

Supporting Information

Gold-catalyzed intermolecular oxidation of *o*-alkynylbiaryls: an easy and practical access to functionalized fluorenes

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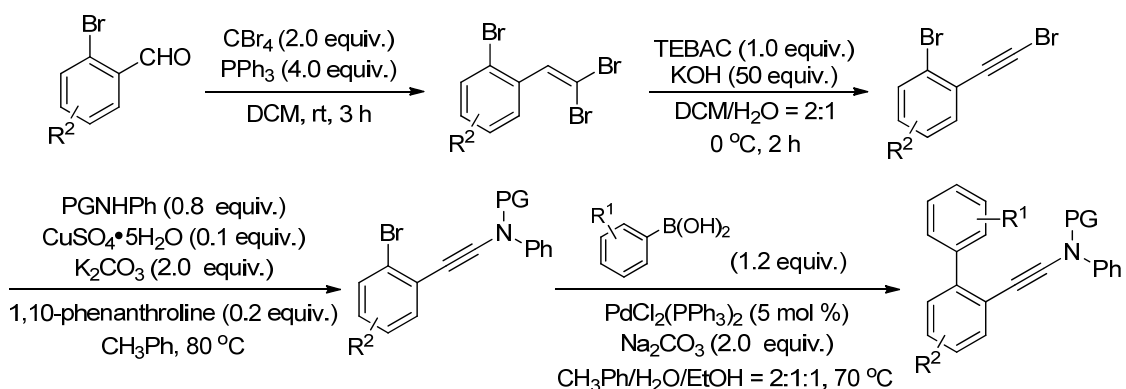
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General Information. Ethyl acetate (ACS grade), hexanes (ACS grade) and anhydrous 1, 2-dichloroethane (ACS grade) were obtained commercially and used without further purification. Methylene chloride, tetrahydrofuran and diethyl ether were purified according to standard methods unless otherwise noted. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh). Infrared spectra were recorded on a Nicolet AVATER FTIR330 spectrometer as thin film and are reported in reciprocal centimeter (cm^{-1}). Mass spectra were recorded with Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer using electron spray ionization.

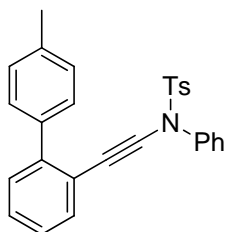
^1H NMR spectra were recorded on a Bruker AV-400 spectrometer and a Bruker AV-500 spectrometer in chloroform- d_3 . Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet, coupling constant(s) in Hz, integration).

^{13}C NMR spectra were recorded on on a Bruker AV-400 spectrometer and a Bruker AV-500 spectrometer in chloroform- d_3 . Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard.

Compounds **1a-1m** were prepared according to the known procedures.¹



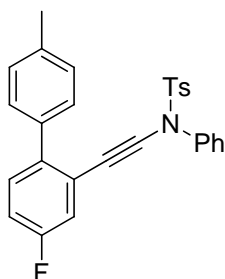
4-methyl-N-((4'-methyl-[1,1'-biphenyl]-2-yl)ethynyl)-N-phenylbenzenesulfonamide (1a)



1a

^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.06 (m, 17H), 2.37 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.6, 143.3, 138.8, 137.7, 136.8, 132.9, 132.6, 129.3, 129.0, 128.8, 128.7, 128.1, 127.9, 126.7, 126.1, 121.1, 85.3, 70.3, 21.6, 21.2; IR (neat): 3059, 3025, 2921, 2235, 1594, 1490, 1480, 1373, 1174, 758, 691, 576; MS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{23}\text{NNaO}_2\text{S}]^+$: 460.1; Found: 460.1; HRMS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{23}\text{NNaO}_2\text{S}]^+$: 460.1342; Found: 460.1350.

N-((4-fluoro-4'-methyl-[1,1'-biphenyl]-2-yl)ethynyl)-4-methyl-N-phenylbenzenesulfonamide (1b)

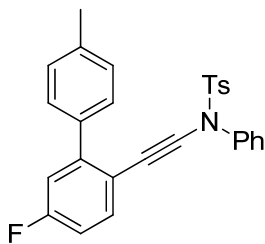


1b

^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.21 (m, 8H), 7.16 – 6.97 (m, 8H), 2.37 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.3 (d, $J = 245.0$ Hz), 144.8, 139.4 (d, $J = 3.2$ Hz), 138.5, 137.0, 136.8, 132.8, 130.8 (d, $J = 8.6$ Hz), 129.3, 129.0, 128.9, 128.8, 128.1, 128.0, 126.1, 122.7 (d, $J = 9.8$ Hz), 118.6 (d, $J = 22.8$ Hz), 115.1 (d, $J = 21.2$ Hz), 86.2, 69.5, 21.6, 21.1; IR (neat): 3064, 3028, 2922, 2235, 1596, 1487, 1374, 1175, 811,

691, 577; MS (ES⁺) Calculated for [C₂₈H₂₂FNNaO₂S]⁺: 478.1; Found: 478.1; HRMS (ES⁺) Calculated for [C₂₈H₂₂FNNaO₂S]⁺: 478.1247; Found: 478.1255.

