SUPPORTING INFORMATION

# A Metal-Free Route to Substituted Imidazolidines via Ring-Opening Cyclization (ROC) of Activated Aziridines with *N*-Benzylanilines: DA-COP Catalyzed Photo-Oxidative C-H Activation

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**Experimental Materials**

All the commercially available reagents and solvents were used without further purification. *Tris*(4-bromophenyl)amine, $Pd(PPh_3)_4$, and cuprous iodide were purchased from Sigma-Aldrich chemical co., Ethynyl trimethyl silane, Tetrahydrofuran (THF), and Triethylamine ($NEt_3$), DMF, Acetonitrile, Phenanthrene-9,10-dione, Bromopyrrolidine-2,5-dione, Chloramine-T•$3H_2O$, PTAB were obtained from Spectrochem Pvt. Ltd.

**Physical Measurements**

NMR spectra were recorded either on a JEOL 400 MHz spectrometer or JEOL 500 MHz spectrometer operating and mentioned in each synthesis procedure. The following notations have been used to describe splitting patterns of $^1H$ NMR signals: s = singlet, d = doublet, t = triplet, m = multiplate, dd = doublet of doublets and ddd = doublet of doublet of doublets. High-resolution mass Spectra (HRMS) were recorded on an Agilent 6538 Ultra High Definition (UHD) Accurate-Mass Q-TOF-LC/MS system using electrospray ionization (ESI) mode. Elemental analyses were carried out using a Thermo Fischer Flash 2000 Elemental Analyzer. Thermogravimetric analyses (TGA) were performed using Metler Toledo instrument under $N_2$ atmosphere (flow rate = 50 mL $min^{-1}$, temperature range 30-800 ˚C, and heating rate = 3 ˚C $min^{-1}$). FT-IR spectra were measured utilizing a Bruker IFS 66 v/S spectrophotometer (KBr pellets, 4000-400 $cm^{-1}$). UV-Vis spectrum was recorded on Perkin Elmer Lambda 900 UV-Vis Spectrometer. Field Emission Scanning Electron Microscopic (FESEM) samples were prepared by dispersing organic polymers in acetonitrile followed by drop-casting on aluminum foil. Micrographs were recorded on JSM-7100F, JEOL.

**Photocatalytic device:**

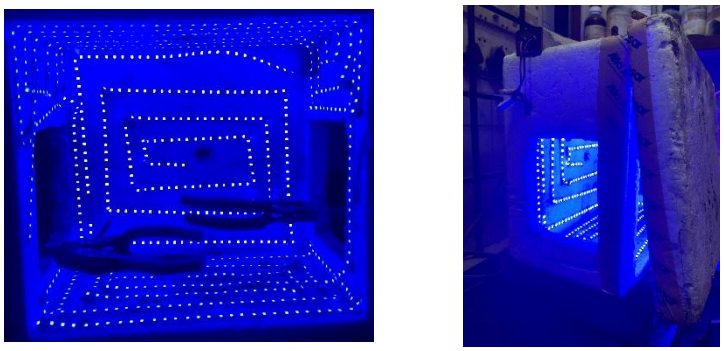


**Figure S1:** A generic LED strap wrapped in a Thermocol box.

**X-ray crystallographic studies:**

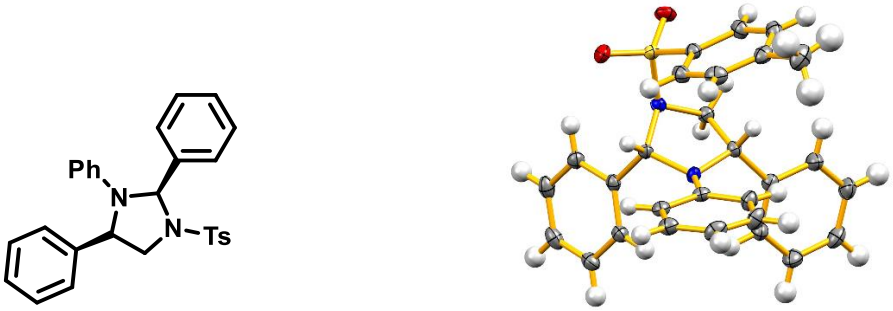



**Figure S2:** ORTEP diagram of compound **10a** (CCDC 2295792) with 50% ellipsoid probability.

Single crystal samples were prepared by slow evaporation in the presence of a solvent mixture of dichloromethane/*n*-pentane (1:9). The crystals used in the analysis were glued to glass fiber and mounted on a Bruker SMART APEX CCD diffractometer with, graphite monochromated Mo-Ka (0.71073 Å) radiation at 100(2) K. Cell constants were obtained from the least-squares refinement of three-dimensional centroids through CCD recording narrow ω rotation frames, completing almost all reciprocal space in the stated θ range. All data were collected with SMART 5.628 and were integrated with the SAINT[1] program. An empirical absorption correction was applied to collect reflections with SADABS[2] using XPREP.[3] The structures were solved with SHELXT and refined with the SHELXL–2018/3[4,5], incorporated into the Olex2 1.3–alpha crystallographic collective package[6]. The space group of the compounds was determined based on the lack of systematic absence and intensity statistics. Full-matrix least squares/difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms are fixed by using geometrical constraints using idealized geometries. All the hydrogen atoms have been defined isotropically. OMIT command was used to remove the insufficient quality data at a low angle with h k l value -2, 0, 2.; -1, 0, 3.; 1, 1, 0.; 2, 0, 0.; -1, 1, 1.

| **Table S1 Crystal data and structure refinement for 10a.** | |
|---|---|
| Identification code | CCDC 2295792 |
| Empirical formula | $C_{56}H_{52}N_4O_4S_2$ |
| Formula weight | 909.13 |

| | |
|---|---|
| Temperature/K | 100(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ (14) |
| a/Å | 18.3937(9) |
| b/Å | 9.9807(5) |
| c/Å | 26.3497(13) |
| α/° | 90 |
| β/° | 104.753(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 4677.9(4) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.291 |
| μ/mm$^{-1}$ | 0.167 |
| F(000) | 1920.0 |
| Reflections collected | 74560 |
| Independent reflections | 11675 [$R_{int}$ = 0.0542, $R_{sigma}$ = 0.0363] |
| Data/restraints/parameters | 11675/0/597 |
| Goodness-of-fit on $F^2$ | 1.077 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0462, $wR_2$ = 0.1049 |
| Final R indexes [all data] | $R_1$ = 0.0629, $wR_2$ = 0.1157 |

$^{a}R1 = \sum ||F_o| - |Fc||/\sum|F_o|$. $^{b}wR_2 = \{\sum [w\,(|Fo|^2 - |Fc|^2)^2]/\sum [w(|Fo|^2)^2]\}^{1/2}$

**References:**


1. SAINT+ 6.02ed.; Bruker AXS, Madison, WI, 1999.
2. Sheldrick, G. M. SADBAS, Empirical Absorption Correction Program, University of Göttingen, Göttingen, Germany, 1997.
3. XPREP, 5.1ed. Siemens Industrial Automation Inc., Madison, WI, 1995.
4. G.M. Sheldrick, *SHELXL-2016*, *Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 2014.
5. G. M. Sheldrick, *Acta Crystallogr. C Struct. Chem. ACTA CRYSTALLOGR C* 2015, **C71**, 3–8.
6. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339–341.

***General procedure for the synthesis of 2,3,4-triaryl-1-tosylimidazolidine*.** (±)-**10a**

In single neck round-bottom flask, aziridine (±)-**8a** (0.110 mmol), benzylaniline **7a** (0.111 mmol) dissolved in MeOH (0.1mL) were introduced and the reaction mixture was kept for stirring at room temperature. The progress of the reaction was monitored by TLC analysis. After completion, the crude product was purified by flash column chromatography on silica gel using 7% ethyl acetate in petroleum ether as the eluent to obtain the pure product (±)-**9a** (0.107 mmol). In the second step, compound (±)-**9a** (0.107 mmol), **TPA-PQ** (5.0 mg) and MeOH (1.5 mL) were taken in a single neck round-bottom flask followed by the purging the reaction mixture with oxygen for 15 min and the reaction mixture was put for stirring under $O_2$ atmosphere using $O_2$-balloon in the presence of Blue LED (18W) light source. The completion of the reaction was monitored by TLC analysis. After completion, the reaction mixture was filtered out to recover the polymer catalyst and the crude concentrate was purified by flash column chromatography on a silica gel (200-400 mesh) using 3% ethyl acetate in petroleum ether as the eluent to afford the pure product (±)-**10a**.

**Selected Spectral Data**

***Synthesis of tris(4-((trimethylsilyl)ethynyl)phenyl)amine (1a)*.**

In a double neck round-bottom flask, *tris*(4-bromophenyl)amine (**1**) (300 mg, 0.622 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (216 mg, 0.186 mmol, 0.3 equiv.), CuI (82.0 mg, 0.424 mmol, 0.6 equiv.) and trimethylsilyl acetylene (1.20 mL, 7.468 mmol, 12.0 equiv.) were kept under an Ar atmosphere. A mixture of DMF (6 mL) and triethylamine (3 mL) was thoroughly degassed using freeze-pump-thaw process and added to the reaction flask. The reaction mixture was heated at 70 ˚C for 12 h. The progress of the reaction was monitored by TLC analysis. After the completion, the resulting mixture was concentrated by a rotary evaporator under vacuum and the crude compound was purified using flash column chromatography to afford the compound **1a** (0.561 mmol, 300 mg) in 90% yield as a light-yellow solid: mp = 162-164 ˚C; $R_f$ = 0.70 (in10% ethyl acetate in petroleum ether); IR $\nu_{max}$ (KBr, $cm^{-1}$) 3034, 2956, 2897, 2157, 1917, 1595, 1505, 1493, 1408, 1320, 1281, 1270, 1248, 1226, 1177, 1114, 1012, 867, 835, 758, 725, 696, 649, 635, 595, 545; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.33 (d, 6H, $J$ = 10.0 Hz), 6.95 (d, 6H, $J$ = 10.0 Hz), 0.23 (s, 27H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) $\delta$ 146.9, 133.2, 123.9, 117.8, 104.9, 94.0, 0.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{33}H_{40}NSi_3$ is 534.2464; found 534.2446.

***Synthesis of tris(4-ethynyl phenyl)amine (1b).***

In a single neck round-bottom flask, *tris*(4-((trimethylsilyl) ethynyl) phenyl)amine (**1a**) (287 mg, 0.538 mmol, 1.0 equiv.) and $Na_2CO_3$ (223 mg, 2.096 mmol, 4.0 equiv.) were dissolved in MeOH (5.0 mL) and the reaction mixture was kept on stirring at room temperature for 3 h. The completion of the reaction was observed by TLC. After completion, the reaction mixture was filtered out and the crude compound was purified by flash column chromatography to afford the desilylated product **1b** (0.441 mmol, 140 mg) in 82% yield as a light-yellow solid: mp = 108-110 ˚C; $R_f$ = 0.40 (in10% ethyl acetate in petroleum ether); IR $\nu_{max}$ (KBr, $cm^{-1}$) 3277, 3266, 3067, 3036, 2101, 1598, 1498, 1318, 1288, 1271, 1175, 1110, 836, 761, 723, 674, 662, 639, 558, 539; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.37 (d, 6H, $J$ = 10.0 Hz), 7.00 (d, 6H, $J$ = 10.0 Hz), 3.04 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) $\delta$ 147.1,133.4, 124.0, 116.9, 83.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{16}N$ is 318.1278; found 318.1275.

***Synthesis of 2,7-dibromophenanthrene-9,10-dione (4).***

In a single neck round-bottom flask, phenanthrene-9,10-dione (**2**) (1.0 g, 4.082 mmol, 1.0 equiv.) was mixed in 27 mL of conc. $H_2SO_4$ **(**98%) followed by the addition of 1-bromopyrrolidine-2,5-dione (**3**) (1.20 g, 10.282 mmol, 2.5 equiv.), the reaction mixture was kept on stirring at room temperature for 8 h. After completion of the reaction, ice water was added to the reaction mixture to give an orange precipitate. The precipitate was filtered out to afford compound **4** (1.30 g, 3.551 mmol) in 86% yield as a deep orange solid: mp = 272-274 ˚C; IR$\nu_{max}$ (KBr, $cm^{-1}$) 3100, 3067, 1677, 1580, 1460, 1400, 1308, 1292, 1265, 1223, 1204, 1141,1079, 904, 826, 707, 456; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 8.19 (d, 2H, $J$ = 10.0 Hz), 8.02 (d, 2H, $J$ = 3.0 Hz), 7.90 (dd, 2H, $J$ = 2.5, 5.0 Hz); HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_7Br_2O_2$ is 366.8787, found 366.8786.

***Synthesis of TPA-PQ.***

In a double neck round-bottom flask *tris*(4-((trimethylsilyl)ethynyl) phenyl)amine (**1b**) (110 mg, 0.346 mmol, 1.0 equiv.), 2,7-dibromophenanthrene-9,10-dione (**4**) (190 mg, 0.519 mmol, 1.5 equiv.) and $Pd(PPh_3)_4$ (120 mg, 0.103 mmol, 0.3 equiv.) were kept under Ar atmosphere. A mixture of DMF (6 mL) and triethylamine (3 mL) was thoroughly degassed using freeze-pump-thaw process and added to the reaction flask. The reaction mixture was stirred at 90-100 ˚C for 12 h for completion of the cross-coupling reaction. After the completion of the reaction, a black precipitate was obtained. The precipitate was purified by washing with THF and followed by boiling DMF to remove the oligomer units that can be present in the reaction mixture. The polymer residue was further Soxhlated by THF to remove the residual palladium catalyst to afford the polymer (**TPA-PQ**) as a black solid. The obtained black solid polymer

was dried under vacuum at 90 ˚C for 4 h to give 50 mg of the pure polymer (**TPA-PQ**). IR $\nu_{max}$ (KBr, $cm^{-1}$) 3032, 2188, 1681, 1589, 1498, 1436, 1315, 1266, 1175, 1104, 997, 913, 828, 747, 723, 691, 650, 628; Anal. Calcd. for $C_{54}H_{30}N_2O_2$: C, 66.15; H, 4.56; N, 2.76. Found: C, 66.69; H, 4.42, N, 2.87.

***General procedure for the synthesis of (±)-2-phenyl-N-tosyl aziridine (8a) and derivatives*.**

In a double-neck RB flask, chloramine-T trihydrate (2.762 g, 9.601 mmol, 1.1 equiv.), PTAB (328 mg, 0.873 mmol, 0.1 equiv.) were taken under an Ar environment, and after the addition of $CH_3CN$ (15 mL), the reaction mixture was kept for stirring for 30 min at room temperature. Next, styrene (1.0 mL, 8.728 mmol, 1.0 equiv.) was added to the reaction mixture dropwise and left for stirring at the same temperature for 5 h. After completion, the reaction was quenched with water, and the mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous $Na_2SO_4$, and the solvent was evaporated under reduced pressure. The crude concentrate was purified by flash column chromatography on a silica gel using 5% ethyl acetate in petroleum ether as the eluent to afford the pure product (±)-2-phenyl-*N*-tosyl aziridine (**8a**) (1383 mg, 5.062 mmol) as a white solid in 58% yield: mp 88-89 ˚C; $R_f$ = 0.43 (in 20% ethyl acetate in petroleum ether); IR $\upsilon_{max}$ (KBr, $cm^{-1}$) 3036, 2958, 1667, 1594, 1494, 1458, 1379, 1156; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.87 (d, 2H, $J$ = 8.6 Hz), 7.33 (d, 2H, $J$ = 8.0 Hz), 7.29-7.26 (m, 3H), 7.22-7.20 (m, 2H), 3.77 (dd, 1H, $J$ = 7.4, 4.0 Hz), 2.98 (d, 1H, $J$ = 7.4 Hz), 2.43 (s, 3H), 2.38 (d, 1H, $J$ = 4.6 Hz); $^{13}$C {$^1$H} NMR ($CDCl_3$, 125 MHz) $\delta$ 144.7, 135.2, 135.1, 129.8, 128.6, 128.4, 128.0, 126.6, 41.1, 36.0, 21.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{16}NO_2S$ is 274.0897; found 274.0896.

***General procedure for the synthesis of N-benzylamine (7a) and its derivative (7b, 7c)*.**

In a double neck round-bottom flask, aniline (1.5 mL, 16.838 mmol, 2.0 equiv.), $CsCO_3$ (6.0 g, 16.838 mmol, 2.0 equiv.), 10 mL acetonitrile as the solvent were introduced followed by the dropwise addition of benzyl bromide (1.0 mL, 8.419 mmol, 1.0 equiv.) under Ar atmosphere. The reaction mixture was kept for stirring at room temperature for 24 h. The progress of the reaction was monitored by TLC analysis. After completion, the reaction was quenched by water and the organic layer was extracted by ethyl acetate and after removal of the solvent under reduced pressure a crude concentrate was obtained which was purified by flash column chromatography to afford the pure product **7a** (800 mg, 4.365 mmol) in 52% yield as semi-solid: $R_f$ = 0.60 (in 10% ethyl acetate in petroleum ether); IR $\upsilon_{max}$ (KBr, $cm^{-1}$) 3419, 3083, 3052, 3025, 2920, 2853, 1602, 1506, 1471, 1452, 1430, 1360, 1298, 1267, 1252, 1179, 1154, 1113, 1098, 1177, 1064, 869, 731, 749, 693, 510; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.87 (d, 2H, $J$ = 8.6

Hz), 7.33 (d, 2H, *J* = 8.0 Hz), 7.29-7.26 (m, 3H), 7.22-7.20 (m, 2H), 3.77 (dd, 1H, *J* = 7.4, 4.0 Hz), 2.98 (d, 1H, *J* = 7.4 Hz), 2.43 (s, 3H), 2.38 (d, 1H, *J* = 4.6 Hz); $^{13}C$ {$^{1}H$} NMR ($CDCl_3$, 125 MHz) $\delta$ 144.7, 135.2, 135.1, 129.8, 128.6, 128.4, 128.0, 126.6, 41.1, 36.0, 21.7; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}N$ is 184.1121; found 184.1121.

***N-(2-(Benzyl(phenyl)amino)-2-phenylethyl)-4-methylbenzenesulfonamide (*(±)*-9a).***

The general method A described above was followed when racemic (±)-2-phenyl-*N*-tosyl aziridine (**8a)** (30.1 mg, 0.109 mmol, 1.0 equiv.) was reacted with *N*-benzylaniline (**7a)** (20.0 mg, 0.110 mmol, 1.01 equiv.) in MeOH (0.1 mL) as the solvent at room temperature for 7 h to afford the ring-opening product (±)-**9a** (49.0 mg, 0.107 mmol) in 98% yield as a white solid: mp 118-120 ˚C; $R_f$ = 0.30 (in 20% ethyl acetate in petroleum ether); IR $\nu_{max}$ (KBr, $cm^{-1}$) 3060, 3029, 2925, 1597, 1501, 1451, 1383, 1329, 1248, 1185, 1161, 1093, 1029, 988, 895, 814, 749, 697, 665, 551, 513; $^{1}H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 7.50 (d, 2H, *J* = 5.0 Hz), 7.08-7.30 (m, 14H), 6.77-6.83 (m, 3H), 5.09 (dd, 1H, *J* = 5.0, 10.0 Hz), 4.67 (dd, 1H, *J* = 5.0, 10.0 Hz), 4.28 (d, 1H, *J* = 15.0 Hz), 4.17 (d, 1H, *J* = 20.0 Hz), 3.54-3.59 (m, 1H), 3.28-3.33 (m, 1H), 2.40 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) $\delta$ 149.1, 143.5, 139.2, 137.3, 136.5, 129.8, 129.3, 128.91, 128.87, 128.0, 127.5, 127.2, 21.5, 44.4, 50.6, 62.6, 116.2, 119.5, 126.8, 127.1; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{29}N_2O_2S$, is 457.1944; found 457.1991.

***2,3,4-Triphenyl-1-tosylimidazolidine (*(±)*-10a).***

The general method A described above was followed when racemic (±)-2-phenyl-1-tosylaziridine (**8a**) (30.0 mg, 0.109 mmol, 1.0 equiv.) was reacted with *N*-benzylaniline (**7a**) (20.0 mg, 0.110 mmol, 1.01 equiv.) in MeOH (0.1 mL) as the solvent at room temperature for 7 h to afford the ring-opening product **(±)-9a** (49.0 mg, 0.107 mmol) in 98% yield as a white solid. In the second step, a single neck round-bottom flask was charged with **(±)-9a** (49.0 mg, 0.107 mmol), **TPA-PQ** (5.0 mg), and MeOH (1.5 mL), purged with oxygen and left for stirring in the presence of Blue LED (18 W) light source for 42 h to afford the cyclized product **(±)-10a** (32.0 mg, 0.070 mmol) in 65% yield as a white solid: mp = 168-170 ˚C; $R_f$ = 0.50 (in 10% ethyl acetate in petroleum ether); IR $\nu_{max}$ (KBr, $cm^{-1}$) 3030, 2956, 2924, 2854, 1925, 1741, 1598, 1503, 1450, 1400, 1347, 1303, 1233, 1212, 1195, 1166, 1120, 1088, 1058, 1026, 1007, 990, 958, 931, 883, 860, 843, 814, 749, 694, 671, 626, 617, 603, 578, 543, 510; $^{1}H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 7.74 (d, 2H, *J* = 10.0 Hz), 7.60 (d, 2H, *J* = 10.0 Hz), 7.35-7.44 (m, 3H), 7.19-7.27 (m, 5H), 7.04 (t, 2H, *J* = 5.0 Hz), 6.98 (d, 2H, *J* = 10.0 Hz), 6.75 (t, 1H, *J* = 5.0 Hz), 6.38 (s, 1H), 6.25 (d, 2H, *J* = 10.0 Hz), 4.28 (dd, 1H, *J* =5.0, 15.0 Hz), 3.89 (dd, 1H, *J* = 5.0,

15.0 Hz), 3.23 (dd, 1H, *J* = 10.0, 15.0 Hz), 2.28 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) $\delta$ 147.3, 144.5, 139.8, 139.4, 134.9, 129.9, 129.0, 128.8, 128.7, 128.6, 127.9, 127.6, 127.3, 126.3, 118.8, 113.3, 80.4, 63.2, 54.2, 21.5; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{27}N_2O_2S$, is 455.1788; found 455.1795.

***4-(4-(Tert-butyl)phenyl)-2,3-diphenyl-1-tosylimidazolidine ((±)-10b).***

The general method A described above was followed when racemic (±)-2-(4-(*tert*-butyl)phenyl)-1-tosylaziridine (**8b)** (36.2 mg, 0.110 mmol, 1.0 equiv.) was reacted with *N*-benzylaniline (**7a)** (20.0 mg, 0.111 mmol, 1.01 equiv.) in MeOH (0.1 mL) as the solvent at room temperature for 6 h to afford the ring-opening product **(±)-9b** (42.0 mg, 0.082 mmol) in 74% yield as a white solid. In the second step, single neck round-bottom flask was charged with **(±)-9b** (42.0 mg, 0.082 mmol), **TPA-PQ** (5.0 mg) and MeOH (1.5 mL), purged with oxygen and left for stirring in the presence of Blue LED (18W) light source for 70 h to afford the cyclized product **(±)-10b** (29.0 mg, 0.057 mmol) in 69% yield as a white solid: mp = 141-143 ˚C; $R_f$ = 0.52 (in 10% ethyl acetate in petroleum ether; IR $\nu_{max}$ (KBr, $cm^{-1}$) 3056, 2963, 2926, 1597, 1502, 1449, 1343, 1237, 1218, 1196, 1169, 1120, 1088, 1052, 989, 959, 941, 865, 831, 814, 742, 702, 686, 670, 623, 582, 566, 541, 509; $^{1}H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 7.74 (d, 2H, *J* = 5.0 Hz), 7.59 (d, 2H, *J* = 10.0 Hz),1.24 (s, 9H), 7.35-7.44 (m, 3H), 7.24-7.26 (m, 3H), 7.11 (d, 2H, *J* = 10.0 Hz), 7.03-7.06 (m, 2H, *J* = 5.0 Hz), 6.96 (d, 2H, *J* = 10.0 Hz), 6.74 (t, 1H, *J* = 5.0 Hz), 6.36 (s, 1H), 6.25 (dd, 2H, *J* = 10.0 Hz), 4.26 (dd, 1H, *J* = 5.0, 15.0 Hz), 3.85 (dd, 1H, *J* = 5.0, 10.0 Hz), 3.23 (dd, 1H, *J* = 10.0, 15.0 Hz), 2.28 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) $\delta$ 150.8, 147.4, 144.4, 139.8, 136.2, 134.9, 129.8, 128.8, 128.7, 128.5, 127.6, 127.3, 126.1, 125.9, 118.7, 113.3, 80.4, 62.8, 54.2, 34.6, 31.3, 21.5; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{35}N_2O_2S$, is 511.2414; found 511.2424.

