

Supplementary Information

Light-Promoted Catalyst-Free and Redox-Neutral Hydrosulfonylation of Unactivated Alkenes Using Sulfinic Acid

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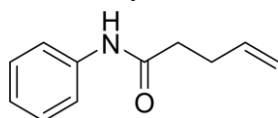
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I. General information

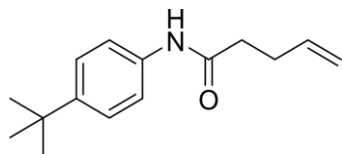
Unless otherwise noted, all chemicals and anhydrous solvents were purchased from commercial suppliers (Merck, Bidepharm, Adamas) and used as received. Commercial unavailable substrates were synthesized according to literature. ^1H NMR, ^{13}C NMR spectra were recorded on a Bruker AVANCE-III HD (600 MHz) spectrometer. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference (CDCl_3 : 7.26 ppm ^1H NMR, 77.16 ppm ^{13}C NMR). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), brs (broad singlet). High-resolution mass spectra (HRMS) were obtained on an Agilent 6475 Triple Quadrupole Liquid Chromatography/Mass Spectrometer. Flash column chromatography was performed on Merck 60 (0.040-0.063 mm) mesh silica gel and run under positive air pressure. Analytical thin layer chromatography (TLC) was performed with Merck pre-coated TLC plates (silica gel 60F-254, layer thickness 0.25 mm). Visualization was achieved by short wave (254 nm) ultraviolet light or by staining with potassium permanganate (KMnO_4) or phosphomolybdic acid (PMA), followed by heating. UV-Vis absorption spectra was taken at ambient temperature using Edinburgh FS5 spectrofluorometer. The Kessil PR160 series ($\lambda_{\text{max}} = 390$ nm, 40 W) was used as the LED light source for the photochemical reactions. Spectral output can be found on: <https://www.kessil.com/science/PR160L.php>. All reactions were carried out in Schlenk tube (20 mL) under an argon atmosphere with magnetic stirring after repeated freeze-pump-thaw. The isolated yield was the purified state by flash chromatography over silica gel.

II. Preparation of starting materials

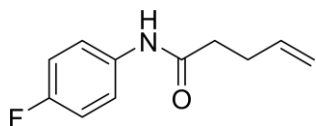
Commercially unavailable alkenes **2** were prepared according to reported procedures.^[1-6] The spectra data of **2h-2o**^[1] and **2ad**^[4] are in accordance with the corresponding literature. Sulfinic acids **1** were synthesized following known procedure.^[7]



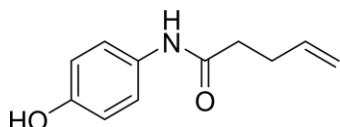
N-phenylpent-4-enamide (2h): ^1H NMR (600 MHz, CDCl_3) δ 7.50 (d, $J = 7.9$ Hz, 2H), 7.31 (t, $J = 7.9$ Hz, 2H), 7.10 (t, $J = 7.4$ Hz, 1H), 5.89 (ddt, $J = 16.8, 10.2, 6.1$ Hz, 1H), 5.13 (dd, $J = 17.2, 1.8$ Hz, 1H), 5.06 (dd, $J = 10.2, 1.8$ Hz, 1H), 2.54 – 2.41 (m, 4H).



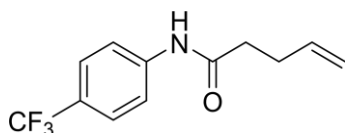
N-(4-(tert-butyl)phenyl)pent-4-enamide (2i): ^1H NMR (600 MHz, CDCl_3) δ 7.42 (d, $J = 8.7$ Hz, 2H), 7.33 (d, $J = 8.7$ Hz, 2H), 5.88 (ddt, $J = 16.8, 10.2, 6.2$ Hz, 1H), 5.12 (dd, $J = 17.2, 1.7$ Hz, 1H), 5.07 – 5.01 (m, 1H), 2.51 – 2.42 (m, 4H), 1.30 (s, 9H).



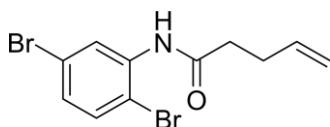
***N*-(4-fluorophenyl)pent-4-enamide (2j):** $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.52 – 7.40 (m, 2H), 7.00 (t, $J = 8.7$ Hz, 2H), 5.87 (ddt, $J = 16.8, 10.2, 6.1$ Hz, 1H), 5.12 (dq, $J = 17.1, 1.6$ Hz, 1H), 5.06 (dt, $J = 10.3, 1.5$ Hz, 1H), 2.71 – 2.30 (m, 4H).



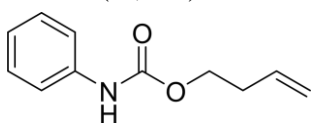
***N*-(4-hydroxyphenyl)pent-4-enamide (2k):** $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.51 – 7.36 (m, 4H), 7.30 (s, 1H), 5.87 (ddt, $J = 16.7, 10.4, 6.2$ Hz, 1H), 5.12 (dd, $J = 17.2, 1.6$ Hz, 1H), 5.06 (dd, $J = 10.4, 1.6$ Hz, 1H), 2.56 – 2.41 (m, 4H).



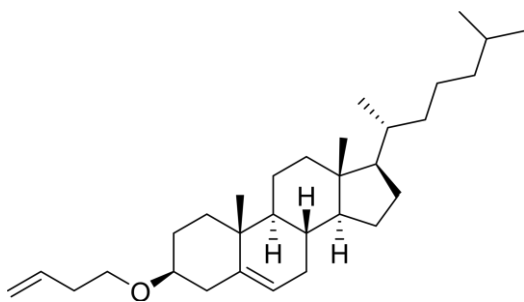
***N*-(4-(trifluoromethyl)phenyl)pent-4-enamide (2l):** $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.63 (d, $J = 8.4$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.44 (s, 1H), 5.98 – 5.79 (m, 1H), 5.13 (dd, $J = 17.0, 1.6$ Hz, 1H), 5.07 (dd, $J = 10.0, 1.6$ Hz, 1H), 2.52 – 2.46 (m, 4H).



***N*-(2,5-dibromophenyl)pent-4-enamide (2m):** $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.61 (s, 1H), 7.60 (d, $J = 2.3$ Hz, 1H), 7.37 (d, $J = 8.5$ Hz, 1H), 7.10 (dd, $J = 8.5, 2.3$ Hz, 1H), 5.88 (ddt, $J = 16.4, 10.1, 6.2$ Hz, 1H), 5.14 (dd, $J = 17.2, 1.6$ Hz, 1H), 5.08 (dd, $J = 10.2, 1.6$ Hz, 1H), 2.59 – 2.47 (m, 4H).



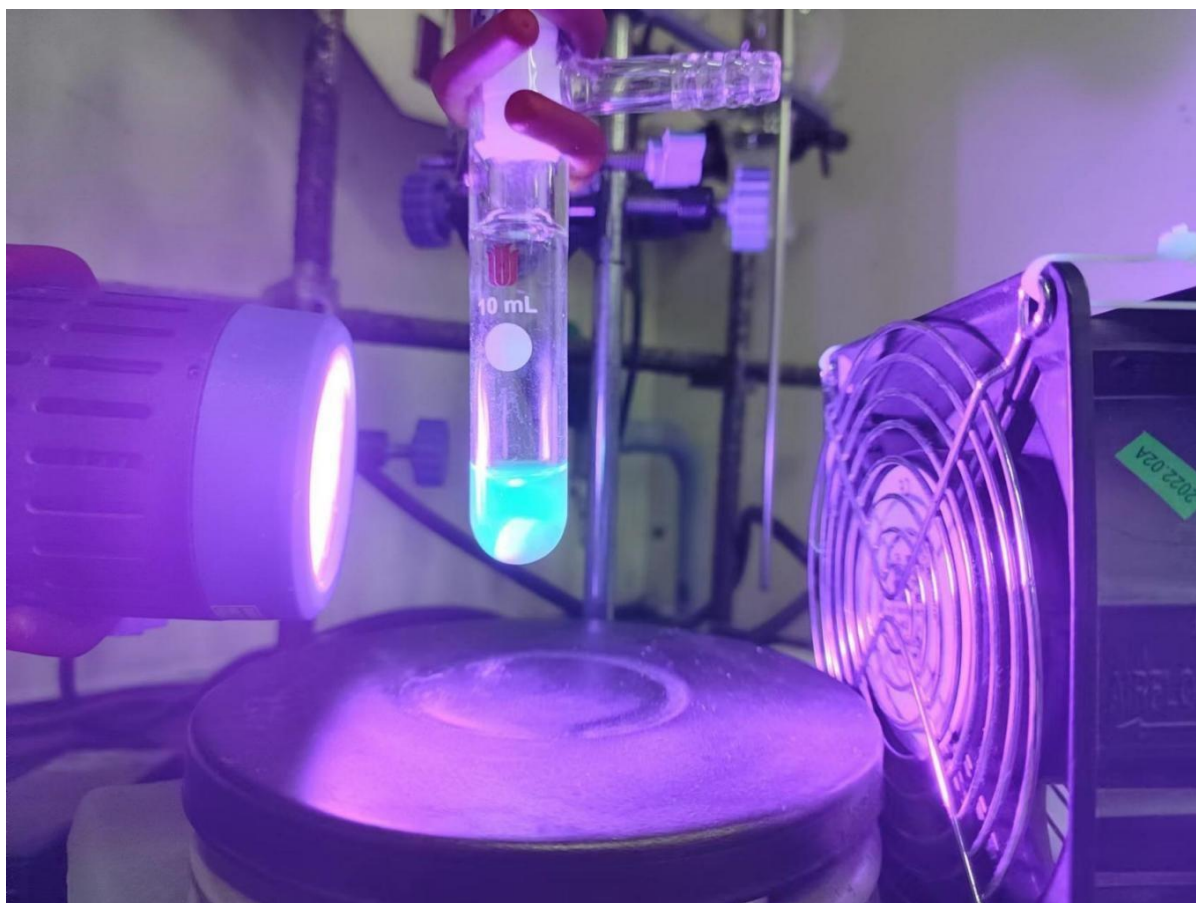
But-3-en-1-yl phenylcarbamate (2o): $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.39 (d, $J = 8.1$ Hz, 2H), 7.29 (dd, $J = 8.6, 7.3$ Hz, 2H), 7.08 – 7.02 (m, 1H), 6.83 (s, 1H), 5.82 (ddt, $J = 17.0, 10.3, 6.7$ Hz, 1H), 5.32 – 5.02 (m, 2H), 4.22 (t, $J = 6.7$ Hz, 2H), 2.43 (dtd, $J = 6.7, 5.3, 1.4$ Hz, 2H).



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-(but-3-en-1-yloxy)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene (2ad). ¹H NMR (600 MHz, CDCl₃) δ 5.93 (ddt, *J* = 17.2, 10.3, 5.6 Hz, 1H), 5.34 (dt, *J* = 5.4, 2.1 Hz, 1H), 5.27 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.15 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.06 – 3.99 (m, 2H), 3.21 (tt, *J* = 11.3, 4.5 Hz, 1H), 2.37 (ddd, *J* = 13.2, 4.8, 2.4 Hz, 1H), 2.27 – 2.17 (m, 1H), 2.09 – 1.94 (m, 2H), 1.93 – 1.77 (m, 5H), 1.63 – 1.03 (m, 21H), 1.00 (s, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.6, 2.7 Hz, 6H), 0.68 (s, 3H).

III. Reaction Optimization

Typical reaction setup



Supplementary Figure 1. The experimental setup for light-promoted reactions.

Reaction irradiated by a Kessil LED (390 nm) light source was running at ambient temperature. A fan was used to cool down the reaction mixture.

Optimization on styrene hydrosulfonylation

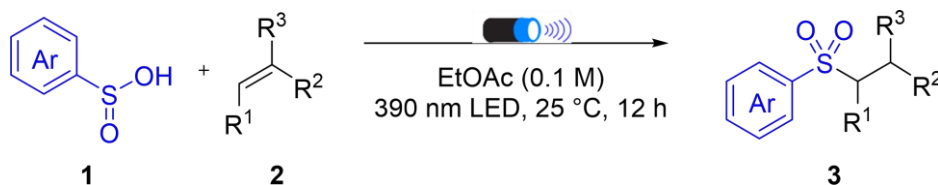
Supplementary Table 1. Selected optimization results for styrene hydrosulfonylation.^a

entry	additives	X equiv	yield of 3ae (%) ^b
1	none	-	22
2	TolSH	0.2	20
3	(TMS) ₃ SiH	0.2	22
4	PhNO ₂	0.2	0
5	Methyl 3-mercaptopropanoate	0.2	32
6	Methyl 2-mercaptobenzoate	0.2	36
7	Triisopropylsilanethiol	0.2	34
8	Hantzsch ester	0.2	40
9	Hantzsch ester	0.5	50
10	Hantzsch ester	2.0	73

^aReaction conditions: 0.2 mmol of **2b** and 0.24 mmol of **1a** in 2 mL of MeCN under argon atmosphere unless otherwise specified. ^bYields estimated by ¹H NMR analysis with dibromomethane as an internal standard.

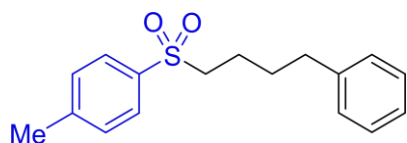
IV. General procedures for light-promoted hydrosulfonylation reaction

General procedure I: hydrosulfonylation of aliphatic alkenes

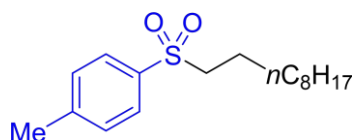


A 20 mL Schlenk tube equipped with a magnetic stir bar was charged with sulfinic acid **1** (0.24 mmol) and aliphatic alkene **2** (0.2 mmol). Then, 2.0 mL of ethyl acetate was added. The Schlenk tube was connected to Schlenk line and freeze-pump-thaw was performed for three times to completely remove air inside the reaction mixture. Eventually the Schlenk tube was refilled with an atmosphere of argon at room temperature and sealed. The reaction vessel was placed in front of a 390 nm Kessil LED (40W) and adequately illuminated. Then the reaction was running at ambient temperature (~25 °C) using a fan to cool down the reaction mixture and stopped after 12 h. The solvent was removed under reduced pressure and the crude

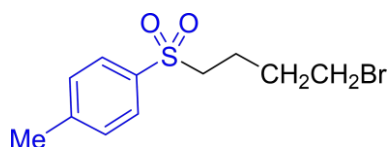
mixture was purified by silica gel column chromatography or prepared TLC (eluent: hexane/diethyl ether or hexane/ethyl acetate; 20/1 – 5/1) to give the corresponding product **3**.



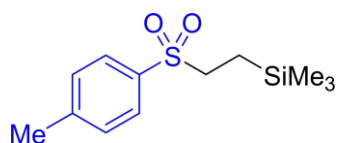
Methyl-4-((4-phenylbutyl)sulfonyl)benzene (3a). Following the general procedure I, the title compound (56.5 mg) was obtained in 98% yield. the NMR data is in line with the literature.^[8] ¹H NMR (600 MHz, CDCl₃) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.32 (, *J* = 8.2 Hz, 2H), 7.29 – 7.22 (m, 2H), 7.20 – 7.15 (m, 1H), 7.14 – 7.07 (m, 2H), 3.14 – 3.02 (m, 2H), 2.58 (t, *J* = 7.5 Hz, 2H), 2.45 (s, 3H), 1.79 – 1.72 (m, 2H), 1.71 – 1.65 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 144.60, 141.31, 136.23, 129.89 (2C), 128.43 (2C), 128.32 (2C), 128.09 (2C), 126.01, 56.21, 35.30, 30.01, 22.39, 21.63. HRMS ESI [M+H]⁺ calculated for C₁₇H₂₁O₂S 289.1262, found 289.1255.



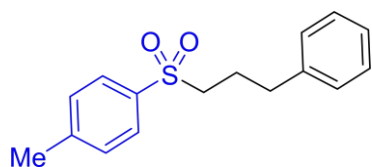
1-(Decylsulfonyl)-4-methylbenzene (3b). Following the general procedure I, the title compound (58.7 mg) was obtained in 99% yield. ¹H NMR (600 MHz, CDCl₃) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 3.31 – 2.83 (m, 2H), 2.44 (s, 3H), 1.81 – 1.59 (m, 2H), 1.43 – 1.29 (m, 2H), 1.29 – 1.01 (m, 12H), 0.86 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 144.53, 136.30, 129.86 (2C), 128.08 (2C), 56.42, 31.83, 29.41, 29.22, 29.22, 28.99, 28.27, 22.71, 22.65, 21.62, 14.09. HRMS ESI [M+H]⁺ calculated for C₁₇H₂₉O₂S 297.1883, found 297.1867.



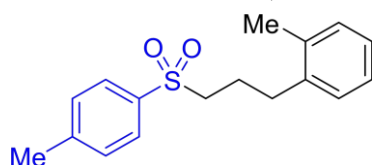
1-((4-Bromobutyl)sulfonyl)-4-methylbenzene (3c). Following the general procedure I, the title compound (53.6 mg) was obtained in 92% yield. ¹H NMR (600 MHz, CDCl₃) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 3.36 (t, *J* = 6.4 Hz, 2H), 3.17 – 2.94 (t, *J* = 7.7 Hz, 2H), 2.44 (s, 3H), 1.95 (dq, *J* = 8.8, 6.3 Hz, 2H), 1.91 – 1.84 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 144.84, 135.99, 130.00 (2C), 128.08 (2C), 55.31, 32.27, 30.94, 21.66, 21.61. HRMS ESI [M+H]⁺ calculated for C₁₁H₁₆BrO₂S 291.0049, found 291.0036.



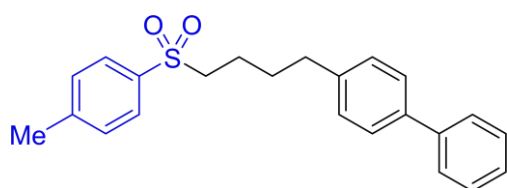
Trimethyl(2-tosylethyl)silane (3d). Following the general procedure I, the title compound (50.8 mg) was obtained in 99% yield ¹H NMR (600 MHz, CDCl₃) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 3.00 – 2.94 (m, 2H), 2.45 (s, 3H), 0.94 – 0.87 (m, 2H), 0.00 (s, 9H). ¹³C NMR (151 MHz, CDCl₃) δ 146.53, 137.81, 131.88 (2C), 130.31 (2C), 54.84, 23.67, 11.23, 0.00 (3C). HRMS ESI [M+H]⁺ calculated for C₁₂H₂₁O₂SSi 257.1026, found 257.1021.



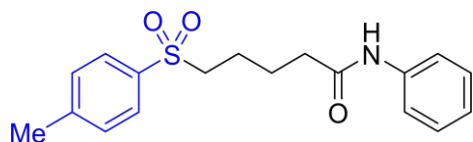
Methyl-4-((3-phenylpropyl)sulfonyl)benzene (3e). Following the general procedure I, the title compound (54.3 mg) was obtained in 99% yield. ^1H NMR (600 MHz, CDCl_3) δ 7.75 (d, $J = 8.2$ Hz, 2H), 7.34 (d, $J = 7.9$ Hz, 2H), 7.29 – 7.23 (m, 2H), 7.21 – 7.17 (m, 1H), 7.09 (d, $J = 6.8$ Hz, 2H), 3.08 – 3.03 (m, 2H), 2.68 (t, $J = 7.5$ Hz, 2H), 2.44 (s, 3H), 2.06 – 2.00 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 144.67, 139.96, 136.17, 129.93 (2C), 128.61 (2C), 128.40 (2C), 128.08 (2C), 126.42, 55.57, 34.13, 24.29, 21.64. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{16}\text{H}_{19}\text{O}_2\text{S}$ 275.1100, found 275.1094.



Methyl-2-(3-tosylpropyl)benzene (3f). Following the general procedure I, the title compound (52.5 mg) was obtained in 91% yield. ^1H NMR (600 MHz, CDCl_3) δ 7.77 (d, $J = 8.3$ Hz, 2H), 7.37 – 7.33 (m, 2H), 7.16 – 7.08 (m, 3H), 7.06 – 7.01 (m, 1H), 3.15 – 3.07 (m, 2H), 2.69 (t, $J = 7.7$ Hz, 2H), 2.45 (s, 3H), 2.24 (s, 3H), 2.07 – 1.95 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 144.68, 138.20, 136.19, 135.93, 130.47, 129.93 (2C), 128.84, 128.08 (2C), 126.55, 126.12, 55.81, 31.58, 23.03, 21.65, 19.26. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{21}\text{O}_2\text{S}$ 289.1257, found 289.1249.

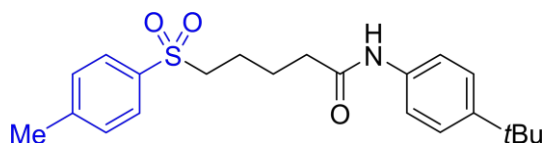


4-(3-Tosylpropyl)-1,1'-biphenyl (3g). Following the general procedure I, the title compound (61.2 mg) was obtained in 84% yield. ^1H NMR (600 MHz, CDCl_3) δ 7.81 – 7.73 (m, 2H), 7.60 – 7.55 (m, 2H), 7.51 – 7.48 (m, 2H), 7.46 – 7.40 (m, 2H), 7.36 – 7.31 (m, 3H), 7.22 – 7.15 (m, 2H), 3.14 – 2.97 (m, 2H), 2.63 (t, $J = 7.4$ Hz, 2H), 2.44 (s, 3H), 1.93 – 1.67 (m, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 144.64, 140.98, 140.41, 139.01, 136.20, 129.91 (2C), 128.10 (2C), 128.77(3C), 127.17 (2C), 127.12 (2C), 126.99 (2C), 56.21, 34.91, 29.97, 22.39, 21.63. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{23}\text{H}_{25}\text{O}_2\text{S}$, 365.1570, found 365.1554.

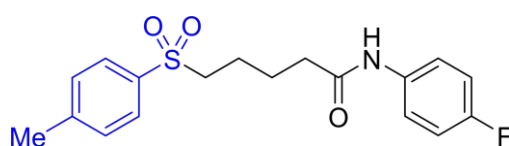


N-Phenyl-5-tosylpentanamide (3h). Following the general procedure I, the title compound (58.3 mg) was obtained in 88% yield. ^1H NMR (600 MHz, CDCl_3) δ 7.76 (d, $J = 8.3$ Hz, 2H), 7.72 (s, 1H), 7.52 – 7.46 (d, $J = 8.3$ Hz, 2H), 7.36 – 7.31 (d, $J = 7.9$ Hz, 2H), 7.30 – 7.25 (m, 2H), 7.08 (tt, $J = 7.2, 1.2$ Hz, 1H), 3.15 – 3.01 (m, 2H), 2.43 (s, 3H), 2.38 – 2.27 (m, 2H), 1.86 – 1.71 (m, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.51, 144.88, 137.94, 135.97, 130.01

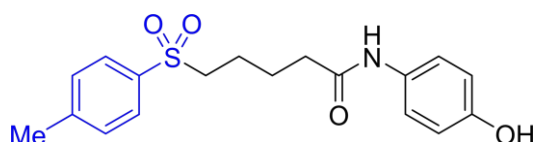
(2C), 128.94 (2C), 127.99 (2C), 124.24, 119.89 (2C), 55.94, 36.62, 24.06, 22.24, 21.64. HRMS ESI $[M+H]^+$ calculated for $C_{18}H_{22}NO_3S$ 332.1315, found 332.1300.



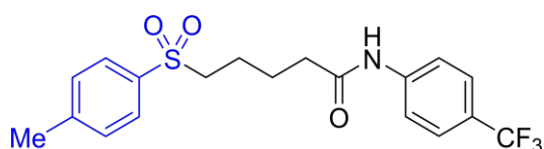
(4-(Tert-butyl)phenyl)-5-tosylpentanamide (3i). Following the general procedure I, the title compound (69.0 mg) was obtained in 89% yield. 1H NMR (600 MHz, $CDCl_3$) δ 7.77 – 7.73 (d, $J = 8.3$ Hz, 2H), 7.61 (s, 1H), 7.42 – 7.37 (d, $J = 8.3$ Hz, 2H), 7.34 – 7.27 (m, 4H), 3.13 – 3.08 (m, 2H), 2.42 (s, 3H), 2.36 – 2.31 (m, 2H), 1.79 (p, $J = 3.3$ Hz, 4H), 1.28 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.37, 147.22, 144.83, 135.99, 135.26, 130.00 (2C), 128.00 (2C), 125.74 (2C), 119.73 (2C), 55.94, 36.58, 34.35, 31.36 (3C), 24.11, 22.27, 21.63. HRMS ESI $[M+H]^+$ calculated for $C_{22}H_{30}NO_3S$ 388.1946, found 388.1926.



(4-Fluorophenyl)-5-tosylpentanamide (3j). Following the general procedure I, the title compound (61.5 mg) was obtained in 88% yield. 1H NMR (600 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.75 (d, $J = 8.2$ Hz, 2H), 7.50 – 7.40 (m, 2H), 7.33 (d, $J = 8.2$ Hz, 2H), 6.95 (t, $J = 8.7$ Hz, 2H), 3.11 (m, 2H), 2.43 (s, 3H), 2.37 – 2.31 (m, 2H), 1.80 (p, $J = 3.7$ Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.51, 159.27 (d, $^1J_{C-F} = 243.3$ Hz), 144.98, 135.94, 133.97 (d, $^4J_{C-F} = 2.9$ Hz), 130.04 (2C), 127.95 (2C), 121.69 (d, $^3J_{C-F} = 7.8$ Hz) (2C), 115.51 (d, $^2J_{C-F} = 22.4$ Hz) (2C), 55.92, 36.43, 24.05, 22.17, 21.63. ^{19}F NMR (565 MHz, $CDCl_3$) δ -118.16. HRMS ESI $[M+H]^+$ calculated for $C_{18}H_{21}FNO_3S$ 350.1226, found 350.1202.

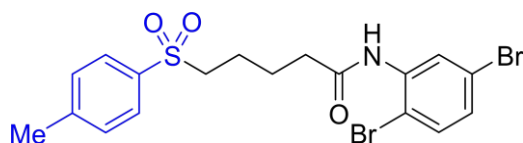


(4-Hydroxyphenyl)-5-tosylpentanamide (3k). Following the general procedure I, the title compound (47.3 mg) was obtained in 68% yield. 1H NMR (600 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.75 (d, $J = 8.2$ Hz, 2H), 7.42 – 7.36 (m, 4H), 7.33 (d, $J = 8.2$ Hz, 2H), 3.15 – 3.07 (m, 2H), 2.43 (s, 3H), 2.39 – 2.28 (m, 2H), 1.87 – 1.77 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.58, 145.01, 137.06, 135.90, 131.87 (2C) 130.05 (2C), 127.95 (2C), 121.40 (2C), 116.71, 55.89, 36.56, 23.97, 22.14, 21.66. HRMS ESI $[M+H]^+$ calculated for $C_{18}H_{22}NO_4S$ 348.1270, found 348.1249.

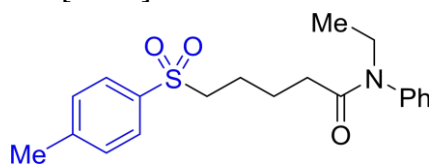


5-Tosyl-N-(4-(trifluoromethyl)phenyl)pentanamide (3l). Following the general procedure I, the title compound (64.7 mg) was obtained in 81% yield. 1H NMR (600 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.75 (d, $J = 8.2$ Hz, 2H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.51 (d, $J = 8.4$ Hz, 2H), 7.33 (d, $J = 8.2$ Hz, 2H), 3.33 – 3.04 (m, 2H), 2.42 (d, $J = 8.0$ Hz, 5H), 1.83 (p, $J = 2.9$ Hz, 4H). ^{13}C

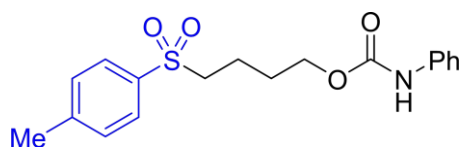
NMR (151 MHz, CDCl₃) δ 170.89, 145.11, 141.10, 135.84, 130.08 (2C), 127.92 (2C), 126.15 (q, $^3J_{C-F} = 3.8$ Hz) (2C), 125.82 (q, $^2J_{C-F} = 33.0$ Hz), 124.10 (q, $^1J_{C-F} = 271.6$ Hz), 119.33 (2C), 55.89, 36.58, 23.89, 22.10, 21.61. ^{19}F NMR (565 MHz, CDCl₃) δ -62.10. HRMS ESI [M+H]⁺ calculated for C₁₉H₂₁F₃NO₃S 400.1194, found 400.1171.



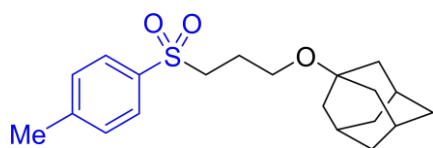
N-(2,5-Dibromophenyl)-5-tosylpentanamide (3m). Following the general procedure I, the title compound (48.0 mg) was obtained in 49% yield. ^1H NMR (600 MHz, CDCl₃) δ 8.53 – 8.50 (s, 1H), 7.77 (d, $J = 8.2$ Hz, 2H), 7.54 (s, 1H), 7.37 (d, $J = 8.5$ Hz, 1H), 7.34 (d, $J = 8.2$ Hz, 2H), 7.10 (dd, $J = 8.5, 2.4$ Hz, 1H), 3.15 – 3.10 (m, 2H), 2.43 (d, $J = 5.0$ Hz, 5H), 1.83 (p, $J = 3.0, 2.6$ Hz, 4H). ^{13}C NMR (151 MHz, CDCl₃) δ 170.11, 144.75, 136.58, 136.21, 133.10, 129.94 (2C), 128.15, 128.04 (2C), 124.65, 122.01, 55.94, 36.87, 23.81, 22.31, 21.58. HRMS ESI [M+H]⁺ calculated for C₁₈H₂₀Br₂NO₃S 487.9531, found 487.9344.



N-Ethyl-N-phenyl-5-tosylpentanamide (3n). Following the general procedure I, the title compound (62.6 mg) was obtained in 87% yield. ^1H NMR (600 MHz, CDCl₃) δ 7.71 (d, $J = 8.2$ Hz, 2H), 7.40 (dd, $J = 8.4, 7.2$ Hz, 2H), 7.34 (d, $J = 7.2$ Hz, 1H), 7.31 (d, $J = 8.2$ Hz, 2H), 7.08 (dd, $J = 8.4, 1.3$ Hz, 2H), 3.68 (q, $J = 7.1$ Hz, 2H), 2.95 (t, $J = 7.5$ Hz, 2H), 2.41 (s, 3H), 1.96 (m, 2H), 1.59 (m, 4H), 1.05 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl₃) δ 171.38, 144.61, 142.18, 136.12, 129.87 (2C), 129.79 (2C), 128.34 (2C), 128.04, 128.02 (2C), 56.09, 44.01, 33.68, 24.04, 22.34, 21.60, 13.04. HRMS ESI [M+H]⁺ calculated for C₂₀H₂₆NO₃S 360.1633, found 360.1617.

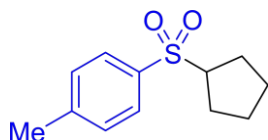


4-Tosylbutyl phenylcarbamate (3o). Following the general procedure I, the title compound (39.6 mg) was obtained in 57% yield. ^1H NMR (600 MHz, CDCl₃) δ 7.78 (d, $J = 8.3$ Hz, 2H), 7.41 – 7.33 (m, 4H), 7.30 (dd, $J = 8.6, 7.3$ Hz, 2H), 7.10 – 7.03 (m, 1H), 6.71 (s, 1H), 4.13 (t, $J = 6.1$ Hz, 2H), 3.23 – 3.03 (t, $J = 7.7$ Hz, 2H), 2.43 (s, 3H), 2.01 – 1.80 (m, 2H), 1.79 – 1.72 (m, 2H). ^{13}C NMR (151 MHz, CDCl₃) δ 153.36, 144.73, 137.78, 136.20, 129.94 (2C), 129.05 (2C), 128.06 (2C), 123.53, 118.76 (2C), 64.00, 55.84, 27.63, 21.56, 19.60. HRMS ESI [M+H]⁺ calculated for C₁₈H₂₂NO₄S 348.1270, found 348.1249.

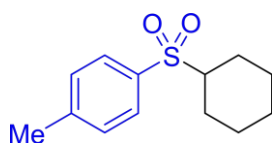


(3s,5s,7s)-1-(3-Tosylpropoxy)adamantane (3p). Following the general procedure I, the title compound (30.7 mg) was obtained in 44% yield. ^1H NMR (600 MHz, CDCl₃) δ 7.77 (d, $J =$

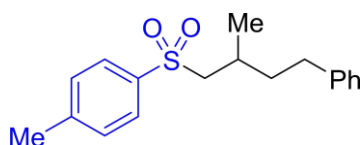
8.2 Hz, 2H), 7.34 (d, $J = 8.2$ Hz, 2H), 3.44 (t, $J = 6.0$ Hz, 2H), 3.24 – 3.10 (m, 2H), 2.44 (s, 3H), 2.24 – 2.05 (m, 3H), 1.96 – 1.85 (m, 2H), 1.73 – 1.51 (m, 12H). ^{13}C NMR (151 MHz, CDCl_3) δ 144.53, 136.29, 129.86 (2C), 128.13 (2C), 72.22, 57.58, 53.86, 41.49 (3C), 36.40 (3C), 30.44 (3C), 24.23, 21.61. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{20}\text{H}_{29}\text{O}_3\text{S}$ 349.1832, found 349.1828.



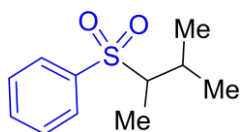
1-(Cyclopentylsulfonyl)-4-methylbenzene (3q). Following the general procedure I, the title compound (44.0 mg) was obtained in 98% yield. ^1H NMR (600 MHz, CDCl_3) δ 7.76 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 8.2$ Hz, 2H), 3.46 (tt, $J = 8.7, 7.2$ Hz, 1H), 2.43 (s, 3H), 2.16 – 2.07 (m, 2H), 1.94 – 1.80 (m, 2H), 1.79 – 1.70 (m, 2H), 1.63 – 1.53 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 144.35, 136.06, 129.77 (2C), 128.48 (2C), 64.28, 27.28 (2C), 25.85 (2C), 21.61. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{12}\text{H}_{17}\text{O}_2\text{S}$ 225.0949, found 225.0937.



1-(Cyclohexylsulfonyl)-4-methylbenzene (3r). Following the general procedure I, the title compound (45.8 mg) was obtained in 96% yield. ^1H NMR (600 MHz, CDCl_3) δ 7.73 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 8.2$ Hz, 2H), 2.86 (tt, $J = 12.1, 3.4$ Hz, 1H), 2.43 (s, 3H), 2.10 – 2.01 (m, 2H), 1.83 (dt, $J = 13.0, 3.1$ Hz, 2H), 1.66 (dt, $J = 3.4, 1.6$ Hz, 1H), 1.42– 1.34 (m, 2H), 1.26 – 1.16 (m, 2H), 1.13 (tt, $J = 12.6, 3.2$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 144.39, 134.44, 129.61 (2C), 129.03 (2C), 63.57, 25.58 (2C), 25.12 (2C), 25.08, 21.54. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{13}\text{H}_{19}\text{O}_2\text{S}$ 239.1100, found 239.1103.

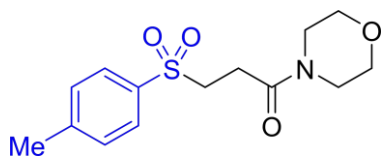


1-Methyl-4-((2-methyl-4-phenylbutyl)sulfonyl)benzene (3s). Following the general procedure I, the title compound (36.3 mg) was obtained in 60% yield. ^1H NMR (600 MHz, CDCl_3) δ 7.74 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 8.2$ Hz, 2H), 7.27 – 7.22 (m, 2H), 7.19 – 7.15 (m, 1H), 7.10 – 7.08 (m, 2H), 3.10 (dd, $J = 14.2, 5.0$ Hz, 1H), 2.94 (dd, $J = 14.2, 7.4$ Hz, 1H), 2.64– 2.47 (m, 2H), 2.45 (s, 3H), 2.14 – 2.03 (m, 1H), 1.79 - 1.72 (m, 1H), 1.59 - 1.52 (m, 1H), 1.12 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 144.49, 141.54, 137.07, 129.90 (2C), 128.40 (2C), 128.34 (2C), 127.92 (2C), 125.91, 62.58, 38.33, 32.72, 28.32, 21.63, 19.88. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{23}\text{O}_2\text{S}$ 303.1413, found 303.1404.

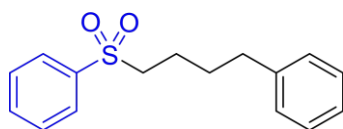


((3-Methylbutan-2-yl)sulfonyl)benzene (3t). Following the general procedure I, the title compound (38.2 mg) was obtained in 90% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.88 (d, $J =$

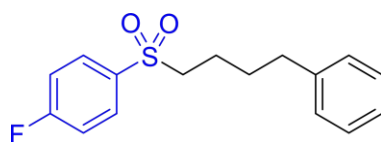
7.2 Hz, 2H), 7.64 (t, $J = 7.4$ Hz, 1H), 7.56 (t, $J = 7.6$ Hz, 2H), 3.11 – 2.84 (m, 1H), 2.58 – 2.47 (m, 1H), 1.20 (d, $J = 7.1$ Hz, 3H), 1.03 (d, $J = 6.8$ Hz, 3H), 0.99 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 138.82, 131.99, 129.23 (2C), 128.77 (2C), 64.86, 26.41, 22.08, 16.79, 7.99. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{11}\text{H}_{17}\text{O}_2\text{S}$ 217.0944, found 217.0936.



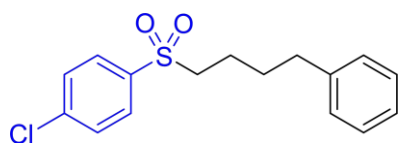
1-Morpholino-3-tosylpropan-1-one (3u). Following the general procedure I, the title compound (58.9 mg) was obtained in 99% yield. ^1H NMR (600 MHz, CDCl_3) δ 7.78 (d, $J = 8.2$ Hz, 2H), 7.35 (d, $J = 8.2$ Hz, 2H), 3.66 (t, $J = 4.9$ Hz, 2H), 3.62 (t, $J = 4.9$ Hz, 2H), 3.54 (dd, $J = 5.6, 4.1$ Hz, 2H), 3.46 – 3.40 (m, 4H), 2.82 – 2.76 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 167.55, 144.99, 136.08, 130.02 (2C), 127.95 (2C), 66.68, 66.41, 51.99, 45.75, 42.23, 25.90, 21.65. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{14}\text{H}_{20}\text{NO}_4\text{S}$ 298.1113, found 298.1095.



((4-Phenylbutyl)sulfonyl)benzene (3v). Following the general procedure I, the title compound (48.3 mg) was obtained in 88% yield. ^1H NMR (600 MHz, CDCl_3) δ 7.91 – 7.86 (m, 2H), 7.68 – 7.62 (m, 1H), 7.56 (ddt, $J = 7.9, 6.5, 1.2$ Hz, 2H), 7.28 – 7.22 (m, 2H), 7.20 – 7.14 (m, 1H), 7.12 – 7.07 (m, 2H), 3.12 – 3.06 (m, 2H), 2.58 (t, $J = 7.5$ Hz, 2H), 1.80 – 1.72 (m, 2H), 1.72 – 1.65 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 141.24, 139.18, 133.65, 129.28 (2C), 128.44 (2C), 128.32 (2C), 128.06 (2C), 126.04, 56.12, 35.28, 29.99, 22.29. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{16}\text{H}_{19}\text{O}_2\text{S}$ 275.1100, found 275.1092.

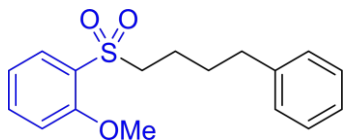


1-Fluoro-4-((4-phenylbutyl)sulfonyl)benzene (3w). Following the general procedure I, the title compound (53.8 mg) was obtained in 92% yield. ^1H NMR (600 MHz, CDCl_3) δ 7.88 (dd, $J = 8.9, 5.0$ Hz, 2H), 7.28 – 7.20 (m, 4H), 7.19 – 7.16 (m, 1H), 7.10 (dd, $J = 7.9, 1.1$ Hz, 2H), 3.14 – 3.02 (m, 2H), 2.59 (t, $J = 7.2$ Hz, 2H), 1.80 – 1.66 (m, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 165.81 (d, $^1J_{\text{C-F}} = 256.1$ Hz), 141.15, 135.19 (d, $^4J_{\text{C-F}} = 3.2$ Hz), 130.94 (d, $^3J_{\text{C-F}} = 9.5$ Hz) (2C), 128.46 (2C), 128.32 (2C), 126.08, 116.60 (d, $^2J_{\text{C-F}} = 22.7$ Hz) (2C), 56.27, 35.24, 29.90, 22.30. ^{19}F NMR (565 MHz, CDCl_3) δ -103.61. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{16}\text{H}_{18}\text{FO}_2\text{S}$ 293.1006, found 293.0999.

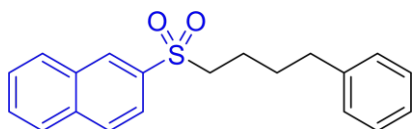


1-Chloro-4-((4-phenylbutyl)sulfonyl)benzene (3x). Following the general procedure I, the title compound (54.4 mg) was obtained in 88% yield. ^1H NMR (600 MHz, CDCl_3) δ 7.80 (d,

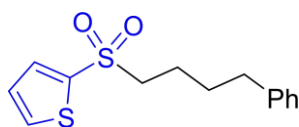
$J = 8.6$ Hz, 2H), 7.52 (d, $J = 8.6$ Hz, 2H), 7.25 (ddd, $J = 7.6, 6.6, 1.2$ Hz, 2H), 7.22 – 7.14 (m, 1H), 7.13 – 7.06 (m, 2H), 3.25 – 2.99 (m, 2H), 2.59 (t, $J = 7.2$ Hz, 2H), 1.81 – 1.64 (m, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 141.12, 140.45, 137.58, 129.63 (2C), 129.59 (2C), 128.47 (2C), 128.32 (2C), 126.09, 56.16, 35.21, 29.89, 22.25. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{16}\text{H}_{18}\text{ClO}_2\text{S}$ 309.0711, found 309.0704.



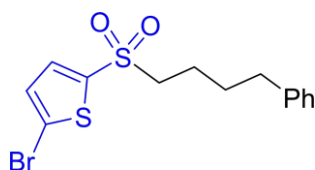
1-Methoxy-2-((4-phenylbutyl)sulfonyl)benzene (3y). Following the general procedure I, the title compound (47.5 mg) was obtained in 78% yield. ^1H NMR (600 MHz, CDCl_3) δ 7.93 (dd, $J = 7.6, 1.8$ Hz, 1H), 7.58 (ddd, $J = 8.3, 7.6, 1.8$ Hz, 1H), 7.26 – 7.21 (m, 2H), 7.18 – 7.14 (m, 1H), 7.11 – 7.06 (m, 3H), 7.03 (dd, $J = 8.3, 0.9$ Hz, 1H), 3.95 (s, 3H), 3.39 – 3.33 (t, $J = 7.5$ Hz, 2H), 2.58 (t, $J = 7.3$ Hz, 2H), 1.78 – 1.66 (m, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 157.34, 141.43, 135.57, 130.58, 128.41 (2C), 128.34 (2C), 126.91, 125.98, 120.79, 112.36, 56.33, 54.22, 35.29, 30.09, 22.07. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{21}\text{O}_3\text{S}$ 305.1206, found 305.1199.