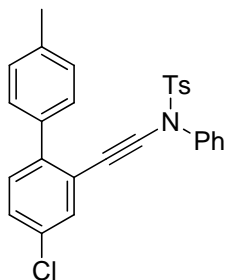
N-((5-fluoro-4'-methyl-[1,1'-biphenyl]-2-yl)ethynyl)-4-methyl-N-phenylbenzenesulfonamide (1c)



1c

¹H NMR (500 MHz, CDCl₃) δ 7.45 (dd, 1H, *J* = 8.5 Hz, *J* = 6.0 Hz), 7.37 (d, 2H, *J* = 8.0 Hz), 7.32 (d, 2H, *J* = 8.0 Hz), 7.25 – 7.19 (m, 3H), 7.13 (t, 4H, *J* = 7.5 Hz), 7.08 – 7.02 (m, 3H), 6.94 (td, 1H, *J* = 8.5 Hz, *J* = 2.5 Hz), 2.38 (s, 3H), 2.36 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 162.1 (d, *J* = 247.9 Hz), 145.8 (d, *J* = 8.0 Hz), 144.7, 138.7, 137.4, 136.7, 134.5 (d, *J* = 8.5 Hz), 133.0, 129.3, 128.9, 128.8(3), 128.8(2), 128.1, 128.0, 126.1, 117.1 (d, *J* = 3.1 Hz), 116.2 (d, *J* = 34.6 Hz), 114.0 (d, *J* = 21.8 Hz), 84.9, 69.3, 21.5, 21.1; IR (neat): 3063, 2922, 2237, 1597, 1488, 1371, 1355, 1175, 822, 772, 691, 579; MS (ES⁺) Calculated for [C₂₈H₂₂FNNaO₂S]⁺: 478.1; Found: 478.1; HRMS (ES⁺) Calculated for [C₂₈H₂₂FNNaO₂S]⁺: 478.1247; Found: 478.1254.

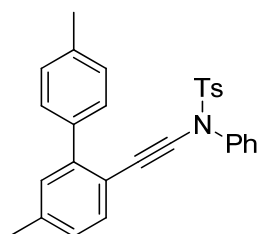
N-((4-chloro-4'-methyl-[1,1'-biphenyl]-2-yl)ethynyl)-4-methyl-N-phenylbenzenesulfonamide (1d)



1d

^1H NMR (400 MHz, CDCl_3) δ 7.44 (s, 1H), 7.37 (d, 2H, $J = 8.0$ Hz), 7.31 – 7.22 (m, 7H), 7.16 – 7.06 (m, 6H), 2.38 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.8, 141.5, 138.5, 137.2, 136.6, 132.8, 132.5, 131.8, 130.5, 129.4, 128.9, 128.8, 128.1, 128.0, 128.0, 126.1, 122.7, 86.4, 69.4, 21.6, 21.2; IR (neat): 3062, 3027, 2922, 2855, 2233, 1590, 1490, 1479, 1375, 1175, 811, 691, 575; MS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{22}\text{ClNNaO}_2\text{S}]^+$: 494.1; Found: 494.1; HRMS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{22}\text{ClNNaO}_2\text{S}]^+$: 494.0952; Found: 494.0956.

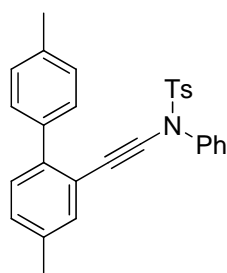
N-((4',5-dimethyl-[1,1'-biphenyl]-2-yl)ethynyl)-4-methyl-N-phenylbenzenesulfonamide (1e)



1e

^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.36 (m, 3H), 7.31 (d, 2H, $J = 8.0$ Hz), 7.20 (d, 3H, $J = 8.0$ Hz), 7.16 – 7.01 (m, 8H), 2.36 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.5, 143.4, 138.9, 138.0, 137.8, 136.7, 132.8, 132.6, 130.0, 129.2, 129.0, 128.7, 128.6, 128.0, 127.8, 127.6, 126.0, 117.9, 84.5, 70.2, 21.5, 21.3, 21.1; IR (neat): 3027, 2921, 2235, 1594, 1489, 1372, 1174, 817, 691, 579; MS (ES^+) Calculated for $[\text{C}_{29}\text{H}_{25}\text{NNaO}_2\text{S}]^+$: 474.2; Found: 474.2; HRMS (ES^+) Calculated for $[\text{C}_{29}\text{H}_{25}\text{NNaO}_2\text{S}]^+$: 474.1498; Found: 474.1505.

