Electronic Supplementary Material (ESI) for ChemComm.

Asymmetric Radical Alkylation of *N*-Sulfinimines under Visible Light Photocatalytic Conditions

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Electronic Supporting Information

for

Contents

1. General methods and materials

NMR spectra were acquired on a BRUKER AVANCE 300 MHz spectrometer running at 300 MHz for ^{1}H and 75 MHz for ^{13}C, and are internally referenced to residual solvent signals ($CDCl_3$ referenced at δ 7.26 ppm for ^{1}H NMR and δ 77.2 ppm for ^{13}C NMR, DMSO-d_6 referenced at δ 2.50 ppm for ^{1}H NMR, acetone-d_6 referenced at δ 2.05 ppm for ^{1}H NMR). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, dd = double doublet, ddd = double double doublet, dt = double triplet, t = triplet, td = triple doublet, tt = triple triplet, q = quartet, p = quintuplet, h = hextuplet, hept = heptuplet, m = multiplet), coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. The diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture through integration of diagnostic signals.

High-Resolution Mass Spectra (HRMS) were obtained on an Agilent Technologies 6120 Quadrupole LC/MS coupled with an SFC Agilent Technologies 1260 Infinity Series instrument for the MS (ESI) (Electrospray Ionization). MassWorks software version 4.0.0.0 (Cerno Bioscience) was used for the formula identification. MassWorks is an MS calibration software which calibrates isotope profiles to achieve high mass accuracy and enables elemental composition determination on conventional mass spectrometers of unit mass resolution allowing highly accurate comparisons between calibrated and theoretical spectra.

Optical rotations were measured on a Perkin-Elmer 241 MC Polarimeter and are reported as follows: $[\alpha]_D^{r.t.}$ (c in g/100 mL, solvent).

Cyclic Voltammetry (CV) experiments were recorded on an IVIUM Technologies CompactStat controlled by IviumSoft version 2.124 offering a compliance voltage of up to ± 100 V (available at the counter electrode), ± 10 V scan range and ± 1 A current range. HPLC grade DCM was used for electrochemical measurements. Tetra-n-butylammonium hexafluorophosphate (Fluorochem) was used as supporting electrolyte at 0.05 M concentration. A conventional three-electrode cell was used, containing a coiled Pt wire acting as counter electrode and a Ag/AgCl saturated solution (Metrohm) as reference electrode. All cyclic voltammetry experiments were performed using a glassy carbon working electrode (A = 0.071 cm^2) (Metrohm). Redox-active species were dissolved at 0.5 mM concentration, and these solutions were thoroughly purged with Ar and kept under an inert atmosphere throughout the measurements.

Emission intensities were recorded on a JASCO Spectrofluorometer FP-8600 equipped with a TC-815 Peltier thermostated single cell holder (water-cooled) controlled by Spectra Manager Version 2.10.01. DMSO was used for all luminescence quenching experiments. All $Ir(ppy)_3$ solutions were excited at 420 nm, observing the maximum emission peak at 518 nm. In a typical experiment, the appropriate amount of quencher would be added to the DMSO solution of $Ir(ppy)_3$ (30 μM) in a Teflon-top 10x10 mm precision cell made of Quartz SUPRASIL®. After degassing with Ar for 1 min, the emission spectra of the samples were collected.

UV-Visible spectra for determination of the quantum yield were recorded on an Agilent 8453 UV-visible Spectroscopy System controlled by UV-visible ChemStation Software Version B.02.01.

Commercial grade reagents and solvents were purchased from Sigma-Aldrich, Alfa Aesar, Fluorochem, TCI Chemicals and used as received without further purification unless otherwise stated. DCM, THF, acetonitrile and toluene were purified by passing through a Pure Solv™ column drying system from Innovative Technology, Inc. Anhydrous DMF and DMSO were acquired from commercial sources. Iridium (III) photocatalysts **3c**, **3d**, and **3e** are commercially available from Sigma-Aldrich, as well as ruthenium (II) photocatalyst **3a**. Iridium photocatalyst **3b** was purchased from TCI Chemicals. (*R*)-*p*-Toluenesulfinamide and (*R*)-2-methyl-2-propanesulfinamide are commercially available from Sigma-Aldrich. (*R*)-2,4,6-Triisopropylbenzenesulfinamide and (*S*)-2,4,6-trimethylbenzenesulfinamide are commercially available from Fluorochem. (*S*)-2-Methoxy-1-naphthalenesulfinamide was previously synthesized in our research group.[1]

Analytical TLC was performed using pre-coated aluminum-backed plates (Merck Kieselgel 60 F_{254}) and visualized by ultraviolet irradiation. Stain solutions are indicated in each case if employed, using heat as developing agent. Chromatographic purification of products was accomplished by flash chromatography (FC) using silica gel (Merck Geduran® Si 60) or porous silica gel (LSI Medience Corporation Iatrobeads 6RS-8060). Celite® 512 medium (Sigma-Aldrich) was used for filtration. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

A 23 W household light bulb was used as white light source. A custom made “light box” was used with 5 strips of blue LEDs (15 W, 3 W per strip) attached around a test tube rack (see Figure S1). A fan was used to maintain the temperature inside the “box” at room temperature.

Figure S1. Experimental setup employed during photoredox reactions.

2. Substrate synthesis

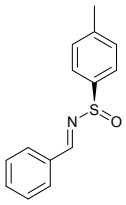
2.1. Synthesis of *N*-sulfinimines **1**

All *N*-sulfinimines were prepared following Davis' methodology except for **1b**, which was prepared following Ellman's procedure.[2]

General procedure:

A solution of the corresponding enantiopure sulfinamide (1.0 equiv) in DCM (0.05 M) was added to an oven-dried sealed tube equipped with a magnetic stir bar, followed by addition of aldehyde (1.0 equiv) and $Ti(OEt)_4$ (technical grade, 20% Ti, 4.0 equiv). After being refluxed overnight and monitored by TLC (ninhydrin stain solution), the mixture was cooled upon completion. Once at room temperature, the reaction mixture was quenched with several drops of a saturated solution of $NaHCO_3$. The resulting suspension was filtered through a plug of celite, and the filter cake was washed with DCM (2 x 10 mL). The filtrate was transferred to a separatory funnel where the organic layer was washed with water, extracted, dried with $MgSO_4$ and concentrated. The *N*-sulfinimines were purified by flash chromatography using silica gel.

(*R*,*E*)-*N*-Benzylidene-4-methylbenzenesulfinamide (1a)[2a]

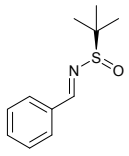


1a

The general procedure was followed with 155.2 mg of (*R*)-*p*-toluenesulfinamide (1.00 mmol), 102 μL of benzaldehyde (1.00 mmol) and 839 μL of $Ti(OEt)_4$ (4.00 mmol) in 20 mL of DCM. Column chromatography (4:1 cyclohexane:EtOAc) afforded **1a** (193.0 mg, 79% yield, white solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.75 (s, 1H), 7.86 – 7.84 (m, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.43 (m, 3H), 7.32 (d, *J* = 8.1 Hz, 2H), 2.40 (s, 3H).

(*R*,*E*)-*N*-Benzylidene-2-methylpropane-2-sulfinamide (1b)[2b]

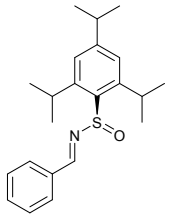


1b

The general procedure was followed with 121.2 mg of (*R*)-*tert*-butanesulfinamide (1.00 mmol), 102 μL of benzaldehyde (1.00 mmol) and 839 μL of $Ti(OEt)_4$ (4.00 mmol) in 20 mL of DCM. Column chromatography (4:1 cyclohexane:EtOAc) afforded **1b** (186.2 mg, 89% yield, yellow oil).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.59 (s, 1H), 7.87 – 7.84 (m, 2H), 7.53 – 7.45 (m, 3H), 1.27 (s, 9H).

(*R*,*E*)-*N*-Benzylidene-2,4,6-triisopropylbenzenesulfinamide (1c)[3a]

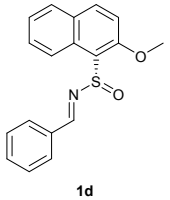


1c

The general procedure was followed with 53.5 mg of (*R*)-2,4,6-triisopropylbenzenesulfinamide (0.20 mmol), 20 μL of benzaldehyde (0.20 mmol) and 168 μL of $Ti(OEt)_4$ (0.80 mmol) in 4 mL of DCM. Column chromatography (4:1 cyclohexane:EtOAc) afforded **1c** (64.4 mg, 90% yield, white solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.86 (s, 1H), 7.85 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.52 – 7.41 (m, 3H), 7.09 (s, 2H), 3.86 (hept, *J* = 6.8 Hz, 2H), 2.89 (hept, *J* = 6.9 Hz, 1H), 1.30 (d, *J* = 6.8 Hz, 6H), 1.25 (d, *J* = 6.9 Hz, 6H), 1.15 (d, *J* = 6.8 Hz, 6H).

(*S*,*E*)-*N*-Benzylidene-2-methoxynaphthalene-1-sulfinamide (1d)[4]

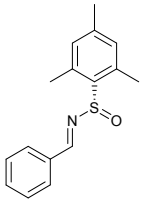


1d

The general procedure was followed with 66.4 mg of (*S*)-2-methoxy-1-naphthalenesulfinamide (0.30 mmol), 30 μL of benzaldehyde (0.30 mmol) and 252 μL of $Ti(OEt)_4$ (1.20 mmol) in 6 mL of DCM. Column chromatography (4:1 cyclohexane:EtOAc) afforded **1d** (55.0 mg, 59% yield, white solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.05 (s, 1H), 8.59 (d, *J* = 8.7 Hz, 1H), 7.98 (d, *J* = 9.1 Hz, 1H), 7.89 – 7.85 (m, 2H), 7.83 – 7.79 (m, 1H), 7.53 – 7.35 (m, 5H), 7.29 (d, *J* = 9.2 Hz, 1H), 3.97 (s, 3H).

(*S*,*E*)-*N*-Benzylidene-2,4,6-trimethylbenzenesulfinamide (1e)[3]

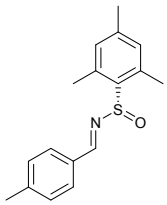


1e

The general procedure was followed with 183.3 mg of (*S*)-2,4,6-trimethylbenzenesulfinamide (1.00 mmol), 102 μL of benzaldehyde (1.00 mmol) and 839 μL of $Ti(OEt)_4$ (4.00 mmol) in 20 mL of DCM. Column chromatography (4:1 cyclohexane:EtOAc) afforded **1e** (231.5 mg, 85% yield, white solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.85 (s, 1H), 7.85 – 7.83 (m, 2H), 7.51 – 7.40 (m, 3H), 6.85 (s, 2H), 2.51 (s, 6H), 2.27 (s, 3H).

(*S*,*E*)-2,4,6-Trimethyl-*N*-(4-methylbenzylidene)benzenesulfinamide (1f)[5]

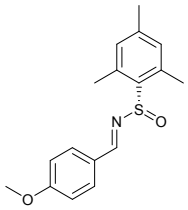


1f

The general procedure was followed with 64.1 mg of (*S*)-2,4,6-trimethylbenzenesulfinamide (0.35 mmol), 41 μL of 4-methylbenzaldehyde (0.35 mmol) and 294 μL of $Ti(OEt)_4$ (1.40 mmol) in 7 mL of DCM. Column chromatography (4:1 cyclohexane:EtOAc) afforded **1f** (68.0 mg, 68% yield, white solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.79 (s, 1H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.84 (s, 2H), 2.49 (s, 6H), 2.39 (s, 3H), 2.27 (s, 3H).

(*S*,*E*)-*N*-(4-Methoxybenzylidene)-2,4,6-trimethylbenzenesulfinamide (1g)[3b,6]

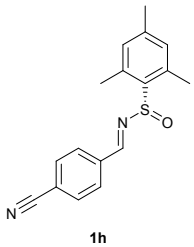


1g

The general procedure was followed with 91.6 mg of (*S*)-2,4,6-trimethylbenzenesulfinamide (0.50 mmol), 61 μL of 4-methoxybenzaldehyde (0.50 mmol) and 419 μL of $Ti(OEt)_4$ (2.00 mmol) in 10 mL of DCM. Column chromatography (4:1 cyclohexane:EtOAc) afforded **1g** (110.8 mg, 74% yield, white solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.75 (s, 1H), 7.80 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.85 (s, 2H), 3.85 (s, 3H), 2.50 (s, 6H), 2.28 (s, 3H).

(*S*,*E*)-*N*-(4-Cyanobenzylidene)-2,4,6-trimethylbenzenesulfinamide (1h)

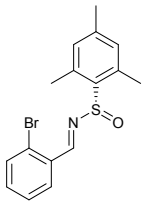


1h

The general procedure was followed with 91.6 mg of (*S*)-2,4,6-trimethylbenzenesulfinamide (0.50 mmol), 81.5 mg of 4-formylbenzonitrile (0.50 mmol) and 419 μL of $Ti(OEt)_4$ (2.00 mmol) in 10 mL of DCM. Column chromatography (4:1 cyclohexane:EtOAc) afforded **1h** (115.6 mg, 78% yield, light brown solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.84 (s, 1H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 6.86 (s, 2H), 2.47 (s, 6H), 2.27 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 159.8, 142.2, 138.6, 137.5, 134.8, 132.8, 131.1, 129.9, 118.2, 115.7, 21.3, 19.0. **HRMS calculated for $C_{17}H_{17}N_2OS$ [M+H]$^+$**: 297.1056, found: 297.1093. $[\alpha]_D^{20}$ = 78.7 (c = 0.91, $CHCl_3$).

(*S*,*E*)-*N*-(2-Bromobenzylidene)-2,4,6-trimethylbenzenesulfinamide (1i)

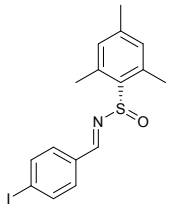


1i

The general procedure was followed with 73.3 mg of (*S*)-2,4,6-trimethylbenzenesulfinamide (0.40 mmol), 47 μL of 2-bromobenzaldehyde (0.40 mmol) and 335 μL of $Ti(OEt)_4$ (1.60 mmol) in 8 mL of DCM. Column chromatography (4:1 cyclohexane:EtOAc) afforded **1i** (112.7 mg, 80% yield, yellow solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.26 (s, 1H), 8.01 – 7.98 (m, 1H), 7.34 – 7.60 (m, 1H), 7.33 – 7.30 (m, 2H), 6.85 (s, 2H), 2.52 (s, 6H), 2.27 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 160.8, 141.8, 138.5, 135.1, 133.5, 133.3, 132.8, 130.9, 129.9, 127.7, 126.3, 21.2, 18.2. **HRMS calculated for $C_{16}H_{17}BrNOS$ [M+H]$^+$**: 350.0209, found: 350.0202. $[\alpha]_D^{20}$ = 236.5 (c = 1.44, $CHCl_3$).

(*S*,*E*)-*N*-(4-Iodobenzylidene)-2,4,6-trimethylbenzenesulfinamide (1j)

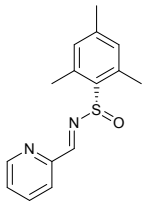


1j

The general procedure was followed with 73.3 mg of (*S*)-2,4,6-trimethylbenzenesulfinamide (0.40 mmol), 92.8 mg of 4-iodobenzaldehyde (0.40 mmol) and 335 μL of $Ti(OEt)_4$ (1.60 mmol) in 8 mL of DCM. Column chromatography (4:1 cyclohexane:EtOAc) afforded **1j** (124.6 mg, 78% yield, light brown solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.75 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 6.86 (s, 2H), 2.48 (s, 6H), 2.28 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 160.8, 142.0, 138.6, 138.4, 135.3, 133.4, 131.0, 130.9, 100.0, 21.3, 19.0. **HRMS calculated for $C_{16}H_{17}INOS$ [M+H]$^+$**: 398.0070, found: 398.0099. $[\alpha]_D^{20}$ = 35.3 (c = 0.34, $CHCl_3$).

(*S*,*E*)-2,4,6-Trimethyl-*N*-(pyridin-2-ylmethylene)benzenesulfinamide (1k)[6]

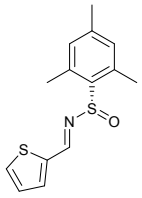


1k

The general procedure was followed with 73.3 mg of (*S*)-2,4,6-trimethylbenzenesulfinamide (0.40 mmol), 38 μL of 2-pyridinecarboxaldehyde (0.40 mmol) and 335 μL of $Ti(OEt)_4$ (1.60 mmol) in 8 mL of DCM. Column chromatography (4:1 cyclohexane:EtOAc) afforded **1k** (61.6 mg, 56% yield, orange solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.92 (s, 1H), 8.72 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.96 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.76 (td, *J* = 7.7, 1.7 Hz, 1H), 7.36 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 6.84 (s, 2H), 2.49 (s, 6H), 2.25 (s, 3H).

(*S*,*E*)-2,4,6-Trimethyl-*N*-(thien-2-ylmethylene)benzenesulfinamide (1l)



1l

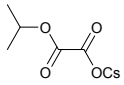
The general procedure was followed with 27.5 mg of (*S*)-2,4,6-trimethylbenzenesulfinamide (0.15 mmol), 14 μL of thiophene-2-carbaldehyde (0.15 mmol) and 126 μL of $Ti(OEt)_4$ (0.60 mmol) in 3 mL of DCM. Column chromatography (4:1 cyclohexane:EtOAc) afforded **1l** (35.0 mg, 84% yield, light brown solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.92 (s, 1H), 7.59 – 7.56 (m, 2H), 7.14 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.85 (s, 2H), 2.50 (s, 6H), 2.27 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 154.8, 141.8, 140.2, 138.7, 135.6, 134.0, 132.7, 130.9, 128.2, 21.2, 19.0. **HRMS calculated for $C_{14}H_{16}NOS_2$ [M+H]$^+$**: 278.0668, found: 278.0655. $[\alpha]_D^{20}$ = -28.5 (c = 1.37, $CHCl_3$).

2.2. Synthesis of radical precursors **2**

All radical precursors were prepared according to previously described methodologies in the literature.[7]

Cesium 2-isopropoxy-2-oxoacetate (2b)[7a]



2b

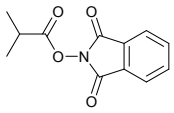
2-Isopropanol (1.5 mL, 20 mmol, 1.0 equiv) was dissolved in 40 mL of THF (0.5 M). Triethylamine (2.9 mL, 21 mmol, 1.05 equiv) and 4-dimethylaminopyridine (DMAP, 61 mg, 0.5 mmol, 0.025 equiv) were successively added, followed by drop-wise addition of methyl chloro(oxo)acetate (1.9 mL, 21 mmol, 1.05 equiv). The reaction mixture was stirred for 1 h at room temperature, then quenched with sat. brine (50 mL). The layers were separated and the organic extracts were washed again with sat. brine:water 1:1 (50 mL). The organic extracts were then treated with 1 M $CsOH_{(aq)}$ (19 mL, 19 mmol, 0.95 equiv), and the mixture was shaken until the intermediate methyl oxalate was consumed (< 5 min, judged by TLC). *n*-Hexane (75 mL) was added, and the aqueous phase was collected. The organic extracts were washed with a second portion of water (10 mL), and the combined aqueous phases were concentrated under reduced pressure to give **2b** (4.30 g, 83% yield, orange solid).

^{1}H NMR (300 MHz, DMSO-d_6): δ 4.88 (hept, *J* = 6.3, 1H), 1.19 (d, *J* = 6.2, 6H).

2.2.1. Synthesis of *N*-acyloxyphthalimides

Over a solution of alkyl carboxylic acid (1.0 equiv.) and *N*-hydroxyphthalimide (NHP, 1.1 equiv.) in DCM (0.22 M), *N*,*N'*-dicylcohexylcarbodiimide (DCC, 1.0 equiv.) was added at 0 ºC. The reaction mixture was stirred at the same temperature for 30 min and continued stirring at room temperature until complete consumption of the alkyl carboxylic acid (followed by ^{1}H NMR). The resulting suspension was filtered through a plug of celite and the filter cake was washed with DCM (2 x 20 mL). The filtrate was concentrated, and the *N*-acyloxyphthalimides were purified by flash chromatography using silica gel.

