SUPPLEMENTARY INFORMATION

Denitrogenation of Tosylhydrazones: Synthesis of Aryl Alkyl Sulfones Catalyzed by Phenalenyl-Based Molecule

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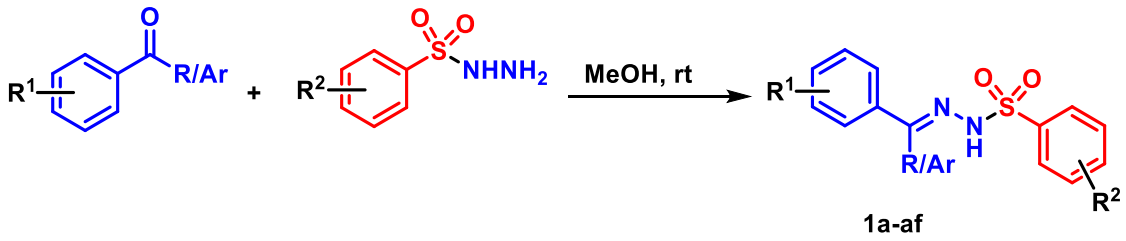
Contents:

I. Experimental Section

General information:

All catalytic and controlled reactions were performed under an oxygen-free atmosphere (Argon or nitrogen) using standard Schlenk techniques. All solvents used in the experiments were dried over a sodium/benzophenone mixture or CaH_2 and distilled before use. All chemicals were purchased from Sigma-Aldrich or Merck or Spectrochem or Alfa Aesar and used as received. Irradiation of the reaction mixture was achieved using a 40 W Kessil PR160L-456 nm LED. Analytical thin-layer chromatography (TLC) was performed on a Merck 60 F254 silica gel plate (0.25 mm thickness). Column chromatography was performed on Merck 60 silica gel (100-200 mesh). The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECS 400 MHz spectrometer and a Bruker Avance III 500 MHz spectrometer in $CDCl_3$ with residual non-deuterated solvent ($CDCl_3$, 7.26/77.0) as an internal standard. Chemical shifts (δ) are given in ppm, and *J* values are given in Hz. All chemical shifts were reported in ppm using tetramethylsilane as a reference. Chemical shifts (δ) downfield from the reference standard were assigned positive values. Evaporation of solvents was performed under reduced pressure using a rotary evaporator. High-resolution mass spectra (HRMS) were obtained on a Bruker maXis impact. EPR spectroscopic measurements were performed on a Bruker (X-band) spectrometer. UV-Vis measurements were carried out on a PerkinElmer Lambda 35 spectrophotometer. Luminescence experiments were carried out on an FLS1000 fluorescence spectrometer from Edinburgh Instruments. All the glassware and NMR tubes used for experiments were kept in an oven at 120 ℃ overnight (12h). Various phenalenyl (PLY)-based molecules were prepared following the reported literature procedures.[1-2]

Experimental Procedures for the Preparation of Starting Materials



Scheme S1. General procedure for the synthesis of tosylhydrazones.

The aldehydes (1.0 equiv.) were added slowly (dropwise/portion wise) to a clear solution of hydrazide (1.0 mmol) in MeOH (5.0 mL). Then, the reaction mixture was stirred at room temperature until complete conversion was observed by TLC. In most of the cases, the hydrazine was precipitated as a white solid. Next, the mixture was cooled down to 0 ℃, filtered, washed with a small amount of cold diethyl ether, and dried *in vacuo* to give the title compounds. The tosylhydrazones **1a-1v** are synthesized earlier[3], and **1w-1af** are newly reported (Figure S1).

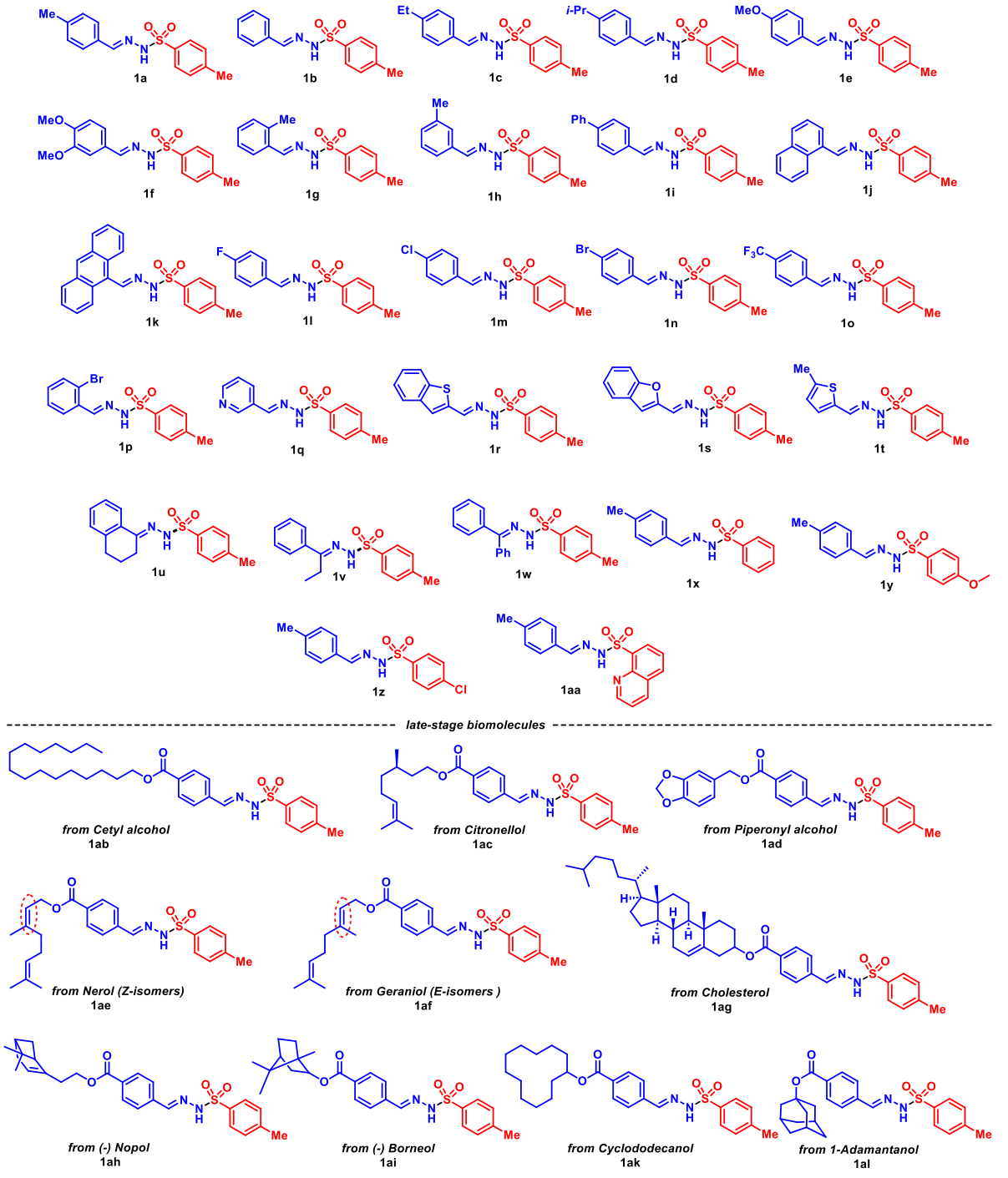
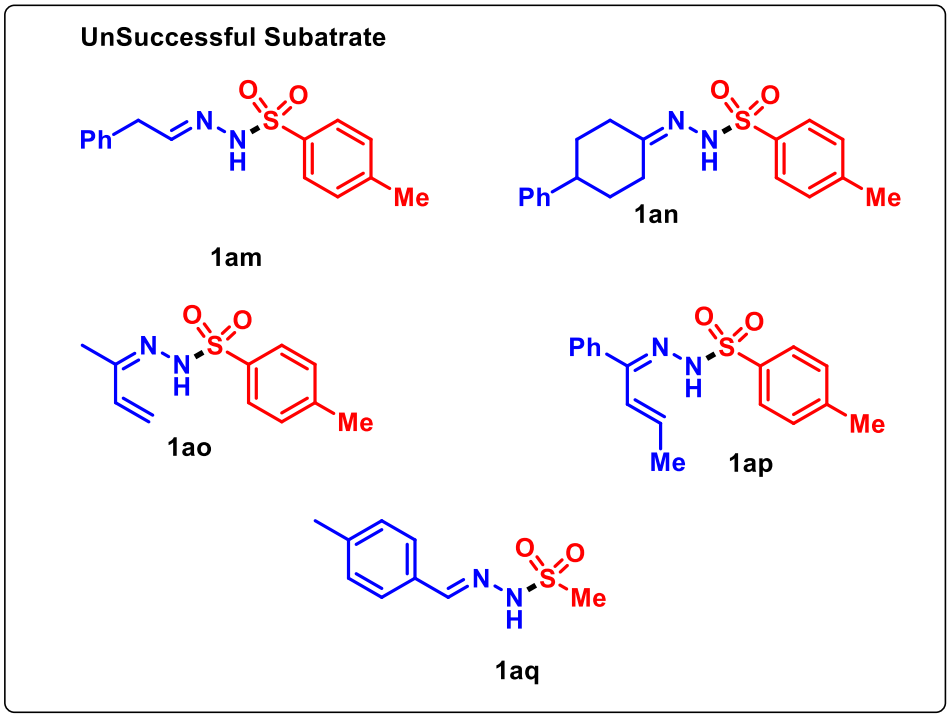


Figure S1. Tosylhydrazone motifs are included in the manuscript.

Unsuccessful Substrate included in the manuscript.

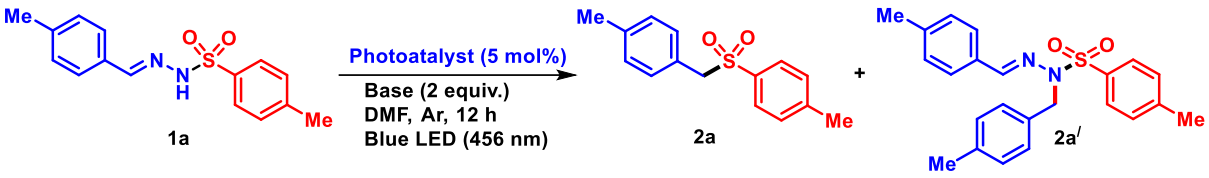


Procedure for optimization of denitrogenative sulfonylation of tosylhydrazones.

1a (0.3 mmol, 86.5 mg), photocatalyst (5 mol%, 0.015 mmol, 3.2 mg), and base (0.9 mmol, 156.7 mg) were taken in an oven-dried 25 mL high-pressure J-Young tube fitted with a teflon cap equipped with a stir bar. Subsequently, 1.5 mL solvent was added to the reaction mixture, and the tube was closed properly. In the Schlenk line, a freeze-pump-thaw cycle was applied twice to maintain an inert atmosphere. Next, argon was purged into the reaction mixture. The reaction tube was closed properly and placed under blue LED irradiation at 456 nm for 12 h. After completion of the reaction, the internal standard, 1,4-dimethoxybenzene (0.1 mmol, 13.8 mg), was added to the crude reaction mixture, and the product was extracted in 25 mL ethyl acetate and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and yields were determined from ^{1}H-NMR spectroscopy of the crude reaction mixture. The desired product, 1-methyl-4-((4-methylbenzyl)sulfonyl)benzene (**2a**), was purified by column chromatography on silica gel (100-200 mesh) using hexane/EtOAc mixture as an eluent.

Optimization of the Reaction Conditions

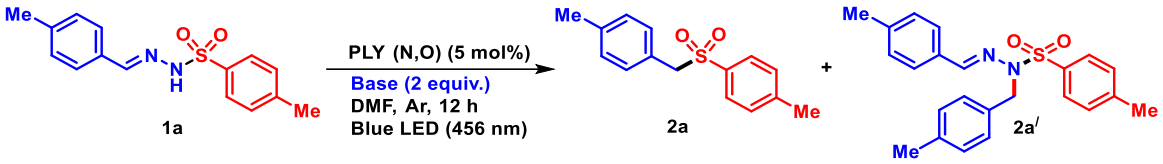
Table S1. Photocatalyst investigation for the denitrogenative sulfonylation reaction of tosylhydrazones



Entry	Catalyst (5 mol%)	Base (3 equiv.)	Solvent	NMR Yield (2a, 2a/) %[a]
1.	**PLY (N,O)**	**K_2HPO_4**	**DMF**	**87, 6**
2.	PLY (O,O)	K_2HPO_4	DMF	70, 5
3.	Rose Bengal	K_2HPO_4	DMF	NR
4.	Eosin Y	K_2HPO_4	DMF	NR
5.	Riboflavin	K_2HPO_4	DMF	NR
6.	Rohdamine B	K_2HPO_4	DMF	25, < 5%
7.	4CzIPN	K_2HPO_4	DMF	62, 5
8.	[Acr-Mes]ClO_4	K_2HPO_4	DMF	NR
9.	PTH	K_2HPO_4	DMF	11, -

[a]The reactions were carried out using **1a** (0.3 mmol), photocatalyst (5 mol%, 0.015 mmol), K_2HPO_4 (3 equiv., 0.9 mmol), and DMF (1.5 mL). Product conversion was determined using 1,4-dimethoxybenzene as the internal standard. NR = No reaction.

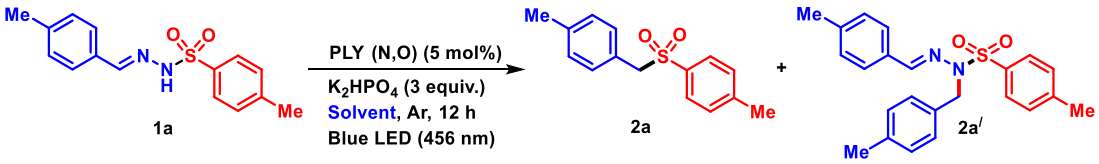
Table S2. Investigation of the most suitable base for the denitrogenative sulfonylation reaction of tosylhydrazones



Entry	Catalyst (5 mol%)	Base	Solvent	NMR Yield (2a, 2a/) %[a]
1.	PLY (N,O)	K_2HPO_4 (2 equiv.)	DMF	60, 5%
2.	PLY (N,O)	K_2CO_3 (2 equiv.)	DMF	40, < 5%
3.	PLY (N,O)	K_3PO_4 (2 equiv.)	DMF	11, -
4.	PLY (N,O)	KO^{t}Bu (2 equiv.)	DMF	11, -

[a]The reactions were carried out using **1a** (0.3 mmol), PLY (N,O) ligand (5 mol%), base (2 equiv.), and DMF (1.5 mL). Product conversion was determined using 1,4-dimethoxybenzene as the internal standard.

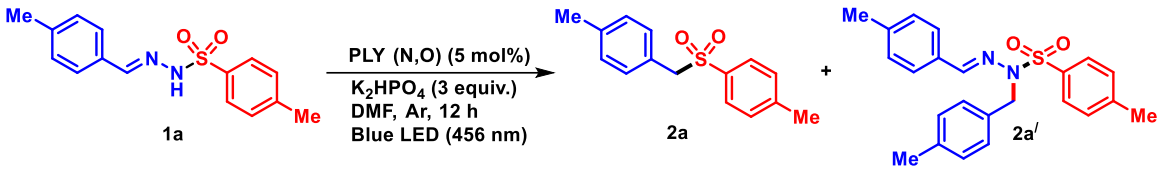
Table S3. Investigation of the most suitable solvent for the denitrogenative sulfonylation reaction of tosylhydrazones



Entry	Catalyst (5 mol%)	Base (3 equiv.)	Solvent	NMR Yield (2a, 2a/) %[a]
1.	PLY (N,O)	K_2HPO_4	1,4-dioxane	28, < 5%
2.	PLY (N,O)	K_2HPO_4	DMSO	64, 6
3	PLY (N,O)	K_2HPO_4	ACN	19, < 5%
4	PLY (N,O)	K_2HPO_4	THF	39, < 5%
5	**PLY (N,O)**	**K_2HPO_4**	**DMF**	**87, 6**

[a]The reactions were carried out using **1a** (0.3 mmol), PLY (N,O) ligand (5 mol%), K_2HPO_4 (3 equiv.), and solvent (1.5 mL). Product conversion was determined using 1,4-dimethoxybenzene as the internal standard.

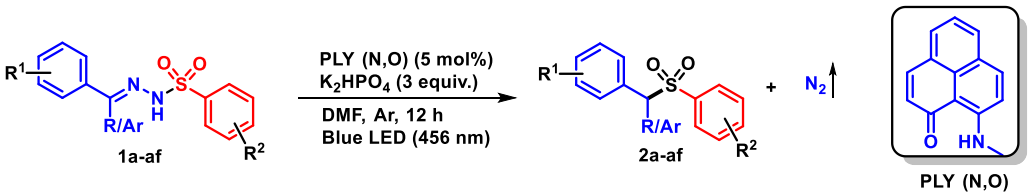
Table S4. Control experiments for the denitrogenative sulfonylation reaction of tosylhydrazones



Entry	Catalyst (5 mol%)	Base (3 equiv.)	Solvent	NMR Yield (2a, 2a′) %[a]
1.	-	K_2HPO_4	DMF	NR
2[b].	PLY (N,O)	K_2HPO_4	DMF	77, 5
3[c].	PLY (N,O)	K_2HPO_4	DMF	NR
4.	PLY (N,O)	-	DMF	12, -
5[d].	PLY (N,O)	K_2HPO_4	DMF	NR

[a]The reactions were carried out using **1a** (0.3 mmol), PLY (N,O) ligand (5 mol%), K_2HPO_4 (3 equiv.), and DMF (1.5 mL). Product conversion was determined using 1,4-dimethoxybenzene as the internal standard. [b]440 nm kessil blue LED was used instead of 456 nm. [c]Dark condition. [d]Under air. NR = No reaction.

General procedure for the denitrogenative sulfonylation of tosylhydrazones



Scheme S2. Denitrogenative sulfonylation of tosylhydrazones catalyzed by PLY (N,O)

Tosylhydrazones **1a-af** (0.3 mmol)], PLY (N,O) (5 mol%, 0.015 mmol, 3.2 mg), K_2HPO_4 (0.9 mmol, 156.7 mg) were taken in an oven-dry 25 mL high-pressure J-Young tube with a Teflon cap equipped with a stir bar. Subsequently, 1.5 mL DMF was added to the reaction mixture, and the tube was closed properly. In the Schlenk line, a freeze-pump-thaw cycle was applied twice to maintain an inert atmosphere. Next, argon was purged into the reaction mixture. The reaction tube

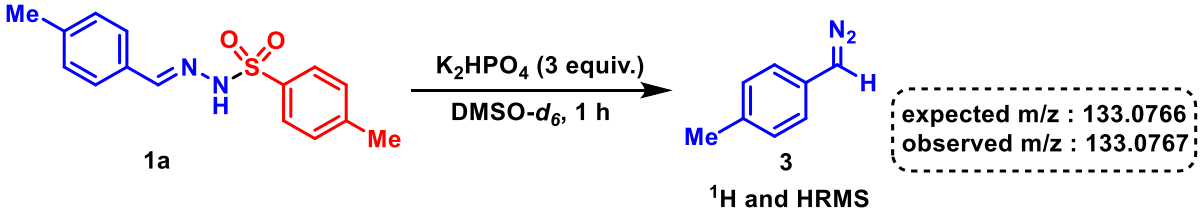
was closed properly and placed under blue LED irradiation at 456 nm for 12 h. After completion of the reaction, the product was extracted in 25 mL ethyl acetate and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel (100-200 mesh) using a hexane/EtOAc mixture to obtain the pure desired products, which were characterized by NMR spectroscopy.

II. Mechanistic studies

Control experiments for mechanistic investigations.

To prove the mechanistic course for the denitrogenative sulfonylation of tosylhyrazones through the transition metal-free phenalenyl ligand-catalyzed pathway, we performed several control experiments.

a. Involvement of diazo intermediate.



Scheme S3. *In situ* generation of the diazo intermediate from tosylhydrazone **1a**.

To check the generation of intermediates in the reaction mixture, an *in situ* ^{1}H NMR study was performed [16].

A 2.5 mL screw cap NMR tube was charged with **1a** (0.05 mmol, 14.4 mg) and K_2HPO_4 (2 equiv., 0.1 mmol, 17.4 mg) in 0.6 mL DMSO-d_6 under an argon atmosphere. The reaction mixture was allowed to stir for 1 h and then *in situ* ^{1}H NMR spectrum was measured, and deprotonation of N-H proton of **1a** was observed (compound **9**), confirmed by the disappearance of peak at 11.34 ppm (see Figure S2, middle spectrum). The same reaction mixture was further stirred for another 30 min under the argon atmosphere and ^{1}H NMR and high-resolution mass spectrometry (HRMS), was performed and the formation of the diazo intermediate (**3**) was confirmed (Figure S2, lower spectra).

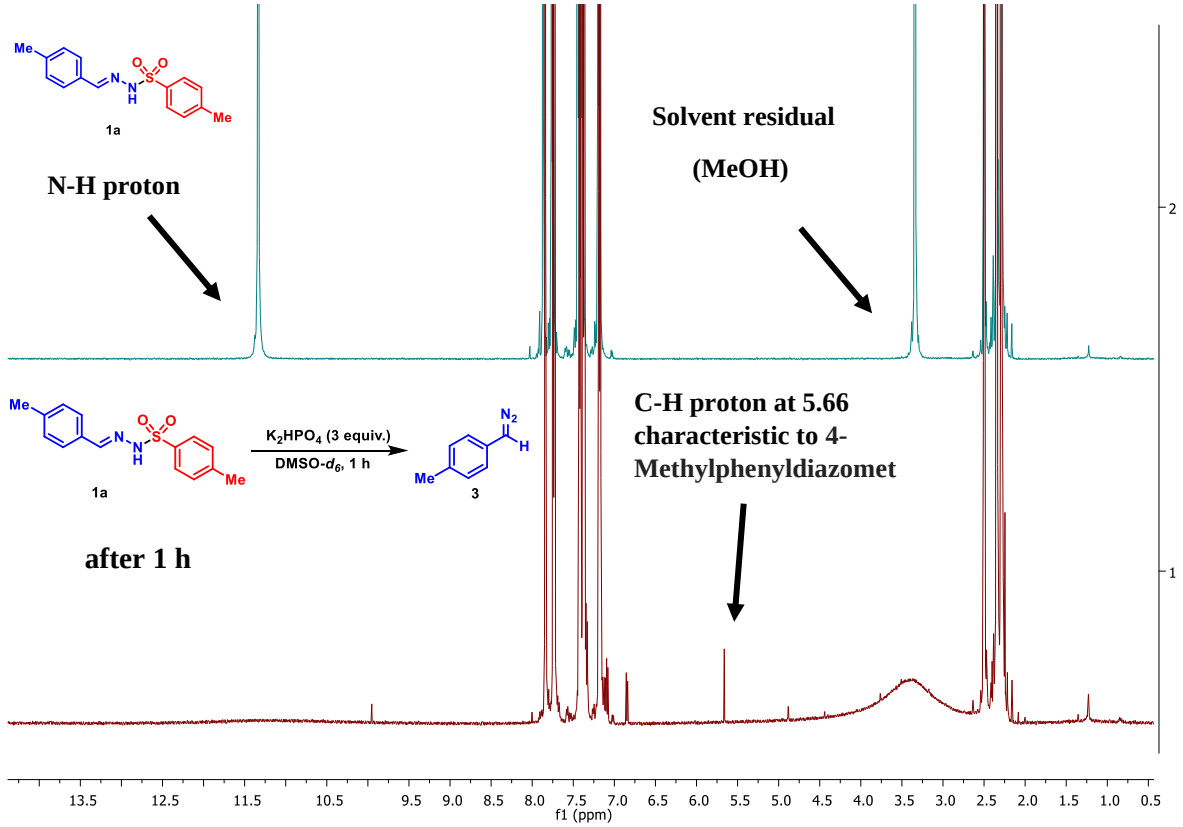


Figure S2. Stacked ^{1}H NMR spectra (DMSO-d_6) of **1a** (top) and **3** (below) after 1h.

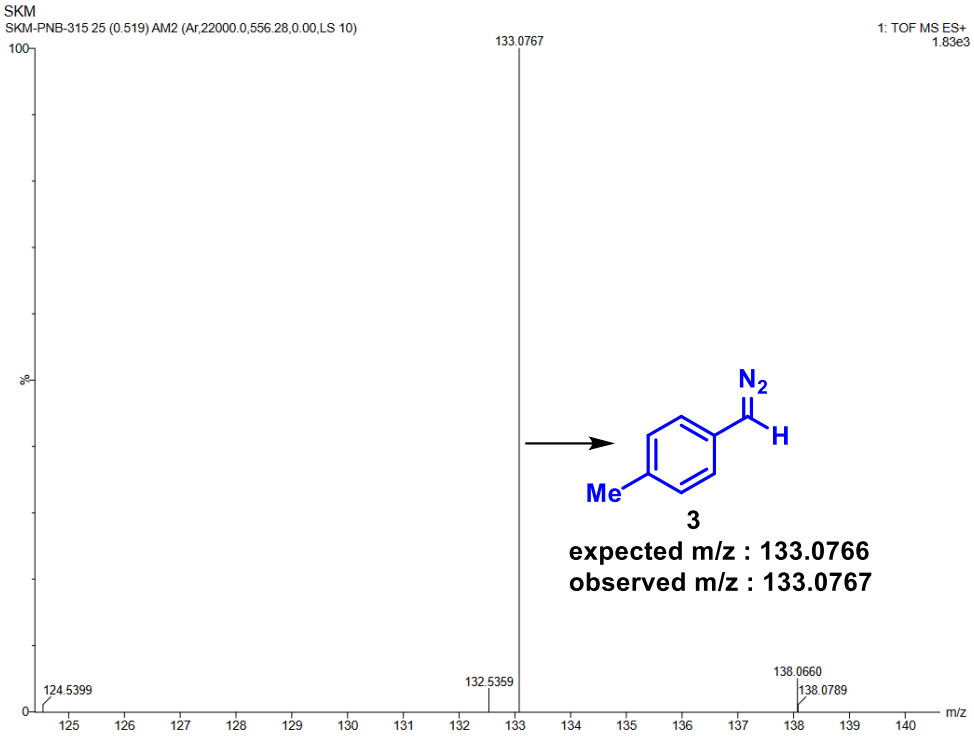
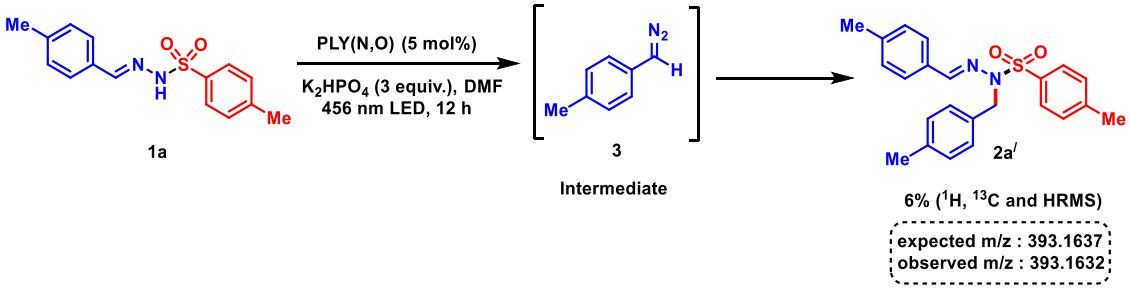


Figure S3. HRMS of diazo intermediate **3** obtained from tosylhydrazone **1a**.

b. Detection and characteriazation of N-alkylated tosylhydrazone (2a′) as a side product from a catalytic mixture.

1) Detection of carbene intermediate in catalytic system



Scheme S4. Detection and characterization of N-alkylated tosylhydrazone (**2a′**) from tosylhydrazone **1a**.

The compound **2a′** was detected under the optimized reaction condition (Scheme S2) and was purified by column chromatography over silica gel (100-200 mesh) using hexane/EtOAc mixture to yield the pure desired products, which was characterized by NMR spectroscopy (^{1}H, ^{13}C) and HRMS [m/z 393.1632 (observed), 393.1637 (expected)].

The crude product was purified by column chromatography using silica gel (100-200 mesh) with 7% of EtOAc in hexane and obtained as colourless liquid (6% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ (ppm) 7.84 (d, *J* = 8.2 Hz, 2H), 7.64 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 6.3 Hz, 4H), 4.75 (s, 2H), 2.42 (s, 3H), 2.33 (s, 3H), 2.31 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298K): δ (ppm) 148.2, 143.9, 140.4, 132.5, 129.5, 129.2, 128.2, 127.4, 127.0, 52.1, 21.5, 21.4, 21.0.

HRMS (TOF) m/z: $[M + H]^+$ Calcd for $C_{36}H_{36}NaO_2$ 393.1637; Found 393.1632.

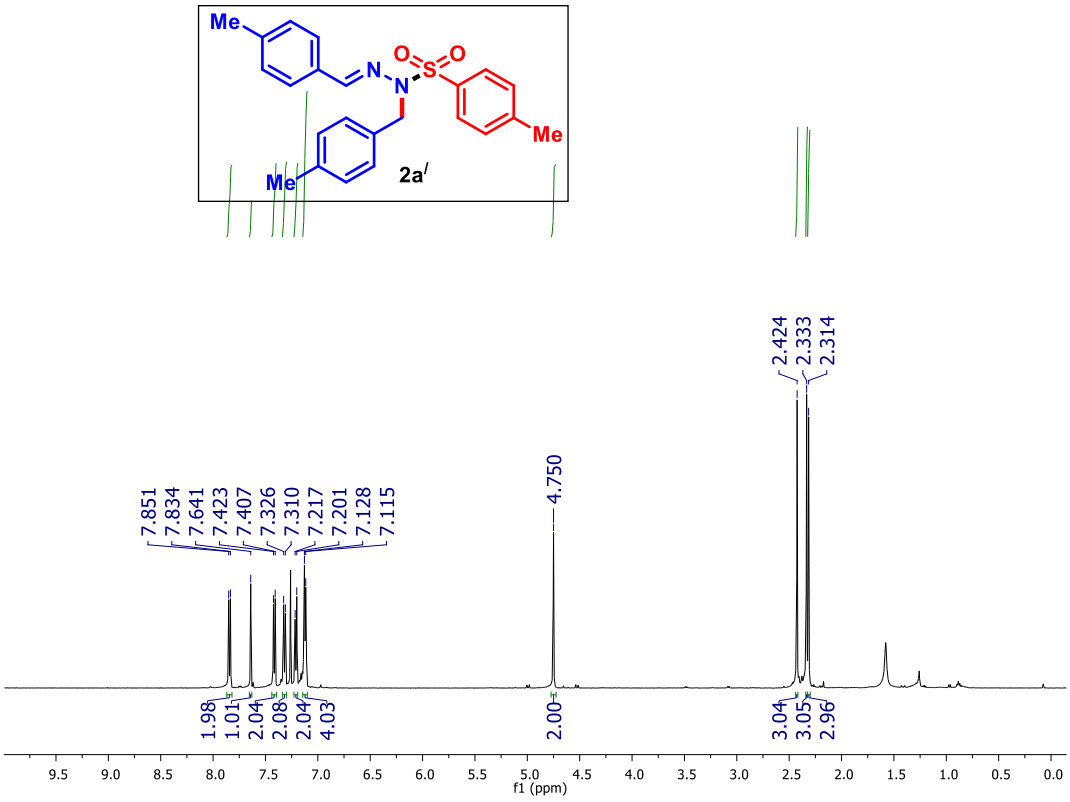


Figure S4. ^{1}H NMR spectrum ($CDCl_3$) of (*E*)-4-methyl-N-(4-methylbenzyl)-N'-(4-methylbenzylidene)benzenesulfonohydrazide (**2a$^{/}$**).

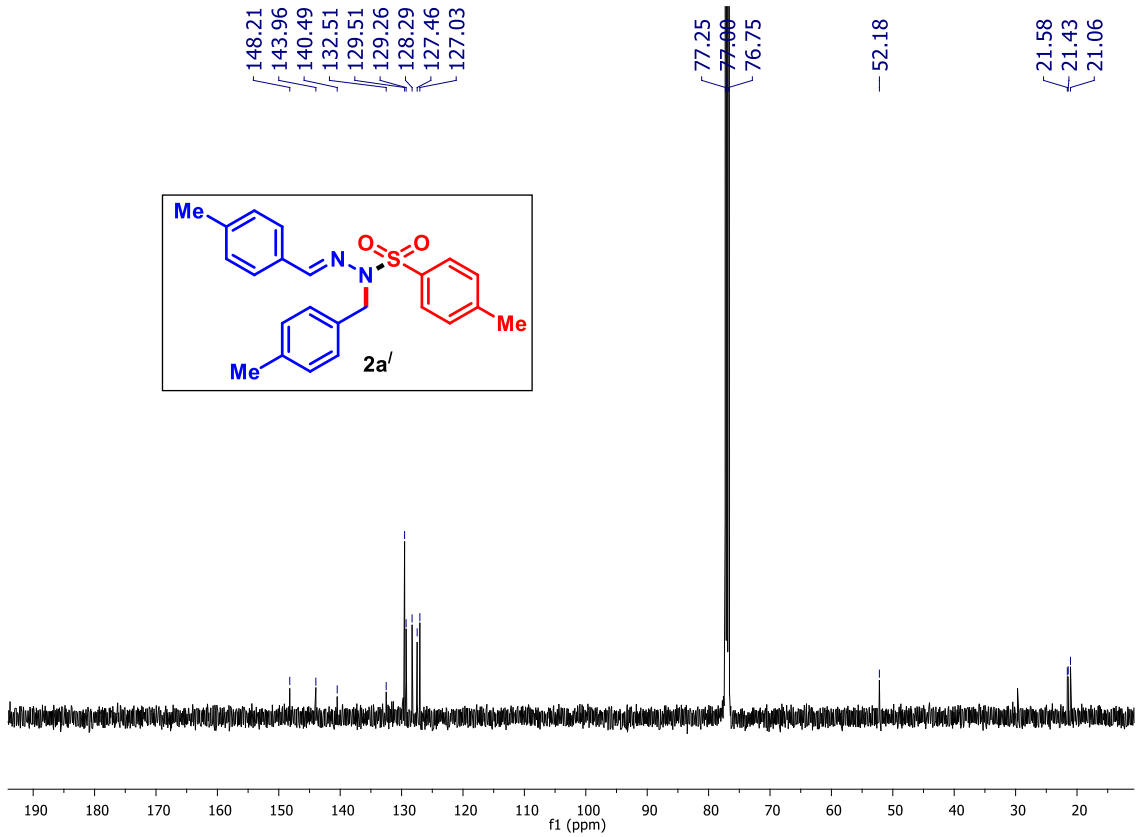


Figure S5. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of (*E*)-4-methyl-N-(4-methylbenzyl)-N'-(4-methylbenzylidene)benzenesulfonohydrazide (**2a**$^{/}$).

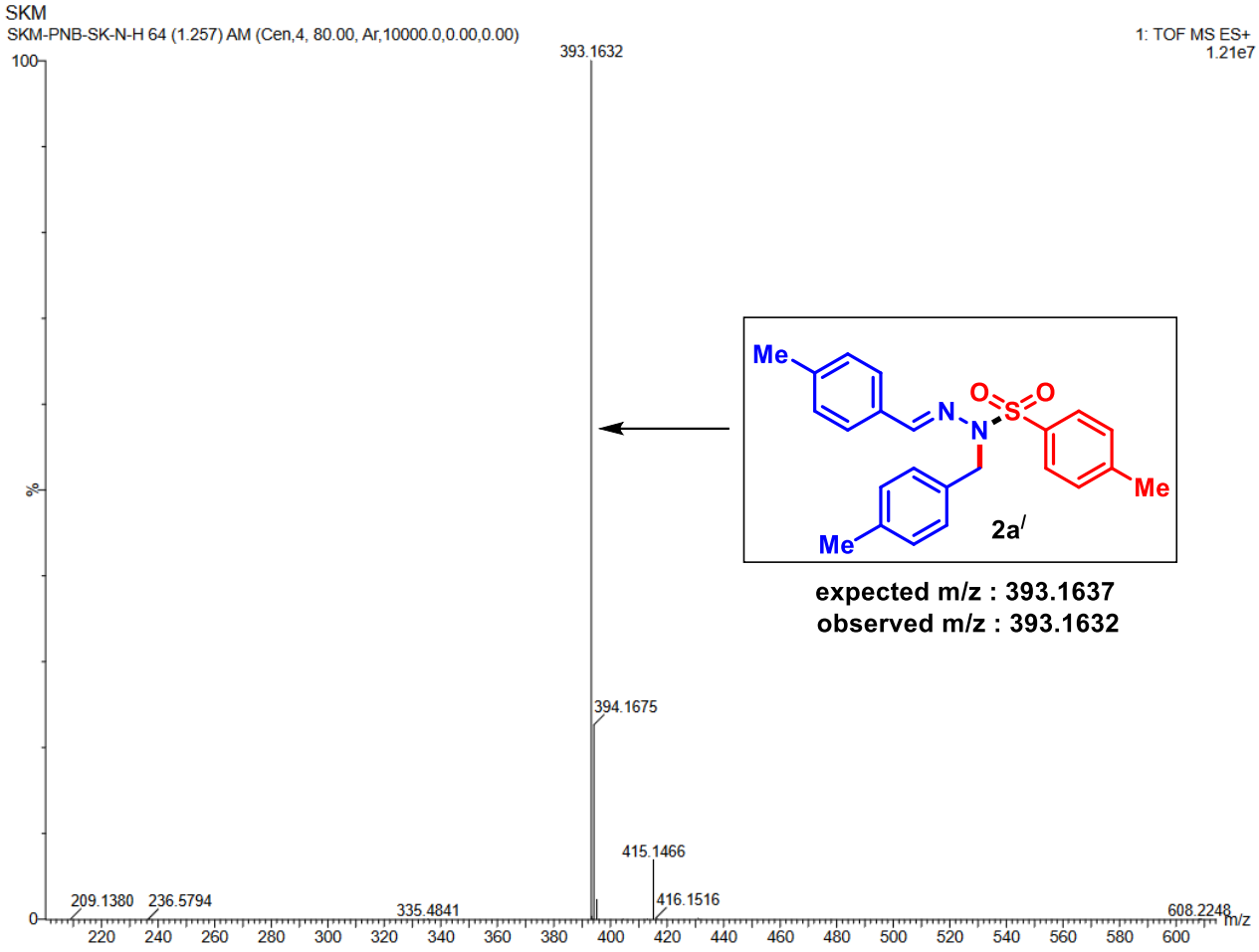
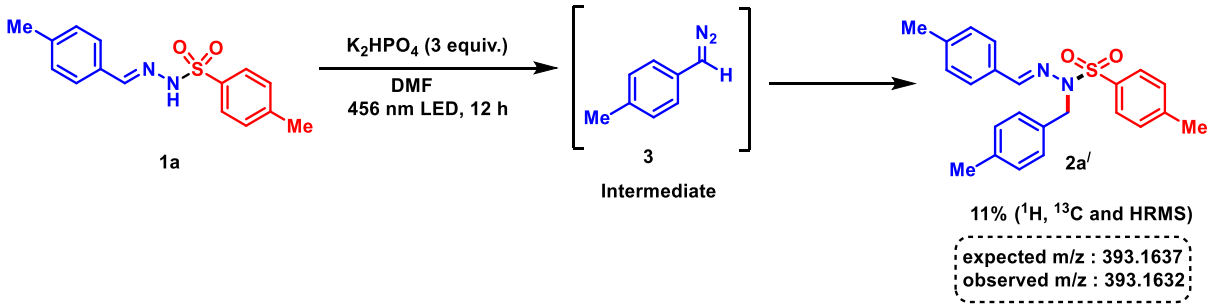


Figure S6. HRMS of carbene trapped intermediate (**2a**/).

2) Detection of carbene in the absence of PLY (N,O) :



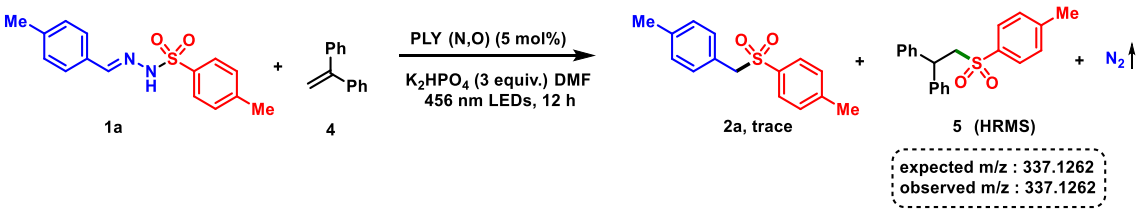
Scheme S5. Formation of N-alkylated tosylhydrazone (**2a**/) from tosylhydrazone **1a** in the absence of PLY (N,O).

Tosylhydrazone **1a** (0.3 mmol, 86.4 mg) and K_2HPO_4 (0.9 mmol, 156.7 mg) were taken in a 25 mL high-pressure J-Young tube fitted with a teflon cap equipped with a stir bar. Subsequently, 1.5 mL DMF was added to the reaction mixture, and the tube was closed properly. In the Schlenk line, a freeze-pump-thaw cycle was applied twice to maintain an inert atmosphere. Next, argon was

purged into the reaction mixture. The reaction tube was closed properly and placed under blue LED irradiation (456 nm) for 12 h. After completion of the reaction, the product was extracted in 25 mL ethyl acetate and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and **2a′** was purified by column chromatography on silica gel (100-200 mesh) using hexane/EtOAc mixture to yield the pure desired products, which were further characterized by NMR spectroscopy (^{1}H, ^{13}C) and HRMS [m/z 393.1632 (observed), 393.1637 (expected)].

*These two experiments unarguably validate the involvement of carbene intermediate in the catalytic mixture and for the formation of the carbene intermediate, from tosylhydrazone **1a**, no PLY (N,O) is required. The formation of 2a′ can be explained by denitrogenation of **3** in the presence of light to generate a carbene, which undergoes an insertion reaction into the N-H bond of substrate **1a**.*

c. Sulfinate radical trapping experiment *via* adducts formation with 1,1-diphenylethylene



Scheme S6. Trapping of sulfinate radical intermediate with 1,1-diphenylethylene.

Tosylhydrazone **1a** (0.3 mmol, 86.4 mg), PLY (N,O) (5 mol%, 0.015 mmol, 3.2 mg), K_2HPO_4 (0.9 mmol, 156.7 mg) and 1,1-diphenylethylene **4** (0.6 mmol, 106 μL) were taken in a 25 mL high-pressure J-Young tube with a Teflon cap equipped with a stir bar. Subsequently, 1.5 mL DMF was added to the reaction mixture, and the tube was closed properly. In the Schlenk line, a freeze-pump-thaw cycle was applied twice to maintain an inert atmosphere. Next, argon was purged into the reaction mixture. The reaction tube was closed properly and placed under blue LED irradiation (456 nm) for 12 h. After completion of the reaction, the product was extracted in 25 mL ethyl acetate and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the NMR yields were determined from ^{1}H NMR spectroscopy using 1,4-dimethoxybenzene as the internal standard (0.1 mmol). In ^{1}H NMR spectroscopy, a trace amount (< 5%) of **2a** was observed. Also, the crude reaction mixture was characterized through HRMS spectroscopy in acetonitrile (Figure S7), and the corresponding mass of trapped sulfinate radical (**7**) [m/z 337.1262 (observed), 337.1262 (expected)] was found.

This observation suggests the involvement of the sulfinate radical during the PLY (N,O) catalyzed

denitrogenative sulfonylation reaction.

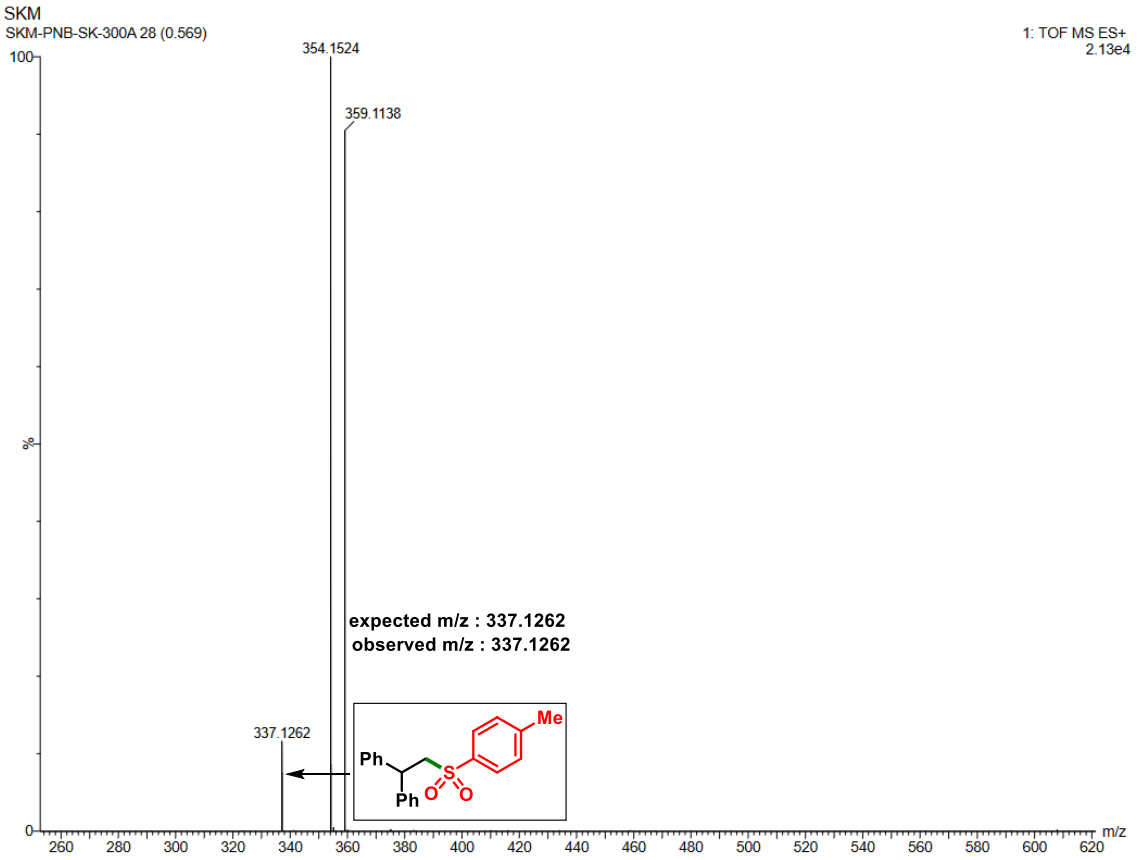
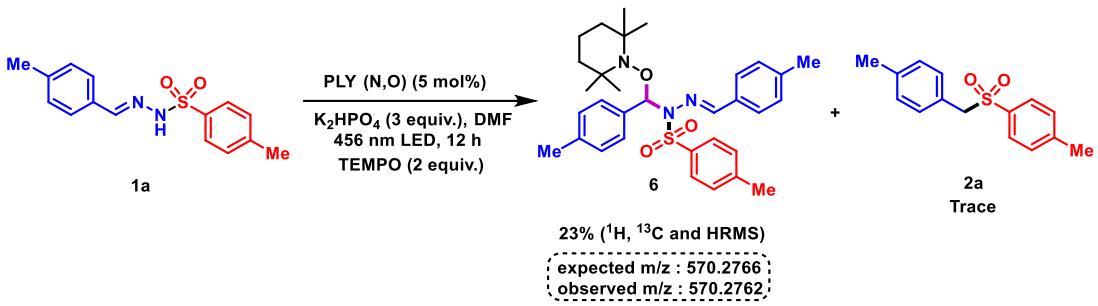


Figure S7. HRMS spectrum of 1,1-diphenylethylene trapped product with tosylhydrazone **1a**.

d. The effect of TEMPO on the denitrogenative sulfonylation of tosylhydrazone 1a.



Scheme S7. The effect of TEMPO on the denitrogenative sulfonylation of **1a**.

Tosylhydrazone **1a** (0.3 mmol, 86.4 mg), PLY (N,O) (5 mol%, 0.015 mmol, 3.2 mg), K_2HPO_4 (0.9 mmol, 156.7 mg) and TEMPO (0.6 mmol, 93.7 mg) were taken in a 25 mL high-pressure J-Young tube fitted with a teflon cap equipped with a stir bar. Subsequently, 1.5 mL DMF was added to the reaction mixture, and the tube was closed properly. In the Schlenk line, a freeze-pump-thaw cycle was applied twice to maintain an inert atmosphere. Next, argon was purged into the reaction mixture. The reaction tube was closed properly and placed under blue LED irradiation (456 nm) for 12 h. After completion of the reaction, the product was extracted in 25 mL ethyl acetate and

dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the NMR yields were determined from ^{1}H NMR spectroscopy using 1,4-dimethoxybenzene as the internal standard. In ^{1}H NMR spectroscopy, a trace amount (< 5%) of **2a** was observed. Also, the crude reaction mixture was characterized through HRMS spectroscopy in acetonitrile (Figure S3), and the corresponding mass of trapped carbene intermediate with TEMPO (**6**) [m/z 570.2762 (observed), 570.2766 (expected)] was found, which was further characterized by NMR spectroscopy (^{1}H and ^{13}C).

The crude product was purified by column chromatography using silica gel (100-200 mesh) with 5% of EtOAc in hexane and obtained as brown solid (23% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 8.01 (d, J = 7.5 Hz, 2H), 7.95 (s, 1H), 7.37 (d, J = 7.4 Hz, 2H), 7.33 (s, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.24 (s, 1H), 7.22 (s, 1H), 7.13 (d, J = 7.4 Hz, 2H), 7.06 (d, J = 7.5 Hz, 2H), 2.45 (s, 3H), 2.34 (s, 3H), 2.28 (s, 3H), 1.72 – 1.58 (m, 3H), 1.59 – 1.53 (m, 3H), 1.35 (m, 3H), 1.24 (m, 3H), 1.13 (m, 3H), 0.97 (m, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 144.3, 142.5, 138.6, 136.5, 135.3, 131.7, 131.2, 128.1, 128.0, 127.9, 127.7, 126.0, 125.8, 92.3, 60.4, 58.7, 39.9, 31.9, 31.7, 20.6, 20.3, 20.0, 19.8, 16.0.

HRMS (TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{41}N_3O_3SNa$ 570.2766; Found 570.2762.

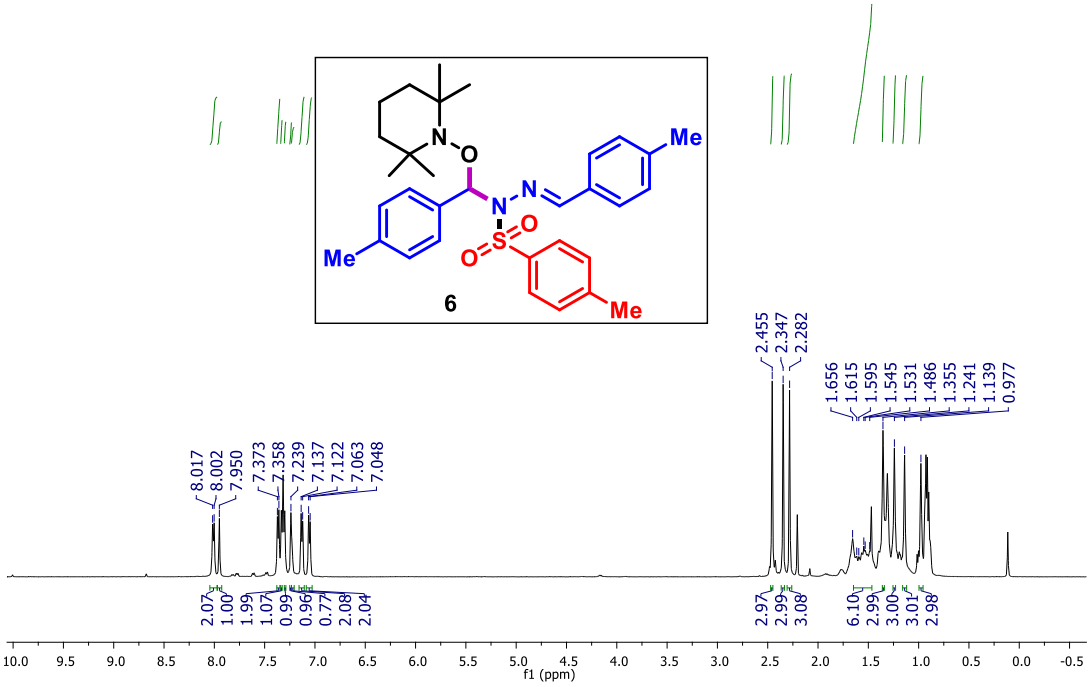


Figure S8. ^{1}H NMR spectrum ($CDCl_3$) of (R,*E*)-4-methyl-N'-(4-methylbenzylidene)-N-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)(*p*-tolyl)methyl)benzenesulfonohydrazide (**6**).

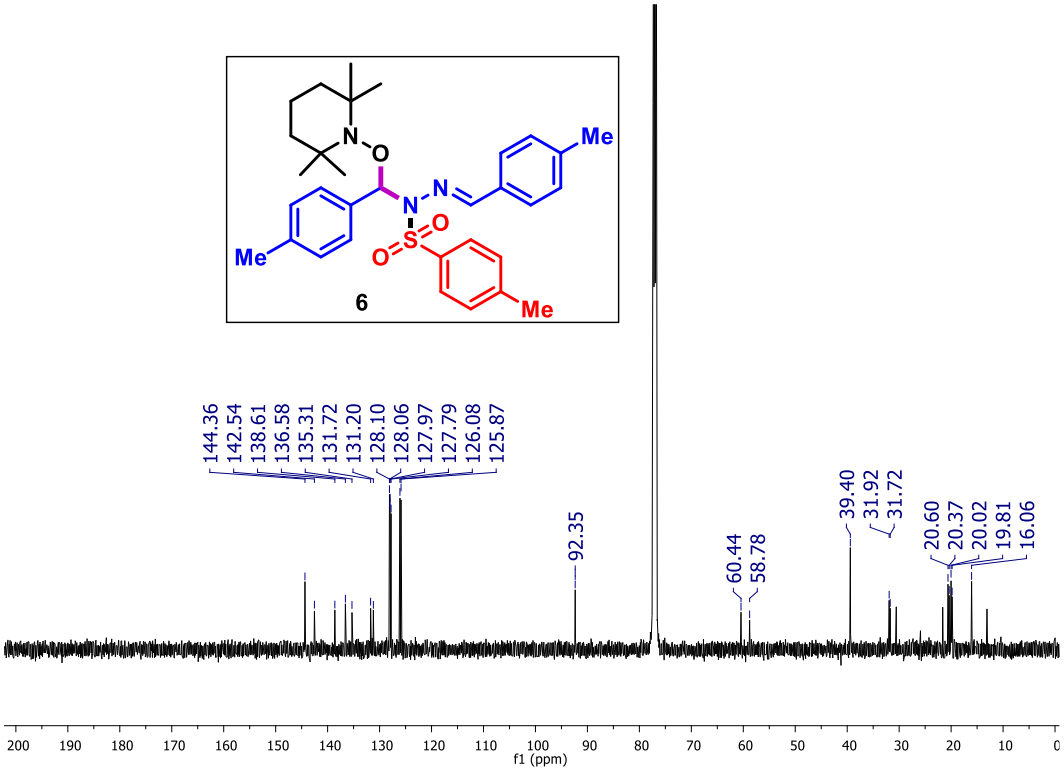


Figure S9. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of (R,*E*)-4-methyl-N'-(4-methylbenzylidene)-N-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)(*p*-tolyl)methyl)benzenesulfonohydrazide (**6**).

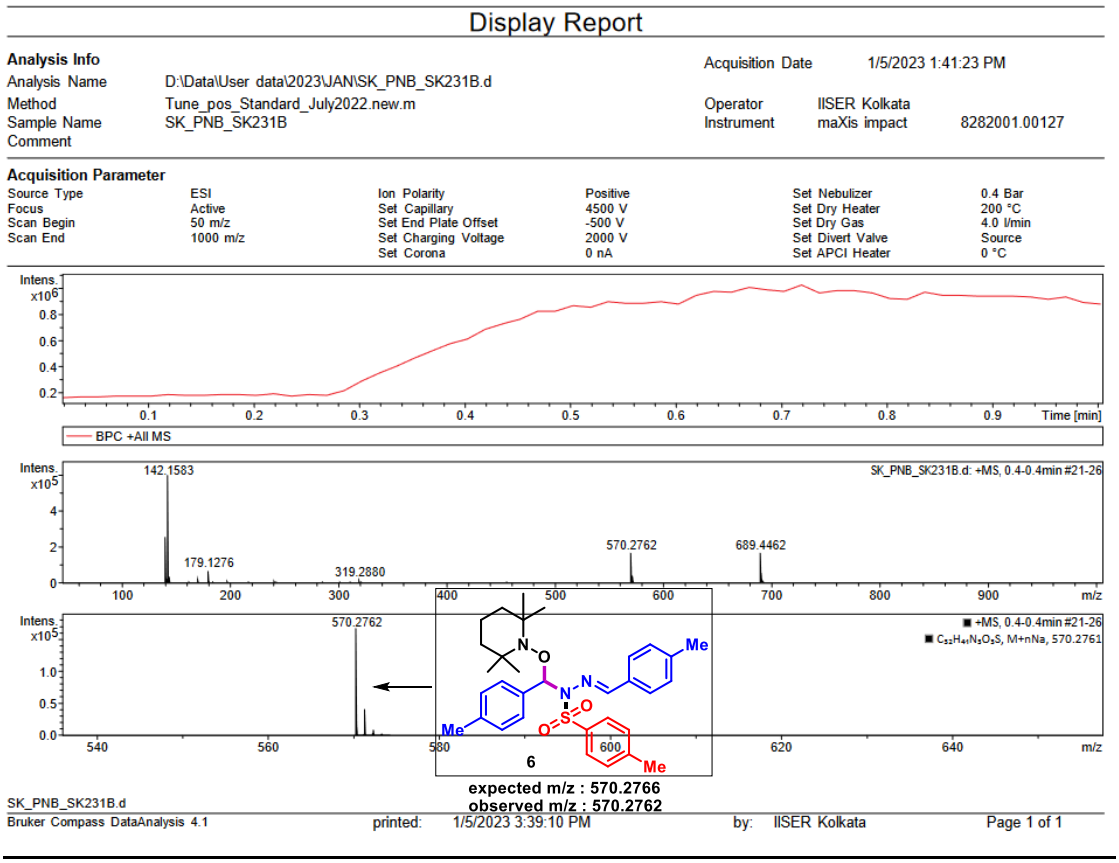
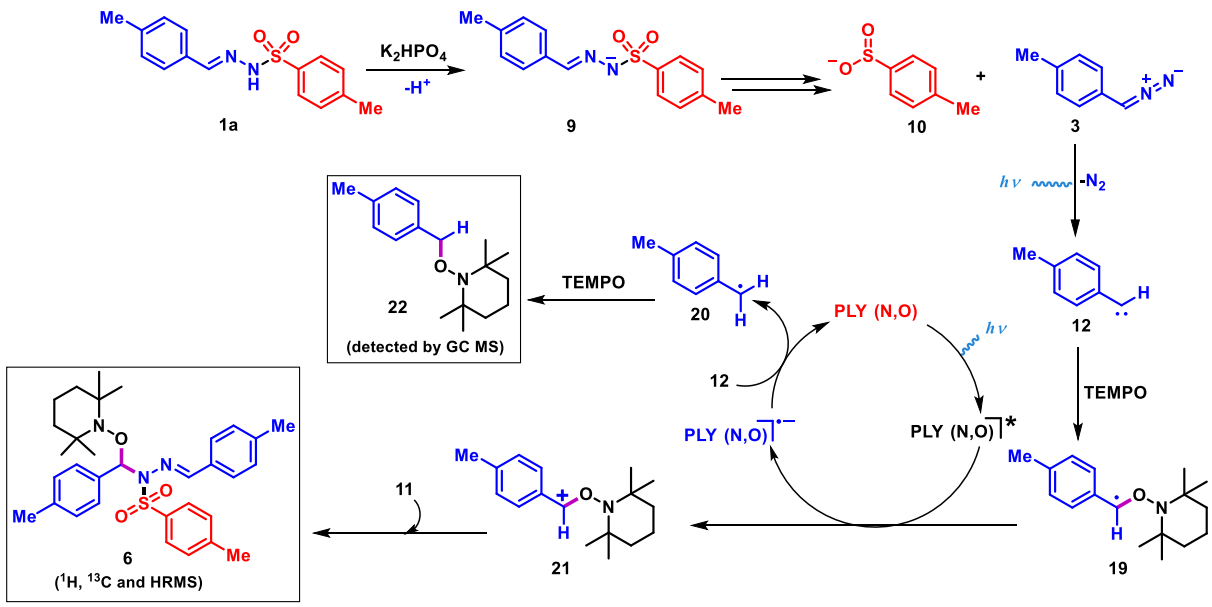


Figure S10. HRMS spectrum of TEMPO trapped product with tosylhydrazone **1a**.



Scheme S8. Proposed mechanism for the effect of TEMPO on the denitrogenative sulfonylation of **1a**.

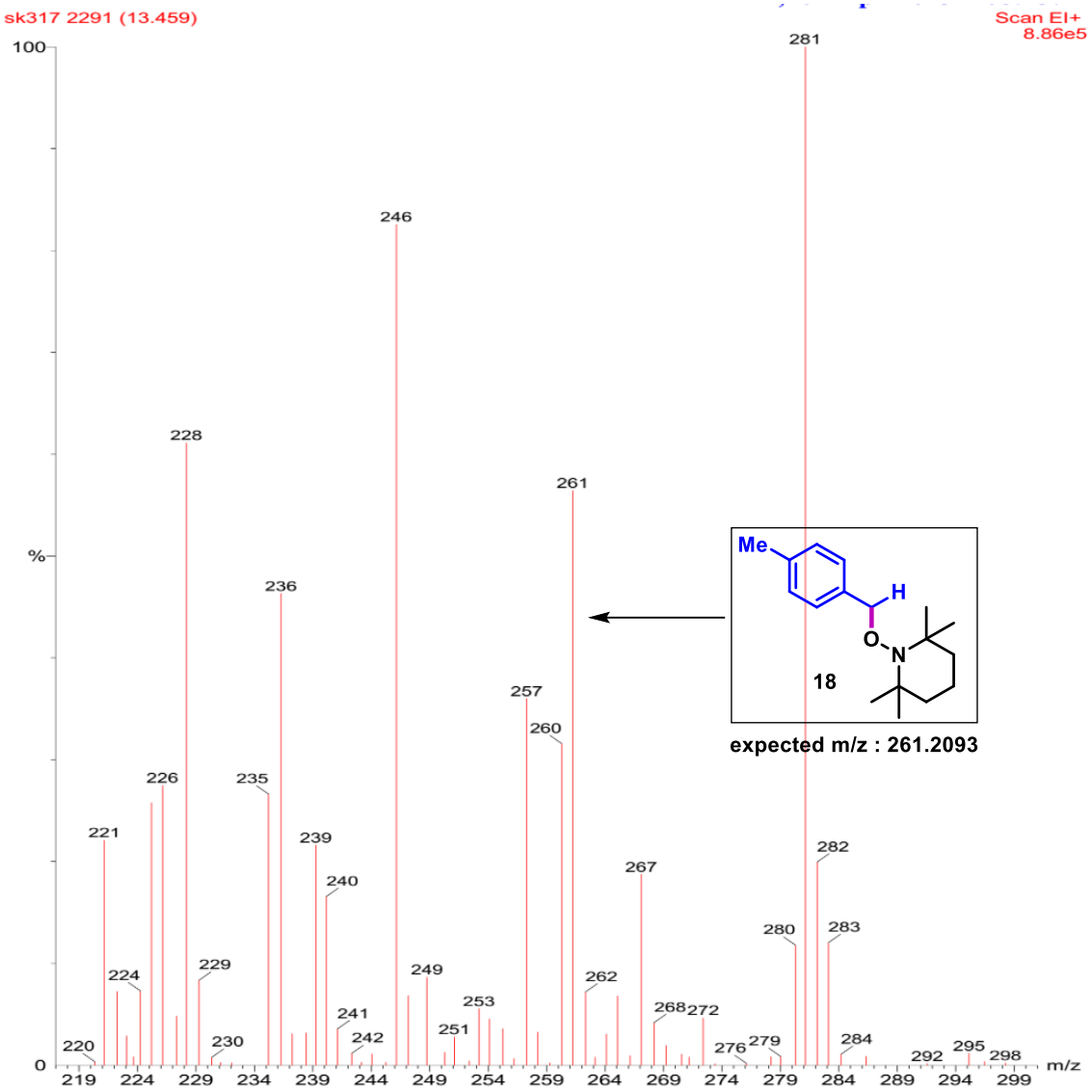
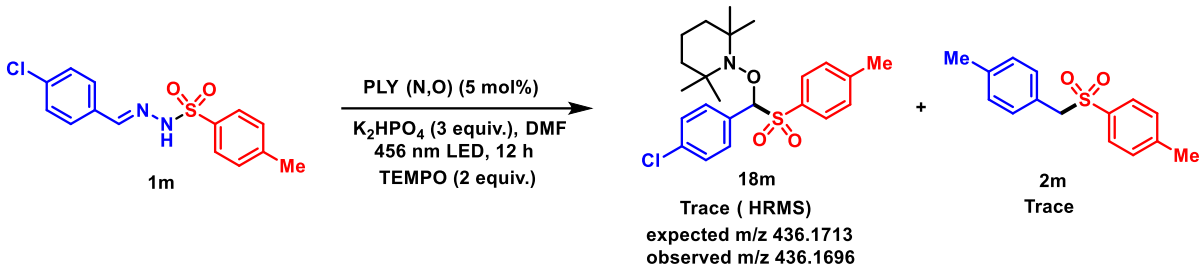


Figure S11. GC-MS spectrum of TEMPO trapped product (**18**).

In TEMPO-trapping control experiment scheme 3d, we have also characterized **18m**, a TEMPO trapped species corresponding to **13m** through mass spectroscopy.



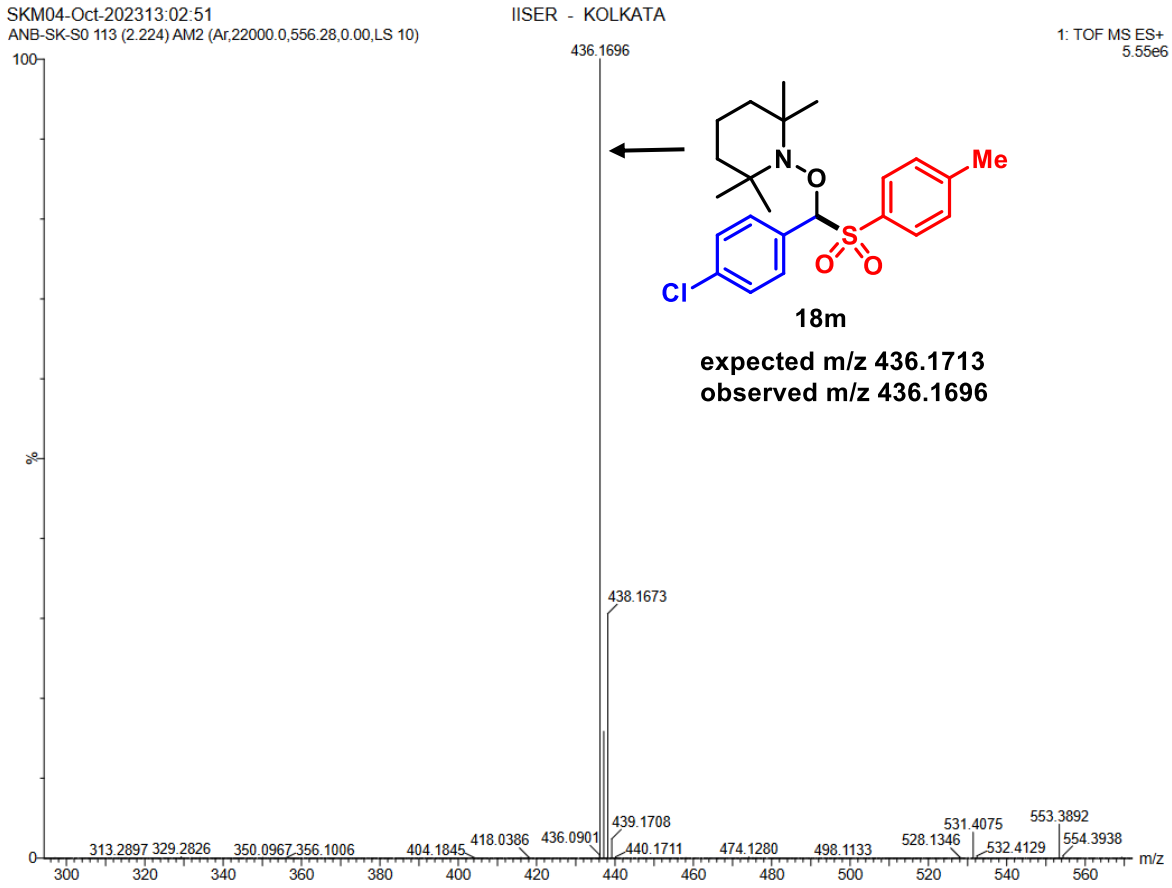
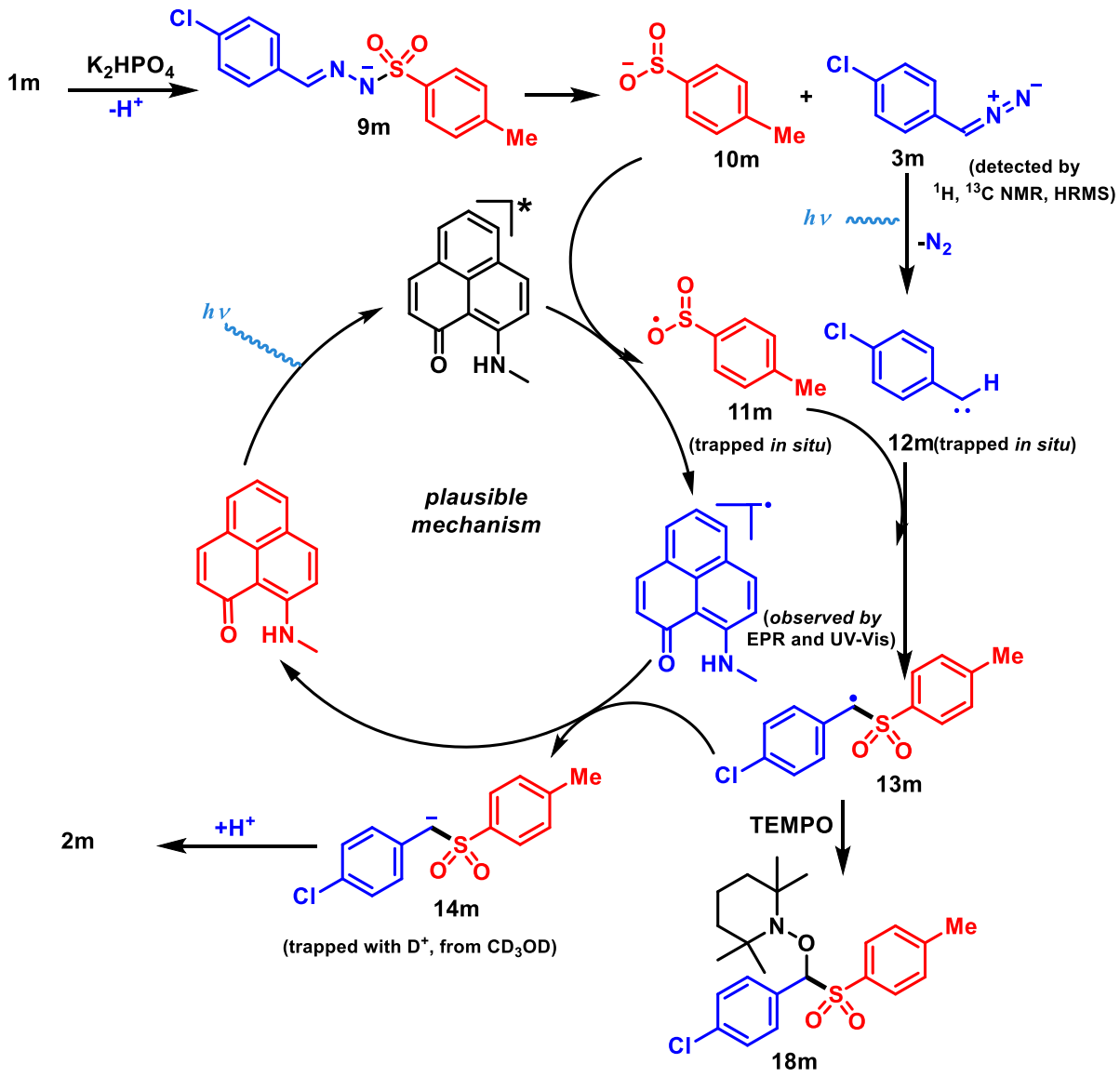


Figure S12. HRMS spectrum of TEMPO trapped product **18m** with tosylhydrazone **1m**.



Scheme S9. Proposed mechanism for the effect of TEMPO-trapping experiment to obtain **18m**.

e. Cross-over Experiment

Scheme S10. Cross-over experiment between **1a** and benzenesulfinic acid sodium salt **7**.

Tosylhydrazone **1a** (0.3 mmol, 86.4 mg), PLY (N,O) (5 mol%, 0.015 mmol, 3.2 mg), K_2HPO_4 (0.9 mmol, 156.7 mg), and benzenesulfinic acid sodium salt **7** (0.3 mmol, 49.2 mg) were taken in a 25 mL high-pressure J-Young tube fitted with a teflon cap and equipped with a stir bar. Subsequently, 1.5 mL DMF was added to the reaction mixture, and the tube was closed properly. In the Schlenk

line, a freeze-pump-thaw cycle was applied twice to maintain an inert atmosphere. Next, argon was purged into the reaction mixture. The reaction tube was closed properly and placed under blue LED irradiation (456 nm) for 12 h. After completion of the reaction, the product was extracted in 25 mL ethyl acetate and dried over anhydrous sodium sulfate. Next, the solvent was removed under reduced pressure. In addition to this, **2a** and **2u** were purified by column chromatography on silica gel (100-200 mesh) using hexane/EtOAc mixture to yield the pure desired products, which were further characterized by NMR spectroscopy and a 1:4.3 ratio of **2a** and **2u** was obtained.

From this experiment, we can conclude that the sulfinate was oxidized in the presence of the PLY-photocatalyst to form the sulfinate radical and the reaction proceeded via a stepwise mechanism.

The crude product was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (yield 91% and **2a: 2u** = 1: 4.3).

