Supporting Information

Catalytic divergent synthesis of imidazoles via reaction condition-dependent [3 + 2] cyclization of TosMIC

Cheng Zhao,[a†] Man-Zhen Gu,[a†] Yi-Yuan Chen,[a] Xiao-Wei Hu,[a] Yi-Bing Xu,[a] Xiao-Min Lin,[a] Xin-Ni Liu,[a] Long Chen,[d] Guo-Shu Chen,[a] and Yun-Lin Liu*[a,b,c]

Email: ylliu@gzhu.edu.cn

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1. General Information

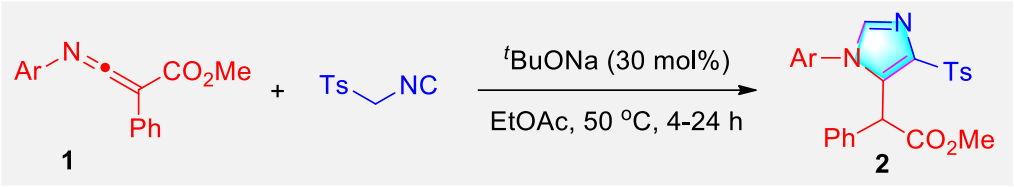
Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker DPX-400 spectrometer. Chemical shifts are reported in ppm from $CDCl_3$ with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad.

Anhydrous solvents such as CH_2Cl_2, CH_3CN, THF, toluene, and EtOAc, and the catalysts such as Et_3N, DABCO, DBU, Ag_2CO_3, ^{t}BuOLi, ^{t}BuONa, and ^{t}BuOK were purchased from Energy Chemical. Unless otherwise stated, all purchased reagents were used without further purification. The; All reactions involving air- or moisture-sensitive compounds were carried out under nitrogen atmosphere in dried Schlenk tube. The ketenimines **1**[1] was prepared using the literature procedures.

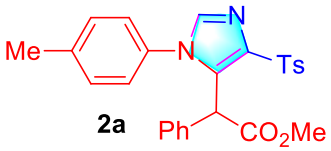
References

[1] (a) P. Lu and Y. Wang, *Chem. Soc. Rev.*, 2012, **41**, 5687; (b) Y. Cheng, Y.-G. Ma, X.-R. Wang and J.-M. Mo, *J. Org. Chem.*, 2009, **74**, 850.

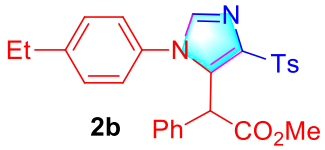
2. General procedure and spectral data of products 2.



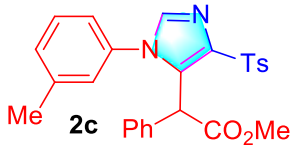
General Procedure: Under nitrogen atmosphere, ketenimines **1** (0.1 mmol), *p*-toluenesulfonylmethyl isocyanide (TosMIC) (0.12 mmol), ^{t}BuONa (30 mol%), and EtOAc (1.0 mL) were successively added to a oven-dried 10 mL schlenk tube. The reaction mixture was then stirred at 50 °C for 4-24 h, and monitored by TLC. After completion, the reaction mixture was cooled down to room temperature and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/EtOAc (5:1 to 1:1) as the eluent to afford the 1,4,5-trisubstituted imidazoles **2**.



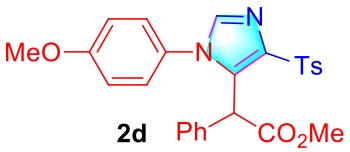
The reaction was run at 50 °C for 4 h, affording product **2a** in 97% yield as a yellow solid (44.6 mg, m.p. 176-178 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 2.43 (s, 3H), 3.71 (s, 3H), 6.10 (s, 1H), 6.78 (ABd, *J* = 8.0 Hz, 2H), 6.89 (ABd, *J* = 7.6 Hz, 2H), 7.05 (ABd, *J* = 8.0 Hz, 2H), 7.09-7.18 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.45 (s, 1H), 7.94 (ABd, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.00, 144.16, 140.02, 139.27, 138.25, 134.62, 133.41, 131.99, 129.66, 129.62, 128.94, 128.14, 128.00, 127.22, 52.58, 46.24, 21.63, 21.13; HRMS (ESI): Exact mass calcd for $C_{26}H_{25}N_2O_4S$ $[M+H]^+$: 461.1530, Found: 461.1530.



The reaction was run at 50 °C for 4 h, affording product **2b** in 84% yield as a yellow solid (39.8 mg, m.p. 180-183 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, *J* = 8.0 Hz, 3H), 2.43 (s, 3H), 2.65 (q, *J* = 7.6 Hz, 2H), 3.72 (s, 3H), 6.13 (s, 1H), 6.81 (d, *J* = 7.6 Hz, 2H), 6.86 (d, *J* = 7.2 Hz, 2H), 7.06-7.16 (m, 5H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.46 (s, 1H), 7.94 (ABd, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.04, 146.27, 144.16, 139.25, 138.24, 134.55, 133.40, 132.15, 129.62, 128.89, 128.49, 128.12, 127.97, 127.29, 127.16, 52.58, 46.27, 28.47, 21.63, 15.53; HRMS (ESI): Exact mass calcd for $C_{27}H_{27}N_2O_4S$ $[M+H]^+$: 475.1686, Found: 475.1674.

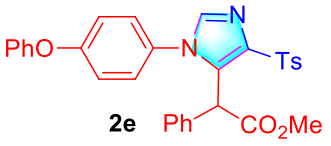


The reaction was run at 50 °C for 4 h, affording product **2c** in 90% yield as a yellow solid (41.4 mg, m.p. 81-84 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.20 (s, 3H), 2.43 (s, 3H), 3.72 (s, 3H), 6.12 (s, 1H), 6.54 (s, 1H), 6.80 (d, *J* = 5.6 Hz, 1H), 6.87 (d, *J* = 7.2 Hz, 2H), 7.10 (t, *J* = 6.8 Hz, 2H), 7.14-7.18 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.46 (s, 1H), 7.95 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.99 144.20, 139.28, 139.10, 138.20, 134.50, 134.41, 133.31, 130.44, 129.64, 128.93, 128.83, 128.09, 128.07, 127.97, 127.16, 124.49, 52.58, 46.29, 21.63, 20.99; HRMS (ESI): Exact mass calcd for $C_{26}H_{25}N_2O_4S$ $[M+H]^+$: 461.1530, Found: 461.1517.



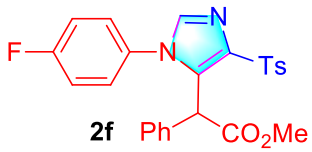
2d

The reaction was run at 50 °C for 8 h, affording product **2d** in 58% yield as a yellow solid (27.6 mg, m.p. 191-193 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.72 (s, 3H), 3.80 (s, 3H), 6.13 (s, 1H), 6.73 (ABd, *J* = 8.8 Hz, 2H), 6.80 (ABd, *J* = 8.4 Hz, 2H), 6.88 (ABd, *J* = 6.8 Hz, 2H), 7.10-7.18 (m, 3H), 7.33 (d, *J* = 8 Hz, 2H), 7.44 (s, 1H), 7.94 (ABd, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.04, 160.29, 144.19, 139.51, 138.17, 138.13, 134.59, 133.58, 129.64, 128.86, 128.74, 128.17, 127.95, 127.23, 127.10, 114.08, 55.56, 52.61, 46.21, 21.64; HRMS (ESI): Exact mass calcd for $C_{26}H_{25}N_2O_5S$ $[M+H]^+$: 477.1479, Found: 477.1431.



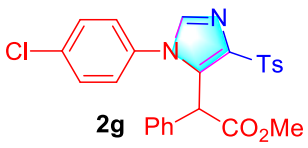
2e

The reaction was run at 50 °C for 14 h, affording product **2e** in 45% yield as a yellow solid (24.2 mg, m.p. 114-116 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.74 (s, 3H), 6.24 (s, 1H), 6.78-6.84 (m, 4H), 6.88 (d, *J* = 6.8 Hz, 2H), 7.02 (d, *J* = 7.6 Hz, 2H), 7.13-7.20 (m, 4H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.46 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.09, 158.67, 155.79, 144.26, 139.48, 138.47, 138.23, 134.55, 133.50, 130.04, 129.69, 129.11, 129.05, 128.79, 128.25, 127.98, 127.28, 124.43, 119.64, 118.13, 52.65, 46.26, 21.64; HRMS (ESI): Exact mass calcd for $C_{31}H_{27}N_2O_5S$ $[M+H]^+$: 539.1635, Found: 539.1623.



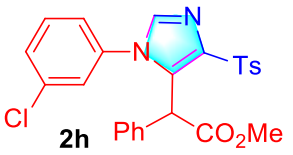
2f

The reaction was run at 50 °C for 4 h, affording product **2f** in 87% yield as a brown solid (40.4 mg, m.p. 189-191 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.74 (s, 3H), 6.31 (s, 1H), 6.80 (ABd, *J* = 7.2 Hz, 2H), 6.83-6.91 (m, 4H), 7.07-7.17 (m, 3H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.42 (s, 1H), 7.96 (ABd, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.08, 162.83 (d, *J* = 249.1 Hz), 144.33, 139.45, 138.75, 138.19, 134.40, 133.37, 130.70 (d, *J* = 3.3 Hz), 129.72, 129.69, 129.60, 128.57, 128.30, 127.95, 127.32, 115.86 (d, *J* = 22.9 Hz), 52.65, 46.25, 21.64; HRMS (ESI): Exact mass calcd for $C_{25}H_{22}FN_2O_4S$ $[M+H]^+$: 465.1279, Found: 465.1272.



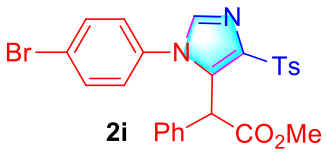
2g

The reaction was run at 50 °C for 4 h, affording product **2g** in 84% yield as a yellow solid (40.3 mg, m.p. 191-193 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.74 (s, 3H), 6.31 (s, 1H), 6.79-6.82 (m, 4H), 7.08-7.12 (m, 2H), 7.14-7.18 (m, 3H), 7.34 (ABd, *J* = 8.0 Hz, 2H), 7.42 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.08, 144.36, 139.26, 138.90, 138.16, 135.84, 134.36, 133.28, 133.23, 129.73, 129.07, 128.99, 128.60, 128.33, 127.97, 127.37, 52.68, 46.28, 21.65; HRMS (ESI): Exact mass calcd for $C_{25}H_{22}ClN_2O_4S$ $[M+H]^+$: 481.0983, Found: 481.0972.



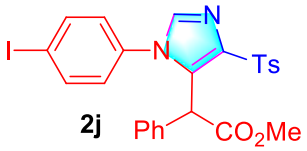
2h

The reaction was run at 50 °C for 4 h, affording product **2h** in 93% yield as a yellow solid (44.6 mg, m.p. 142-144 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.75 (s, 3H), 6.33 (s, 1H), 6.74 (s, 1H), 6.79 (d, *J* = 3.6 Hz, 2H), 6.86 (d, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 6.8 Hz, 2H), 7.14-7.19 (m, 2H), 7.32-7.36 (m, 3H), 7.42 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.98, 144.38, 139.10, 138.76, 138.06, 135.63, 134.49, 134.04, 133.19, 129.90, 129.83, 129.72, 128.52, 128.26, 128.00, 127.89, 127.45, 125.97, 52.69, 46.25, 21.63; HRMS (ESI): Exact mass calcd for $C_{25}H_{22}ClN_2O_4S$ $[M+H]^+$: 481.0983, Found: 481.0972.



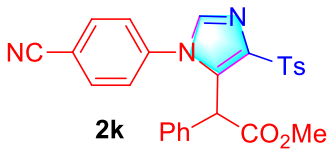
2i

The reaction was run at 50 °C for 4 h, affording product **2i** in 92% yield as a yellow solid (48.2 mg, m.p. 178-180 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.74 (s, 3H), 6.31 (s, 1H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 7.08-7.12 (m, 2H), 7.14-7.18 (m, 1H), 7.32-7.36 (m, 4H), 7.42 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.06, 144.36, 139.18, 138.89, 138.14, 134.33, 133.74, 133.22, 132.07, 129.73, 129.24, 128.59, 128.33, 127.95, 127.37, 123.88, 52.68, 46.27, 21.65; HRMS (ESI): Exact mass calcd for $C_{25}H_{22}BrN_2O_4S$ $[M+H]^+$: 525.0478, Found: 525.0477.



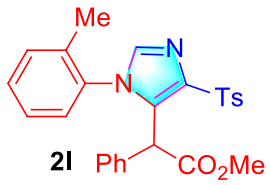
2j

The reaction was run at 50 °C for 4 h, affording product **2j** in 88% yield as a yellow solid (50.3 mg, m.p. 152-154 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.74 (s, 3H), 6.28 (s, 1H), 6.60 (ABd, *J* = 8.0 Hz, 2H), 6.80 (ABd, *J* = 7.2 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 2H), 7.15-7.18 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.41 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.94 (ABd, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.05, 144.36, 139.09, 138.80, 138.07, 134.38, 134.26, 133.15, 129.71, 129.31, 128.58, 128.31, 127.91, 127.34, 95.47, 52.70, 46.26, 21.64; HRMS (ESI): Exact mass calcd for $C_{25}H_{22}IN_2O_4S$ $[M+H]^+$: 573.0340, Found: 573.0330.



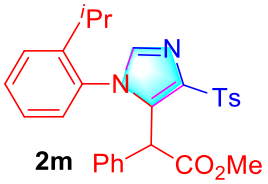
2k

The reaction was run at 50 °C for 4 h, affording product **2k** in 91% yield as a brown solid (42.8 mg, m.p. 218-220 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.77 (s, 3H), 6.46 (s, 1H), 6.72 (d, *J* = 7.2 Hz, 2H), 7.00 (d, *J* = 8 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.37 (d, *J* = 8.0 Hz 2H), 7.42 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.13, 144.60, 139.49, 138.98, 138.63, 137.90, 134.09, 133.05, 132.57, 129.83, 128.73, 128.46, 128.31, 127.91, 127.55, 117.36, 113.48, 52.82, 46.26, 21.67; HRMS (ESI): Exact mass calcd for $C_{26}H_{22}N_3O_4S$ $[M+H]^+$: 472.1326, Found: 472.1308.



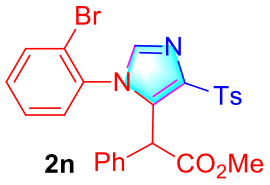
2l

The reaction was run at 50 °C for 24 h, affording product **2l** as an inseparable mixture of two diastereoisomers (2.4:1 ratio) in 67% yield (30.8 mg, yellow solid, m.p. 62-64 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (s, 3H), 1.57 (s, 1.3H), 2.44 (s, 4.1H), 3.70 (s, 1.25H), 3.76 (s, 3H), 5.39 (s, 0.36H), 6.16 (s, 1H), 6.79 (d, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 0.37H), 6.98-7.04 (m, 3.7H), 7.11-7.23 (m, 4.85H), 7.33-7.45 (m, 6H), 7.97-8.01 (m, 2.7H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.26, 169.87, 144.21, 138.93, 138.61, 138.35, 138.04, 137.97, 136.82, 134.64, 133.57, 133.20, 131.33, 130.89, 130.38, 129.70, 129.57, 129.40, 129.35, 128.63, 128.39, 128.25, 128.20, 128.19, 128.03, 127.96, 127.61, 127.31, 126.88, 126.51, 99.88, 91.57, 52.63, 46.20, 21.67, 16.66; HRMS (ESI): Exact mass calcd for $C_{26}H_{25}N_2O_4S$ $[M+H]^+$: 461.1530, Found: 461.1536.



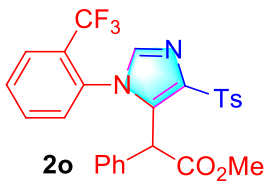
2m

The reaction was run at 50 °C for 24 h, affording product **2m** as an inseparable mixture of two diastereoisomers (1.4:1 ratio) in 57% yield (27.8 mg, yellow solid, m.p. 189-191 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.49 (d, *J* = 6.8 Hz, 2H), 0.82 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz 2H), 1.03 (d, *J* = 6.8 Hz, 3H), 2.07 (sep, *J* = 6.8 Hz, 0.8H), 2.24 (sep, *J* = 6.8 Hz, 1H), 2.44 (s, 5H), 3.75 (s, 2H), 3.76 (s, 3H), 5.20 (s, 0.64H), 5.50 (s, 1H), 6.92-6.95 (m, 3H), 6.99 (dd, *J* = 8.0, 0.8 Hz, 0.8H), 7.02-7.05 (m, 1.4H), 7.11-7.16 (m, 3H), 7.17-7.23 (m, 4H), 7.31-7.38 (m, 5.5H), 7.43-7.49 (m, 3.7H), 7.98 (d, *J* = 8.4 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 1.4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.12, 170.02, 147.08, 146.73, 144.16, 144.15, 138.92, 138.83, 138.25, 138.22, 138.04, 137.97, 134.10, 134.05, 133.61, 133.40, 131.75, 131.48, 130.93, 130.75, 129.59, 129.54, 129.52, 129.34, 128.50, 128.40, 128.38, 128.21, 128.16, 127.56, 127.48, 127.26, 126.99, 126.68, 126.43, 52.86, 52.70, 47.32, 46.84, 27.71, 27.49, 25.80, 25.51, 22.25, 21.66, 21.64, 21.39; HRMS (ESI): Exact mass calcd for $C_{28}H_{29}N_2O_4S$ $[M+H]^+$: 489.1843, Found: 489.1836.



2n

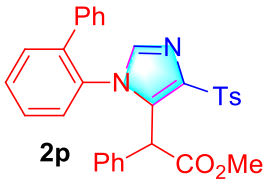
The reaction was run at 50 °C for 24 h, affording product **2n** in 54% yield as an inseparable mixture of two diastereoisomers (3:1 ratio) (28.3 mg, yellow solid, m.p. 68-70 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 1H), 2.44 (s, 3H), 3.69 (s, 1H), 3.78 (s, 3H), 5.73 (s, 0.3H), 6.27 (s, 1H), 6.75 (d, *J* = 7.2 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 0.4H), 6.99-7.05 (m, 3H), 7.08-7.12 (m 1H), 7.17-7.25 (m, 2H), 7.31-7.40 (m, 6H), 7.43-7.46 (m, 1H), 7.51 (s, 0.3H), 7.64 (d, *J* = 8.0 Hz, 0.3H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.58, 144.26, 139.36, 138.34, 136.22, 134.63, 134.08, 133.25, 132.94, 132.66, 131.60, 131.43, 131.41, 130.50, 130.16, 129.79, 129.73, 129.58, 129.15, 129.05, 128.45, 128.37, 128.19, 128.14, 127.89, 127.81, 127.58, 127.26, 123.25, 52.71, 46.54, 46.30, 21.67; HRMS (ESI): Exact mass calcd for $C_{25}H_{22}BrN_2O_4S$ $[M+H]^+$: 525.0478, Found: 525.0472.



2o

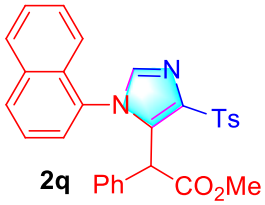
The reaction was run at 50 °C for 24 h, affording product **2o** as an inseparable mixture of two diastereoisomers (3.3:1 ratio) in 68% yield (35.0 mg, yellow solid, m.p. 149-151 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 1H), 2.45 (s, 3H), 3.69 (s, 1H), 3.77 (s, 3H), 5.73 (s, 0.3H), 5.93 (s, 1H), 6.74 (d, *J* = 7.6 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 0.3H), 7.01-7.05 (m, 2.7H), 7.09-7.12 (m, 1H), 7.16-7.22 (m, 1H), 7.33-7.38 (m, 3.8H), 7.44-7.63 (m, 5H), 7.75 (d, *J* = 7.6 Hz, 0.3H), 7.95 (d, *J* = 8.4 Hz, 0.6H), 7.99 (d, *J*

= 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.45, 169.30, 144.30, 139.48, 139.29, 139.27, 139.01, 138.89, 138.59, 138.18, 137.90, 134.31, 133.47, 133.15, 132.95, 132.71, 132.47, 131.82, 131.26, 130.65, 130.59, 130.57, 129.69, 129.58, 129.22, 128.91, 128.32, 128.19, 128.07, 127.92, 127.70, 127.59, 127.39, 127.33, 127.28, 121.98 (q, *J* = 272.6 Hz), 52.79, 52.66, 47.06, 46.17, 21.66; HRMS (ESI): Exact mass calcd for $C_{26}H_{22}F_3N_2O_4S$ $[M+H]^+$: 515.1247, Found: 515.1237.



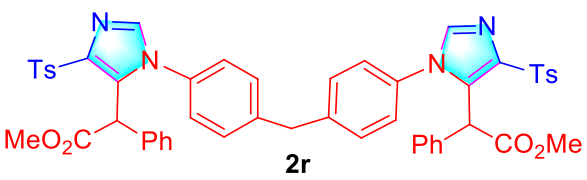
2p

The reaction was run at 50 °C for 24 h, affording product **2p** an inseparable mixture of two diastereoisomers (2.7:1 ratio) in 66% yield (34.5 mg, yellow solid, m.p. 158-160 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 1H), 2.44 (s, 3H), 3.62 (s, 1H), 3.67 (s, 3H), 5.43 (s, 1H), 5.64 (s, 0.36H), 6.56 (d, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 6.8 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 1H), 7.04-7.06 (m, 4H), 7.11-7.21 (m, 10H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.37-7.43 (m, 1H), 7.49-7.60 (m, 3H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.08, 143.95, 140.06, 139.31, 139.03, 138.41, 138.39, 137.55, 137.54, 136.37, 134.47, 133.81, 131.79, 131.40, 130.72, 129.69, 129.42, 128.58, 128.53, 128.38, 128.29, 128.29, 128.16, 128.09, 128.03, 127.96, 127.89, 127.73, 127.64, 52.74, 52.70, 47.20, 47.09, 21.64, 21.59; HRMS (ESI): Exact mass calcd for $C_{31}H_{27}N_2O_4S$ $[M+H]^+$: 523.1686, Found: 523.1673.



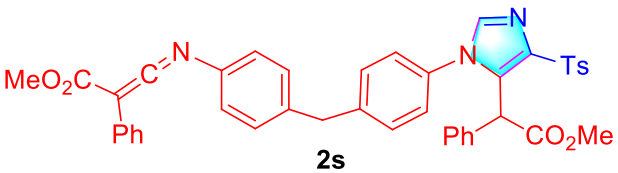
2q

The reaction was run at 50 °C for 24 h, affording product **2q** an inseparable mixture of two diastereoisomers (2.6:1 ratio) in 51% yield (25.3 mg, yellow solid, m.p. 68-70 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 1H), 2.46 (s, 3H), 3.35 (s, 1H), 3.77 (s, 3H), 5.82 (s, 0.36H), 6.06 (s, 1H), 6.62-6.72 (m, 6H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.98-7.05 (m, 1.6H), 7.13 (t, *J* = 8.4 Hz, 0.45H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.29-7.35 (m, 1.6H), 7.38-7.49 (m, 5.5H), 7.51 (s, 1H), 7.59 (s, 0.43H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 0.43H), 7.92-7.97 (m, 2H), 8.03 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.25, 169.39, 144.27, 144.23, 139.86, 139.82, 138.33, 138.12, 138.05, 134.74, 134.41, 134.17, 133.76, 133.51, 133.20, 130.82, 130.77, 130.65, 130.41, 130.21, 130.14, 129.73, 129.61, 129.10, 128.79, 128.20, 128.10, 128.04, 128.00, 127.73, 127.65, 127.56, 127.32, 127.04, 126.79, 126.69, 126.63, 126.24, 124.79, 124.52, 122.29, 121.66, 52.64, 52.35, 46.53, 46.51, 22.66, 21.68; HRMS (ESI): Exact mass calcd for $C_{29}H_{25}N_2O_4S$ $[M+H]^+$: 497.1530, Found: 497.1522.



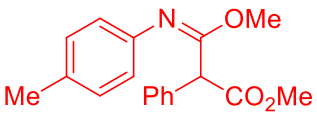
2r

The reaction was run at 50 °C for 24 h, affording product **2r** in 40% yield as a red solid (36.2 mg, m.p. 108-110 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 6H), 3.69 (s, 6H), 3.95 (s, 2H), 6.18 (s, 2H), 6.83-6.87 (m, 8H), 7.02-7.06 (m, 8H), 7.09-7.13 (m, 2H), 7.33 (d, *J* = 7.6 Hz, 4H), 7.45 (s, 2H), 7.93 (ABd, *J* = 7.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.01, 146.27, 144.31, 141.95, 141.91, 139.22, 138.56, 138.08, 134.50, 133.20, 133.09, 129.67, 129.44, 129.43, 128.78, 128.77, 128.14, 127.96, 127.68, 127.21, 52.63, 46.18, 40.82, 21.64; HRMS (ESI): Exact mass calcd for $C_{51}H_{45}N_4O_8S_2$ $[M+H]^+$: 905.2673, Found: 905.2680.



2s

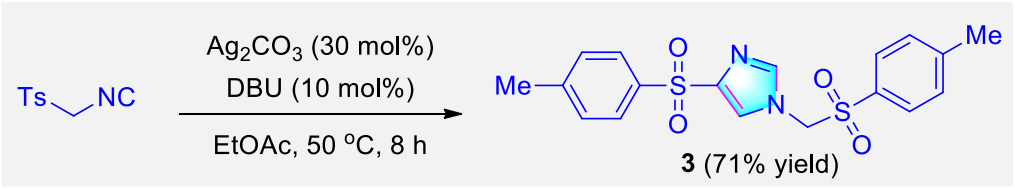
The reaction was run at 50 °C for 24 h, affording product **2s** in 10% yield as a dark-blue oil (7.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.71 (s, 3H), 3.80 (s, 3H), 3.99 (s, 2H), 6.19 (s, 1H), 6.78-6.85 (m, 4H), 7.01-7.06 (m, 4H), 7.08-7.13 (m, 1H), 7.18-7.23 (m, 3H), 7.32-7.35 (m, 6H), 7.44 (s, 1H), 7.53-7.55 (m, 2H), 7.94 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.80, 170.01, 168.04, 144.22, 142.31, 141.06, 139.23, 138.57, 138.24, 134.99, 134.53, 133.28, 133.03, 130.20, 129.94, 129.65, 129.39, 129.34, 129.21, 128.80, 128.62, 128.14, 127.99, 127.70, 127.50, 127.34, 127.19, 126.46, 125.04, 52.60, 51.83, 46.25, 41.04, 21.63; HRMS (ESI): Exact mass calcd for $C_{42}H_{36}N_3O_6S$ $[M+H]^+$: 710.2319, Found: 710.2312.



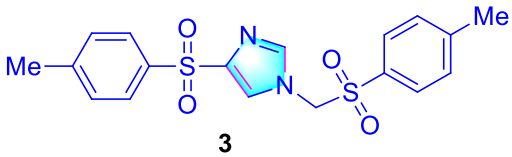
6

The reaction was run at 80 °C for 1.5 h by using K_2CO_3 (30 mol%) as the catalyst and MeOH/DME (2:1) as the solvent, affording product **6** in 81% yield as a yellow oil (24.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.74 (s, 3H), 3.87 (s, 3H), 4.78 (s, 1H), 6.65 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.11 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.20-7.23 (m, 2H), 7.29-7.34 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.62, 158.18, 145.10, 133.94, 132.73, 129.65, 129.43, 128.37, 127.76, 121.01, 54.01, 52.66, 51.76, 20.80; HRMS (ESI): Exact mass calcd for $C_{18}H_{20}NO_3$ $[M+H]^+$: 298.1438, Found: 298.1433.