1,3-Dioxoisoindolin-2-yl isobutyrate (2c)[7b]

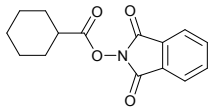


2c

The general procedure was followed with 0.95 mL of isobutyric acid (11 mmol), 1.96 g of NHP (12 mmol) and 2.27 g of DCC (11 mmol) in 50 mL of DCM. Following 13 h, the reaction mixture was filtered through celite, and column chromatography (9:1 cyclohexane:EtOAc) afforded **2c** (1.84 g, 72% yield, white solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 – 7.82 (m, 2H), 7.79 – 7.73 (m, 2H), 2.94 (hept, *J* = 7.0 Hz, 1H), 1.36 (d, *J* = 7.0 Hz, 6H).

1,3-Dioxoisoindolin-2-yl cyclohexanecarboxylate (2d)[7b]

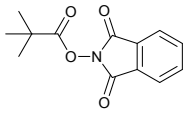


2d

The general procedure was followed with 0.94 g of cyclohexanecarboxylic acid (7.3 mmol), 1.31 g of NHP (8.0 mmol) and 1.51 g of DCC (7.3 mmol) in 35 mL of DCM. Following 13 h, the reaction mixture was filtered through celite, and column chromatography (14:1 *n*-pentane:EtOAc) afforded **2d** (1.22 g, 61% yield, white solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 – 7.70 (m, 2H), 7.68 – 7.64 (m, 2H), 2.62 (tt, *J* = 10.8, 3.7 Hz, 1H), 1.97 (dd, *J* = 13.5, 3.8 Hz, 2H), 1.73 – 1.68 (m, 2H), 1.58 - 1.51 (m, 3H), 1.31 – 1.12 (m, 3H).

1,3-Dioxoisoindolin-2-yl pivalate (2e)[7b]

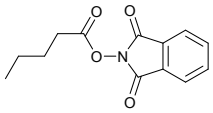


2e

The general procedure was followed with 2.04 g of pivalic acid (20 mmol), 3.59 g of NHP (22 mmol) and 4.13 g of DCC (20 mmol) in 90 mL of DCM. Following 24 h, the reaction mixture was filtered through celite, and column chromatography (9:1 cyclohexane:EtOAc) afforded **2e** (2.91 g, 59% yield, white solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 – 7.85 (m, 2H), 7.81 – 7.76 (m, 2H), 1.44 (s, 9H).

1,3-Dioxoisoindolin-2-yl pentanoate (2f)[8]

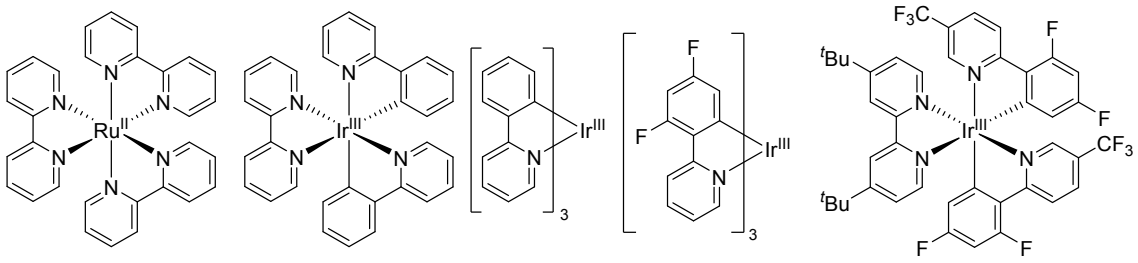


2f

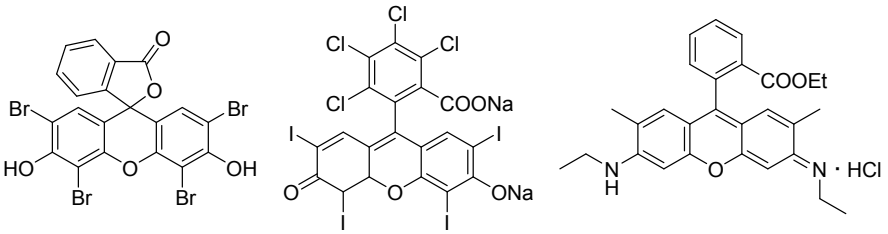
The general procedure was followed with 2.2 mL of pentanoic acid (20 mmol), 3.59 g of NHP (22 mmol) and 4.13 g of DCC (20 mmol) in 90 mL of DCM. Following 24 h, the reaction mixture was filtered through celite, and column chromatography (9:1 cyclohexane:EtOAc) afforded **2f** (3.42 g, 69% yield, white solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 – 7.86 (m, 2H), 7.82 – 7.76 (m, 2H), 2.67 (t, *J* = 7.5 Hz, 2H), 1.78 (p, *J* = 7.6 Hz, 2H), 1.48 (h, *J* = 7.7 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H).

3. Table of photocatalysts (3) used in Table 1



$[Ru(bpy)_3]^{2+}$ **3a** | $[Ir(ppy)_2(bpy)]^+$ **3b** | $Ir(ppy)_3$ **3c** | $Ir(dFppy)_3$ **3d** | $[Ir\{dF(CF_3)ppy\}_2(dtbpy)]^+$ **3e**



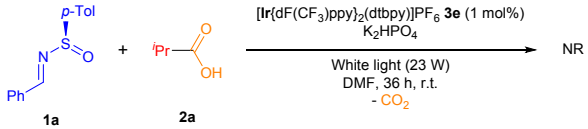
Eosin Y **3f** | Rose Bengal **3g** | Rhodamine 6G **3h**

4. Experimental procedure for photocatalytic alkylations of *N*-sulfinimines

4.1. Initial trials for decarboxylative additions to *N*-sulfinimines

4.1.1. Reaction with carboxylic acid

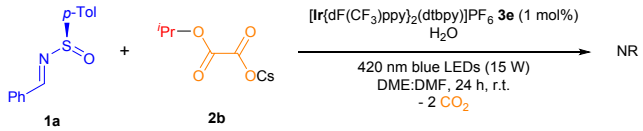
The reaction was performed following MacMillan's procedure.[9]



A dry vial equipped with a magnetic stir bar was charged with $[Ir\{dF(CF_3)ppy\}_2(dtbpy)]PF_6$ **3e** (2 μmol, 0.01 equiv.), (*R*)-*N*-sulfinimine **1a** (0.2 mmol, 1.0 equiv.), isobutyric acid **2a** (0.2 mmol, 1.0 equiv.), K_2HPO_4 (0.24 mmol, 1.2 equiv.), and 0.5 mL of DMF (0.4 M). Evacuation of the sealed vial followed by refill with N_2 was conducted three times at room temperature. The reaction mixture was irradiated (23 W fluorescent lamp, approximate distance was 2 cm from the vial) for 36 h at room temperature. The crude was concentrated and directly analyzed by ^1H NMR spectroscopy, but no reaction was observed.

4.1.2. Reaction with isopropyl cesium oxalate

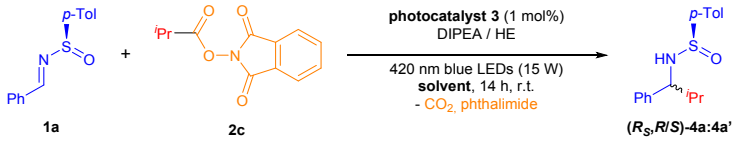
The reaction was performed following Overman's procedure.[7a]



A dry vial equipped with a magnetic stir bar was charged with [Ir{dF(CF_3)ppy}$_2$(dtbpy)]PF_6 **3e** (2.5 μmol, 0.01 equiv.), (*R*)-*N*-sulfinimine **1a** (0.25 mmol, 1.0 equiv.), cesium 2-isopropoxy-2-oxoacetate **2b** (0.28 mmol, 1.1 equiv.) and 2.5 mL of a 3:1 mixture of DME:DMF (DME was previously distilled) (0.1 M), followed by addition of water (2.5 mmol, 10.0 equiv.). Evacuation of the sealed vial followed by refill with N_2 was conducted three times at room temperature. The reaction mixture was irradiated in the "light-box" for 24 h at room temperature. The crude was concentrated and directly analyzed by ^{1}H NMR spectroscopy, but no reaction was observed.

4.2. Development of the asymmetric radical alkylation of *N*-sulfinimines

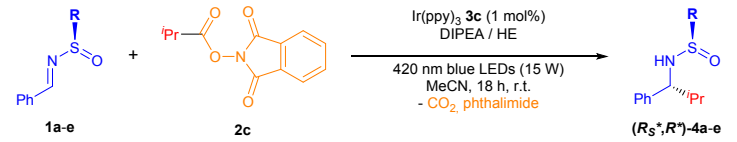
4.2.1. Catalyst and solvent screening



A dry vial equipped with a magnetic stir bar was charged with the corresponding photocatalyst (**3a-h**, 1.0 μmol, 0.01 equiv.), (*R*)-*N*-sulfinimine **1a** (0.15 mmol, 1.5 equiv.), 1,3-dioxoisoindolin-2-yl isobutyrate **2c** (0.10 mmol, 1.0 equiv.), DIPEA (0.2 mmol, 2.0 equiv.), Hantzsch ester (0.15 mmol, 1.5 equiv.) and 1.0 mL of the corresponding solvent (0.1 M). Evacuation of the sealed vial followed by refill with N_2 was conducted three times at room temperature. Extra-precautions were taken with volatile solvents. The reaction mixture was irradiated in the "light-box" for 14 h at room temperature. The crude was concentrated and directly analyzed by ^{1}H NMR spectroscopy.

3c and MeCN were selected as optimal photocatalyst and solvent respectively. At this point, we observed complete conversion in our reaction with 1.5 equiv. of (*R*)-*N*-sulfinimine **1a** and 1.0 equiv. of 1,3-dioxoisoindolin-2-yl isobutyrate **2c**. We established the more expensive substrate **1a** as limiting reagent by reversing the stoichiometric ratio to 1.0 equiv. of **1a** and 1.5 equiv. of **2c**, while still achieving full conversion.

4.2.2. Chiral auxiliary screening

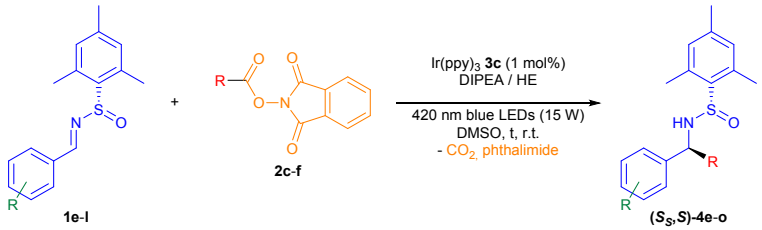


A dry vial equipped with a magnetic stir bar was charged with $Ir(ppy)_3$ **3c** (1.0 μmol, 0.01 equiv.), the corresponding enantiopure *N*-sulfinimine (**1a**-**e**, 0.10 mmol, 1.0 equiv.), 1,3-

dioxoisoindolin-2-yl isobutyrate **2c** (0.15 mmol, 1.5 equiv.), DIPEA (0.2 mmol, 2.0 equiv.), Hantzsch ester (0.15 mmol, 1.5 equiv.) and 1.0 mL of MeCN (0.1 M). Evacuation of the sealed vial followed by refill with N_2 was conducted three times at room temperature. The reaction mixture was irradiated in the "light-box" for 18 h at room temperature. The crude was concentrated and directly analyzed by ^{1}H NMR spectroscopy.

The reaction mixture was transferred with 20 mL of $CHCl_3$ to a separatory funnel where the organic layer was washed with $NH_4OH_{(aq)}$ 25% (3 x 10 mL), dried with $MgSO_4$ and concentrated. Column chromatography using porous silica gel (Iatrobeads) (19:1 cyclohexane:EtOAc) delivered the single diastereoisomer **4e** (10.5 mg, 33% yield, white solid). Isolation of products **4a** and **4c** was also attempted (see section 4.3. for more information).

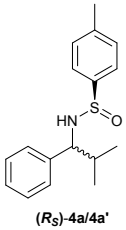
4.3. Asymmetric radical alkylation of *N*-sulfinimines



General procedure:

A dry vial equipped with a magnetic stir bar was charged with $Ir(ppy)_3$ **3c** (1.0 μmol, 0.01 equiv.), the corresponding enantiopure (*S*)-*N*-sulfinimine (**1e-l**, 0.10 mmol, 1.0 equiv.), the corresponding radical precursor (**2c-f**, 0.15 mmol, 1.5 equiv.), DIPEA (0.3 mmol, 3.0 equiv.), Hantzsch ester (0.05 mmol, 0.5 equiv.) and 1.0 mL of DMSO (0.1 M). Evacuation of the sealed vial followed by refill with N_2 was conducted three times at room temperature. The reaction mixture was irradiated in the "light-box" at room temperature. Reaction time is indicated in each case. The reaction mixture was transferred with 20 mL of $CHCl_3$ to a separatory funnel where the organic layer was washed with $NH_4OH_{(aq)}$ 25% (3 x 10 mL), dried with $MgSO_4$ and concentrated. The sulfinamides were purified by column chromatography using silica gel (Iatrobeads).

(*R*)-4-Methyl-*N*-(2-methyl-1-phenylpropyl)benzenesulfinamide (4a/4a')[10]

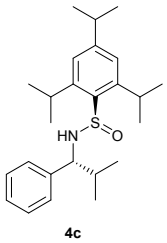

(*R*$_S$)-4a/4a'

The general procedure was followed with 24.3 mg of (*R*,*E*)-*N*-Benzylidene-4-methylbenzenesulfinamide **(1a)** (0.10 mmol), 1,3-dioxoisoindolin-2-yl isobutyrate **2c** (0.15 mmol), 0.7 mg of $Ir(ppy)_3$ **3c** (1.0 μmol), 35.0 μL of DIPEA (0.20 mmol) and 38.0 mg of Hantzsch ester (0.15 mmol) to afford a diastereoisomeric mixture of sufinamides **4a** and **4a'** (66:34; ^{1}H NMR) after 14 h. Column chromatography (9:1 cyclohexane:EtOAc) afforded **4a** and **4a'** (16.0 mg, 56% yield, white solid). **4a** and **4a'** could not be separated.

Major diastereoisomer: **(*R*$_S$,*R*)-4a**; minor diastereoisomer **(*R*$_S$,*S*)-4a'**.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.1 Hz, 2H, ***S***), 7.49 (d, *J* = 8.1 Hz, 2H, ***R***), 7.23 – 7.13 (m, 5H, ***R*** + ***S***), 7.07 – 7.04 (m, 2H, ***R*** + ***S***), 4.35 – 4.33 (m, 1H, ***R*** + ***S***), 4.27 – 4.24 (m, 1H, ***R*** + ***S***), 2.34 (s, 3H, ***R*** + ***S***), 2.20 – 2.09 (m, 1H, ***R***), 1.99 – 1.92 (m, 1H, ***S***), 1.00 (d, *J* = 6.7 Hz, 3H, ***R***), 0.93 (d, *J* = 6.7 Hz, 3H, ***S***), 0.84 (d, *J* = 6.7 Hz, 3H, ***R***), 0.79 (d, *J* = 6.7 Hz, 3H, ***S***).

(*R*)-2,4,6-triisopropyl-*N*-((*R*)-2-methyl-1-phenylpropyl)benzenesulfinamide (4c)

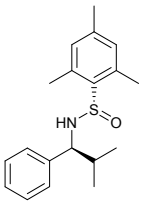


4c

The general procedure was followed with 35.5 mg of (*R*,*E*)-*N*-Benzylidene-4-methylbenzenesulfinamide **(1c)** (0.10 mmol), 1,3-dioxoisoindolin-2-yl isobutyrate **2c** (0.15 mmol), 0.7 mg of $Ir(ppy)_3$ **3c** (1.0 μmol), 35.0 μL of DIPEA (0.20 mmol) and 38.0 mg of Hantzsch ester (0.15 mmol) to afford a diastereoisomeric mixture of sufinamides **4c** and **4c'** (90:10; ^{1}H NMR) after 18 h. Column chromatography (9:1 cyclohexane:EtOAc) afforded **4c** and **4c'** (11.6 mg, 29% yield, white solid). **4c** and **4c'** could not be separated. Signals from the major diastereoisomer were identified through ^{1}H NMR spectroscopy.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 – 7.24 (m, 5H), 7.06 (s, 2H), 4.64 (d, *J* = 5.5 Hz, 1H), 4.25 (t, *J* = 6.0 Hz, 1H), 4.04 – 3.90 (m, 2H), 2.87 (hept, *J* = 6.7 Hz, 1H), 2.29 – 2.17 (m, 1H), 1.24 (dd, *J* = 6.9, 1.8 Hz, 18H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 151.8, 147.6, 141.3, 138.7, 128.5, 127.8, 127.7, 127.6, 123.2, 65.7, 34.5, 33.2, 28.3, 24.5, 24.4, 24.0, 19.5, 18.6. **HRMS calculated for $C_{20}H_{28}NOS$ [M+H]$^+$**: 400.2669, found: 400.2680. $[\alpha]_D^{20}$ = -71.6 (c = 0.89, $CHCl_3$).

(*S*)-2,4,6-Trimethyl-*N*-((*S*)-2-methyl-1-phenylpropyl)benzenesulfinamide (4e)[11]



4e

The general procedure was followed with 27.1 mg of (*S*,*E*)-*N*-benzylidene-2,4,6-trimethylbenzenesulfinamide **1e** (0.10 mmol), 35.0 mg of 1,3-dioxoisoindolin-2-yl isobutyrate **2c** (0.15 mmol), 0.7 mg of $Ir(ppy)_3$ **3c** (1.0 μmol), 52.2 μL of DIPEA (0.30 mmol) and 12.7 mg of Hantzsch ester (0.05 mmol) in 1.0 mL of DMSO. Following 36 h and extraction with $NH_4OH_{(aq)}$, column chromatography (19:1 cyclohexane:EtOAc) afforded **4e** (23.4 mg, 79% yield, white solid).

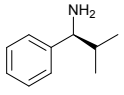
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31 – 7.21 (m, 5H), 6.81 (s, 2H), 4.48 (d, *J* = 5.4 Hz, 1H), 4.21 (t, *J* = 5.9 Hz, 2H), 2.52 (s, 6H), 2.30 – 2.16 (m, 4H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.82 (d, *J* = 6.7 Hz, 3H).

^{1}H NMR (300 MHz, acetone-d_6): δ 7.32 – 7.18 (m, 5H), 6.79 (s, 2H), 5.74 (d, *J* = 8.4 Hz, 1H), 4.10 – 4.05 (m, 1H), 2.47 (s, 6H), 2.22 (s, 3H), 2.07 – 2.00 (m, 1H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.77 (d, *J* = 6.7 Hz, 3H).

Since the chemical shifts, multiplicities and assignments are consistent with the ones reported in the literature for the (*S*,*S*)-isomer,[11b] we can confirm the (*S*,*S*) configuration of our product **4e**.

Desulfinylation of **4e**: hydrolysis with 10.0 equiv. of TFA in MeOH (0.4 M) was performed, affording enantiopure amine **5** with a 73% yield.

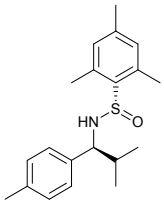
(*S*)-2-methyl-1-phenylpropan-1-amine (**5**)[12]



5

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24 – 7.16 (m, 5H), 3.78 (d, *J* = 8.0 Hz, 1H), 2.21 – 2.10 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.67 (d, *J* = 6.6 Hz, 3H). $[\alpha]_D^{20}$ = -5.7 (c = 0.23, $CHCl_3$); Literature,[12] (*R*)-amine $[\alpha]_D^{20}$ = +6.4 (c = 0.6, $CHCl_3$).

(*S*)-2,4,6-Trimethyl-*N*-((*S*)-2-methyl-1-(*p*-tolyl)propyl)benzenesulfinamide (4f)

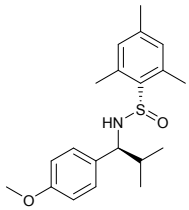


4f

The general procedure was followed with 28.5 mg of (*S*,*E*)-2,4,6-trimethyl-*N*-(4-methylbenzylidene)benzenesulfinamide **1f** (0.10 mmol), 35.0 mg of 1,3-dioxoisoindolin-2-yl isobutyrate **2c** (0.15 mmol), 0.7 mg of $Ir(ppy)_3$ **3c** (1.0 μmol), 52.2 μL of DIPEA (0.30 mmol) and 12.7 mg of Hantzsch ester (0.05 mmol) in 1.0 mL of DMSO. Following 40 h and extraction with $NH_4OH_{(aq)}$, column chromatography (19:1 cyclohexane:EtOAc) afforded **4f** (19.4 mg, 59% yield, white solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.11 (s, 4H), 6.82 (s, 2H), 4.45 (d, *J* = 5.2 Hz, 1H), 4.18 (t, *J* = 5.8 Hz, 1H), 2.52 (s, 6H), 2.32 (s, 3H), 2.27 – 2.15 (m, 4H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.81 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 140.6, 138.7, 138.1, 137.1, 136.6, 132.8, 130.9, 129.1, 127.6, 64.9, 33.0, 29.8, 21.2, 21.1, 19.5, 18.6. **HRMS calculated for $C_{20}H_{28}NOS$ [M+H]$^+$**: 330.1856, found: 330.1890. $[\alpha]_D^{20}$ = 94.2 (c = 1.99, $CHCl_3$).