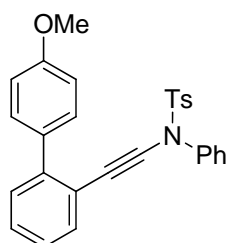
N-((4,4'-dimethyl-[1,1'-biphenyl]-2-yl)ethynyl)-4-methyl-N-phenylbenzenesulfonamide (1f)



1f

^1H NMR (500 MHz, CDCl_3) δ 7.37 (d, 2H, $J = 8.0$ Hz), 7.33 – 7.29 (m, 3H), 7.23 – 7.05 (m, 11H), 2.34 (s, 3H), 2.33 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 144.5, 140.5, 138.8, 137.6, 136.5, 136.4, 132.9, 132.8, 129.2, 129.1, 129.0, 128.8, 128.7, 128.6, 128.0, 127.8, 126.0, 120.7, 84.9, 70.4, 21.5, 21.1, 20.6; IR (neat): 3023, 2921, 2858, 2233, 1595, 1489, 1372, 1174, 811, 691, 575; MS (ES^+) Calculated for $[\text{C}_{29}\text{H}_{25}\text{NNaO}_2\text{S}]^+$: 474.2; Found: 474.2; HRMS (ES^+) Calculated for $[\text{C}_{29}\text{H}_{25}\text{NNaO}_2\text{S}]^+$: 474.1498; Found: 474.1505.

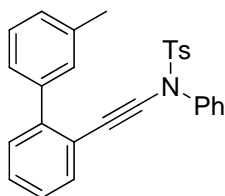
N-((4'-methoxy-[1,1'-biphenyl]-2-yl)ethynyl)-4-methyl-N-phenylbenzenesulfonamide (1g)



1g

^1H NMR (500 MHz, CDCl_3) δ 7.50 – 7.40 (m, 3H), 7.36 – 7.17 (m, 8H), 7.13 – 7.03 (m, 4H), 6.85 (d, $J = 8.5$ Hz, 2H), 3.77 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.0, 144.6, 143.0, 138.8, 133.0, 132.9, 132.6, 130.2, 129.3, 129.2, 128.8, 128.0, 127.9(3), 127.9(2), 126.5, 126.0, 120.9, 85.3, 70.3, 55.1, 21.5; IR (neat): 2924, 2851, 2235, 1609, 1516, 1480, 1372, 1175; MS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{23}\text{NNaO}_3\text{S}]^+$: 476.1; Found: 476.1; HRMS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{23}\text{NNaO}_3\text{S}]^+$: 476.1291; Found: 476.1295.

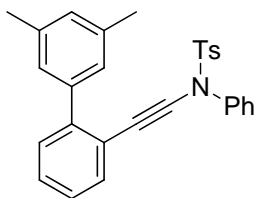
**4-methyl-N-((3'-methyl-[1,1'-biphenyl]-2-yl)ethynyl)-N-phenylbenzenesulfonamide
(1h)**



1h

^1H NMR (400 MHz, CDCl_3) δ 7.47 (d, 1H, $J = 7.6$ Hz), 7.36 – 7.16 (m, 11H), 7.16 – 7.02 (m, 5H), 2.33 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 144.6, 143.3, 140.6, 138.8, 137.6, 132.7, 132.4, 129.9, 129.3, 129.2, 128.8, 127.9(8), 127.9(5), 127.9(2), 127.8, 126.8, 126.1, 125.9, 121.0, 85.3, 70.2, 21.5, 21.3; IR (neat): 3062, 2921, 2236, 1594, 1490, 1454, 1373, 1176; MS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{23}\text{NNaO}_2\text{S}]^+$: 460.1; Found: 460.1; HRMS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{23}\text{NNaO}_2\text{S}]^+$: 460.1342; Found: 460.1351.

