Double C-N Bond Cleavages of N-Alkyl 4-Oxopiperidinium Salts: Access to Unsymmetrical Tertiary Sulfonamides

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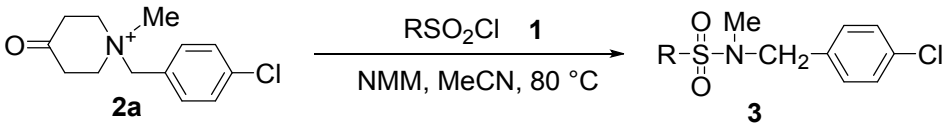
1. General Experimental Information

Analytic methods. All reactions were carried out under air atmosphere. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer or a Bruker 600 MHz spectrometer with $CDCl_3$ as solvent. Chemical shifts of ^{1}H NMR and ^{13}C NMR spectra are reported in parts per million (ppm) with TMS as an internal standard. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, quint = quintet, sx = sextet, sept = septet, m = multiplet and br = broad), and coupling constant (*J*) are in Hz. High resolution mass spectra (HRMS (ESI)) were performed using a 6520B Q-TOF high-resolution mass spectrometer. Column chromatography was performed on silica gel 300-400 mesh. Analytical thin layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. All reagents were purchased from commercial sources and were used as thus.

2. Details of experimental procedures

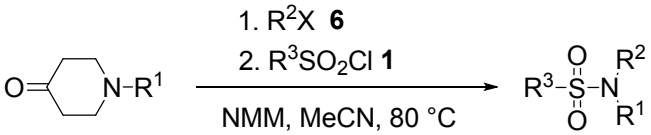
2.1 General procedure for the syntheses of compounds 3



2a **3**

In a 10 mL test tube were charged with sulfonyl chloride **1** (0.5 mmol), N-(4-chlorobenzyl)-N-methyl-4-oxopiperidin-1-ium chloride **2** (165 mg, 0.6 mmol), N-methylmorpholine (165 mg, 1.5 mmol) and acetonitrile (2.0 mL). The reaction mixtures were heated to 80 °C under air for 4h. Upon completion (TLC) and after cooling to ambient temperature, the reaction mixture was dissolved in ethyl acetate (10 mL) and washed successively with water (2×10 mL) and then brine (10 mL). The aqueous phase was further extracted with ethyl acetate (10 mL) and washed as previously. The organic phase was combined, dried over Na_2SO_4 and concentrated. Purification by silica gel column chromatography gave desired sulfonamide products **3**.

2.2 General procedure for the syntheses of compounds 5

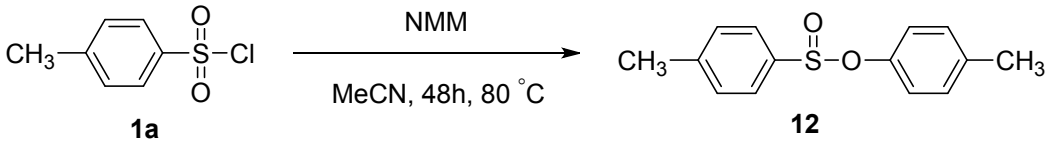


4 **5**

In a 10 mL test tube were charged with N-substituted 4-piperidinone **4** (0.6 mmol), organohalide **6** (0.6 mmol) and MeCN (2 mL). The reaction mixtures were stirred at 50 °C for 24h. Upon completion (TLC), N-methylmorpholine (165 mg, 1.5 mmol) and sulfonyl chloride (0.5 mmol) were added and the reaction mixtures were heated to 80 °C under air for 4 h. After cooling to ambient temperature, the reaction mixture was dissolved in ethyl acetate (10 mL) and washed successively with water (2×10 mL) and then brine (10 mL). The aqueous phase was further extracted with ethyl acetate (10 mL) and washed as previously. The organic phase was combined, dried over Na_2SO_4 and concentrated. Purification by silica gel column chromatography gave desired sulfonamide products **5** .

3. Mechanism screenings

3.1 Decomposition of TsCl in the presence of N-methylmorpholine



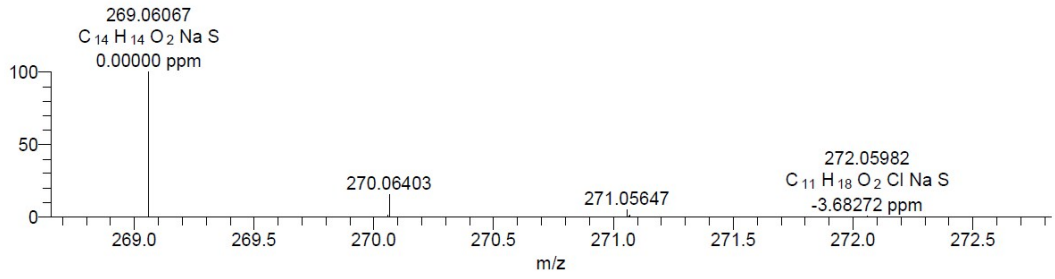
1a **12**

4-Methylbenzenesulfonyl chloride (191 mg, 1.0 mmol) and N-Methylmorpholine (152 mg, 1.5 mmol) were heated in MeCN (2 mL) to 80 °C under air for 48 h to yield **12** in 14.6% (18 mg) yield.

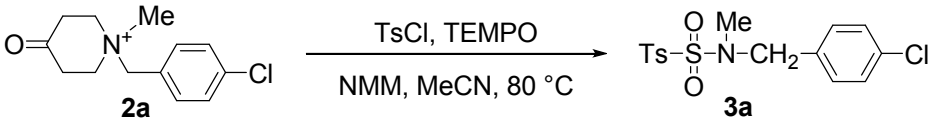
^{1}H NMR(400 MHz, $CDCl_3$) δ (ppm):7.46 (d, *J* = 8.0 Hz, 2H), 7.23 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm):144.4, 141.9, 140.3, 136.3, 130.0, 129.2, 127.4, 124.4, 21.5, 21.3.

HRMS (ESI) *m/z*: Calcd for $C_{14}H_{14}O_2NaS$ $[M+Na]^+$ 269.06067; Found 269.06067.



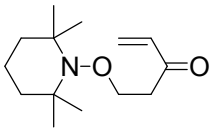
3.2 Trapping radicals with TEMPO



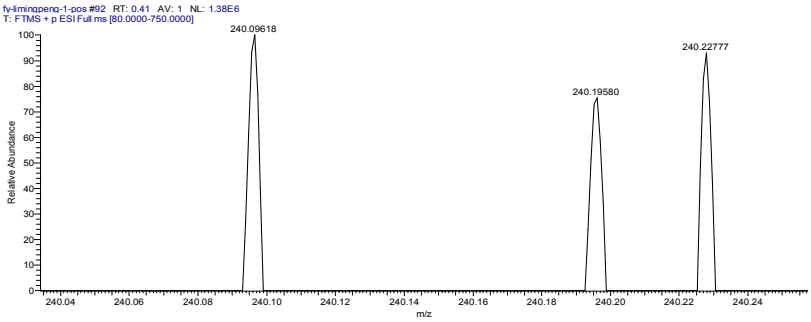
2a **3a**

A solution of 4-methylbenzenesulfonyl chloride (95 mg, 0.5 mmol), 1-(4-chlorobenzyl)-1-methyl-4-oxopiperidin-1-ium chloride (163.5 mg, 0.6 mmol), N-Methylmorpholine (151 mg, 1.5 mmol) and TEMPO (156 mg, 1.0 mmol) in CH_3CN (2.0 mL) were heated to 80 °C under air for 4 h. Then the reaction solution was submitted to HRMS examination. The main radical species or intermediates that are detected by HRMS analysis are listed below.

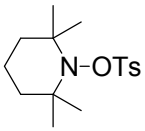
(1) 5-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pent-1-en-3-one (10)



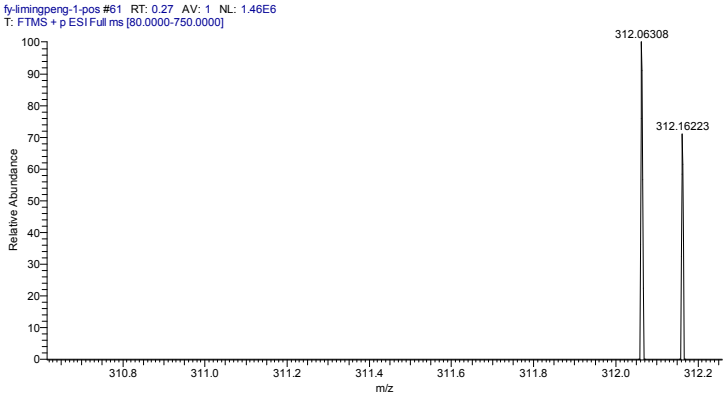
HRMS (ESI) *m/z*: Calcd for $C_{14}H_{26}O_2N$ $[M+H]^+$ 240.19581; Found 240.19580.



(2) 2,2,6,6-tetramethylpiperidin-1-yl 4-methylbenzenesulfonate (11)



HRMS (ESI) *m/z*: Calcd for $C_{16}H_{26}NO_3S$ $[M+H]^+$ 312.16279; Found 312.16223.

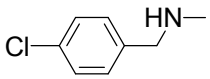


Compoind **11** was also isolated from above reaction system as a main product in 42% isolated yield.

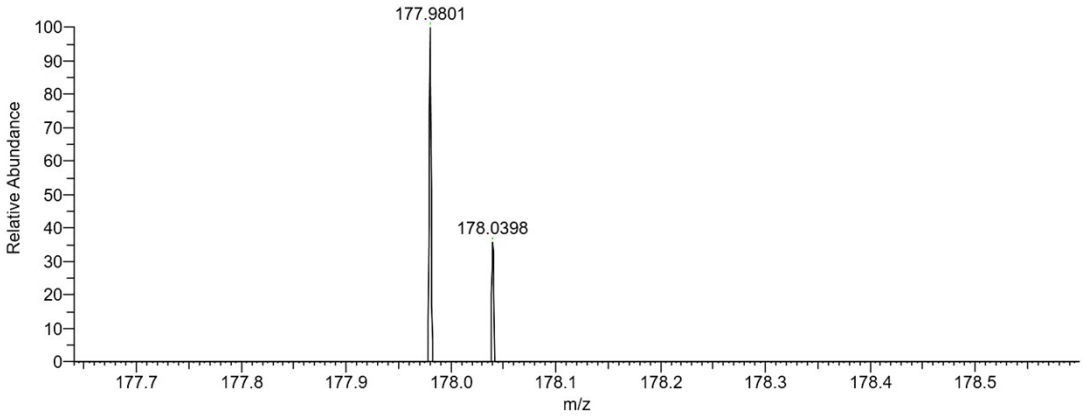
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.48 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 2.29 (s, 3H), 1.72-1.62 (m, 2H), 1.57-1.49 (m, 4H), 1.34 (s, 12H).

^{13}C NMR (151 HMz, DMSO-d_6) δ (ppm): 145.5, 138.4, 128.6, 125.9, 56.1, 34.6, 27.1, 21.2, 16.3.

(3) 1-(4-Chlorophenyl)-N-methylmethanamine (V)

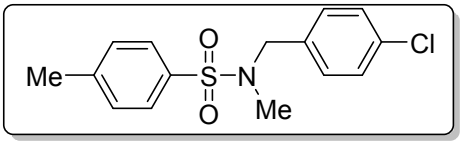


HRMS (ESI) *m/z*: calcd for $C_8H_{11}NClNa$ $[M+Na]^+$ 178.03940; Found 178.0389.



4. Compound characterization data

***N*-(4-Chlorobenzyl)-*N*,4-dimethylbenzenesulfonamide (3a)**



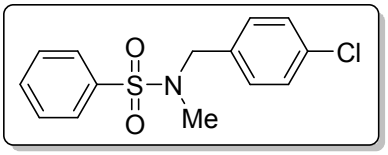
The reaction of 4-methylbenzenesulfonyl chloride (95 mg, 0.5 mmol),1-(4-chlorobenzyl)-1-methyl-4-oxopiperidin-1-ium chloride (163.5 mg, 0.6 mmol) and N-Methylmorpholine (151 mg, 1.5 mmol) in MeCN (2 mL) affords **3a** in 76% (117 mg) yield. White solid; Mp: 82 - 84 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.71 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.09 (s, 2H), 2.58 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 143.9, 134.5, 134.4, 133.9, 130.0, 129.9, 129.0, 127.7, 53.7, 34.6, 21.8.

HRMS (ESI) *m/z*: Calcd for $C_{15}H_{16}O_2NClNaS$ $[M+Na]^+$ 332.04880; Found 332.04868.

***N*-(4-Chlorobenzyl)-*N*-methylbenzenesulfonamide (3b)**



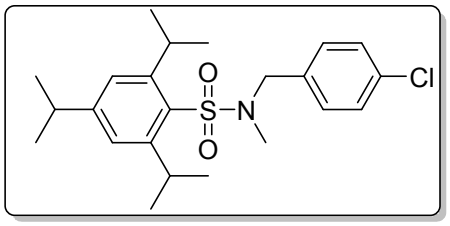
The reaction of benzenesulfonyl chloride (87.5 mg, 0.5 mmol), 1-(4-chlorobenzyl)-1-methyl-4-oxopiperidin-1-ium chloride (327.6 mg, 1.2 mmol) and N-Methylmorpholine (151 mg, 1.5 mmol) in MeCN (2 mL) affords **3b** in 71% (104 mg) yield. White solid; Mp: 61 - 63 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.86 – 7.82 (m, 2H), 7.64 – 7.62 (m, 1H), 7.58 – 7.56 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 4.12 (s, 2H), 2.60 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 137.3, 134.2, 133.8, 132.8, 129.6, 129.2, 128.8, 127.4, 53.5, 34.4.

HRMS (ESI) *m/z*: Calcd for $C_{14}H_{14}O_2NClNaS$ $[M+Na]^+$ 318.03260; Found 318.03262.

***N*-(4-Chlorobenzyl)-2,4,6-triisopropyl-*N*-methylbenzenesulfonamide (3c)**



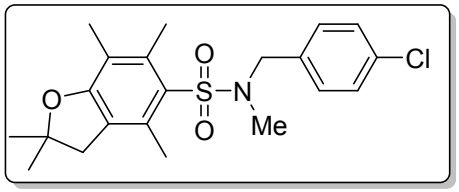
The reaction of 2,4,6-triisopropylbenzenesulfonyl chloride (151 mg, 0.5 mmol), 1-(4-ch lorobenzyl)-1-methyl-4-oxopiperidin-1-ium chloride (327.6 mg, 1.2 mmol) and N-Methylmor pholine (151 mg, 1.5 mmol) in MeCN (2 mL) affords **3c** in 45% (94 mg) yield. White s olid; Mp: 127 - 128 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.30 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.19 (s, 2H), 4.33 (s, 2H), 4.24 – 4.18 (m, 2H), 3.01 – 2.76 (m, 1H), 2.57 (s, 3H), 1.26 (dd, *J* = 4.2, 3.6 Hz, 18H).

^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm): 153.3, 151.6, 134.3, 133.7, 130.4, 130.1, 128.7, 123.9, 51.4, 34.2, 33.0, 29.4, 24.8, 23.5.

HRMS (ESI) (ESI) *m/z*: Calcd for $C_{23}H_{33}O_2NClS$ $[M+H]^+$ 422.19150; Found 422.19150.

***N*-(4-Chlorobenzyl)-*N*,2,2,4,6,7-hexamethyl-2,3-dihydrobenzofuran-5-sulfonamide (3d)**



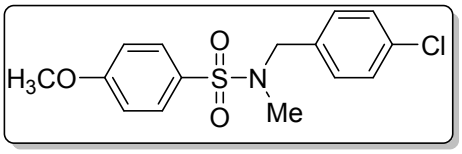
The reaction of 2,2,4,6,7-pentamethyl-2,3-dihydrobenzofuran-5-sulfonyl chloride (144 m g, 0.5 mmol), 1-(4-chlorobenzyl)-1-methyl-4-oxopiperidin-1-ium chloride (327.6 mg, 1.2 m mol) and N-Methylmorpholine (151 mg, 1.5 mmol) in MeCN (2 mL) affords **3d** in 73% (148 mg) yield. White solid; Mp: 124 - 126 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.28(d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 4.23 (s, 2H), 2.99 (s, 2H), 2.58 (s, 3H), 2.55 (s, 3H), 2.51 (s, 3H), 2.13 (s, 3H), 1.49 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 160.1, 140.8, 135.4, 134.7, 133.6, 129.9, 128.7, 125.9, 125.2, 118.2, 86.9, 52.0, 43.2, 32.6, 28.5, 19.3, 17.7, 12.5.

HRMS (ESI) *m/z*: Calcd for $C_{21}H_{27}O_3NClS$ $[M+H]^+$ 408.13947; Found 408.13858.

_N_-(4-Chlorobenzyl)-4-methoxy-_N_-methylbenzenesulfonamide (3e)



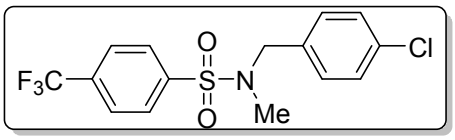
The reaction of 4-methoxybenzenesulfonyl chloride (103 mg, 0.5 mmol), 1-(4-chlorobenzyl)-1-methyl-4-oxopiperidin-1-ium chloride (327.6 mg, 1.2 mmol) and N-Methylmorpholine (151 mg, 1.5 mmol) in MeCN (2 mL) affords **3e** in 80% (130 mg) yield. White solid; Mp: 132 - 134 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.77 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 2H), 4.08 (s, 2H), 3.89 (s, 3H), 2.57 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 163.0, 134.3, 133.7, 129.7, 129.5, 128.8, 114.3, 55.6, 53.5, 34.4 .

HRMS (ESI) *m/z*: Calcd for $C_{15}H_{17}O_3NClS$ $[M+H]^+$ 326.06122; Found 326.06107.

_N_-(4-Chlorobenzyl)-_N_-methyl-4-(trifluoromethyl)benzenesulfonamide (3f)



The reaction of 4-(trifluoromethyl)benzenesulfonyl chloride (121 mg, 0.5 mmol), 1-(4-chlorobenzyl)-1-methyl-4-oxopiperidin-1-ium chloride (327.6 mg, 1.2 mmol) and N-Methylmorpholine (151 mg, 1.5 mmol) in MeCN (2 mL) affords **3f** in 55%(100 mg) yield. White solid; Mp: 86 - 88 °C.

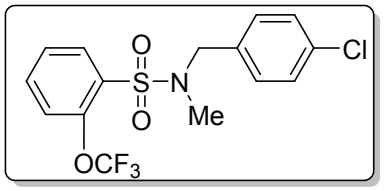
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.96 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 4.16 (s, 2H), 2.65 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 141.1, 135.2 – 133.1 (m), 129.6, 129.0, 127.8, 126.4 (q, *J* = 3.7 Hz), 124.1, 122.3, 110.0, 53.4, 34.4 .

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -63.52 .

HRMS (ESI) *m/z*: Calcd for $C_{16}H_{14}NO_4F_3ClS$ $[M+HCOO]^-$ 408.02842; Found 408.02881.

***N*-(4-Chlorobenzyl)-N-methyl-2-(trifluoromethoxy)benzenesulfonamide (3g)**



The reaction of 2-(trifluoromethoxy)benzenesulfonyl chloride (130 mg, 0.5 mmol), 1-(4-chlorobenzyl)-1-methyl-4-oxopiperidin-1-ium chloride (163.8 mg, 0.6 mmol) and N-Methylmorpholine (151 mg, 1.5 mmol) in MeCN (2 mL) affords **3g** in 41% (77 mg) yield. Colorless liquid.

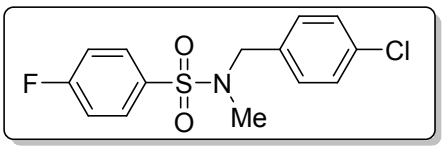
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.07 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.64 (ddd, *J* = 8.4, 7.4, 1.6 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.27 – 7.24 (m, 2H), 4.33 (s, 2H), 2.72 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 146.1, 134.4 (d, *J* = 6.0 Hz), 133.8, 132.0, 131.2, 129.5, 128.8, 126.5, 121.1, 120.2 (d, *J* = 1.9 Hz), 119.4, 53.2, 34.0 .