(*S*)-*N*-((*S*)-1-(4-Methoxyphenyl)-2-methylpropyl)-2,4,6-trimethylbenzenesulfinamide (4g)[11]

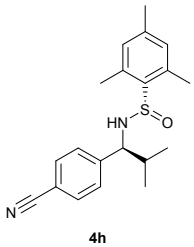


4g

The general procedure was followed with 30.1 mg of (*S*,*E*)-*N*-(4-methoxybenzylidene)-2,4,6-trimethylbenzenesulfinamide **1g** (0.10 mmol), 35.0 mg of 1,3-dioxoisoindolin-2-yl isobutyrate **2c** (0.15 mmol), 0.7 mg of $Ir(ppy)_3$ **3c** (1.0 μmol), 52.2 μL of DIPEA (0.30 mmol) and 12.7 mg of Hantzsch ester (0.05 mmol) in 1.0 mL of DMSO. Following 37 h and extraction with $NH_4OH_{(aq)}$, column chromatography (9:1 cyclohexane:EtOAc) afforded **4g** (21.1 mg, 61% yield, white solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19 – 7.14 (m, 2H), 6.86 – 6.82 (m, 4H), 4.41 (d, *J* = 4.9 Hz, 1H), 4.20 – 4.14 (m, 1H), 3.79 (s, 3H), 2.52 (s, 6H), 2.30 – 2.15 (m, 4H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.81 (d, *J* = 6.7 Hz, 3H).

(*S*)-*N*-((*S*)-1-(4-Cyanophenyl)-2-methylpropyl)-2,4,6-trimethylbenzenesulfinamide (4h)

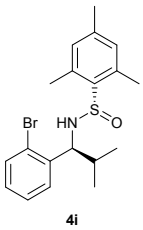


4h

The general procedure was followed with 29.6 mg of (*S*,*E*)-*N*-(4-cyanobenzylidene)-2,4,6-trimethylbenzenesulfinamide **1h** (0.10 mmol), 58.3 mg of 1,3-dioxoisoindolin-2-yl isobutyrate **2c** (0.25 mmol), 0.7 mg of $Ir(ppy)_3$ **3c** (1.0 μmol), 52.2 μL of DIPEA (0.30 mmol) and 12.7 mg of Hantzsch ester (0.05 mmol) in 1.0 mL of DMSO. Following 41 h and extraction with $NH_4OH_{(aq)}$, column chromatography (9:1 cyclohexane:EtOAc) afforded **4h** (21.5 mg, 63% yield, yellow solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 6.77 (s, 2H), 4.48 (d, *J* = 6.0 Hz, 1H), 4.26 (t, *J* = 6.3 Hz, 1H), 2.50 (s, 6H), 2.24 (s, 3H), 2.19 – 2.07 (m, 1H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.82 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 147.0, 141.0, 137.5, 136.7, 132.1, 131.0, 128.2, 118.8, 111.2, 64.4, 33.7, 31.0, 21.0, 19.6, 19.1, 18.9. **HRMS calculated for $C_{20}H_{25}N_2OS$ [M+H]$^+$**: 341.1682, found: 341.1713. $[\alpha]_D^{20}$ = 67.2 (c = 1.99, $CHCl_3$).

(*S*)-*N*-((*S*)-1-(2-Bromophenyl)-2-methylpropyl)-2,4,6-trimethylbenzenesulfinamide (4i)

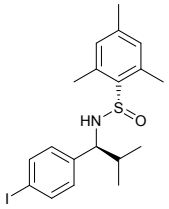


4i

The general procedure was followed with 35.0 mg of (*S*,*E*)-*N*-(2-bromobenzylidene)-2,4,6-trimethylbenzenesulfinamide **1i** (0.10 mmol), 35.0 mg of 1,3-dioxoisoindolin-2-yl isobutyrate **2c** (0.15 mmol), 0.7 mg of $Ir(ppy)_3$ **3c** (1.0 μmol), 52.2 μL of DIPEA (0.30 mmol) and 12.7 mg of Hantzsch ester (0.05 mmol) in 1.0 mL of DMSO. Following 38 h and extraction with $NH_4OH_{(aq)}$, column chromatography (9:1 cyclohexane:EtOAc) afforded **4i** (27.6 mg, 70% yield, orange solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 3.8 Hz, 2H), 7.12 – 7.04 (m, 1H), 6.79 (s, 2H), 4.81 (s, 1H), 4.50 (t, *J* = 7.1 Hz, 1H), 2.52 (s, 6H), 2.31 – 2.14 (m, 4H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 141.3, 140.5, 138.6, 136.6, 133.4, 130.9, 129.3, 128.7, 127.4, 123.2, 33.4, 29.8, 21.1, 20.0, 19.6, 18.5. **HRMS calculated for $C_{19}H_{25}BrNOS$ [M+H]$^+$**: 394.0835, found: 394.0801. $[\alpha]_D^{20}$ = 109.0 (c = 1.53, $CHCl_3$).

(*S*)-*N*-((*S*)-1-(4-Iodophenyl)-2-methylpropyl)-2,4,6-trimethylbenzenesulfinamide (4j)

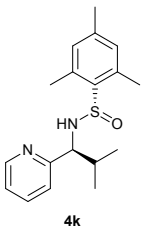


4j

The general procedure was followed with 39.7 mg of (*S*,*E*)-*N*-(4-iodobenzylidene)-2,4,6-trimethylbenzenesulfinamide **1j** (0.10 mmol), 58.3 mg of 1,3-dioxoisoindolin-2-yl isobutyrate **2c** (0.25 mmol), 0.7 mg of $Ir(ppy)_3$ **3c** (1.0 μmol), 52.2 μL of DIPEA (0.30 mmol) and 12.7 mg of Hantzsch ester (0.05 mmol) in 1.0 mL of DMSO. Following 36 h and extraction with $NH_4OH_{(aq)}$, column chromatography (19:1 cyclohexane:EtOAc) afforded **4j** (26.5 mg, 60% yield, yellow solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 – 7.58 (m, 2H), 6.98 – 6.90 (m, 2H), 6.80 (s, 2H), 4.42 (d, *J* = 5.5 Hz, 1H), 4.16 (t, *J* = 6.0 Hz, 1H), 2.51 (s, 6H), 2.26 (s, 3H), 2.15 (h, *J* = 6.7 Hz, 1H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.81 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 140.9, 140.8, 138.1, 137.4, 136.6, 131.0, 129.6, 92.9, 64.4, 33.2, 21.1, 19.6, 19.3, 18.6. **HRMS calculated for $C_{19}H_{25}INOS$ [M+H]$^+$**: 442.0696, found: 442.0698. $[\alpha]_D^{20}$ = 91.1 (c = 1.17, $CHCl_3$).

(*S*)-2,4,6-Trimethyl-*N*-((*S*)-2-methyl-1-(pyridin-2-yl)propyl)benzenesulfinamide (4k)



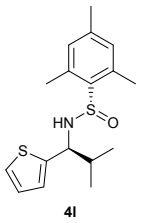
4k

The general procedure was followed with 27.2 mg of (*S*,*E*)-2,4,6-trimethyl-*N*-(pyridin-2-ylmethylene)benzenesulfinamide **1k** (0.10 mmol), 58.3 mg of 1,3-dioxoisoindolin-2-yl isobutyrate **2c** (0.25 mmol), 0.7 mg of $Ir(ppy)_3$ **3c** (1.0 μmol), 52.2 μL of DIPEA (0.30 mmol) and 12.7 mg of Hantzsch ester (0.05 mmol) in 1.0 mL of DMSO. Following 36 h and extraction with $NH_4OH_{(aq)}$, column chromatography (9:1 cyclohexane:EtOAc) afforded **4k** (17.7 mg, 56% yield, brown solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.55 – 8.53 (m, 1H), 7.62 (td, *J* = 7.7, 1.8 Hz, 1H), 7.21 – 7.13 (m, 2H), 6.85 (s, 2H), 6.07 (d, *J* = 7.9 Hz, 1H), 4.24 (dd, *J* = 7.9, 6.1 Hz, 1H), 2.57 (s, 6H), 2.28 (s, 3H), 2.08 – 1.95 (m, 1H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.85 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 160.8, 148.8, 140.5, 139.2, 136.6, 136.5, 130.8, 122.6,

122.3, 65.4, 35.3, 29.9, 21.2, 20.0, 19.6, 17.9. **HRMS calculated for $C_{18}H_{25}N_2OS$ [M+H]$^+$**: 317.1682, found: 317.1689. $[\alpha]_D^{20}$ = 120.9 (c = 1.76, $CHCl_3$).

(*S*)-2,4,6-Trimethyl-*N*-((*S*)-2-methyl-1-(thien-2-yl)propyl)benzenesulfinamide (4l)

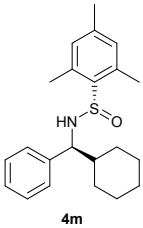


4l

The general procedure was followed with 27.7 mg of (*S*,*E*)-2,4,6-trimethyl-*N*-(thiophen-2-ylmethylene)benzenesulfinamide **1l** (0.10 mmol), 35.0 mg of 1,3-dioxoisoindolin-2-yl isobutyrate **2c** (0.15 mmol), 0.7 mg of Ir(ppy)$_3$ **3c** (1.0 μmol), 52.2 μL of DIPEA (0.30 mmol) and 12.7 mg of Hantzsch ester (0.05 mmol) in 1.0 mL of DMSO. Following 46 h and extraction with $NH_4OH_{(aq)}$, column chromatography (14:1 cyclohexane:EtOAc) afforded **4l** (20.6 mg, 64% yield, yellow solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.00 (d, *J* = 3.1 Hz, 1H), 6.95 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.85 (s, 2H), 4.54 (t, *J* = 6.1 Hz, 1H), 4.45 (d, *J* = 6.4 Hz, 1H), 2.56 (s, 6H), 2.28 – 2.21 (m, 4H), 0.96 (d, *J* = 2.4 Hz, 3H), 0.94 (d, *J* = 2.4 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 145.2, 140.8, 136.6, 131.0, 126.8, 125.6, 124.6, 123.8, 61.4, 34.0, 31.1, 23.8, 21.2, 19.6, 19.0. **HRMS calculated for $C_{17}H_{24}NOS_2$ [M+H]$^+$**: 322.1312, found: 322.1294. $[\alpha]_D^{20}$ = 66.7 (c = 0.18, $CHCl_3$).

(*S*)-*N*-((*S*)-Cyclohexyl(phenyl)methyl)-2,4,6-trimethylbenzenesulfinamide (4m)[11]

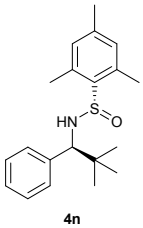


4m

The general procedure was followed with 27.1 mg of (*S*,*E*)-*N*-benzylidene-2,4,6-trimethylbenzenesulfinamide **1e** (0.10 mmol), 41.0 mg of 1,3-dioxoisoindolin-2-yl cyclohexanecarboxylate **2d** (0.15 mmol), 0.7 mg of Ir(ppy)$_3$ **3c** (1.0 μmol), 52.2 μL of DIPEA (0.30 mmol) and 12.7 mg of Hantzsch ester (0.05 mmol) in 1.0 mL of DMSO. Following 40 h and extraction with $NH_4OH_{(aq)}$, column chromatography (9:1 cyclohexane:EtOAc) afforded **4m** (26.3 mg, 74% yield, white solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 – 7.18 (m, 5H), 6.81 (s, 2H), 4.45 (d, J = 5.6 Hz, 1H), 4.21 – 4.17 (m, 1H), 2.51 (s, 6H), 2.26 (s, 3H), 1.96 – 1.91 (m, 1H), 1.84 – 1.63 (m, 4H), 1.60 – 1.52 (m, 1H), 1.32 – 0.7 (m, 5H).

(*S*)-*N*-((*S*)-2,2-Dimethyl-1-phenylpropyl)-2,4,6-trimethylbenzenesulfinamide (4n)

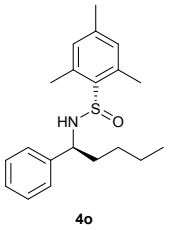


4n

The general procedure was followed with 27.1 mg of (*S*,*E*)-*N*-benzylidene-2,4,6-trimethylbenzenesulfinamide **1e** (0.10 mmol), 37.1 mg of 1,3-dioxoisoindolin-2-yl pivalate **2e** (0.15 mmol), 0.7 mg of Ir(ppy)$_3$ **3c** (1.0 μmol), 52.2 μL of DIPEA (0.30 mmol) and 12.7 mg of Hantzsch ester (0.05 mmol) in 1.0 mL of DMSO. Following 36 h and extraction with $NH_4OH_{(aq)}$, column chromatography (19:1 cyclohexane:EtOAc) afforded **4n** (11.9 mg, 36% yield, white solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 – 7.14 (m, 5H), 6.79 (s, 2H), 4.68 (d, *J* = 7.4 Hz, 1H), 4.06 (d, *J* = 7.3 Hz, 1H), 2.50 (s, 6H), 2.26 (s, 3H), 0.91 (s, 9H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 141.0 140.6, 138.6, 136.6, 130.9, 128.0, 128.0, 127.3, 68.8, 35.9, 26.9, 21.1, 19.1. **HRMS calculated for $C_{20}H_{27}NOSNa$ [M+Na]$^+$**: 352.1706, found: 352.1708. $[\alpha]_D^{20}$ = -5.8 (c = 0.78, $CHCl_3$).

(*S*)-2,4,6-Trimethyl-*N*-((*S*)-1-phenylpentyl)benzenesulfinamide (4o)



4o

The general procedure was followed with 27.1 mg of (*S*,*E*)-*N*-benzylidene-2,4,6-trimethylbenzenesulfinamide **1e** (0.10 mmol), 37.1 mg of 1,3-Dioxoisoindolin-2-yl pentanoate **2f** (0.15 mmol), 0.7 mg of $Ir(ppy)_3$ **3c** (1.0 μmol), 52.2 μL of DIPEA (0.30 mmol) and 12.7 mg of Hantzsch ester (0.05 mmol) in 1.0 mL of DMSO. Following 49 h and extraction with $NH_4OH_{(aq)}$, column chromatography (9:1 cyclohexane:EtOAc) afforded **4n** (13.5 mg, 41% yield, white solid).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 – 7.26 (m, 5H), 6.82 (s, 2H), 4.44 – 4.37 (m, 2H), 2.53 (s, 6H), 2.26 (s, 3H), 2.17 – 2.05 (m, 1H), 1.86 – 1.73 (m, 1H), 1.70 – 1.52 (m, 2H), 1.19 – 1.12 (m, 2H), 0.85 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 142.5, 140.7, 138.2, 136.7, 134.6, 131.0, 128.7, 127.8, 127.3, 126.7, 123.7, 123.6, 58.9, 35.9, 28.2, 22.7, 21.1, 19.5, 14.1. **HRMS calculated for $C_{20}H_{28}NOS$ $[M+H]^+$**: 330.1886, found: 330.1877. $[\alpha]_D^{20}$ = 75.2 (c = 0.49, $CHCl_3$).

5. Mechanistic studies on the asymmetric radical alkylation of *N*-sulfinimines

5.1. Electrochemical analysis of the reaction components

Cyclic voltammetry of 1,3-dioxoisoindolin-2-yl isobutyrate (2c)

Tetra-n-butylammonium hexafluorophosphate (193.7 mg, 0.50 mmol) was added to a 0.5 mM solution of *N*-acyloxyphthalimide **2c** in 10 mL of DCM. The reduction potential was measured at a 50 mV/s scan rate. A completely irreversible reduction was observed with $E_{1/2}^{red}$ = -1.18 V vs SCE.

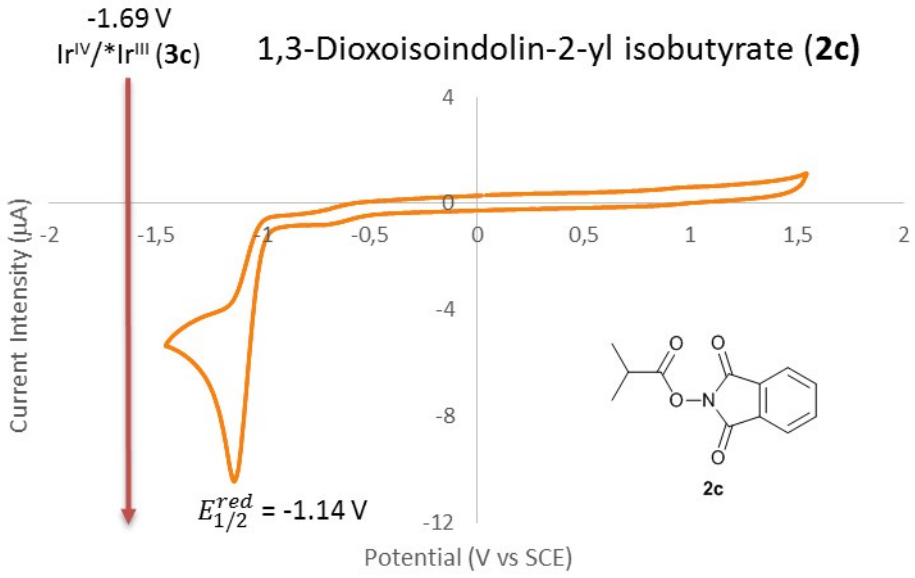


Figure S2. Cyclic voltammetry of **2c**.

As shown in Figure S2, the redox potential associated to the oxidation of the photoexcited state of $Ir(ppy)_3$ is larger than the reduction potential for *N*-acyloxyphthalimide.

Cyclic voltammetry of DIPEA

Tetra-n-butylammonium hexafluorophosphate (193.7 mg, 0.50 mmol) was added to a 0.5 mM solution of DIPEA in 10 mL of DCM. The oxidation potential was measured at a 50 mV/s scan rate. A completely irreversible oxidation was observed with $E_{1/2}^{ox}$ = +0.94 V vs SCE.

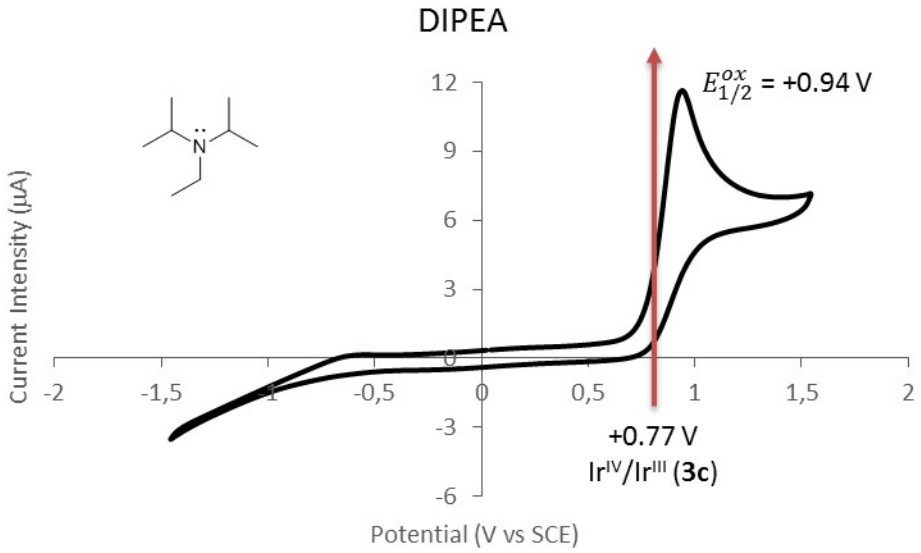


Figure S3. Cyclic voltammetry of DIPEA.

As shown in Figure S3, the redox potential associated to the oxidation of the electron donor DIPEA is larger than the reduction potential for the Ir^{IV} species.

5.2. Stern-Volmer phosphorescence quenching studies

The Stern-Volmer plots displayed in Figure S4 show a linear correlation between the concentration of quencher [Q] and I_0/I according to the equation $I_0/I = K_{SV}\cdot[Q] + 1$.

