Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Visible-light mediated cross-coupling of aryl halides with sodium sulfinates via carbonyl-photoredox/nickel dual catalysis

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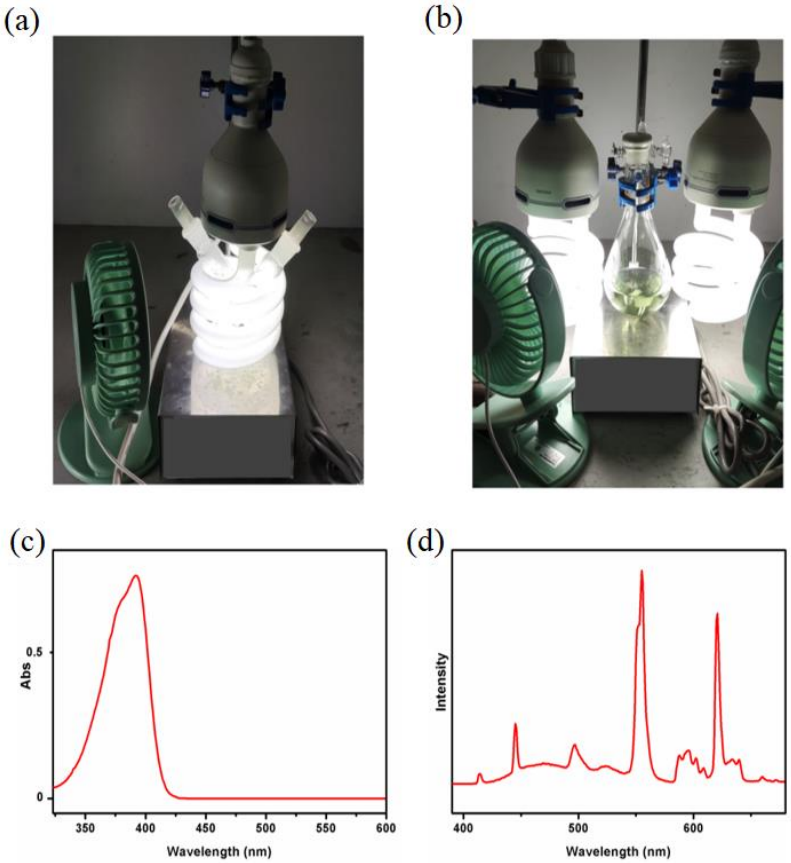


Fig. S1 Reaction set-up with a 45 W CFL (a), gram scale reaction set-up with 2×45 W CFLs (b), the absorbance spectrum of Cl-TXO in DMSO (c), the output spectrum of 45 W CFL (d).

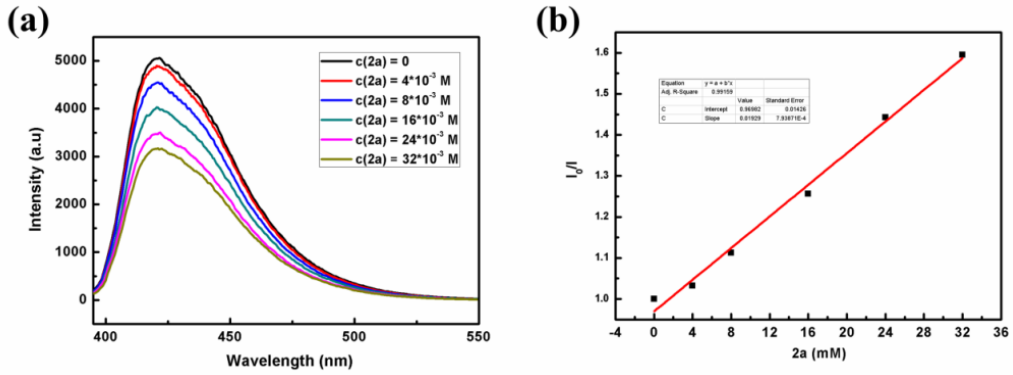


Fig. S2 (a) Emission spectra of Cl-TXO in DMSO (1×10^{-4} mol·L^{-1}) in the presence of increasing **2a** concentrations excited at λ = 374 nm. (b) Stern-Volmer plot of I_0/I versus **2a** concentration in Cl-TXO DMSO solution (I_0 and I represent the intensities of the emission in the absence and presence of the quencher).

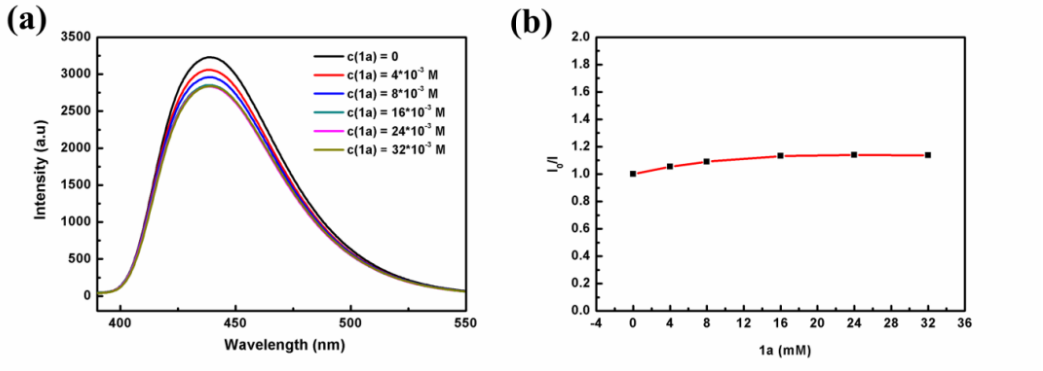


Fig. S3 (a) Emission spectra of Cl-TXO in DMSO (1×10^{-4} mol·L^{-1}) in the presence of increasing **1a** concentrations excited at λ = 374 nm. (b) Stern-Volmer plot of I_0/I versus **1a** concentration in Cl-TXO DMSO solution (I_0 and I represent the intensities of the emission in the absence and presence of the quencher).

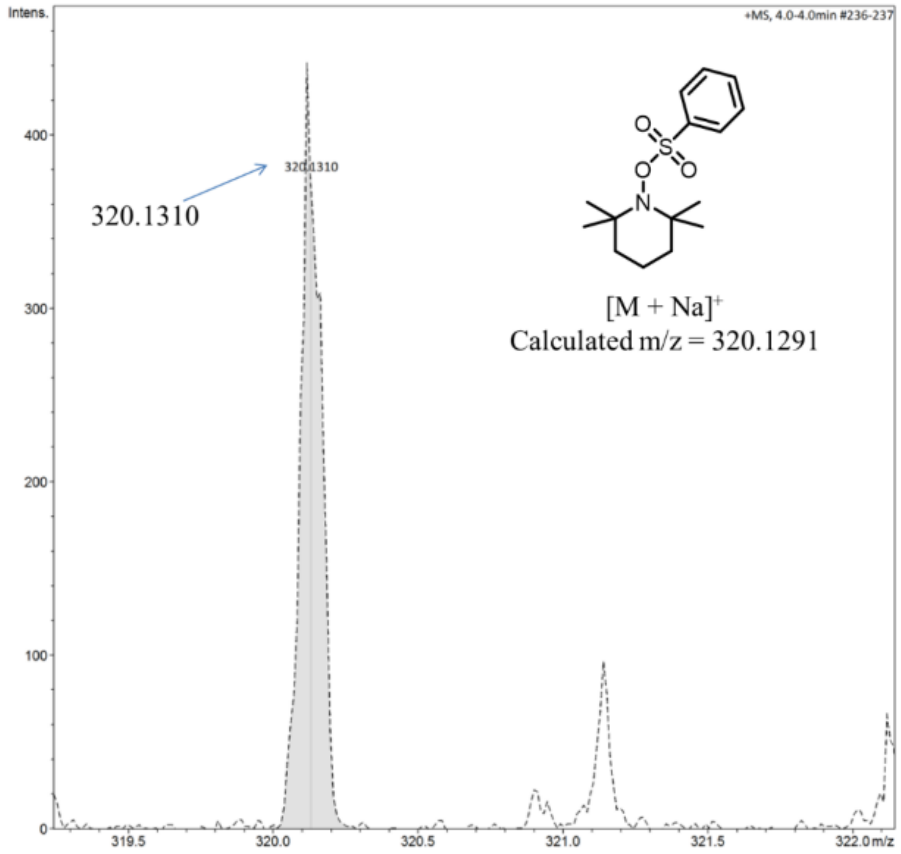


Fig. S4 The positive-ion ESI mass spectrum of 2,2,6,6-tetramethylpiperidin-1-yl benzenesulfonate.

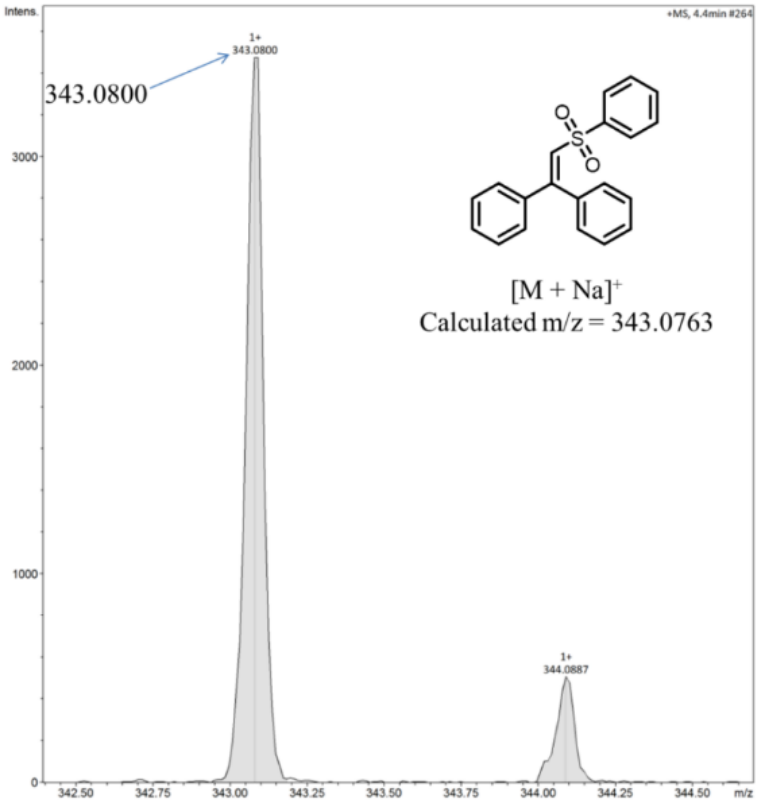


Fig. S5 The positive-ion ESI mass spectrum of (2-(phenylsulfonyl)ethene-1,1-diyl)dibenzene.

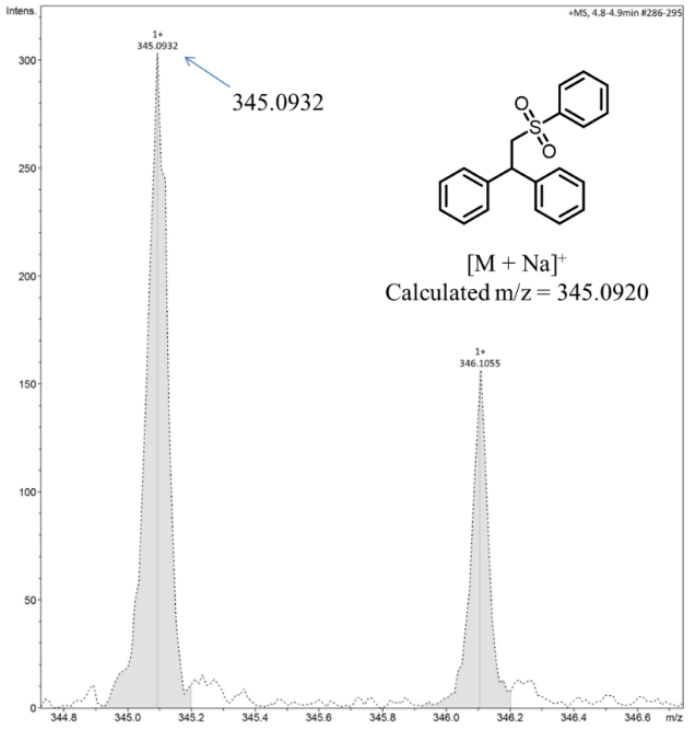
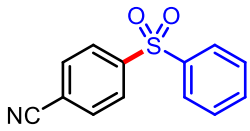


Fig. S6 The positive-ion ESI mass spectrum of (2-(phenylsulfonyl)ethane-1,1-diyl)dibenzene.

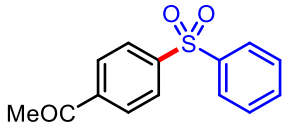
NMR data of products

4-(phenylsulfonyl)benzonitrile (3aa)[S1]



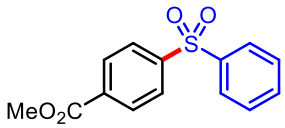
3aa was obtained in 90% yield (43.7 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.06 (d, *J* = 8.5 Hz, 2H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 145.9, 140.1, 134.1, 133.1, 129.7, 128.3, 128.0, 117.2, 116.9. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{13}H_9NO_2SNa^+$ 266.0246; Found 266.0243.

1-(4-(phenylsulfonyl)phenyl)ethan-1-one (3ba)[S1]



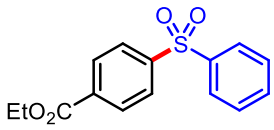
3ba was obtained in 86% yield (44.7 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.11-8.00 (m, 4H), 7.96 (d, *J* = 7.1 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 2H), 2.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 196.7, 145.5, 140.8, 140.4, 133.7, 129.5, 129.1, 128.0, 127.9, 26.9. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{14}H_{12}O_3SNa^+$ 283.0399; Found 283.0416.

methyl 4-(phenylsulfonyl)benzoate (3ca)[S1]



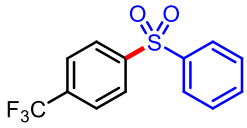
3ca was obtained in 87% yield (48.0 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.15 (d, *J* = 8.7 Hz, 2H), 8.01 (d, *J* = 8.7 Hz, 2H), 7.96 (d, *J* = 7.1 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 2H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 165.5, 145.5, 140.8, 134.3, 133.6, 130.5, 129.5, 127.9, 127.7, 52.7. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{14}H_{12}O_4SNa^+$ 299.0349; Found 299.0335.

ethyl 4-(phenylsulfonyl)benzoate (3da)[S1]



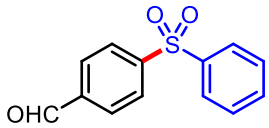
3da was obtained in 88% yield (51.0 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.16 (d, *J* = 8.7 Hz, 2H), 8.01 (d, *J* = 8.7 Hz, 2H), 7.96 (d, *J* = 7.1 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 165.0, 145.3, 140.8, 134.7, 133.6, 130.4, 129.5, 127.8, 127.7, 61.7, 14.2. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{14}O_4SNa^+$ 313.0505; Found 313.0515.

1-(phenylsulfonyl)-4-(trifluoromethyl)benzene (3ea)[S2]



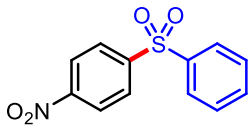
3ea was obtained in 61% yield (34.9 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.08 (d, *J* = 8.2 Hz, 2H), 7.97 (dt, *J* = 3.5, 2.4 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 145.2, 140.6, 134.9 (q, $^{2}J_{C\text{-}F}$ = 33.2 Hz), 133.8, 129.6, 128.2, 127.9, 126.5 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 123.1 (d, $^{1}J_{C\text{-}F}$ = 273.3 Hz). ^{19}F NMR (377 MHz, $CDCl_3$, ppm) δ -63.2. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{13}H_9F_3O_2SNa^+$ 309.0168; Found 309.0177.

4-(phenylsulfonyl)benzaldehyde (3fa)[S1]



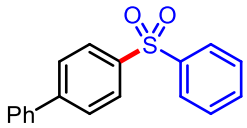
3fa was obtained in 58% yield (28.5 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 10.08 (s, 1H), 8.12 (d, *J* = 8.3 Hz, 2H), 7.99 (dd, *J* = 13.2, 7.8 Hz, 4H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 190.7, 146.7, 140.6, 139.1, 133.8, 130.3, 129.6, 128.4, 128.0. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{13}H_{10}O_3SNa^+$ 269.0243; Found 269.0268.

1-nitro-4-(phenylsulfonyl)benzene (3ga)[S1]



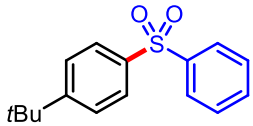
3ga was obtained in 90% yield (47.3 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.46-8.23 (m, 2H), 8.23-8.05 (m, 2H), 8.05-7.91 (m, 2H), 7.74-7.61 (m, 1H), 7.57 (dt, *J* = 8.3, 5.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 150.3, 147.4, 140.0, 134.1, 129.7, 129.0, 128.0, 124.5. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{12}H_9NO_4SNa^+$ 286.0144; Found 286.0173.

4-(phenylsulfonyl)-1,1'-biphenyl (3ha)[S1]



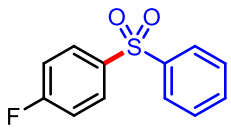
3ha was obtained in 64% yield (37.6 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.00 (t, *J* = 7.5 Hz, 4H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.63-7.49 (m, 5H), 7.43 (dt, *J* = 22.2, 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 146.2, 141.7, 140.1, 139.2, 133.2, 129.3, 129.1, 128.6, 128.2, 128.0, 127.7, 127.4. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{18}H_{14}O_2SNa^+$ 317.0607; Found 317.0614.

1-(tert-butyl)-4-(phenylsulfonyl)benzene (3ia)[S3]



3ia was obtained in 54% yield (29.6 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.95 (d, *J* = 6.9 Hz, 2H), 7.86 (d, *J* = 8.7 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.53-7.47 (m, 4H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 157.1, 142.0, 138.6, 133.0, 129.2, 127.6, 127.5, 126.3, 35.2, 31.0. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{16}H_{18}O_2SNa^+$ 297.0920; Found 297.0895.

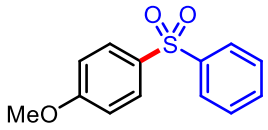
1-fluoro-4-(phenylsulfonyl)benzene (3ja)[S4]



3ja was obtained in 75% yield (35.4 mg) according to the general procedure (petroleum

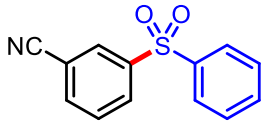
ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.02-7.87 (m, 4H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.22-7.14 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 165.5 (d, $^{1}J_{C\text{-}F}$ = 256.1 Hz), 141.5, 137.7 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 133.3, 130.5 (d, $^{3}J_{C\text{-}F}$ = 9.6 Hz), 129.4, 127.6, 116.6 (d, $^{2}J_{C\text{-}F}$ = 22.7 Hz). ^{19}F NMR (377 MHz, $CDCl_3$, ppm) δ -104.2. QTOF-MS *m/z* [M + Na]$^{+}$ Calcd for $C_{12}H_9FO_2SNa^{+}$ 259.0199; Found 259.0184.

1-methoxy-4-(phenylsulfonyl)benzene (3ka)[S1]



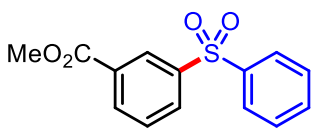
3ka was obtained in 35% yield (17.4 mg) based on 1-bromo-4-methoxybenzene, 57% yield (28.3 mg) based on 1-iodo-4-methoxybenzene according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.90 (dd, *J* = 14.8, 8.0 Hz, 4H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.3 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 163.4, 142.3, 133.1, 132.8, 130.0, 129.2, 127.3, 114.5, 55.6. QTOF-MS *m/z* [M + Na]$^{+}$ Calcd for $C_{13}H_{12}O_3SNa^{+}$ 271.0399; Found 271.0396.

3-(phenylsulfonyl)benzonitrile (3la)[S1]



3la was obtained in 61% yield (29.6 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.22 (s, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.65 (dd, *J* = 15.1, 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 143.5, 140.2, 136.2, 134.0, 131.5, 131.3, 130.4, 129.7, 127.9, 117.0, 114.0. QTOF-MS *m/z* [M + Na]$^{+}$ Calcd for $C_{13}H_9NO_2SNa^{+}$ 266.0246; Found 266.0258.

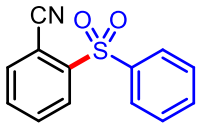
methyl 3-(phenylsulfonyl)benzoate (3ma)



3ma was obtained in 49% yield (27.0 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. M.P. = 60.5-61.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.60 (s,

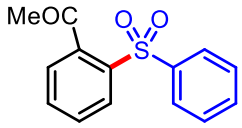
1H), 8.23 (d, *J* = 7.8 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 7.1 Hz, 2H), 7.74-7.56 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 2H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 165.3, 142.4, 141.0, 134.1, 133.5, 131.6, 131.6, 129.6, 129.5, 128.8, 127.8, 52.6. IR (KBr disk) 3076, 2954, 2918, 2850, 1716, 1597, 1444, 1317, 1266, 1153, 1125, 1094, 1023, 999, 974, 925, 847, 820, 744, 712, 684 cm^{-1}. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{14}H_{12}O_4SNa^+$ 299.0349; Found 299.0343.

2-(phenylsulfonyl)benzonitrile (3na)[S1]



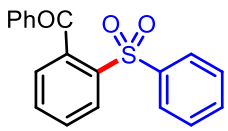
3na was obtained in 47% yield (22.8 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.35 (d, *J* = 7.1 Hz, 1H), 8.09 (d, *J* = 7.2 Hz, 2H), 7.81 (t, *J* = 6.8 Hz, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 143.7, 139.5, 135.7, 134.2, 133.4, 133.3, 129.8, 129.4, 128.7, 115.6, 111.5. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{13}H_9NO_2SNa^+$ 266.0246; Found 266.0251.

1-(2-(phenylsulfonyl)phenyl)ethan-1-one (3oa)[S5]



3oa was obtained in 56% yield (29.1 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 7.0 Hz, 2H), 7.65-7.47 (m, 5H), 7.30 (d, *J* = 7.5 Hz, 1H), 2.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 203.3, 142.4, 141.3, 138.1, 133.4, 133.4, 130.0, 129.9, 129.1, 128.0, 126.0, 32.0. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{14}H_{12}O_3SNa^+$ 283.0399; Found 283.0424.

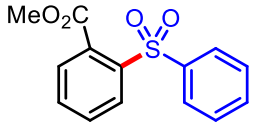
phenyl(2-(phenylsulfonyl)phenyl)methanone (3pa)[S1]



3pa was obtained in 59% yield (38.0 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.22-8.09 (m, 1H), 7.92 (d, *J* = 7.2 Hz, 2H), 7.79 (d, *J* = 7.1 Hz, 2H), 7.64 (d, *J* = 9.1 Hz, 2H), 7.62-7.53 (m, 2H), 7.53-7.42 (m,

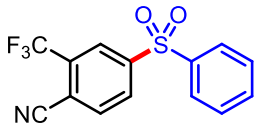
4H), 7.38-7.28 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 195.7, 141.3, 140.0, 139.7, 136.8, 133.7, 133.3, 132.9, 130.2, 130.2, 130.1, 129.1, 128.5, 128.2, 128.1. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{19}H_{14}O_3SNa^+$ 345.0556; Found 345.0551.

methyl 2-(phenylsulfonyl)benzoate (3qa)[S6]



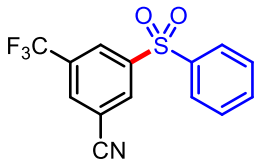
3qa was obtained in 53% yield (29.2 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.20-8.10 (m, 1H), 7.97 (d, *J* = 7.1 Hz, 2H), 7.67-7.61 (m, 2H), 7.61-7.55 (m, 2H), 7.52 (t, *J* = 7.4 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 167.7, 141.5, 139.0, 133.3, 133.2, 130.9, 130.2, 129.2, 129.0, 127.8, 53.0, 29.7. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{14}H_{12}O_4SNa^+$ 299.0349; Found 299.0349.

4-(phenylsulfonyl)-2-(trifluoromethyl)benzonitrile (3ra)[S1]



3ra was obtained in 91% yield (56.6 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.33 (s, 1H), 8.24 (d, *J* = 8.1 Hz, 1H), 8.10-7.88 (m, 3H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 146.6, 139.3, 135.8, 134.6, 134.3 (d, $^2J_{C\text{-}F}$ = 33.7 Hz), 131.3, 130.0, 128.2, 125.8 (q, $^3J_{C\text{-}F}$ = 4.5 Hz), 121.5 (d, $^1J_{C\text{-}F}$ = 274.9 Hz), 114.5, 114.0. ^{19}F NMR (377 MHz, $CDCl_3$, ppm) δ -62.1. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{14}H_8F_3NO_2SNa^+$ 334.0120; Found 334.0133.

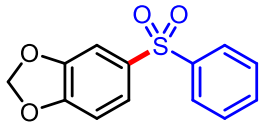
3-(phenylsulfonyl)-5-(trifluoromethyl)benzonitrile (3sa)[S1]



3sa was obtained in 71% yield (44.2 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.39 (d, *J* = 12.6 Hz, 2H), 8.08 (s, 1H), 7.99 (d, *J* = 7.1 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 145.1, 139.3, 134.6, 134.3, 133.5 (d, $^2J_{C\text{-}F}$ = 34.9 Hz), 133.0 (q, $^3J_{C\text{-}F}$ = 3.4 Hz), 130.0, 128.3 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 128.2, 122.0 (q, $^1J_{C\text{-}F}$ = 273.8 Hz), 115.7, 115.2. ^{19}F

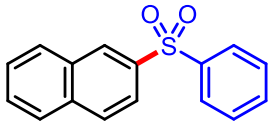
NMR (377 MHz, $CDCl_3$, ppm) δ -63.1. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{14}H_8F_3NO_2SNa^+$ 334.0120; Found 334.0137.

5-(phenylsulfonyl)benzo[*d*][1,3]dioxole (3ta)[S1]



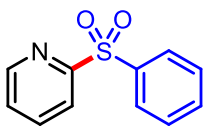
3ta was obtained in 26% yield (13.6 mg) based on 5-bromobenzo[d][1,3]dioxole, 43% yield (22.5 mg) based on 5-iodobenzo[d][1,3]dioxole according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.91 (d, *J* = 7.0 Hz, 2H), 7.59-7.53 (m, 2H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.32 (d, *J* = 1.8 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.05 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 151.9, 148.4, 142.0, 134.9, 133.0, 129.2, 127.4, 123.6, 108.5, 107.9, 102.4. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{13}H_{10}O_4SNa^+$ 285.0192; Found 285.0197.

2-(phenylsulfonyl)naphthalene (3ua)[S1]



3ua was obtained in 54% yield (28.9 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.58 (s, 1H), 8.00 (t, *J* = 7.1 Hz, 3H), 7.93 (d, *J* = 8.7 Hz, 1H), 7.87 (t, *J* = 7.8 Hz, 2H), 7.63 (ddd, *J* = 14.4, 7.1, 1.5 Hz, 2H), 7.57-7.46 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 141.6, 138.4, 135.0, 133.2, 132.2, 129.7, 129.4, 129.3, 129.2, 129.1, 127.9, 127.7, 127.6, 122.7. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{16}H_{12}O_2SNa^+$ 291.0450; Found 291.0454.

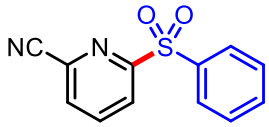
2-(phenylsulfonyl)pyridine (3va)[S7]



3va was obtained in 63% yield (27.6 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.68 (d, *J* = 4.7 Hz, 1H), 8.21 (d, *J* = 7.9 Hz, 1H), 8.07 (d, *J* = 7.1 Hz, 2H), 7.93 (td, *J* = 7.8, 1.7 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.46 (ddd, *J* = 7.7, 4.7, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$,

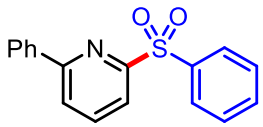
ppm) δ 158.9, 150.5, 139.0, 138.1, 133.8, 129.1, 128.9, 126.9, 122.2. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{11}H_9NO_2SNa^+$ 242.0246; Found 242.0251.

6-(phenylsulfonyl)picolinonitrile (3wa)[S1]



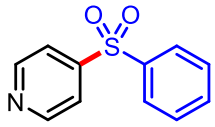
3wa was obtained in 50% yield (24.4 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.42 (dd, *J* = 8.0, 1.0 Hz, 1H), 8.20-7.98 (m, 3H), 7.84 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 160.5, 139.7, 137.4, 134.5, 134.3, 131.1, 129.4, 129.4, 124.8, 115.7. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{12}H_8N_2O_2SNa^+$ 267.0199; Found 267.0187.