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -56.34 .

HRMS (ESI) *m/z*: Calcd for $C_{15}H_{13}O_3NClF_3NaS$ $[M+Na]^+$ 402.01545; Found 402.01499.

***N*-(4-Chlorobenzyl)-4-fluoro-*N*-methylbenzenesulfonamide (3h)**



The reaction of 4-fluorobenzenesulfonyl chloride (97 mg, 0.5 mmol), 1-(4-chlorobenzyl)-1-methyl-4-oxopiperidin-1-ium chloride (327.6 mg, 1.2 mmol) and N-Methylmorpholine (151 mg, 1.5 mmol) in MeCN (2 mL) affords **3h** in 55% (86 mg) yield. White solid; Mp: 80 - 82 °C.

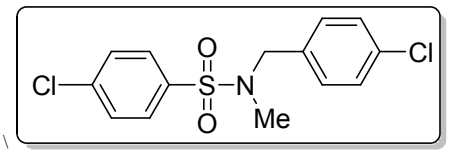
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.86 – 7.84 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.23 (m, 4H), 4.12 (s, 2H), 2.60 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 165.7(d, *J* = 254.9 Hz), 133.9(d, *J* = 4.8 Hz), 130.1, 130.0, 129.6, 128.9, 116.5, 116.4, 53.5, 34.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -103.08 – -109.20 (m).

HRMS (ESI) *m/z*: Calcd for $C_{14}H_{13}O_2NClFNaS$ $[M+Na]^+$ 336.02318; Found 336.02358.

4-Chloro-*N*-(4-chlorobenzyl)-*N*-methylbenzenesulfonamide (3i)



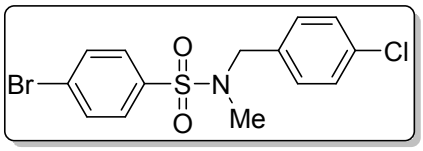
The reaction of 4-chlorobenzenesulfonyl chloride (105 mg, 0.5 mmol), 1-(4-chlorobenzyl)-1-methyl-4-oxopiperidin-1-ium chloride (327.6 mg, 1.2 mmol) and N-Methylmorpholine (151 mg, 1.5 mmol) in MeCN (2 mL) affords **3i** in 53% (87 mg) yield. White solid; Mp: 143 - 144 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.77 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.11 (s, 2H), 2.60 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 139.4, 135.9, 133.9, 133.9, 129.6, 129.5, 128.9, 128.8, 53.5, 34.3.

HRMS (ESI) *m/z*: Calcd for $C_{14}H_{13}O_2NCl_2$ NaS $[M+Na]^+$ 351.99363; Found 351.99355.

4-Bromo-*N*-(4-chlorobenzyl)-*N*-methylbenzenesulfonamide (3j)



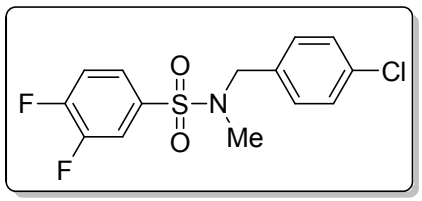
The reaction of 4-bromobenzenesulfonyl chloride (127 mg, 0.5 mmol), 1-(4-chlorobenzyl)-1-methyl-4-oxopiperidin-1-ium chloride (327.6 mg, 1.2 mmol) and N-Methylmorpholine (151 mg, 1.5 mmol) in MeCN (2 mL) affords **3j** in 65% (120 mg) yield. White solid; Mp: 102 - 103 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.71 – 7.68 (m, 4H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.11 (s, 2H), 2.60 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 136.5, 134.0, 133.9, 132.5, 129.7, 128.9, 128.9, 127.8, 53.5, 34.4.

HRMS (ESI) *m/z*: Calcd for $C_{14}H_{13}O_2NBrClNaS$ $[M+Na]^+$ 395.9437; Found 395.9423.

***N*-(4-Chlorobenzyl)-3,4-difluoro-*N*-methylbenzenesulfonamide (3k)**



The reaction of 3,4-difluorobenzenesulfonyl chloride (106 mg, 0.5 mmol), 1-(4-chlorobenzyl)-1-methyl-4-oxopiperidin-1-ium chloride (327.6 mg, 1.2 mmol) and N-Methylmorpholine (151 mg, 1.5 mmol) in MeCN (2 mL) affords **3k** in 54%(89 mg) yield. White solid; Mp: 78 - 79 °C.

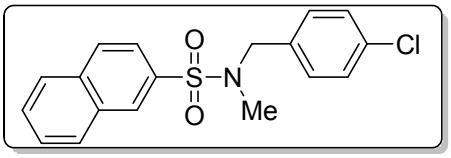
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.35 - 7.37 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.23 (m, 2H), 7.07 (tt, *J* = 8.5, 2.3 Hz, 2H), 4.15 (s, 1H), 2.65 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 163.8 (d, *J* = 11.6 Hz), 162.0, 134.1, 133.5, 129.6, 129.0, 110.8 (dd, *J* = 21.5, 6.5 Hz), 108.4 (t, *J* = 25.0 Hz), 53.5, 34.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -105.65 (dd, *J* = 8.5, 5.8 Hz).

HRMS (ESI) *m/z*: Calcd for $C_{14}H_{12}O_2NClF_2NaS$ $[M+Na]^+$ 354.01375; Found 354.01356.

***N*-(4-Chlorobenzyl)-*N*-methylnaphthalene-2-sulfonamide (3n)**



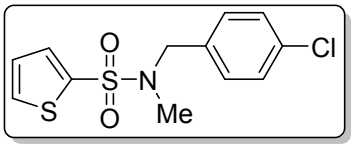
The reaction of naphthalene-2-sulfonyl chloride (113 mg, 0.5 mmol), 1-(4-chlorobenzyl)-1-methyl-4-oxopiperidin-1-ium chloride (327.6 mg, 1.2 mmol) and N-Methylmorpholine (151 mg, 1.5 mmol) in MeCN (2 mL) affords **3n** in 55% (95 mg) yield. White solid; Mp: >200 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.41 (s, 1H), 8.01 (t, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.82 (dd, *J* = 1.8, 1.8 Hz, 1H), 7.70 – 7.59 (m, 2H), 7.31 (d, *J* = 9.0 Hz, 2H), 7.26 (d, *J* = 9.0 Hz, 2H), 4.18 (s, 2H), 2.65 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 139.4, 134.8, 134.4, 134.2, 133.8, 132.3, 129.7, 129.4, 129.2, 128.8, 128.8, 127.9, 127.6, 53.6, 34.4 .

HRMS (ESI) *m/z*: Calcd for $C_{18}H_{17}O_2NClS$ $[M+H]^+$ 346.06630; Found 346.06596.

_N_-(4-Chlorobenzyl)-_N_-methylthiophene-2-sulfonamide (3o)



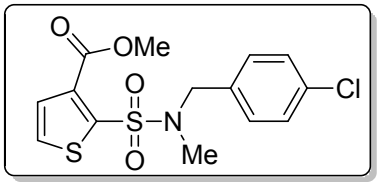
The reaction of thiophene-2-sulfonyl chloride (90 mg, 0.5 mmol), 1-(4-chlorobenzyl)-1-methyl-4-oxopiperidin-1-ium chloride (327.6 mg, 1.2 mmol) and N-Methylmorpholine (151 mg, 1.5 mmol) in MeCN (2 mL) affords **3o** in 45% (67 mg) yield. Yellow viscous oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.62 (dd, *J* = 1.2, 1.2 Hz,1H), 7.45 (dd, *J* = 1.2, 1.8 Hz,1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 6.6 Hz, 2H), 7.15 (dd, *J* = 3.0, 3.6 Hz, 1H), 4.28 (d, *J* = 14.4 Hz, 1H), 4.19 (d, *J* = 14.4 Hz,1H), 2.60 (s, 3H).

^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm): 146.5, 135.0, 133.6, 131.4, 130.1, 129.7, 128.8, 127.9, 54.4, 32.8.

HRMS (ESI) *m/z*: Calcd for $C_{12}H_{13}O_2NClS_2$ $[M+H]^+$ 302.00707; Found 302.00732.

Methyl 2-(_N_-(4-chlorobenzyl)-_N_-methylsulfamoyl)thiophene-3-carboxylate (3p)



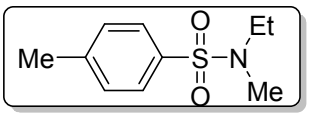
The reaction of methyl 2-(chlorosulfonyl)thiophene-3-carboxylate (120 mg, 0.5 mmol), 1-(4-chlorobenzyl)-1-methyl-4-oxopiperidin-1-ium chloride (327.6 mg, 1.2 mmol) and N-Met hylmorpholine (151 mg, 1.5 mmol) in MeCN (2 mL) affords **3p** in 45% (80 mg) yield. White solid; Mp: 107 - 109 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.51 (s, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 9.6 Hz, 2H), 4.45 (s, 2H), 3.93 (s, 3H), 2.78 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 160.0, 141.7, 134.7, 133.7, 131.5, 129.6, 129.1, 128.8, 110.0, 53.7, 53.0, 34.4.

HRMS (ESI) *m/z*: Calcd for $C_{14}H_{14}O_4NClNaS_2$ $[M+Na]^+$ 381.9950; Found 381.9945.

_N_-Ethyl-_N_,4-dimethylbenzenesulfonamide (5a)[1]

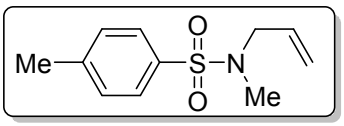


According to general procedure 2.2, **5a** was obtained in 76% (81 mg) isolated yield. White solid; Mp: 28 - 30 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.66 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 3.08 (q, *J* = 7.2 Hz, 2H), 2.72 (s, 3H), 2.42 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 143.2, 134.7, 129.6, 127.3, 44.8, 33.9, 21.4, 13.0.

_N_-Allyl-_N_,4-dimethylbenzenesulfonamide (5b)[2]

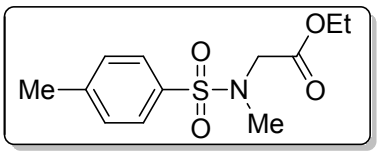


According to general procedure 2.2, **5b** was obtained in 42% (47 mg) yield as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.68 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 5.86 – 5.61 (m, 1H), 5.22 – 5.13 (m, 2H), 3.63 (d, *J* = 6.6 Hz, 2H), 2.66 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 143.3, 134.5, 132.6, 129.6, 127.5, 119.1, 53.0, 34.2, 21.5.

Ethyl 2-(N,4-dimethylphenylsulfonamido)acetate (5c)



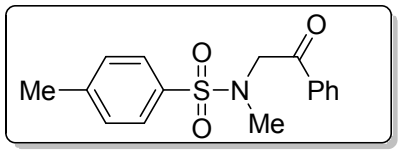
According to general procedure 2.2, **5c** was obtained in 47% (63 mg) yield as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.62 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 4.18 (qt, *J* = 7.1, 3.6 Hz, 2H), 3.90 (d, *J* = 17.4 Hz, 1H), 3.77 (d, *J* = 17.4 Hz, 1H), 2.71 (s, 3H), 2.41 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 169.5, 141.4, 140.5, 129.6, 126.4, 61.2, 52.6, 34.5, 21.3, 14.1.

HRMS (ESI) *m/z*: Calcd for $C_{12}H_{18}O_4NS$ $[M+H]^+$ 272.09511; Found 272.09481.

***N*,4-Dimethyl-*N*-(2-oxo-2-phenylethyl)benzenesulfonamide (5d)**[3]

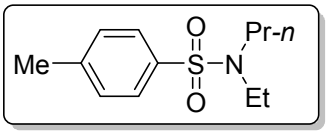


According to general procedure 2.2, **5d** was obtained in 44% (66 mg) isolated yield. Yellowish solid; Mp: 111 - 113 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.98 (d, J = 7.2 Hz, 2H), 7.73 (d, J = 7.8 Hz, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 4.57 (s, 2H), 2.83 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 193.7, 143.6, 134.8, 134.7, 133.8, 129.6, 128.8, 128.3, 127.6, 56.1, 35.6, 21.5.

***N*-Ethyl-4-methyl-*N*-propylbenzenesulfonamide (5e)**[4]

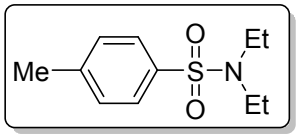


According to general procedure 2.2, **5e** was obtained in 62% (74 mg) isolated yield as a yellowish viscous oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.69 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 3.19(q, *J* = 7.2 Hz, 2H), 3.09 – 3.05 (m, 2H), 2.40 (s, 3H), 1.60 – 1.52 (m, 2H), 1.10 (t, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 142.8, 137.3, 129.5, 127.0, 49.3, 42.6, 22.0, 21.4, 14.1, 11.1.

***N*,*N*-Diethyl-4-methylbenzenesulfonamide (5f)**[5]

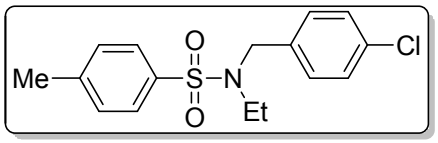


According to general procedure 2.2, **5f** was obtained in 72% (81 mg) isolated yield. White solid; Mp: 59 - 61 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.69 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 3.22 (q, *J* = 7.2 Hz, 4H), 2.41 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 142.9, 137.4, 129.5, 127.0, 42.0, 21.4, 14.1.

***N*-(4-Chlorobenzyl)-*N*-ethyl-4-methylbenzenesulfonamide (5g)**



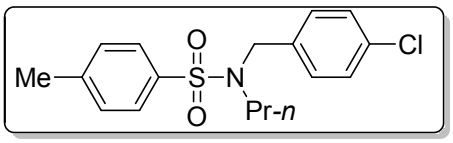
According to general procedure 2.2, **5g** was obtained in 46% (74 mg) isolated yield. White solid; Mp: 56 - 58 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.72 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 1H), 4.29 (s, 2H), 3.18 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 0.92 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 143.3, 137.1, 135.2, 133.5, 129.7, 129.5, 128.7, 127.1, 50.5, 42.5, 21.5, 13.4.

HRMS (ESI) *m/z*: Calcd for $C_{16}H_{19}O_2NClS$ $[M+H]^+$ 324.08195; Found 324.08194.

***N*-(4-Chlorobenzyl)-4-methyl-*N*-propylbenzenesulfonamide (5h)**



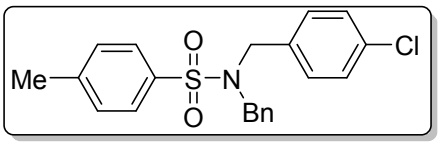
According to general procedure 2.2, **5h** was obtained in 53% (89 mg) isolated yield. White solid; Mp: 79 - 81 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.71 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 4.27 (s, 2H), 3.11 – 3.02 (m, 2H), 2.44 (s, 3H), 1.40 – 1.23 (m, 2H), 0.71 (t, *J* = 15 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 143.3, 134.0, 135.4, 133.5, 129.7, 129.5, 128.7, 127.1, 51.3, 50.1, 21.5, 21.4, 11.1.

HRMS (ESI) *m/z*: Calcd for $C_{14}H_{14}O_2NSCl$ $[M+H]^+$ 338.09760; Found 338.09756.

***N*-Benzyl-*N*-(4-chlorobenzyl)-4-methylbenzenesulfonamide (5i)**



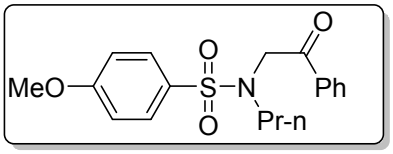
According to general procedure 2.2, **5i** was obtained in 42% (80 mg) isolated yield. White solid; Mp: 179 - 180 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.74 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.22 – 7.20 (m, 3H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.04 – 7.01 (m, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 4.29 (s, 2H), 4.26 (s, 2H), 2.46 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 143.4, 137.5, 135.4, 134.4, 133.4, 129.8, 129.7, 128.5, 128.5, 128.4, 127.7, 127.2, 50.9, 50.0, 21.5.

HRMS (ESI) *m/z*: Calcd for $C_{17}H_{20}O_2NSCl$ $[M+H]^+$ 386.09760; Found 386.09756.

4-Methoxy-*N*-(2-oxo-2-phenylethyl)-*N*-propylbenzenesulfonamide (5j)



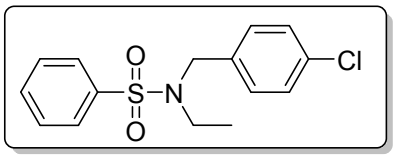
According to general procedure 2.2, **5j** was obtained in 45% (78 mg) isolated yield as a yellowish viscous oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.95 (dd, *J* = 1.2, 1.2 Hz, 2H), 7.80 (d, *J* = 9.0 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 6.97 (d, *J* = 9,.0 Hz, 2H), 4.74 (s, 2H), 3.87 (s, 3H), 3.22 – 3.19 (m, 2H), 1.55 – 1.46 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 194.2, 162.8, 134.9, 133.7, 129.6, 128.8, 128.0, 114.0, 55.5, 52.9, 50.0, 21.2, 11.1.

HRMS (ESI) *m/z*: Calcd for $C_{18}H_{20}O_4NS$ $[M+H]^+$ 348.12641; Found 348.12607.

***N*-(4-Chlorobenzyl)-*N*-ethylbenzenesulfonamide (5k)**



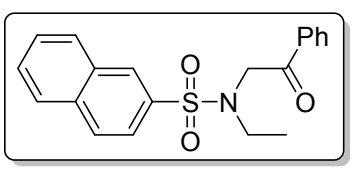
According to general procedure 2.2, **5k** was obtained in 56% (86 mg) isolated yield as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.84 (d, *J* = 7.9 Hz, 2H), 7.62 – 7.57 (m, 1H), 7.53 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.32 (s, 2H), 3.20 (q, *J* = 7.2 Hz, 2H), 0.92 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 140.1, 135.1, 133.6, 132.5, 129.5, 129.2, 128.7, 127.0, 50.5, 42.6, 13.4 .

HRMS (ESI) *m/z*: Calcd for $C_{15}H_{17}O_2NSCl$ $[M+H]^+$ 310.06630; Found 310.06590.

***N*-Ethyl-*N*-(2-oxo-2-phenylethyl)naphthalene-2-sulfonamide (5l)**



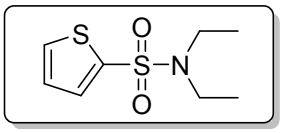
According to general procedure 2.2, **5l** was obtained in 40% (70 mg) isolated yield as a yellowish viscous oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.45 (s, 1H), 7.98 – 7.94 (m, 4H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.85 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.67 – 7.61 (m, 1H), 7.65 – 7.57 (m, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 4.83 (s, 2H), 3.41 (q, *J* = 7.2 Hz, 2H), 1.11 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 194.0, 136.8, 134.9, 134.8, 133.8, 132.1, 129.2, 129.2, 128.8, 128.7, 128.6, 128.0, 127.9, 127.3, 122.9, 52.3, 43.2, 13.4.

HRMS (ESI) *m/z*: Calcd for $C_{20}H_{20}O_3NS$ $[M+H]^+$ 354.11584; Found 354.11576.

***N*,*N*-Diethylthiophene-2-sulfonamide (5m)**[6]

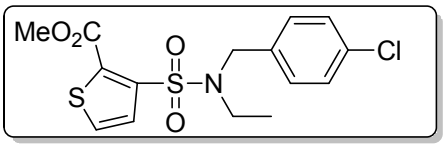


According to general procedure 2.2, **5m** was obtained in 64% (70 mg) yield as a brownish oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.55 (d, *J* = 4.2 Hz, 2H), 7.08 (t, *J* = 4.2 Hz, 1H), 3.25 (q, *J* = 7.2 Hz, 4H), 1.18 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (151 MHz,$CDCl_3$) δ (ppm): 140.8, 131.3, 131.1, 127.2, 42.6, 14.2.

