

## Supporting Information

### Three-Component Functionalized Dihydropyridine Synthesis via a Formal Inverse Electron-Demand Hetero-Diels–Alder Reaction

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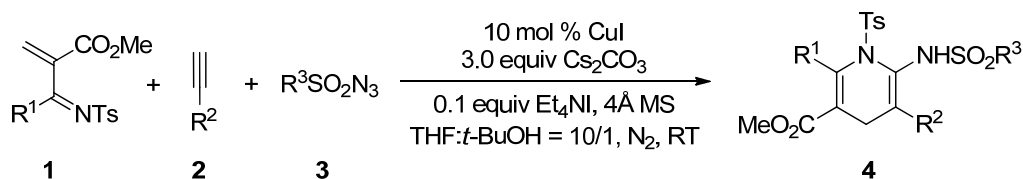
## Experiment section

All reactions were preformed in oven-dried flask under nitrogen atmosphere, otherwise noted. THF and toluene were distilled from Na immediately prior to use while *t*-BuOH from CaH<sub>2</sub>. Thin-layer chromatography (TLC) was performed on silica gel plates (60F–254) using UV-light (254 and 365 nm). Flash chromatography was conducted on silica gel (300–400 mesh). NMR (400 MHz for <sup>1</sup>H NMR, 100 MHz for <sup>13</sup>C NMR) samples were run in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub>, and they were referenced to TMS. High resolution mass spectral (HRMS) analyses were measured using ESI techniques.

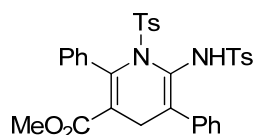
1-azadienes **1** were prepared according to the literature procedures.<sup>[1],[2]</sup>

### General procedure A for the synthesis of product 4

An oven-dried flask was charged with sulfonylazide **3** (0.3 mmol), CuI (3.8 mg, 0.02 mmol), Et<sub>4</sub>Ni (5.1 mg, 0.02 mmol), 1-azadienes **1** (0.2 mmol), 4Å MS (100 mg), evacuated and backfilled with nitrogen. Then THF (5 mL) and *t*-BuOH (0.5 mL) were added. After stirred at room temperature for 10 min, alkyne **2** (0.3 mmol), Cs<sub>2</sub>CO<sub>3</sub> (195 mg, 0.6 mmol) were successively added. The reaction mixture was stirred at 25 °C until 1-azadienes **1** disappeared, monitored by TLC. The mixture was quenched with saturated ammonium chloride (10 mL), and extracted by CH<sub>2</sub>Cl<sub>2</sub> (10 mL x 3). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated in vacuo. The residue was purified by column chromatography on silica gel to provide the desired product **4**.



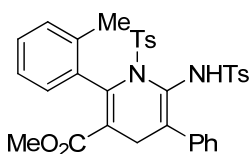
#### Methyl 6-(4-methylphenylsulfonamido)-2,5-diphenyl-1-tosyl-1,4-dihydropyridine-3-carboxylate **4a**



To a mixture of 4-methylbenzenesulfonyl azide (59.2 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), methyl 2-(phenyl(tosylimino)methyl)acrylate (68.7 mg, 0.2 mmol), Et<sub>4</sub>Ni (5.1 mg, 0.02 mmol), 4Å MS (100 mg) in THF (5 mL) and *t*-BuOH (0.5 mL) under N<sub>2</sub> atmosphere, ethynylbenzene (30.6 mg, 0.3 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (195 mg, 0.6 mmol) were added. The

residue was purified by column chromatography on silica gel (n-hexane/EtOAc = 10:1, v/v) to provide **4a** as a white solid (110.6 mg, 90%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 7.49 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.25–7.24 (m, 1H), 7.18–7.10 (m, 9H), 7.01–7.00 (m, 2H), 6.96–6.94 (m, 2H), 6.83 (s, 1H), 3.44 (s, 3H), 2.96 (d, *J* = 20.4 Hz, 1H), 2.31–2.29 ppm (m, 7H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 167.6, 148.0, 145.1, 143.5, 137.0, 136.9, 136.3, 134.7, 134.3, 129.8, 129.8, 129.5, 129.4, 128.4, 128.3, 128.2, 128.1, 127.6, 127.4, 125.9, 121.3, 51.9, 33.1, 21.8, 21.7 ppm; HRMS calc for C<sub>33</sub>H<sub>30</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, [M]<sup>+</sup> 614.1545, found 614.1543.

#### Methyl 6-(4-methylphenylsulfonamido)-5-phenyl-2-(*o*-tolyl)-1-tosyl-1,4-dihydropyridine-3-carboxylate **4b**

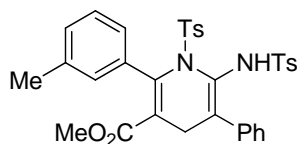


To a mixture of 4-methylbenzenesulfonyl azide (59.2 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), methyl 2-(*o*-tolyl(tosylimino)methyl)acrylate (71.5 mg, 0.2 mmol), Et<sub>4</sub>Ni (5.1 mg, 0.02 mmol), 4Å MS (100 mg) in THF (5 mL) and *t*-BuOH (0.5 mL) under N<sub>2</sub> atmosphere, ethynylbenzene (30.6 mg, 0.3 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (195 mg, 0.6 mmol) were added. The

residue was purified by column chromatography on silica gel (n-hexane/EtOAc = 10:1, v/v) to provide **4b** as a white solid (96.8 mg, 77%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 7.47 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.13–7.07 (m, 5H), 7.05–7.04 (m, 3H), 7.00–6.91 (m, 5H), 6.81 (s, 1H), 3.45 (s, 3H), 2.97 (d, *J* = 20.4 Hz,

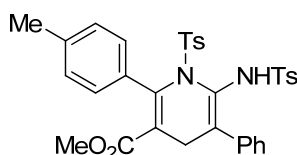
1H), 2.43 (d,  $J$  = 20.4 Hz, 1H), 2.31 (s, 3H), 2.27 (s, 3H), 2.17 ppm (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C, TMS)  $\delta$  = 167.7, 148.2, 144.9, 143.4, 137.2, 136.8, 136.3, 134.5, 134.3, 130.4, 130.3, 129.6, 129.5, 128.4, 128.3, 128.1, 128.1, 127.4, 127.3, 127.2, 125.9, 120.9, 51.8, 33.2, 21.8, 21.6, 21.4 ppm; HRMS calc for  $\text{C}_{34}\text{H}_{32}\text{N}_2\text{O}_6\text{S}_2$ ,  $[\text{M}]^+$  628.1702, found 628.1706.

**Methyl 6-(4-methylphenylsulfonamido)-5-phenyl-2-(m-tolyl)-1-tosyl-1,4-dihydropyridine-3-carboxylate 4c**



To a mixture of 4-methylbenzenesulfonyl azide (59.2 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), methyl 2-(m-tolyl(tosylimino)methyl)acrylate (71.5 mg, 0.2 mmol),  $\text{Et}_4\text{NI}$  (5.1 mg, 0.02 mmol), 4Å MS (100 mg) in THF (5 mL) and *t*-BuOH (0.5 mL) under  $\text{N}_2$  atmosphere, ethynylbenzene (30.6 mg, 0.3 mmol) and  $\text{Cs}_2\text{CO}_3$  (195 mg, 0.6 mmol) were added. The residue was purified by column chromatography on silica gel (n-hexane/EtOAc = 10:1, v/v) to provide **4c** as a white solid (98.1 mg, 78%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C, TMS)  $\delta$  = 7.47 (d,  $J$  = 8.4 Hz, 2H), 7.32 (d,  $J$  = 8.4 Hz, 2H), 7.13–7.07 (m, 5H), 7.04–7.04 (m, 3H), 7.00–6.92 (m, 5H), 6.79 (s, 1H), 3.45 (s, 3H), 2.97 (d,  $J$  = 20.4 Hz, 1H), 2.43 (d,  $J$  = 20.4 Hz, 1H), 2.31 (s, 3H), 2.27 (s, 3H), 2.18 ppm (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C, TMS)  $\delta$  = 167.6, 148.2, 144.9, 143.3, 137.1, 136.7, 136.3, 134.5, 134.5, 134.2, 130.3, 130.2, 129.5, 129.4, 128.3, 128.2, 128.1, 128.0, 127.4, 127.2, 127.2, 125.8, 120.8, 51.8, 33.1, 21.7, 21.6, 21.3 ppm; HRMS calc for  $\text{C}_{34}\text{H}_{32}\text{N}_2\text{O}_6\text{S}_2$ ,  $[\text{M}]^+$  628.1702, found 628.1703.

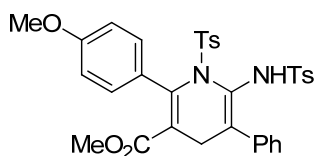
**Methyl 6-(4-methylphenylsulfonamido)-5-phenyl-2-(p-tolyl)-1-tosyl-1,4-dihydropyridine-3-carboxylate 4d**



To a mixture of 4-methylbenzenesulfonyl azide (59.2 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), methyl 2-(p-tolyl(tosylimino)methyl)acrylate (71.5 mg, 0.2 mmol),  $\text{Et}_4\text{NI}$  (5.1 mg, 0.02 mmol), 4Å MS (100 mg) in THF (5 mL) and *t*-BuOH (0.5 mL) under  $\text{N}_2$  atmosphere, ethynylbenzene (30.6 mg, 0.3 mmol) and  $\text{Cs}_2\text{CO}_3$  (195 mg, 0.6 mmol) were added. The residue was purified by column chromatography on silica gel (n-hexane/EtOAc = 10:1, v/v) to provide **4d** as a white solid (103.1 mg, 82%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C, TMS)  $\delta$  = 7.49 (d,  $J$  = 8.4 Hz, 2H), 7.36 (d,  $J$  = 8.4 Hz, 2H), 7.18–7.10 (m, 5H), 7.04–7.01 (m, 4H), 7.00–6.93 (m, 4H), 6.80 (s, 1H), 3.46 (s, 3H), 2.94 (d,  $J$  = 20.4 Hz, 1H), 2.32 (s, 3H), 2.29–2.22 ppm (m, 7H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C, TMS)  $\delta$  = 167.6, 148.1, 145.0, 143.4, 139.5, 137.2, 136.9, 136.3, 134.1, 131.7, 129.6, 129.6, 129.5, 128.3, 128.3, 128.2, 128.0, 128.0, 127.3, 125.7, 120.6, 51.8, 33.0, 21.7, 21.6, 21.6 ppm; HRMS calc for  $\text{C}_{34}\text{H}_{32}\text{N}_2\text{O}_6\text{S}_2$ ,  $[\text{M}]^+$  628.1702, found 628.1702.

**Methyl**

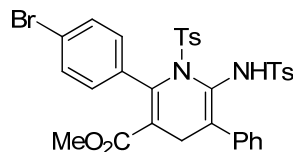
**2-(4-methoxyphenyl)-6-(4-methylphenylsulfonamido)-5-phenyl-1-tosyl-1,4-dihydropyridine-3-carboxylate 4e**



To a mixture of 4-methylbenzenesulfonyl azide (59.2 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), methyl 2-((4-methoxyphenyl)(tosylimino)methyl)acrylate (71.5 mg, 0.2 mmol),  $\text{Et}_4\text{NI}$  (5.1 mg, 0.02 mmol), 4Å MS (100 mg) in THF (5 mL) and *t*-BuOH (0.5 mL) under  $\text{N}_2$  atmosphere, ethynylbenzene (30.6 mg, 0.3 mmol) and  $\text{Cs}_2\text{CO}_3$  (195 mg, 0.6 mmol) were added. The residue was purified by column chromatography on silica gel (n-hexane/EtOAc = 10:1, v/v) to provide **4e** as a white solid (85.1 mg, 66%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C, TMS)  $\delta$  = 7.49 (d,  $J$  = 8.4 Hz, 2H), 7.33 (d,  $J$  = 8.4 Hz, 2H), 7.19–7.07 (m, 7H), 7.01–6.99 (m, 2H), 6.94 (d,  $J$  = 8.4 Hz, 2H), 6.81 (s, 1H), 6.68–6.64 (m, 2H), 3.74 (s, 3H), 3.48 (s, 3H), 2.96 (d,  $J$  = 20.0 Hz, 1H), 2.32–2.27 ppm (m, 7H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C, TMS)  $\delta$  = 167.7, 160.6, 148.2, 144.9, 143.3, 137.4, 136.7, 136.2, 134.5, 131.4, 129.6, 129.4, 128.3, 128.2, 128.0, 128.0, 127.3, 126.8, 125.7, 119.6, 112.9, 55.2, 51.8, 33.0, 21.7, 21.6 ppm; HRMS calc for  $\text{C}_{34}\text{H}_{32}\text{N}_2\text{O}_7\text{S}_2$ ,  $[\text{M}]^+$  644.1651, found 644.1655.

## Methyl

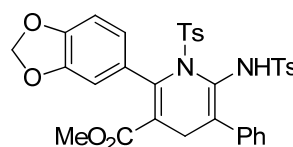
### 2-(4-bromophenyl)-6-(4-methylphenylsulfonamido)-5-phenyl-1-tosyl-1,4-dihydropyridine-3-carboxylate **4f**



To a mixture of 4-methylbenzenesulfonyl azide (59.2 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), methyl 2-((4-bromophenyl)(tosylimino)methyl)acrylate (84.5 mg, 0.2 mmol), Et<sub>4</sub>NI (5.1 mg, 0.02 mmol), 4Å MS (100 mg) in THF (5 mL) and *t*-BuOH (0.5 mL) under N<sub>2</sub> atmosphere, ethynylbenzene (30.6 mg, 0.3 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (195 mg, 0.6 mmol) were added. The residue was purified by column chromatography on silica gel (n-hexane/EtOAc = 10:1, v/v) to provide **4f** as a white solid (102.7 mg, 74%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 7.47 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.25–7.23 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.11–7.05 (m, 5H), 6.97–6.95 (m, 2H), 6.92–6.90 (m, 2H), 6.84 (s, 1H), 3.48 (s, 3H), 3.02 (d, *J* = 20.4 Hz, 1H), 2.41 (d, *J* = 20.4 Hz, 1H), 2.32 (s, 3H), 2.27 ppm (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 167.0, 147.2, 145.2, 143.4, 137.0, 136.6, 136.0, 134.4, 133.4, 131.6, 130.7, 129.7, 129.4, 128.3, 128.3, 128.1, 128.0, 127.2, 125.7, 123.9, 121.5, 52.0, 33.0, 21.8, 21.6 ppm; HRMS calc for C<sub>33</sub>H<sub>29</sub>BrN<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, [M]<sup>+</sup> 692.0650, found 692.0649.

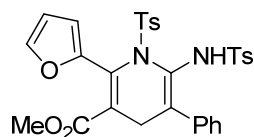
## Methyl

### 2-(benzo[d][1,3]dioxol-5-yl)-6-(4-methylphenylsulfonamido)-5-phenyl-1-tosyl-1,4-dihydropyridine-3-carboxylate **4g**



To a mixture of 4-methylbenzenesulfonyl azide (59.2 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), methyl 2-(benzo[d][1,3]dioxol-5-yl(tosylimino)methyl)acrylate (77.5 mg, 0.2 mmol), Et<sub>4</sub>NI (5.1 mg, 0.02 mmol), 4Å MS (100 mg) in THF (5 mL) and *t*-BuOH (0.5 mL) under N<sub>2</sub> atmosphere, ethynylbenzene (30.6 mg, 0.3 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (195 mg, 0.6 mmol) were added. The residue was purified by column chromatography on silica gel (n-hexane/EtOAc = 10:1, v/v) to provide **4g** as a white solid (114.6 mg, 87%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 7.52 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.18–7.11 (m, 5H), 7.03–6.95 (m, 4H), 6.82 (s, 1H), 6.69 (m, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.52 (s, 1H), 5.88 (d, *J* = 10.0 Hz, 2H), 3.49 (s, 3H), 2.94 (d, *J* = 20.0 Hz, 1H), 2.32–2.28 ppm (m, 7H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 167.6, 148.7, 147.4, 147.0, 145.1, 143.5, 137.5, 136.8, 136.2, 134.3, 129.6, 129.5, 128.3, 128.2, 128.1, 128.0, 127.2, 125.7, 124.4, 120.3, 110.1, 107.5, 101.3, 51.8, 33.0, 21.7, 21.5 ppm; HRMS calc for C<sub>34</sub>H<sub>30</sub>N<sub>2</sub>O<sub>8</sub>S<sub>2</sub>, [M]<sup>+</sup> 658.1444, found 658.1443.

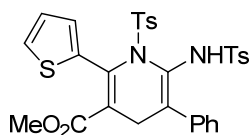
### Methyl 2-(furan-2-yl)-6-(4-methylphenylsulfonamido)-5-phenyl-1-tosyl-1,4-dihydropyridine-3-carboxylate **4h**



To a mixture of 4-methylbenzenesulfonyl azide (59.2 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), methyl 2-(furan-2-yl(tosylimino)methyl)acrylate (66.7 mg, 0.2 mmol), Et<sub>4</sub>NI (5.1 mg, 0.02 mmol), 4Å MS (100 mg) in THF (5 mL) and *t*-BuOH (0.5 mL) under N<sub>2</sub> atmosphere, ethynylbenzene (30.6 mg, 0.3 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (195 mg, 0.6 mmol) were added. The residue was purified by column chromatography on silica gel (n-hexane/EtOAc = 10:1.5, v/v) to provide **4h** as a white solid (73.8 mg, 61%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 7.60 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.35 (d, 1H), 7.2–7.18 (m, 5H), 7.09–7.06 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.71 (s, 1H), 6.33–6.31 (m, 1H), 6.18 (d, *J* = 3.2 Hz, 1H), 3.63 (s, 3H), 2.81 (d, *J* = 21.2 Hz, 1H), 2.32 (s, 3H), 2.28 (s, 3H), 1.68 ppm (d, *J* = 21.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 166.9, 147.4, 145.7, 143.6, 143.5, 137.7, 136.9, 136.2, 135.3, 132.3, 129.9, 129.6, 128.5, 128.4, 128.2, 127.4, 125.8, 122.2, 113.7, 111.6, 52.2, 32.8, 21.8, 21.6 ppm; HRMS calc for C<sub>31</sub>H<sub>28</sub>N<sub>2</sub>O<sub>7</sub>S<sub>2</sub>, [M]<sup>+</sup> 604.1338, found 604.1340.

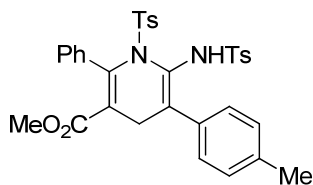
### Methyl 6-(4-methylphenylsulfonamido)-5-phenyl-2-(thiophen-2-yl)-1-tosyl-1,4-dihydropyridine-3-carboxylate **4i**

To a mixture of 4-methylbenzenesulfonyl azide (59.2 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), methyl



2-(thiophen-2-yl(tosylimino)methyl)acrylate (69.9 mg, 0.2 mmol), Et<sub>4</sub>NI (5.1 mg, 0.02 mmol), 4Å MS (100 mg) in THF (5 mL) and *t*-BuOH (0.5 mL) under N<sub>2</sub> atmosphere, ethynylbenzene (30.6 mg, 0.3 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (195 mg, 0.6 mmol) were added. The residue was purified by column chromatography on silica gel (n-hexane/EtOAc = 10:1.5, v/v) to provide **4i** as a white solid (65.8 mg, 53%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 7.73 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.31–7.30 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.13–7.11 (m, 3H), 7.02–6.98 (m, 3H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.85–6.82 (m, 1H), 6.75 (s, 1H), 3.57 (s, 3H), 2.91 (d, *J* = 20.4 Hz, 1H), 2.32 (s, 3H), 2.26 (s, 3H), 2.04 ppm (d, *J* = 20.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 167.1, 145.3, 143.4, 140.1, 137.1, 136.7, 136.1, 136.0, 133.7, 131.3, 129.8, 129.5, 128.7, 128.3, 128.2, 127.3, 126.6, 126.0, 122.0, 52.1, 33.2, 21.8, 21.5 ppm; HRMS calc for C<sub>31</sub>H<sub>28</sub>N<sub>2</sub>O<sub>6</sub>S<sub>3</sub>, [M]<sup>+</sup> 620.1109, found 620.1115.

#### Methyl 6-(4-methylphenylsulfonamido)-2-phenyl-5-(*p*-tolyl)-1-tosyl-1,4-dihydropyridine-3-carboxylate **4j**

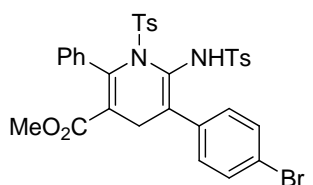


To a mixture of 4-methylbenzenesulfonyl azide (59.2 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), methyl 2-(phenyl(tosylimino)methyl)acrylate (68.7 mg, 0.2 mmol), Et<sub>4</sub>NI (5.1 mg, 0.02 mmol), 4Å MS (100 mg) in THF (5 mL) and *t*-BuOH (0.5 mL) under N<sub>2</sub> atmosphere, 1-ethynyl-4-methylbenzene (34.8 mg, 0.3 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (195 mg, 0.6 mmol) were added. The residue was purified by column

chromatography on silica gel (n-hexane/EtOAc = 10:1, v/v) to provide **4j** as a white solid (71.7 mg, 57%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 7.49 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.25–7.23 (m, 1H), 7.19–7.10 (m, 6H), 6.97–6.95 (m, 2H), 6.92 (m, 4H), 6.83 (s, 1H), 3.44 (s, 3H), 2.94 (d, *J* = 20.4 Hz, 1H), 2.32–2.25 ppm (m, 10H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 167.6, 147.9, 145.0, 143.3, 138.2, 137.1, 134.7, 134.0, 133.2, 129.7, 129.6, 129.3, 128.9, 128.2, 128.0, 127.5, 127.3, 125.3, 121.3, 51.8, 32.9, 21.7, 21.6, 21.3 ppm; HRMS calc for C<sub>34</sub>H<sub>32</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, [M]<sup>+</sup> 628.1702, found 628.1705.

#### Methyl

#### 5-(4-bromophenyl)-6-(4-methylphenylsulfonamido)-2-phenyl-1-tosyl-1,4-dihydropyridine-3-carboxylate **4k**

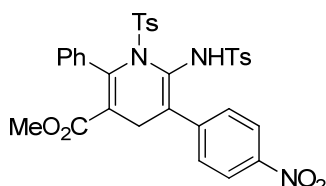


To a mixture of 4-methylbenzenesulfonyl azide (59.2 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), methyl 2-(phenyl(tosylimino)methyl)acrylate (68.7 mg, 0.2 mmol), Et<sub>4</sub>NI (5.1 mg, 0.02 mmol), 4Å MS (100 mg) in THF (5 mL) and *t*-BuOH (0.5 mL) under N<sub>2</sub> atmosphere, 1-bromo-4-ethynylbenzene (54.3 mg, 0.3 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (195 mg, 0.6 mmol) were added. The residue was purified by column chromatography on silica

gel (n-hexane/EtOAc = 10:1, v/v) to provide **4k** as a white solid (86.1 mg, 62%); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 25 °C, TMS) δ = 10.03 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.40–7.27 (m, 11H), 7.08–7.05 (m, 4H), 3.46 (s, 3H), 2.82 (d, *J* = 19.6 Hz, 1H), 2.39 (s, 3H), 2.35 (s, 3H), 1.97 ppm (d, *J* = 19.6 Hz, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 25 °C, TMS) δ = 166.3, 146.3, 144.9, 142.4, 138.2, 135.2, 134.9, 134.2, 134.0, 130.7, 130.1, 129.6, 129.2, 128.9, 128.8, 127.6, 127.4, 126.7, 126.0, 122.1, 121.5, 51.6, 32.1, 21.1, 21.1 ppm; HRMS calc for C<sub>33</sub>H<sub>29</sub>BrN<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, [M]<sup>+</sup> 692.0650, found 692.0653.

#### Methyl

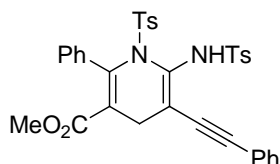
#### 6-(4-methylphenylsulfonamido)-5-(4-nitrophenyl)-2-phenyl-1-tosyl-1,4-dihydropyridine-3-carboxylate **4l**



To a mixture of 4-methylbenzenesulfonyl azide (59.2 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), methyl 2-(phenyl(tosylimino)methyl)acrylate (68.7 mg, 0.2 mmol), Et<sub>4</sub>NI (5.1 mg, 0.02 mmol), 4Å MS (100 mg) in THF (5 mL) and *t*-BuOH (0.5 mL) under N<sub>2</sub> atmosphere, 1-ethynyl-4-nitrobenzene (44.1 mg, 0.3 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (195 mg, 0.6 mmol) were added. The residue was purified by column

chromatography on silica gel (n-hexane/EtOAc = 10:1, v/v) to provide **4l** as a white solid (110.8 mg, 84%); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 25 °C, TMS) δ = 10.21 (s, 1H), 7.91 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.43–7.28 (m, 11H), 7.03–7.01 (m, 2H), 3.47 (s, 3H), 2.95 (d, *J* = 19.2 Hz, 1H), 2.39 (s, 3H), 2.25 (s, 3H), 2.15 ppm (d, *J* = 19.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 25 °C, TMS) δ = 166.2, 146.4, 146.3, 144.9, 142.6, 142.5, 138.1, 134.9, 134.1, 132.8, 129.6, 129.5, 129.3, 129.0, 128.9, 128.1, 127.6, 127.4, 126.1, 122.8, 121.8, 51.6, 32.0, 21.1, 20.8 ppm; HRMS calc for C<sub>33</sub>H<sub>29</sub>N<sub>3</sub>O<sub>8</sub>S<sub>2</sub>, [M]<sup>+</sup> 659.1396, found 659.1397.

