Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Data

Ring expansion/ opening reactions of epoxy ene-amides: Access to azabicyclononene, tetrahydropyridine and tetrazole scaffolds

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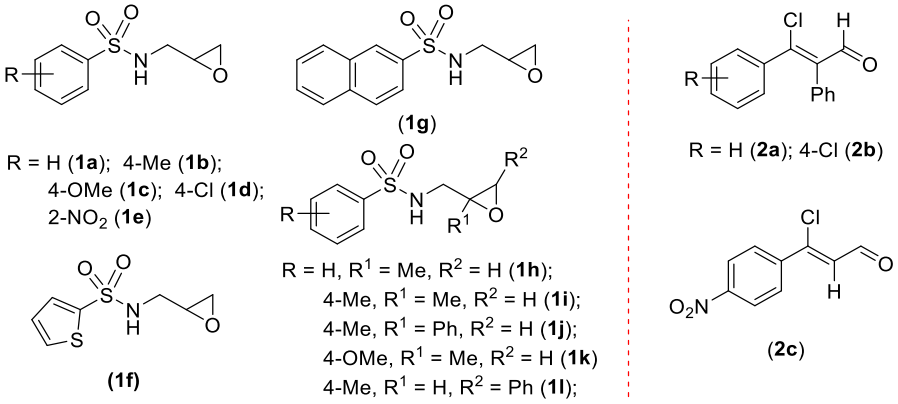
1. General Methods:

All chemicals were procured from Aldrich or local manufacturers and used Further without any purification unless noted. Chemicals were purified when required according to standard procedures.[1] All reactions, unless stated otherwise, were performed in a dry nitrogen atmosphere. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded using 5 mm tubes [field strengths: 400 and 100 MHz for ^{1}H/ ^{13}C using 400 MHz NMR spectrometer; 500 and 125 MHz for ^{1}H, $^{13}C\{^{1}H\}$ using 500 MHz NMR spectrometer] in $CDCl_3$ solution (unless specified otherwise) with shifts referenced to $SiMe_4$ [= 0 for ^{1}H, $^{13}C\{^{1}H\}$]. All *J* values are in Hz. Infrared spectra were recorded neat or by using KBr pellets on an FT/IR spectrometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. For TLC, glass micro slides were

coated with silica-gel-GF254 (mesh size 75) and spots were identified using iodine or UV chamber as appropriate. For column chromatography, silica gel of 100-200 mesh size was used. Mass spectra were recorded using HRMS (ESI-TOF analyzer) equipment. X-ray data for **4aa**, **4db**, **5ba**, **5cb**, **6hc** and **7la** were collected at 298 K on a Bruker AXS-SMART or OXFORD diffractometer using Mo-K_α (= 0.71073 Å) radiation. Structures were solved and refined using standard methods.[2] CCDC nos. are 2237334-2237338 and 2253326.

2. Synthesis of epoxy benzene sulfonamides (1a-1l) and chloro-acrylaldehydes (2a-2c)

The epoxy benzene sulfonamides **1a-1l** and **chloro-acrylaldehydes 2a-2c** used in the present study were prepared by using known literature procedures.[3-6]

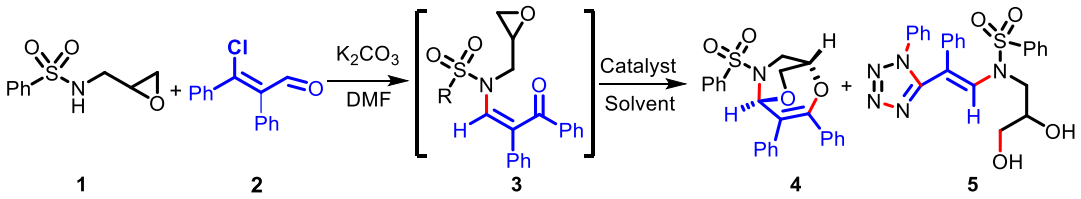


3. Optimization of reaction conditions for the synthesis of 4 and 5

The initial reaction was performed between *N*-oxiranylmethyl benzenesulfonamide **1a** and 3-chloro-2,3-diphenylacrylaldehyde **2a** in the presence of K_2CO_3 in DMF solvent at 80 ^oC. We were able to isolate intermediate **3aa**.[7] The intermediate **3aa** was initially treated with $BF_3{\cdot}OEt_2$ (50 mol%) in $CHCl_3$ at room temperature (25 ^oC) for 5 h and gave the unexpected product dioxa-9-azabicyclonon-3-ene **4aa** [cf. Figure S1 for **4aa**, X-ray] in 78% yield (Table S1, entry 1). Based on this result, we screened Lewis acid catalyst, solvent, additive, reaction temperature, reaction time, and quantity of additive (Table S1). First, the effectiveness of various Lewis acid

catalysts such as $BF_3{\cdot}OEt_2$, $Zn(OTf)_2$, NaOTf, AgOTf, $Cu(OTf)_2$, $SnCl_2$, and $TiCl_4$ was screened (entries 2-7) and $BF_3{\cdot}OEt_2$ was proven to be the best. Even 3 h reaction time was sufficient (entry 8). Next, we checked the effectiveness of solvents such as DCM, DCE, CH_3CN, THF, PEG-400, DMF and DMSO (entries 9-15). The reduction of mol% of catalyst loading (20 mol%) did not affect the yield of the product **4aa** appreciably (entry 16). When we added $TMSN_3$ as an additive, the tetrazole derivative **5aa** was obtained as the sole product (85% yield, entry 17). We investigated the effectiveness of other Lewis acids such as $SnCl_2$ and $Cu(OTf)_2$ (entry 18 and 19) but these were not as good as $BF_3{\cdot}OEt_2$. Changing the solvent to DCM marginally lowered the yield to 80% (entry 20). Absence of the Lewis acid catalyst did not lead to either **4aa** or **5aa** (entry 21).

Table S1. Optimization of reaction conditions[a]



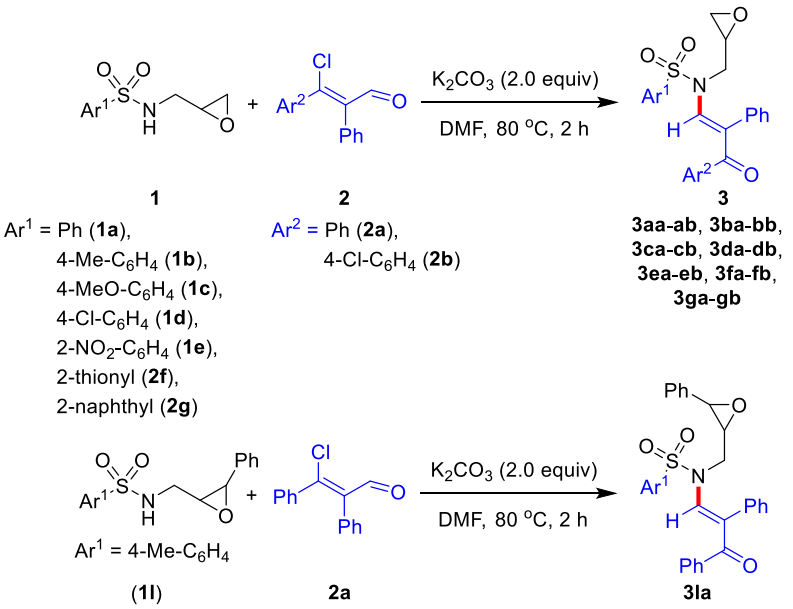
Entry	Catalyst	Additive	Solvent	Temp (°C)	Time (h)	Yield of 4**aa** (%)[b]	Yield of 5**aa** (%)
1	$BF_3{\cdot}OEt_2$	--	$CHCl_3$	25	5	78	--
2	$Zn(OTf)_2$	--	$CHCl_3$	25	5	--	--
3	Na(OTf)	--	$CHCl_3$	25	5	--	--
4	Ag(OTf)	--	$CHCl_3$	25	5	--	--
5	$Cu(OTf)_2$	--	$CHCl_3$	25	5	40	--
6	$SnCl_2$	--	$CHCl_3$	25	5	55	--
7	$TiCl_4$	--	$CHCl_3$	25	5	--	--

8	$BF_3{\cdot}OEt_2$	--	$CHCl_3$	25	3	78	
9	$BF_3{\cdot}OEt_2$	--	DCM	25	3	72	--
10	$BF_3{\cdot}OEt_2$	--	DCE	25	3	20	--
11	$BF_3{\cdot}OEt_2$	--	CH_3CN	25	3	30	--
12	$BF_3{\cdot}OEt_2$	--	THF	25	3	--	--
13	$BF_3{\cdot}OEt_2$	--	PEG-400	25	3	--	--
14	$BF_3{\cdot}OEt_2$	--	DMF	25	3	--	--
15	$BF_3{\cdot}OEt_2$	--	DMSO	25	3	--	--
16	**$BF_3{\cdot}OEt_2$**	**--**	**$CHCl_3$**	**25**	**3**	**78**	**--**
17	**$BF_3{\cdot}OEt_2$**	**$TMSN_3$**	**$CHCl_3$**	**25**	**3**	**--**	**85**
18	$SnCl_2$	$TMSN_3$	$CHCl_3$	25	3	--	65
19	$Cu(OTf)_2$	$TMSN_3$	$CHCl_3$	25	3	--	60
20	$BF_3{\cdot}OEt_2$	$TMSN_3$	DCM	25	3	--	80
21		$TMSN_3$	$CHCl_3$	25	3	--	--

[a]Reaction conditions: **3aa** (83.9 mg, 0.20 mmol), with catalyst (50 mol % for entries 1-15 and 20 mol% for entries 16-21), and additive (Me_3SiN_3, 52.6 µL, 2.0 equiv) in dry $CHCl_3$ (3.0 mL) at 25 ^oC (rt). Yields given are after isolation.

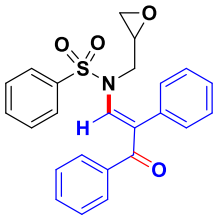
4 (a). General procedure for the synthesis of compounds 3aa-gb and **3la:**

Substrate **3ca** was prepared by following the procedure described in our previous work.[7] The compounds **3aa-ab**, **3ba-bb**, **3cb**, **3da-db**, **3ea-eb**, **3fa-fb, 3ga-gb** and **3lb** are new.



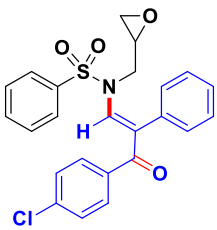
To a mixture of 3-chloro-2,3-diphenylacrylaldehyde **2a** (48.5 mg, 0.20 mmol 1.0 equiv), K_2CO_3 (55.2 mg, 0.40 mmol, 2.0 equiv) in dry DMF (5 mL), *N*-(oxiran-2-ylmethyl)benzenesulfonamide **1a** (64.0 mg, 0.30 mmol, 1.5 equiv), was added. The resulting reaction mixture was heated for 2 h on an oil bath maintained at 80 ^oC. After the completion of the reaction as monitored by TLC, ethyl acetate (30 mL) was added and the solution was washed with water (3 × 30 mL), then with brine solution (3 × 15 mL); the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic portion was dried over anhydrous Na_2SO_4 then the solvent was evaporated under the reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate 9: 1) to obtain compound **3aa**.as a mixture of *E* and *Z* isomers (1:25 ratio). Crystallization was done from an ethyl acetate-hexane mixture (1:20). Other compounds were prepared similarly.

(E)-N-(oxiran-2-ylmethyl)-N-(3-oxo-2,3-diphenylprop-1-en-1-yl)benzenesulfonamide **(3aa).** Following the general procedure, the reaction of **1a** (64.0 mg, 0.30 mmol) with **2a** (48.5 mg, 0.20 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), after column chromatography (EtOAc:hexane = 1:9) afforded **3aa** as a white solid. Yield 69 mg (82%). Mp 103-104 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 7.85-7.82 (m, 2H), 7.74-7.70 (m, 3H), 7.63-7.59 (m, 2H), 7.57-7.53 (m, 2H), 7.46-7.43 (m, 2H), 7.32-7.29 (m, 3H), 7.05-7.02 (m, 2H), 3.36-3.28 (m, 2H), 2.81-2.78 (m, 1H), 2.59-2.58 (m, 1H), 2.23-2.22 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.8, 138.6. 138.5, 138.2, 134.1, 133.8, 132.0, 130.0, 129.6_0, 129.5_6, 128.6, 128.5, 128.3, 128.0, 127.0, 49.7, 48.5, 45.8 ppm; IR (Neat): 2921, 1633, 1588, 1445, 1356, 1283, 1162 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{22}NO_4S$ $[M+H]^+$: *m/z* 420.1264. Found: 420.1265.



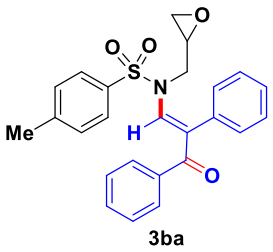
3aa

(E)-N-(3-(4-chlorophenyl)-3-oxo-2-phenylprop-1-en-1-yl)-N-(oxiran-2-ylmethyl)benzenesulfonamide **(3ab).** Following the general procedure, the reaction of **1a** (64.0 mg, 0.30 mmol) with **2b** (55.4 mg, 0.20 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), after column chromatography (EtOAc:hexane = 1:9) afforded **3ab** as a white solid. Yield 78 mg (86%). Mp 105-106 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 7.83-7.82 (m, 2H), 7.72-7.69 (m, 1H), 7.63-7.59 (m, 4H), 7.52 (s, 1H), 7.39-7.37 (m, 2H), 7.31-7.27 (m, 3H), 7.00-6.98 (m, 2H), 3.36-3.24 (m, 2H), 2.78-2.75 (m, 1H), 2.56 (dd → t, *J* = 4.5 Hz, 1H), 2.20-2.18 (dd, *J* = 4.5, 2.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.4, 138.5. 138.4, 138.2, 136.9, 133.9, 131.1, 130.0, 129.6, 128.7, 128.6, 127.6, 127.4, 49.8, 48.5, 45.7 ppm; IR (Neat): 3076, 1638, 1588, 1445, 1356, 1274, 1163 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{21}ClNO_4S$ $[M+H]^+$: *m/z* 454.0874. Found: 454.0877.



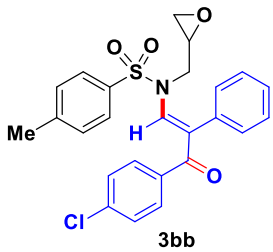
3ab

***(E)-4-methyl-N-(oxiran-2-ylmethyl)-N-(3-oxo-2,3-diphenylprop-1-en-1-yl)benzenesulfonamide* (3ba).** Following the general procedure, the reaction of **1b** (68.2 mg, 0.30 mmol) with **2a** (48.5 mg, 0.20 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), after column chromatography (EtOAc:hexane = 1:9) afforded **3ba** as a white solid. Yield 81 mg (87%). Mp 88-89 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 7.71-7.69 (m, 4H), 7.56-7.53 (m, 2H), 7.46-7.43 (m, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.33-7.31 (m, 3H), 7.08-7.07 (m, 2H), 3.33-3.32 (m, 2H), 2.79-2.76 (m, 1H), 2.58 (dd→t, *J* = 4.0 Hz, 1H), 2.50 (s, 3H), 2.22-2.21 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.9, 145.0. 139.0, 138.7, 135.2, 134.2, 132.0, 130.2, 129.6, 128.6, 128.5, 128.3, 127.5, 127.3, 49.7, 48.4, 45.9, 21.7 ppm; IR (Neat): 2992, 1641, 1592, 1414, 1348, 1274, 1168 cm^{-1}; HRMS (ESI): Calcd. for $C_{25}H_{24}NO_4S$ $[M+H]^+$: *m/z* 434.1421. Found: 434.1425.



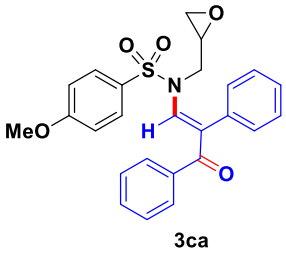
3ba

***(E)-N-(3-(4-chlorophenyl)-3-oxo-2-phenylprop-1-en-1-yl)-4-methyl-N-(oxiran-2-ylmethyl)benzenesulfonamide* (3bb).** Following the general procedure, the reaction of **1b** (68.2 mg, 0.30 mmol) with **2b** (55.4 mg, 0.20 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), after column chromatography (EtOAc:hexane = 1:9) afforded **3bb** as a white solid. Yield 78 mg (86%). Mp 119-120 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 7.73-7.71 (m, 2H), 7.65-7.62 (m, 2H), 7.55 (s, 1H), 7.41-7.39 (m, 4H), 7.34-7.31 (m, 3H), 7.07-7.05 (m, 2H), 3.38-3.29 (m, 2H), 2.79-2.76 (m, 1H), 2.58-2.56 (m, 1H), 2.51 (s, 3H), 2.21-2.20 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.5, 145.1. 138.9, 138.2, 137.0, 135.2, 134.0, 131.0, 130.2, 130.1, 128.7, 128.6, 127.4, 127.0, 49.7, 48.3, 45.8, 21.7 ppm; IR (Neat): 2922, 1650, 1553, 1491, 1360, 1243, 1164 cm^{-1}; HRMS (ESI): Calcd. for $C_{25}H_{23}ClNO_4S$ $[M+H]^+$: *m/z* 468.1031. Found: 468.1036.



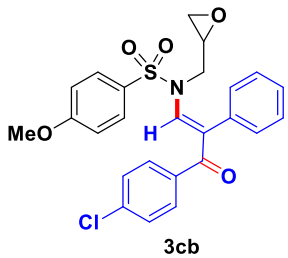
3bb

***(E)-4-methoxy-N-(oxiran-2-ylmethyl)-N-(3-oxo-2,3-diphenylprop-1-en-1-yl)benzenesulfonamide* (3ca).**[7] Following the general procedure, the reaction of **1c** (73.0 mg, 0.30 mmol) with **2a** (48.5 mg, 0.20 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), after column chromatography (EtOAc:hexane = 1:9) afforded **3ca** as a white solid. Yield 69 mg (77%). Mp 129-130 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 9.0 Hz, 2H), 7.70-7.68 (m, 2H), 7.57-7.53 (m, 2H), 7.45-7.42 (m, 2H), 7.33-7.32 (m, 3H), 7.11-7.09 (m, 2H), 7.04 (d, *J* = 9.0 Hz, 2H), 3.93 (s, 3H), 3.34-3.33 (m, 2H), 2.79-2.76 (m, 1H), 2.58 (dd → t, *J* = 4.5 Hz, 1H), 2.22-2.20 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 195.9, 163.9, 139.3. 138.7, 134.3, 131.9, 130.2, 129.7, 129.6, 128.6, 128.4, 128.3, 126.9, 114.7, 55.8, 49.7, 48.3, 45.9 ppm; IR (Neat): 2916, 1636, 1591, 1494, 1348, 1260, 1150 cm^{-1}; HRMS (ESI): Calcd. for $C_{25}H_{24}NO_5S$ $[M+H]^+$: *m/z* 450.1370. Found: 450.1367.



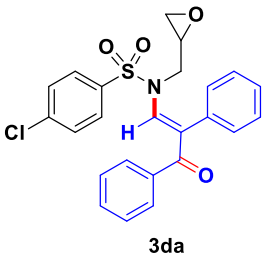
3ca

***(E)-N-(3-(4-chlorophenyl)-3-oxo-2-phenylprop-1-en-1-yl)-4-methoxy-N-(oxiran-2-ylmethyl)benzenesulfonamide* (3cb).** Following the general procedure, the reaction of **1c** (73.0 mg, 0.30 mmol) with **2b** (55.4 mg, 0.20 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), after column chromatography (EtOAc:hexane = 1:9) afforded **3cb** as a white solid. Yield 82 mg (88%). Mp 87-88 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 7.78-7.75 (m, 2H), 7.64-7.61 (m, 2H), 7.56 (s, 1H), 7.40-7.38 (m, 2H), 7.33-7.32 (m, 3H), 7.09-7.04 (m, 4H), 3.94 (s, 3H), 3.39-3.28 (m, 2H), 2.78-2.75 (m, 1H), 2.57 (dd → t, *J* = 5.0 Hz, 1H), 2.20-2.19 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 194.6, 163.9, 139.3. 138.2, 137.1, 134.1, 131.0, 130.2, 129.7, 129.4, 128.7, 128.6, 126.4, 114.7, 55.9, 49.7, 48.2, 45.8 ppm; IR (Neat): 2925, 1650, 1593, 1552, 1495, 1358, 1244, 1163 cm^{-1}; HRMS (ESI): Calcd. for $C_{25}H_{23}ClNO_5S$ $[M+H]^+$: *m/z* 484.0980. Found: 484.0977.



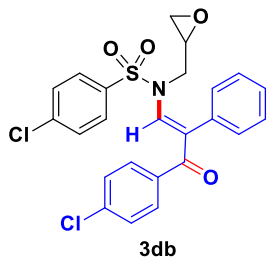
3cb

***(E)-4-chloro-N-(oxiran-2-ylmethyl)-N-(3-oxo-2,3-diphenylprop-1-en-1-yl)benzenesulfonamide* (3da).** Following the general procedure, the reaction of **1d** (74.3 mg, 0.30 mmol) with **2a** (48.5 mg, 0.20 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), after column chromatography (EtOAc:hexane = 1:9) afforded **3da** as a white solid. Yield 68 mg (75%). Mp 102-103 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 7.76-7.73 (m, 2H), 7.69-7.67 (m, 2H), 7.56-7.52 (m, 3H), 7.44-7.41 (m, 3H), 7.32-7.30 (m, 3H), 7.09-7.05 (m, 2H), 3.39-3.25 (m, 2H), 2.78-2.75 (m, 1H), 2.58 (dd → t, *J* = 4.5 Hz, 1H), 2.22-2.21 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 195.6, 140.6, 138.4. 137.8, 136.6, 134.0, 132.1, 130.0, 129.8, 129.6, 128.9, 128.7, 128.6, 128.5, 128.3 49.6, 48.7, 45.7 ppm; IR (Neat): 3062, 1652, 1559, 1443, 1364, 1252, 1165 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{21}ClNO_4S$ $[M+H]^+$: *m/z* 454.0874. Found: 454.0873.



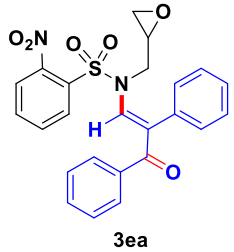
3da

***(E)-4-chloro-N-(3-(4-chlorophenyl)-3-oxo-2-phenylprop-1-en-1-yl)-N-(oxiran-2-ylmethyl)benzenesulfonamide* (3db).** Following the general procedure, the reaction of **1d** (74.3 mg, 0.30 mmol) with **2b** (55.4 mg, 0.20 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), after column chromatography (EtOAc:hexane = 1:9) afforded **3db** as a white solid. Yield 83 mg (85%). Mp 130-131 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 7.80-7.78 (m, 2H), 7.66-7.63 (m, 2H), 7.60-7.57 (m, 2H), 7.47 (s, 1H), 7.42-7.39 (m, 2H), 7.35-7.32 (m, 3H), 7.08-7.05 (m, 2H), 3.41 (dd, *J* = 15.0, 4.0 Hz, 1H), 3.28 (dd, *J* = 16.0, 6.0 Hz, 1H), 2.80-2.77 (m, 1H), 2.60-2.59 (m, 1H), 2.23 (dd, *J* = 4.5, 2.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 194.3, 140.7, 138.5. 137.9, 136.7, 136.6, 133.9, 131.1, 130.0, 129.9, 128.9, 128.8, 128.7, 128.1, 49.7, 48.7, 45.7 ppm; IR (Neat): 3073, 1650, 1554, 1479, 1365, 1244, 1167 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{20}Cl_2NO_4S$ $[M+H]^+$: *m/z* 488.0485. Found: 488.0486.



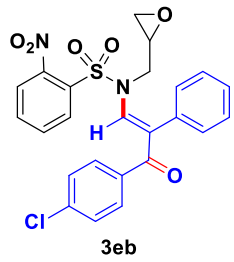
3db

(E)-2-nitro-N-(oxiran-2-ylmethyl)-N-(3-oxo-2,3-diphenylprop-1-en-1-yl)benzenesulfonamide **(3ea).** Following the general procedure, the reaction of **1e** (78.4 mg, 0.30 mmol) with **2a** (48.5 mg, 0.20 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), after column chromatography (EtOAc:hexane = 1:9) afforded **3ea** as a semisolid. Yield 77 mg (83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.0 Hz, 1H), 7.84-7.78 (m, 2H), 7.77-7.73 (m, 3H), 7.55-7.52 (m, 1H), 7.48 (s, 1H), 7.44-7.41 (m, 2H), 7.32-7.31 (m, 3H), 7.14-7.12 (m, 2H), 3.56 (dd, *J* = 16.0, 3.5 Hz, 1H), 3.34 (dd, *J* = 16.0, 5.5 Hz, 1H), 2.92-2.89 (m, 1H), 2.63 (dd→t, *J* = 4.0 Hz, 1H), 2.33-2.32 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 195.8, 147.8, 138.3. 137.1, 134.9, 133.9, 132.3, 132.2, 131.8, 131.6, 129.9, 129.7, 129.4, 128.7, 128.4, 124.9, 50.0, 48.9, 45.6 ppm; IR (Neat): 3020, 1648, 1539, 1442, 1363, 1275, 1166 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{21}N_2O_6S$ $[M+H]^+$: *m/z* 465.1115. Found: 465.1116.



3ea

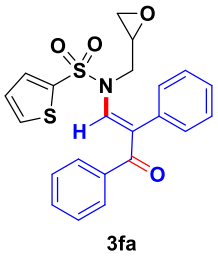
(E)-N-(3-(4-chlorophenyl)-3-oxo-2-phenylprop-1-en-1-yl)-2-nitro-N-(oxiran-2-ylmethyl)benzenesulfonamide **(3eb).** Following the general procedure, the reaction of **1e** (78.4 mg, 0.30 mmol) with **2b** (55.4 mg, 0.20 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), after column chromatography (EtOAc:hexane = 1:9) afforded **3eb** as a white solid. Yield 87 mg (87%). Mp 146-147 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08-8.06 (m, 1H), 7.85-7.79 (m, 2H), 7.78-7.76 (m, 1H), 7.73-7.70 (m, 2H), 7.50 (s, 1H), 7.41-7.38 (m, 2H), 7.33-7.30 (m, 3H), 7.14-7.10 (m, 2H), 3.56 (dd, *J* = 16.0, 3.5 Hz, 1H), 3.32 (dd, *J* = 16.0, 6.0 Hz, 1H), 2.90-2.87 (m, 1H), 2.62-2.60 (m, 1H), 2.31-2.29 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 194.4, 147.8, 138.6. 137.1, 136.6, 135.0, 133.8, 132.3, 131.9, 131.5, 131.2, 129.9, 128.8, 128.7_3, 128.6_7, 124.9, 49.9, 48.9, 45.5 ppm; IR (Neat):



3eb

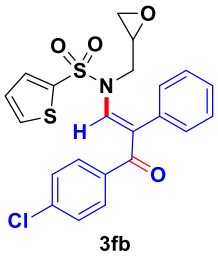
3020, 1652, 1539, 1355, 1264, 1164 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{20}ClN_2O_6S$ $[M+H]^+$: *m/z* 499.0725. Found: 499.0724.

(E)-N-(oxiran-2-ylmethyl)-N-(3-oxo-2,3-diphenylprop-1-en-1-yl)thiophene-2-sulfonamide **(3fa).** Following the general procedure, the reaction of **1f** (65.8 mg, 0.30 mmol) with **2a** (48.5 mg, 0.20 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), after column chromatography (EtOAc:hexane = 1:9) afforded **3fa** as a white solid. Yield 64 mg (75%). Mp 134-135 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 7.75-7.74 (m, 3H), 7.67-7.66 (m, 1H), 7.56-7.53 (m, 1H), 7.46-7.43 (m, 3H), 7.35-7.32 (m, 3H), 7.21-7.19 (m, 1H), 7.12-7.10 (m, 2H), 3.38-3.28 (m, 2H), 2.85-2.82 (m, 1H), 2.62 (dd → t, *J* = 4.5 Hz, 1H), 2.26-2.25 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 195.6, 138.2_9, 138.2_7. 137.6, 134.0, 133.5_4, 133.4_8, 132.2, 129.9, 129.7, 129.4, 128.7, 128.6, 128.3, 127.9, 49.6, 49.0, 45.9 ppm; IR (Neat): 3073, 1637, 1590, 1443, 1361, 1282, 1161 cm^{-1}; HRMS (ESI): Calcd. for $C_{22}H_{20}NO_4S_2$ $[M+H]^+$: *m/z* 426.0828. Found: 426.0825.



3fa

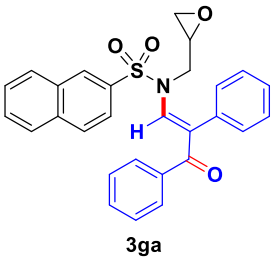
(E)-N-(3-(4-chlorophenyl)-3-oxo-2-phenylprop-1-en-1-yl)-N-(oxiran-2-ylmethyl)thiophene-2-sulfonamide **(3fb).** Following the general procedure, the reaction of **1f** (65.8 mg, 0.30 mmol) with **2b** (55.4 mg, 0.20 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), after column chromatography (EtOAc:hexane = 1:9) afforded **3fb** as a white solid. Yield 79 mg (86%). Mp 111-112 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 7.75-7.73 (m, 1H), 7.68-7.65 (m, 3H), 7.44 (s, 1H), 7.40-7.39 (m, 2H), 7.33-7.31 (m, 3H), 7.20-7.18 (m, 1H), 7.09-7.05 (m, 2H), 3.37-3.25 (m, 2H), 2.82-2.79 (m, 1H), 2.60-2.58 (m, 1H), 2.23-2.21 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 195.7, 138.3, 138.2. 137.7, 134.0, 133.6, 133.5, 132.2, 131.1, 129.9, 129.4, 128.7, 128.6, 128.3, 127.9, 49.7, 49.0, 45.9 ppm; IR (Neat):



3fb

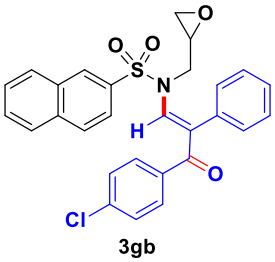
3093, 1638, 1590, 1362, 1283, 1161 cm^{-1}; HRMS (ESI): Calcd. for $C_{22}H_{19}ClNO_4S_2$ $[M+H]^+$: *m/z* 460.0439. Found: 460.0434.

***(E)-N-(oxiran-2-ylmethyl)-N-(3-oxo-2,3-diphenylprop-1-en-1-yl)naphthalene-2-sulfonamide* (3ga).** Following the general procedure, the reaction of **1g** (79.0 mg, 0.30 mmol) with **2a** (48.5 mg, 0.20 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), after column chromatography (EtOAc:hexane = 1:9) afforded **3ga** as a white solid. Yield 71 mg (76%). Mp 123-124 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 8.38-8.37 (m, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 7.98-7.96 (m, 2H), 7.77-7.64 (m, 5H), 7.60 (s, 1H), 7.52-7.49 (m, 1H), 7.39-7.135 (m, 2H),7.29-7.27 (m, 1H), 7.26-7.23 (m, 2H), 7.06-7.03 (m, 2H), 3.41-3.33 (m, 2H), 2.80-2.77 (m, 1H), 2.55 (dd → t, *J* = 4.5 Hz, 1H), 2.22-2.21 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 195.8, 138.9, 138.7. 135.2, 134.9, 134.1, 132.1, 132.0, 130.1, 130.0, 129.6, 129.5, 129.4, 128.6, 128.5, 128.3, 128.1, 127.5, 122.0, 49.8, 48.5, 45.9 ppm; IR (Neat): 2996, 1641, 1590, 1443, 1351, 1274, 1167 cm^{-1}; HRMS (ESI): Calcd. for $C_{28}H_{24}NO_4S$ $[M+H]^+$: *m/z* 470.1421. Found: 470.1419.



3ga

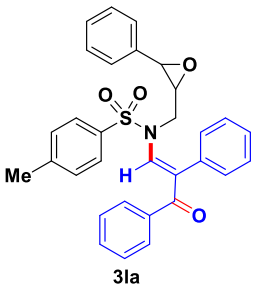
***(E)-N-(3-(4-chlorophenyl)-3-oxo-2-phenylprop-1-en-1-yl)-N-(oxiran-2-ylmethyl)naphthalene-2-sulfonamide* (3gb)** Following the general procedure, the reaction of **1g** (79.0 mg, 0.30 mmol) with **2b** (55.4 mg, 0.20 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), after column chromatography (EtOAc:hexane = 1:9) afforded **3gb** as a white solid. Yield 87 mg (86%). Mp 145-146 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 8.39-8.38 (m, 1H), 8.05 (d, *J* = 9.0 Hz, 1H), 7.98 (d, *J* = 9.0 Hz, 2H), 7.78-7.76 (m, 1H), 7.75-7.72 (m, 1H), 7.71-7.68 (m, 1H), 7.58-7.56 (m, 3H), 7.32-7.29 (m, 2H), 7.28-7.23 (m, 3H), 7.04-7.01 (m, 2H), 3.44-3.32 (m, 2H), 2.80-2.76 (m, 1H), 2.55 (dd → t, *J* = 4.5 Hz, 1H), 2.21-2.20 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 194.5, 139.0, 138.2. 137.0,



3gb

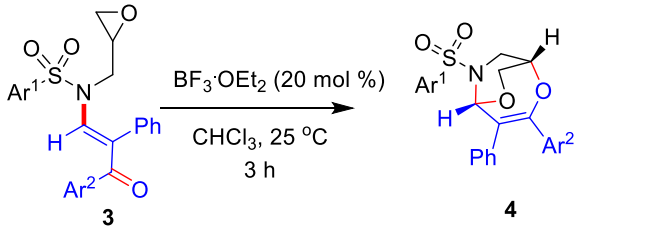
135.2, 134.8, 134.0, 132.1, 131.0, 130.1, 129.7, 129.5, 128.7, 128.6, 128.2, 128.1, 127.0, 121.9, 49.7, 48.4, 45.8 ppm; IR (Neat): 3062, 1641, 1586, 1354, 1270, 1168 cm^{-1}; HRMS (ESI): Calcd. for $C_{28}H_{23}ClNO_4S$ $[M+H]^+$: *m/z* 504.1031. Found: 504.1037.

(E)-4-methyl-N-(3-oxo-2,3-diphenylprop-1-en-1-yl)-N-((3-phenyloxiran-2-yl)methyl)benzenesulfonamide **(3la)** Following the general procedure, the reaction of **1l** (91.0 mg, 0.30 mmol) with **2a** (48.5 mg, 0.20 mmol) using K_2CO_3 (55.2 mg, 0.40 mmol) after column chromatography (EtOAc:hexane = 1:9) afforded **3la** as a semi solid. Yield 83 mg (81%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72-7.68 (m, 4H), 7.58 (s, 1H), 7.55-7.52 (m, 1H), 7.44-7.41 (m, 2H), 7.37-7.34 (m, 5H), 7.31-7.29 (m, 2H), 7.28-7.26 (m, 1H), 7.15-7.013 (m, 2H), 7.06 (d, *J* = 6.5 Hz, 2H), 3.50-3.39 (m, 3H), 2.81-2.80 (m, 1H), 2.49 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 195.9, 145.1, 138.9. 138.7, 136.1, 135.2, 134.2, 132.0, 130.2, 129.6, 128.7, 128.5, 128.3, 127.4, 125.7, 59.7, 57.7, 48.0, 21.7 ppm; IR (Neat): 2927, 1733, 1649, 1594, 1444, 1356, 1241, 1163 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{28}NO_4S$ $[M+H]^+$: *m/z* 510.1734. Found: 510.1735.



3la

4 (b). General procedure for the synthesis of compounds 4aa-4gb:



3
3aa-ab, 3ba-bb, 3ca-cb, 3da-db, 3ea-eb, 3fa-fb, 3ga-gb

4
4aa-ab, 4ba-bb, 4ca-cb, 4da-db, 4ea-eb, 4fa-fb, 4ga-gb

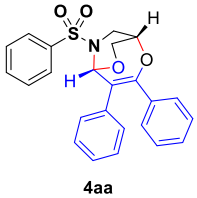
(i) Procedure: To a solution of *N*-(oxiran-2-ylmethyl)-*N*-(3-oxo-2,3-diphenylprop-1-en-1-yl)benzenesulfonamide **3aa** (83.9 mg, 0.2 mmol 1.0 equiv) in dry $CHCl_3$ (2 mL), $BF_3{\cdot}OEt_2$ (5.0

µL, 0.04 mmol, 0.2 equiv) was added. The resulting reaction mixture was stirred for 3 h at rt (25 ^{o}C). After the completion of the reaction as monitored by TLC, DCM (10 mL) was added and the solution was washed with water (3 × 10 mL), then brine solution (3 × 10 mL); the aqueous layer was extracted with DCM (3 × 10 mL). The combined organic portion was dried over anhydrous Na_2SO_4, the solvent was evaporated under the reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate 9: 1) to obtain compound **4aa** as a white solid. Crystallization was done from an ethyl acetate-hexane mixture (1:20). Other compounds were prepared similarly.

(ii) Alternative procedure:

We could also achieve the formation of **4** by starting with 3-chloro-2,3-diphenylacrylaldehyde (0.20 mmol 1.0 equiv), K_2CO_3 (0.40 mmol, 2.0 equiv) in dry DMF (5 mL) and epoxy benzene sulfonamide (0.30 mmol 1.5 equiv). The resulting mixture was heated for 2 h on an oil bath maintained at 80 ^{o}C. After the completion of the reaction as monitored by TLC, the solvent was removed and $BF_3{\cdot}OEt_2$ (20 mol%) in $CHCl_3$ (2 mL) was added at 25 ^{o}C. The mixture was stirred for 3 h, without isolating the intermediate compound **3**. Removal of DMF was necessary for this method.

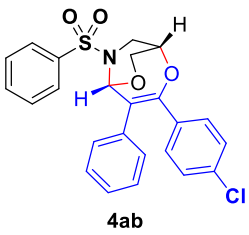
3,4-diphenyl-9-(phenylsulfonyl)-2,6-dioxa-9-azabicyclo[3.2.2]non-3-ene **(4aa).** Following the general procedure, the reaction of **3aa** (83.9 mg, 0.2 mmol) with $BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol) after column chromatography (EtOAc:hexane = 1:9) afforded **4aa** as a white solid. Yield 62 mg (74%). Mp 182-183 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.5 Hz, 2H), 7.62-7.59 (m, 1H), 7.53-7.50 (m, 2H), 7.21-7.15 (m, 10H), 6.05 (s, 1H), 4.59-4.56 (m, 2H), 4.28 (dt, *J* = 12.0, 2.5 Hz, 1H), 3.79 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.62 (dd, *J* = 12.0, 3.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 153.1, 138.9, 138.2, 135.4,



4aa

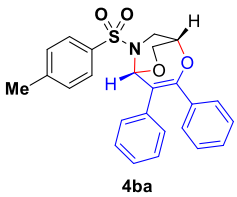
133.0, 130.1, 129.6, 129.1, 128.6, 128.5, 127.7, 127.7_4, 126.6_8, 114.5, 85.6, 72.4, 67.7, 48.6 ppm; IR (Neat): 2919, 2970, 1635, 1446, 1349, 1262, 1161 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{22}NO_4S$ $[M+H]^+$: *m/z* 420.1264. Found: 420.1261.

3-(4-chlorophenyl)-4-phenyl-9-(phenylsulfonyl)-2,6-dioxa-9-azabicyclo[3.2.2]non-3-ene **(4ab).** Following the general procedure, the reaction of **3ab** (90.8 mg, 0.2 mmol) with $BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol) after column chromatography (EtOAc:hexane = 1:9) afforded **4ab** as a white solid. Yield 69 mg (76%). Mp 134-135 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90-7.89 (m, 2H), 7.62-7.59 (m, 1H), 7.53-7.50 (m, 2H), 7.25-7.18 (m, 3H), 7.16-7.08 (m, 6H), 6.03 (s, 1H), 4.59-4.53 (m, 2H), 4.27 (dt, *J* = 12.0, 2.5 Hz, 1H), 3.79 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.61 (dd, *J* = 12.0, 3.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 151.9, 138.6, 138.1, 134.4, 133.8, 133.1, 130.9, 130.0, 128.7, 128.0, 127.7, 127.0, 115.0, 85.6, 72.6, 67.6, 48.5 ppm; IR (Neat): 2866, 1633, 1487, 1445, 1353, 1163 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{21}ClNO_4S$ $[M+H]^+$: *m/z* 454.0874. Found: 454.0878.



4ab

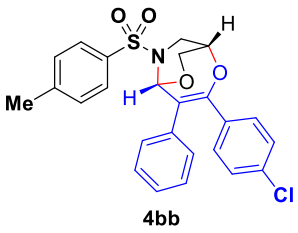
3,4-diphenyl-9-tosyl-2,6-dioxa-9-azabicyclo[3.2.2]non-3-ene **(4ba).** Following the general procedure, the reaction of **3ba** (86.7 mg, 0.2 mmol) with $BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol) after column chromatography (EtOAc:hexane = 1:9) afforded **4ba** as a white solid. Yield 68 mg (78%). Mp 175-176 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.20-7.15 (m, 10H), 6.03 (s, 1H), 4.58-4.55 (m, 2H), 4.28-4.26 (m, 1H), 3.79 (dd, *J* = 12.0, 3.5 Hz, 1H), 3.60 (dd, *J* = 12.0, 2.5 Hz, 1H) 2.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 153.0, 143.8, 138.9, 135.4, 135.2, 130.1, 129.7, 129.6, 128.5, 128.5, 127.7, 126.7, 114.5, 85.6, 72.5, 67.6, 48.5, 21.6 ppm; IR



4ba

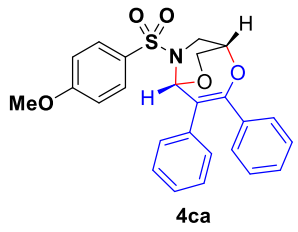
(Neat): 2926, 2862, 1634, 1446, 1341, 1316, 1252, 1159 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{24}NO_4S$ $[M+H]^+$: *m/z* 434.1421. Found: 434.1420.