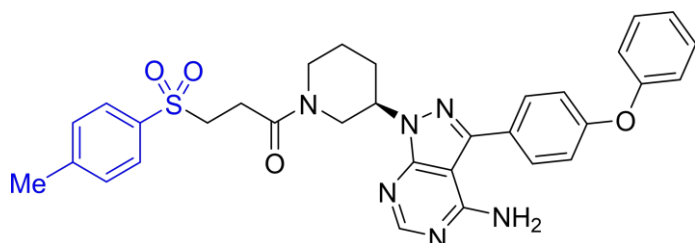
((4-Phenylbutyl)sulfonyl)naphthalene (3z). Following the general procedure I, the title compound (43.5 mg) was obtained in 67% yield. ^1H NMR (600 MHz, CDCl_3) δ 8.47 (d, $J = 1.8$ Hz, 1H), 8.00 (dd, $J = 9.0, 2.1$ Hz, 2H), 7.97 – 7.91 (m, 1H), 7.85 (dd, $J = 8.6, 1.9$ Hz, 1H), 7.77–7.56 (m, 2H), 7.21 (dd, $J = 8.0, 6.7$ Hz, 2H), 7.17 – 7.11 (m, 1H), 7.09 – 7.05 (m, 2H), 3.21 – 3.15 (m, 2H), 2.57 (t, $J = 7.6$ Hz, 2H), 1.83 – 1.74 (m, 2H), 1.74 – 1.67 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 140.18, 134.96, 134.29, 131.17, 128.86, 128.57, 128.42, 128.25, 127.37 (2C), 127.25 (2C), 126.98, 126.70, 124.98, 121.72, 55.13, 34.22, 28.98, 21.35. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{20}\text{H}_{21}\text{O}_2\text{S}$ 325.1257, found 325.1249.



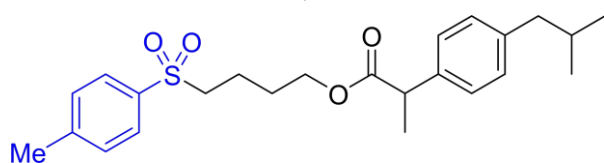
2-((4-phenylbutyl)sulfonyl)thiophene (3aa). Following the general procedure I, the title compound (43.5 mg) was obtained in 91% yield. ^1H NMR (600 MHz, CDCl_3) δ 7.70 (dd, $J = 5.0, 1.3$ Hz, 1H), 7.66 (dd, $J = 3.8, 1.4$ Hz, 1H), 7.28 – 7.25 (m, 2H), 7.20 – 7.17 (m, 1H), 7.15 (dd, $J = 5.0, 3.8$ Hz, 1H), 7.13 – 7.11 (m, 2H), 3.23 – 3.18 (m, 2H), 2.61 (t, $J = 7.6$ Hz, 2H), 1.86 – 1.79 (m, 2H), 1.75 – 1.69 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 141.23, 140.16, 134.08, 133.94, 128.47(2C), 128.36(2C), 127.94, 126.07, 57.57, 35.29, 29.89, 22.67. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{14}\text{H}_{17}\text{O}_2\text{S}_2$ 281.0664, found 281.0659.



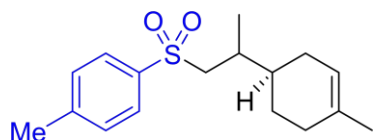
2-bromo-5-((4-phenylbutyl)sulfonyl)thiophene (3ab). Following the general procedure I, the title compound (61.1 mg) was obtained in 85% yield. ¹H NMR (600 MHz, CDCl₃) δ 7.39 (d, *J* = 4.0 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.12 (dd, *J* = 5.4, 3.4 Hz, 3H), 3.19 – 3.15 (t, *J* = 7.5 Hz, 2H), 2.62 (t, *J* = 7.5 Hz, 2H), 1.87 – 1.79 (m, 2H), 1.73 (p, *J* = 7.6 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 140.05, 139.81, 133.24, 129.92, 127.45(2C), 127.31(2C), 125.08, 121.05, 56.39, 34.17, 28.76, 21.55. HRMS ESI [M+H]⁺ calculated for C₁₄H₁₆BrO₂S₂ 358.9770, found 358.9776.



1-(3-(4-Amino-3-(4-phenoxyphenyl)-1H-pyrazolo[3,4-d]pyrimidin-1-yl)piperidin-1-yl)-3-tosylpropan-1-one (3ac). Following the general procedure I, the title compound (69.2 mg) was obtained in 58% yield as a mixture of 2 rotamers (1:1).^[9] ¹H NMR (600 MHz, CDCl₃) δ 8.38 (s, 0.5H), 8.32 (s, 0.5H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.43 – 7.35 (m, 3H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.21 – 7.14 (m, 3H), 7.08 (t, *J* = 7.4 Hz, 2H), 5.93 (s, 2H), 4.91– 4.81 (m, 1H), 4.69 (dd, *J* = 12.9, 4.4 Hz, 0.5H), 4.38 (dt, *J* = 13.3, 4.1 Hz, 0.5H), 4.01 (dd, *J* = 13.4, 4.2 Hz, 0.5H), 3.86 (d, *J* = 13.7 Hz, 0.5H), 3.80 – 3.73 (m, 0.5H), 3.58 – 3.39 (m, 2H), 3.31 (dd, *J* = 12.8, 10.7 Hz, 0.5H), 3.22 – 3.14 (m, 0.5H), 2.91 – 2.88 (m, 2H), 2.78 – 2.75 (m, 0.5H), 2.45 (s, 1.5H), 2.43 (s, 1.5H), 2.38 – 2.32 (m, 1H), 2.26– 2.22 (m, 1H), 2.05 – 2.00 (m, 0.5H), 1.93 – 1.89 (m, 0.5H), 1.77 – 1.68 (m, 0.5H), 1.66 – 1.57 (m, 0.5H). ¹³C NMR (151 MHz, CDCl₃) δ 167.69, 167.61, 158.88, 158.85, 157.29, 156.37, 155.18, 154.44, 154.24, 153.96, 145.10, 144.98, 144.49, 143.36, 136.27, 136.24, 130.13, 130.09, 130.06, 130.03, 128.12, 128.09, 127.48, 124.26, 119.74, 119.29, 119.27, 53.33, 52.58, 52.26, 52.22, 49.62, 46.12, 45.60, 42.28, 31.71, 30.19, 29.96, 26.40, 26.29, 25.02, 23.78, 22.77. HRMS ESI [M+H]⁺ calculated for C₃₂H₃₃N₆O₄S 597.2279, found 597.2264.

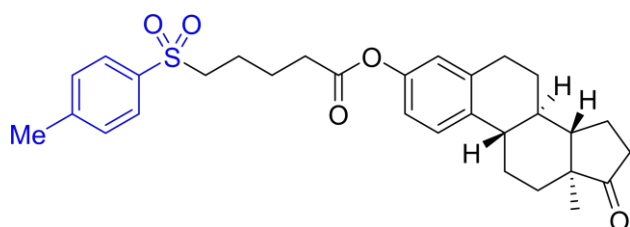


5-Tosylbutyl 2-(4-isobutylphenyl)propanoate (3ad). Following the general procedure I, the title compound (58.3 mg) was obtained in 70% yield. ¹H NMR (600 MHz, CDCl₃) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 4.01 (td, *J* = 6.0, 3.2 Hz, 2H), 3.64 (q, *J* = 7.1 Hz, 1H), 3.01 (td, *J* = 7.1, 2.0 Hz, 2H), 2.44 (m, 5H), 1.89 - 1.81(m, 1H), 1.74 – 1.60 (m, 4H), 1.44 (d, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 174.62, 144.72, 140.60, 137.58, 136.09, 129.93 (2C), 129.37 (2C), 128.08 (2C), 127.10 (2C), 63.54, 55.72, 45.08, 45.03, 30.18, 27.18, 22.41 (2C), 21.64, 19.61, 18.38. HRMS ESI [M+H]⁺ calculated for C₂₄H₃₃O₄S 417.2094, found 417.2083.

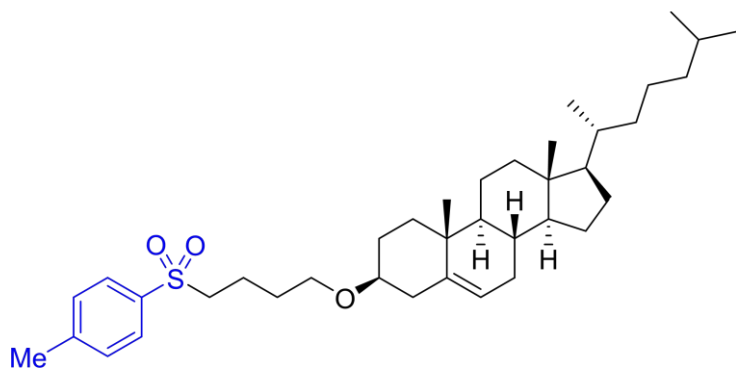


1-Methyl-4-((2-((R)-4-methylcyclohex-3-en-1-yl)propyl)sulfonyl)benzene (3ae).

Following the general procedure I, the title compound (39.8 mg) was obtained in 68% yield. The separated 2 doublet peaks located at 1.05 ppm and 1.03 ppm in ^1H NMR, assigned to methyl group attached to tertiary carbon, indicate the product is a mixture of 2 diastereomers with *d.r.* estimated as 1:1. ^1H NMR (600 MHz, CDCl_3) δ 7.78 (d, $J = 8.3$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 5.45 – 5.25 (m, 1H), 3.13 – 3.08 (m, 1H), 2.91 – 2.86 (m, 1H), 2.44 (s, 3H), 2.17 – 2.00 (m, 1H), 1.89 (m, 3H), 1.59 (s, 3H), 1.58 – 1.45 (m, 2H), 1.35 – 1.18 (m, 2H), 1.05 (d, $J = 6.9$ Hz, 1.5H), 1.03 (d, $J = 6.9$ Hz, 1.5H). ^{13}C NMR (151 MHz, CDCl_3) δ 144.56, 144.55, 137.31, 137.27, 134.18, 134.12, 129.97, 128.01, 120.15, 120.10, 60.89, 60.70, 38.79, 38.73, 32.72, 30.63, 30.49, 28.55, 27.44, 26.32, 25.29, 23.44, 21.72, 16.94, 16.59. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{25}\text{O}_2\text{S}$ 293.1570, found 293.1567.

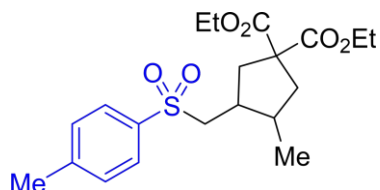


(8R,9S,13S,14S)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 5-tosylpentanoate (3af). Following the general procedure I, the title compound (50.9 mg) was obtained in 50% yield. ^1H NMR (600 MHz, CDCl_3) δ 7.78 (d, $J = 8.2$ Hz, 2H), 7.35 (d, $J = 8.2$ Hz, 2H), 7.28 – 7.24 (m, 1H), 6.78 (dd, $J = 8.4, 2.5$ Hz, 1H), 6.76 (d, $J = 2.5$ Hz, 1H), 3.16 – 3.05 (m, 2H), 2.94 – 2.83 (m, 2H), 2.62 – 2.51 (m, 2H), 2.51 – 2.46 (m, 1H), 2.44 (s, 3H), 2.41 – 2.35 (m, 1H), 2.27 (td, $J = 10.7, 4.1$ Hz, 1H), 2.16 – 2.12 (m, 1H), 2.08 – 1.97 (m, 2H), 1.98 – 1.92 (m, 1H), 1.82 (dt, $J = 7.3, 2.8$ Hz, 4H), 1.68 – 1.39 (m, 6H), 0.90 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.59, 148.41, 144.76, 138.06, 137.47, 136.09, 129.98 (2C), 128.09 (2C), 126.41, 121.49, 118.65, 55.95, 50.42, 47.94, 44.14, 37.99, 35.86, 33.66, 31.55, 29.40, 26.32, 25.75, 23.57, 22.30, 21.66, 21.59, 13.83. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{30}\text{H}_{37}\text{O}_5\text{S}$ 509.2362, found 509.2333.

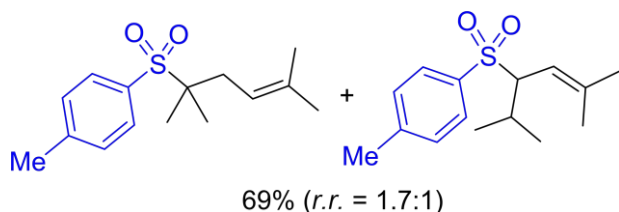


(3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-3-(4-tosylbutoxy)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene (3ag). Following the general procedure I, the title compound (62.1 mg) was obtained in 52% yield.

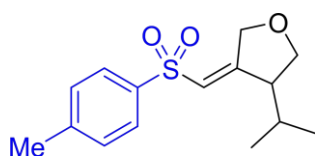
^1H NMR (600 MHz, CDCl_3) δ 7.79 (d, $J = 8.3$ Hz, 2H), 7.36 (d, $J = 8.3$ Hz, 2H), 5.33 – 5.29 (m, 1H), 3.49 (t, $J = 6.0$ Hz, 2H), 3.21 – 3.16 (m, 2H), 3.05 (tt, $J = 11.0, 4.4$ Hz, 1H), 2.45 (s, 3H), 2.25 (ddd, $J = 13.2, 4.8, 2.3$ Hz, 1H), 2.14 – 2.06 (m, 1H), 2.02 – 1.91 (m, 4H), 1.87 – 1.76 (m, 3H), 1.54 – 1.21 (m, 13H), 1.19 – 1.02 (m, 7H), 1.01 – 0.98 (m, 3H), 0.97 (s, 3H), 0.91 (d, $J = 6.6$ Hz, 3H), 0.86 (d, $J = 6.6, 3\text{H}$), 0.85 (d, $J = 6.6, 3\text{H}$), 0.67 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 144.60, 140.71, 136.27, 129.89 (2C), 128.13 (2C), 121.72, 79.18, 65.49, 56.77, 56.16, 53.74, 50.18, 42.33, 39.78, 39.53, 39.03, 37.15, 36.84, 36.19, 35.79, 31.94, 31.88, 28.34, 28.23, 28.02, 24.29, 23.83 (2C), 22.83, 22.57, 21.63, 21.06, 19.36, 18.72, 11.86. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{38}\text{H}_{61}\text{O}_3\text{S}$ 597.4336, found 597.4330.



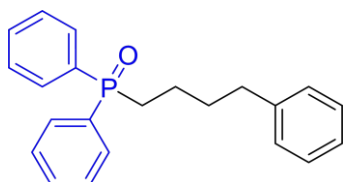
Diethyl 3-methyl-4-(tosylmethyl)cyclopentane-1,1-dicarboxylate (5a). Following the general procedure I, the title compound (65.0 mg) was obtained in 82% yield, as a mixture of 2 diastereomers (*d. r.* = 93:7). ^1H NMR (600 MHz, CDCl_3 , major isomer) δ 7.78 (d, $J = 8.2$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 4.48 – 3.87 (m, 4H), 3.13 (dd, $J = 14.1, 5.0$ Hz, 1H), 3.03 (dd, $J = 14.1, 8.4$ Hz, 1H), 2.52 – 2.44 (m, 1H), 2.45 (s, 3H), 2.45 – 2.35 (m, 2H), 2.32 – 2.25 (m, 1H), 2.22 – 2.13 (m, 1H), 1.96 (dd, $J = 13.9, 5.1$ Hz, 1H), 1.22 (t, $J = 7.1$ Hz, 6H), 0.83 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3 , major isomer) δ 172.60, 172.46, 144.82, 136.85, 130.07 (2C), 128.14 (2C), 61.73, 61.70, 58.75, 57.01, 41.13, 37.96, 37.24, 36.40, 21.77, 15.09, 14.13 (2C). HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{20}\text{H}_{29}\text{O}_6\text{S}$ 397.1679, found 397.1663.



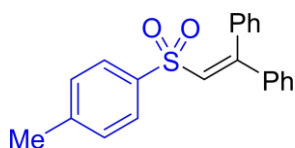
1-((2,5-Dimethylhex-4-en-2-yl)sulfonyl)-4-methylbenzene + 1-((2,5-dimethylhex-4-en-3-yl)sulfonyl)-4-methylbenzene (5b). Following the general procedure I, the title compound (36.8 mg) was obtained in 69% yield, as an inseparable mixture of 2 regioisomers (*r. r.* = 1.7:1). ^1H NMR (500 MHz, CDCl_3) δ 7.73 (d, $J = 7.9$ Hz, 1.7*2H), 7.64 (d, $J = 7.8$ Hz, 2H), 7.31 (d, $J = 7.9$ Hz, 1.7*2H), 7.25 (d, $J = 7.8$ Hz, 2H), 5.52 (d, $J = 15.8$ Hz, 1H), 5.31 (dd, $J = 15.8, 6.9$ Hz, 1H), 5.03 (t, $J = 7.9$ Hz, 1.7*1H), 2.42 (s, 1.7*3H), 2.40 (s, 3H), 2.37 (d, $J = 7.8$ Hz, 1.7*2H), 2.31-2.20 (m, 1H), 1.69 (s, 1.7*3H), 1.55 (s, 1.7*3H), 1.38 (s, 6H), 1.21 (s, 1.7*6H), 0.90 (d, $J = 6.7$ Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 144.54, 144.41, 141.75, 136.52, 132.61, 132.45, 130.82, 130.67, 129.46, 128.96, 126.06, 117.25, 64.10, 63.66, 32.95, 31.36, 26.19, 22.10, 21.74, 21.29, 20.41, 18.12. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{15}\text{H}_{23}\text{O}_2\text{S}$ 267.1413, found 267.1409.



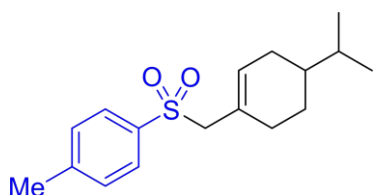
(Z)-3-Isopropyl-4-(tosylmethylene)tetrahydrofuran (5c). Following the general procedure I, the title compound (23.6 mg) was obtained in 42% yield. ^1H NMR (600 MHz, CDCl_3) δ 7.77 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 6.16 (td, $J = 2.5, 1.8$ Hz, 1H), 4.88 – 4.76 (m, 2H), 3.85 (dd, $J = 9.0, 6.9$ Hz, 1H), 3.77 (dd, $J = 9.0, 5.3$ Hz, 1H), 2.69 (dt, $J = 6.9, 5.3, 1.8$ Hz, 1H), 2.44 (s, 3H), 1.88 (m, 1H), 0.94 (d, $J = 6.9$ Hz, 3H), 0.84 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 160.27, 143.44, 137.57, 128.92 (2C), 126.14 (2C), 120.49, 69.44, 67.66, 50.81, 29.52, 20.60, 19.93, 16.86. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{15}\text{H}_{21}\text{O}_3\text{S}$ 281.1211, found 281.1189.



Diphenyl(4-phenylbutyl)phosphine oxide (9a). Following the general procedure I, the title compound (40.8 mg) was obtained in 61% yield. The spectra data was in line with the literature.^[10] ^1H NMR (600 MHz, CDCl_3) δ 7.74 – 7.69 (m, 4H), 7.53 – 7.48 (m, 2H), 7.45 (tdd, $J = 8.3, 2.5, 1.0$ Hz, 4H), 7.24 (dd, $J = 8.3, 6.9$ Hz, 2H), 7.17 – 7.13 (m, 1H), 7.12 – 7.09 (m, 2H), 2.58 (t, $J = 7.5$ Hz, 2H), 2.31 – 2.24 (m, 2H), 1.76 – 1.64 (m, 4H). HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{22}\text{H}_{24}\text{OP}$ 335.1559, found 335.1546.



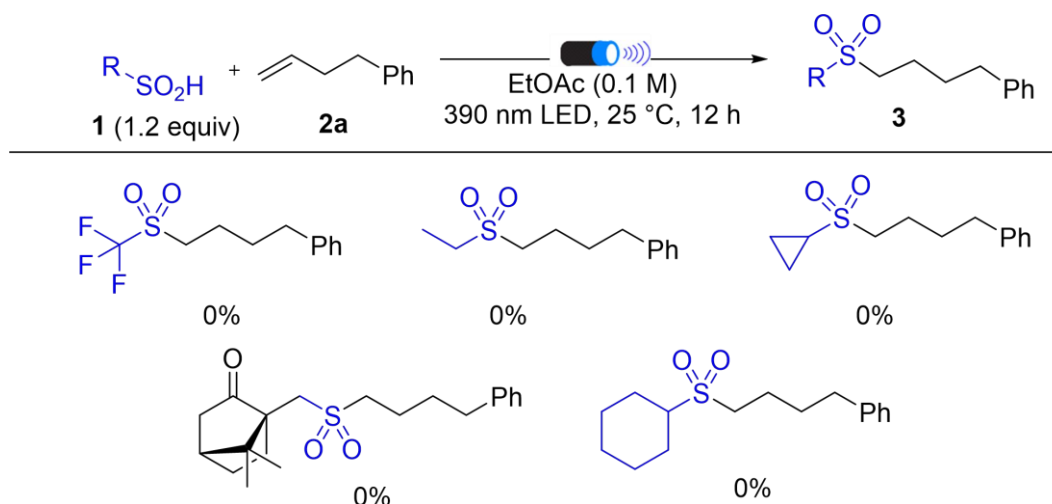
(2-Tosylethene-1,1-diyl)dibenzene (11). Following the general procedure I, the title compound (24.0 mg) was obtained in 36% yield. ^1H NMR (600 MHz, CDCl_3) δ 7.47 (d, $J = 8.3$ Hz, 2H), 7.36 (tdd, $J = 5.7, 4.2, 2.9$ Hz, 2H), 7.30 (dd, $J = 8.3, 7.1$ Hz, 4H), 7.23 – 7.18 (m, 2H), 7.16 – 7.13 (m, 2H), 7.10 (dd, $J = 8.2, 1.3$ Hz, 2H), 6.99 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 154.72, 143.75, 139.26, 138.64, 135.59, 130.22, 129.79 (2C), 129.34 (2C), 128.97, 128.84, 128.57 (2C), 128.21 (2C), 127.81 (2C), 127.71 (2C), 21.56. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{19}\text{O}_2\text{S}$ 335.1100, found 335.1089.



1-(((4-Isopropylcyclohex-1-en-1-yl)methyl)sulfonyl)-4-methylbenzene (13). Following the general procedure I, the title compound (35.1 mg) was obtained in 60% yield. ^1H NMR (600 MHz, CDCl_3) δ 7.69 (d, $J = 8.2$ Hz, 2H), 7.29 (d, $J = 8.2$ Hz, 2H), 5.38 (dd, $J = 5.1, 2.5$ Hz, 1H), 3.64 (s, 2H), 2.41 (s, 3H), 2.08 (dd, $J = 4.9, 2.5$ Hz, 2H), 1.98–1.92 (m, 1H), 1.73 – 1.68 (m, 1H), 1.65–1.61 (m, 1H), 1.42–1.38 (m, 1H), 1.19–1.16 (m, 1H), 1.14–1.07 (m, 1H), 0.84 (d, $J = 6.8$ Hz, 3H), 0.82 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 144.43, 135.70, 132.68, 129.49 (2C), 128.47 (2C), 126.03, 64.54, 39.18, 31.93, 29.36, 29.33, 26.13,

21.63, 19.87, 19.60. HRMS ESI $[M+H]^+$ calculated for $C_{17}H_{25}O_2S$ 293.1575, found 293.1555.

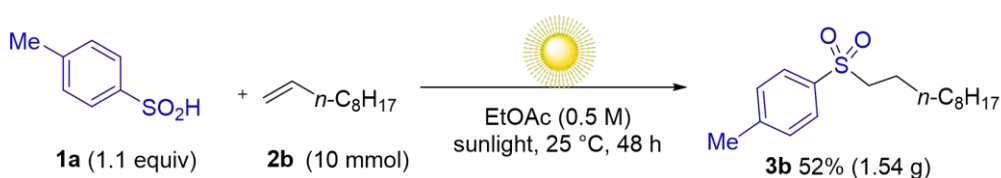
Scope limitation



Supplementary Figure 2. Unsuccessful attempt using alkylsulfonic acids

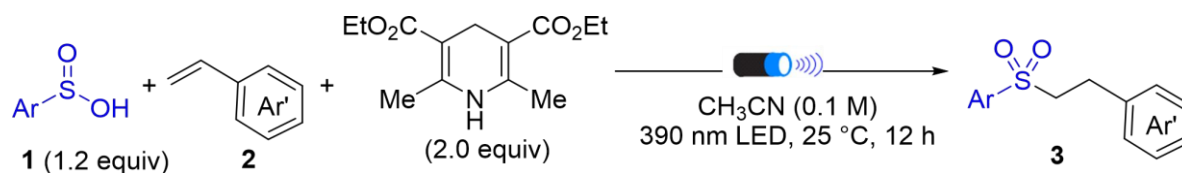
Sunlight-promoted gram-scale synthesis

Thanks to the sunny weather in Nanjing in Mar 2024, we have performed the sunlight-promoted gram-scale synthesis of **3b** successfully, albeit with longer reaction time and lower yields (Supplementary Figure 3). Reaction mixture was kept stirring not only under sunshine, but also in darkness (covered by aluminium foil) during night and cloudy or rainy daytime. However, only the reaction time under sunshine was accumulated, which is reasonable since light ON/OFF experiments indicated that our reaction was shut down without light irradiation (Supplementary Figure 8). The preliminary gram-scale synthesis was performed under moderate sunlight in the spring of Nanjing, China. We believe that the yield can be higher with more powerful sunlight.

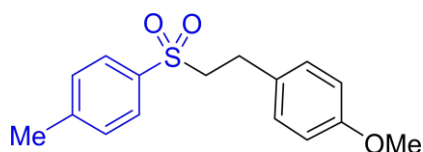


Supplementary Figure 3. Gram-scale synthesis of **3b** under sunlight.

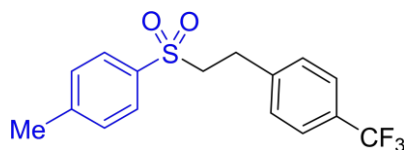
General procedure II: hydrosulfonylation of styrene



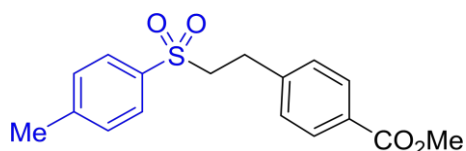
A 20 mL Schlenk tube equipped with a magnetic stir bar was charged with Hantzsch ester (0.4 mmol), sulfinic acid **1** (0.24 mmol), and styrene **2** (0.2 mmol). Then, 2.0 mL of acetyl acetate was added. The Schlenk tube was connected to Schlenk line and freeze-pump-thaw was performed for three times to completely remove air inside the reaction mixture. Eventually the Schlenk tube was refilled with an atmosphere of argon at room temperature and sealed. The reaction vessel was placed in front of the 390 nm Kessil LED (40 W) and ensured to be adequately illuminated. Then the reaction was running at ambient temperature (~25 °C) using a fan to cool down the reaction mixture and stopped after 12 h. The solvent was removed under reduced pressure and the crude mixture was purified by silica gel column chromatography or prepared TLC (eluent: hexane/diethyl ether or hexane/ethyl acetate; 20/1 – 10/1) to give the corresponding product **3**.



1-Methoxy-4-(2-tosylethyl)benzene (3ah). Following the general procedure II, the title compound (42.4 mg) was obtained in 73% yield. ^1H NMR (600 MHz, CDCl_3) δ 7.81 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), 6.79 (d, J = 8.7 Hz, 2H), 3.76 (s, 3H), 3.33 – 3.25 (m, 2H), 3.07 – 2.94 (m, 2H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 158.64, 144.88, 136.26, 133.82, 130.09 (2C), 129.43 (2C), 128.25 (2C), 114.33 (2C), 58.01, 55.41, 28.14, 21.78. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{16}\text{H}_{19}\text{O}_3\text{S}$ 291.1049, found 291.1043.

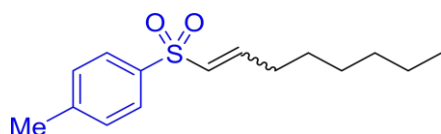
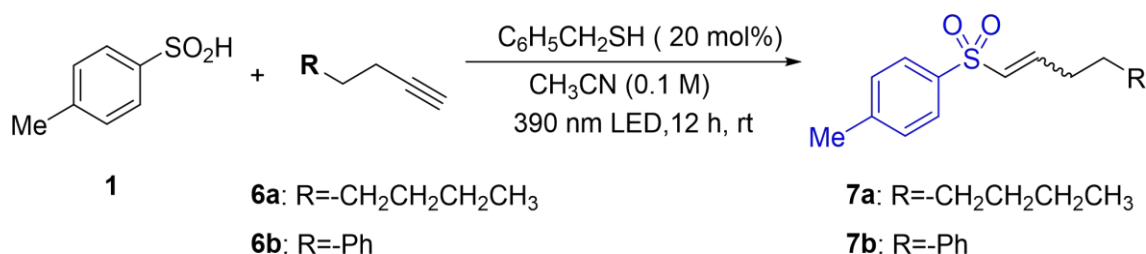


1-Methyl-4-((4-(trifluoromethyl)phenethyl)sulfonyl)benzene (3ai). Following the general procedure II, the title compound (36.8 mg) was obtained in 56% yield. ^1H NMR (600 MHz, CDCl_3) δ 7.78 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 3.46 – 3.21 (m, 2H), 3.22 – 2.94 (m, 2H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 144.94, 141.67, 136.08, 129.99 (2C), 129.37 (d, $^2J_{\text{C-F}}$ = 32.4 Hz), 128.69 (2C), 128.08 (2C), 125.69 (q, $^3J_{\text{C-F}}$ = 3.8 Hz) (2C), 124.02 (q, $^1J_{\text{C-F}}$ = 272.0 Hz), 57.08, 28.71, 21.55. ^{19}F NMR (565 MHz, CDCl_3) δ -62.58. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{16}\text{H}_{16}\text{F}_3\text{O}_2\text{S}$ 329.0818, found 329.0814.



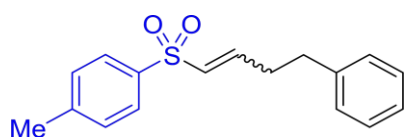
Methyl 4-(2-tosylethyl)benzoate (3aj). Following the general procedure II, the title compound (38.2 mg) was obtained in 60% yield. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.92 (d, $J = 8.2$ Hz, 2H), 7.80 (d, $J = 8.3$ Hz, 2H), 7.36 (d, $J = 8.2$ Hz, 2H), 7.18 (d, $J = 8.3$ Hz, 2H), 3.89 (s, 3H), 3.37 – 3.32 (m, 2H), 3.11 – 3.07 (m, 2H), 2.45 (s, 3H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 166.68, 144.92, 142.87, 136.07, 130.07 (2C), 129.99 (2C), 128.96, 128.33 (2C), 128.11 (2C), 57.09, 52.03, 28.85, 21.57. HRMS ESI $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{19}\text{O}_4\text{S}$ 319.0999, found 319.0988.

Hydrosulfonylation of alkyne



1-Methyl-4-(2-(octylsulfonyl)vinyl)benzene (7a)

A mixture of 4-methylphenylsulfonic acid (**1a**, 0.2 mmol, 31.2 mg), 1-octyne (**6a**, 0.24 mmol, 35 μL) and benzyl thiol (20.0 mol%, 5 μL) in MeCN (2.0 mL, 0.1 M) was stirred under argon atmosphere and irradiation of a 390 nm Kessil LED (40 W) for 12 h. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20/1) to afford product **7a** as an inseparable mixture of geometrical isomers (41.5 mg, 77%, $E/Z = 56:44$ as indicated by $^1\text{H NMR}$ spectroscopy). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.79 (d, $J = 8.3$ Hz, 0.44 \times 2H), 7.75 (d, $J = 8.2$ Hz, 0.56 \times 2H), 7.36–7.29 (m, (0.56+0.44) \times 2H), 6.95 (dt, $J = 15.1, 6.9$ Hz, 0.56 \times 1H), 6.34–6.16 (m, 0.56 \times 1H+0.44 \times 2H), 2.64 (qd, $J = 7.5, 1.4$ Hz, 0.44 \times 2H), 2.43 (s, 0.44 \times 3H), 2.43 (s, 0.56 \times 3H), 2.21 (qd, $J = 7.1, 1.6$ Hz, 0.56 \times 2H), 1.40 (m, (0.56+0.44) \times 2H), 1.28–1.21 (m, (0.56+0.44) \times 6H), 0.86 (m, (0.56+0.44) \times 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 147.26, 146.83, 144.32, 144.25, 139.12, 137.94, 130.73, 130.68, 129.96, 129.92, 127.71, 127.43, 31.64, 31.58, 31.56, 28.96, 28.80, 28.76, 27.87, 27.67, 22.63, 22.58, 21.74, 21.71, 14.14, 14.11.

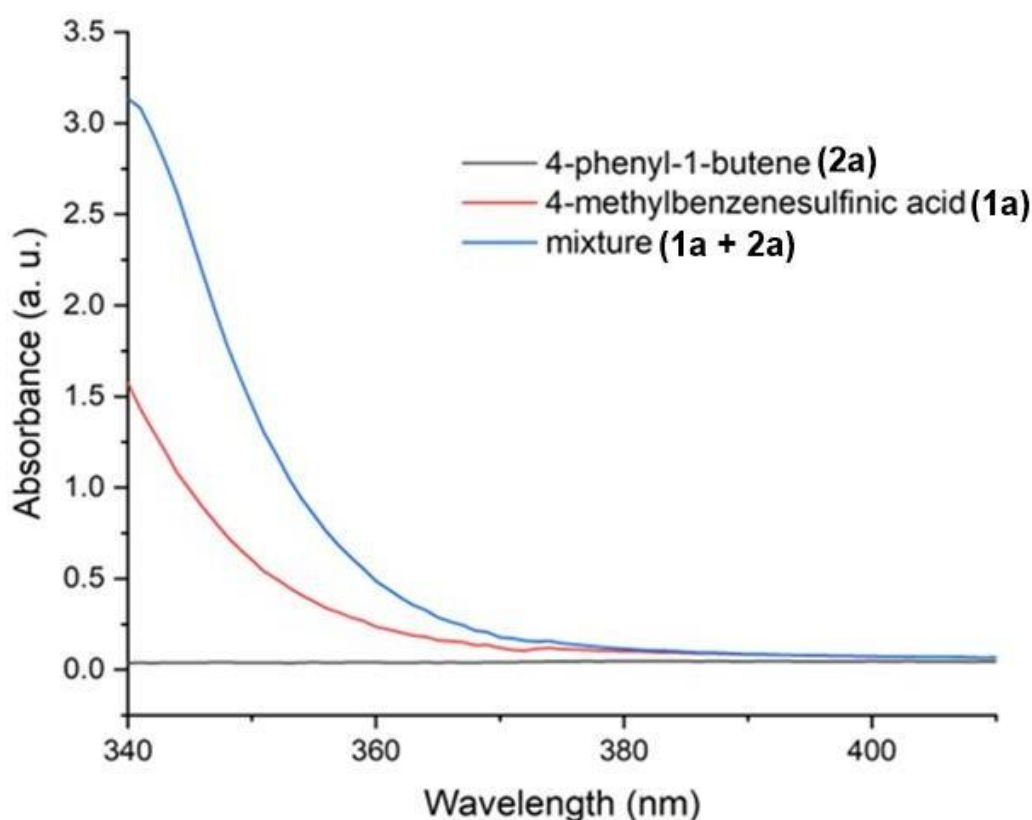


1-Methyl-4-((4-phenylbut-1-en-1-yl)sulfonyl)benzene (**7b**)

A mixture of 4-methyl-phenylsulfonic acid (**1a**, 0.2 mmol, 31.2 mg), 4-phenyl-1-butyne (**6b**, 0.24 mmol, 34 μ L) and benzyl thiol (20.0 mol%, 5 μ L) in MeCN (2.0 mL, 0.1M) was stirred under an argon atmosphere and irradiation of a 390 nm Kessil LEDs(40 W) for 12 h. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (petroleumether/EtOAc = 20/1) to afford product **7b** as an inseparable mixture of geometrical isomers (37.2 mg, 65%, *E/Z* = 40:60 indicated by ^1H NMR spectroscopy). ^1H NMR (500 MHz, CDCl_3) δ 7.79–7.65 (m, (0.60+0.40) \times 2H), 7.36–7.18 (m, (0.60+0.40) \times 6H), 7.14 (d, J = 7.5 Hz, (0.60+0.40) \times 1H), 6.99 (dt, J = 14.3, 7.0 Hz, 0.40 \times 1H), 6.39 – 6.20 (m, (0.40 \times 1H +0.6 \times 2H), 3.04 (q, J = 7.3 Hz, 0.6 \times 2H), 2.79 (q, J = 7.5Hz, (0.60+0.40) \times 2H), 2.57 (q, J = 7.3 Hz, 0.4 \times 2H), 2.46 (s, (0.60+0.40) \times 3H). ; ^{13}C NMR (126 MHz, CDCl_3) δ 145.58, 145.41, 144.38, 144.30, 140.44, 140.10, 138.78, 137.73, 131.46, 131.19, 129.95, 128.67, 128.62, 128.58, 128.43, 127.72, 127.41, 126.47, 126.37, 34.85, 34.01, 33.21, 29.23, 21.72 (2C).

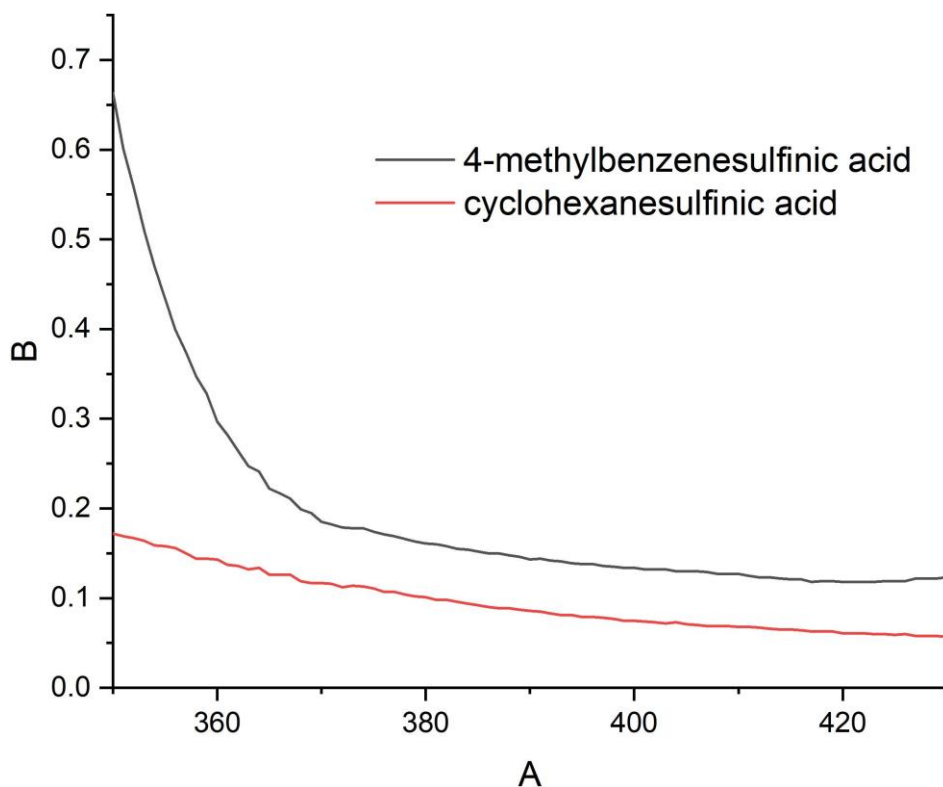
V. Mechanistic studies

UV-Vis absorption spectra



Supplementary Figure 4. Absorption spectrum of 4-phenyl-1-butene **2a** (0.3 mg, 0.002 mmol) in 3 mL ethyl acetate (black line); absorption spectrum of 4-methylbenzenesulfonic

acid **1a** (0.3 mg, 0.002 mmol) in 3 mL ethyl acetate (red line); absorption spectrum of mixture of **1a** (0.3 mg, 0.002 mmol) and **2a** (0.3 mg, 0.002 mmol) in 3 mL ethyl acetate (blue line).



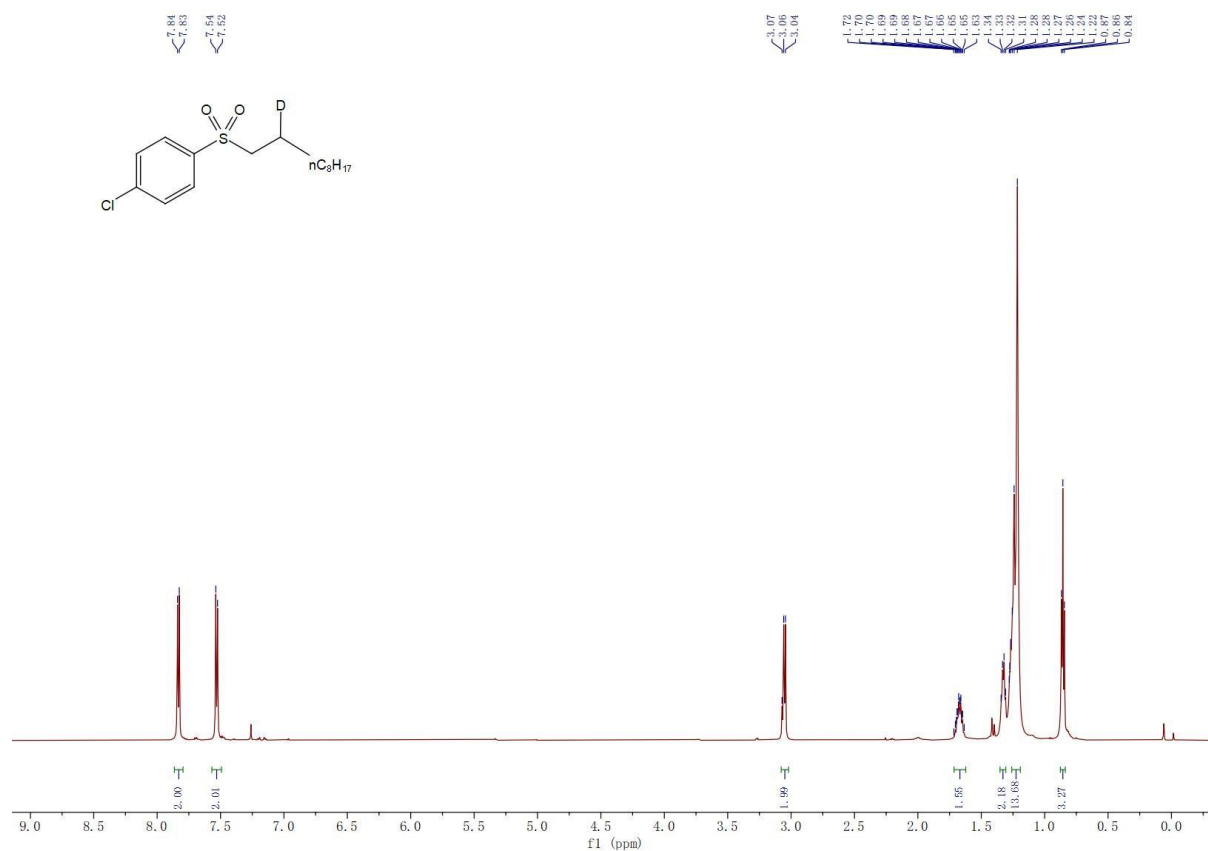
Supplementary Figure 5. Absorption spectrum of 4-methylbenzenesulfonic acid **1a** (0.3 mg, 0.002 mmol) in 3 mL ethyl acetate (black line); absorption spectrum of cyclohexanesulfonic acid (0.3 mg, 0.002 mmol) in 3 mL ethyl acetate (red line).

