Supporting Information

Base-promoted cascade *5-exo-dig* annulation/carboxylation of *o*-(1-alkynyl)benzenesulfonamides with CO_2: divergent synthesis of mono- or gem-dicarboxylic esters

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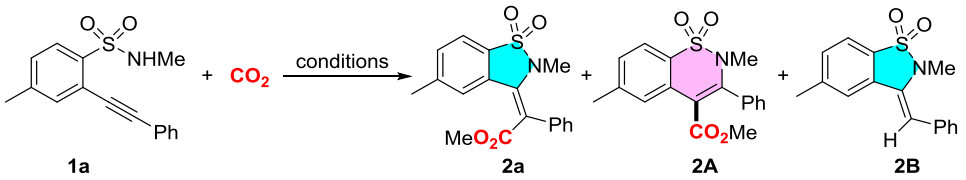
I. General Information

Chemicals were used as received without special purification unless stated otherwise. ^{1}H and ^{13}C NMR were recorded at ambient temperature on a 400 or 300 MHz NMR spectrometer (100 or 75 MHz for ^{13}C NMR). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0 ppm) as the internal standard. NMR analysis was carried out at 298 K unless noted otherwise. HRMS was obtained on an ESI-LC-MS/MS spectrometer.

II. Evaluation of Conditions[a]

Initially, *N*,4-dimethyl-2-(phenylethynyl)benzenesulfon amide **1a** was selected as the model substrate to optimize the reaction conditions (Table S1). Firstly, the reaction of **1a** with CO_2 was conducted by using 3 equiv of K_2CO_3 as the base in DMF at 60 °C, the *5-exo-dig* annulation/carboxylation product **2a** was isolated in 36% yield, along with the generation of 6-*endo*-dig analogous **2A** in 32% yield, amination-protonation product **2B** in 21% yield, respectively. The structure of **2a** was ambiguously confirmed by X-ray crystallography analysis (for details, please see Supporting Information, Figure S1). For further improving the reaction efficiency, then, other common bases were tested, Na_2CO_3 gave **2a** in a decreased yield (25%, entry 2), while KO^{t}Bu and Cs_2CO_3 only could result in a messy mixture (entry 3) or almost no reaction (entry 4). Among the solvent screening, DMSO gave a slightly better result (45%, entry 5). However, DMAc only resulted in **2a** in 14% yield (entry 6), and the reaction could not occur in MeCN (entry 7). The attempt to improve the reaction efficiency by adding some Lewis acids failed. None of the desired acid **2a** could be detected. Instead, only the full formation of the protonated product **2B** was observed (entry 8). Further elevating the reaction temperature to 80 °C has no positive effect (38%, entry 9). However, lowering the temperature to 40 °C could improve the yield of **2a** to 50% (entry 10). Delightedly, the employment of dry DMSO improved the yield to 61% (entry 11). Particularly, when the reaction was conduct at room temperature for about 48 h, the yield of **2a** could be further increased to 76% (entries 12-13). Control experiments revealed that the reaction could not take place without base or CO_2, respectively (entry 14).

Table S1 Evaluation of Conditions[a]



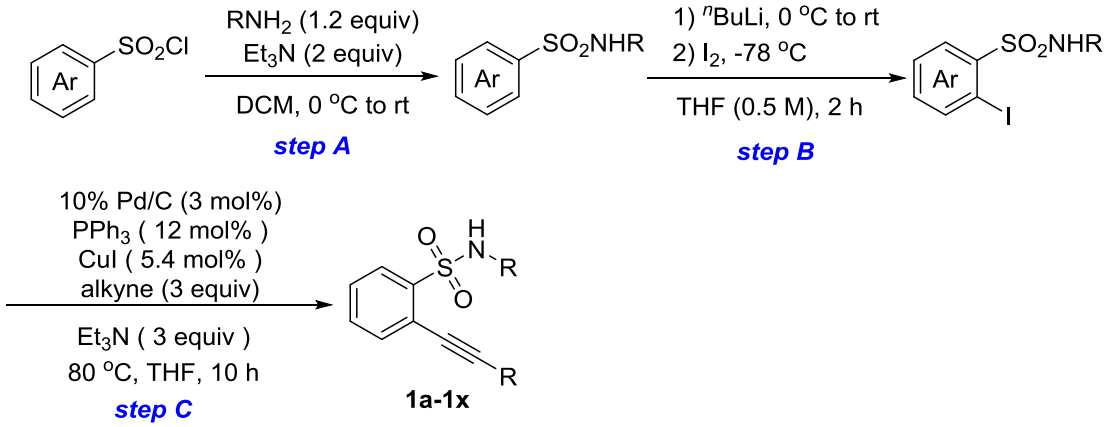
entry	base	solvent	T (°C)	**2a** yield [b] (%)
1	K_2CO_3	DMF	60	36
2	Na_2CO_3	DMF	60	25
3	KO^tBu	DMF	60	messy
4	Cs_2CO_3	DMF	60	trace
5	K_2CO_3	DMSO	60	45
6	K_2CO_3	DMAc	60	14
7	K_2CO_3	MeCN	60	0
8[c]	K_2CO_3	DMSO	60	0
9	K_2CO_3	DMSO	80	38
10	K_2CO_3	DMSO	40	50
11[d]	K_2CO_3	DMSO	40	61
12	K_2CO_3	DMSO	25	68
13[e]	K_2CO_3	DMSO	25	76
14[f]	K_2CO_3	DMSO	25	N.R

[a] Reaction conditions: **1a** (0.1 mmol), base (0.3 mmol), CO_2 (1 atm), solvent (1 mL), 12 h, in a sealed Schlenk tube, unless otherwise noted. Then, MeI (0.4 mmol), 50 °C (oil bath), 1 h. [b] Isolated yield. [c] $Cu(OTf)_2$ or AgOAc (10 mol%) was added, [d] dry DMSO was used. [e] 48 h. [f] without K_2CO_3 or CO_2. N.R. = no reaction.

III. Synthesis and Characterization of Starting Materials

General Procedure A

(1) *o*-(1-Alkynyl)benzenesulfonamides are **1a-1x** prepared according to the known methods.[1] **1a-1x** are all known compounds (Note: commercially available *N*,4-dimethylbenzenesulfonamide was used for the synthesis of **1a-1d, 1l-1x** directly, and 2-bromobenzenesulfonyl chloride was used for the synthesis of **1f** directly.)



Step A: Primary amine (12 mmol, 1.2 equiv) and Et_3N (20 mmol, 2 equiv) were added to round bottom flask, then benzenesulfonyl chloride (10 mmol, 1 equiv) in dichloromethane was injected into it at 0 °C. After the mixture was stirred until TLC showed that benzenesulfonyl chloride was totally consumed at room temperature. Water was added to the reaction mixture and extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate: petroleum ether) on silica gel or recrystallized from ethyl acetate/petroleum ether to give the corresponding products.

Step B: To a solution of sulfonamide (1.0 equiv.) in anhydrous THF (0.5 M), *n*-butyllithium (2.5 M in hexanes, 2.1 equiv) was added dropwise at 0 °C. The

[1] (a) D. K. Barange, T. C. Nishad, N. K. Swamy, V. Bandameedi, D. Kumar, B. R. Sreekanth, K. Vyas, M. Pal, *J. Org. Chem.* 2007, **72**, 8547–8550. (b) B. M. Rao, J. S. Yadav, B. Sridharb, B. V. S. Reddy, *Org. Biomol. Chem.*, 2018, 16, 5163–5166.

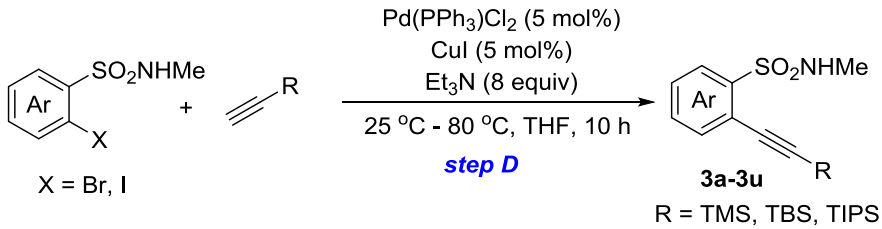
reaction mixture was stirred at 0 °C for 15 minutes and then warmed to room temperature. After stirring for one hour at room temperature the solution was cooled to –78 °C and stirred for further 15 minutes. Then, a solution of iodine (1.1 equiv.) in anhydrous THF (0.73 M) was added until the brown colour persisted. The reaction mixture was stirred for one hour at –78 °C and subsequently quenched by addition of NH_4Cl (sat. aq. solution) followed by NaS_2O_5 (sat. aq. solution). The aqueous phase was extracted with EtOAc (3 x15 ml), the combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. Separation by flash column chromatography afforded sulfonamides **II-8** as colorless solids.

Step C: A mixture of 2-iodo-*N*-methyl bezenesulfonamide (10 mmol, 1.0 equiv), 10% Pd/C (3 mol%, 0.3 mmol, 31.9 mg), PPh_3 (12 mol%, 1.2 mmol, 314.7 mg), CuI (5.4 mol%, 0.54 mmol, 102.8 mg) and Et_3N (3 equiv., 30 mmol, 4.2 mL) in acetonitrile (20 mL) was stirred at 25 °C for 30 min under nitrogen. To this mixture was added appropriate terminal alkyne (15 mmol) slowly with stirring. The reaction mixture was then stirred at 80 °C for 10 h, cooled to room temperature, diluted with EtOAc (50 mL) and filtered through celite. The filtrate was collected and concentrated under vacuum. The residue was purified by column chromatography (SiO_2) to afford the desired product.

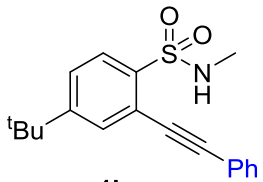
(2) *o*-(1-Alkynyl)benzenesulfonamides **3a-3u** are prepared according to the known methods. (*Note: commercially available 2-bromobenzenesulfonyl chloride was used for the synthesis of **3a-3e, 3s-3u** directly. The corresponding 2-bromobenzenesulfonyl chlorides for the synthesis of **3o-3r** were prepared according to the reported procedure.*[2] *Other iodine analogous was prepared according to step **A** and **B.***)

General Procedure B

[2] N. Radhoff, A. Studer, *Angew. Chem. Int. Ed.*, 2021, **60**, 3561–3565.



Step D:[3] A mixture of 2-iodo-*N*-methyl bezenesulfonamide[4] (10 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (5 mol%), terminal alkyne (15 mmol, 1.5 equiv) and triethylamine (80 mmol, 8 equiv) in tetrahydrofuran (20 mL) was stirred at 25 °C for 30 min under nitrogen. To this mixture was added appropriate terminal alkyne (15 mmol) slowly with stirring. The reaction mixture was then stirred at 80 °C for 10 h, cooled to room temperature, diluted with EtOAc (50 mL) and filtered through celite. The filtrate was collected and concentrated under vacuum. The residue was purified by column chromatography (SiO_2) to afford the desired products (50 – 90%). **3a-3b**, **3d-3f** are known compounds.[5] **3c, 3g-3t** are new compounds and their characterization data are listed as follows.



1j

4-(*tert*-Butyl)-*N*-methyl-2-(phenylethynyl)benzenesulfonamide (**1j**) was prepared as a brown solid from 4-(tert-butyl)-2-iodo-N-methylbenzenesulfonamide (1.76 g, 5 mmol) and ethynylbenzene according to the General Procedure A (eluent: petroleum

[3] Y. Tao, S. R. Gilbertson, *Chem. Commun.*, 2018, **54**, 11292—11295.

[4] F. W. Friese, C. Mück-Lichtenfeld, A. Studer, *Nat. Commun.*, 2018, **9**, 2808.

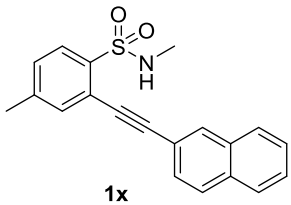
[5]. (a) Y. Ohta, H. Chiba, S. Oishi, N. Fujii, H. Ohno, *J. Org. Chem.*, 2009, **74**, 7052—7058. (b) D. K. Rayabarapu, A. Zhou, K. O. Jeon, T. Samarakoon, A. Rolfe, H. Siddiqui, P. R. Hanson, *Tetrahedron*, 2009, **65**, 3180—3188.

ether / ethyl acetate: 5:1) in 70% yield (1.14 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 2.0 Hz, 1H), 7.62 – 7.59 (m, 2H), 7.48 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.41 – 7.38 (m, 3H), 5.05 (q, *J* = 5.5 Hz, 1H), 2.61 (d, *J* = 5.4 Hz, 3H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 136.4, 131.7, 131.3, 129.7, 129.3, 128.6, 125.6, 121.9, 120.1, 96.6, 86.1, 35.0, 30.9, 29.5.

HRMS (ESI–TOF) *m*/*z* [M + H]$^{+}$: calcd. for $[C_{19}H_{22}NO_2S]^{+}$ 328.1366, found 328.1356.



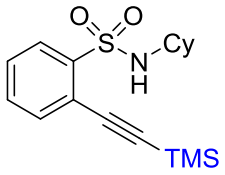
1x

***N*,4-Dimethyl-2-(naphthalen-2-ylethynyl)benzenesulfonamide** (**1x**) was prepared as a yellow solid from 2-iodo-*N*,4-dimethylbenzenesulfonamide (0.93 g, 3 mmol) and 1-ethynylnaphthalene according to the General Procedure A (eluent: petroleum ether / ethyl acetate: 5:1) in 90% yield (0.90 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (brs, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.86 (dd, *J* = 7.2, 3.7 Hz, 3H), 7.61 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.58 (d, *J* = 1.6 Hz, 1H), 7.56 – 7.53 (m, 2H), 7.29 (dt, *J* = 8.1, 1.2 Hz, 1H), 5.08 (q, *J* = 5.5 Hz, 1H), 2.62 (d, *J* = 5.5 Hz, 3H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 136.3, 134.6, 133.1, 132.8, 132.0, 129.8, 129.1, 128.3, 127.9, 127.8 (2C), 127.2, 126.8, 120.4, 119.1, 97.3, 86.0, 29.5, 21.1.

HRMS (ESI–TOF) *m*/*z* [M + H]$^{+}$: calcd. for $[C_{20}H_{18}NO_2S]^{+}$ 336.1053, found 336.1048.



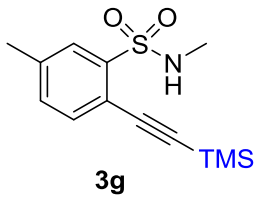
3c

***N*-Cyclohexyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide** (**3c**) was prepared as a black oil from 2-bromo-*N*-cyclohexylbenzenesulfonamide (1.59 g, 5 mmol) and ethynyltrimethylsilane according to the General Procedure B (eluent: petroleum ether / ethyl acetate: 5:1) in 75% yield (1.25 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.59 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.49 – 7.40 (m, 2H), 5.30 (d, *J* = 7.0 Hz, 1H), 3.05 (s, 1H), 1.75 – 1.58 (m, 4H), 1.48 – 1.43 (m, 1H), 1.21 – 1.11 (m, 5H), 0.28 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 134.4, 131.7, 128.7, 128.3, 119.9, 103.8, 101.8, 52.7, 33.5, 25.0, 24.3, -0.48.

HRMS (ESI–TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{17}H_{26}NO_2SSi]^+$ 336.1448, found 336.1443.



3g

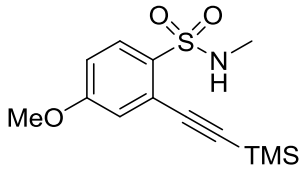
***N*,5-Dimethyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide** (**3g**) was prepared as a brown oil from 2-iodo-*N*,5-dimethylbenzenesulfonamide (1.56 g, 5 mmol) and ethynyltrimethylsilane according to the General Procedure B (eluent: petroleum ether / ethyl acetate: 5:1) in 70% yield (0.98 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 1.8 Hz, 1H), 7.22 – 7.19 (m, 1H), 5.15 (q, *J* = 5.5 Hz, 1H), 2.52 (d, *J* = 5.5 Hz, 3H), 2.32 (s, 3H), 0.23 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 136.9, 134.8, 129.4, 129.3, 119.7, 102.8, 101.2, 29.2, 20.9, -0.7.

HRMS (ESI–TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{13}H_{20}NO_2SSi]^+$ 282.0979, found

282.0975.



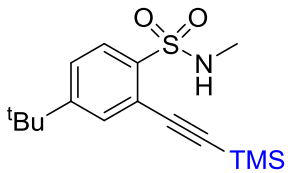
3h

4-Methoxy-*N*-methyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide (3h) was prepared as a brown oil from 2-iodo-4-methoxy-*N*-methylbenzenesulfonamide (1.64 g, 5 mmol) and ethynyltrimethylsilane according to the General Procedure B (eluent: petroleum ether / ethyl acetate: 5:1) in 85% yield (1.26 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.9 Hz, 1H), 7.08 (d, *J* = 2.7 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.7 Hz, 1H), 5.09 (q, *J* = 5.5 Hz, 1H), 3.83 (s, 3H), 2.55 (d, *J* = 5.5 Hz, 3H), 0.27 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 131.6, 131.6, 121.6, 119.5, 114.1, 103.2, 101.0, 55.7, 29.4, -0.6.

HRMS (ESI–TOF) *m*/*z* [M + Na]$^{+}$: calcd. for $[C_{13}H_{19}NNaO_3SSi]^{+}$ 320.0747, found 320.0742.



3i

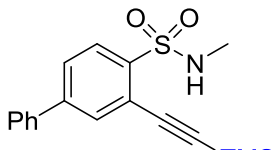
4-(*tert*-Butyl)-*N*-methyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide (3i) was prepared as a yellow solid from 4-(tert-butyl)-2-iodo-*N*-methylbenzenesulfonamide (1.77 g, 5 mmol) and ethynyltrimethylsilane according to the General Procedure B (eluent: petroleum ether / ethyl acetate: 5:1) in 85% yield (1.37 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H),

7.46 (dd, *J* = 8.4, 2.0 Hz, 1H), 5.20 (q, *J* = 5.5 Hz, 1H), 2.59 (d, *J* = 5.4 Hz, 3H), 1.32 (s, 9H), 0.29 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 137.0, 131.6, 129.4, 126.0, 119.6, 102.6, 101.8, 35.0, 30.9, 29.4, -0.4.

HRMS (ESI–TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{16}H_{25}NNaO_2SSi]^+$ 346.1267, found 346.1263.



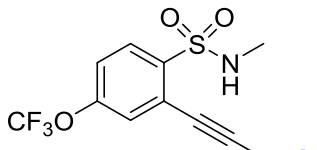
3j

***N*-Methyl-3-((trimethylsilyl)ethynyl)-[1,1'-biphenyl]-4-sulfonamide (3j)** was prepared as a brown solid from 3-iodo-*N*-methyl-[1,1'-biphenyl]-4-sulfonamide (1.87 g, 5 mmol) and ethynyltrimethylsilane according to the General Procedure B (eluent: petroleum ether / ethyl acetate: 5:1) in 90% yield (1.54 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 1.9 Hz, 1H), 7.66 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.61 – 7.59 (m, 2H), 7.50 – 7.42 (m, 3H), 5.25 (q, *J* = 5.4 Hz, 1H), 2.65 (d, *J* = 5.5 Hz, 3H), 0.32 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 138.4, 138.3, 133.0, 130.1, 129.0, 128.7, 127.2, 127.2, 120.5, 103.6, 101.3, 29.5, -0.5.

HRMS (ESI–TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{18}H_{22}NO_2SSi]^+$ 344.1135, found 344.1136.



3k

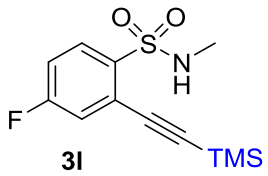
***N*-Methyl-4-(trifluoromethoxy)-2-((trimethylsilyl)ethynyl)benzenesulfonamide (3k)** was prepared as a red oil from

2-iodo-*N*-methyl-4-(trifluoromethoxy)benzenesulfonamide (1.91 g, 5 mmol) and ethynyltrimethylsilane according to the General Procedure B (eluent: petroleum ether / ethyl acetate: 5:1) in 65% yield (1.14 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.8 Hz, 1H), 7.45 (dt, *J* = 1.9, 1.0 Hz, 1H), 7.29 (ddd, *J* = 8.7, 2.5, 1.1 Hz, 1H), 5.16 (q, *J* = 5.4 Hz, 1H), 2.63 (d, *J* = 5.4 Hz, 3H), 0.30 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 138.5, 131.6, 126.0, 122.5, 120.6, 120.1 (q, $J_{C\text{-}F}$ = 260.8 Hz), 105.77, 99.70, 29.43, -0.6.

HRMS (ESI–TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{13}H_{17}F_3NO_3SSi]^+$ 352.0645, found 352.0638.



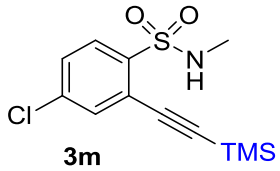
3l

4-Fluoro-*N*-methyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide (3l) was prepared as a red oil from 4-fluoro-2-iodo-*N*-methylbenzenesulfonamide (1.58 g, 5 mmol) and ethynyltrimethylsilane according to the General Procedure B (eluent: petroleum ether / ethyl acetate: 5:1) in 60% yield (0.86 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.8, 5.5 Hz, 1H), 7.32 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.18 – 7.13 (m, 1H), 5.13 (d, *J* = 5.4 Hz, 1H), 2.61 (d, *J* = 5.4 Hz, 3H), 0.30 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2 (d, $J_{C\text{-}F}$ = 256.3 Hz), 136.4, 132.2 (d, $J_{C\text{-}F}$ = 9.1 Hz), 122.8 (d, $J_{C\text{-}F}$ = 10.1 Hz), 121.5 (d, $J_{C\text{-}F}$ = 24.2 Hz), 116.2, 116.0, 105.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 29.4, -0.6.

HRMS (ESI–TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{12}H_{17}FNO_2SSi]^+$ 286.0728, found 286.0723.



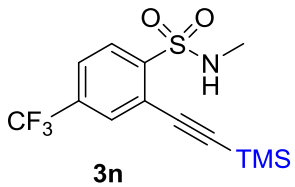
3m

4-Chloro-*N*-methyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide (3m) was prepared as a yellow oil from 4-chloro-2-iodo-*N*-methylbenzenesulfonamide (1.65 g, 5 mmol) and ethynyltrimethylsilane according to the General Procedure B (eluent: petroleum ether / ethyl acetate: 5:1) in 70% yield (1.05 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 1H), 7.60 (d, *J* = 2.1 Hz, 1H), 7.42 (dd, *J* = 8.5, 2.1 Hz, 1H), 5.14 (q, *J* = 5.4 Hz, 1H), 2.60 (d, *J* = 5.4 Hz, 3H), 0.29 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 138.4, 134.1, 130.8, 128.9, 121.8, 105.3, 99.8, 29.4, -0.6.

HRMS (ESI–TOF) *m*/*z* [M + H]$^{+}$: calcd. for $[C_{12}H_{17}ClNO_2SSi]^{+}$ 302.0432, found 302.0424.



3n

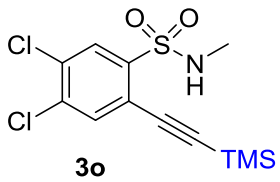
***N*-Methyl-4-(trifluoromethyl)-2-((trimethylsilyl)ethynyl)benzenesulfonamide (3n)** was prepared as a red solid from 2-iodo-*N*-methyl-4-(trifluoromethyl)benzenesulfonamide (1.83 g, 5 mmol) and ethynyltrimethylsilane according to the General Procedure B (eluent: petroleum ether / ethyl acetate: 5:1) in 68% yield (1.14 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.13 (m, 1H), 7.87 (d, *J* = 1.8 Hz, 1H), 7.70 (ddd, *J* = 8.2, 1.9, 0.8 Hz, 1H), 5.22 (q, *J* = 5.3 Hz, 1H), 2.63 (d, *J* = 5.4 Hz, 3H), 0.30 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 134.1 (q, $J_{C\text{-}F}$ = 33.5 Hz), 131.3 (q, $J_{C\text{-}F}$ = 3.7

Hz), 130.0, 125.3 (q, J_{C-F} = 3.6 Hz), 122.7 (q, J_{C-F} = 274.1 Hz), 121.2, 106.0, 99.8, 29.3, -0.7.

HRMS (ESI–TOF) *m*/*z* [M + H]$^+$: calcd. for [$C_{13}H_{17}F_3NO_2SSi$]$^+$ 336.0696, found 336.0690.



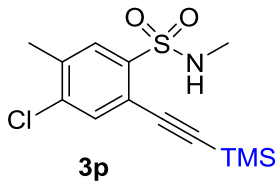
3o

4,5-Dichloro-*N*-methyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide (3o) was prepared as a yellow oil from 4,5-dichloro-2-iodo-*N*-methylbenzenesulfonamide (1.82 g, 5 mmol) and ethynyltrimethylsilane according to the General Procedure B (eluent: petroleum ether / ethyl acetate: 5:1) in 65% yield (1.09g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.68 (s, 1H), 5.14 (q, *J* = 5.3 Hz, 1H), 2.62 (d, *J* = 5.4 Hz, 3H), 0.27 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 136.7, 135.6, 133.3, 131.1, 119.6, 106.0, 98.9, 29.4, -0.7.

HRMS (ESI–TOF) *m*/*z* [M + H]$^+$: calcd. for [$C_{12}H_{17}Cl_2NO_2SSi$]$^+$ 336.0043, found 336.0041.



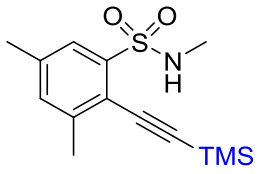
3p

4-chloro-*N*,5-dimethyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide (3p) was prepared as a white solid from 4-chloro-2-iodo-*N*,5-dimethylbenzenesulfonamide (1.73 g, 5 mmol) and ethynyltrimethylsilane according to the General Procedure B (eluent: petroleum ether / ethyl acetate: 5:1) in 63% yield (0.99g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 0.8 Hz, 1H), 7.60 (s, 1H), 5.17 – 5.13 (q, *J* = 5.4 Hz, 1H), 2.60 (d, *J* = 5.5 Hz, 3H), 2.43 (s, 3H), 0.28 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 138.1, 137.7, 134.5, 131.6, 118.8, 104.0, 100.0, 29.4, 20.1, -0.5.

HRMS (ESI–TOF) *m*/*z* [M + H]$^{+}$: calcd. for $[C_{13}H_{19}ClNO_2SSi]^{+}$ 316.0589, found 316.0582.



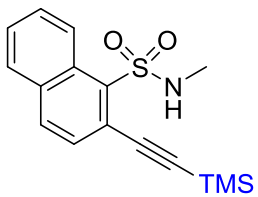
3q

***N*,3,5-Trimethyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide (3q)** was prepared as a white solid from 2-iodo-*N*,3,5-trimethylbenzenesulfonamide (1.63 g, 5 mmol) and ethynyltrimethylsilane according to the General Procedure B (eluent: petroleum ether / ethyl acetate: 5:1) in 60% yield (0.89g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.68 (m, 1H), 7.23 (d, *J* = 1.8 Hz, 1H), 5.34 (q, *J* = 5.5 Hz, 1H), 2.59 (d, *J* = 5.5 Hz, 3H), 2.45 (s, 3H), 2.37 (s, 3H), 0.29 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 139.8, 138.9, 134.2, 127.7, 116.4, 107.4, 100.3, 29.5, 21.4, 20.9, -0.3.

HRMS (ESI–TOF) *m*/*z* [M + H]$^{+}$: calcd. for $[C_{14}H_{22}NO_2SSi]^{+}$ 296.1135, found 296.1125.



3r

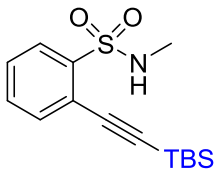
N-methyl-2-((trimethylsilyl)ethynyl)naphthalene-1-sulfonamide **(3r)** was prepared as a yellow oil from 2-iodo-*N*-methylnaphthalene-1-sulfonamide (1.74 g, 5 mmol) and ethynyltrimethylsilane according to the General

Procedure B (eluent: petroleum ether / ethyl acetate: 5:1) in 50% yield (0.79g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, *J* = 8.9 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.67 – 7.57 (m, 3H), 5.90 (q, *J* = 5.5 Hz, 1H), 2.75 (d, *J* = 5.3 Hz, 3H), 0.33 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 133.8, 132.4, 130.3, 130.1, 128.6, 128.5, 127.5, 126.0, 119.8, 105.4, 103.6, 29.7, -0.5.

HRMS (ESI–TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{16}H_{20}NO_2SSi]^+$ 318.0979, found 318.0971.



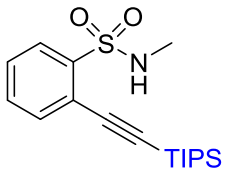
3s

2-((*tert*-Butyldimethylsilyl)ethynyl)-*N*-methylbenzenesulfonamide (3s) was prepared as a brown oil from 2-bromo-*N*-methylbenzenesulfonamide (1.25 g, 5 mmol) and tert-butyl(ethynyl)dimethylsilane according to the General Procedure B (eluent: petroleum ether / ethyl acetate: 5:1) in 80% yield (1.24 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.65 – 7.63 (m, 1H), 7.54 – 7.44 (m, 2H), 5.27 (q, *J* = 5.4 Hz, 1H), 2.58 (d, *J* = 5.5 Hz, 3H), 1.00 (s, 9H), 0.23 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 134.7, 132.1, 129.4, 128.8, 120.2, 102.3, 101.9, 29.3, 26.0, 16.7, -4.9.

HRMS (ESI–TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{15}H_{24}NO_2SSi]^+$ 310.1292, found 310.1288.



3t

***N*-Methyl-2-((triisopropylsilyl)ethynyl)benzenesulfonamide (3t)** was prepared as a white solid from 2-bromo-*N*-methylbenzenesulfonamide (1.25 g, 5 mmol) and ethynyltriisopropylsilane according to the General Procedure B (eluent: petroleum ether / ethyl acetate: 5:1) in 85% yield (1.49 g).

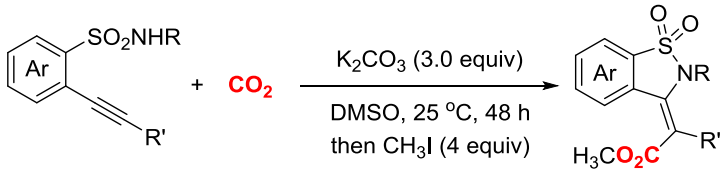
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.66 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.54 – 7.45 (m, 2H), 5.37 (d, *J* = 5.8 Hz, 1H), 2.59 (d, *J* = 5.5 Hz, 3H), 1.28 – 1.09 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 135.1, 132.1, 129.4, 128.7, 120.4, 103.1, 100.8, 29.3, 18.6, 11.3.

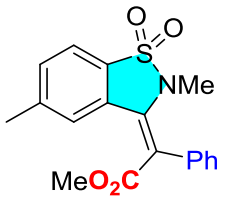
HRMS (ESI–TOF) *m*/*z* [M + H]$^{+}$: calcd. for $[C_{18}H_{30}NO_2SSi]^{+}$ 352.1761, found 352.1763.

IV. Synthesis of Mono-Carboxylic Esters

General Procedure C



Under air, to an over-dried 20 mL Schlenk tube equipped with a Teflon cap was added o-(1-alkynyl)benzene sulfonamides (0.2 mmol), K_2CO_3 (0.6 mmol, 3 equiv, 82.8 mg) and DMSO (2.0 mL). The reaction vessel was evacuated to about -0.1 MPa (last 30 seconds per time) and backfilled with CO_2 (1 atm) in three times. Then, the Schlenk tube was stirred at 25 °C for 48 h. After that, MeI (0.8 mmol, 4 equiv, 52 μL) was added into the reaction mixture, and the reaction mixture was stirred at 50 °C for about 1 h, then, the reaction mixture was terminated by saturated brine and extracted with ethyl acetate (EA) for at least 6 times (2 mL × 6). Subsequently, the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography to give the desired product.



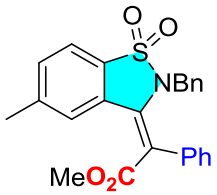
2a

Methyl (*E*)-2-(2,5-dimethyl-1,1-dioxidobenzo[d]isothiazol-3(2*H*)-ylidene)-2-phenylacetate (2a) was prepared as a brown oil from N,4-dimethyl-2-(phenylethynyl)benzenesulfonamide (57.0 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 75% yield with the ratio of Z/*E* configuration in 1:5 (51.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 0.2H), 7.47 (s, 1H), 7.45 – 7.40 (m, 2H), 7.39 (s, 1H), 7.37 – 7.34 (m, 3H), 3.87 (s, 3H), 2.68 (s, 0.6H), 2.66 (s, 3H), 2.48 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 144.1, 137.5, 134.8, 131.9, 130.3, 129.8, 128.7, 128.5, 127.8, 124.7, 121.2, 113.3, 53.0, 31.8, 22.2.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{18}H_{17}NNaO_4S]^+$ 366.0770, found 366.0777.



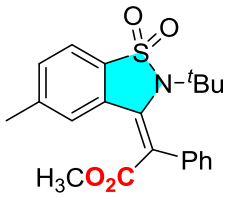
2b

Methyl (*E*)-2-(2-benzyl-5-methyl-1,1-dioxidobenzo[d]isothiazol-3(2*H*)-ylidene)-2-phenylacetate (2b) was prepared as a brown oil from N-benzyl-4-methyl-2-(phenylethynyl)benzenesulfonamide (72.2 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 53% yield with the ratio of Z/*E* configuration in 1:10 (44.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 0.1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.40 (s, 1H), 7.35 – 7.28 (m, 3.7H), 7.24 – 7.20 (m, 0.3H), 7.20 – 7.09 (m, 5H), 6.93 – 6.90 (m, 0.2H), 6.75 – 6.74 (m, 2H), 5.18 (s, 0.2H), 4.43 (s, 2H), 3.78 (s, 3H), 3.54 (s, 0.3H), 2.46 (s, 3H), 2.02 (s, 0.3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 144.0, 143.5, 134.6, 134.1, 133.9, 131.7, 131.5, 131.2, 130.4, 129.8, 129.1, 128.7, 128.4, 127.9 (2C), 127.3, 127.0, 124.3, 121.2, 121.0, 116.4, 52.8, 52.1, 47.9, 46.7, 22.2, 21.7.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{24}H_{21}NNaO_4S]^+$ 442.1083, found 442.1086.



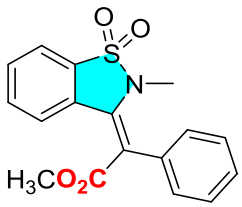
2c

Methyl (*E*)-2-(2-(*tert*-butyl)-5-methyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)-2-phenylacetate (2c) was prepared as a brown oil from N-(tert-butyl)-4-methyl-2-(phenylethynyl)benzenesulfonamide (65.4 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 38% yield with the ratio of Z/*E* configuration in 1:19 (29.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.71 (s, 1H), 7.66 – 7.64 (m, 2H), 7.42 – 7.35 (m, 4H), 3.78 (s, 0.16H), 3.47 (s, 3H), 2.46 – 2.45 (m, 3.16H), 1.14 (s, 9H), 1.07 (s, 0.5 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 143.1, 142.8, 139.0, 133.7, 130.1, 129.9, 129.6, 128.6, 128.1, 126.6, 124.4, 122.6, 65.5, 52.6, 30.8, 21.9.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{21}H_{23}NNaO_4S]^+$ 408.1240, found 408.1244.



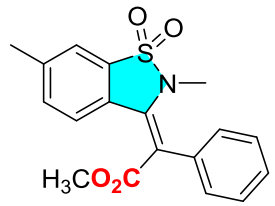
2f

Methyl (*E*)-2-(2-methyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)-2-phenylacetate (2f) was prepared as a brown oil from *N*-methyl-2-(phenylethynyl)benzenesulfonamide (54.2 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 52% yield (34.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 1H), 7.75 – 7.71 (m, 1H), 7.67 – 7.61 (m, 2H), 7.43 – 7.34 (m, 5H), 3.87 (s, 3H), 2.67 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 137.1, 134.6, 133.1, 132.3, 130.9, 129.9, 129.7, 128.6, 128.5, 124.3, 121.3, 113.8, 52.9, 31.7.

HRMS (ESI-TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{17}H_{16}NO_4S]^+$ 330.0795, found 330.0787.



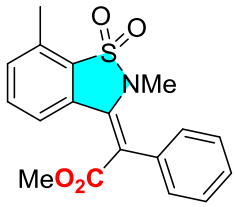
2g

Methyl (*E*)-2-(2,6-dimethyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)-2-phenylacetate (2g) was prepared as a brown oil from N,5-dimethyl-2-(phenylethynyl)benzenesulfonamide (57.0 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 66% yield with the ratio of *Z*/*E* configuration in 1:2.8 (45.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.78 (m, 0.35H), 7.66 (s, 1H), 7.62 – 7.58 (m, 1.7H), 7.48 – 7.34 (m, 8H), 3.85 (s, 3H), 3.53 (s, 1.06H), 2.91 (s, 1.06H), 2.66 (s, 3H), 2.49 (s, 3H), 2.39 (s, 1.06H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 166.6, 146.2, 142.2, 137.7, 136.6, 134.9, 134.8, 134.3(2C), 132.5, 132.1, 130.3, 130.1, 129.8, 128.6, 128.4, 128.2, 127.9, 127.4, 124.3, 121.3, 119.7, 115.4, 112.8, 52.9, 52.1, 33.2, 31.8, 21.4, 20.3.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{18}H_{17}NNaO_4S]^+$ 366.0770, found 366.0774.



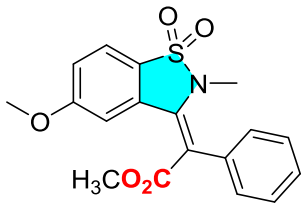
2h

Methyl (*E*)-2-(2,7-dimethyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)-2-phenylacetate (2h) was prepared as colorless oil from *N*,2-dimethyl-6-(phenylethynyl)benzenesulfonamide (57.0 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 17% yield with the ratio of *Z*/*E* configuration in 1:3.3 (11.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.67 (brs, 0.3H), 7.60 (t, *J* = 7.6 Hz, 0.6H), 7.48 – 7.39 (m, 6H), 7.37 – 7.35 (m, 3H), 3.87 (s, 3H), 3.86 (s, 0.9H), 2.66 (s, 3.9H), 2.50 (s, 0.9H), 2.48 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 144.1, 142.3, 137.5, 134.9, 134.3, 132.0, 130.4, 129.9, 129.8, 128.7 (2C), 128.6, 127.9, 124.7, 124.4, 121.4, 121.2, 119.9, 113.3, 53.0, 31.8 (2C), 22.2, 21.4.

HRMS (ESI-TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{18}H_{18}NO_4S]^+$ 344.0951, found 344.0947.



2i

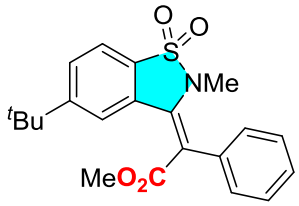
Methyl (*E*)-2-(5-methoxy-2-methyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)-2-phenylacetate (2i) was prepared as a brown oil from 4-methoxy-*N*-methyl-2-(phenylethynyl)benzenesulfonamide (60.2 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 71%

yield (51.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.6 Hz, 1H), 7.40 – 7.35 (m, 5H), 7.19 (d, *J* = 2.1 Hz, 1H), 7.13 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 2.65 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 163.4, 137.2, 134.8, 132.2, 129.7, 128.7, 128.5, 124.7, 122.8, 117.6, 113.6, 108.9, 55.8, 53.0, 31.9.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{18}H_{17}NNaO_5S]^+$ 382.0720, found 382.0724.



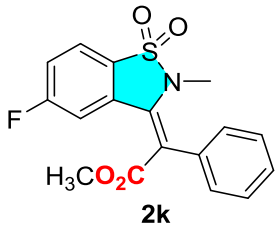
2j

Methyl (E)-2-(5-(*tert*-butyl)-2-methyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)-2-phenylacetate (2j) was prepared as colorless oil from 4-(*tert*-butyl)-*N*-methyl-2-(phenylethynyl)benzenesulfonamide (65.4 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 65% yield (50.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.78 (m, 2H), 7.67 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.43 – 7.36 (m, 5H), 3.89 (s, 3H), 2.66 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 157.2, 137.4, 134.8, 130.1, 129.8, 129.7, 128.7 (2C), 128.5, 121.1, 121.0, 113.2, 53.0, 35.6, 31.9, 31.1.

HRMS (ESI-TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{21}H_{24}NO_4S]^+$ 386.1421, found 386.1418.



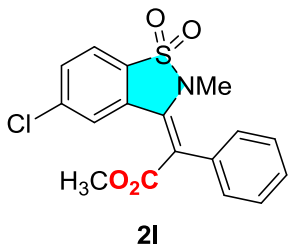
2k

Methyl (*E*)-2-(5-methoxy-2-methyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)-2-phenylacetate (2k) was prepared as a brown oil from 4-fluoro-N-methyl-2-(phenylethynyl)benzenesulfonamide (57.8 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 72% yield (50.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.6, 5.0 Hz, 1H), 7.44 – 7.38 (m, 4H), 7.37 – 7.31 (m, 3H), 3.88 (s, 3H), 2.66 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 165.2 ($J_{C\text{-}F}$ = 254.7 Hz), 136.3 ($J_{C\text{-}F}$ = 3.1 Hz), 134.4, 132.9 ($J_{C\text{-}F}$ = 10.2 Hz), 129.7, 128.8, 128.7, 128.5 ($J_{C\text{-}F}$ = 2.8 Hz), 123.5 ($J_{C\text{-}F}$ = 10.1 Hz), 118.8 (q, $J_{C\text{-}F}$ = 24.6 Hz), 115.1, 111.8 ($J_{C\text{-}F}$ = 27.0 Hz), 53.2, 32.0.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{17}H_{14}FNNaO_4S]^+$ 370.0520, found 370.0520.



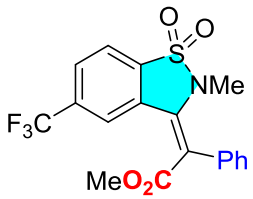
2l

Methyl (*E*)-2-(5-chloro-2-methyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)-2-phenylacetate (2l) was prepared as a brown oil from 4-chloro-N-methyl-2-(phenylethynyl)benzenesulfonamide (61.0 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 77% yield (56.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 1H), 7.69 – 7.68 (m, 1H), 7.59 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.44 – 7.34 (m, 5H), 3.88 (s, 3H), 2.66 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 139.8, 136.0, 134.3, 131.8, 131.1, 130.8, 129.7, 128.8, 128.7, 124.7, 122.5, 115.0, 53.2, 32.0.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{17}H_{14}ClNNaO_4S]^+$ 386.0224, found 386.0232.



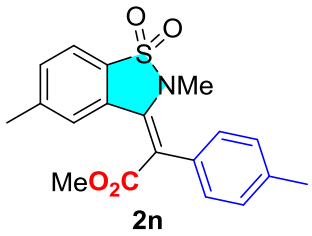
2m

Methyl (*E*)-2-(2-methyl-1,1-dioxido-5-(trifluoromethyl)benzo[d]isothiazol-3(2H)-ylidene)-2-phenylacetate (2m) was prepared as a brown oil from N-methyl-2-(phenylethynyl)-4-(trifluoromethyl)benzenesulfonamide (67.8 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) g in 85% yield with the ratio of Z/*E* configuration in 1:13.6 (67.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 0.1H), 8.07 – 8.05 (m, 0.1H), 8.02 – 8.00 (m, 1H), 7.98 (s, 1H), 7.89 – 7.86 (m, 1H), 7.82 – 7.79 (m, 0.1H), 7.56 – 7.46 (m, 0.46H), 7.46 – 7.36 (m, 5H), 3.88 (s, 3H), 3.40 (s, 0.24H), 3.05 (s, 0.24H), 2.69 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 167.1, 135.7, 135.4 ($J_{C\text{-}F}$ = 1.7 Hz), 135.3, 135.0, 134.1, 131.0, 129.7, 129.0, 128.9, 128.8, 127.7 ($J_{C\text{-}F}$ = 3.6 Hz), 122.9 ($J_{C\text{-}F}$ = 274.6 Hz), 122.8, 122.3, 121.8 (q, $J_{C\text{-}F}$ = 4.2 Hz), 115.7, 53.1, 52.2, 35.1, 32.0.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{18}H_{14}F_3NNaO_4S]^+$ 420.0488, found 420.0491.



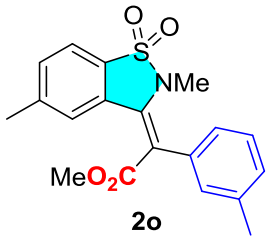
2n

Methyl (*E*)-2-(2,5-dimethyl-1,1-dioxidobenzo[d]isothiazol-3(2*H*)-ylidene)-2-(*p*-tolyl) acetate (2n) was prepared as a brown oil from *N*,4-dimethyl-2-(*p*-tolylethynyl)benzenesulfonamide (59.8 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 72% yield (51.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.43(m, 2H), 7.28 – 7.22 (m, 4H, overlapped with $CDCl_3$), 3.89 (s, 3H), 2.71 (s, 3H), 2.49 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 144.0, 138.6, 137.0, 131.8, 130.4, 129.8, 129.6 (2C), 129.4, 124.5, 121.1, 113.5, 52.9, 31.8, 22.1, 21.3.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{19}H_{19}NNaO_4S]^+$ 380.0927, found 380.0924.



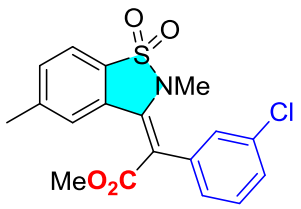
2o

Methyl (*E*)-2-(2,5-dimethyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)-2-(m-tolyl) acetate (2o) was prepared as a brown oil from *N*,4-dimethyl-2-(*m*-tolylethynyl)benzenesulfonamidee (59.8 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 69% yield (51.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.28 – 7.23 (m, 1H), 7.14 – 7.13 (m, 3H), 3.84 (s, 3H), 2.64 (s, 3H), 2.44 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 144.0, 138.4, 136.9, 134.6, 131.8, 130.3, 130.2, 129.8, 129.3, 128.5, 126.9, 124.5, 121.1, 113.4, 52.9, 31.6, 22.1, 21.4.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{19}H_{19}NNaO_4S]^+$ 380.0927, found 380.0935.



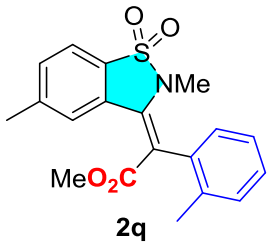
2p

Methyl (*E*)-2-(3-chlorophenyl)-2-(2,5-dimethyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)acetate (2p) was prepared as a brown oil from 2-((3-chlorophenyl)ethynyl)-N,4-dimethylbenzenesulfonamide (63.8 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 38% yield (28.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.41 – 7.37 (m, 1H), 7.34 – 7.30 (m, 2H), 7.24 – 7.21 (m, 1H), 3.79 (s, 3H), 3.24 (s, 3H), 2.11 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 143.8, 139.4, 138.0, 135.2, 132.0, 130.8, 130.6, 130.3, 130.0, 129.1, 129.0, 127.0, 121.2, 109.8, 52.7, 30.6, 22.0.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{18}H_{16}ClNNaO_4S]^+$ 400.0381, found 400.0386.



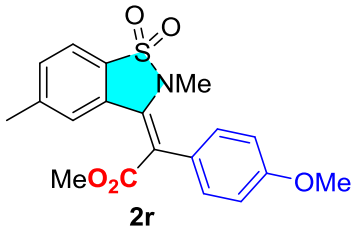
2q

Methyl (*E*)-2-(2,5-dimethyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)-2-(o-tolyl) acetate (2q) was prepared as a brown oil from N,4-dimethyl-2-(o-tolylethynyl)benzenesulfonamide (59.8 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 67% yield (47.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.58 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.21 (m, 4H), 3.82 (s, 3H), 2.50 (s, 3H), 2.48 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 144.0, 138.0, 137.7, 134.4, 131.9, 130.6, 130.3, 129.8, 129.7, 128.9, 126.0, 125.1, 121.1, 111.9, 52.8, 30.1, 22.2, 19.8.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{19}H_{19}NNaO_4S]^+$ 380.0927, found 380.0929.



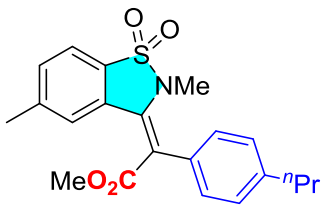
2r

Methyl (*E*)-2-(2,5-dimethyl-1,1-dioxidobenzo[d]isothiazol-3(2*H*)-ylidene)-2-(4-methoxyphenyl)acetate (2r) was prepared as a brown oil from 2-((4-methoxyphenyl)ethynyl)-N,4-dimethylbenzenesulfonamide (63.02 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 53% yield (39.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9, Hz, 1H), 7.44 – 7.41 (m, 2H), 7.30-7.27 (m, 2H), 6.94-6.92 (m, 2H), 3.87 (s, 3H), 3.84 (s, 3H), 2.70 (s, 3H), 2.47 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 159.6, 144.0, 136.9, 131.7, 131.0, 130.5, 129.9, 126.8, 124.5, 121.1, 114.1, 113.4, 55.3, 52.9, 31.8, 22.2.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{19}H_{19}NNaO_5S]^+$ 396.0876, found 396.0884.



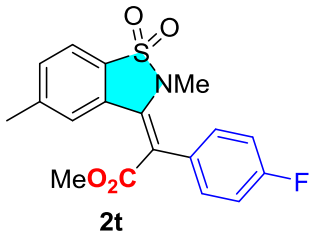
2s

Methyl (*E*)-2-(2,5-dimethyl-1,1-dioxidobenzo[*d*]isothiazol-3(2*H*)-ylidene)-2-(4-propylphenyl)acetate (2s) was prepared as a brown oil from *N*,4-dimethyl-2-((4-propylphenyl)ethynyl)benzenesulfonamide (65.4 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 66% yield with the ratio of Z/*E* configuration in 1:15 (50.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 0.07H), 7.45 – 7.41 (m, 2H), 7.28 – 7.26 (m, 2H), 7.22 – 7.20 (m, 2H), 3.87 (s, 3H), 3.79 (s, 0.2H), 3.25 (s, 0.2H), 2.68 (s, 3H), 2.65 – 2.59 (m, 2H), 2.47 (s, 3H), 1.69 – 1.64 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 144.0, 143.3, 137.0, 131.9, 131.7, 131.4, 130.4 (2C), 129.8, 129.6, 129.5, 128.7, 127.1, 124.5, 121.1, 120.8, 113.6, 52.9, 37.7, 31.6, 24.2, 22.1, 13.8.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{21}H_{23}NNaO_4S]^+$ 408.1240, found 408.1241.



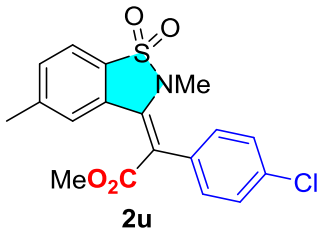
2t

Methyl (*E*)-2-(2,5-dimethyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)-2-(4-fluoro phenyl)acetate (2t) was prepared as a brown oil from A name could not be generated for this structure. (60.6 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 65% yield with the ratio of *Z*/*E* configuration in 1:10 (45.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 0.1H), 7.46 – 7.43 (m, 2H), 7.36 – 7.29 (m, 2.2H), 7.18 – 7.13 (m, 0.2H), 7.13 – 7.08 (m, 2H), 3.86 (s, 3H), 3.78 (s, 0.3H), 3.23 (s, 0.3H), 2.67 (s, 3H), 2.47 (s, 3H), 2.11 (s, 0.3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 162.5 ($J_{C\text{-}F}$=250.6 Hz), 144.1, 138.0, 132.1, 131.6 ($J_{C\text{-}F}$= 8.3 Hz), 130.8 ($J_{C\text{-}F}$= 3.6 Hz), 130.2, 129.9, 124.7, 121.2, 115.9 ($J_{C\text{-}F}$= 21.8 Hz), 112.2, 53.0, 31.9, 22.2.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{18}H_{16}FNNaO_4S]^+$ 384.0676, found 384.0681.



2u

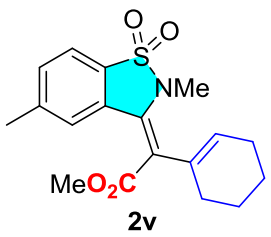
Methyl (*E*)-2-(4-chlorophenyl)-2-(2,5-dimethyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)acetate (2u) was prepared as a brown oil from 2-((4-chlorophenyl)ethynyl)-N,4-dimethylbenzenesulfonamide. (63.8 mg, 0.2

mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 53% yield with the ratio of *Z*/*E* configuration in 1:6.6 (40.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 0.15H), 7.47 – 7.43 (m, 2H), 7.40 – 7.37 (m, 2.15H), 7.31 – 7.27 (m, 2.45H), 7.00 (s, 0.15H), 6.00 (s, 0.15H), 3.87 (s, 3H), 3.18 (s, 0.45H), 2.69 (s, 3H), 2.48 (s, 3H), 2.23 (s, 0.45H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 144.2, 143.4, 138.4, 134.5, 133.9, 133.6, 133.4, 132.2, 131.2, 131.1, 130.9, 130.2, 130.0, 129.0 (2C), 124.9, 124.8, 121.2, 121.0, 111.9, 104.8, 53.0, 32.1, 29.7, 26.3, 22.2, 22.0.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{18}H_{16}ClNNaO_4S]^+$ 400.0381, found 400.0385.



