SUPPORTING INFORMATION

Dioxygen Concentration-Dependent Selective Hydroxysulfonylation of Olefins by Rose Bengal-Sensitized Photocatalysis

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1. General aspects

All the chemicals were used as received from commercial sources without any further purification. For the synthesis, solvents were distilled and dried, whenever necessary prior to use. Silica gel (100–200 m mesh) column chromatography was conducted to purify the compounds. ^{1}H and ^{13}C NMR spectra were recorded using 400 and 500 MHz NMR spectrometers. High-resolution mass spectra (HRMS) were recorded using an ESI-QTOF mass spectrometer. All reactions were performed using oven-dried glassware and reaction vials.

2. Reaction setup

Typically, the reactions were carried out by irradiating the reaction mixtures contained in glass vials fitted with O_2 balloon with blue radiation from the light source (Kessil® PR160-440 nm lamp) with 100% intensity. An ambient temperature was maintained during the photoirradiation with a connected compact fan. The approximate distance between the glass vial and the LED lamp source was 4 cm.

3. KI/Starch test for the detection of hydrogen peroxide (H_2O_2) in the reaction

To establish the formation of H_2O_2 as the by-product of hydroxysulfonylation reactions, KI/starch test was performed as follows. The reaction mixture containing **1a** (0.25 mmol), **2a** (0.50 mmol), and Rose Bengal (2 mol%) in 1 mL of EtOH was irradiated under O_2 atmosphere with Blue-LED light for 4 h. Subsequently, the solution of potassium iodide (KI) was added to the reaction mixture followed by starch. The colour of the resulting solution was found to turn light-brown instantaneously.

Solution A: The reaction mixture after 4 h of irradiation with Blue-LED light (λ = 440 nm).

Solution B: Observed brown coloration after the addition of the solutions of KI and starch to solution A.

4. Absorption spectra of rose bengal and methylene blue and emission spectra of blue-LED

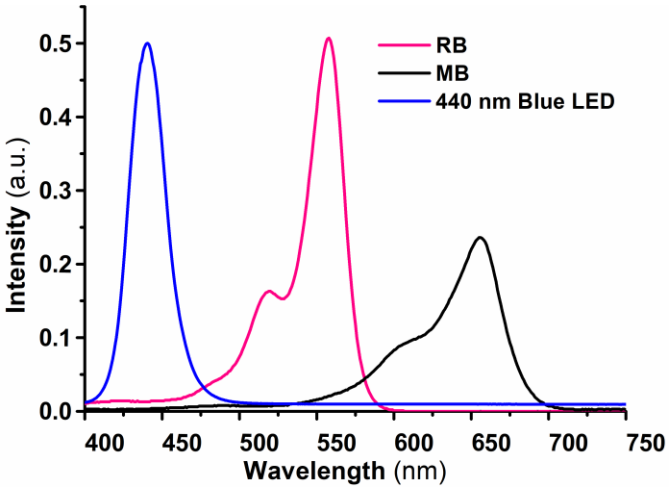


Fig. S1. UV−vis spectra of rose bengal (6 μM) and methylene blue (6 μM) at 25 °C in EtOH and 440 nm blue-LED emission spectrum.

5. ^{1}H NMR monitoring studies

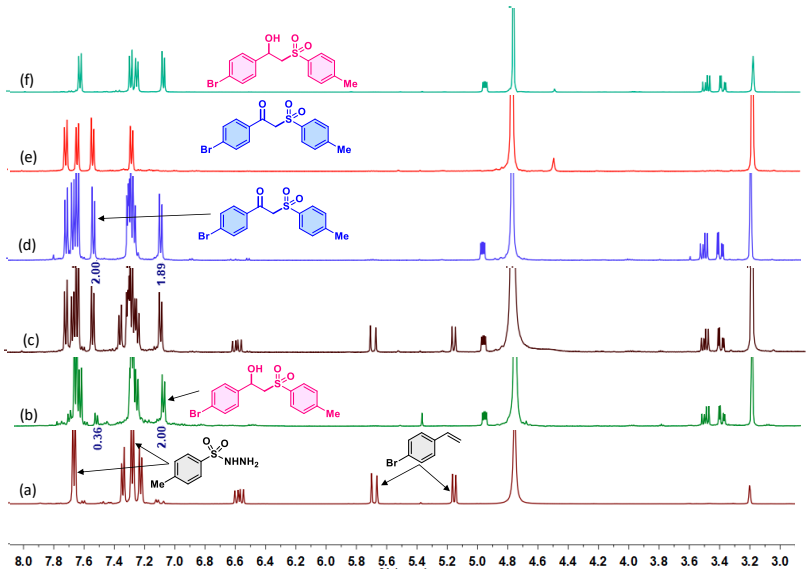


Fig. S2. ^{1}H NMR spectroscopic monitoring of the reaction of 4-bromostyrene (**1F**) and *p*-toluenesulfonyl hydrazide (**2b**) in 1 mL of CD_3OD under 45 W Blue LED irradiation: (a) at 0 h, (b) after 4 h under O_2, (c) after 10 h under air and (d) after 24 h under air. (e) ^{1}H NMR of **4Fb** in CD_3OD. (f) ^{1}H NMR spectrum of **3Fb** in CD_3OD.

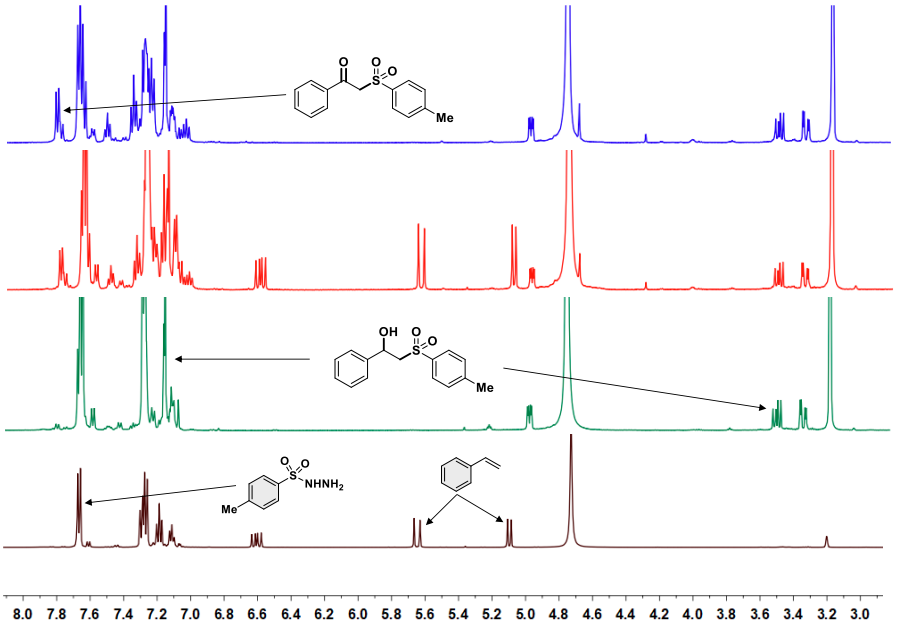


Fig. S3. ^{1}H NMR spectroscopic monitoring of the reaction of styrene (**1A**) and *p*-toluenesulfonyl hydrazide (**2b**) in 1 mL of CD_3OD under 45 W Blue LED irradiation: (a) at 0 h, (b) after 4 h under O_2, (c) after 10 h under air and (d) after 24 h under air.

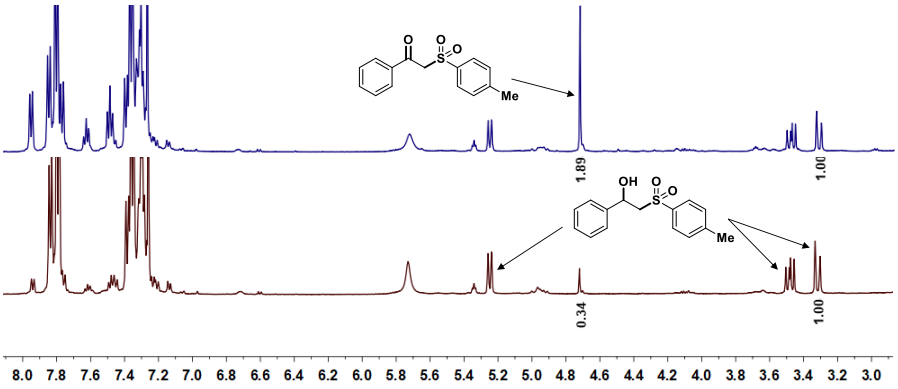


Fig. S4. ^{1}H NMR of the reaction mixture of the reaction of styrene (**1A**) and *p*-toluenesulfonyl hydrazide (**2b**) in 1 mL of CD_3OD under 45 W blue LED irradiation: (a) under air after 24 h in $CDCl_3$ and (b) under O_2 atmosphere after 4 h in $CDCl_3$.

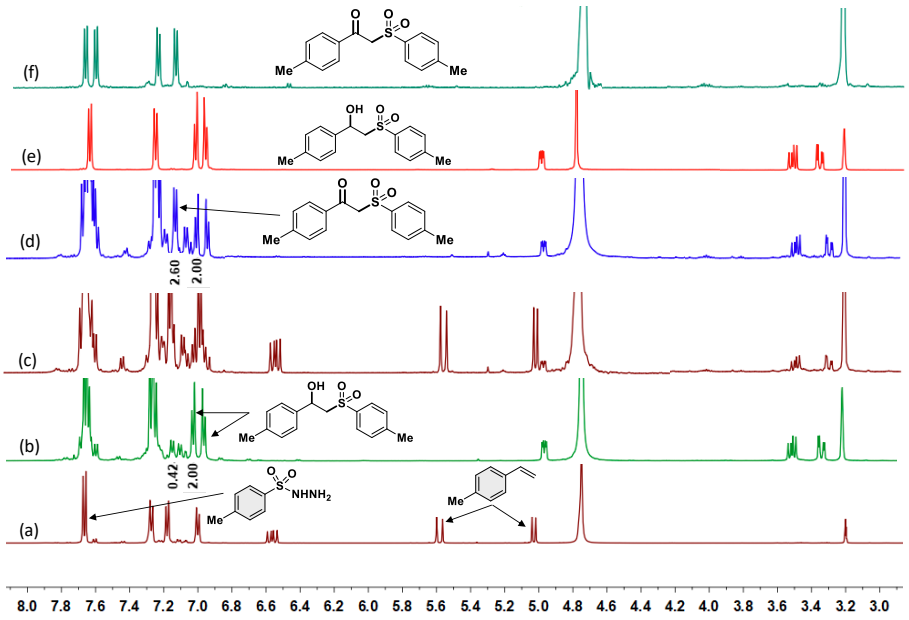
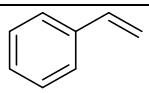
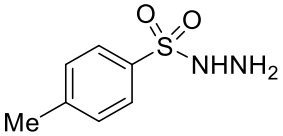
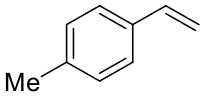
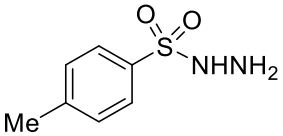
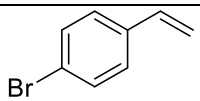
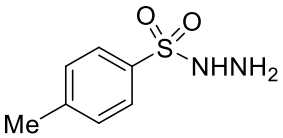


Fig. S5. ^{1}H NMR spectroscopic monitoring of the reaction of 4-methylstyrene (**1B**) and *p*-toluenesulfonyl hydrazide (**2b**) in 1 mL of CD_3OD under 45 W blue LED irradiation (a) at 0 h, (b) after 4 h under O_2, (c) after 10 h under air and (d) after 24 h under air. (e) ^{1}H NMR of **3Bb** in CD_3OD. (f) ^{1}H NMR spectrum of **4Bb** in CD_3OD.

Table S1 ^{1}H monitoring studies

Entry	Alkene	Sulfonyl hydrazide	Medium	Reaction time (h)	Product distribution β-Hydroxysulfone (3): β-Ketosulfone (4)
1			O_2	4	**3Ab**:**4Ab** = 86:14
2			Air	24	**3Ab**:**4Ab** = 51:49
3			O_2	4	**3Bb**:**4Bb** = 83:17
4			Air	24	**3Bb**:**4Bb** = 44:56
5			O_2	4	**3Fb**:**4Fb** = 85:15
6			Air	24	**3Fb**:**4Fb** = 48:52

6. Representative general procedure: To a glass vial equipped with a septum was charged olefin **1** (0.25 mmol), sulfonyl hydrazide **2**/*N*-hydroxy sulfonamide **5** (0.50 mmol), Rose Bengal (2 mol%) and 1 mL of ethanol. The resulting reaction mixture was purged with O_2 through a septum with the help of a balloon filled with O_2 for 5 min. The contents were stirred under irradiation with a 45 W Blue-LED light under O_2 atmosphere maintained with an oxygen-filled balloon. The progress of the reaction was monitored with thin layer chromatography. After completion of the reaction, the solvent was removed in vacuo, the resulting residue was washed with H_2O and the organic matter was extracted with EtOAc (30 mL × 3). The combined organic extract was dried over anhyd. Na_2SO_4 and the solvent removed in vacuo. The resultant crude product was subjected to silica-gel column chromatography using hexane/EtOAc (9:1) to obtain pure *β*-hydroxysulfone.

1-Phenyl-2-tosylethan-1-ol (**3Ab**):[1] Colorless solid (53 mg, 77%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.26 (m, 5H), 5.25 (dd, *J* = 10.0, 1.6 Hz, 1H), 3.48 (dd, *J* = 14.0, 10.0 Hz, 1H), 3.32 (dd, *J* = 14.0, 1.6 Hz, 1H), 2.47 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.4, 140.7, 136.2, 130.2, 128.8, 128.4, 128.1, 125.7, 68.5, 64.0, 21.8.

1-(*p*-Tolyl)-2-tosylethan-1-ol (**3Bb**):[1] Colorless liquid (59 mg, 81%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.20 (dd, *J* = 10.0, 1.6 Hz, 1H), 3.47 (dd, *J* = 14.0, 10.0 Hz, 1H), 3.30 (dd, *J* = 14.0, 1.6 Hz, 1H), 2.46 (s, 3H), 2.31 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.2, 138.2, 137.9, 136.3, 130.1, 129.4, 128.1, 125.7, 68.4, 64.0, 21.7, 21.2.

1-(4-(*tert*-Butyl)phenyl)-2-tosylethan-1-ol (**3Cb**):[5] Colorless solid (63 mg, 76%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 5.23 (dd, *J* = 10.0, 1.5 Hz, 1H), 3.50 (dd, *J* = 14.0, 10.0 Hz, 1H), 3.33 (dd, *J* = 14.0, 1.5 Hz, 1H), 3.12 – 2.96 (bs, 1H), 2.46 (s, 3H), 1.28 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.5, 145.2, 137.7, 136.3, 130.1, 128.1, 125.7, 125.5, 68.4, 63.9, 34.6, 31.3, 21.7.

1-(4-Fluorophenyl)-2-tosylethan-1-ol (**3Db**):[1] Colorless solid (61 mg, 84%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.27 (m, 2H), 7.01 (t, *J*

= 8.5 Hz, 2H), 5.25 (dd, *J* = 10.0, 1.5 Hz, 1H), 3.44 (dd, *J* = 14.0, 10.0 Hz, 1H), 3.29 (dd, *J* = 14.0, 1.5 Hz, 1H), 2.47 (s, 3H), 2.16 (s, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.6, 161.7, 145.5, 136.4 (d, *J* = 52.9 Hz), 130.3, 128.1, 127.5 (d, *J* = 8.8 Hz), 115.8 (d, *J* = 21.5 Hz), 68.0, 64.1, 21.8.

1-(4-Chlorophenyl)-2-tosylethan-1-ol (**3Eb**):[1] Colorless solid (63 mg, 81%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 5.24 (dd, *J* = 10.0, 1.0 Hz, 1H), 3.42 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.28 (dd, *J* = 14.4, 1.0 Hz, 1H), 2.47 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.6, 139.2, 136.1, 134.2, 130.3, 129.0, 128.1, 127.2, 68.0, 64.0, 21.8.

1-(4-Bromophenyl)-2-tosylethan-1-ol (**3Fb**):[1] Colorless solid (69 mg, 78%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 5.22 (dd, *J* = 10.0, 1.5 Hz, 1H), 3.42 (dd, *J* = 14.0, 10.0 Hz, 1H), 3.28 (dd, *J* = 14.0, 1.5 Hz, 1H), 2.47 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.5, 139.7, 136.0, 131.9, 130.3, 128.1, 127.5, 122.3, 68.0, 63.8, 21.8.

1-(4-Nitrophenyl)-2-tosylethan-1-ol (**3Gb**):[5] Colorless solid (47 mg, 58%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 5.43 – 5.37 (m, 1H), 4.05 (bs, 1H), 3.43 (dd, *J* = 14.2, 10.0 Hz, 1H), 3.32 (dd, *J* = 14.2, 2.0 Hz, 1H), 2.47 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.8, 147.7, 145.8, 135.8, 130.4, 128.1, 126.7, 124.0, 67.7, 63.7, 21.8.

