Supporting Information

Deciphering Light-Triggered Mg^{2+}-Assisted $FeCl_3$ Ion-Pairing: An Efficient Photo-Oxidant for Chemo-Divergent Functionalization of 3-Arylidene Indoline

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I. General Information

1. Materials and instruments:

All reactions involving air- or moisture-sensitive reagents were carried out under a dry argon atmosphere with oven-dried reaction vessels. The reactions that required heating utilised an oil bath. Solvents, reagents, and chemicals were purchased from Aldrich, Alfa aesar, Merck, SRL, Spectrochem, and Process Chemicals. Unless otherwise noted, all commercial reagents involved in the transformation reactions were used as received from the commercial suppliers. Standard procedures were utilized for drying solvents, and they were distilled before use.

Reactions were monitored visualizing TLC plates (made of silica gel, Merck silica gel 60, F254) under UV light (254 and 365 nm) chamer, colour change in an I_2 vapour chamber, or by solvent charring using an aqueous acid/alcohol (H_2SO_4/MeOH/H_2O) mixture, or KMnO4 or vanillin solution.

^1H and ^{13}C NMR spectra were recorded on a Bruker (300 and 400 MHz) spectrometer in $CDCl_3$ solvent using tetramethylsilane (TMS) as the internal standard. Chemical shifts were measured in parts per million (δ ppm) referenced to 0.00 ppm for TMS and relative to the signal of $CDCl_3$, defined at δ 7.26 ppm for ^1H and δ 76.74 ppm for ^{13}C. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Coupling constants, *J*, were reported in Hertz units (Hz).

HRMS (m/z) were measured using EI and ESI techniques (JEOL-JMS 700 and Q-Tof Micro mass spectrometer, respectively). HRMS (m/z) data were recorded in ESI (Q-Tof and Orbitrap, positive ion) and EI (magnetic sector, positive ion) mode. All the HRMS data were obtained in acetonitrile solvent.

Melting points were determined in a capillary melting point apparatus and are uncorrected.

UV-vis absorption spectra were recorded using a Shimadzu UV 1800 spectrometer. Steady-state luminescence spectra were acquired by a Horiba Fluoromax-4 spectrofluorometer.

The electrochemical measurements were performed using a computerized CHI760E electrochemical workstation with a three-electrode system: a 1 mm platinum wire counter electrode (for oxidation), an Ag/AgCl electrode as the reference electrode, and a 3 mm glassy carbon working electrode (for reduction). Cyclic voltametric data (CV) were collected in N_2-purged as well as O_2-purged acetonitrile solution of the substrate (ca.1 mM) at 25°C, using the

supporting electrolyte, tetrabutylammonium perchlorate (TBAP), (ca. 0.1 M). The acquired scan rate for CV measurements was set to 100 mV/sec. Polishing the glassy carbon working electrode utilised a fine polishing suspension of alumina on a polishing pad, following a figure-eight pattern with even pressure, and thorough rinsing with dry acetonitrile solvent.

Electron Paramagnetic Resonance (EPR) spectral data were evaluated for the sample using a standard quartz EPR tube on a JEOL JES-FA200 X-band spectrometer. Instrument settings: microwave frequency, 9.458 GHz; microwave power, 0.998 mW; modulation frequency, 100 kHz.

Resonance Raman (rR) spectroscopy data were obtained using a Trivista 555 spectrograph (Princeton Instruments) and 413.1 nm excitation from a Kr^+ laser (Coherent, Sabre Innova SBRC-DBW-K).

Single-crystal X-ray diffraction intensity data were obtained using a Bruker D8 QUEST area detector diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The low-temperature single crystal X-ray diffraction (SXRD) intensity data were collected by using a BRUKER APEX II diffractometer equipped with a CCD area detector, a MoKα (λ=0.7174 Å) radiation source, and a Peltier temperature controller that can maintain temperatures between 80 K and 400 K.

- **Reaction Set-up:**

The Material of the Irradiation Vessel: Borosilicate reaction tube (Single and dual chamber reactor, unless otherwise noted)

Light Source[1]:

Brand: PHILIPS

Model: Tornado-G-5M

Broadband source：λ_{max} = 545 nm.

Two 32 W white CFL spiral bulbs (λ_{max} = 545 nm) were set up 3 cm apart from the reaction tube without using any filters.

2. Computational Method (DFT study):

All the theoretical calculations were performed using DFT (Density Functional Theory) with the Gaussian 09 software package. For geometry optimizations, the 6-31G(d,p) basis set was

used for C, N, O, S, and H elements. Based on these optimized geometries, single-point calculations were carried out with the 6-311+G(2d,2p) basis set for all elements. Analytical frequency calculations of the transition states were performed to confirm the stationary points at the same basis set level as the geometry optimizations. The reported energies are Gibbs free energies, which include zero-point vibrational corrections, thermal corrections, and entropy corrections at 298 K. These corrections were calculated as single-point corrections on the optimized structures using the same basis set combination as for the geometry optimizations, with the conductor-like polarizable continuum model (CPCM) method applied. All energies were also corrected for dispersion effects via single-point calculations using the DFT method based on the optimized geometries.

II. Experimental Section

1. Additional optimization of the reaction conditions.

A) Screening with different iron catalysts, additives and oxygen sources in MeCN using a single-chamber reaction vessel

				Yield (%)		
Entry	**Catalyst**	**Additives**	**Oxygen Source**	**2a**	**3a**	**4a**
1	$FeCl_3$ (10 mol%)	excluding $MgSO_4$	O_2-balloon	0	48	21
2	$FeCl_3$ (10 mol%)	$MgSO_4$ (3 mol%)	O_2-balloon	11	52	16
3	$FeCl_3$ (10 mol%)	$MgSO_4$ (3 mol%)		0	40	27
4	$FeCl_3$ (10 mol%)	$MgSO_4$ (10 mol%)		0	35	41
5	$FeCl_3$ (10 mol%)	$MgSO_4$ (30 mol%)		0	22	44
6	$FeCl_3$ (10 mol%)	$MgSO_4$ (3 mol%)/ PTSA (5 mol%)/ H_2O (5 µL)	O_2-balloon	0	45	trace
7	$FeCl_3$ (10 mol%)	$MgSO_4$ (10 mol%)/ PTSA (5 mol%)/ H_2O (5 µL)	O_2-balloon	0	59	trace
8	$FeCl_3$ (10 mol%)	Na_2SO_4 (1 equiv.)	O_2-balloon	0	48	trace
9	$FeCl_3$ (10 mol%)	$MgCl_2$ (30 mol%)	O_2-balloon	12	49	17
10	$FeCl_3$ (10 mol%)	$MgCl_2$ (30 mol%)/ Na_2SO_4 (1 equiv.)	O_2-balloon	26	38	24
11	$FeCl_3$ (10 mol%)	PTSA (5 mol%)	O_2-balloon	0	73	0
12	$FeCl_3$ (10 mol%)	AcOH (5 mol%)	O_2-balloon	0	62	0
13	$FeCl_3$ (10 mol%)	PTSA (5 mol%)/H_2O (5 µL)	O_2-balloon	0	84	0
14	$FeCl_3$ (10 mol%)	H_2O (5 µL)	O_2-balloon	0	72	0
15	$FeCl_3$ (10 mol%)	H_2O_2 (1 % V/V)		0	81	0
16	$FeCl_3$ (10 mol%)	LiBr (10 Mol%)		0	0	68
17	Li[$FeCl_3Br$] (10 mol %)			0	0	75
18	$FeBr_3$ (10 mol%)	PTSA (5 mol%)	O_2-balloon	0	42	51

Table S1. Optimization of the reaction conditions[a]. [a]Typical reaction conditions for accessing divergent C-3 functionalization of 3-arylidene indolines. In a single-chamber reaction vessel, 1a (0.50 mmol), iron catalyst (0.05 mmol), 2x32 W White CFL (λ_{max}= 545 nm), 50 ºC, 2 h.

B) Screening with common state-of-the-art singlet oxygen ($^1O_2$) sources for the photodimerization reaction in MeCN using a double-chamber reaction vessel

	Chamber A	Chamber B		Yield (%)
Entry	**$^1O_2$ generator**	**Catalyst**	**Oxygen Source**	**2a**
1	$FeCl_3$ (50 mol%)/ $MgSO_4$ (1 equiv.)		O_2-balloon	0
2	EOSIN Y (50 mol%)	$FeCl_3$ (2 mol%)	O_2-balloon	46
3	Rose Bengal (50 mol%)	$FeCl_3$ (2 mol%)	O_2-balloon	41
4	Rhodamine B (50 mol%)	$FeCl_3$ (2 mol%)	O_2-balloon	38

Table S2. Optimization of the reaction conditions[a]. [a]Typical reaction conditions for accessing 1,2-diindolyl ethanes from 3-arylidene indolines in a double-chamber reaction vessel. Chamber A: Dioxygen-activation catalyst (0.25 mmol), O_2-balloon, MeCN (2 ml), and Chamber B: 1a (0.50 mmol), Fe-catalyst (0.01 mmol), MeCN (2 ml), and both the reaction chambers were set up under 2x32 W White CFL exposure at 50 ºC for 2 h.

2. General Experimental Procedure:

All the substrates, 3-arylidene indolines (**1**) employed for the divergent synthesis of 3-functionalized indoles were accessed by utilizing our previously established protocols.[2]

A. Representative experimental procedure for the synthesis of *trans*-1,2-diindolyl ethanes and their Characterizations:

(1*R*,2*S*)-1,2-diphenyl-1,2-bis(1-tosyl-1*H*-indol-3-yl)ethane (**2a**):

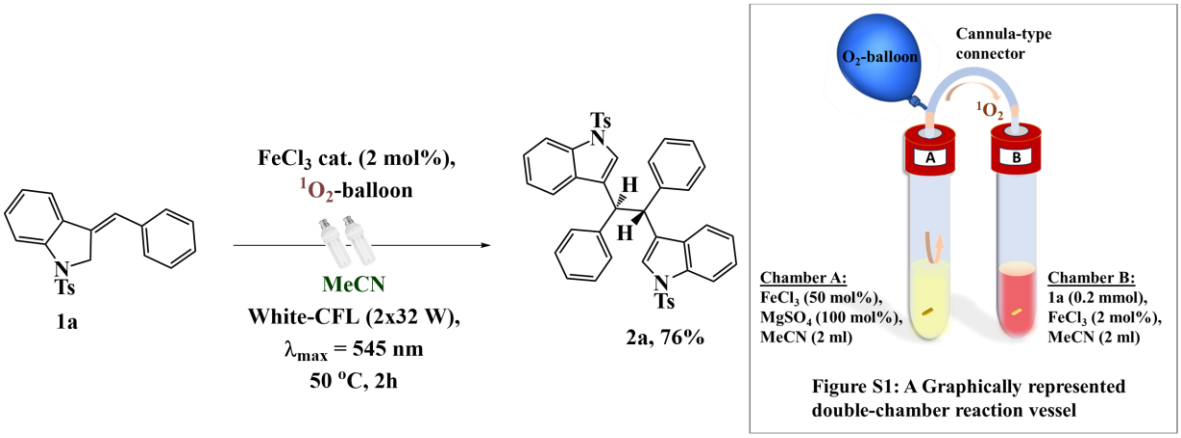


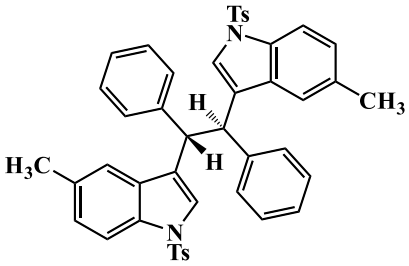
Figure S1: A Graphically represented double-chamber reaction vessel

Scheme S1

For the synthesis of the photodimerized product, **2a**, a double-chamber (chamber A and B) reaction vessel was devised, where two reaction vessels were adjusted with a cannula-type connector for easy transfer of oxygen gas between these vessels. To a solution of $FeCl_3$ (ca. 0.05 M) in MeCN was added 1 equivalent of anhydrous $MgSO_4$ in the reaction chamber A, which is equipped with an oxygen balloon. In another chamber B, to a solution of **1a** (72 mg, 0.2 mmol) in MeCN (2 ml) was added a catalytic amount of $FeCl_3$ (~1 mg, 0.004 mmol). The reaction was continued at 50 °C for 2 h under an oxygen atmosphere and with White CFL (λ_{max} = 545 nm, 2x32 W) exposure. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with DCM for 3 times, washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with Hexane/EtOAc 95:5 (v/v) to afford an off-white solid product **2a** in 76% yield (0.15 mmol, 108 mg). m.p. 188-189 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 2H), 7.47 – 7.45 (m, 1H), 7.43 (s, 1H), 7.39 (s, 2H), 7.32 – 7.29 (m, 6H), 7.28 (d, *J* = 1.1 Hz, 1H), 7.23 – 7.17 (m, 3H), 7.05 (d, *J* = 0.8 Hz, 3H), 7.03 – 7.01 (m, 6H), 6.99 – 6.96 (m, 3H), 4.80 (s, 2H), 2.31 (s, 6H).^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8, 140.9, 135.2,

134.6, 130.7, 129.8, 128.4, 128.0, 126.5, 126.2, 125.3, 124.9, 123.6, 123.1, 119.7, 113.8, 48.3, 21.5. HRMS (ESI, m/z) calculated for $C_{44}H_{37}N_2O_4S_2^+$: 721.2189, found: 721.2191.

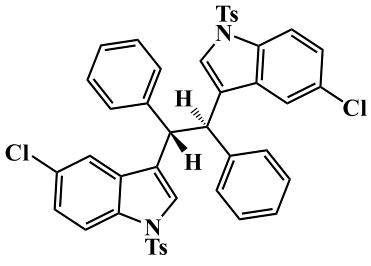
(1*R*,2*S*)-1,2-bis(5-methyl-1-tosyl-1*H*-indol-3-yl)-1,2-diphenylethane (**2b**):



2b

Yield: 72% (0.14 mmol, 105 mg). off-White semi-solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.30 (s, 2H), 7.27 (d, *J* = 1.7 Hz, 2H), 7.25 (s, 2H), 7.18 (dt, *J* = 1.6, 0.8 Hz, 2H), 7.10 (d, *J* = 1.6 Hz, 1H), 7.07 (d, *J* = 1.6 Hz, 1H), 7.04 – 7.03 (m, 2H), 7.00 (d, *J* = 2.2 Hz, 5H), 6.96 – 6.93 (m, 3H), 4.71 (s, 2H), 2.35 (s, 6H), 2.29 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.7, 140.9, 134.5, 133.5, 133.3, 131.00, 129.7, 128.4, 127.9, 126.4, 126.2, 125.2, 123.1, 119.6, 113.5, 48.2, 21.5, 21.5. HRMS (ESI, m/z) calculated for $C_{46}H_{41}N_2O_4S_2^+$: 749.2502, found: 749.2508.

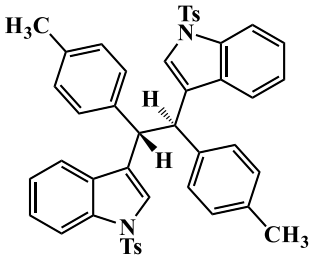
(1*R*,2*S*)-1,2-bis(5-chloro-1-tosyl-1*H*-indol-3-yl)-1,2-diphenylethane (**2c**):



2c

Yield: 66% (0.13 mmol, 105 mg). Yellowish semi-solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.33 (m, 3H), 7.31 – 7.30 (m, 4H), 7.28 – 7.27 (m, 3H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.06 – 7.00 (m, 8H), 6.88 – 6.84 (m, 4H), 4.72 (s, 2H), 2.31 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 140.8, 137.4, 135.2, 134.7, 130.8, 129.8, 129.1, 127.7, 127.1, 126.2, 125.6, 125.4, 124.9, 123.6, 123.0, 119.8, 113.7, 48.2, 21.5, 21.3. HRMS (EI, m/z) calculated for $C_{44}H_{35}Cl_2N_2O_4S_2^+$: 789.1410, found: 789.1408.

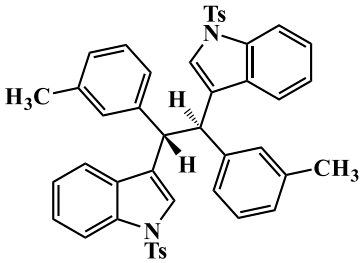
(1*R*,2*S*)-1,2-di-p-tolyl-1,2-bis(1-tosyl-1*H*-indol-3-yl)ethane (**2d**):



2d

Yield: 75% (0.14 mmol, 105 mg). off-White amorphous solid. m.p. 169-176 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.92 (m, 2H), 7.48 – 7.44 (m, 2H), 7.36 (s, 2H), 7.29 (s, 2H), 7.26 (d, *J* = 2.0 Hz, 3H), 7.22 – 7.17 (m, 2H), 7.01 (dd, *J* = 7.4, 1.3 Hz, 4H), 6.86 (d, *J* = 3.3 Hz, 8H), 4.77 (s, 2H), 2.30 (s, 6H), 2.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 137.9, 135.8, 135.2, 134.7, 130.8, 129.7, 128.7, 128.3, 126.2, 125.7, 124.8, 123.5, 122.9, 119.7, 113.7, 47.7, 21.5, 20.9. HRMS (ESI, m/z) calculated for $C_{46}H_{41}N_2O_4S_2^+$: 749.2502, found: 749.2511.

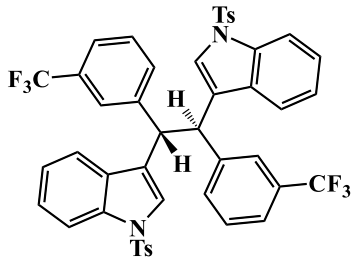
(1*R*,2*S*)-1,2-di-*m*-tolyl-1,2-bis(1-tosyl-1*H*-indol-3-yl)ethane (**2e**):



2e

Yield: 73% (0.14 mmol, 109 mg). Off-white semi-solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.30 (s, 2H), 7.27 (d, *J* = 1.8 Hz, 2H), 7.25 (s, 2H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.19 – 7.17 (m, 2H), 7.08 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.03 – 7.01 (m, 4H), 7.00 (d, *J* = 2.1 Hz, 4H), 6.96 (s, 1H), 6.93 (dt, *J* = 5.7, 2.6 Hz, 3H), 4.71 (s, 2H), 2.35 (s, 6H), 2.29 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8, 141.1, 134.6, 133.6, 133.4, 131.12, 130.0, 129.9, 129.7, 128.5, 128.1, 127.4, 126.5, 126.3, 125.3, 123.2, 122.6, 119.6, 113.6, 48.4, 21.7, 21.6. HRMS (ESI, m/z) calculated for $C_{46}H_{41}N_2O_4S_2^+$: 749.2502, found: 749.2502.

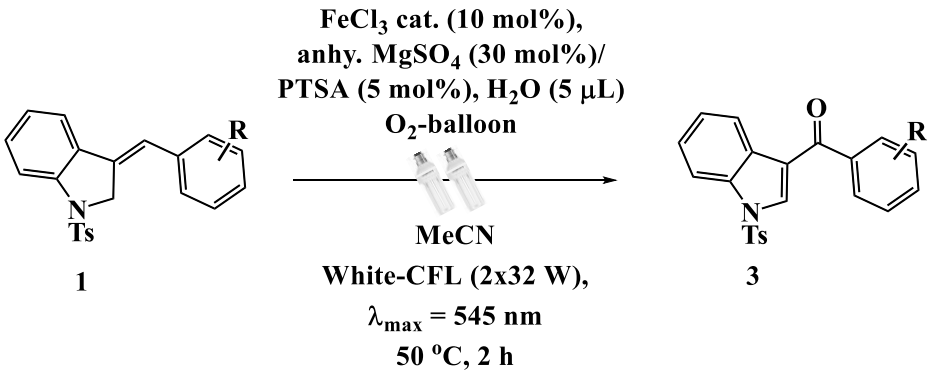
(1*R*,2*S*)-1,2-bis(1-tosyl-1*H*-indol-3-yl)-1,2-bis(3-(trifluoromethyl)phenyl)ethane (**2f**):



2f

Yield: 75% (0.15 mmol, 128 mg). off-White solid. m.p. 202-203 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 8.05 (s, 1H), 7.64 (d, *J* = 1.6 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 1.9 Hz, 2H), 7.40 (d, *J* = 2.1 Hz, 4H), 7.19 – 7.15 (m, 4H), 7.08 – 7.04 (m, 6H), 6.94 (dd, *J* = 6.6, 3.0 Hz, 4H), 4.80 (s, 2H), 2.38 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.57, 140.11, 136.61, 134.31, 130.14, 130.08, 128.29, 128.25, 126.87, 126.32, 125.81, 124.85, 124.64, 121.92, 117.19, 114.09, 77.34, 77.23, 77.02, 76.71, 48.08, 29.72, 21.61. HRMS (ESI, m/z) calculated for $C_{46}H_{35}F_6N_2O_4S_2^+$: 857.1937, found: 857.1936.

B. Representative experimental procedure for the synthesis of 3-acyl indoles and their Characterizations:

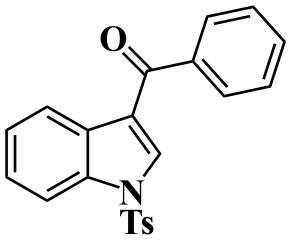


1 **3**

Scheme S2

To a solution of **1** (0.2 mmol) in MeCN (2 ml) was added a catalytic amount of $FeCl_3$ (0.02 mmol), PTSA (0.01 mmol), anhydrous $MgSO_4$ (0.06 mmol), and H_2O (5 μL). The reaction was continued at 50 °C for 2 h under an oxygen atmosphere and with White CFL (λ_{max} = 545 nm, 2x32 W) exposure. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with DCM for 3 times, washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with Hexane/EtOAc 95:5 (v/v) to afford the desired product **3**.

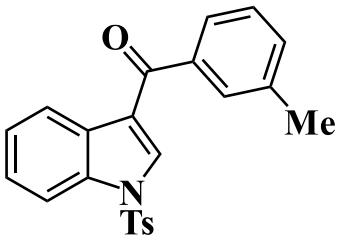
Phenyl(1-tosyl-1*H*-indol-3-yl)methanone (**3a**):



3a

Yield: 84% (0.16 mmol, 63 mg). Off-white solid. ^{1}H NMR (400 MHz, CDCl3) δ 8.62 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.53 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.22 (s, 1H), 8.17 – 8.13 (m, 2H), 7.90 – 7.87 (m, 2H), 7.69 – 7.65 (m, 1H), 7.58 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.37 – 7.34 (m, 2H), 7.32 (s, 1H), 7.28 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 147.2, 146.4, 146.2, 138.6, 134.39, 133.2, 132.6, 131.8, 129.9, 128.9, 128.8, 128.6, 121.3, 120.5, 117.4, 21.8. HRMS (EI, m/z) calculated for $C_{22}H_{18}NO_3S^+$: 376.1002, found: 376.1098.

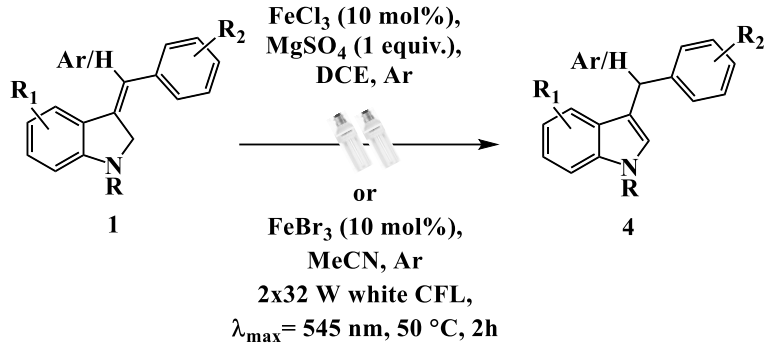
m-Tolyl(1-tosyl-1*H*-indol-3-yl)methanone (**3b**):



3b

Yield: 79% (0.16 mmol, 61 mg). Off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.30 (m, 1H), 8.04 (s, 1H), 8.03 – 8.00 (m, 1H), 7.83 – 7.80 (m, 2H), 7.70 – 7.66 (m, 2H), 7.47 – 7.38 (m, 4H), 7.30 (s, 1H), 7.28 (s, 1H), 2.49 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 145.9, 139.3, 138.6, 135.0, 134.6, 133.5, 133.2, 130.2, 129.5, 128.6, 128.5, 127.1, 126.3, 125.9, 124.8, 122.9, 120.6, 113.2, 21.6, 21.5. HRMS (ESI, m/z) calculated for $C_{23}H_{20}NO_3S^+$: 390.1158, found: 390.1158.

C. Representative experimental procedure for the synthesis of 3-alky indoles and their Characterizations:



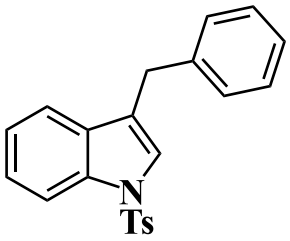
Scheme S3

(A) To a solution of **1** (0.2 mmol) in DCE (2 ml) was added a catalytic amount of $FeCl_3$ (0.02 mmol) and anhydrous $MgSO_4$ (1 equiv.), or

(B) To a solution of **1** (0.2 mmol) in MeCN was added a catalytic amount of $FeBr_3$ (0.02 mmol).

Reactions were continued at 50 °C for 2 h under an inert atmosphere and with White CFL (λ_{max} = 545 nm, 2x32 W) exposure. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with DCM for 3 times, washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with Hexane/EtOAc 99:1 (v/v) to afford the desired product **4**.

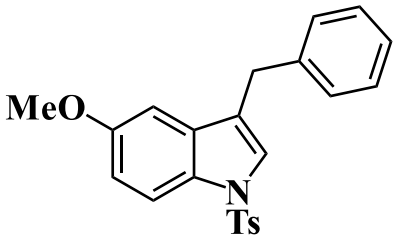
3-Benzyl-1-tosyl-1*H*-indole (**4a**):



4a

Yield: (A) 62 % (0.12 mmol, 45 mg); (B) 91% (0.18 mmol, 66 mg). White semi-solid. ^{1}H NMR (400 MHz, CDCl3) δ 8.01 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.77 – 7.74 (m, 2H), 7.41 – 7.38 (m, 1H), 7.31 (ddd, *J* = 7.6, 3.4, 2.2 Hz, 4H), 7.26 – 7.22 (m, 5H), 7.19 (dd, *J* = 7.8, 1.0 Hz, 1H), 4.03 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 139.0, 135.6, 135.4, 130.9, 129.8, 128.6, 128.5, 126.8, 126.4, 124.7, 124.0, 123.1, 122.5, 119.8, 113.8, 31.4, 21.5. HRMS (ESI, m/z) calculated for $C_{22}H_{20}NO_2S^+$: 362.1209, found: 362.1209.

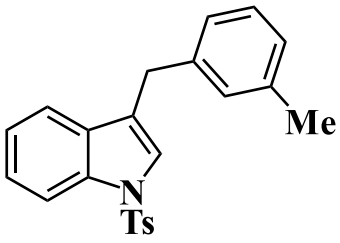
3-Benzyl-5-methoxy-1-tosyl-1*H*-indole (**4b**):



4b

Yield: (A) 65 % (0.13 mmol, 51 mg); (B) 92% (0.18 mmol, 72 mg). White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 9.0 Hz, 1H), 7.72 – 7.69 (m, 2H), 7.33 – 7.30 (m, 1H), 7.26 (t, *J* = 1.7 Hz, 1H), 7.23 – 7.18 (m, 6H), 6.94 – 6.90 (m, 1H), 6.79 (d, *J* = 2.4 Hz, 1H), 3.98 (s, 2H), 3.76 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 144.7, 138.9, 135.2, 131.9, 130.3, 129.8, 128.6, 128.6, 126.7, 126.5, 124.9, 122.6, 114.8, 113.4, 102.4, 100.0, 55.6, 31.4, 21.6. HRMS (ESI, m/z) calculated for $C_{23}H_{22}NO_3S^+$: 392.1315, found: 362.392.1319.

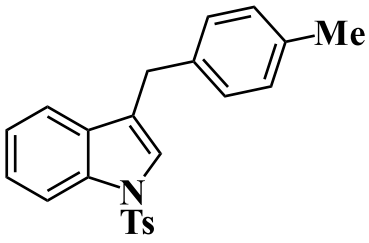
3-(3-Methylbenzyl)-1-tosyl-1*H*-indole (**4c**):



4c

Yield: (A) 62 % (0.12 mmol, 46 mg); (B) 87% (0.17 mmol, 65 mg). White semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 1H), 7.76 – 7.74 (m, 2H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.31 (m, 1H), 7.30 (s, 1H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.19 (dd, *J* = 7.7, 3.4 Hz, 2H), 7.04 (q, *J* = 7.7 Hz, 3H), 3.99 (s, 2H), 2.36 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 138.6, 138.1, 135.6, 135.3, 130.9, 129.8, 129.4, 128.4, 127.2, 126.8, 125.7, 124.7, 124.0, 123.1, 122.6, 119.8, 113.8, 31.3, 21.6, 21.4. HRMS (ESI, m/z) calculated for $C_{23}H_{22}NO_2S^+$: 376.1366, found: 376.1367.