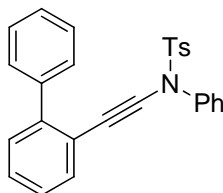
N-((3',5'-dimethyl-[1,1'-biphenyl]-2-yl)ethynyl)-4-methyl-N-phenylbenzenesulfonamide (1i)



1i

^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.45 (m, 1H), 7.34 – 7.19 (m, 8H), 7.04 – 6.95 (m, 6H), 6.97 (s, 1H), 2.34 (s, 3H), 2.27 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.5, 143.4, 140.6, 138.8, 137.5, 132.7, 132.4, 129.4, 129.2, 128.9, 128.8, 128.0, 127.9, 127.8, 127.0, 126.8, 125.9, 121.0, 85.2, 70.4, 21.5, 21.2; IR (neat): 3062, 3029, 2920, 2857, 2236, 1596, 1490, 1374, 1175, 759, 691, 584; MS (ES^+) Calculated for $[\text{C}_{29}\text{H}_{25}\text{NNaO}_2\text{S}]^+$: 474.2; Found: 474.2; HRMS (ES^+) Calculated for $[\text{C}_{29}\text{H}_{25}\text{NNaO}_2\text{S}]^+$: 474.1498; Found: 474.1507.

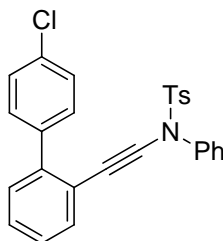
N-([1,1'-biphenyl]-2-ylethynyl)-4-methyl-N-phenylbenzenesulfonamide (1j)



1j

^1H NMR (400 MHz, CDCl_3) δ 7.53 – 7.49 (m, 3H), 7.36 – 7.33 (m, 5H), 7.30 – 7.21 (m, 6H), 7.11 (d, 2H, $J = 8.4$ Hz), 7.07 (d, 2H, $J = 8.0$ Hz), 2.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.6, 143.3, 140.7, 138.8, 132.8, 132.6, 129.4, 129.3, 129.2, 128.9, 128.1, 128.1, 128.0, 127.2, 127.0, 126.1, 121.1, 85.4, 70.2, 21.6; IR (neat): 3060, 2924, 2236, 1593, 1490, 1374, 1175, 755, 692, 568; MS (ES^+) Calculated for $[\text{C}_{27}\text{H}_{21}\text{NNaO}_2\text{S}]^+$: 446.1; Found: 446.1; HRMS (ES^+) Calculated for $[\text{C}_{27}\text{H}_{21}\text{NNaO}_2\text{S}]^+$: 446.1185; Found: 446.1193.

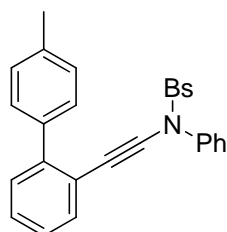
N-((4'-chloro-[1,1'-biphenyl]-2-yl)ethynyl)-4-methyl-N-phenylbenzenesulfonamide (1k)



1k

^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, 1H, $J = 7.6$ Hz), 7.42 (d, 2H, $J = 8.0$ Hz), 7.37 – 7.23 (m, 10H), 7.16 (d, 2H, $J = 8.0$ Hz), 7.07 (d, 2H, $J = 7.6$ Hz), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.8, 141.9, 138.9, 138.5, 133.1, 132.8, 132.6, 130.4, 129.3, 129.0, 128.9, 128.0, 127.8, 127.3, 126.0, 120.9, 85.7, 69.6, 21.5; IR (neat): 3063, 2920, 2849, 2234, 1594, 1490, 1476, 1374, 1173, 760, 691, 585; MS (ES^+) Calculated for $[\text{C}_{27}\text{H}_{20}\text{ClNNaO}_2\text{S}]^+$: 480.1; Found: 480.1; HRMS (ES^+) Calculated for $[\text{C}_{27}\text{H}_{20}\text{ClNNaO}_2\text{S}]^+$: 480.0795; Found: 480.0802.

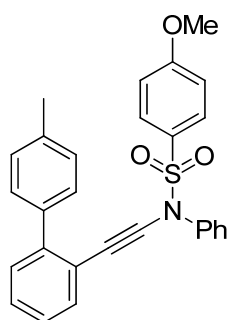
**4-bromo-N-((4'-methyl-[1,1'-biphenyl]-2-yl)ethynyl)-N-phenylbenzenesulfonamide
(1l)**



1l

^1H NMR (500 MHz, CDCl_3) δ 7.50 – 7.46 (m, 1H), 7.46 – 7.38 (m, 4H), 7.35 – 7.30 (m, 2H), 7.28 – 7.16 (m, 8H), 7.10 – 7.06 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.5, 138.5, 137.8, 137.0, 134.6, 132.6, 131.9, 129.4, 129.4, 129.1, 129.0, 128.9, 128.8, 128.2, 128.2, 126.8, 126.1, 120.7, 84.7, 70.6, 21.2; IR (neat): 3059, 2921, 2853, 2236, 1572, 1489, 1390, 1378, 1181, 821, 742, 604; MS (ES^+) Calculated for $[\text{C}_{27}\text{H}_{20}\text{BrNNaO}_2\text{S}]^+$: 524.0; Found: 524.0; HRMS (ES^+) Calculated for $[\text{C}_{27}\text{H}_{20}\text{BrNNaO}_2\text{S}]^+$: 524.0290; Found: 524.0299.