2-phenyl-6-(phenylsulfonyl)pyridine (3xa)[S8]



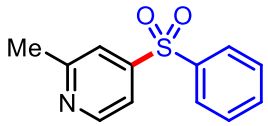
3xa was obtained in 42% yield (24.8 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.16 (d, *J* = 7.1 Hz, 2H), 8.11 (d, *J* = 7.2 Hz, 1H), 8.02-7.91 (m, 3H), 7.87 (d, *J* = 7.4 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.49-7.40 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 158.7, 158.0, 138.9, 138.7, 137.1, 133.7, 130.1, 129.2, 128.9, 128.8, 127.0, 123.1, 119.8. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{17}H_{13}NO_2SNa^+$ 318.0559; Found 318.0544.

4-(phenylsulfonyl)pyridine (3ya)[S1]



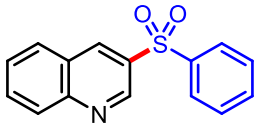
3ya was obtained in 72% yield (31.5 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.83 (dd, *J* = 4.5, 1.6 Hz, 2H), 7.98 (d, *J* = 7.1 Hz, 2H), 7.77 (dd, *J* = 4.5, 1.6 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 151.2, 149.8, 139.7, 134.2, 129.7, 128.2, 120.6. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{11}H_9NO_2SNa^+$ 242.0246; Found 242.0253.

2-methyl-4-(phenylsulfonyl)pyridine (3za)[S9]



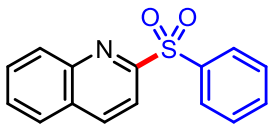
3za was obtained in 52% yield (24.2 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.69 (d, *J* = 5.2 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 2H), 7.64 (t, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 3H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 160.7, 150.6, 149.9, 139.9, 134.1, 129.6, 128.1, 120.1, 117.7, 24.7. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{12}H_{11}NO_2SNa^+$ 256.0403; Found 256.0432.

3-(phenylsulfonyl)quinoline (3a'a)[S2]



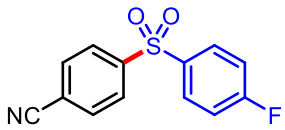
3a'a was obtained in 88% yield (47.3 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.28 (d, *J* = 2.3 Hz, 1H), 8.83 (d, *J* = 2.1 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 7.1 Hz, 2H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.89 (ddd, *J* = 8.5, 7.0, 1.4 Hz, 1H), 7.69 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 149.4, 147.1, 141.0, 137.0, 134.7, 133.8, 132.8, 129.6, 129.6, 129.2, 128.4, 127.8, 126.4. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{11}NO_2SNa^+$ 292.0403; Found 292.0380.

2-(phenylsulfonyl)quinoline (3b'a)[S1]



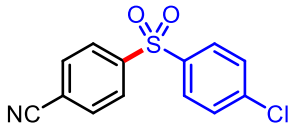
3b'a was obtained in 45% yield (24.1 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.39 (d, *J* = 8.5 Hz, 1H), 8.30-8.07 (m, 4H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.80 (t, *J* = 7.7 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 158.1, 147.5, 139.1, 138.7, 133.7, 131.0, 130.4, 129.2, 129.1, 129.1, 128.9, 127.7, 117.7. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{11}NO_2SNa^+$ 292.0403; Found 292.0378.

4-((4-fluorophenyl)sulfonyl)benzonitrile (3ab)[S1]



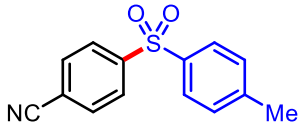
3ab was obtained in 83% yield (43.3 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.04 (d, *J* = 8.6 Hz, 2H), 7.97 (dd, *J* = 8.9, 5.0 Hz, 2H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.26-7.19 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 166.0 (d, $^{1}J_{C\text{-}F}$ = 257.6 Hz), 145.7, 136.2, 133.2, 130.9 (d, $^{3}J_{C\text{-}F}$ = 9.6 Hz), 128.2, 117.1, 117.1 (d, $^{2}J_{C\text{-}F}$ = 22.7 Hz), 117.1. ^{19}F NMR (377 MHz, $CDCl_3$, ppm) δ -102.3. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{13}H_8FNO_2SNa^+$ 284.0152; Found 284.0167.

4-((4-chlorophenyl)sulfonyl)benzonitrile (3ac)[S2]



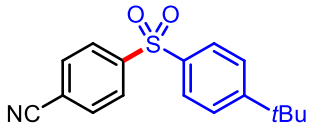
3ac was obtained in 57% yield (31.6 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.04 (d, *J* = 8.7 Hz, 2H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 145.5, 141.0, 138.6, 133.2, 130.0, 129.4, 128.3, 117.2, 117.0. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{13}H_8ClNO_2SNa^+$ 299.9856; Found 299.9878.

4-tosylbenzonitrile (3ad)[S1]



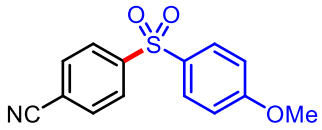
3ad was obtained in 65% yield (33.4 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.04 (d, *J* = 8.6 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 146.3, 145.3, 137.1, 133.0, 130.3, 128.1, 128.0, 117.2, 116.7, 21.6. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{14}H_{11}NO_2SNa^+$ 280.0403; Found 280.0431.

4-((4-(tert-butyl)phenyl)sulfonyl)benzonitrile (3ae)[S1]



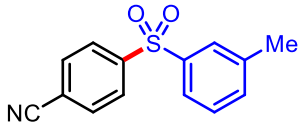
3ae was obtained in 89% yield (53.2mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.05 (d, *J* = 8.5 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 158.2, 146.2, 137.0, 133.0, 128.2, 127.9, 126.7, 117.2, 116.7, 35.3, 31.0. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{17}H_{17}NO_2SNa^+$ 322.0872; Found 322.0859.

4-((4-methoxyphenyl)sulfonyl)benzonitrile (3af)[S1]



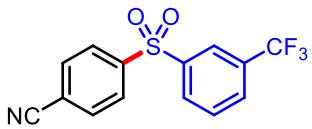
3af was obtained in 59% yield (32.2 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.02 (d, *J* = 8.7 Hz, 2H), 7.88 (d, *J* = 9.0 Hz, 2H), 7.78 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 9.0 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 164.1, 146.6, 133.0, 131.4, 130.3, 128.0, 117.2, 116.5, 114.9, 55.8. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{14}H_{11}NO_3SNa^+$ 296.0352; Found 296.0359.

4-(m-tolylsulfonyl)benzonitrile (3ag)[S1]



3ag was obtained in 55% yield (28.3 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.75 (s, 2H), 7.47-7.39 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 146.0, 140.0, 139.9, 134.9, 133.1, 129.5, 128.3, 128.2, 125.2, 117.2, 116.8, 21.4. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{14}H_{11}NO_2SNa^+$ 280.0403; Found 280.0386.

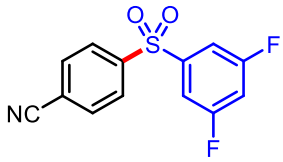
4-((3-(trifluoromethyl)phenyl)sulfonyl)benzonitrile (3ah)[S1]



3ah was obtained in 62% yield (38.6 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.22 (s, 1H), 8.14 (d, *J* = 7.9 Hz, 1H), 8.08 (d, *J* = 8.7 Hz, 2H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.72 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 144.9, 141.6, 133.3, 132.5 (d, $^{2}J_{C-F}$ = 33.7 Hz),

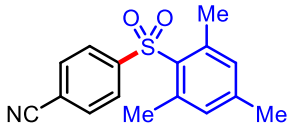
131.2, 130.7 (q, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 130.5, 128.5, 125.0 (q, $^{3}J_{C\text{-}F}$ = 3.9 Hz), 122.9 (d, $^{1}J_{C\text{-}F}$ = 273.1 Hz), 117.6, 116.9. ^{19}F NMR (377 MHz, $CDCl_3$, ppm) δ -62.9. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{14}H_8F_3NO_2SNa^+$ 334.0120; Found 334.0134.

4-((3,5-difluorophenyl)sulfonyl)benzonitrile (3ai)[S1]



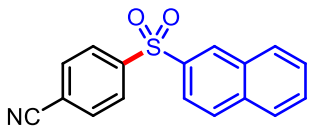
3ai was obtained in 82% yield (45.8 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.06 (d, *J* = 8.6 Hz, 2H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 3.9 Hz, 2H), 7.07 (t, *J* = 8.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 163.1 (dd, $^{1}J_{C\text{-}F}$ = 256.9 Hz), 144.5, 143.5 (t, $^{3}J_{C\text{-}F}$ = 8.2 Hz), 133.4, 128.6, 117.8, 116.9, 111.6 (dd, $^{2}J_{C\text{-}F}$ = 28.4 Hz), 109.8 (t, $^{2}J_{C\text{-}F}$ = 24.9 Hz). ^{19}F NMR (377 MHz, $CDCl_3$, ppm) δ -103.9. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{13}H_7F_2NO_2SNa^+$ 302.0058; Found 302.0074.

4-(mesitylsulfonyl)benzonitrile (3aj)[S1]



3aj was obtained in 58% yield (33.1 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 6.98 (s, 2H), 2.57 (s, 6H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 147.6, 144.4, 140.3, 132.8, 132.5, 132.3, 126.8, 117.3, 116.3, 22.8, 21.1. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{16}H_{15}NO_2SNa^+$ 308.0716; Found 308.0733.

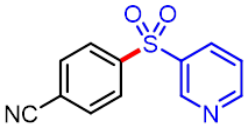
4-(naphthalen-2-ylsulfonyl)benzonitrile (3ak)[S1]



3ak was obtained in 60% yield (35.2 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.59 (s, 1H), 8.11 (d, *J* = 8.6 Hz, 2H), 7.99 (dd, *J* = 13.4, 8.3 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.84 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.79 (d, *J* = 8.6 Hz, 2H), 7.73-7.60 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 145.9, 136.8, 135.3, 133.1, 132.2, 130.1, 129.9, 129.7, 129.5, 128.3, 128.0, 128.0, 122.4, 117.2, 116.9.

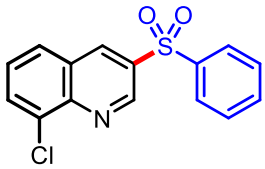
QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{17}H_{11}NO_2SNa^+$ 316.0403; Found 316.0434.

4-(pyridin-3-ylsulfonyl)benzonitrile (3al)[S10]



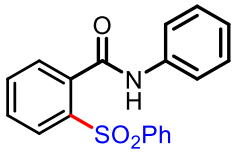
3al was obtained in 50% yield (24.4 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.16 (d, *J* = 2.0 Hz, 1H), 8.85 (dd, *J* = 4.8, 1.4 Hz, 1H), 8.23 (ddd, *J* = 8.1, 2.3, 1.7 Hz, 1H), 8.09 (d, *J* = 8.7 Hz, 2H), 7.85 (d, *J* = 8.7 Hz, 2H), 7.51 (ddd, *J* = 8.1, 4.9, 0.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 154.4, 148.9, 144.9, 137.0, 135.5, 133.4, 128.4, 124.1, 117.6, 116.9. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{12}H_8N_2O_2SNa^+$ 267.0199; Found 267.0187.

8-chloro-3-(phenylsulfonyl)quinolone (3c'a)[S1]



3c'a was obtained in 80% yield (48.5 mg) according to the general procedure (petroleum ether/EtOAc, 5:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.37 (d, *J* = 2.2 Hz, 1H), 8.85 (d, *J* = 2.2 Hz, 1H), 8.03 (dd, *J* = 5.3, 3.4 Hz, 2H), 7.99 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.91 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.70-7.58 (m, 2H), 7.58-7.51 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 147.8, 145.5, 140.6, 137.2, 135.8, 134.1, 134.0, 132.7, 129.7, 128.4, 128.2, 127.9, 127.8. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{10}ClNO_2SNa^+$ 326.0013; Found 326.0028.

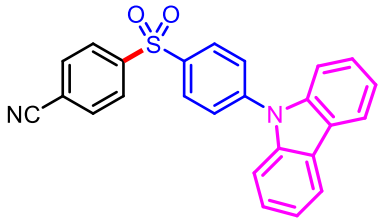
N-phenyl-2-(phenylsulfonyl)benzamide (3d'a)



3d'a was obtained in 83% yield (56.0 mg) according to the general procedure (petroleum ether/EtOAc, 3:1): white solid. M.P. = 185.6-187.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.24-8.12 (m, 2H), 7.97-7.78 (m, 2H), 7.70-7.59 (m, 3H), 7.55 (dd, *J* = 14.6, 7.5 Hz, 3H), 7.41 (t,

J = 7.8 Hz, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 164.9, 140.2, 138.1, 137.6, 136.7, 133.8, 133.7, 130.5, 130.0, 129.2, 129.1, 129.1, 128.1, 124.9, 120.2. IR (KBr disk) 3255, 3197, 3134, 3066, 2353, 2165, 1962, 1662, 1598, 1540, 1492, 1441, 1315, 1264, 1156, 1120, 1085, 1055, 1024, 998, 971, 924, 888, 840, 754, 684 cm^{-1}. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{19}H_{15}NO_3SNa^+$ 360.0665; Found 360.0687.

4-((4-(9H-carbazol-9-yl)phenyl)sulfonyl)benzonitrile (4)



A 10 mL test tube was charged with 4-((4-fluorophenyl)sulfonyl)benzonitrile (0.4 mmol), carbazole (0.4 mmol), K_2CO_3 (0.6 mmol) in degased, dry DMF (6 mL).The reaction was stirred under an nitrogen atmosphere at 100 °C for 24 h. Next, the mixture was cooled to room temperature and poured into ice water slowly, stired for 30 min. After that, this mixture was filtered. The filter cake was dried via suction filtration, washed with water, distilled water, anhydrous methanol, respectively. The crude product was obtained in 91% yiled (148.5 mg), white solid. M.P. = 202.8-204.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.14 (dd, *J* = 15.7, 8.0 Hz, 6H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.6 Hz, 2H), 7.41 (q, *J* = 8.3 Hz, 4H), 7.32 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 145.6, 143.3, 139.8, 138.0, 133.3, 129.9, 128.4, 127.3, 126.4, 124.1, 121.2, 120.6, 117.2, 117.1, 109.6. IR (KBr disk) 3098, 3057, 2231, 1587, 1500, 1443, 1312, 1240, 1212, 1148, 1100, 1011, 972, 934, 909, 839, 794, 746, 721, 679, 626 cm^{-1}. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{25}H_{16}N_2O_2SNa^+$ 431.0825; Found 431.0841.

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NMR spectra

Fig. S7 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 4-(phenylsulfonyl)benzonitrile (**3aa**) in $CDCl_3$

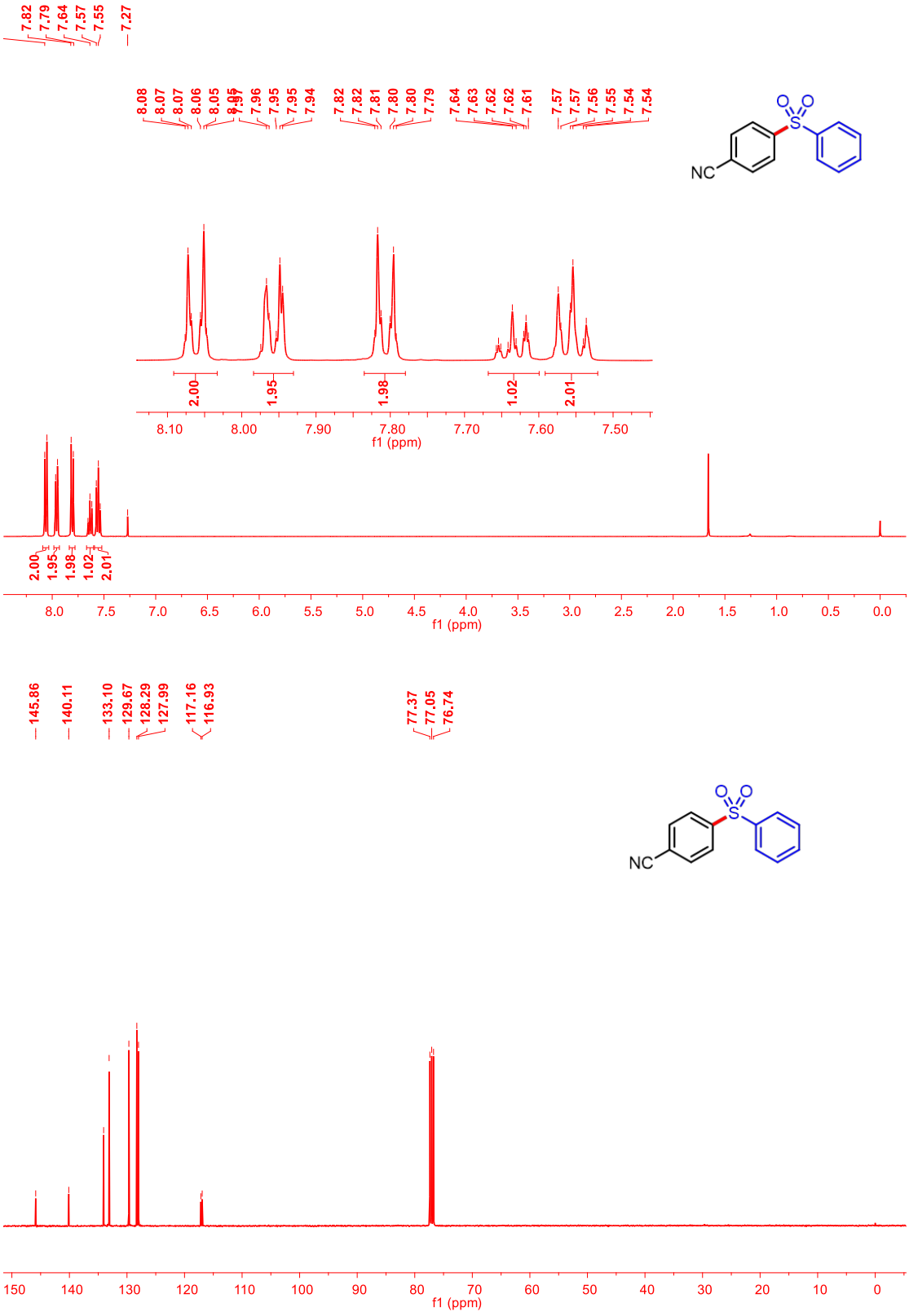


Fig. S8 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 1-(4-(phenylsulfonyl)phenyl)ethan-1-one (**3ba**) in $CDCl_3$

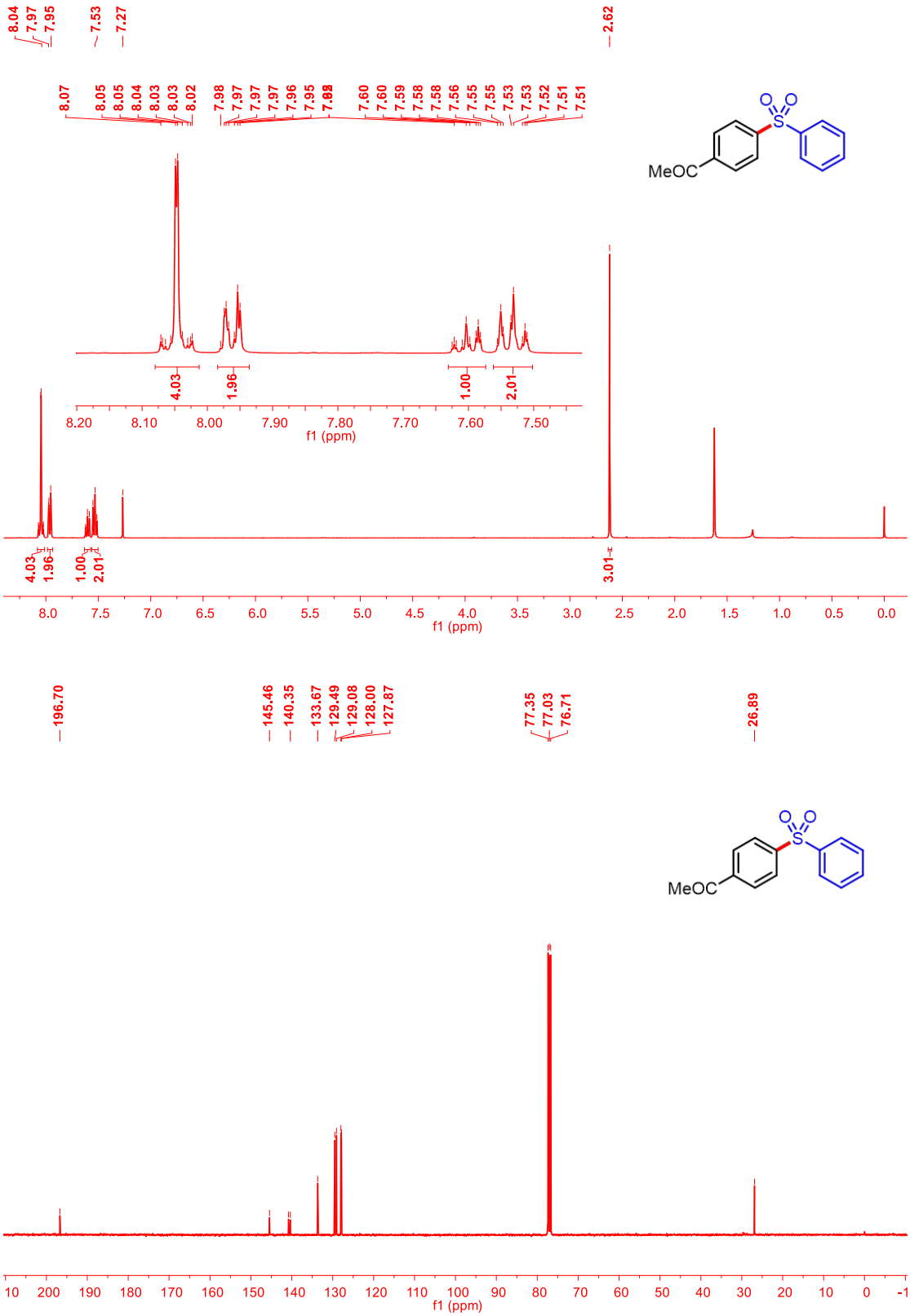


Fig. S9 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for methyl 4-(phenylsulfonyl)benzoate (**3ca**) in $CDCl_3$

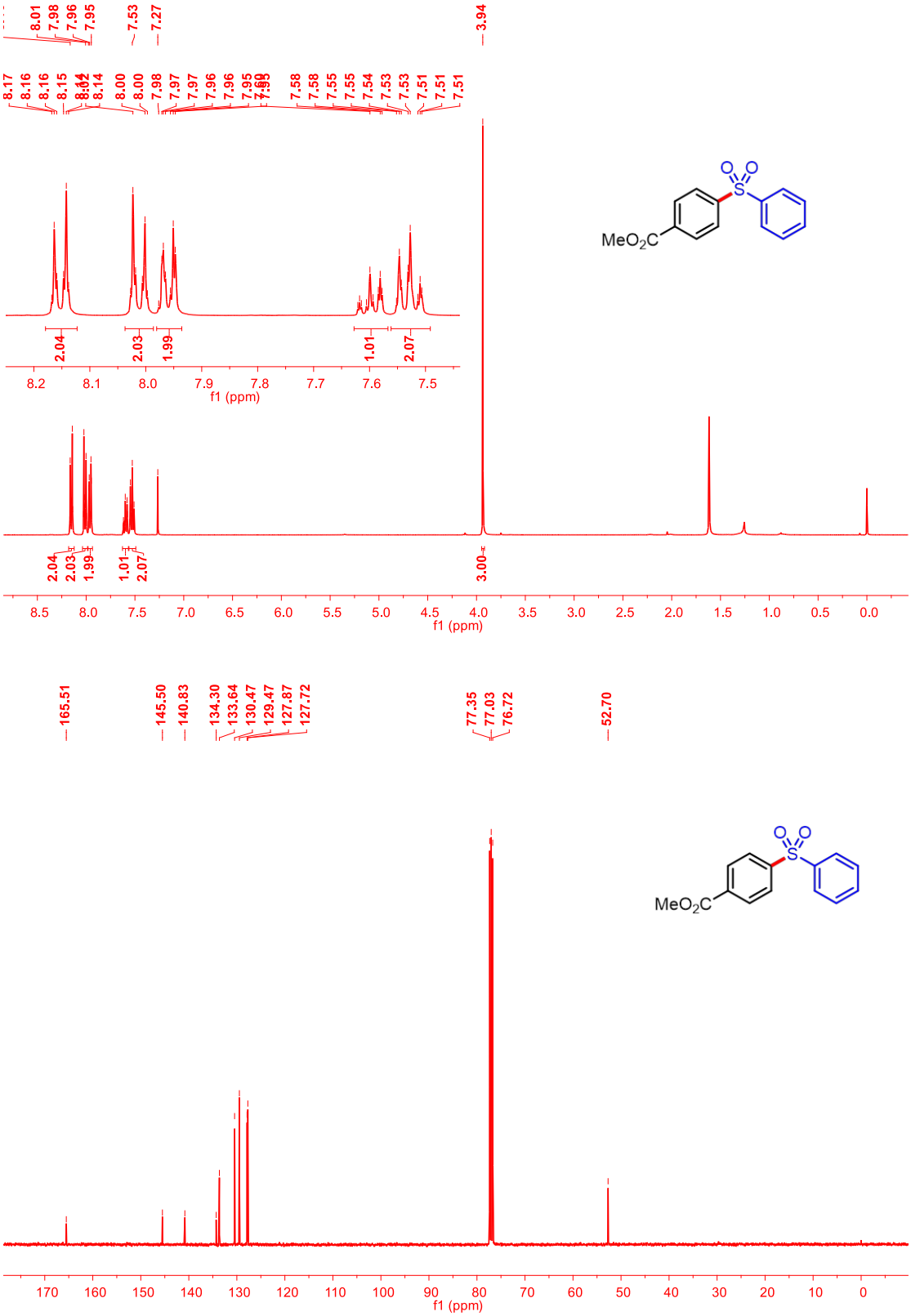


Fig. S10 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for ethyl 4-(phenylsulfonyl)benzoate (**3da**) in $CDCl_3$