1-(*m*-Tolyl)-2-tosylethan-1-ol (**3Hb**): Colorless liquid (51 mg, 71%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.11 – 7.09 (m, 3H), 5.22 (dd, *J* = 10.0, 1.0 Hz, 1H), 3.48 (dd, *J* = 14.3, 10.0 Hz, 1H), 3.32 (dd, *J* = 14.3, 1.0 Hz, 1H), 2.47 (s, 3H), 2.31 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.3, 140.7, 138.6, 136.3, 130.2, 129.2, 128.8, 128.1, 126.4, 122.8, 68.6, 64.1, 21.8, 21.5; **HRMS** (**ESI**) m/z: [M+Na^+] calcd for $C_{16}H_{18}SO_3Na$ 313.0874; found 313.0874.

1-(3-Methoxyphenyl)-2-tosylethan-1-ol (**3Ib**): Colorless liquid (49 mg, 64%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.88 – 6.77 (m, 3H), 5.25 – 5.19 (m, 1H), 3.77 (s, 3H), 3.46 (dd, *J* = 14.0, 10.0 Hz, 1H), 3.31 (dd, *J* =

14.0, 1.7 Hz, 1H), 3.12 (bs, 1H), 2.46 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.9, 145.3, 142.4, 136.2, 130.2, 129.9, 128.1, 117.9, 113.9, 111.1, 68.4, 64.0, 55.3, 21.8; **HRMS** (**ESI**) m/z: [M+Na^+] calcd for $C_{16}H_{18}SO_4Na$ 329.0818; found 329.0811.

1-(3-Bromophenyl)-2-tosylethan-1-ol (**3Jb**): Colorless solid (59 mg, 67%): mp = 124–126 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.36 (m, 4H), 7.24 – 7.17 (m, 2H), 5.22 (dd, *J* = 10.0, 1.5 Hz, 1H), 3.43 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.30 (dd, *J* = 14.4, 1.5 Hz, 1H), 2.72 (bs, 1H), 2.47 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6, 143.0, 136.0, 131.5, 130.4, 130.3, 128.9, 128.1, 124.4, 122.9, 67.9, 63.9, 21.8; **HRMS** (**ESI**) m/z: [M+Na^+] calcd for $C_{15}H_{15}BrSO_3Na$ 376.9817; found 376.9814.

1-(Naphthalen-1-yl)-2-tosylethan-1-ol (**3Kb**): Colorless solid (68 mg, 84%): mp = 118–120 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.87 – 7.83 (m, 1H), 7.76 (dd, *J* = 11.9, 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.38 (m, 5H), 6.05 (dd, *J* = 7.2, 3.9 Hz, 1H), 3.84 (s, 1H), 3.51 – 3.48 (m, 2H), 2.49 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.5, 136.1, 136.0, 133.8, 130.3, 129.4, 129.3, 128.8, 128.3, 126.7, 125.8, 125.7, 123.3, 121.8, 65.3, 63.6, 21.8; **HRMS** (**ESI**) m/z: [M+Na^+] calcd for $C_{19}H_{18}BrSO_3Na$ 349.0869; found 349.0861.

2-Phenyl-1-tosylpropan-2-ol (**3Lb**):[1] Colorless solid (66 mg, 91%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.18 – 7.15 (m, 4H), 4.65 (s, 1H), 3.70 (d, *J* = 14.5 Hz, 1H), 3.59 (d, *J* = 14.5 Hz, 1H), 2.38 (s, 3H), 1.70 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.6, 144.5, 137.4, 129.8, 128.3, 127.6, 127.2, 124.7, 73.2, 66.7, 30.8, 21.6.

1-((4-Methoxyphenyl)sulfonyl)-2-phenylpropan-2-ol (**3Ld**):[1] Colorless liquid (67 mg, 88%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.21 – 7.14 (m, 3H), 6.81 (d, *J* = 8.5 Hz, 2H), 4.68 (s, 1H), 3.83 (s, 3H), 3.69 (d, *J* = 14.5 Hz, 1H), 3.59 (d, *J* = 14.5 Hz, 1H), 1.68 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.6, 144.6, 132.0, 129.8, 128.3, 127.2, 124.7, 114.4, 73.2, 66.9, 55.8, 30.9.

1-(Naphthalen-2-ylsulfonyl)-2-phenylpropan-2-ol (**3Lf**):[1] Colorless solid (68 mg, 84%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.86 (t, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.55 (m, 3H), 7.25 (d, *J* = 7.5 Hz, 2H), 7.04 (t, *J* = 7.5 Hz, 2H), 6.94 (t, *J* = 7.0 Hz, 1H), 4.69 (s, 1H), 3.82 (d, *J* = 14.8 Hz, 1H), 3.69 (d, *J* = 14.8 Hz, 1H), 1.70 (s, 3H); **^{13}C NMR** (126 MHz,

$CDCl_3$) δ 144.2, 137.0, 135.1, 132.0, 129.9, 129.6, 129.5, 129.4, 128.2, 127.9, 127.6, 127.4, 124.7, 122.0, 73.3, 66.6, 31.0.

1-((4-Nitrophenyl)sulfonyl)-2-phenylpropan-2-ol (**3Lg**):[3] Colorless solid (65 mg, 81%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 7.15 – 7.10 (m, 3H), 4.36 (s, 1H), 3.86 (d, *J* = 15.0 Hz, 1H), 3.72 (d, *J* = 15.0 Hz, 1H), 1.67 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.4, 145.4, 143.7, 129.1, 128.5, 127.6, 124.9, 124.1, 73.1, 66.9, 31.3.

2-Phenyl-1-(thiophen-2-ylsulfonyl)propan-2-ol (**3Li**):[7] Colorless solid (59 mg, 83%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 5.0 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.26 – 7.16 (m, 4H), 6.93 (t, *J* = 5.0 Hz, 1H), 4.47 (s, 1H), 3.86 (d, *J* = 14.5 Hz, 1H), 3.72 (d, *J* = 14.5 Hz, 1H), 1.72 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.4, 141.4, 134.3, 134.2, 128.4, 127.8, 127.4, 124.7, 73.3, 68.2, 30.8.

2-(2-Bromophenyl)-1-tosylpropan-2-ol (**3Mb**): Colorless solid (85 mg, 93%): mp = 148–150 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.11 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.00 (td, *J* = 7.8, 1.6 Hz, 1H), 5.14 (s, 1H), 4.80 (d, *J* = 15.0 Hz, 1H), 3.64 (d, *J* = 15.0 Hz, 1H), 2.36 (s, 3H), 1.73 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.4, 142.1, 135.8, 134.6, 129.4, 129.1, 128.6, 127.9, 127.9, 120.1, 73.3, 62.2, 28.2, 21.7; **HRMS** (**ESI**) m/z: [M+K^+] calcd for $C_{16}H_{17}BrSO_3K$ 406.9713; found 406.9710.

1-(4-Bromophenyl)-2-((4-methoxyphenyl)sulfonyl)ethan-1-ol (**3Fd**):[5] Colorless solid (76 mg, 82%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 2H), 5.22 (d, *J* = 10.0 Hz, 1H), 3.90 (s, 3H), 3.42 (dd, *J* = 14.0, 10.0 Hz, 1H), 3.30 – 3.24 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.3, 139.8, 132.0, 130.5, 130.3, 127.5, 122.3, 114.8, 68.1, 64.1, 55.9.

2-(Phenylsulfonyl)-1-(*p*-tolyl)ethan-1-ol (**3Ba**):[4] Colorless solid (56 mg, 82%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.27 – 5.21 (m, 1H), 3.50 (dd, *J* = 14.5, 10.0 Hz,

1H), 3.33 (dd, *J* = 14.5, 1.8 Hz, 1H), 2.31 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.3, 138.3, 137.8, 134.2, 129.5, 129.5, 128.1, 125.7, 68.4, 64.0, 21.2.

2-((4-Isopropylphenyl)sulfonyl)-1-(*p*-tolyl)ethan-1-ol (**3Bc**): Colorless solid (60 mg, 76%): mp = 58–60 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.28 – 5.21 (m, 1H), 3.48 (dd, *J* = 14.0, 10.2 Hz, 1H), 3.32 (dd, *J* = 14.0, 1.6 Hz, 1H), 3.01 (m, 1H), 2.83 (bs, 1H), 2.31 (s, 3H), 1.29 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.9, 138.2, 137.8, 136.6, 129.5, 128.2, 127.7, 125.7, 68.4, 64.0, 34.4, 23.7, 21.2; **HRMS** (**ESI**) m/z: [M+Na^+] calcd for $C_{18}H_{22}SO_3Na$ 341.1187; found 341.1182.

2-((4-Methoxyphenyl)sulfonyl)-1-(*p*-tolyl)ethan-1-ol (**3Bd**): Colorless liquid (66 mg, 87%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 5.22 – 5.17 (m, 1H), 3.89 (s, 3H), 3.46 (dd, *J* = 14.3, 10.0 Hz, 1H), 3.29 (dd, *J* = 14.3, 1.8 Hz, 1H), 2.86 (bs, 1H), 2.31 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.1, 138.2, 137.8, 130.6, 130.3, 129.5, 125.7, 114.7, 68.5, 64.2, 55.8, 21.2; **HRMS** (**ESI**) m/z: [M+Na^+] calcd for $C_{16}H_{18}SO_4Na$ 329.0818; found 329.0809.

2-((4-Chlorophenyl)sulfonyl)-1-(*p*-tolyl)ethan-1-ol (**3Be**):[5] Colorless solid (66 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.14 (m, 4H), 5.23 (dd, *J* = 9.9, 2.0 Hz, 1H), 3.52 (dd, *J* = 14.0, 9.9 Hz, 1H), 3.32 (dd, *J* = 14.0, 2.0 Hz, 1H), 2.90 (bs, 1H), 2.32 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.8, 138.4, 137.9, 137.7, 129.7, 129.6, 129.5, 125.7, 68.5, 64.0, 21.2.

2-(Naphthalen-2-ylsulfonyl)-1-(*p*-tolyl)ethan-1-ol (**3Bf**): Colorless solid (65 mg, 80%): mp = 112–114 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.01 (t, *J* = 8.1 Hz, 2H), 7.96 – 7.88 (m, 2H), 7.72 – 7.63 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 5.27 (dd, *J* = 9.8, 1.7 Hz, 1H), 3.59 (dd, *J* = 14.5, 9.8 Hz, 1H), 3.42 (dd, *J* = 14.5, 1.7 Hz, 1H), 2.27 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.2, 137.7, 136.0, 135.5, 132.2, 130.1, 129.9, 129.6, 129.6, 129.4, 128.1, 127.9, 125.7, 122.5, 68.5, 63.9, 21.1; **HRMS** (**ESI**) m/z: [M+Na^+] calcd for $C_{19}H_{18}SO_3Na$ 349.0869; found 349.0860.

2-((4-Nitrophenyl)sulfonyl)-1-(*p*-tolyl)ethan-1-ol (**3Bg**): Colorless solid (59 mg, 74%): mp = 126–128 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.6 Hz, 2H), 8.13 (d, *J* = 8.6 Hz, 2H), 7.15 (m, 4H), 5.30 (dd, *J* = 9.8, 2.0 Hz, 1H), 3.62 (dd, *J* = 14.6, 9.8 Hz, 1H), 3.40 (dd, *J* = 14.6, 2.0 Hz, 1H), 2.32 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.9, 145.4, 138.8, 137.5, 129.8, 129.7, 125.7, 124.5, 68.8, 64.0, 21.2; **HRMS** (**ESI**) m/z: [M+Na^+] calcd for $C_{15}H_{15}NSO_5Na$ 344.0568; found 344.0562.

2-(*n*-Butylsulfonyl)-1-(*p*-tolyl)ethan-1-ol (**3Bh**): Colorless solid (41 mg, 65%): mp = 69–71 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 5.32 (dd, *J* = 10.0, 1.8 Hz, 1H), 3.40 (dd, *J* = 14.6, 10.0 Hz, 1H), 3.16 – 3.07 (m, 3H), 2.35 (s, 3H), 1.87 – 1.79 (m, 2H), 1.51 – 1.43 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.5, 138.3, 129.7, 125.7, 68.9, 60.5, 54.5, 23.9, 21.8, 21.2, 13.6; **HRMS** (**ESI**) m/z: [M+Na^+] calcd for $C_{13}H_{20}SO_3Na$ 279.1025; found 279.1021.

2-(Thiophen-2-ylsulfonyl)-1-(*p*-tolyl)ethan-1-ol (**3Bi**): Colorless liquid (43 mg, 61%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 4.5 Hz, 2H), 7.20 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.27 (d, *J* = 10.0 Hz, 1H), 3.62 (dd, *J* = 14.5, 10.0 Hz, 1H), 3.50 (s, 1H), 3.44 (d, *J* = 14.5 Hz, 1H), 2.32 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.3, 140.2, 138.4, 137.7, 134.6, 129.6, 128.2, 125.7, 68.7, 65.5, 21.2; **HRMS** (**ESI**) m/z: [M+Na^+] calcd for $C_{13}H_{24}S_2O_3Na$ 305.0277; found 305.0270.

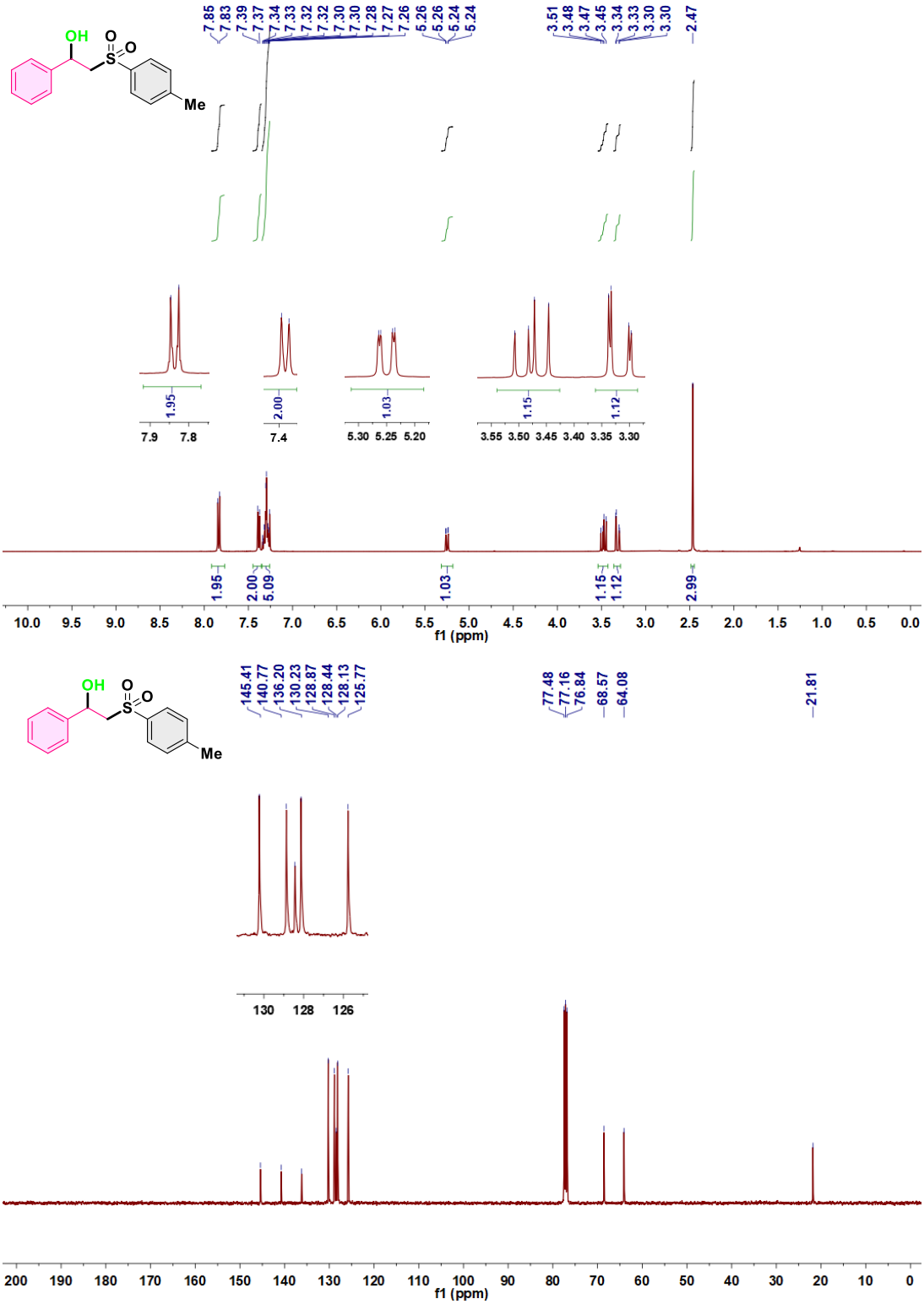


Fig. S6. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 1-phenyl-2-tosylethan-1-ol (**3Ab**) in $CDCl_3$.