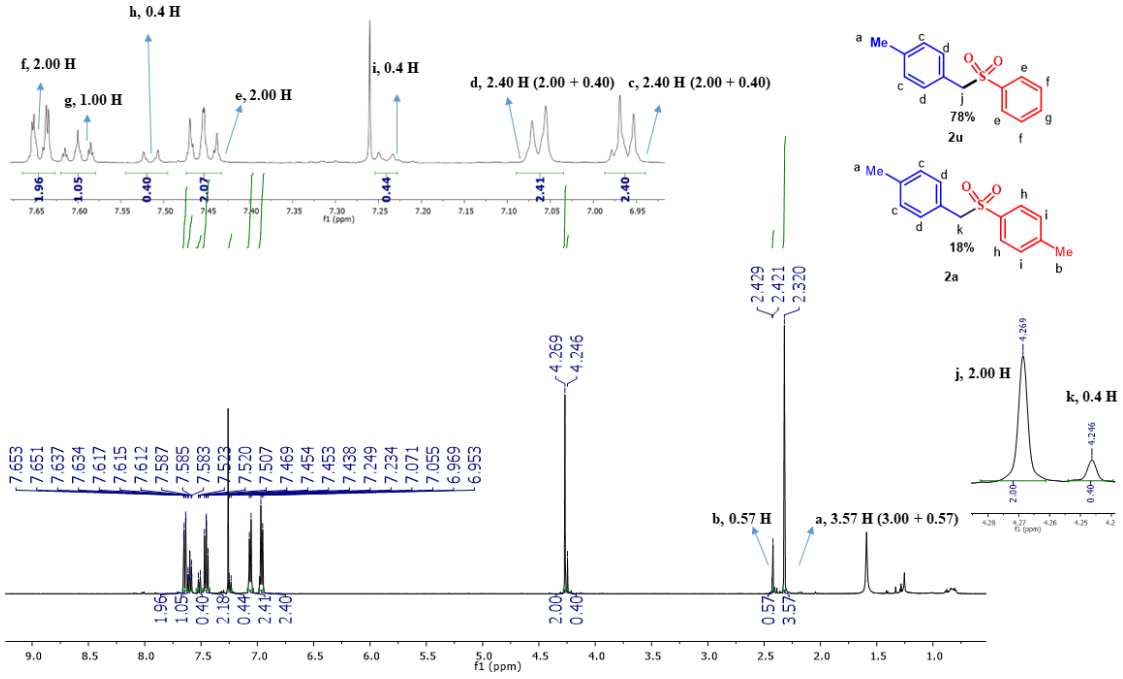
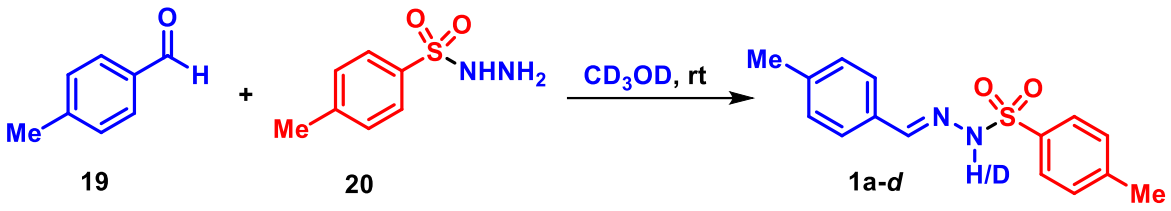


Figure S13. ^{1}H NMR spectrum ($CDCl_3$) of cross-over experiment, (**2a** : **2u** = 1: 4.3).

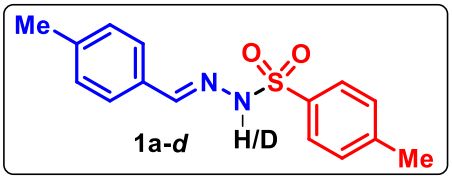
f. Isotope-labelling study

Synthesis of deuterium incorporated tosylhydrazone 1a-*d*:



Scheme S11. Preparation of D-incorporated tosylhydrazone **1a-*d***.

In an oven-dried Schlenk tube, the aldehyde (**19**) (1.0 equiv.) was added dropwise slowly to a clear solution of hydrazide (**20**) (1.0 mmol) in CD_3OD (5.0 mL). Then, the reaction mixture was stirred at room temperature until complete conversion was observed by TLC. The hydrazine was precipitate slowly as a white solid. Subsequently, the mixture was cooled down to 0 ℃, filtered, washed with a small amount of cold diethyl ether, and dried *in vacuo* to give the corresponding deuterium-incorporated compound (**1a-*d***).



^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) δ 8.04 (brs, 0.5 H), 7.87 (d, J = 8.3 Hz, 2H), 7.74 (s, 1H), 7.47 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 7.9 Hz, 2H), 2.39 (s, 3H), 2.34 (s, 3H).

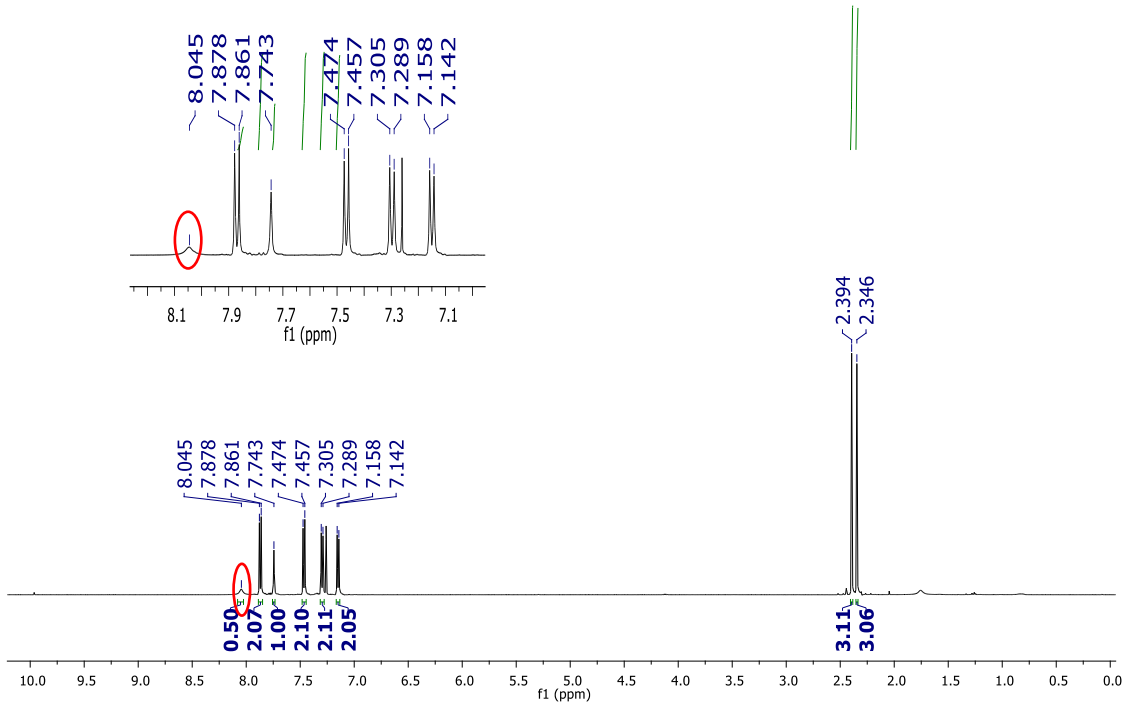
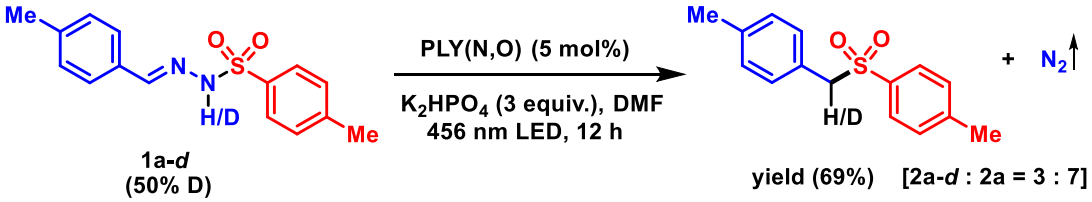


Figure S14. ^{1}H NMR spectrum of D-incorporated tosylhydrazone **1a-*d*.**

1) Reaction with D-incorporated 1a-*d*:



Scheme S12. Deuterium labelling experiment with **1a-*d***.

D-incorporated tosylhydrazone **1a-*d*** (0.3 mmol, 86.4 mg), PLY (N,O) (5 mol%, 0.015 mmol, 3.2 mg), K_2HPO_4 (0.9 mmol, 156.7 mg) were taken in a 25 mL high-pressure J-Young tube fitted with a teflon cap and equipped with a stir bar. Subsequently, 1.5 mL DMF was added to the reaction mixture, and the tube was closed properly. In the Schlenk line, a freeze-pump-thaw cycle was applied twice to maintain an inert atmosphere. Next, argon was purged into the reaction mixture. The reaction tube was closed properly and placed under blue LED irradiation (456 nm) for 12 h. After completion of the reaction, the product was extracted in 25 mL ethyl acetate and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. In addition to this, **2a** and **2a-*d*** were purified by column chromatography on silica gel (100-200 mesh) using

hexane/EtOAc mixture to yield the pure desired products, which were further characterized by NMR spectroscopy and a 3:7 ratio of **2a-*d*** and **2a** was obtained.

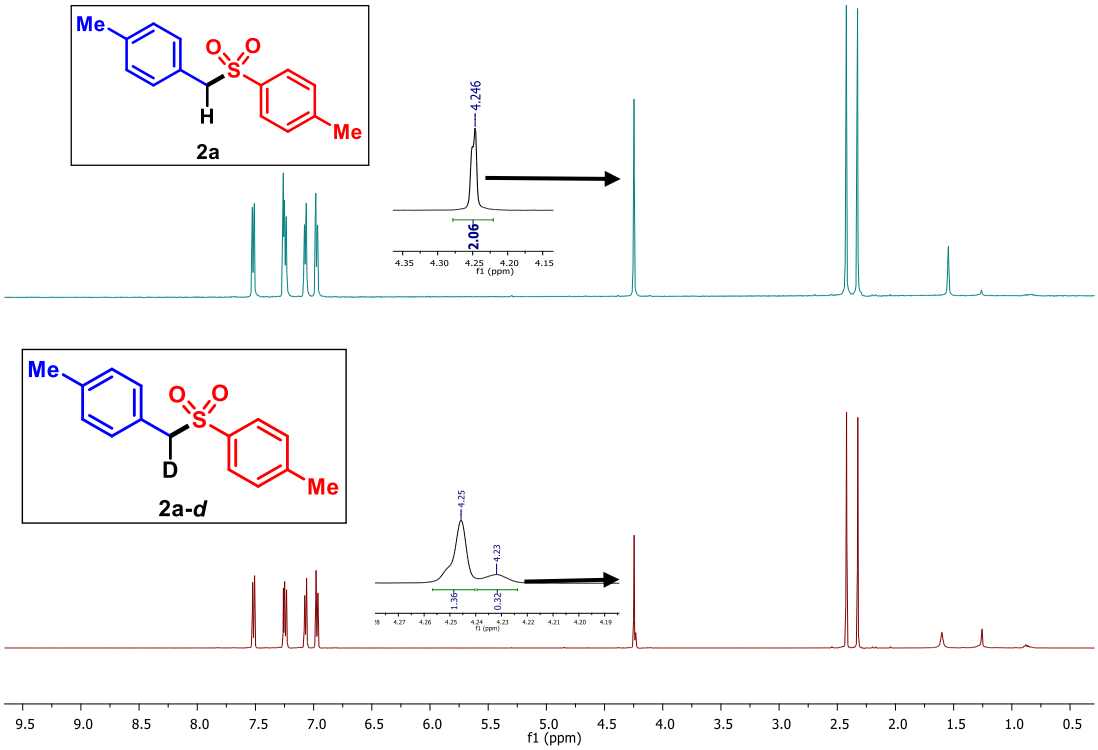
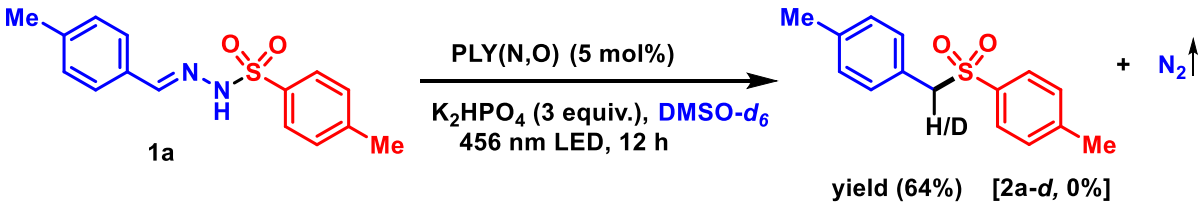


Figure S15. ^{1}H NMR spectra ($CDCl_3$) of **2a** (above) and **2a-*d*** (below).

2) Reaction with D-incorporated DMSO-d_6:

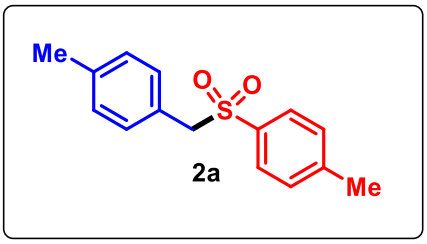


Scheme S13. Deuterium labelling experiment with DMSO-d_6.

Tosylhydrazone **1a** (0.3 mmol, 86.4 mg), PLY (N,O) (5 mol%, 0.015 mmol, 3.2 mg), K_2HPO_4 (0.9 mmol, 156.7 mg) were taken in a 25 mL high-pressure J-Young tube fitted with a teflon cap and equipped with a stir bar. Subsequently, 1 mL DMSO-d_6 was added to the reaction mixture, and the tube was closed properly. In the Schlenk line, a freeze-pump-thaw cycle was applied twice to maintain an inert atmosphere. Next, argon was purged into the reaction mixture. The reaction tube was closed properly and placed under blue LED irradiation (456 nm) for 12 h. After completion of the reaction, the product was extracted in 25 mL ethyl acetate and dried over anhydrous sodium sulfate. Then, the solvent was removed under reduced pressure. In addition to this, **2a** and **2a-*d***

were purified by column chromatography on silica gel (100-200 mesh) using hexane/EtOAc mixture to yield the pure desired products, which were further characterized by NMR spectroscopy and no deuterium incorporated sulfone was obtained.

1-methyl-4-((4-methylbenzyl)sulfonyl)benzene (2a): [6]



^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.52 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 7.9 Hz, 2H), 7.07 (d, J = 7.8 Hz, 2H), 6.97 (d, J = 7.9 Hz, 2H), 4.25 (s, 2H), 2.42 (s, 3H), 2.33 (s, 3H).

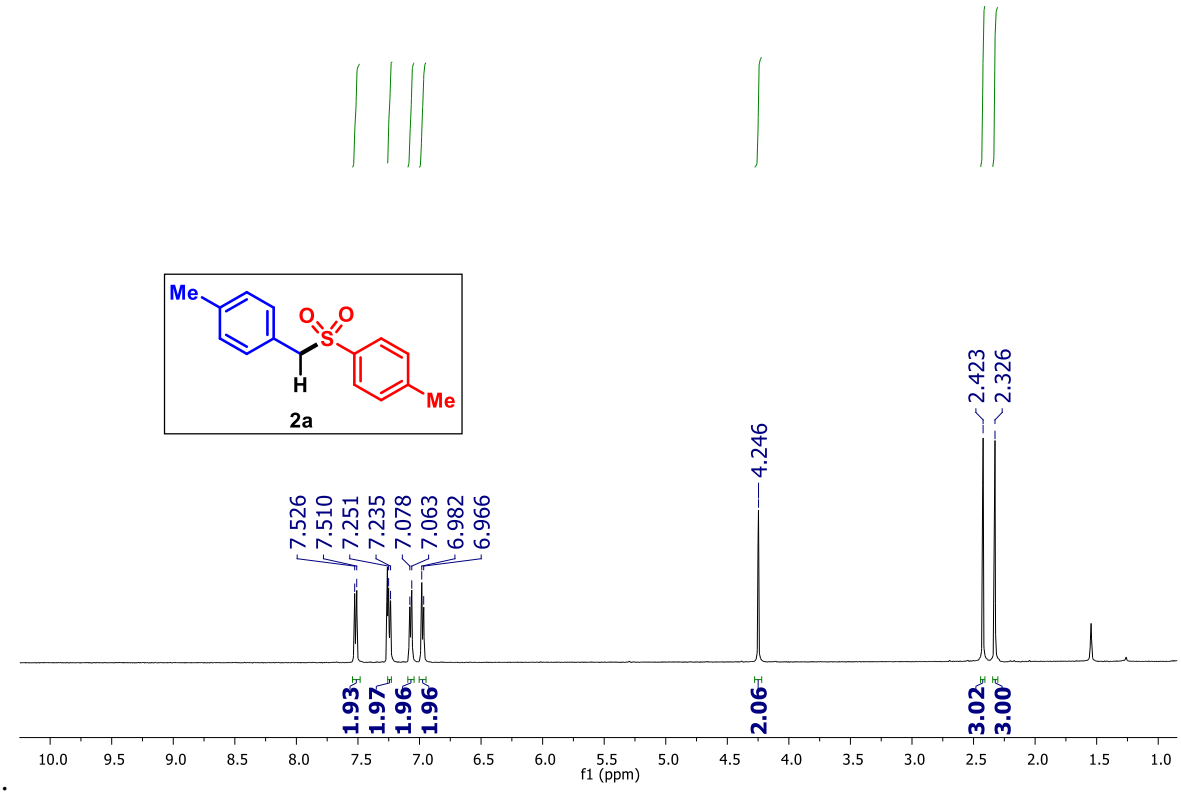
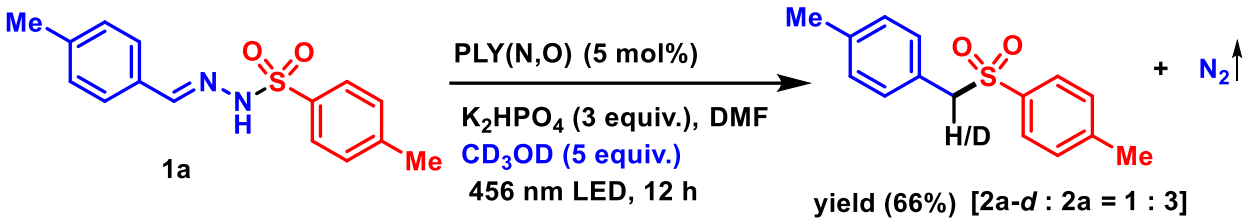


Figure S16. ^{1}H NMR spectrum ($CDCl_3$) of **2a**.

3. Reaction with CD_3OD:



Scheme S13. Deuterium labelling experiment with CD_3OD.

Tosylhydrazone **1a** (0.3 mmol, 86.4 mg), PLY (N,O) (5 mol%, 0.015 mmol, 3.2 mg), K_2HPO_4 (0.9 mmol, 156.7 mg) and CD_3OD (5.0 equiv., 1.5 mmol, 60 mL) were taken in a 25 mL high-pressure J-Young tube fitted with a teflon cap and equipped with a stir bar. Subsequently, 1.5 mL DMF was added to the reaction mixture, and the tube was closed properly. In the Schlenk line, a freeze-pump-thaw cycle was applied twice to maintain an inert atmosphere. Next, argon was purged into the reaction mixture. The reaction tube was closed properly and placed under blue LED irradiation (456 nm) for 12 h. After completion of the reaction, the product was extracted in 25 mL ethyl acetate and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. In addition to this, **2a** and **2a-*d*** were purified by column chromatography on silica gel (100-200 mesh) using hexane/EtOAc mixture to yield the pure desired products, which were further characterized by NMR spectroscopy and a 1:3 ratio of **2a-*d*** and **2a** was obtained.

From these three experiments described above, we can conclude that the solvent is not the source of proton during the protonation step, i.e. the last step of the catalytic mixture. The N-H proton of the substrate is the source of hydrogen.

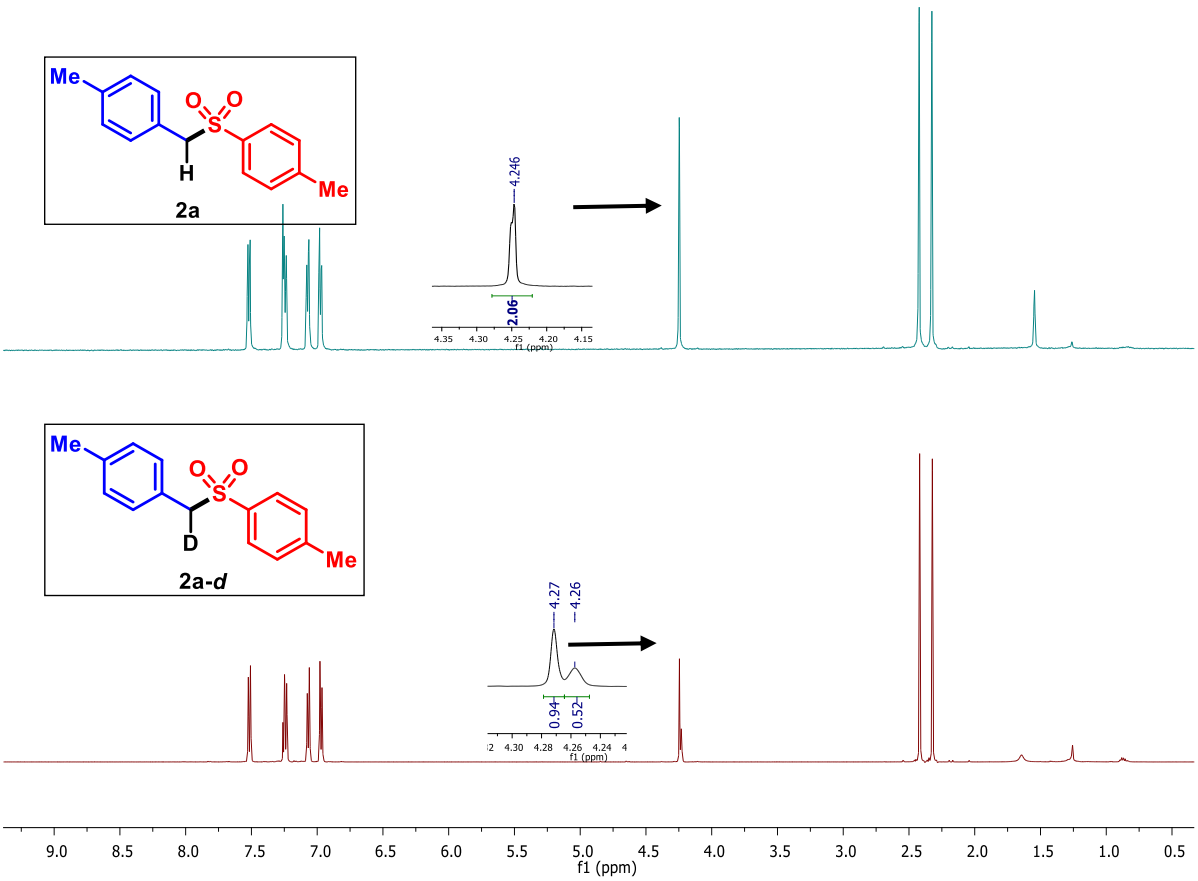


Figure S17. ^{1}H NMR spectra ($CDCl_3$) of **2a** (above) and **2a-*d*** (below).

III. Spectroscopic studies:

The PLY (N,O) (**L1**) solution was prepared in DMF solvent. The concentration of **L1** was fixed to 50 µM in the case of EPR study, Uv-Vis studies, and fluorescence quenching studies.

EPR Study.

An EPR spectrum of PLY (N,O) was recorded before and after the addition of the sodium *p*-toluenesulfinate (**8**) under blue LED irradiation.

First, PLY (N,O) was exposed under the light in DMF for 1 minute and analyzed with Bruker (X-band) EPR spectrometer at 77K, which gave no signal (Figure S17).

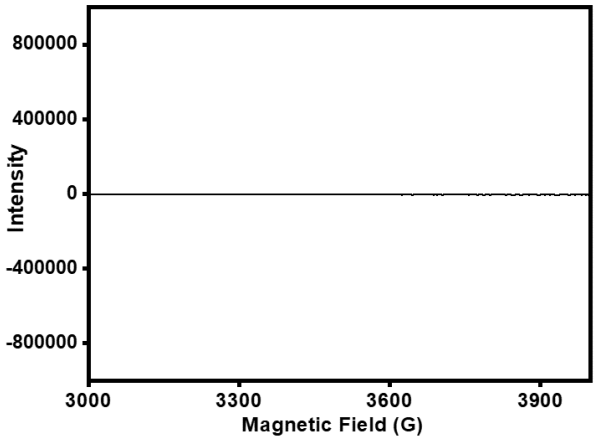
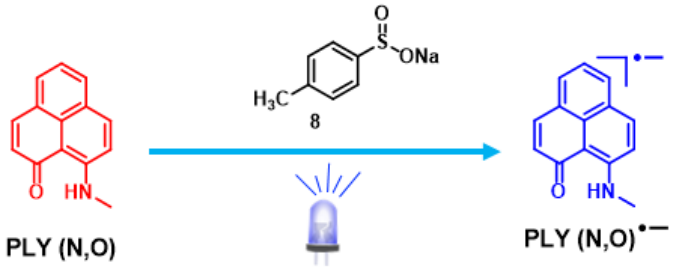


Figure S18. The EPR spectrum of PLY (N,O) under blue LED light irradiation (λ= 456 nm, Kessil lamp, 40 W).

Next, PLY (N,O) was excited with light in the presence of sodium *p*-toluenesulfinate (**8**). The X-band EPR measurement of this solution was also carried out at 77K, and a sharp signal was observed with g = 1.996, indicating the formation of a photoinduced phenalenyl-based radical (Figure S18).



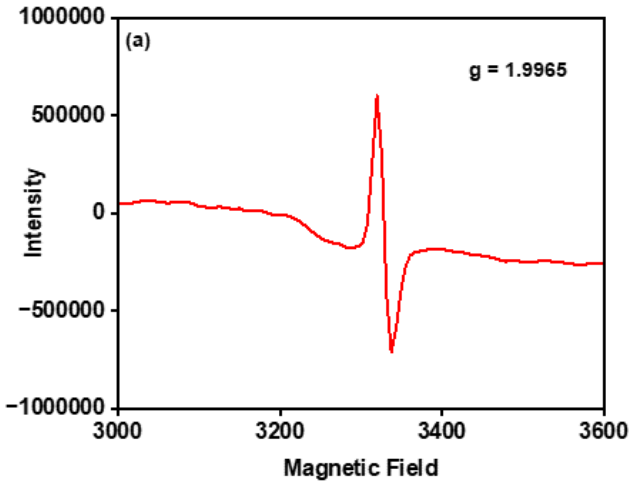


Figure S19. The EPR spectral signature shows the *in situ* formation of PLY (N,O) radical anion in the presence of sodium *p*-toluenesulfinate (**8**) with blue LED light irradiation (λ= 456 nm, Kessil

lamp, 40 W).

After that, an EPR spectrum of PLY (N,O) was recorded in the presence of sodium *p*-toluenesulfinate (**8**) in DMF without any light irradiation. The X-band EPR measurement of this solution was also carried out at 77K and no EPR signal was observed (Figure S19).

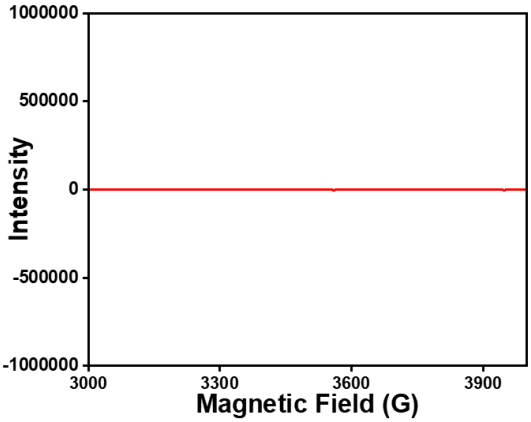


Figure S20. The EPR spectrum of mixture of PLY (N,O) with sodium *p*-toluenesulfinate without light irradiation.

UV-Vis spectroscopic studies between PLY (N,O) and sodium *p*-toluenesulfinate (8).

A 50 mM solution of PLY (N,O) was prepared in DMF, and 300 mM sodium *p*-toluenesulfinate (**8**) was added to it, and absorption spectra were recorded at a different time interval under irradiation with 456 nm kessil blue LED. During this experiment, the absorption peaks corresponding to free PLY (N,O) undergo a sharp decline in their intensity over time upon the addition of sulfinate (**8**) under photoirradiation, followed by the appearance of a new band with vibronic features in the region 550-650 nm (inset, Figure S20), which is consistent with the generation of PLY-based radical species.

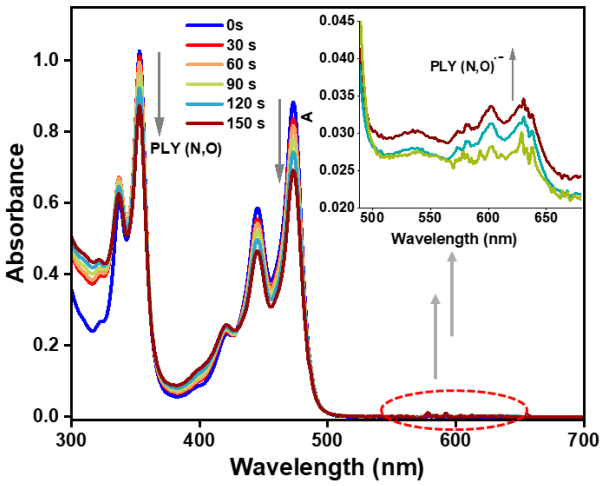


Figure S21. Absorption spectra showing the consumption of PLY (N,O) and generation of PLY (N,O) radical anion in the presence of sodium *p*-toluenesulfinate upon irradiation with kessil blue

LED (456 nm).

This finding indicates the interaction between sodium sulfinate and PLY (N,O) upon irradiation resulting in a photoinduced electron transfer (PET) from sodium sulfinate to the excited state of PLY (N,O) forming PLY-based radical anion.

Stern-Volmer Fluorescence Quenching Studies

Luminescence experiments were carried out on an FLS1000 fluorescence spectrometer from Edinburgh Instruments, equipped with a 450 W Xe lamp. PLY (N,O) solutions were excited at 440 nm, and emission intensity at 490 nm was collected. All the measurements were carried out by mixing a 50 ×10 $^{-6}$ M solution in dry degassed DMF and the appropriate amount of quencher in a screw top 1.0 cm quartz cuvette. I_0 is the intensity without quencher and I is the intensity with quencher. Plots were drawn according to the Stern-Volmer equation. Stern-Volmer equation $I_0/I = 1+k_q[Q]$.

Emission quenching studies with sodium p-toluenesulfinate (8), (diazomethylene)dibenzene, K_2HPO_4 and 1a

The increasing amount of quencher were added to a solution of PLY (N,O) in DMF. After each addition, emission spectra were recorded.

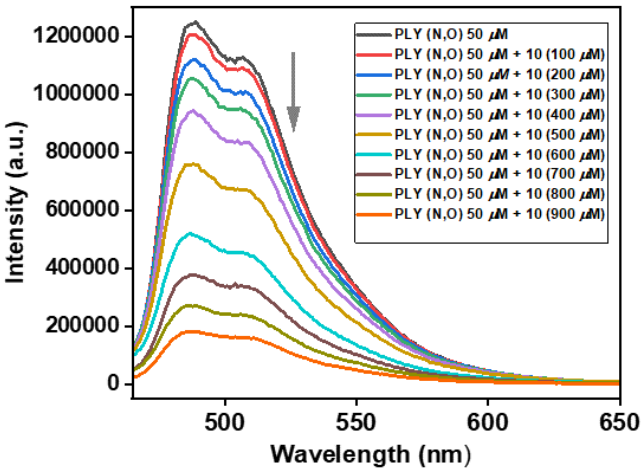


Figure S22. Fluorescence quenching of sodium *p*-toluenesulfinate (**8**)

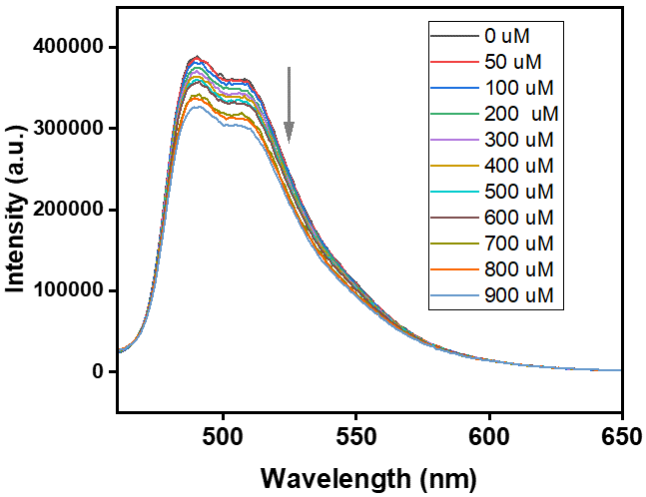


Figure S23. Fluorescence quenching of (diazomethylene)dibenzene

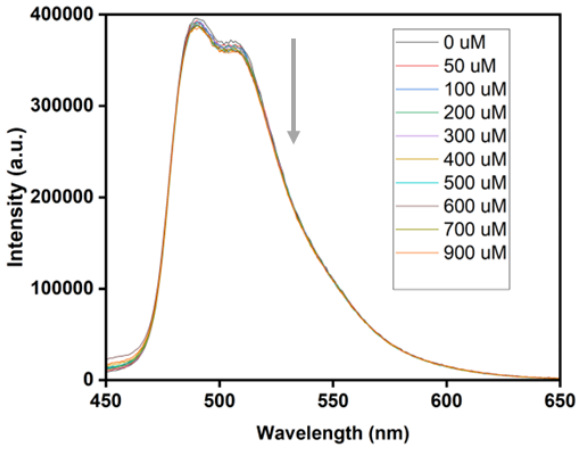


Figure S24. Fluorescence quenching of K_2HPO_4

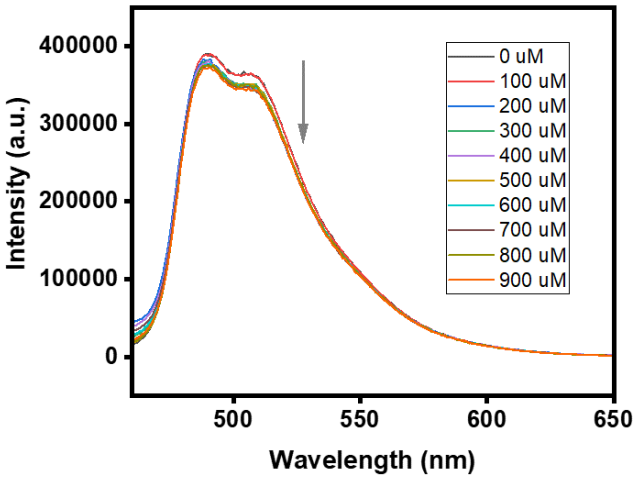


Figure S25. Fluorescence quenching of 1a

Stern-Volmer plots

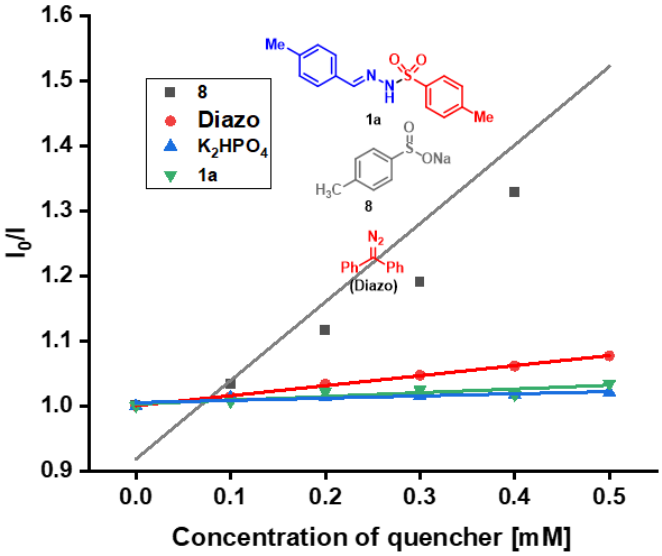


Figure S26. Stern-Volmer plot of PLY (N,O) at different quenchers

The reported excited-state lifetime for PLY (N,O) (3.3 ns) was used for k_q calculations.[4]

Table S5. k_q calculations of 8, diazo, K_2HPO_4, 1a

Compound	k_q ($M^{-1}s^{-1}$)
8	**3.01×10^8**
Diazo	**4.66×10^7**
K_2HPO_4	**1.02×10^7**
1a	**1.75×10^7**

Quantum Yield Calculation

The photon flux was determined by using standard ferrioxalate actinometry.[5] A 0.15 M solution of ferrioxalate was made by mixing 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4.

A buffered solution was prepared by mixing 50 mg of 1,10-phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. Both solutions were kept in the dark.

To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 60.0 seconds at λ = 456 nm placing 8 cm away from the 40 W Kessil blue LED lamp. After irradiation, 0.35 mL of the 1,10-phenanthroline solution was added to the cuvette. The solution was then kept for 1 h in the dark so that all the ferrous ions completely coordinate with the 1,10-phenanthroline. A non-irradiated sample was also prepared and allowed to rest for about 1 h in the dark.

After 1 h, the absorbance of both solutions was measured at 510 nm and the conversion was calculated using the equation:

$$mol\ Fe^{2+} = \frac{V.\Delta A}{\varepsilon.I}$$

where V is the total volume of the solution after the addition of phenanthroline (0.00235 L), ΔA (0.672 from the average of two experiments) is the difference in the absorbance between the irradiated and non-irradiated solutions at 510 nm, Ɛ is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}) and l is the path length (1 cm).

$$\therefore mol\ Fe^{2+} = \frac{0.00235L * 0.672}{1 * 11100\ Lcm{-}1\ mol{-}1} = 1.423\ \text{X}\ 10^{-7}\ \text{mol.}$$

The photon flux can be calculated using the equation:

$$Photon\ flux = \frac{mol\ Fe^{2+}}{\phi.t.f}$$

Where ϕ is the quantum yield of the ferrioxalate actinometer (1.10 for a 0.15 M solution at λ = 456 nm), t is the time for which the sample is irradiated (60 s), f is the fraction of light absorbed at 456 nm

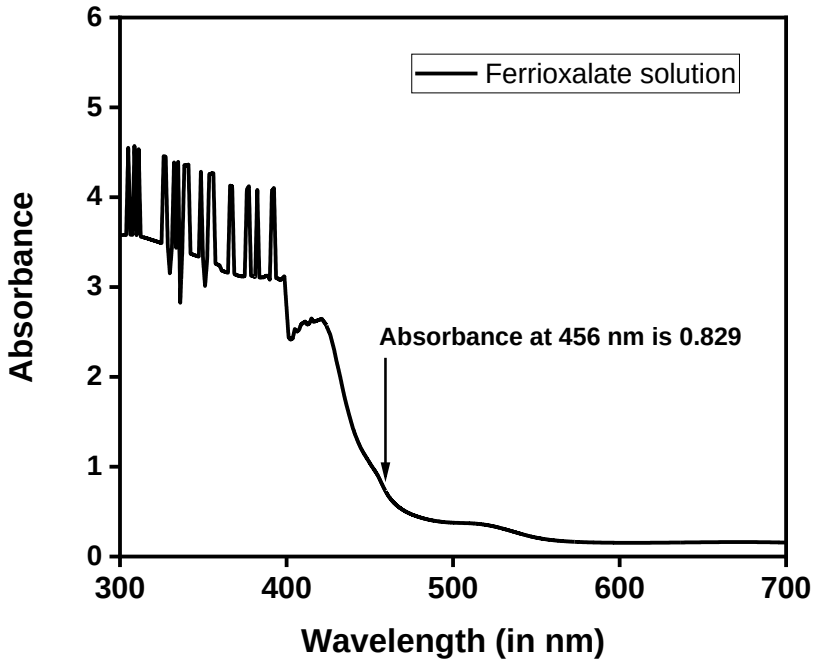


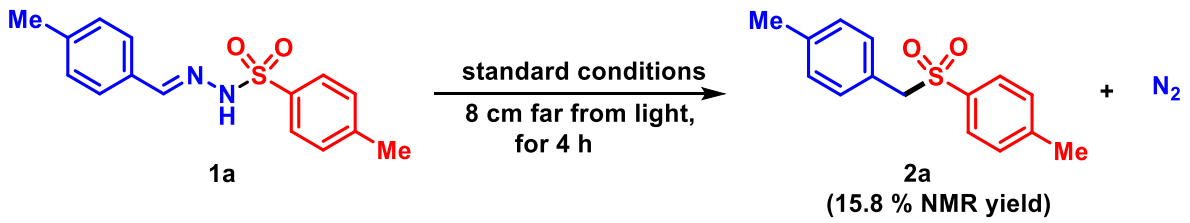
Figure S27. Absorbance of the ferrioxalate actinometer solution.

$f = 1 - 10^{-A}$ Where A = 0.829 at 456 nm

$f = 1 - 10^{-0.829} = 1 - 0.148 = 0.852$

$\therefore Photon\ flux = \frac{1.423*10^{-7}}{1.1*60*0.852} = 2.533 * 10^{-8}\ Einstein\ s^{-1}$

In an oven-dried high-pressure J-Young tube (25 ml) with a teflon cap equipped with a stir bar, PLY (N,O) (5 mol%, 0.015 mmol), K_2HPO_4 (3 equiv. 0.9 mmol), and **1a** (0.3 mmol) were taken, followed by addition of dry DMF (1.5 mL) were added sequentially. The tube was closed properly and connected with the Schlenk line, the freeze-pump and thaw cycle were done twice to evacuate any gasses present. After coming to room temperature Ar gas was charged into the reaction mixture, and it was kept under the irradiation of blue LED of 456 nm light for 4 h, with a fan to maintain the room temperature, placing 8 cm away from 40 W Kessil blue LED lamp. After completion of the reaction, the mixture was extracted with 25 mL ethyl acetate (EtOAc) and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and NMR yield was determined from ^{1}H NMR spectroscopy using 1,4-dimethoxybenzene (0.1 mmol) as an internal standard. The yield was found to be 15.8 % (12.3 mg and 4.74 X 10^{-5} mol).



The quantum yield was calculated as follows:

$$\varphi = \frac{mol\ product}{\text{flux.t.f}} = \frac{4.74*10^{-5}}{2.533*10^{-8}*4*3600\ s*0.944} = 0.14$$

$$\varphi = 0.14$$

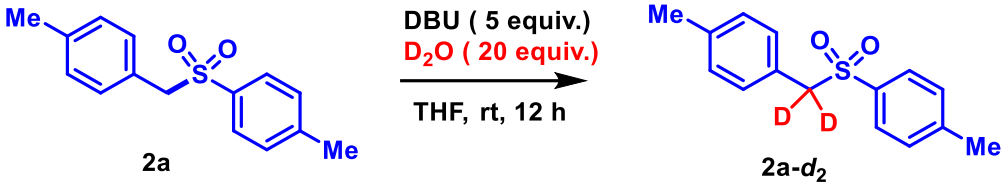
Where flux is the photon flux determined by ferrioxalate actinometry (2.533 X 10^{-8} Einstein/s), t is the time (14,400 s), and f ($1 - 10^{-A}$ where A is 1.257, f = 0.944) is the fraction of light absorbed by PLY (N,O) at 456 nm under the reaction condition mentioned above.

IV. Synthetic Applications

To show the utilization of above-mentioned products, we have performed different reactions with alkyl, aryl sulfones for access various synthetic derivatives.

Deuterium labelling

At first, we did the double deuteration at benzylic position to obtain di-deuterated sulfone.[10]



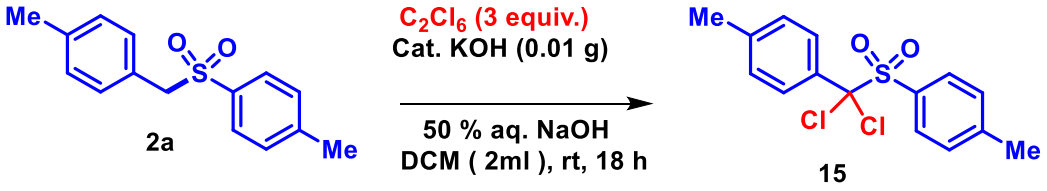
Reaction conditions: To a solution of **2a** (0.4 mmol) in 2 ml of THF, 5.0 equiv. of DBU, and 20.0 equiv. of D_2O was added and the mixture was stirred for 18 h, under Ar atmosphere. After completion of the reaction EtOAc and H_2O work-up was done and then it was purified using column chromatography in 7% EtOAc and hexane mixture. The product **2a-*d*$_2$** was isolated in 86% yield.

^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ (ppm) 7.54 (d, J = 8.2 Hz, 2 H), 7.26 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H), 2.34 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 144.6, 138.6, 135.1, 130.6, 129.5, 129.2, 128.6, 125.0, 61.9, 21.6, 21.2.

HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{14}D_2O_2SNa$ 285.0894; found 285.0882

Dichlorination



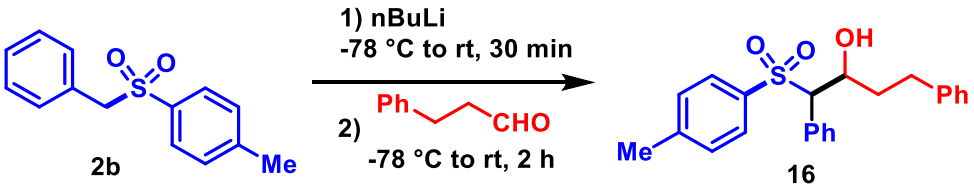
Reaction conditions: For synthesis of dichlorinated benzylic sulfone **15**, we have taken **2a** (0.4 mmol) in 2.0 ml of DCM, 3.0 equiv. of C_2Cl_6, and 50% aqueous NaOH (5 ml) solution and then catalytic amount of KOH (0.01g, 0.18 mmol) was added and the mixture was stirred for 18 h, under Ar atmosphere [11]. After completion of reaction DCM and H_2O work-up was done and then it was prurified using column chromatography in 5 % EtOAc and Hexane mixture. The compound obtained as a white solid in 79% yield.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.65 (dd, *J* = 12.2, 8.3 Hz, 4 H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 2.46 (s, 3H), 2.39 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 146.3, 141.5, 132.2, 129.74, 129.71, 129.14, 128.9, 128.6, 99.9, 21.8, 21.2.

HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{14}Cl_2O_2SNa$ 352.9969; found 352.9967.

Synthesis of β-hydroxy sulfone



Reaction conditions: For synthesis of sulfone derived alcohol **16**, we have taken **2a** (1.0 mmol) in 2.0 ml of dry THF and vacuum was given for 2 h. Subsequently, 1.1 equiv. of *n*-BuLi (1.1 mmol, 1.0 ml of 1.3 M *n*-BuLi in hexane) was added at -78 °C and the reaction mixture was stirred for 30 min at the same temperature. Next, to the resultant reaction mixture 2-phenyl propanal (1.2 equiv. 160 µl) was added over 20 min at -78 °C and then warmed the reaction mixture to rt and continued the stirring for another 2 h.[13] After completion of reaction EtOAc and aqueous NH_4Cl work-up was done and then it was purified using column chromatography. The compound **16** was obtained as inseparable mixture of two diastereomers (white solid, *dr* = 2.3:1, 57% yield).

Characterization of Major isomer:

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.48-7.44 (m, 1H), 7.34-7.30 (m, 2H), 7.27-7.23 (m, 2H), 7.19 (dd, *J* = 4.4, 3.2 Hz, 2H), 7.16-7.13 (m, 3H), 7.04-6.98 (m, 2H), 6.92 (d, *J* = 7.2 Hz, 2H), 4.78-4.74 (m, 1H), 4.15 (d, *J* = 9.5 Hz, 1H), 2.75-2.61 (m, 2H), 2.376 (s, 3H), 1.62-1.54 (m, 2H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 144.9, 141.5, 134.2, 131.2, 130.2, 129.4, 129.3, 128.9, 128.5, 128.4, 128.2, 125.6, 76.9, 69.0, 36.3, 30.7, 21.6.

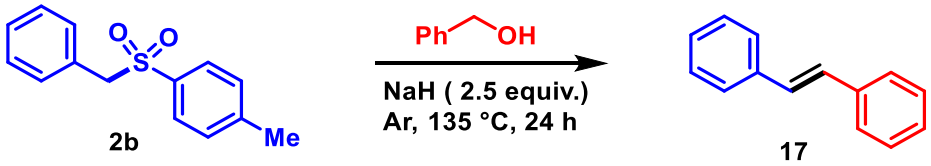
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{23}H_{24}NaO_3S$ 403.1314; found 403.1349.

Characterization peaks of Minor isomer:

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.36 (d, *J* = 7.1), 7.30-7.27 (m), 7.24-7.21 (m), 7.18-7.15 (m), 7.12-7.07 (m) 3.95 (d, *J* = 2.4 Hz), 2.82-2.75 (m), 2.361 (s), 1.69-1.61 (m).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 144.7, 141.2, 134.8, 131.2, 129.6, 129.4, 128.8, 128.6, 128.4, 128.37, 128.36, 125.9, 74.6, 68.5, 36.6, 31.9, 21.56.

Alkenylation reaction



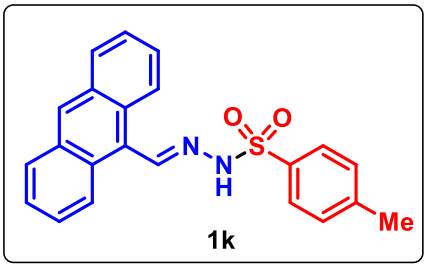
Reaction conditions: For the synthesis of olefin **17**, we have taken **2a** (1.0 mmol) in 1.0 ml of benzyl alcohol, 2.5 equiv. of NaH (2.5 equiv. 60 mg) was added in the inert condition and the reaction mixture was stirred for 24 h at 135 °C [12]. After completion of the reaction DCM and H_2O work-up was done and then it was purified using column chromatography. The compound **17** was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as a white solid. The compound **17** was purified by column chromatography using silica gel (100-200 mesh) in normal hexane and obtained as a white solid in 61% yield

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.57-7.52 (m, 4 H), 7.39 (t, *J* = 7.6 Hz, 4H), 7.32-7.27 (m, 2H), 714 (s, 2H) .

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 137.3, 128.7, 128.6, 127.6, 126.5.

V. The analytical and spectral characterization data of the catalytic products.

(*E*)-N'-(anthracen-9-ylmethylene)-4-methylbenzenesulfonohydrazide (1k):



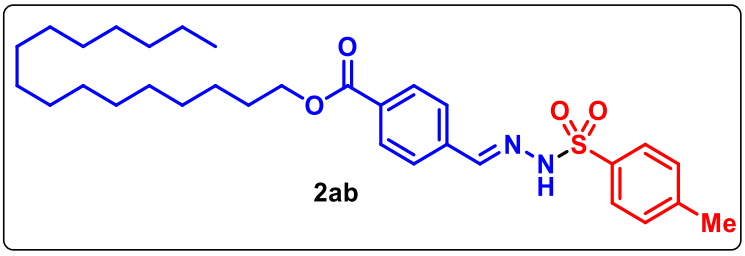
The crude product was obtained as yellow solid (67% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ (ppm) 8.56 (brs, 1H), 8.27 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.78 (d, J = 7.5 Hz, 2H), 7.61 – 7.55 (m, 3H), 7.51 (d, J = 7.3 Hz, 2H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 2H), 2.51 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298K): δ (ppm) 144.8, 135.4, 131.1, 129.9, 129.6, 129.1, 128.2, 128.0, 127.5, 125.9, 124.0, 21.6.

HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{19}N_2O_2S$ 375.1167; found 375.1162.

hexadecyl (*E*)-4-((2-tosylhydrazineylidene)methyl)benzoate (1ab):



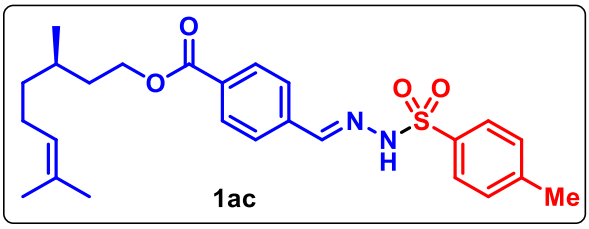
The crude product was obtained as white solid (73% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ (ppm) 8.14 (brs, 1H), 8.05 – 7.95 (m, 2H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.78 (s, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.30 (t, *J* = 6.7 Hz, 2H), 2.41 (s, 3H), 1.82 – 1.69 (m, 2H), 1.25 (brs, 26H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298K): δ (ppm) 166.0, 146.0, 144.5, 137.1, 135.1, 131.9, 130.1, 129.8, 129.7, 129.5, 129.5, 127.9, 127.1, 65.4, 31.9, 29.6, 29.6, 29.5, 29.5, 29.3, 29.2, 28.6,26.0, 22.6, 21.6, 14.1.

HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{31}H_{47}N_2O_4S$ 543.3256; found 543.3258.

(R)-3,7-dimethyloct-6-en-1-yl (*E*)-4-((2-tosylhydrazineylidene)methyl)benzoate (**1ac**):



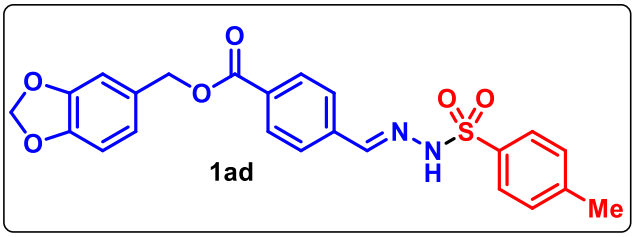
The crude product was obtained as white solid (69% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ (ppm) 8.17 (brs, 1H), 8.0 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.77 (s, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.09 (ddd, *J* = 7.1, 4.2, 1.4 Hz, 1H), 4.43 – 4.27 (m, 2H), 2.41 (s, 3H), 2.09 – 1.91 (m, 2H), 1.86 -1.70 (m, 2H), 1.67 (d, *J* = 1.0 Hz, 3H), 1.66 -1.62 (m, 1H), 1.60 (s, 3H), 1.45 -1.35 (m, 1H), 1.23 (dddd, *J* = 13.5, 9.2, 7.6, 6.1 Hz, 1H), 0.96 (d, *J* = 6.5 Hz, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298K): δ (ppm) 166.0, 145.9, 144.4, 137.1, 135.1, 131.8, 131.4, 129.8, 129.7, 127.9, 127.1, 124.5, 63.7, 36.9, 35.4, 29.5, 25.6, 25.3, 21.6, 19.4, 17.6.

HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{33}N_2O_4S$ 457.2202; found 455.2005.

benzo[d][1,3]dioxol-5-ylmethyl (*E*)-4-((2-tosylhydrazineylidene)methyl)benzoate (1ad):



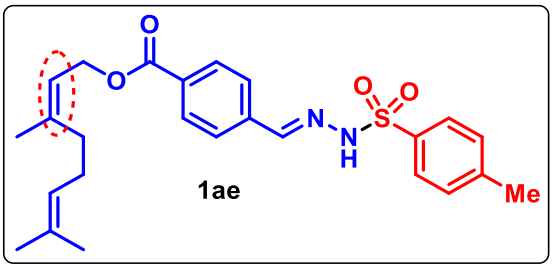
The crude product was obtained as white solid (59% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ (ppm) 8.16 (brs, 1H), 8.05 – 7.7 (m, 2H), 7.90 – 7.86 (m, 2H), 7.76 (s, 1H), 7.64 – 7.58 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.95 – 6.85 (m, 2H), 6.81 (d, *J* = 7.8 Hz, 1H), 5.97 (s, 2H), 5.25 (s, 2H), 2.40 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298K): δ (ppm) 165.7, 147.8, 147.7, 145.9, 144.5, 137.3, 135.1, 131.4, 129.9, 129.7, 129.5, 127.9, 127.1, 122.3, 108.0, 108.2, 101.1, 66.9, 21.5.

HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{21}N_2O_6S$ 453.1120; found 453.1179.

(*Z*)-3,7-dimethylocta-2,6-dien-1-yl 4-((*E*)-(2-tosylhydrazineylidene)methyl)benzoate (1ae):



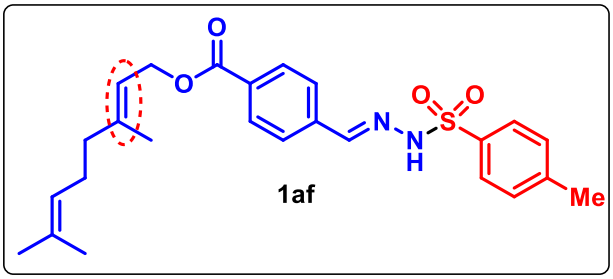
The crude product was obtained as white solid (71% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ (ppm) 8.33 (brs, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.78 (s, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.50 – 5.54 (m, 1H), 5.11 (tdd, *J* = 5.6, 2.8, 1.4 Hz, 1H), 4.80 (dd, *J* = 7.2 , 0.7 Hz, 2H), 2.40 (s, 3H), 2.18 (dd, *J* = 11.1, 4.6 Hz, 2H), 2.11 (dd, *J* = 14.8, 7.4 Hz, 2H), 1.79 (d, *J* = 1.1 Hz, 3H), 1.66 (d, *J* = 0.9 Hz, 3H), 1.60 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298K): δ (ppm) 166.0, 146.1, 144.4, 142.9, 137.1, 135.1, 132.2, 131.8, 129.8, 129.7, 127.9, 127.0, 123.5, 119.0, 61.8, 32.2, 26.6, 25.6, 23.4, 21.5, 17.6.

HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{31}N_2O_4S$ 455.2202; found 455.2005.

(*E*)-3,7-dimethylocta-2,6-dien-1-yl 4-((*E*)-(2-tosylhydrazineylidene)methyl)benzoate (1af):



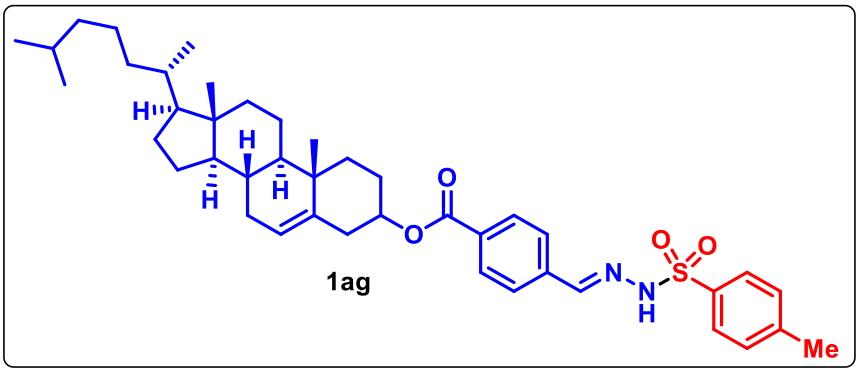
The crude product was obtained as white solid (64% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ (ppm) 8.62 (brs, 1H), 8.07 – 7.96 (m, 2H), 7.90 – 7.84 (m, 2H), 7.80 (s, 1H), 7.61 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.45 (ddd, *J* = 8.3, 5.9, 1.2 Hz, 1H), 5.14 – 5.03 (m, 1H), 4.83 (d, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 2.11 (d, *J* = 6.6 Hz, 2H), 2.08 (d, *J* = 7.5 Hz, 2H), 1.76 (d, *J* = 0.9 Hz, 3H), 1.67 (d, *J* = 0.9 Hz, 3H), 1.60 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298K): δ 166.0, 146.2, 144.4, 142.6, 137.2, 135.1, 131.8, 131.7, 129.8, 129.7, 127.8, 127.0, 123.6, 118.1, 62.1, 39.4, 26.2, 25.6, 21.5, 17.6, 16.5.

HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{25}H_{30}N_2O_4SNa$ 477.1824; found 477.1890.

(8R,9R,10S,13S,14R,17S)-10,13-dimethyl-17-((S)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-((*E*)-(2-tosylhydrazineylidene)methyl)benzoate (1ag):



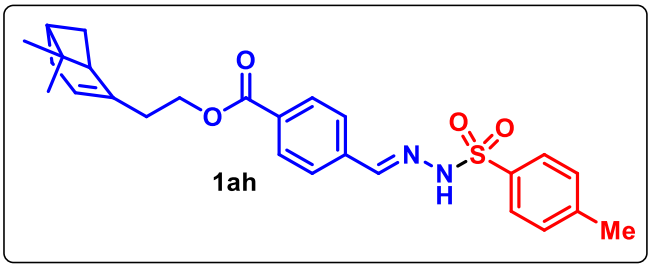
The crude product was obtained as white solid (52% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 8.13 (brs, 1H), 8.01 (d, J = 8.3 Hz, 2H), 7.87 (d, J = 8.3 Hz, 2H), 7.77 (s, 1H), 7.62 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 5.42 (s, 1H), 4.91 – 4.78 (m, 1H), 2.45 (d J = 7.6 Hz, 2H), 2.41 (s, 3H), 2.05 – 1.95 (m, 4H), 1.97 – 1.82 (m, 2H), 1.76 – 1.60 (m, 7H), 1.55 - 1.49 (m, 3H), 1.21 – 1.11 (m, 7H), 1.06 (s, 3H), 1.04 – 0.96 (m, 3H), 0.92 (d, J = 6.5 Hz. 3H), 0.87 (d, J = 8.3 Hz, 3H), 0.86 (d, J = 7.2 Hz, 3H), 0.69 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 165.3, 146.0, 144.4, 135.2, 132.2, 129.8, 129.7, 127.0, 122.8, 74.9, 56.6, 56.1, 50.0, 42.3, 39.7, 39.5, 38.5, 37.0, 36.6, 36.1, 35.7, 31.9, 31.8, 28.2, 28.0, 23.8, 22.8, 22.5, 21.5, 21.0, 19.3, 18.7, 11.8.

HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{42}H_{59}N_2O_4S$ 687.4196; found 687.4246.

2-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl(*E*)-4-((2-tosylhydrazineylidene)methyl)benzoate (1ah):



The crude product was obtained as white solid (57% yield).

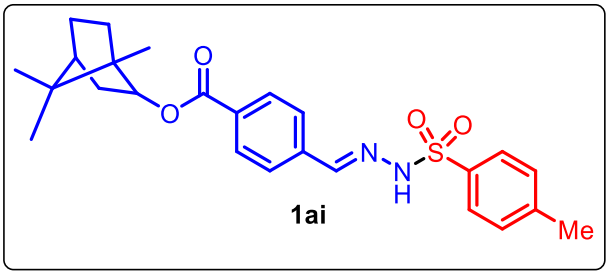
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 8.15 (brs, 1H), 8.04 – 7.97 (m, 2H), 7.88 (d, J = 8.3 Hz, 2H), 7.77 (s, 1H), 7.6 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 5.43 – 5.30 (m, 1H), 4.40 – 4.27

(m, 2H), 2.43 -2. 41 (m, 1H), 2.41 (s, 3H), 2.37 – 2.36 (m, 1H), 2.37 (dd, *J* = 5.6, 2.9 Hz, 1H), 2.23 (q, *J* = 17.5 Hz, 2H), 2.13 – 2.07 (m, 2H), 1.27 (s, 3H), 1.16 (d, *J* = 8.5 Hz, 1H), 0.82 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 165.9, 145.9, 144.4, 144.1, 137.1, 135.1, 131.8, 129.8, 129.7, 127.9, 127.1, 119.0, 63.5, 45.7, 40.7, 38.0, 35.9, 31.6, 31.3, 26.2, 21.5, 21.1.

HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{31}N_2O_4S$ 467.2004; found 467.2013.

1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl (*E*)-4-((2-tosylhydrazineylidene)methyl)benzoate (1ai):



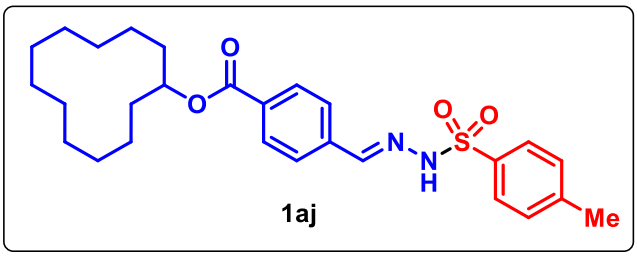
The crude product was obtained as white solid (61% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 8.33 (brs, 1H), 8.05 – 7.99 (m, 2H), 7.90 – 7.85 (m, 2H), 7.80 (s, 1H), 7.68 – 7.61 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.10 (ddd, *J* = 9.9, 3.3, 2.2 Hz, 1H), 2.47 (ddd, J = 9.3, 5.3, 3.4 Hz, 1H), 2.41 (s, 3H), 2.15 – 2.04 (m, 1H), 1.74 (t, *J* = 4.5 Hz, 1H), 1.44 – 1.36 (m, 1H), 1.35 – 1.25 (m, 1H), 1.10 (dd, *J* = 13.8, 3.5 Hz, 1H), 0.96 (s, 3H), 0.91 (s, 3H), 0.90 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 166.2, 146.1, 144.4, 137.2, 135.1, 132.1, 129.7, 127.9, 127.1, 80.8, 49.1, 47.8, 44.9, 36.8, 28.0, 27.3, 21.5, 19.6, 18.8, 13.5.

HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{31}N_2O_4S$ 455.2005; found 455.1916.

cyclododecyl (*E*)-4-((2-tosylhydrazineylidene)methyl)benzoate (1aj):



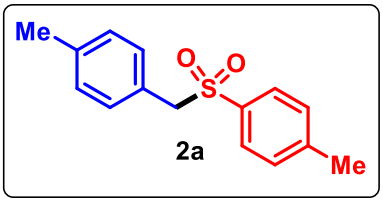
The crude product was obtained as white solid (56% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 8.39 (brs, 1H), 7.99 (d, J = 8.3 Hz, 2H), 7.87 (d, J = 8.2 Hz, 2H), 7.79 (s, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 5.26-5.22 (m, 1H), 2.40 (s, 3H), 1.87-1.79 (m, 4H), 1.68-1.61 (m, 2H), 1.49-1.33 (m, 16H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 166.2, 146.1, 144.4, 137.2, 135.1, 132.1, 129.7, 127.9, 127.1, 80.8, 49.1, 47.8, 44.9, 36.8, 28.0, 27.3, 21.5, 19.6, 18.8, 13.5.

HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{36}N_2O_4S$ 485.2474; found 485.2477.

1-methyl-4-((4-methylbenzyl)sulfonyl)benzene (2a):[6]

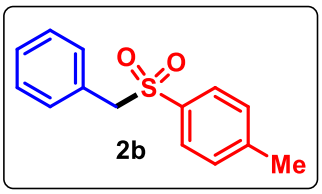


The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (82% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.52 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 7.9 Hz, 2H), 7.07 (d, J = 7.8 Hz, 2H), 6.97 (d, J = 7.9 Hz, 2H), 4.25 (s, 2H), 2.42 (s, 3H), 2.33 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 144.5, 138.6, 135.1, 130.6, 129.4, 129.2, 128.6, 125.1, 62.6, 21.6, 21.2. HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{16}NaO_2S$ is 283.0769; found 283.0761.

1-(benzylsulfonyl)-4-methylbenzene (2b):[6]

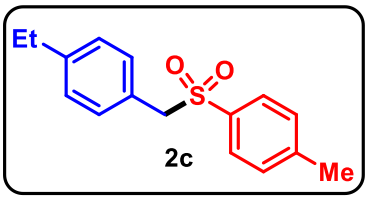


The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (78% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.50 (d, J = 7.9 Hz, 2H), 7.31 (t, J = 7.2 Hz, 1H), 7.25 (dd, J_1 = 17.0 Hz and J_2 = 7.8 Hz, 4H), 7.09 (d, J = 7.4 Hz, 2H), 4.29 (s, 2H), 2.42 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 144.6, 135.0, 130.8, 129.4, 128.6, 128.6, 128.5, 128.3, 62.9, 21.6. HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{14}H_{14}NaO_2S$ is 269.0612; found 269.0609.

1-ethyl-4-(tosylmethyl)benzene (2c):

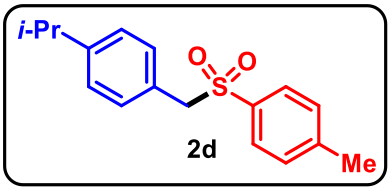


The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (81% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.52 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 7.9 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 7.00 (d, J = 7.8 Hz, 2H), 4.25 (s, 2H), 2.62 (d, J = 7.6 Hz, 2H), 2.42 (s, 3H), 1.21 (t, J = 7.6 Hz, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 144.5, 138.6, 135.1, 130.6, 129.4, 129.2, 128.6, 125.1, 62.6, 28.5, 21.6, 15.4. HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{19}O_2S$ is 275.1106; found 275.1102.

1-isopropyl-4-(tosylmethyl)benzene (2d):

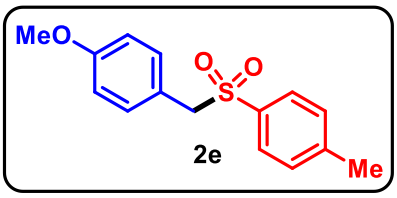


The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (81% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.52 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 7.02 (d, J = 8.1 Hz, 2H), 4.24 (s, 2H), 2.87 (dt, J = 13.8, 6.9 Hz, 1H), 2.42 (s, 3H), 1.22 (s, 3H), 1.20 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 149.6, 144.5, 135.2, 130.7, 129.4, 128.5, 126.6, 125.3, 62.6, 33.7, 23.8, 21.5. HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{20}O_2S$ 289.1262; found 289.1262.

1-methoxy-4-(tosylmethyl)benzene (2e): [6]

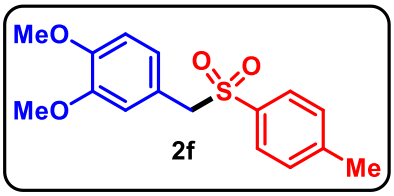


The compound was purified by column chromatography using silica gel (100-200 mesh) with 9% of EtOAc in hexane and obtained as white solid (67% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.51 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 7.9 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 8.5, Hz, 2H), 4.24 (s, 2H), 3.79 (s, 3H), 2.42 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 160.0, 144.6, 135.1, 132.0, 129.5, 128.6, 120.1, 114.0, 62.2, 55.2, 21.6. HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{16}NaO_3S$ 299.0718; found 299.0710.

1,2-dimethoxy-4-(tosylmethyl)benzene (2f): [6]

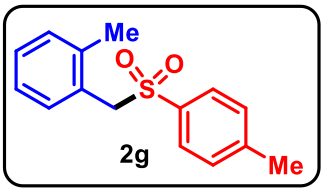


The compound was purified by column chromatography using silica gel (100-200 mesh) with 9% of EtOAc in hexane and obtained as white solid (66% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.52 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 6.74 (d, J = 8.2 Hz, 1H), 6.63 (dd, J = 8.2, 2.0 Hz, 1H), 6.64 (d, J = 2.0 Hz, 1H), 4.22 (s, 2H), 3.85 (s, 3H), 3.87 (s, 3H), 2.41 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 149.4, 148.7, 144.55, 135.0, 129.4, 128.7, 123.5, 120.5, 113.5, 110.9, 62.6, 55.8, 55.7, 21.5. HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{18}NaO_4S$ 329.0823; found 329.0823.

1-methyl-2-(tosylmethyl)benzene (2g): [6]

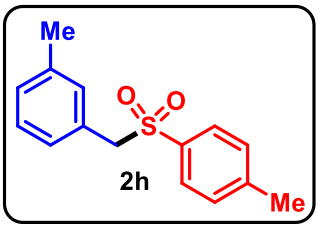


The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (58% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.52 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.2 (dd, J = 11.4, 4.7 Hz, 1H), 7.10 (dd, J = 14.4, 7.3 Hz, 2H), 7.02 (d, J = 7.4 Hz, 1H), 4.35 (s, 2H), 2.42 (s, 3H), 2.11 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 144.8, 138.4, 135.6, 132.0, 130.7, 129.7, 129.0, 128.7, 126.8, 126.1, 60.2, 21.7, 19.5. HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{16}NaO_2S$ is 283.0769; found 283.0761.

1-methyl-3-(tosylmethyl)benzene (2h): [6]

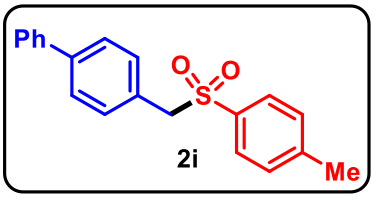


The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (59% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.54 (d, J = 8.3 Hz, 2H), 7.28-7.26 (m, 2H), 7.19 – 7.12 (m, 2H), 6.95(s, 1H), 6.87 (dd, J_1 = 5.0 Hz and J_1 = 3.4 Hz, 1H), 4.27 (s, 2H), 2.44 (s, 3H), 2.29 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ 144.6, 138.2, 135.1, 131.5, 129.4, 128.7, 128.3, 128.0, 127.8, 60.2, 21.5, 21.1. HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{16}NaO_2S$ is 283.0769; found 283.0761.

4-(tosylmethyl)-1,1'-biphenyl (2i): [6]

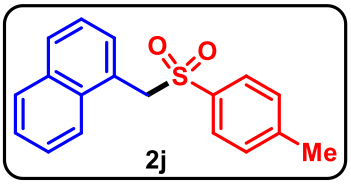


The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (66% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.62 - 7.57 (m, 4H), 7.55 – 7.51 (m, 2H), 7.47 (dd, *J* = 10.4, 4.8 Hz, 2H), 7.41 – 7.36 (m, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.2 (d, *J* = 8.2 Hz, 2H), 4.36 (s, 2H), 2.44 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 144.6, 141.5, 140.2, 135.1, 131.2, 129.5, 128.8, 128.6, 127.6, 127.1, 127.0, 62.5, 21.6. HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{20}H_{18}NaO_2S$ 345.0920; found 345.0925.

1-(tosylmethyl)naphthalene (2j): [6]

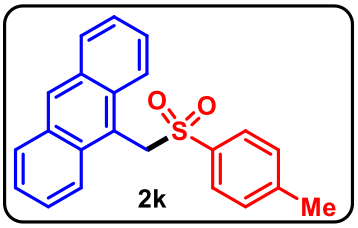


The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (61% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.83 (t, *J* = 8.1 Hz, 3H), 7.48 (d, J = 8.2 Hz, 2H), 7.45 – 7.39 (m, 2H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.0 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 4.80 (s, 2H), 2.36 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 144.6, 135.1, 133.7, 132.1, 130.5, 129.6, 129.4, 128.6, 128.6, 126.5, 125.8, 125.0, 124.6, 123.6, 59.9, 21.5. HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{20}H_{18}NaO_2S$ 319.0769; found 319.0765.

9-(tosylmethyl)anthracene (2k):



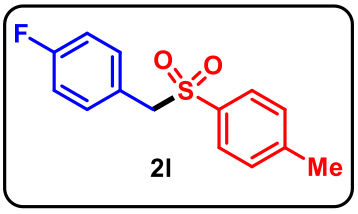
The compound was purified by column chromatography using silica gel (100-200 mesh) with 7% of EtOAc in hexane and obtained as white solid (38% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 8.47 (s, 1H), 8.04-8.00 (m, 2H), 7.99-7.96 (m, 2H), 7.48 – 7.38 (m, 6H), 7.07 (d, *J* = 7.9 Hz, 2H), 5.43 (s, 2H), 2.32 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 144.7, 135.5, 131.4, 131.3, 129.5, 129.4, 129.0, 128.5, 126.6, 125.0, 124.2, 120.0, 119.8, 55.8, 21.5.

HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{18}O_2SNa$ 369.0925; found 369.0974.

1-fluoro-4-(tosylmethyl)benzene (2l): [6]

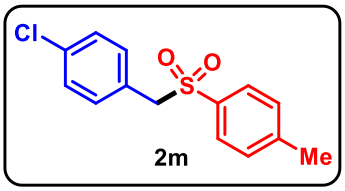


The compound was purified by column chromatography using silica gel (100-200 mesh) with 9% of EtOAc in hexane and obtained as light-yellow solid (55% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.53 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 7.09 (dd, J = 8.6 5.3 Hz, 2H), 6.98 (t, J = 8.6 Hz, 2H), 4.27 (s, 2H), 2.44 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 163.0 (d, J = 248 Hz), 144.8, 134.8, 132.5 (d, J = 8.4 Hz), 129.6, 128.6, 124.2 (d, J = 3.7 Hz), 115.6 (d, J = 21.9 Hz), 62.0, 21.6. HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{14}H_{13}FO_2SNa$ 287.0518; found 287.0513

1-chloro-4-(tosylmethyl)benzene (2m): [6]

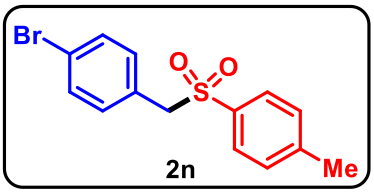


The compound was purified by column chromatography using silica gel (100-200 mesh) with 9% of EtOAc in hexane and obtained as white solid (54% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.54 (d, J = 8.3 Hz, 2H), 7.28 (dd, J = 10.4, 6.8 Hz, 4H), 7.05 (d, J = 8.4 Hz, 2H), 4.33 (s, 2H), 2.43 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 145.0, 135.0, 134.8, 132.1, 130.0, 128.8, 128.6, 126.8, 62.1, 21.6. HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{14}H_{13}ClO_2SNa$ 303.0222; found 303.0232

1-bromo-4-(tosylmethyl)benzene (2n): [6]

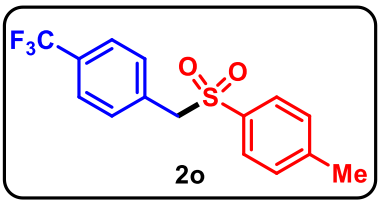


The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (63% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.53 (dd, J = 8.1, 4.8 Hz, 4H), 7.27 (d, J = 8.7 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 4.27 (s, 2H), 2.45 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 144.9, 134.7, 132.3, 131.7, 129.6, 128.5, 127.3, 123.1, 62.2, 21.6. HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{14}H_{13}BrNaO_2S$ 346.9717; found 346.9708.