**Methyl 6-(4-methylphenylsulfonamido)-2-phenyl-5-(phenylethynyl)-1-tosyl-1,4-dihydropyridine-3-carboxylate 4m**



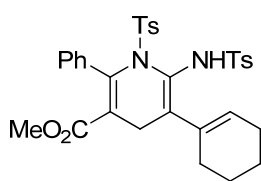
To a mixture of 4-methylbenzenesulfonyl azide (59.2 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), methyl 2-(phenyl(tosylimino)methyl)acrylate (68.7 mg, 0.2 mmol), Et<sub>4</sub>Ni (5.1 mg, 0.02 mmol), 4 Å MS (100 mg) in THF (5 mL) and *t*-BuOH (0.5 mL) under N<sub>2</sub> atmosphere, buta-1,3-diyn-1-ylbenzene (37.8 mg, 0.3 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (195 mg, 0.6 mmol) were added. The residue was purified by column chromatography on silica gel

(n-hexane/EtOAc = 15:1, v/v) to provide **4m** as a yellow solid (74.1 mg, 58%); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 25 °C, TMS) δ = 10.54 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.45–7.42 (m, 4H), 7.39–7.36 (m, 4H), 7.35–7.26 (m, 4H), 7.25–7.23 (m, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 3.48 (s, 3H), 2.82 (d, *J* = 18.4 Hz, 1H), 2.55 (d, *J* = 18.4 Hz, 1H), 2.41 (s, 3H), 2.07 ppm (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 25 °C, TMS) δ = 166.3, 146.0, 144.7, 142.9, 137.9, 135.1, 135.0, 134.2, 131.4, 129.5, 129.4, 129.1, 128.8, 128.2, 127.7, 127.5, 126.6, 121.9, 121.0, 111.3, 94.8, 84.6, 51.7, 30.7, 21.1, 20.7 ppm; HRMS calc for C<sub>35</sub>H<sub>30</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, [M]<sup>+</sup> 638.1545, found 638.1544.

**Gram-scale manipulation:**

An entry was conducted by using 4-methylbenzenesulfonyl azide (1.78 g, 9.0 mmol), CuI (114.1 mg, 0.6 mmol), methyl 2-(phenyl(tosylimino)methyl)acrylate (2.06 g, 6.0 mmol), Et<sub>4</sub>Ni (51 mg, 0.2 mmol), 4 Å MS (1.5 g) in THF (80 mL) and *t*-BuOH (8 mL) under N<sub>2</sub> atmosphere, buta-1,3-diyn-1-ylbenzene (1.13 g, 9.0 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (5.85 g, 18 mmol). The crude product was purified by silica gel chromatography on silica gel (n-hexane/EtOAc = 15:1, v/v) to provide **4m** (2.49 g, 65 %).

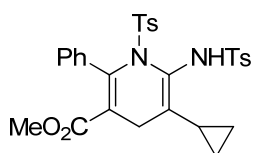
**Methyl 5-(cyclohex-1-en-1-yl)-6-(4-methylphenylsulfonamido)-2-phenyl-1-tosyl-1,4-dihydropyridine-3-carboxylate 4n**



To a mixture of 4-methylbenzenesulfonyl azide (59.2 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), methyl 2-(phenyl(tosylimino)methyl)acrylate (68.7 mg, 0.2 mmol), Et<sub>4</sub>Ni (5.1 mg, 0.02 mmol), 4 Å MS (100 mg) in THF (5 mL) and *t*-BuOH (0.5 mL) under N<sub>2</sub> atmosphere, 1-ethynylcyclohex-1-ene (31.8 mg, 0.3 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (195 mg, 0.6 mmol) were added. The residue was purified by column chromatography on silica gel

(n-hexane/EtOAc = 10:1, v/v) to provide **4n** as a white solid (53.2 mg, 43%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 7.71 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.41–7.20 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.13–7.09 (m, 2H), 6.91 (d, *J* = 7.2 Hz, 2H), 6.78 (s, 1H), 5.57 (s, 1H), 3.41 (s, 3H), 2.69 (d, *J* = 20.4 Hz, 1H), 2.36–2.35 (m, 6H), 2.19–2.15 (m, 1H), 1.92–1.84 (m, 3H), 1.51–1.42 (m, 3H), 1.35–1.32 ppm (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 167.8, 147.4, 145.0, 143.7, 139.3, 137.9, 134.9, 133.7, 129.7, 129.6, 129.4, 129.3, 128.1, 127.6, 127.4, 123.9, 121.8, 51.7, 30.8, 26.9, 25.5, 22.4, 21.8, 21.6, 21.5 ppm; HRMS calc for C<sub>33</sub>H<sub>34</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, [M]<sup>+</sup> 618.1858, found 618.1852.

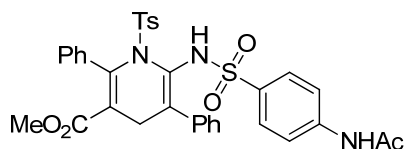
**Methyl 5-cyclopropyl-6-(4-methylphenylsulfonamido)-2-phenyl-1-tosyl-1,4-dihydropyridine-3-carboxylate 4o**



To a mixture of 4-methylbenzenesulfonyl azide (59.2 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), methyl 2-(phenyl(tosylimino)methyl)acrylate (68.7 mg, 0.2 mmol), Et<sub>4</sub>NI (5.1 mg, 0.02 mmol), 4Å MS (100 mg) in THF (5 mL) and *t*-BuOH (0.5 mL) under N<sub>2</sub> atmosphere, ethynylcyclopropane (19.8 mg, 0.3 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (195 mg, 0.6 mmol) were added.

The residue was purified by column chromatography on silica gel (n-hexane/EtOAc = 10:1, v/v) to provide **4o** as a white solid (47.5 mg, 41%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 7.79 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.20–7.18 (m, 3H), 7.07–7.03 (m, 2H), 7.00 (s, 1H), 6.61 (d, *J* = 7.6 Hz, 2H), 3.37 (s, 3H), 2.40–2.38 (m, 6H), 1.97–1.90 (m, 2H), 1.29–1.24 (m, 1H), 0.62–0.59 (m, 1H), 0.53–0.49 (m, 1H), 0.33–0.32 (m, 1H), 0.25–0.21 ppm (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 168.0, 147.1, 145.3, 143.9, 140.3, 138.0, 135.0, 132.8, 130.0, 129.7, 129.3, 129.1, 128.1, 127.7, 127.3, 124.0, 121.2, 51.7, 25.4, 21.8, 21.7, 13.3, 4.9, 4.8 ppm; HRMS calc for C<sub>30</sub>H<sub>30</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, [M]<sup>+</sup> 578.1545, found 578.1547.

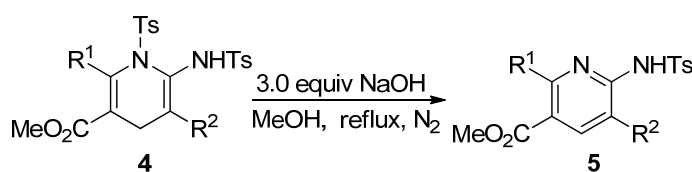
#### Methyl 1-(4-acetamidophenyl)-6-(4-methylphenylsulfonamido)-2,5-diphenyl-1,4-dihydropyridine-3-carboxylate **4p**



To a mixture of 4-acetamidobenzenesulfonyl azide (72.1 mg, 0.3 mmol), CuI (3.8 mg, 0.02 mmol), methyl 2-(phenyl(tosylimino)methyl)acrylate (68.7 mg, 0.2 mmol), Et<sub>4</sub>NI (5.1 mg, 0.02 mmol), 4Å MS (100 mg) in THF (5 mL) and *t*-BuOH (0.5 mL) under N<sub>2</sub> atmosphere, ethynylbenzene (30.6 mg, 0.3 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (195 mg, 0.6 mmol) were added. The residue was purified by

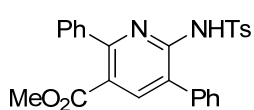
column chromatography on silica gel (n-hexane/EtOAc = 5:1, v/v) to provide **4p** as a white solid (72.4 mg, 55%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 7.87 (s, 1H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.36–7.31 (m, 5H), 7.27–7.23 (m, 4H), 7.18–7.17 (m, 3H), 7.08–7.07 (m, 2H), 7.03 (s, 1H), 3.53 (s, 3H), 3.02 (d, *J* = 20.4 Hz, 1H), 2.41 (s, 3H), 2.33 (d, *J* = 20.4 Hz, 1H), 2.16 ppm (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 169.0, 167.5, 147.7, 145.2, 142.1, 137.3, 136.0, 134.6, 134.0, 134.0, 129.7, 129.6, 129.4, 128.4, 128.2, 128.0, 127.6, 125.7, 121.6, 119.1, 51.9, 33.1, 24.7, 21.7 ppm; HRMS calc for C<sub>34</sub>H<sub>31</sub>N<sub>3</sub>O<sub>7</sub>S<sub>2</sub>, [M]<sup>+</sup> 657.1603, found 657.1600.

#### General procedure B for the synthesis of compound **5**



To a solution of **5** (0.3 mmol, 1.0 equiv) in MeOH (10 mL), NaOH (0.6 mmol, 3.0 equiv) was added under nitrogen atmosphere and the mixture was heated to reflux. The reaction was monitored by TLC and stopped at the desired time. The solvent was removed under vacuum and the residue was purified through column chromatography on silica gel (n-hexane/EtOAc = 15:1, v/v) to afford the pure product **5**.

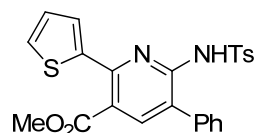
#### Methyl 6-(4-methylphenylsulfonamido)-2,5-diphenylnicotinate **5a**



To a solution of **4a** (184.2 mg, 0.3 mmol) in MeOH (10 mL), NaOH (36 mg, 0.9 mmol) was added under nitrogen atmosphere and the mixture was heated to reflux. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified through column chromatography on silica gel (n-hexane/EtOAc = 15:1, v/v) to afford the pure product **5a** as a white solid (125.2mg, 91%); <sup>1</sup>H NMR (400 MHz,

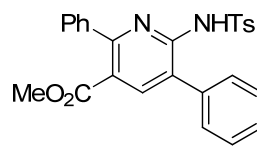
DMSO-*d*<sub>6</sub>, 25 °C, TMS)  $\delta$  = 10.76 (s, 1H), 7.94 (s, 1H), 7.80–7.52 (d, *J* = 8.0 Hz, 2H), 7.60–7.54 (m, 4H), 7.51–7.42 (m, 4H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 3.63 (s, 3H), 2.38 ppm (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 25 °C, TMS)  $\delta$  = 167.2, 154.8, 149.2, 142.8, 140.9, 138.9, 138.1, 135.4, 129.0, 128.9, 128.8, 128.6, 128.2, 127.8, 127.4, 124.4, 121.6, 52.2, 21.0 ppm; HRMS calc for C<sub>26</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>S, [M]<sup>+</sup> 458.1300, found 458.1302.

#### Methyl 6-(4-methylphenylsulfonamido)-5-phenyl-2-(thiophen-2-yl)nicotinate **5i**



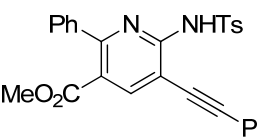
To a solution of **4i** (186.2 mg, 0.3 mmol) in MeOH (10 mL), NaOH (36 mg, 0.9 mmol) was added under nitrogen atmosphere and the mixture was heated to reflux. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified through column chromatography on silica gel (n-hexane/EtOAc = 15:1, v/v) to afford the pure product **5i** as a white solid (110.1 mg, 79%); <sup>1</sup>H NMR (400 MHz, DMSO, 25 °C, TMS)  $\delta$  : 7.99 (d, *J* = 8.0 Hz, 2H), 7.69 (s, 1H), 7.45–7.41 (m, 4H), 7.33–7.30 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.01–6.99 (m, 1H), 3.74 (s, 3H), 2.30 ppm (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO, 25 °C, TMS)  $\delta$  : 168.1, 149.3, 148.4, 144.3, 141.7, 140.4, 136.5, 134.4, 129.9, 129.3, 129.2, 129.1, 129.0, 128.8, 128.7, 128.6, 128.5, 127.5, 122.0, 120.2, 52.6, 21.6 ppm; HRMS calc for C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>, [M]<sup>+</sup> 464.0864, found 464.0863.

#### Methyl 5-(4-bromophenyl)-6-(4-methylphenylsulfonamido)-2-phenylnicotinate **5k**



To a solution of **4k** (208.9 mg, 0.3 mmol) in MeOH (10 mL), NaOH (36 mg, 0.9 mmol) was added under nitrogen atmosphere and the mixture was heated to reflux. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified through column chromatography on silica gel (n-hexane/EtOAc = 15:1, v/v) to afford the pure product **5i** as a white solid (133.8 mg, 83%); <sup>1</sup>H NMR (400 MHz, DMSO, 25 °C, TMS)  $\delta$  : 10.82 (s, 1H), 7.94 (s, 1H), 7.78–7.73 (m, 4H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.45–7.40 (m, 3H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.19–7.17 (m, 2H), 3.62 (s, 3H), 2.37 ppm (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO, 25 °C, TMS)  $\delta$  : 167.2, 155.1, 142.9, 140.7, 138.7, 138.1, 134.6, 131.7, 131.3, 129.0, 128.9, 128.6, 127.8, 127.4, 123.2, 121.7, 52.2, 21.0 ppm; HRMS calc for C<sub>26</sub>H<sub>21</sub>BrN<sub>2</sub>O<sub>4</sub>S, [M]<sup>+</sup> 536.0405, found 536.0401.

#### Methyl 6-(4-methylphenylsulfonamido)-2-phenyl-5-(phenylethynyl)nicotinate **5m**



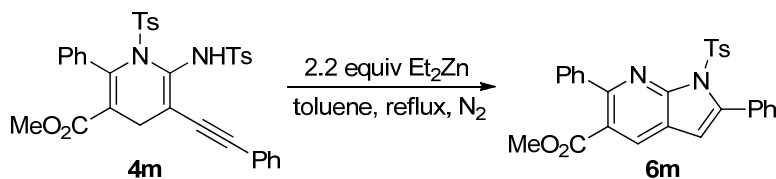
To a **4m** (191.6 mg, 0.3 mmol) in MeOH (10 mL), NaOH (36 mg, 0.9 mmol) was added under nitrogen atmosphere and the mixture was heated to reflux. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified through column chromatography on silica gel (n-hexane/EtOAc = 15:1, v/v) to afford the pure product **5m** as a white solid (97.0 mg, 67%); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 25 °C, TMS)  $\delta$  = 11.29 (s, 1H), 8.22 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.74–7.71 (m, 2H), 7.52–7.41 (m, 6H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.25–7.22 (m, 2H), 3.64 (s, 3H), 2.36 ppm (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 25 °C, TMS)  $\delta$  = 166.8, 155.1, 151.6, 143.3, 143.0, 138.2, 137.8, 131.8, 129.4, 129.2, 129.2, 128.7, 128.7, 127.9, 127.5, 121.8, 120.9, 105.7, 97.2, 82.7, 52.3, 21.0 ppm; HRMS calc for C<sub>28</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>S, [M]<sup>+</sup> 482.1300, found 482.1296.

#### Synthesis of compound **6m**

To a solution of **4m** (191.4 mg, 0.3 mmol) in anhydrous toluene (5 mL), Et<sub>2</sub>Zn (0.44 mL, 0.66 mmol, 1.5N in toluene) was added under nitrogen atmosphere. Then the mixture was heated to reflux. The reaction was monitored by TLC and stopped at the desired time. The mixture was quenched carefully with H<sub>2</sub>O (10 mL) at 0 °C, and



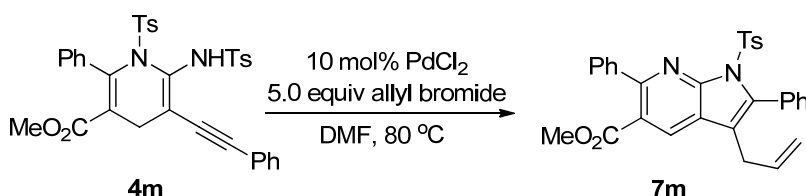
extracted by CH<sub>2</sub>Cl<sub>2</sub> (10 mL x 3). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated in vacuo. The solvent was concentrated under vacuum and the residue was purified through column chromatography on silica gel (n-hexane/EtOAc = 15:1, v/v) to afford the pure product **6m** as a white solid (75.3g, 52%).



#### Methyl 2,6-diphenyl-1-tosyl-1H-pyrrolo[2,3-b]pyridine-5-carboxylate **6m**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 8.23 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.65–7.62 (m, 4H), 7.53–7.50 (m, 6H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.59 (s, 1H), 3.72 (s, 3H), 2.36 ppm (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 169.2, 154.0, 149.8, 145.2, 143.8, 140.2, 135.5, 132.4, 131.0, 129.8, 129.3, 129.1, 129.0, 128.6, 128.5, 128.0, 127.8, 123.3, 119.8, 108.2, 52.4, 21.7 ppm; HRMS calc for C<sub>28</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>S, [M]<sup>+</sup> 482.1300, found 482.1301.

#### Synthesis of compound **7m**



To a solution of **4m** (191.4 mg, 0.3 mmol), PdCl<sub>2</sub> (0.03 mmol, 0.1 equiv) in DMF (2 mL), 3-bromoprop-1-ene (1.5 mmol, 5.0 equiv) was added at 80 °C. The reaction was monitored by TLC and stopped at the desired time. The solvent was concentrated under vacuum and the residue was purified through column chromatography on silica gel (n-hexane/EtOAc = 15:1, v/v) to afford the pure product **7m** as yellow oil (83.1 mg, 53%).

#### Methyl 3-allyl-2,6-diphenyl-1-tosyl-1H-pyrrolo[2,3-b]pyridine-5-carboxylate **7m**

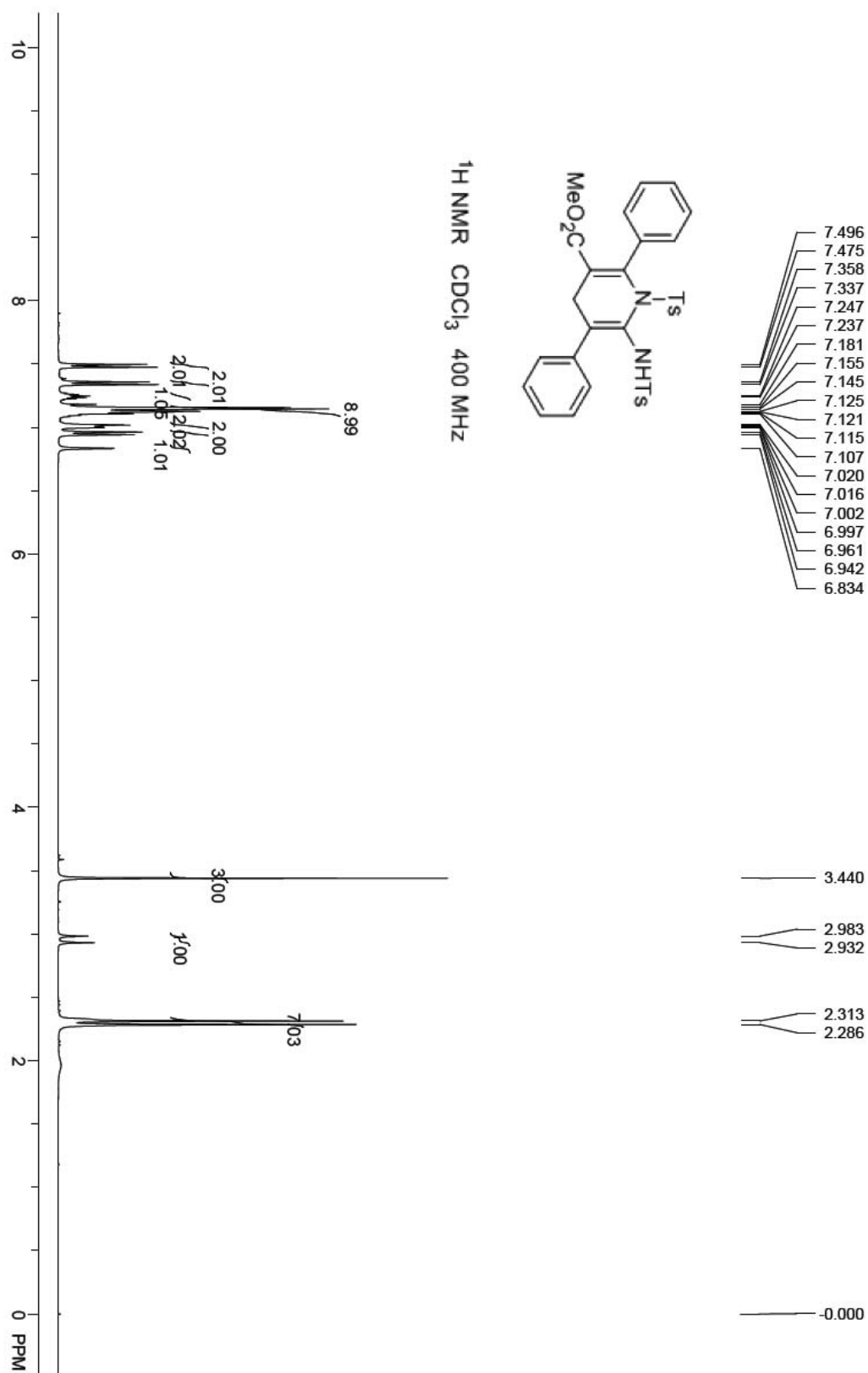
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 8.08 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.55–7.53 (m, 2H), 7.44–7.36 (m, 8H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.83–5.79 (m, 1H), 4.95 (dd, *J*<sub>1</sub> = 1.6 Hz, *J*<sub>2</sub> = 10.4 Hz, 1H), 4.83 (dd, *J*<sub>1</sub> = 1.6 Hz, *J*<sub>2</sub> = 17.2 Hz, 1H), 3.61 (s, 3H), 3.17–3.16 (m, 2H), 2.26 ppm (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 169.4, 154.1, 149.2, 145.0, 140.3, 139.2, 135.7, 135.4, 131.1, 130.4, 130.0, 129.3, 129.0, 128.5, 128.5, 128.0, 127.9, 122.9, 120.4, 116.9, 116.3, 52.4, 28.6, 21.7 ppm; HRMS calc for C<sub>31</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>S, [M]<sup>+</sup> 522.1613, found 522.1612.

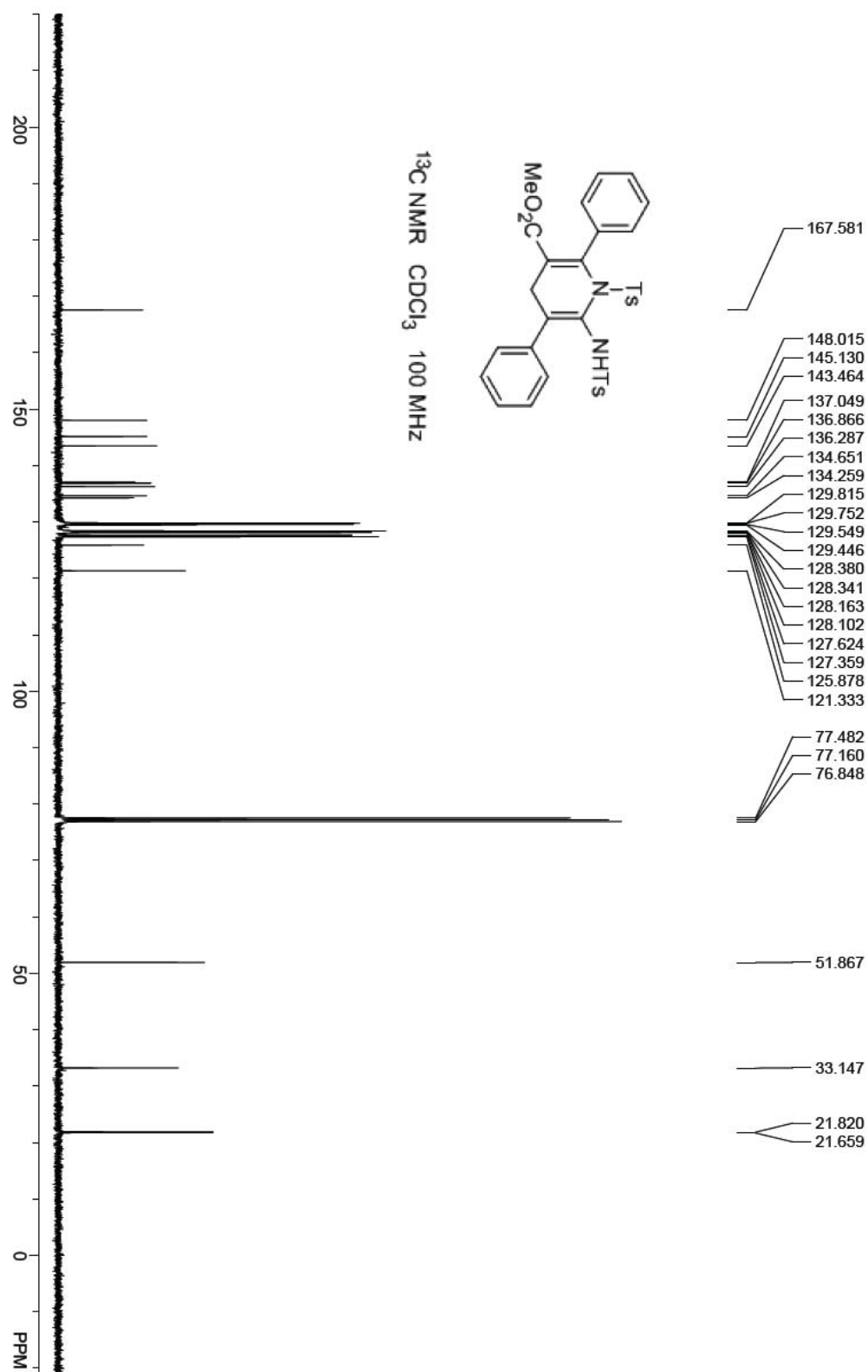
#### References:

1. Liu, H.; Zhang, Q.; Wang, L.; Tong, X. *Chem. Eur. J.* **2010**, *16*, 1968.
2. Jiang, X.; Shi, X.; Wang, S.; Sun, T.; Cao, Y.; Wang, R. *Angew. Chem., Int. Ed.* **2012**, *51*, 2084.