Deuterium-labeling experiment



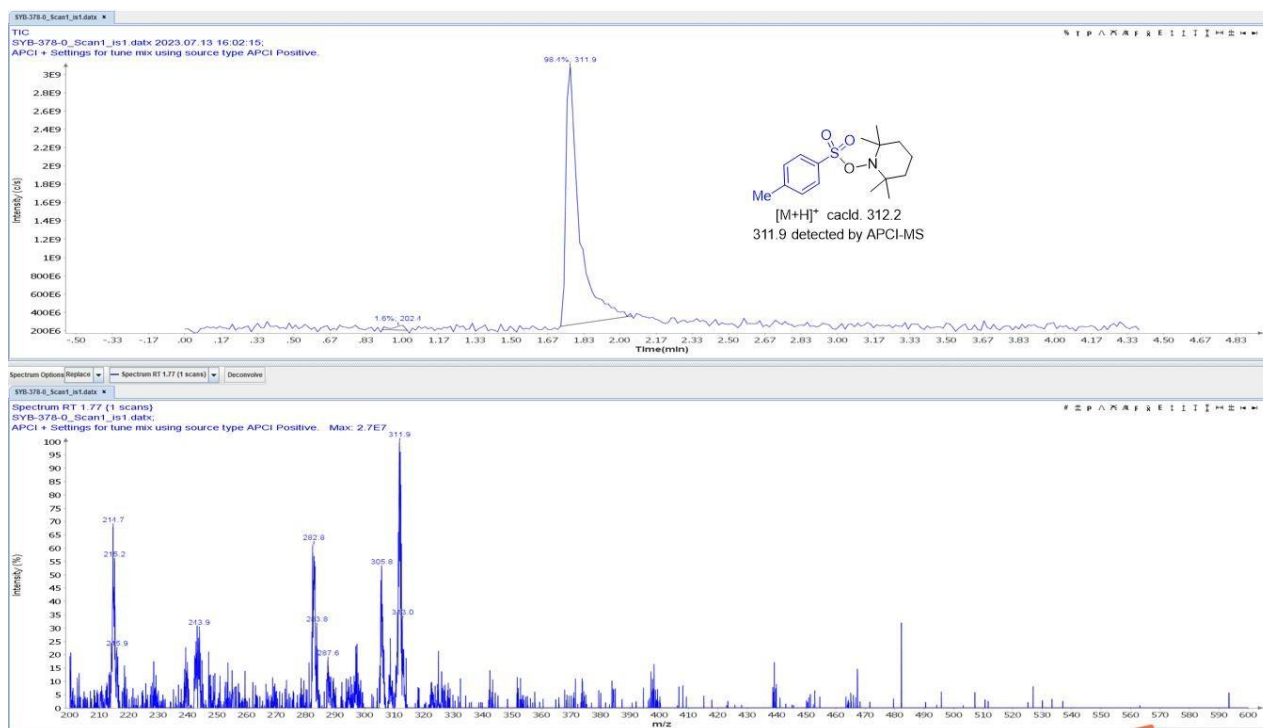
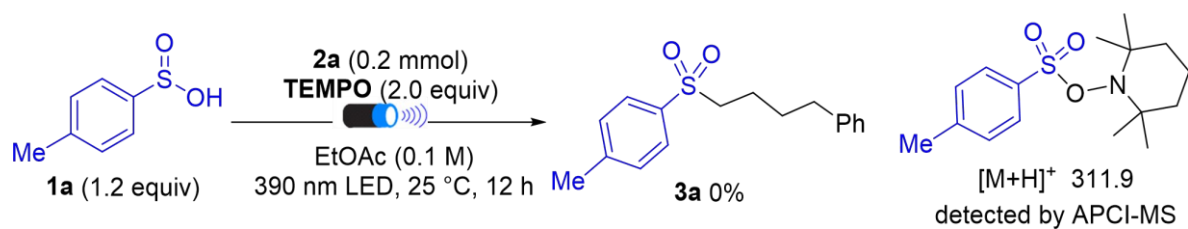
Following the general procedure I, except that deuterated water (2.0 mmol, 36 μ L) was added to the reaction mixture, the title compound (58.3 mg) was obtained in 96% yield, with 44% deuteration at C_β of the sulfone moiety.

^1H NMR (600 MHz, CDCl_3) δ 7.83 (d, $J = 8.3$ Hz, 2H), 7.53 (d, $J = 8.2$ Hz, 2H), 3.15–3.04 (m, 2H), 1.73 – 1.63 (m, 1.56H), 1.36 – 1.33 (m, 2H), 1.28 – 1.12 (m, 12H), 0.86 (t, $J = 7.0$ Hz, 3H).



Supplementary Figure 6. Deuterium incorporation in alkene hydrodesulfonation.

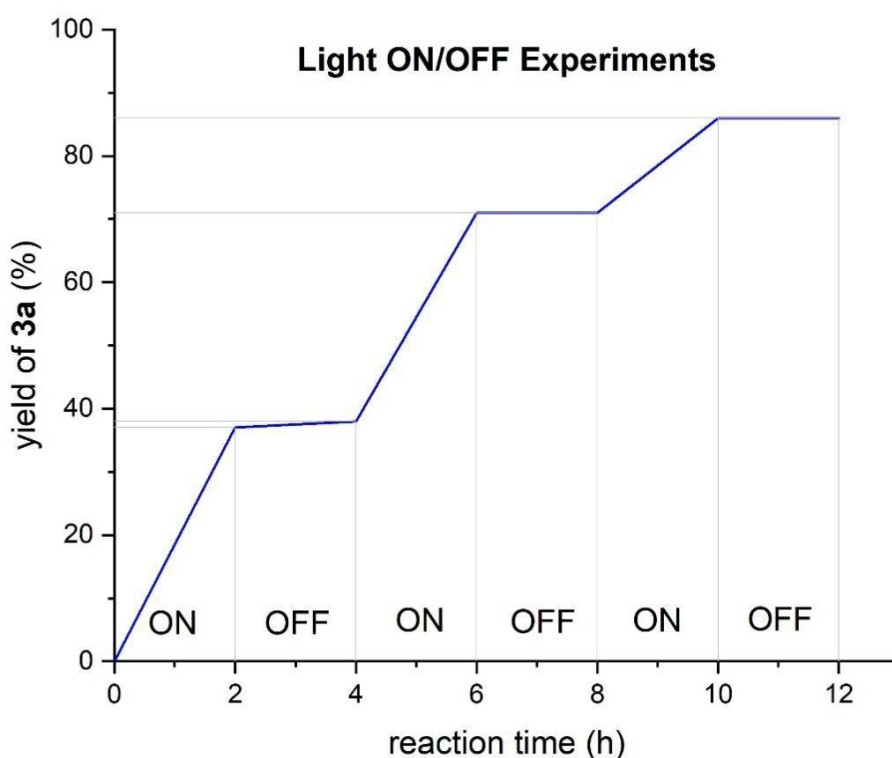
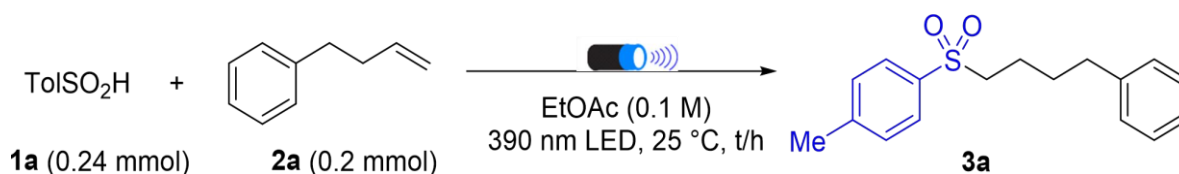
Trapping of sulfonyl radical by TEMPO



Supplementary Figure 7. Observation of adduct of TEMPO and sulfonyl radical by mass spectroscopy.

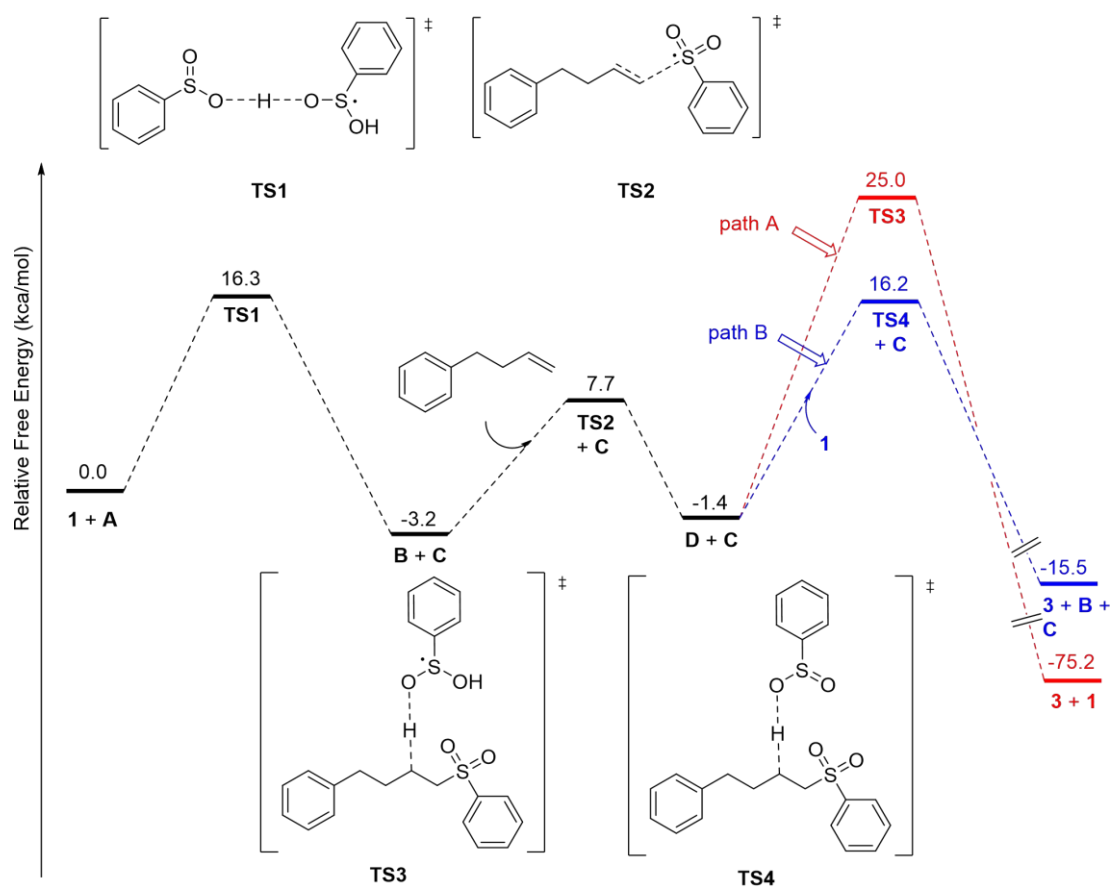
Light on/off experiments over time

To examine the impact of light, we conducted experiments under alternating periods of irradiation and darkness (Supplementary Figure 8). These resulted in an interruption of the reaction progress in the absence of light and recuperation of reactivity on further illumination, which allows temporal control over the entire reaction period. These results demonstrate that light is a necessary component of the reaction, while they do not definitively rule out a radical-chain process.



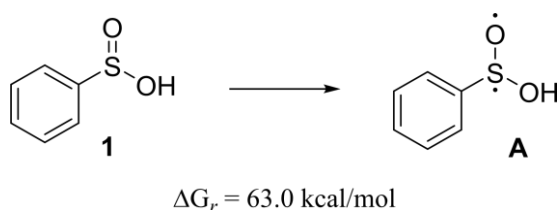
Supplementary Figure 8. Time profile of the transformation with the light ON/OFF over time.

DFT calculation



result at M06-2X-SMD(acetonitrile)/Def2-TZVP// M06-2X-SMD(acetonitrile)/Def2-SVP

Supplementary Figure 9. Density functional theory (DFT) calculation on energy profile of this transformation.



Supplementary Figure 10. Density functional theory (DFT) calculation on relative energy gap between **1** and **A**.

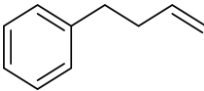
Computational details

Computational Methods

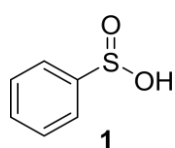
Density functional theory (DFT) calculations were conducted with the Gaussian 16 program.^[11] Geometry optimization was performed using M06-2X functional,^[12] with def2-SVP basis set.^[13] Frequency calculations were performed to confirm stationary points as

minima or transition states using the same method with the optimizations. Single-point energy calculations were then performed on the stationary points by using M06-2X functional with def2-TZVP basis set.^[13] All the calculations were simulated in acetonitrile with the SMD model.^[14] Single-point energies corrected by Gibbs free energy corrections were used to as the solution phase Gibbs free energies. All the energies in this paper correspond to the reference state of 1 mol L⁻¹, 298.15 K.

Energy data (a.u.)

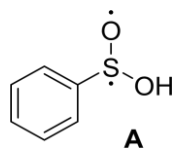
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B	0.066200		-780.2290554
C	0.085684		-781.4048655
D	0.243213		-1168.485214
3	0.257707		-1169.147953
	0.154774		-388.2399094
TS1	0.166505		-1561.614391
TS2	0.238967		-1168.46646
TS3	0.343017		-1949.859087
TS4	0.338093		-1949.337628

Cartesian coordinates

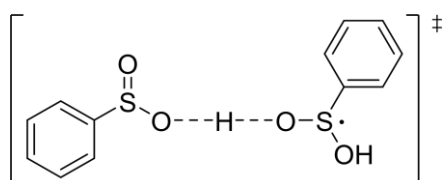


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C	0.701021000	1.198826000	0.071736000
C	2.087124000	1.241615000	0.232017000
C	2.838440000	0.070559000	0.129657000
H	2.805054000	-2.064747000	-0.211283000
H	0.331242000	-2.158194000	-0.495303000
H	0.085795000	2.097242000	0.145211000
H	2.580278000	2.193268000	0.436800000

H	3.922018000	0.108431000	0.253917000
S	-1.696278000	-0.067274000	-0.421618000
O	-2.165414000	1.280092000	-0.012344000
O	-2.028062000	-1.153995000	0.770962000
H	-1.618529000	-0.862224000	1.609485000

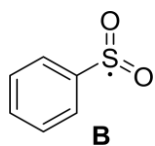


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C	-0.705860000	1.210748000	-0.051603000
C	-0.077338000	-0.038504000	-0.001865000
C	-0.819482000	-1.223410000	0.047371000
C	-2.209915000	-1.152090000	0.049103000
C	-2.851964000	0.086626000	0.001207000
H	-2.597073000	2.230125000	-0.089529000
H	-0.116362000	2.123624000	-0.094919000
H	-0.307998000	-2.185201000	0.083836000
H	-2.793976000	-2.072858000	0.088524000
H	-3.941914000	0.137158000	0.002511000
S	1.697878000	-0.195292000	-0.005824000
O	1.983061000	-1.688245000	-0.071742000
O	2.037946000	1.720063000	0.093922000
H	3.002634000	1.775315000	-0.043841000

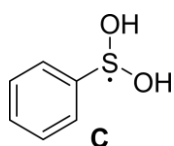


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C	3.026523000	-1.517996000	0.353293000
C	3.397392000	0.816981000	-0.257315000
C	4.384518000	-1.648847000	0.643904000
H	2.336817000	-2.356393000	0.461803000
C	4.751134000	0.670195000	0.039451000
H	2.998888000	1.766562000	-0.618169000
C	5.241834000	-0.558441000	0.488725000
H	4.772687000	-2.607732000	0.990762000

H	5.426385000	1.518254000	-0.084035000
H	6.302987000	-0.665918000	0.719514000
H	-0.187683000	1.569043000	-1.498021000
O	-1.148443000	2.097447000	-1.124175000
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C	-2.919351000	-0.488277000	1.315177000
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C	-3.790076000	-1.555988000	1.113701000
H	-2.563743000	-0.244341000	2.313379000
C	-3.811589000	-1.122276000	-1.262189000
H	-2.602953000	0.535645000	-1.936965000
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H	-4.115780000	-2.145284000	1.972232000
H	-4.155883000	-1.367798000	-2.267903000
H	-4.920562000	-2.715134000	-0.315588000
O	-1.494504000	1.692939000	2.244283000
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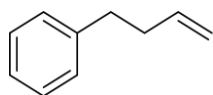


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H	-0.199197000	-2.160180000	-0.091217000
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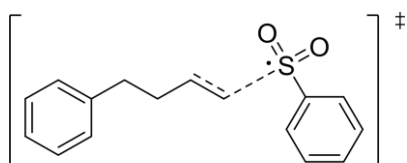


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C	2.840815000	0.035797000	0.041517000
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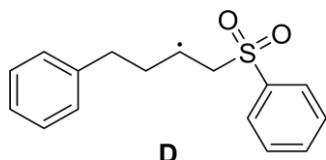


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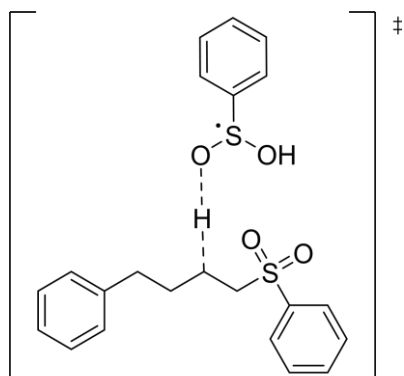


TS2

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C	5.828004000	1.298575000	0.634492000
C	6.259243000	1.076750000	-0.673929000
H	5.957613000	-0.074123000	-2.477528000
H	4.074007000	-1.391826000	-1.539706000
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H	1.556045000	-0.495931000	-0.563924000
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C	-5.673597000	-0.732157000	-0.100080000
H	-3.926109000	-1.874852000	-0.697972000
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H	-5.654268000	2.574000000	0.751002000
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H	-7.210760000	0.648886000	0.519493000



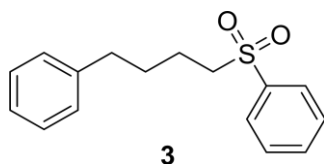
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C	-4.681883000	0.624573000	-1.194805000
C	-5.742088000	1.376839000	-0.686231000
C	-6.186610000	1.166731000	0.619609000
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H	-4.023836000	-1.308315000	1.522522000
H	-4.338156000	0.791080000	-2.218981000
H	-6.224084000	2.128997000	-1.313931000
H	-7.016825000	1.752525000	1.018465000
C	-2.873824000	-1.127520000	-0.942151000
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H	-2.918170000	-1.164697000	-2.041139000
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H	-1.503366000	-0.461374000	0.592865000
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C	-0.360946000	-1.280731000	-1.013450000
C	0.967458000	-0.652699000	-1.153227000
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O	1.768763000	-1.725736000	1.148525000
C	3.358276000	0.153150000	0.197683000
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C	4.372513000	-0.791316000	0.043693000
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C	5.665462000	-0.343139000	-0.220547000
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H	6.938013000	1.370691000	-0.530605000



TS3

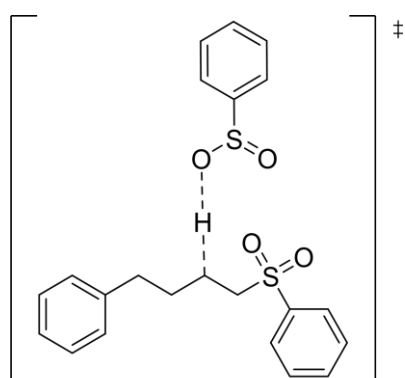
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H	-3.293577000	-2.540923000	-0.086832000
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C	2.041432000	4.351350000	-1.554730000
H	0.017904000	3.657679000	-1.929267000
C	3.045751000	3.596789000	0.521037000
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H	2.103512000	4.928842000	-2.478132000

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H	4.027471000	4.883552000	-0.904682000
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H	3.431983000	-1.065799000	1.846306000
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H	6.706107000	-3.267824000	-1.191172000
H	5.788828000	-1.368742000	2.569333000
H	7.431947000	-2.464749000	1.053815000
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TS4

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C	-4.430682000	3.665000000	-1.290467000
C	-4.668514000	4.267359000	-0.054444000
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H	-2.920392000	2.114633000	1.927721000
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H	-2.378704000	0.074178000	0.578178000
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C	-0.730277000	1.073859000	-0.387861000
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S	2.432658000	1.003736000	0.583300000
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C	4.167835000	0.771099000	0.260602000
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C	4.829162000	-0.289521000	0.878440000
C	6.171961000	1.457265000	-0.857983000
H	4.266091000	2.479842000	-1.055597000
C	6.185067000	-0.471730000	0.613417000
H	4.290617000	-0.950902000	1.559383000
C	6.851434000	0.398334000	-0.252661000
H	6.700245000	2.136868000	-1.528187000
H	6.724088000	-1.292758000	1.088177000
H	7.913619000	0.251032000	-0.455251000
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S	-0.531353000	-3.254878000	-1.222860000
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O	0.671394000	-3.361162000	-0.353637000
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C	-1.692034000	-2.950695000	1.265486000
C	-4.228977000	-2.393571000	0.206677000
H	-3.313222000	-2.652436000	-1.738544000
C	-2.762553000	-2.674370000	2.117811000
H	-0.694915000	-3.174663000	1.648772000
C	-4.024270000	-2.396092000	1.589268000
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H	-2.609272000	-2.679088000	3.198153000
H	-4.858410000	-2.184254000	2.260296000

VI. Advances of green metrics on atom economy (AE) and real mass

efficiency (RME)

$$\text{Atom economy (AE)} = \frac{\text{Formula weight of product (g}\cdot\text{mol}^{-1})}{\text{Formula weight of all reactants used in reaction (g}\cdot\text{mol}^{-1})}$$

$$\text{Reaction mass efficiency (RME)} = \frac{\text{Mass of product (g)}}{\text{Total mass of reactants used in reaction (g)}}$$

Reaction scheme: $\text{R-SO}_2\text{-X} + \text{R}^1\text{-CH=CH-R}^2\text{-R}^3 \xrightarrow{\text{conditions described in ref.}} \text{R-SO}_2\text{-CH(R}^1\text{)-CH(R}^2\text{)-R}^3$

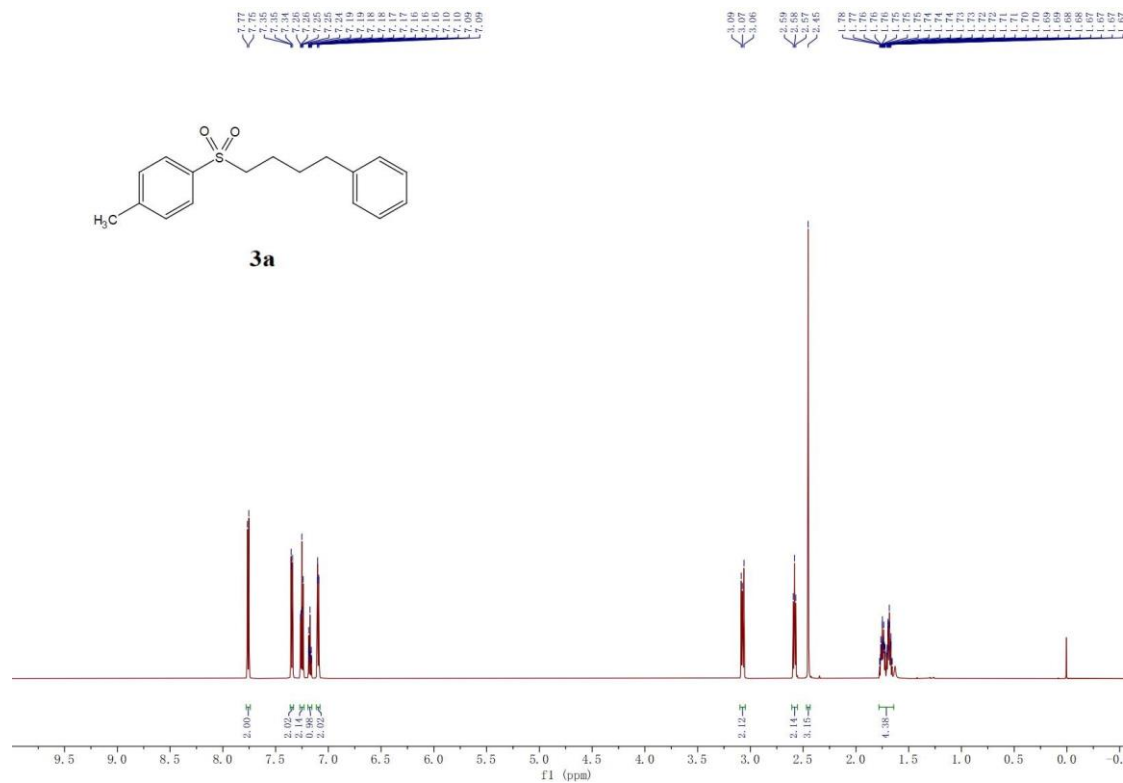
Chemical structures shown: **this work** (4-methylphenyl), **ref:11** (4-fluorophenyl), **ref:13** (4-methylphenyl), **ref:14** (phenyl), **ref:15** (phenyl), **ref:17** (phenyl), **ref:18** (4-methylphenyl), **ref:19** (phenyl), **ref:20** (4-fluorophenyl).

ref.	X	reactants				3	Yield (%)	AE (%)	RME (%)
		1 (equiv)	1 Molecular Weight (g/mol)	2 (equiv)	2 Molecular Weight (g/mol)				
this work	H	1.2	156.20	1	132.20	288.41	99%	100.00%	89.33%
ref:11	Cl	2.5	194.60	1	147.18	307.34	90%	89.92%	43.65%
ref:13	Cl	2.5	190.64	1	84.16	240.36	72%	87.47%	30.86%
ref:14	Na	1.65	164.15	1	175.23	317.40	98%	93.52%	69.73%
ref:15	Na	1.6	164.15	1	224.43	366.60	80%	94.34%	60.21%
ref:17	Na	4	164.15	1	118.18	260.35	74%	92.21%	24.87%
ref:18	N=CH-Ar	1	289.35	2.5	70.09	226.29	84%	62.96%	40.92%

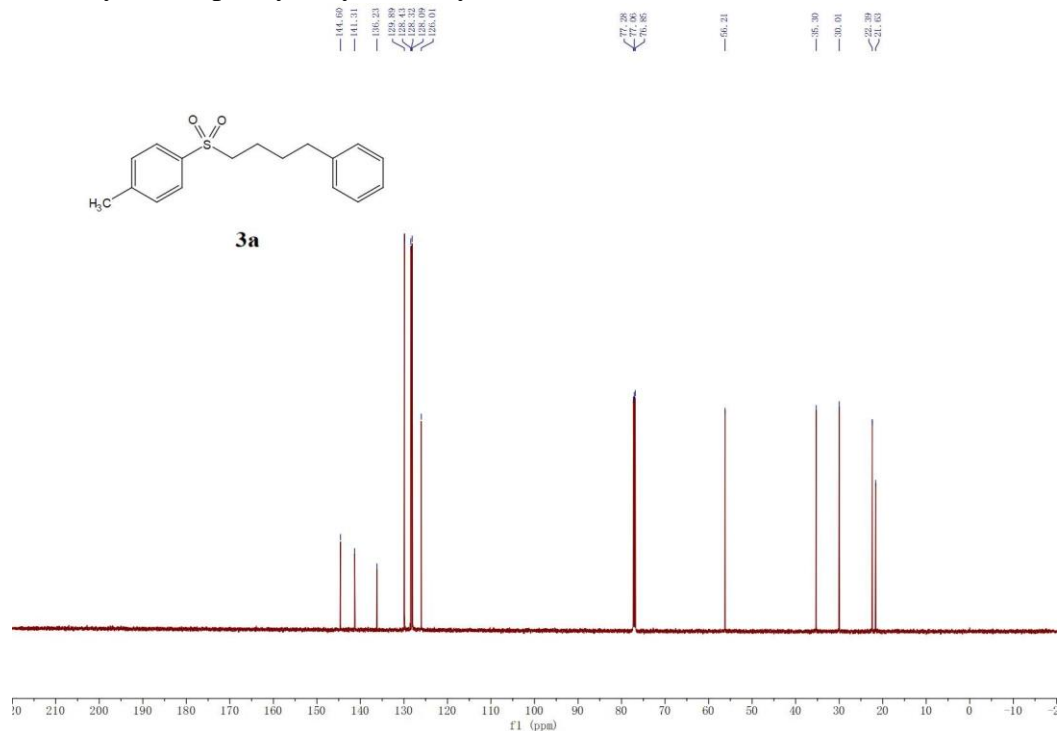
Supplementary Figure 11. Advances of this work regarding green metrics on AE and RME

VII. NMR spectra

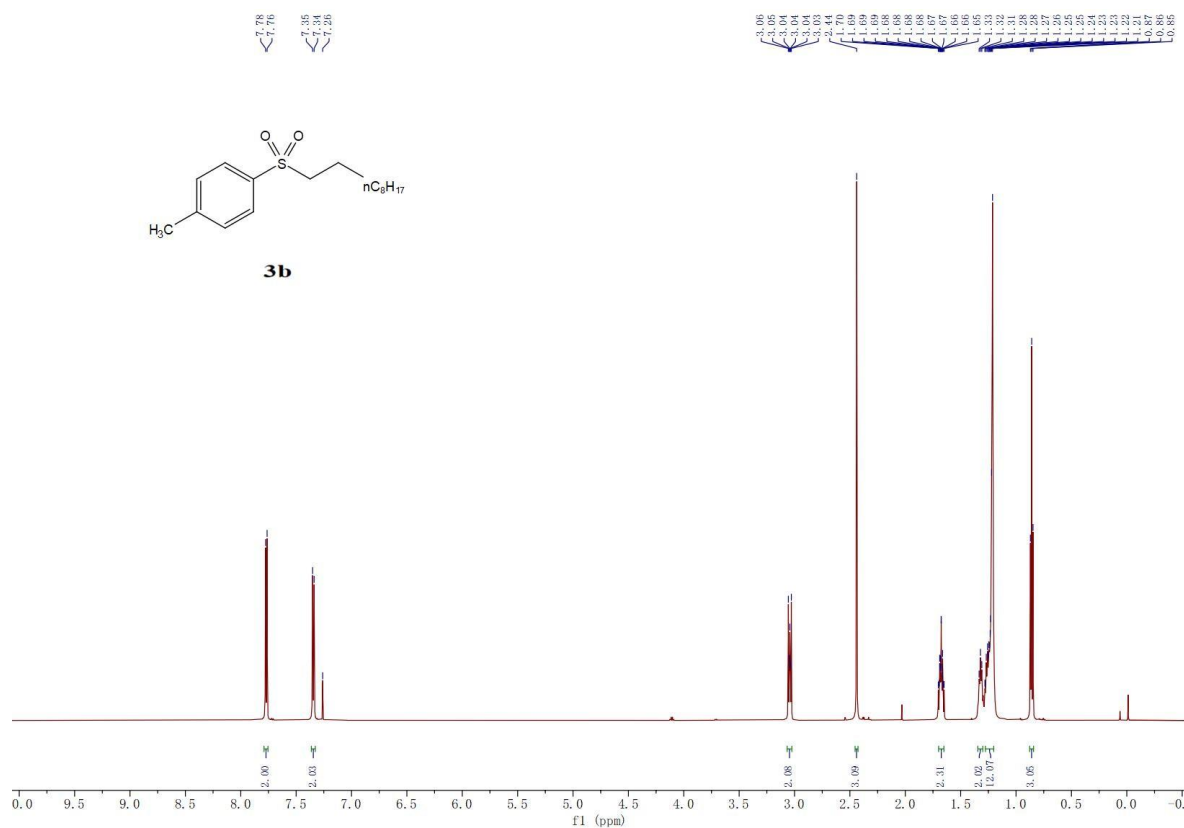
Supplementary Figure 12 ^1H NMR (600 MHz, CDCl_3) of 1-methyl-4-((4-phenylbutyl)sulfonyl)benzene (**3a**)



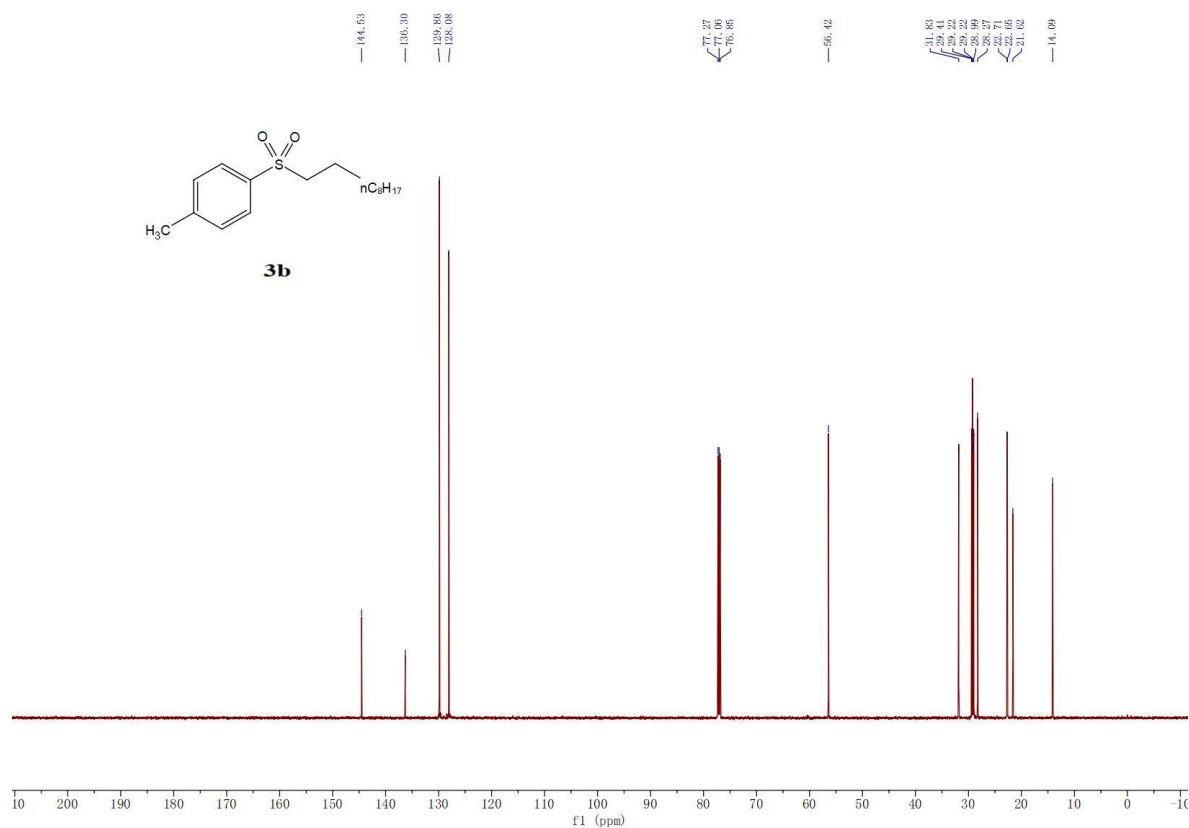
Supplementary Figure 13 ^{13}C NMR (151 MHz, CDCl_3) of 1-methyl-4-((4-phenylbutyl)sulfonyl)benzene (**3a**)



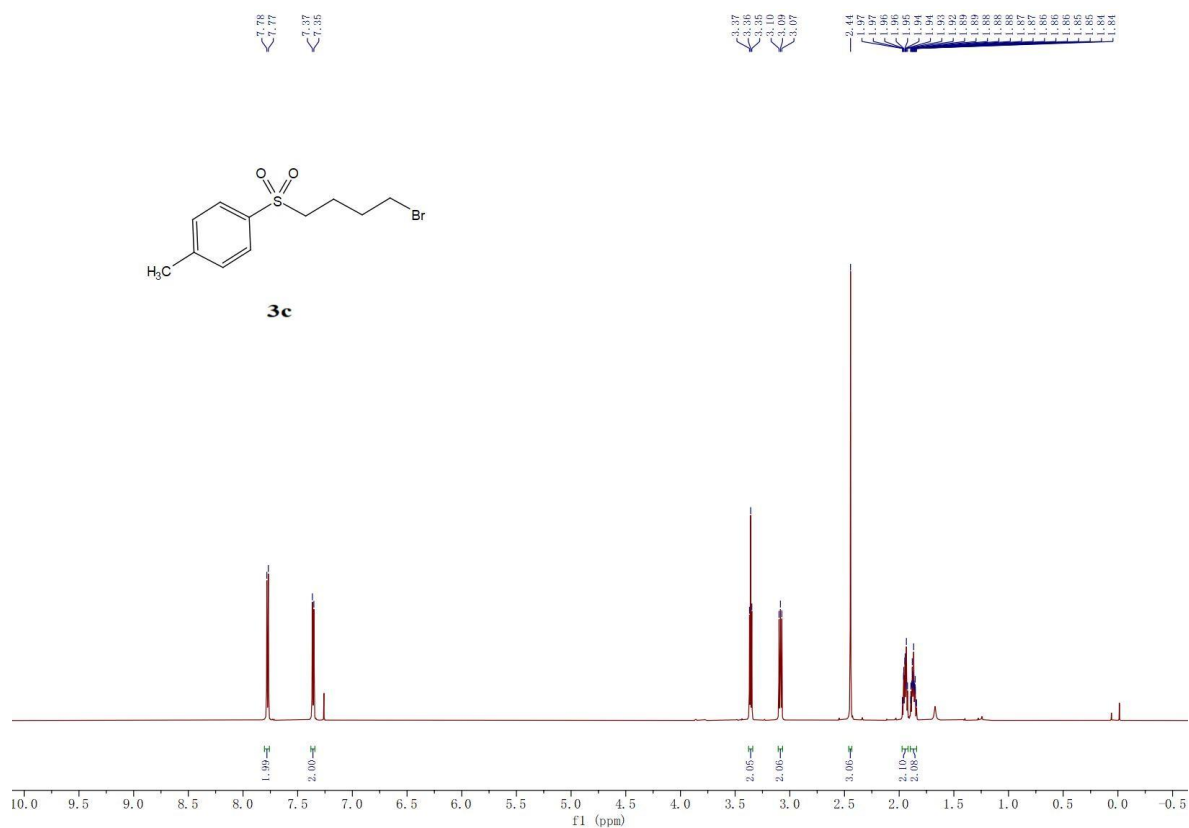
Supplementary Figure 14 | ^1H NMR (600 MHz, CDCl_3) of 1-(decylsulfonyl)-4-methylbenzene (**3b**)



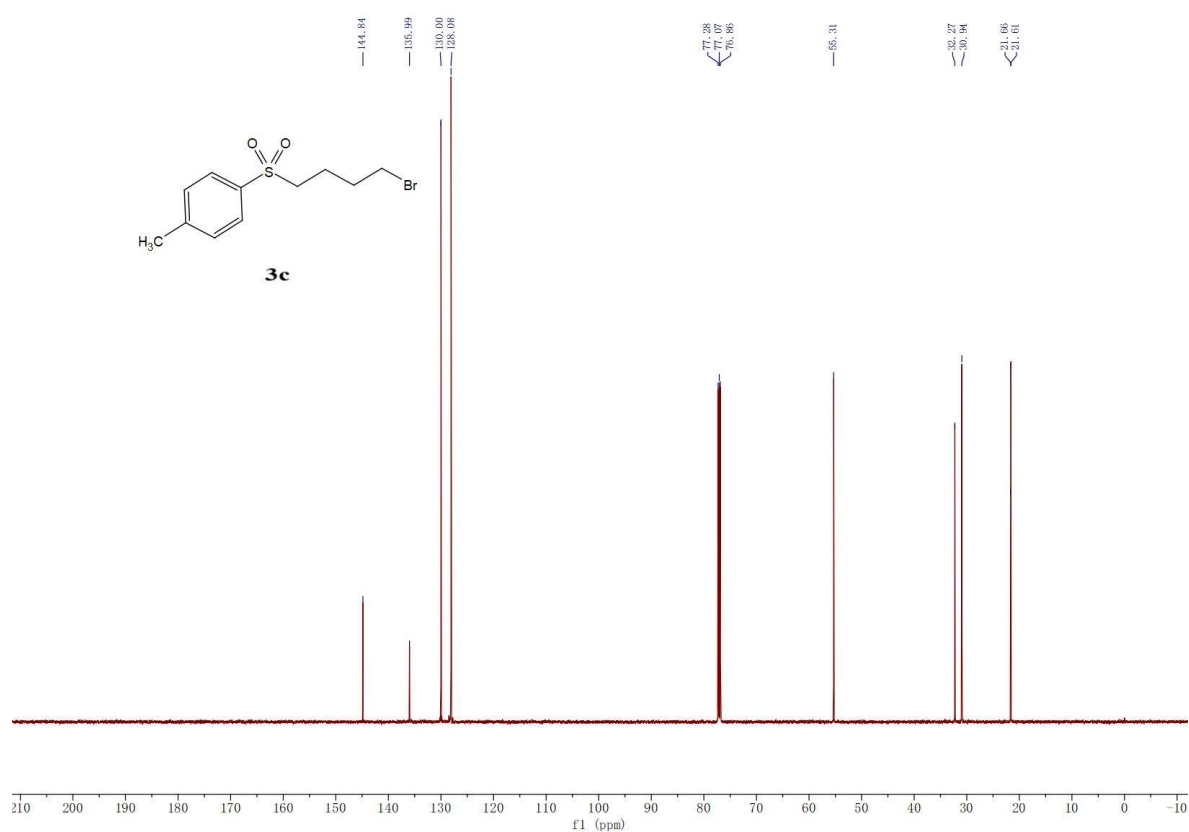
Supplementary Figure 15 | ^{13}C NMR (151 MHz, CDCl_3) of 1-(decylsulfonyl)-4-methylbenzene (**3b**)



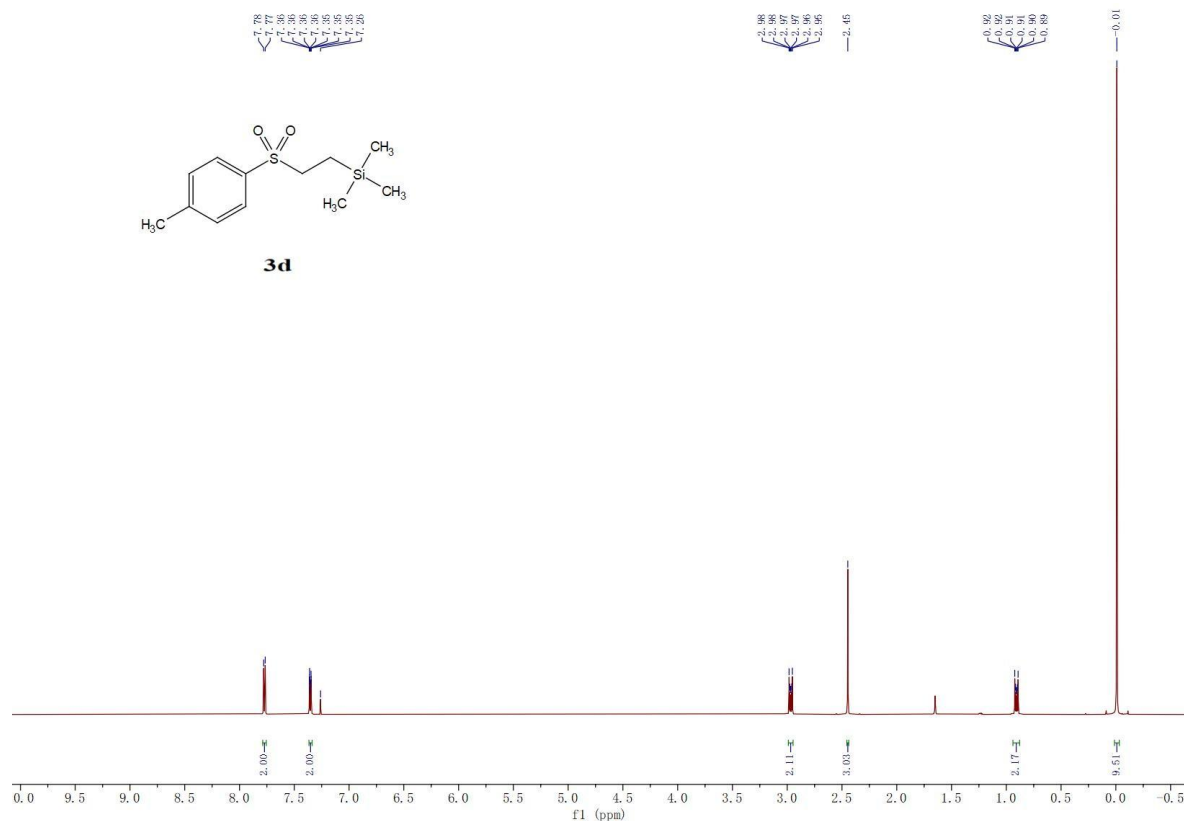
Supplementary Figure 16 | ^1H NMR (600 MHz, CDCl_3) of 1-((4-bromobutyl)sulfonyl)-4-methylbenzene (**3c**)