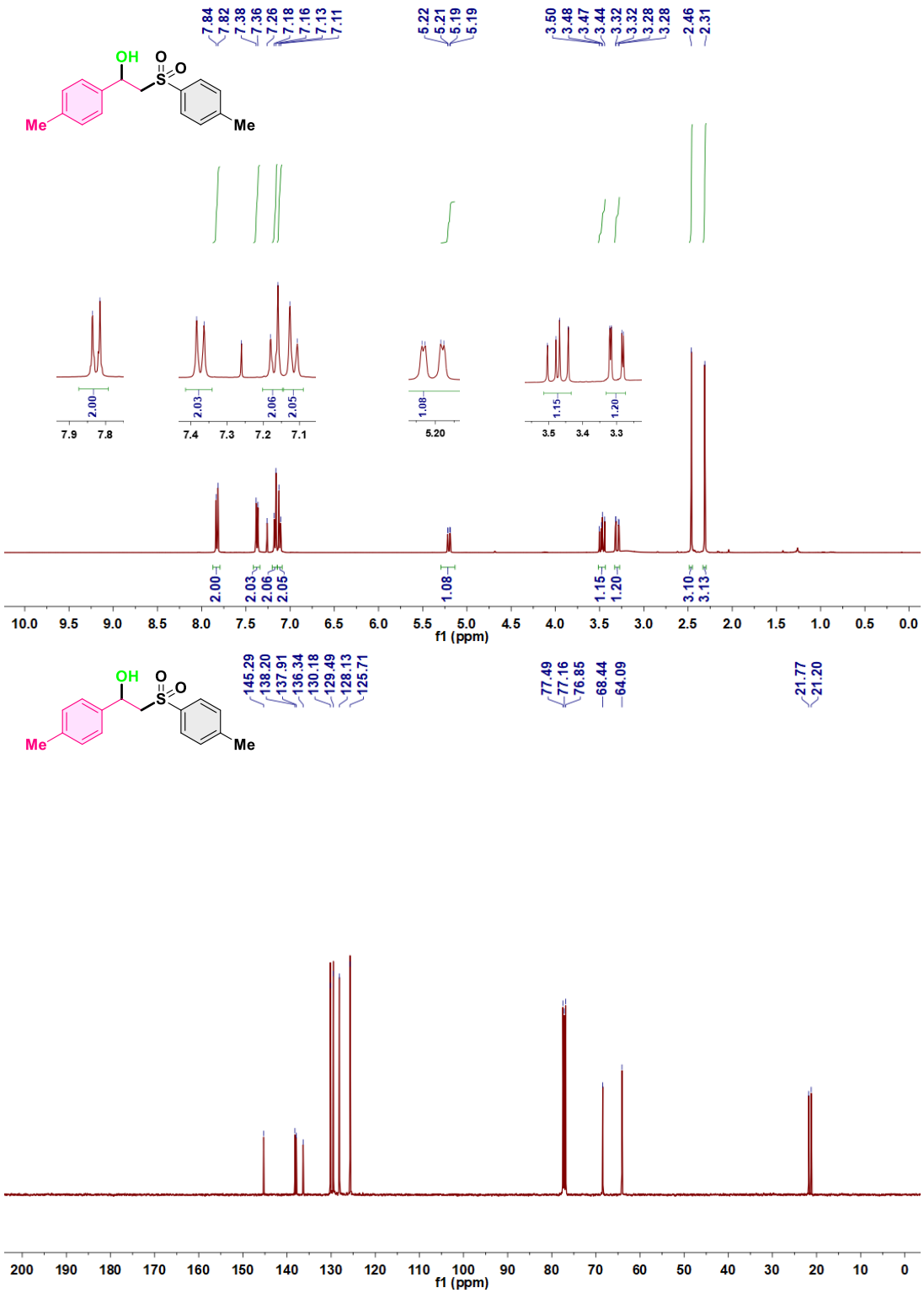


Fig. S7. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 1-(*p*-tolyl)-2-tosylethan-1-ol (**3Bb**) in $CDCl_3$.

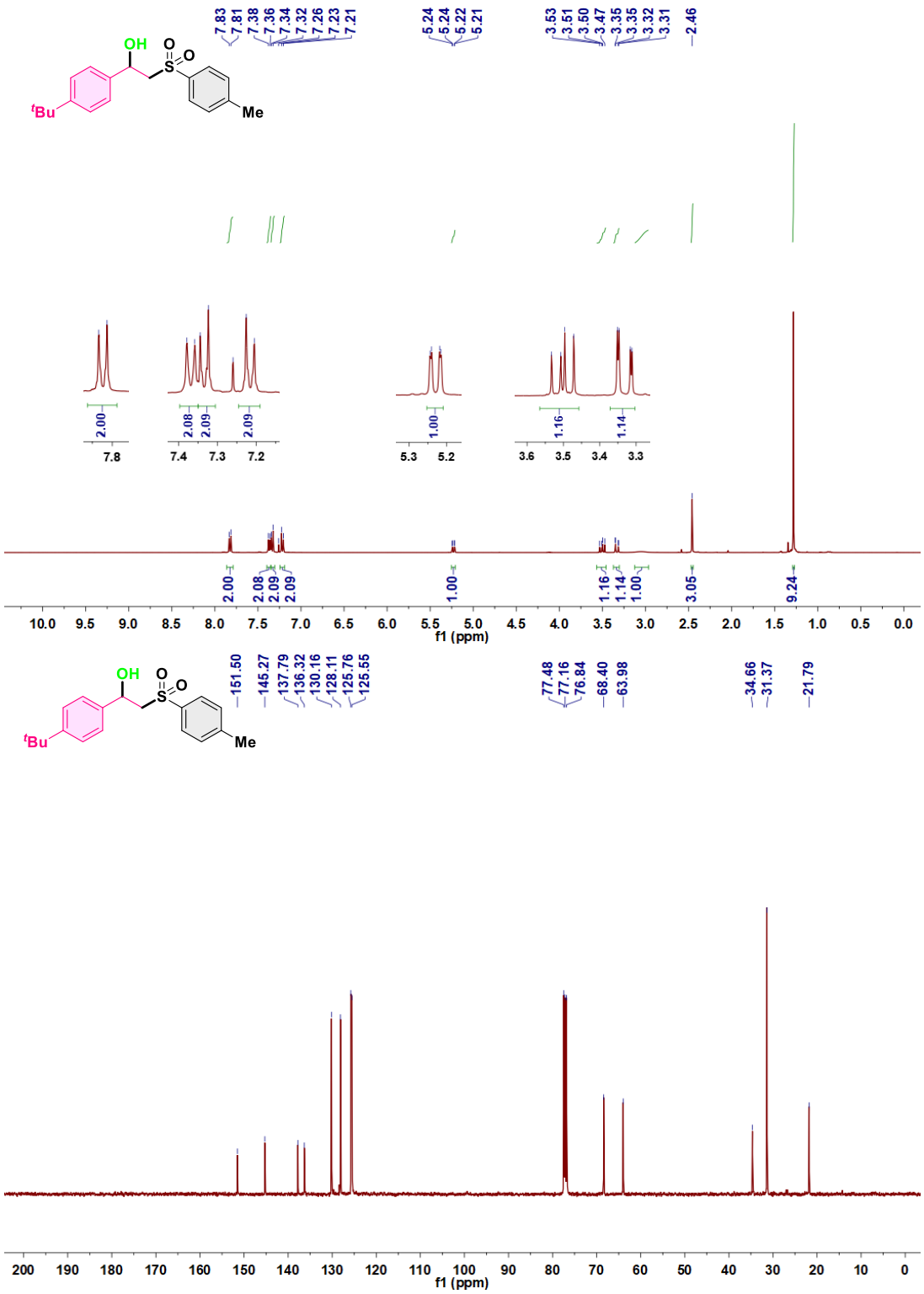


Fig. S8. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 1-(4-(*tert*-butyl)phenyl)-2-tosylethan-1-ol (**3Cb**) in $CDCl_3$.

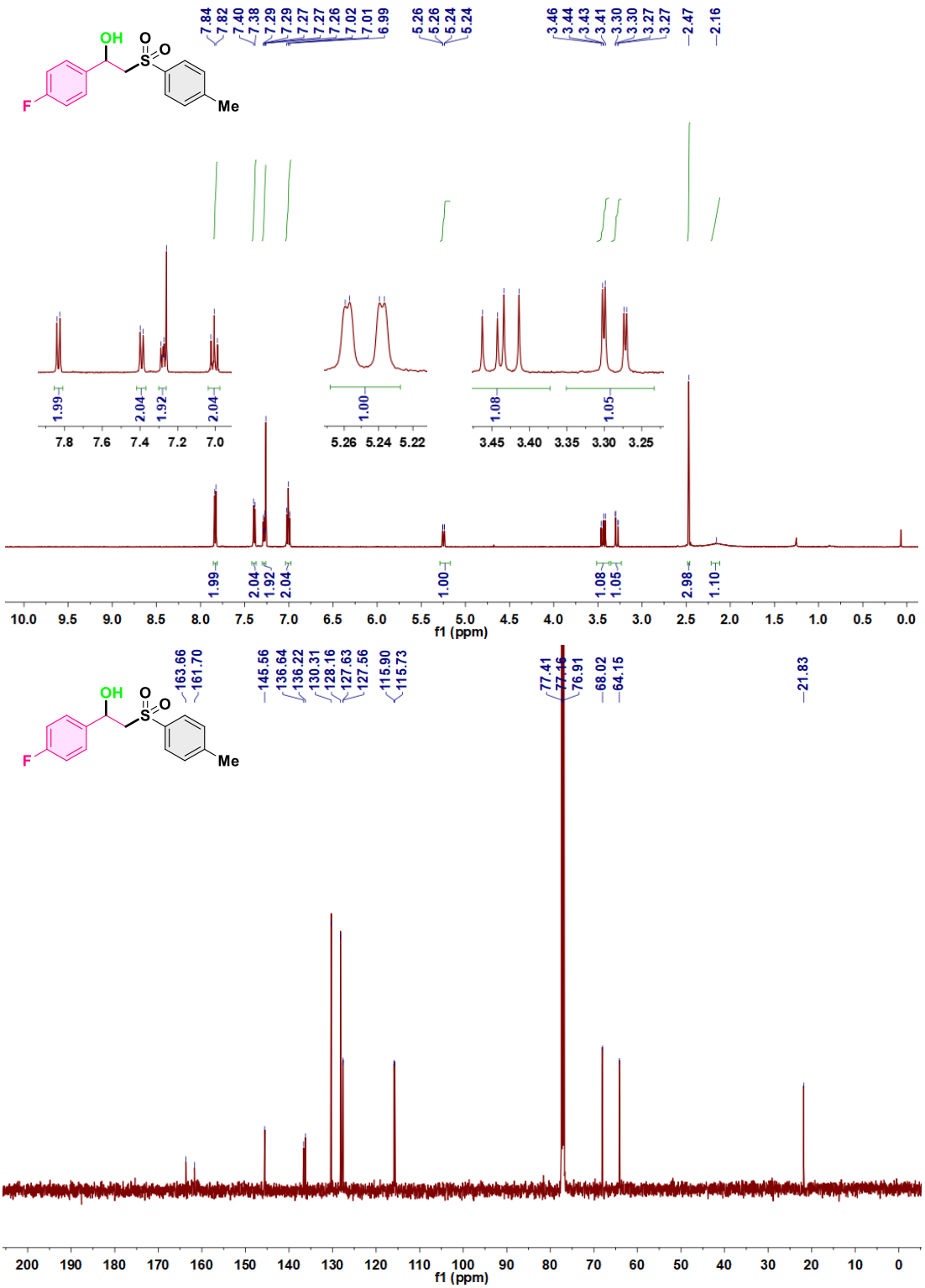


Fig. S9. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra of 1-(4-fluorophenyl)-2-tosylethan-1-ol (**3Db**) in $CDCl_3$.

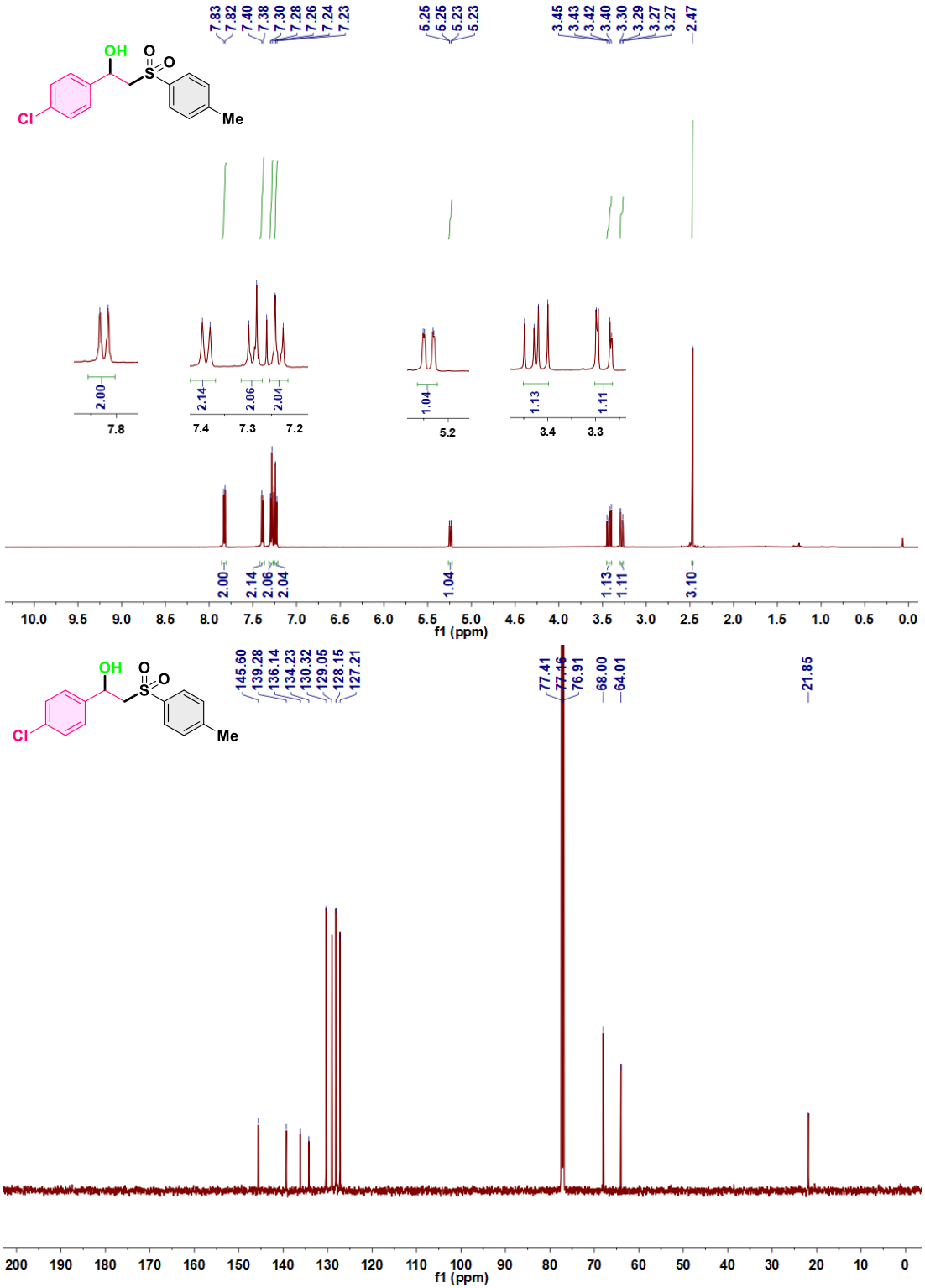


Fig. S10. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra of 1-(4-chlorophenyl)-2-tosylethan-1-ol (**3Eb**) in $CDCl_3$.