1-methyl-4-((4-(trifluoromethyl)benzyl)sulfonyl)benzene (2o): [8]



The compound was purified by column chromatography using silica gel (100-200 mesh) with 9% of EtOAc in hexane and obtained as white solid (66% yield).

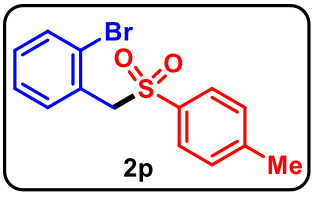
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.53 (dd, J = 8.1, 4.8 Hz, 4H), 7.25 (dd, J_1 = 17.4 Hz and J_2 = 8.4 Hz, 4H), 4.33 (s, 2H), 2.43 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 145.1, 134.8, 132.3, 131.2, 130.0, 128.6, 125.5 (q, J = 3.7 Hz), 122.7, 62.3, 21.6.

^{19}F NMR (CDCl3, 376 MHz, 298 K): δ (ppm) - 62.76.

HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{14}F_3O_2S$ 315.0667; found 315.0668

1-bromo-2-(tosylmethyl)benzene (2p): [6]

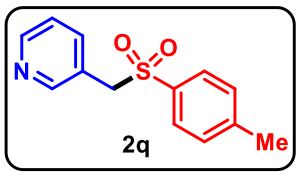


White solid, Yield: 47%. The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.51 (d, J = 8.1 Hz, 2H), 7.46 (dd, J = 10.9, 8.1 Hz, 2H), 7.31 (t, J = 7.5 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H) 7.17 (t, J = 7.5 Hz, 1H), 4.56 (s, 2H), 2.41 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 144.8, 135.2, 132.9, 132.9, 130.2, 129.5, 128.7, 128.4, 127.6, 125.9, 61.6, 21.6. HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{14}BrO_2$ 324.9898; found 324.9891.

3-(tosylmethyl)pyridine (2q): [9]

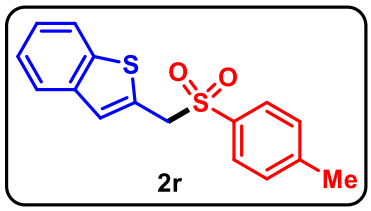


The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (45% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.54 (d, J = 8.3 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.24 (d, J = 7.9 Hz, 2H), 7.11 (td, J = 7.6 and 1.1 Hz, 1H), 6.92 (t, J = 9.0 Hz, 1H), 4.38 (s, 2H), 2.42 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 163.9, 162.0, 144.8, 134.7, 132.5, 129.5, 128.5, 124.1, 124.1, 115.6, 115.5, 61.9, 21.6.

2-(tosylmethyl)benzo[b]thiophene (2r):



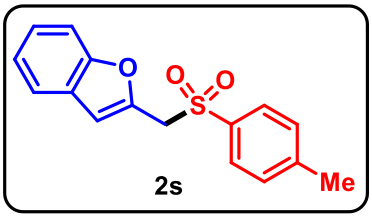
The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (59% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.77 – 7.75 (m, 1H), 7.70 – 7.68 (m, 1H), 7.64 (d, J = 8.3 Hz, 2H), 7.34 – 7.32 (m, 2H), 7.26-7.25 (m, 2H), 7.12 (s, 1H), 4.58 (s, 2H), 2.42 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 145.0, 140.7, 139.2, 134.7, 129.7, 128.7, 127.0, 124.9, 124.5, 123.8, 122.2, 58.0, 21.6.

HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{14}O_2S_2Na$ 325.0333; found 325.0319.

2-(tosylmethyl)benzofuran (2s):



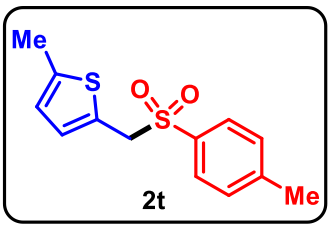
The compound was purified by column chromatography using silica gel (100-200 mesh) with 10% of EtOAc in hexane and obtained as white solid (65% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.65 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 7.6 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.27 (d, J = 9.4 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 6.67 (s, 1H), 4.52 (s, 2H), 2.43 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 155.2, 145.1, 145.0, 135.3, 130.0, 128.5, 128.0, 125.0, 123.0, 121.2, 111.3, 108.8, 56.5, 21.7.

HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{14}O_3SNa$ 309.0561; found 309.0556.

2-methyl-5-(tosylmethyl)thiophene (2t):



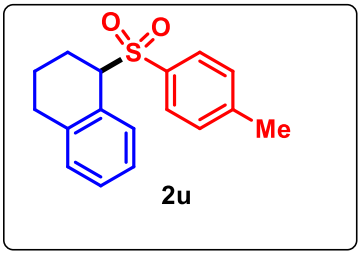
The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (72% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.61 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 6.65 – 6.49 (s, 2H), 4.40 (s, 2H), 2.43 (s, 6H).

, **^{13}C {^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 144.7, 142.2, 134.7, 130.1, 129.5, 128.6, 126.0, 125.3, 57.6, 21.6, 15.3.

HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{13}H_{14}O_2S2Na$ 289.0333; found 289.0328.

1-(tosylmethyl)-1,2,3,4-tetrahydronaphthalene (2u):



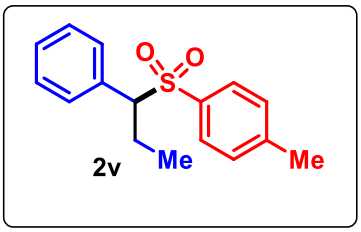
The compound was purified by column chromatography using silica gel (100-200 mesh) with 7% of EtOAc in hexane and obtained as a brown solid (47% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.51 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.24 (ddd, *J* = 8.9, 5.7, 1.7 Hz, 3H), 7.14 – 7.07 (m, 2H), 4.38 (dd, *J* = 6.3, 3.9 Hz, 1H), 2.67 – 2.54 (m, 2H), 2.43 (s, 3H), 2.39 (dd, *J* = 6.8, 4.0 Hz, 1H), 2.09 – 2.02 (m, 2H), 1.62 – 1.58 (m, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 144.5, 139.8, 134.8, 131.7, 129.4, 129.3, 129.2, 128.4, 127.0, 125.6, 64.6, 28.6, 23.8, 21.6, 19.2.

HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{17}H_{18}O_2S_2Na$ 309.0925; found 309.0930.

(S)-1-methyl-4-((1-phenylpropyl)sulfonyl)benzene (2v):



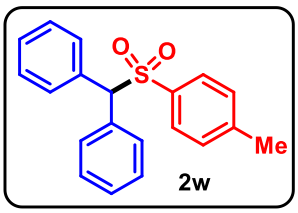
The compound was purified by column chromatography using silica gel (100-200 mesh) with 6% of EtOAc in hexane and obtained as a brown solid (53% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.39 (d, *J* = 8.3 Hz, 2H), 7.29-7.22 (m, 3H), 7.18-7.13 (m, 2H), 7.12-7.08 (m, 2H), 3.92 (dd, *J* = 11.6, 3.7, 1 H), 2.48-2.44 (m, 1H), 2.38 (s, 3H), 2.18-2.08 (m, 1H), 0.085 (t, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 144.3, 134.5, 132.2, 129.9, 129.2, 129.0, 128.6, 128.4, 73.1, 21.5, 21.0, 11.5.

HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{18}O_2SNa$ 297.0925; found 297.0922.

(tosylmethylene)dibenzene (2w): [6]

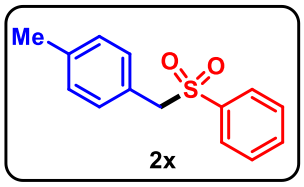


The compound was purified by column chromatography using silica gel (100-200 mesh) with 7% of EtOAc in hexane and obtained as white solid (29% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.55 – 7.51 (m, 4H), 7.49 (d, J = 8.3 Hz, 2H), 7.33 – 7.29 (m, 6H), 7.15 (d, J = 7.9 Hz, 2H), 5.26 (s, 1H), 2.37 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 144.4, 133.1, 129.9, 129.2, 129.0, 128.6, 128.5, 76.5, 21.6. HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{20}H_{18}O_2SNa$ 345.0925; found 345.0931

1-methyl-4-((phenylsulfonyl)methyl)benzene (2x): [7]

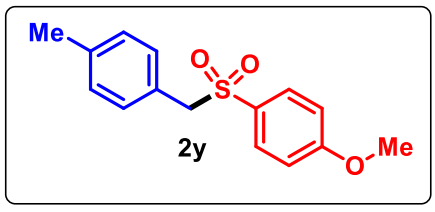


The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (60% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.67 – 7.63 (m, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 7.06 (d, J = 7.9 Hz, 2H), 6.96 (d, J = 8.0 Hz, 2H), 4.27 (s, 2H), 2.32 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 138.7, 138.0, 133.6, 130.6, 129.2, 128.8, 128.6, 124.9, 62.5, 21.1. HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{14}H_{14}O_2SNa$ 269.0612; found 269.0611.

1-methoxy-4-((4-methylbenzyl)sulfonyl)benzene (2y):



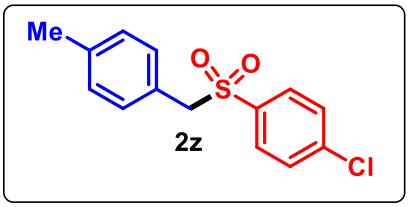
The compound was purified by column chromatography using silica gel (100-200 mesh) with 9% of EtOAc in hexane and obtained as a white solid (67% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.54 (d, J = 9.0 Hz, 2 H), 7.07 (d, J = 7.8 Hz, 2H), 6.96 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 4.24 (s, 2H), 3.85 (s, 3H), 2.32 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 163.6, 138.6, 130.7, 130.6, 129.5, 129.2, 125.3, 113.9, 62.7, 55.6, 21.2.

HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{16}O_3SNa$ 299.0718; found 299.0710.

1-chloro-4-((4-methylbenzyl)sulfonyl)benzene (2z):

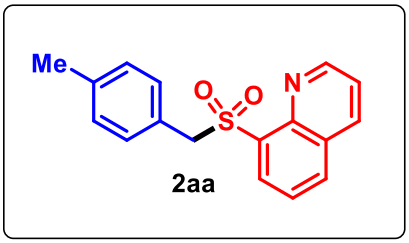


The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as a white solid (61% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.54 (d, J = 8.7 Hz, 2 H), 7.42 (d, J = 8.7 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 4.27 (s, 2H), 2.33 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 140.4, 138.9, 136.4, 130.6, 130.1, 129.4, 129.2, 124.7, 62.6, 21.2. HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{14}H_{13}ClO_2SNa$ 303.0222; found 303.0232

8-((4-methylbenzyl)sulfonyl)quinoline (2aa):



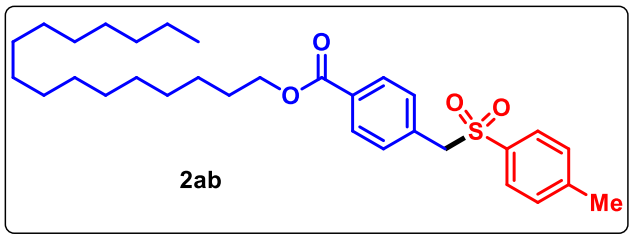
The compound was purified by column chromatography using silica gel (100-200 mesh) with 18% of EtOAc in hexane and obtained as a brown solid (51% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 9.26-9.09 (m, 1H), 8.28 (dd, J = 13.6, 7.8 Hz, 2H), 8.06 (d, J = 8.1 Hz, 1H), 7.61 (dd, J = 8.3, 4.2 Hz, 1H), 7.55 (t, J = 7.7 Hz, 1H), 6.95 (m, 4H), 5.12 (s, 2H), 2.23 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 151.5, 144.3, 138.3, 136.7, 135.3, 134.2, 132.7, 130.5, 129.1, 128.7, 125.5, 125.4, 122.2, 61.3, 21.1.

HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{17}H_{15}O_2NSNa$ 3230.0721; found 320.0725.

hexadecyl 4-(tosylmethyl)benzoate (2ab):



2ab

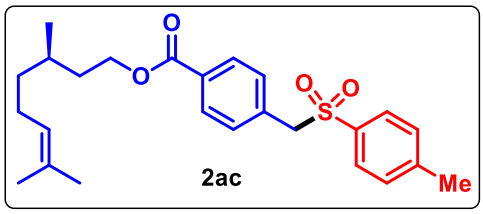
The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (57% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.93 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 4.33 (s, 2H), 4.30 (t, J = 6.7 Hz, 2H), 2.42 (s, 3H), 1.78-1.72 (m, 2H), 1.44-1.9 (m, 2H), 1.38-1.21 (m, 24H), 0.88 (t, J = 6.9 Hz, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 166.1, 145.0, 134.8, 133.1, 130.8, 129.7, 129.6, 128.6, 65.4, 62.7, 32.0, 29.67, 29.65, 29.63, 29.57, 29.52, 29.34, 29.27, 28.8, 26.0, 22.7, 21.6, 14.1. (*Aliphatic peaks are overlapped*).

HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{31}H_{46}O_4SNa$ 537.3015; found 537.3036

(R)-3,7-dimethyloct-6-en-1-yl 4-(tosylmethyl)benzoate (2ac):



2ac

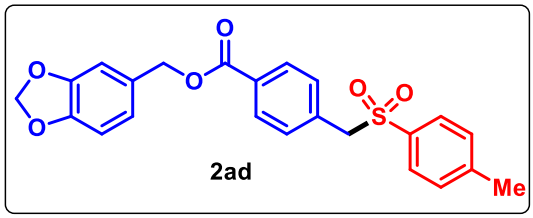
The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (65% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.92 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 5.09 (s, 1H), 4. 35 – 4.33 (m, 4H), 2.42 (s, 3H), 2.07-1.93 (m, 2H), 1.83 – 1.76 (m, 1H), 1.67-1.62 (m, 4H), 1.60-1.56 (m, 4H), 1.41-1.6 (m, 1H), 1.27-1.22 (m, 1H), 0.96 (d, J = 6.5 Hz, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 166.1, 145.0, 134.8, 133.2, 131.4, 130.8, 129.7, 129.6, 128.6, 124.5, 63.8, 62.7, 37.0, 35.5, 29.6, 25.7, 25.4, 21.6, 19.5, 17.7.

HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{33}O_4S$ 429.2100; found 429.2180.

benzo[d][1,3]dioxol-5-ylmethyl 4-(tosylmethyl)benzoate (2ad):



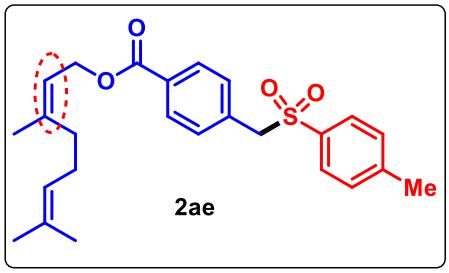
The compound was purified by column chromatography using silica gel (100-200 mesh) with 9% of EtOAc in hexane and obtained as white solid (54% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.94 (d, J = 7.7 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 7.7 Hz, 2H), 7.15 (d, J = 7.7 Hz, 2H), 6.92 (d, J = 11.9 Hz, 2H), 6.81 (d, J = 7.7 Hz, 1H), 5.97 (s, 2H), 5.24 (s, 2H), 4.33 (s, 2H), 2.42 (s, 3H),

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 165.9, 147.9, 147.7, 145.0, 133.4, 130.8, 130.4, 129.8, 129.6, 129.5, 128.6, 122.3, 109.0, 108.3, 101.2, 66.9, 62.7, 21.

HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{23}H_{20}O_6SNa$ 447.0878; found 447.0847.

(*Z*)-3,7-dimethylocta-2,6-dien-1-yl 4-(tosylmethyl)benzoate (2ae):



The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (66% yield).

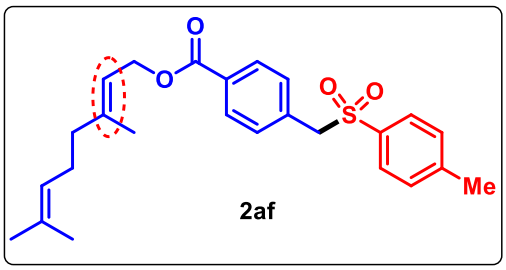
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.93 (dd, J = 8.3, 2.5 Hz, 2H), 7.49 (dd, J = 8.3, 3.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.14 (dd, J = 8.2, 3.7 Hz, 2H), 5.46 (dd J = 15.4, 7.6 Hz, 1H), 5.14 – 5.05 (m, 1H), 4.81 (dd, J = 16.0, 7.1 Hz, 2H), 4.33 (s, 2H), 2.41 (s, 3H), 2.18 (dd, J = 11.1, 4.4 Hz, 1H), 2.11 (t, J = 6.7 Hz, 2H), 2.09 – 2.04 (m, 1H), 1.78 (d, J = 16.8 H, 3H), 1.66 (s, 3H), 1.59 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 166.1, 145.0, 143.0, 142.6, 134.7, 133.1, 132.2, 131.9, 130.7, 129.7, 129.6, 128.6, 123.7, 123.5, 119.0, 118.2, 62.7, 62.1, 61.8, 39.5, 32.2, 26.6, 26.2, 25.7, 25.6, 23.5, 21.6, 17.7, 17.6, 16.5.

Due to the isomerization of the red circled double bond, we observed 2:1 ratio of product (*E*: *Z*). *i.e.* why, the carbon numbers are excess. The isomerization is due to the tosyl radical addition.

HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{31}O_4S$ 427.1943; found 427.1917.

(*E*)-3,7-dimethylocta-2,6-dien-1-yl 4-(tosylmethyl)benzoate (2af):



The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (74% yield).

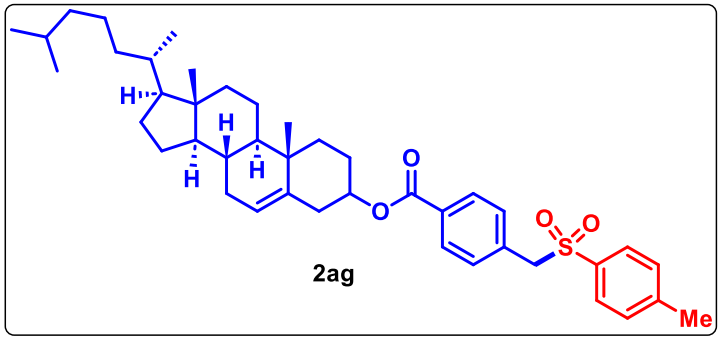
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.92 (dd, *J* = 8.3, 2.4 Hz, 2H), 7.48 (dd, *J* = 8.2, 3.0 Hz, 2H), 7.23 (d, *J* = 8.41 Hz, 2H), 7.14 (dd, *J* = 8.2, 3.7 Hz, 2H), 5.45 (t *J* = 7.4 Hz, 1H), 5.14 – 5.04 (m, 1H), 4.81 (dd, J = 15.9, 7.1 Hz, 2H), 4.33 (s, 2H), 2.41 (s, 3H), 2.17 (d, *J* = 7.5 Hz, 1H), 2.11 (t, *J* = 6.8 Hz, 2H), 2.09 (d, J = 7.2 Hz, 1H), 1.77 (d, J = 16.6 H, 3H), 1.66 (s, 3H), 1.59 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 166.1, 145.0, 142.9, 142.6, 134.7, 133.1, 132.2, 131.8, 130.7, 129.7, 129.6, 128.6, 123.7, 123.5, 119.0, 118.1, 62.6, 62.0, 61.8, 39.5, 32.2, 26.6, 26.2, 25.64, 25.62, 23.5, 21.6, 17.65, 17.63, 16.5.

Due to the isomerization of the red circled double bond, we observed 2:1 ratio of product (*E*: *Z*). *i.e.* why, the carbon numbers are excess. The isomerization is due to the tosyl radical addition.

HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{25}H_{30}O_4SNa$ 449.1762; found 449.1758.

(8R,9R,10S,13S,14R,17S)-10,13-dimethyl-17-((S)-5-methylhexan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(tosylmethyl)benzoate (2ag):



2ag

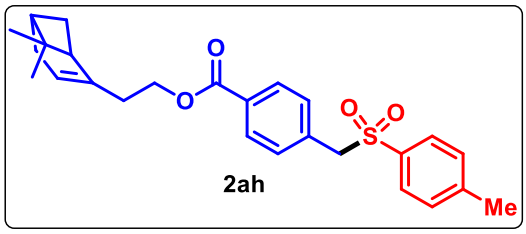
The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (43% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.93 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 7.9 Hz, 2H), 7.15 (dd, J = 8.4 Hz, 2H), 5.41 (d J = 4.3 Hz, 1H), 5.01 – 4.71 (m, 1H), 4.33 (s, 2H), 2.45 (d, J = 7.7 Hz, 2H), 2.42 (s, 3H), 2.01 – 1.90 (m, 4H), 1.89 – 1.69 (m, 2H), 1.62 – 1.45 (m, 7H), 1.42 -1.31 (m, 3H), 1.23 – 1.09 (m, 7H), 1.06 (s, 3H), 1.05 – 0.96 (m, 3H), 0.92 (d, J = 6.5 Hz. 3H), 0.87 (d, J = 2.3 Hz, 3H), 0.86 (d, J = 2.2 Hz, 3H), 0.69 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 165.4, 145.0, 139.5, 134.8, 133.0, 131.0, 130.7, 129.65, 129.63, 128.6, 122.8, 74.9, 62.6, 56.6, 56.1, 50.0, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.7, 31.9, 31.8, 28.2, 28.0, 27.8, 24.3, 23.8, 22.8, 22.5, 21.6, 21.0, 19.3, 18.7, 11.4.

HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{41}H_{56}O_4SNa$ 681.3954; found 681.3947.

2-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl 4-(tosylmethyl)benzoate (2ah):



2ah

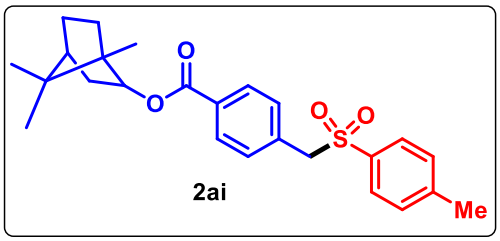
The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (52% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.91 (d, J = 7.8 Hz, 2H), 7.49 (d, J = 7.8 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 7.5 Hz, 2H), 5.35 (s, 1H), 4.33 (s, 4H), 2.42-2.37 (m, 4H), 2.29-2.19 (m, 2H), 2.10 (s, 2H), 1.27 (s, 3H), 1.16 (d, J = 8.4, 1H), 0.83 (s, 3H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 166.0, 145.0, 144.1, 134.8, 133.2, 130.8, 130.7, 129.7, 129.6, 128.6, 119.0, 63.5, 62.7, 45.8, 40.7, 38.0, 36.0, 31.7, 31.4, 26.2, 21.6, 21.1.

HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{31}O_4S$ 439.1943; found 439.1964.

1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-(tosylmethyl)benzoate (2ai):



2ai

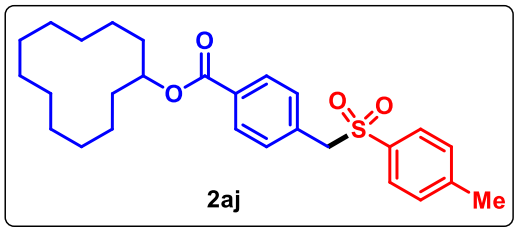
The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (64% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.97 (d, J = 7.9 Hz, 2H), 7.54 (d, J = 7.9 Hz, 2H), 7.28 (d, J = 7.2 Hz, 2H), 7.20 (d, J = 7.9 Hz, 2H), 5.13 (d, J = 9.5 Hz, 1H), 4.36 (s, 2H), 2.51 - 2.44 (m, 4H), 2.14 – 2.09 (m, 1H), 1.85-1.80 (m, 1H), 1.76 (s, 1H), 1.45-1.40 (m, 1H), 1.35-1.30 (m, 1H), 1.13 (d, J = 13.8 Hz, 1H), 0.96 (s, 3H), 0.93 (d, J = 4 Hz, 6H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 166.3, 145.0, 134.8, 133.0, 131.1, 130.8, 129.7, 129.6, 128.6, 80.8, 62.9, 49.1, 47.9, 44.9, 36.8, 28.0, 27.3, 21.6, 19.7, 18.9, 13.6.

HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{31}O_4S$ 427.1943; found 427.1917.

cyclododecyl 4-(tosylmethyl)benzoate (2aj):



2aj

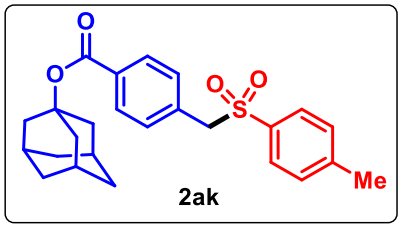
The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (59% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.94 (d, J = 7.6 Hz, 2H), 7.53 (d, J = 7.6 Hz, 2H), 7.27 (d, J = 7.9 Hz, 2H), 7.17 (d, J = 7.7 Hz, 2H), 5.26 (s, 1H), 4.35 (s, 2H), 2.44 (s, 3H), 1.91 – 1.75 (m, 2H), 1.67 (s, 2H), 1.44 (d, J = 39.3 Hz, 18H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 165.7, 144.9, 134.8, 133.0, 131.2, 130.7, 129.63, 129.61, 128.6, 73.2, 62.6, 29.1, 24.2, 23.9, 23.3, 23.1, 21.6, 20.8.

HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{27}H_{36}O_4SNa$ 479.2232; found 479.2227

(3s,5s,7s)-adamantan-1-yl 4-(tosylmethyl)benzoate (2ak):



The compound was purified by column chromatography using silica gel (100-200 mesh) with 8% of EtOAc in hexane and obtained as white solid (42% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.89 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 4.34 (s, 2H), 2.44 (s, 3H), 2.25 (d J = 11.4 Hz, 9H), 1.72 (t, J = 7.5 Hz, 6H).

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm) 165.6, 146.1, 144.4, 137.1, 135.2, 132.3, 129.8, 129.7, 127.9, 127.1, 73.4, 29.1, 24.2, 24.0, 23.3, 23.1, 21.6, 20.8.

HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{25}H_{28}O_4SNa$ 447.1606; found 447.1645.

VI. ^{1}H and ^{13}C NMR spectra of the products.

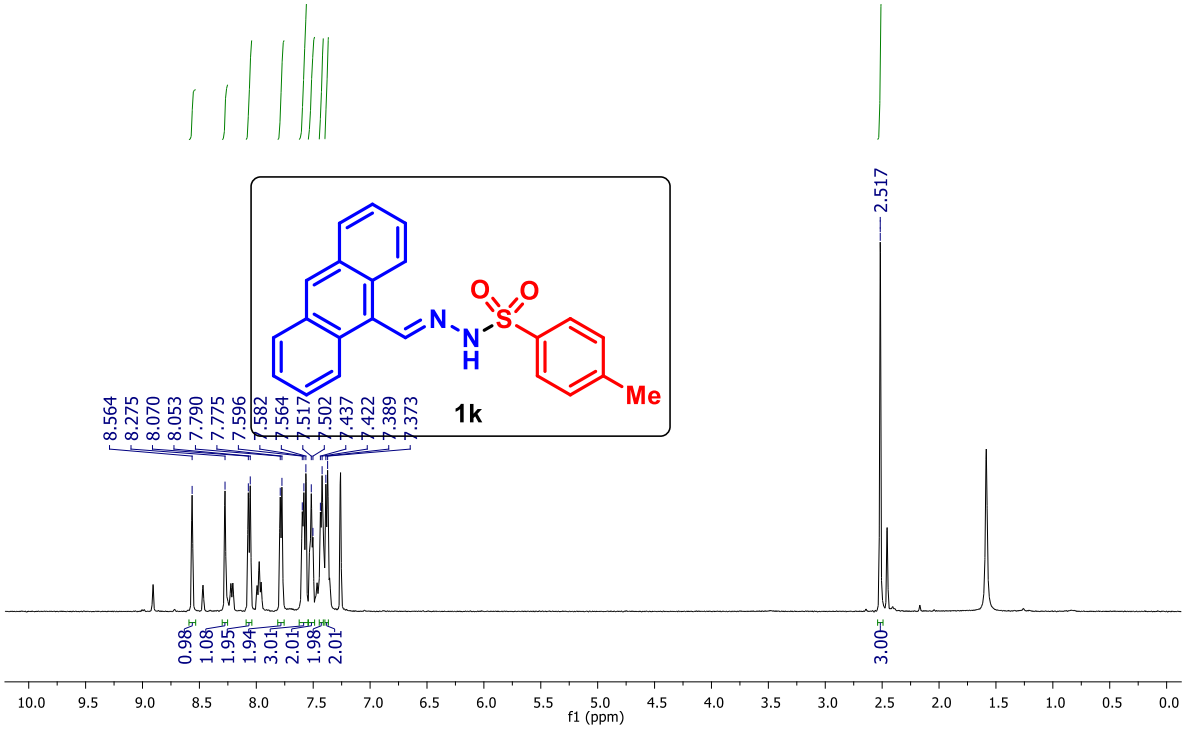


Figure S28. ^{1}H NMR spectrum ($CDCl_3$) of (*E*)-N'-(anthracen-9-ylmethylene)-4-methylbenzenesulfonohydrazide (**1k**).

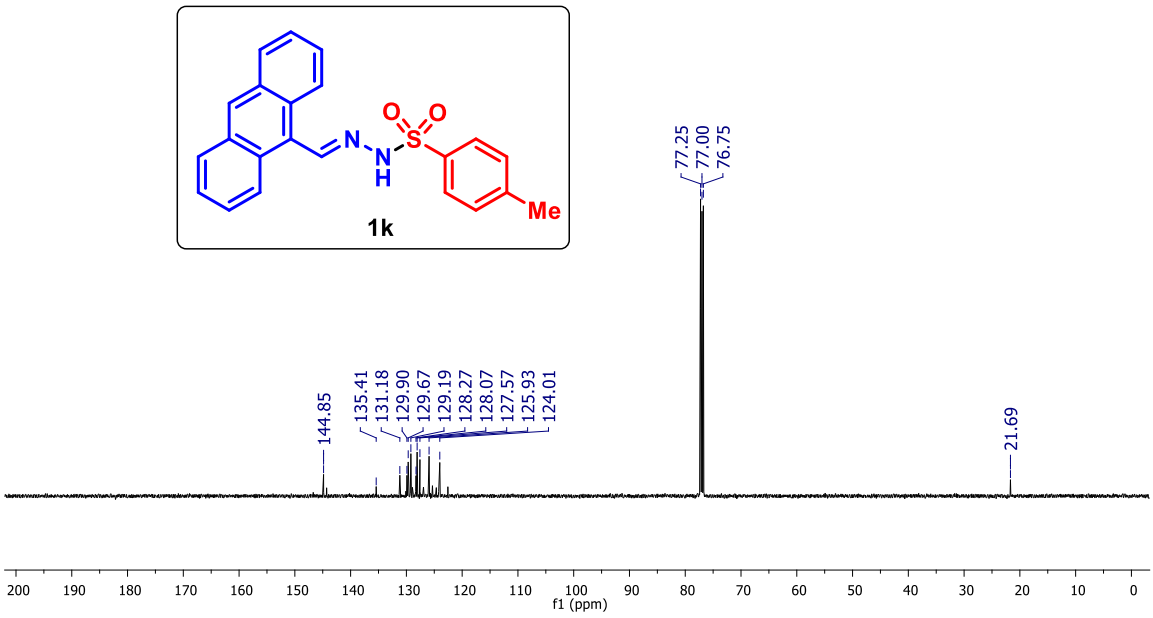


Figure S29. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of (*E*)-N'-(anthracen-9-ylmethylene)-4-methylbenzenesulfonohydrazide (**1k**).

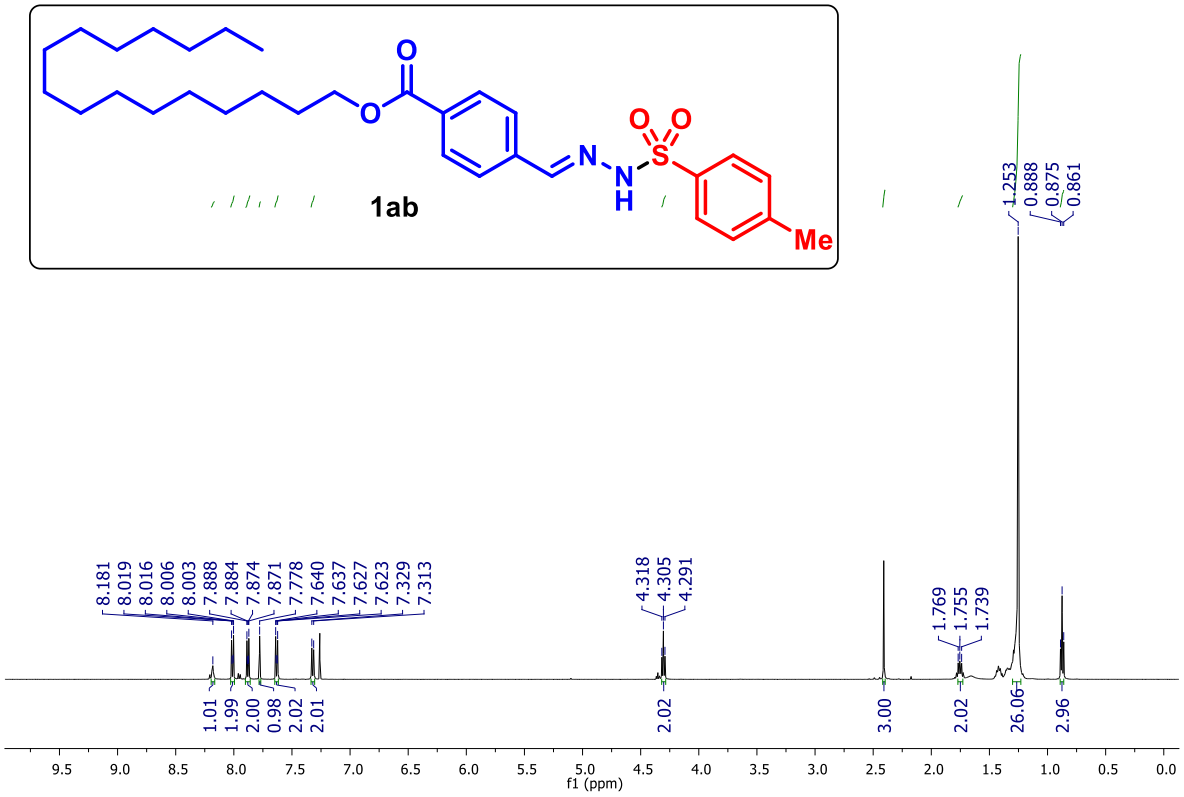


Figure S30. ^{1}H NMR spectrum ($CDCl_3$) of hexadecyl (*E*)-4-((2-tosylhydrazineylidene)methyl)benzoate (**1ab**).

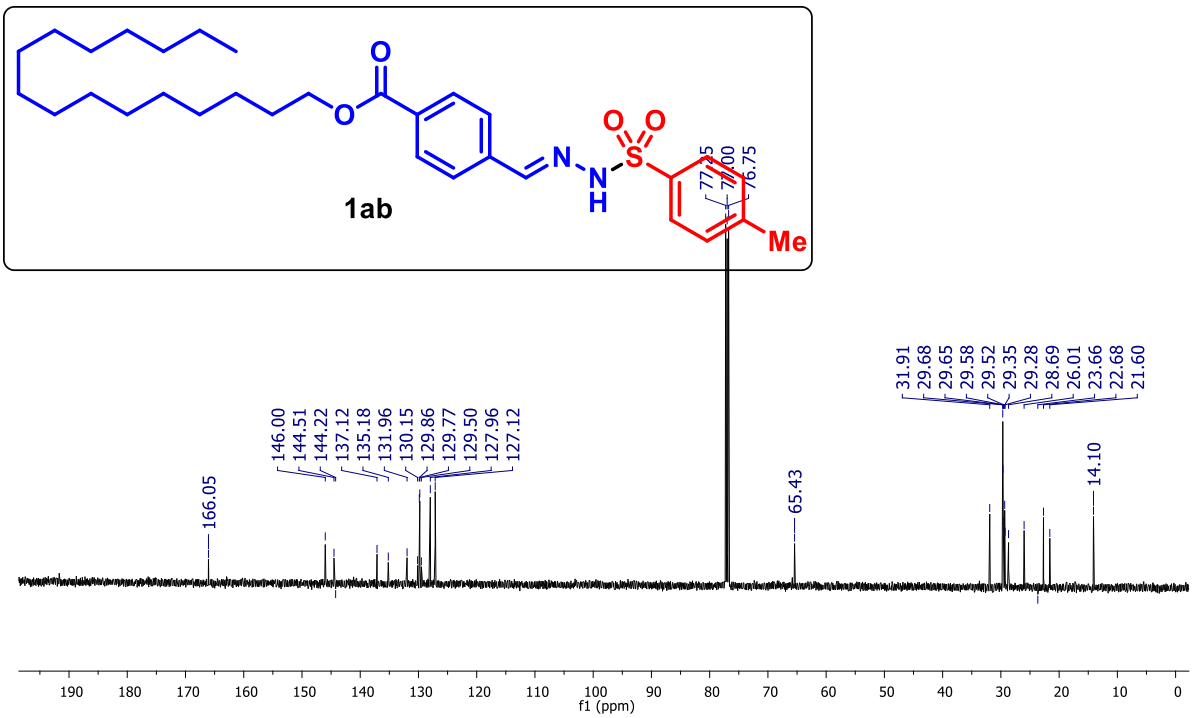


Figure S31. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of hexadecyl (*E*)-4-((2-tosylhydrazineylidene)methyl)benzoate (**1ab**).

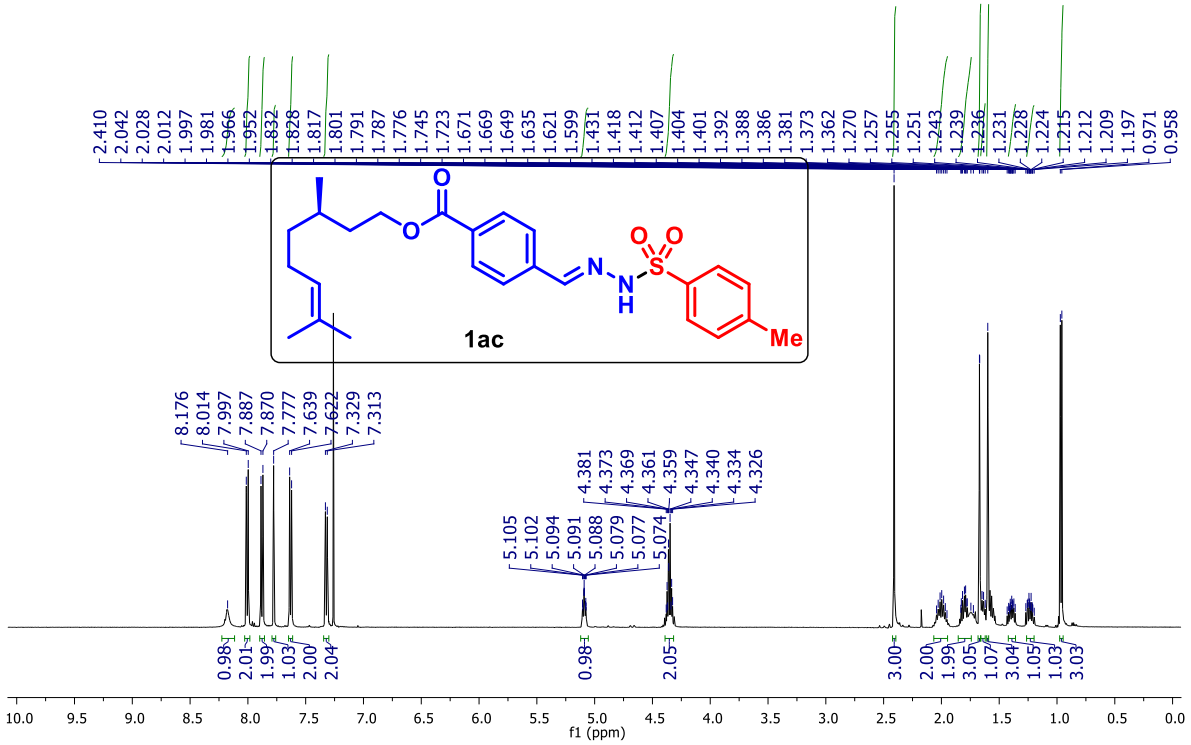


Figure S32. ^{1}H NMR spectrum ($CDCl_3$) of (R)-3,7-dimethyloct-6-en-1-yl (*E*)-4-((2-tosylhydrazineylidene)methyl)benzoate (**1ac**).

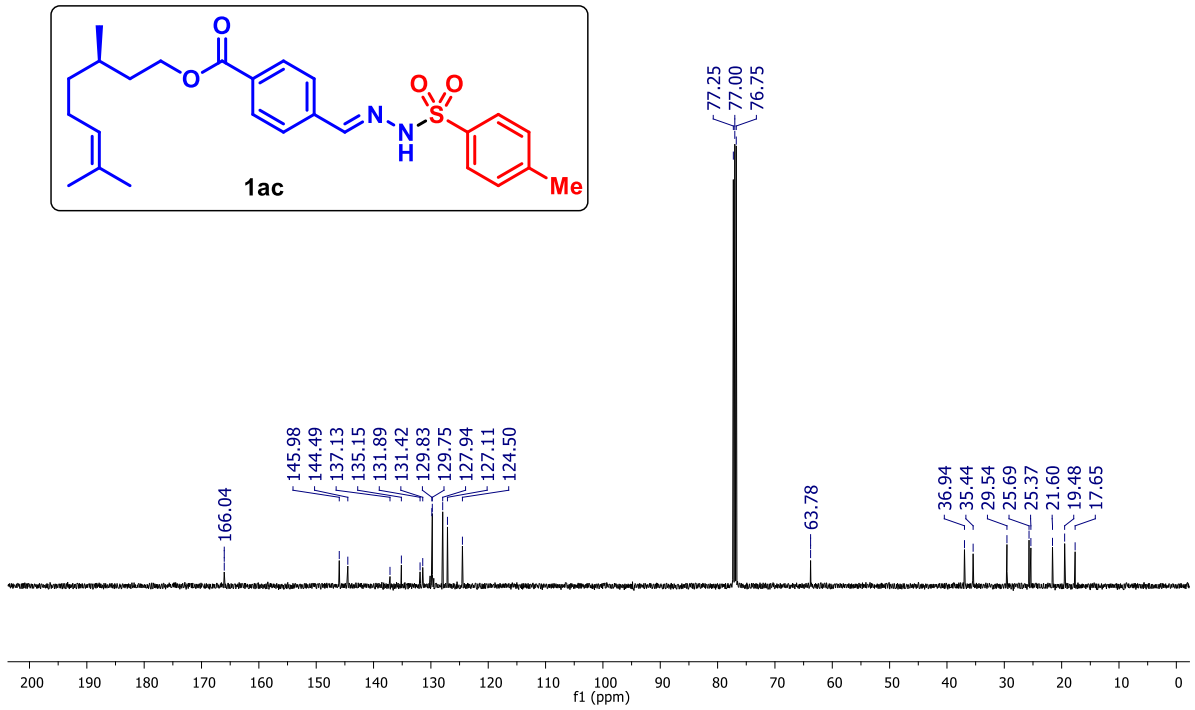


Figure S33. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of (R)-3,7-dimethyloct-6-en-1-yl (*E*)-4-((2-tosylhydrazineylidene)methyl)benzoate (**1ac**).

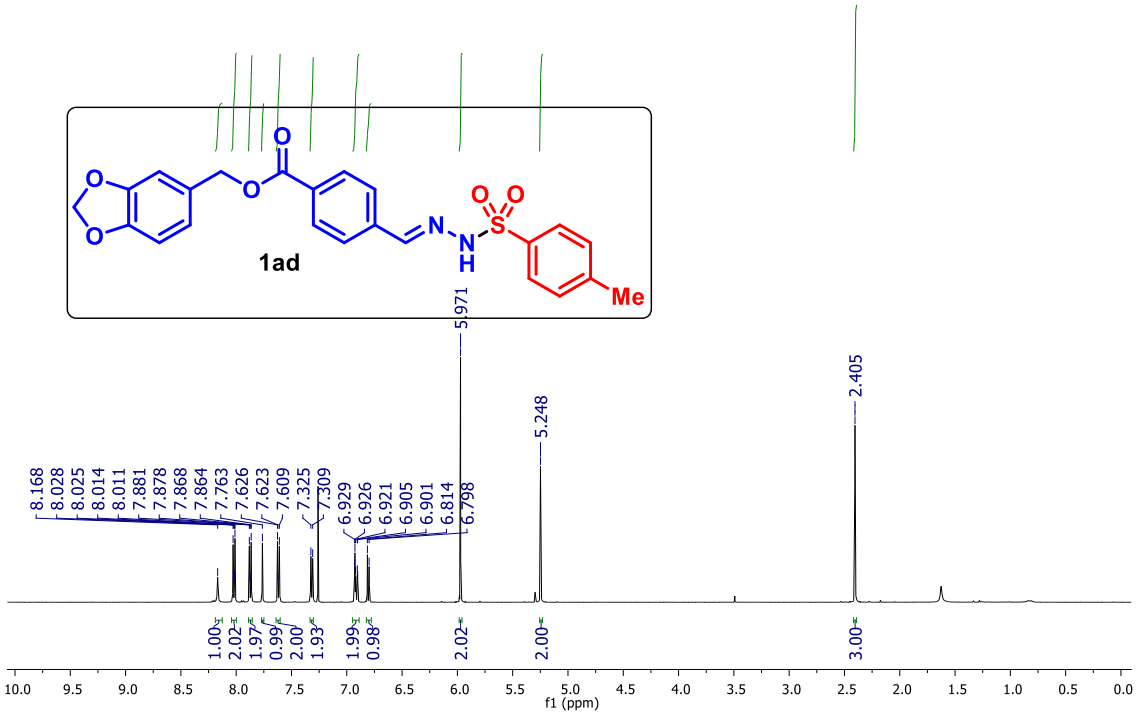


Figure S34. ^{1}H NMR spectrum ($CDCl_3$) of benzo[d][1,3]dioxol-5-ylmethyl (*E*)-4-((2-tosylhydrazineylidene)methyl)benzoate (**1ad**).

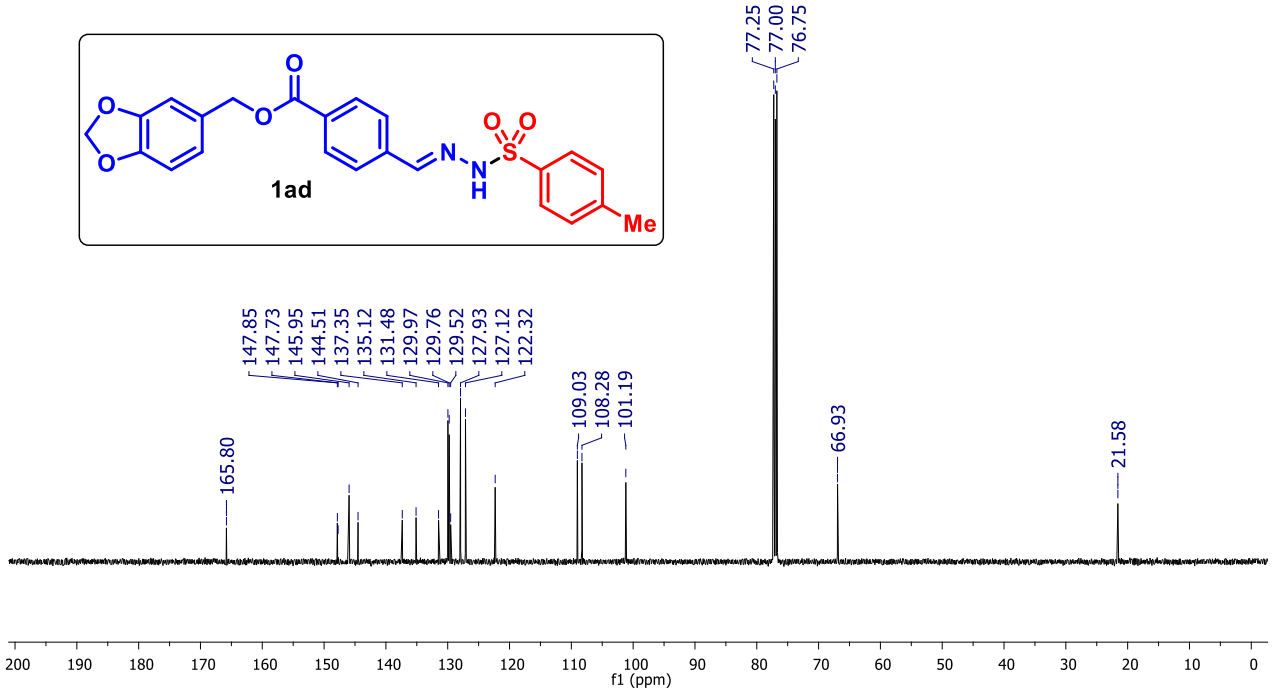


Figure S35. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of benzo[d][1,3]dioxol-5-ylmethyl (*E*)-4-((2-tosylhydrazineylidene)methyl)benzoate (**1ad**).

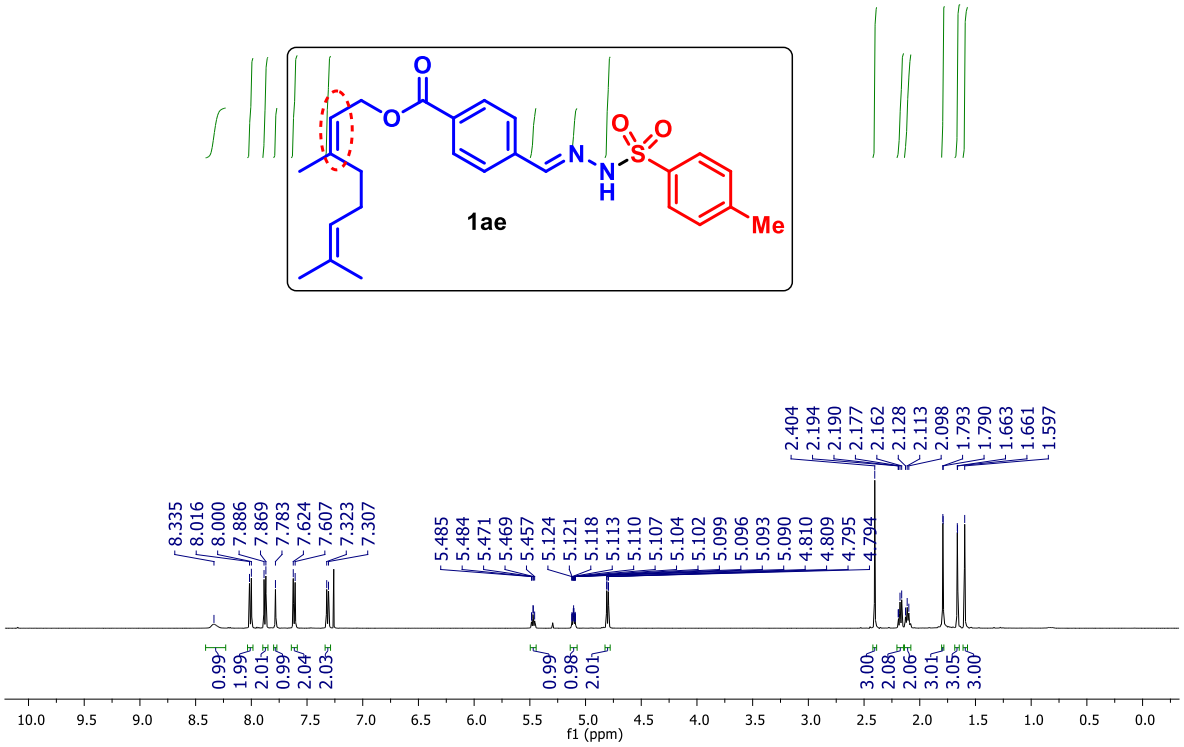


Figure S36. ^{1}H NMR spectrum ($CDCl_3$) of **(***Z***)**-3,7-dimethylocta-2,6-dien-1-yl 4-((*E*)-(2-tosylhydrazineylidene)methyl)benzoate (**1ae**).

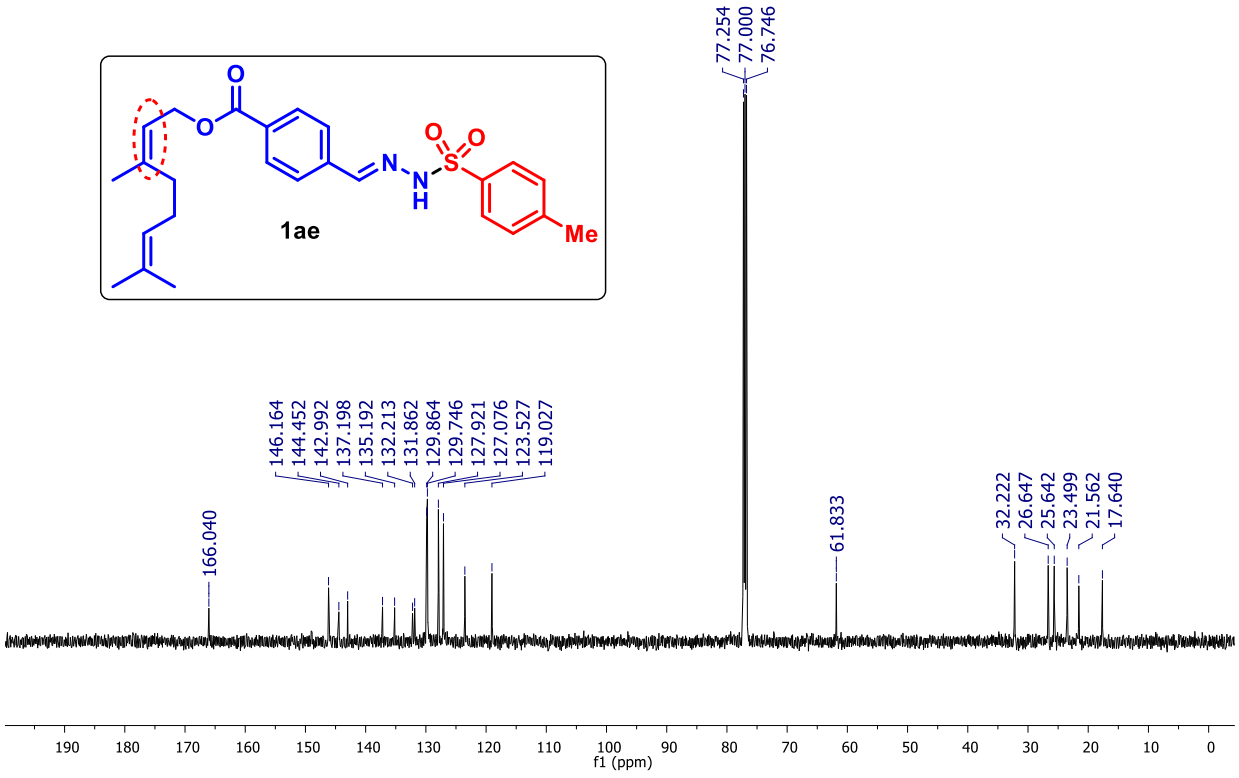


Figure S37. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of **(***Z***)**-3,7-dimethylocta-2,6-dien-1-yl 4-((*E*)-(2-tosylhydrazineylidene)methyl)benzoate (**1ae**).

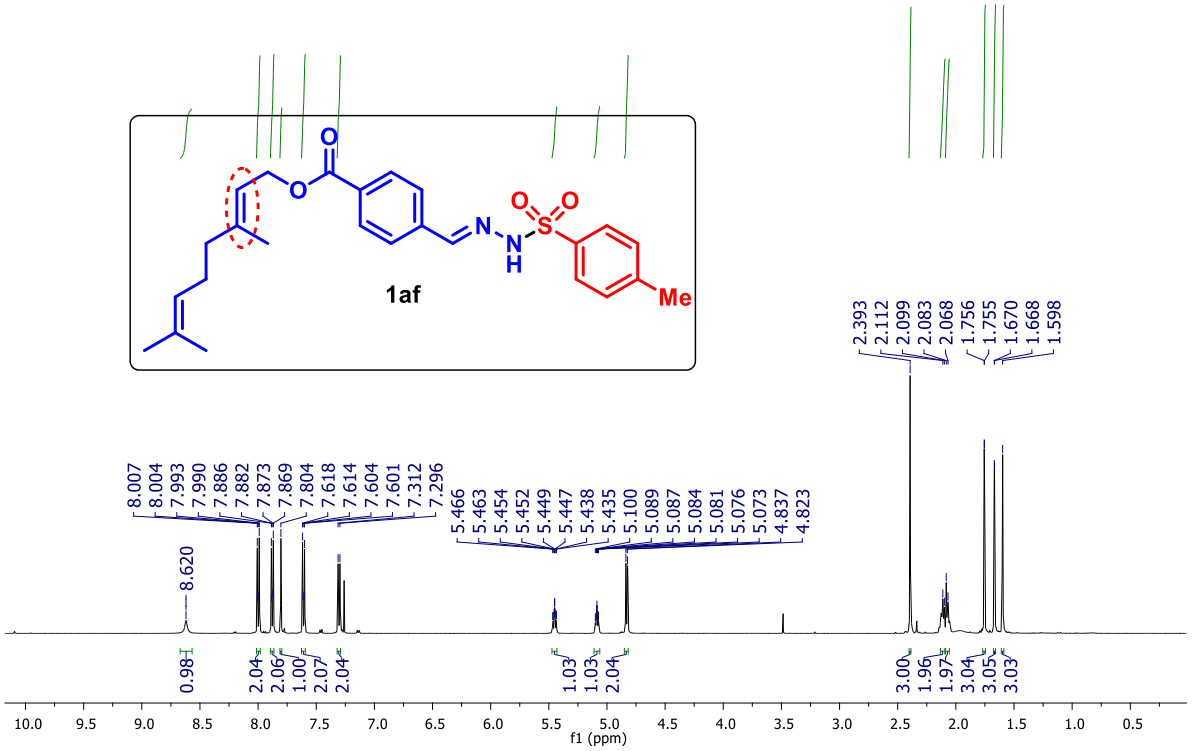


Figure S38. ^{1}H NMR spectrum ($CDCl_3$) of (*E*)-3,7-dimethylocta-2,6-dien-1-yl 4-((*E*)-(2-tosylhydrazineylidene)methyl)benzoate (**1af**).

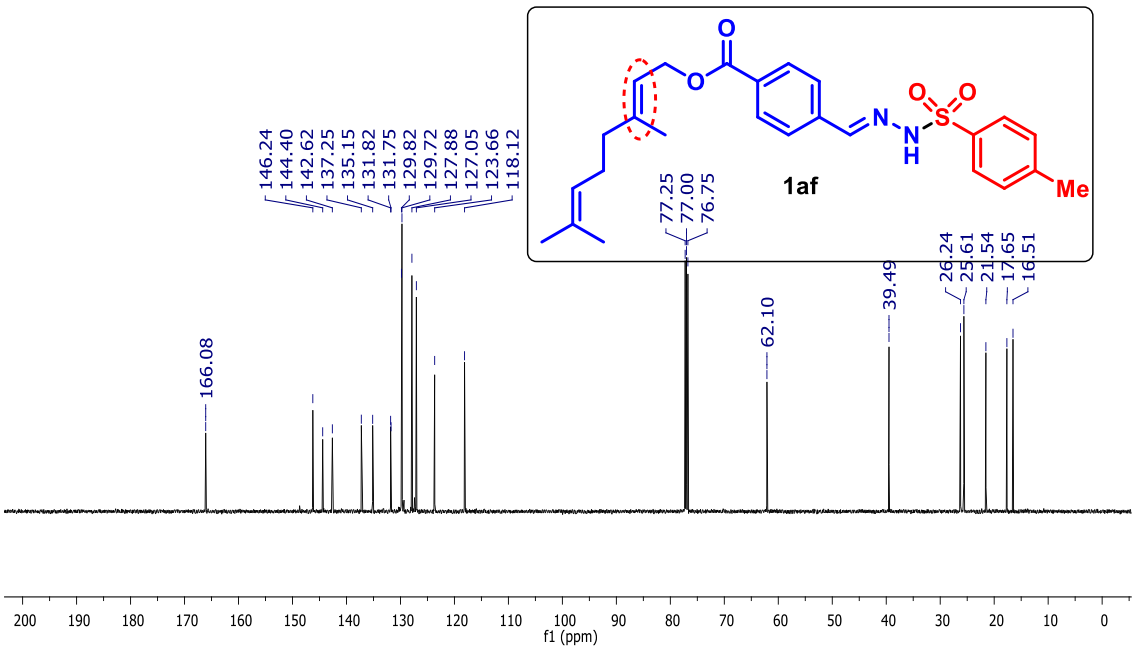


Figure S39. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of (*E*)-3,7-dimethylocta-2,6-dien-1-yl 4-((*E*)-(2-tosylhydrazineylidene)methyl)benzoate (**1af**).

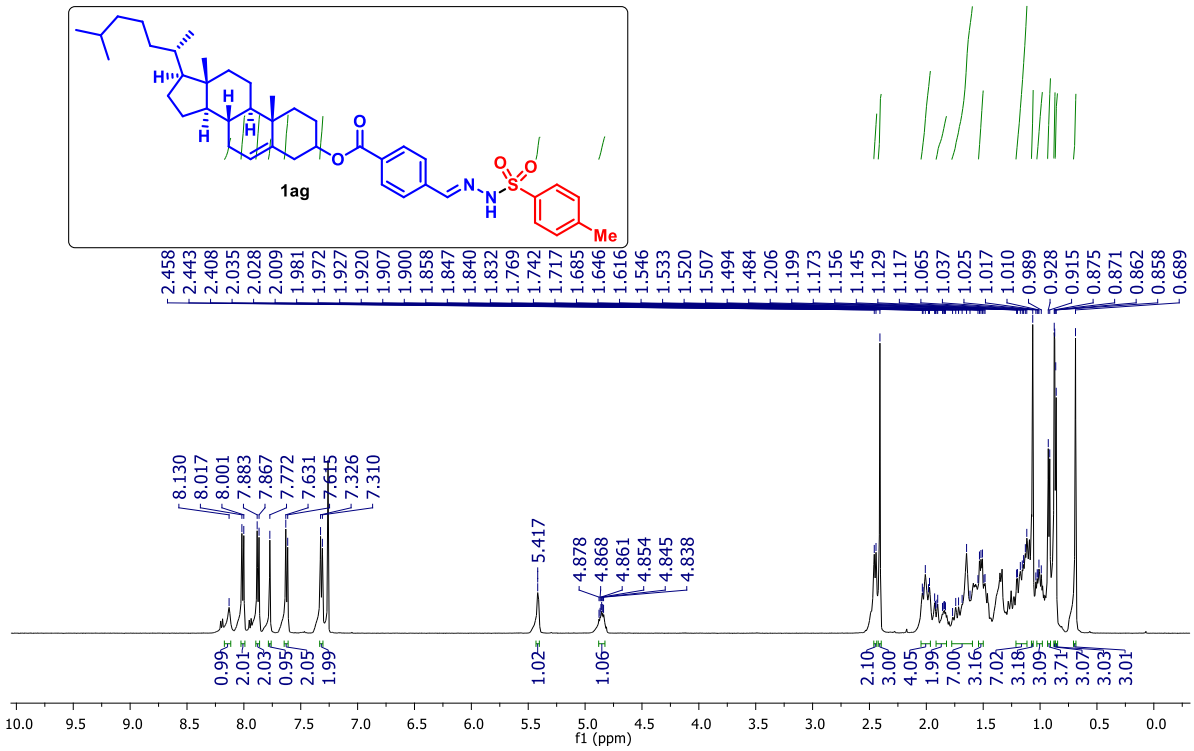


Figure S40. ^{1}H NMR spectrum ($CDCl_3$) of (8R,9R,10S,13S,14R,17S)-10,13-dimethyl-17-((S)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-((*E*)-(2-tosylhydrazineylidene)methyl)benzoate (**1ag**).

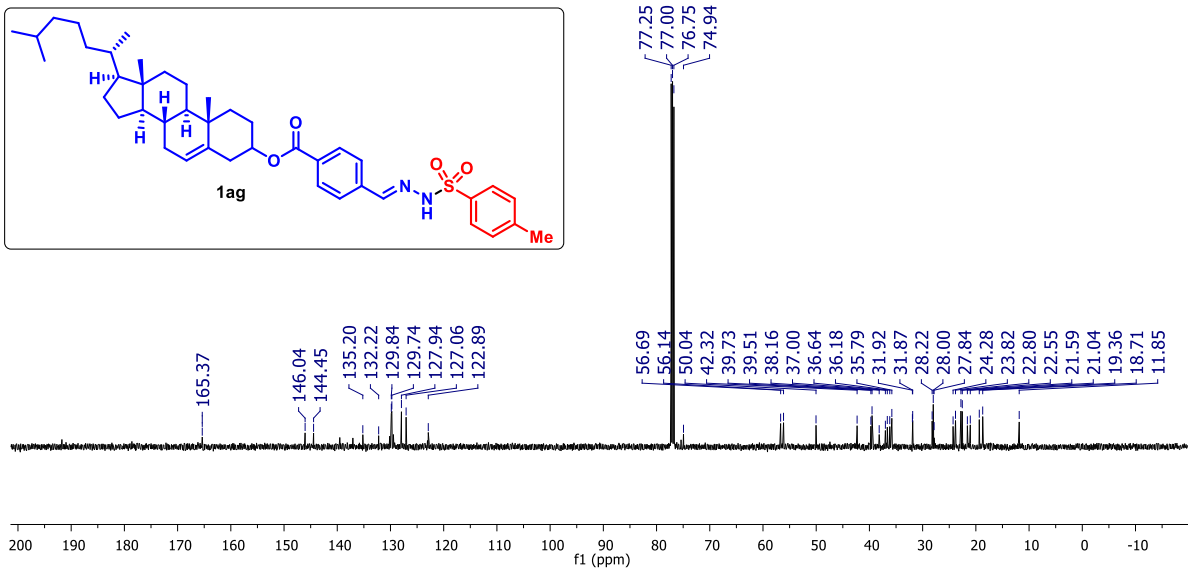


Figure S41. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of (8R,9R,10S,13S,14R,17S)-10,13-dimethyl-17-((S)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-((*E*)-(2-tosylhydrazineylidene)methyl)benzoate (**1ag**).

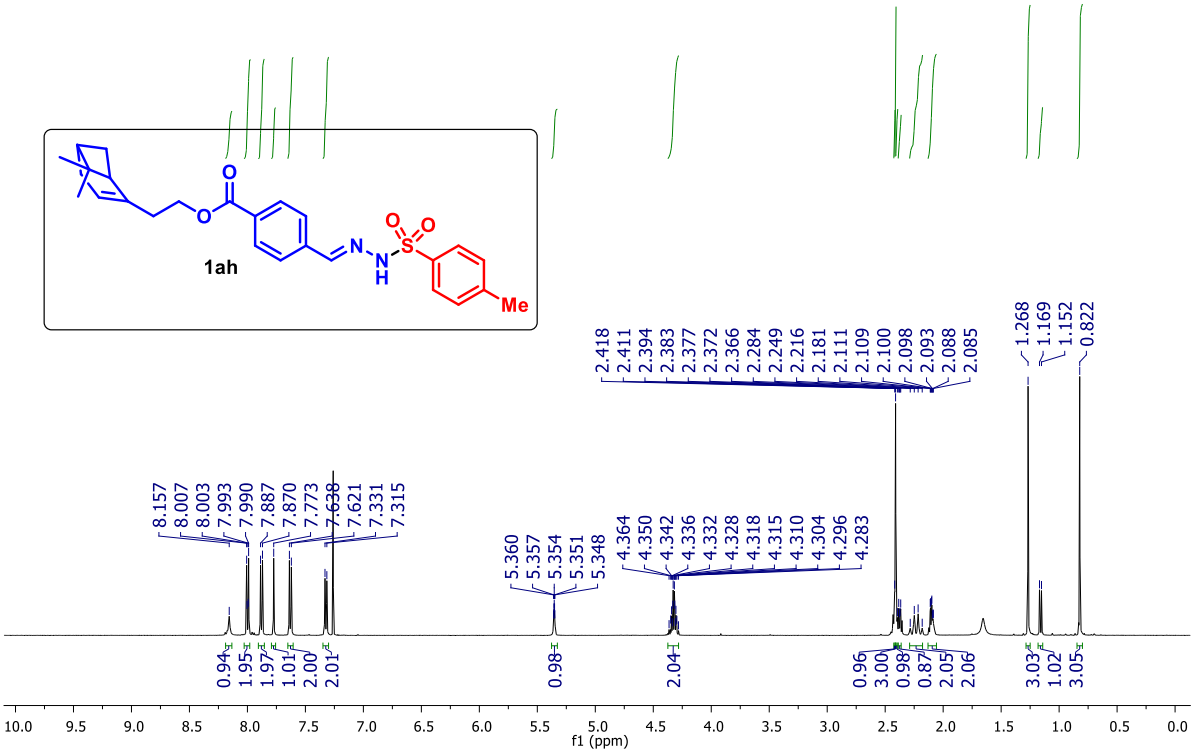


Figure S42. ^{1}H NMR spectrum ($CDCl_3$) of 2-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl(*E*)-4-((2-tosylhydrazineylidene)methyl)benzoate (**1ah**).

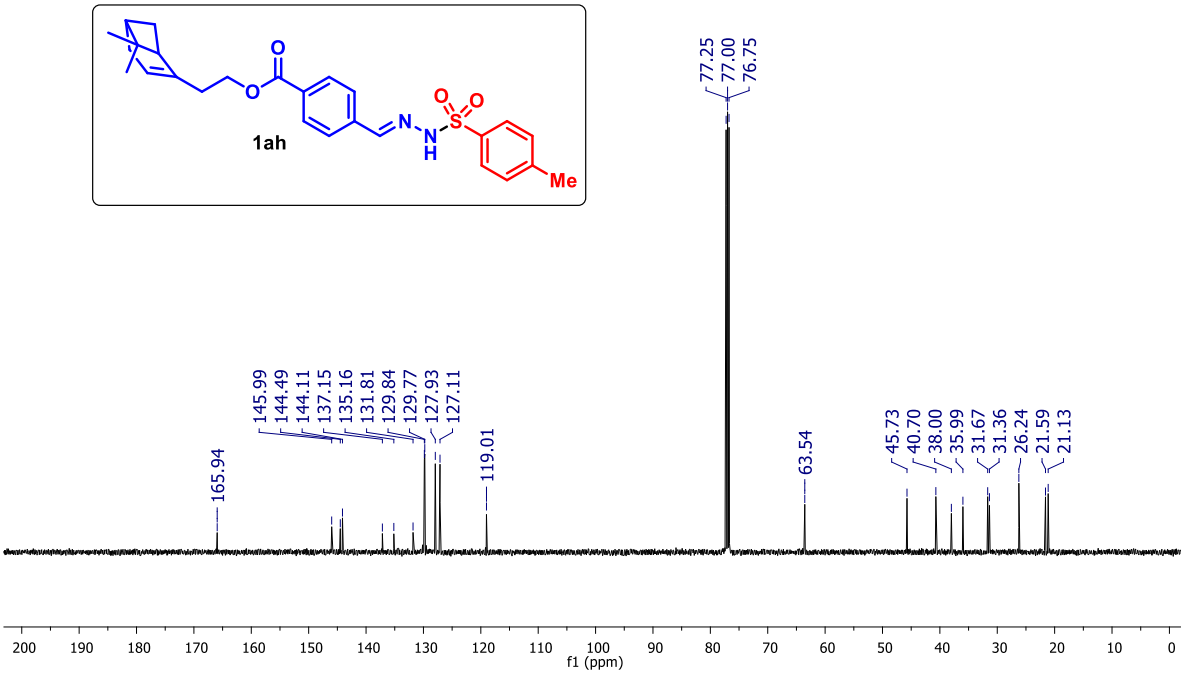


Figure S43. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 2-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl(*E*)-4-((2-tosylhydrazineylidene)methyl)benzoate (**1ah**).

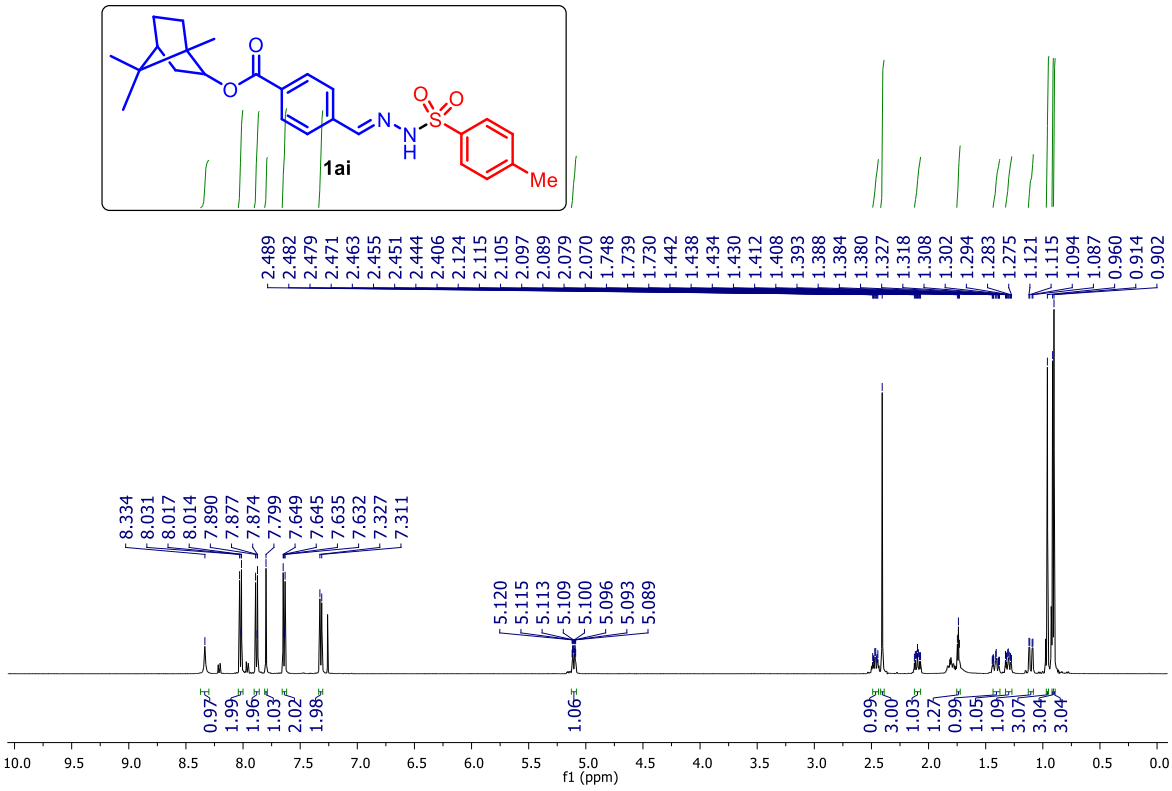


Figure S44. ^{1}H NMR spectrum ($CDCl_3$) of 1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl (*E*)-4-((2-tosylhydrazineylidene)methyl)benzoate (**1ai**).