***2,3-Diphenyl-4-(p-tolyl)-1-tosylimidazolidine ((±)-10c).***

The general method A described above was followed when racemic (±)-2-(*p*-tolyl)-1-tosylaziridine (**9c**) (31.6 mg, 0.110 mmol, 1.01 equiv.) was reacted with *N*-benzylaniline (**7a)** (20.0 mg, 0.111 mmol, 1.01 equiv.) in MeOH (0.1 mL) as solvent at room temperature for 5 h to afford the ring-opening product **(±)-9c** (45.0 mg, 0.096 mmol) in 87% yield as a white solid. In the second step, single neck round-bottom flask was charged with **(±)-9c** (32.0 mg, 0.068 mmol), **TPA-PQ** (5.0 mg), and MeOH (1.5 mL), purged with oxygen and left for stirring in the presence of Blue LED (18W) light source for 70 h to afford the cyclized product **(±)-10c** (24.0 mg, 0.051mmol) as a white solid in 75% yield: mp = 152-154 ˚C; $R_f$ = 0.54 (in 10% ethyl

acetate in petroleum ether); IR $\nu_{max}$ (KBr, $cm^{-1}$) 2921, 1598, 1500, 1449, 1350, 1207, 1164, 1089, 1019, 960, 813, 749, 694, 671, 581, 543, 512; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 7.73 (d, 2H, $J$ = 7.5 Hz), 7.59 (d, 2H, $J$ = 8.0 Hz), 7.35-7.43 (m, 3H), 6.97 (d, 2H, $J$ = 8.5 Hz), 6.74 (t, 1H, $J$ =7.0 Hz), 6.24 (d, 2H, $J$ = 8.0 Hz), 4.25 (dd, 1H, $J$ = 7.0, 13.5 Hz), 2.27 (s, 3H), 7.01-7.09 (m, 6H), 6.36 (s,1H), 3.85 (dd, 1H, $J$ = 7.0, 10.5 Hz), 3.21(dd, 1H, $J$ = 10.0, 15.0 Hz), 2.28 (s, 3H);$^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) $\delta$ 147.0, 144.4, 139.8, 137.6, 136.3, 134.9, 129.8, 129.7, 128.8, 128.7, 128.5, 127.6, 21.1, 127.3, 126.3, 118.7, 113.2, 80.4, 62.9, 54.2, 21.6,; HRMS (ESI) m/z: $[M+H]^+$ calcd for, $C_{29}H_{29}N_2O_2S$ is 469.1944; found 469.1940.

***4-(2-Chlorophenyl)-2,3-diphenyl-1-tosylimidazolidine ((±)-10d).***

The general method A described above was followed when (±)-2-(2-chlorophenyl)-1-tosylaziridine (**8d**) (33.8 mg, 0.110 mmol, 1.0 equiv.) was reacted with *N*-benzylaniline (**7a**) (20.3 mg, 0.111 mmol, 1.01 equiv.) in MeOH (0.1 mL) as the solvent at room temperature for 10 h to afford the ring-opening product **(±)-9d** (42.0 mg, 0.085 mmol) in 77% yield as a white solid. In the second step, single neck round-bottom flask was charged with **(±)-9d** (42.0 mg, 0.085 mmol), **TPA**-**PQ** (5.0 mg), and MeOH (1.5 mL), purged with oxygen and left for stirring in the presence of Blue LED (18W) light source for 6 days to afford the cyclized product **(±)-10d** (25.0 mg, 0.051 mmol) in 60% yield as a white solid: mp = 184-186 ˚C; $R_f$ = 0.40 (in 10% ethyl acetate in petroleum ether); IR $\nu_{max}$ (KBr, $cm^{-1}$) 3042, 2924, 2853, 1736, 1595, 1504, 1492, 1469, 1446, 1351, 1322, 1301, 1229, 1208, 1167, 1154, 1091, 1060, 1045, 1031, 1008, 991, 957, 928, 880, 859, 848, 808, 755, 737, 722, 698, 673, 627, 579, 544, 513, 454, 429; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 7.76 (d, 2H, $J$ = 10.0 Hz), 7.61 (d, 2H, $J$ = 10.0 Hz), 7.03-7.45 (m, 5H), 7.02-7.15 (m, 4H), 6.94 (d, 2H, $J$ = 10.0 Hz), 6.76 (t, 1H, $J$ = 5.0 Hz), 6.38 (s, 1H), 6.13 (d, 2H, $J$ = 10.0 Hz), 4.58 (dd, 1H, $J$ = 10.0, 13.5 Hz), 4.17 (dd, 1H, $J$ = 5.0, 10.0 Hz), 3.11 (dd, 1H, $J$ = 10.0, 15.0 Hz), 2.26 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) $\delta$ 147.1, 144.6, 139.8, 136.5, 134.6, 132.3, 129.9, 129.8, 129.1, 128.9, 128.8, 128.6, 127.8, 127.7, 127.6, 127.1, 21.5, 119.1, 113.3, 80.5, 60.8, 52.1; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{26}ClN_2O_2S$ is 489.1398; found 489.1403.

Note: when the reaction mixture was purged with $O_2$ for 2 h, the cyclization step was completed in 96 h with slight increment in yield (64%) of the product (±)-**10d**.

***4-(3-Chlorophenyl)-2,3-diphenyl-1-tosylimidazolidine ((±)-10e).***

The general method A described above was followed when (±)-2-(3-chlorophenyl)-1-tosylaziridine (**8e)** (33.8 mg, 0.110 mmol, 1.0 equiv.) was reacted with *N*-benzylaniline (**7a)**

(20.3 mg, 0.111 mmol, 1.01 equiv.) in MeOH (0.1 mL) as the solvent at room temperature for 15 h to afford the ring-opening product **(±)-9e** (43.0 mg, 0.087 mmol) in 79% yield as a white solid. In the second step, single neck round-bottom flask was charged with **(±)-9e** (43.0 mg, 0.087 mmol), **TPA**-**PQ** (5.0 mg), and MeOH (1.5 mL), purged with oxygen and left for stirring in the presence of Blue LED (18W) light source for 7 days to afford the cyclized product **(±)-10e** (20.0 mg, 0.041 mmol) in 47% yield as a white solid: mp = 180-182 ˚C; $R_f$ = 0.35 (in 10% ethyl acetate in petroleum ether); IR $\nu_{max}$ (KBr, $cm^{-1}$) 3061, 2956, 2923, 2853, 1737, 1597, 1576, 1501, 1463, 1350, 1332, 1261, 1233, 1209, 1165, 1089, 1019, 960, 864, 800, 771, 749, 693, 671, 628, 585, 565, 544, 514; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.72 (d, 2H, $J$ = 5.0 Hz), 7.59 (d, 2H, $J$ = 10.0 Hz), 7.36-7.45 (m, 3H), 7.05-7.19 (m, 6H), 6.98 (d, 2H, $J$ = 10.0 Hz), 6.78 (t, 1H, $J$ =10.0 Hz), 6.38 (s, 1H), 6.23 (d, 2H, $J$ = 10.0 Hz), 4.28 (dd, 1H, $J$ = 5.0 Hz, 15.0 Hz), 3.85 (dd, 1H, $J$ = 10.0 Hz, 10.3Hz), 3.20 (dd, 1H, $J$ = 10.0, $J$ = 15.0 Hz), 2.29 (s, 3H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 125 MHz) $\delta$ 147.0, 144.6, 141.7, 139.5, 134.9, 134.7, 130.4, 129.9, 128.9, 128.8, 128.7, 128.2, 127.5, 127.2, 126.5, 124.5, 119.1, 113.2, 80.4, 62.9, 54.1, 21.6; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{26}ClN_2O_2S$ is 489.1398; found 489.1376.

***4-(4-Chlorophenyl)-2,3-diphenyl-1-tosylimidazolidine ((±)-10f).***

The general method A described above was followed when (±)-2-(4-chlorophenyl)-1-tosylaziridine (**8f)** (33.8 mg, 0.110 mmol, 1.0 equiv.) was reacted with *N*-benzylaniline (**7a)** (20.3 mg, 0.111 mmol, 1.01 equiv.) in MeOH (0.1 mL) as the solvent at room temperature for 10 h to afford the ring-opening product **(±)-9f** (46.0 mg, 0.094 mmol) in 85% yield as a white solid. In the second step, single neck round-bottom flask charged with **(±)-9f** (46.0 mg, 0.094 mmol), **TPA**-**PQ** (5.0 mg), and MeOH (1.5 mL), was purged with oxygen and left for stirring in the presence of Blue LED (18W) light source for 6 days to afford the cyclized product **(±)-10f** (22.0 mg, 0.045 mmol) in 48% yield as a white solid: mp = 156-158 ˚C; $R_f$ = 0.48 (in 10% ethyl acetate in petroleum ether); IR $\nu_{max}$ (KBr, $cm^{-1}$) 2924, 2854, 1597, 1497, 1448, 1402, 1348, 1301, 1234, 1210, 1159, 1090, 1014, 956, 942, 922, 883, 847, 822, 809, 751, 739, 720, 692, 681, 669, 649, 623 604, 579, 546, 527, 505, 473, 453; $^1$H NMR ($CDCl_3$, 500 MHz) 7.69 (d, 2H, $J$ = 10.0 Hz), 7.59 (d, 2H, $J$ = 5.0 Hz), 7.35-7.43 (m, 3H ), 7.22 (d, 2H, $J$ = 10.0 Hz), 7.13 (d, 2H, $J$ = 5.0 Hz), 7.05 (t, 2H, $J$ = 8.0 Hz), 6.97 (d, 2H, $J$ = 10.0 Hz), 6.76 (t, 1H, $J$ = 7.25 Hz), 6.37 (s, 1H), 6.22 (d, 2H, $J$ =10.0 Hz), 4.27 (dd, 1H, $J$ = 5.0, 15.0 Hz), 3.88 (dd, 1H, $J$ = 7.5, 10.5 Hz), 3.18 (dd, 1H, $J$ = 11.0, 13.5 Hz), 2.23 (s, 3H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 125 MHz) $\delta$ 147.0, 144.6, 139.6, 138.0, 134.8, 133.6, 129.9, 129.2, 128.9, 128.8, 128.7, 127.8,

127.6, 127.2, 119.1, 113.2, 80.4, 62.6, 54.0, 21.5; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{26}ClN_2O_2S$ is 489.1398; found 489.1399.

***2,3-Diphenyl-1-tosyl-4-(4-(trifluoromethyl)phenyl)imidazolidine ((±)-10g).***

The general method A described above was followed when (±)-1-tosyl-2-(4-(trifluoromethyl)phenyl)aziridine (**8g**) (37.5 mg, 0.110 mmol, 1.0 equiv.) was reacted with *N*-benzylaniline (**7a**) (20.3 mg, 0.111 mmol, 1.01 equiv.) in MeOH (0.1 mL) as the solvent at room temperature for 23 h to afford the ring-opening product **(±)-9g** (48.0 mg, 0.091 mmol) in 83% yield as a white solid. In the second step, single neck round-bottom flask was charged with **(±)-9g** (48.0 mg, 0.091 mmol), **TPA-PQ** (5.0 mg) and MeOH (1.5 mL), purged with oxygen and left for stirring in the presence of Blue LED (18W) light source for 6 days to afford the cyclized product **(±)-10g** (20.0 mg, 0.038 mmol) in 42% yield as a white solid: mp = 83-85 ˚C; $R_f$ = 0.41 (in 10% ethyl acetate in petroleum ether); IR $\nu_{max}$ (KBr, $cm^{-1}$) 3063, 2962, 2925, 2853, 1620, 1598, 1502, 1449, 1417, 1351, 1324, 1264, 1234, 1203, 1164, 1124, 1090, 1067, 1017, 992, 960, 929, 863, 835, 814, 779, 750, 739, 694, 677, 673, 644, 624, 603, 577, 546, 532, 520; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.70 (d, 2H, $J$ = 10.0 Hz), 7.60 (d, 2H, $J$ = 10.0 Hz), 7.52 (d, 2H, $J$ = 5.0 Hz), 7.31-7.44 (m, 5H), 6.98 (d, 2H, $J$ = 10.0 Hz), 6.78 (t, 1H, $J$ = 10.0 Hz), 6.40 (s, 1H), 6.21 (d, 2H , $J$ = 5.0 Hz), 4.32 (dd, 1H, $J$ = 5.0, 10.0 Hz), 3.97 (dd, 1H, $J$ = 7.0, 10.5 Hz), 3.20 (dd, 1H, $J$ = 10.0, 15.0 Hz), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) $\delta$ 145.8 (d, $J$ = 287.5 Hz), 143.6, 139.5, 134.7, 129.9, 128.9 (d, $J$ = 25 Hz) , 128.7, 127.6, 127.1, 126.7, 126.1 ( d, $J$ = 12.5 Hz), 119.2, 113.2, 80.5, 62.8, 53.9, 21.6; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{26}F_3N_2O_2S$ is 523.1662; found 523.1653.

***1-((4-Methoxyphenyl)sulfonyl)-2,3,4-triphenylimidazolidine ((±)-10h).***

The general method A described above was followed when (±)-1-((4-methoxyphenyl)sulfonyl)-2-phenylaziridine (**8h**) (31.8 mg, 0.110 mmol, 1.0 equiv.) was reacted with *N*-benzylaniline (**7a**) (20.3 mg, 0.111 mmol, 1.01 equiv.) in MeOH (0.1 mL) as the solvent at room temperature for 8 h to afford the ring-opening product **(±)-9h** (43.0 mg, 0.091 mmol) in 83% yield as a white solid. In the second step, single neck round-bottom flask was charged with (±)-**9h** (30.0 mg, 0.063 mmol), **TPA-PQ** (5.0 mg) and MeOH (1.5 mL), purged with oxygen and left for stirring in the presence of Blue LED (18 W) light source for 50 h to afford the cyclized product (±)-**10h** (27.0 mg, 0.057 mmol) in 90% yield as a white solid: mp = 153-155 ˚C; $R_f$ = 0.30 (in 10% ethyl acetate in petroleum ether); IR $\nu_{max}$ (KBr, $cm^{-1}$) 3029, 2964, 2925, 1655, 1593, 1494, 1450, 1438, 1415, 1345, 1310, 1265, 1231, 1213, 1198,

1154, 1112, 1089, 1060, 1027, 1013, 958, 946, 928, 883, 862, 840, 813, 803, 753, 715, 694, 676, 629, 603, 580, 551, 524, 503; $^{1}$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.74 (d, 2H, $J$ = 9.5 Hz), 7.64 (d, 2H, $J$ = 9.0 Hz), 7.35-7.44 (m, 3H), 7.19-7.27 (m, 5H), 7.05 (dd, 2H, $J$ = 7.5, 8.5 Hz), 6.74 (t, 1H, $J$ = 7.0 Hz), 6.64 (d, 2H, $J$ = 12.0 Hz), 6.38 (s, 1H), 6.27 (d, 2H, $J$ = 9.0 Hz), 4.26 (dd, 1H, $J$ = 7.5, 13.5 Hz), 3.88 (dd, 1H, $J$ = 7.0, 10.5 Hz), 3.73 (s, 3H), 3.23 (dd, 1H, $J$ = 10.5, 13.5 Hz); $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 125 MHz) $\delta$ 163.6, 147.4, 139.7, 139.4, 129.7, 129.4, 128.99, 128.9, 128.7, 128.6, 127.9, 127.2, 126.4, 118.7, 114.4, 113.3, 80.5, 63.3, 55.6, 54.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{27}N_2O_3S$ is 471.1737; found 471.1740.

***1-((4-(Tert-butyl)phenyl)sulfonyl)-2,3,4-triphenylimidazolidine ((±)-10i).***

The general method A described above was followed (±)-1-((4-(*tert*-butyl)phenyl)sulfonyl)-2-phenylaziridine (**8i**) (34.7 mg, 0.110 mmol, 1.0 equiv.) was reacted with *N*-benzylaniline (**7a**) (20.3 mg, 0.111 mmol, 1.01 equiv.) in MeOH (0.1 mL) as the solvent at room temperature for 8 h to afford the ring-opening product (±)-**9i** (46.0 mg, 0.092 mmol) in 84% yield as a white solid. In the second step, single neck round-bottom flask was charged with (±)-**9i** (42.0 mg, 0.084 mmol), **TPA**-**PQ** (5.0 mg), and MeOH (1.5 mL), purged with oxygen and left for stirring in the presence of Blue LED (18 W) light source for 7 days to afford the cyclized product (±)-**10i** (34.0 mg, 0.068 mmol) in 81% yield as a white solid. mp = 150-152 ˚C; $R_f$ = 0.54 (in 10% ethyl acetate in petroleum ether); IR $\nu_{max}$ (KBr, $cm^{-1}$) 3088, 3006, 3064, 3026, 2959, 2941, 2873, 1595, 1500, 1464, 1451, 1400, 1363, 1349, 1331, 1318, 1305, 1272, 1233, 1214, 1198, 1168, 1113, 1086, 1053, 1028, 1007, 991, 962, 943, 925, 883, 872, 861, 843, 769, 753, 731, 694, 649, 632, 607, 582, 554, 544, 528, 503, 528, 512, 503; $^{1}$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.74 (d, 2H, $J$ = 10.0 Hz), 7.63 (d, 2H, $J$ = 10.0 Hz), 7.35-7.44 (m, 3H), 7.16-7.27 (m, 7H), 7.03 (t, 2H, $J$ = 8.0 Hz), 6.74 (t, 1H, $J$ = 7.0 Hz), 6.42 (s, 1H), 6.22 (d, 2H, $J$ = 10.0 Hz), 4.26 (dd, 1H, $J$ = 5.0, 15.0 Hz), 3.70 (dd, 1H, $J$ = 5.0, 10.0 Hz), 3.23 (dd, 1H, $J$ = 10.5, 13.5 Hz), 1.25 (s, 9H); $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 125 MHz) $\delta$ 157.5, 147.3, 139.7, 139.4, 134.8, 128.9, 128.7, 128.5, 127.9, 127.4, 127.3, 126.3, 118.7, 113.2, 80.3, 63.3, 54.2, 35.1, 31.0; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{31}H_{33}N_2O_2S$ is 497.2257; found 497.2271.

Note: when the reaction mixture was purged with $O_2$ for 2 h, the cyclization step was completed in 96 h with slight increment in yield (86%) of the product (±)-**10i.**

***2,3,4-Triphenyl-1-(phenylsulfonyl)imidazolidine ((±)-10j).***

The general method A described above was followed (±)-2-phenyl-1-(phenylsulfonyl)aziridine (**8j**) (28.5 mg, 0.107 mmol, 1.0 equiv.) was reacted with *N*-benzylaniline (**7a**) (20.3 mg, 0.108

mmol, 1.01 equiv.) in MeOH (0.1 mL) as the solvent at room temperature for 9 h to afford the ring-opening product (±)-**9j** (46.0 mg, 0.104 mmol) in 97% yield as a white solid. In the second step, single neck round-bottom flask was charged with (±)-**9j** (44.0 mg, 0.099 mmol), **TPA-PQ** (5.0 mg) and MeOH (1.5 mL), purged with oxygen and left for stirring in the presence of Blue LED (18 W) light source for 80 h to afford the cyclized product (±)-**10j** (28.0 mg, 0.063 mmol) in 64% yield as a white solid: mp = 153-155 ˚C; $R_f$ = 0.40 (in 10% ethyl acetate in petroleum ether); IR $\nu_{max}$ (KBr, $cm^{-1}$) 3057, 2954, 2924, 2854, 1743, 1599, 1498, 1447, 1351, 1334, 1309, 1233, 1210, 1167, 1089, 1060, 1028, 1016, 998, 958, 929, 882, 860, 848, 809, 766, 739, 718, 699, 688, 632, 604, 586, 558, 513, 502, 454; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.72 (t, 4H, $J$ = 10.0 Hz), 7.35-7.45(m, 4H), 7.18.7.26 (m, 7H), 7.04 (t, 2H, $J$ = 10.0 Hz), 6.74 (t, 1H, $J$ = 9.0 Hz), 6.42(s, 1H), 6.25 (d, 2H, $J$ =10.0 Hz), 4.25 (dd, 1H, $J$ =5.0, 15.0 Hz), 3.82 (dd, 1H, $J$ = 10.0, 15.0 Hz), 3.24 (dd, 1H, $J$ = 15.0, 20.0 Hz); $^{13}$C{$^1$H} NMR ($CDCl_3$, 125 MHz) $\delta$ 147.1, 139.7, 139.2, 138.0, 133.4, 129.3, 129.0, 128.9, 128.7, 128.6, 127.9, 127.6, 127.3, 126.3, 118.9, 113.4, 80.4, 63.3, 54.1; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{25}N_2O_2S$ is 441.1631; found 441.1628

***1-((4-Fluorophenyl)sulfonyl)-2,3,4-triphenylimidazolidine ((±)-10k).***

The general method A described above was followed (±)-1-((4-fluorophenyl)sulfonyl)-2-phenylaziridine (**8k**) (51.8 mg, 0.187 mmol, 1.0 equiv.) was reacted with *N*-benzylaniline (**7a**) (34.4 mg, 0.188 mmol, 1.01 equiv.) in MeOH (0.1 mL) as the solvent at room temperature for 8 h to afford the ring-opening product (±)-**9k** (83.0 mg, 0.180 mmol) in 96% yield as a white solid. In the second step, single neck round-bottom flask was charged with (±)-**9k** (76.0 mg, 0.165 mmol), **TPA-PQ** (5.0 mg) and MeOH (1.5 mL), purged with oxygen and left for stirring in the presence of Blue LED (18 W) light source for 7 days to afford the cyclized product (±)-**10k** (40.0 mg, 0.087 mmol) in 53% yield as a white solid: mp = 80-82 ˚C; $R_f$ = 0.25 (in 10% ethyl acetate in petroleum ether); IR $\nu_{max}$ (KBr, $cm^{-1}$) 3061, 2924, 1592, 1493, 1450, 1404, 1353, 1292, 1236, 1213, 1169, 1154, 1088, 1028, 1009, 991, 959, 838, 818, 750, 659, 674, 625, 577, 544, 517; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.69-7.73 (m, 4H), 7.37-7.44 (m, 3H), 7.20-7.28 (m, 5H), 7.07 (dd, 2H, $J$ = 7.0, 9.0 Hz), 6.87 (t, 2H, $J$ = 8.5 Hz), 6.77 (t, 1H, $J$ = 7.5 Hz), 6.39 (s, 1H), 6.30 (d, 2H, $J$ = 9.0 Hz), 4.27 (dd, 1H, $J$ = 7.0, 14.0 Hz), 3.94 (dd, 1H, $J$ = 7.0, 10.5 Hz), 3.27 (dd, 1H, $J$ = 10.0, 13.5 Hz); $^{13}$C{$^1$H} NMR ($CDCl_3$, 125 MHz) $\delta$ 165.6 (d, $J$ = 300 Hz), 147.1, 139.2 (d, $J$ = 62.5 Hz), 134.1, 130.2 (d, $J$ =12.5 Hz), 129.0, 128.75, 128.7, 128.0, 127.2, 126.3, 119.1, 116.6, 116.4, 113.2, 80.5, 63.3, 54.1; HRMS (ESI) m/z: $[M+H]^+$ calcd for,

$C_{27}H_{24}FN_2O_2S$ is 459.1537; found 459.1524.