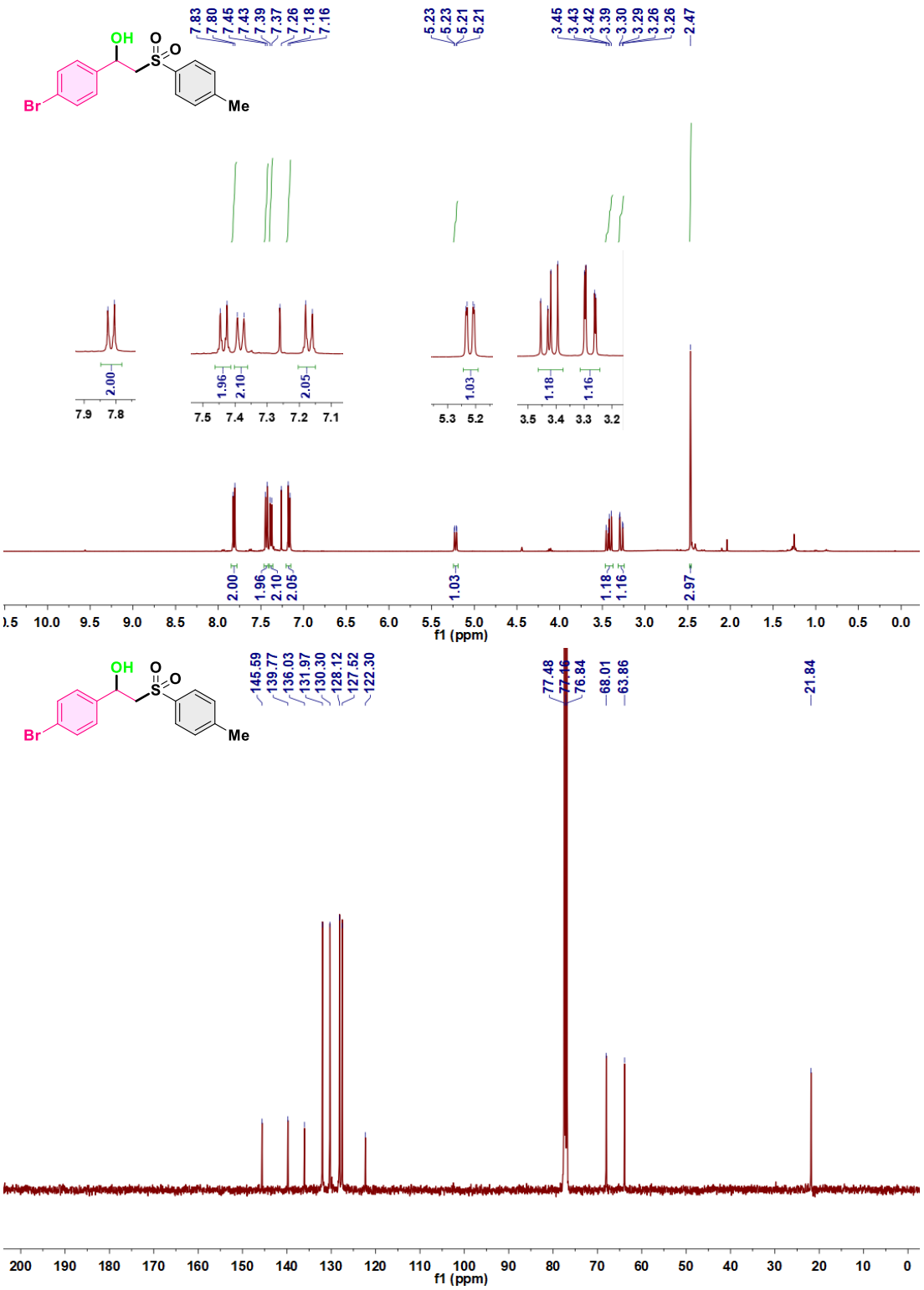


Fig. S11. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 1-(4-bromophenyl)-2-tosylethan-1-ol (**3Fb**) in $CDCl_3$.

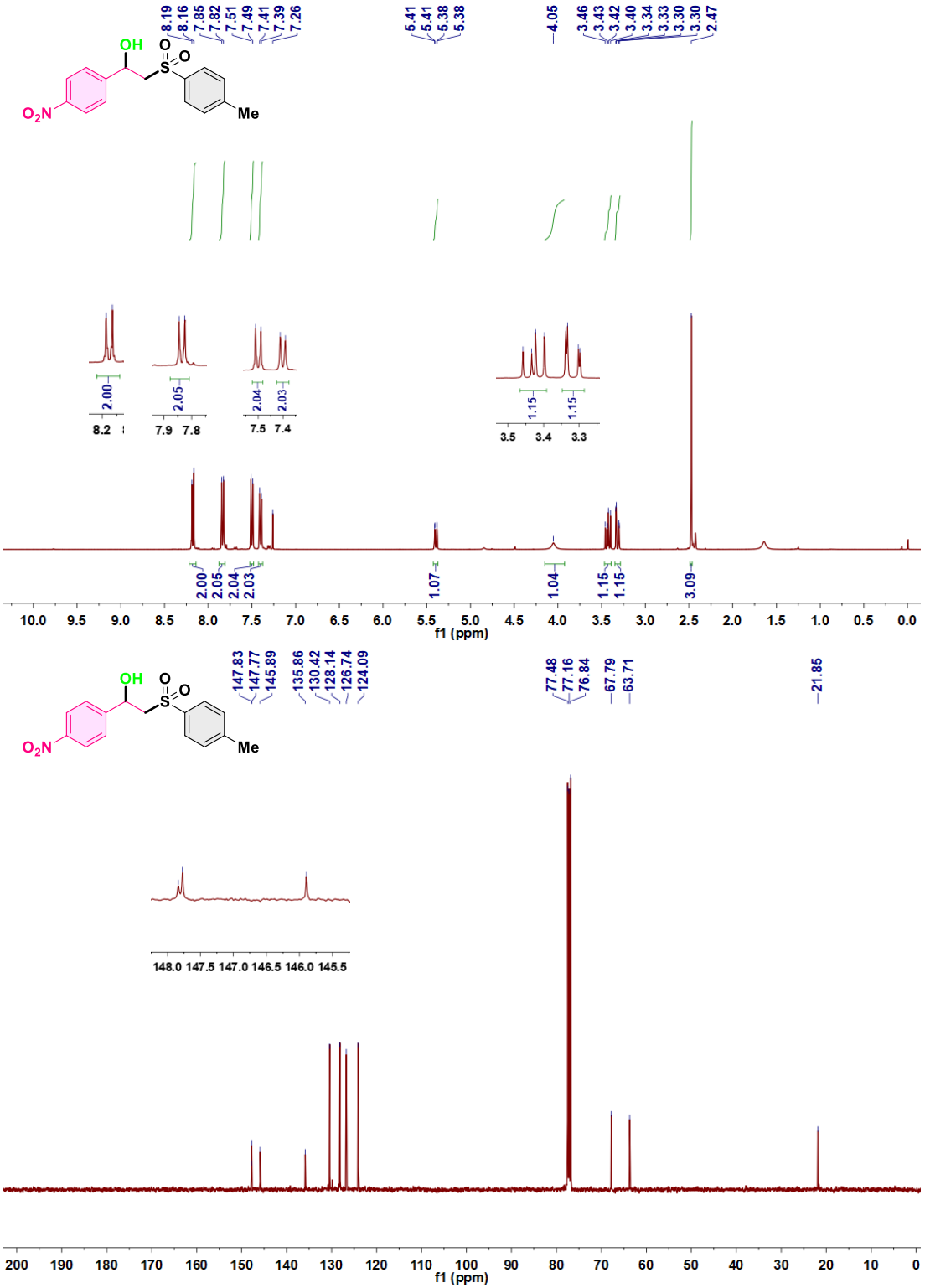


Fig. S12. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 1-(4-nitrophenyl)-2-tosylethan-1-ol (**3Gb**) in $CDCl_3$.

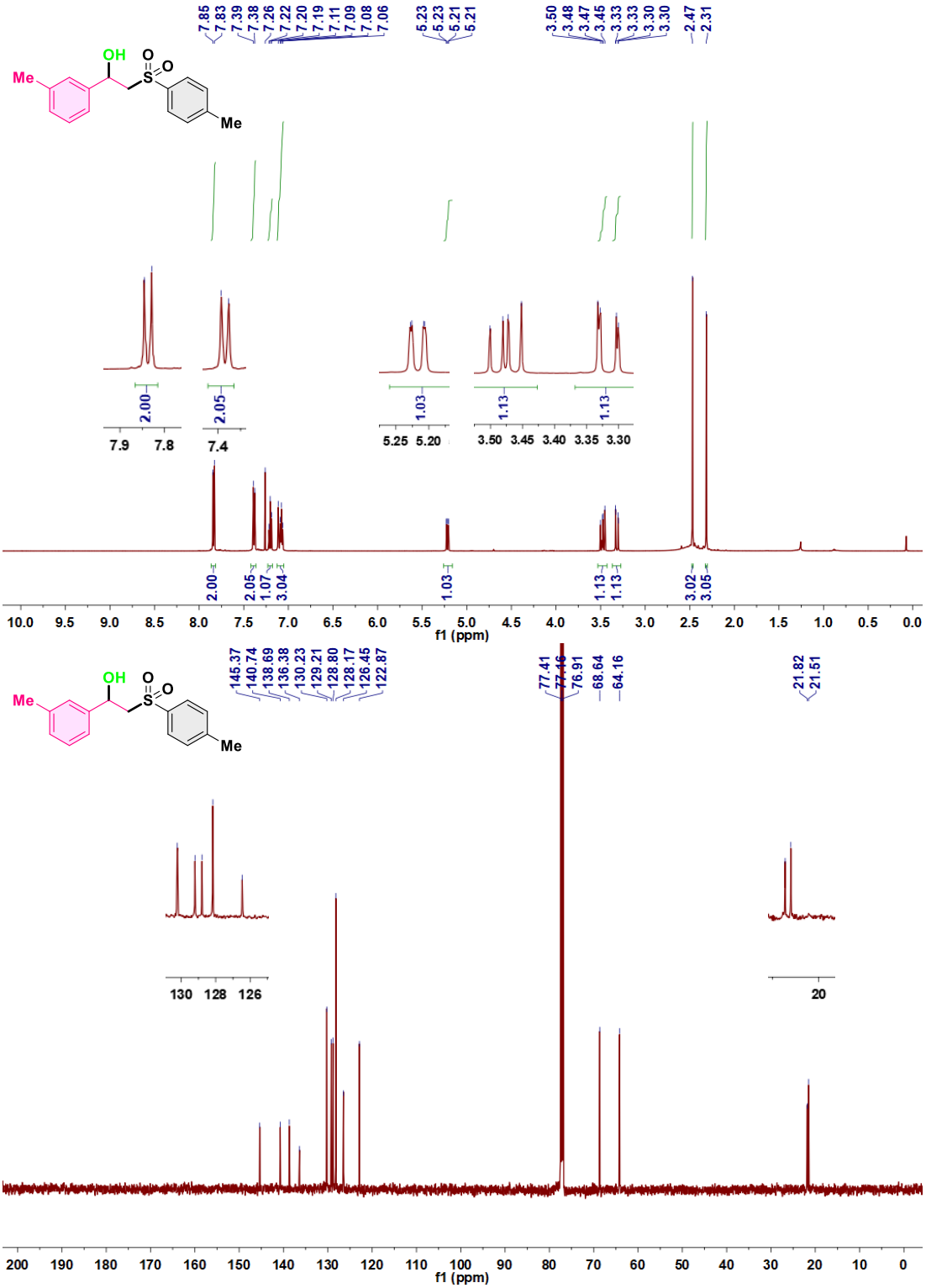


Fig. S13. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra of 1-(*m*-tolyl)-2-tosylethan-1-ol (**3Hb**) in $CDCl_3$.

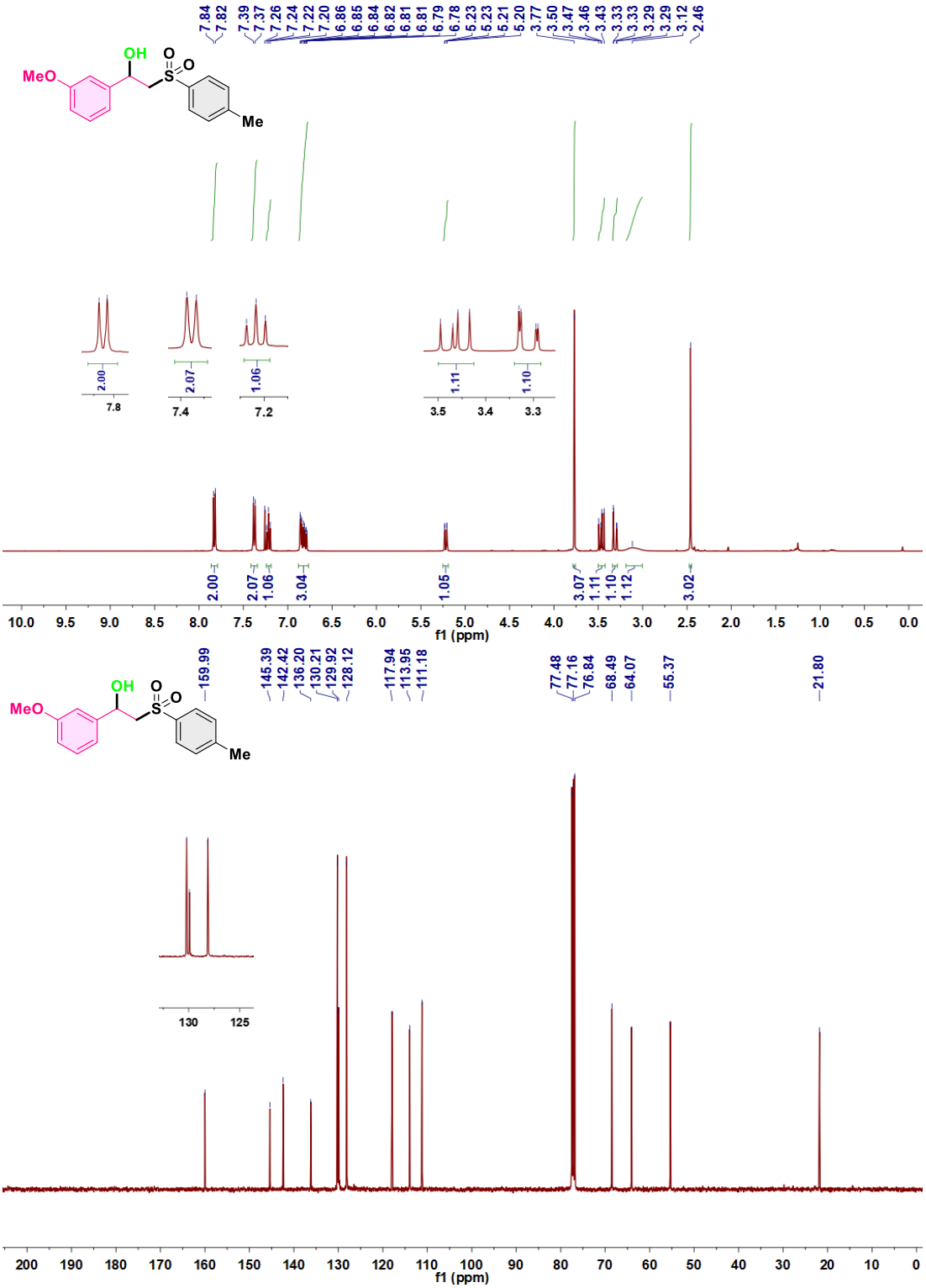


Fig. S14. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 1-(3-methoxyphenyl)-2-tosylethan-1-ol (**3Ib**) in $CDCl_3$.

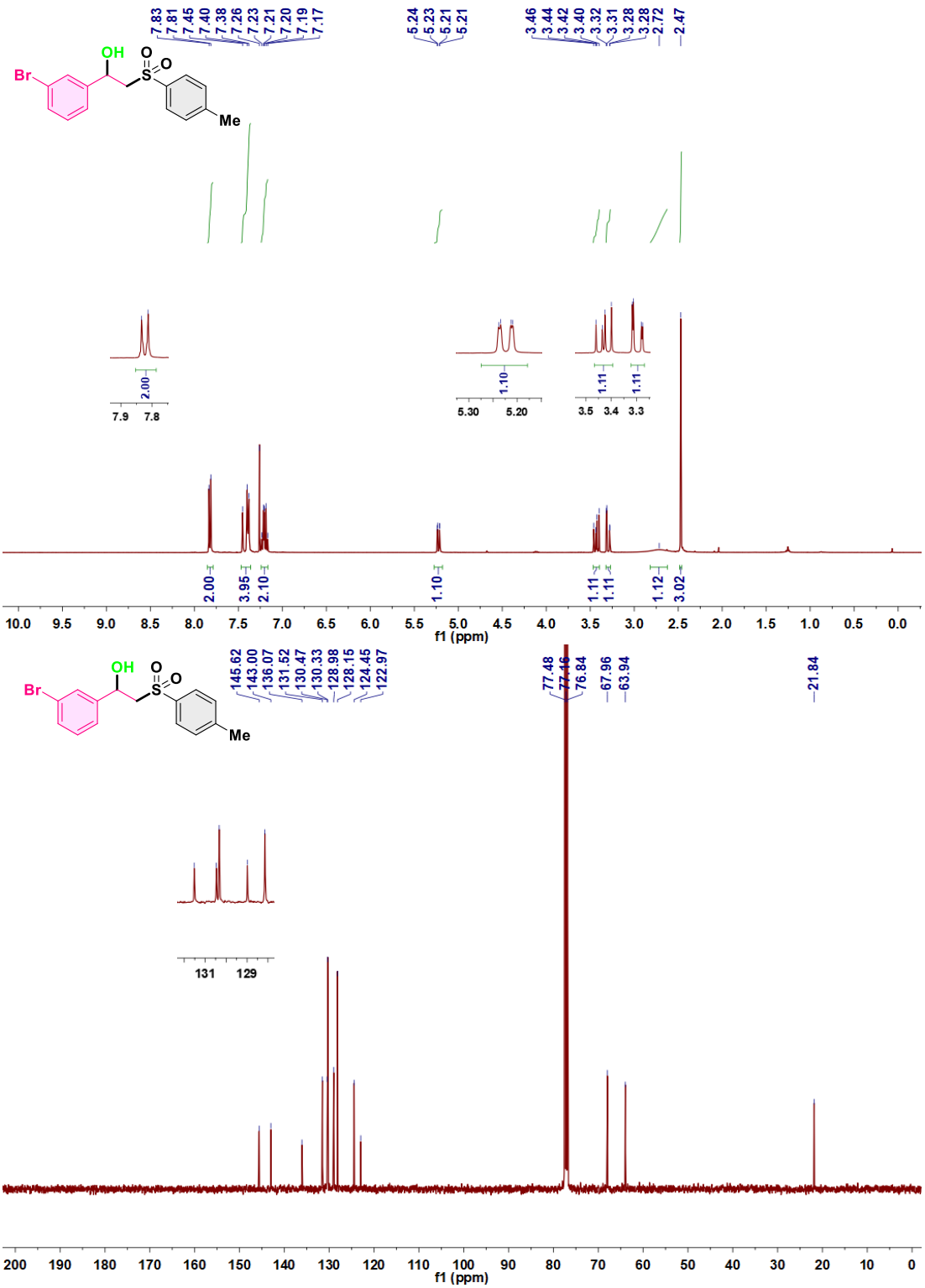


Fig. S15. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 1-(3-bromophenyl)-2-tosylethan-1-ol (**3Jb**) in $CDCl_3$.