2v

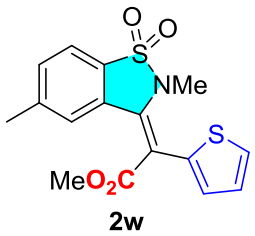
Methyl (*E*)-2-(cyclohex-1-en-1-yl)-2-(2,5-dimethyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)acetate (2v) was prepared as a brown oil from 2-(cyclohex-2-en-1-ylethynyl)-N,4-dimethylbenzenesulfonamide (57.8 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 74% yield with the ratio of *Z*/*E* configuration in 1:1 (51.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.38 (s, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.28 – 6.25 (m, 1H), 6.01 – 5.99 (m, 1H), 3.73(s, 3H), 3.16(s, 3H), 2.80 (s, 6H), 2.43 (s, 3H), 2.35 (s, 3H), 2.29 – 2.26 (m, 2H), 2.24 – 2.20 (m, 2H), 2.17 – 2.10 (m, 4H), 1.74 – 1.70 (m, 2H), 1.67 – 1.58 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 148.2, 142.7, 142.6, 136.5, 135.3, 134.5,

134.3, 133.1, 130.3, 130.1, 128.5, 128.2, 127.8, 125.6, 122.5, 121.6, 120.6, 113.2, 97.8, 84.6, 52.0, 37.7, 32.9, 28.6, 27.1, 25.7, 25.5, 22.3, 22.1, 21.9, 21.6, 21.3, 21.0.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for [$C_{18}H_{21}NNaO_4S$]$^+$ 370.1083, found 370.1086.



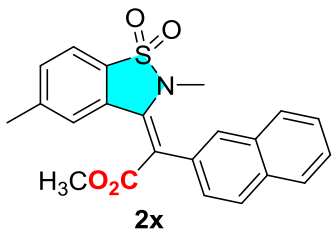
2w

Methyl (*Z*)-2-(2,5-dimethyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)-2-(thiophen-2-yl)acetate (2w) was prepared as a brown oil from N,4-dimethyl-2-(thiophen-2-ylethynyl)benzenesulfonamide (58.0 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 48% yield with the ratio of Z/*E* configuration > 20:1 (33.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.51 – 7.50 (m, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.12 – 7.10 (m, 1H), 7.02 – 7.00 (m, 1H), 6.19 (s, 1H), 3.80 (s, 3H), 3.25 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 143.9, 141.0, 137.4, 131.9, 130.3, 129.8, 129.7, 128.5, 127.8, 127.2, 120.9, 102.4, 52.6, 30.6, 22.0.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for [$C_{16}H_{15}NNaO_4S_2$]$^+$ 372.0335, found 372.0335.



2x

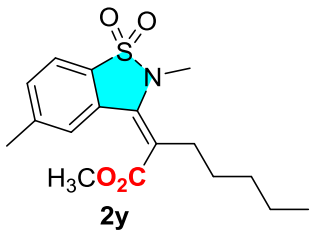
Methyl

(*E*)-2-(2,5-dimethyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)-2-(naphthalen-2-yl)acetate (**2x**) was prepared as a yellow solid from N,4-dimethyl-2-(naphthalen-2-ylethynyl)benzenesulfonamide (67.0 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 64% yield with the ratio of *Z*/*E* configuration in 1:12 (50.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 3.4H), 7.82 – 7.81 (m, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 0.1H), 7.54 – 7.51 (m, 3.2H), 7.48 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.46 – 7.44 (m, 1H), 7.10 (m, 0.1H), 3.90 (s, 3H), 3.24 (s, 0.25H), 2.67 (s, 3H), 2.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 144.1, 143.2, 137.8, 132.9, 132.8, 132.2, 132.0, 130.9, 130.3, 130.0, 129.9, 129.1, 128.4, 128.3 (2C), 128.2, 127.7 (2C), 127.5, 127.0, 126.9, 126.8, 126.5, 126.2, 125.0, 124.7, 121.2, 120.9, 113.2, 53.0, 32.0, 26.3, 22.2, 21.8.

HRMS (ESI-TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{22}H_{20}NO_4S]^+$ 394.1108, found 394.1107.



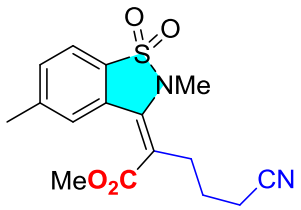
2y

Methyl (*E*)-2-(2,5-dimethyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)heptanoate (**2y**) was prepared as a brown oil from 2-(hept-1-yn-1-yl)-N,4-dimethylbenzenesulfonamide (55.8 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 30% yield (20.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 1H), 7.28 – 7.27(m, 2H), 3.90 (s, 3H), 3.28 (s, 3H), 2.60 – 2.56 (m, 2H), 2.42 (s, 3H), 1.71 – 1.65 (m, 2H), 1.40 – 1.33 (m, 4H), 0.91 – 0.90 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 146.0, 142.6, 130.4, 128.6, 128.3, 125.7, 121.6, 115.2, 52.3, 31.6, 31.4, 31.3, 27.6, 22.2, 21.9, 13.9.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{17}H_{23}NNaO_4S]^+$ 360.1240, found 360.1234.



2z

(*E*)-Methyl 5-cyano-2-(2,5-dimethyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)pentanoate (2z) was prepared as a brown oil from 2-(5-cyanopent-1-yn-1-yl)-N,4-dimethylbenzenesulfonamide (55.2 mg, 0.2 mmol) and CO_2 (1 atm) (eluent: dichloromethane / petroleum ether: 1:1) in 45% yield (30.2 mg).

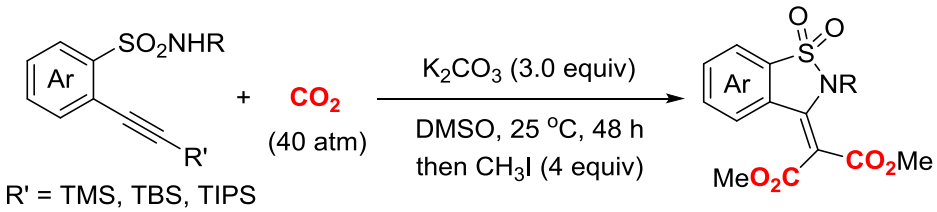
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.34 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.29 (brs, 1H), 3.96 (s, 3H), 3.20 (s, 3H), 2.78 (t, *J* = 7.0 Hz, 2H), 2.50 (t, *J* = 6.7 Hz, 2H), 2.44 (s, 3H), 2.04 (t, *J* = 6.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 143.0, 142.9, 129.8, 129.5, 128.8, 126.2, 122.0, 119.3, 119.1, 53.0, 32.6, 29.3, 23.5, 21.9, 15.8.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{16}H_{18}N_2NaO_4S]^+$ 357.0879, found 357.0882.

V. Synthesis of Gem-Dicarboxylic Esters

General Procedure D



Under air, to an over-dried 20 mL vessel was added *o*-(1-alkynyl)benzene sulfonamide (0.2 mmol), K_2CO_3 (0.6 mmol, 3 equiv, 82.8 mg) and DMSO (2.0 mL). The vessel was fixed into a stainless steel autoclave. Then the autoclave was sealed and CO_2 was introduced from a cylinder. The reaction was carried out at 25 °C under magnetic stirring for 48 h and the pressure was kept constant (40 atm) during the reaction. As the reaction was completed, the vessel was cooled to room temparature and the pressure was released slowly to atmospheric pressure. After that, MeI (0.8 mmol, 4 equiv, 52 μL) was added into the reaction mixture, and the reaction mixture was stirred at room temperature for about 2 h. Then, the reaction mixture was saturated brine and extracted with ethyl acetate (EA) for at least 6 times (2 mL × 6). Subsequently, the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography to give the desired product.

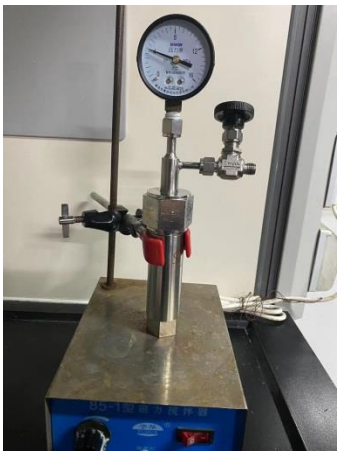
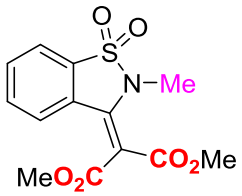


Figure S1 The setup for the synthesis of gem-dicarboxylic esters



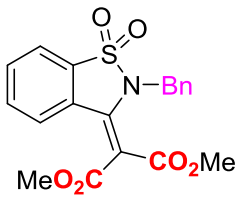
4a

Dimethyl 2-(2-methyl-1,1-dioxidobenzo[d]isothiazol-3(2*H*)-ylidene)malonate (**4a**) was prepared as an oil from *N*-methyl-2-((trimethylsilyl)ethynyl)benzene sulfonamide **3a** (53.4 mg, 0.2 mmol) and CO_2 (4 MPa) according to the General Procedure **D** (eluent: ethyl acetate / petroleum ether: 1:5) in 65% yield (40.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.88(m, 1H), 7.76 – 7.64 (m, 3H), 3.89 (s, 3H), 3.85 (s, 3H), 3.19 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 164.3, 145.3, 133.7, 132.6, 132.1, 128.2, 125.9, 121.7, 101.9, 53.2, 52.8, 30.7.

HRMS (ESI–TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{13}H_{13}NNaO_6S]^+$ 334.0356, found 334.0352.



4b

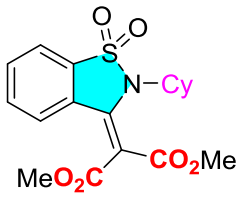
Dimethyl 2-(2-benzyl-1,1-dioxidobenzo[d]isothiazol-3(2*H*)-ylidene)malonate (**4b**) was prepared as an oil from *N*-benzyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide **3b** (68.6 mg, 0.2 mmol) and CO_2 (4 MPa) according to the General Procedure **D** (eluent: ethyl acetate / petroleum ether: 1:5) in 55% yield (42.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.96 (m, 1H), 7.77 – 7.73 (m, 1H), 7.70 –

7.66 (m, 1H), 7.62 – 7.60 (m, 1H), 7.30 – 7.26 (m, 3H), 7.19 – 7.16 (m, 2H), 5.13 (s, 2H), 3.78 (s, 3H), 3.52 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 163.4, 140.7, 133.7, 132.5, 132.4, 131.8, 128.6, 128.4, 128.0, 127.6, 125.5, 121.8, 104.2, 53.2, 52.4, 46.8.

HRMS (ESI–TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{19}H_{18}NO_6S]^+$ 388.0849, found 388.0852.



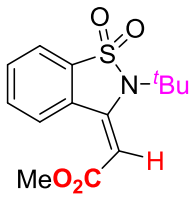
4c

Dimethyl 2-(2-cyclohexyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)malonate (**4c**) was prepared as an oil from N-cyclohexyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide (67.0 mg, 0.2 mmol) and CO_2 (4 MPa) according to the General Procedure **D** (eluent: ethyl acetate / petroleum ether: 1:5) in 40% yield (30.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.70 – 7.59 (m, 3H), 3.86 (s, 6H), 3.80 – 3.75 (m, 1H), 2.18 – 2.15 (m, 4H), 1.89 – 1.85 (m, 2H), 1.66 – 1.62 (m, 1H), 1.22 – 1.13 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 165.1, 144.2, 133.6, 133.2, 132.4, 129.0, 125.5, 120.8, 104.2, 62.5, 53.0, 29.5, 26.6, 25.1.

HRMS (ESI–TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{18}H_{21}NNaO_6S]^+$ 402.0982, found 402.0981.



4d'

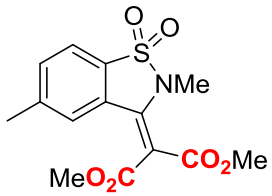
Metyl

(*E*)-2-(2-(tert-butyl)-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)acetate (**4d'**) was prepared as an oil from N-(tert-butyl)-2-((trimethylsilyl)ethynyl)benzenesulfonamide (61.8mg, 0.2 mmol) and CO_2 (4 MPa) according to the General Procedure **D** (eluent: ethyl acetate / petroleum ether: 1:5) in 80% yield (47.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 – 9.01 (m, 1H), 7.78 – 7.74 (m, 1H), 7.68 – 7.61 (m, 2H), 5.82 (s, 1H), 3.79 (s, 3H), 1.83 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 143.4, 133.6, 133.1, 131.7, 128.5, 127.6, 120.1, 98.6, 59.7, 51.8, 28.6.

HRMS (ESI–TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{14}H_{18}NO_4S]^+$ 296.0951, found 296.0952.



4f

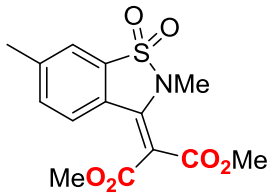
Dimethyl

2-(2,5-dimethyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)malonate (**4f**) was prepared as an oil from N,4-dimethyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide (56.2 mg, 0.2 mmol) and CO_2 (4 MPa) according to the General Procedure **D** (eluent: ethyl acetate / petroleum ether: 1:5) in 64% yield (41.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.9 Hz, 1H), 7.52 – 7.48 (m, 2H), 3.88 (s, 3H), 3.84 (s, 3H), 3.18 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 164.4, 145.6, 144.8, 133.5, 129.5, 128.5, 126.2, 121.4, 101.4, 53.1, 52.8, 30.8, 22.2.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{14}H_{15}NNaO_6S]^+$ 348.0512, found 348.0512.



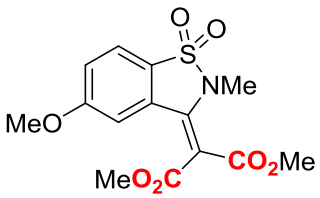
4g

Dimethyl 2-(2,6-dimethyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)malonate (**4g**) was prepared as an oil from N,5-dimethyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide (56.2 mg, 0.2 mmol) and CO_2 (4 MPa) according to the General Procedure **D** (eluent: ethyl acetate / petroleum ether: 1:5) in 62% yield (40.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.68 (m, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.47 – 7.44 (m, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.18 (s, 3H), 2.51 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 164.5, 145.7, 144.2, 134.6, 132.3, 125.8, 125.6, 121.7, 101.2, 53.1, 52.7, 30.7, 21.5.

HRMS (ESI–TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{14}H_{16}NO_6S]^+$ 326.0693, found 326.0691.



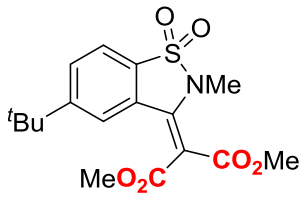
4h

Dimethyl 2-(5-methoxy-2-methyl-1,1-dioxidobenzo[d]isothiazol-3(2*H*)-ylidene)malonate (**4h**) was prepared as an oil from 4-methoxy-N-methyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide (59.4 mg, 0.2 mmol) and CO_2 (4 MPa) according to the General Procedure **D** (eluent: ethyl acetate / petroleum ether: 1:5) in 65% yield (44.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.6 Hz, 1H), 7.23 – 7.17 (m, 2H), 3.88 (s, 3H), 3.87 (s, 3H), 3.84 (s, 3H), 3.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 164.4, 163.7, 145.4, 130.5, 124.2, 123.1, 118.8, 110.9, 101.7, 56.0, 53.2, 52.8, 30.9.

HRMS (ESI–TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{14}H_{16}NO_7S]^+$ 342.0642, found 342.0641.



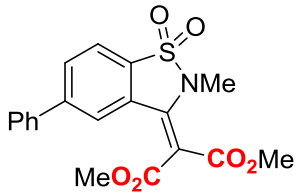
4i

Dimethyl 2-(5-(tert-butyl)-2-methyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)malonate (**4i**) was prepared as an oil from 4-(tert-butyl)-*N*-methyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide (64.6 mg, 0.2 mmol) and CO_2 (4 MPa) according to the General Procedure **D** (eluent: ethyl acetate / petroleum ether: 1:5) in 65% yield (47.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 2H), 7.74 (dd, *J* = 8.2, 1.6 Hz, 1H), 3.90 (s, 3H), 3.84 (s, 3H), 3.18 (s, 3H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 164.3, 157.8, 145.9, 130.3, 129.3, 128.2, 122.8, 121.2, 101.2, 53.1, 52.7, 35.7, 31.0, 30.8.

HRMS (ESI–TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{17}H_{21}NNaO_6S]^+$ 390.0982, found 390.0979.



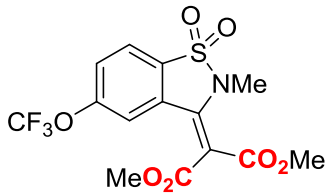
4j

Dimethyl 2-(2-methyl-1,1-dioxido-5-phenylbenzo[d]isothiazol-3(2*H*)-ylidene)malonate (**4j**) was prepared as an oil from *N*-methyl-3-((trimethylsilyl)ethynyl)-[1,1'-biphenyl]-4-sulfonamide (68.6 mg, 0.2 mmol) and CO_2 (4 MPa) according to the General Procedure **D** (eluent: ethyl acetate / petroleum ether: 1:5) in 67% yield (51.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.87 (m, 3H), 7.55 – 7.45 (m, 5H), 3.88 (s, 3H), 3.86 (s, 3H), 3.22 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 164.3, 147.1, 145.2, 138.7, 131.5, 130.5, 129.3, 129.0, 128.9, 127.3, 124.7, 121.9, 101.9, 53.2, 52.8, 30.8.

HRMS (ESI–TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{19}H_{18}NO_6S]^+$ 388.0849, found 388.0848.



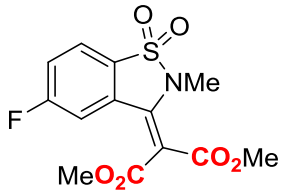
4k

Dimethyl 2-(2-methyl-1,1-dioxido-5-(trifluoromethoxy)benzo[d]isothiazol-3(2*H*)-ylidene)malonate (**4k**) was prepared as an oil from N-methyl-4-(trifluoromethoxy)-2-((trimethylsilyl)ethynyl)benzenesulfonamide (70.2 mg, 0.2 mmol) and CO_2 (4 MPa) according to the General Procedure **D** (eluent: ethyl acetate / petroleum ether: 1:5) in 60% yield (47.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 1H), 7.66 – 7.65 (m, 1H), 7.56 – 7.53 (m, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.20 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 164.1, 152.8, 143.5, 130.8, 130.2, 124.9, 123.5, 120.1 (q, J_{C-F} = 261.5 Hz), 118.3, 103.4, 53.3, 53.0, 30.9.

HRMS (ESI–TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{14}H_{13}F_3NO_7S]^+$ 396.0359, found 396.0359.



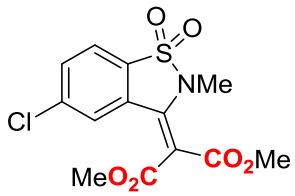
4l

Dimethyl 2-(5-fluoro-2-methyl-1,1-dioxidobenzo[*d*]isothiazol-3(2*H*)-ylidene)malonate (**4l**) was prepared as an oil from 4-fluoro-*N*-methyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide (57.0 mg, 0.2 mmol) and CO_2 (4 MPa) according to the General Procedure **D** (eluent: ethyl acetate / petroleum ether: 1:5) in 65% yield (42.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.6, 4.9 Hz, 1H), 7.50 (dd, *J* = 9.6, 2.2 Hz, 1H), 7.44 – 7.39 (m, 1H), 3.90 (s, 3H), 3.85 (s, 3H), 3.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 165.4 (d, J_{C-F} = 253.8 Hz), 164.1, 143.7 (d, J_{C-F} = 2.8 Hz), 131.1 (d, J_{C-F} = 11.0 Hz), 128.2 (d, J_{C-F} = 3.0 Hz), 123.9 (d, J_{C-F} = 10.0 Hz), 120.4 (d, J_{C-F} = 24.0 Hz), 113.6 (d, J_{C-F} = 27.0 Hz), 103.0, 53.3, 52.9, 30.7.

HRMS (ESI–TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{13}H_{12}FNNaO_6S]^+$ 352.0262, found 352.0262.



4m

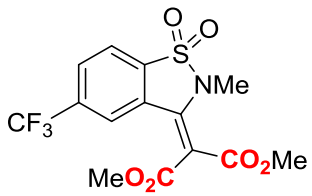
Dimethyl 2-(5-chloro-2-methyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)malonate (**4m**) was prepared as an oil from 4-chloro-N-methyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide (60.2 mg,

0.2 mmol) and CO_2 (4 MPa) according to the General Procedure **D** (eluent: ethyl acetate / petroleum ether: 1:5) in 60% yield (41.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 1.6 Hz, 1H), 7.67 (dd, *J* = 8.3, 1.7 Hz, 1H), 3.91 (s, 3H), 3.85 (s, 3H), 3.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 164.1, 143.7, 140.4, 132.8, 130.4, 123.0, 126.3, 122.7, 103.0, 53.3, 52.9, 30.7.

HRMS (ESI–TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{13}H_{12}ClNNaO_6S]^+$ 367.9966, found 367.9969.



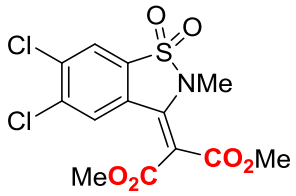
4n

Dimethyl 2-(2-methyl-1,1-dioxido-5-(trifluoromethyl)benzo[d]isothiazol-3(2H)-ylidene)malonate (**4n**) was prepared as a oil from N-methyl-4-(trifluoromethyl)-2-((trimethylsilyl)ethynyl)benzenesulfonamide (67.0 mg, 0.2 mmol) and CO_2 (4 MPa) according to the General Procedure **D** (eluent: ethyl acetate / petroleum ether: 1:5) in 70% yield (53.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.03 (m, 2H), 7.98 – 7.95 (m, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.21 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 164.0, 143.4, 135.7 (d, J_{C-F} = 33.4 Hz), 135.0, 129.5 (q, J_{C-F} = 3.3 Hz), 129.2, 123.5 (q, J_{C-F} = 4.0 Hz), 122.6 (q, J_{C-F} = 274.6 Hz), 122.5, 103.6, 53.3, 53.1, 30.8.

HRMS (ESI–TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{14}H_{12}F_3NNaO_6S]^+$ 402.0230, found 402.0233.



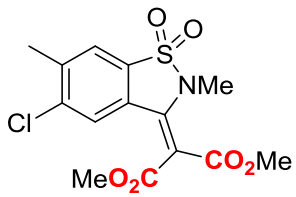
4o

Dimethyl 2-(5,6-dichloro-2-methyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)malonate (**4o**) was prepared as an oil from 4,5-dichloro-N-methyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide (67.0 mg, 0.2 mmol) and CO_2 (4 MPa) according to the General Procedure **D** (eluent: ethyl acetate / petroleum ether: 1:5) in 50% yield (37.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.92 (s, 1H), 3.91 (s, 3H), 3.86 (s, 3H), 3.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 164.1, 143.1, 138.9, 137.7, 131.4, 128.1, 127.6, 123.2, 103.4, 53.4, 53.0, 30.8.

HRMS (ESI–TOF) *m/z* [M + H]$^+$: calcd. for $[C_{13}H_{12}Cl_2NO_6S]^+$ 379.9757, found 379.9756.



4p

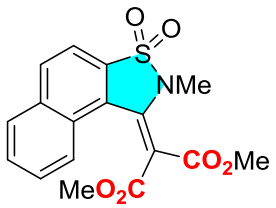
Dimethyl 2-(5-chloro-2,6-dimethyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)malonate (**4p**) was prepared as an oil from 4-chloro-N,5-dimethyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide (63.0 mg, 0.2 mmol) and CO_2 (4 MPa) according to the General Procedure **D** (eluent: ethyl acetate / petroleum ether: 1:5) in 62% yield (44.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.73 (m, 2H), 3.90 (s, 3H), 3.84 (s, 3H), 3.17

(s, 3H), 2.51 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 164.2, 144.2, 142.2, 140.6, 130.4, 127.3, 126.6, 123.1, 102.1, 53.2, 52.9, 30.7, 20.7.

HRMS (ESI–TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{14}H_{15}ClNO_6S]^+$ 360.0303, found 360.0307.



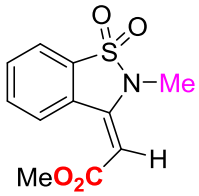
4r

Dimethyl 2-(2-methyl-3,3-dioxidonaphtho[1,2-d]isothiazol-1(2H)-ylidene)malonate (**4r**) was prepared as an oil from *N*-methyl-1-((trimethylsilyl)ethynyl)naphthalene-2-sulfonamide (63.4 mg, 0.2 mmol) and CO_2 (4 MPa) according to the General Procedure **D** (eluent: ethyl acetate / petroleum ether: 1:5) in 35% yield (25.2 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.06 (d, *J* = 8.9 Hz, 1H), 7.98 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.81 – 7.74 (m, 2H), 7.62 (d, *J* = 8.9 Hz, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 3.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 164.4, 146.0, 134.6, 134.0, 129.9, 129.7, 128.7, 128.6, 127.3, 124.7, 123.9, 120.5, 102.4, 53.2, 52.8, 30.9.

HRMS (ESI–TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{17}H_{16}NO_6S]^+$ 362.0693, found 362.0686.



4a'

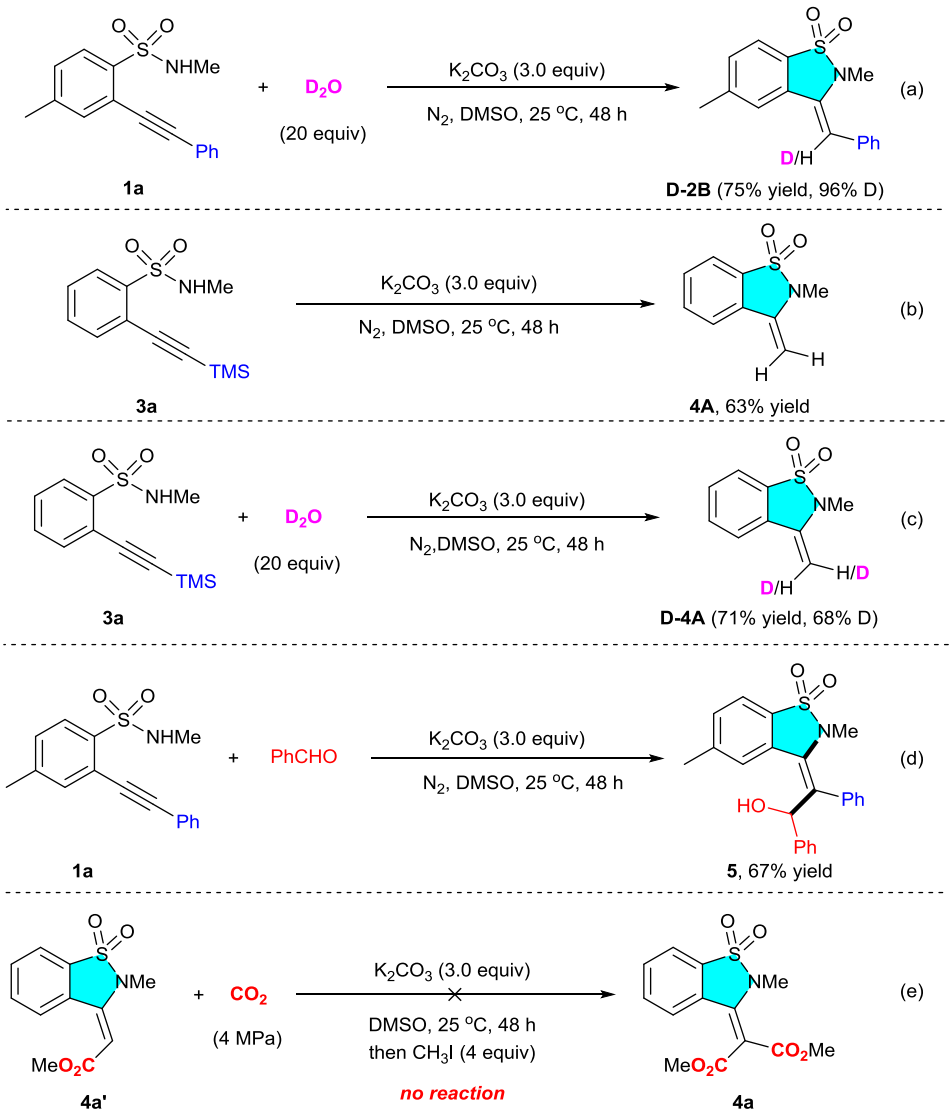
Methyl (E)-2-(2-methyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)acetate was prepared as an oil from 2-ethynyl-N-methylbenzenesulfonamide (39.0mg, 0.2 mmol) and CO_2 (4 MPa) (eluent: ethyl acetate / petroleum ether: 1:5) in 81% yield (41.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.88 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.77 – 7.65 (m, 2H), 5.36 (s, 1H), 3.79 (s, 3H), 3.16 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 144.7, 133.8, 133.1, 132.0, 129.6, 127.5, 121.0, 94.7, 51.7, 26.4.

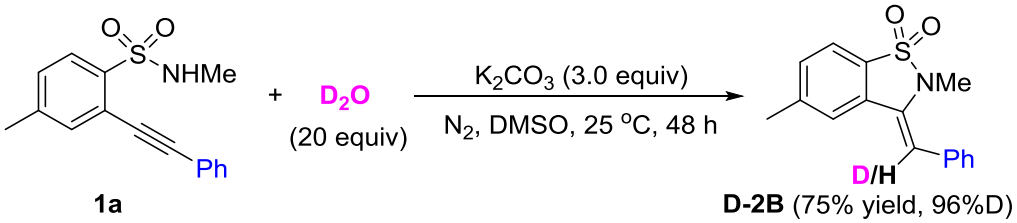
HRMS (ESI–TOF) *m*/*z* [M + Na]$^+$: calcd. for $[C_{11}H_{11}NNaO_4S]^+$ 276.0301, found 276.0307.

VI. The Control Experiment and Proposed Mechanism



Scheme S1. Control experiments

(a) The isotope labelling experiment of 1a with D_2O

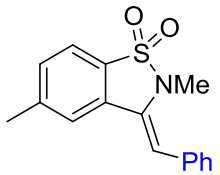


O-(1-Alkynyl)benzene sulfonamides **1a** (0.2 mmol, 57.0 mg), K_2CO_3 (0.6 mmol, 82.8 mg), D_2O (72.3 μL, 4.0 mmol, 20 equiv) and DMSO (2.0 mL) was added into a 20 mL Schlenk tube equipped with a Teflon cap. The reaction

vessel was evacuated to about -0.1 MPa (last 30 seconds per time) and backfilled with N_2 in three times. Then, the Schlenk tube was stirred at 25 °C for 48 h. After that, the reaction mixture was diluted by 5 mL saturated brine and extracted with ethyl acetate (EA) for at least 6 times (2 mL × 6). Subsequently, the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (PE/EA 5/1) to give the D-labelled compound **D-2B** as a slight yellow oil in 75% yield (42.9 mg, 96%D) with the *dr* of 1:5.8.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1.22H), 7.58 (brs, 1H), 7.44 – 7.36 (m, 6H), 7.31 – 7.26 (m, 1.2H), 6.94 (s, 0.16H), 6.59 (s, 0.04H), 3.20 (s, 0.52H), 2.94 (s, 3H), 2.50 (s, 3H), 2.18 (s, 0.52H).

Compound **2B was synthesized by the reported procedure**[6]



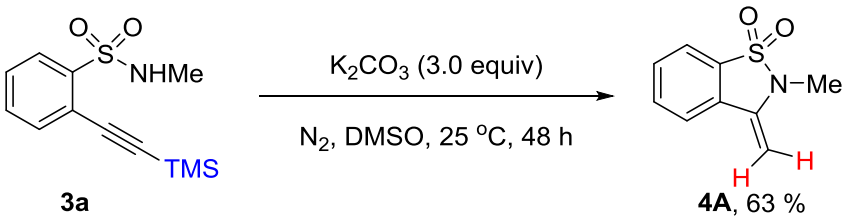
2B

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.58 (s, 1H), 7.43 – 7.35 (m, 5H), 7.31 – 7.26 (m, 1H + overlapped with $CDCl_3$), 6.59 (s, 1H), 2.94 (s, 3H), 2.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 134.1, 134.0, 132.8, 131.0, 129.6, 128.9, 128.2, 127.4, 120.9, 120.9, 105.5, 32.1, 21.9.

(b) The control experiment with 3a

[6] A. S. Reddy, A. L. S. Kumari, S. Saha, K. C. K. Swamy, *Adv. Synth. Catal.*, 2016, **358**, 1625–1638.



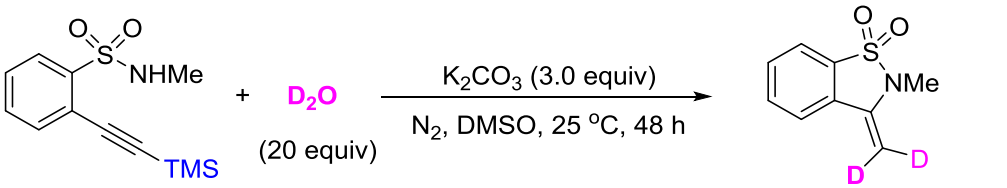
3a **4A**, 63 %

N-Methyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide (0.2 mmol, 53.4 mg), K_2CO_3 (3 equiv, 82.8 mg) and DMSO (2 mL) was added into a 20 mL Schlenk tube equipped with a Teflon cap. The reaction vessel was evacuated to about -0.1 MPa (last 30 seconds per time) and backfilled with N_2 in three times. Then, the Schlenk tube was stirred at room temperature for 48 h. After that, the reaction mixture was diluted by 5 mL saturated brine and extracted with ethyl acetate (EA) for at least 6 times (2 mL × 6) and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (PE/EA= 5/1) to give the compound **4A** in 63% yield (24.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.61 – 7.56 (m, 1H), 5.00 (t, *J* = 2.2 Hz, 1H), 4.47 (t, *J* = 2.2 Hz, 1H), 3.15 (d, *J* = 1.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 133.0, 132.0, 130.3, 121.4, 121.0, 84.6, 25.8.

(c) The isotope labelling experiment of 3a with D_2O



3a **D-4A** (71% yield, 68%D)

N-Methyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide **3a** (0.2 mmol, 53.4

mg), K_2CO_3 (0.6 mmol, 82.8 mg), D_2O (72.3 μL, 4.0 mmol, 20 equiv) and DMSO (2.0 mL) was added into a 20 mL Schlenk tube equipped with a Teflon cap. The reaction vessel was evacuated to about -0.1 MPa (last 30 seconds per time) and backfilled with N_2 in three times. Then, the Schlenk tube was stirred at 25 °C for 48 h. After that, the reaction mixture was diluted by 5 mL saturated brine and extracted with ethyl acetate (EA) for at least 6 times (2 mL × 6). Subsequently, the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (PE/EA 5/1) to give the D-labelled compound **D-4A** as a white solid in 71% yield (28.1 mg, 68% D).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.79 (m, 1H), 7.73 – 7.70 (m, 1H), 7.65 – 7.61 (m, 1H), 7.58 – 7.54 (m, 1H), 4.98 (d, *J* = 2.8 Hz, 0.32H), 4.45 (d, *J* = 2.8 Hz, 0.32H), 3.12 (s, 3H).

(d) The carbon anion trapping reaction with PhCHO

1a **5**, 67%, *Z*/*E* = 1:12

O-(1-Alkynyl)benzene sulfonamides **1a** (0.2 mmol, 57.0 mg), K_2CO_3 (0.6 mmol, 82.8 mg), PhCHO (40.6 μL, 0.4 mmol) and DMSO (2.0 mL) was added into a 20 mL Schlenk tube equipped with a Teflon cap. The reaction vessel was evacuated to about -0.1 MPa (last 30 seconds per time) and backfilled with N_2 in three times. Then, the Schlenk tube was stirred at 25 °C for 48 h. After that, the reaction mixture was diluted by 5 mL saturated brine and extracted with ethyl acetate (EA) for at least 6 times (2 mL × 6). Subsequently, the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash

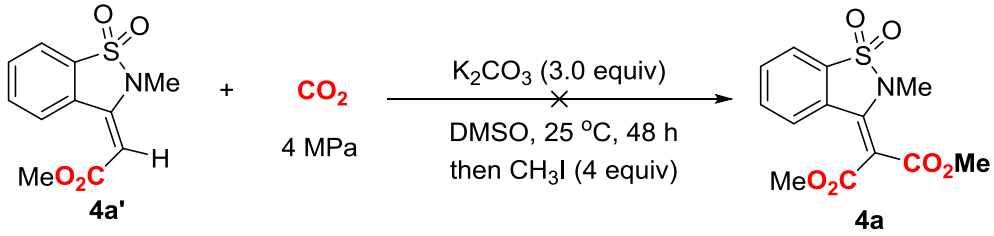
chromatography (PE/EA 5/1) to give compound **5** as a colorless oil in 67% yield (52.4 mg) with the *Z*/*E* ratio of 1:12.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.4 Hz, 0.24H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.69 (s, 1H), 7.48 – 7.45 (m, 0.42H), 7.42 – 7.38 (m, 3H), 7.36 – 7.28 (m, 3.5H), 7.25 – 7.22 (m, 3H), 7.08 – 7.05 (m, 2H), 6.47 (s, 1H), 2.62 – 2.61 (m, 0.5H), 2.50 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 140.7, 135.3, 134.5, 133.5, 132.8, 132.2, 130.8, 130.3, 128.5, 128.4, 128.1 (2C), 127.7, 126.2 (2C), 121.4, 72.0, 33.3, 22.2.

HRMS (ESI-TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{23}H_{22}NO_3S]^+$ 392.1315, found 392.1309.

(e) Control experiment of **4a'** and CO_2

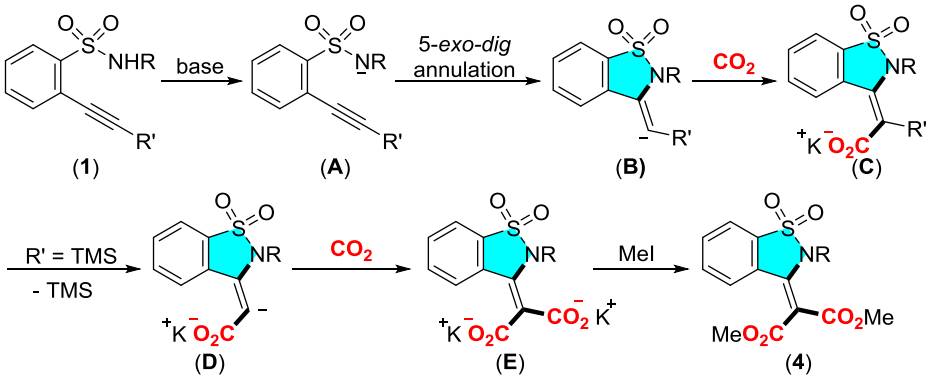


Under air, to an over-dried 20 mL vessel was added **4a'** (0.2 mmol, 50.6 mg), K_2CO_3 (0.6 mmol, 3 equiv, 82.8 mg) and DMSO (2.0 mL). The vessel was fixed into a stainless steel autoclave. Then the autoclave was sealed and CO_2 was introduced from a cylinder. The reaction was carried out at 25 °C under magnetic stirring for 48 h and the pressure was kept constant (4 MPa) during the reaction. As the reaction was completed, the vessel was cooled to room temperature and the pressure was released slowly to atmospheric pressure. After that, MeI (0.8 mmol, 4 equiv, 52 μL) was added into the reaction mixture, and the reaction mixture was stirred at room temperature for about 2 h. After the analyzing by TLC, none of newly generated product could be detected, only **4a'** could be detected.

Based on the above results and some relative works,[7] a reasonable

[7] (a) D. Rambabu, N. S. P. V. Murthy, K. R. S. Prasad, A. Kandale, G. S. Deora, M. V.

mechanism is proposed in Scheme S1. Firstly, the sulfamine group in *o*-(1-alkynyl)benzenesulfonamide **1** is deprotonated by base, affording the sulfamide anion **A**. Next, 5-*exo-dig* annulation of intermediate **A** generates the vinyl anion intermediate **B**. Sequentially, nucleophilic addition of its vinyl anion to CO_2 leads to intermediate **C**. Then, esterification of **C** furnishes the product **2**. Alternatively, when the alkyne bounded with TMS, desilylation would lead to the carbon anion **D**, which undergoes sequential carboxylation with a second molecule of CO_2 and esterification to afford the double carboxylation product **4**.

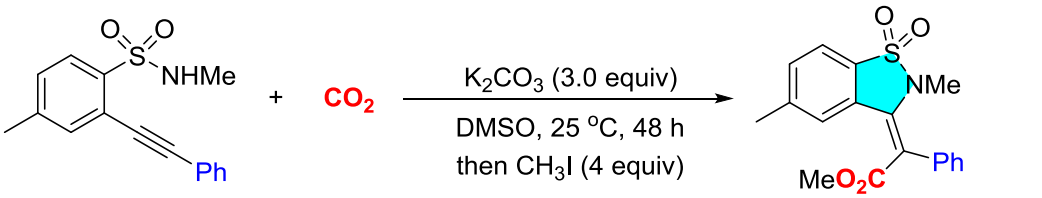


Scheme S2. Proposed Mechanism

B. Rao and M. Pal, *Tetrahedron Lett.*, 2012, **53**, 6577–6583. (b) S. Debnath and S. Mondal, *J. Org. Chem.*, 2015, **80**, 3940–3948. (c) B. M. Rao, J. S. Yadav, B. Sridharb and B. V. S. Reddy, *Org. Biomol. Chem.*, 2018, **16**, 5163–5166. (d) Q. Xiao, J. Sheng, Z. Chen and J. Wu, *Chem. Commun.*, 2013, **49**, 8647–8649.

VII. Gram-Scale Reaction and Derivation

(a) Gram-scale reaction of 1a and CO_2

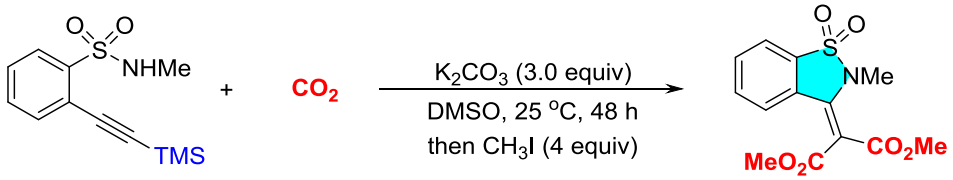


1a, 1 g

2a (840.3 mg, 70% yield)

Under air, to an over-dried 100 mL Schlenk tube equipped with a Teflon cap was o-(1-alkynyl)benzene sulfonamides **1a** (3.5 mmol, 1.0 g), K_2CO_3 (10.5 mmol, 3 equiv, 1.45 g) and DMSO (20.0 mL). The reaction vessel was evacuated to about -0.1 MPa (last 30 seconds per time) and backfilled with CO_2 (1 atm) in three times. Then, the Schlenk tube was stirred at 25 °C for 48 h. After that, MeI (14.0 mmol, 4 equiv, 0.88 mL) was added into the reaction mixture, and the reaction mixture was stirred at 50 °C for about 1 h, then, the reaction mixture was saturated brine and extracted with ethyl acetate (EA) for at least 6 times (10 mL × 6). Subsequently, the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (dichloromethane / petroleum ether: 1:1) to give the pure desired product 2**a** (70%, 840.3 mg).

(b) Gram-scale reaction of 3a and CO_2



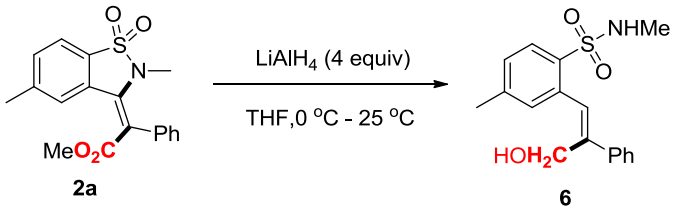
3a, 1 g

4a (734.7 mg, 60% yield)

Under air, to an over-dried 100 mL polytetrafluoroethylene (PTFE) reaction vessel, *N*-methyl-2-((trimethylsilyl)ethynyl)benzenesulfonamide **3a** (3.75 mmol, 1.0 g), K_2CO_3 (11.2 mmol, 3 equiv, 1.55 g) and DMSO (20.0 mL) was added sequentially. The vessel was fixed into a stainless-steel autoclave

with a pressure-regulating system. Then the autoclave was sealed and CO_2 was introduced from a cylinder (4 MPa). Then, the autoclave was stirred at 25 °C for 48 h. After that, MeI (15.0 mmol, 4 equiv, 0.94 mL) was added into the reaction mixture, and the reaction mixture was stirred at 25 °C for about 1 h, then, the reaction mixture was saturated brine and extracted with ethyl acetate (EA) for at least 6 times (10 mL × 6). Subsequently, the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (ethyl acetate / petroleum ether: 1:5) to give the pure desired product **4a** (60%, 734.7 mg).

(c) Reduction of 2a by $LiAlH_4$



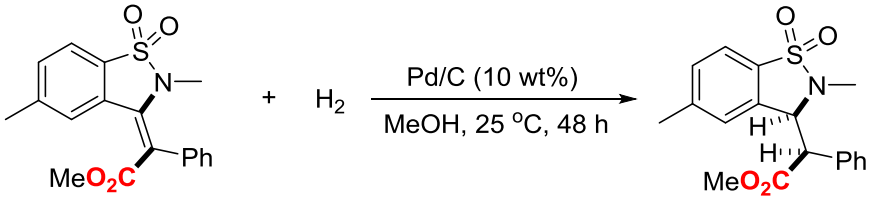
Under N_2, to a 50 mL round bottom flask equipped with a stir bar was added **2a** (0.5 mmol, 171.6 mg), anhydrous THF (4 mL) and the reaction mixture was cooled down to 0 °C. Then, $LiAlH_4$ (2 mmol, 75.9 mg, 4 equiv) was added to the mixture slowly. After that, the reaction mixture was allowed to warm to room temperature and stirred overnight. Upon completion (monitored by TLC), it was quenched with aqueous NaOH solution and filtered through a plug of celite. Then, the reaction mixture was extracted with ethyl acetate (3 × 15 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography to afford compound **6** as a white solid in 69% yield (109.1 mg).

^{1}H NMR (300 MHz, $CDCl_3$) 7.84 (d, J = 8.0 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.24 – 7.20 (m, 3H + overlapped with $CDCl_3$), 7.10 – 7.01 (m, 3H), 6.71 (s, 1H), 5.57 (brs, 1H), 4.55 (s, 2H), 2.56 (d, J = 5.1 Hz, 3H), 2.06 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 142.5, 137.4, 135.8, 133.6, 133.1, 129.9, 128.6, 128.4, 127.6, 127.3, 122.8, 66.9, 28.9, 21.1.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for [$C_{17}H_{19}NNaO_3S$]$^+$ 340.0978, found 340.0980.

(d) Reduction of 2a by H_2



2a **7**, 60 % yield *dr* = 1:8

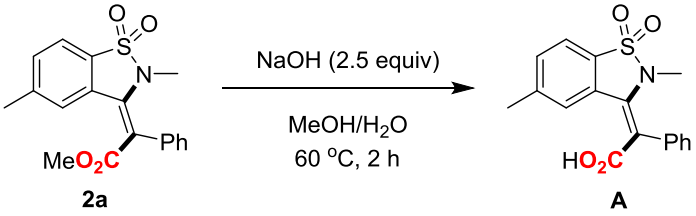
In a 10 mL vial, 10 wt% Pd/C (22.0 mg, 0.01 mmol) was added to a solution of compound **2a** (64.1 mg, 0.225 mmol) in MeOH (4.0 mL) at room temperature. The 10 mL vial was placed in a 100 mL reaction still which was filled with H_2 (40 atm). The reaction mixture was then stirred for 48 h at 25 °C. Upon completion, the mixture was filtered through a pad of Celite. The filtrate was concentrated in vacuo and the residue purified by flash column chromatography (3:1 petroleum ether: EtOAc) to obtain **(e)** in 60% yield (46.6 mg) with the *dr* ratio of about 1:8.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 0.16H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.44 – 7.27 (m, 4H), 7.20 – 7.15 (m, 3.24H), 5.71 (brs, 1H), 4.83 (d, *J* = 9.4 Hz, 0.14H), 4.78 (d, *J* = 10.3 Hz, 1H), 3.94 (d, *J* = 9.3 Hz, 0.16H), 3.91 (d, *J* = 10.4 Hz, 1H), 3.73 (s, 3H), 3.70 (s, 0.36H), 2.98 (s, 3H), 2.41 (s, 0.36H), 2.39 (s, 0.36H), 2.08 (s, 3H).

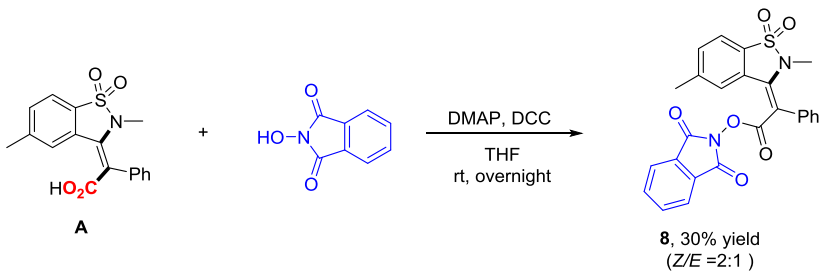
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 143.6, 142.3, 136.3, 134.8, 134.4, 133.0, 130.5, 130.2, 129.5, 129.0, 128.9, 128.8, 128.5, 128.2, 126.4, 125.0, 121.2, 120.8, 67.2, 66.5, 57.4, 57.1, 52.5, 52.3, 36.2, 33.5, 21.8, 21.4.

HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$: calcd. for [$C_{18}H_{19}NNaO_4S$]$^+$ 368.0927, found 368.0930.

(e) The reaction of 2a with 2-hydroxyisoindoline-1,3-dione



Methyl (*E*)-2-(2,5-dimethyl-1,1-dioxidobenzo[d]isothiazol-3(2H)-ylidene)-2-phenylacetate (68.6 mg, 0.2 mmol), NaOH (0.5 mmol, 2.5 equiv, 20 mg) was dissolved into a mixture of MeOH (6 mL) and H_2O (3 mL). The obtained solution was heated at 60 °C for 2 h in oil bath. After cooled to room temperature, ethyl acetate and H_2O was added and the water phase was collected. Then 1 mol/L HCl was added to adjust the pH to 1 and followed by the extraction by ethyl acetate. The collected organic phase was dried by $MgSO_4$ and evaporated in vacuo. The obtained white solid was used in the next step without further purification.



To a solution of **A** in THF (2 mL) was added 2-hydroxyisoindoline-1,3-dione (41 mg, 1.66 equiv, 0.33 mmol), 4-dimethylaminopyridine (1.2 mg, 5 mol%) and dicyclohexylcarbodiimide (62 mg, 1.5 equiv, 0.3 mmol) sequentially. Then, the reaction mixture was stirred at room temperature overnight. The mixture was filtered and evaporated in vacuo. The obtained crude was then purified by silica chromatography (2:1 petroleum ether: EtOAc) to give pure **8** (28.5 mg, 30% yield) with the *Z*/*E* ratio of 2:1.

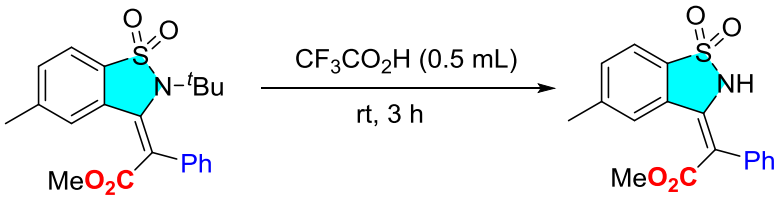
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 0.5H), 7.92 (dd, *J* = 5.5, 3.1 Hz, 1H), 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.83 – 7.77 (m, 3.5H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.58 (dd,

J = 6.8, 2.9 Hz, 2H), 7.52 (m, 4H), 7.48 – 7.38 (m, 2H), 7.35 (d, J = 8.0 Hz, 1H), 6.14 (s, 1H), 3.36 (s, 3H), 2.74 (s, 1.5H), 2.61 (s, 1.5H), 2.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 163.1, 162.6, 162.2, 162.1, 161.5, 148.8, 145.4, 144.9, 144.1, 142.9, 134.9, 134.7 (2C), 134.6, 134.0, 133.0, 132.5, 131.7, 130.8, 130.7, 129.8 (2C), 129.5, 129.4, 129.3 (2C), 129.1, 129.0, 128.9, 128.8, 128.7, 127.9, 126.7, 126.5, 124.0, 123.9, 123.8, 121.1, 121.0, 105.1, 103.5, 31.6, 31.5, 21.9, 21.8.

HRMS (ESI-TOF) m/z [M + H]$^+$: calcd. for $[C_{25}H_{19}N_2O_6S]^+$ 475.0958, found 475.0972.