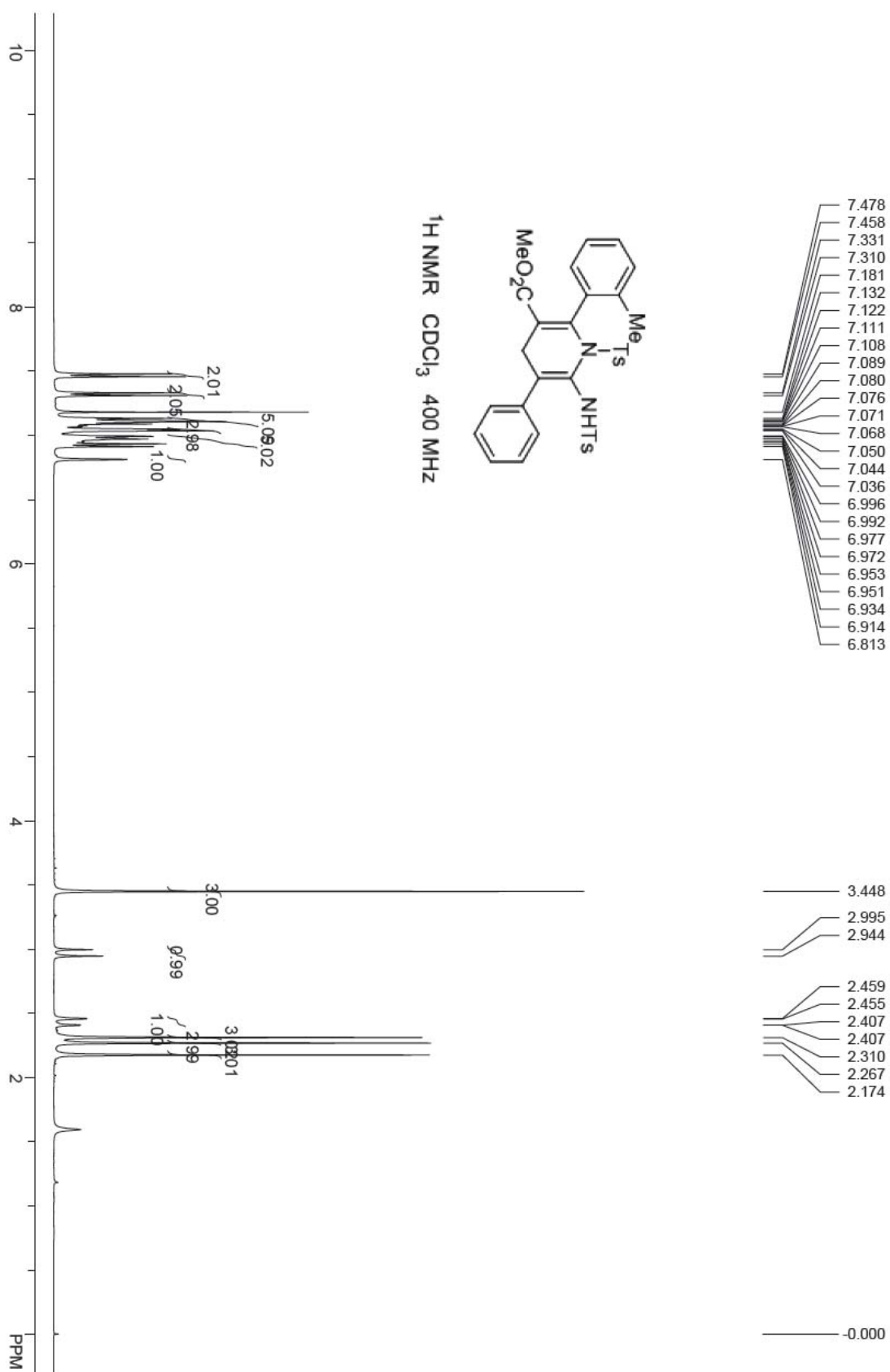
## NMR spectra

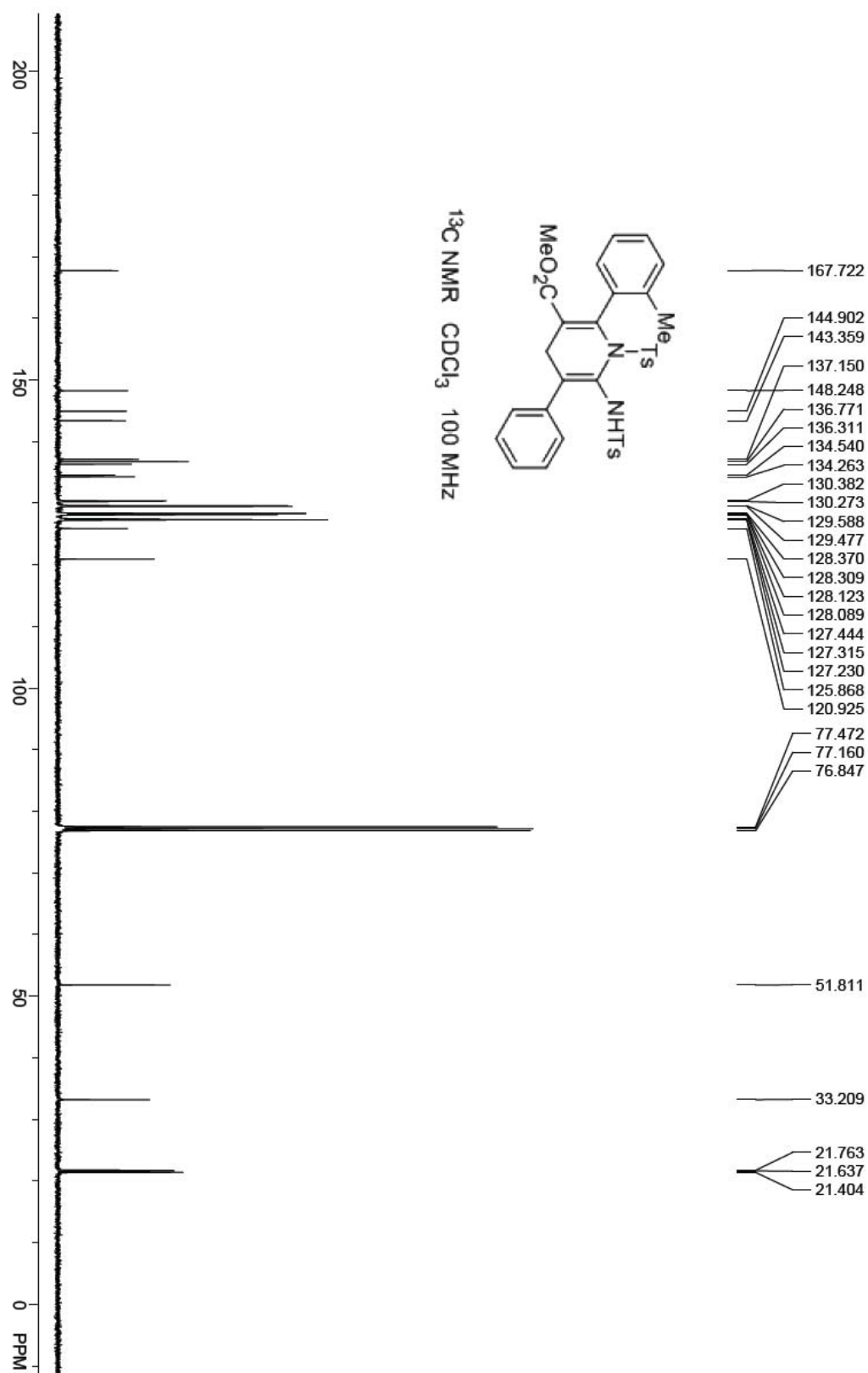
Methyl 6-(4-methylphenylsulfonamido)-2,5-diphenyl-1-tosyl-1,4-dihydropyridine-3-carboxylate 4a



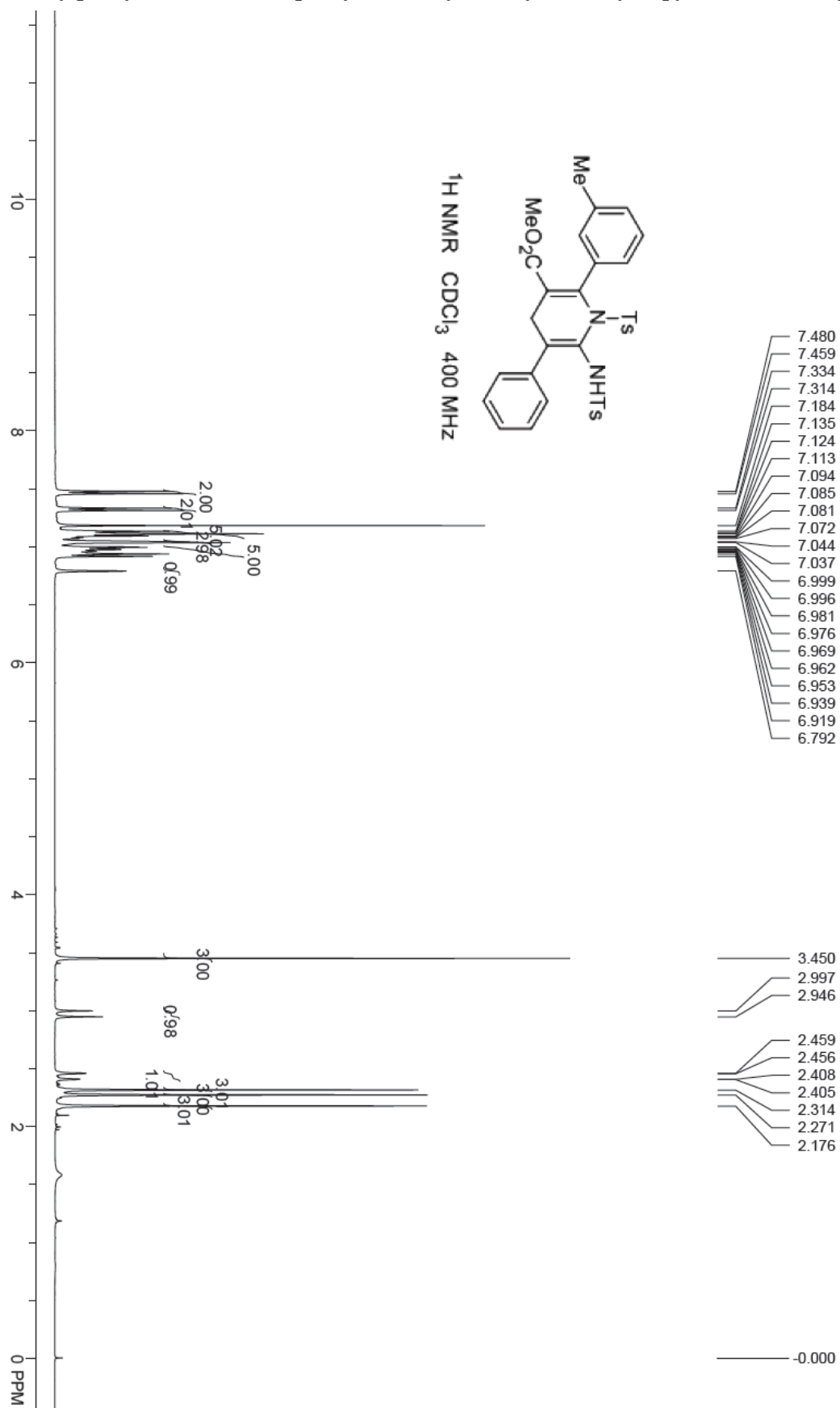


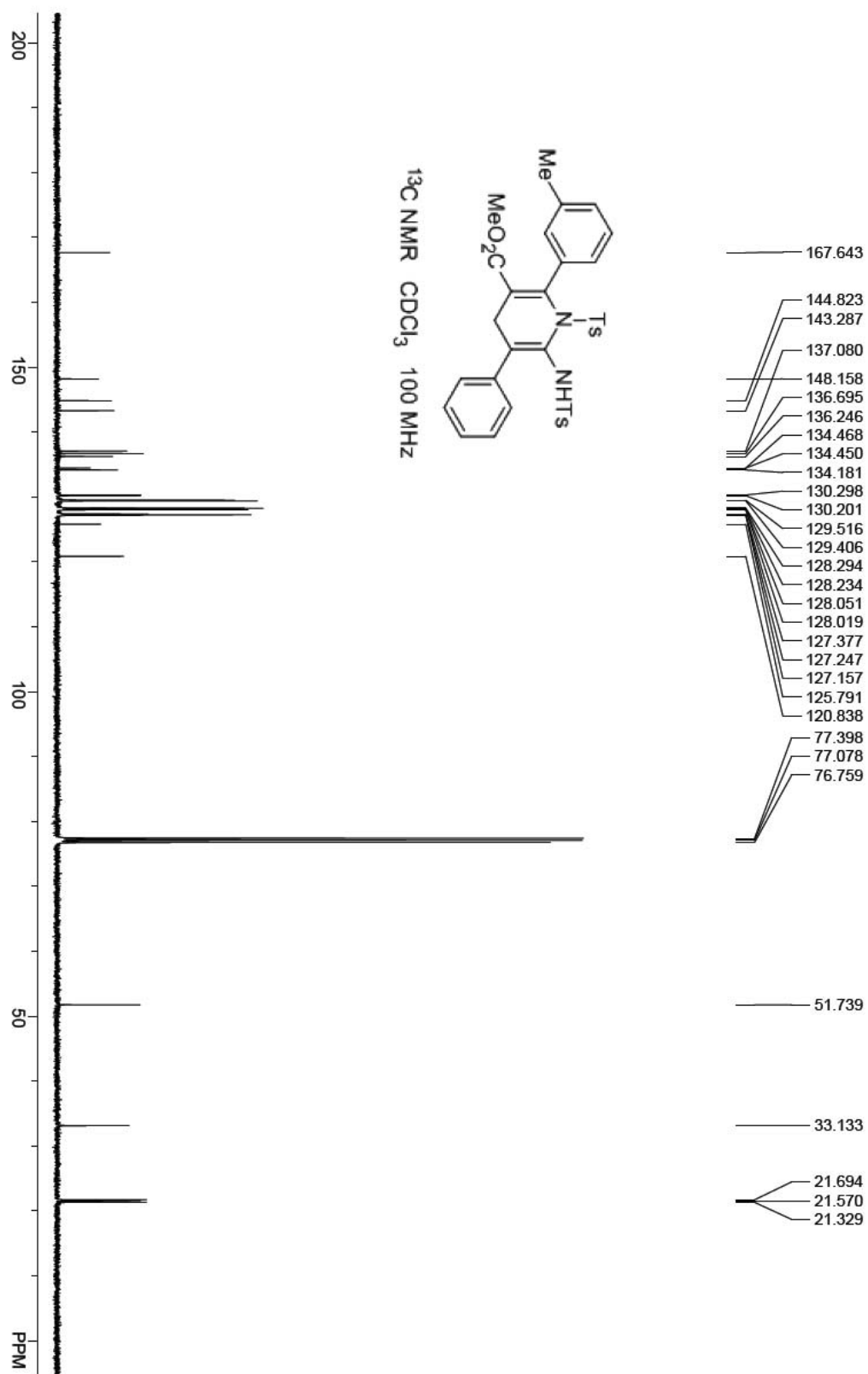
Methyl 6-(4-methylphenylsulfonamido)-5-phenyl-2-(o-tolyl)-1-tosyl-1,4-dihydropyridine-3-carboxylate 4b



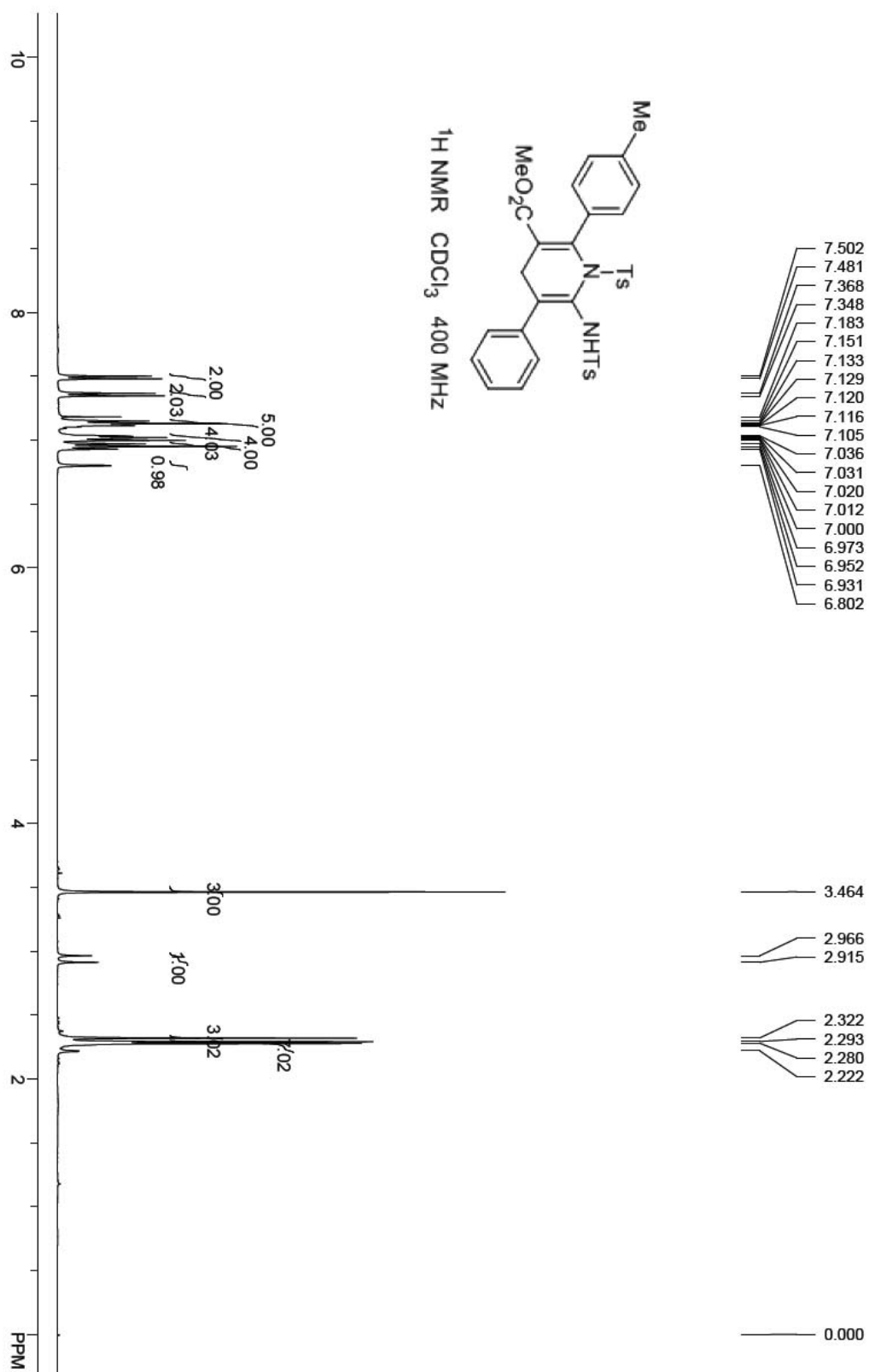


Methyl 6-(4-methylphenylsulfonamido)-5-phenyl-2-(m-tolyl)-1-tosyl-1,4-dihydropyridine-3-carboxylate 4c

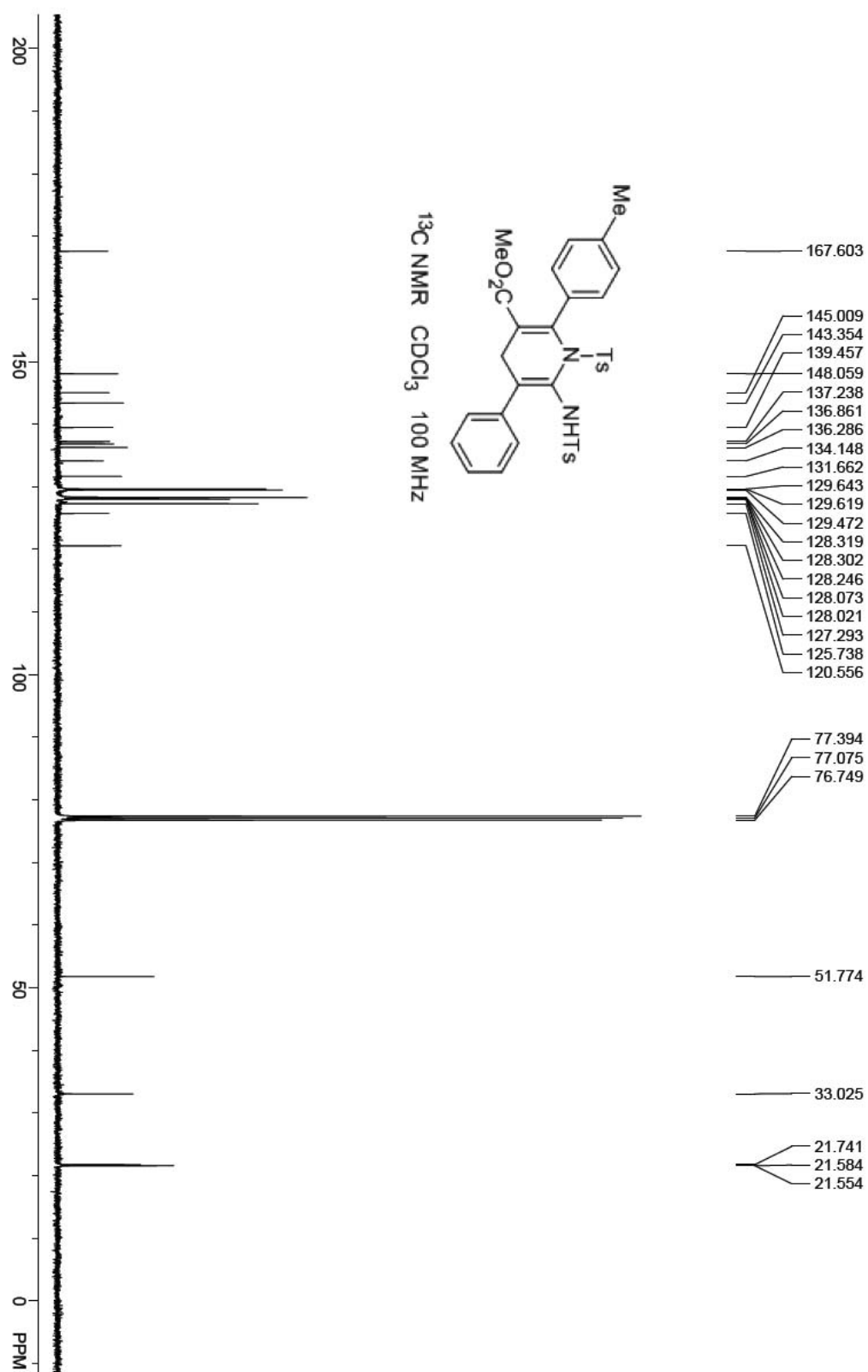




Methyl 6-(4-methylphenylsulfonamido)-5-phenyl-2-(p-tolyl)-1-tosyl-1,4-dihydropyridine-3-carboxylate 4d