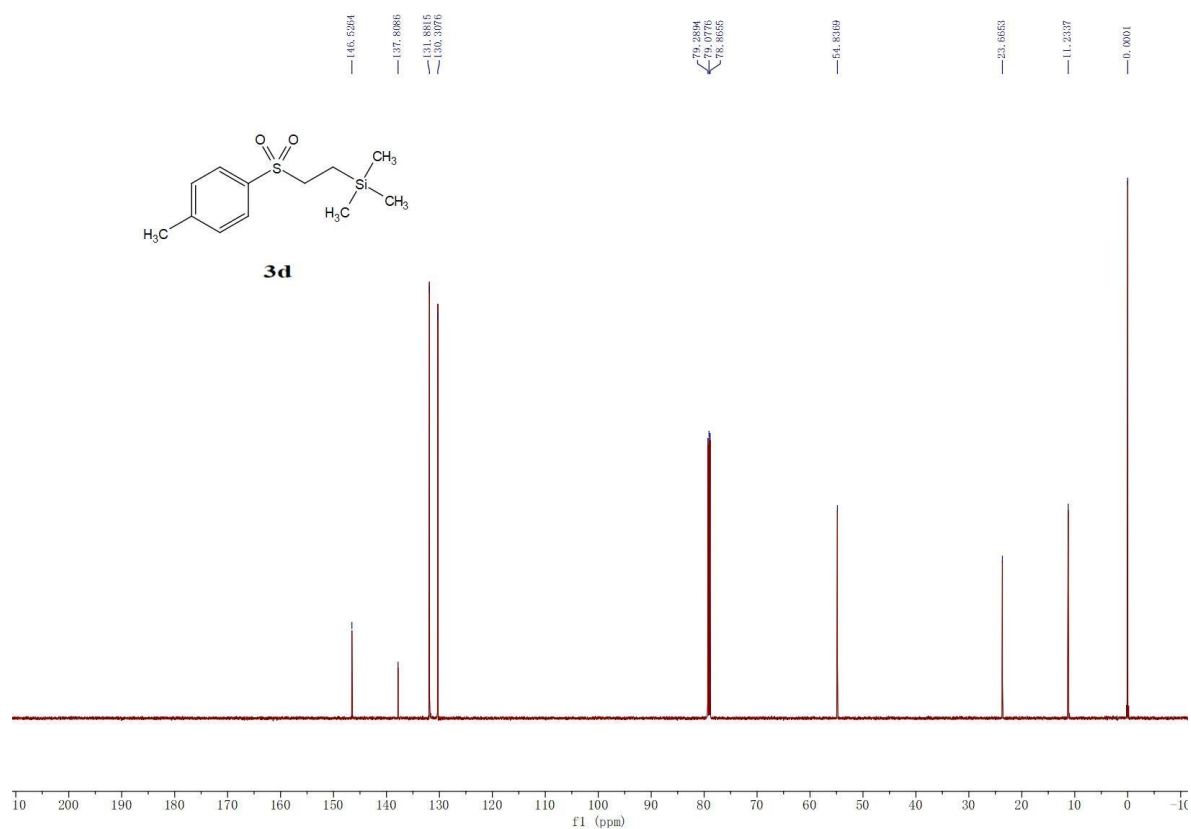
Supplementary Figure 17 | ^{13}C NMR (151 MHz, CDCl_3) of 1-((4-bromobutyl)sulfonyl)-4-methylbenzene (**3c**)



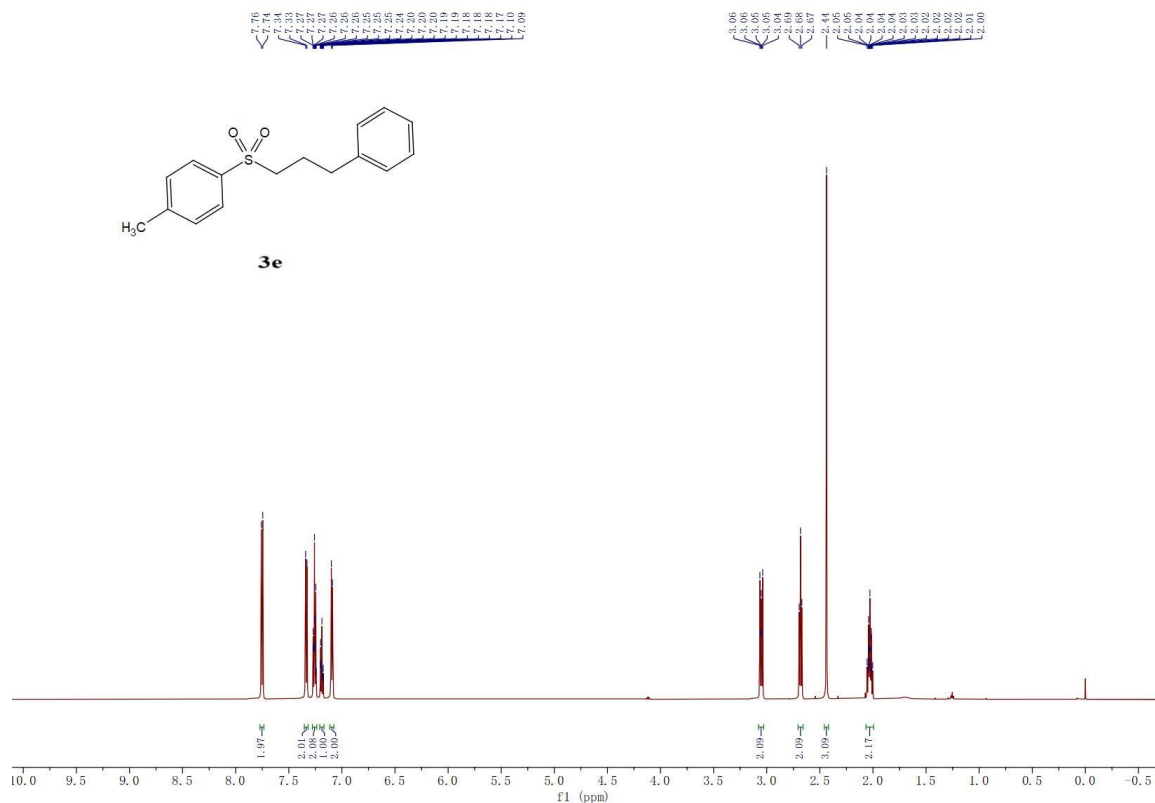
Supplementary Figure 18 ^1H NMR (600 MHz, CDCl_3) of trimethyl(2-tosylethyl)silane (**3d**)



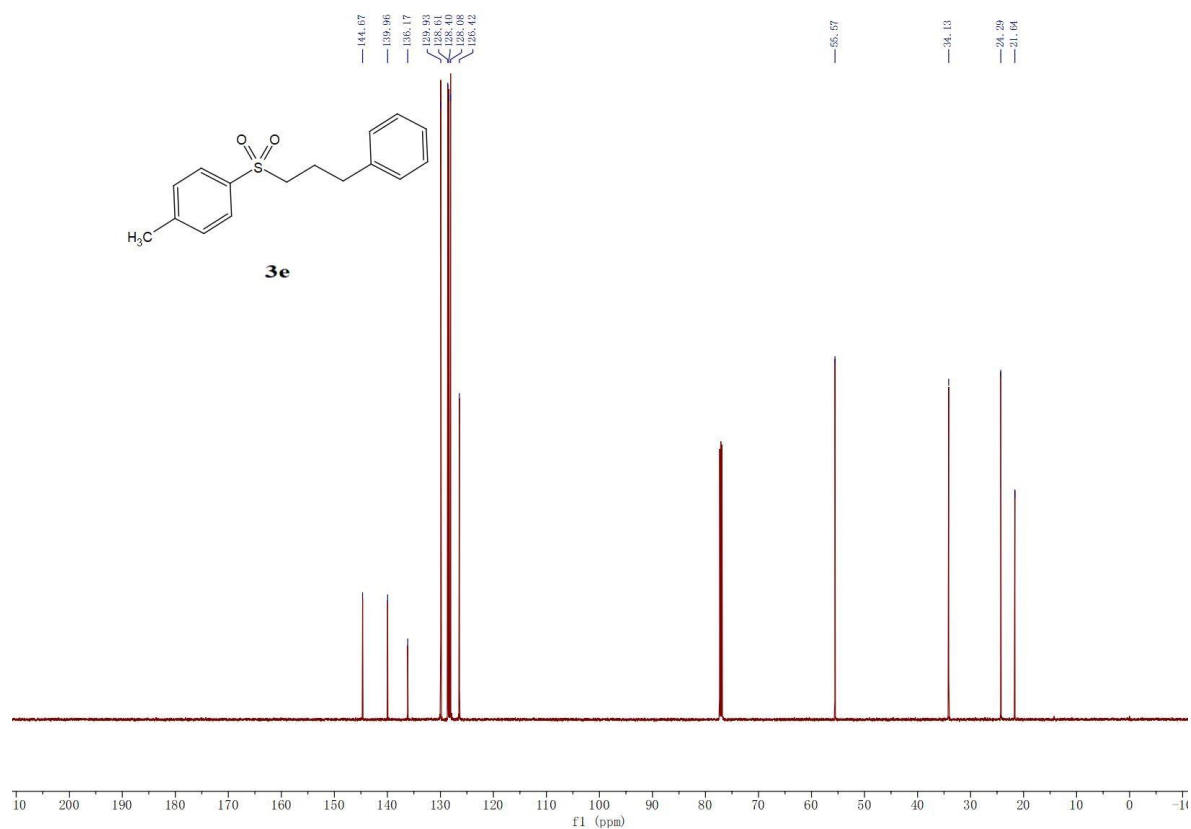
Supplementary Figure 19 ^{13}C NMR (151 MHz, CDCl_3) of trimethyl(2-tosylethyl)silane (**3d**)



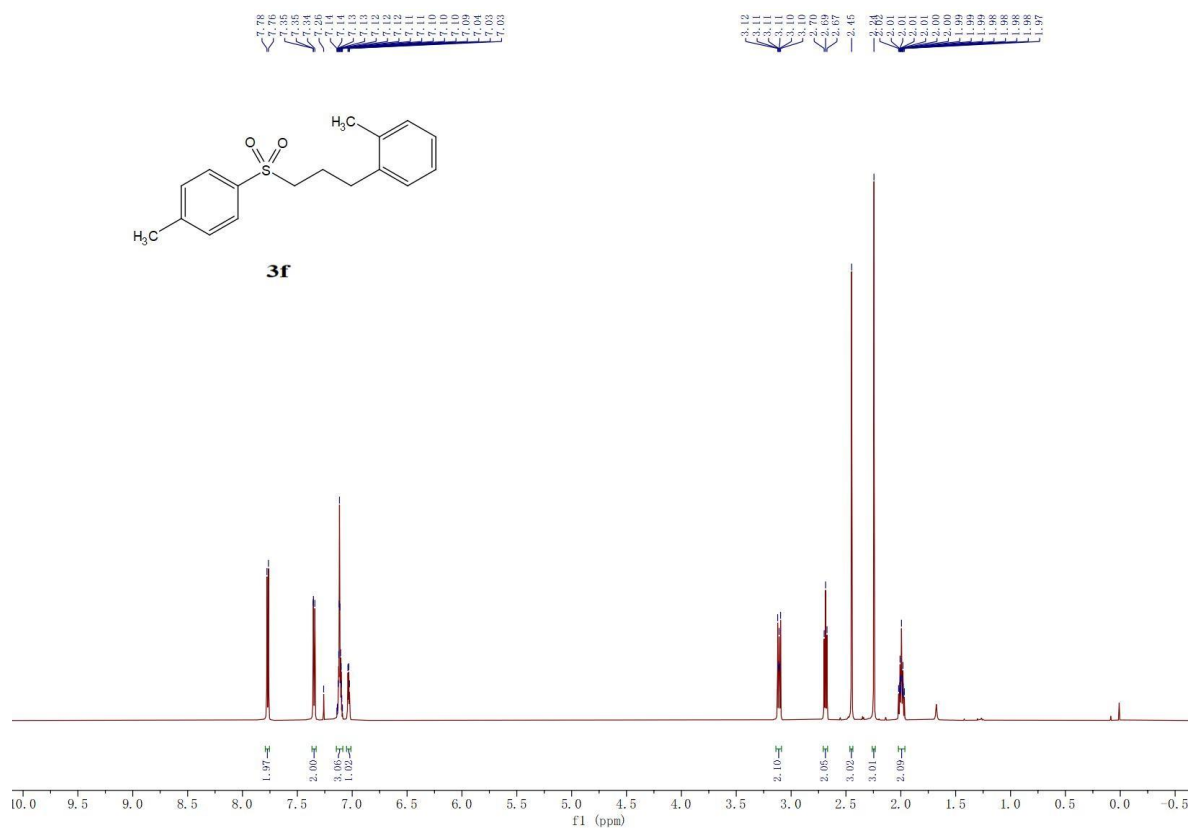
Supplementary Figure 20 | ^1H NMR (600 MHz, CDCl_3) of 1-methyl-4-((3-phenylpropyl)sulfonyl)benzene (**3e**)



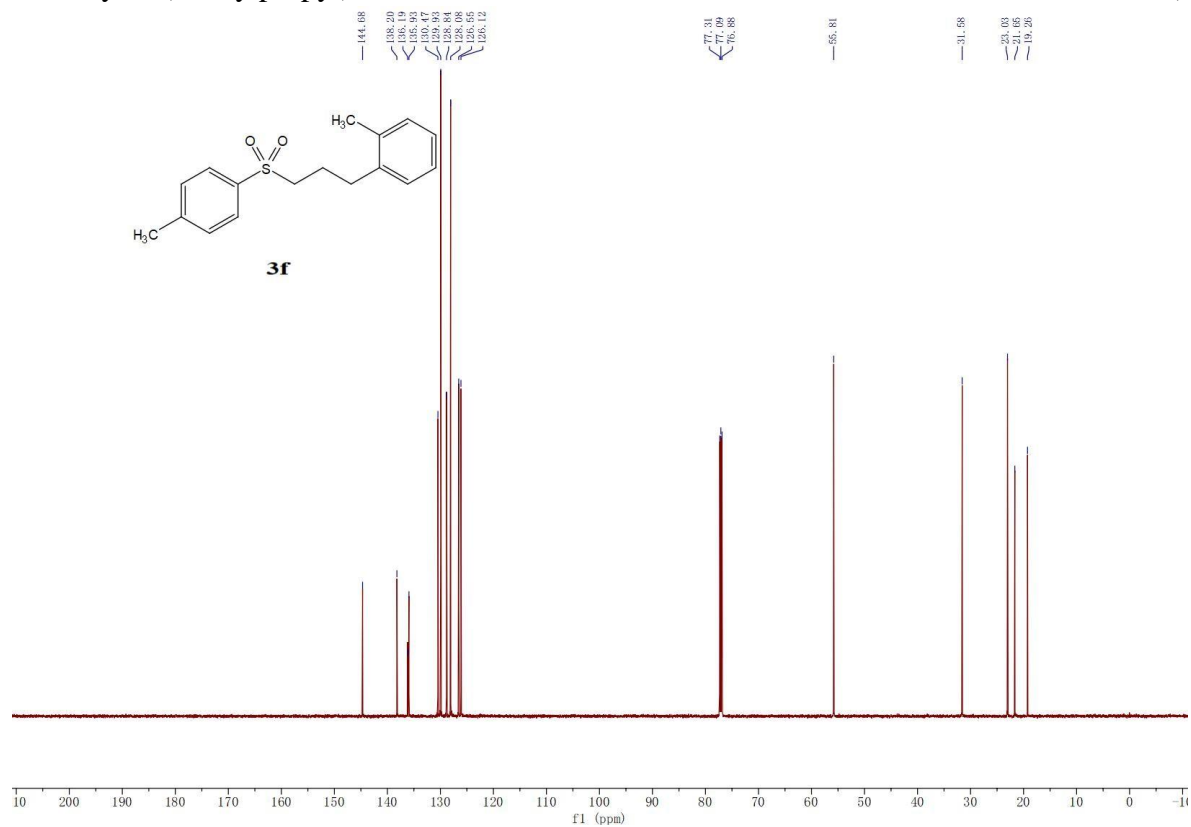
Supplementary Figure 21 | ^{13}C NMR (151 MHz, CDCl_3) of 1-methyl-4-((3-phenylpropyl)sulfonyl)benzene (**3e**)



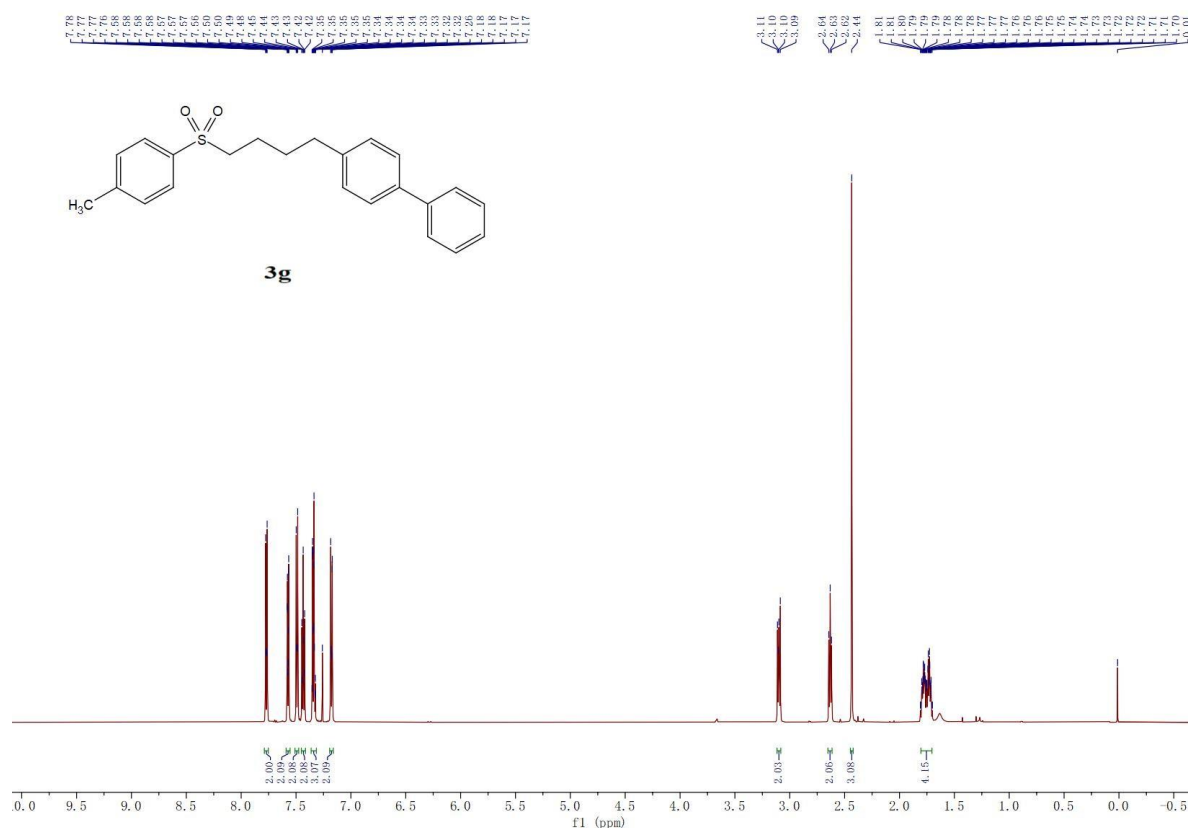
Supplementary Figure 22 ^1H NMR (600 MHz, CDCl_3) of 1-methyl-2-(3-tosylpropyl)benzene (**3f**)



Supplementary Figure 23 ^{13}C NMR (151 MHz, CDCl_3) of 1-methyl-2-(3-tosylpropyl)benzene (**3f**)



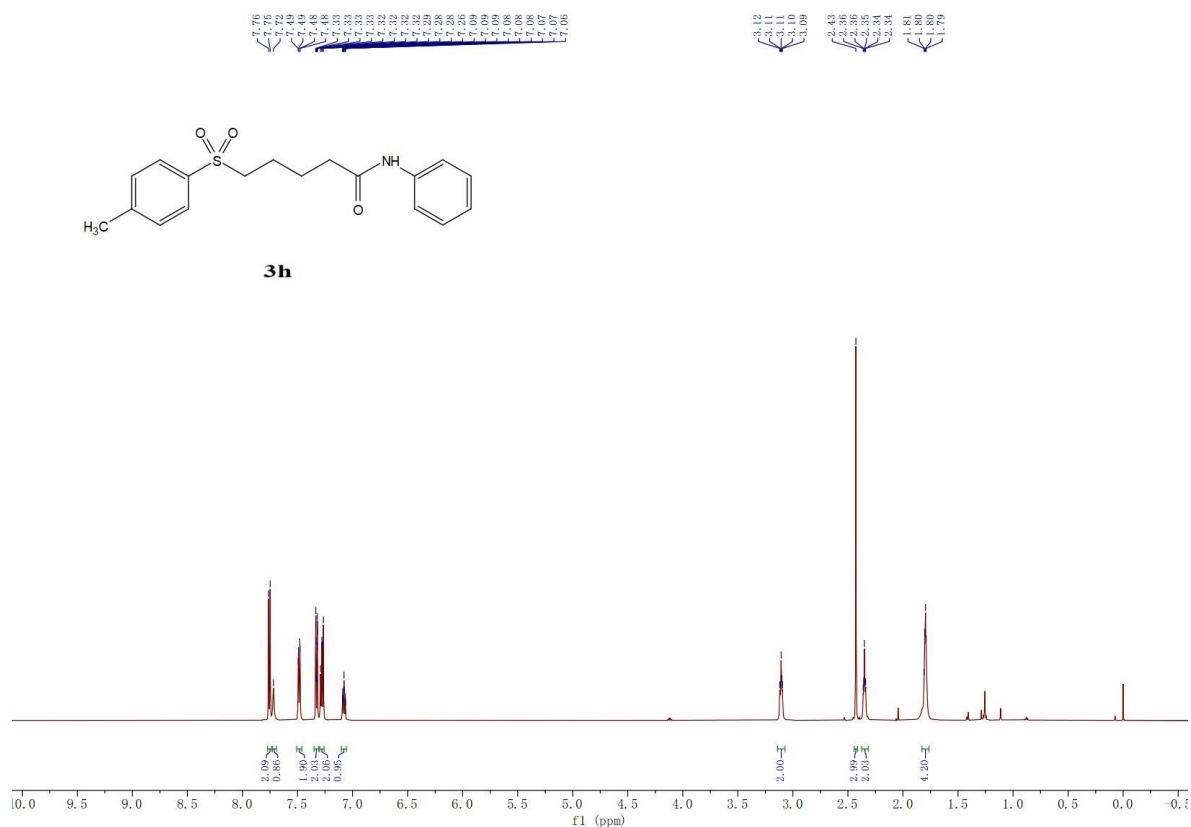
Supplementary Figure 24 ^1H NMR (600 MHz, CDCl_3) of 4-(3-tosylpropyl)-1,1'-biphenyl (**3g**)



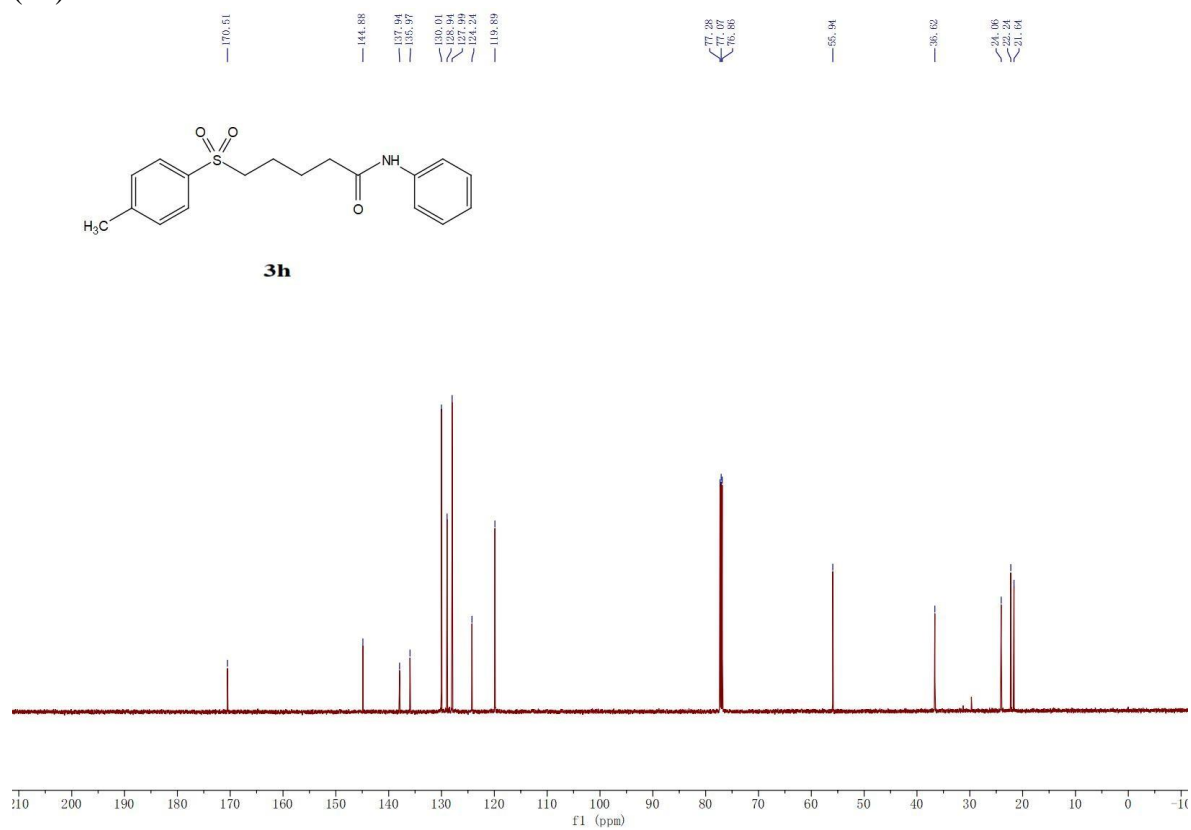
Supplementary Figure 25 ^{13}C NMR (151 MHz, CDCl_3) of 4-(3-tosylpropyl)-1,1'-biphenyl (**3g**)



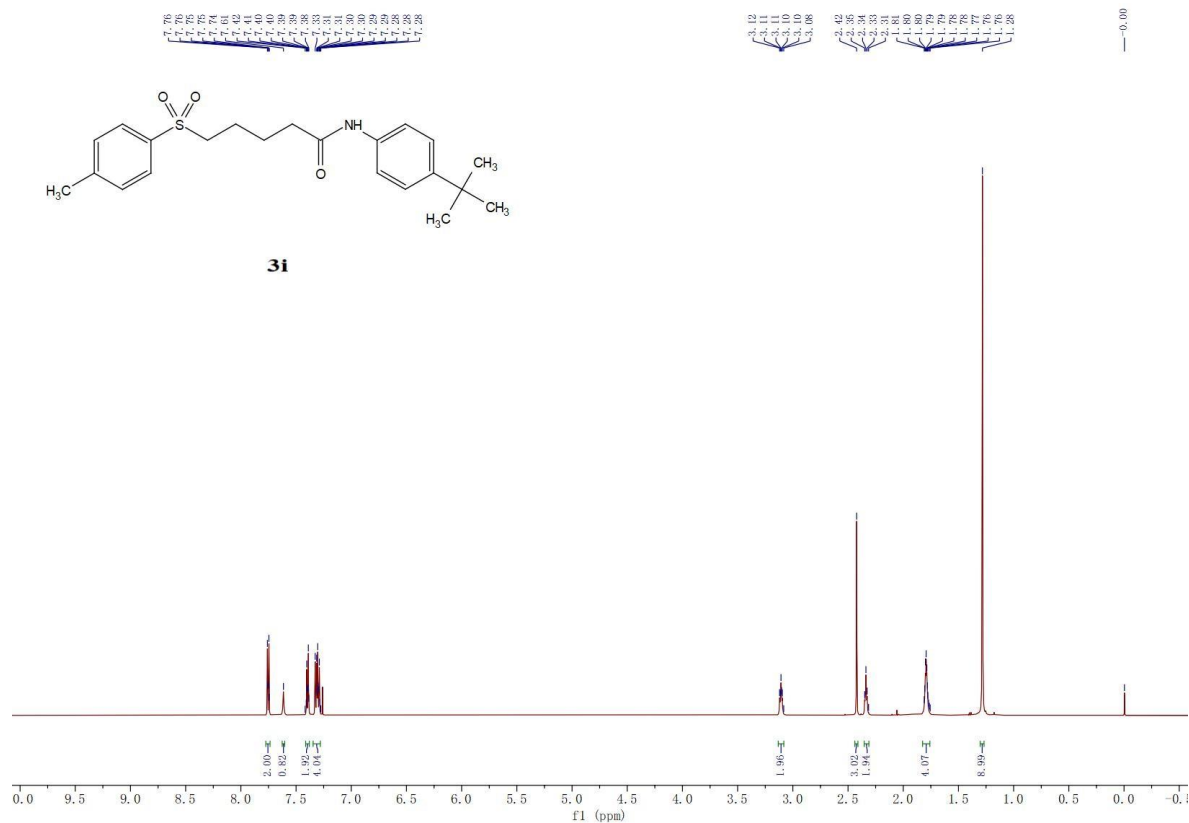
Supplementary Figure 26 ^1H NMR (600 MHz, CDCl_3) of N-phenyl-5-tosylpentanamide (**3h**)



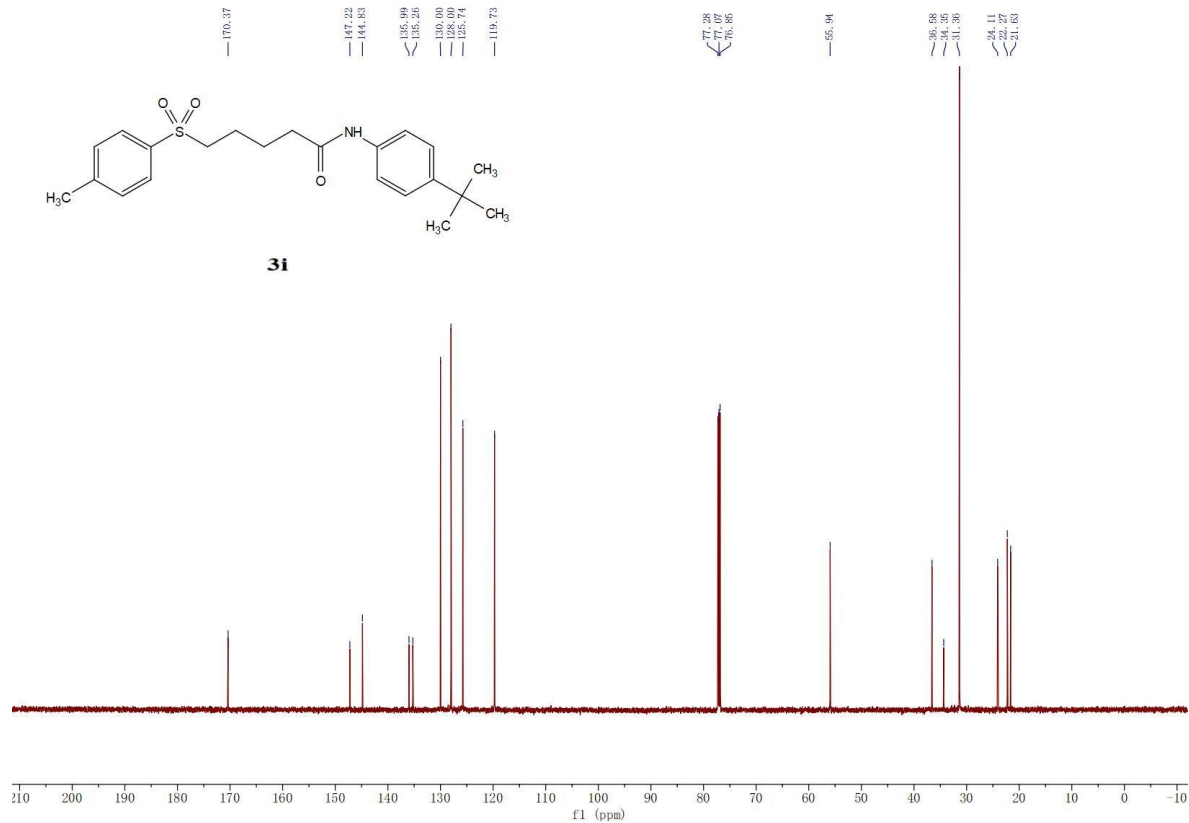
Supplementary Figure 27 ^{13}C NMR (151 MHz, CDCl_3) of N-phenyl-5-tosylpentanamide (**3h**)



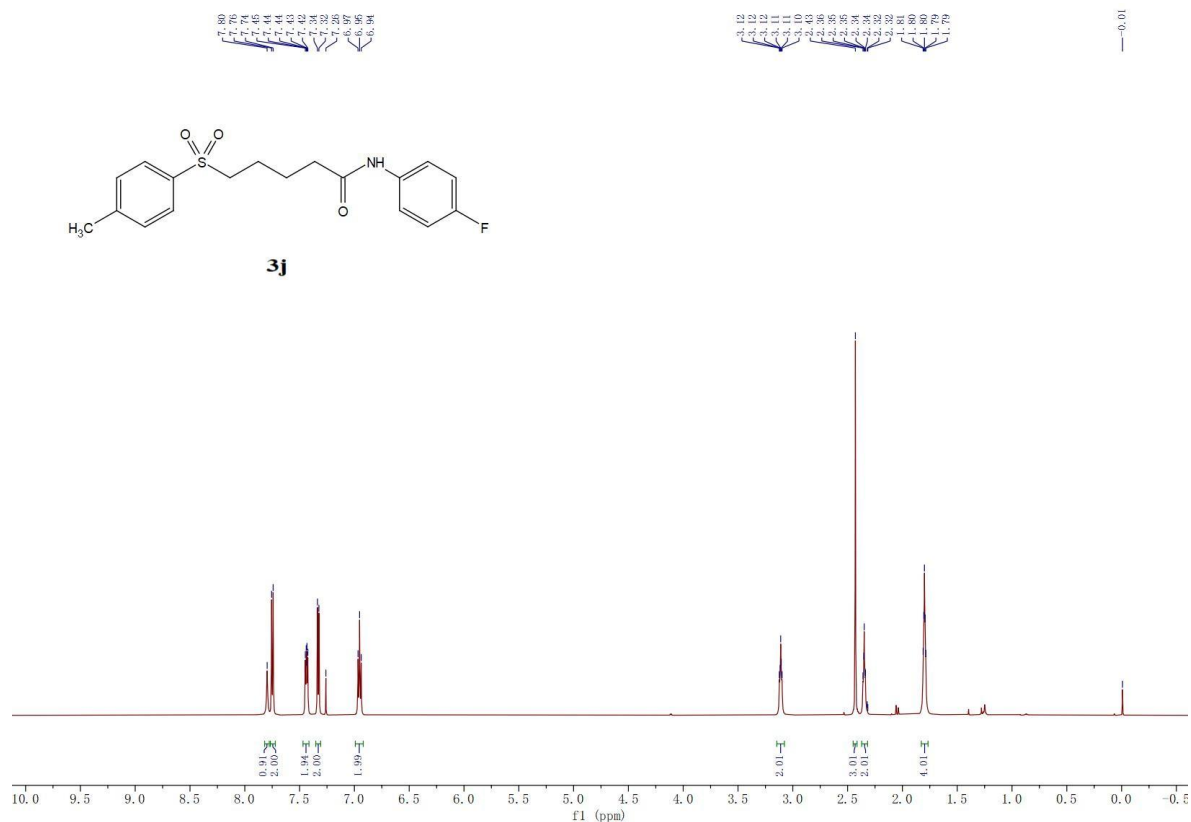
Supplementary Figure 28 | ^1H NMR (600 MHz, CDCl_3) of N-(4-(tert-butyl)phenyl)-5-tosylpentanamide (**3i**)



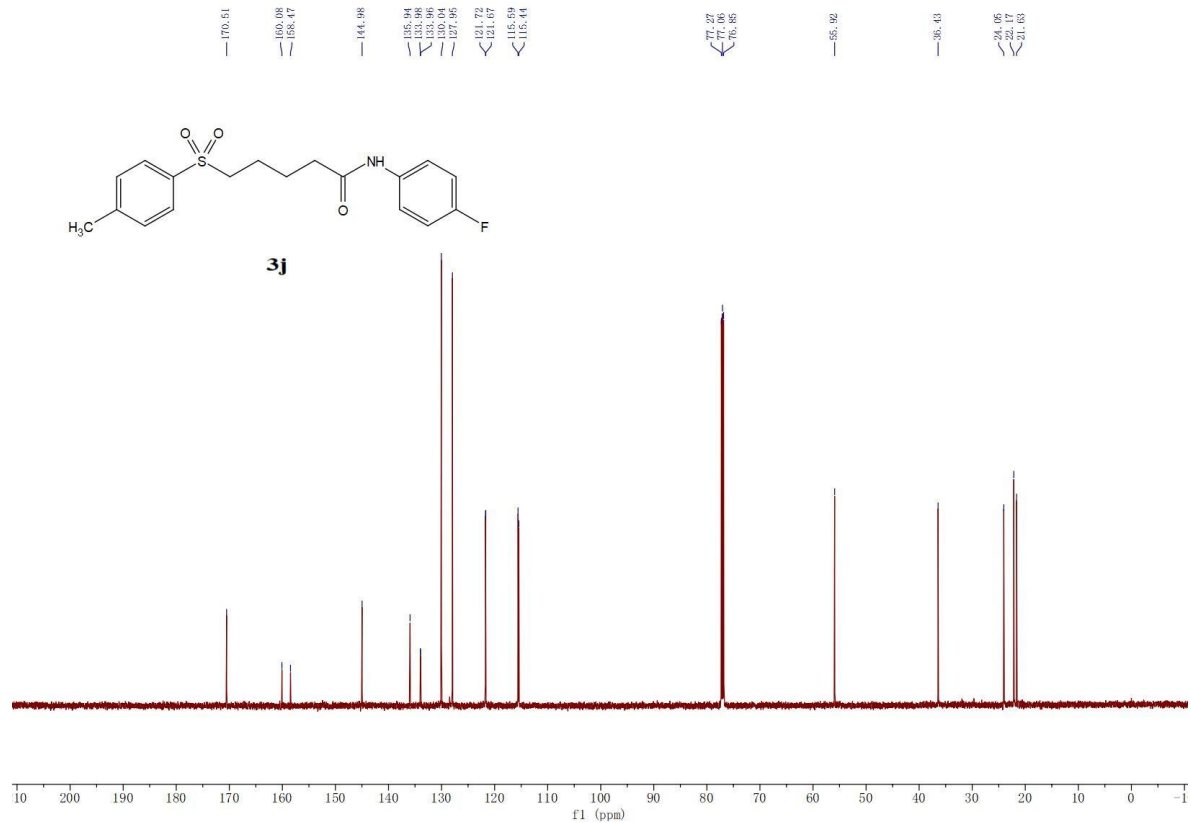
Supplementary Figure 29 | ^{13}C NMR (151 MHz, CDCl_3) of N-(4-(tert-butyl)phenyl)-5-tosylpentanamide (**3i**)



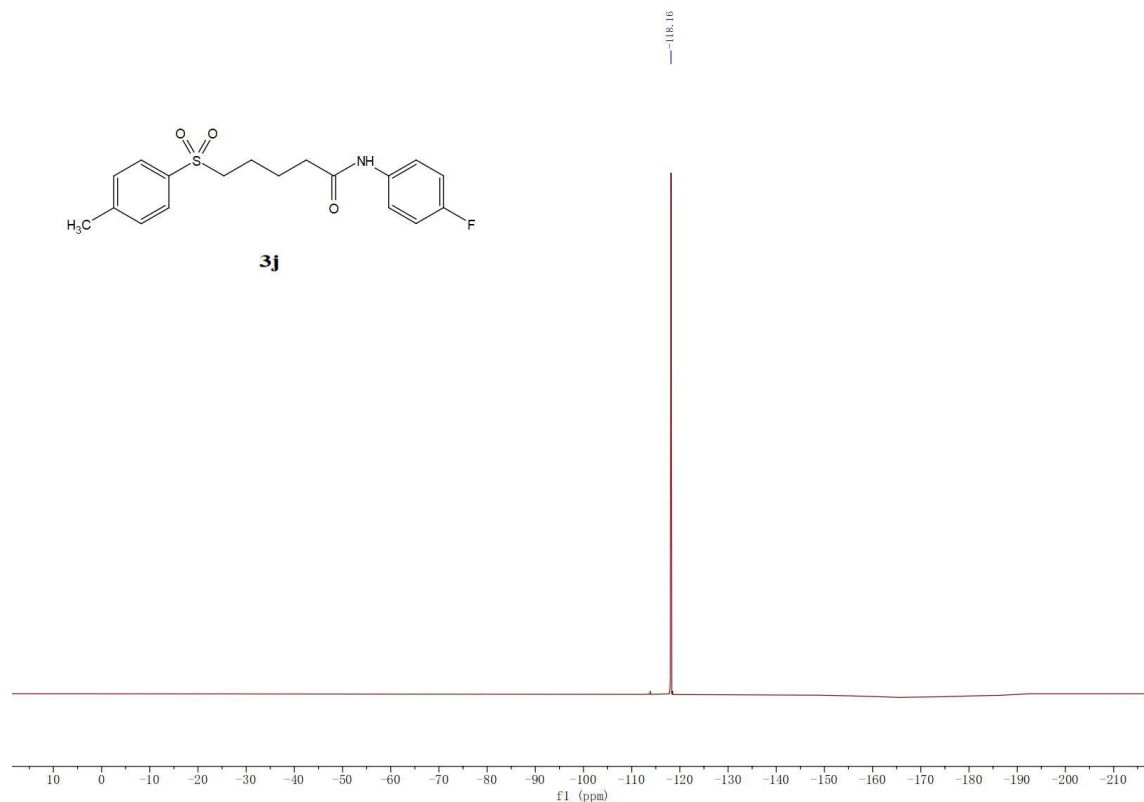
Supplementary Figure 30 ^1H NMR (600 MHz, CDCl_3) of N-(4-fluorophenyl)-5-tosylpentanamide (**3j**)



