

School of Chemistry, Physics and Mechanical Engineering,

Queensland University of Technology (QUT), 2 George St, Brisbane, Queensland 4001, Australia.

Aix Marseille Université, CNRS, ICR UMR 7273, 13397 Marseille, France.

Email: j.blinco@qut.edu.au

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General Procedure

All starting materials and reagents were purchased from Sigma Aldrich and used without further purification. All reactions were monitored with Merck Silica Gel 60 F254 TLC plates and visualized with UV light. Silica gel column chromatography was performed using silica gel 60 Å (230 - 400 mesh) with eluents as specified. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra at 100 MHz. Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra run in $CDCl_3$ are reported in ppm relative to the solvent residual peak: proton (δ = 7.28 ppm) and carbon (δ = 77.20 ppm). Multiplicity is indicated as follows: s (singlet); br s (broad singlet); d (doublet); dd (doublet of doublets); t (triplet); m (multiplet). Coupling constants are reported in Hertz (Hz). Mass spectra were recorded using electrospray as the ionization technique in positive ion mode. All mass spectra samples were prepared as solutions in methanol.

Infrared spectra were recorded as neat samples using a Nicolet 870 Nexus Fourier Transform infrared spectrometer equipped with a DTGS TEC detector and an Attenuated Total Reflectance (ATR) accessory (Nicolet Instrument Corp., Madison, WI) using a Smart Endurance single reflection ATR accessory equipped with a composite diamond IRE with a 0.75 mm^2 sampling surface and a ZnSe focussing element. An Optical Path Difference (OPD) velocity of 0.6329 cm s^{-1} and a gain of 8 were used. Spectra were collected in the spectral range 4000-525 cm^{-1} with a minimum of 16 scans, and 4 cm^{-1} resolution.

Analytical HPLC was performed on a Hewlett Packard 1100 series HPLC, using an Agilent prep-C18 scalar column (10 μm, 4.6 × 150 mm) at a flow rate of 1 mL/min.

LC-MS analysis was performed on an Agilent 6520 QTOF LC/MS instrument with a 1290 Infinity HPLC system and UV detector (set at 220 nm) coupled to a 6520 Accurate-Mass QTOF mass spectrometer. An Agilent prep-C18 Scalar (10 μm, 4.6 x 150 nm) C-18 column was set up in line before the UV detector and QTOF mass spectrometer.

GC-MS analysis was performed on an Agilent HP6890 gas chromatograph with a HP5973 mass spectrometer detector using an Agilent 19091S-413 HP5-MS column. Each sample had an injection volume of 10 μL. The inlet temperature was set at 200 °C in a split set up with a 20:1 ratio giving a total flow rate of 27.8 mL/min. The oven temperature was set to ramp over 25 minutes starting at 100 °C and increasing at a ramp rate of 10 °C per min reaching a maximum temperature of 250 °C followed by 20 minutes of isothermal heating at 250 °C.

UV-Vis spectroscopic analysis was performed using a Shimadzu UV-1800 UV spectrometer. A scan speed of 600 nm/min was used on a spectral window of 200-500 nm with a slit width of 1.0 nm. Solutions were analysed in quartz fluorescence spectroscopy cells with a concurrent cell containing blank solvent.

Electron Paramagnetic Resonance spectroscopy was performed using a Magnettech MS400 Miniscope EPR spectrometer with a H03 Temperature controller. Samples measured in NMR tubes

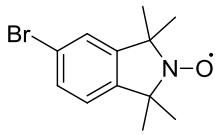
used a B0 field of 3358 Gauss (G) with a sweep width of 120 G and a sweep time of 120 seconds. A signal modulation of 500 mG and microwave attenuation of 10 decibels were applied.

Photoirradiation experiments were performed using a RAYONET Photochemical Chamber Reactor with 350 nm FL8BL-B UV-B bulbs (16 bulbs) arranged in the circular chamber. Samples were positioned in a sample carousel 6 cm away from the nearest bulb.

Melting points were measured on a Gallenkamp Variable Temperature Apparatus by the capillary method and are uncorrected.

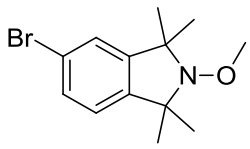
Experimental Procedures

5-Bromo-1,1,3,3-tetramethylisoindol-2-yloxyl (18)



To a solution of 5-bromo-1,1,3,3-tetramethylisoindoline (6.03 g, 23.72 mmol, 1.0 eq.) in dichloromethane (150 mL) was added mCPBA (77 % purity) (6.92 g, 30.84 mmol, 1.3 eq.) in portions. The reaction was maintained for two hours at room temperature. 2M sodium hydroxide was then added and the resulting mixture stirred vigorously for 15 minutes. The reaction mixture was then extracted with dichloromethane. The combined organic extracts were then washed with water followed by a saturated solution of brine, dried over anhydrous sodium sulphate and concentrated in vacuo. Purification via silica gel column chromatography (diethyl ether:*n*-hexanes; 1:2) afforded 5-bromo-1,1,3,3-tetramethylisoindol-2-yloxyl (**18**) as an orange solid (5.94 g, 93 % yield). M.p. 100 - 101 °C. Rf = 0.40, diethyl ether : n-hexanes; 1 : 2. HRMS (ESI) m/z: calculated for $C_{12}H_{15}BrNONa$ [M+Na]+ 291.0229; found 291.02305.

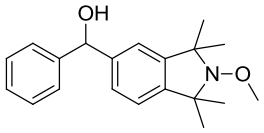
5-Bromo-2-methoxy-1,1,3,3-tetramethylisoindoline (8)



To a solution of 5-bromo-1,1,3,3-tetramethylisoindol-2-yloxyl (**18**) (5.90 g, 21.92 mmol, 1.0 eq.) in dimethyl sulfoxide (80 mL) was added iron(II) sulphate heptahydrate (12.19 g, 43.84 mmol, 2.0 eq.). The reaction was placed in an ice bath and 10 mL of aqueous hydrogen peroxide (30 %) added in portions (2 mL dropwise at 10 minutes intervals). After one hour the reaction mixture was diluted with water and extracted with diethyl ether. The combined

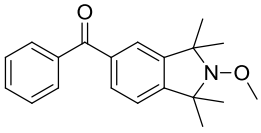
organic extracts were then washed with a saturated solution of brine, dried over anhydrous sodium sulphate and concentrated *in vacuo*. Purification via silica gel column chromatography (diethyl ether:n-hexanes; 1:19) afforded 5-bromo-2-methoxy-1,1,3,3-tetramethylisoindoline (**8**) as a low melting white solid (5.54 g, 89 % yield). Rf = 0.52, diethyl ether : n-hexanes; 1 : 19. ^{1}H NMR (400 MHz CDCl3): δ (ppm) = 7.35 (dd, J = 8.0, 2.0 Hz, 1H, H_{arom}), 7.22 (d, J = 2.0 Hz, 1H, H_{arom}), 6.97 (d, J = 8.0 Hz, 1H, H_{arom}), 3.77 (s, 3H, OCH_3), 1.41 (br s, 12H, 4×CH_3). HRMS (ESI) m/z: calculated for $C_{13}H_{19}BrNO$ [M+H]+ 284.0645; found 284.0643.