3. General procedure and spectral data of product 3.



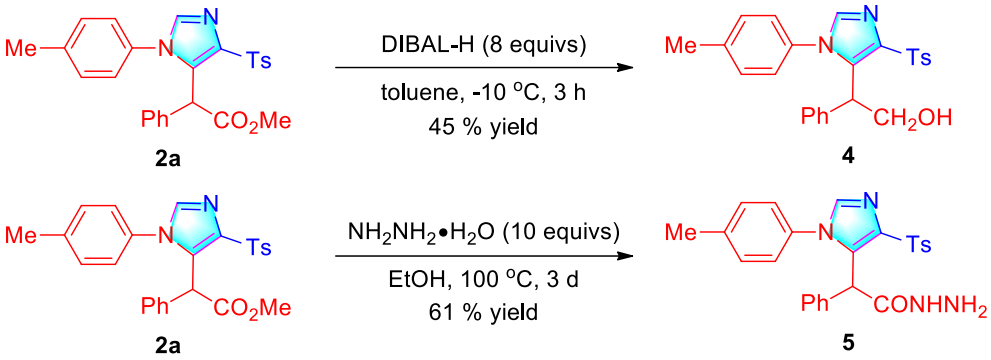
General Procedure: Under nitrogen atmosphere, *p*-toluenesulfonylmethyl isocyanide (TosMIC) (0.10 mmol), Ag_2CO_3 (30 mol%), DBU (10 mol%), and EtOAc (1.0 mL) were successively added to a oven-dried 10 mL schlenk tube. The reaction mixture was then stirred at 50 °C for 8 h, and monitored by TLC. After completion, the reaction mixture was cooled down to room temperature and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/EtOAc (3:1) as the eluent to afford the 1,4-disubstituted imidazole **3**.



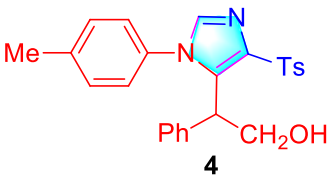
3

The reaction was run at 50 °C for 8 h, affording product **3** in 71% yield as a white solid (27.7 mg, m.p. 184-186 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 6H), 5.14 (s, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.29 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.39 (s, 1H), 7.44 (ABd, *J* = 8.0 Hz, 2H), 7.85 (ABd, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.90, 144.50, 143.21, 139.46, 137.30, 131.20, 130.49, 129.77, 128.64, 127.90, 123.72, 66.34, 21.80, 21.63.

4. Further transformations of product 2a.



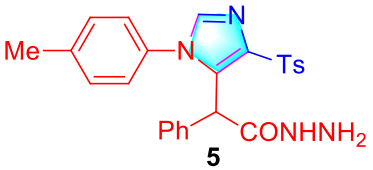
The preparation of 4: Under nitrogen atmosphere, **2a** (46.0 mg, 0.10 mmol) and toluene (3.0 mL) were added to an oven-dried 10 mL Schlenk tube. The reaction mixture was then cooled down to -10 °C followed by the drop wise addition of DIBAL-H (0.8 mmol). After the full consumption of **2a** (ca. 3 h), 1 mol/L of sodium hydroxide solution (5 mL) was added to quench the reaction. The resulting mixture was extracted with ethyl acetate for three times (8 mL × 3). The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/EtOAc (3:2) as the eluent to afford the desired product **4** in 45 % yield as a yellow solid (19.4 mg, m.p. 82-84 °C).



4

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.42 (s, 3H), 2.70 (s, 1H), 4.18-4.22 (m, 1H), 4.37 (t, *J* = 10 Hz, 1H), 4.92 (t, *J* = 8.8 Hz, 1H), 6.81 (d, *J* = 7.2 Hz, 2H), 6.86 (dd, *J* = 6.8 Hz, 2H), 7.08-7.15 (m, 5H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.42 (s, 1H), 7.82 (ABd, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.24, 140.10, 138.93, 138.53, 137.96, 137.80, 136.38, 132.18, 129.77, 129.65, 128.31, 128.10, 127.88, 127.29, 126.81, 63.32, 43.20, 21.64, 21.15; HRMS (ESI): Exact mass calcd for $C_{25}H_{25}N_2O_3S$ $[M+H]^+$: 433.1580, Found: 433.1572.

The preparation of 5: **2a** (46.0 mg, 0.10 mmol), MeOH (3.0 mL), and hydrazine hydrate were added to a 25 mL sealed tube. The reaction mixture was then stirred at 100 °C for 3 d. After completion, the sealed tube was cooled down to room temperature, and the solution was extracted with ethyl acetate for three times (10 mL × 3). The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography using MeOH/EtOAc (1:3) as the eluent to afford the desired product **5** in 61 % yield as a yellow solid (28.1 mg, m.p. 82-84 °C).



5

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.77 (s, 1H), 2.36 (s, 3H), 2.42 (s, 3H), 3.88 (s, 1H), 5.46 (s, 1H), 6.86 (ABd, *J* = 8.0 Hz, 2H), 7.06-7.10 (m, 4H), 7.15 (s, 1H), 7.20-7.22 (m, 3H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.47 (s, 1H), 7.98 (ABd, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.02, 144.25, 140.13, 139.12, 138.19, 137.90, 134.13, 133.40, 131.71, 129.70, 129.62, 129.20, 128.89, 128.19, 127.98, 127.36, 47.51, 21.65, 21.14; HRMS (ESI): Exact mass calcd for $C_{25}H_{25}N_4O_3S$ $[M+H]^+$: 461.1642, Found: 461.1647.

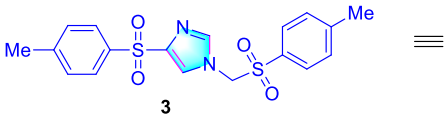
5. X-Ray crystallographic data for compounds 2a and 3.

Data intensity of compound **2a** was collected using a Bruker 'Bruker APEX-II CCD' diffractometer at 179.99 (10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. CCDC 2209195.

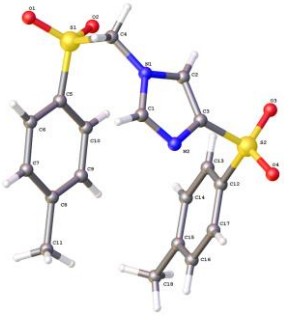
X-ray structure of product **2a**
CCDC 2209195

Empirical formula	$C_{26}H_{24}N_2O_4S$
Formula weight	460.53
Temperature/K	179.99(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.4115(7)
b/Å	17.4920(18)
c/Å	13.8909(10)
α/°	90
β/°	94.077(7)
γ/°	90
Volume/Å^3	2281.0(3)
Z	4
ρ_{calc}g/cm^3	1.341
μ/mm^{-1}	0.178
F(000)	968.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.658 to 59.292
Index ranges	-12 ≤ h ≤ 11, -24 ≤ k ≤ 15, -18 ≤ l ≤ 19
Reflections collected	11730
Independent reflections	5383 [R_{int} = 0.0395, R_{sigma} = 0.0733]
Data/restraints/parameters	5383/0/301
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0878, wR_2 = 0.1989
Final R indexes [all data]	R_1 = 0.1321, wR_2 = 0.2275
Largest diff. peak/hole / e Å^{-3}	1.53/-0.68

Data intensity of compound **3** was collected using a Bruker 'Bruker APEX-II CCD' diffractometer at 180.00 (10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. CCDC 2209196.



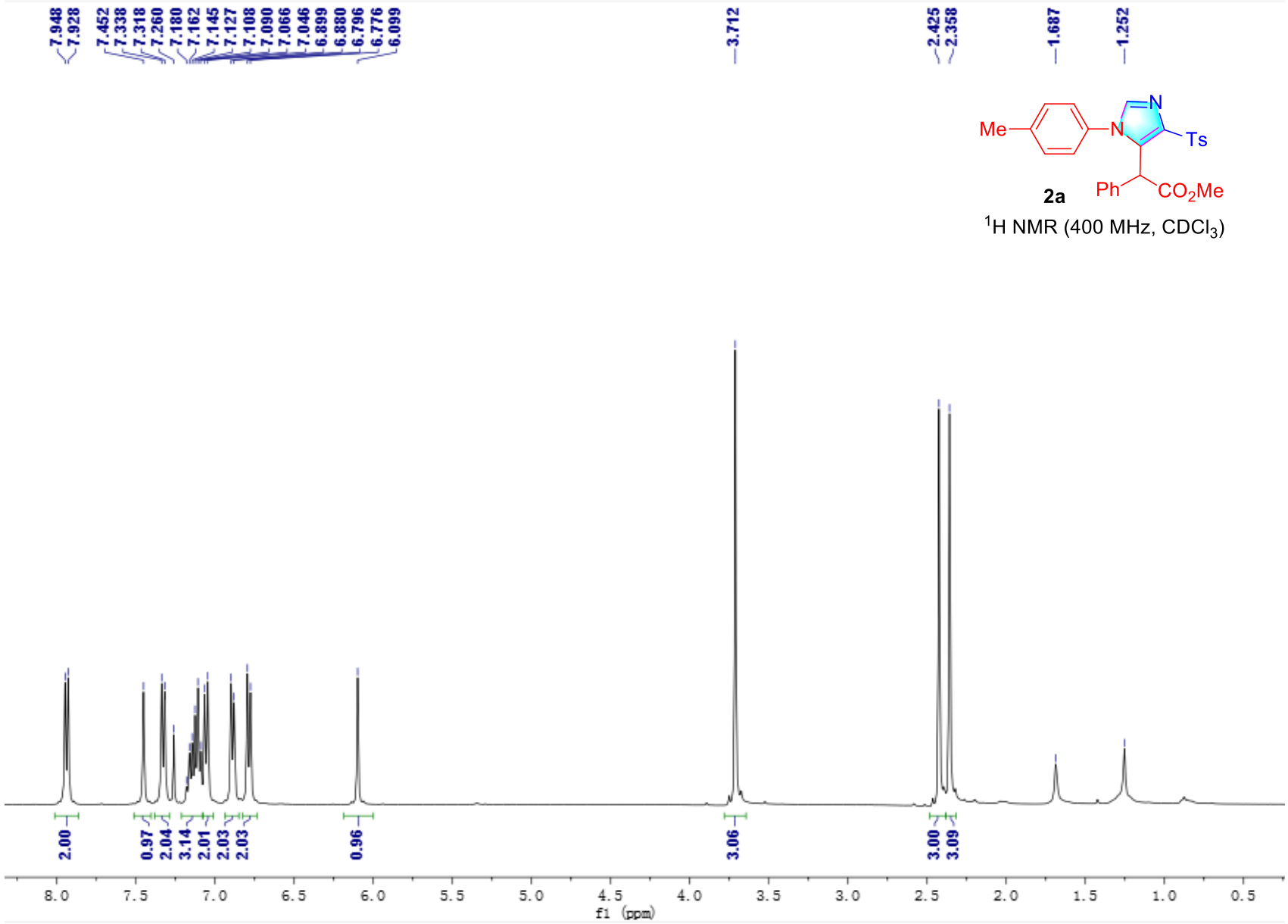
3

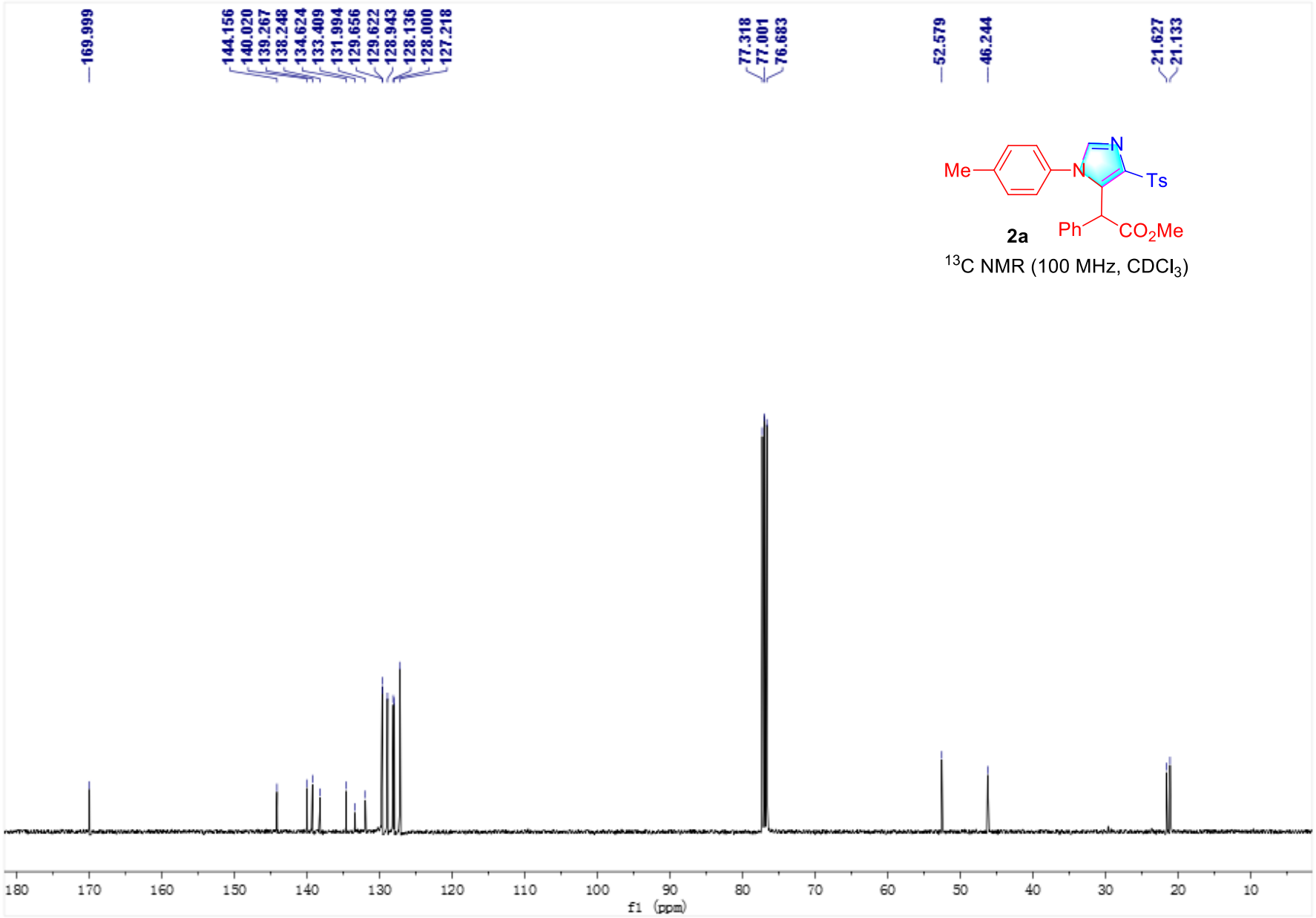


X-ray structure of product **3**
CCDC 2209196

Empirical formula	$C_{18}H_{18}N_2O_4S_2$
Formula weight	390.46
Temperature/K	180.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	5.9384(2)
b/Å	19.6239(8)
c/Å	15.6970(7)
α/°	90
β/°	99.037(4)
γ/°	90
Volume/Å^3	1806.54(13)
Z	4
ρ_{calc}g/cm^3	1.436
μ/mm^{-1}	2.908
F(000)	816.0
Crystal size/mm^3	0.14 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.268 to 147.738
Index ranges	-6 ≤ h ≤ 7, -24 ≤ k ≤ 17, -16 ≤ l ≤ 19
Reflections collected	6926
Independent reflections	3569 [R_{int} = 0.0553, R_{sigma} = 0.0761]
Data/restraints/parameters	3569/0/237
Goodness-of-fit on F^2	1.092
Final R indexes [I>=2σ (I)]	R_1 = 0.0806, wR_2 = 0.2106
Final R indexes [all data]	R_1 = 0.0971, wR_2 = 0.2253
Largest diff. peak/hole / e Å^{-3}	0.98/-0.63

6. Copies of ^{1}H NMR and ^{13}C NMR spectra of compounds 2-6.

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46.244
21.627
21.133
Me
N
N
Ts
Ph
CO2Me
2a
13C NMR (100 MHz, CDCl3)
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140
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120
110
100
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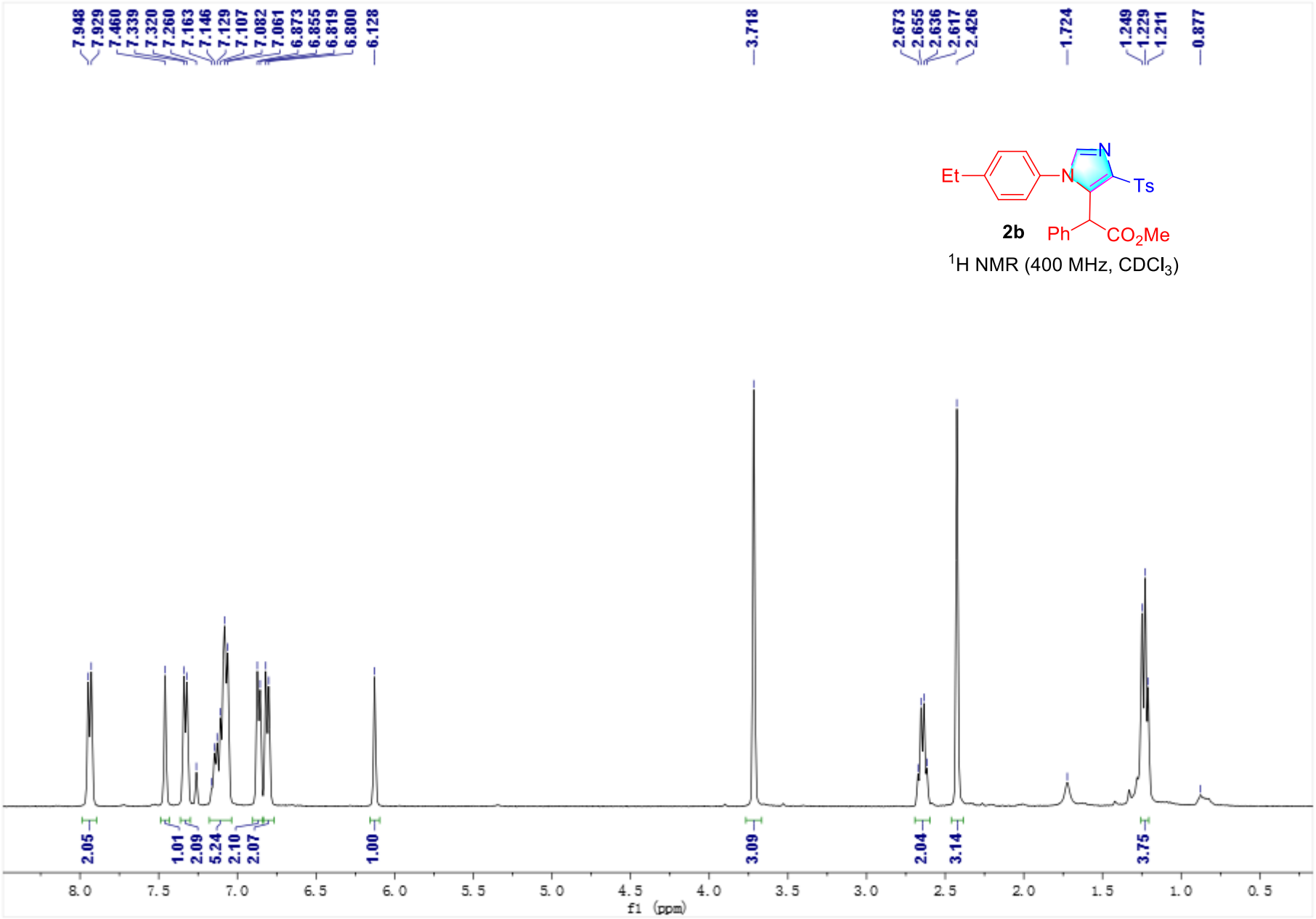
f1 (ppm)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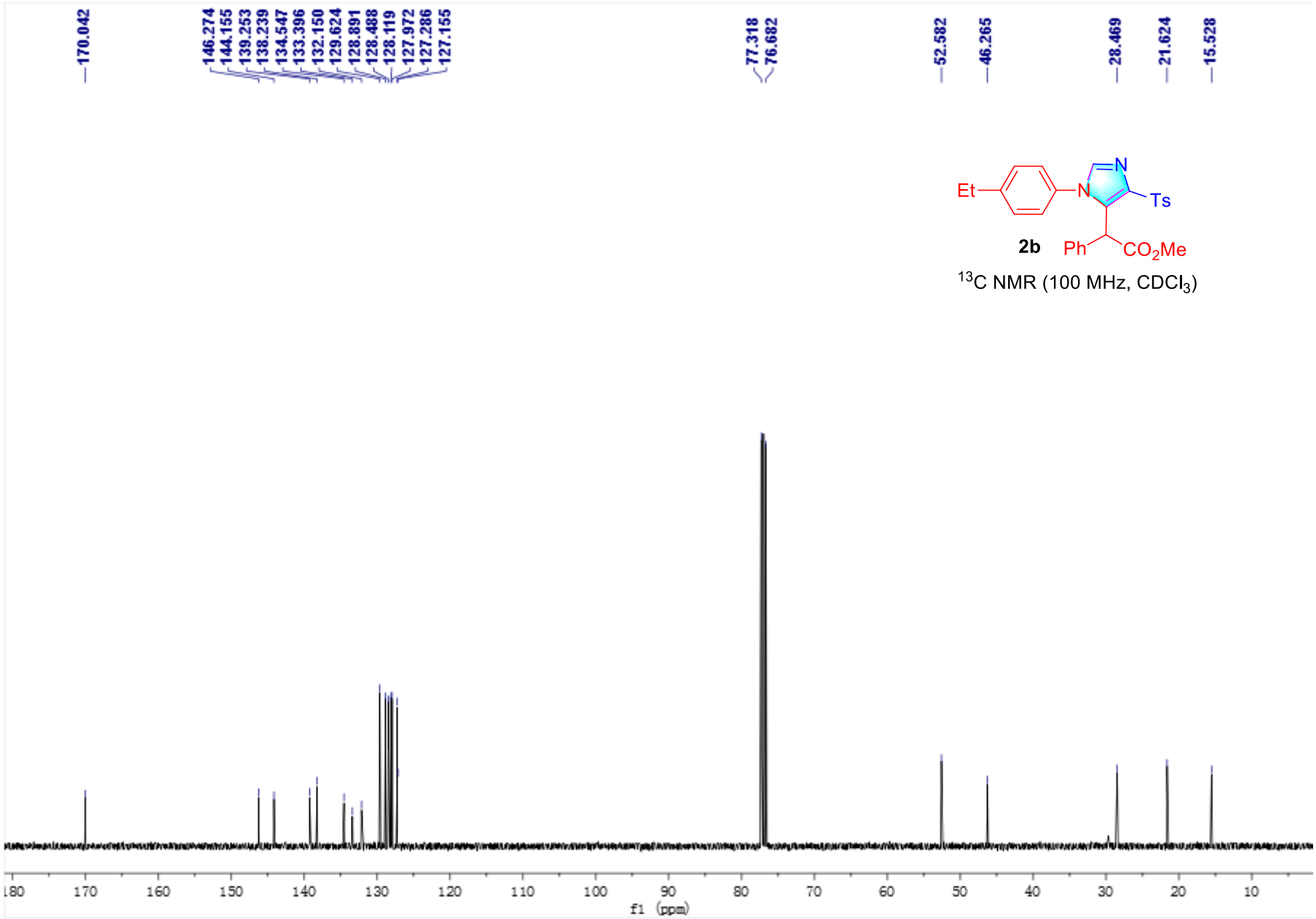
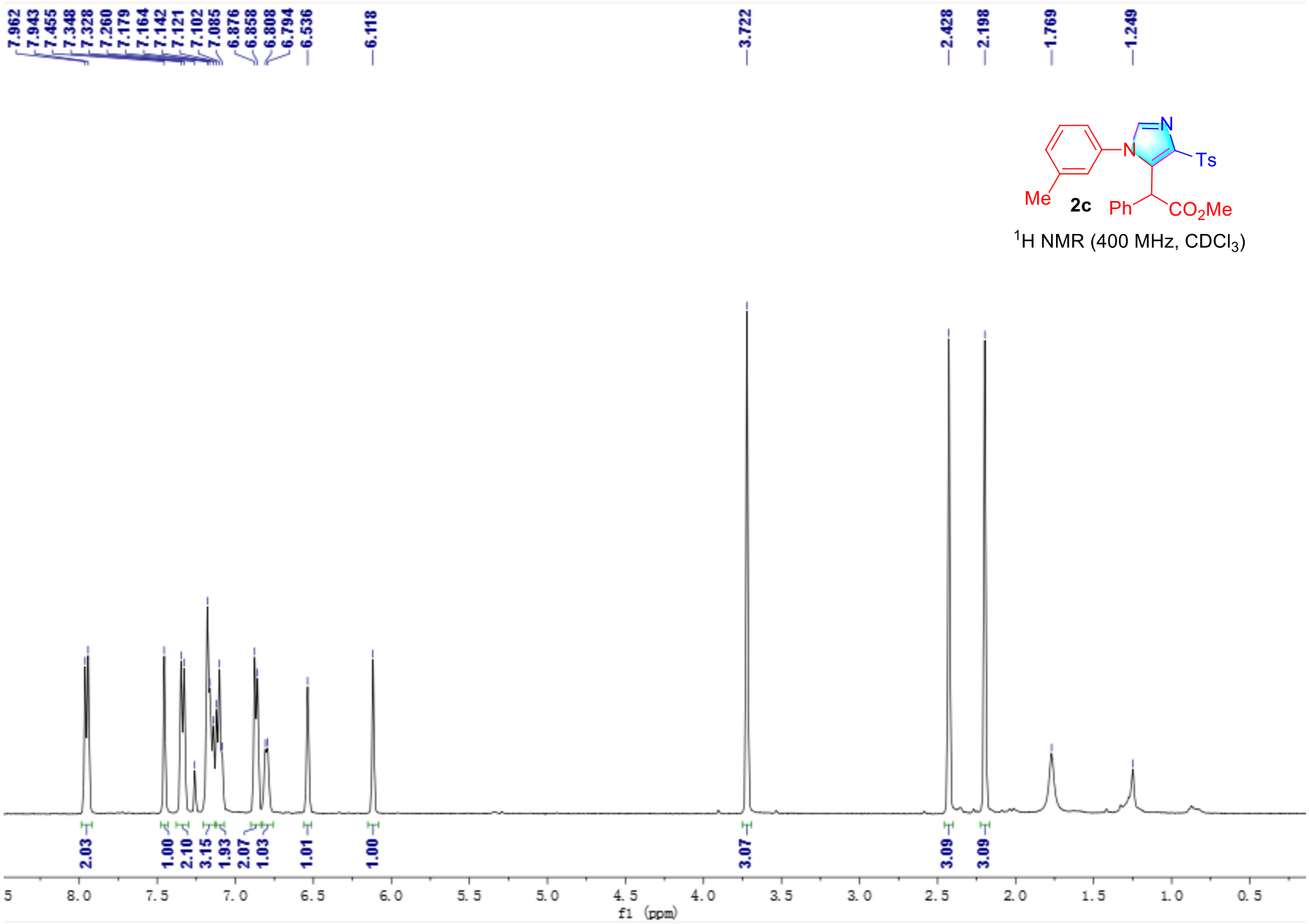
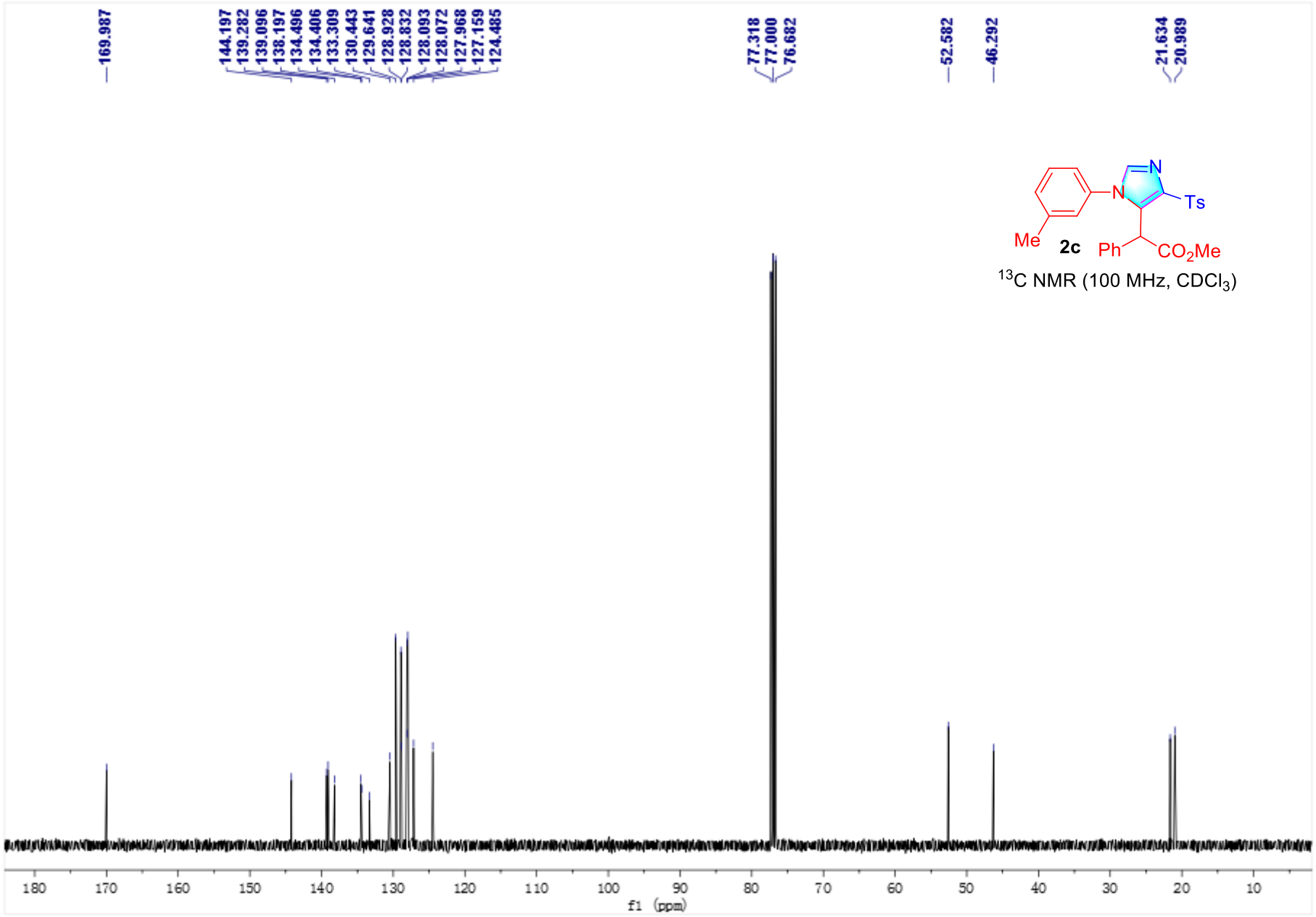
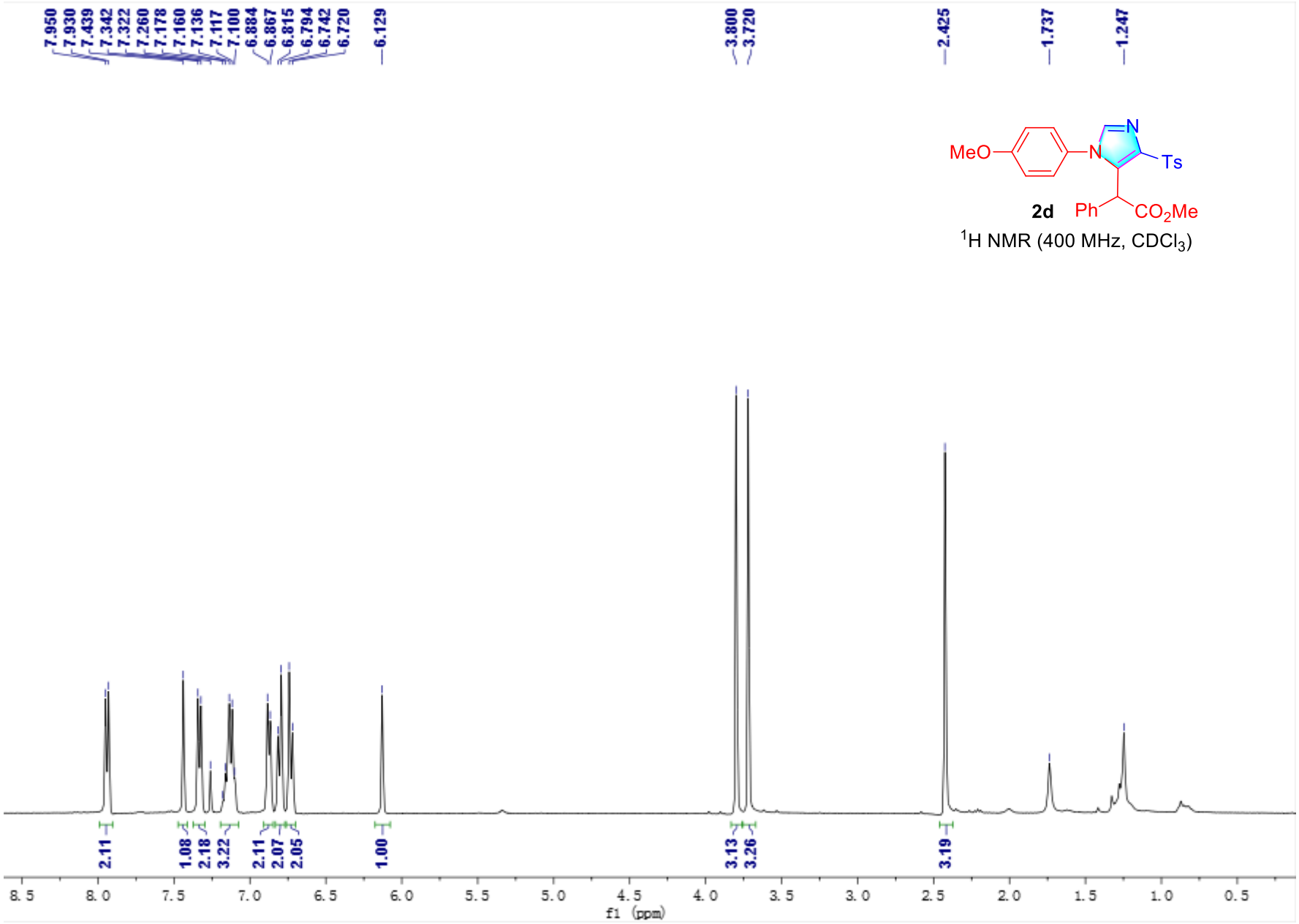
7.061
6.873
6.855
6.819
6.800
6.128
3.718
2.673
2.655
2.636
2.617
2.426
1.724
1.249
1.229
1.211
0.877
Et
N
N
Ts
Ph
CO2Me
2b
1H NMR (400 MHz, CDCl3)
2.05
1.01
2.09
5.24
2.10
2.07
1.00
3.09
2.04
3.14
3.75
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