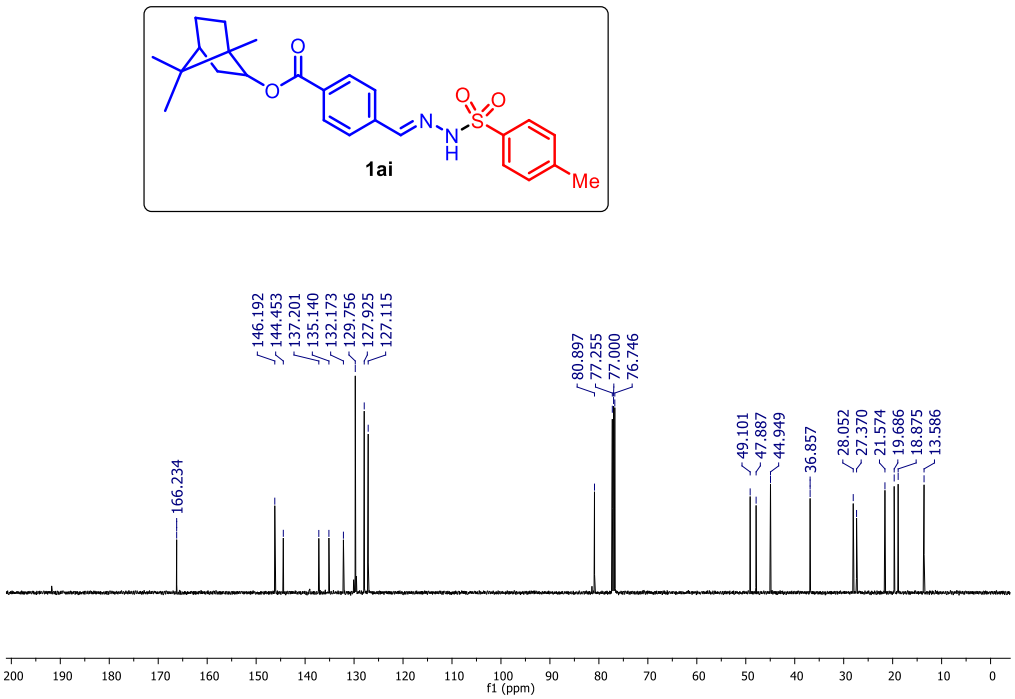


Figure S45. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl (*E*)-4-((2-tosylhydrazineylidene)methyl)benzoate (**1ai**).

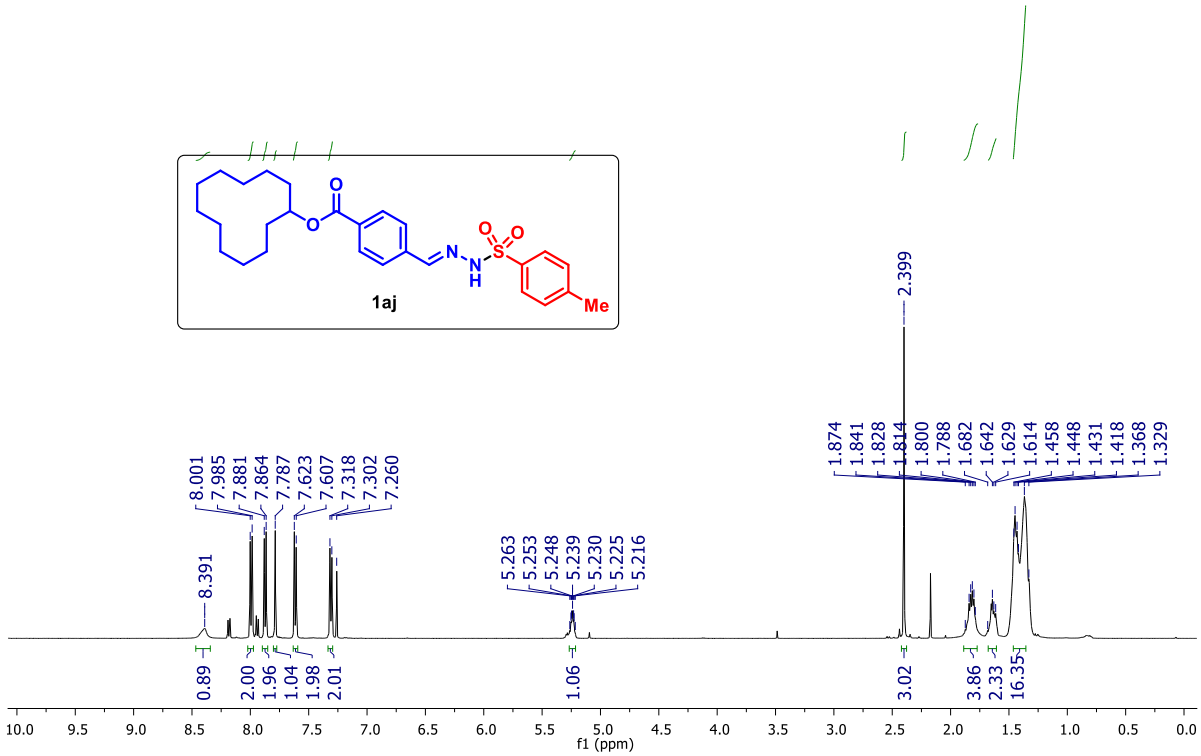


Figure S46. ^{1}H NMR spectrum ($CDCl_3$) of cyclododecyl (*E*)-4-((2-tosylhydrazineylidene)methyl)benzoate (**1aj**).

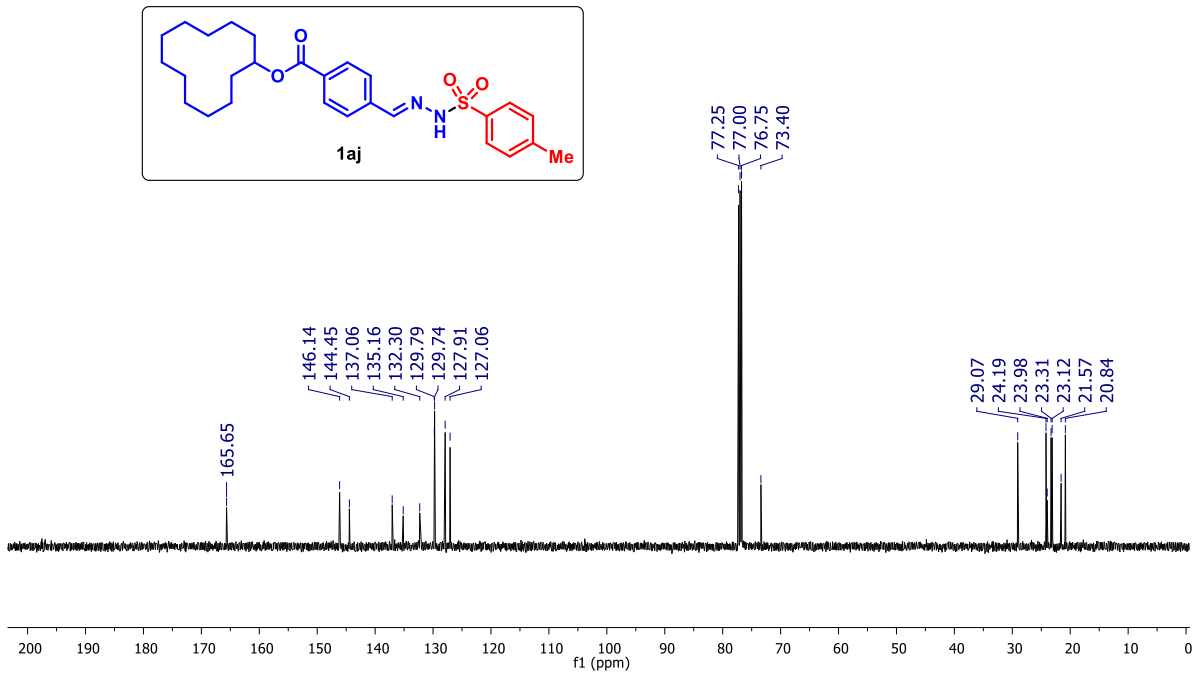


Figure S47. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of cyclododecyl (*E*)-4-((2-tosylhydrazineylidene)methyl)benzoate (**1aj**).

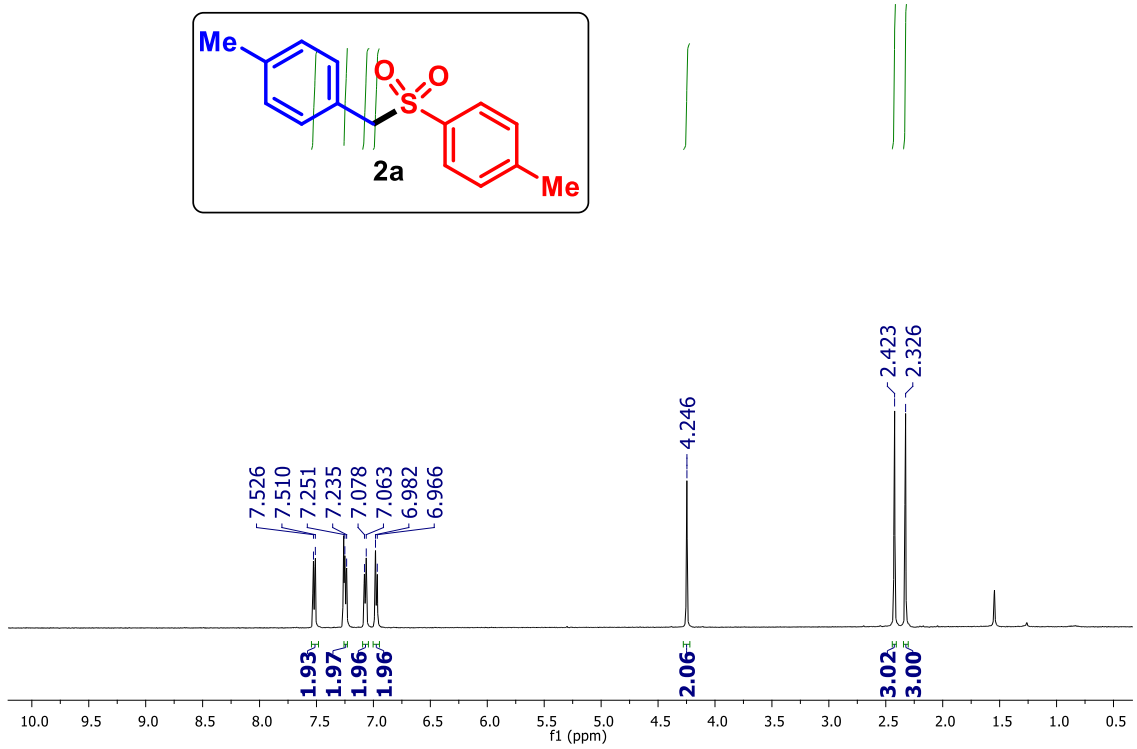


Figure S48. ^{1}H NMR spectrum ($CDCl_3$) of 1-methyl-4-((4-methylbenzyl)sulfonyl)benzene (**2a**).[6]

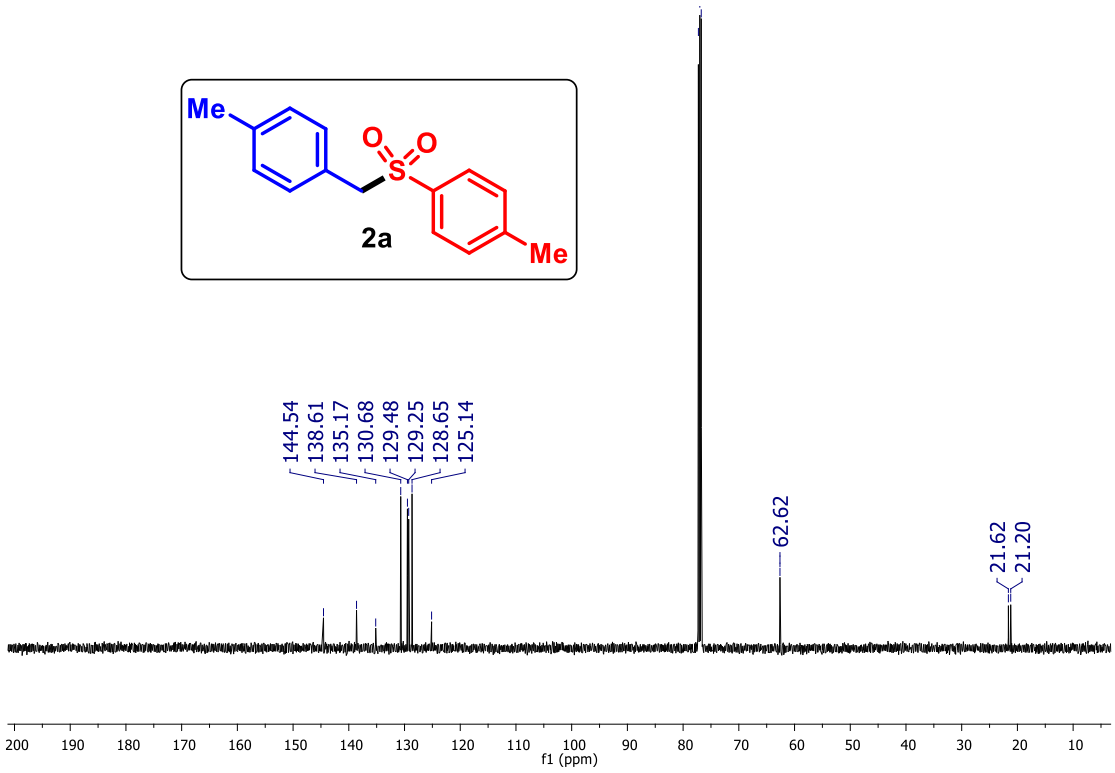


Figure S49. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1-methyl-4-((4-methylbenzyl)sulfonyl)benzene (**2a**). [6]

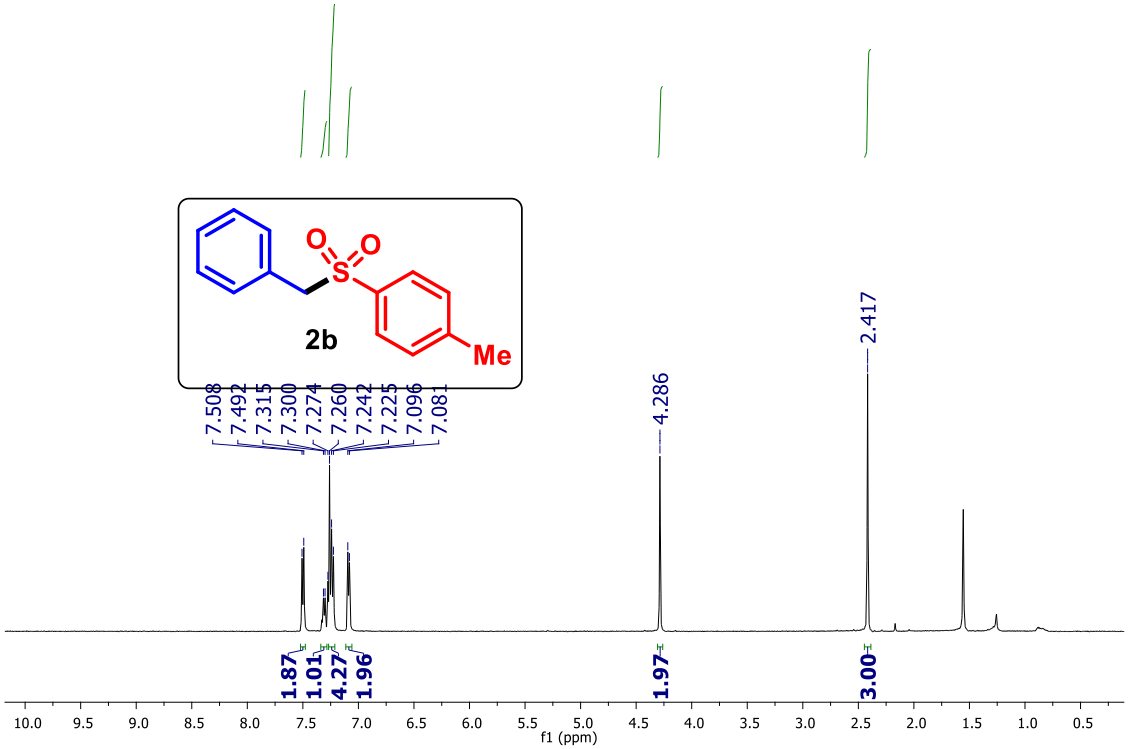


Figure S50. ^{1}H NMR spectrum ($CDCl_3$) of 1-(benzylsulfonyl)-4-methylbenzene (**2b**). [6]

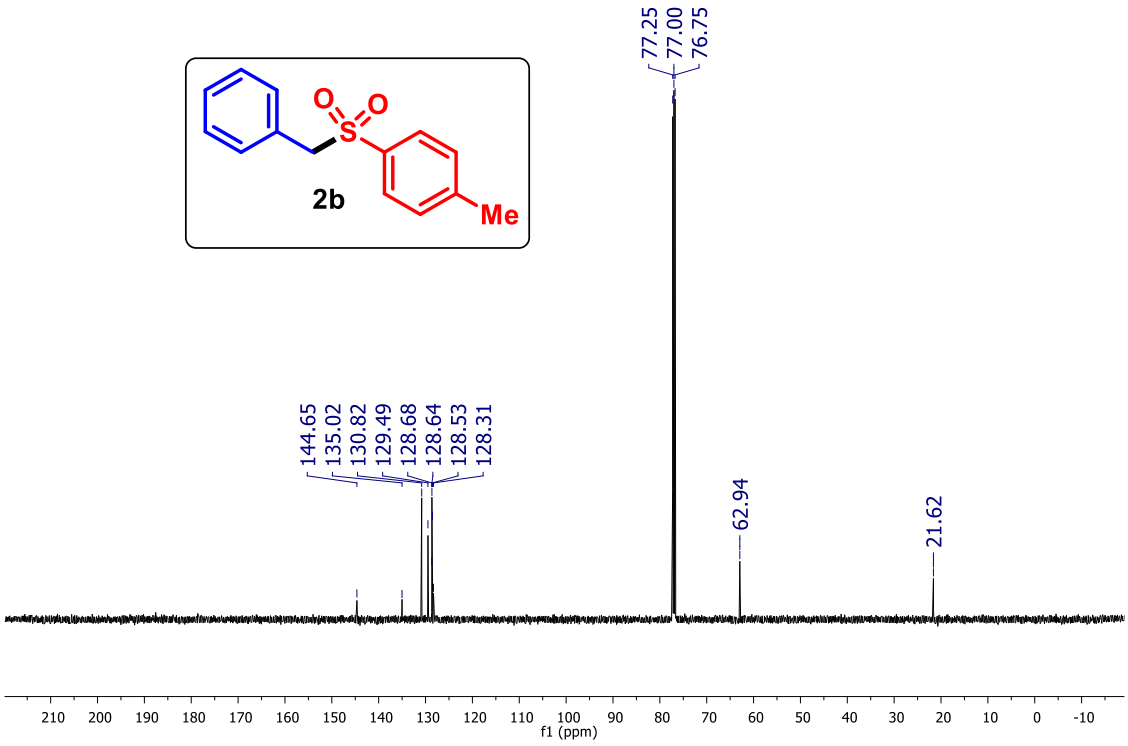


Figure S51. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1-(benzylsulfonyl)-4-methylbenzene (**2b**). [6]

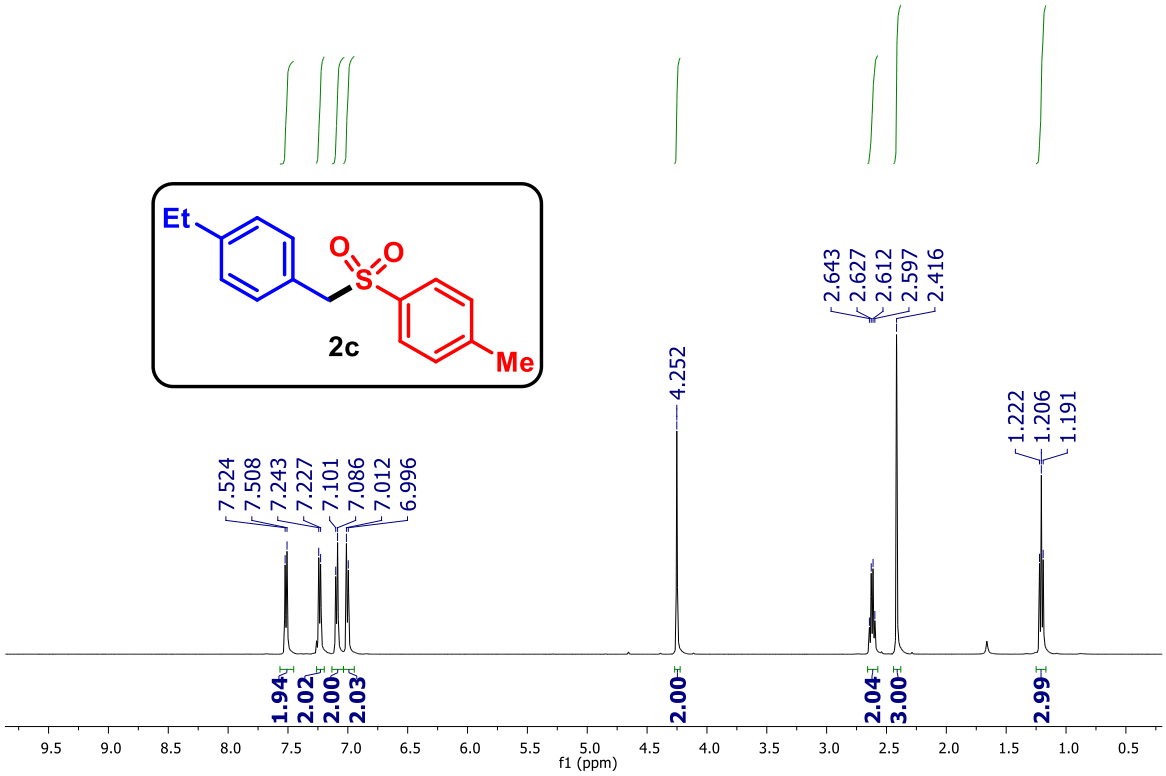


Figure S52. ^{1}H NMR spectrum ($CDCl_3$) of 1-ethyl-4-(tosylmethyl)benzene (**2c**).

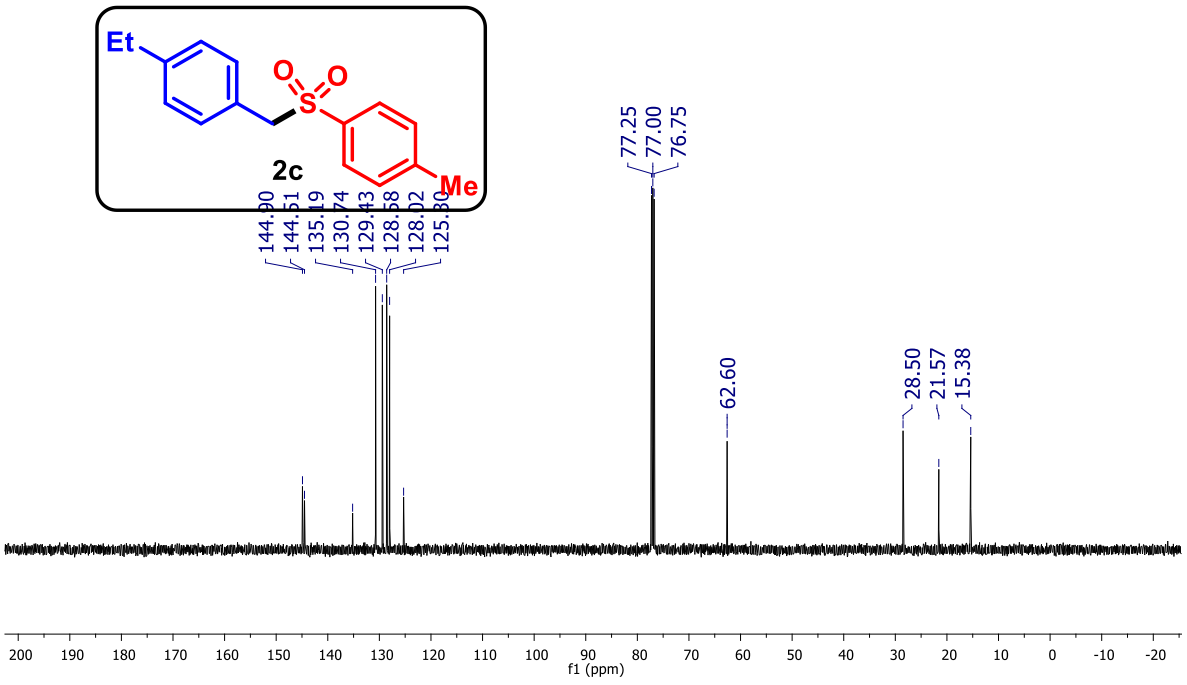


Figure S53. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1-ethyl-4-(tosylmethyl)benzene (**2c**).

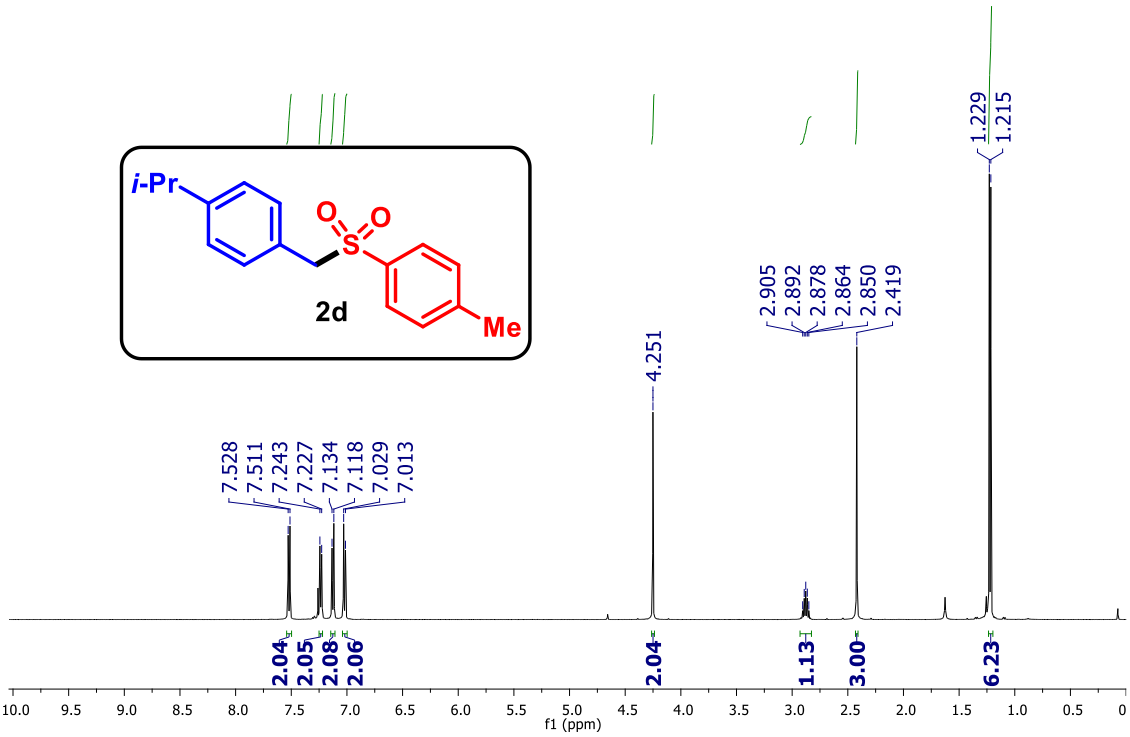


Figure S54. ^{1}H NMR spectrum ($CDCl_3$) of 1-isopropyl-4-(tosylmethyl)benzene (**2d**).

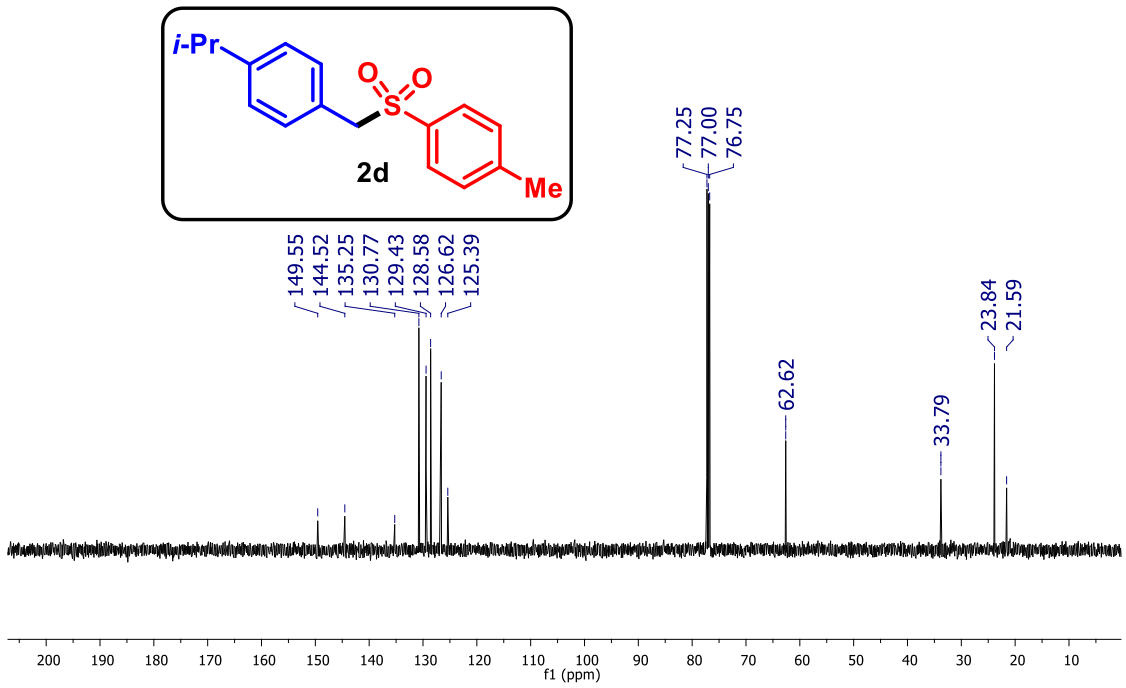


Figure S55. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1-isopropyl-4-(tosylmethyl)benzene (**2d**).

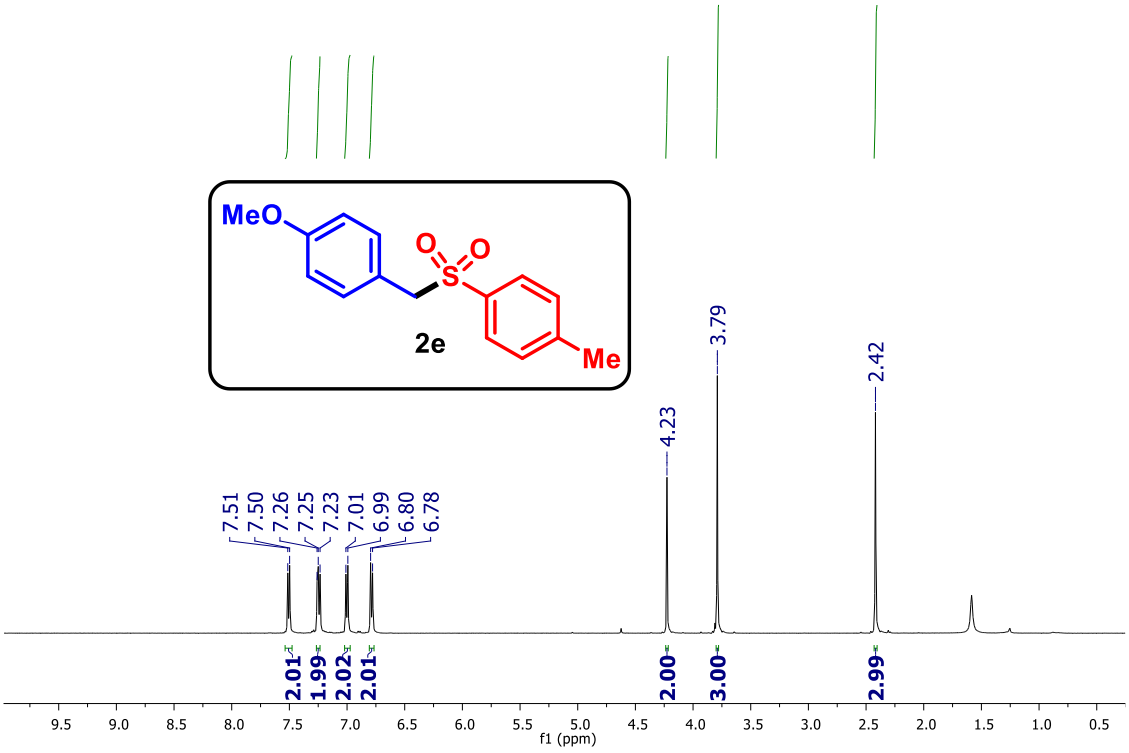


Figure S56. ^{1}H NMR spectrum ($CDCl_3$) of 1-methoxy-4-(tosylmethyl)benzene (**2e**). [6]

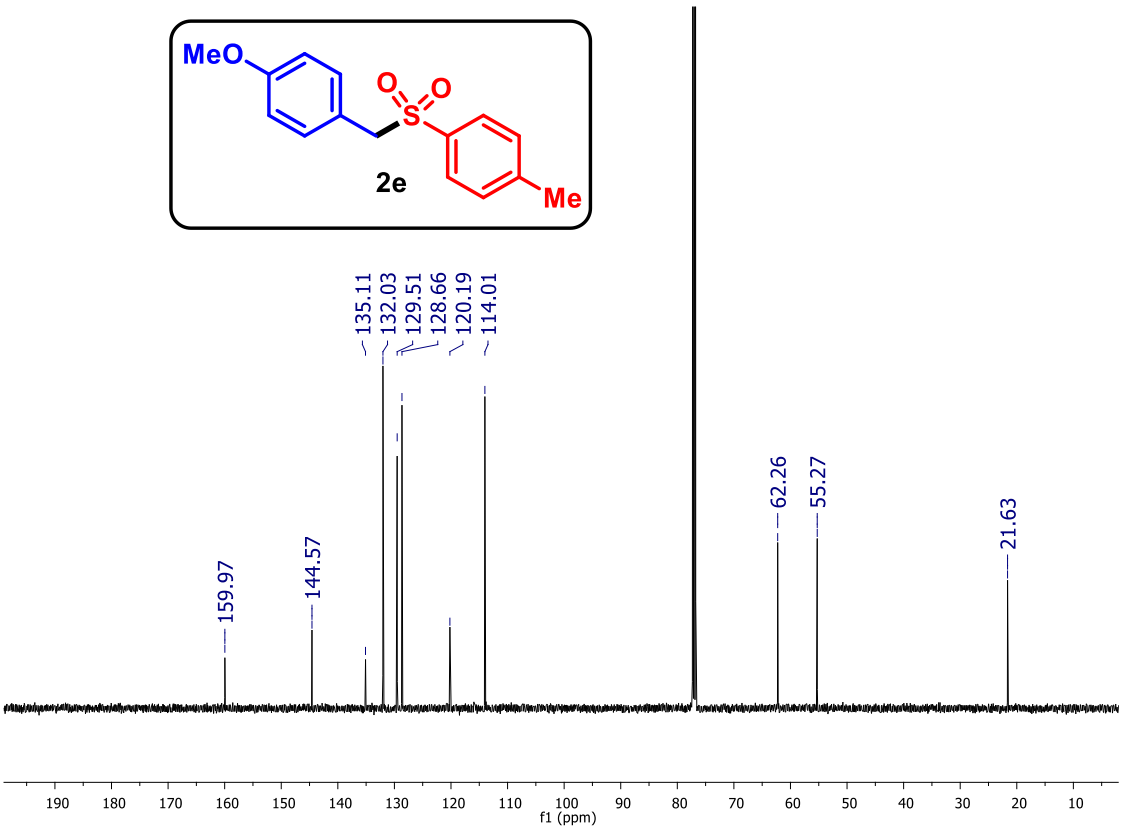


Figure S57. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1-methoxy-4-(tosylmethyl)benzene (**2e**). [6]

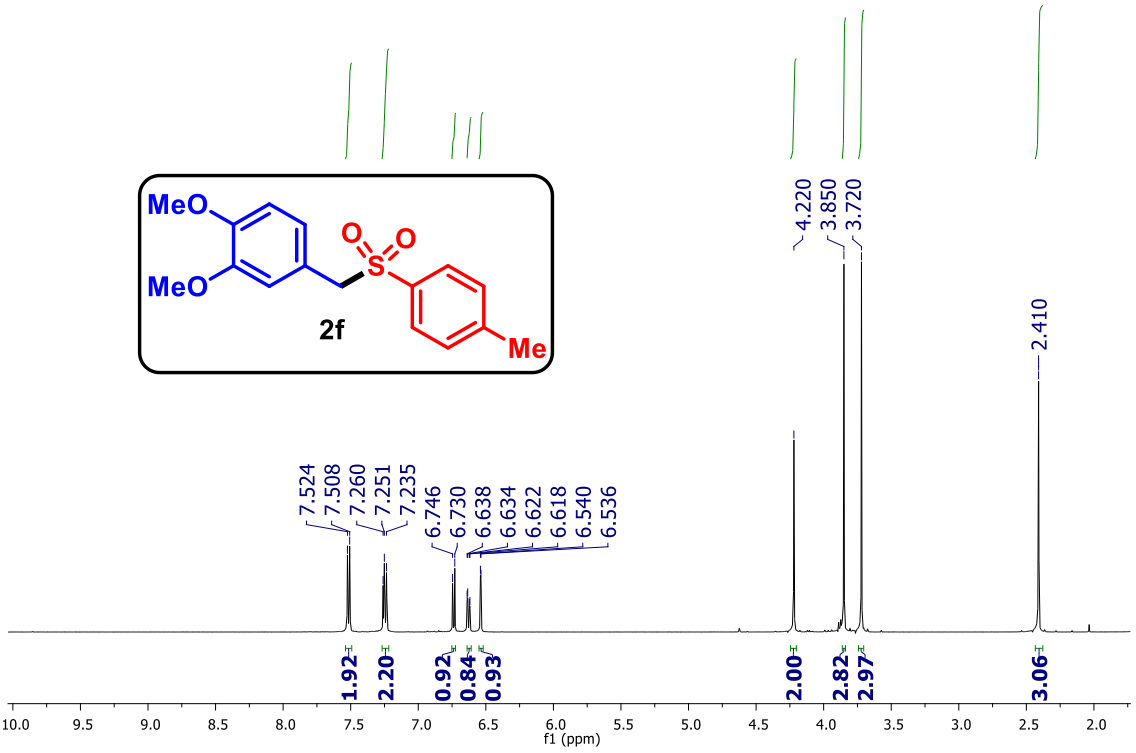


Figure S58. ^{1}H NMR spectrum ($CDCl_3$) of 1,2-dimethoxy-4-(tosylmethyl)benzene (**2f**). [6]

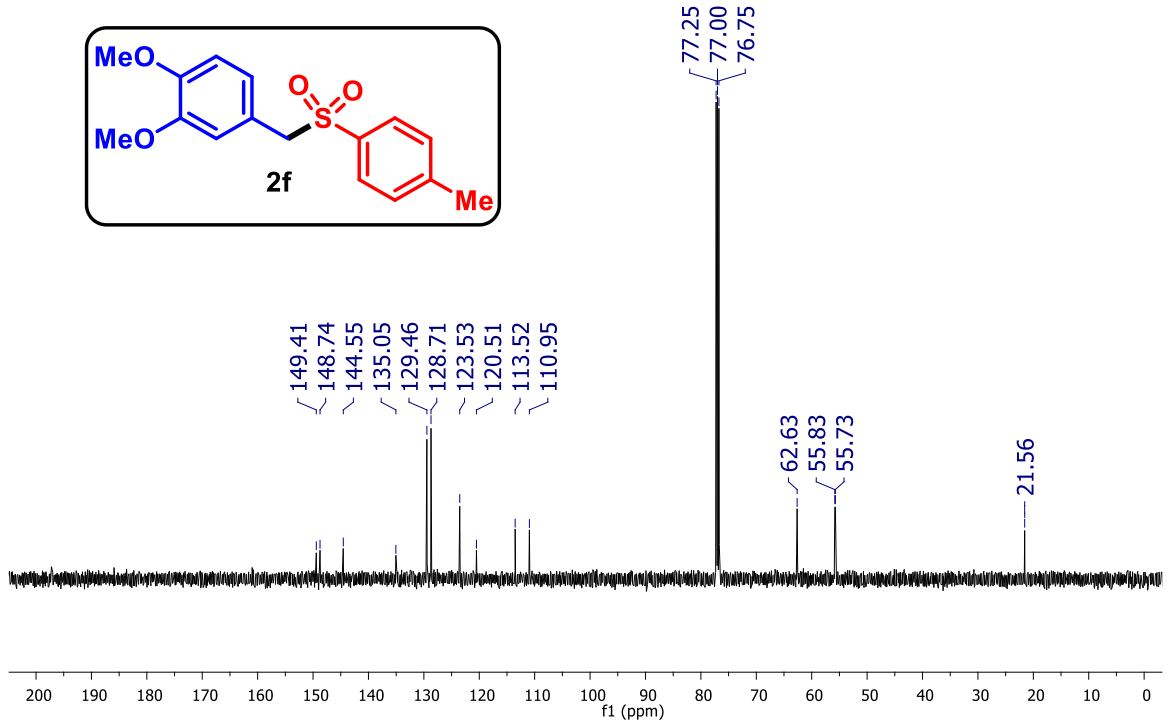


Figure S59. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1,2-dimethoxy-4-(tosylmethyl)benzene (**2f**). [6]

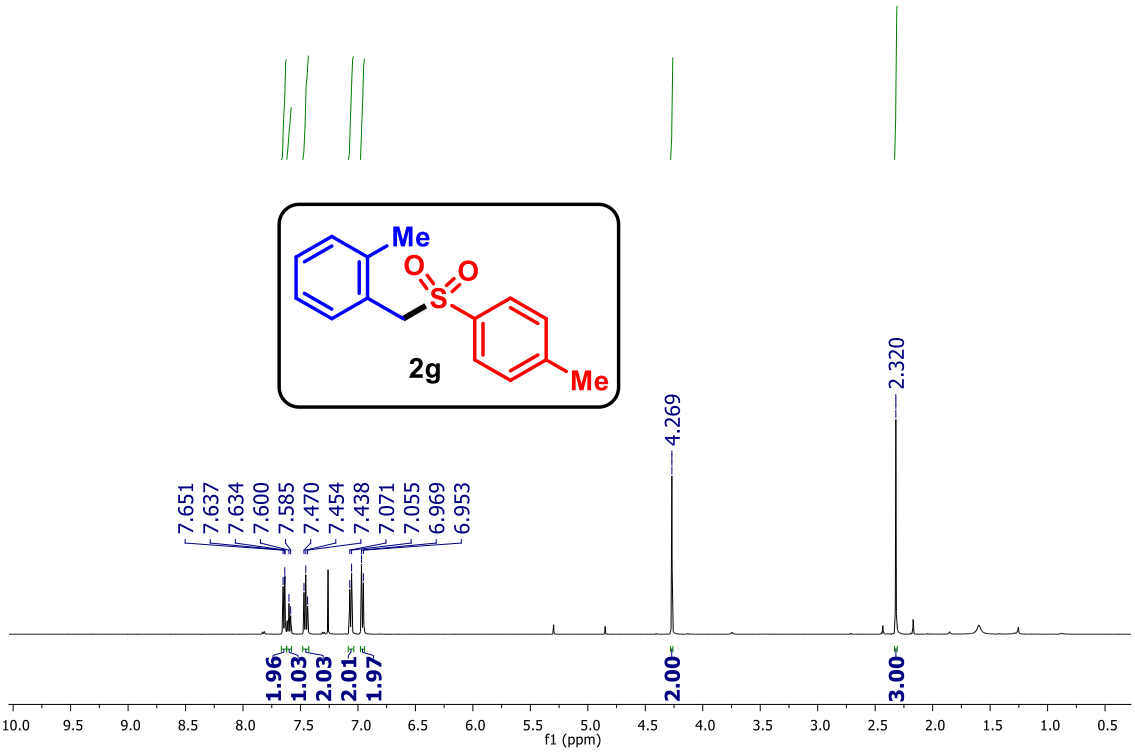


Figure S60. ^{1}H NMR spectrum ($CDCl_3$) of 1-methoxy-4-(tosylmethyl)benzene (**2g**). [6]

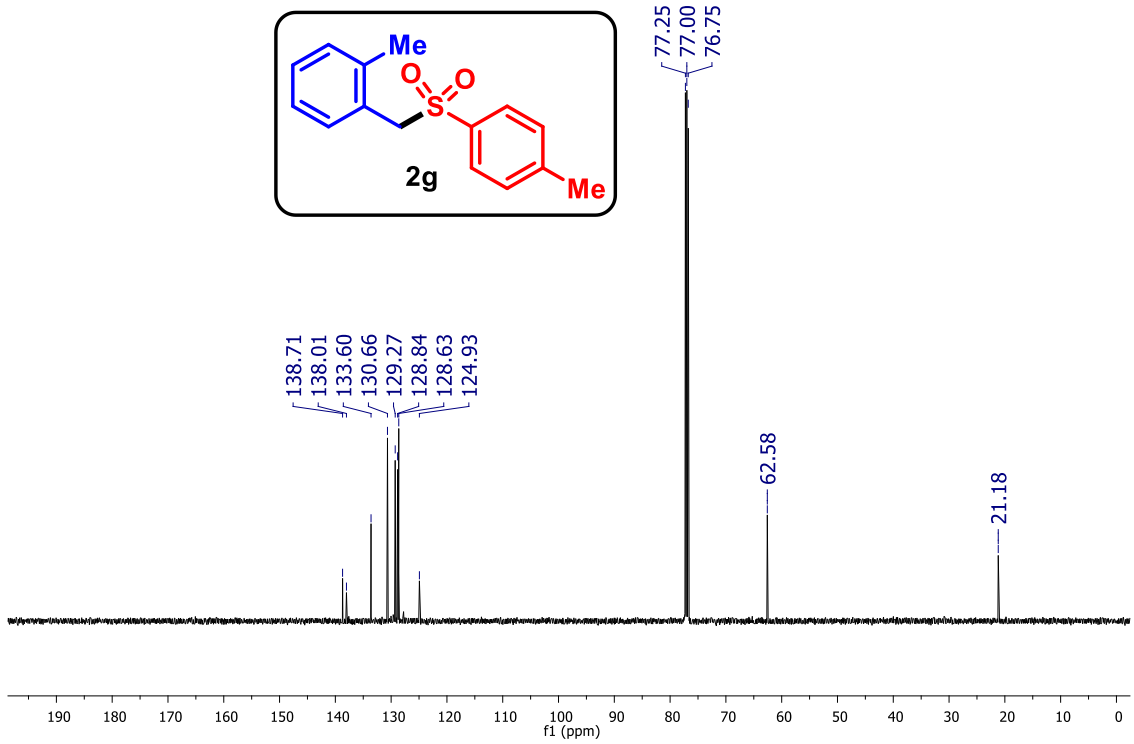


Figure S61. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1-methoxy-4-(tosylmethyl)benzene (**2g**). [6]

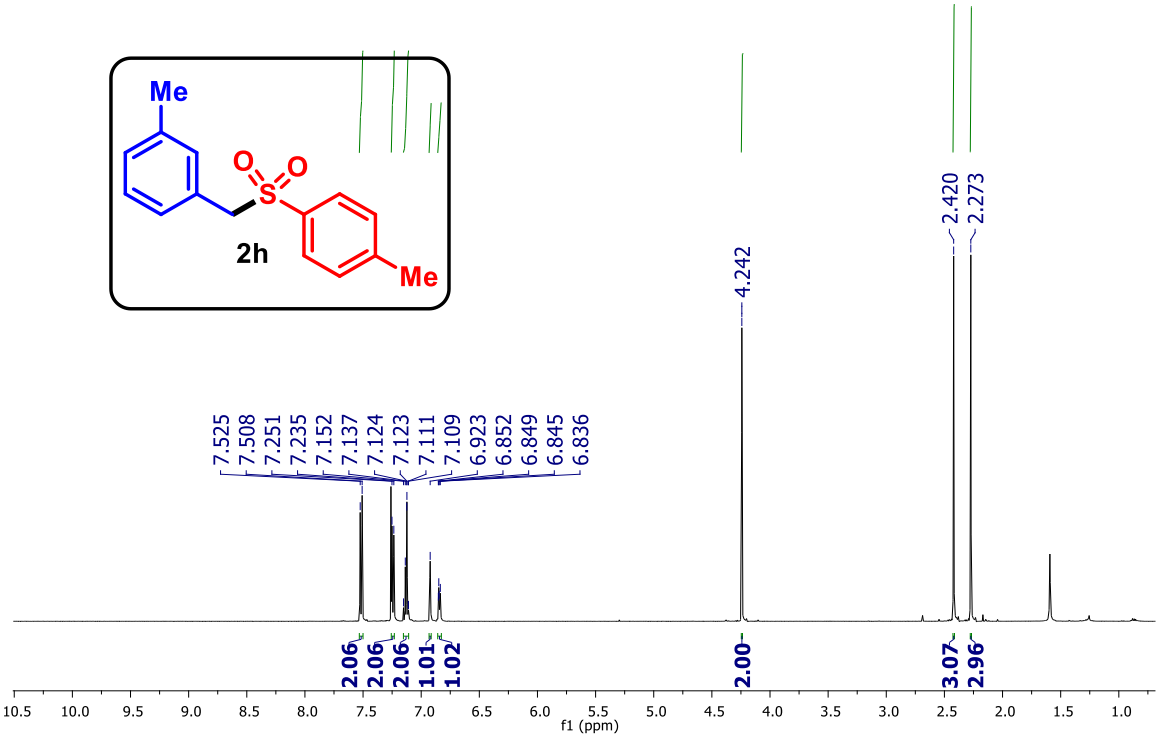


Figure S62. ^{1}H NMR spectrum ($CDCl_3$) of 1-methoxy-4-(tosylmethyl)benzene (**2h**). [6]

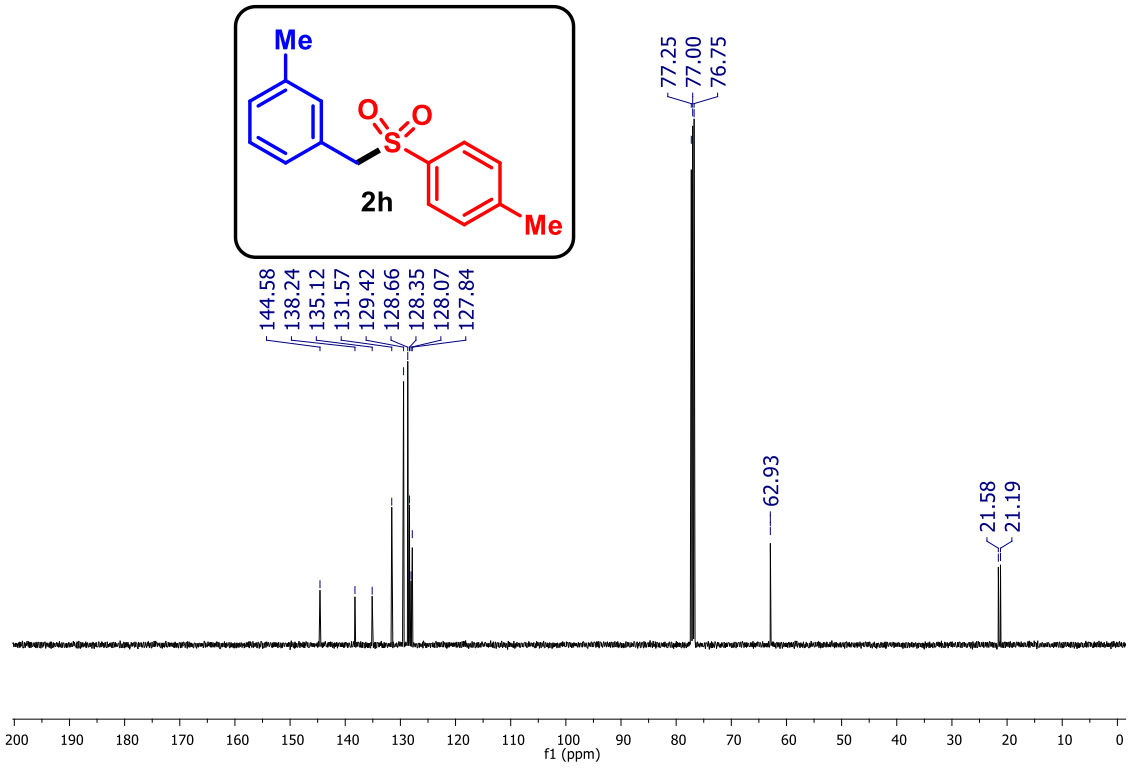


Figure S63. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1-methoxy-4-(tosylmethyl)benzene (**2h**). [6]

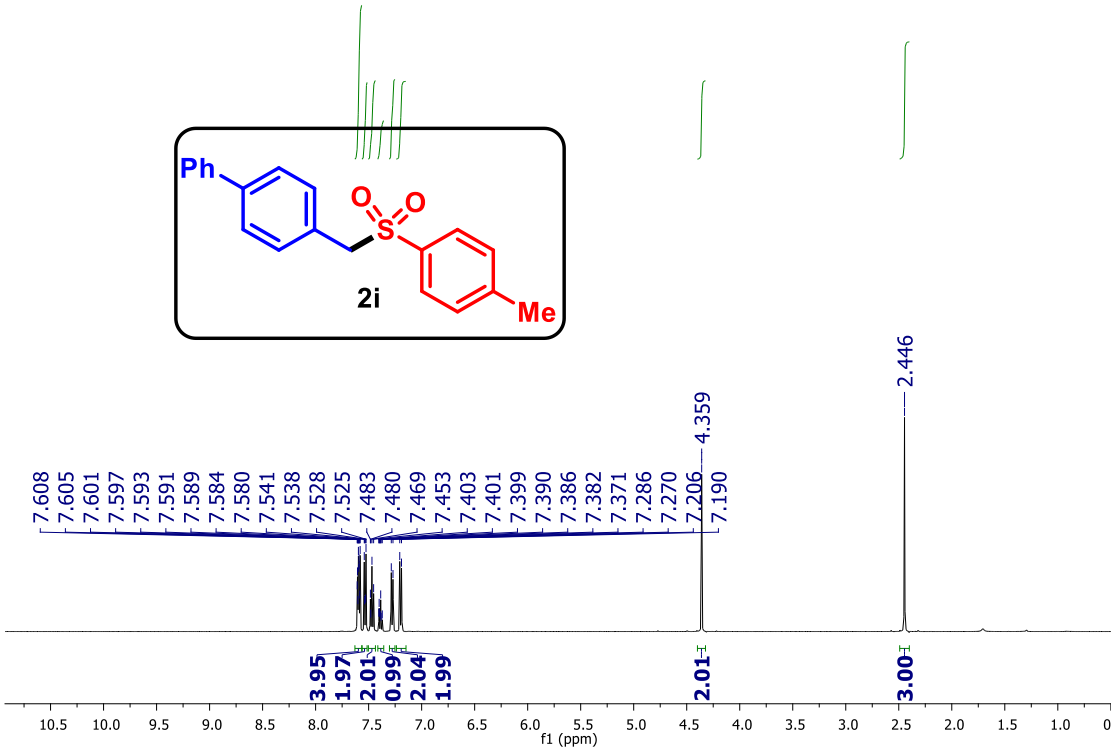


Figure S64. ^{1}H NMR spectrum ($CDCl_3$) of 4-(tosylmethyl)-1,1'-biphenyl (**2i**). [6]

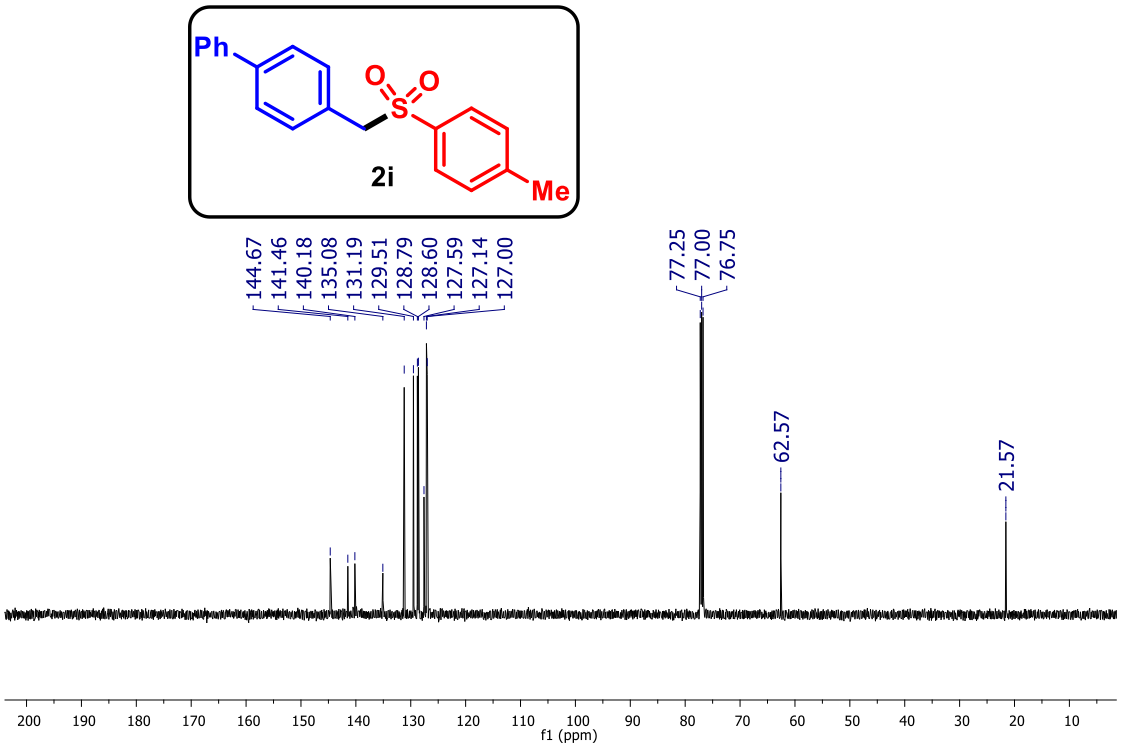


Figure S65. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 4-(tosylmethyl)-1,1'-biphenyl (**2i**). [6]

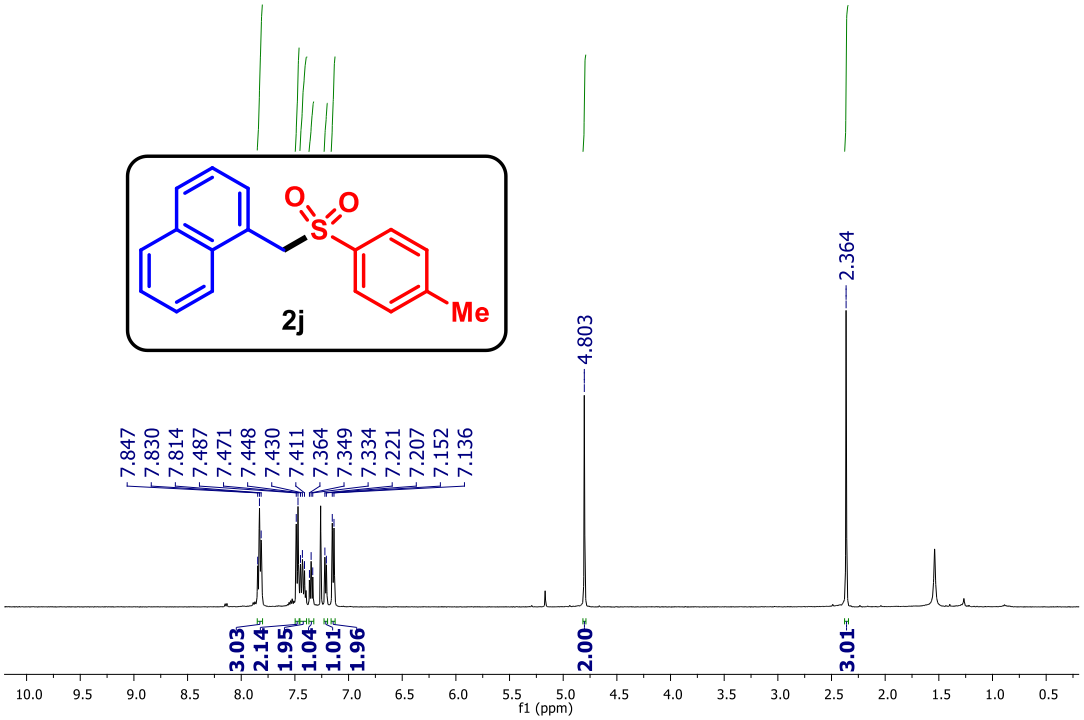


Figure S66. ^{1}H NMR spectrum ($CDCl_3$) of 1-(tosylmethyl)naphthalene (**2j**). [6]

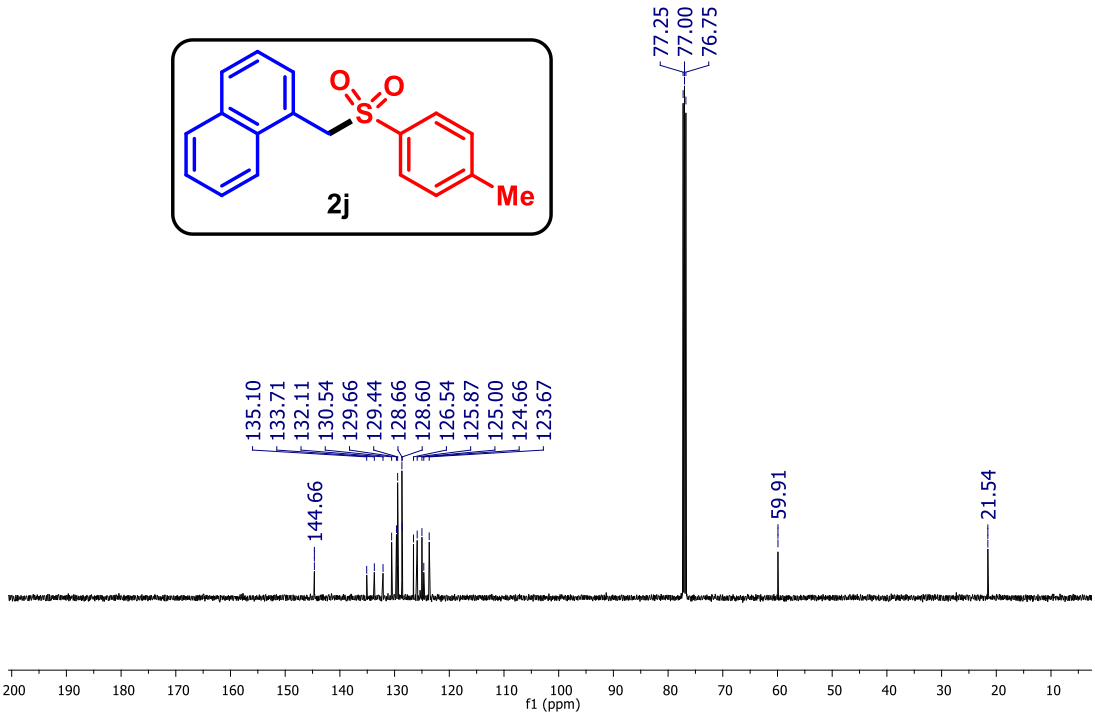


Figure S67. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1-(tosylmethyl)naphthalene (**2j**).

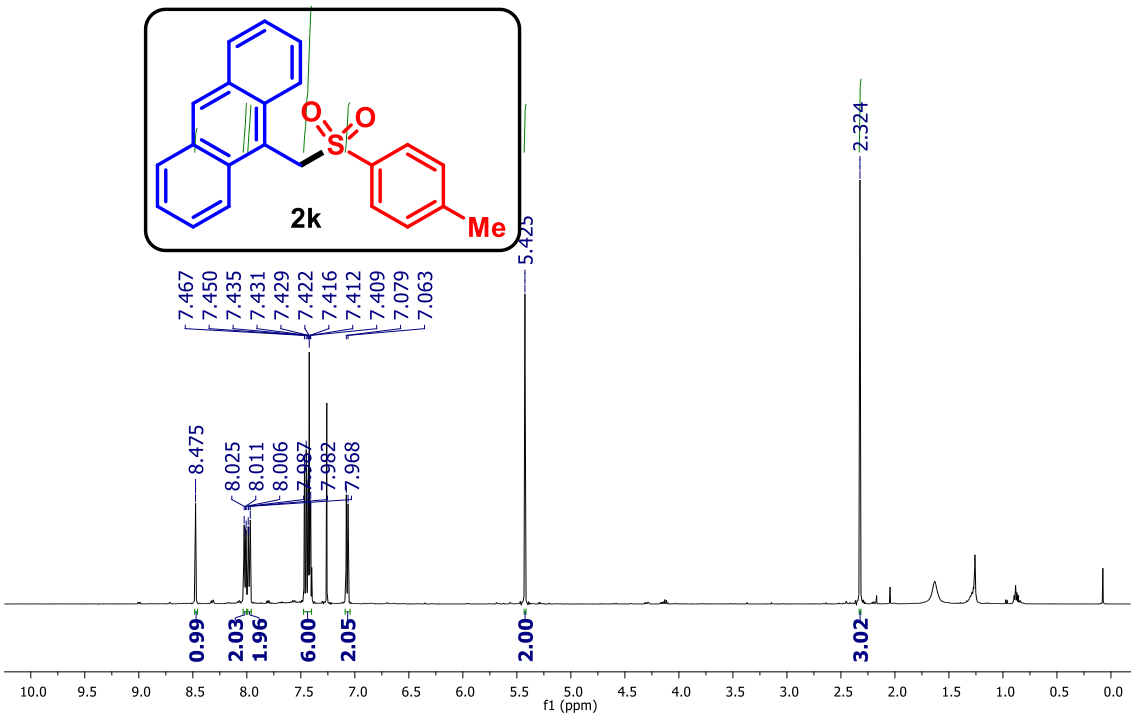


Figure S68. ^{1}H NMR spectrum ($CDCl_3$) of 9-(tosylmethyl)anthracene (**2k**).

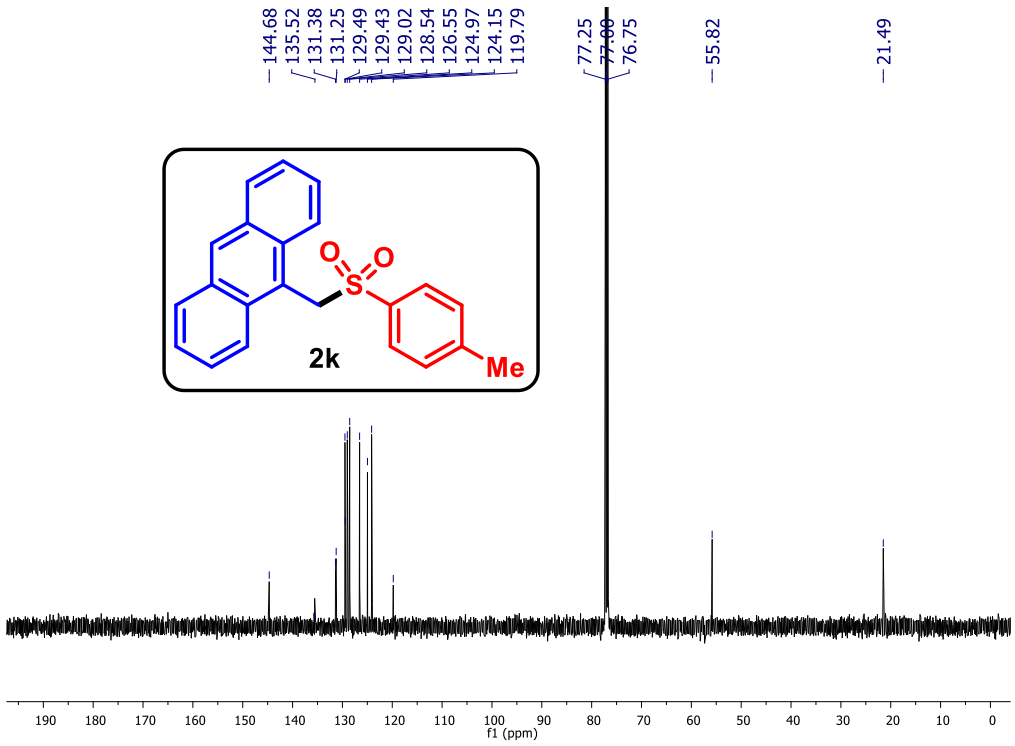


Figure S69. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 9-(tosylmethyl)anthracene (**2k**).