3-(4-chlorophenyl)-4-phenyl-9-tosyl-2,6-dioxa-9-azabicyclo[3.2.2]non-3-ene **(4bb).** Following the general procedure, the reaction of **3bb** (93.6 mg, 0.2 mmol) with $BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol) after column chromatography (EtOAc:hexane = 1:9) afforded **4bb** as a white solid. Yield 71 mg (76%). Mp 172-173 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.24-7.19 (m, 3H), 716-7.14 (m, 2H), 7.13-7.08 (m, 4H), 6.01 (s, 1H), 4.58-4.52 (m, 2H), 4.26 (dt, *J* = 12.5, 2.5 Hz, 1H), 3.79 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.59 (dd, *J* = 12.5, 3.5 Hz, 1H) 2.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 151.9, 143.9, 138.6, 135.1, 134.4, 133.8, 130.9, 130.0, 129.8, 128.7, 128.0, 127.7, 127.0, 115.0, 85.5, 72.6, 67.6, 48.5, 21.6 ppm; IR (Neat): 2921, 2868, 1629, 1487, 1351, 1175, 1161 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{23}ClNO_4S$ $[M+H]^+$: *m/z* 468.1031. Found: 468.1034.



4bb

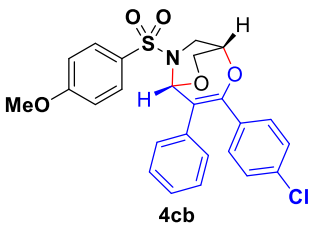
9-((4-methoxyphenyl)sulfonyl)-3,4-diphenyl-2,6-dioxa-9-azabicyclo[3.2.2]non-3-ene **(4ca).** Following the general procedure, the reaction of **3ca** (89.9 mg, 0.2 mmol) with $BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol) after column chromatography (EtOAc:hexane = 1:9) afforded **4ca** as a white solid. Yield 69 mg (77%). Mp 146-147 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.19-7.16 (m, 10H), 6.96 (d, *J* = 8.5 Hz, 2H), 6.03 (s, 1H), 4.58-4.55 (m, 2H), 4.26 (d, *J* = 12.5 Hz, 1H), 387 (s, 3H), 3.79 (dd, *J* = 12.0, 3.5 Hz, 1H), 3.60 (dd, *J* = 12.0, 2.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 163.2, 153.0, 139.0, 135.4, 130.1, 129.9, 129.8, 129.6, 128.5_3, 128.4_7, 127.7, 126.7, 114.5, 114.3, 85.6, 72.5, 67.7, 55.6, 48.5 ppm; IR (Neat): 1634,



4ca

1601, 1499, 1345, 1262, 1175, 1160 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{24}NO_5S$ $[M+H]^+$: *m/z* 450.1370. Found: 450.1373.

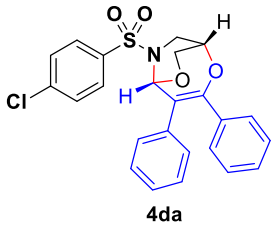
3-(4-chlorophenyl)-9-((4-methoxyphenyl)sulfonyl)-4-phenyl-2,6-dioxa-9-azabicyclo[3.2.2]non-3-ene **(4cb).** Following the general procedure, the reaction of **3cb** (96.8 mg, 0.2 mmol) with



4cb

$BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol) after column chromatography (EtOAc:hexane = 1:9) afforded **4cb** as a white solid. Yield 72 mg (74%). Mp 165-166 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83-7.81 (m, 2H), 7.24-7.19 (m, 3H), 7.16-7.08 (m, 6H), 6.97-6.95 (m, 2H), 6.01 (s, 1H), 4.58-4.53 (m, 2H), 4.23 (d, *J* = 12.5 Hz, 1H), 388 (s, 3H), 3.81-3.78 (m, 1H), 3.58 (dd, *J* = 12.0, 3.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 163.2, 151.8, 138.6, 134.3, 133.9, 130.8, 130.0, 129.8, 129.7, 128.6, 127.9, 126.9, 115.0, 114.2, 85.5, 72.6, 67.6, 55.6, 48.5 ppm; IR (Neat): 2922, 1630, 1594, 1494, 1349, 1310, 1224, 1177 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{23}ClNO_5S$ $[M+H]^+$: *m/z* 484.0980. Found: 484.0980.

9-((4-chlorophenyl)sulfonyl)-3,4-diphenyl-2,6-dioxa-9-azabicyclo[3.2.2]non-3-ene **(4da).** Following the general procedure, the reaction of **3da** (90.8 mg, 0.2 mmol) with $BF_3{\cdot}OEt_2$ (5.0

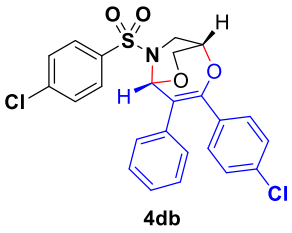


4da

µL, 0.04 mmol) after column chromatography (EtOAc:hexane = 1:9) afforded **4db** as a white solid. Yield 64 mg (70%). Mp 145-146 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82-7.80 (m, 2H), 7.47-7.44 (m, 2H), 7.22-7.16 (m, 4H), 7.16-7.12 (m, 6H), 6.02 (s, 1H), 4.62-4.58 (m, 2H), 4.27 (dt, *J* = 12.5 Hz, 3.0 Hz, 1H), 3.86 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.59 (dd, *J* = 12.0, 3.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 153.2, 139.5, 138.8, 136.8, 135.2, 130.0, 129.5, 129.4, 129.0, 128.6, 128.5, 127.7, 126.8, 114.2, 85.7, 72.4, 67.7, 48.6 ppm; IR (Neat): 2868, 1633,

1446, 1353, 1258, 1163, 1088 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{21}ClNO_4S$ $[M+H]^+$: *m/z* 454.0874. Found: 454.0870.

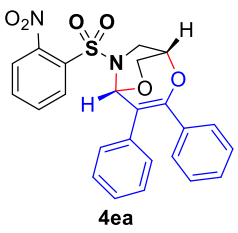
3-(4-chlorophenyl)-9-((4-chlorophenyl)sulfonyl)-4-phenyl-2,6-dioxa-9-azabicyclo[3.2.2]non-3-ene **(4db).** Following the general procedure, the reaction of **3db** (97.8 mg, 0.2 mmol) with



4db

$BF_3{\cdot}OEt_2$ (5.0 μL, 0.04 mmol) after column chromatography (EtOAc:hexane = 1:9) afforded **4db** as a white solid. Yield 67 mg (68%). Mp 202-203 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82-7.79 (m, 2H), 7.48-7.45 (m, 2H), 7.25-7.18 (m, 3H), 7.14-7.11 (m, 4H), 7.09-7.07 (m, 2H), 6.00 (s, 1H), 4.62-4.56 (m, 2H), 4.26 (dt, *J* = 12.5, 2.5 Hz, 1H), 3.86 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.58 (dd, *J* = 12.0, 3.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 152.0, 139.6, 138.4, 136.6, 134.5, 133.6, 130.8, 129.9, 129.4, 129.0, 128.7, 128.0, 127.0, 114.7, 85.6, 72.5, 67.6, 48.6 ppm; IR (Neat): 2924, 1628, 1485, 1382, 1224, 1165, 1089 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{20}Cl_2NO_4S$ $[M+H]^+$: *m/z* 488.0485. Found: 488.0486.

9-((2-nitrophenyl)sulfonyl)-3,4-diphenyl-2,6-dioxa-9-azabicyclo[3.2.2]non-3-ene **(4ea).** Following the general procedure, the reaction of **3ea** (93.1 mg, 0.2 mmol) with $BF_3{\cdot}OEt_2$ (5.0 μL,

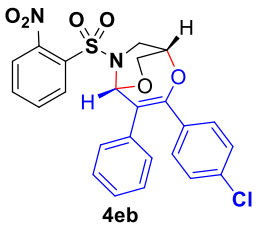


4ea

0.04 mmol) after column chromatography (EtOAc:hexane = 1:9) afforded **4ea** as a white solid. Yield 60 mg (64%). Mp 160-161 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.69-7.63 (m, 2H), 7.58-7.55 (m, 1H), 7.22-7.19 (m, 3H), 7.17-7.13 (m, 5H), 7.11-7.09 (m, 2H), 6.04 (s, 1H), 4.74-4.67 (m, 2H), 4.27 (dt, *J* = 12.5, 2.0 Hz, 1H), 4.12 (dd, *J* = 12.0, 3.5 Hz, 1H), 3.99 (dd, *J* = 12.0, 3.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 153.5, 148.5, 138.6, 135.2, 133.7, 132.3, 131.8, 130.4, 130.1, 129.6, 128.7, 128.5, 127.7, 126.7, 124.2, 114.2, 85.7, 72.8, 67.9, 48.8 ppm;

IR (Neat): 2951, 1538, 1442, 1359, 1269, 1166 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{21}N_2O_6S$ $[M+H]^+$: *m/z* 465.1115. Found: 465.1118.

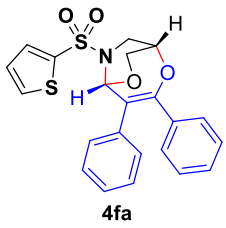
3-(4-chlorophenyl)-9-((2-nitrophenyl)sulfonyl)-4-phenyl-2,6-dioxa-9-azabicyclo[3.2.2]non-3-ene **(4eb).** Following the general procedure, the reaction of **3eb** (99.8 mg, 0.2 mmol) with



4eb

$BF_3{\cdot}OEt_2$ (5.0 μL, 0.04 mmol) after column chromatography (EtOAc:hexane = 1:9) afforded **4eb** as a white solid. Yield 63 mg (63%). Mp 89-90 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.70-7.63 (m, 2H), 7.59-7.56 (m, 1H), 7.16-7.08 (m, 9H), 6.02 (s, 1H), 4.74 (s, 1H), 4.66 (d, *J* = 12.0 Hz, 2H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.15 (dd, *J* = 12.0, 3.5 Hz, 1H), 3.97 (dd, *J* = 12.0, 2.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 152.3, 148.5, 138.2, 134.5, 133.8, 133.7, 132.2, 131.8, 130.9, 130.4, 130.0, 128.7, 128.0, 127.0, 124.2, 114.7, 85.6, 72.9, 67.8, 48.7 ppm; IR (Neat): 2921, 2852, 1629, 1542, 1456, 1356, 1260, 1166 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{20}ClN_2O_6S$ $[M+H]^+$: *m/z* 499.0725. Found: 499.0724.

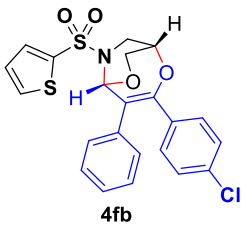
3,4-diphenyl-9-(thiophen-2-ylsulfonyl)-2,6-dioxa-9-azabicyclo[3.2.2]non-3-ene **(4fa).** Following the general procedure, the reaction of **3fa** (85.1 mg, 0.2 mmol) with $BF_3{\cdot}OEt_2$ (5.0 μL,



4fa

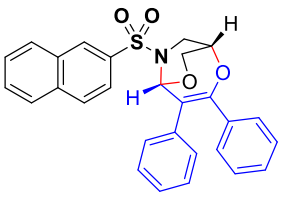
0.04 mmol) after column chromatography (EtOAc:hexane = 1:9) afforded **4fa** as a white solid. Yield 61 mg (72%). Mp 194-195 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67-7.61 (m, 2H), 7.20-7.16 (m, 10H), 7.12-7.10 (m, 1H), 6.02 (s, 1H), 4.64-4.61 (m, 2H), 4.35 (dt, *J* = 12.0, 2.5 Hz, 1H), 3.90 (dd, *J* = 12.5, 4.5 Hz, 1H), 3.69 (dd, *J* = 12.0, 3.0 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 153.3, 138.8, 138.4, 135.3, 132.8, 132.4, 130.1, 129.6, 128.6, 128.5, 127.7, 127.5, 126.7, 114.1, 85.8, 72.3, 67.6, 48.8 ppm; IR (Neat): 2922, 2871, 1632, 1444, 1351, 1265, 1157 cm^{-1}; HRMS (ESI): Calcd. for $C_{22}H_{20}NO_4S_2$ $[M+H]^+$: *m/z* 426.0828. Found: 426.0830.

***3-(4-chlorophenyl)-4-phenyl-9-(thiophen-2-ylsulfonyl)-2,6-dioxa-9-azabicyclo[3.2.2]non-3-ene* (4fb).** Following the general procedure, the reaction of **3fb** (92.0 mg, 0.2 mmol) with $BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol) after column chromatography (EtOAc:hexane = 1:9) afforded **4fb** as a white solid. Yield 67 mg (73%). Mp 145-146 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 3.0 Hz, 1H), 7.60 (d, *J* = 4.5 Hz, 1H), 7.22-7.17 (m, 3H), 7.14-7.06 (m, 7H), 5.97 (s, 1H), 4.62-4.56 (m, 2H), 4.31 (d, *J* = 12.0 Hz, 1H), 3.88 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.66 (dd, *J* = 12.0, 2.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 152.1, 138.5, 138.3, 134.5, 133.7, 132.8, 132.5, 130.9, 130.0, 128.7, 128.0, 127.6, 127.0, 114.6, 85.7, 72.5, 67.6, 48.8 ppm; IR (Neat): 2928, 1635, 1489, 1350, 1261, 1224, 1158 cm^{-1}; HRMS (ESI): Calcd. for $C_{22}H_{19}ClNO_4S_2$ $[M+H]^+$: *m/z* 460.0439. Found: 460.0440.



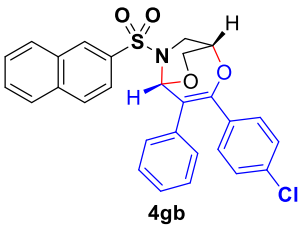
4fb

***9-(naphthalen-2-ylsulfonyl)-3,4-diphenyl-2,6-dioxa-9-azabicyclo[3.2.2]non-3-ene* (4ga).** Following the general procedure, the reaction of **3ga** (93.9 mg, 0.2 mmol) with $BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol) after column chromatography (EtOAc:hexane = 1:9) afforded **4ga** as a white solid. Yield 66 mg (70%). Mp 197-198 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.44 (s, 1H), 7.94-7.88 (m, 3H), 7.85-7.83 (m, 1H), 7.66-7.59 (m, 2H), 7.17-7.09 (m, 10H), 6.12 (s, 1H), 4.55-4.52 (m, 2H), 4.30 (dt, *J* = 12.0, 2.5 Hz, 1H), 3.76 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.65 (dd, *J* = 12.0, 3.0 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 153.1, 138.9, 135.3, 135.1, 135.0, 132.1, 130.0, 129.5$_3$, 129.4$_7$, 129.3, 129.2, 128.9, 128.5$_2$, 128.4$_5$, 127.9, 127.7, 127.5, 126.7, 122.7, 114.5, 85.6, 72.4, 67.6, 48.6 ppm; IR (Neat): 2926, 2850, 1633, 1344, 1318, 1256, 1176 cm^{-1}; HRMS (ESI): Calcd. for $C_{28}H_{24}NO_4S$ $[M+H]^+$: *m/z* 470.1421. Found: 470.1422.



4ga

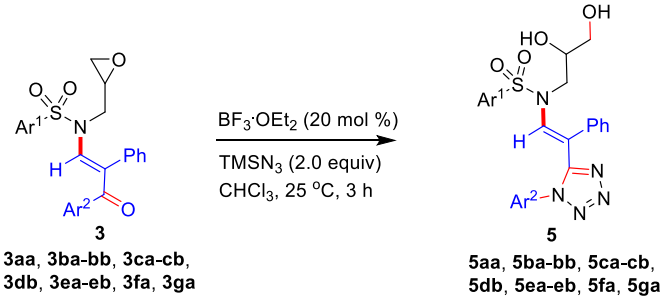
***3-(4-chlorophenyl)-9-(naphthalen-2-ylsulfonyl)-4-phenyl-2,6-dioxa-9-azabicyclo[3.2.2]non-3-ene* (4gb).** Following the general procedure, the reaction of **3gb** (100.8 mg, 0.2 mmol) with



4gb

$BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol) after column chromatography (EtOAc:hexane = 1:9) afforded **4gb** as a white solid. Yield 74 mg (73%). Mp 164-165 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.46-8.46 (m, 1H), 7.97-7.91 (m, 3H), 7.85 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 7.69-7.66 (m, 1H), 7.65-7.61 (m, 1H), 7.23-7.18 (m, 3H), 7.17-7.13 (m, 2H), 7.11-7.09 (m, 2H), 7.08-7.05 (m, 2H), 6.12 (s, 1H), 4.59-4.51 (m, 2H), 4.32 (dt, J = 12.0, 2.5 Hz, 1H), 3.81 (dd, J = 12.0, 4.0 Hz, 1H), 3.66 (dd, J = 12.5, 3.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 151.9, 138.6, 135.0, 134.9$_6$, 134.4, 133.8, 132.1, 130.9, 130.0, 129.5, 129.4, 129.3, 129.0, 128.7, 128.0, 127.6, 127.0, 122.7, 115.0, 85.6, 72.6, 67.6, 48.6 ppm; IR (Neat): 2855, 1635, 1490, 1344, 1318, 1255, 1160 cm^{-1}; HRMS (ESI): Calcd. for $C_{28}H_{23}ClNO_4S$ $[M+H]^+$: *m/z* 504.1031. Found: 504.1030.

4 (c). General procedure for the synthesis of tetrazoles 5aa-5gb:



3
3aa, **3ba-bb**, **3ca-cb**, **3db**, **3ea-eb**, **3fa**, **3ga**

5
5aa, **5ba-bb**, **5ca-cb**, **5db**, **5ea-eb**, **5fa**, **5ga**

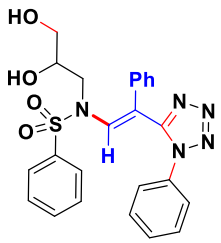
(i) To a solution of N-(oxiran-2-ylmethyl)-N-(3-oxo-2,3-diphenylprop-1-en-1-yl)benzenesulfonamide **3aa** (83.9 mg, 0.2 mmol 1.0 equiv) in dry $CHCl_3$ (2 mL), $BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol, 0.2 equiv) and $TMSN_3$ (52.6 µL, 0.40 mmol, 2.0 equiv) were added. The resulting mixture was stirred for 3 h at rt (25 ^{o}C). After the completion of the reaction (TLC), DCM (10 mL) was added, the solution was washed with water (3 × 10 mL) and then with brine

solution (3 × 10 mL); the aqueous layer was extracted with DCM (3 × 10 mL). The combined organic portion was dried over anhydrous Na_2SO_4, the solvent was evaporated under the reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate 3: 2) to obtain compound **5aa** .as a white solid.

(ii) Alternative procedure:

We could also achieve the formation of **5** by starting with 3-chloro-2,3-diphenylacrylaldehyde (0.20 mmol 1.0 equiv), K_2CO_3 (0.40 mmol, 2.0 equiv) in dry DMF (5 mL) and epoxy benzene sulfonamide (0.30 mmol 1.5 equiv). The resulting reaction mixture was heated for 2 h on an oil bath maintained at 80 ^oC. After the completion of the reaction as monitored by TLC, the solvent was removed. To this mixture $BF_3{\cdot}OEt_2$ (20 mol%) and $TMSN_3$ (2.0 equiv) in $CHCl_3$ (2 mL) were added at 25 ^oC. The contents were stirred for 3 h, without isolating the intermediate compound **3**. Work-up was similar to (i) above. Removal of DMF was necessary for this method.

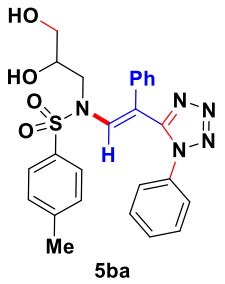
(E)-N-(2,3-dihydroxypropyl)-N-(2-phenyl-2-(1-phenyl-1H-tetrazol-5-yl)vinyl)benzenesulfonamide **(5aa).** Following the general procedure, the reaction of **3aa** (83.9 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol) and $TMSN_3$ (52.6 µL, 0.40 mmol) after column chromatography (EtOAc:hexane = 2:3) afforded **5aa** as a white solid. Yield 81 mg (85%). Mp 131-132 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.75-7.72 (m, 1H), 7.65-7.62 (m, 2H), 7.37-7.34 (m, 1H), 7.30-7.28 (m, 3H), 7.18-7.12 (m, 3H), 7.17 (d, *J* =7.5 Hz, 2H), 7.15-7.12 (m, 1H), 6.72 (d, *J* =7.0 Hz, 2H) 3.58-3.58 (m, 1H), 3.33-3.24 (m, 2H), 3.11 (dd, *J* = 11.5, 4.5 Hz, 1H), 3.02 (dd, *J* = 15.0, 4.5 Hz, 1H), 2.80 (bs, 1H), 2.17 (bs, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 154.3, 138.0, 133.8, 133.6, 132.4, 132.2, 129.9, 129.5,129.3, 129.1, 129.0, 128.6, 127.4,



5aa

125.2, 115.9, 68.6, 63.4, 50.0, ppm; IR (Neat): 3381, 1608, 1495, 1449, 1358, 1180,1166, cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{24}N_5O_4S$ $[M+H]^+$: *m/z* 478.1544. Found: 478.1546.

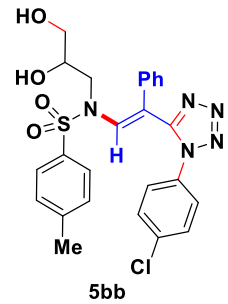
***(E)-N-(2,3-dihydroxypropyl)-4-methyl-N-(2-phenyl-2-(1-phenyl-1H-tetrazol-5-yl)vinyl)benzenesulfonamide* (5ba).** Following the general procedure, the reaction of **3ba** (98.3



5ba

mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol) and $TMSN_3$ (52.6 µL, 0.40 mmol) after column chromatography (EtOAc:hexane = 2:3) afforded **5ba** as a white solid. Yield 81 mg (82%). Mp 120-121 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8 Hz, 2H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.38-7.35 (m, 1H), 7.32-7.28 (m, 2H), 7.24 (s, 1H), 7.19 (d, *J* = 7.5 Hz, 2H), 7.16-7.13 (m, 1H), 7.09-7.06 (m, 2H), 6.79 (d, *J* = 7.0 Hz, 2H), 3.55 (bs, 1H), 3.29-3.25 (m, 2H), 3.11-3.03 (m, 2H), 2.55 (bs, 1H), 2.52 (s, 3H), 2.03 (bs, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 154.3, 144.8 134.9, 133.8, 132.5, 132.4, 130.1, 129.9, 129.4, 129.2, 129.1, 128.6, 127.6, 125.2, 115.7, 68.7, 63.4, 50.1, 21.8 ppm; IR (Neat): 3360, 2920, 1593, 1496, 1445, 1350, 1162, cm^{-1}; HRMS (ESI): Calcd. for $C_{25}H_{26}N_5O_4S$ $[M+H]^+$: *m/z* 492.1700. Found: 492.1701.

***(E)-N-(2-(1-(4-chlorophenyl)-1H-tetrazol-5-yl)-2-phenylvinyl)-N-(2,3-dihydroxypropyl)-4-methylbenzenesulfonamide* (5bb)**. Following the general procedure, the reaction of **3bb** (93.6

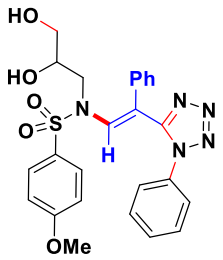


5bb

mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol) and $TMSN_3$ (52.6 µL, 0.40 mmol) after column chromatography (EtOAc:hexane = 2:3) afforded **5bb** as a white solid. Yield 88 mg (84%). Mp 123-124 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.21 (s, 1H), 7.18-7.15 (m, 2H), 7.12-7.09 (m, 1H), 7.04-7.01 (m, 4H), 6.70-6.68 (m, 2H), 3.49-3.47 (m, 1H), 3.23-3.15 (m, 2H), 3.03-2.95 (m, 2H), 2.57 (bs, 1H), 2.44 (s, 3H), 1.97 (bs, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 154.5, 144.8 136.0, 135.0, 132.7, 132.4, 132.3, 130.1,

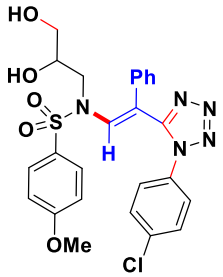
129.4, 129.3, 129.1, 128.7, 127.5, 126.5, 114.8, 68.7, 63.4, 50.0, 21.7 ppm; IR (Neat): 3330, 2920, 1622, 1494, 1348, 1161, 1089, cm^{-1}; HRMS (ESI): Calcd. for $C_{25}H_{25}ClN_5O_4S$ $[M+H]^+$: *m/z* 526.1310. Found: 526.1309.

(E)-N-(2,3-dihydroxypropyl)-4-methoxy-N-(2-phenyl-2-(1-phenyl-1H-tetrazol-5-yl)vinyl)benzenesulfonamide **(5ca).** Following the general procedure, the reaction of **3ca** (89.9 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol) and $TMSN_3$ (52.6 µL, 0.40 mmol) after column chromatography (EtOAc:hexane = 2:3) afforded **5ca** as a white solid. Yield 84 mg (83%). Mp 149-150 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.81-7.78 (m, 2H), 7.38-7.34 (m, 1H), 7.33-7.29 (m, 2H), 7.25 (s, 1H), 7.21-7.18 (m, 2H), 7.17-7.13 (m, 1H), 7.10-7.06 (m, 4H), 6.83-6.82 (m, 2H), 3.95 (s, 3H), 3.57-3.53 (m, 1H), 3.31-3.23 (m, 2H), 3.11-3.03 (m, 2H), 2.63 (bs, 1H), 2.07 (bs, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 163.7, 154.4, 133.8 132.5, 129.9, 129.8, 129.4, 129.1, 129.0, 128.6, 125.2, 114.9, 114.6, 68.5, 63.4, 55.9, 50.0 ppm; IR (Neat): 3372, 2945, 1594, 1497, 1344, 1256, 1153 cm^{-1}; HRMS (ESI): Calcd. for $C_{25}H_{26}N_5O_5S$ $[M+H]^+$: *m/z* 508.1649. Found: 508.1647.



5ca

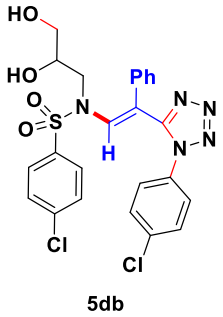
(E)-N-(2-(1-(4-chlorophenyl)-1H-tetrazol-5-yl)-2-phenylvinyl)-N-(2,3-dihydroxypropyl)-4-methoxybenzenesulfonamide **(5cb).** Following the general procedure, the reaction of **3cb** (96.8 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol) and $TMSN_3$ (52.6 µL, 0.40 mmol) after column chromatography (EtOAc:hexane = 2:3) afforded **5cb** as a white solid. Yield 85 mg (78%). Mp 152-153 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.83-7.80 (m, 2H), 7.32 (s, 1H), 7.27-7.24 (m, 2H), 7.21-7.18 (m, 1H), 7.14-7.11 (m, 4H), 7.10-7.07 (m, 2H), 6.82-6.81 (m, 2H), 3.96 (s, 3H), 3.59-3.56 (m, 1H), 3.32 (dd, *J* = 15.0, 8.0 Hz, 1H), 3.23 (dd, *J* = 11.5, 3.0 Hz, 1H), 3.10-3.04 (m,



5cb

2H), 2.81 (bs, 1H), 2.15 (bs, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 163.8, 136.0 132.8, 132.4, 132.3, 129.8, 129.5, 129.3, 129.2, 128.7, 126.4, 114.6, 114.4, 68.6, 63.3, 55.8, 50.0 ppm; IR (Neat): 3300, 2922, 1623, 1594, 1495, 1346, 1251, 1157 cm^{-1}; HRMS (ESI): Calcd. for $C_{25}H_{25}ClN_5O_5S$ $[M+H]^+$: *m/z* 542.1249. Found: 542.1251.

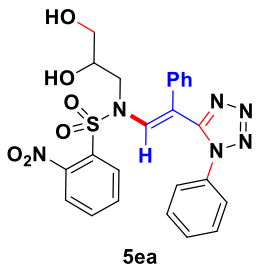
(E)-4-chloro-N-(2-(1-(4-chlorophenyl)-1H-tetrazol-5-yl)-2-phenylvinyl)-N-(2,3-dihydroxypropyl)benzenesulfonamide **(5db).** Following the general procedure, the reaction of



5db

3db (97.8 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol) and $TMSN_3$ (52.6 µL, 0.40 mmol) after column chromatography (EtOAc:hexane = 2:3) afforded **5db** as a white solid. Yield 86 mg (79%). Mp 195-196 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.30 (s, 1H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.22-7.19 (m, 1H), 7.15-7.10 (m, 4H), 6.81 (d, *J* = 7.0 Hz, 2H), 3.60-3.58 (m, 1H), 3.36 (dd, *J* = 15.0, 8.5 Hz, 1H), 3.23 (dd, *J* =11.3, 3.0 Hz, 1H), 3.10-3.03 (m, 2H), 2.82 (bs, 1H), 2.12 (bs, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 155.0, 139.2 137.1, 135.1, 133.3, 133.0, 130.3, 129.7, 129.5, 129.1, 128.7, 128.0, 116.6, 69.2, 63.8, 51.3 ppm; IR (Neat): 3371, 2944, 1627, 1493, 1351, 1280, 1166 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{22}Cl_2N_5O_5S$ $[M+H]^+$: *m/z* 546.0764. Found: 546.0768.

(E)-N-(2,3-dihydroxypropyl)-2-nitro-N-(2-phenyl-2-(1-phenyl-1H-tetrazol-5-yl)vinyl)benzenesulfonamide **(5ea).** Following the general procedure, the reaction of **3ea** (93.1

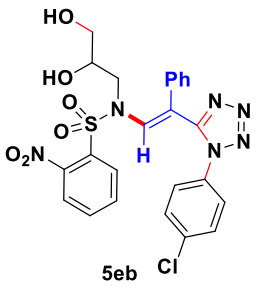


5ea

mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol) and $TMSN_3$ (52.6 µL, 0.40 mmol) after column chromatography (EtOAc:hexane = 2:3) afforded **5ea** as a white solid. Yield 81 mg (78%). Mp 118-119 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, *J* = 7.5 Hz, 1H), 7.79-7.71 (m, 3H), 7.39 (s, 1H), 7.23-7.20 (m, 1H), 7.17-7.14 (m, 2H), 7.11-7.09 (m, 2H), 7.06-7.03 (m, 1H), 7.00-6.97 (m, 2H), 6.76

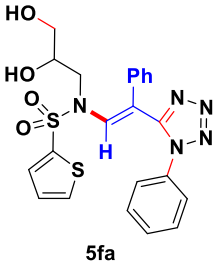
(d, *J* = 7.0 Hz, 2H), 3.62-3.61 (m, 1H), 3.38 (dd, *J* = 15.0, 9.0 Hz, 1H), 3.20 (dd, *J* =11.5, 3.0 Hz, 2H), 3.06-3.02 (m, 2H), 2.34 (bs, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 154.4, 147.8 134.8, 133.6, 132.5, 132.2, 131.9, 131.5, 131.4, 129.9, 129.3, 129.1, 128.6, 125.3, 124.6, 115.1, 68.1, 63.5, 50.0 ppm; IR (Neat): 3341, 1541, 1479, 1363, 1163 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{23}N_6O_6S$ $[M+H]^+$: *m/z* 523.1394. Found: 523.1395.

(E)-N-(2-(1-(4-chlorophenyl)-1H-tetrazol-5-yl)-2-phenylvinyl)-N-(2,3-dihydroxypropyl)-2-nitrobenzenesulfonamide **(5eb).** Following the general procedure, the reaction of **3eb** (99.8 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol) and $TMSN_3$ (52.6 µL, 0.40 mmol) after column chromatography (EtOAc:hexane = 2:3) afforded **5eb** as a white solid. Yield 85 mg (76%). Mp 89-90 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (d, *J* = 7.5 Hz, 1H), 7.89-7.80 (m, 3H), 7.52 (s, 1H), 7.22-7.09 (m, 7H), 6.87 (d, *J* = 7.0 Hz, 2H), 3.76-3.69 (b, 1H), 3.50-3.42 (m, 1H), 3.35-3.25 (m, 2H), 3.16-3.08 (m, 2H), 2.33 (bs, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 154.5, 147.9 136.0, 134.8, 132.5, 132.2, 132.1, 132.0, 131.6, 131.4, 129.4, 129.3, 128.8, 126.6, 124.7, 114.0, 68.1, 63.4, 49.9 ppm; IR (Neat): 3350, 2922, 1619, 1541, 1495, 1364, 1165 cm^{-1}; HRMS (ESI): Calcd. for $C_{24}H_{22}ClN_6O_6S$ $[M+H]^+$: *m/z* 557.1005. Found: 557.1006.



5eb

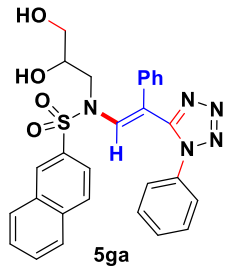
(E)-N-(2,3-dihydroxypropyl)-N-(2-phenyl-2-(1-phenyl-1H-tetrazol-5-yl)vinyl)thiophene-2-sulfonamide **(5fa).** Following the general procedure, the reaction of **3fa** (85.1 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol) and $TMSN_3$ (52.6 µL, 0.40 mmol) after column chromatography (EtOAc:hexane = 2:3) afforded **5fa** as a white solid. Yield 79 mg (82%). Mp 150-151 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.70 (dd, *J* = 4.0, 1.5 Hz, 1H), 7.37-7.33 (m, 1H), 7.31-7.30 (m, 2H), 7.24-7.20 (m, 4H), 7.17-7.14 (m, 1H), 7.11-7.08 (m, 2H), 6.82-6.81 (m, 2H), 3.62-



5fa

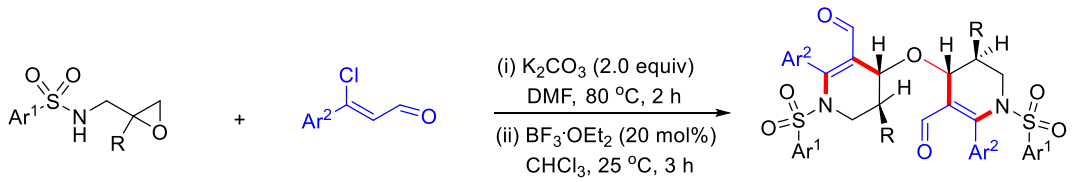
3.58 (m, 1H), 3.36-3.27 (m, 2H), 3.14 (dd, *J* = 11.5, 5.0 Hz, 1H), 3.06 (dd, *J* = 15.5, 4.5 Hz, 1H), 2.83 (bs, 1H), 2.23 (bs, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 154.1, 137.9 133.7, 133.5, 133.3, 132.3, 131.8, 130.0, 129.3, 129.2, 128.7, 128.0, 125.1, 117.6, 68.6, 63.3, 50.6 ppm; IR (Neat): 3381, 2922, 1605, 1495, 1357, 1158 cm^{-1}; HRMS (ESI): Calcd. for $C_{22}H_{22}N_5O_4S_2$ $[M+H]^+$: *m/z* 484.1108. Found: 484.1106.

(E)-N-(2,3-dihydroxypropyl)-N-(2-phenyl-2-(1-phenyl-1H-tetrazol-5-yl)vinyl)naphthalene-2-sulfonamide **(5ga).** Following the general procedure, the reaction of **3ga** (93.9 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol) and $TMSN_3$ (52.6 µL, 0.40 mmol) after column chromatography (EtOAc:hexane = 2:3) afforded **5ga** as a white solid. Yield 81 mg (77%). Mp 66-67 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.46 (s, 1H), 8.06-8.03 (m, 2H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.81-7.79 (m, 1H), 7.75-7.67 (m, 2H), 7.37 (s, 1H), 7.26-7.23 (m, 1H), 7.13-7.04 (m, 5H), 6.96-6.93 (m, 2H), 6.63 (d, *J* = 7.0 Hz, 2H), 3.61-3.58 (m, 1H), 3.66 (dd, *J* = 15.0, 8.0 Hz, 1H), 3.25 (dd, *J* = 11.5, 3.0 Hz, 1H), 3.12-3.04 (m, 2H), 2.88 (bs, 1H), 2.21 (bs, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 154.3, 135.2 134.9, 133.7, 132.4, 132.2, 129.8, 129.5_0, 129.4_5, 129.3, 129.1, 129.0_4, 128.9_7, 128.5, 128.1, 125.1, 122.2, 115.6, 68.7, 63.3, 50.1 ppm; IR (Neat): 3391, 2922, 1730, 1618, 1498, 1347, 1158 cm^{-1}; HRMS (ESI): Calcd. for $C_{28}H_{26}N_5O_4S$ $[M+H]^+$: *m/z* 528.1700. Found: 528.1706.



5ga

4. (d) Synthesis of tetrahydropyridine-3-carbaldehydes 6hc-kc: ***Representative procedure for the synthesis of compound 6hc***



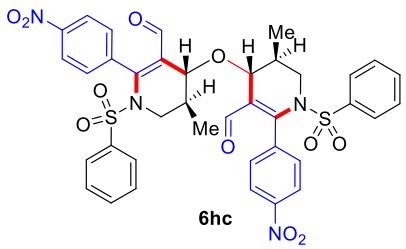
Ar^1 = Ph, R = Me (**1h**);
Ph, R = Ph (**1i**);
4-Me-C_6H_4, R = Me (**1j**);
4-Me-C_6H_4, R = Ph (**1k**);
4-MeO-C_6H_4, R = Me (**1l**);

Ar^2 = 4-NO_2-C_6H_4 (**2c**)

6hc, **6ic**, **6jc**, **6kc**, **6lc**

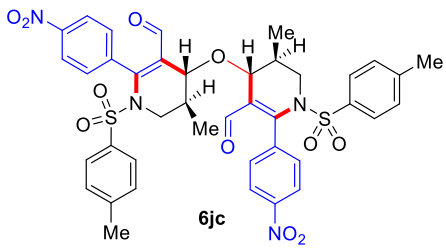
To a mixture of *(Z)*-3-chloro-3-(4-nitrophenyl)acrylaldehyde **2c** (63.5 mg, 0.30 mmol, 1.0 equiv) and K_2CO_3 (82.9 mg, 0.60 mmol, 2.0 equiv) in dry DMF (5 mL), *N*-((2-methyloxiran-2-yl)methyl)benzenesulfonamide **1h** (79.0 mg, 0.36 mmol, 1.2 equiv) was added. The resulting mixture was heated for 2 h on an oil-bath maintained at 80 ^oC. After the completion of the reaction as monitored by TLC, ethyl acetate (30 mL) was added and the solution was washed with water (3 × 30 mL) and then with brine solution (3 × 15 mL); the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic portion was dried over anhydrous Na_2SO_4, the solvent was evaporated under the reduced pressure. This whole residue was dissolved in in dry $CHCl_3$ (2 ml), and $BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol, 0.2 equiv) was added. The resulting mixture was stirred for 3 h at rt (25 ^oC). After the completion of the reaction as monitored by TLC, DCM (10 mL) was added and the solution was washed with water (3 × 10 mL), then brine solution (3 × 10 mL); the aqueous layer was extracted with DCM (3 × 10 mL). The combined organic portion was dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate 1: 4) to obtain compound **6hc** as a light-yellow solid. Using the same molar quantities, the remaining compounds were prepared.

5-formyl-3-methyl-6-(4-nitrophenyl)-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridin-4-yl)oxy)-5-methyl-2-(4-nitrophenyl)-1-(phenylsulfonyl)-1,4,5,6-tetrahydropyridine-3-carbaldehyde **(6hc).**



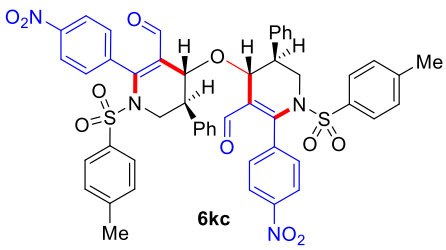
Yellow solid. Yield 65 mg (83%). Mp 167-168 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.80 (s, 2H), 8.21 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 2H), 7.86 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 2H), 7.59-7.56 (m, 2H), 7.46 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 2H), 7.39-7.33 (m, 8H), 6.96 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 2H), 4.43 (d, J = 12.0 Hz, 2H), 4.20 (s, 2H), 3.48 (dd, J_1 = 12.5 Hz, J_2 = 2.0 Hz, 2H), 2.96-2.95 (m, 2H), 0.97 (d, J = 7.0 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 190.0, 153.8, 148.3 140.4, 137.5, 133.7, 133.4, 130.8, 129.1, 126.9, 122.6, 122.1, 120.5, 68.0, 48.2, 27.5, 13.8 ppm; IR (Neat): 2968, 1737, 1664, 1645, 1510, 1367, 1346, 1164 cm^{-1}; HRMS (ESI): Calcd. for $C_{38}H_{35}N_4O_{11}S_2$ $[M+H]^+$: *m/z* 787.1738. Found: 787.1732.

5-formyl-3-methyl-6-(4-nitrophenyl)-1-tosyl-1,2,3,4-tetrahydropyridin-4-yl)oxy)-5-methyl-2-(4-nitrophenyl)-1-tosyl-1,4,5,6-tetrahydropyridine-3-carbaldehyde **(6ic).** White solid. Yield 63 mg



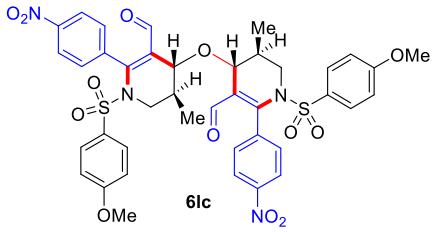
(77%). Mp 185-186 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.81 (s, 2H), 8.22 (d, J = 7.5 Hz, 2H), 7.92 (d, J = 7.5 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.25-7.17 (m, 8H), 7.03 (d, J = 8.0 Hz, 2H), 4.41 (d, J = 12.5 Hz, 2H), 4.21 (s, 2H), 3.49 (d, J = 12.0 Hz, 2H), 2.97-2.96 (m, 2H), 2.44 (s, 6H), 0.97 (d, J = 7.0 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 190.0, 154.0, 148.3, 145.0, 137.7, 137.4, 133.3, 130.8, 129.7, 127.0, 122.5, 122.1, 120.2, 68.0, 48.1, 27.5, 21.6, 13.8 ppm; IR (Neat): 2969, 2861, 1738, 1552, 1343, 1315, 1149 cm^{-1}; HRMS (ESI): Calcd. for $C_{40}H_{39}N_4O_{11}S_2$ $[M+H]^+$: *m/z* 815.2051. Found: 815.2055.

5-formyl-6-(4-nitrophenyl)-3-phenyl-1-tosyl-1,2,3,4-tetrahydropyridin-4-yl)oxy)-2-(4-nitrophenyl)-5-phenyl-1-tosyl-1,4,5,6-tetrahydropyridine-3-carbaldehyde **(6jc).** White solid.