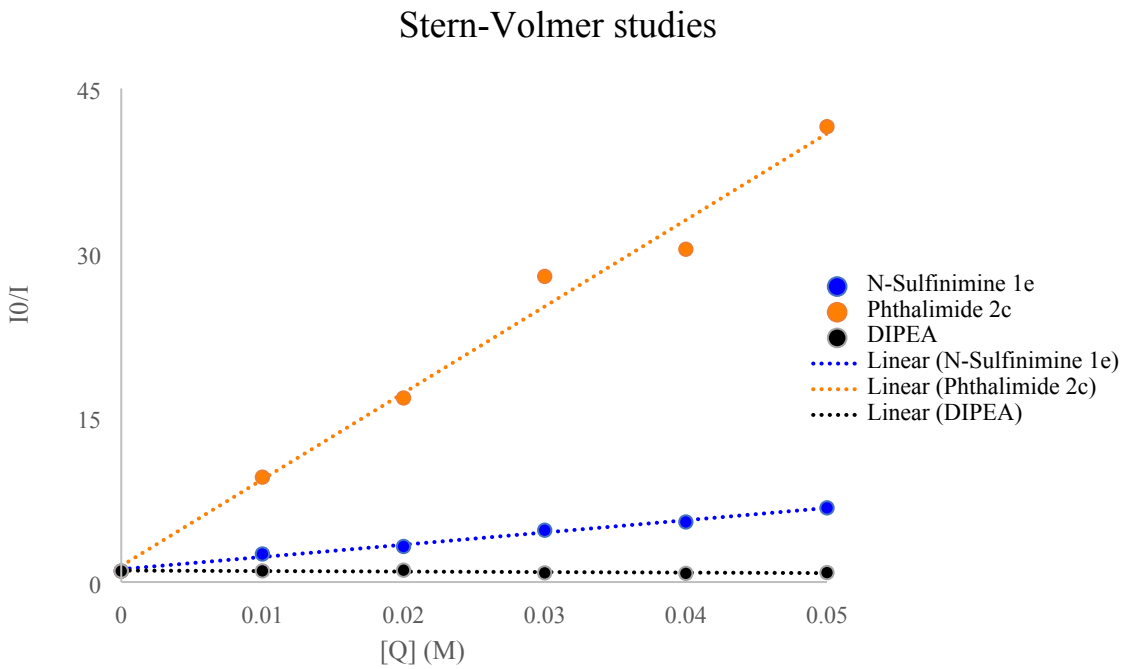


Figure S4. $Ir(ppy)_3$ phosphorescence emission quenching by different components.

The data plotted in the chart confirms the lack of interaction between DIPEA and $^*Ir(ppy)_3$. Additionally, it presents the possibility of *N*-sulfinimine **1e** quenching

photoexcited catalyst **3c**. However, the quenching behavior of phthalimide **2c** is considerably higher. Therefore, the initial step must involve the oxidative quenching of the photoexcited *$Ir(ppy)_3$ by **2c**.

5.3. Quantum yield measurement

5.3.1. Preliminary setup

A potassium ferrioxalate solution was prepared as actinometer following the procedure described by the IUPAC (subcommittee in photochemistry).[13] The procedure is based on the decomposition under irradiation of ferric ions to ferrous ions, which can be complexed by 1,10-phenanthroline. This photochemical transformation has a known quantum yield (ϕ) and the complexation of Fe^{2+} with 1,10-phenanthroline can be monitored by UV-Visible absorption since its extinction coefficient at 510 nm is also known (ε =11100 $M^{-1}\cdot cm^{-1}$). Therefore, the transformed moles can be related with the moles of photons absorbed by the equation ϕ = transformed moles/absorbed photons.

Green crystals of $K_3[Fe(C_2O4)_3]\cdot 3H_2O$ were prepared according to the following procedure: 55.3 g of potassium oxalate monohydrate (0.30 mol, 3.0 equiv.) were dissolved in 80 mL of water (3.75 M) at 90 ºC. Then, 16.2 g of $FeCl_3$ (0.10 mol, 1.0 equiv.) were added to the solution and it was stirred for 10 min while cooling to room temperature. The precipitate was filtered and recrystallized in water (24.6 g, 50% yield).

The following solutions were prepared and stored in a dark environment prior to use:

- **Potassium ferrioxalate solution 0.012 M**: 59.0 mg of $K_3[Fe(C_2O_4)]\cdot 3H_2O$ and 28 μL of H_2SO_4 (96%) were added to a 10 mL volumetric flask and filled to the mark with Milli-Q water.
- **1,10-Phenanthroline 0.01 M**: 99.1 mg of 1,10-phenanthroline monohydrate were added to a 50 mL volumetric flask and filled to the mark with Milli-Q water.
- **Buffer solution**: 4.94 g of NaOAc and 1 mL of H_2SO_4 (96%) were added to a 100 mL volumetric flask and filled to the mark with Milli-Q water.
- **Model reaction solution**: 27.1 mg of (*S*,*E*)-*N*-benzylidene-2,4,6-trimethylbenzenesulfinamide **1e** (0.10 mmol), 35.0 mg of 1,3-dioxoisoindolin-2-yl isobutyrate **2c** (0.15 mmol), 0.7 mg of $Ir(ppy)_3$ **3c** (1.0 μmol), 52.2 μL of DIPEA (0.30 mmol) and 12.7 mg of Hantzsch ester were added to a dry vial. The components were dissolved in 1.0 mL of DMSO. Evacuation of the sealed vial followed by refill with N_2 was conducted three times at room temperature.

5.3.2. Actinometry measurements

2.0 mL of potassium ferrioxalate solution (0.012 M) were introduced into a sealed vial under dark conditions while being stirred. Then, the 420 nm blue LEDs were switched on. Every 60 s the light was switched off and a 0.1 mL aliquot was taken. To each aliquot, 2.0 mL of buffer solution and 0.5 mL of 1,10-phenanthroline 0.01 M solution were added and the final volume was raised to 10 mL with Milli-Q water. As a blank sample, a solution was prepared with 0.1 mL of non-irradiated potassium ferrioxalate solution (0.012 M), 2.0 mL of buffer solution and 0.5 mL of 1,10-phenanthroline 0.01 M solution in a 10 mL volumetric flask filled with Milli-Q water to the mark.

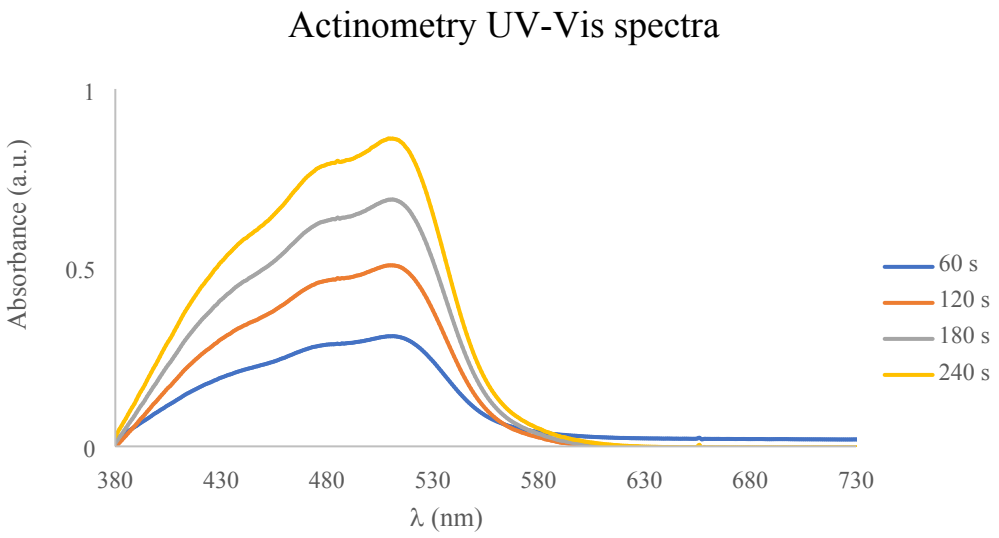


Figure S5. UV-Visible spectra recorded at different irradiation time intervals.

The number of photochemically produced Fe^{2+} moles after each time interval is determined using the Beer-Lambert law:

$$moles\ of\ Fe^{2+} = \frac{V_1 \cdot V_3 \cdot \Delta A_{510}}{1000 \cdot V_2 \cdot l \cdot \varepsilon_{510}}$$

where V_1 is the irradiated volume (noting that the initial volume is 2.0 mL but it changes as the aliquots are taken); V_2 is the aliquot volume (0.1 mL), V_3 is the final volume after addition of 1,10-phenanthroline and buffer solutions (10 mL), l refers to the optical pathway (1 cm) and ε_{510} is the extinction coefficient of the complex formed by Fe^{2+} and 1,10-phenanthroline (*ca.* 11100 $M^{-1} \cdot cm^{-1}$).

The generated moles of Fe^{2+} (x) are plotted as a function of time (t) in Figure S6.

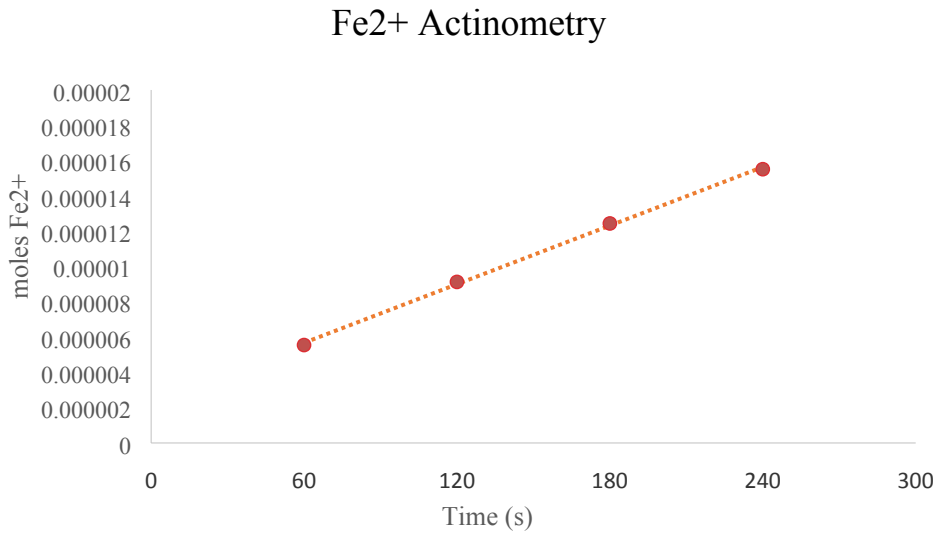


Figure S6. Plotted data of generated moles of Fe^{2+}.

The slope of the plotted trendline (dx/dt) was correlated to the moles of incident photons by unit of time ($^{0}q_{n,p}$) using the following equation:

$$q_{n,p}^{0} = \frac{dx/dt}{\phi_{420} \cdot \left[1 - 10^{A_{420}}\right]}$$

Where ϕ_{420} is the quantum yield of the actinometer reaction at the irradiated wavelength, in this case being 1.02 at 420 nm.[14] A_{420} is the absorbance of the actinometer solution (ferrioxalate) at the irradiated wavelength (420 nm), obtaining a value of 1.04.

Therefore, the moles of incident photons by unit of time ($q_{n,p}^{0}$) was determined to be $6.48 \cdot 10^{-8}$ einstein·s^{-1}.

5.3.3. Quantum yield determination

The model reaction solution (1.0 mL) was irradiated at specific time intervals in order to control the conversion of the process. Every 60 min, a 0.1 mL aliquot was taken from the reaction mixture (always under inert atmosphere). The solvent of the aliquot was removed under reduced pressure and a ^{1}H NMR spectrum in $CDCl_3$ was recorded.

The generated moles of product **4e** (x) are plotted as a function of time (t) in Figure S7.

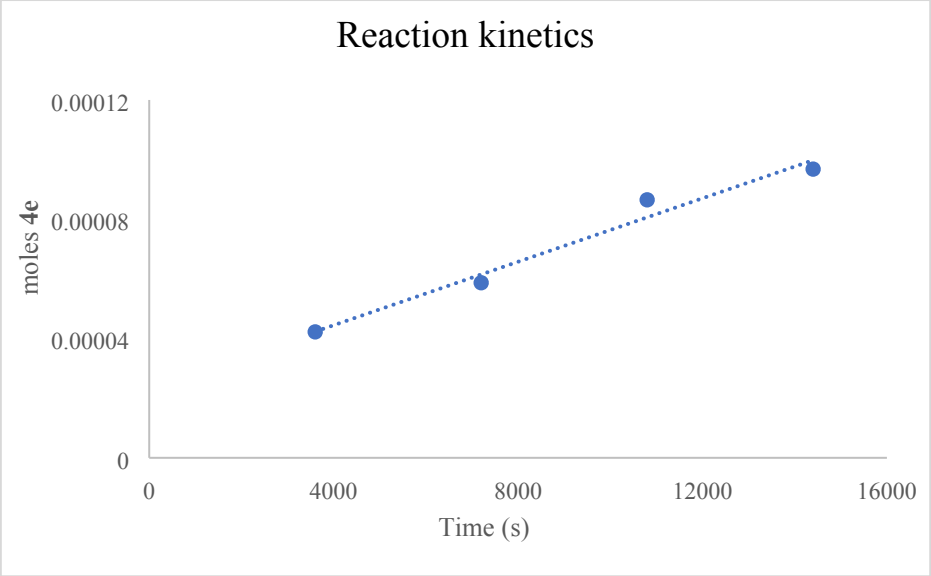


Figure S7. Plotted data of generated moles of product **4e**.

Lastly, the absorbance of the model reaction solution at the irradiated wavelength was measured, obtaining a value of 19.44.

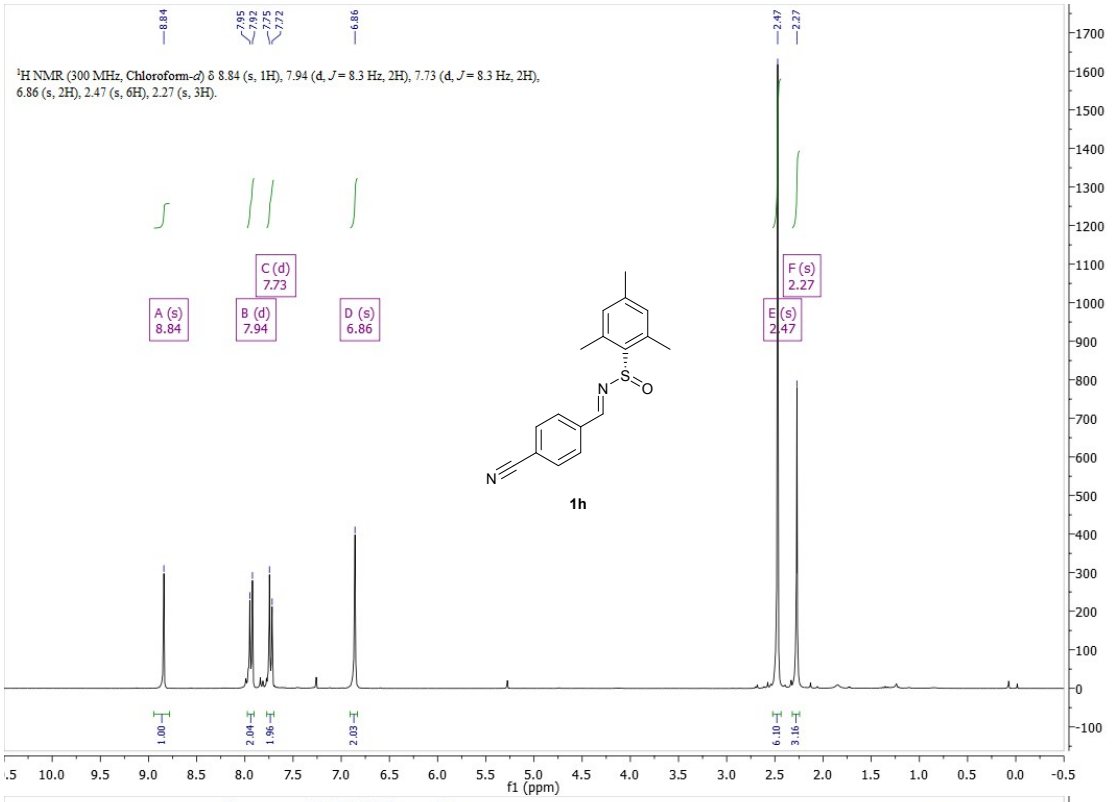
Therefore, the quantum yield of the reaction could be calculated:

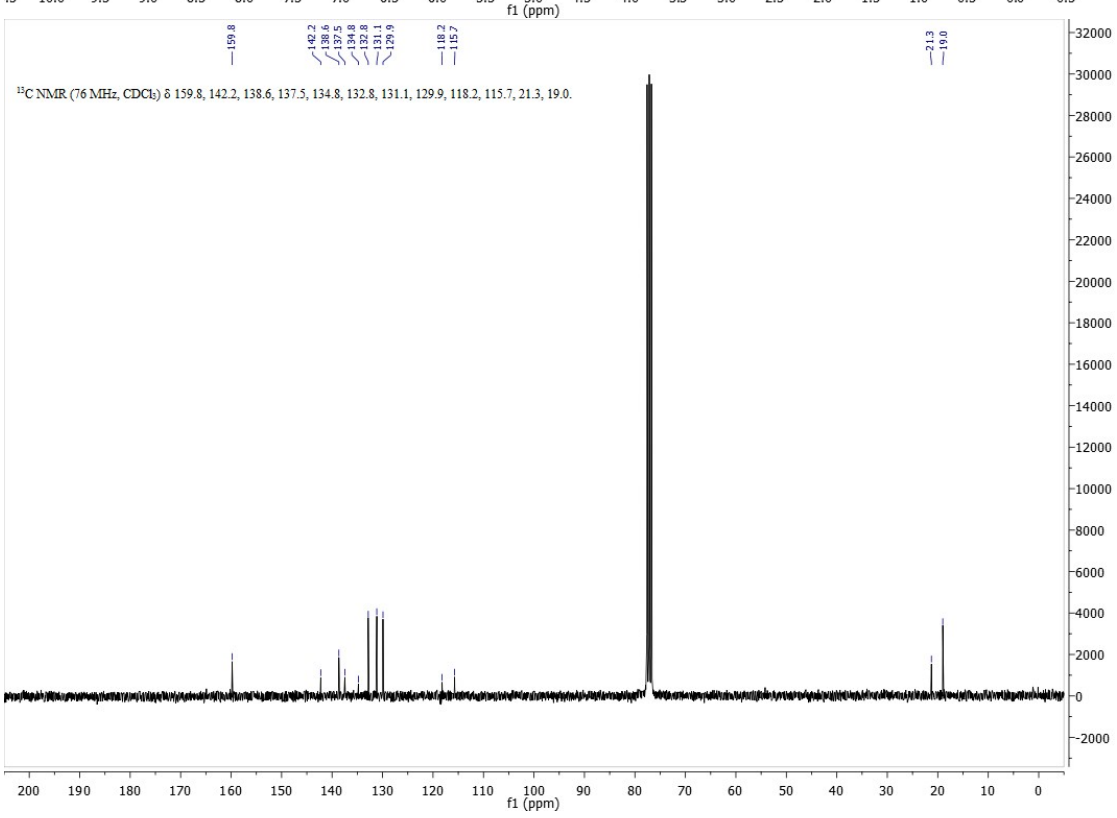
$$\phi_{420} = \frac{dx/dt}{q_{n,p}^{0} \cdot \left[1 - 10^{A_{420}}\right]} = 0.077$$

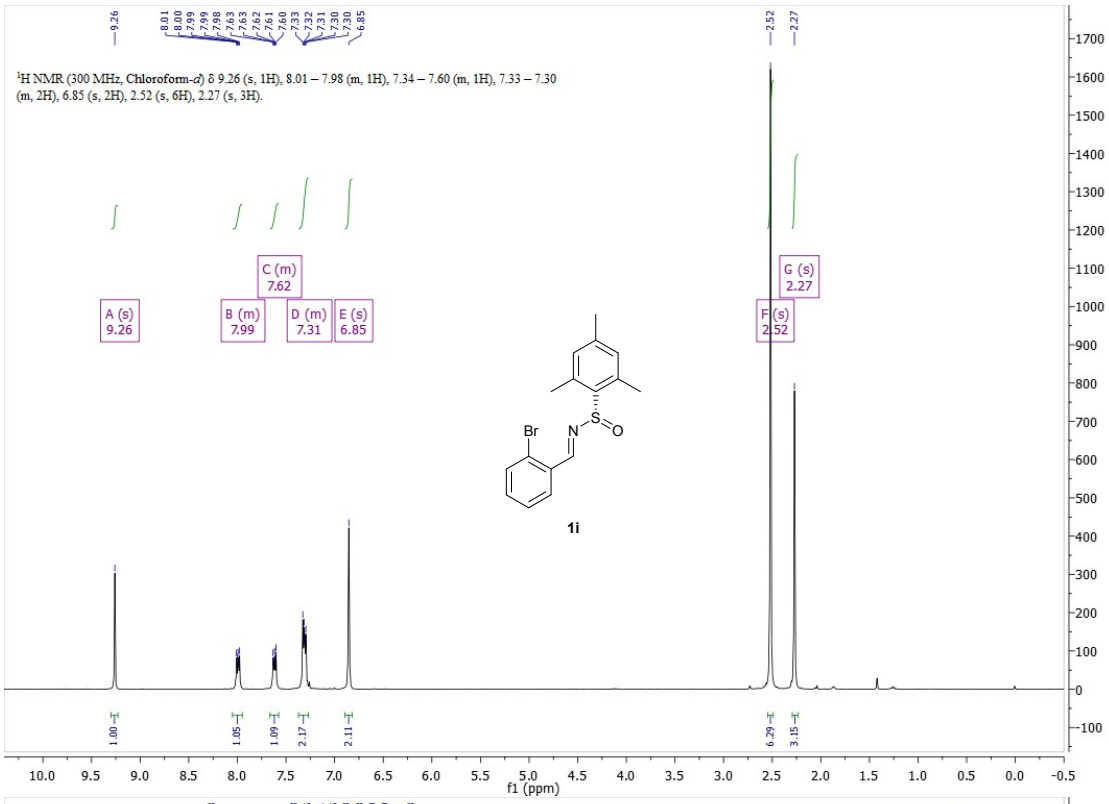
Where dx/dt is the slope of the plotted trendline in Figure S7, $q_{n,p}^{0}$ is the previously determined number of moles of incident photons by unit of time, and A_{420} is the absorbance of the model reaction solution at the irradiated wavelength (420 nm).