***3-(4-Methoxyphenyl)-2,4-diphenyl-1-tosylimidazolidine ((±)-10l).***

The general method A described above was followed (±)-2-phenyl-1-tosylaziridine (**8a)** (30.1 mg, 0.110 mmol, 1.0 equiv) was reacted with *N*-benzyl-4-methoxyaniline (**7b**) (23.7 mg, 0.111 mmol, 1.01 equiv.) in MeOH (0.1 mL) as the solvent at room temperature for 3 h to afford the ring-opening product (±)-**9l** (48.0 mg, 0.098 mmol) in 89% yield as white solid. In the second step, single neck round-bottom flask was charged with (±)-**9l** (48.0 mg, 0.098 mmol), **TPA-PQ** (5.0 mg) and MeOH (1.5 mL), purged with oxygen and left for stirring in the presence of Blue LED (18 W) light source for 4 days to afford the cyclized product (±)-**10l** (25.0 mg, 0.051 mmol) in 52% yield as a white solid. mp =140-142 ˚C; $R_f$ = 0.35 (in 10% ethyl acetate in petroleum ether); IR $\nu_{max}$ (KBr, $cm^{-1}$) 2923, 2841, 1595, 1513, 1453, 1356, 1297, 1265, 1246, 1211, 1163, 1116, 1086, 1008, 1029, 943, 962, 859, 811, 759, 740, 698, 668, 625, 606, 590, 575, 544, 522; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.73 (d, 2H, *J* = 5.0 Hz), 7.60 (d, 2H, *J* = 10.0 Hz ), 7.35-7.43 (m, 3H), 7.23-7.27 (m, 5H), 7.03 (d, 2H, *J* = 10.0 Hz), 6.63 (d, 2H, *J* = 10.0 Hz), 6.27 (s, 1H), 6.20 (d, 2H, *J* = 10.0 Hz), 4.22-4.28 (m, 1H), 3.89 (dd, 1H, *J* = 5.0, 10.0 Hz), 3.70 (s, 3H), 3.22 (dd, 1H, *J* = 10.0, 20.0 Hz), 3.21 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) $\delta$ 152.9, 144.4, 141.6, 140.2, 139.4, 135.1, 129.9, 129.0, 128.7, 128.5, 127.9, 127.6, 127.3, 126.4, 114.5, 114.3, 81.0, 63.5, 55.8, 54.2, 21.5; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{29}N_2O_3S$ is 485.1893; found 485.1915.

Note: when the reaction mixture was purged with $O_2$ for 2 h, the cyclization step was completed in 78 h with slight increment in yield (58%) of the product (±)-**10l**.

***3-Phenyl-1-tosyl-1,2,3,5,6,10b-hexahydroimidazo[2,1-a] isoquinoline ((±)-10n).***

The general method A described above was followed (±)-2-phenyl-1-tosylaziridine (**8a**) (51.3 mg, 0.184 mmol, 1.0 equiv) was reacted with 1,2,3,4-tetrahydroisoquinoline (**7d)** (24.0 $\mu$L, 0.185 mmol, 1.01 equiv.) in MeOH (0.1 mL) as the solvent at room temperature for 5 min to afford the inseparable mixture of ring-opening products (±)-**9n** (2.5:1) (72.0 mg, 0.177 mmol) in 96% yield as semi-solid. In the second step, single neck round-bottom flask was charged with (±)-**9n** (72.0 mg, 0.177 mmol), **TPA-PQ** (5.0 mg) and MeOH (1.5 mL), purged with oxygen and left for stirring in the presence of Blue LED (18 W) light source for 24 h to afford the cyclized product (±)-**10n** (20.0 mg, 0.049 mmol) in 28% yield as a white solid; mp = 185-187 ˚C; $R_f$ = 0.50 (in 10% ethyl acetate in petroleum ether); IR $\nu_{max}$ (KBr, $cm^{-1}$) 3034, 2924, 2868, 1599, 1491, 1456, 1432, 1340, 1301, 1292, 1214, 1165, 1156, 1128, 1110, 1088, 1018,

998, 951, 895, 881, 861, 839, 785, 771, 760, 751, 665, 613, 589, 544, 516, 484, 464, 440; $^{1}$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.95 (d, 1H, *J* = 10.0 Hz), 7.83 ( d, 2H, *J* = 10.0 Hz), 7.38 (d, 2H, *J* = 5.0 Hz), 7.23 (t, 1H, *J* =5.0 Hz), 7.18-7.23 (m, 4H), 7.05 (d, 1H, *J* = 10.0 Hz), 6.86 (d, 2H, *J* = 10.0 Hz), 5.93 (s, 1H), 4.09 (t, 1H, *J* = 10.0 Hz), 3.69 (dd, 1H, *J* = 7.5, 10.0 Hz), 3.17 (t, 1H, *J* = 10.0 Hz), 3.06-3.13 (m, 1H), 2.86-2.93 (m, 1H), 2.72 (dd, 1H, *J* = 5.0, 15.0 Hz), 2.52 (s, 3H), 2.37 (dd, 1H *J* = 5.0, 15.0 Hz);$^{13}$C{$^{1}$H} NMR ($CDCl_3$, 125 MHz) $\delta$ 144.0, 138.8, 134.9, 134.1, 134.0, 129.8, 129.1, 128.7, 128.5, 128.2, 127.7, 127.6, 76.4, 127.2, 60.8, 55.6, 41.5, 21.8, 21.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for, $C_{24}H_{25}N_2O_2S$ is 405.163; found 405.1608.

***(2R,4R)-2,3,4-triphenyl-1-tosylimidazolidine [(2R,4R)-10a].***

The general method A described above was followed when racemic (*S*)-2-phenyl-1-tosylaziridine (*S*-**8a**) (30.1 mg, 0.109 mmol, 1.0 equiv.) was reacted with *N*-benzylaniline (**2a**) (20.2 mg, 0.110 mmol, 1.01 equiv.) in MeOH (0.1 mL) as the solvent at room temperature for 7 h to afford the ring-opening chiral product (*3R*)-**9a** (49.0 mg, 0.107 mmol) in 98% yield as a white solid. In the second step, single neck round-bottom flask was charged with ring opening chiral product (*3R*)-**9a** (49.0 mg, 0.107 mmol), **TPA-PQ** (5.0 mg) and MeOH (1.5 mL), purged with oxygen and left for stirring in the presence of Blue LED (18 W) light source for 42 h to afford the cyclized product (*2R,4R*)**-10a** (32.0 mg, 0.070 mmol) in 65% yield as a white solid. mp = 168-170 ˚C; $R_f$ = 0.50 (in 10% ethyl acetate in petroleum ether); $[\alpha]^{25}_{D}$ -0.55 (*c* 0.027 in $C_2H_4Cl_2$), the optical purity was determined by chiral HPLC analysis (OD-H, *n*-hexane/isopropanol = 99/1, flow rate = 1.0 mL/min), $t_R$ = 14.97 min (minor), 11.83 min (major); IR $\nu_{max}$ (KBr, $cm^{-1}$) 3030, 2956, 2924, 2854, 1925, 1741, 1598, 1503, 1450, 1400, 1347, 1303, 1233, 1212, 1195, 1166, 1120, 1088, 1058, 1026, 1007, 990, 958, 931, 883, 860, 843, 814, 749, 694, 671, 626, 617, 603, 578, 543, 510; $^{1}$HNMR ($CDCl_3$, 500 MHz) $\delta$ 7.74 (d, 2H, *J* = 10.0 Hz), 7.60 (d, 2H, *J* = 10.0 Hz), 7.35-7.44 (m, 3H), 7.19-7.27 (m, 5H), 7.04 (t, 2H, *J* = 5.0 Hz), 6.98 (d, 2H, *J* = 10.0 Hz), 6.75 (t, 1H, *J* = 5.0 Hz), 6.38 (s, 1H), 6.25 (d, 2H, *J* = 10.0 Hz), 4.28 (dd, 1H, *J* =5.0, 15.0 Hz), 3.89 (dd, 1H, *J* = 5.0, 15.0 Hz), 3.23 (dd, 1H, *J* = 10.0, 15.0 Hz), 2.28 (s, 3H); $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 125 MHz) $\delta$ 147.3, 144.5, 139.8, 139.4, 134.9, 129.9, 129.0, 128.8, 128.7, 128.6, 127.9, 127.6, 127.3, 126.3, 118.8, 113.3, 80.4, 63.2, 54.2, 21.5; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{27}N_2O_2S$, is 455.1788; found 455.1795.

## Material characterization:

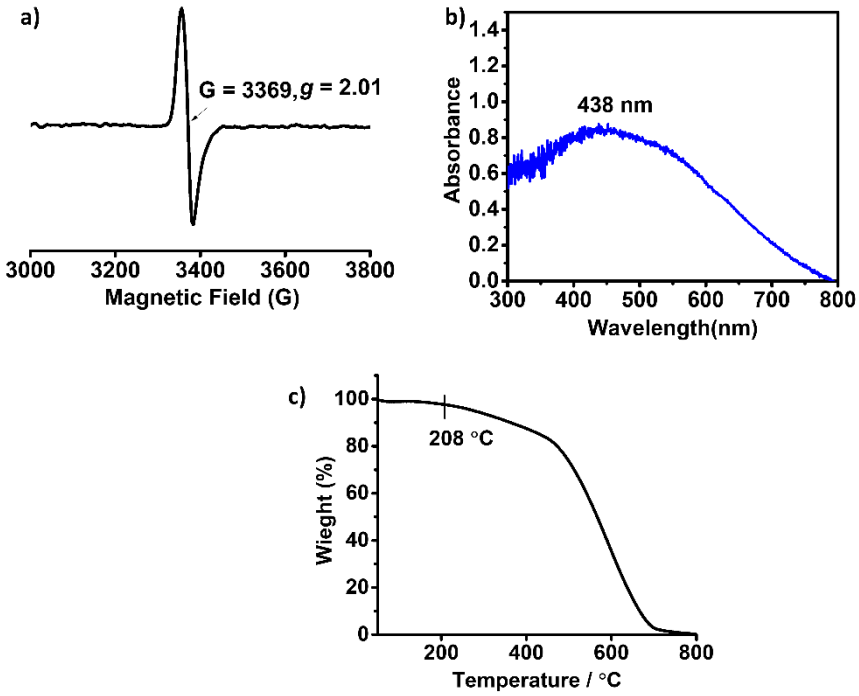



**Figure S3**: (a) EPR spectrum of **TPA-PQ** at room temperature, (b) Uv-Vis spectrum in solid state; and (c) TGA plot of **TPA-PQ**.

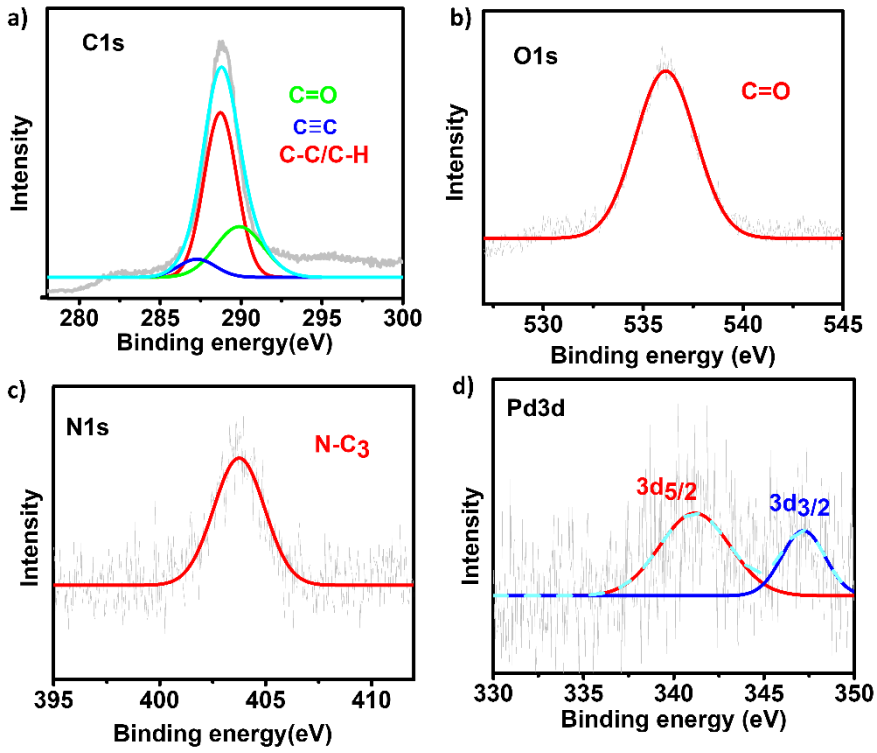



**Figure S4**: XPS analysis of **TPA-PQ**.

**Electrochemical Study:**

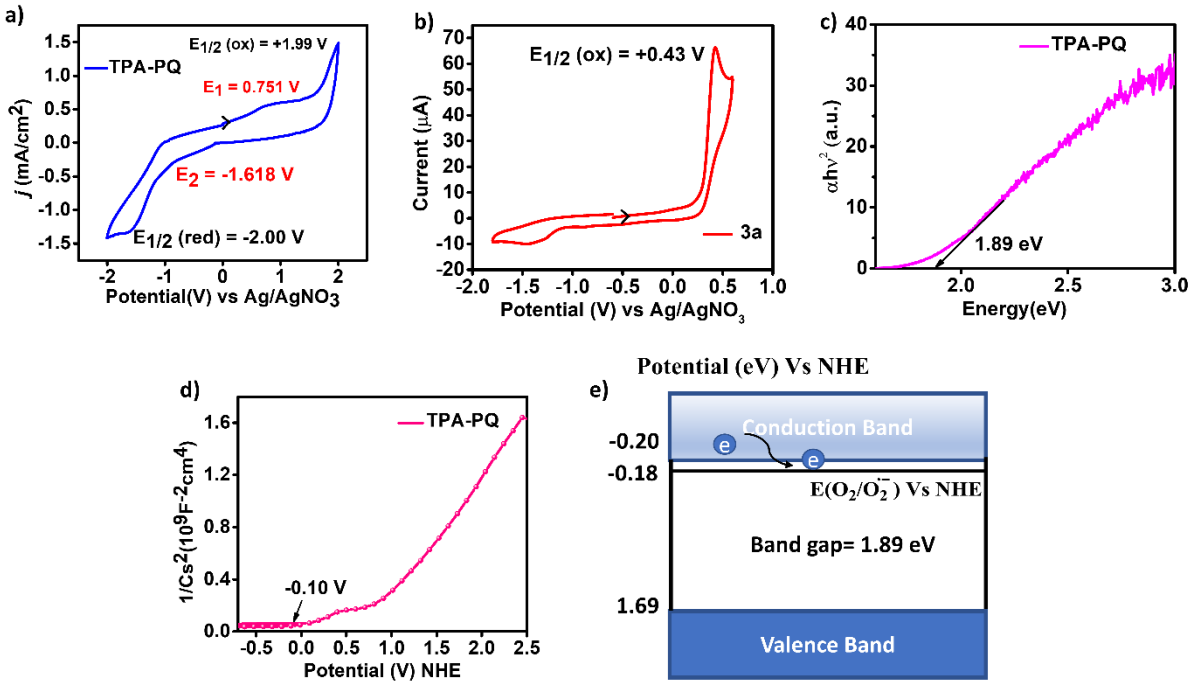



**Figure S5:** (a) Cyclic voltammetry of **TPA-PQ** in 0.1 M TBAP electrolyte containing solution of acetonitrile; (b) Cyclic voltammetry of **9a** in 0.1 M TBAP electrolyte containing solution of MeOH; (c) Tauc plot of **TPA-PQ**, (d) Mott–Schottky (MS) analysis for flat band potential of TPA-PQ; and (e) Schematic representation of band positioning of **TPA-PQ** demonstrating feasibility of the electron transfer from **TPA-PQ** to $O_2$.

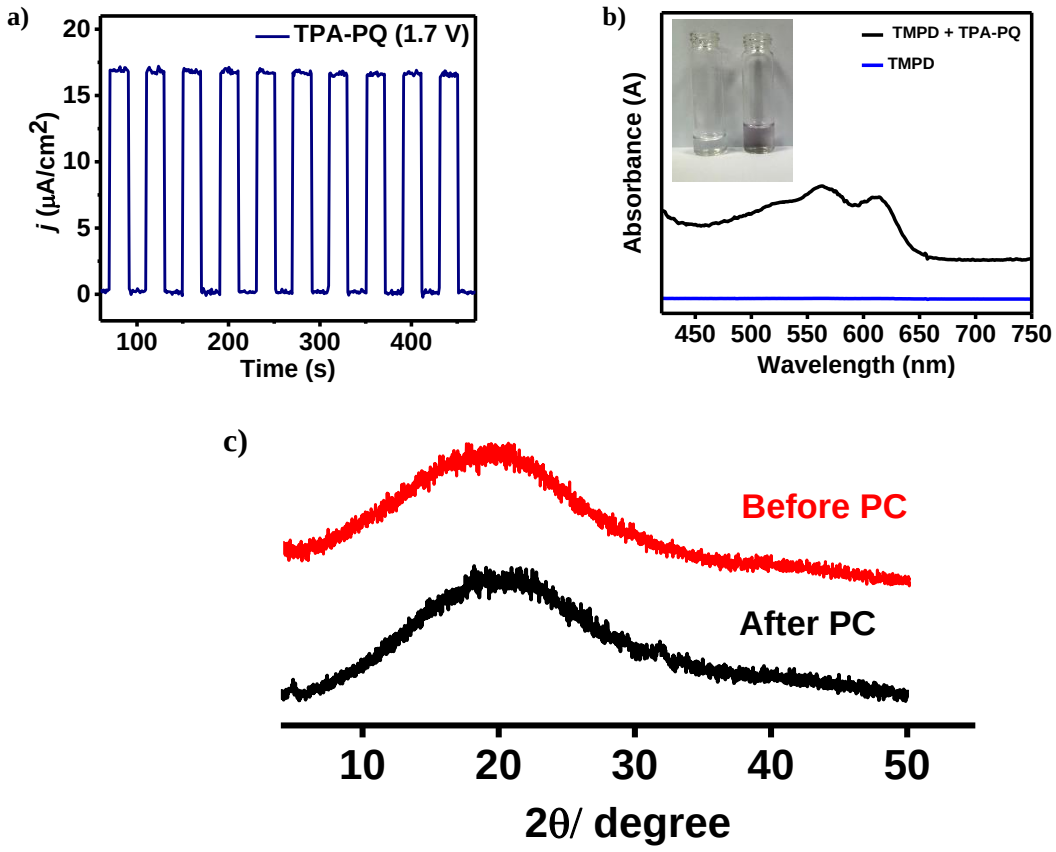
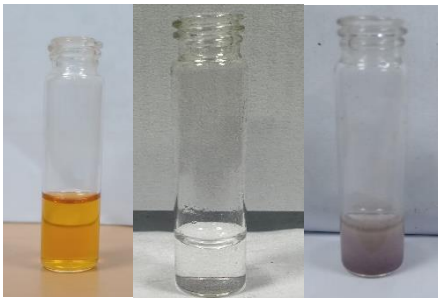



**Figure S6**: (a) Photocurrent measurement of **TPA-PQ** in 0.1M TBAP solution in $CH_3CN$; (b) UV-visible absorption spectra for evidence in favor of the formation of TMPD cationic radical upon irradiation of suspension of **TPA-PQ** in 0.1M of TMPD in methanol and in the presence of oxygen; and (c) PXRD plot of **TPA-PQ** before and after photocatalysis**.**

**KI/starch test for the detection of hydrogen peroxide ($H_2O_2$) in the reaction:**

For the detection of $H_2O_2$ as an intermediate during the photo-oxidative C-H activation reaction**,** KI/starch test was performed. For this purpose, the reaction mixture contains the starting material (±)-**9a** (49 mg), **TPA-PQ** (5.0mg) and methanol (1.5 mL) as solvent in the presence of $O_2$ atmosphere and kept the reaction mixture under blue LED for 42 h after the completion of the reaction, observed by TLC. The reaction mixture was filtered off with the help of Whatman filter paper to recover the catalyst and kept the filtrate for starch/KI test. The preparation of the starch/KI solution, A solution of KI (0.05 M), starch (4 mg/mL) and glacial acetic acid (0.5 M) in 2mL $H_2O$ was prepared (Solution **B**). When, 100 μL of solution **A** was added into solution **B**, the colour of the resulting solution (Solution **C**) immediately changes to dark purple which verify the presence of $H_2O_2$ in the reaction mixture. The colour change arises

due to the formation of the complex between starch and triiodide ions in which the latter was produced by the oxidation of KI by $H_2O_2$.



**Solution A** **Solution B** **Solution C**

**Figure S7**: (A) The reaction mixture after completion of reaction (B) KI and starch in $H_2O$ (C) After the addition of 100 µL of solution A in solution B.

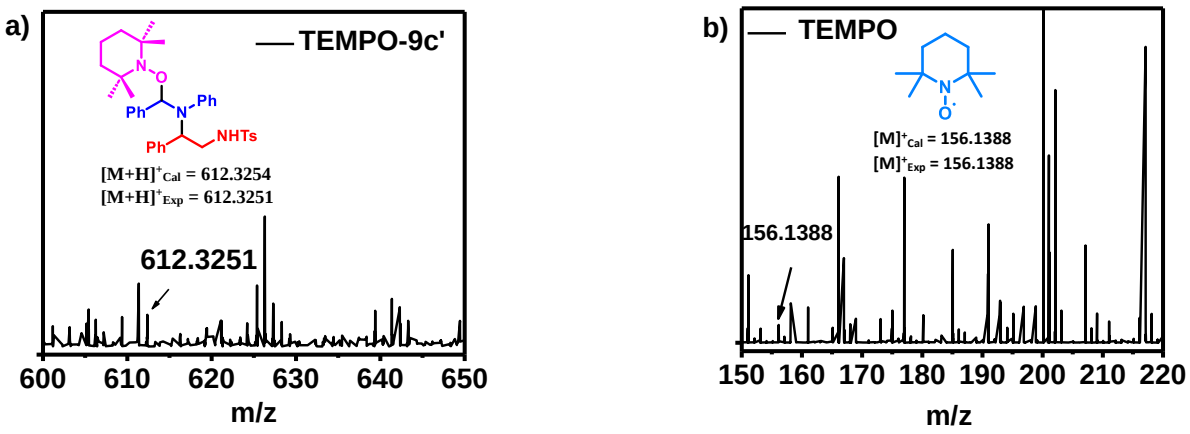



**Figure S8**: ESI-MS spectra of (a) the **TEMPO-9c'** adduct and (b) **TEMPO** formed in the quenching experiment involving the radical trapping by **TEMPO** and singlet oxygen trapping by **2,2,6,6-Tetramethylpiperidine** respectively.