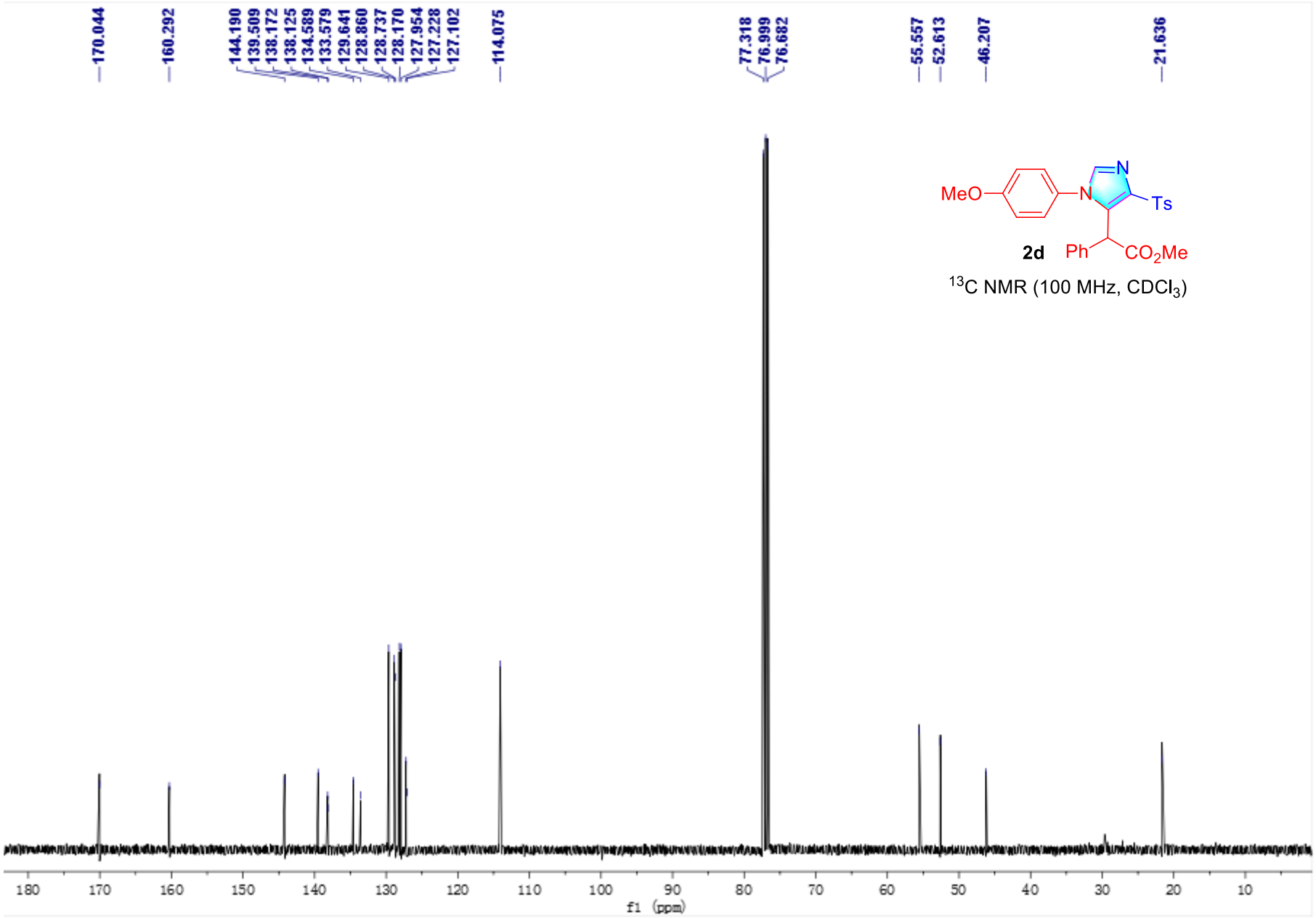


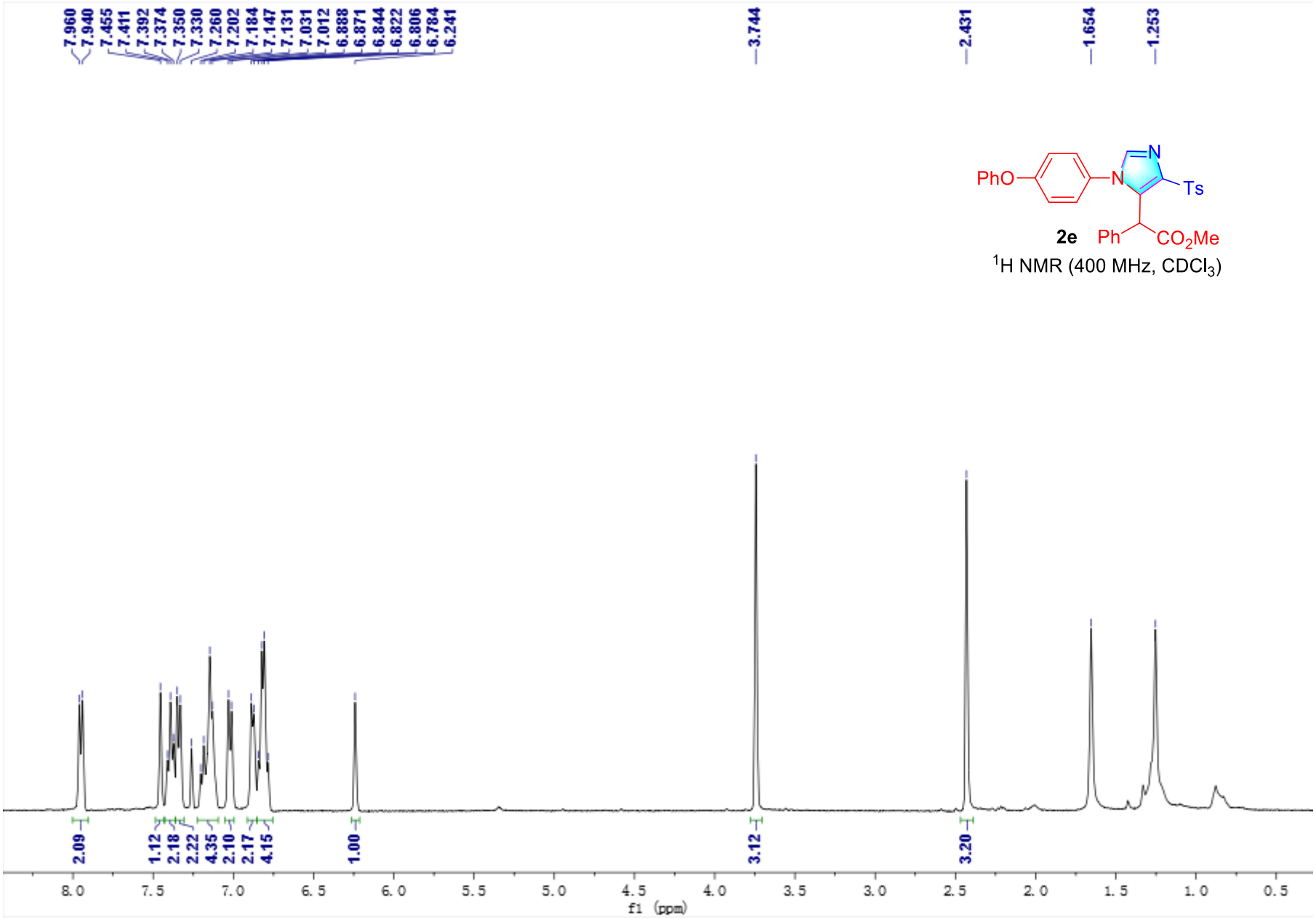
^{13}C NMR (100 MHz, $CDCl_3$)

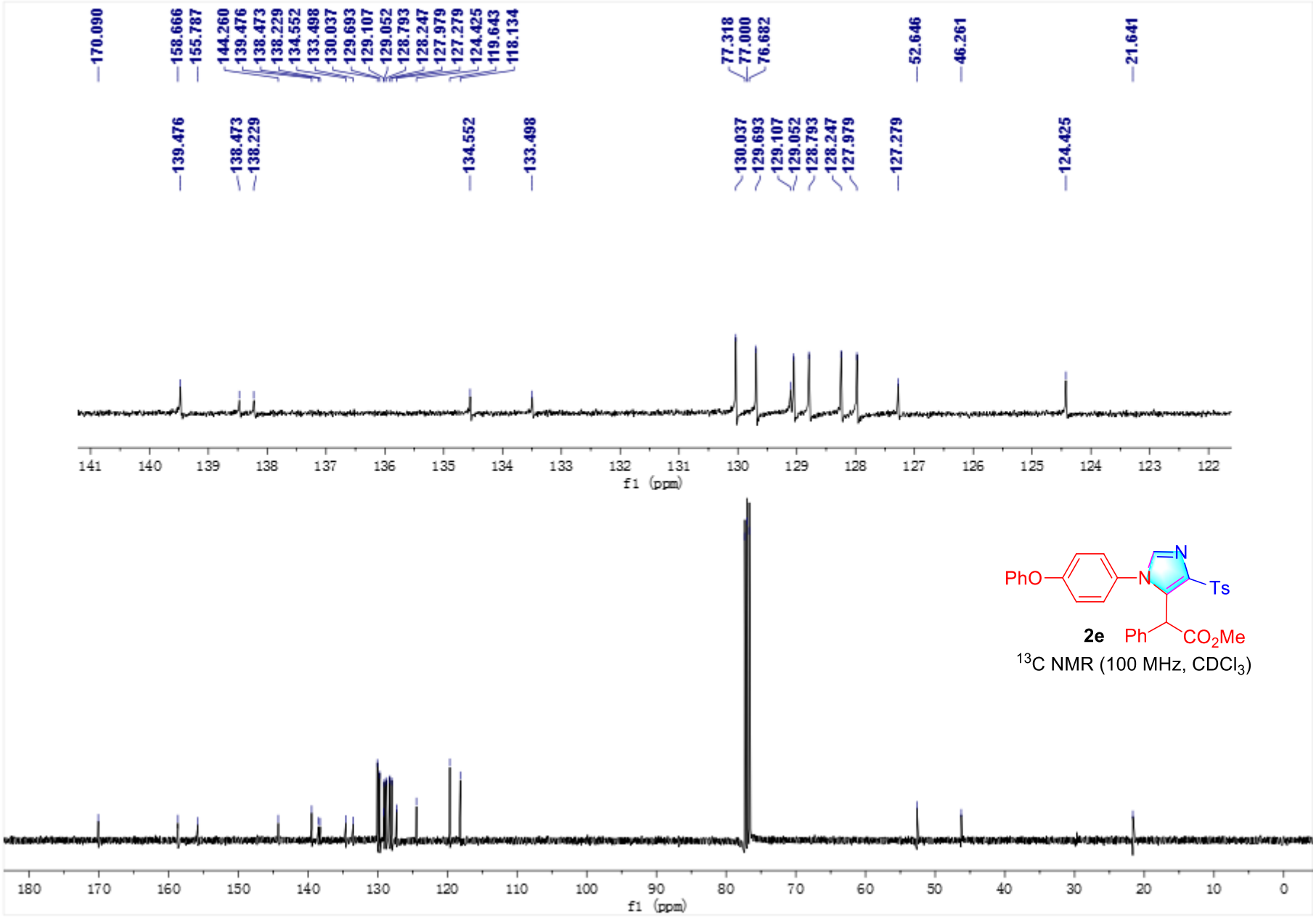

7.962
7.943
7.455
7.348
7.328
7.260
7.179
7.164
7.142
7.121
7.102
7.085
6.876
6.858
6.808
6.794
6.536
6.118
3.722
2.428
2.198
1.769
1.249
Me
2c
Ph
CO2Me
Ts
N
1H NMR (400 MHz, CDCl3)
2.03
1.00
2.10
3.15
1.93
2.07
1.03
1.01
1.00
3.07
3.09
3.09
f1 (ppm)

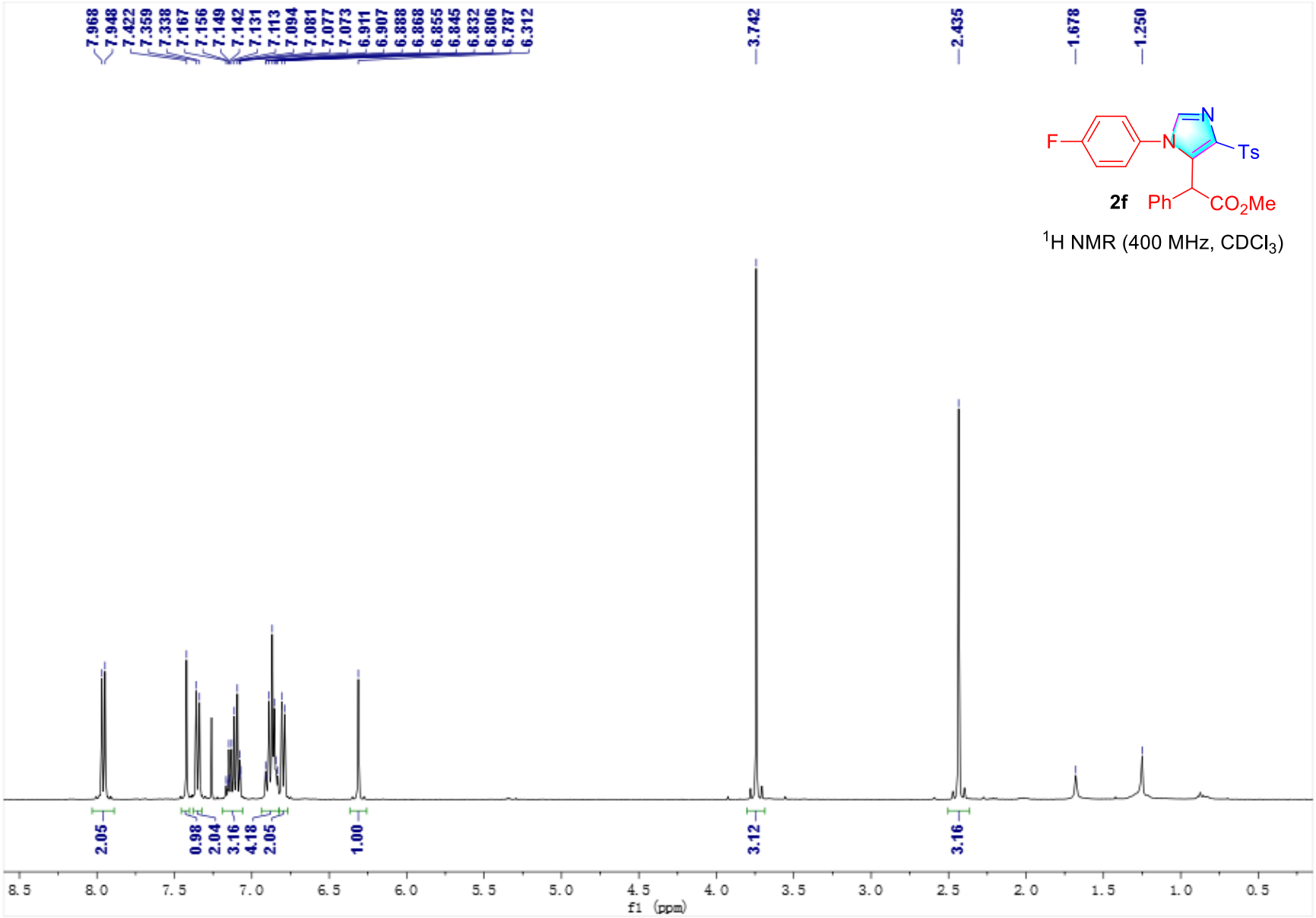

169.987
144.197
139.282
139.096
138.197
134.496
134.406
133.309
130.443
129.641
128.928
128.832
128.093
128.072
127.968
127.159
124.485
77.318
77.000
76.682
52.582
46.292
21.634
20.989
N
N
Ts
Me
2c
Ph
CO2Me
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

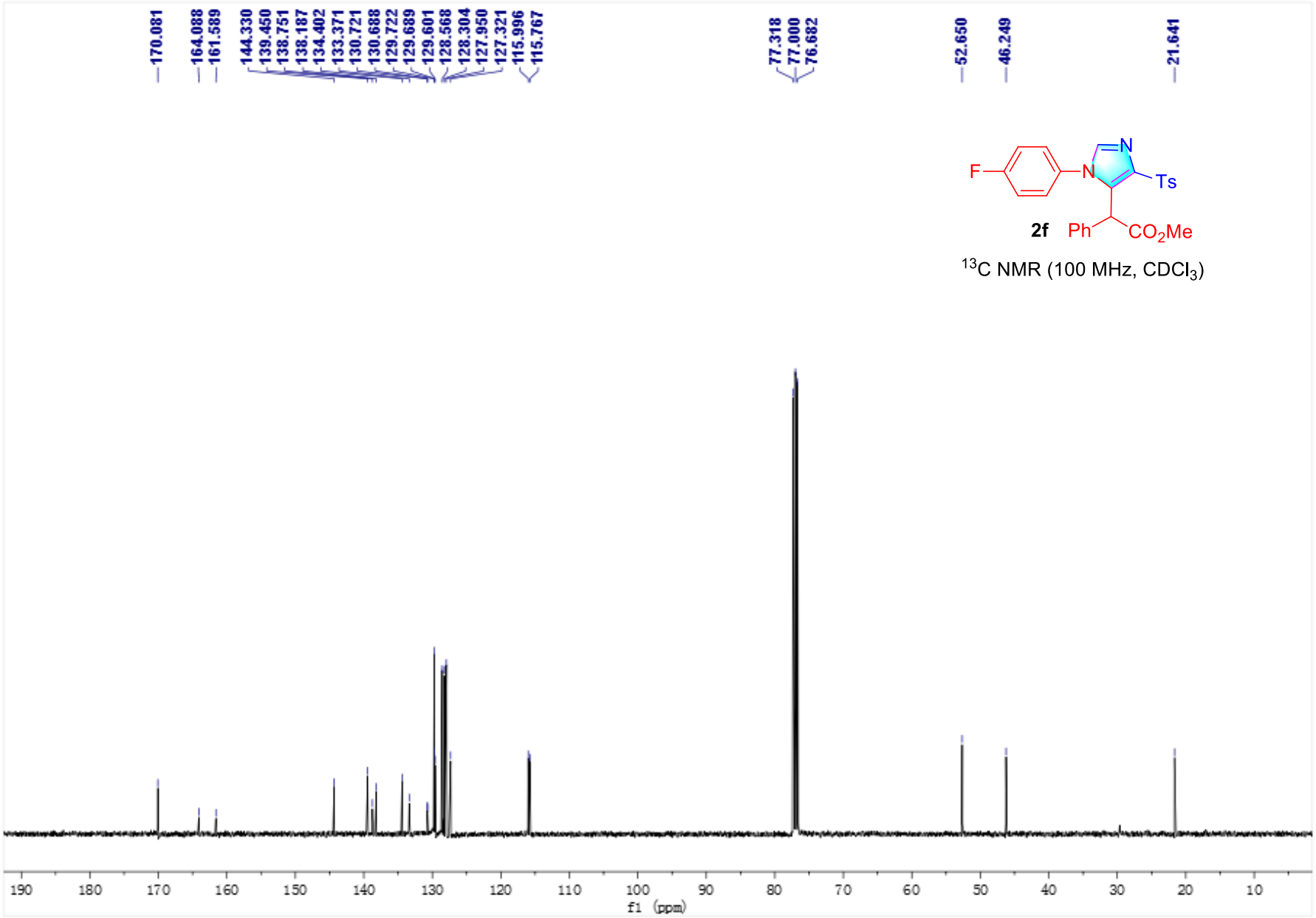

7.950
7.930
7.439
7.342
7.322
7.260
7.178
7.160
7.136
7.117
7.100
6.884
6.867
6.815
6.794
6.742
6.720
6.129
3.800
3.720
2.425
1.737
1.247
MeO
N
N
Ts
Ph
CO2Me
2d
1H NMR (400 MHz, CDCl3)
2.11
1.08
2.18
3.22
2.11
2.07
2.05
1.00
3.13
3.26
3.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

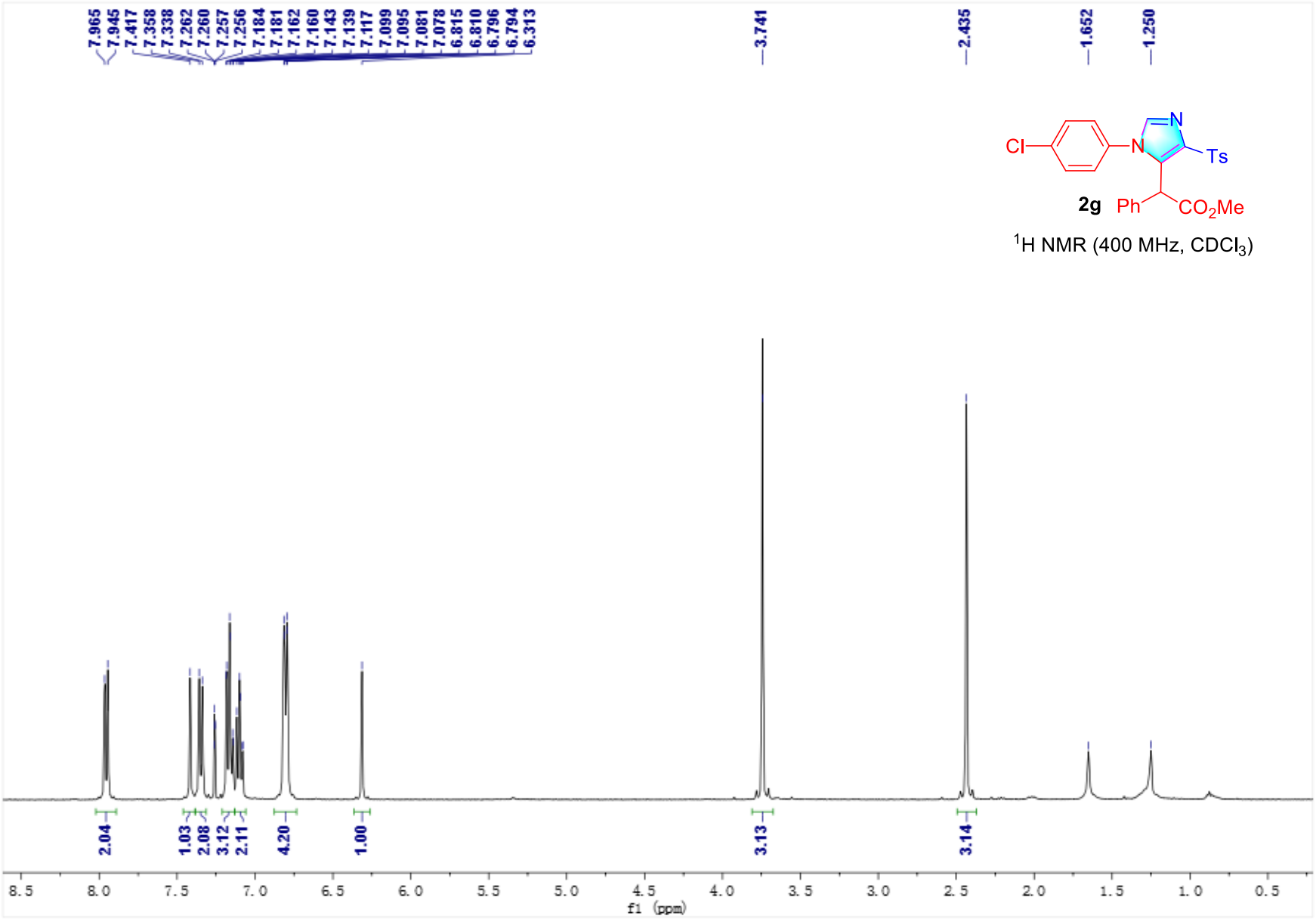

170.044
160.292
144.190
139.509
138.172
138.125
134.589
133.579
129.641
128.860
128.737
128.170
127.954
127.228
127.102
114.075
77.318
76.999
76.682
55.557
52.613
46.207
21.636
MeO
N
N
Ts
Ph
CO2Me
2d
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