(f) Derivation of 2c



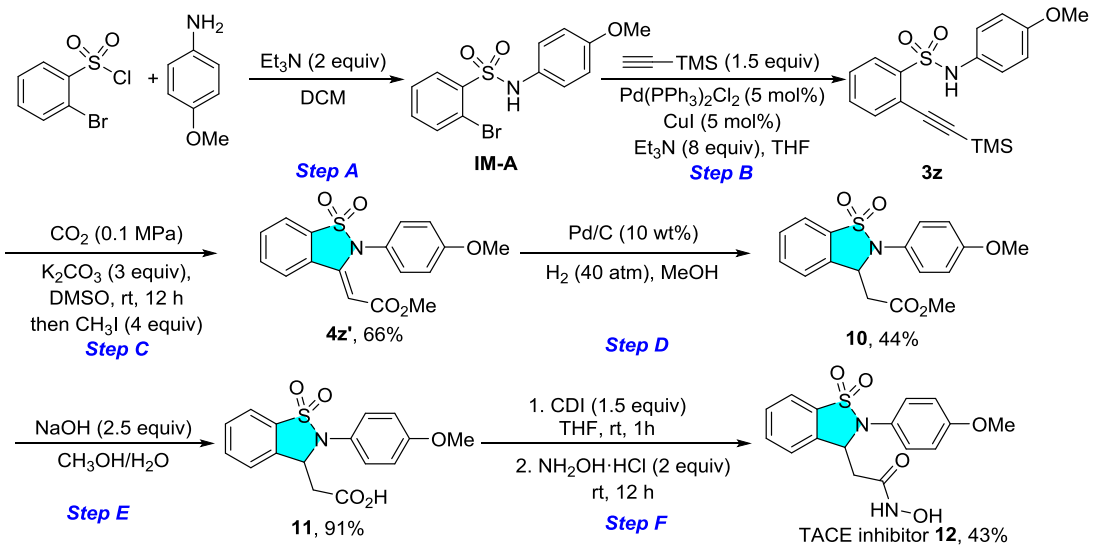
A solution of **2c** (77.0 mg, 0.2 mmol) in CF_3CO_2H (0.5 mL) was stirred at room temperature for about 3 h. Then, the mixture was terminated by saturated brine water and extracted by ethyl acetate. The collected organic phase was dried by Na_2SO_4 and evaporated in vacuo. The obtained crude was then purified by silica chromatography (1:1 petroleum ether: EtOAc) to give **2c′** as colorless oil in 31% yield (20.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.57 (dd, J = 7.4, 2.2 Hz, 2H), 7.49 – 7.46 (m, 3H), 7.35 (d, J = 8.0 Hz, 1H), 3.47 (s, 3H), 2.49 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 143.2, 142.5, 134.6, 130.9, 130.8, 128.9, 128.8, 128.6, 128.5, 126.1, 121.3, 111.4, 52.2, 22.0.

HRMS (ESI-TOF) m/z [M + H]$^+$: calcd. for $[C_{17}H_{16}NO_4S]^+$ 330.0795, found 330.0792.

IIX. Synthesis of TACE Inhibitor



Procedure:

Steps A-B: Firstly, the *o*-(1-alkynyl)benzenesulfonamide **3z** was synthesized according to the General Procedure **B** by using 2-bromobenzenesulfonyl chloride (2.5 g, 10 mmol) and 4-methoxyaniline (1.5 g, 12 mmol), furnishing **IM-A** in 86% yield (2.9 g, 8.6 mmol). Then, Sonogashira reaction of **IM-A** with ethynyltrimethylsilane (1 g, 10.3 mmol) lead to **3z** as yellow oil in 75% yield (2.3 g, 6.5 mmol).

Steps C: Then, the mono-carboxylation reaction of **3z** with CO_2 was conducted according to General Procedure C furnished product **4z'** as brown oil in 66% yield (1.5 g, 4.3 mmol).

Steps D-E: In a 20 mL vial, 10 wt % Pd/C (34.5 mg) was added to a solution of compound **4z'** (345 mg, 1 mmol) in MeOH (10 mL) at room temperature. The 20 mL vial was placed in a 100 mL reaction still which was filled with H_2 (40 atm). The reaction mixture was then stirred for 48 h at 25 ^{o}C. Upon completion, the mixture was filtered through a pad of Celite. The filtrate was concentrated in vacuo and the residue purified by flash column chromatography (5:1 petroleum ether: EtOAc) to obtain **10** as colorless oil in 44% yield (152.7 mg).

In a 50 mL round bottle flask, compound **11** (173.5 mg, 0.5 mmol), NaOH (1.25 mmol, 2.5 equiv, 50 mg) was dissolved into a mixture of MeOH (10 mL) and H_2O (5 mL). The obtained solution was heated at 65 ^oC for 3 h in oil bath. After cooled to room temperature, ethyl acetate and H_2O was added and the water phase was collected. Then 1 mol/L HCl was added to adjust the pH to 1 and followed by the extraction by ethyl acetate. The collected organic phase was dried by $MgSO_4$ and evaporated in vacuo, furnishing compound **10** as a white solid in 91% yield (151.5 mg), which was used in the next step without further purification.

Steps F: To a solution of compound **12** in THF (2 mL) was added 1,1'-carbonyldiimidazole (48 mg, 1.5 equiv, 0.3 mmol). The reaction mixture was stirred at room temperature for 1h. Then hydroxylamine hydrochloride (27.8 mg, 2 equiv, 0.4 mmol) was added, then, the reaction mixture was stirred at room temperature overnight. The mixture was filtered and evaporated in vacuo. The obtained crude was then purified by silica chromatography (1:1 petroleum ether: EtOAc) to give pure **11** (29.9 mg, 43% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (brs, 1H), 7.78 (d, *J* = 7.3 Hz, 1H), 7.53 (q, *J* = 7.4, 6.9 Hz, 2H), 7.43 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 2H), 5.35 – 5.34 (m, 1H), 3.78 (s, 3H), 2.71 – 2.67 (m, 1H), 2.48 – 2.45 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 149.0, 136.1, 134.2, 133.3, 129.9, 129.1, 125.9, 124.3, 121.5, 115.2, 59.6, 55.5, 37.1.

HRMS (ESI-TOF) *m*/*z* [M + H]$^+$: calcd. for $[C_{16}H_{17}N_2O_5S]^+$ 349.0853, found 349.0847.

IX. Crystallographic Data of 2a and 4f

(a) X-Ray crystallographic data of 2a

The crystal structures have been deposited at the Cambridge Crystallographic Data Centre (2174206, **2a**). The data can be obtained free of charge via the internet at https://www.ccdc.cam.ac.uk/structures/. The measurements were taken in a Bruker APEX-II CCD diffractometer. The crystal was kept at 128.0 K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the SHELXL refinement package using Least Squares minimisation.

Method of crystallization: A solution of **2a** in ethyl acetate and hexane was evaporated the solvent slowly at room temperature.

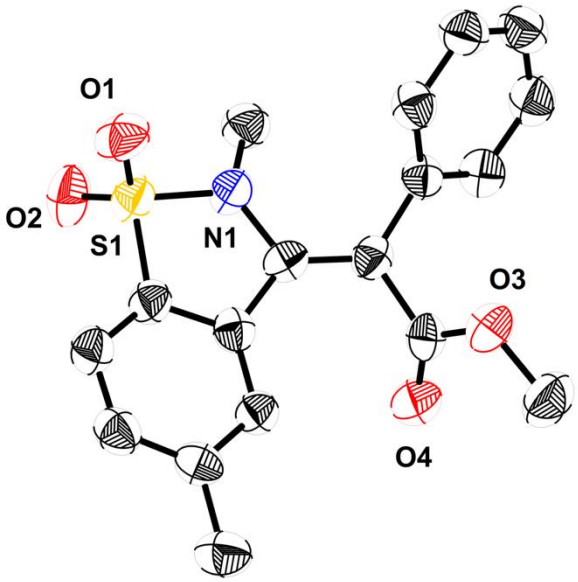


Figure S1. Solid state structure of **2a**. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity.

Table S1 Crystallographic data of complex **2a**

CCDC number	2348034
Empirical formula	$C_{18}H_{17}NO_4S$
Formula weight	343.38
Temperature [K]	128.00

Crystal system	monoclinic
Space group (number)	$P2_1/c$ (14)
a [Å]	9.907(4)
b [Å]	10.099(4)
c [Å]	17.406(7)
α [°]	90
β [°]	104.78(3)
γ [°]	90
Volume [Å^3]	1683.8(12)
Z	4
ρ_{calc} [gcm^{-3}]	1.355
μ [mm^{-1}]	1.239
F(000)	720
Crystal size [mm^3]	0.3×0.2×0.2
Crystal colour	clear light colourless
Crystal shape	block
Radiation	GaK_α (λ=1.34138 Å)
2θ range [°]	8.88 to 105.94 (0.84 Å)
Index ranges	−11 ≤ h ≤ 11
	−12 ≤ k ≤ 7
	−20 ≤ l ≤ 20
Reflections collected	11571
Independent reflections	2909
	R_{int} = 0.1688
	R_{sigma} = 0.1287
Completeness to θ = 52.968°	98.0 %
Data / Restraints / Parameters	2909/0/221
Goodness-of-fit on F^2	0.998
Final R indexes	R_1 = 0.0818
[I≥2σ(I)]	wR_2 = 0.2078
Final R indexes	R_1 = 0.1198
[all data]	wR_2 = 0.2496
Largest peak/hole [eÅ^{-3}]	0.38/-0.46
Extinction coefficient	0.039(6)

(b) X-Ray crystallographic data of 4f

The crystal structures have been deposited at the Cambridge Crystallographic Data Centre (2280046, **4f**). The data can be obtained free of charge via the internet at https://www.ccdc.cam.ac.uk/structures/. The

measurements were taken in a Bruker APEX-II CCD diffractometer. The crystal was kept at 128.0 K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the SHELXL refinement package using Least Squares minimisation.

Method of crystallization: A solution of **4f** in ethyl acetate and hexane was evaporated the solvent slowly at room temperature.

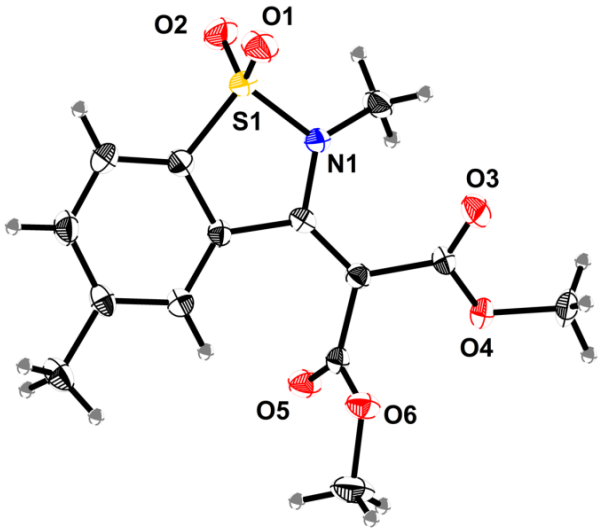
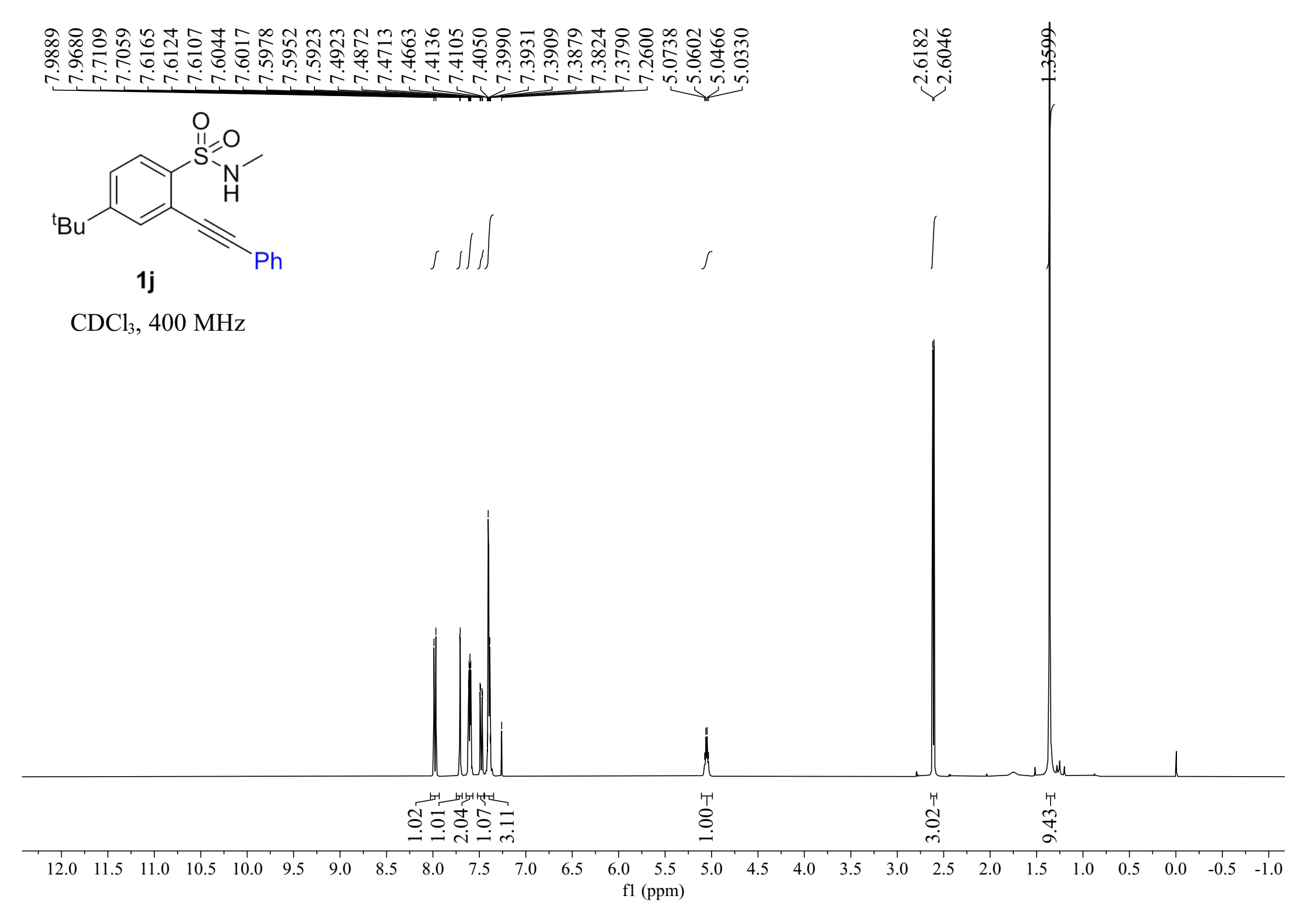


Figure S2. Solid state structure of **4f**. Thermal ellipsoids are drawn at the 30% probability level.

Table S2 Crystallographic data of complex **4f**

CCDC number	2280046
Empirical formula	$C_{14}H_{15}NO_6S$
Formula weight	325.33
Temperature [K]	150.00
Crystal system	triclinic
Space group (number)	$P\bar{1}$ (2)
a [Å]	7.9471(6)
b [Å]	7.9767(6)
c [Å]	12.2761(10)
α [°]	74.518(2)
β [°]	88.476(3)
γ [°]	84.620(2)
Volume [Å^3]	746.66(10)

Z	2
ρ_{calc} [gcm^{-3}]	1.447
μ [mm^{-1}]	0.246
F(000)	340
Crystal size [mm^3]	0.3×0.2×0.2
Crystal colour	clear light colourless
Crystal shape	block
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	5.15 to 55.11 (0.77 Å)
Index ranges	−10 ≤ h ≤ 10
	−10 ≤ k ≤ 10
	−15 ≤ l ≤ 15
Reflections collected	14032
Independent reflections	3395
	R_{int} = 0.0634
	R_{sigma} = 0.0514
Completeness to θ = 25.242°	98.9 %
Data / Restraints / Parameters	3395/0/203
Absorption correction	0.5337/0.7456
T_{min}/T_{max} (method)	(multi-scan)
Goodness-of-fit on F^2	1.079
Final R indexes	R_1 = 0.0539
[I≥2σ(I)]	wR_2 = 0.1171
Final R indexes	R_1 = 0.0733
[all data]	wR_2 = 0.1375
Largest peak/hole [eÅ^{-3}]	0.45/−0.61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7.7109
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7.6165
7.6124
7.6107
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7.6017
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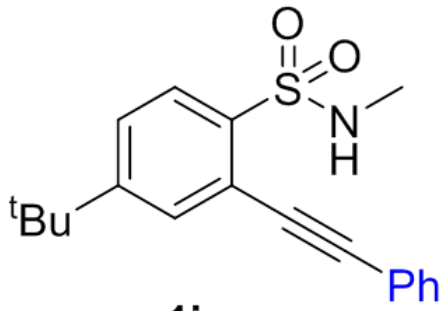
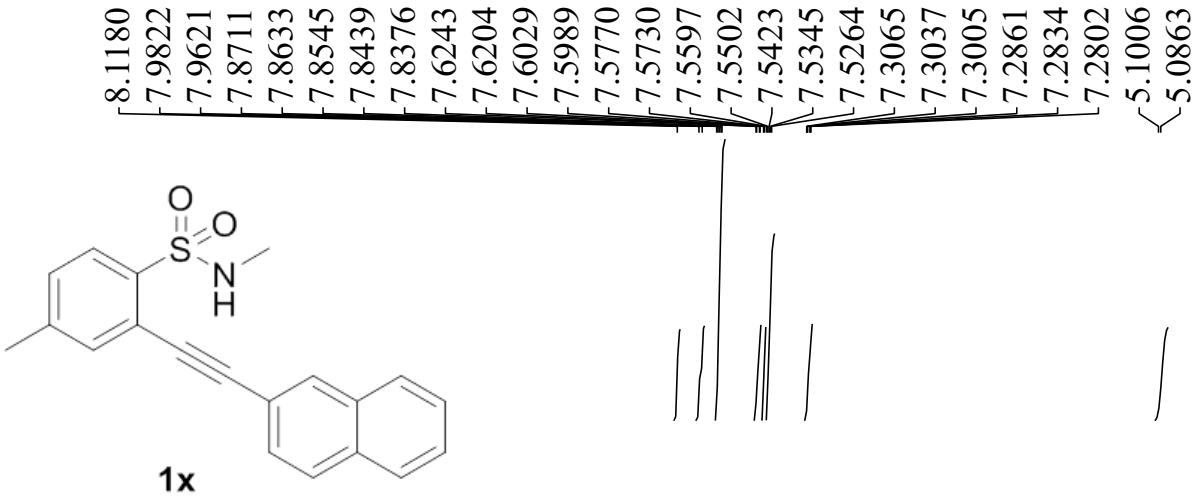
7.5952
7.5923
7.4923
7.4872
7.4713
7.4663
7.4136
7.4105
7.4050
7.3990
7.3931
7.3909
7.3879
7.3824
7.3790
7.2600
5.0738
5.0602
5.0466
5.0330
2.6182
2.6046
1.3599
O
O
S
N
H
tBu
Ph
1j
CDCl3, 400 MHz
1.02
1.01
2.04
1.07
3.11
1.00
3.02
9.43
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



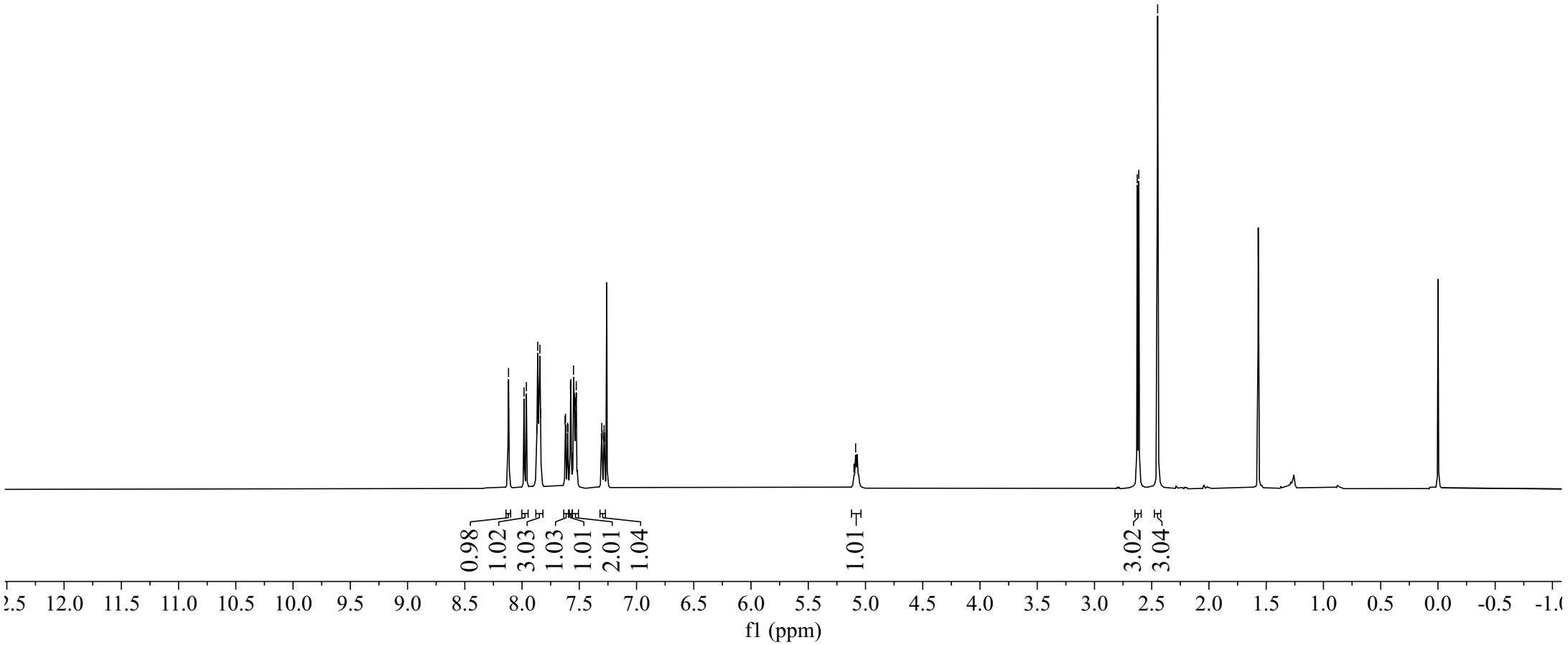
1j

$CDCl_3$, 101 MHz



1x

$CDCl_3$, 400 MHz



143.03
136.34
134.57
133.13
132.77
131.97
129.80
129.10
128.31
127.88
127.83
127.75
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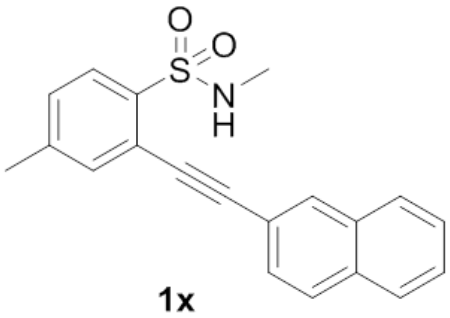
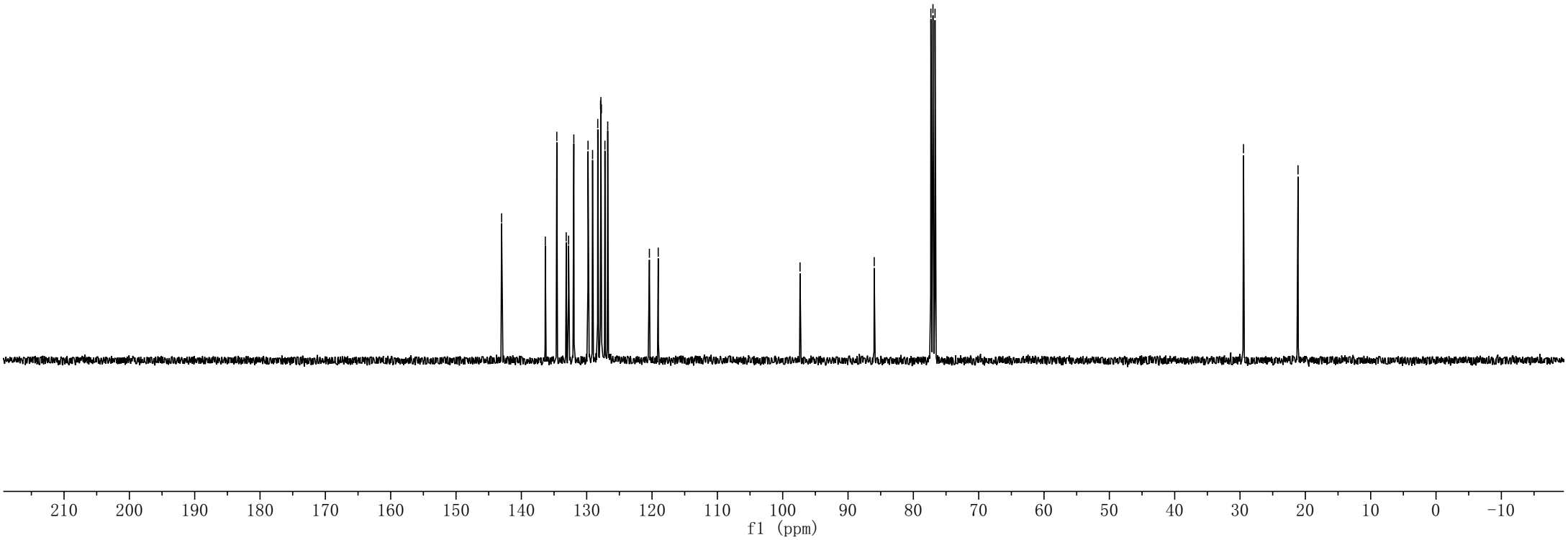
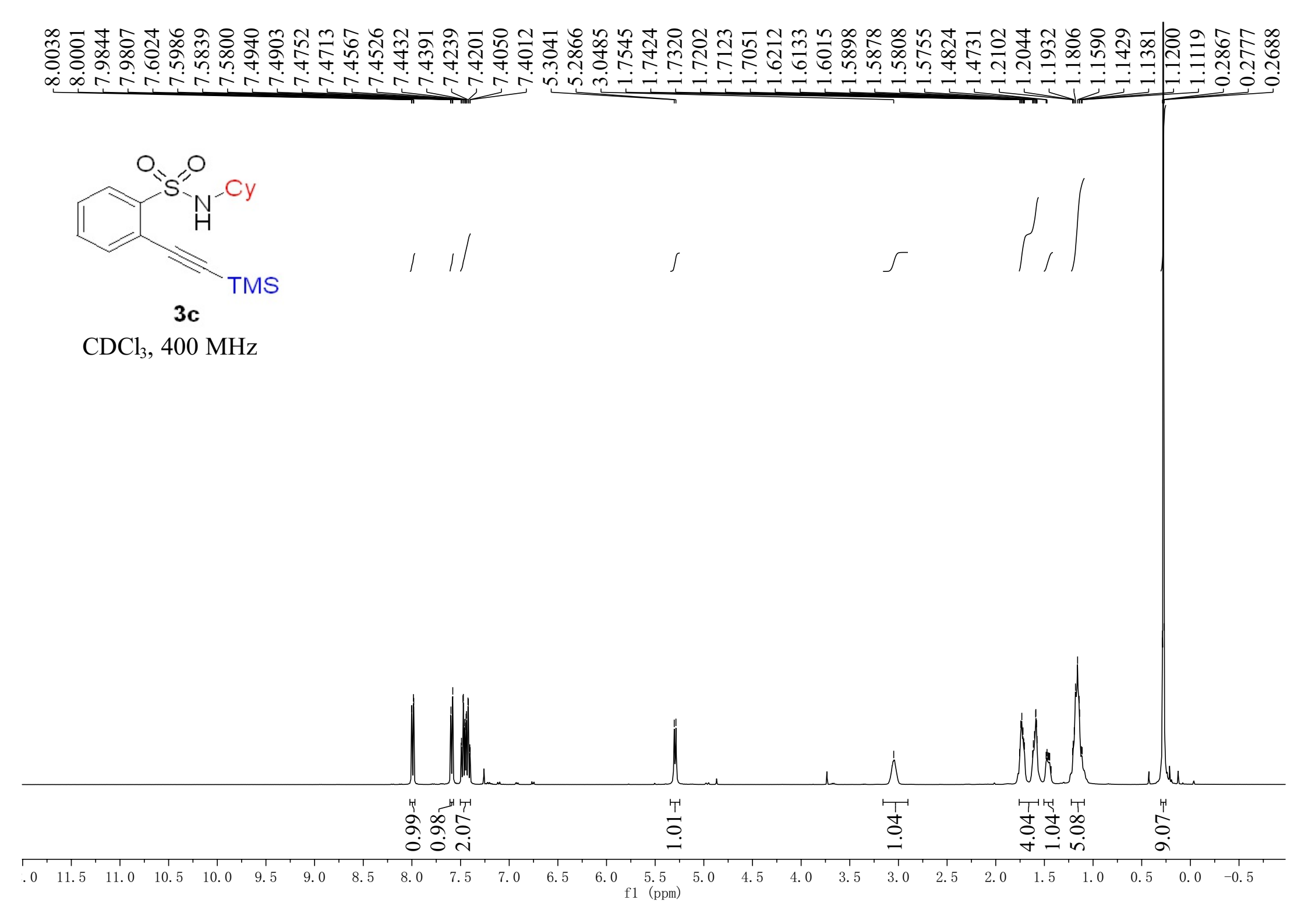
126.78
120.40
119.05
97.34
85.99
77.32
77.00
76.68
29.47
21.12



1x

$CDCl_3$, 101 MHz

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7.4201
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7.4012
5.3041
5.2866
3.0485
1.7545
1.7424
1.7320
1.7202
1.7123
1.7051
1.6212
1.6133
1.6015
1.5898
1.5878
1.5808
1.5755
1.4824
1.4731
1.2102
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1.1119
0.2867
0.2777
0.2688
O
O
S
N
H
Cy
TMS
3c
CDCl3, 400 MHz
0.99
0.98
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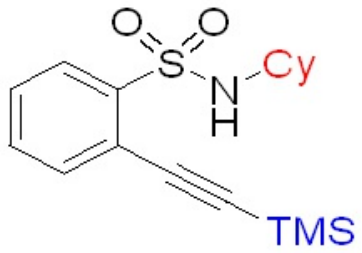
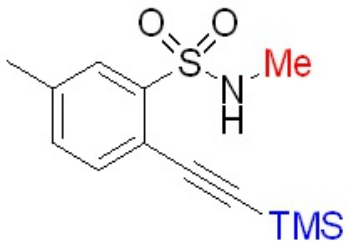
1.01
1.04
4.04
1.04
5.08
9.07
f1 (ppm)



3c

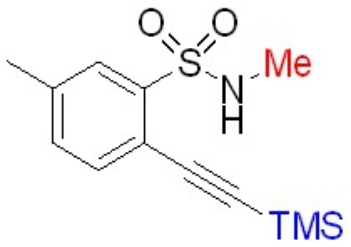
$CDCl_3$, 101 MHz

142.75
134.36
131.73
128.66
128.29
119.91
103.84
101.80
77.32
77.00
76.68
52.71
33.46
25.02
24.28
-0.48



3g

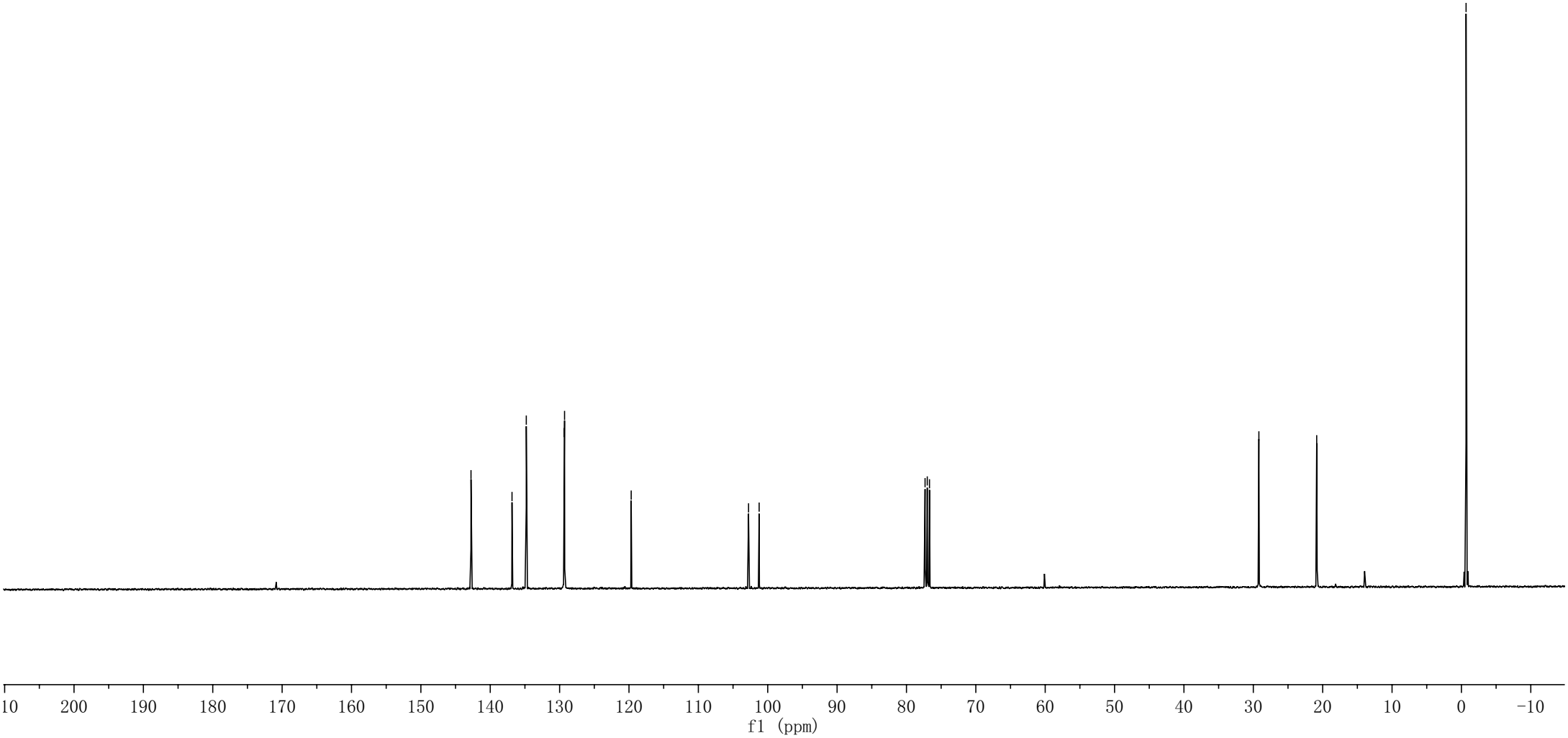
$CDCl_3$, 400 MHz

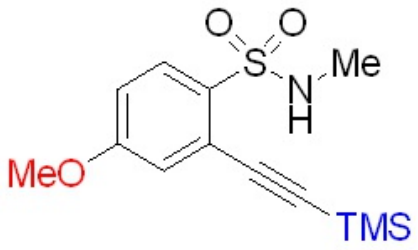


3g

142.77
136.86
134.80
129.35
129.29
119.68
102.76
101.24
77.32
77.00
76.68
29.20
20.86
-0.67

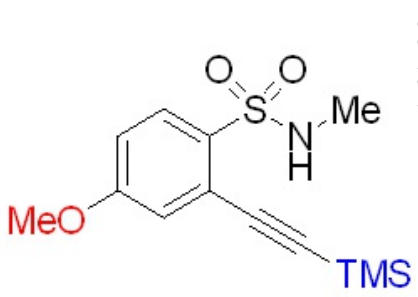
$CDCl_3$, 101 MHz





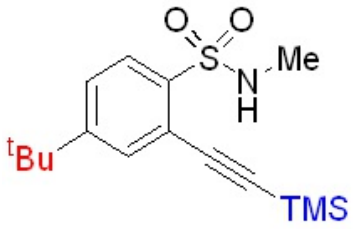
3h

$CDCl_3$, 400 MHz



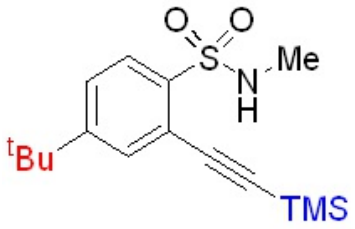
3h

$CDCl_3$, 101 MHz



3i

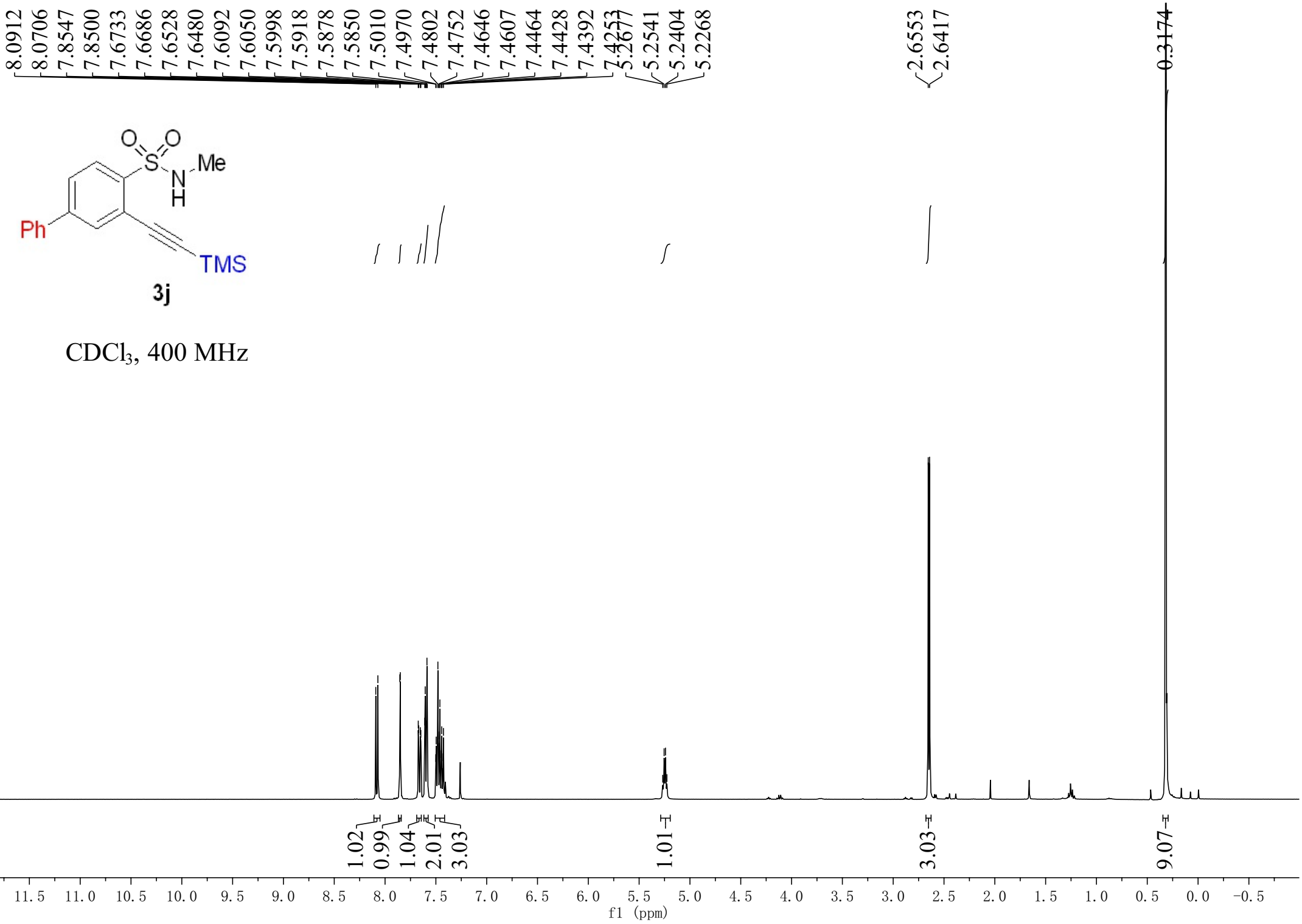
$CDCl_3$, 400 MHz

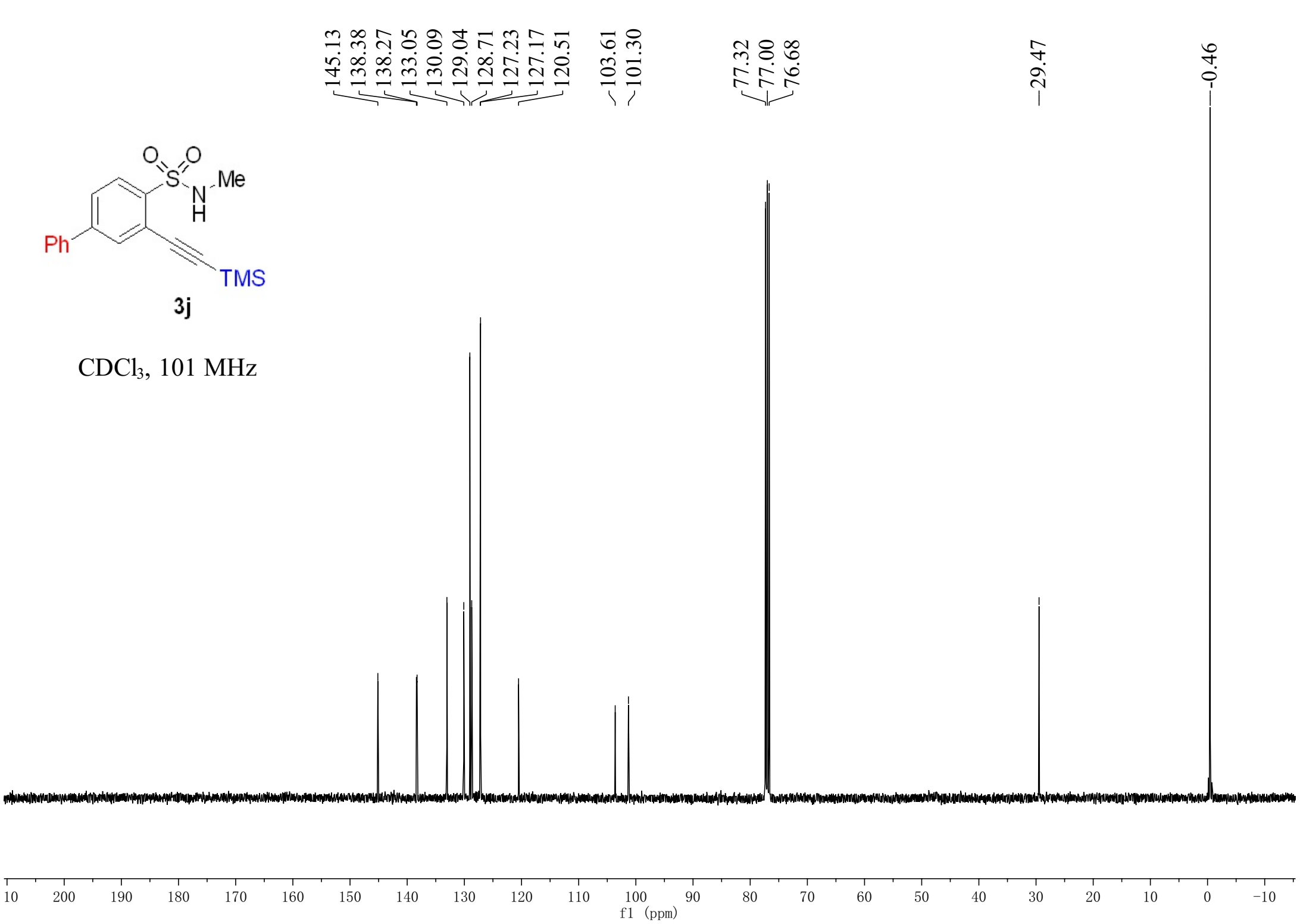


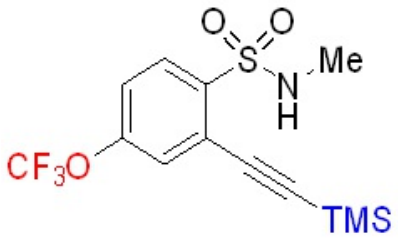
3i

155.86
137.02
131.65
129.42
125.98
119.59
102.62
101.81
77.32
77.00
76.68
34.97
30.86
29.43
-0.45

$CDCl_3$, 101 MHz

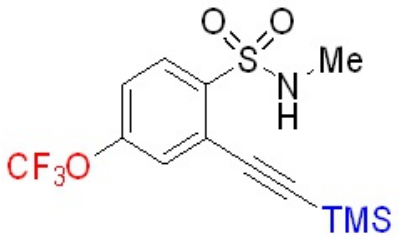

8.0912
8.0706
7.8547
7.8500
7.6733
7.6686
7.6528
7.6480
7.6092
7.6050
7.5998
7.5918
7.5878
7.5850
7.5010
7.4970
7.4802
7.4752
7.4646
7.4607
7.4464
7.4428
7.4392
7.4253
7.4177
5.2541
5.2404
5.2268
2.6553
2.6417
0.3174
O
O
S
N
H
Me
Ph
TMS
3j
CDCl3, 400 MHz
1.02
0.99
1.04
2.01
3.03
1.01
3.03
9.07
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


145.13
138.38
138.27
133.05
130.09
129.04
128.71
127.23
127.17
120.51
103.61
101.30
77.32
77.00
76.68
29.47
-0.46
O
O
S
N
H
Me
Ph
TMS
3j
CDCl3, 101 MHz
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3k

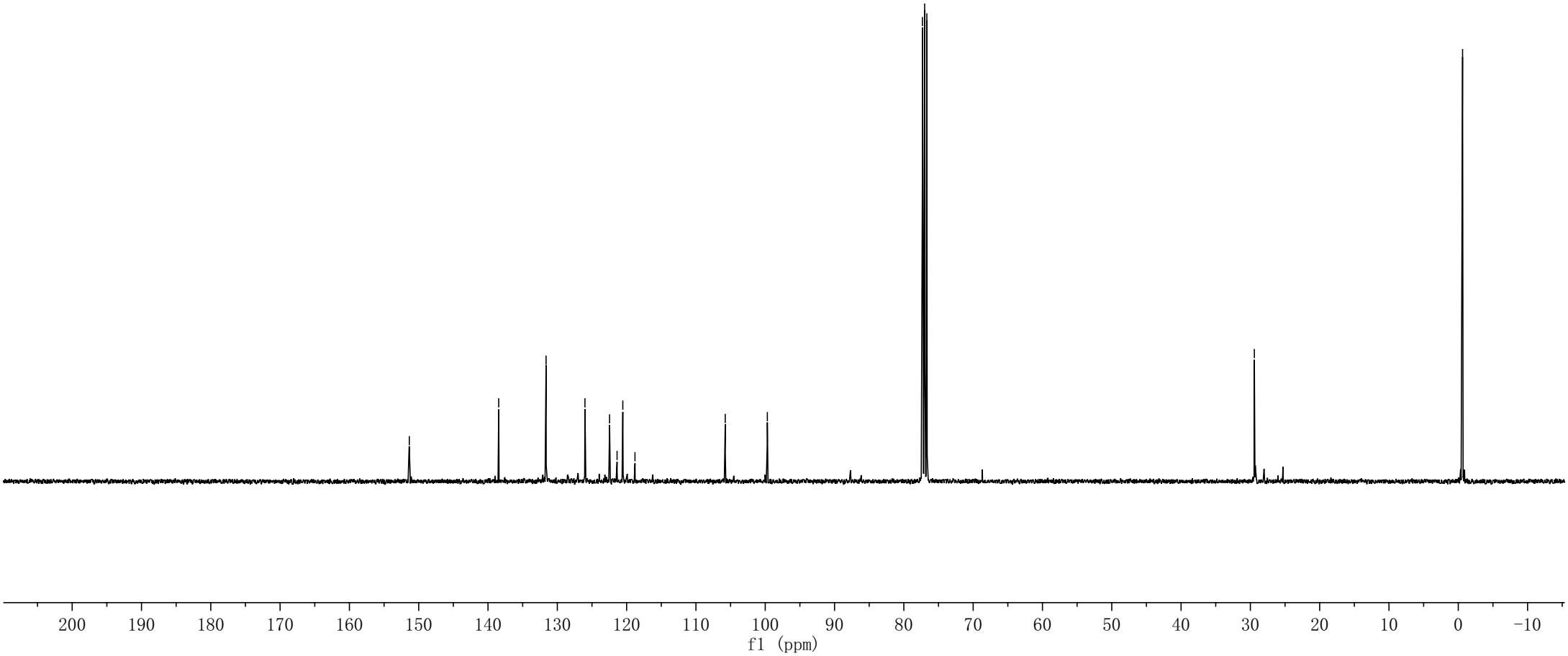
$CDCl_3$, 400 MHz

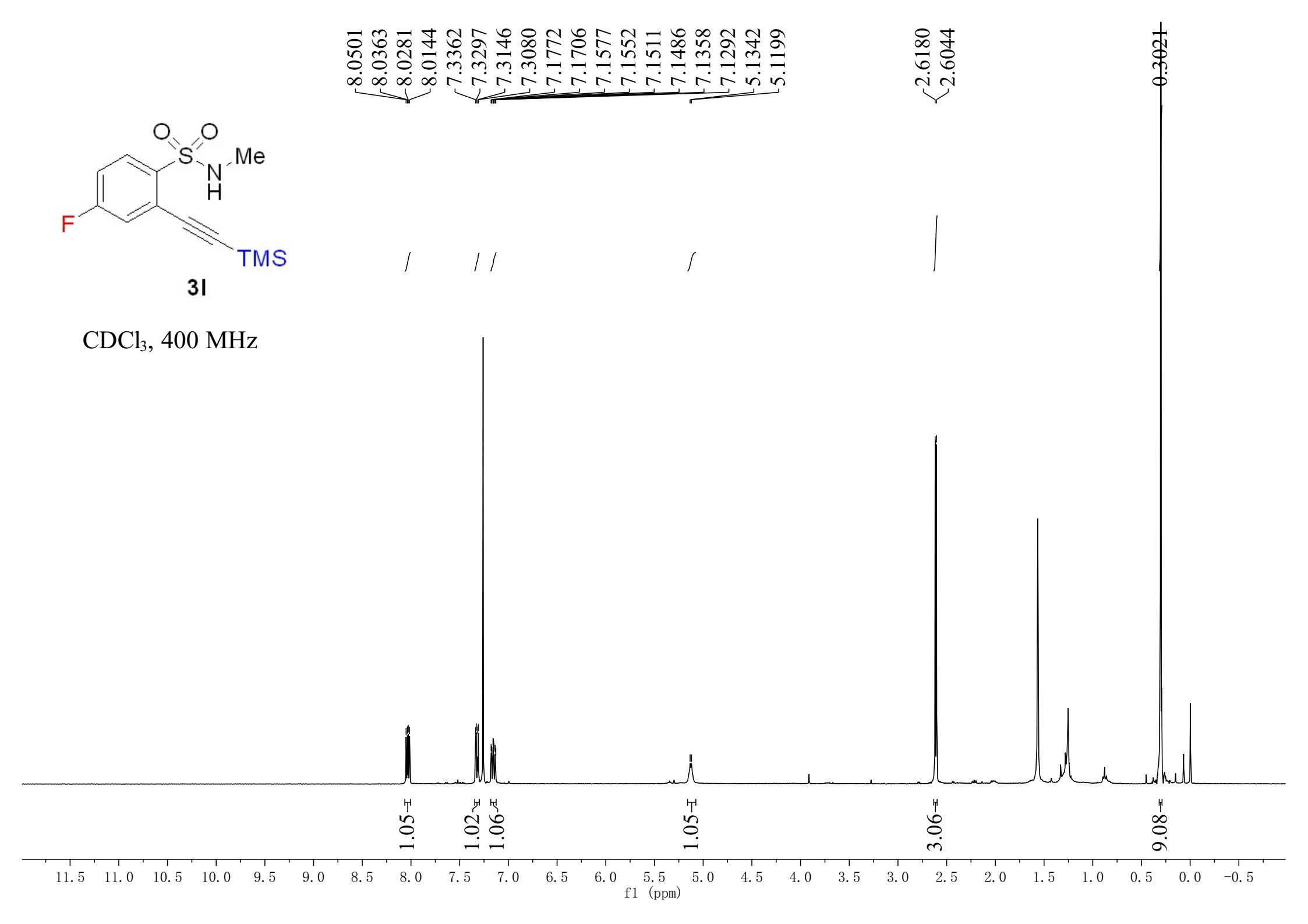


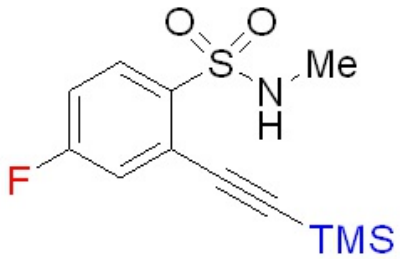
3k

$CDCl_3$, 101 MHz

151.36
138.46
131.62
126.01
122.46
121.38
120.55
118.80
105.77
99.70
77.32
77.00
76.68
29.43
-0.62

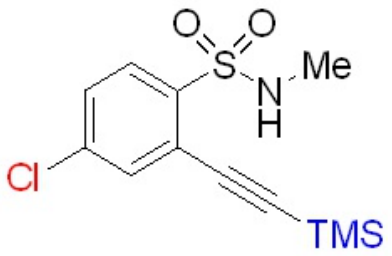



8.0501
8.0363
8.0281
8.0144
7.3362
7.3297
7.3146
7.3080
7.1772
7.1706
7.1577
7.1552
7.1511
7.1486
7.1358
7.1292
5.1342
5.1199
2.6180
2.6044
0.3021
O
O
S
N
H
Me
F
TMS
3l
CDCl3, 400 MHz
1.05
1.02
1.06
1.05
3.06
9.08
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