**Copies of NMR spectra:**

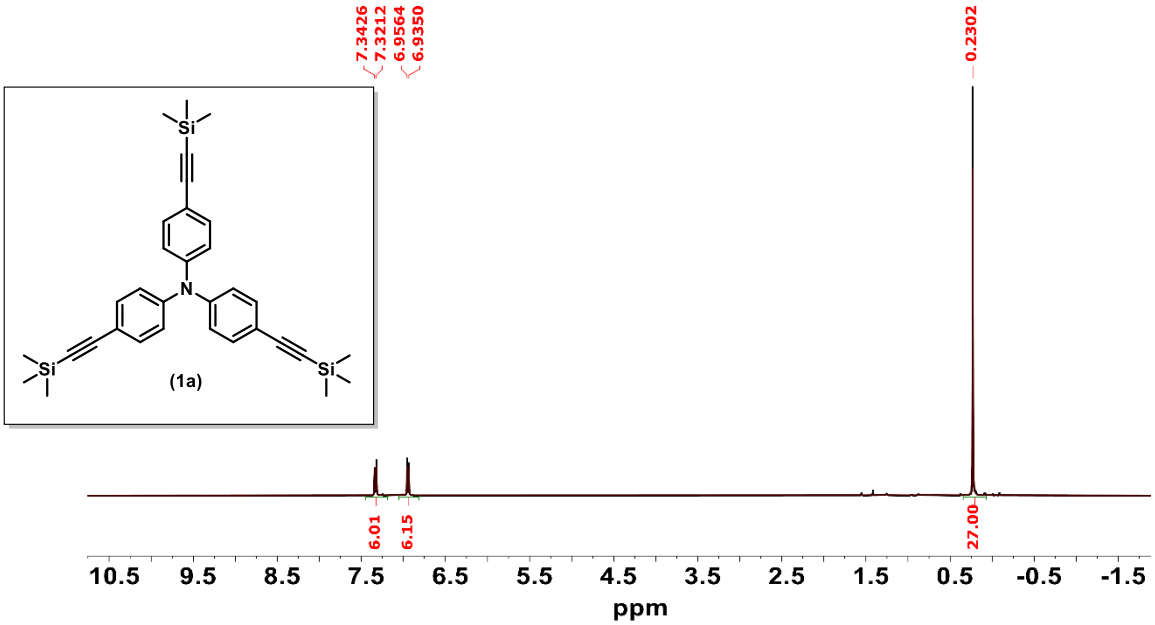



**Figure S9:** $^{1}$H NMR spectrum of compound **1a** (500 MHz, $CDCl_3$).

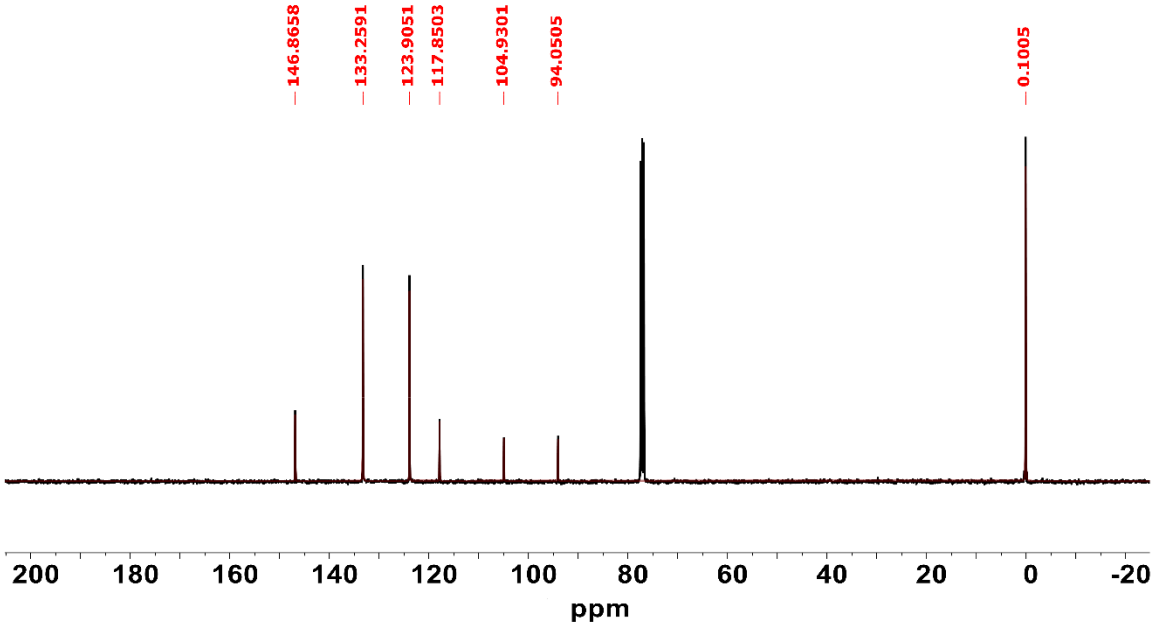



**Figure S10:** $^{13}C\{^{1}H\}$ NMR spectrum of compound **1a** (125 MHz, $CDCl_3$).

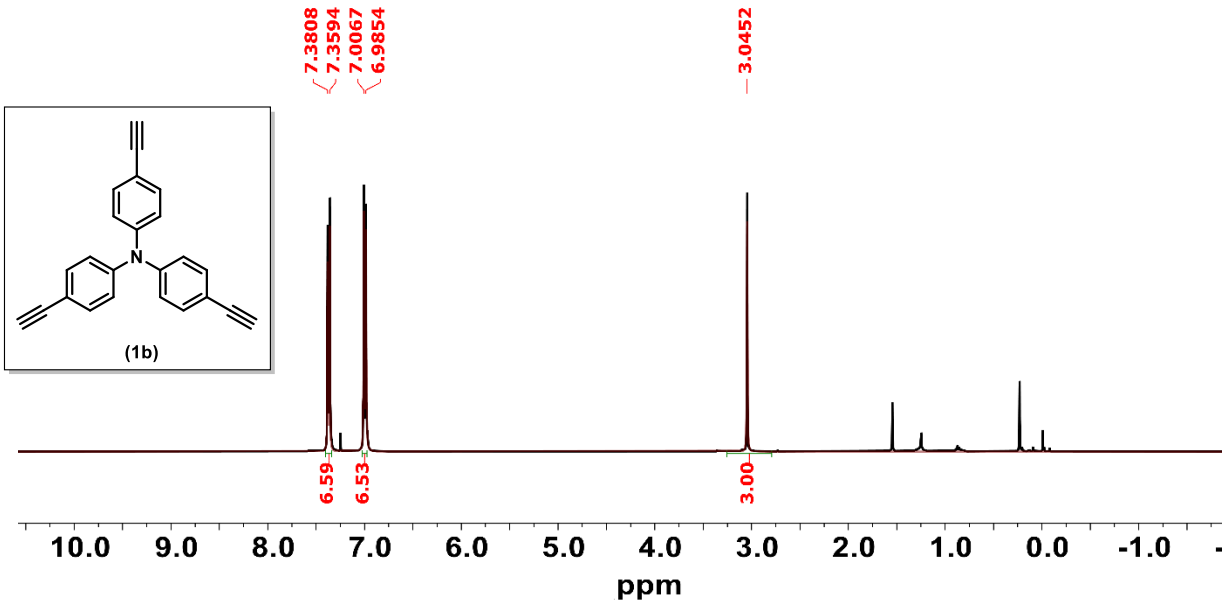



**Figure S11:** $^{1}$H NMR spectrum of compound **1b** (500 MHz, $CDCl_3$).

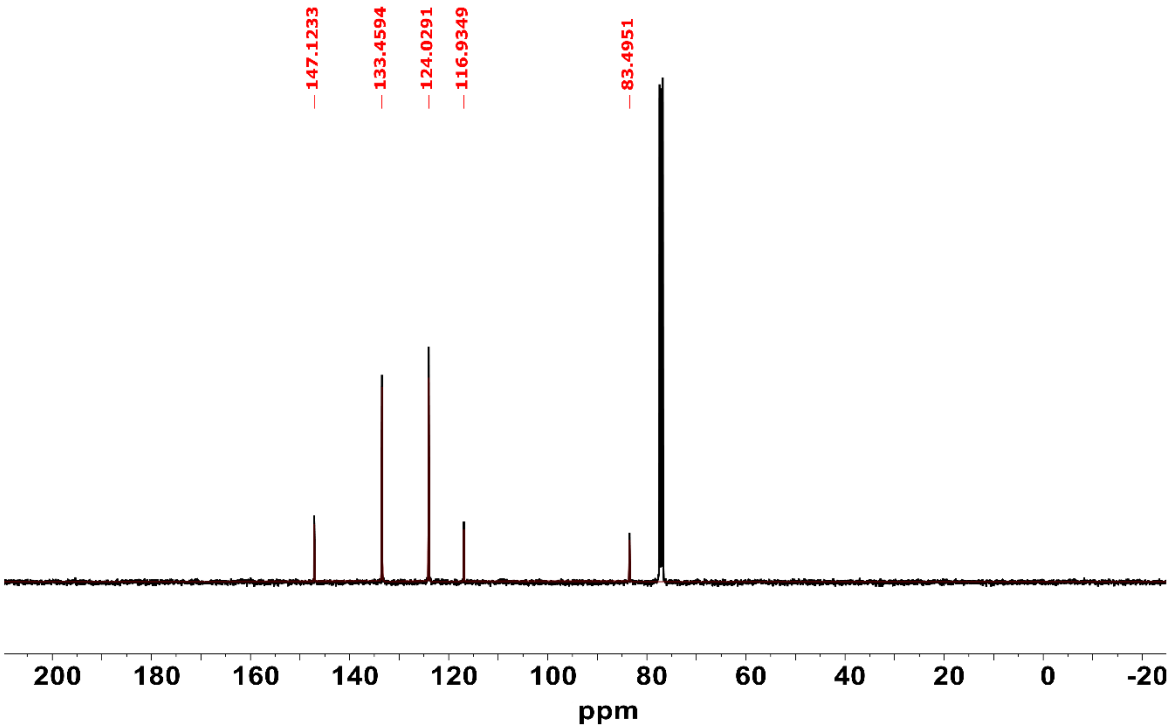



**Figure S12:** $^{13}C\{^{1}H\}$ NMR spectrum of compound **1b** (125 MHz, $CDCl_3$).

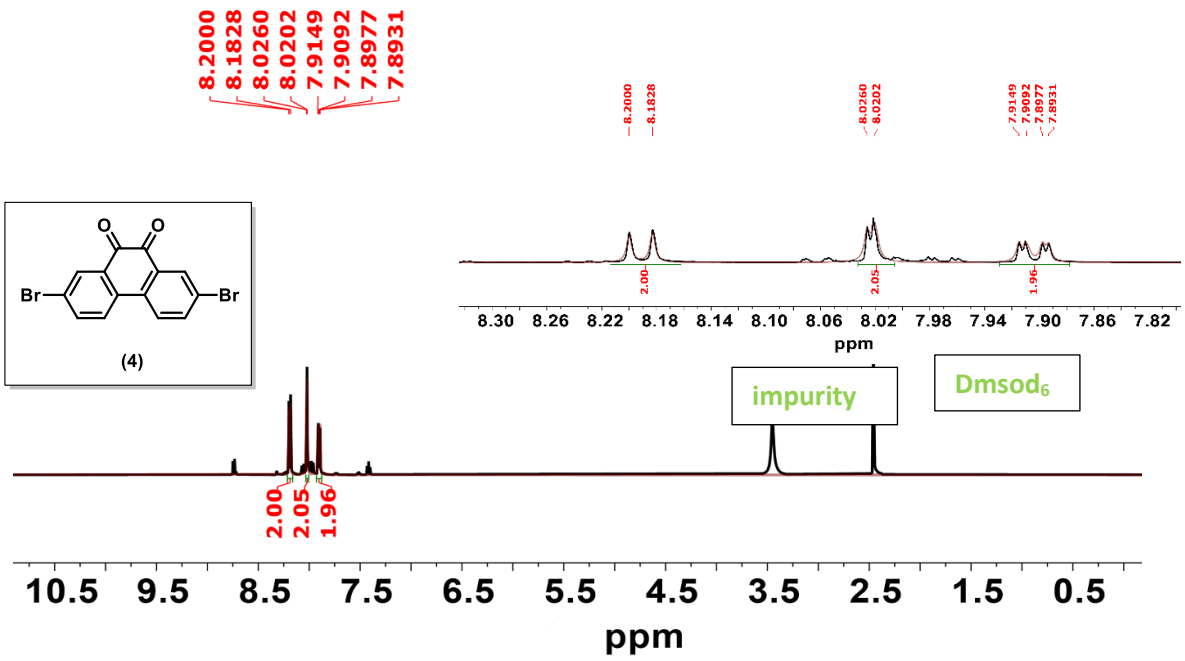



**Figure S13**: $^{1}$H NMR spectrum of compound **4** (500 MHz, poor soluble in dmsod$_6$).

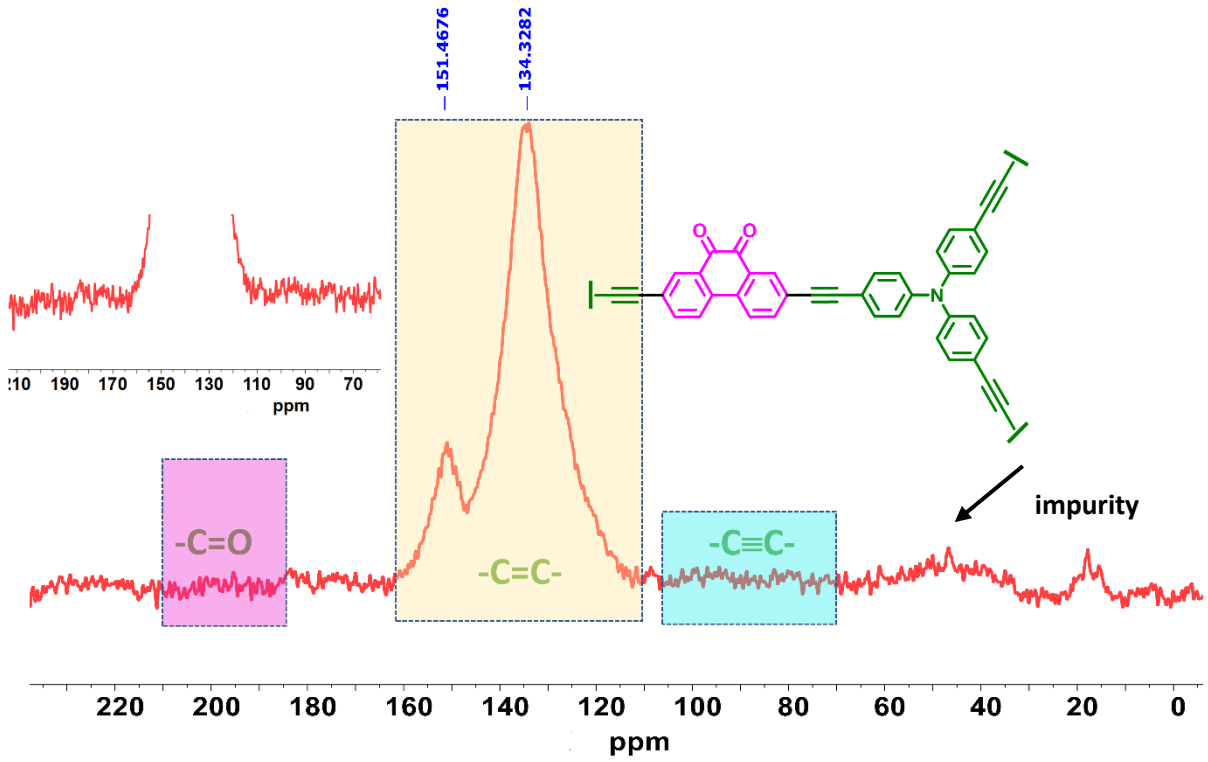



**Figure S14:** Solid State $^{13}$C NMR of **TPA-PQ**.

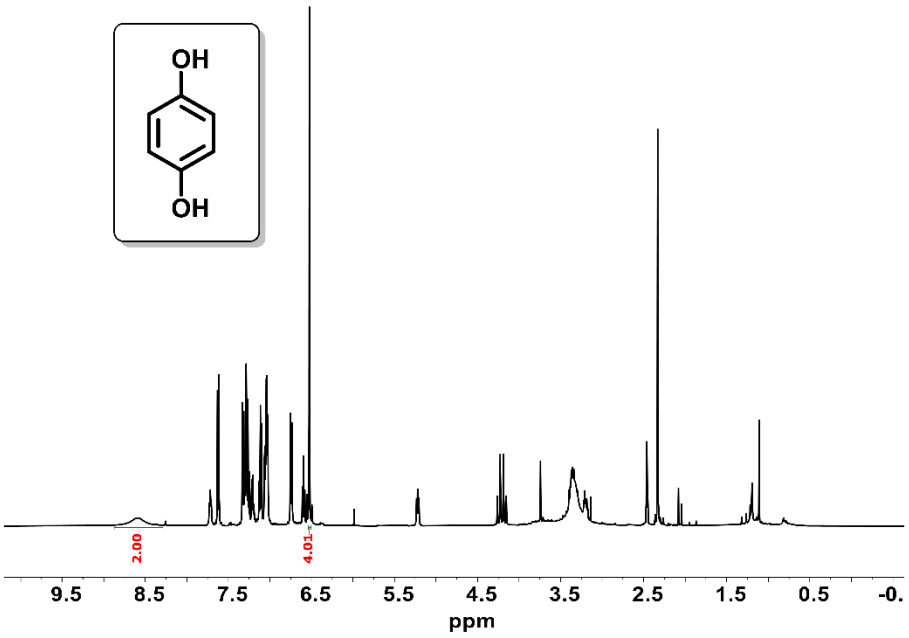



**Figure S15:** $^{1}$H NMR spectrum of crude product (500 MHz, dmso$_6$) after the irradiation of compound (±)-**9a**, Benzoquinone as superoxide quencher and **TPA-PQ** as photocatalyst.