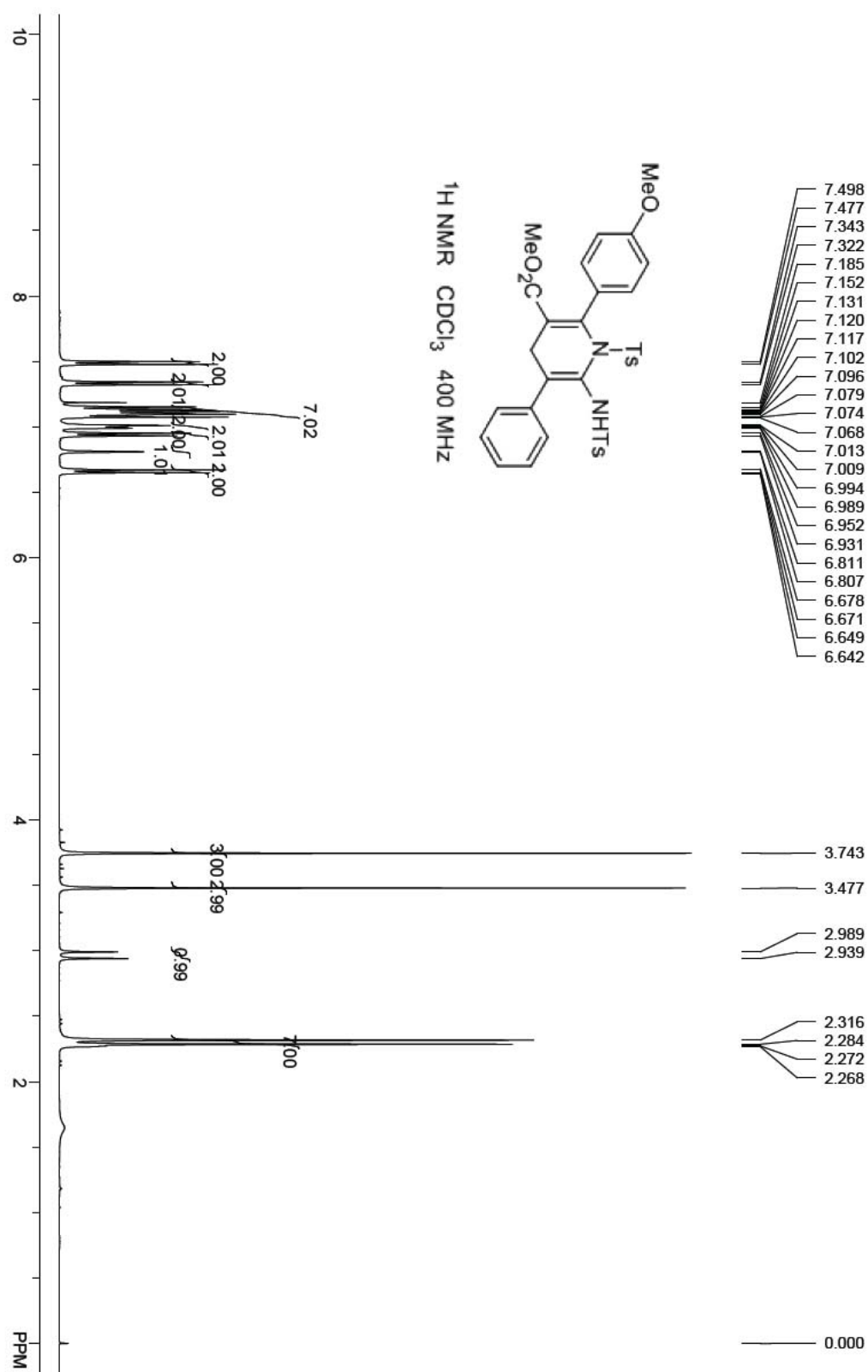


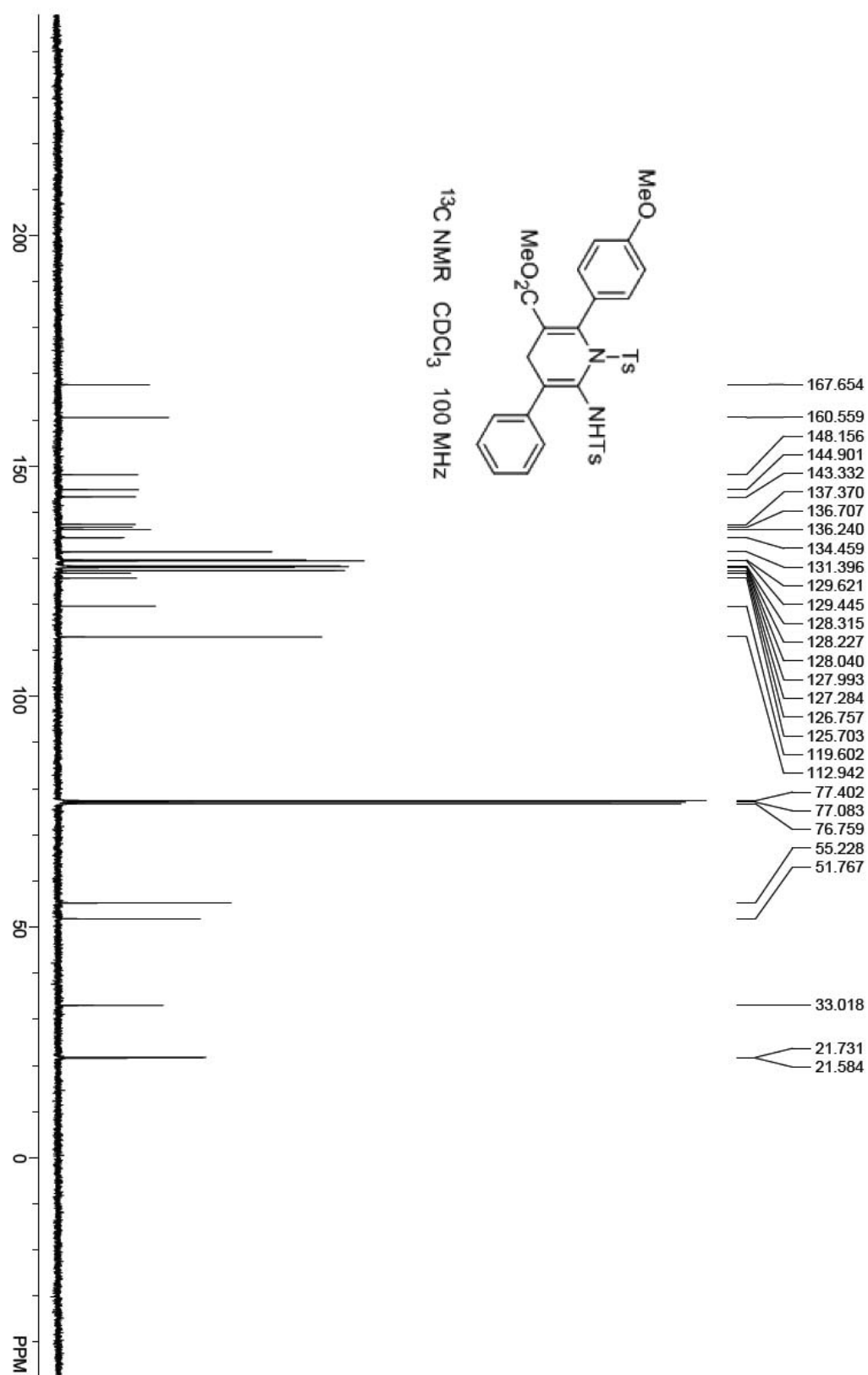




Methyl

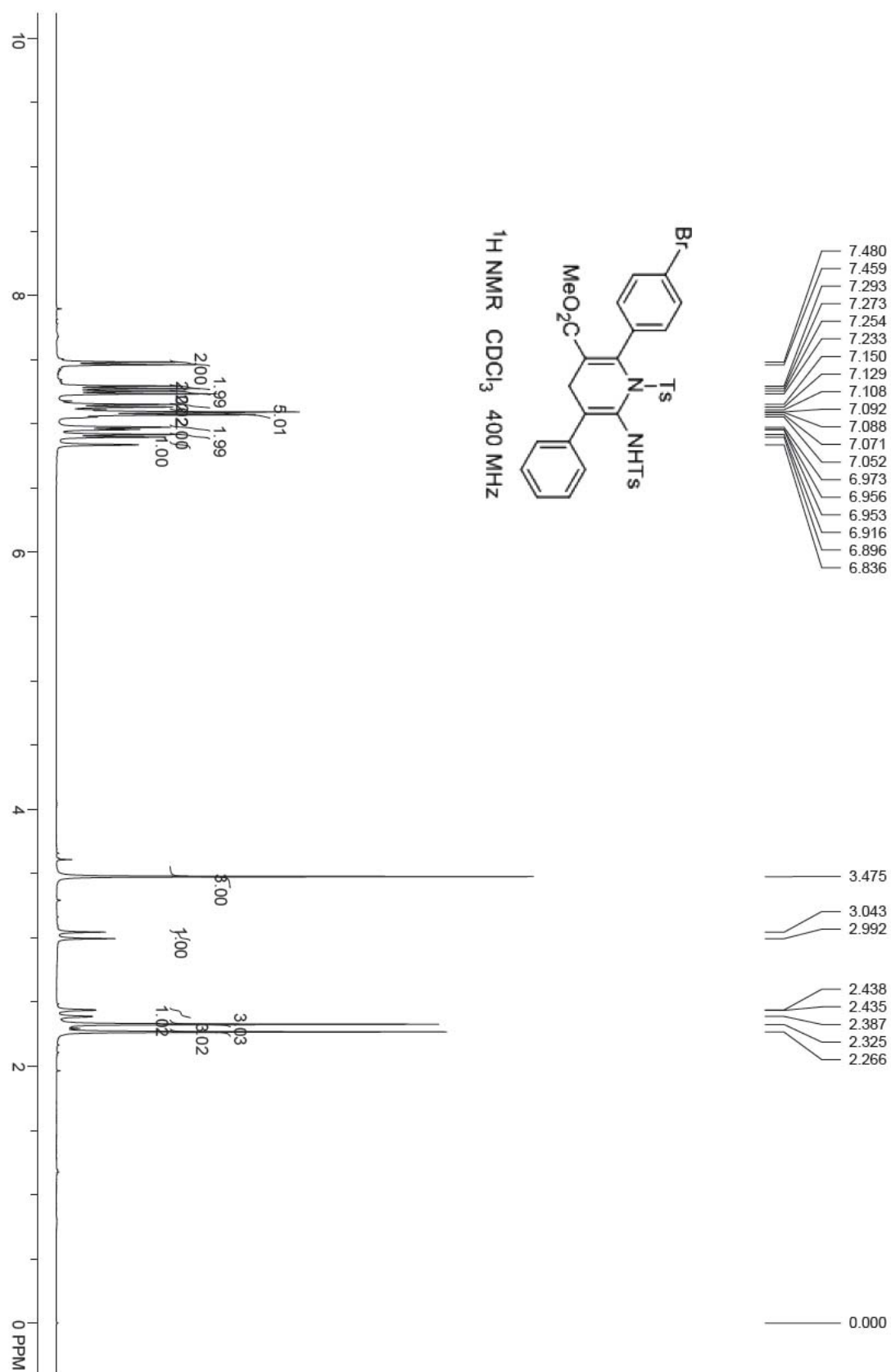
2-(4-methoxyphenyl)-6-(4-methylphenylsulfonamido)-5-phenyl-1-tosyl-1,4-dihydropyridine-3-carboxylate 4e

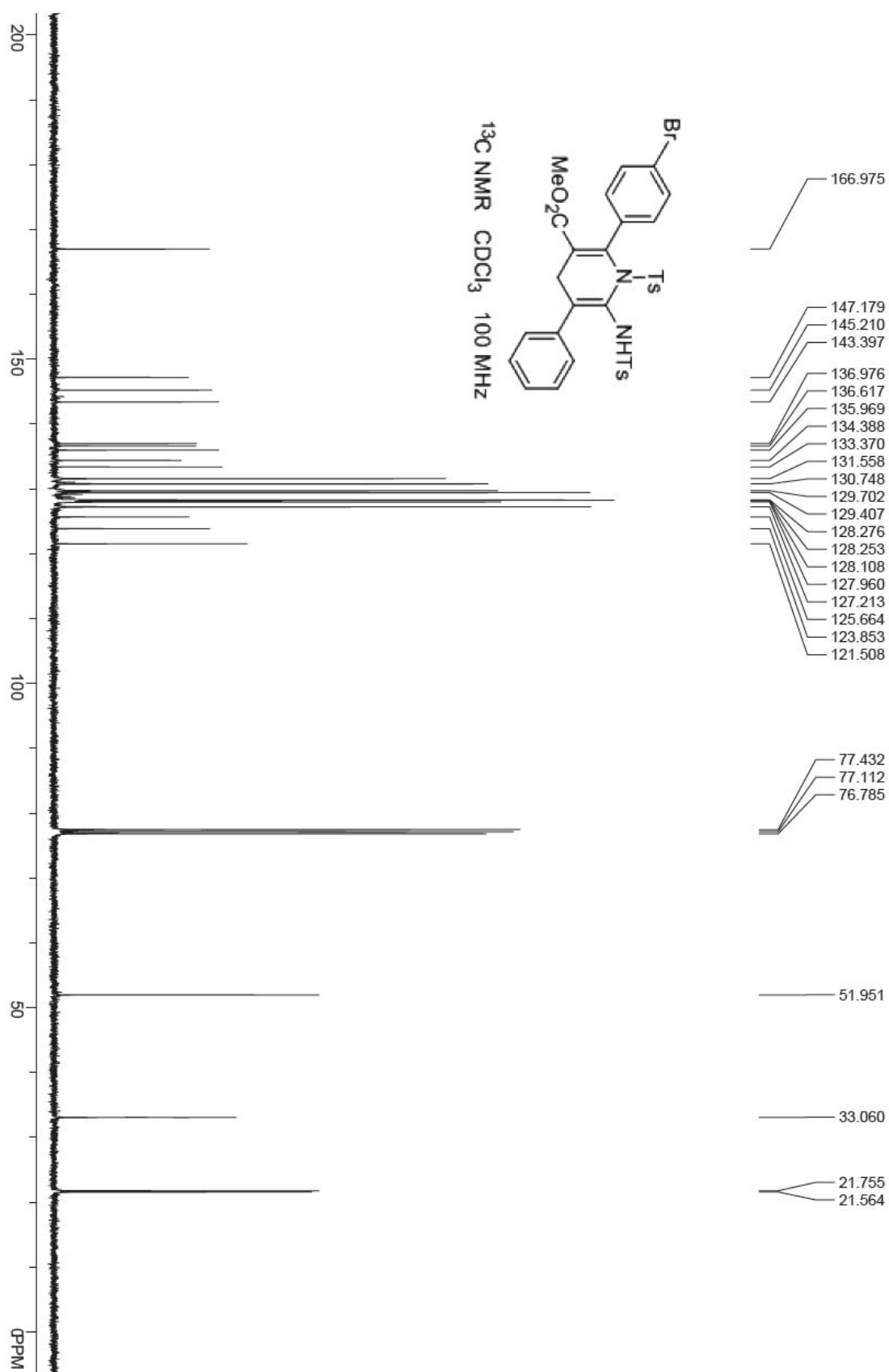




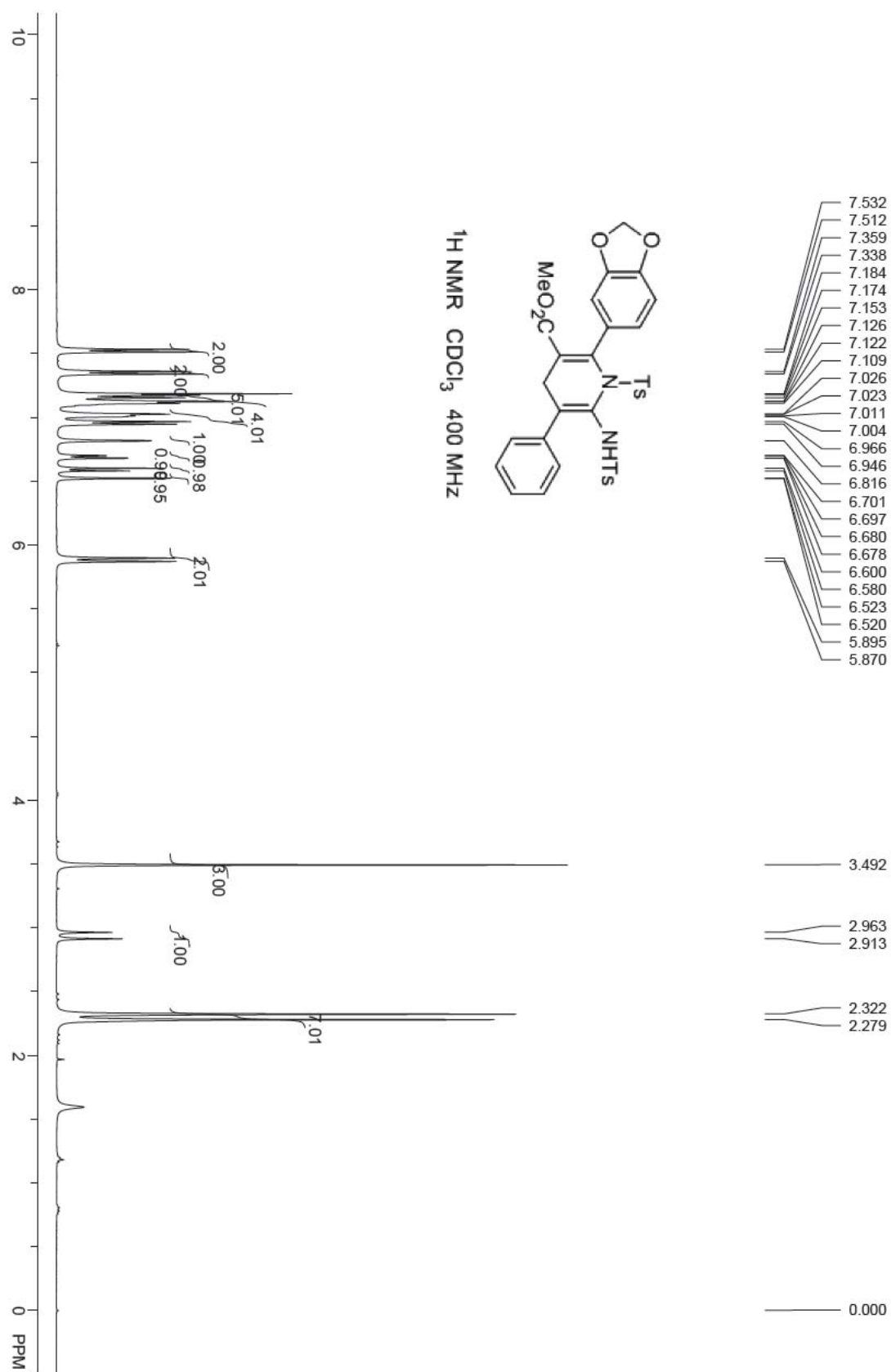
Methyl

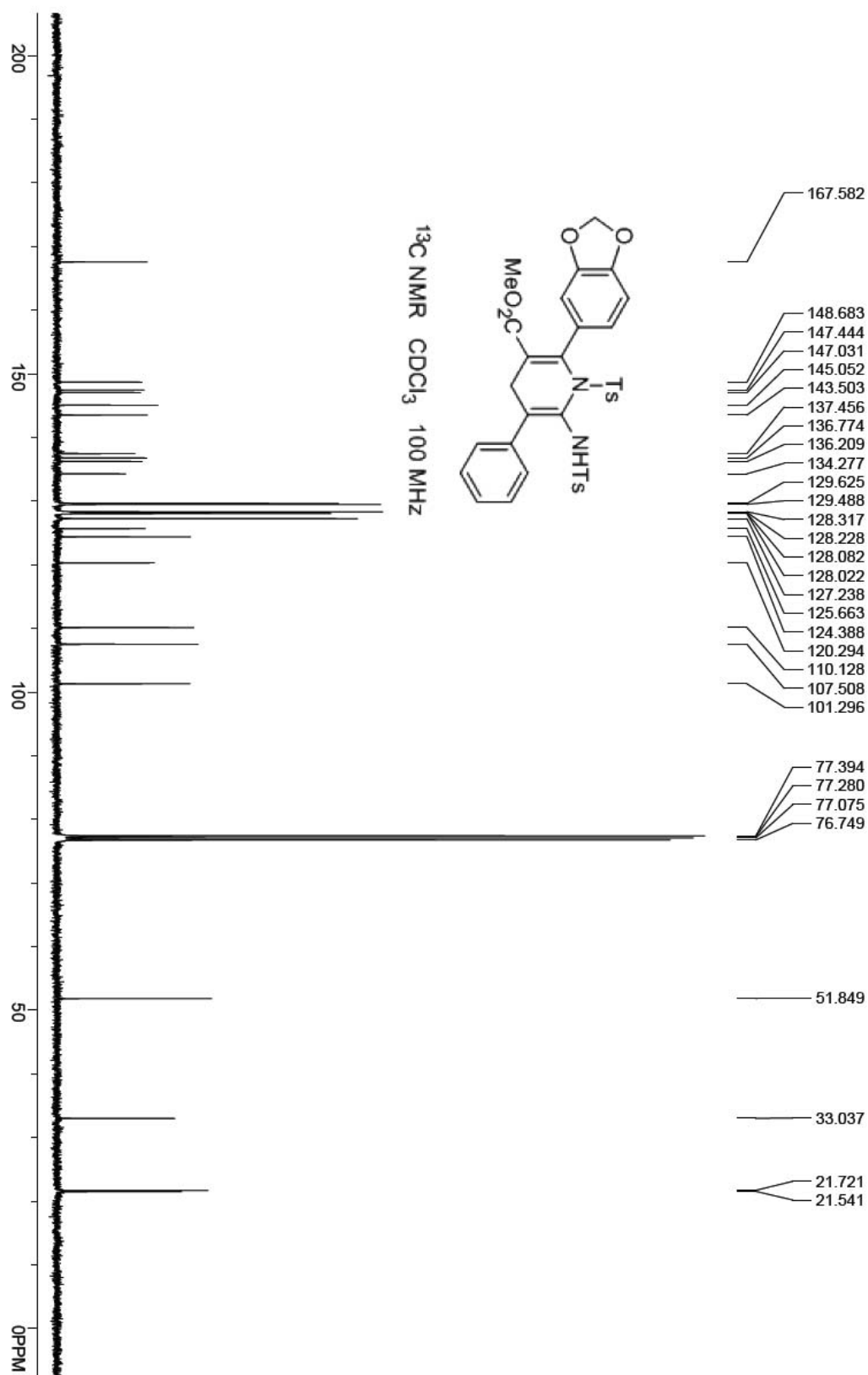
2-(4-bromophenyl)-6-(4-methylphenylsulfonamido)-5-phenyl-1-tosyl-1,4-dihydropyridine-3-carboxylate **4f**



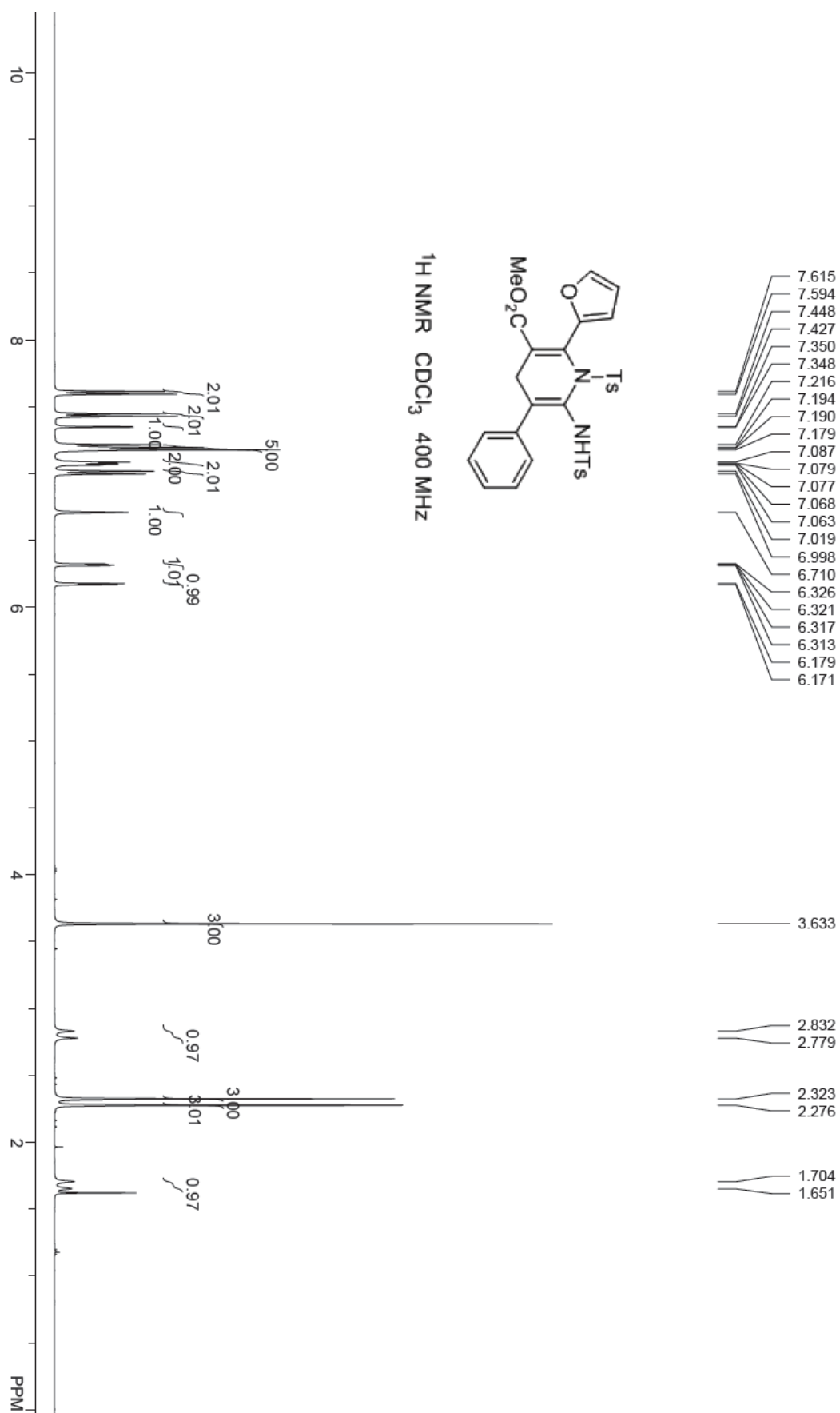


2-(Benzo[d][1,3]dioxol-5-yl)-6-(4-methylphenylsulfonamido)-5-phenyl-1-tosyl-1,4-dihydropyridine-3-carboxylate 4g