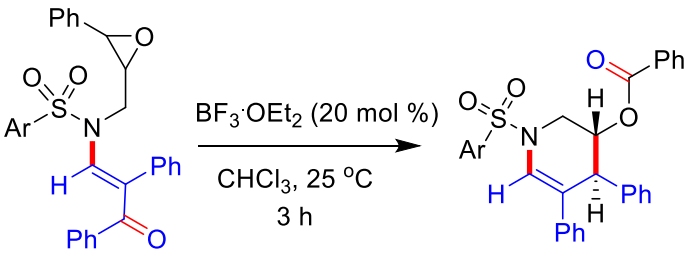
Yield 71 mg (76%). Mp 138-139 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.85 (s, 2H), 8.26 (d, *J* = 7.0 Hz, 2H), 7.99 (d, *J* = 7.5 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 2H),7.34 (s, 6H), 7.20 (d, *J* = 5.0 Hz, 4H), 6..96 (d, *J* = 8.0 Hz, 4H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 8.0 Hz, 4H), 4.89 (s, 2H), 4.78 (d, *J* = 12.5 Hz, 2H), 4.22 (s, 2H), 3.92-3.89 (m, 2H), 2.38 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 189.3, 155.3, 148.3, 144.9, 138.2, 137.0, 136.4, 132.2, 132.0, 129.5, 128.8, 127.6, 127.3, 127.2, 122.2, 120.0, 65.8, 48.3, 38.0, 21.6 ppm; IR (Neat): 2921, 2852, 1734, 1656, 1521, 1345, 1163 cm^{-1}; HRMS (ESI): Calcd. for $C_{50}H_{42}N_4NaO_{11}S_2$ $[M+Na]^+$: *m/z* 961.2184. Found: 961.2181.

5-formyl-1-((4-methoxyphenyl)sulfonyl)-3-methyl-6-(4-nitrophenyl)-1,2,3,4-tetrahydropyridin-4-yl)oxy)-1-((4-methoxyphenyl)sulfonyl)-5-methyl-2-(4-nitrophenyl)-1,4,5,6-tetrahydropyridine-3-carbaldehyde **(6kc).** Yellow solid. Yield 61 mg (72%). Mp 165-166 ^{o}C; ^{1}H



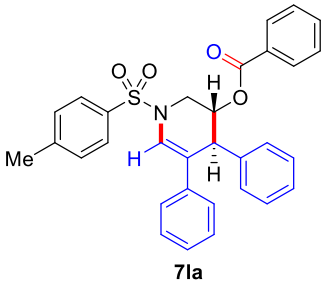
NMR (500 MHz, $CDCl_3$): δ 8.81 (s, 2H), 8.22 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.26 (s, 4H), 7.07 (d, *J* = 7.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 4H), 4.40 (d, *J* = 12.5 Hz, 2H), 4.21 (s, 2H), 3.88 (s, 6H), 3.48 (d, *J* = 12.5 Hz, 2H), 2.96-2.95 (m, 2H), 0.97 (d, *J* = 7.0 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 190.0, 163.8, 154.1, 148.3, 137.8, 133.2, 131.7, 130.9, 129.3, 122.5, 122.1, 120.0, 114.2, 68.0, 55.9, 48.0, 27.6, 13.9 ppm; IR (Neat): 2924, 1656, 1564, 1494, 1345, 1267, 1160 cm^{-1}; HRMS (ESI): Calcd. for $C_{40}H_{38}NaN_4O_{13}S_2$ $[M+Na]^+$: *m/z* 869.1769. Found: 869.1773.

4. (e) Synthesis of tetrahydropyridin-3-yl benzoate 7la:



Ar = 4-Me-C_6H_4

4,5-diphenyl-1-tosyl-1,2,3,4-tetrahydropyridin-3-yl benzoate **(7la).** The procedure was the same as described earlier for azabicyclononenes **4aa-gb**. Thus the reaction of **3la** (101.9 mg, 0.2 mmol) with $BF_3{\cdot}OEt_2$ (5.0 µL, 0.04 mmol) after column chromatography (EtOAc:hexane = 1:9) afforded **7la** as a white solid. Yield 66 mg (65%). Mp 169-170 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73-7.66 (m, 5H), 7.55-7.52 (m, 1H), 7.36-7.33 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.24-7.21 (m, 5H), 7.15-7.12 (m, 5H), 5.34 (s, 1H), 4.12 (s, 1H), 3.97 (d, *J* = 13.5 Hz, 1H), 3.27 (d, *J* = 13.5 Hz, 1H), 2.23 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 165.7, 143.9, 139.9. 138.7, 134.9, 133.2, 129.9, 129.7, 129.5, 128.9, 128.6, 128.4, 128.2, 127.5, 127.1, 126.7, 125.1, 123.0, 115.1, 70.7, 44.6, 41.6, 21.5 ppm; IR (Neat): 3056, 1713, 1647, 1599, 1451, 1348, 1263, 1162 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{28}NO_4S$ $[M+H]^+$: *m/z* 510.1734. Found: 510.1731. Crystallization was done from ethyl acetate-hexane mixture (1:20).



7la

(5) Crystal data and molecular structures

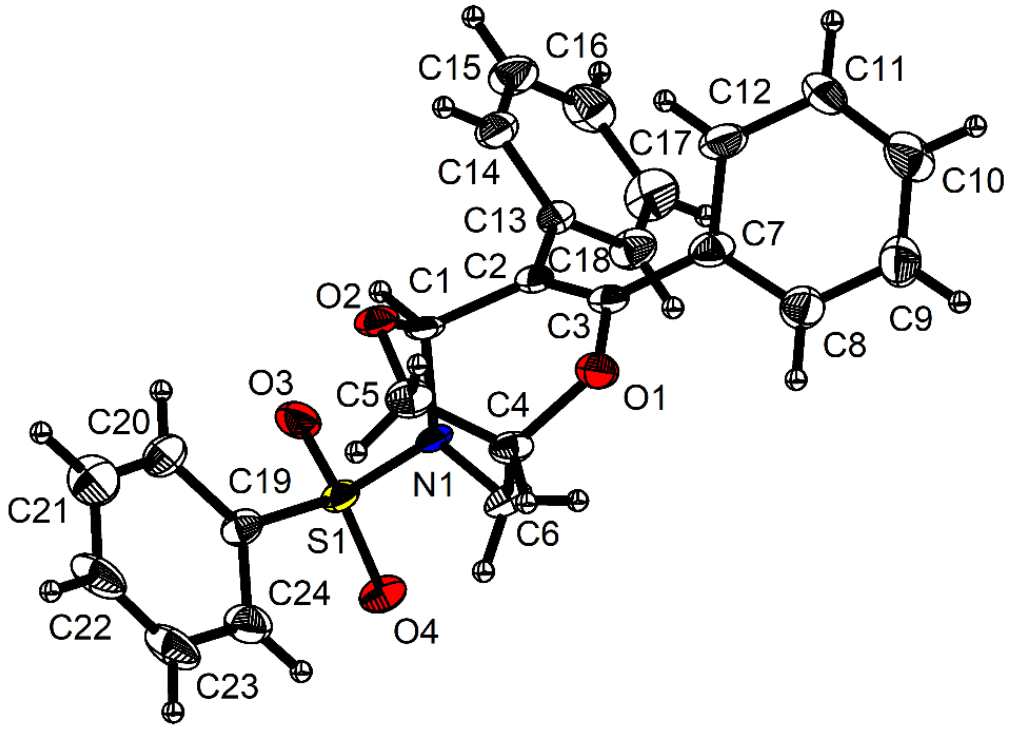


Figure S1. ORTEP view of 3,4-diphenyl-9-(phenylsulfonyl)-2,6-dioxa-9-azabicyclo[3.2.2]non-3-ene **4aa** with 30% probability of ellipsoids. ***Crystal data****:* $C_{24}H_{21}NO_4S$, M = 419.48, Orthorhombic, Space group P 2(1) 2(1) 2(1), a = 5.9615(2), b = 14.5594(7), c = 23.8714(11) Å, V = 2071.92(16)Å^3, α = 90, β = 90, γ = 90^o, Z = 4, μ = 0.187 mm^{-1}, data/restraints/parameters: 3376/0/265, R indices (>2sigma(I)): R1 = 0.0952, *w*R2 (all data) = 0.2916. Selected bond parameters: S1-N1 1.616(8), N1-C1 1.467(10), N1-C6 1.504(12), O2-C1 1.420(11), O2-C5 1.442(12), C4-C5 1.495(14), C4-C6 1.509(13), C1-C2 1.530(13), C3-C2 1.339(14), O1-C3 1.387(11), O1-C4 1.470(11), C2-C13 1.507(13), C3-C7 1.466(15) (Å). CCDC No: 2237334.

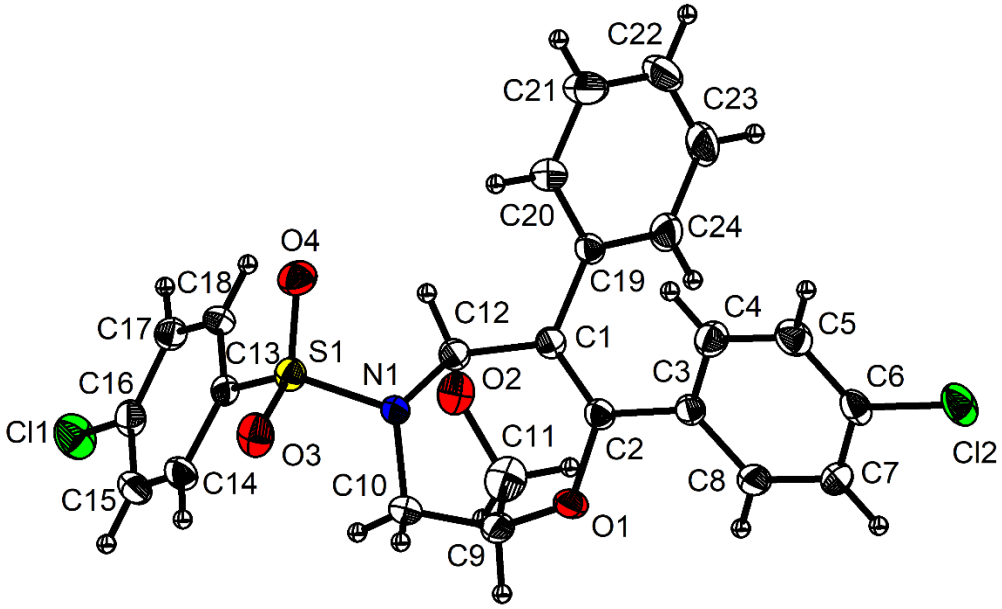
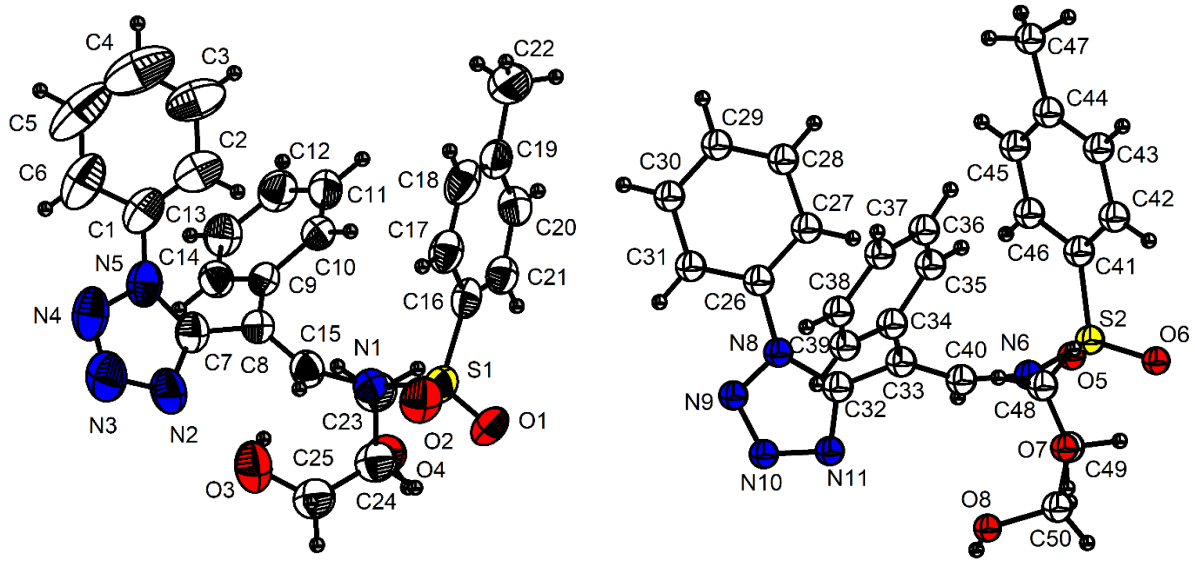


Figure S2. ORTEP view of 3-(4-chlorophenyl)-9-((4-chlorophenyl)sulfonyl)-4-phenyl-2,6-dioxa-9-azabicyclo[3.2.2]non-3-ene **4db** with 30% probability of ellipsoids. ***Crystal data:*** $C_{24}H_{19}Cl_2NO_4S$, M = 488.39, Monoclinic, Space group P 1 21/c 1, a = 12.9092(17), b = 6.0215(7), c = 29.195(4) Å, V = 2242.7(5)Å^3, α = 90, β = 98.799 (5), γ = 90^o, Z = 4, μ = 0.415 mm^{-1}, data/restraints/parameters: 5135/0/289, R indices (>2sigma(I)): R1 = 0.0490 (3649), *w*R2 (all data) = 0.1441 (5135). Selected bond parameters: S1-N1 1.6464(19, N1-C12 1.465(3), N1-C10 1.480(3), O2-C12 1.427(3), O2-C11 1.448(4), C9-C10 1.500(4), C9-C11 1.515(4), C1-C12 1.517(3), C1-C2 1.338(3), O1-C9 1.446(3), O1-C2 1.373(3), C3-C2 1.493(3), C1-C19 1.490(3) (Å). CCDC No: 2237335



Molecule-1 (**5ba**) Molecule-2 (**5ba**)

Figure S3. ORTEP view of (*E*)-*N*-(2,3-dihydroxypropyl)-4-methyl-N-(2-phenyl-2-(1-phenyl-1H-tetrazol-5-yl)vinyl)benzenesulfonamide **5ba** with 30% probability of ellipsoids. ***Crystal data:*** $C_{25}H_{24}N_5O_4S$, M = 491.56, Monoclinic, Space group P 1 21/c 1, a = 20.3465(7), b = 10.9821(3), c = 23.9221(9) Å, V = 4954.2(3) Å^3, α = 90, β = 112.054 (4), γ = 90^o ,Z= 4, μ = 0.172 mm^{-1}; data/restraints/parameters: 8741/0/631, R indices (I> 2sigma(I)): R1 = 0.1008 (5049), wR2 (all data) = 0.3473 (8741). Selected bond parameters: S1-N1 1.642(5), N1-C15 1.423(7), N1-C23 1.487(8), C23-C24 1.492(9), C24-C25 1.434(9), C8-C7 1.461(8), C9-C8 1.469(7), C8-C15 1.343(7), O4-C24 1.466(8), O3-C25 1.422(9), C7-N2 1.340(8), N5-C7 1.335(8), N5-C1 1.444(10), N2-N3 1.347(8), N4-N3 1.268(9), N5-N4 1.379(8) (Å). Molecule-2: S2-N6 1.646(5), N6-C48 1.477(7), N6-C40 1.408(7), C48-C49 1.380(12), C50-C49 1.321(12), C33-C40 1.340(7), C34-C33 1.481(7), C33-C32 1.470(7), O7-C49 1.446(10), O8-C50 1.400(11), N11-C32 1.327(7), N8-C26 1.440(7), N8-C32 1.333(6), N8-N9 1.348(6), N9-N10 1.272(7), N11-N11 1.371(7). CCDC No: 2237336.

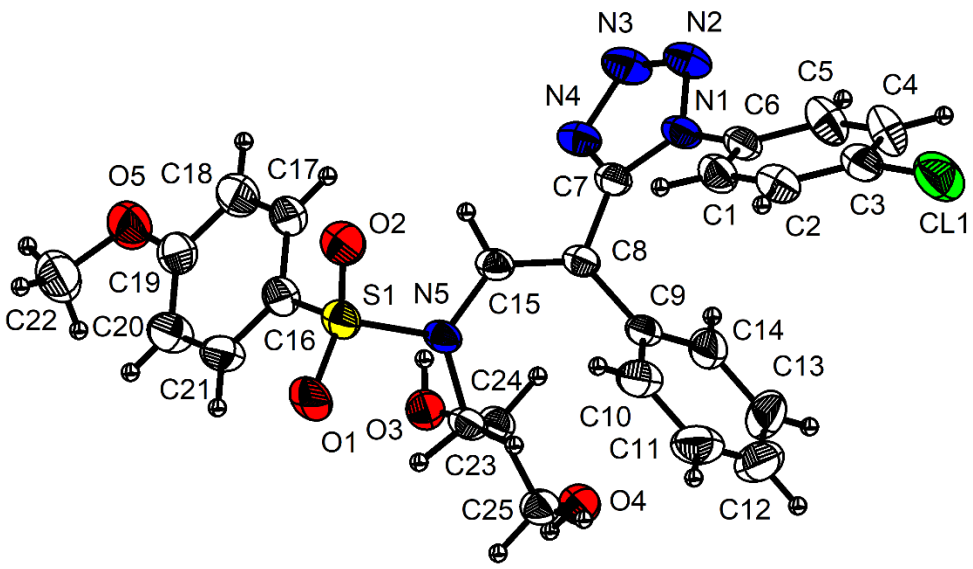


Figure S4. ORTEP view of (*E*)-*N*-(2-(1-(4-chlorophenyl)-1H-tetrazol-5-yl)-2-phenylvinyl)-N-(2,3-dihydroxypropyl)-4-methoxybenzenesulfonamide **5cb** with 30% probability of ellipsoids. ***Crystal data****:* $C_{25}H_{24}ClN_5O_5S$, M = 542.00, Triclinic, Space group $P\bar{1}$, a = 10.4254(3), b = 11.9858(4), c = 12.4011(3) Å, V = 1403.61(8) $Å^3$, α = 69.515(3), β = 75.700(3), γ = 88.454(3)^o ,Z= 2, μ = 0.398 mm^{-1}; data/restraints/parameters: 5921/0/331, R indices (I> 2sigma(I)): R1 = 0.0530 (3605), wR2 (all data) = 0.1622 (5921). Selected bond parameters: S1-N5 1.6622(18), N5-C23 1.487(2), N5-C15 1.395(3), C24-C23 1.528(3), C24-C25 1.503(3), C8-C15 1.343(3), C8-C9 1.475(3), C8-C7 1.456(3), O4-C25 1.412(3), O3-C24 1.411(2), N1-C7 1.355(3), N1-C6 1.423(3), N1-N2 1.365(2), N2-N3 1.273(3), N4-N3 1.363(3), N4-C7 1.320(3) (Å) CCDC No: 2237337

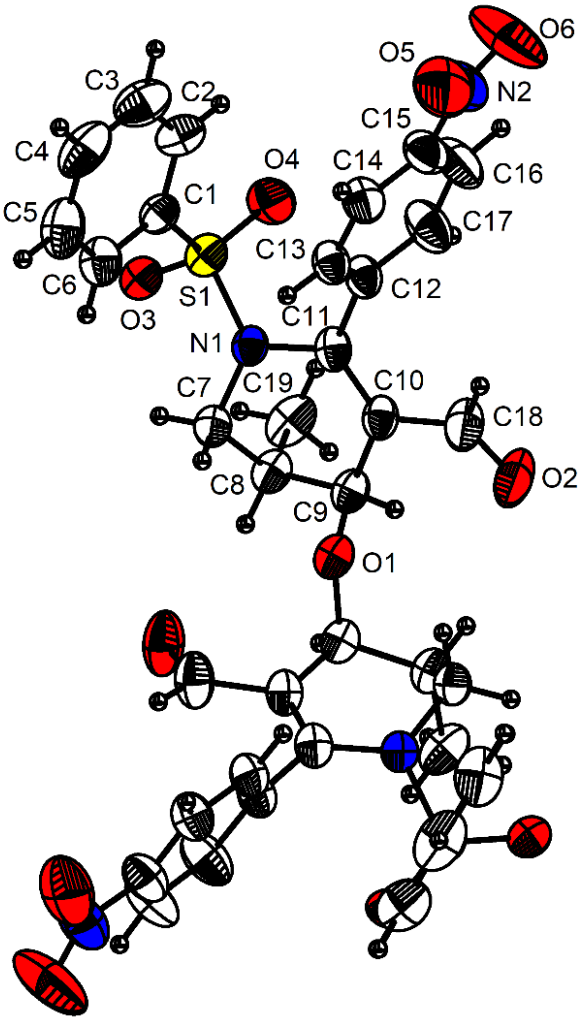
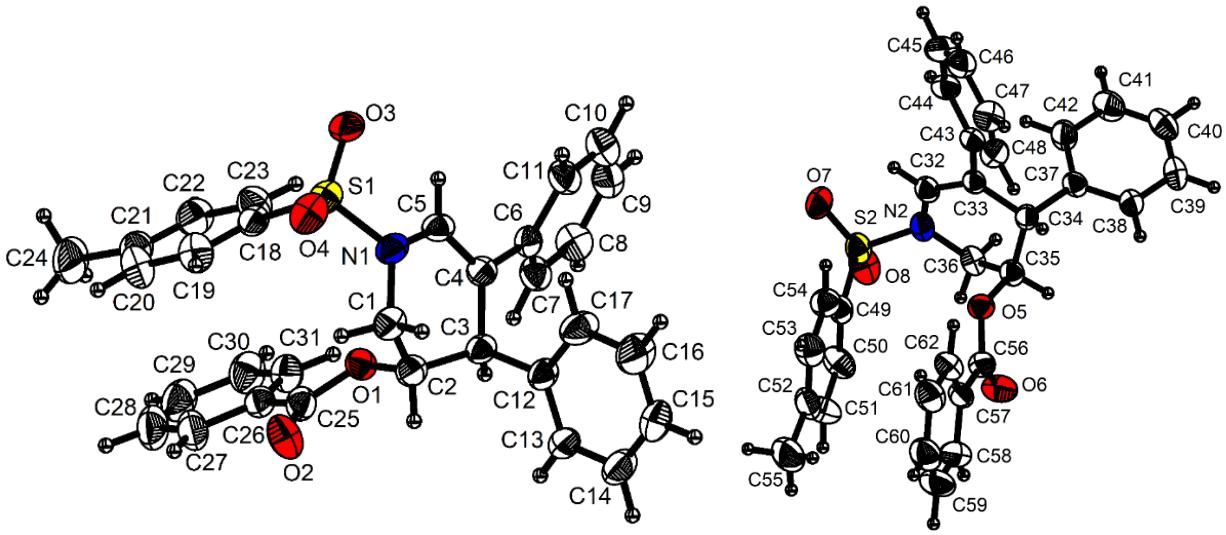


Figure S5. ORTEP view of 5-formyl-3-methyl-6-(4-nitrophenyl)-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridin-4-yl)oxy)-5-methyl-2-(4-nitrophenyl)-1-(phenylsulfonyl)-1,4,5,6-tetrahydropyridine-3-carbaldehyde **6hc** with 30% probability of ellipsoids. ***Crystal data:*** $C_{38}H_{34}N_4O_{11}S_2$, M = 786.81, orthorhombic, Space group P b c n, a = 25.8268(11), b = 16.2750(7), c = 10.0472(5) Å, V = 4223.2 (3) Å^3, α = 90, β = 90, γ = 90, Z= 4, μ = 0.185 mm^{-1}, data/restraints/parameters: 3723/0/244, R indices (I> 2sigma(I)): R1 = 0.0579 (2260), wR2 (all data) = 0.1784 (3723). Selected bond parameters: S1-N1 1.677(2), N1-C7 1.475(4), N1-C11 1.399(4), C7-C8 1.519(4), C9-C8 1.515(4), C9-C10 1.492(4), C11-C10 1.348(4), C10-C18 1.463(5), C11-C12 1.493(4), O1-C9 1.445(3) (Å) CCDC No: 2237338.



Molecule-1 (**7la**) Molecule-2 (**7la**)

Figure S6. ORTEP view of 4,5-diphenyl-1-tosyl-1,2,3,4-tetrahydropyridin-3-yl benzoate **7la** with 30% probability of ellipsoids. ***Crystal data:*** $C_{31}H_{27}NO_4S$, M = 509.59, Triclinic, Space group $P\bar{1}$, a = 7.1998(5), b = 16.6494(10), c = 21.1710(14) Å, V = 2652.7(3) Å^3, α = 76.121(5), β = 83.698 (5), γ = 89.177(5)^o, Z= 4, μ = 0.159 mm^{-1}; data/restraints/parameters: 8720/578/669, R indices (I> 2sigma(I)): R1 = 0.0954 (3545), wR2 (all data) = 0.3113 (8720). Selected bond parameters: S1-N1 1.642(5), N1-C1 1.465(7), N1-C5 1.414(7), C2-C1 1.509(7), C3-C2 1.525(7), C4-C3 1.497(7), C4-C5 1.333(7), O1-C2 1.459(6), O1-C25 1.359(7), O2-C25 1.201(7) (Å). Molecule-2: S2-N2 1.643(5), N2-C32 1.394(7), N2-C36 1.467(7), C32-C33 1.326(7), C34-C33 1.491(7), C34-C35 1.539(7), C35-C36 1.508(7), O5-C35 1.458(6), O5-C56 1.351(7), O6-C56 1.211(7) (Å). CCDC No: 2253326.

(6) References

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(7) ^{1}H and ^{13}C{^{1}H} NMR spectra