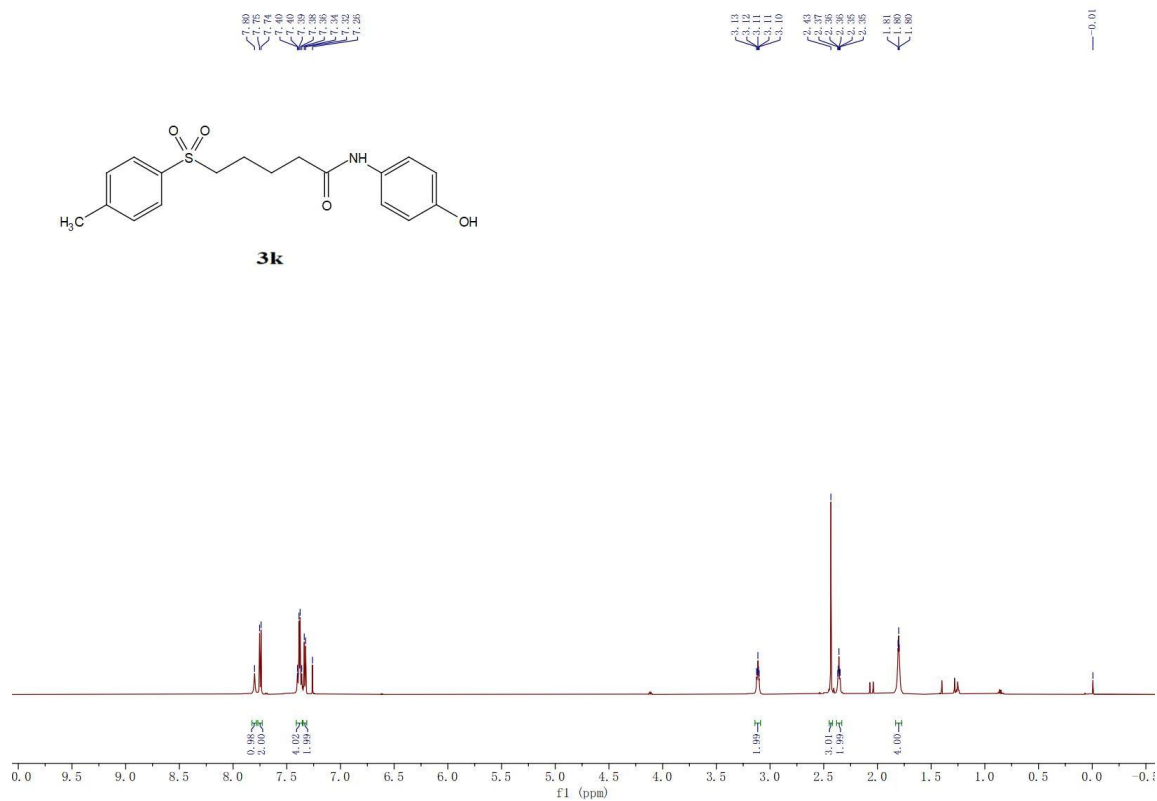
Supplementary Figure 31 ^{13}C NMR (151 MHz, CDCl_3) of N-(4-fluorophenyl)-5-tosylpentanamide (**3j**)



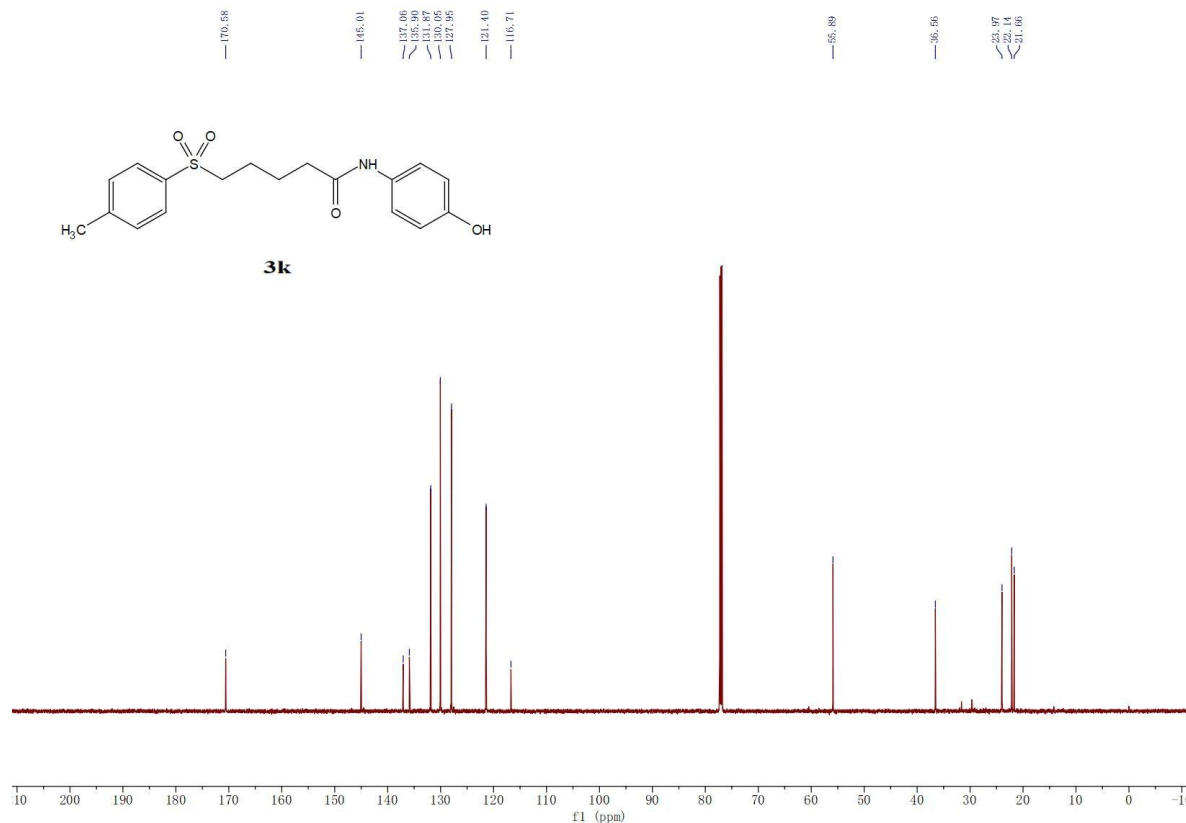
Supplementary Figure 32 ^{19}F NMR (151 MHz, CDCl_3) of N-(4-fluorophenyl)-5-tosylpentanamide (3j)



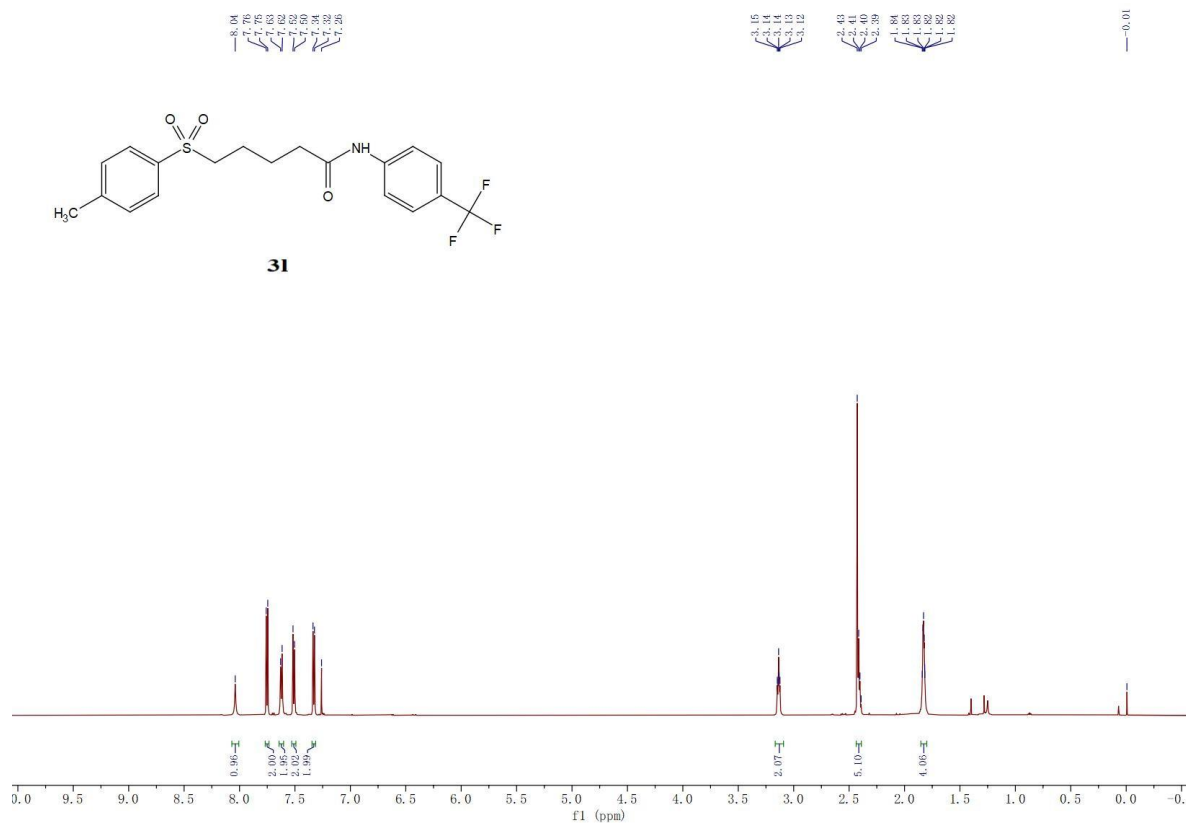
Supplementary Figure 33 ^1H NMR (600 MHz, CDCl_3) of N-(4-hydroxyphenyl)-5-tosylpentanamide (3k)



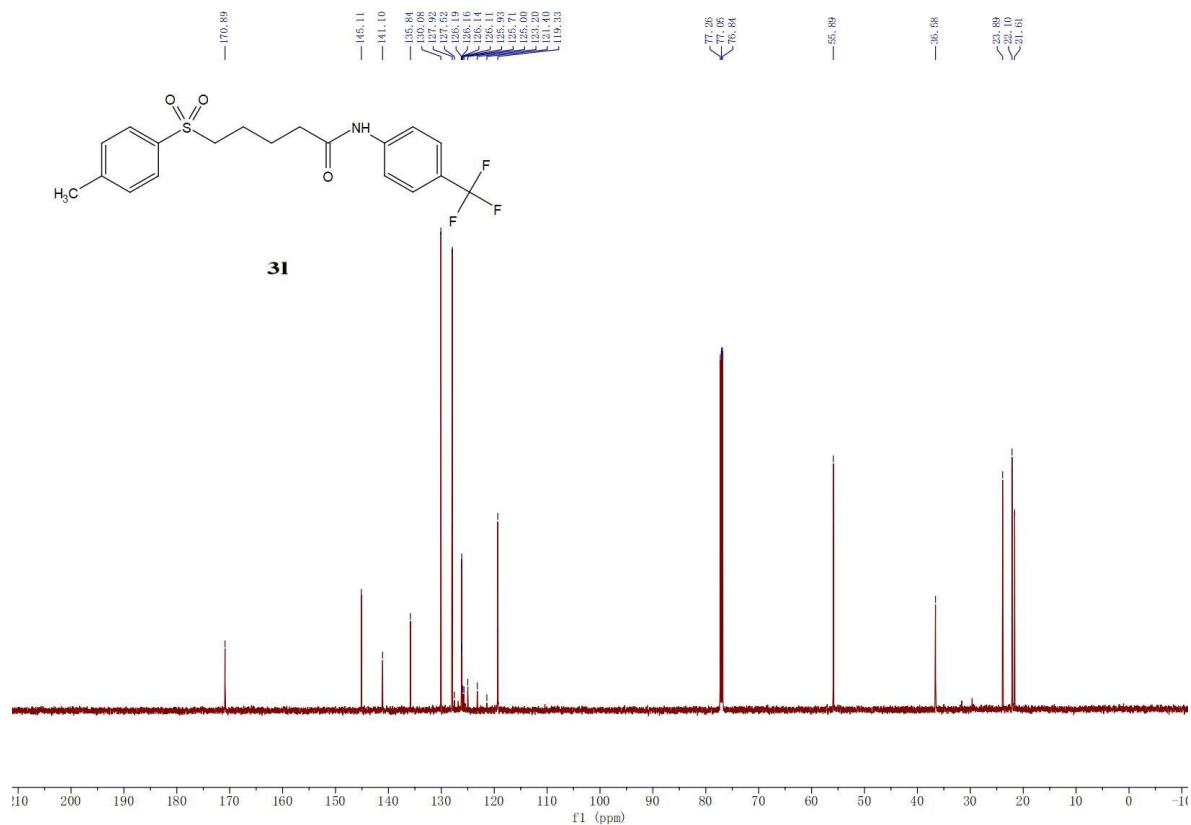
Supplementary Figure 34 ^{13}C NMR (151 MHz, CDCl_3) of N-(4-hydroxyphenyl)-5-tosylpentanamide (**3k**)



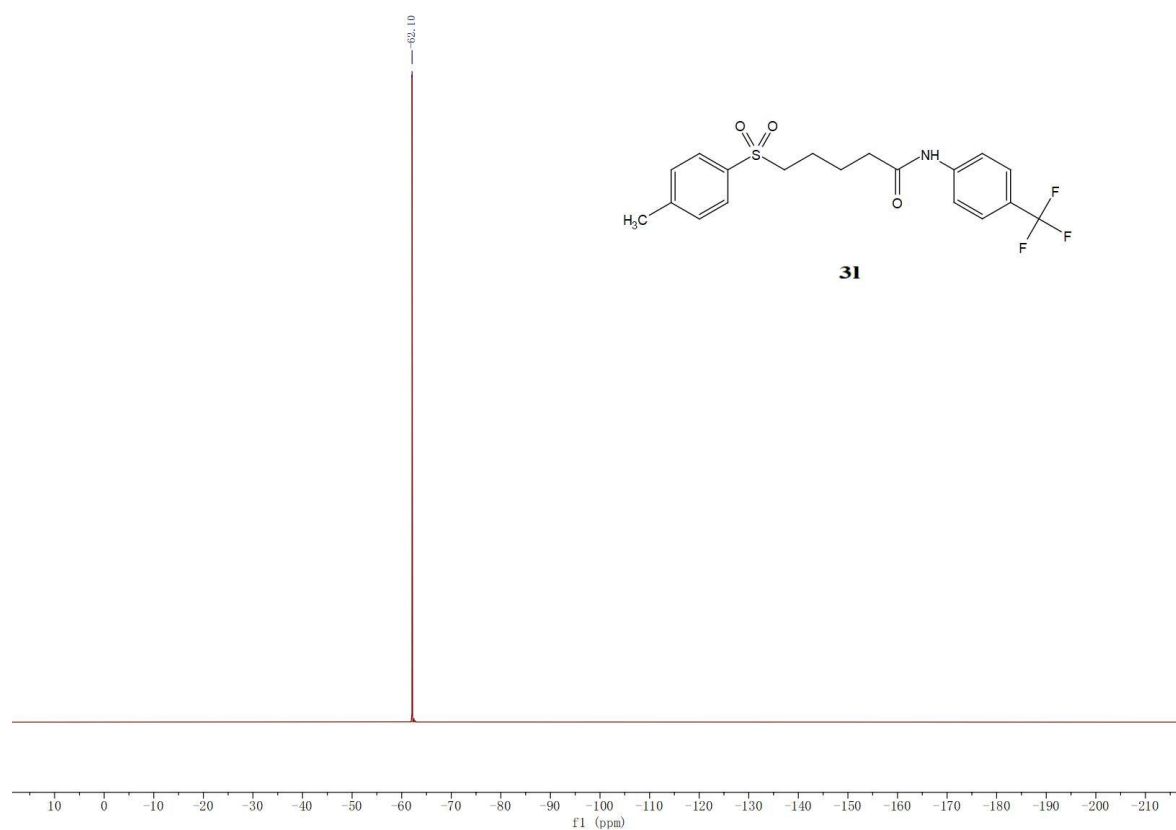
Supplementary Figure 35 ^1H NMR (600 MHz, CDCl_3) of 5-tosyl-N-(4-(trifluoromethyl)phenyl)pentanamide (**3l**)



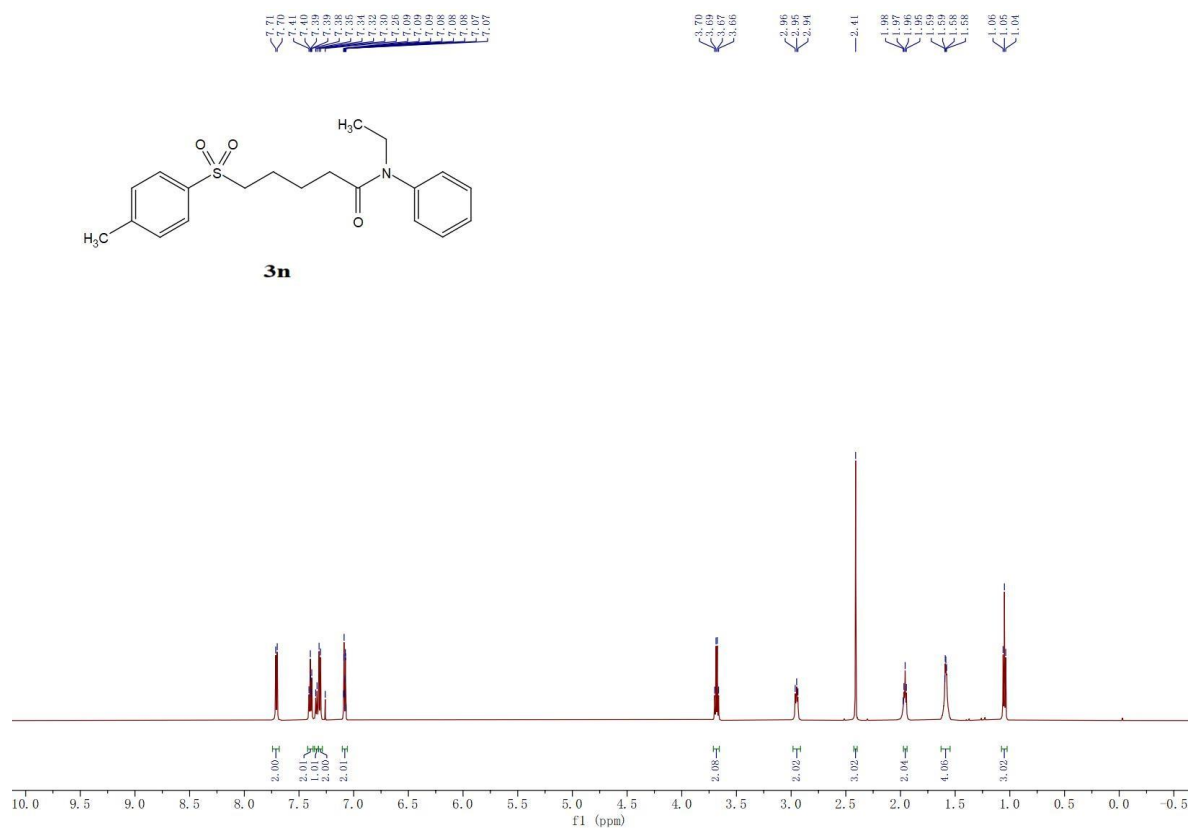
Supplementary Figure 36 ^{13}C NMR (151 MHz, CDCl_3) of 5-tosyl-N-(4-(trifluoromethyl)phenyl)pentanamide (**31**)



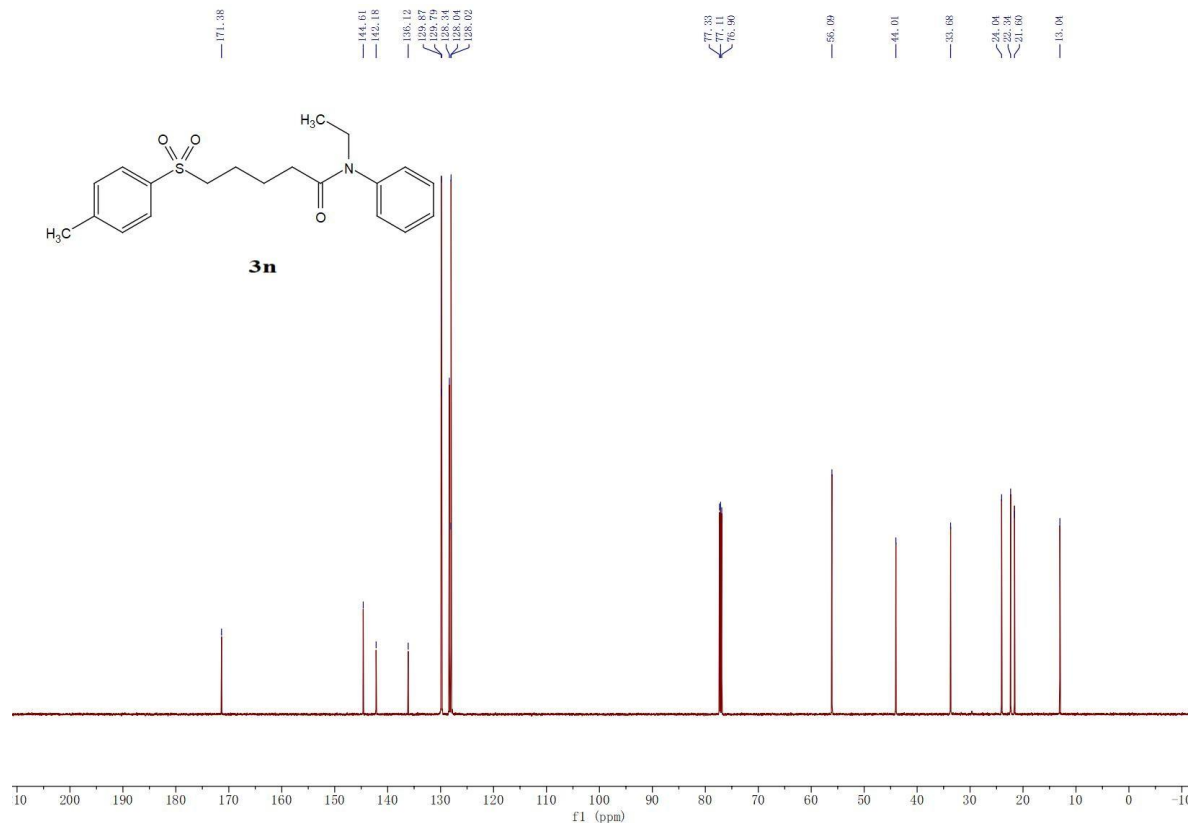
Supplementary Figure 37 ^{19}F NMR (565 MHz, CDCl_3) of 5-tosyl-N-(4-(trifluoromethyl)phenyl)pentanamide (**31**)



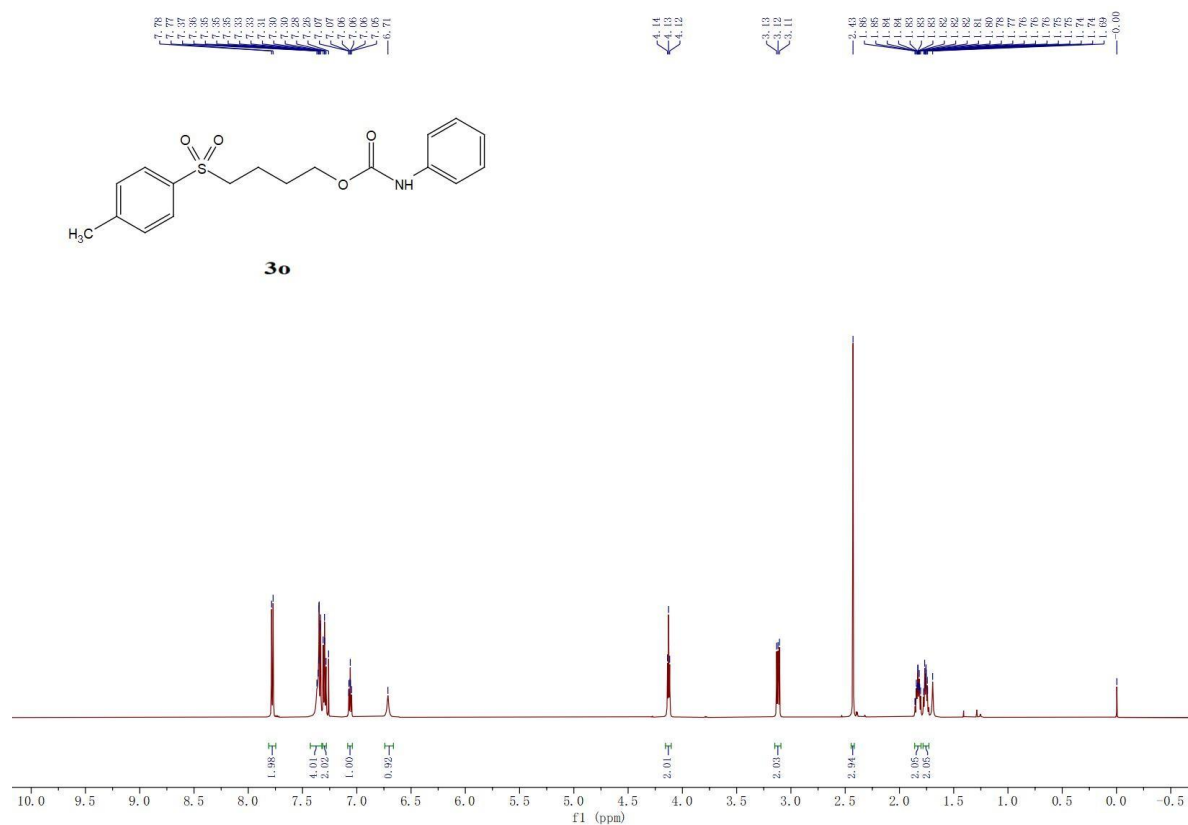
Supplementary Figure 40 ^1H NMR (600 MHz, CDCl_3) of N-ethyl-N-phenyl-5-tosylpentanamide (**3n**)



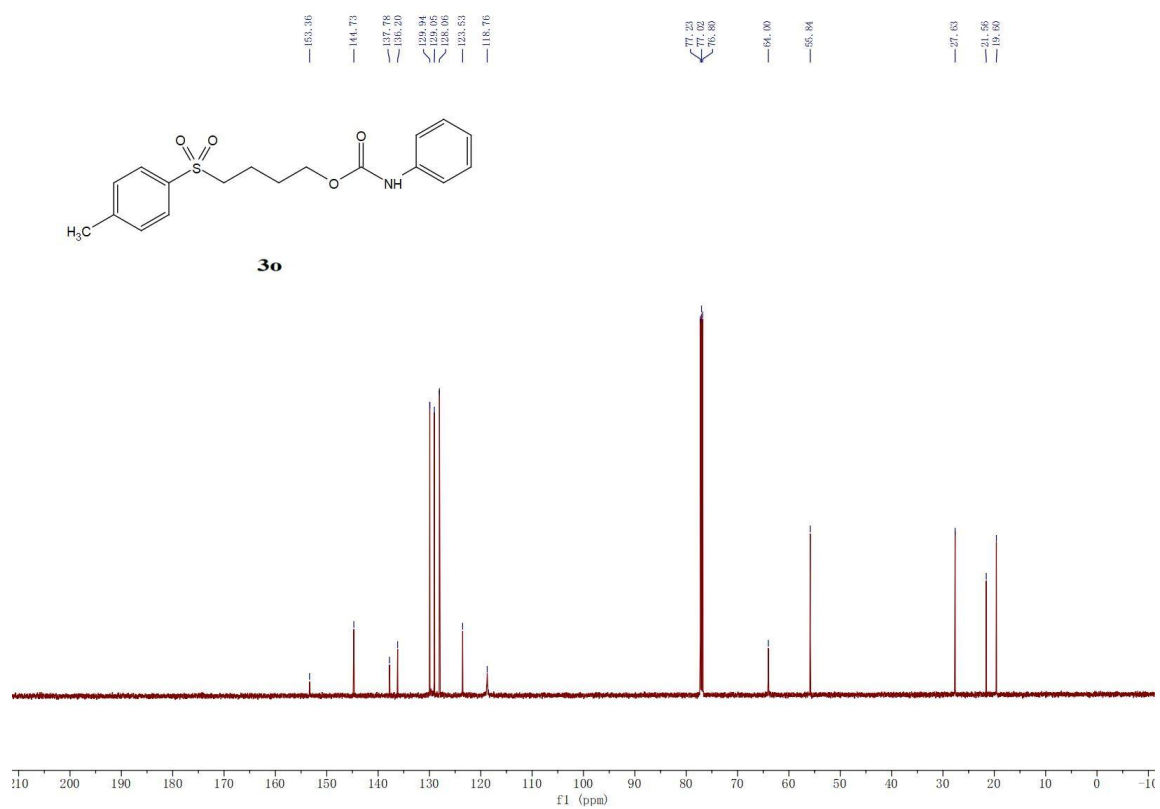
Supplementary Figure 41 ^{13}C NMR (151 MHz, CDCl_3) of N-ethyl-N-phenyl-5-tosylpentanamide (**3n**)



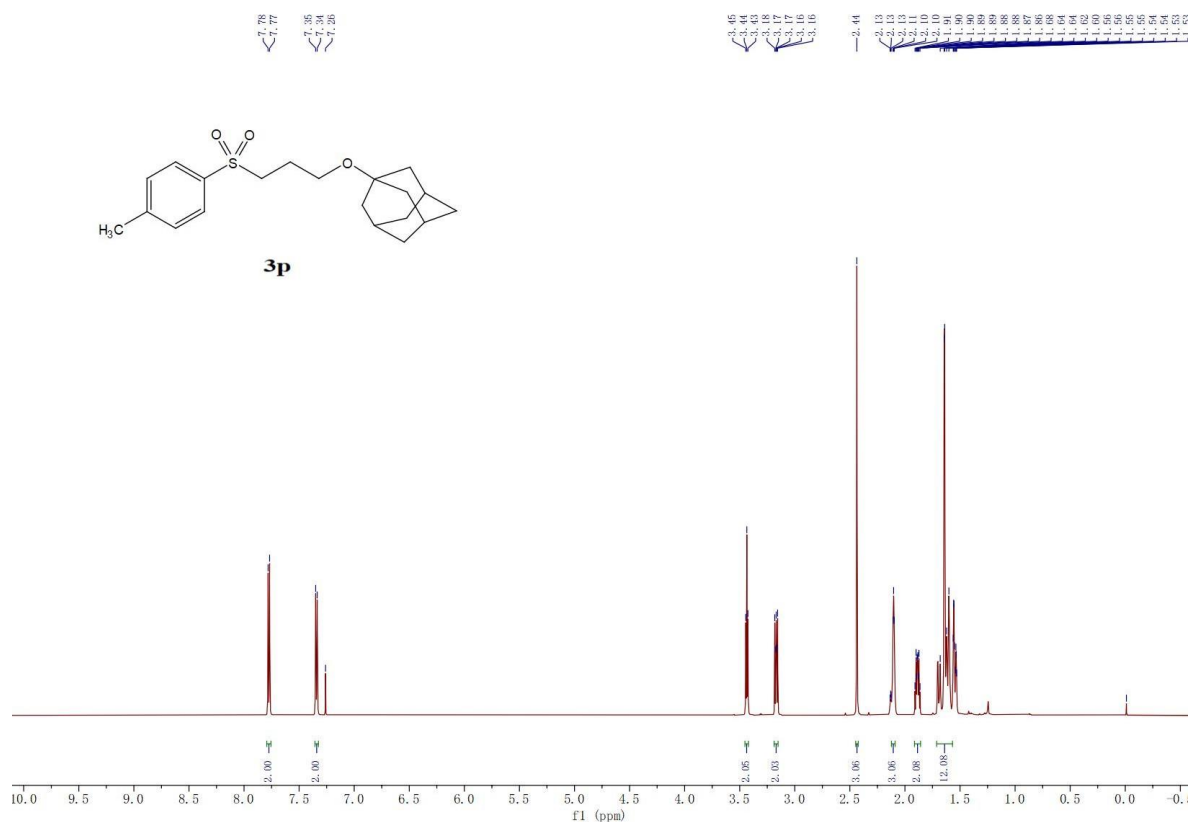
Supplementary Figure 42 ^1H NMR (600 MHz, CDCl_3) of 4-tosylbutyl phenylcarbamate (**3o**)



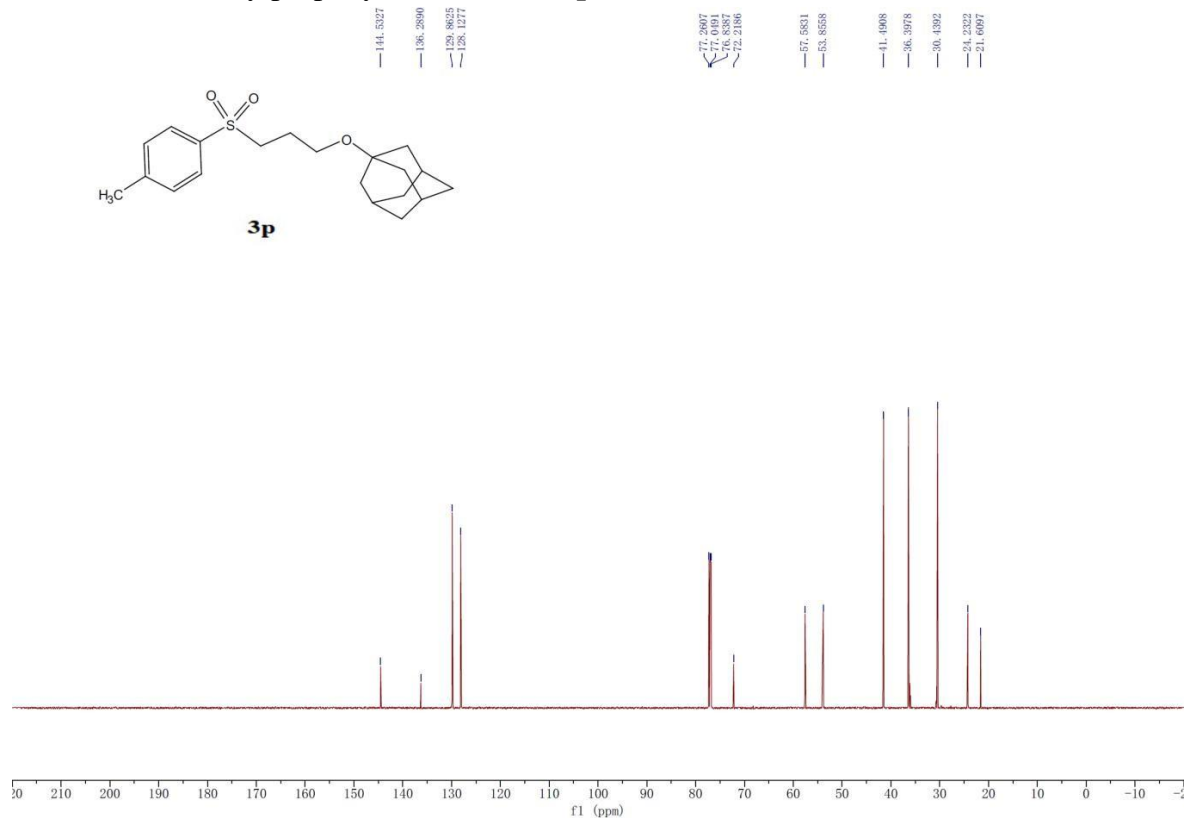
Supplementary Figure 43 ^{13}C NMR (151 MHz, CDCl_3) of 4-tosylbutyl phenylcarbamate (**3o**)



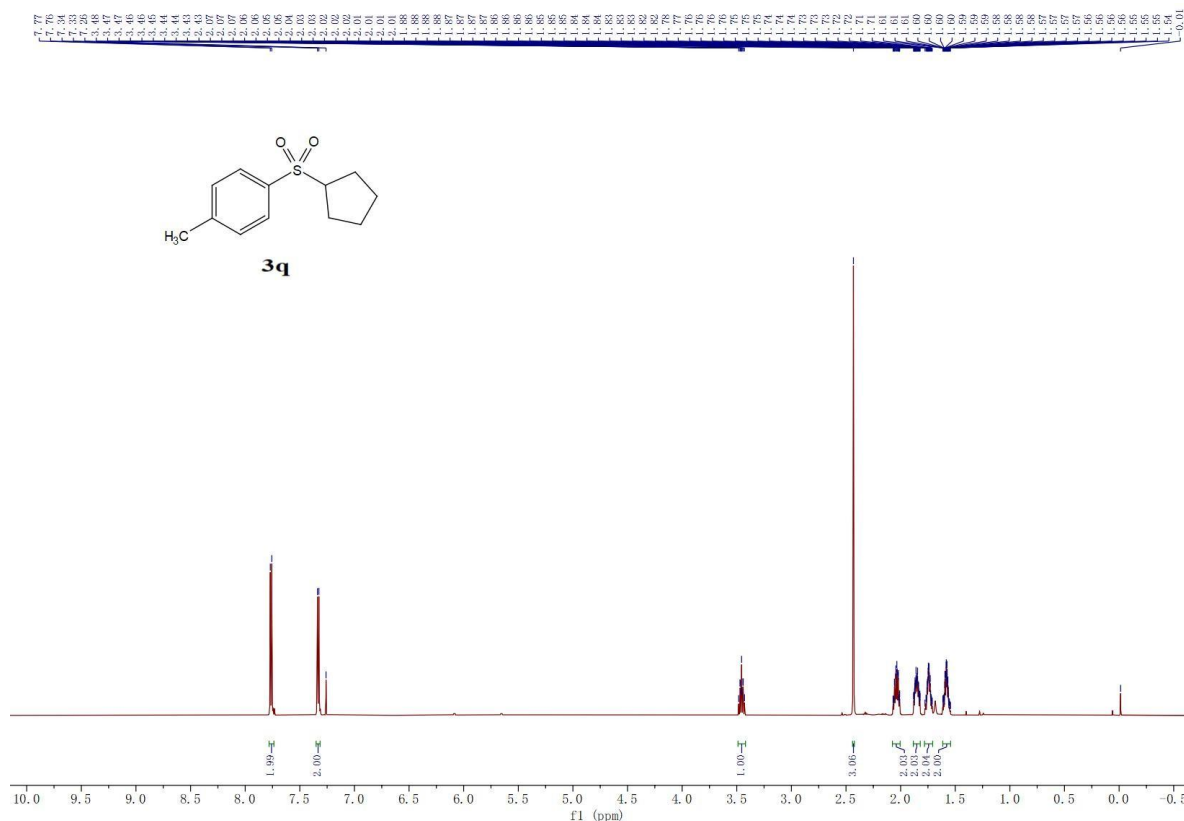
Supplementary Figure 44 ^1H NMR (600 MHz, CDCl_3) of (3s,5s,7s)-1-(3-tosylpropoxy)adamantane (**3p**)



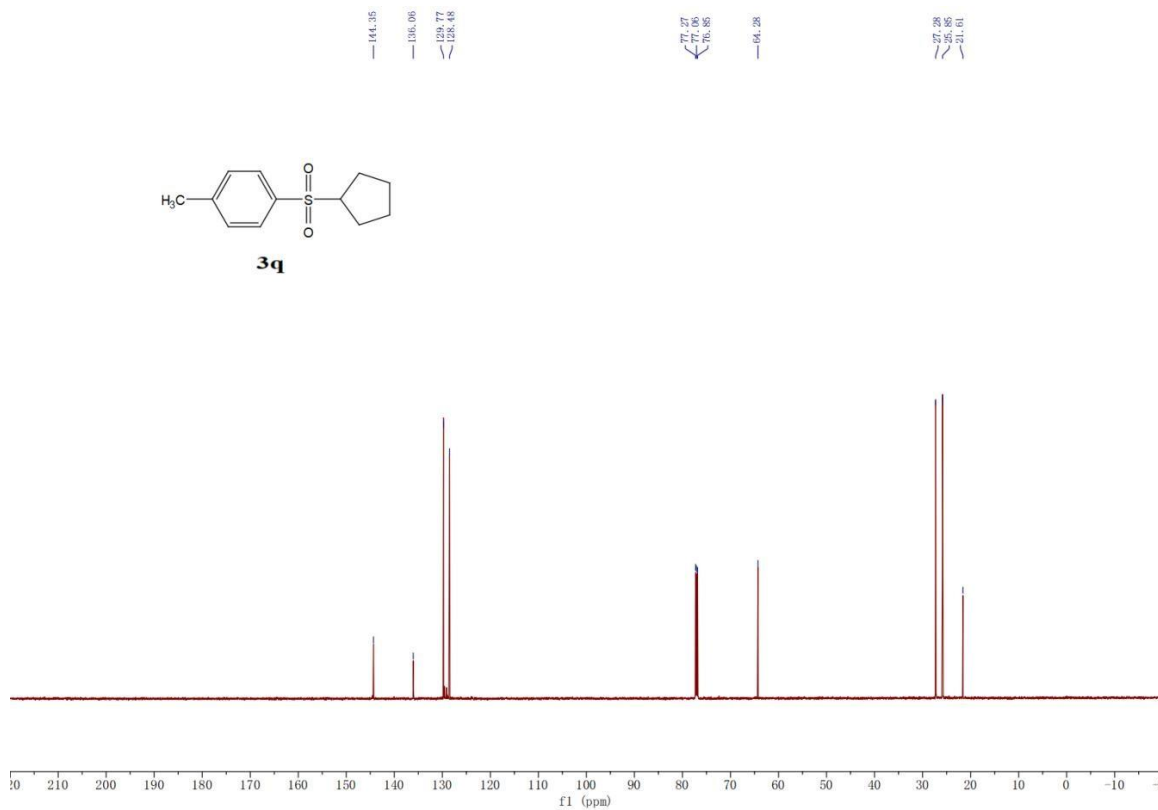
Supplementary Figure 45 ^{13}C NMR (151 MHz, CDCl_3) of (3s,5s,7s)-1-(3-tosylpropoxy)adamantane (**3p**)



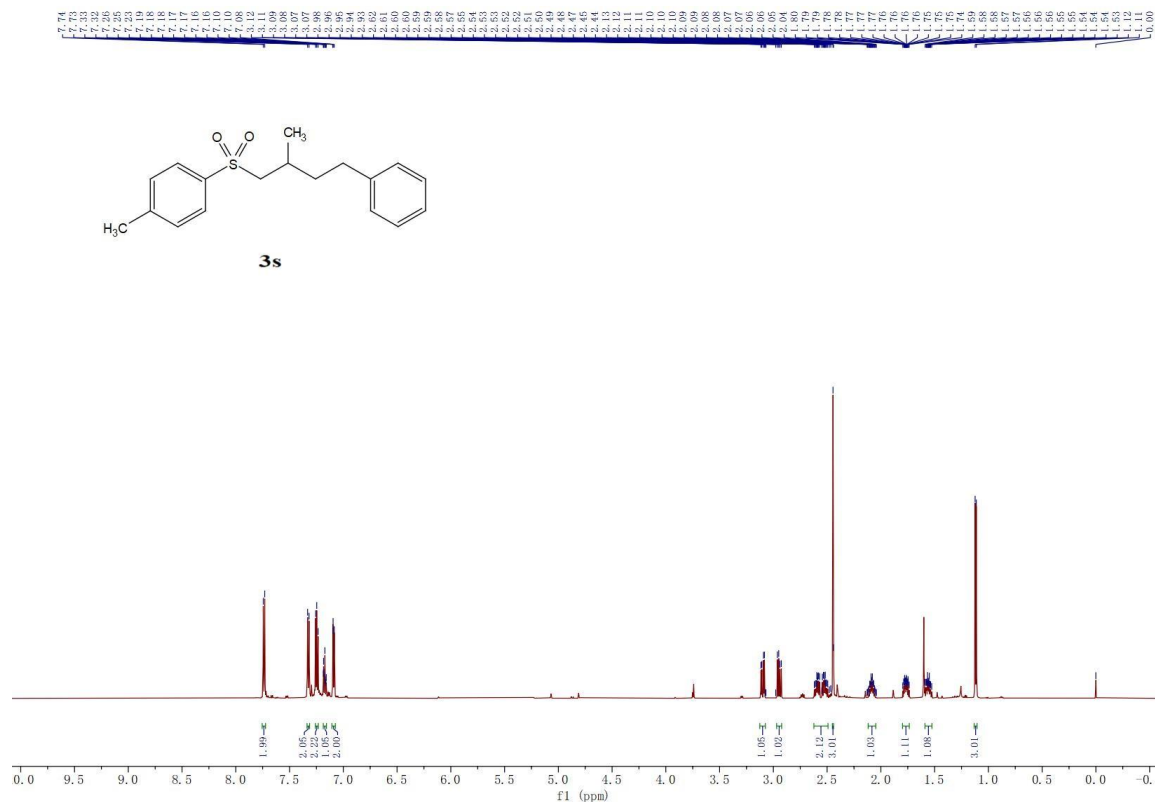
Supplementary Figure 46 ^1H NMR (600 MHz, CDCl_3) of 1-(cyclopentylsulfonyl)-4-methylbenzene (**3q**)