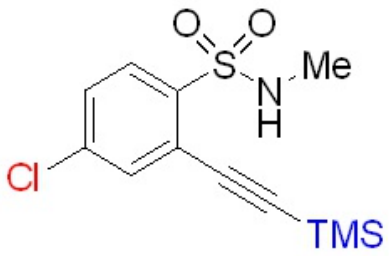
3l

$CDCl_3$, 101 MHz



3m

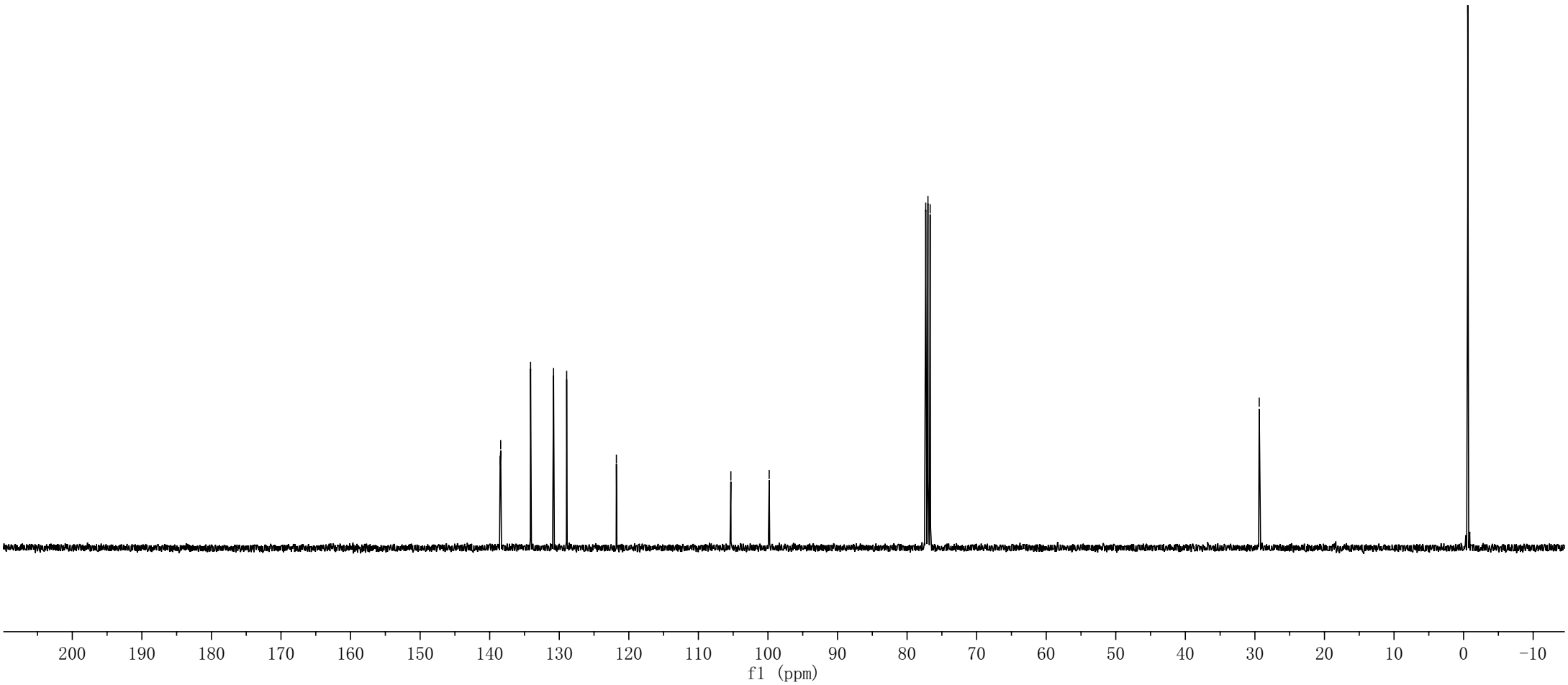
$CDCl_3$, 400 MHz

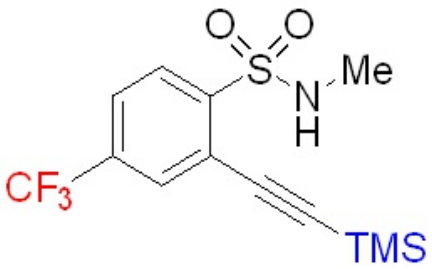


3m

138.50
138.42
134.12
130.82
128.93
121.79
105.33
99.82
77.32
77.00
76.68
29.38
-0.60

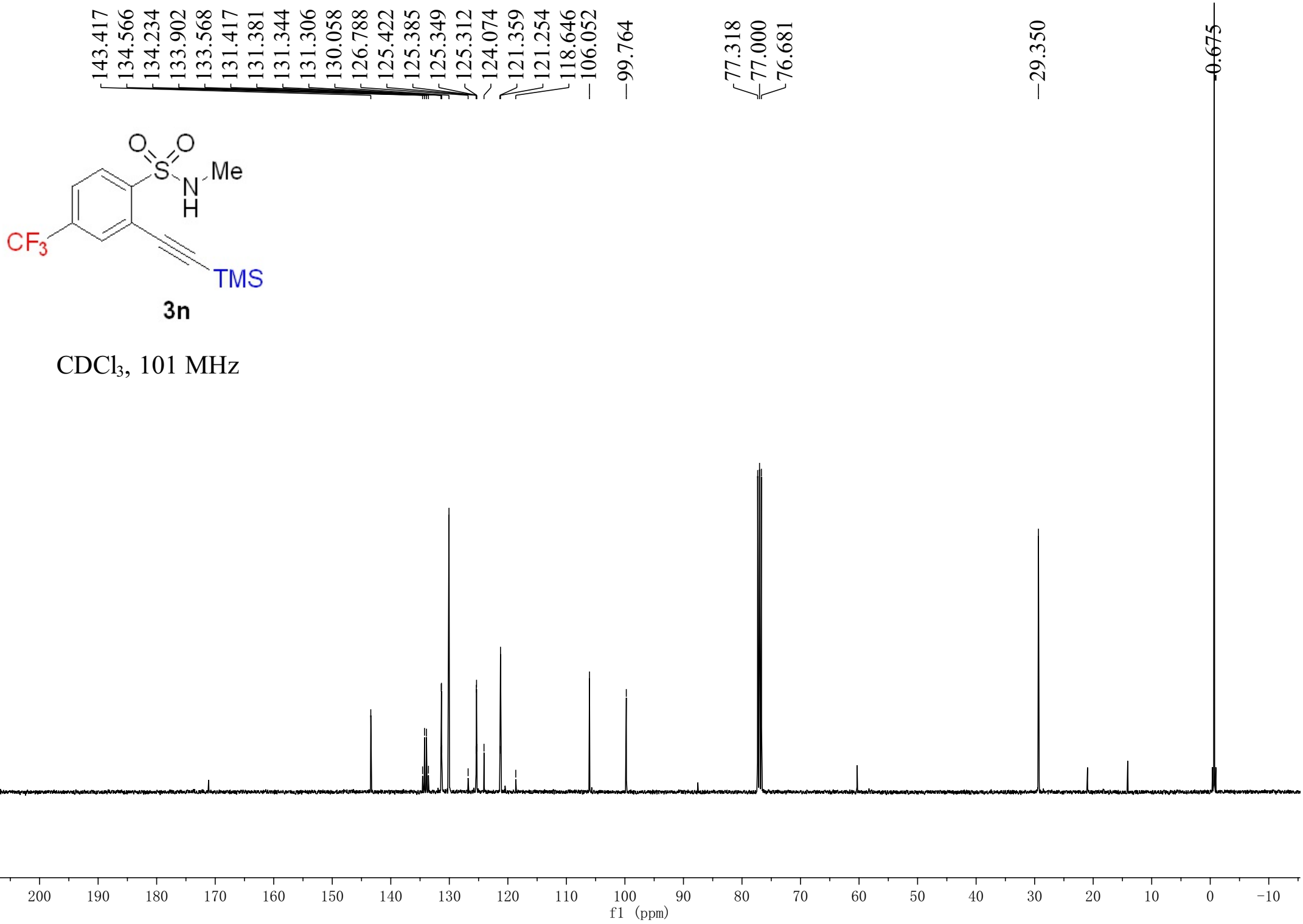
$CDCl_3$, 101 MHz

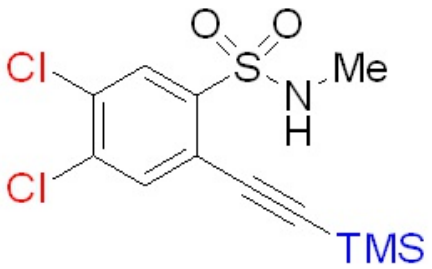




3n

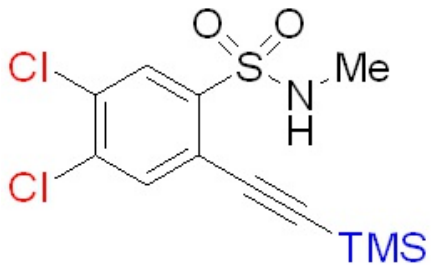
$CDCl_3$, 400 MHz


143.417
134.566
134.234
133.902
133.568
131.417
131.381
131.344
131.306
130.058
126.788
125.422
125.385
125.349
125.312
124.074
121.359
121.254
118.646
106.052
99.764
77.318
77.000
76.681
29.350
0.675
O
O
S
N
H
Me
CF3
TMS
3n
CDCl3, 101 MHz
f1 (ppm)



3o

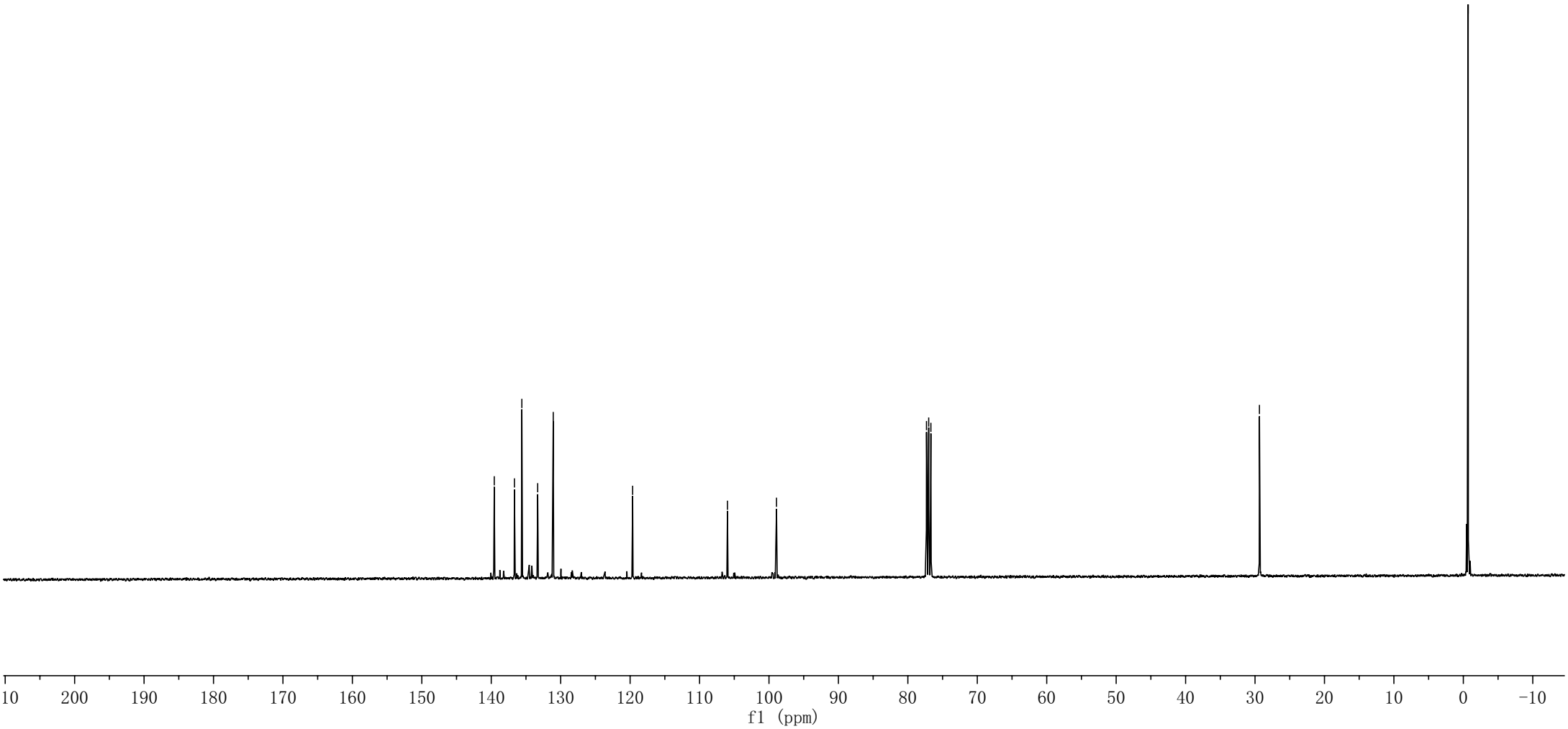
$CDCl_3$, 400 MHz

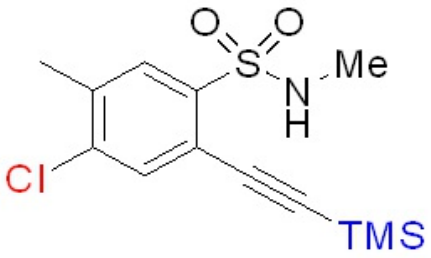


3o

139.57
136.66
135.59
133.31
131.07
119.64
105.98
98.92
77.32
77.00
76.68
29.36
-0.70

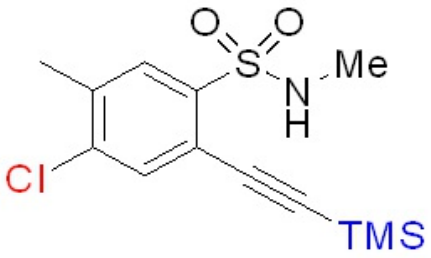
$CDCl_3$, 101 MHz





3p

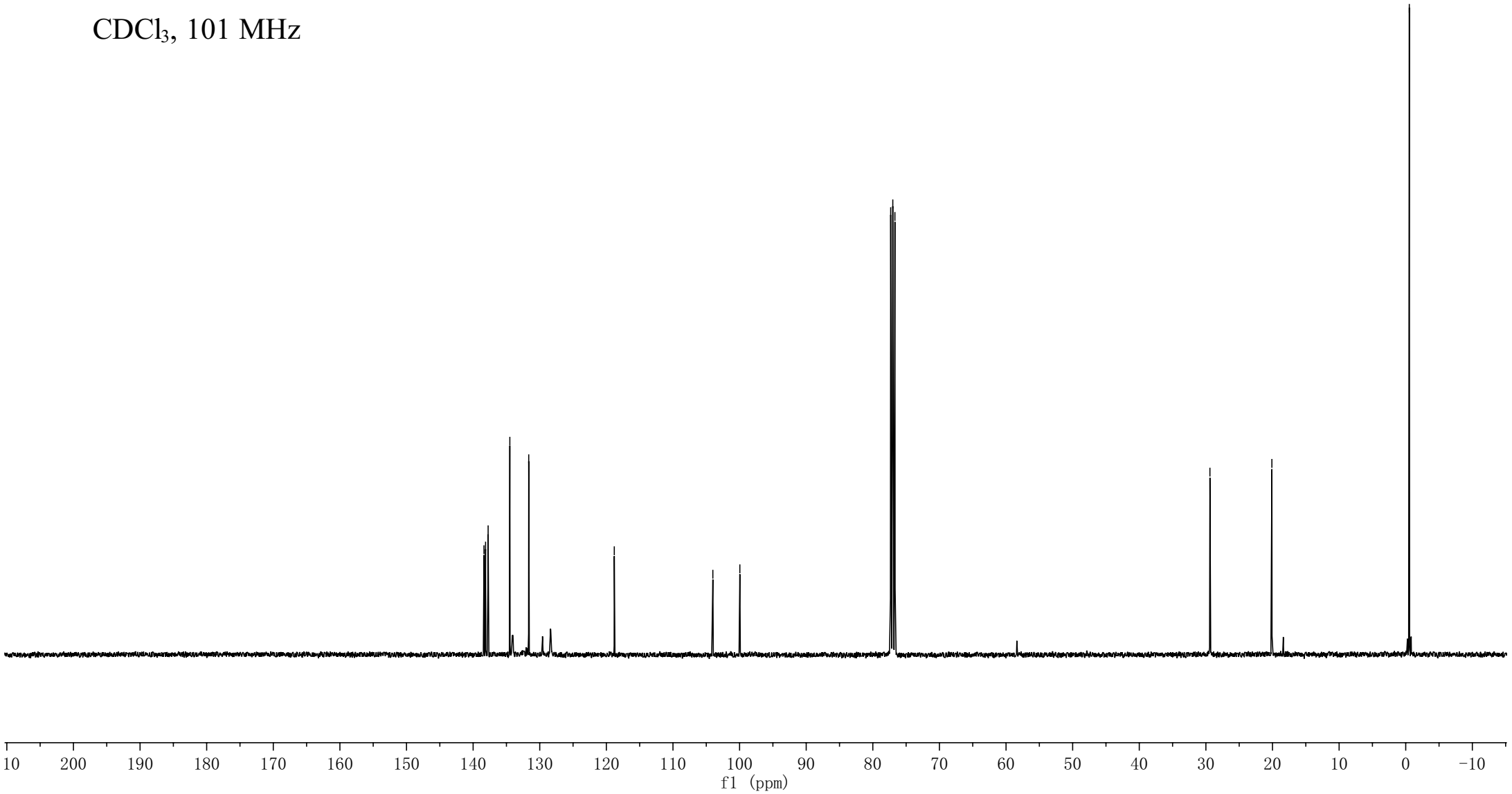
$CDCl_3$, 400 MHz

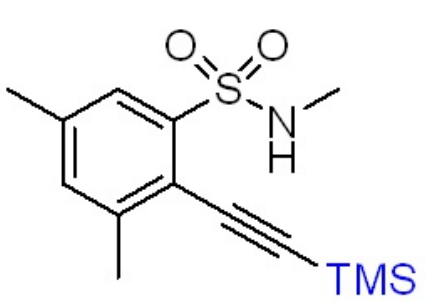


3p

138.37
138.13
137.75
134.49
131.65
118.81
104.01
99.96
77.32
77.00
76.68
29.39
20.09
-0.54

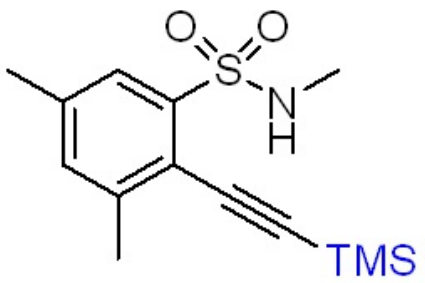
$CDCl_3$, 101 MHz





3q

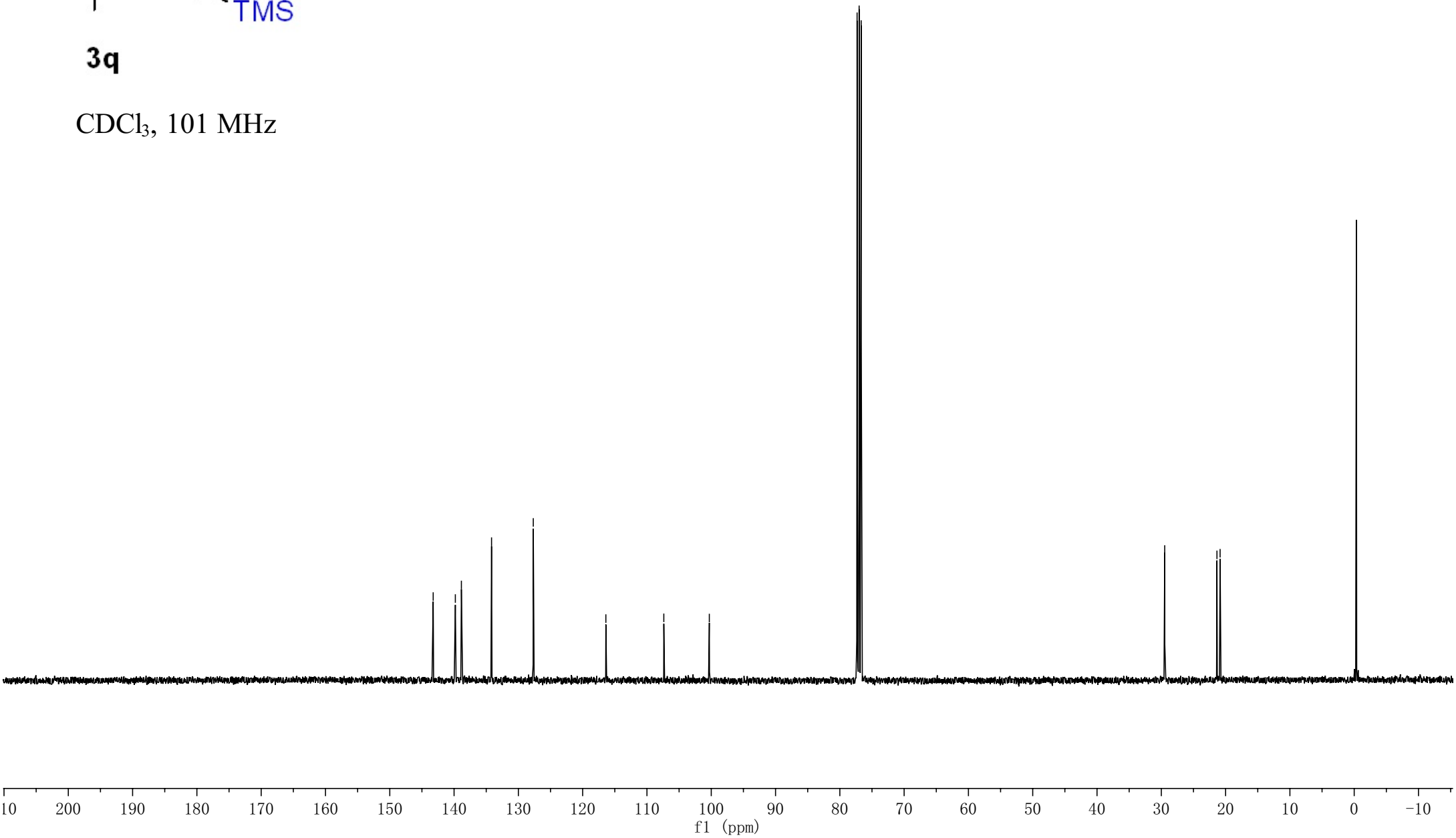
$CDCl_3$, 400 MHz

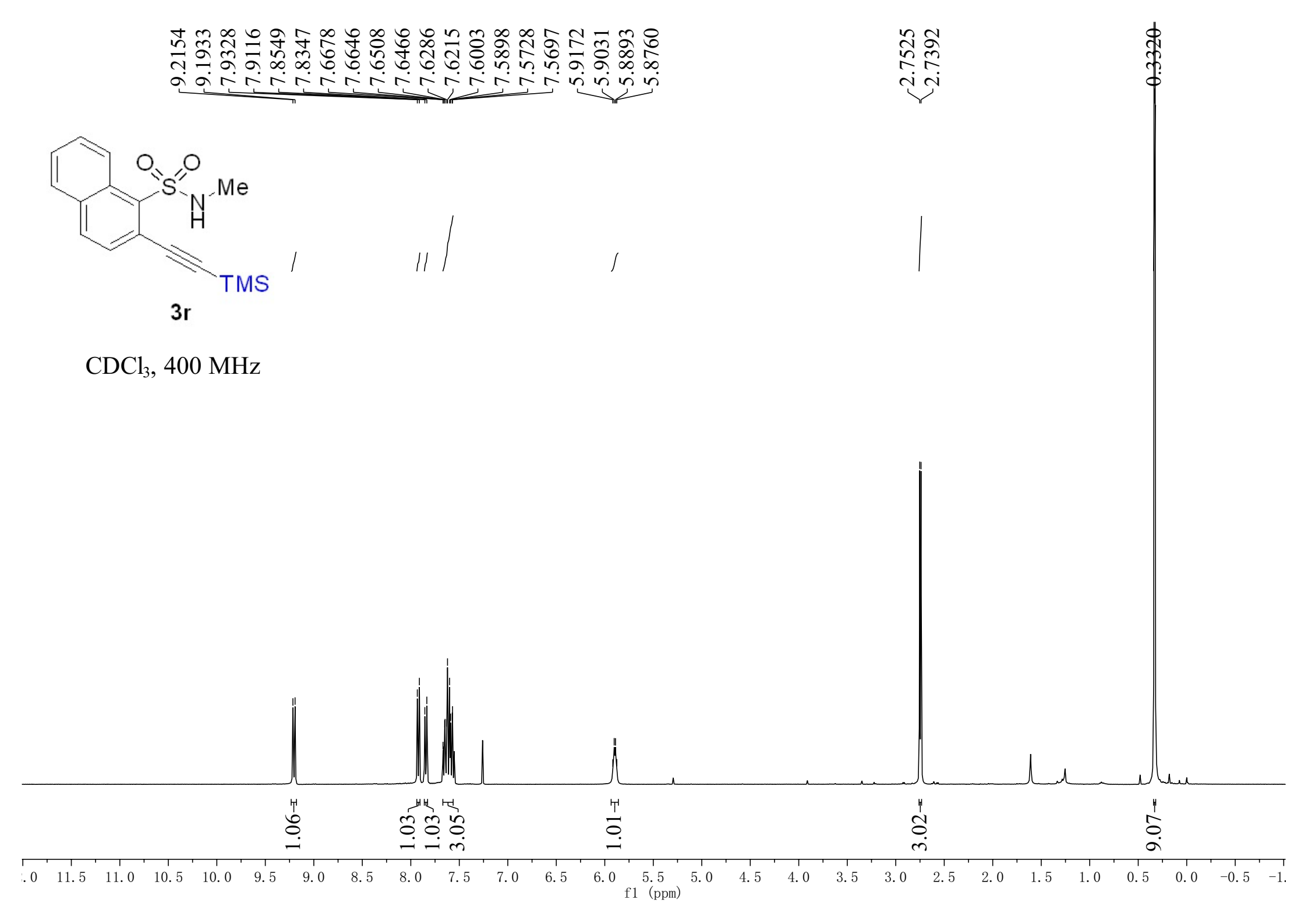


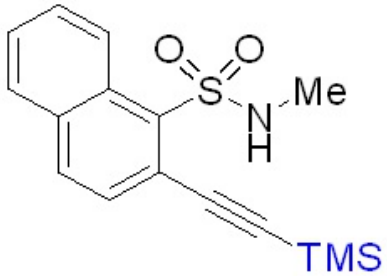
3q

$CDCl_3$, 101 MHz

143.25
139.80
138.86
134.17
127.68
116.39
107.38
100.30
77.32
77.00
76.68
29.47
21.35
20.86
-0.34

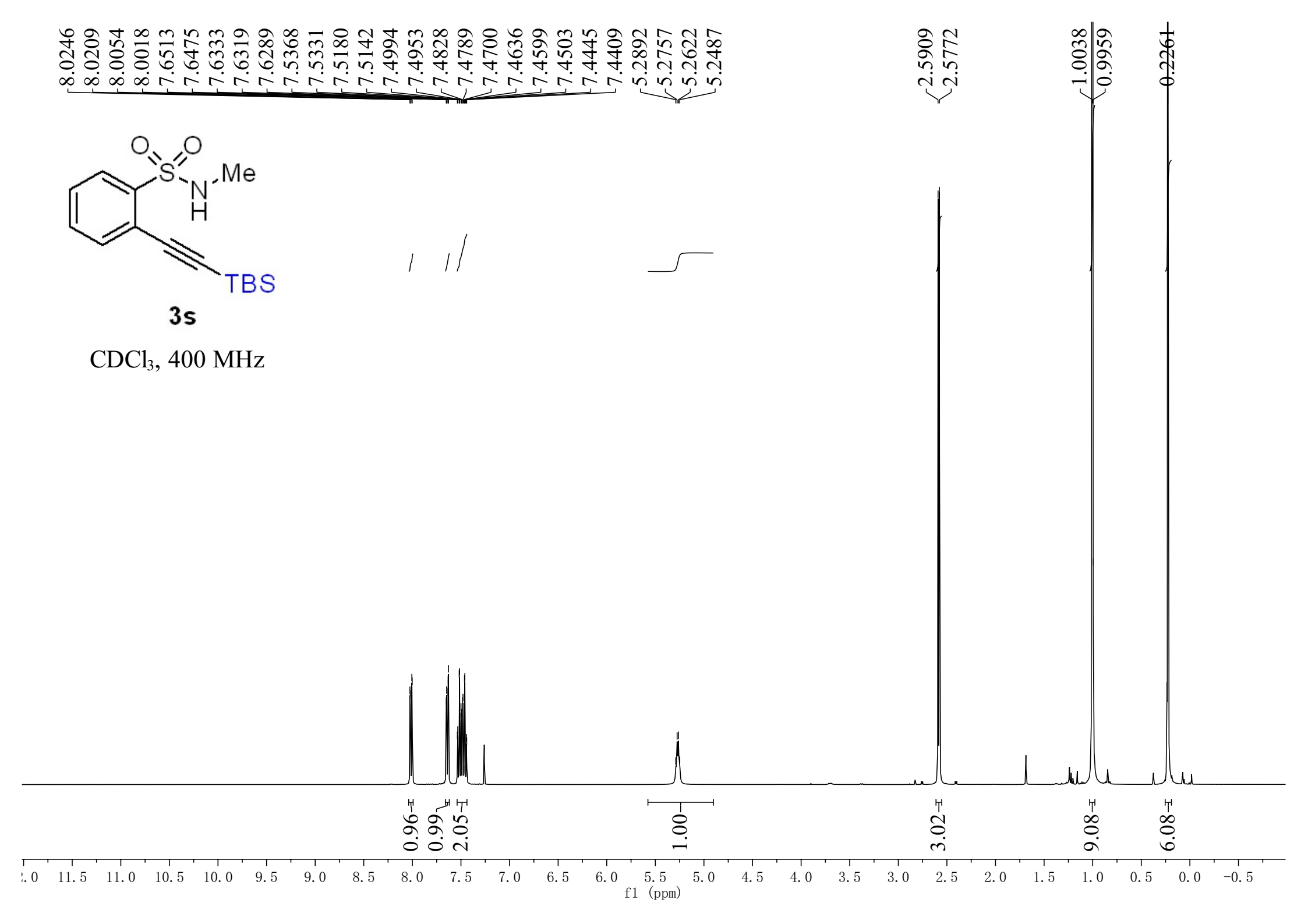



9.2154
9.1933
7.9328
7.9116
7.8549
7.8347
7.6678
7.6646
7.6508
7.6466
7.6286
7.6215
7.6003
7.5898
7.5728
7.5697
5.9172
5.9031
5.8893
5.8760
2.7525
2.7392
0.3320
O
O
S
N
H
Me
TMS
3r
CDCl3, 400 MHz
1.06
1.03
1.03
3.05
1.01
3.02
9.07
f1 (ppm)



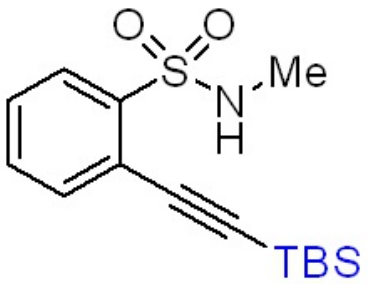
3r

$CDCl_3$, 101 MHz



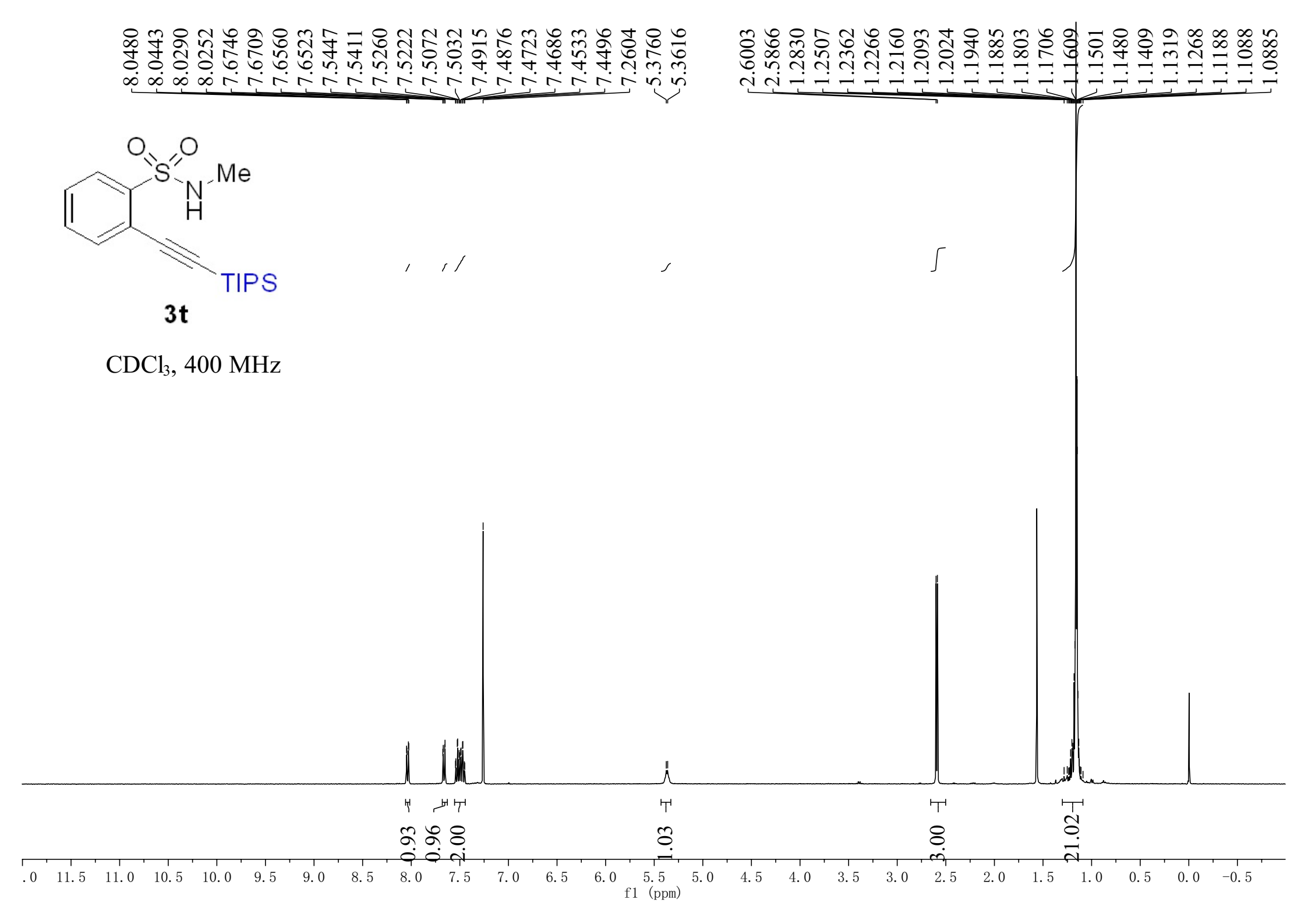
3s

$CDCl_3$, 400 MHz



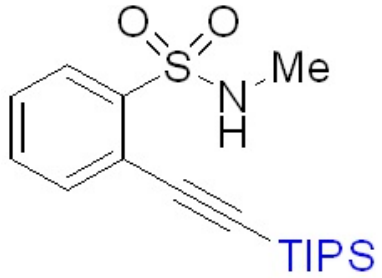
3s

$CDCl_3$, 101 MHz



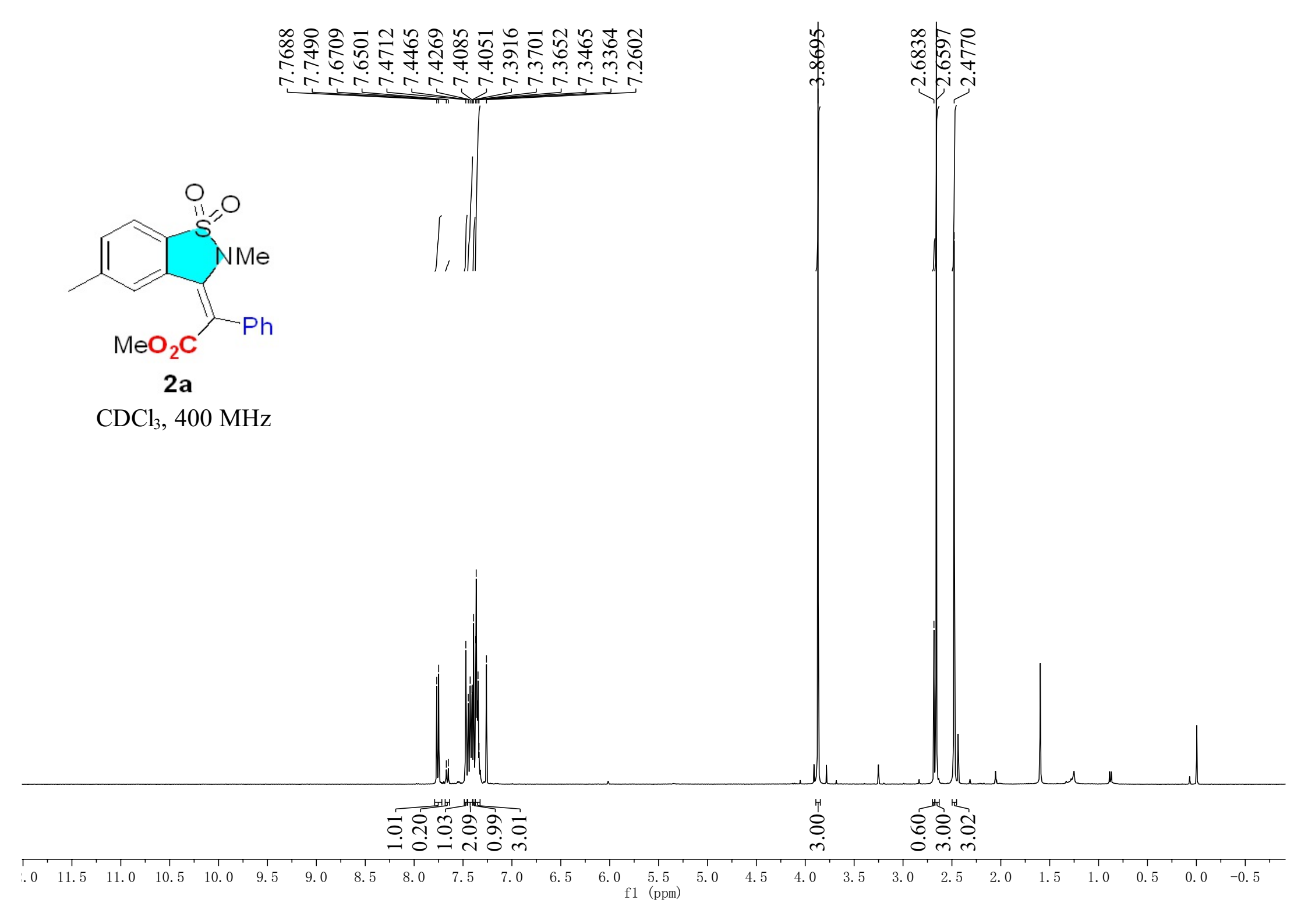
3t

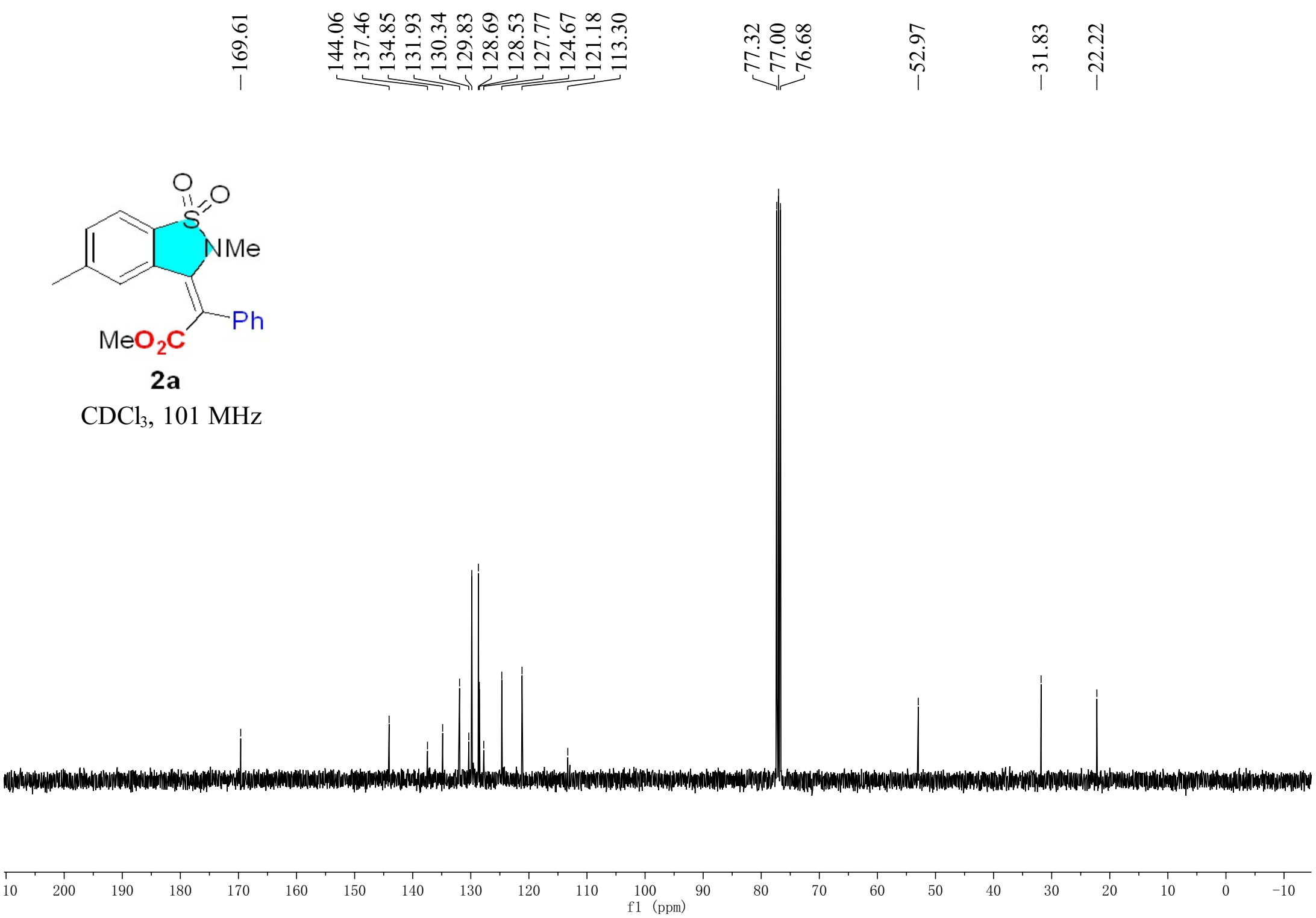
$CDCl_3$, 400 MHz

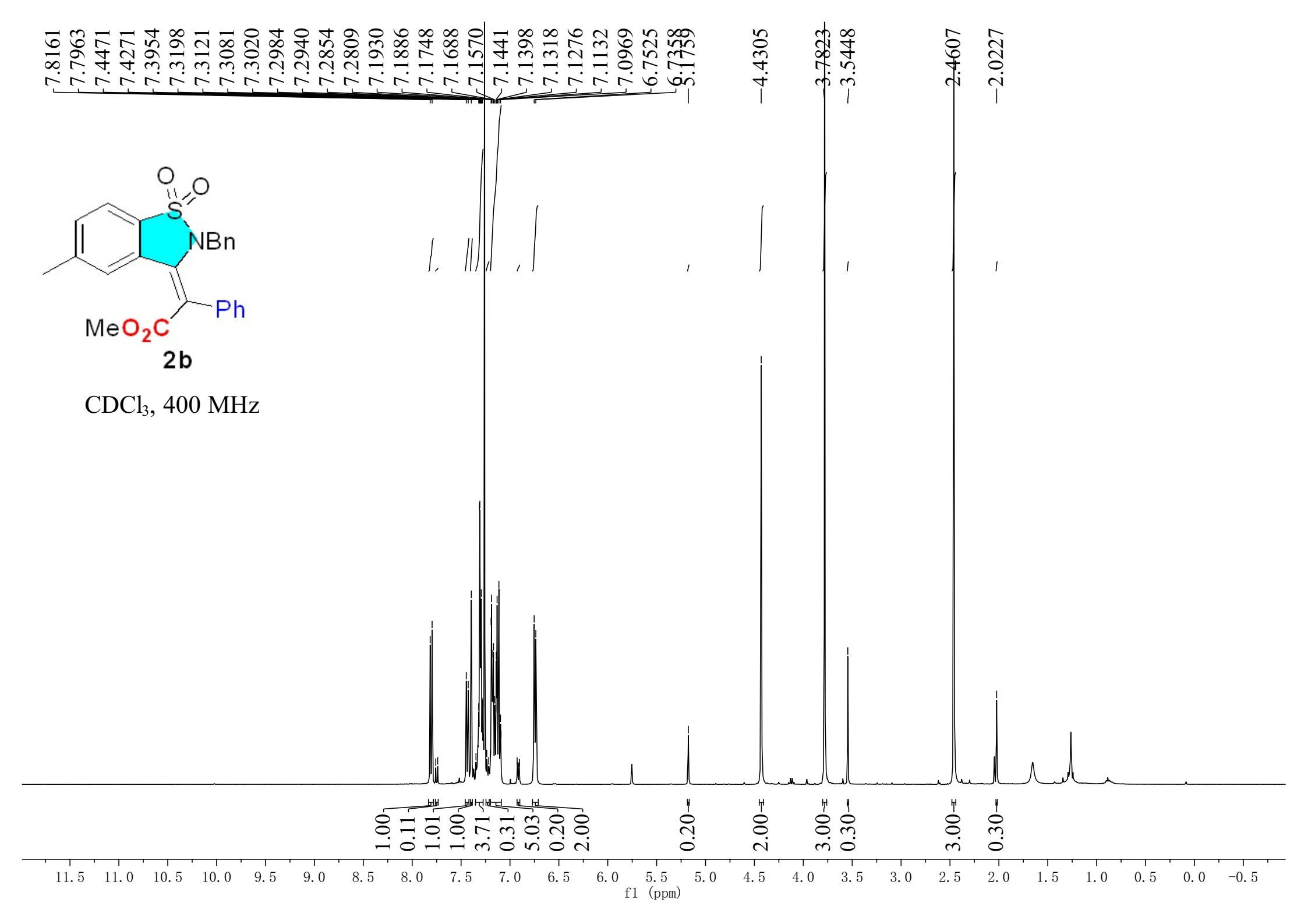


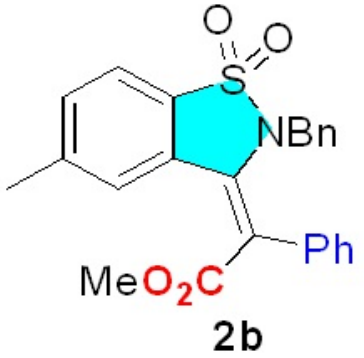
3t

$CDCl_3$, 101 MHz


7.7688
7.7490
7.6709
7.6501
7.4712
7.4465
7.4269
7.4085
7.4051
7.3916
7.3701
7.3652
7.3465
7.3364
7.2602
3.8695
2.6838
2.6597
2.4770
O
O
S
NMe
Ph
MeO2C
2a
CDCl3, 400 MHz
1.01
0.20
1.03
2.09
0.99
3.01
3.00
0.60
3.00
3.02
f1 (ppm)

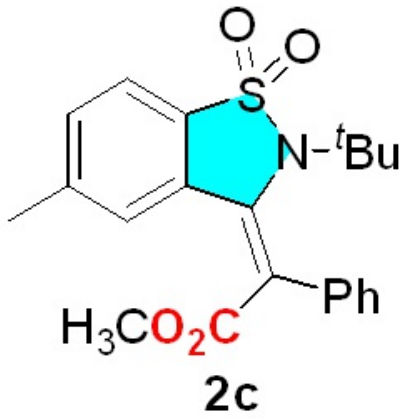

169.61
144.06
137.46
134.85
131.93
130.34
129.83
128.69
128.53
127.77
124.67
121.18
113.30
77.32
77.00
76.68
52.97
31.83
22.22
O
O
S
NMe
Ph
MeO2C
2a
CDCl3, 101 MHz
f1 (ppm)


7.8161
7.7963
7.4471
7.4271
7.3954
7.3198
7.3121
7.3081
7.3020
7.2984
7.2940
7.2854
7.2809
7.1930
7.1886
7.1748
7.1688
7.1570
7.1441
7.1398
7.1318
7.1276
7.1132
7.0969
6.7525
6.7358
5.1759
4.4305
3.7823
3.5448
2.4607
2.0227
O
O
S
NBn
Ph
MeO2C
2b
CDCl3, 400 MHz
1.00
0.11
1.01
1.00
3.71
0.31
5.03
0.20
2.00
0.20
2.00
3.00
0.30
3.00
0.30
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



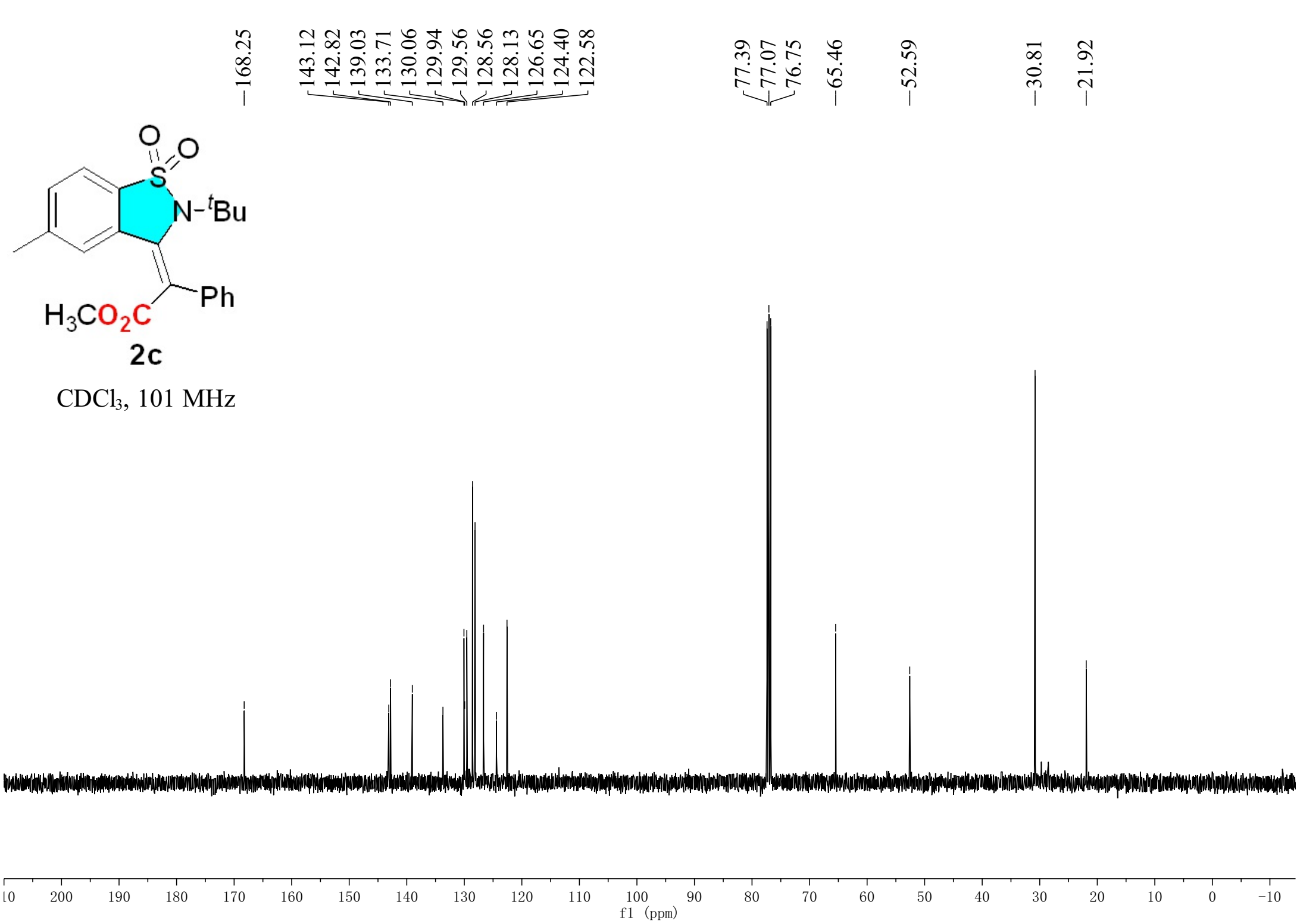
2b

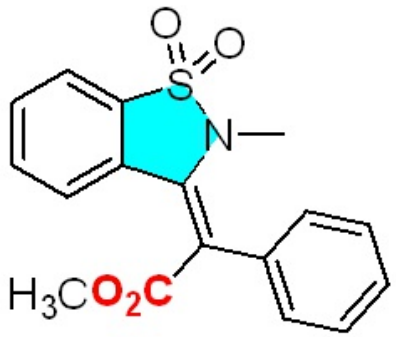
$CDCl_3$, 101 MHz



2c

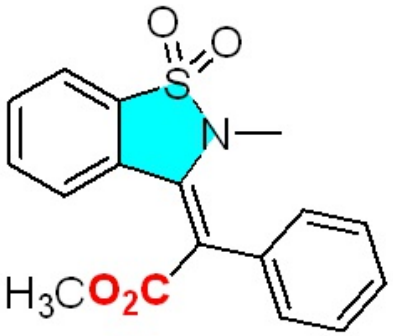
$CDCl_3$, 400 MHz


168.25
143.12
142.82
139.03
133.71
130.06
129.94
129.56
128.56
128.13
126.65
124.40
122.58
77.39
77.07
76.75
65.46
52.59
30.81
21.92
O
O
S
N-tBu
Ph
H3CO2C
2c
CDCl3, 101 MHz
f1 (ppm)