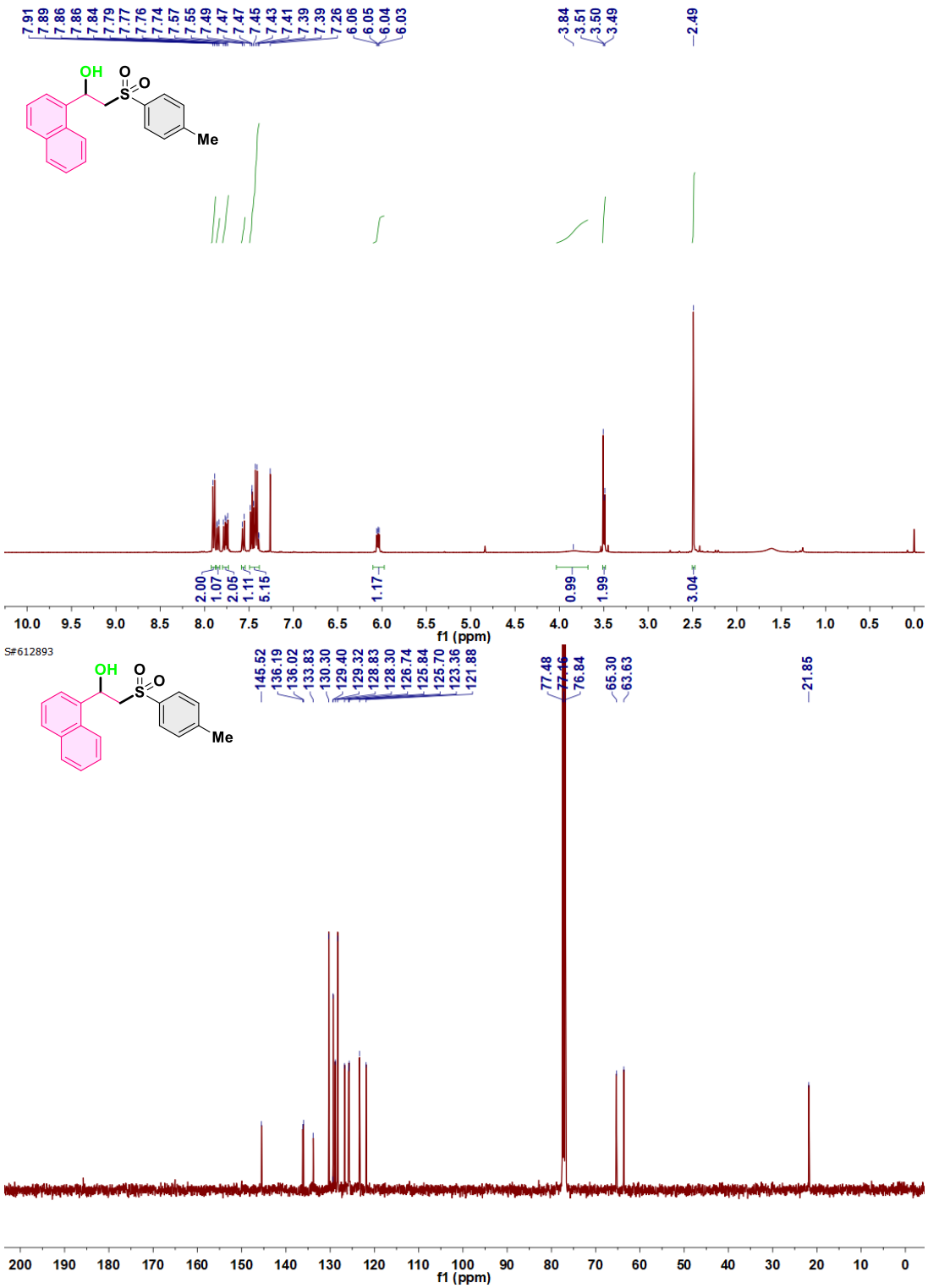


Fig. S16. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 2-(2-bromophenyl)-1-tosylpropan-2-ol (**3Kb**) in $CDCl_3$.

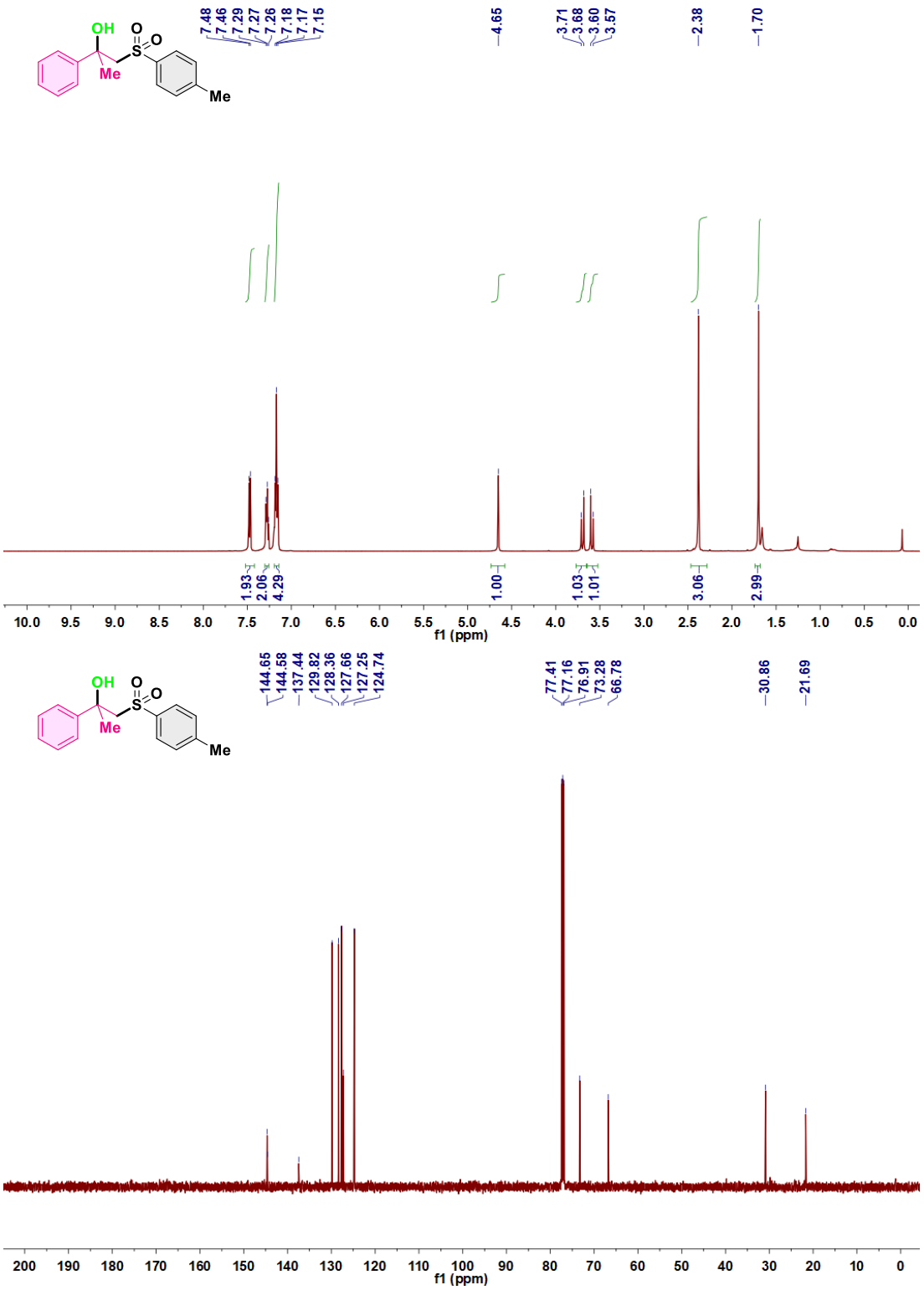


Fig. S17. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra of 2-phenyl-1-tosylpropan-2-ol (**3Lb**) in $CDCl_3$.

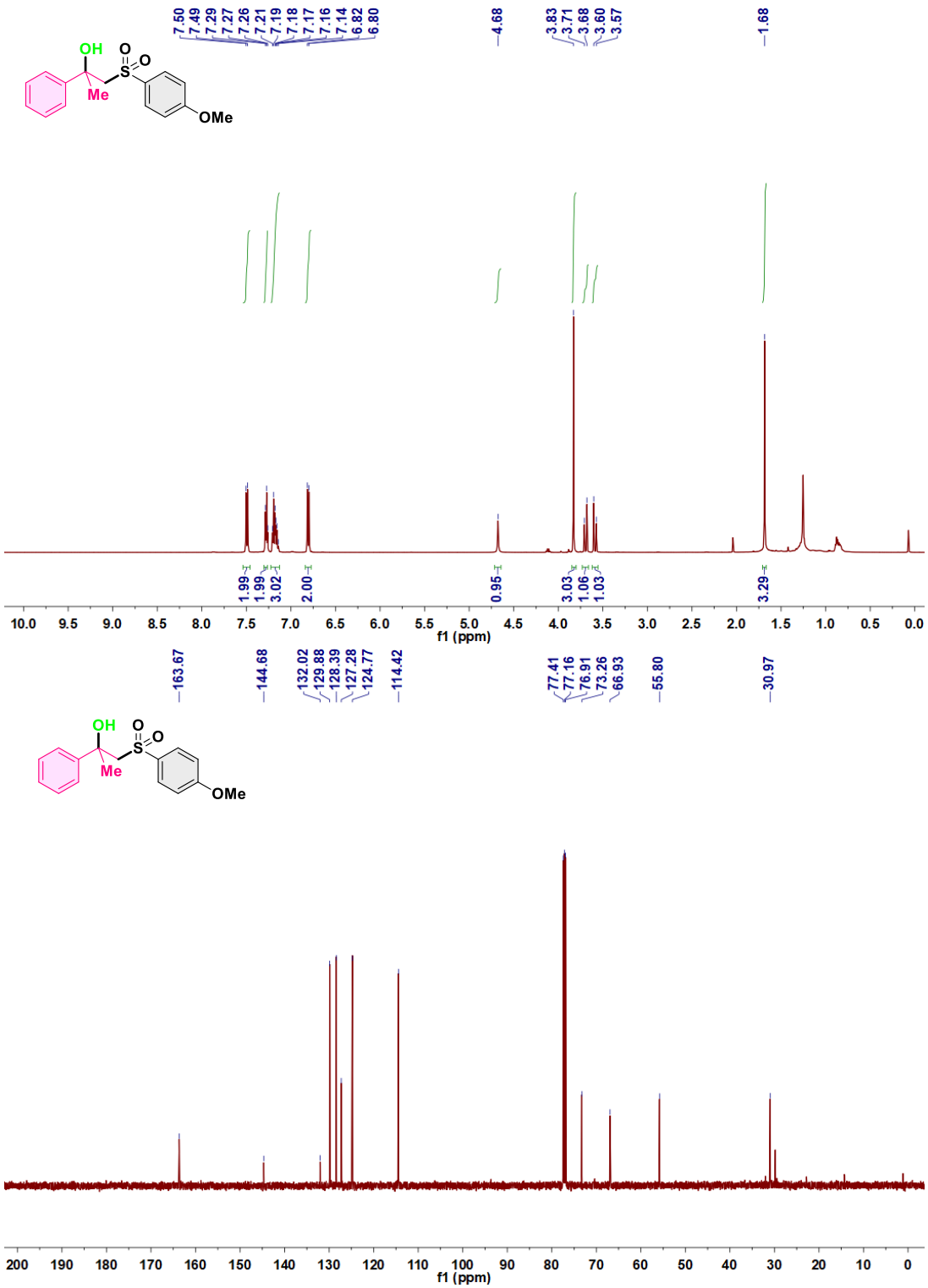


Fig. S18. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra of 1-((4-methoxyphenyl)sulfonyl)-2-phenylpropan-2-ol (**3LLd**) in $CDCl_3$.

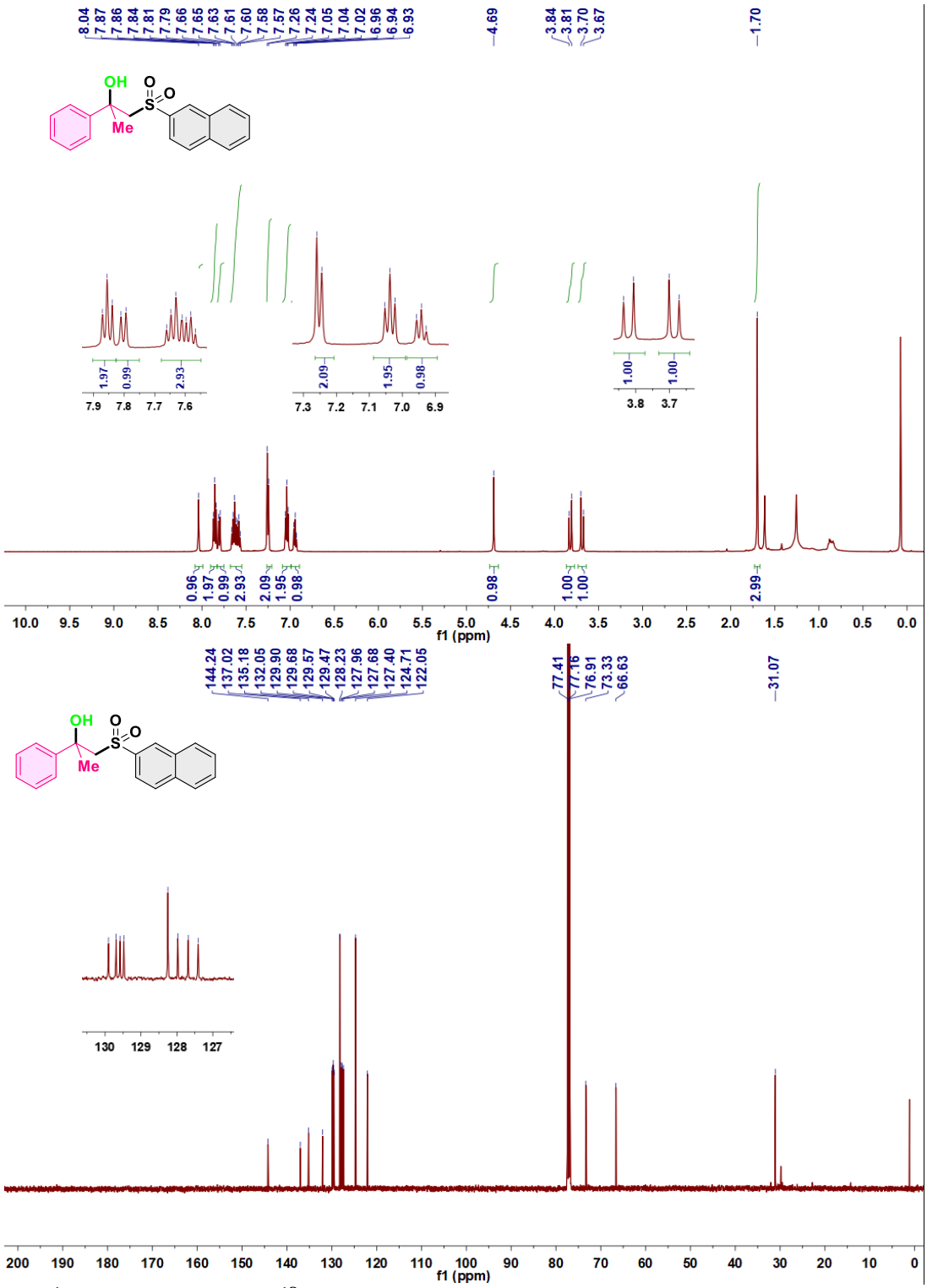


Fig. S19. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra of 1-(naphthalen-2-ylsulfonyl)-2-phenylpropan-2-ol (**3Lf**) in $CDCl_3$.