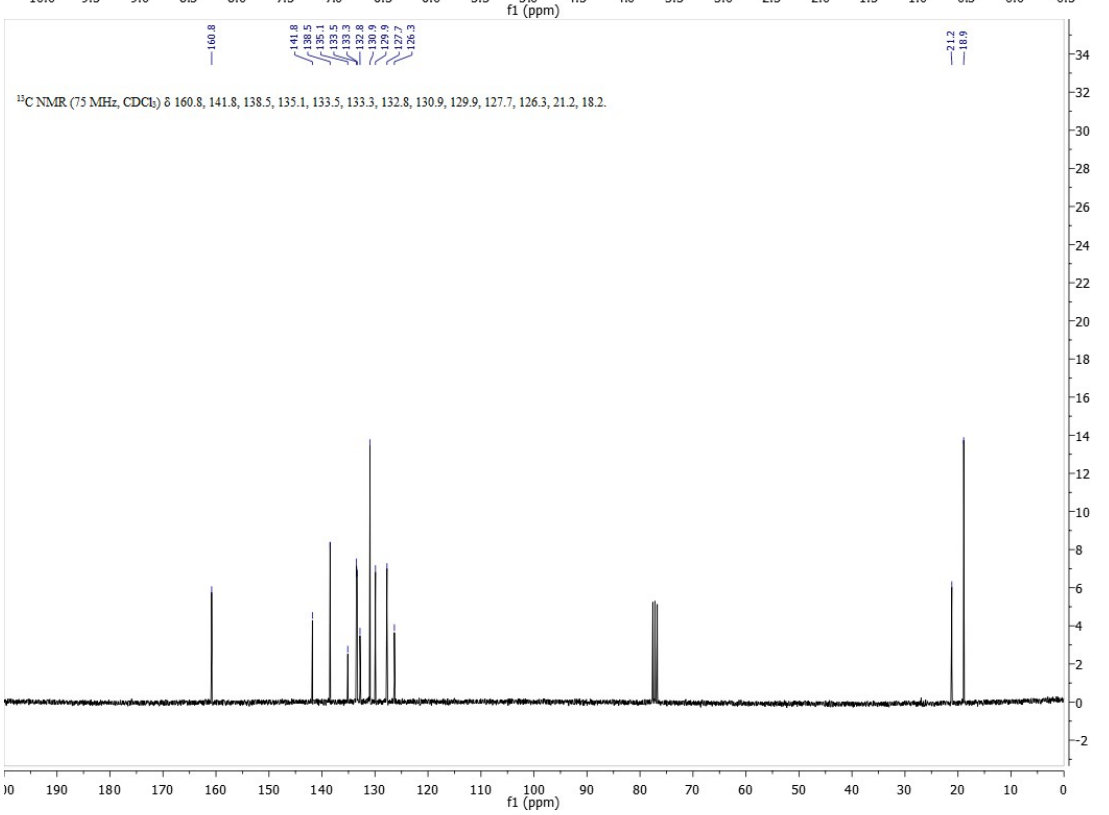
Since ϕ_{420} = 0.077, the photocatalyst must absorb 13 photons to afford one equivalent of product **4e**, indicating that a chain propagation-type mechanism is not taking place.

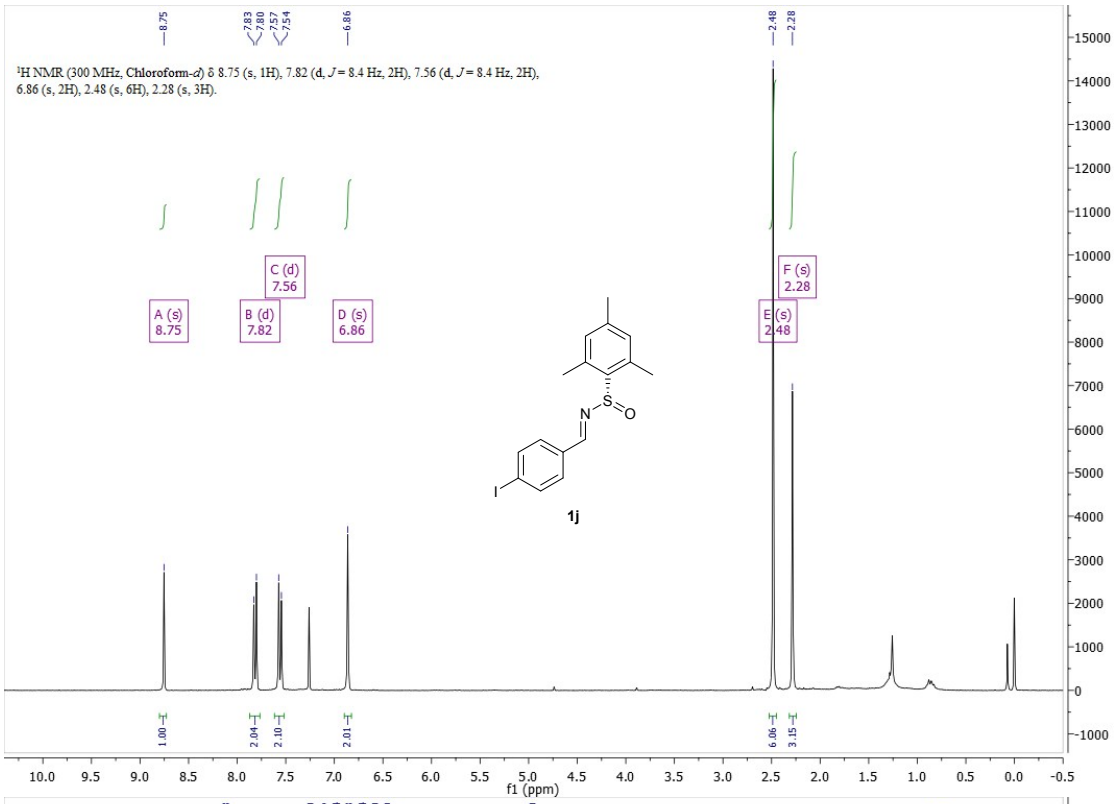
6. NMR spectral data



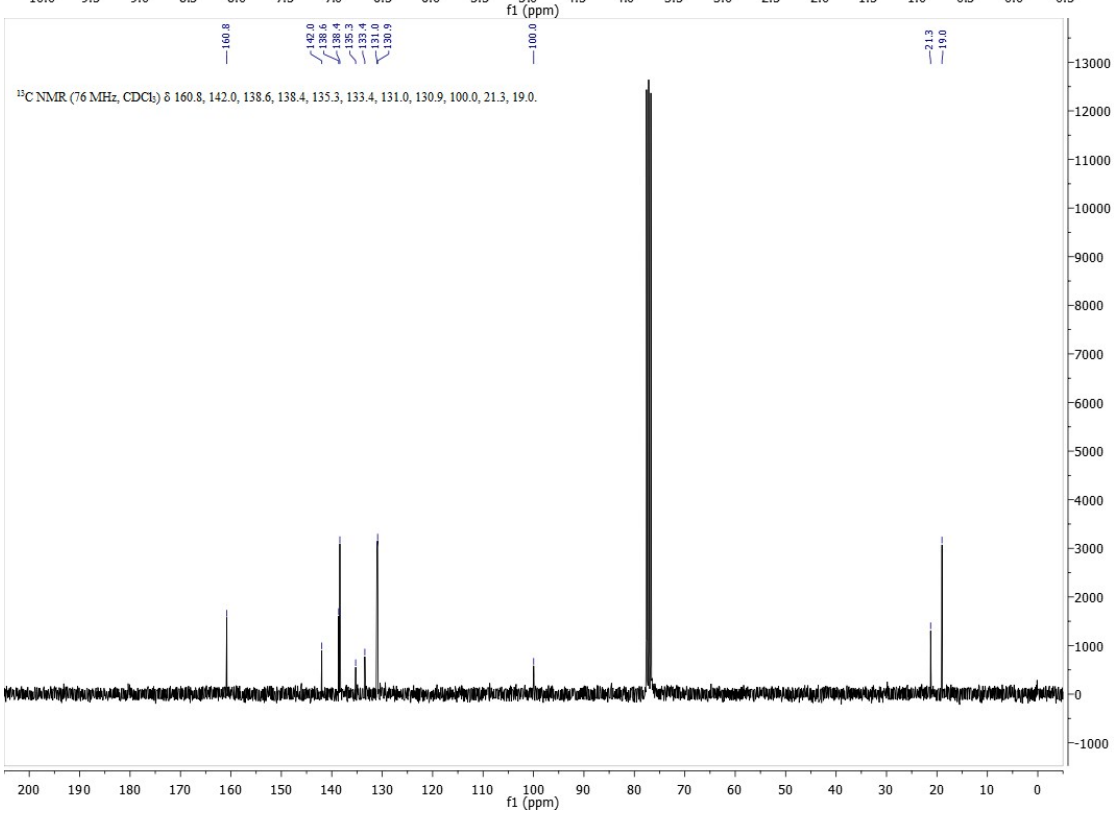


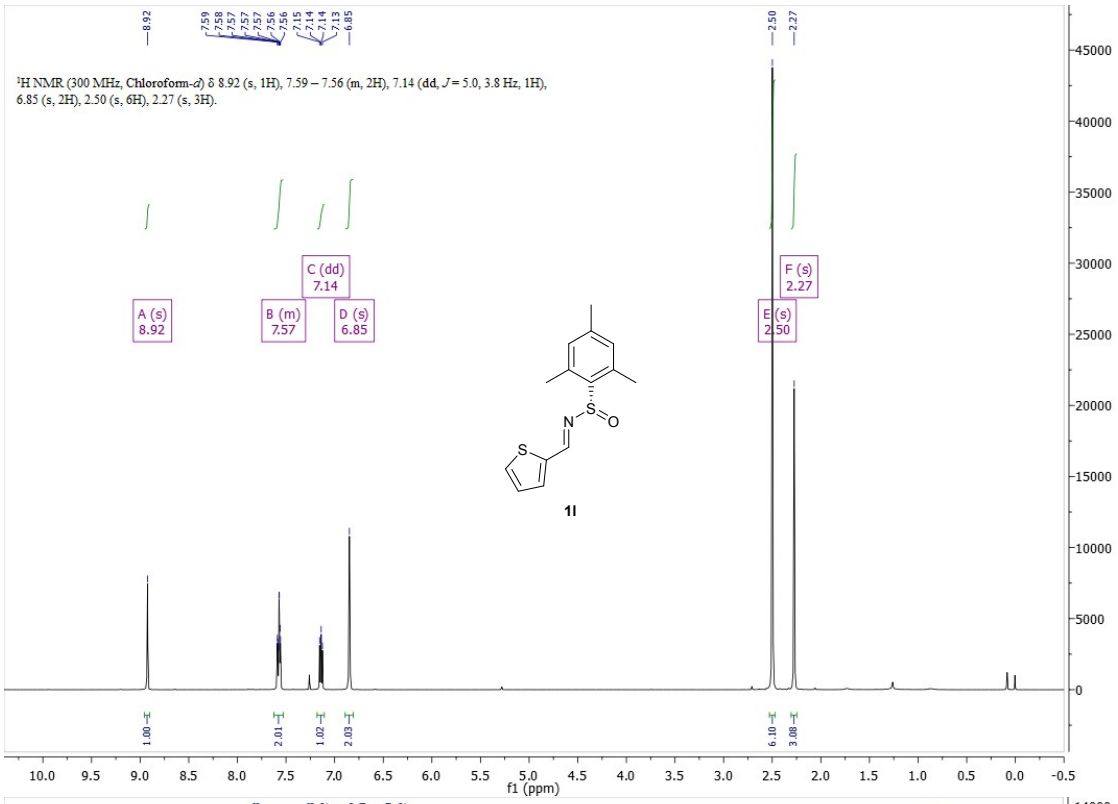

9.26
8.01
8.00
7.99
7.99
7.98
7.63
7.62
7.61
7.60
7.33
7.32
7.31
7.30
6.85
2.52
2.27
[1]H NMR (300 MHz, Chloroform-d) δ 9.26 (s, 1H), 8.01 – 7.98 (m, 1H), 7.34 – 7.60 (m, 1H), 7.33 – 7.30 (m, 2H), 6.85 (s, 2H), 2.52 (s, 6H), 2.27 (s, 3H).
A (s) 9.26
B (m) 7.99
C (m) 7.62
D (m) 7.31
E (s) 6.85
F (s) 2.52
G (s) 2.27
Br
N
S
O
1i
1.00
1.05
1.09
2.17
2.11
6.29
3.15
f1 (ppm)


160.8
141.8
138.5
135.1
133.5
133.3
132.8
130.9
129.9
127.7
126.3
21.2
18.9
[13]C NMR (75 MHz, CDCl3) δ 160.8, 141.8, 138.5, 135.1, 133.5, 133.3, 132.8, 130.9, 129.9, 127.7, 126.3, 21.2, 18.2.
f1 (ppm)

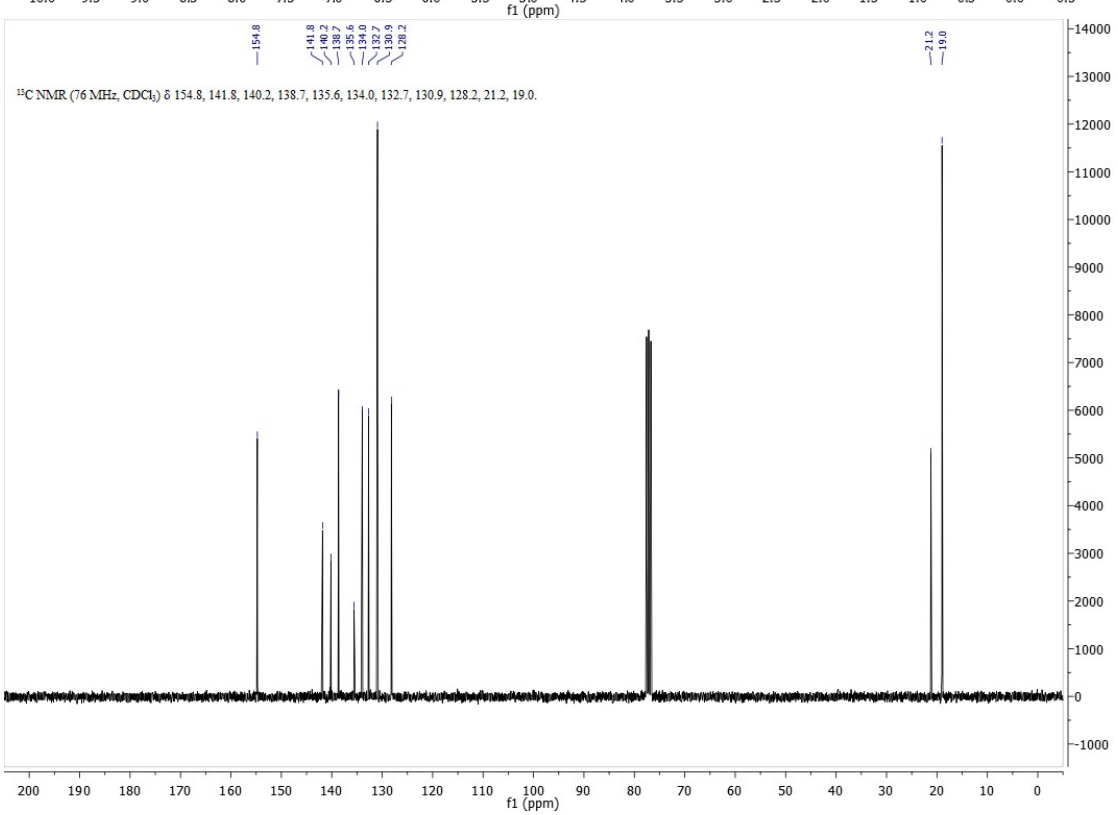

8.75
7.83
7.80
7.57
7.54
6.86
2.48
2.28
^{1}H NMR (300 MHz, Chloroform-d) δ 8.75 (s, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 6.86 (s, 2H), 2.48 (s, 6H), 2.28 (s, 3H).
A (s) 8.75
B (d) 7.82
C (d) 7.56
D (s) 6.86
E (s) 2.48
F (s) 2.28
1.00
2.04
2.10
2.01
6.06
3.15
f1 (ppm)