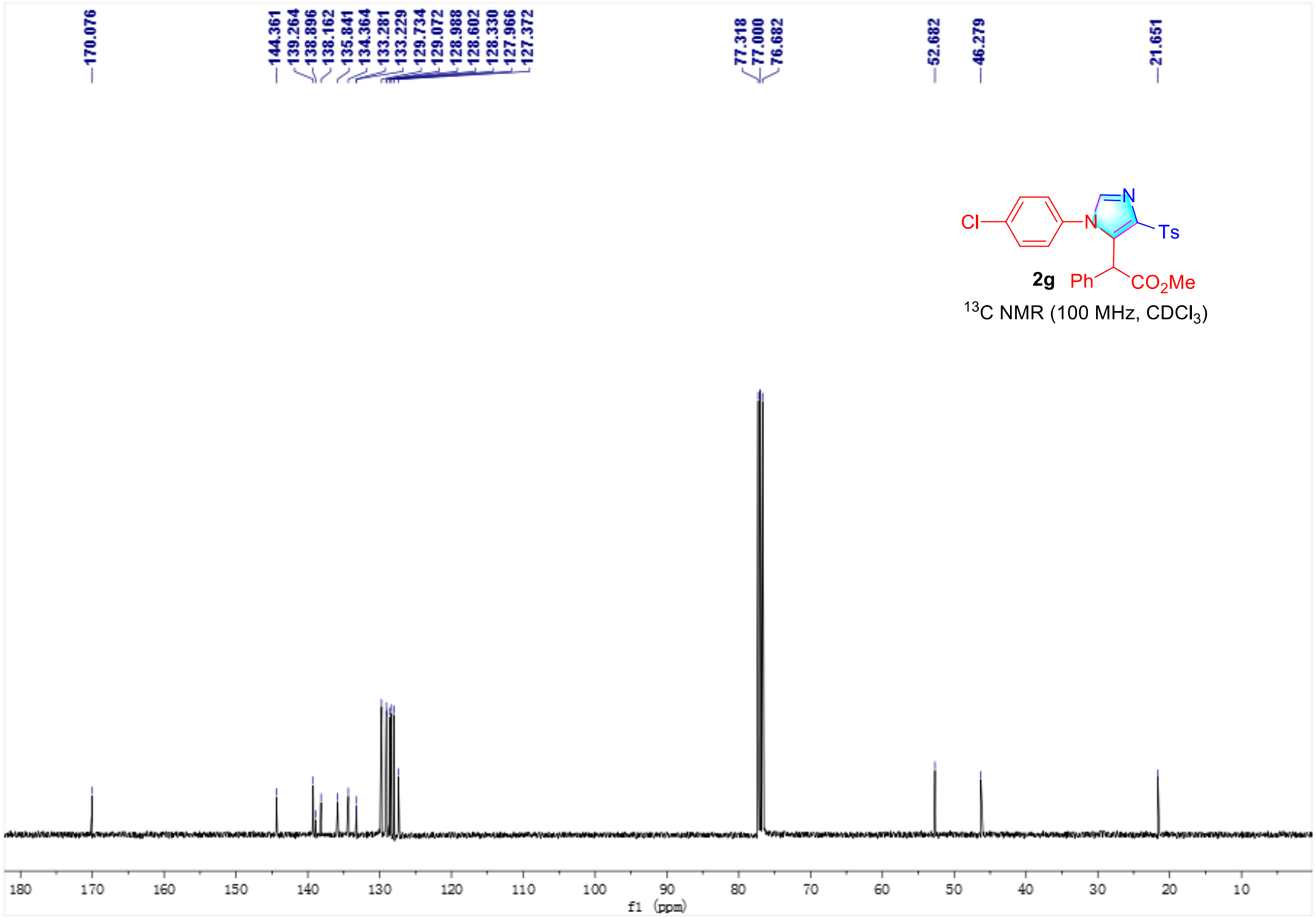

7.960
7.940
7.455
7.411
7.392
7.374
7.350
7.330
7.260
7.202
7.184
7.147
7.131
7.031
7.012
6.888
6.871
6.844
6.822
6.806
6.784
6.241
3.744
2.431
1.654
1.253
PhO
N
N
Ts
Ph
CO2Me
2e
1H NMR (400 MHz, CDCl3)
2.09
1.12
2.18
2.22
4.35
2.10
2.17
4.15
1.00
3.12
3.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

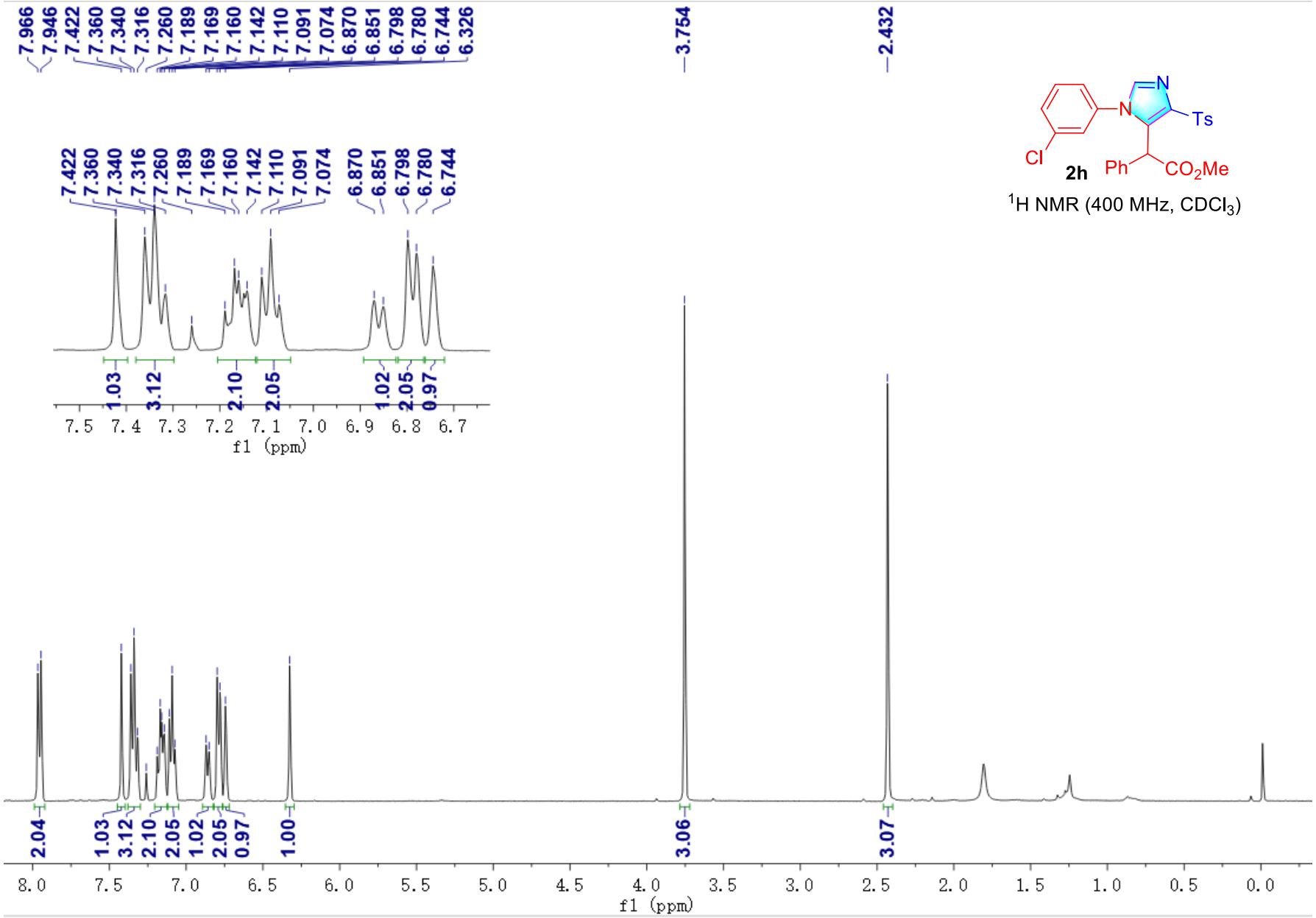

170.090
158.666
155.787
144.260
139.476
138.473
138.229
134.552
133.498
130.037
129.693
129.107
129.052
128.793
128.247
127.979
127.279
124.425
119.643
118.134
77.318
77.000
76.682
52.646
46.261
21.641
f1 (ppm)
PhO
N
N
Ts
Ph
CO2Me
2e
13C NMR (100 MHz, CDCl3)

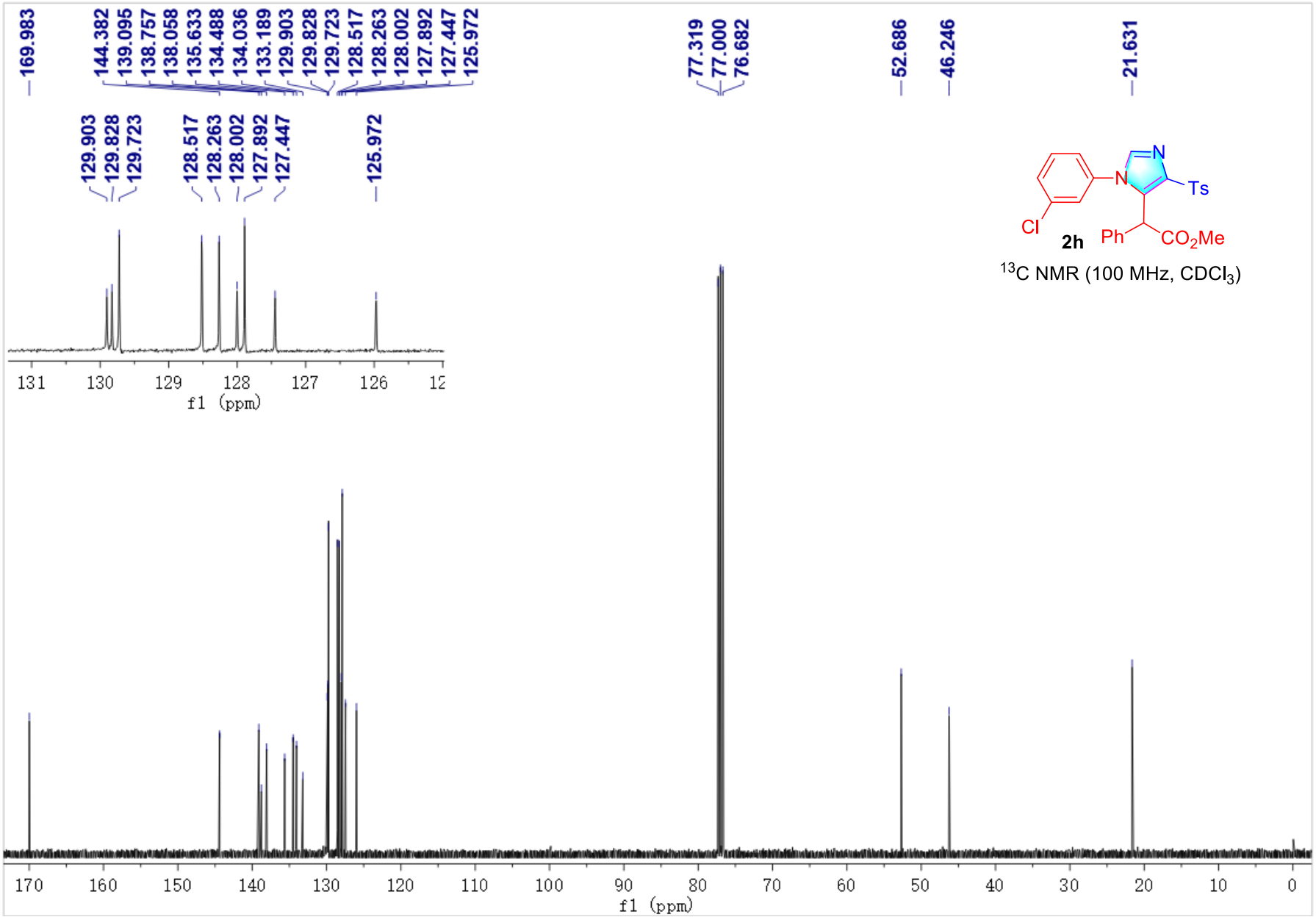

7.968
7.948
7.422
7.359
7.338
7.167
7.156
7.149
7.142
7.131
7.113
7.094
7.081
7.077
7.073
6.911
6.907
6.888
6.868
6.855
6.845
6.832
6.806
6.787
6.312
3.742
2.435
1.678
1.250
F
N
N
Ts
2f
Ph
CO2Me
1H NMR (400 MHz, CDCl3)
2.05
0.98
2.04
3.16
4.18
2.05
1.00
3.12
3.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

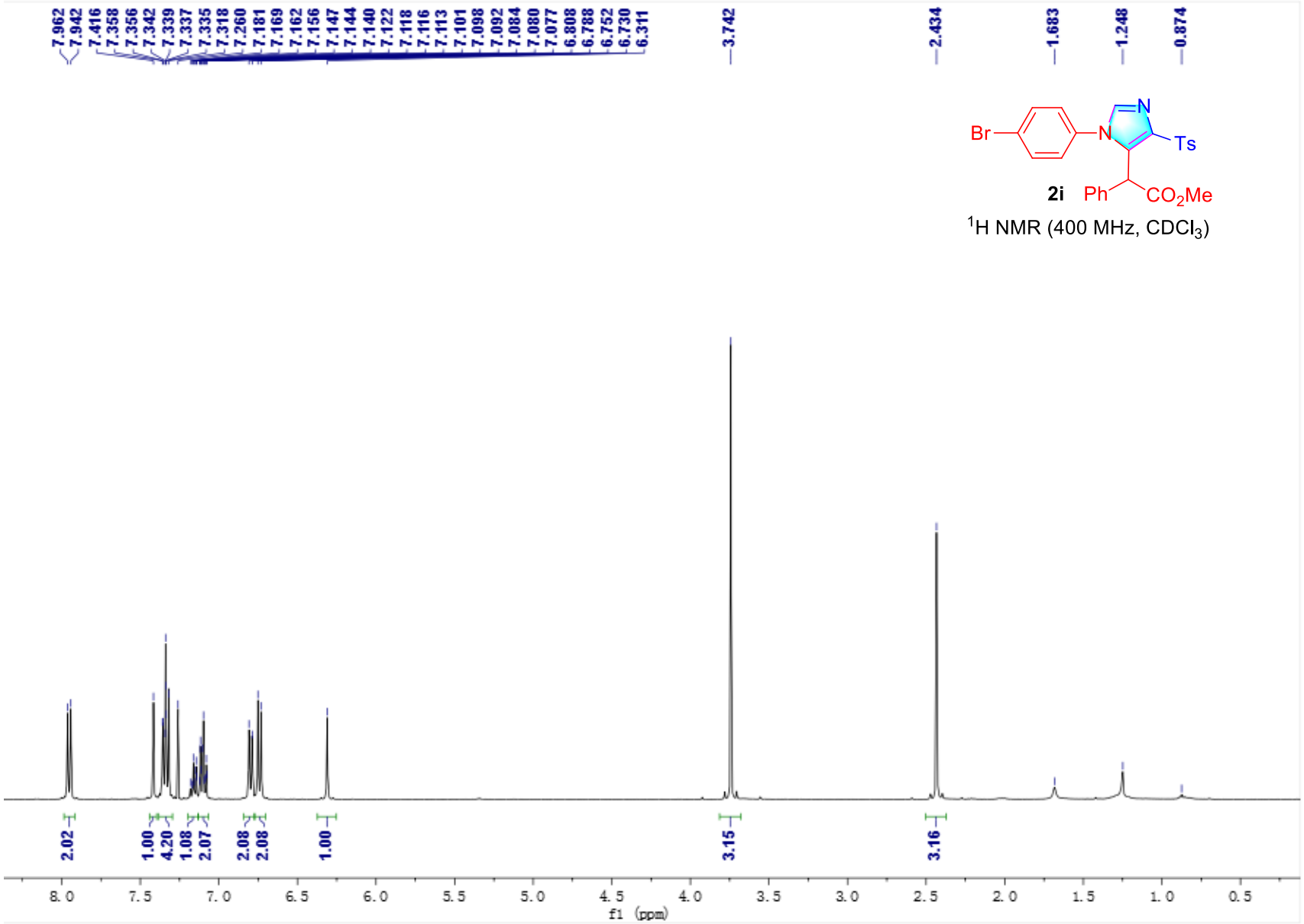

170.081
164.088
161.589
144.330
139.450
138.751
138.187
134.402
133.371
130.721
130.688
129.722
129.689
129.601
128.568
128.304
127.950
127.321
115.996
115.767
77.318
77.000
76.682
52.650
46.249
21.641
F
N
N
Ts
Ph
CO2Me
2f
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

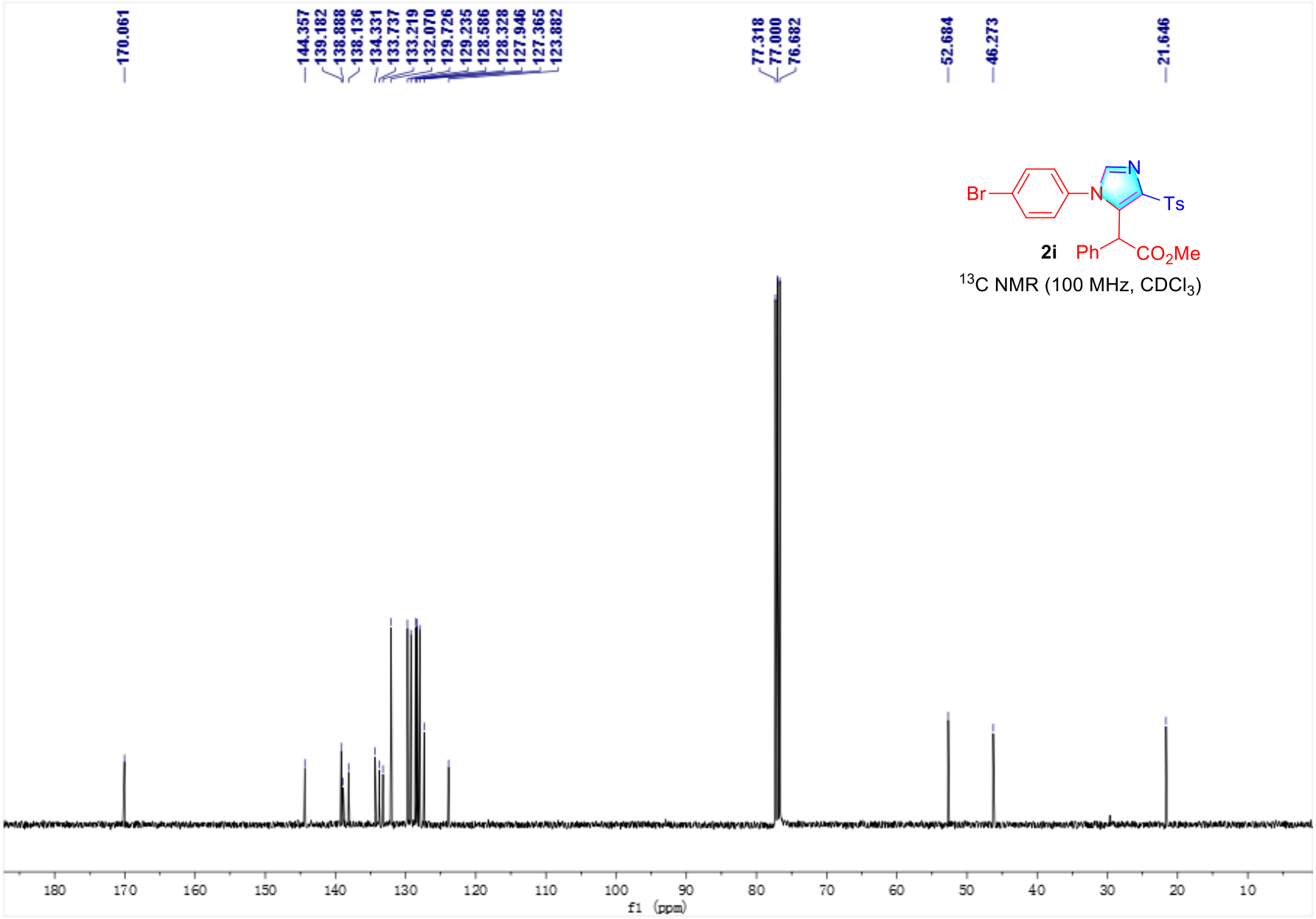

7.965
7.945
7.417
7.358
7.338
7.262
7.260
7.257
7.256
7.184
7.181
7.162
7.160
7.143
7.139
7.117
7.099
7.095
7.081
7.078
6.815
6.810
6.796
6.794
6.313
3.741
2.435
1.652
1.250
Cl
N
N
Ts
Ph
CO2Me
2g
1H NMR (400 MHz, CDCl3)
2.04
1.03
2.08
3.12
2.11
4.20
1.00
3.13
3.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

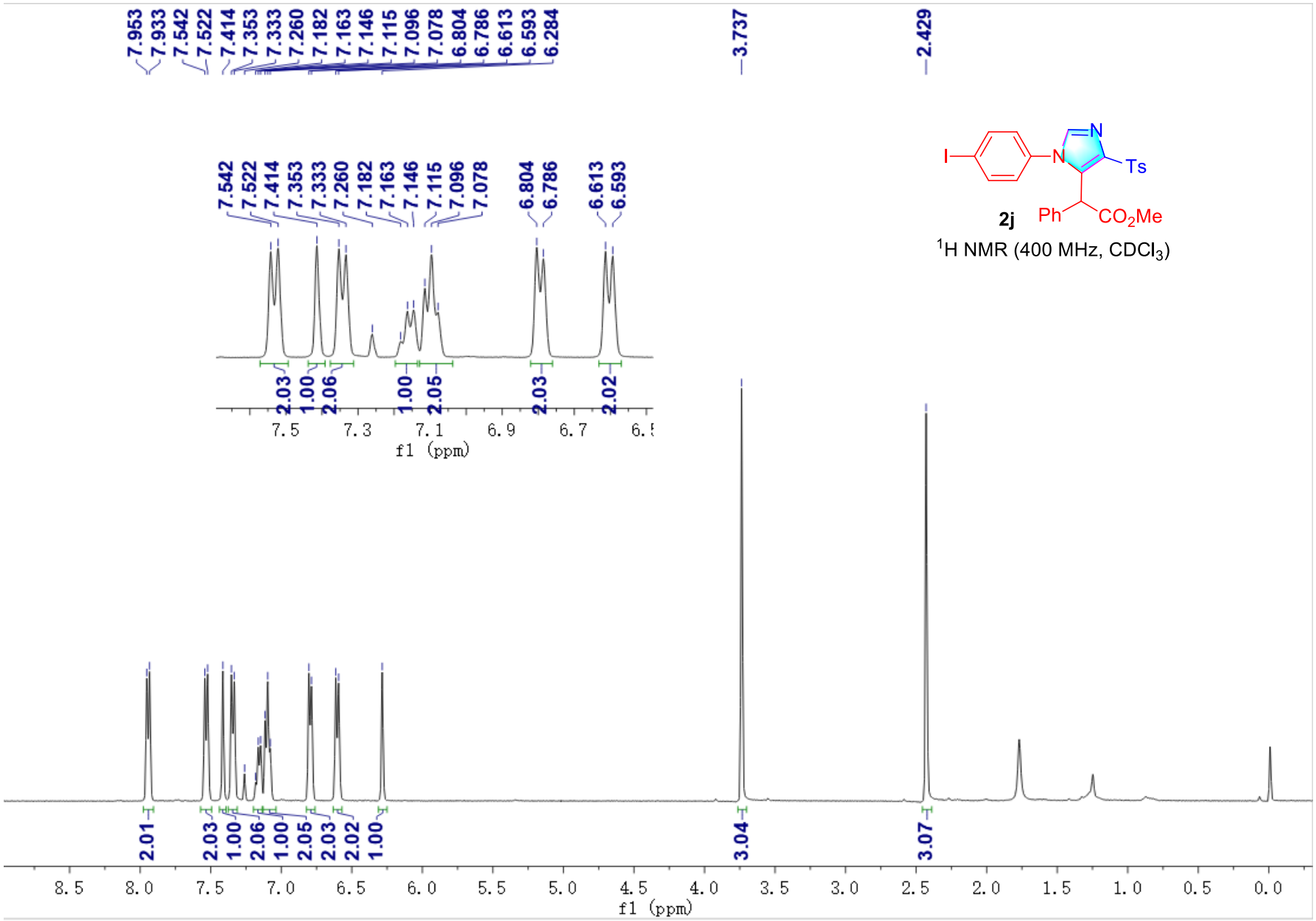

170.076
144.361
139.264
138.896
138.162
135.841
134.364
133.281
133.229
129.734
129.072
128.988
128.602
128.330
127.966
127.372
77.318
77.000
76.682
52.682
46.279
21.651
Cl
N
N
Ts
Ph
CO2Me
2g
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