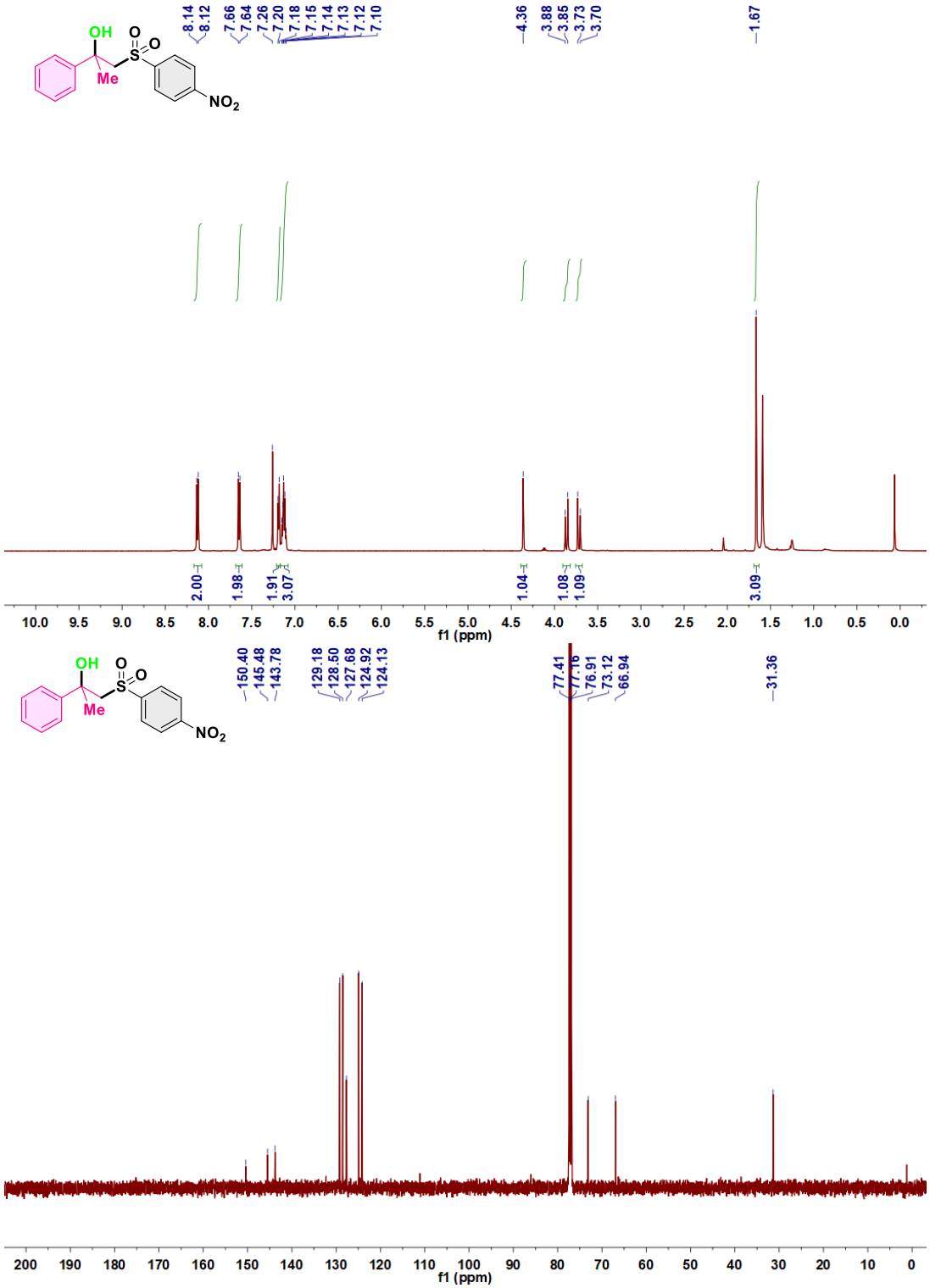


Fig. S20. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra of 1-((4-nitrophenyl)sulfonyl)-2-phenylpropan-2-ol (**3Lg**) in $CDCl_3$.

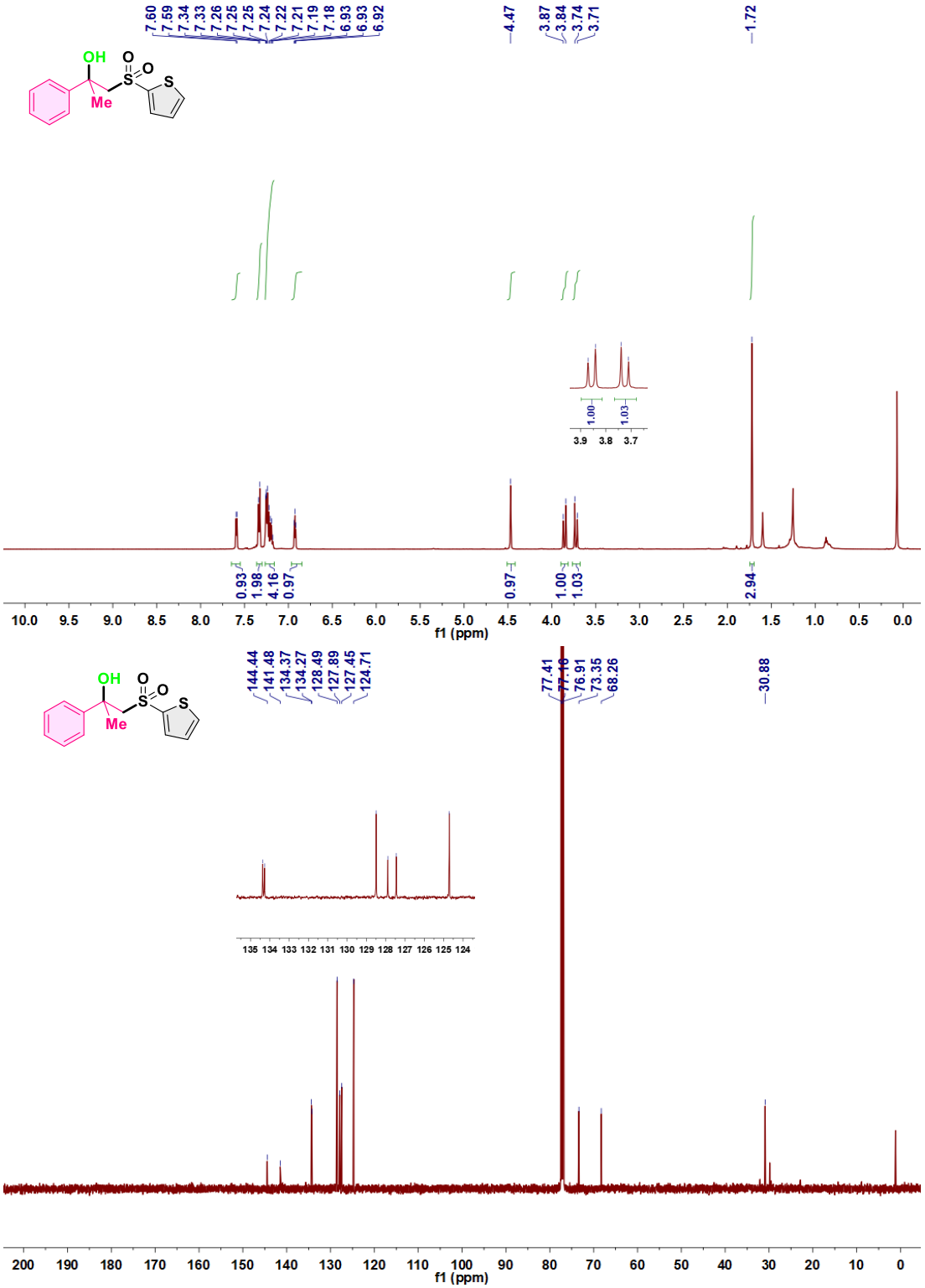


Fig. S21. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra of 2-phenyl-1-(thiophen-2-ylsulfonyl)propan-2-ol (**3Li**) in $CDCl_3$.

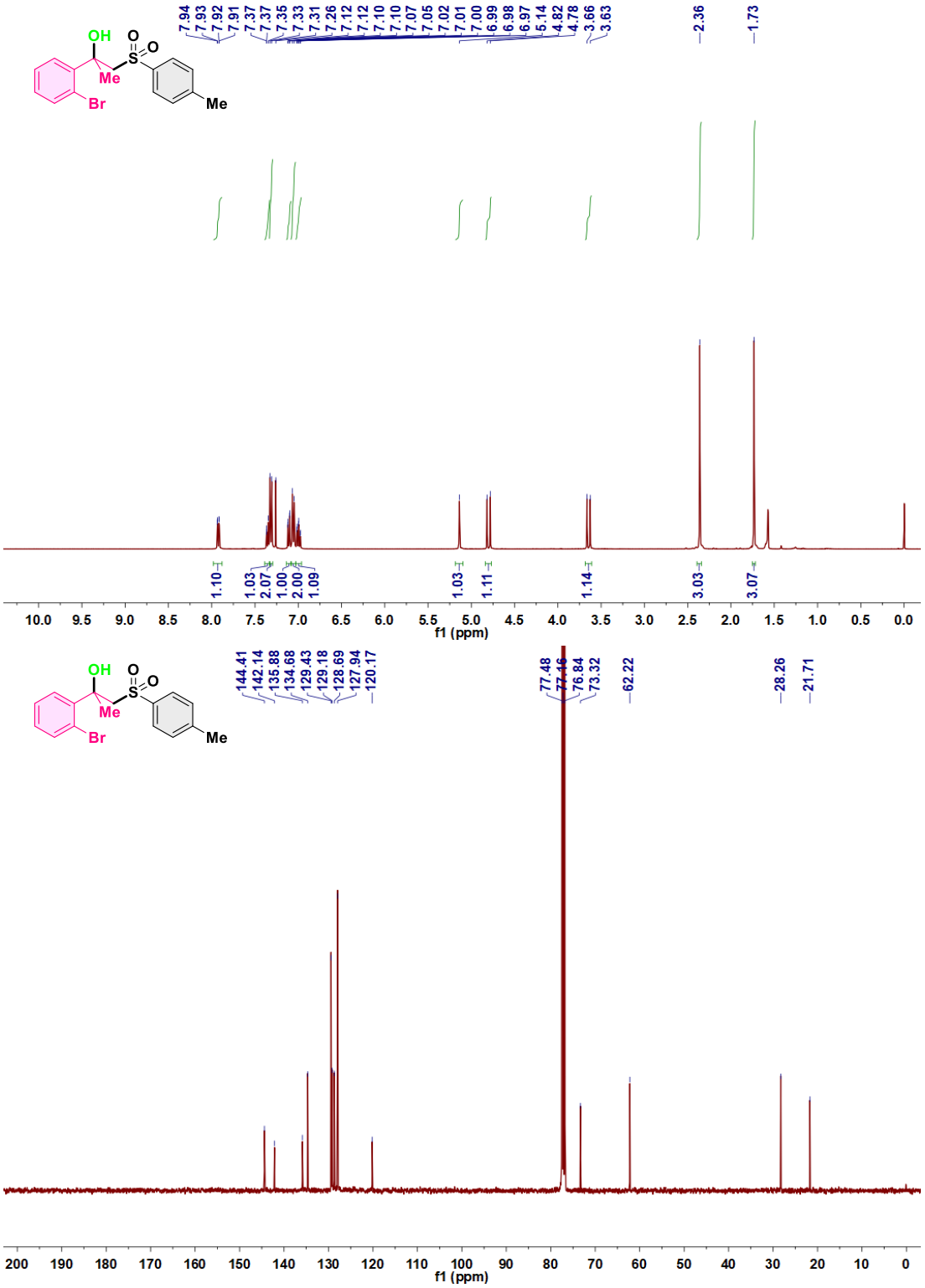


Fig. S22. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 2-(2-bromophenyl)-1-tosylpropan-2-ol (**3Mb**) in $CDCl_3$.

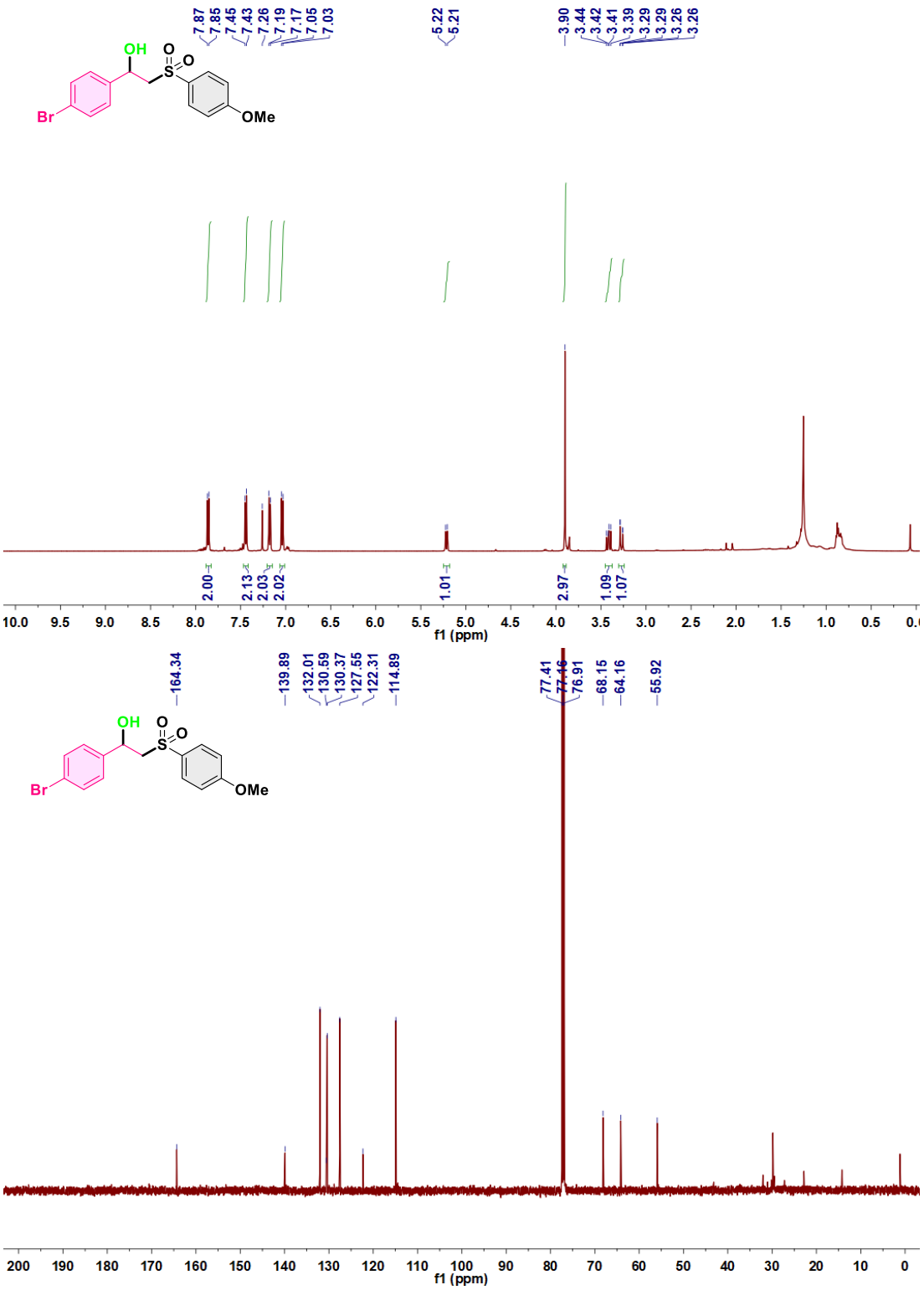


Fig. S23. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra of 1-(4-bromophenyl)-2-((4-methoxyphenyl)sulfonyl)ethan-1-ol (**3Fd**) in $CDCl_3$.

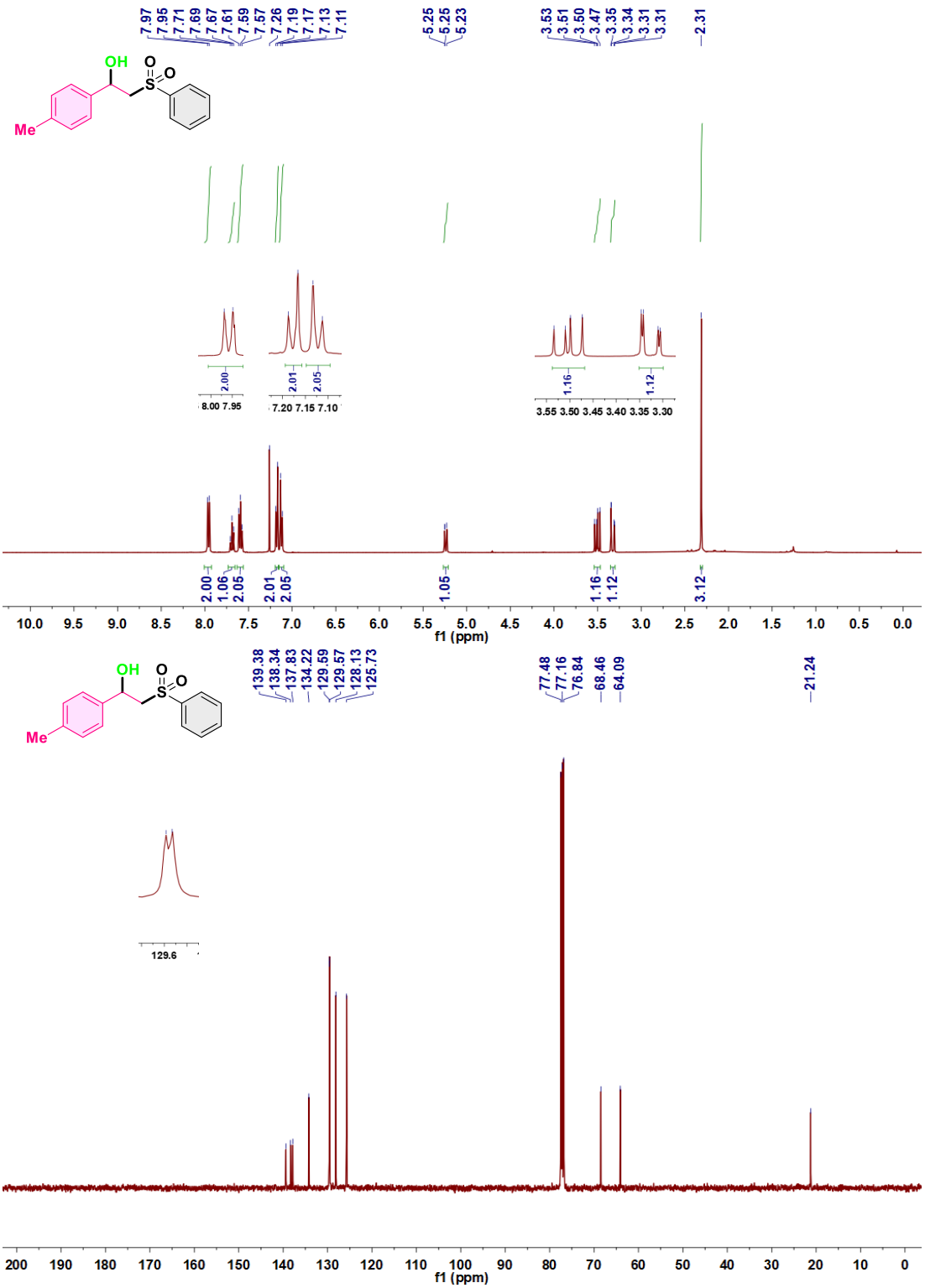


Fig. S24. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 2-(phenylsulfonyl)-1-(*p*-tolyl)ethan-1-ol (**3Ba**) in $CDCl_3$.