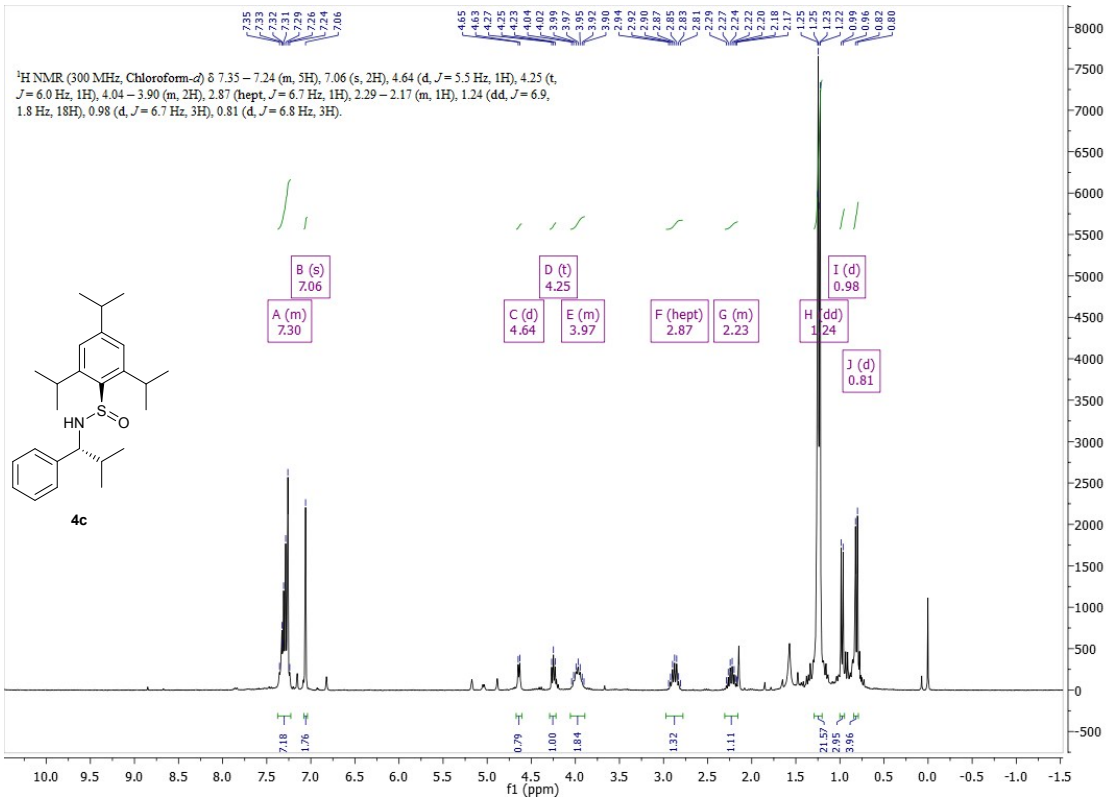
1j

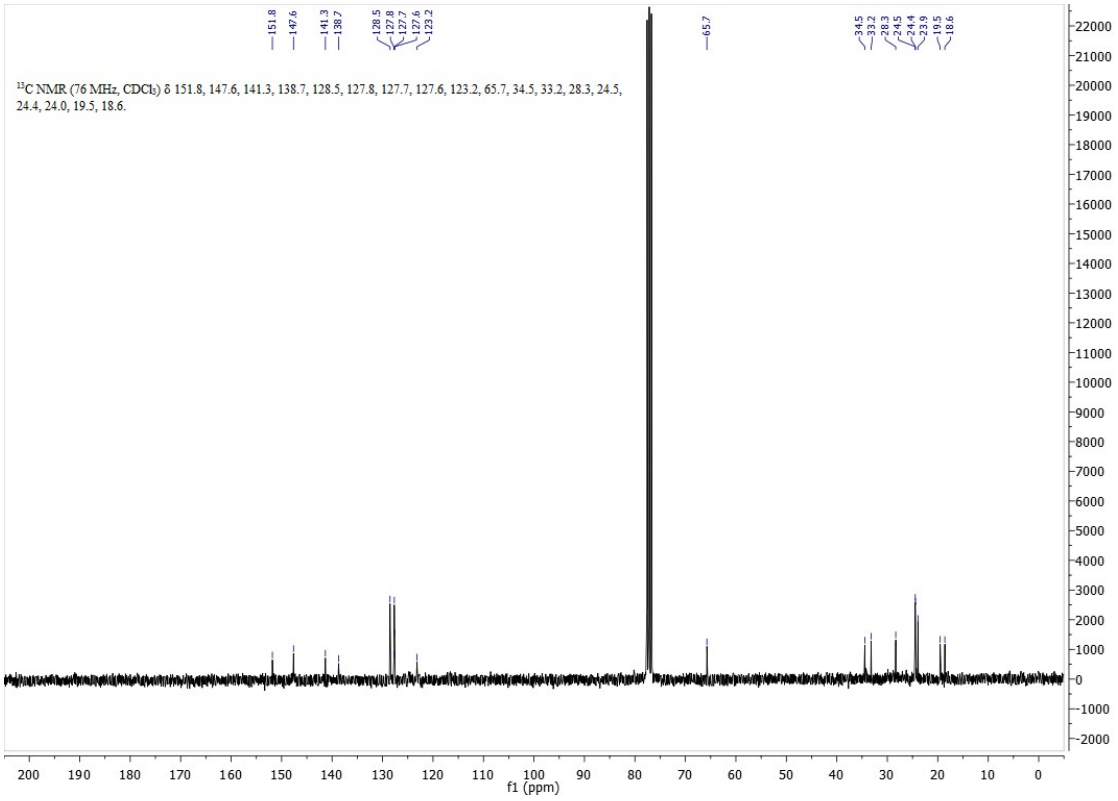

160.8
142.0
138.6
138.4
135.3
133.4
131.0
130.9
100.0
21.3
19.0
^{13}C NMR (76 MHz, $CDCl_3$) δ 160.8, 142.0, 138.6, 138.4, 135.3, 133.4, 131.0, 130.9, 100.0, 21.3, 19.0.
f1 (ppm)

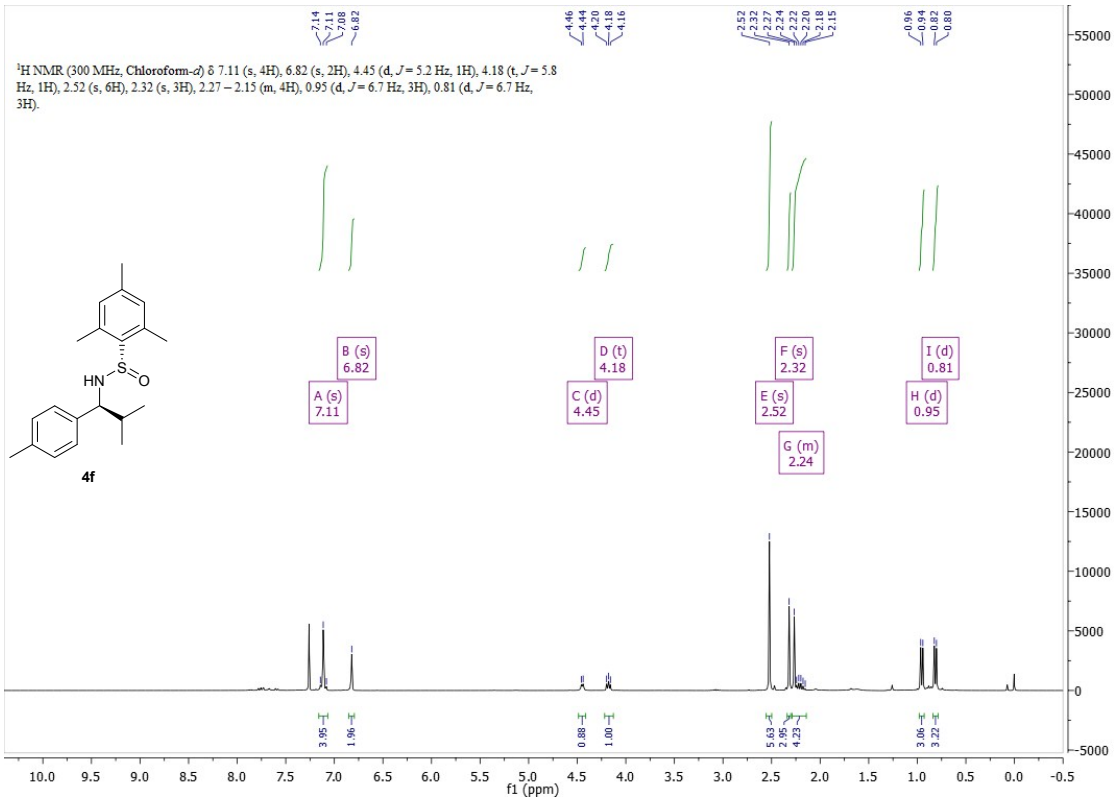

8.92
7.59
7.58
7.57
7.57
7.57
7.57
7.56
7.56
7.15
7.14
7.14
7.13
6.85
2.50
2.27
^{1}H NMR (300 MHz, Chloroform-d) δ 8.92 (s, 1H), 7.59 – 7.56 (m, 2H), 7.14 (dd, J = 5.0, 3.8 Hz, 1H), 6.85 (s, 2H), 2.50 (s, 6H), 2.27 (s, 3H).
A (s) 8.92
B (m) 7.57
C (dd) 7.14
D (s) 6.85
E (s) 2.50
F (s) 2.27
1.00
2.01
1.02
2.03
6.10
3.08
f1 (ppm)

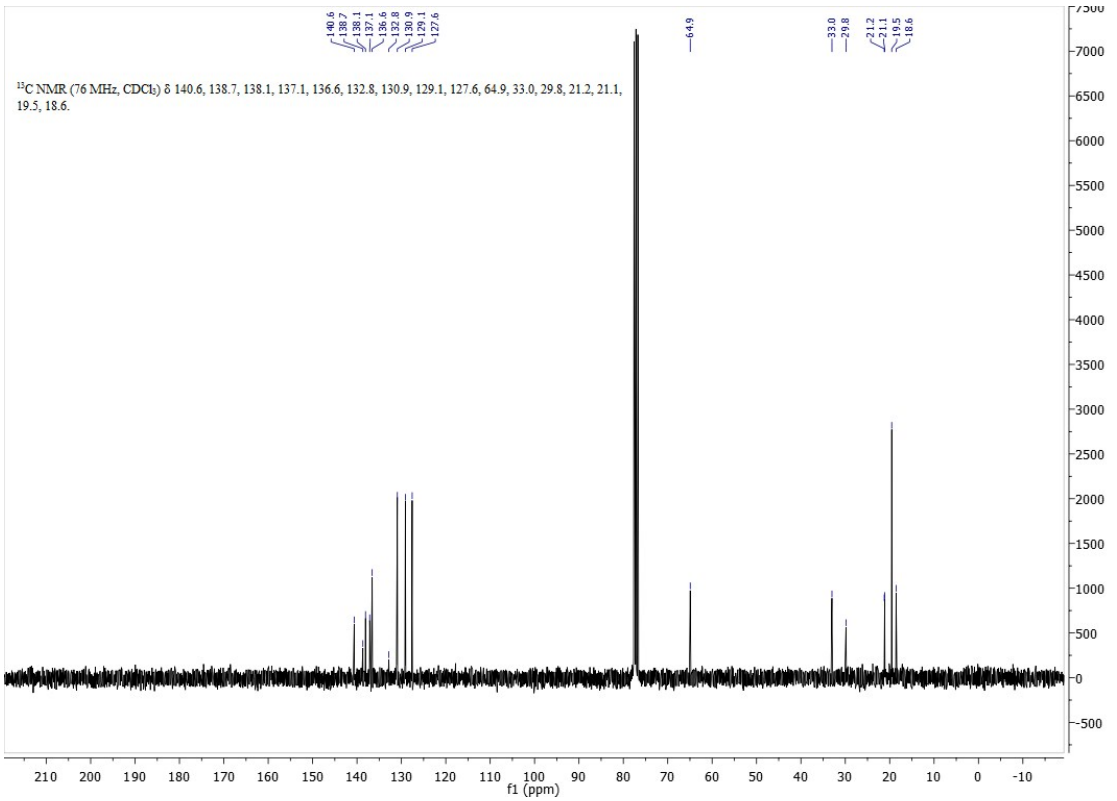
1l

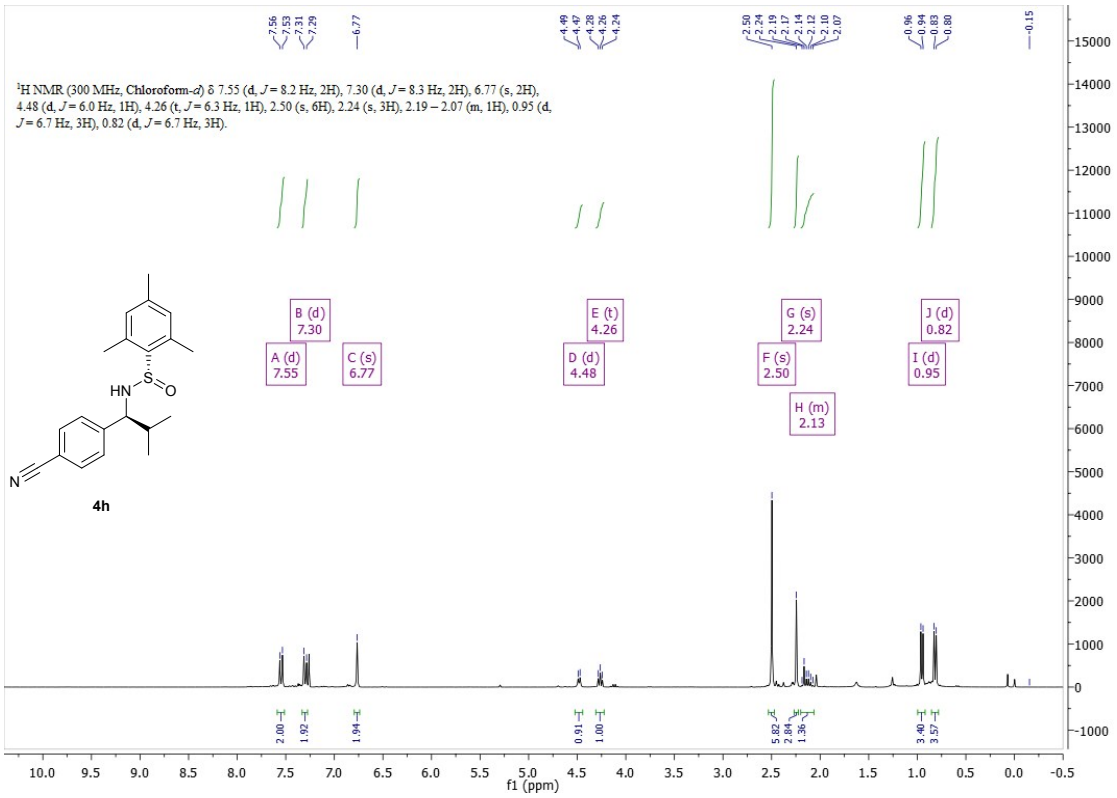

154.8
141.8
140.2
138.7
135.6
134.0
132.7
130.9
128.2
21.2
19.0
^{13}C NMR (76 MHz, $CDCl_3$) δ 154.8, 141.8, 140.2, 138.7, 135.6, 134.0, 132.7, 130.9, 128.2, 21.2, 19.0.
f1 (ppm)

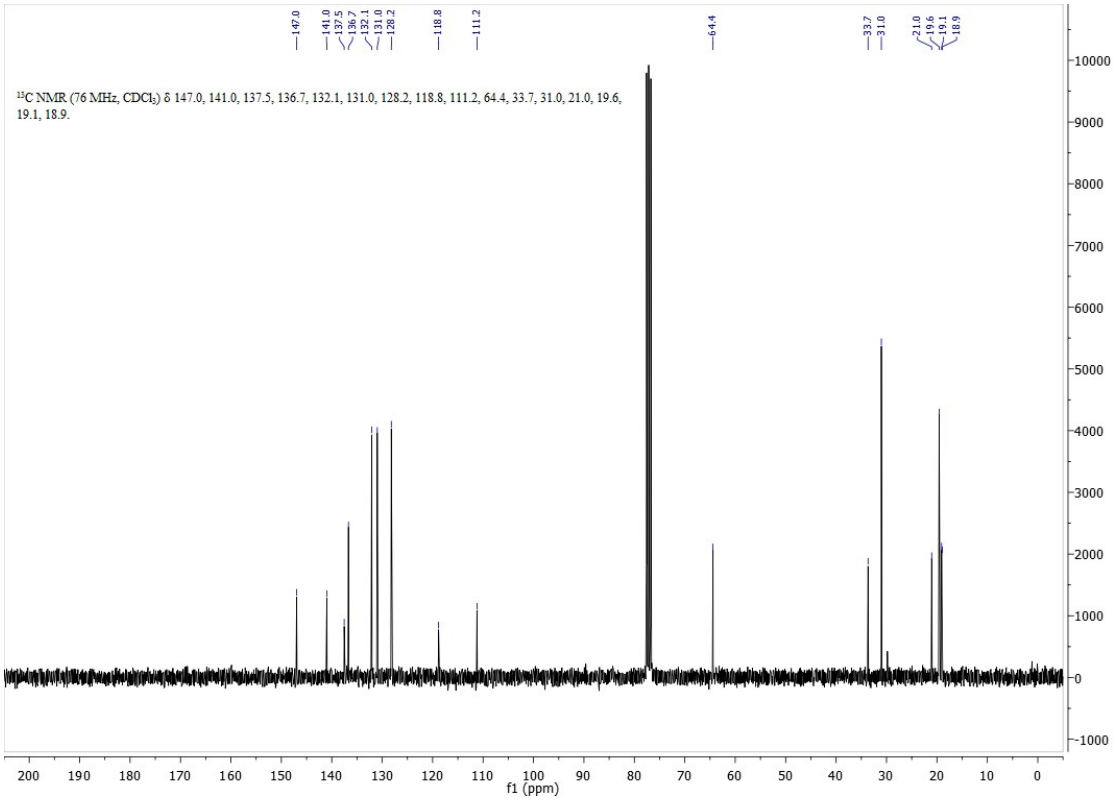

7.35 7.33 7.32 7.31 7.29 7.26 7.24 7.06
4.65 4.63 4.27 4.25 4.23 4.04 4.02 3.99 3.97 3.95 3.92 3.90 2.94 2.92 2.90 2.87 2.85 2.83 2.81 2.29 2.27 2.24 2.22 2.20 2.18 2.17 1.25 1.23 1.22 0.99 0.96 0.82 0.80
^{1}H NMR (300 MHz, Chloroform-d) δ 7.35 – 7.24 (m, 5H), 7.06 (s, 2H), 4.64 (d, J = 5.5 Hz, 1H), 4.25 (t, J = 6.0 Hz, 1H), 4.04 – 3.90 (m, 2H), 2.87 (hept, J = 6.7 Hz, 1H), 2.29 – 2.17 (m, 1H), 1.24 (dd, J = 6.9, 1.8 Hz, 18H), 0.98 (d, J = 6.7 Hz, 3H), 0.81 (d, J = 6.8 Hz, 3H).
B (s) 7.06
D (t) 4.25
I (d) 0.98
A (m) 7.30
C (d) 4.64
E (m) 3.97
F (hept) 2.87
G (m) 2.23
H (dd) 1.24
J (d) 0.81
HN
S
O
4c
7.18 1.76 0.79 1.00 1.84 1.32 1.11 21.57 2.95 3.96
f1 (ppm)

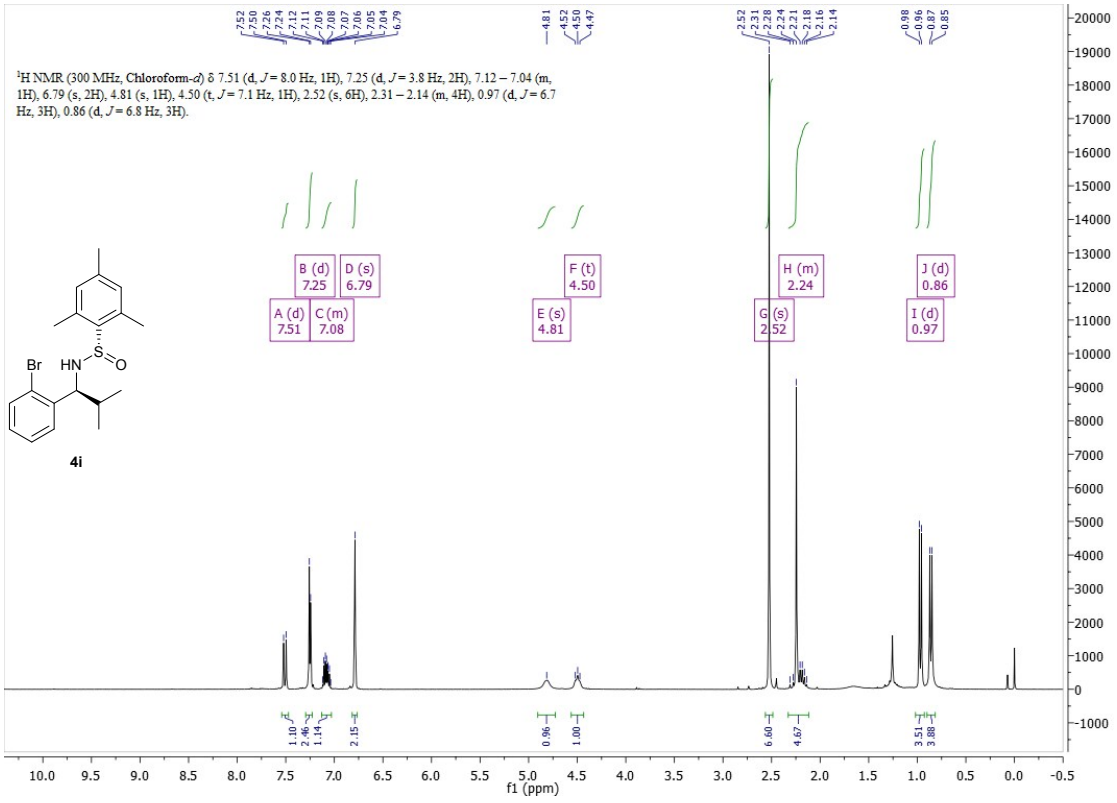

151.8 147.6 141.3 138.7 128.5 127.8 127.7 127.6 123.2 65.7 34.5 33.2 28.3 24.5 24.4 24.0 19.5 18.6
^{13}C NMR (76 MHz, CDCl$_3$) δ 151.8, 147.6, 141.3, 138.7, 128.5, 127.8, 127.7, 127.6, 123.2, 65.7, 34.5, 33.2, 28.3, 24.5, 24.4, 24.0, 19.5, 18.6.
f1 (ppm)