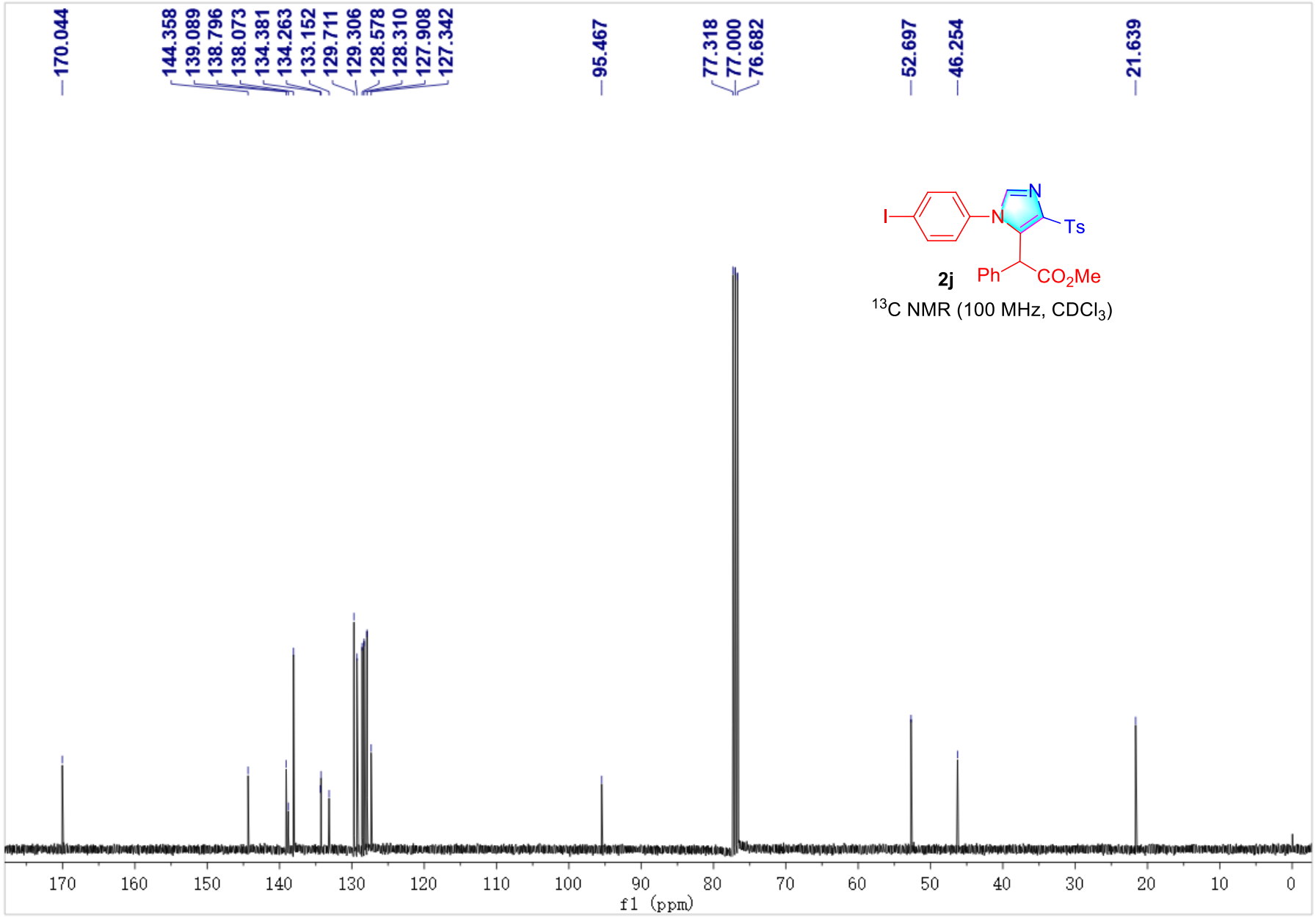

7.966
7.946
7.422
7.360
7.340
7.316
7.260
7.189
7.169
7.160
7.142
7.110
7.091
7.074
6.870
6.851
6.798
6.780
6.744
6.326
3.754
2.432
1.03
3.12
2.10
2.05
1.02
2.05
0.97
f1 (ppm)
2.04
1.00
3.06
3.07
Cl
N
N
Ts
Ph
CO2Me
2h
1H NMR (400 MHz, CDCl3)

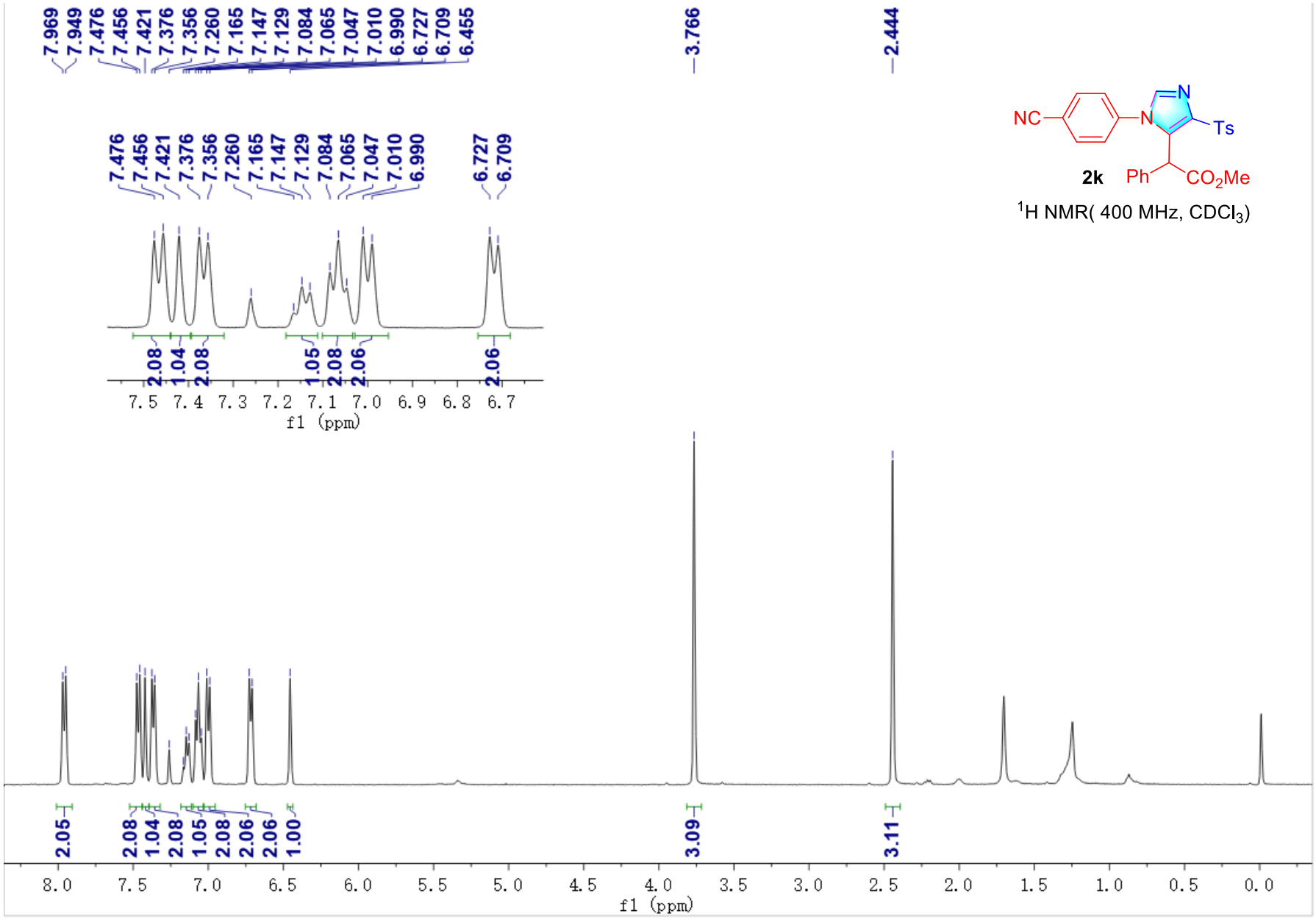

169.983
144.382
139.095
138.757
138.058
135.633
134.488
134.036
133.189
129.903
129.828
129.723
128.517
128.263
128.002
127.892
127.447
125.972
77.319
77.000
76.682
52.686
46.246
21.631
f1 (ppm)
2h
13C NMR (100 MHz, CDCl3)

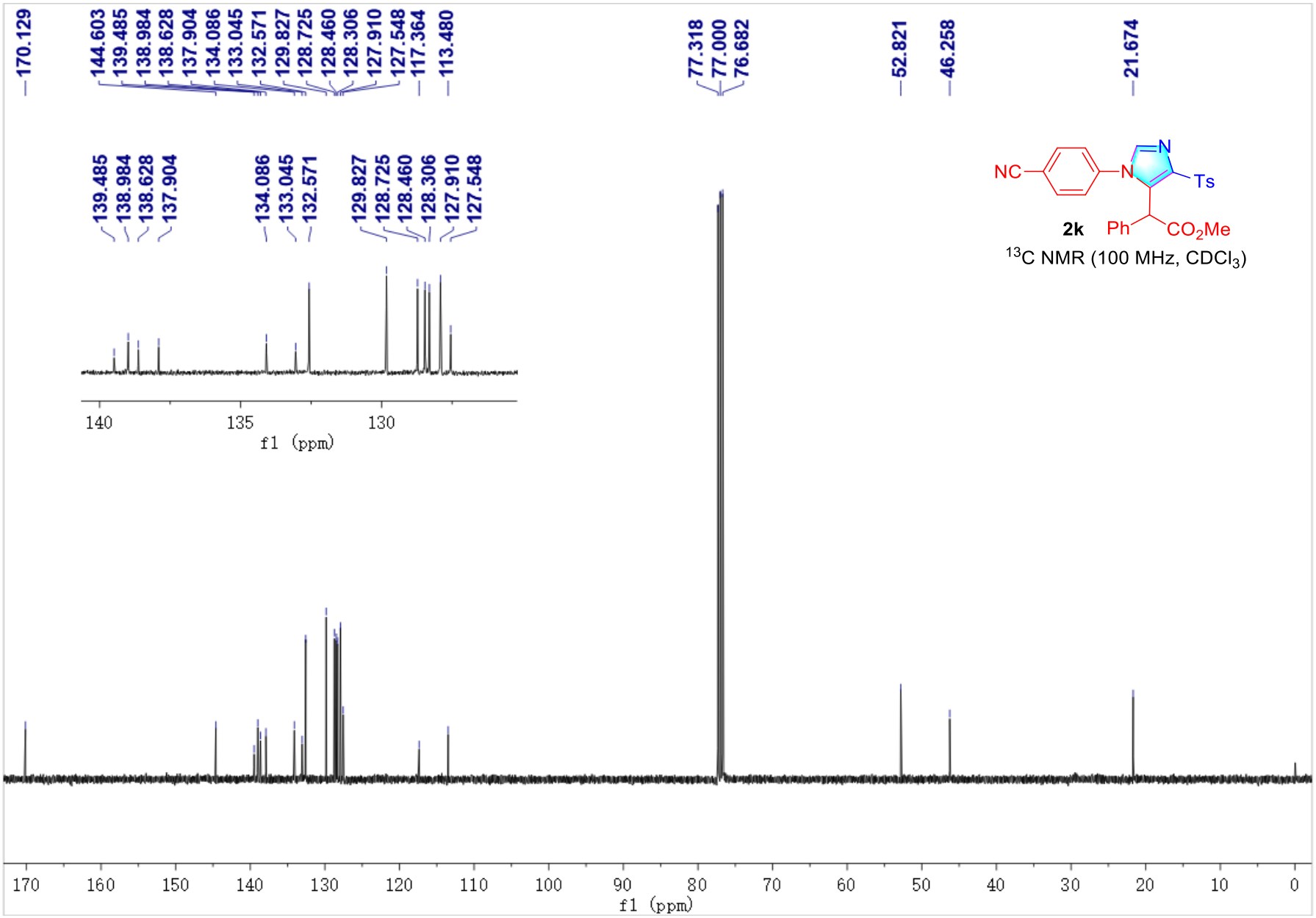

7.962
7.942
7.416
7.358
7.356
7.342
7.339
7.337
7.335
7.318
7.260
7.181
7.169
7.162
7.156
7.147
7.144
7.140
7.122
7.118
7.116
7.113
7.101
7.098
7.092
7.084
7.080
7.077
6.808
6.788
6.752
6.730
6.311
3.742
2.434
1.683
1.248
0.874
Br
N
N
Ts
Ph
CO2Me
2i
1H NMR (400 MHz, CDCl3)
2.02
1.00
4.20
1.08
2.07
2.08
2.08
1.00
3.15
3.16
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
f1 (ppm)

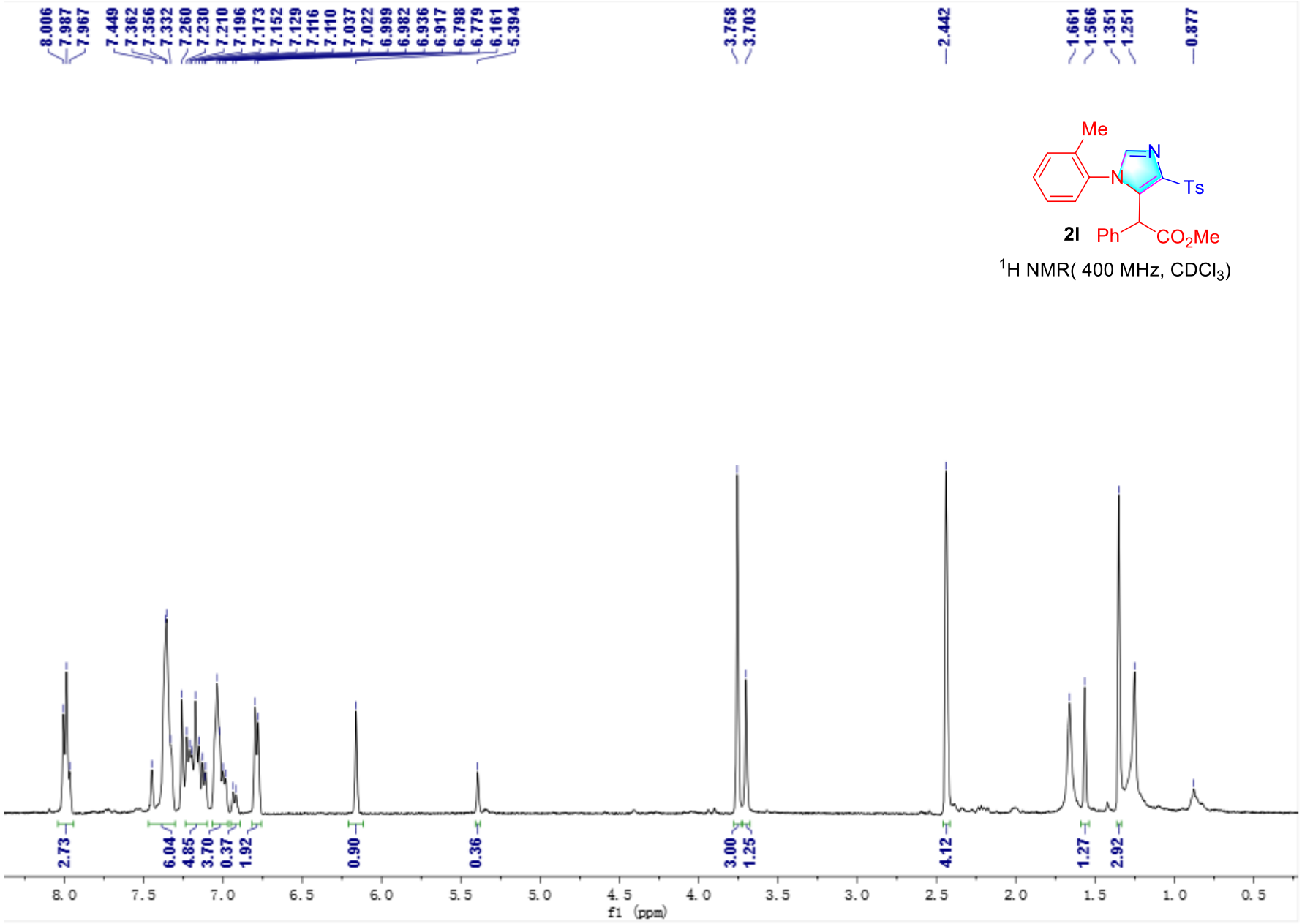

170.061
144.357
139.182
138.888
138.136
134.331
133.737
133.219
132.070
129.726
129.235
128.586
128.328
127.946
127.365
123.882
77.318
77.000
76.682
52.684
46.273
21.646
Br
N
N
Ts
Ph
CO2Me
2i
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.953
7.933
7.542
7.522
7.414
7.353
7.333
7.260
7.182
7.163
7.146
7.115
7.096
7.078
6.804
6.786
6.613
6.593
6.284
3.737
2.429
2.03
1.00
2.06
1.00
2.05
2.03
2.02
f1 (ppm)
I
N
N
Ts
Ph
CO2Me
2j
1H NMR (400 MHz, CDCl3)
2.01
2.03
1.00
2.06
1.00
2.05
2.03
2.02
1.00
3.04
3.07
f1 (ppm)


170.044
144.358
139.089
138.796
138.073
134.381
134.263
133.152
129.711
129.306
128.578
128.310
127.908
127.342
95.467
77.318
77.000
76.682
52.697
46.254
21.639
I
N
N
Ts
Ph
CO2Me
2j
13C NMR (100 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

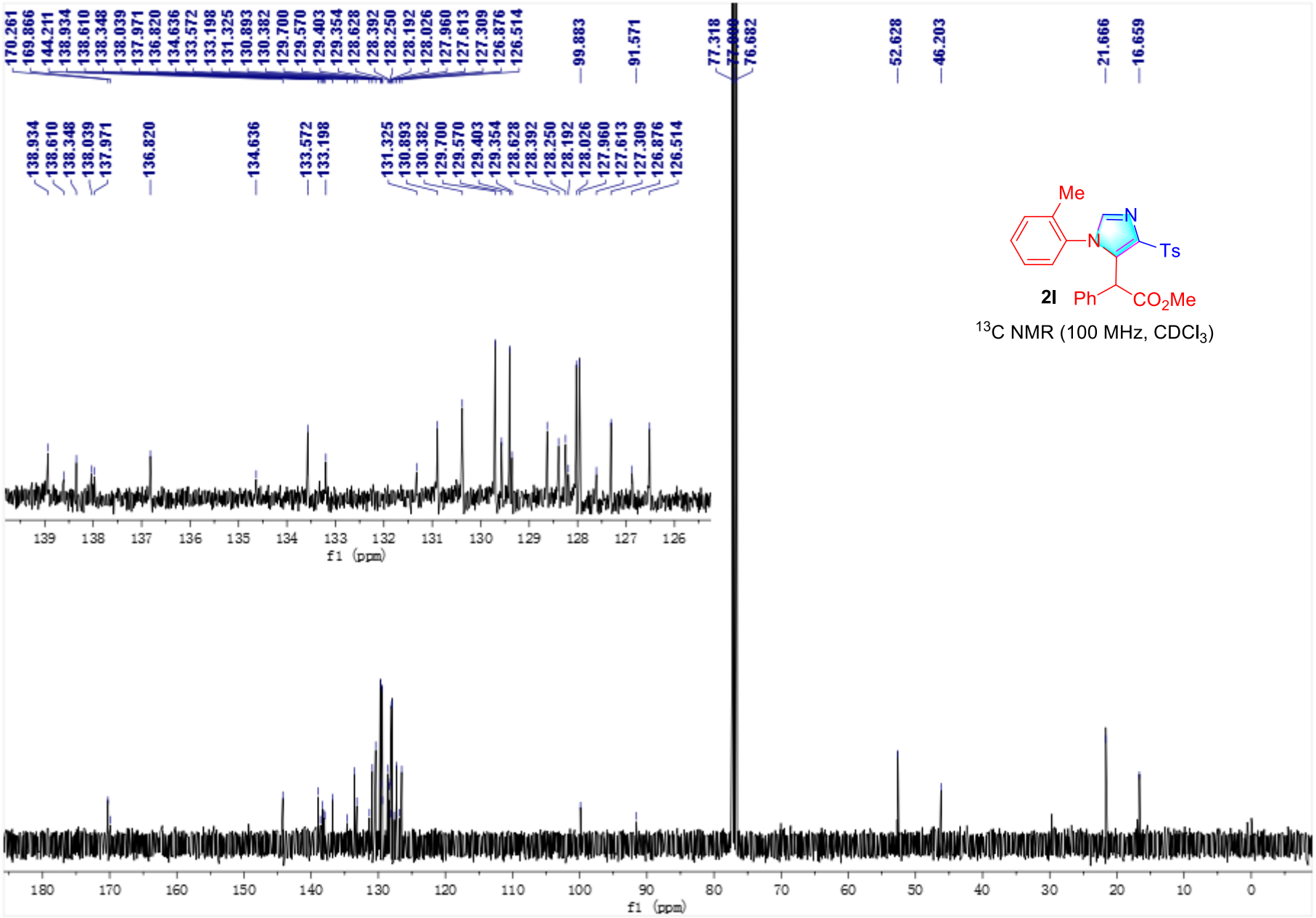

7.969
7.949
7.476
7.456
7.421
7.376
7.356
7.260
7.165
7.147
7.129
7.084
7.065
7.047
7.010
6.990
6.727
6.709
6.455
3.766
2.444
NC
N
N
Ts
Ph
CO2Me
2k
1H NMR(400 MHz, CDCl3)
2.08
1.04
2.08
1.05
2.08
2.06
2.06
f1 (ppm)
2.05
2.08
1.04
2.08
1.05
2.08
2.06
2.06
1.00
3.09
3.11
f1 (ppm)

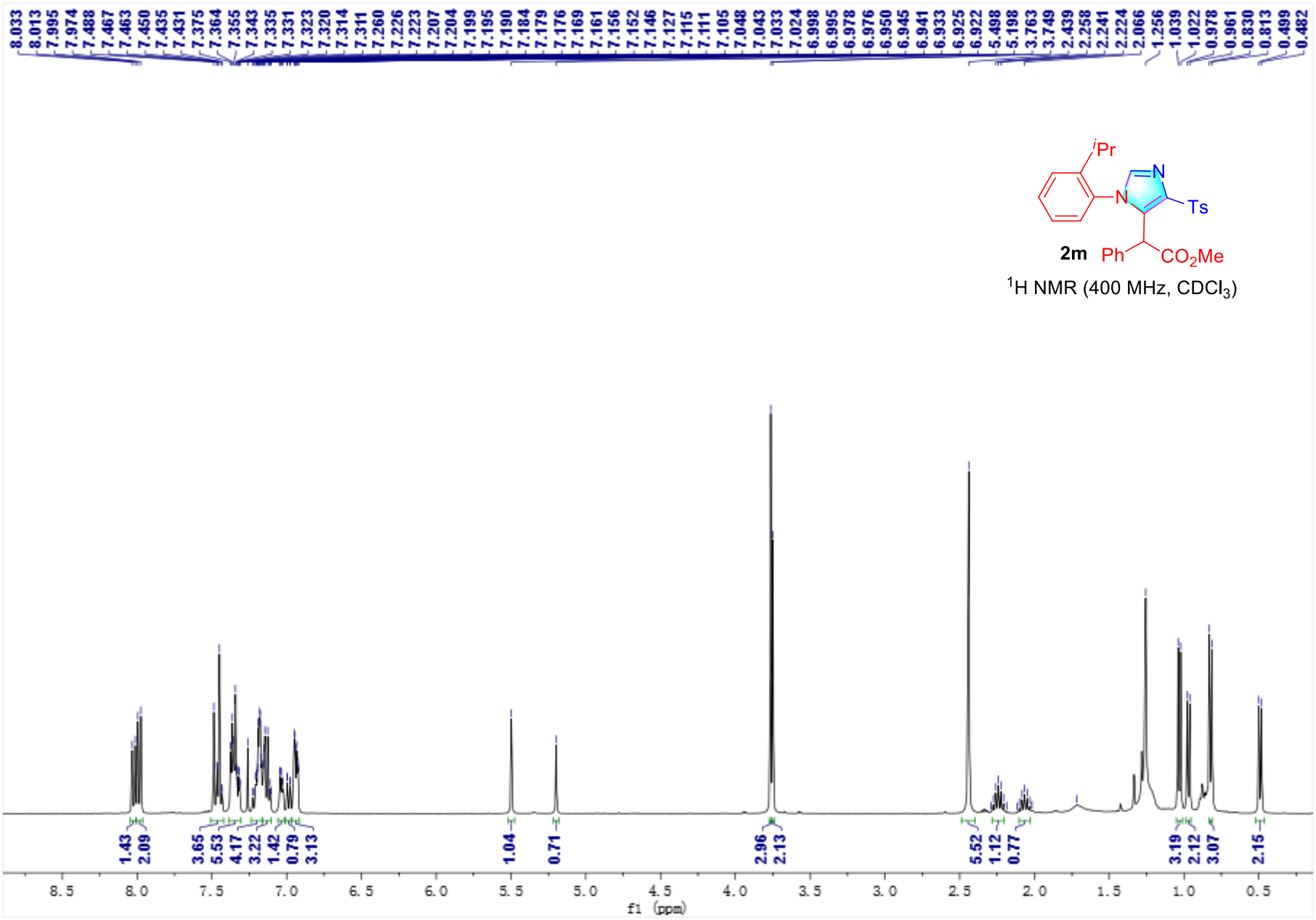

170.129
144.603
139.485
138.984
138.628
137.904
134.086
133.045
132.571
129.827
128.725
128.460
128.306
127.910
127.548
117.364
113.480
77.318
77.000
76.682
52.821
46.258
21.674
NC
N
N
Ts
Ph
CO2Me
2k
13C NMR (100 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