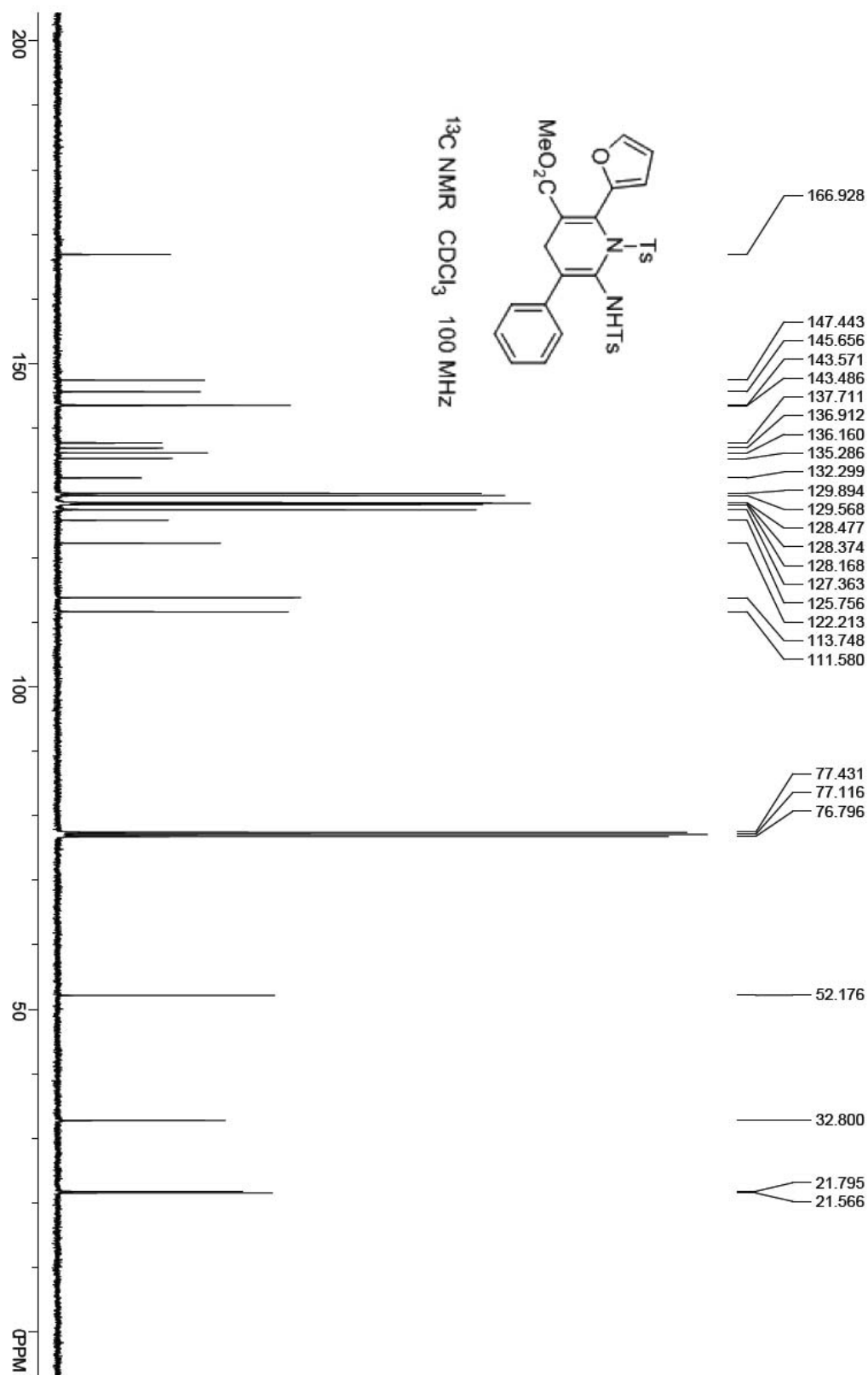




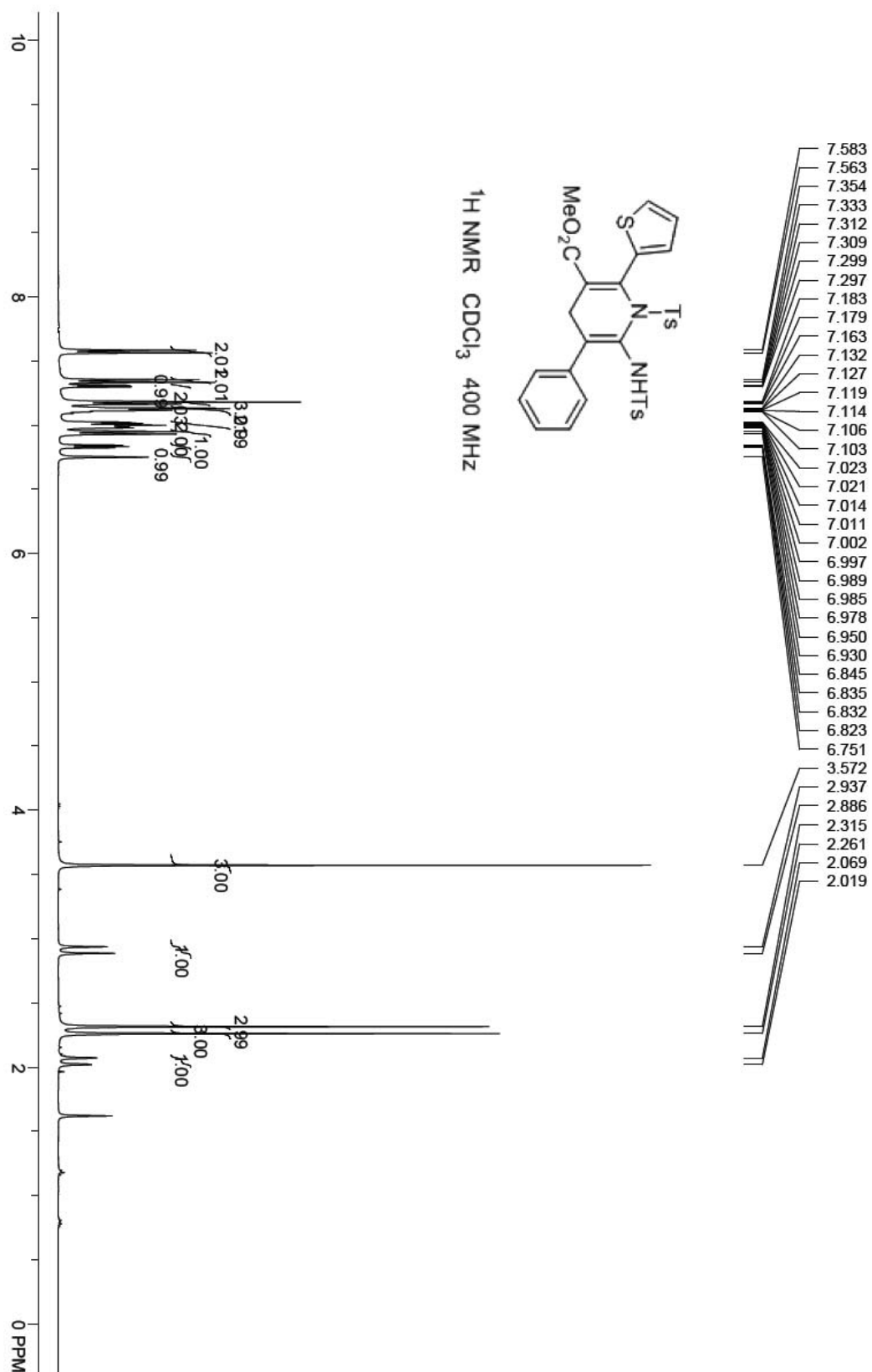
Methyl 2-(furan-2-yl)-6-(4-methylphenylsulfonamido)-5-phenyl-1-tosyl-1,4-dihydropyridine-3-carboxylate  
4h

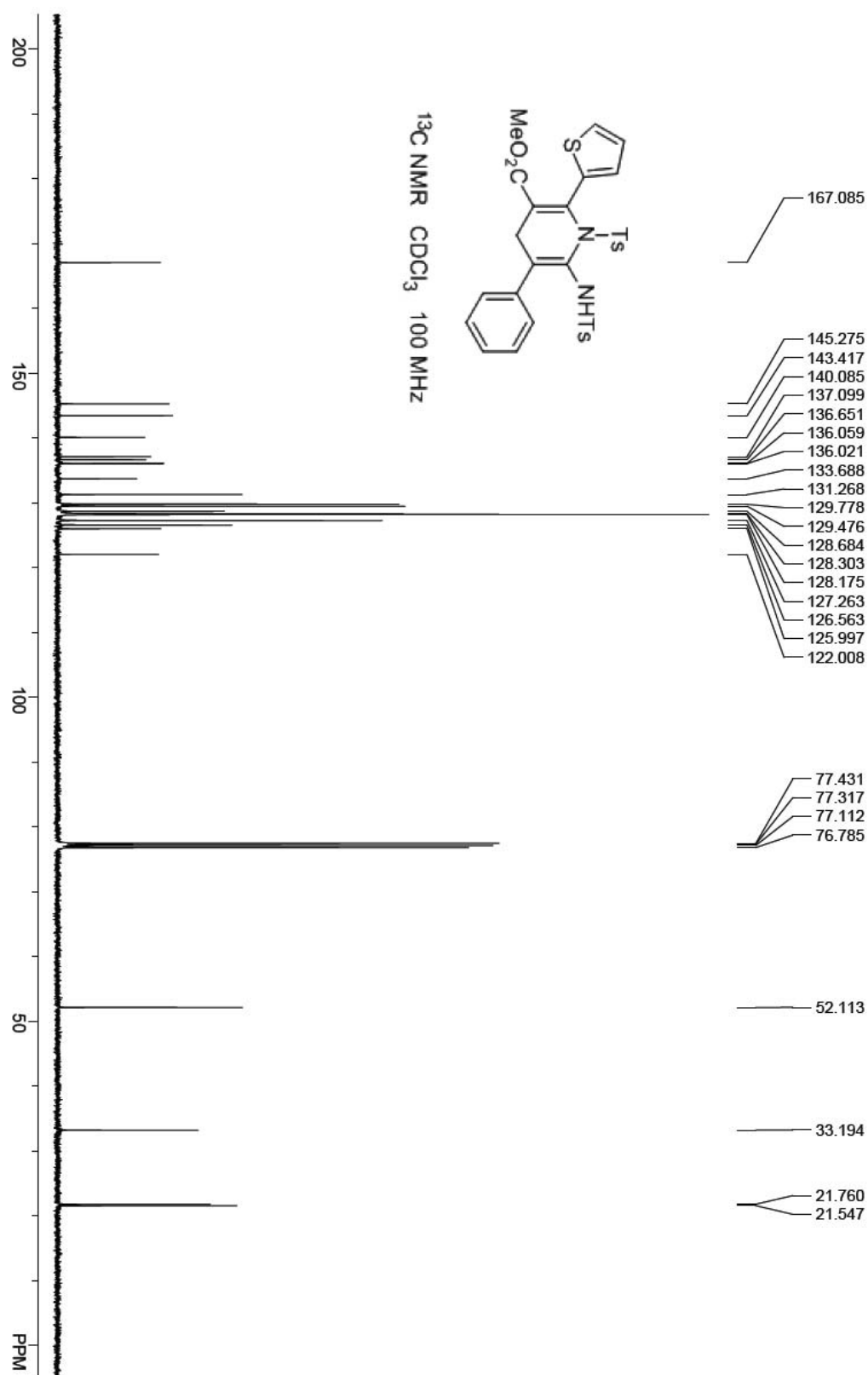




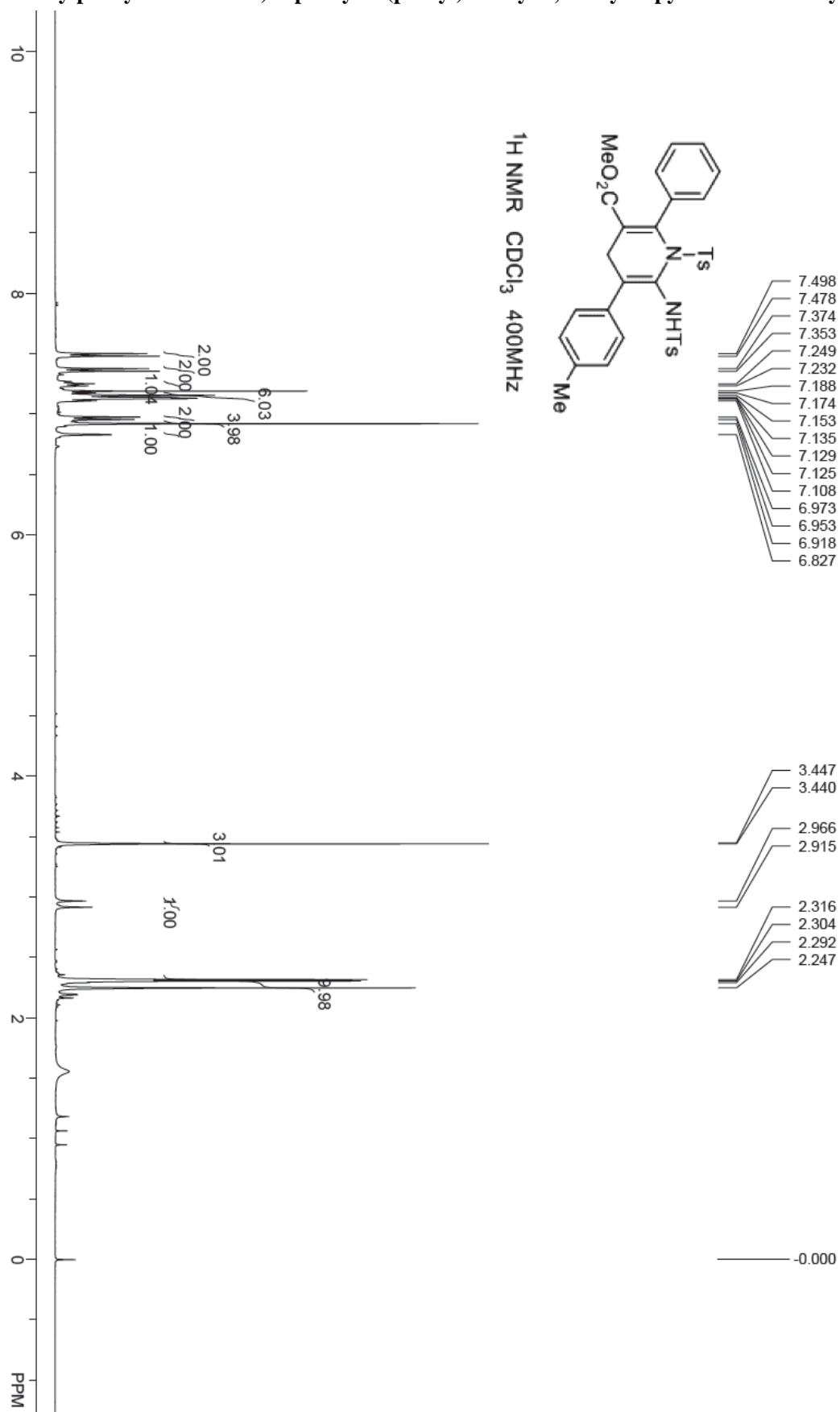


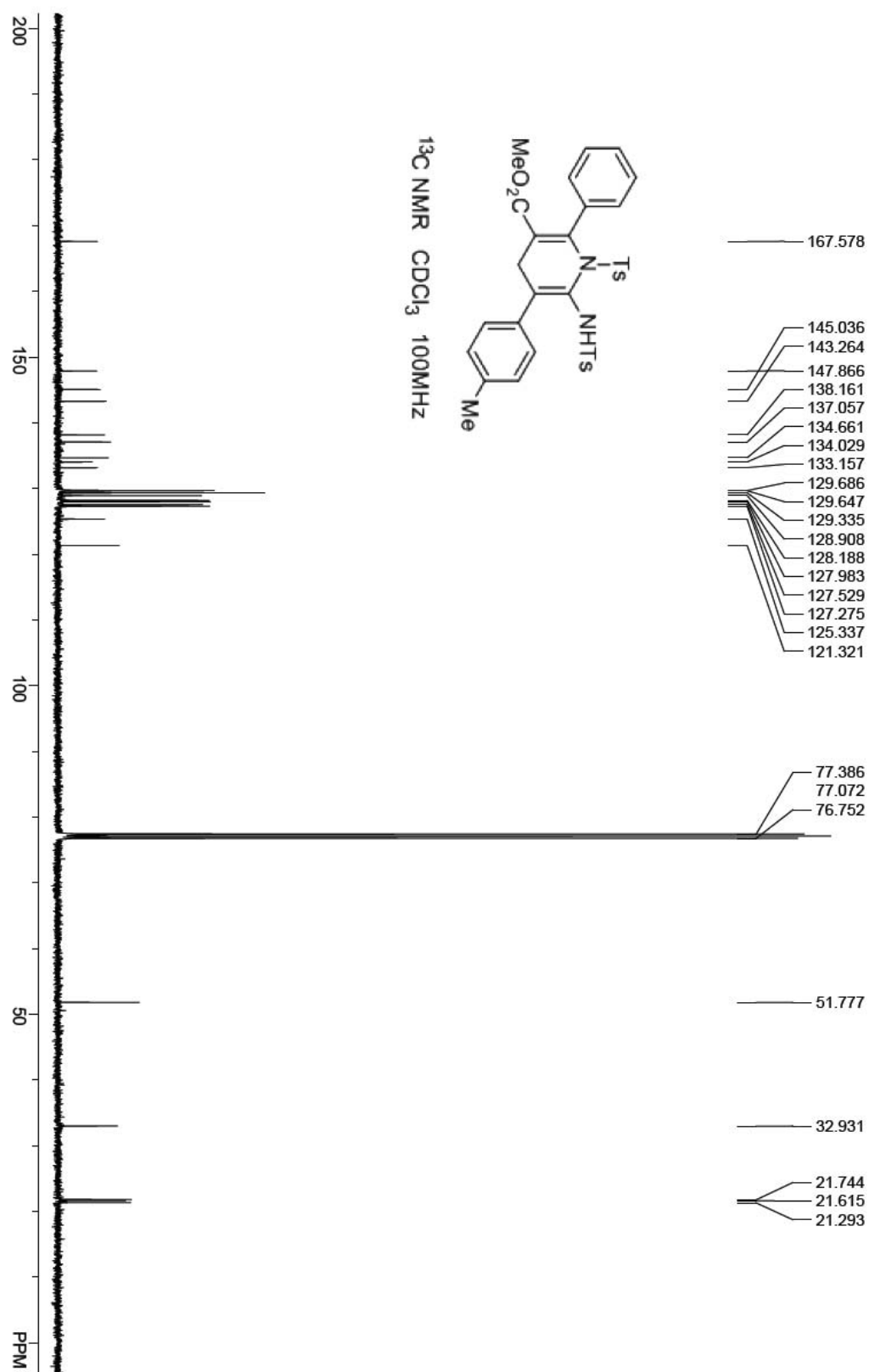
Methyl 6-(4-methylphenylsulfonamido)-5-phenyl-2-(thiophen-2-yl)-1-tosyl-1,4-dihydropyridine-3-carboxylate  
4i





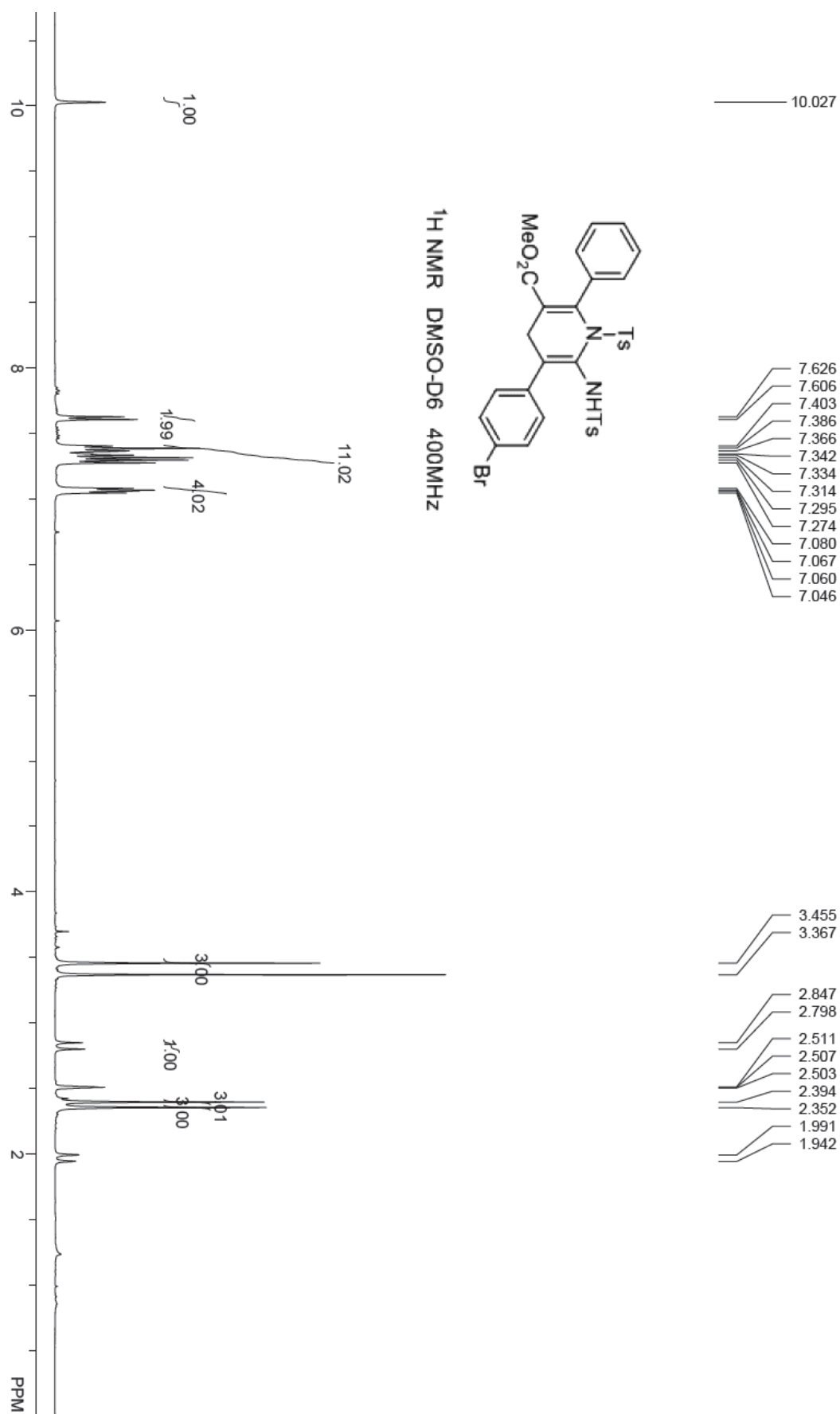
Methyl 6-(4-methylphenylsulfonamido)-2-phenyl-5-(p-tolyl)-1-tosyl-1,4-dihydropyridine-3-carboxylate 4j