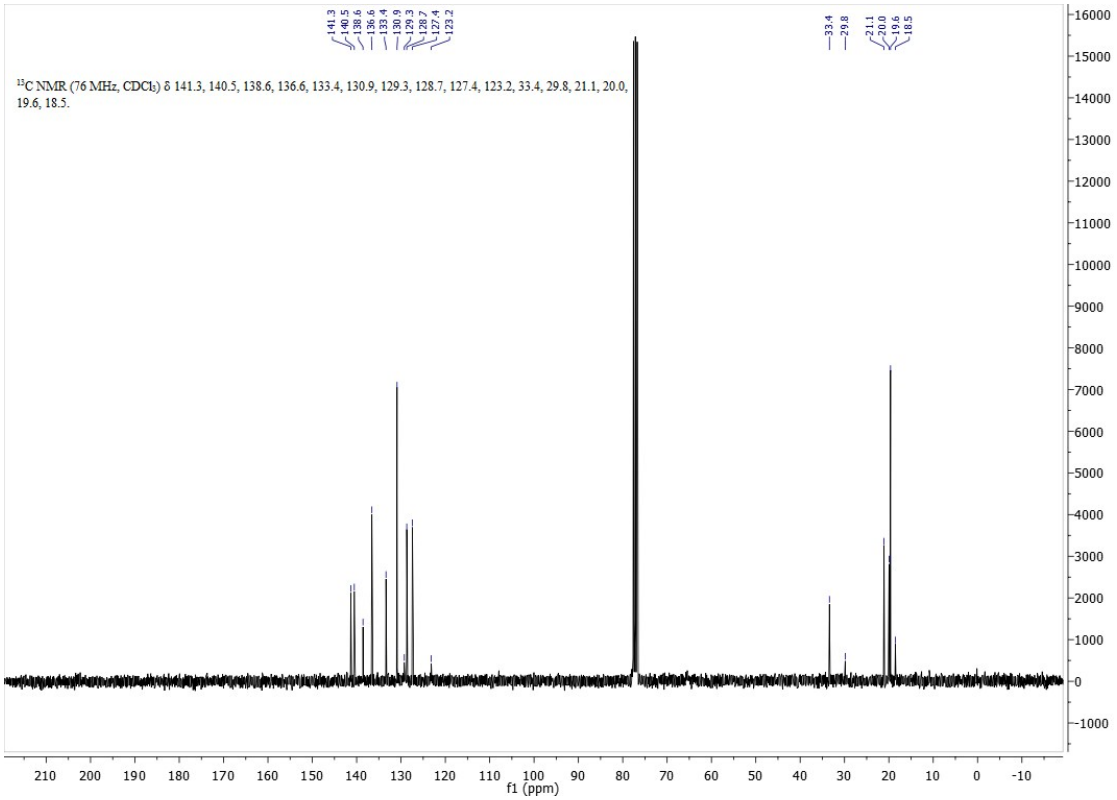

7.14
7.11
7.08
6.82
4.46
4.44
4.20
4.18
4.16
2.52
2.32
2.27
2.24
2.22
2.20
2.18
2.15
0.96
0.94
0.82
0.80
^{1}H NMR (300 MHz, Chloroform-d) δ 7.11 (s, 4H), 6.82 (s, 2H), 4.45 (d, J = 5.2 Hz, 1H), 4.18 (t, J = 5.8 Hz, 1H), 2.52 (s, 6H), 2.32 (s, 3H), 2.27 – 2.15 (m, 4H), 0.95 (d, J = 6.7 Hz, 3H), 0.81 (d, J = 6.7 Hz, 3H).
HN
S
O
4f
B (s) 6.82
A (s) 7.11
D (t) 4.18
C (d) 4.45
F (s) 2.32
E (s) 2.52
G (m) 2.24
I (d) 0.81
H (d) 0.95
3.95
1.96
0.88
1.00
5.63
2.95
4.23
3.06
3.22
f1 (ppm)

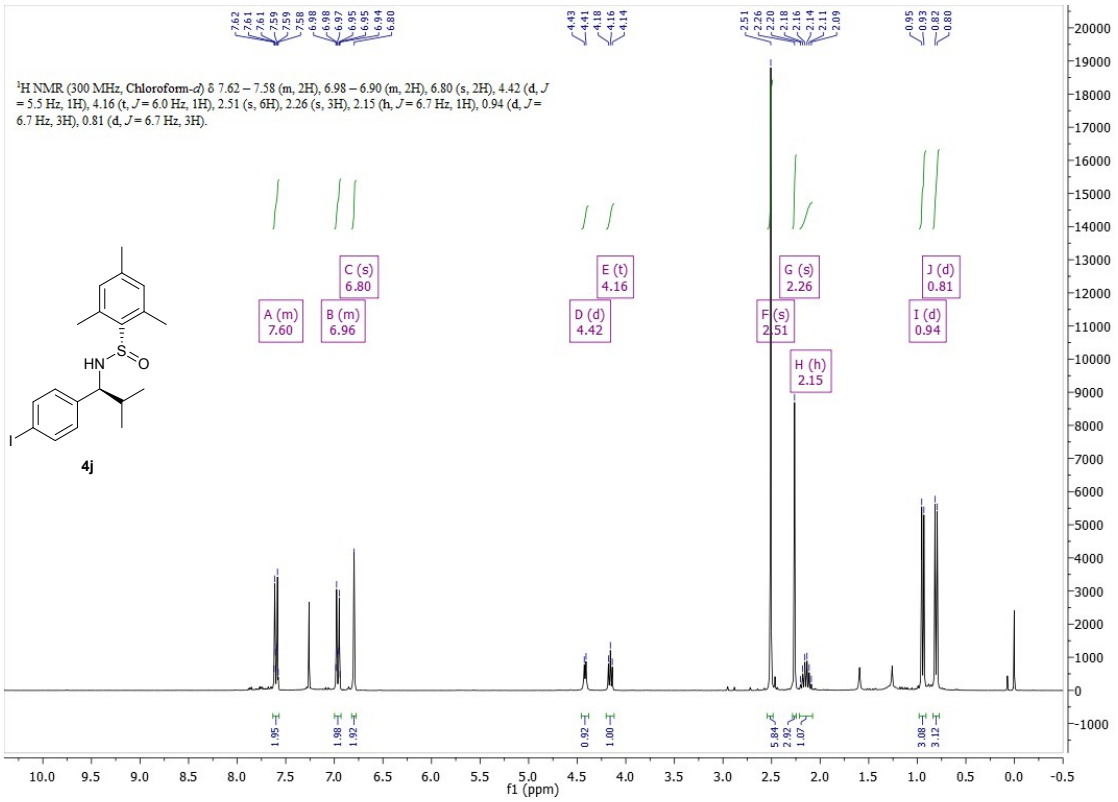

140.6
138.7
138.1
137.1
136.6
132.8
130.9
129.1
127.6
64.9
33.0
29.8
21.2
21.1
19.5
18.6
^{13}C NMR (76 MHz, $CDCl_3$) δ 140.6, 138.7, 138.1, 137.1, 136.6, 132.8, 130.9, 129.1, 127.6, 64.9, 33.0, 29.8, 21.2, 21.1, 19.5, 18.6.
f1 (ppm)

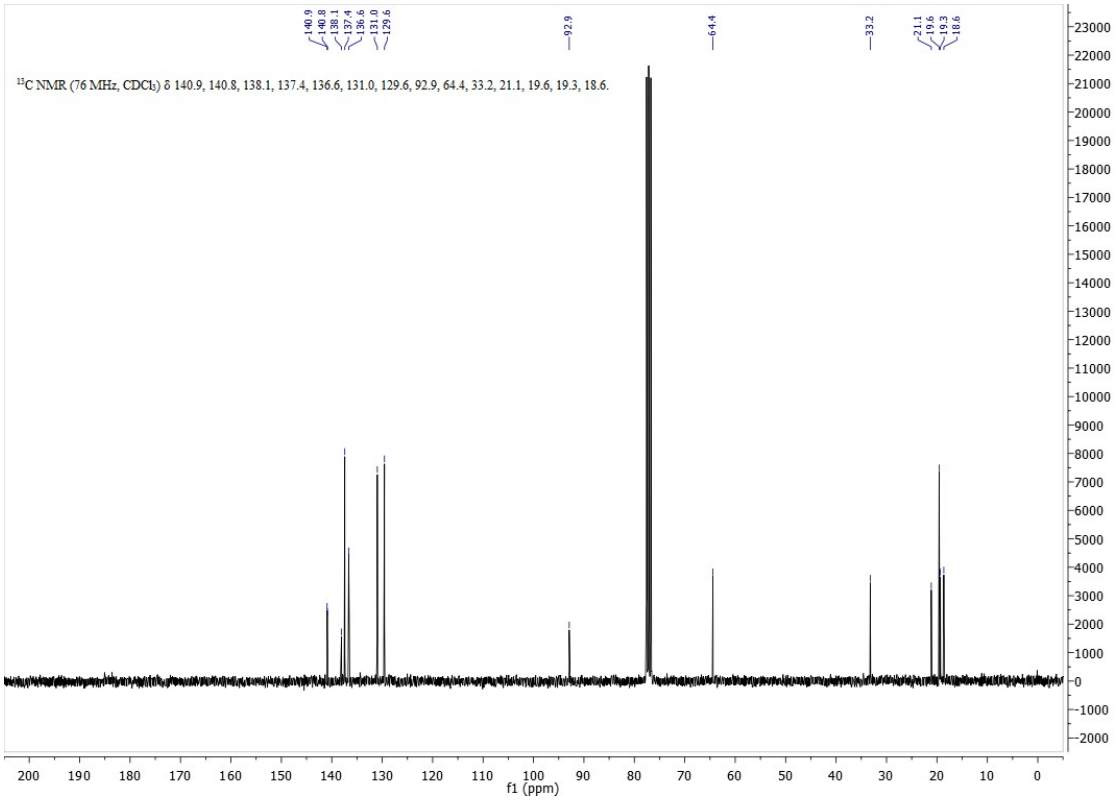

7.56
7.53
7.31
7.29
6.77
4.49
4.47
4.28
4.26
4.24
2.50
2.24
2.19
2.17
2.14
2.12
2.10
2.07
0.96
0.94
0.83
0.80
0.15
¹H NMR (300 MHz, Chloroform-d) δ 7.55 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 6.77 (s, 2H), 4.48 (d, J = 6.0 Hz, 1H), 4.26 (t, J = 6.3 Hz, 1H), 2.50 (s, 6H), 2.24 (s, 3H), 2.19 – 2.07 (m, 1H), 0.95 (d, J = 6.7 Hz, 3H), 0.82 (d, J = 6.7 Hz, 3H).
B (d) 7.30
A (d) 7.55
C (s) 6.77
E (t) 4.26
D (d) 4.48
G (s) 2.24
F (s) 2.50
H (m) 2.13
J (d) 0.82
I (d) 0.95
HN
S
O
N
4h
2.00
1.92
1.94
0.91
1.00
5.82
2.84
1.36
3.40
3.57
f1 (ppm)

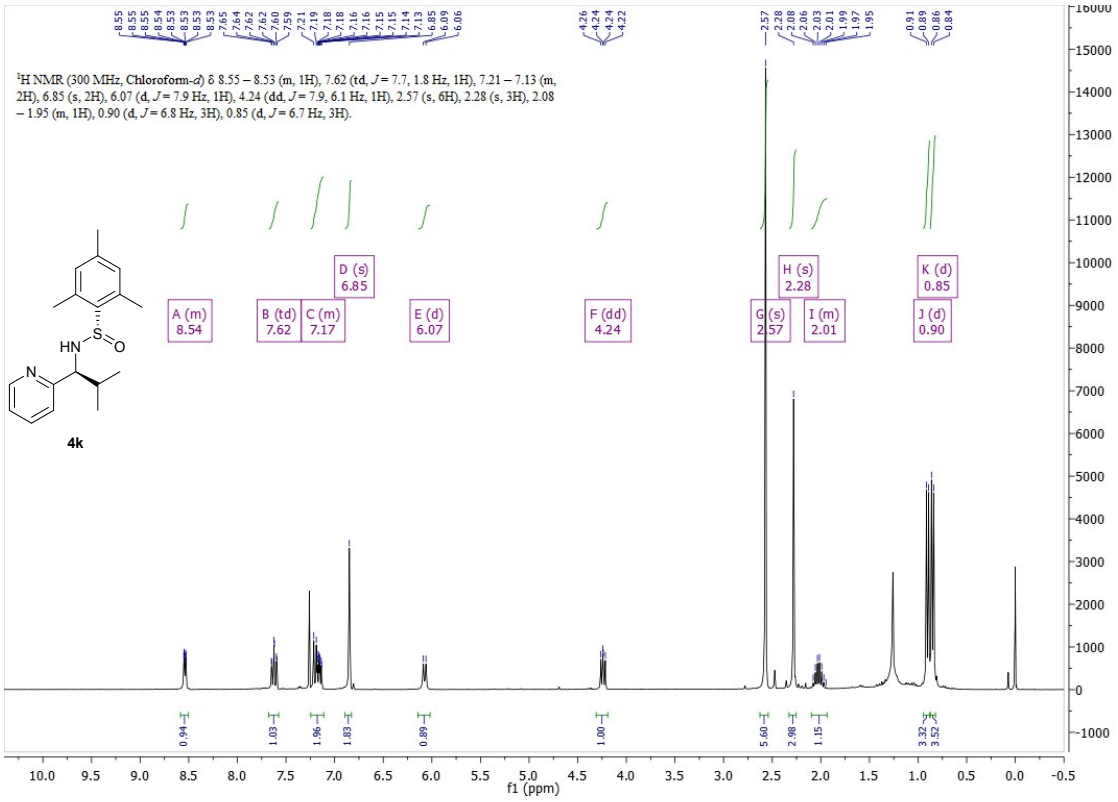

147.0
141.0
137.5
136.7
132.1
131.0
128.2
118.8
111.2
64.4
33.7
31.0
21.0
19.6
19.1
18.9
¹³C NMR (76 MHz, CDCl₃) δ 147.0, 141.0, 137.5, 136.7, 132.1, 131.0, 128.2, 118.8, 111.2, 64.4, 33.7, 31.0, 21.0, 19.6, 19.1, 18.9.
f1 (ppm)


7.52
7.50
7.26
7.24
7.12
7.11
7.09
7.08
7.07
7.06
7.05
7.04
6.79
4.81
4.52
4.50
4.47
2.52
2.31
2.28
2.24
2.21
2.18
2.16
2.14
0.98
0.96
0.87
0.85
^{1}H NMR (300 MHz, Chloroform-d) δ 7.51 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 3.8 Hz, 2H), 7.12 – 7.04 (m, 1H), 6.79 (s, 2H), 4.81 (s, 1H), 4.50 (t, J = 7.1 Hz, 1H), 2.52 (s, 6H), 2.31 – 2.14 (m, 4H), 0.97 (d, J = 6.7 Hz, 3H), 0.86 (d, J = 6.8 Hz, 3H).
B (d) 7.25
D (s) 6.79
A (d) 7.51
C (m) 7.08
F (t) 4.50
E (s) 4.81
H (m) 2.24
G (s) 2.52
J (d) 0.86
I (d) 0.97
Br
HN
S
O
4i
1.10
2.46
1.14
2.15
0.96
1.00
6.60
4.67
3.51
3.88
f1 (ppm)

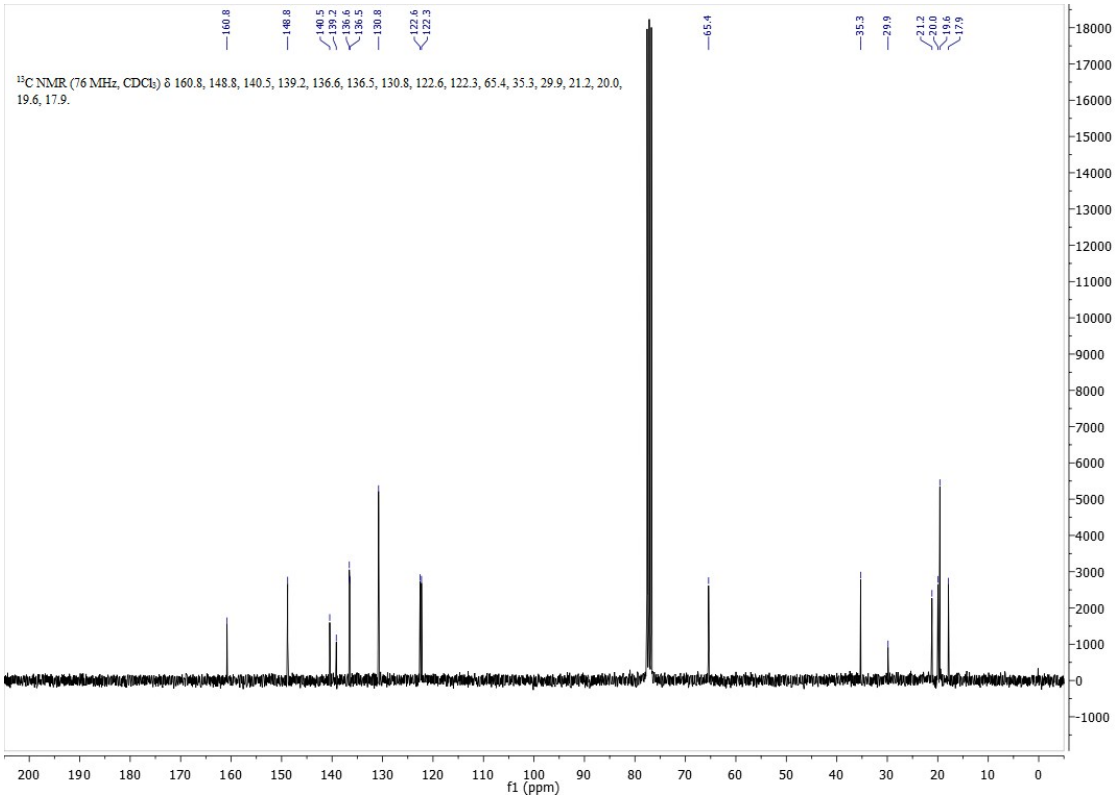

141.3
140.5
138.6
136.6
133.4
130.9
129.3
128.7
127.4
123.2
33.4
29.8
21.1
20.0
19.6
18.5
^{13}C NMR (76 MHz, $CDCl_3$) δ 141.3, 140.5, 138.6, 136.6, 133.4, 130.9, 129.3, 128.7, 127.4, 123.2, 33.4, 29.8, 21.1, 20.0, 19.6, 18.5.
f1 (ppm)

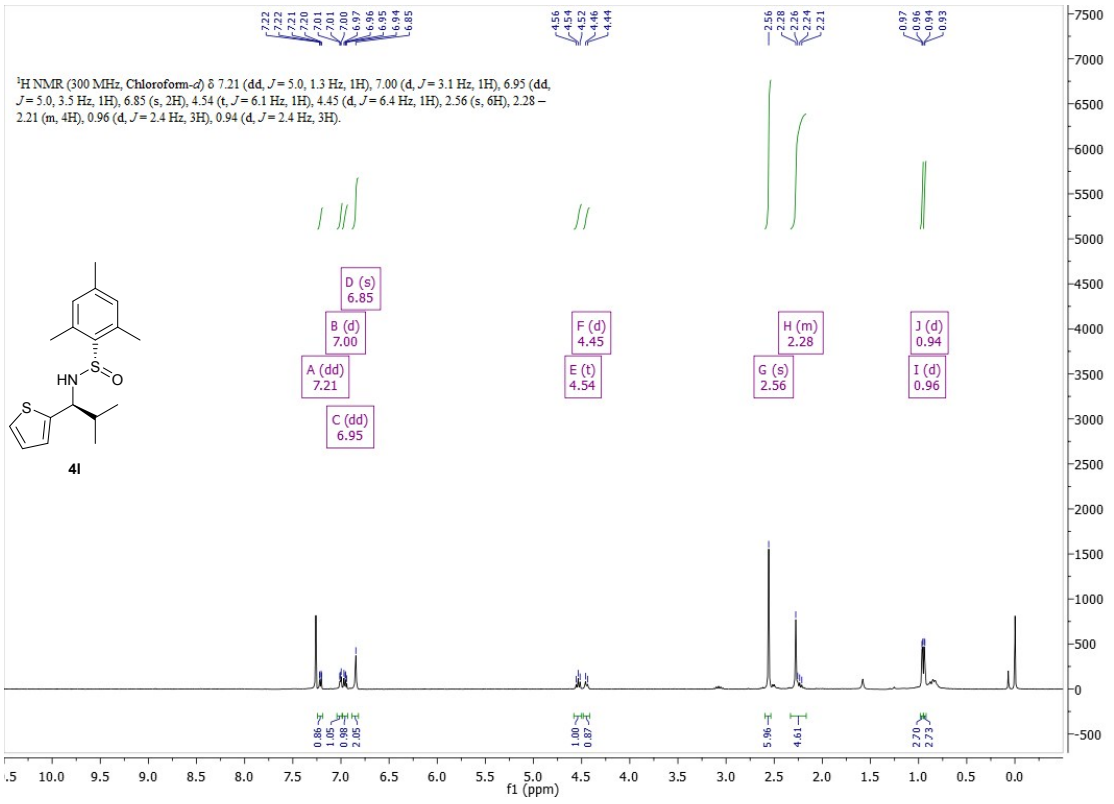

^{1}H NMR (300 MHz, Chloroform-d) δ 7.62 – 7.58 (m, 2H), 6.98 – 6.90 (m, 2H), 6.80 (s, 2H), 4.42 (d, J = 5.5 Hz, 1H), 4.16 (t, J = 6.0 Hz, 1H), 2.51 (s, 6H), 2.26 (s, 3H), 2.15 (h, J = 6.7 Hz, 1H), 0.94 (d, J = 6.7 Hz, 3H), 0.81 (d, J = 6.7 Hz, 3H).
A (m) 7.60
B (m) 6.96
C (s) 6.80
D (d) 4.42
E (t) 4.16
F (s) 2.51
G (s) 2.26
H (h) 2.15
I (d) 0.94
J (d) 0.81
HN
S
O
I
4j
f1 (ppm)