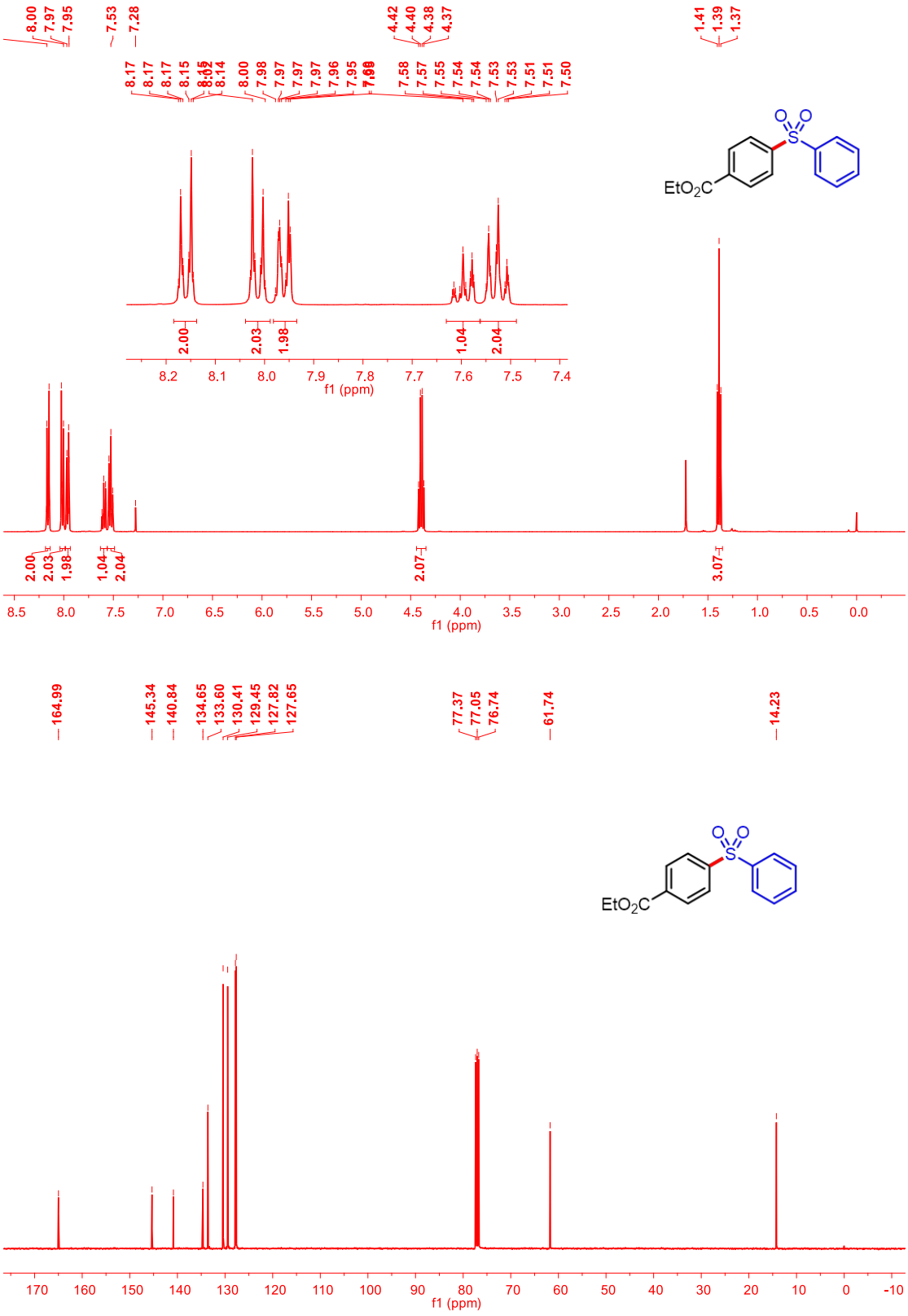
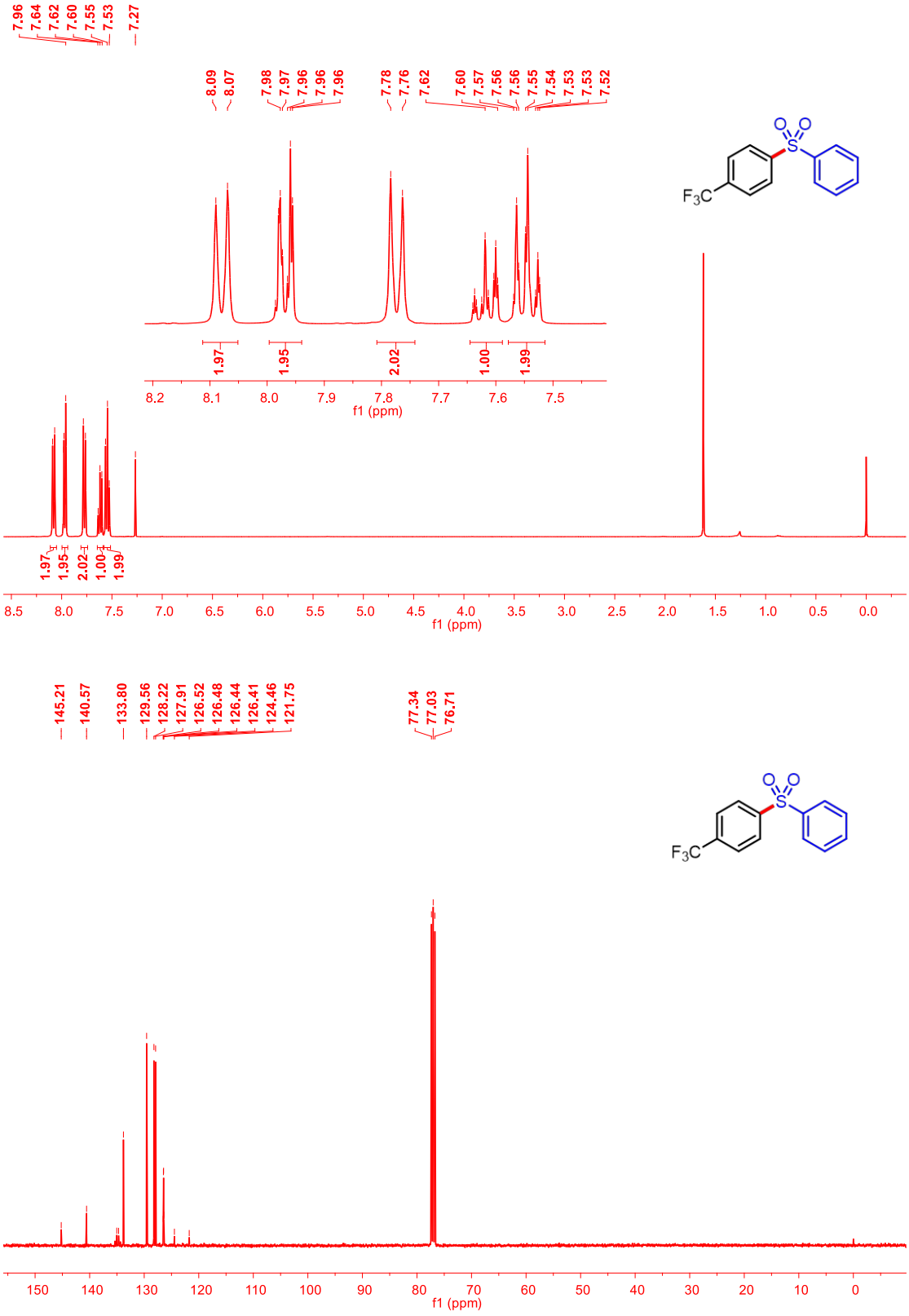
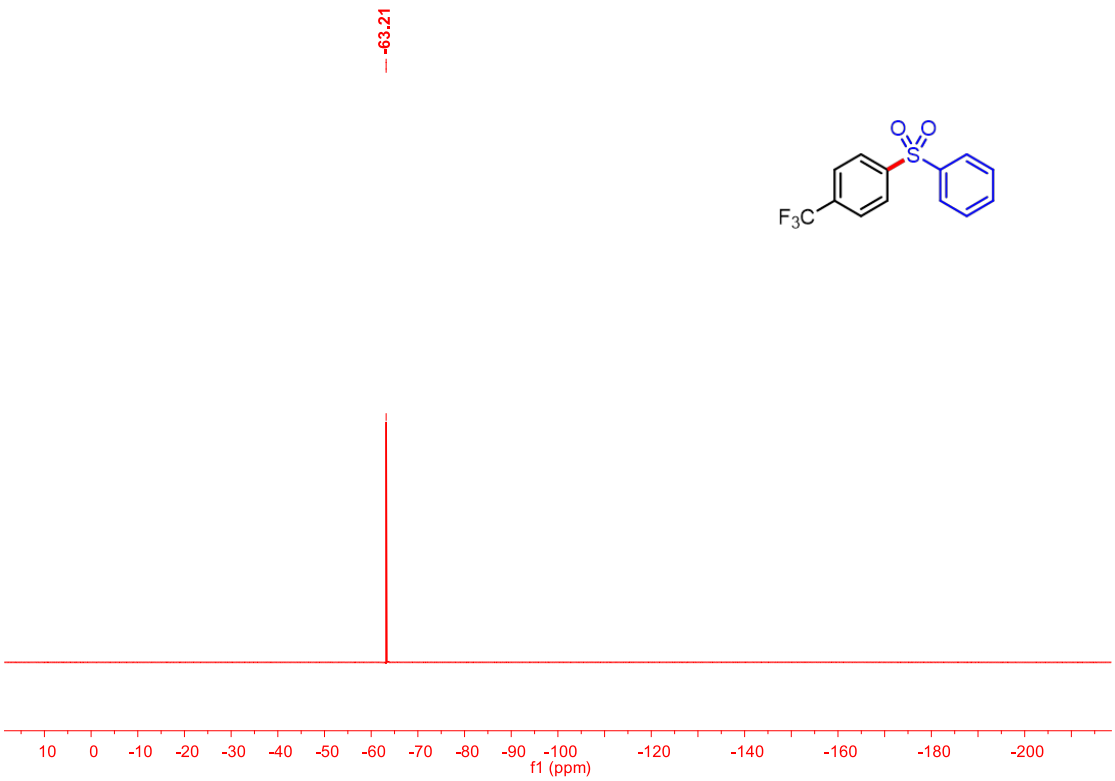


Fig. S11 The ^{1}H (400 MHz), ^{13}C (101 MHz), ^{19}F (377 MHz) NMR spectra for 1-(phenylsulfonyl)-4-(trifluoromethyl)benzene (**3ea**) in $CDCl_3$

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F3C
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-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

Fig. S12 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 4-(phenylsulfonyl)benzaldehyde (**3fa**) in $CDCl_3$

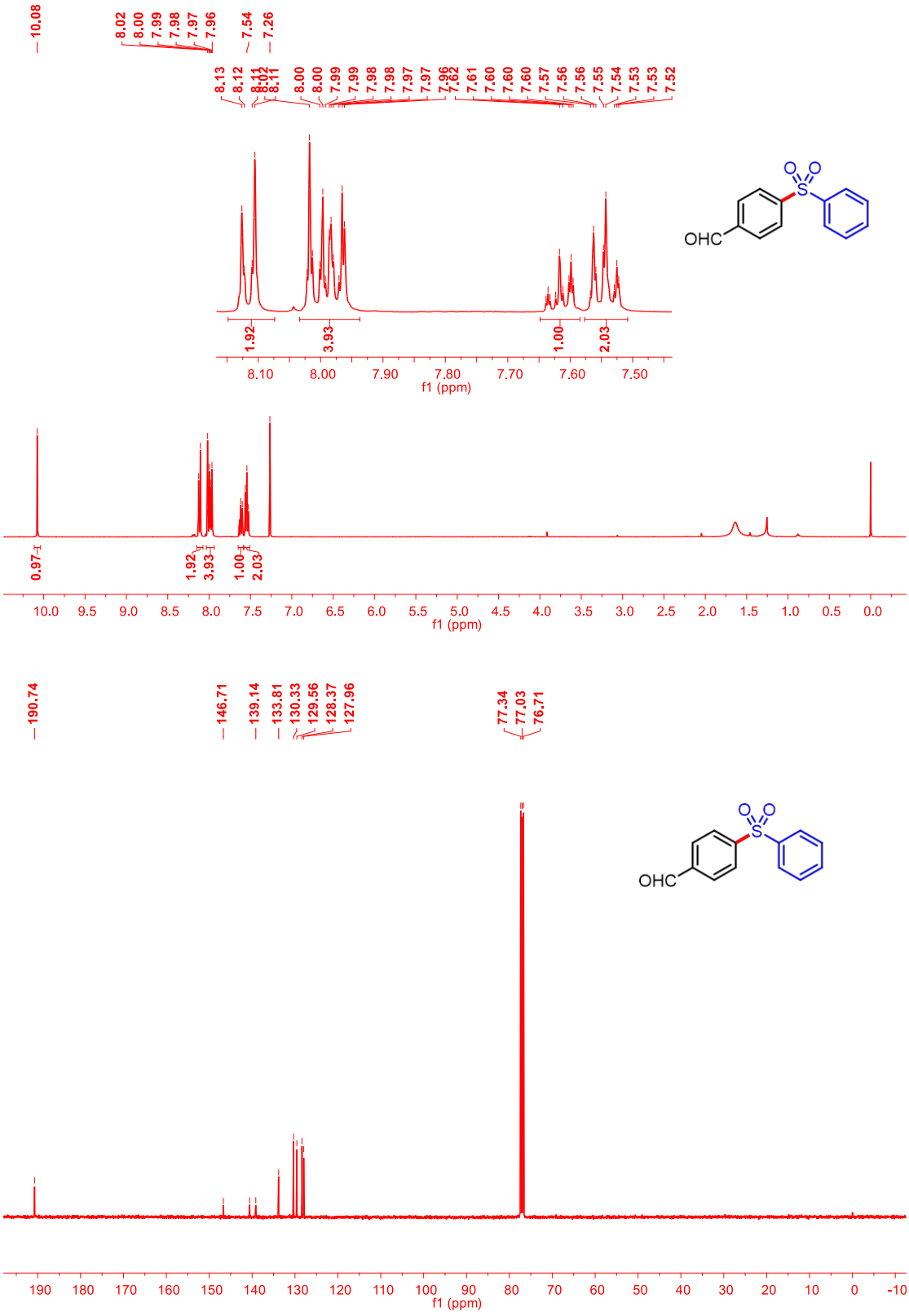
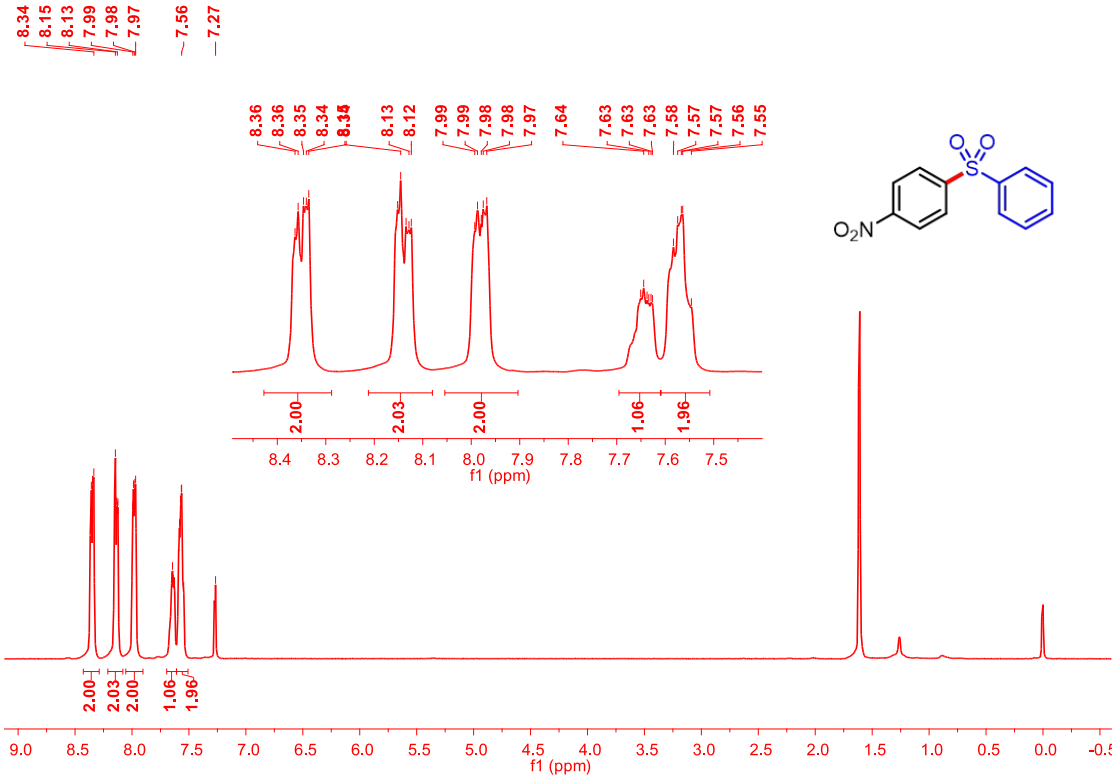


Fig. S13 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 1-nitro-4-(phenylsulfonyl)benzene (**3ga**) in $CDCl_3$



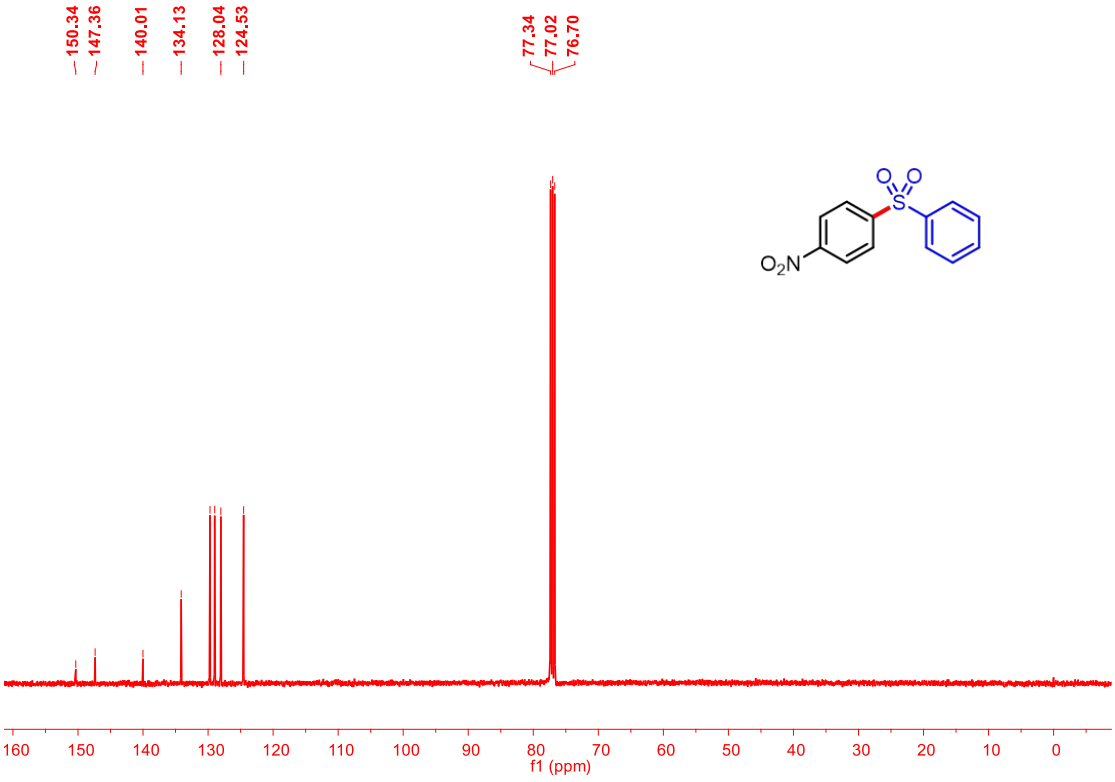


Fig. S14 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 4-(phenylsulfonyl)-1,1'-biphenyl (**3ha**) in $CDCl_3$

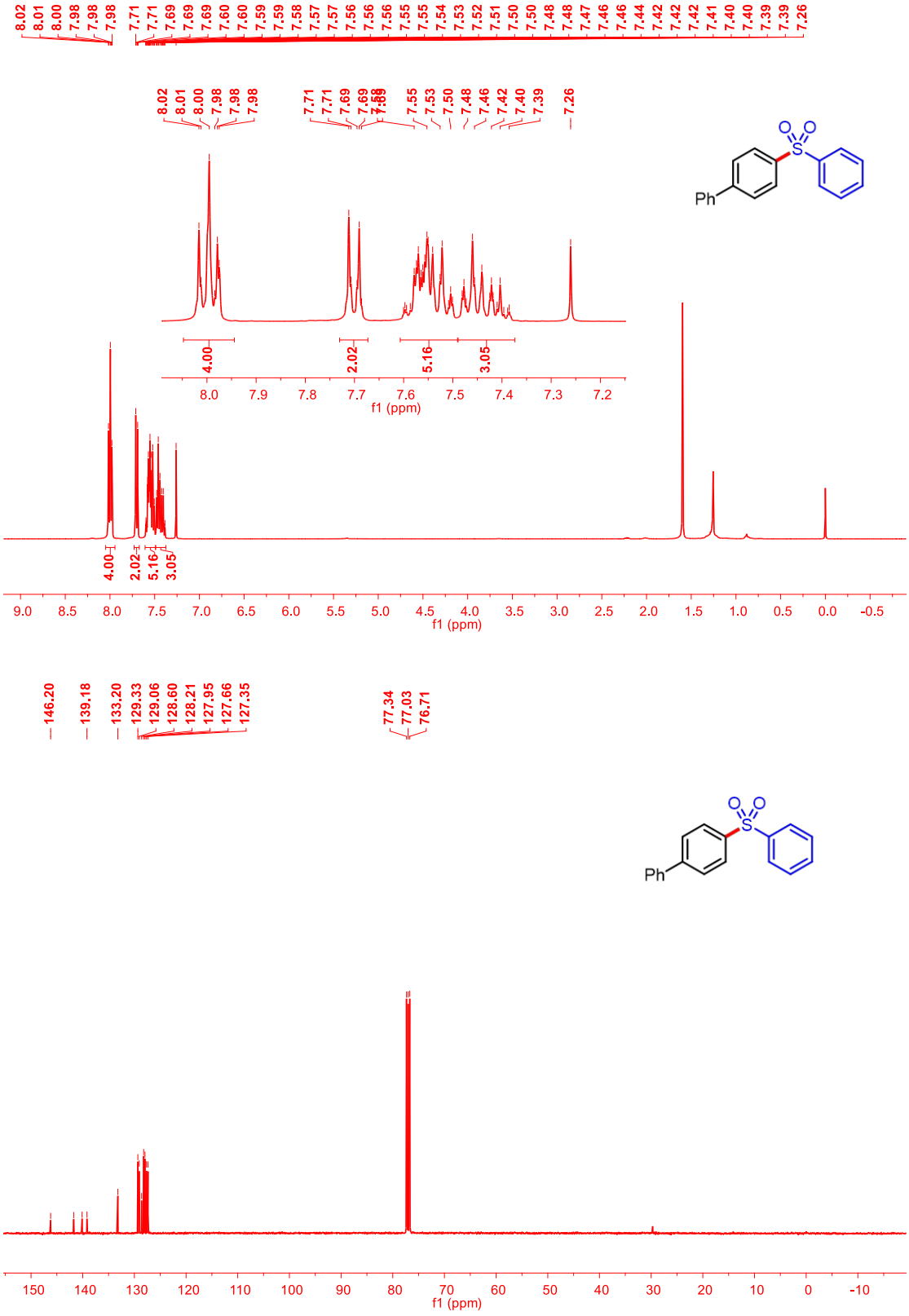
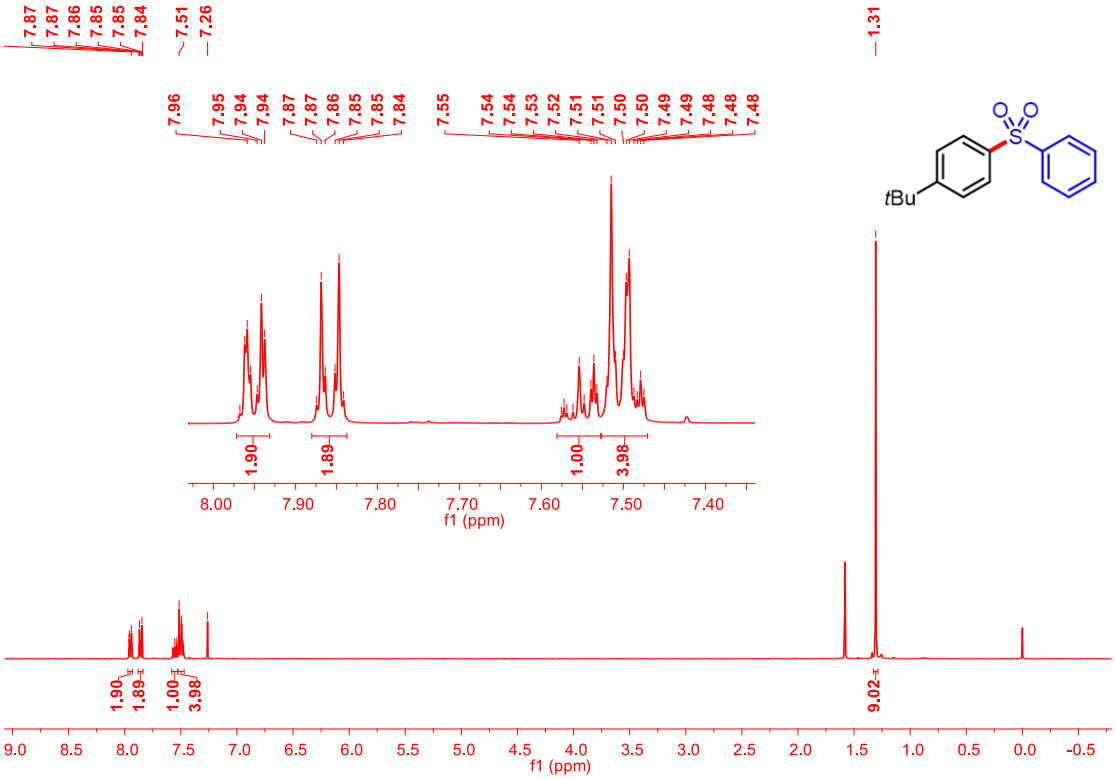


Fig. S15 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 1-(tert-butyl)-4-(phenylsulfonyl)benzene (**3ia**) in $CDCl_3$



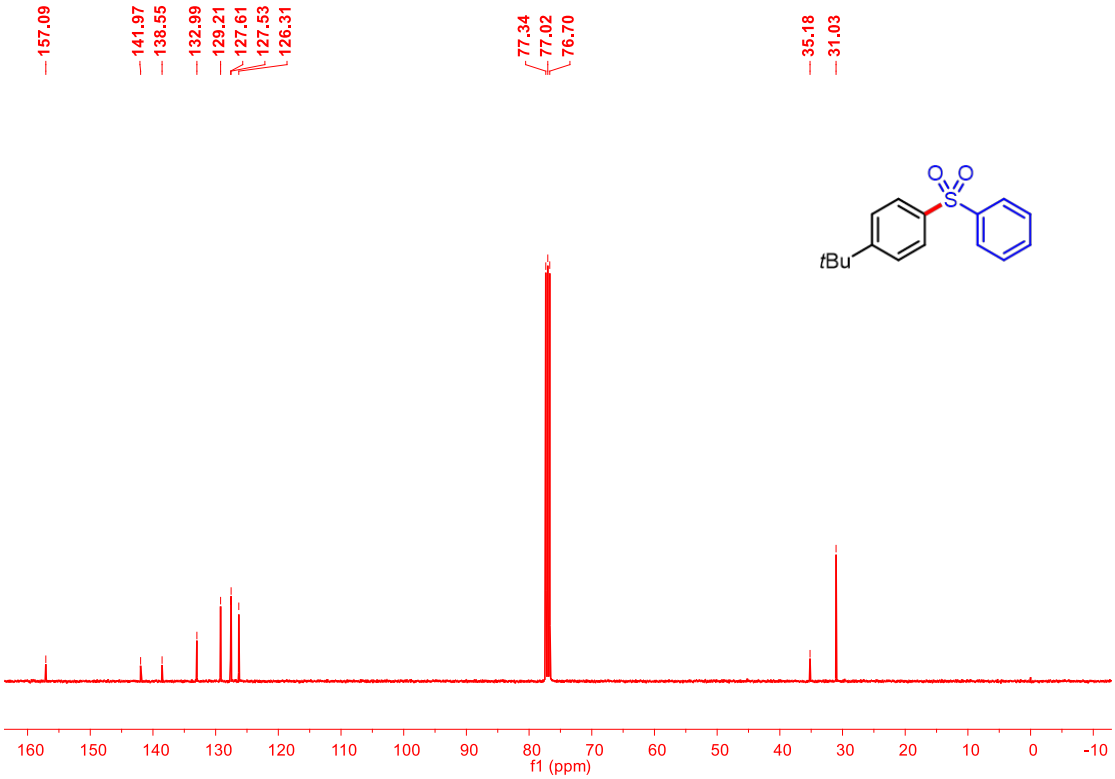
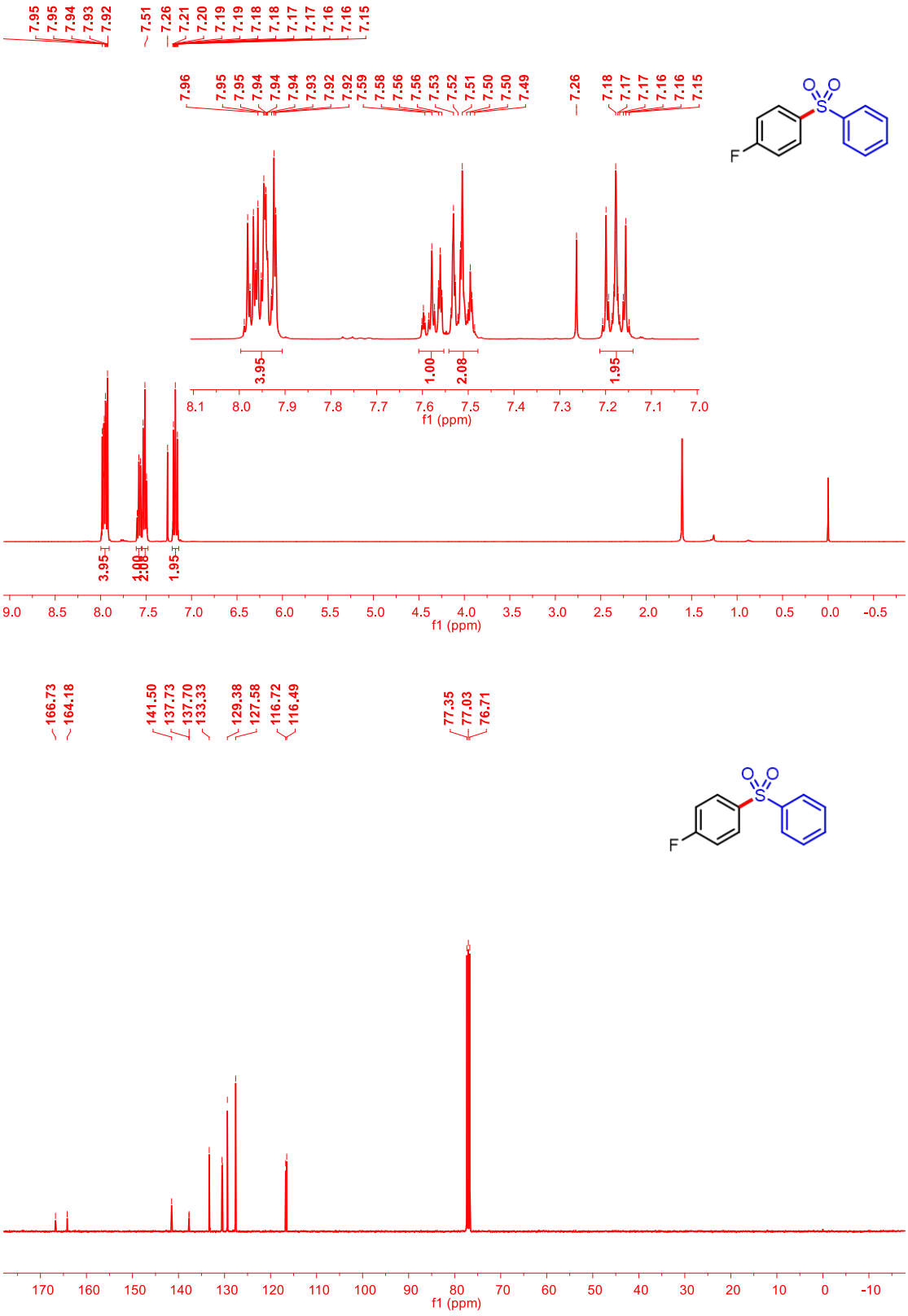