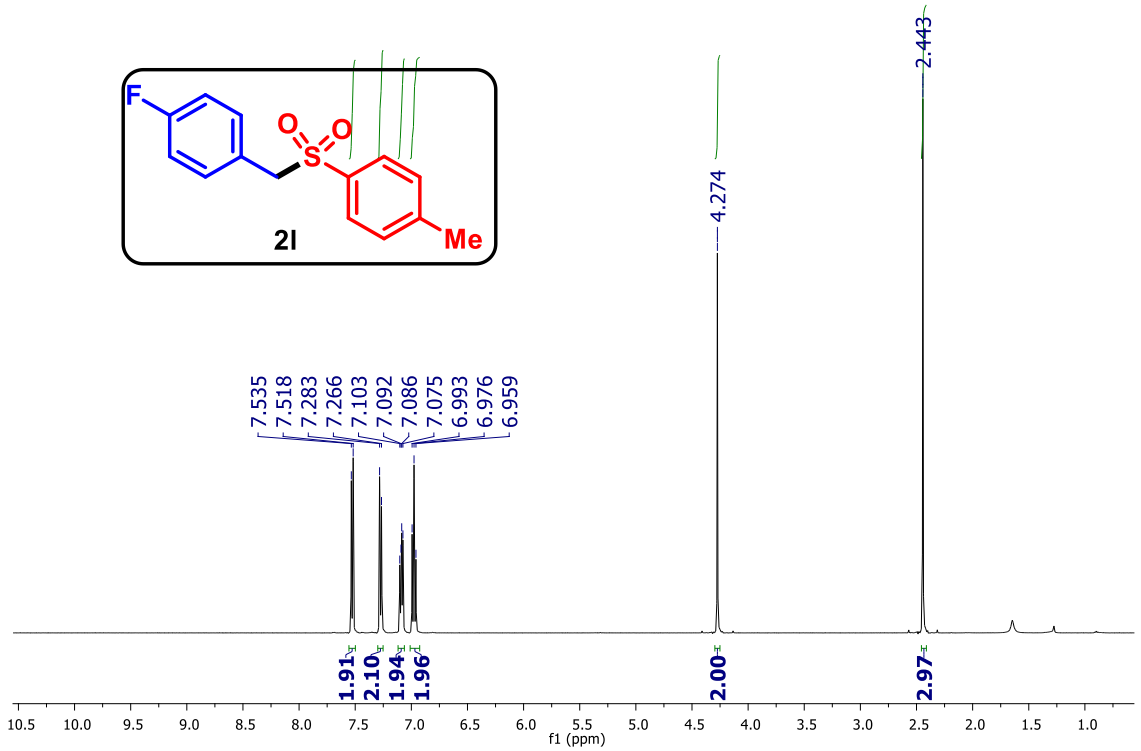


Figure S70. ^{1}H NMR spectrum ($CDCl_3$) of 1-fluoro-4-(tosylmethyl)benzene (**2l**). [6]

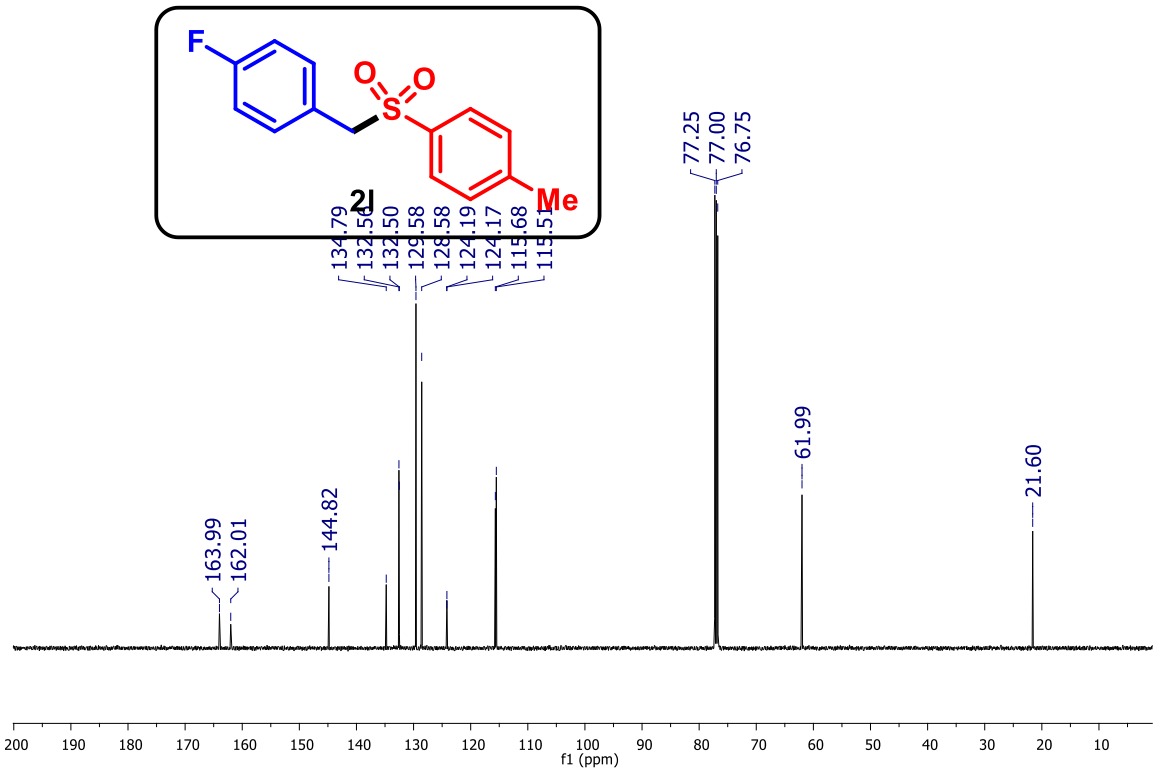


Figure S71. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1-fluoro-4-(tosylmethyl)benzene (**2l**). [6]

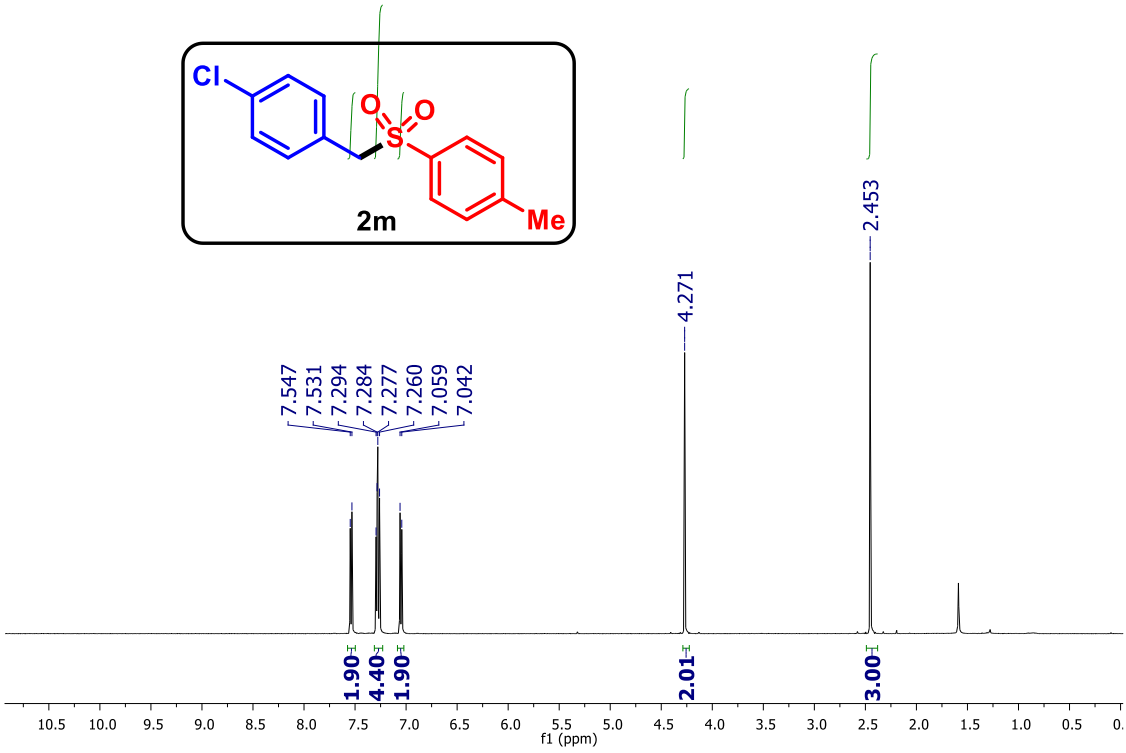


Figure S72. ^{1}H NMR spectrum ($CDCl_3$) of 1-chloro-4-(tosylmethyl)benzene (**2m**). [6]

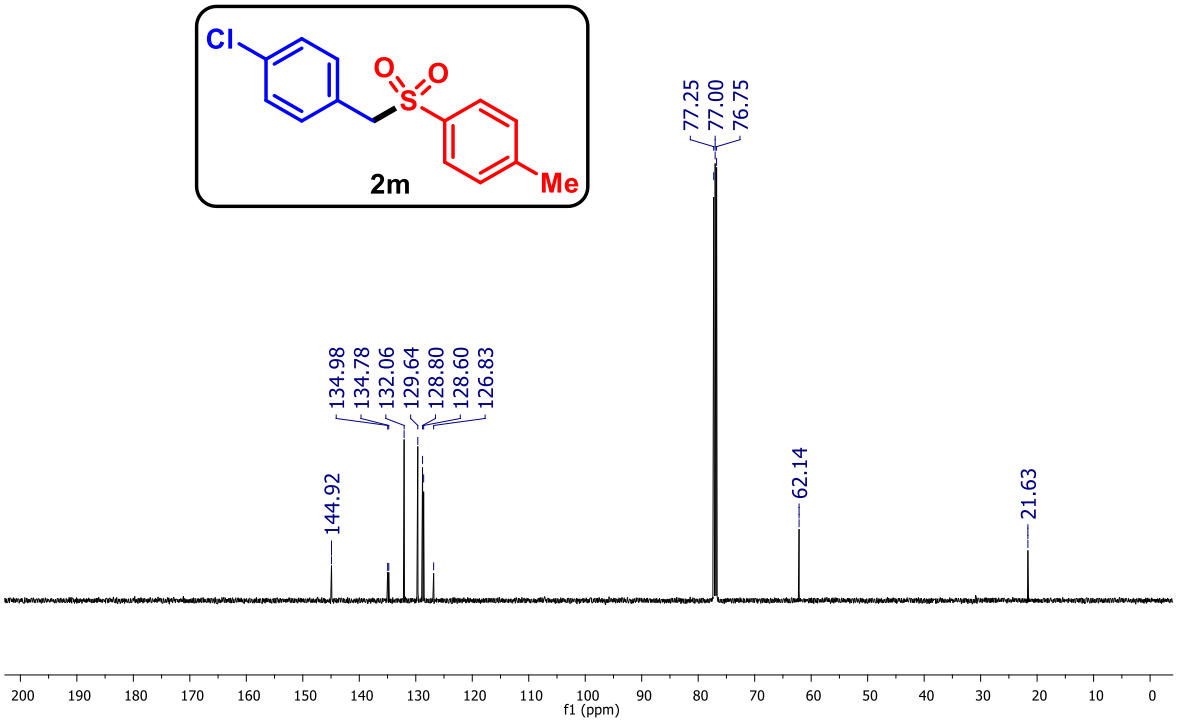


Figure S73. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1-chloro-4-(tosylmethyl)benzene (**2m**). [6]

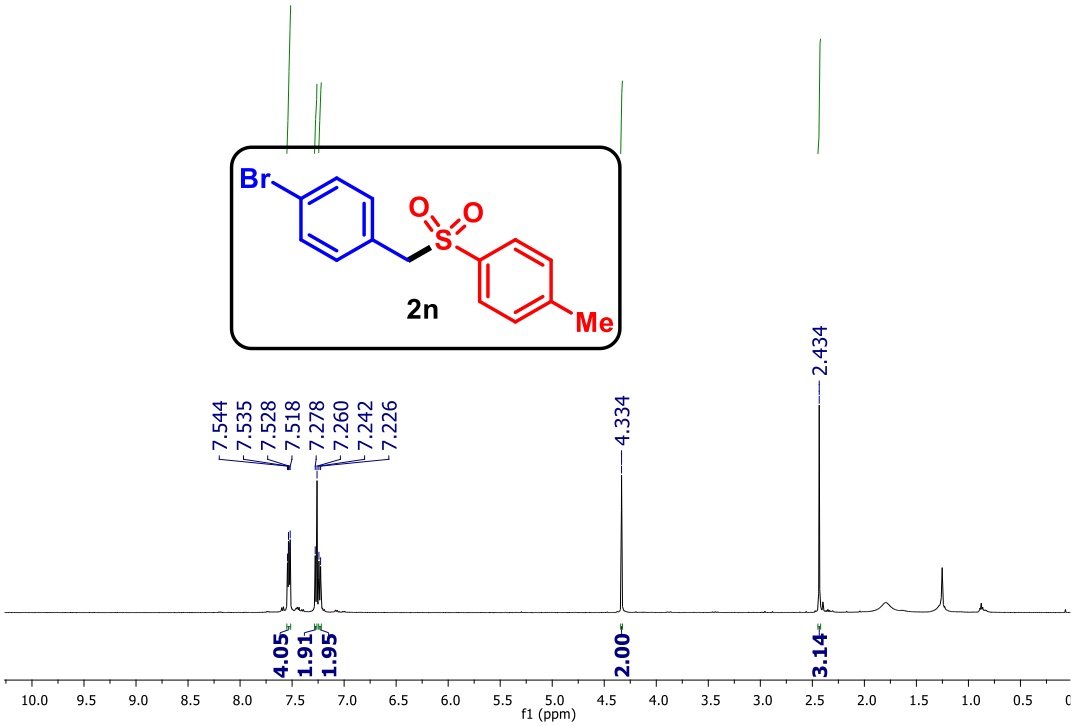


Figure S74. ^{1}H NMR spectrum ($CDCl_3$) of 1-bromo-4-(tosylmethyl)benzene (**2n**). [6]

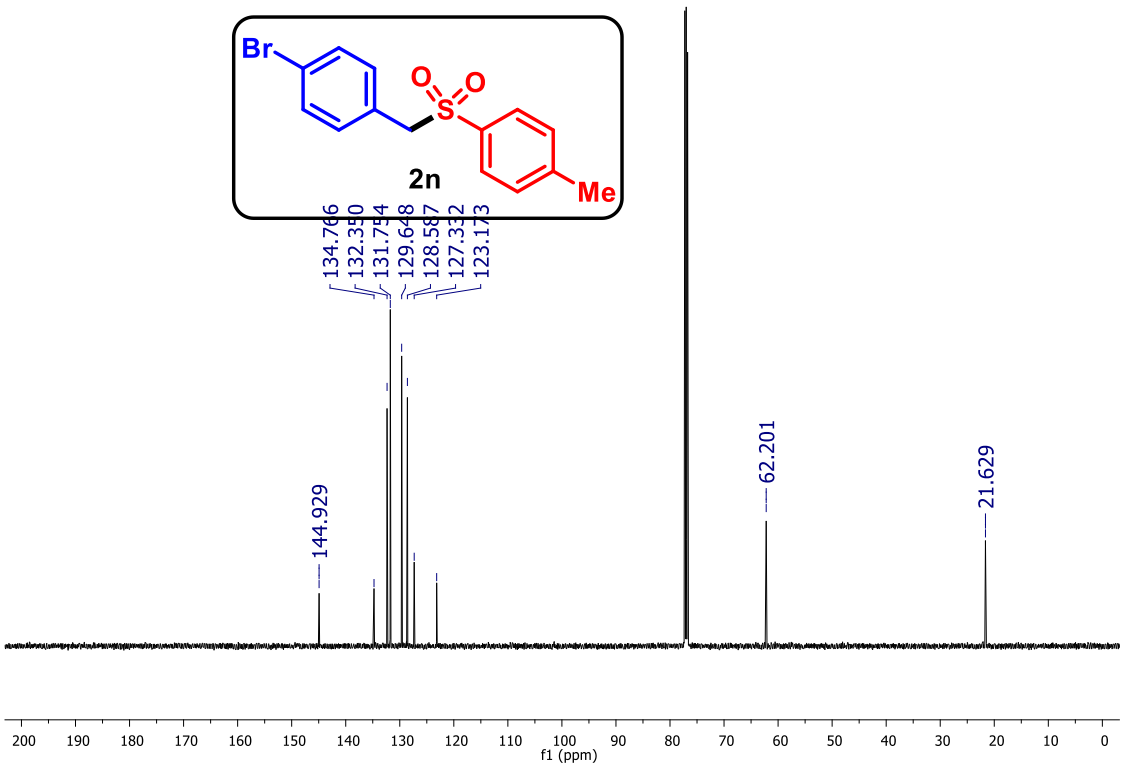


Figure S75. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1-bromo-4-(tosylmethyl)benzene (**2n**). [6]

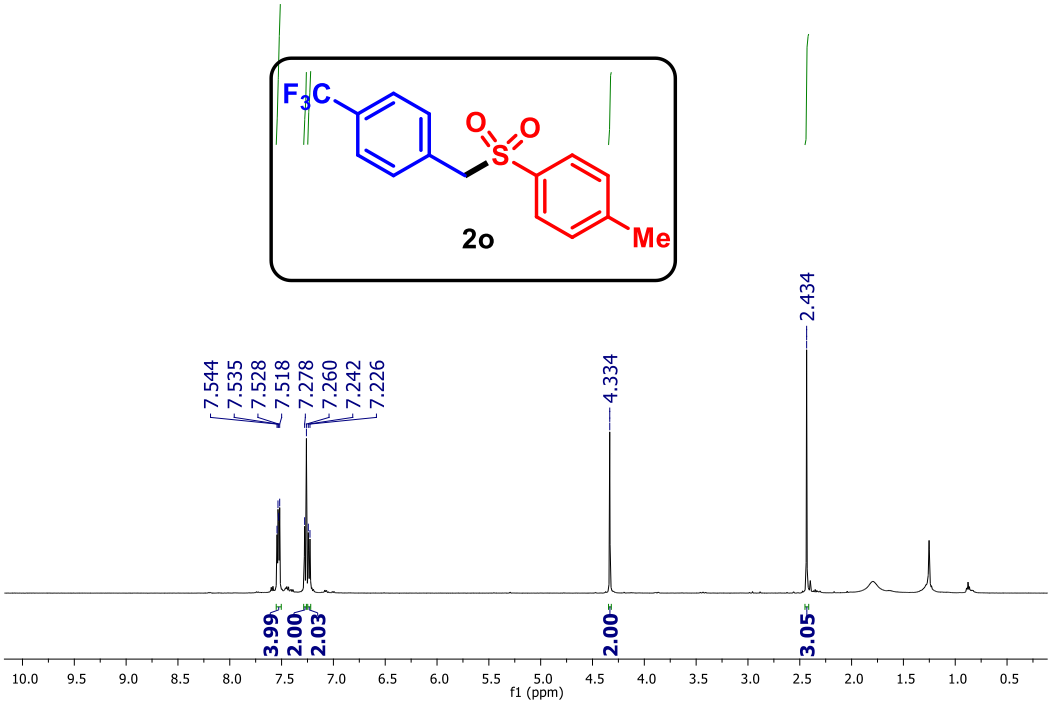


Figure S76. ^{1}H NMR spectrum ($CDCl_3$) of 1-methyl-4-((4-(trifluoromethyl)benzyl)sulfonyl)benzene (**2o**). [6]

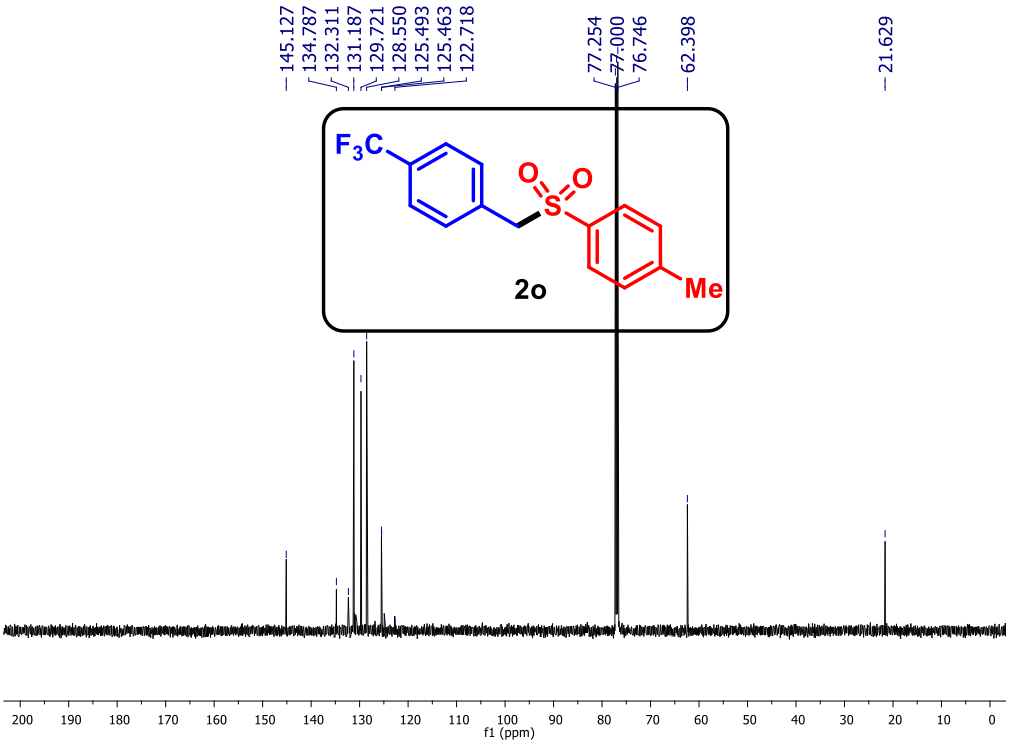


Figure S77. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1-methyl-4-((4-(trifluoromethyl)benzyl)sulfonyl)benzene (**2o**). [6]

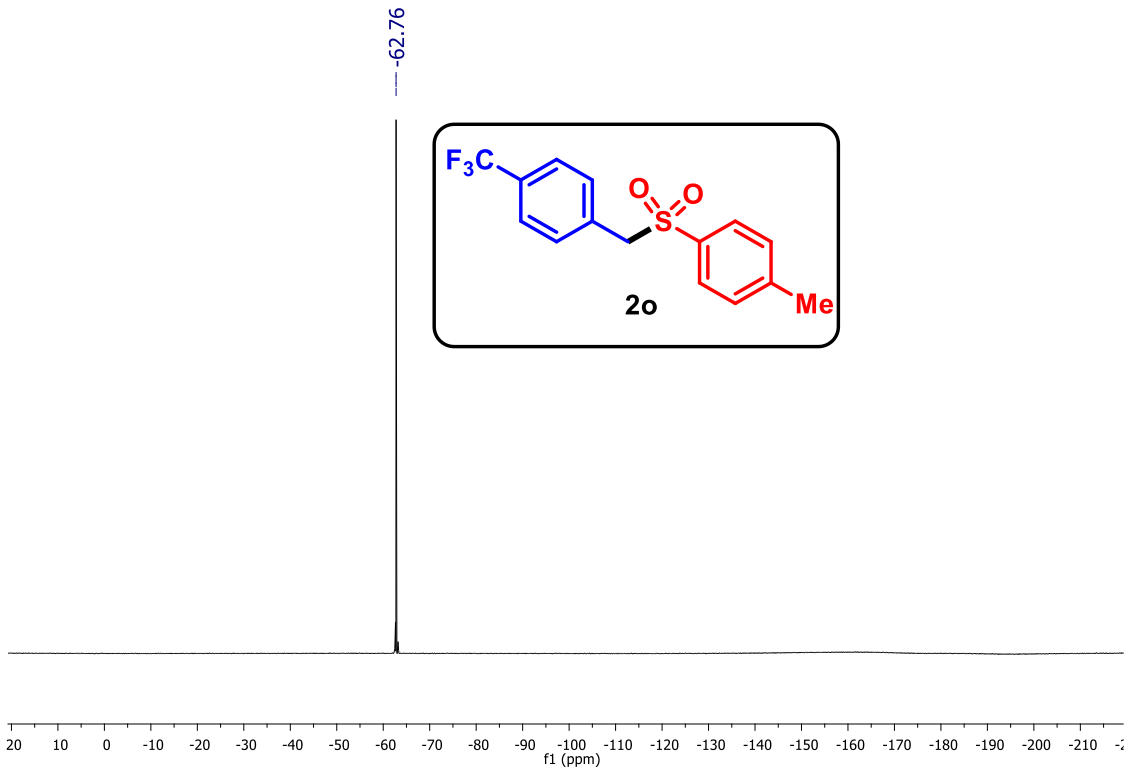


Figure S78. ^{19}F NMR spectrum ($CDCl_3$) of 1-methyl-4-((4-(trifluoromethyl)benzyl)sulfonyl)benzene (**2o**). [6]

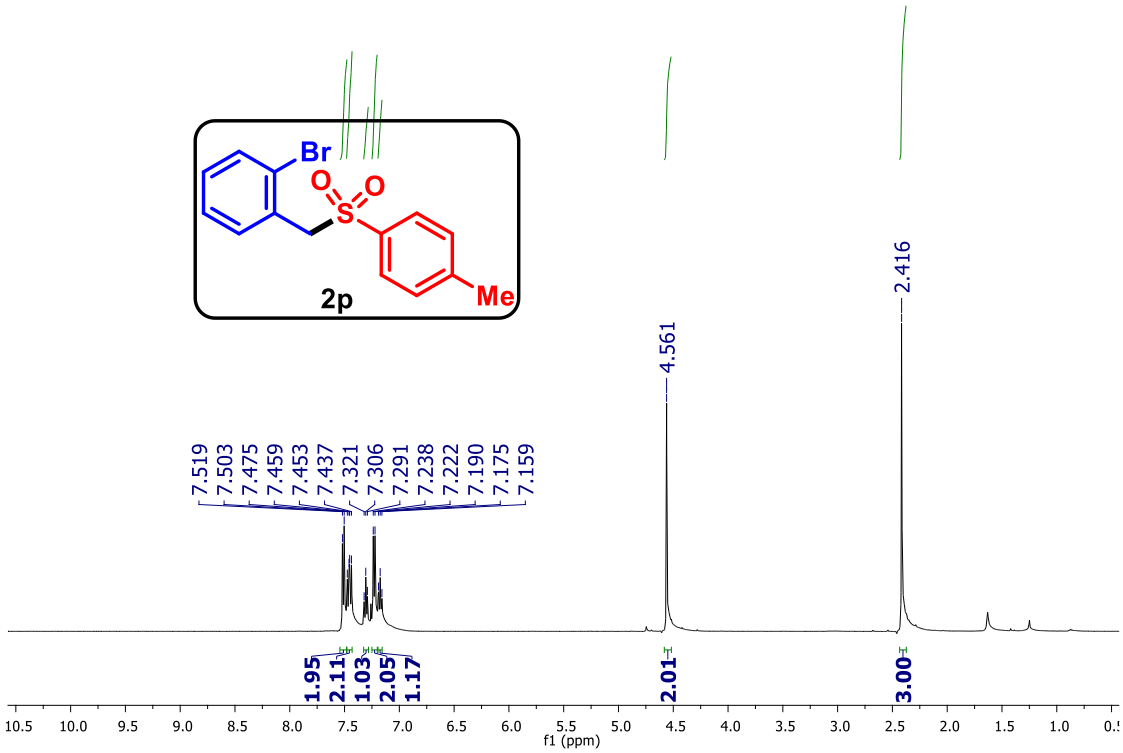


Figure S79. ^{1}H NMR spectrum ($CDCl_3$) of 1-bromo-2-(tosylmethyl)benzene (**2p**). [6]

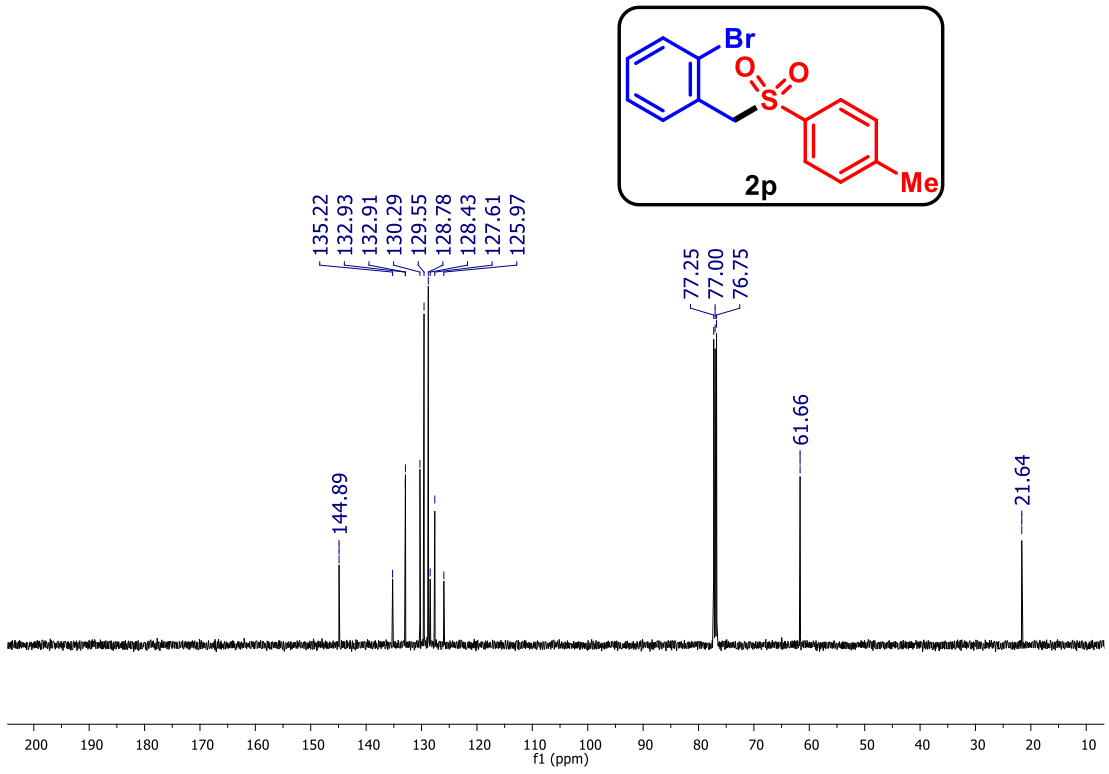


Figure S80. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1-bromo-2-(tosylmethyl)benzene (**2p**). [6]

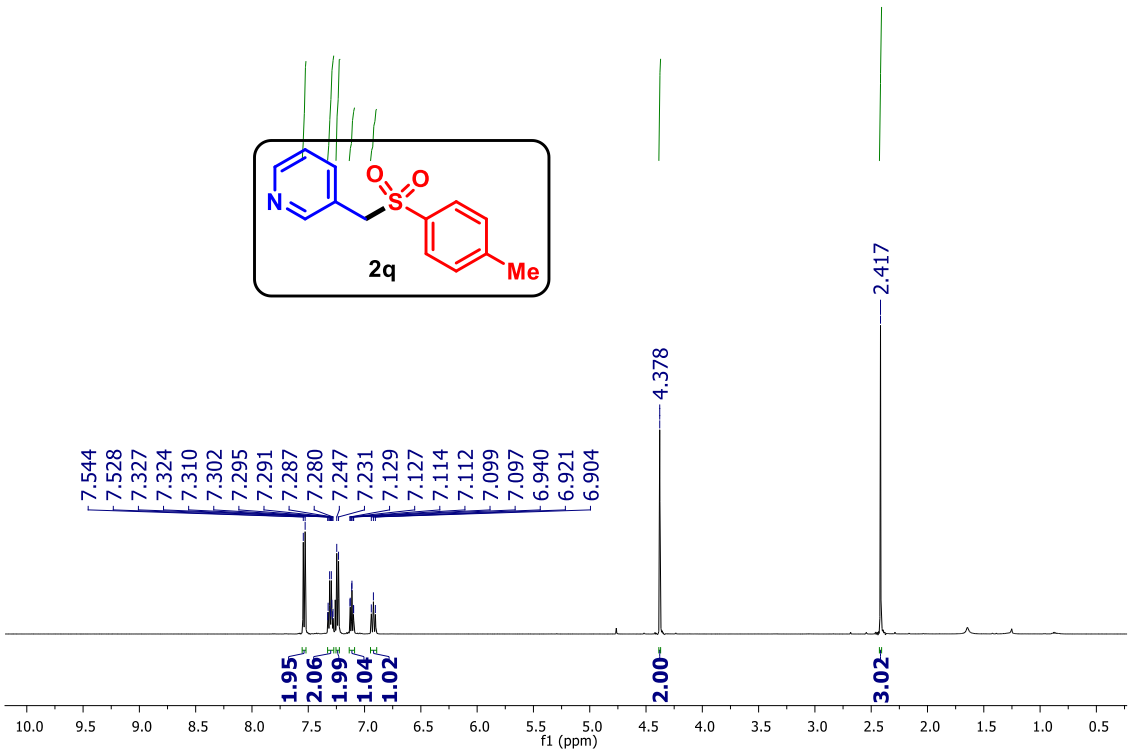


Figure S81. ^{1}H NMR spectrum ($CDCl_3$) of 3-(tosylmethyl)pyridine (**2q**). [9]

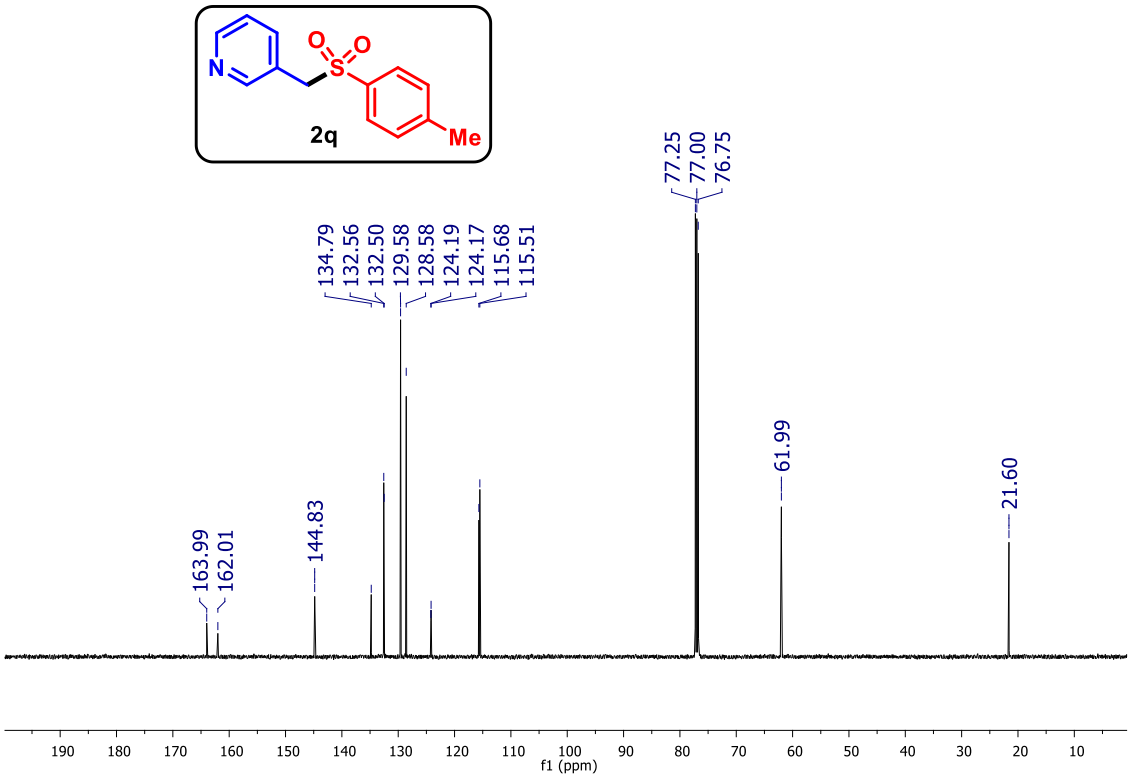


Figure S82. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 3-(tosylmethyl)pyridine (**2q**). [9]

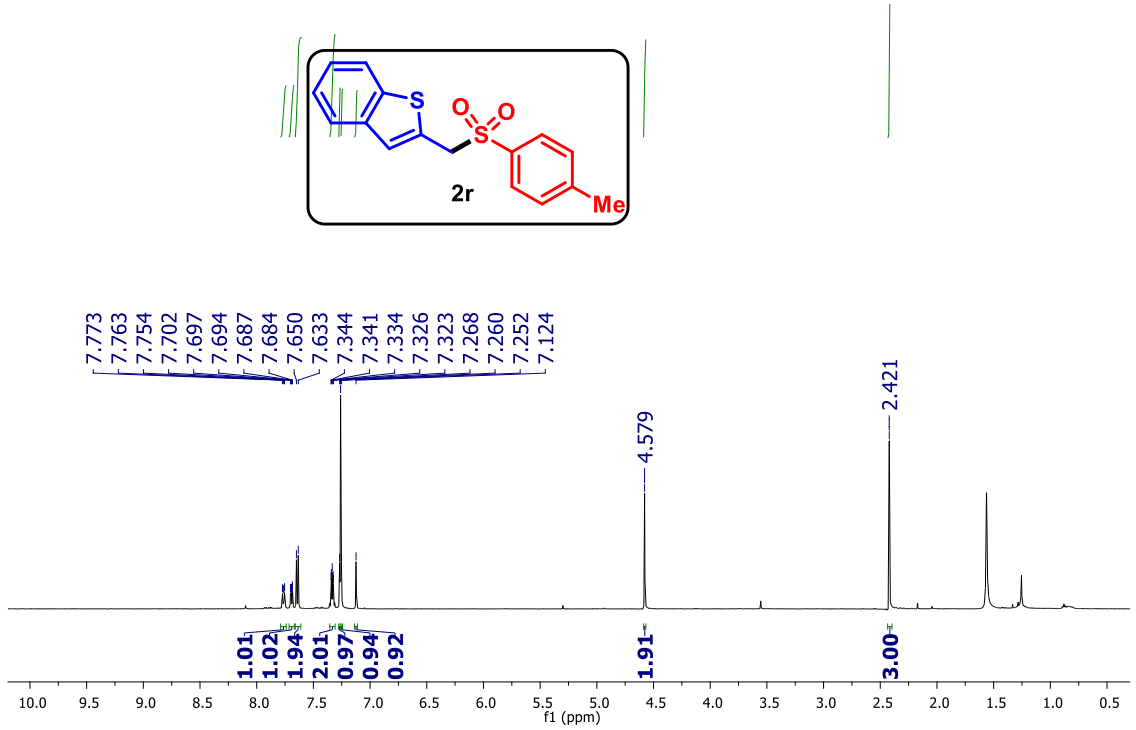


Figure S83. ^{1}H NMR spectrum ($CDCl_3$) of 2-(tosylmethyl)benzo[*b*]thiophene (**2r**).

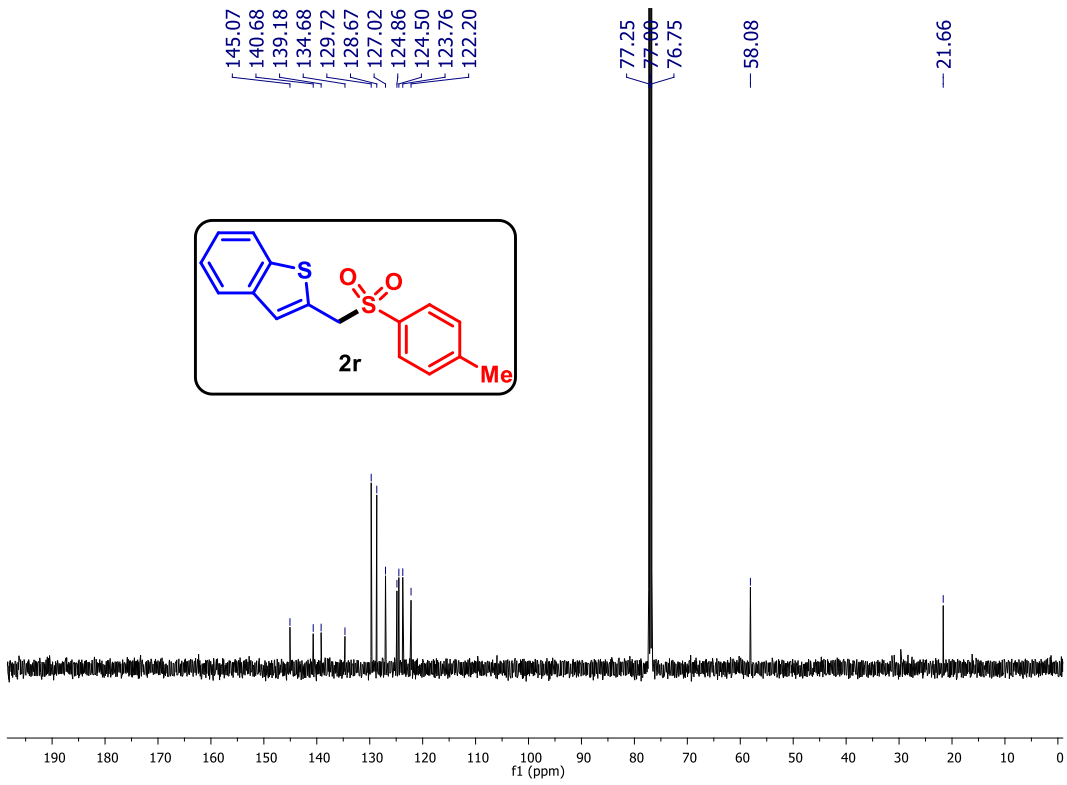


Figure S84. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 2-(tosylmethyl)benzo[*b*]thiophene (**2r**).

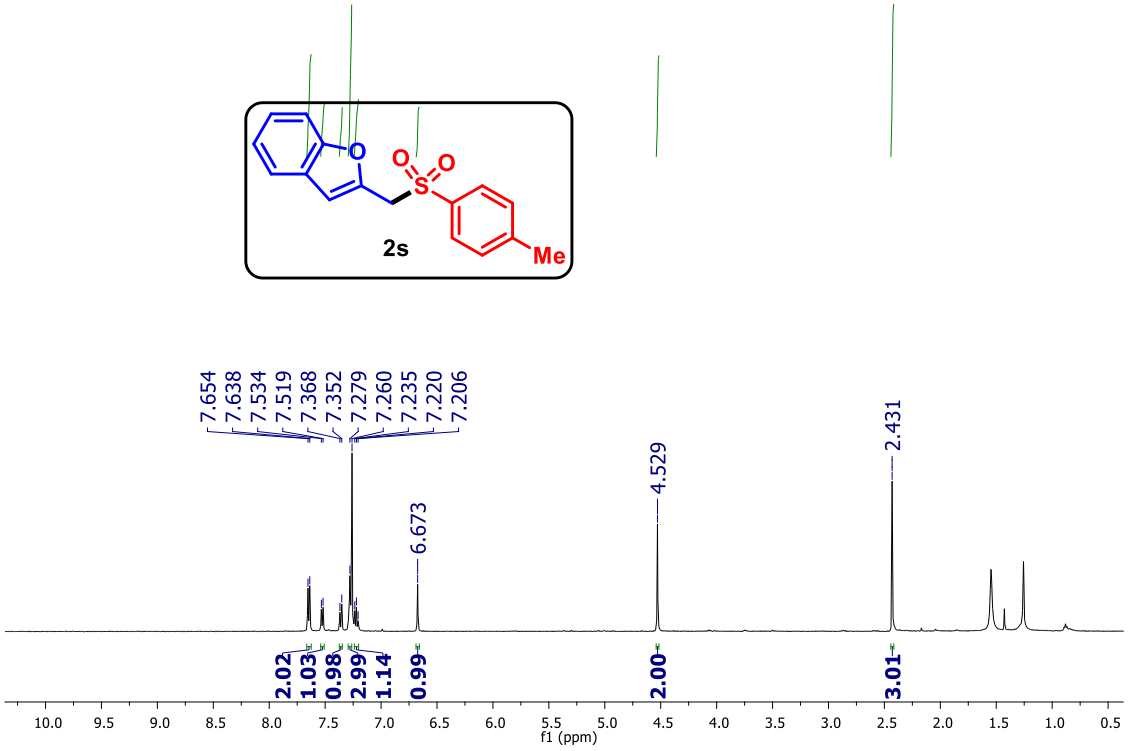


Figure S85. ^{1}H NMR spectrum ($CDCl_3$) of 2-(tosylmethyl)benzofuran (**2s**).

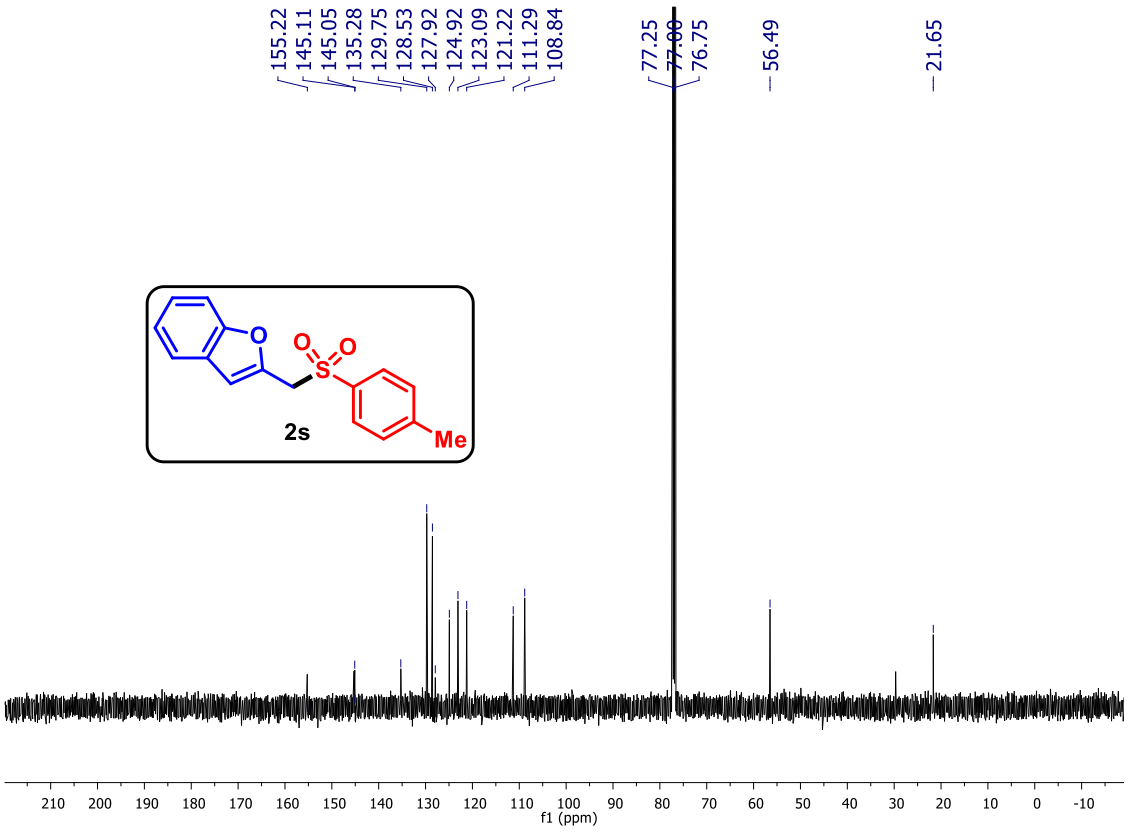


Figure S86. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 2-(tosylmethyl)benzofuran (**2s**).

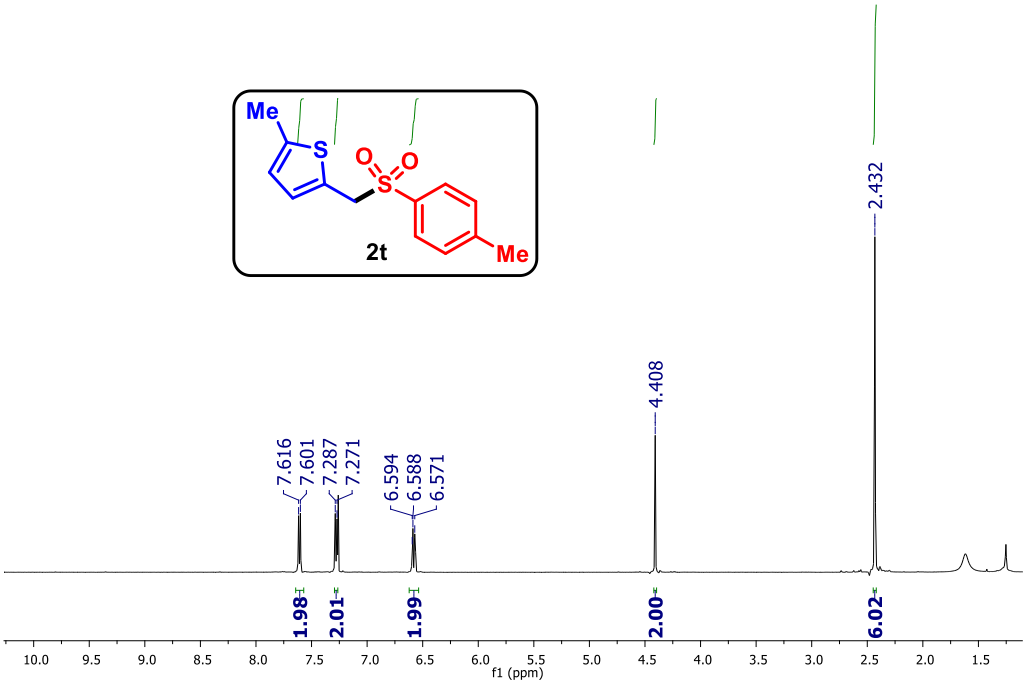


Figure S87. ^{1}H NMR spectrum ($CDCl_3$) of 2-methyl-5-(tosylmethyl)thiophene (**2t**).

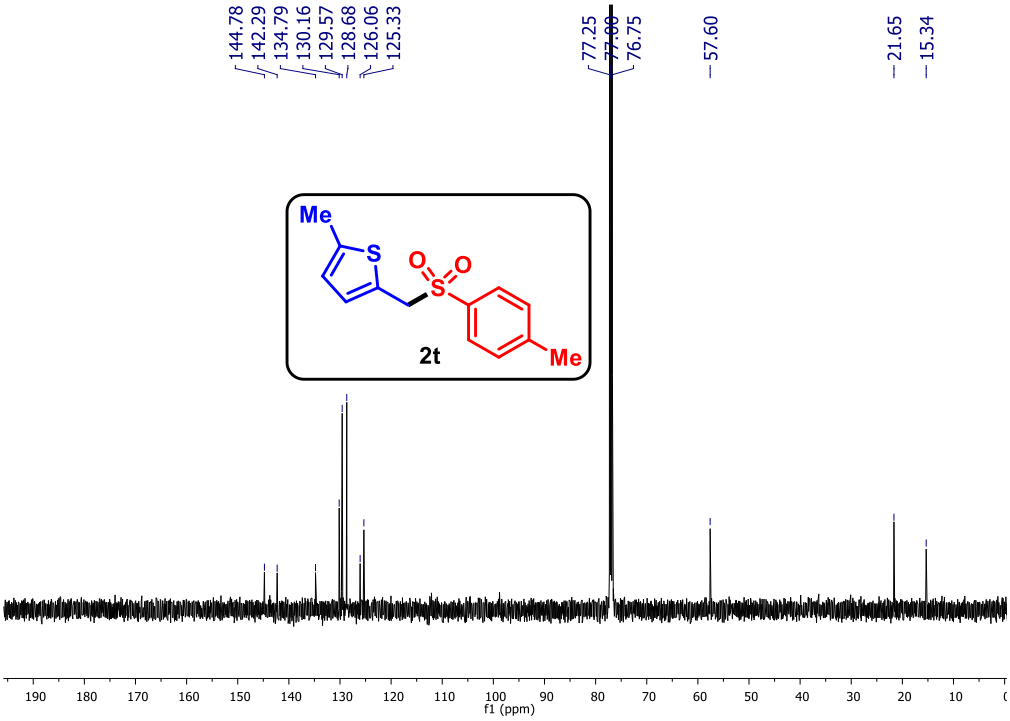


Figure S88. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 2-methyl-5-(tosylmethyl)thiophene (**2t**).

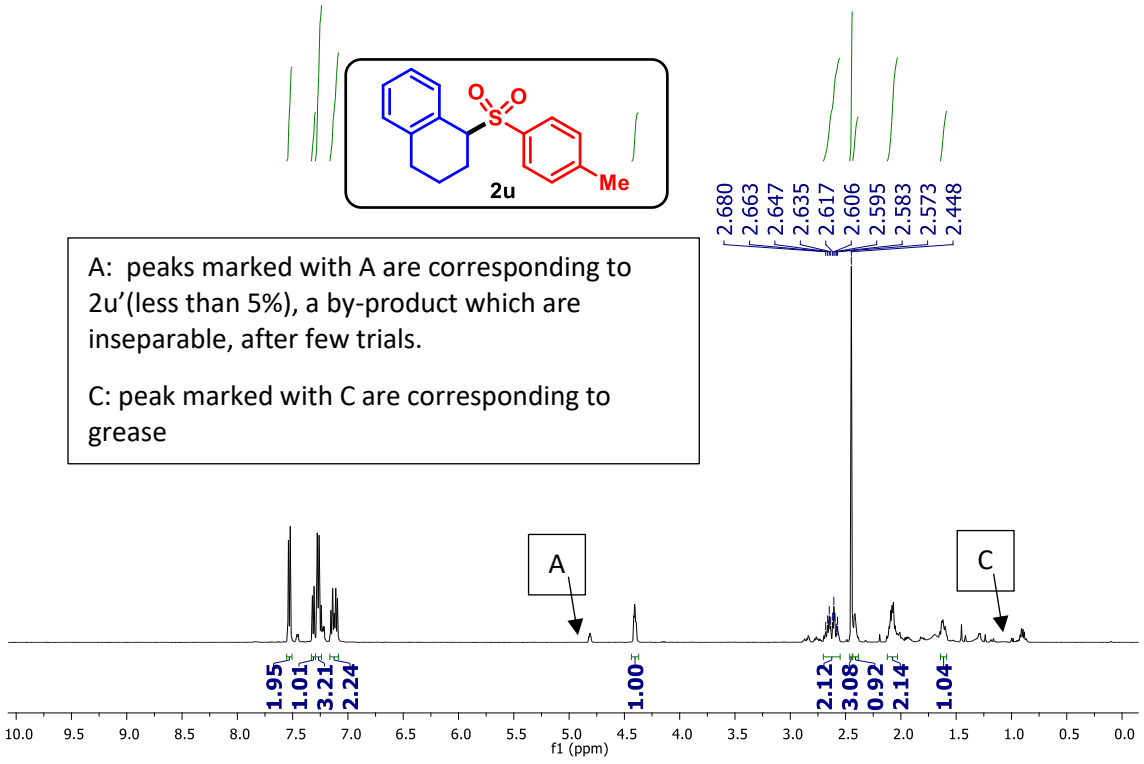


Figure S89. ^{1}H NMR spectrum ($CDCl_3$) of 1-(tosylmethyl)-1,2,3,4-tetrahydronaphthalene (**2u**). [6]

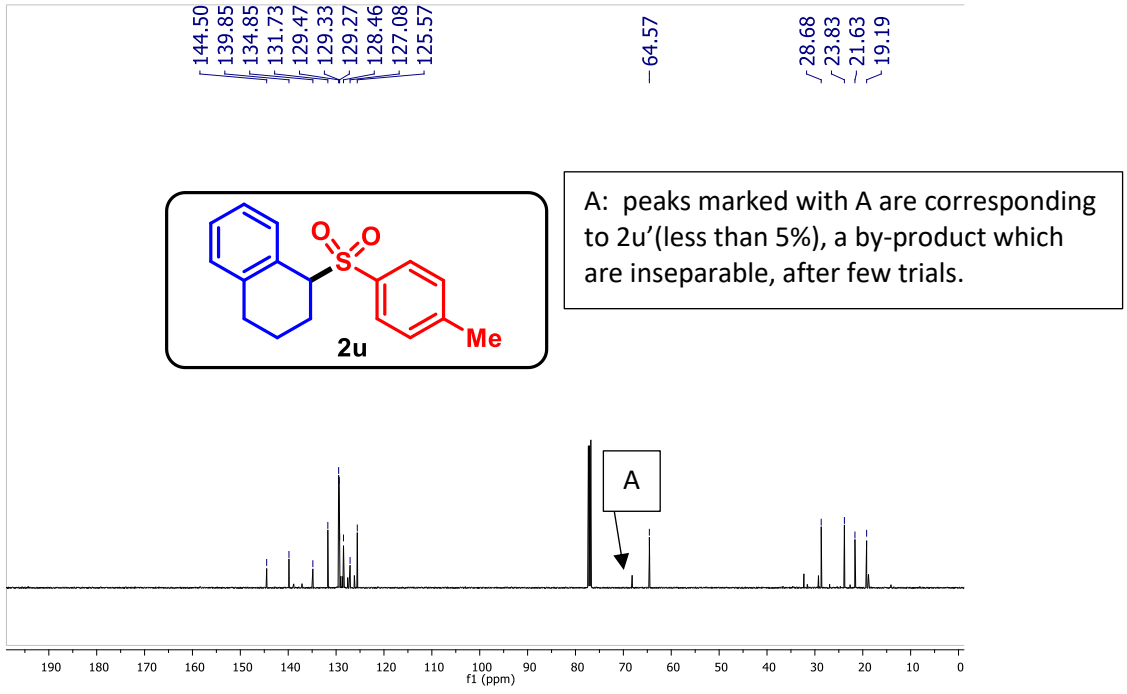


Figure S90. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1-(tosylmethyl)-1,2,3,4-tetrahydronaphthalene (**2u**).

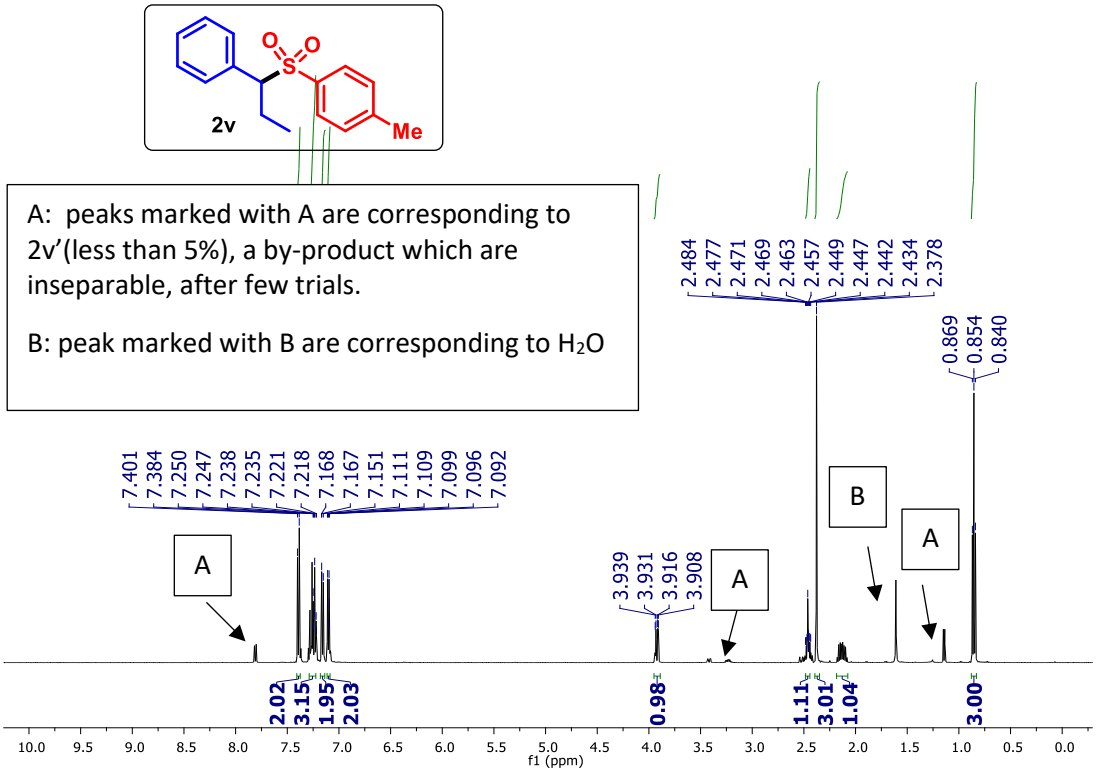


Figure S91. ^{1}H NMR spectrum ($CDCl_3$) of (S)-1-methyl-4-((1-phenylpropyl)sulfonyl)benzene(**2v**).[14]

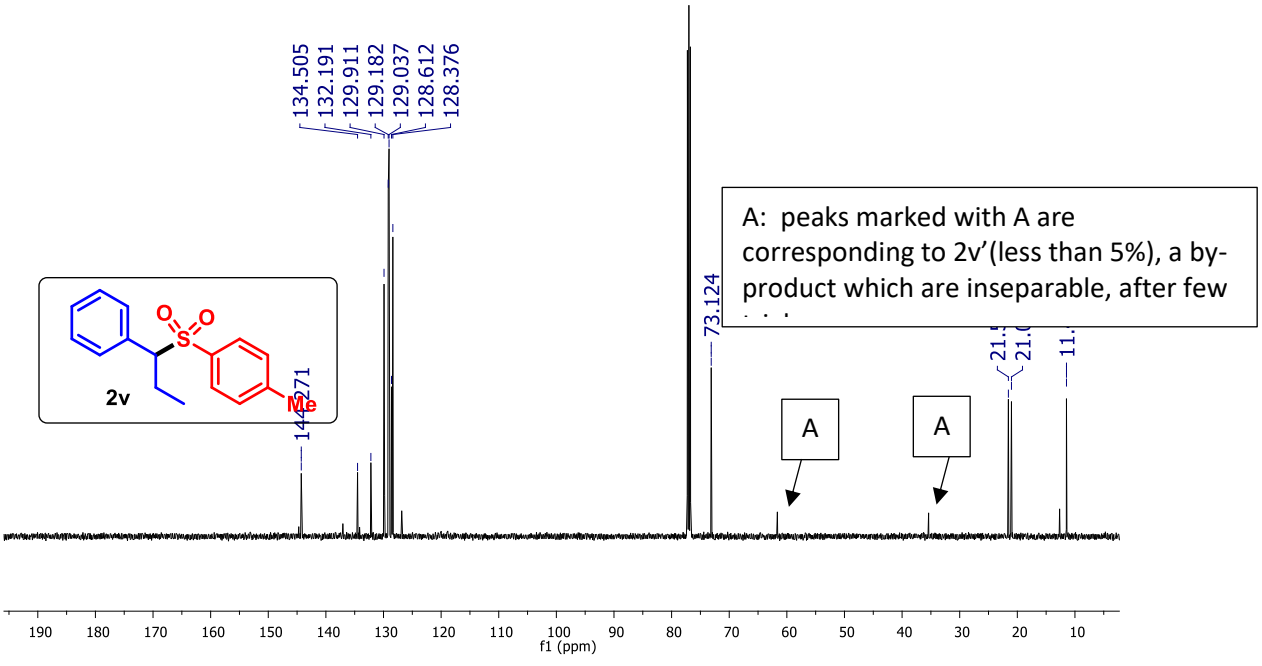


Figure S92. ^{13}C **{**^{1}H} NMR spectrum ($CDCl_3$) of (S)-1-methyl-4-((1-phenylpropyl)sulfonyl)benzene(**2v**).[14]

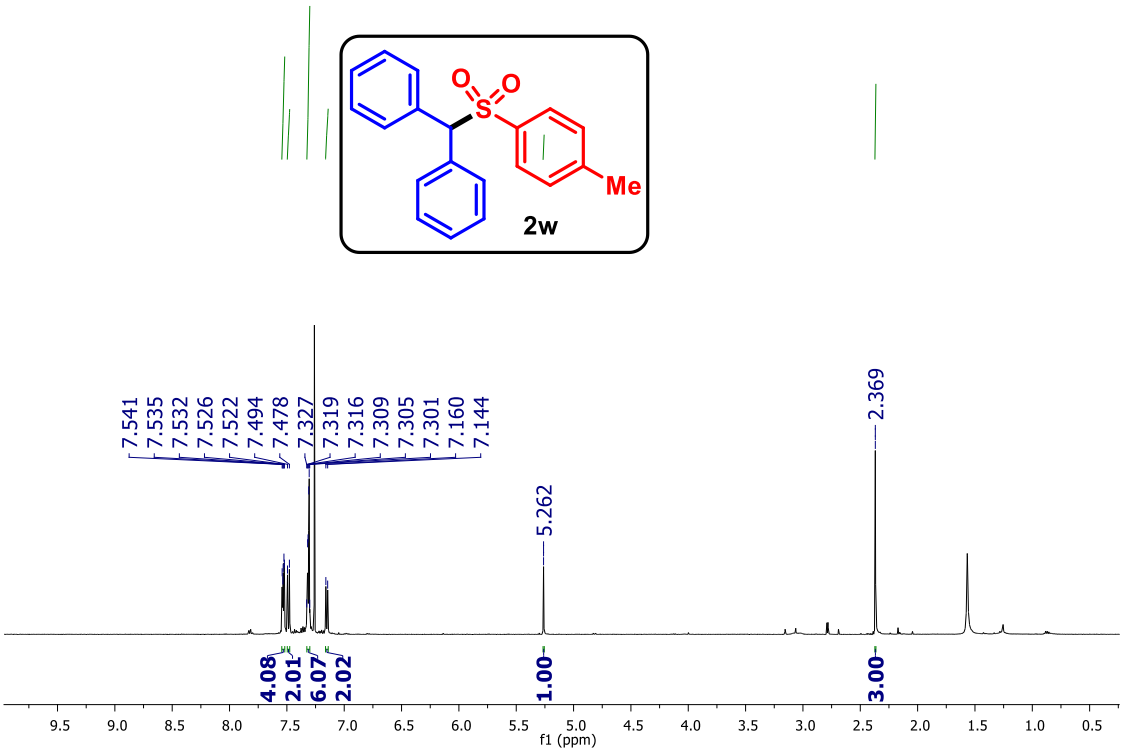


Figure S93. ^{1}H NMR spectrum ($CDCl_3$) of (tosylmethylene)dibenzene (**2w**). [6]

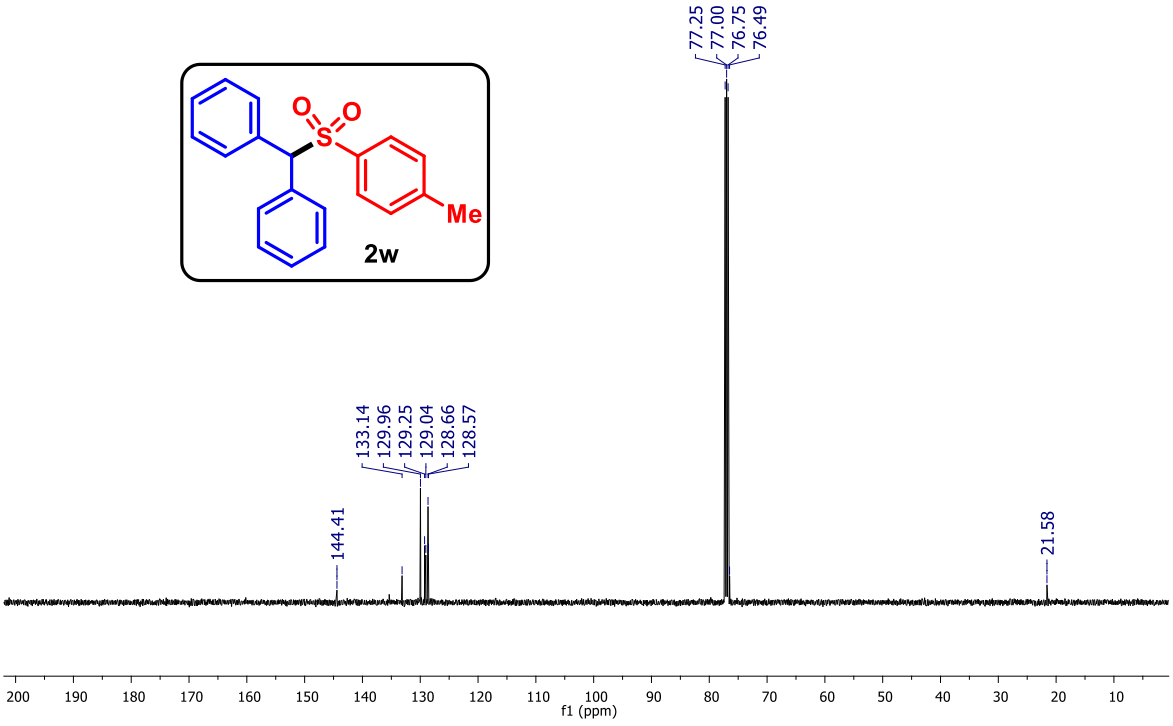


Figure S94. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of (tosylmethylene)dibenzene (**2w**).

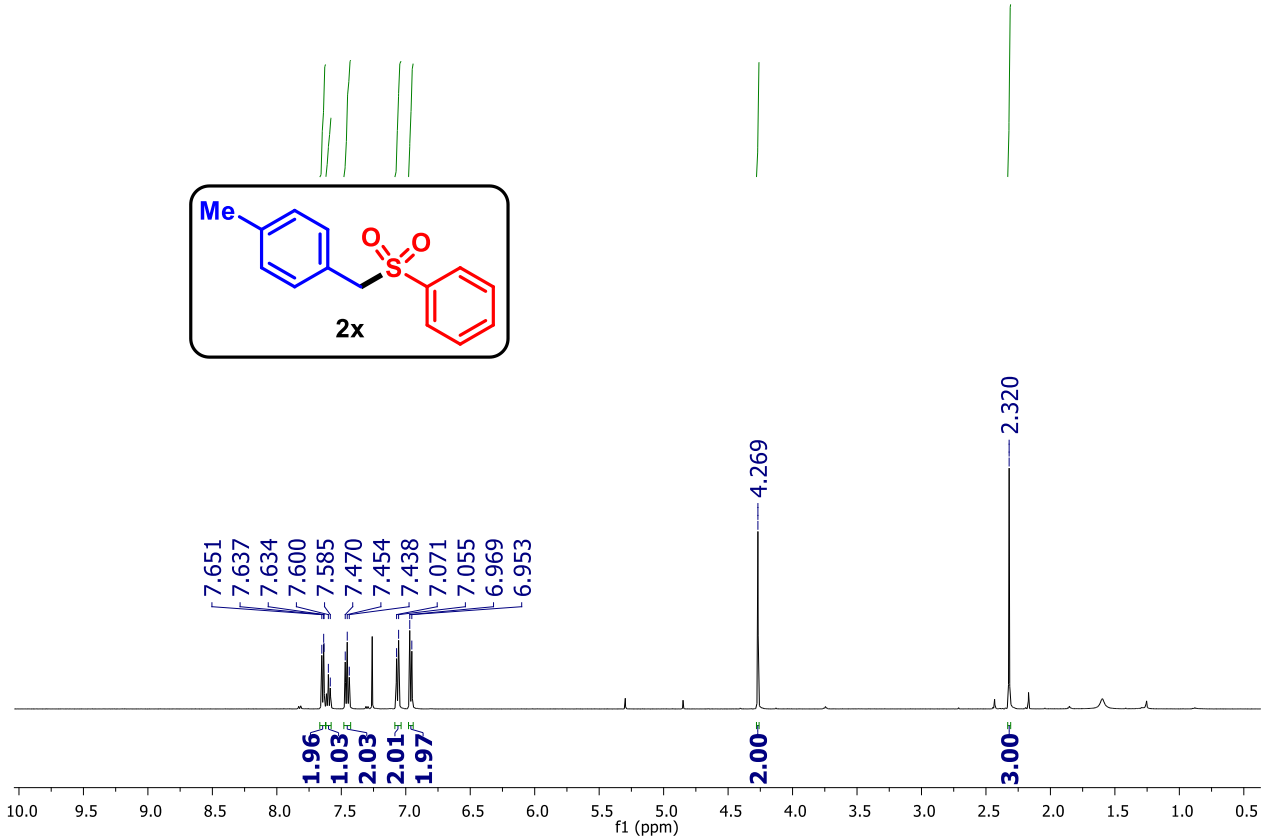


Figure S95. ^{1}H NMR spectrum ($CDCl_3$) of 1-methyl-4-((phenylsulfonyl)methyl)benzene (**2x**). [7]

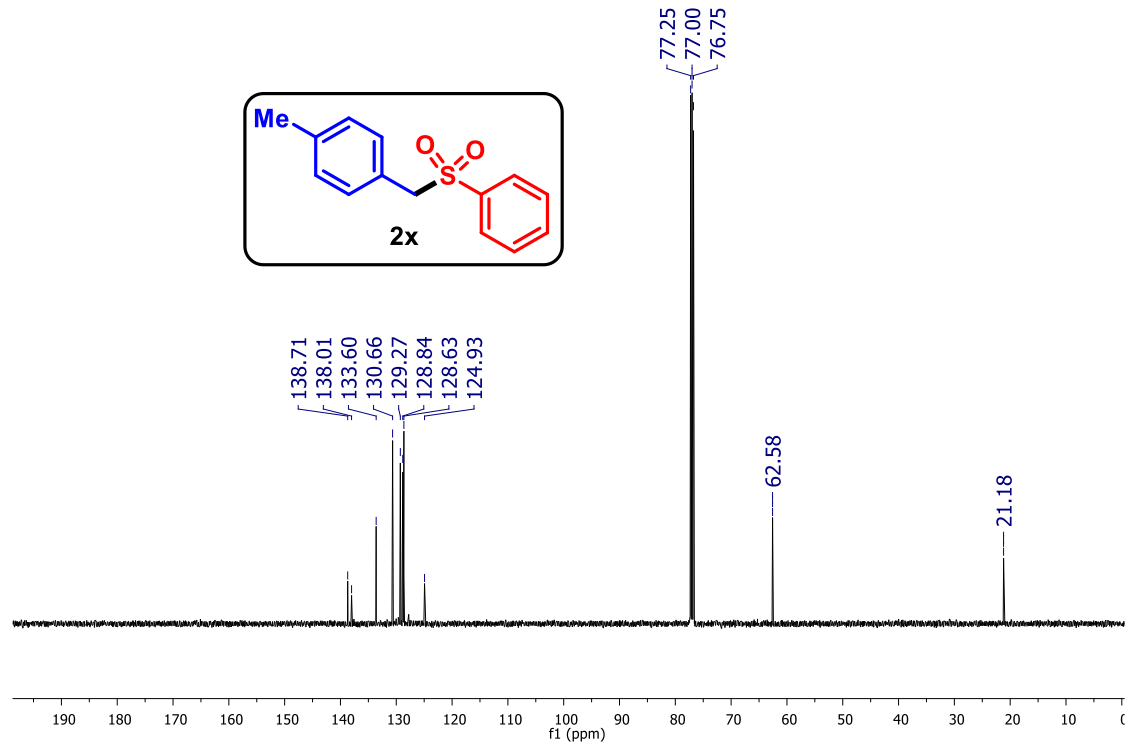


Figure S96. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1-methyl-4-((phenylsulfonyl)methyl)benzene (**2x**). [7]

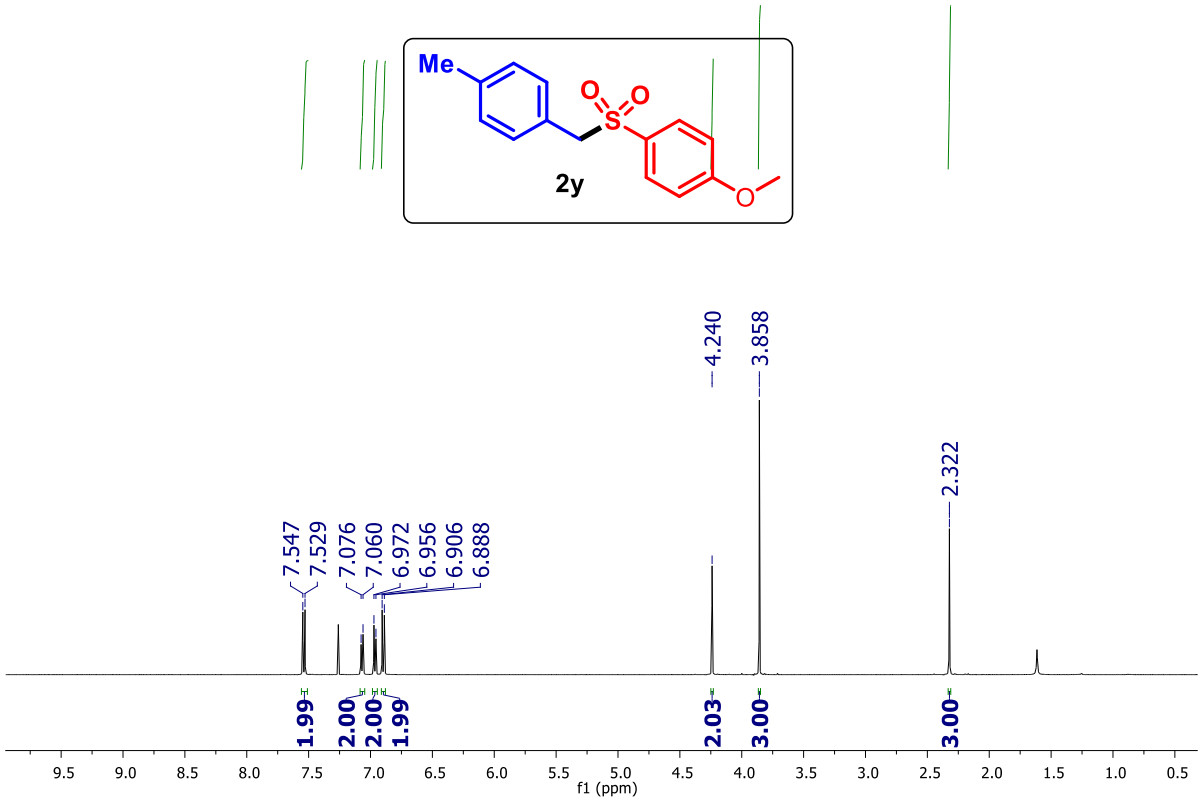


Figure S97. ^{1}H NMR spectrum ($CDCl_3$) of 1-methoxy-4-((4-methylbenzyl)sulfonyl)benzene(**2y**). [6]

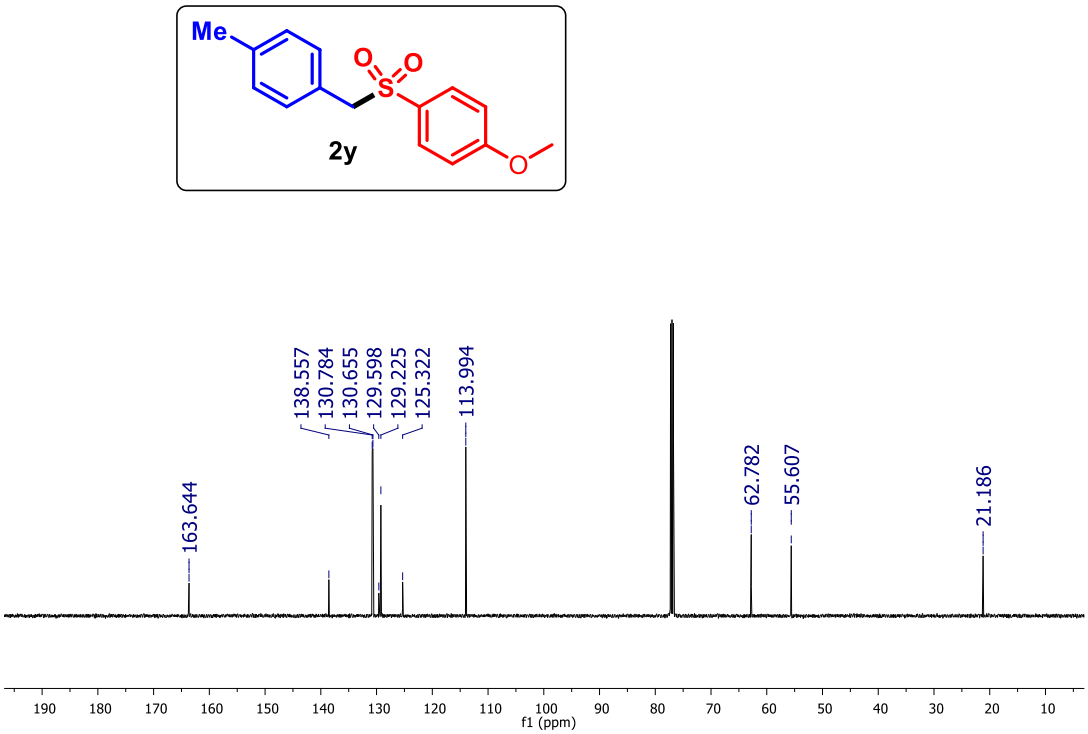


Figure S98. ^{13}C **{**^{1}H} NMR spectrum ($CDCl_3$) of 1-methoxy-4-((4-methylbenzyl)sulfonyl)benzene**(2y)**.