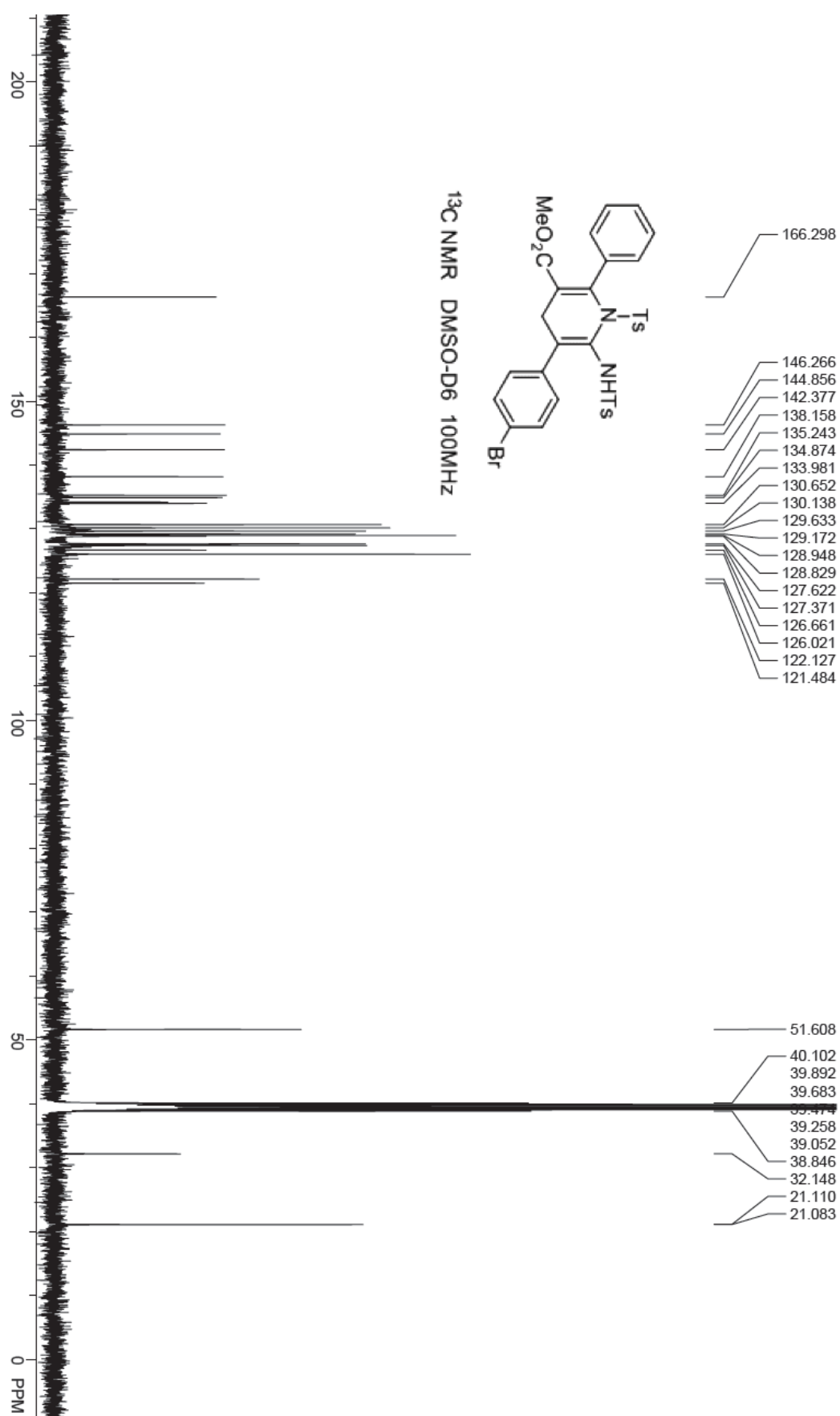




Methyl

5-(4-bromophenyl)-6-(4-methylphenylsulfonamido)-2-phenyl-1-tosyl-1,4-dihydropyridine-3-carboxylate 4k

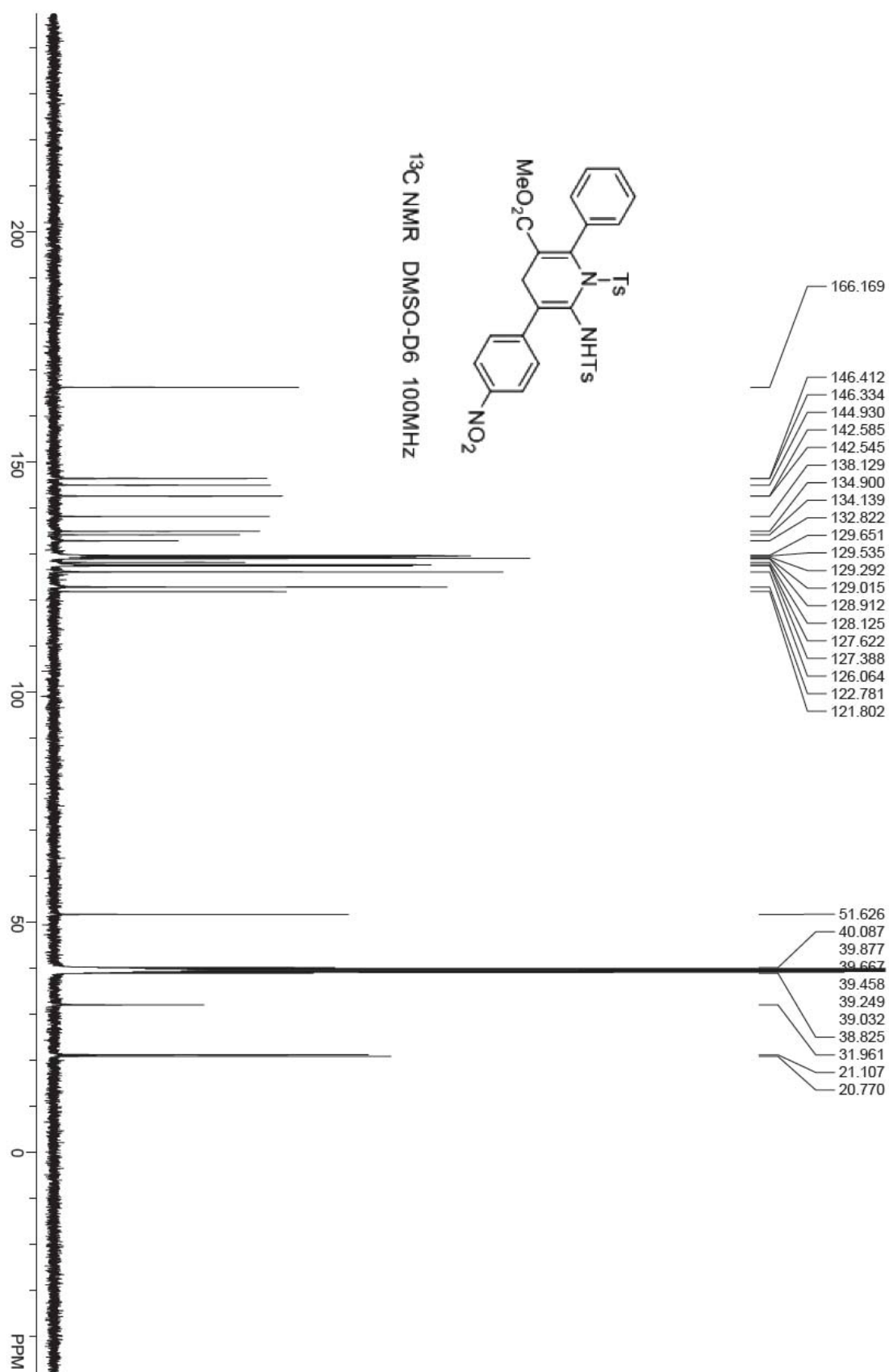




**6-(4-methylphenylsulfonamido)-5-(4-nitrophenyl)-2-phenyl-1-tosyl-1,4-dihydropyridine-3-carboxylate 4l**

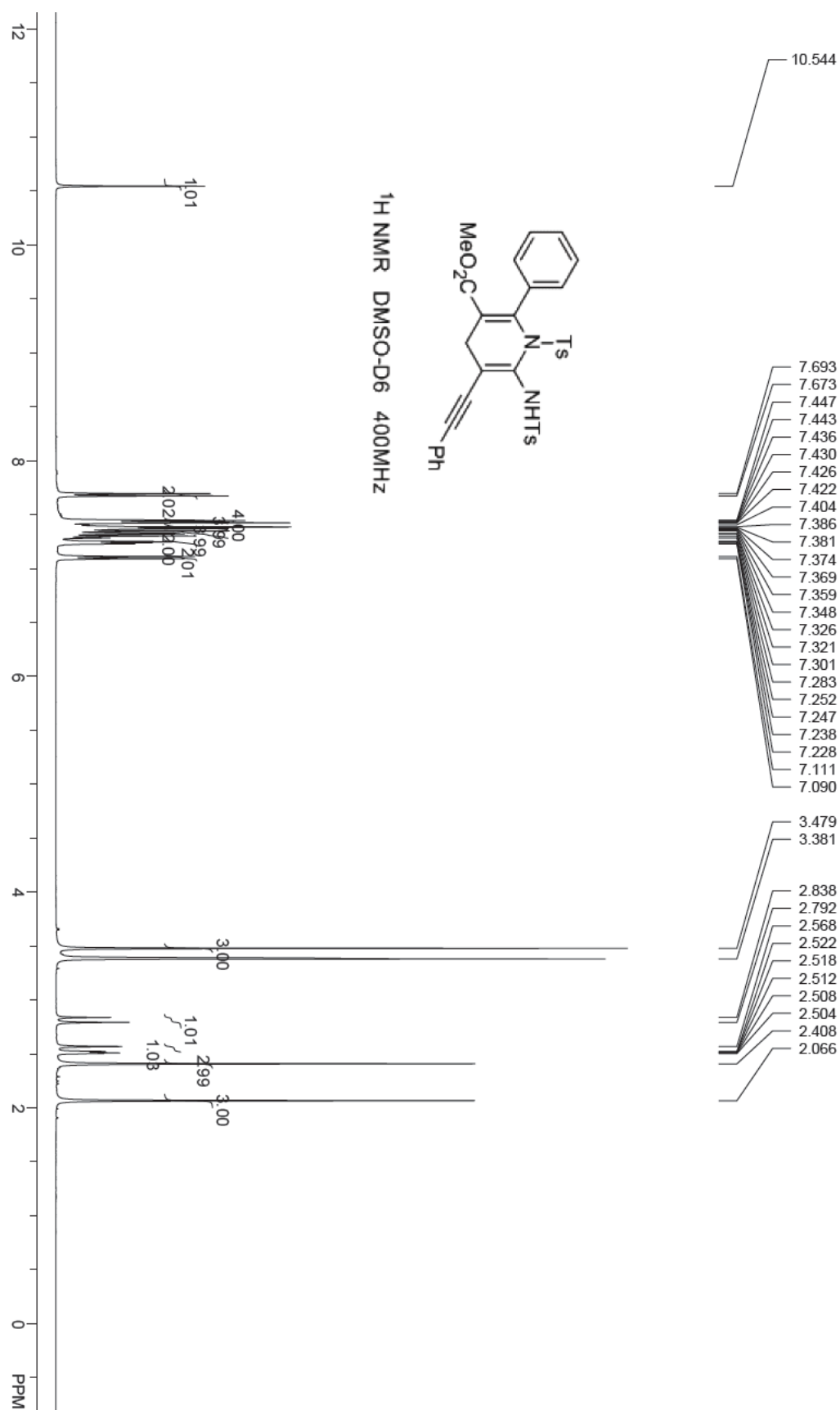


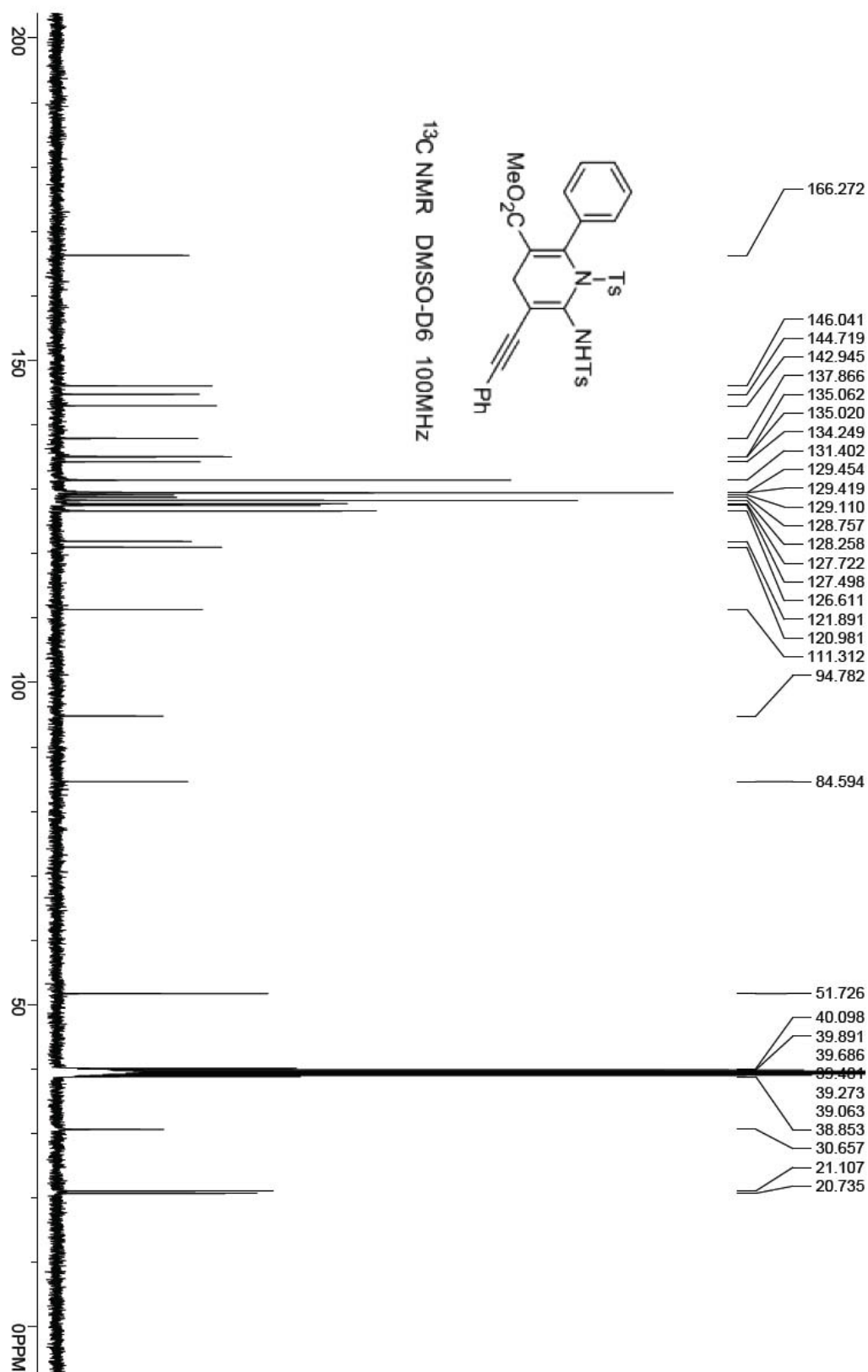




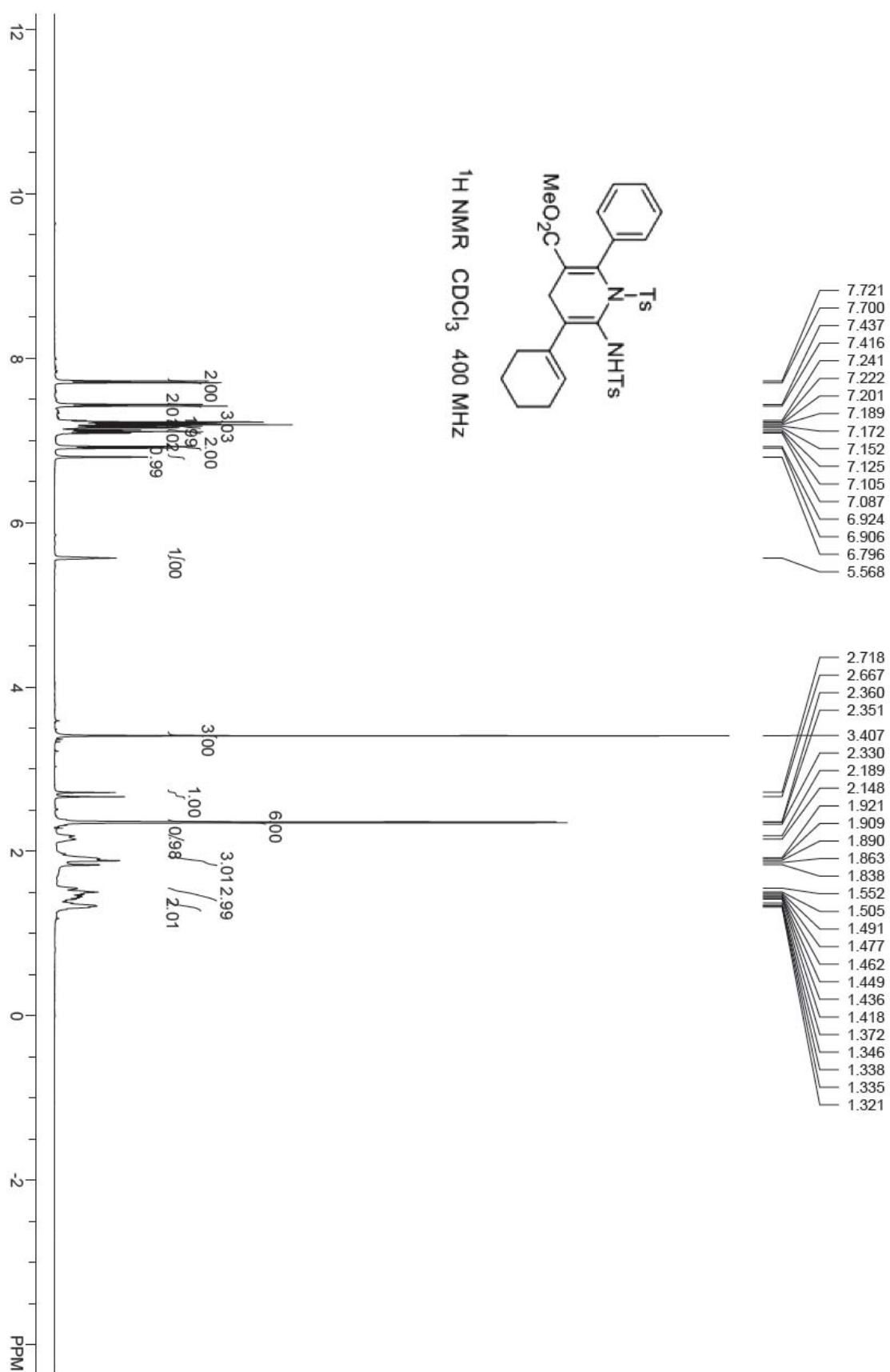
# Methyl

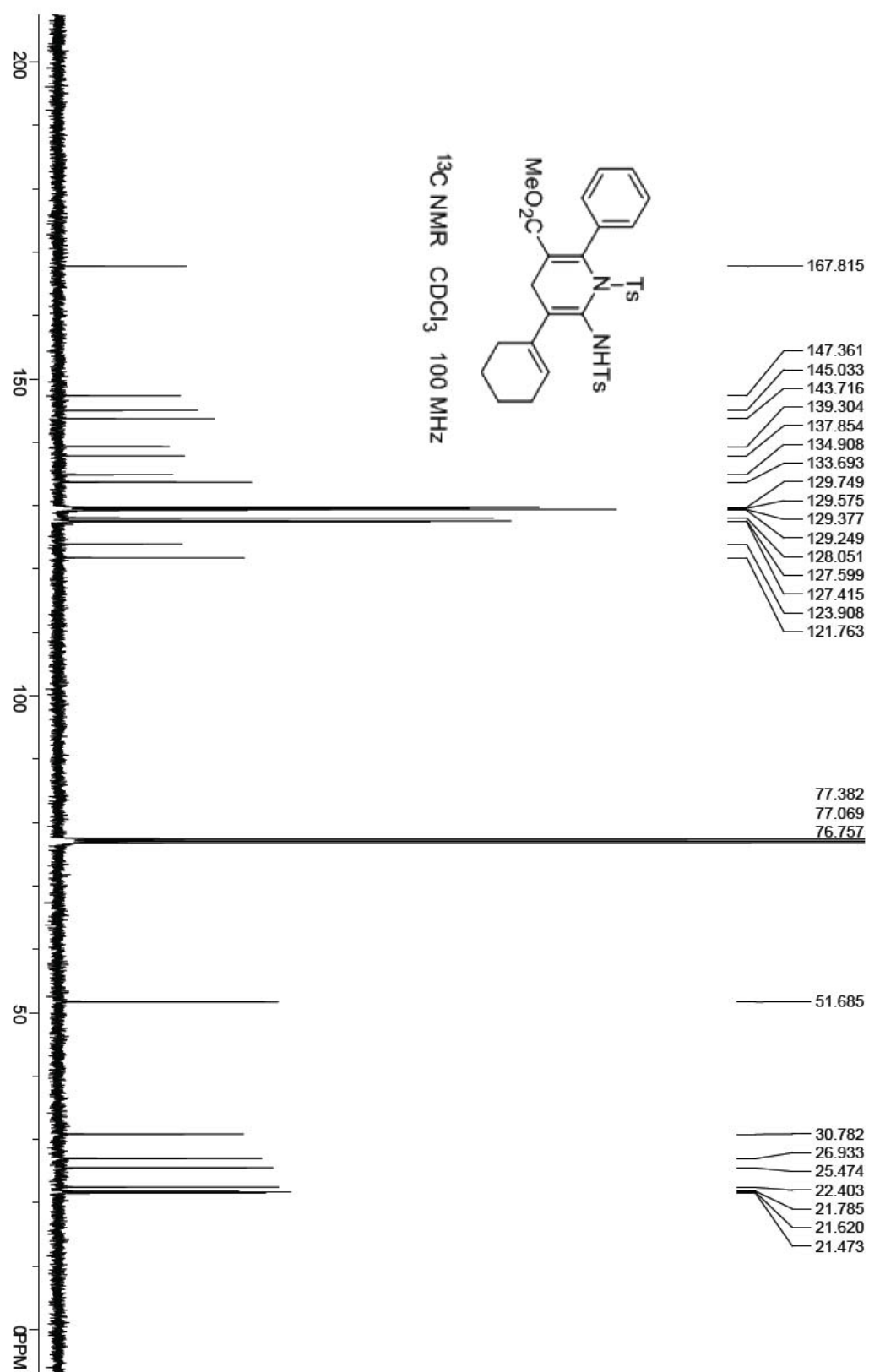
## 6-(4-methylphenylsulfonamido)-2-phenyl-5-(phenylethynyl)-1-tosyl-1,4-dihydropyridine-3-carboxylate 4m