Fig. S16 The ^{1}H (400 MHz), ^{13}C (101 MHz), ^{19}F (377 MHz) NMR spectra for 1-fluoro-4-(phenylsulfonyl)benzene (**3ja**) in $CDCl_3$



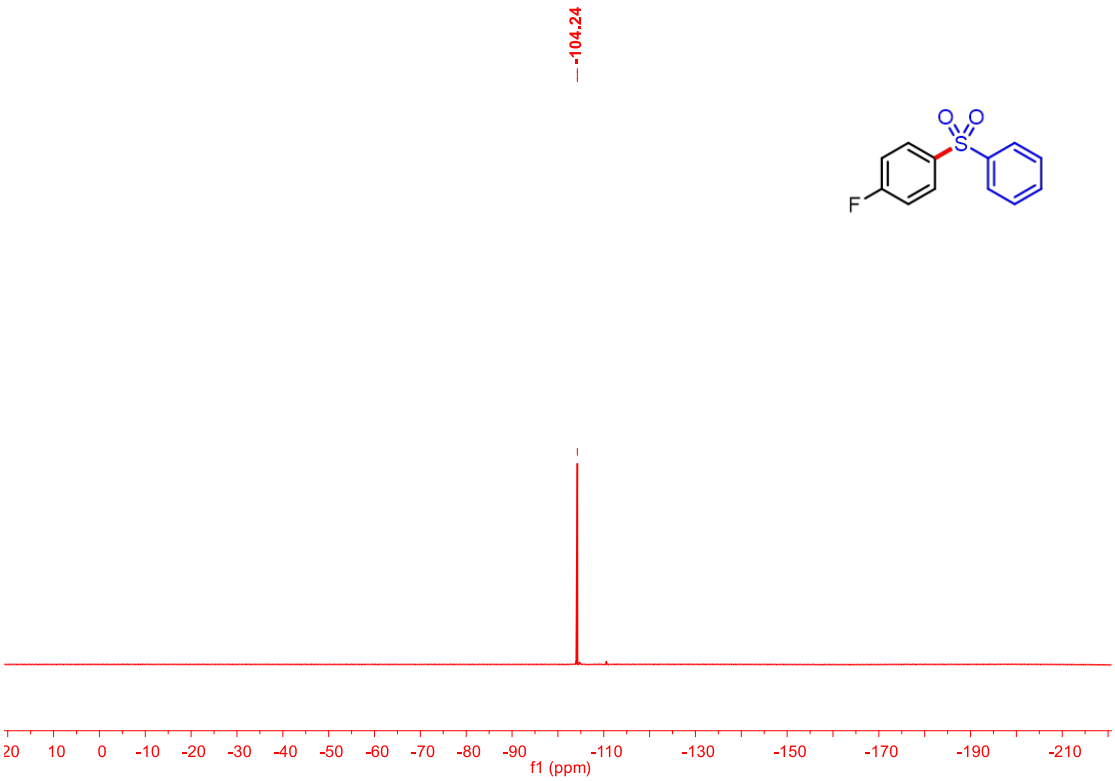
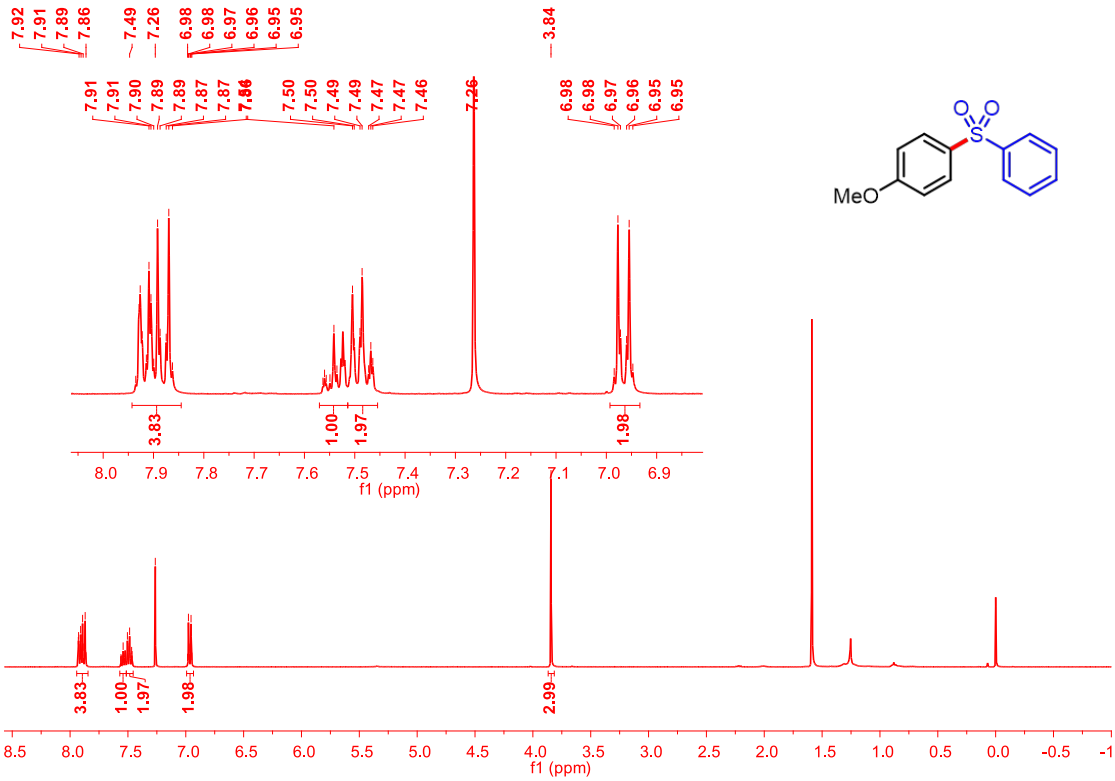

-104.24
O
O
S
F
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

Fig. S17 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 1-methoxy-4-(phenylsulfonyl)benzene (**3ka**) in $CDCl_3$



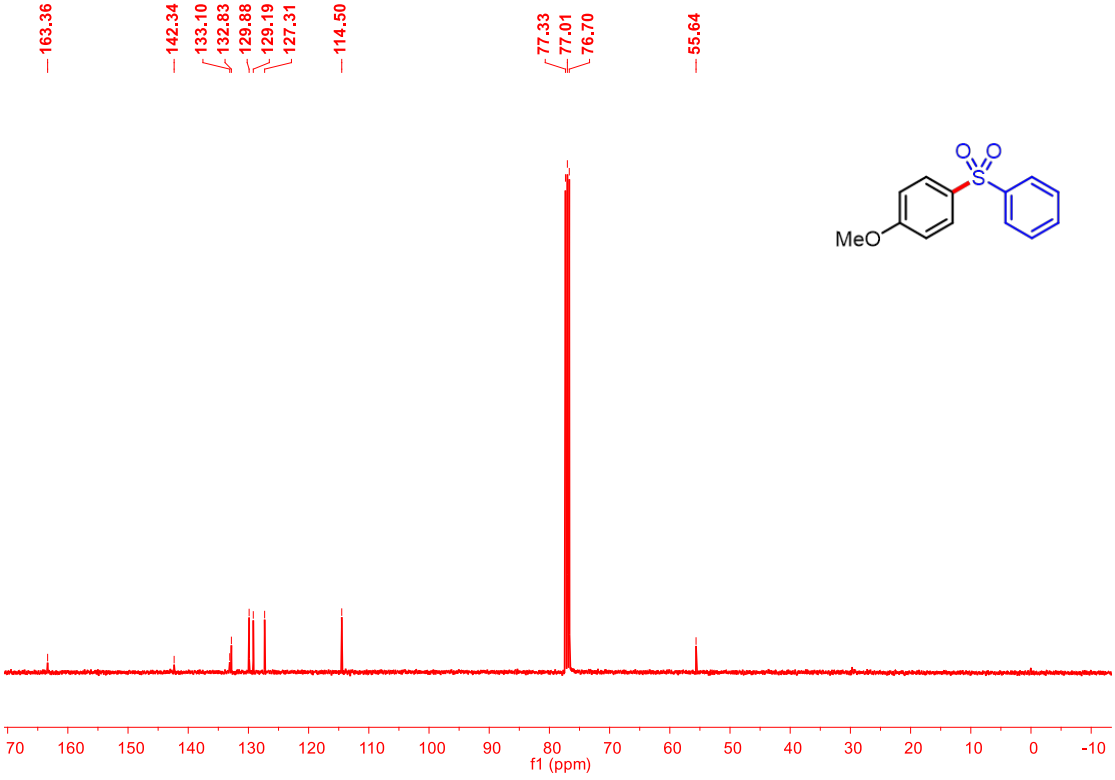


Fig. S18 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 3-(phenylsulfonyl)benzonitrile (**3la**) in $CDCl_3$

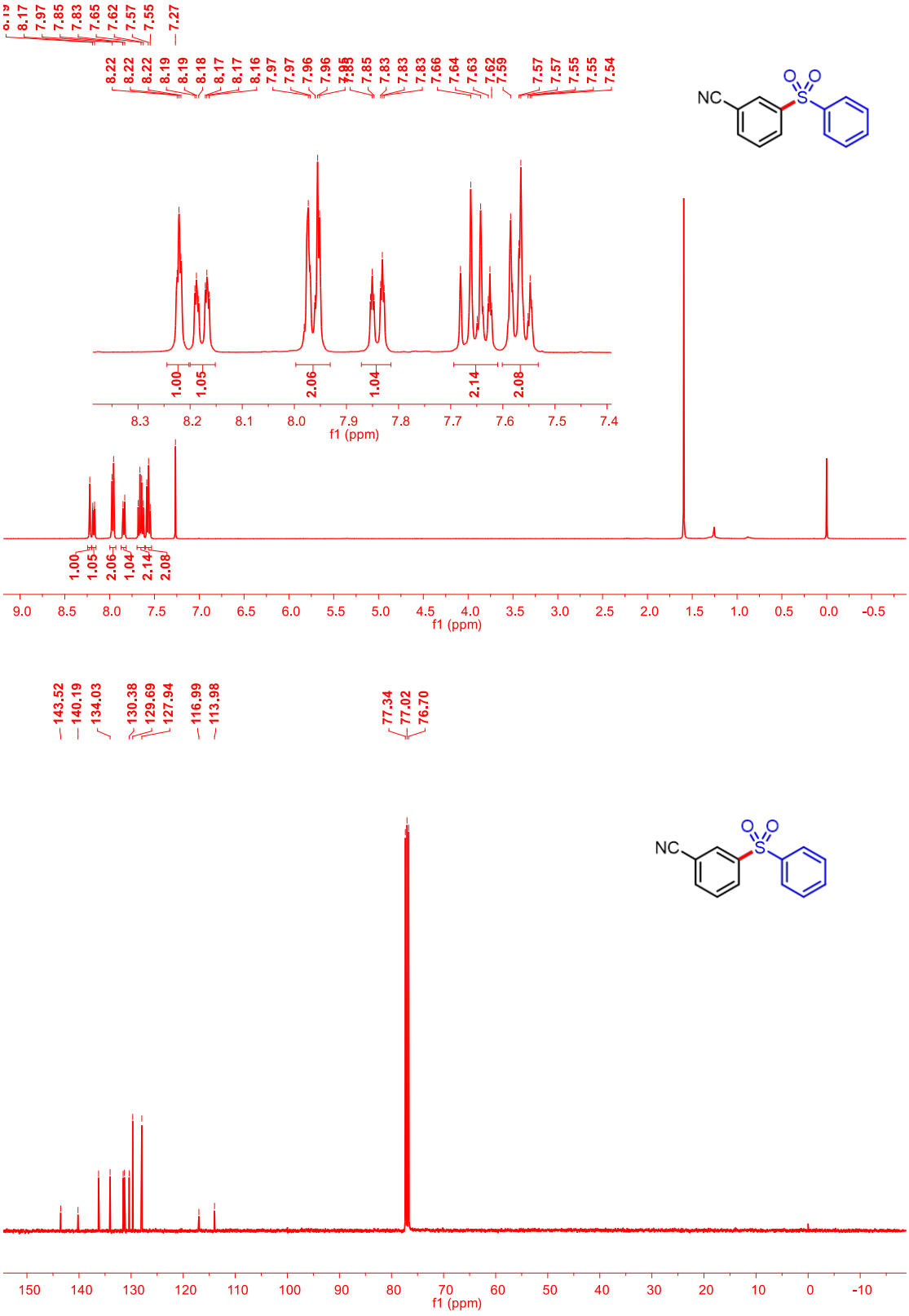


Fig. S19 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for methyl 3-(phenylsulfonyl)benzoate (**3ma**) in $CDCl_3$

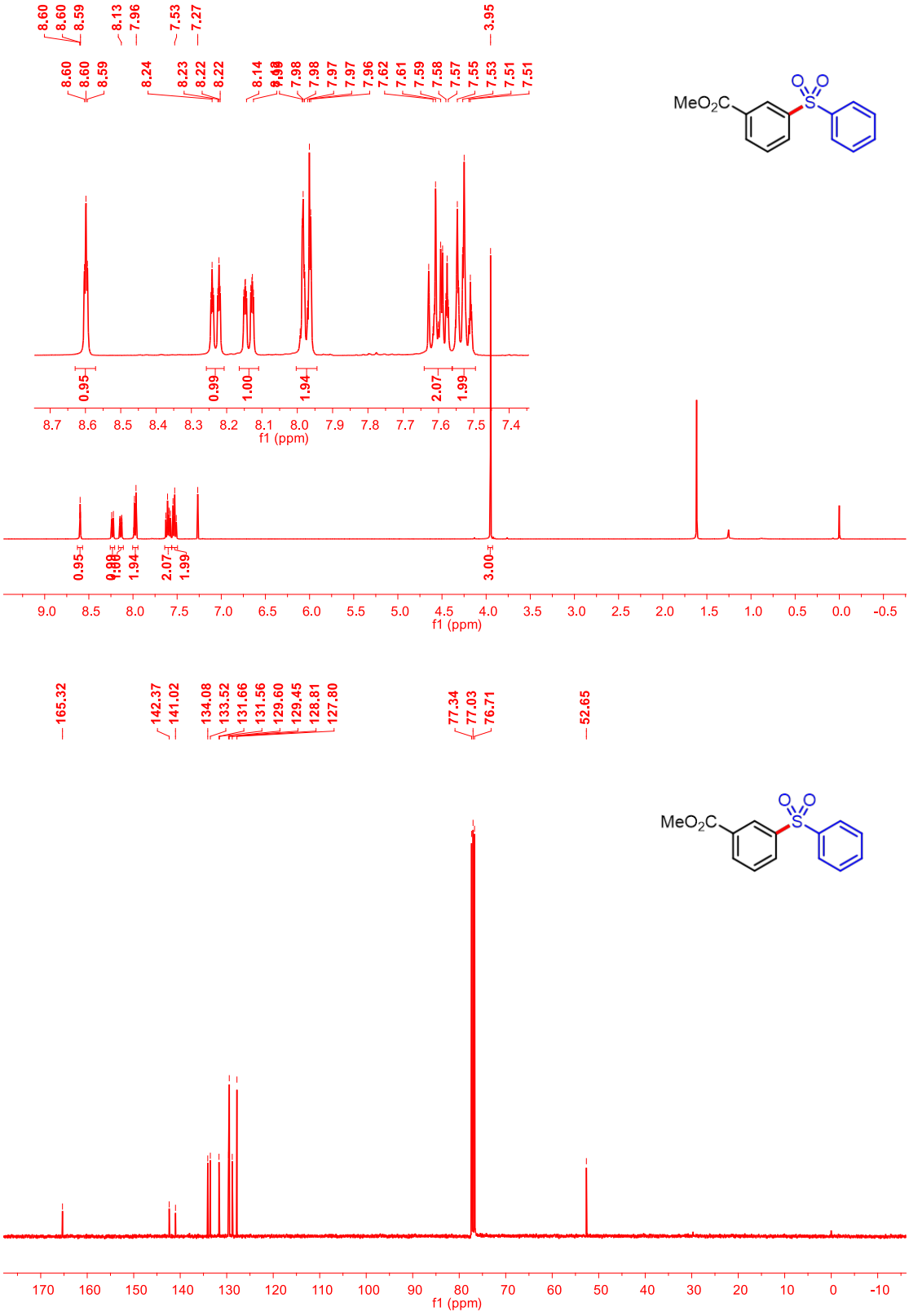


Fig. S20 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 2-(phenylsulfonyl)benzonitrile (**3na**) in $CDCl_3$

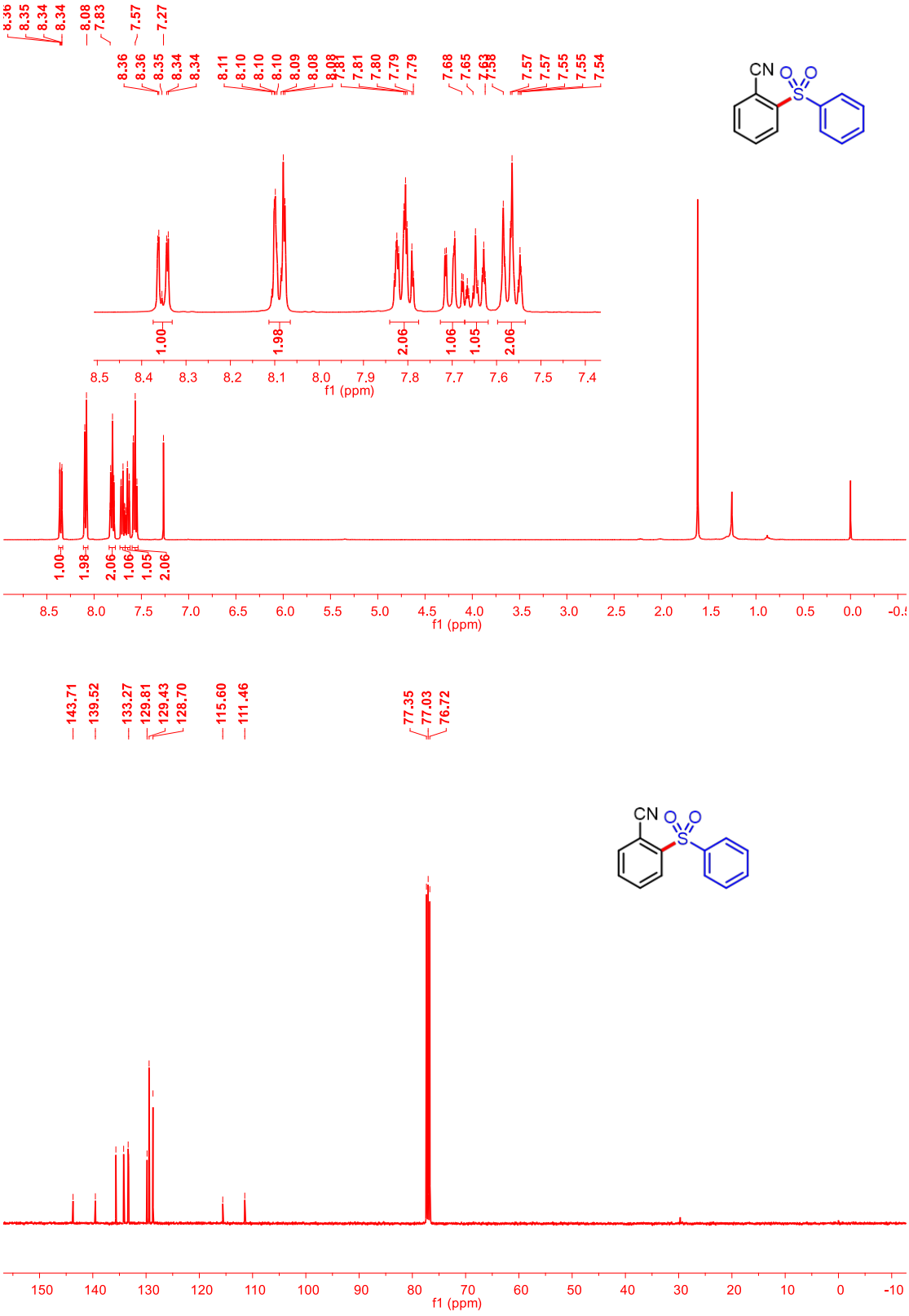


Fig. S21 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 1-(2-(phenylsulfonyl)phenyl)ethan-1-one (**3oa**) in $CDCl_3$

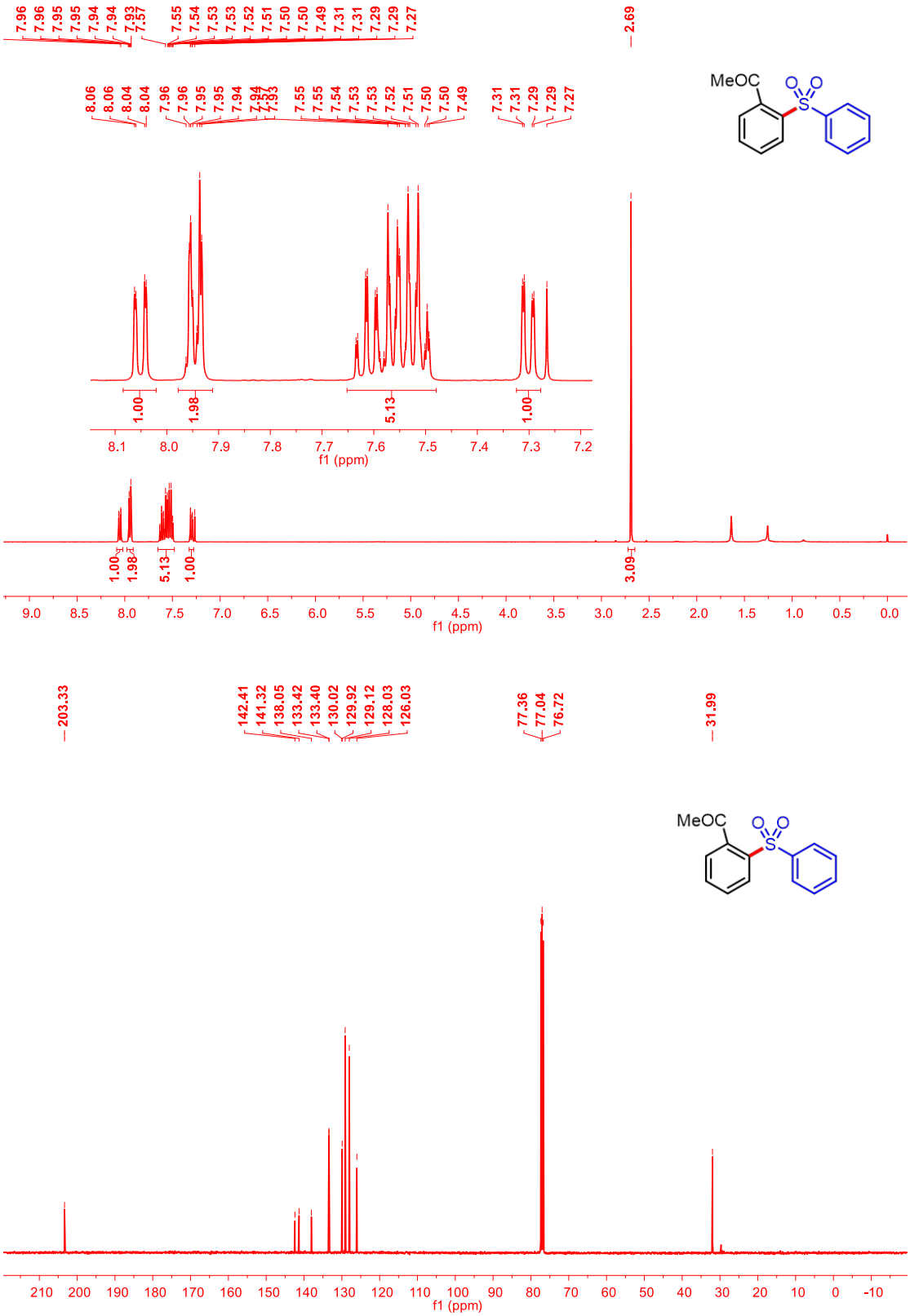


Fig. S22 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for phenyl(2-(phenylsulfonyl)phenyl)methanone (**3pa**) in $CDCl_3$

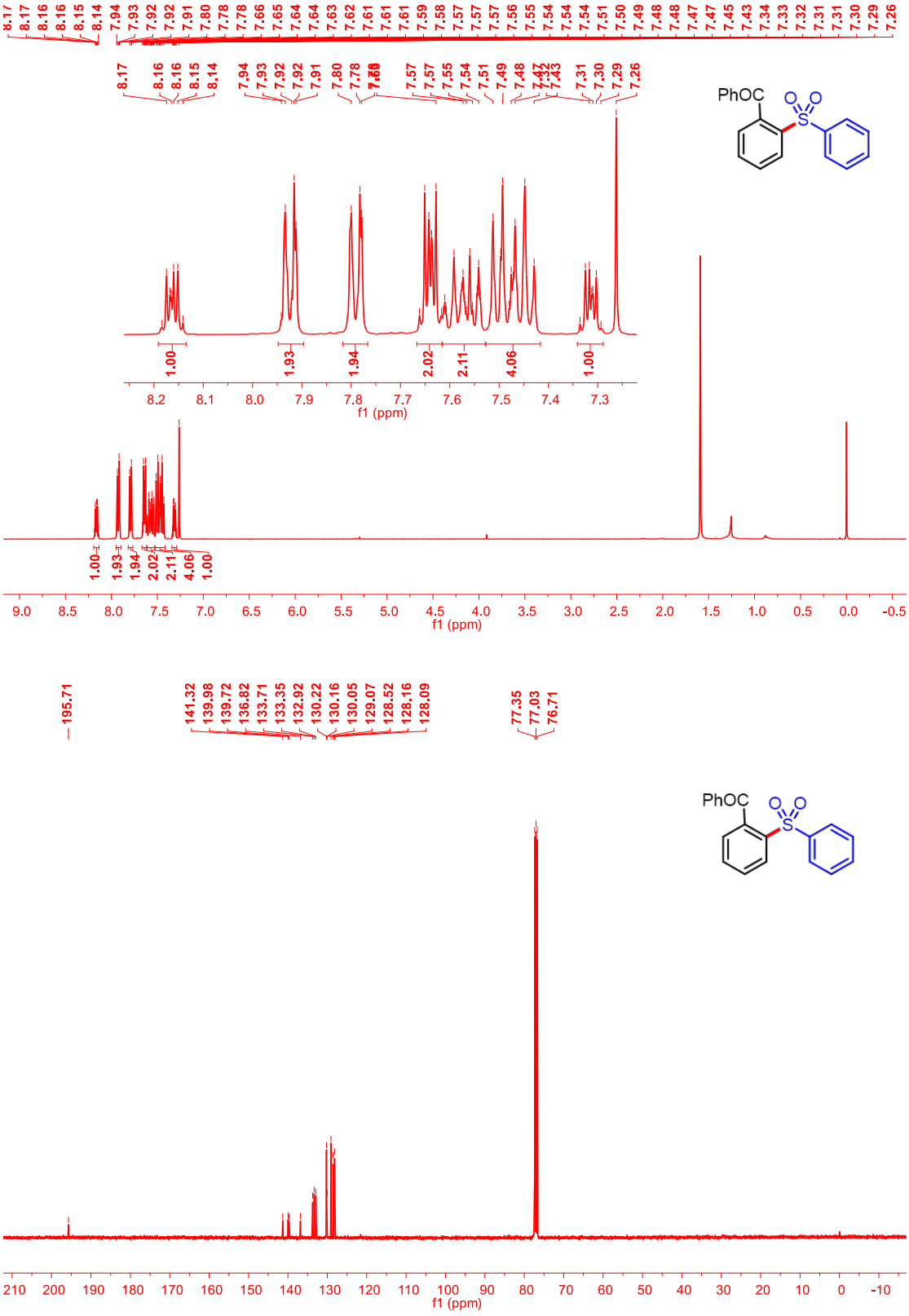


Fig. S23 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for methyl 2-(phenylsulfonyl)benzoate (**3qa**) in $CDCl_3$