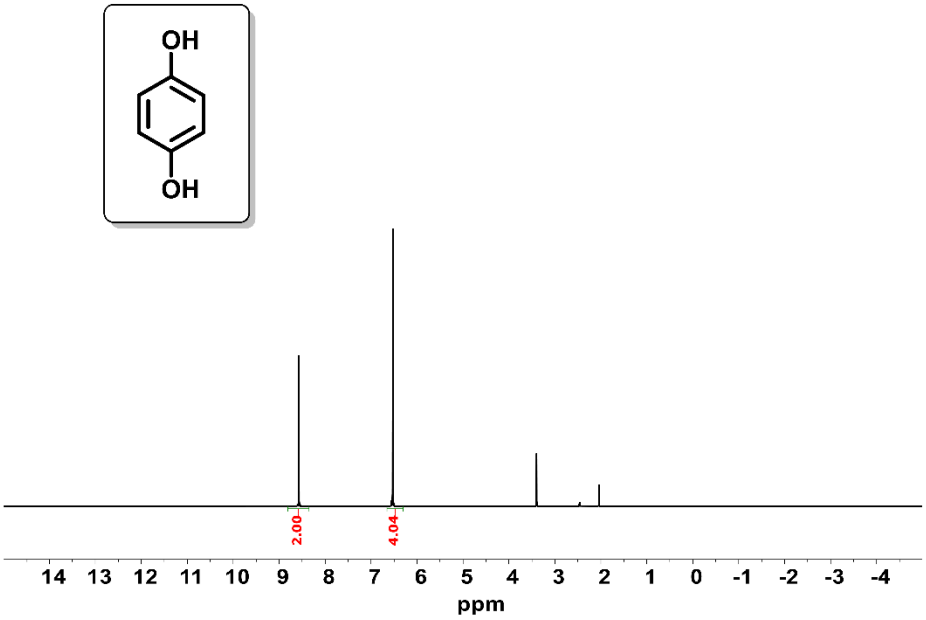



**Figure S16:** $^{1}$H NMR spectrum of Pure Hydroquinone (500 MHz, dmso$_6$).

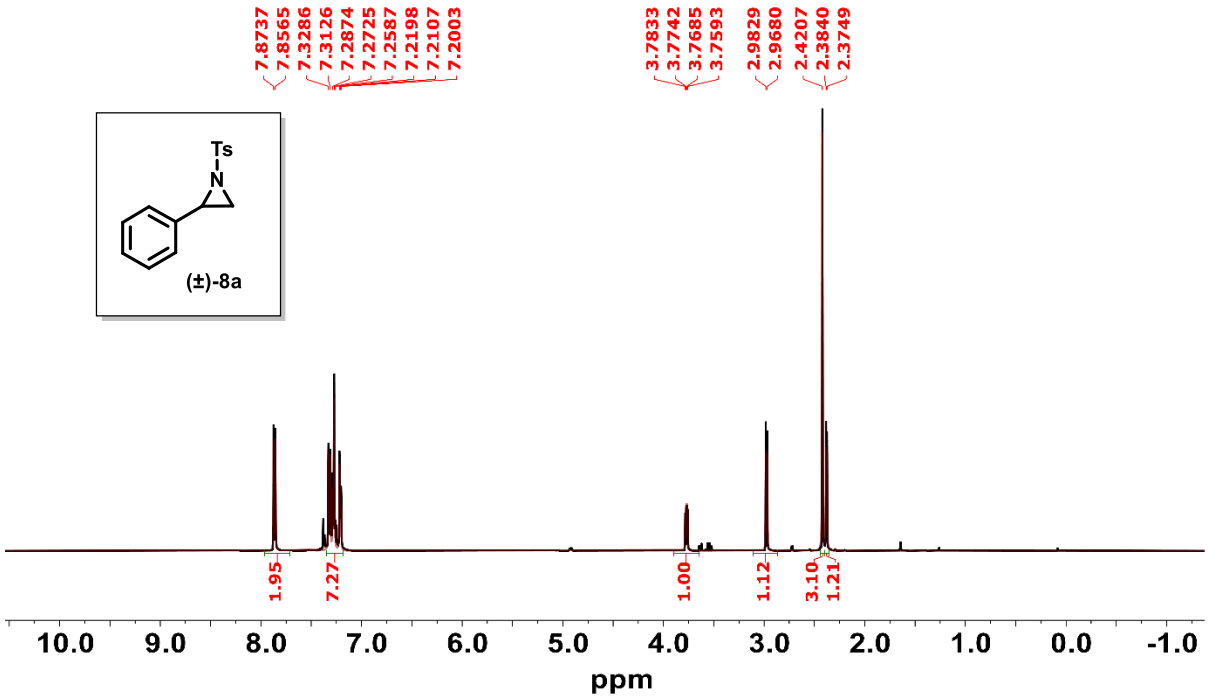



**Figure S17:** $^{1}$H NMR spectrum of (±)-**8a** (400 MHz, $CDCl_3$).

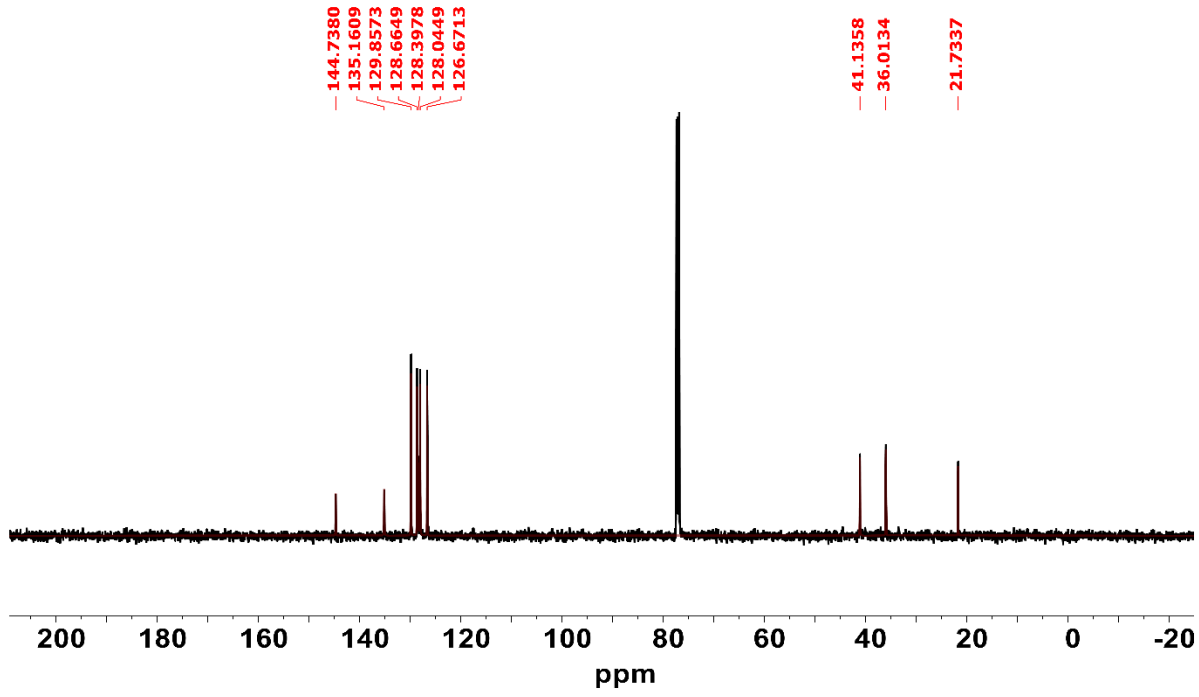



**Figure S18:** $^{13}C\{^{1}H\}$ NMR spectrum of (±)-**8a** (100 MHz, $CDCl_3$).

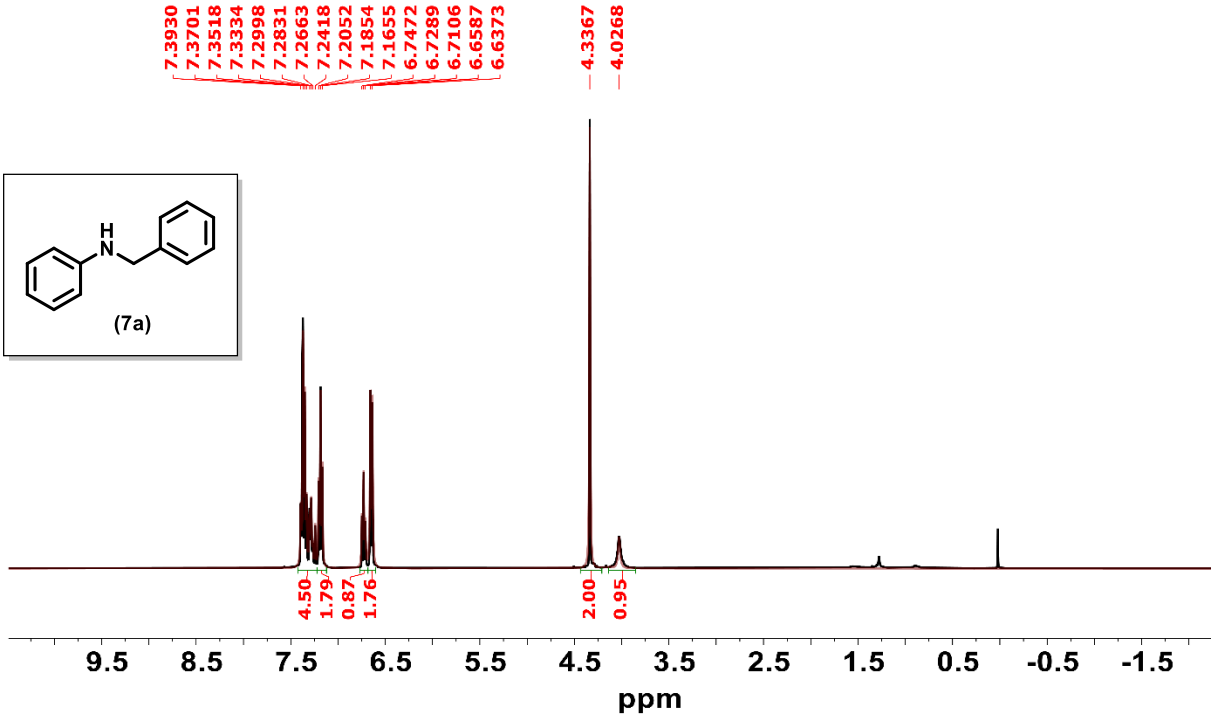



**Figure S19:** $^{1}$H NMR spectrum of **7a** (400 MHz, $CDCl_3$).

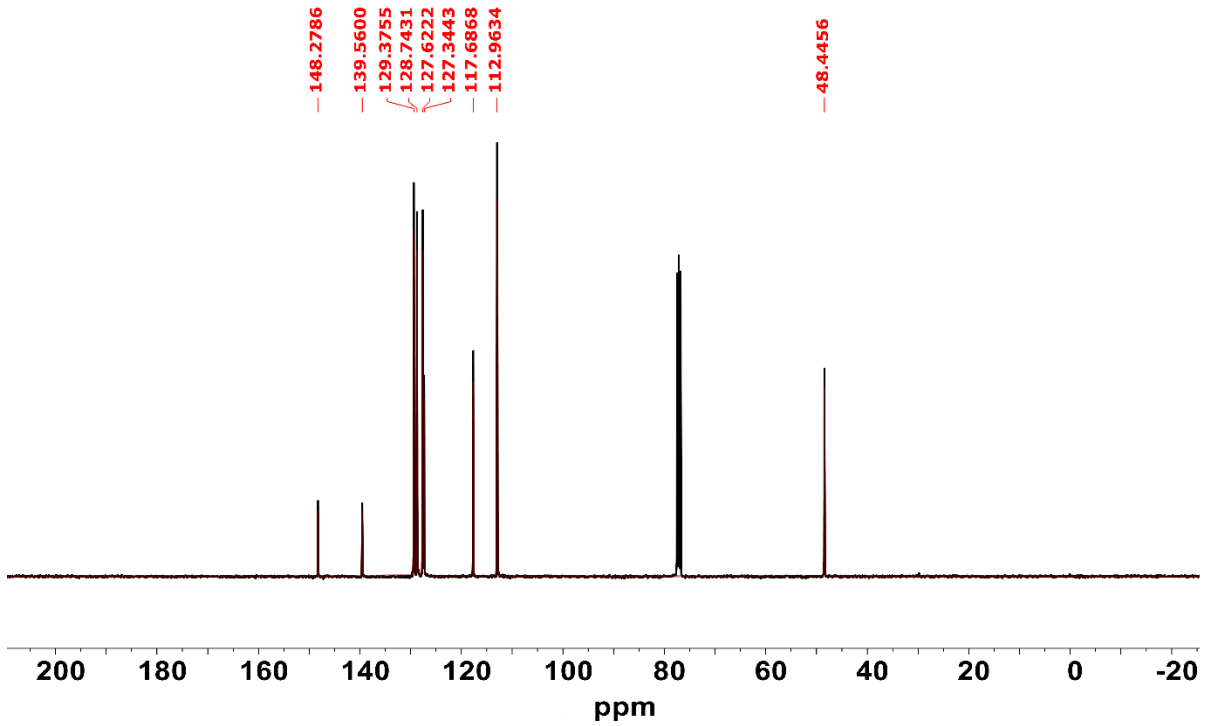



**Figure S20:** $^{13}C\{^{1}H\}$ NMR spectrum of **7a** (100 MHz, $CDCl_3$).

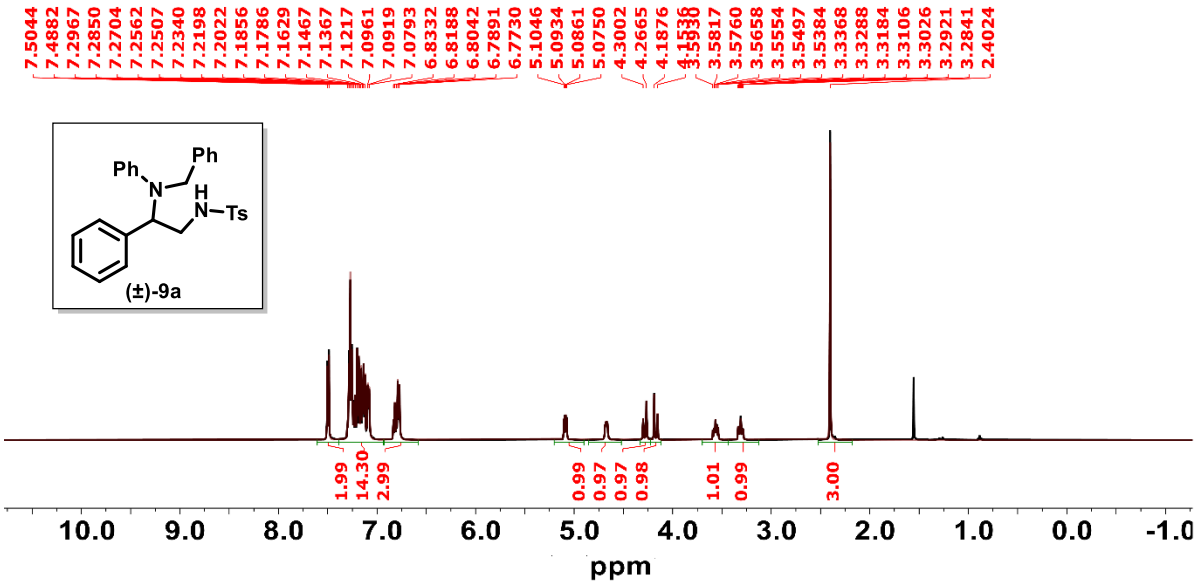



**Figure S21:** $^{1}$H NMR spectrum of (±)-**9a** (500 MHz, $CDCl_3$).

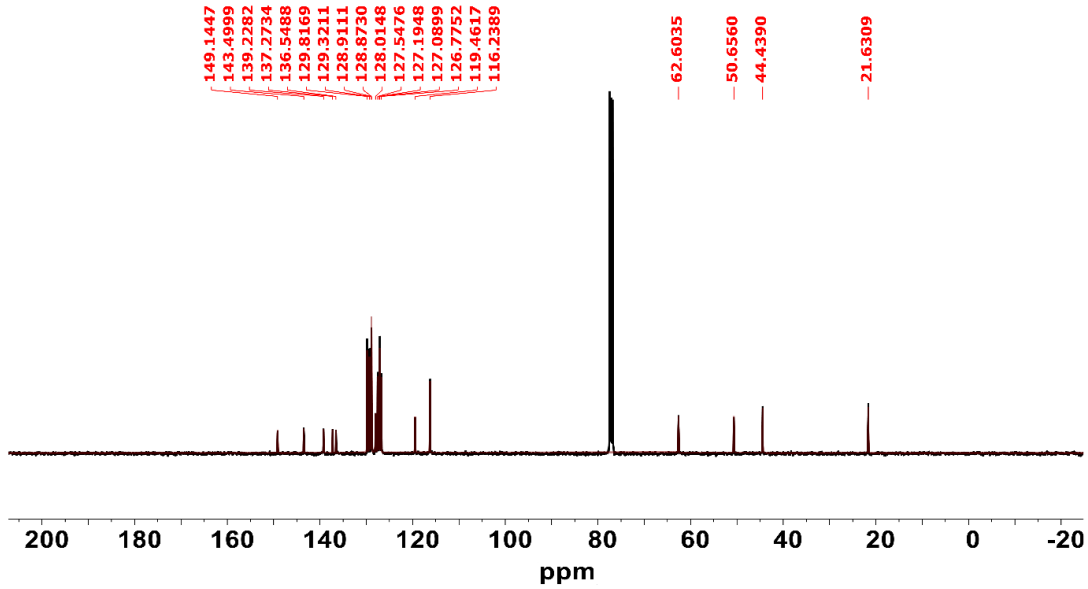



**Figure S22:** $^{13}C\{^{1}H\}$ NMR spectrum of (±)-**9a** (125 MHz, $CDCl_3$).

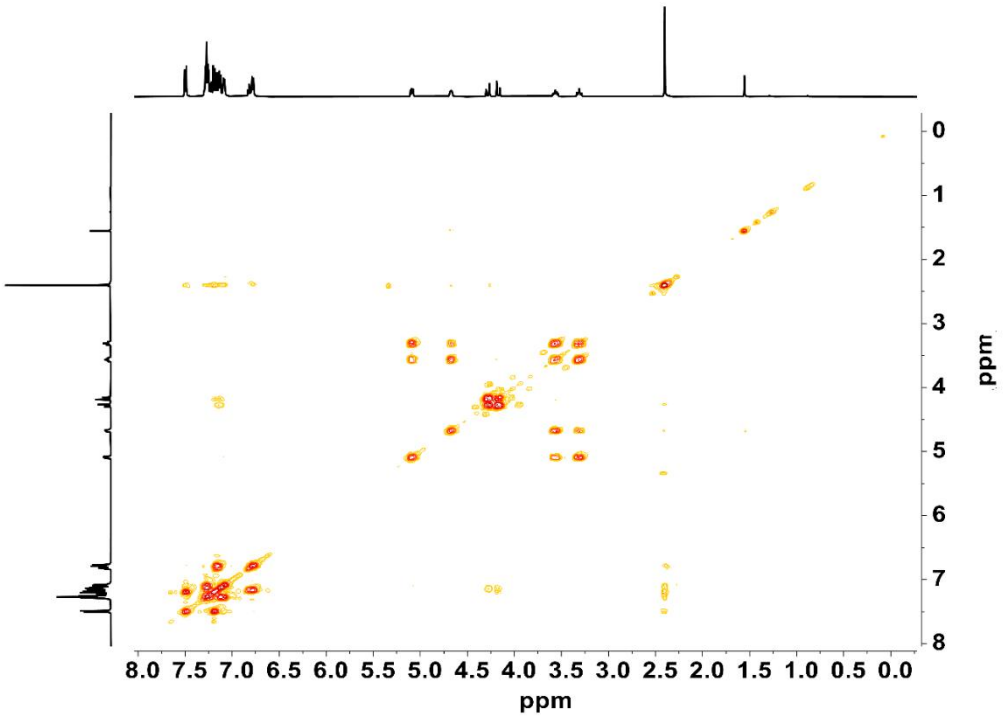



**Figure S23**. $^{1}$H-$^{1}$H COSY NMR spectrum (±)-**9a** (500 MHz, $CDCl_3$).

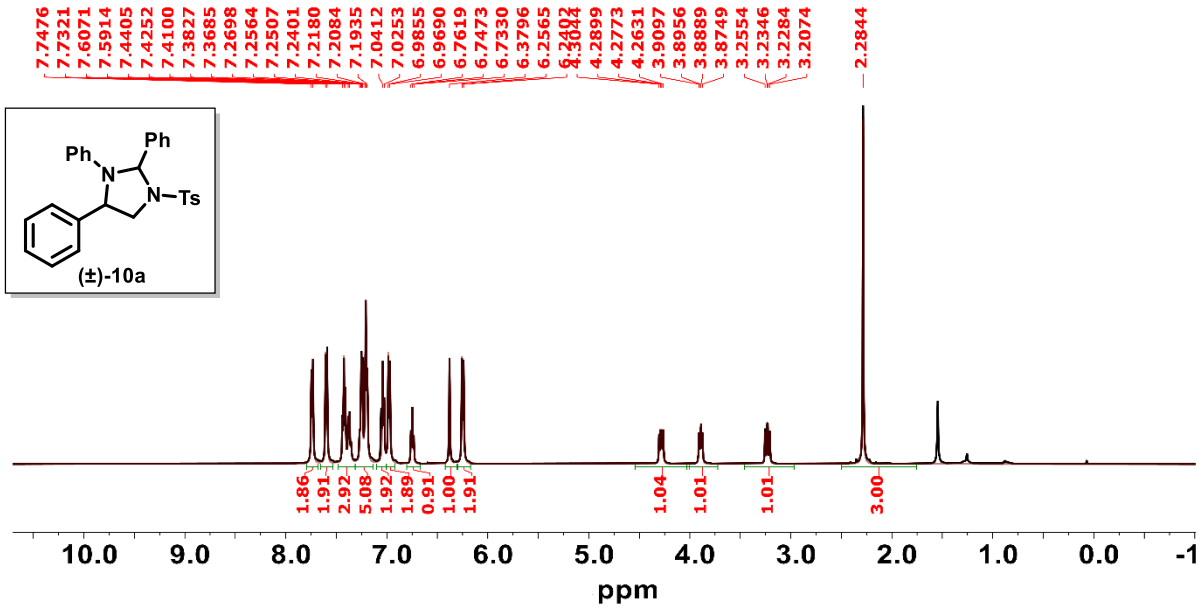



**Figure S24**: $^{1}$H NMR spectrum of (±)-**10a** (500 MHz, $CDCl_3$).

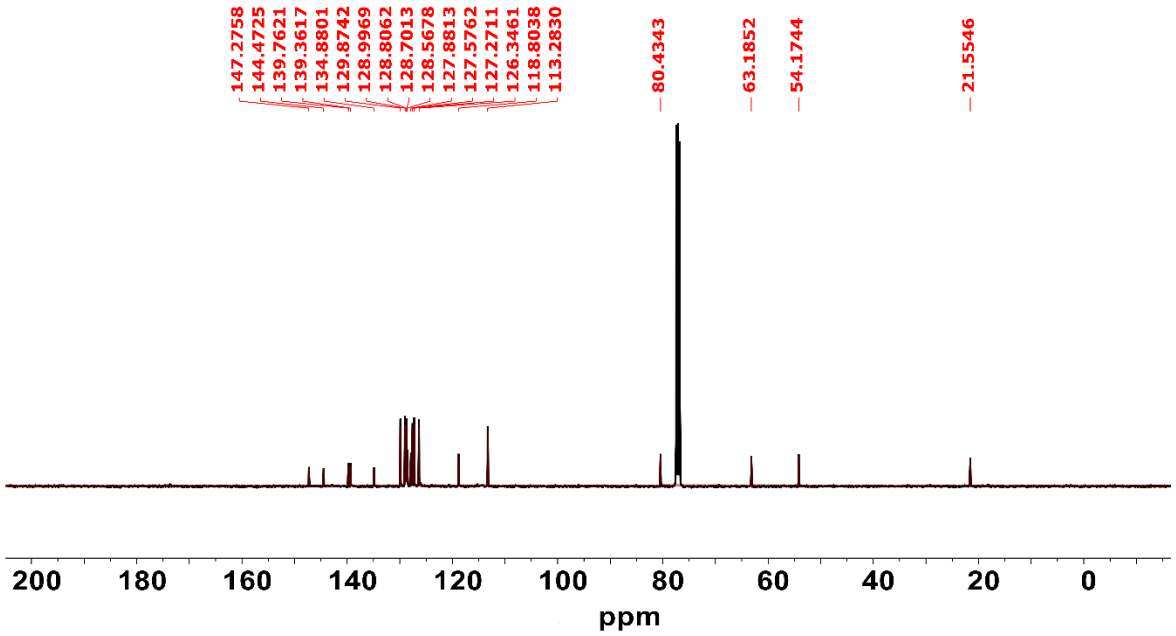



**Figure S25:** $^{13}C\{^{1}H\}$ NMR spectrum of (±)-**10a** (125 MHz, $CDCl_3$).

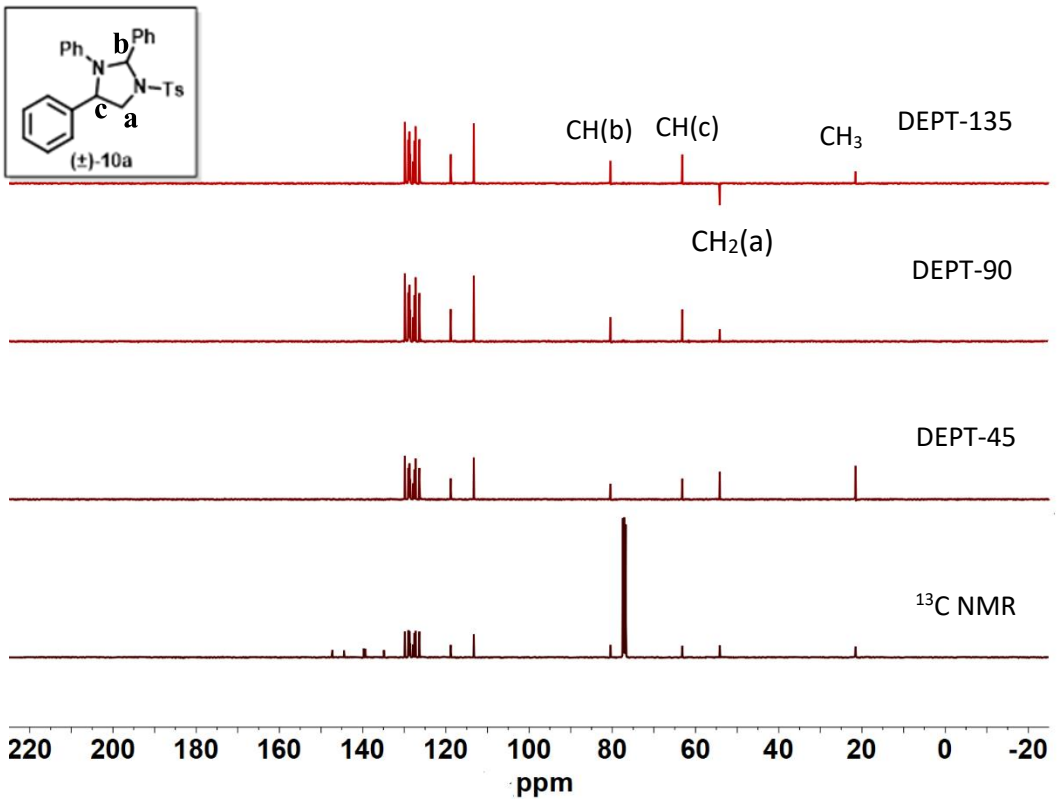