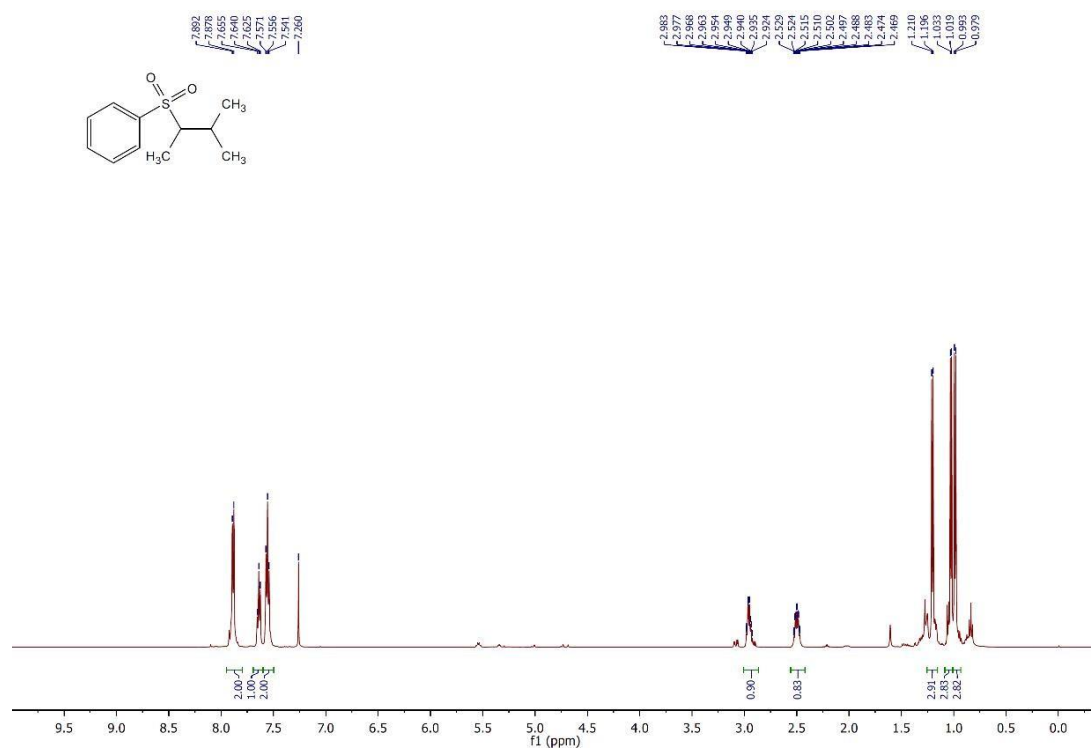
Supplementary Figure 47 ^{13}C NMR (151 MHz, CDCl_3) of 1-(cyclopentylsulfonyl)-4-methylbenzene (**3q**)



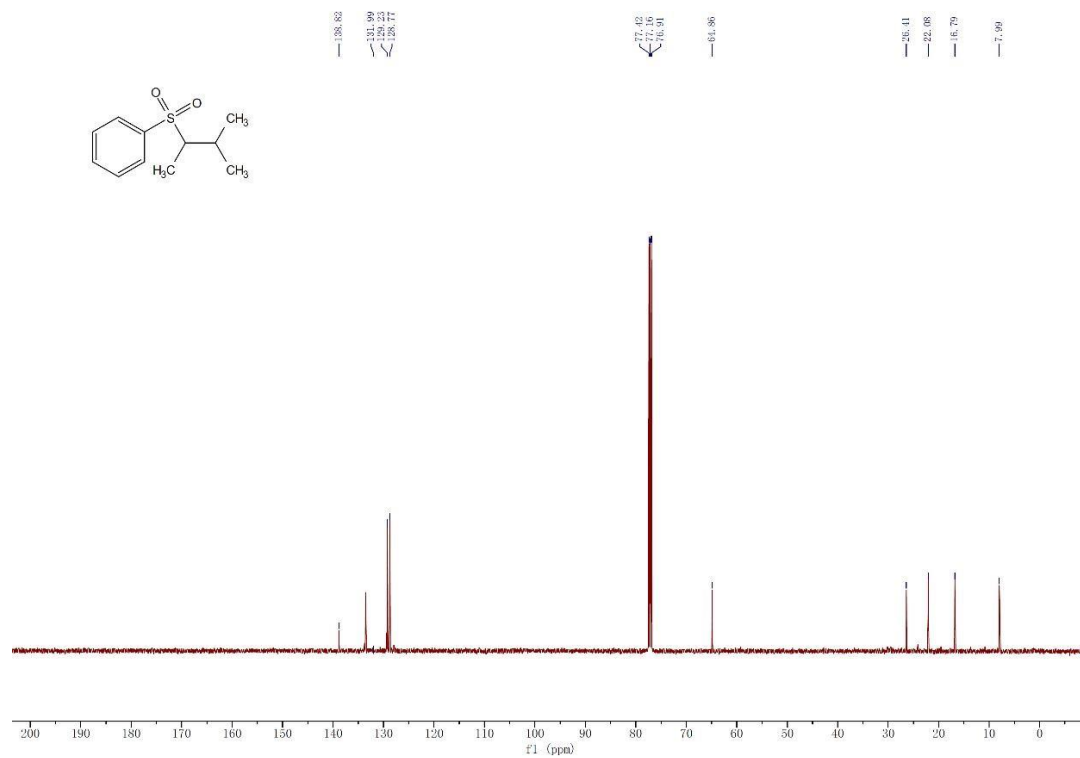
Supplementary Figure 50 ^1H NMR (600 MHz, CDCl_3) of 1-methyl-4-((2-methyl-4-phenylbutyl)sulfonyl)benzene (**3s**)



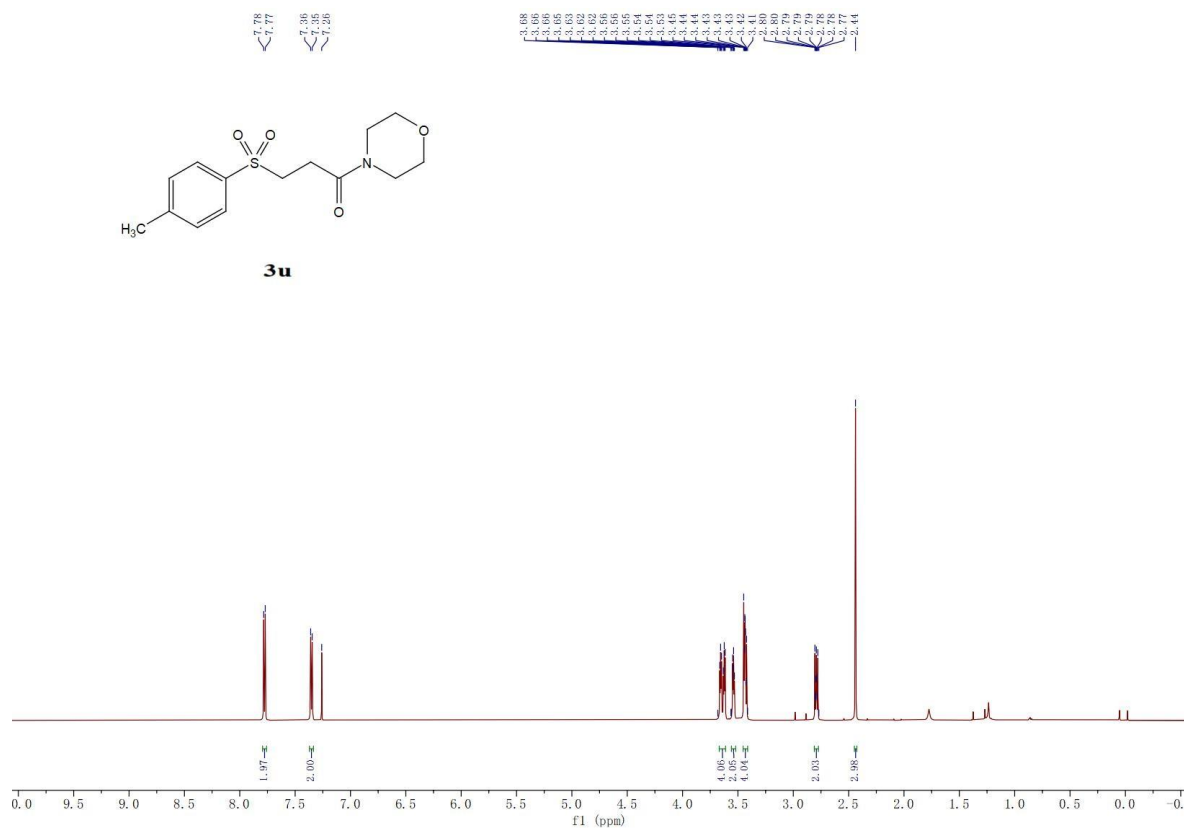
Supplementary Figure 52 ^1H NMR (500 MHz, CDCl_3) of ((3-Methylbutan-2-yl)sulfonyl)benzene (**3t**)



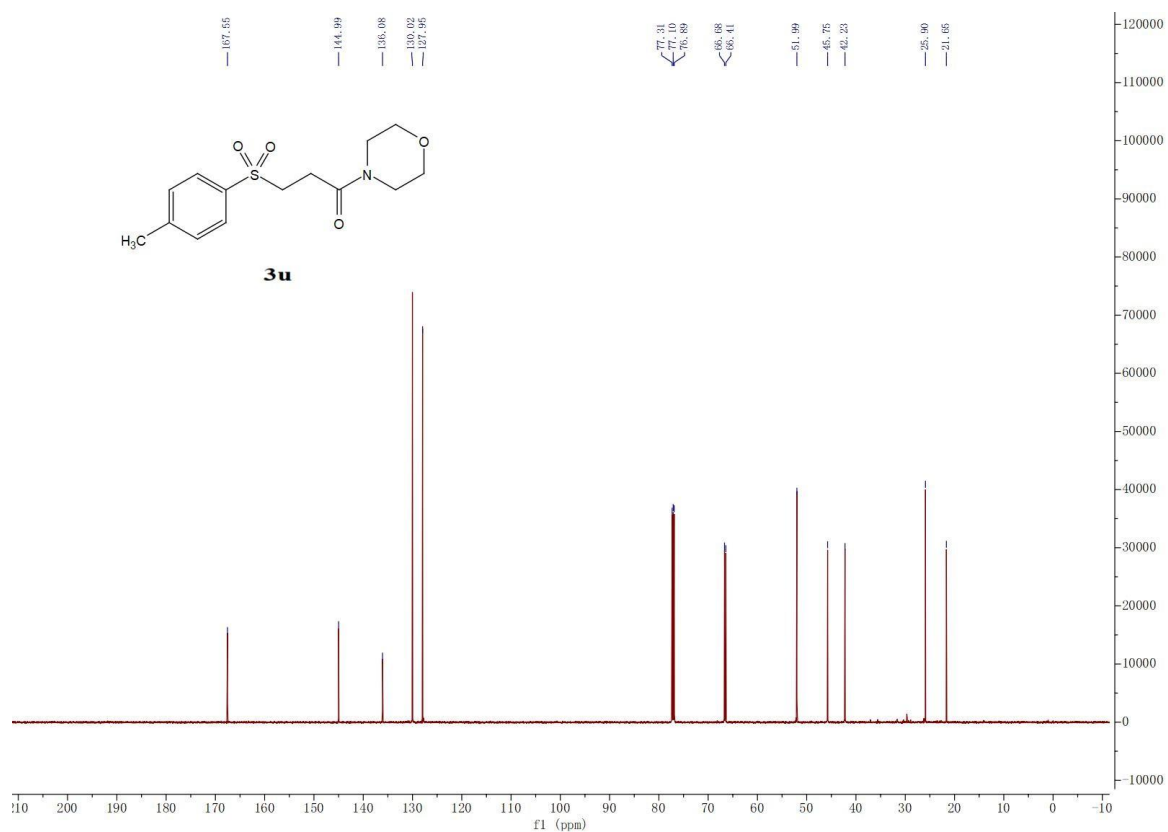
Supplementary Figure 53 ^{13}C NMR (126 MHz, CDCl_3) of ((3-Methylbutan-2-yl)sulfonyl)benzene (**3t**)



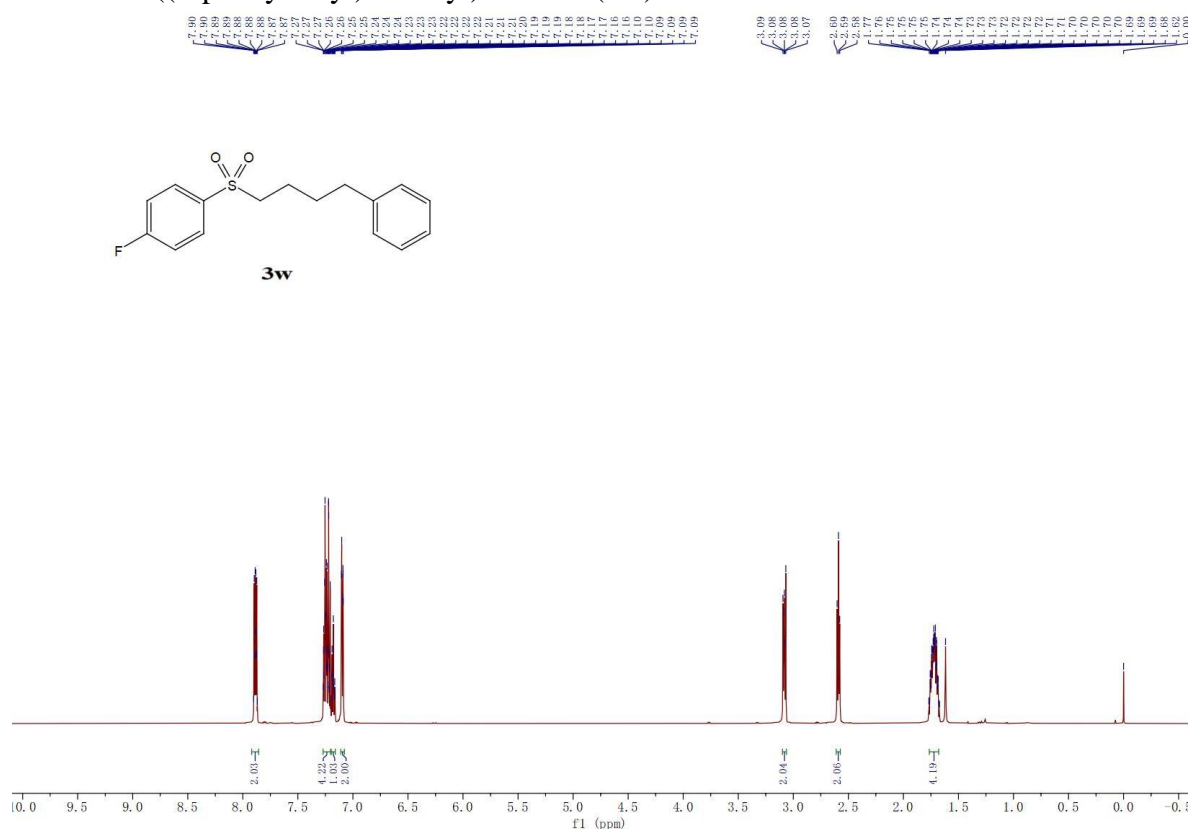
Supplementary Figure 54 ^1H NMR (600 MHz, CDCl_3) of 1-morpholino-3-tosylpropan-1-one (**3u**)



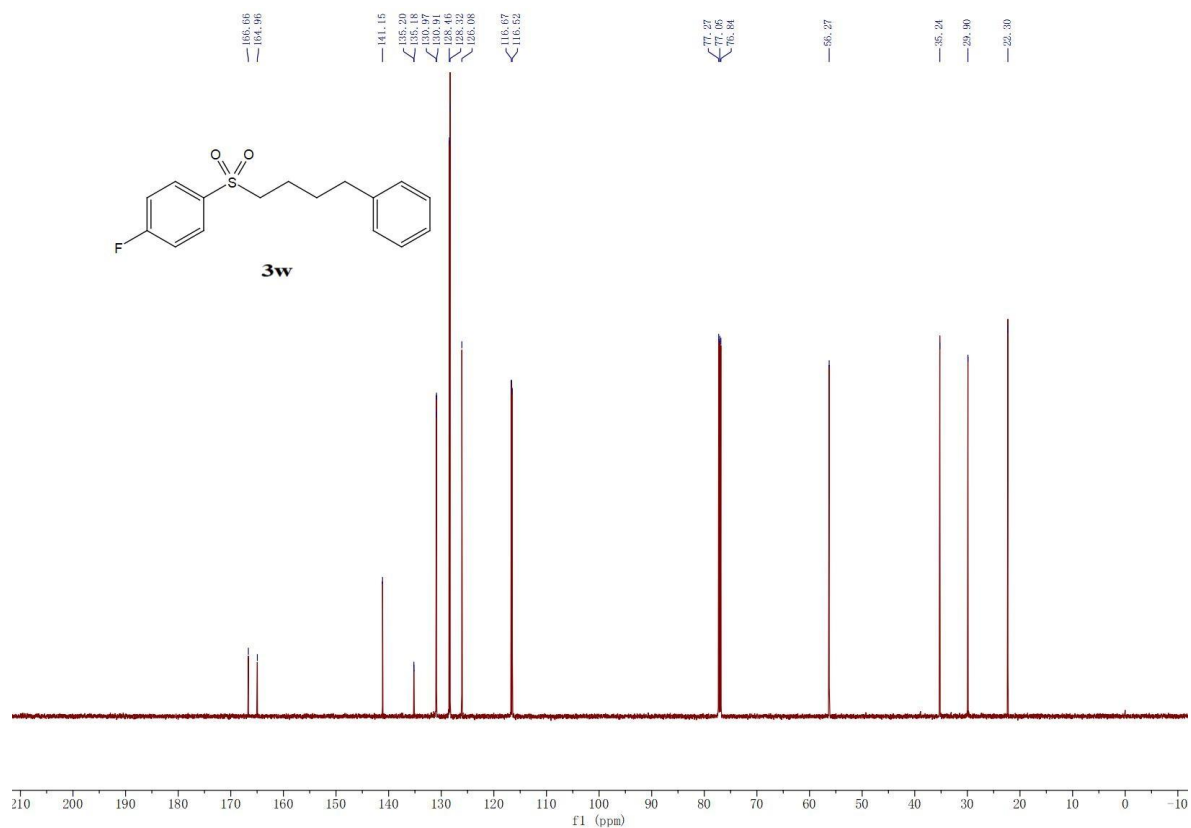
Supplementary Figure 55 ^{13}C NMR (151 MHz, CDCl_3) of 1-morpholino-3-tosylpropan-1-one (**3u**)



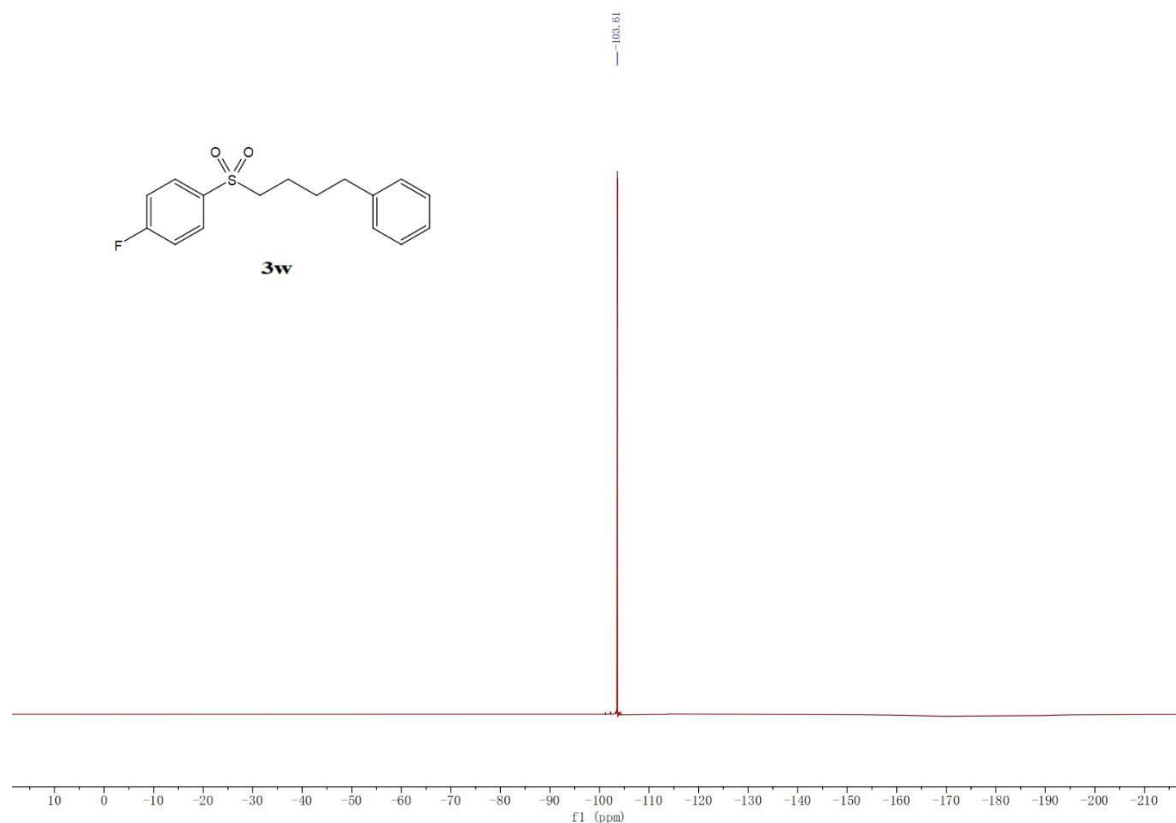
Supplementary Figure 58 ^1H NMR (600 MHz, CDCl_3) of 1-fluoro-4-((4-phenylbutyl)sulfonyl)benzene (**3w**)



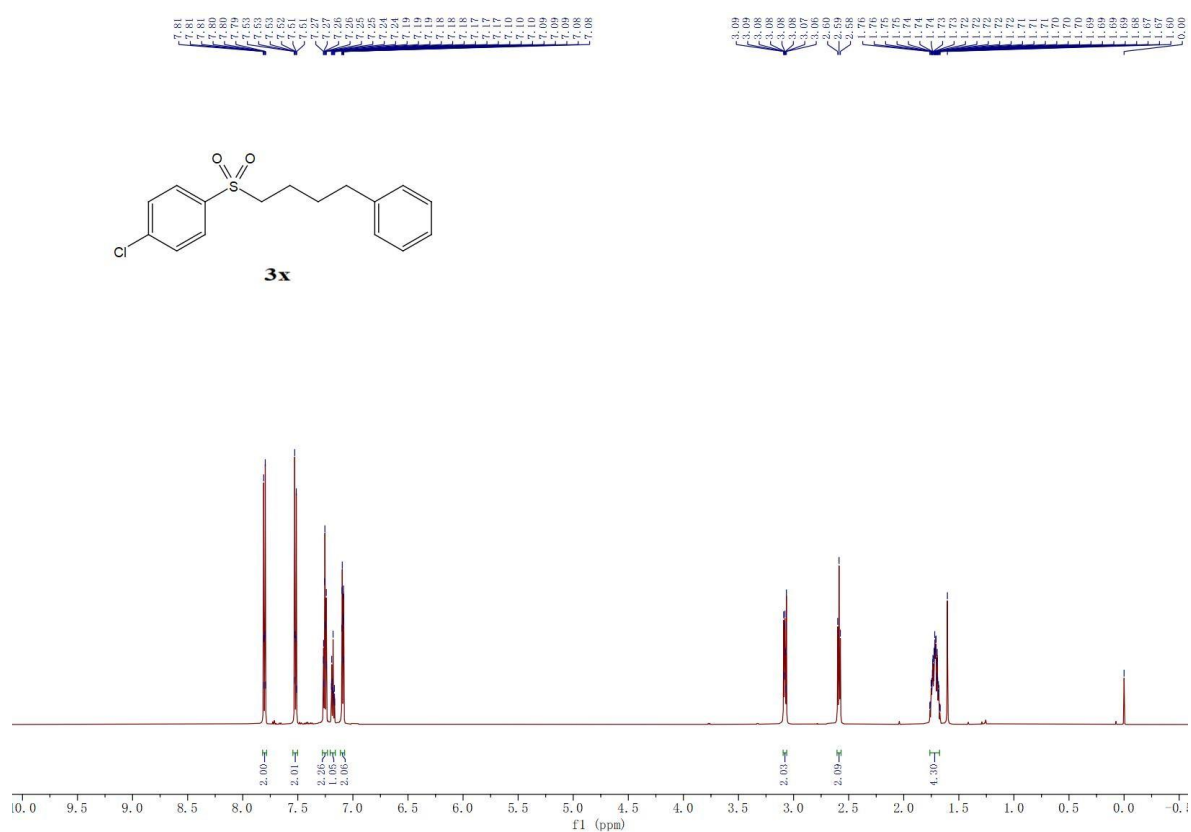
Supplementary Figure 59 ^{13}C NMR (151 MHz, CDCl_3) of 1-fluoro-4-((4-phenylbutyl)sulfonyl)benzene (**3w**)



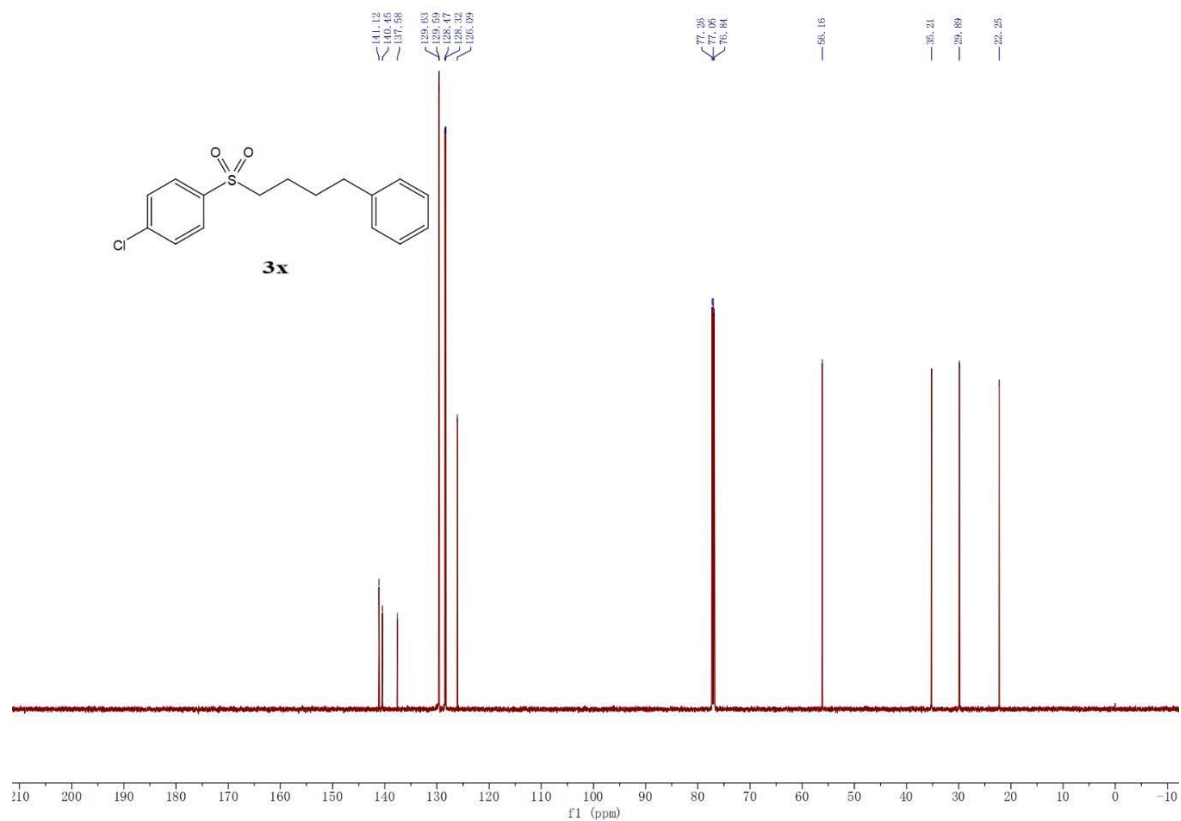
Supplementary Figure 60 ^{19}F NMR (565 MHz, CDCl_3) of 1-fluoro-4-((4-phenylbutyl)sulfonyl)benzene (**3w**)



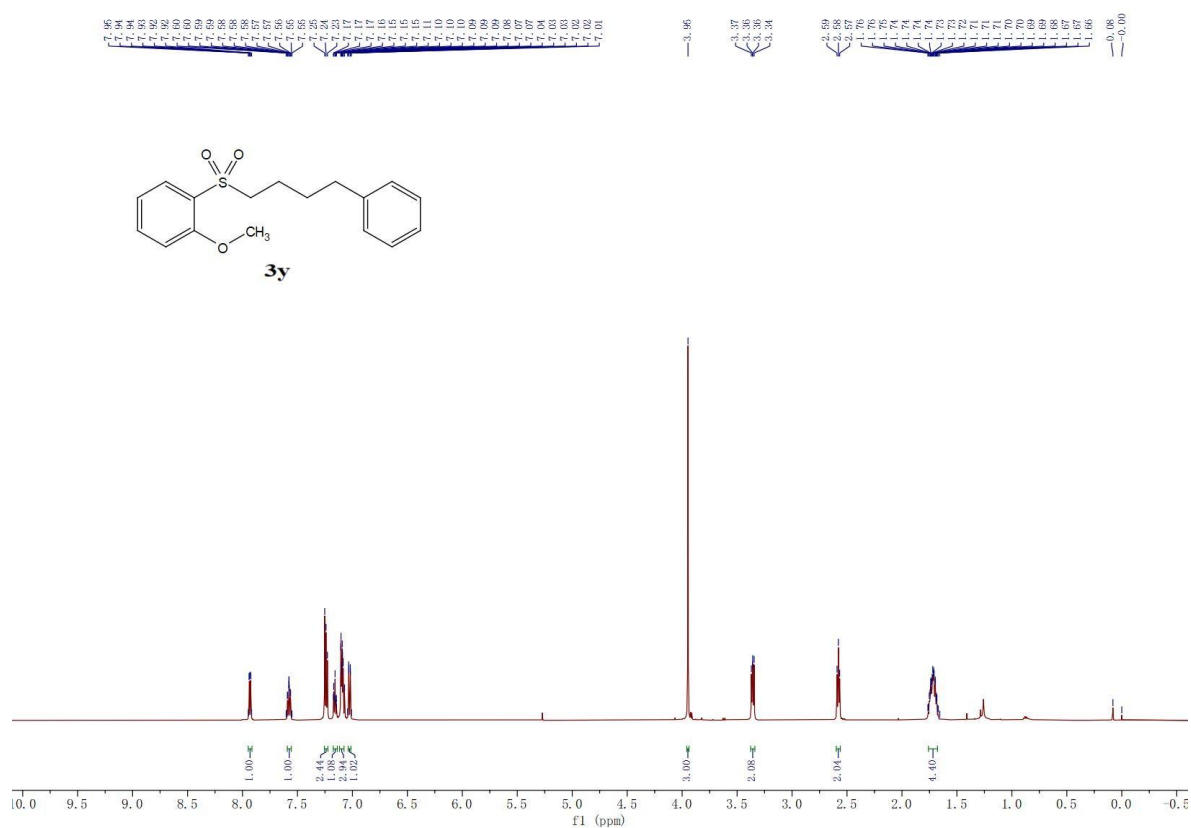
Supplementary Figure 61 ^1H NMR (600 MHz, CDCl_3) of 1-chloro-4-((4-phenylbutyl)sulfonyl)benzene (**3x**)



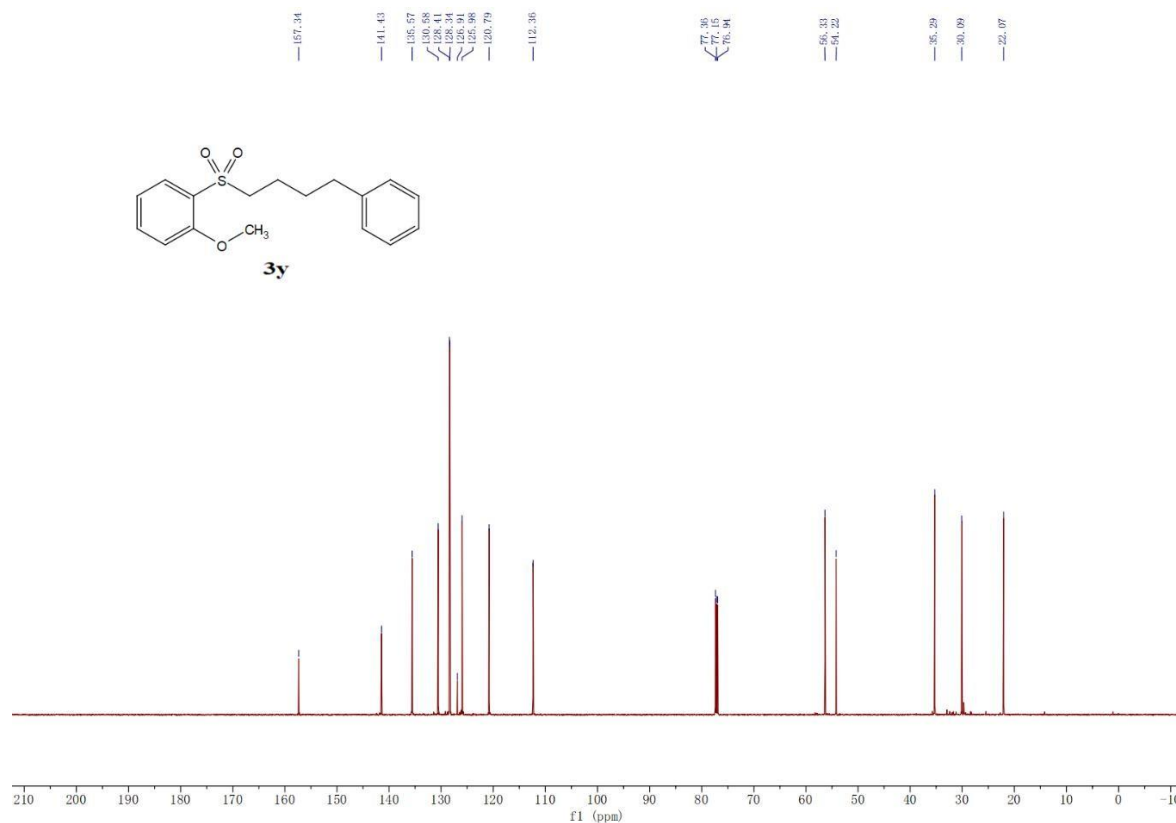
Supplementary Figure 62 ^{13}C NMR (151 MHz, CDCl_3) of 1-chloro-4-((4-phenylbutyl)sulfonyl)benzene (**3x**)



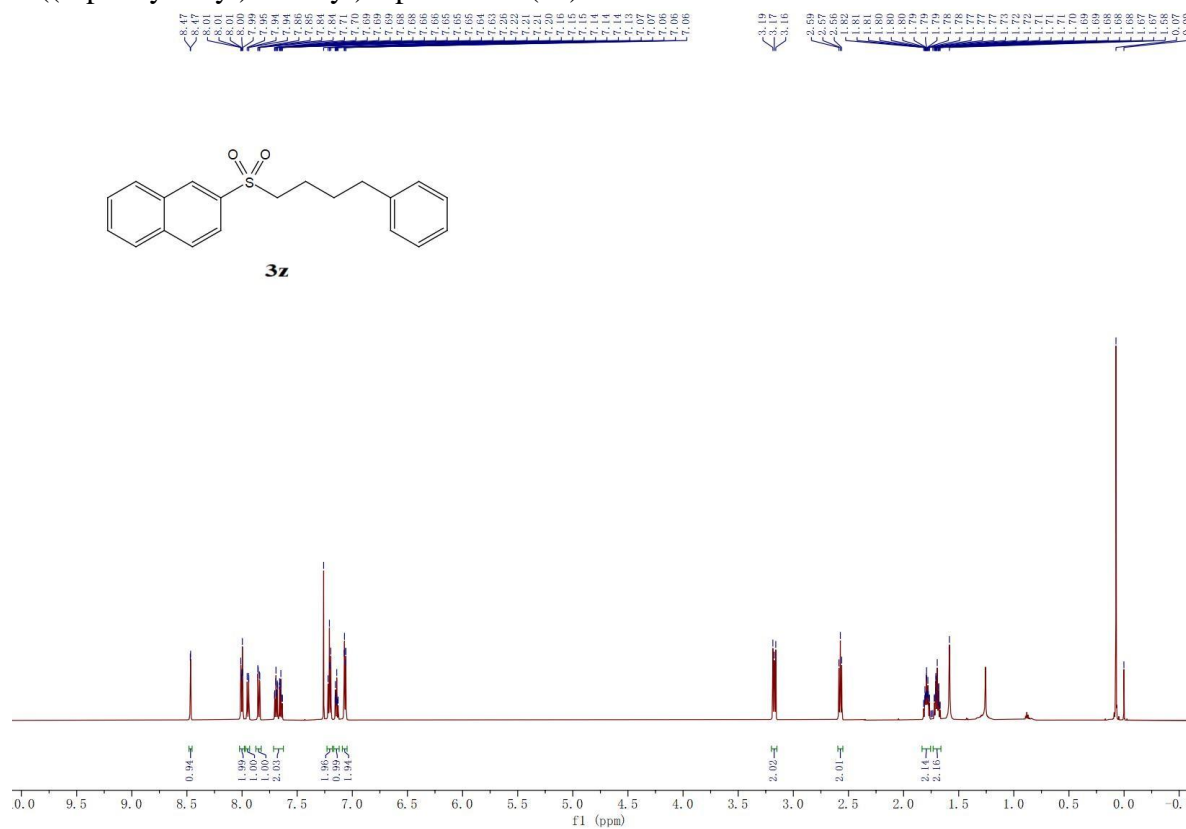
Supplementary Figure 63 ^1H NMR (600 MHz, CDCl_3) of 1-methoxy-2-((4-phenylbutyl)sulfonyl)benzene (**3y**)



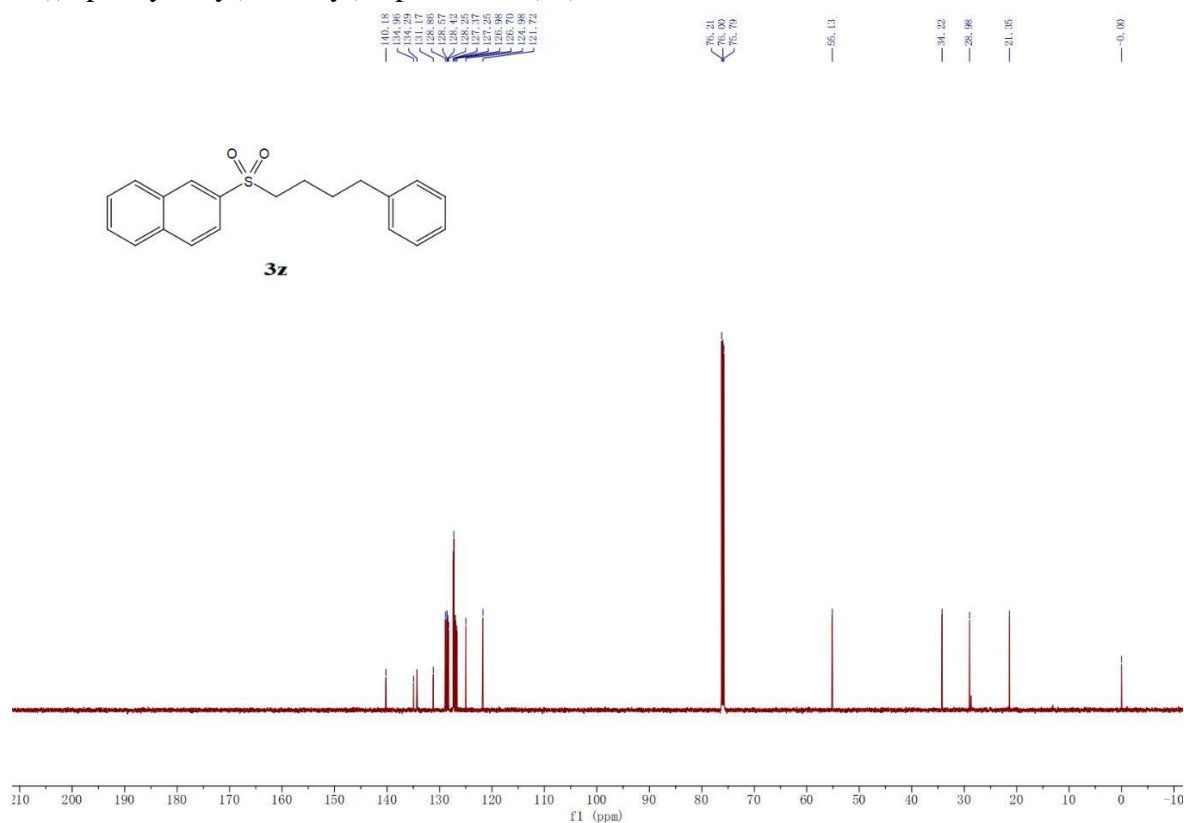
Supplementary Figure 64 ^{13}C NMR (151 MHz, CDCl_3) of 1-methoxy-2-((4-phenylbutyl)sulfonyl)benzene (**3y**)



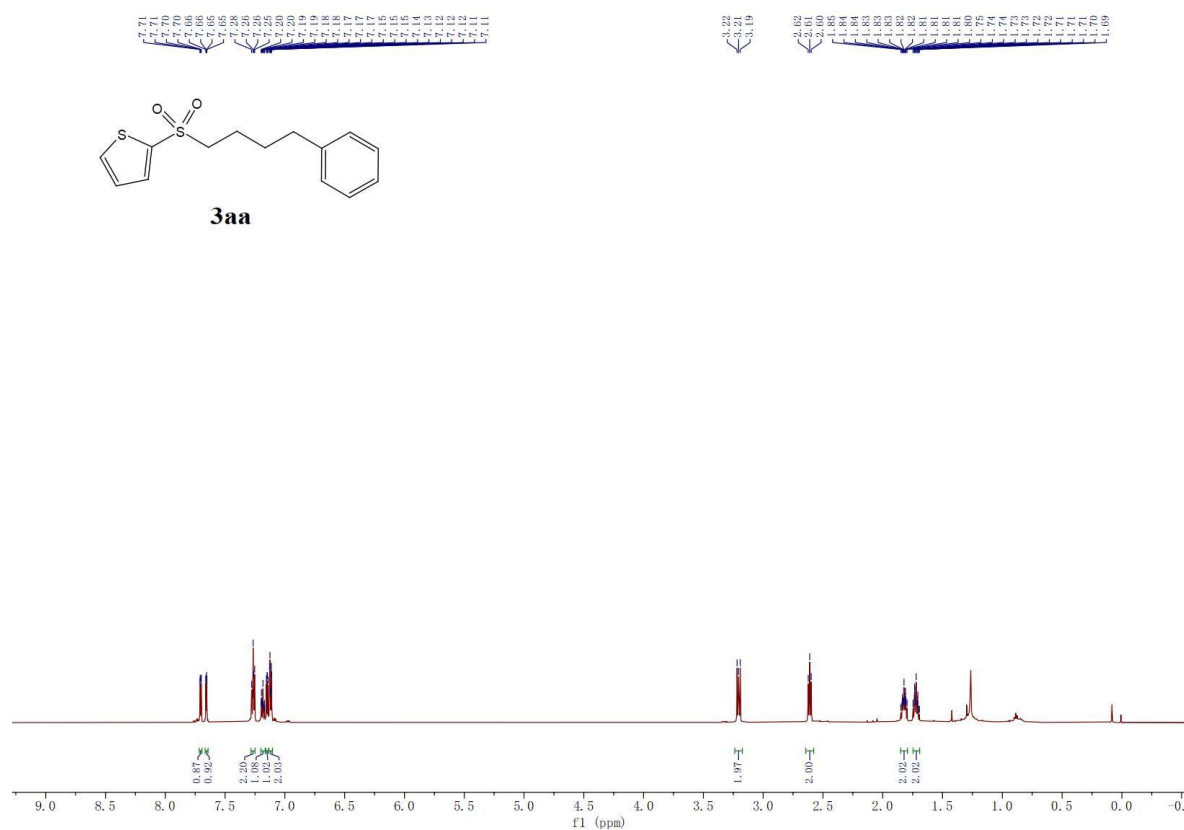
Supplementary Figure 65 ^1H NMR (600 MHz, CDCl_3) of 2-((4-phenylbutyl)sulfonyl)naphthalene (**3z**)