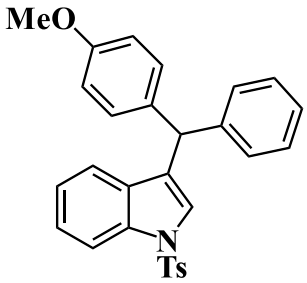
3-(4-Methylbenzyl)-1-tosyl-1*H*-indole (**4d**):



4d

Yield: (A) 59 % (0.12 mmol, 44 mg); (B) 84% (0.16 mmol, 63 mg). White semi-solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.76 – 7.73 (m, 2H), 7.39 (ddd, *J* = 7.8, 1.3, 0.8 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.27 (d, *J* = 1.2 Hz, 1H), 7.24 – 7.17 (m, 3H), 7.11 (s, 4H), 3.98 (d, *J* = 1.2 Hz, 2H), 2.37 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.68, 135.90, 135.61, 135.39, 130.92, 129.76, 129.22, 128.51, 126.77, 124.65, 123.93, 123.08, 122.77, 119.77, 113.80, 77.33, 77.01, 76.70, 30.96, 21.53, 21.01. HRMS (ESI, m/z) calculated for $C_{23}H_{22}NO_2S^+$: 376.1366, found: 376.1366.

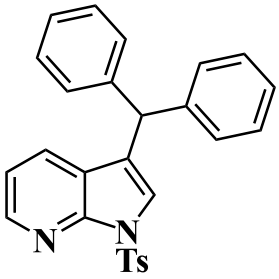
3-((4-Methoxyphenyl)(phenyl)methyl)-1-tosyl-1*H*-indole (**4e**):



4e

Yield: (A) 67 % (0.13 mmol, 63 mg); (B) 92% (0.16 mmol, 86 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.67 – 7.65 (m, 2H), 7.27 (s, 1H), 7.25 (s, 2H), 7.24 – 7.23 (m, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.11 – 7.09 (m, 2H), 7.07 – 7.06 (m, 2H), 7.03 – 7.01 (m, 2H), 6.90 (d, *J* = 1.4 Hz, 1H), 6.82 – 6.79 (m, 2H), 5.45 (s, 1H), 3.78 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 144.9, 142.5, 135.90, 135.2, 134.3, 130.6, 129.9, 128.8, 128.6, 127.2, 126.9, 126.8, 125.8, 124.8, 123.2, 120.6, 113.9, 113.9, 55.32, 47.8, 21.7.

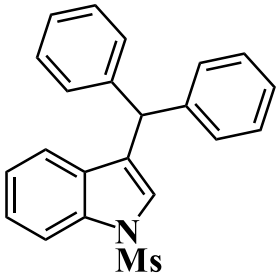
3-Benzhydryl-1-tosyl-1*H*-pyrrolo[2,3-b]pyridine (**4f**):



4f

Yield: (A) 61 % (0.12 mmol, 54 mg); (B) 86 % (0.17 mmol, 75 mg). Yellowish White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 4H), 7.34 (t, *J* = 1.1 Hz, 1H), 7.32 – 7.30 (m, 1H), 7.27 (ddd, *J* = 7.8, 1.7, 0.9 Hz, 3H), 7.17 (dt, *J* = 7.9, 1.6 Hz, 4H), 6.51 (dd, *J* = 7.8, 5.0 Hz, 1H), 6.41 (dd, *J* = 7.8, 1.7 Hz, 1H), 4.81 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 147.9, 144.4, 140.9, 140.7, 138.2, 135.5, 132.2, 129.6, 129.4, 129.0, 128.9, 128.9, 128.4, 128.2, 128.1, 128.1, 127.1, 123.0, 117.8, 54.1, 21.7.

3-Benzhydryl-1-(methylsulfonyl)-1*H*-indole (**4g**):



4g

Yield: (A) 66 % (0.13 mmol, 48 mg); (B) 90 % (0.18 mmol, 65 mg). Yellowish White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.29 (dd, *J* = 7.0, 1.3 Hz, 2H), 7.28 – 7.26 (m, 2H), 7.25 (s, 1H), 7.18 – 7.16 (m, 4H), 7.14 – 7.12 (m, 2H), 6.81 (d, *J* = 1.4 Hz, 1H), 5.53 (d, *J* = 1.3 Hz, 1H), 3.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 140.7, 135.8, 132.8, 130.2, 130.1, 128.9, 128.9, 128.8, 127.2, 125.7, 125.3, 125.3, 123.5, 120.9, 113.3, 48.1, 40.7.

III. Mechanistic Investigation

A. *In situ* formation of Fe-IP and its characterization:

To a solution of anhydrous $MgSO_4$ (1 equiv.) (Figure S1. (i)A), $FeCl_3$ (0.5 mmol) was added. The transparent solution immediately turned a deep brown colour (Figure S1. (i)B), which, upon light exposure (2x32 W white CFL, λ_{max}= 545 nm), turned into a pale-yellow solution (Figure S1. (i)C) within an hour. Afterwards, the solution was filtered, and this filtrate (Fe-IP) was used for the subsequent experiments.

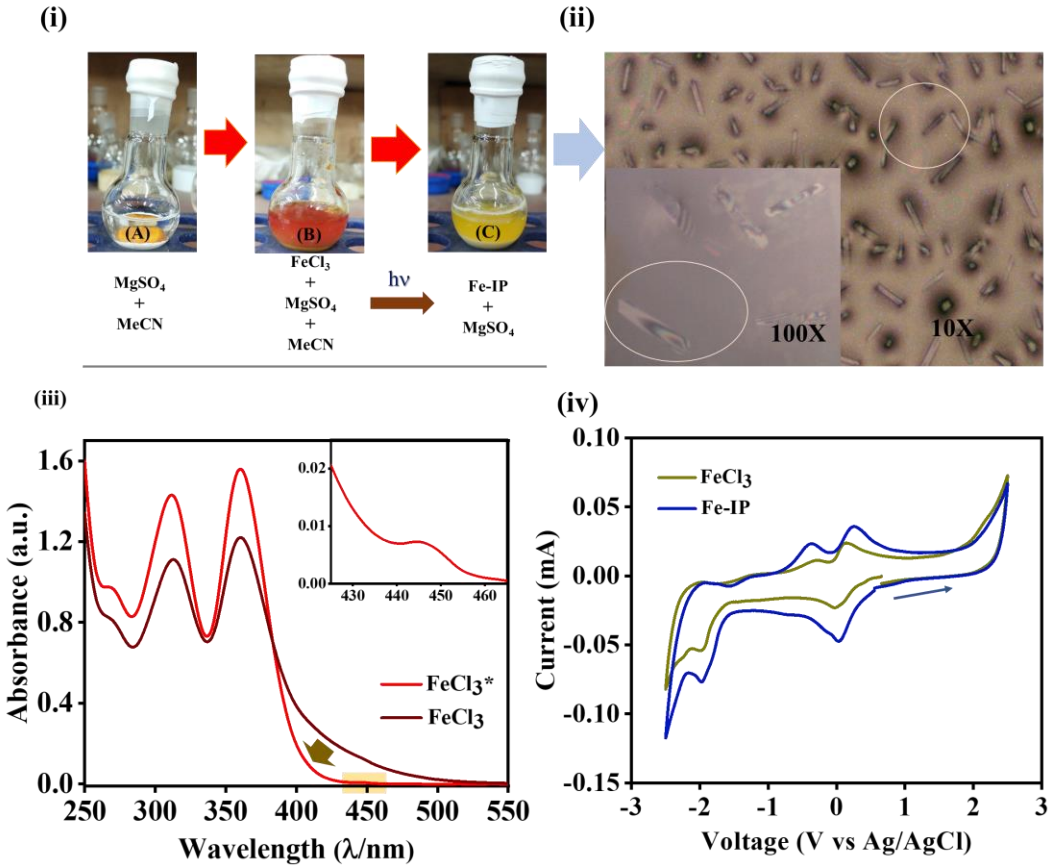


Figure S1. Formation of a mixed valence ion pair of iron(III) in MeCN (Fe-IP).

First, an image was produced with curiosity, taking a few drops of the filtrate on a glass slide under a Confocal Raman Microscope (Horiba Scientific XploRA Plus Confocal Raman Microscope; Laser: 532 nm; Objective: 10x and Numerical aperture: 0.25), and some crystals were observed in the mixture (Figure S1. (ii))

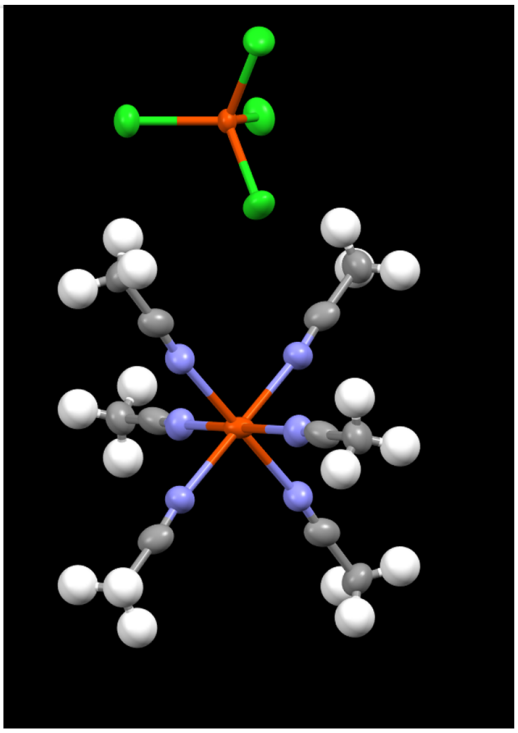
UV-vis spectroscopic experiment (Figure S1. (iii)) was done maintaining the concentration of the filtrate at ca. 10^{-4} M at RT. Cyclic voltammetry (Figure S1. (iv)) was performed using this

filtrate (1 mM) at a scan rate of 100 mV/s at RT. Pt working electrode was used for oxidation, while the glassy carbon electrode was used for reduction. $FeCl_3$* refers to the irradiated solution of $FeCl_3$ in MeCN without filtration.

Single Crystal Structure of Fe-IP:

To the pale-yellow filtrate of irradiated $FeCl_3$ (in the presence of anhydrous $MgSO_4$ in MeCN), taken in a vial, n-hexane was added slowly. The vial was then capped and stored in a refrigerator. After 2 days, the formation of some solid crystals was observed, and then these were sent for low-temperature SXRD study. The SXRD analysis provided the structure of Fe-IP as follows.

Identifier	mo_pd111023_0m_a
Literature Reference	*Unknown* (0)
Formula	$Cl_{1.333}$ $Fe_{0.333}$,C_2 H_3 $Fe_{0.167}$ N
Compound Name	
Synonym	
Space Group	P $\bar{3}$ (147)
Cell Lengths	**a** 11.630(3) **b** 11.630(3) **c** 6.1171(18)
Cell Angles	**α** 90 **β** 90 **γ** 120
Cell Volume	716.532
Z, Z'	**Z**: 6 **Z'**: 0
R-Factor (%)	12.07
Disorder	
Polymorph	



Crystal Structure of Fe-IP

Figure S2

B. Interaction of Fe-IP with molecular oxygen:

To investigate the interaction of the mixed valence ion pair of iron(III), Fe-IP, we irradiated the $FeCl_3$ in MeCN in the presence of anhydrous $MgSO_4$ and oxygen. Next, with the filtrate of

the reaction mixture, cyclic voltammetry and resonance Raman spectroscopy were performed with vigorous purging of O_2 into the solution.

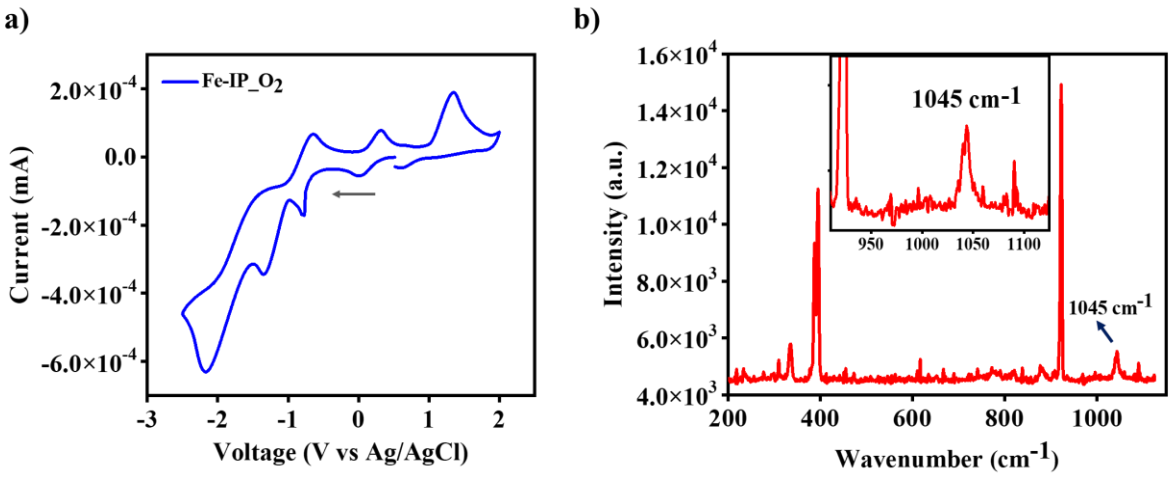


Figure S3. a) Cyclic Voltametric experiment for profiling dioxygen reduction by Fe-IP. The experiment was done with an O_2-saturated solution of Fe-IP in MeCN at room temperature at a scan rate of 100 mV/s. Pt working electrode was used for oxidation, while the glassy carbon electrode was used for reduction. b) Resonance Raman spectra of transient Fe-$O_2^{\bullet-}$ radical intermediate at 77K.

C. Photocatalysis by Fe-IP for the divergent functionalization of 3-arylidene indolines:

1. UV-vis spectroscopic study:

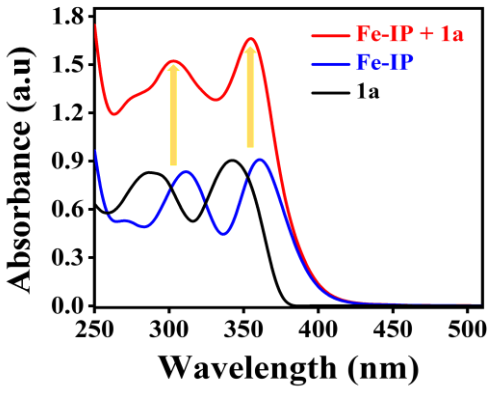


Figure S4. Absorption spectral shift by the reaction mixture (ca. 10^{-4} M) of **1a** and Fe-IP in MeCN at RT.

2. Photoluminescence study:

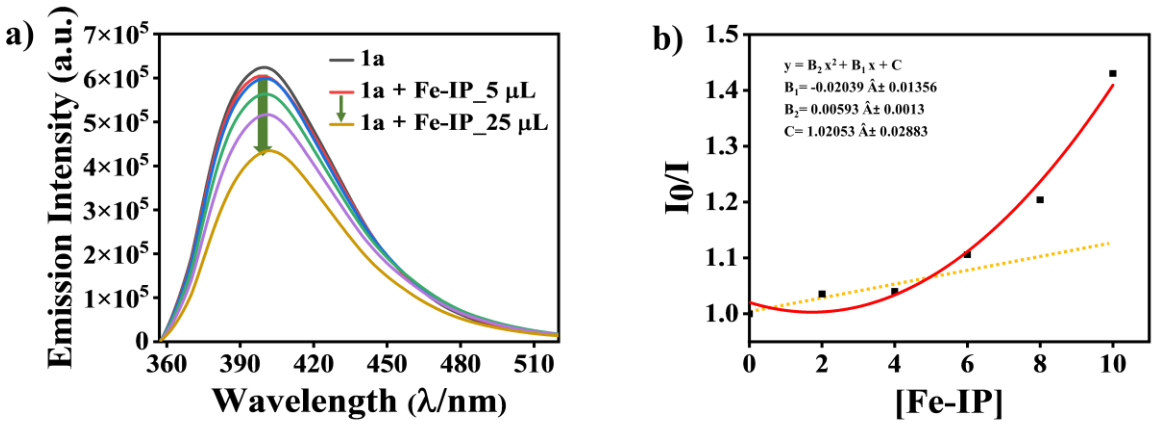


Figure S5. (a) Emission spectral changes of **1a** ($1x10^{-5}$ M) with gradual addition of Fe-IP ($1x10^{-5}$ M) in MeCN at RT. (b) The non-linear Stern-Volmer plot reveals the combination of static and dynamic quenching by Fe-IP.

3. Cyclic voltametric experiment:

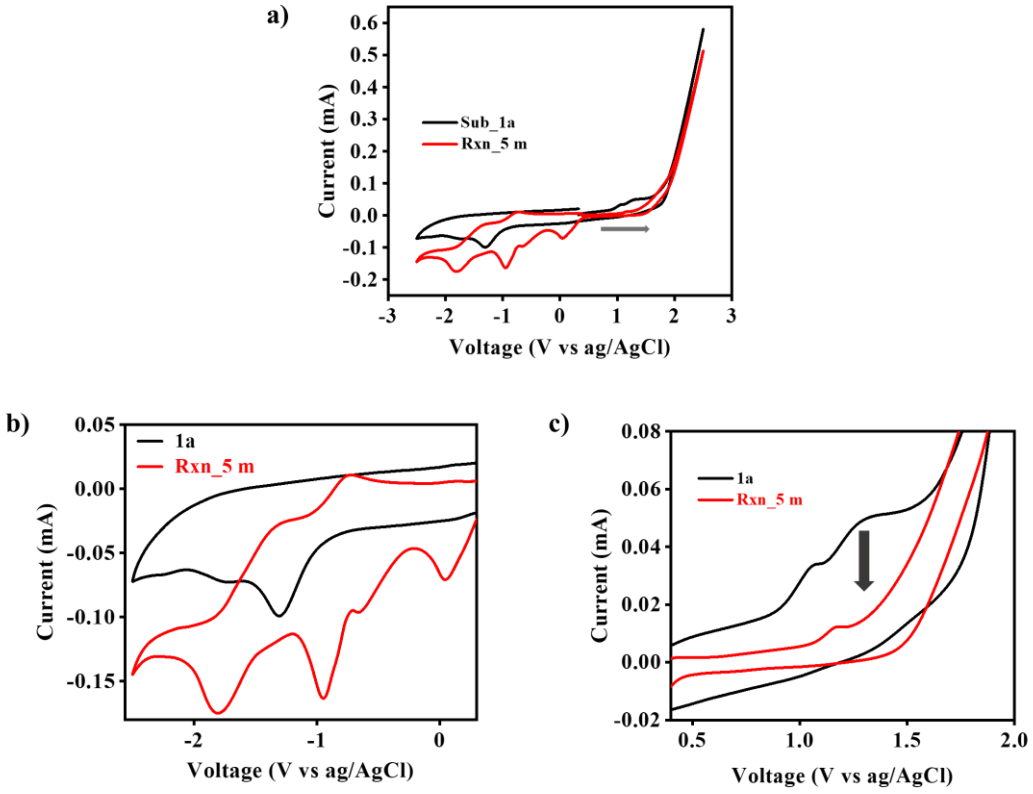


Figure S6. Cyclic voltammograms of **1a** and the reaction mixture in aerated (O_2) MeCN at a scan rate of 100 mV/s at RT. Pt working electrode was used for oxidation, while the glassy carbon electrode was used for reduction.

4. Electron Paramagnetic Resonance (EPR) study:

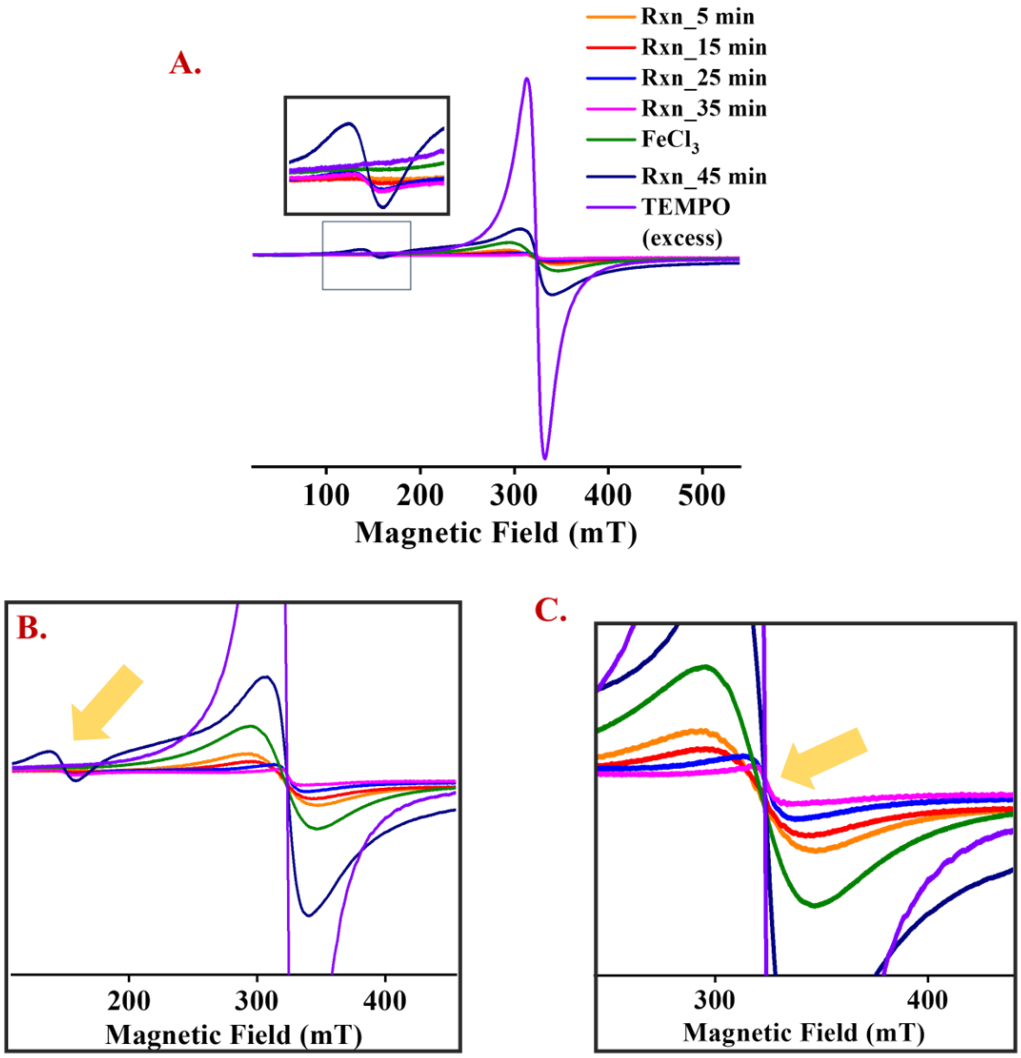
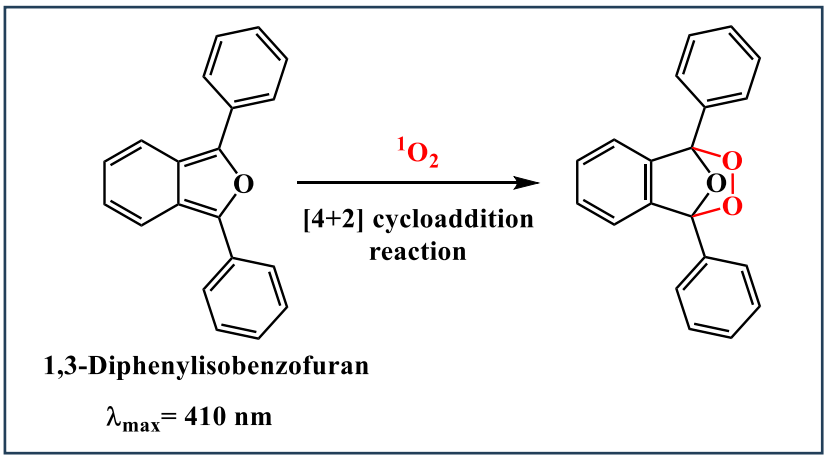


Figure S7. Progressive EPR spectra of $FeCl_3$ photocatalyzed functionalization of 3-arylidene indolines in MeCN at 77K. Generation of Fe(III) in different ligand environments, as well as organic radicals as reactive intermediates.

5. 1,3-Diphenylisobenzofuran (DPBF)-quenching experiment:

UV-vis spectra were recorded with a mixture of substrate, **1a** and DPBF in MeCN (ca. 10^{-5} M). The rapidly decreasing absorption intensity at λ_{max}= 410 nm for DPBF indicates the involvement of ROS ($^1O_2$) in dimerization reaction because DPBF undergoes highly specific rapid [4+2] cycloaddition reaction with singlet oxygen.



Scheme S4

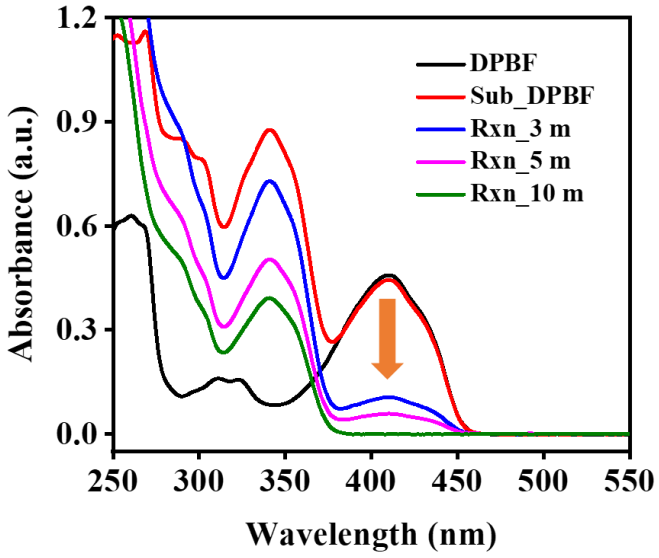


Figure S8: DPBF quenching in the presence of ROS.

6. Investigation, Isolation and Characterization of organic reaction intermediate:

To understand the intermediates involved in the divergent photo-functionalization of 3-arylidene indolines using the $FeCl_3$ photocatalyst, we first performed reactions in a double-chamber setup in MeCN under an oxygen atmosphere at 50 °C, and collected aliquots at different time intervals for ^1H NMR analysis. The spectral changes observed in $CDCl_3$ are as follows.

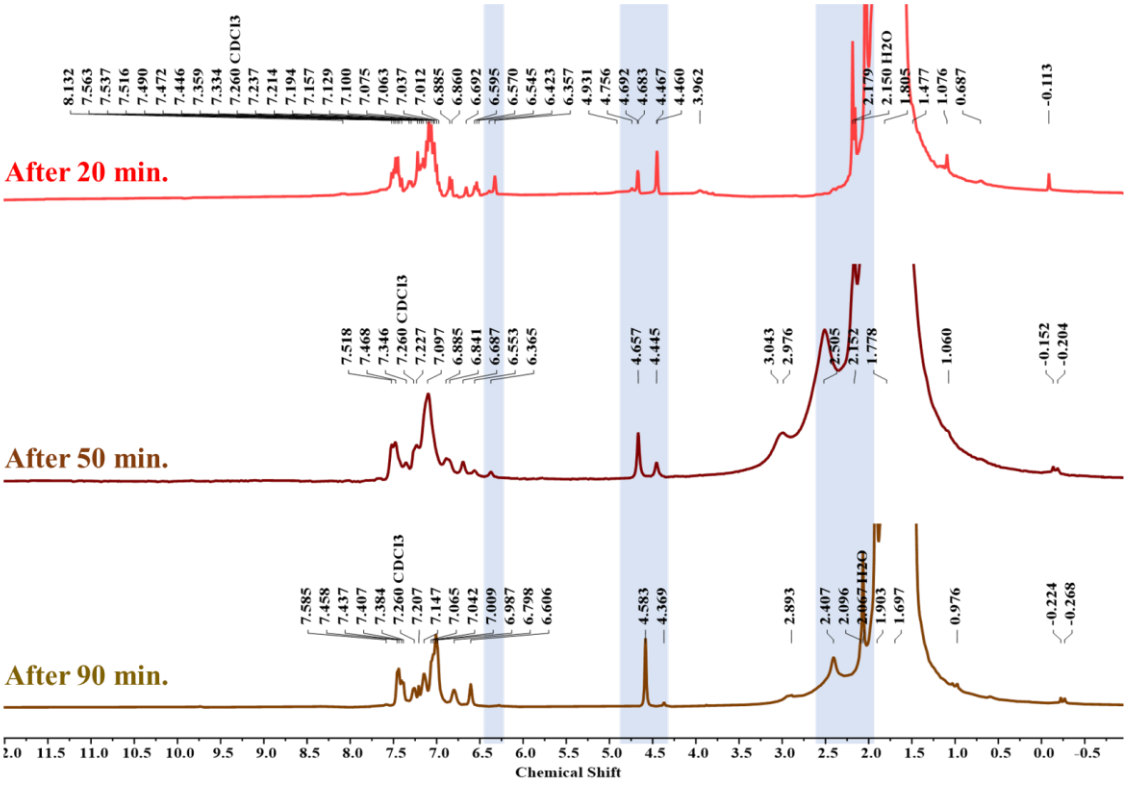
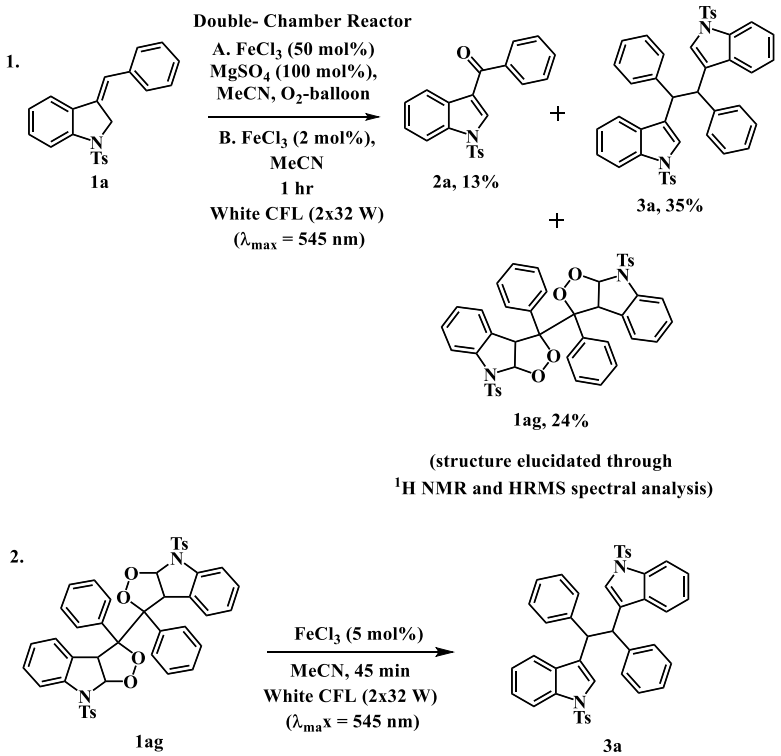


Figure S9: ^{1}H NMR spectral changes for the photodimerization of 3-arylidene indolines in different time intervals.