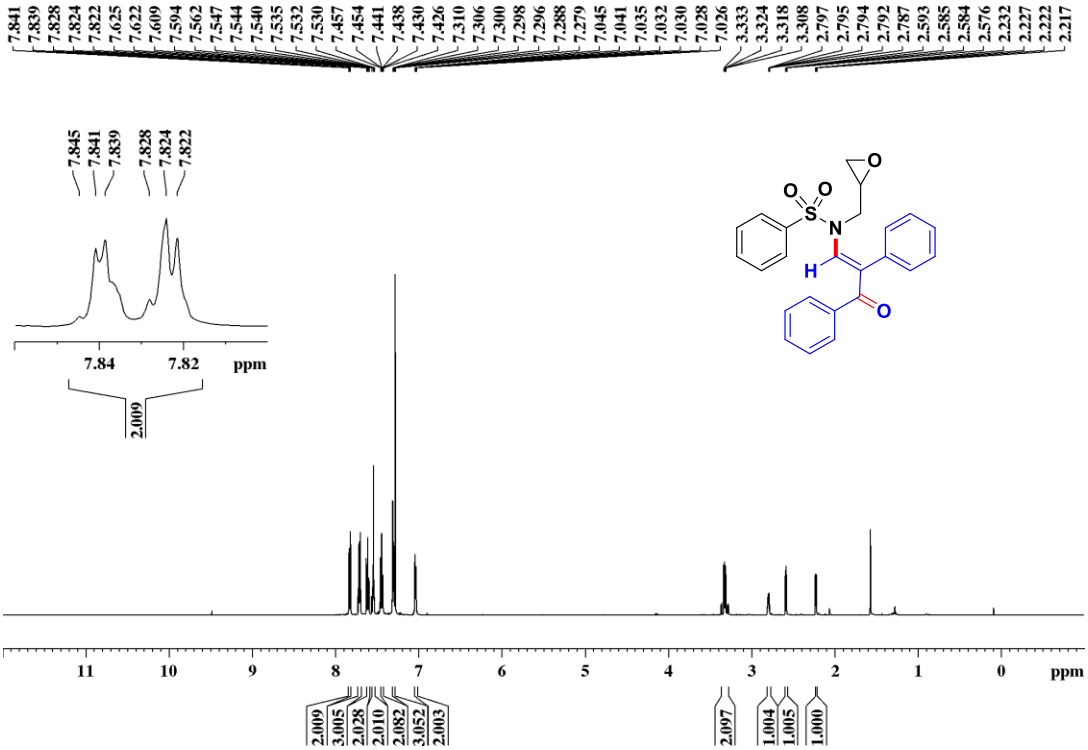

Figure S7. ^{1}H NMR spectrum of compound 3aa

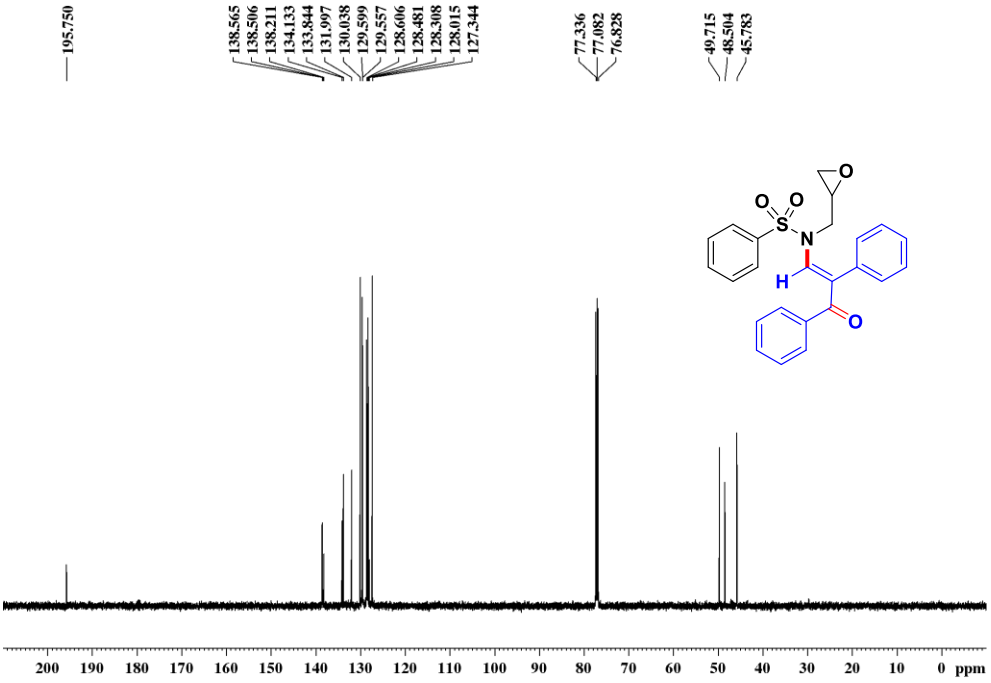

Figure S8. ^{13}C{^{1}H} NMR spectrum of compound 3aa

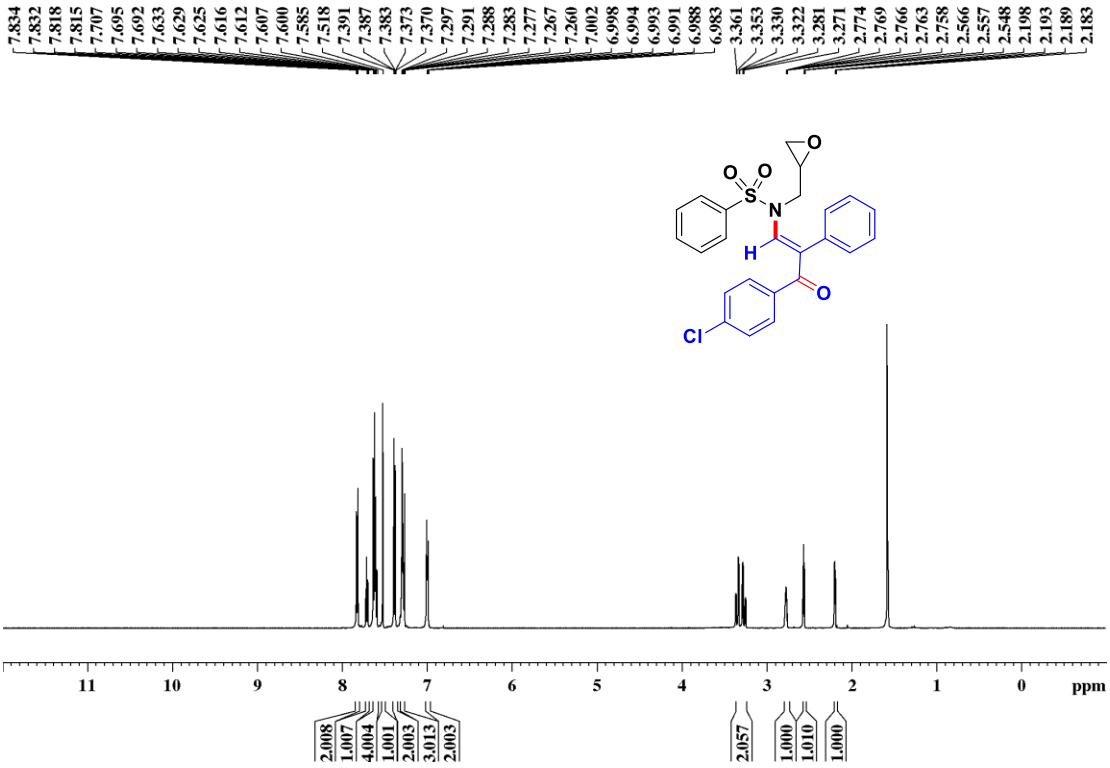

Figure S9. ^{1}H NMR spectrum of compound 3ab

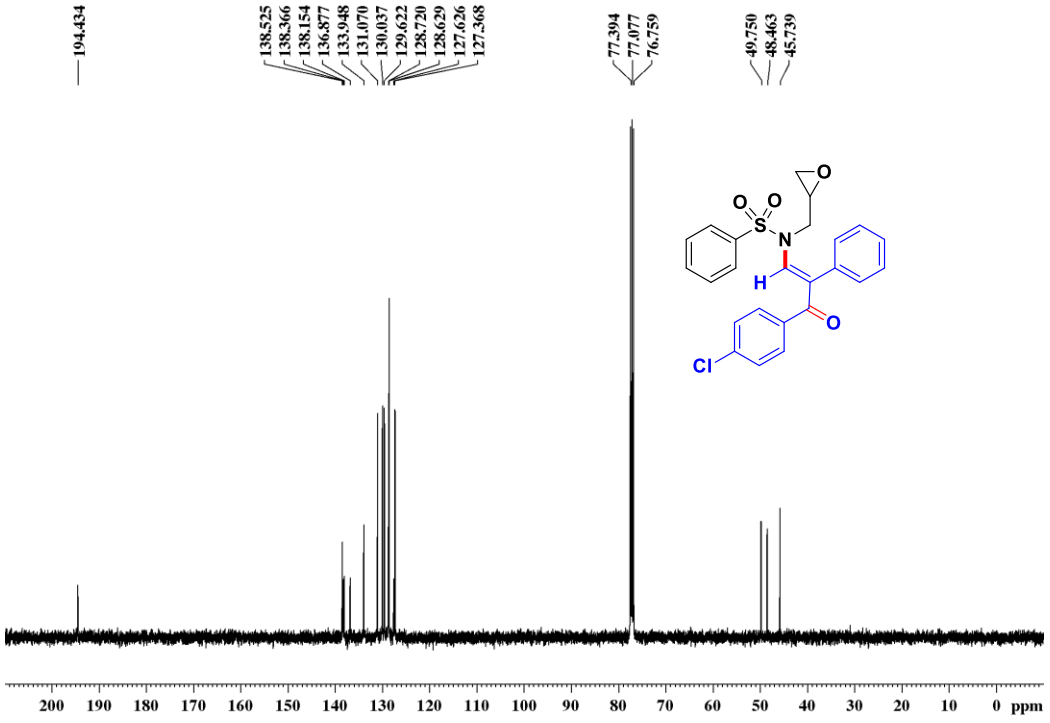

Figure S10. ^{13}C{^{1}H} NMR spectrum of compound 3ab

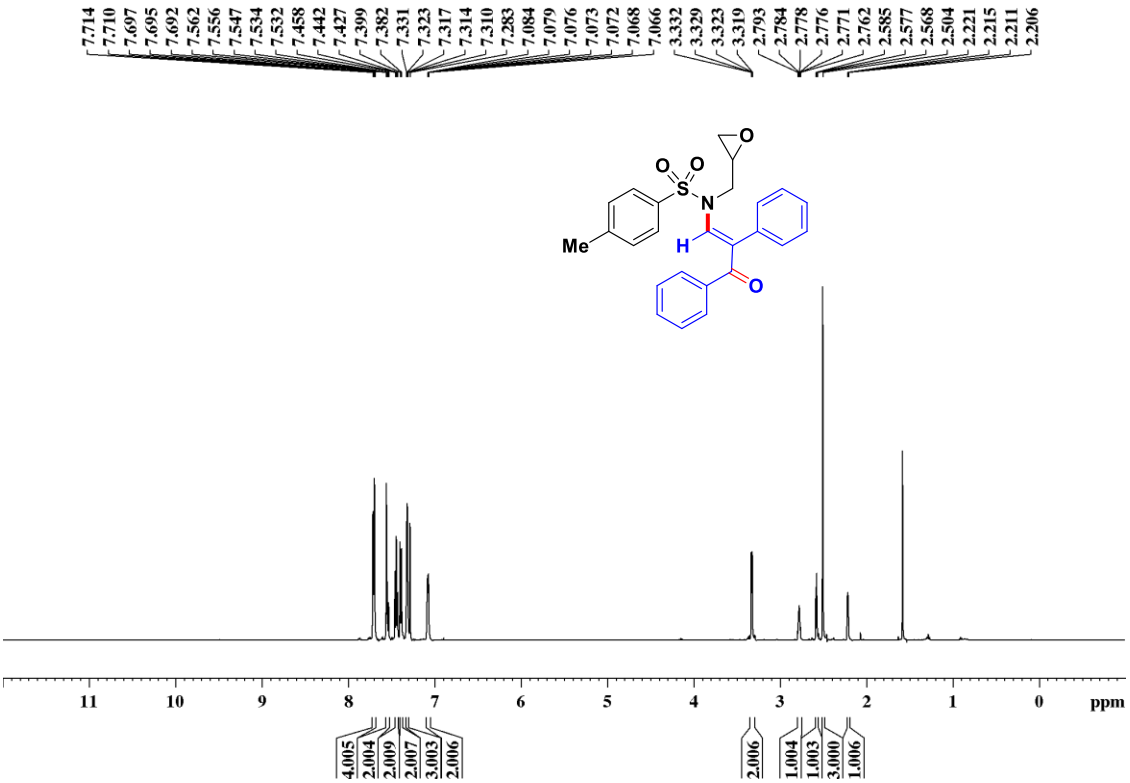

Figure S11. ^{1}H NMR spectrum of compound 3ba

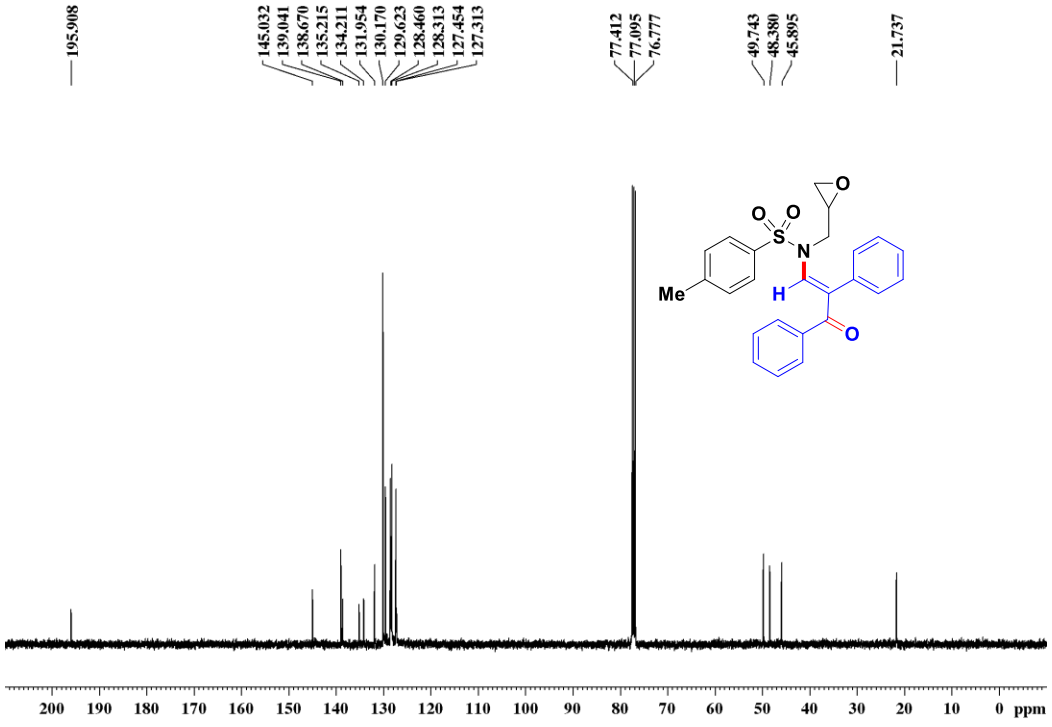

Figure S12. ^{13}C{^{1}H} NMR spectrum of compound 3ba

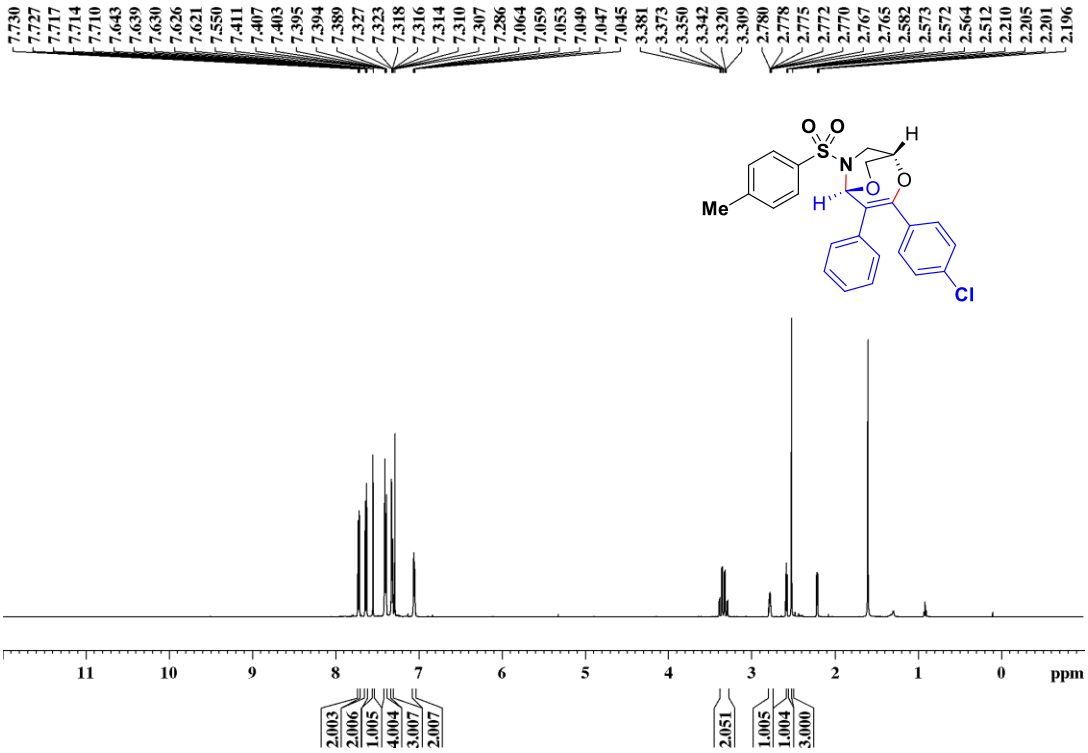

Figure S13. ^{1}H NMR spectrum of compound 3bb

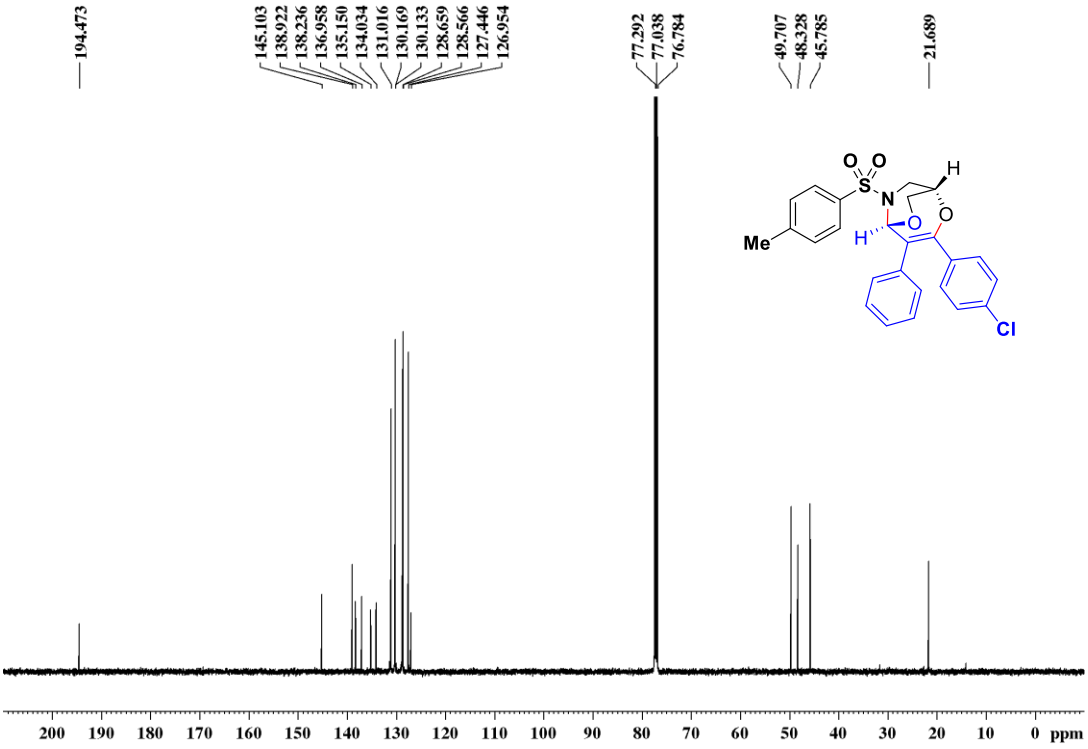

Figure S14. ^{13}C{^{1}H} NMR spectrum of compound 3bb

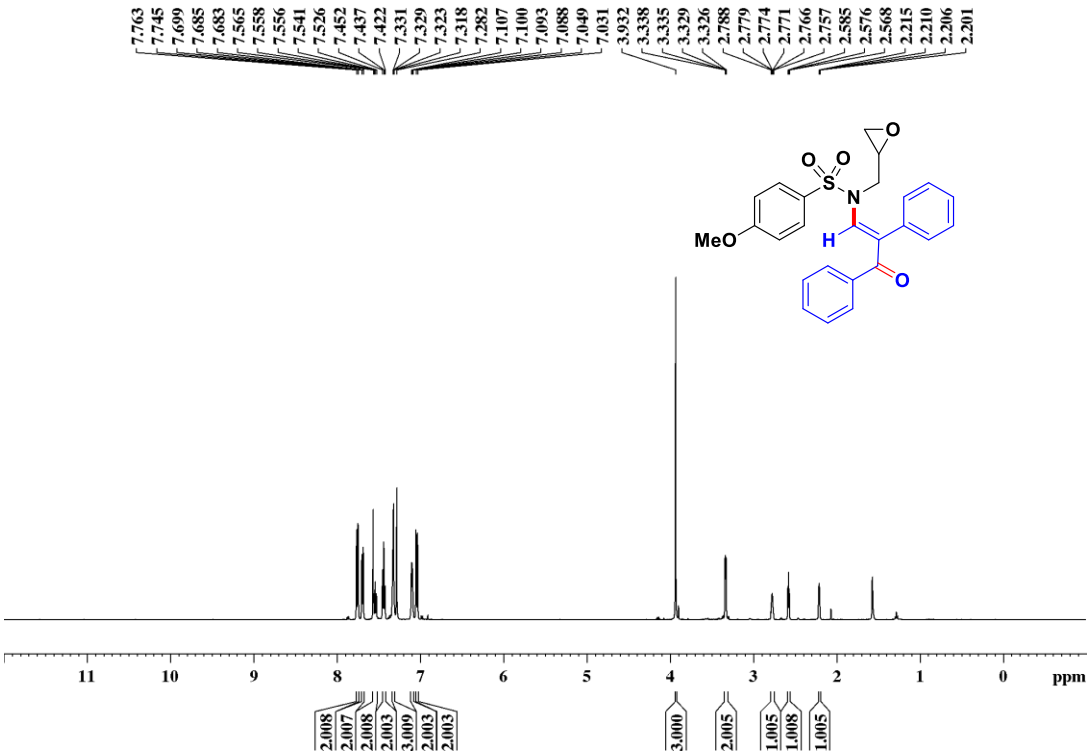

Figure S15. ^{1}H NMR spectrum of compound 3ca

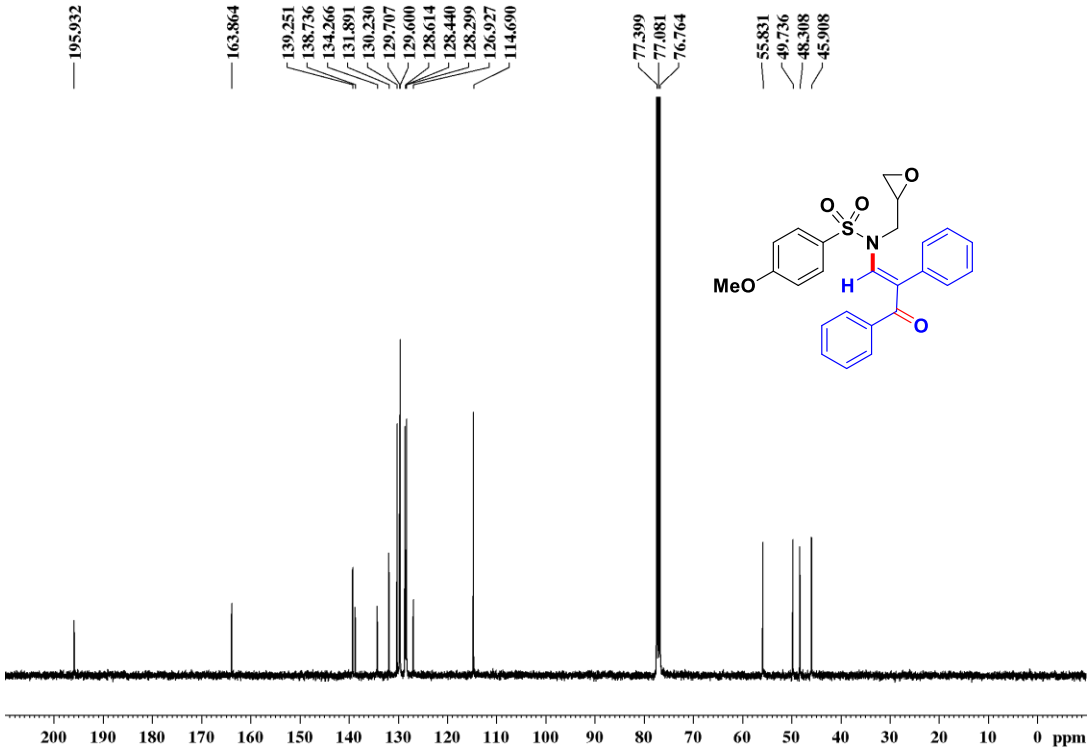

Figure S16. ^{13}C{^{1}H} NMR spectrum of compound 3ca

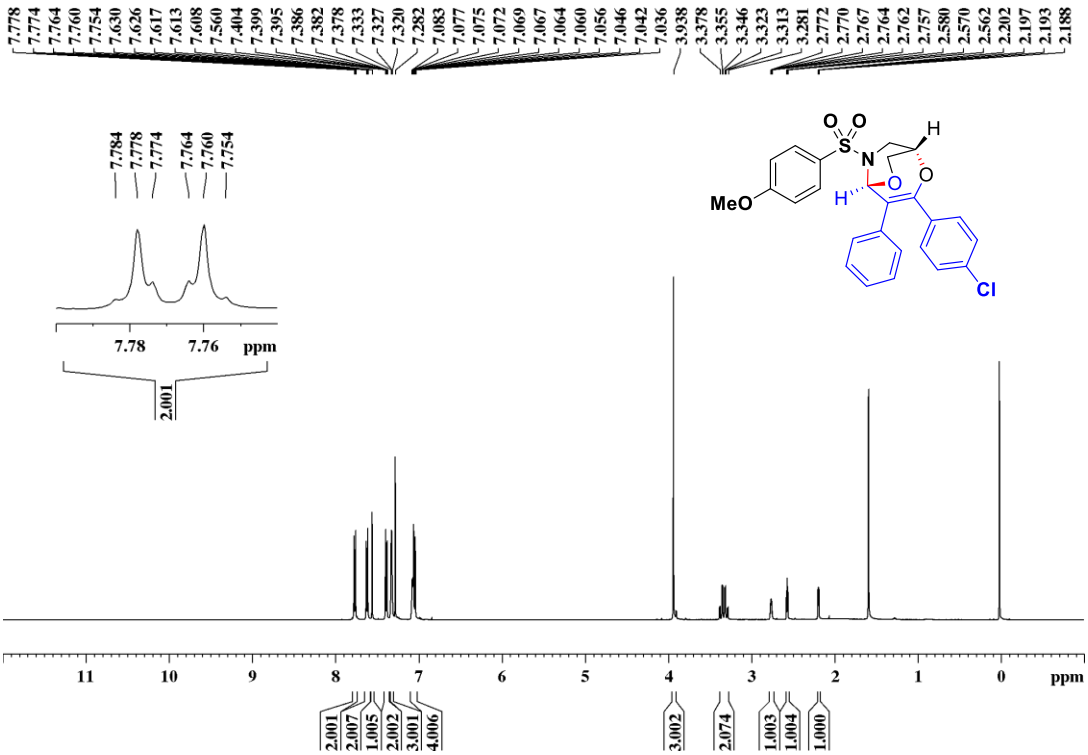

Figure S17. ^{1}H NMR spectrum of compound 3cb

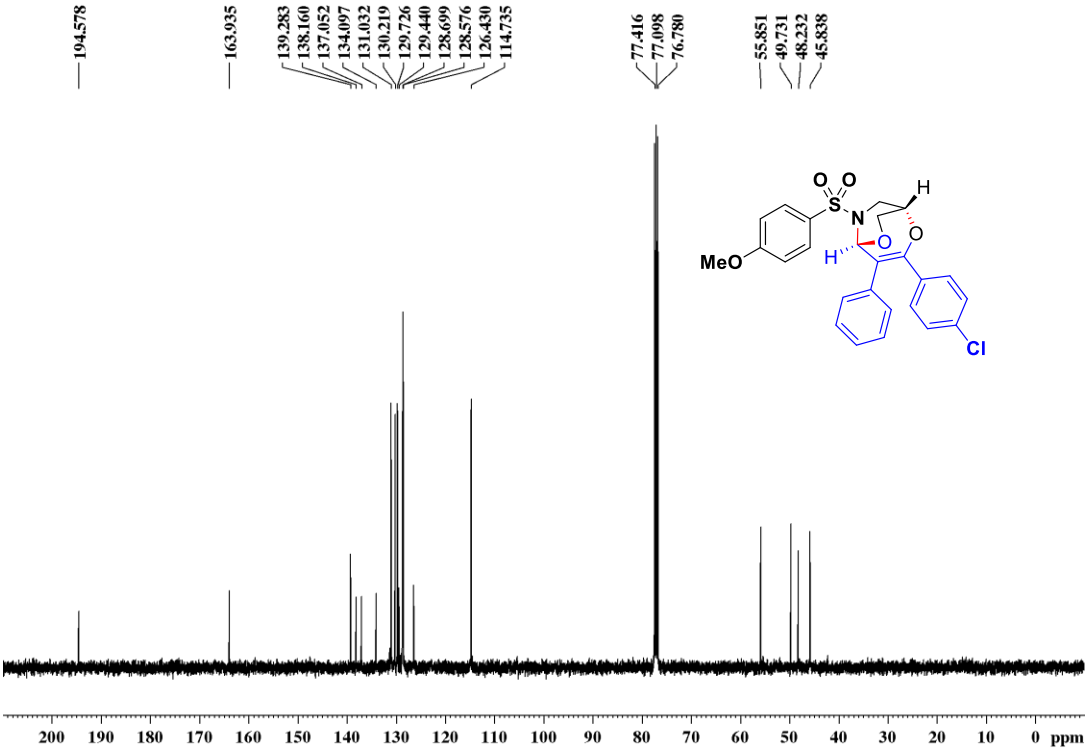

Figure S18. ^{13}C{^{1}H} NMR spectrum of compound 3cb

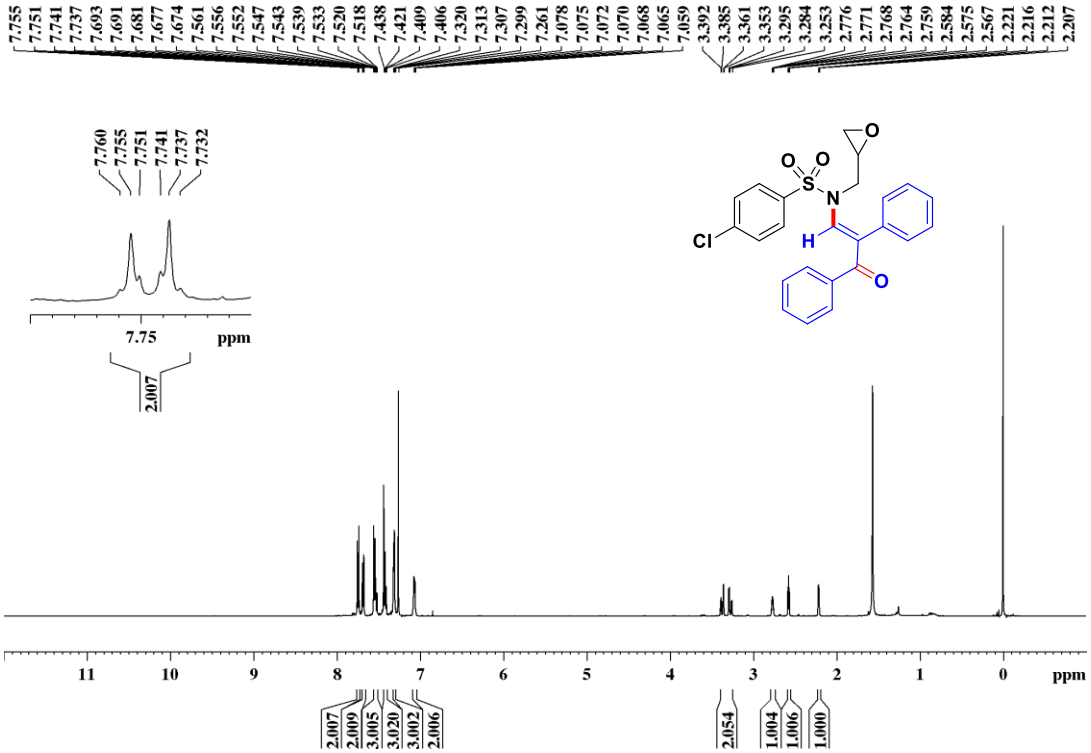

Figure S19. ^{1}H NMR spectrum of compound 3da

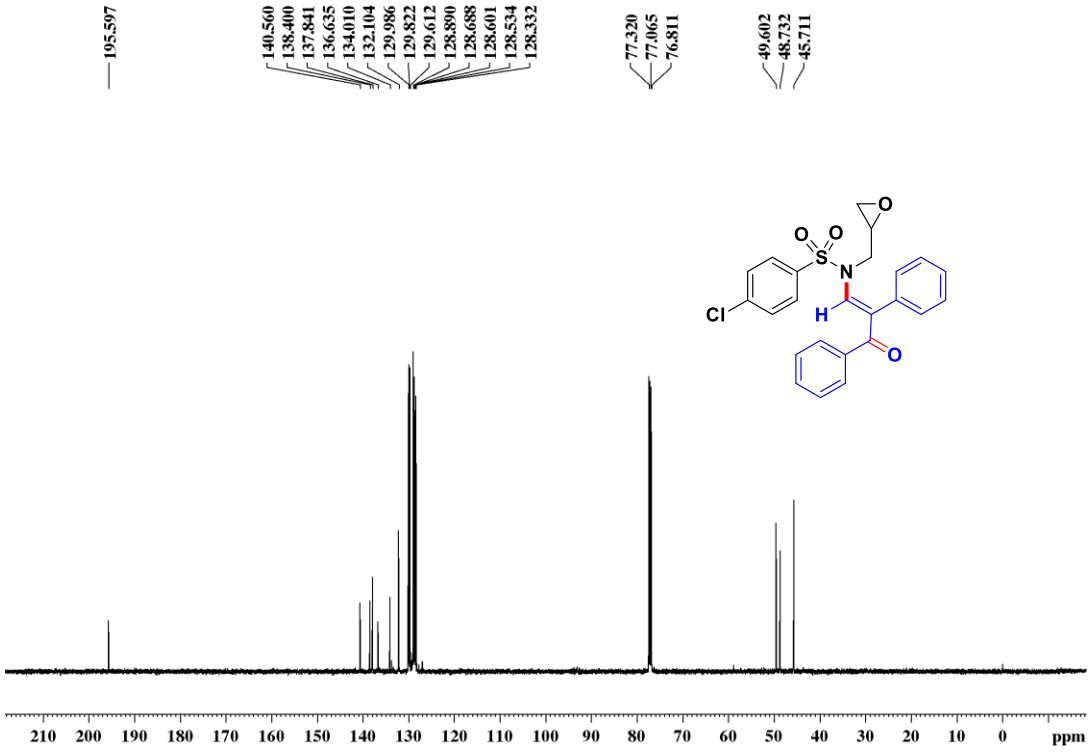

Figure S20. ^{13}C{^{1}H} NMR spectrum of compound 3da

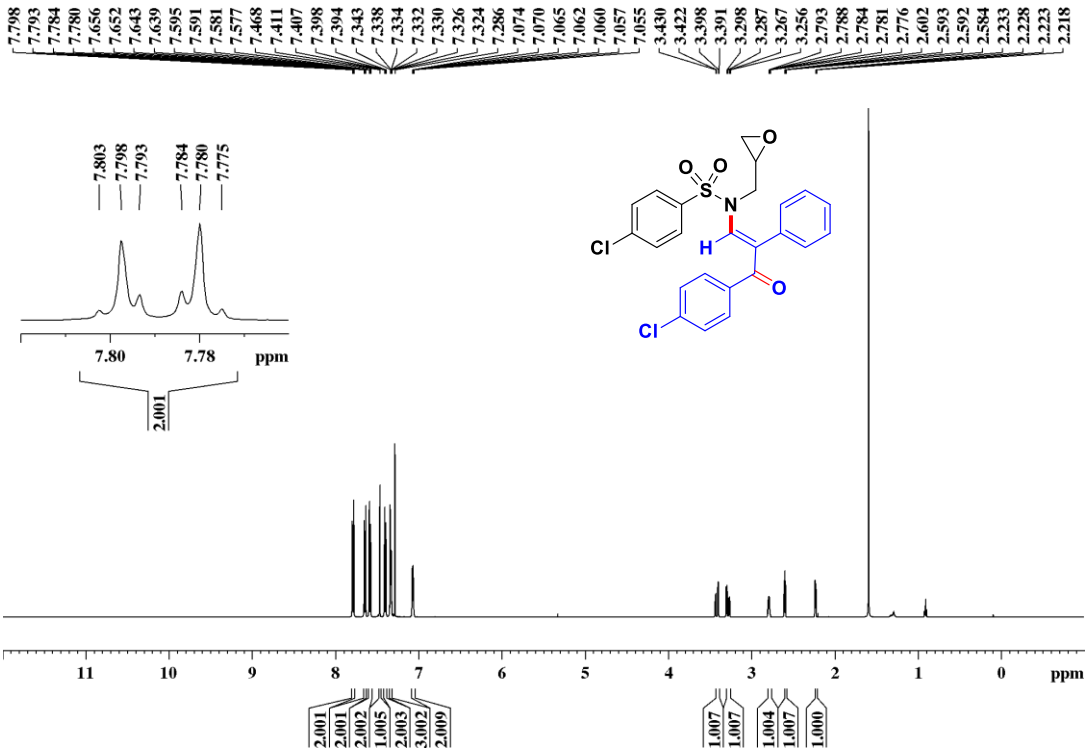

Figure S21. ^{1}H NMR spectrum of compound 3db

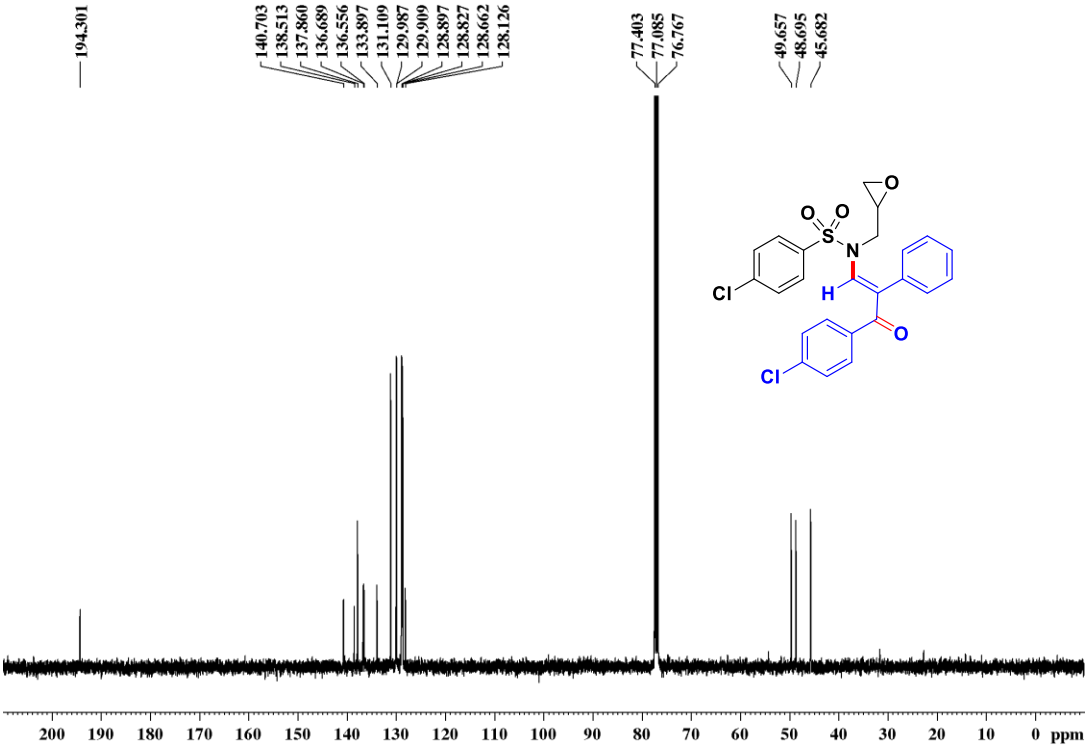

Figure S22. ^{13}C{^{1}H} NMR spectrum of compound 3db

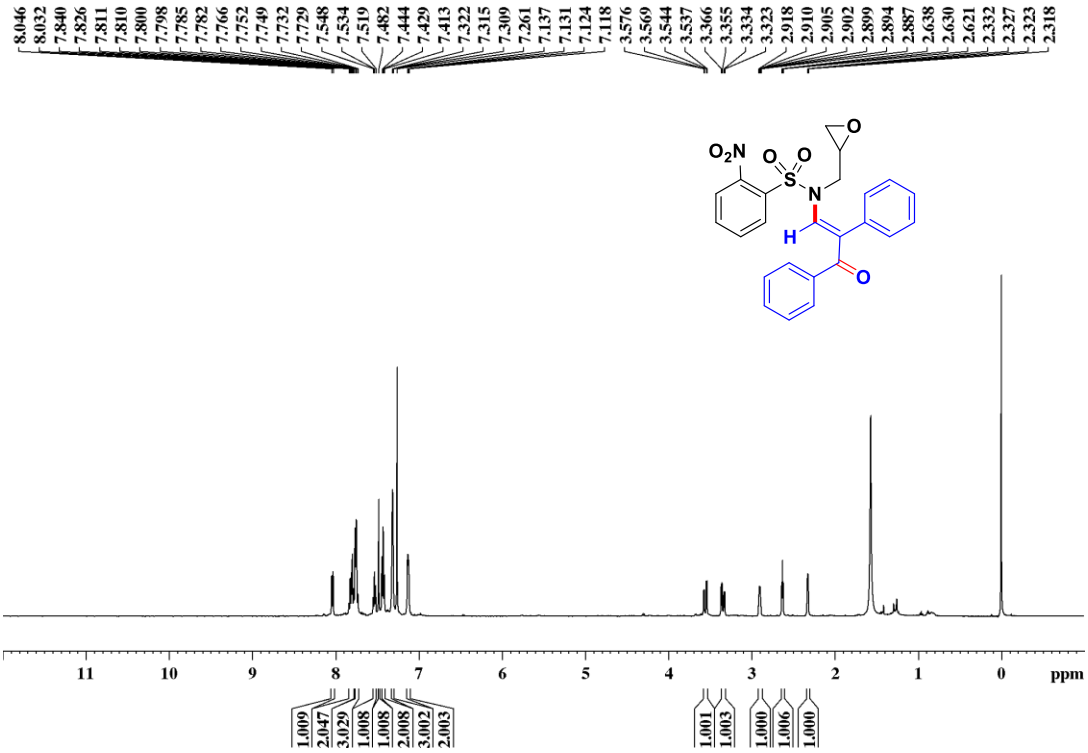

Figure S23. ^{1}H NMR spectrum of compound 3ea

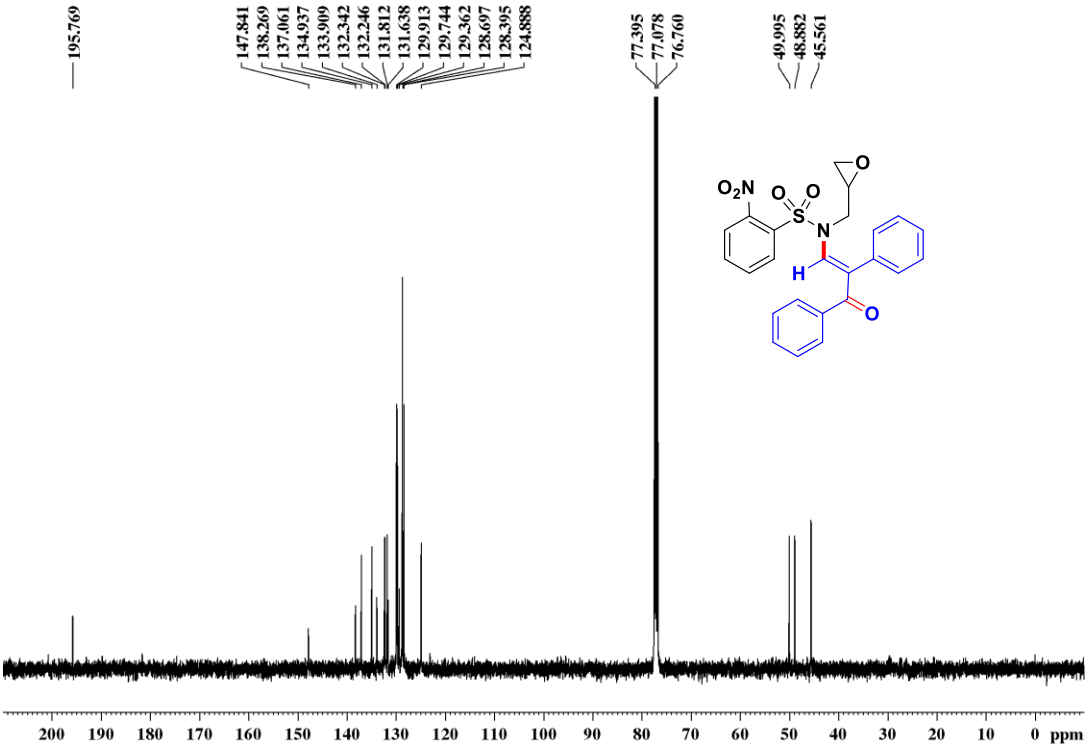