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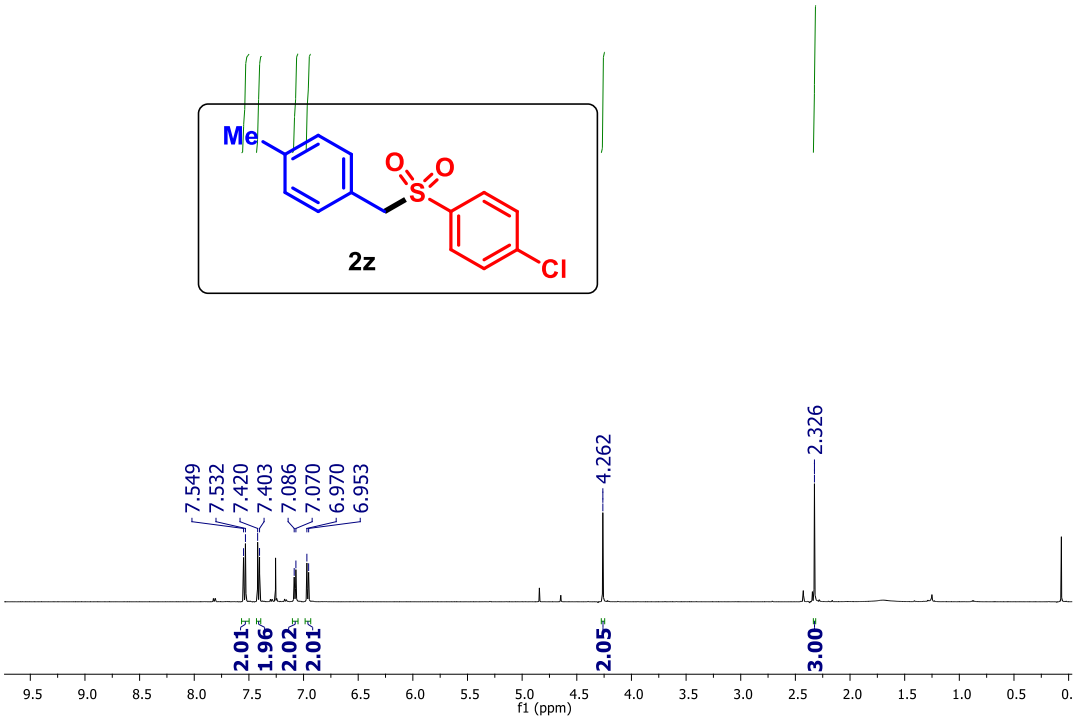


Figure S99. ^{1}H NMR spectrum ($CDCl_3$) of 1-chloro-4-((4-methylbenzyl)sulfonyl)benzene(**2z**). [6]

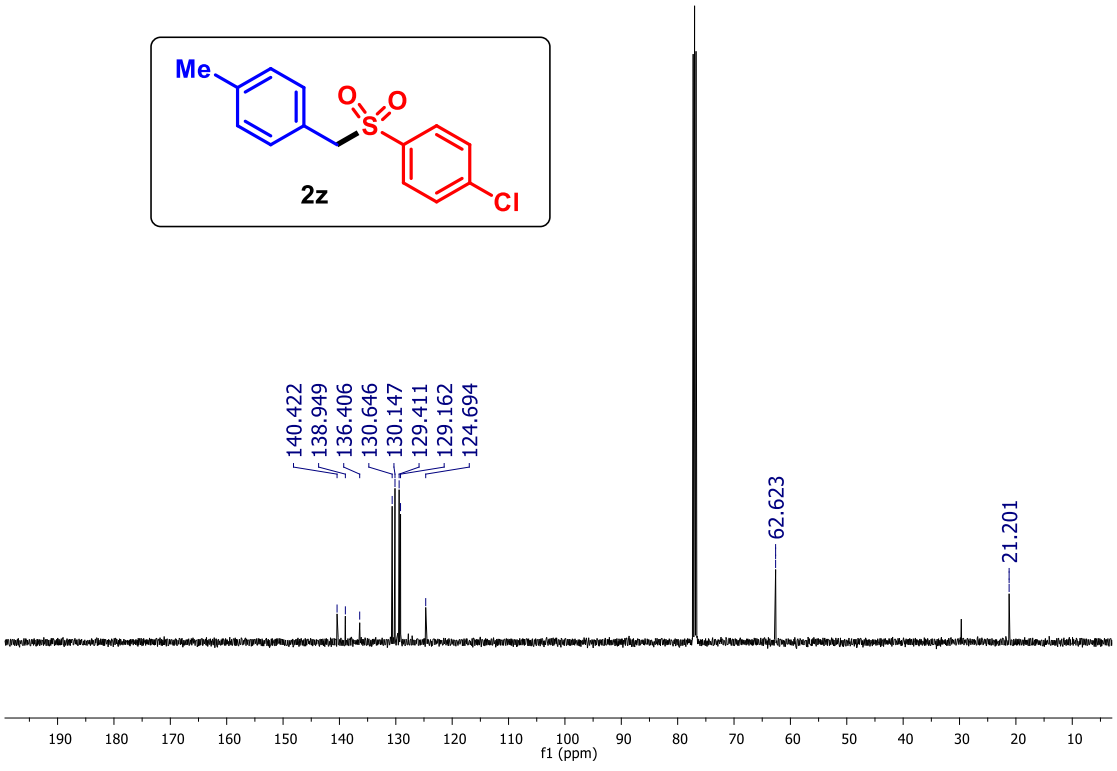


Figure S100. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1-chloro-4-((4-methylbenzyl)sulfonyl)benzene(**2z**). [6]

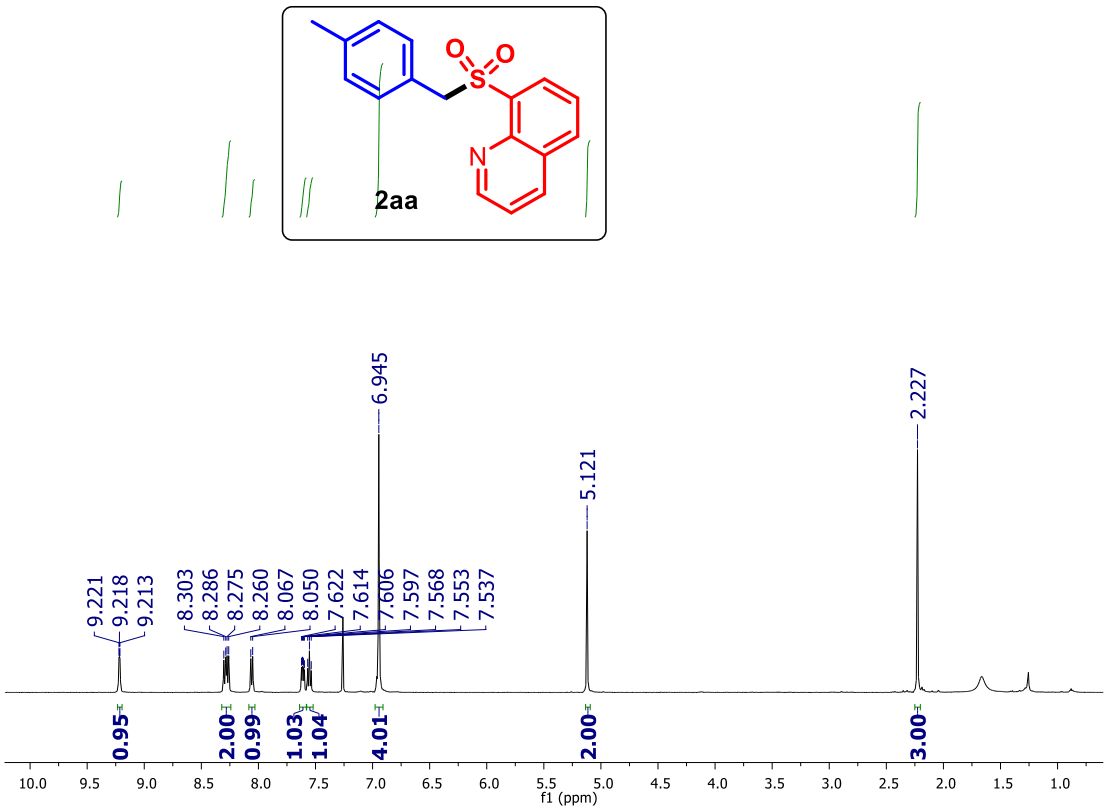


Figure S101. ^{1}H NMR spectrum ($CDCl_3$) of 8-(tosylmethyl)quinoline(**2aa**).[15]

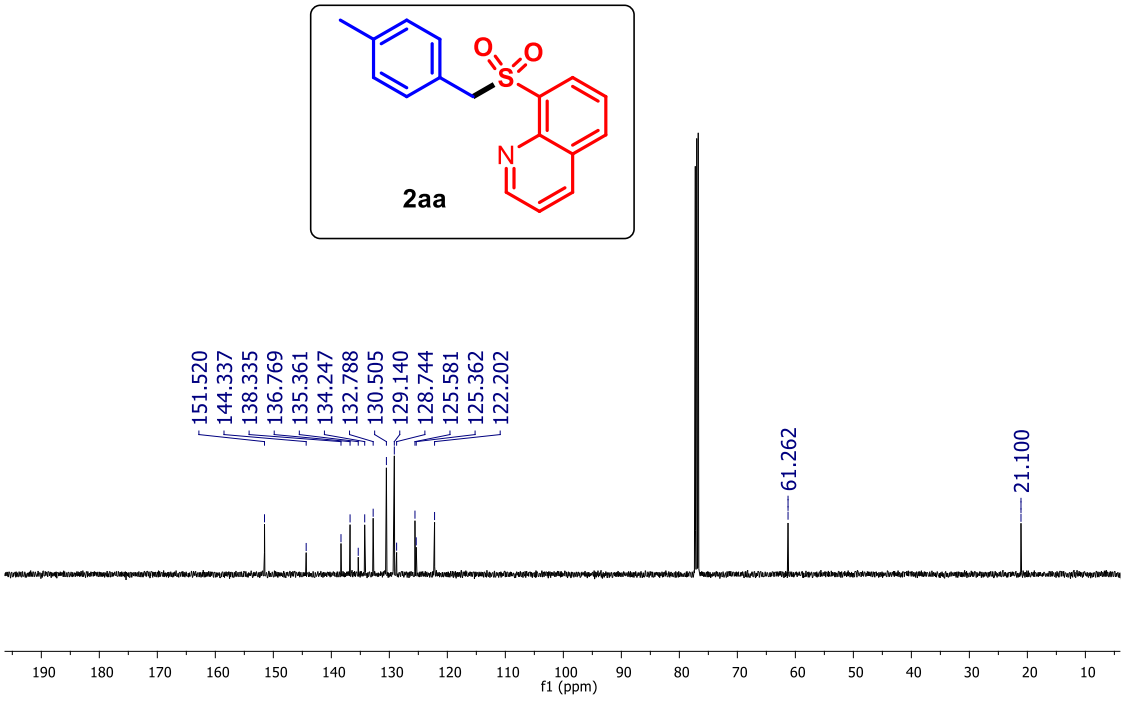


Figure S102. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 8-(tosylmethyl)quinoline(**2aa**).[15]

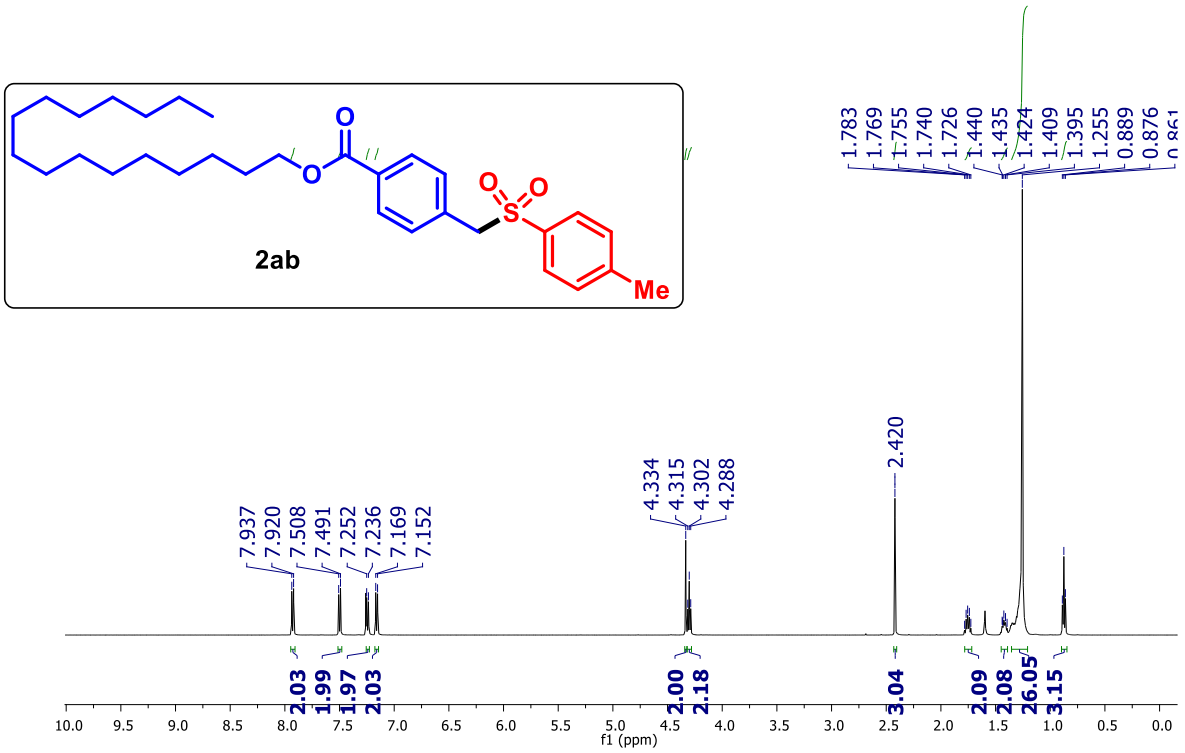


Figure S103. ^{1}H NMR spectrum ($CDCl_3$) of hexadecyl 4-(tosylmethyl)benzoate (**2ab**).

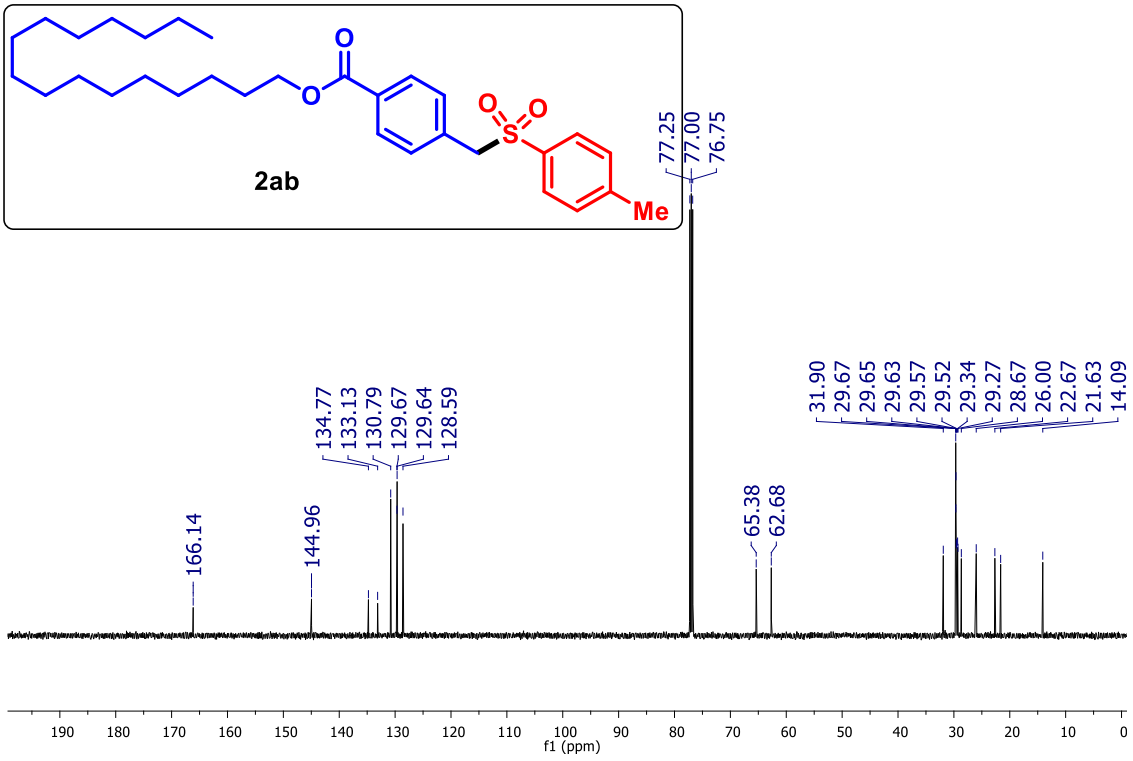


Figure S104. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of hexadecyl 4-(tosylmethyl)benzoate (**2ab**).

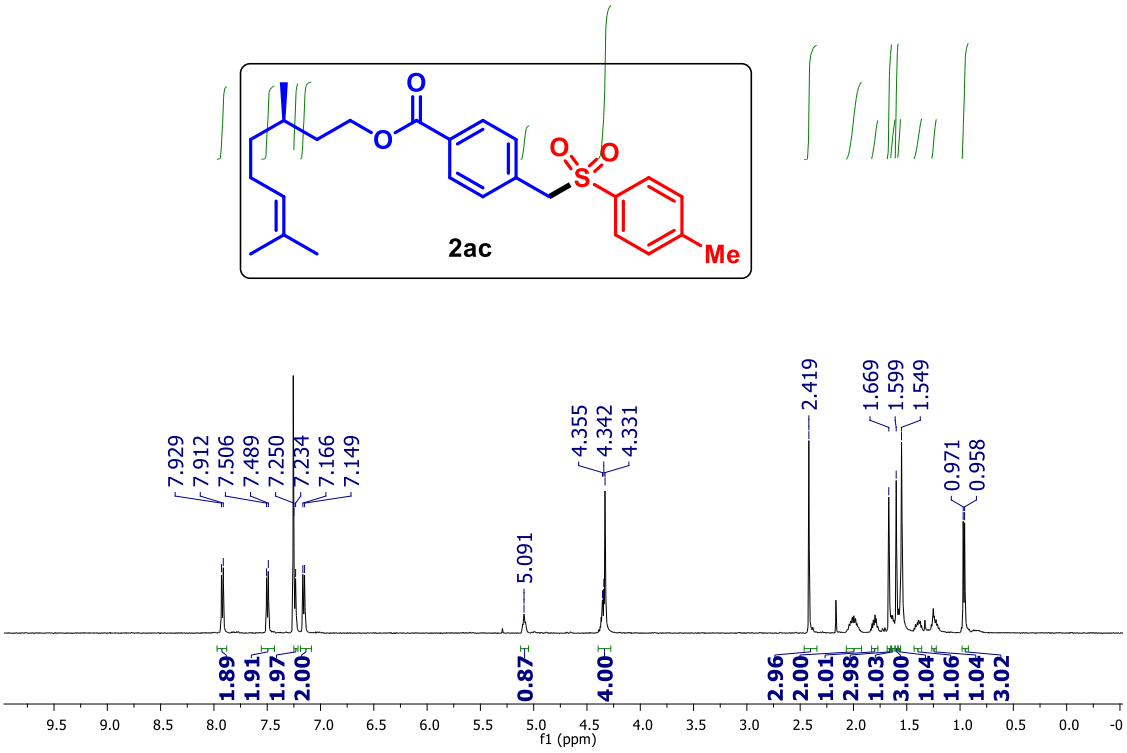


Figure S105. ^{1}H NMR spectrum ($CDCl_3$) of (R)-3,7-dimethyloct-6-en-1-yl 4-(tosylmethyl)benzoate (**2ac**).

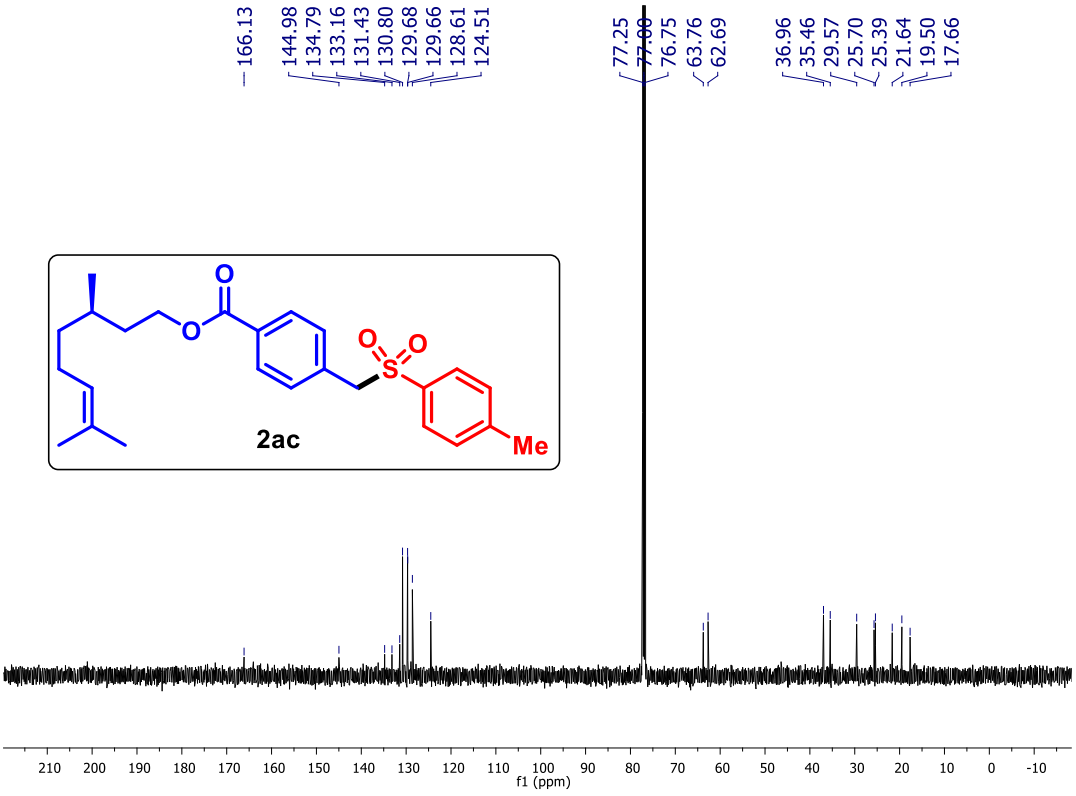


Figure S106. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of (R)-3,7-dimethyloct-6-en-1-yl 4-(tosylmethyl)benzoate (**2ac**).

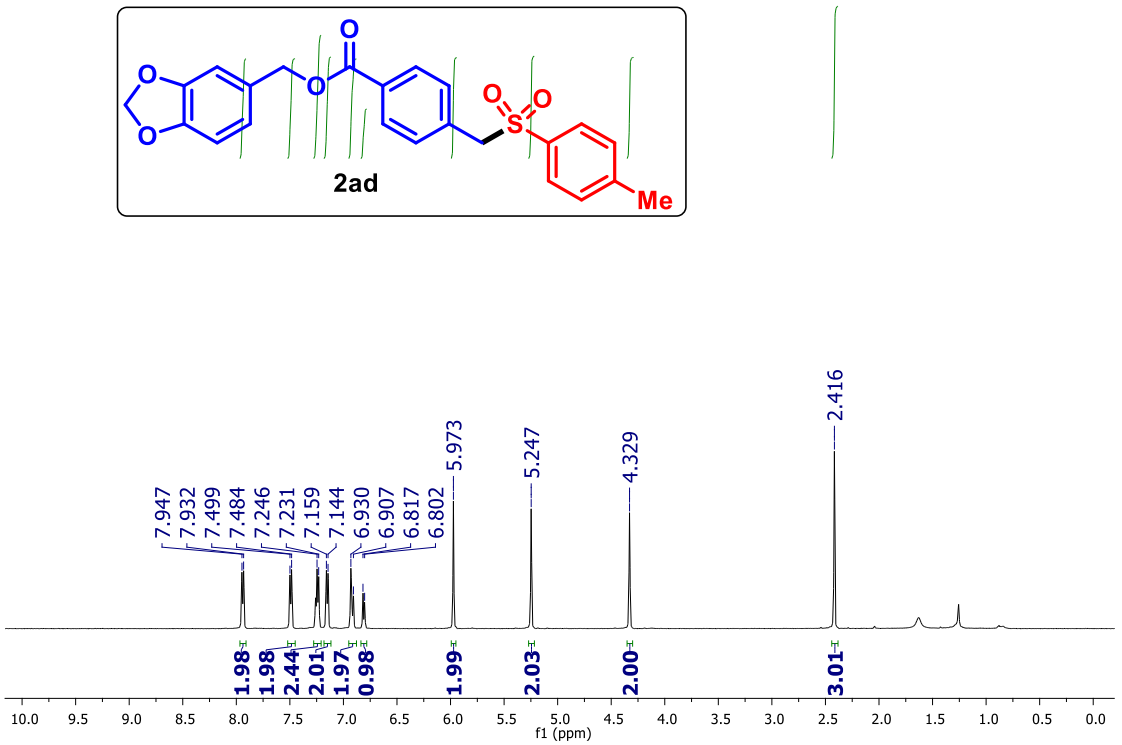


Figure S107. ^{1}H NMR spectrum ($CDCl_3$) of benzo[d][1,3]dioxol-5-ylmethyl 4-(tosylmethyl)benzoate (**2ad**).

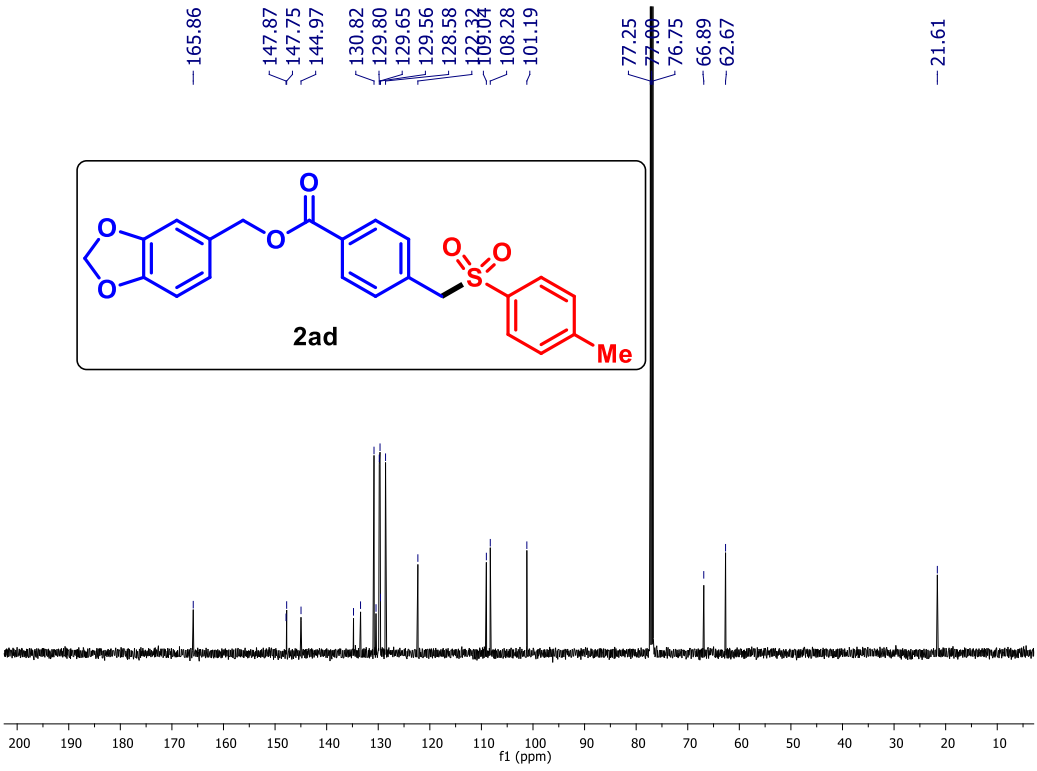


Figure S108. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of benzo[d][1,3]dioxol-5-ylmethyl 4-(tosylmethyl)benzoate (**2ad**).

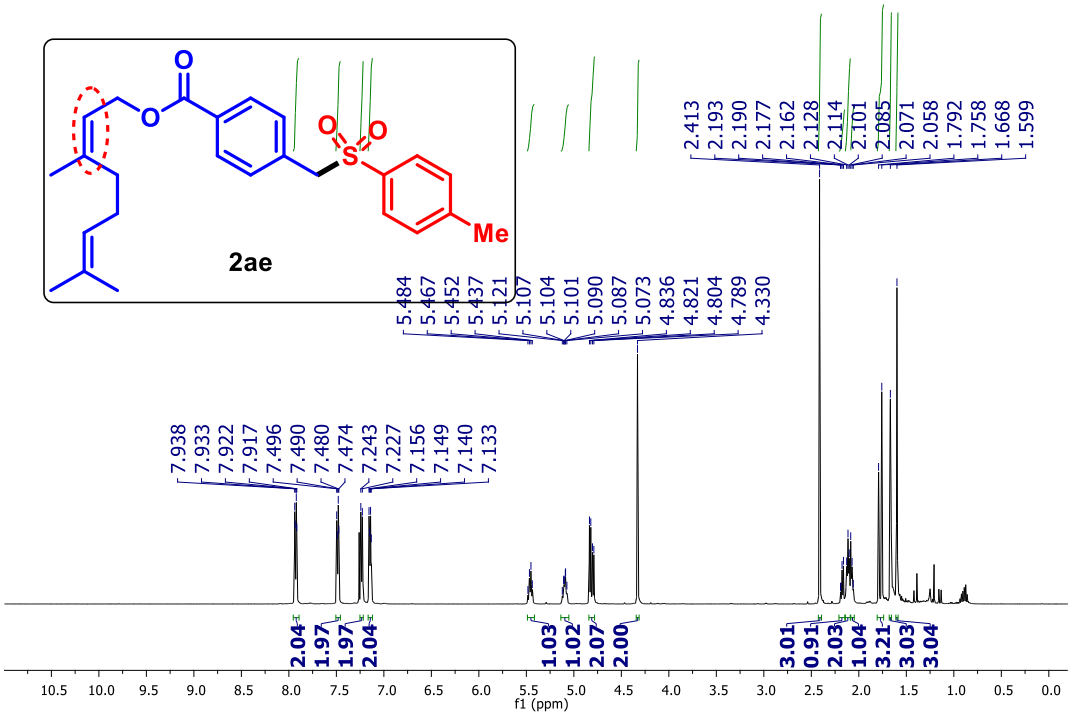


Figure S109. ^{1}H NMR spectrum ($CDCl_3$) of (*Z*)-3,7-dimethylocta-2,6-dien-1-yl 4-(tosylmethyl)benzoate (**2ae**).

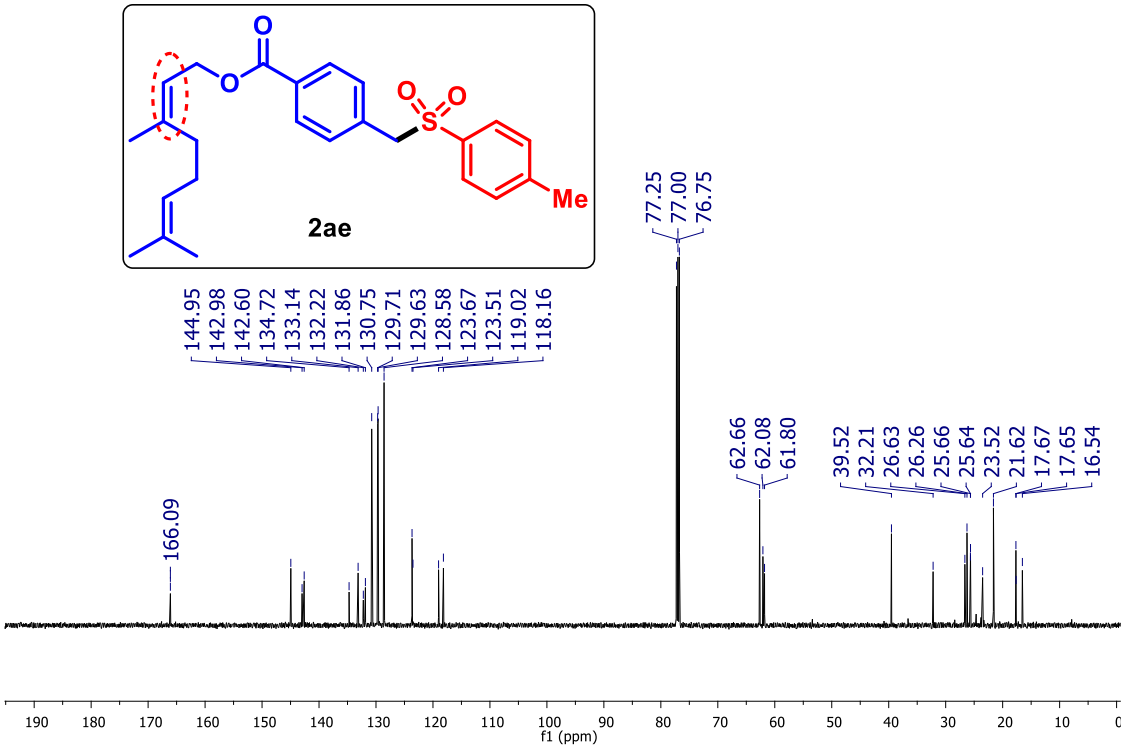


Figure S110. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of (*Z*)-3,7-dimethylocta-2,6-dien-1-yl 4-(tosylmethyl)benzoate (**2ae**).

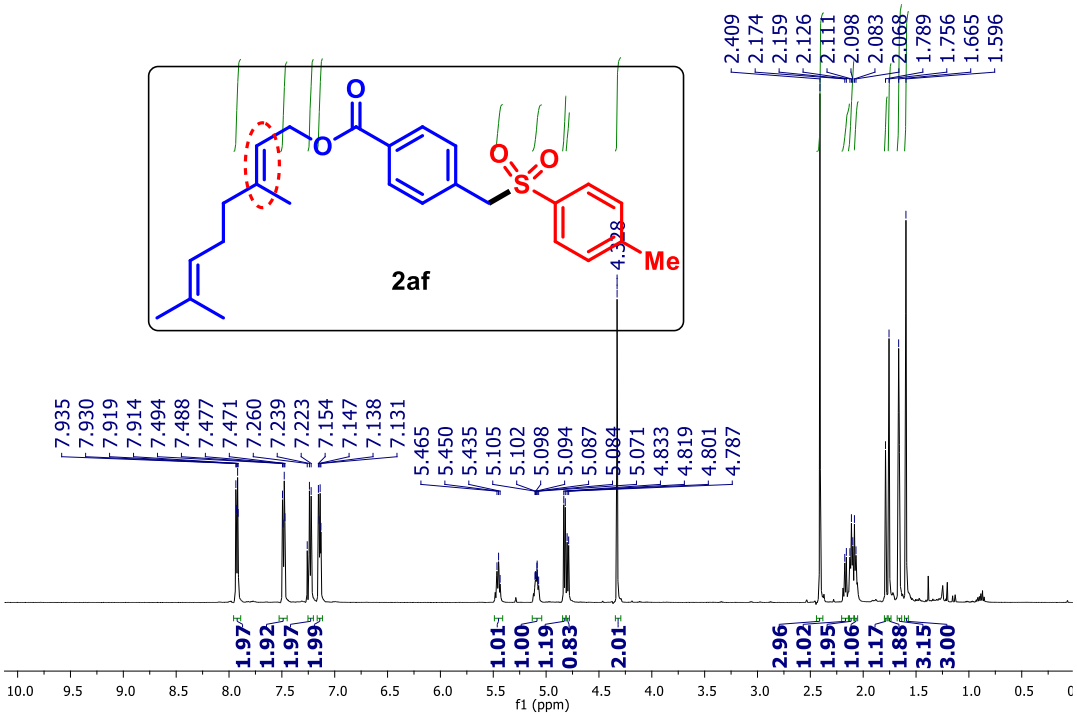


Figure S111. ^{1}H NMR spectrum ($CDCl_3$) of (*E*)-3,7-dimethylocta-2,6-dien-1-yl 4-(tosylmethyl)benzoate (**2af**).

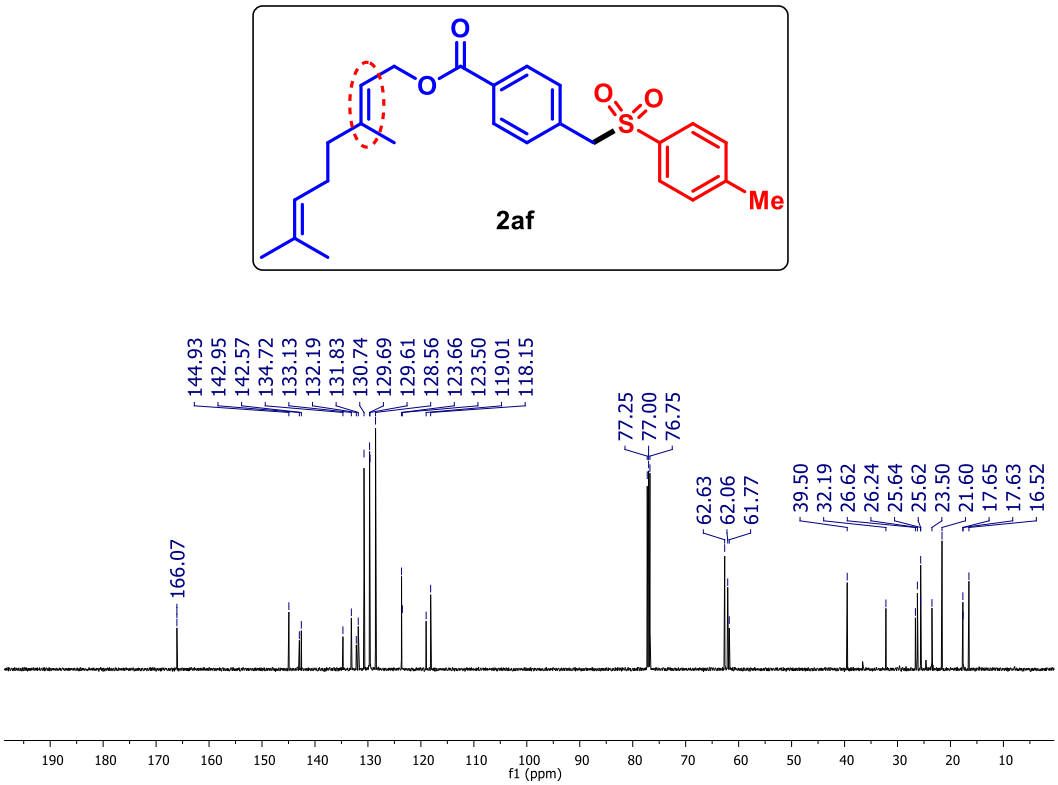


Figure S112. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of (*E*)-3,7-dimethylocta-2,6-dien-1-yl 4-(tosylmethyl)benzoate (**2af**)

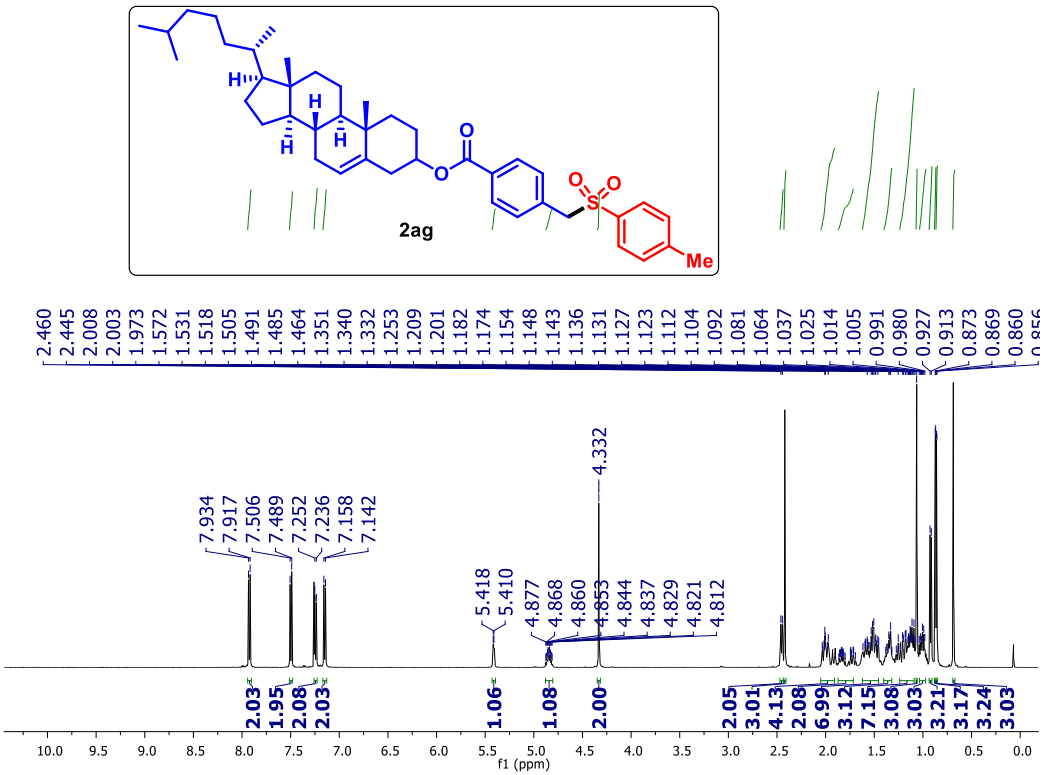


Figure S113. ^{1}H NMR spectrum ($CDCl_3$) of (8R,9R,10S,13S,14R,17S)-10,13-dimethyl-17-((S)-5-methylhexan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(tosylmethyl)benzoate (**2ag**).

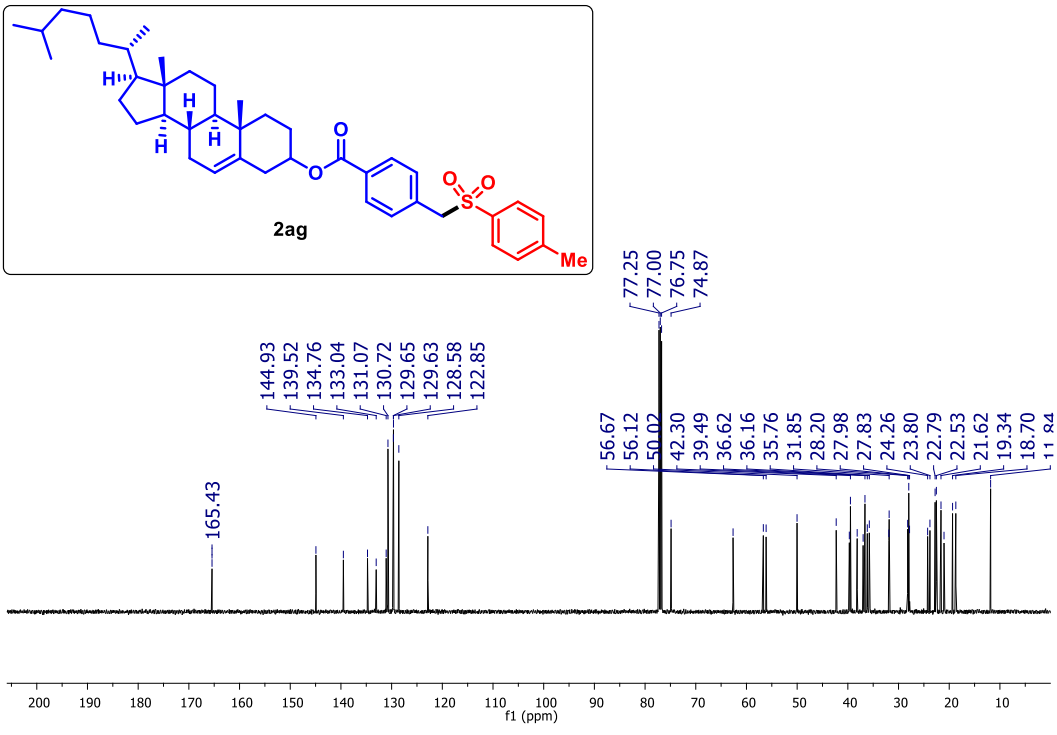


Figure S114. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of (8R,9R,10S,13S,14R,17S)-10,13-dimethyl-17-((S)-5-methylhexan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(tosylmethyl)benzoate (**2ag**).

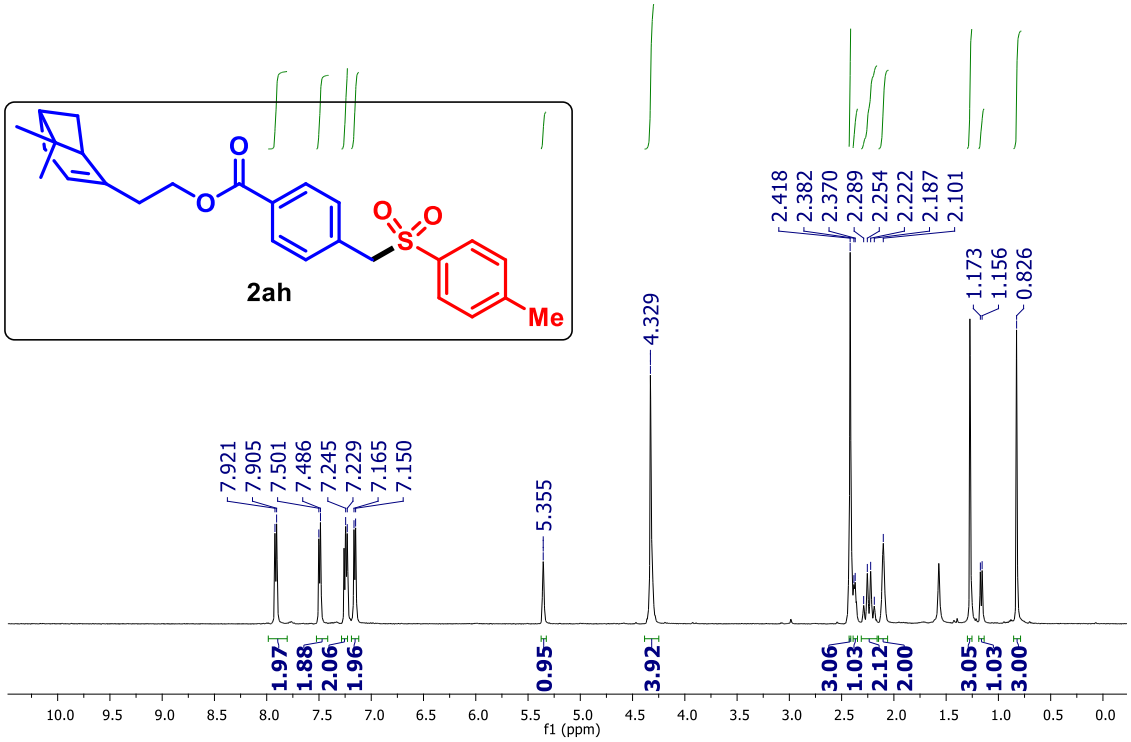


Figure S115. ^{1}H NMR spectrum ($CDCl_3$) of 2-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl 4-(tosylmethyl)benzoate (**2ah**).

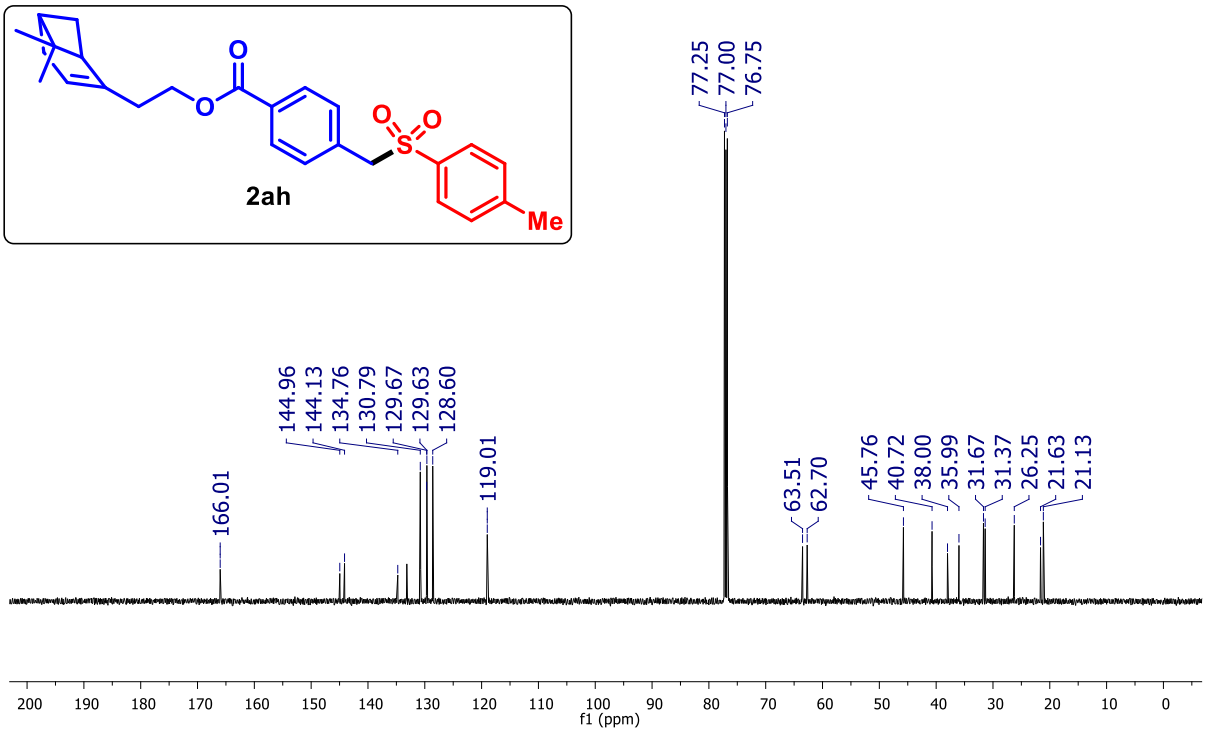


Figure S116. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 2-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl 4-(tosylmethyl)benzoate (**2ah**).

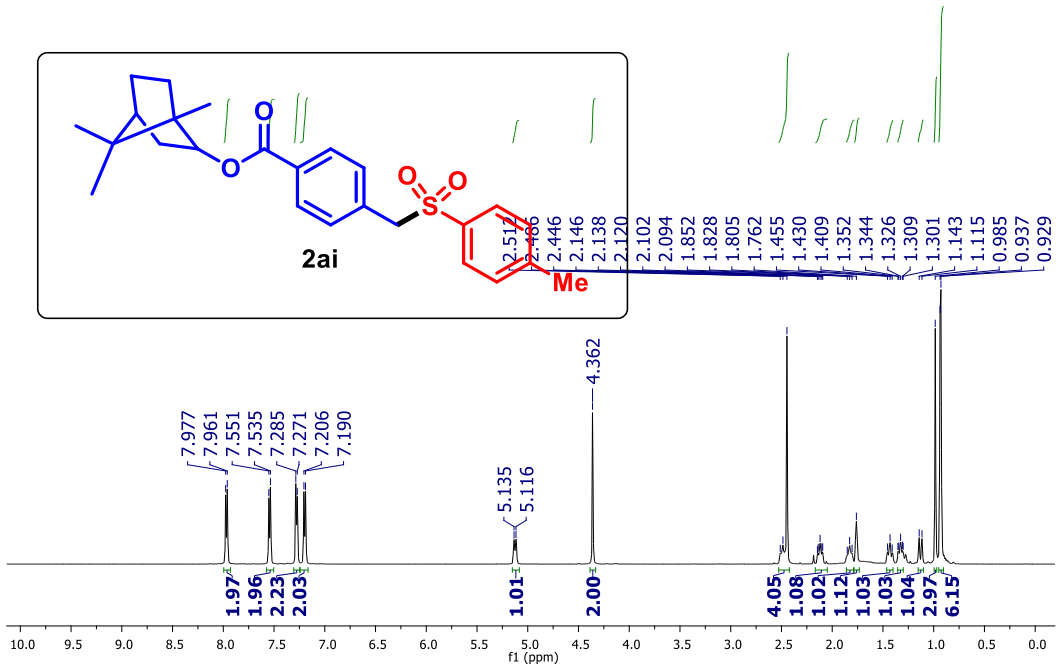


Figure S117. ^{1}H NMR spectrum ($CDCl_3$) of 1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-(tosylmethyl)benzoate (**2ai**).

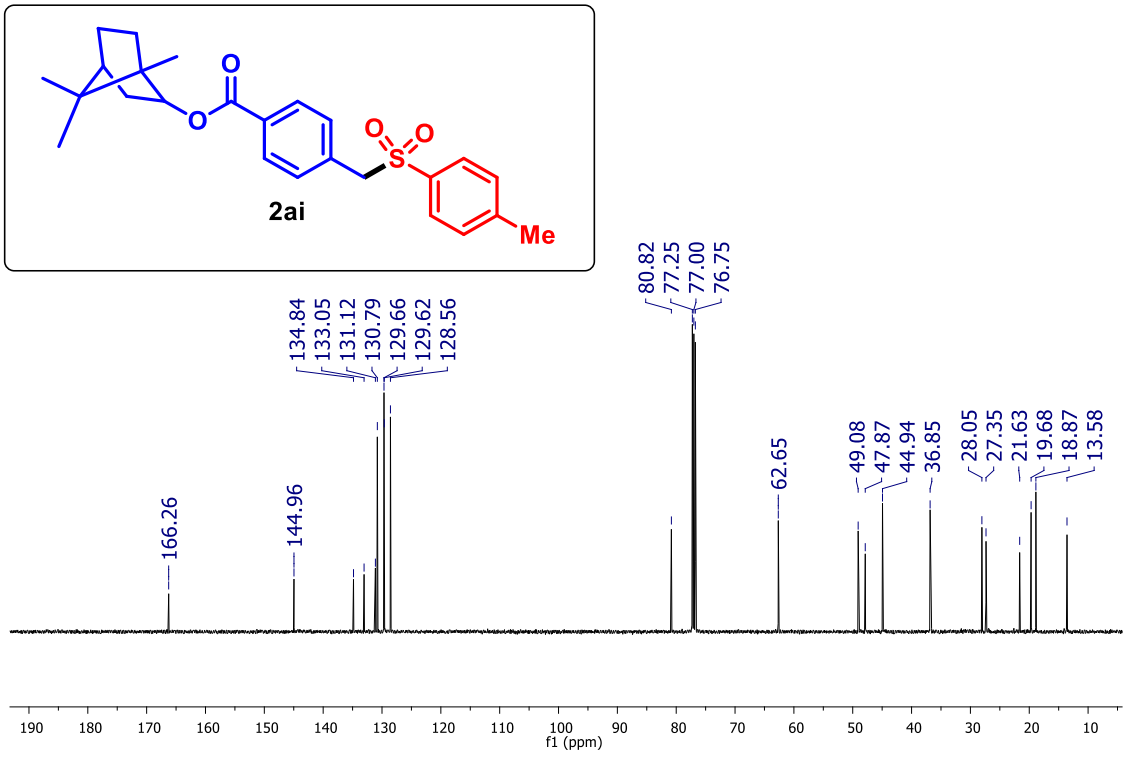


Figure S118. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-(tosylmethyl)benzoate (**2ai**).

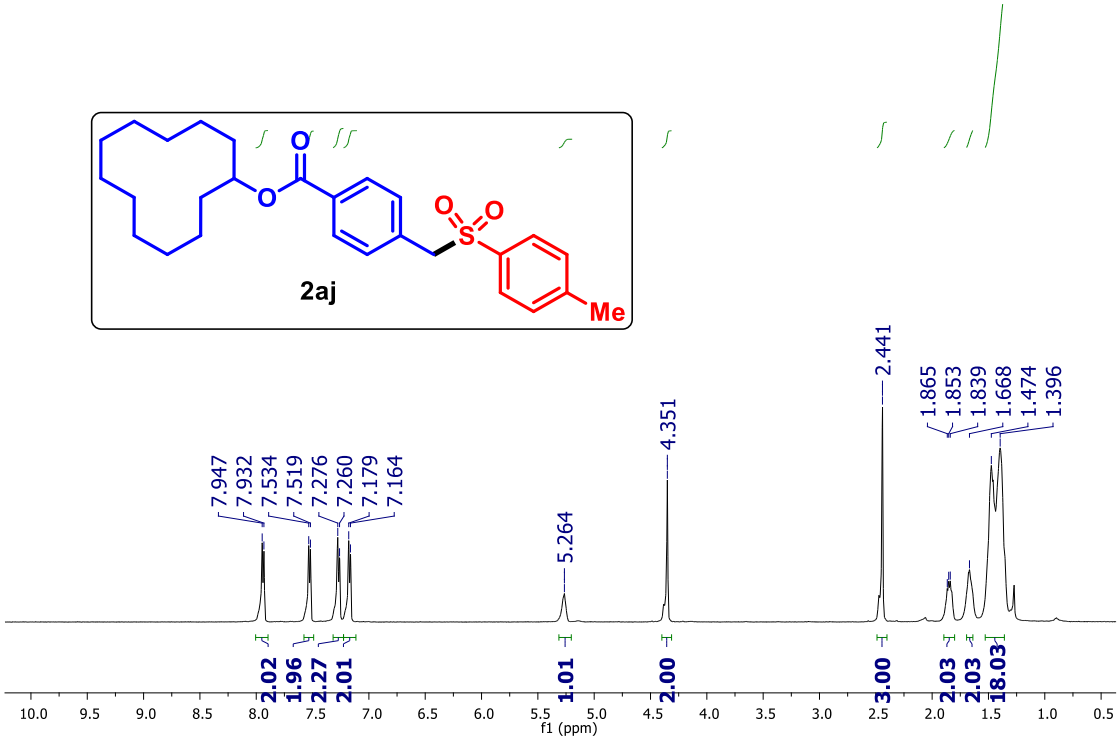


Figure S119. ^{1}H NMR spectrum ($CDCl_3$) of cyclododecyl 4-(tosylmethyl)benzoate (**2aj**).

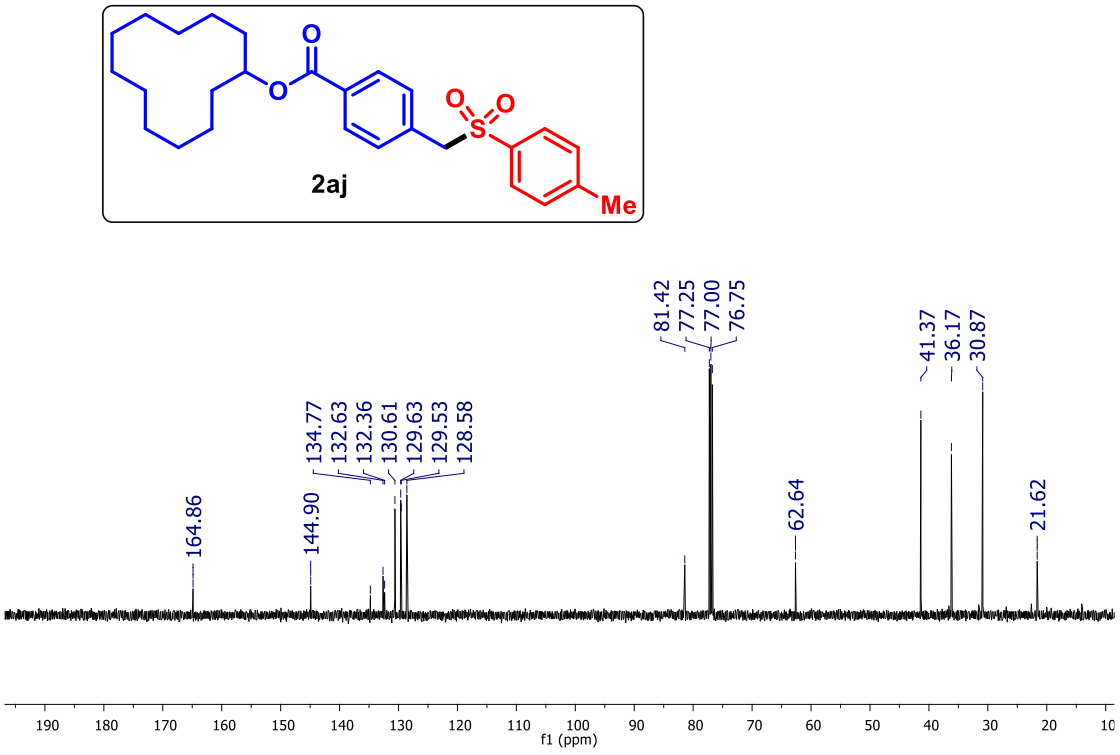


Figure S120. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of cyclododecyl 4-(tosylmethyl)benzoate (**2aj**).

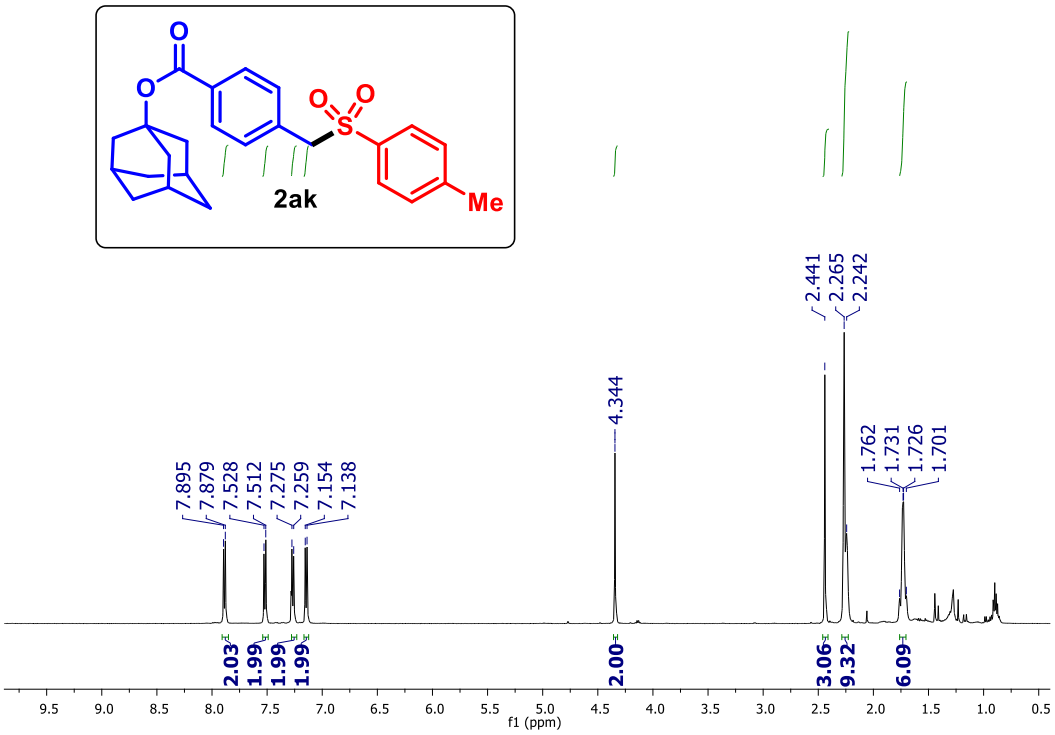


Figure S121. ^{1}H NMR spectrum ($CDCl_3$) of (3s,5s,7s)-adamantan-1-yl 4-(tosylmethyl)benzoate (**2ak**).

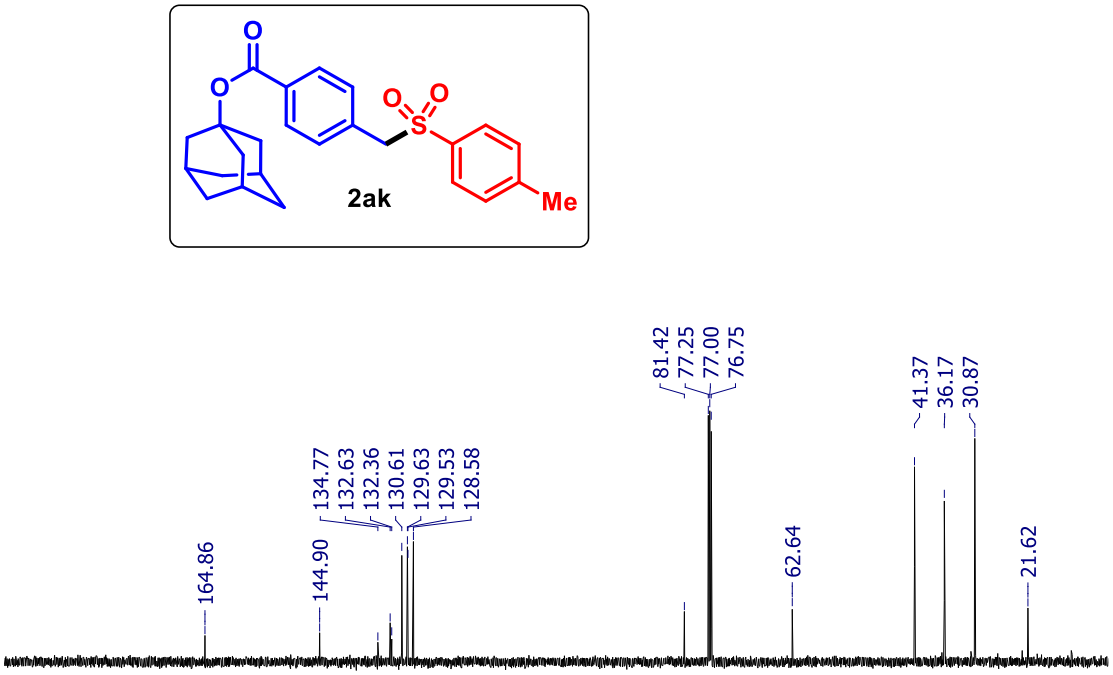


Figure S122. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of (3s,5s,7s)-adamantan-1-yl 4-(tosylmethyl)benzoate (**2ak**).

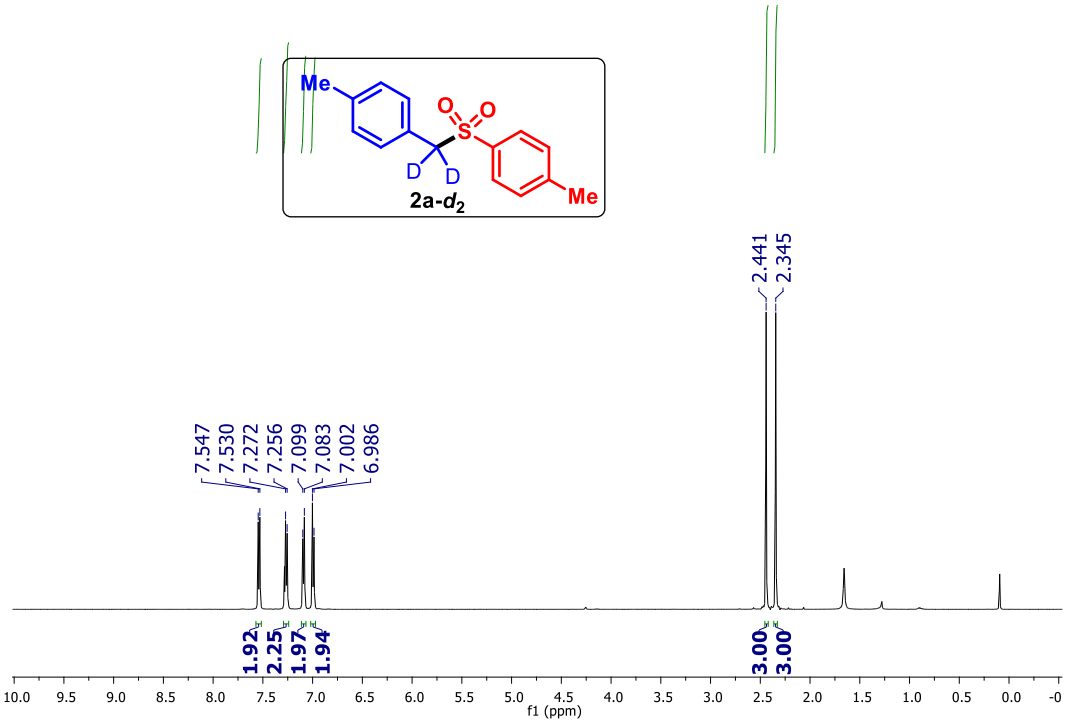


Figure S123. ^{1}H NMR spectrum ($CDCl_3$) of 1-methyl-4-((p-tolylmethyl-d2)sulfonyl)benzene **2a-*d*$_2$.**

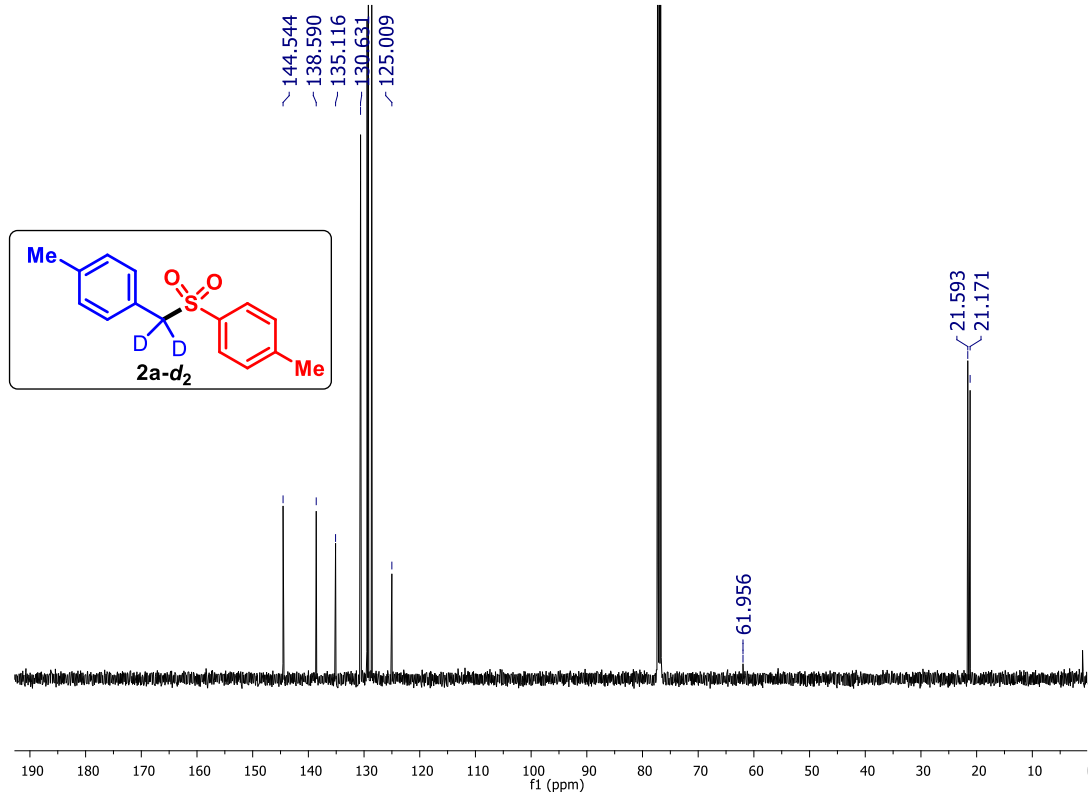


Figure S124. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1-methyl-4-((p-tolylmethyl-d2)sulfonyl)benzene **2a-*d*$_2$.**

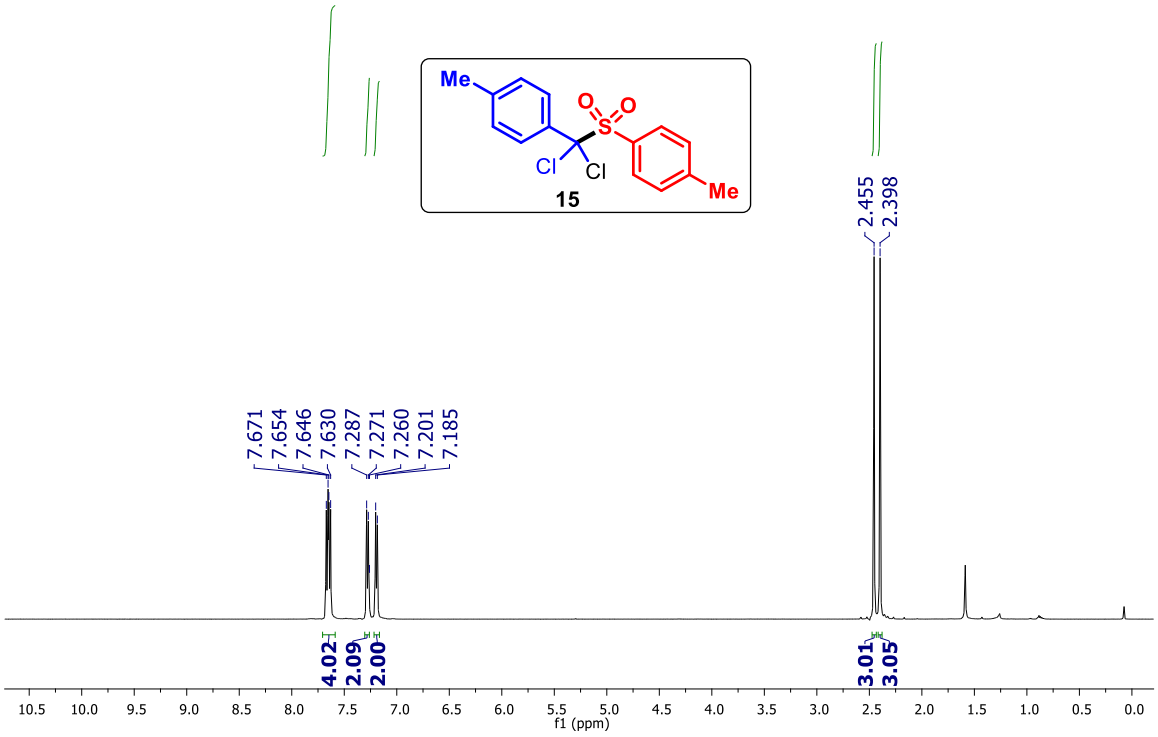


Figure S125. ^{1}H NMR spectrum ($CDCl_3$) of 1-((dichloro(p-tolyl)methyl)sulfonyl)-4-methylbenzene **15**.