Isolation of the reaction intermediate **1ag** involved in the photodimerization of **1a**:

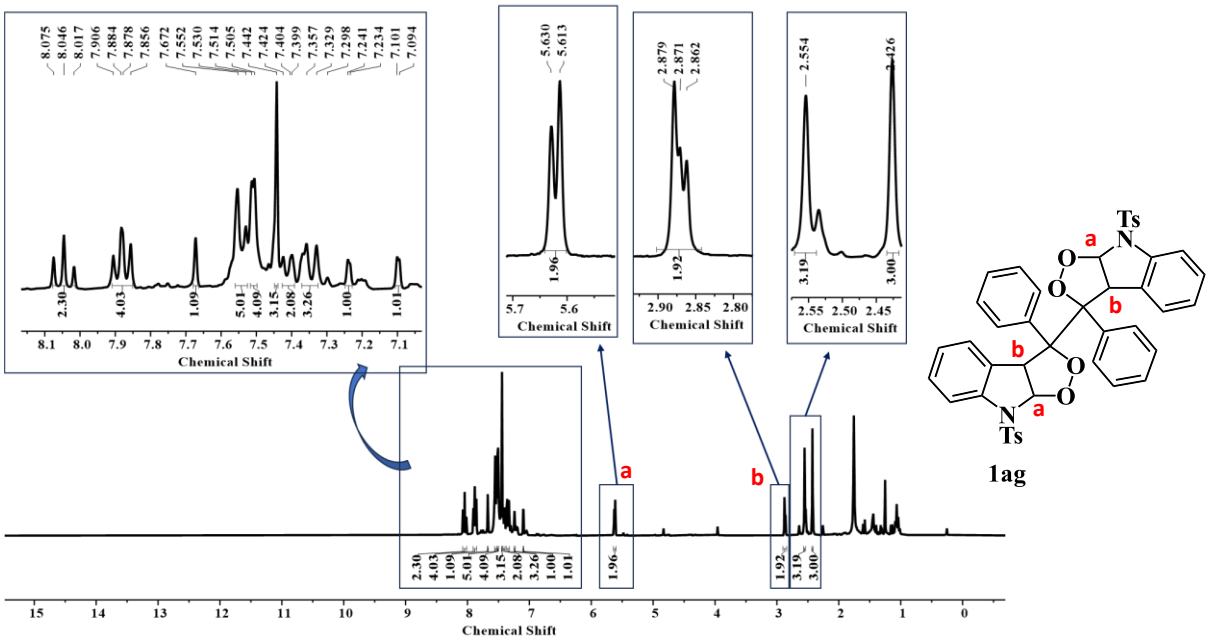


Scheme S5

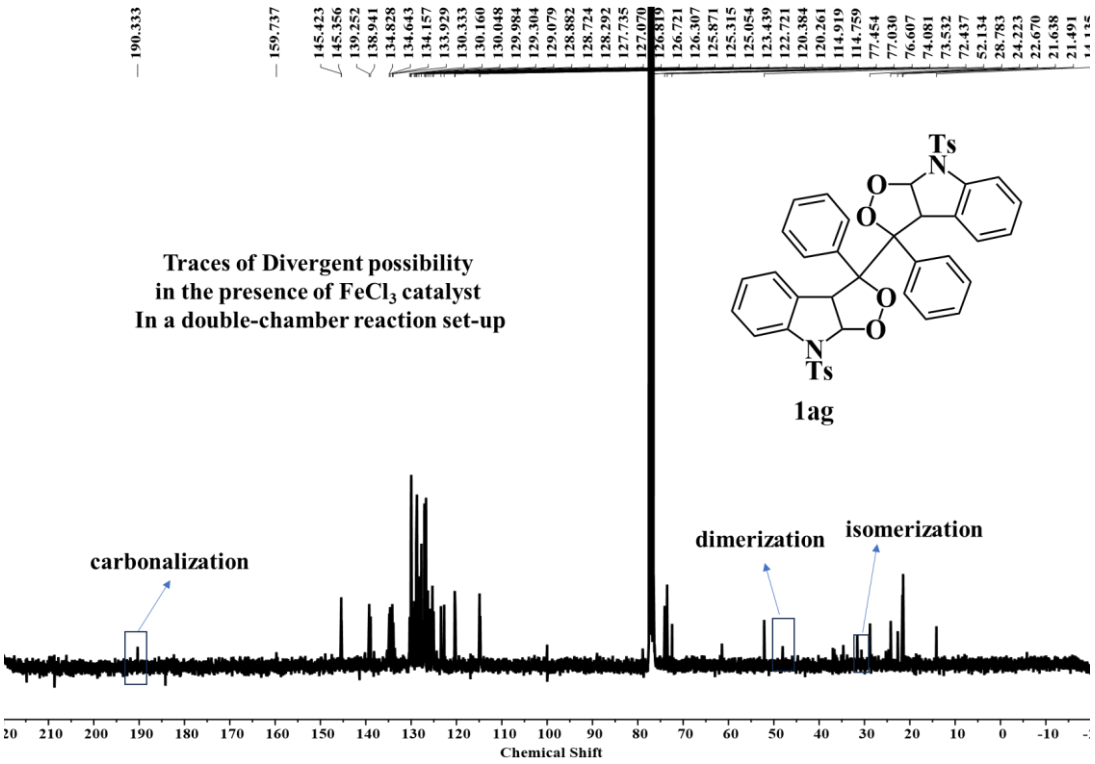
In an afore-mentioned double-chamber reaction set-up, to a solution of $FeCl_3$ (ca. 0.05 M) in MeCN was added 1 equivalent of anhydrous $MgSO_4$ in the reaction chamber A, which is equipped with an oxygen balloon. In another chamber B, to a solution of **1a** (72 mg, 0.2 mmol) in MeCN (2 ml) was added a catalytic amount of $FeCl_3$ (~1 mg, 0.004 mmol). The reaction was continued at 50 °C under an oxygen atmosphere and with White CFL (λ_{max} = 545 nm, 2x32 W) exposure. After 1 h, the reaction was stopped, the crude reaction mixture was then extracted with DCM for 3 times, washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with Hexane/EtOAc 99:2 (v/v) to afford an off-white amorphous solid intermediate product **1ag,** which is unstable as evidenced in the NMR spectra. This product was characterized through ^1H and ^{13}C NMR spectroscopy. ^1H NMR (300 MHz, $CDCl^3$) δ 8.05 (t, *J* = 8.7 Hz, 2H), 7.91 – 7.85 (m, 4H), 7.67 (s, 1H), 7.54 (d, *J* = 6.8 Hz, 5H), 7.51 (d, *J* = 2.7 Hz, 4H), 7.44 (s, 3H), 7.43 – 7.39 (m, 2H), 7.37 – 7.32 (m, 3H), 7.24 (d, *J* = 2.2 Hz, 1H), 7.10 (d, *J* = 2.3 Hz, 1H), 5.62 (d, *J* = 5.0 Hz, 2H), 2.90 – 2.84 (m, 2H), 2.55 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.3, 159.7, 145.4, 145.4, 139.3, 138.9, 134.8, 134.6, 134.2, 133.9, 130.3, 130.2, 130.1, 129.9, 129.3, 129.1, 128.9, 128.7, 128.3, 127.7, 127.1, 126.8, 126.7, 126.3, 125.9, 125.3, 125.1, 123.4, 122.7, 120.4, 120.3, 114.9, 114.8, 100.0, 74.1, 73.5, 72.4, 61.5, 52.1, 48.1, 36.9, 34.7, 31.6, 28.8, 24.2, 22.7, 21.6, 21.5, 14.1.

Further, when the product **1ag** was treated with $FeCl_3$, **2a** was afforded in a major amount.

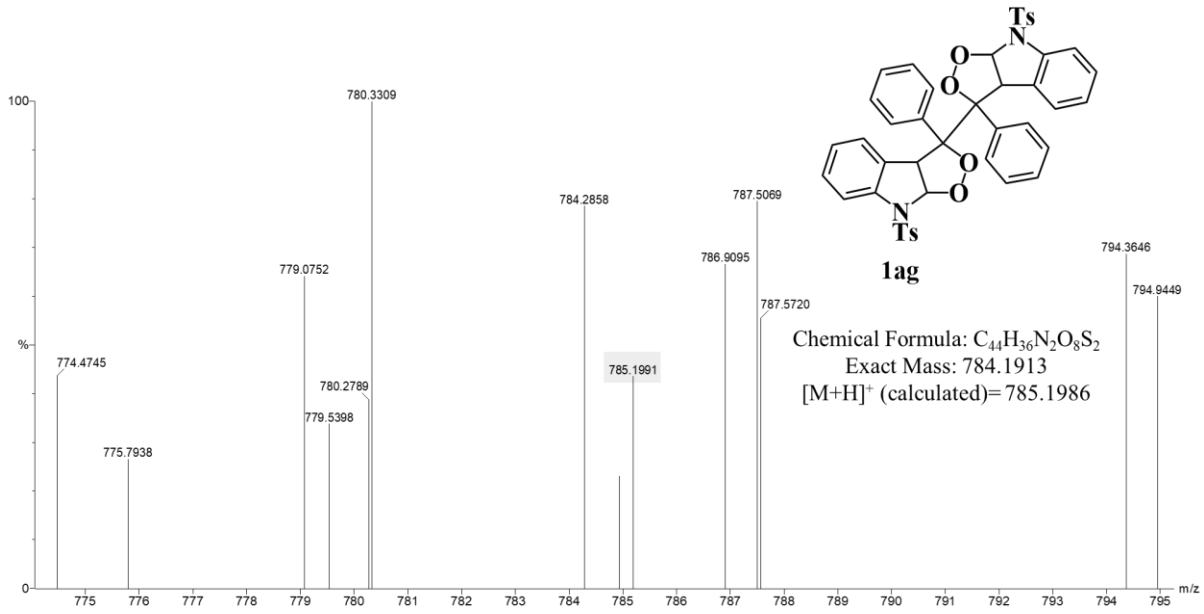
^1H NMR spectra of isolated intermediate **1ag**:



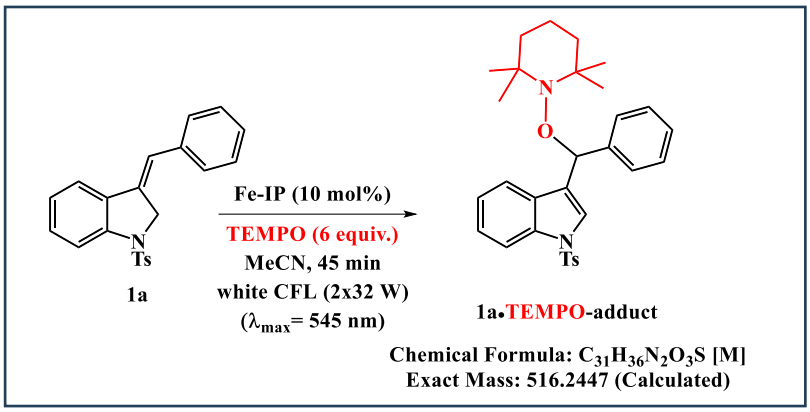
^{13}C NMR spectra of isolated intermediate **1ag**:

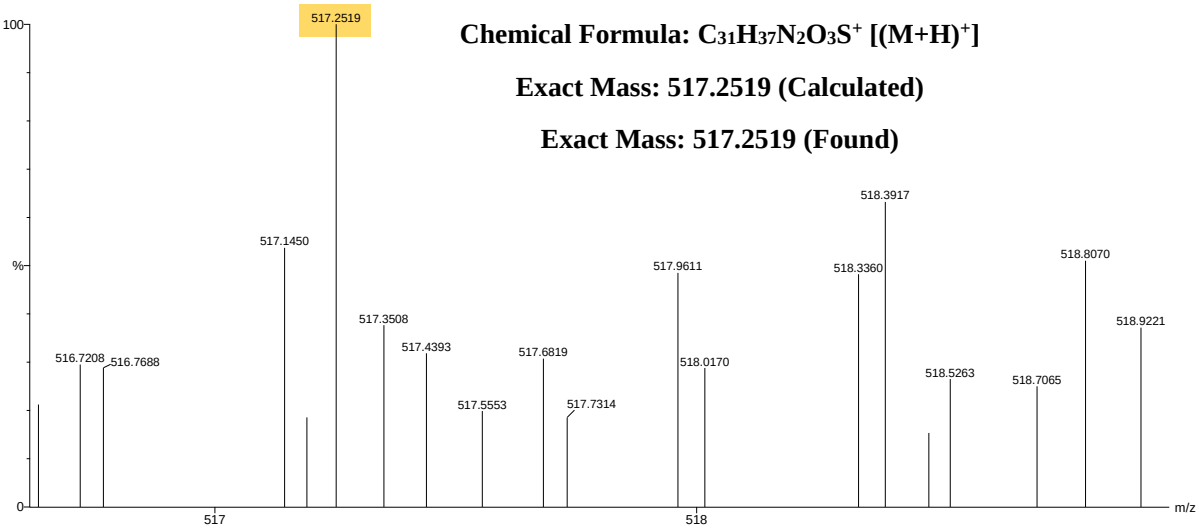


HRMS spectra of the intermediate **1ag**:



HRMS spectra of the intermediate **1a.TEMPO** adduct in Radical quenching study:





Computational Study:

1a

Optimization Parameters

Item	Value	Threshold	Converged?
Maximum Force	0.000003	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.001232	0.001800	YES
RMS Displacement	0.000140	0.001200	YES

Predicted change in Energy= -5.424184D-10

Optimization completed.

-- Stationary point found.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.343018	3.994238	-1.724824
2	6	0	1.484962	3.937419	-0.917441
3	6	0	1.626056	2.966563	0.077010
4	6	0	0.597167	2.036109	0.229798
5	6	0	-0.565323	2.086124	-0.565038
6	6	0	-0.688145	3.073750	-1.546445
7	7	0	0.480922	0.987367	1.175212
8	6	0	-1.485760	1.024296	-0.154568
9	16	0	1.786982	0.132487	1.836052
10	8	0	2.819809	1.120907	2.143933
11	8	0	1.191079	-0.722348	2.862545
12	6	0	2.402001	-0.932209	0.531029
13	6	0	1.996664	-2.267625	0.489463
14	6	0	2.455522	-3.085203	-0.542498
15	6	0	3.310089	-2.589146	-1.535275
16	6	0	3.709172	-1.245368	-1.462785
17	6	0	3.264661	-0.413673	-0.439830
18	6	0	3.783000	-3.470893	-2.665056
19	6	0	-2.724498	0.817462	-0.657765
20	6	0	-3.735866	-0.187336	-0.338363
21	6	0	-4.984306	-0.084640	-0.990202
22	6	0	-6.011012	-0.990673	-0.749246
23	6	0	-5.822739	-2.038005	0.155240
24	6	0	-4.595545	-2.163271	0.807956
25	6	0	-3.565618	-1.256342	0.567654
26	6	0	-0.783409	0.245025	0.942686

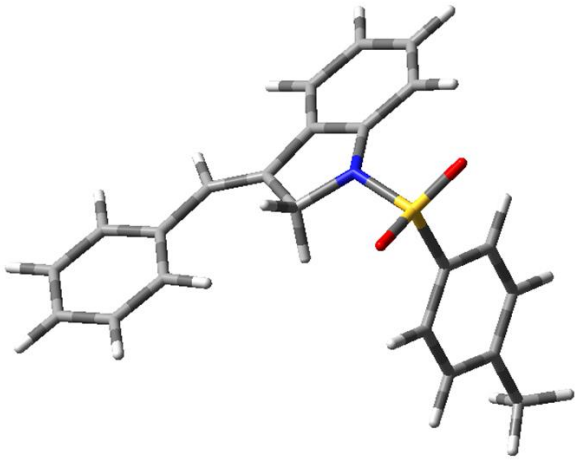
27	1	0	0.255975	4.762870	-2.486297
28	1	0	2.276701	4.667936	-1.054601
29	1	0	2.496056	2.938423	0.719778
30	1	0	-1.577751	3.122857	-2.167222
31	1	0	1.356781	-2.658876	1.272420
32	1	0	2.150394	-4.127594	-0.570748
33	1	0	4.385842	-0.847802	-2.214379
34	1	0	3.595130	0.616781	-0.381177
35	1	0	3.692932	-4.530388	-2.411371
36	1	0	3.189521	-3.297374	-3.571037
37	1	0	4.827728	-3.268254	-2.919367
38	1	0	-3.040016	1.518889	-1.428140
39	1	0	-5.140980	0.727865	-1.695040
40	1	0	-6.959398	-0.880081	-1.267072
41	1	0	-6.621289	-2.748093	0.347644
42	1	0	-4.435442	-2.975539	1.511202
43	1	0	-2.628153	-1.395992	1.089303
44	1	0	-1.357111	0.200877	1.872951
45	1	0	-0.572734	-0.785955	0.629037

Sum of electronic and zero-point Energies= -1452.778608

Sum of electronic and thermal Energies= -1452.756486

Sum of electronic and thermal Enthalpies= -1452.755542

Sum of electronic and thermal Free Energies= -1452.833063



1ab

Optimization Parameters

Item	Value	Threshold	Converged?
Maximum Force	0.000026	0.000450	YES
RMS Force	0.000004	0.000300	YES
Maximum Displacement	0.000540	0.001800	YES
RMS Displacement	0.000141	0.001200	YES

Predicted change in Energy= -1.446900D-08

Optimization completed.

-- Stationary point found.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.255938	4.031146	1.569812
2	6	0	-1.399909	3.928430	0.762216

3	6	0	-1.544814	2.896276	-0.162515
4	6	0	-0.515093	1.956723	-0.237061
5	6	0	0.645145	2.041027	0.563084
6	6	0	0.773450	3.099846	1.468830
7	7	0	-0.358915	0.831614	-1.075926
8	6	0	0.856688	0.210682	-0.772624
9	6	0	1.530907	0.926452	0.211801
10	16	0	-1.625886	-0.021312	-1.869463
11	8	0	-2.528603	0.999881	-2.393566
12	8	0	-0.940130	-0.982806	-2.729156
13	6	0	-2.465542	-0.916381	-0.569902
14	6	0	-3.550906	-0.328153	0.082209
15	6	0	-4.178604	-1.027126	1.110084
16	6	0	-3.741536	-2.302658	1.494786
17	6	0	-2.650680	-2.868216	0.818291
18	6	0	-2.008875	-2.187120	-0.212058
19	6	0	-4.449101	-3.063862	2.588698
20	6	0	2.784920	0.684824	0.825141
21	6	0	3.824263	-0.235290	0.459000
22	6	0	4.861164	-0.494190	1.393765
23	6	0	5.891782	-1.378472	1.108370
24	6	0	5.938934	-2.031919	-0.128386
25	6	0	4.944722	-1.772778	-1.077079
26	6	0	3.907115	-0.891698	-0.796145
27	1	0	-0.168933	4.854716	2.271918
28	1	0	-2.183400	4.675390	0.846538
29	1	0	-2.407731	2.835161	-0.813360
30	1	0	1.664783	3.198645	2.081049
31	1	0	1.114953	-0.700698	-1.283823

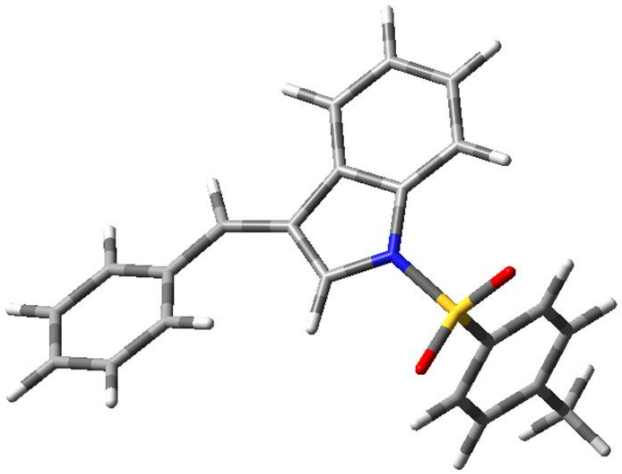
32	1	0	-3.901354	0.651300	-0.220982
33	1	0	-5.024505	-0.574950	1.620303
34	1	0	-2.301300	-3.857853	1.099184
35	1	0	-1.177656	-2.635978	-0.743907
36	1	0	-4.904302	-2.387108	3.317022
37	1	0	-5.251885	-3.685931	2.174071
38	1	0	-3.763624	-3.729183	3.120985
39	1	0	2.981178	1.270232	1.720290
40	1	0	4.831765	0.007388	2.357680
41	1	0	6.664747	-1.561098	1.849573
42	1	0	6.745786	-2.722471	-0.353881
43	1	0	4.986556	-2.253583	-2.050408
44	1	0	3.182813	-0.666144	-1.569477

Sum of electronic and zero-point Energies= -1452.167510

Sum of electronic and thermal Energies= -1452.146300

Sum of electronic and thermal Enthalpies= -1452.145356

Sum of electronic and thermal Free Energies= -1452.220864



1ac

Optimization Parameters

Item	Value	Threshold	Converged?
Maximum Force	0.000018	0.000450	YES
RMS Force	0.000004	0.000300	YES
Maximum Displacement	0.001553	0.001800	YES
RMS Displacement	0.000308	0.001200	YES

Predicted change in Energy= -1.838180D-08

Optimization completed.

-- Stationary point found.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.014400	4.259128	-0.993374
2	6	0	1.167713	3.977994	-0.292384
3	6	0	1.353310	2.758546	0.359286
4	6	0	0.315451	1.836782	0.265100
5	6	0	-0.887505	2.100863	-0.421293
6	6	0	-1.055587	3.333200	-1.055244
7	7	0	0.205347	0.527371	0.804941
8	6	0	-0.988792	0.006658	0.530632
9	6	0	-1.755787	0.932525	-0.239158
10	16	0	1.468291	-0.409705	1.736036

11	8	0	2.052954	0.591512	2.610873
12	8	0	0.690708	-1.549112	2.201379
13	6	0	2.616755	-0.903460	0.486011
14	6	0	3.796223	-0.170563	0.316911
15	6	0	4.705357	-0.588956	-0.649015
16	6	0	4.458424	-1.721277	-1.441427
17	6	0	3.266271	-2.437612	-1.238421
18	6	0	2.342476	-2.044042	-0.278130
19	6	0	5.466767	-2.181821	-2.460818
20	6	0	-3.022508	0.745809	-0.762651
21	6	0	-3.998501	-0.269555	-0.489721
22	6	0	-5.018240	-0.475408	-1.453153
23	6	0	-5.971078	-1.468073	-1.274755
24	6	0	-5.949713	-2.250161	-0.115261
25	6	0	-4.978490	-2.031410	0.871403
26	6	0	-4.013871	-1.051904	0.693172
27	1	0	-0.125594	5.219784	-1.484873
28	1	0	1.950165	4.727661	-0.243628
29	1	0	2.247646	2.555683	0.933740
30	1	0	-1.973553	3.576351	-1.581044
31	1	0	-1.222967	-1.002711	0.834901
32	1	0	4.006959	0.687197	0.944852
33	1	0	5.627200	-0.031699	-0.784395
34	1	0	3.066111	-3.322093	-1.835479

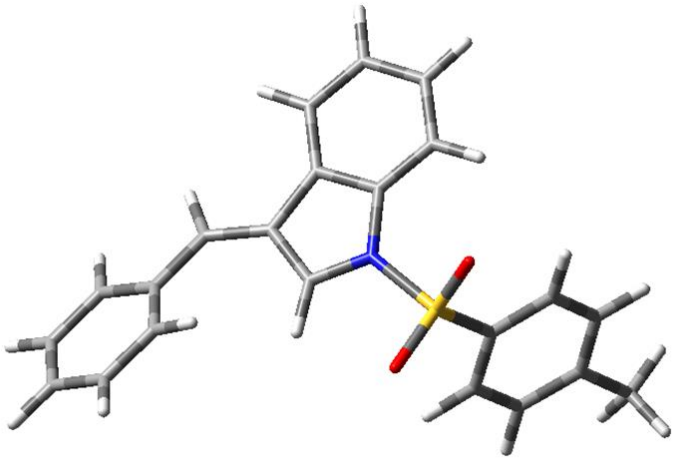
35	1	0	1.439383	-2.620080	-0.109781
36	1	0	6.048469	-1.345571	-2.856409
37	1	0	6.173723	-2.885832	-2.005302
38	1	0	4.986179	-2.697053	-3.296263
39	1	0	-3.324367	1.479239	-1.509870
40	1	0	-5.032510	0.136693	-2.350176
41	1	0	-6.736218	-1.628409	-2.026711
42	1	0	-6.705593	-3.014734	0.034057
43	1	0	-4.995844	-2.612846	1.787123
44	1	0	-3.314220	-0.840689	1.493808

Sum of electronic and zero-point Energies= -1452.167516

Sum of electronic and thermal Energies= -1452.146306

Sum of electronic and thermal Enthalpies= -1452.145362

Sum of electronic and thermal Free Energies= -1452.22087



1ad

Optimization Parameters

Item Value Threshold Converged?

Maximum Force 0.000005 0.000450 YES

RMS Force 0.000001 0.000300 YES

Maximum Displacement 0.000824 0.001800 YES

RMS Displacement 0.000222 0.001200 YES

Predicted change in Energy=-1.234268D-09

Optimization completed.

-- Stationary point found.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.610370	2.905224	-0.011438
2	6	0	0.547118	2.021868	0.182203
3	6	0	-0.659408	2.119404	-0.544636
4	6	0	-0.797964	3.128289	-1.504353
5	6	0	0.258525	4.009310	-1.715654
6	6	0	1.446898	3.897119	-0.976172
7	7	0	0.400648	0.946799	1.084829
8	6	0	-0.854072	0.361694	0.889531
9	6	0	-1.559452	1.055351	-0.090376
10	16	0	1.679034	0.095437	1.862330
11	8	0	2.642062	1.110769	2.279734

12	8	0	1.007954	-0.790324	2.810182
13	6	0	2.417178	-0.900691	0.575145
14	6	0	1.877941	-2.158464	0.292859
15	6	0	2.443962	-2.921848	-0.723661
16	6	0	3.538751	-2.450310	-1.463654
17	6	0	4.064664	-1.189521	-1.149131
18	6	0	3.512545	-0.408453	-0.136659
19	6	0	4.124546	-3.275329	-2.582883
20	6	0	-2.887703	0.887001	-0.553117
21	6	0	-3.800124	-0.199974	-0.336705
22	6	0	-3.422573	-1.471761	0.165419
23	6	0	-4.363616	-2.477511	0.351177
24	6	0	-5.710266	-2.261495	0.042255
25	6	0	-6.103529	-1.022414	-0.476086
26	6	0	-5.168186	-0.015455	-0.667959
27	1	0	2.512749	2.834267	0.582206
28	1	0	-1.714007	3.221172	-2.079970
29	1	0	0.162235	4.796465	-2.457216
30	1	0	2.253844	4.602478	-1.150013
31	1	0	1.047152	-2.537441	0.877236
32	1	0	2.034676	-3.904422	-0.941429
33	1	0	4.923148	-0.815463	-1.699820
34	1	0	3.934554	0.557460	0.114608
35	1	0	4.053774	-4.345873	-2.370258

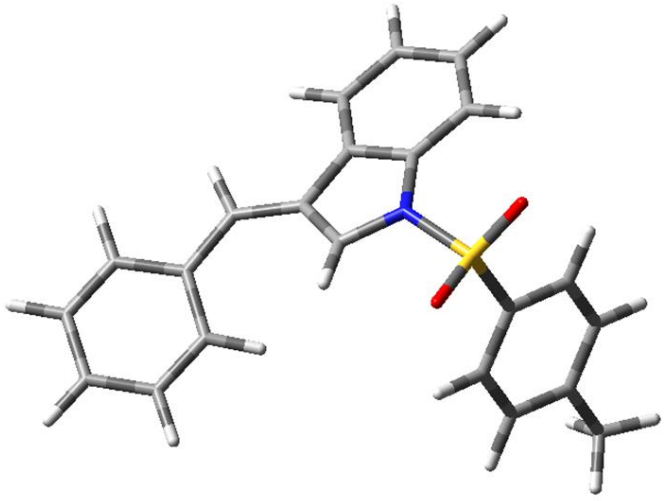
36	1	0	3.588026	-3.093668	-3.522253
37	1	0	5.175940	-3.029102	-2.754231
38	1	0	-3.281355	1.710202	-1.144619
39	1	0	-2.378186	-1.681075	0.362855
40	1	0	-4.044134	-3.443798	0.731502
41	1	0	-6.440838	-3.050399	0.192524
42	1	0	-7.144628	-0.845319	-0.730712
43	1	0	-5.483122	0.945066	-1.067542
44	1	0	-1.162684	-0.430880	1.550103

Sum of electronic and zero-point Energies= -1452.167359

Sum of electronic and thermal Energies= -1452.145319

Sum of electronic and thermal Enthalpies= -1452.144375

Sum of electronic and thermal Free Energies= -1452.222245



1ae

Optimization Parameters

Item Value Threshold Converged?