(Hydroxy(phenyl)methyl)-2-methoxy-1,1,3,3-tetramethylisoindoline (9)



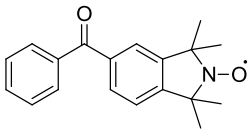
A solution of 5-bromo-2-methoxy-1,1,3,3-tetramethylisoindoline (**8**) (1.00 g, 3.52 mmol, 1.0 eq.) in THF (50 mL) was cooled to - 78 °C and placed under an inert atmosphere of argon. To this solution was added *n*-butyllithium (1.6 M in *n*-hexanes) (2.4 mL, 3.87 mmol, 1.1 eq.) dropwise. The reaction was then allowed to stir for 15 minutes, maintaining a constant temperature of reaction (- 78 ± 5 °C). A solution of benzaldehyde (1.08 mL, 10.56 mmol, 3.0 eq.) in THF (50 mL) was then added dropwise, maintaining a constant temperature of reaction (- 78 ± 5 °C), until the addition was complete. The reaction was then allowed to return to room temperature over two hours and then quenched by the addition of water (50 mL). The resulting mixture was extracted with dichloromethane (3 × 100 mL) and the combined organic extracts washed with a saturated solution of brine (50 mL), dried over anhydrous sodium sulphate and concentrated *in vacuo*. Purification via silica gel column chromatography (dichloromethane : diethyl ether; 19 : 1) afforded 5-(hydroxy(phenyl)methyl)-2-methoxy-1,1,3,3-tetramethylisoindoline (**9**) as a colourless oil (1.04 g, 95 % yield). R_f = 0.40, dichloromethane : diethyl ether; 19 : 1.^{1}H NMR (400 MHz $CDCl_3$): δ (ppm) = 7.42 – 7.35 (m, 4H, H_{arom}), 7.31 – 7.28 (m, 1H, H_{arom}), 7.21 (dd, *J* = 7.6, 1.6 Hz, 1H, H_{arom}), 7.19 (d, *J* = 1.6 Hz, 1H, H_{arom}), 7.06 (d, *J* = 7.6 Hz, 1H, H_{arom}), 5.86 – 5.85 (m, 1H, CH), 3.79 (s, 3H, OCH_3), 2.26 – 2.24 (m, 1H, OH), 1.44 (br s, 12H, 4×CH_3). ^{13}C NMR (100 MHz $CDCl_3$): δ (ppm) = 145.71, 144.85, 144.00, 143.14, 128.65, 127.72, 126.73, 125.95, 121.74, 119.81, 76.61, 67.30, 67.08, 65.65, 30.23, 30.23. HRMS (ESI) *m/z*: calculated for $C_{20}H_{26}NO_2$ $[M+H]^+$ 312.1958; found 312.1977.

5-Benzoyl-2-methoxy-1,1,3,3-tetramethylisoindoline (10)



To a solution of 5-(hydroxy(phenyl)methyl)-2-methoxy-1,1,3,3-tetramethylisoindoline (**9**) (910 mg, 2.92 mmol, 1.0 eq.) in dichloromethane (100 mL) was added pyridinium chlorochromate (756 mg, 3.51 mmol, 1.2 eq.). The reaction was maintained for 2.5 hours at room temperature. The reaction mixture was then filtered through celite, eluting with dichloromethane, and concentrated *in vacuo*. Purification via silica gel column chromatography (dichloromethane) afforded 5-benzoyl-2-methoxy-1,1,3,3-tetramethylisoindoline (**10**) as a white solid after extensive concentration *in vacuo* (850 mg, 94 % yield). M.p. 69 - 70 °C. R_f = 0.38, dichloromethane ^{1}H NMR (400 MHz $CDCl_3$): δ (ppm) = 7.82 (d, *J* = 7.6 Hz, 2H, H_{arom}), 7.68 (d, *J* = 8.0 Hz, 1H, H_{arom}), 7.61 (t, *J* = 7.6 Hz, 2H, H_{arom}), 7.51 (t, *J* = 7.6 Hz, 2H, H_{arom}), 7.20 (d, *J* = 8.0 Hz, 1H, H_{arom}), 3.82 (s, 3H, OCH_3), 1.49 (br s, 12H, 4×CH_3). ^{13}C NMR (100 MHz $CDCl_3$): δ (ppm) = 196.70, 150.35, 145.83, 138.05, 137.04, 132.41, 130.13, 130.05, 128.40, 123.52, 121.44, 67.39, 67.24, 65.69, 29.57, 25.22. HRMS (ESI) *m/z*: calculated for $C_{20}H_{24}NO_2$ $[M+H]^+$ 310.1802; found 310.1795. HRMS (ESI) *m/z*: calculated for $C_{20}H_{23}NO_2Na$ $[M+Na]^+$ 332.1621; found 332.1607.

5-Benzoyl-1,1,3,3-tetramethylisoindolin-2-yloxyl (11)

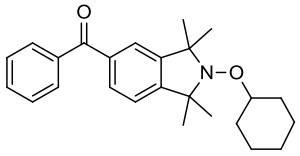


To a solution of 5-benzoyl-2-methoxy-1,1,3,3-tetramethylisoindoline (**10**) (600 mg, 1.94 mmol, 1.0 eq.) in dichloromethane (100 mL) was added *m*-CPBA (77 % purity) (957 mg, 4.27 mmol, 2.2 eq.) in portions. The reaction was maintained for one hour at room temperature. 2M sodium hydroxide (100 mL) was then added and the resulting mixture stirred vigorously for 15 minutes. The reaction mixture was then extracted with dichloromethane (3 × 100 mL). The combined organic extracts were then washed with water (50 mL) followed by a saturated solution of brine (50 mL), dried over anhydrous sodium sulphate and concentrated *in vacuo*. Purification via silica gel column chromatography (dichloromethane : diethyl ether; 19 : 1) followed by recrystallization from methanol afforded 5-benzoyl-1,1,3,3-tetramethylisoindolin-2-yloxyl (**11**) as small orange needles (526 mg, 92 % yield). M.p. 149 - 150 °C. R_f = 0.35, dichloromethane : diethyl ether; 19 : 1. ^{1}H NMR (400 MHz $CDCl_3$): δ (ppm) = 7.88 (br s, 2H, H_{arom}), 7.67 (t, *J* = 6.8 Hz, 1H, H_{arom}), 7.55 (br s, 1H, H_{arom}). HRMS (ESI) *m/z*: calculated for $C_{19}H_{21}NO_2$ $[M+H]^+$ 295.1567; found 295. 1566. HRMS (ESI) *m/z*: calculated for $C_{19}H_{20}NO_2Na$ $[M+Na]^+$ 317.1386; found 317.1388.

General procedure for the preparative scale generation and isolation of photoirradiation products 14, 16 and 17

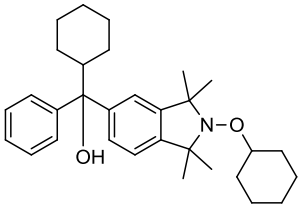
Two 10 mM solutions of 11 in cyclohexane (30 mg in 10 mL) were degassed with three freeze-pump-thaw cycles and bubbled with a stream of argon for 1 hour and sealed in quartz reaction vessels. One solution was irradiated with 350 nm light for 10 minutes to predominantly generate the intermediate **14** which was isolated by normal phase silica column chromatography (Et2O:Hexane, 1:2). The remaining solution was irradiated with 350 nm light for 30 minutes to generate the two products **16** and **17** concurrently, the two products were isolated using normal phase silica column chromatography (Et2O:Hexane, 1:2).