**Figure S26**: DEPT $^{13}C$ NMR spectrum of (±)-**10a** ($CDCl_3$, 500 MHz).

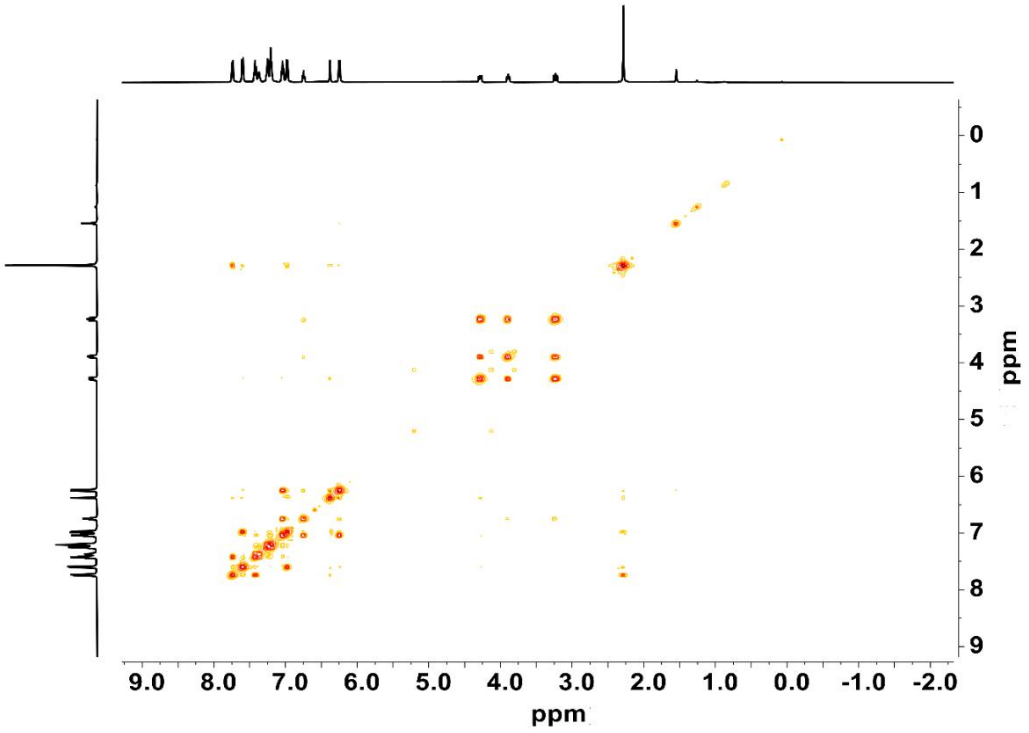



**Figure S27**: $^{1}$H-$^{1}$H COSY NMR spectrum of (±)-**10a** ($CDCl_3$, 500 MHz).

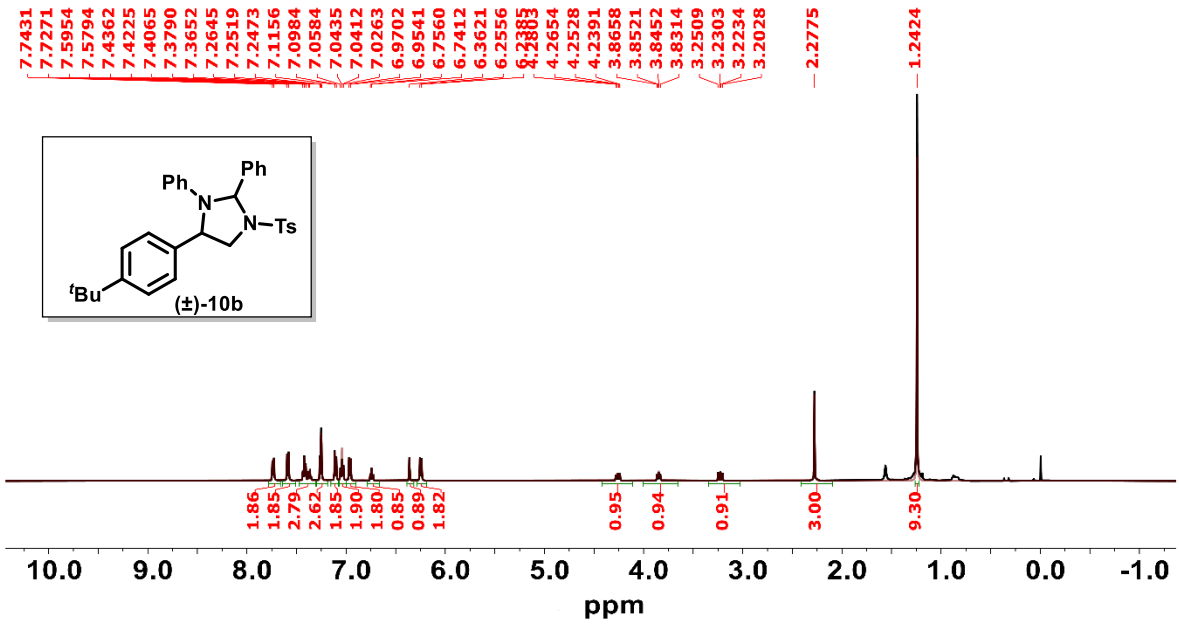



**Figure S28**: $^{1}$H NMR spectrum of (±)-**10b** (500 MHz, $CDCl_3$).

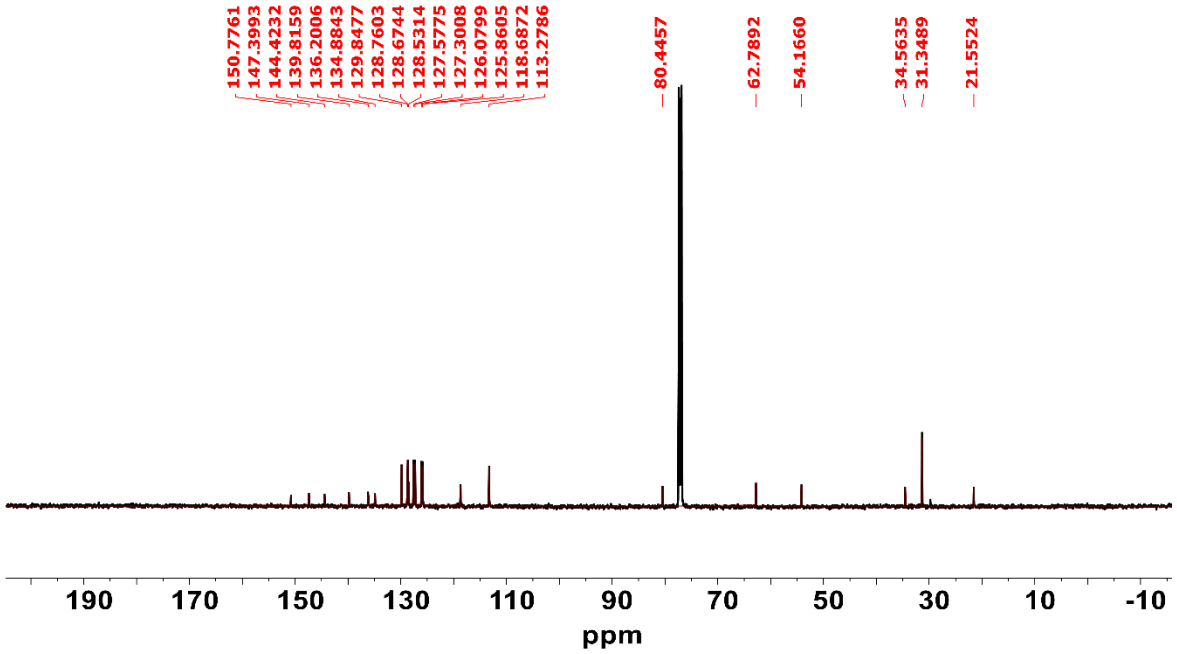



**Figure S29:** $^{13}C\{^{1}H\}$ NMR spectrum of (±)-**10b** (125 MHz, $CDCl_3$).

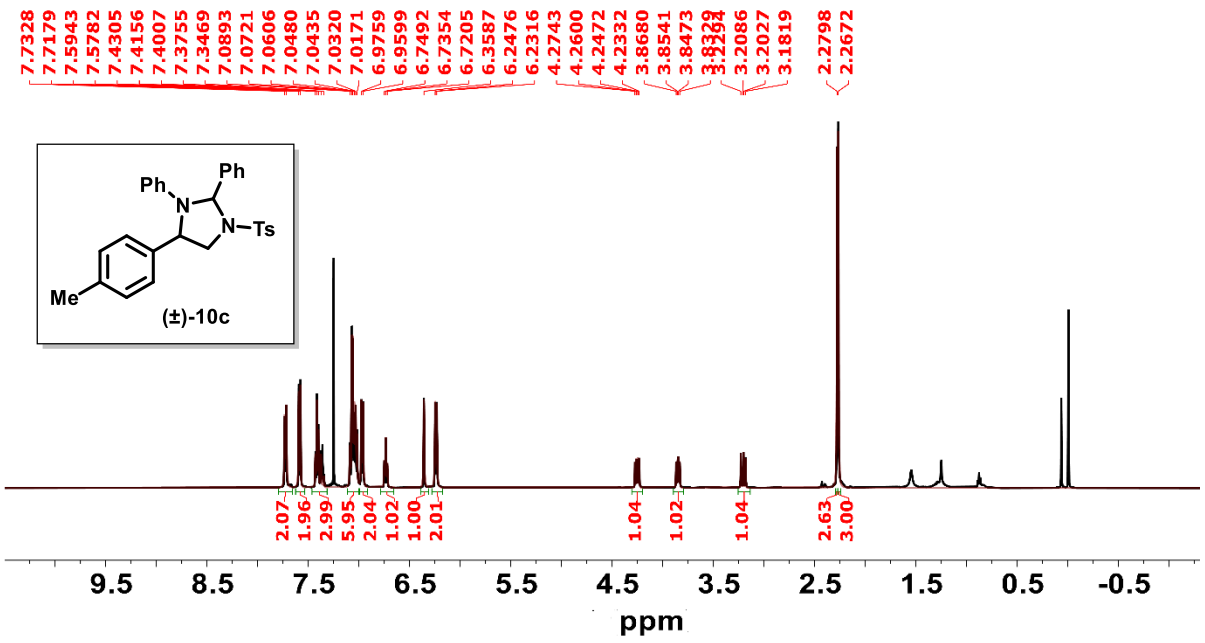



**Figure S30**: $^{1}H$ NMR spectrum of (±)-**10c** (500 MHz, $CDCl_3$.

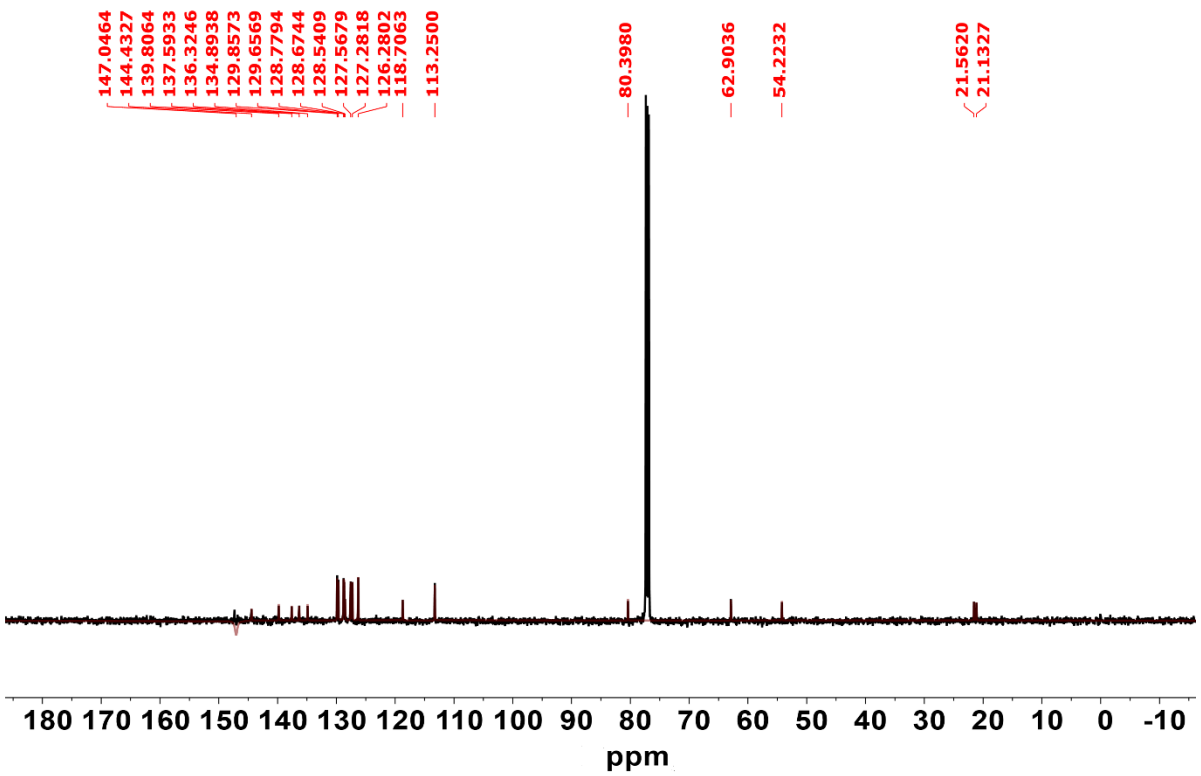



**Figure S31:** $^{13}C\{^{1}H\}$ NMR spectrum of (±)-**10c** (125 MHz, $CDCl_3$).

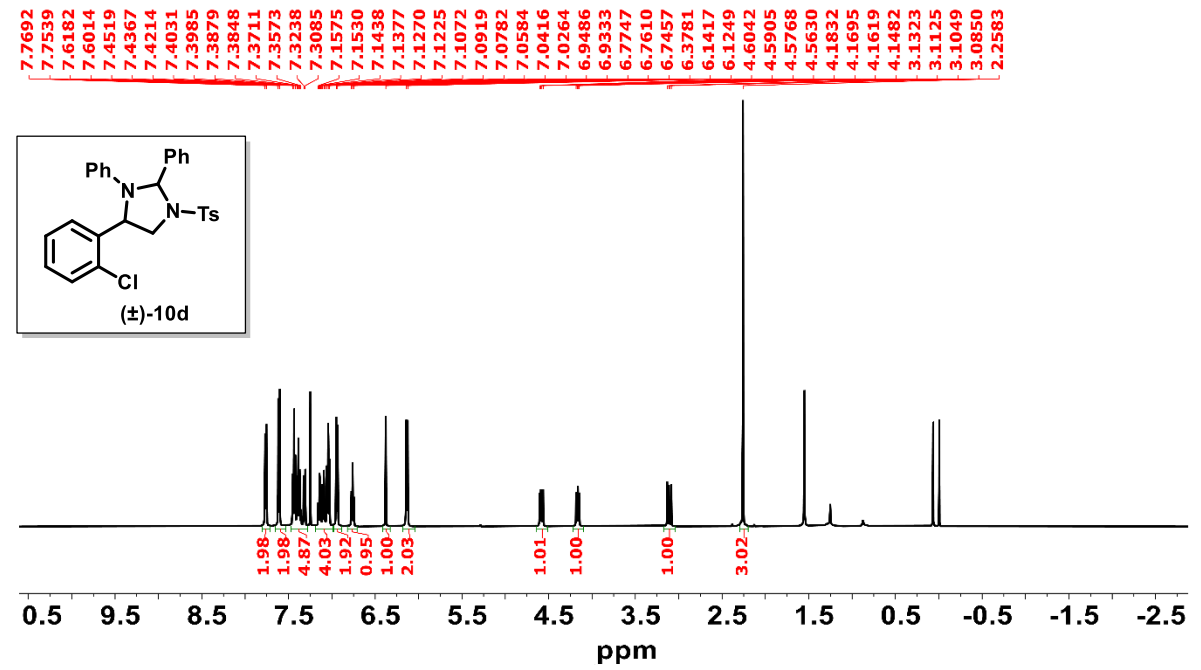



**Figure S32**: $^{1}H$ NMR spectrum of (±)-**10d** (500 MHz, $CDCl_3$).

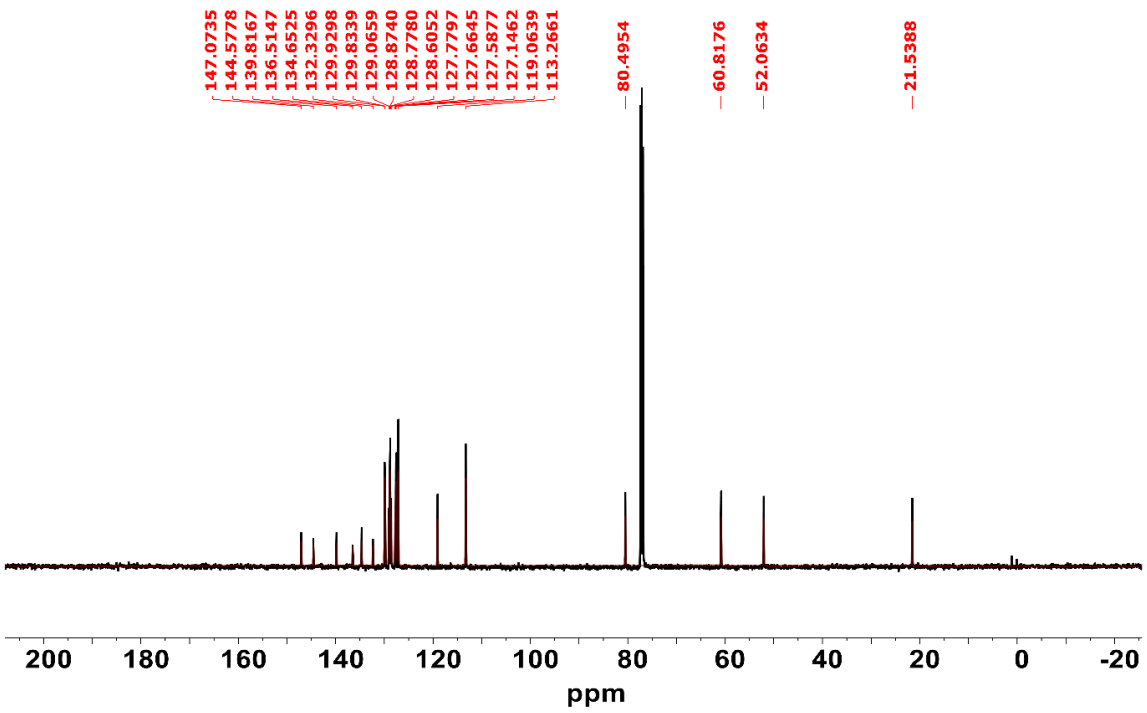



**Figure S33:** $^{13}C\{^{1}H\}$ NMR spectrum of (±)-**10d** (125 MHz, $CDCl_3$).

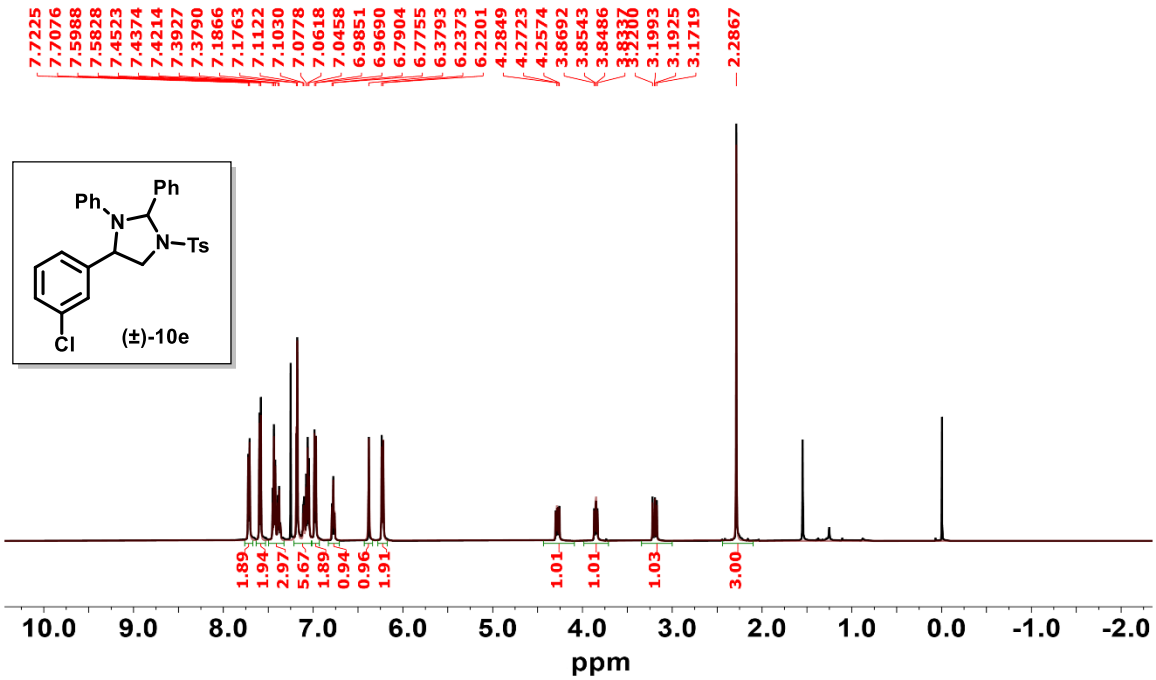



**Figure S34**: $^{1}H$ NMR spectrum of (±)-**10e** (500 MHz, $CDCl_3$.

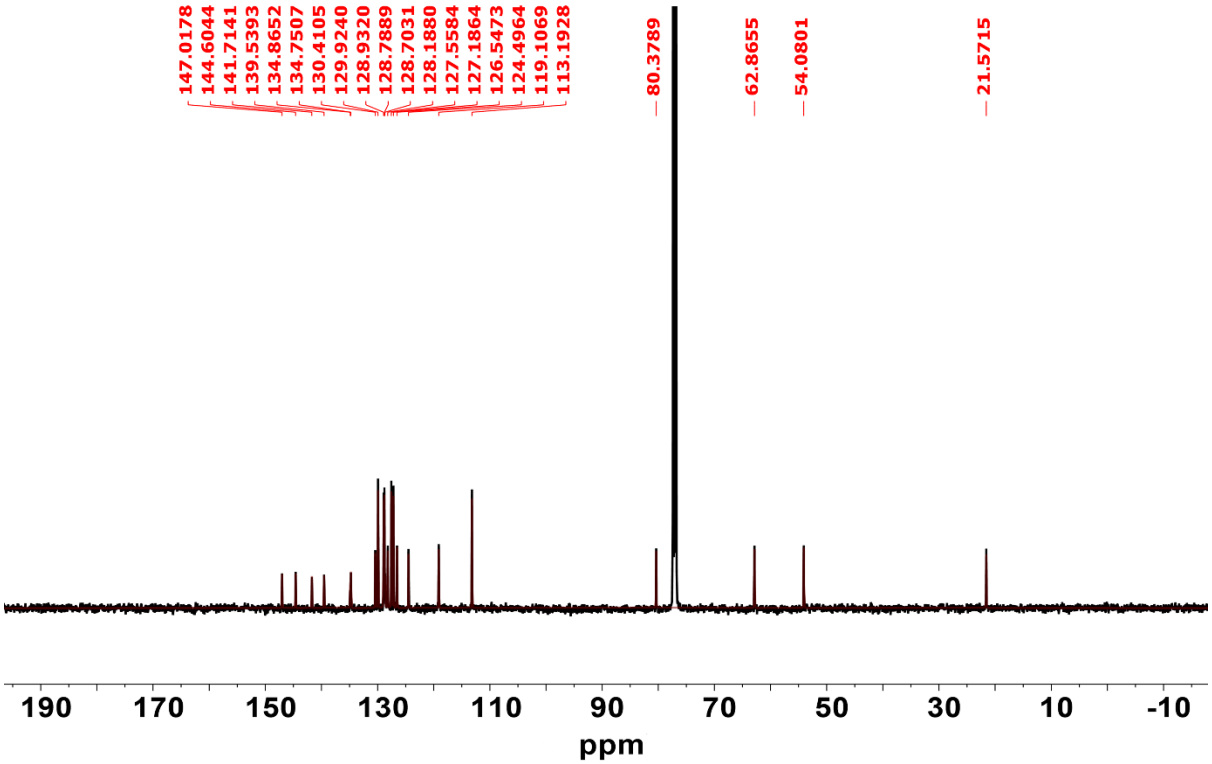