Methyl 2-(*N*-(4-chlorobenzyl)-*N*-ethylsulfamoyl)thiophene-3-carboxylate (5n)



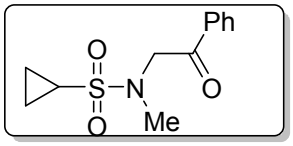
According to general procedure 2.2, **5n** was obtained in 47% (87 mg) isolated yield as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.50 (d, *J* = 5.2 Hz, 1H), 7.47 (d, *J* = 5.4 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 4.59 (s, 1H), 3.92 (s, 2H), 3.33 (q, *J* = 7.2 Hz, 2H), 0.97 (t, *J* = 7.1 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 156.0, 143.6, 135.4, 133.4, 132.8, 131.6, 129.4, 129.1, 128.7, 53.0, 50.3, 42.0, 13.1 .

HRMS (ESI) *m/z*: Calcd for $C_{15}H_{17}O_4NClS_2$ $[M+H]^+$ 374.02820; Found 374.02796.

***N*-Methyl-*N*-(2-oxo-2-phenylethyl)cyclopropanesulfonamide (5o)**



According to general procedure 2.2, **5o** was obtained in 46% (58 mg) isolated yieldas a yellowish viscous oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.95 (d, *J* = 7.8 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 4.79 (s, 2H), 3.05 (s, 3H), 2.62 (tt, *J* = 8.0, 4.9 Hz, 1H), 1.20 – 1.14 (m, 2H), 1.03 (dd, *J* = 2.4, 2.4 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 194.6, 134.6, 134.0, 128.9, 127.9, 56.4, 35.9, 28.9, 5.1.

HRMS (ESI) *m/z*: Calcd for $C_{12}H_{15}O_3NNaS$ $[M+H]^+$ 276.06649; Found 276.06619.

References:

[1] Y. Cai; R. Zhang, *Synlett,* **2017**, *28*, 1630.

[2] W. Zhang, Z. Zou,Y. Wang, *Angew.Chem*. **2019**, *131*, 634.

[3] S.-H. Su, M.-D. Su, *RSC Adv.,* **2016**, *6*, 80712.

[4] F.Zhang, D. Zheng, *Org. Lett*., **2018**, *20*, 1167.

[5] Z.Zhang, Y.-H. Liu, *Tetrahedron,* **2019**, *75*, 2763.

[6] Y. Fu, Q.-S. Xu, C.-Z. Shi, *Adv. Syn. Catal*., **2018**, *360*, 3502.

5. Copies of NMR spectra of compounds

***N*-(4-Chlorobenzyl)-*N*,4-dimethylbenzenesulfonamide (3a)**

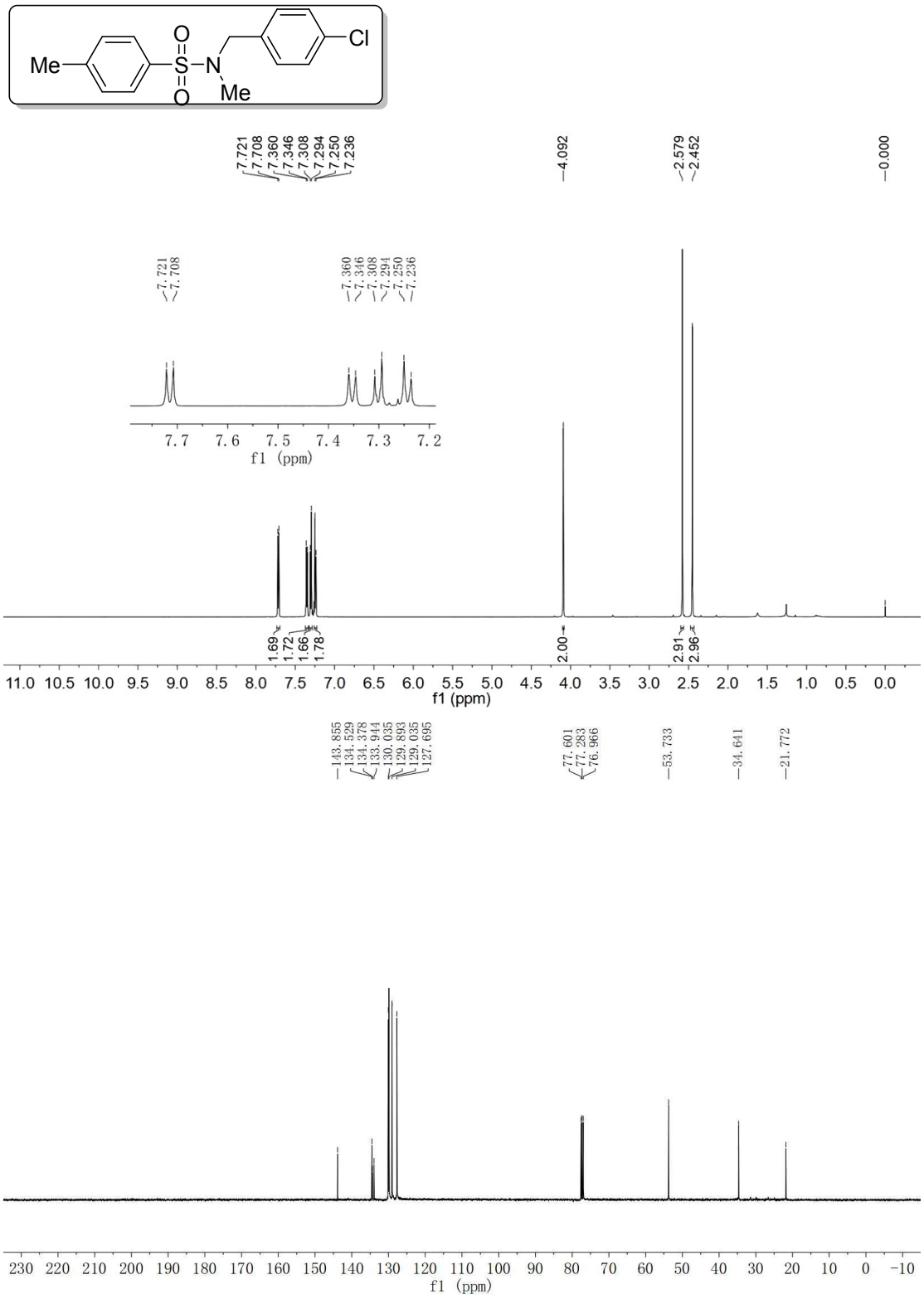


Figure S1. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 3a in $CDCl_3$.

***N*-(4-Chlorobenzyl)-*N*-methylbenzenesulfonamide (3b)**

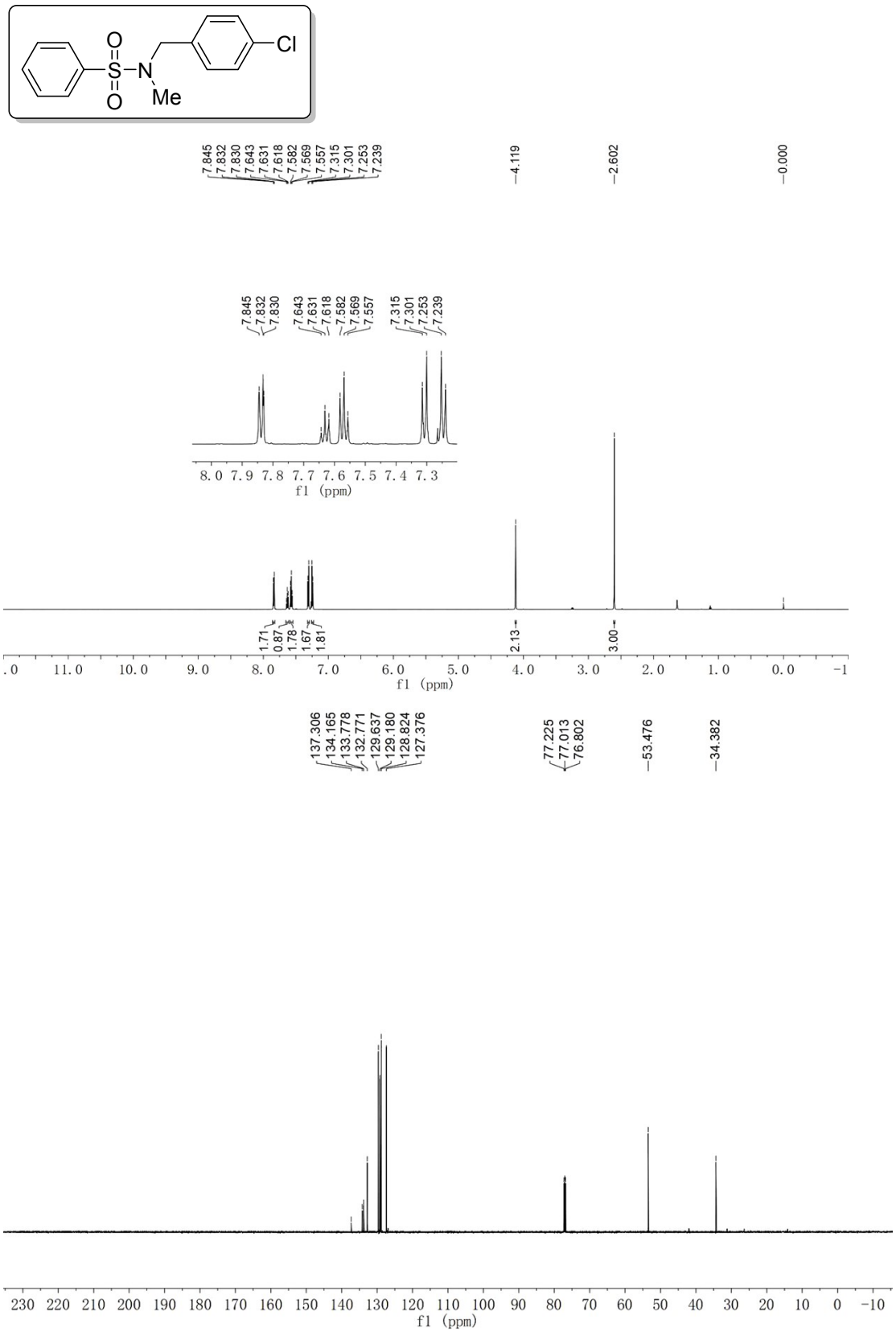


Figure S2. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 3b in $CDCl_3$.

***N*-(4-Chlorobenzyl)-2,4,6-triisopropyl-*N*-methylbenzenesulfonamide (3c)**

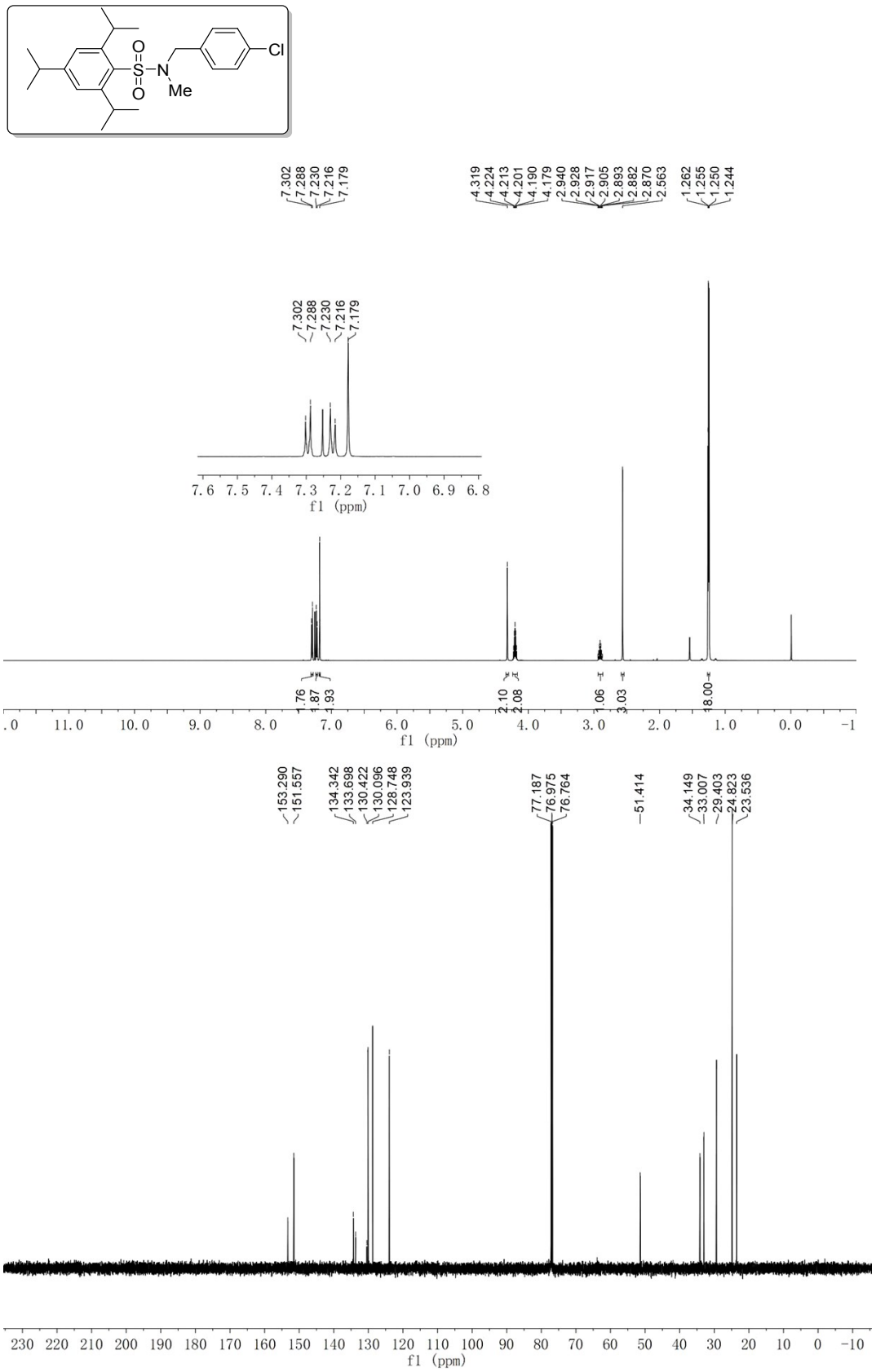


Figure S3. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 3c in $CDCl_3$.

N-(4-Chlorobenzyl)-*N*,2,2,4,6,7-hexamethyl-2,3-dihydrobenzofuran-5-sulfonamide (3d)

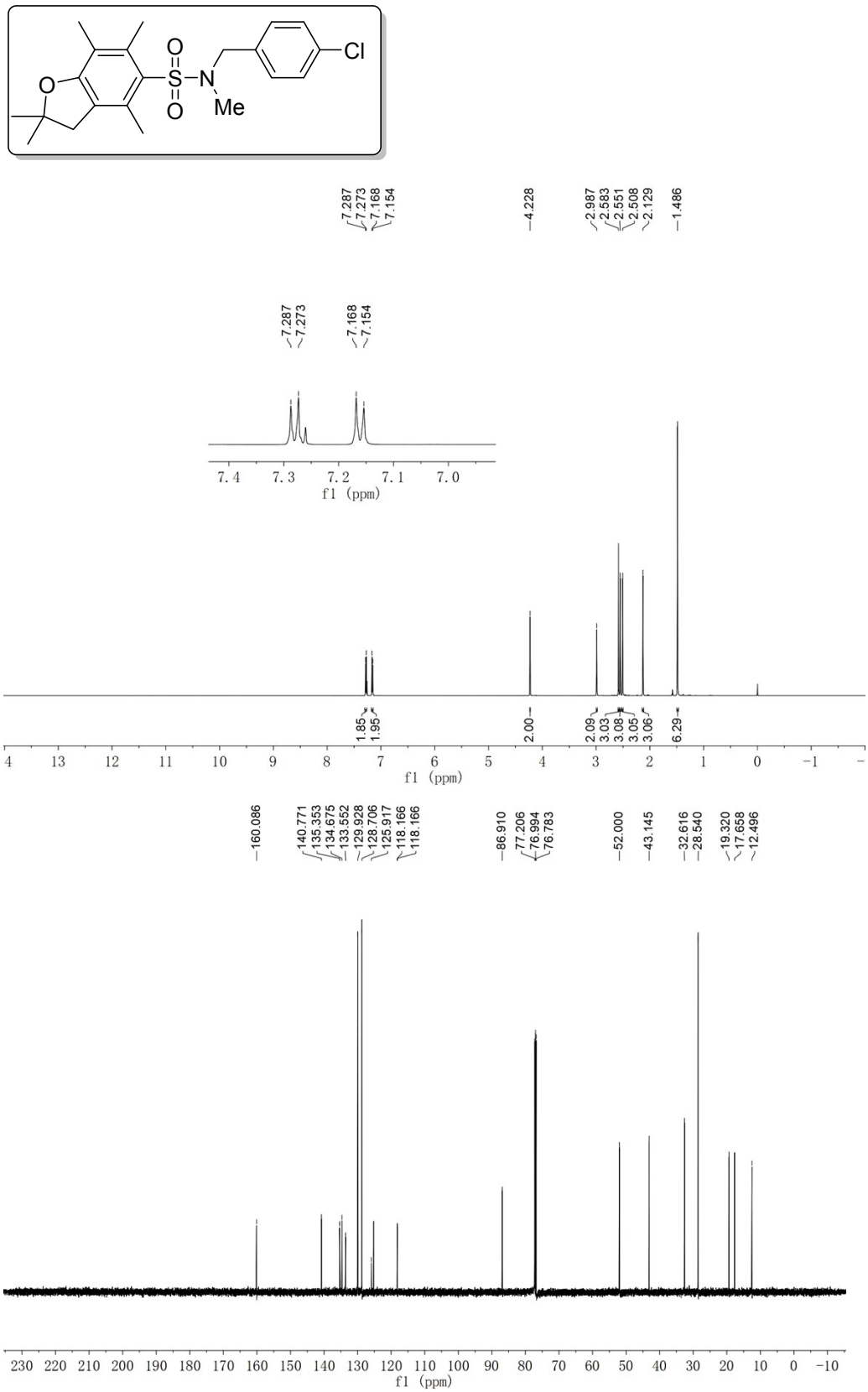


Figure S4. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 3d in $CDCl_3$.

***N*-(4-Chlorobenzyl)-4-methoxy-*N*-methylbenzenesulfonamide (3e)**

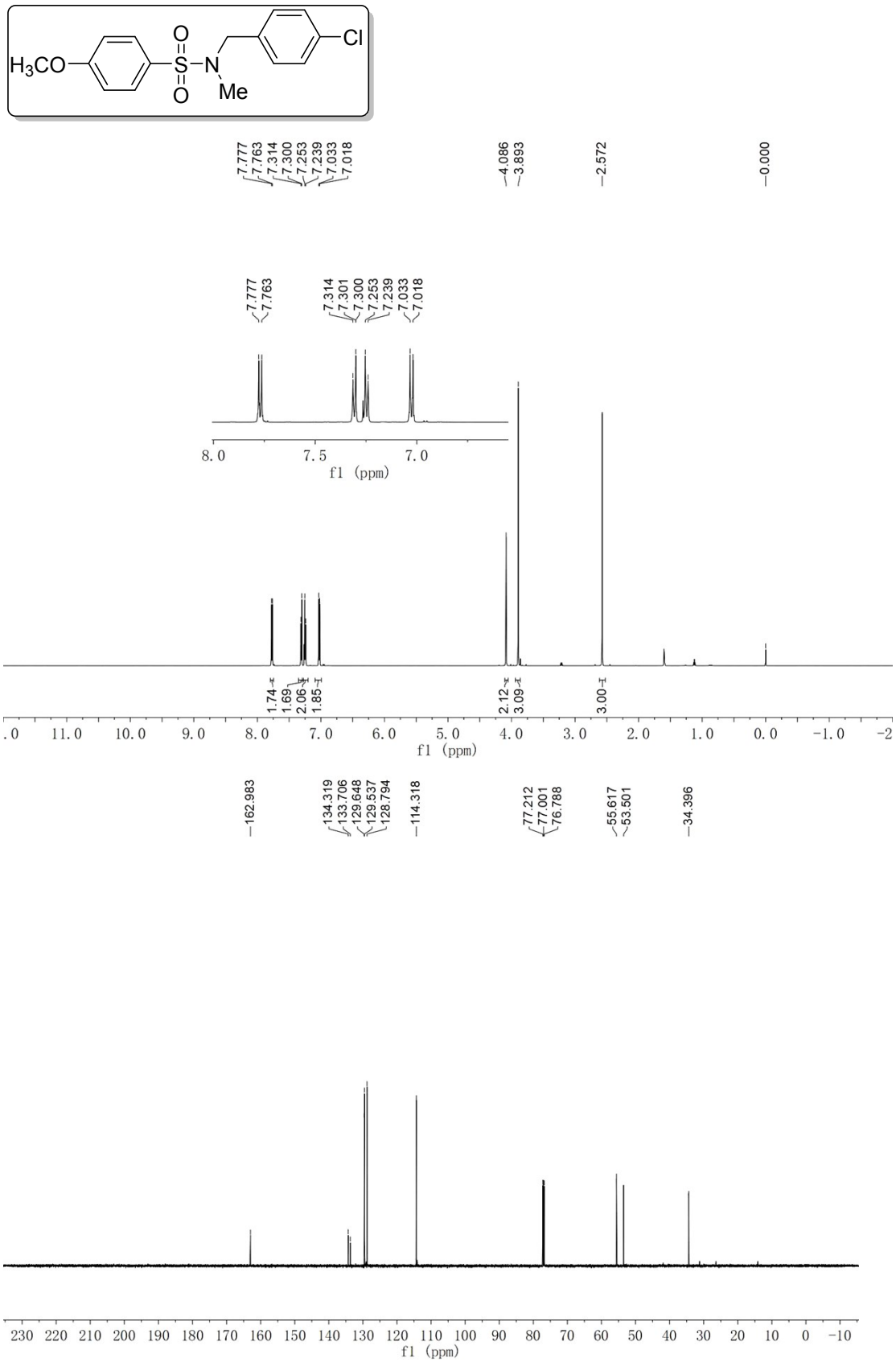


Figure S5. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 3e in $CDCl_3$.