(2-(cyclohexyloxy)-1,1,3,3-tetramethylisoindolin-5-yl)(phenyl)methanone (**14**)



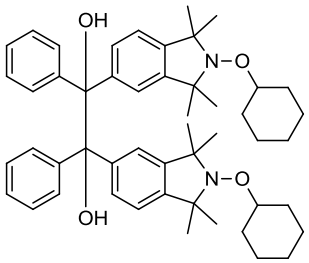
^{1}H NMR (400 MHz $CDCl_3$): δ (ppm) = 7.80 (dd, 2H, H_{arom}), 7.66 (dd, 1H, H_{arom}), 7.59 (t, 2H, H_{arom}), 7.48 (t, 2H, H_{arom}), 7.18 (d, 1H, H_{arom}), 3.71 (septet, 1H, $OC\underline{H}_1(CH_2)_2$), 2.10 (d, 2H, CH_2), 2.10 (d, 2H, CH_2), 1.78 (d, 2H, CH_2), 1.53 (d, 6H, CH_2), 1.38 (m, 6H, CH_3), 1.31 (m, 4H, CH_2). ^{13}C NMR (100 MHz $CDCl_3$): δ (ppm) = 196.63, 150.52, 145.93, 137.93, 136.77, 132.22, 129.98, 129.82, 128.23, 123.53, 121.41, 81.83, 67.52, 67.37, 32.50, 30.40, 25.94, 25.21, 24.49. HRMS (ESI) *m/z*: calculated for $C_{25}H_{31}NO_2$ $[M+H]^+$ 378.2427; found 378.2371.

Cyclohexyl(2-(cyclohexyloxy)-1,1,3,3-tetramethylisoindolin-5-yl)(phenyl)methanol (**16**)



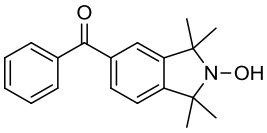
^{1}H NMR (400 MHz $CDCl_3$): δ (ppm) = 7.46 (d, 2H, H_{arom}), 7.29 (d, 2H, H_{arom}), 7.22 (m, 2H, H_{arom}), 7.17 (tt, 1H, H_{arom}), 6.97 (d, 1H, H_{arom}), 3.67 (septet, 1H, $OC\underline{H}_1(CH_2)_2$), 2.40 (tt, 1H, $Ar_2COHC\underline{H}_1(CH_2)_2$), 2.09 (d, 2H, CH_2), 2.03 (s, 1H, $Ar_2CO\underline{H}R_1(CH_2)_2$), 1.75 (m, 6H, CH_2), 1.45 (m, 8H, CH_2), 1.30 (m, 12H, CH_3), 1.10 (m, 4H, CH_2). HRMS (ESI) *m/z*: calculated for $C_{31}H_{43}NO_2$ $[M+H]^+$ 462.3366; found 462.3308.

1,2-bis(2-(cyclohexyloxy)-1,1,3,3-tetramethylisoindolin-5-yl)-1,2-diphenylethane-1,2-diol (**17**)



^{1}H NMR (400 MHz $CDCl_3$): δ (ppm) = 7.36 (s, 1H, H_{arom}), 7.30 (br s, 3H, H_{arom}), 7.19 (br s, 6H, H_{arom}), 7.12 (br s, 2H, H_{arom}), 6.98 (m, 2H, H_{arom}), 6.88 (d, 2H, H_{arom}), 3.64 (br s, 2H, $OC\underline{H}_1(CH_2)_2$), 2.98 (br s, 2H, $Ar_2CO\underline{H}R_1(CH_2)_2$), 2.04 (br s, 4H, CH_2), 1.76 (br s, 4H, CH_2), 1.53 (d, 2H, CH_2), 1.42 (s, 6H, CH_2), 1.24 (m, 24H, CH_3), 1.08 (m, 4H, CH_2). ^{13}C NMR (100 MHz $CDCl_3$): δ (ppm) = 146.46, 144.11, 143.39, 128.60, 127.97, 127.82, 127.25, 126.20, 125.78, 121.12, 120.53, 81.72, 80.53, 77.22, 67.41, 67.30, 67.08, 67.01, 45.94, 34.86, 32.54, 31.59, 30.26, 27.28, 26.91, 26.70, 26.51, 25.98, 25.28, 24.51, 14.14. HRMS (ESI) *m/z*: calculated for $C_{50}H_{64}N_2O_4$ $[(M/2)+H]^+$ 379.2511; found 379.2457.

Identification of (2-hydroxy-1,1,3,3-tetramethylisoindolin-5-yl)(phenyl)methanone (**12**)



The formation of hydroxyl amine **12** could be observed in the reaction mixture for the photolysis of **11** using LC-MS analysis and the method stated previously. The nitroxide had a typical elution time of 2.17 minutes and the hydroxyl amine species appeared at 1.87 minutes (See figure X below). The hydroxyl amine could be generated by treating **11** with the reducing agent phenylhydrazine, which produced a peak at the same retention with protonated and sodiated mass signals matching the hydroxylamine **12**. HRMS (ESI) *m/z*: calculated for $C_{19}H_{21}NO_2$ $[M+H]^+$ 296.1645; found 269.1639. HRMS (ESI) *m/z*: calculated for $C_{19}H_{21}NO_2Na$ $[M+Na]^+$ 318.1459; found 318.1457.