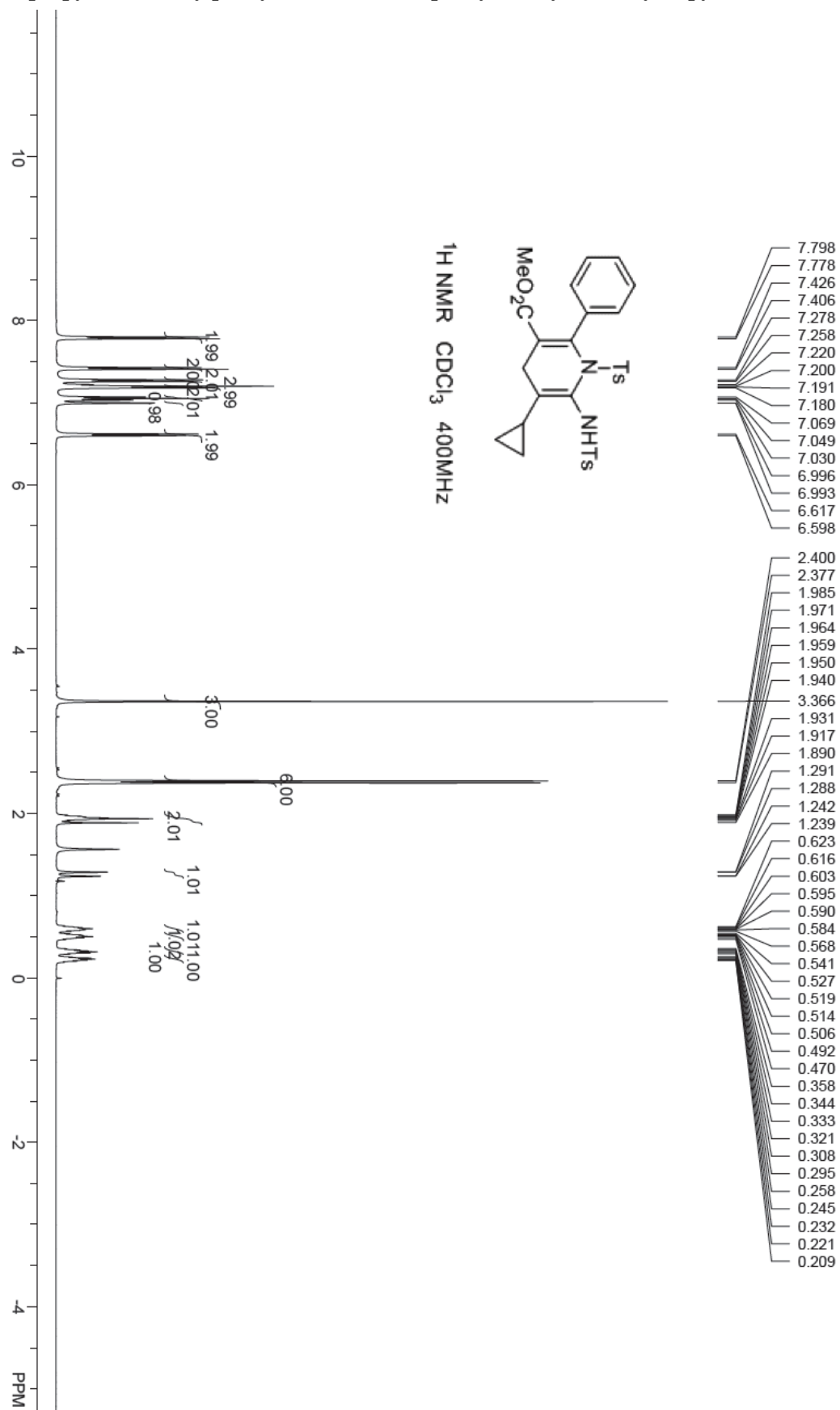


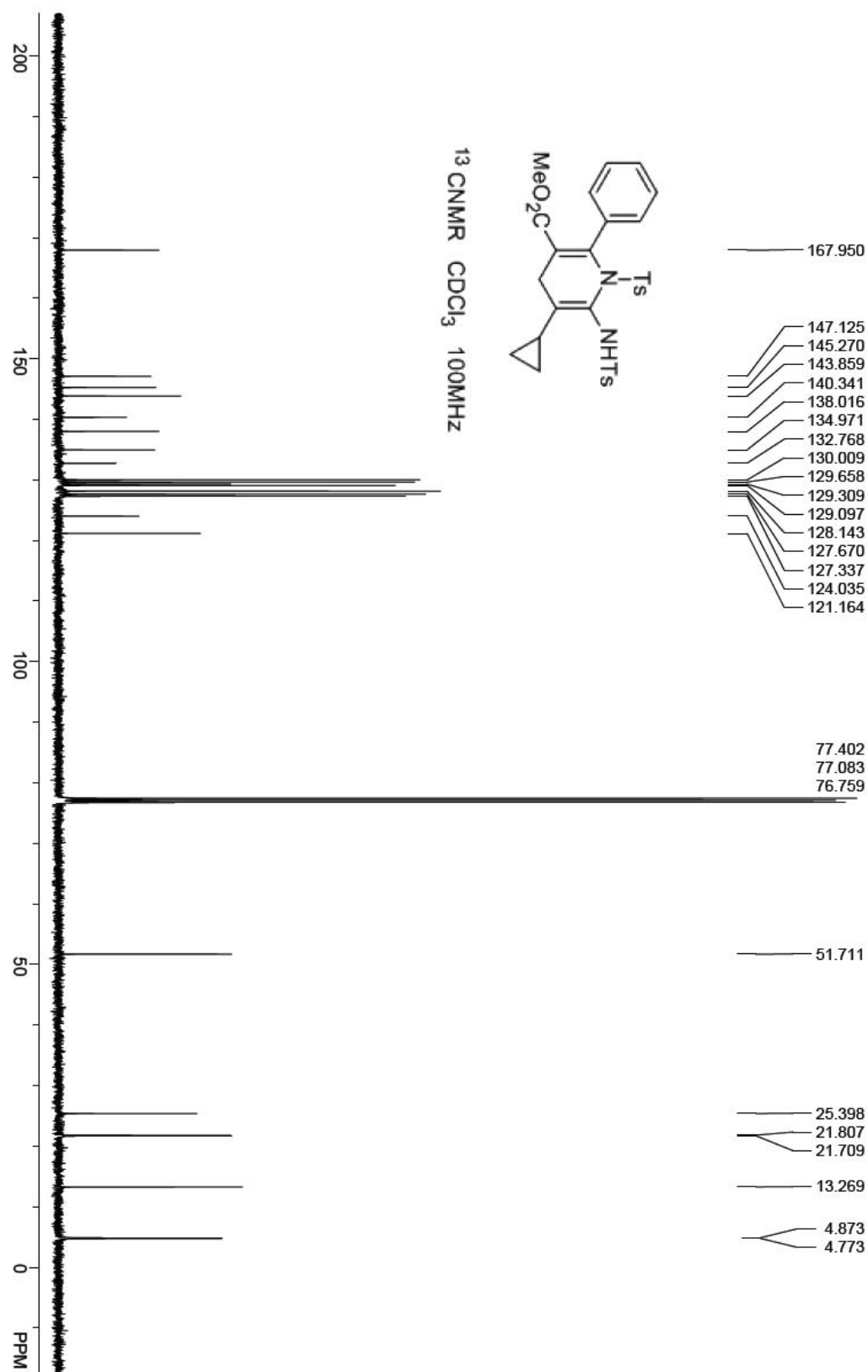
**Methyl5-(cyclohex-1-en-1-yl)-6-(4-methylphenylsulfonamido)-2-phenyl-1-tosyl-1,4-dihydropyridine-3-carboxylate 4n**



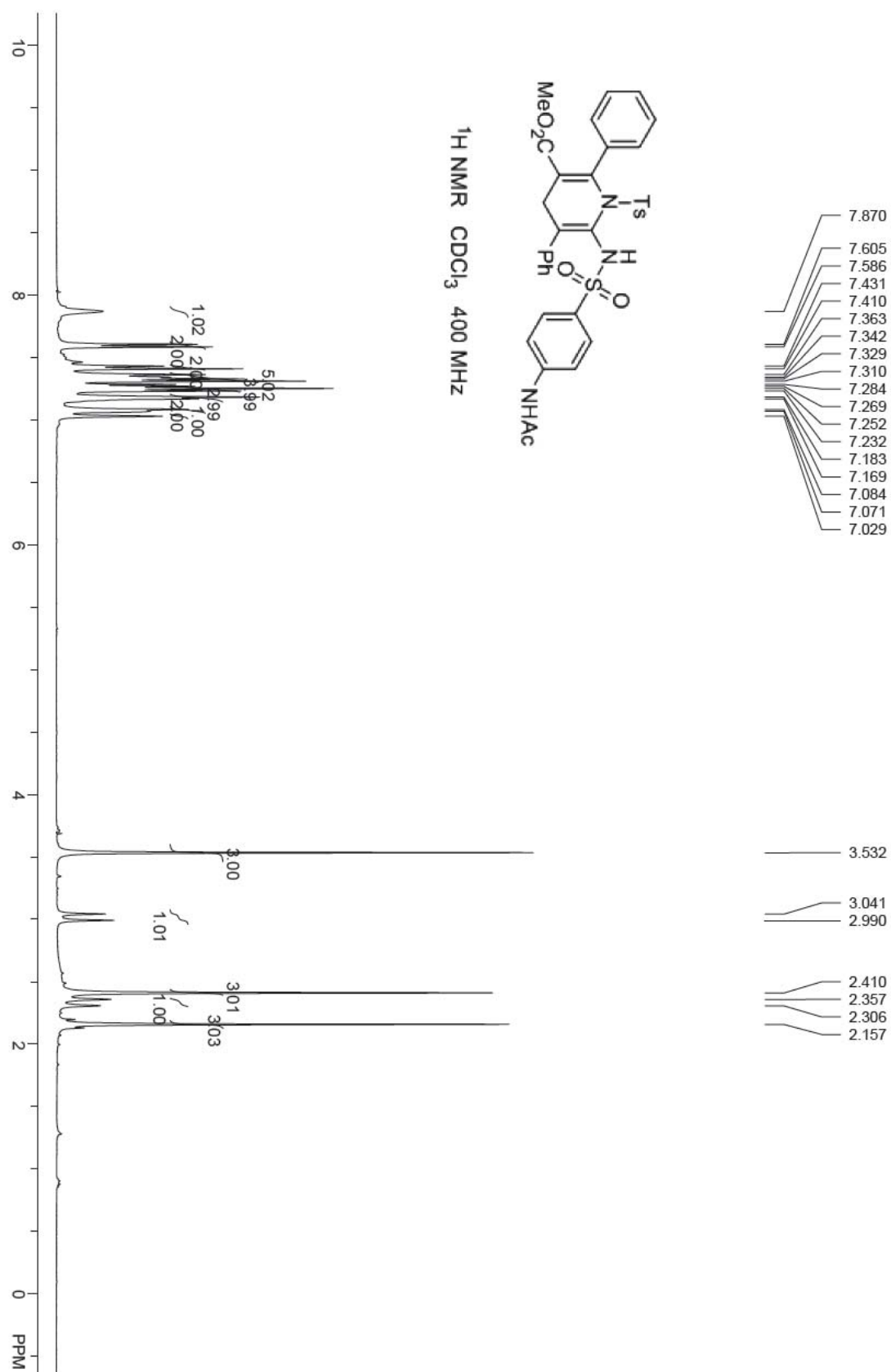


Methyl5-cyclopropyl-6-(4-methylphenylsulfonamido)-2-phenyl-1-tosyl-1,4-dihydropyridine-3-carboxylate 4o

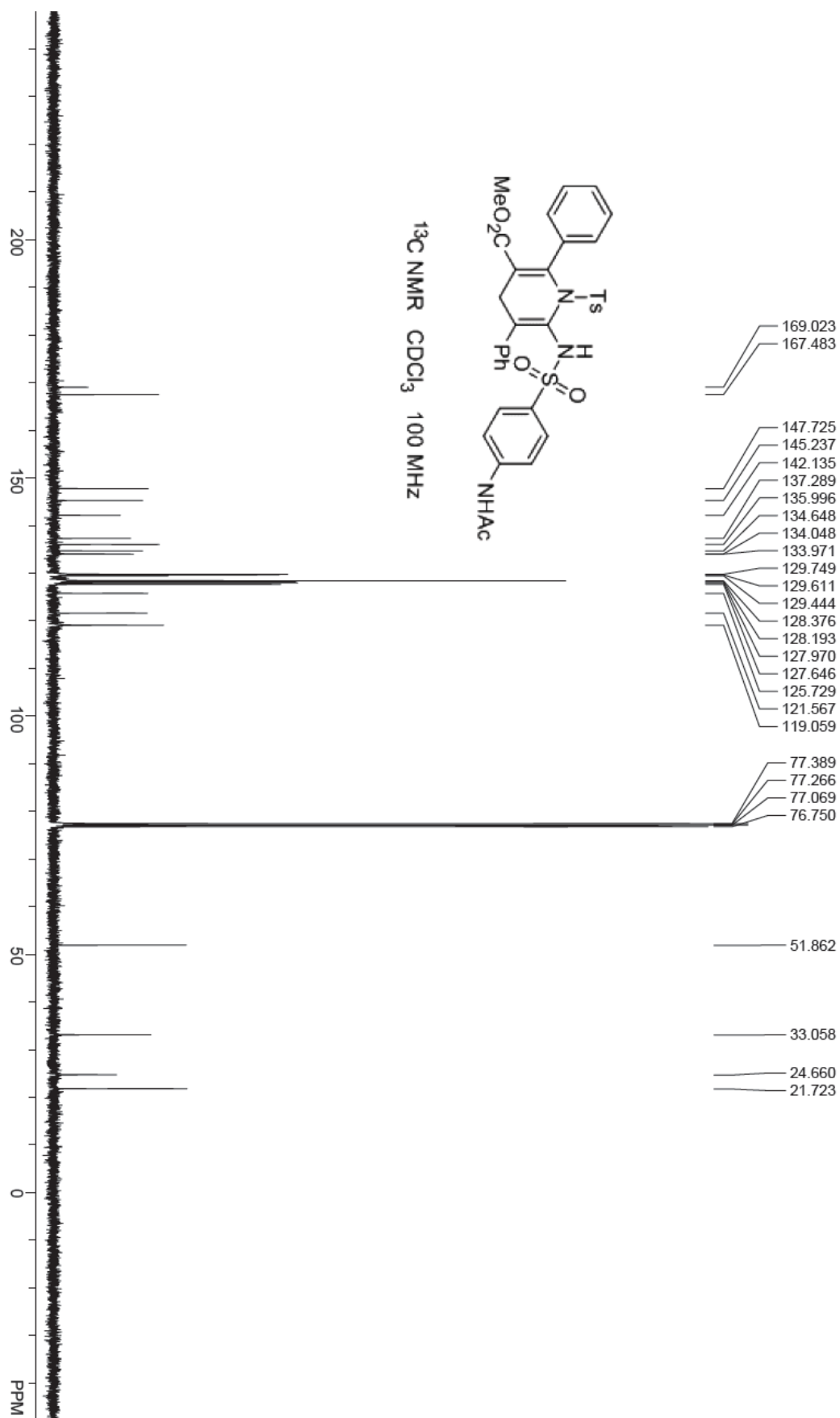




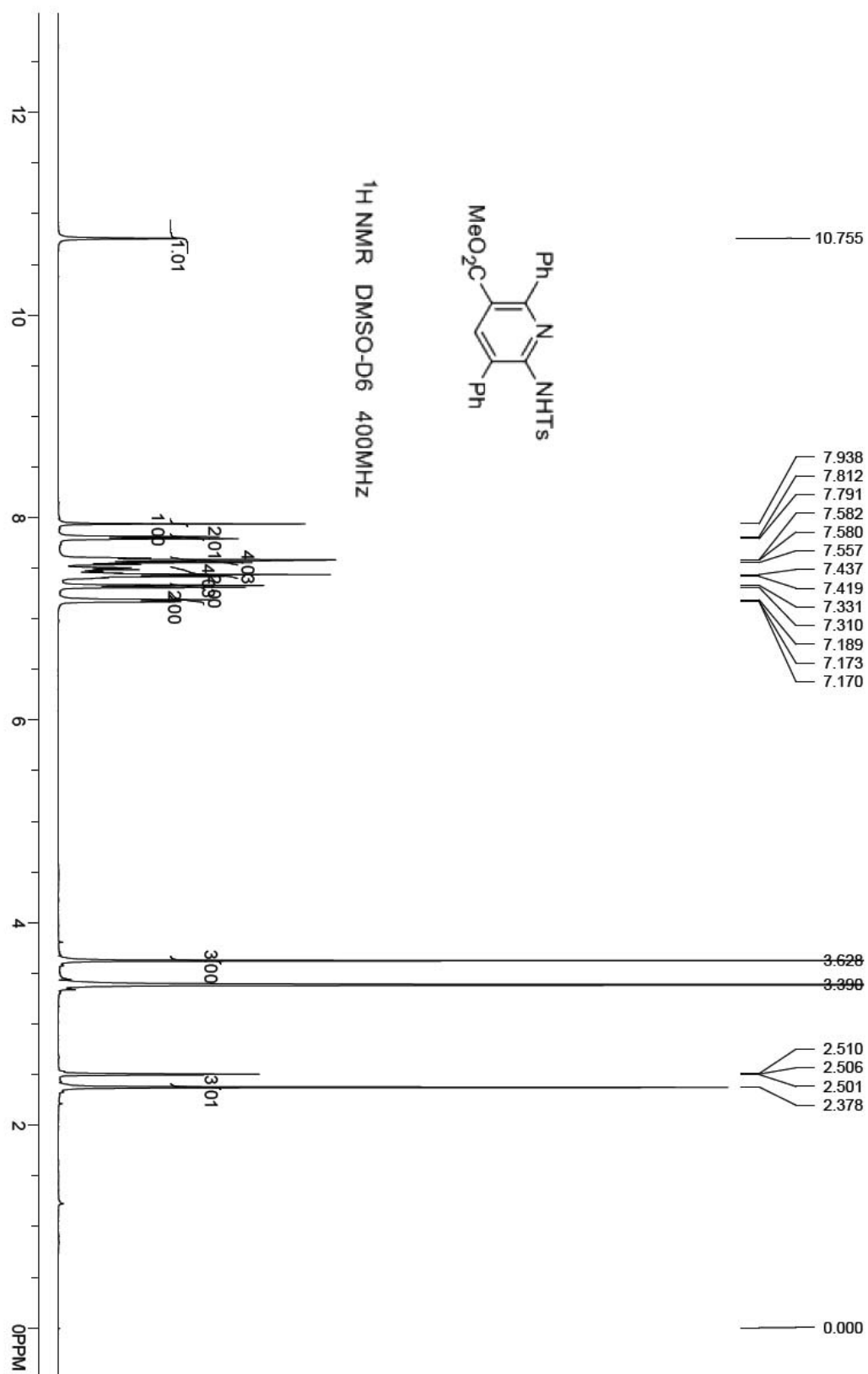
**Methyl1-(4-acetamidophenyl)-6-(4-methylphenylsulfonamido)-2,5-diphenyl-1,4-dihydropyridine-3-carboxylate 4p**

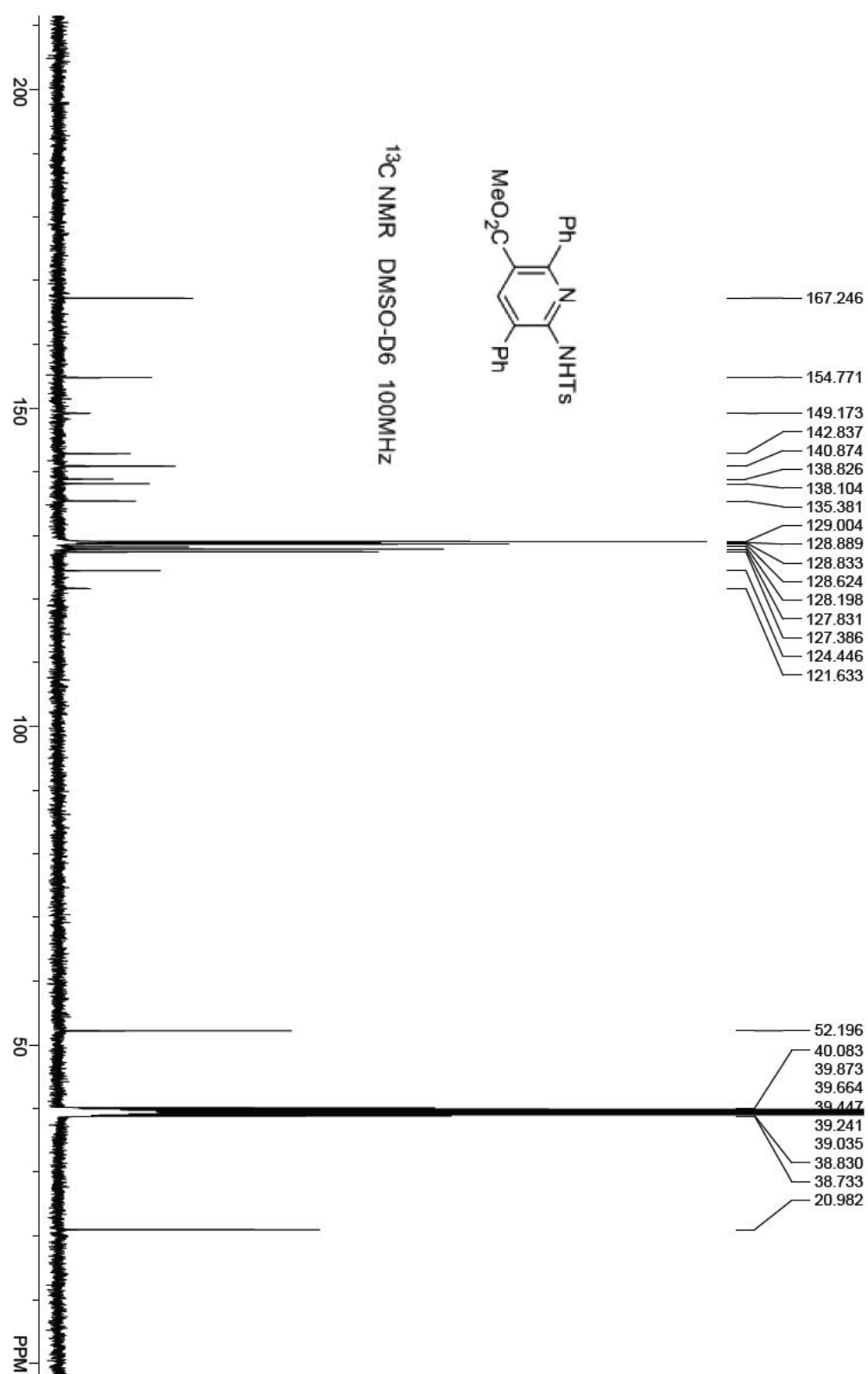




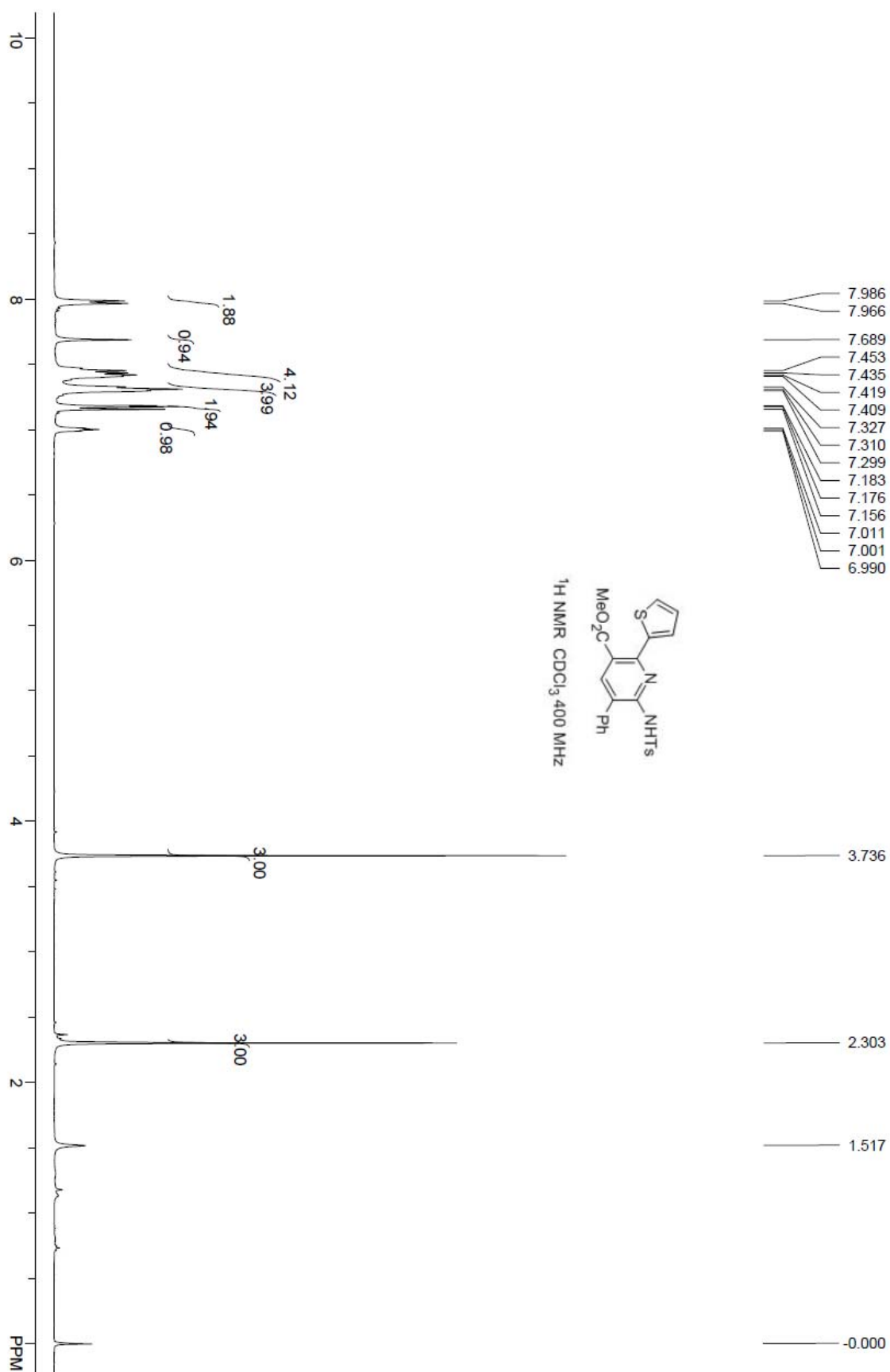


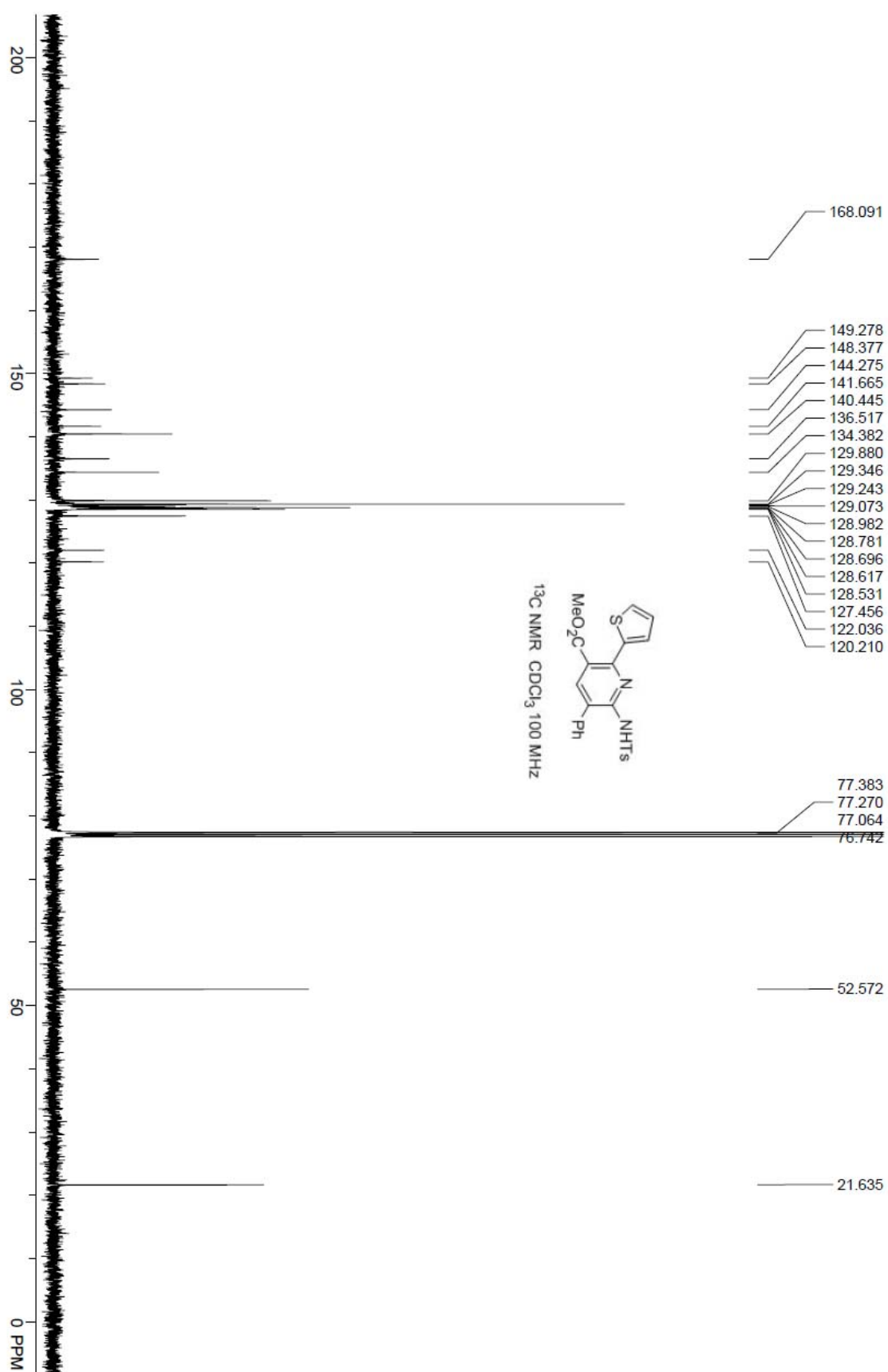
Methyl 6-(4-methylphenylsulfonamido)-2,5-diphenylnicotinate 5a