Figure S24. ^{13}C{^{1}H} NMR spectrum of compound 3ea

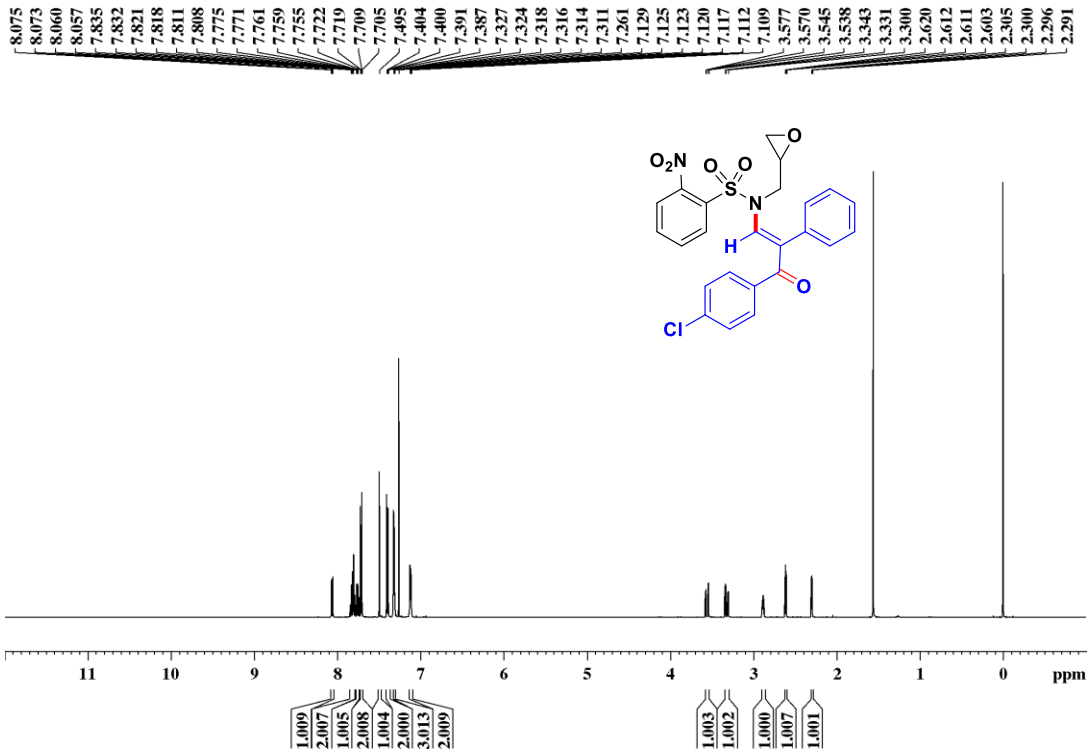

Figure S25. ^{1}H NMR spectrum of compound 3eb

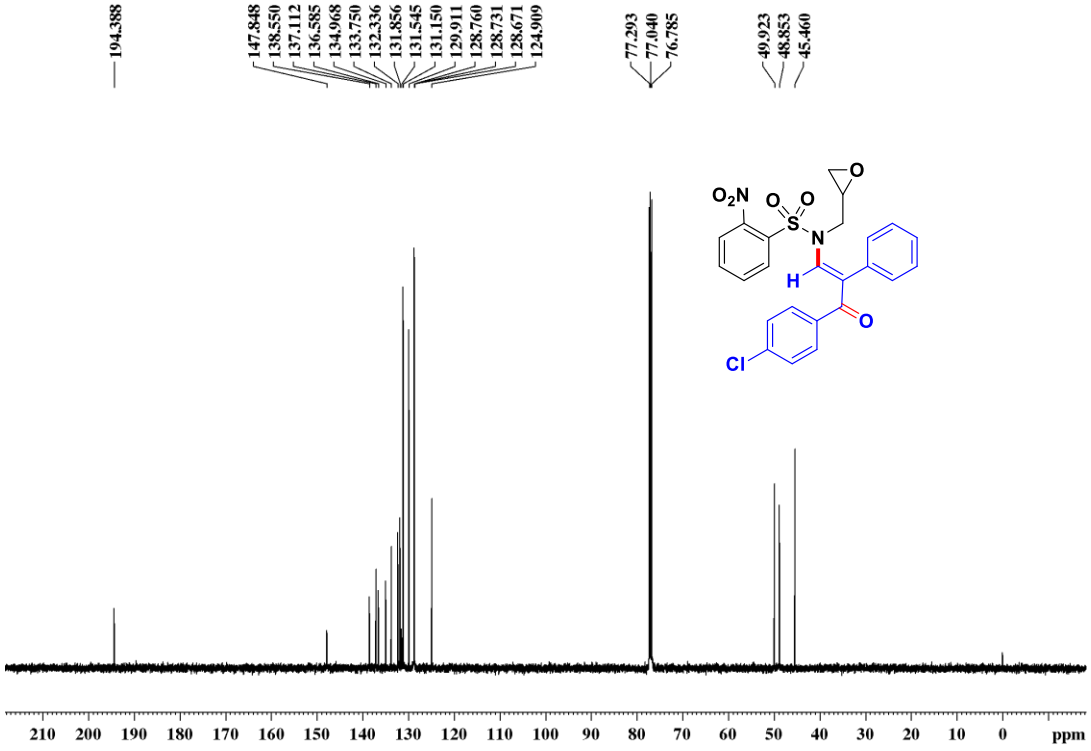

Figure S26. ^{13}C{^{1}H} NMR spectrum of compound 3eb

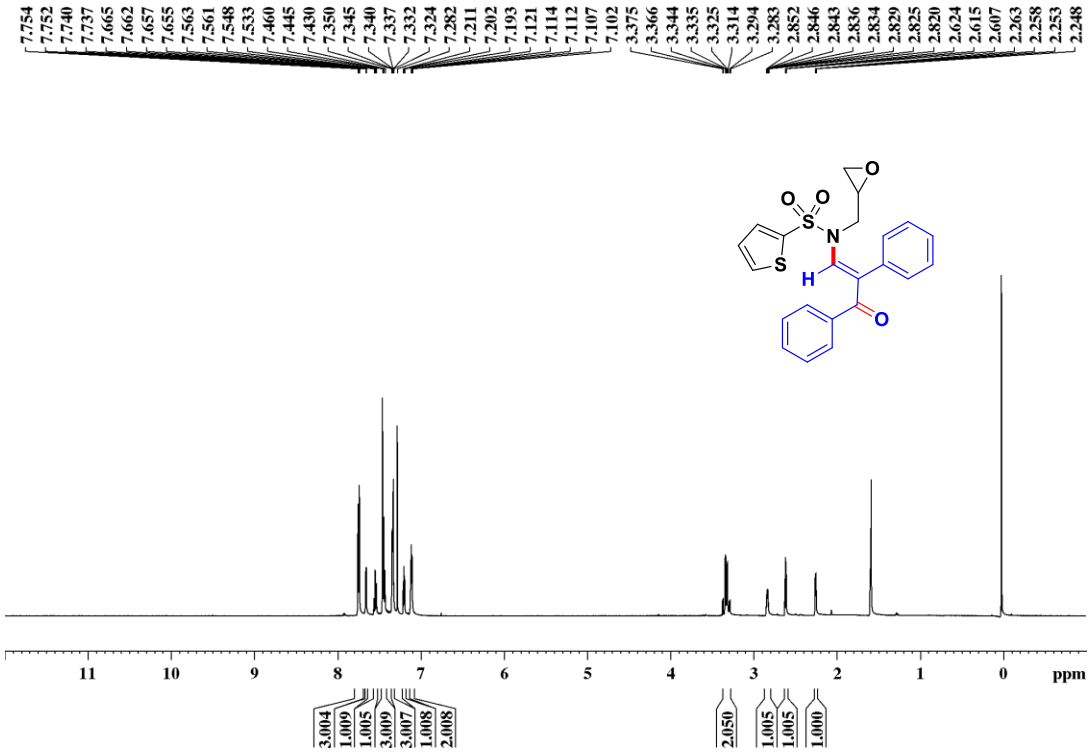

Figure S27. ^{1}H NMR spectrum of compound 3fa

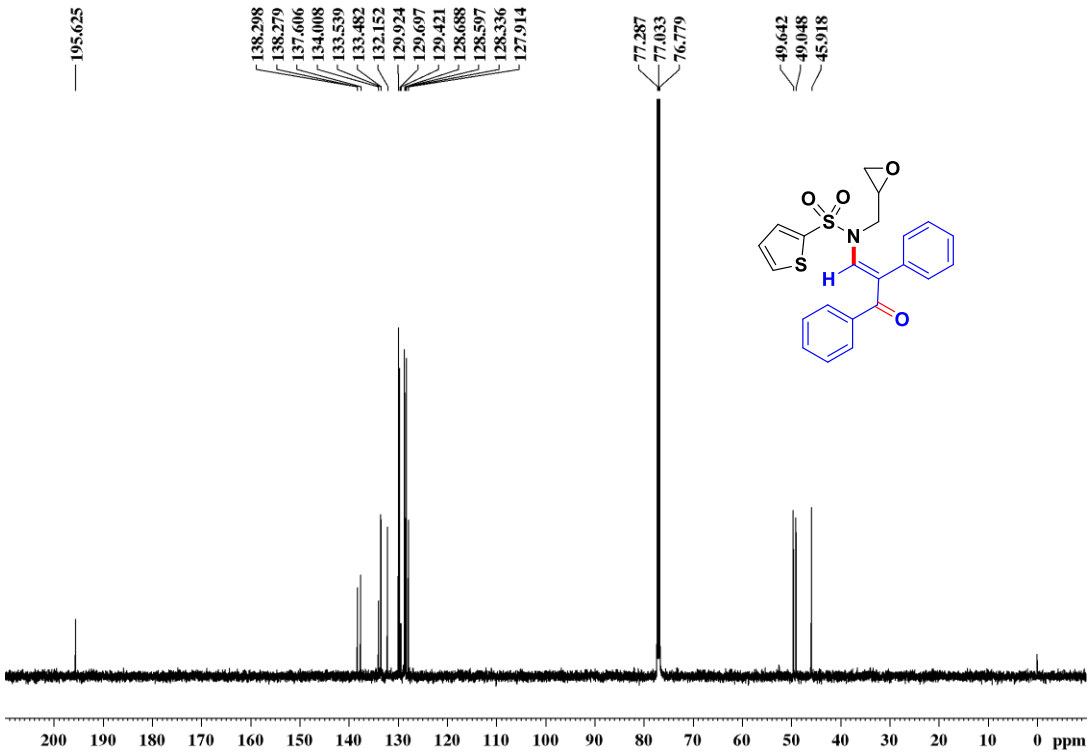

Figure S28. ^{13}C{^{1}H} NMR spectrum of compound 3fa

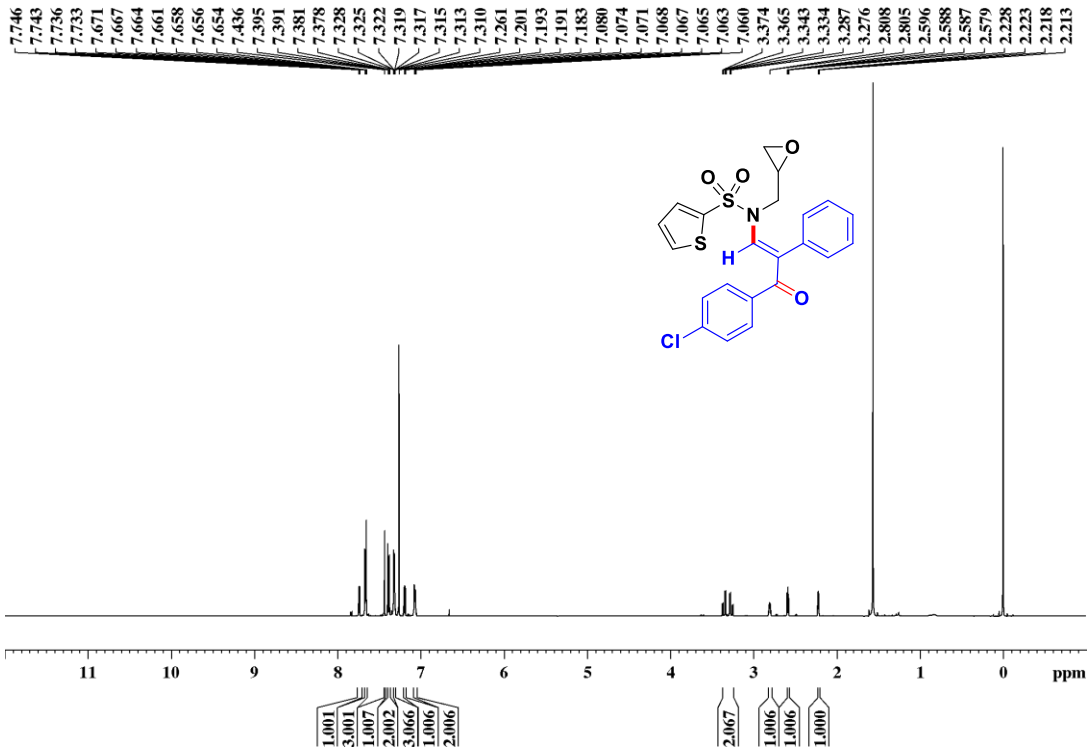

Figure S29. ^{1}H NMR spectrum of compound 3fb

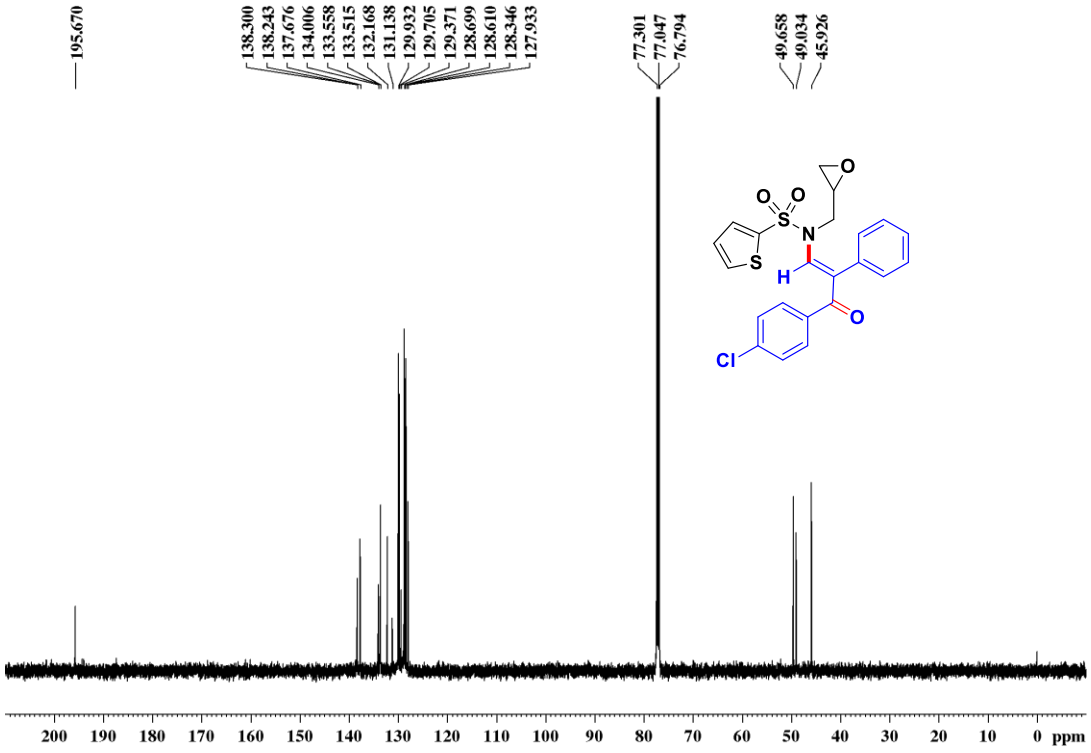

Figure S30. ^{13}C{^{1}H} NMR spectrum of compound 3fb

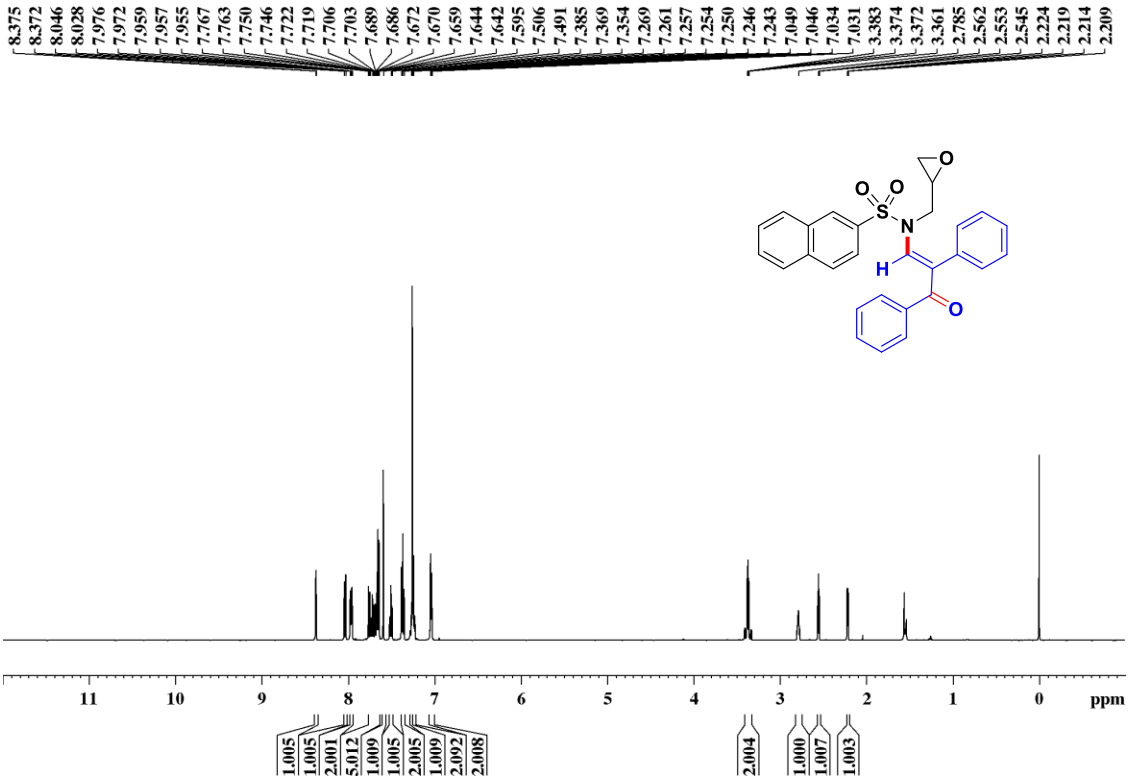

Figure S31. ^{1}H NMR spectrum of compound 3ga

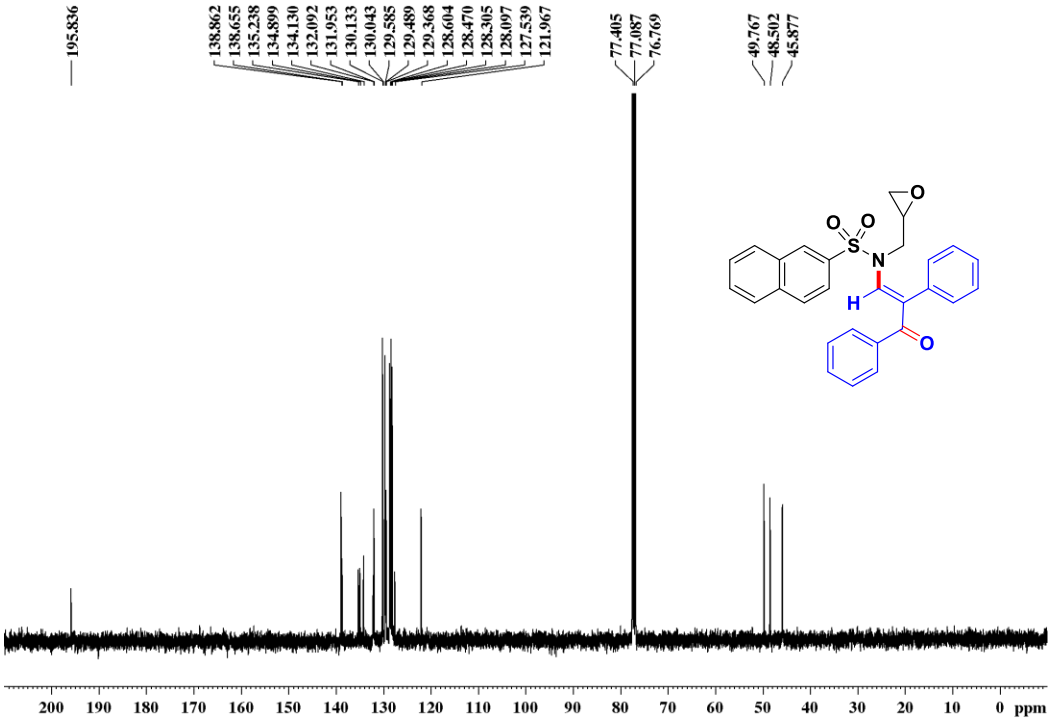

Figure S32. ^{13}C{^{1}H} NMR spectrum of compound 3ga

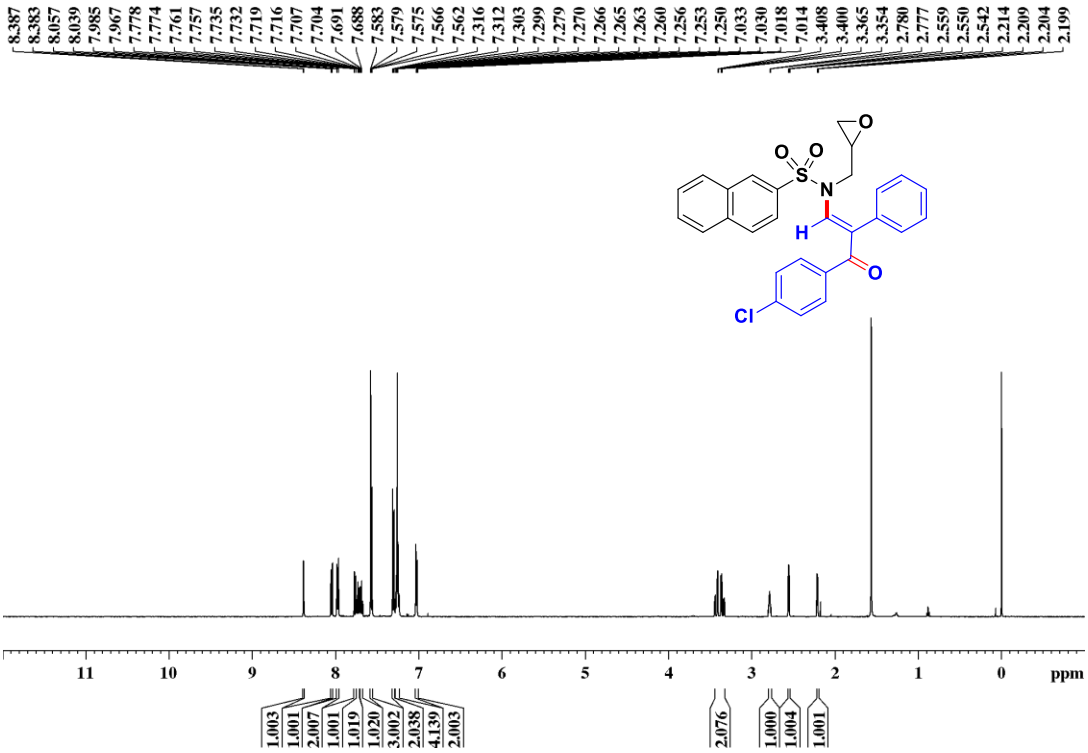

Figure S33. ^{1}H NMR spectrum of compound 3gb

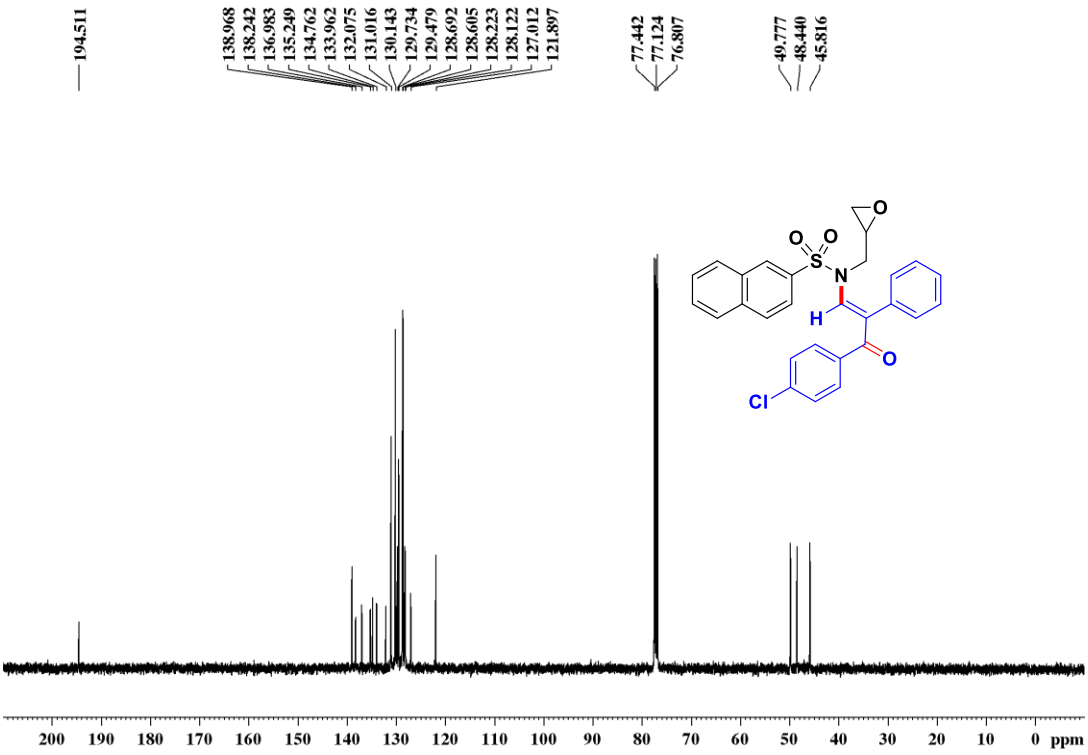

Figure S34. ^{13}C{^{1}H} NMR spectrum of compound 3gb

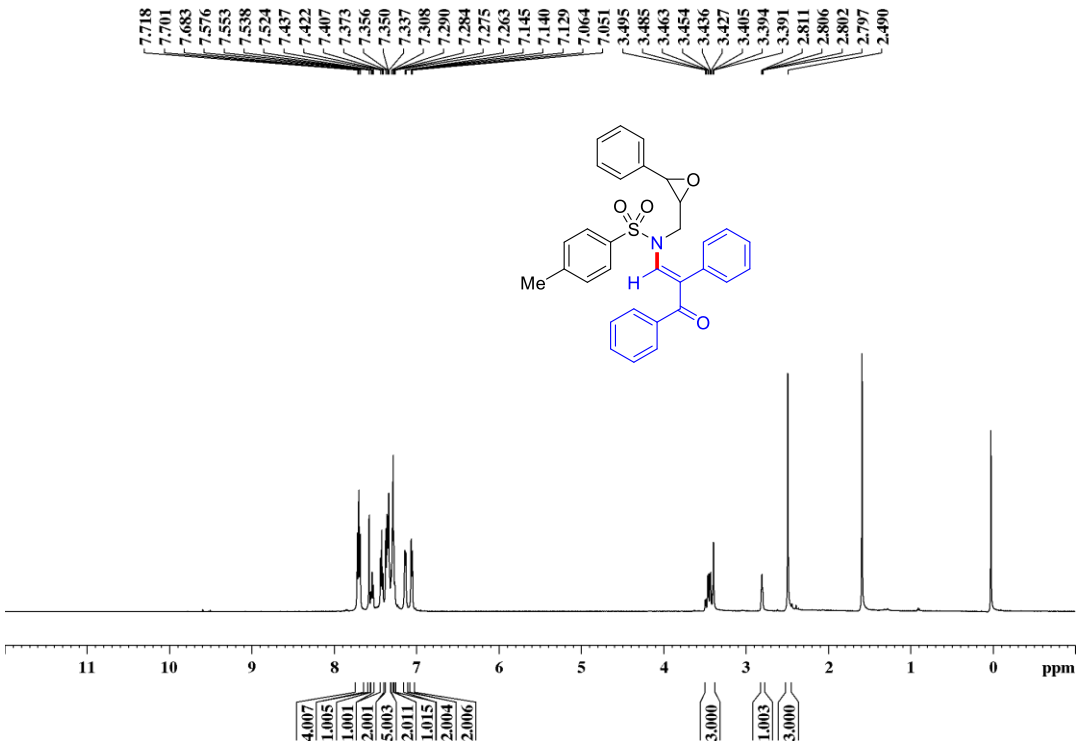

Figure S35. ^{1}H NMR spectrum of compound 3la

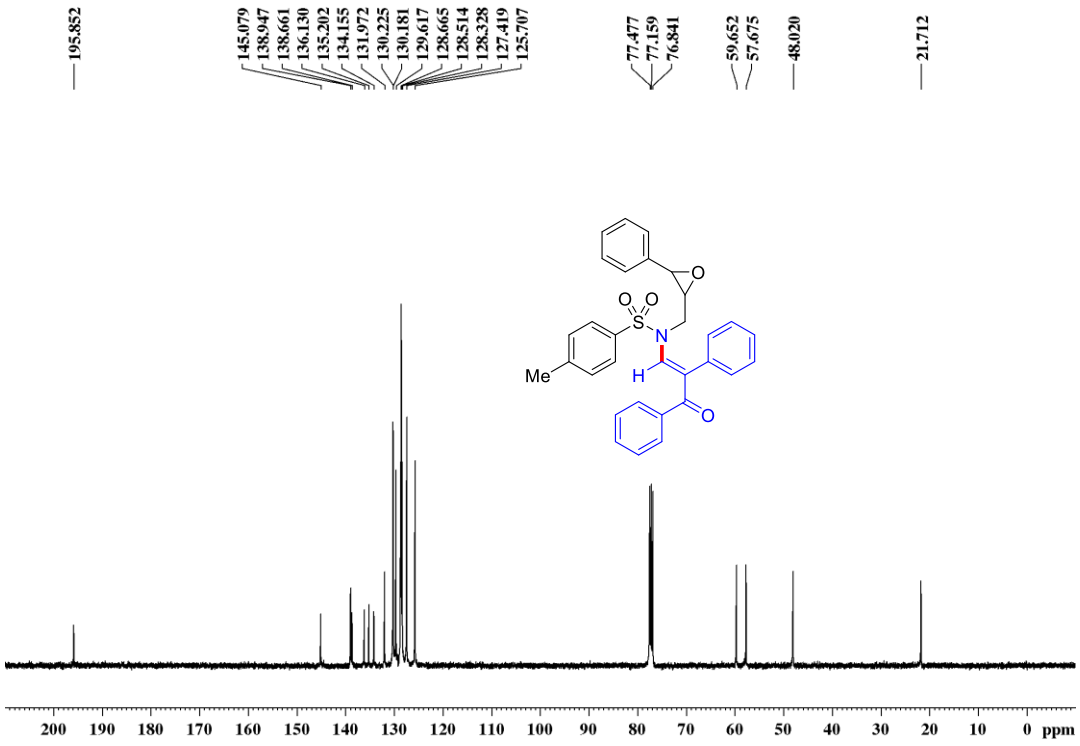

Figure S36. ^{13}C{^{1}H} NMR spectrum of compound 3la

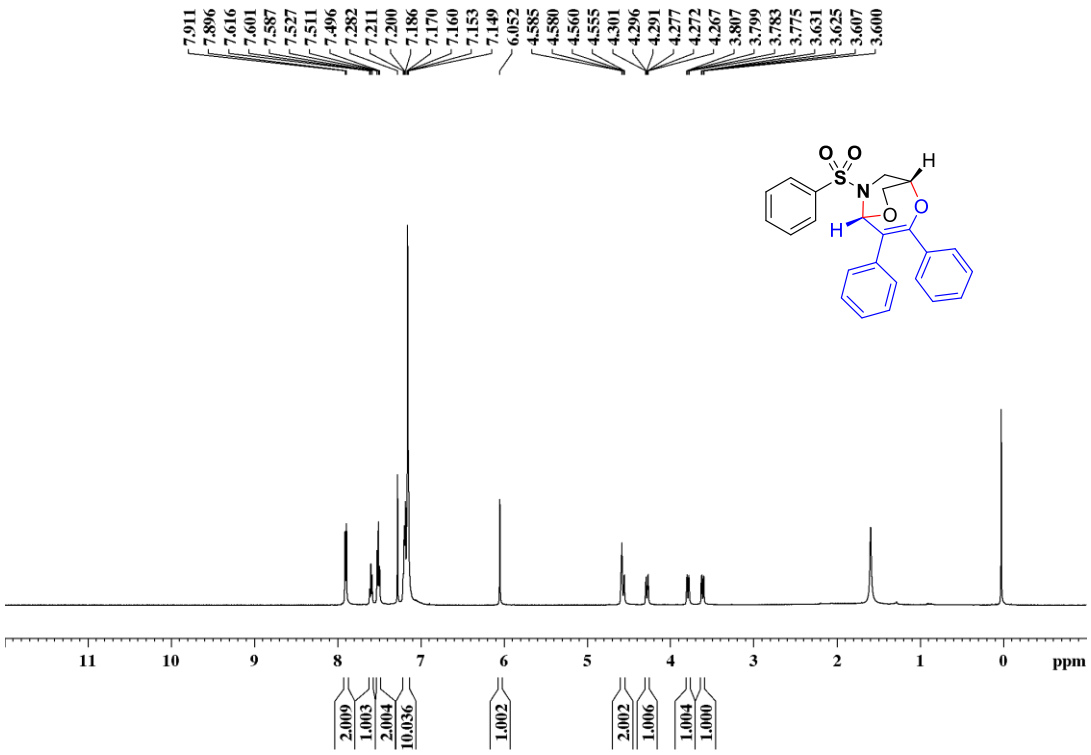

Figure S37. ^{1}H NMR spectrum of compound 4aa

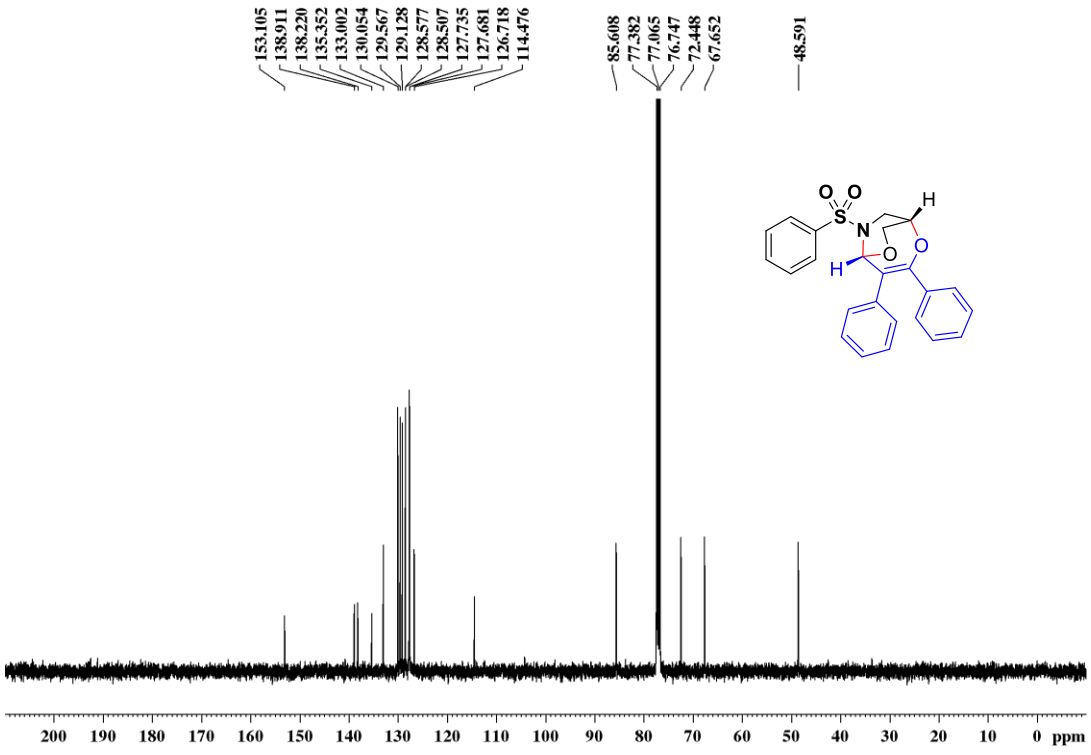

Figure S38. ^{13}C{^{1}H} NMR spectrum of compound 4aa

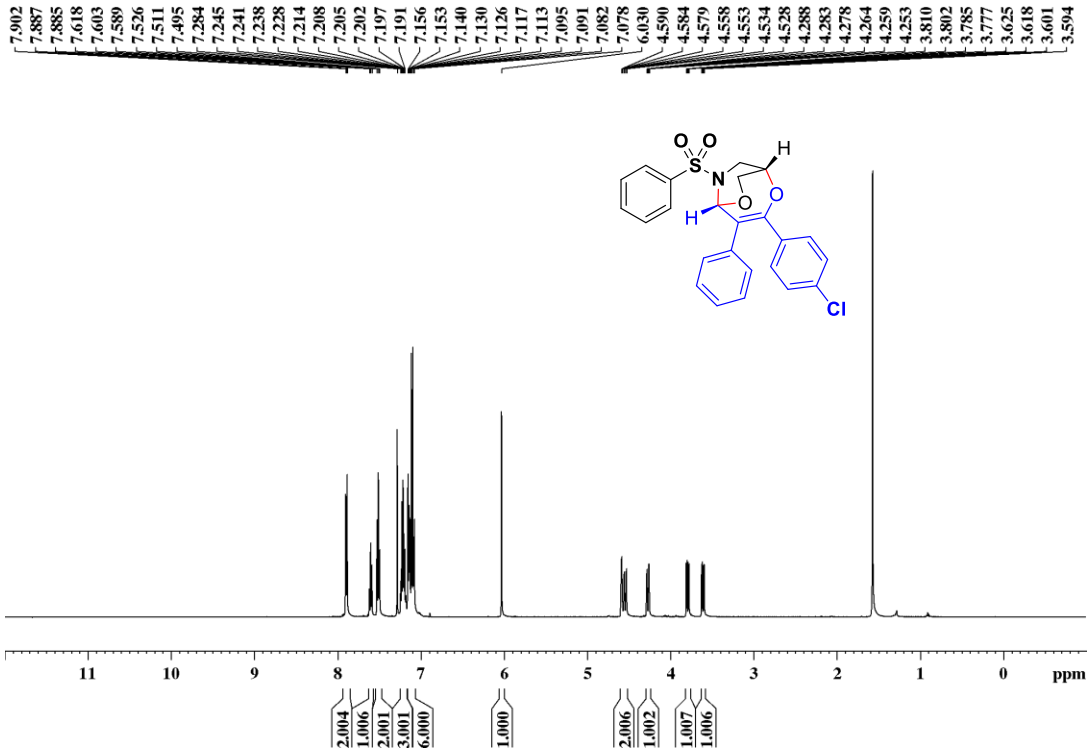

Figure S39. ^{1}H NMR spectrum of compound 4ab

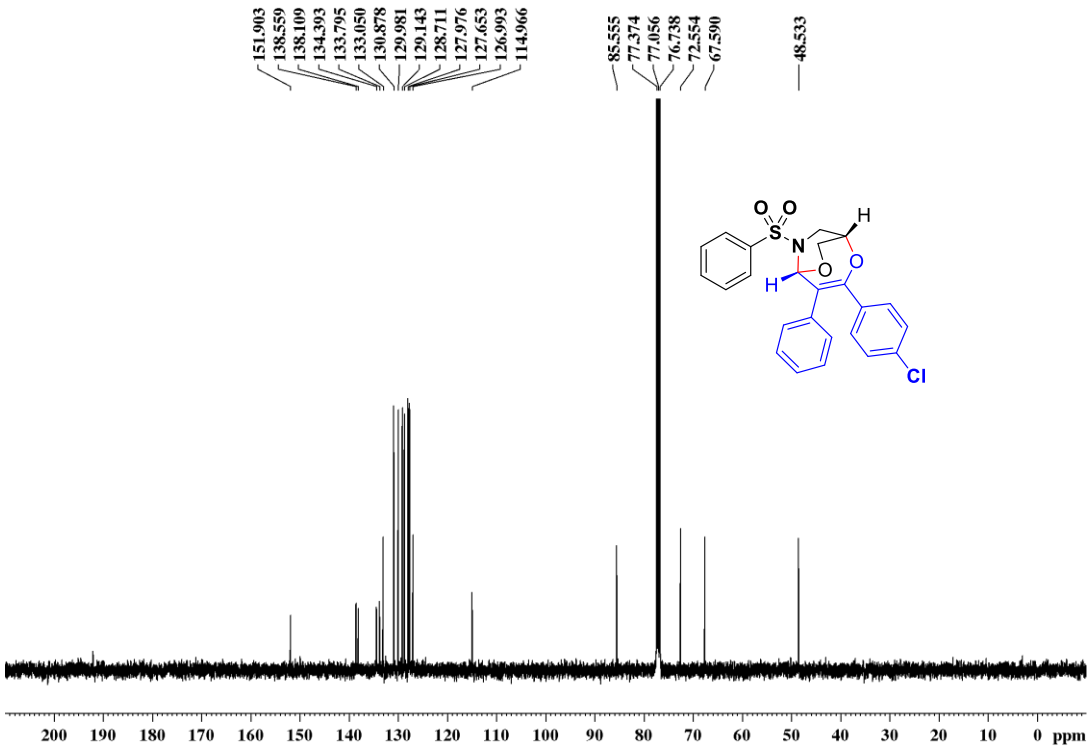

Figure S40. ^{13}C{^{1}H} NMR spectrum of compound 4ab

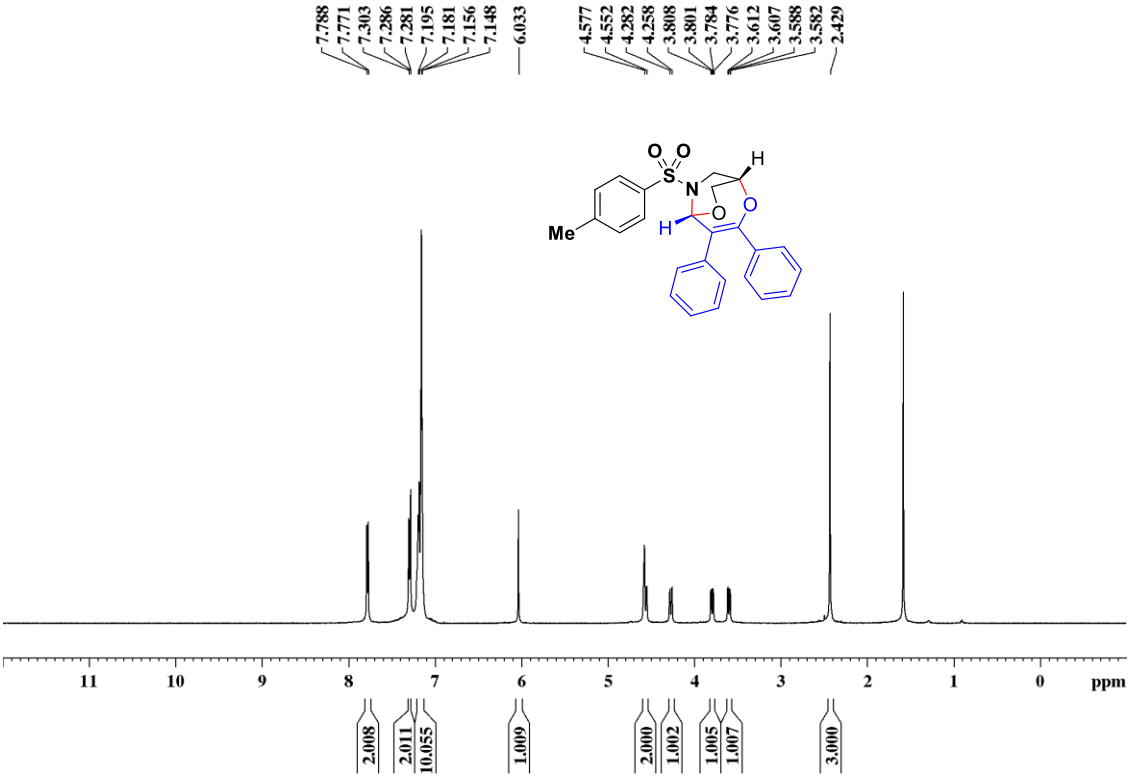

Figure S41. ^{1}H NMR spectrum of compound 4ba

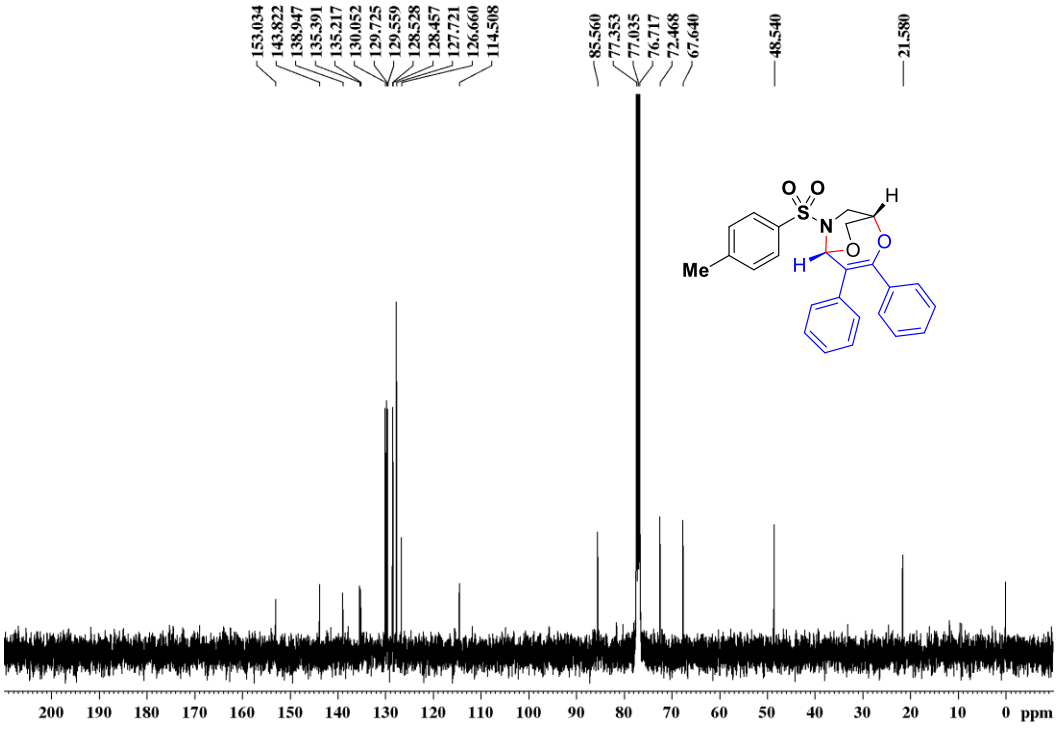