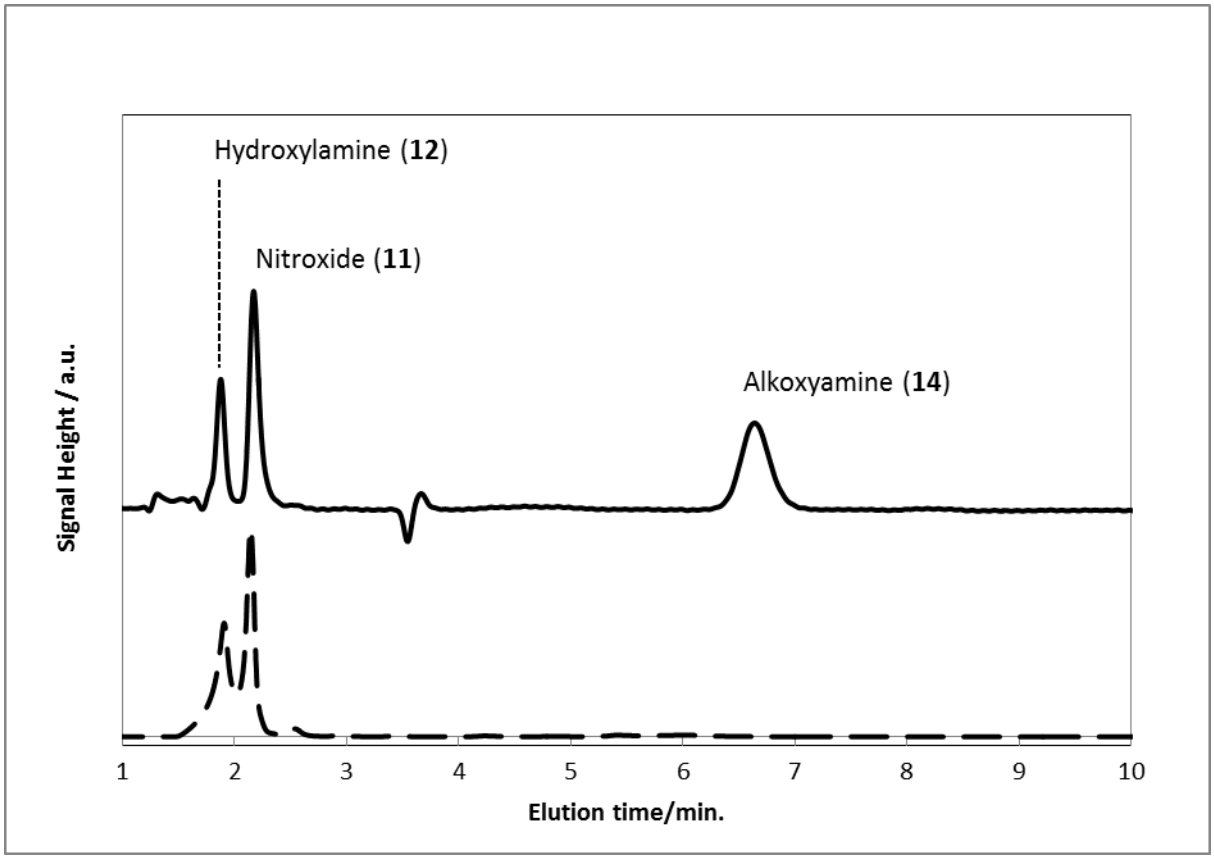


Figure S1: LC-MS chromatogram of products formed from **11** after 5 minutes of photolysis (solid line) and the products formed by treating **11** with a reducing agent phenylhydrazine (dashed line).

Spectral Data for Synthesised Compounds

NMR Spectra

Figure S2: ^{1}H NMR spectra of 5-bromo-2-methoxy-1,1,3,3-tetramethylisoindoline

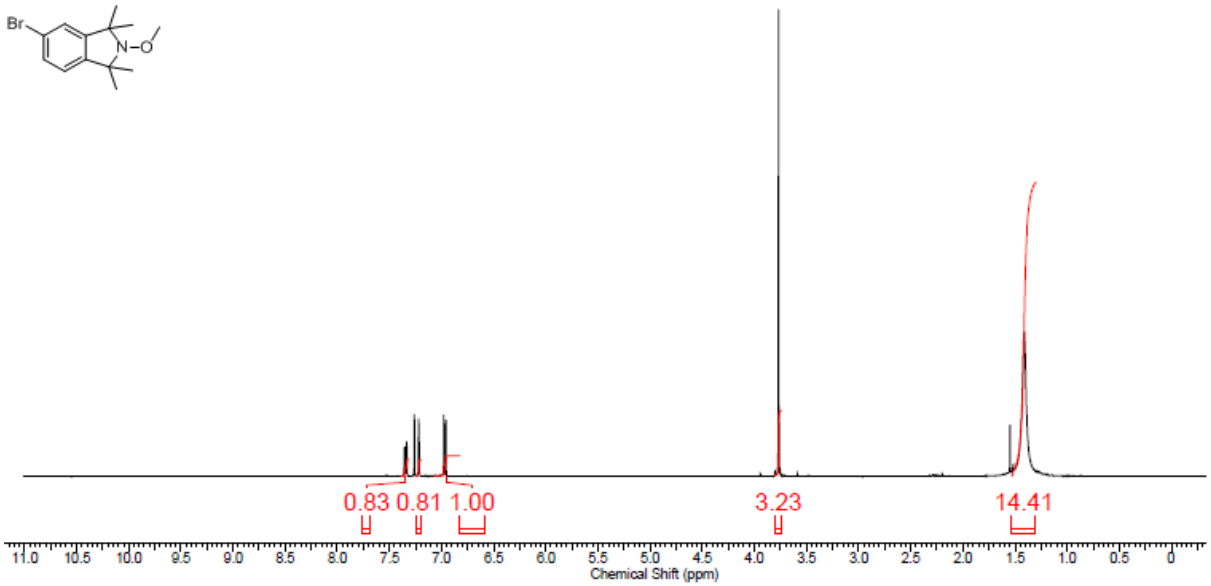


Figure S3: ^{1}H NMR spectra of 5-(hydroxy(phenyl)methyl)-2-methoxy-1,1,3,3-tetramethylisoindoline (**9**)

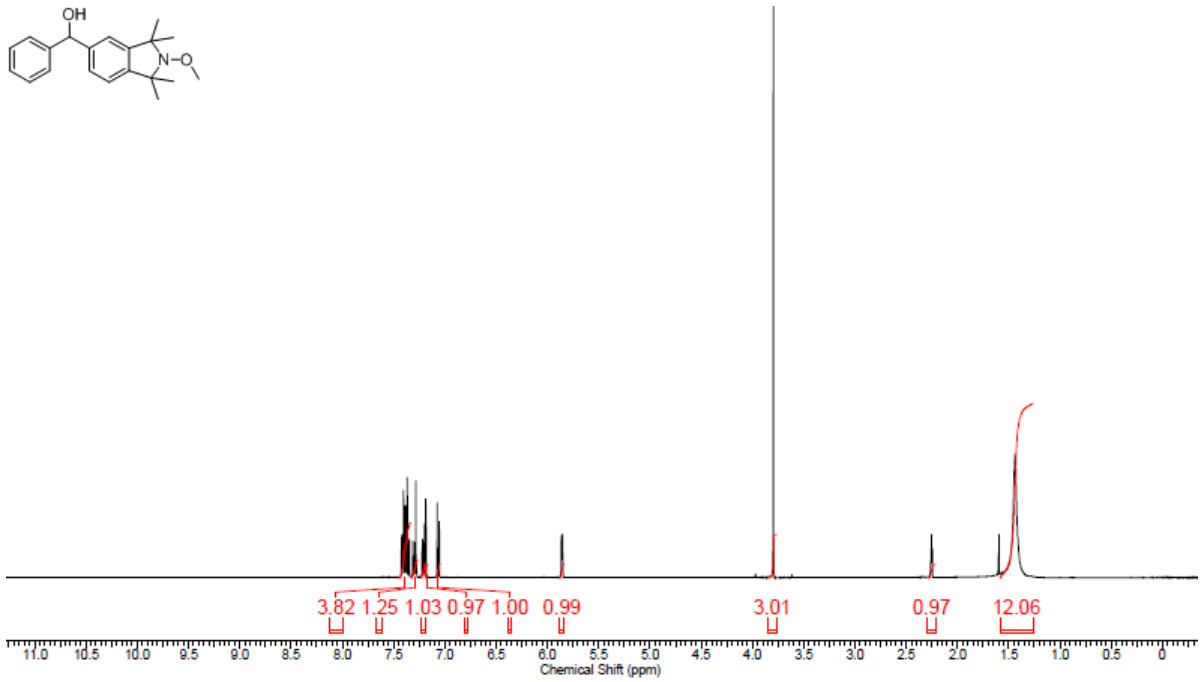


Figure S4: ^{13}C NMR spectra of 5-(hydroxy(phenyl)methyl)-2-methoxy-1,1,3,3-tetramethylisoindoline (**9**)