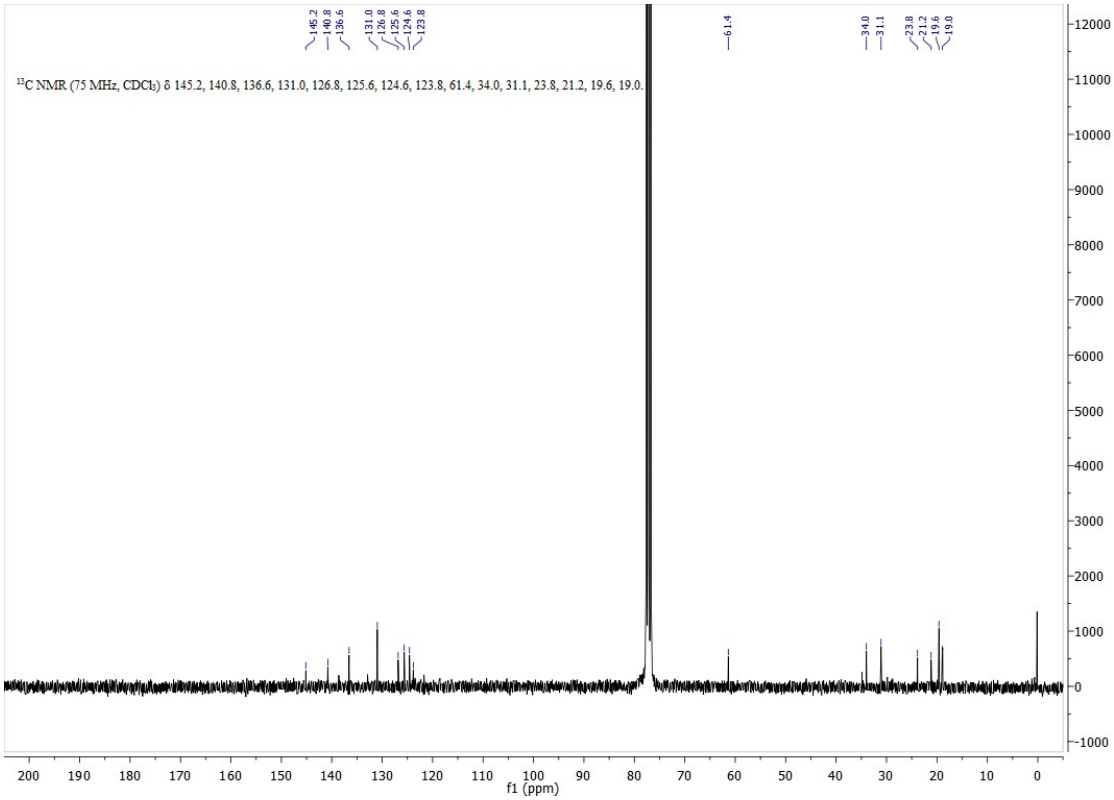

^{13}C NMR (76 MHz, CDCl$_3$) δ 140.9, 140.8, 138.1, 137.4, 136.6, 131.0, 129.6, 92.9, 64.4, 33.2, 21.1, 19.6, 19.3, 18.6.
f1 (ppm)

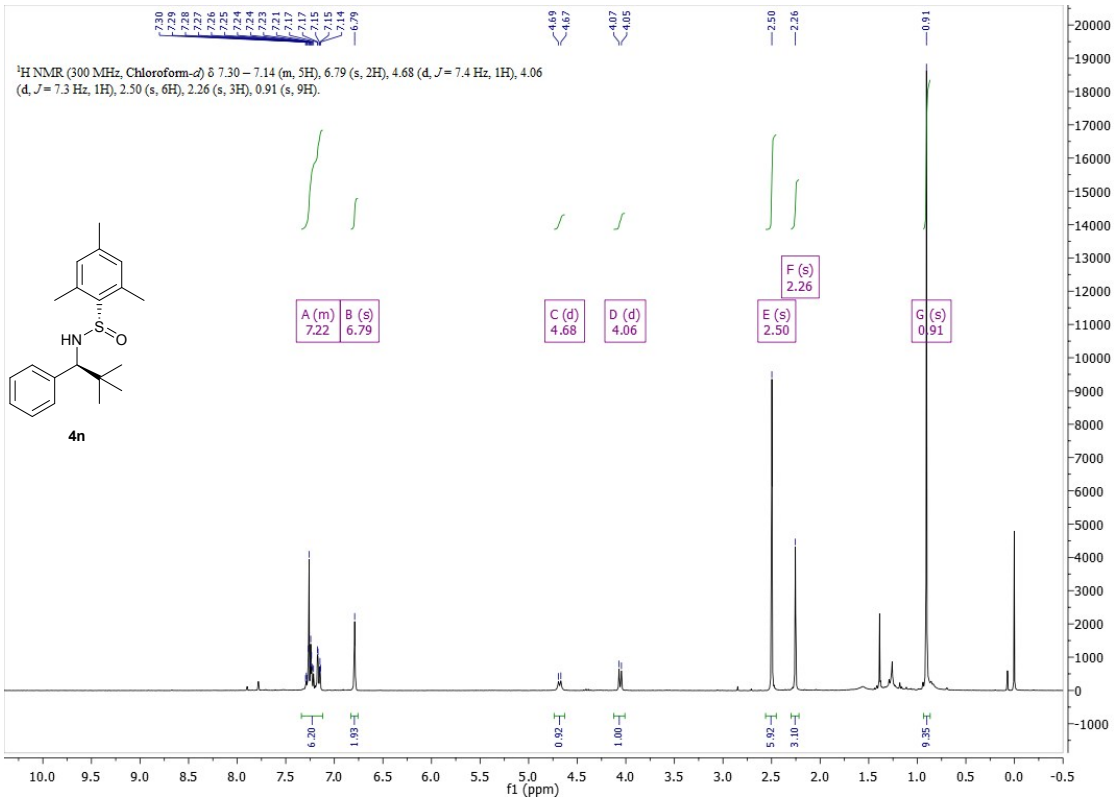

8.55 8.55 8.55 8.54 8.53 8.53 8.53 7.65 7.64 7.62 7.62 7.60 7.59 7.21 7.19 7.18 7.16 7.16 7.15 7.15 7.14 7.13 6.85 6.09 6.06
4.26 4.24 4.24 4.22
2.57 2.28 2.08 2.06 2.03 2.01 1.99 1.97 1.95
0.91 0.89 0.86 0.84
^{1}H NMR (300 MHz, Chloroform-d) δ 8.55 – 8.53 (m, 1H), 7.62 (td, J = 7.7, 1.8 Hz, 1H), 7.21 – 7.13 (m, 2H), 6.85 (s, 2H), 6.07 (d, J = 7.9 Hz, 1H), 4.24 (dd, J = 7.9, 6.1 Hz, 1H), 2.57 (s, 6H), 2.28 (s, 3H), 2.08 – 1.95 (m, 1H), 0.90 (d, J = 6.8 Hz, 3H), 0.85 (d, J = 6.7 Hz, 3H).
A (m) 8.54
B (td) 7.62
C (m) 7.17
D (s) 6.85
E (d) 6.07
F (dd) 4.24
G (s) 2.57
H (s) 2.28
I (m) 2.01
J (d) 0.90
K (d) 0.85
HN
N
O
S
0.94
1.03
1.96
1.83
0.89
1.00
5.60
2.98
1.15
3.32
3.52
f1 (ppm)

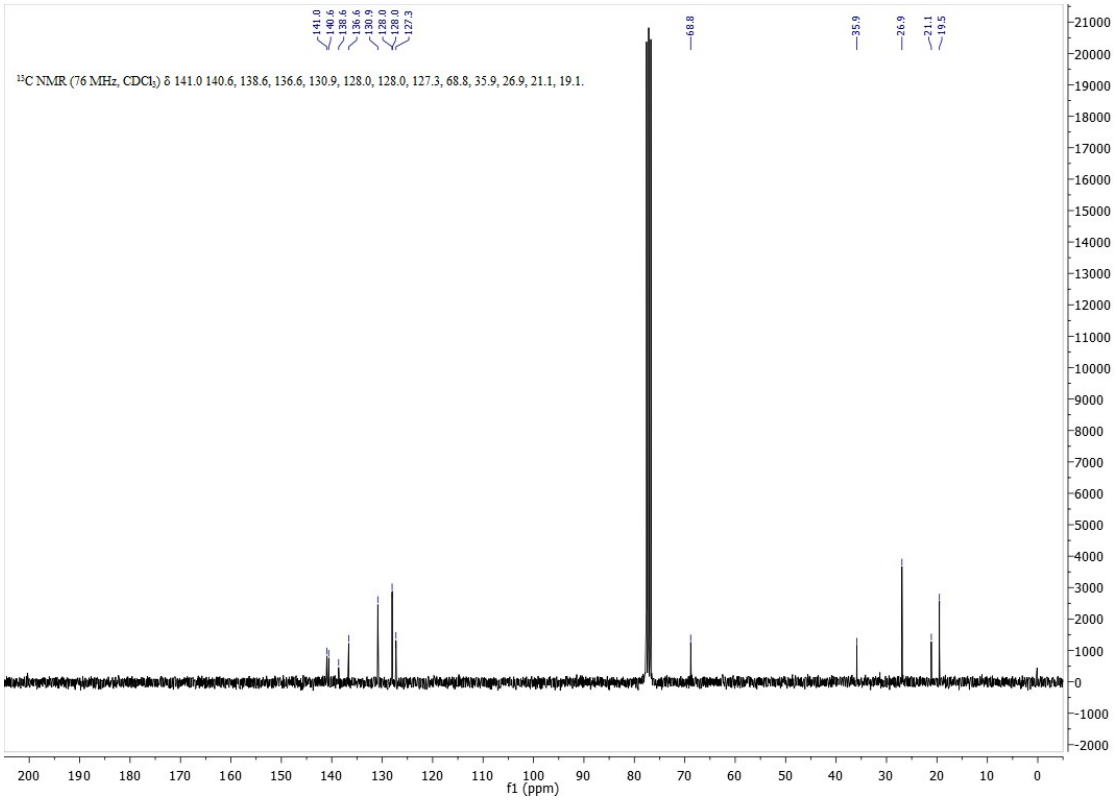
4k

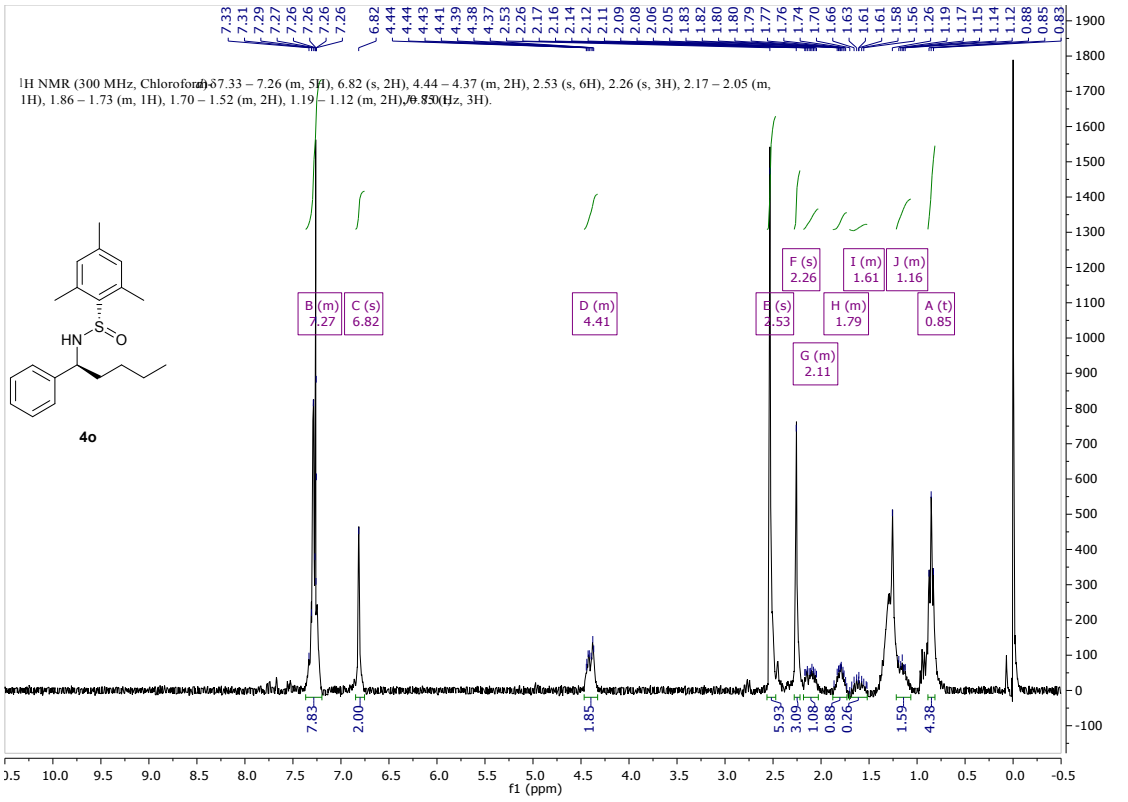

160.8
148.8
140.5
139.2
136.6
136.5
130.8
122.6
122.3
65.4
35.3
29.9
21.2
20.0
19.6
17.9
^{13}C NMR (76 MHz, $CDCl_3$) δ 160.8, 148.8, 140.5, 139.2, 136.6, 136.5, 130.8, 122.6, 122.3, 65.4, 35.3, 29.9, 21.2, 20.0, 19.6, 17.9.
f1 (ppm)

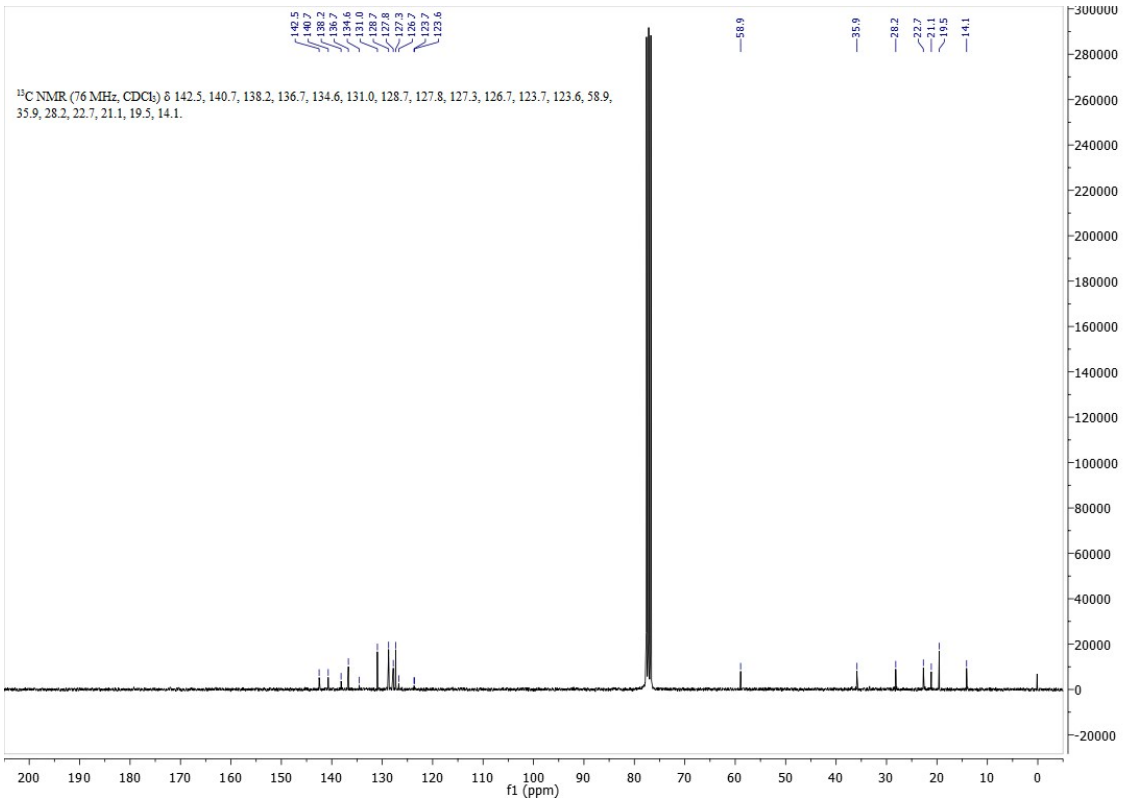

^{1}H NMR (300 MHz, Chloroform-d) δ 7.21 (dd, J = 5.0, 1.3 Hz, 1H), 7.00 (d, J = 3.1 Hz, 1H), 6.95 (dd, J = 5.0, 3.5 Hz, 1H), 6.85 (s, 2H), 4.54 (t, J = 6.1 Hz, 1H), 4.45 (d, J = 6.4 Hz, 1H), 2.56 (s, 6H), 2.28 – 2.21 (m, 4H), 0.96 (d, J = 2.4 Hz, 3H), 0.94 (d, J = 2.4 Hz, 3H).
D (s) 6.85
B (d) 7.00
A (dd) 7.21
C (dd) 6.95
F (d) 4.45
E (t) 4.54
H (m) 2.28
G (s) 2.56
J (d) 0.94
I (d) 0.96
HN
S
O
S
4l
f1 (ppm)


^{13}C NMR (75 MHz, CDCl$_3$) δ 145.2, 140.8, 136.6, 131.0, 126.8, 125.6, 124.6, 123.8, 61.4, 34.0, 31.1, 23.8, 21.2, 19.6, 19.0.
f1 (ppm)


^{1}H NMR (300 MHz, Chloroform-d) δ 7.30 – 7.14 (m, 5H), 6.79 (s, 2H), 4.68 (d, J = 7.4 Hz, 1H), 4.06 (d, J = 7.3 Hz, 1H), 2.50 (s, 6H), 2.26 (s, 3H), 0.91 (s, 9H).
A (m) 7.22
B (s) 6.79
C (d) 4.68
D (d) 4.06
E (s) 2.50
F (s) 2.26
G (s) 0.91
4n
f1 (ppm)


^{13}C NMR (76 MHz, $CDCl_3$) δ 141.0 140.6, 138.6, 136.6, 130.9, 128.0, 128.0, 127.3, 68.8, 35.9, 26.9, 21.1, 19.1.
f1 (ppm)


1H NMR (300 MHz, Chloroform-d) δ 7.33 – 7.26 (m, 5H), 6.82 (s, 2H), 4.44 – 4.37 (m, 2H), 2.53 (s, 6H), 2.26 (s, 3H), 2.17 – 2.05 (m, 1H), 1.86 – 1.73 (m, 1H), 1.70 – 1.52 (m, 2H), 1.19 – 1.12 (m, 2H), 0.85 (t, J = 7.3 Hz, 3H).
B (m) 7.27
C (s) 6.82
D (m) 4.41
E (s) 2.53
F (s) 2.26
G (m) 2.11
H (m) 1.79
I (m) 1.61
J (m) 1.16
A (t) 0.85
4o
f1 (ppm)


13C NMR (76 MHz, CDCl3) δ 142.5, 140.7, 138.2, 136.7, 134.6, 131.0, 128.7, 127.8, 127.3, 126.7, 123.7, 123.6, 58.9, 35.9, 28.2, 22.7, 21.1, 19.5, 14.1.
f1 (ppm)

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