Maximum Force 0.000005 0.000450 YES

RMS Force 0.000001 0.000300 YES

Maximum Displacement 0.000798 0.001800 YES

RMS Displacement 0.000130 0.001200 YES

Predicted change in Energy=-1.932187D-09

Optimization completed.

-- Stationary point found.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.005896	2.396177	2.356678
2	6	0	0.631692	2.592213	2.563573
3	6	0	-0.320281	2.199992	1.614370
4	6	0	0.139492	1.618773	0.439625
5	6	0	1.534318	1.420361	0.201577
6	6	0	2.465809	1.807394	1.185087
7	7	0	-0.585447	1.084583	-0.648725
8	6	0	0.341050	0.663738	-1.717306
9	6	0	1.692878	0.804676	-1.068107
10	8	0	0.269317	-0.699252	-2.148867
11	8	0	1.393087	-1.410024	-1.501389

12	6	0	2.460794	-0.423585	-1.480090
13	16	0	-2.233804	1.357930	-0.987533
14	8	0	-2.657700	2.576525	-0.295118
15	8	0	-2.340372	1.232478	-2.441304
16	6	0	-3.051670	-0.031168	-0.208522
17	6	0	-2.666809	-1.335166	-0.535733
18	6	0	-3.353165	-2.398231	0.039555
19	6	0	-4.419641	-2.184037	0.929070
20	6	0	-4.782628	-0.866717	1.231170
21	6	0	-4.105833	0.215910	0.668197
22	6	0	-5.142875	-3.354440	1.549549
23	6	0	3.540349	-0.926691	-0.552615
24	6	0	4.883907	-0.782286	-0.914561
25	6	0	5.897190	-1.212353	-0.056800
26	6	0	5.572556	-1.808497	1.162259
27	6	0	4.232353	-1.969264	1.520939
28	6	0	3.219347	-1.526661	0.671913
29	1	0	2.713855	2.710786	3.116776
30	1	0	0.291162	3.058032	3.483351
31	1	0	-1.376621	2.358106	1.785913
32	1	0	3.525640	1.653518	1.015367
33	1	0	0.145196	1.249650	-2.620564
34	1	0	2.859862	-0.314460	-2.499310
35	1	0	-1.836982	-1.509182	-1.213538

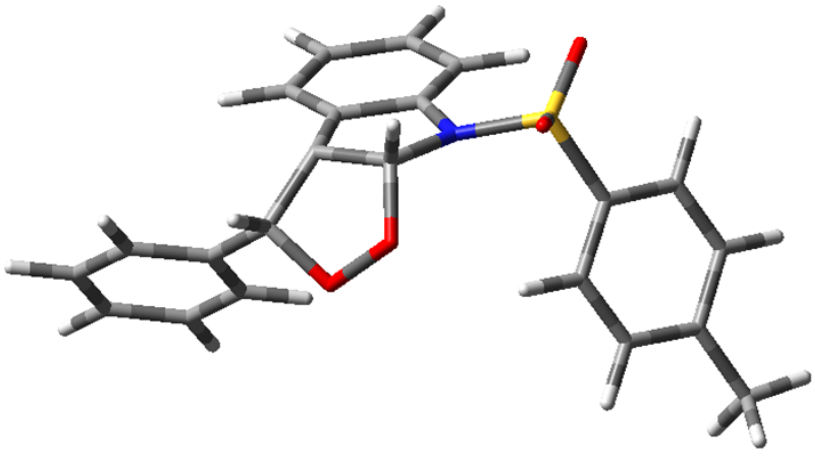
36	1	0	-3.057359	-3.414768	-0.205654
37	1	0	-5.606239	-0.681217	1.914891
38	1	0	-4.387284	1.236752	0.900375
39	1	0	-5.462387	-4.072304	0.786811
40	1	0	-4.491763	-3.894744	2.246734
41	1	0	-6.028215	-3.031424	2.102896
42	1	0	5.137978	-0.331871	-1.870564
43	1	0	6.936787	-1.090921	-0.346166
44	1	0	6.359563	-2.151571	1.827383
45	1	0	3.974851	-2.439234	2.465514
46	1	0	2.177933	-1.652754	0.945856

Sum of electronic and zero-point Energies= -1602.485351

Sum of electronic and thermal Energies= -1602.464141

Sum of electronic and thermal Enthalpies= -1602.463197

Sum of electronic and thermal Free Energies= -1602.538705



1ae´

Optimization Parameters

Item	Value	Threshold	Converged?
Maximum Force	0.000012	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.000872	0.001800	YES
RMS Displacement	0.000197	0.001200	YES

Predicted change in Energy=-2.875383D-09

Optimization completed.

-- Stationary point found.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.975275	2.996065	-2.131915
2	6	0	0.140034	3.516974	-1.451950
3	6	0	0.743213	2.825913	-0.404642
4	6	0	0.206191	1.581464	-0.066025
5	6	0	-0.917604	1.038802	-0.738182
6	6	0	-1.515976	1.765892	-1.778341
7	7	0	0.562122	0.664373	0.939703
8	6	0	-0.298017	-0.439535	0.862668
9	6	0	-1.211951	-0.240630	-0.128488

10	16	0	2.055142	0.588773	1.788813
11	8	0	2.456867	1.974160	2.014430
12	8	0	1.812438	-0.350471	2.880010
13	6	0	3.197325	-0.161014	0.636032
14	6	0	3.320681	-1.551797	0.607380
15	6	0	4.196318	-2.131395	-0.306515
16	6	0	4.951607	-1.345145	-1.188858
17	6	0	4.808759	0.048727	-1.132391
18	6	0	3.939286	0.649236	-0.225725
19	6	0	5.920908	-1.982252	-2.153880
20	6	0	-2.317924	-1.165217	-0.533903
21	8	0	-2.049149	-2.448562	0.173579
22	8	0	-2.651563	-3.460328	-0.416946
23	6	0	-3.725287	-0.702492	-0.222530
24	6	0	-4.775396	-1.085966	-1.065851
25	6	0	-6.087333	-0.713008	-0.774405
26	6	0	-6.360272	0.045080	0.365169
27	6	0	-5.317832	0.427916	1.211816
28	6	0	-4.006306	0.056743	0.919741
29	1	0	-1.426126	3.570194	-2.935538
30	1	0	0.533682	4.487451	-1.738386
31	1	0	1.578185	3.243519	0.143327
32	1	0	-2.392032	1.377767	-2.288748
33	1	0	-0.179742	-1.260003	1.551540

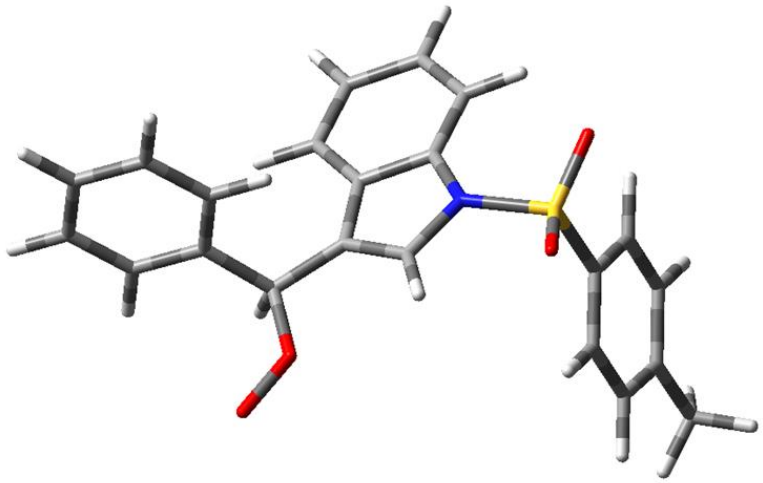
34	1	0	2.751584	-2.162845	1.298857
35	1	0	4.297636	-3.212709	-0.332613
36	1	0	5.389188	0.673866	-1.805143
37	1	0	3.844968	1.727638	-0.175472
38	1	0	5.599249	-2.987589	-2.439251
39	1	0	6.029456	-1.385901	-3.064066
40	1	0	6.916522	-2.073311	-1.702521
41	1	0	-2.240464	-1.412171	-1.597723
42	1	0	-4.562564	-1.685412	-1.946081
43	1	0	-6.894141	-1.013448	-1.436316
44	1	0	-7.381031	0.338787	0.591823
45	1	0	-5.525687	1.018650	2.098988
46	1	0	-3.195449	0.359966	1.574583

Sum of electronic and zero-point Energies= -1602.502283

Sum of electronic and thermal Energies= -1602.481073

Sum of electronic and thermal Enthalpies= -1602.480129

Sum of electronic and thermal Free Energies= -1602.555637



1af

Optimization Parameters

Item	Value	Threshold	Converged?
Maximum Force	0.000007	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.001454	0.001800	YES
RMS Displacement	0.000251	0.001200	YES

Predicted change in Energy= -4.369456D-09

Optimization completed.

-- Stationary point found.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.469510	-2.323675	1.486917
2	6	0	-0.046860	-1.627683	0.392418

3	6	0	-1.434125	-1.467955	0.229047
4	6	0	-2.318426	-2.022758	1.148606
5	6	0	-1.812233	-2.732024	2.242282
6	6	0	-0.431941	-2.869805	2.405390
7	7	0	0.637539	-0.996418	-0.669707
8	6	0	-0.333371	-0.502187	-1.712158
9	6	0	-1.725338	-0.616317	-0.991129
10	8	0	-0.060839	0.686020	-2.251513
11	8	0	-1.349759	1.684372	-0.456591
12	6	0	-2.179440	0.788731	-0.552562
13	6	0	-3.607024	1.023511	-0.200439
14	6	0	-3.928429	2.221201	0.464877
15	6	0	-5.245930	2.507309	0.803436
16	6	0	-6.263685	1.605739	0.473764
17	6	0	-5.957567	0.418479	-0.193966
18	6	0	-4.636223	0.123794	-0.527874
19	16	0	2.259993	-1.241595	-1.074539
20	8	0	2.716912	-2.514762	-0.500879
21	8	0	2.337358	-1.044315	-2.528025
22	6	0	3.120253	0.085978	-0.244558
23	6	0	2.687436	1.404166	-0.426254
24	6	0	3.402095	2.431488	0.178787
25	6	0	4.542235	2.167535	0.958676
26	6	0	4.948219	0.836985	1.119830

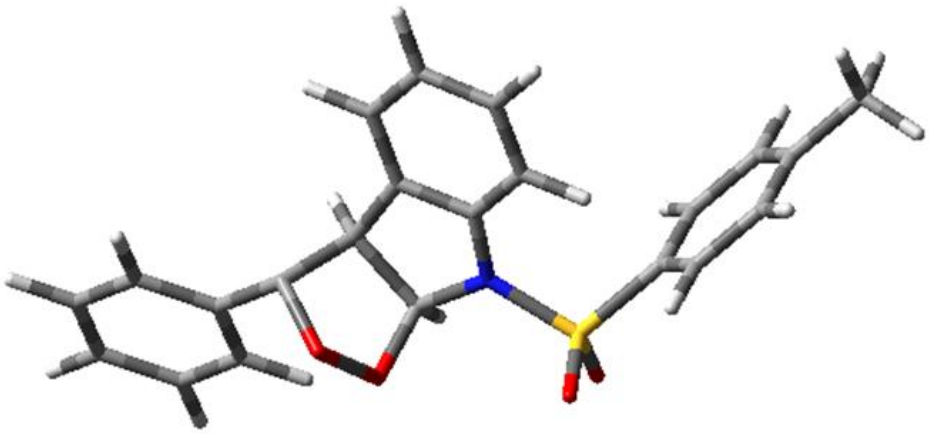
27	6	0	4.245781	-0.210703	0.522381
28	6	0	5.297902	3.299036	1.609917
29	1	0	1.535383	-2.453180	1.616362
30	1	0	-3.389126	-1.900304	1.024268
31	1	0	-2.493271	-3.169555	2.964691
32	1	0	-0.042364	-3.414997	3.259678
33	1	0	-0.325081	-1.227126	-2.549581
34	1	0	-2.461652	-1.069637	-1.656760
35	1	0	-3.129625	2.912275	0.709507
36	1	0	-5.483196	3.430708	1.322062
37	1	0	-7.293118	1.830243	0.735395
38	1	0	-6.746378	-0.278452	-0.457517
39	1	0	-4.424882	-0.798724	-1.056009
40	1	0	1.799530	1.610687	-1.015584
41	1	0	3.070266	3.457587	0.047714
42	1	0	5.824428	0.612557	1.720716
43	1	0	4.562406	-1.239018	0.652351
44	1	0	5.614325	4.038549	0.866670
45	1	0	4.666686	3.824413	2.335236
46	1	0	6.186600	2.938824	2.133114

Sum of electronic and zero-point Energies= -1602.563729

Sum of electronic and thermal Energies= -1602.542519

Sum of electronic and thermal Enthalpies= -1602.541575

Sum of electronic and thermal Free Energies= -1602.617083



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Optimization Parameters

Item	Value	Threshold	Converged?
Maximum Force	0.000015	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.001426	0.001800	YES
RMS Displacement	0.000206	0.001200	YES

Predicted change in Energy= -2.107112D-09

Optimization completed.

-- Stationary point found.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-1.082045	2.194415	-3.037939
2	6	0	0.282596	2.529689	-2.995917
3	6	0	1.036375	2.360475	-1.837834
4	6	0	0.384396	1.832067	-0.721281
5	6	0	-0.991463	1.490104	-0.739754
6	6	0	-1.727756	1.681496	-1.919245
7	7	0	0.854222	1.574419	0.580167
8	6	0	-0.203345	1.050880	1.338809
9	6	0	-1.334462	1.002079	0.581493
10	16	0	2.490803	1.372277	1.055212
11	8	0	3.253543	2.375354	0.317069
12	8	0	2.452466	1.329787	2.514660
13	6	0	2.945787	-0.248796	0.451841
14	6	0	2.687648	-1.368906	1.246299
15	6	0	3.035004	-2.628418	0.767942
16	6	0	3.634601	-2.788112	-0.490987
17	6	0	3.889463	-1.644668	-1.259797
18	6	0	3.549419	-0.374100	-0.799791
19	6	0	3.982123	-4.162945	-1.006775
20	6	0	-2.702026	0.581836	1.054772
21	8	0	-2.510085	0.169290	2.419661
22	8	0	-3.826020	-0.007485	3.006504
23	6	0	-3.329379	-0.525024	0.220904
24	6	0	-2.638769	-1.723134	0.001903

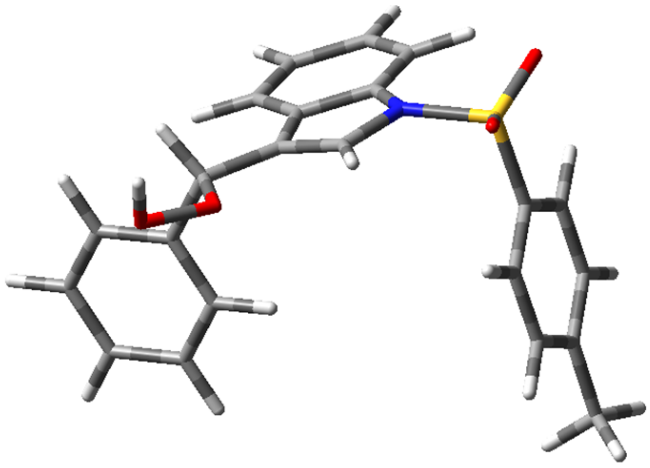
25	6	0	-3.223491	-2.747943	-0.738077
26	6	0	-4.504950	-2.585549	-1.272338
27	6	0	-5.199762	-1.396165	-1.056219
28	6	0	-4.613789	-0.373161	-0.307254
29	1	0	-1.640017	2.343824	-3.957365
30	1	0	0.759656	2.939711	-3.880952
31	1	0	2.079105	2.648247	-1.792730
32	1	0	-2.780575	1.422551	-1.957879
33	1	0	-0.045116	0.799642	2.374458
34	1	0	2.244457	-1.247702	2.228315
35	1	0	2.845744	-3.502219	1.385396
36	1	0	4.367105	-1.748019	-2.229983
37	1	0	3.765602	0.508894	-1.389594
38	1	0	4.365451	-4.804205	-0.207460
39	1	0	3.096835	-4.658523	-1.423558
40	1	0	4.735104	-4.115971	-1.797755
41	1	0	-3.377118	1.450512	1.049289
42	1	0	-3.824507	0.733287	3.635568
43	1	0	-1.641694	-1.844203	0.414844
44	1	0	-2.680151	-3.674162	-0.902068
45	1	0	-4.958312	-3.384063	-1.852491
46	1	0	-6.198488	-1.265381	-1.462635
47	1	0	-5.161760	0.548128	-0.125643

Sum of electronic and zero-point Energies= -1603.126015

Sum of electronic and thermal Energies= -1603.104805

Sum of electronic and thermal Enthalpies= -1603.103861

Sum of electronic and thermal Free Energies= -1603.179369



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Optimization Parameters

Item	Value	Threshold	Converged?
Maximum Force	0.000004	0.000450	YES
RMS Force	0.000000	0.000300	YES
Maximum Displacement	0.001750	0.001800	YES
RMS Displacement	0.000213	0.001200	YES

Predicted change in Energy= -8.198590D-10

Optimization completed.

-- Stationary point found.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.380831	2.003426	-0.533927
2	6	0	-5.036492	3.267141	0.310140
3	6	0	-3.963731	3.263324	1.154102
4	6	0	-3.124447	1.986050	1.244857
5	6	0	-3.427558	0.908573	0.530202
6	6	0	-4.614717	0.879527	-0.434351
7	7	0	-1.917698	1.734421	2.061033
8	6	0	-1.240595	0.639959	1.307003
9	6	0	-2.397454	-0.175207	0.833439
10	16	0	-0.913552	3.103085	2.267486
11	8	0	-1.657199	4.153640	2.976802
12	8	0	0.271478	2.727397	3.051240
13	8	0	-0.581763	0.996715	0.043051
14	8	0	-1.374516	0.538258	-0.981374
15	6	0	-0.403044	3.710748	0.674132
16	6	0	0.398621	2.802016	-0.276146
17	6	0	0.787348	3.264985	-1.489043
18	6	0	0.427227	4.699838	-1.917076
19	6	0	-0.278326	5.499471	-1.080923
20	6	0	-0.719999	4.973347	0.297443
21	6	0	0.868955	5.226061	-3.295311

22	6	0	-1.889009	-0.709150	-0.431746
23	6	0	-2.977419	-1.367538	-1.299787
24	6	0	-3.209556	-2.887912	-1.221052
25	6	0	-4.167471	-3.467535	-1.984617
26	6	0	-5.023757	-2.605954	-2.931084
27	6	0	-0.775663	-1.752248	-0.221180
28	6	0	-4.819407	-1.268018	-3.000545
29	6	0	-3.730853	-0.609223	-2.132869
30	6	0	0.370405	-1.125760	0.535071
31	6	0	1.227217	-0.758291	-0.637659
32	8	0	0.359391	-0.709939	-1.748693
33	8	0	-0.216130	-1.978794	-1.523677
34	6	0	-1.378087	-2.968815	0.505790
35	6	0	-2.547984	-2.776994	1.488690
36	6	0	-3.078143	-3.847650	2.128447
37	6	0	-2.510632	-5.256236	1.872421
38	6	0	-1.481129	-5.425062	1.007419
39	6	0	-0.878649	-4.208396	0.280580
40	6	0	1.363045	-1.992844	1.327508
41	6	0	2.350324	-2.390115	0.530398
42	7	0	2.082701	-1.953062	-0.842432
43	6	0	1.326634	-2.372286	2.810095
44	6	0	2.363733	-3.104906	3.308728
45	6	0	3.543733	-3.529626	2.384677

46	6	0	3.540490	-3.191640	1.063115
47	16	0	3.468253	-1.602225	-1.781139
48	8	0	4.288735	-2.813978	-1.915324
49	8	0	3.053520	-1.141408	-3.113594
50	6	0	4.419003	-0.327391	-0.981589
51	6	0	3.788971	1.052867	-0.718155
52	6	0	4.512945	2.023112	-0.108985
53	6	0	5.965746	1.745272	0.319977
54	6	0	6.520236	0.530639	0.087780
55	6	0	5.697524	-0.571780	-0.604487
56	6	0	6.788442	2.847487	1.012556
57	1	0	-6.222130	2.017540	-1.194984
58	1	0	-5.644450	4.143714	0.227110
59	1	0	-3.716452	4.127484	1.734671
60	1	0	-4.836806	0.006261	-1.011349
61	1	0	-0.498824	0.158849	1.909637
62	1	0	-2.787789	-0.885689	1.531724
63	1	0	0.648759	1.805062	0.021337
64	1	0	1.344423	2.633640	-2.149283
65	1	0	-0.528594	6.496423	-1.378350
66	1	0	-1.277074	5.604792	0.957685
67	1	0	0.921499	4.411998	-3.987779
68	1	0	0.160268	5.947136	-3.645648
69	1	0	1.831996	5.684556	-3.210135

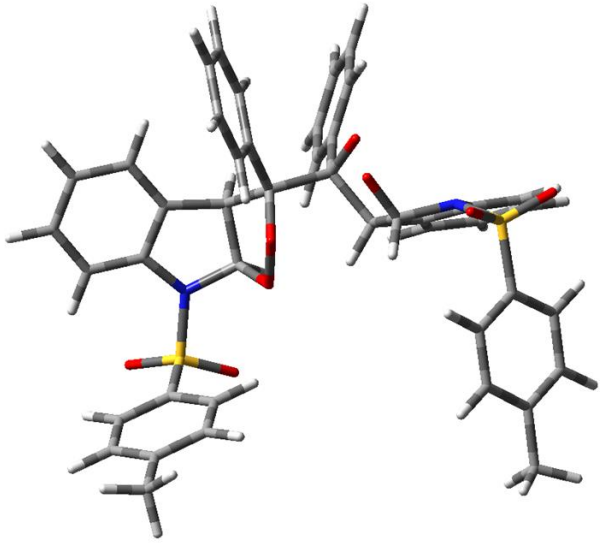
70	1	0	-2.614622	-3.486590	-0.563451
71	1	0	-4.328819	-4.523888	-1.929902
72	1	0	-5.780170	-3.063532	-3.533912
73	1	0	-5.414304	-0.669338	-3.658239
74	1	0	-3.569431	0.447034	-2.187772
75	1	0	-0.053070	-0.376627	1.171033
76	1	0	1.825493	0.108242	-0.447486
77	1	0	-2.942224	-1.798327	1.666612
78	1	0	-3.890915	-3.714331	2.811432
79	1	0	-2.929164	-6.101585	2.377485
80	1	0	-1.086832	-6.403731	0.829627
81	1	0	-0.065784	-4.341714	-0.402368
82	1	0	0.514215	-2.069215	3.436986
83	1	0	2.367606	-3.387733	4.340671
84	1	0	4.360445	-4.090797	2.788419
85	1	0	4.343598	-3.481034	0.418051
86	1	0	2.779627	1.245936	-1.016136
87	1	0	4.075238	2.982074	0.074049
88	1	0	7.529745	0.337674	0.385613
89	1	0	6.135434	-1.530737	-0.787762
90	1	0	6.460130	3.806434	0.669518
91	1	0	6.652166	2.781814	2.071858
92	1	0	7.824556	2.720201	0.777587

Sum of electronic and zero-point Energies= -3205.078719

Sum of electronic and thermal Energies= -3205.057509

Sum of electronic and thermal Enthalpies= -3205.056565

Sum of electronic and thermal Free Energies= -3205.132073



2a

Optimization Parameters

Item	Value	Threshold	Converged?
Maximum Force	0.000009	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.001438	0.001800	YES
RMS Displacement	0.000227	0.001200	YES

Predicted change in Energy= -1.471185D-08

Optimization completed.

-- Stationary point found.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.712213	-2.778318	-2.739045
2	6	0	-4.961563	-2.720366	-2.096523
3	6	0	-5.126317	-2.043585	-0.891551
4	6	0	-4.002754	-1.410638	-0.355455
5	6	0	-2.731849	-1.459463	-0.980858
6	6	0	-2.595589	-2.161857	-2.187891
7	7	0	-3.844440	-0.668646	0.829088
8	6	0	-2.514132	-0.229188	0.901733
9	6	0	-1.802318	-0.708969	-0.157817
10	16	0	-5.091653	0.057861	1.753400
11	8	0	-6.173929	-0.920684	1.818430
12	8	0	-4.419277	0.565694	2.947368
13	6	0	-5.643442	1.449832	0.774892
14	6	0	-4.950895	2.660234	0.858104
15	6	0	-5.375210	3.734178	0.081707
16	6	0	-6.482329	3.621248	-0.772908
17	6	0	-7.159425	2.395550	-0.830628
18	6	0	-6.750440	1.307493	-0.062749
19	6	0	-6.951634	4.803238	-1.585109
20	6	0	-0.320909	-0.503092	-0.421005

21	6	0	0.574022	-1.491160	0.407305
22	6	0	0.044373	0.970990	-0.234120
23	6	0	-0.008033	1.835634	-1.336620
24	6	0	0.251921	3.199723	-1.199203
25	6	0	0.568748	3.729024	0.053513
26	6	0	0.631564	2.878873	1.158821
27	6	0	0.375230	1.514387	1.015022
28	6	0	0.138074	-2.947061	0.218562
29	6	0	2.050997	-1.323749	0.133435
30	6	0	-0.685551	-3.568691	1.165058
31	6	0	-1.104804	-4.888582	0.993621
32	6	0	-0.703119	-5.609898	-0.130511
33	6	0	0.122004	-5.002667	-1.078605
34	6	0	0.540186	-3.683732	-0.903393
35	6	0	3.115235	-1.855838	0.965444
36	6	0	4.350430	-1.539562	0.348975
37	7	0	4.046575	-0.859514	-0.843981
38	6	0	2.651681	-0.719744	-0.930961
39	16	0	5.113804	0.124018	-1.754881
40	8	0	6.374230	-0.609281	-1.844506
41	8	0	4.344845	0.504819	-2.937835
42	6	0	5.376956	1.575672	-0.743388
43	6	0	6.588552	1.727497	-0.068992
44	6	0	6.785654	2.860919	0.717632

45	6	0	5.791325	3.839967	0.841188
46	6	0	4.582637	3.657145	0.151583
47	6	0	4.366848	2.536402	-0.643385
48	6	0	6.022050	5.077680	1.673158
49	6	0	3.118161	-2.575873	2.169534
50	6	0	4.336357	-2.938372	2.732547
51	6	0	5.550278	-2.608880	2.103988
52	6	0	5.578343	-1.912688	0.898429
53	1	0	-3.617708	-3.324117	-3.672910
54	1	0	-5.814858	-3.223878	-2.540817
55	1	0	-6.078394	-2.027004	-0.376346
56	1	0	-1.630165	-2.235066	-2.678014
57	1	0	-2.209970	0.383633	1.735337
58	1	0	-4.104437	2.759281	1.528235
59	1	0	-4.840297	4.677860	0.142859
60	1	0	-8.021564	2.290401	-1.483233
61	1	0	-7.286198	0.366316	-0.098318
62	1	0	-6.113536	5.435413	-1.892213
63	1	0	-7.487037	4.484631	-2.483553
64	1	0	-7.635886	5.430793	-1.000945
65	1	0	-0.155995	-0.744495	-1.477950
66	1	0	0.408926	-1.256063	1.466437
67	1	0	-0.264645	1.435394	-2.314474
68	1	0	0.202546	3.847384	-2.069977

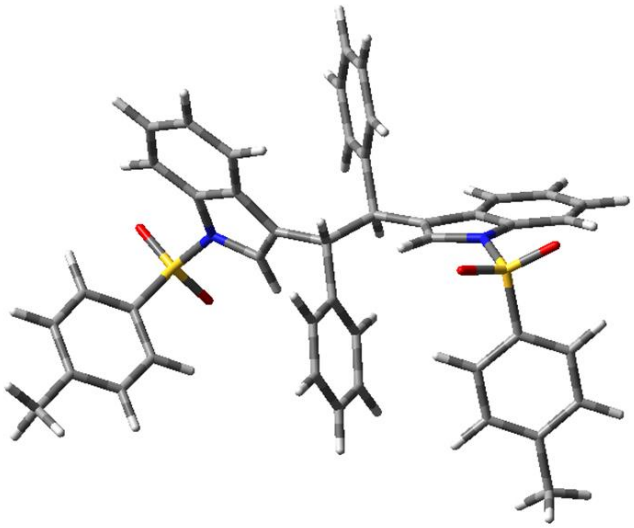
69	1	0	0.761891	4.792047	0.166931
70	1	0	0.883543	3.275772	2.138126
71	1	0	0.443833	0.873347	1.888487
72	1	0	-1.009632	-3.011766	2.040216
73	1	0	-1.744471	-5.351272	1.739592
74	1	0	-1.025838	-6.638176	-0.264599
75	1	0	0.448021	-5.558665	-1.953097
76	1	0	1.201637	-3.226898	-1.634202
77	1	0	2.237663	-0.199577	-1.779300
78	1	0	7.362107	0.975648	-0.172640
79	1	0	7.728311	2.985291	1.243269
80	1	0	3.795706	4.400699	0.238364
81	1	0	3.430704	2.414076	-1.176779
82	1	0	6.784096	4.909671	2.438851
83	1	0	6.363658	5.911187	1.047165
84	1	0	5.103228	5.401757	2.170728
85	1	0	2.183585	-2.856361	2.645104
86	1	0	4.352798	-3.494966	3.664745
87	1	0	6.487441	-2.915079	2.558956
88	1	0	6.510043	-1.686825	0.395041

Sum of electronic and zero-point Energies= -2904.384553

Sum of electronic and thermal Energies= -2904.339520

Sum of electronic and thermal Enthalpies= -2904.338576

Sum of electronic and thermal Free Energies= -2904.472391



3a

Optimization Parameters

Item	Value	Threshold	Converged?
Maximum Force	0.000009	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.001438	0.001800	YES
RMS Displacement	0.000227	0.001200	YES

Predicted change in Energy= -1.471185D-08

Optimization completed.