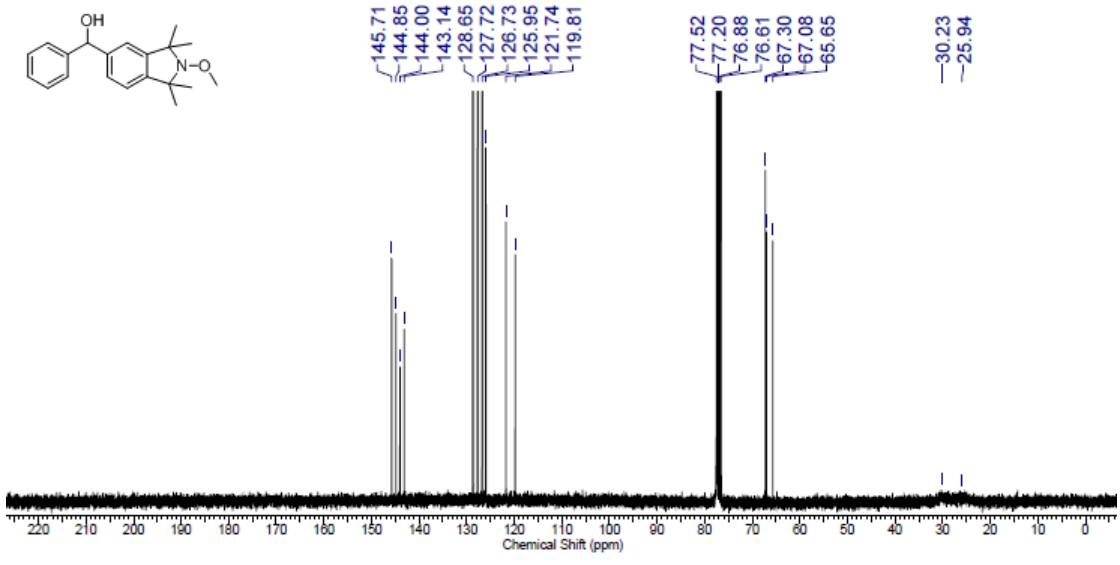


Figure S5: ^{1}H NMR spectra of 5-benzoyl-2-methoxy-1,1,3,3-tetramethylisoindoline (**10**)

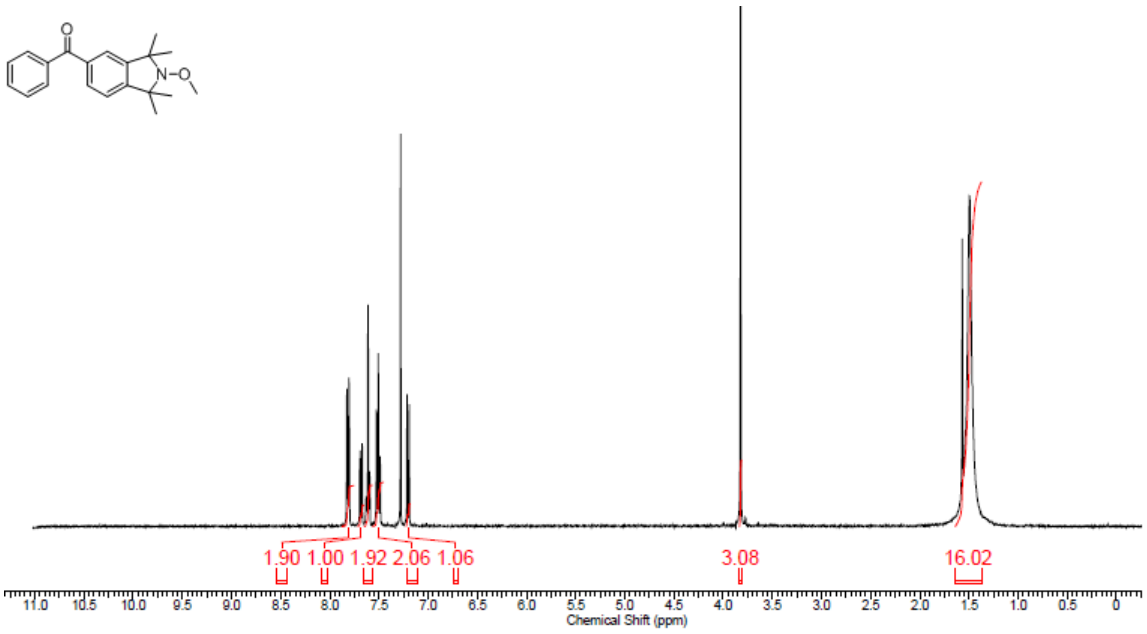


Figure S6: ^{13}C NMR spectra of 5-benzoyl-2-methoxy-1,1,3,3-tetramethylisoindoline (**10**)

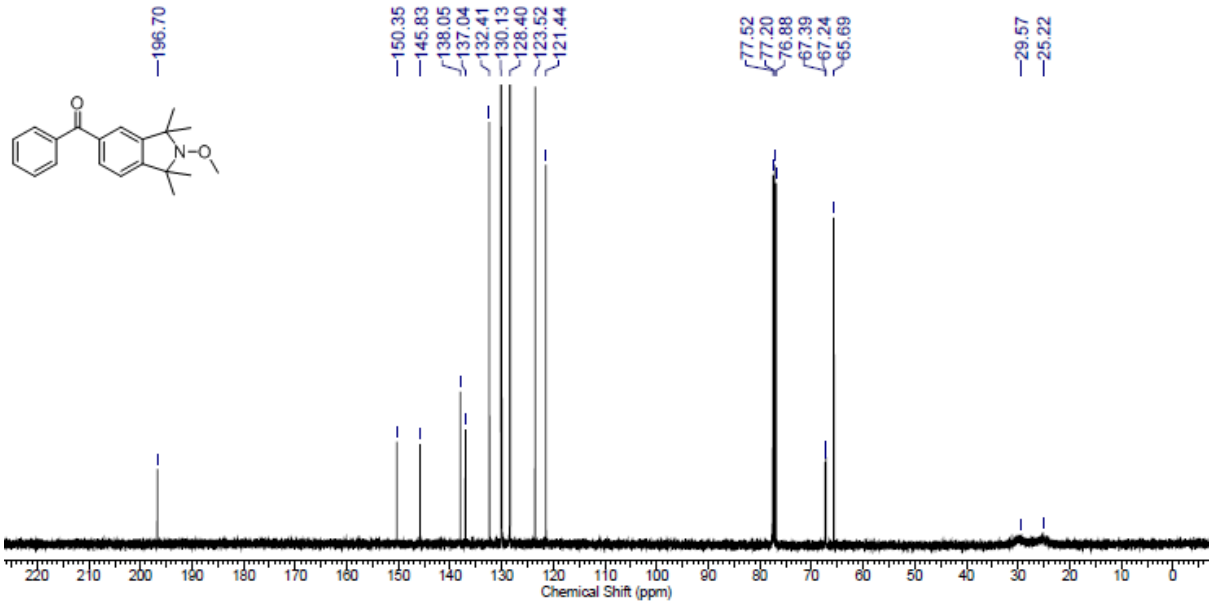


Figure S7: ^{1}H NMR spectra of 5-benzoyl-1,1,3,3-tetramethylisoindolin-2-yloxyl (**11**)