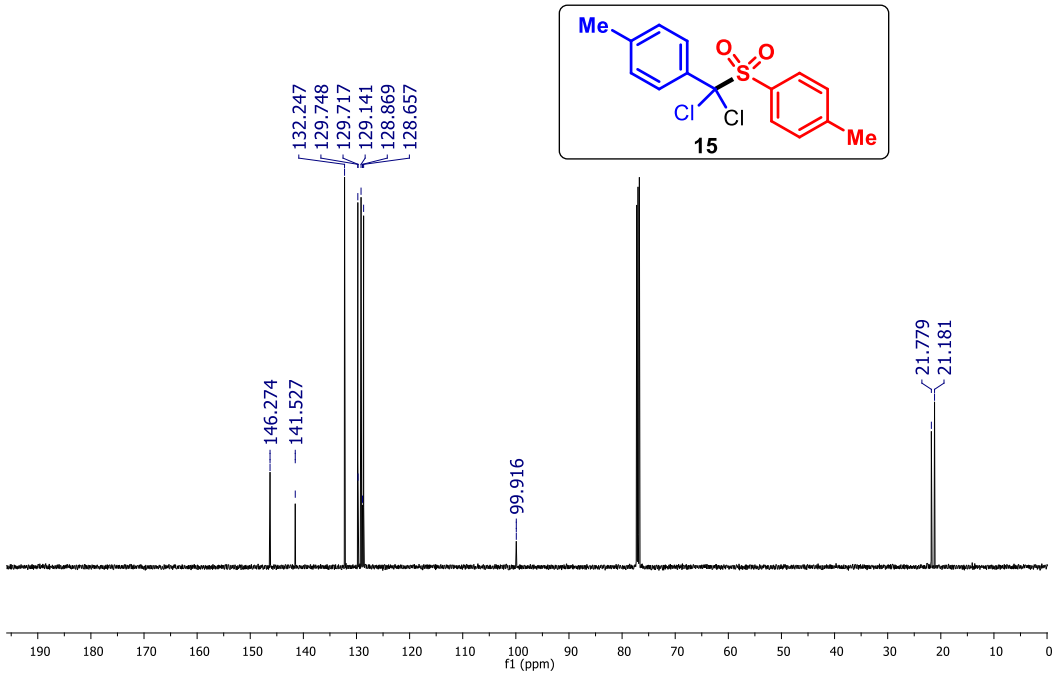
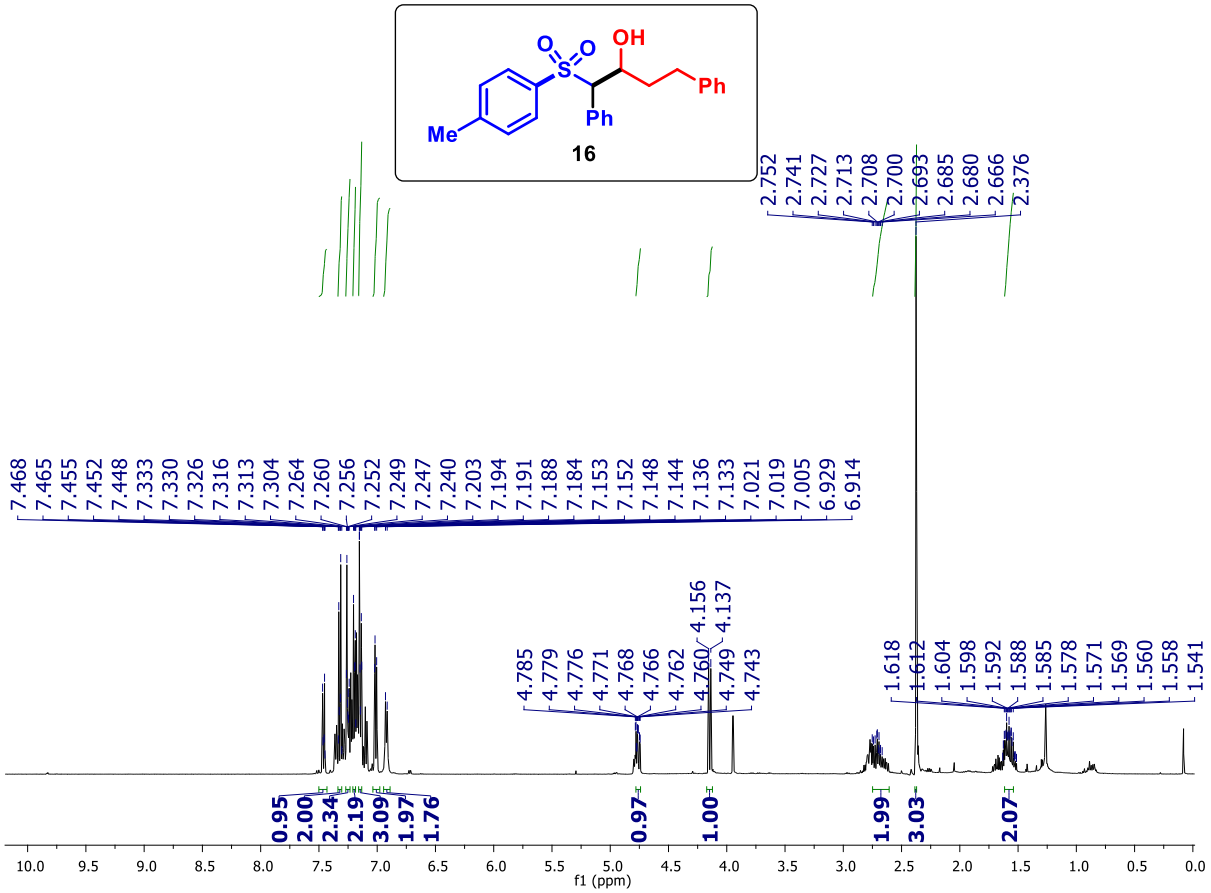


Figure S126. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of 1-((dichloro(p-tolyl)methyl)sulfonyl)-4-methylbenzene**15**



.**Figure S127.** ^{1}H NMR spectrum ($CDCl_3$) of (1R,2S)-1,4-diphenyl-1-tosylbutan-2-ol **16.**

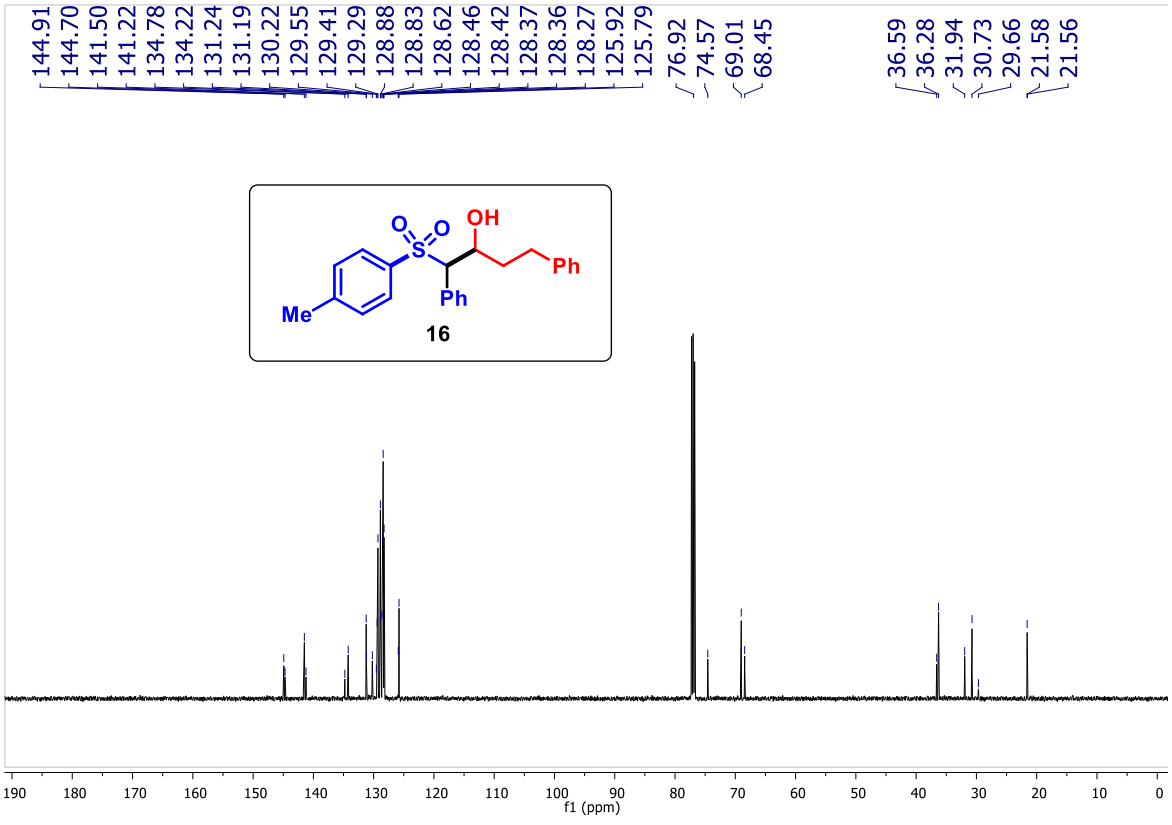


Figure S128. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of (1R,2S)-1,4-diphenyl-1-tosylbutan-2-ol **16.**

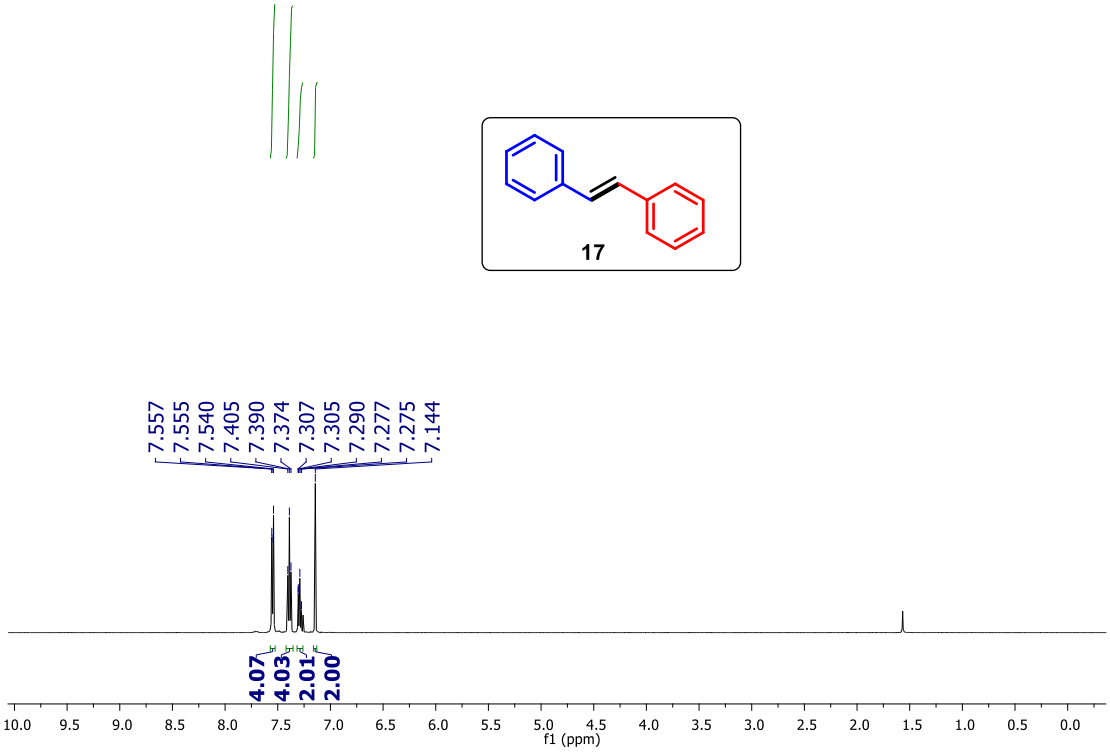


Figure S129. ^{1}H NMR spectrum ($CDCl_3$) of (E)-1,2-diphenylethene **17**. [12]

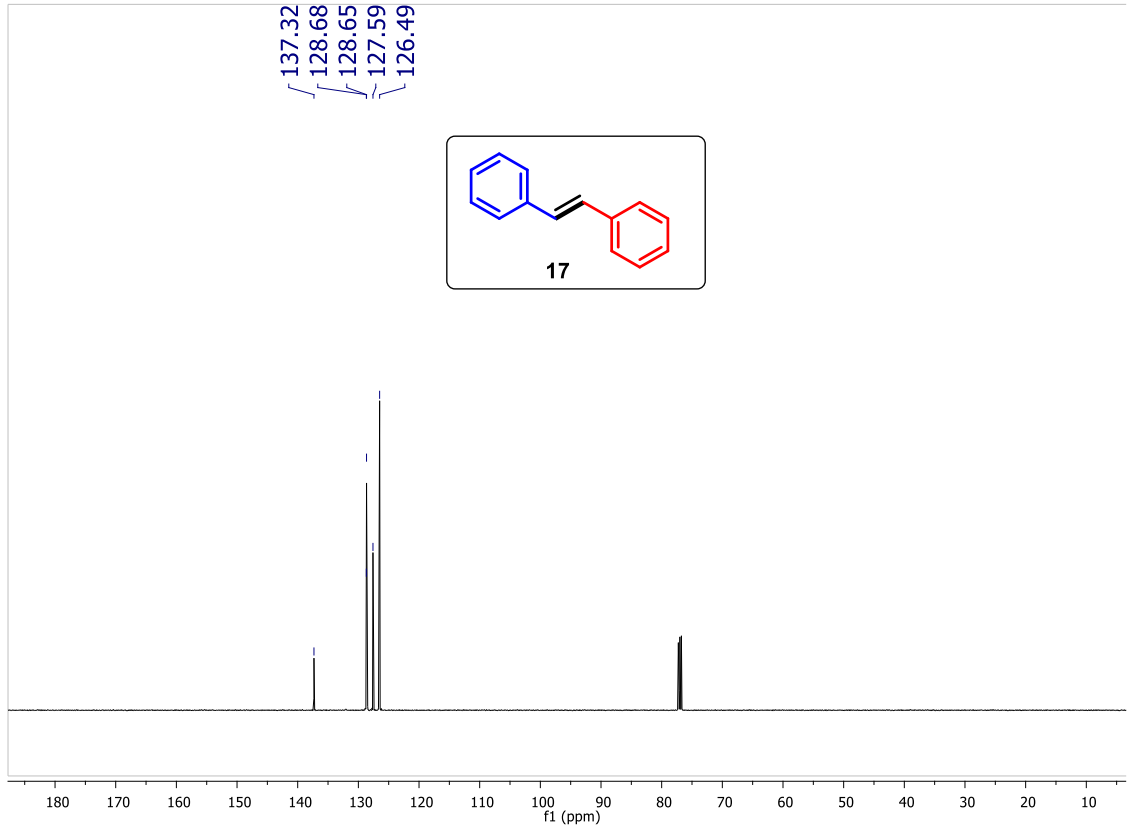
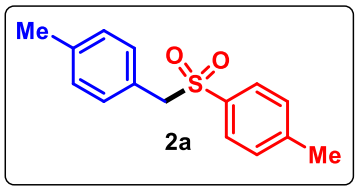


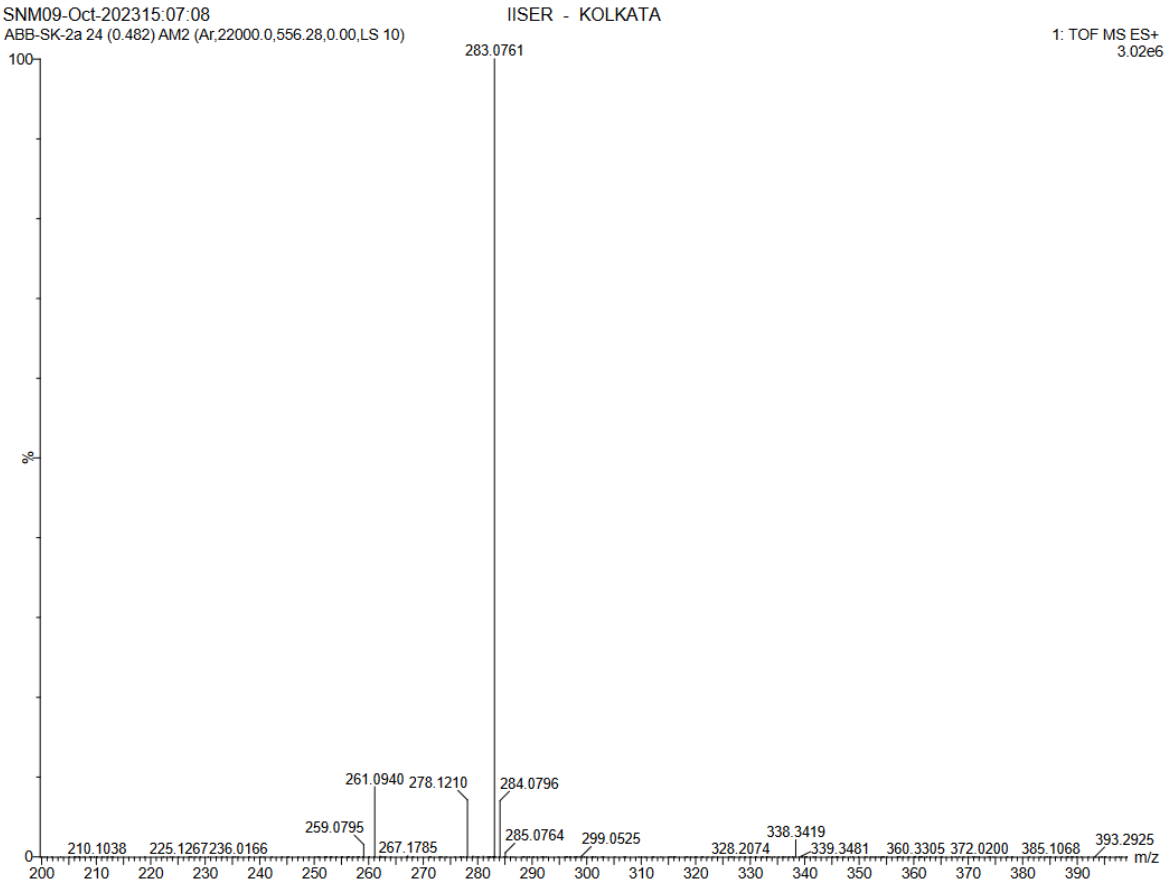
Figure S130. ^{13}C {^{1}H} NMR spectrum ($CDCl_3$) of (E)-1,2-diphenylethene **17**. [12]

VII. HRMS Spectra

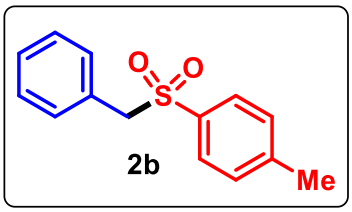
1-Methyl-4-((4-methylbenzyl)sulfonyl)benzene (2a):[6]



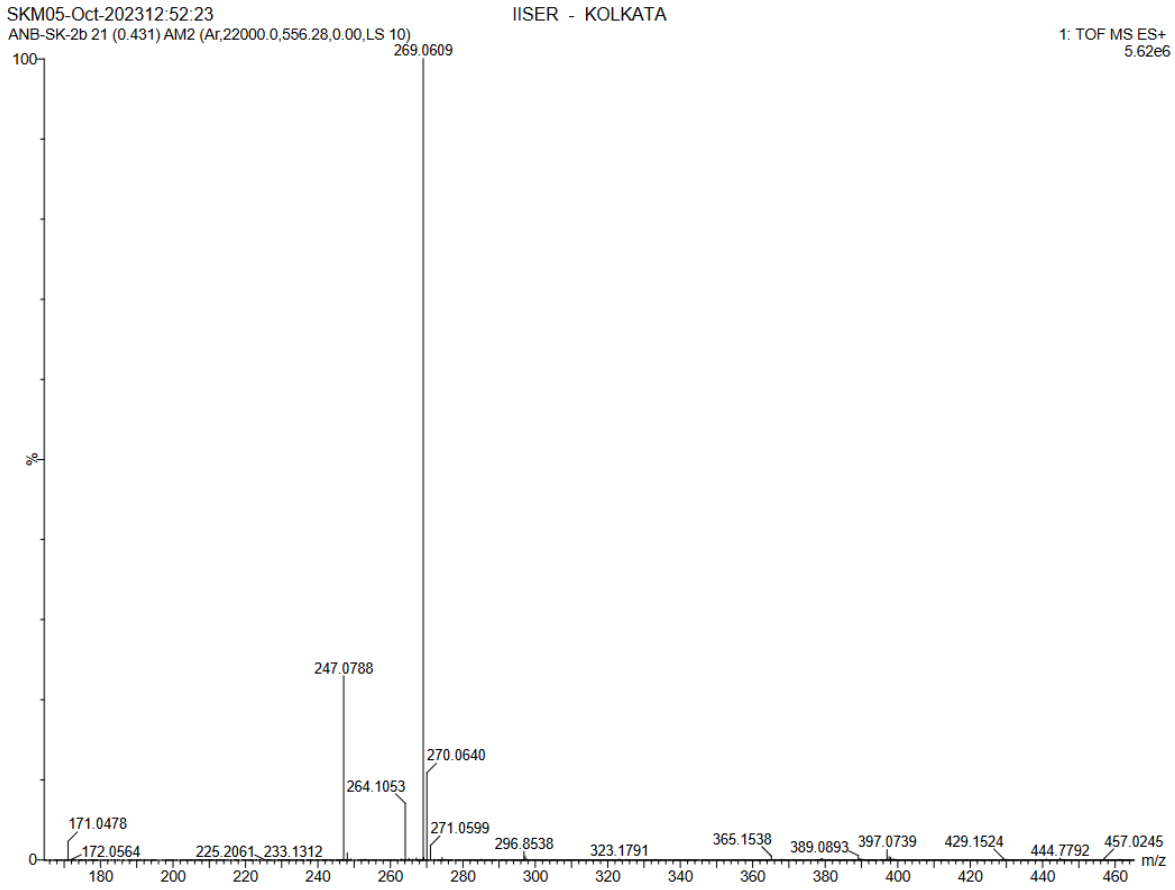
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{16}NaO_2S$ is 283.0764; found 283.0761.



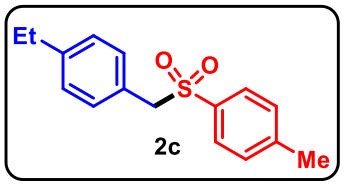
1-(Benzylsulfonyl)-4-methylbenzene (2b):[6]



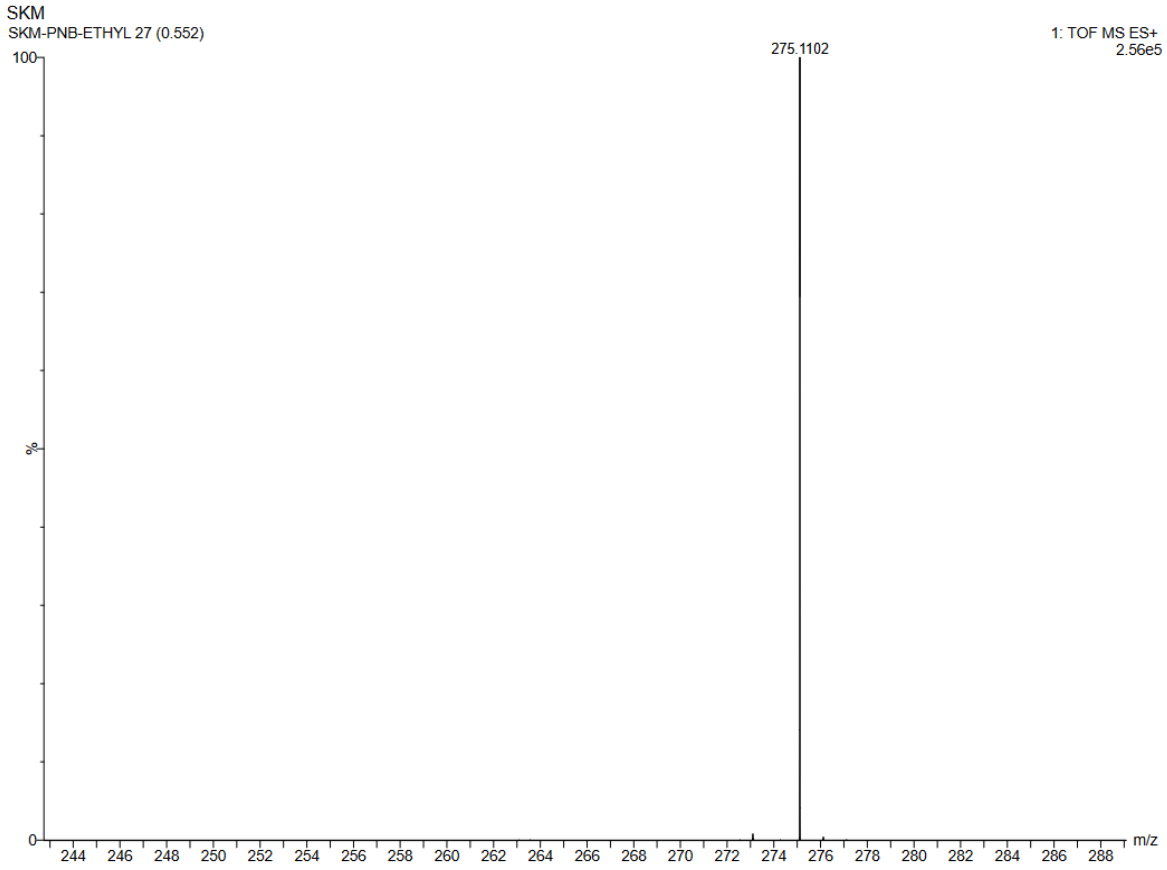
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{14}H_{14}NaO_2S$ is 269.0607; found 269.0609.



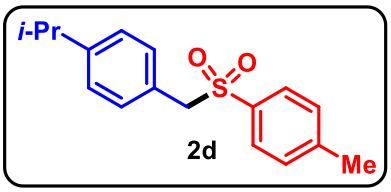
1-Ethyl-4-(tosylmethyl)benzene (2c):



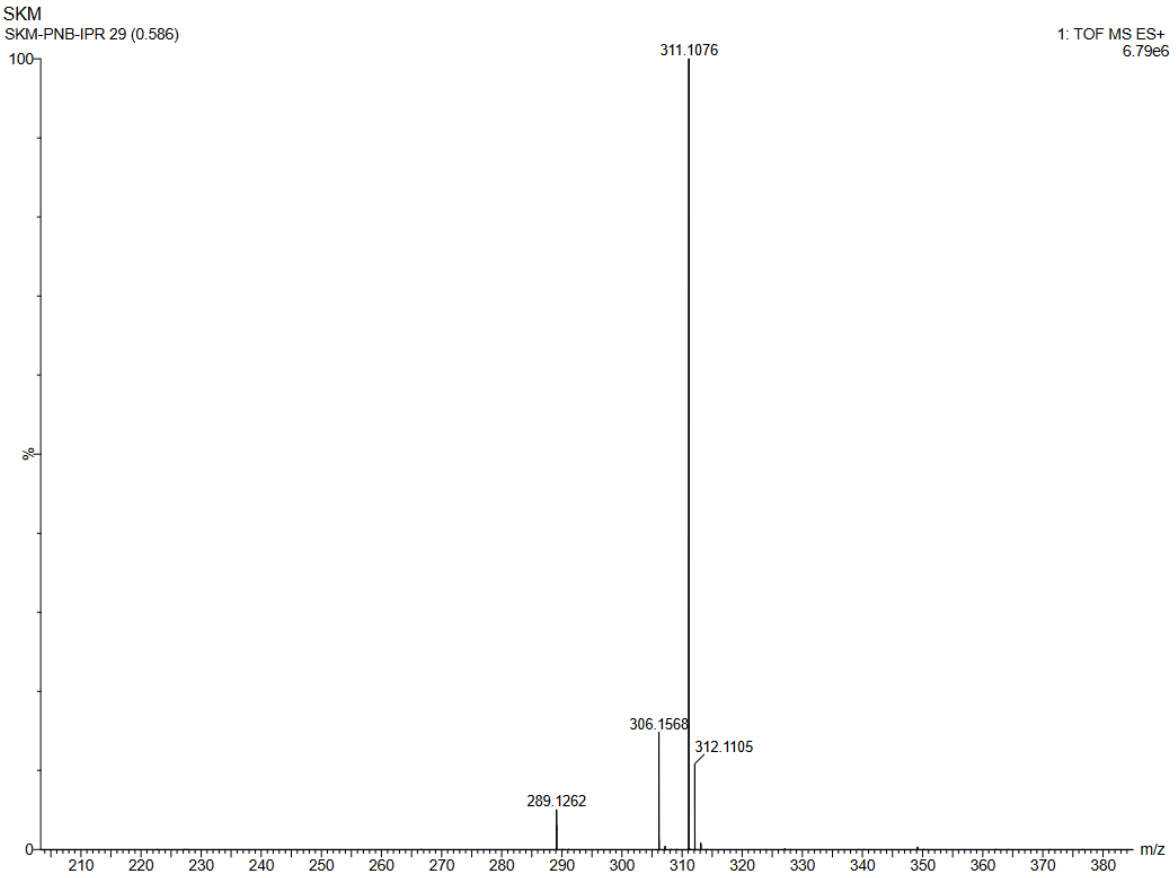
HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{19}O_2S$ is 275.1101; found 275.1102.



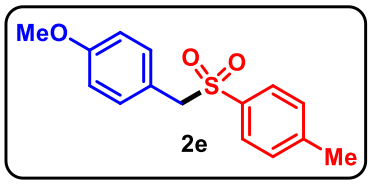
1-Isopropyl-4-(tosylmethyl)benzene (2d):



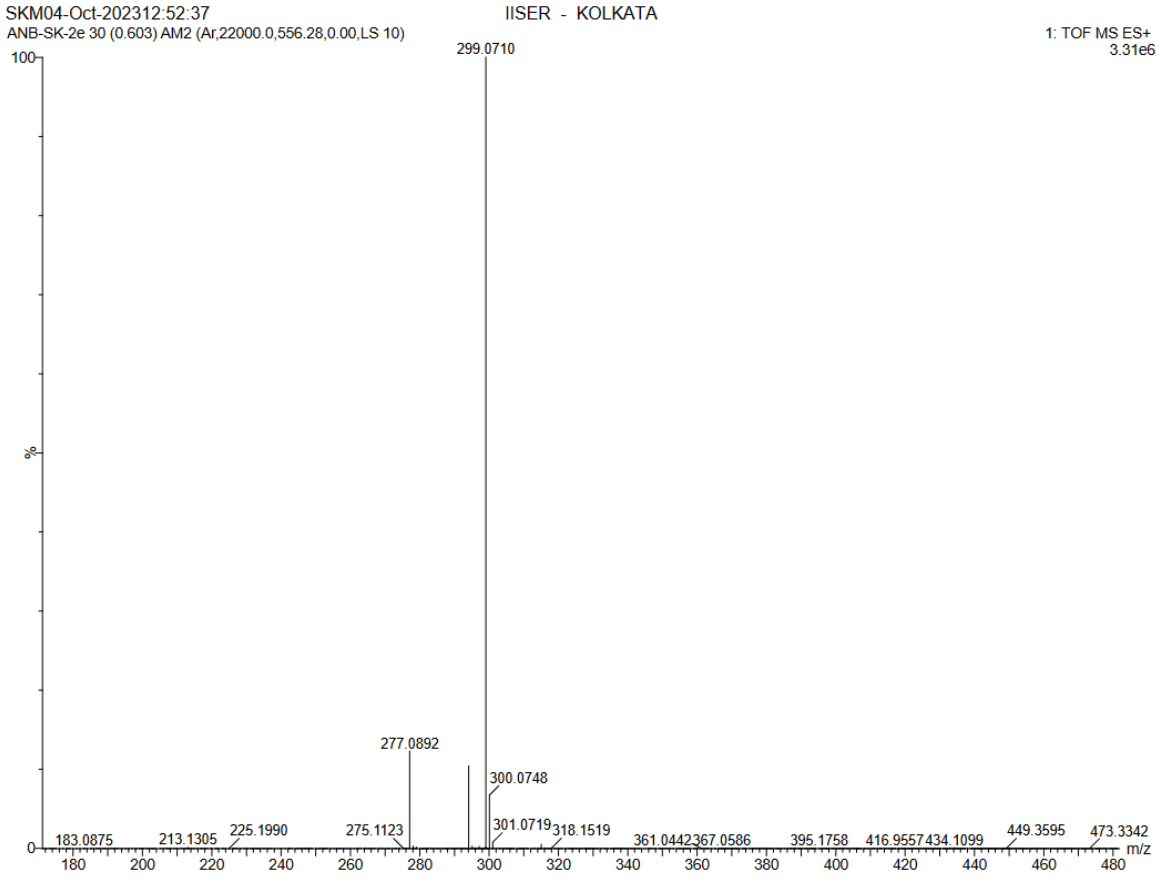
HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{20}O_2S$ 289.1262; found 289.1262.



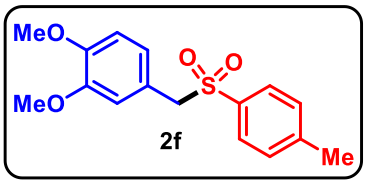
1-Methoxy-4-(tosylmethyl)benzene (2e): [6]



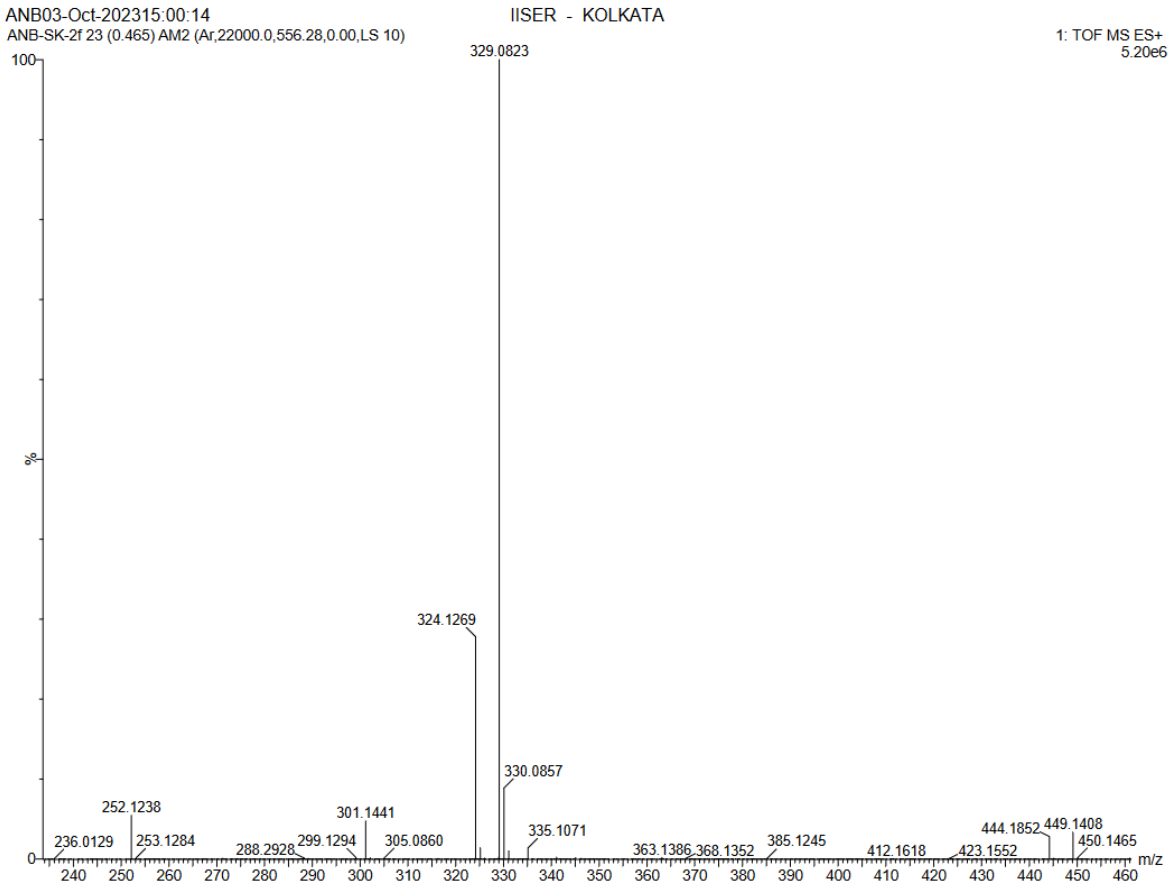
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{16}NaO_3S$ 299.0713; found 299.0710.



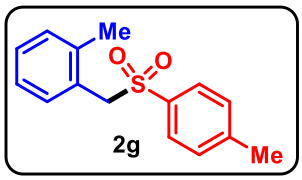
1,2-Dimethoxy-4-(tosylmethyl)benzene (2f): [6]



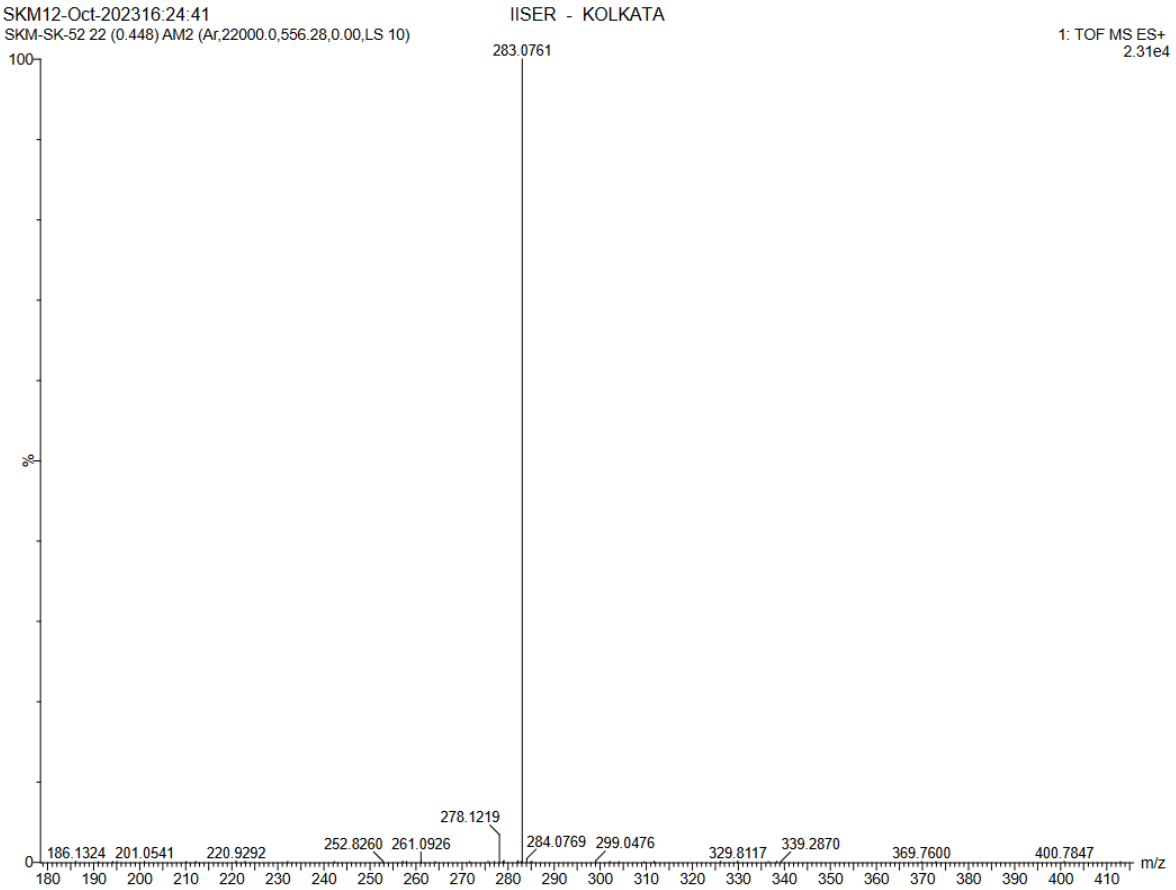
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{18}NaO_4S$ 329.0818; found 329.0823.



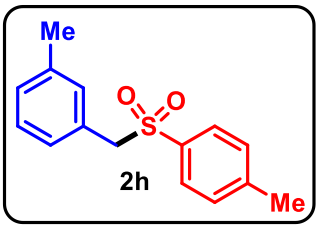
1-Methyl-2-(tosylmethyl)benzene (2g): [6]



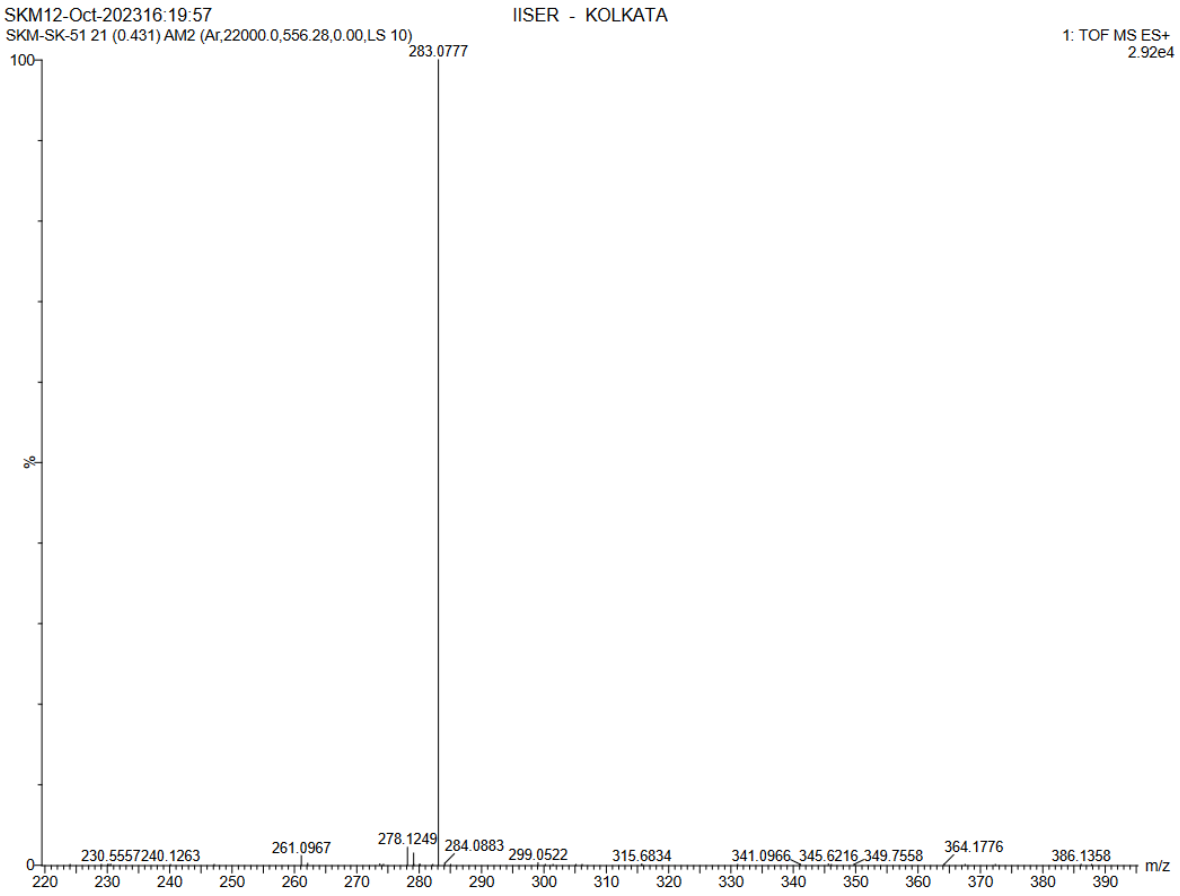
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{16}NaO_2S$ is 283.0761; found 283.0761.



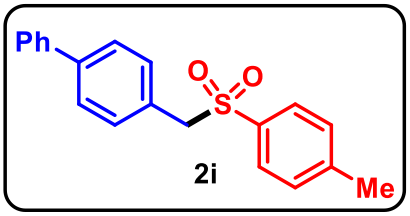
1-Methyl-3-(tosylmethyl)benzene (2h): [6]



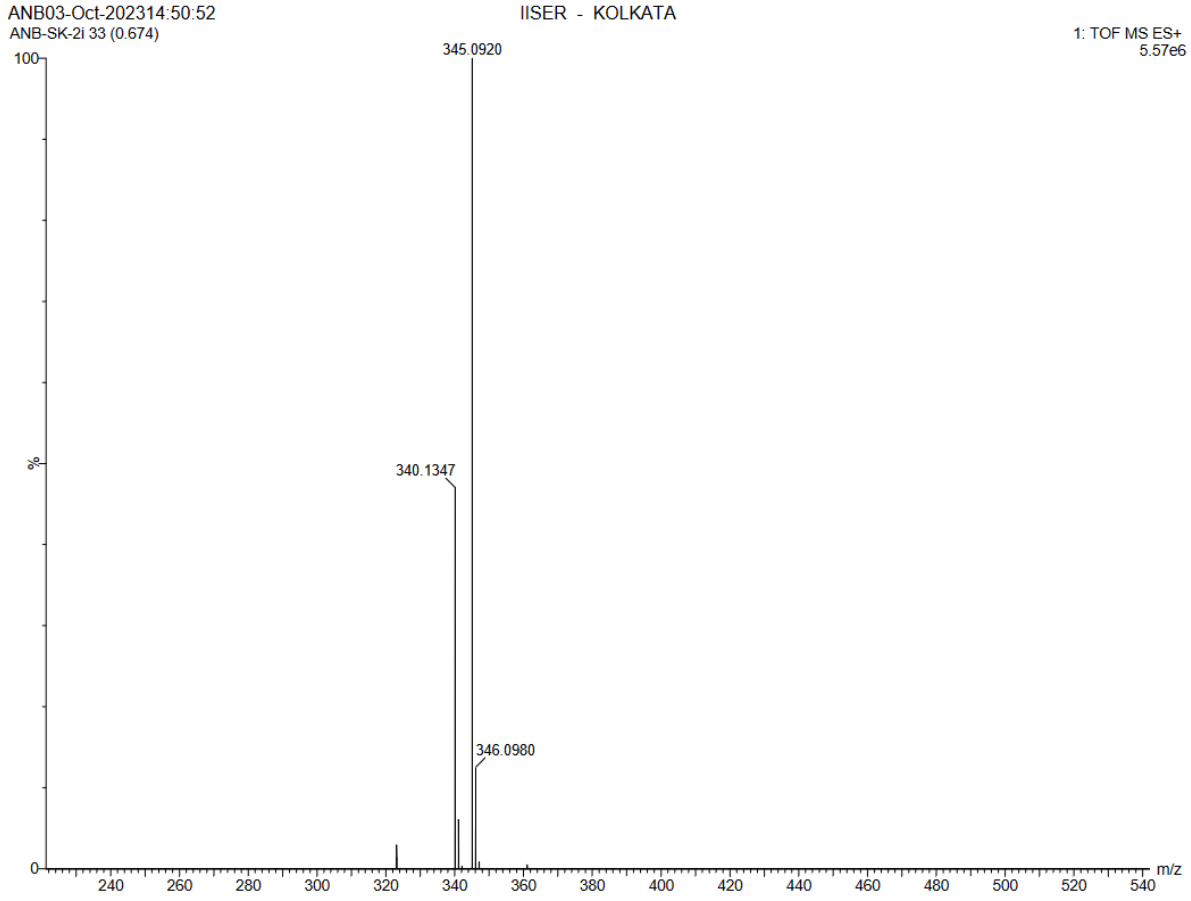
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{16}NaO_2S$ is 283.0761; found 283.0777.



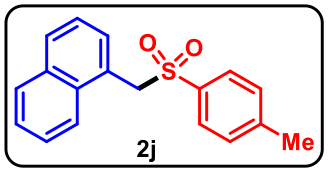
4-(Tosylmethyl)-1,1'-biphenyl (2i): [6]



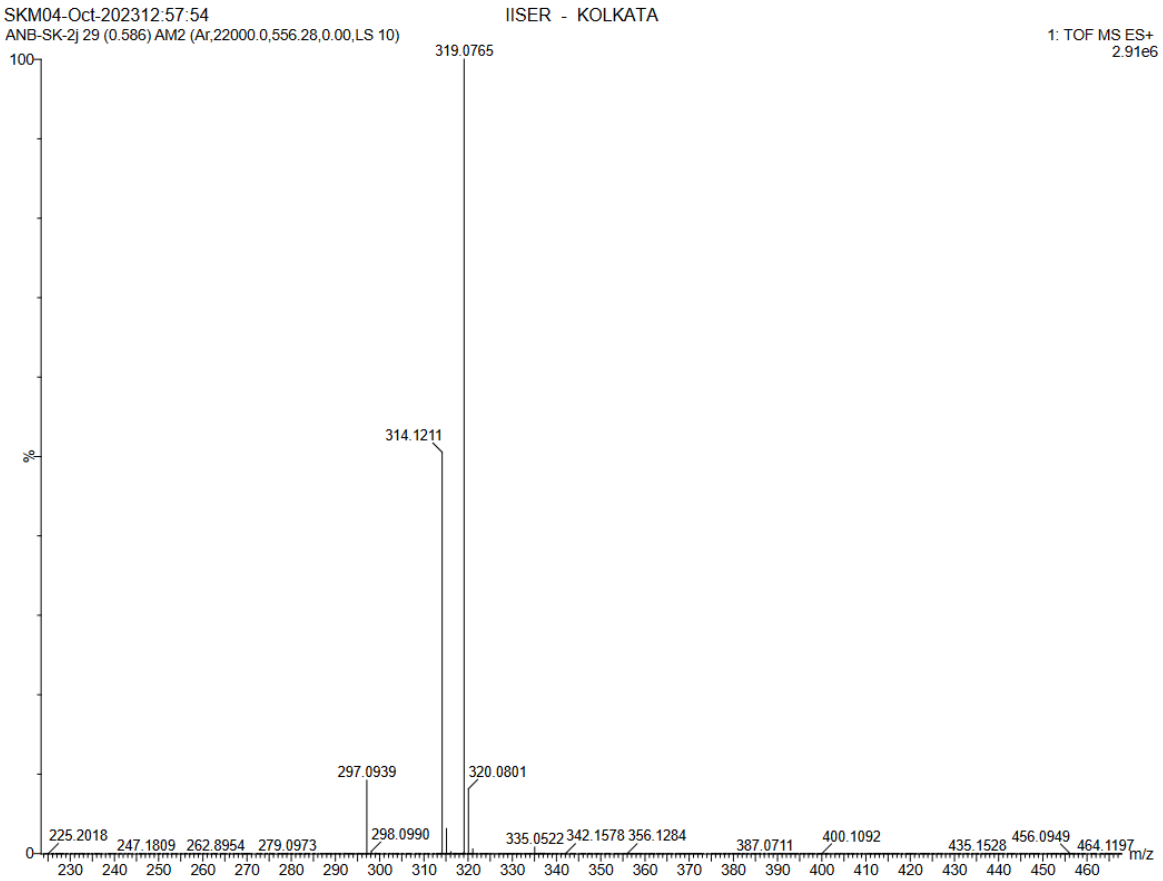
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{20}H_{18}NaO_2S$ 345.0920; found 345.0920.



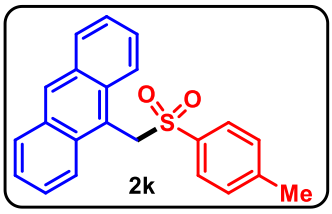
1-(Tosylmethyl)naphthalene (2j): [6]



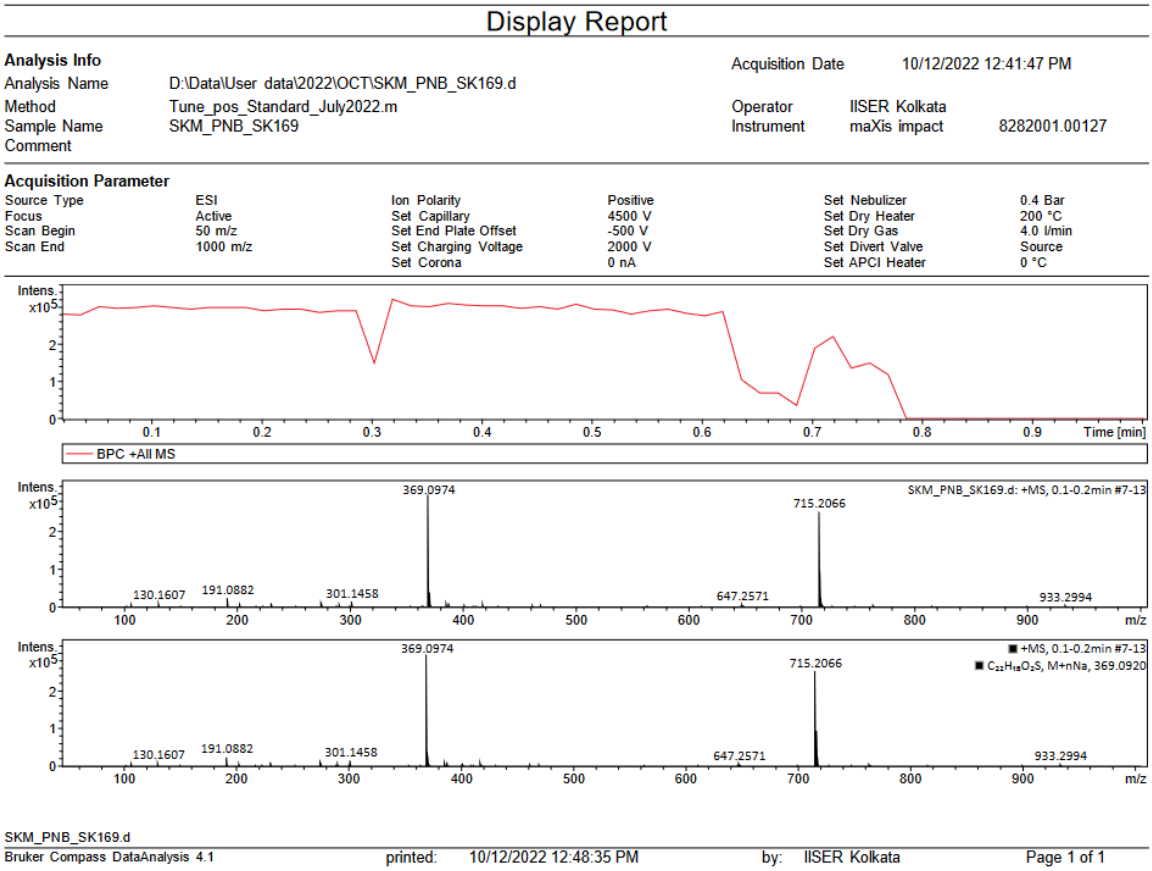
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{20}H_{18}NaO_2S$ 319.0764; found 319.0765.



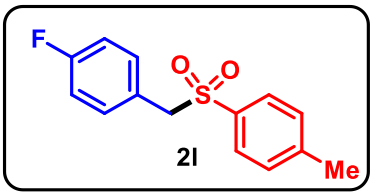
9-(Tosylmethyl)anthracene (2k):



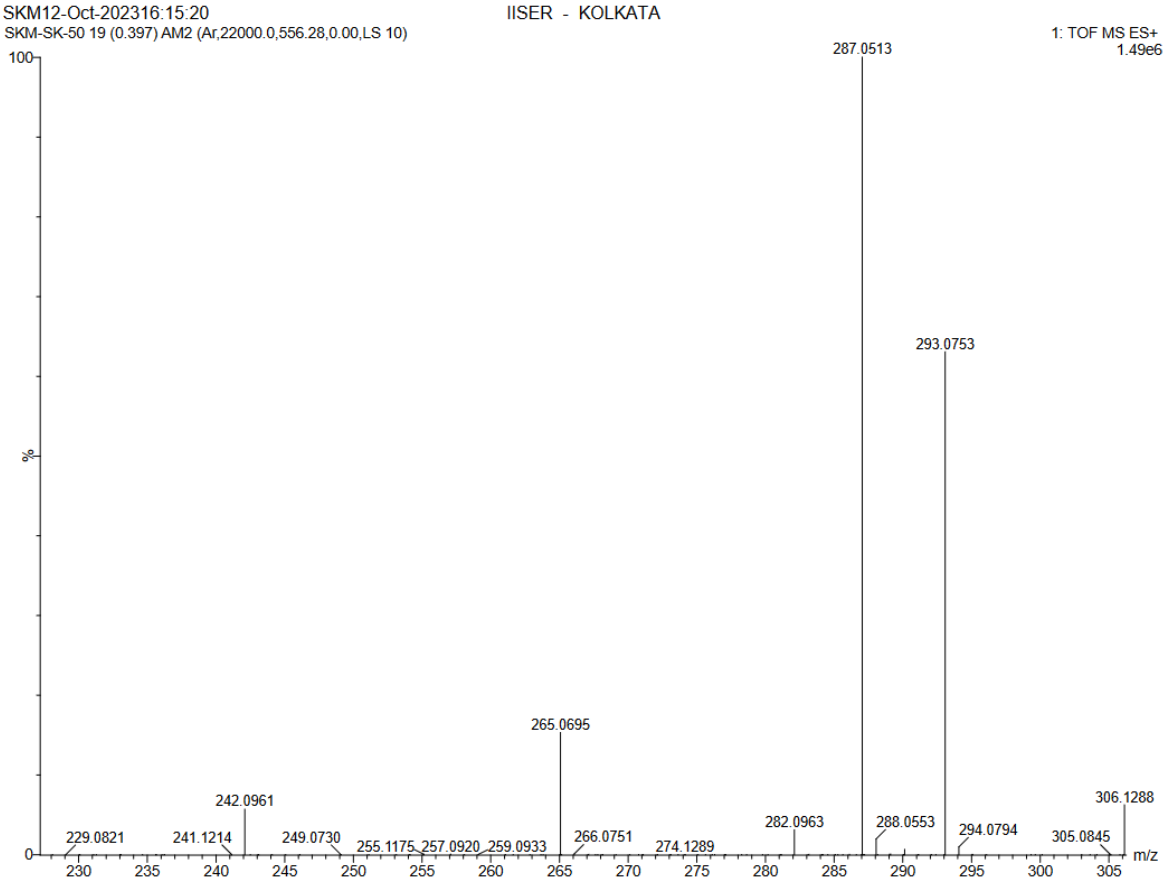
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{18}O_2SNa$ 369.0920; found 369.0974.



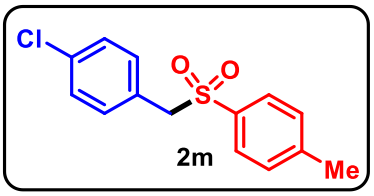
1-Fluoro-4-(tosylmethyl)benzene (2l): [6]



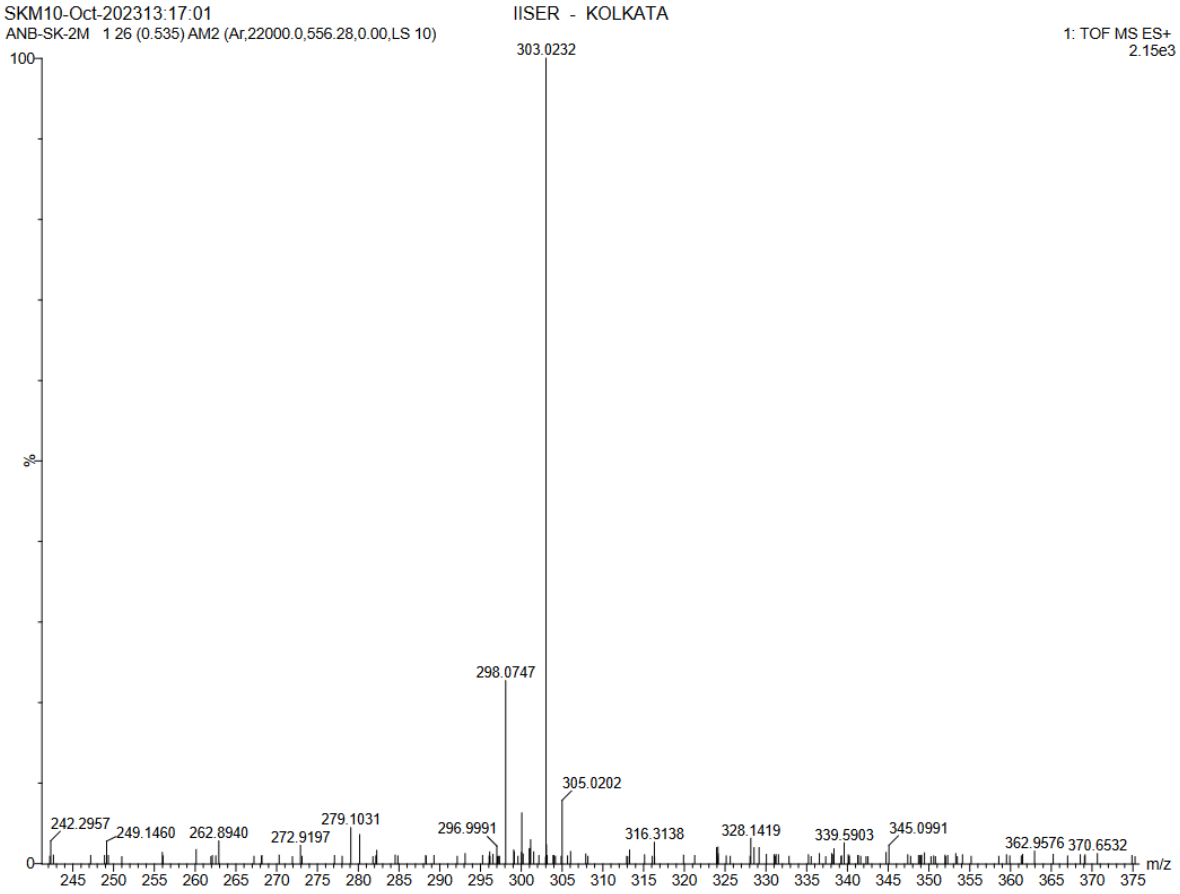
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{14}H_{13}FO_2SNa$ 287.0515; found 287.0513



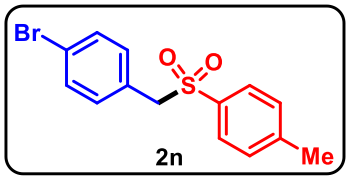
1-Chloro-4-(tosylmethyl)benzene (2m): [6]



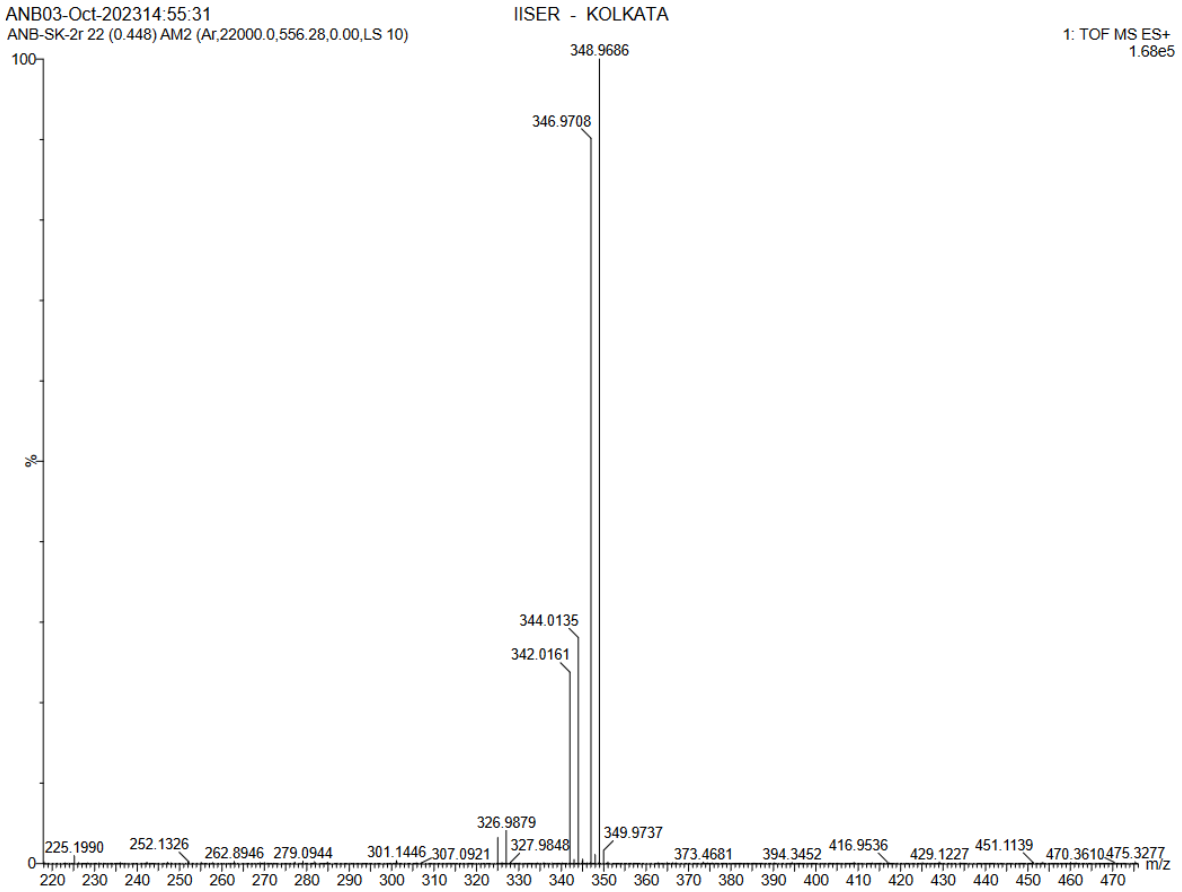
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{14}H_{13}ClO_2SNa$ 303.0217; found 303.0232



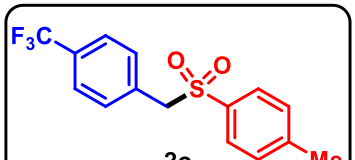
1-Bromo-4-(tosylmethyl)benzene (2n): [6]



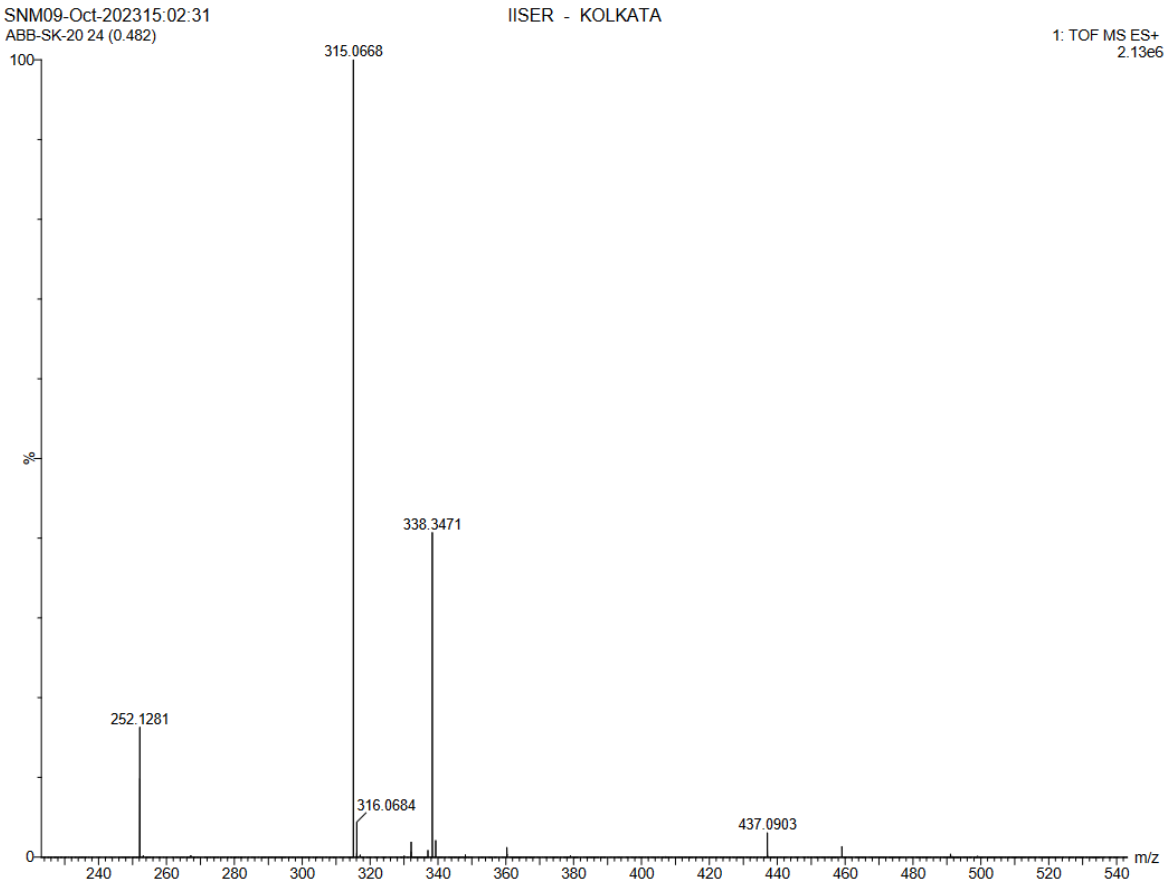
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{14}H_{13}BrNaO_2S$ 346.9712; found 346.9708.



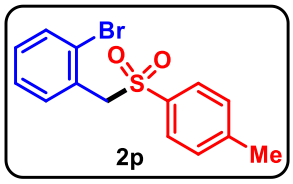
1-Methyl-4-((4-(trifluoromethyl)benzyl)sulfonyl)benzene (2o): [8]



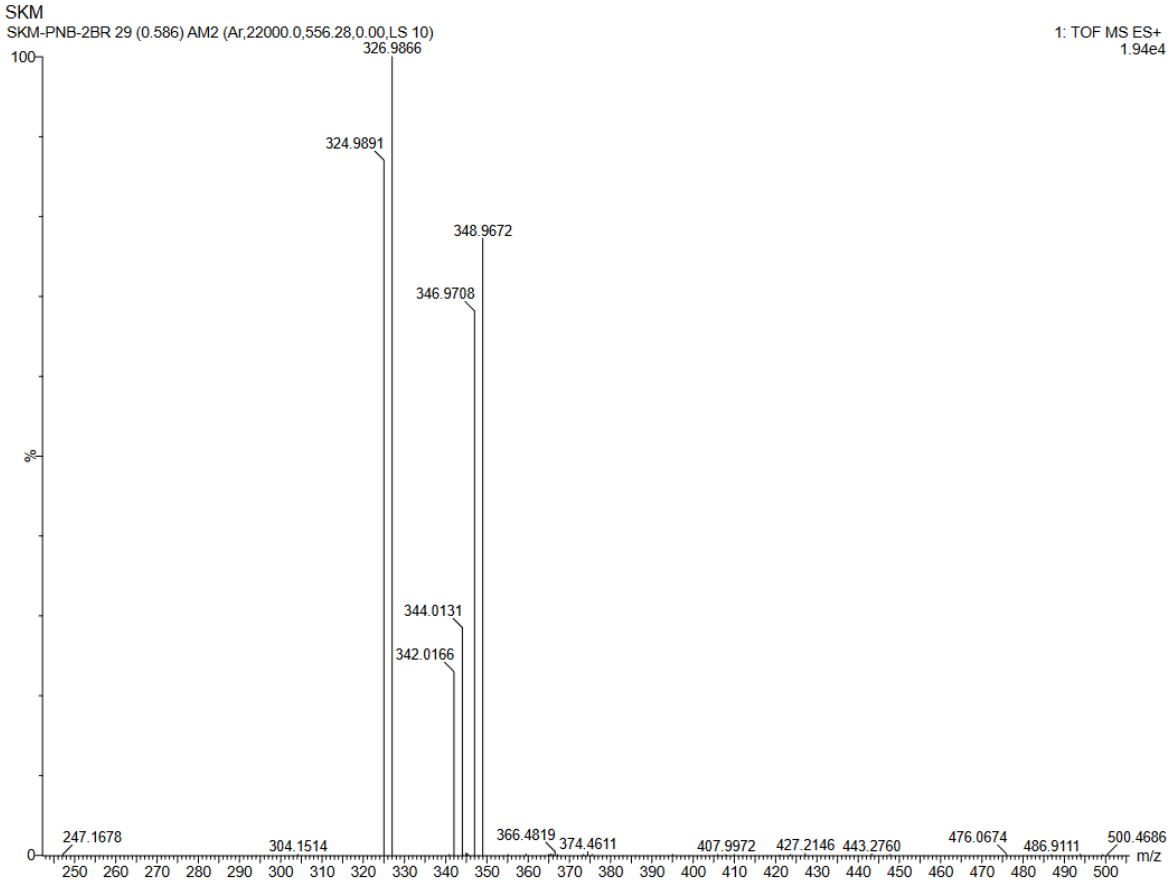
HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{14}F_3O_2S$ 315.0662; found 315.0668.



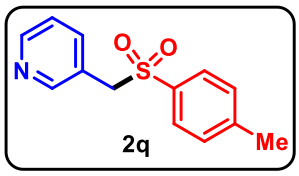
1-Bromo-2-(tosylmethyl)benzene (2p): [6]



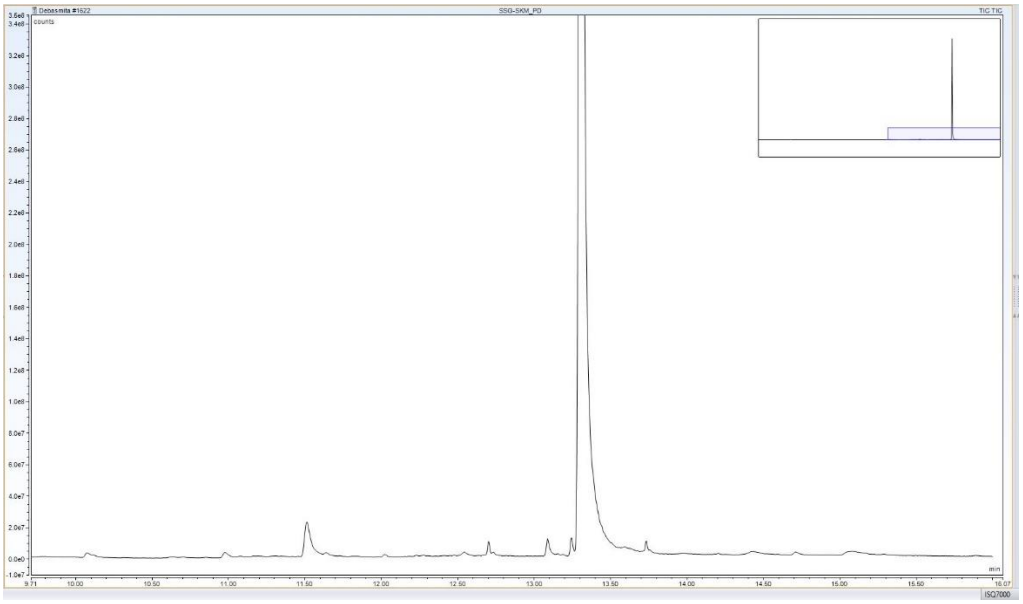
HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{14}BrO_2$ 324.9888; found 324.9891.

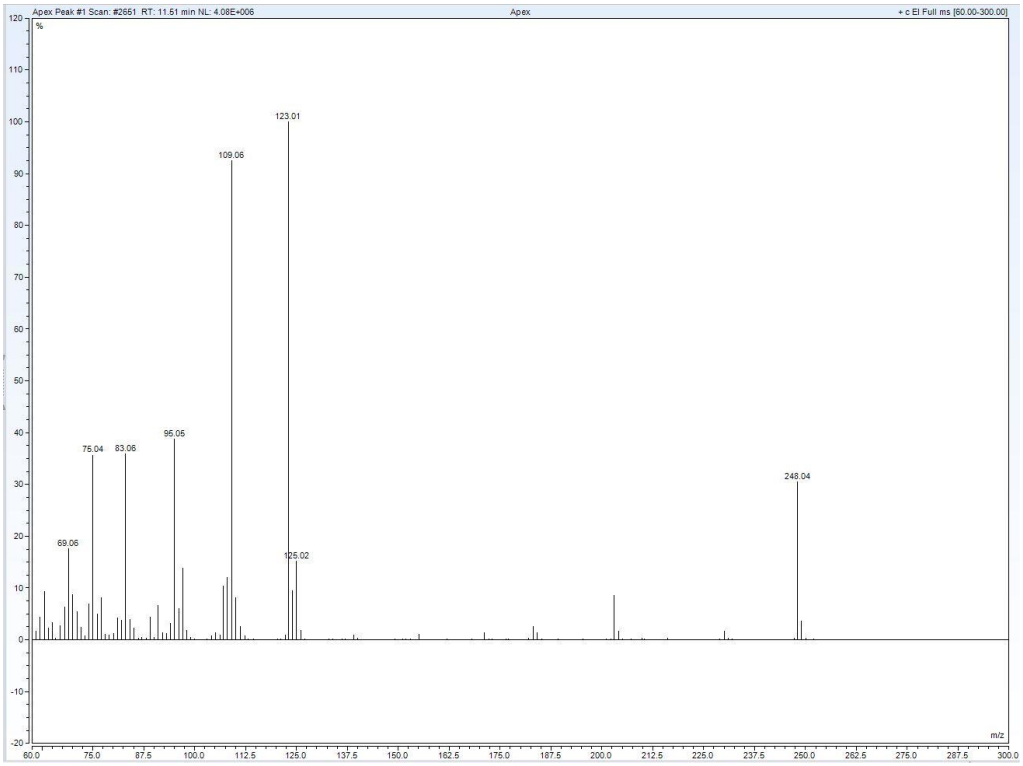


3-(Tosylmethyl)pyridine (2q): [9]

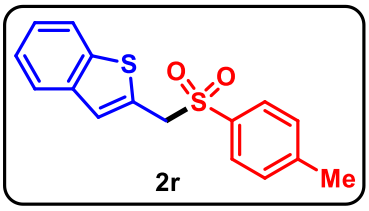


GC MS $[M + H]^+$ calcd for $C_{13}H_{14}O_2SN$: 248.07; found 248.04;

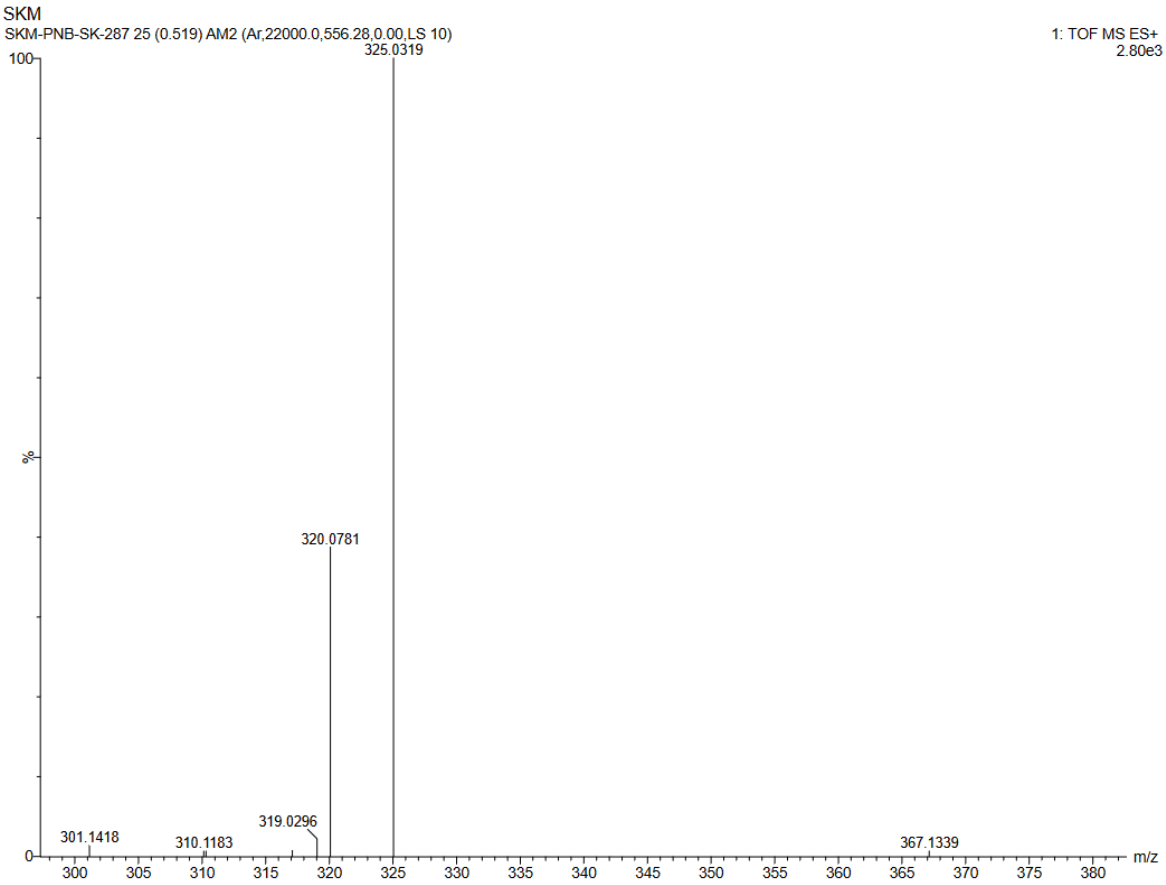




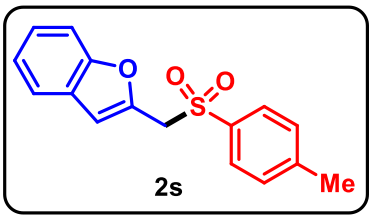
2-(Tosylmethyl)benzo[b]thiophene (2r):



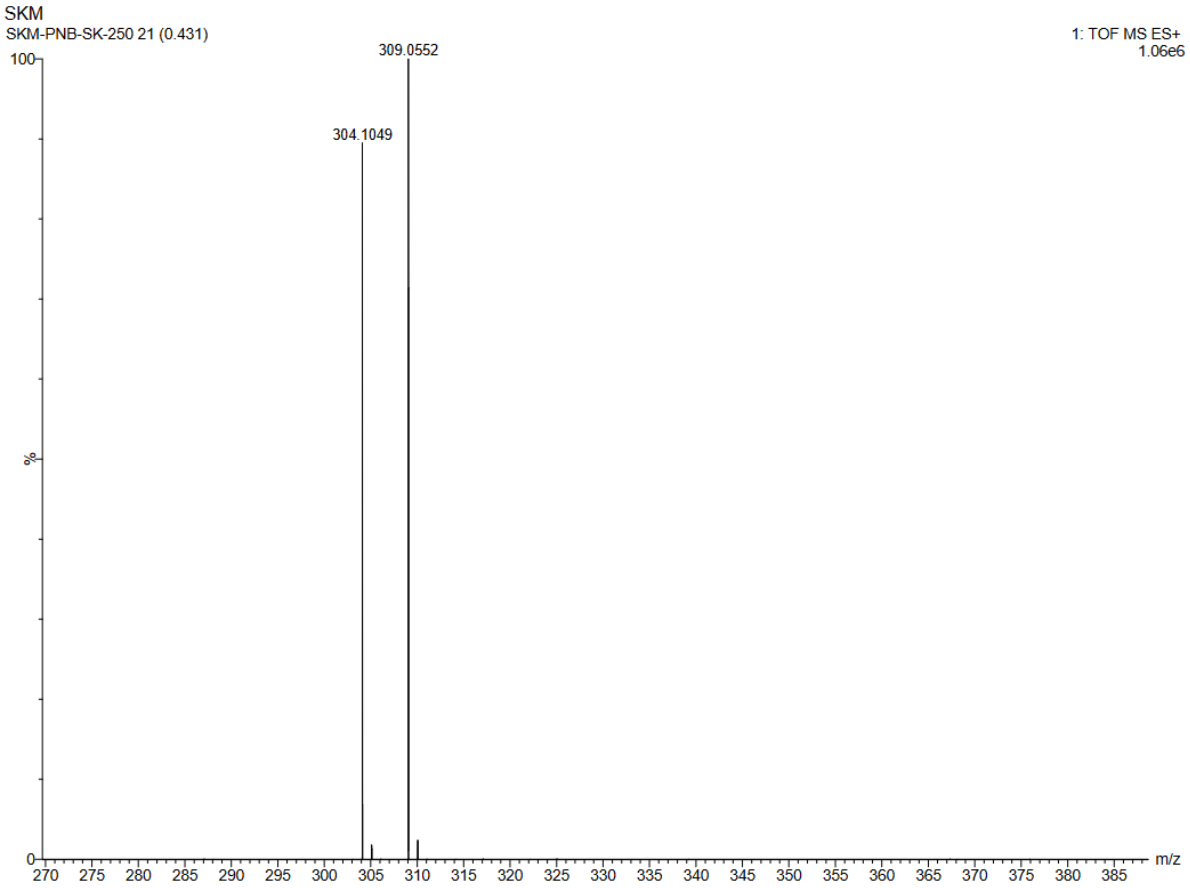
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{14}O_2S_2Na$ 325.0328; found 325.0319.