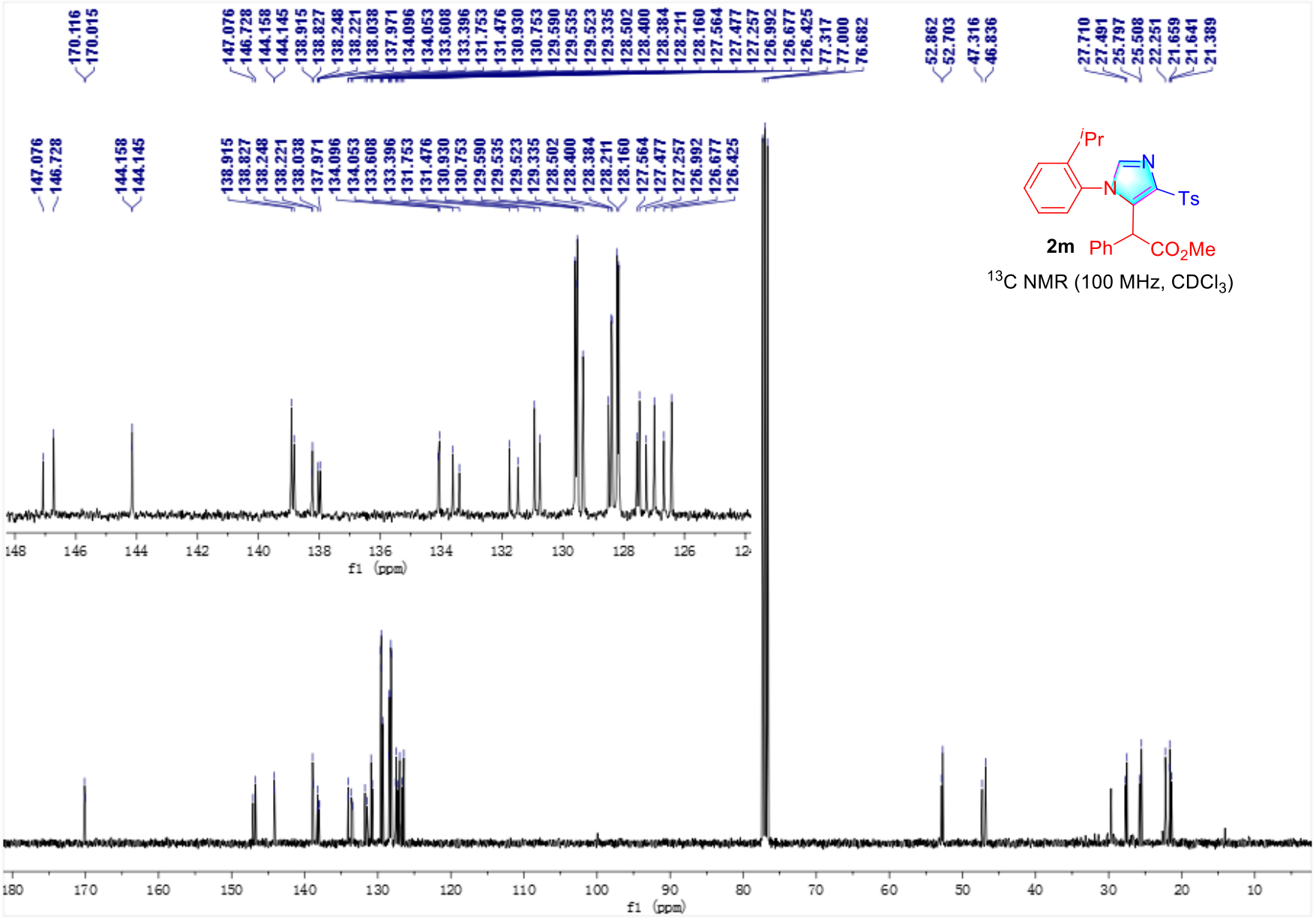


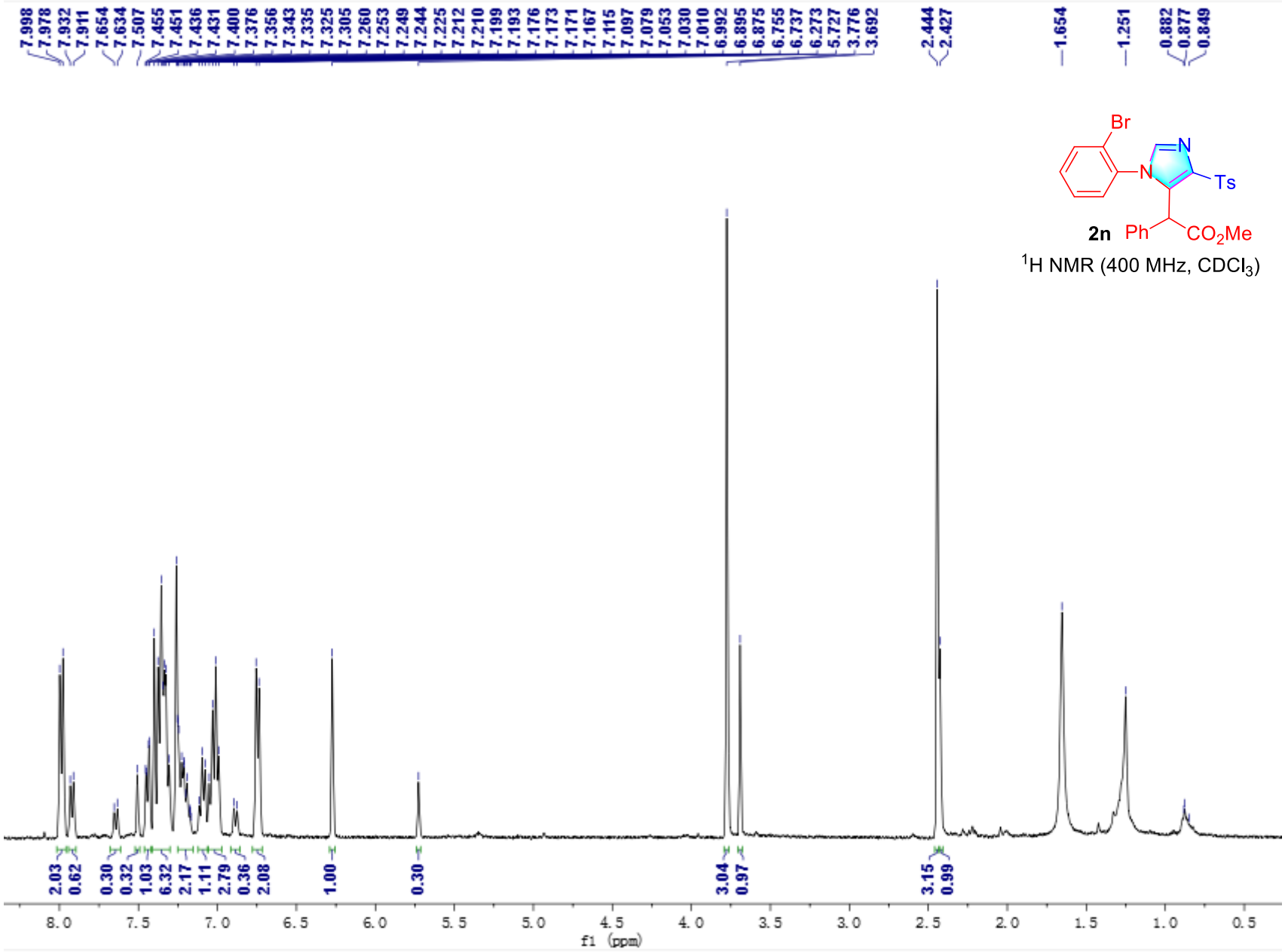
2l

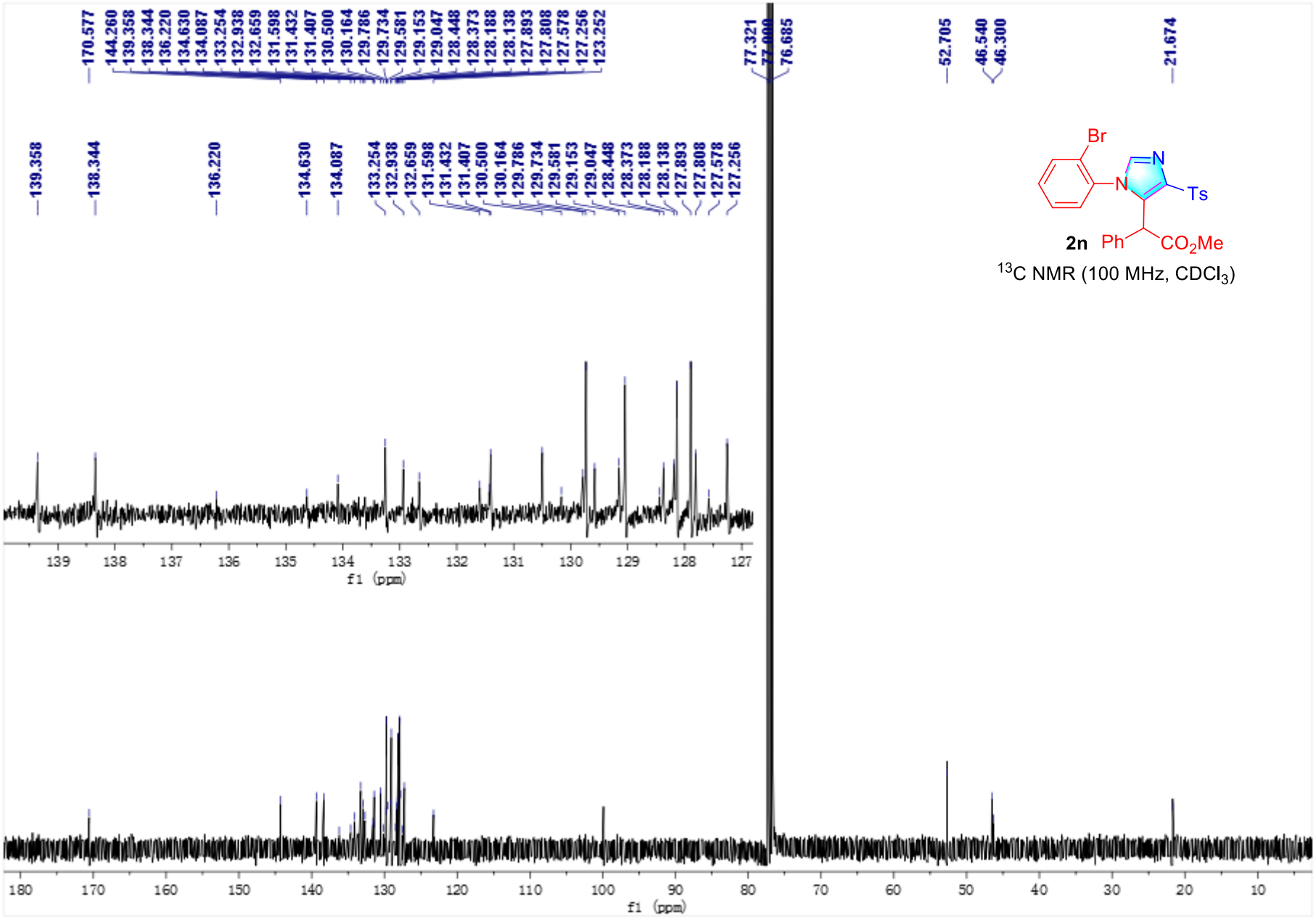
^{1}H NMR(400 MHz, $CDCl_3$)

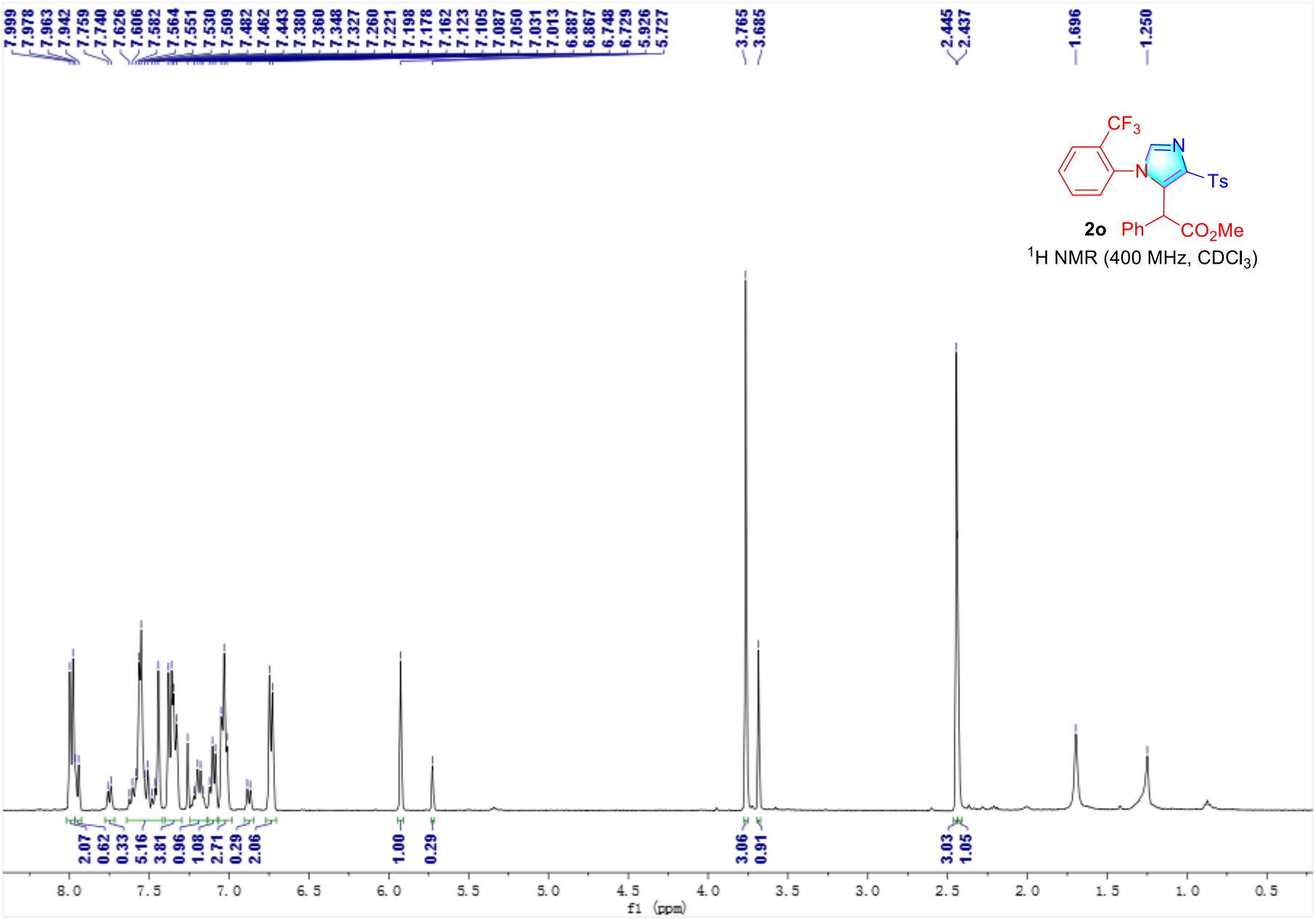

170.261
169.866
144.211
138.934
138.610
138.348
138.039
137.971
136.820
134.636
133.572
133.198
131.325
130.893
130.382
129.700
129.570
129.403
129.354
128.628
128.392
128.250
128.192
128.026
127.960
127.613
127.309
126.876
126.514
99.883
91.571
77.318
77.000
76.682
52.628
46.203
21.666
16.659
Me
N
N
Ts
Ph
CO2Me
2l
13C NMR (100 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

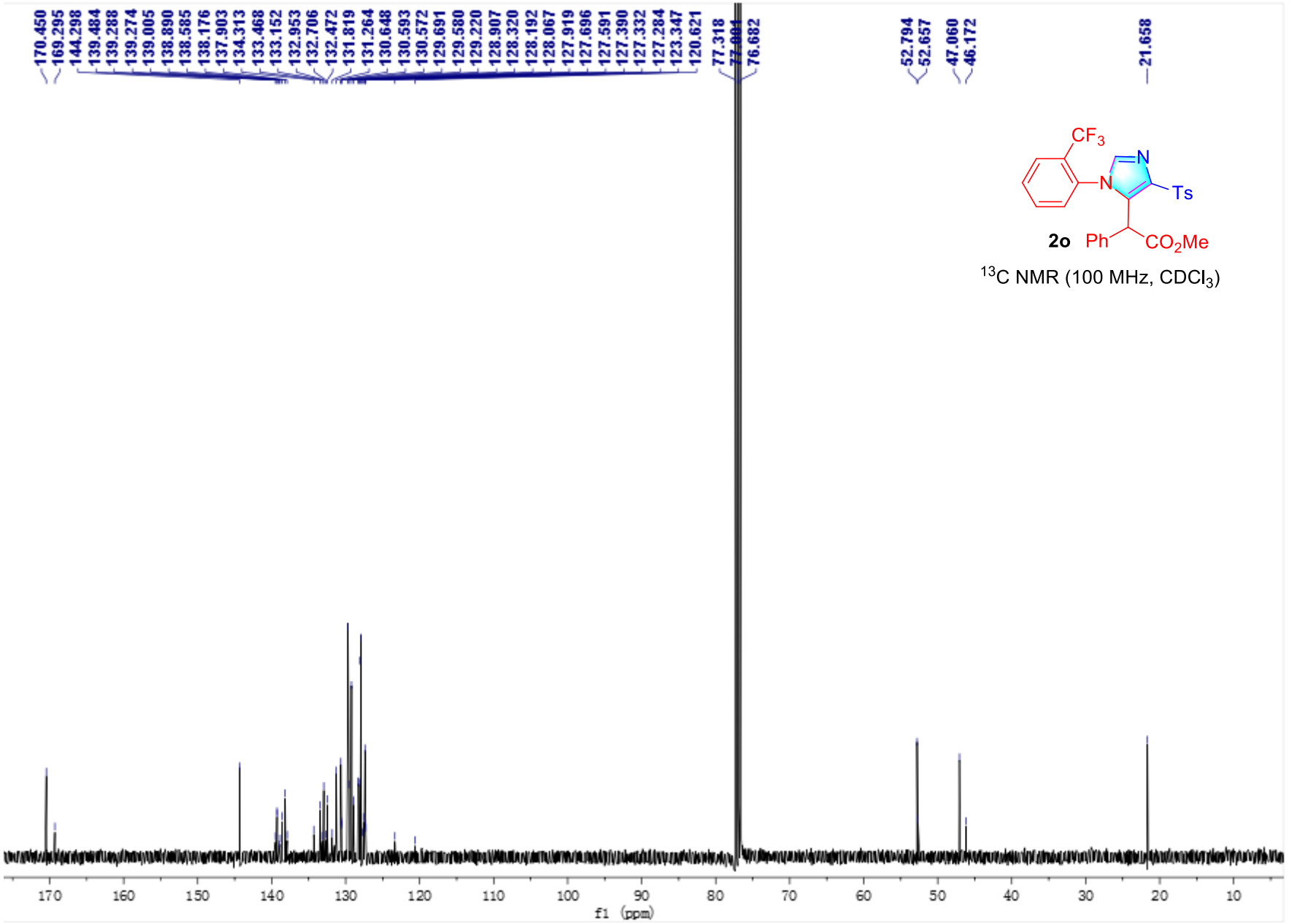

8.033 8.013 7.995 7.974 7.488 7.467 7.463 7.450 7.435 7.431 7.375 7.364 7.355 7.343 7.335 7.331 7.323 7.320 7.314 7.311 7.260 7.226 7.223 7.207 7.204 7.199 7.195 7.190 7.184 7.179 7.176 7.169 7.161 7.156 7.152 7.146 7.127 7.115 7.111 7.105 7.048 7.043 7.033 7.024 6.998 6.995 6.978 6.976 6.950 6.945 6.941 6.933 6.925 6.922 5.498 5.198 3.763 3.749 2.439 2.258 2.241 2.224 2.066 1.256 1.039 1.022 0.978 0.961 0.830 0.813 0.499 0.482
iPr
N
N
Ts
Ph
CO2Me
2m
1H NMR (400 MHz, CDCl3)
1.43 2.09 3.65 5.53 4.17 3.22 1.42 0.79 3.13 1.04 0.71 2.96 2.13 5.52 1.12 0.77 3.19 2.12 3.07 2.15
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
f1 (ppm)

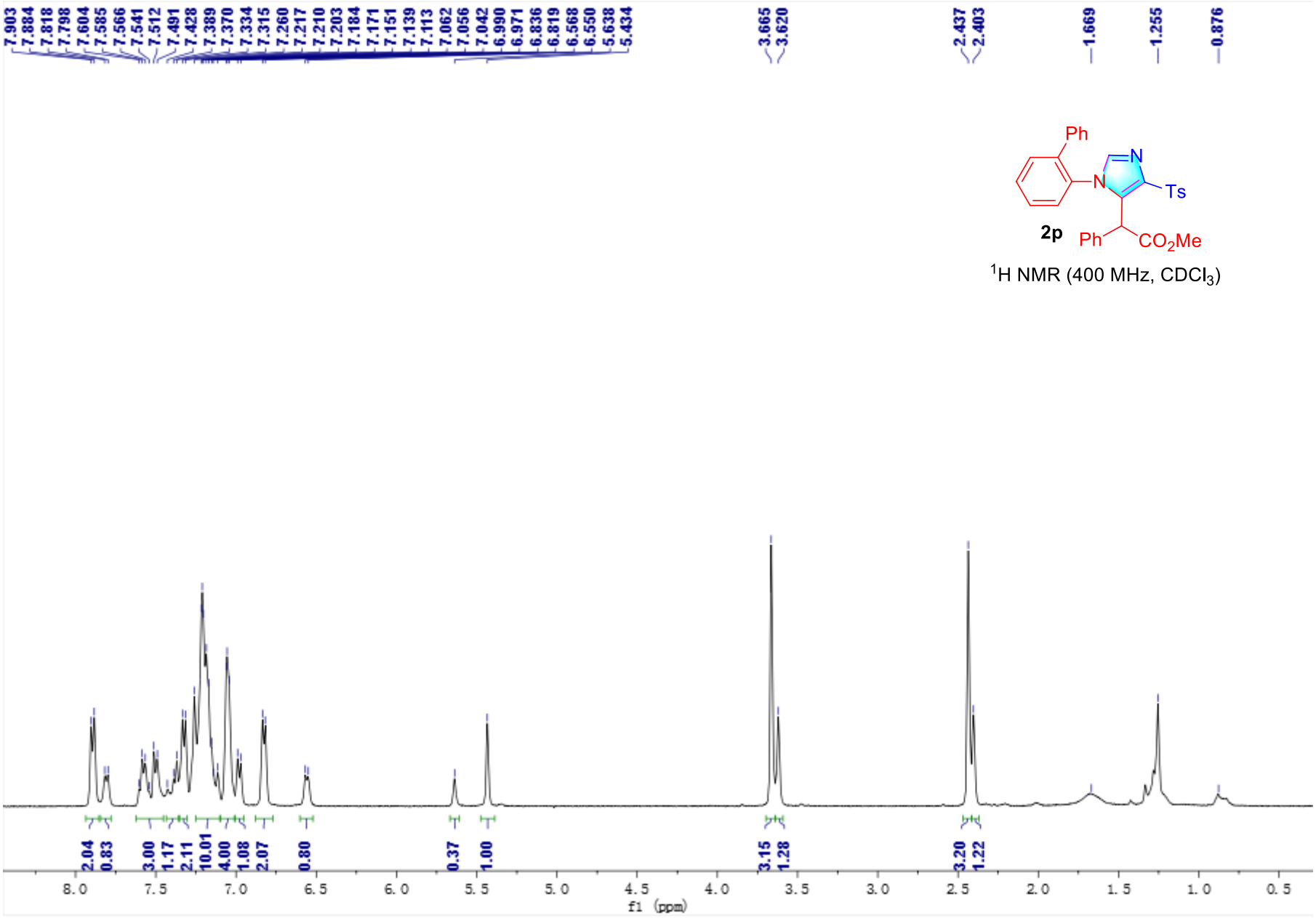

170.116
170.015
147.076
146.728
144.158
144.145
138.915
138.827
138.248
138.221
138.038
137.971
134.096
134.053
133.608
133.396
131.753
131.476
130.930
130.753
129.590
129.535
129.523
129.335
128.502
128.400
128.384
128.211
128.160
127.564
127.477
127.257
126.992
126.677
126.425
77.317
77.000
76.682
52.862
52.703
47.316
46.836
27.710
27.491
25.797
25.508
22.251
21.659
21.641
21.389
iPr
N
N
Ts
2m
Ph
CO2Me
13C NMR (100 MHz, CDCl3)
f1 (ppm)
f1 (ppm)


7.998
7.978
7.932
7.911
7.654
7.634
7.507
7.455
7.451
7.436
7.431
7.400
7.376
7.356
7.343
7.335
7.325
7.305
7.260
7.253
7.249
7.244
7.225
7.212
7.210
7.199
7.193
7.176
7.173
7.171
7.167
7.115
7.097
7.079
7.053
7.030
7.010
6.992
6.895
6.875
6.755
6.737
6.273
5.727
3.776
3.692
2.444
2.427
1.654
1.251
0.882
0.877
0.849
Br
N
N
Ts
Ph
CO2Me
2n
1H NMR (400 MHz, CDCl3)
2.03
0.62
0.30
0.32
1.03
6.32
2.17
1.11
2.79
0.36
2.08
1.00
0.30
3.04
0.97
3.15
0.99
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
f1 (ppm)

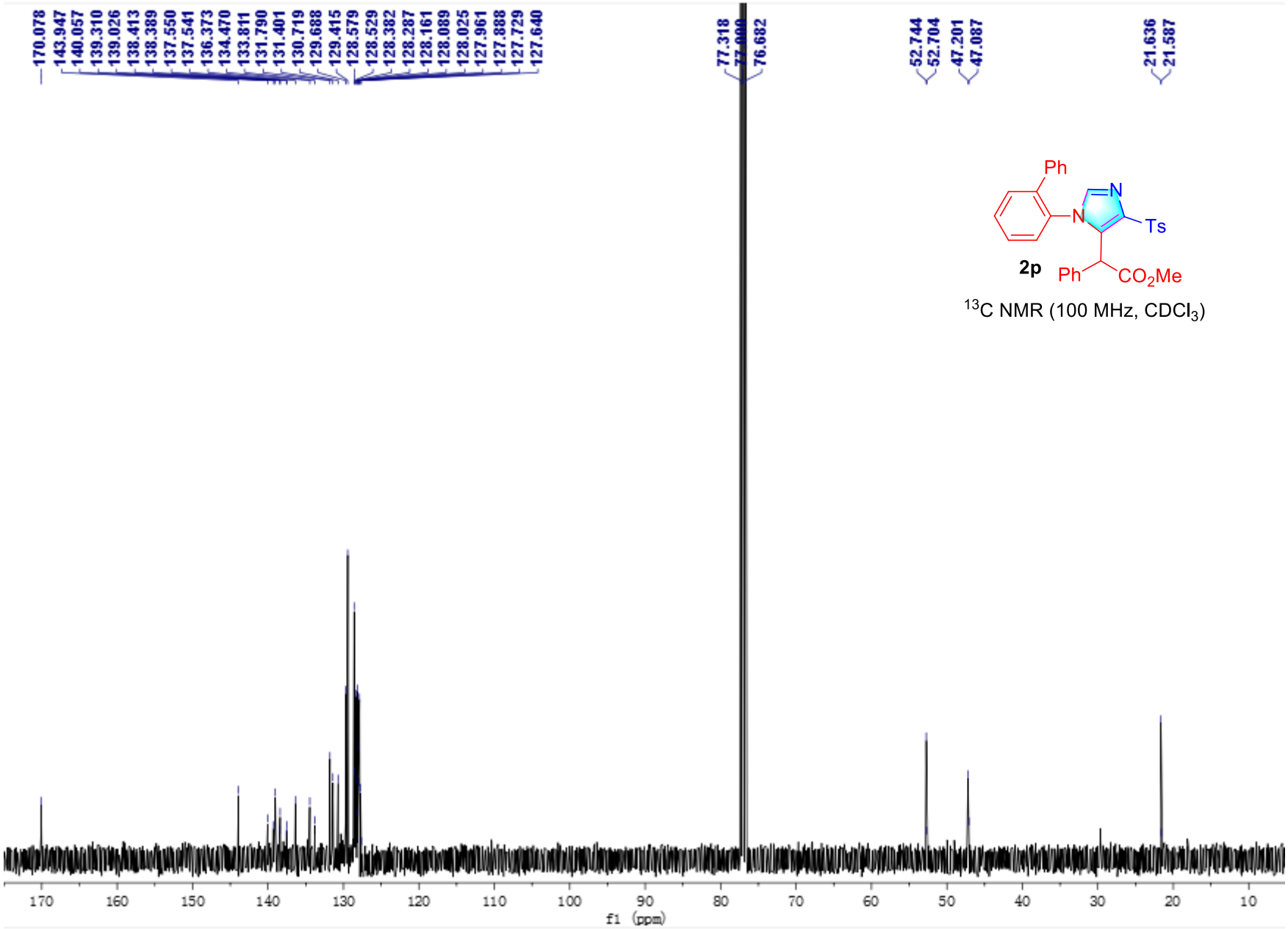

170.577
144.260
139.358
138.344
136.220
134.630
134.087
133.254
132.938
132.659
131.598
131.432
131.407
130.500
130.164
129.786
129.734
129.581
129.153
129.047
128.448
128.373
128.188
128.138
127.893
127.808
127.578
127.256
123.252
77.321
77.000
76.685
52.705
46.540
46.300
21.674
Br
N
N
Ts
Ph
CO2Me
2n
13C NMR (100 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

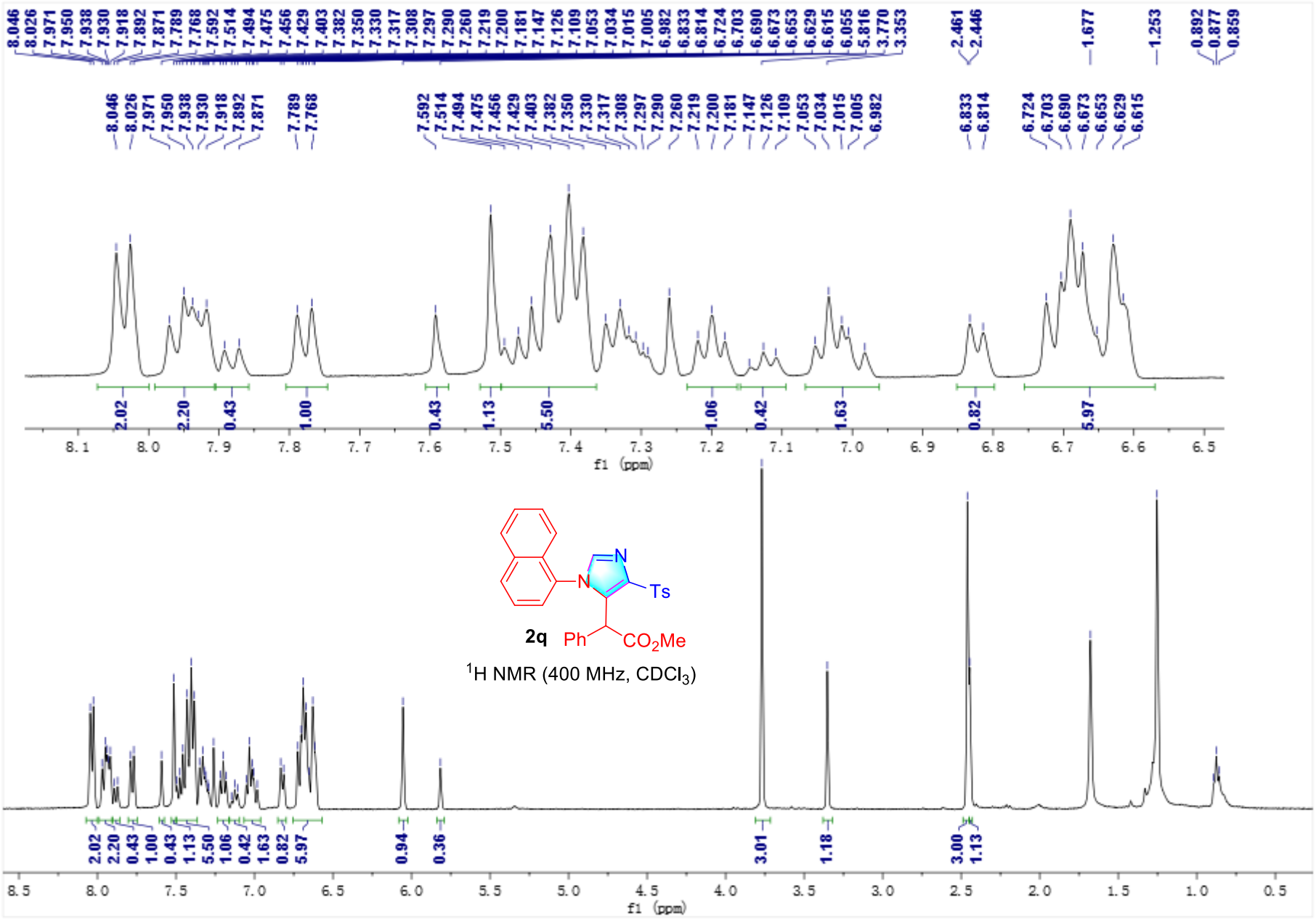

7.999
7.978
7.963
7.942
7.759
7.740
7.626
7.606
7.582
7.564
7.551
7.530
7.509
7.482
7.462
7.443
7.380
7.360
7.348
7.327
7.260
7.221
7.198
7.178
7.162
7.123
7.105
7.087
7.050
7.031
7.013
6.887
6.867
6.748
6.729
5.926
5.727
3.765
3.685
2.445
2.437
1.696
1.250
CF3
N
N
Ts
Ph
CO2Me
2o
1H NMR (400 MHz, CDCl3)
2.07
0.62
0.33
5.16
3.81
0.96
1.08
2.71
0.29
2.06
1.00
0.29
3.06
0.91
3.03
1.05
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
f1 (ppm)