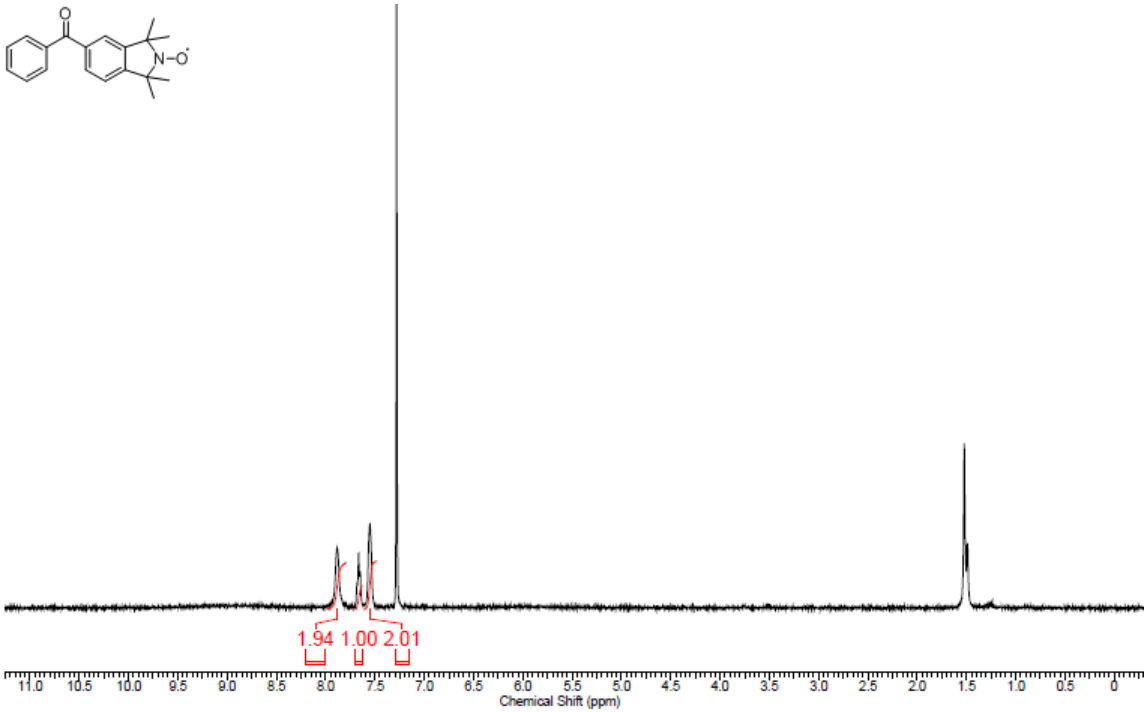


Figure S8: ^{1}H NMR spectra of 5-(hydroxy(phenyl)methyl)-2-methoxy-1,1,3,3-tetramethylisoindoline (**14**)

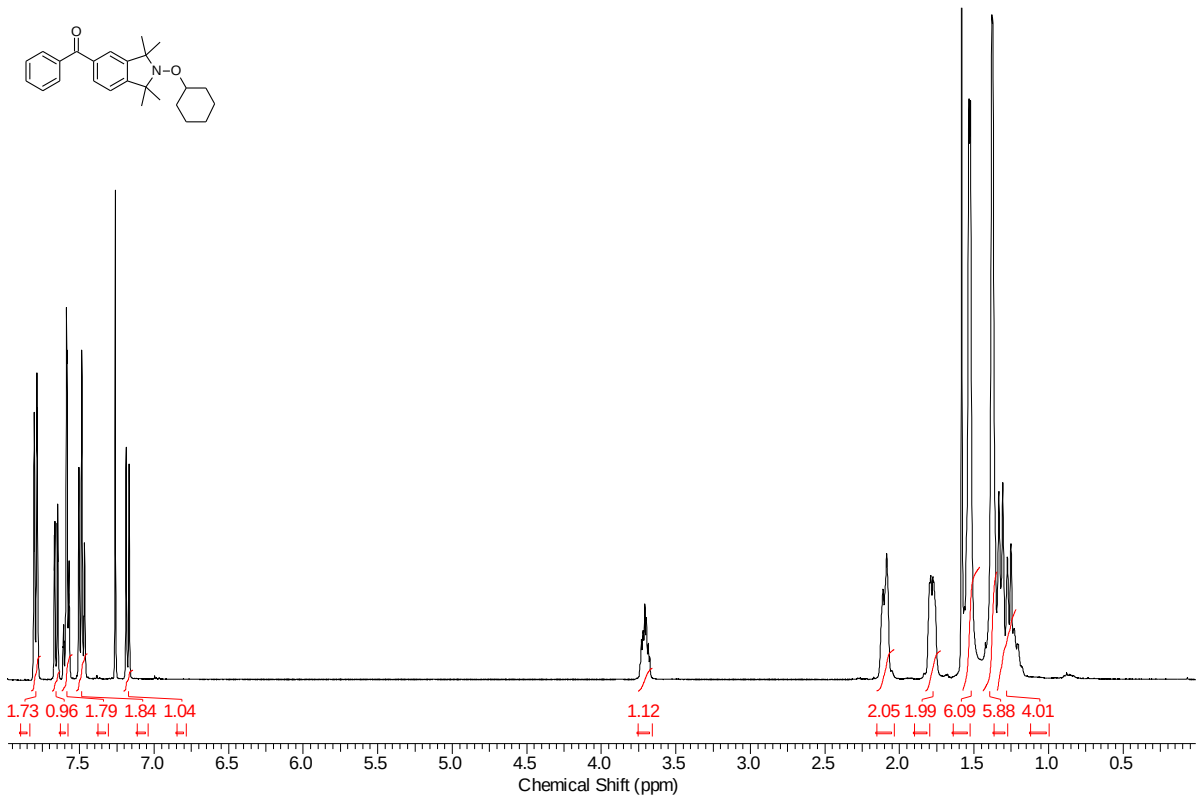


Figure S9: ^{13}C NMR spectra of 5-(hydroxy(phenyl)methyl)-2-methoxy-1,1,3,3-tetramethylisoindoline (**14**)

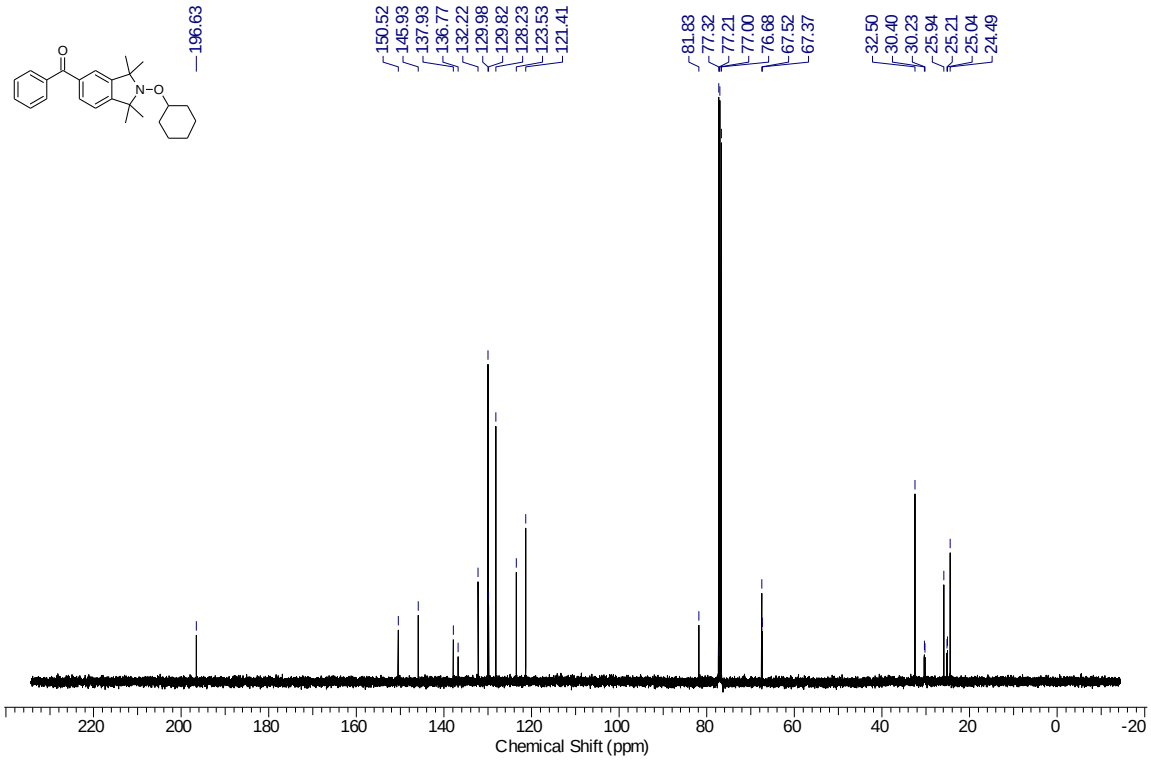


Figure S10: ^{1}H NMR spectra of 5-(hydroxy(phenyl)methyl)-2-methoxy-1,1,3,3-tetramethylisoindoline (**16**)