***N*-(4-Chlorobenzyl)-*N*-methyl-4-(trifluoromethyl)benzenesulfonamide (3f)**

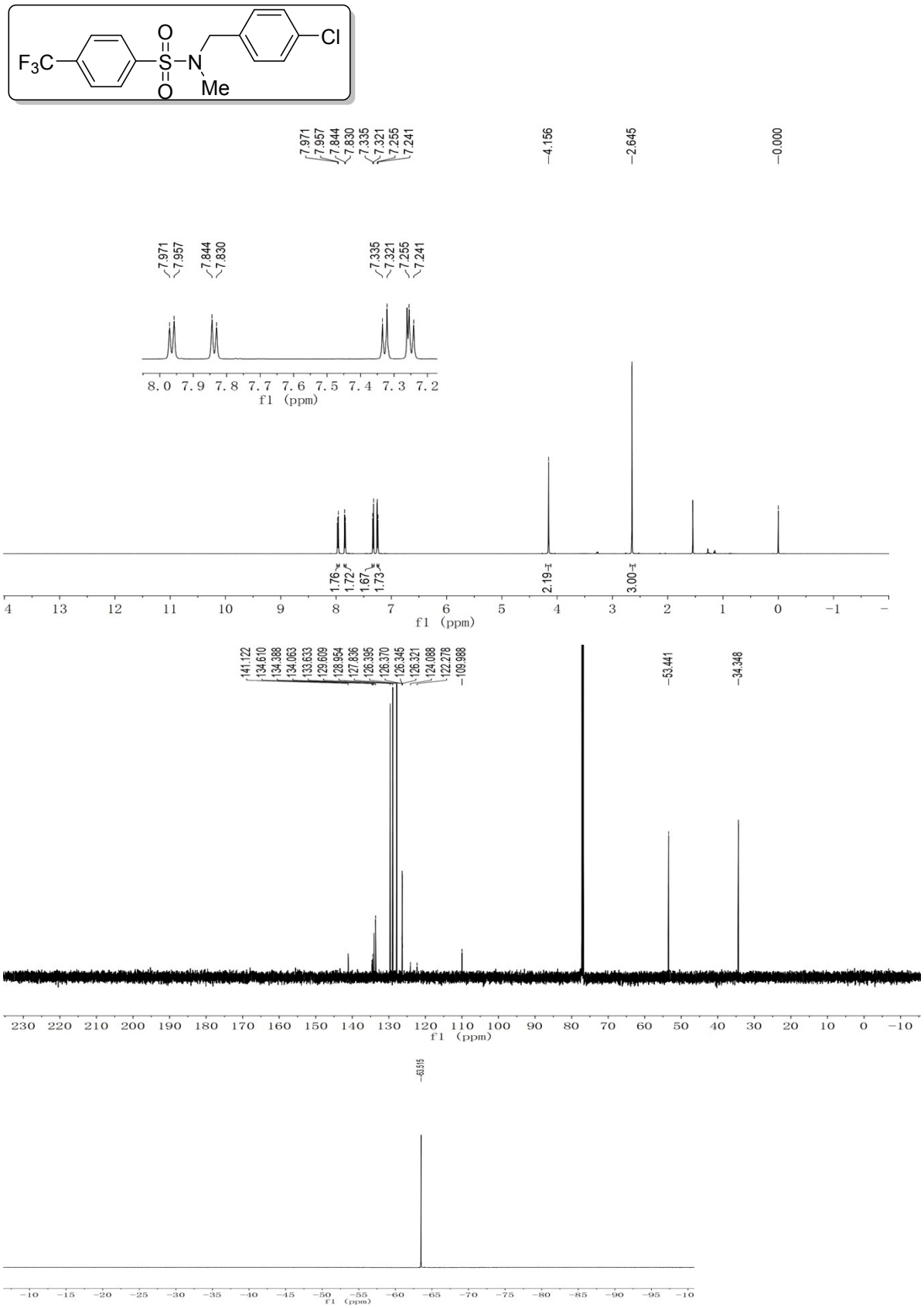


Figure S6. ^{1}H (600 MHz), ^{13}C (151 MHz) and ^{19}F (376 M) NMR spectra of 3f in $CDCl_3$.

***N*-(4-Chlorobenzyl)-*N*-methyl-2-(trifluoromethoxy)benzenesulfonamide (3g)**

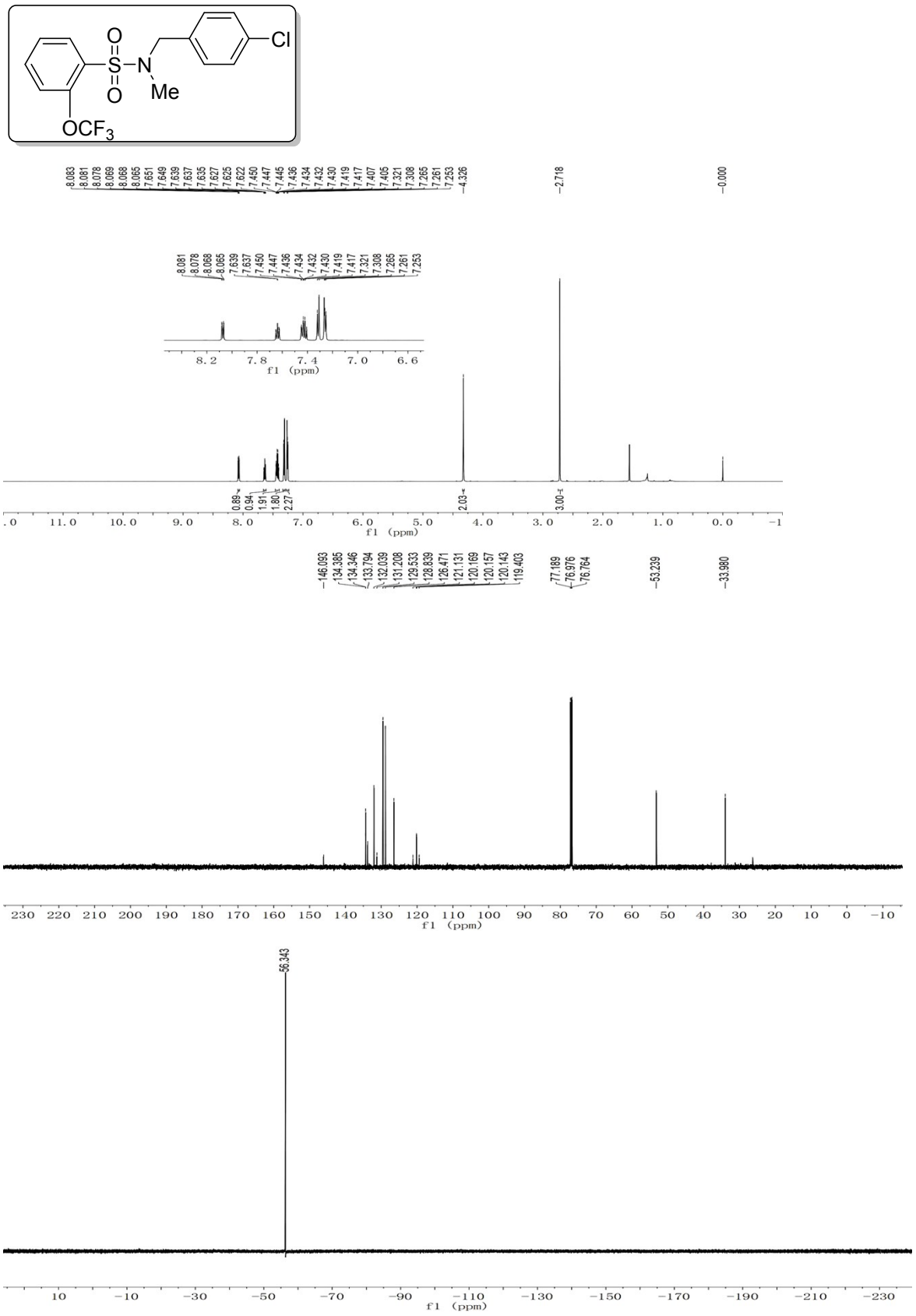


Figure S7. ^{1}H (600 MHz), ^{13}C (151 MHz) and ^{19}F (376 M) NMR spectra of 3g in $CDCl_3$.

***N*-(4-Chlorobenzyl)-4-fluoro-*N*-methylbenzenesulfonamide (3h)**

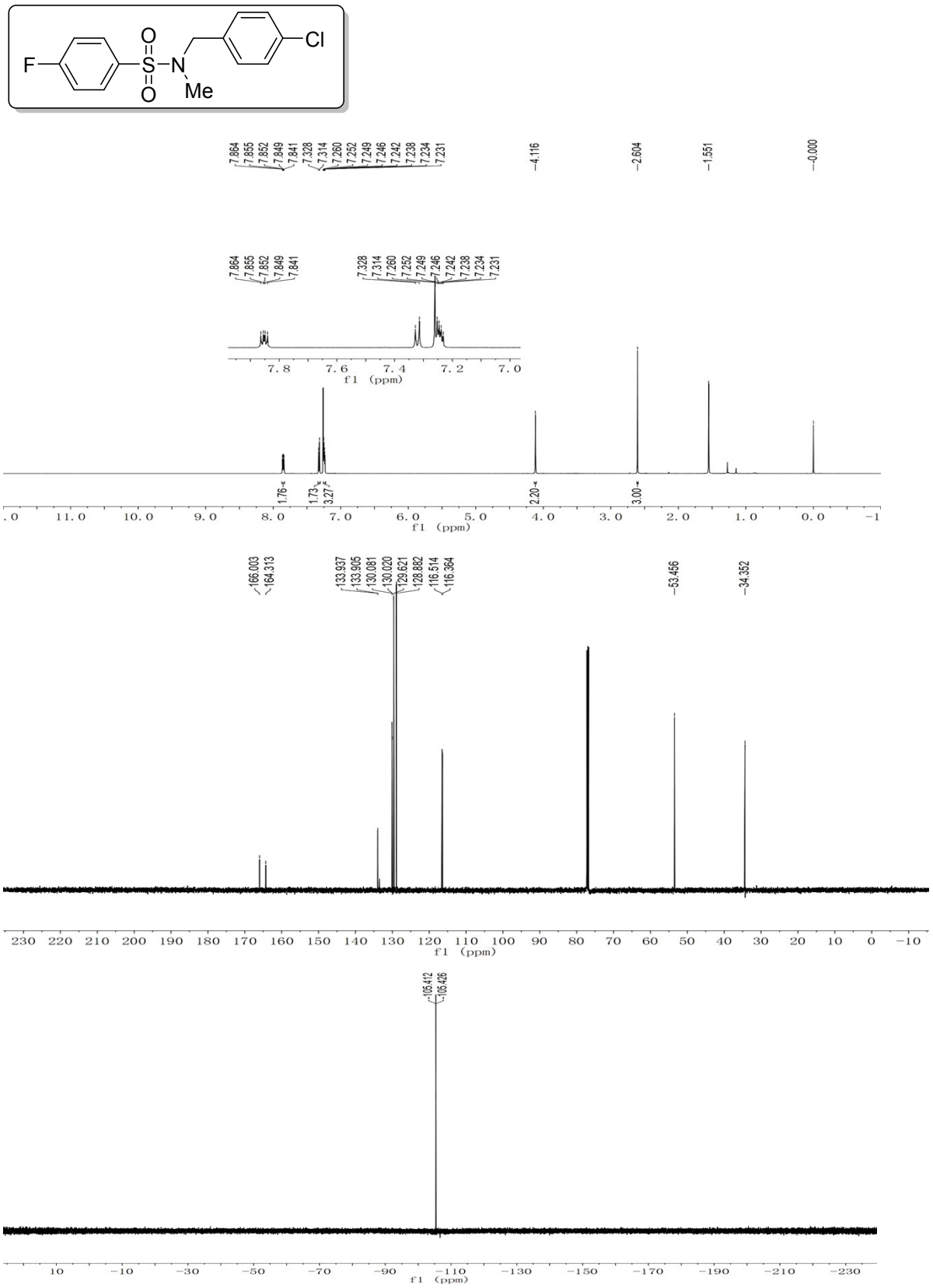


Figure S8. ^{1}H (600 MHz), ^{13}C (151 MHz) and ^{19}F (376 M) NMR spectra of 3h in $CDCl_3$.

4-Chloro-*N*-(4-chlorobenzyl)-*N*-methylbenzenesulfonamide (3i)

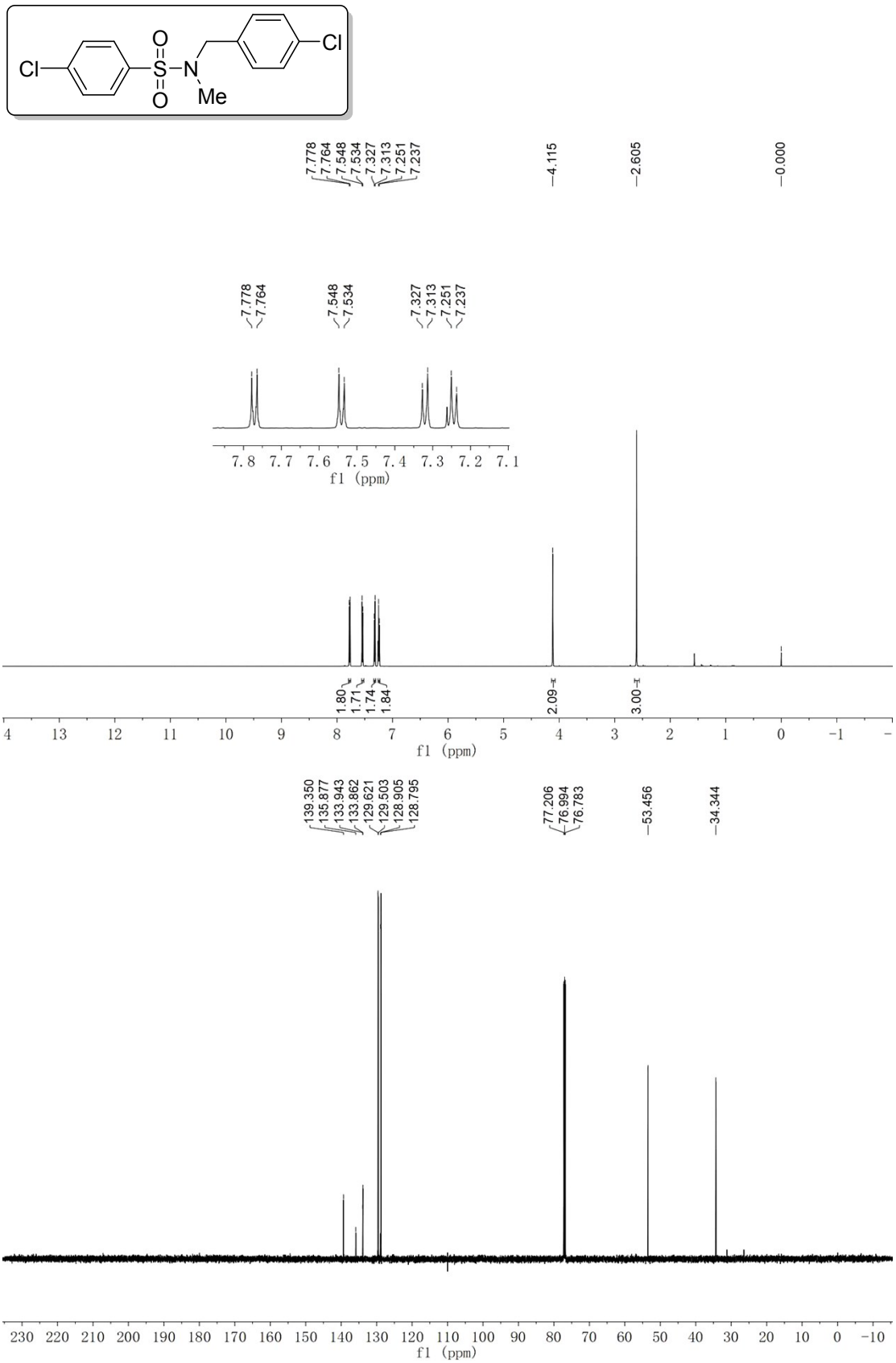


Figure S9. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 3i in $CDCl_3$.

4-bromo-*N*-(4-chlorobenzyl)-*N*-methylbenzenesulfonamide (3j)

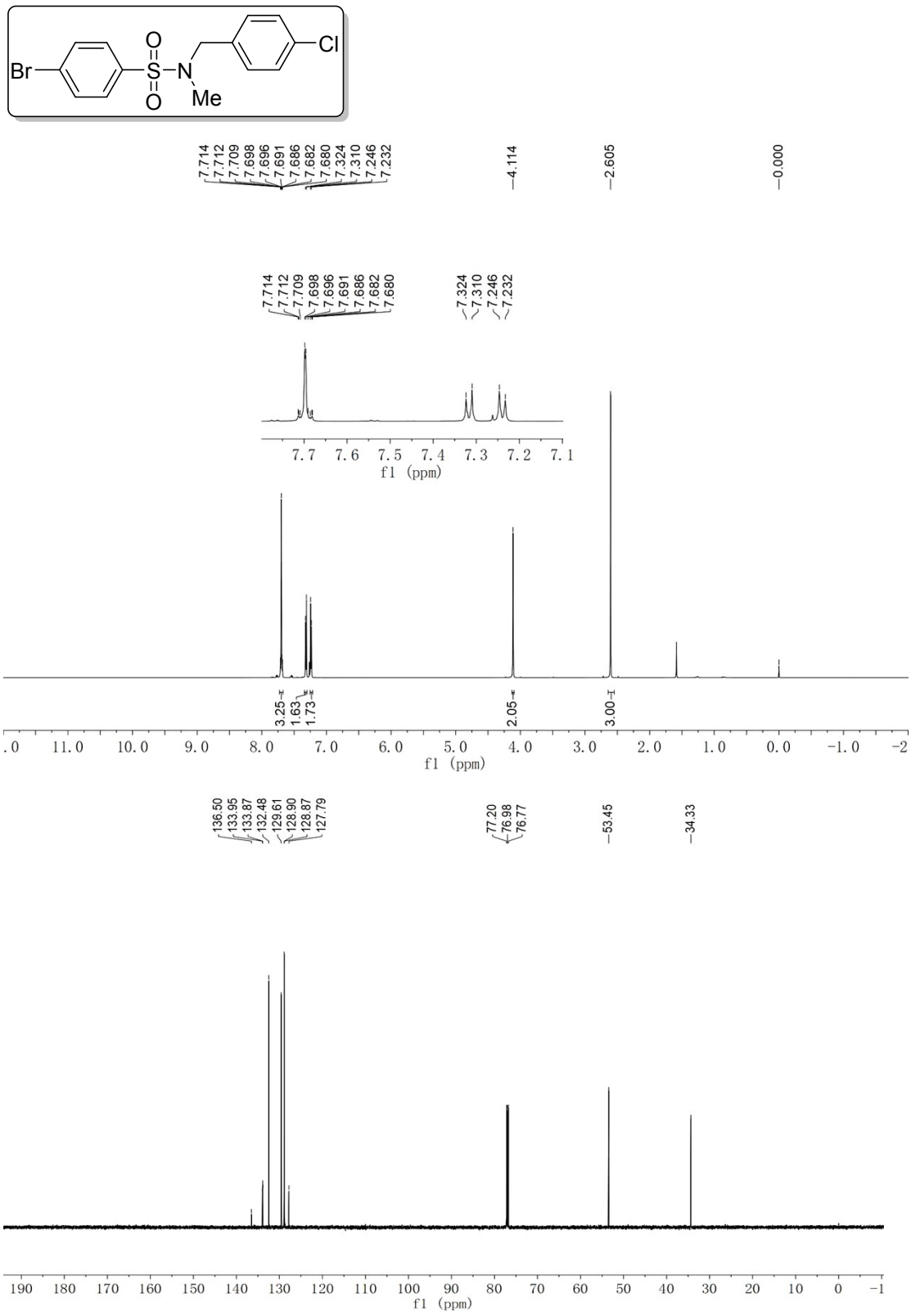


Figure S10. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 3j in $CDCl_3$.