-- Stationary point found.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	0.074224	4.172675	-1.496032
2	6	0	1.287507	4.041754	-0.797345
3	6	0	1.514594	2.978701	0.072033
4	6	0	0.488592	2.040698	0.207167
5	6	0	-0.740773	2.154530	-0.483446
6	6	0	-0.948319	3.243807	-1.342376
7	7	0	0.398515	0.881772	1.008622
8	6	0	-0.833386	0.280100	0.796621
9	6	0	-1.565065	1.019638	-0.101146
10	16	0	1.676525	0.089161	1.855744
11	8	0	2.550263	1.148863	2.347392
12	8	0	1.000502	-0.855263	2.740733
13	6	0	2.537559	-0.831361	0.588788
14	6	0	2.162426	-2.152373	0.334753
15	6	0	2.830074	-2.862487	-0.659442
16	6	0	3.862793	-2.274233	-1.404102
17	6	0	4.224489	-0.950180	-1.116074
18	6	0	3.571583	-0.222362	-0.124974
19	6	0	4.557789	-3.042083	-2.501115
20	6	0	-2.959150	0.798588	-0.528499
21	8	0	-3.593641	1.707139	-1.061834
22	6	0	-3.622227	-0.529563	-0.296678
23	6	0	-5.009041	-0.532720	-0.080475
24	6	0	-5.691364	-1.730059	0.111170

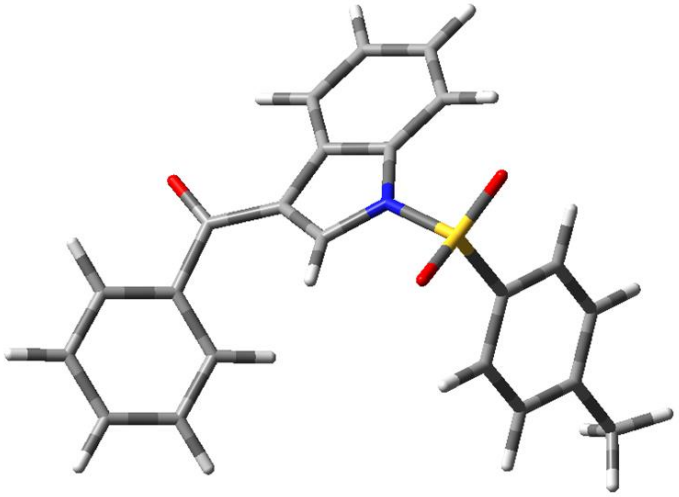
25	6	0	-5.000947	-2.944599	0.063125
26	6	0	-3.627249	-2.954101	-0.180286
27	6	0	-2.938645	-1.753058	-0.355413
28	1	0	-0.069573	5.022487	-2.156453
29	1	0	2.061467	4.792661	-0.924647
30	1	0	2.431460	2.898372	0.641857
31	1	0	-1.896934	3.346511	-1.854112
32	1	0	-1.093840	-0.602858	1.358002
33	1	0	1.380015	-2.617313	0.924041
34	1	0	2.550209	-3.893803	-0.854994
35	1	0	5.033867	-0.483912	-1.670634
36	1	0	3.869660	0.793517	0.105565
37	1	0	4.539403	-4.118531	-2.310374
38	1	0	4.065119	-2.871937	-3.466271
39	1	0	5.600494	-2.730777	-2.608924
40	1	0	-5.530928	0.418178	-0.067599
41	1	0	-6.762005	-1.719953	0.292925
42	1	0	-5.534241	-3.879891	0.206311
43	1	0	-3.091753	-3.897056	-0.240878
44	1	0	-1.876200	-1.768463	-0.573934

Sum of electronic and zero-point Energies= -1526.823755

Sum of electronic and thermal Energies= -1526.801089

Sum of electronic and thermal Enthalpies= -1526.800145

Sum of electronic and thermal Free Energies= -1526.878906



4a

Optimization Parameters

Item	Value	Threshold	Converged?
Maximum Force	0.000041	0.000450	YES
RMS Force	0.000003	0.000300	YES
Maximum Displacement	0.001520	0.001800	YES
RMS Displacement	0.000267	0.001200	YES

Predicted change in Energy=-5.059318D-09

Optimization completed.

-- Stationary point found.

Standard orientation:

Center Atomic Atomic Coordinates (Angstroms)

Number Number Type X Y Z

---

1 6 0 0.523943 4.170796 -1.673995

2 6 0 1.611707 3.984376 -0.803147

3 6 0 1.630332 2.947903 0.127284

4 6 0 0.529347 2.089132 0.150253

5 6 0 -0.579113 2.259271 -0.716258

6 6 0 -0.575453 3.320562 -1.633318

7 7 0 0.234732 0.985274 0.972239

8 6 0 -1.541874 1.217912 -0.417782

9 16 0 1.352498 0.064829 1.886126

10 8 0 2.310820 1.020582 2.435380

11 8 0 0.528664 -0.796443 2.730569

12 6 0 2.196592 -0.961184 0.686910

13 6 0 1.664582 -2.211602 0.363559

14 6 0 2.315952 -2.997241 -0.582937

15 6 0 3.488069 -2.553796 -1.213507

16 6 0 4.003755 -1.299406 -0.859492

17 6 0 3.367966 -0.497802 0.085805

18 6 0 4.166732 -3.401617 -2.261309

19 6 0 -3.659237 -0.169964 -0.635545

20 6 0 -4.477262 -0.120277 0.500877

21 6 0 -5.175633 -1.249631 0.929463

22 6 0 -5.066922 -2.449713 0.224933

23 6 0 -4.255266 -2.511865 -0.908722

24 6 0 -3.556601 -1.380550 -1.332337

25 6 0 -1.012126 0.463210 0.583766

26 1 0 0.540952 4.995526 -2.380158

27 1 0 2.452652 4.669999 -0.845309

28 1 0 2.451727 2.825290 0.821858

29 1 0 -1.419103 3.475694 -2.299700

30 1 0 0.770033 -2.566356 0.862927

31 1 0 1.911876 -3.974770 -0.831375

32 1 0 4.919857 -0.947101 -1.325220

33 1 0 3.781269 0.463015 0.369219

34 1 0 4.070960 -4.467942 -2.037104

35 1 0 3.717644 -3.235137 -3.248208

36 1 0 5.230698 -3.163355 -2.342189

37 1 0 -4.567584 0.812117 1.052553

38 1 0 -5.806604 -1.190966 1.811664

39 1 0 -5.612942 -3.328483 0.555251

40 1 0 -4.167890 -3.440318 -1.465995

41 1 0 -2.927106 -1.434539 -2.217248

42 1 0 -1.415239 -0.390078 1.105449

43 6 0 -2.884437 1.052376 -1.084871

44 1 0 -2.734916 1.010779 -2.172034

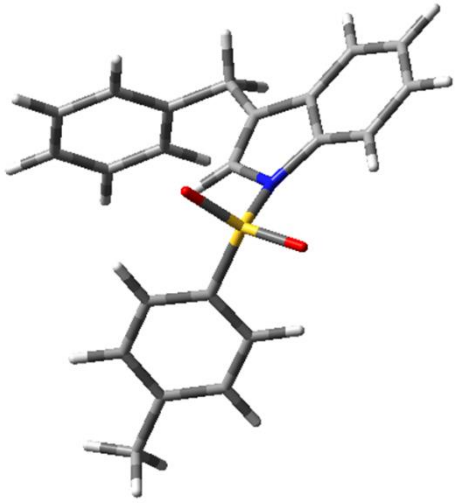
45 1 0 -3.485566 1.954006 -0.903443

Sum of electronic and zero-point Energies= -1452.789412

Sum of electronic and thermal Energies= -1452.767130

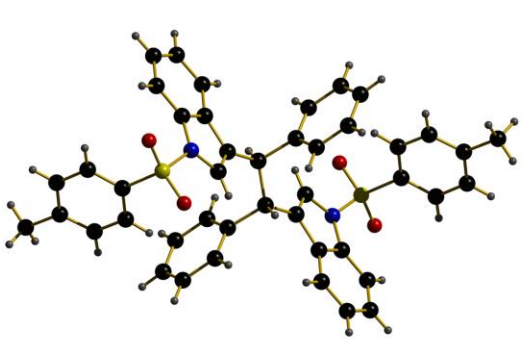
Sum of electronic and thermal Enthalpies= -1452.766186

Sum of electronic and thermal Free Energies= -1452.845424



IV. Crystal Structure of the representative dimerized product, 2a:

Empirical formula	$C_{44}H_{36}N_2O_4S_2$
Formula weight	720.87
Temperature/K	273.15
Crystal system	triclinic
Space group	P-1
a/Å	8.5846(8)
b/Å	10.3006(10)
c/Å	12.9846(12)
α/°	70.921(3)
β/°	77.705(3)
γ/°	68.783(3)
Volume/Å^3	1005.71(17)
Z	1
ρ_{calc}g/cm^3	1.19
μ/mm^{-1}	0.175
F(000)	378
Crystal size/mm^3	0.22 × 0.15 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.41 to 50.7
Index ranges	$-10 \le h \le 10$, $-12 \le k \le 12$, $-15 \le l \le 15$
Reflections collected	19423
Independent reflections	3678 [R_{int} = 0.0894, R_{sigma} = 0.0850]
Data/restraints/parameters	3678/0/236
Goodness-of-fit on F^2	1.189
Final R indexes [I>=2σ (I)]	R_1 = 0.1285, wR_2 = 0.2358
Final R indexes [all data]	R_1 = 0.1669, wR_2 = 0.2516
Largest diff. peak/hole / e Å^{-3}	0.35/-0.34

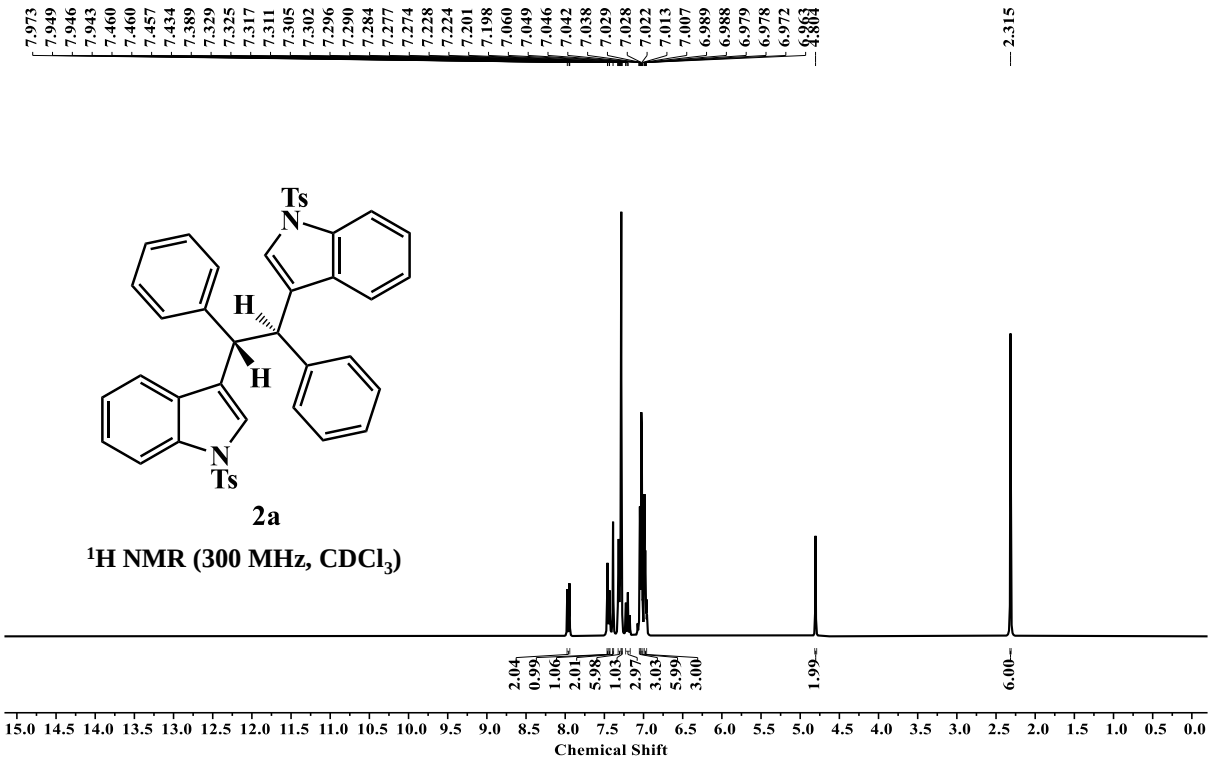


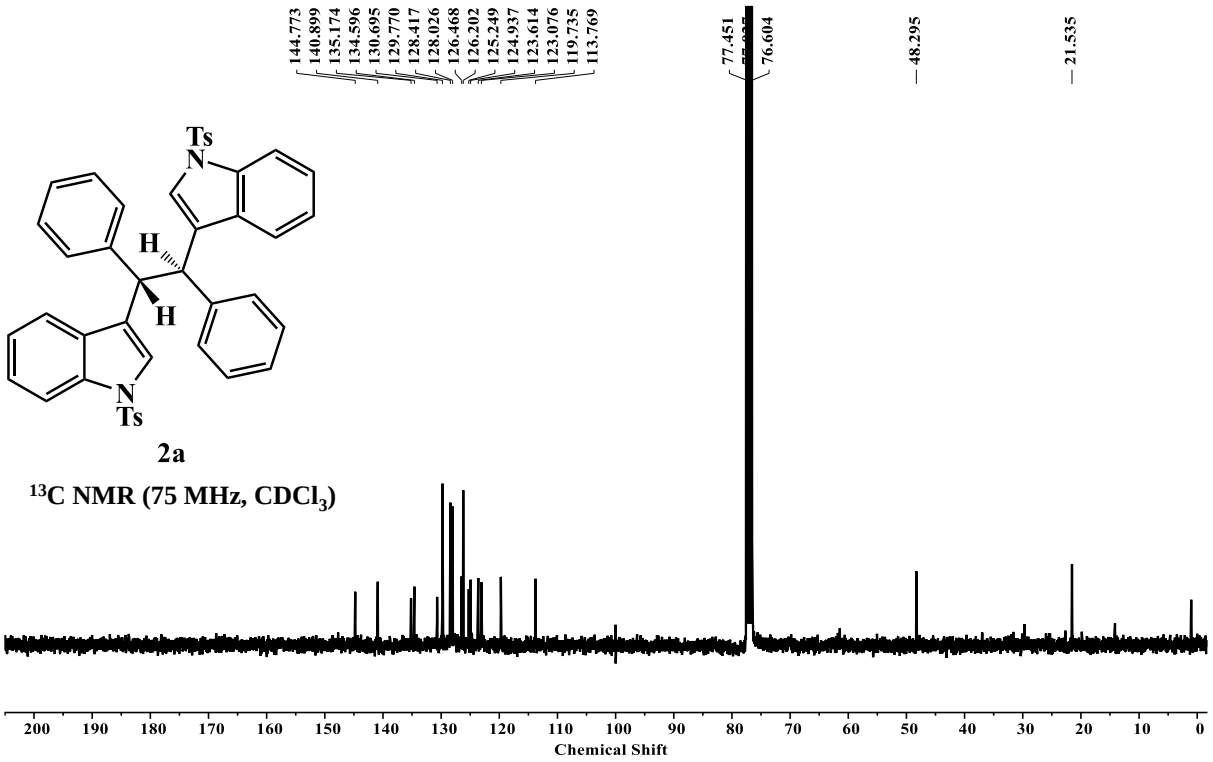
Crystal structure of 2a

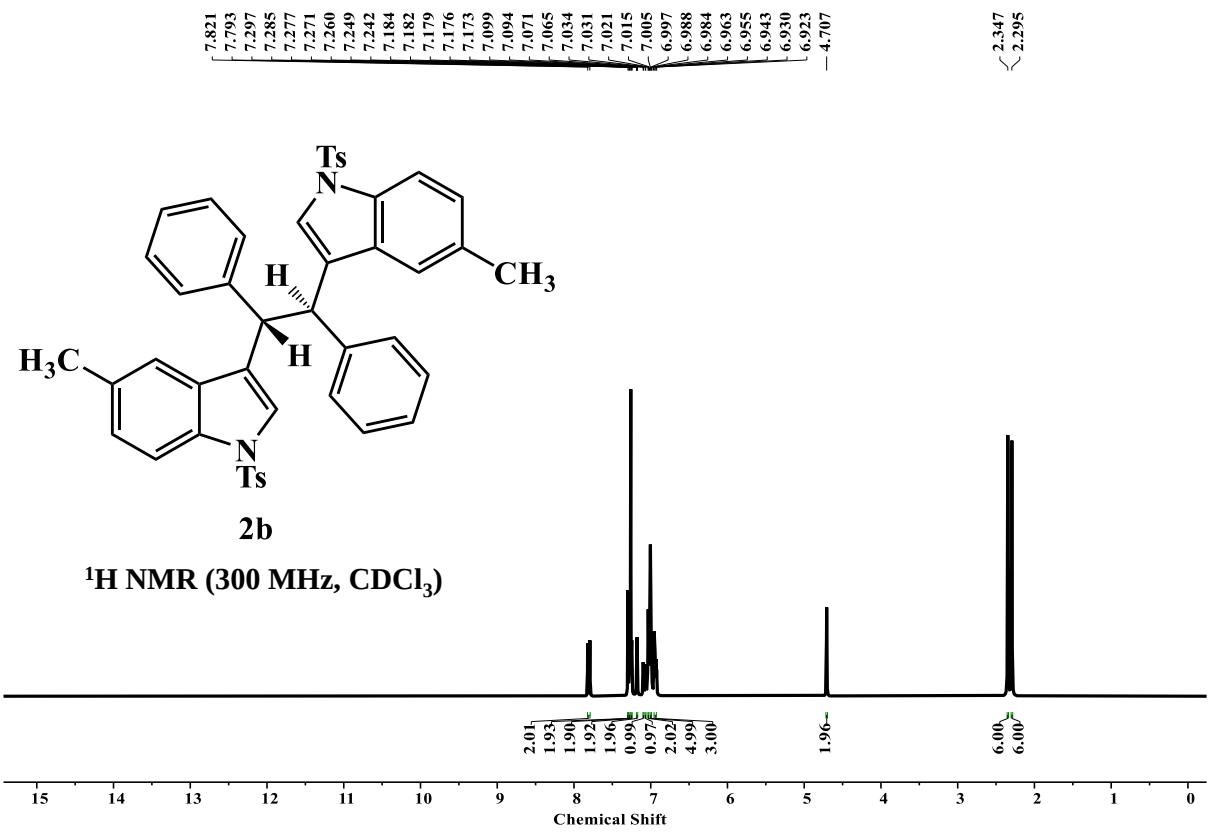
CCDC No. 2388099

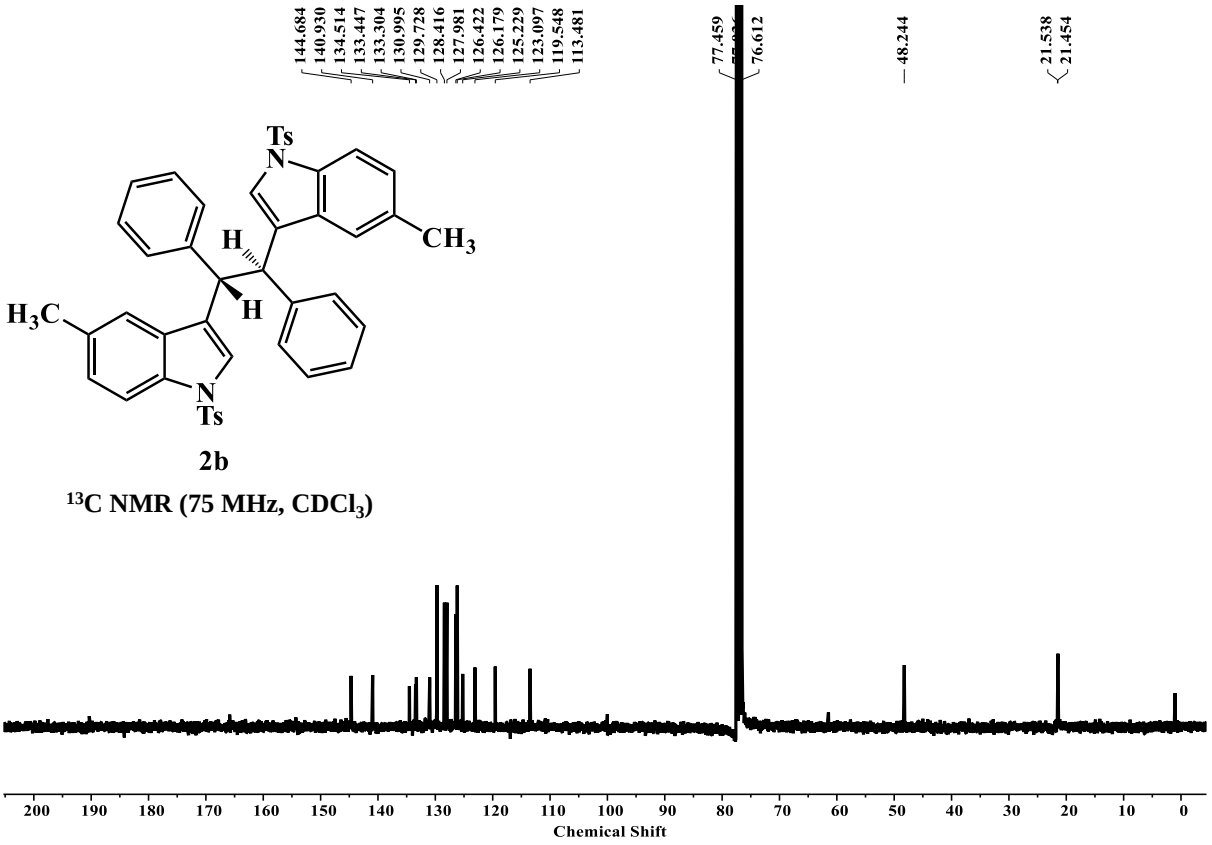
Figure S10

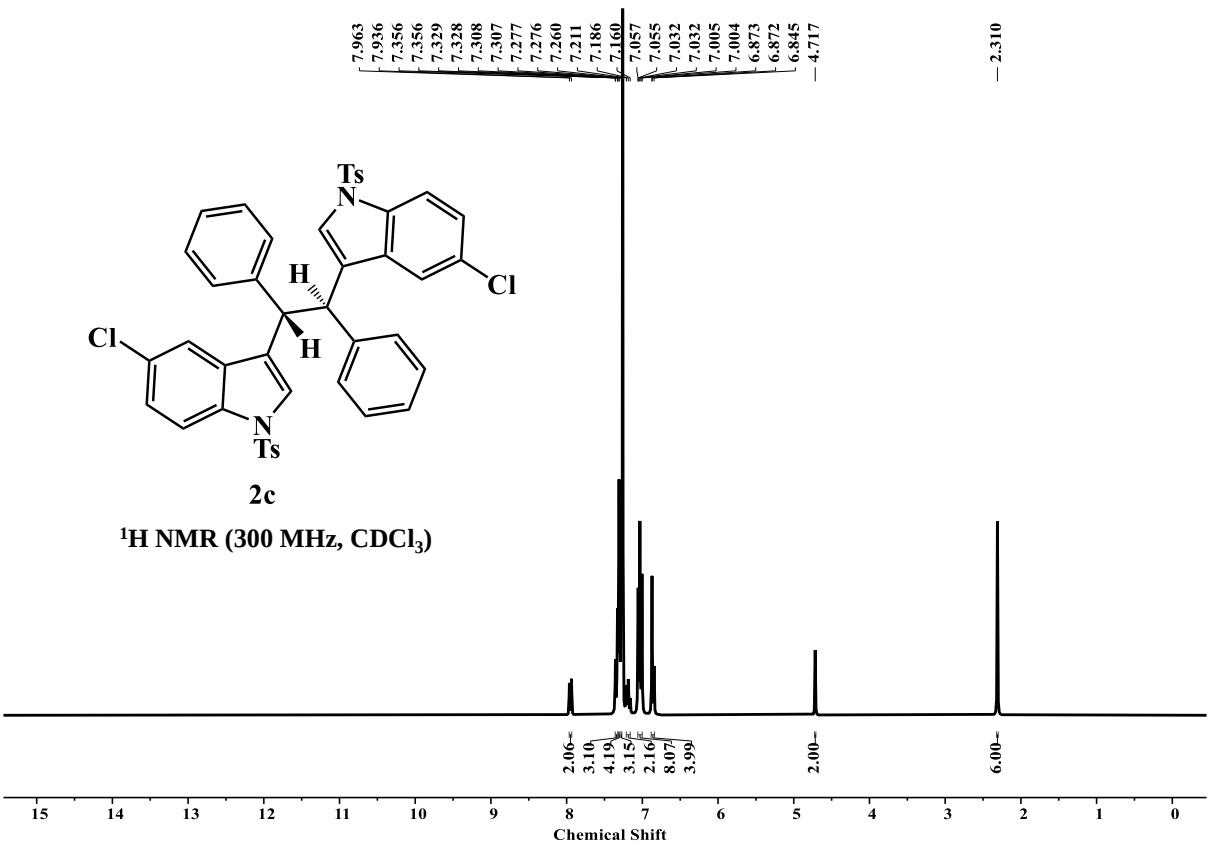
V. Copies of NMR spectra:





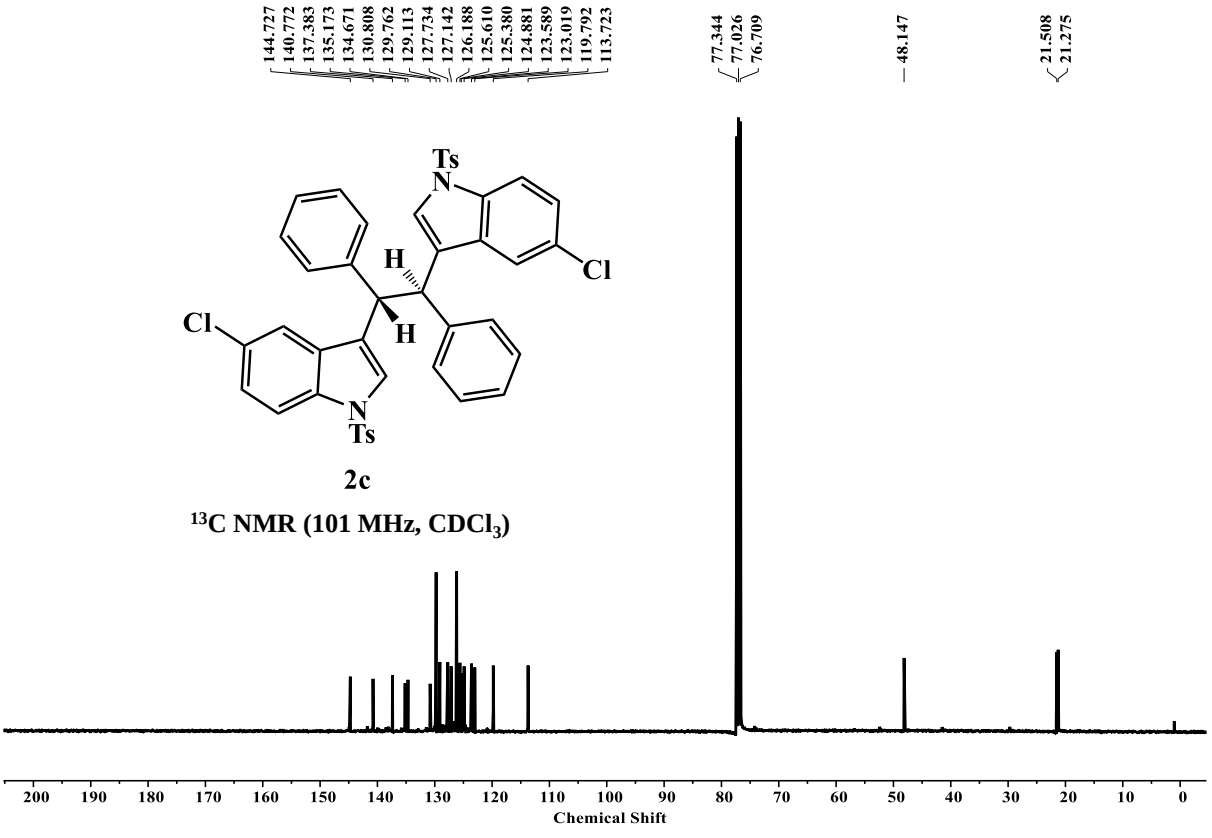

7.821
7.793
7.297
7.285
7.277
7.271
7.260
7.249
7.242
7.184
7.182
7.179
7.176
7.173
7.099
7.094
7.071
7.065
7.034
7.031
7.021
7.015
7.005
6.997
6.988
6.984
6.963
6.955
6.943
6.930
6.923
4.707
2.347
2.295
Ts
N
H
CH3
H3C
H
N
Ts
2b
1H NMR (300 MHz, CDCl3)
2.01
1.93
1.90
1.92
1.96
0.99
0.97
2.02
4.99
3.00
1.96
6.00
6.00
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift


144.684
140.930
134.514
133.447
133.304
130.995
129.728
128.416
127.981
126.422
126.179
125.229
123.097
119.548
113.481
77.459
76.612
48.244
21.538
21.454
Ts
N
H
CH3
H3C
H
N
Ts
2b
13C NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift



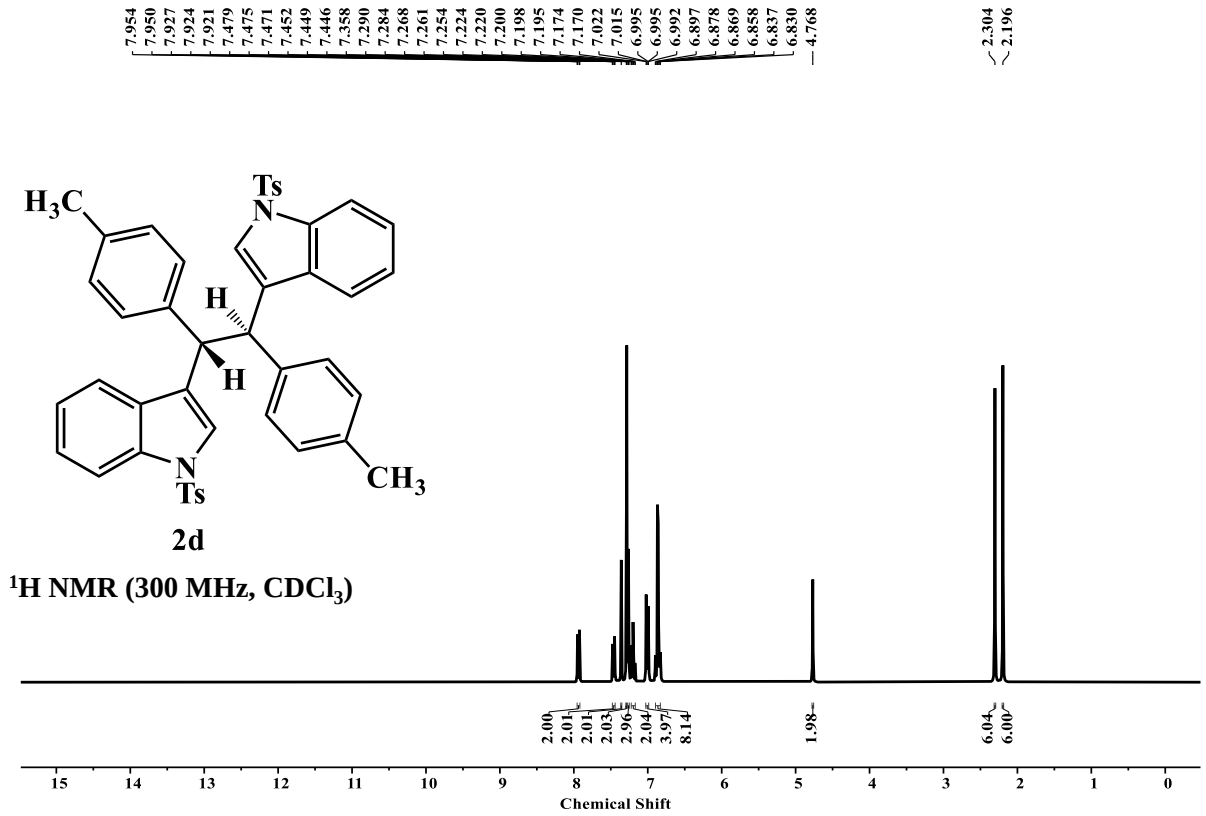
2c

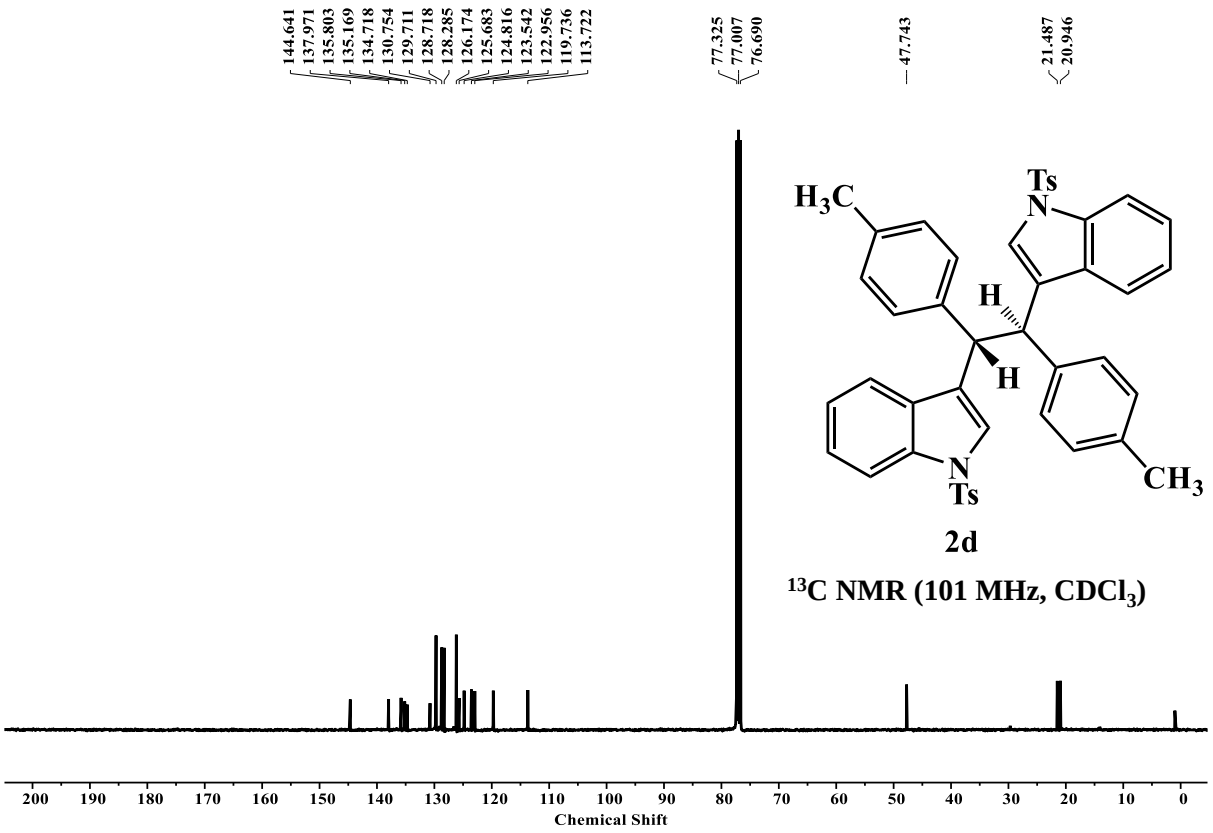
^{1}H NMR (300 MHz, $CDCl_3$)

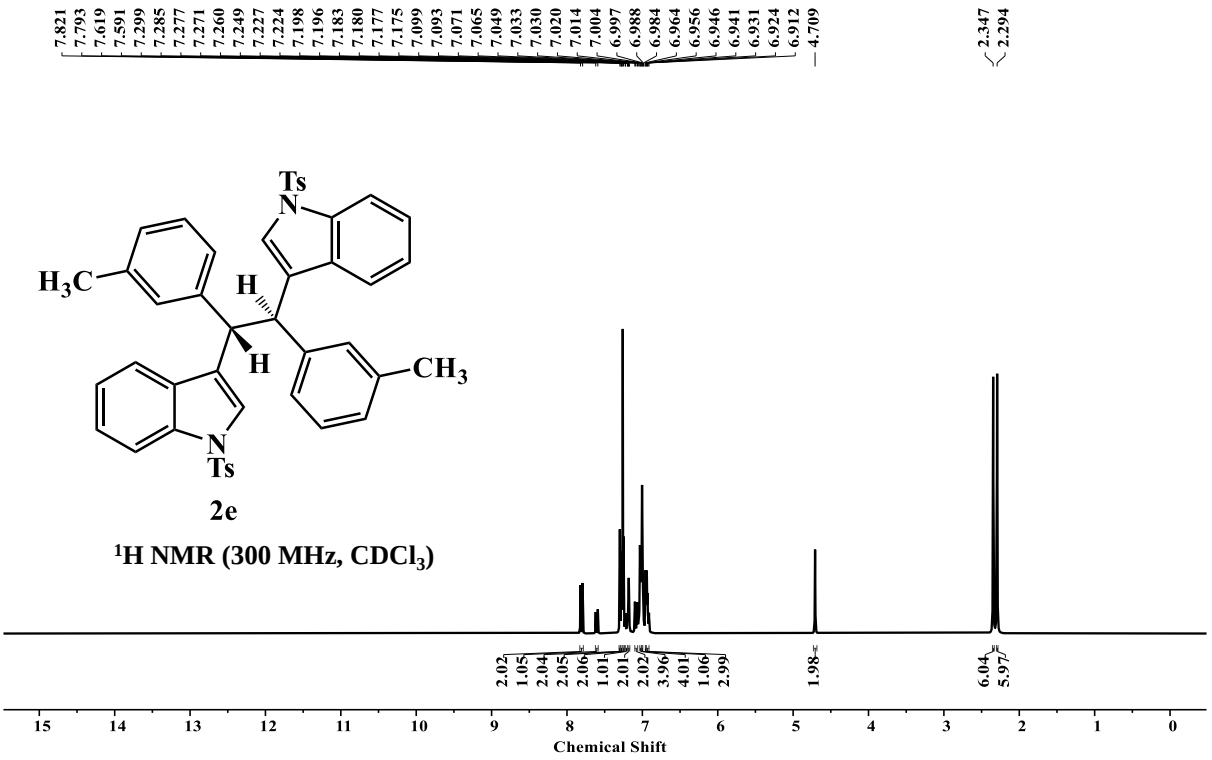


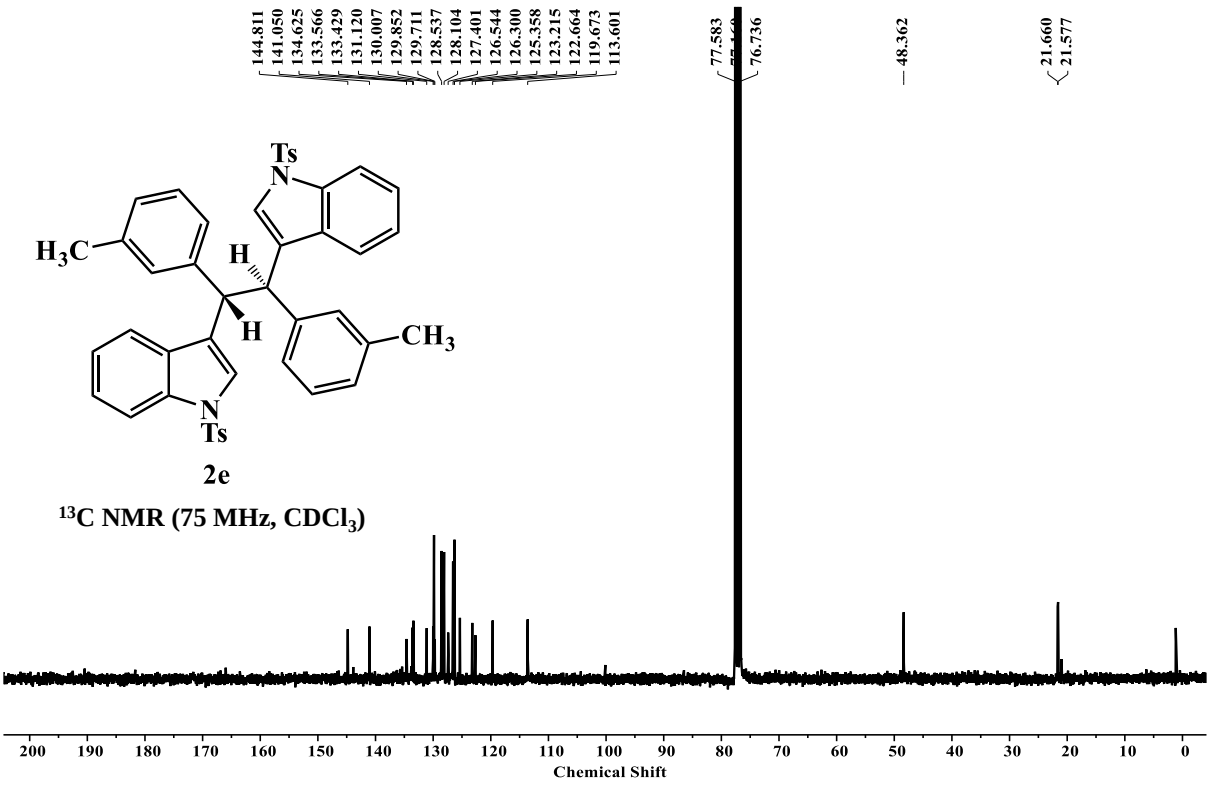
2c

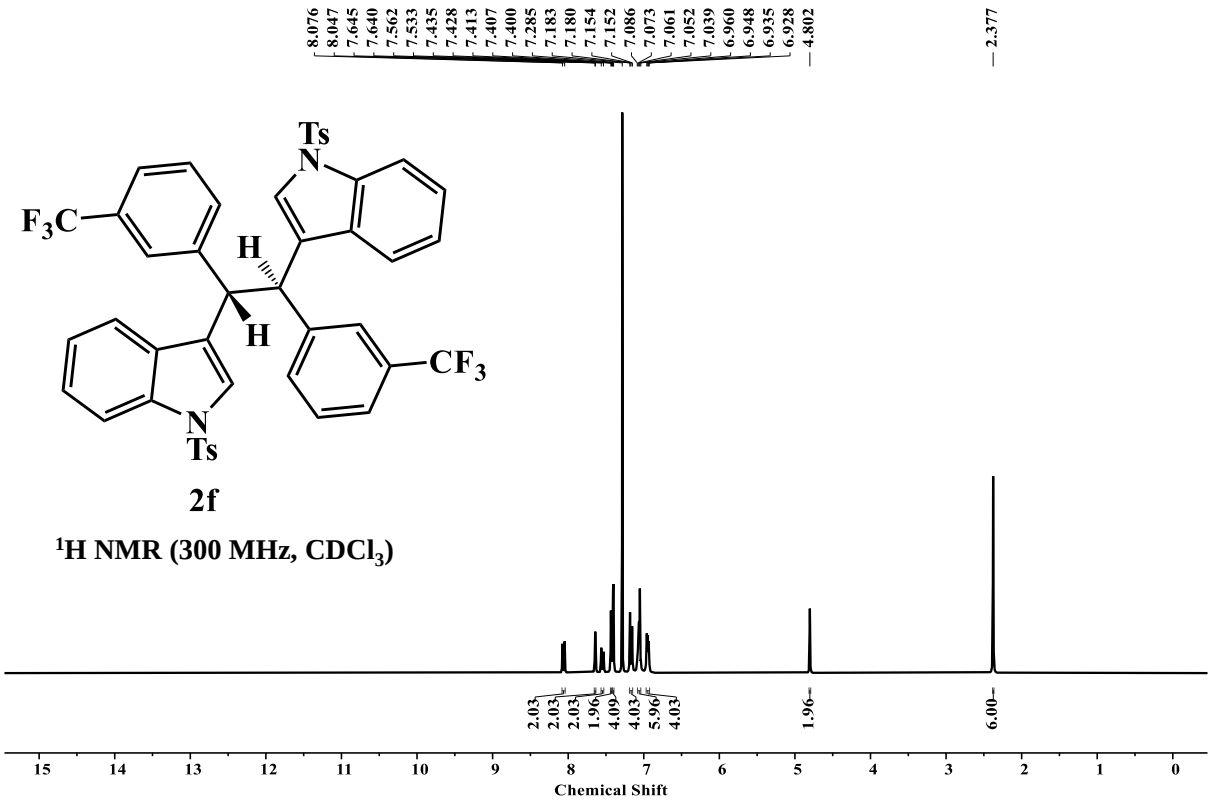
^{13}C NMR (101 MHz, $CDCl_3$)

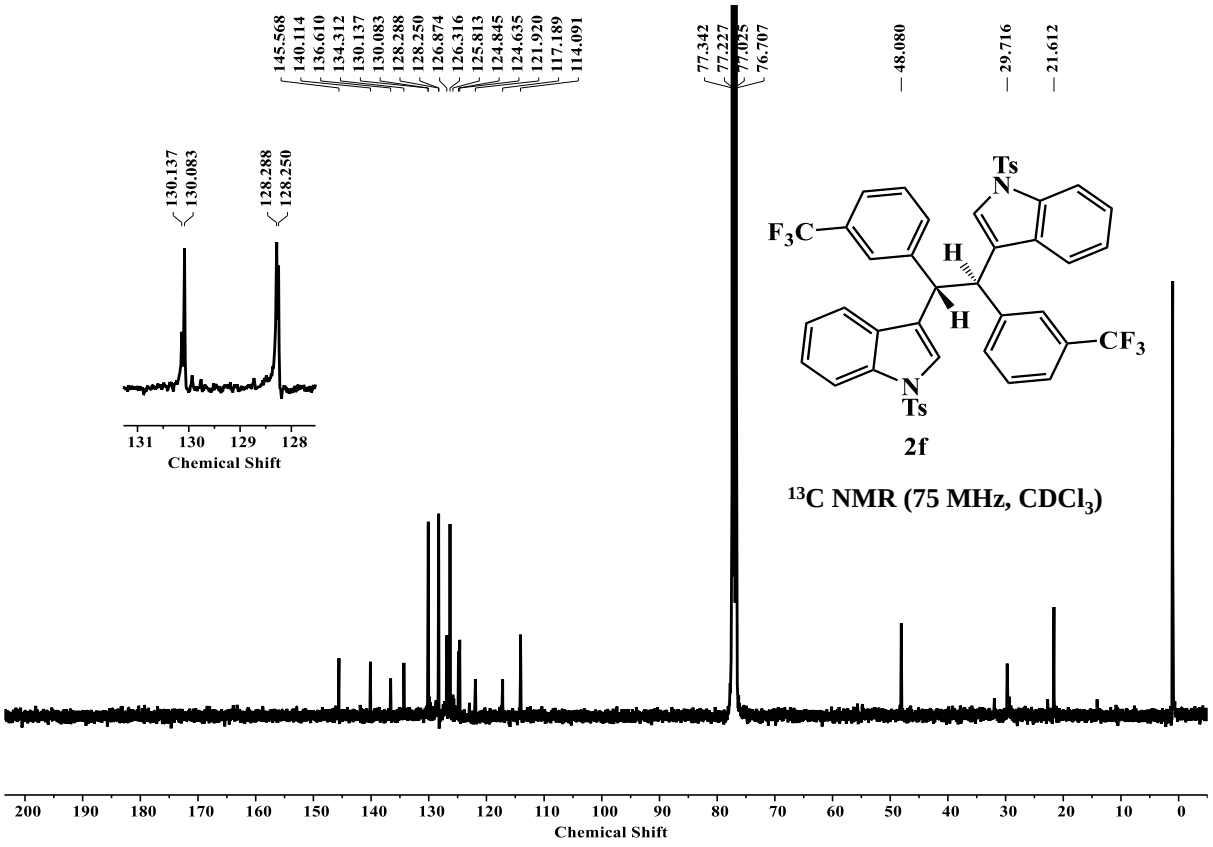

7.954
7.950
7.927
7.924
7.921
7.479
7.475
7.471
7.452
7.449
7.446
7.358
7.290
7.284
7.268
7.261
7.254
7.224
7.220
7.200
7.198
7.195
7.174
7.170
7.022
7.015
6.995
6.995
6.992
6.897
6.878
6.869
6.858
6.837
6.830
4.768
2.304
2.196
Ts
N
H
H
N
Ts
CH3
2d
1H NMR (300 MHz, CDCl3)
2.00
2.01
2.01
2.03
2.96
2.04
3.97
8.14
1.98
6.04
6.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
Chemical Shift

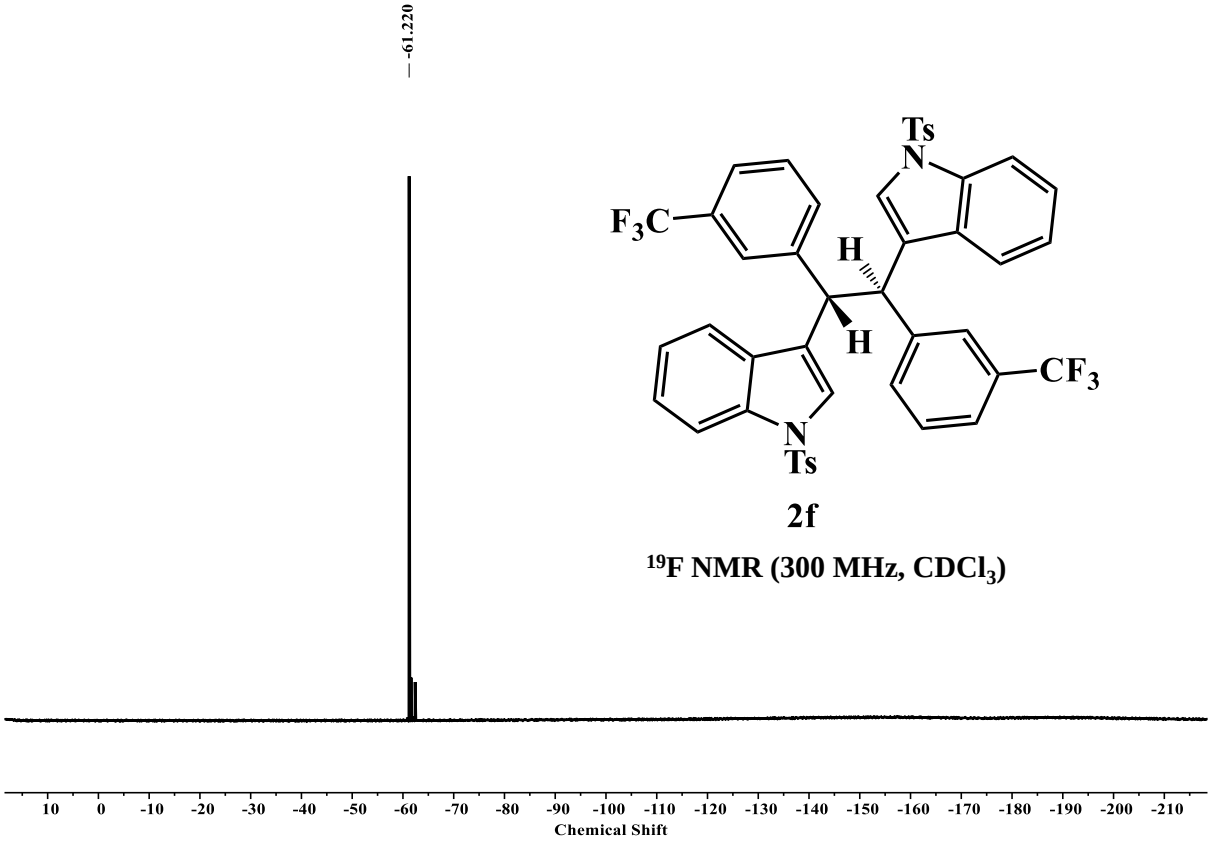

144.641
137.971
135.803
135.169
134.718
130.754
129.711
128.718
128.285
126.174
125.683
124.816
123.542
122.956
119.736
113.722
77.325
77.007
76.690
47.743
21.487
20.946
H3C
Ts
N
H
H
N
Ts
CH3
2d
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift


7.821
7.793
7.619
7.591
7.299
7.285
7.277
7.271
7.260
7.249
7.227
7.224
7.198
7.196
7.183
7.180
7.177
7.175
7.099
7.093
7.071
7.065
7.049
7.033
7.030
7.020
7.014
7.004
6.997
6.988
6.984
6.964
6.956
6.946
6.941
6.931
6.924
6.912
4.709
2.347
2.294
Ts
N
H3C
H
H
CH3
N
Ts
2e
1H NMR (300 MHz, CDCl3)
2.02
1.05
2.04
2.05
2.06
1.01
2.01
2.02
3.96
4.01
1.06
2.99
1.98
6.04
5.97
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift


144.811
141.050
134.625
133.566
133.429
131.120
130.007
129.852
129.711
128.537
128.104
127.401
126.544
126.300
125.358
123.215
122.664
119.673
113.601
77.583
76.736
48.362
21.660
21.577
Ts
N
H3C
H
H
CH3
N
Ts
2e
13C NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift

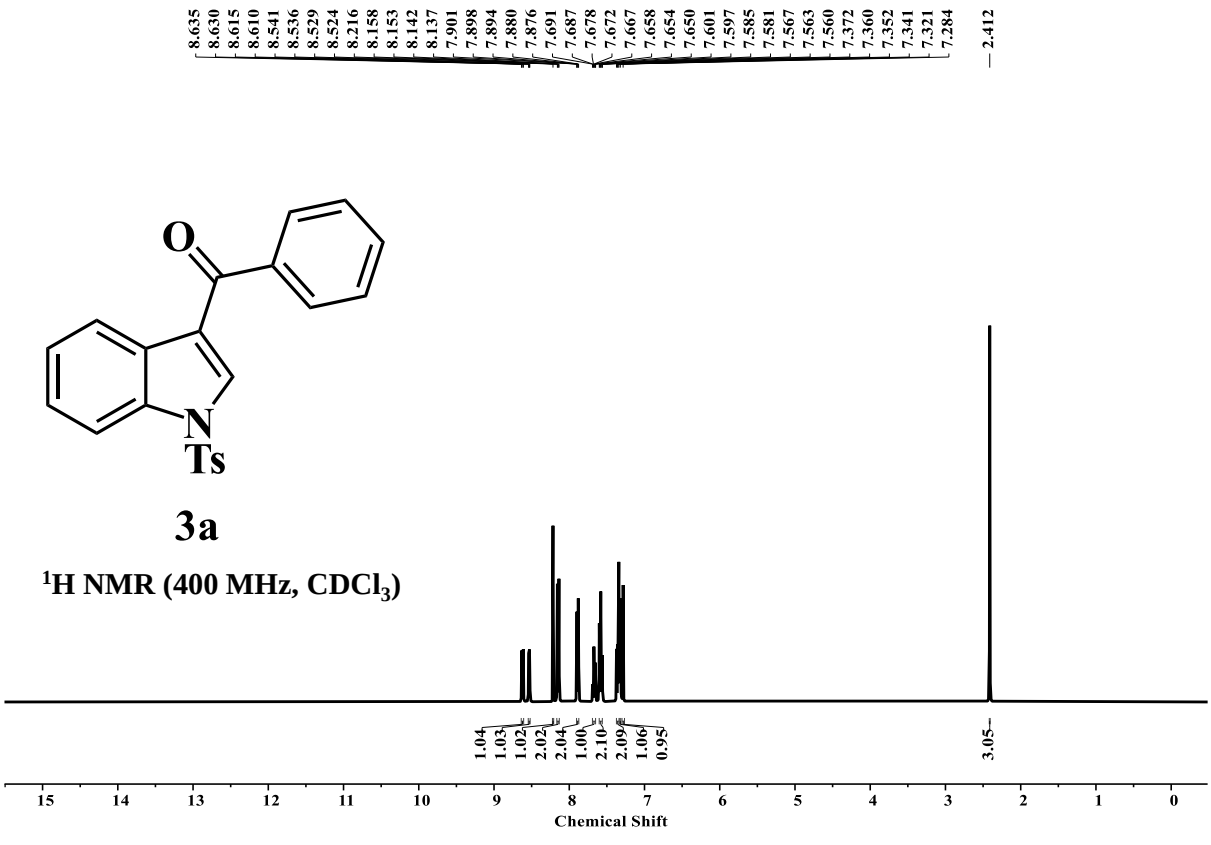

8.076
8.047
7.645
7.640
7.562
7.533
7.435
7.428
7.413
7.407
7.400
7.285
7.183
7.180
7.154
7.152
7.086
7.073
7.061
7.052
7.039
6.960
6.948
6.935
6.928
4.802
2.377
Ts
N
F3C
H
H
CF3
N
Ts
2f
1H NMR (300 MHz, CDCl3)
2.03
2.03
2.03
1.96
4.09
4.03
5.96
4.03
1.96
6.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
Chemical Shift