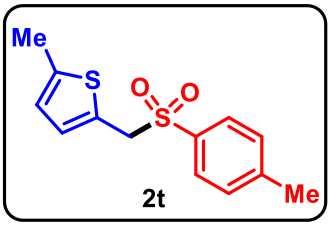
2-(Tosylmethyl)benzofuran (2s):



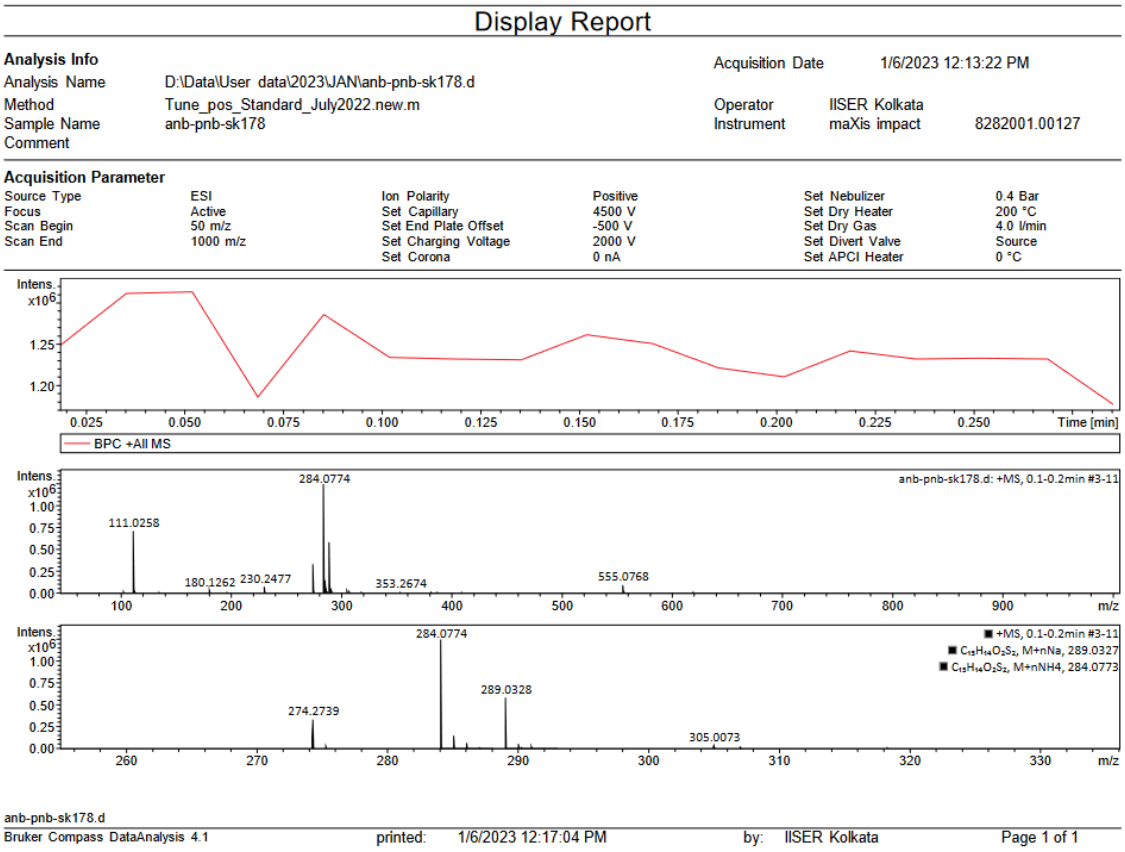
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{14}O_3SNa$ 309.0556; found 309.0552.



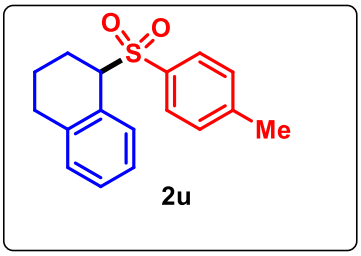
2-Methyl-5-(tosylmethyl)thiophene (2t):



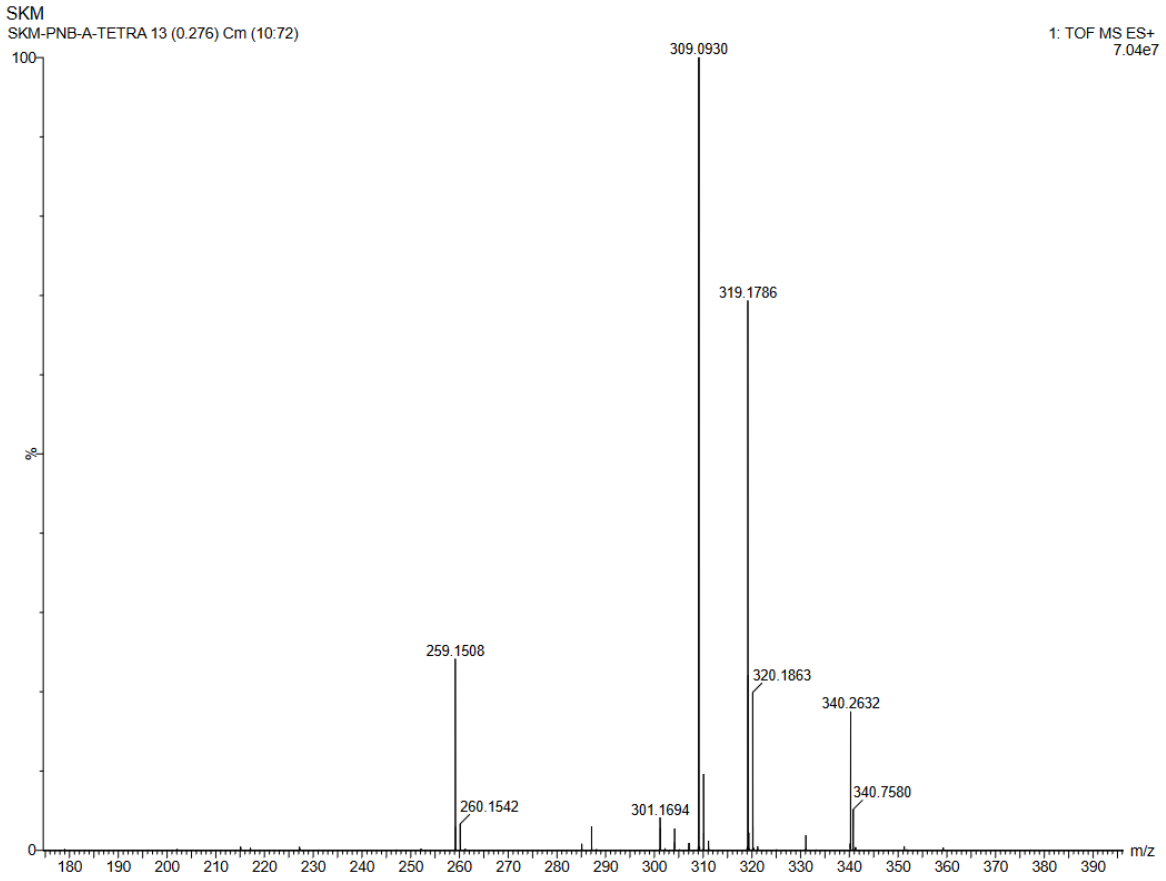
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{13}H_{14}O_2S2Na$ 289.0328; found 289.0328.



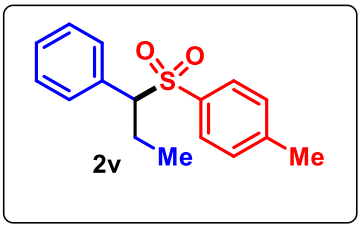
1-(Tosylmethyl)-1,2,3,4-tetrahydronaphthalene (2u):



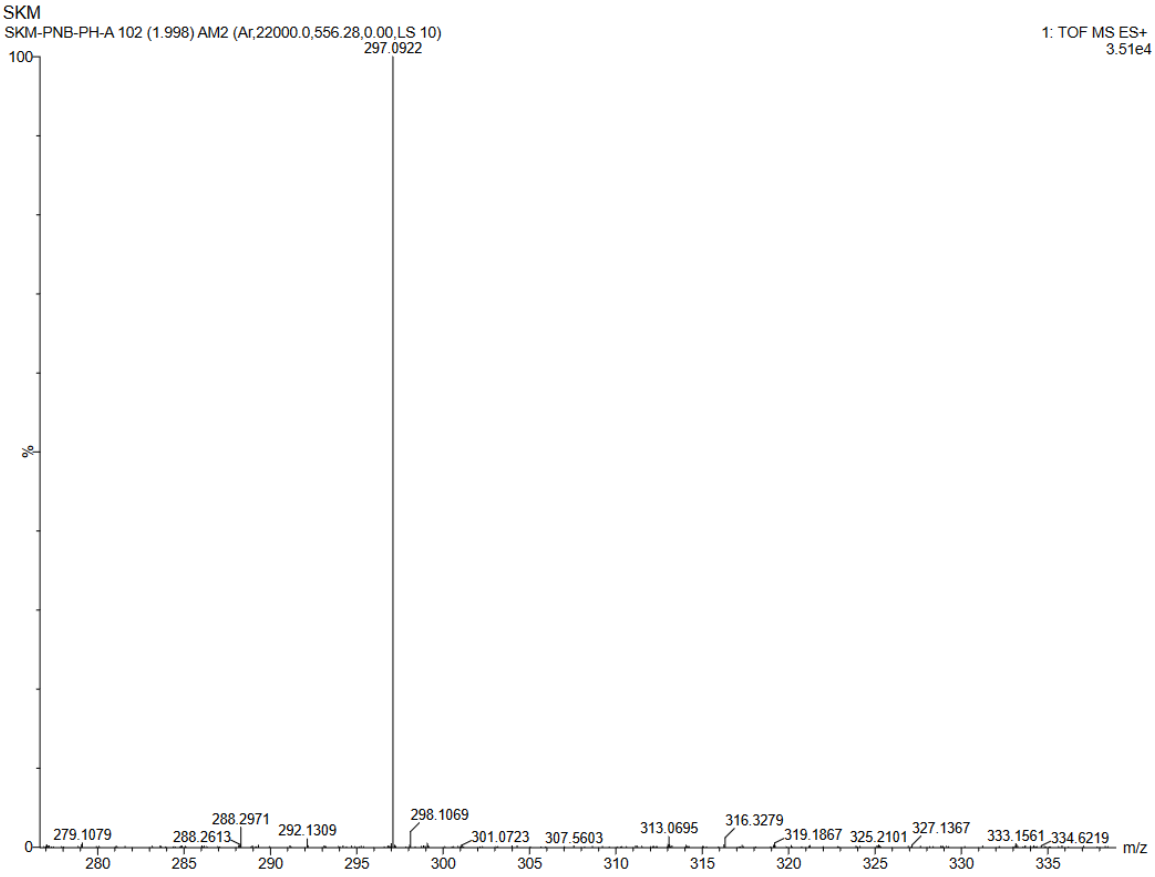
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{17}H_{18}O_2S_2Na$ 309.0920; found 309.0930.



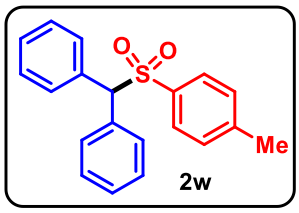
(S)-1-Methyl-4-((1-phenylpropyl)sulfonyl)benzene (2v):



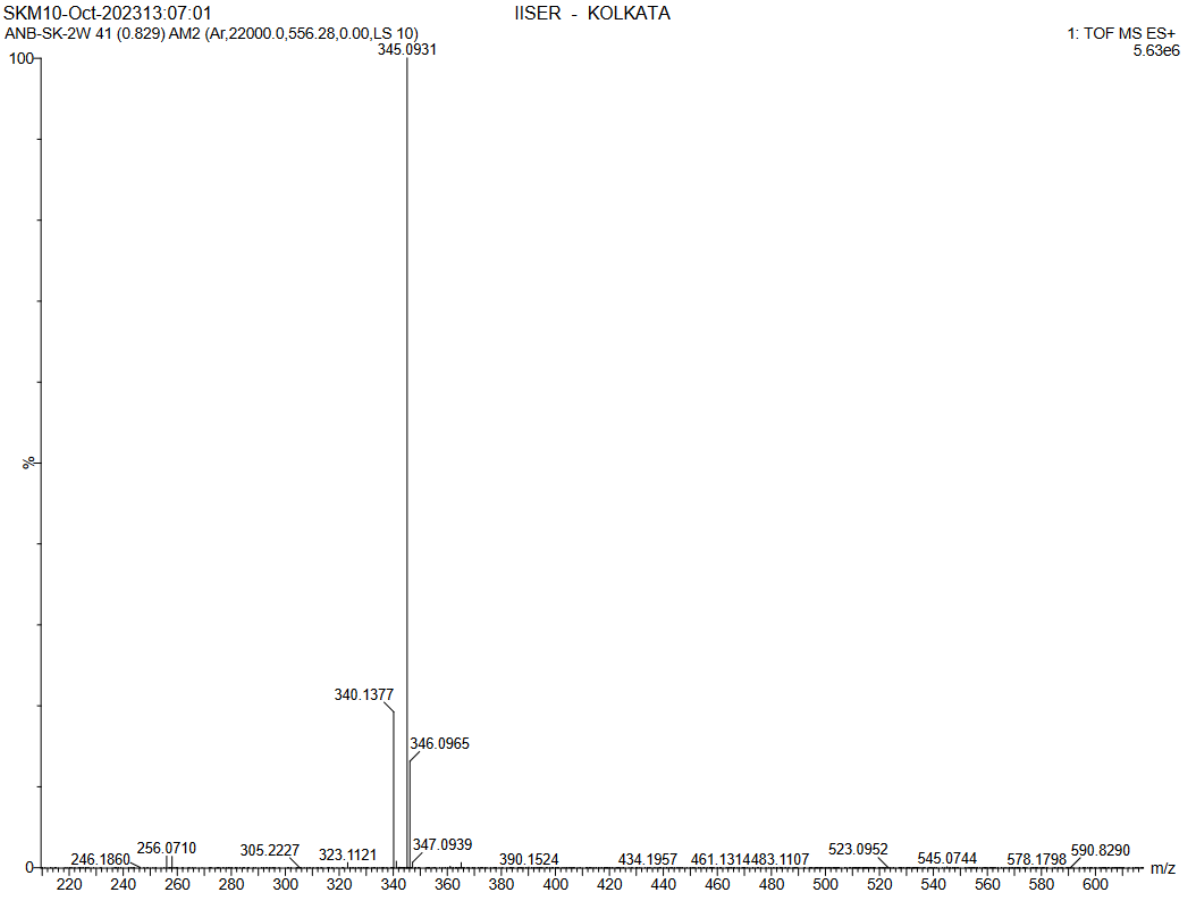
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{18}O_2SNa$ 297.0920; found 297.0922.



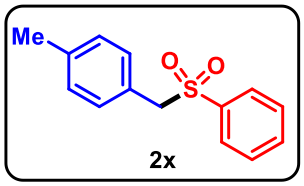
(Tosylmethylene)dibenzene (2w): [6]



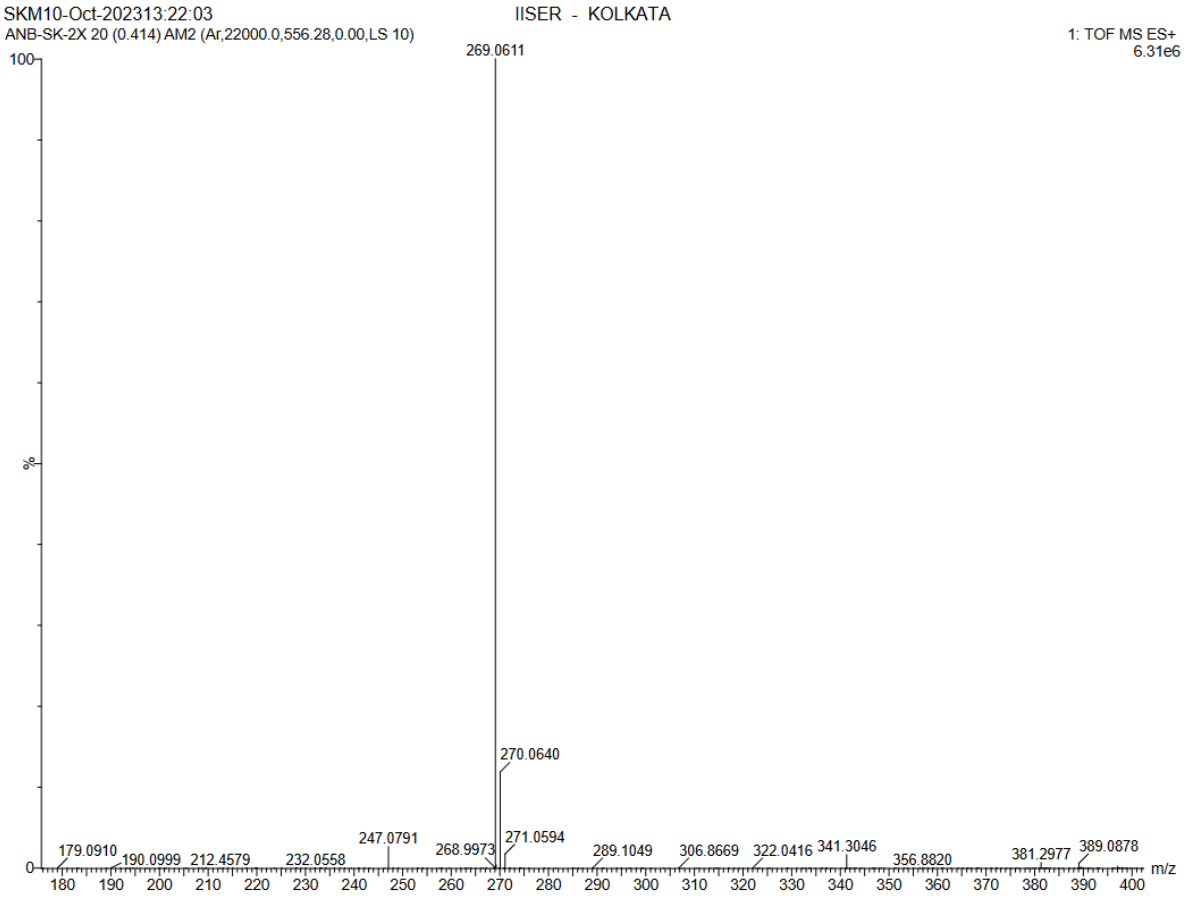
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{20}H_{18}O_2SNa$ 345.0920; found 345.0931



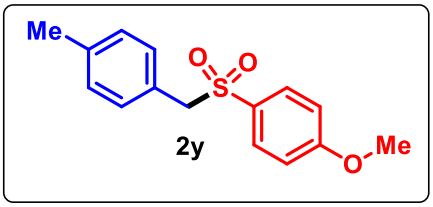
1-Methyl-4-((phenylsulfonyl)methyl)benzene (2x): [7]



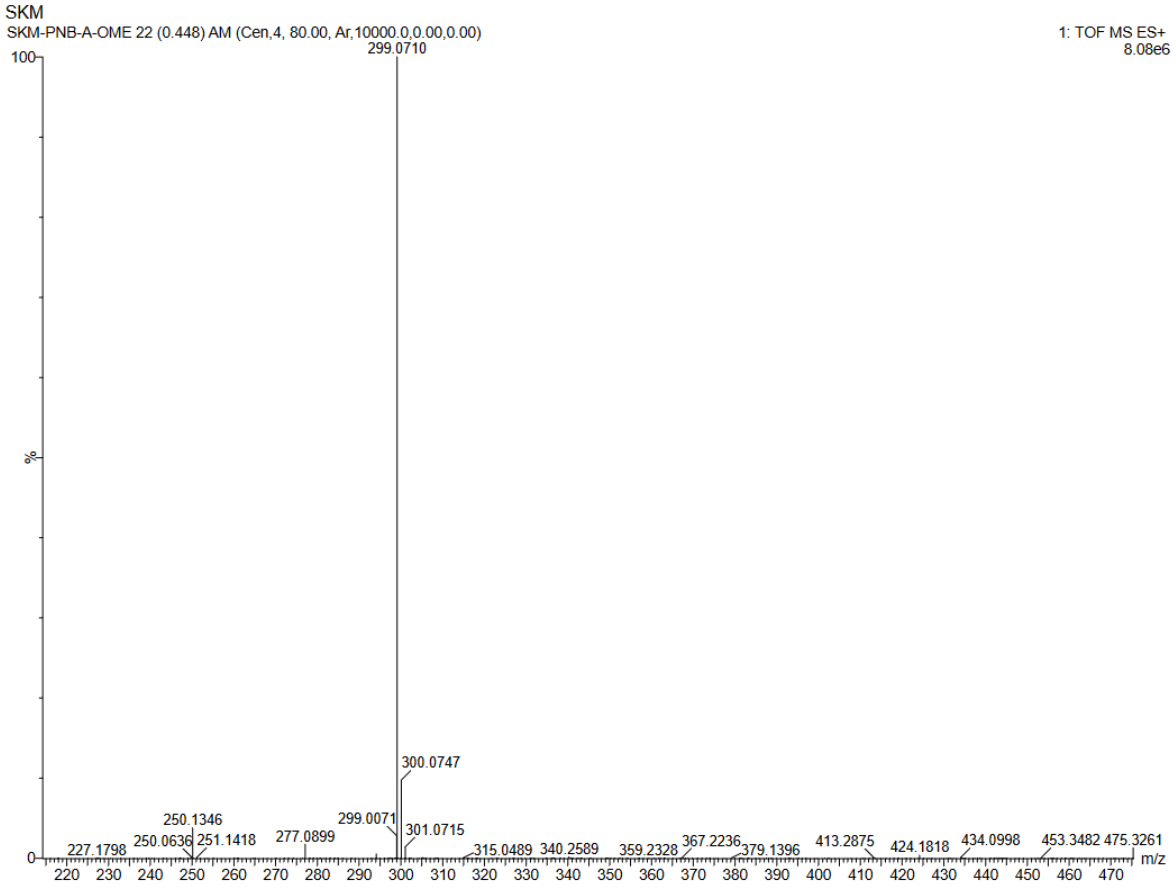
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{14}H_{14}O_2SNa$ 269.0607; found 269.0611.



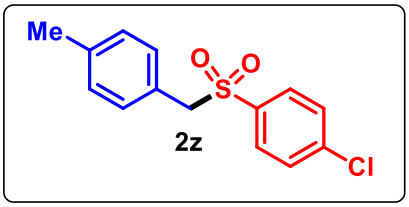
1-Methoxy-4-((4-methylbenzyl)sulfonyl)benzene (2y):



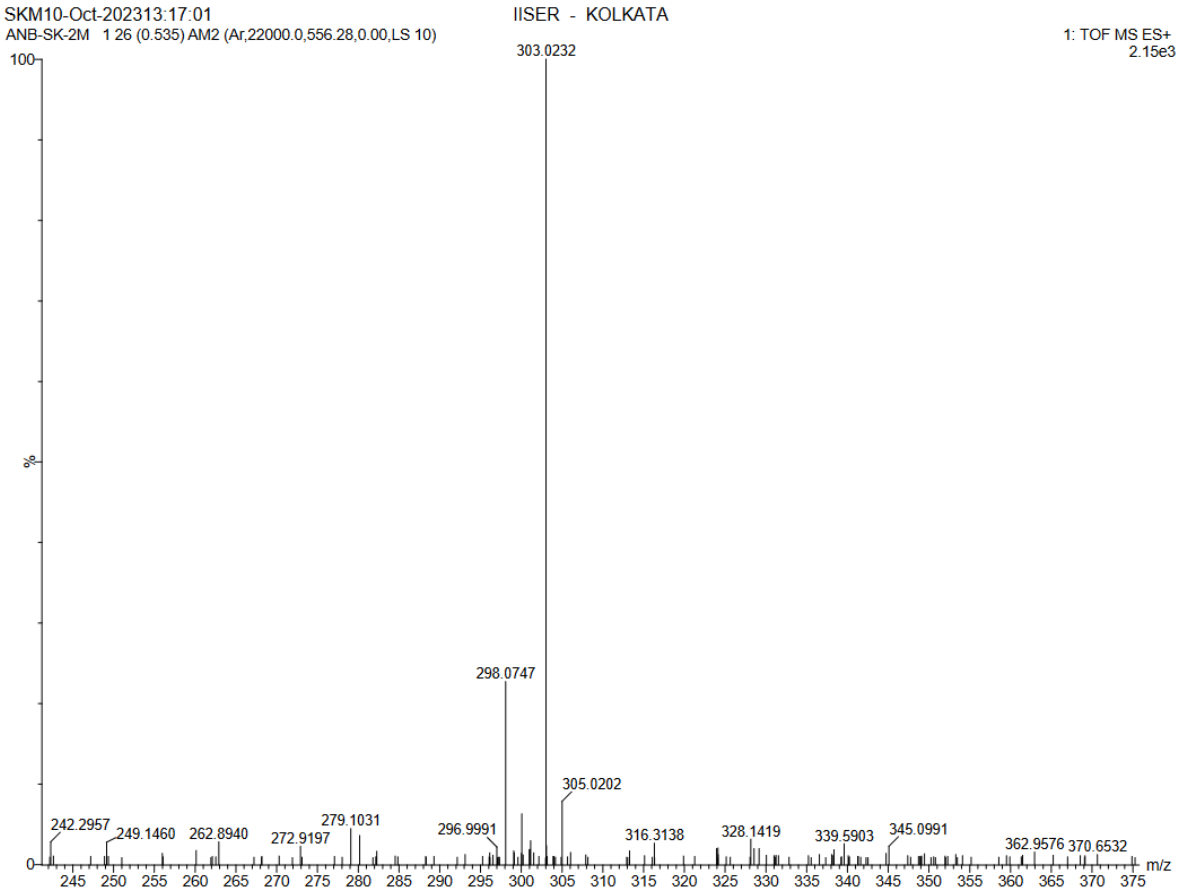
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{16}O_3SNa$ 299.0713; found 299.0710.



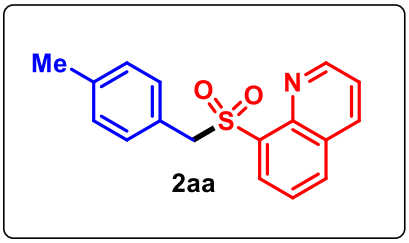
1-Chloro-4-((4-methylbenzyl)sulfonyl)benzene (2z):



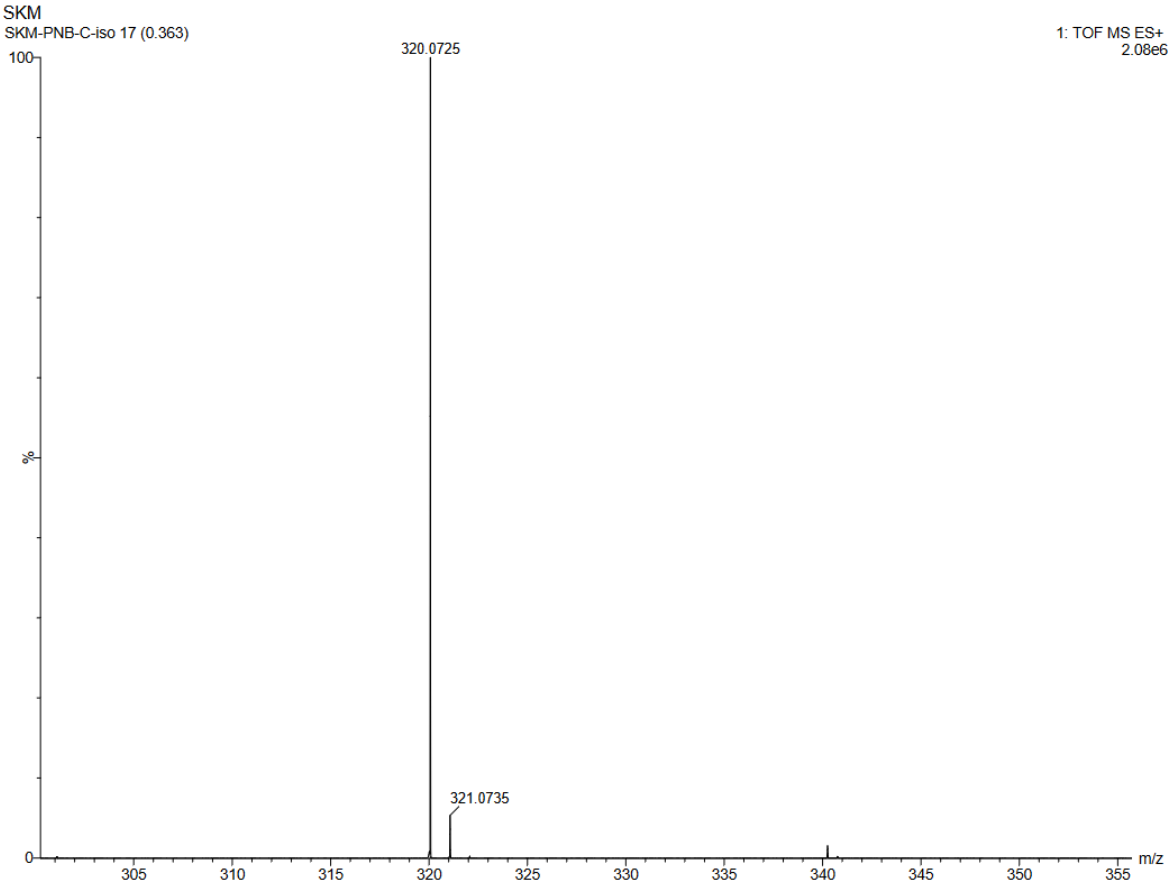
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{14}H_{13}ClO_2SNa$ 303.0217; found 303.0232



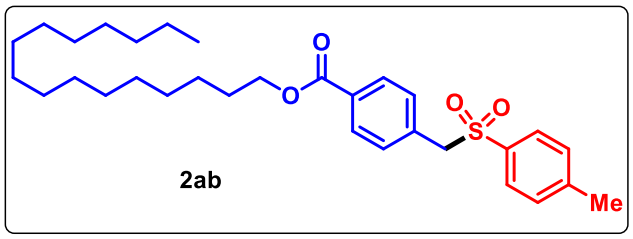
8-((4-Methylbenzyl)sulfonyl)quinoline (2aa):



HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{17}H_{15}O_2NSNa$ 320.0717; found 320.0725.

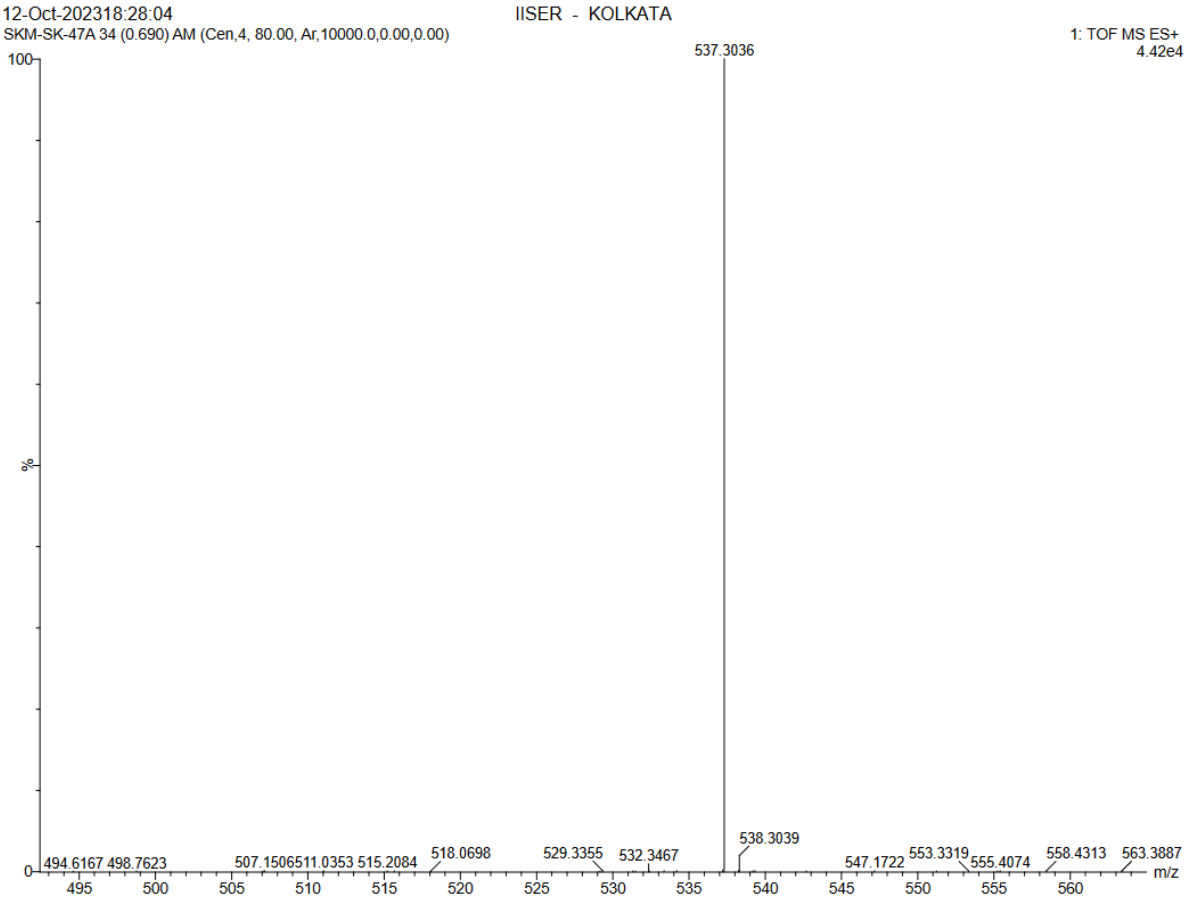


Hexadecyl 4-(tosylmethyl)benzoate (2ab):

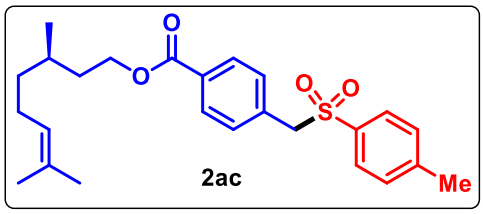


2ab

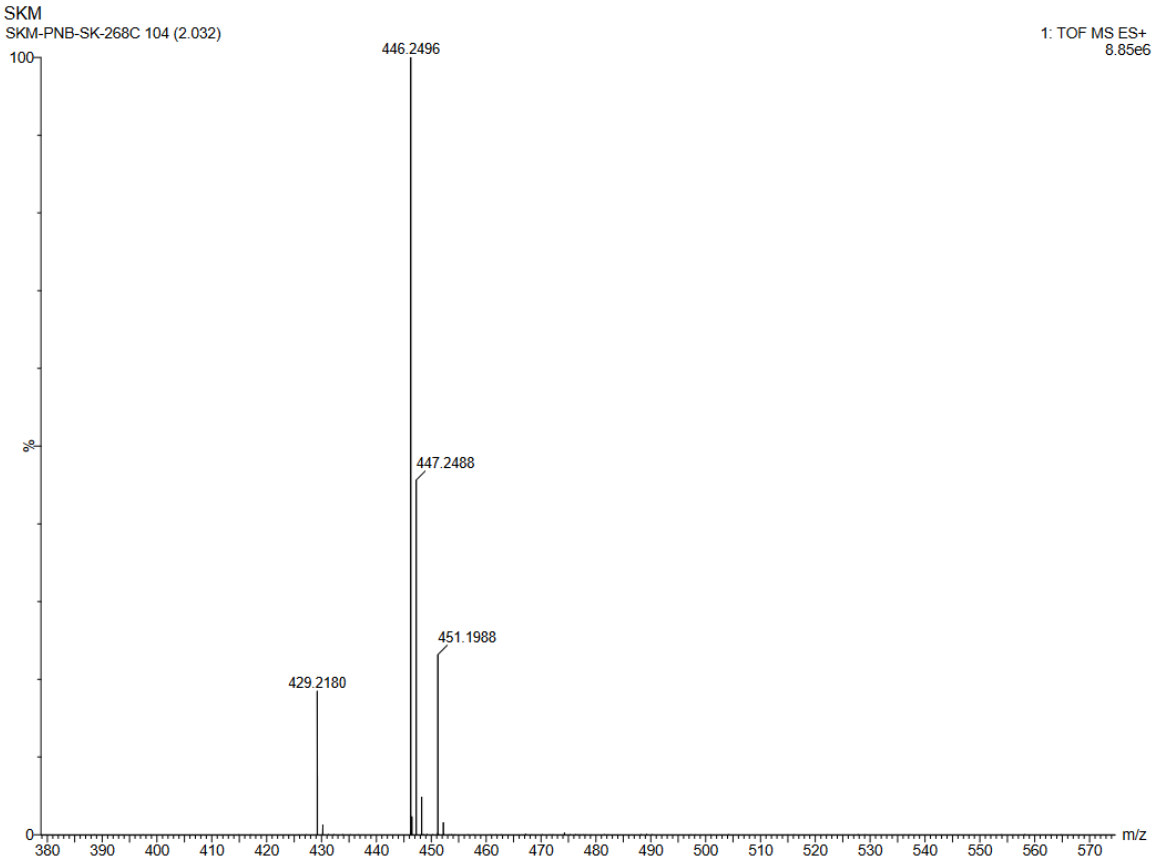
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{31}H_{46}O_4SNa$ 537.3015; found 537.3036



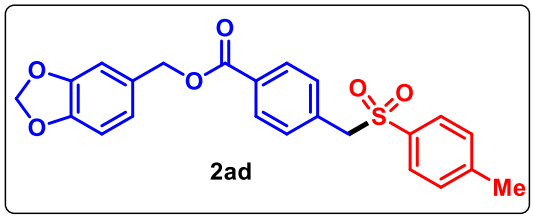
(R)-3,7-Dimethyloct-6-en-1-yl 4-(tosylmethyl)benzoate (2ac):



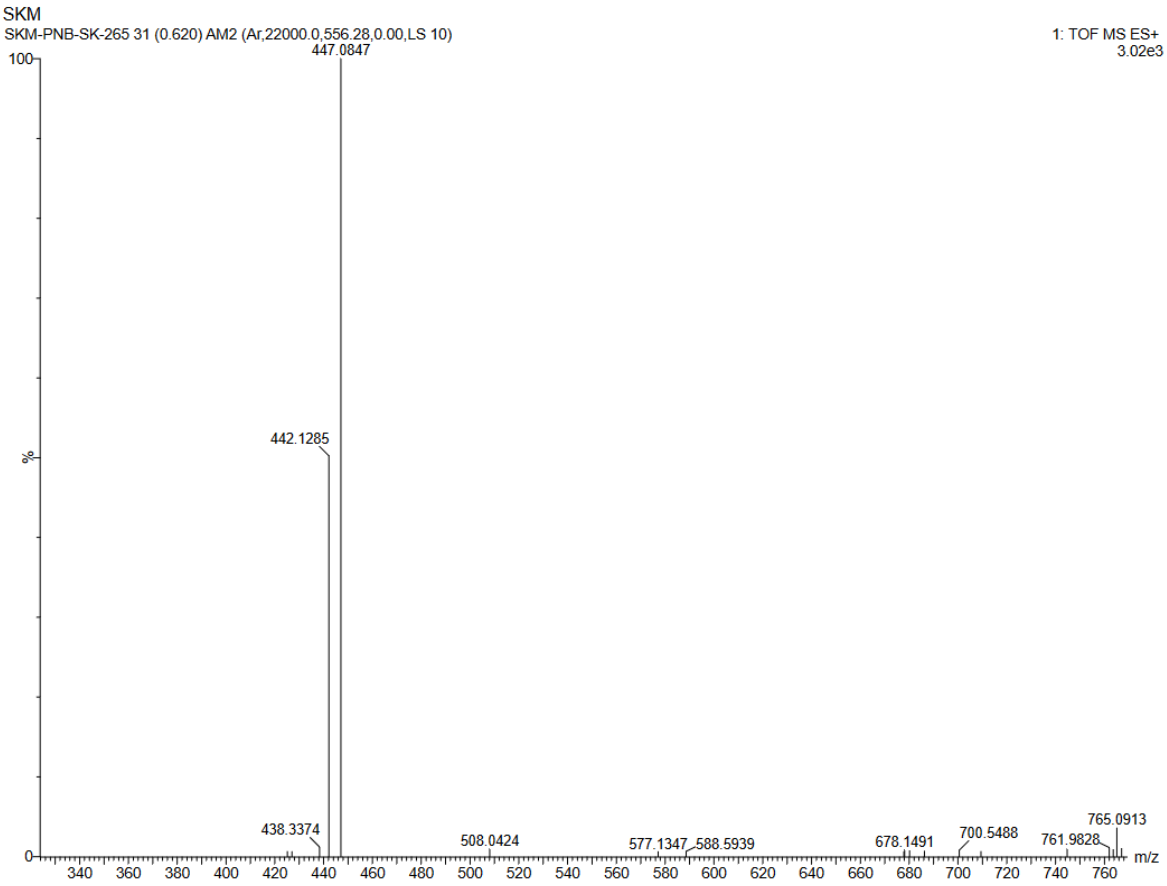
HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{33}O_4S$ 429.2100; found 429.2180.



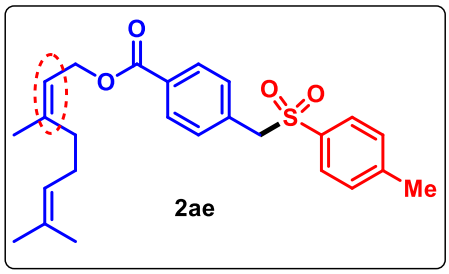
Benzo[d][1,3]dioxol-5-ylmethyl 4-(tosylmethyl)benzoate (2ad):



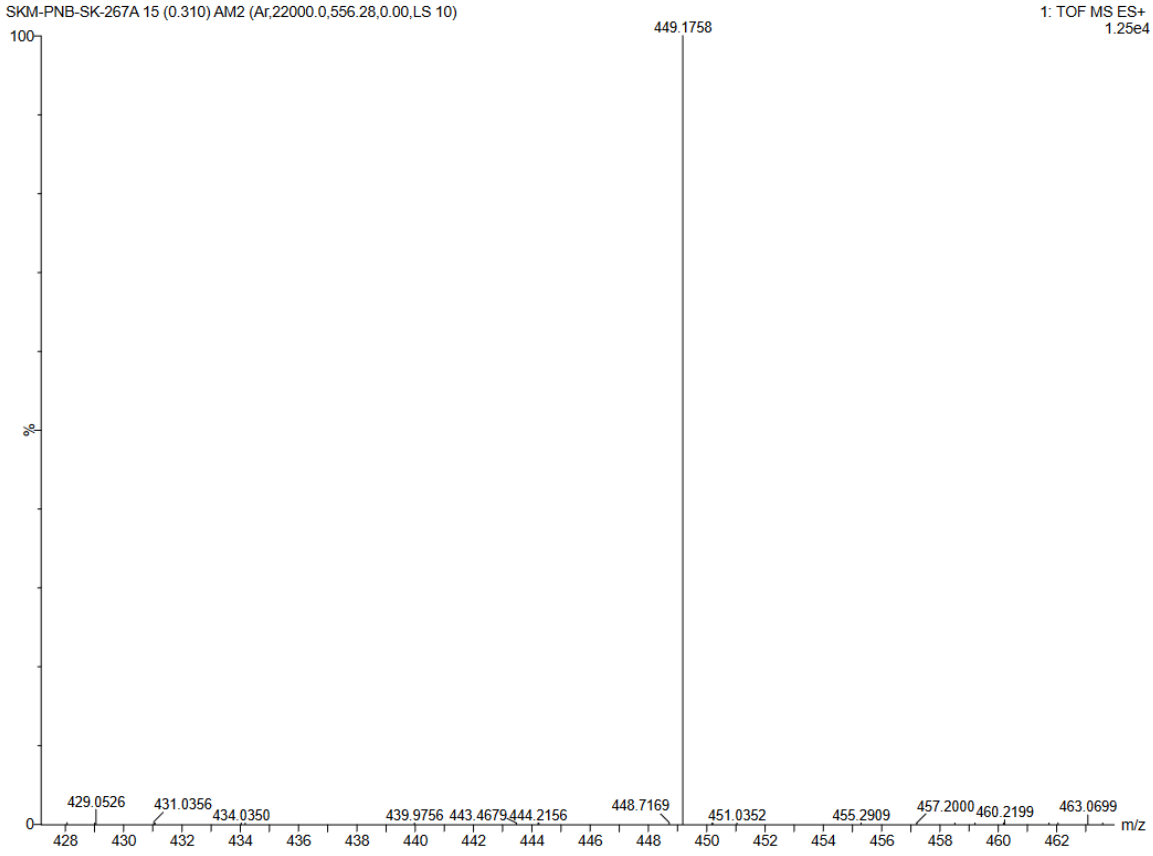
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{23}H_{20}O_6SNa$ 447.0878; found 447.0847.



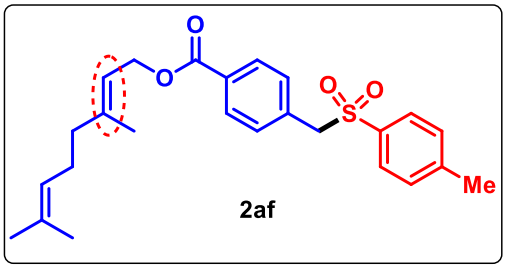
(*Z*)-3,7-Dimethylocta-2,6-dien-1-yl 4-(tosylmethyl)benzoate (2ae):



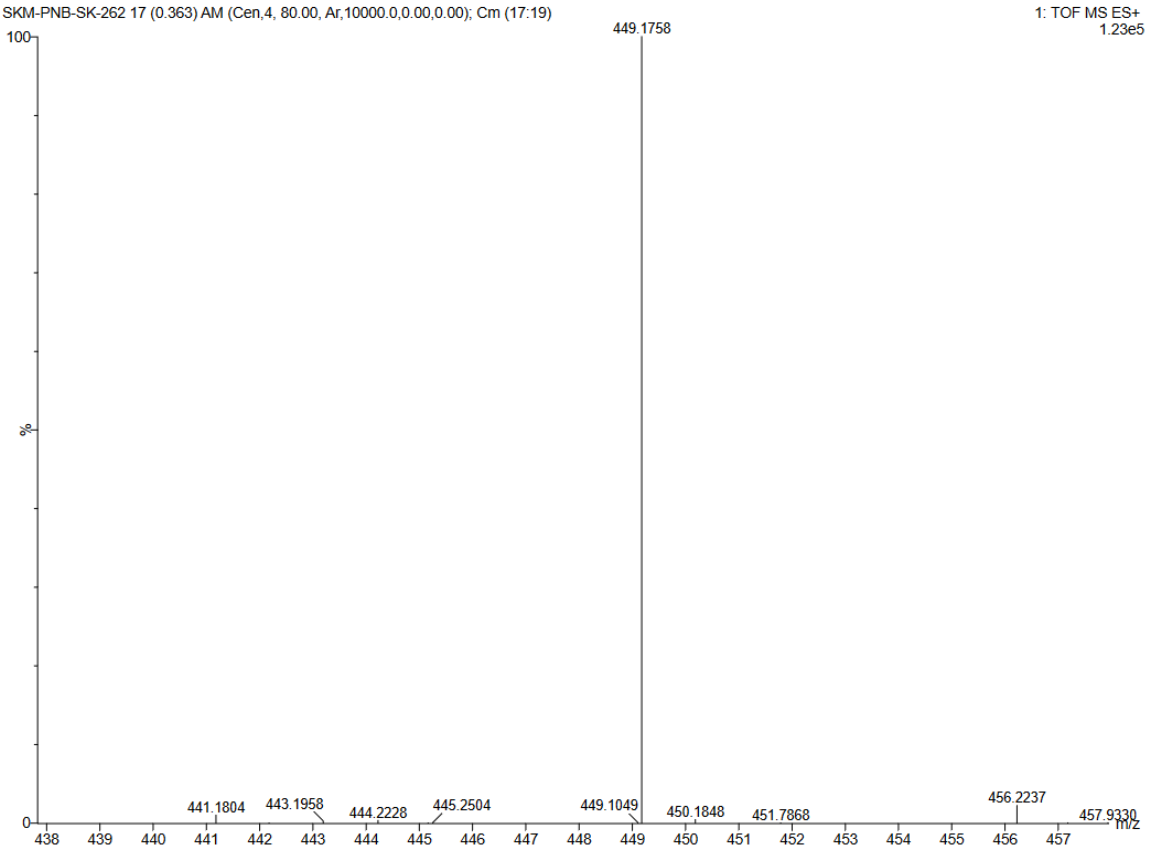
HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{31}O_4S$ 427.1943; found 427.1917.



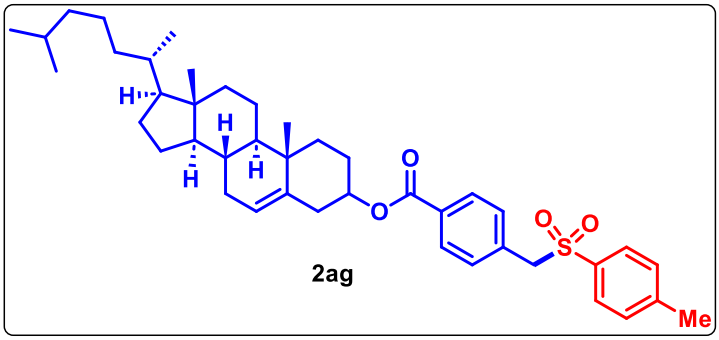
(*E*)-3,7-Dimethylocta-2,6-dien-1-yl 4-(tosylmethyl)benzoate (2af):



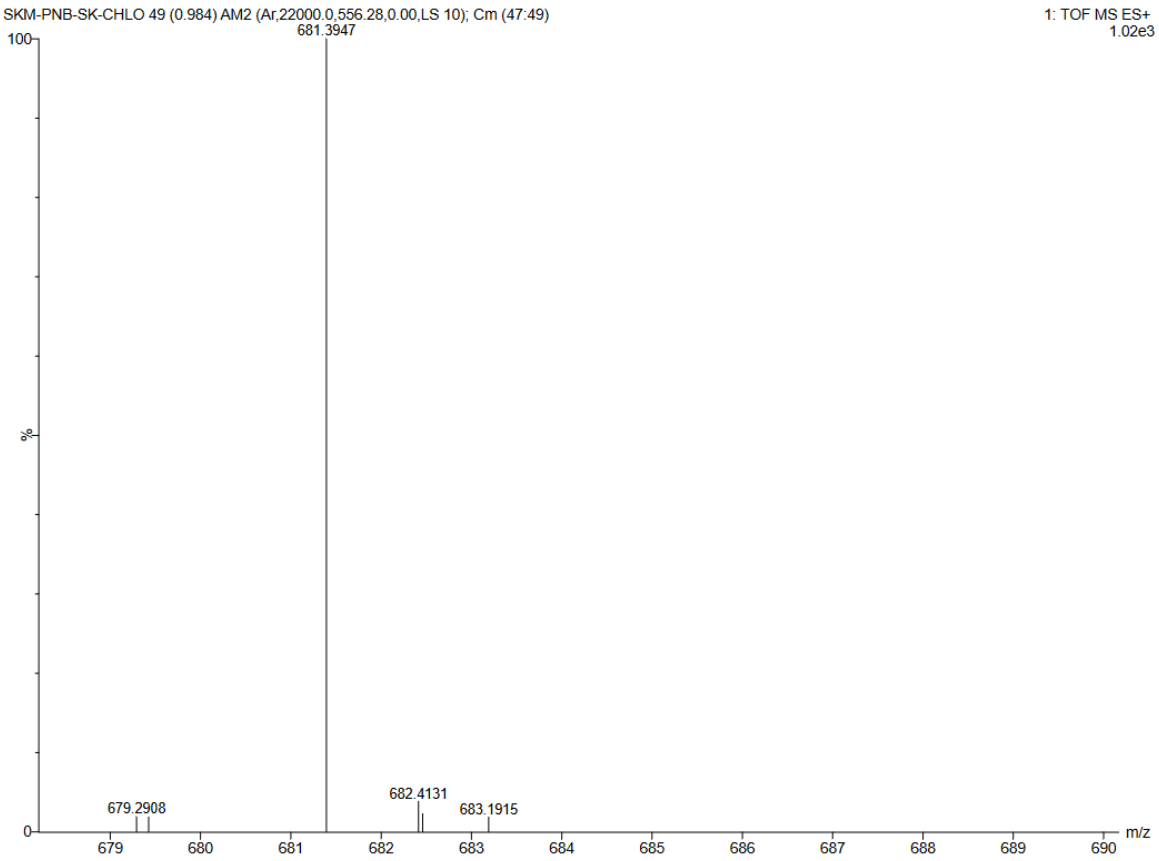
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{25}H_{30}O_4SNa$ 449.1762; found 449.1758.



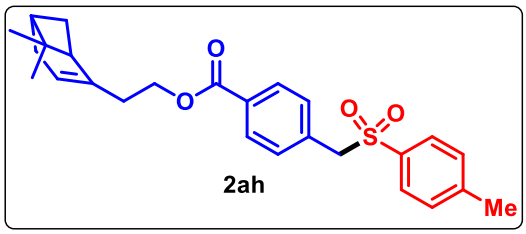
(8R,9R,10S,13S,14R,17S)-10,13-Dimethyl-17-((S)-5-methylhexan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(tosylmethyl)benzoate (2ag):



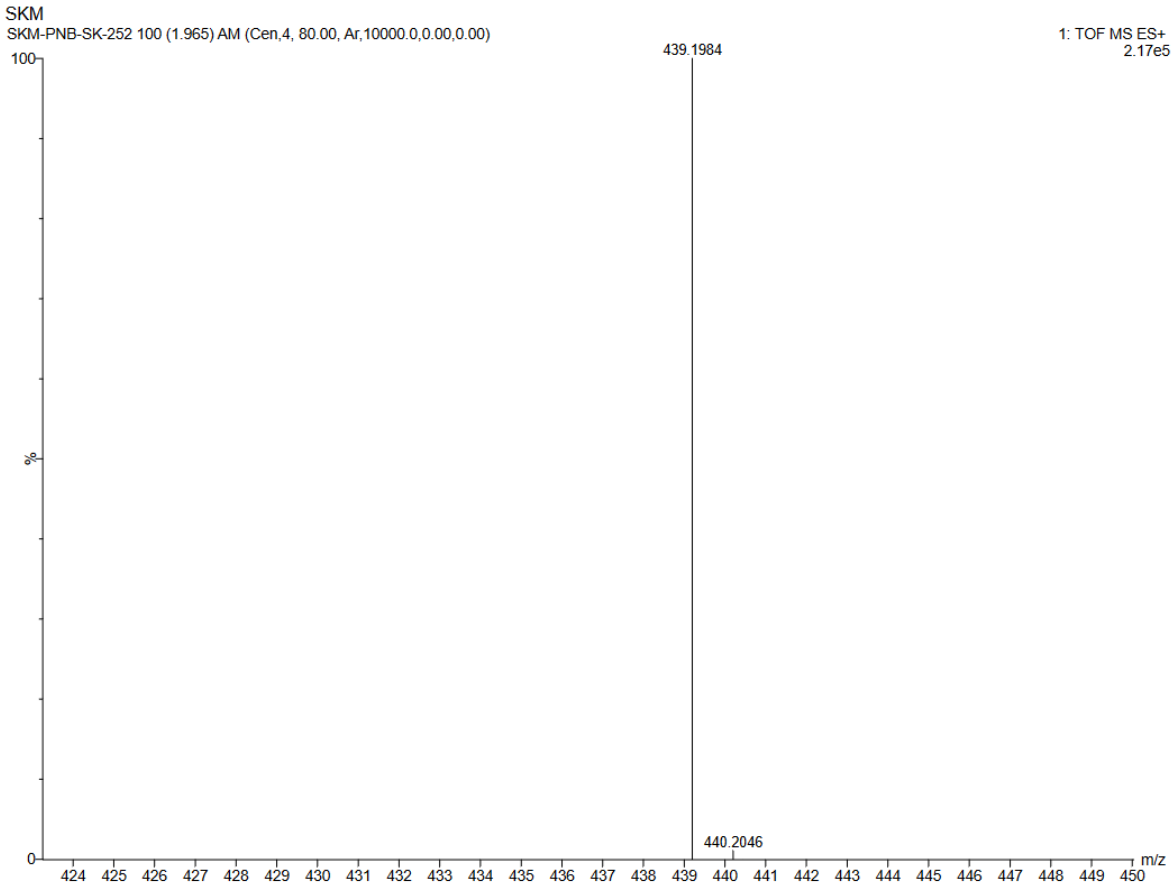
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{41}H_{56}O_4SNa$ 681.3954; found 681.3947.



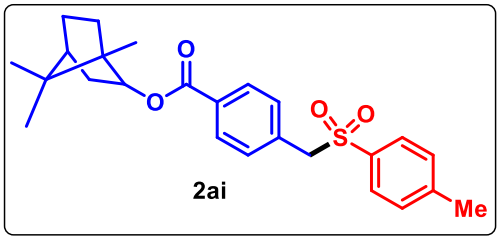
2-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl 4-(tosylmethyl)benzoate (2ah):



HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{31}O_4S$ 439.1943; found 439.1964.

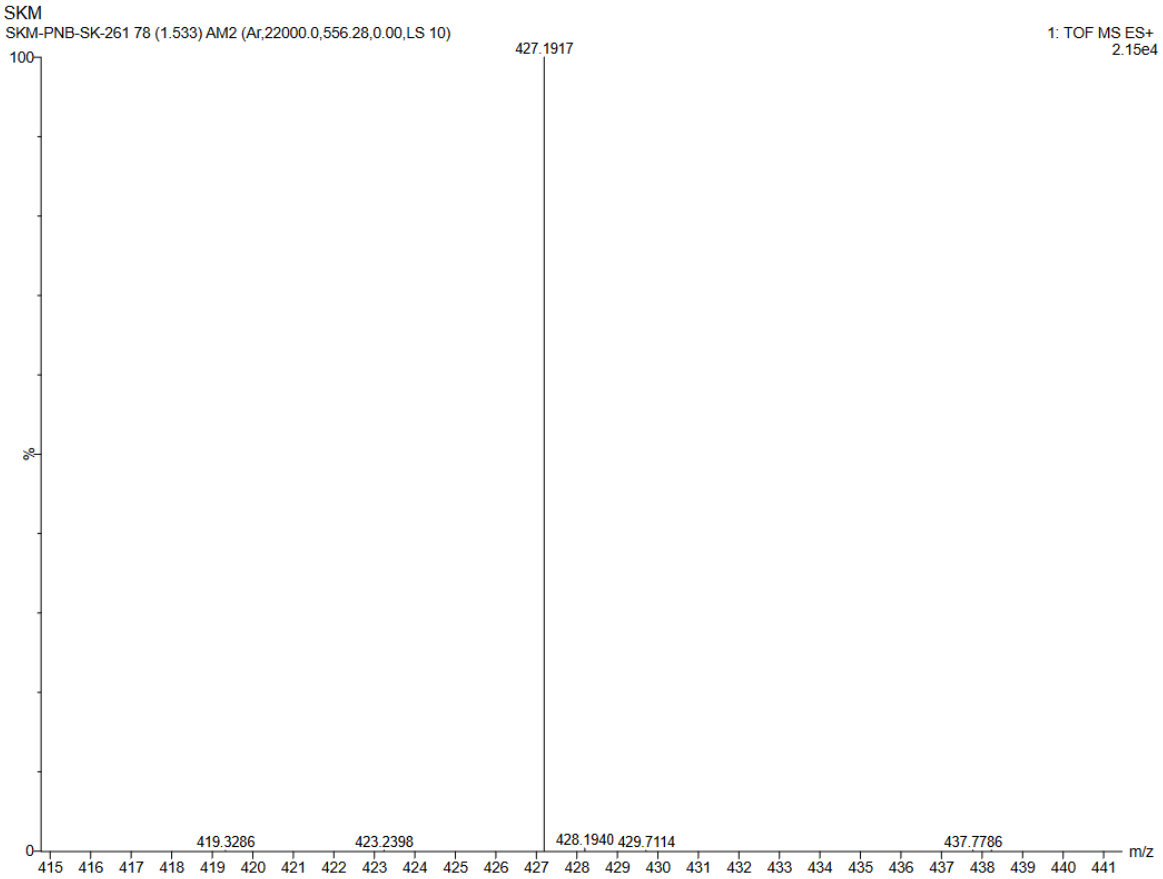


1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 4-(tosylmethyl)benzoate (2ai):

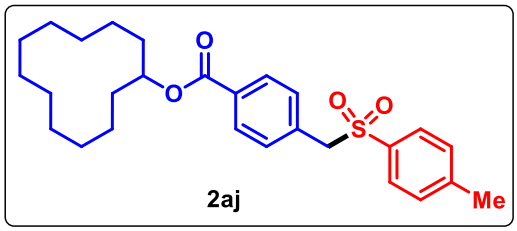


2ai

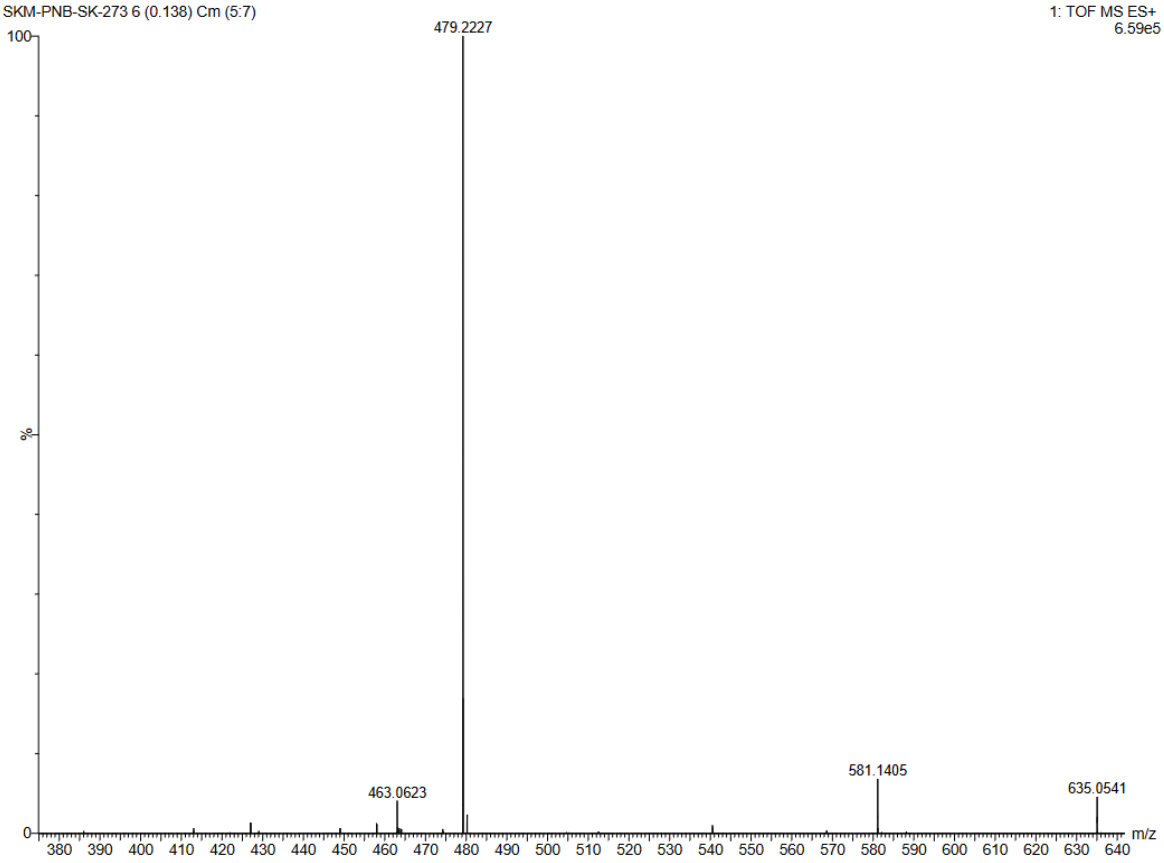
HRMS (TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{31}O_4S$ 427.1943; found 427.1917.



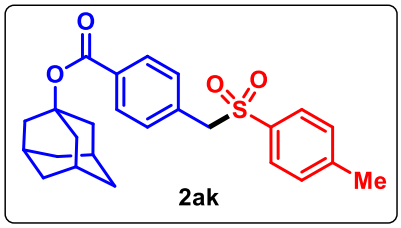
Cyclododecyl 4-(tosylmethyl)benzoate (2aj):



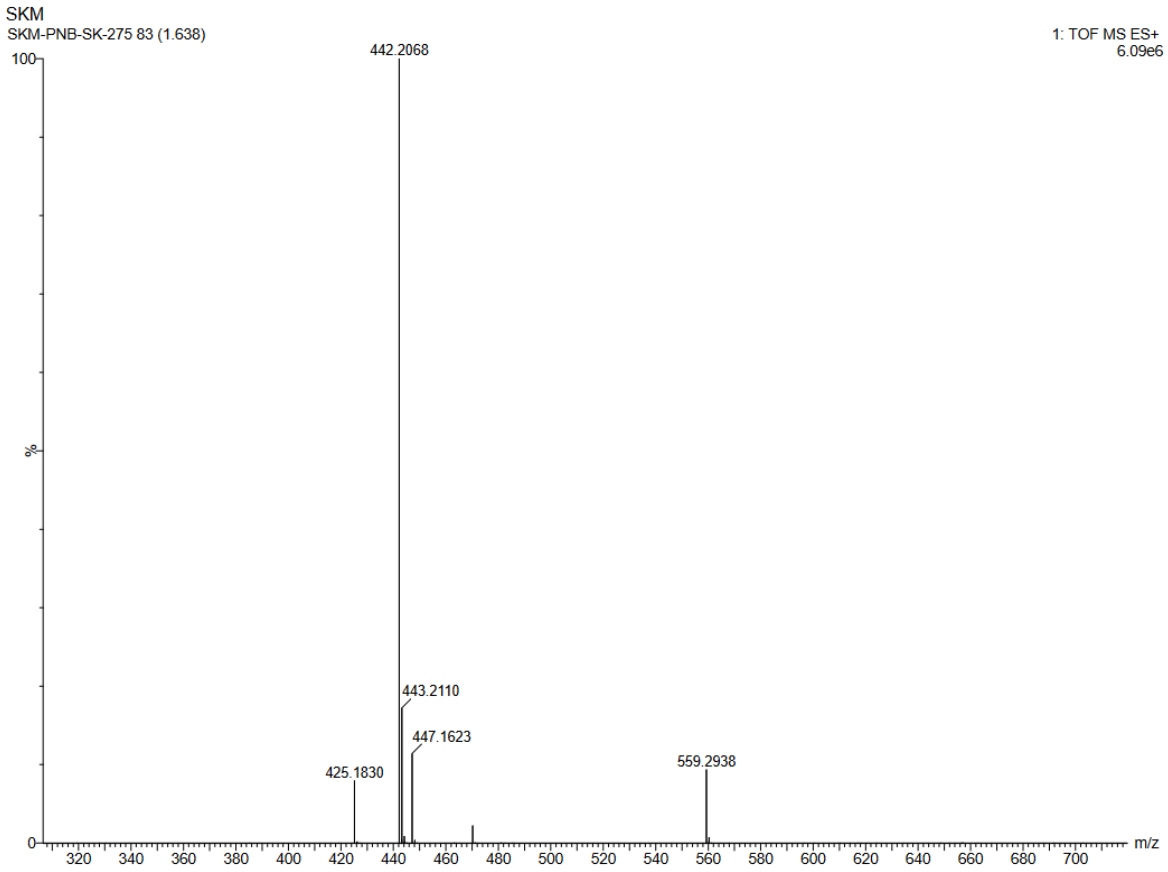
HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{27}H_{36}O_4SNa$ 479.2232; found 479.2227



(3s,5s,7s)-Adamantan-1-yl 4-(tosylmethyl)benzoate (2ak):



HRMS (TOF) m/z: $[M + Na]^+$ calcd for $C_{25}H_{28}O_4SNa$ 447.1606; found 447.1623.



VIII. References

1. Mandal, S.; Itkis, M. E.; Chi, X.; Samanta, S.; Lidsky, D.; Reed, R. W.; Oakley, R. T.; Tham, F. S.; Haddon, R. C. New Family of Aminophenalenyl-Based Neutral Radical Molecular Conductors: Synthesis, Structure, and Solid-State Properties. *J. Am. Chem. Soc*. **2005**, *127*, 8185−8196.
2. Haddon, R. C.; Rayford, R.; Hirani, A. M. 2-Methyl- and 5-Methyl-9-Hydroxyphenalenone. *J. Org. Chem.* **1981**, *46*, 4587-4588.
3. Li, H.; Shangguan, X.; Zhang, Z.; Huang, S.; Zhang, Y.; Wang, J. Formal Carbon Insertion of N-Tosylhydrazone into B−B and B−Si Bonds: gem-Diborylation and gem-Silylborylation of sp3 Carbon. *Org. Lett*. **2014**, *16*, 448−451.
4. Cismesia, M. A.; Yoon, T. P. Characterizing Chain Processes in Visible Light Photoredox Catalysis. *Chem. Sci*. **2015**, *6*, 5426–5434.
5. Datta, P.; Goswami. T.; Kandoth, N.; Banik, A.; Ahmed, J.; Bhaskaran, A. S.; Saha, R.; Kuniyil, R.; Ghosh, H. N.; Mandal, S. K. Generation of Photoinduced Phenalenyl-Based Radicals: Towards Designing Reductive C C Coupling Catalysis. *ChemPhotoChem*, **2023**, DOI: org/10.1002/cptc.202300033.
6. Huang, X.; Chen, X.; Xie, H.; Tan, Z.; Jiang, H.; Zeng, W. Visible-Light-Catalyzed in Situ Denitrogenative Sulfonylation of Sulfonylhydrazones. *Org. Lett.* **2021**, *23*, 6784−6788.
7. Idris, A. M.; Lee, S. Highly Reactive Palladium-Catalyzed and Acetonitrile-Mediated Three-Component Reactions for Arylsulfone Synthesis. *Org. Lett.* **2022**, *24*, 8520−8525.
8. Tilby, M. J.; Dewez, D. F.; Pantaine, L. R. E.; Hall, A.; Martinez-Lamenca, C.; Willis, M. C. Photocatalytic Late-Stage Functionalization of Sulfonamides via Sulfonyl Radical Intermediates. *ACS Catal.* **2022**, *12*, 6060−6067.
9. Knauber, T.; Tucker, J. Palladium Catalyzed Monoselective α-Arylation of Sulfones and Sulfonamides with 2,2,6,6-Tetramethylpiperidine·ZnCl·LiCl Base and Aryl Bromides. *J. Org. Chem.* **2016**, *81*, 5636−5648.
10. Landge, V. G., Yadav, V., Subaramanian, M., Dangarh, P., & Balaraman, E. Nickel(ii)-catalyzed direct olefination of benzyl alcohols with sulfones with the liberation of H2. *Chem. Comm.* **2019**, 55, 6130–6133.
11. Meyers, C. Y., Chan-Yu-King, R., Hua, D. H., Kolb, V. M., Matthews, W. S., Parady, T. E., Horii, T., Sandrock, P. B., Hou, Y., & Xie, S. Unexpected Differences in the α-Halogenation and Related Reactivity of Sulfones with Perhaloalkanes in KOH−t-BuOH. *J. of Org. Chem.*, **2019**, 68, 500–511.
12. Yao, C., Li, Q., Wang, M., Ning, X., & Kang, Y. (E)-Specific direct Julia-olefination of aryl alcohols without extra reducing agents promoted by bases. *Chem. Comm.* **2015**, 51, 7729–7732.
13. Orita, A., Yasui, A. Y., & Otera, J. Automated Synthesis: Utilization of MEDLEY in Synthetic Processes. *Org. Proc. Res. Dev.* **2000**, 4, 337–341.

14. Reddy, M. A., Reddy, P. P., & Sreedhar, B.. Iron(III) Chloride-Catalyzed Direct Sulfonylation of Alcohols with Sodium Arenesulfinates. Reddy, M. A., Reddy, P. P., & Sreedhar, B. (2010). Iron(III) Chloride-Catalyzed Direct Sulfonylation of Alcohols with Sodium Arenesulfinates. *Adv. Synth. & Catal.* **2010**, *352*, 1861–1869.
15. Li, Y., Liu, T., Qiu, G., & Wu, J. Catalyst-Free Sulfonylation of (Hetero)aryl Iodides with Sodium Dithionite. *Adv. Synth. & Catal.* **2019**, *361*, 1154–1159.
16. F. I. Jari, Fishbein J.C. Mechanisms of Benzyl Group Transfer in the Decay of (E)-Arylmethanediazoates and Aryldiazomethanes in Aqueous Solutions *J. Am. Chem. Soc.* **1995**, *117*, 4228–4239.