***N*-(4-Chlorobenzyl)-3,4-difluoro-*N*-methylbenzenesulfonamide (3k)**

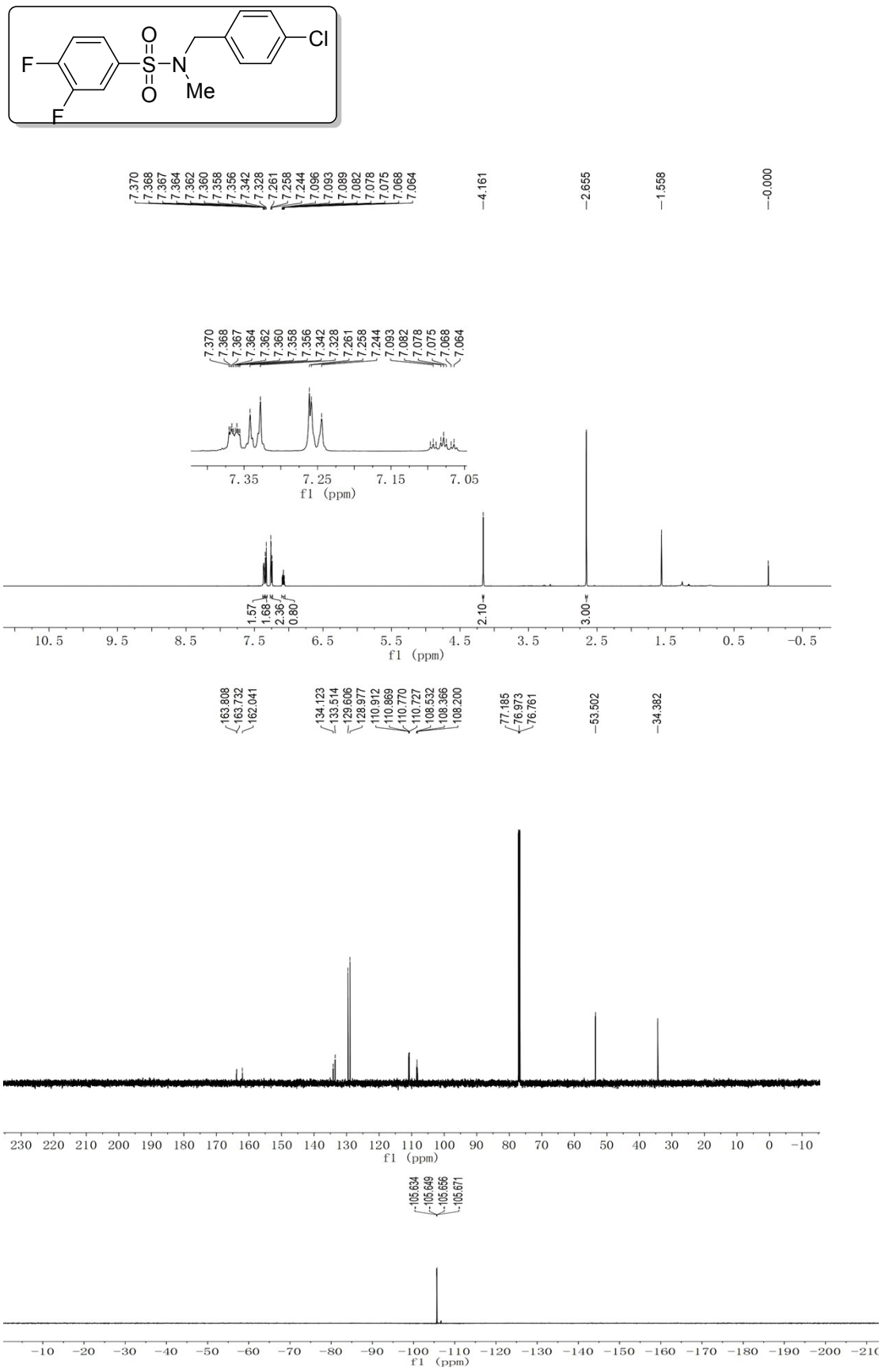


Figure S11. ^{1}H (600 MHz), ^{13}C (151 MHz) and ^{19}F (376 M) NMR spectra of 3k in $CDCl_3$.

***N*-(4-Chlorobenzyl)-*N*-methylnaphthalene-2-sulfonamide (3n)**

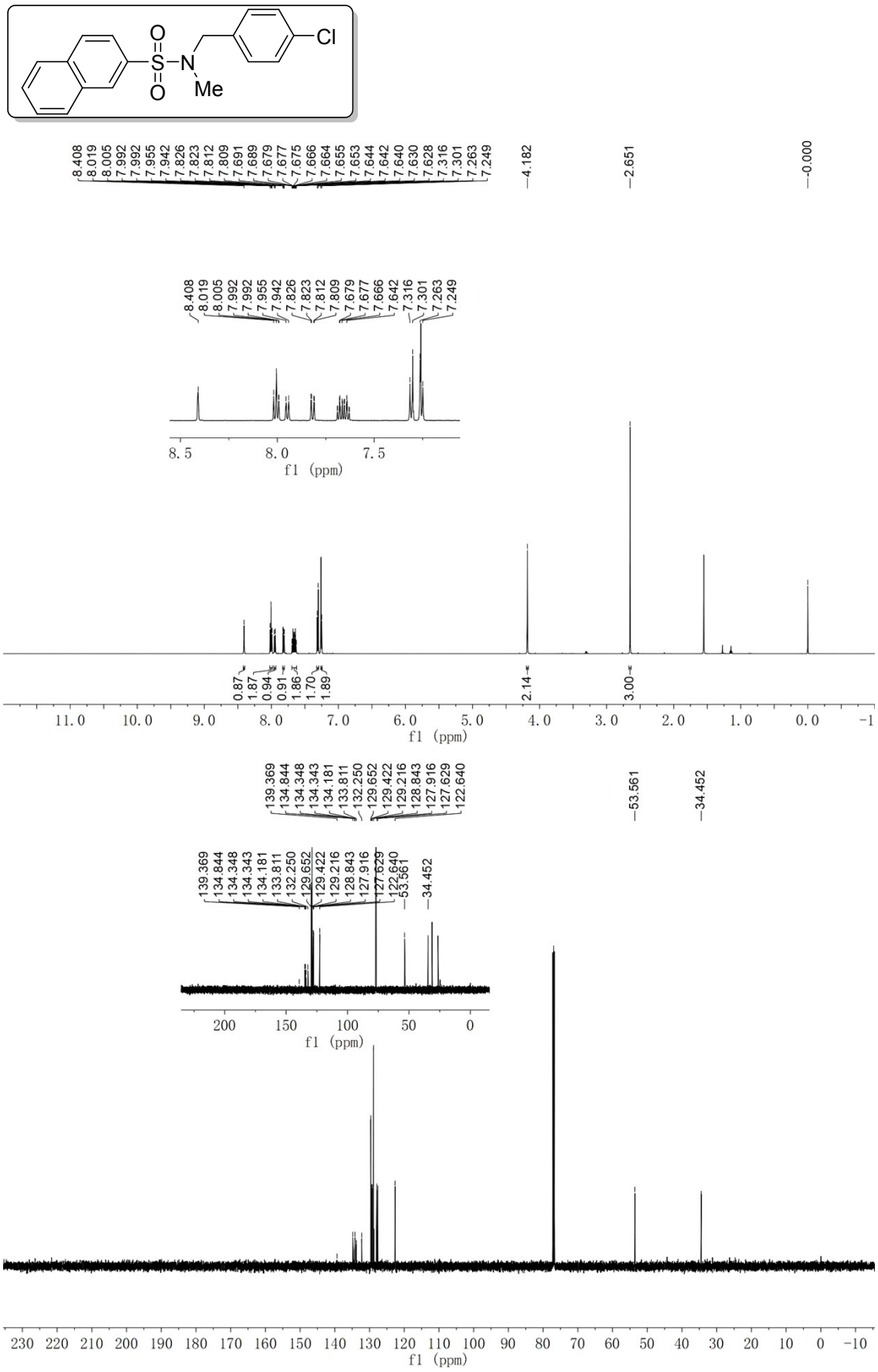


Figure S12. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 3n in $CDCl_3$.

***N*-(4-Chlorobenzyl)-*N*-methylthiophene-2-sulfonamide (3o)**

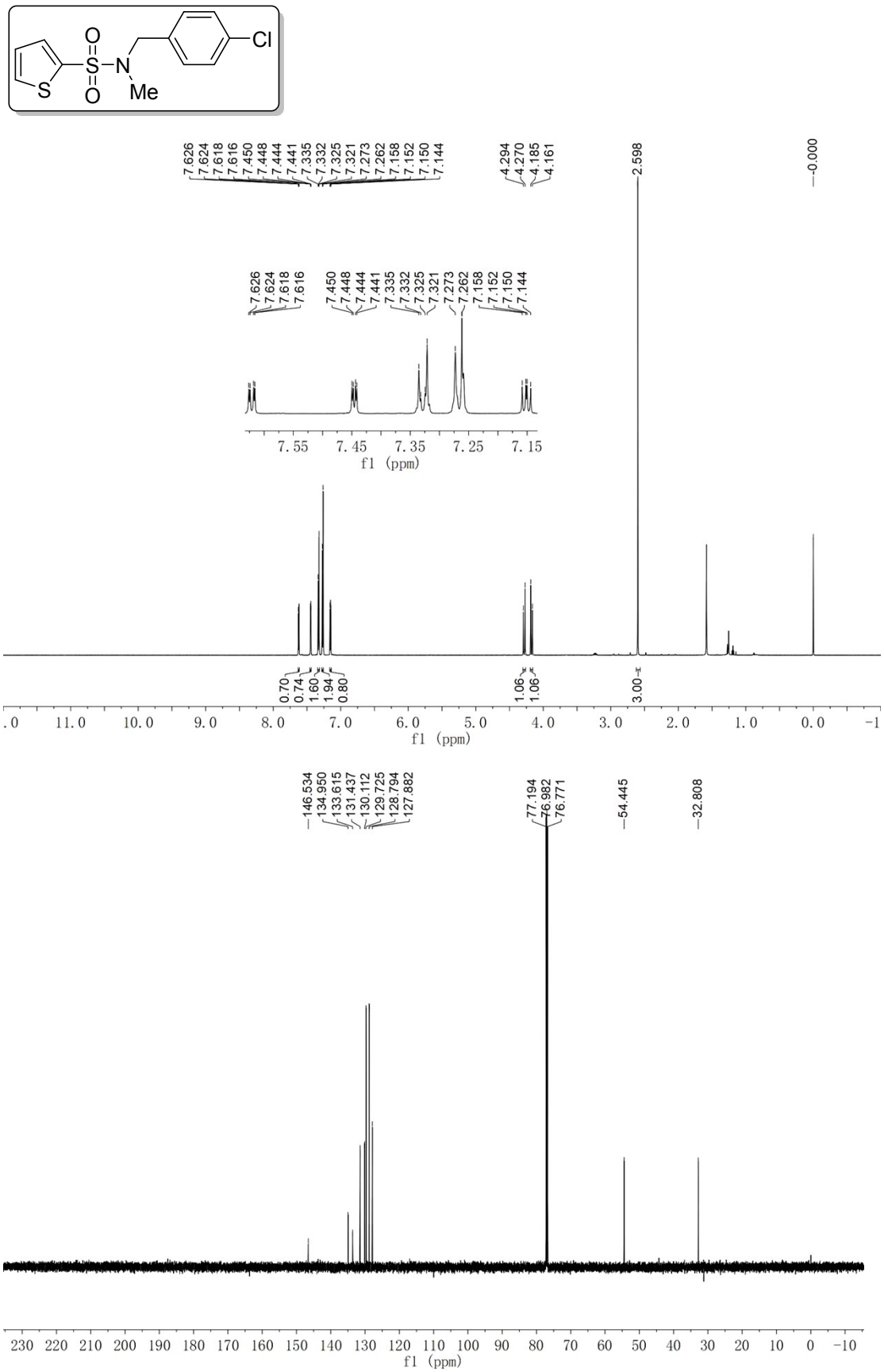


Figure S13. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 3o in $CDCl_3$.

Methyl2-(*N*-(4-chlorobenzyl)-*N*-methylsulfamoyl)thiophene-3-carboxylate (3p)

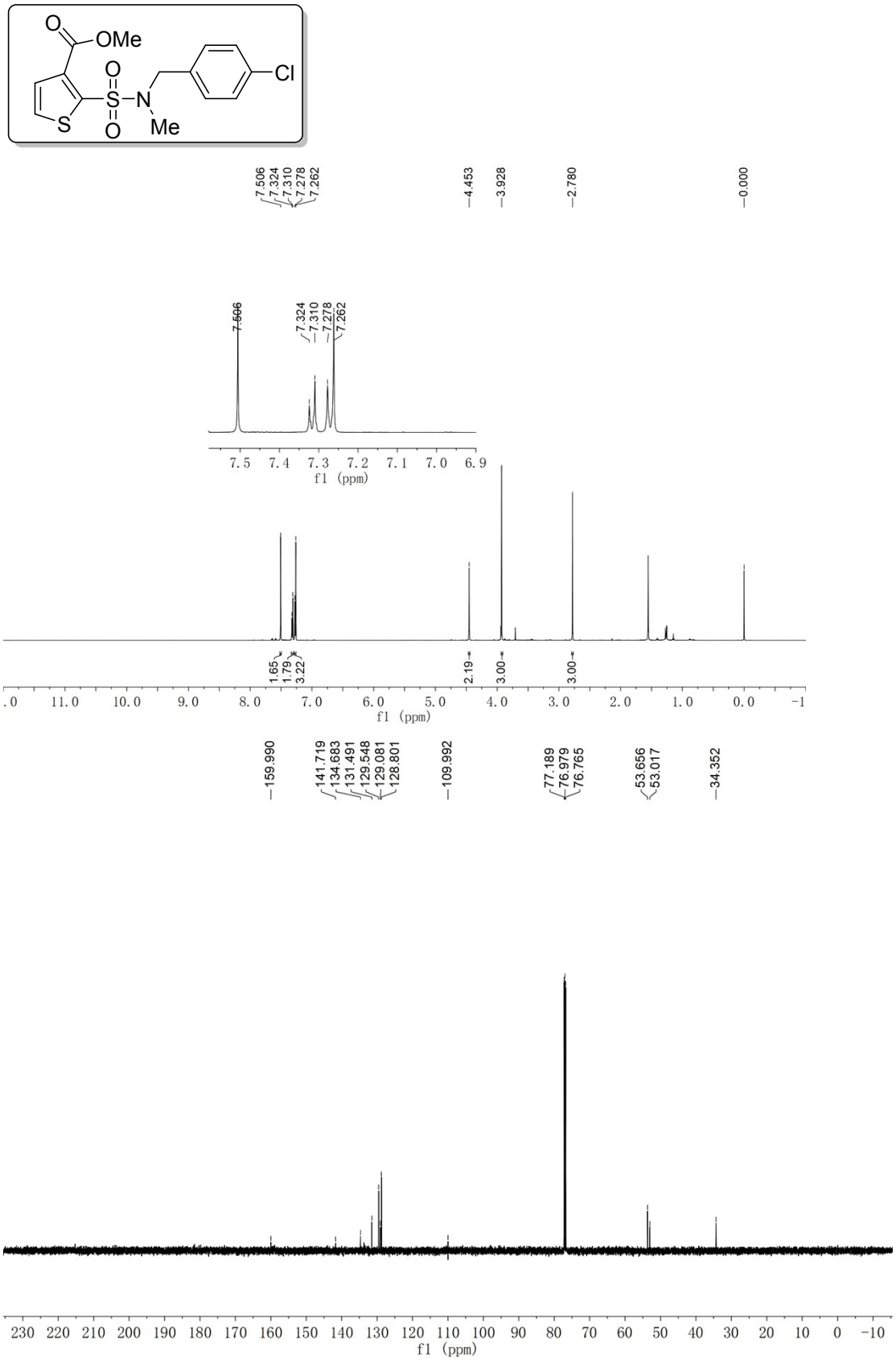


Figure S14. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 3p in $CDCl_3$.

***N*-Ethyl-*N*,4-dimethylbenzenesulfonamide (5a)**

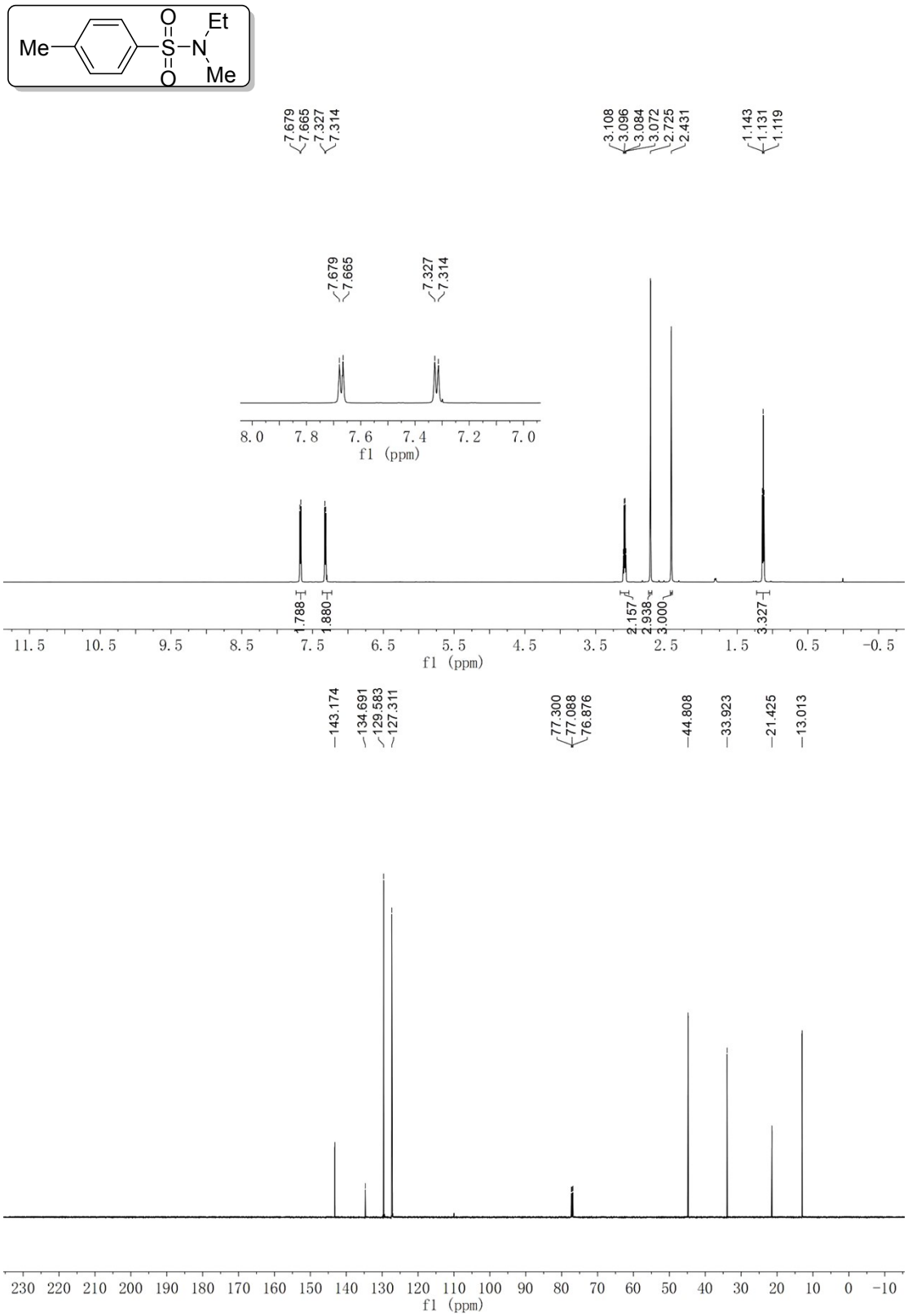


Figure S15. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 5a in $CDCl_3$.