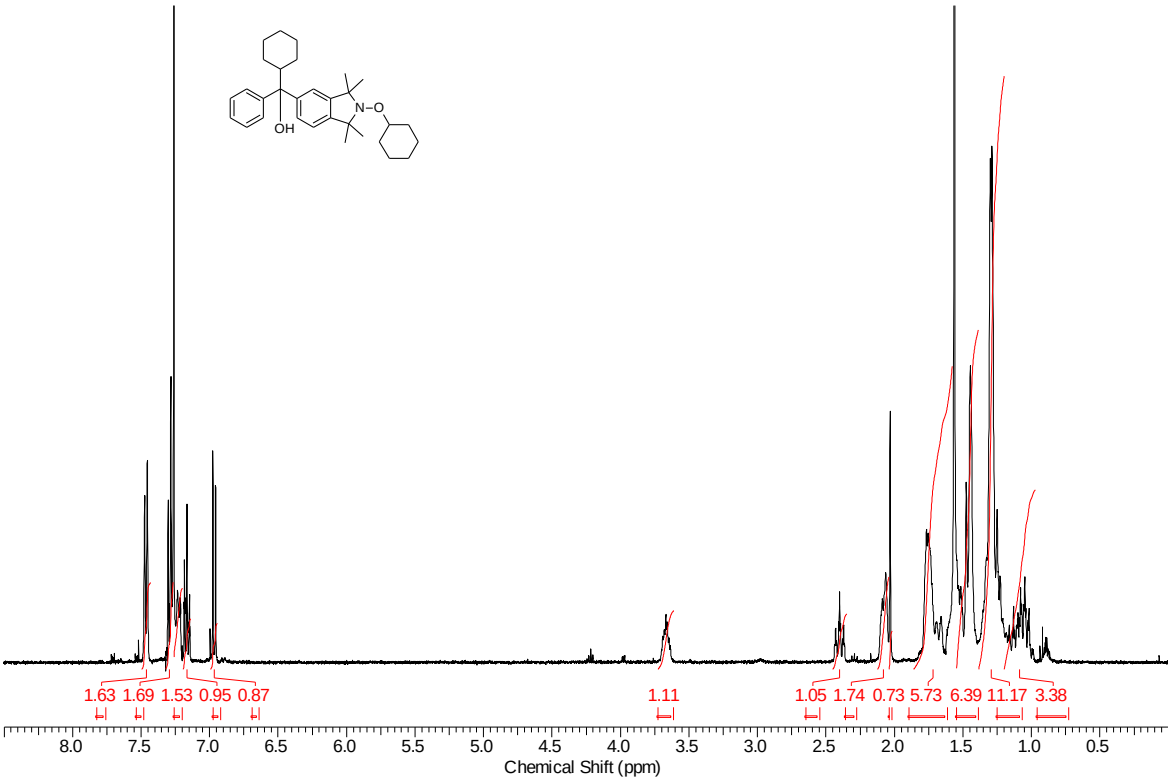


Figure S11: ^{1}H NMR spectra of 5-(hydroxy(phenyl)methyl)-2-methoxy-1,1,3,3-tetramethylisoindoline (**17**)

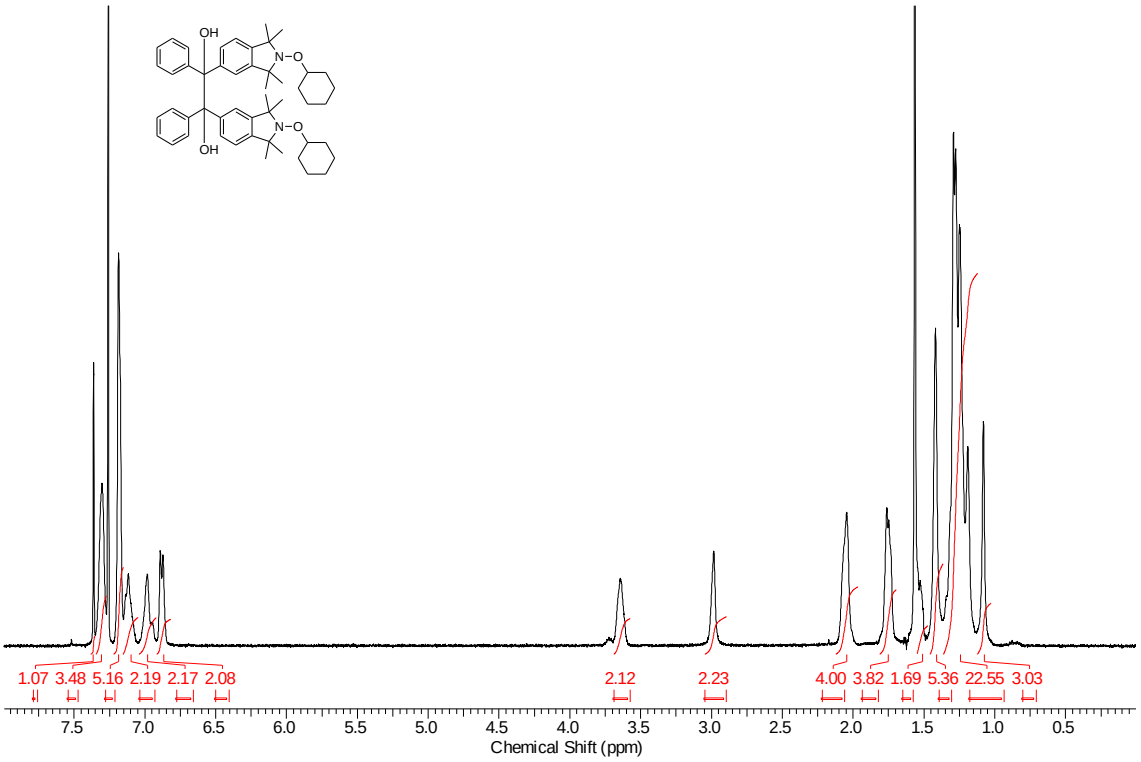
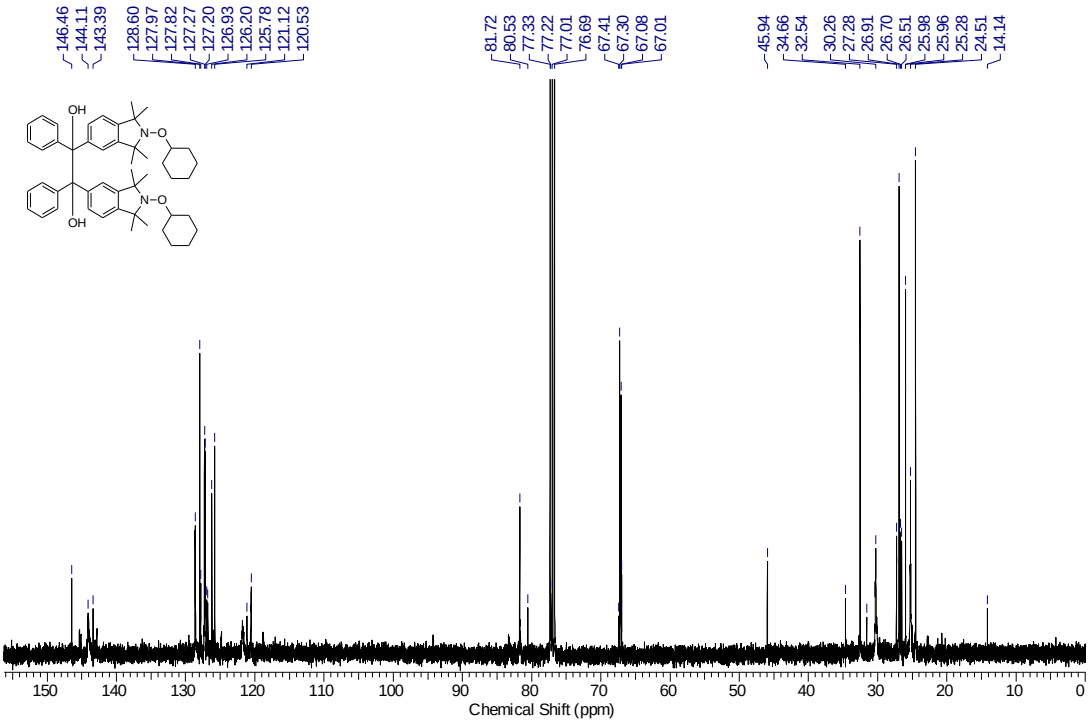
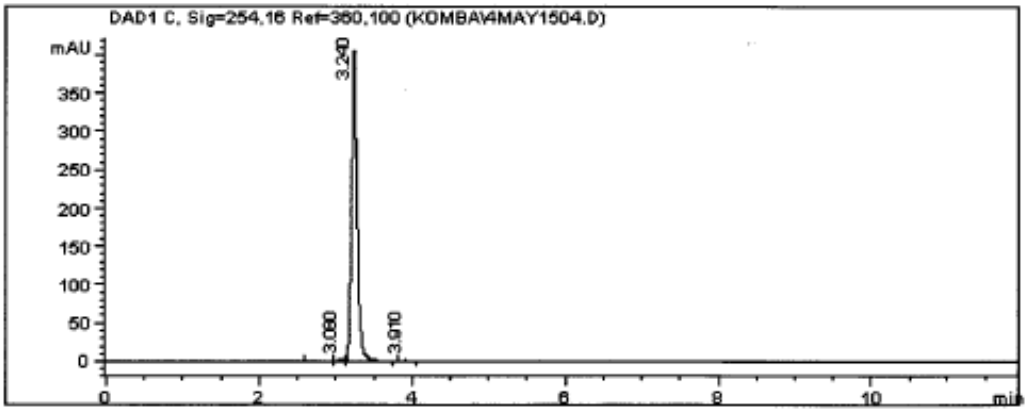