Figure S42. ^{13}C{^{1}H} NMR spectrum of compound 4ba

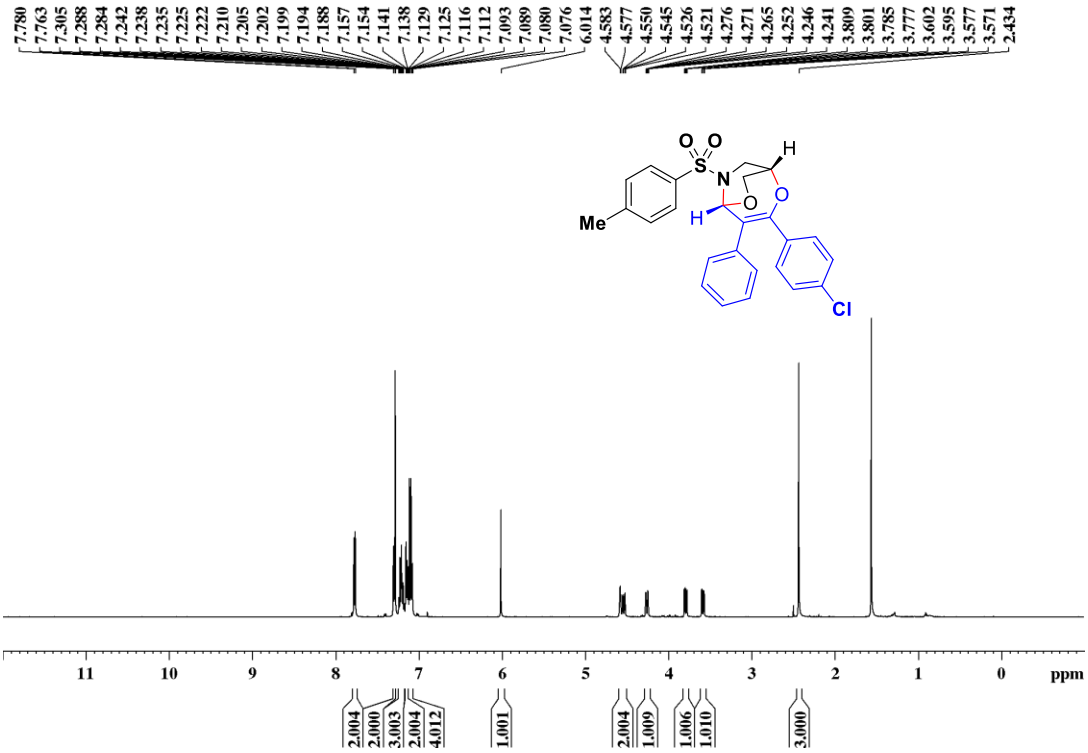

Figure S43. ^{1}H NMR spectrum of compound 4bb

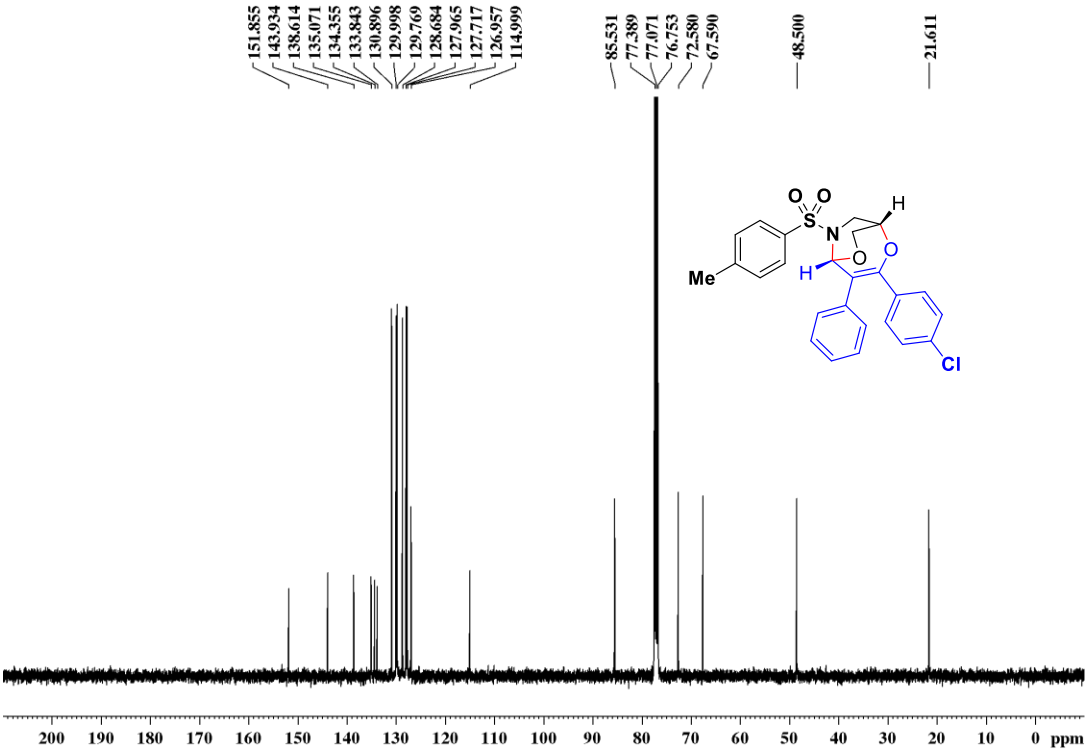

Figure S44. ^{13}C{^{1}H} NMR spectrum of compound 4bb

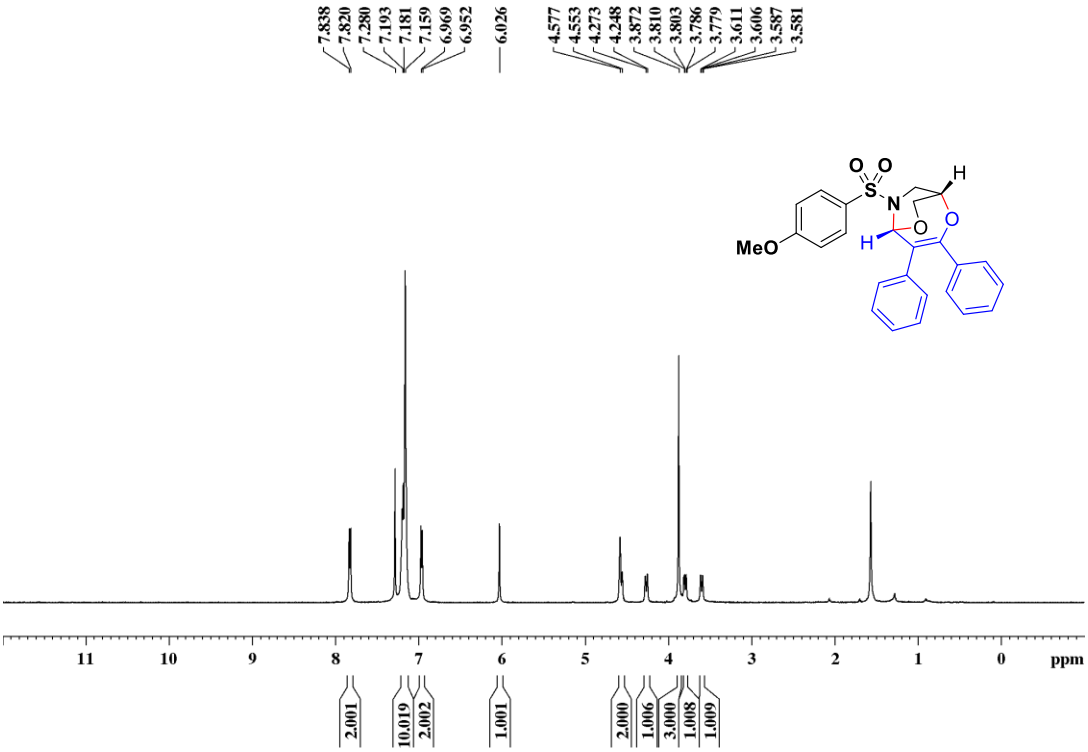

Figure S45. ^{1}H NMR spectrum of compound 4ca

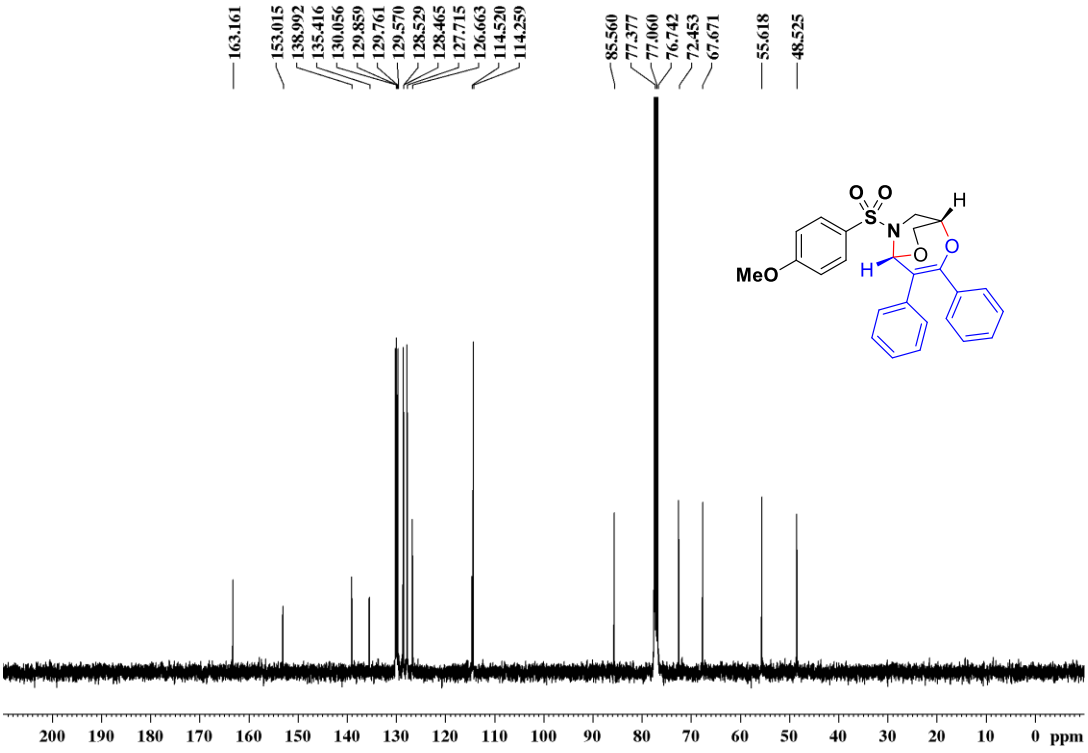

Figure S46. ^{13}C{^{1}H} NMR spectrum of compound 4ca

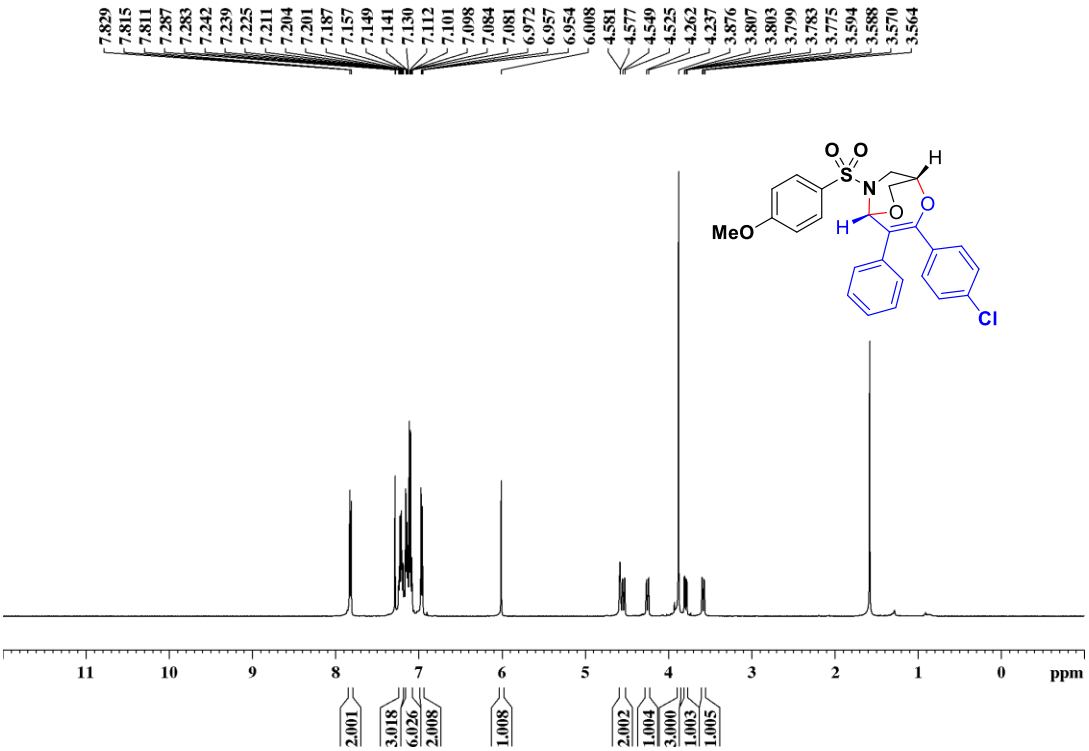

Figure S47. ^{1}H NMR spectrum of compound 4cb

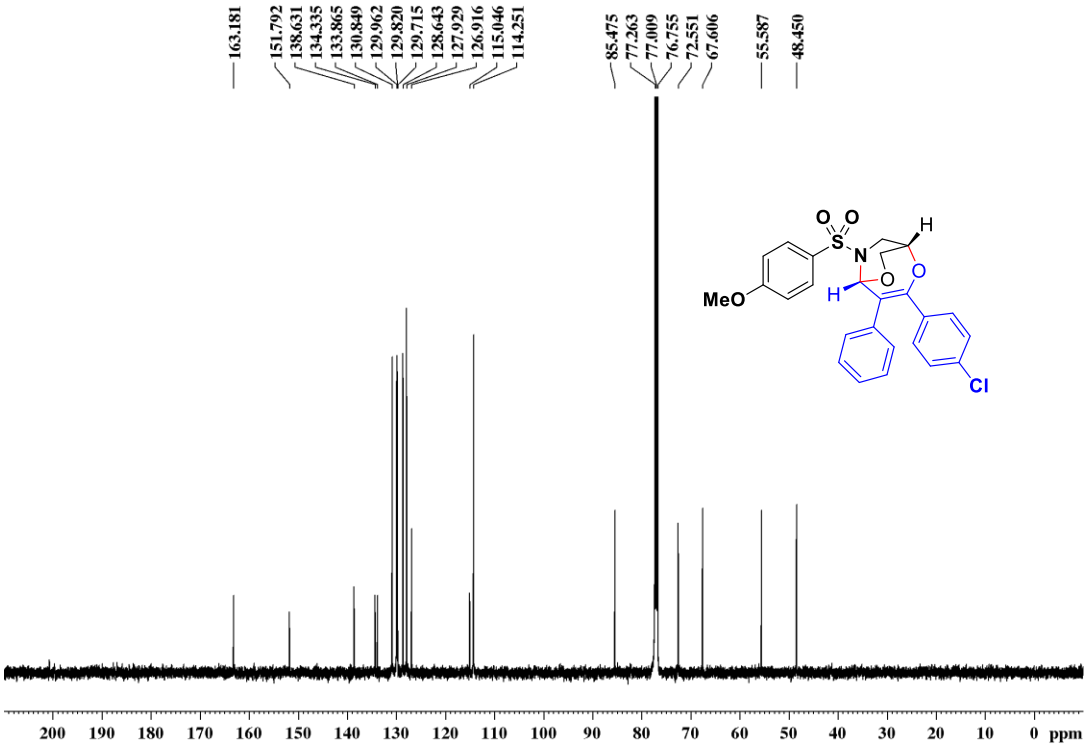

Figure S48. ^{13}C{^{1}H} NMR spectrum of compound 4cb

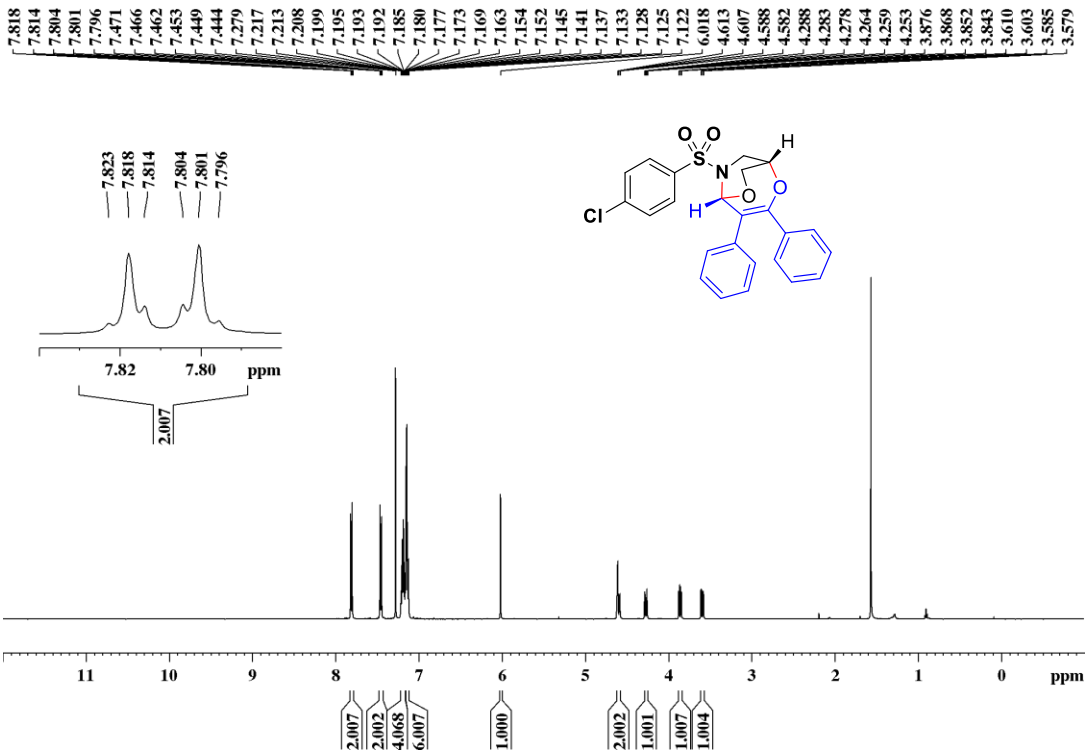

Figure S49. ^{1}H NMR spectrum of compound 4da

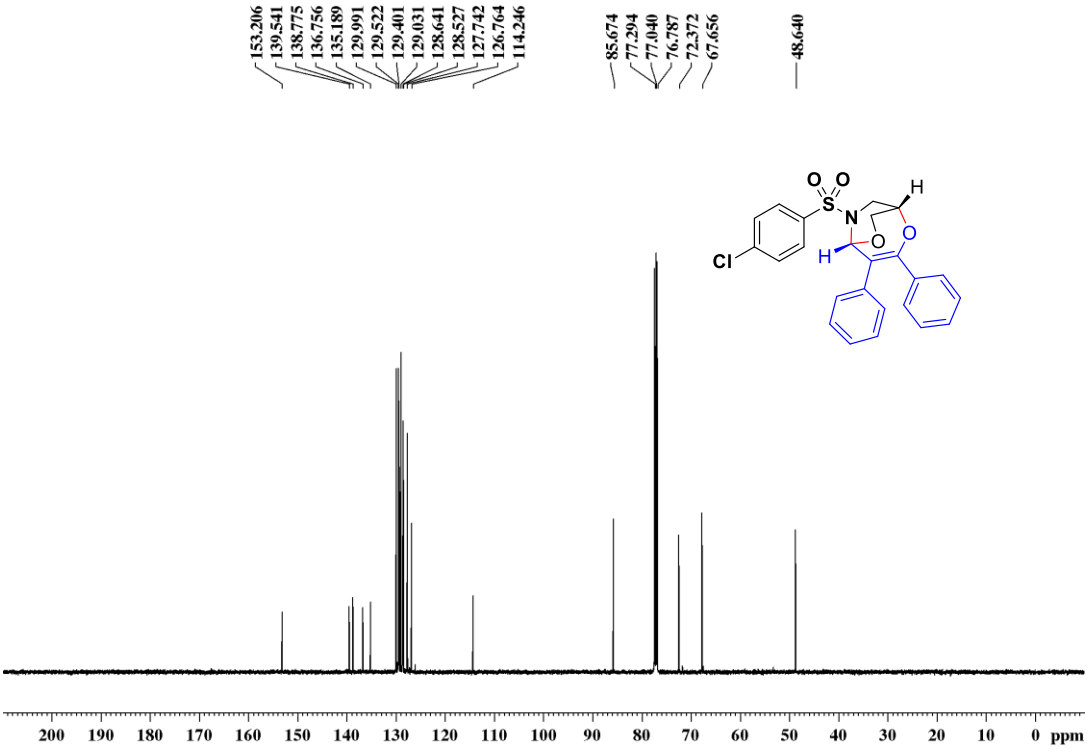

Figure S50. ^{13}C{^{1}H} NMR spectrum of compound 4da

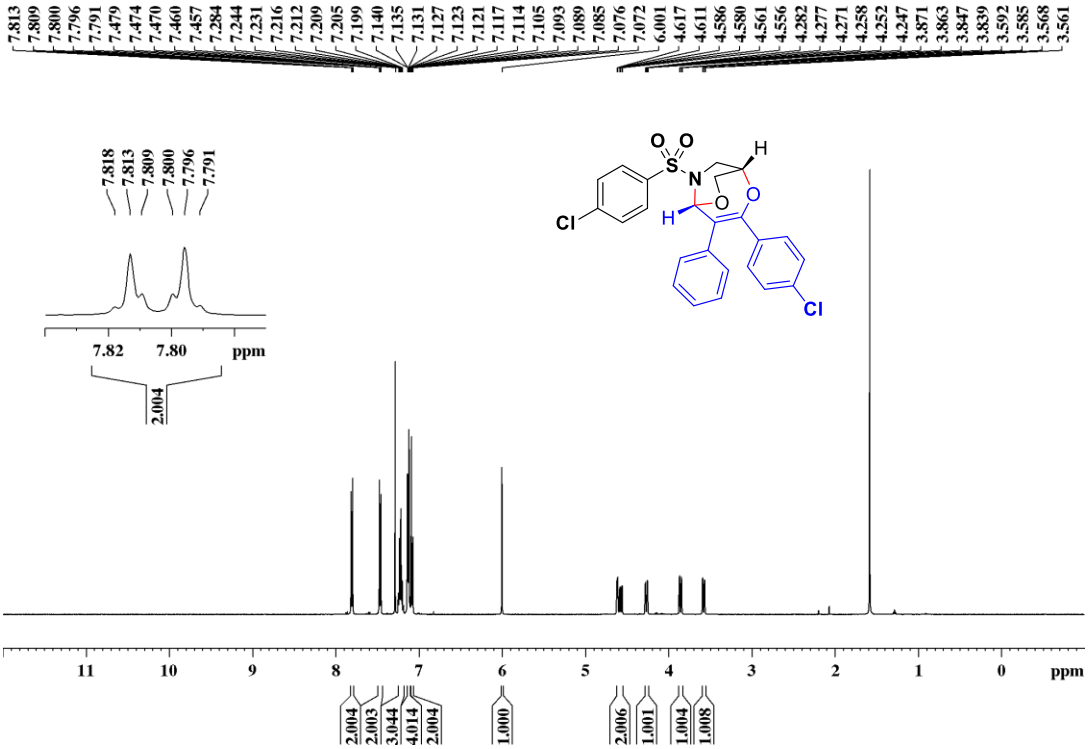

Figure S51. ^{1}H NMR spectrum of compound 4db

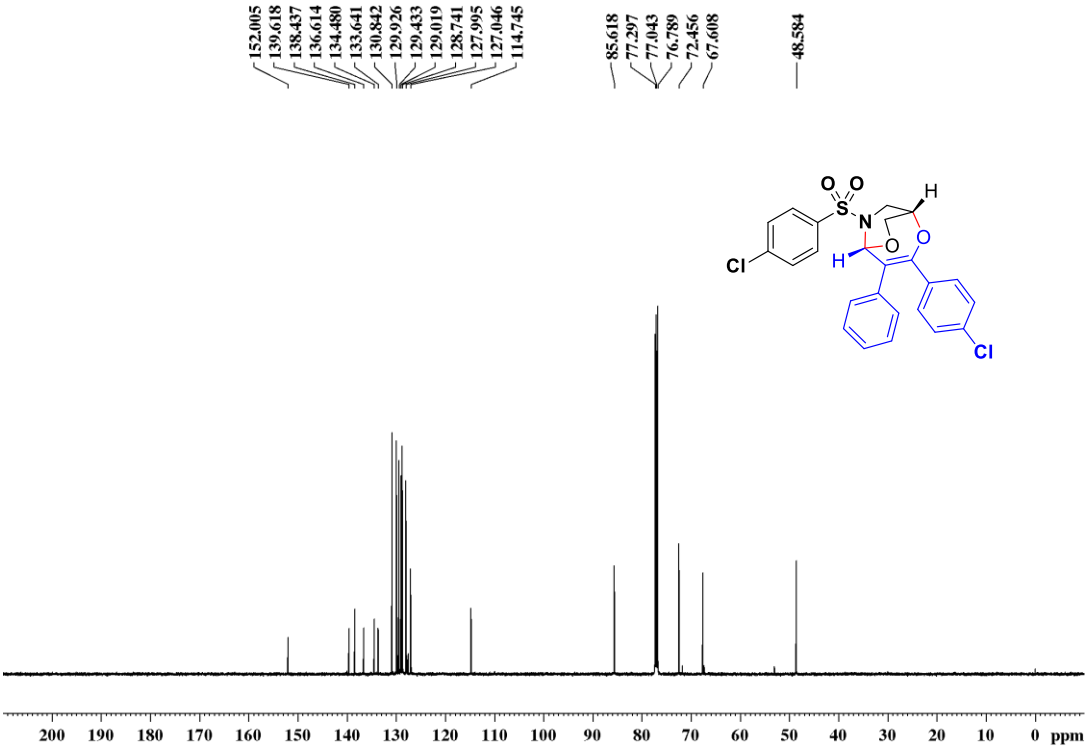

Figure S52. ^{13}C{^{1}H} NMR spectrum of compound 4db

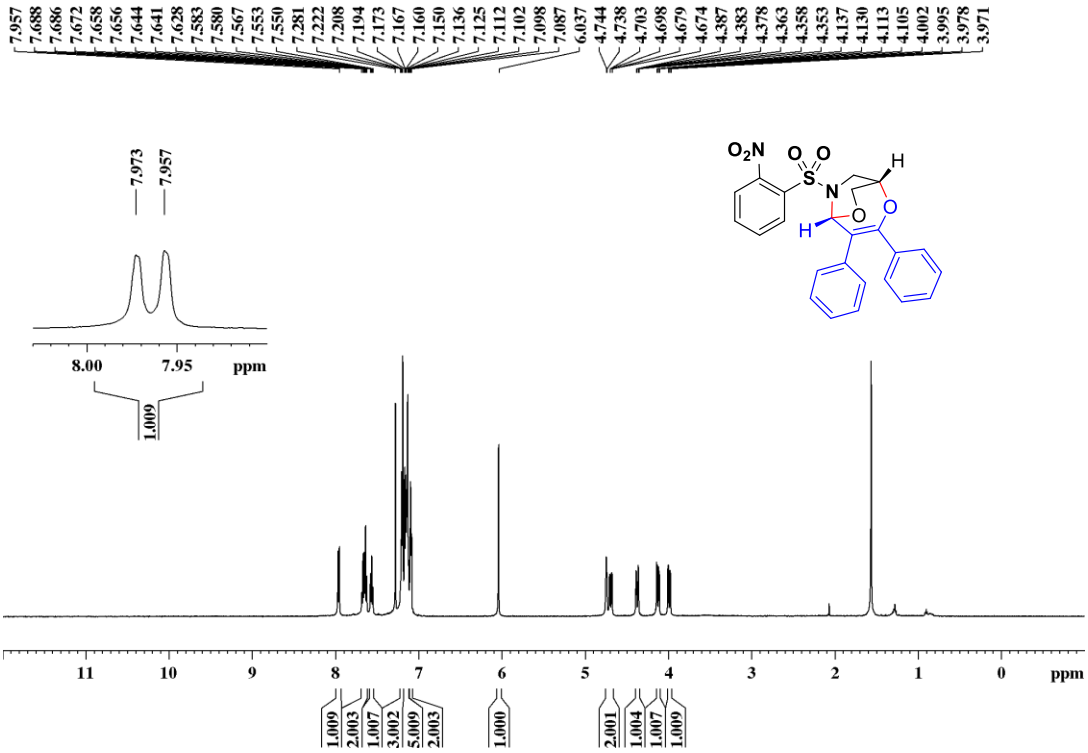

Figure S53. ^{1}H NMR spectrum of compound 4ea

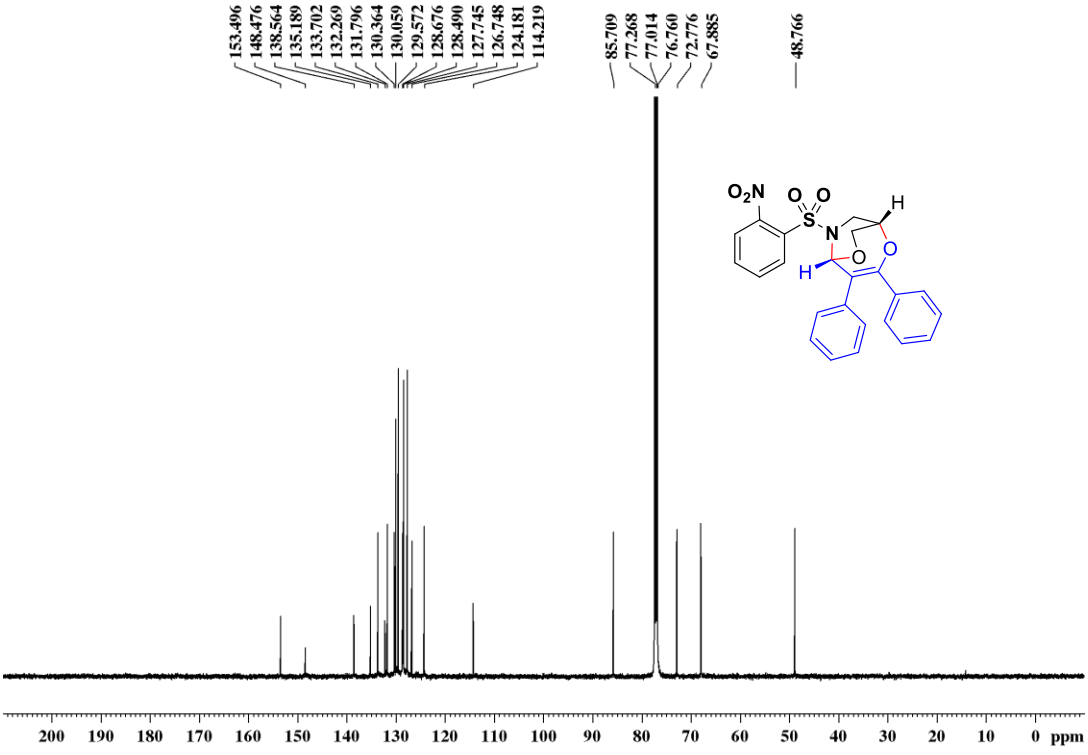

Figure S54. ^{13}C{^{1}H} NMR spectrum of compound 4ea

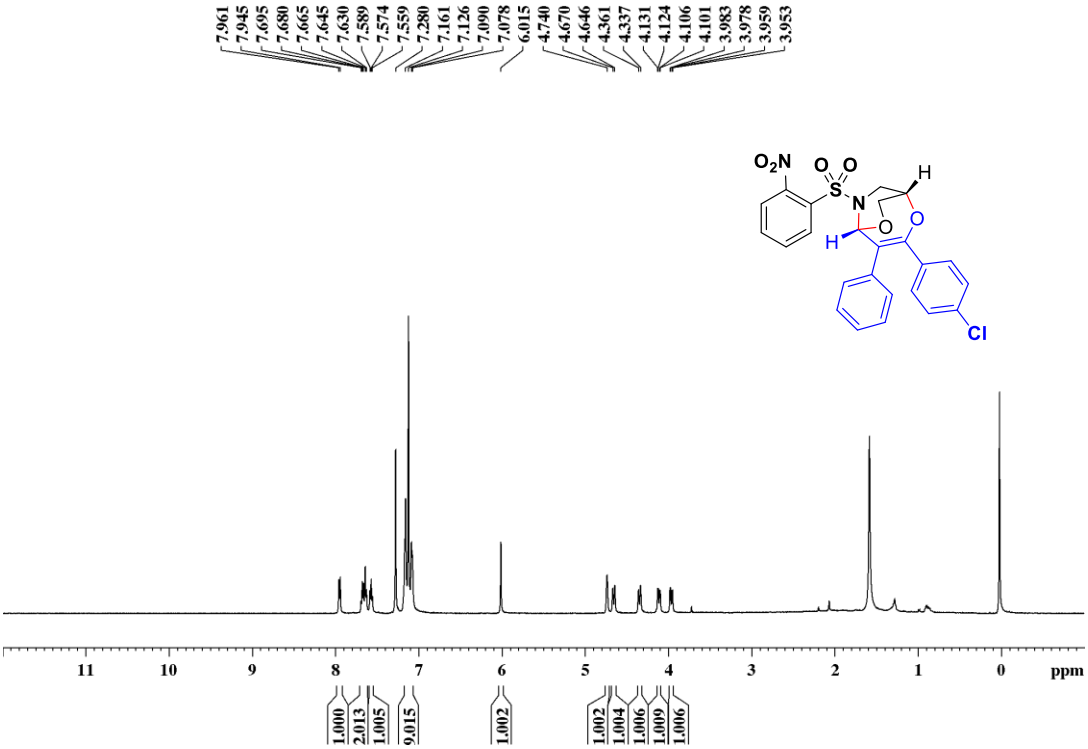

Figure S55. ^{1}H NMR spectrum of compound 4eb

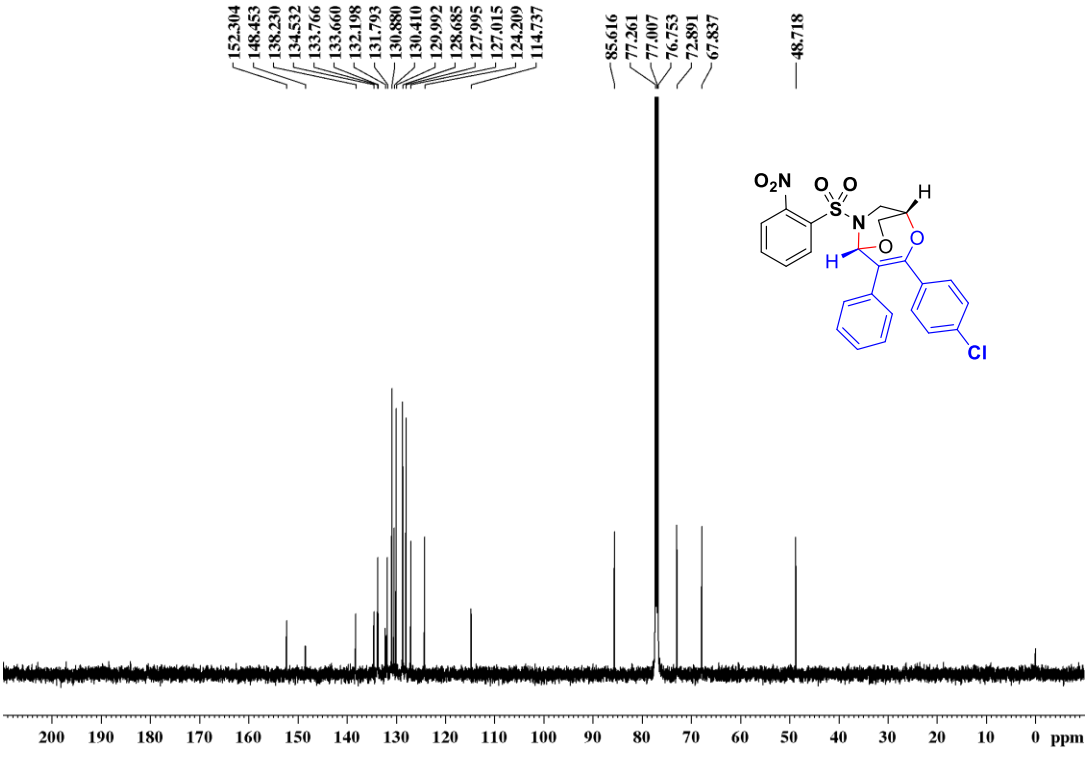

Figure S56. ^{13}C{^{1}H} NMR spectrum of compound 4eb

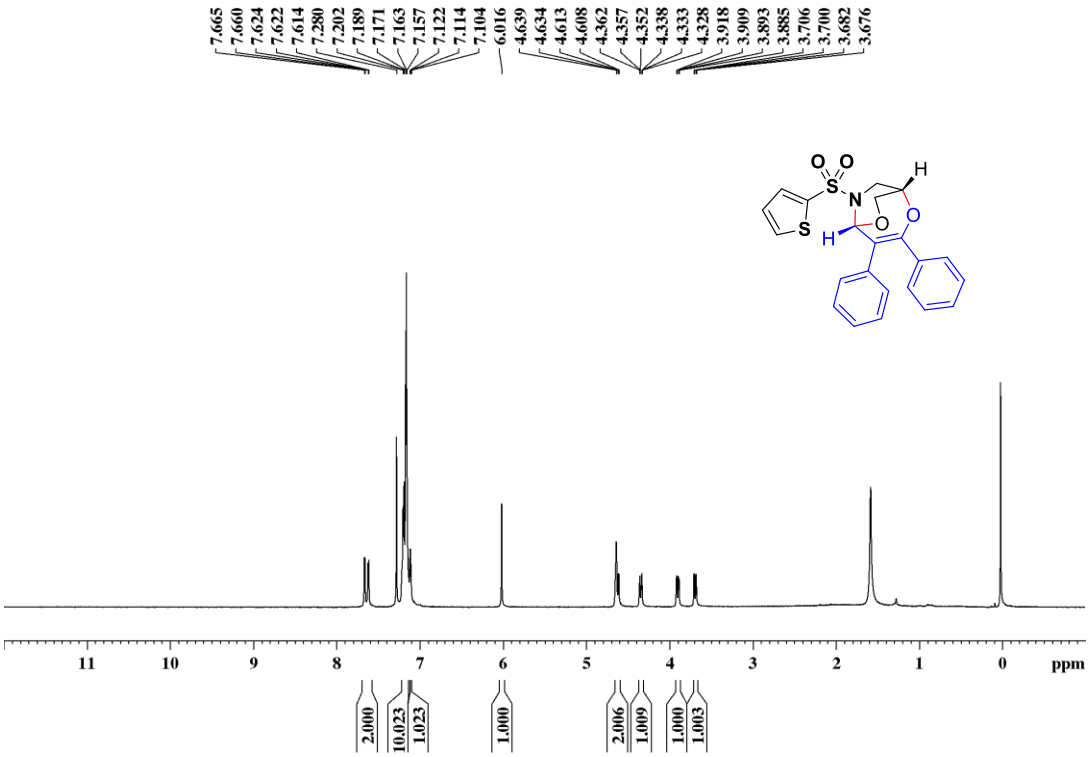

Figure S57. ^{1}H NMR spectrum of compound 4fa

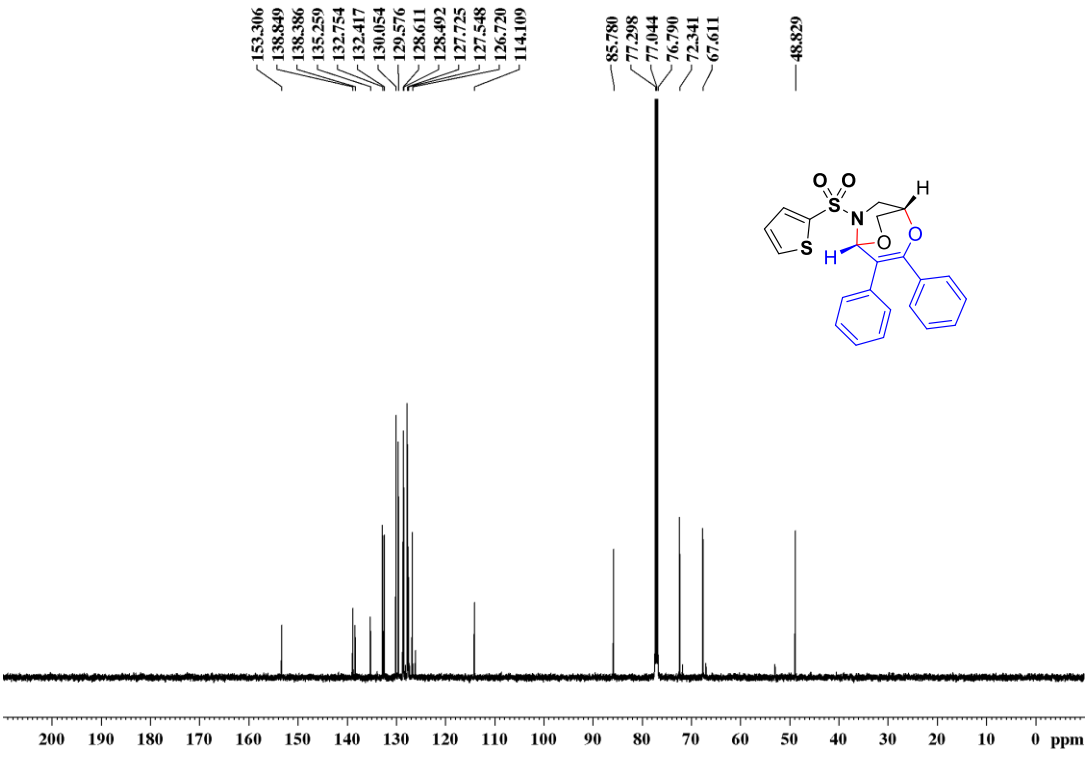

Figure S58. ^{13}C{^{1}H} NMR spectrum of compound 4fa

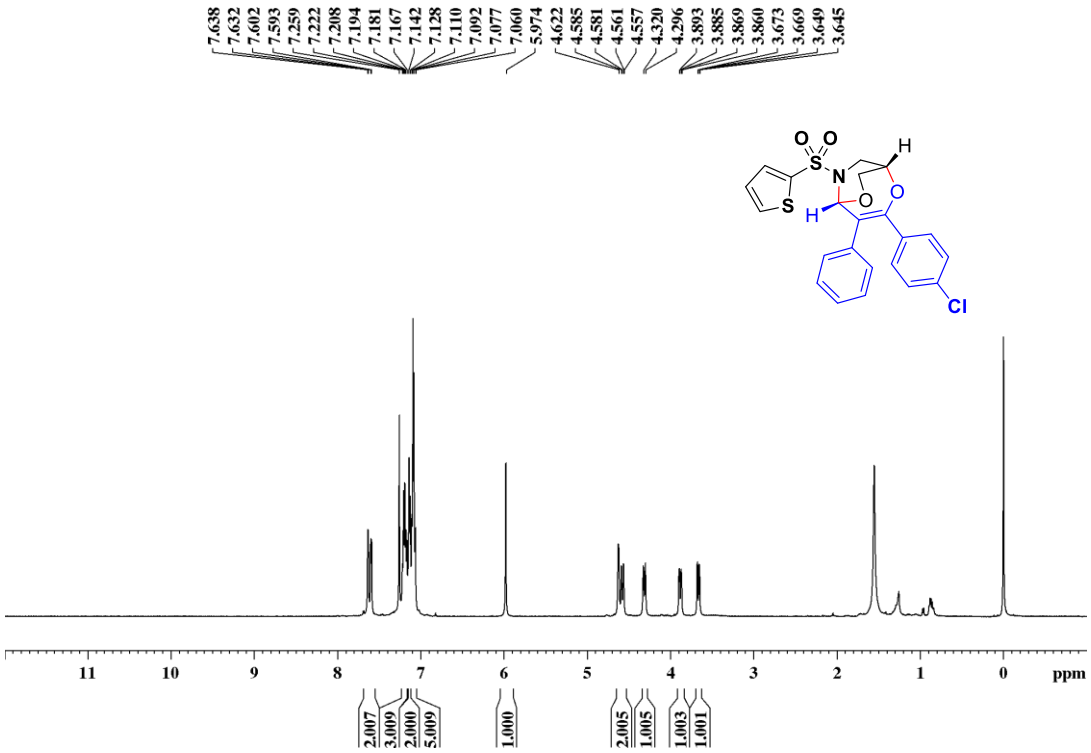

Figure S59. ^{1}H NMR spectrum of compound 4fb