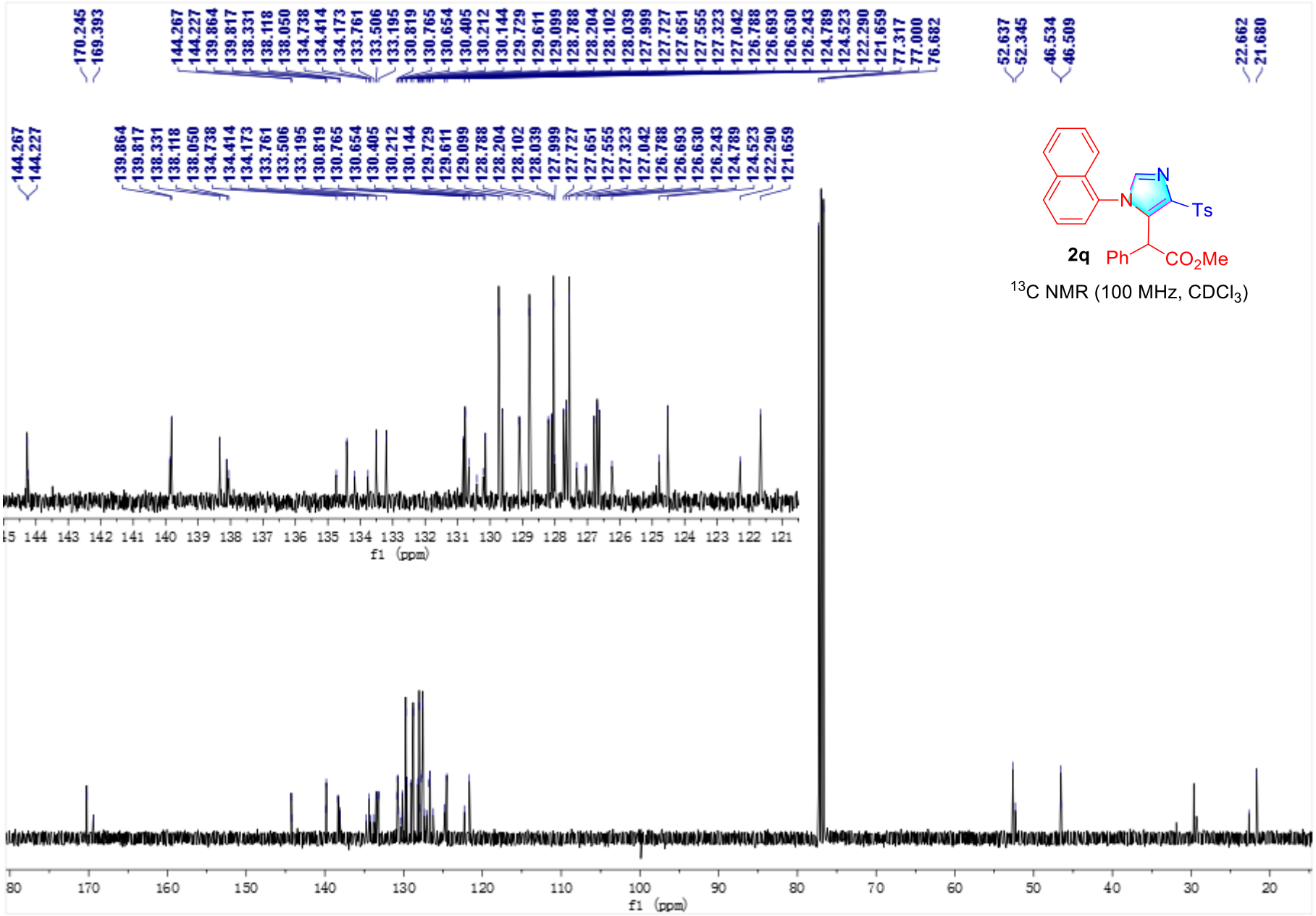

170.450
169.295
144.298
139.484
139.288
139.274
139.005
138.890
138.585
138.176
137.903
134.313
133.468
133.152
132.953
132.706
132.472
131.819
131.264
130.648
130.593
130.572
129.691
129.580
129.220
128.907
128.320
128.192
128.067
127.919
127.696
127.591
127.390
127.332
127.284
123.347
120.621
77.318
77.084
76.682
52.794
52.657
47.060
46.172
21.658
CF3
N
N
Ts
Ph
CO2Me
2o
13C NMR (100 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



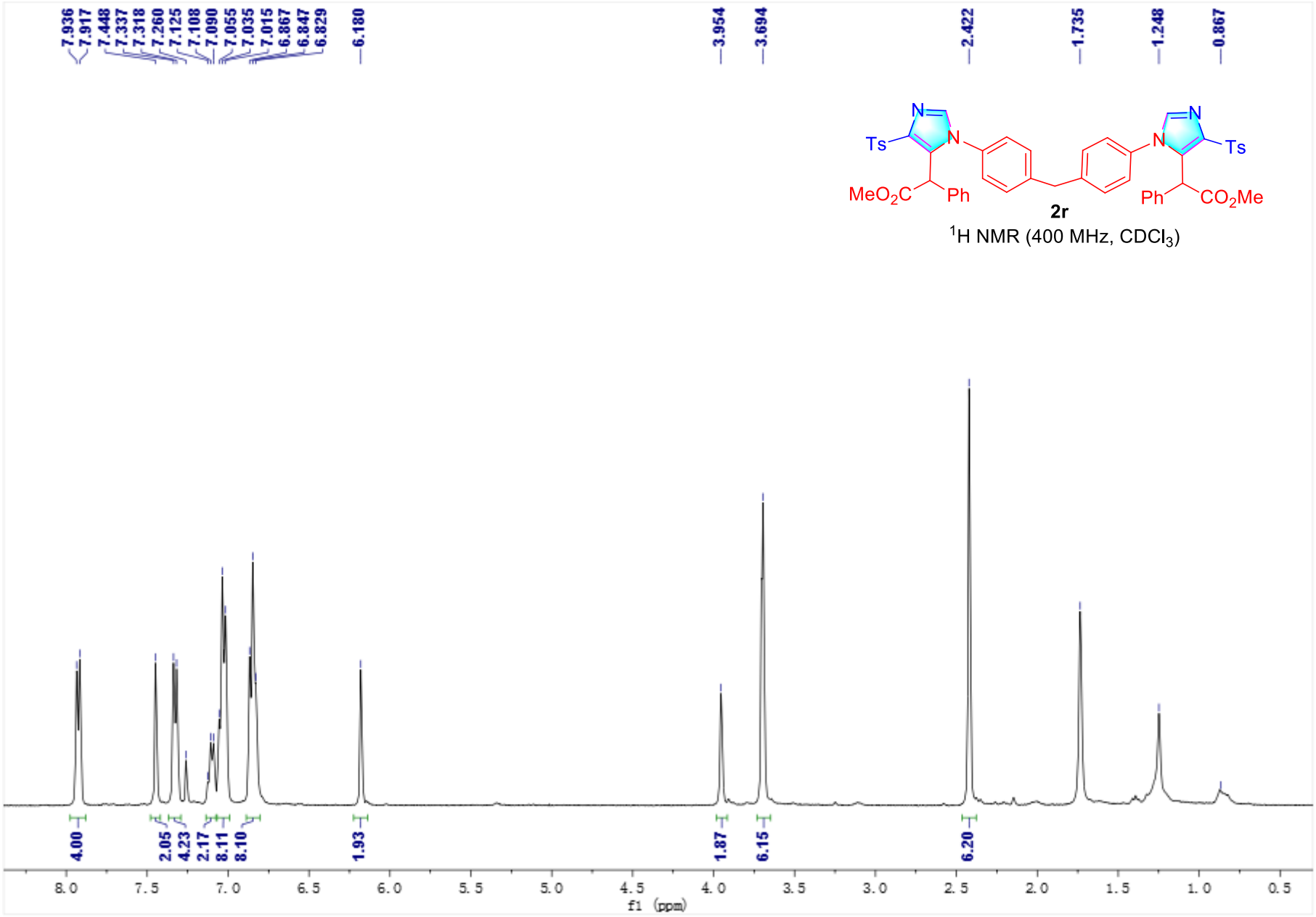
^{1}H NMR (400 MHz, $CDCl_3$)

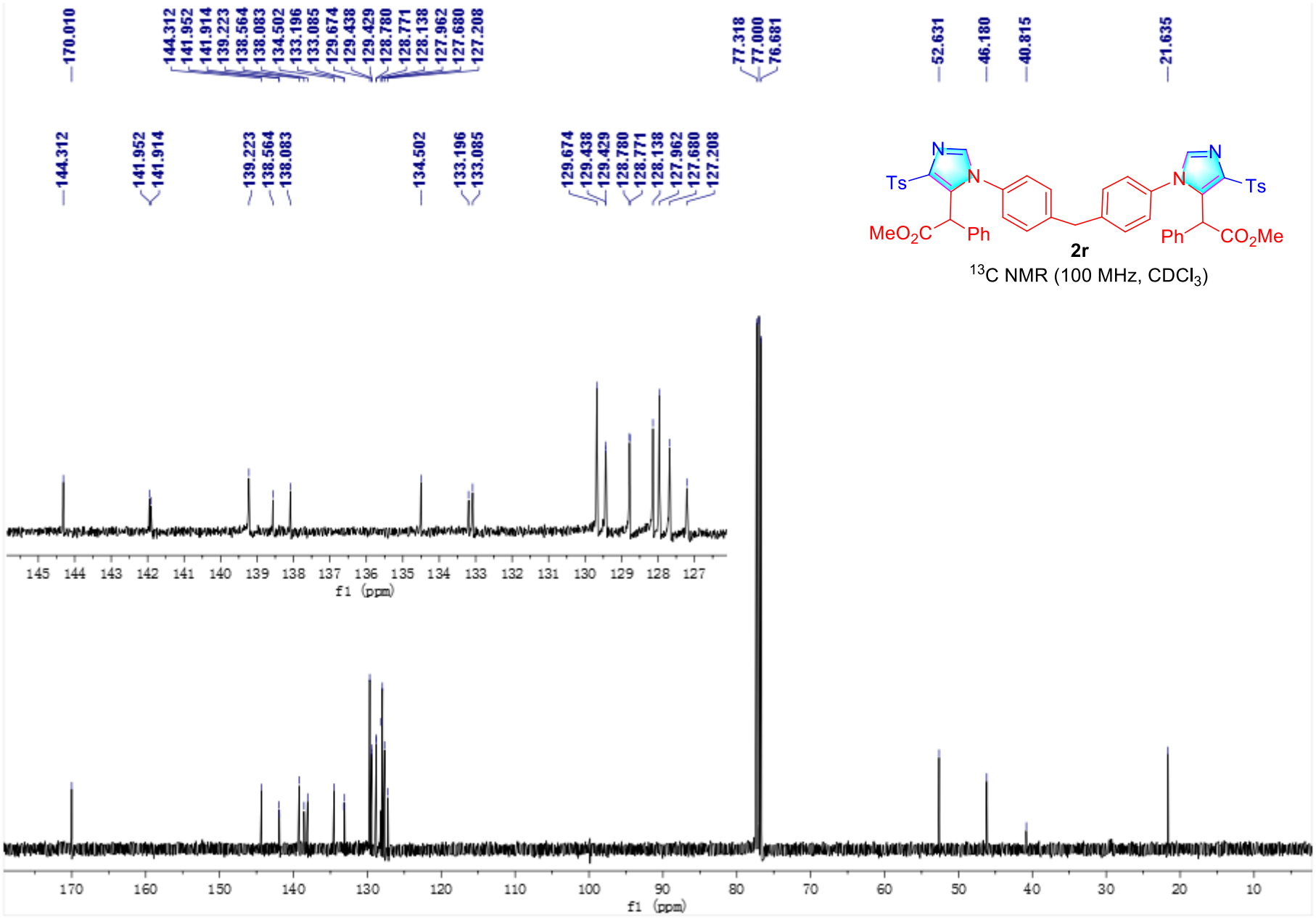

170.078
143.947
140.057
139.310
139.026
138.413
138.389
137.550
137.541
136.373
134.470
133.811
131.790
131.401
130.719
129.688
129.415
128.579
128.529
128.382
128.287
128.161
128.089
128.025
127.961
127.888
127.729
127.640
77.318
77.000
76.682
52.744
52.704
47.201
47.087
21.636
21.587
Ph
N
N
Ts
2p
Ph
CO2Me
13C NMR (100 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

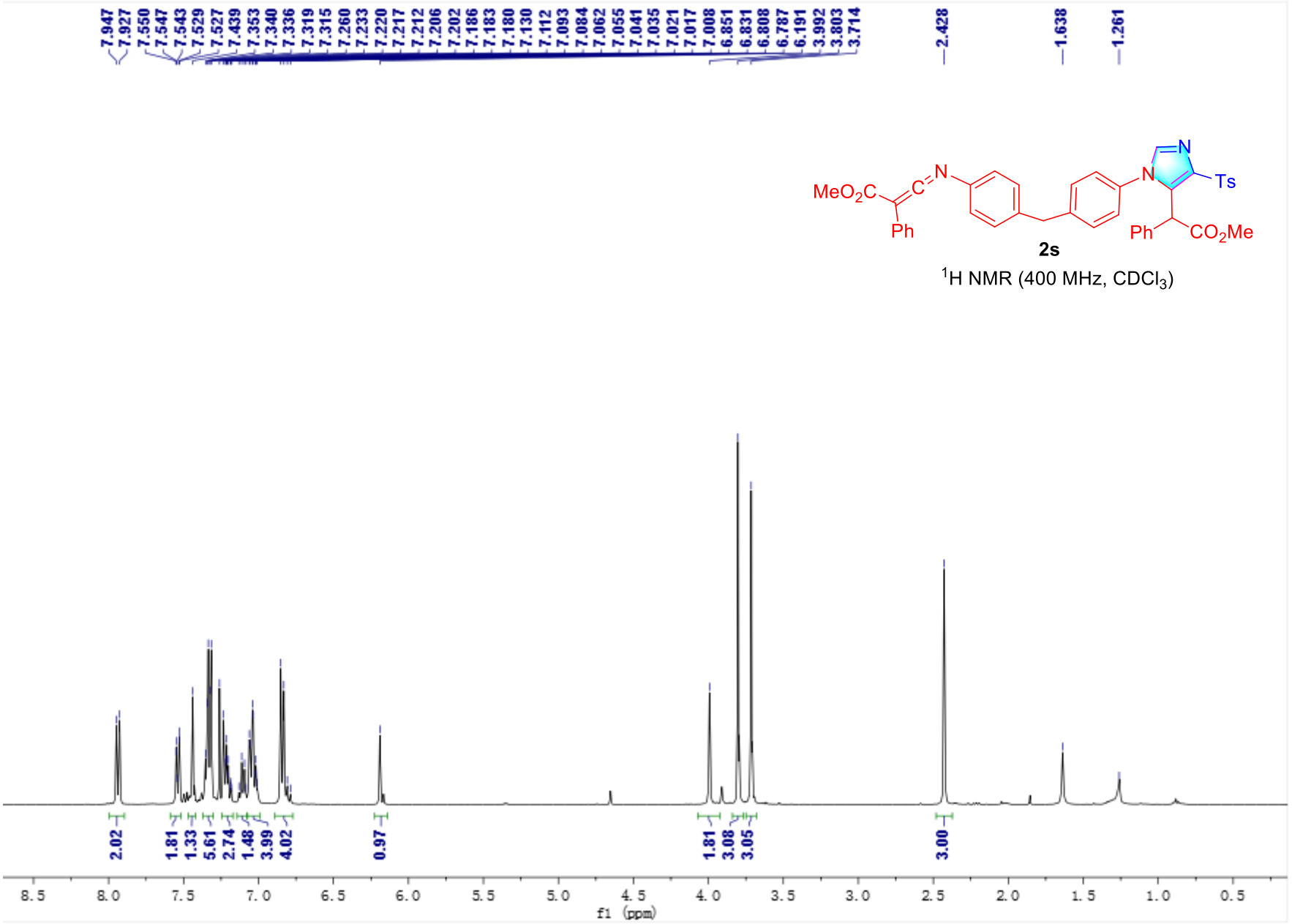

2q
Ph
CO2Me
Ts
1H NMR (400 MHz, CDCl3)
f1 (ppm)

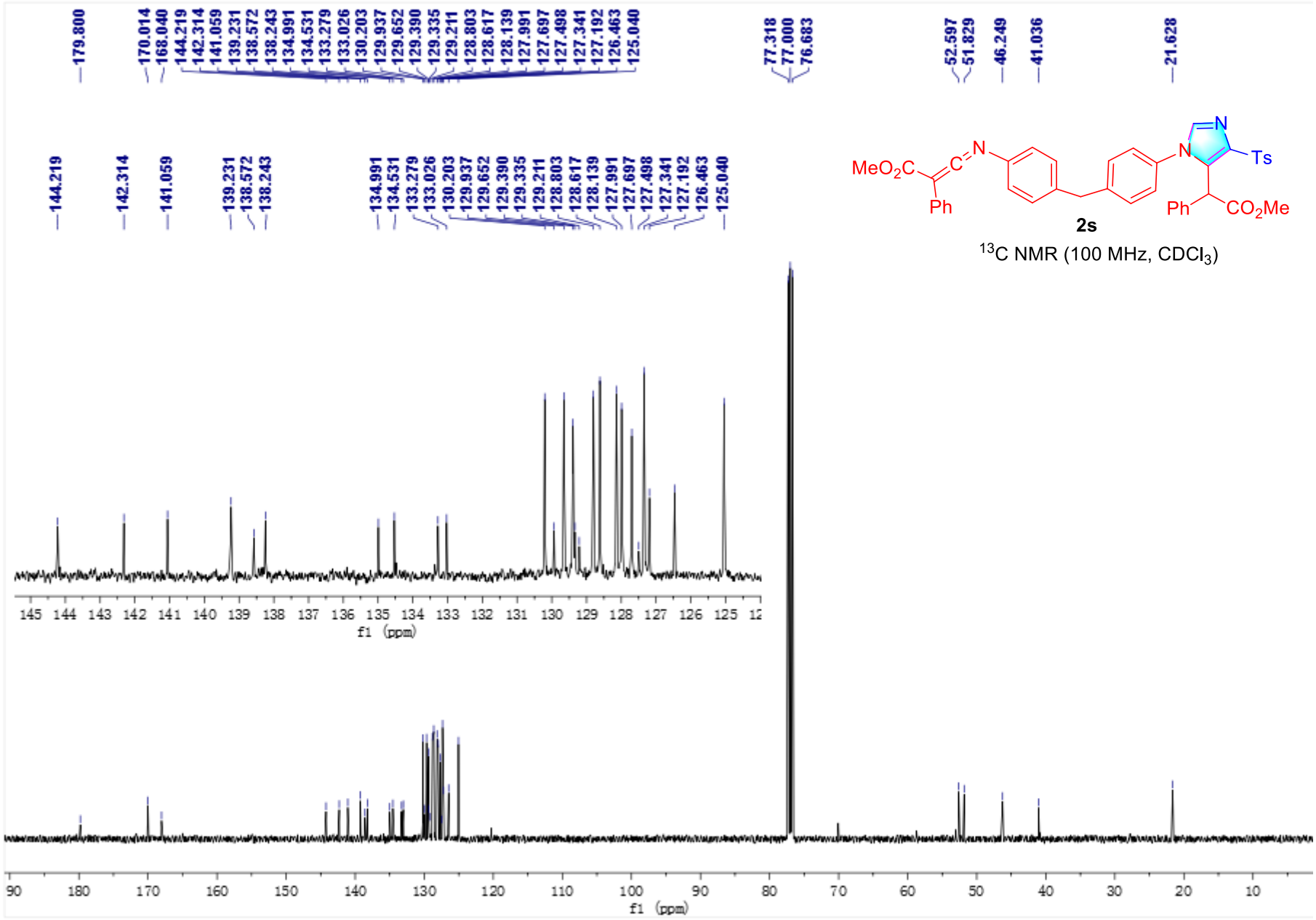


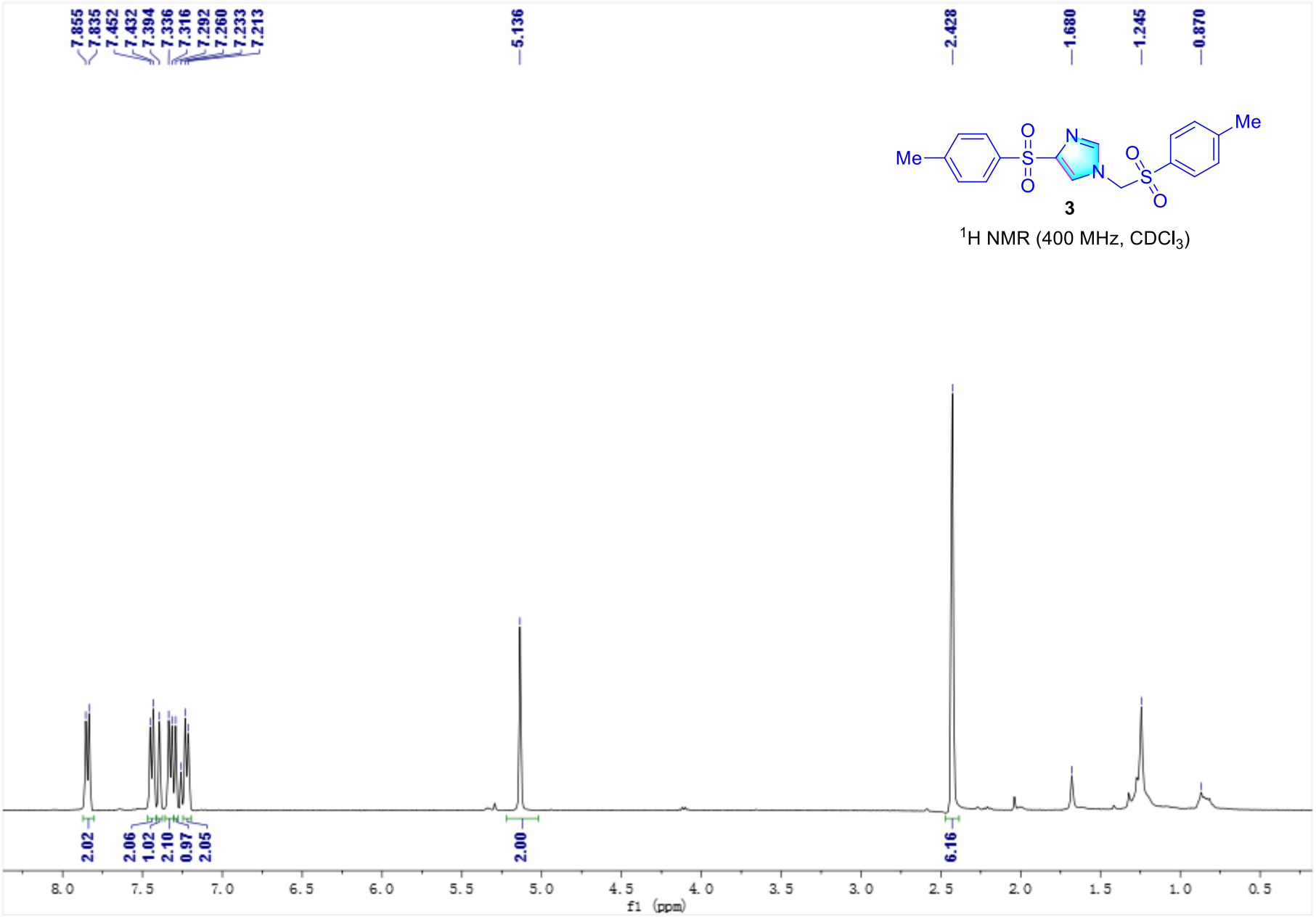
^{13}C NMR (100 MHz, $CDCl_3$)

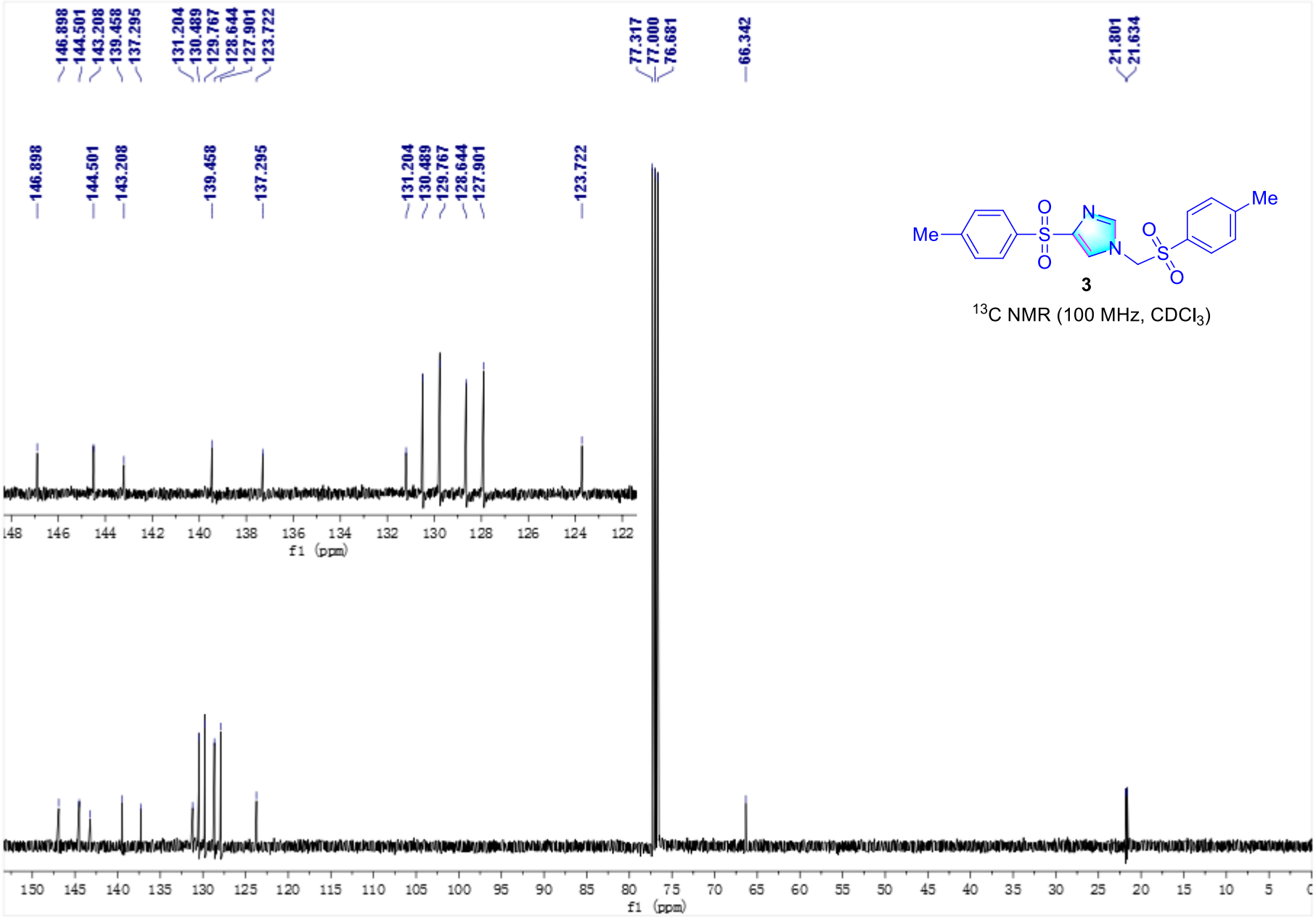

7.936
7.917
7.448
7.337
7.318
7.260
7.125
7.108
7.090
7.055
7.035
7.015
6.867
6.847
6.829
6.180
3.954
3.694
2.422
1.735
1.248
0.867
Ts
N
N
MeO2C
Ph
Ph
CO2Me
2r
1H NMR (400 MHz, CDCl3)
4.00
2.05
4.23
2.17
8.11
8.10
1.93
1.87
6.15
6.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