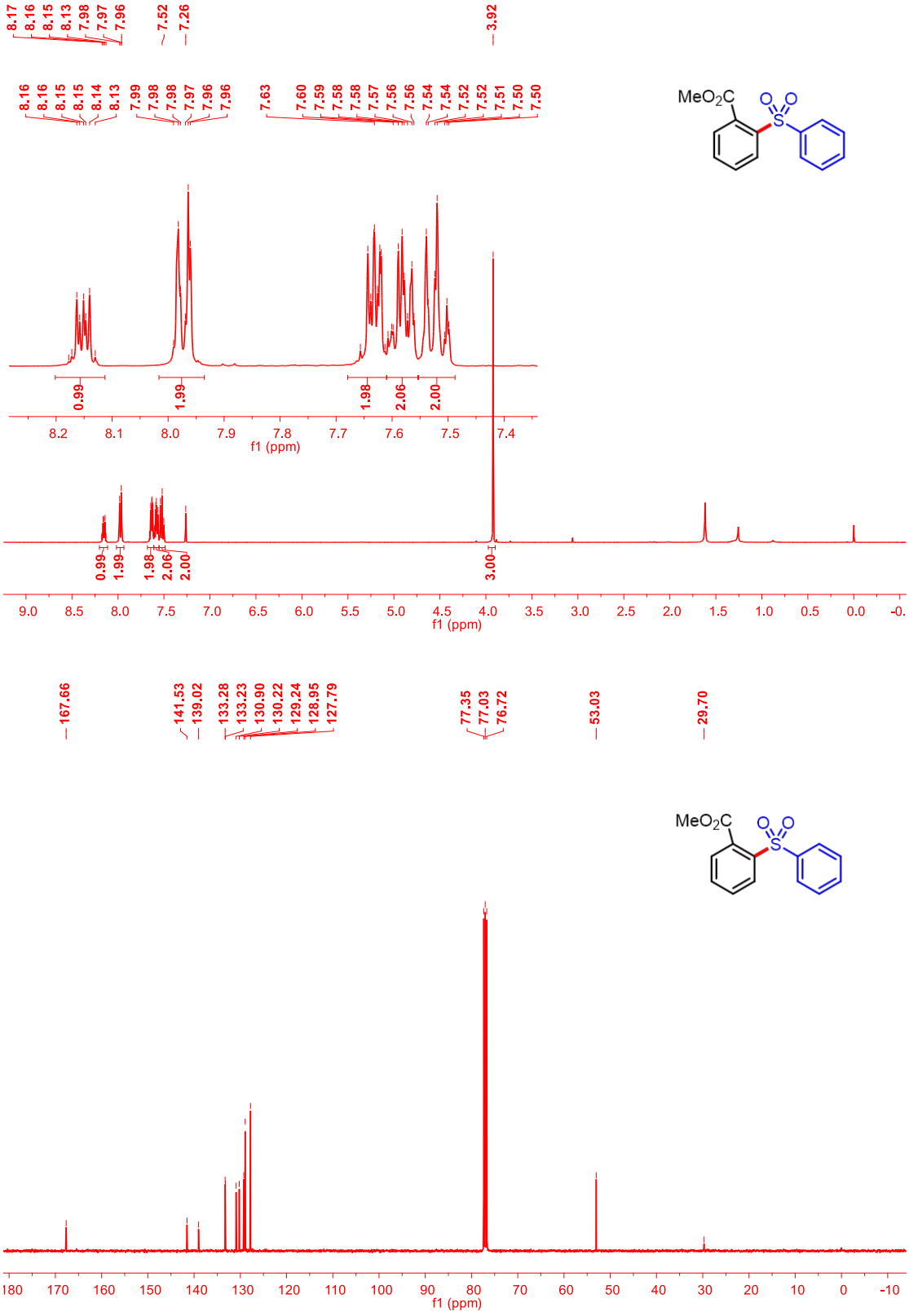
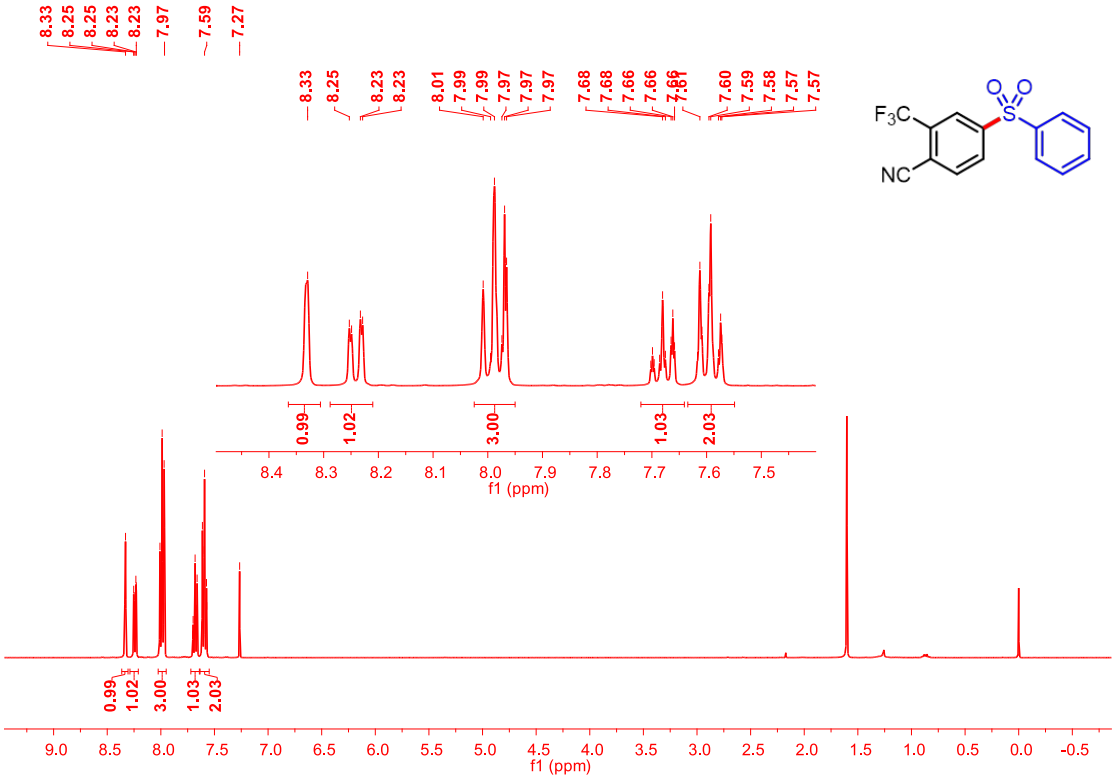
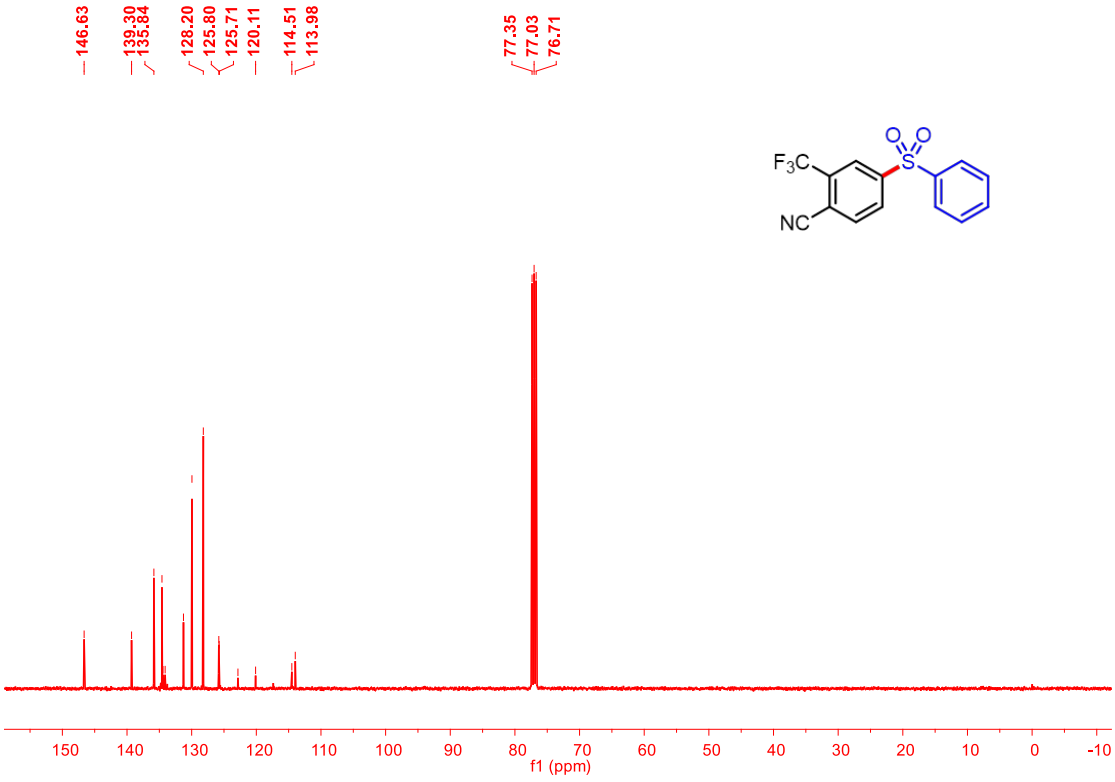


Fig. S24 The ^{1}H (400 MHz), ^{13}C (101 MHz), ^{19}F (377 MHz) NMR spectra for 4-(phenylsulfonyl)-2-(trifluoromethyl)benzonitrile (**3ra**) in $CDCl_3$





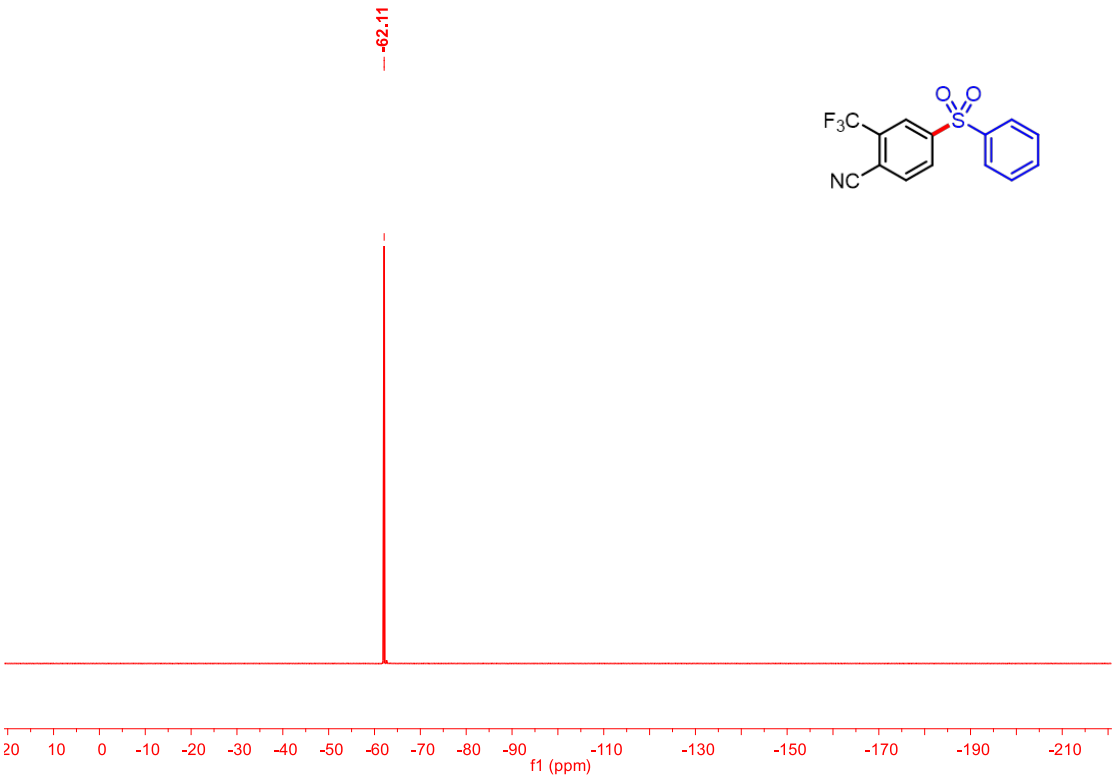
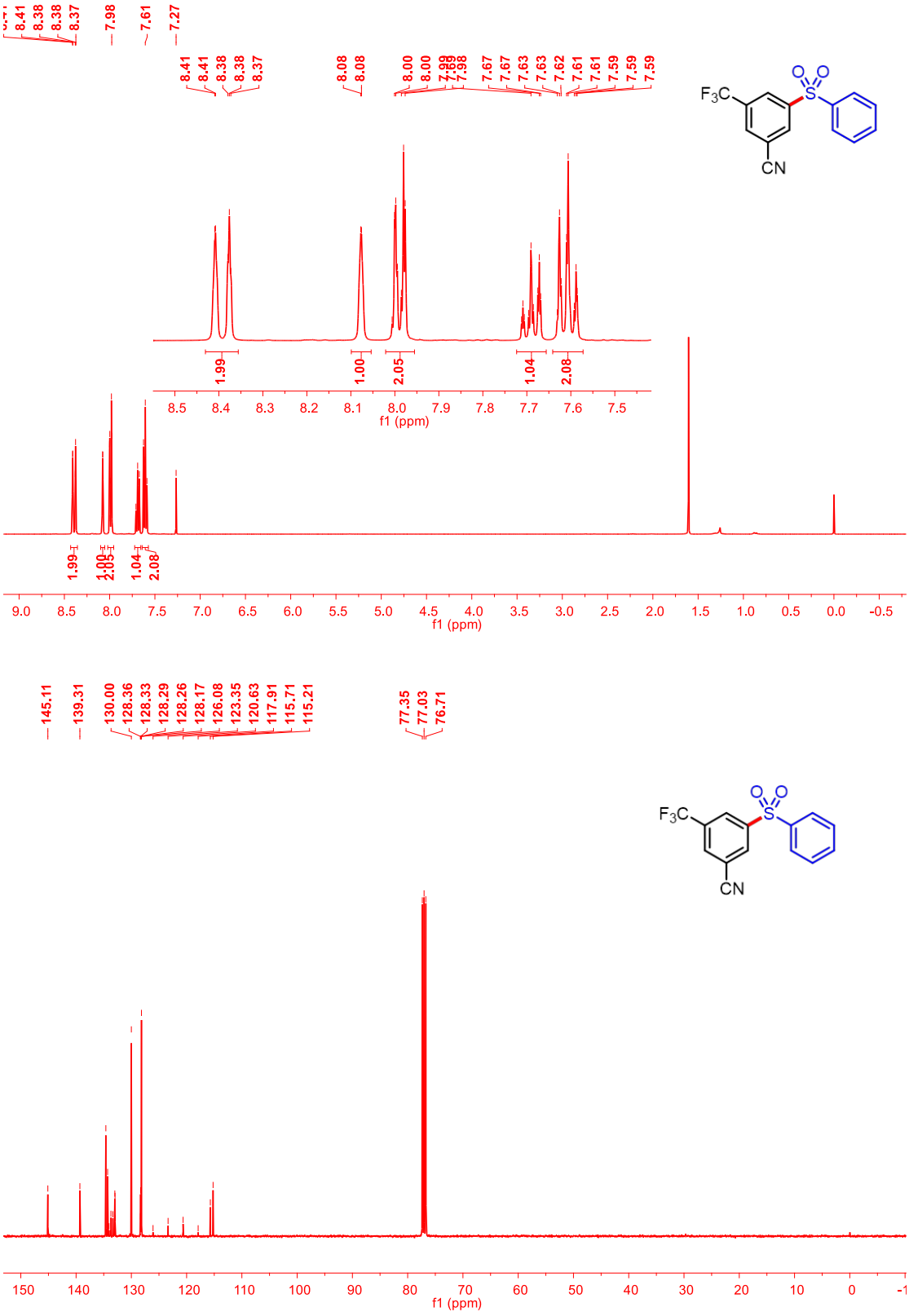

-62.11
F3C
NC
O
O
S
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

Fig. S25 The ^{1}H (400 MHz), ^{13}C (101 MHz), ^{19}F (377 MHz) NMR spectra for 3-(phenylsulfonyl)-5-(trifluoromethyl)benzonitrile (**3sa**) in $CDCl_3$



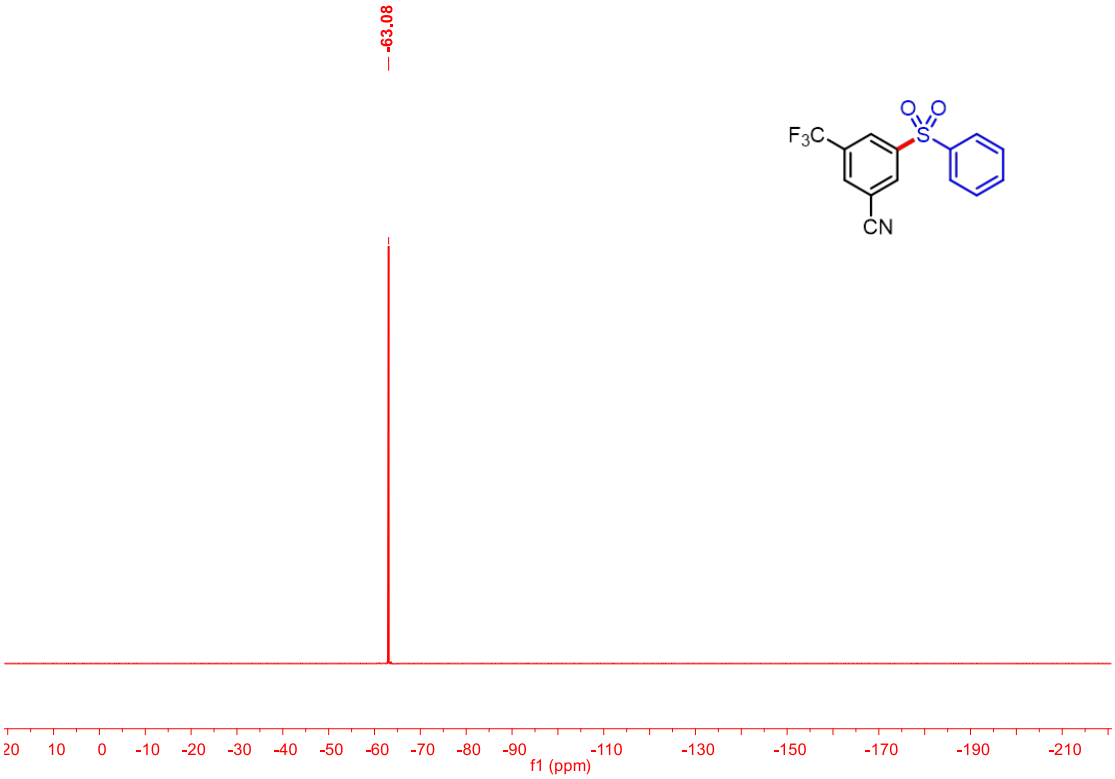

-63.08
F3C
O
O
S
CN
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

Fig. S26 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 5-(phenylsulfonyl)benzo[d][1,3]dioxole (**3ta**) in $CDCl_3$

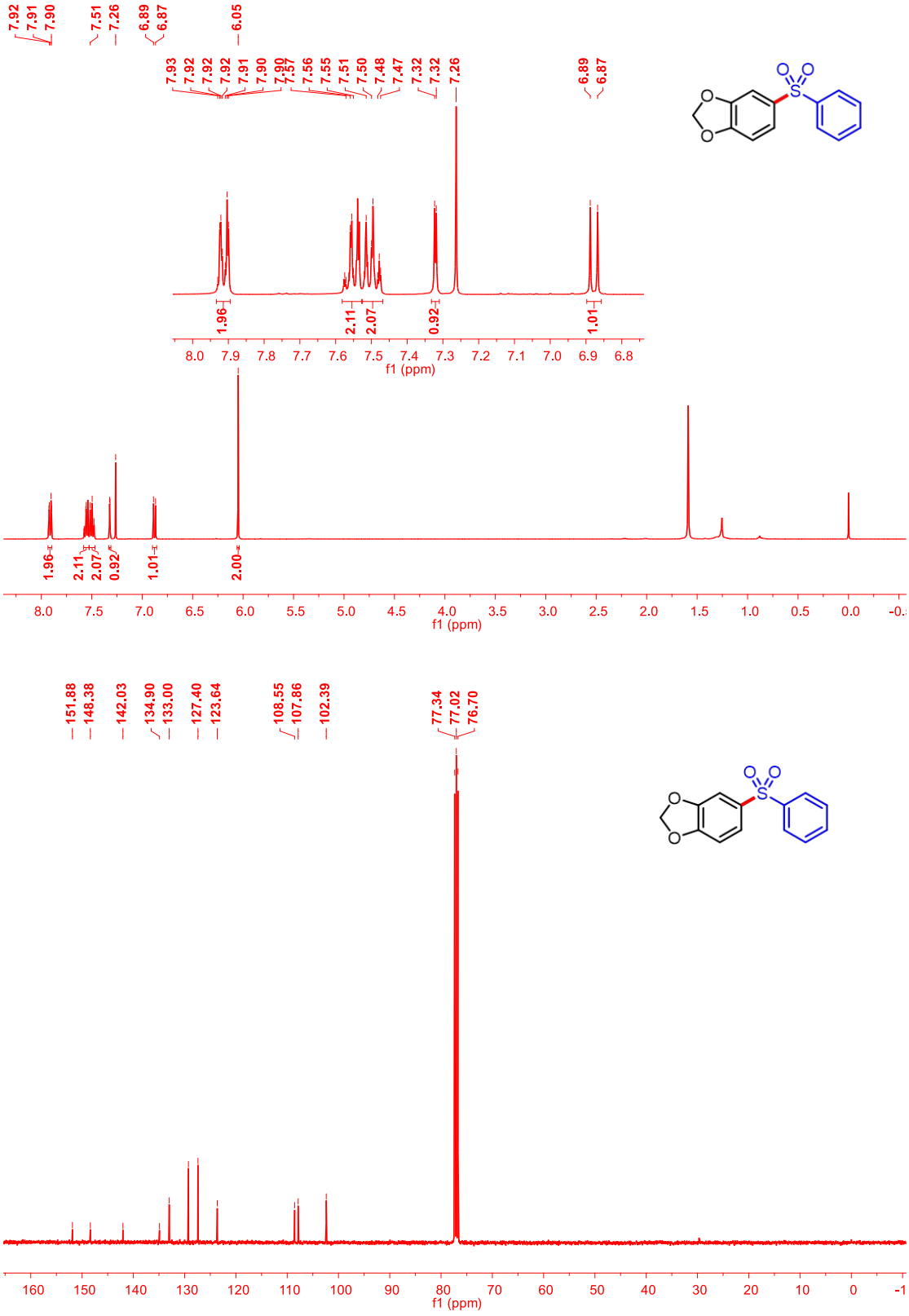


Fig. S27 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 2-(phenylsulfonyl)naphthalene (**3ua**) in $CDCl_3$

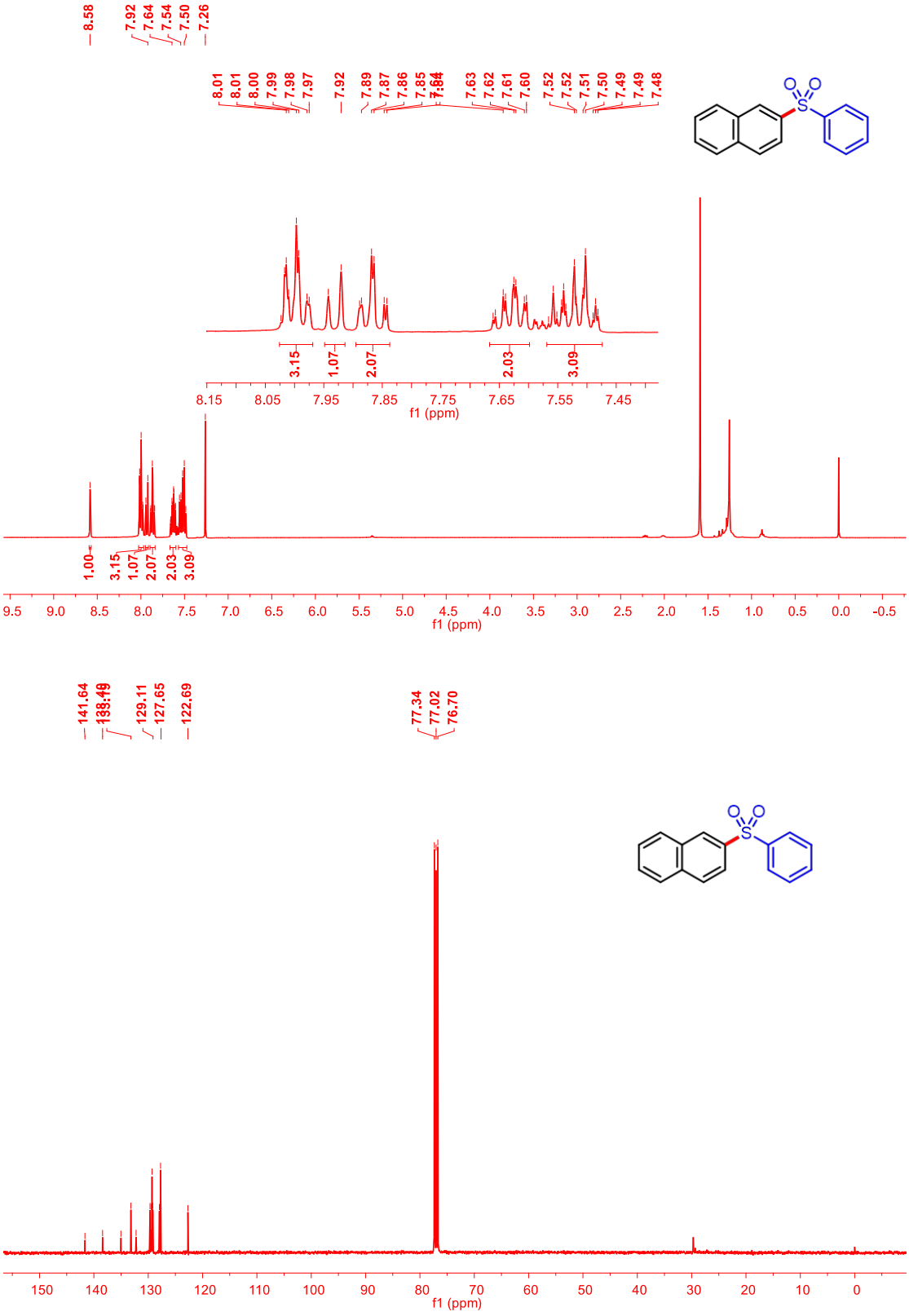


Fig. S28 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 2-(phenylsulfonyl)pyridine (**3va**) in $CDCl_3$