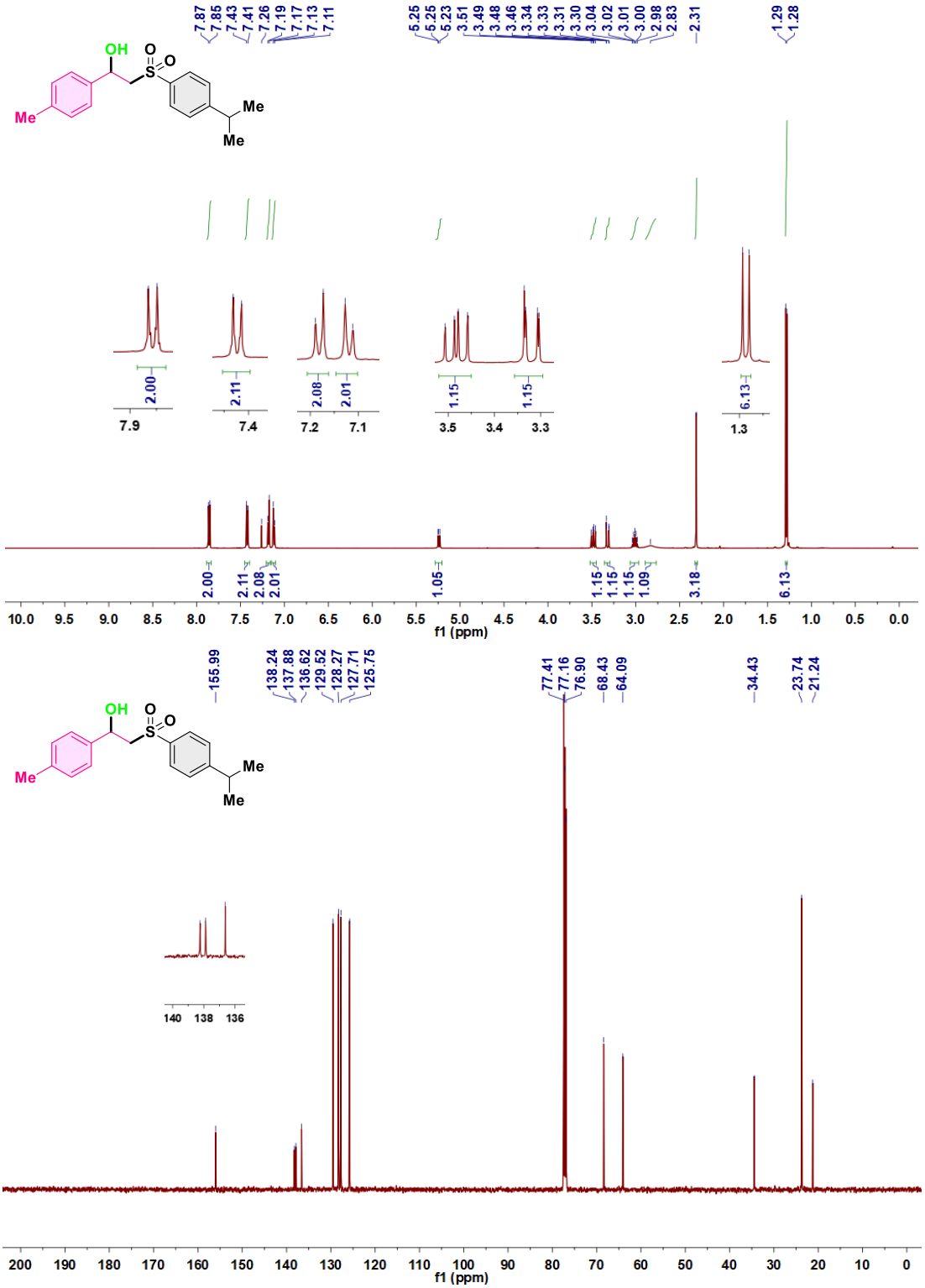


Fig. S25. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra of 2-((4-isopropylphenyl)sulfonyl)-1-(*p*-tolyl)ethan-1-ol (**3Bc**) in $CDCl_3$.

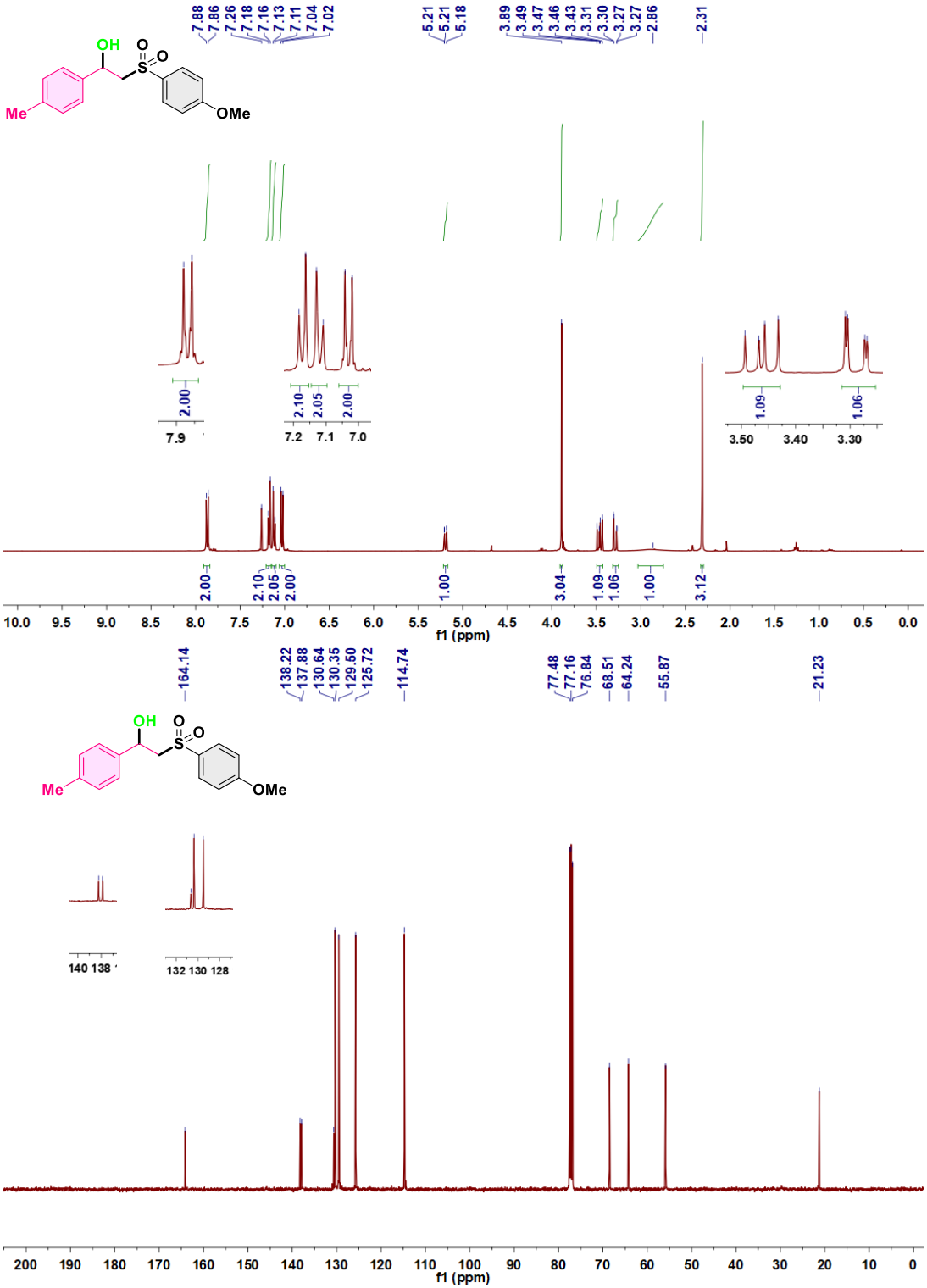


Fig. S26. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 2-((4-methoxyphenyl)sulfonyl)-1-(*p*-tolyl)ethan-1-ol (**3Bd**) in $CDCl_3$.

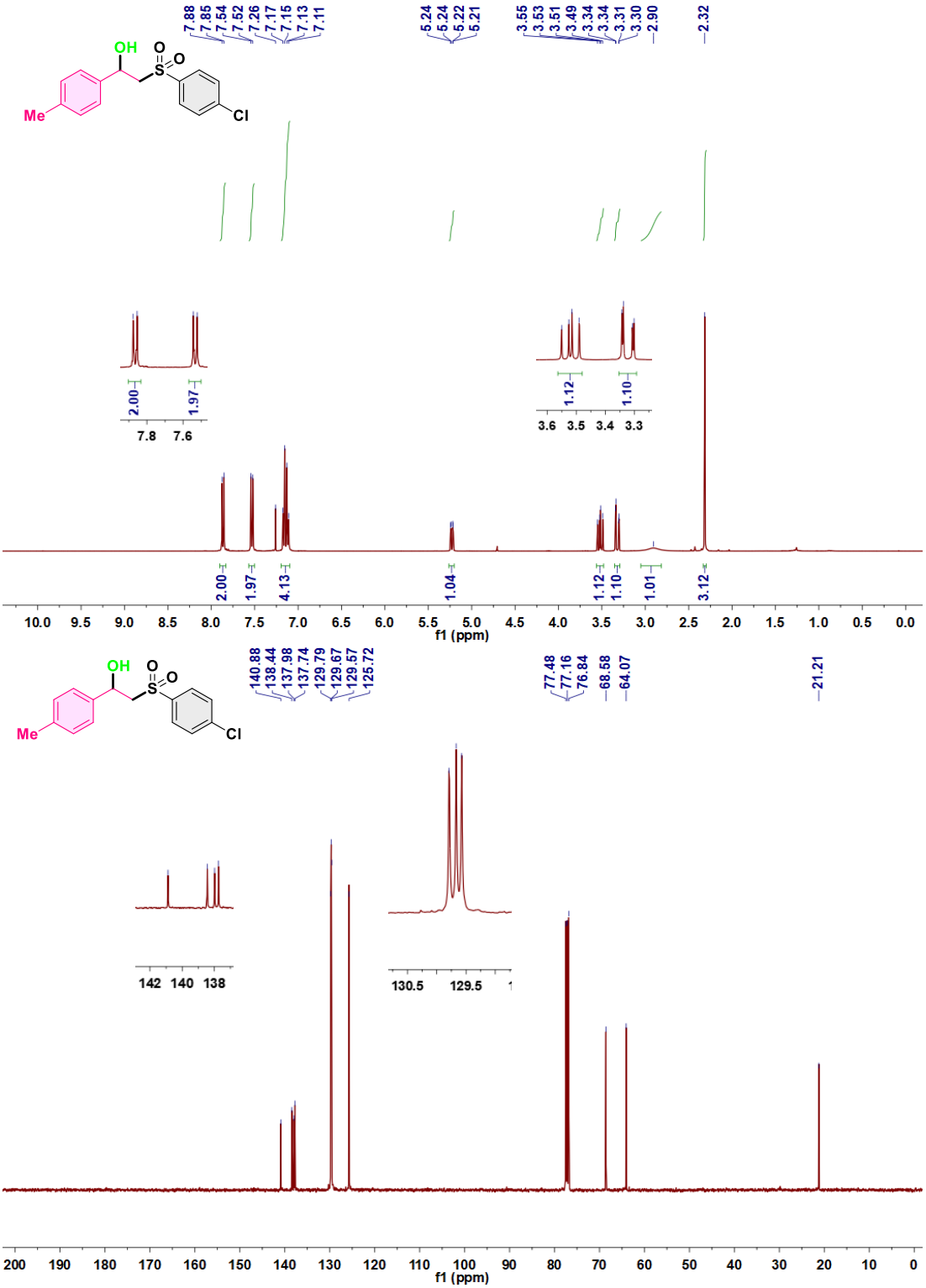


Fig. S27. ^{1}H (400 MHz) and ^{13}C NMR (126 MHz) spectra of 2-((4-chlorophenyl)sulfonyl)-1-(*p*-tolyl)ethan-1-ol (**3Be**) in $CDCl_3$.

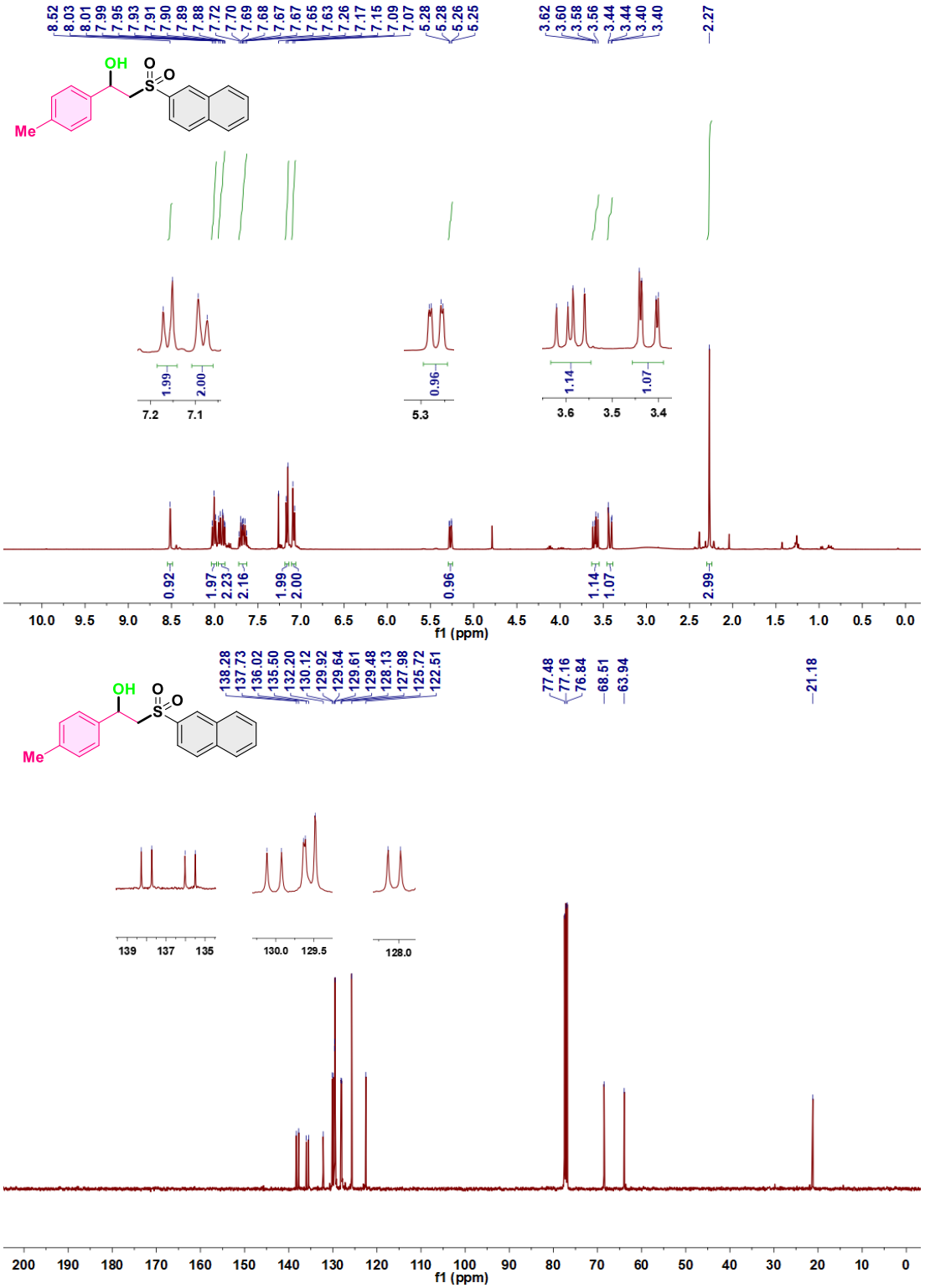


Fig. S28. ^{1}H (400 MHz) and ^{13}C (126 MHz) NMR spectra of 2-(naphthalen-2-ylsulfonyl)-1-(*p*-tolyl)ethan-1-ol (**3Bf**) in $CDCl_3$.