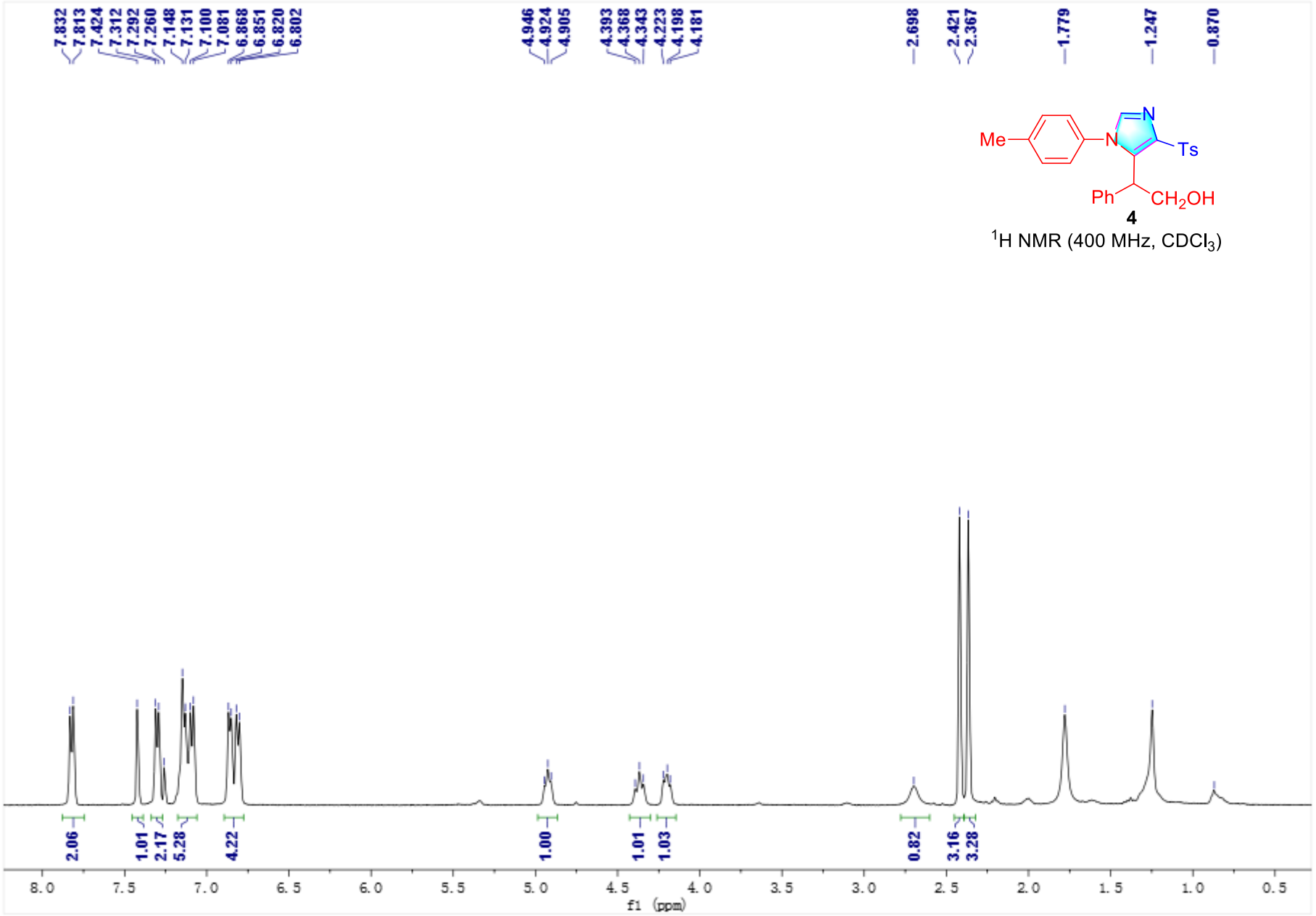

170.010
144.312
141.952
141.914
139.223
138.564
138.083
134.502
133.196
133.085
129.674
129.438
129.429
128.780
128.771
128.138
127.962
127.680
127.208
77.318
77.000
76.681
52.631
46.180
40.815
21.635
Ts
N
MeO2C
Ph
CO2Me
2r
13C NMR (100 MHz, CDCl3)
f1 (ppm)

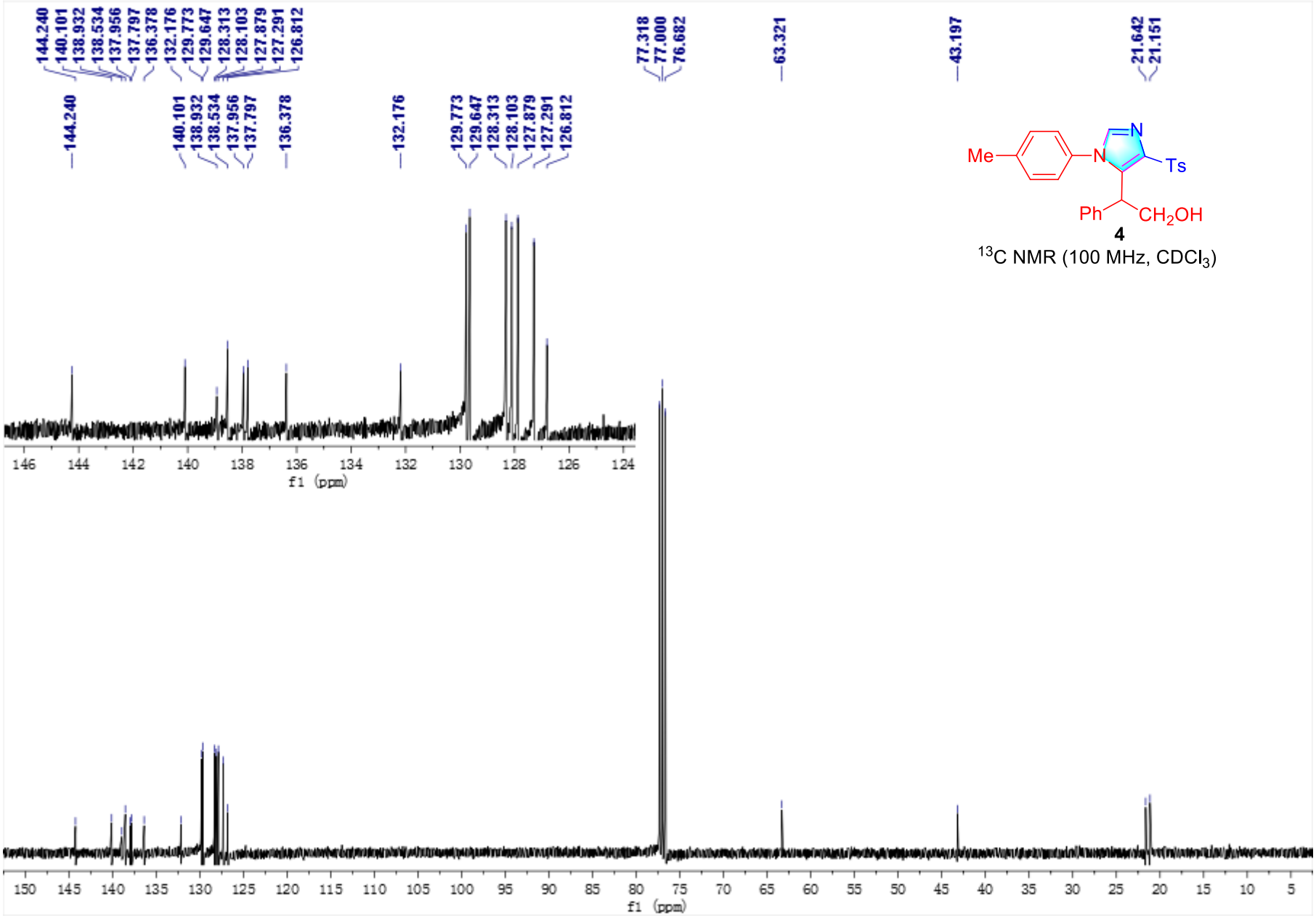

7.947
7.927
7.550
7.547
7.543
7.529
7.527
7.439
7.353
7.340
7.336
7.319
7.315
7.260
7.233
7.220
7.217
7.212
7.206
7.202
7.186
7.183
7.180
7.130
7.112
7.093
7.084
7.062
7.055
7.041
7.035
7.021
7.017
7.008
6.851
6.831
6.808
6.787
6.191
3.992
3.803
3.714
2.428
1.638
1.261
MeO2C
C
N
Ph
N
N
Ts
Ph
CO2Me
2s
1H NMR (400 MHz, CDCl3)
2.02
1.81
1.33
5.61
2.74
1.48
3.99
4.02
0.97
1.81
3.08
3.05
3.00
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
f1 (ppm)

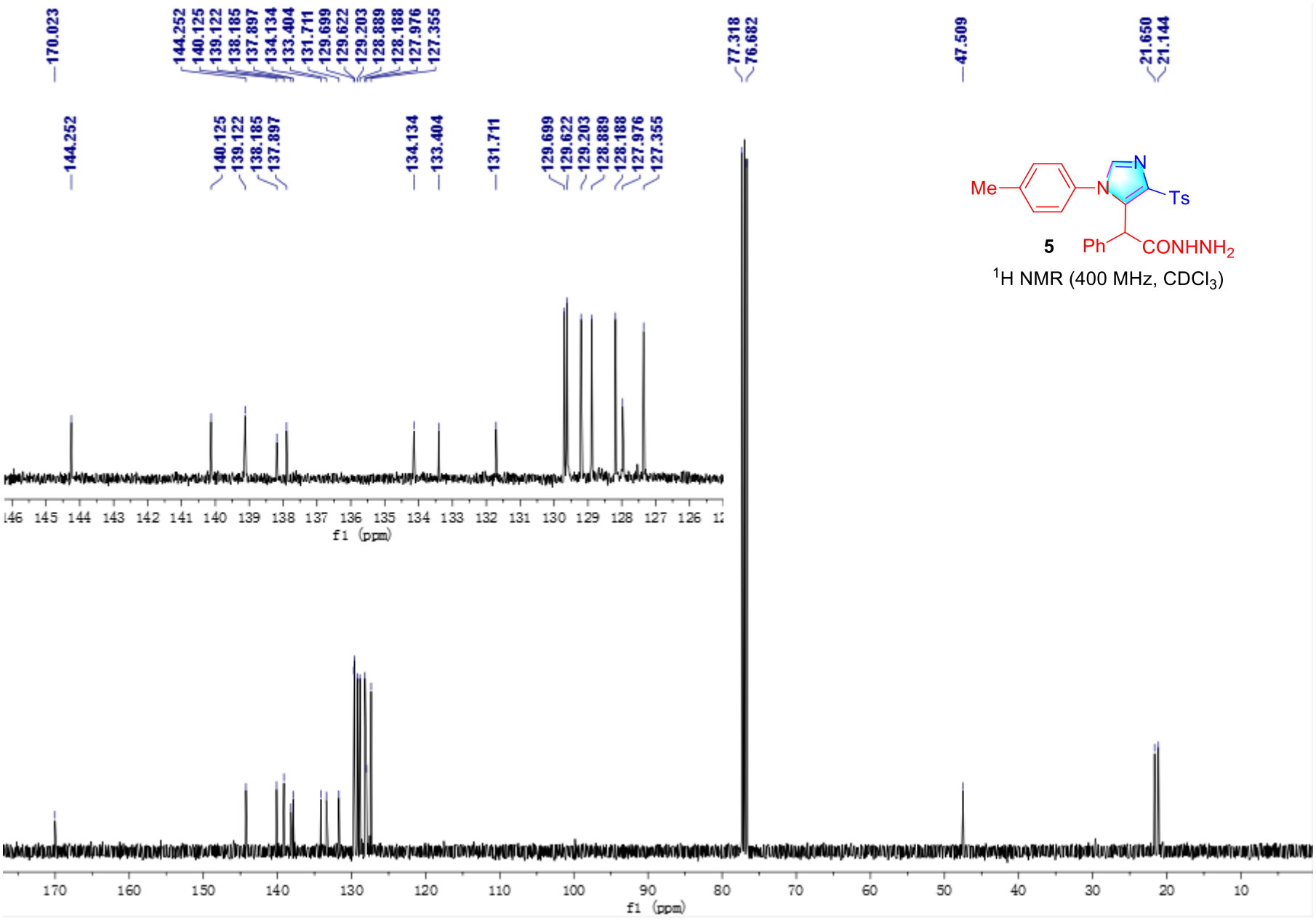

179.800
170.014
168.040
144.219
142.314
141.059
139.231
138.572
138.243
134.991
134.531
133.279
133.026
130.203
129.937
129.652
129.390
129.335
129.211
128.803
128.617
128.139
127.991
127.697
127.498
127.341
127.192
126.463
125.040
77.318
77.000
76.683
52.597
51.829
46.249
41.036
21.628
MeO2C
C
N
Ph
N
Ts
Ph
CO2Me
2s
13C NMR (100 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

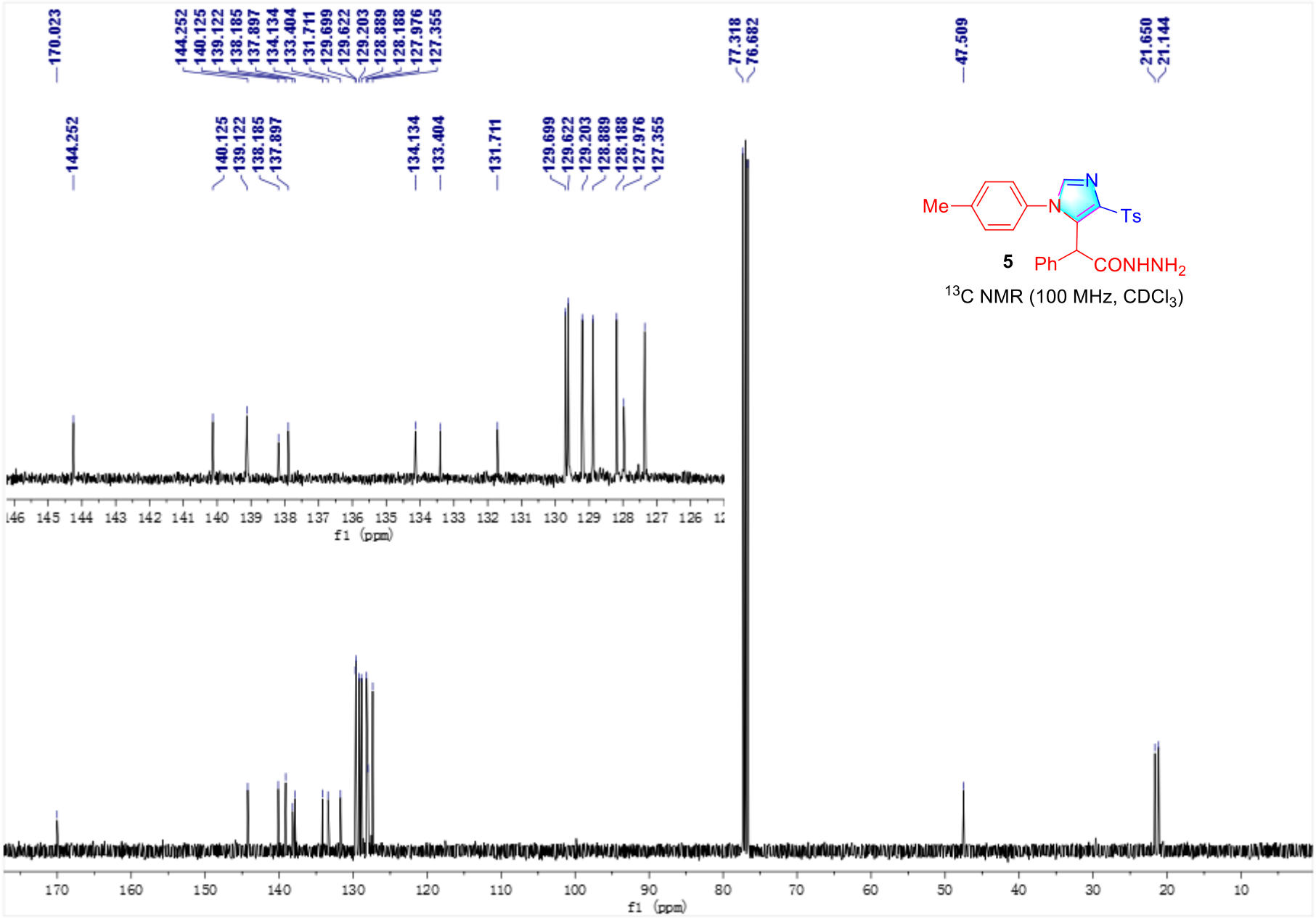

7.855
7.835
7.452
7.432
7.394
7.336
7.316
7.292
7.260
7.233
7.213
5.136
2.428
1.680
1.245
0.870
Me
Me
3
1H NMR (400 MHz, CDCl3)
2.02
2.06
1.02
2.10
0.97
2.05
2.00
6.16
f1 (ppm)

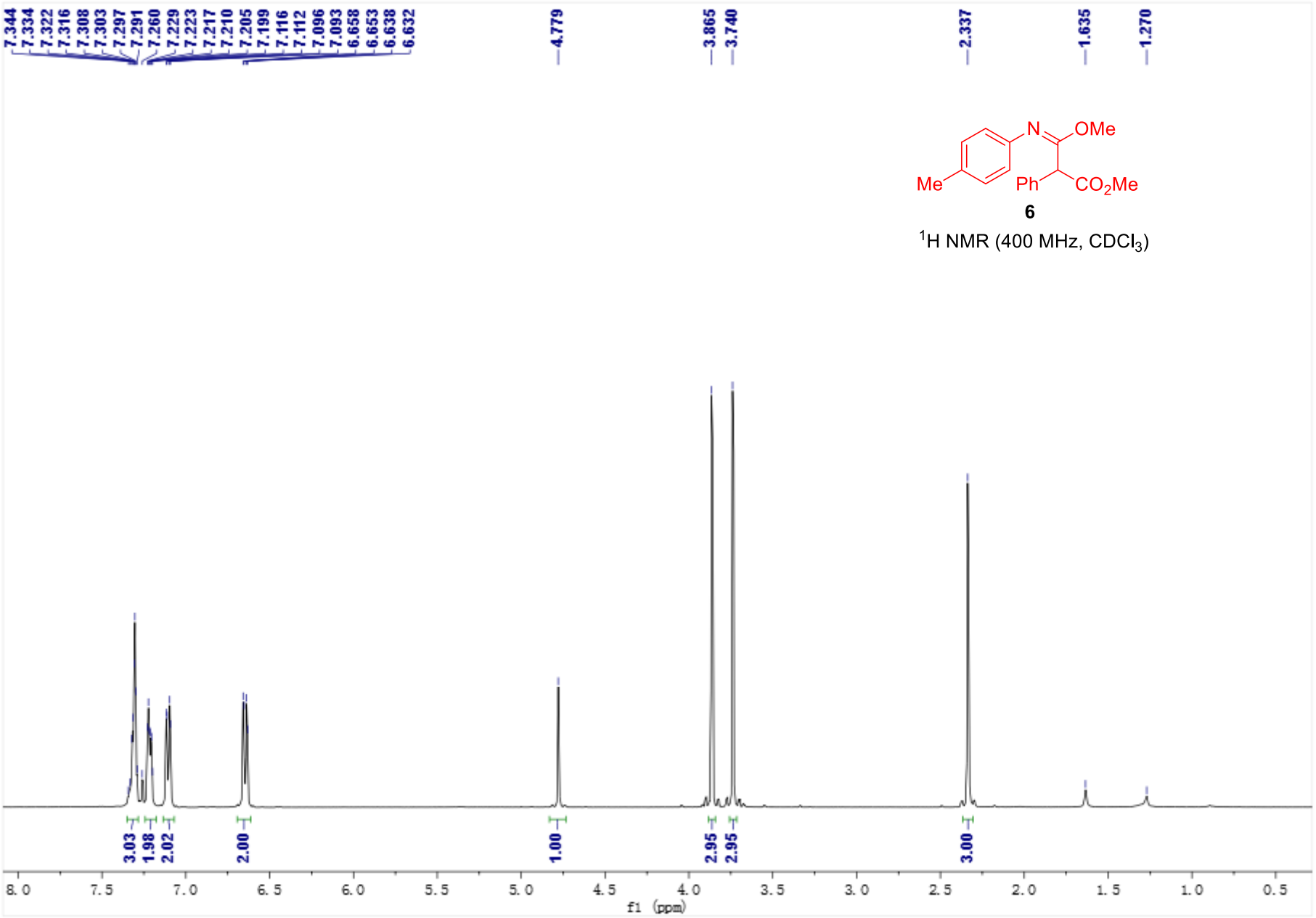

146.898
144.501
143.208
139.458
137.295
131.204
130.489
129.767
128.644
127.901
123.722
77.317
77.000
76.681
66.342
21.801
21.634
Me
Me
3
13C NMR (100 MHz, CDCl3)
f1 (ppm)

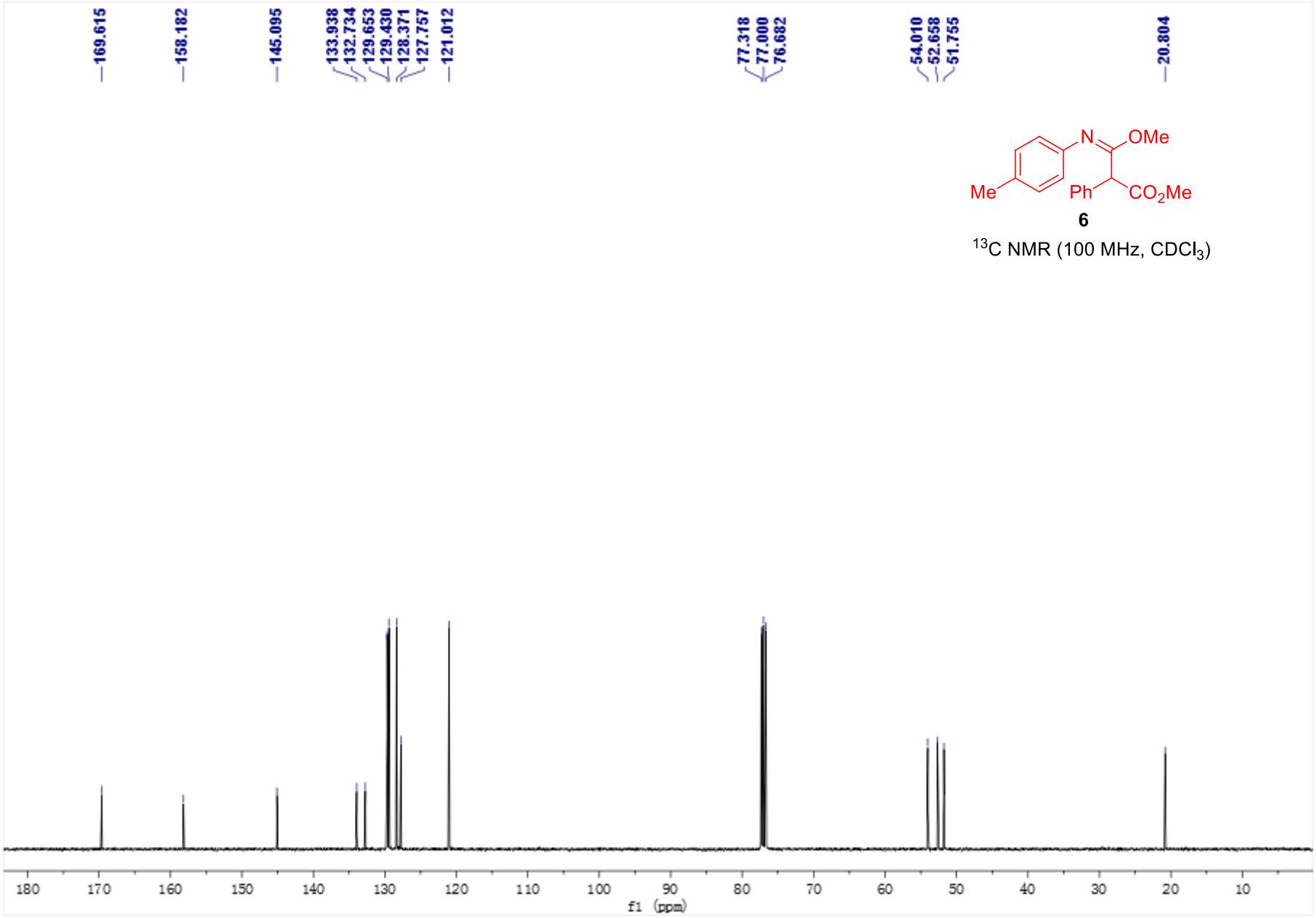

7.832
7.813
7.424
7.312
7.292
7.260
7.148
7.131
7.100
7.081
6.868
6.851
6.820
6.802
4.946
4.924
4.905
4.393
4.368
4.343
4.223
4.198
4.181
2.698
2.421
2.367
1.779
1.247
0.870
Me
N
N
Ts
Ph
CH2OH
4
1H NMR (400 MHz, CDCl3)
2.06
1.01
2.17
5.28
4.22
1.00
1.01
1.03
0.82
3.16
3.28
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


144.240
140.101
138.932
138.534
137.956
137.797
136.378
132.176
129.773
129.647
128.313
128.103
127.879
127.291
126.812
77.318
77.000
76.682
63.321
43.197
21.642
21.151
Me
N
N
Ts
Ph
CH2OH
4
13C NMR (100 MHz, CDCl3)
f1 (ppm)
f1 (ppm)


170.023
144.252
140.125
139.122
138.185
137.897
134.134
133.404
131.711
129.699
129.622
129.203
128.889
128.188
127.976
127.355
77.318
76.682
47.509
21.650
21.144
Me
N
N
Ts
Ph
CONHNH2
5
1H NMR (400 MHz, CDCl3)
f1 (ppm)


170.023
144.252
140.125
139.122
138.185
137.897
134.134
133.404
131.711
129.699
129.622
129.203
128.889
128.188
127.976
127.355
77.318
76.682
47.509
21.650
21.144
Me
N
N
Ts
Ph
CONHNH2
5
13C NMR (100 MHz, CDCl3)
f1 (ppm)
f1 (ppm)


7.344
7.334
7.322
7.316
7.308
7.303
7.297
7.291
7.260
7.229
7.223
7.217
7.210
7.205
7.199
7.116
7.112
7.096
7.093
6.658
6.653
6.638
6.632
4.779
3.865
3.740
2.337
1.635
1.270
N
OMe
Me
Ph
CO2Me
6
1H NMR (400 MHz, CDCl3)
3.03
1.98
2.02
2.00
1.00
2.95
2.95
3.00
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
f1 (ppm)



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^{13}C NMR (100 MHz, $CDCl_3$)