145.568
140.114
136.610
134.312
130.137
130.083
128.288
128.250
126.874
126.316
125.813
124.845
124.635
121.920
117.189
114.091
77.342
77.227
77.025
76.707
48.080
29.716
21.612
130.137
130.083
128.288
128.250
131 130 129 128
Chemical Shift
Ts
N
F3C
H
H
CF3
N
Ts
2f
13C NMR (75 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift



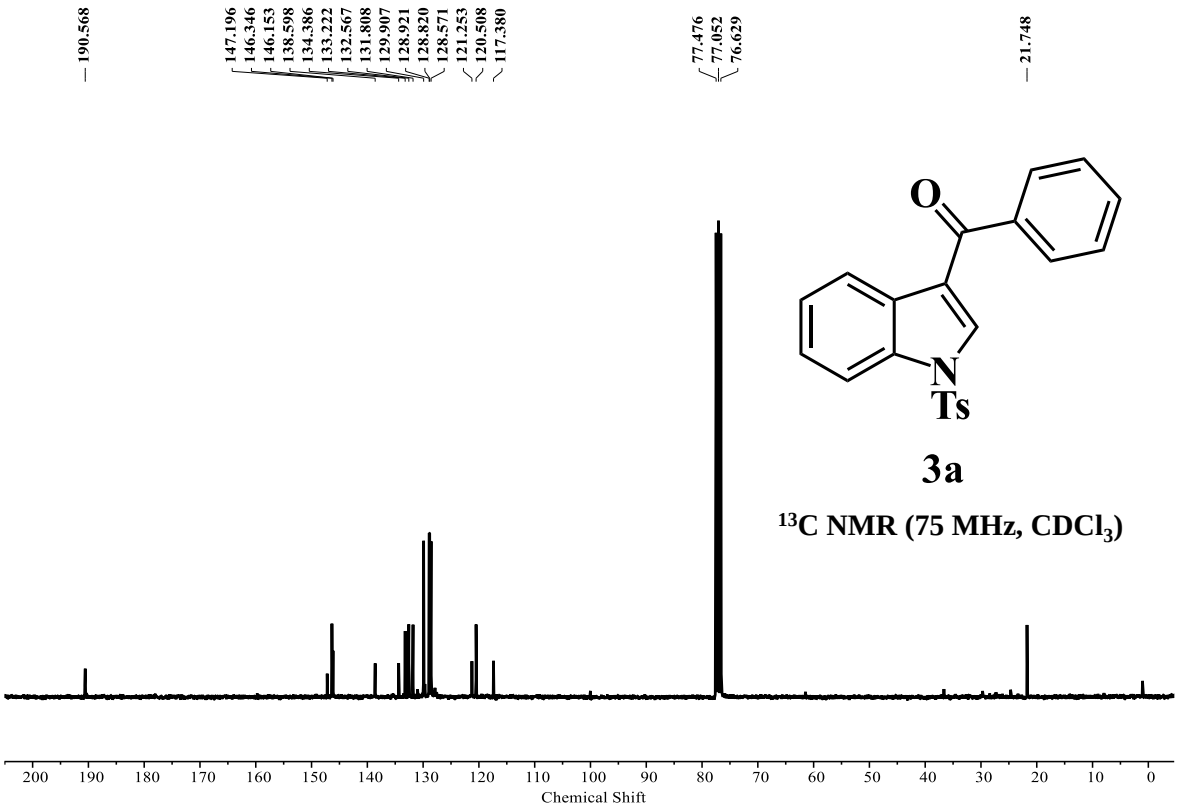
2f

^{19}F NMR (300 MHz, $CDCl_3$)



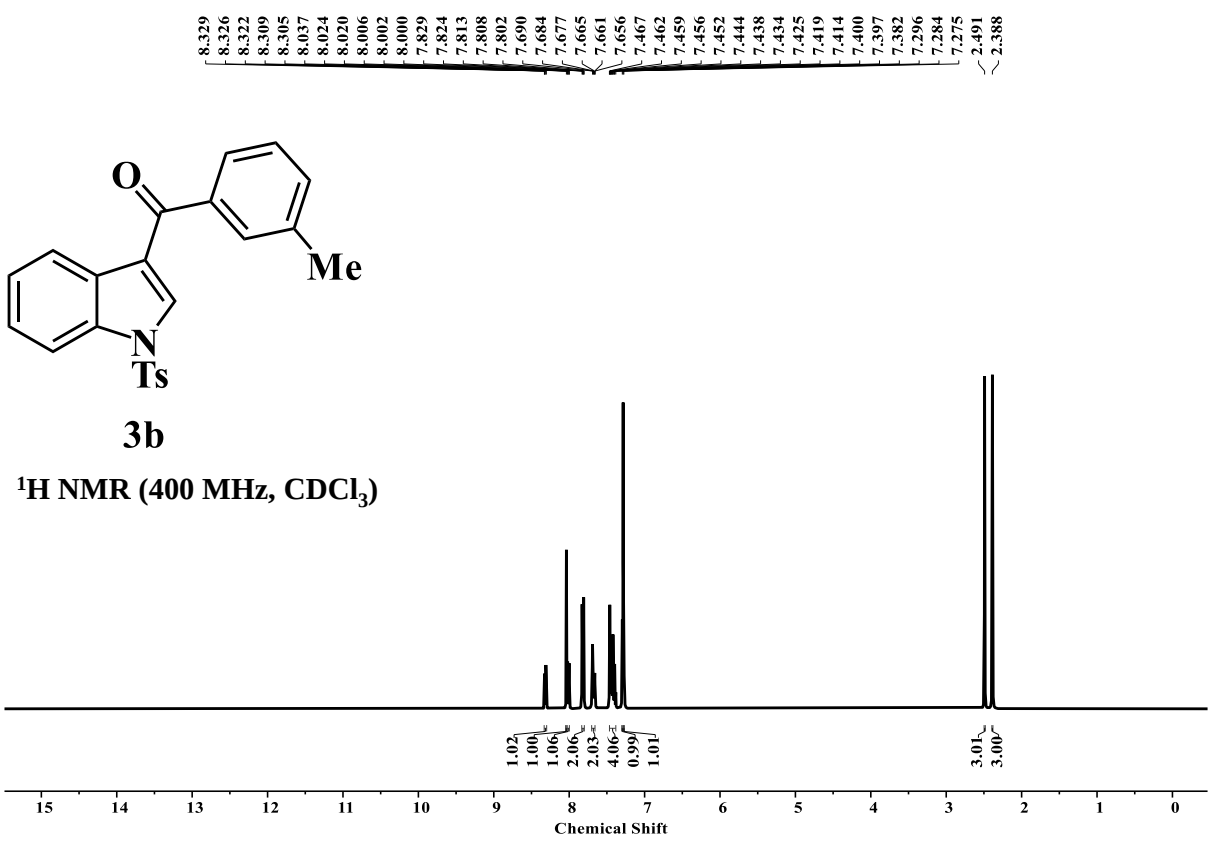
3a

^{1}H NMR (400 MHz, $CDCl_3$)



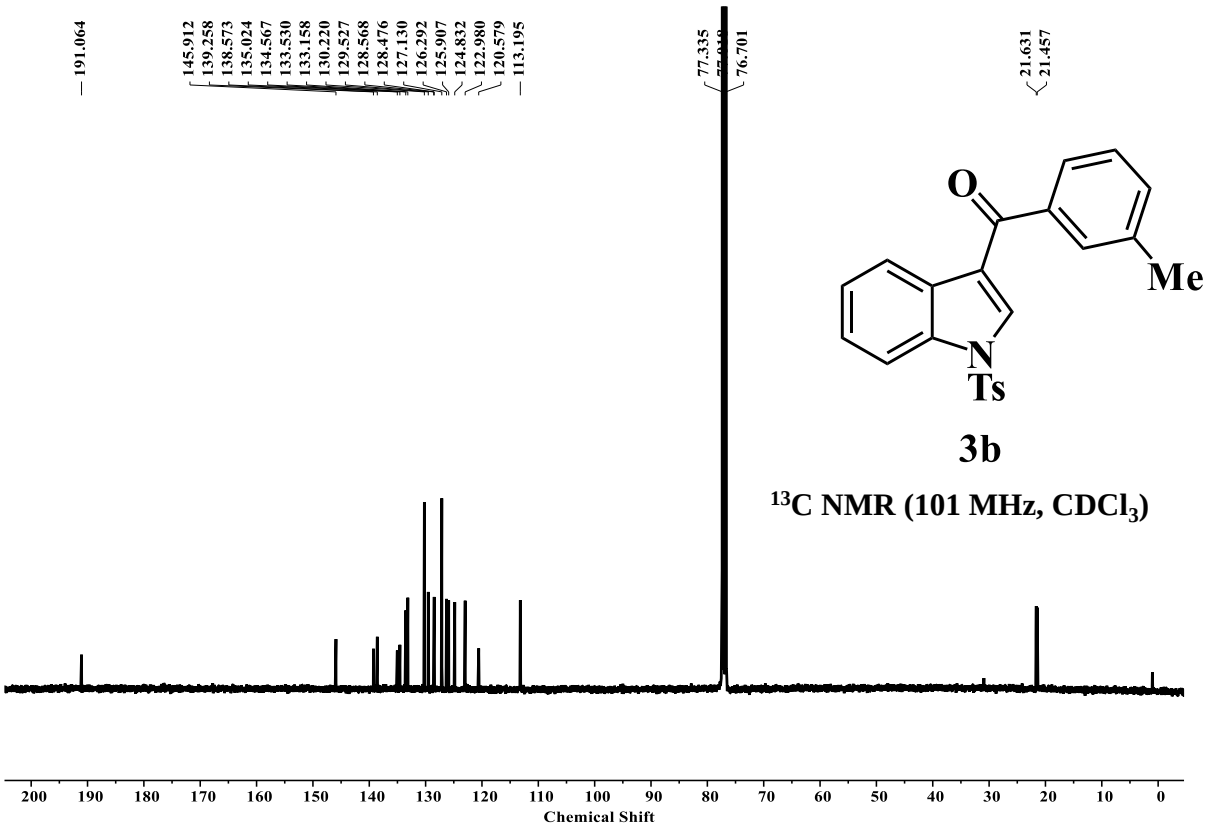
3a

^{13}C NMR (75 MHz, $CDCl_3$)



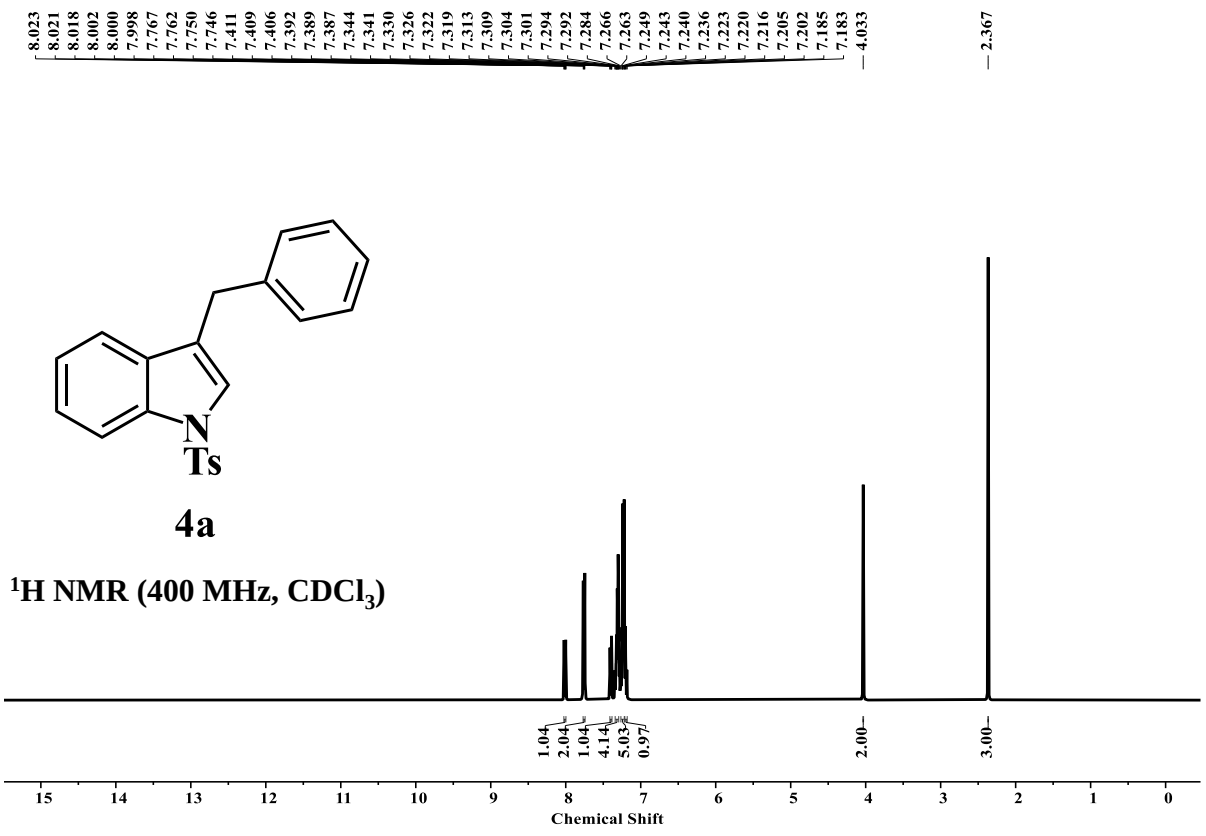
3b

^{1}H NMR (400 MHz, $CDCl_3$)



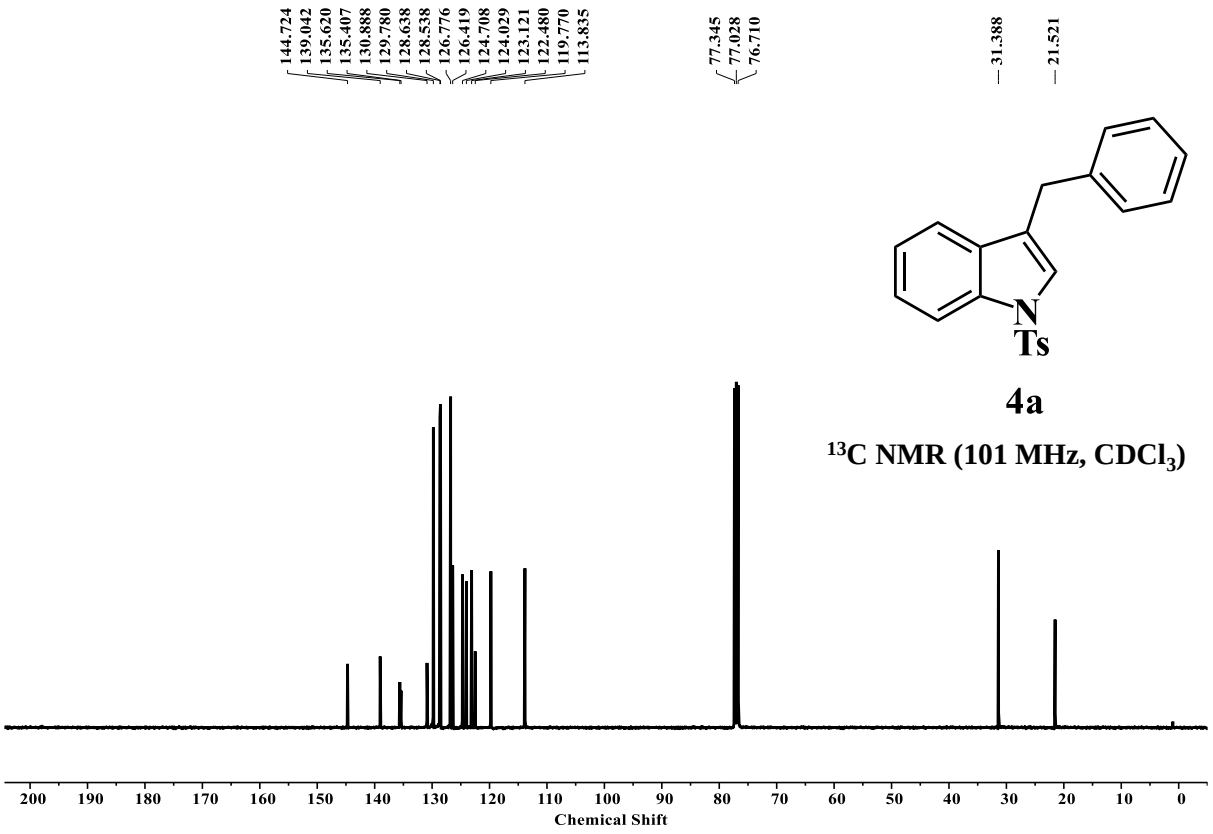
3b

^{13}C NMR (101 MHz, $CDCl_3$)



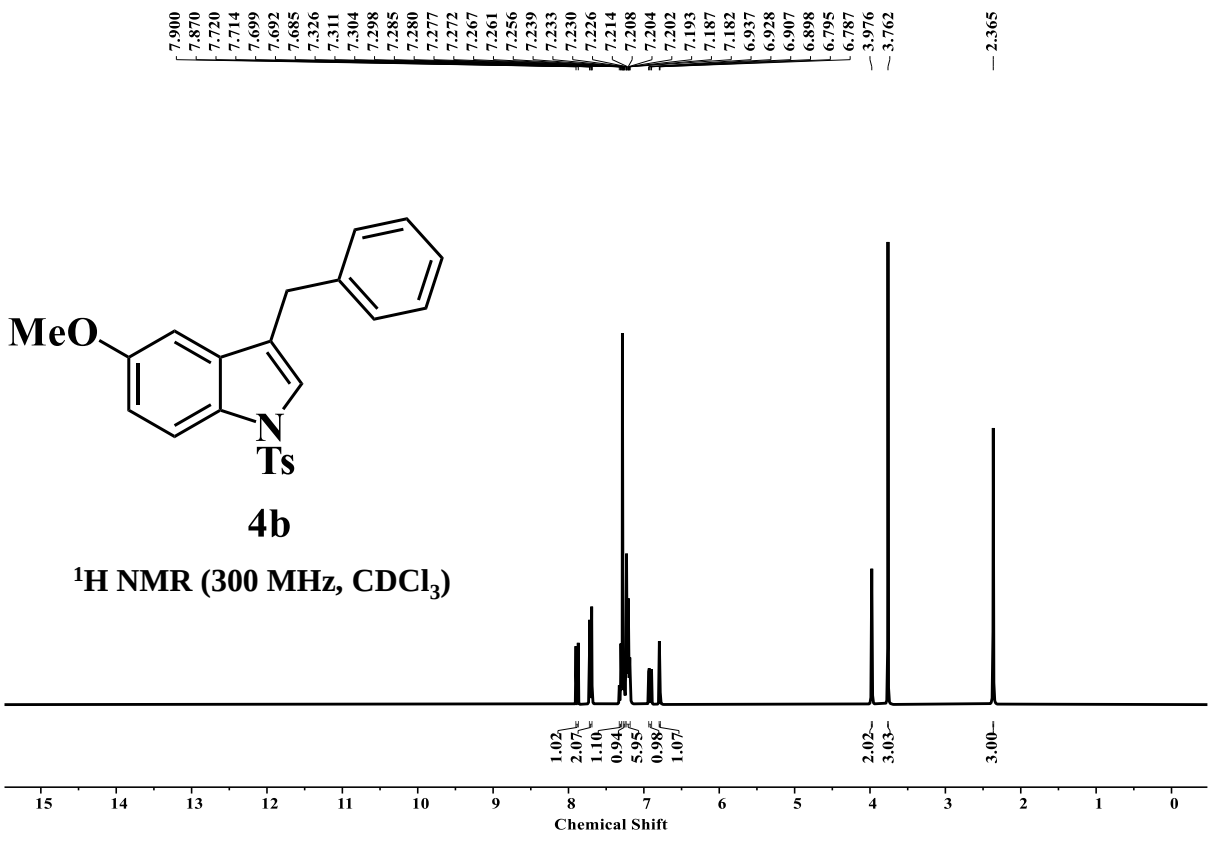
4a

^{1}H NMR (400 MHz, $CDCl_3$)



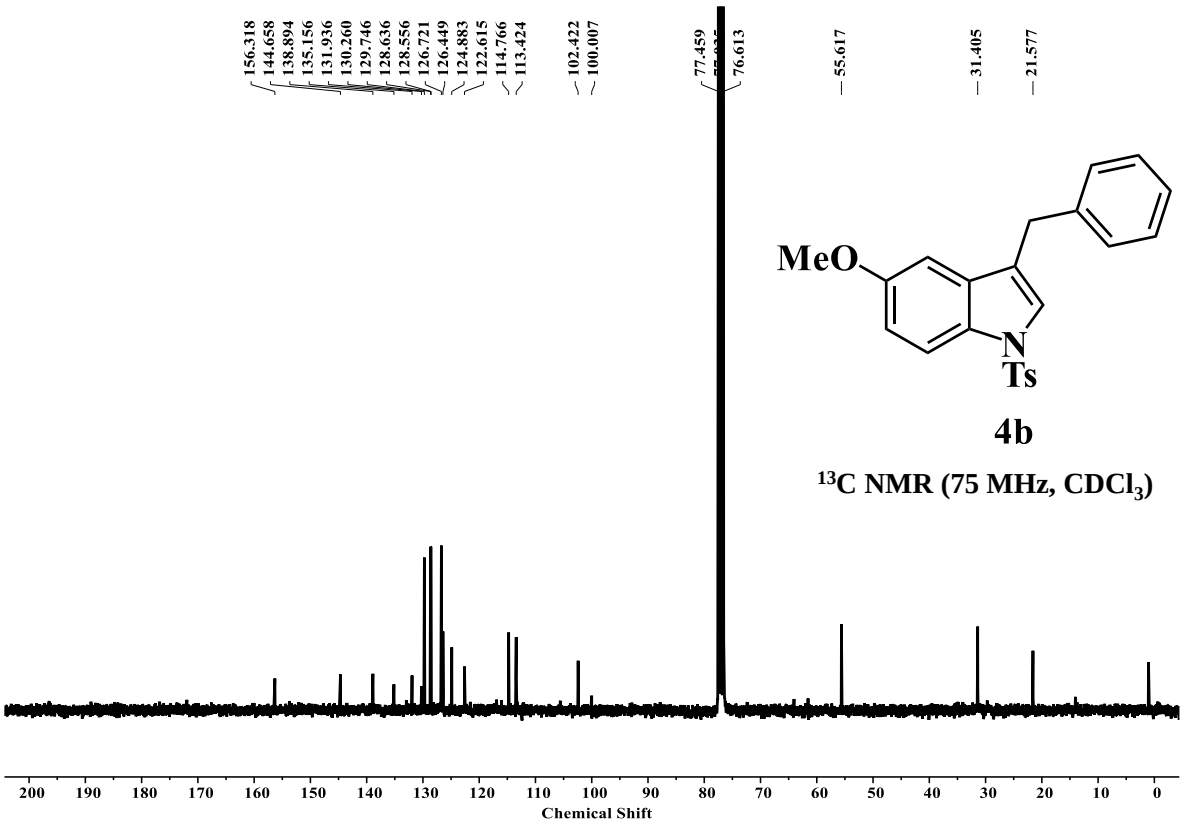
4a

^{13}C NMR (101 MHz, $CDCl_3$)



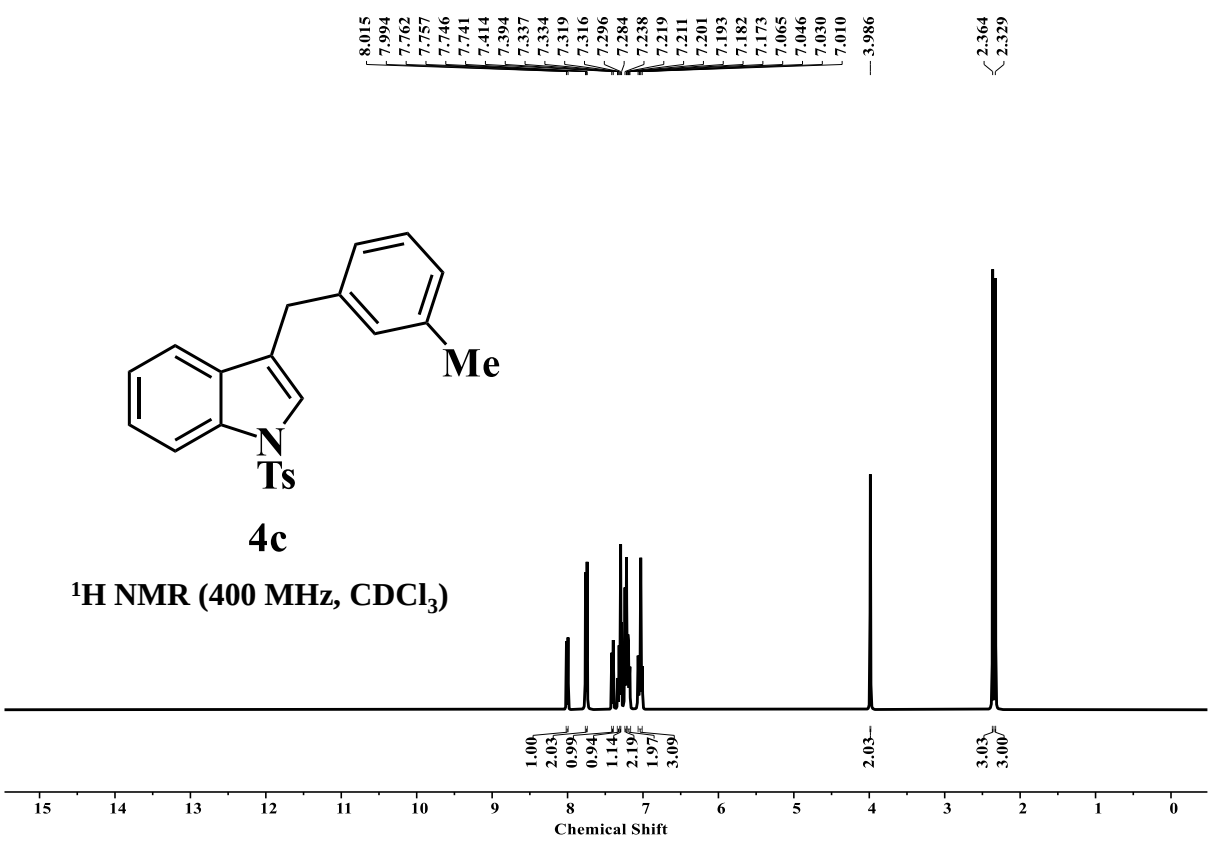
4b

^{1}H NMR (300 MHz, $CDCl_3$)