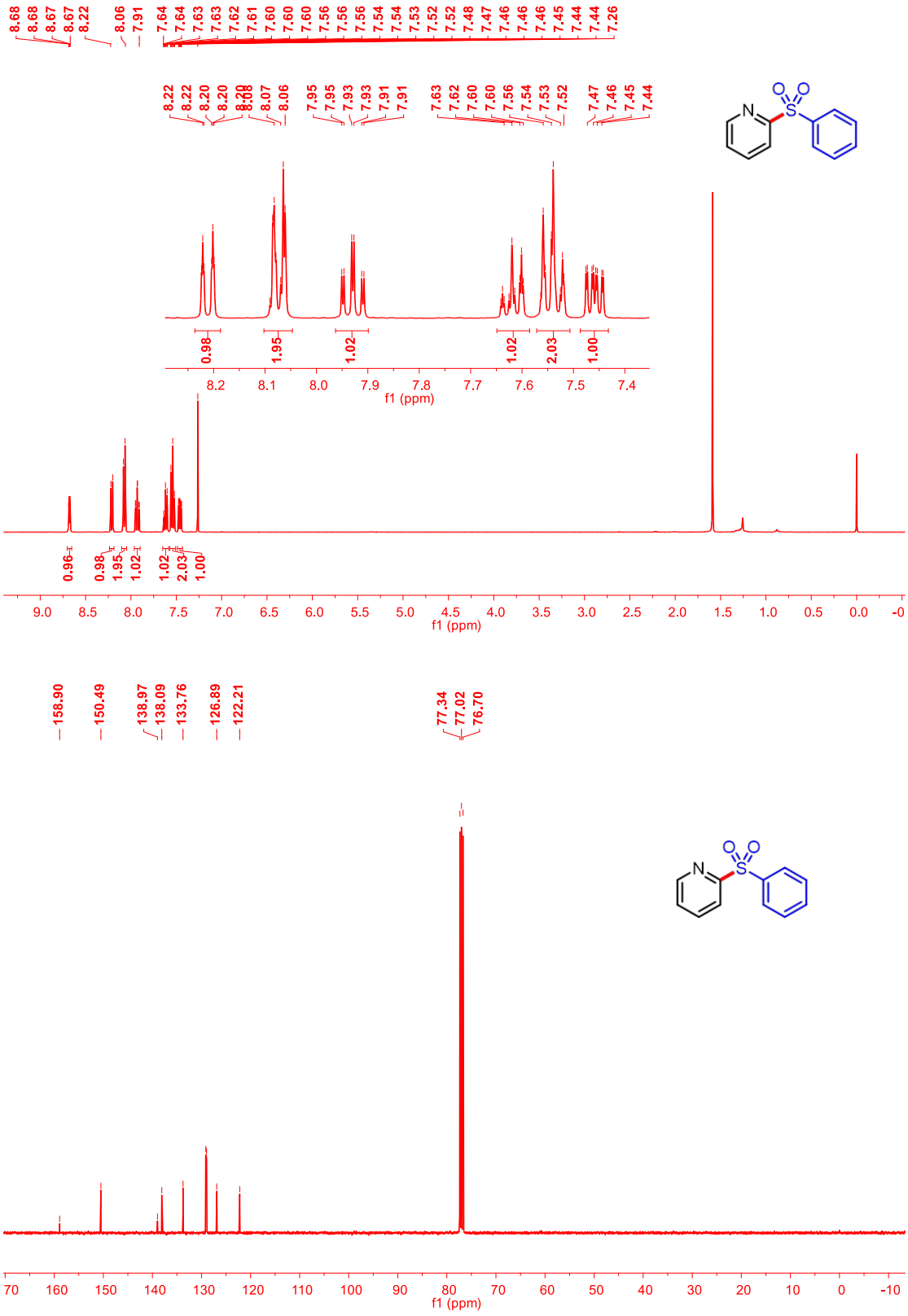


Fig. S29 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 6-(phenylsulfonyl)picolinonitrile (**3wa**) in $CDCl_3$

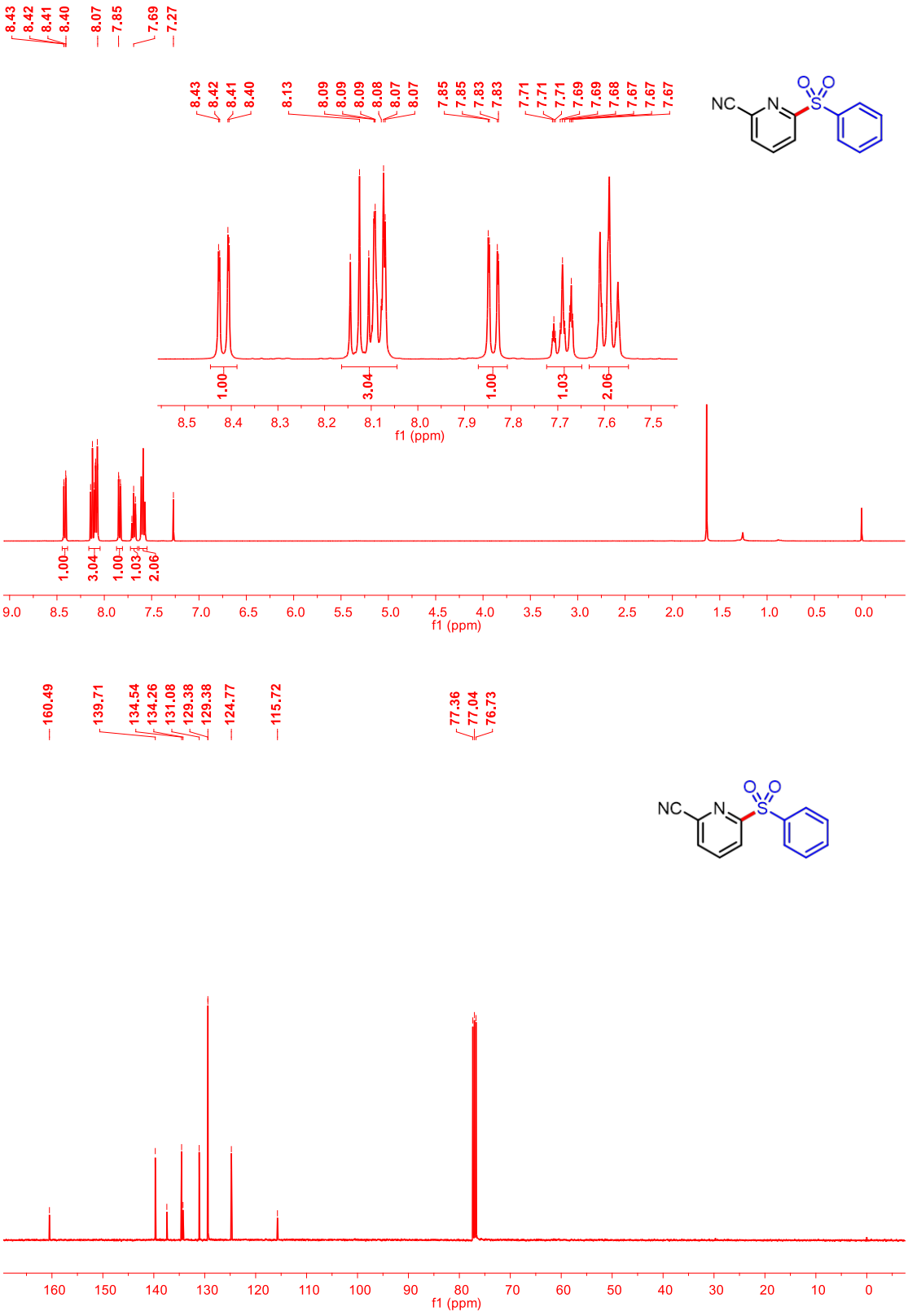


Fig. S30 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 2-phenyl-6-(phenylsulfonyl)pyridine (**3xa**) in $CDCl_3$

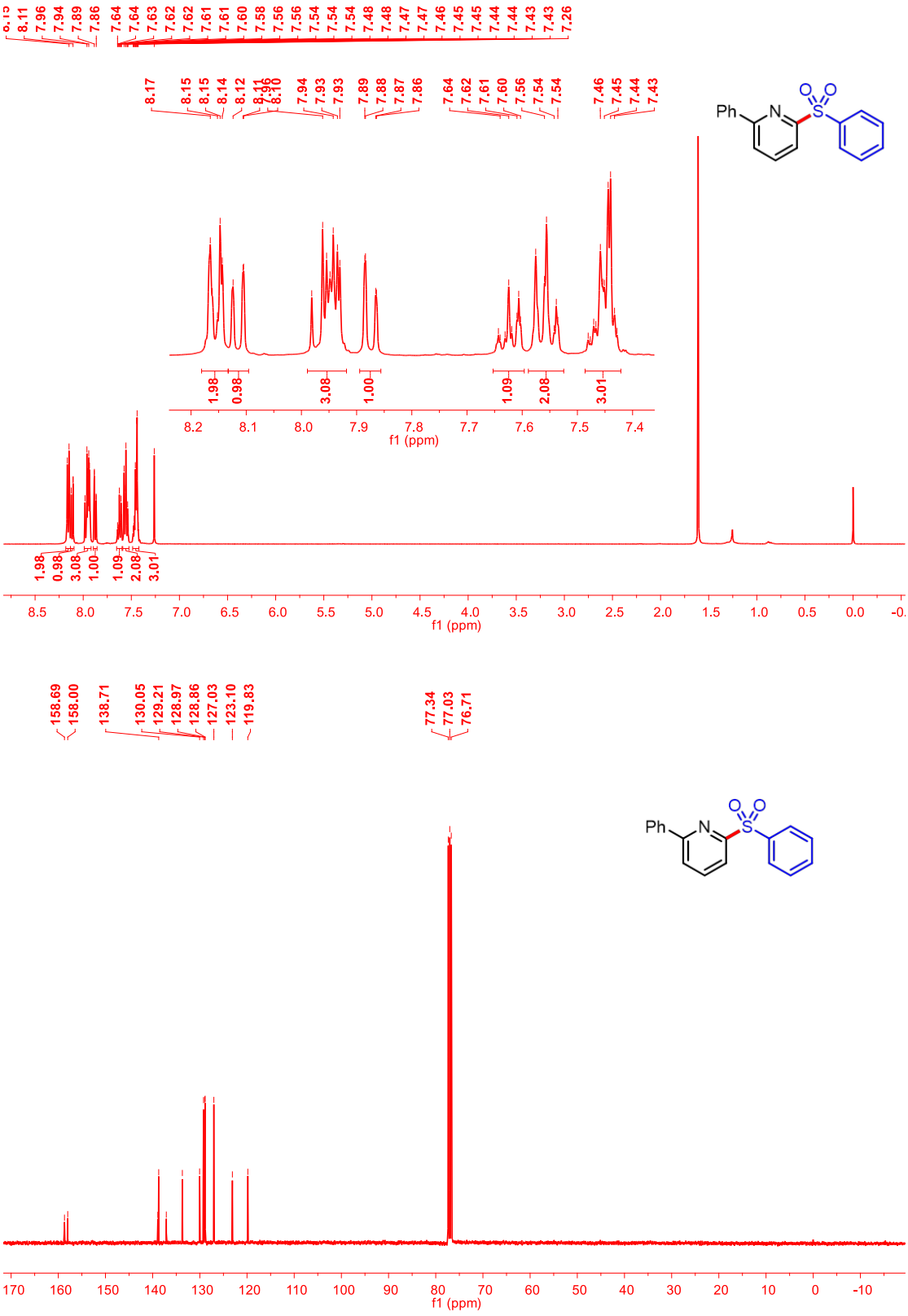


Fig. S31 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 4-(phenylsulfonyl)pyridine (**3ya**) in $CDCl_3$

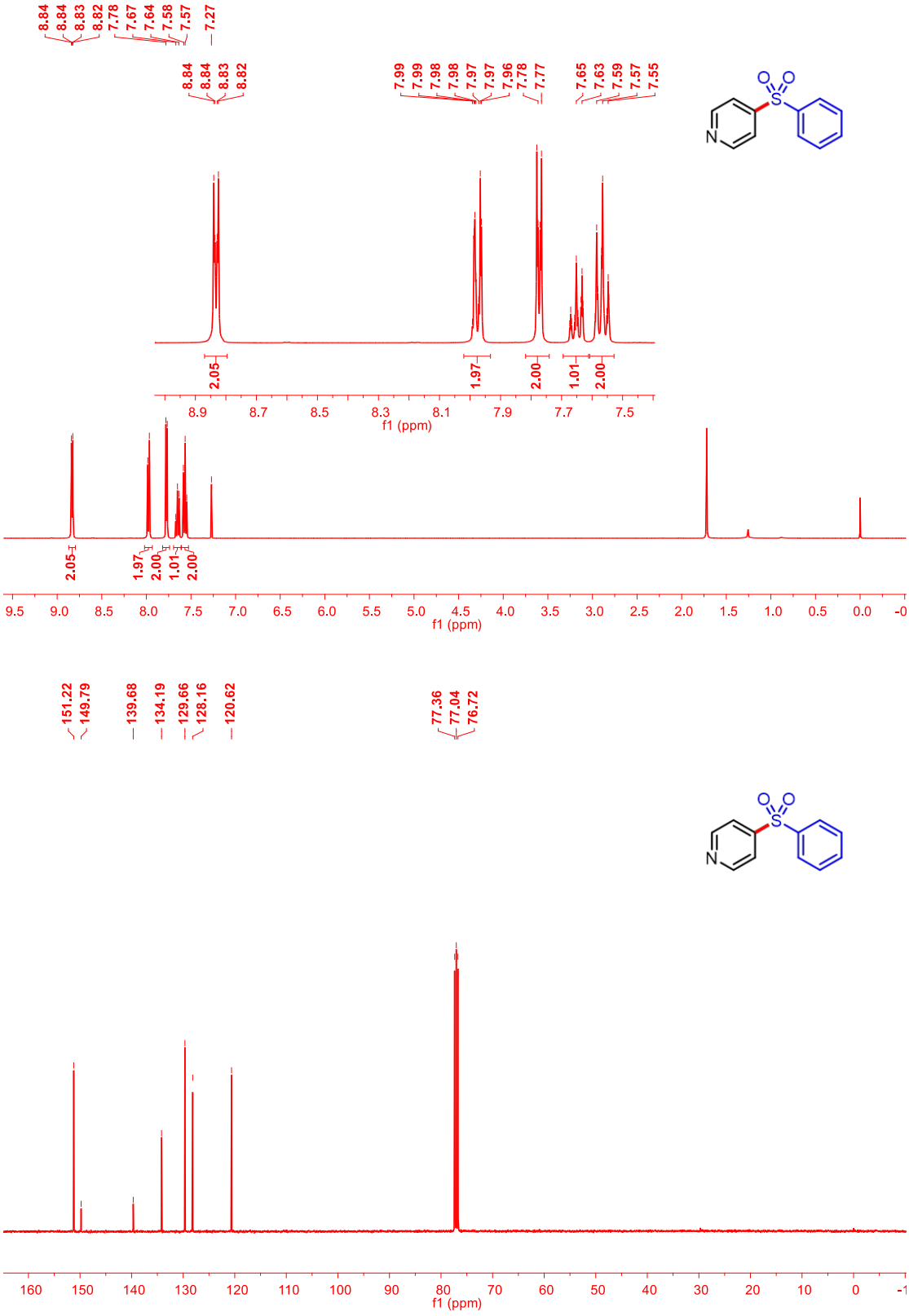


Fig. S32 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 2-methyl-4-(phenylsulfonyl)pyridine (**3za**) in $CDCl_3$

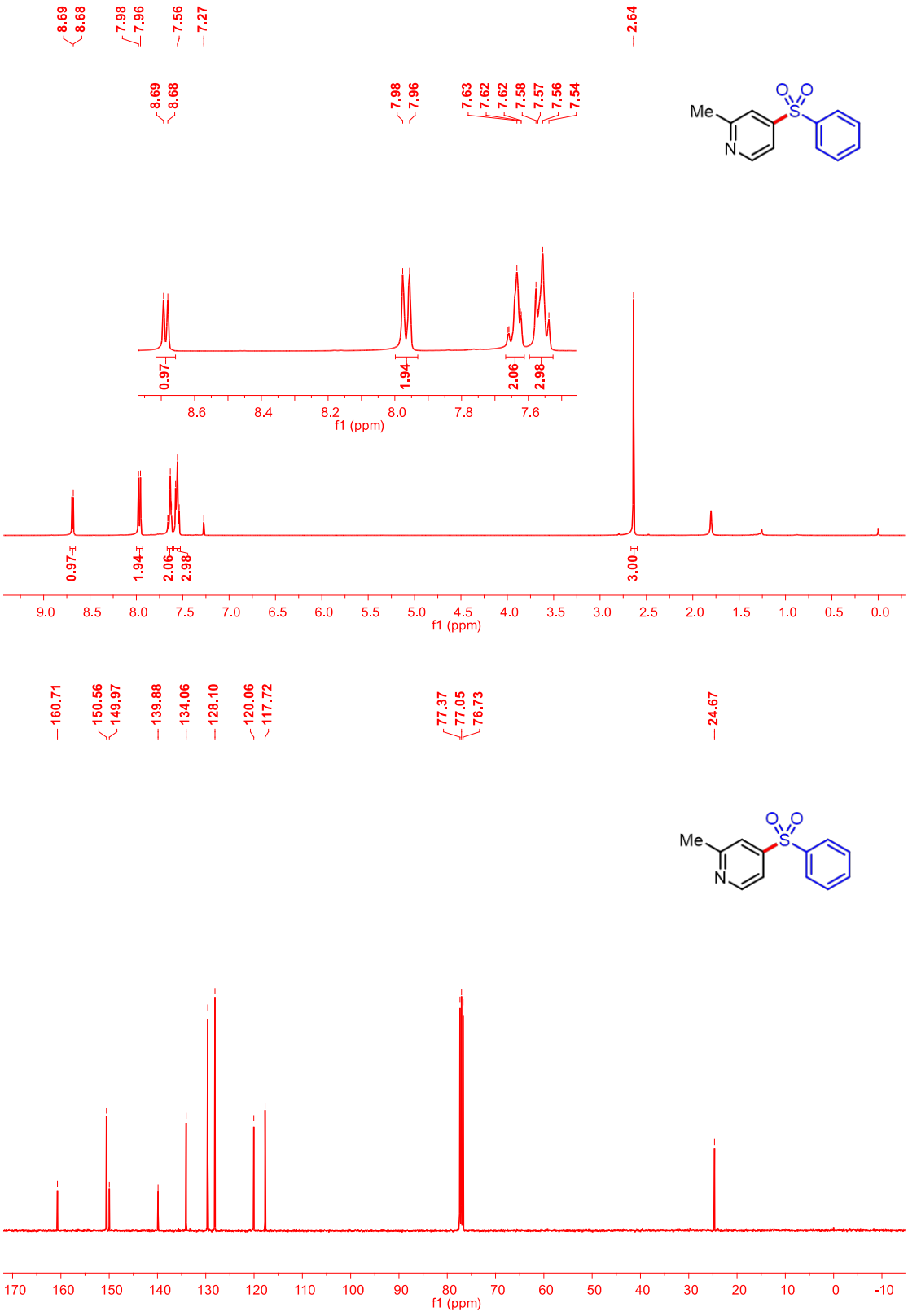


Fig. S33 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 3-(phenylsulfonyl)quinoline (**3a'a**) in $CDCl_3$

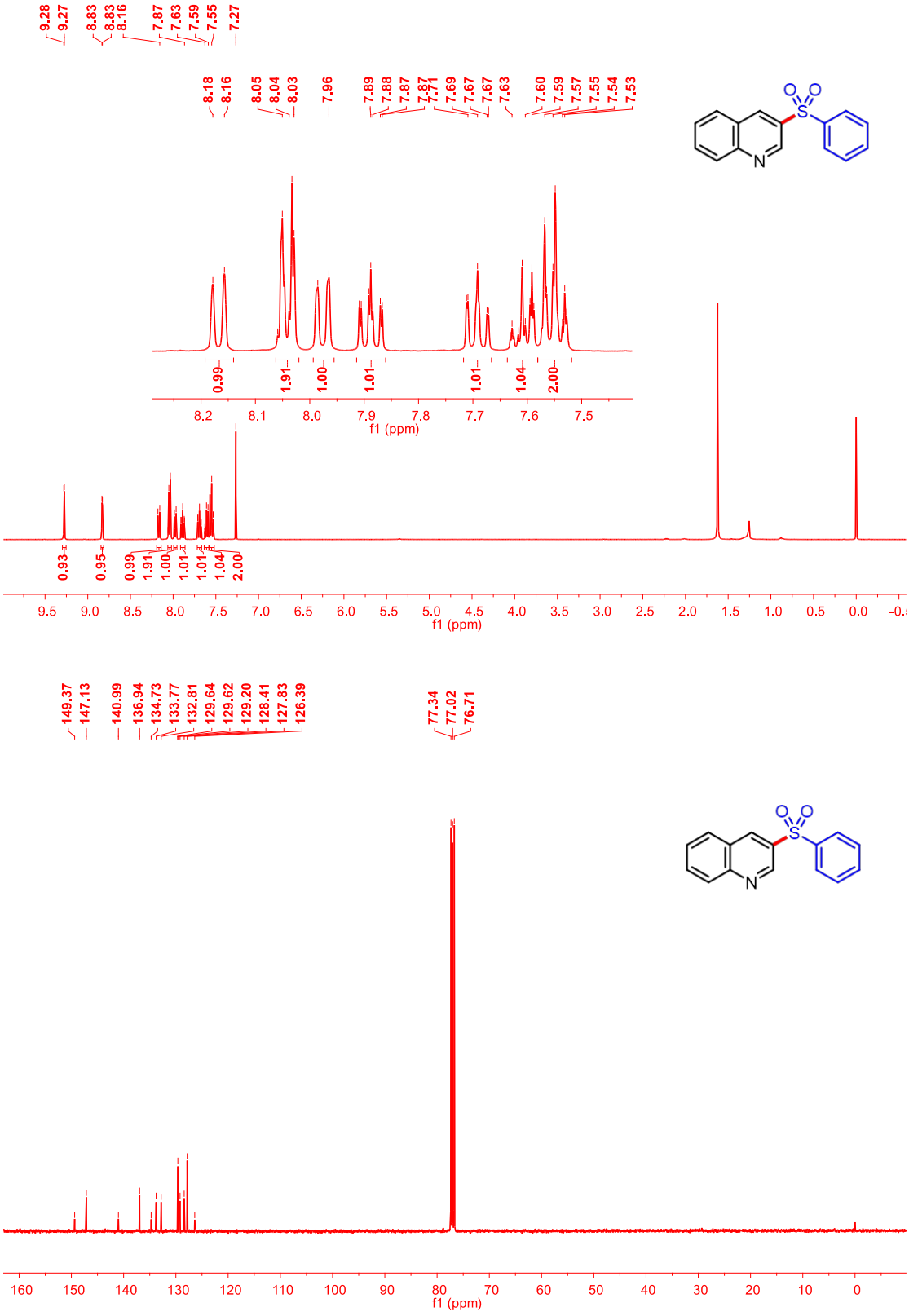


Fig. S34 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 2-(phenylsulfonyl)quinoline (**3b'a**) in $CDCl_3$

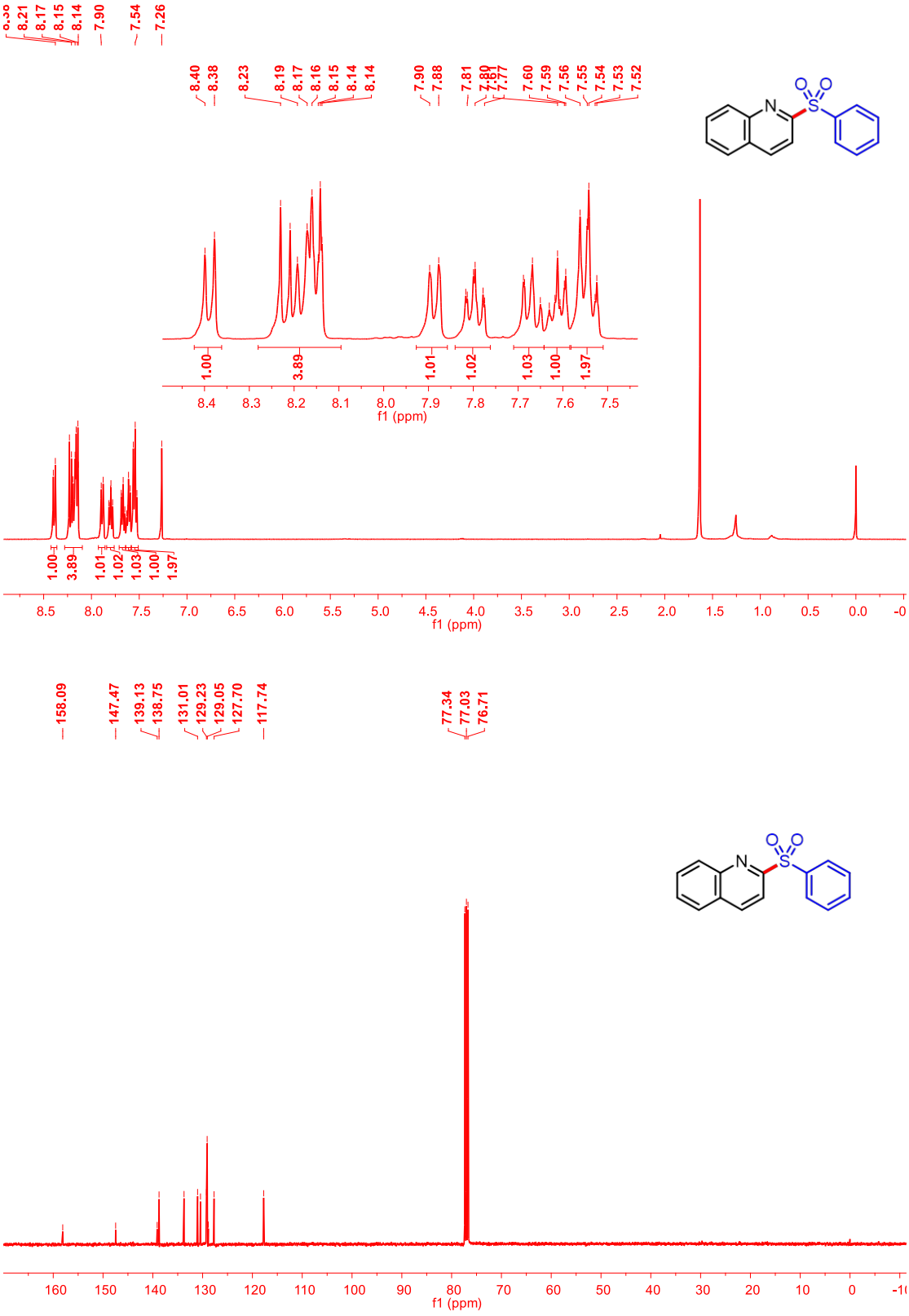
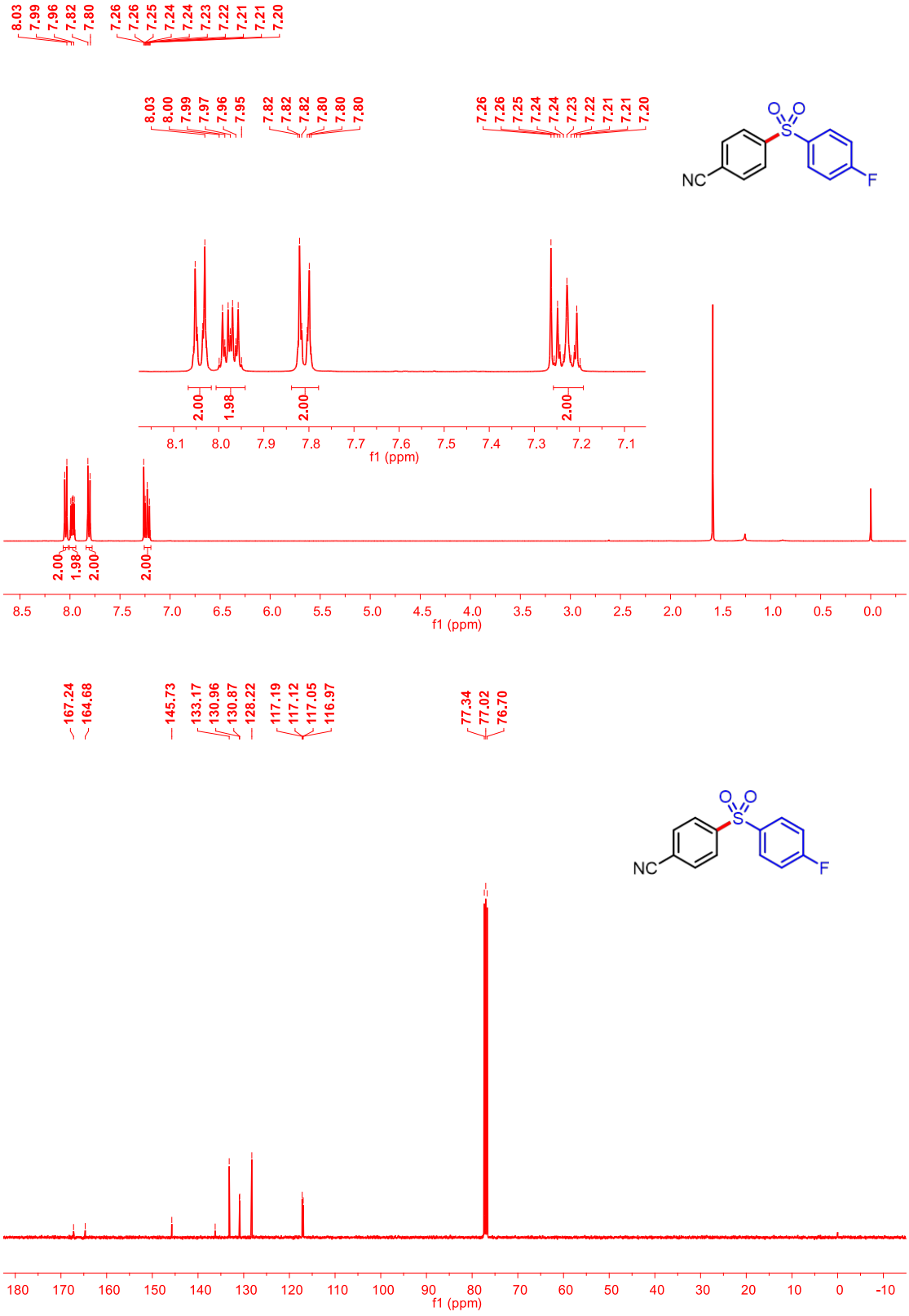