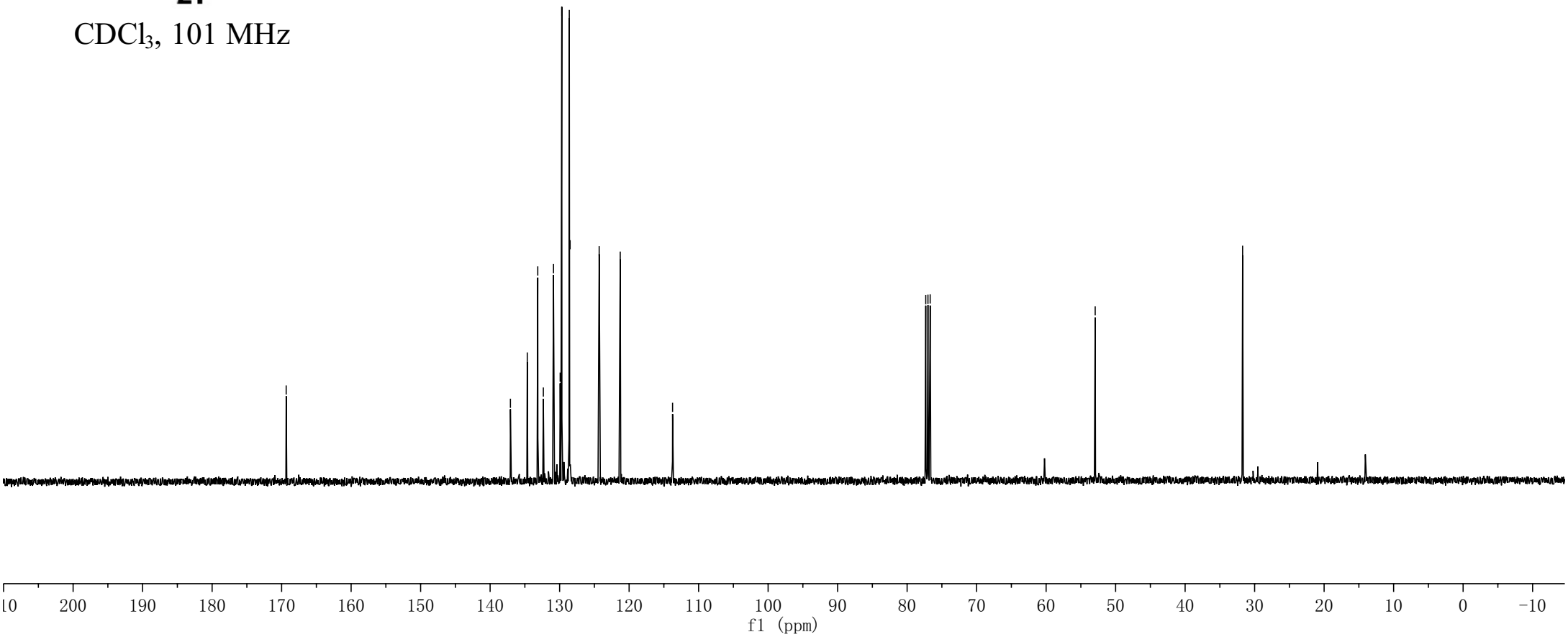
2f

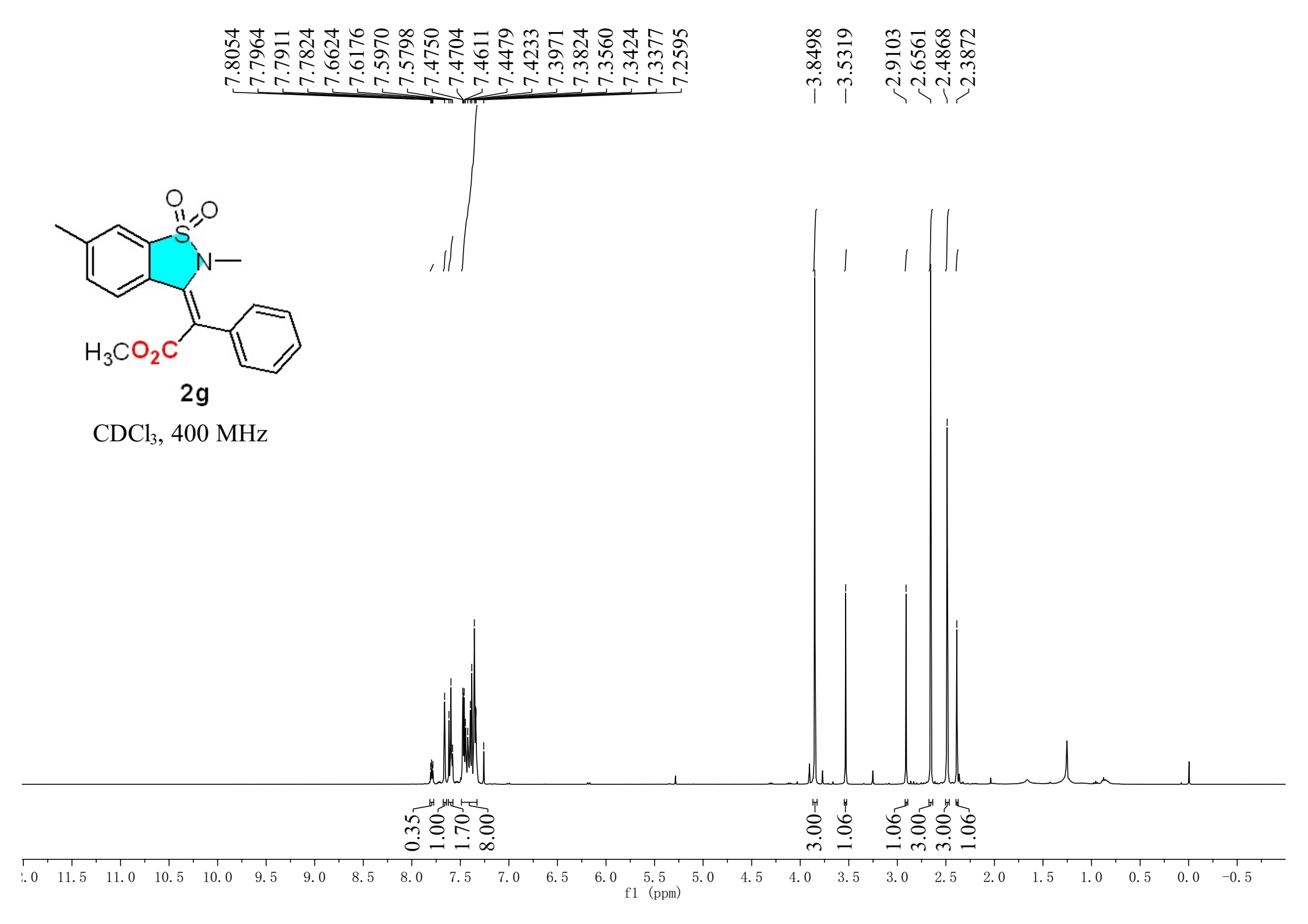
$CDCl_3$, 400 MHz



2f

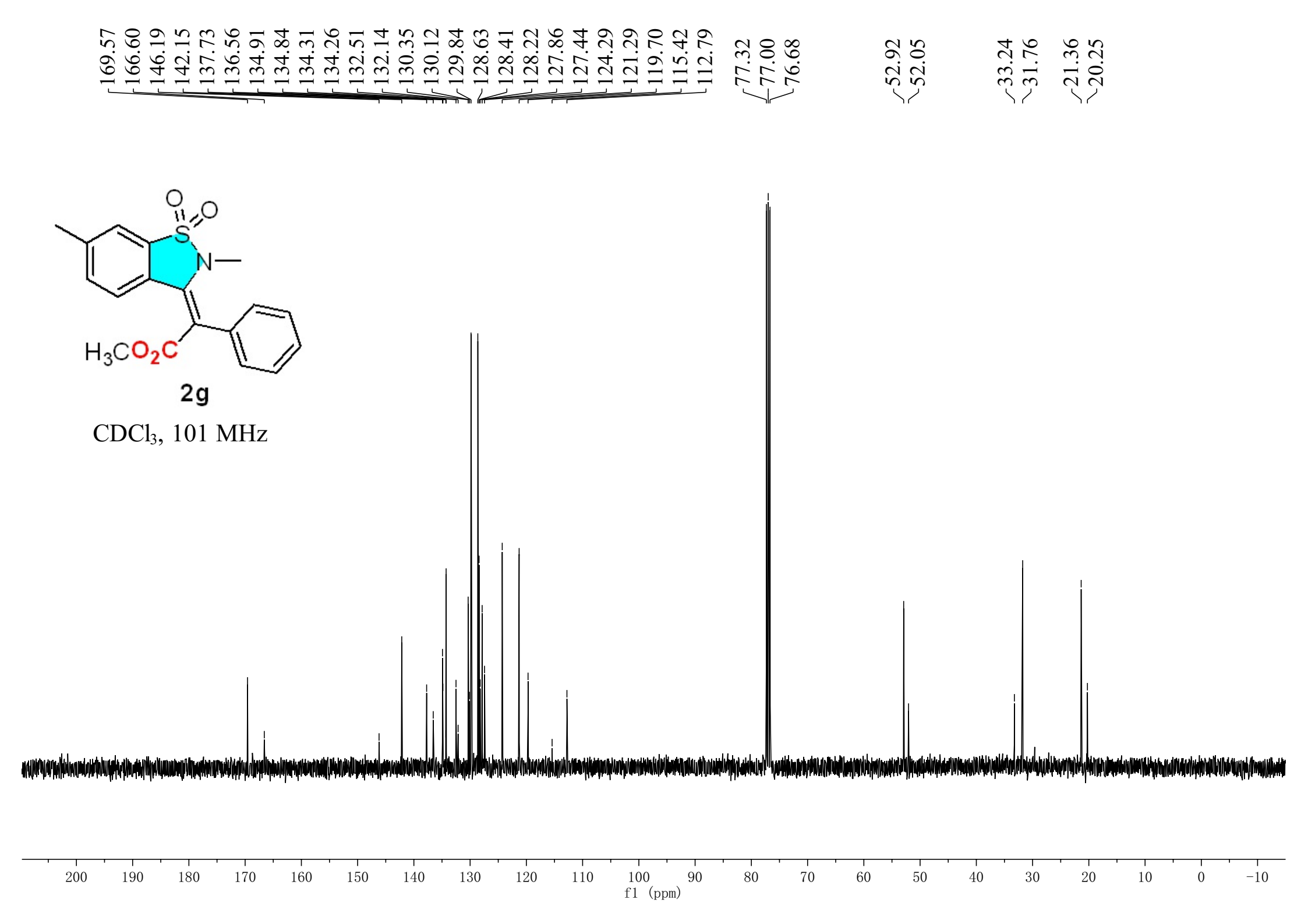
$CDCl_3$, 101 MHz

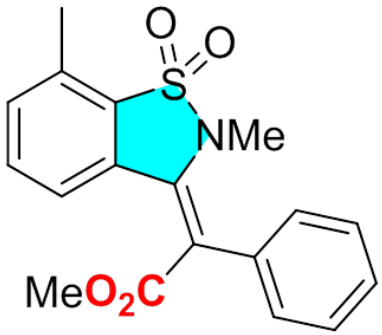




2g

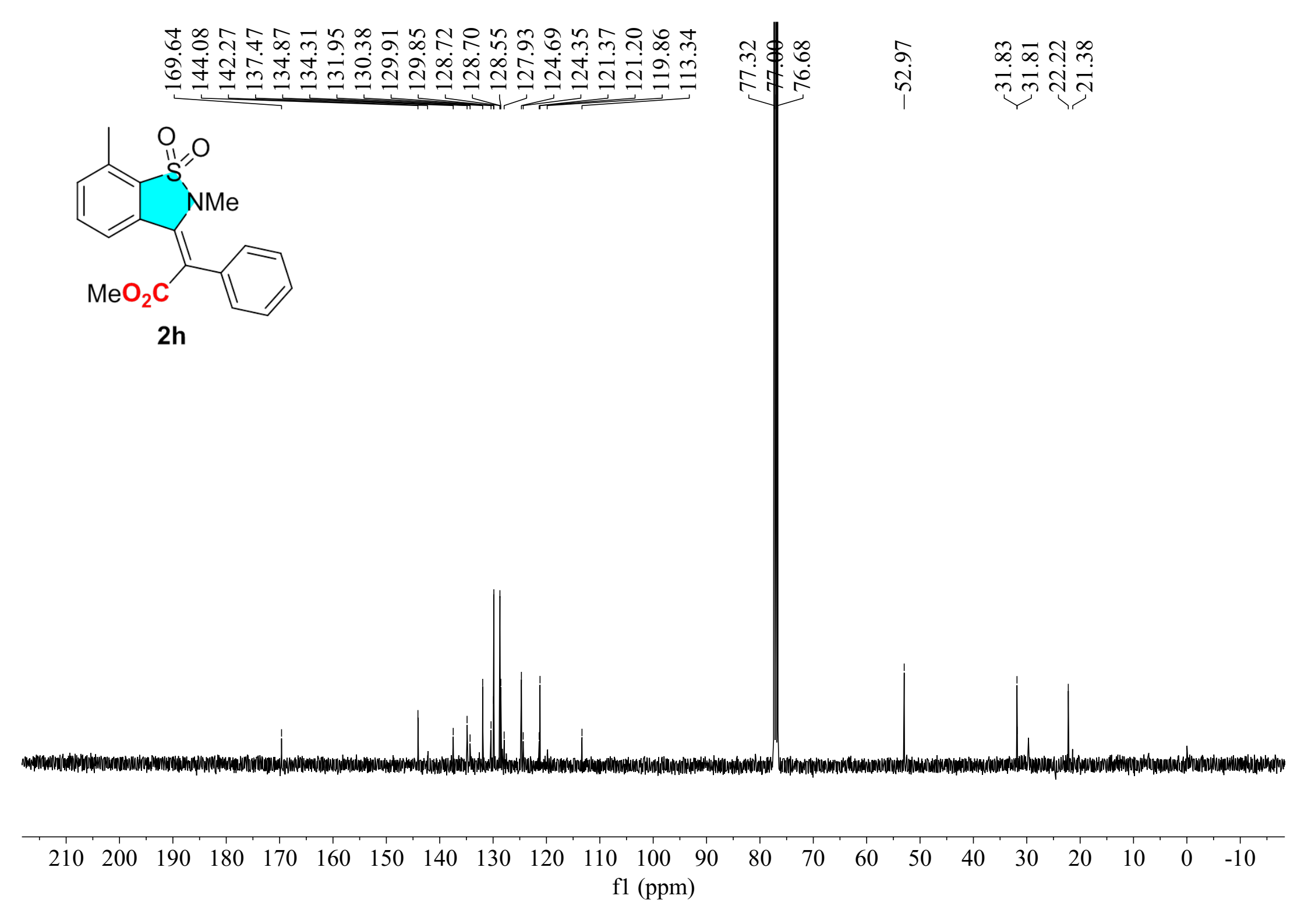
$CDCl_3$, 400 MHz

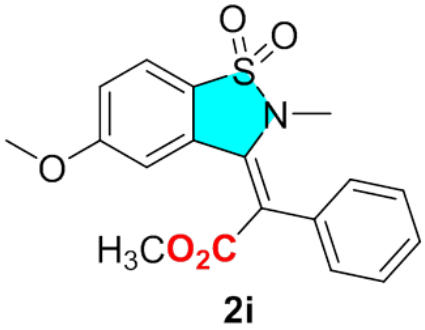

169.57
166.60
146.19
142.15
137.73
136.56
134.91
134.84
134.31
134.26
132.51
132.14
130.35
130.12
129.84
128.63
128.41
128.22
127.86
127.44
124.29
121.29
119.70
115.42
112.79
77.32
77.00
76.68
52.92
52.05
33.24
31.76
21.36
20.25
O
O
S
N
H3CO2C
2g
CDCl3, 101 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
O
S
NMe
MeO2C

2h

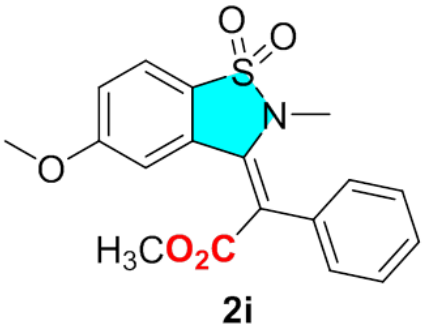
7.7729
7.7530
7.6699
7.6206
7.6001
7.5828
7.4842
7.4769
7.4718
7.4497
7.4307
7.4268
7.4127
7.4085
7.3949
7.3900
7.3811
7.3742
7.3688
7.3589
7.3507
7.2629
3.8726
3.8575
2.6623
2.4988
2.4813
1.00
0.30
0.65
6.00
3.01
3.00
0.90
3.90
0.92
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.
f1 (ppm)


169.64
144.08
142.27
137.47
134.87
134.31
131.95
130.38
129.91
129.85
128.72
128.70
128.55
127.93
124.69
124.35
121.37
121.20
119.86
113.34
77.32
77.00
76.68
52.97
31.83
31.81
22.22
21.38
O
O
S
NMe
MeO2C
2h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



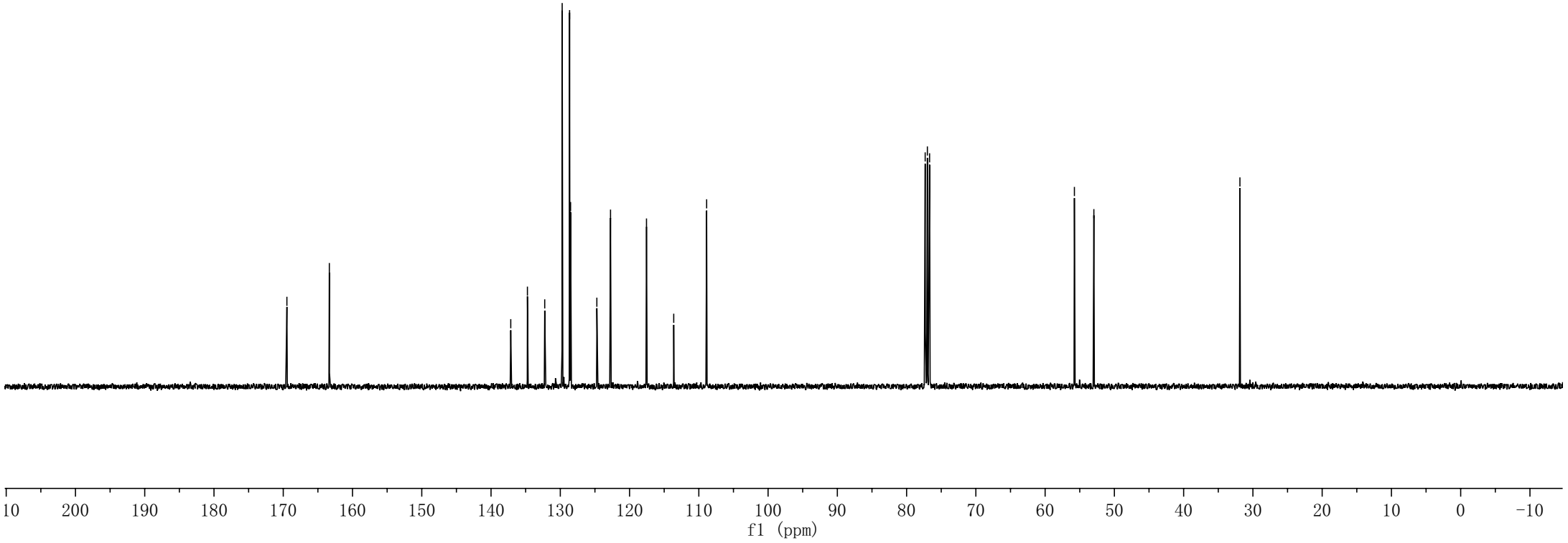
2i

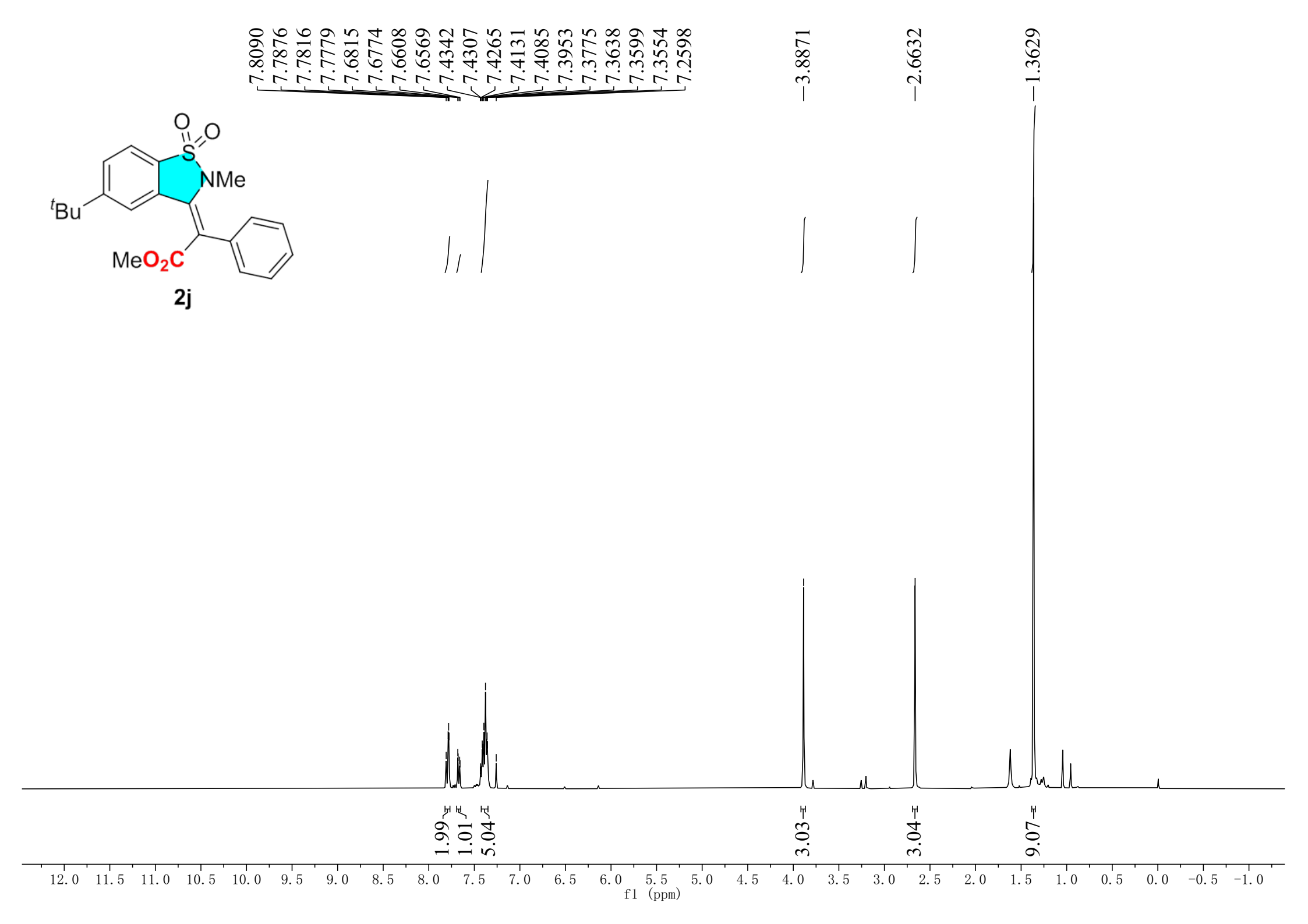
$CDCl_3$, 400 MHz

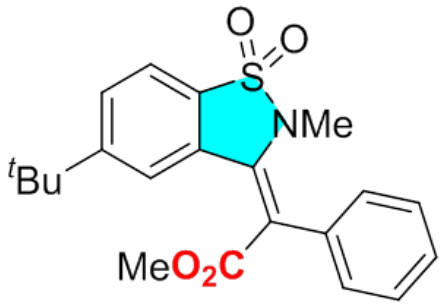


2i

$CDCl_3$, 101 MHz

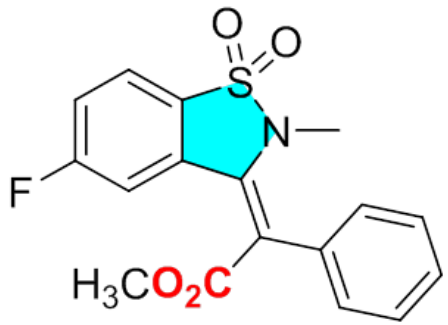



7.8090
7.7876
7.7816
7.7779
7.6815
7.6774
7.6608
7.6569
7.4342
7.4307
7.4265
7.4131
7.4085
7.3953
7.3775
7.3638
7.3599
7.3554
7.2598
3.8871
2.6632
1.3629
O
O
S
NMe
tBu
MeO2C
2j
1.99
1.01
5.04
3.03
3.04
9.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


O
O
S
NMe
tBu
MeO2C

2j

169.71
157.17
137.36
134.83
130.06
129.77
129.72
128.73
128.71
128.52
121.09
120.97
113.21
77.32
77.00
76.68
53.03
35.63
31.86
31.10
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



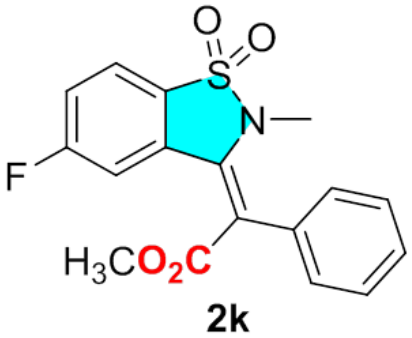
2k

$CDCl_3$, 400 MHz

7.8823
7.8699
7.8609
7.8485
7.4435
7.4382
7.4192
7.4144
7.4009
7.3863
7.3825
7.3664
7.3619
7.3464
7.3337
7.3283
7.3130
7.3077
7.2605
3.8759
2.6595

1.00
4.00
3.10
3.00
3.00

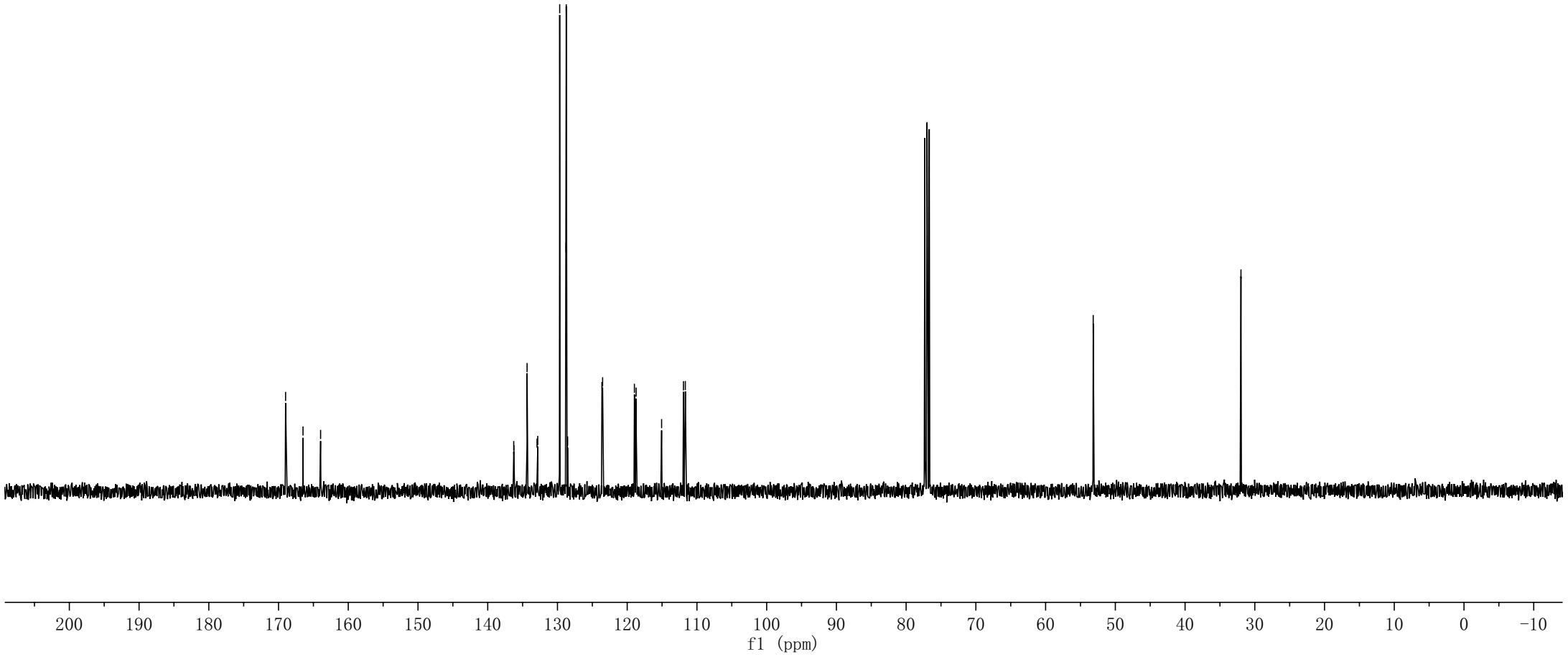
f1 (ppm)

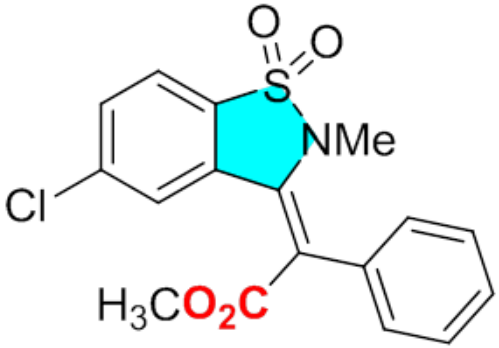


2k

$CDCl_3$, 101 MHz

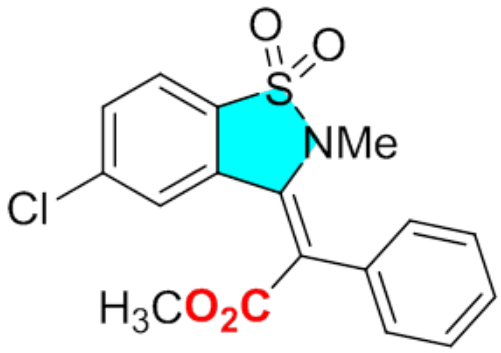
168.9891
166.4900
163.9679
136.2728
136.2424
134.3577
132.9300
132.8291
129.6819
128.7813
128.7410
128.5732
128.5456
123.6263
123.5263
118.9655
118.7220
115.0665
111.9314
111.6644
53.1725
31.9843





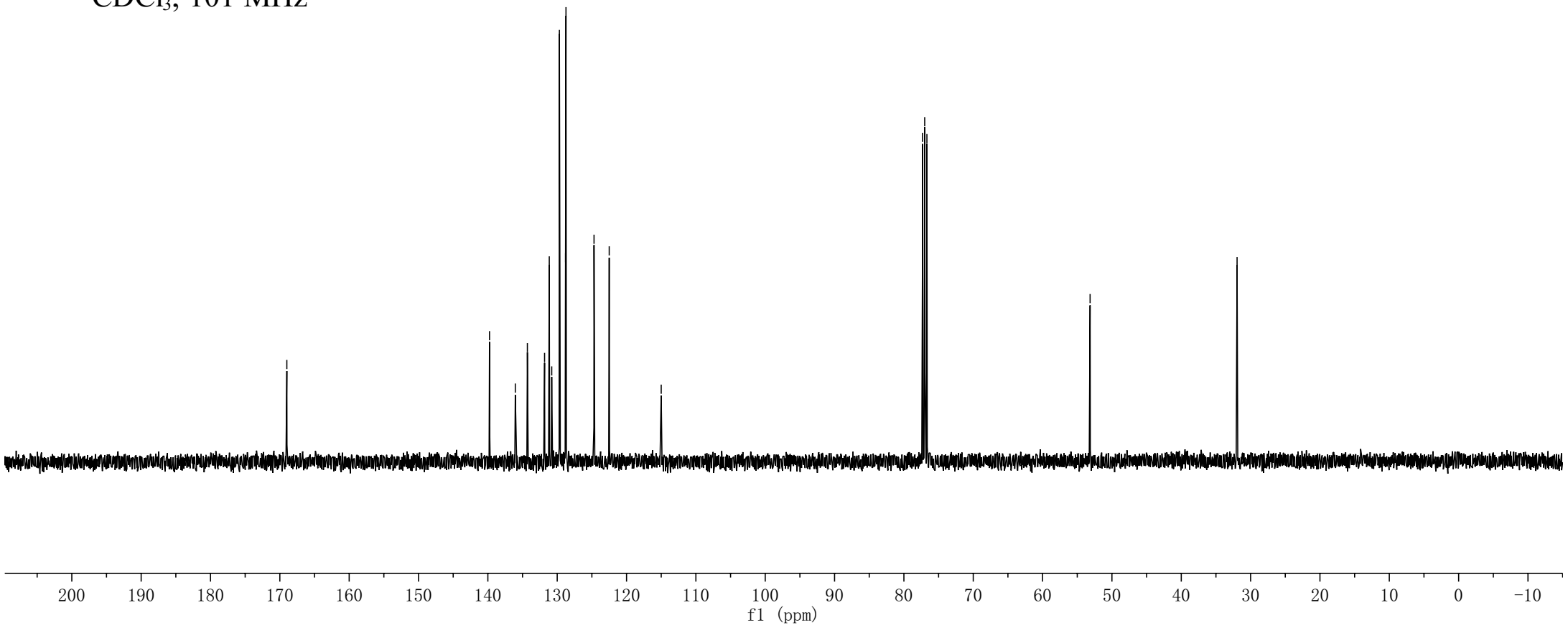
2l

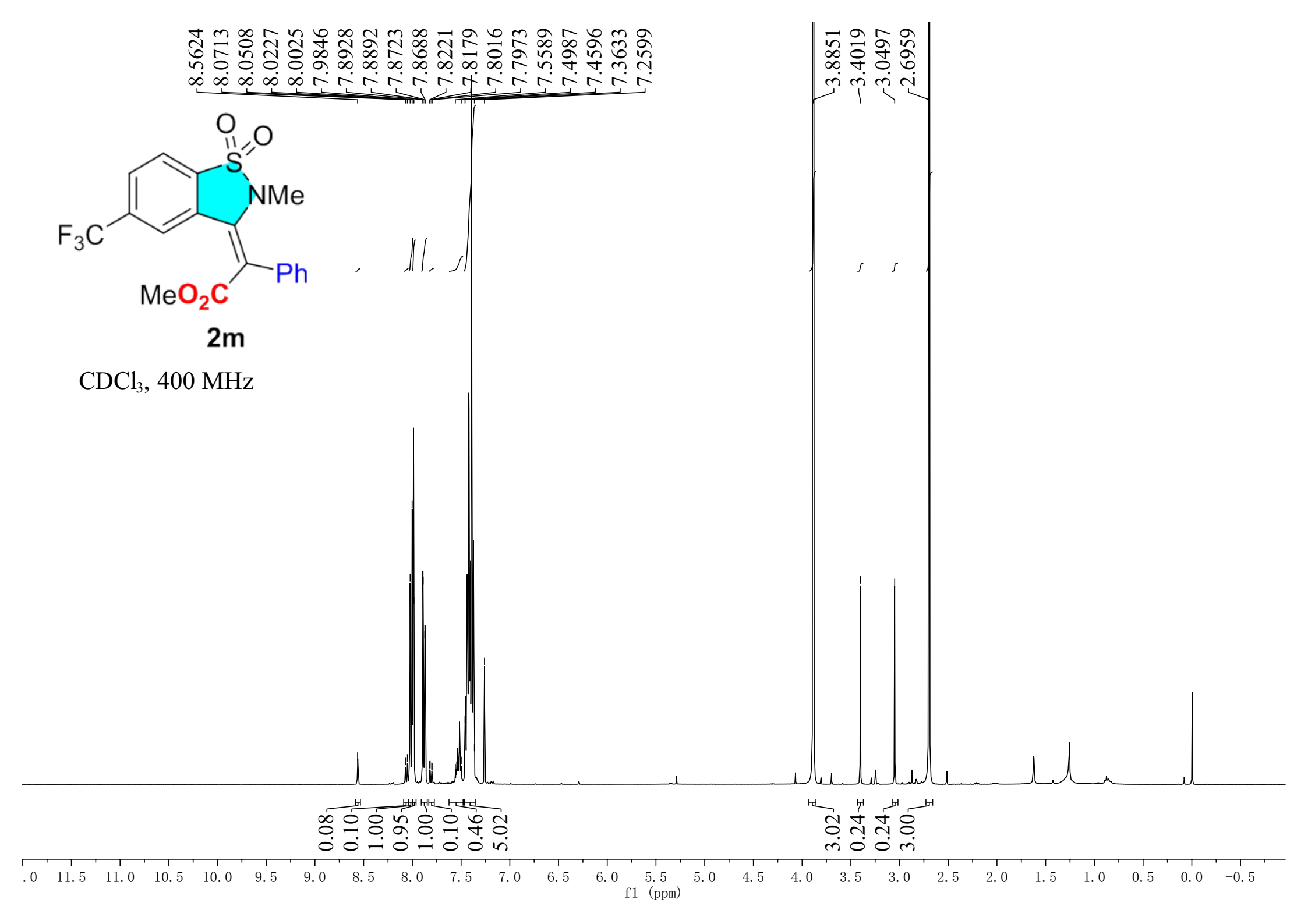
$CDCl_3$, 400 MHz



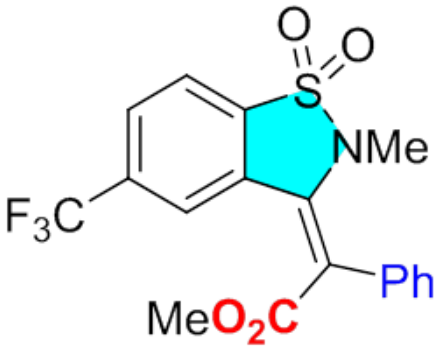
2l

$CDCl_3$, 101 MHz



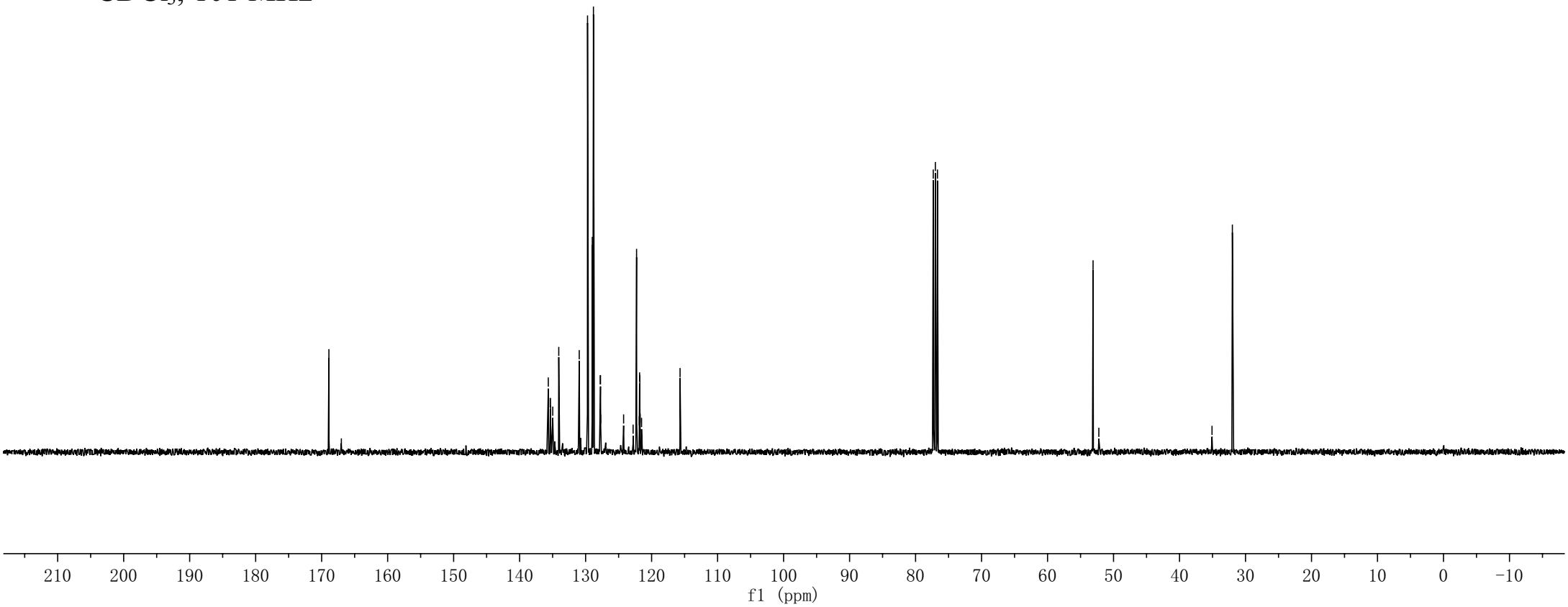

8.5624
8.0713
8.0508
8.0227
8.0025
7.9846
7.8928
7.8892
7.8723
7.8688
7.8221
7.8179
7.8016
7.7973
7.5589
7.4987
7.4596
7.3633
7.2599
3.8851
3.4019
3.0497
2.6959
O
O
S
NMe
F3C
Ph
MeO2C
2m
CDCl3, 400 MHz
0.08
0.10
1.00
0.95
1.00
0.10
0.46
5.02
3.02
0.24
0.24
3.00
f1 (ppm)

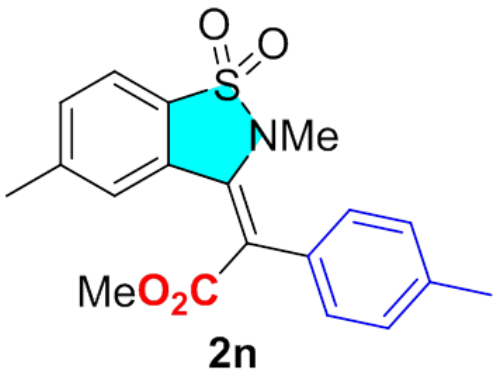
168.9006
167.0132
135.6553
135.3602
135.3494
135.3085
134.9798
134.0698
130.9648
129.7087
128.9874
128.8627
128.8132
127.8159
127.7805
127.7460
127.7119
124.2418
122.8042
122.2784
121.8649
121.8231
121.7812
121.7401
121.5235
115.6879
77.3187
77.0008
76.6828
53.1029
52.2273
35.0769
31.9927



2m

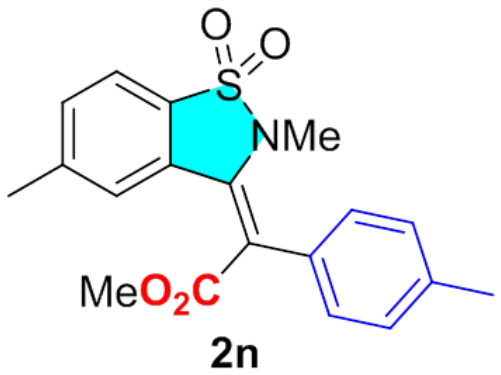
$CDCl_3$, 101 MHz





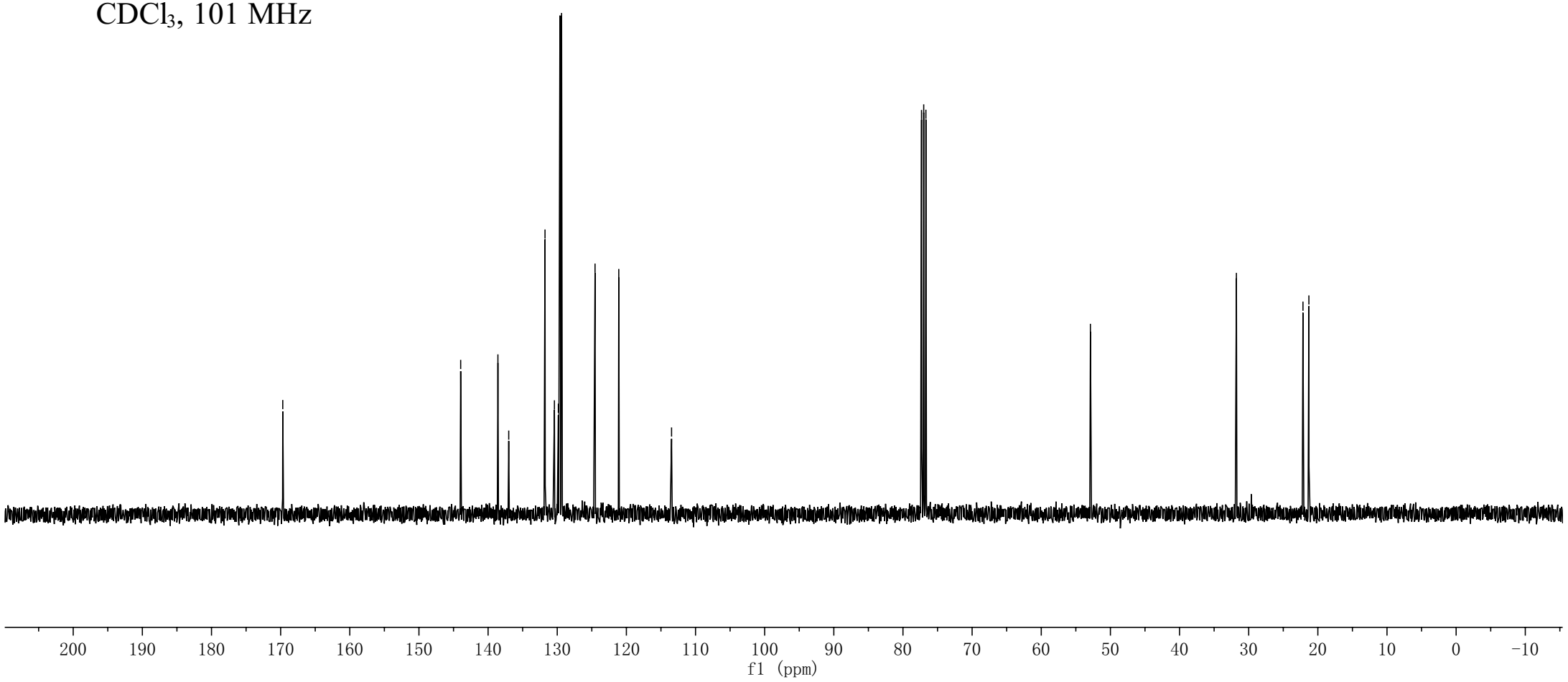
2n

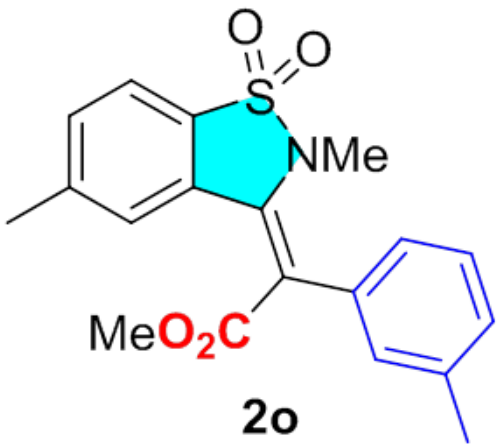
$CDCl_3$, 400 MHz



2n

$CDCl_3$, 101 MHz

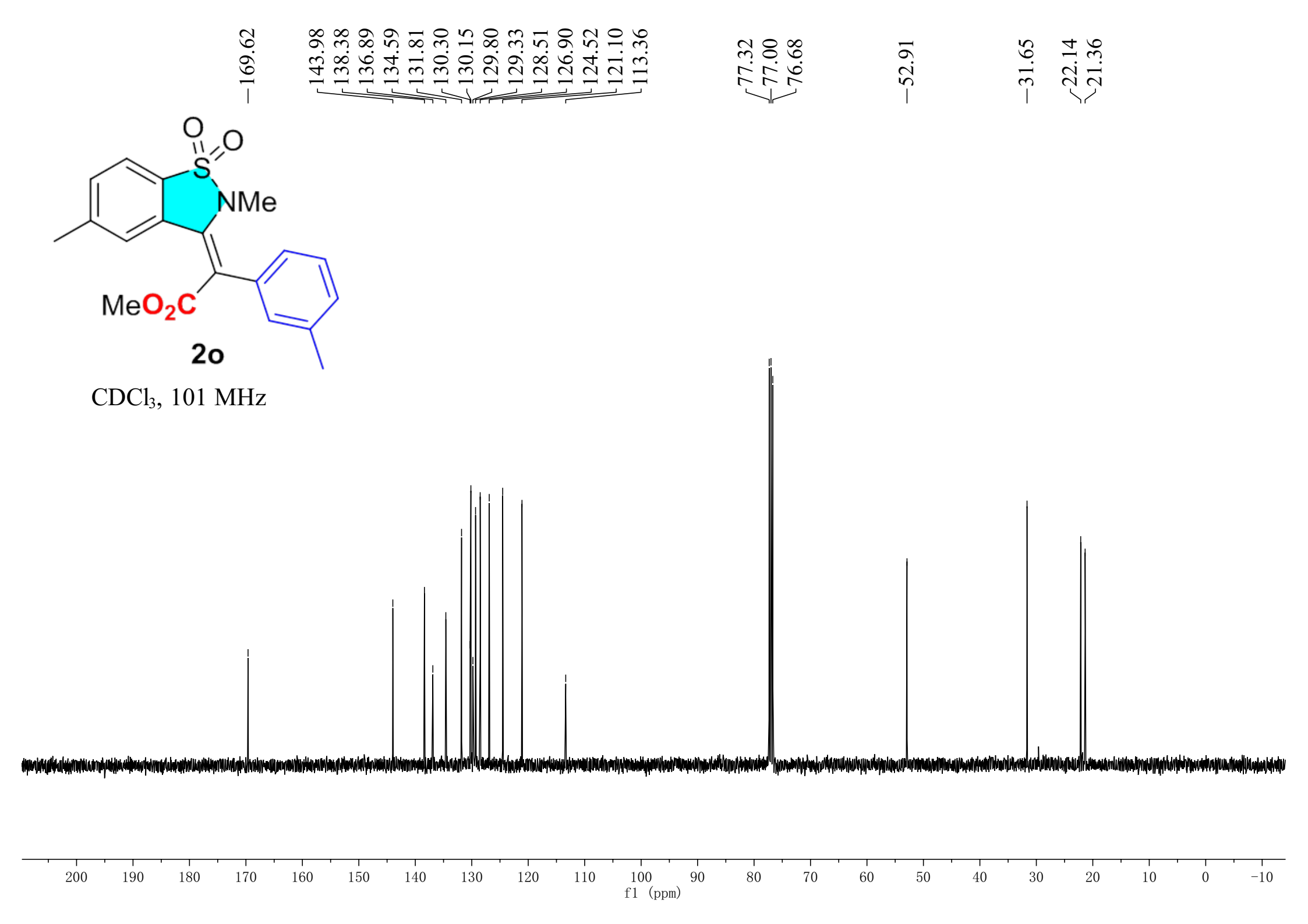


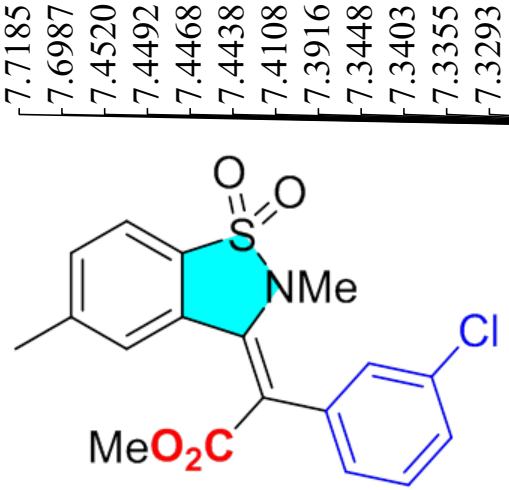


2o

$CDCl_3$, 400 MHz

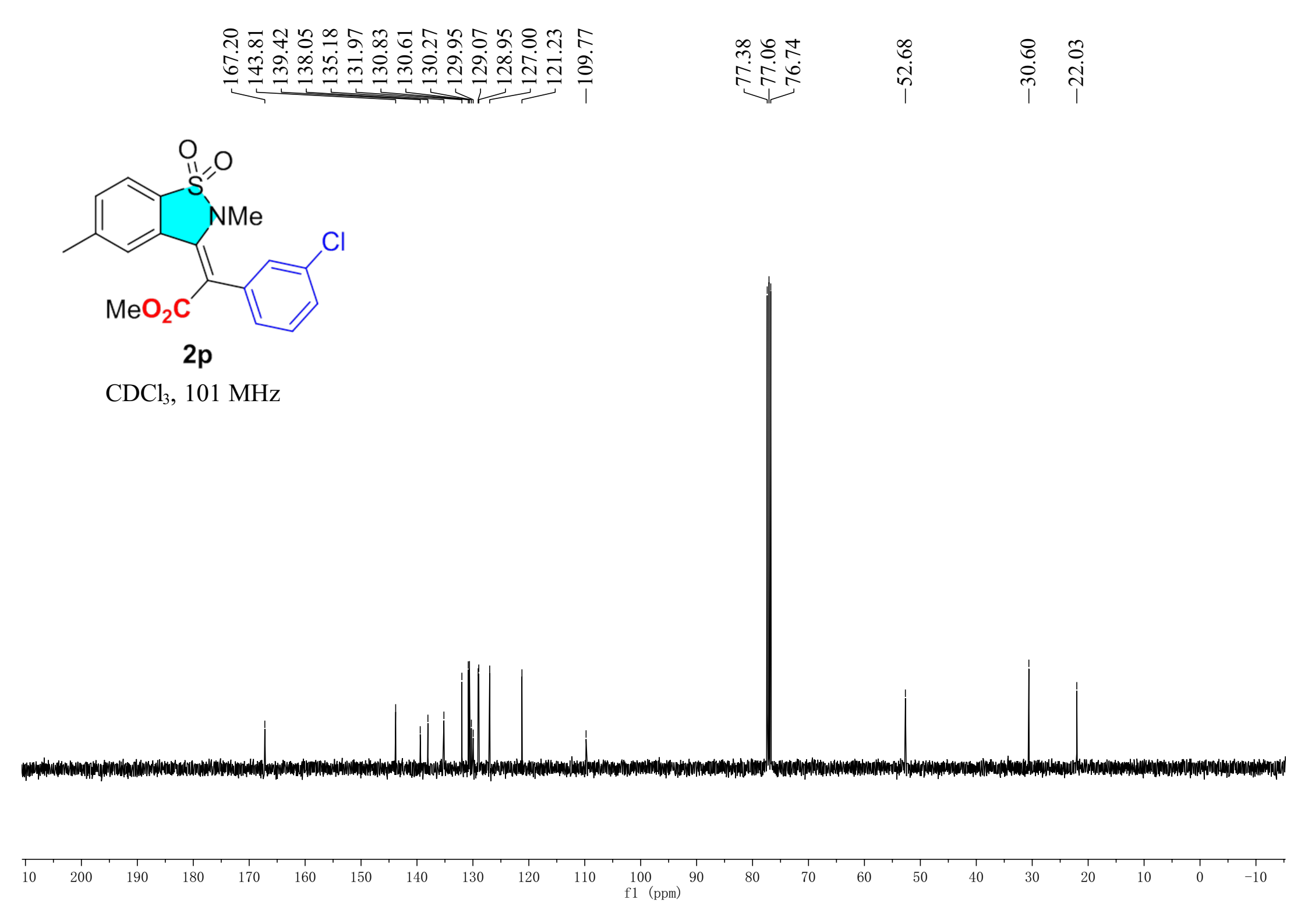
7.7325
7.7128
7.4163
7.4076
7.3871
7.2817
7.2602
7.2415
7.2348
7.1426
7.1263
3.8403
2.6412
2.4408
2.3424
1.01
2.03
1.19
3.03
2.93
3.00
3.02
3.10
f1 (ppm)