***N*-Allyl-*N*,4-dimethylbenzenesulfonamide (5b)**

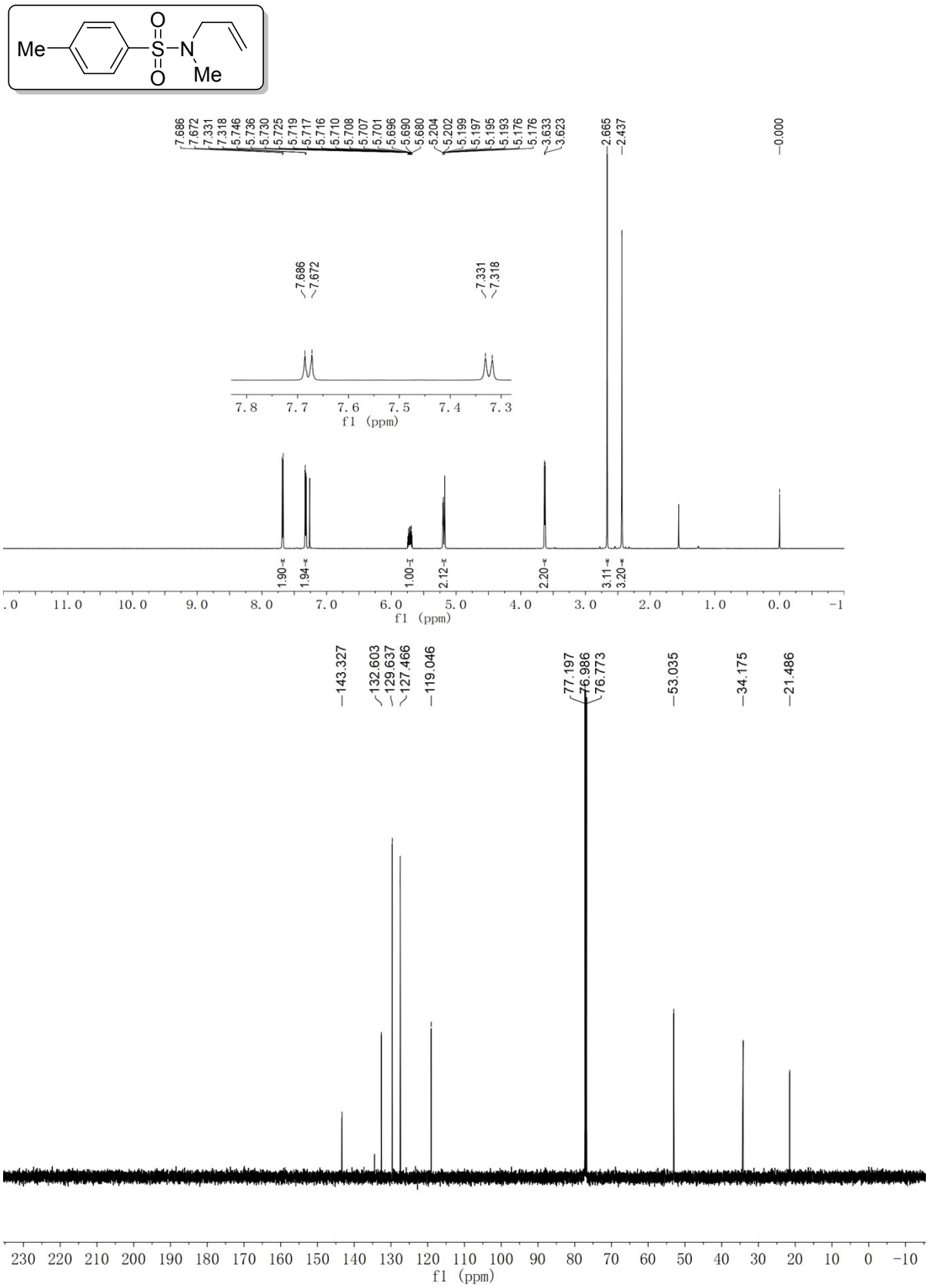


Figure S16. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 5b in $CDCl_3$.

Ethyl *N*-methyl-*N*-tosylglycinate (5c)

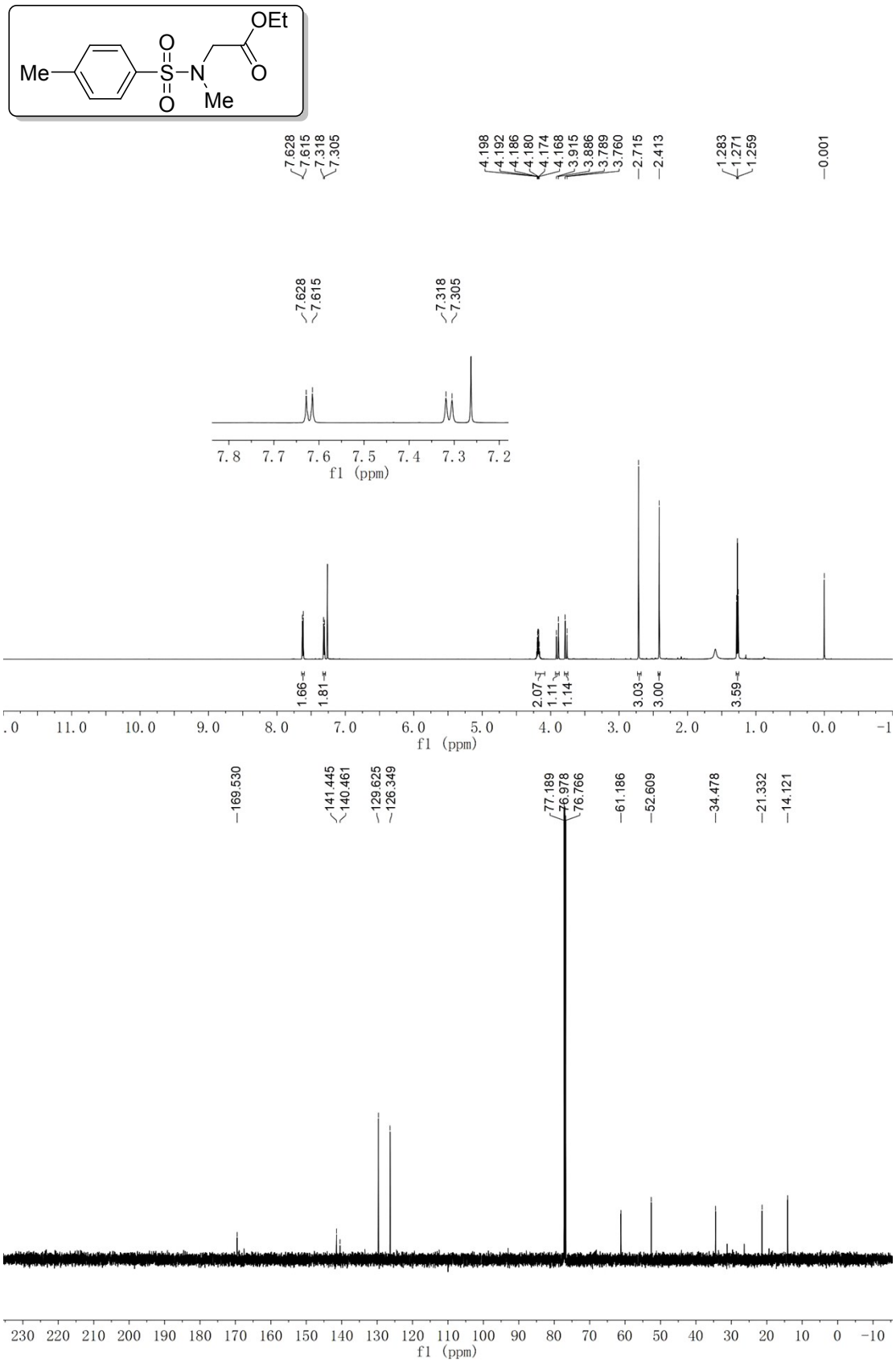


Figure S17. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 5c in $CDCl_3$.

***N*,4-Dimethyl-*N*-(2-oxo-2-phenylethyl)benzenesulfonamide (5d)**

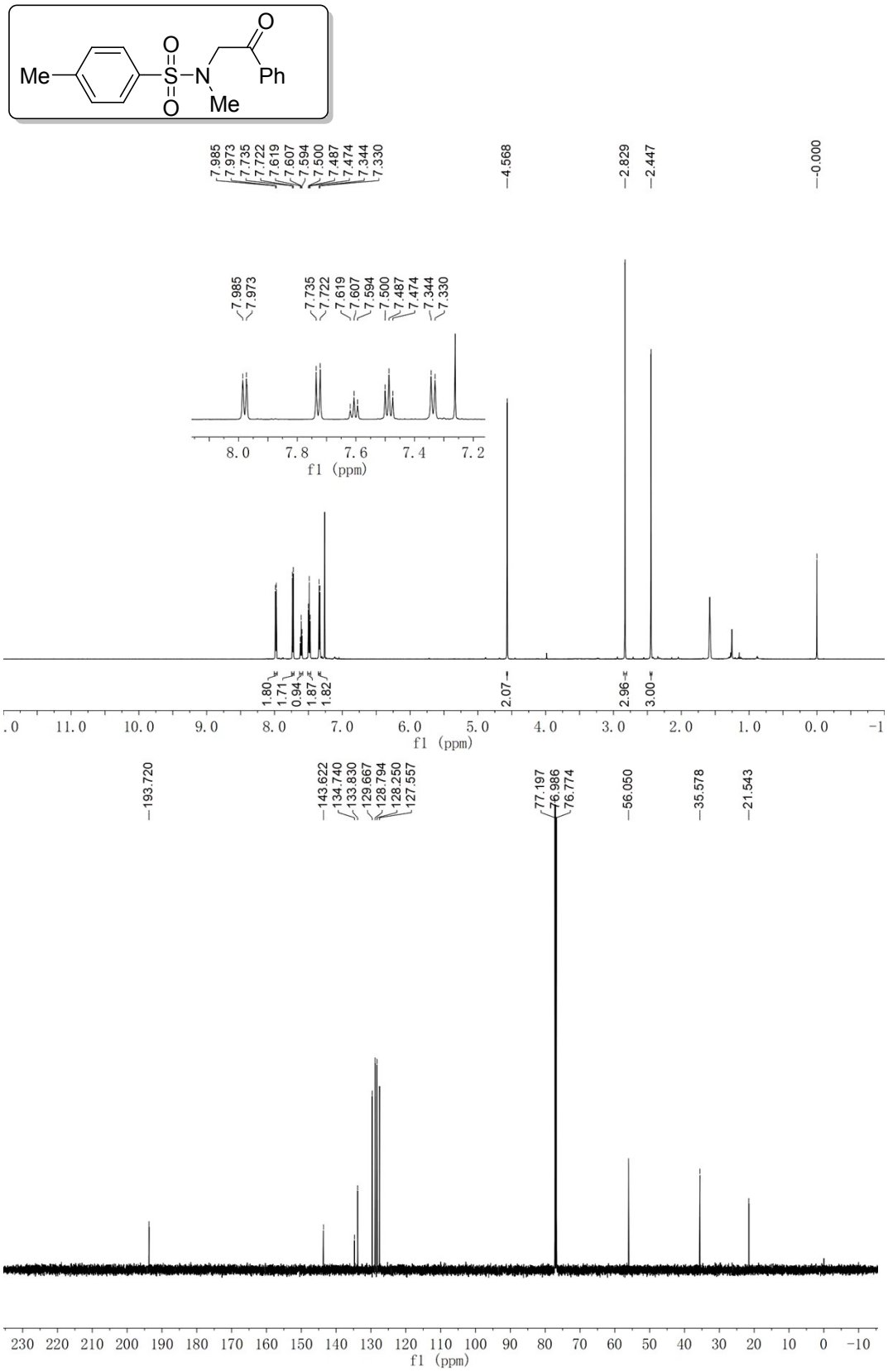


Figure S18. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 5d in $CDCl_3$.

***N*-Ethyl-4-methyl-*N*-propylbenzenesulfonamide (5e)**

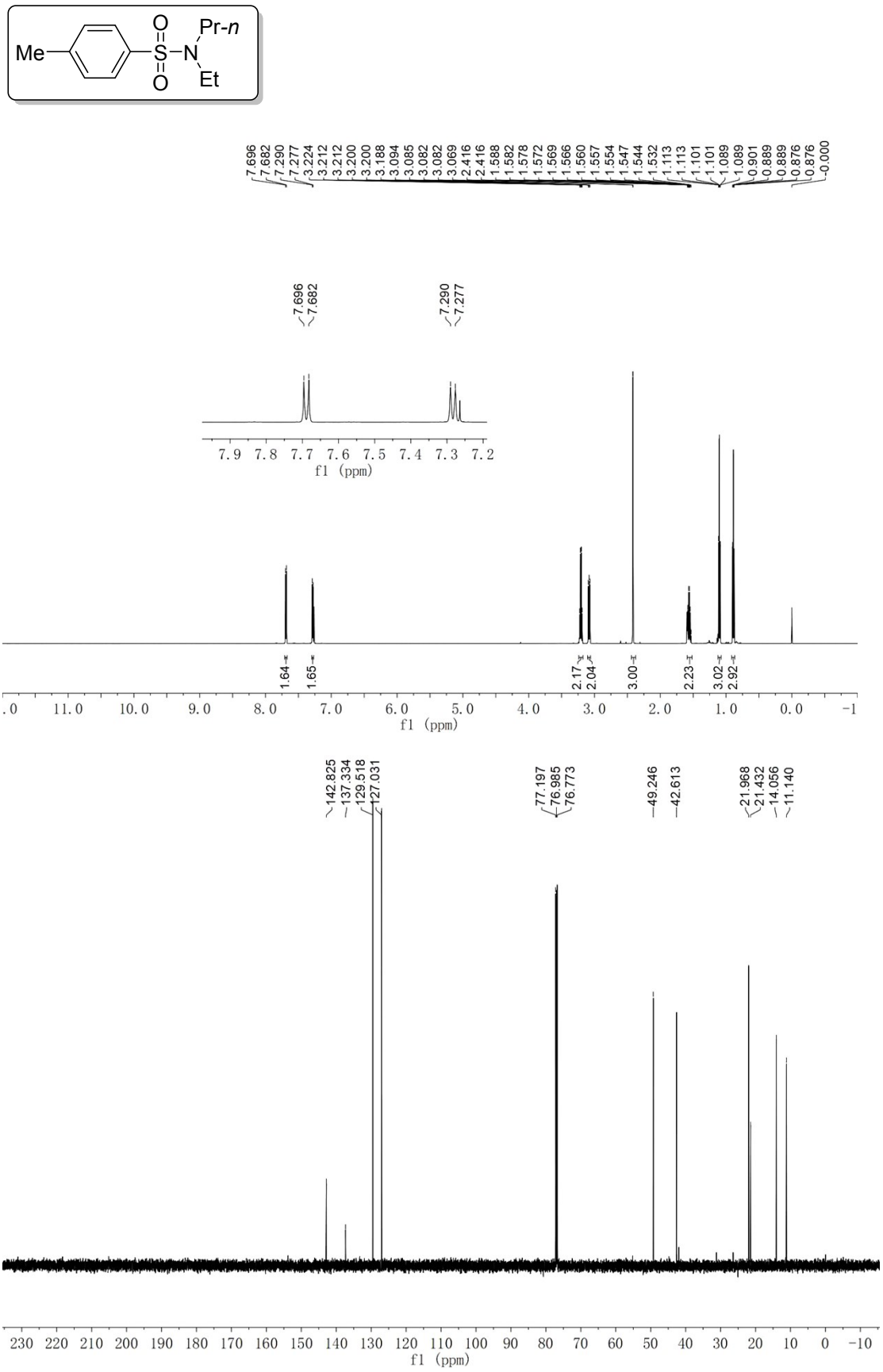


Figure S19. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 5e in $CDCl_3$.

***N*,*N*-diethyl-4-methylbenzenesulfonamide (5f)**

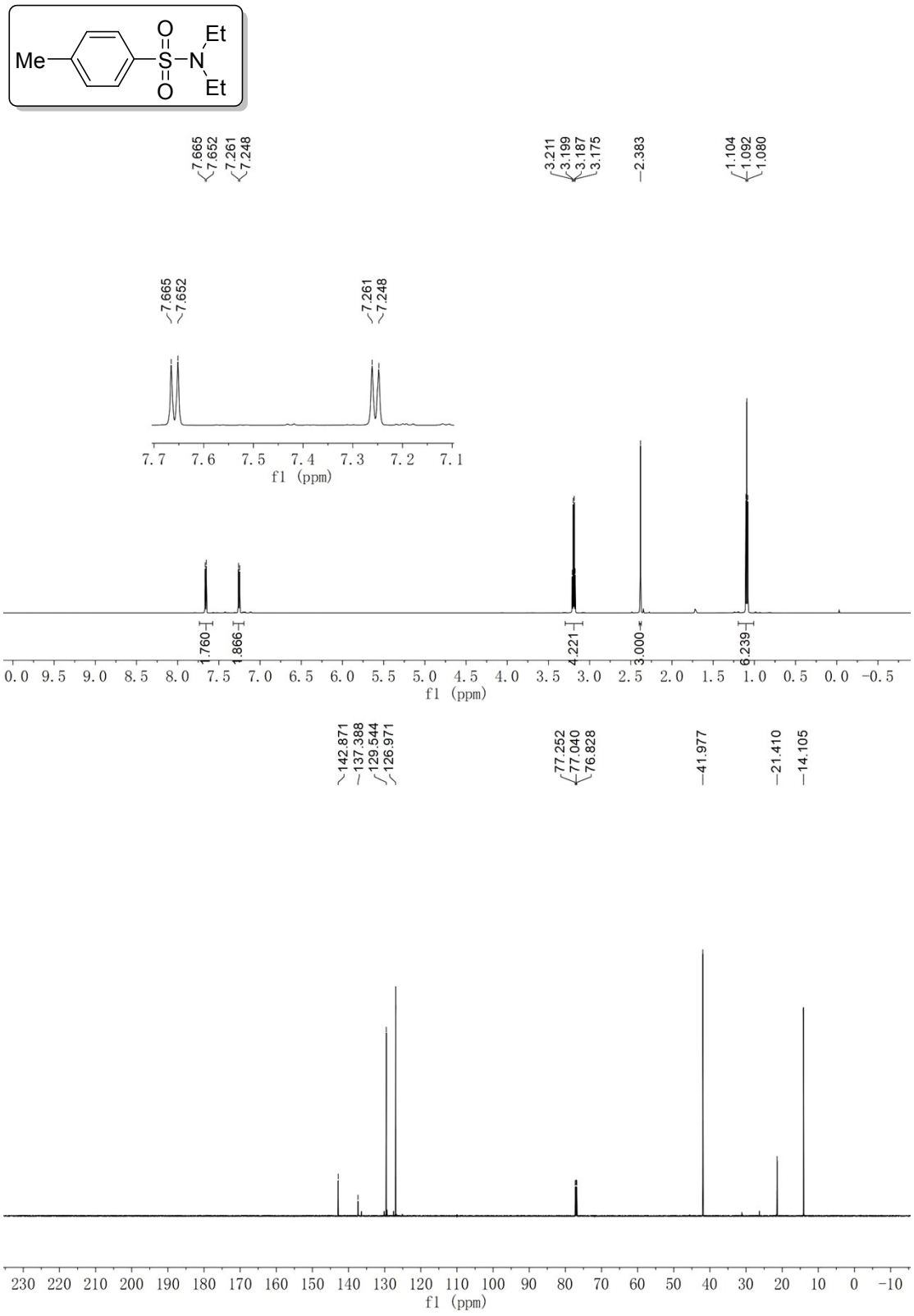


Figure S20. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 5f in $CDCl_3$.