**Figure S35:** $^{13}C\{^{1}H\}$ NMR spectrum of (±)-**10e** (125 MHz, $CDCl_3$).

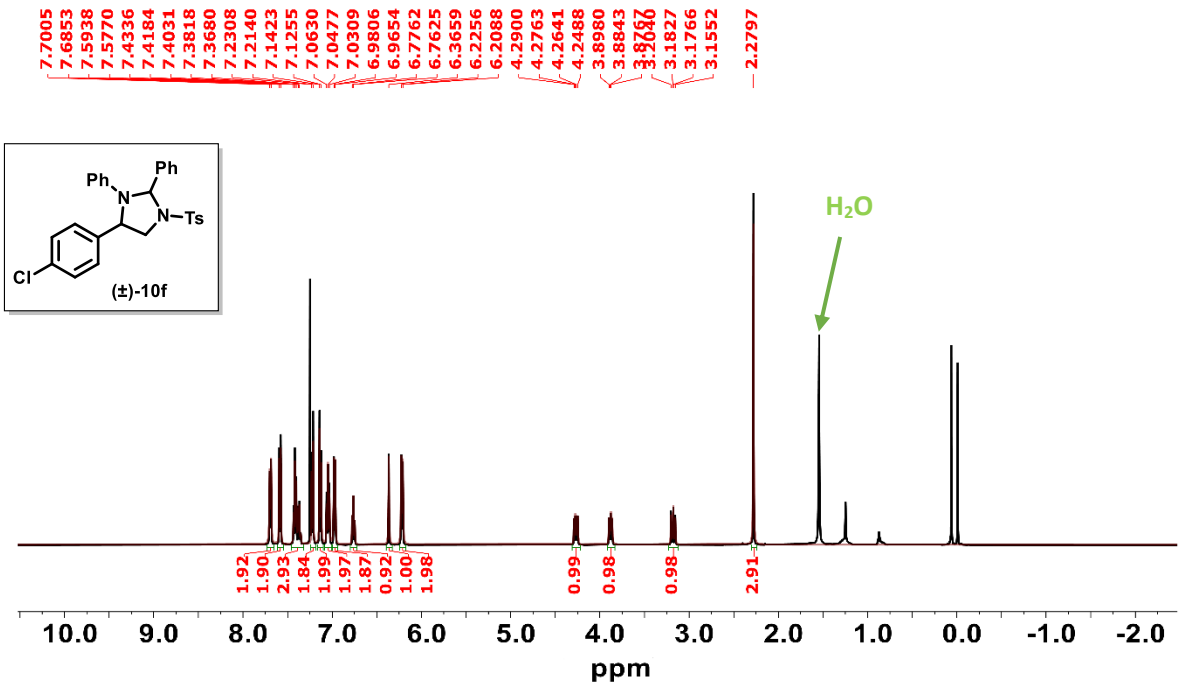



**Figure S36**: $^{1}H$ NMR spectrum of (±)-**10f** (500 MHz, $CDCl_3$).

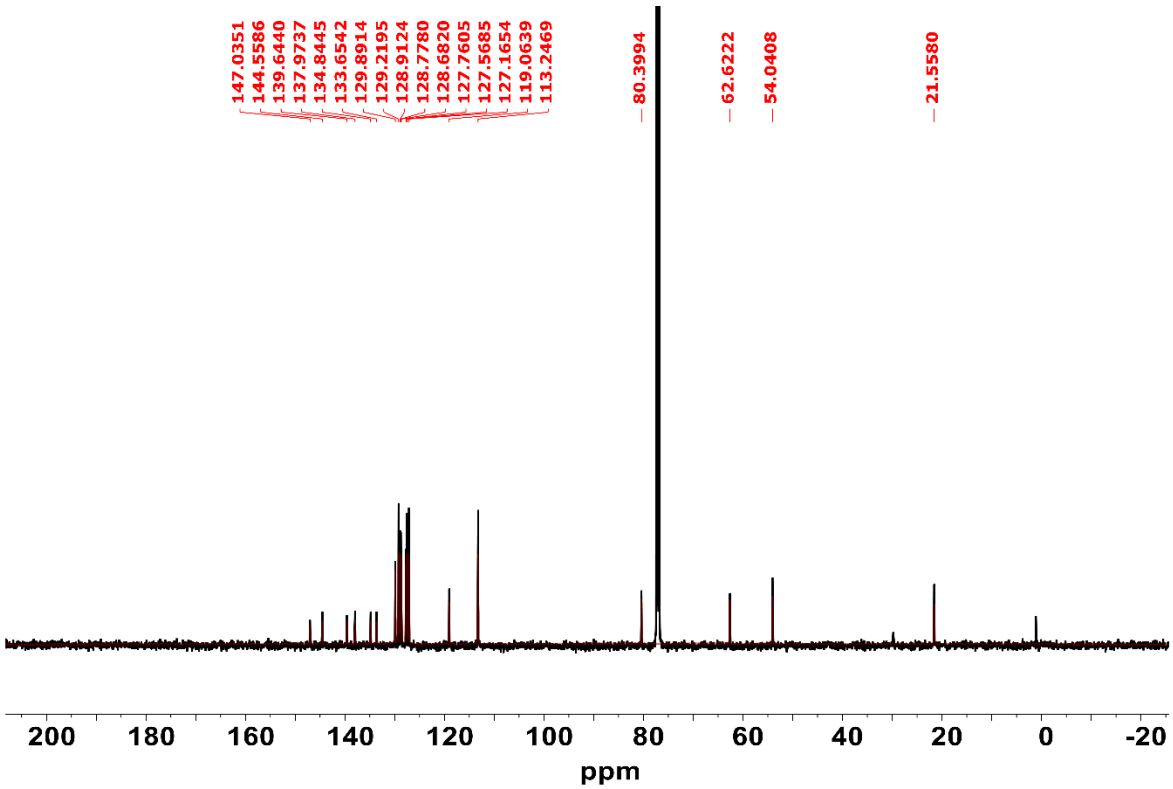



**Figure S37:** $^{13}C\{^{1}H\}$ NMR spectrum of (±)-**10f** (125 MHz, $CDCl_3$).

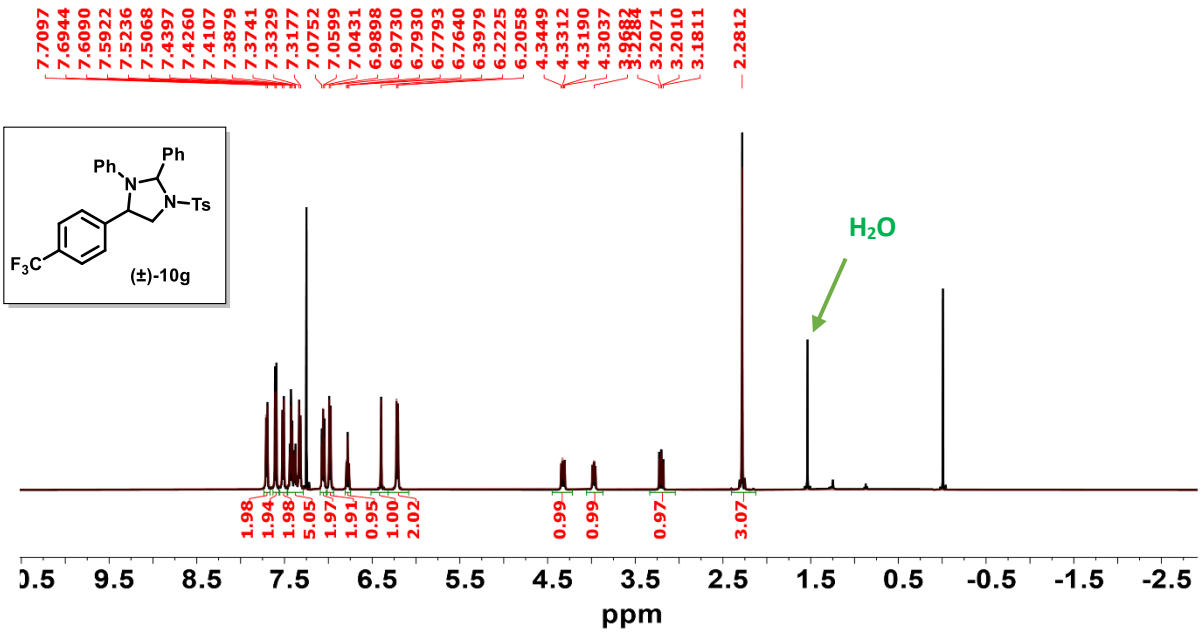



**Figure S38**: $^{1}H$ NMR spectrum of (±)-**10g** (500 MHz, $CDCl_3$.

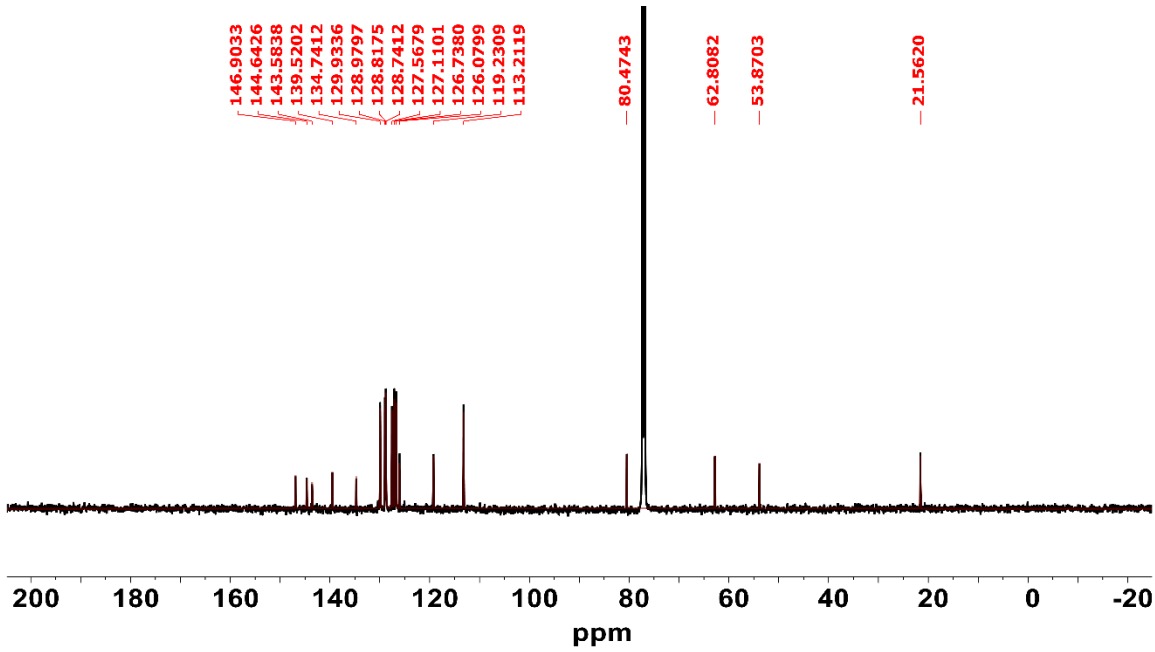



**Figure S39:** $^{13}C\{^{1}H\}$ NMR spectrum of (±)-**10g** (125 MHz, $CDCl_3$).

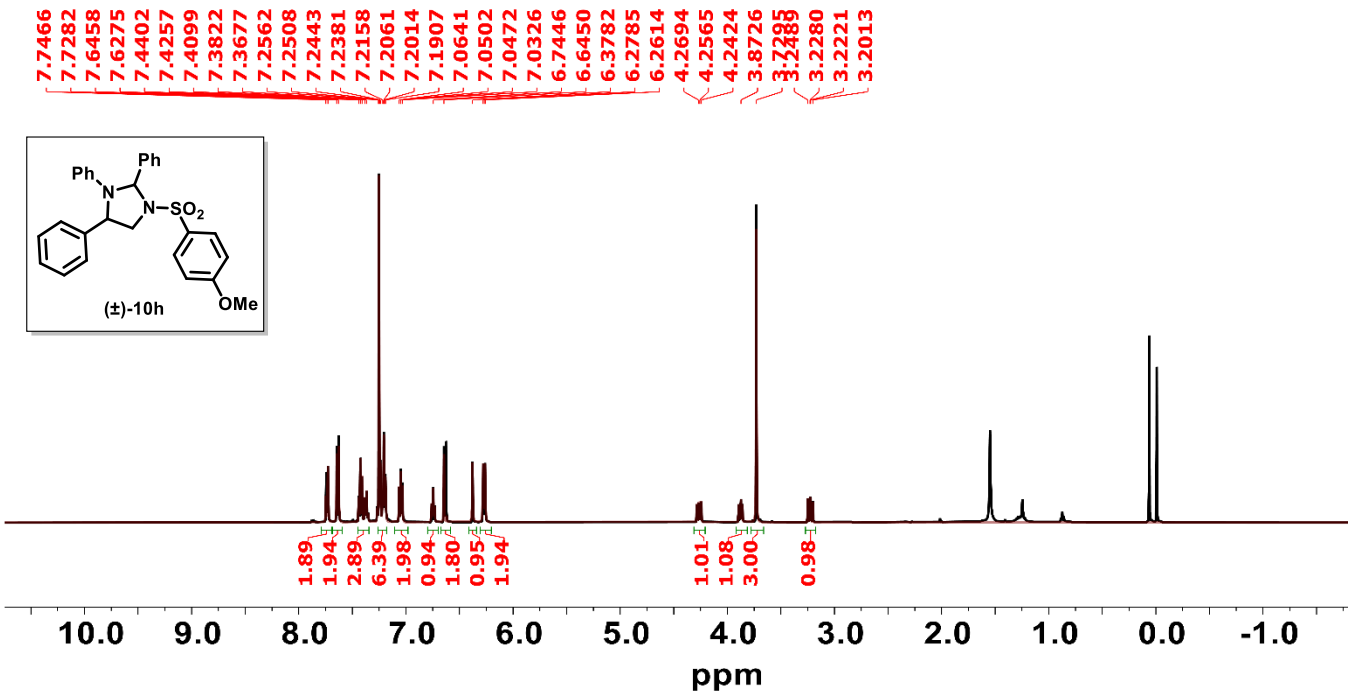



**Figure S40**: $^{1}H$ NMR spectrum of (±)-**10h** (500 MHz, $CDCl_3$).

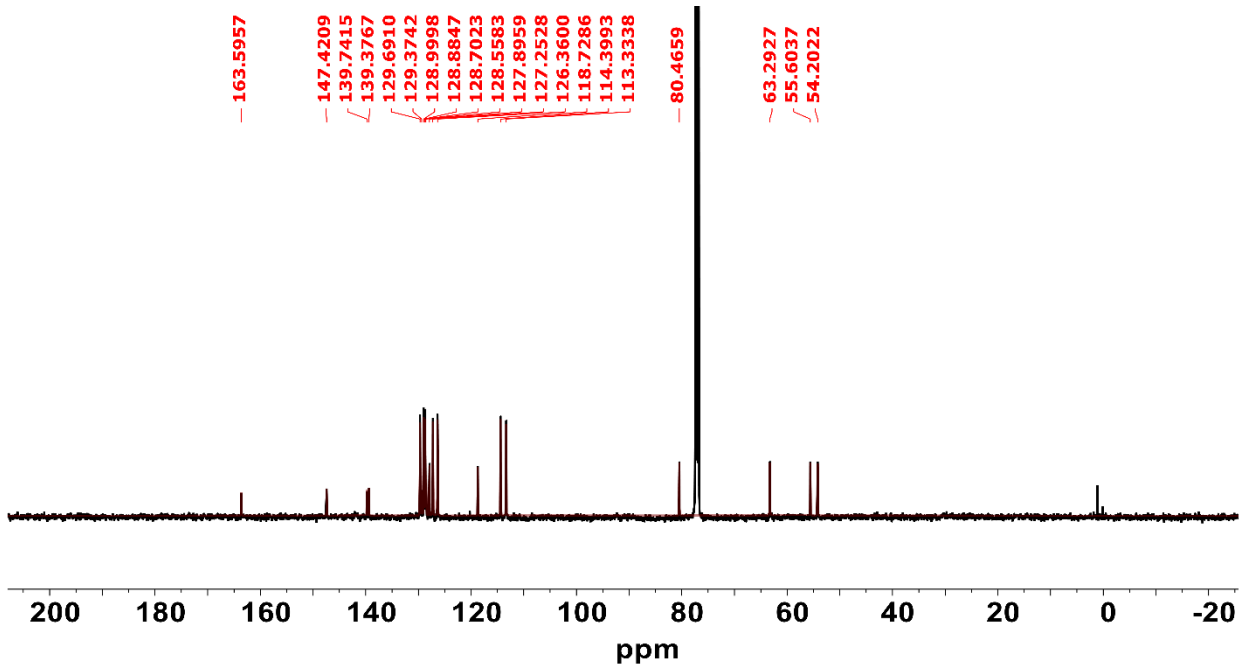



**Figure S41:** $^{13}C\{^{1}H\}$ NMR spectrum of (±)-**10h** (125 MHz, $CDCl_3$).

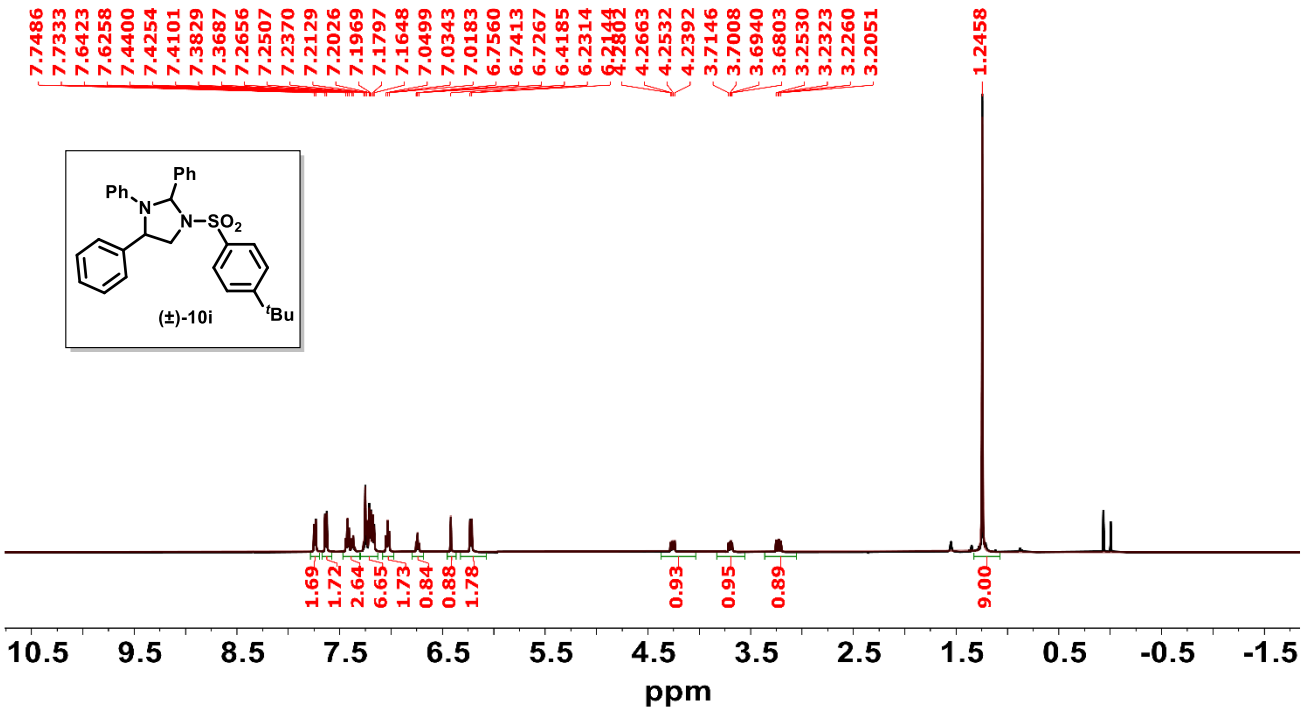



**Figure S42**: $^{1}H$ NMR spectrum of (±)-**10i** (500 MHz, $CDCl_3$).

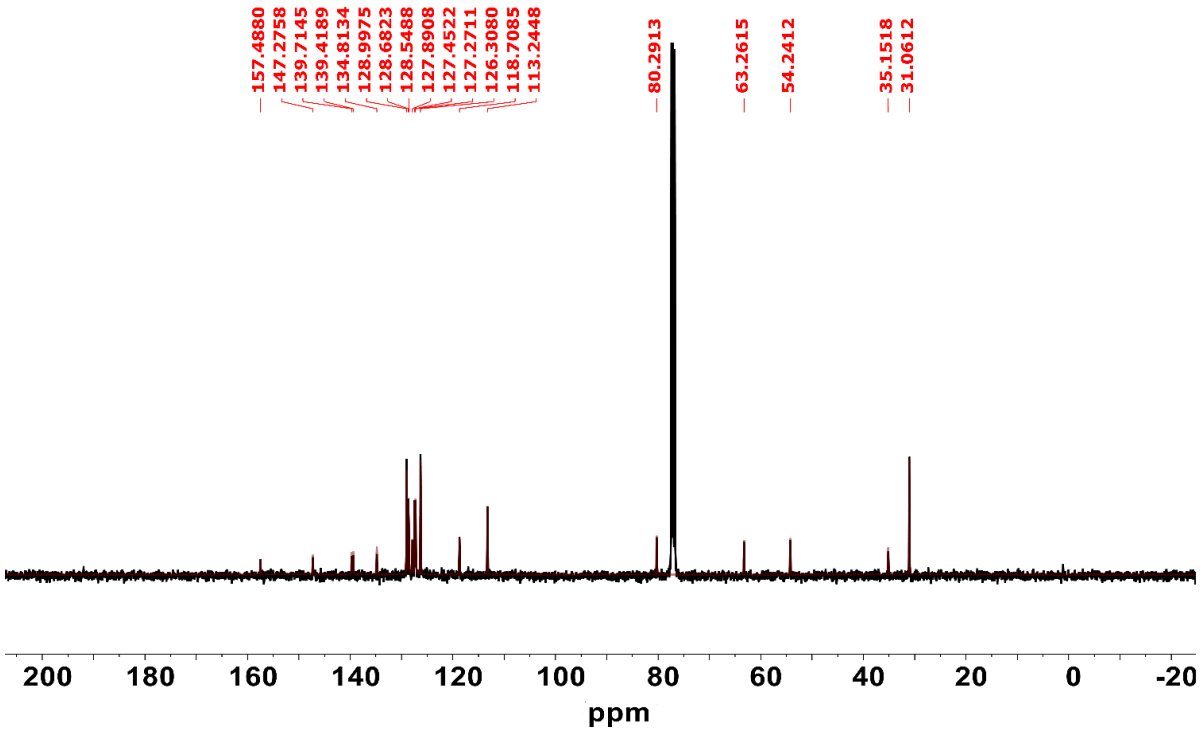



**Figure S43:** $^{13}C\{^{1}H\}$ NMR spectrum of (±)-**10i** (125 MHz, $CDCl_3$).

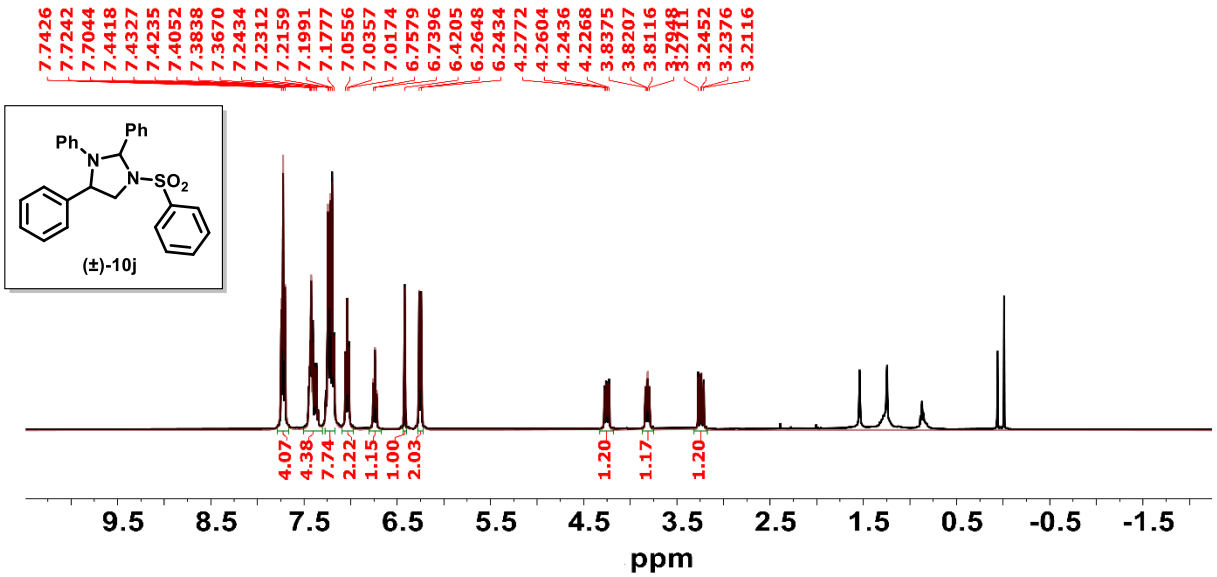



**Figure S44**: $^{1}H$ NMR spectrum of (±)-**10j** (500 MHz, $CDCl_3$).

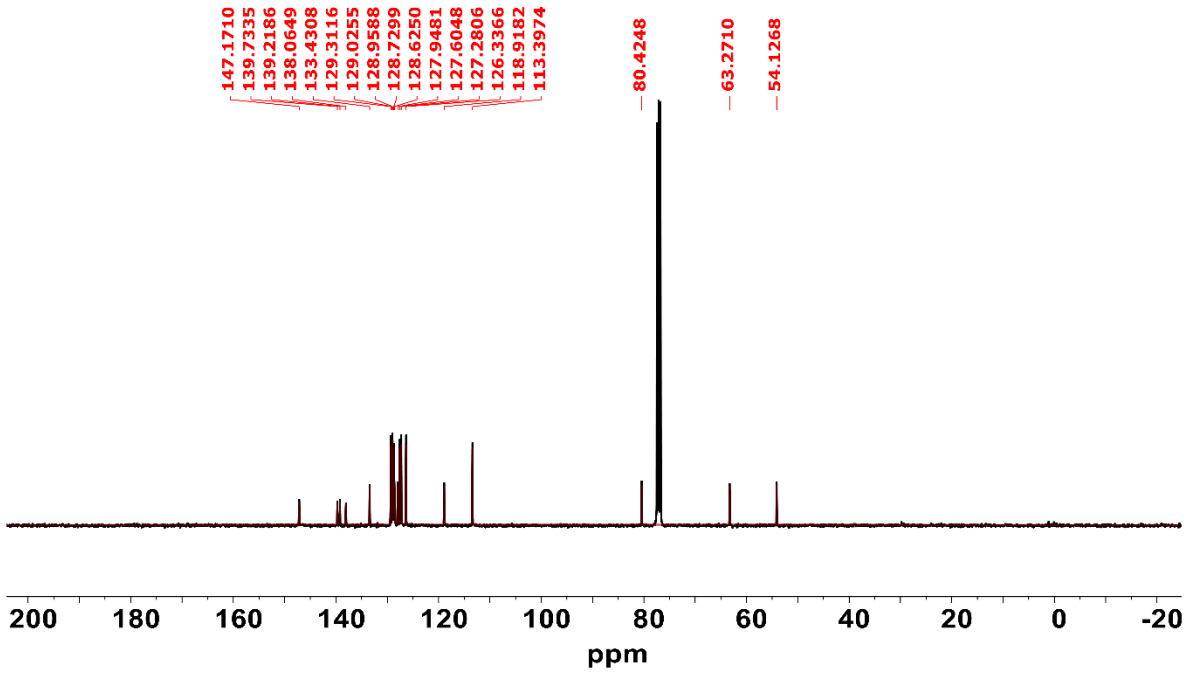