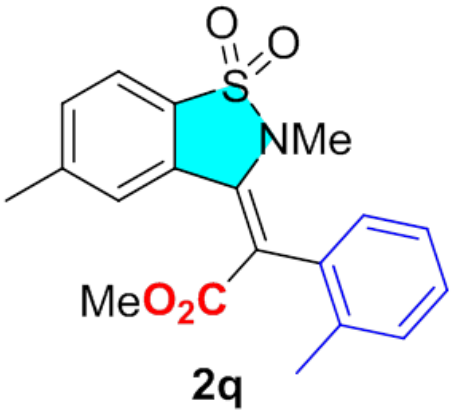

169.62
143.98
138.38
136.89
134.59
131.81
130.30
130.15
129.80
129.33
128.51
126.90
124.52
121.10
113.36
77.32
77.00
76.68
52.91
31.65
22.14
21.36
O
O
S
NMe
MeO2C
2o
CDCl3, 101 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



2p

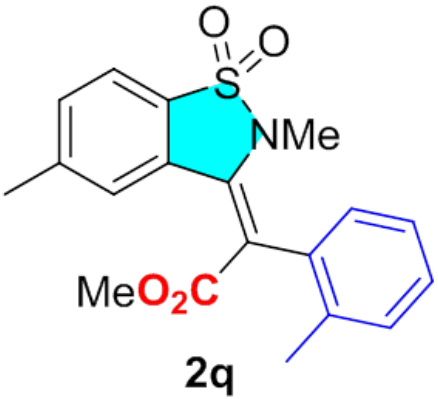
$CDCl_3$, 400 MHz


167.20
143.81
139.42
138.05
135.18
131.97
130.83
130.61
130.27
129.95
129.07
128.95
127.00
121.23
109.77
77.38
77.06
76.74
52.68
30.60
22.03
O
O
S
NMe
Cl
MeO2C
2p
CDCl3, 101 MHz
f1 (ppm)



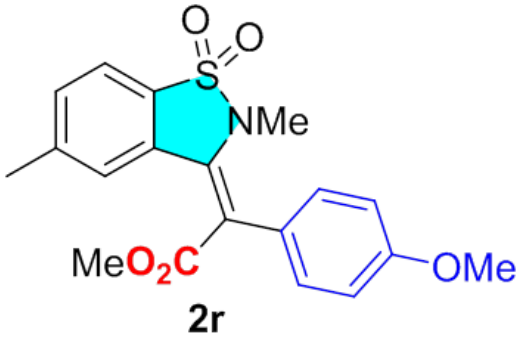
2q

$CDCl_3$, 400 MHz



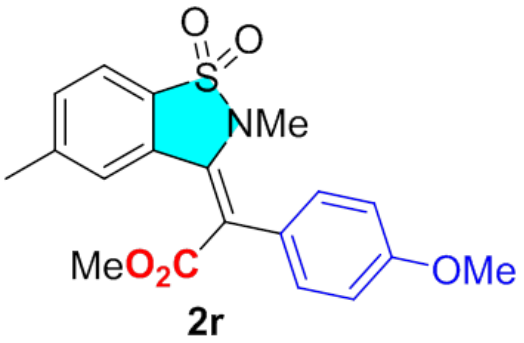
2q

$CDCl_3$, 101 MHz



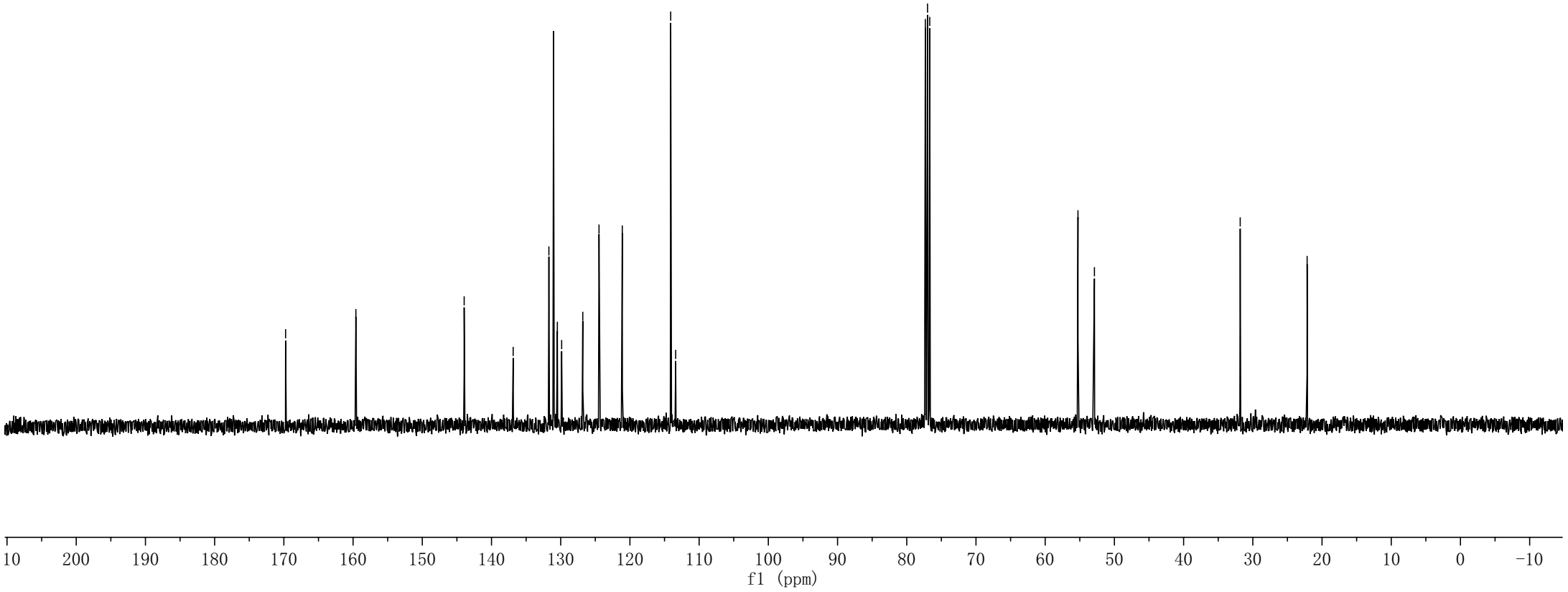
2r

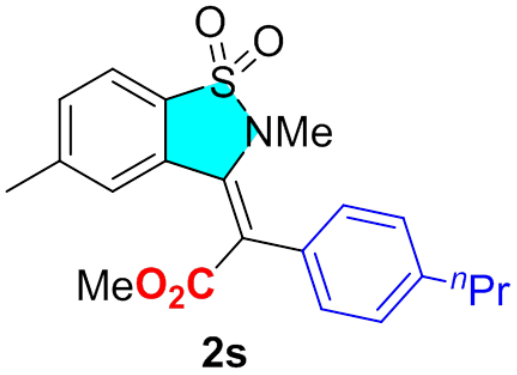
$CDCl_3$, 400 MHz



2r

$CDCl_3$, 101 MHz



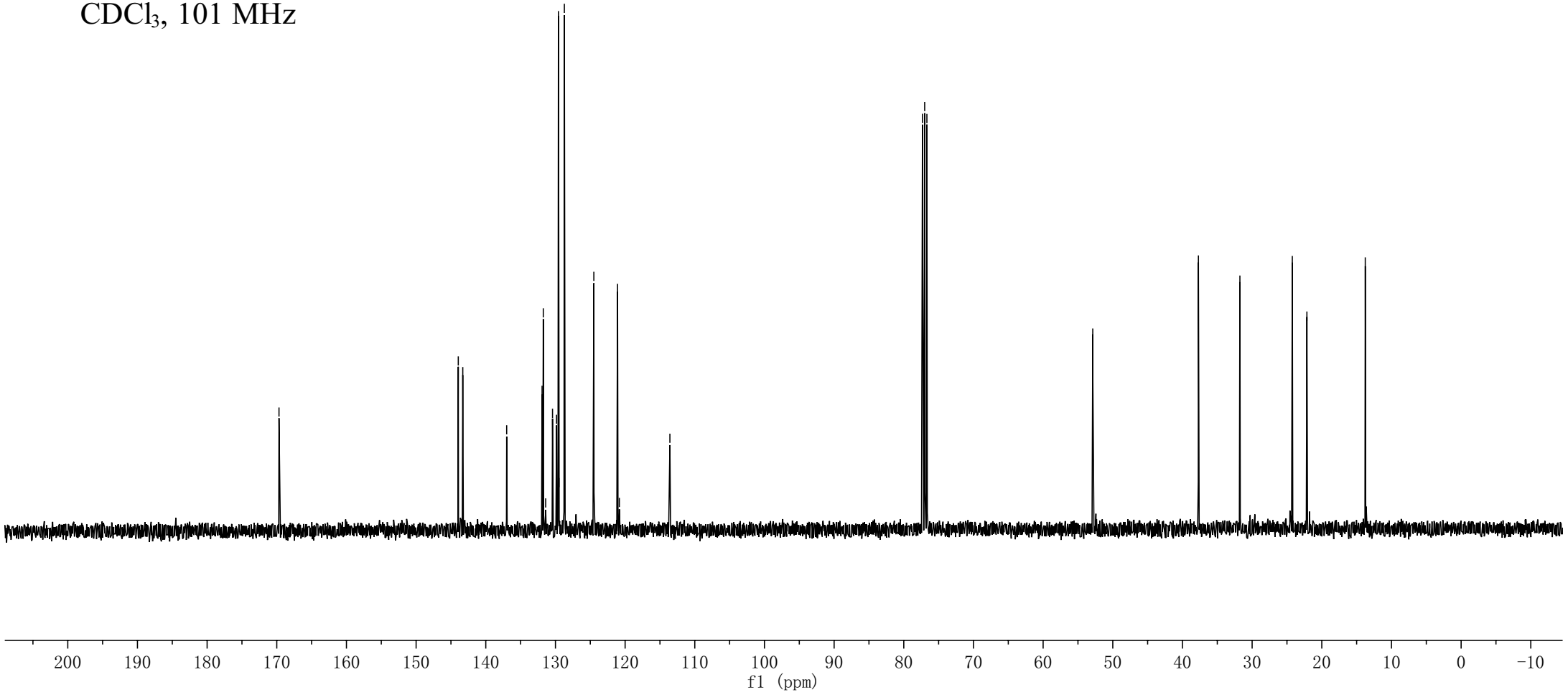


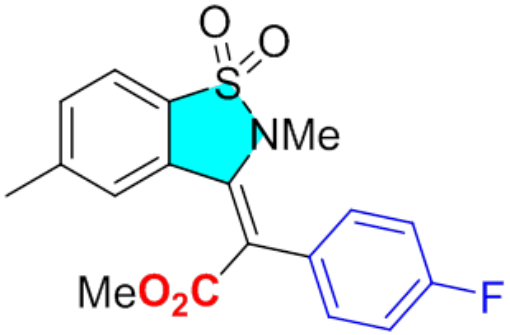
2s

$CDCl_3$, 400 MHz

2s

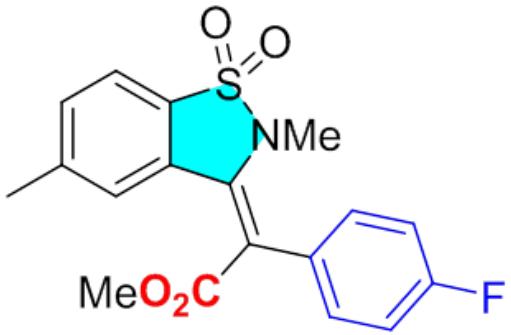
$CDCl_3$, 101 MHz





2t

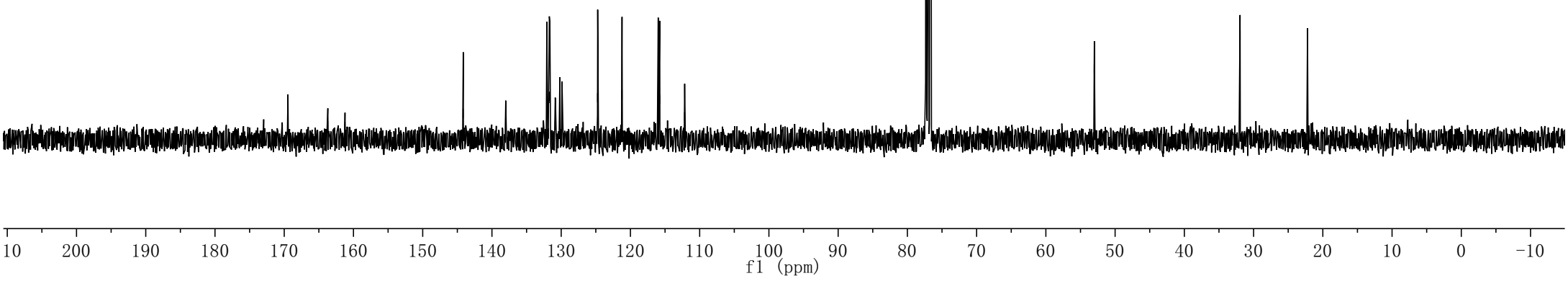
$CDCl_3$, 400 MHz

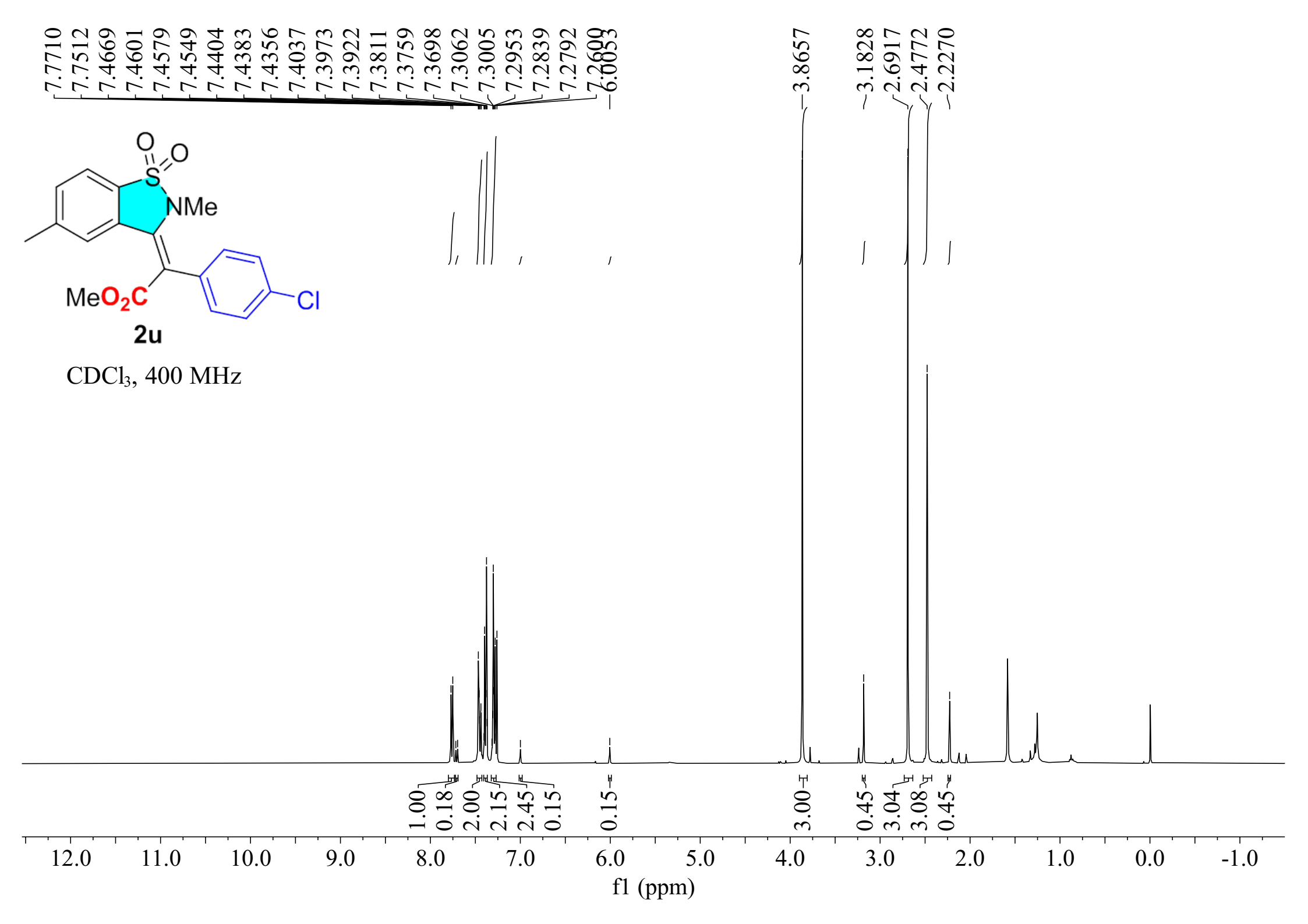


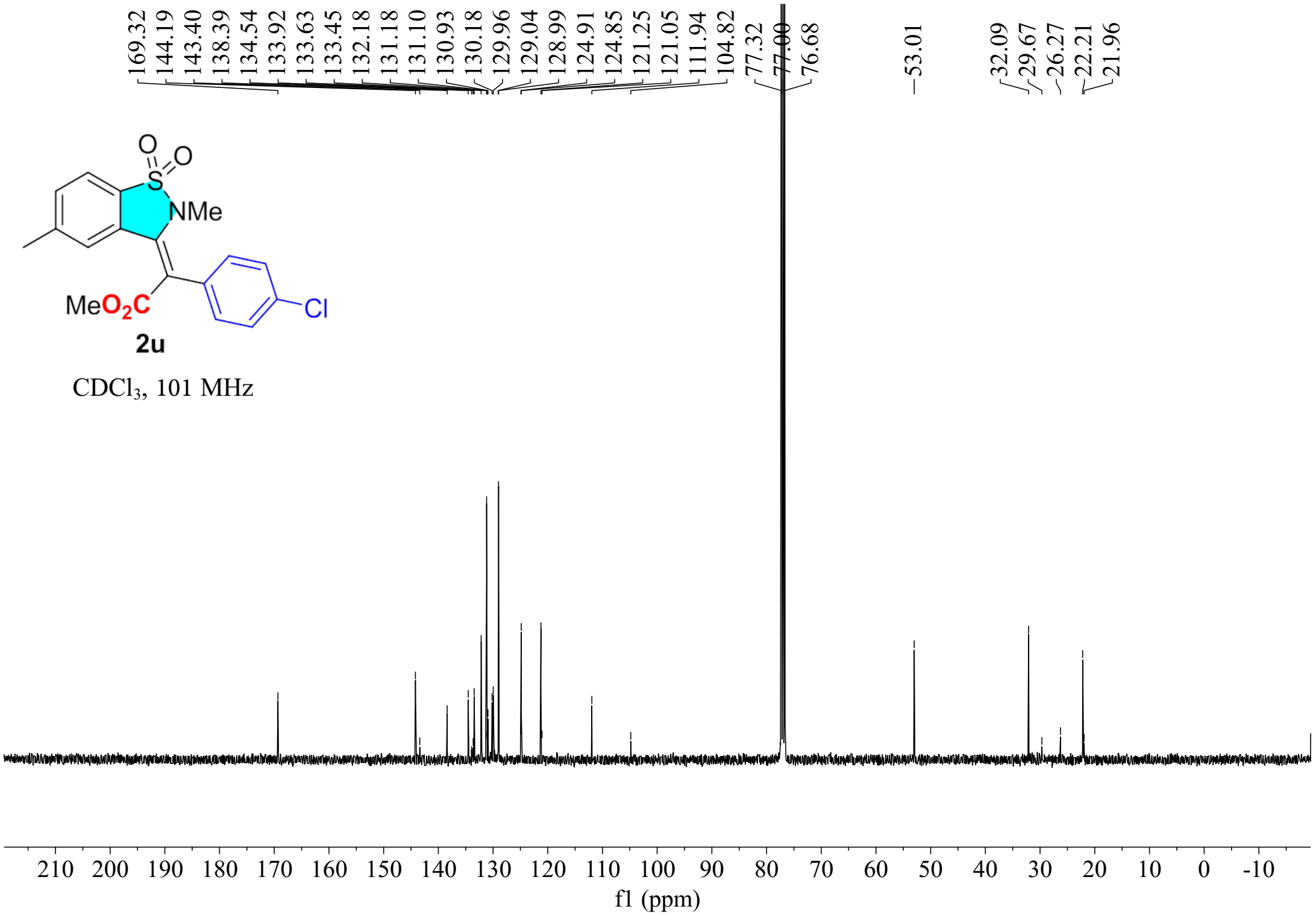
2t

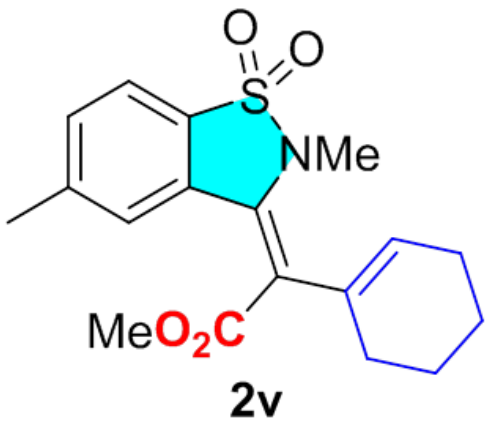
$CDCl_3$, 101 MHz

169.4779
163.7187
161.2372
144.1605
138.0170
132.0882
131.7279
131.6454
130.8708
130.8350
130.2096
129.8948
124.7410
121.2235
115.9975
115.7817
112.1755
77.3180
77.0007
76.6836
53.0044
31.9541
22.2146



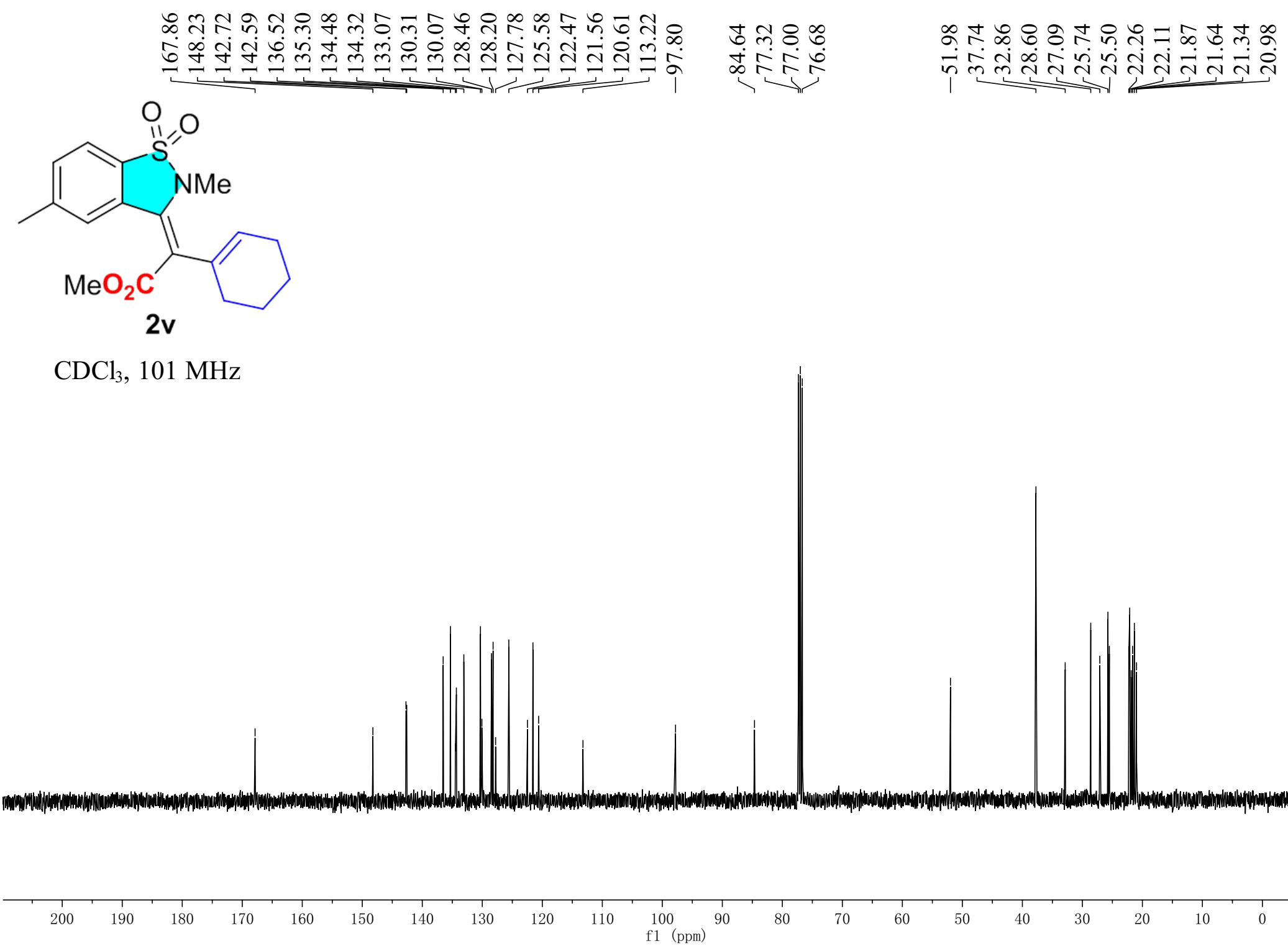

7.7710
7.7512
7.4669
7.4601
7.4579
7.4549
7.4404
7.4383
7.4356
7.4037
7.3973
7.3922
7.3811
7.3759
7.3698
7.3062
7.3005
7.2953
7.2839
7.2792
7.2600
6.0053
3.8657
3.1828
2.6917
2.4772
2.2270
O
O
S
NMe
MeO2C
Cl
2u
CDCl3, 400 MHz
1.00
0.18
2.00
2.15
2.45
0.15
0.15
3.00
0.45
3.04
3.08
0.45
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

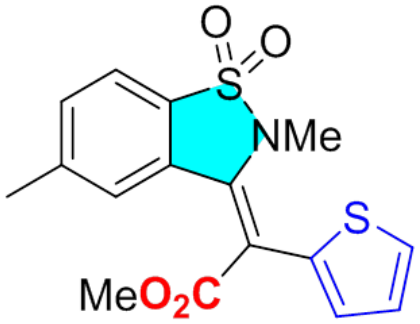

169.32
144.19
143.40
138.39
134.54
133.92
133.63
133.45
132.18
131.18
131.10
130.93
130.18
129.96
129.04
128.99
124.91
124.85
121.25
121.05
111.94
104.82
77.32
77.00
76.68
53.01
32.09
29.67
26.27
22.21
21.96
O
O
S
NMe
MeO2C
Cl
2u
CDCl3, 101 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



2v

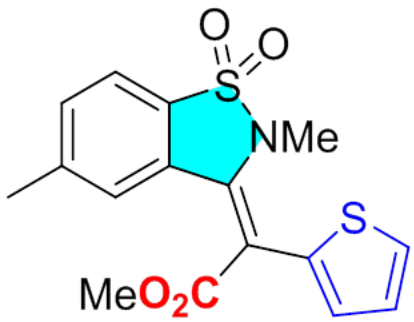
$CDCl_3$, 400 MHz


167.86
148.23
142.72
142.59
136.52
135.30
134.48
134.32
133.07
130.31
130.07
128.46
128.20
127.78
125.58
122.47
121.56
120.61
113.22
97.80
84.64
77.32
77.00
76.68
51.98
37.74
32.86
28.60
27.09
25.74
25.50
22.26
22.11
21.87
21.64
21.34
20.98
O
O
S
NMe
MeO2C
2v
CDCl3, 101 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



2w

$CDCl_3$, 400 MHz

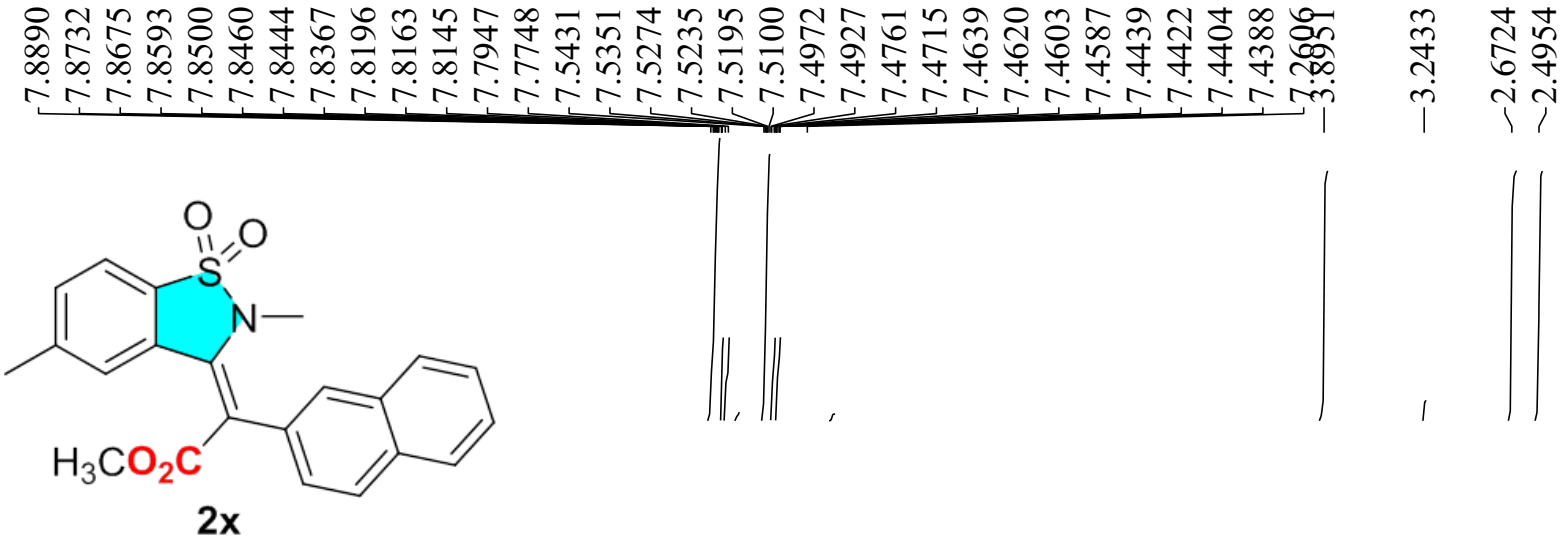


2w

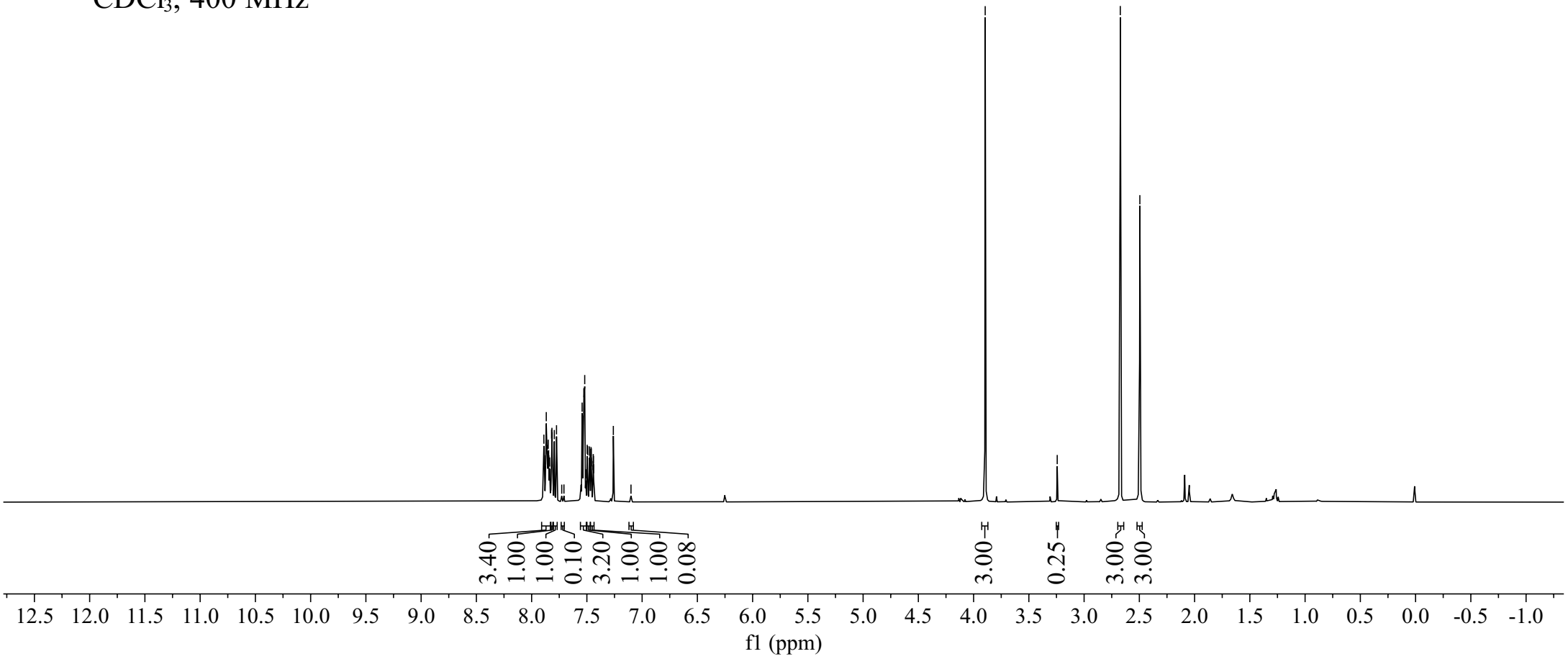
$CDCl_3$, 101 MHz

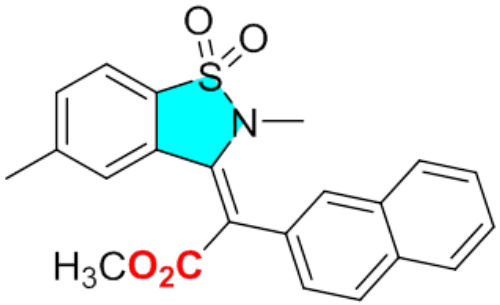
166.82
143.88
141.04
137.36
131.92
130.26
129.81
129.66
128.47
127.85
127.17
120.91
102.38
77.32
77.00
76.68
52.61
30.63
21.98

f1 (ppm)



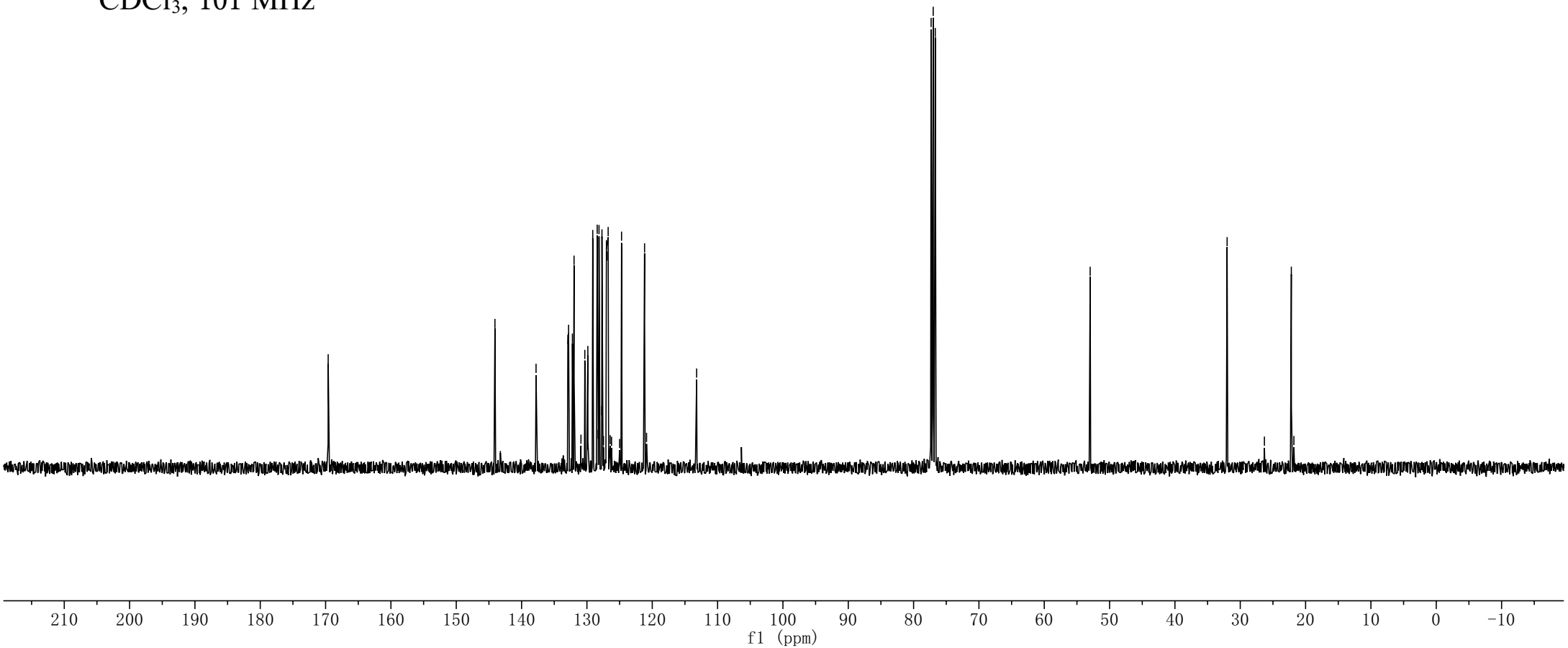
$CDCl_3$, 400 MHz

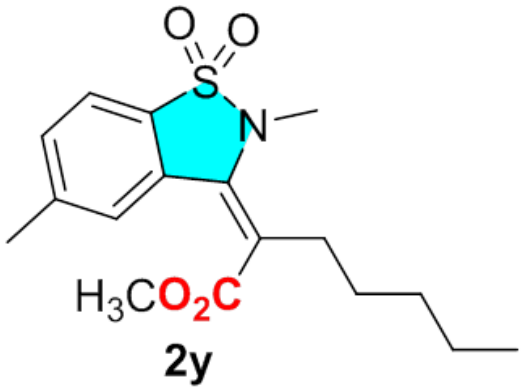




2x

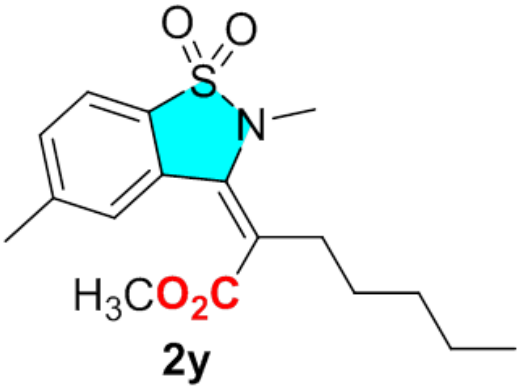
$CDCl_3$, 101 MHz





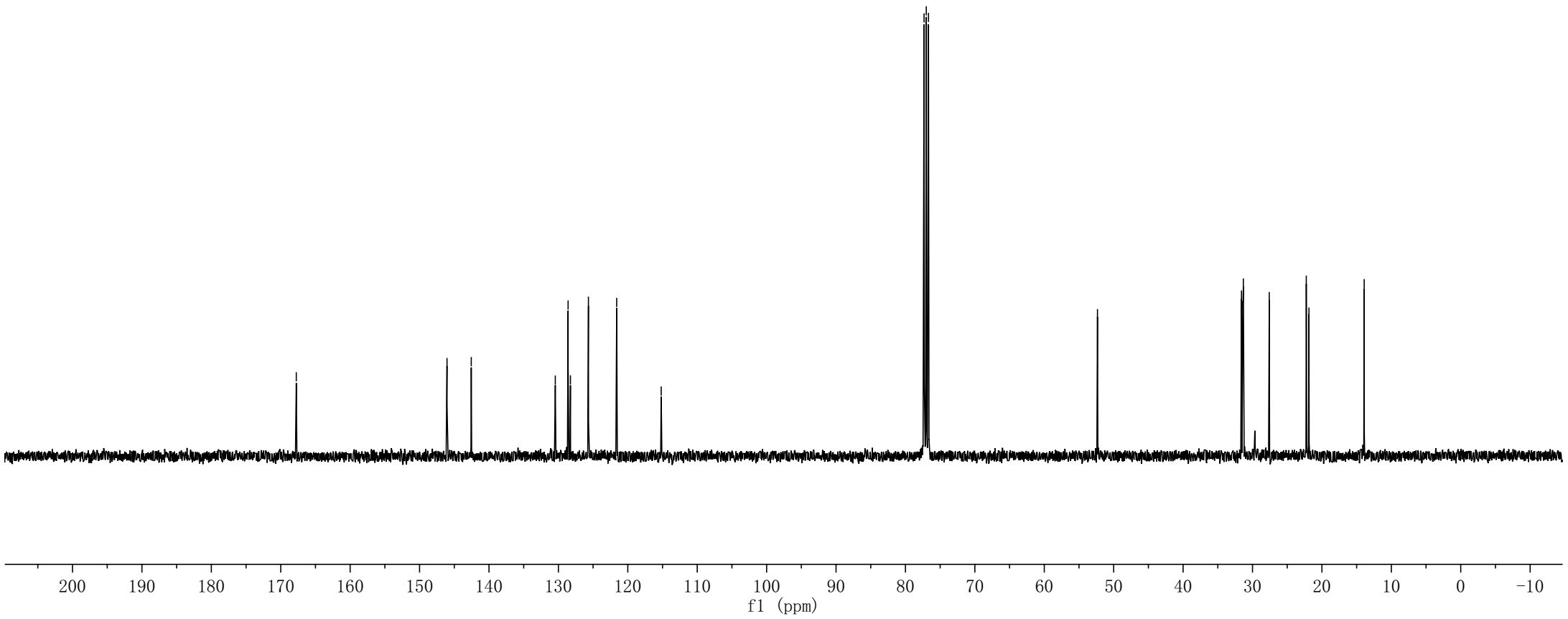
2y

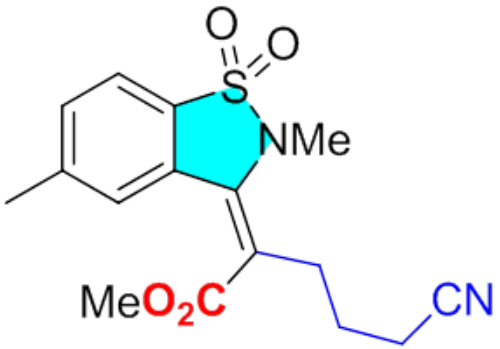
$CDCl_3$, 400 MHz



2y

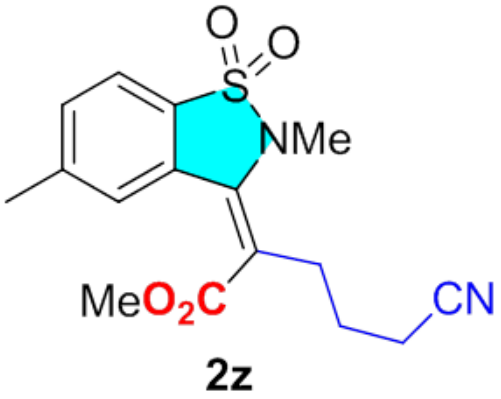
$CDCl_3$, 101 MHz





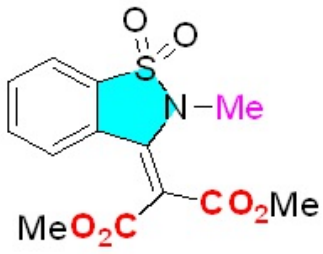
2z

$CDCl_3$, 400 MHz



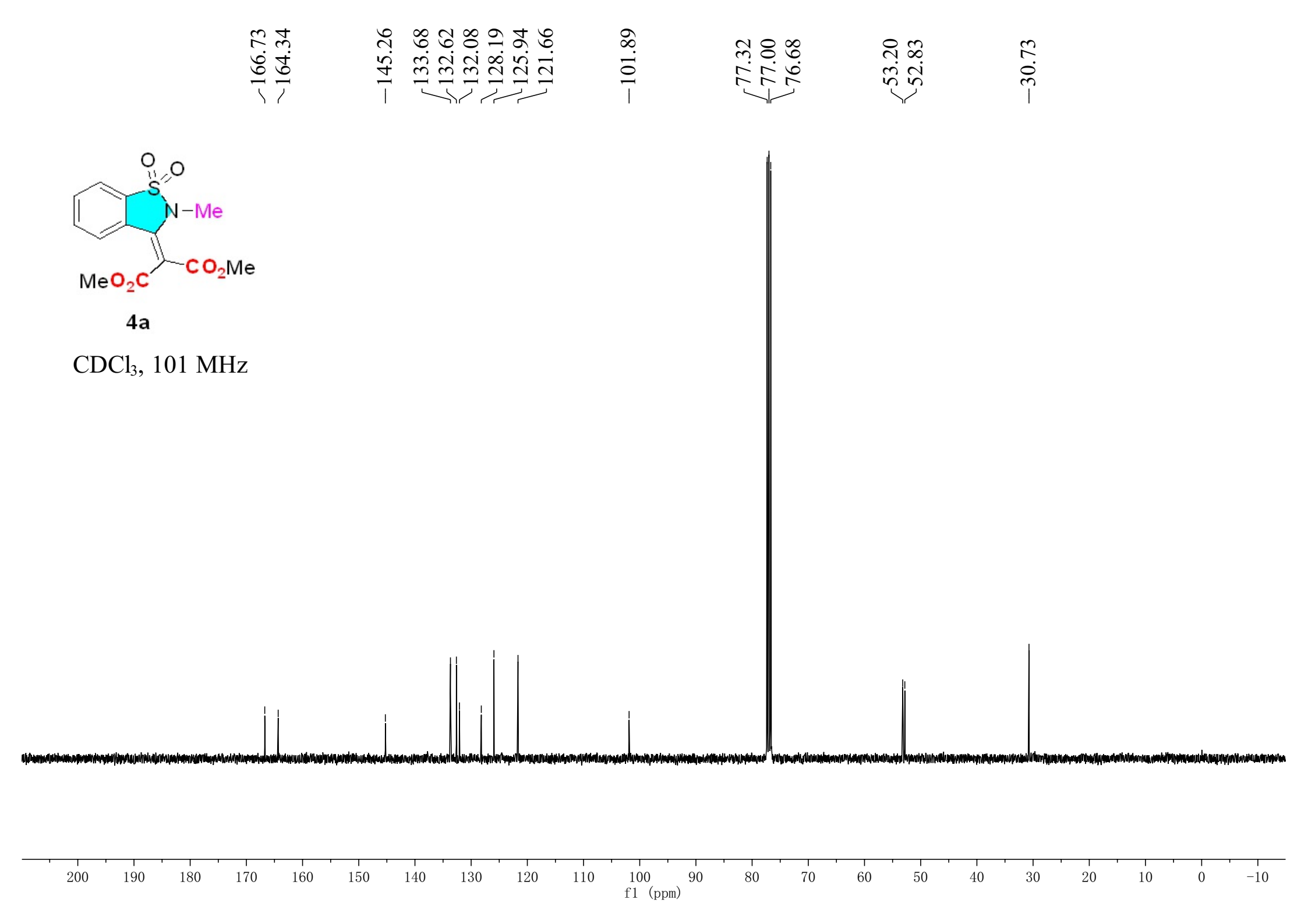
2z

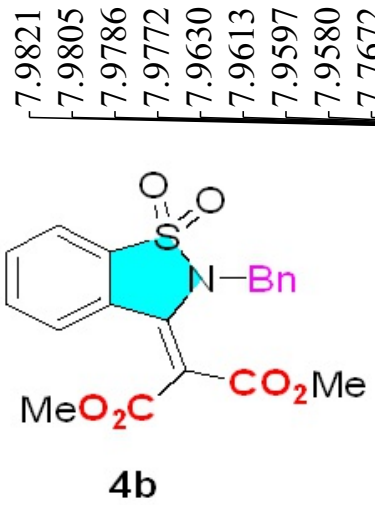
$CDCl_3$, 101 MHz



4a

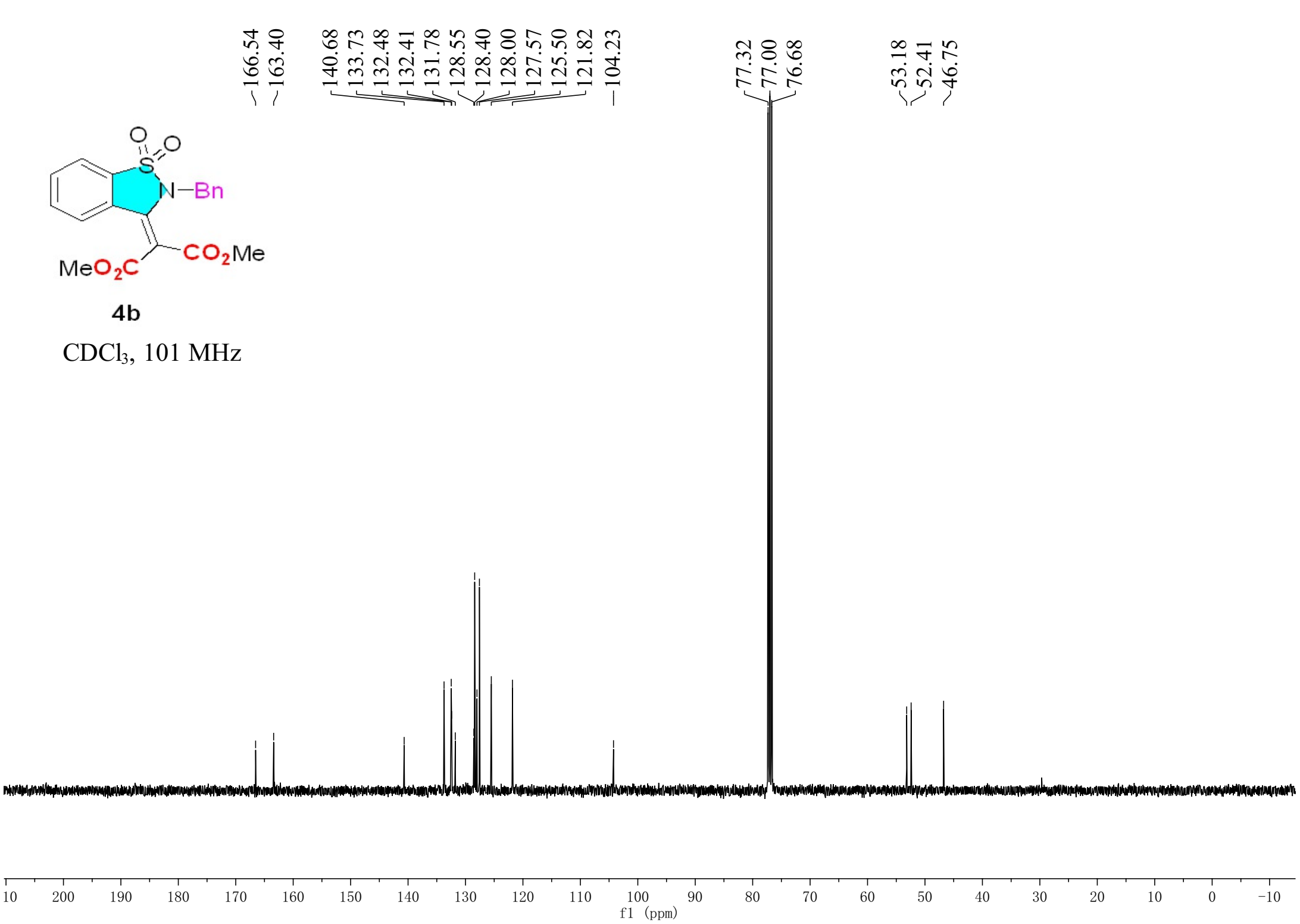
$CDCl_3$, 400 MHz

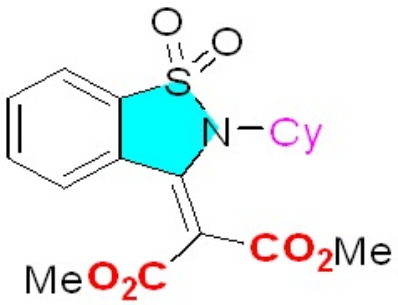

166.73
164.34
145.26
133.68
132.62
132.08
128.19
125.94
121.66
101.89
77.32
77.00
76.68
53.20
52.83
30.73
O
O
S
N–Me
CO2Me
MeO2C
4a
CDCl3, 101 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