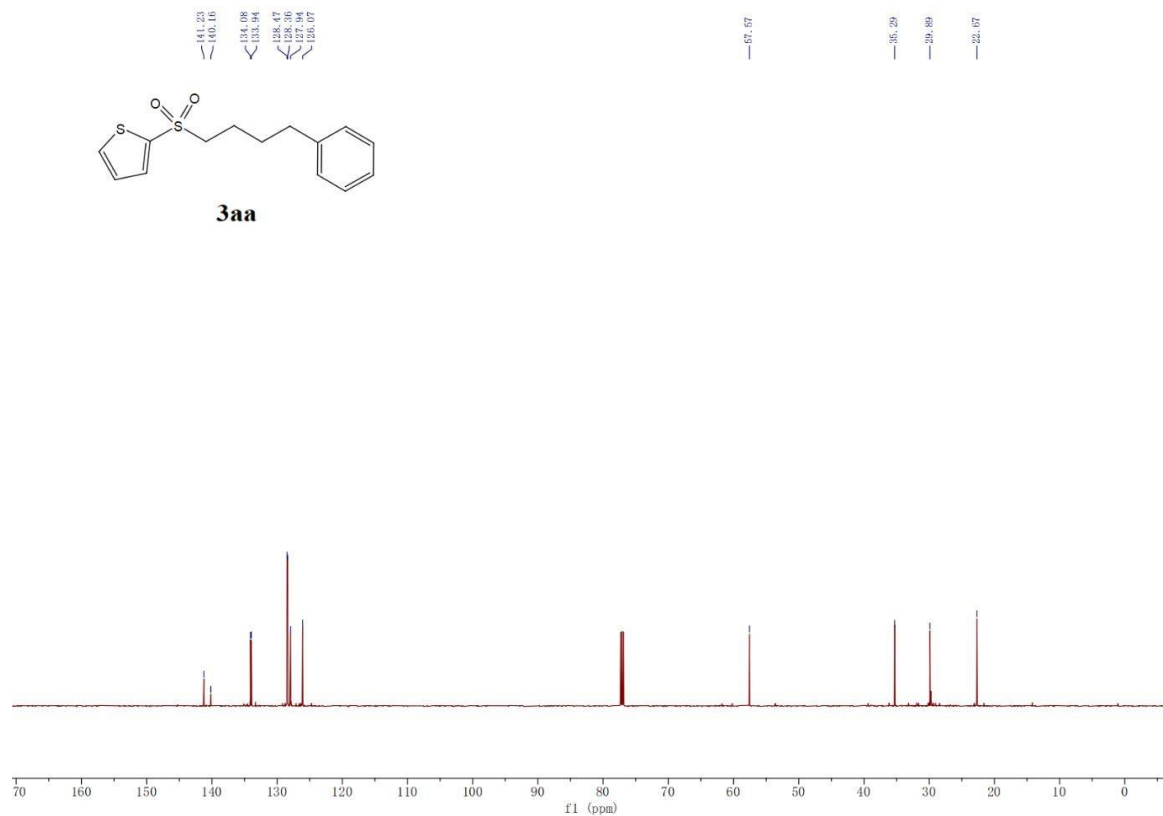
Supplementary Figure 66 ^{13}C NMR (151 MHz, CDCl_3) of 2-((4-phenylbutyl)sulfonyl)naphthalene (**3z**)



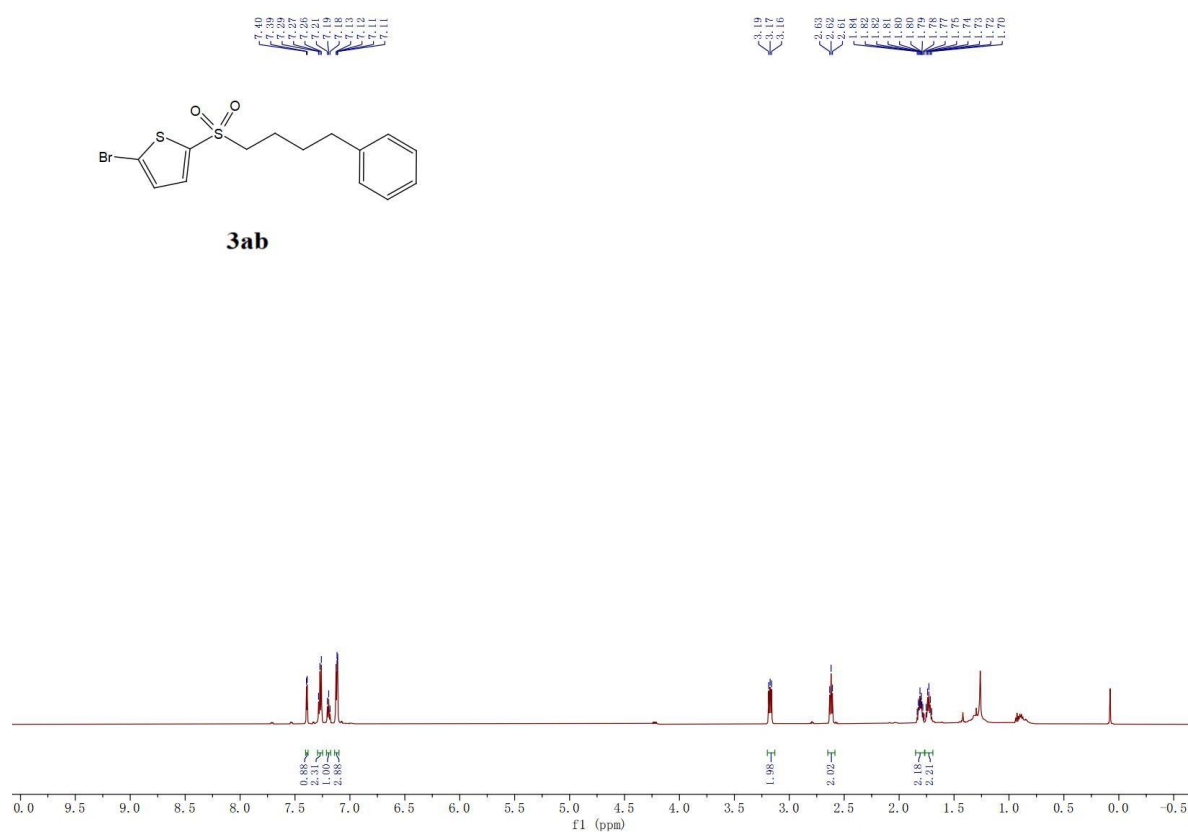
Supplementary Figure 67 ^1H NMR (600 MHz, CDCl_3) of 2-bromo-5-((4-phenylbutyl)sulfonyl)thiophene (**3aa**)



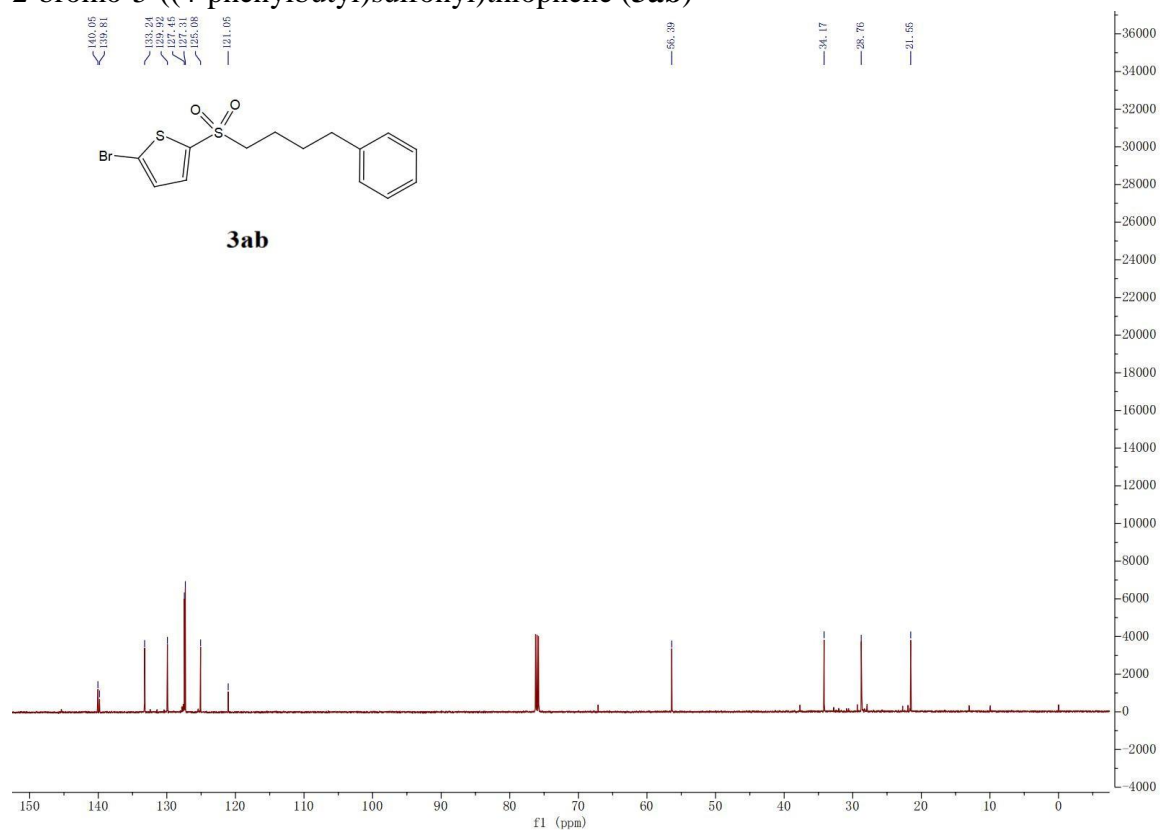
Supplementary Figure 68 ^{13}C NMR (151 MHz, CDCl_3) of 2-((4-phenylbutyl)sulfonyl)thiophene (**3aa**)



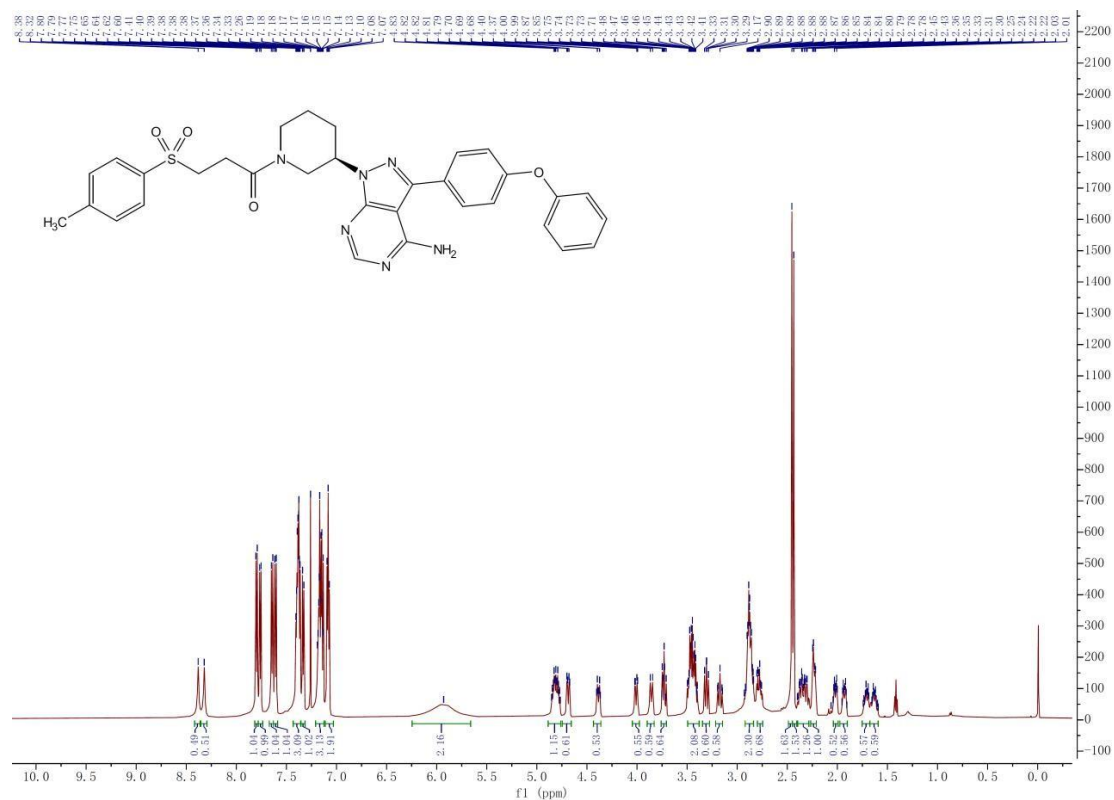
Supplementary Figure 69 ^1H NMR (600 MHz, CDCl_3) of 2-((4-phenylbutyl)sulfonyl)ethene-1,1-diyl)dibenzene (**3ab**)



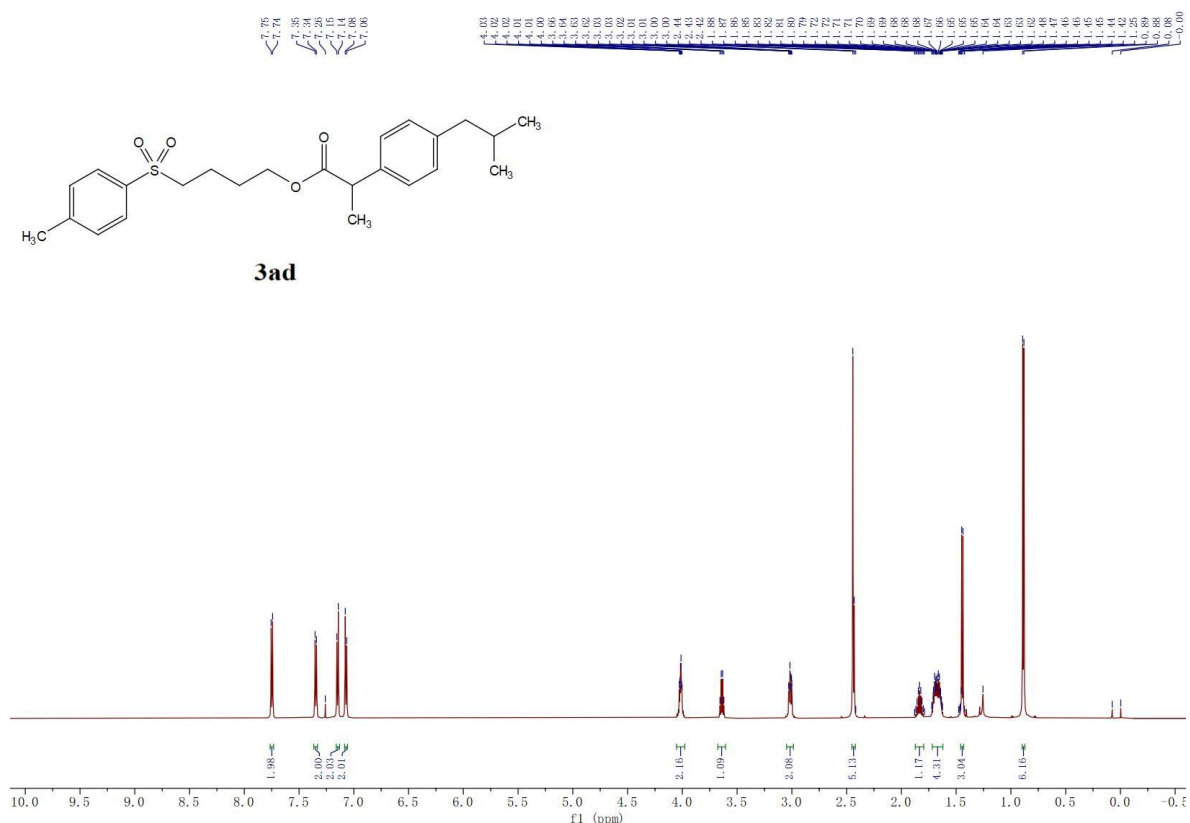
Supplementary Figure 70 ^{13}C NMR (151 MHz, CDCl_3) of 2-bromo-5-((4-phenylbutyl)sulfonyl)thiophene (**3ab**)



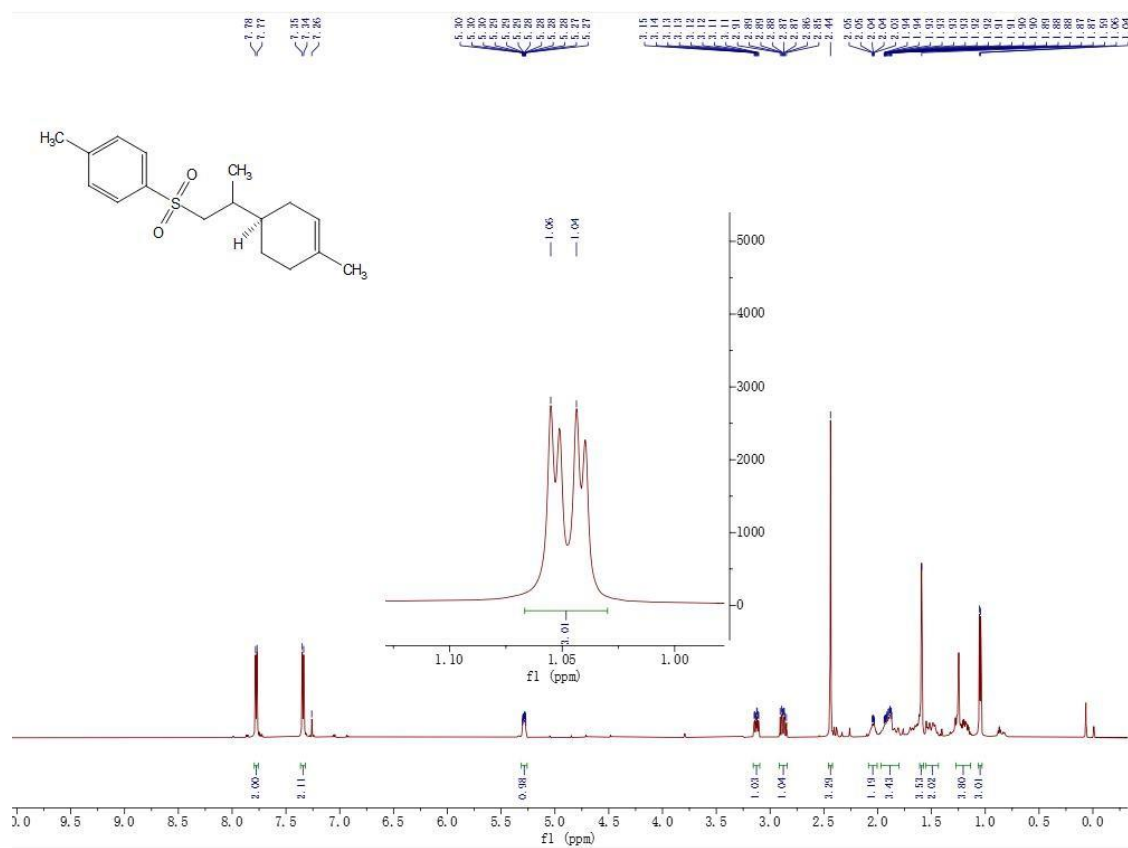
Supplementary Figure 71 ^1H NMR (600 MHz, CDCl_3) of 1-(3-(4-amino-3-(4-phenoxyphenyl)-1H-pyrazolo[3,4-d]pyrimidin-1-yl)piperidin-1-yl)-3-tosylpropan-1-one (**3ac**)



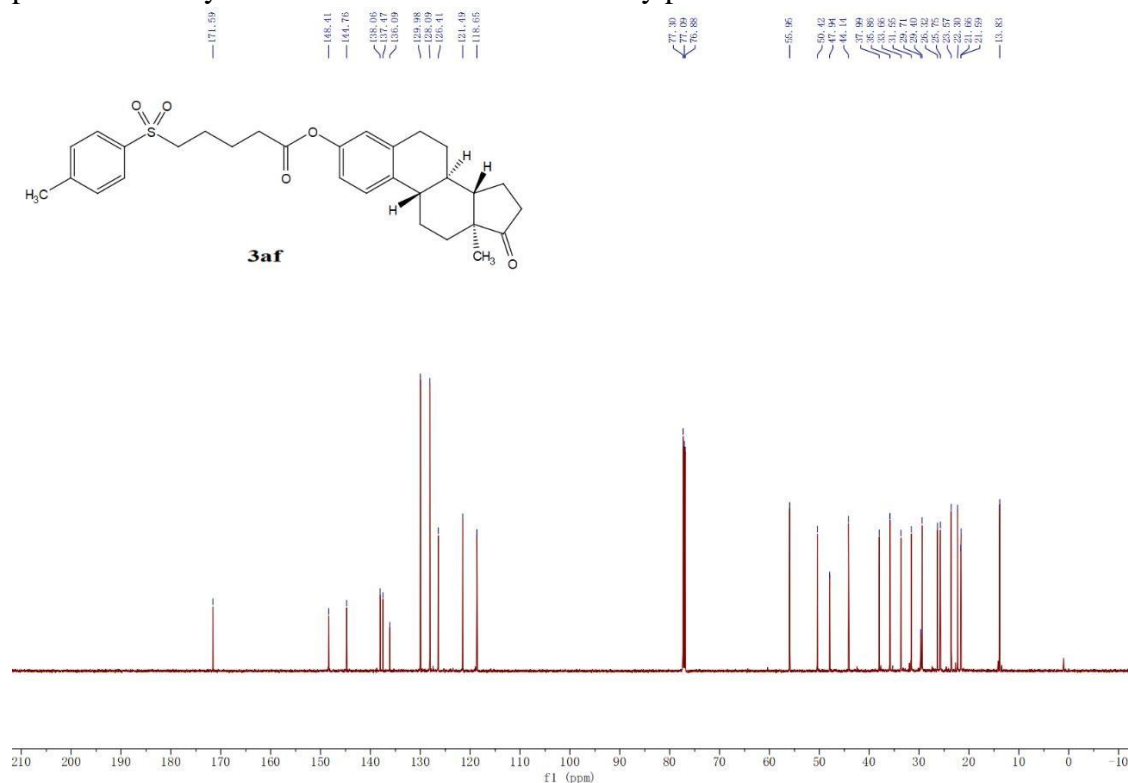
Supplementary Figure 74 ^{13}C NMR (151 MHz, CDCl_3) of 4-tosylbutyl 2-(4-isobutylphenyl)propanoate (**3ad**)



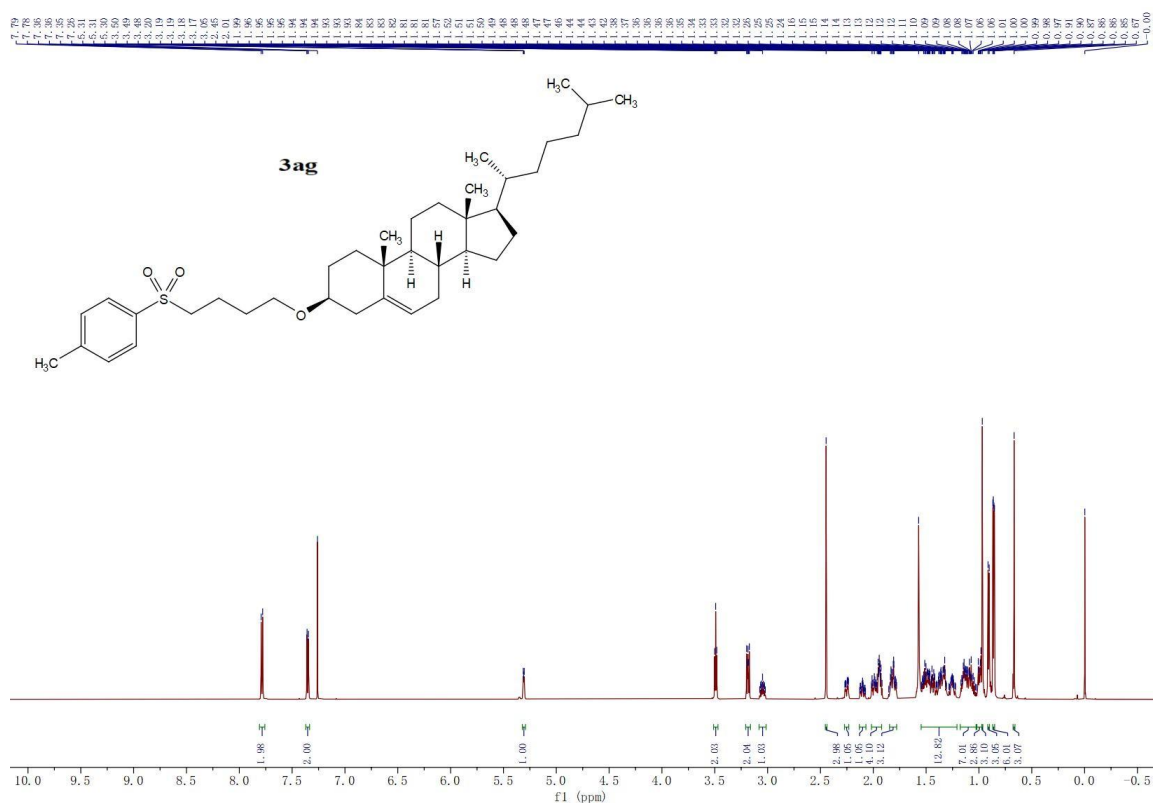
Supplementary Figure 75 ^1H NMR (600 MHz, CDCl_3) of 1-methyl-4-((2-((R)-4-methylcyclohex-3-en-1-yl)propyl)sulfonyl)benzene (**3ae**)



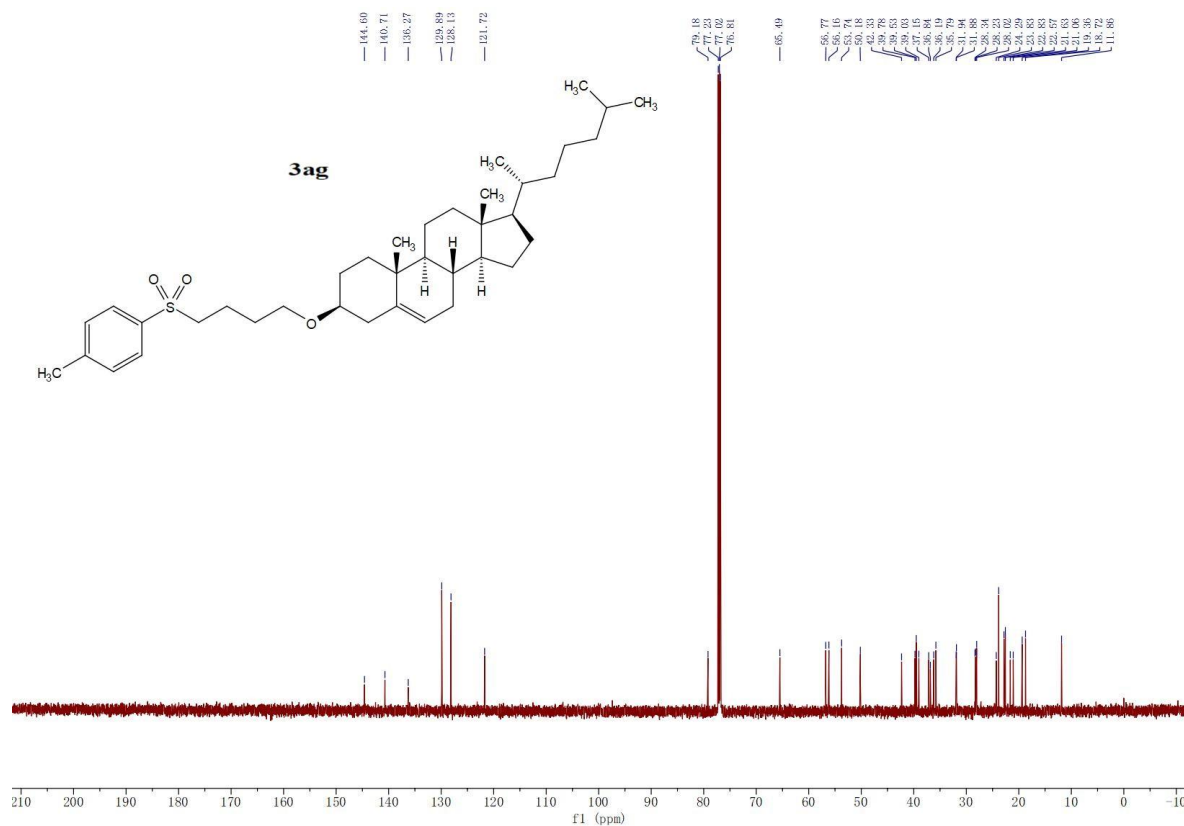
Supplementary Figure 78 ^{13}C NMR (151 MHz, CDCl_3) of (8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 5-tosylpentanoate (**3af**)



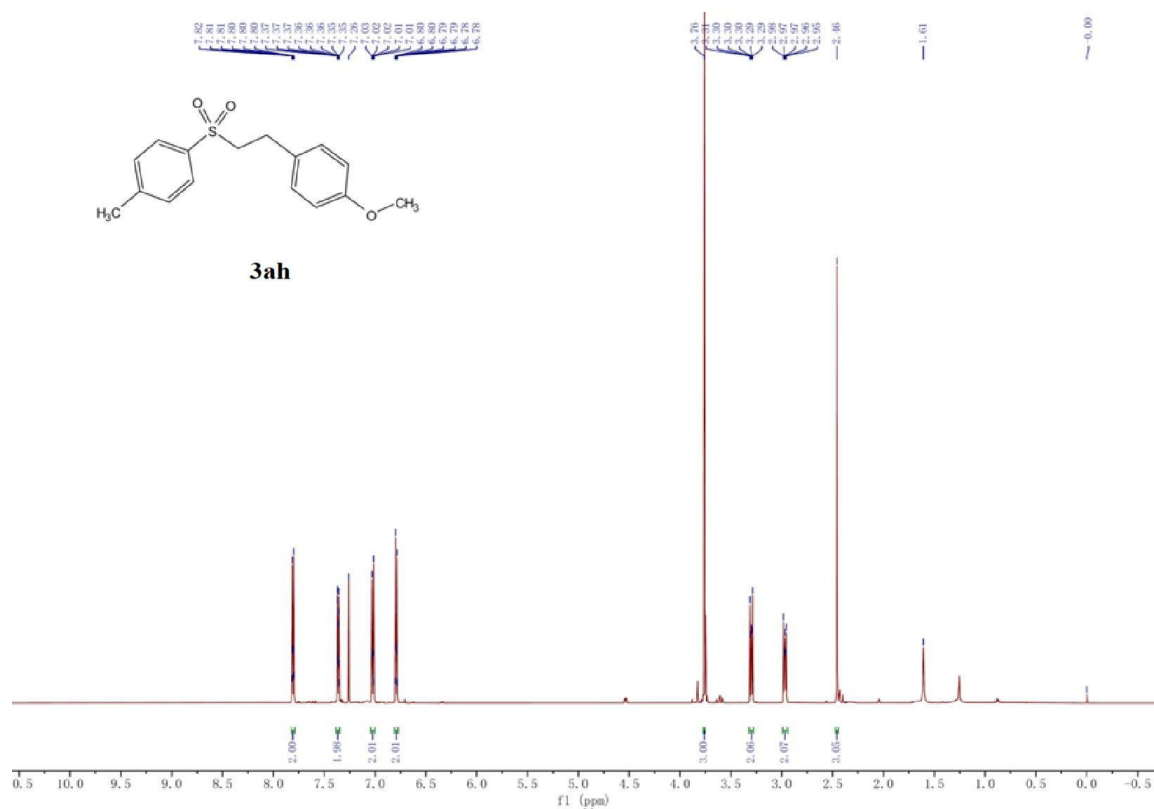
Supplementary Figure 79 ^1H NMR (600 MHz, CDCl_3) of (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-3-(4-tosylbutoxy)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene (**3ag**)



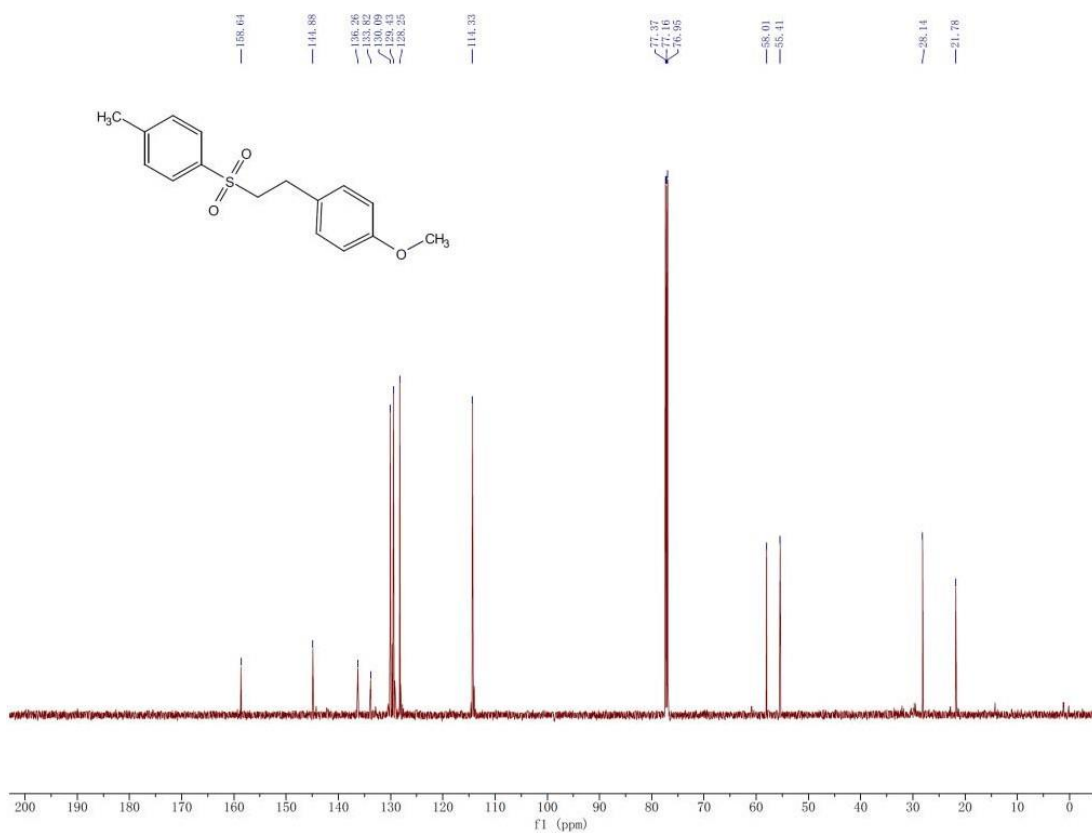
Supplementary Figure 80 ^{13}C NMR (151 MHz, CDCl_3) of (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-3-(4-tosylbutoxy)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene (**3ad**)



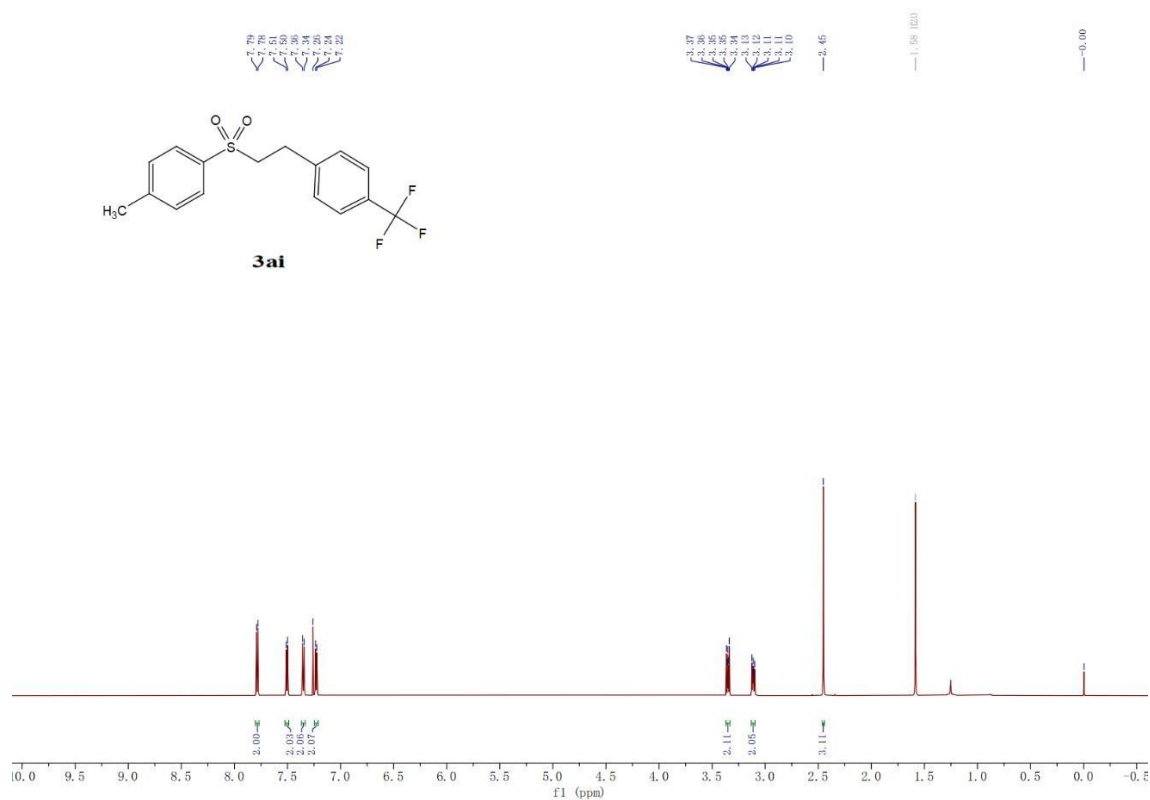
Supplementary Figure 81 ^1H NMR (600 MHz, CDCl_3) of 1-methoxy-4-(2-tosylethyl)benzene (**3ah**)



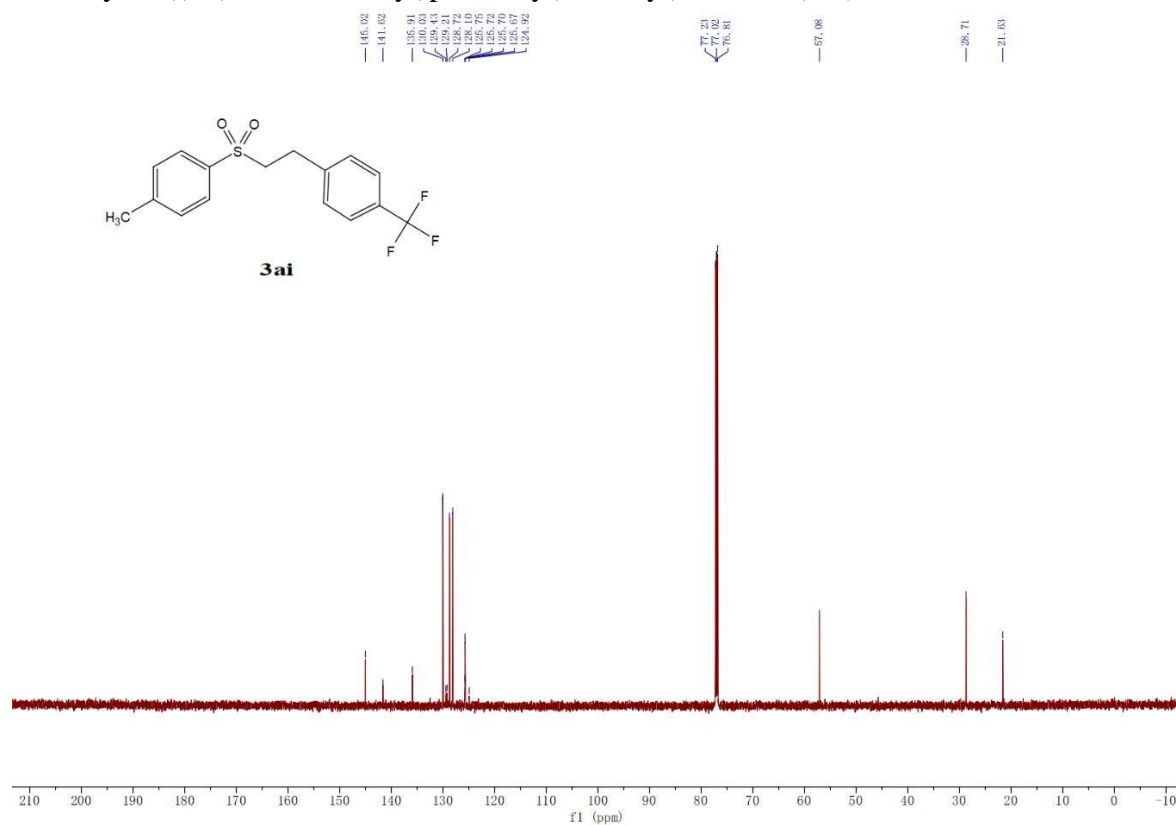
Supplementary Figure 82 ^{13}C NMR (151 MHz, CDCl_3) of 1-methoxy-4-(2-tosylethyl)benzene (**3ah**)



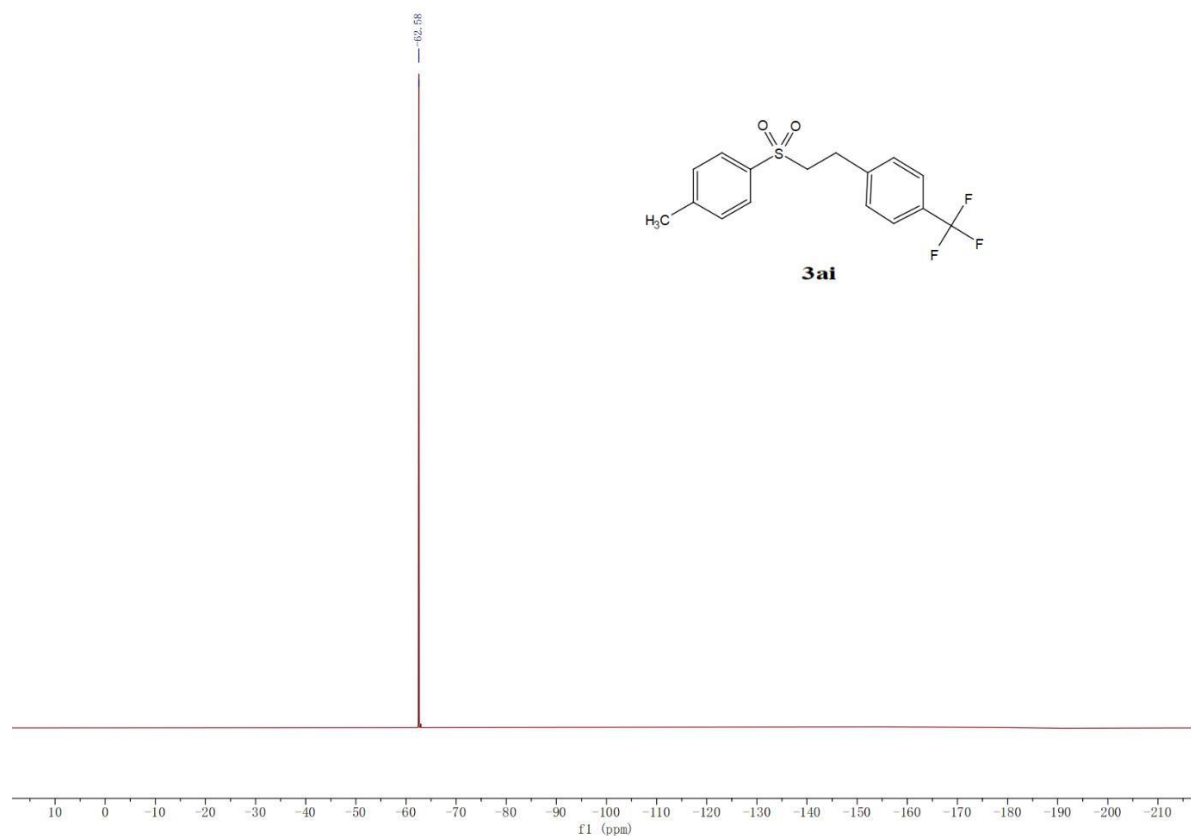
Supplementary Figure 83 ^1H NMR (600 MHz, CDCl_3) of 1-methyl-4-((4-(trifluoromethyl)phenethyl)sulfonyl)benzene (**3ai**)