***N*-(4-Chlorobenzyl)-*N*-ethyl-4-methylbenzenesulfonamide (5g)**

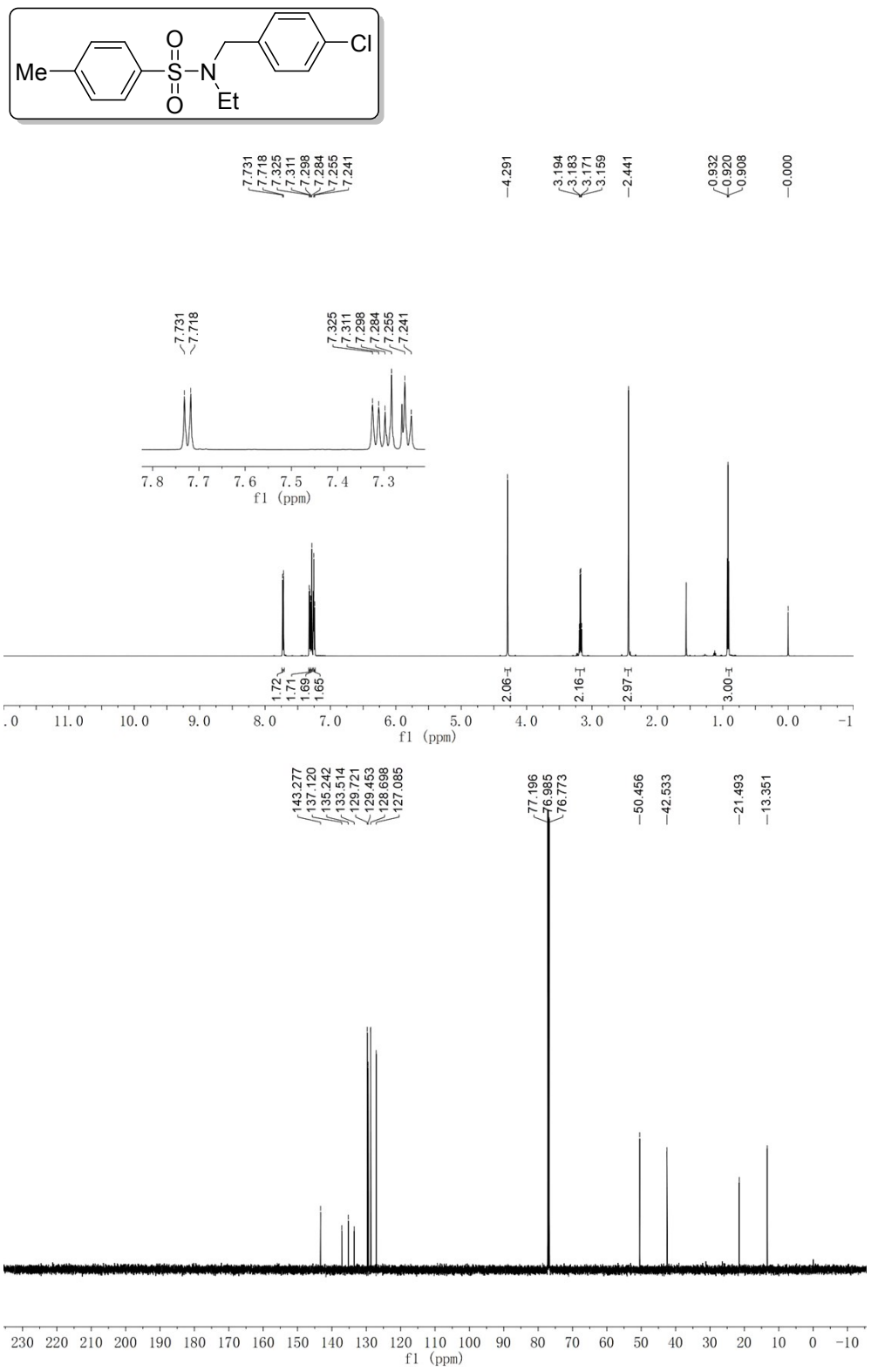


Figure S21. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 5g in $CDCl_3$.

N-(4-Chlorobenzyl)-4-methyl-*N*-propylbenzenesulfonamide (5h)

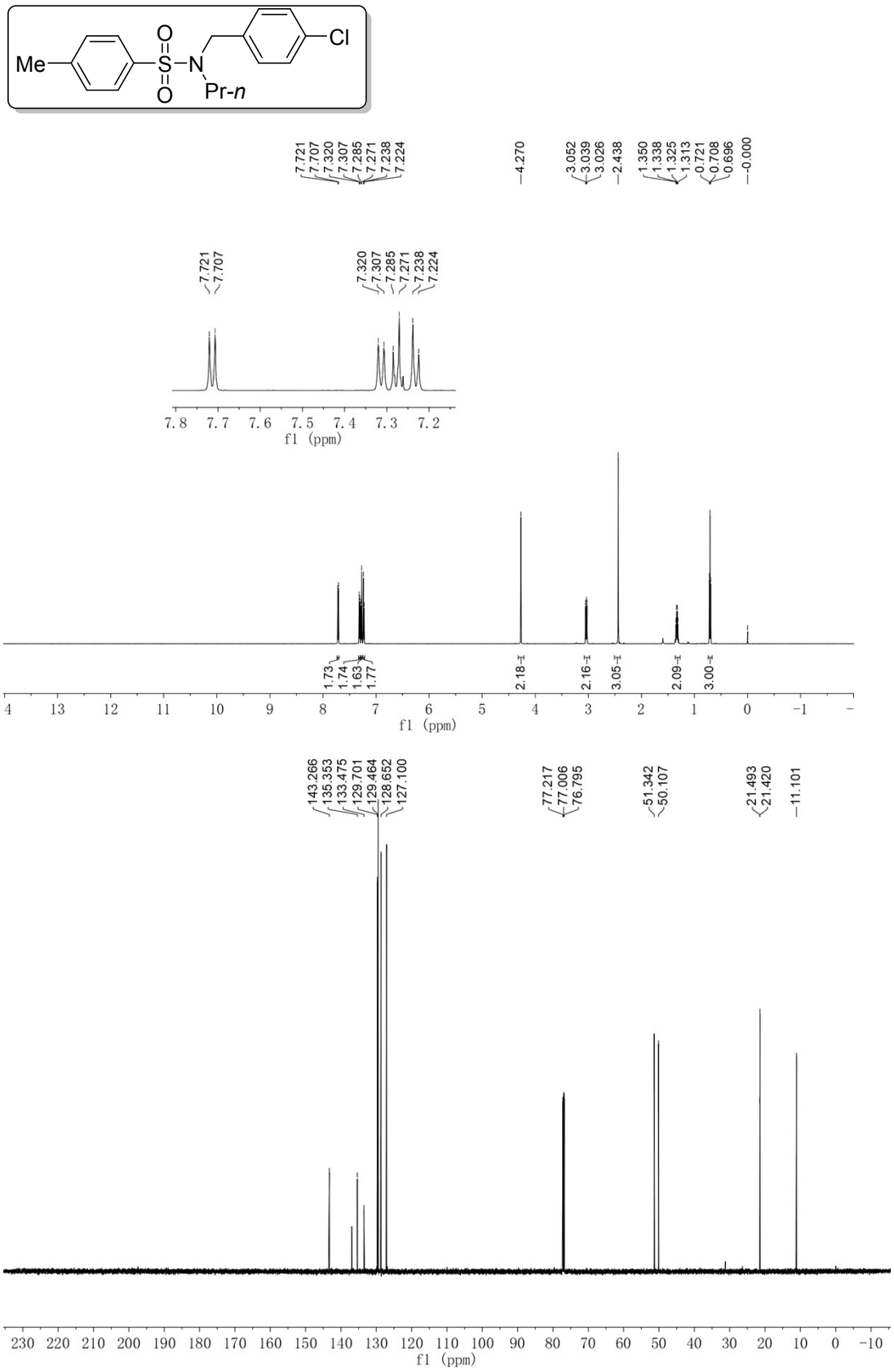


Figure S22. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 5h in $CDCl_3$.

***N*-Benzyl-*N*-(4-chlorobenzyl)-4-methylbenzenesulfonamide (5i)**

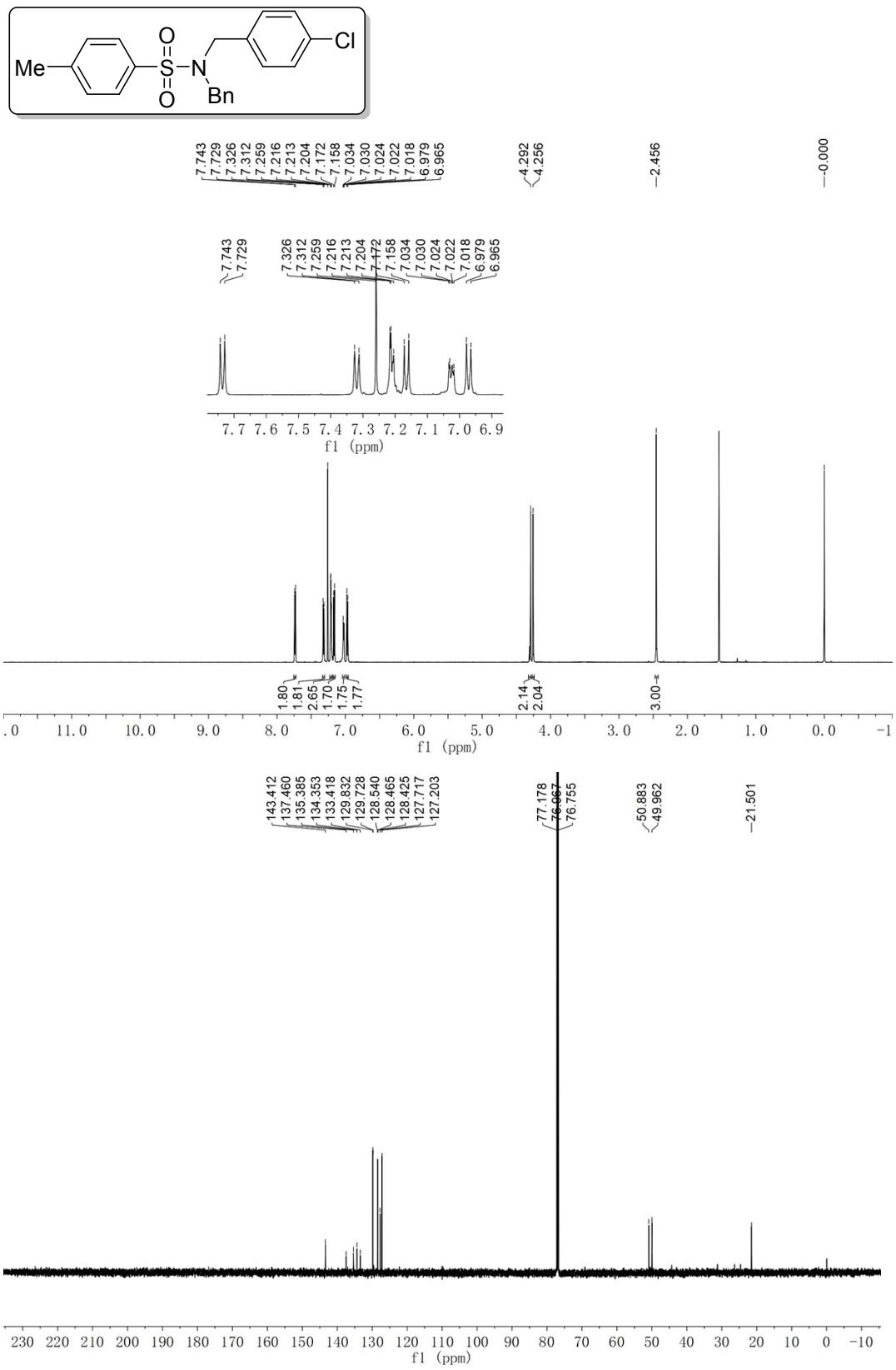


Figure S23. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 5i in $CDCl_3$.

4-Methoxy-*N*-(2-oxo-2-phenylethyl)-*N*-propylbenzenesulfonamide (5j)

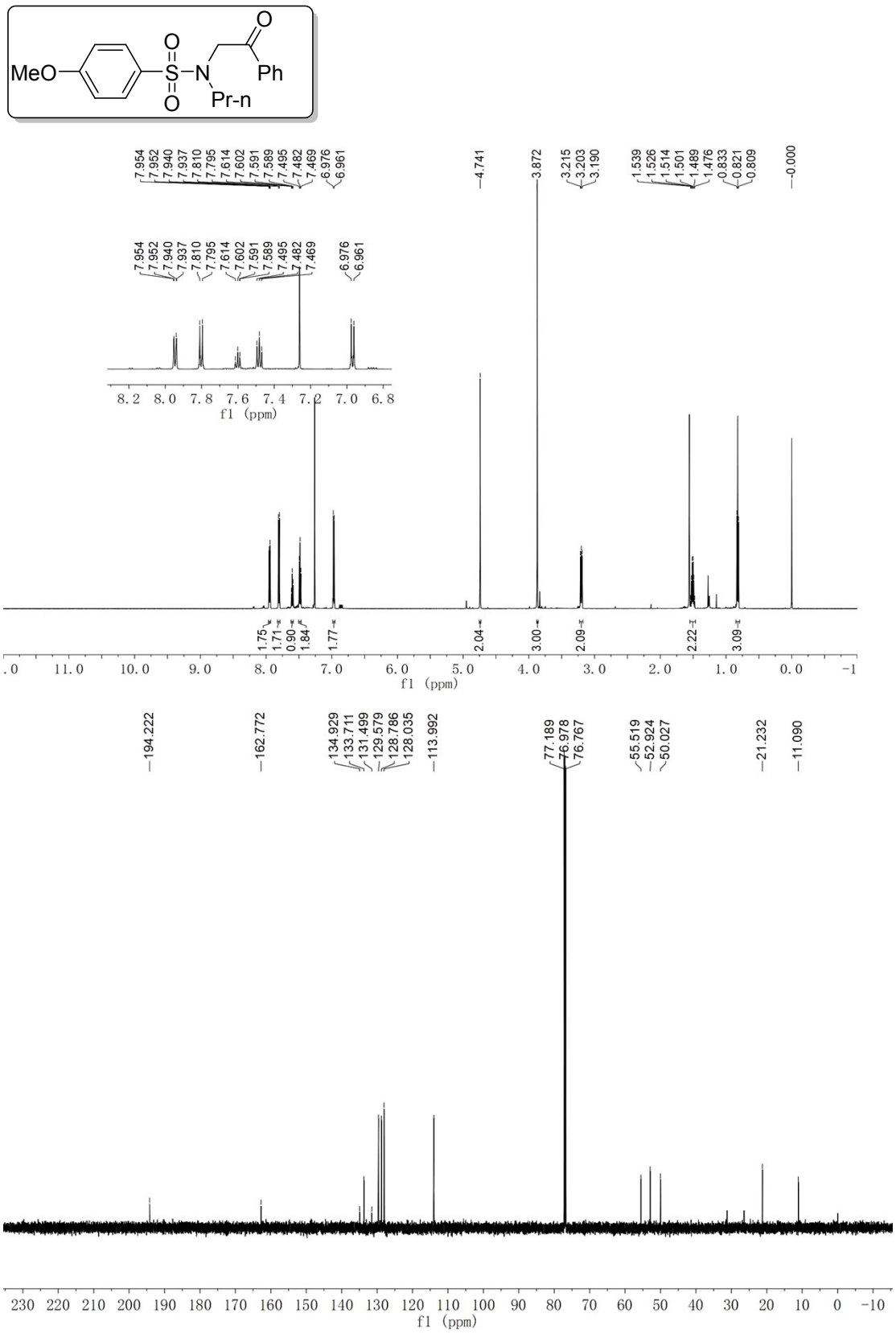


Figure S24. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 5j in $CDCl_3$.

***N*-(4-Chlorobenzyl)-*N*-ethylbenzenesulfonamide (5k)**

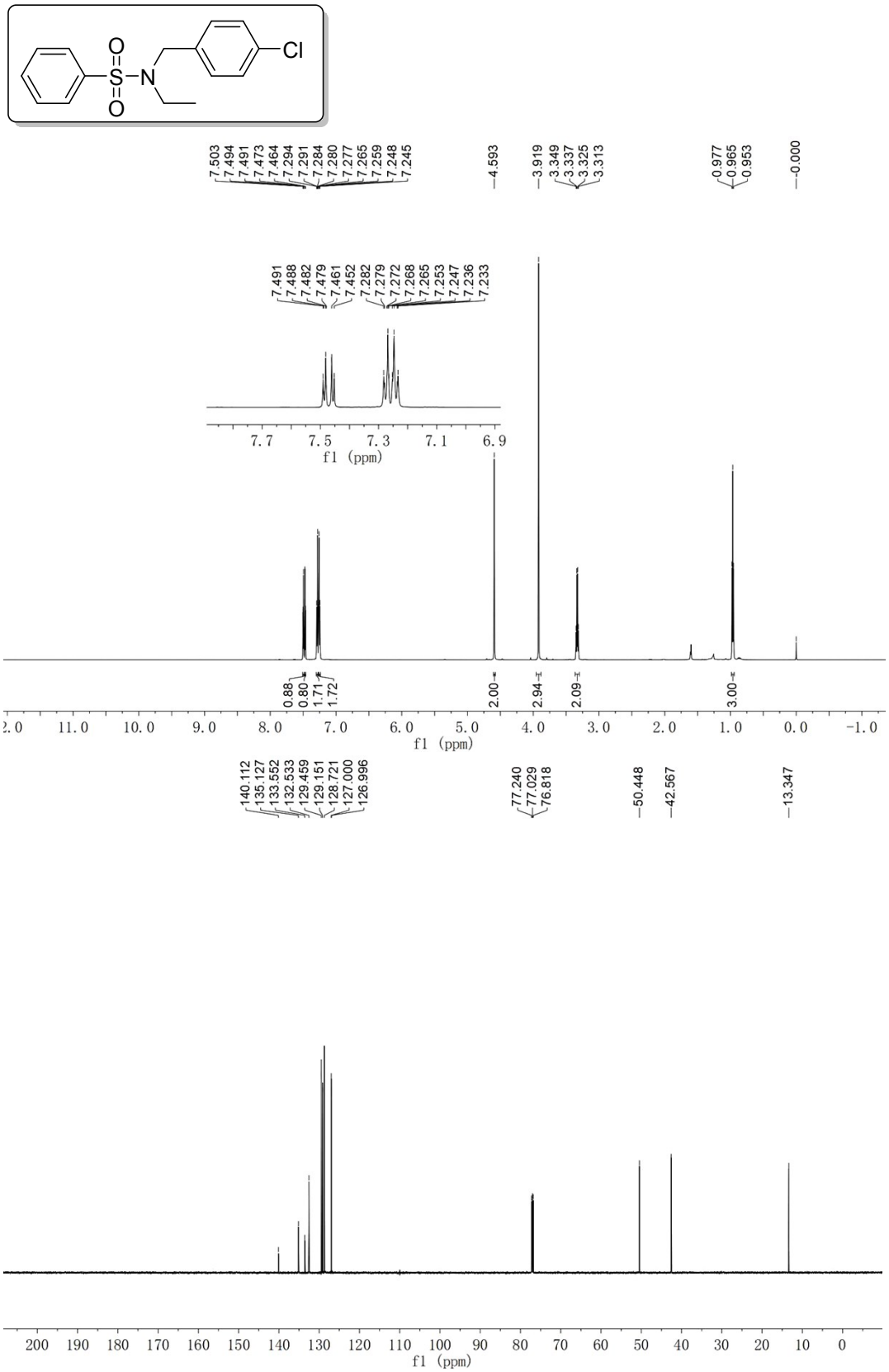


Figure S25. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 5k in $CDCl_3$.