4b

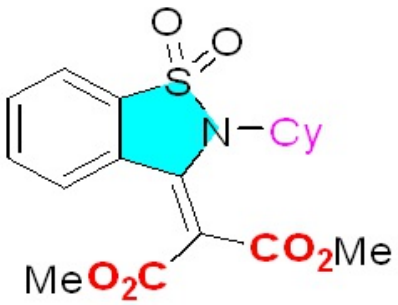
$CDCl_3$, 400 MHz


166.54
163.40
140.68
133.73
132.48
132.41
131.78
128.55
128.40
128.00
127.57
125.50
121.82
104.23
77.32
77.00
76.68
53.18
52.41
46.75
O
O
S
N—Bn
CO2Me
MeO2C
4b
CDCl3, 101 MHz
f1 (ppm)



4c

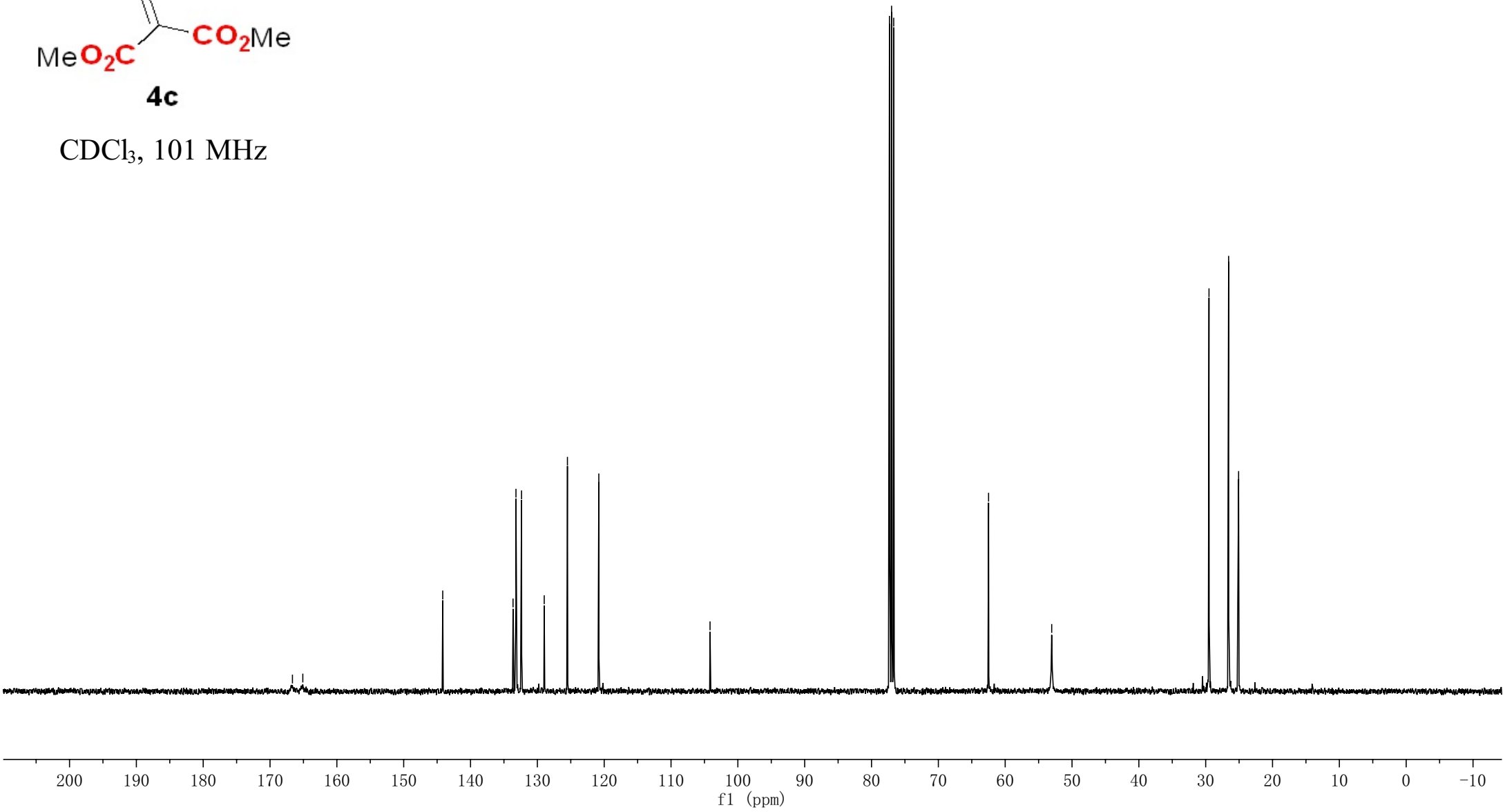
$CDCl_3$, 400 MHz

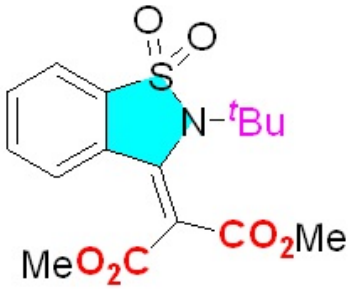


4c

$CDCl_3$, 101 MHz

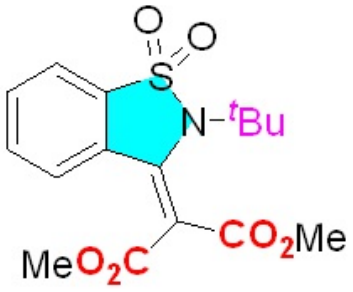
166.65
165.09
144.16
133.64
133.20
132.37
128.97
125.50
120.80
104.16
77.32
77.00
76.68
62.49
53.04
29.51
26.57
25.08





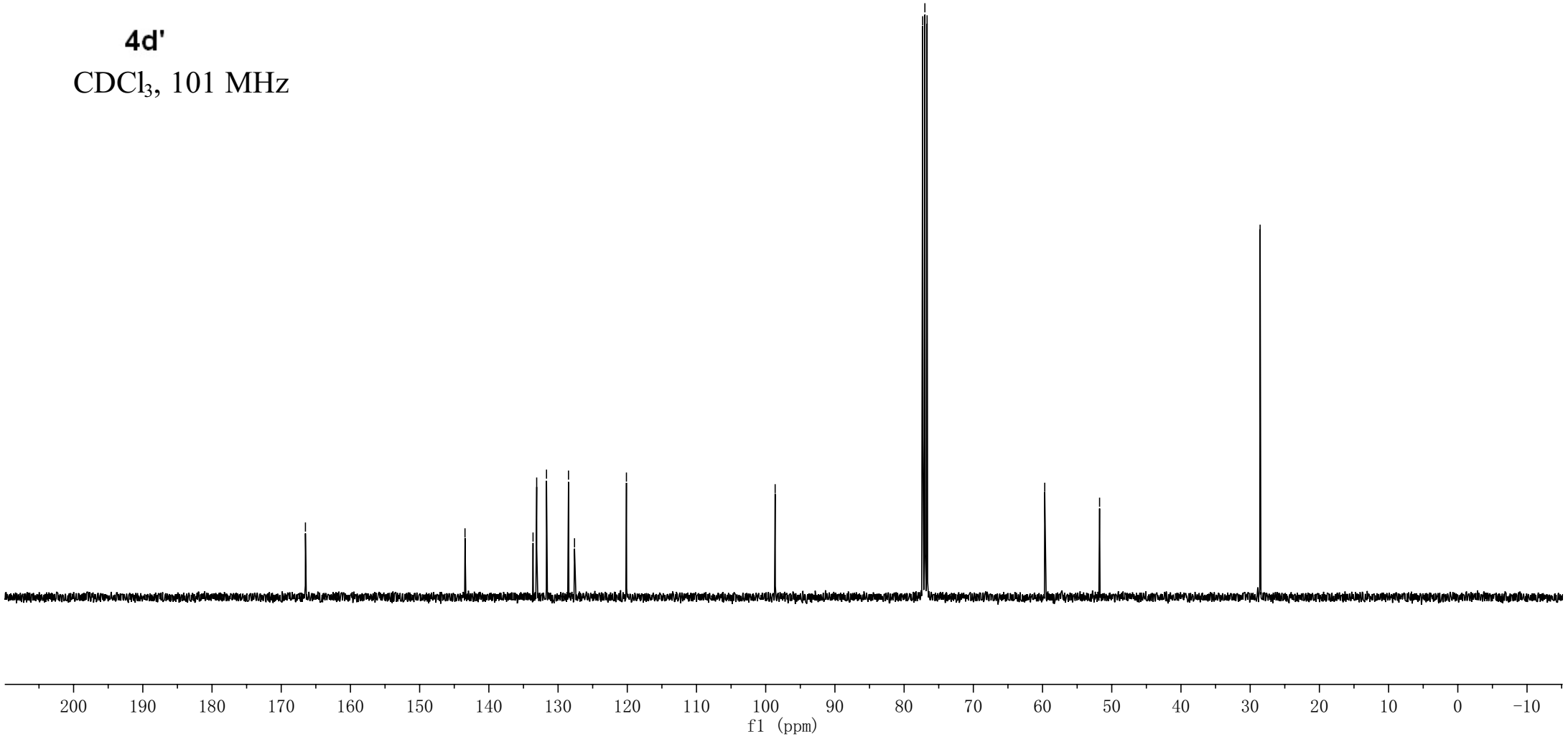
4d'

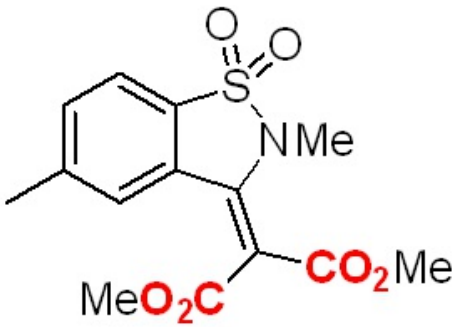
$CDCl_3$, 400 MHz



4d'

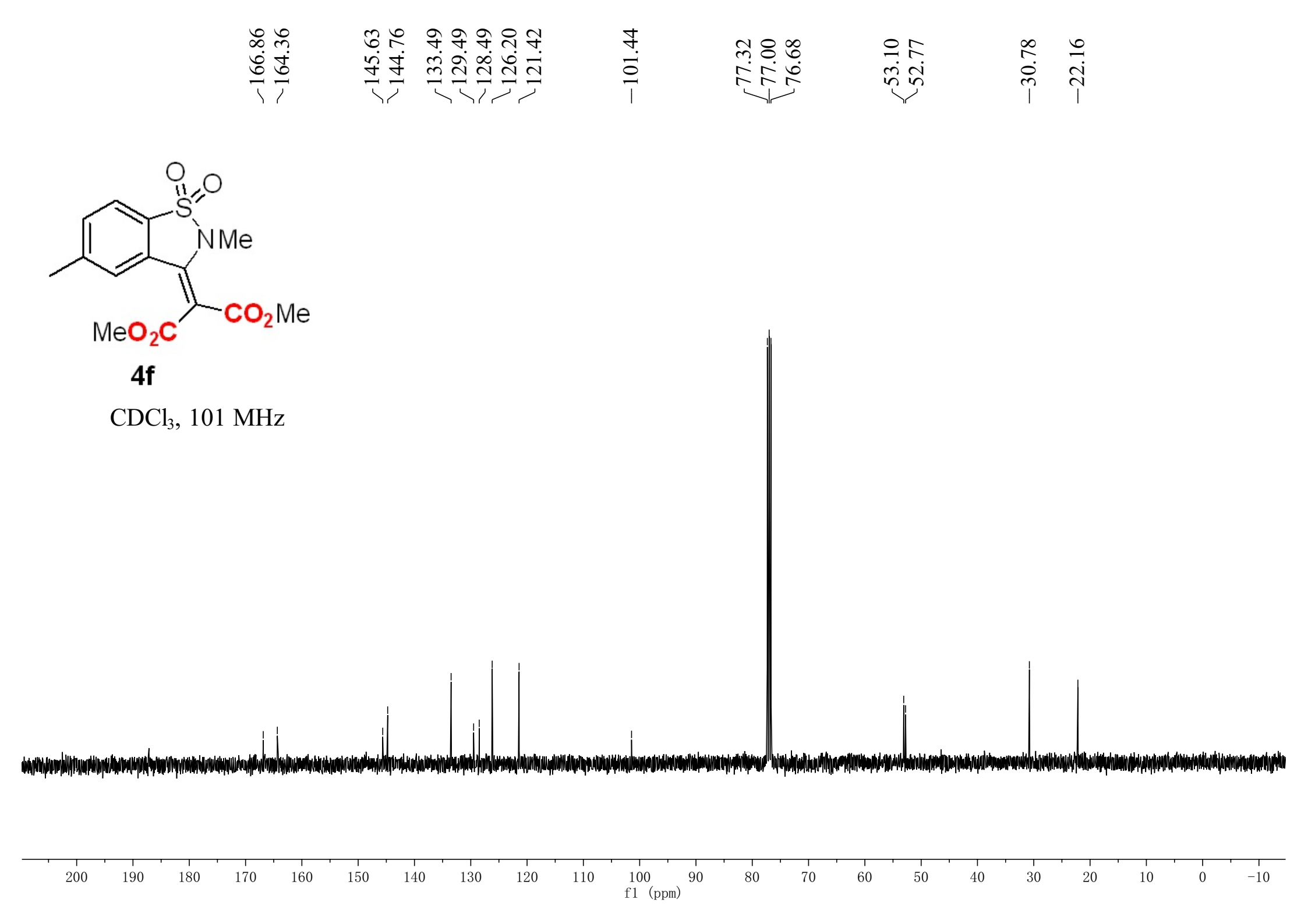
$CDCl_3$, 101 MHz

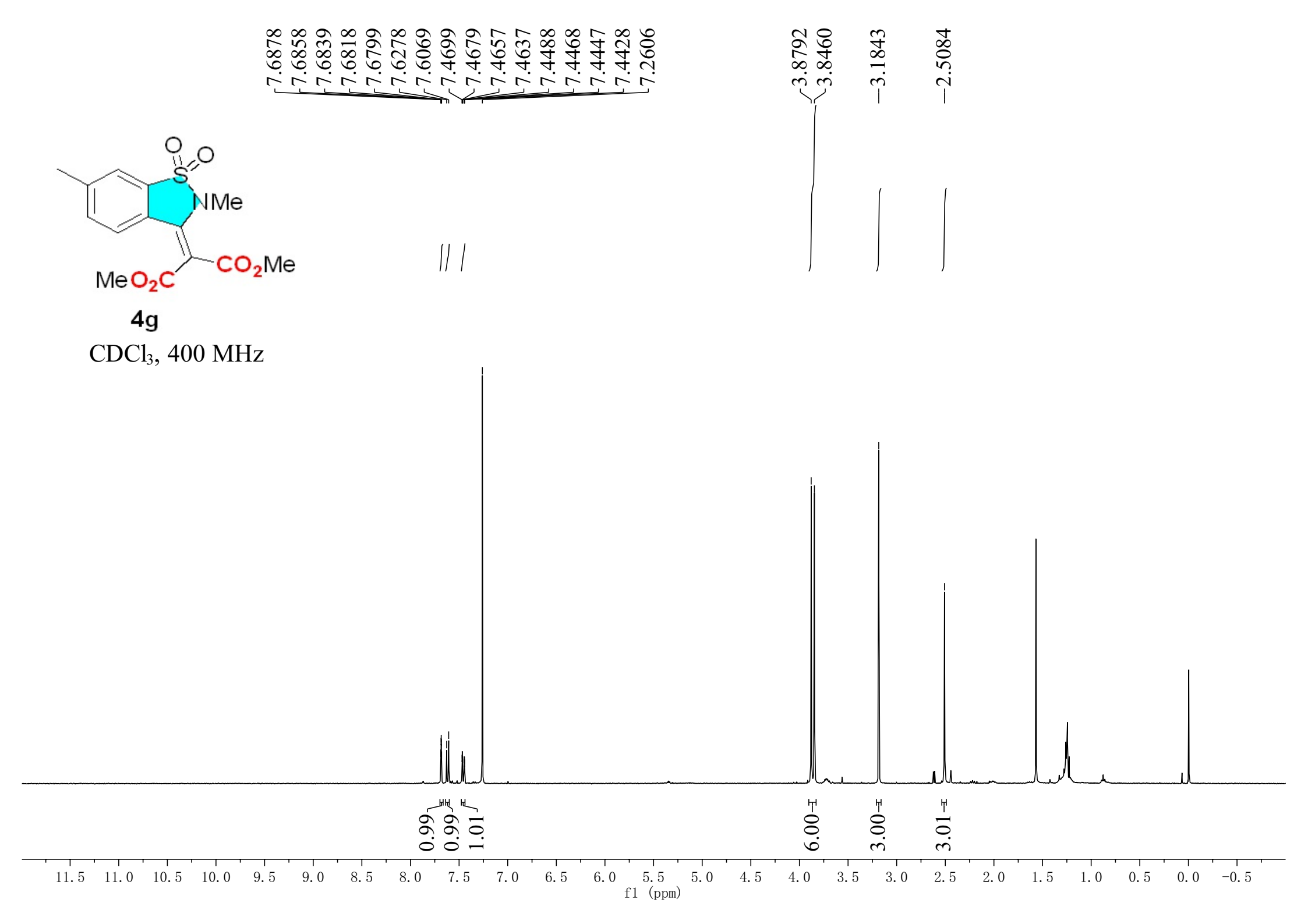


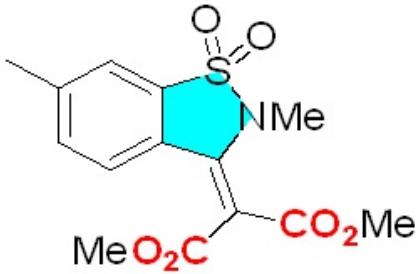


4f

$CDCl_3$, 400 MHz


166.86
164.36
145.63
144.76
133.49
129.49
128.49
126.20
121.42
101.44
77.32
77.00
76.68
53.10
52.77
30.78
22.16
NMe
CO2Me
MeO2C
4f
CDCl3, 101 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.6878
7.6858
7.6839
7.6818
7.6799
7.6278
7.6069
7.4699
7.4679
7.4657
7.4637
7.4488
7.4468
7.4447
7.4428
7.2606
3.8792
3.8460
3.1843
2.5084
NMe
CO2Me
MeO2C
4g
CDCl3, 400 MHz
0.99
0.99
1.01
6.00
3.00
3.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

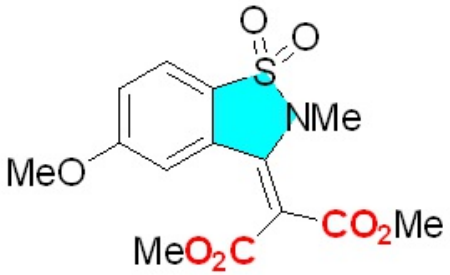


4g

$CDCl_3$, 101 MHz

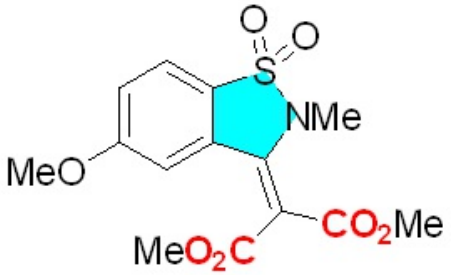
166.87
164.48
145.73
144.23
134.64
132.28
125.78
125.60
121.69
101.15
77.32
77.00
76.68
53.09
52.73
30.70
21.54

f1 (ppm)



4h

$CDCl_3$, 400 MHz

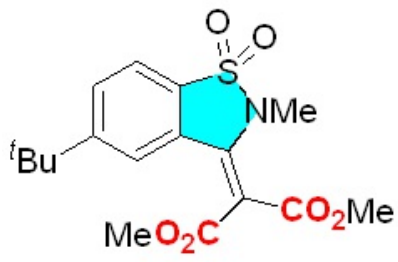


4h

$CDCl_3$, 101 MHz

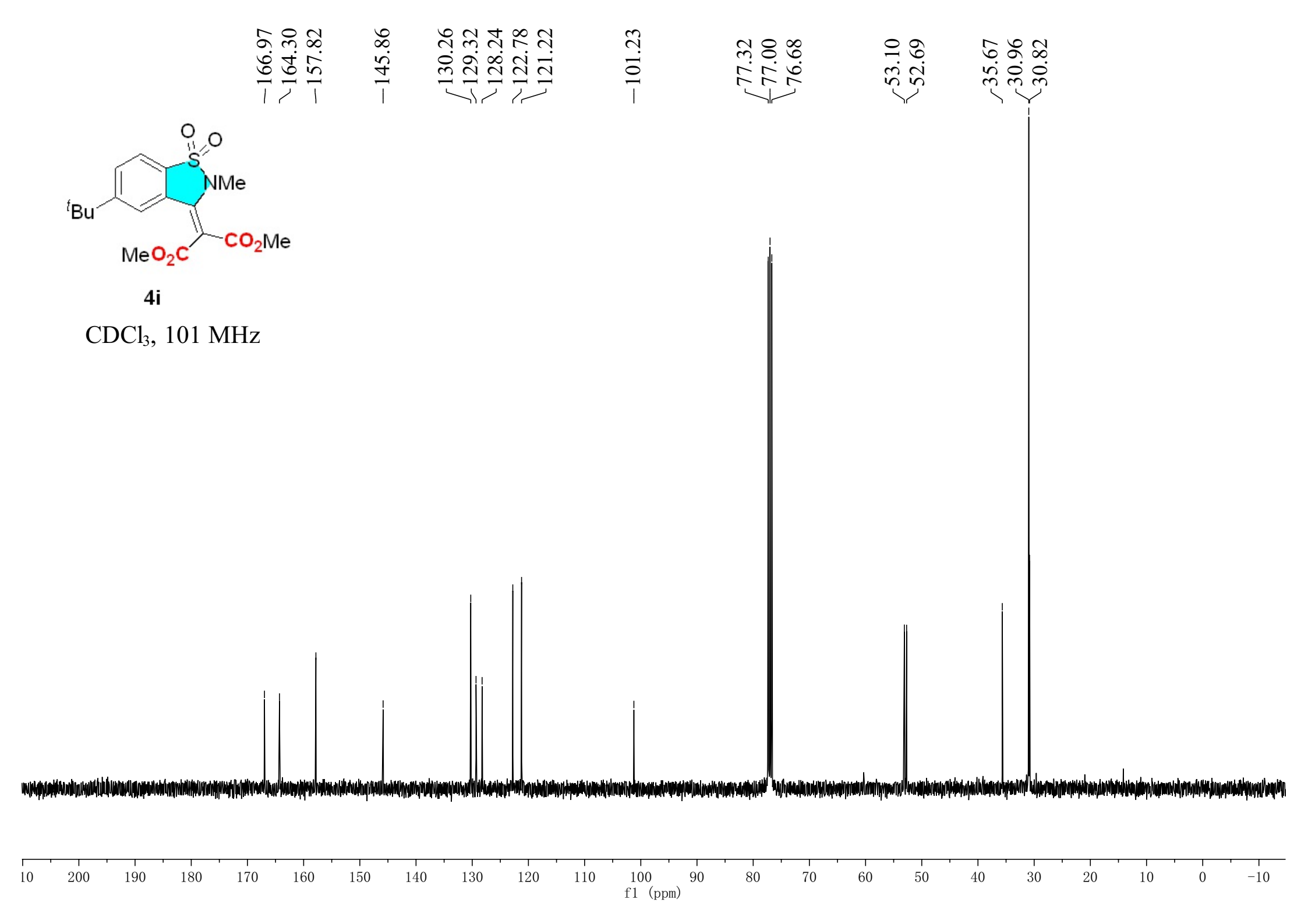
166.83
164.38
163.71
145.36
130.52
124.16
123.10
118.77
110.88
101.72
55.99
53.19
52.82
30.88

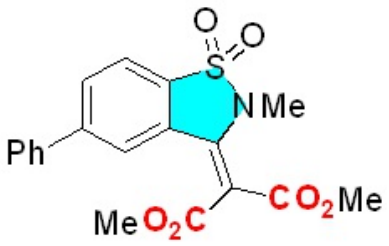
f1 (ppm)



4i

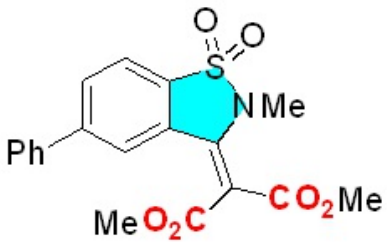
$CDCl_3$, 400 MHz


166.97
164.30
157.82
145.86
130.26
129.32
128.24
122.78
121.22
101.23
77.32
77.00
76.68
53.10
52.69
35.67
30.96
30.82
O
O
S
NMe
tBu
CO2Me
MeO2C
4i
CDCl3, 101 MHz
f1 (ppm)



4j

$CDCl_3$, 400 MHz

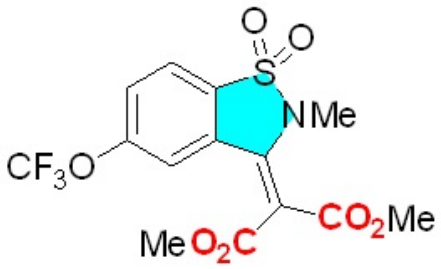


4j

$CDCl_3$, 101 MHz

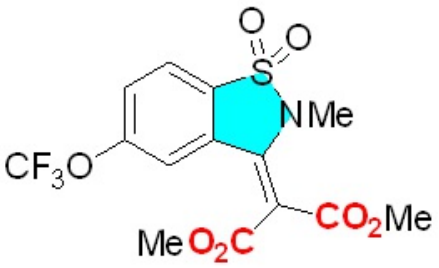
166.83
164.28
147.10
145.22
138.68
131.49
130.52
129.30
129.05
128.88
127.28
124.66
121.92
101.92
77.32
77.00
76.68
53.21
52.80
30.83

f1 (ppm)



4k

$CDCl_3$, 400 MHz



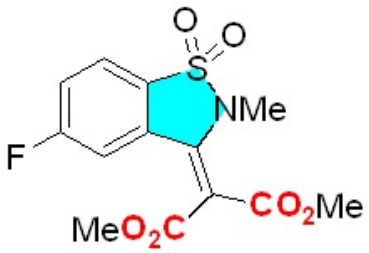
4k

$CDCl_3$, 101 MHz

166.18
164.07
152.76
143.50
130.76
130.19
124.88
123.52
121.41
118.82
118.32
103.35
77.37
77.05
76.74
53.35
53.08
30.88

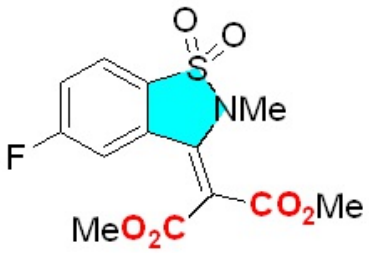
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

f1 (ppm)



4l

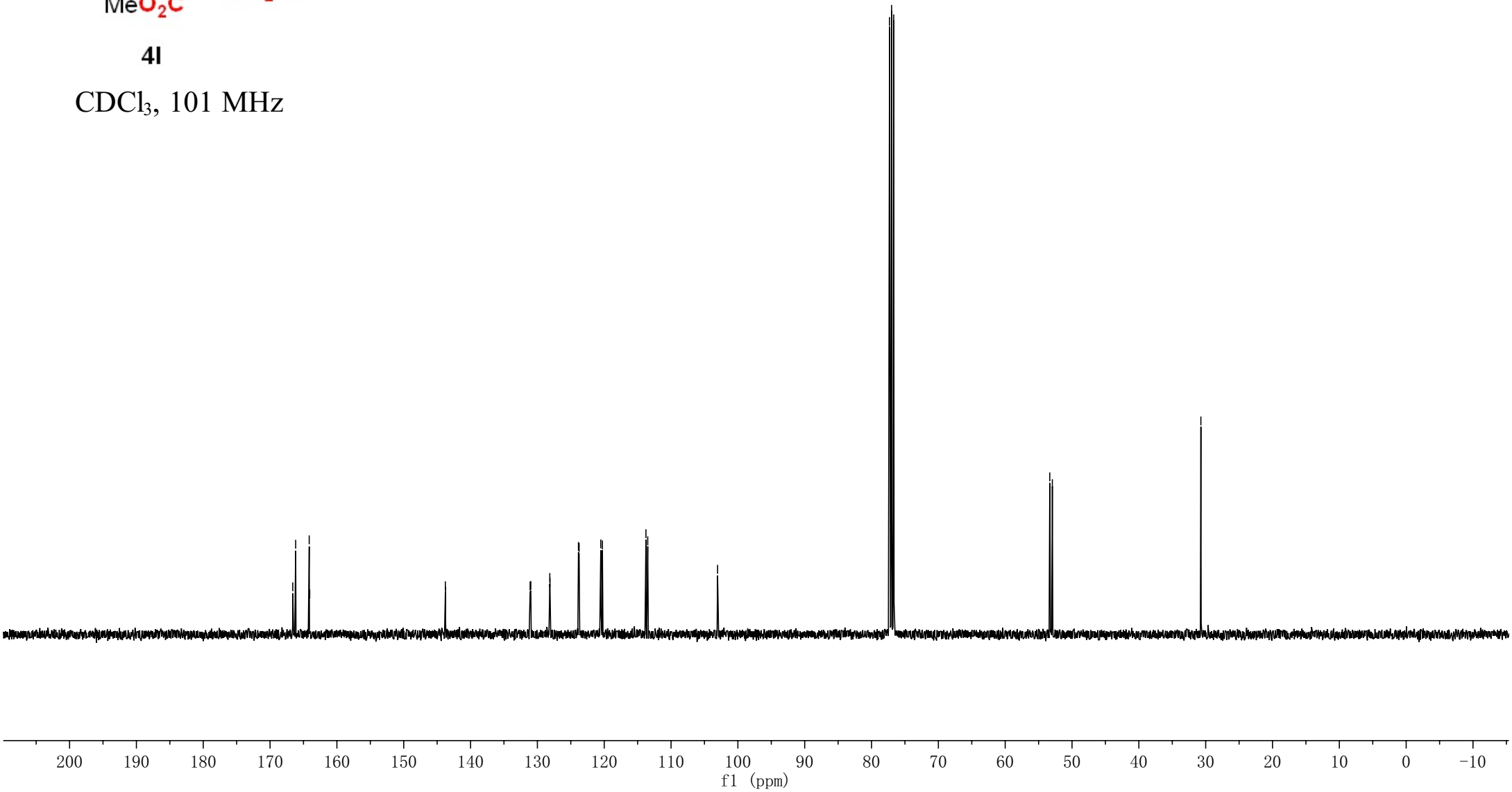
$CDCl_3$, 400 MHz

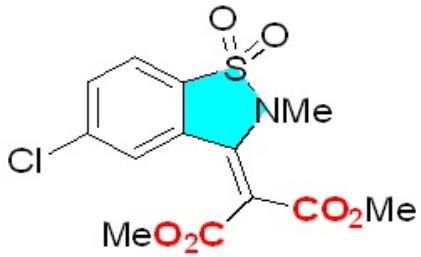


4l

$CDCl_3$, 101 MHz

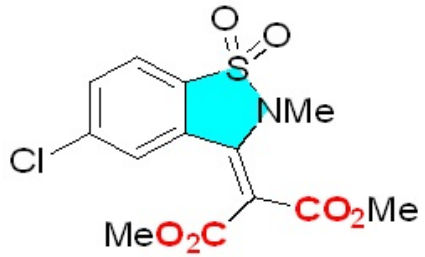
166.6044
166.1670
164.1405
164.0671
143.7704
143.7420
131.0869
130.9836
128.1415
128.1126
123.8544
123.7565
120.5120
120.2695
113.7560
113.4864
103.0355
77.3181
77.0003
76.6824
53.3299
52.9463
30.7179





4m

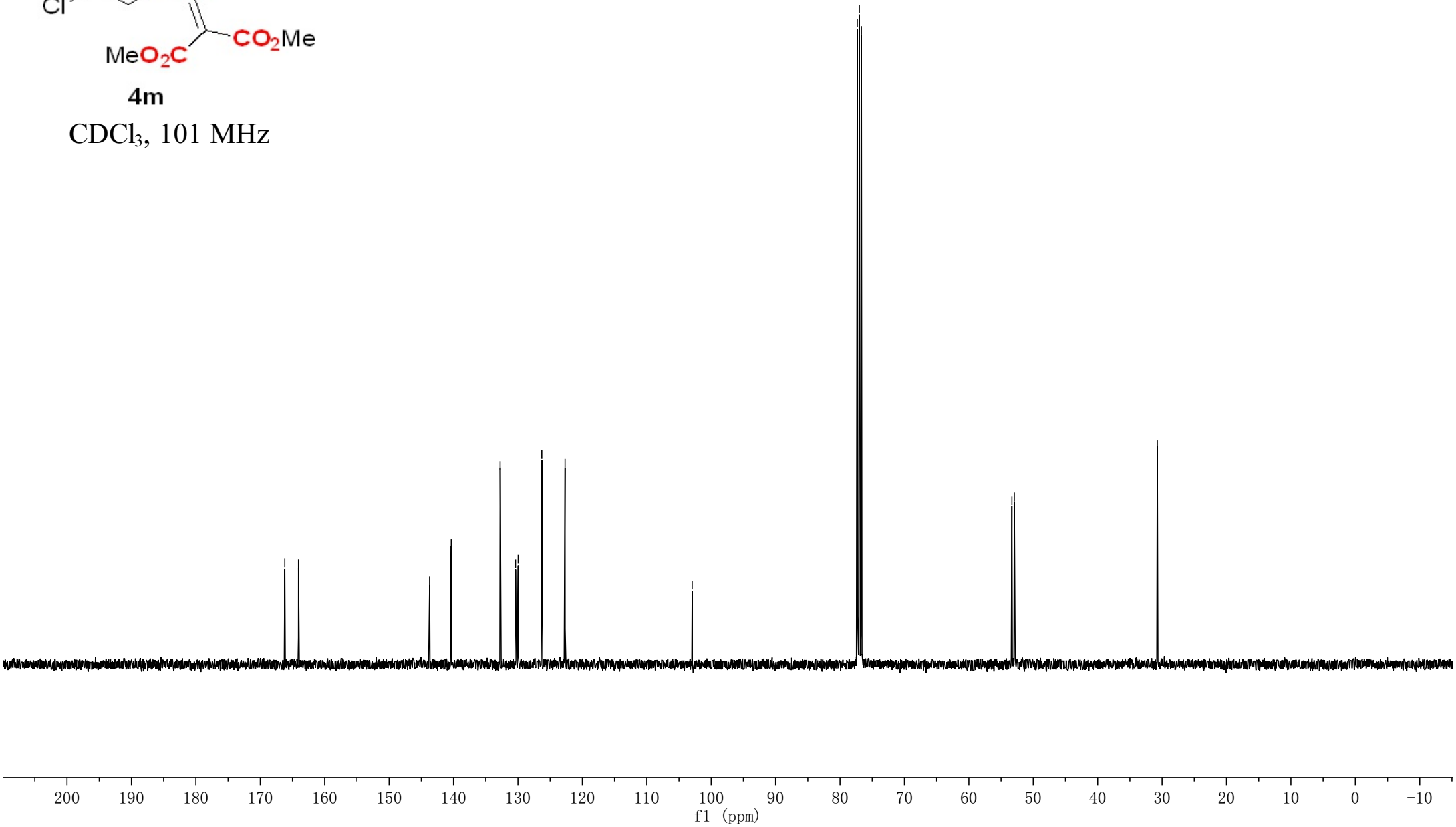
$CDCl_3$, 400 MHz

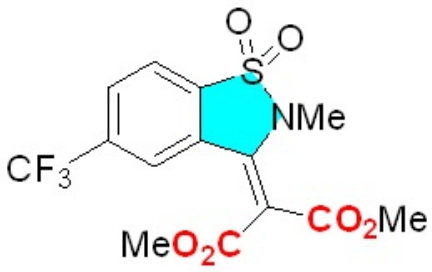


4m

$CDCl_3$, 101 MHz

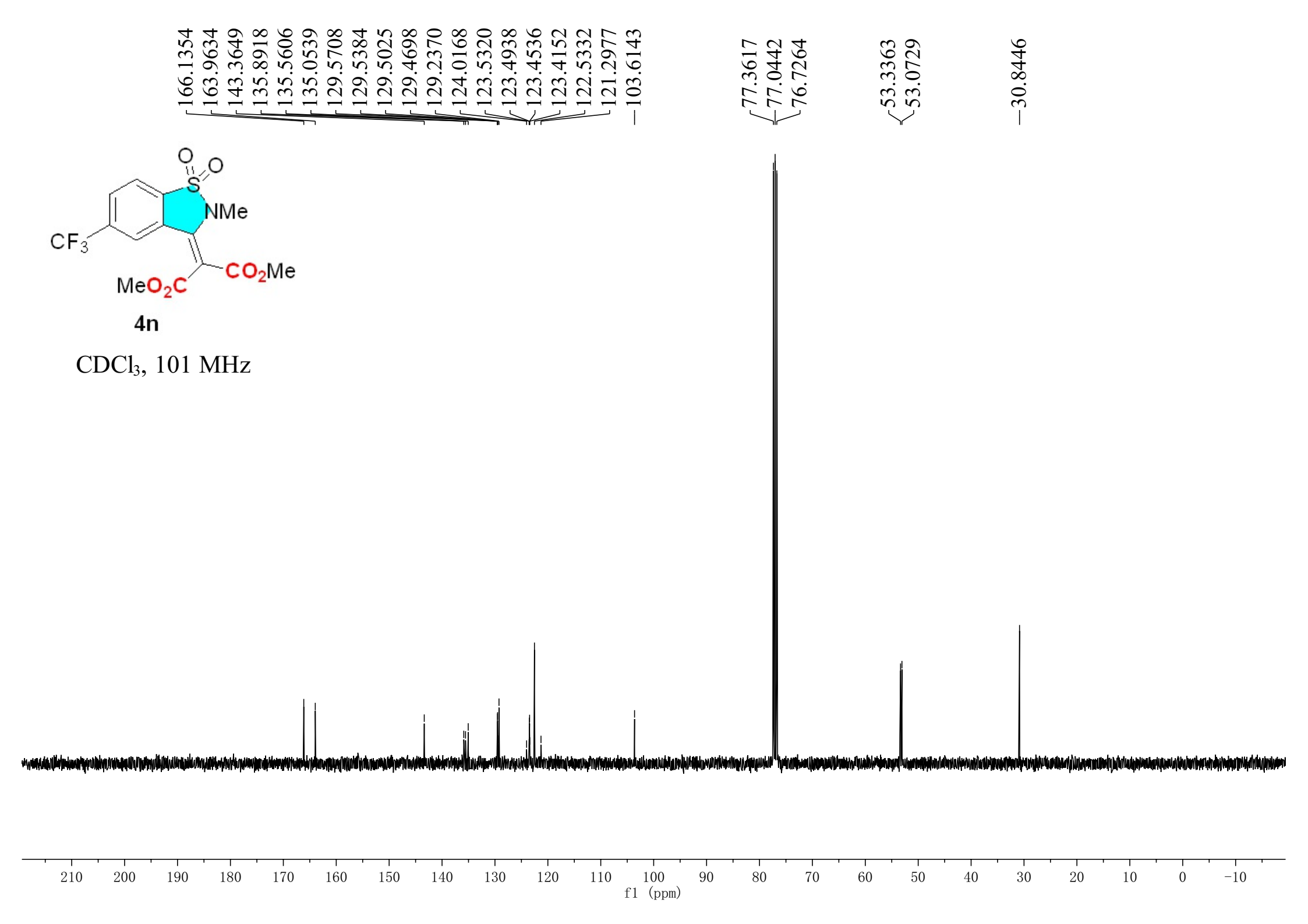
166.19
164.06
143.71
140.35
132.76
130.37
129.96
126.30
122.68
102.95
77.32
77.00
76.68
53.31
52.94
30.74

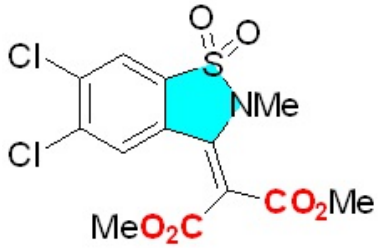




4n

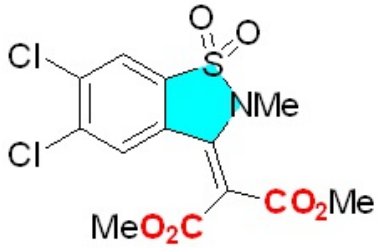
$CDCl_3$, 400 MHz


166.1354
163.9634
143.3649
135.8918
135.5606
135.0539
129.5708
129.5384
129.5025
129.4698
129.2370
124.0168
123.5320
123.4938
123.4536
123.4152
122.5332
121.2977
103.6143
77.3617
77.0442
76.7264
53.3363
53.0729
30.8446
O
O
S
NMe
CF3
MeO2C
CO2Me
4n
CDCl3, 101 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



4o

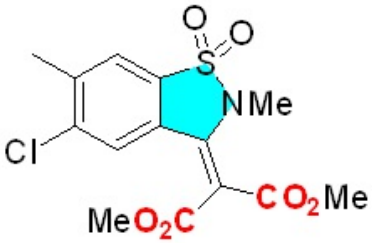
$CDCl_3$, 400 MHz



4o

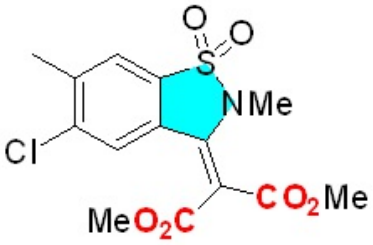
$CDCl_3$, 101 MHz

166.04
164.06
143.10
138.86
137.71
131.37
128.09
127.62
123.19
103.37
77.32
77.00
76.68
53.38
53.04
30.78



4p

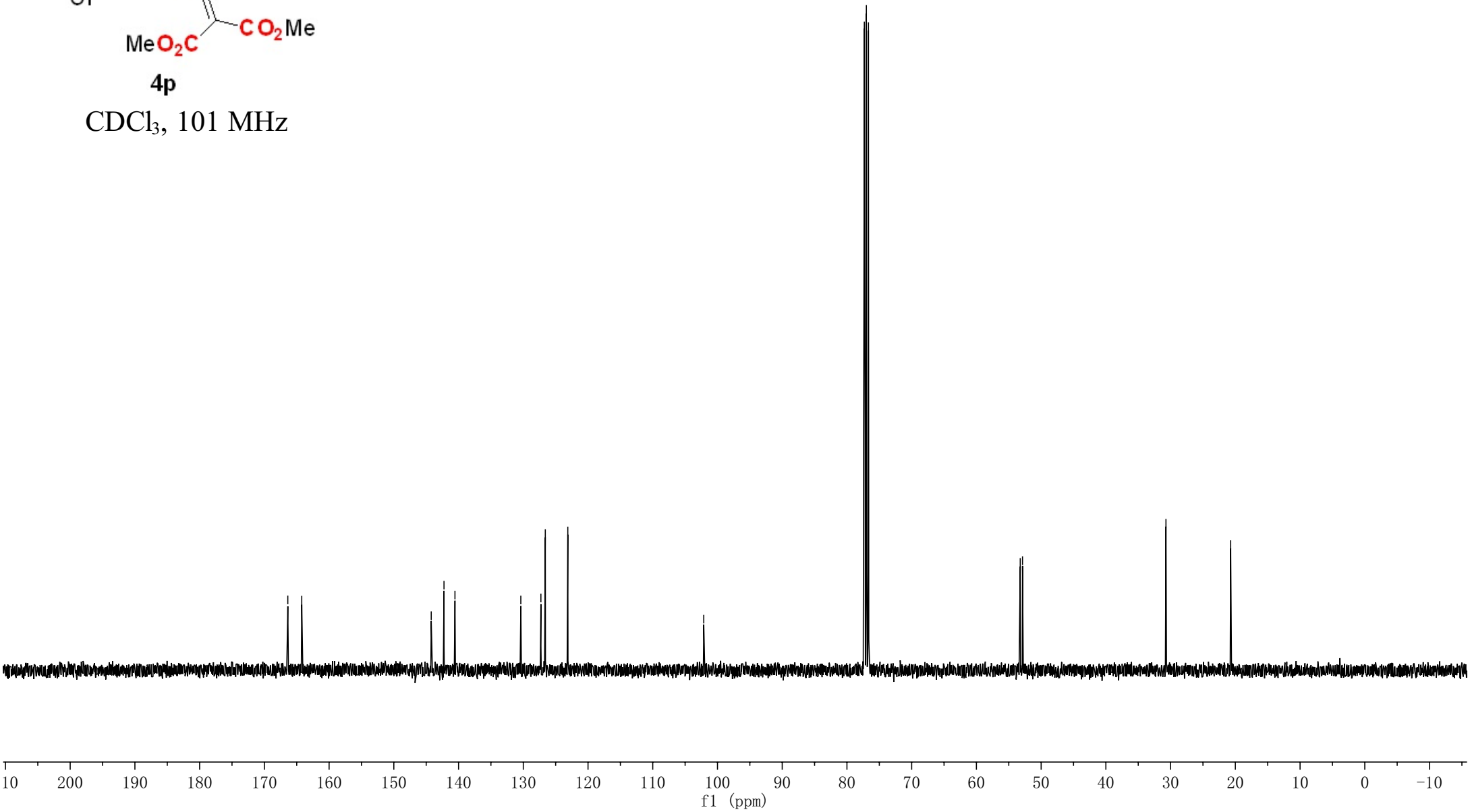
$CDCl_3$, 400 MHz

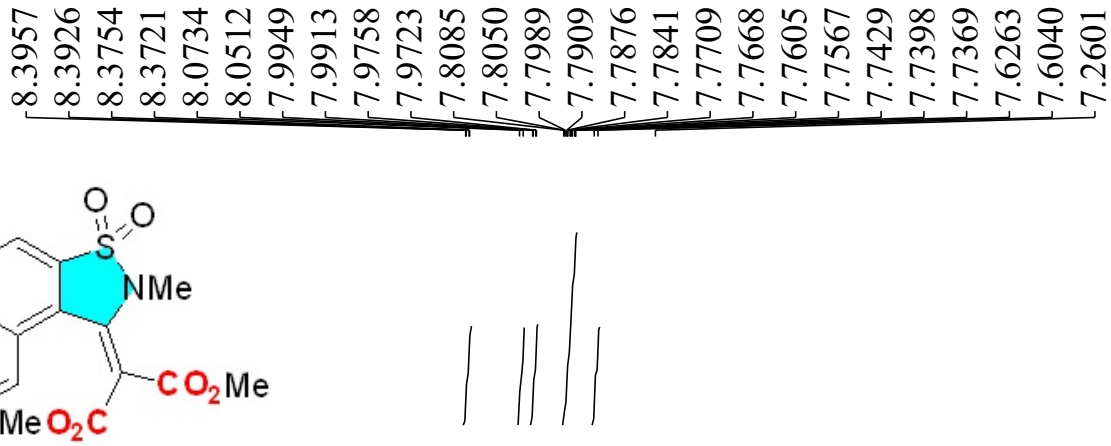


4p

$CDCl_3$, 101 MHz

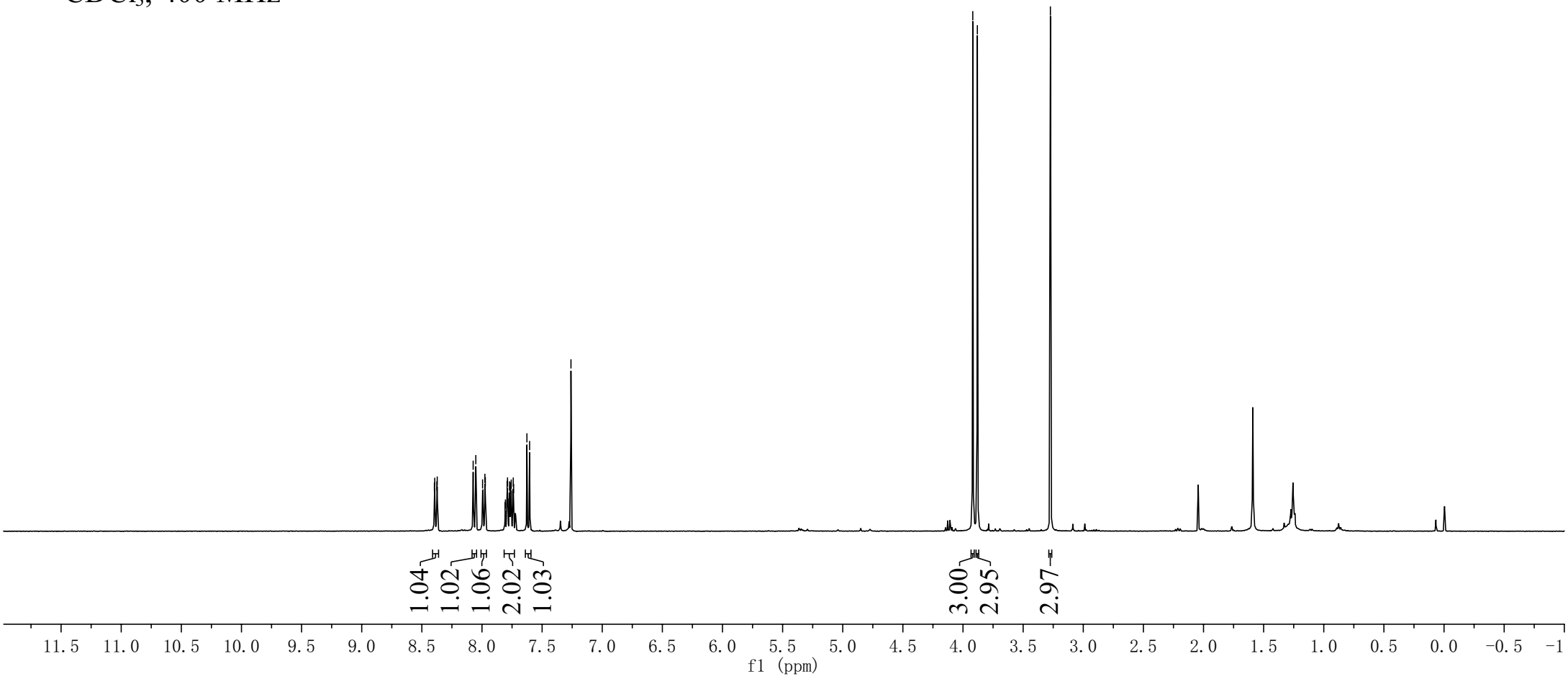
166.38
164.22
144.22
142.25
140.56
130.38
127.28
126.60
123.12
102.12
77.32
77.00
76.68
53.23
52.88
30.72
20.72