Figure S12: ^{13}C NMR spectra of 5-(hydroxy(phenyl)methyl)-2-methoxy-1,1,3,3-tetramethylisoindoline (**17**)



HPLC Data

Figure S12: HPLC trace of 5-(hydroxy(phenyl)methyl)-2-methoxy-1,1,3,3-tetramethylisoindoline (**9**)

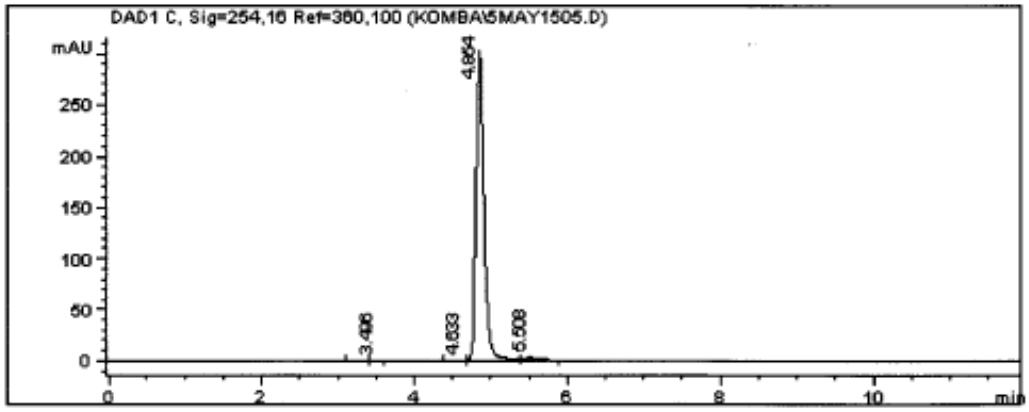


Peak No.	Time (Min)	Area	Area (%)
1	2.885	6.248	0.298
2	3.080	12.103	0.577
3	3.240	2070.949	98.764
4	3.910	7.571	0.361

Conditions and other information

Column: Agilent prep C18 Scala 4.6x150mm
injection size: 2uL

Figure 13: HPLC trace of 5-benzoyl-2-methoxy-1,1,3,3-tetramethylisoindoline (**10**)

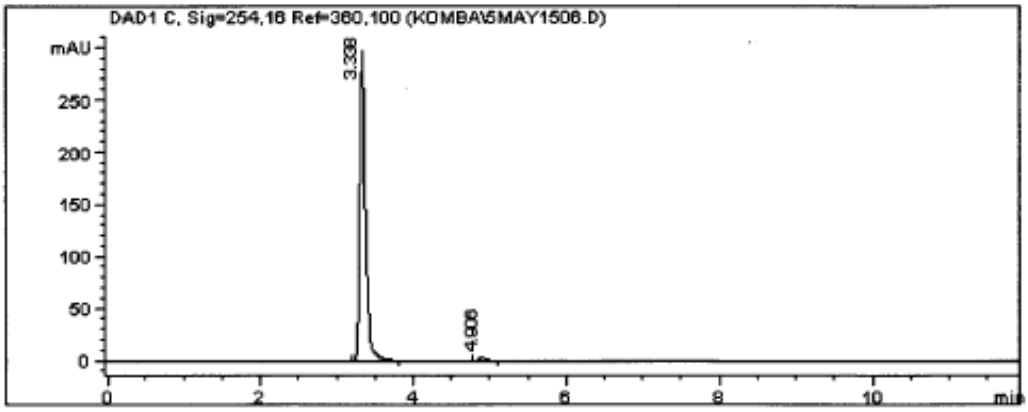


Peak No.	Time (Min)	Area	Area (%)
1	3.282	6.668	0.299
2	3.496	5.027	0.226
3	4.633	6.181	0.278
4	4.854	2178.161	97.824
5	5.508	30.580	1.373

Conditions and other information

Column: Agilent prep C18 Scala 4.6x150mm
injection size: 2uL

Figure S14: HPLC trace of 5-benzoyl-1,1,3,3-tetramethylisoindolin-2-yloxyl (**11**)



Peak No.	Time (Min)	Area	Area (%)
1	3.338	1557.471	98.874
2	4.906	17.733	1.126

Conditions and other information

Column: Agilent prep C18 Scala 4.6x150mm

injection size: 2uL

Figure S15: UV-Vis spectra of **11** in cyclohexane showing the π-π* absorption band at 250 nm (dashed line) and the n-π* absorption band at 347 nm (solid line).