Ethyl-*N*-(2-oxo-2-phenylethyl)naphthalene-2-sulfonamide (5l)

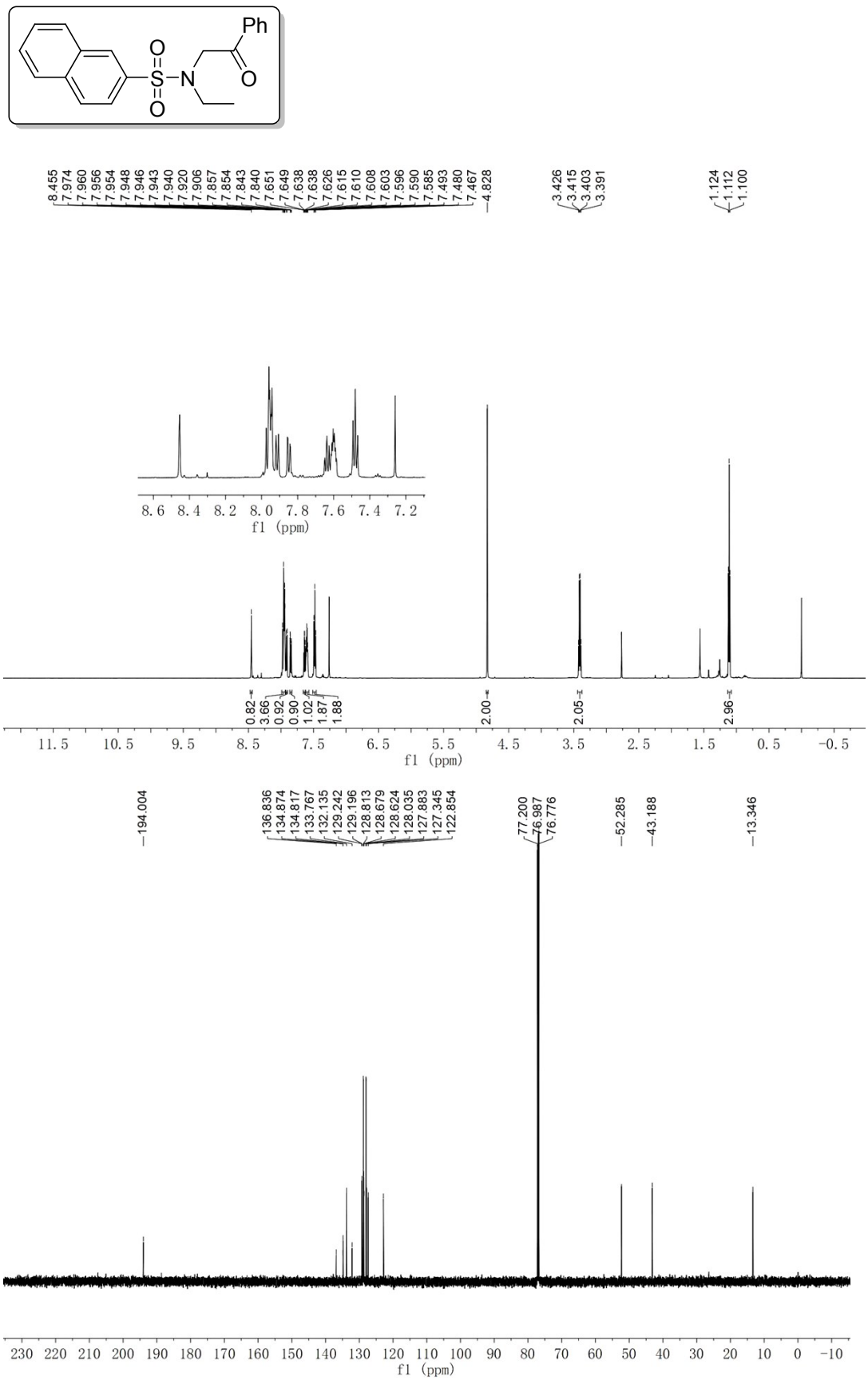


Figure S26. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 5l in $CDCl_3$.

***N*,*N*-Diethylthiophene-2-sulfonamide (5m)**

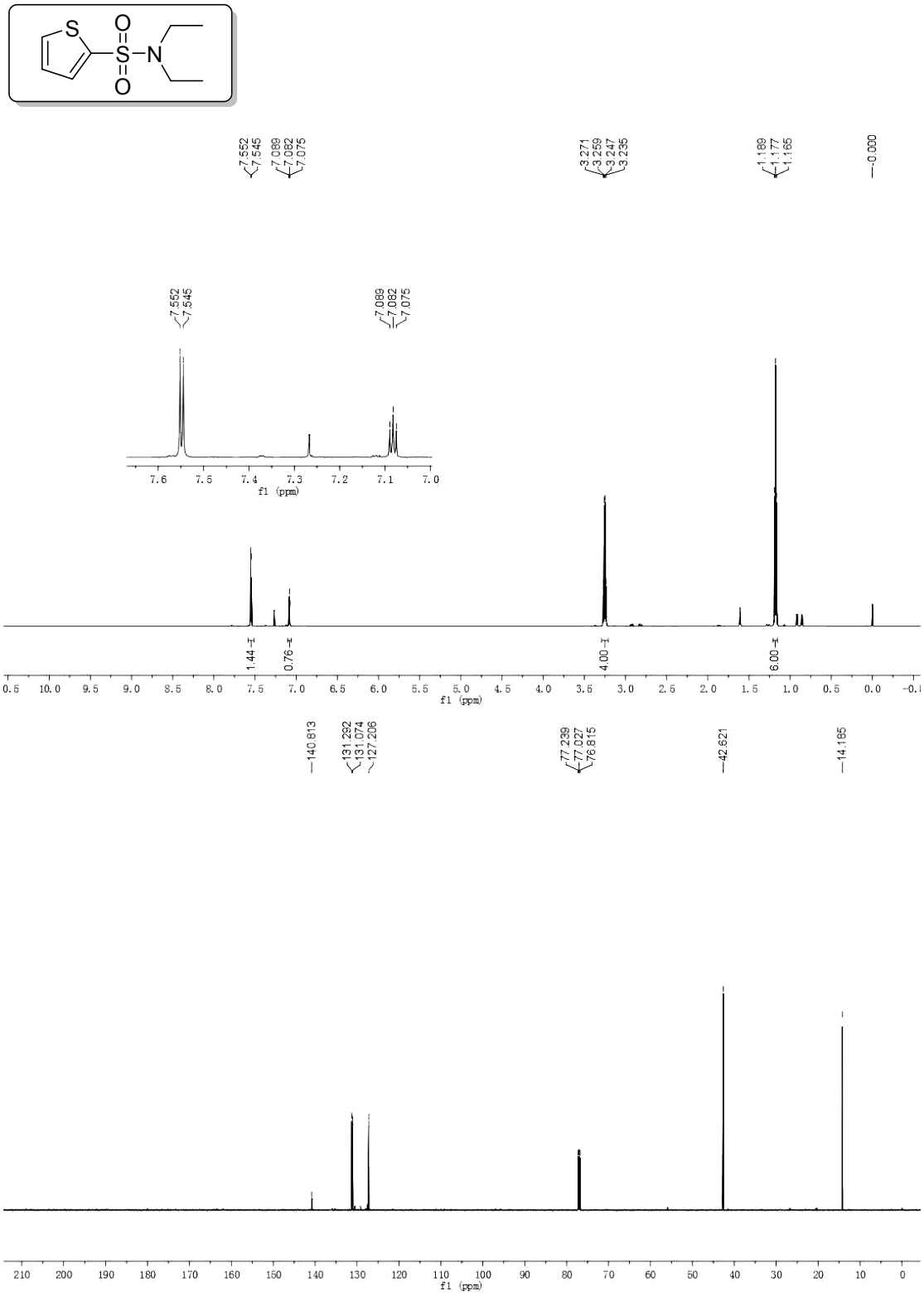


Figure S27. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 5m in $CDCl_3$.

Methyl 2-(*N*-(4-chlorobenzyl)-*N*-ethylsulfamoyl)thiophene-3-carboxylate (5n)

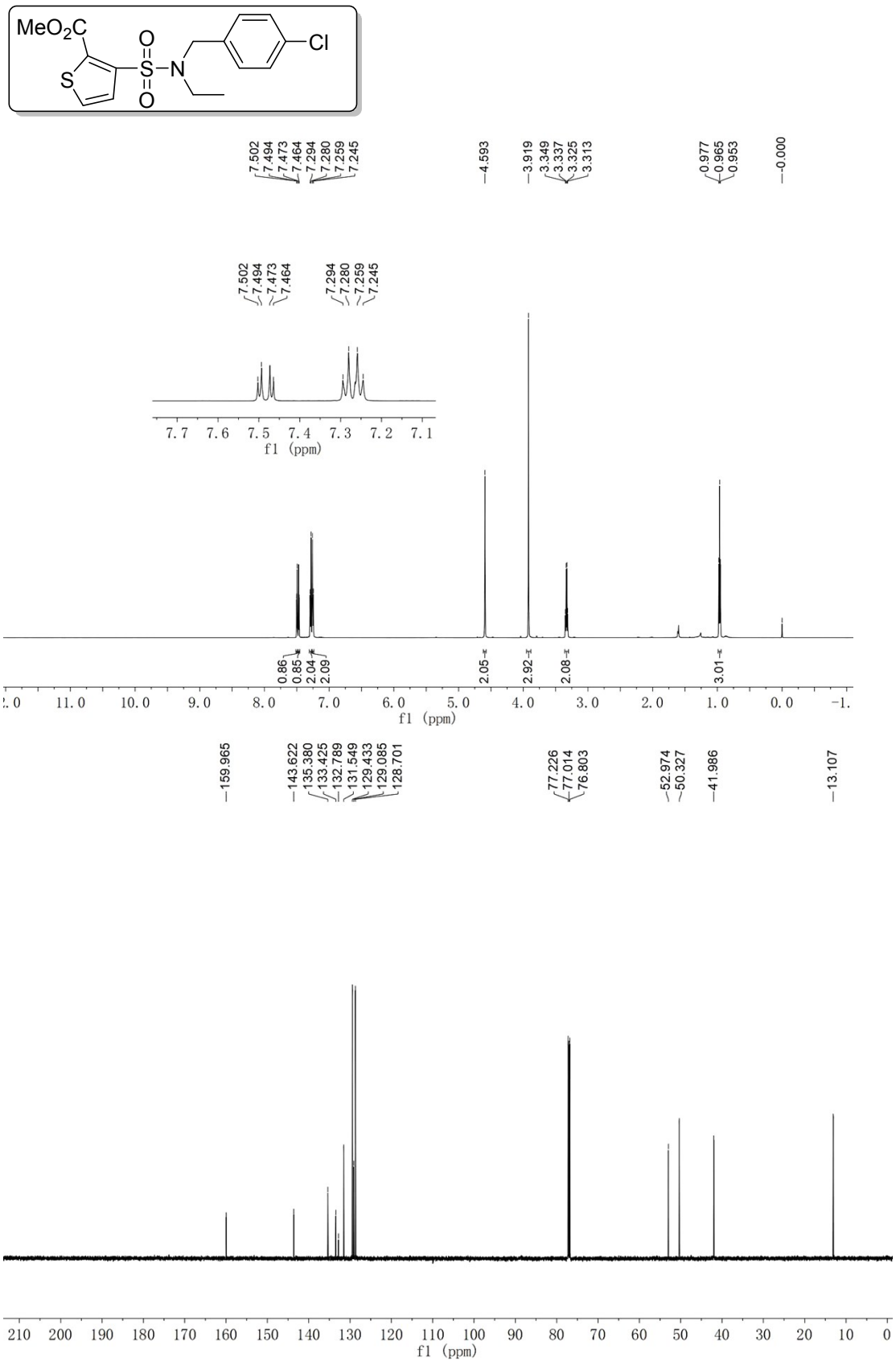


Figure S28. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 5n in $CDCl_3$.

***N*-Methyl-*N*-(2-oxo-2-phenylethyl)cyclopropanesulfonamide (5o)**

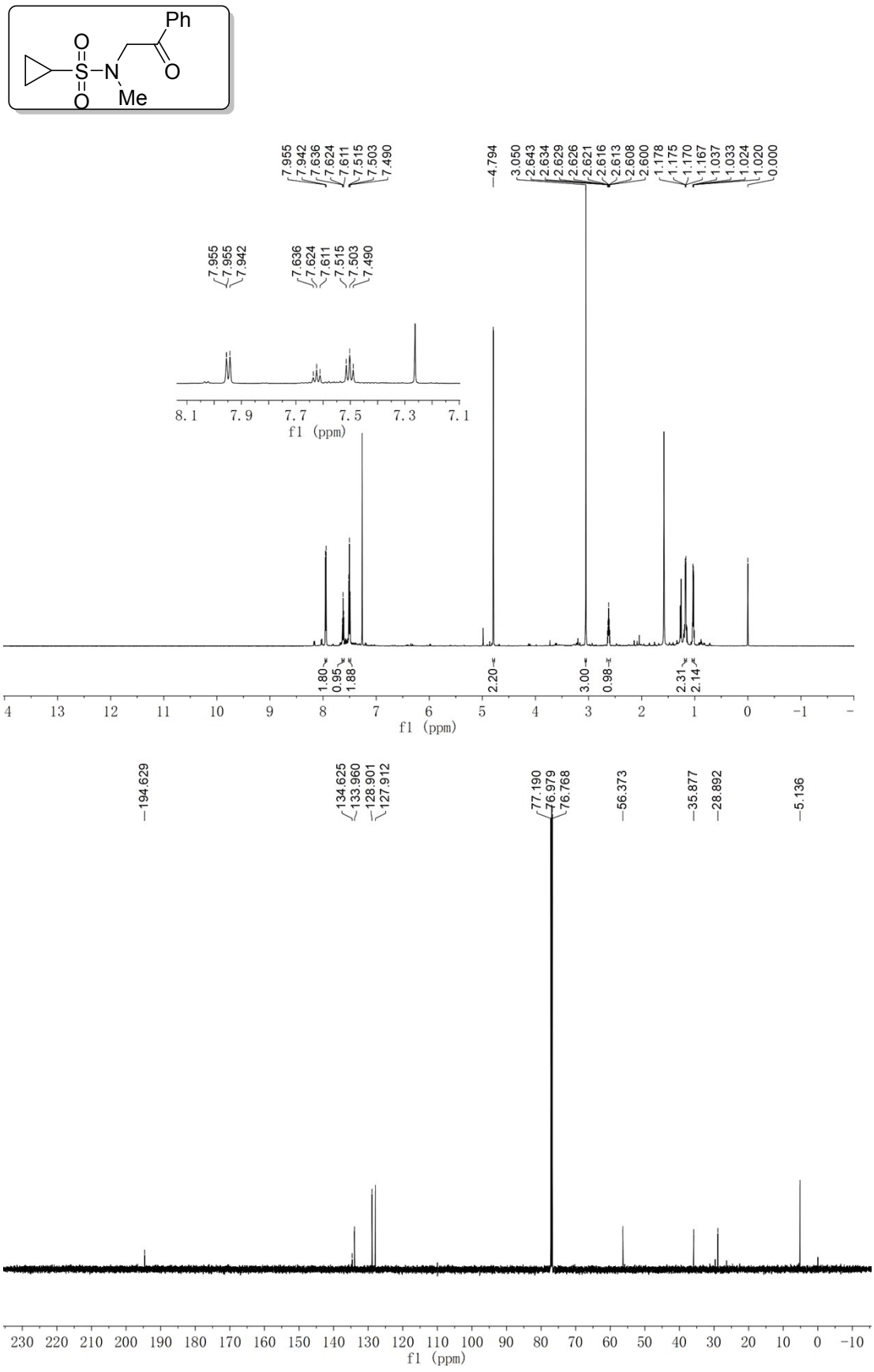


Figure S29. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 5o in $CDCl_3$.

2,2,6,6-Tetramethylpiperidin-1-yl 4-methylbenzenesulfonate (11)

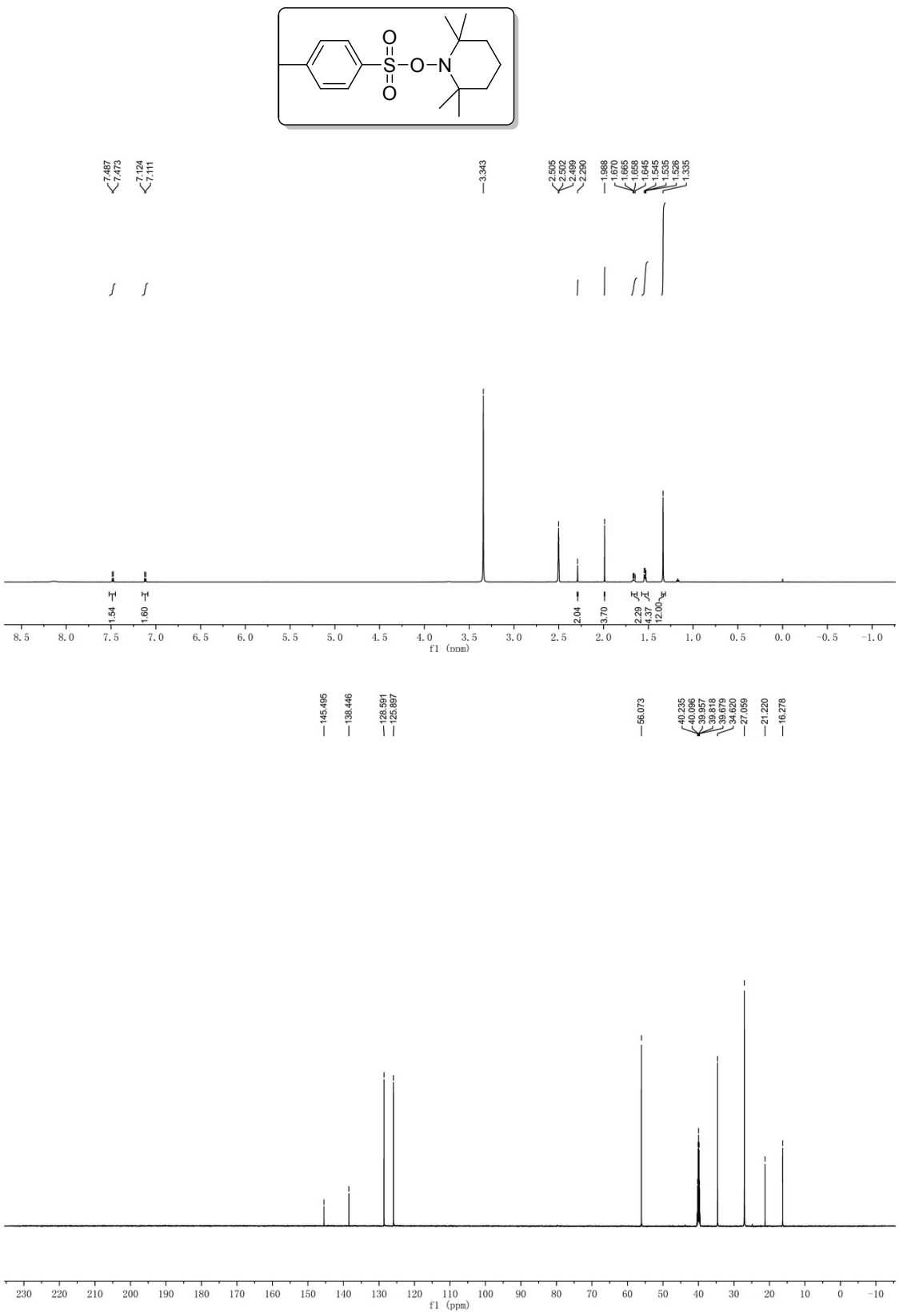


Figure S30. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of 11 in $CDCl_3$.