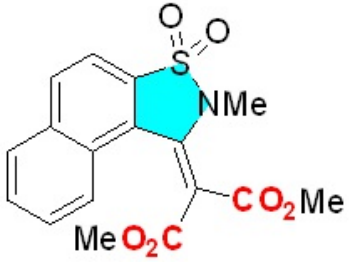




4r

$CDCl_3$, 400 MHz



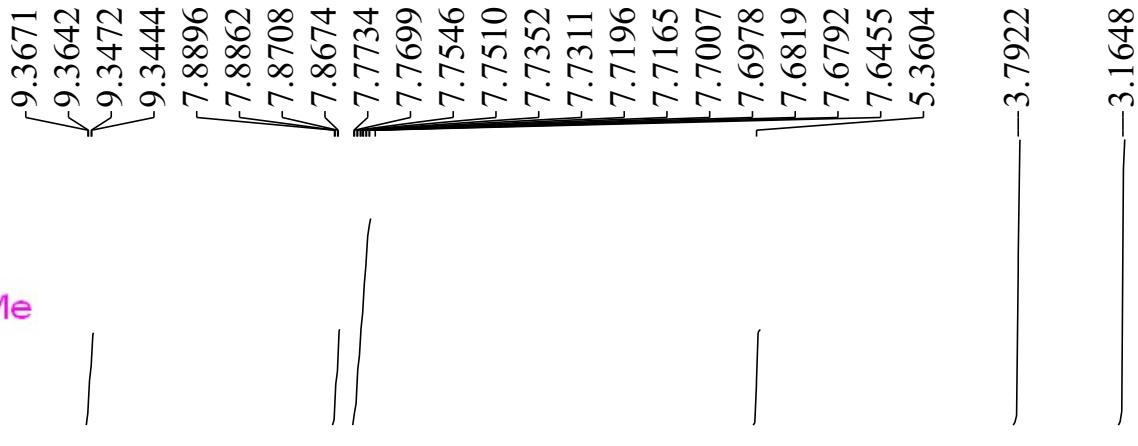


4r

$CDCl_3$, 101 MHz

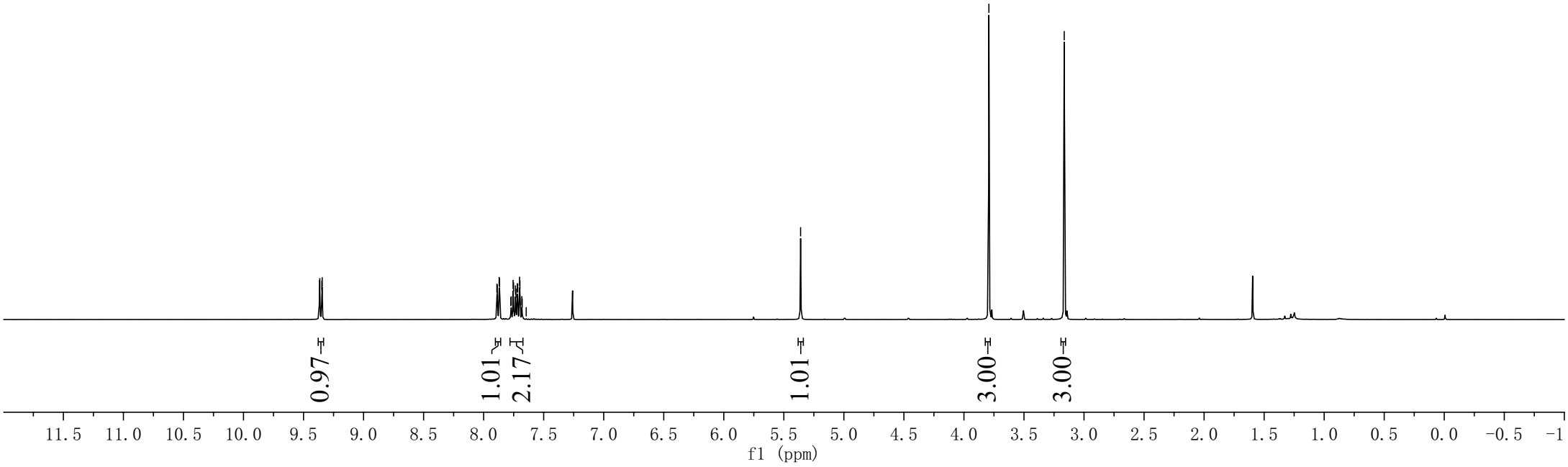
166.89
164.44
146.02
134.64
134.04
129.86
129.67
128.68
128.59
127.26
124.69
123.86
120.48
102.44
77.32
77.00
76.68
53.21
52.85
30.90

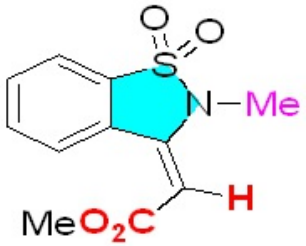
f1 (ppm)



4a'

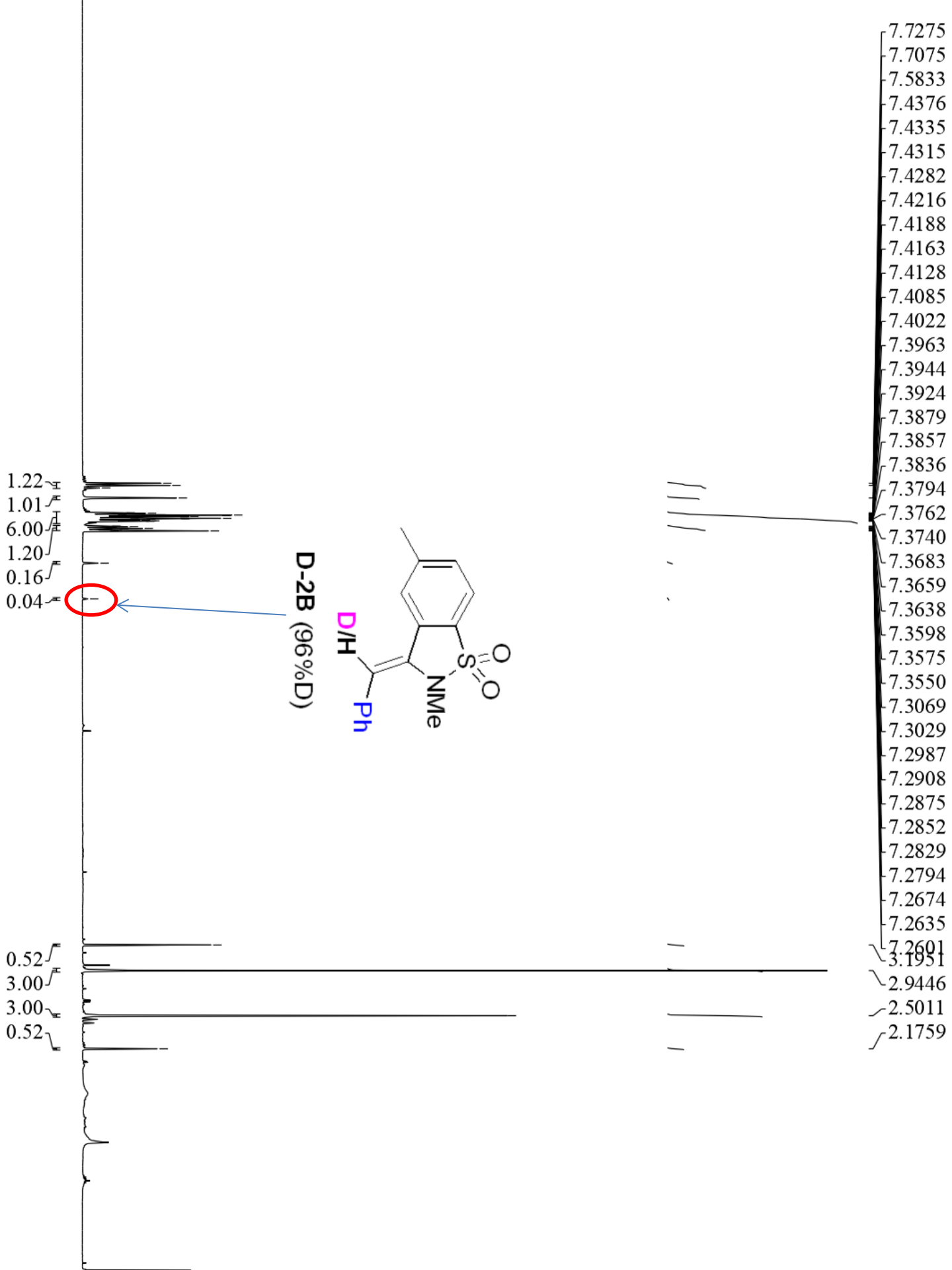
$CDCl_3$, 400 MHz

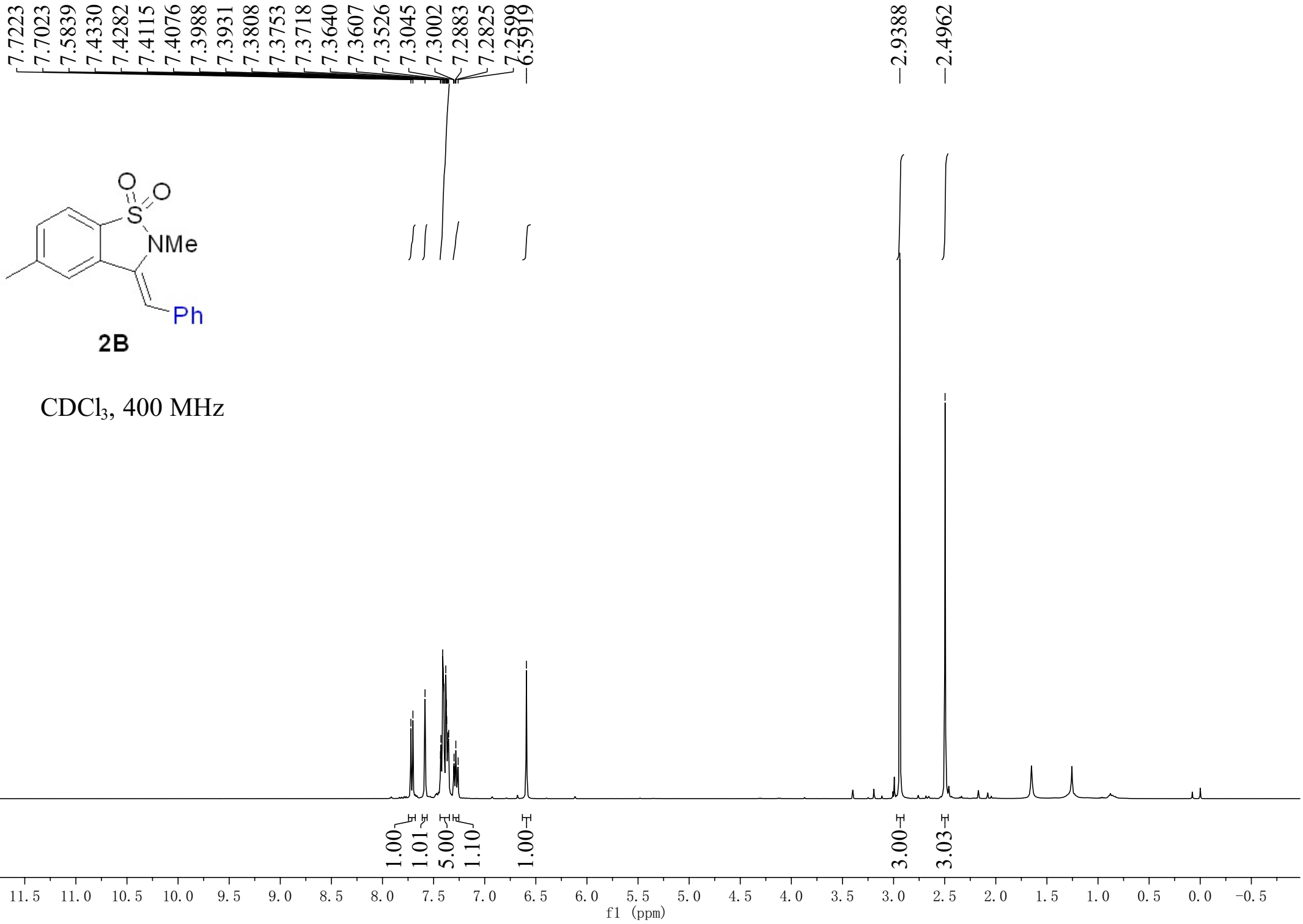




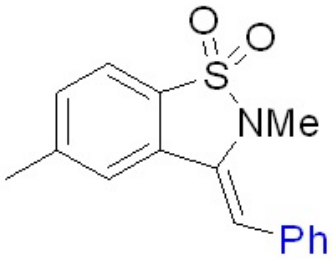
4a'

$CDCl_3$, 101 MHz


7.7275
7.7075
7.5833
7.4376
7.4335
7.4315
7.4282
7.4216
7.4188
7.4163
7.4128
7.4085
7.4022
7.3963
7.3944
7.3924
7.3879
7.3857
7.3836
7.3794
7.3762
7.3740
7.3683
7.3659
7.3638
7.3598
7.3575
7.3550
7.3069
7.3029
7.2987
7.2908
7.2875
7.2852
7.2829
7.2794
7.2674
7.2635
7.2601
3.1951
2.9446
2.5011
2.1759
1.22
1.01
6.00
1.20
0.16
0.04
0.52
3.00
3.00
0.52
D-2B (96%D)
D/H
Ph
NMe
S
O
O

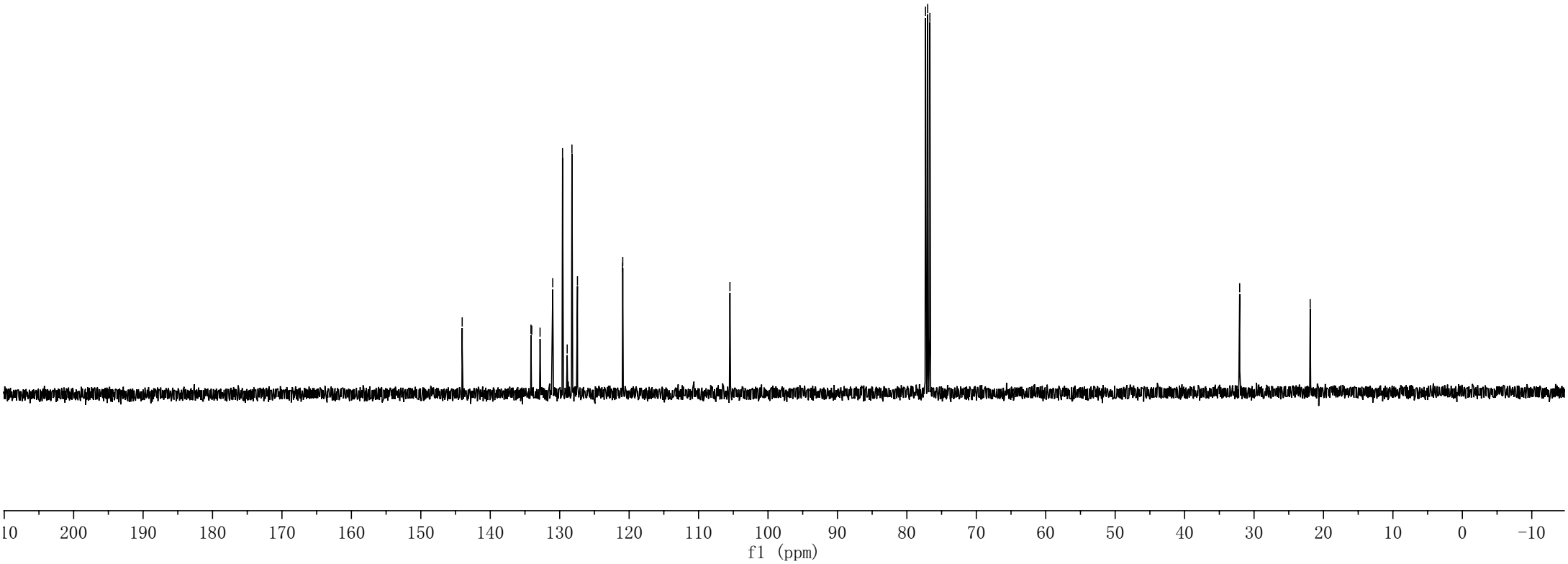

7.7223
7.7023
7.5839
7.4330
7.4282
7.4115
7.4076
7.3988
7.3931
7.3808
7.3753
7.3718
7.3640
7.3607
7.3526
7.3045
7.3002
7.2883
7.2825
7.2599
6.5919
2.9388
2.4962
O
O
S
NMe
Ph
2B
CDCl3, 400 MHz
1.00
1.01
5.00
1.10
1.00
3.00
3.03
f1 (ppm)

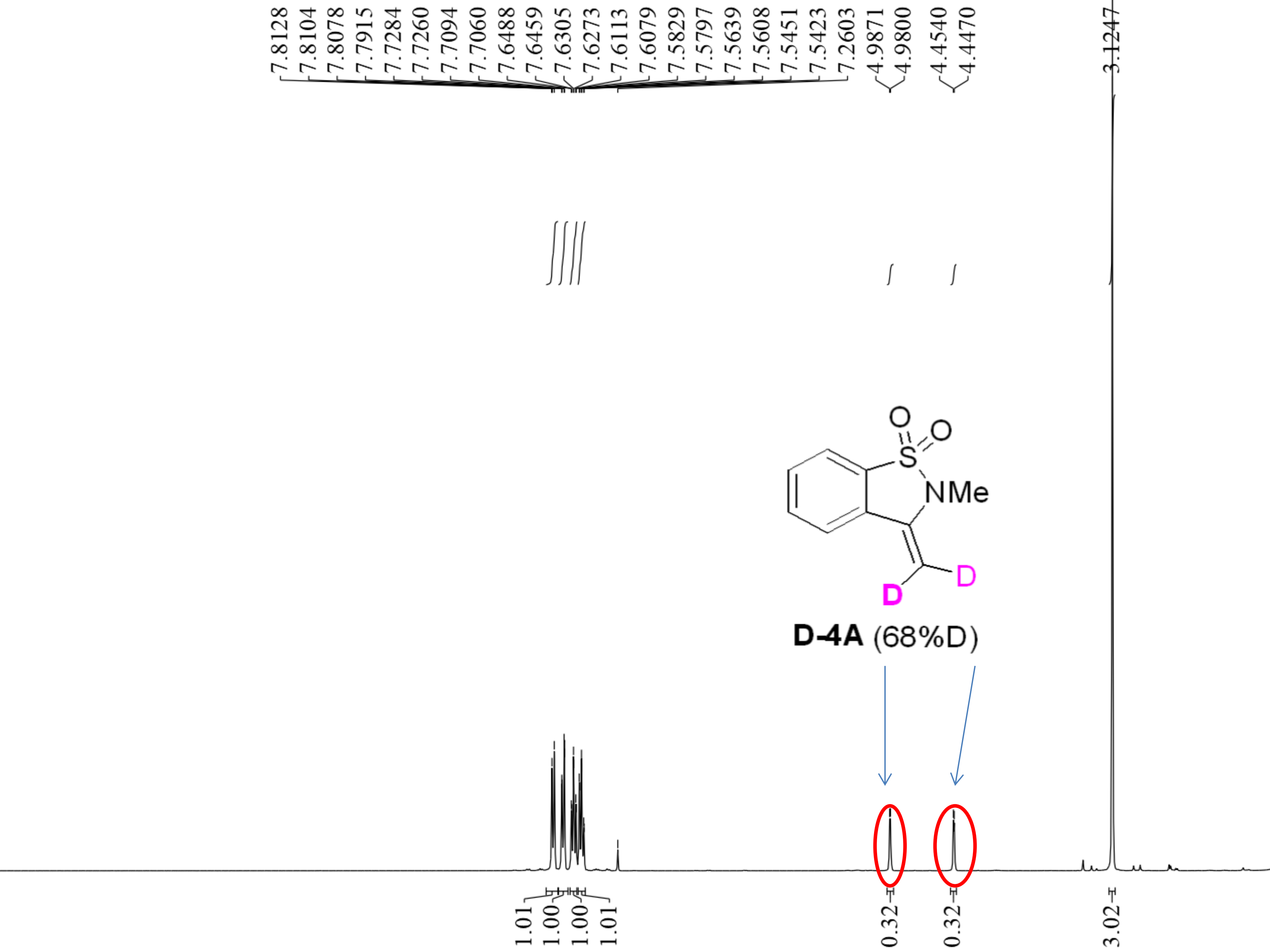
144.04
134.14
134.02
132.83
131.00
129.59
128.92
128.23
127.44
120.94
120.92
105.48
77.32
77.00
76.68
32.07
21.91

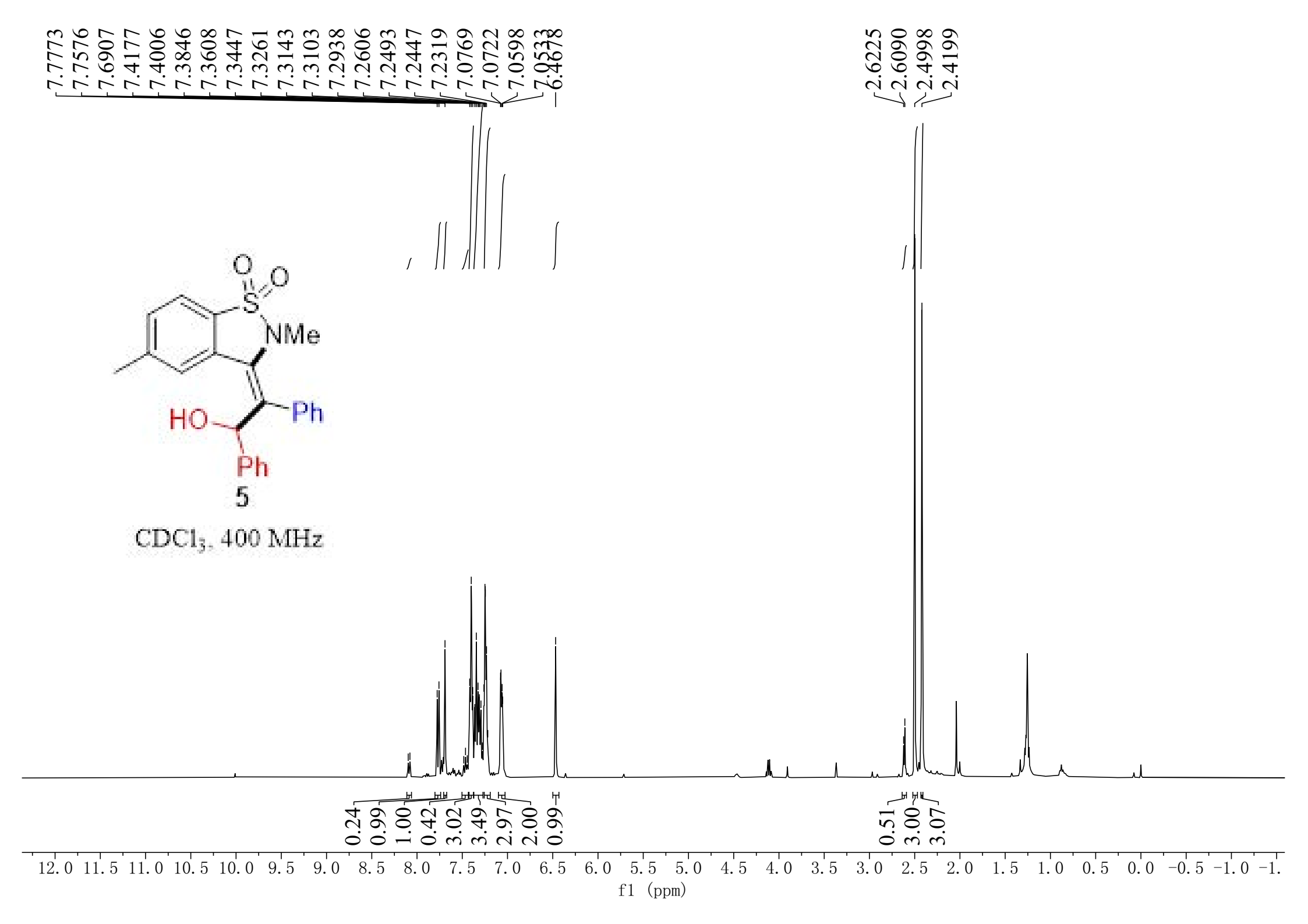


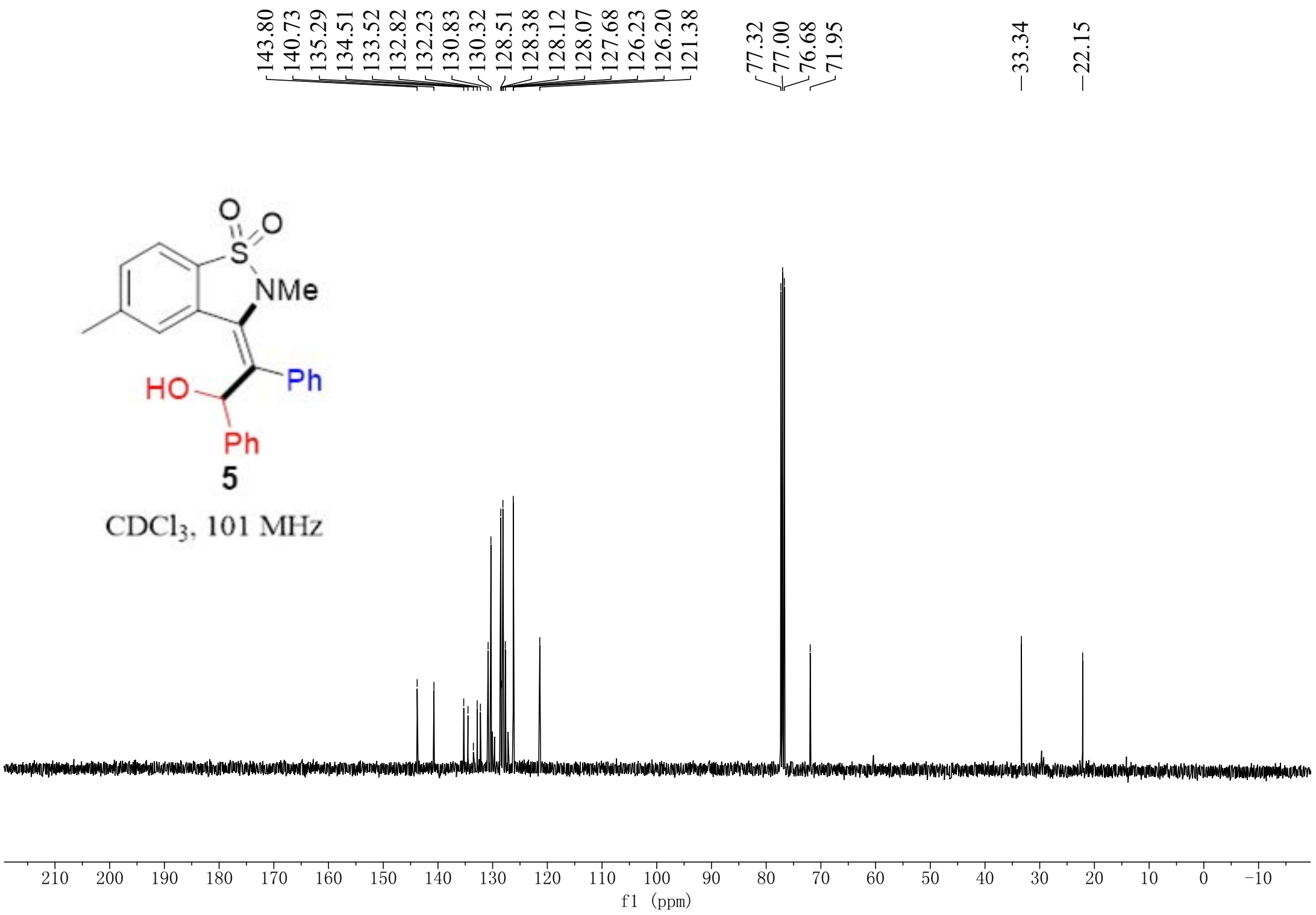
2B

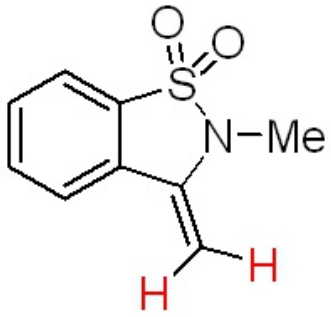
$CDCl_3$, 101 MHz




7.8128
7.8104
7.8078
7.7915
7.7284
7.7260
7.7094
7.7060
7.6488
7.6459
7.6305
7.6273
7.6113
7.6079
7.5829
7.5797
7.5639
7.5608
7.5451
7.5423
7.2603
4.9871
4.9800
4.4540
4.4470
3.1247
O
O
S
NMe
D
D
D-4A (68%D)
1.01
1.00
1.00
1.01
0.32
0.32
3.02

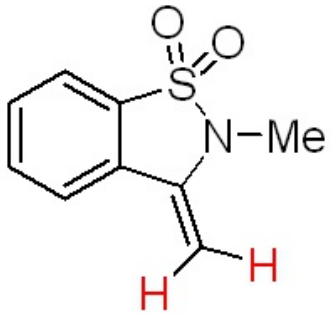

7.7773
7.7576
7.6907
7.4177
7.4006
7.3846
7.3608
7.3447
7.3261
7.3143
7.3103
7.2938
7.2606
7.2493
7.2447
7.2319
7.0769
7.0722
7.0598
2.6225
2.6090
2.4998
2.4199
O
O
S
NMe
HO
Ph
Ph
5
CDCl3, 400 MHz
0.24
0.99
1.00
0.42
3.02
3.49
2.97
2.00
0.99
0.51
3.00
3.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.
f1 (ppm)


143.80
140.73
135.29
134.51
133.52
132.82
132.23
130.83
130.32
128.51
128.38
128.12
128.07
127.68
126.23
126.20
121.38
77.32
77.00
76.68
71.95
33.34
22.15
O
O
S
NMe
HO
Ph
Ph
5
CDCl3, 101 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



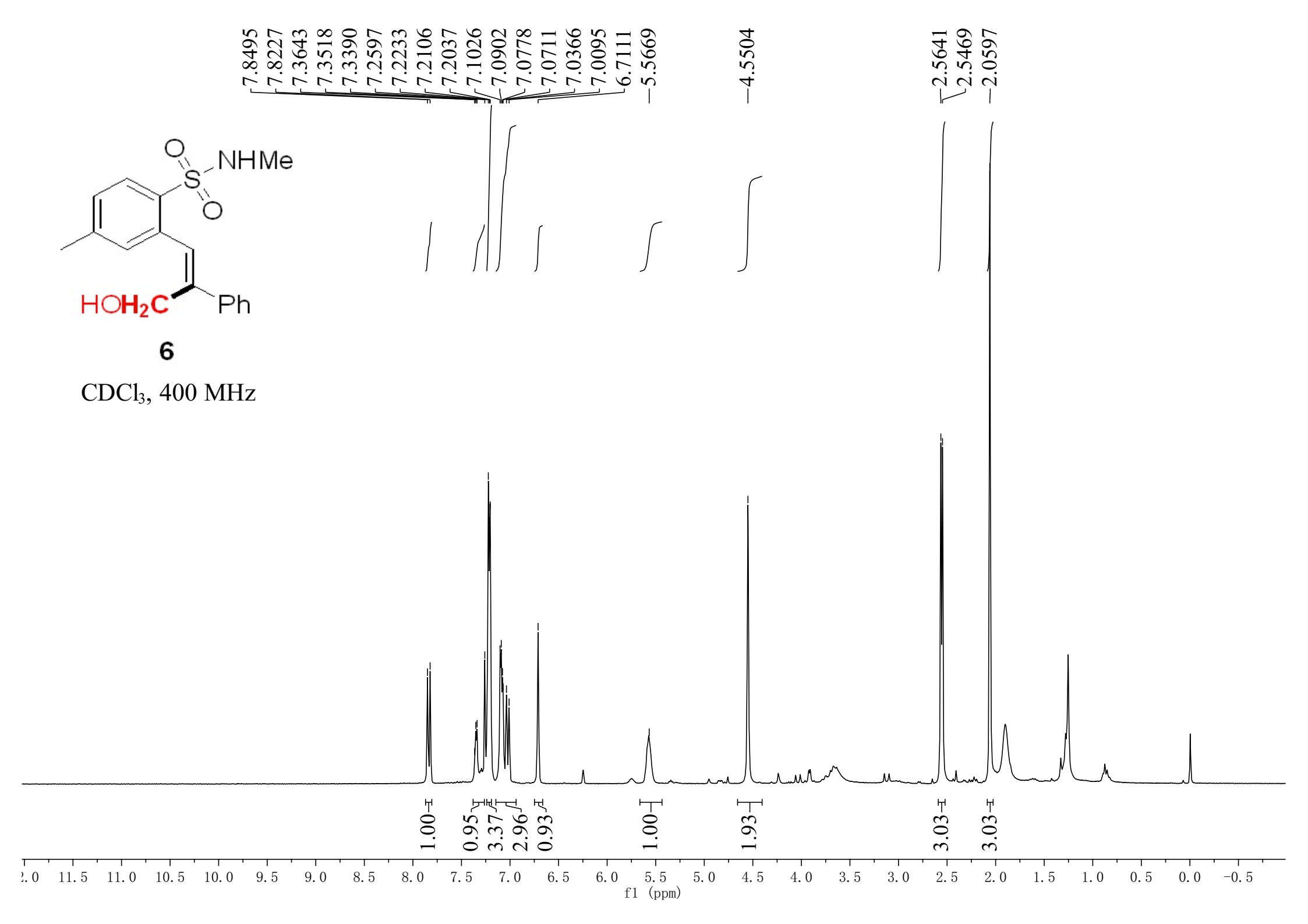
4A

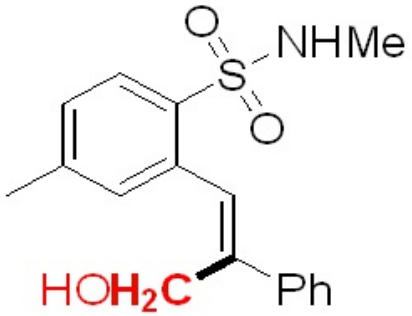
$CDCl_3$, 400 MHz



4A

$CDCl_3$, 101 MHz


7.8495
7.8227
7.3643
7.3518
7.3390
7.2597
7.2233
7.2106
7.2037
7.1026
7.0902
7.0778
7.0711
7.0366
7.0095
6.7111
5.5669
4.5504
2.5641
2.5469
2.0597
NHMe
HOH2C
Ph
6
CDCl3, 400 MHz
1.00
0.95
3.37
2.96
0.93
1.00
1.93
3.03
3.03
f1 (ppm)



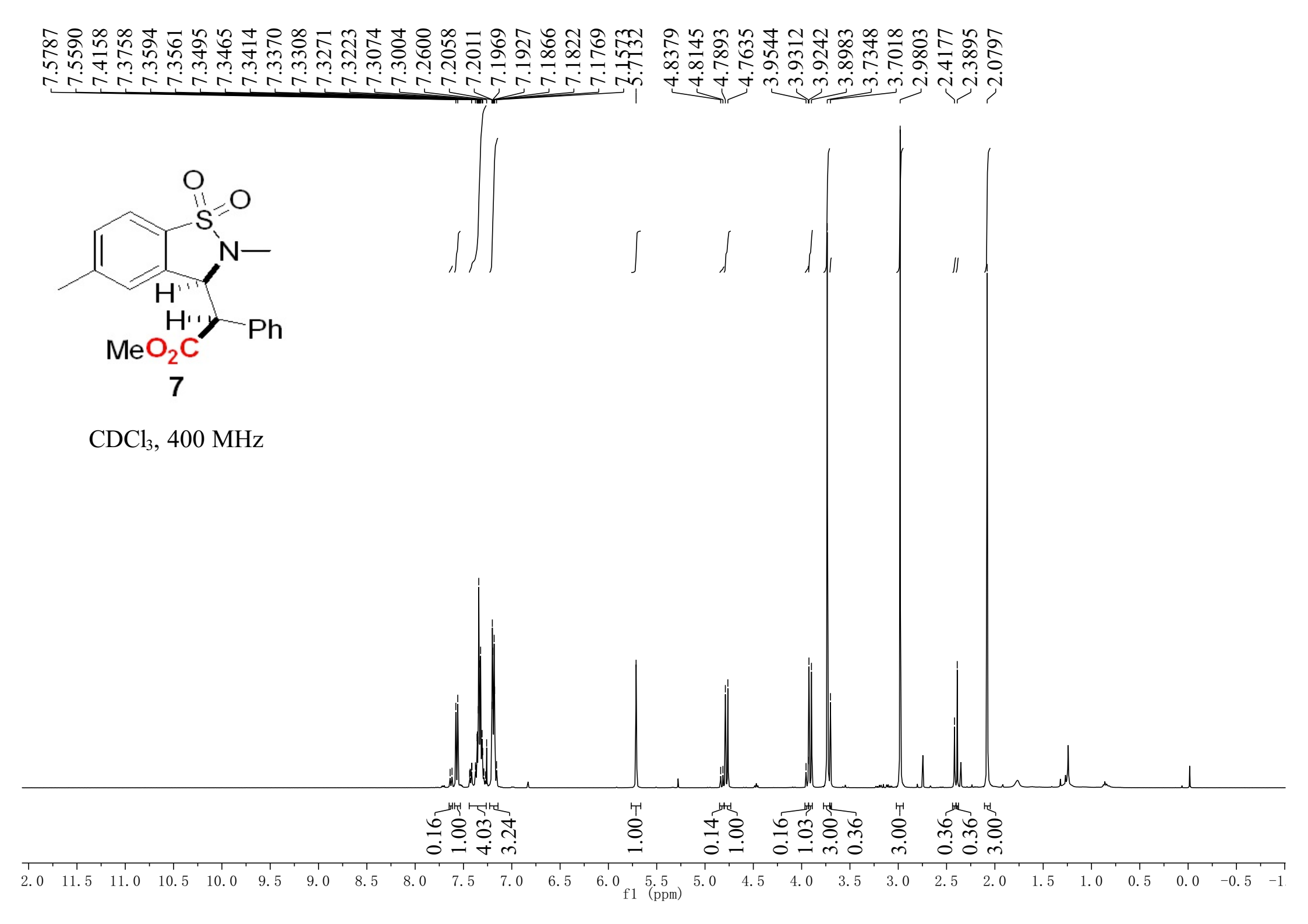
6

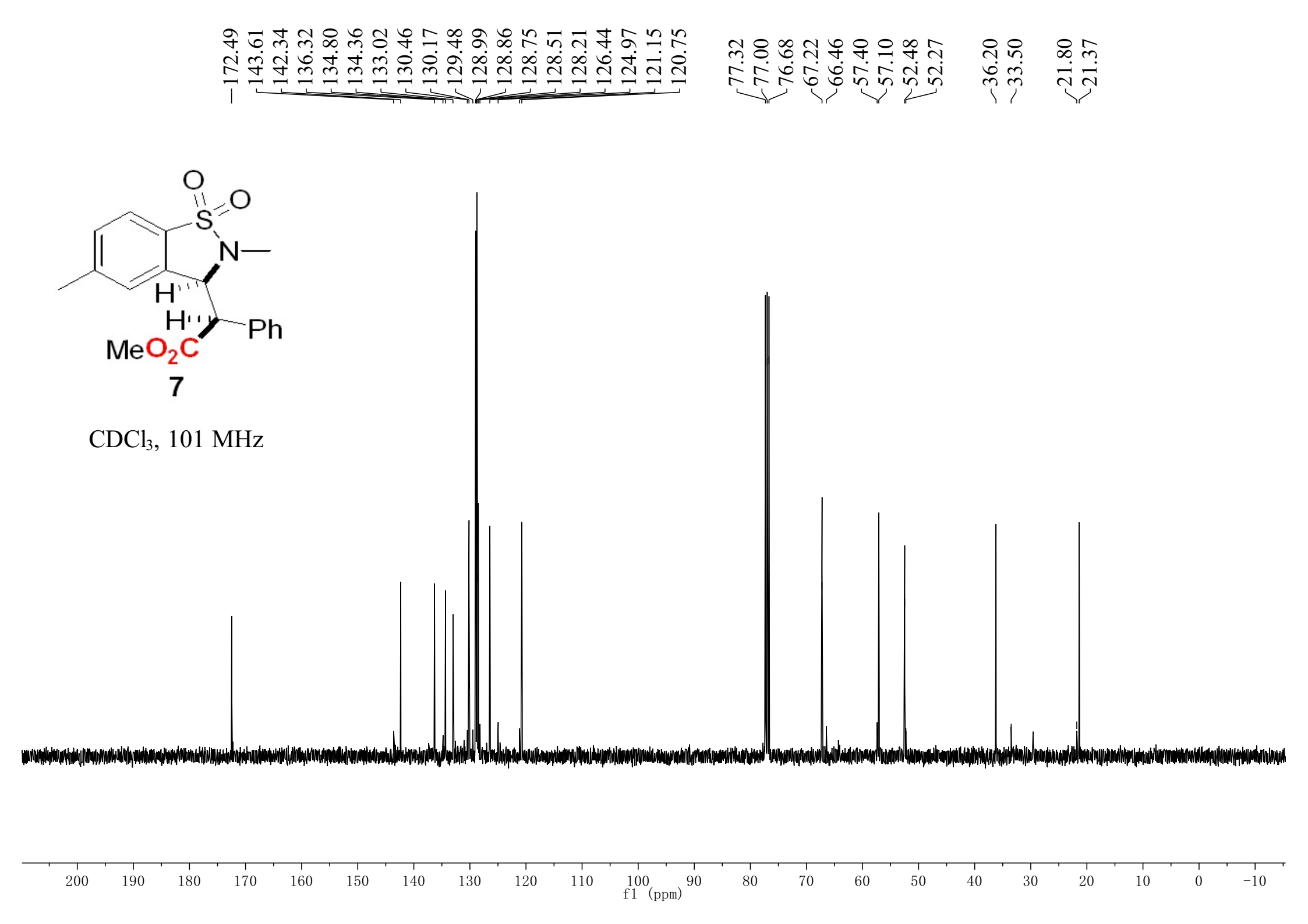
$CDCl_3$, 101 MHz

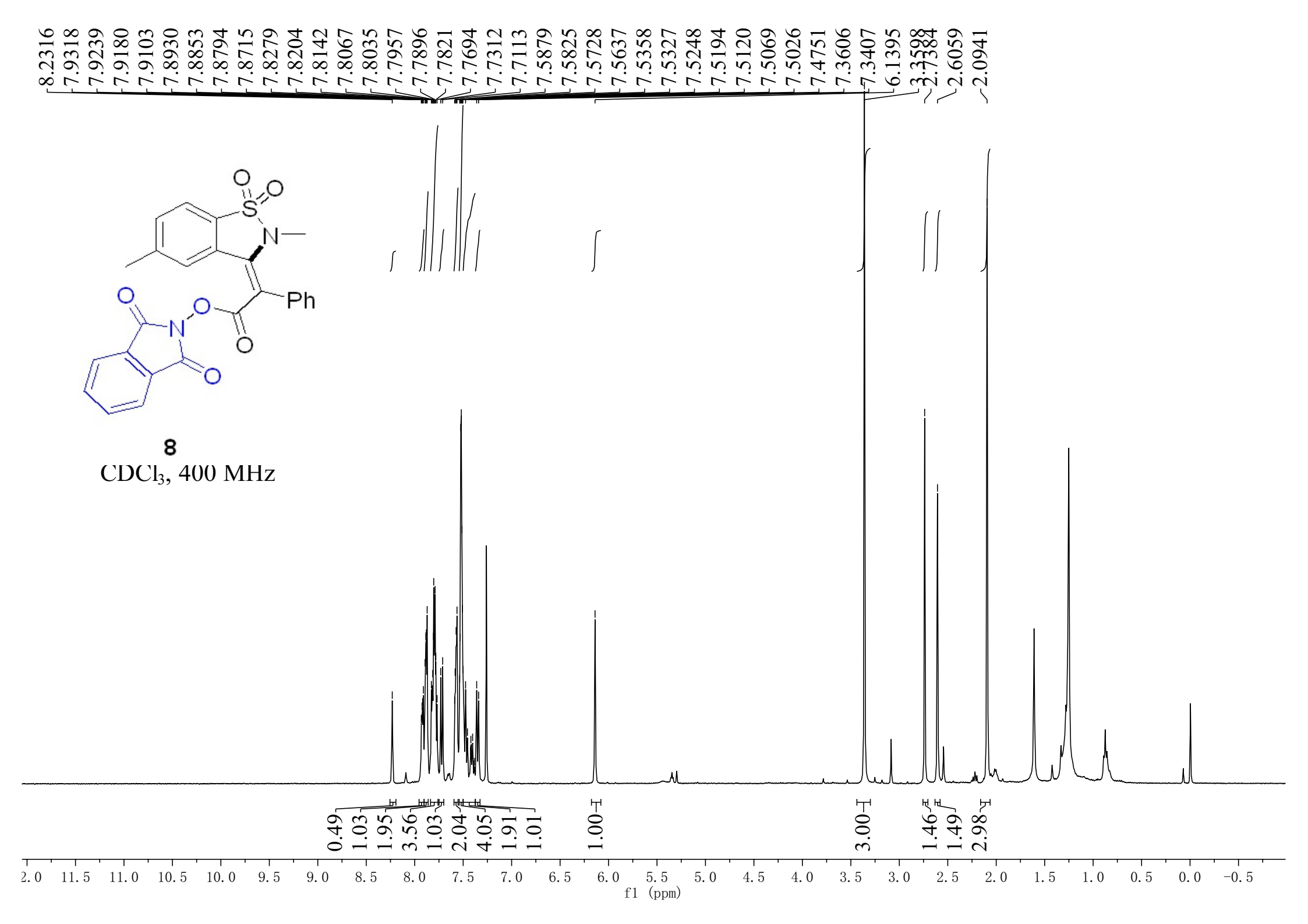
144.40
142.53
137.43
135.83
133.61
133.13
129.91
128.64
128.42
127.65
127.34
122.79
77.42
77.00
76.58
66.91
28.88
21.07

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

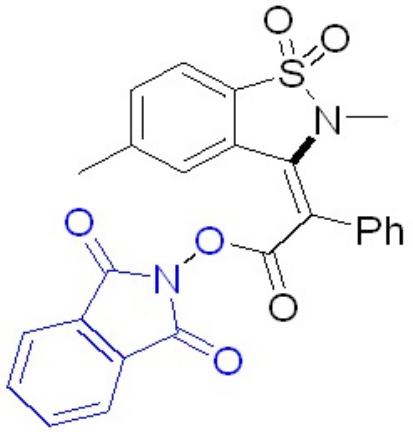

7.5787
7.5590
7.4158
7.3758
7.3594
7.3561
7.3495
7.3465
7.3414
7.3370
7.3308
7.3271
7.3223
7.3074
7.3004
7.2600
7.2058
7.2011
7.1969
7.1927
7.1866
7.1822
7.1769
7.1573
7.1132
4.8379
4.8145
4.7893
4.7635
3.9544
3.9312
3.9242
3.8983
3.7348
3.7018
2.9803
2.4177
2.3895
2.0797
O
O
S
N
H
H
Ph
MeO2C
7
CDCl3, 400 MHz
0.16
1.00
4.03
3.24
1.00
0.14
1.00
0.16
1.03
3.00
0.36
3.00
0.36
0.36
3.00
f1 (ppm)


172.49
143.61
142.34
136.32
134.80
134.36
133.02
130.46
130.17
129.48
128.99
128.86
128.75
128.51
128.21
126.44
124.97
121.15
120.75
77.32
77.00
76.68
67.22
66.46
57.40
57.10
52.48
52.27
36.20
33.50
21.80
21.37
O
O
S
N
H
H
Ph
MeO2C
7
CDCl3, 101 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



8

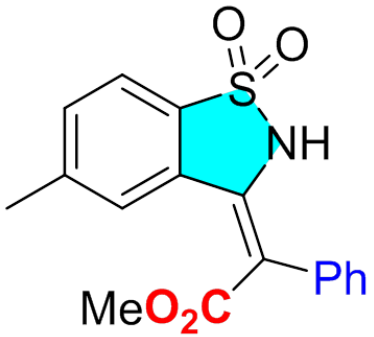
$CDCl_3$, 400 MHz



8

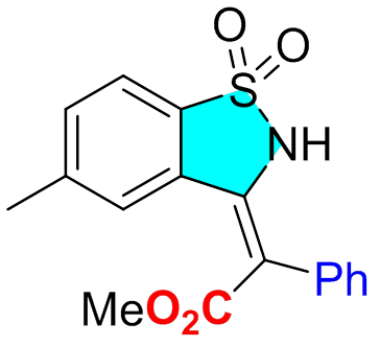
$CDCl_3$, 101 MHz

166.2 163.2 162.7 162.3 162.2 161.6 145.5 145.0 144.2 135.0 134.8 134.8 134.7 134.1 133.1 132.6 131.8 130.9 130.8 129.9 129.9 129.6 129.5 129.4 129.4 129.2 129.1 129.0 128.9 128.8 128.0 126.8 126.6 124.1 124.0 123.9 121.2 121.1 105.2 103.6 31.7 31.6 22.0



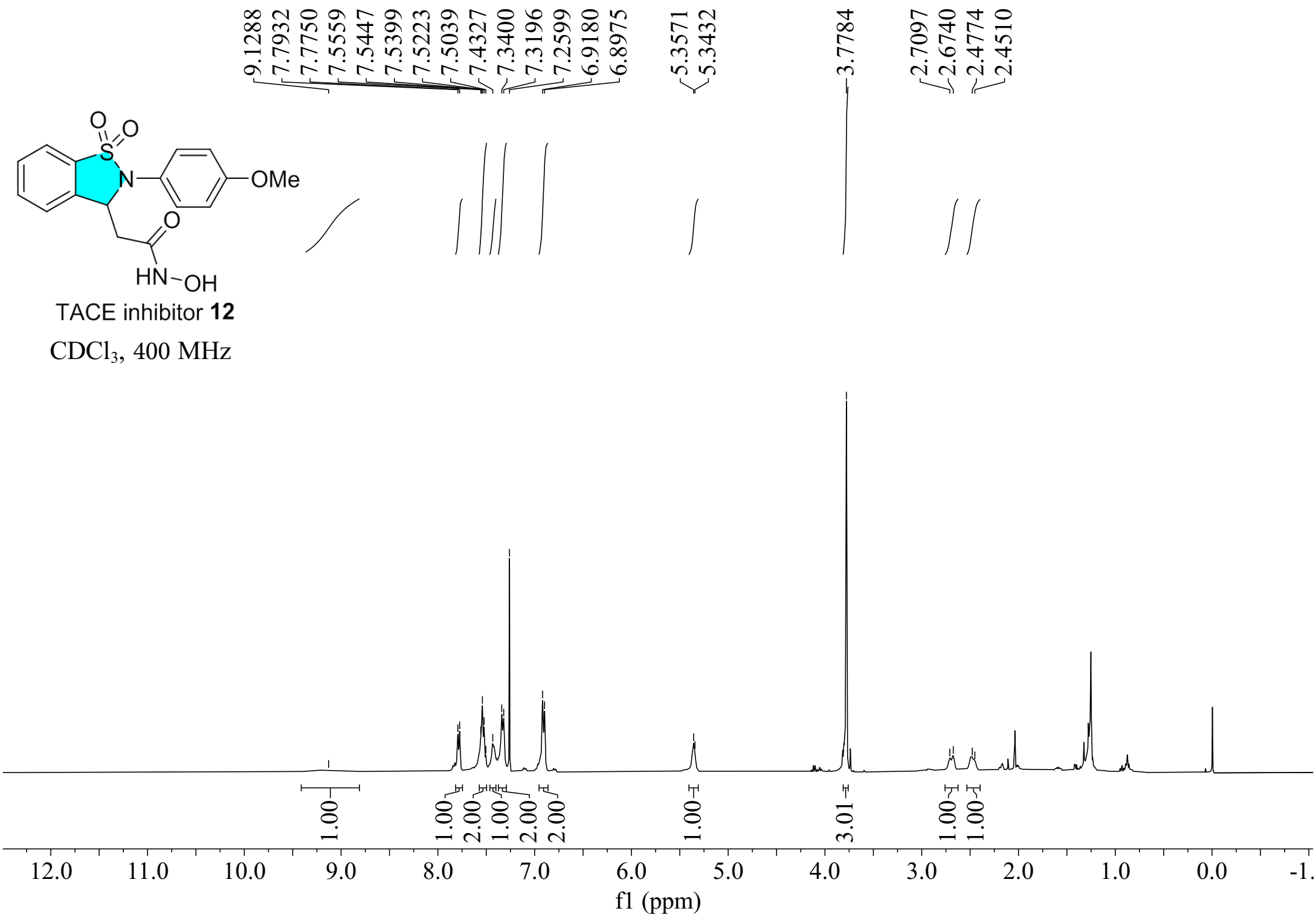
9

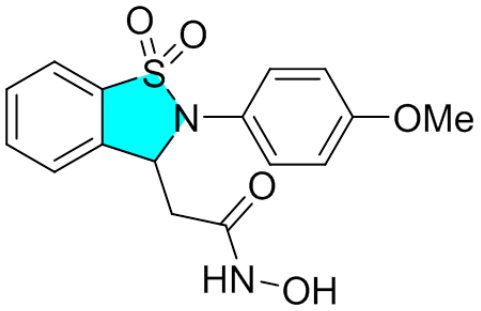
$CDCl_3$, 400 MHz



9

$CDCl_3$, 101 MHz


9.1288
7.7932
7.7750
7.5559
7.5447
7.5399
7.5223
7.5039
7.4327
7.3400
7.3196
7.2599
6.9180
6.8975
5.3571
5.3432
3.7784
2.7097
2.6740
2.4774
2.4510
O
O
S
N
OMe
O
HN
OH
TACE inhibitor 12
CDCl3, 400 MHz
1.00
1.00
2.00
1.00
2.00
2.00
1.00
3.01
1.00
1.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.
f1 (ppm)



TACE inhibitor **12**

$CDCl_3$, 101 MHz

159.57
148.98
136.06
134.16
133.31
129.89
129.10
125.92
124.31
121.52
115.17
77.32
77.00
76.68
59.65
55.52
37.09