Fig. S35 The ^{1}H (400 MHz), ^{13}C (101 MHz) and ^{19}F (377 MHz) NMR spectra for 4-((4-fluorophenyl)sulfonyl)benzonitrile (**3ab**) in $CDCl_3$



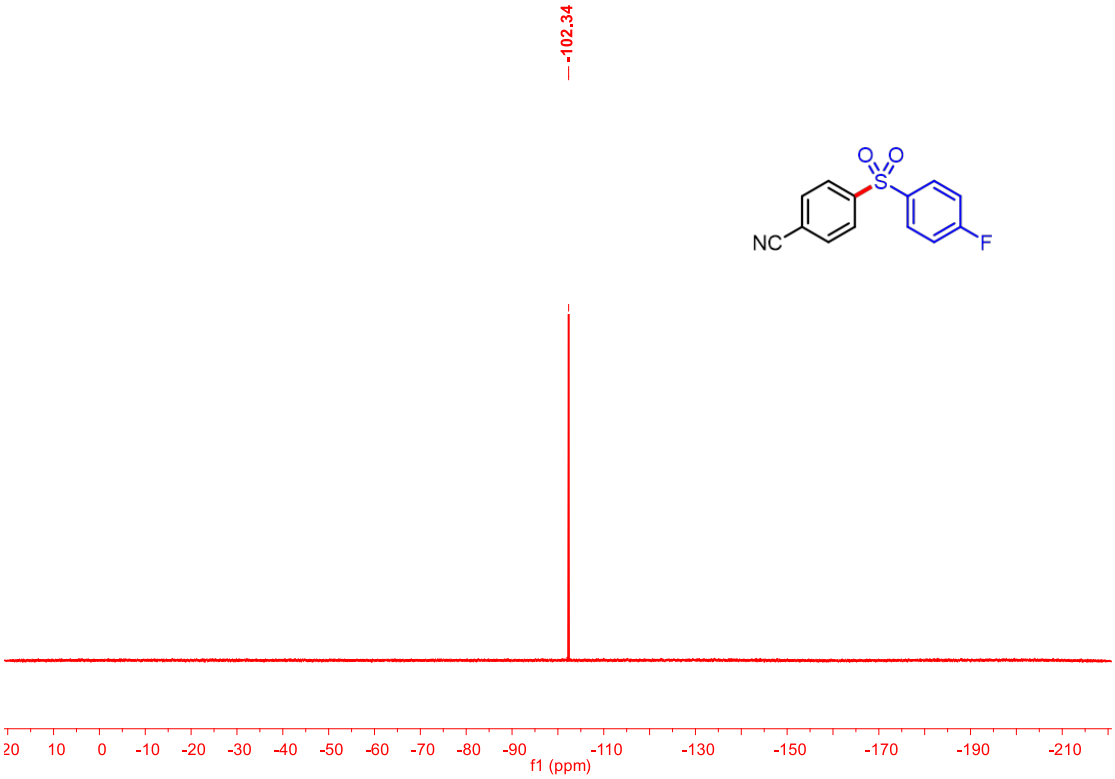

-102.34
O
O
S
NC
F
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

Fig. S36 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 4-((4-chlorophenyl)sulfonyl)benzonitrile (**3ac**) in $CDCl_3$

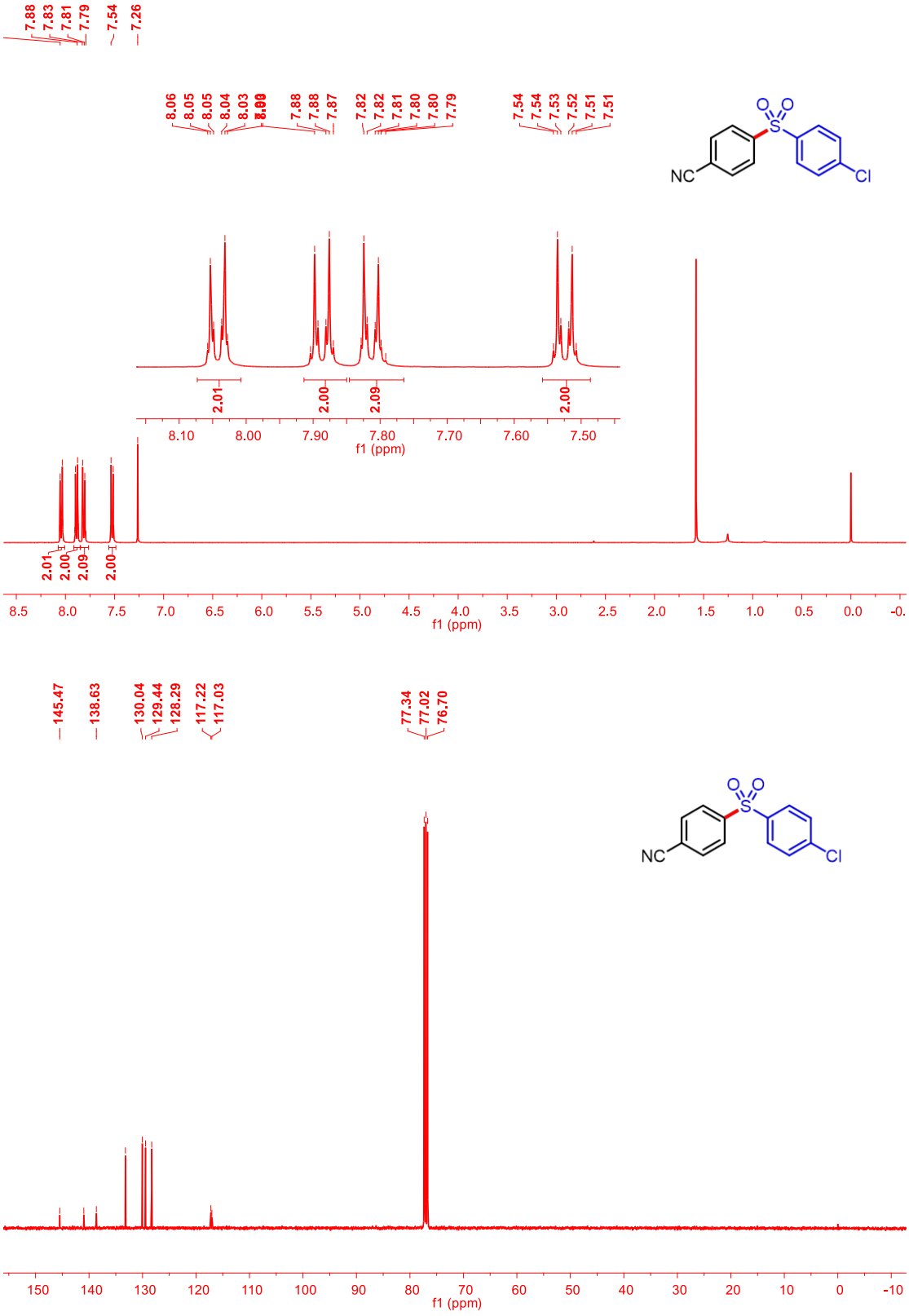


Fig. S37 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 4-tosylbenzonitrile (**3ad**) in $CDCl_3$

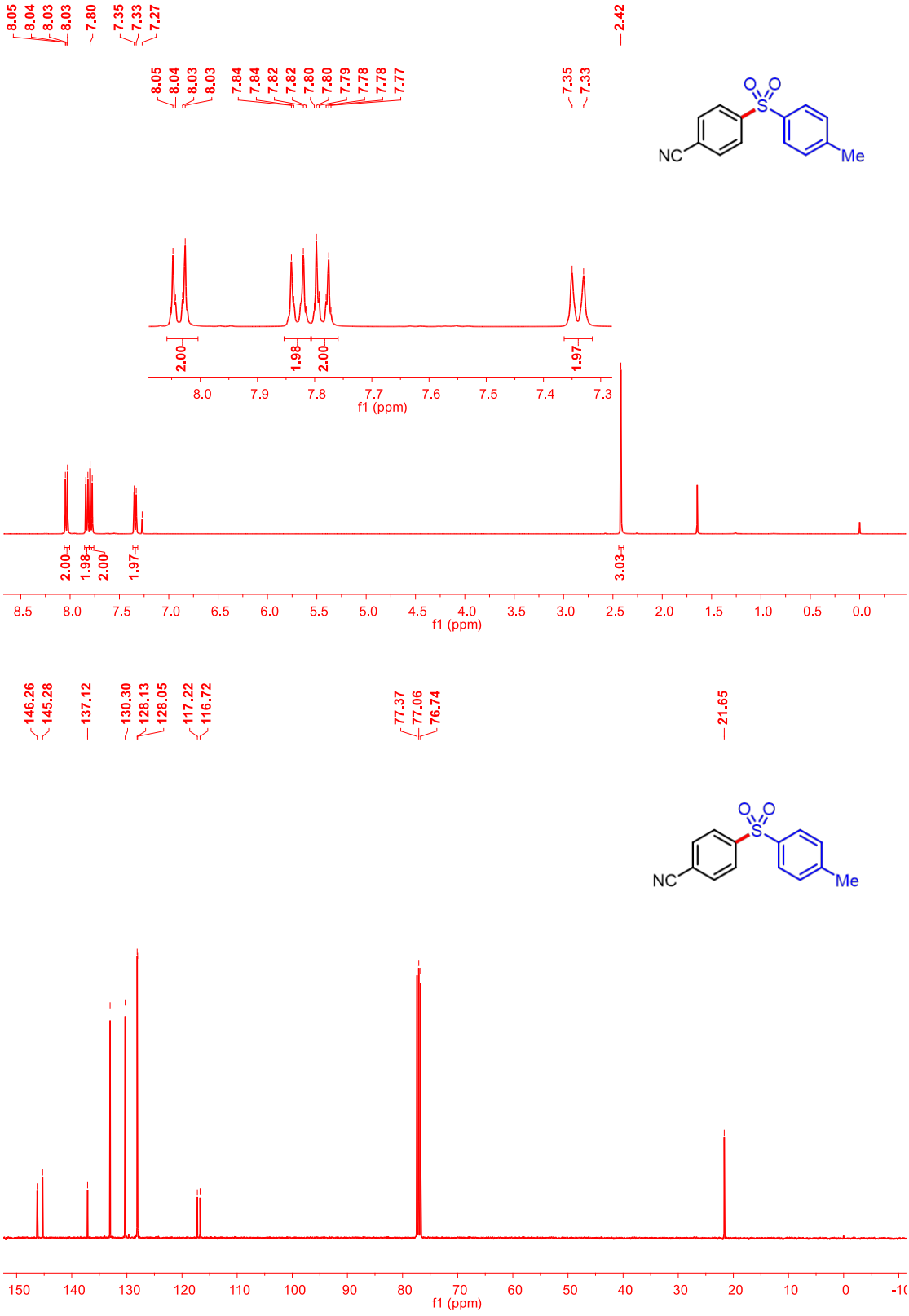


Fig. S38 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 4-((4-(tert-butyl)phenyl)sulfonyl)benzonitrile (**3ae**) in $CDCl_3$

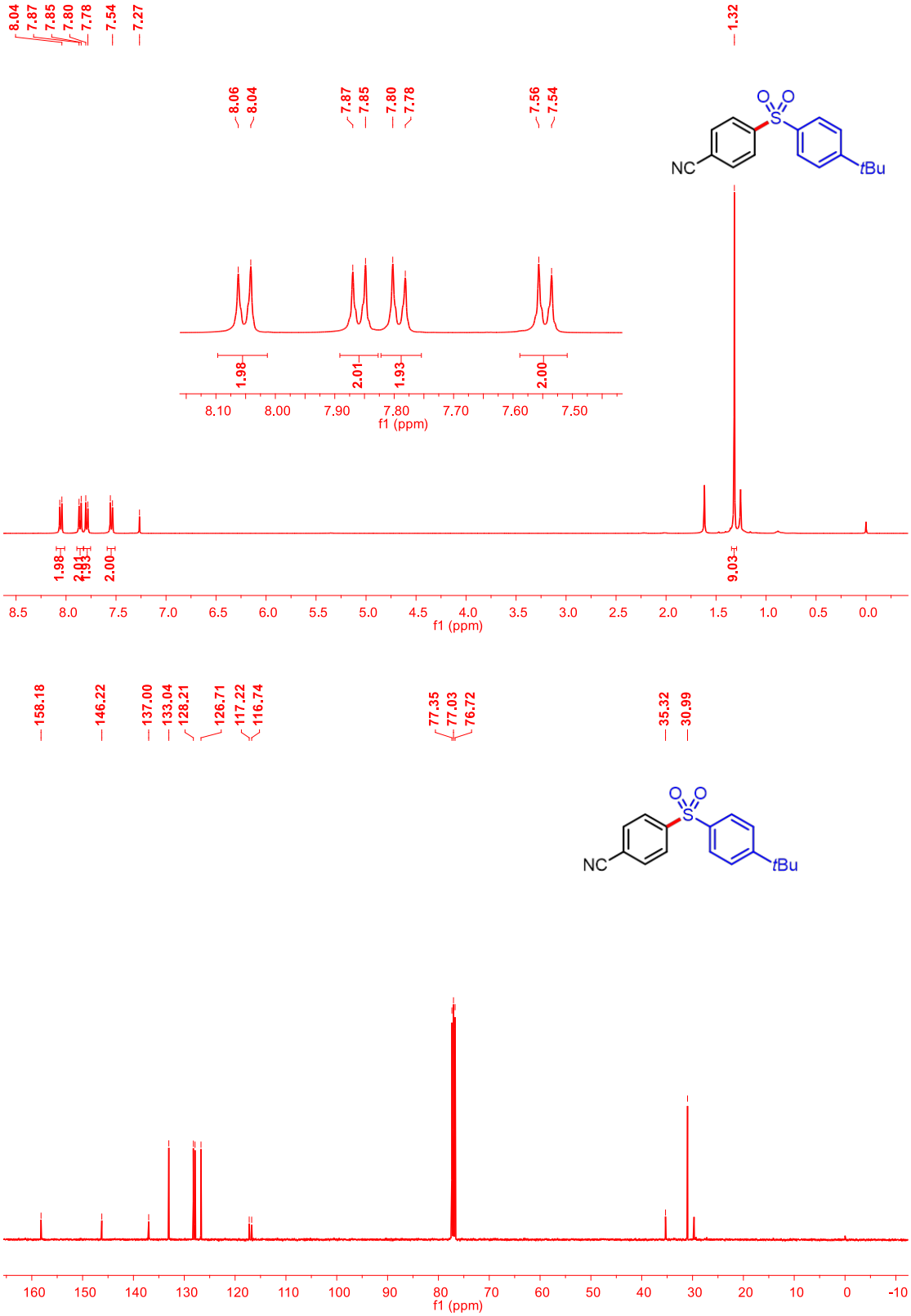


Fig. S39 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 4-((4-methoxyphenyl)sulfonyl)benzonitrile (**3af**) in $CDCl_3$

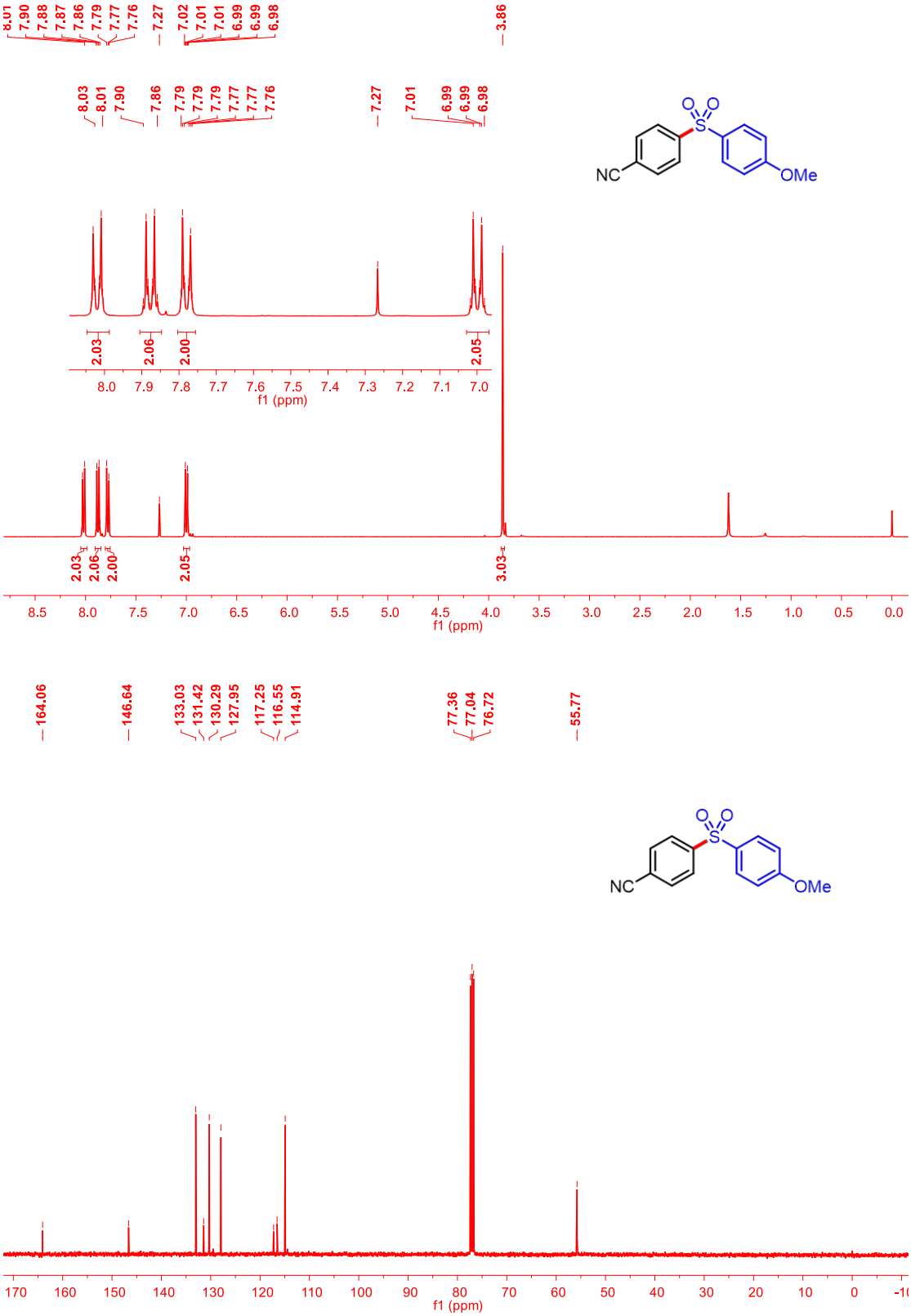


Fig. S40 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 4-(m-tolylsulfonyl)benzonitrile (**3ag**) in $CDCl_3$

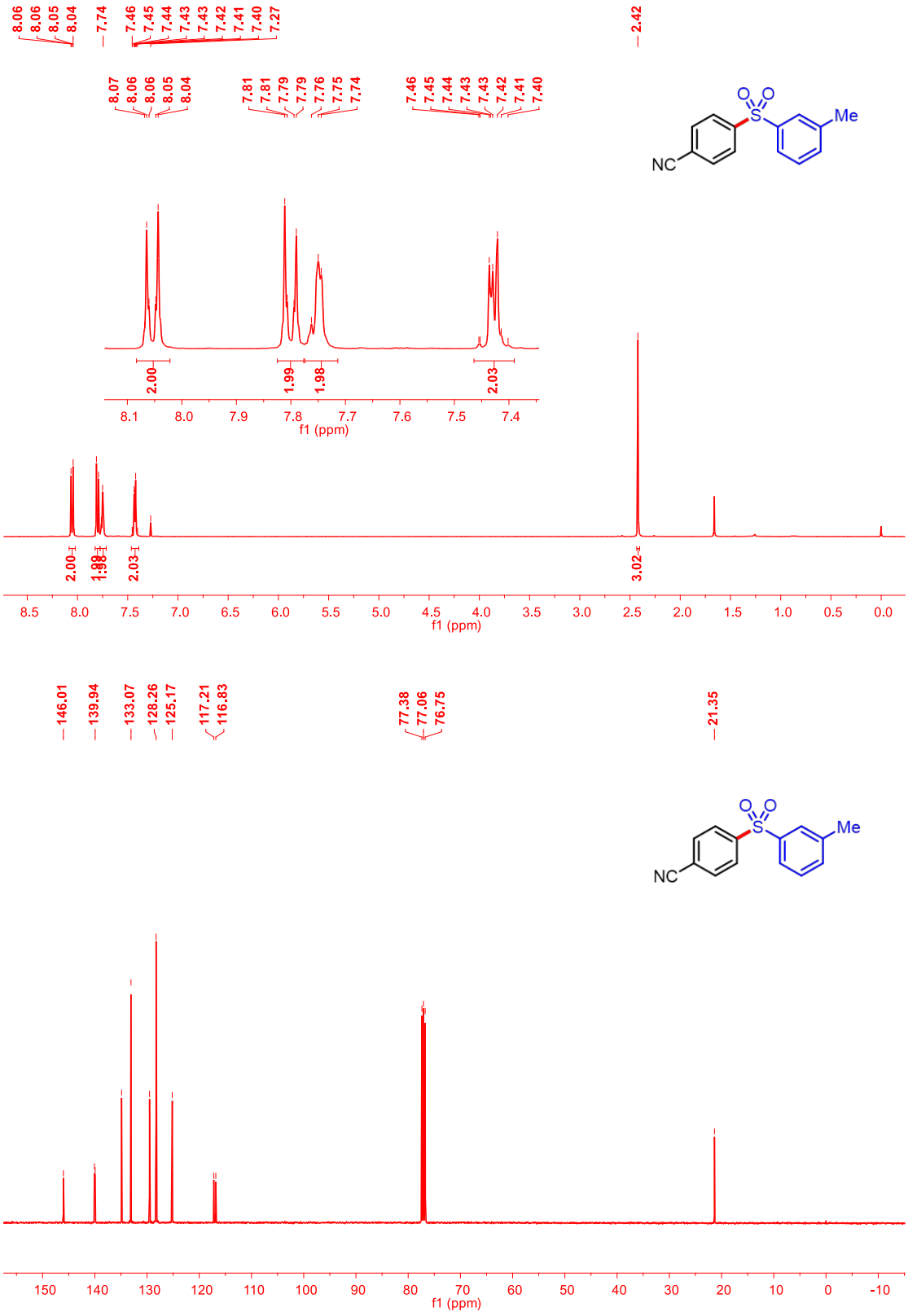
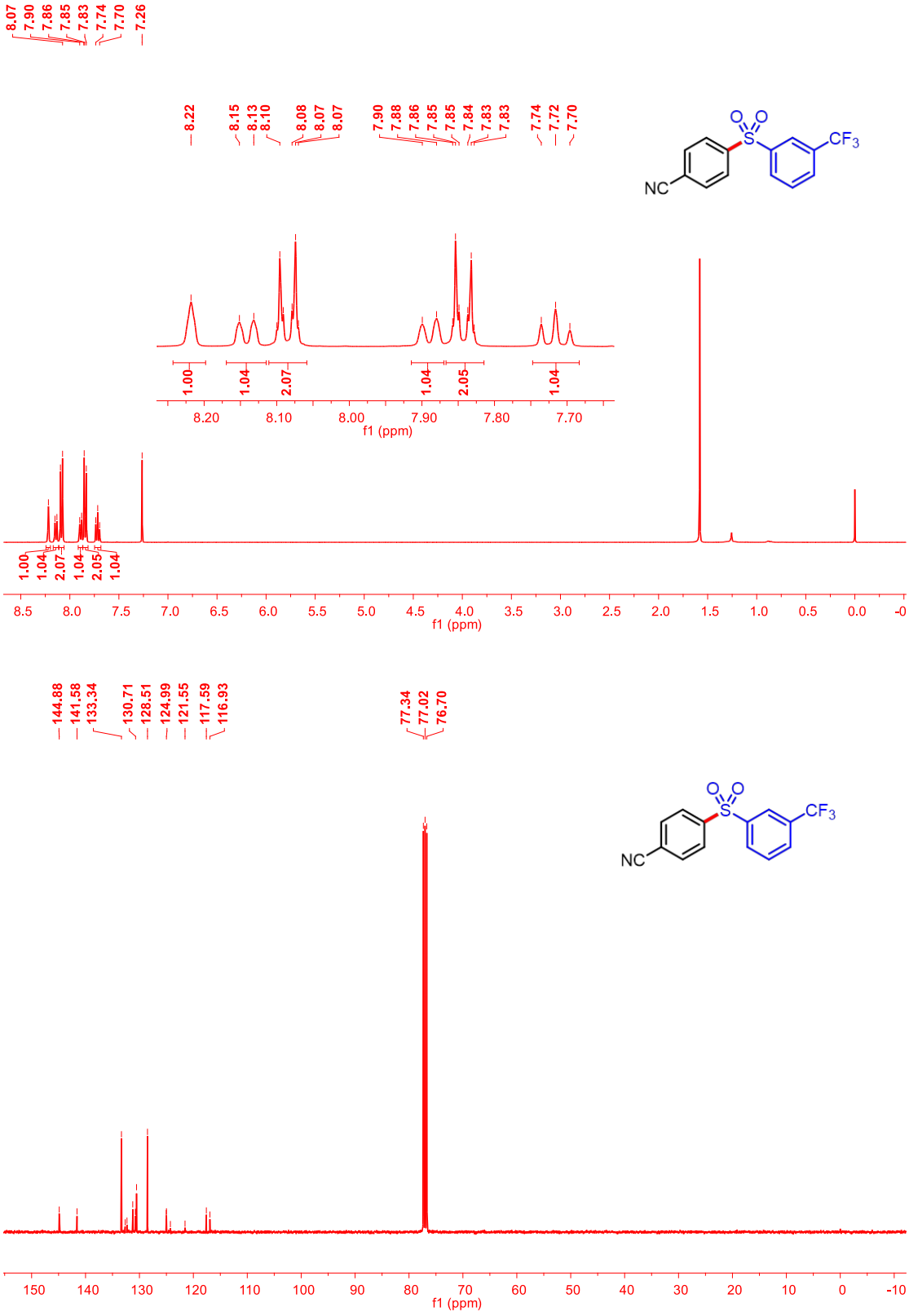


Fig. S41 The ^{1}H (400 MHz), ^{13}C (101 MHz), and ^{19}F (377 MHz) NMR spectra for 4-((3-(trifluoromethyl)phenyl)sulfonyl)benzonitrile (**3ah**) in $CDCl_3$