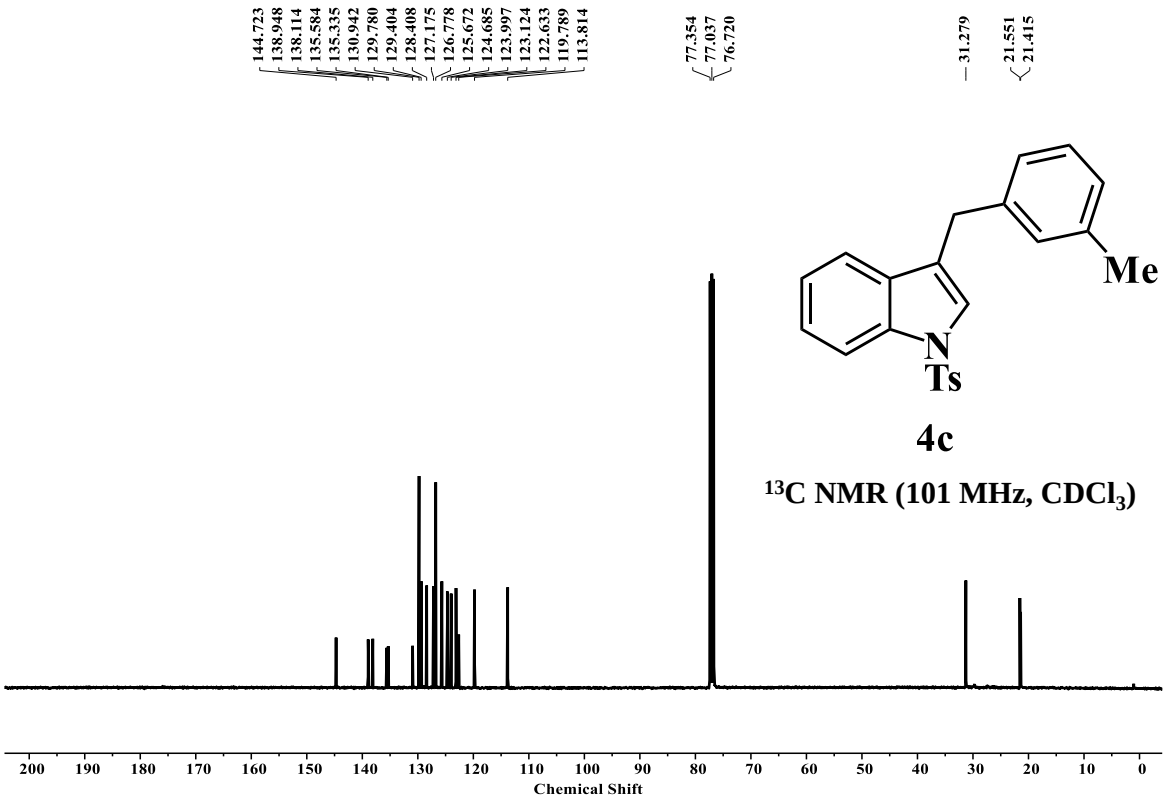
4b

^{13}C NMR (75 MHz, $CDCl_3$)



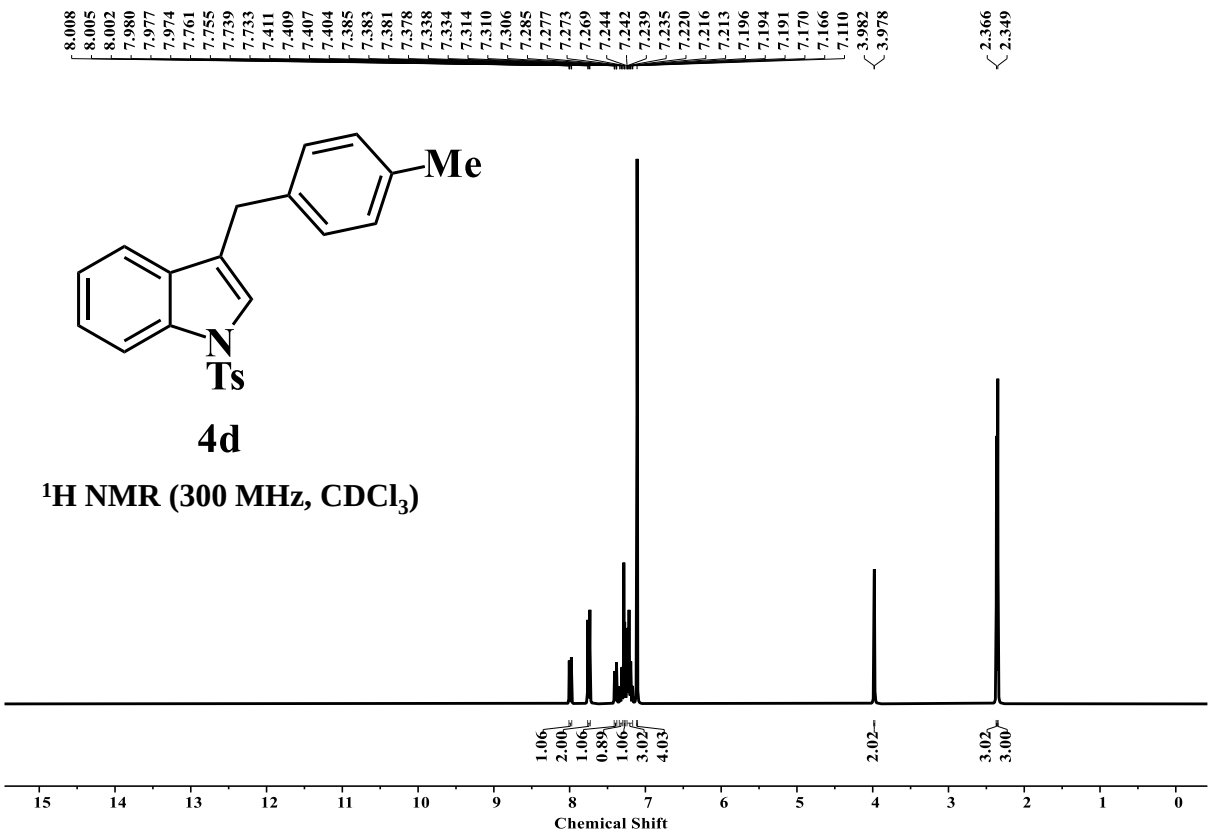
4c

^{1}H NMR (400 MHz, $CDCl_3$)



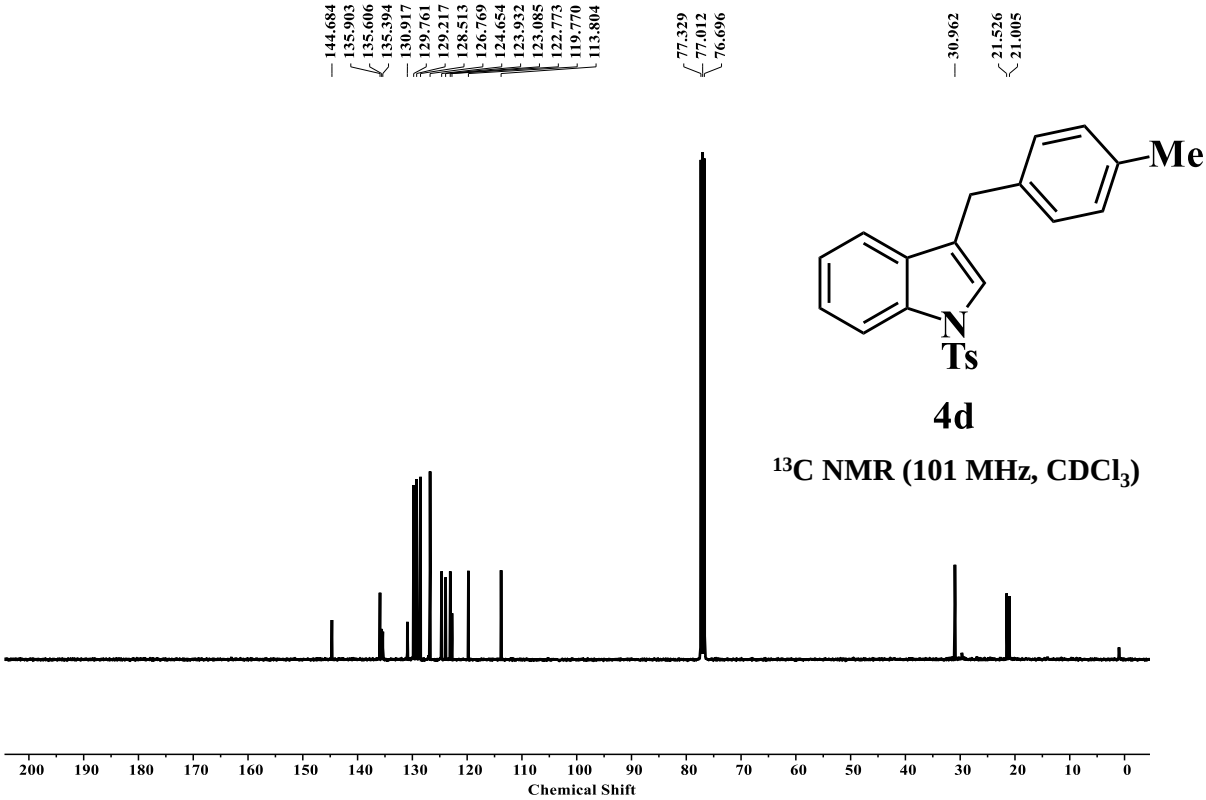
4c

^{13}C NMR (101 MHz, $CDCl_3$)



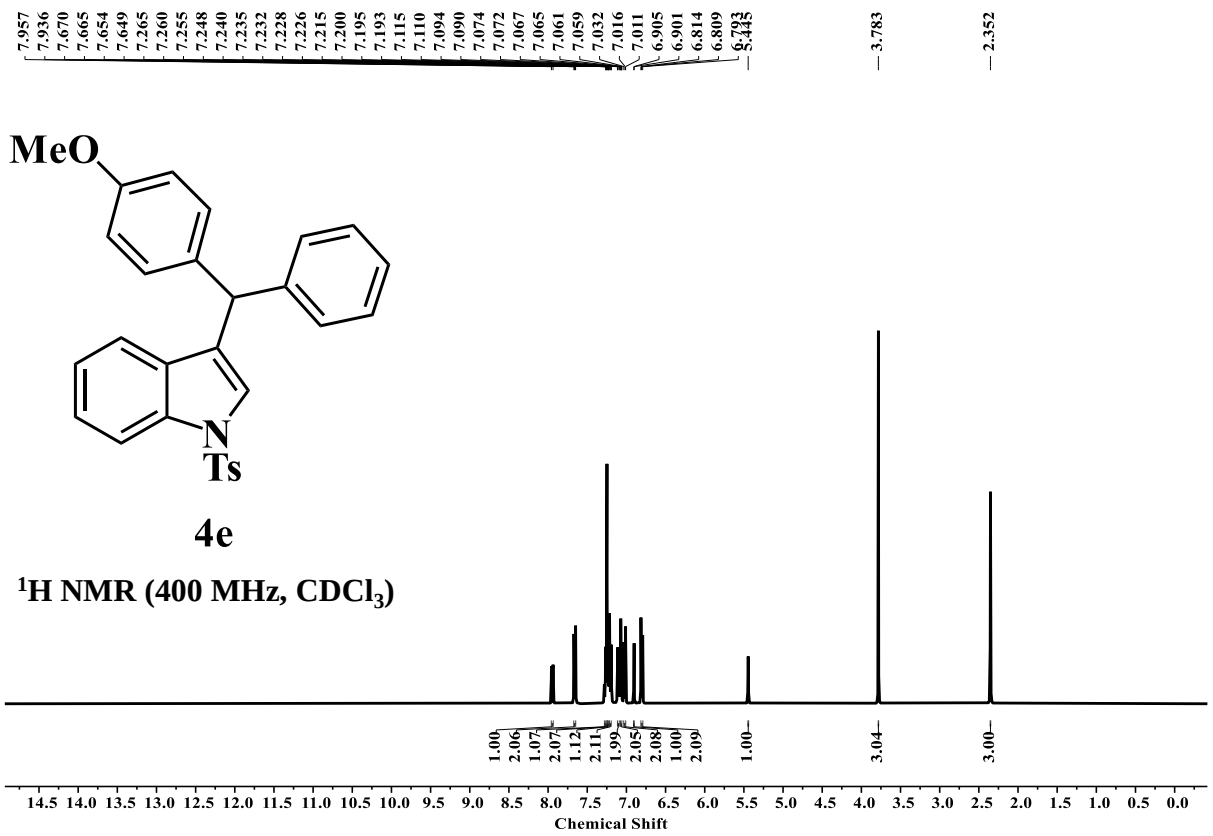
4d

^{1}H NMR (300 MHz, $CDCl_3$)



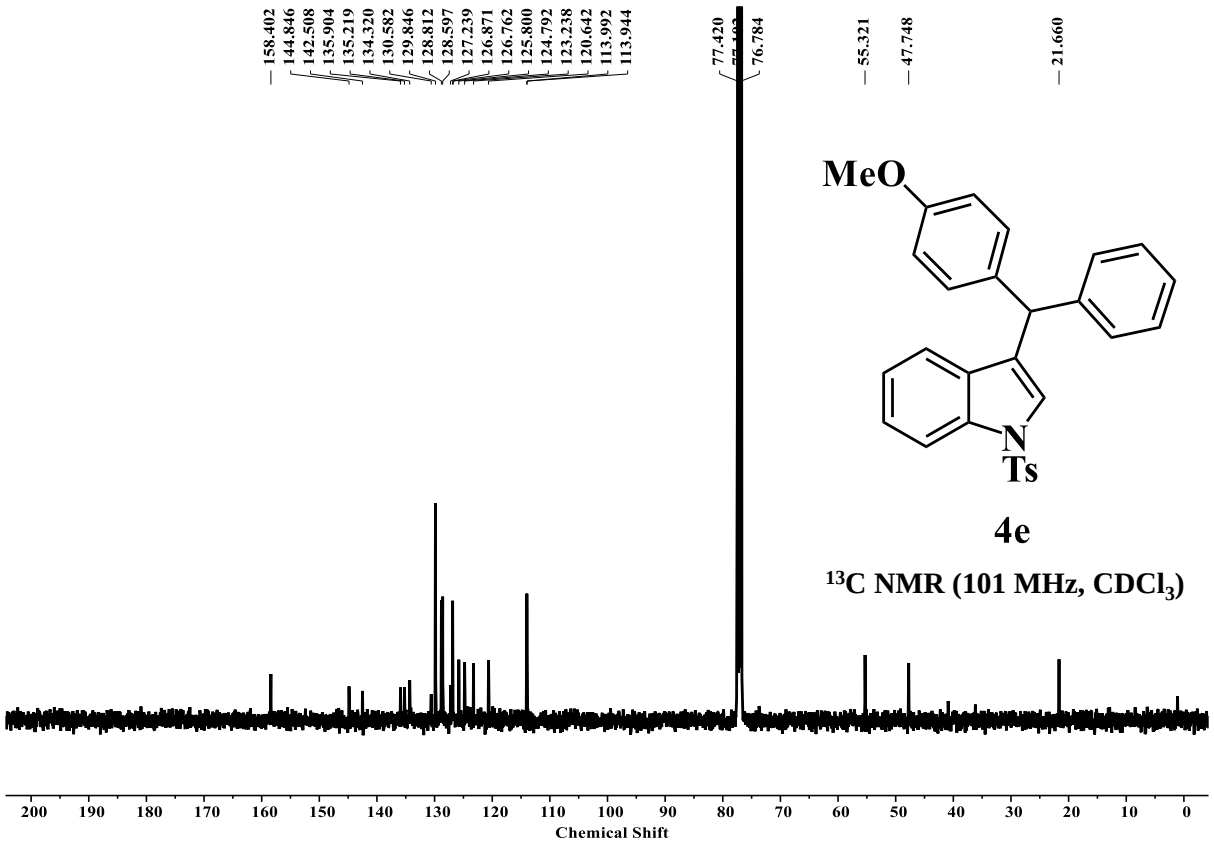
4d

^{13}C NMR (101 MHz, $CDCl_3$)



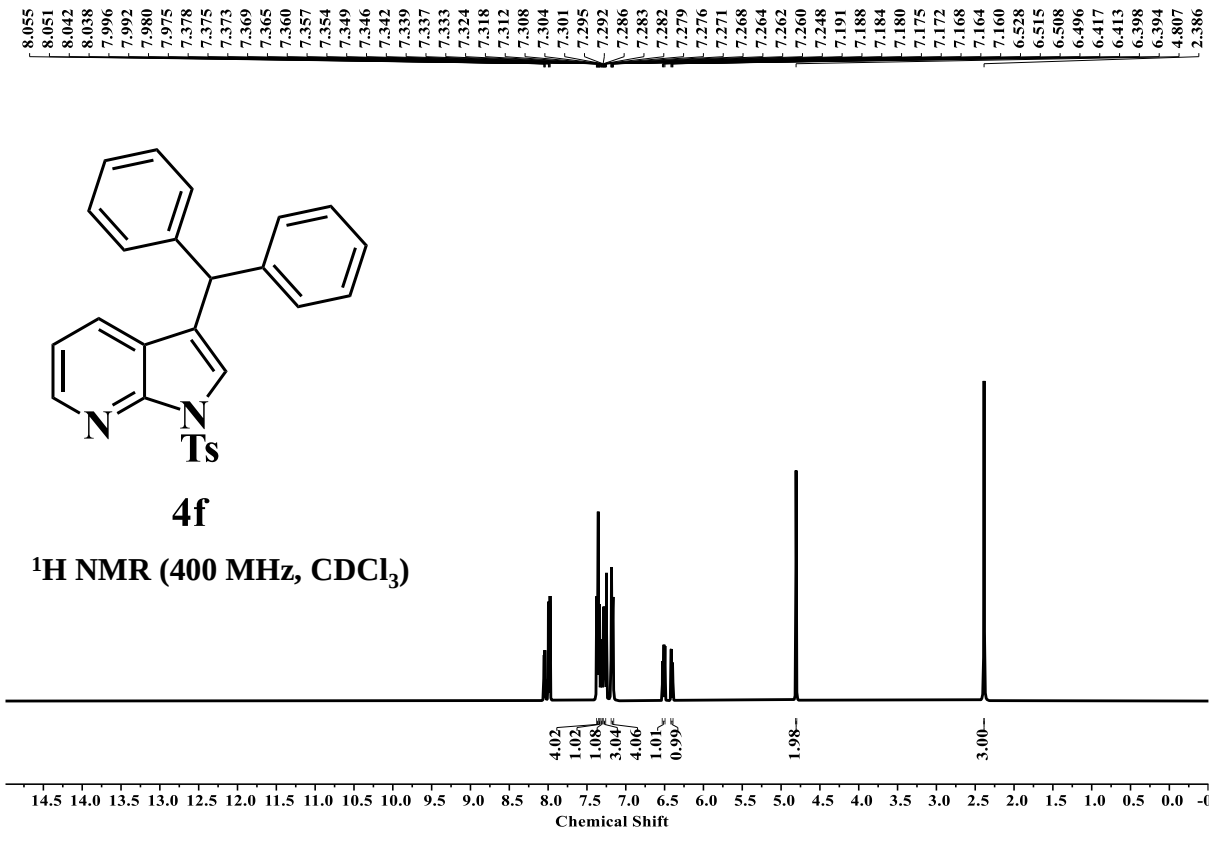
4e

^{1}H NMR (400 MHz, $CDCl_3$)



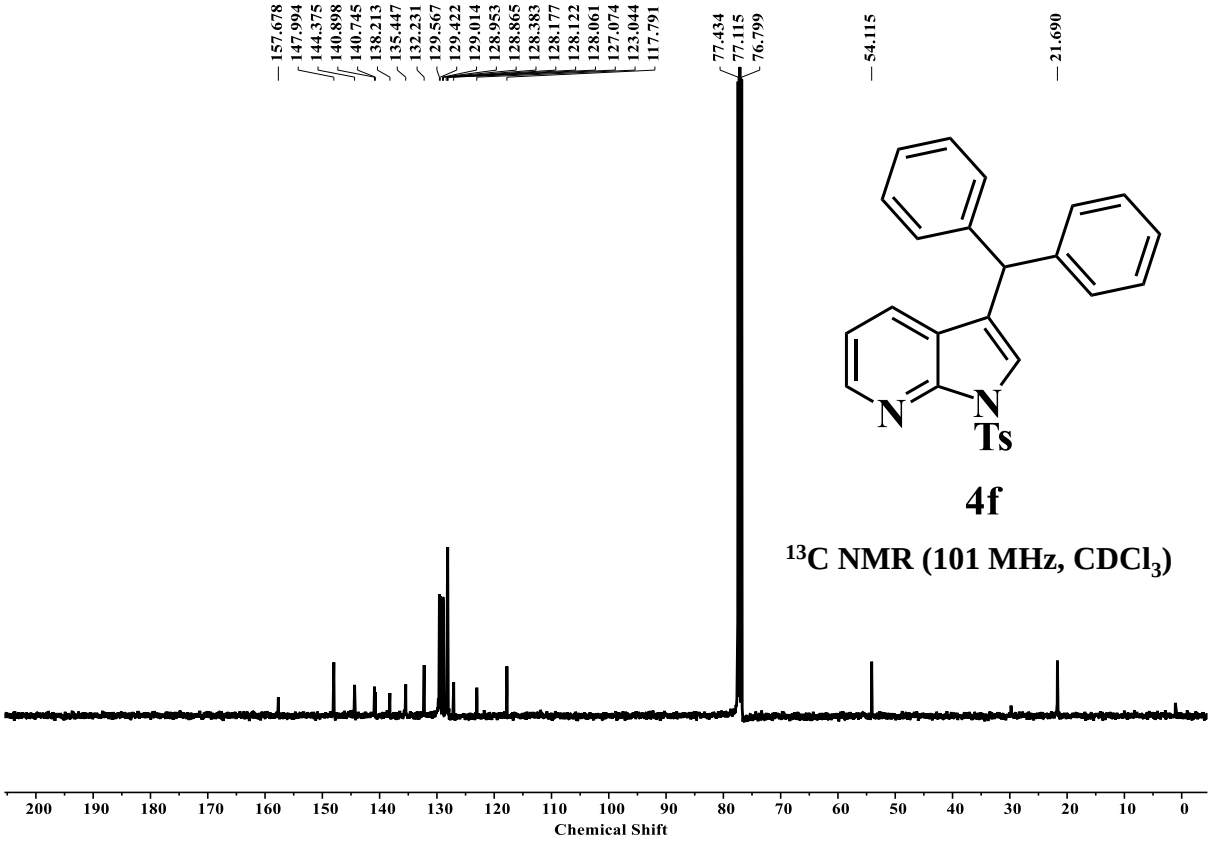
4e

^{13}C NMR (101 MHz, $CDCl_3$)



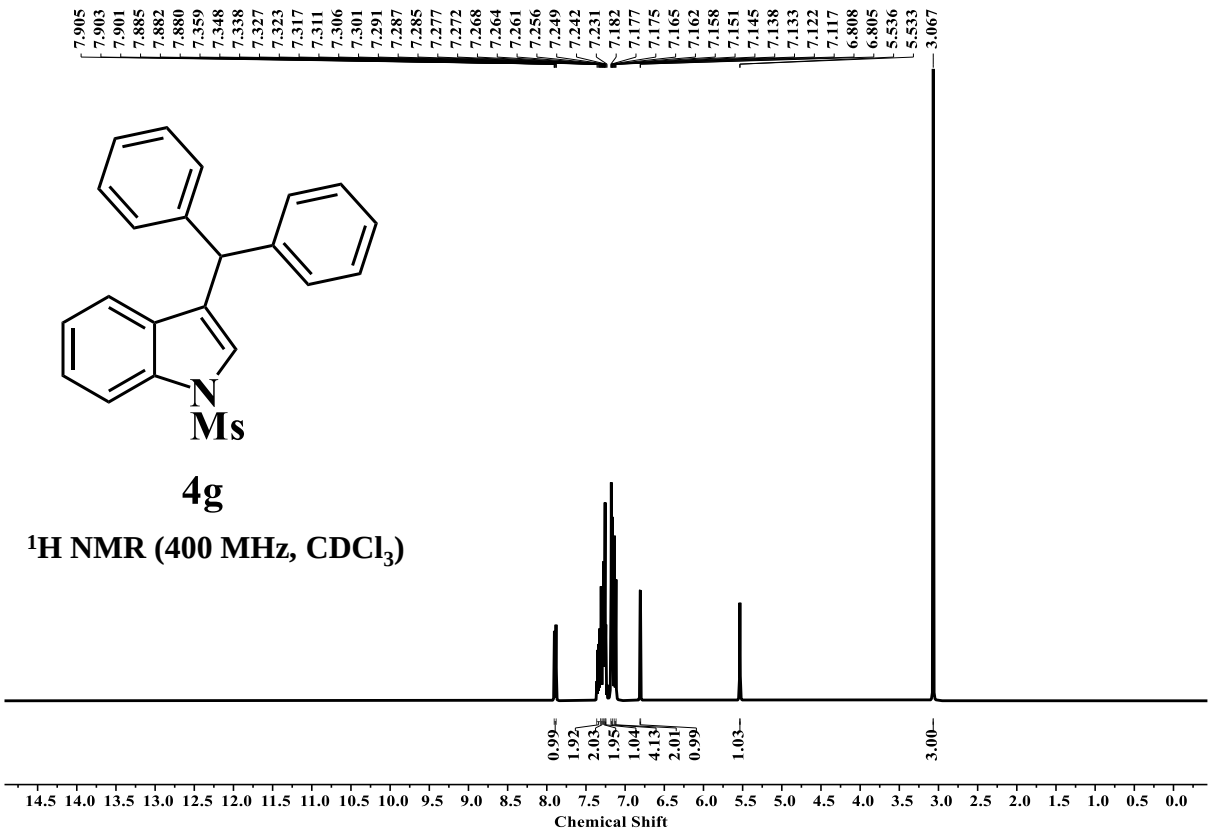
4f

^{1}H NMR (400 MHz, $CDCl_3$)



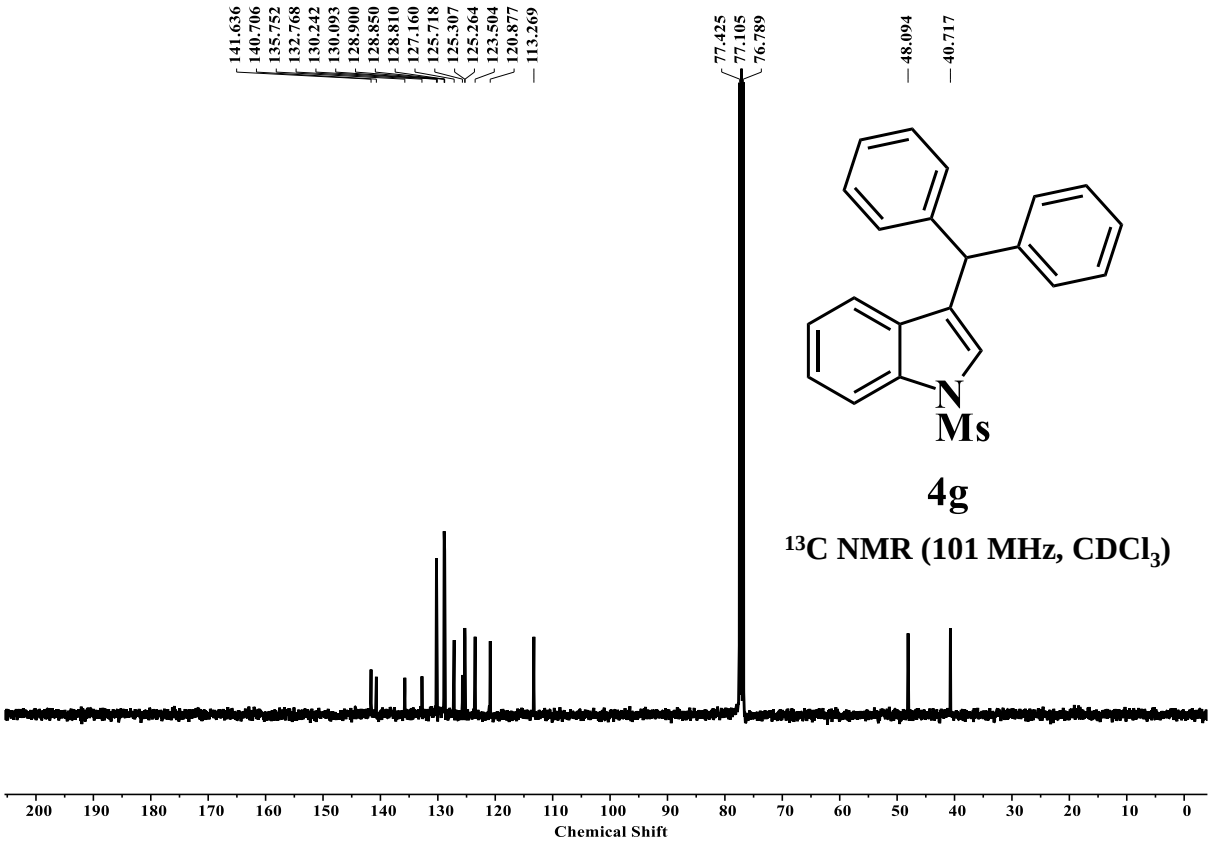
4f

^{13}C NMR (101 MHz, $CDCl_3$)



4g

^{1}H NMR (400 MHz, $CDCl_3$)



VI. Supplementary References:

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   b) R. Chanda, B. Chakraborty, G. Rana and U. Jana, *Eur. J. Org. Chem.*, **2020**, *1*, 61–65.

   c) Kar, A.; Chakraborty, B.; Kundal, S.; Rana, G.; Jana, U., *Org. Biomol. Chem.*, **2021**, *19*, 906.

   d) G. Rana, A. Kar, S. Kundal, D. Musib and U. Jana, *J. Org. Chem.*, **2023**, *88*, 838–851.

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