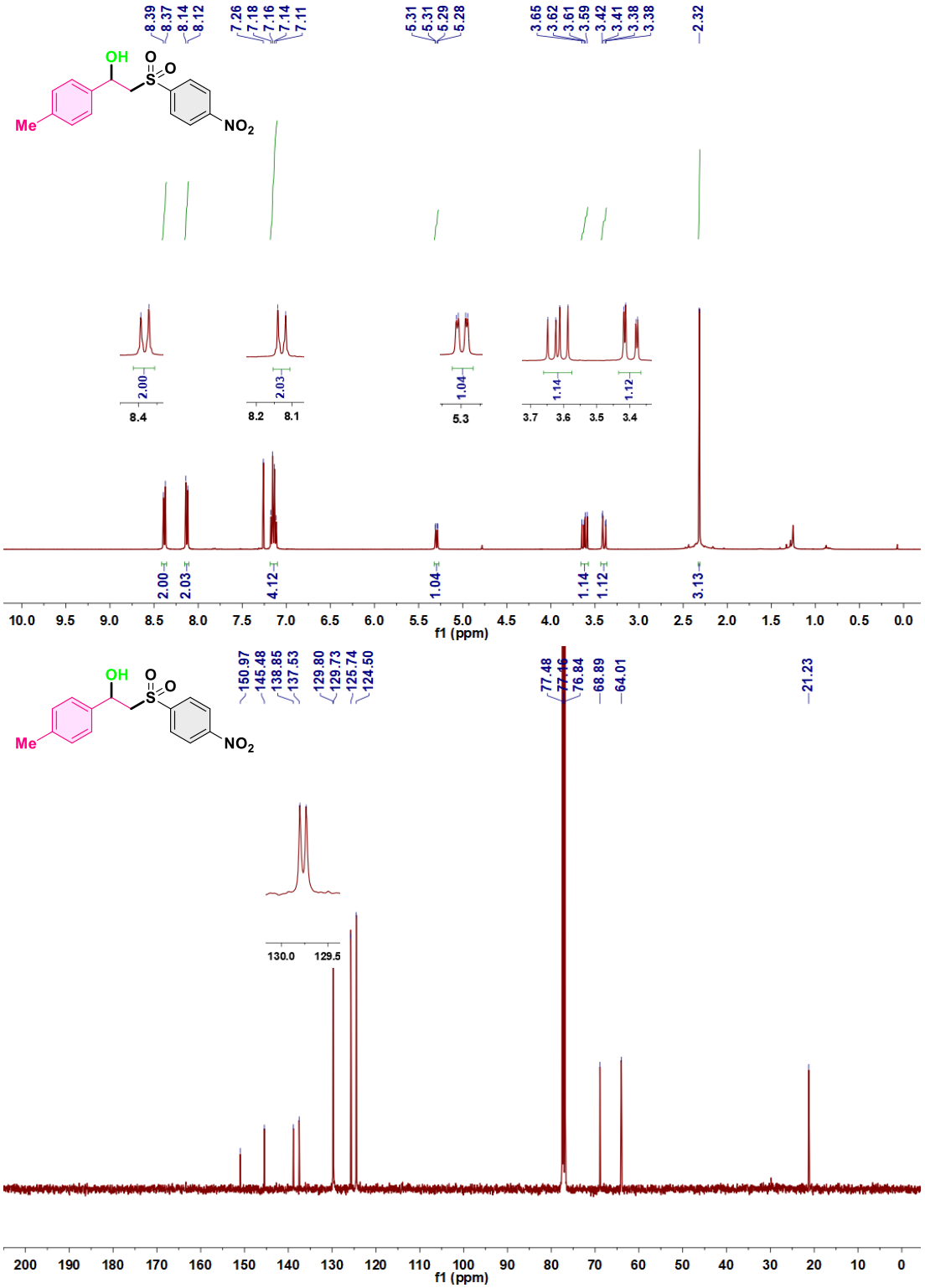


Fig. S29. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 2-((4-nitrophenyl)sulfonyl)-1-(*p*-tolyl)ethan-1-ol (**3Bg**) in $CDCl_3$.

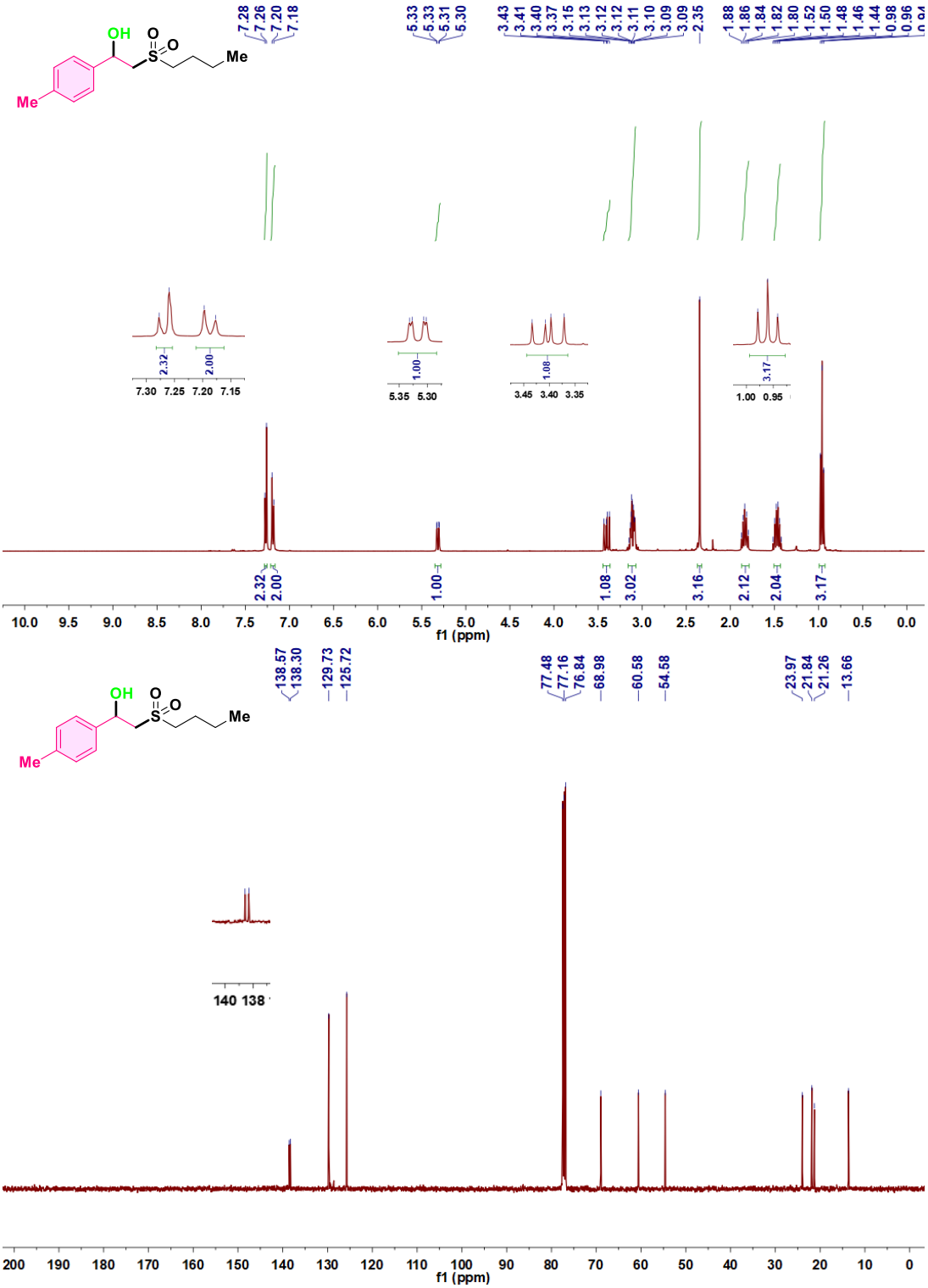


Fig. S30. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 2-(*n*-butylsulfonyl)-1-(*p*-tolyl)ethan-1-ol (**3Bh**) in $CDCl_3$.

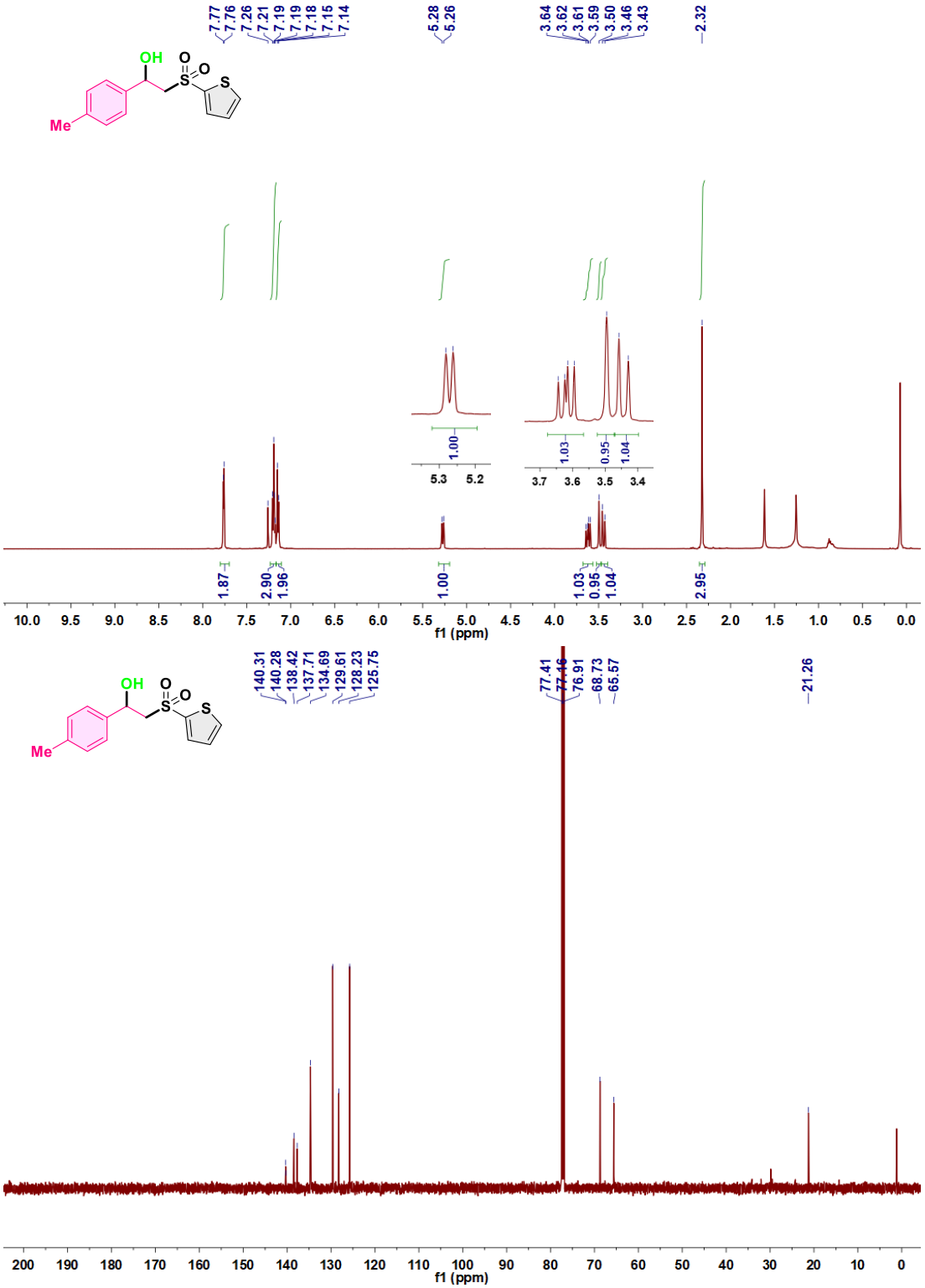


Fig. S31. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra of 2-(thiophen-2-ylsulfonyl)-1-(*p*-tolyl)ethan-1-ol (**3Bi**) in $CDCl_3$.

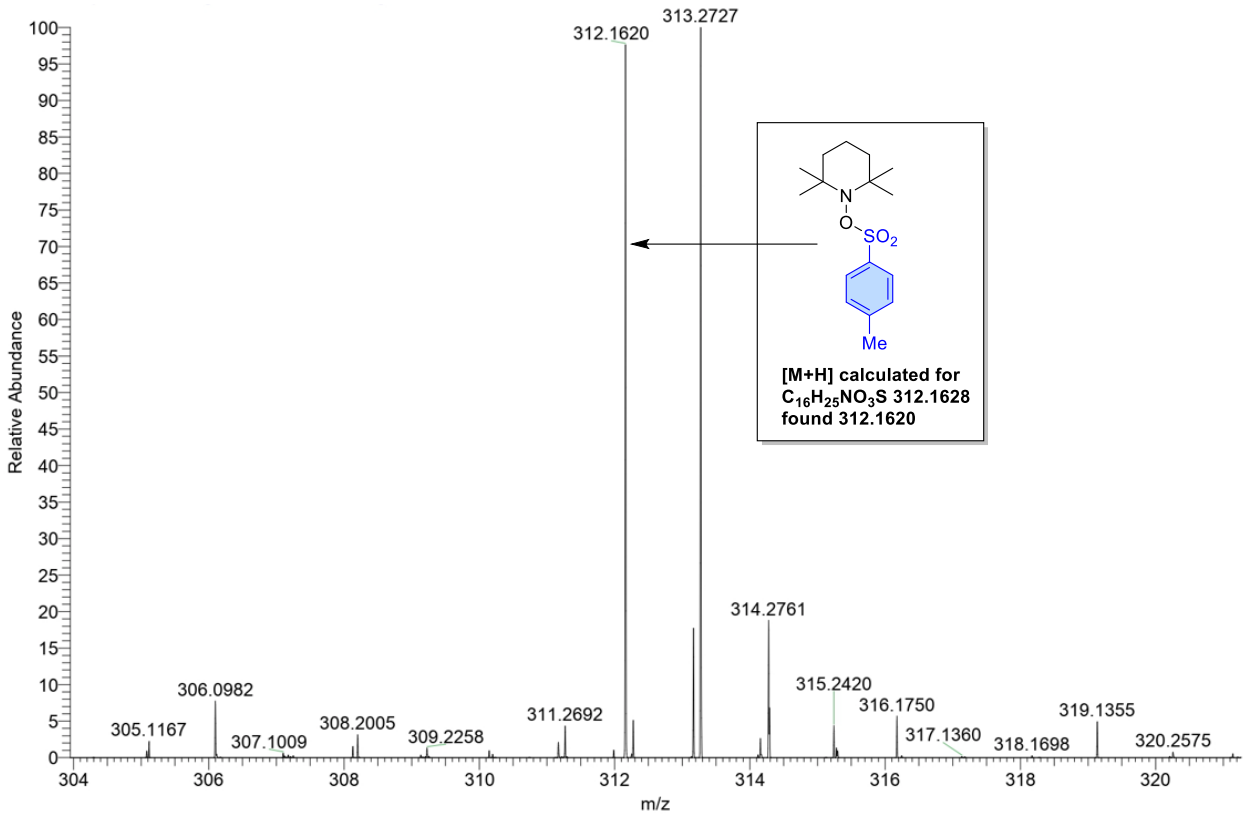


Fig. S32: HR-MS spectrum of the reaction mixture in the presence of TEMPO.

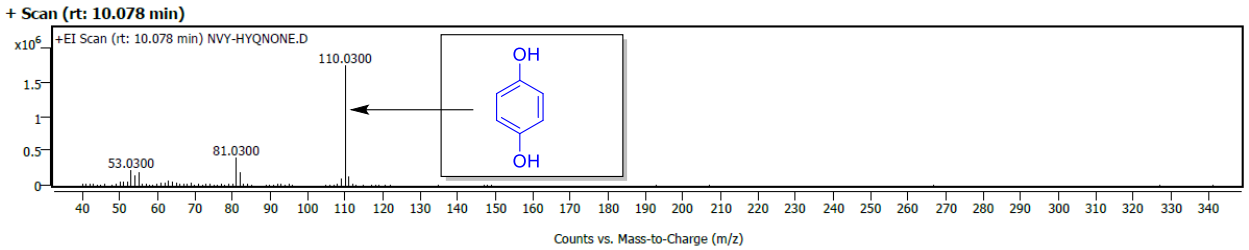


Fig.S33: GC-MS (EI) spectrum of the reaction mixture in the presence of *p*-benzoquinone.

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