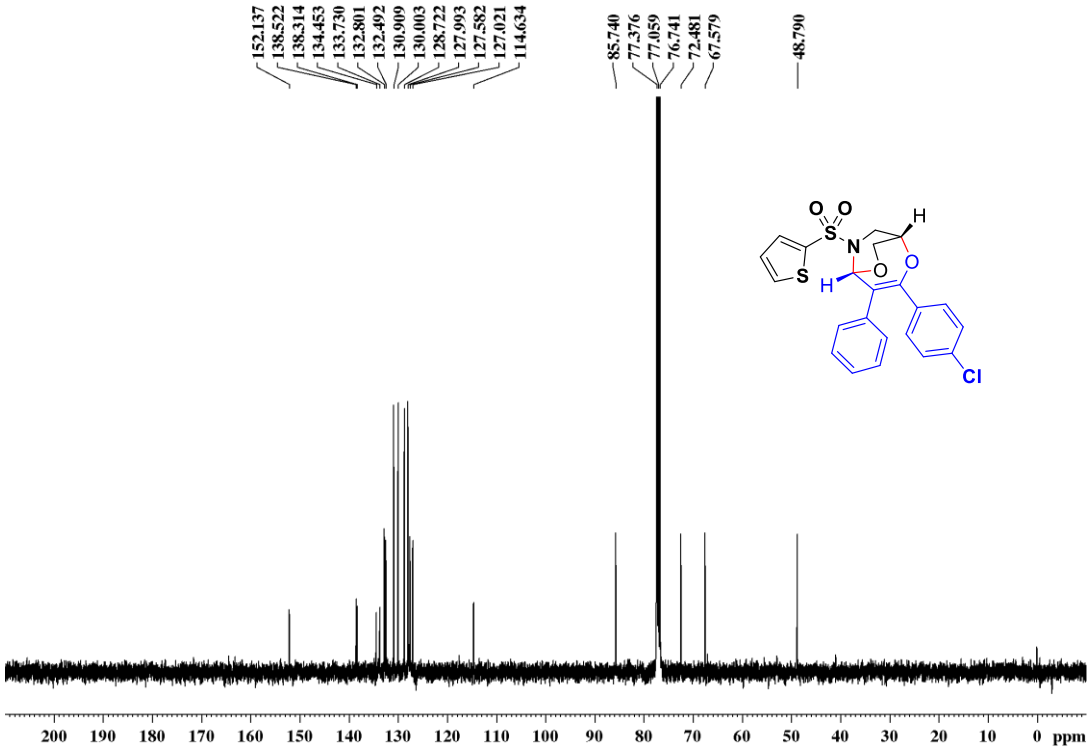

Figure S60. ^{13}C{^{1}H} NMR spectrum of compound 4fb

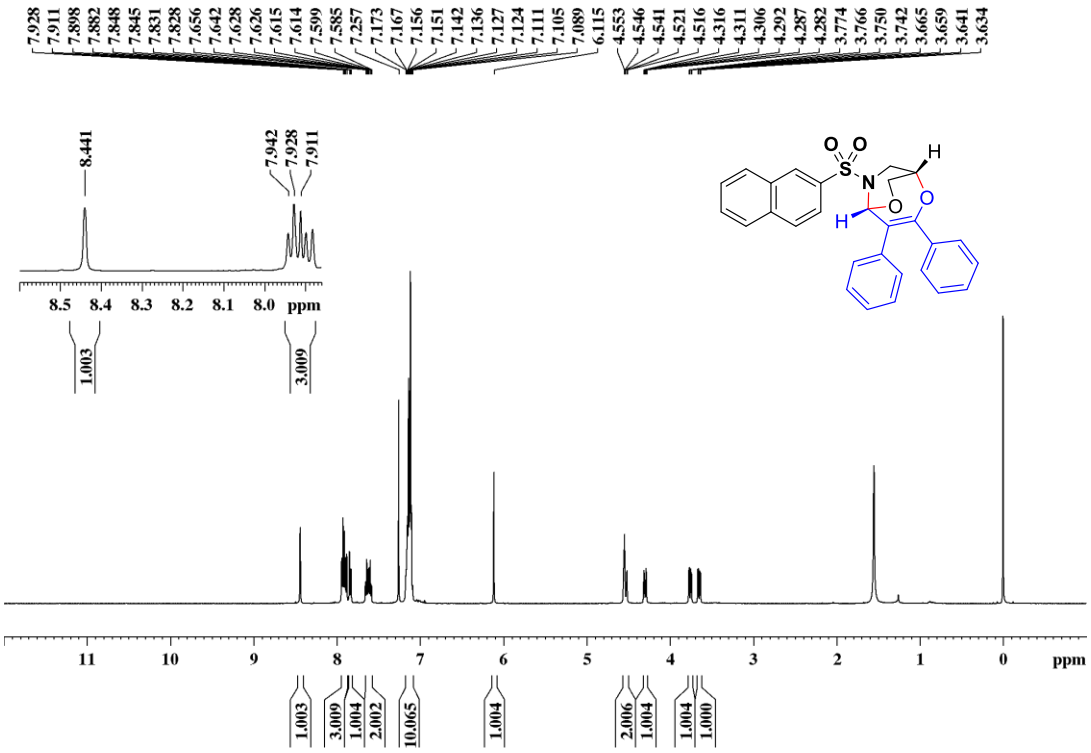

Figure S61. ^{1}H NMR spectrum of compound 4ga

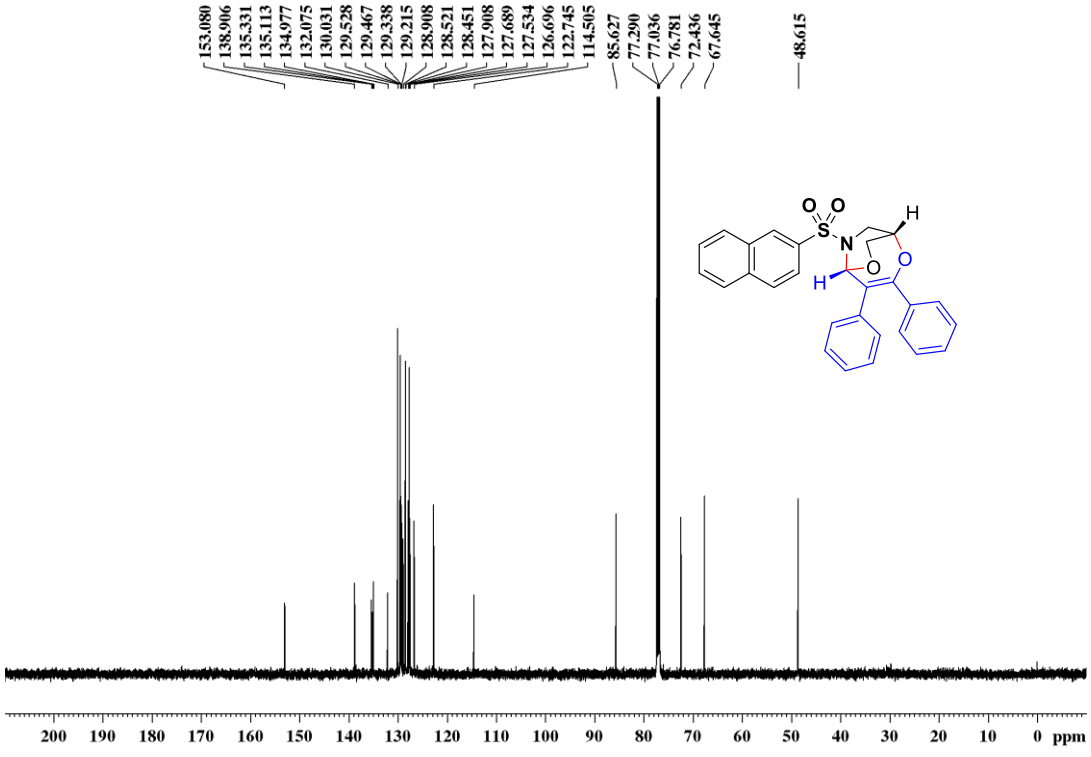

Figure S62. ^{13}C{^{1}H} NMR spectrum of compound 4ga

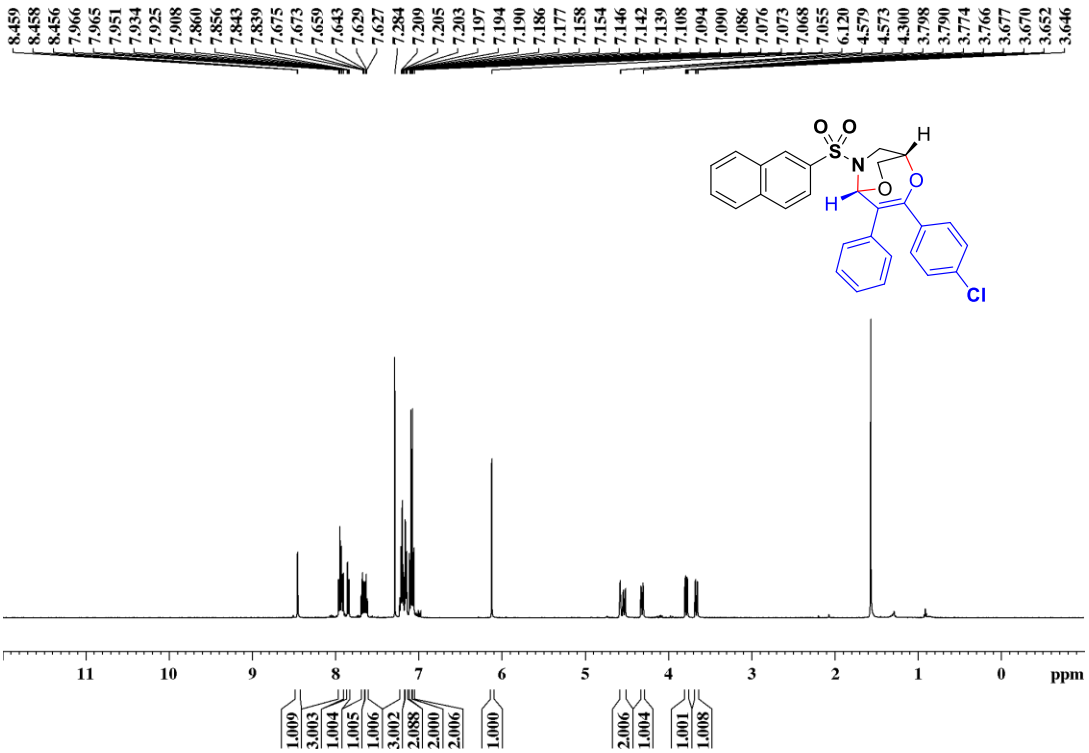

Figure S63. ^{1}H NMR spectrum of compound 4gb

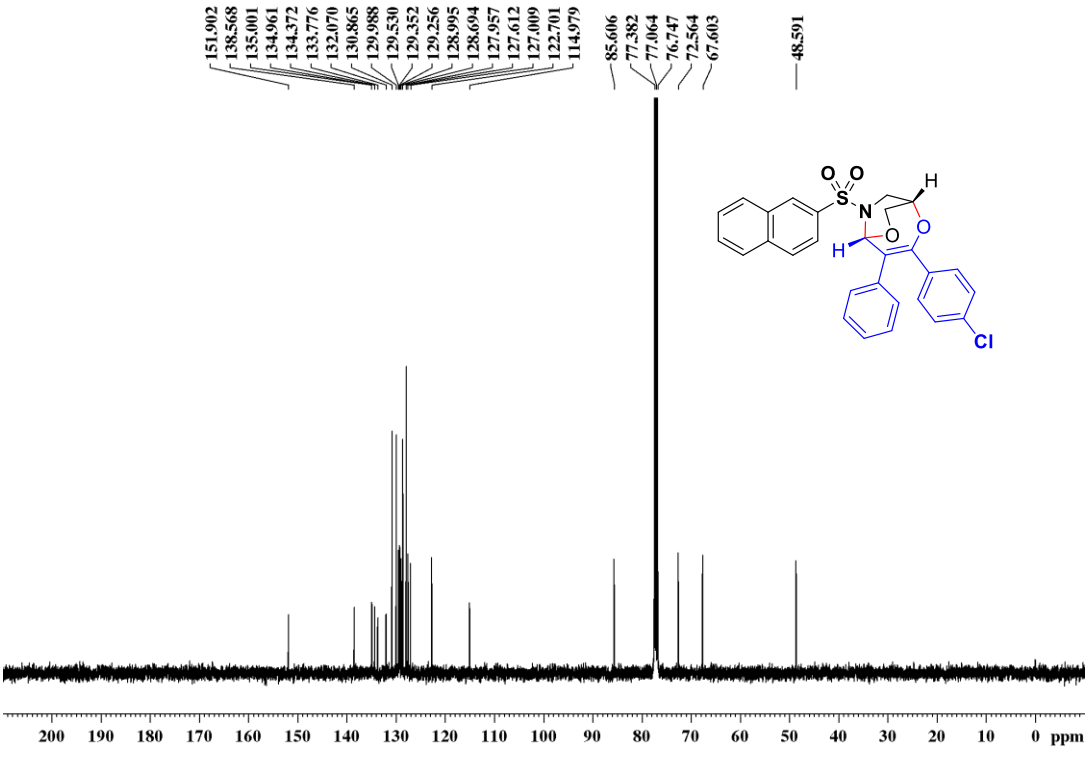

Figure S64. ^{13}C{^{1}H} NMR spectrum of compound 4gb

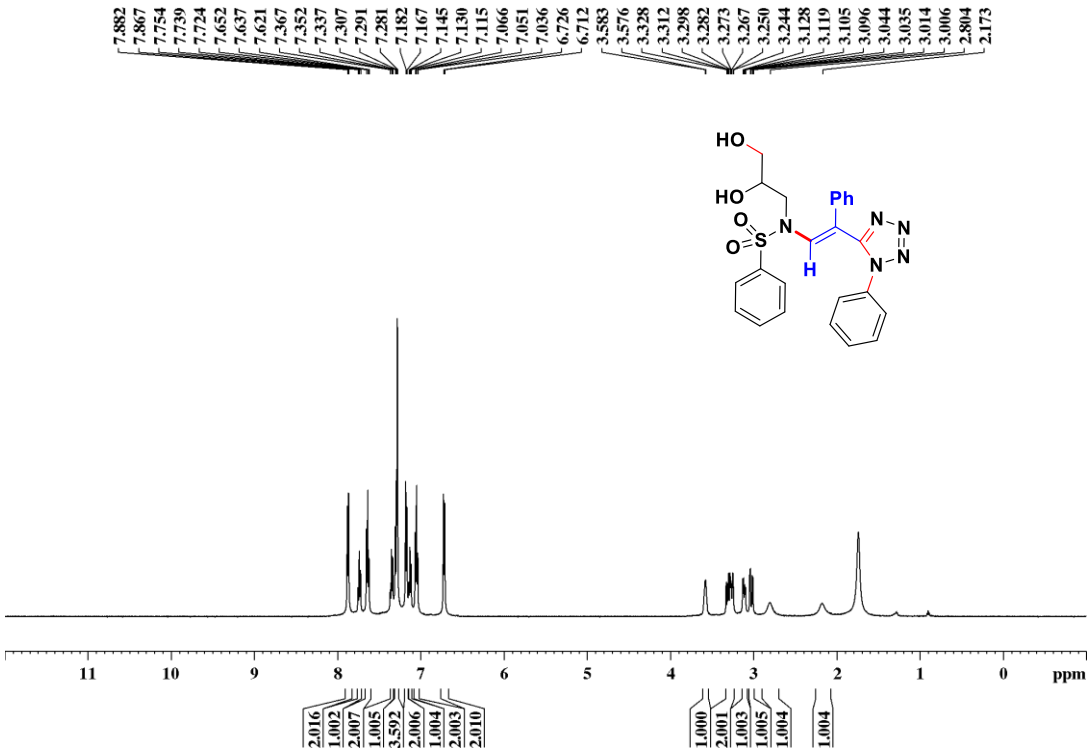

Figure S65. ^{1}H NMR spectrum of compound 5aa

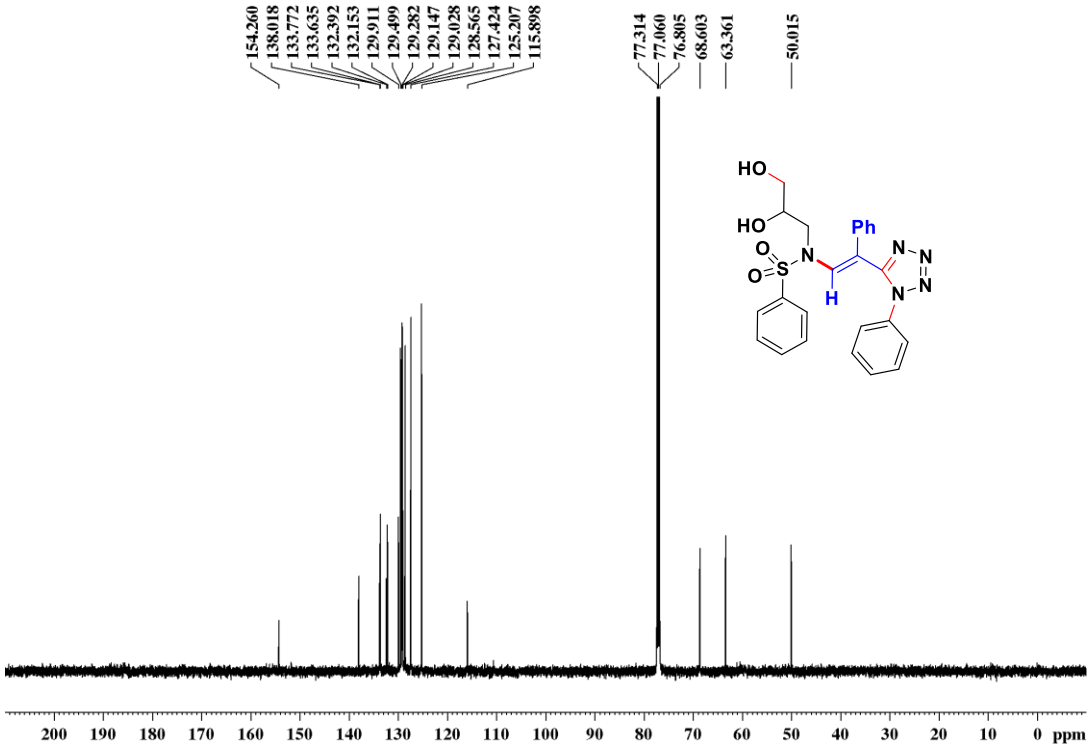

Figure S66. ^{13}C{^{1}H} NMR spectrum of compound 5aa

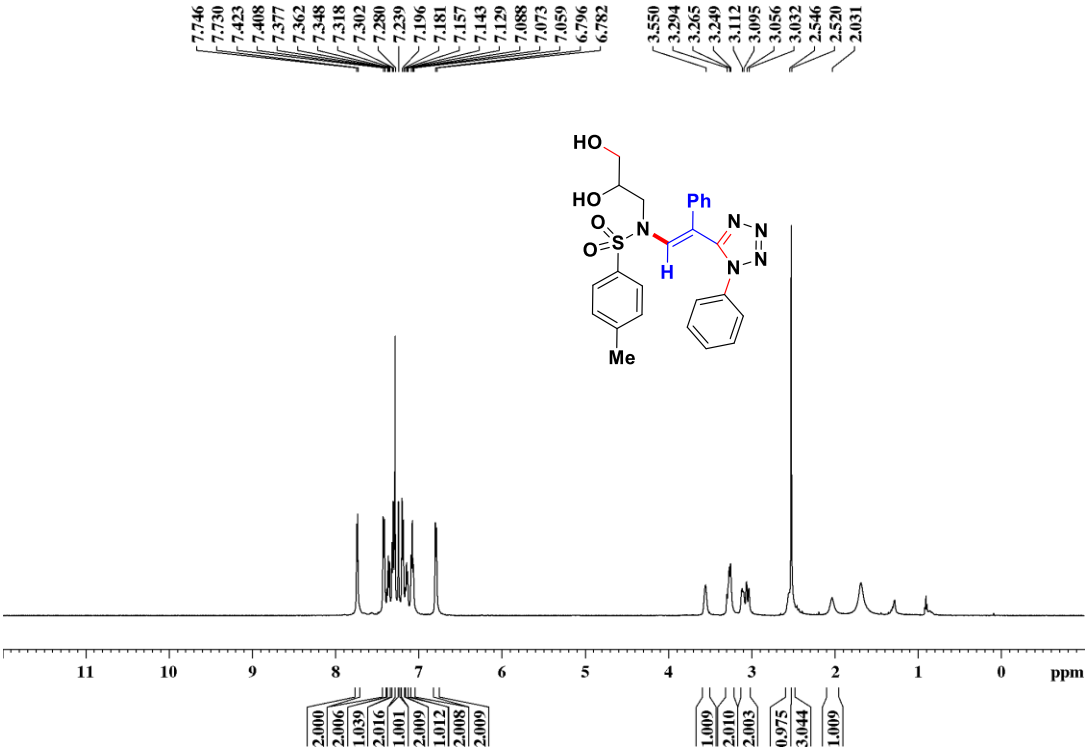

Figure S67. ^{1}H NMR spectrum of compound 5ba

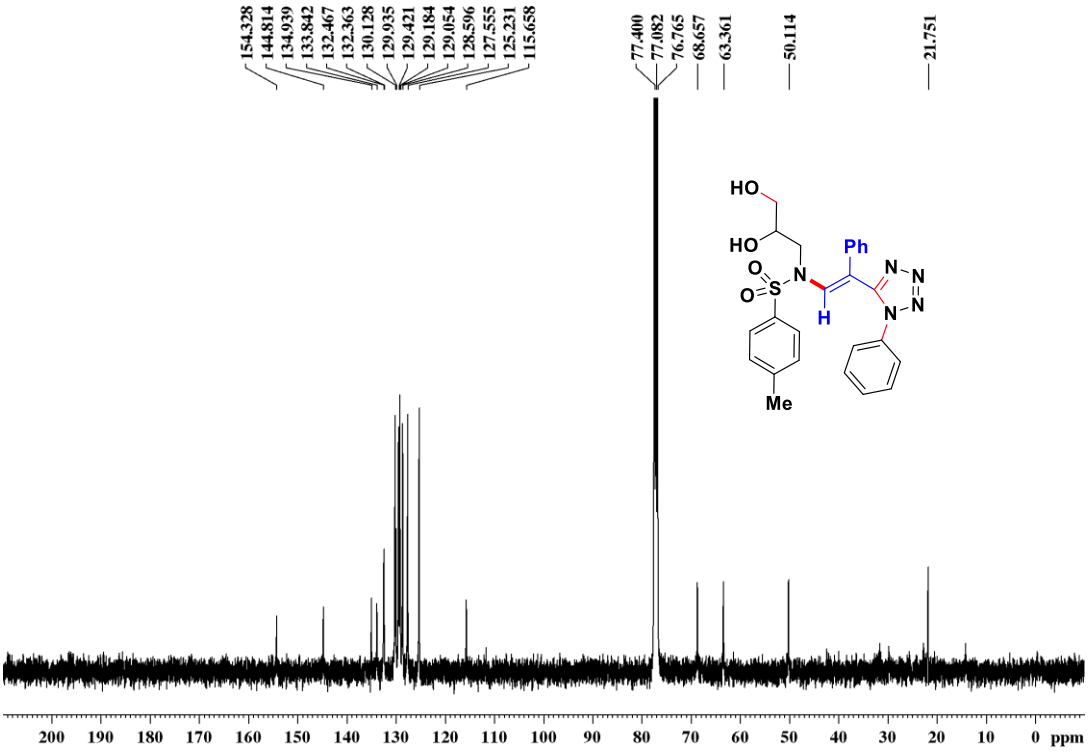

Figure S68. ^{13}C{^{1}H} NMR spectrum of compound 5ba

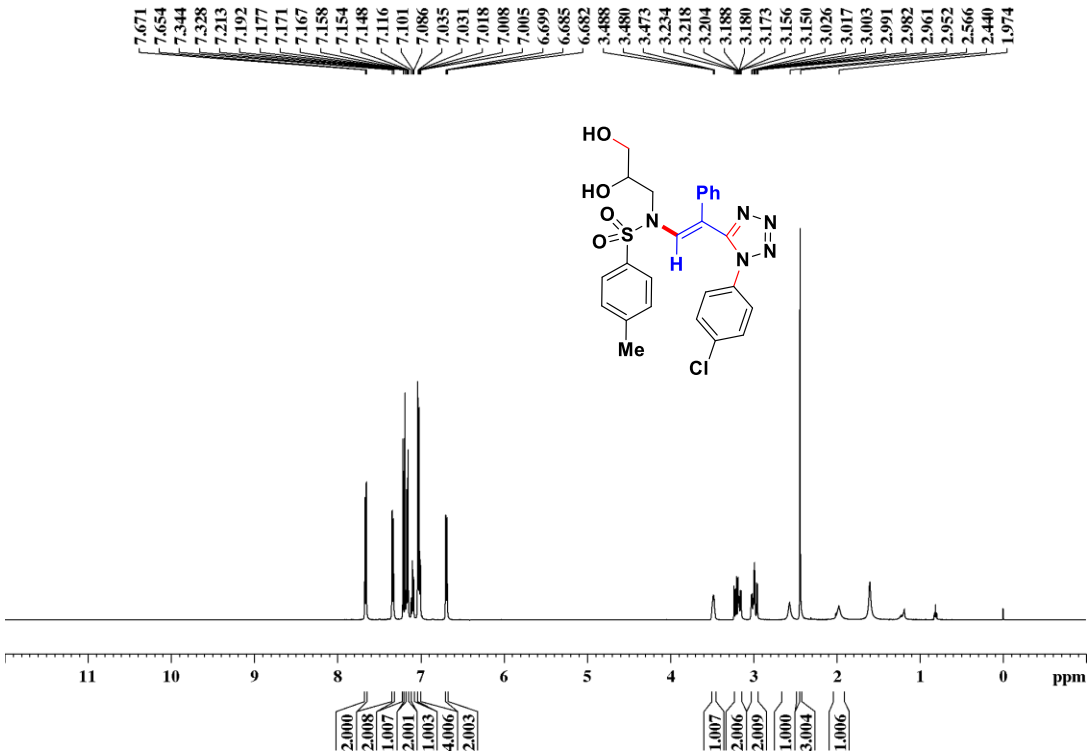

Figure S69. ^{1}H NMR spectrum of compound 5bb

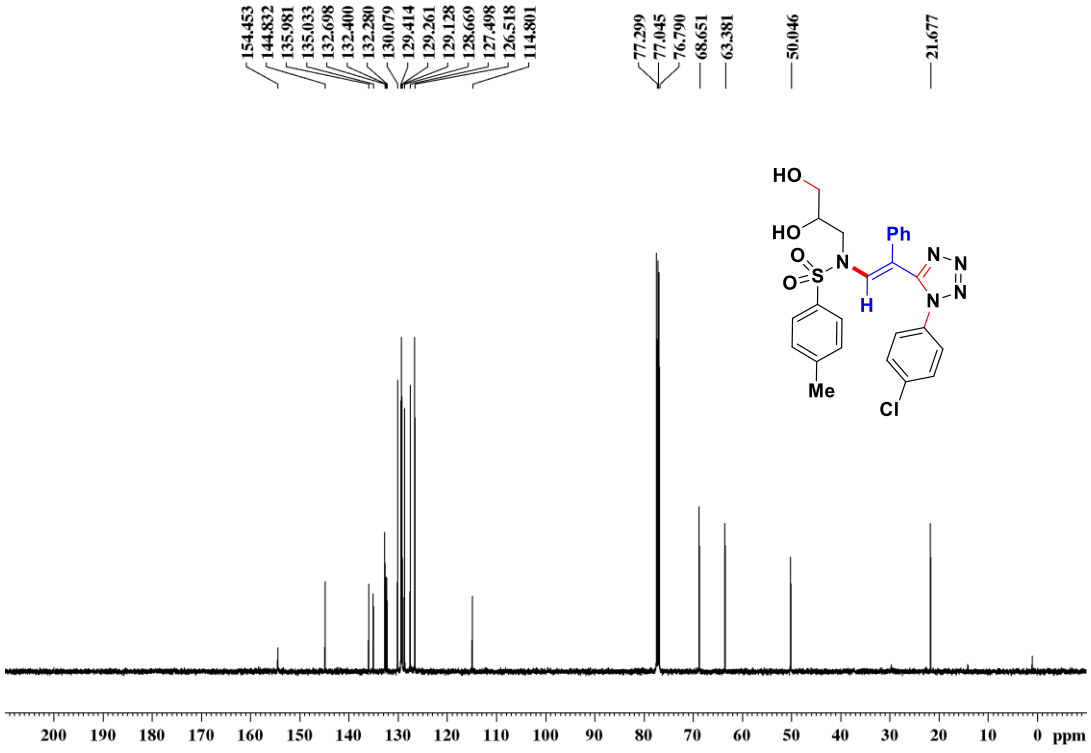

Figure S70. ^{13}C{^{1}H} NMR spectrum of compound 5bb

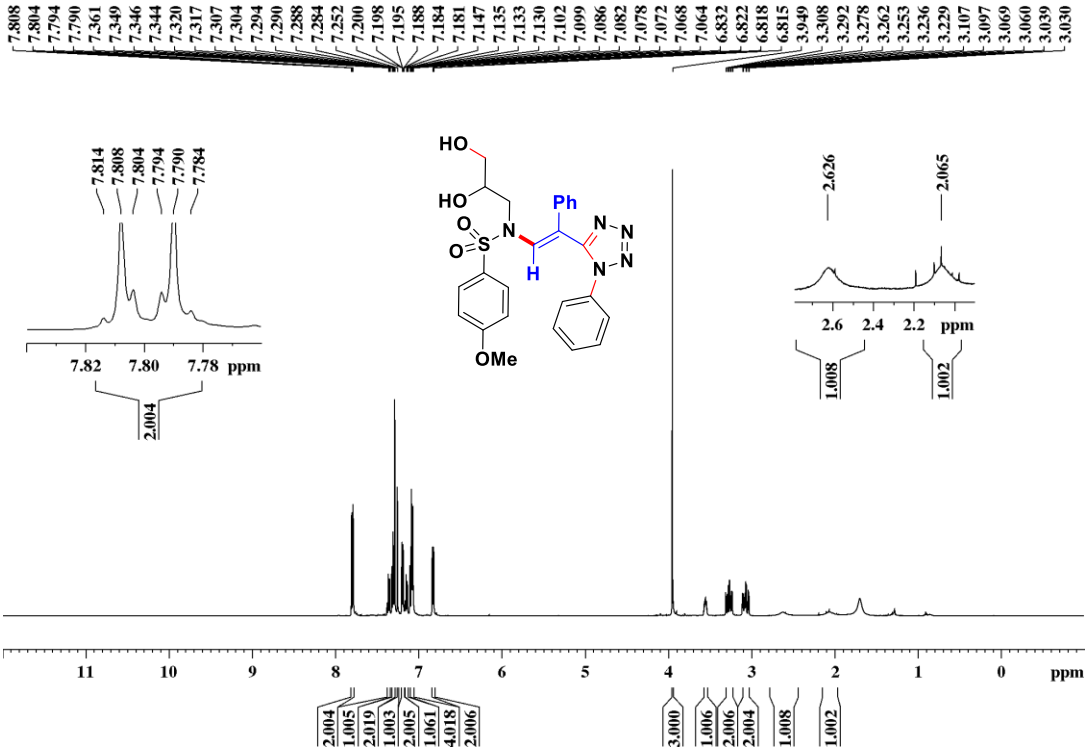

Figure S71. ^{1}H NMR spectrum of compound 5ca

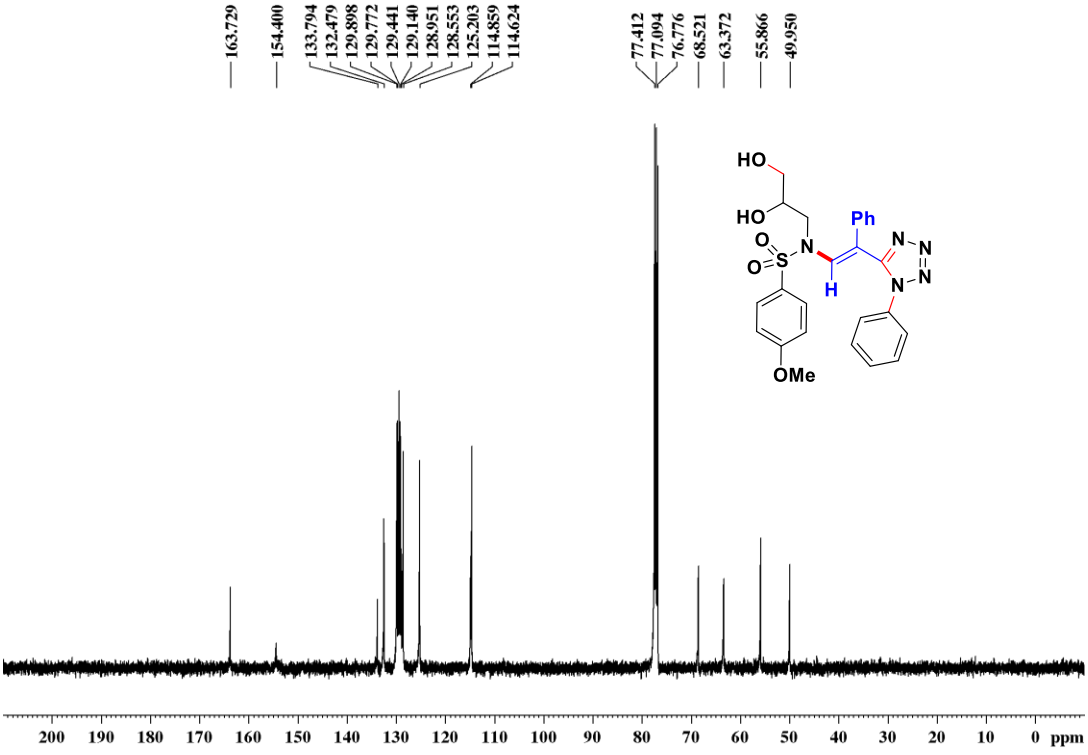

Figure S72. ^{13}C{^{1}H} NMR spectrum of compound 5ca

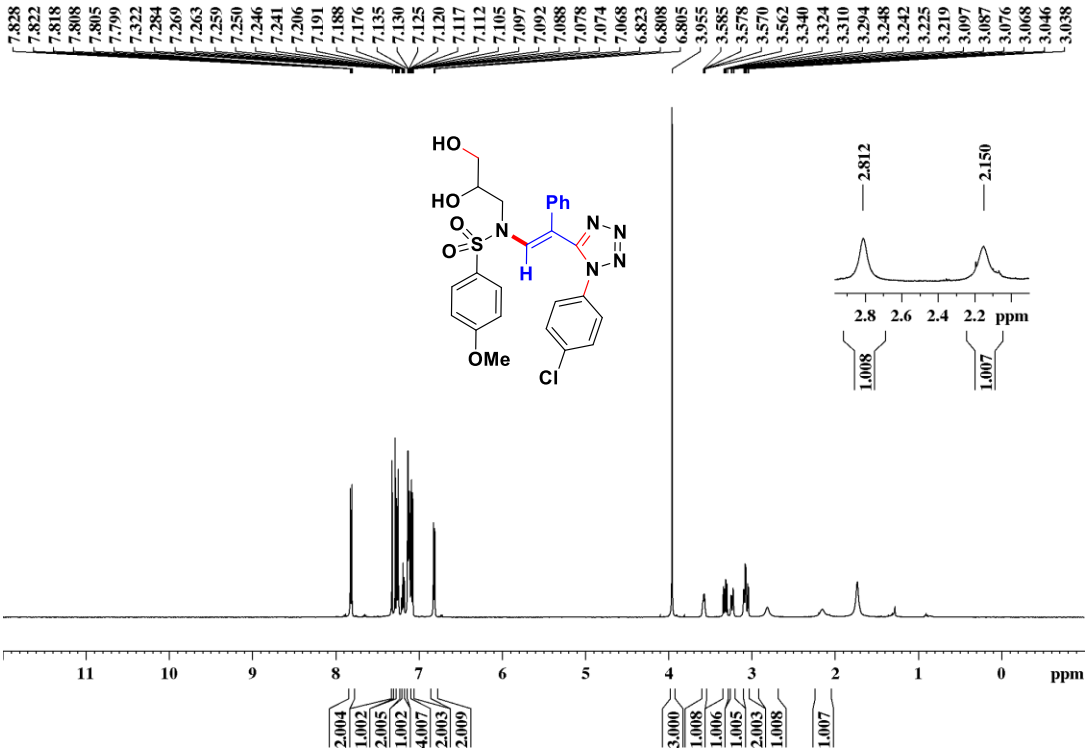

Figure S73. ^{1}H NMR spectrum of compound 5cb

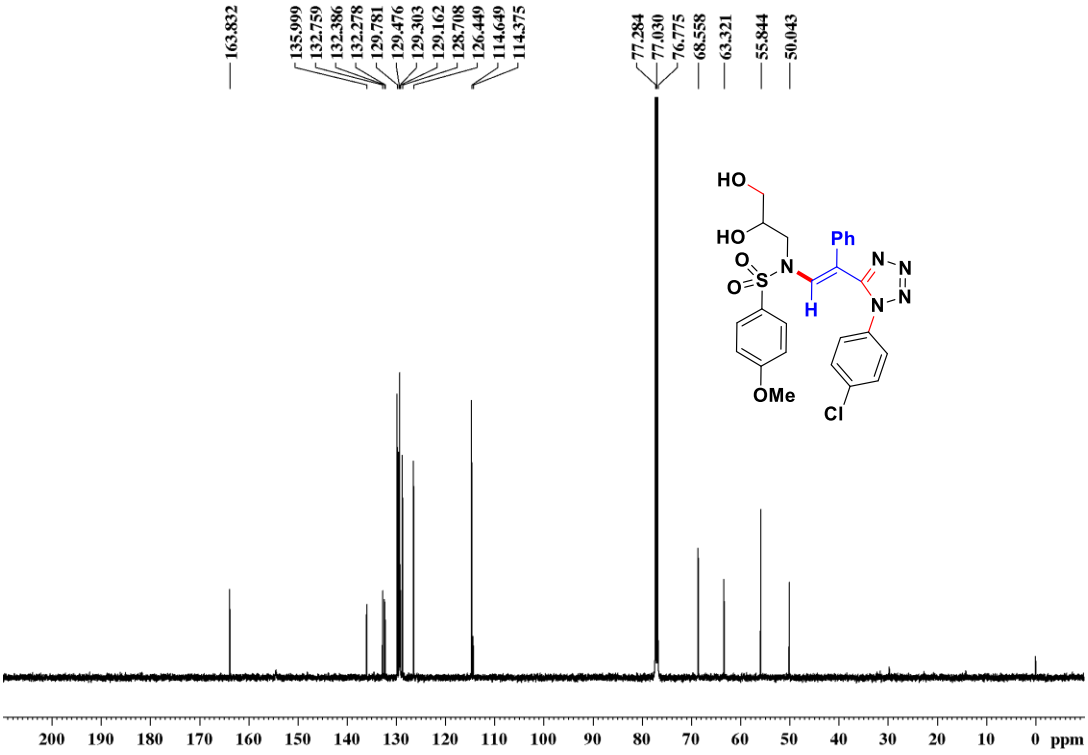

Figure S74. ^{13}C{^{1}H} NMR spectrum of compound 5cb

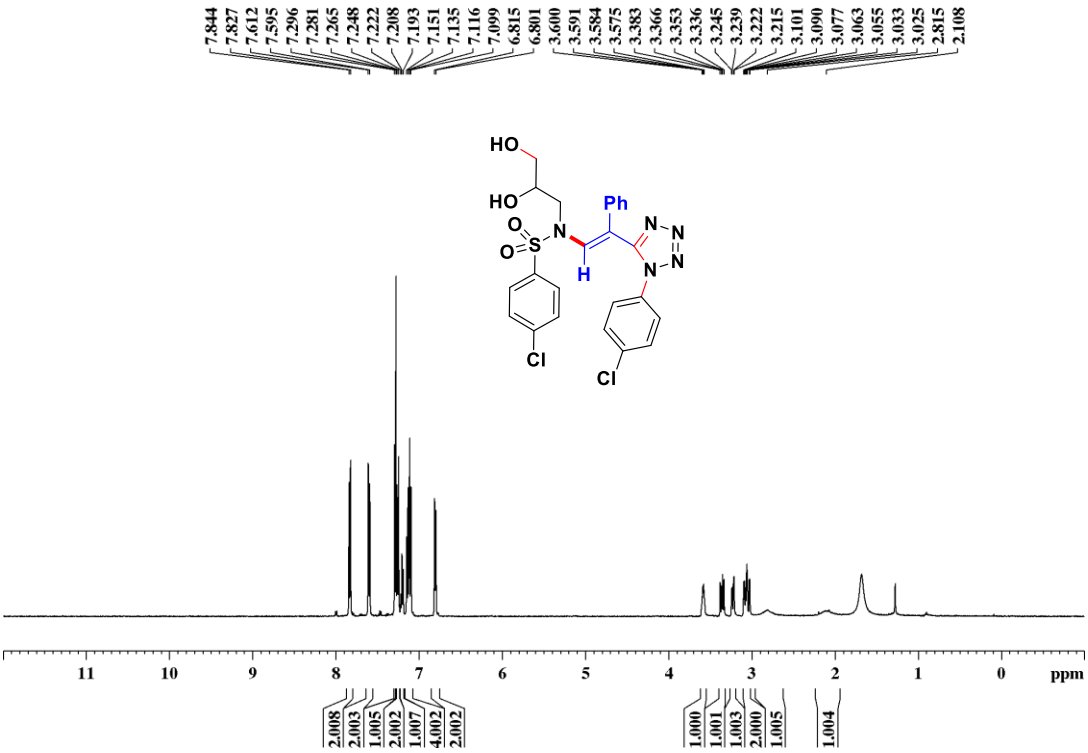

Figure S75. ^{1}H NMR spectrum of compound 5db

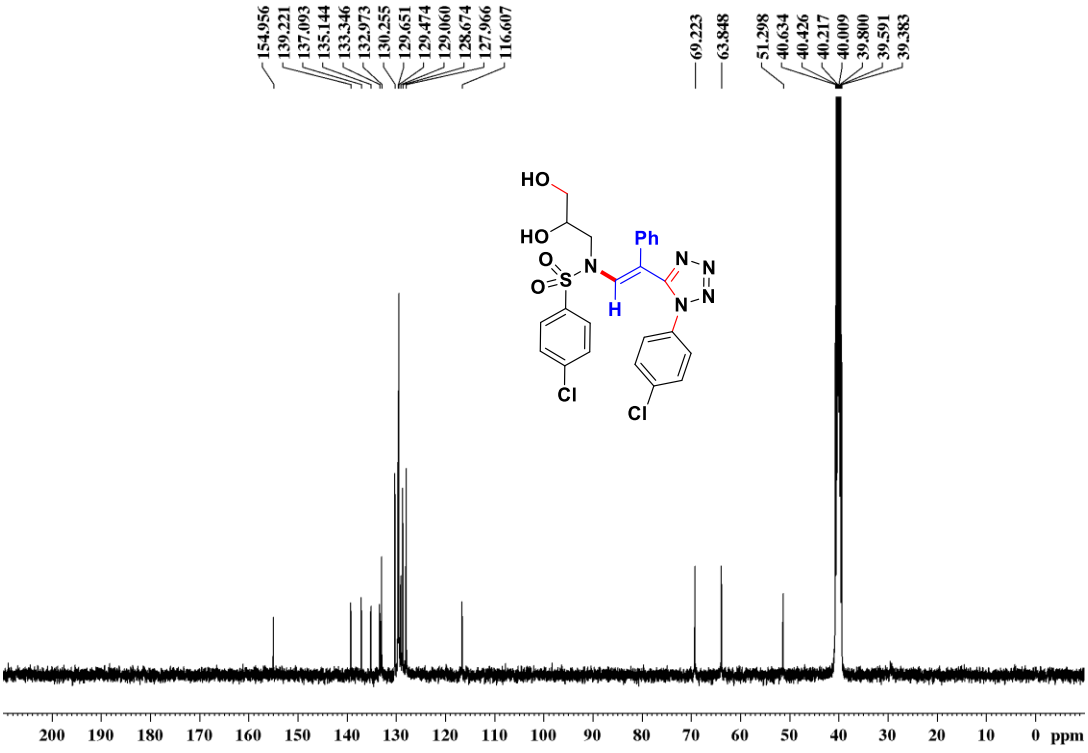

Figure S76. ^{13}C{^{1}H} NMR spectrum of compound 5db

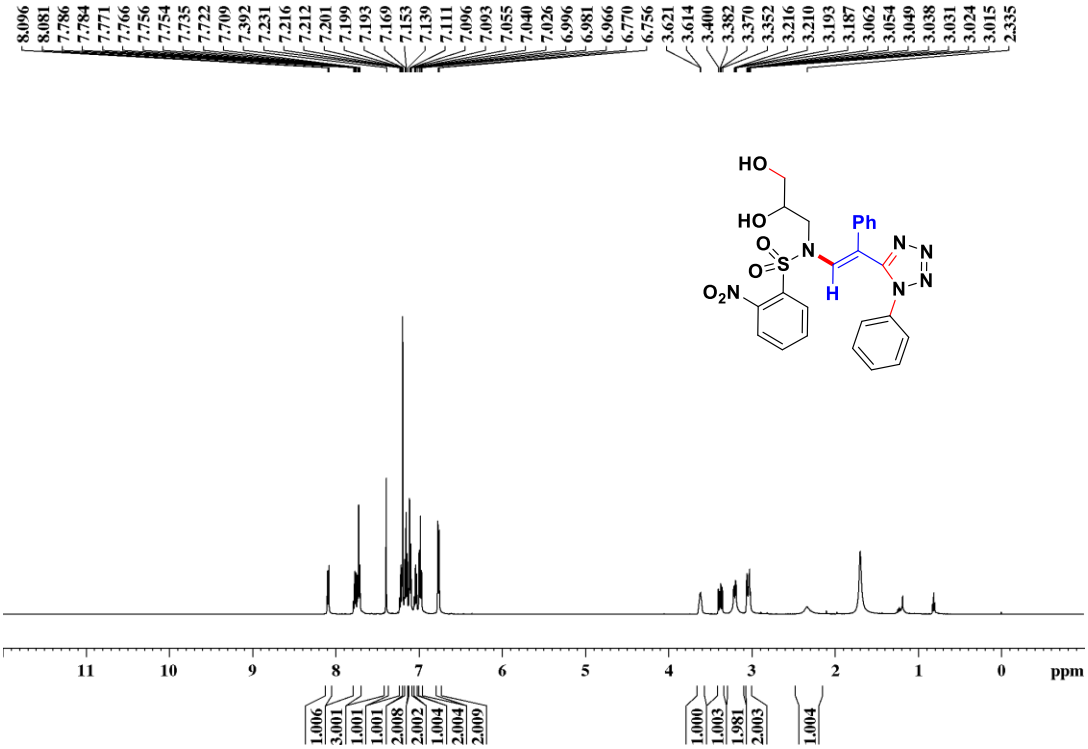