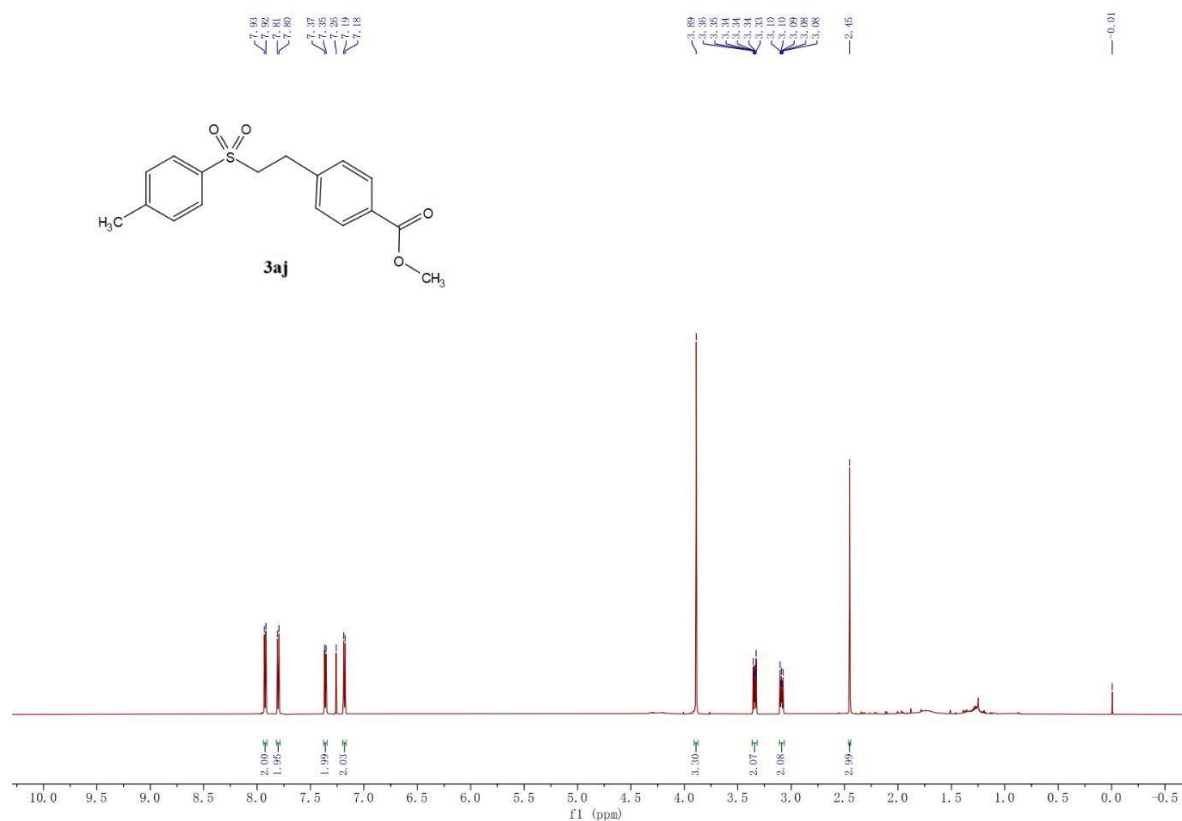
Supplementary Figure 84 ^{13}C NMR (151 MHz, CDCl_3) of 1-methyl-4-((4-(trifluoromethyl)phenethyl)sulfonyl)benzene (**3ai**)



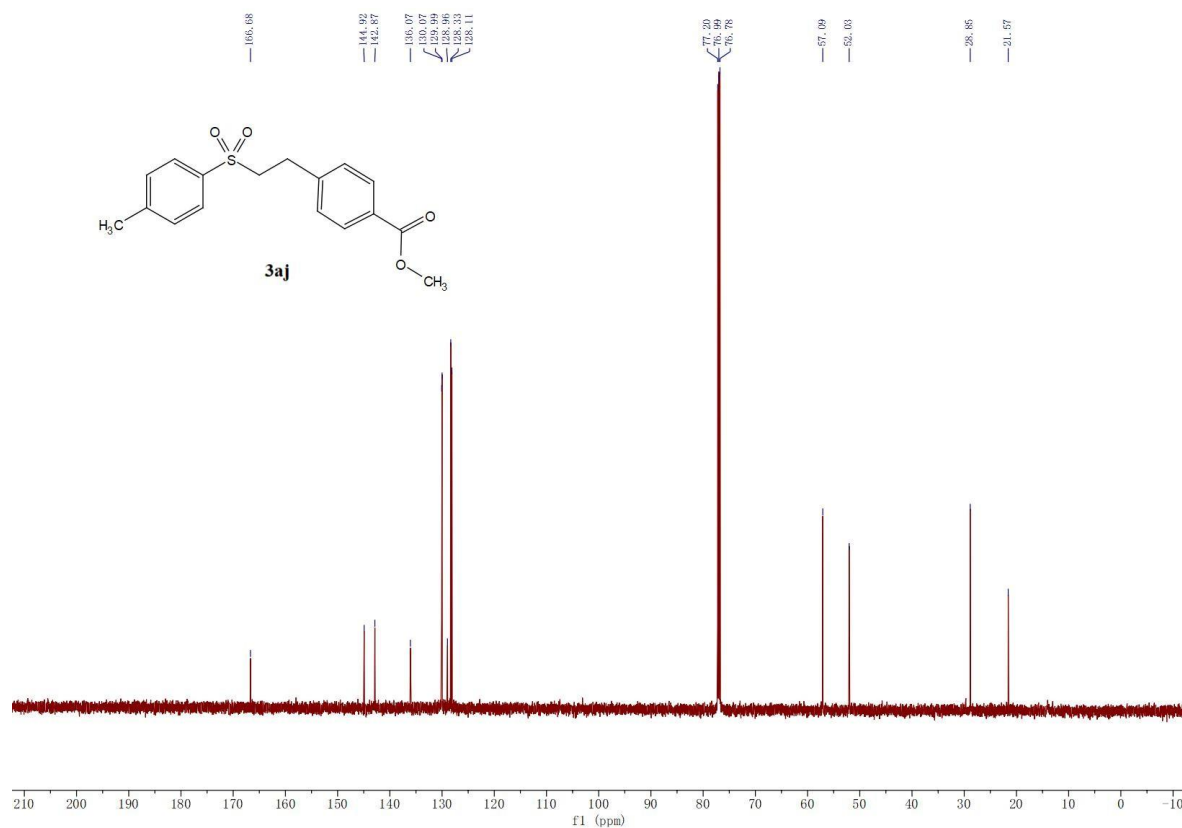
Supplementary Figure 85 ^{19}F NMR (565 MHz, CDCl_3) of 1-methyl-4-((4-(trifluoromethyl)phenethyl)sulfonyl)benzene (**3ai**)



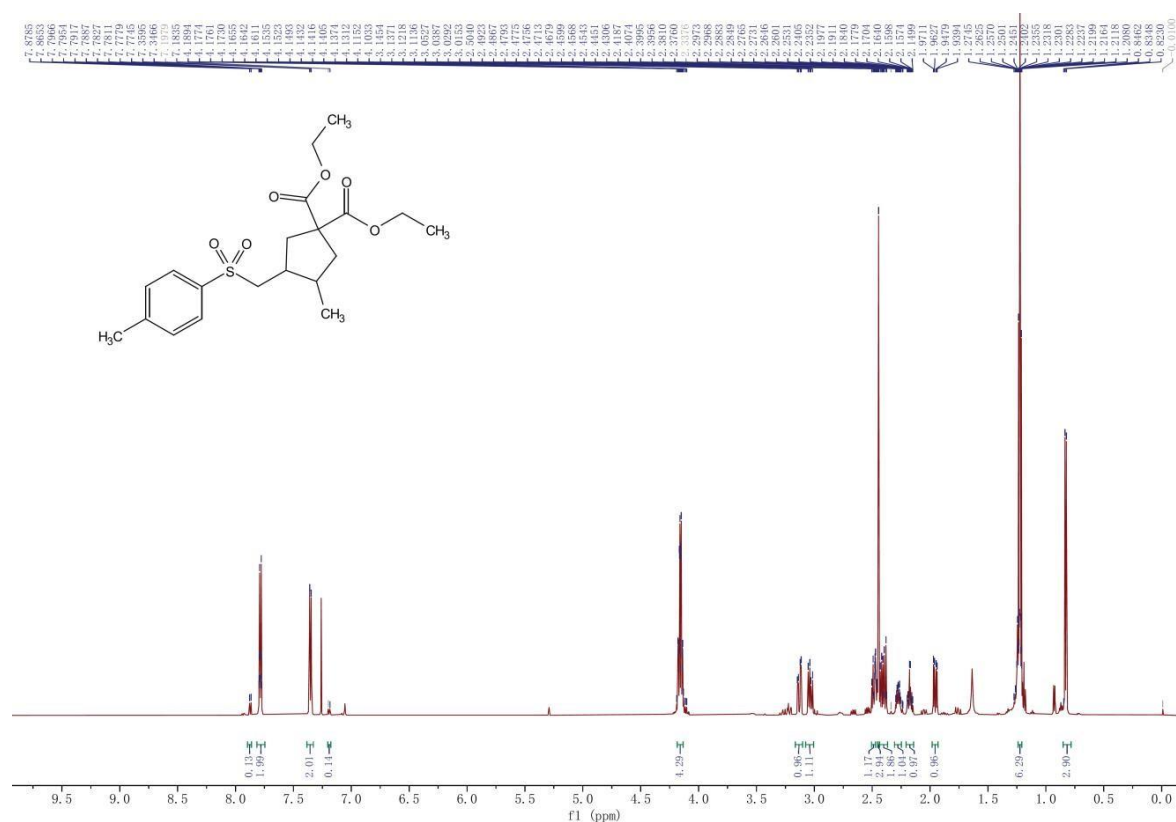
Supplementary Figure 86 ^1H NMR (600 MHz, CDCl_3) of methyl 4-(2-tosylethyl)benzoate (**3aj**)



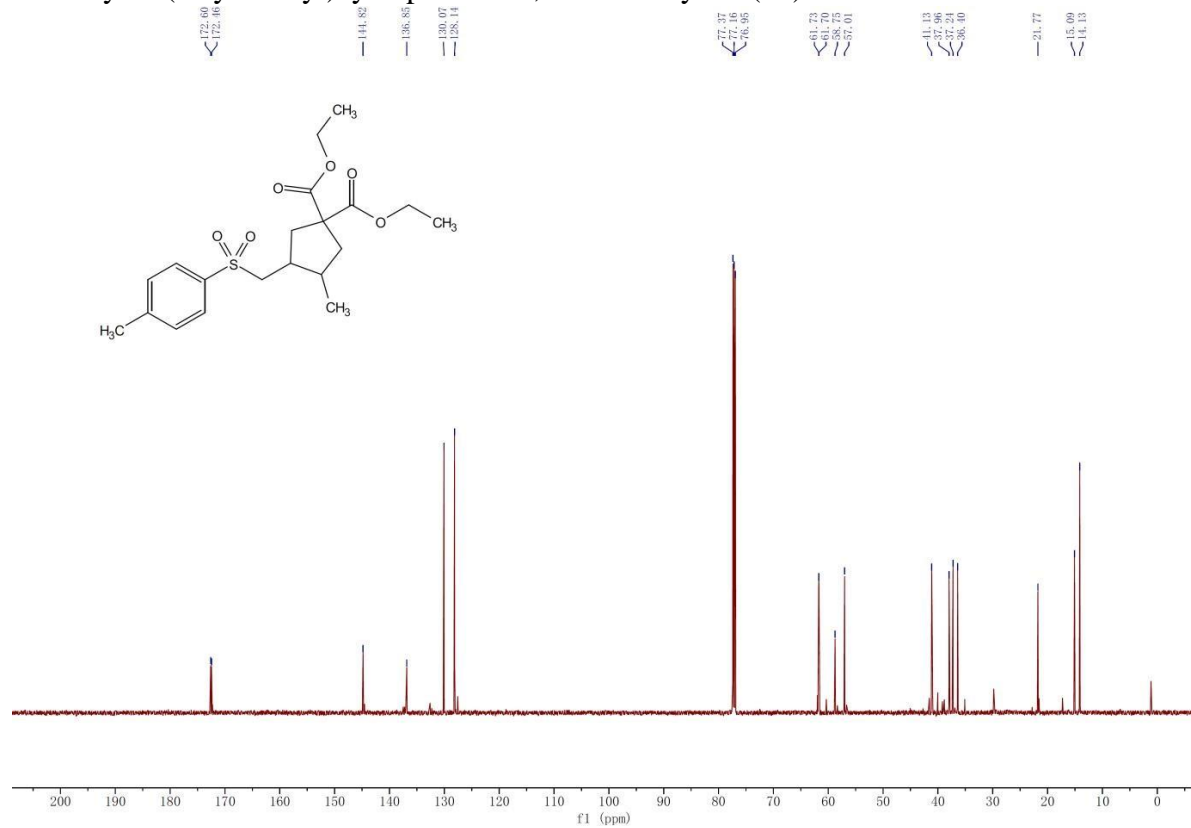
Supplementary Figure 87 ^{13}C NMR (151 MHz, CDCl_3) of methyl 4-(2-tosylethyl)benzoate (**3aj**)



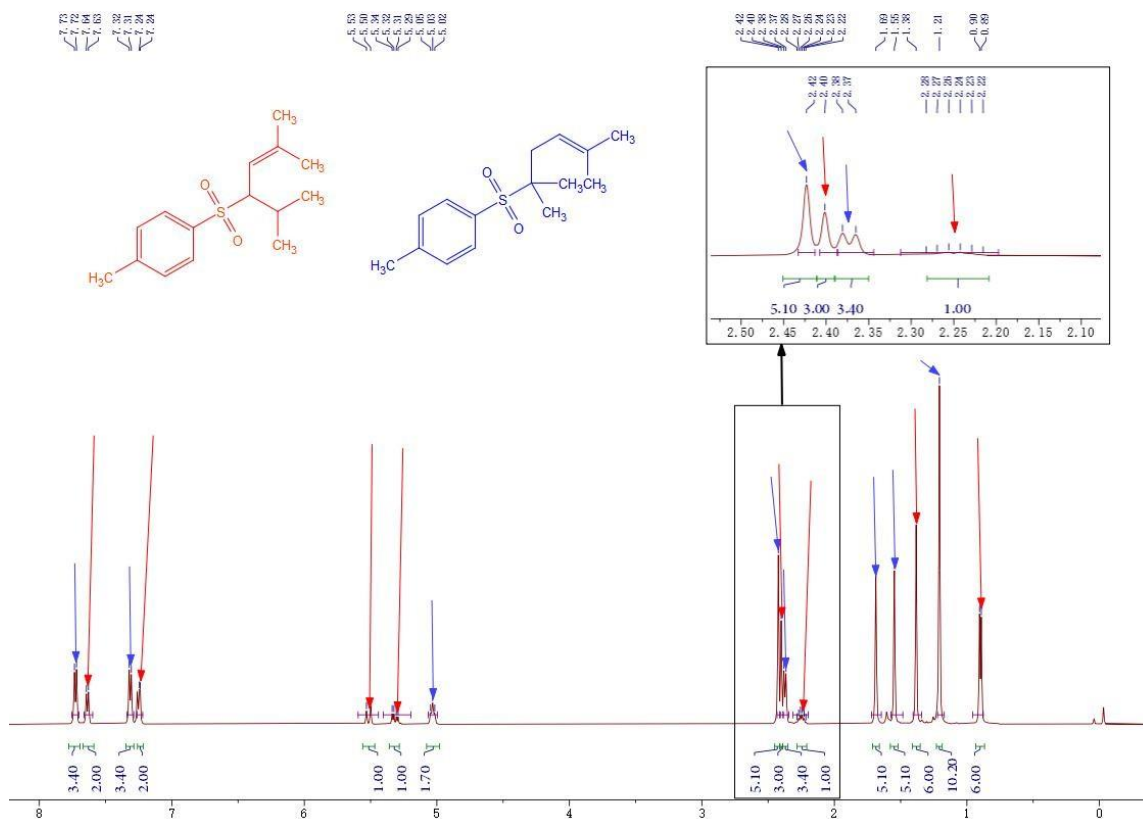
Supplementary Figure 88 ^1H NMR (600 MHz, CDCl_3) of diethyl 3-methyl-4-(tosylmethyl)cyclopentane-1,1-dicarboxylate (**5a**)



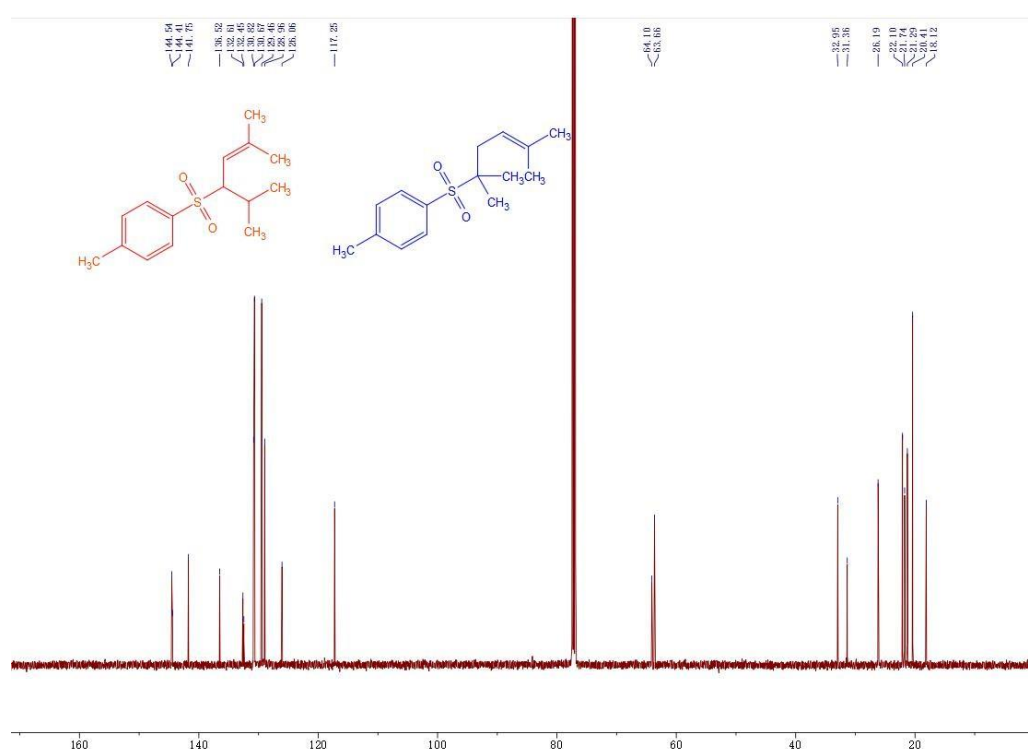
Supplementary Figure 89 ^{13}C NMR (151 MHz, CDCl_3) of diethyl 3-methyl-4-(tosylmethyl)cyclopentane-1,1-dicarboxylate (**5a**)



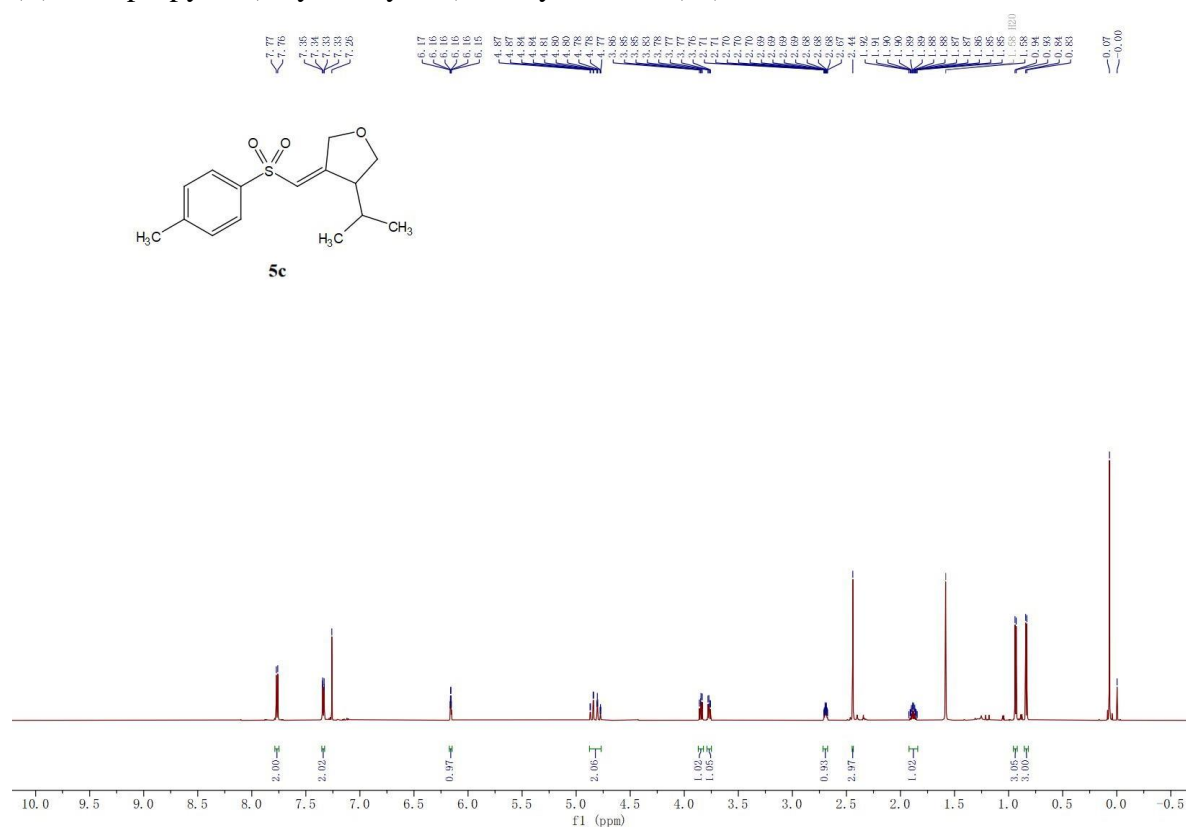
Supplementary Figure 90 ^1H NMR (600 MHz, CDCl_3) of
 1-((2,5-dimethylhex-4-en-2-yl)sulfonyl)-4-methylbenzene
 &
 1-((2,5-dimethylhex-4-en-3-yl)sulfonyl)-4-methylbenzene (**5b**)



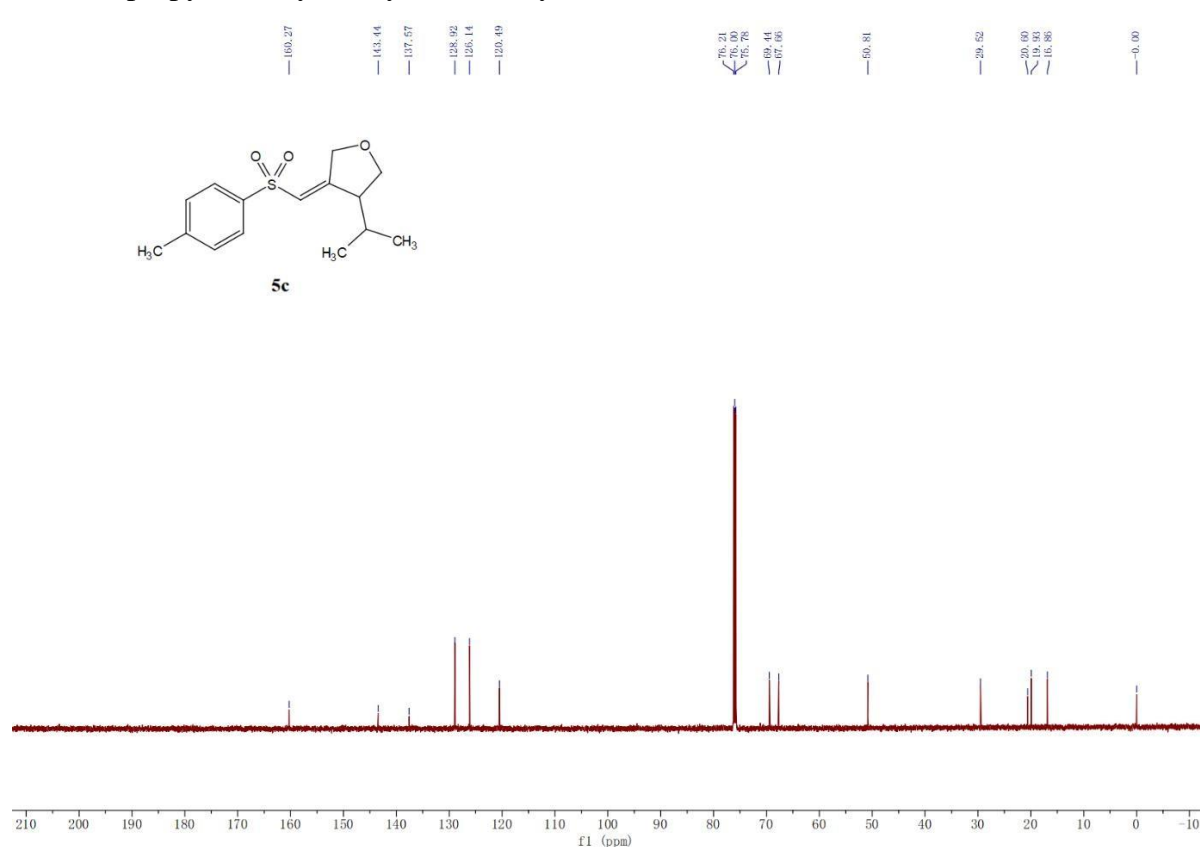
Supplementary Figure 91 ^{13}C NMR (151 MHz, CDCl_3) of
 1-((2,5-dimethylhex-4-en-2-yl)sulfonyl)-4-methylbenzene
 &
 1-((2,5-dimethylhex-4-en-3-yl)sulfonyl)-4-methylbenzene (**5b**)



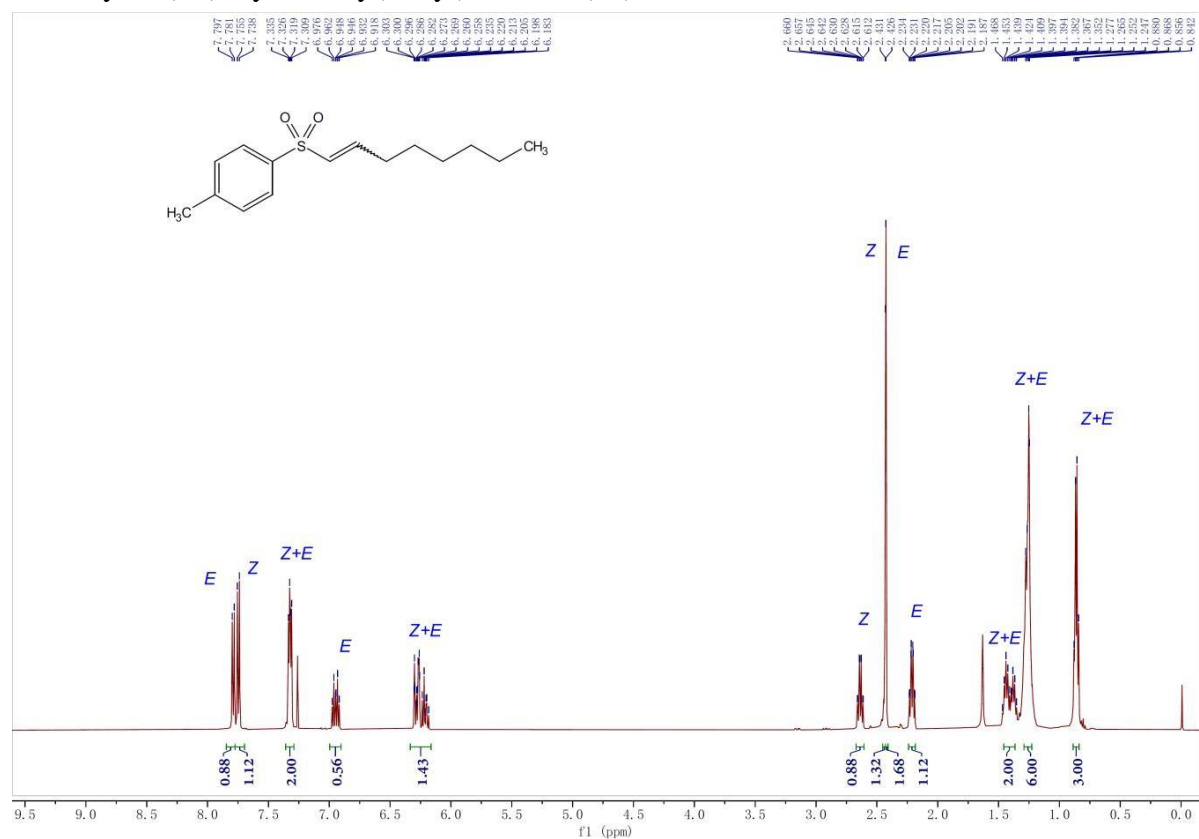
Supplementary Figure 92 ^1H NMR (600 MHz, CDCl_3) of (Z)-3-isopropyl-4-(tosylmethylene)tetrahydrofuran (**5c**)



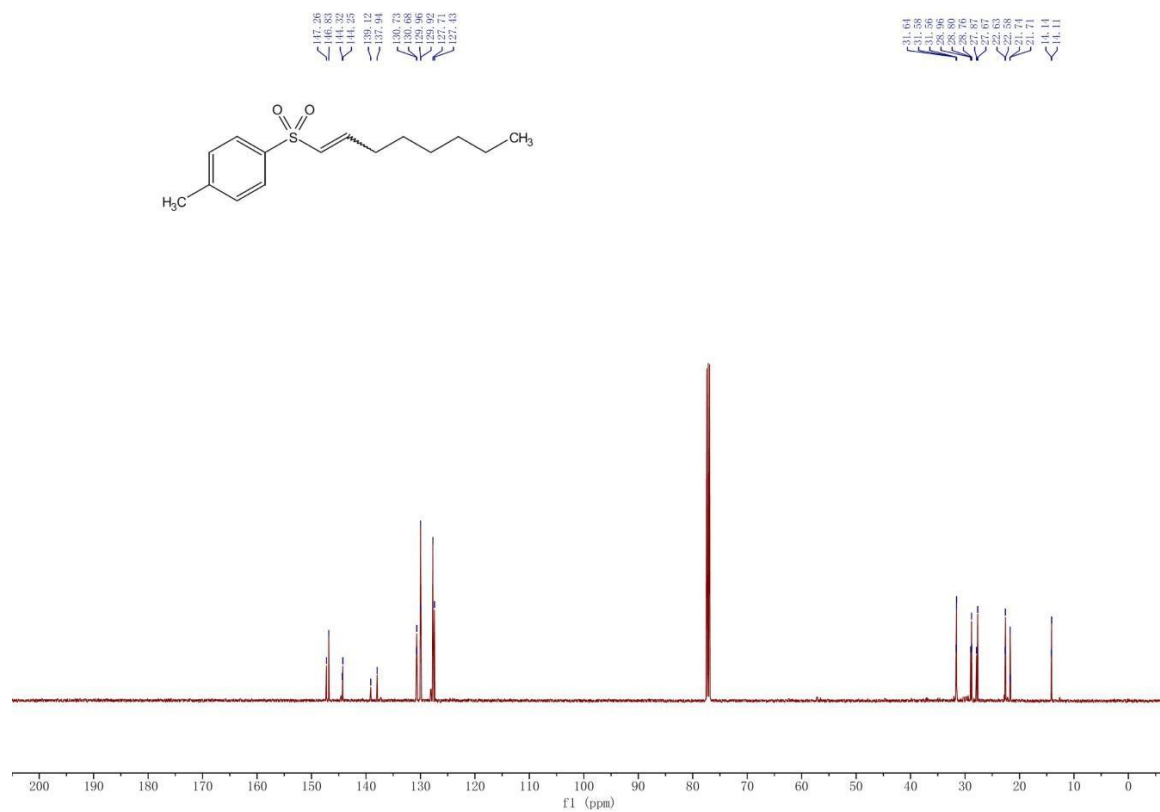
Supplementary Figure 93 ^{13}C NMR (151 MHz, CDCl_3) of (Z)-3-isopropyl-4-(tosylmethylene)tetrahydrofuran (**5c**)



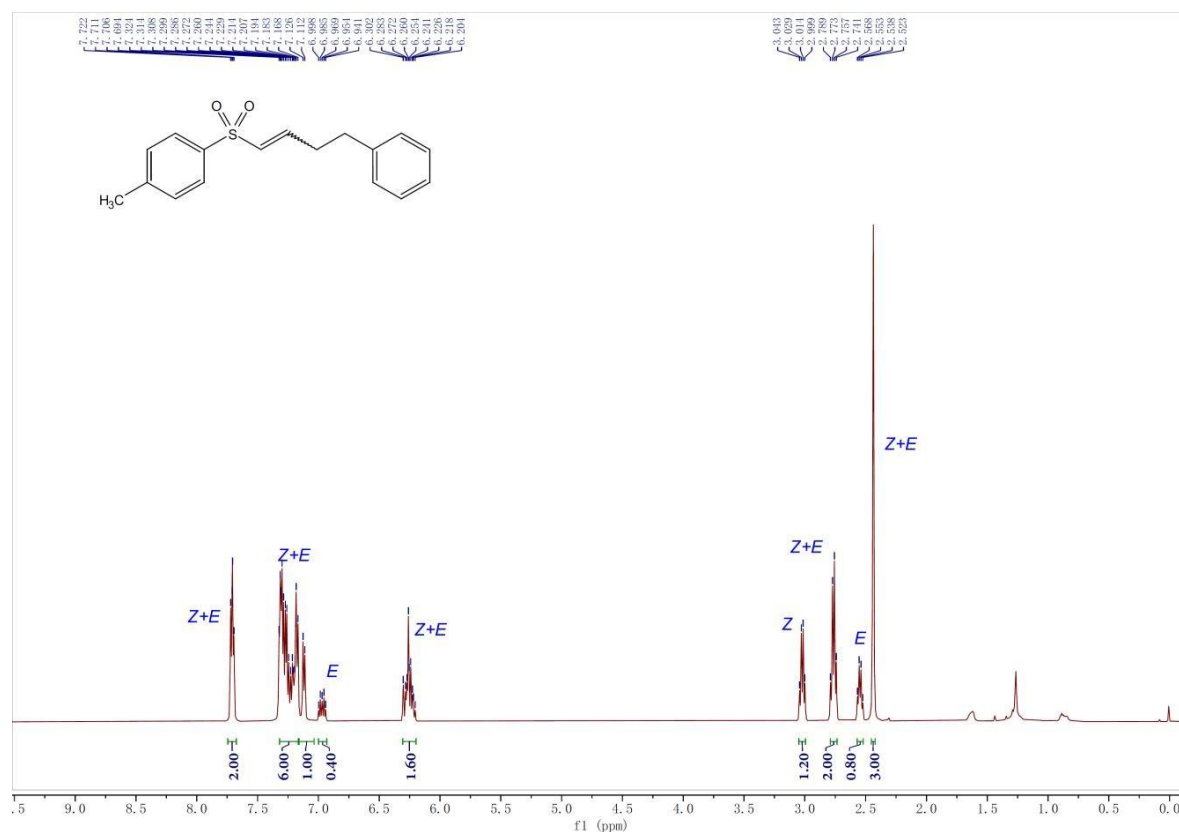
Supplementary Figure 94 ^1H NMR (500 MHz, CDCl_3) of 1-methyl-4-(2-(octylsulfonyl)vinyl)benzene (**7a**)



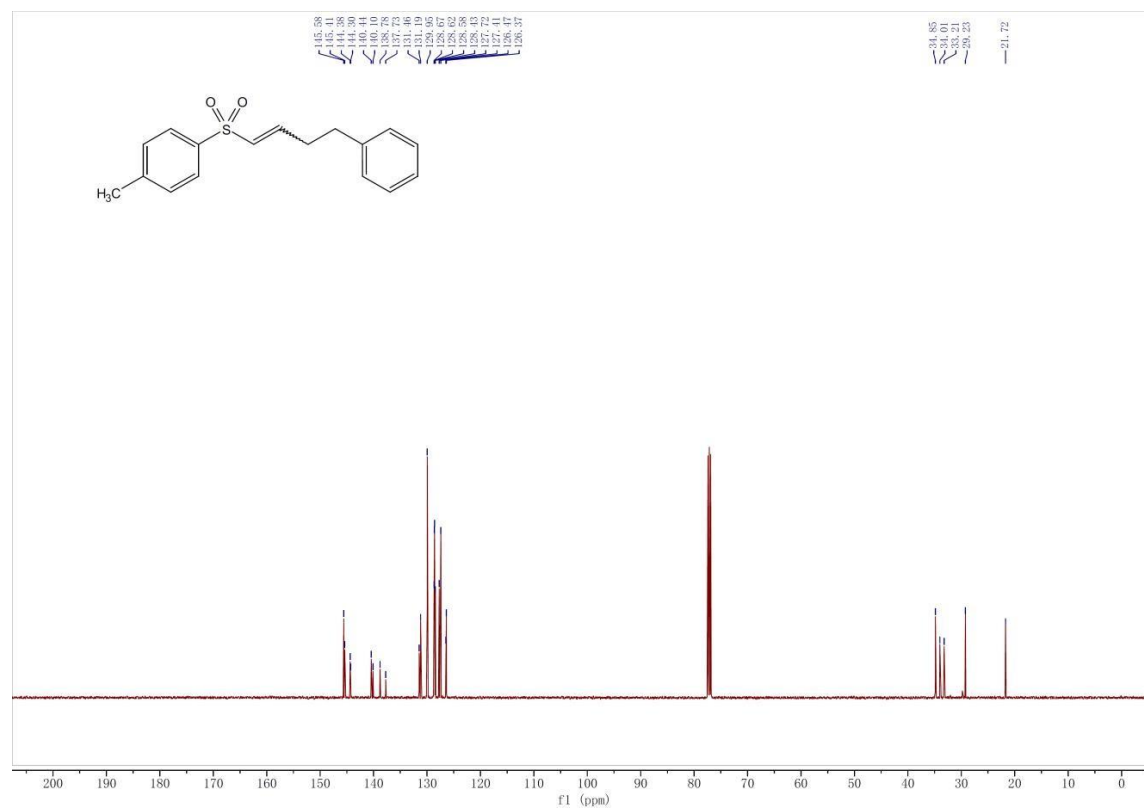
Supplementary Figure 95 ^{13}C NMR (126 MHz, CDCl_3) of 1-methyl-4-(2-(octylsulfonyl)vinyl)benzene (**7a**)



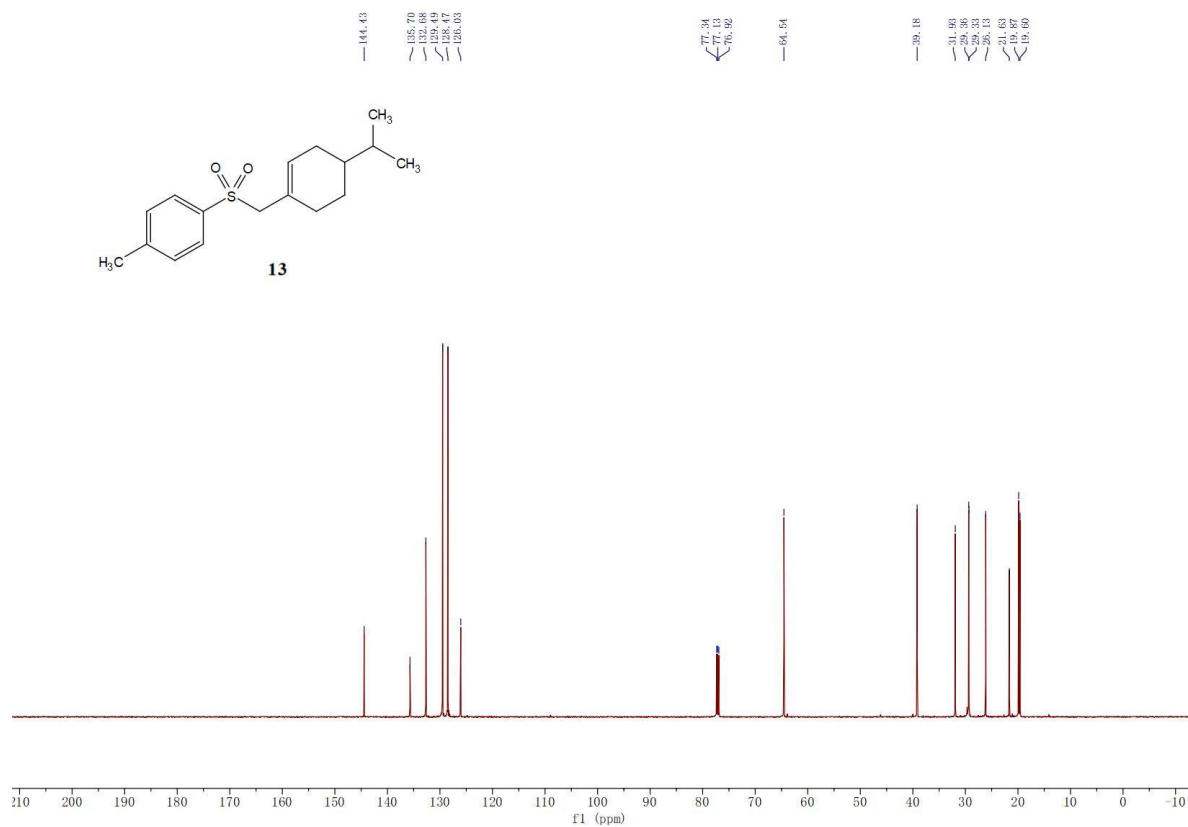
Supplementary Figure 96 ^1H NMR (500 MHz, CDCl_3) of 1-methyl-4-((4-phenylbut-1-en-1-yl)sulfonyl)benzene (**7b**)



Supplementary Figure 97 ^{13}C NMR (126 MHz, CDCl_3) of 1-methyl-4-((4-phenylbut-1-en-1-yl)sulfonyl)benzene (**7b**)



Supplementary Figure 102 ^{13}C NMR (151 MHz, CDCl_3) of 1-(((4-isopropylcyclohex-1-en-1-yl)methyl)sulfonyl)-4-methylbenzene (**13**)



Supplementary References

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