**Figure S45:** $^{13}C\{^{1}H\}$ NMR spectrum of (±)-**10j** (125 MHz, $CDCl_3$).

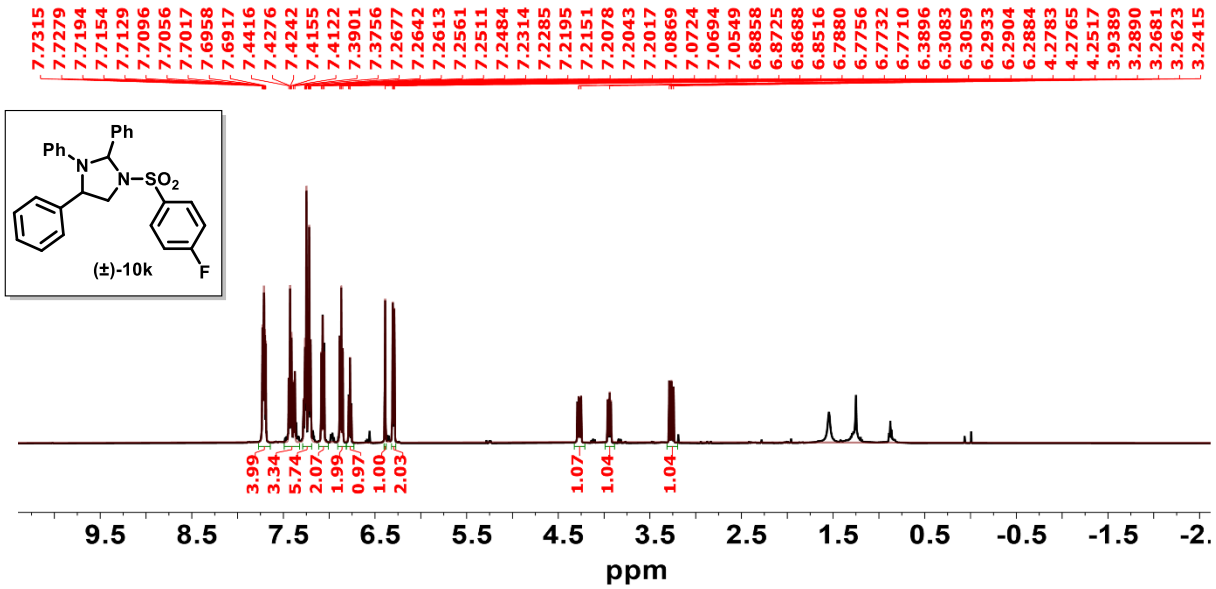



**Figure S46**: $^{1}H$ NMR spectrum of (±)-**10k** (500 MHz, $CDCl_3$).

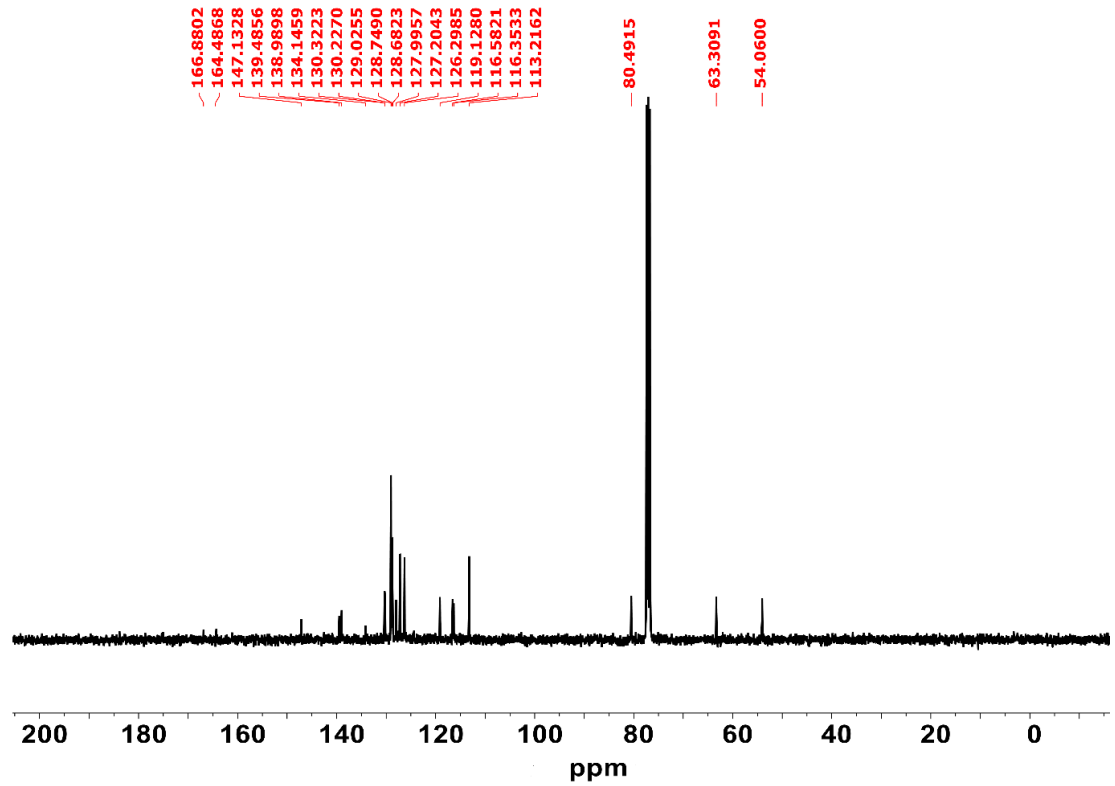



**Figure S47:** $^{13}C\{^{1}H\}$ NMR spectrum of (±)-**10k** (125 MHz, $CDCl_3$).

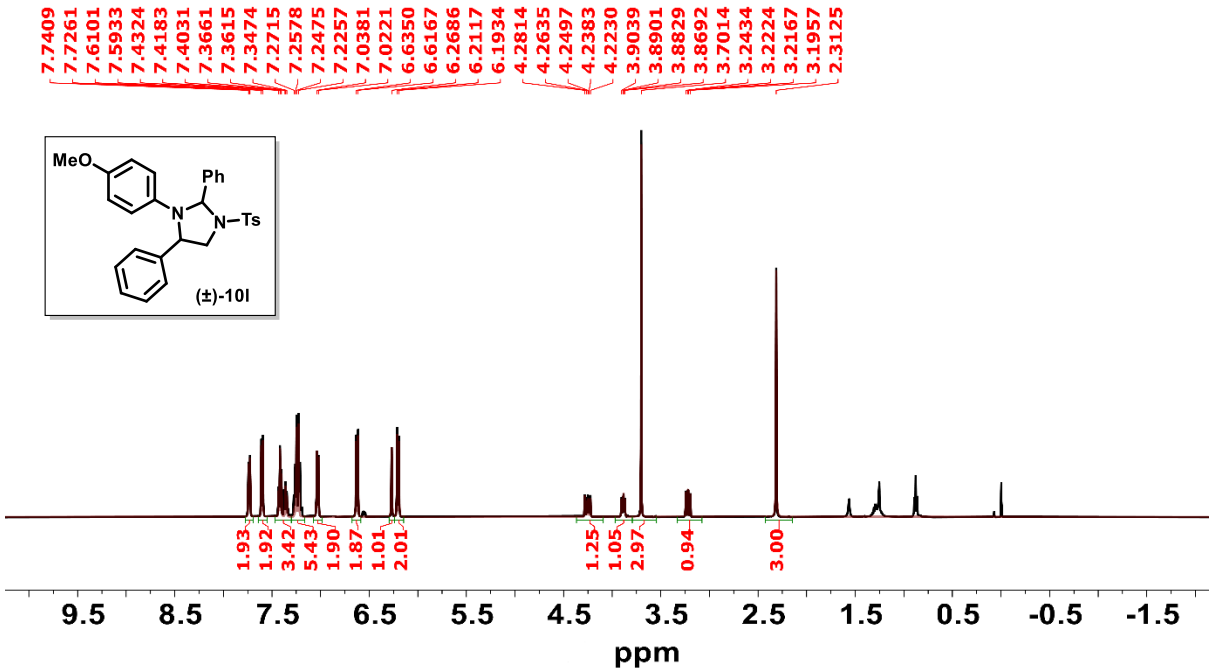



**Figure S48**: $^{1}H$ NMR spectrum of (±)-**10l** (500 MHz, $CDCl_3$).

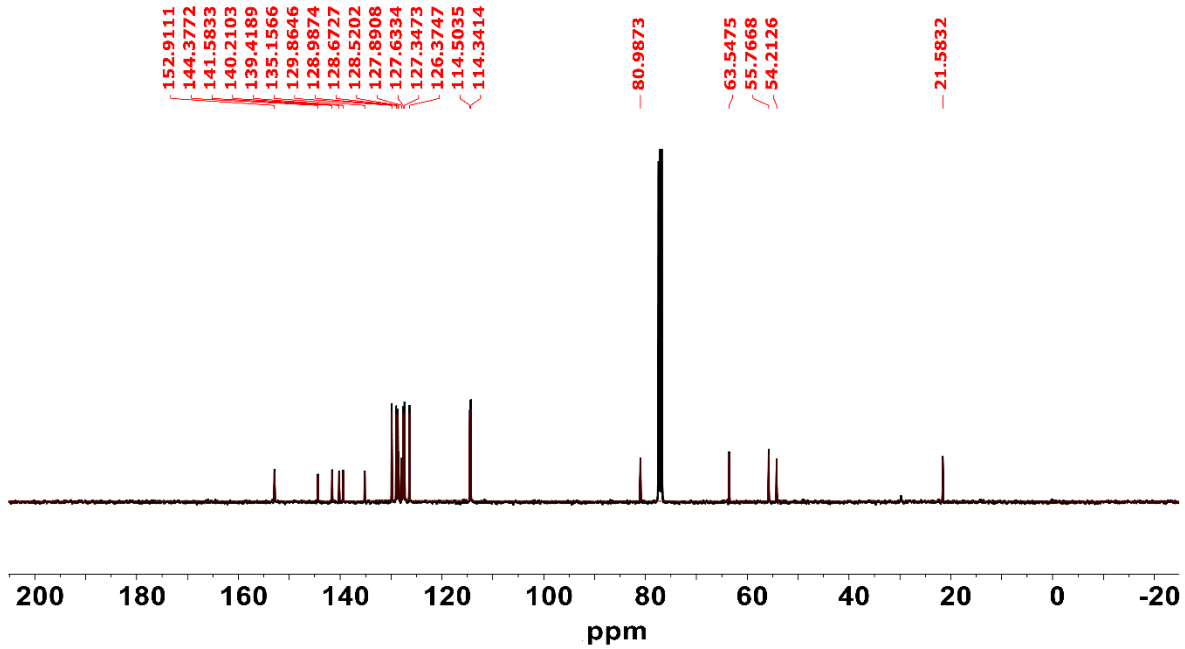



**Figure S49:** $^{13}C\{^{1}H\}$ NMR spectrum of (±)-**10l** (125 MHz, $CDCl_3$).

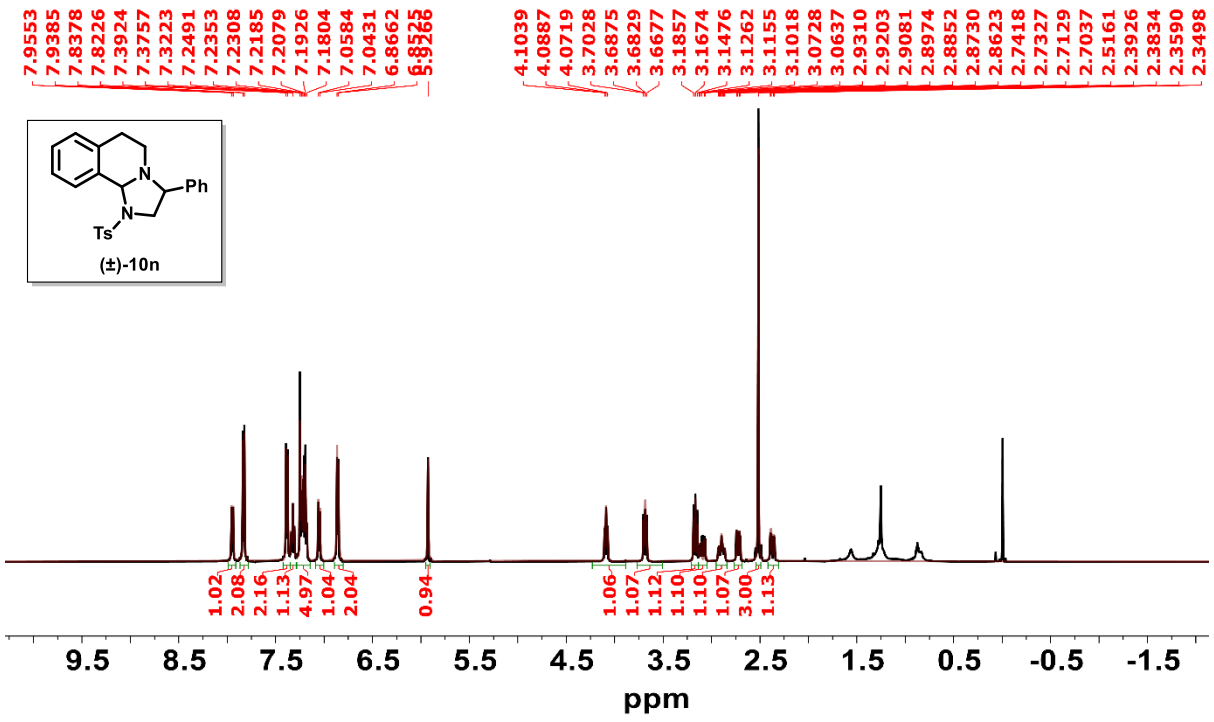



**Figure S50**: $^{1}H$ NMR spectrum of (±)-**10n** (500 MHz, $CDCl_3$).

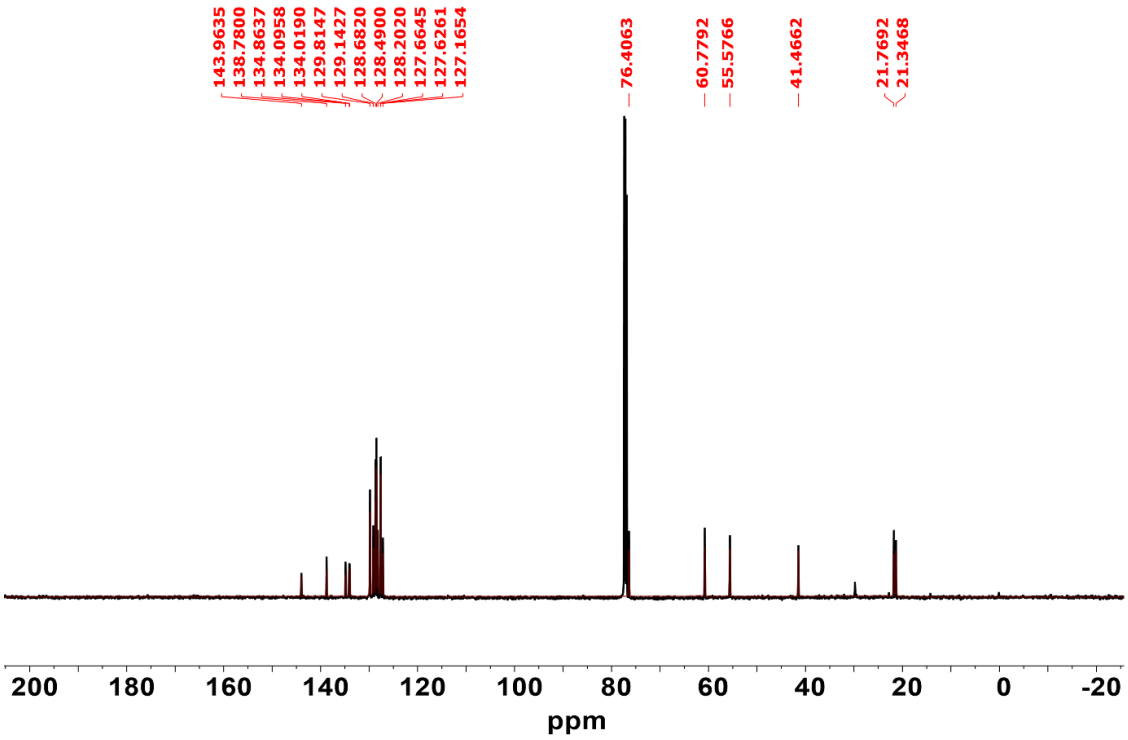



**Figure S51:** $^{13}C\{^{1}H\}$ NMR spectrum of (±)-**10n** (125 MHz, $CDCl_3$).

# HPLC chromatogram for %ee determination:

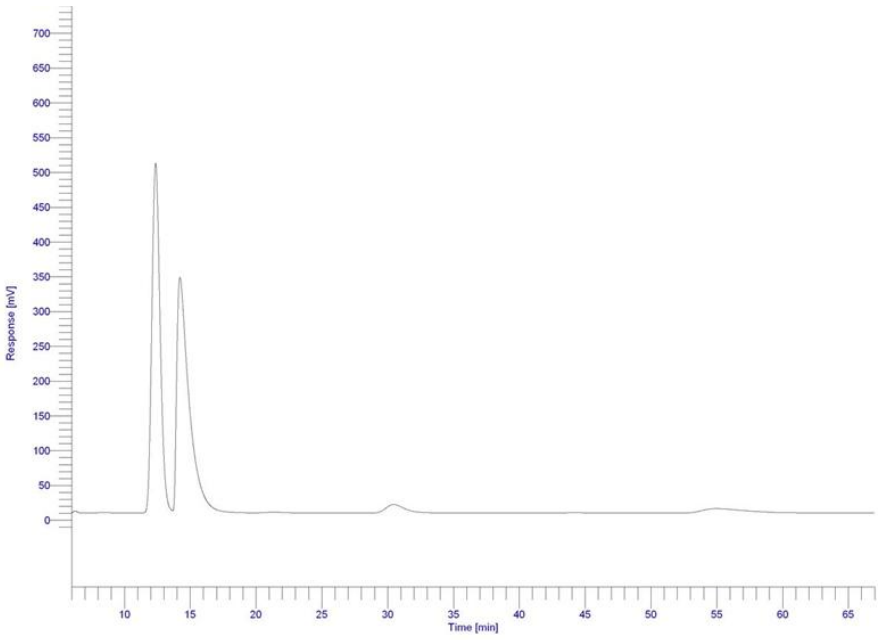


**Figure S52**: HPLC chromatogram of (±)-**10a** (OD-H, isopropanol/Hexane = 1/99, 1.0 mL/ min, 860psi) $t_R$ = 12.38 min, 14.22 min.

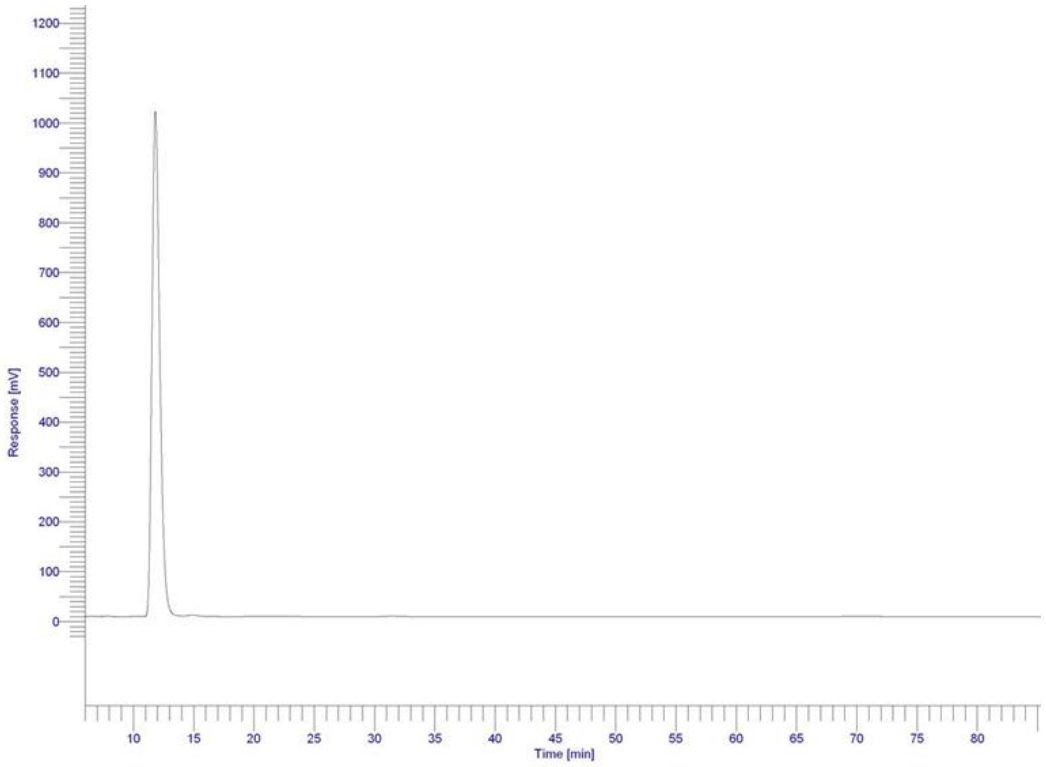



**Figure S53**: HPLC chromatogram of (*2R,4R*)**-10a** (OD-H, isopropanol/hexane = 1/99, 1.0 mL/ min, 860 psi) $t_R$ = 11.83 min, 14.97min.