Figure S77. ^{1}H NMR spectrum of compound 5ea

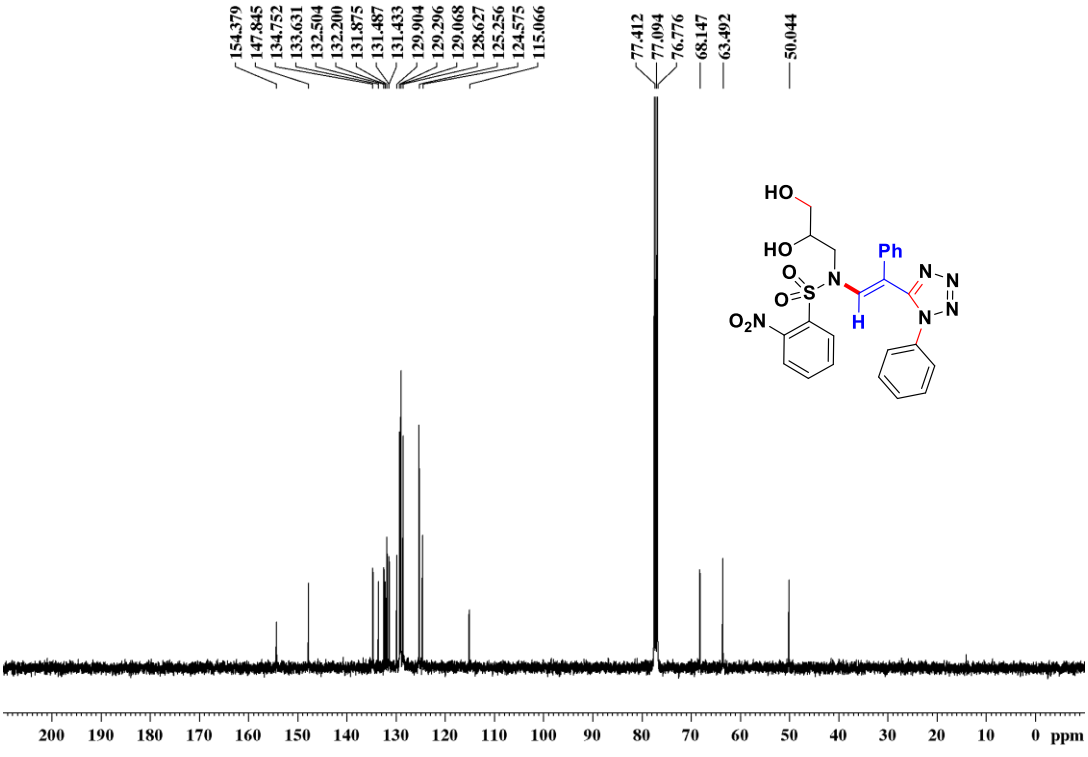

Figure S78. ^{13}C{^{1}H} NMR spectrum of compound 5ea

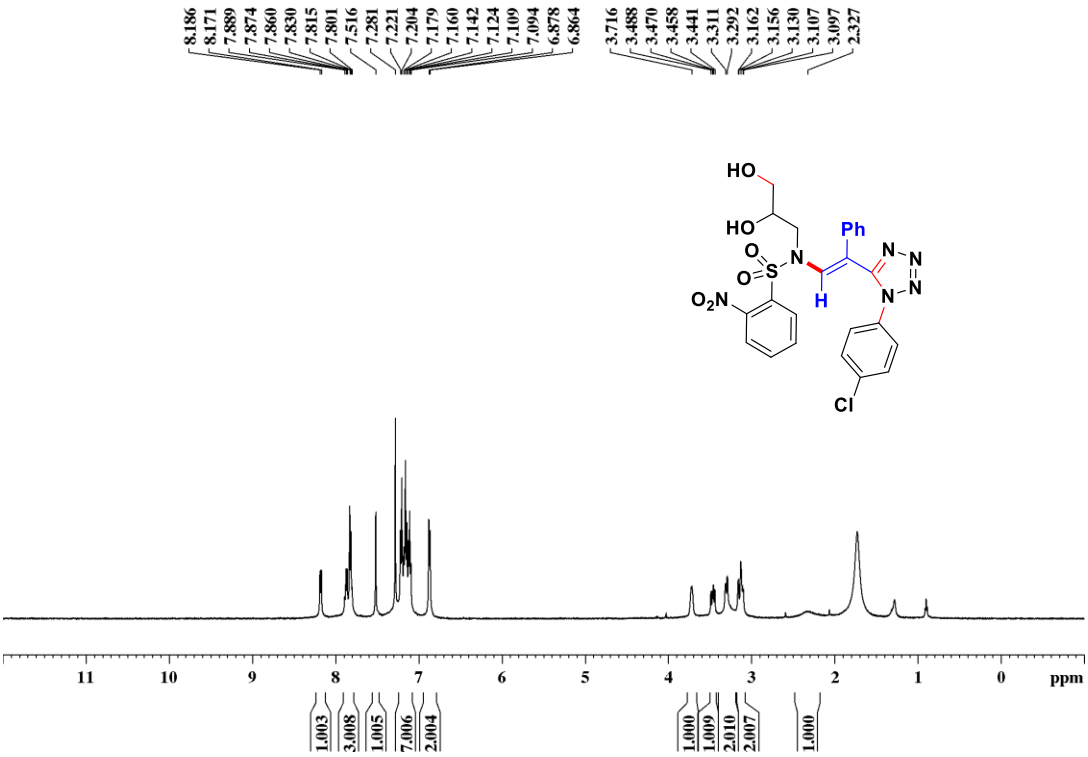

Figure S79. ^{1}H NMR spectrum of compound 5eb

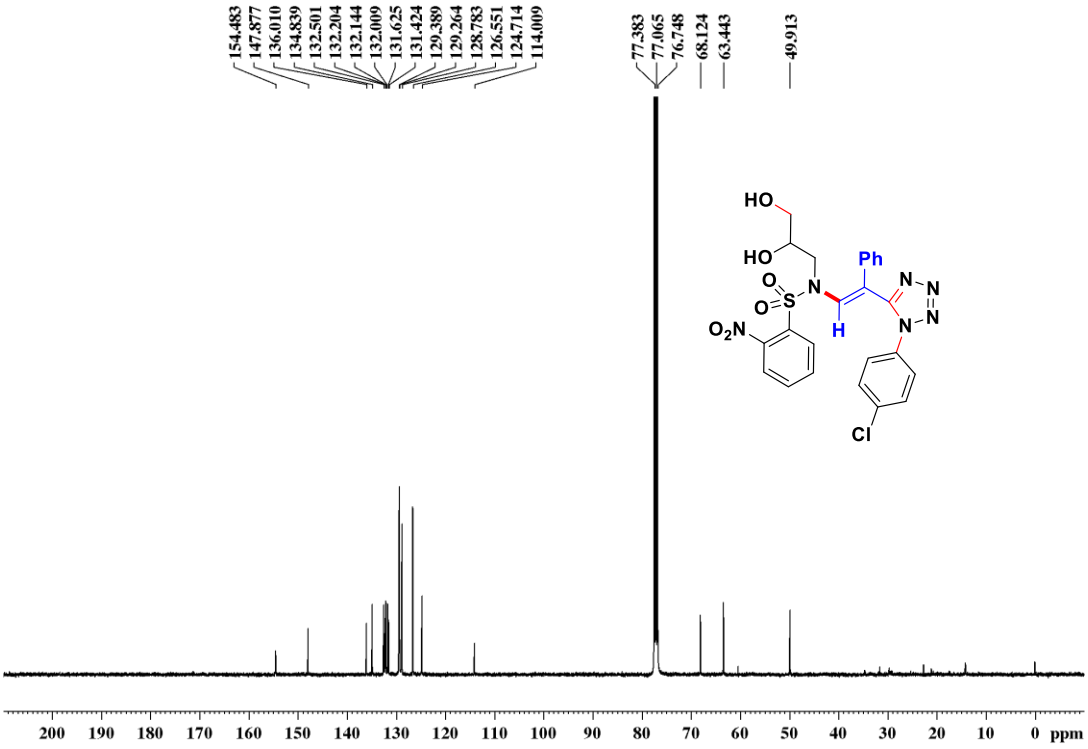

Figure S80. ^{13}C{^{1}H} NMR spectrum of compound 5eb

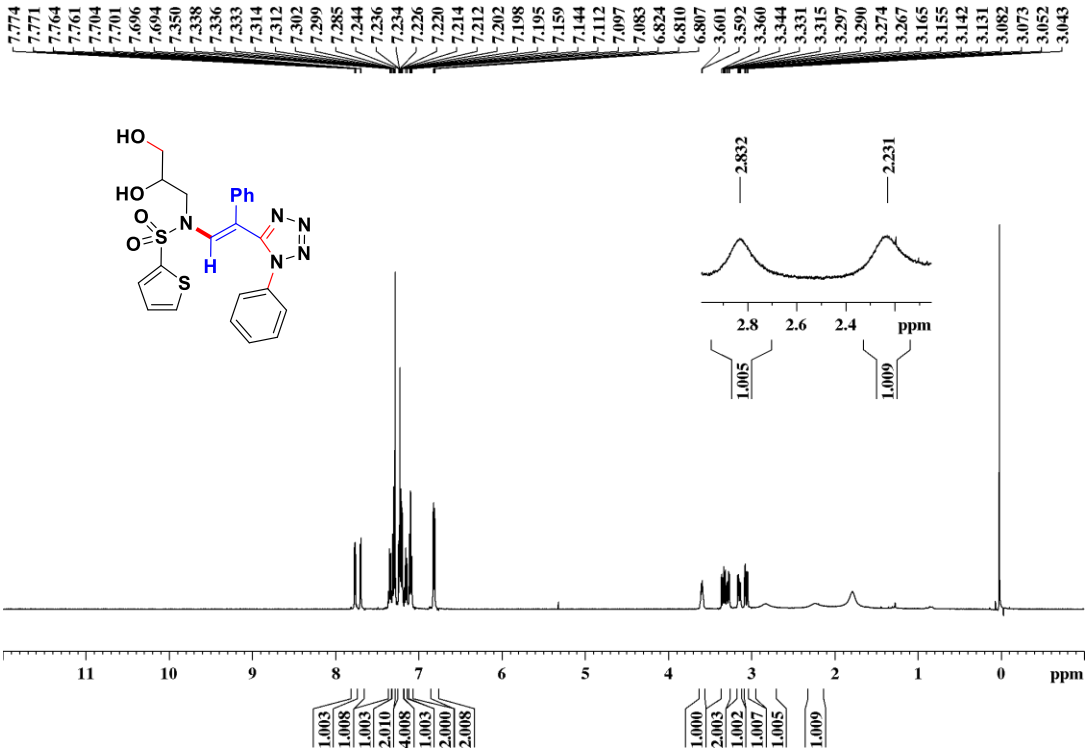

Figure S81. ^{1}H NMR spectrum of compound 5fa

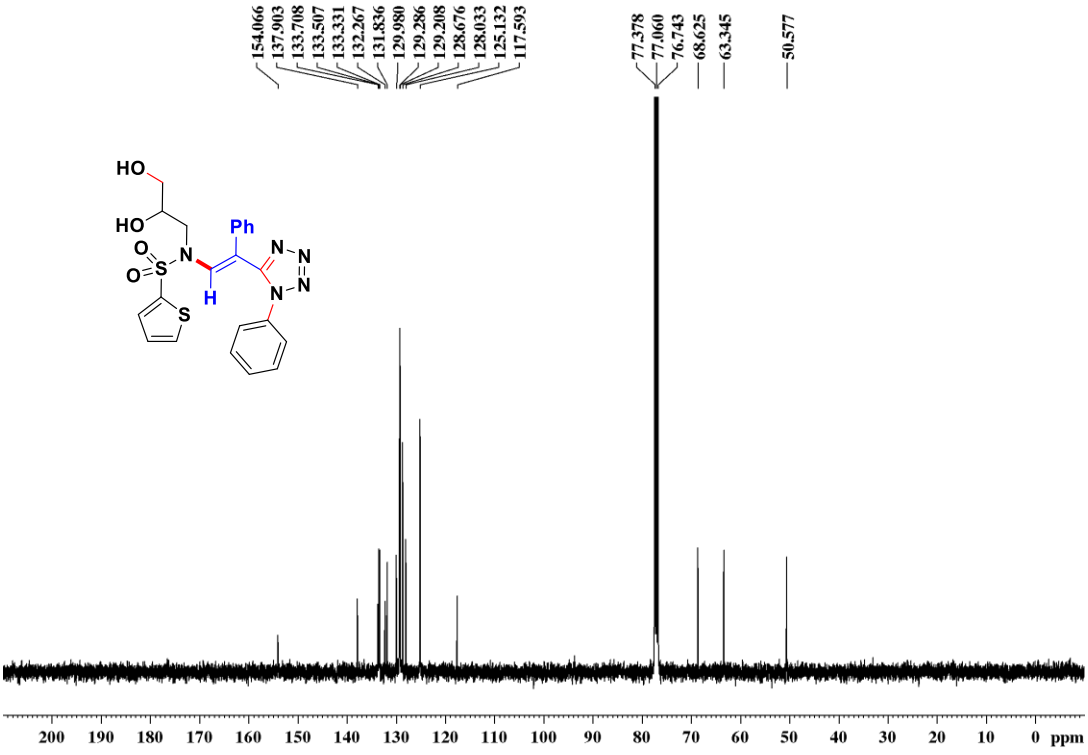

Figure S82. ^{13}C{^{1}H} NMR spectrum of compound 5fa

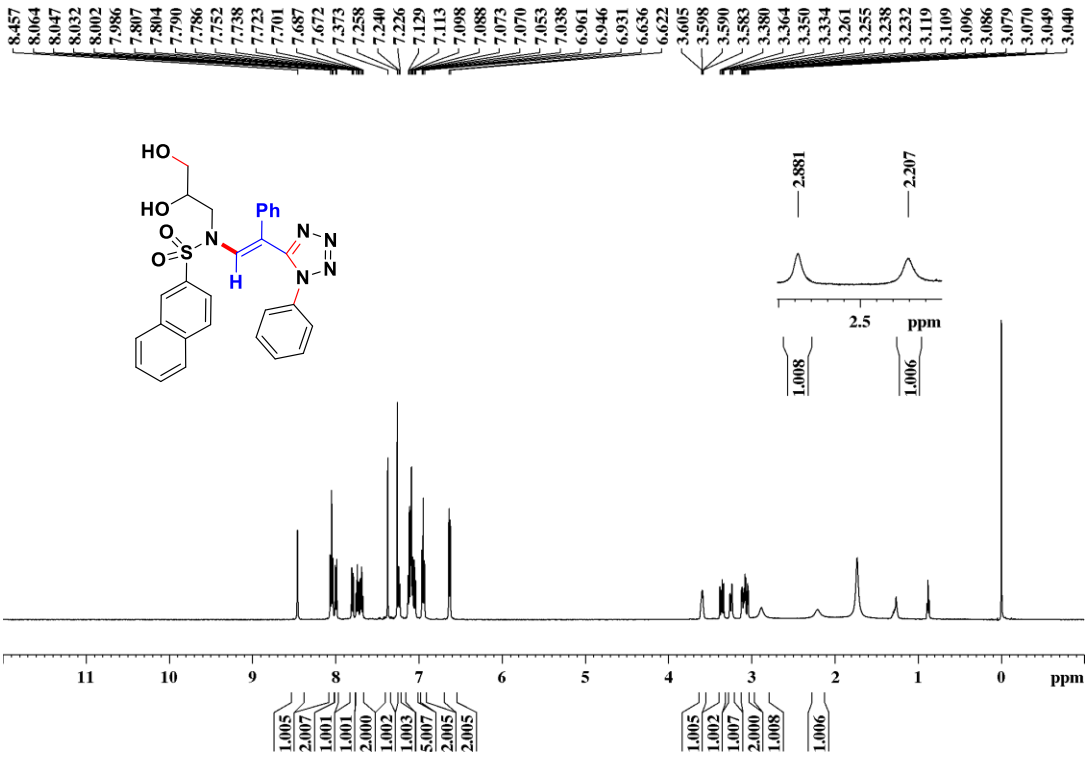

Figure S83. ^{1}H NMR spectrum of compound 5ga

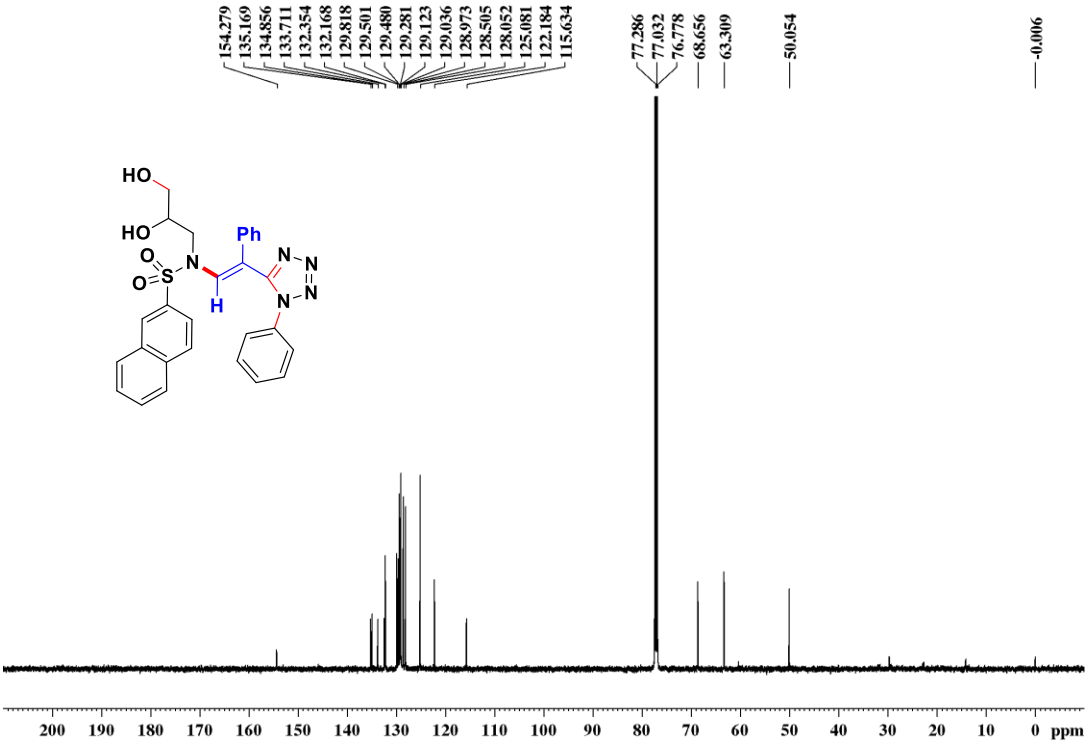

Figure S84. ^{13}C{^{1}H} NMR spectrum of compound 5ga

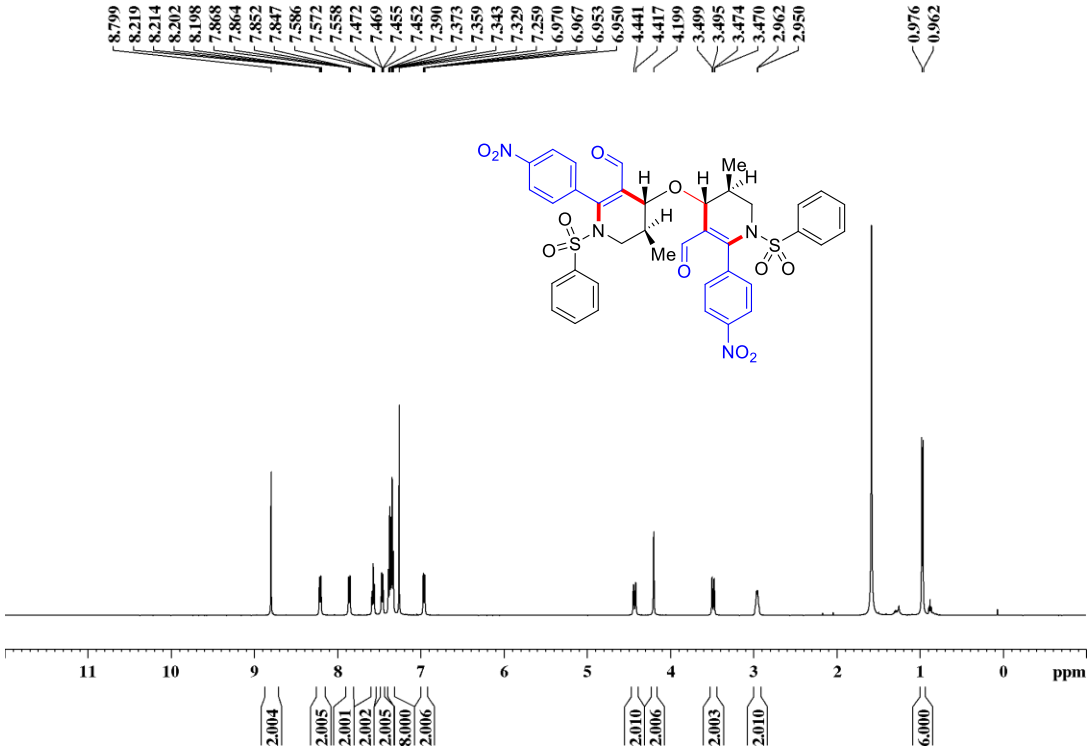

Figure S85. ^{1}H NMR spectrum of compound 6hc

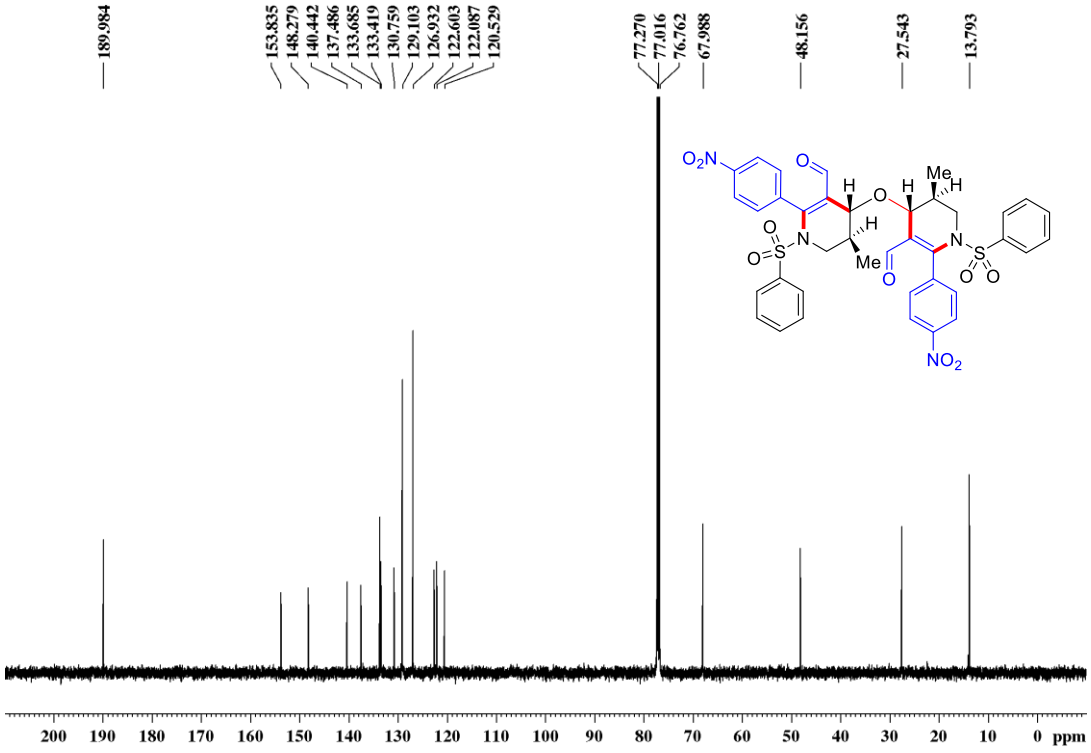

Figure S86. ^{13}C{^{1}H} NMR spectrum of compound 6hc

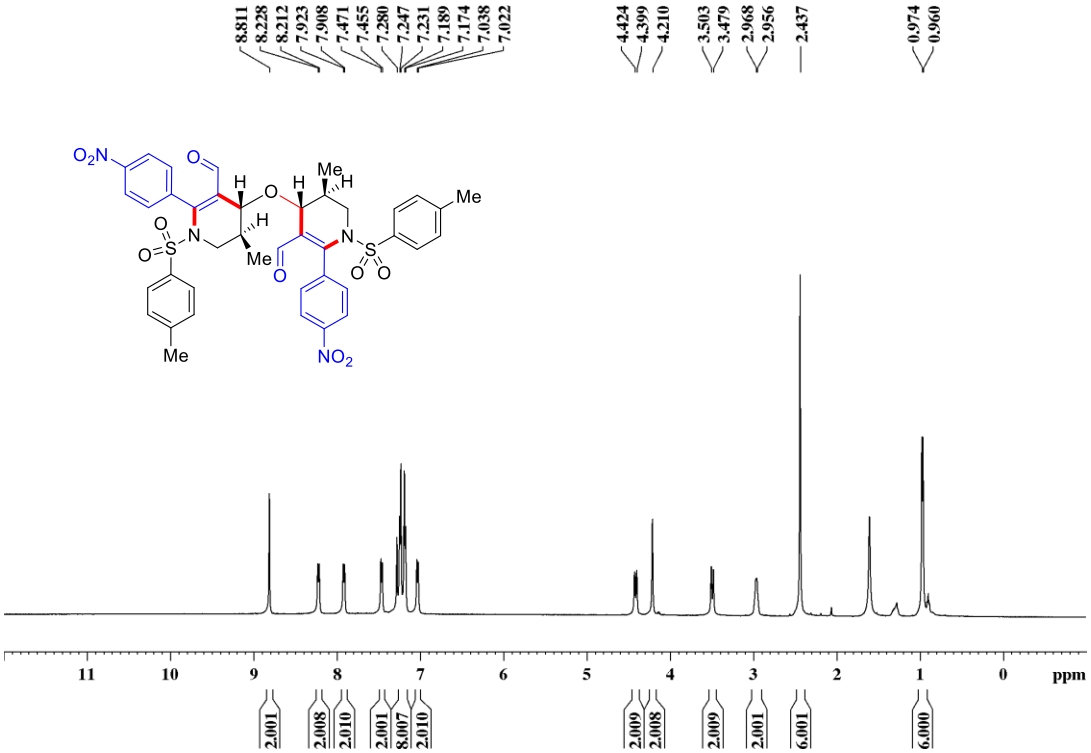

Figure S87. ^{1}H NMR spectrum of compound 6ic

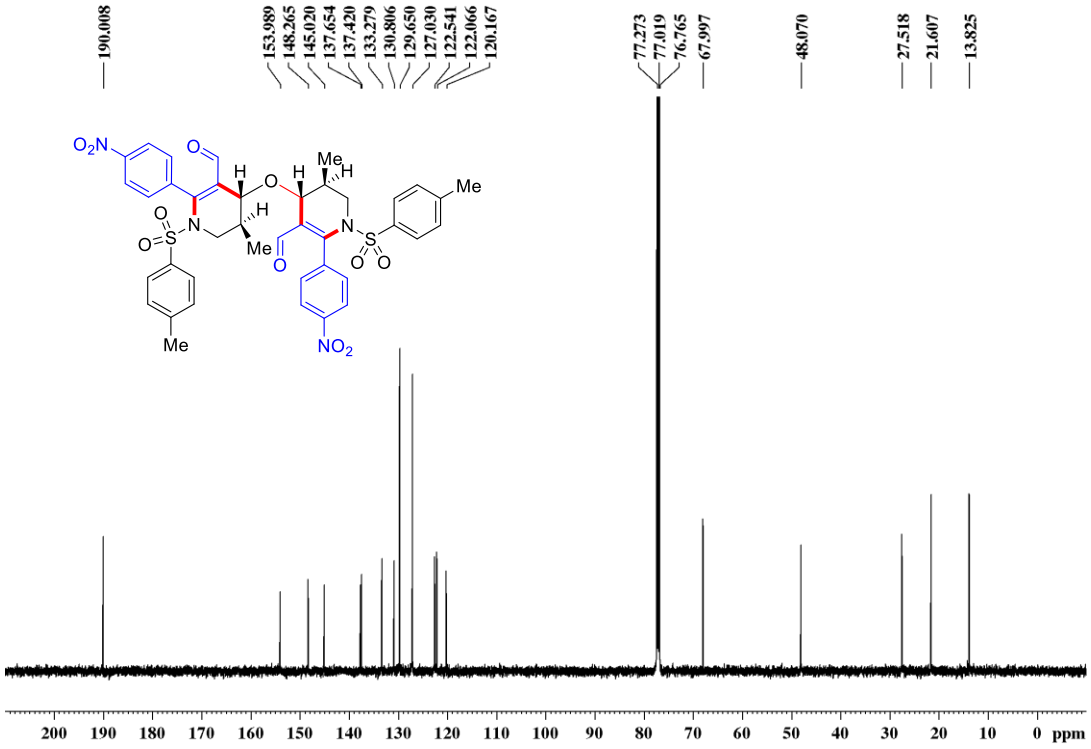

Figure S88. ^{13}C{^{1}H} NMR spectrum of compound 6ic

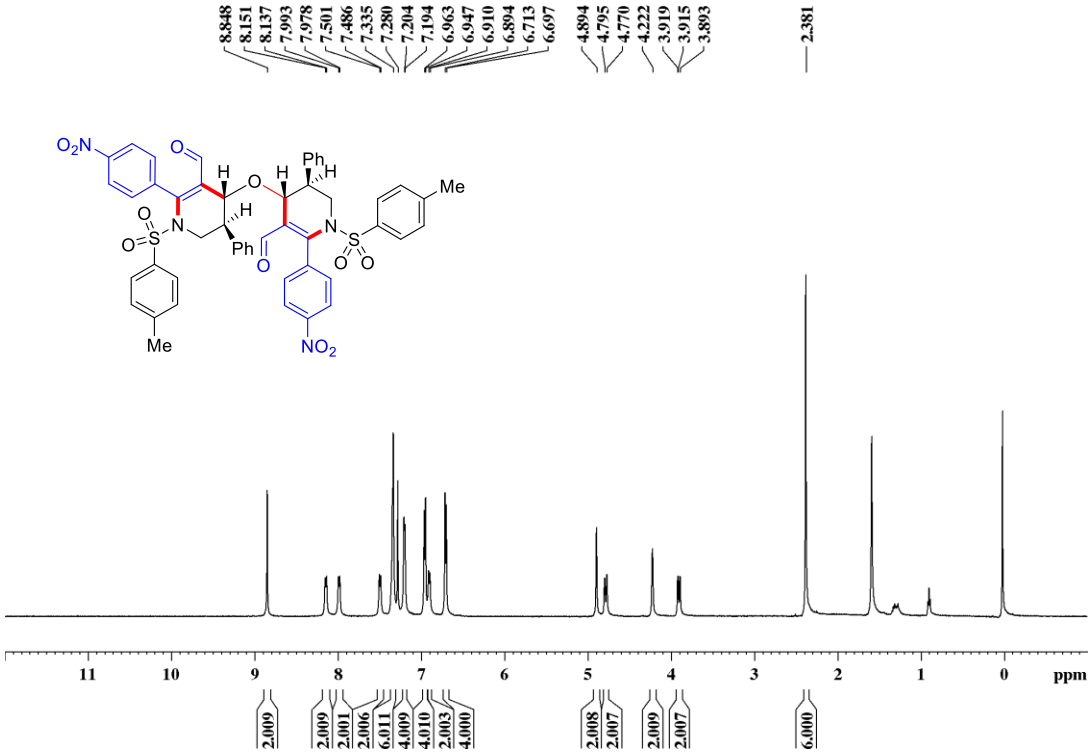

Figure S89. ^{1}H NMR spectrum of compound 6jc

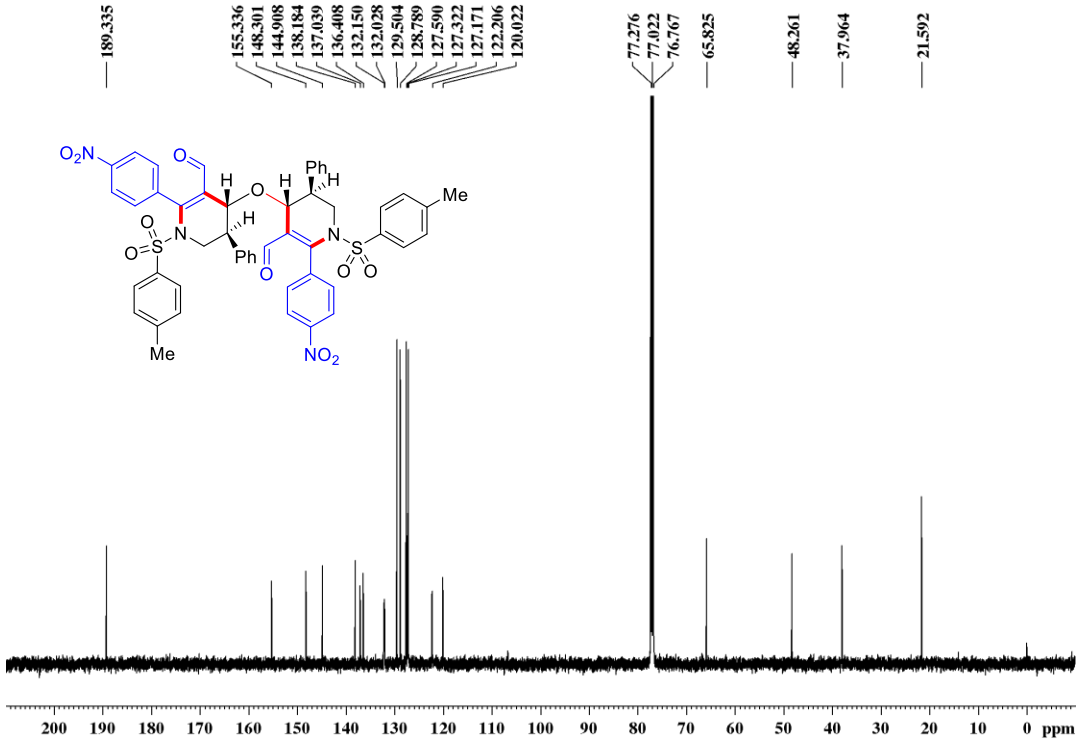

Figure S90. ^{13}C{^{1}H} NMR spectrum of compound 6jc

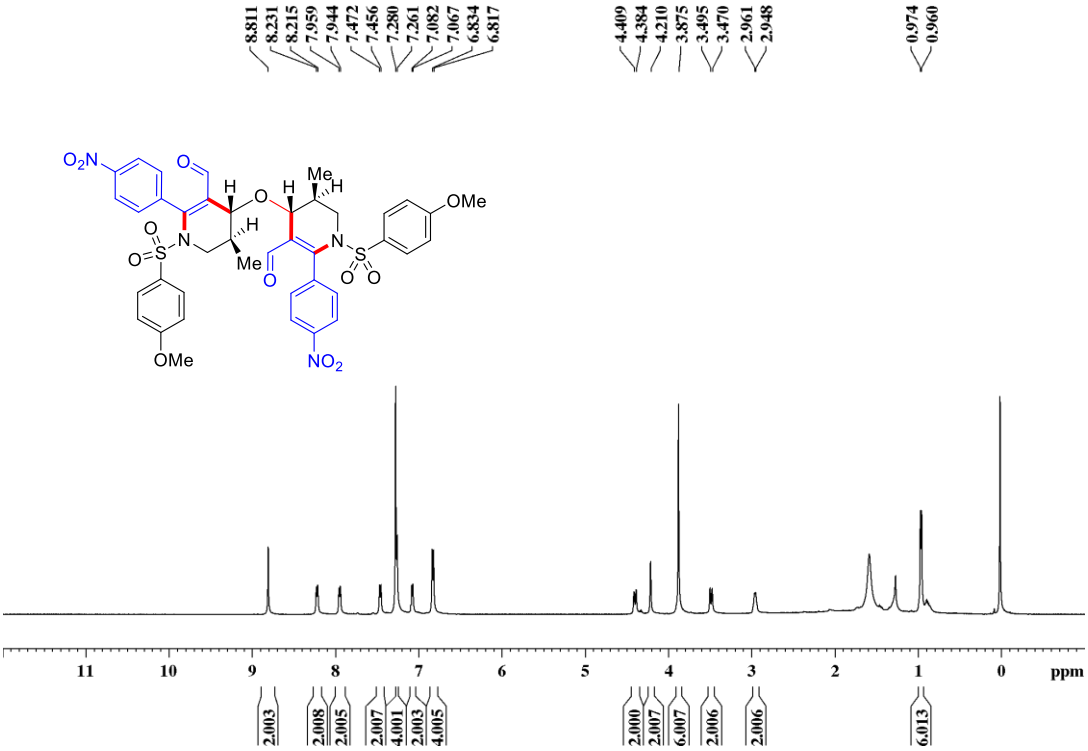

Figure S91. ^{1}H NMR spectrum of compound 6kc

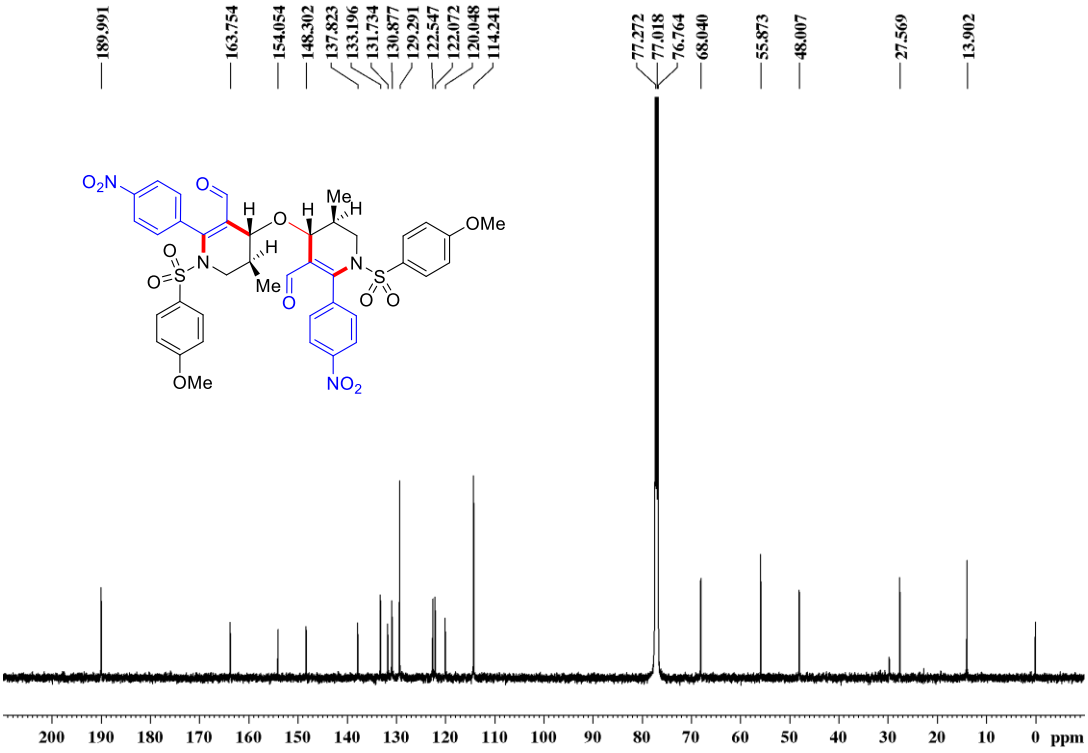

Figure S92. ^{13}C{^{1}H} NMR spectrum of compound 6kc

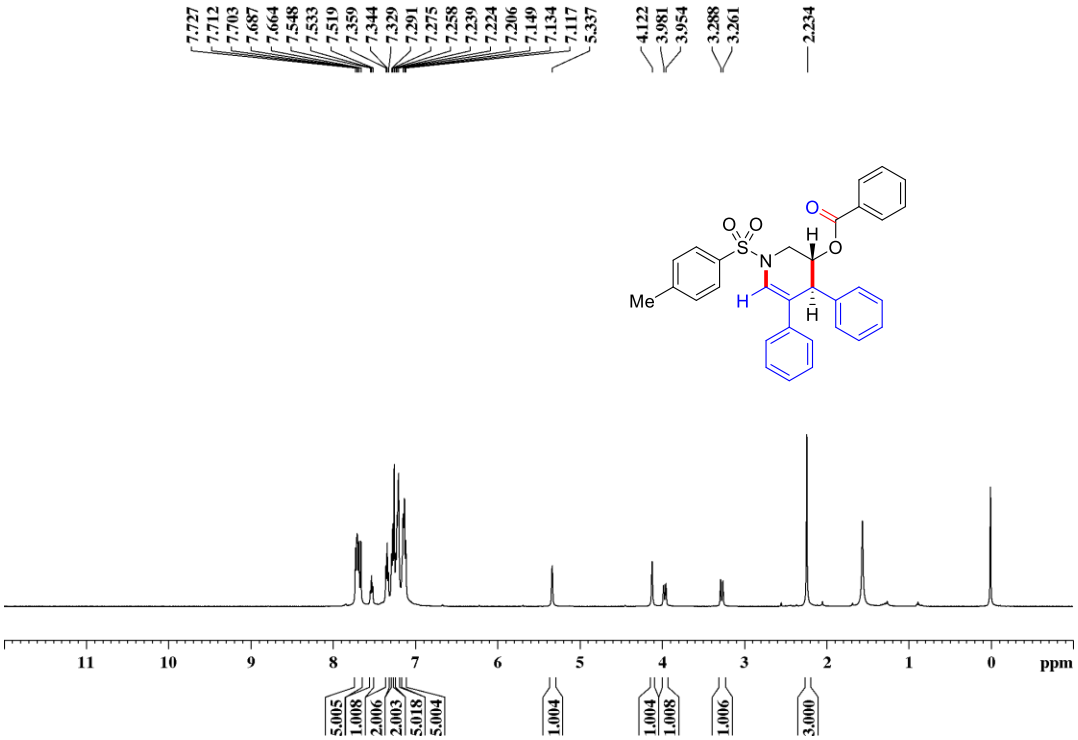

Figure S93. ^{1}H NMR spectrum of compound 7la

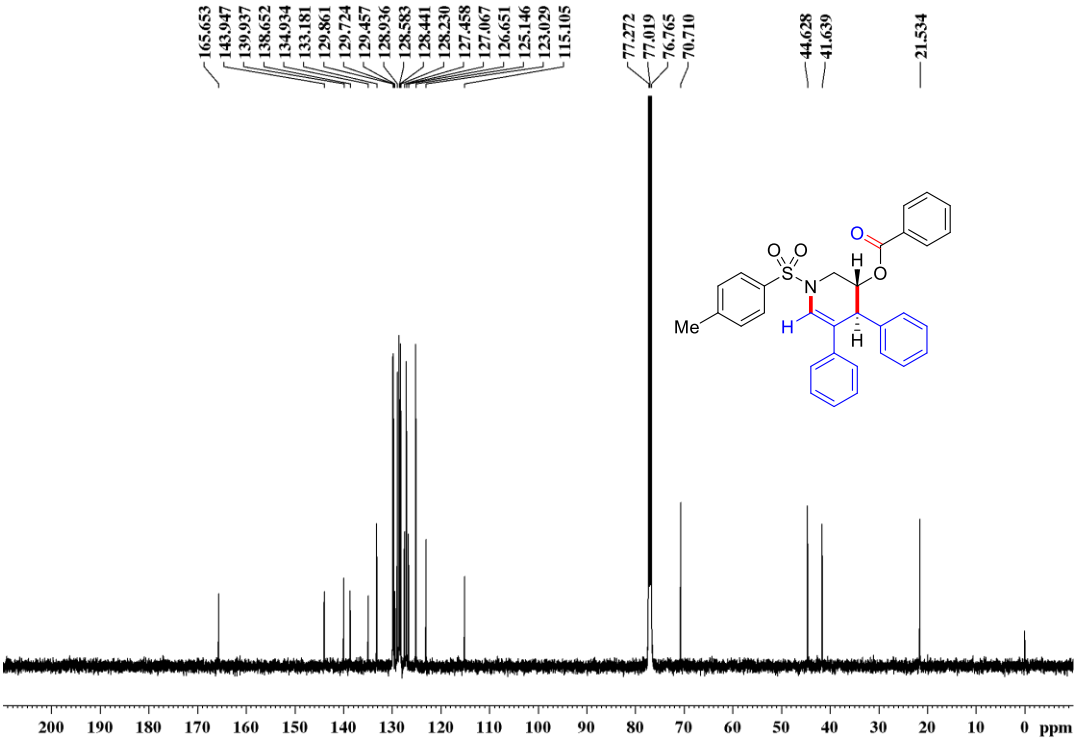

Figure S94. ^{13}C{^{1}H} NMR spectrum of compound 7la