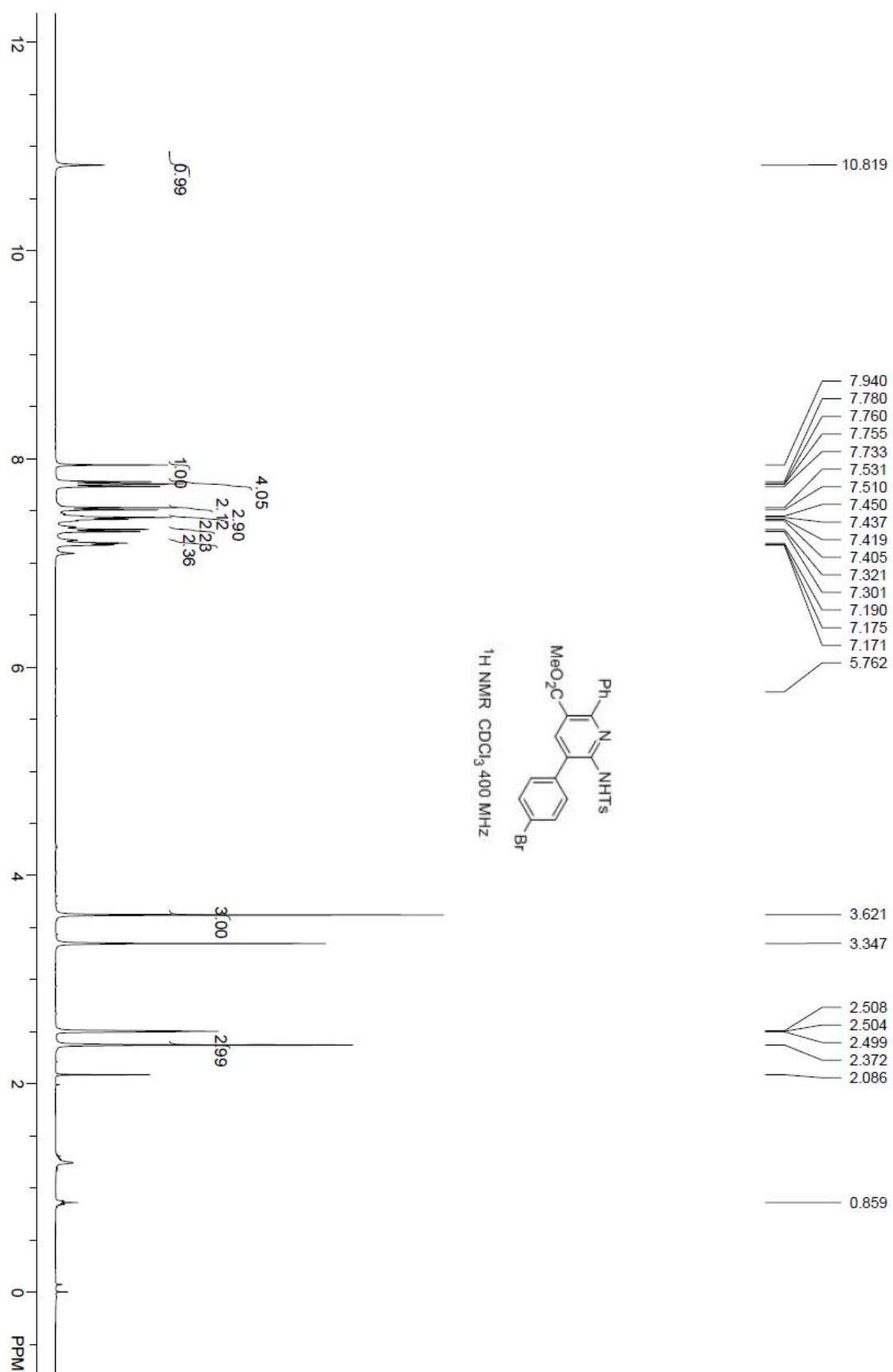


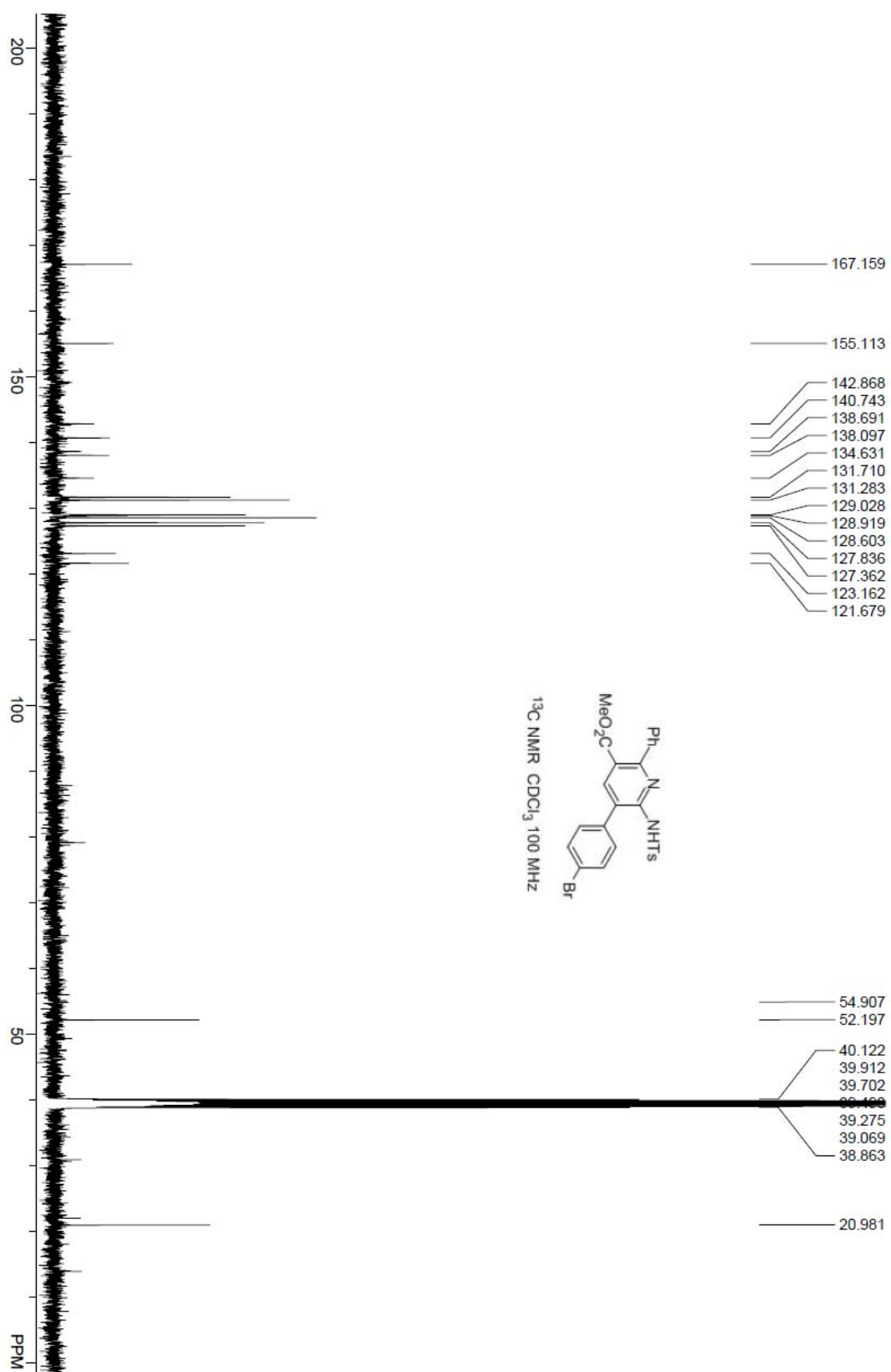
Methyl 6-(4-methylphenylsulfonamido)-5-phenyl-2-(thiophen-2-yl)nicotinate 5i



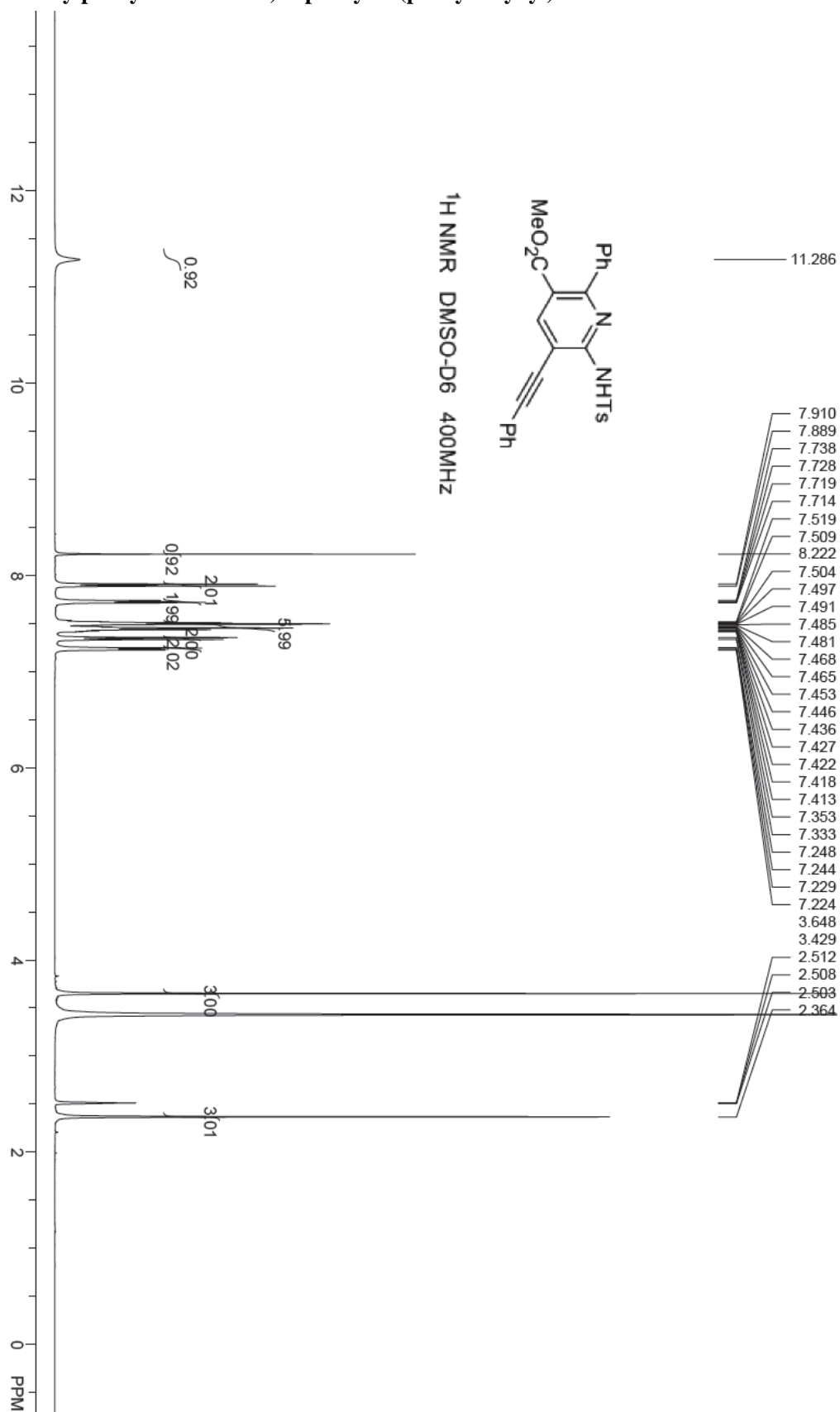


Methyl 5-(4-bromophenyl)-6-(4-methylphenylsulfonamido)-2-phenylnicotinate 5k

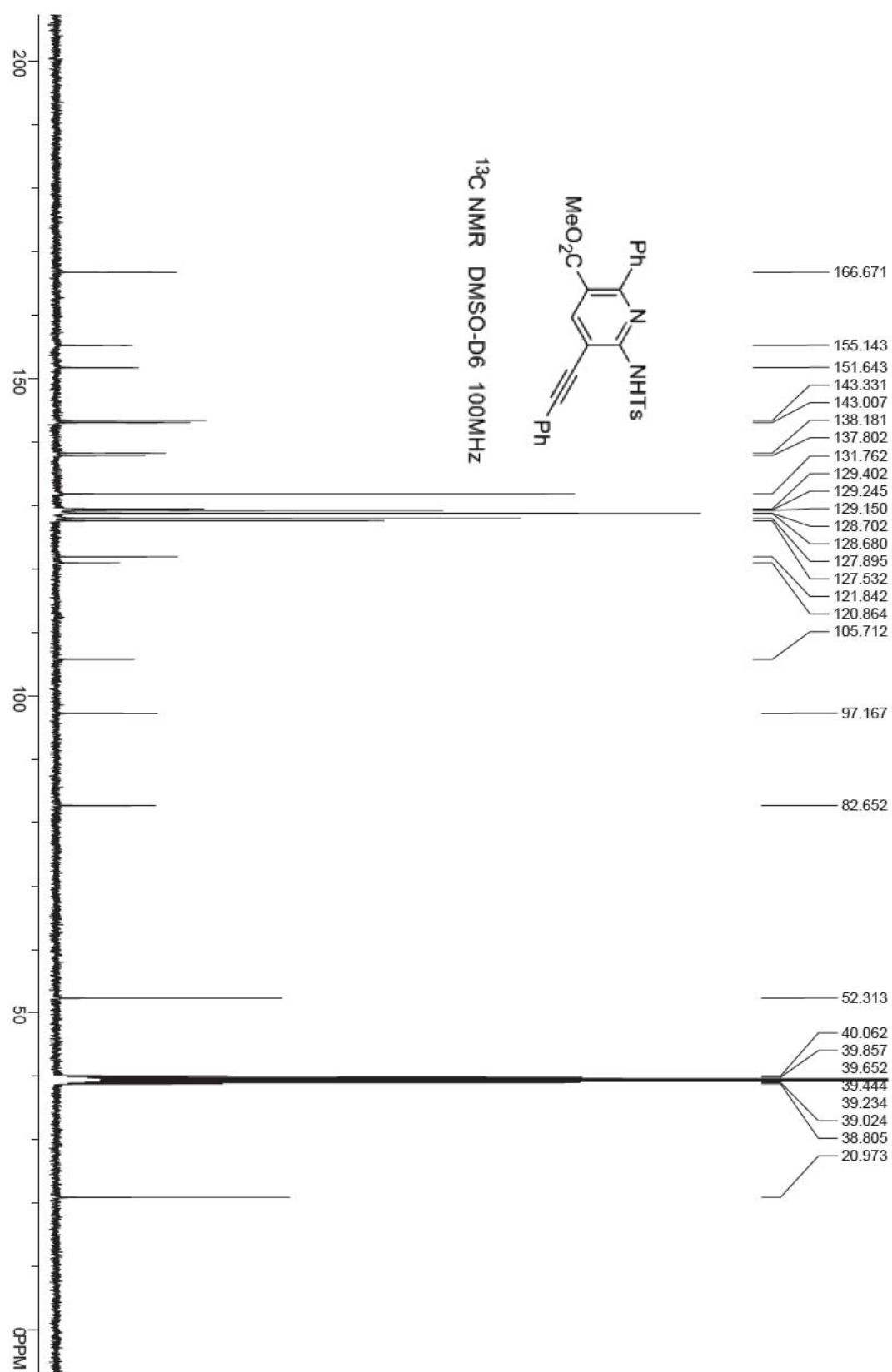




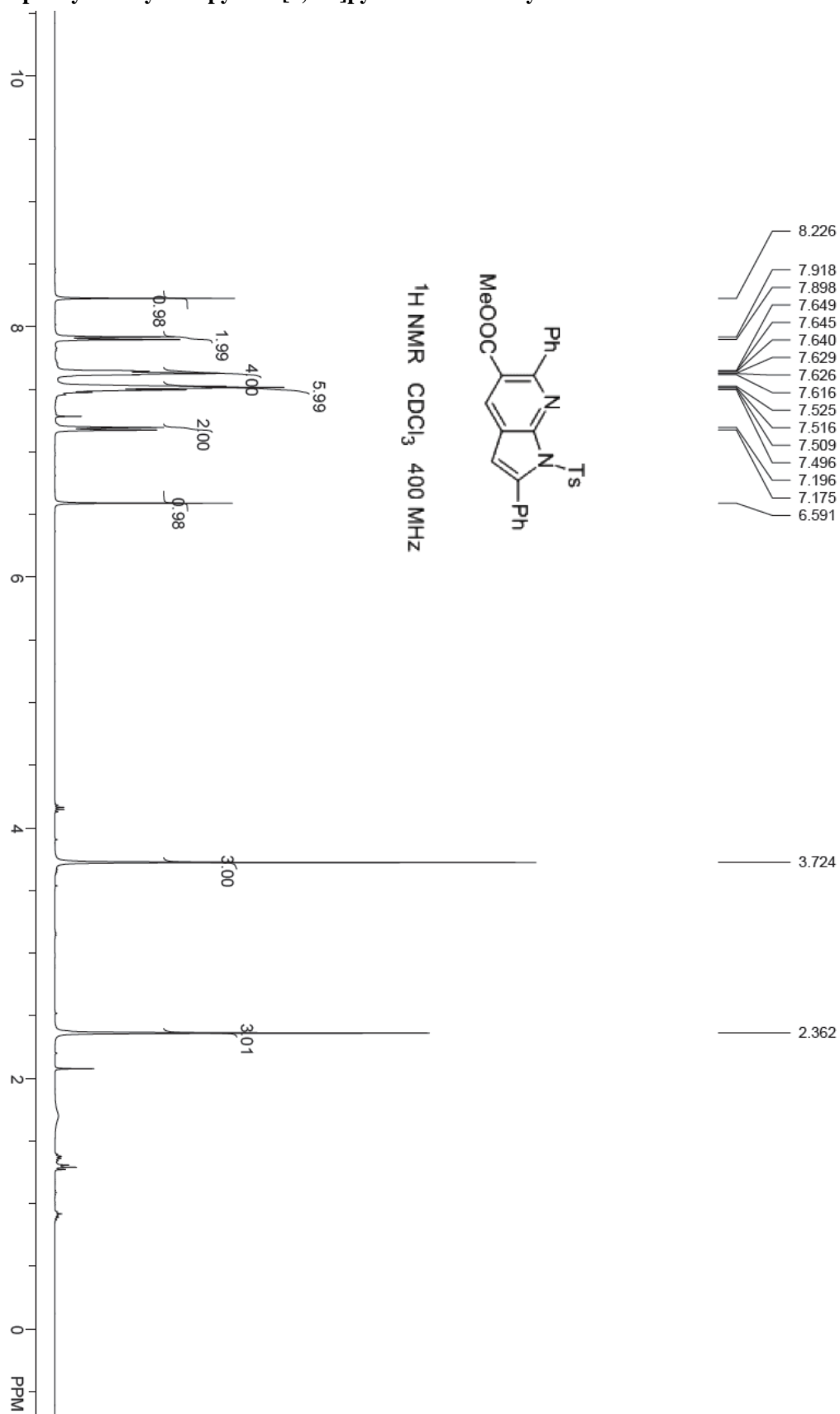
Methyl 6-(4-methylphenylsulfonamido)-2-phenyl-5-(phenylethynyl)nicotinate 5m

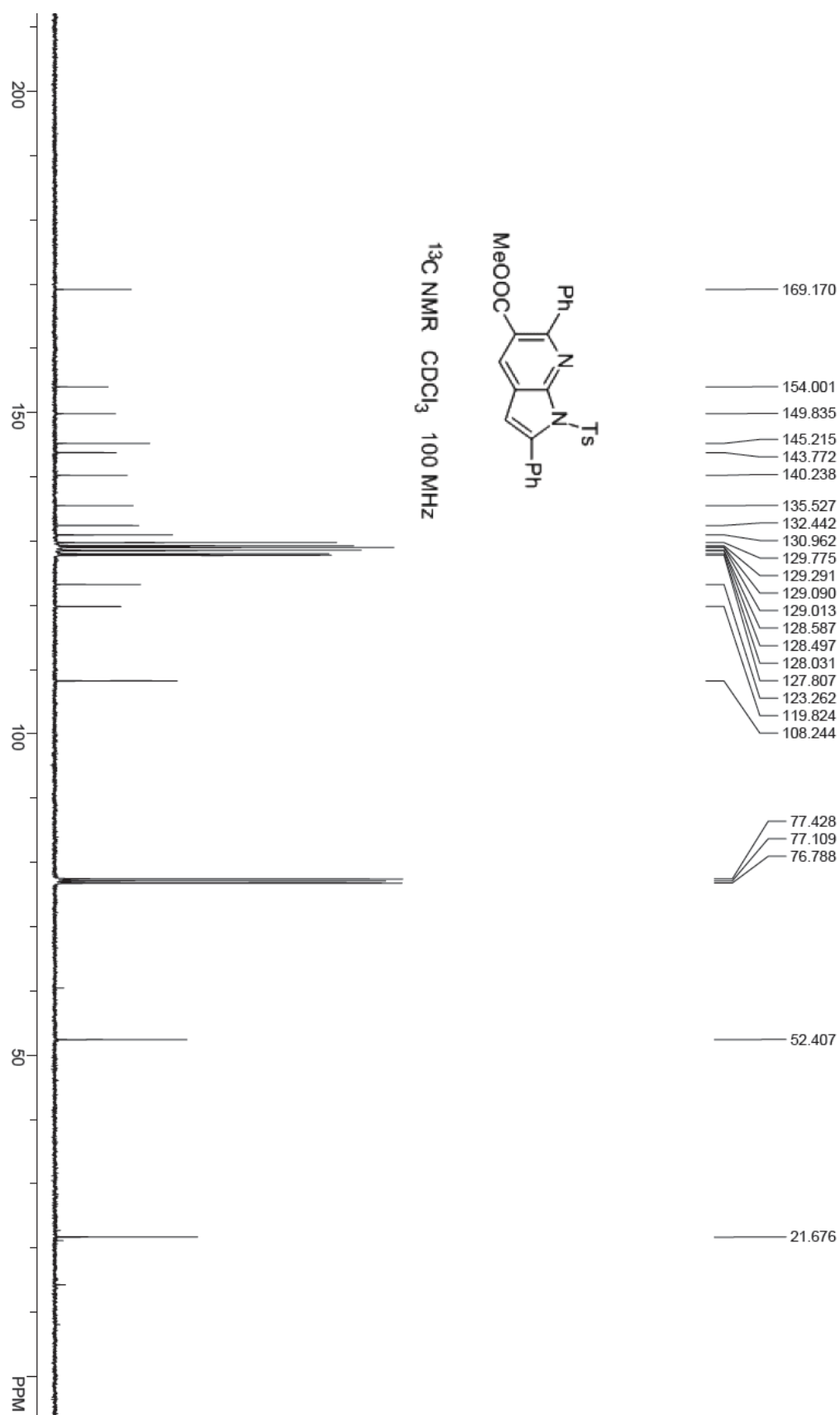






Methyl 2,6-diphenyl-1-tosyl-1H-pyrrolo[2,3-b]pyridine-5-carboxylate 6m





Methyl 3-allyl-2,6-diphenyl-1-tosyl-1H-pyrrolo[2,3-b]pyridine-5-carboxylate 7m