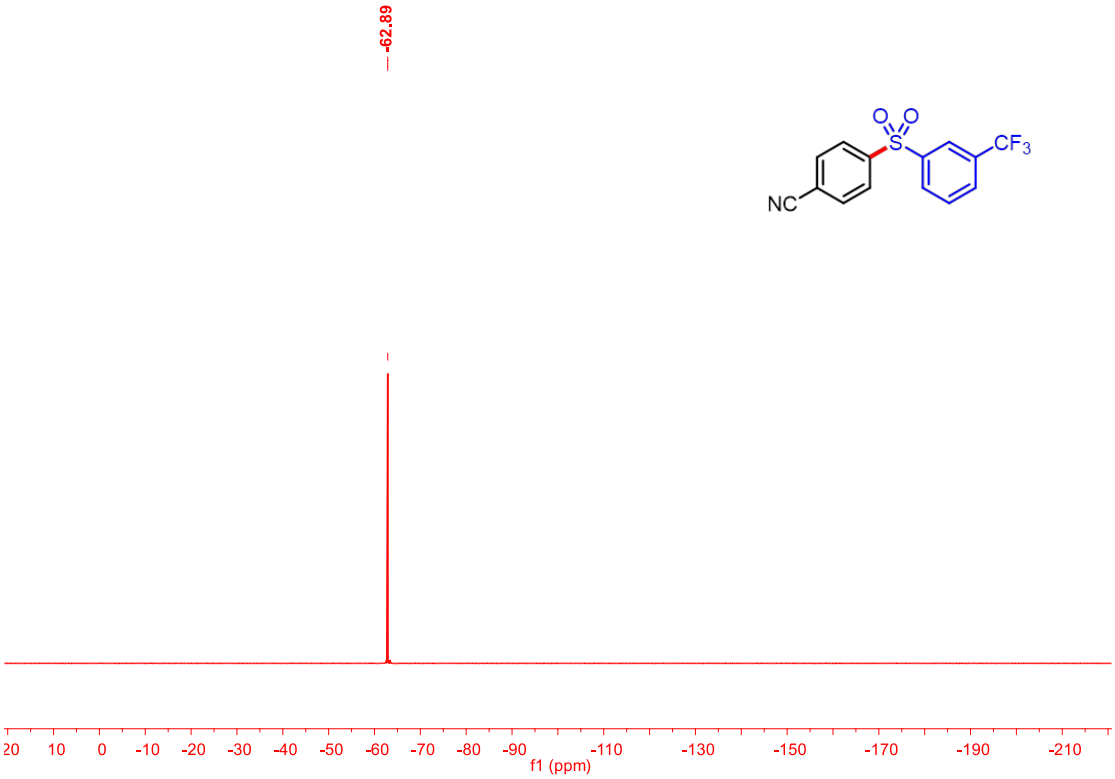
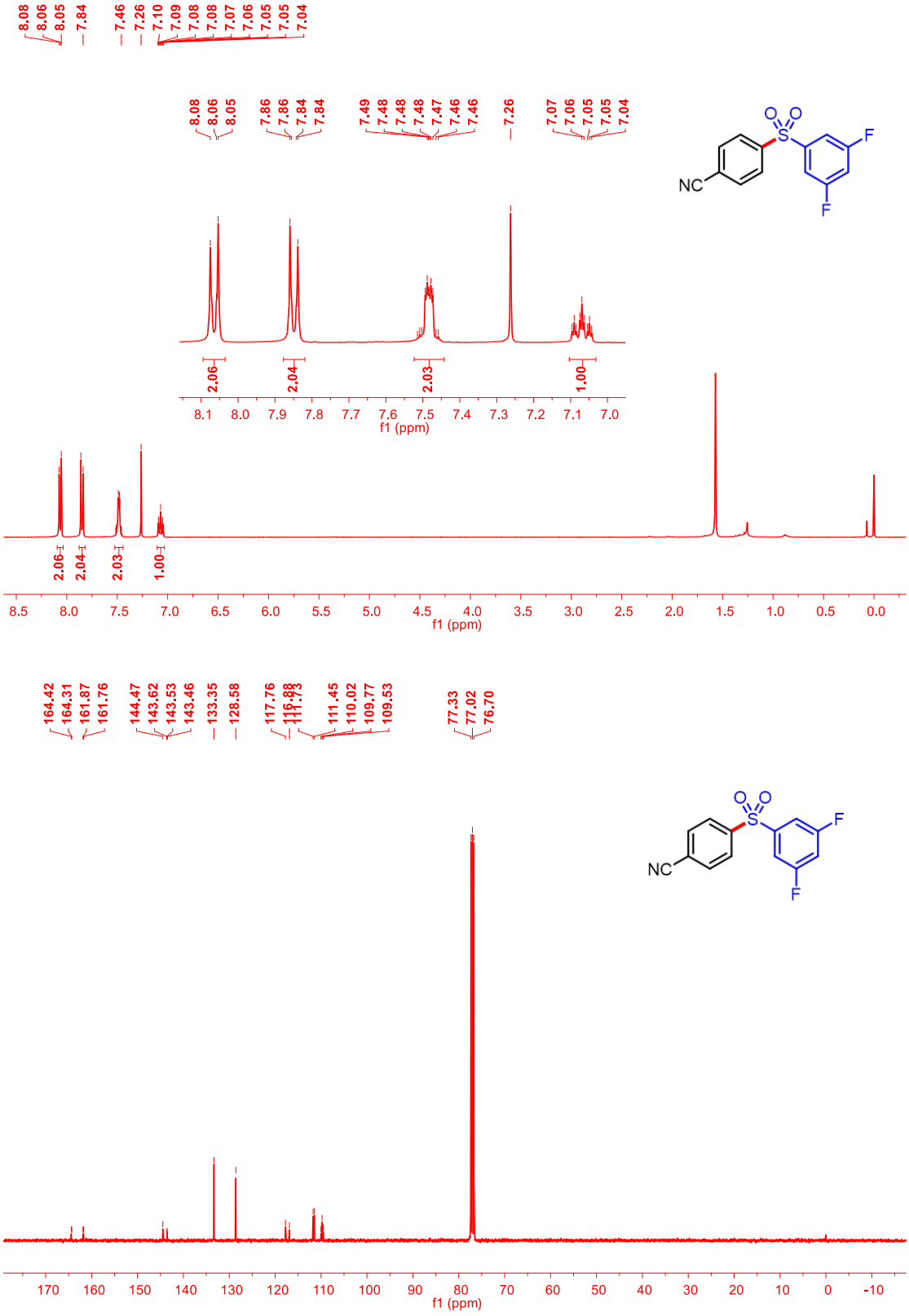

-62.89
NC
CF3
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

Fig. S42 The ^{1}H (400 MHz), ^{13}C (101 MHz) and ^{19}F (377 MHz) NMR spectra for 4-((3,5-difluorophenyl)sulfonyl)benzonitrile (**3ai**) in $CDCl_3$



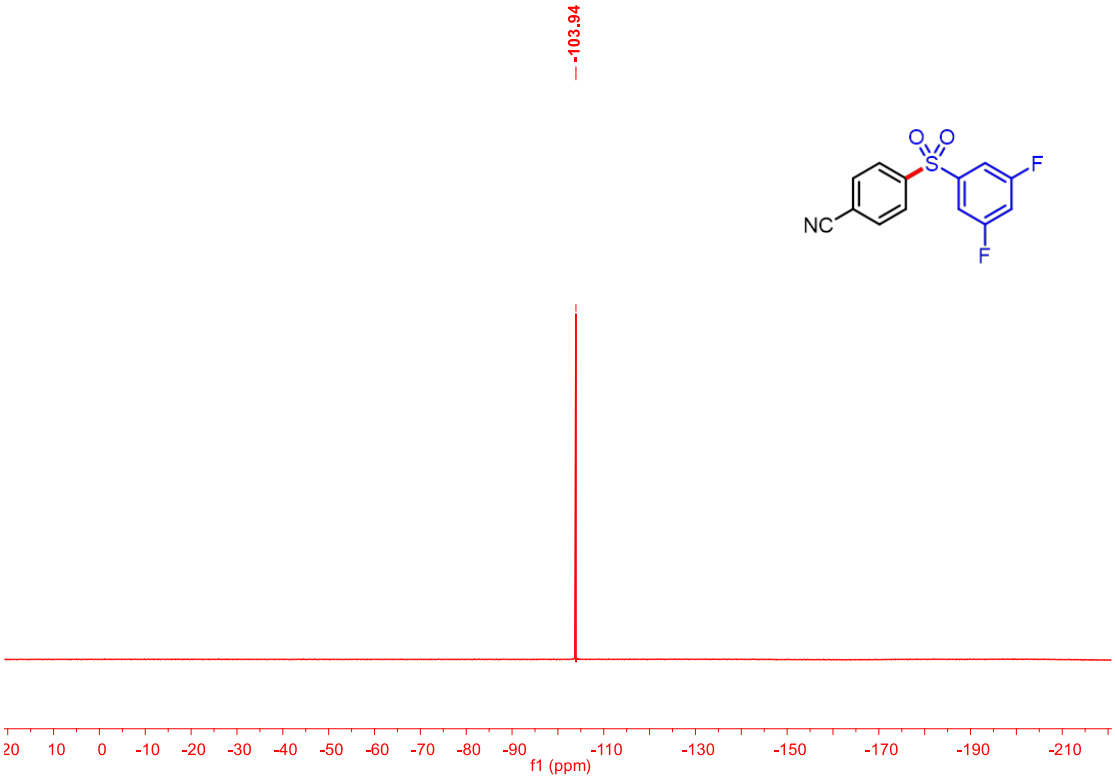

-103.94
O
O
S
F
NC
F
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

Fig. S43 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 4-(mesitylsulfonyl)benzonitrile (**3aj**) in $CDCl_3$

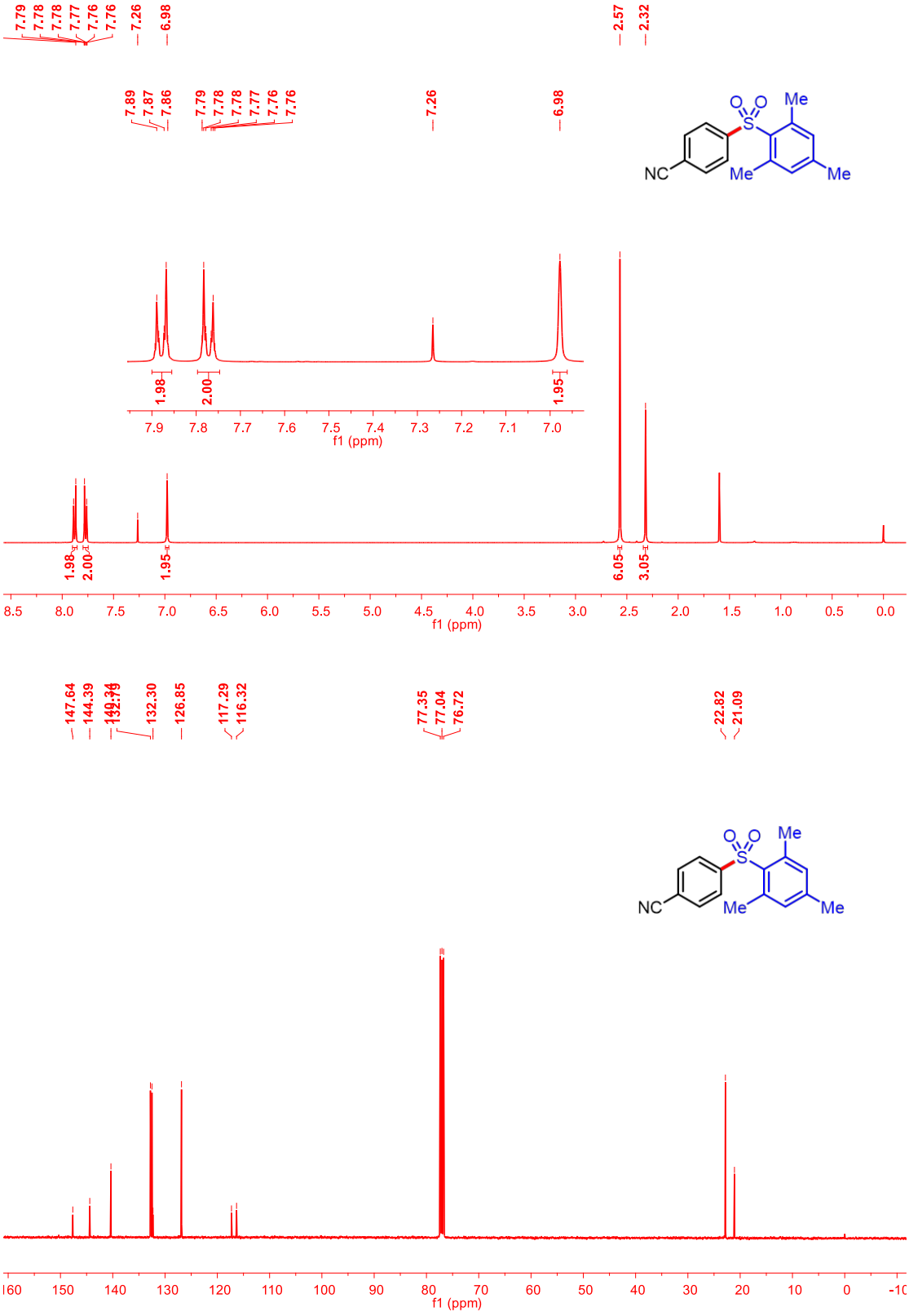


Fig. S44 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 4-(naphthalen-2-ylsulfonyl)benzonitrile (**3ak**) in $CDCl_3$

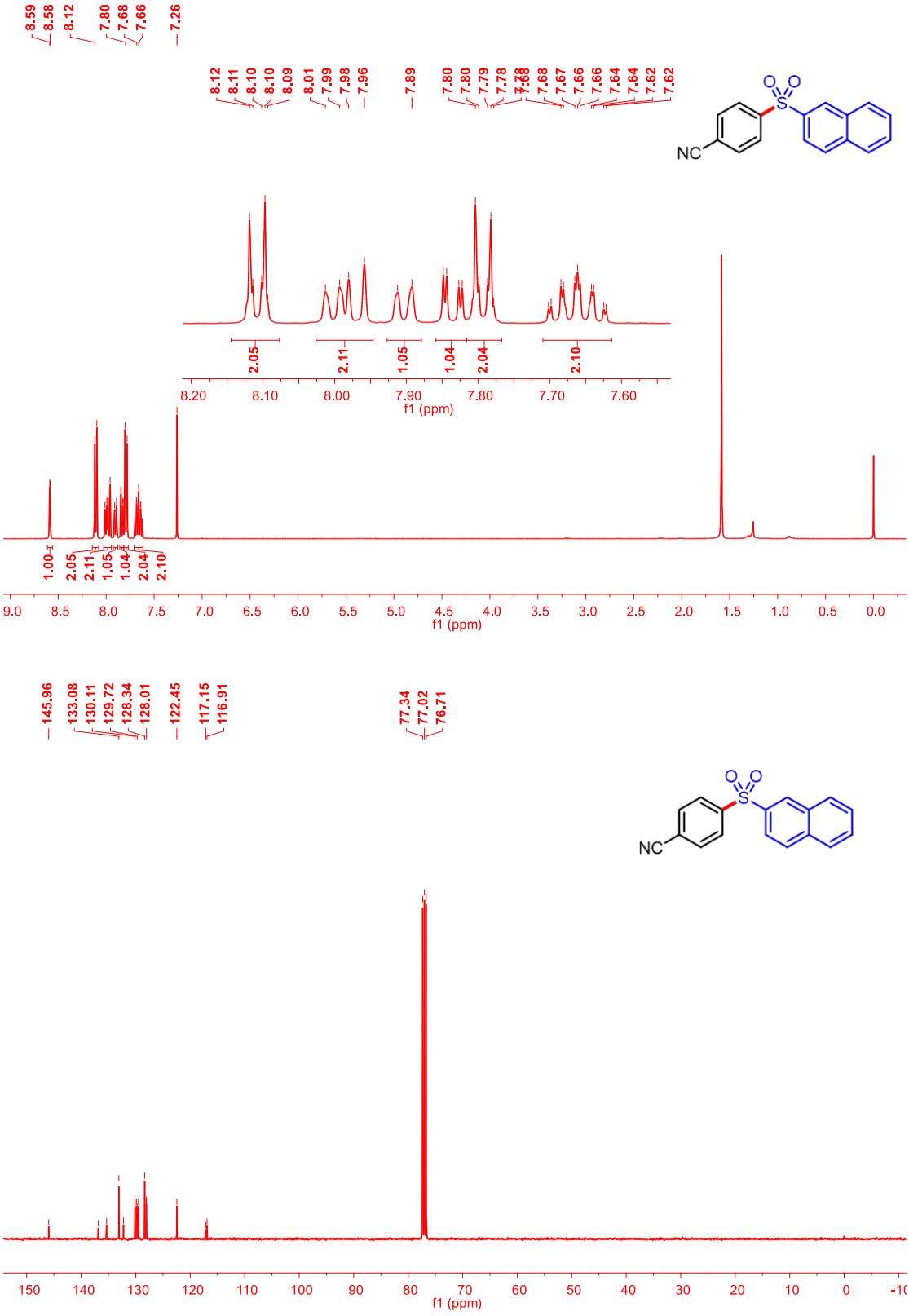


Fig. S45 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 4-(pyridin-3-ylsulfonyl)benzonitrile (**3al**) in $CDCl_3$

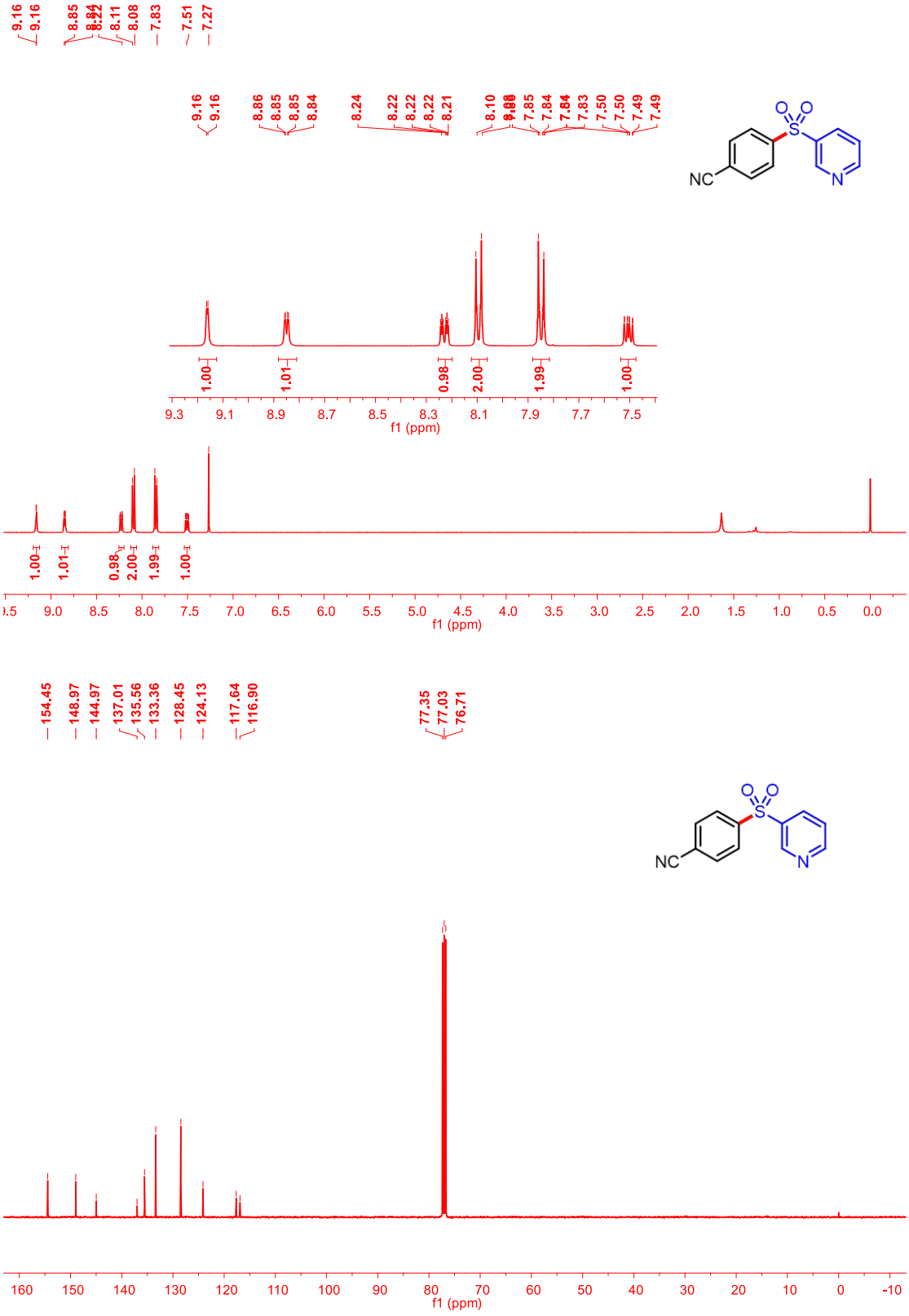


Fig. S46 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 8-chloro-3-(phenylsulfonyl)quinoline (**3c'a**) in $CDCl_3$

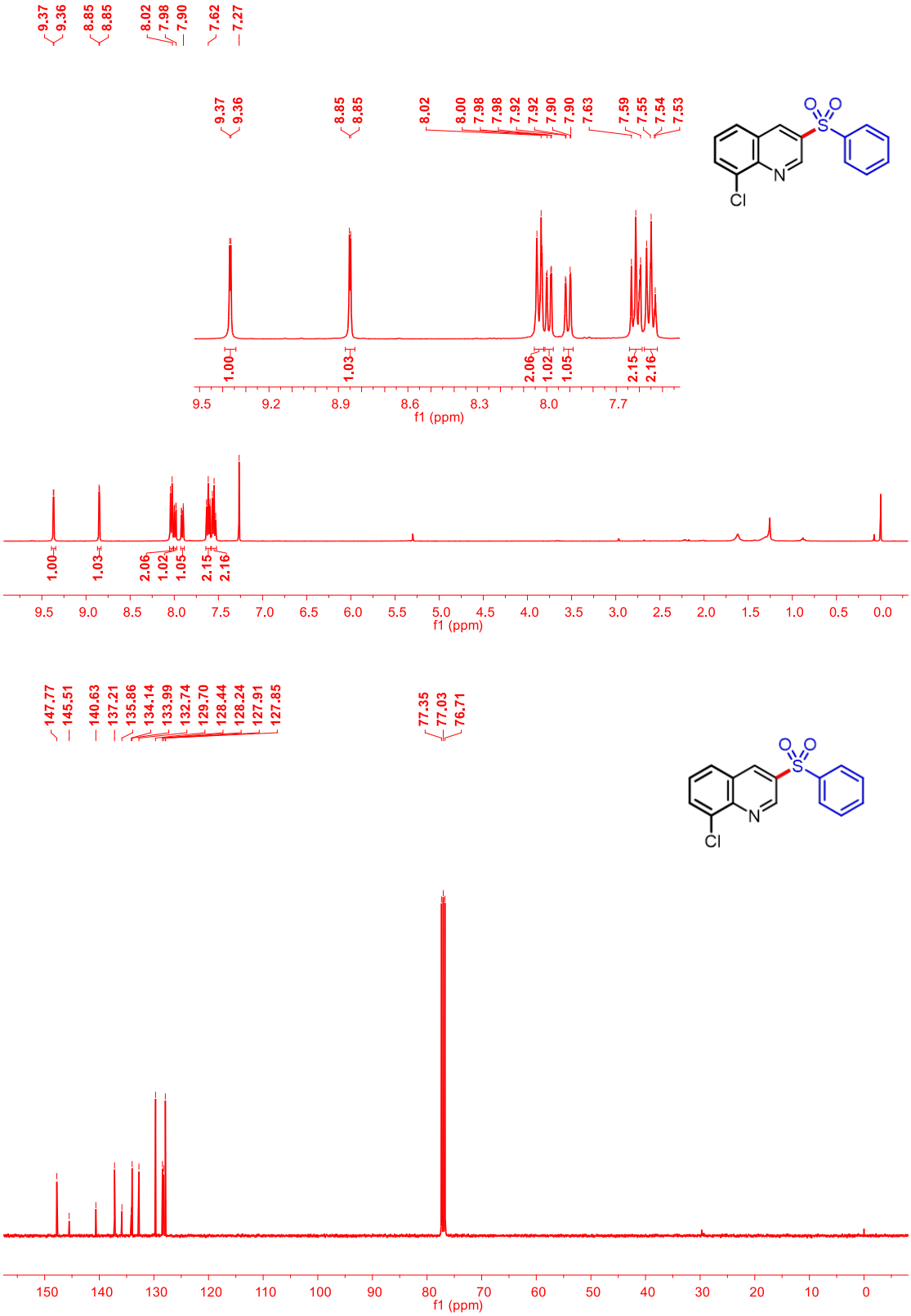


Fig. S47 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for N-phenyl-2-(phenylsulfonyl)benzamide (**3d'a**) in $CDCl_3$

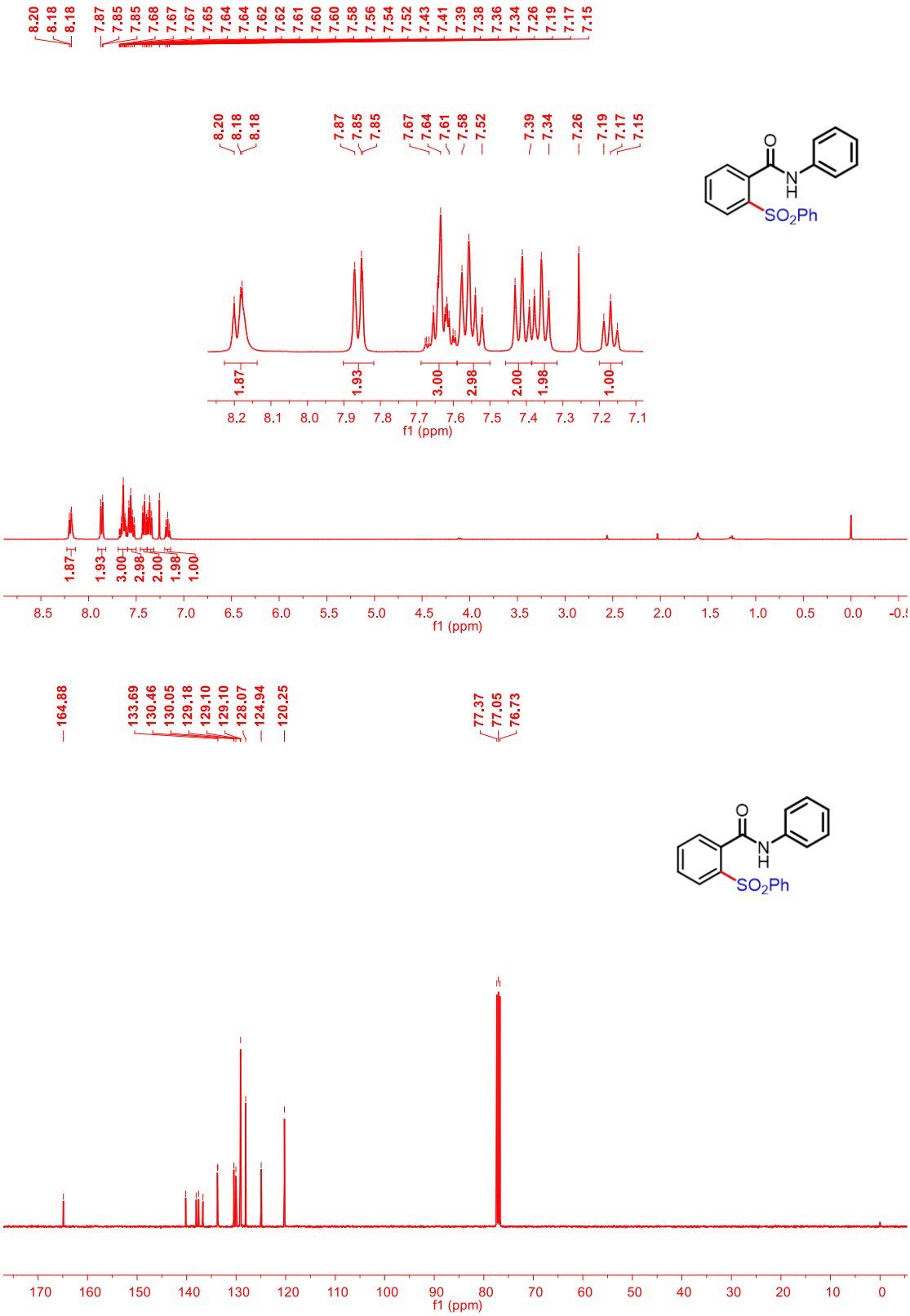


Fig. S48 The ^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra for 4-((4-(9H-carbazol-9-yl)phenyl)sulfonyl)benzonitrile (**4**) in $CDCl_3$