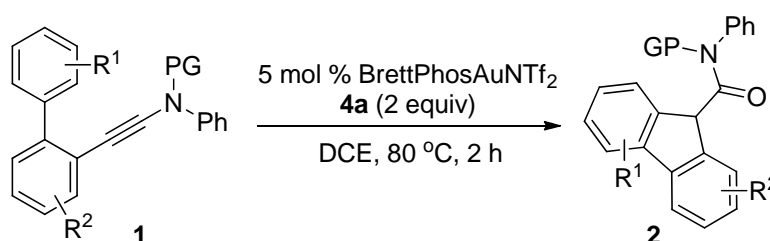
**4-methoxy-N-((4'-methyl-[1,1'-biphenyl]-2-yl)ethynyl)-N-phenylbenzenesulfonamide
(1m)**



1m

^1H NMR (400 MHz, CDCl_3) δ 7.47 (dd, 1H, $J = 7.2$ Hz, $J = 6.4$ Hz), 7.39 (d, 2H, $J = 8.0$ Hz), 7.36 – 7.18 (m, 8H), 7.14 (d, 2H, $J = 8.0$ Hz), 7.08 (dd, 2H, $J = 8.0$ Hz, $J = 1.6$ Hz), 6.75 (d, 2H, $J = 8.8$ Hz), 3.77 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.6,

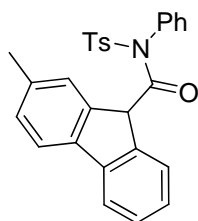
143.2, 138.8, 137.7, 136.8, 132.5, 130.2, 129.2, 129.0, 128.8, 128.7, 127.9, 127.2, 126.7, 126.1, 121.0, 113.8, 85.4, 70.3, 55.5, 21.1; IR (neat): 3058, 3023, 2922, 2234, 1593, 1495, 1371, 1112, 832, 691, 674; MS (ES⁺) Calculated for [C₂₈H₂₃NNaO₃S]⁺: 476.1; Found: 476.1; HRMS (ES⁺) Calculated for [C₂₈H₂₃NNaO₃S]⁺: 476.1291; Found: 476.1294.



General procedure:

8-Ethylquinoline *N*-oxide (103.9 mg, 0.60 mmol) and BrettPhosAuNTf₂ (15.3 mg, 0.015 mmol) were added to a solution of the *o*-alkynylbiaryls **1** (0.30 mmol) in DCE (6.0 mL) at room temperature. The reaction mixture was stirred at 80 °C and the progress of the reaction was monitored by TLC. The reaction typically took 2 h. Upon completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the desired products **2**.

2-methyl-N-phenyl-N-tosyl-9H-fluorene-9-carboxamide (**2a**)

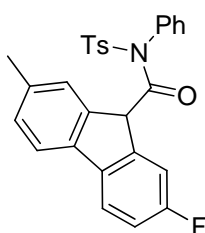


2a

Compound **2a** was prepared in 77% yield according to the general procedure (Table 2, entry 1). ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, 2H, *J* = 8.0 Hz), 7.40 – 7.29 (m, 5H), 7.26 – 7.13 (m, 4H), 7.10 – 7.00 (m, 3H), 6.75 (d, 2H, *J* = 7.6 Hz), 4.76 (s, 1H), 2.44 (s,

3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.5, 144.8, 141.6, 141.1, 140.7, 138.9, 137.3, 135.7, 133.7, 130.7, 129.3, 129.2, 128.9, 128.5, 128.0, 126.8, 124.7, 124.1, 121.6, 119.9, 119.9, 56.1, 21.6, 21.5; IR (neat): 2924, 2853, 1695, 1591, 1485, 1350, 1137, 747, 697, 567; MS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{23}\text{NNaO}_3\text{S}]^+$: 476.1; Found: 476.1; HRMS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{23}\text{NNaO}_3\text{S}]^+$: 476.1291; Found: 476.1295.

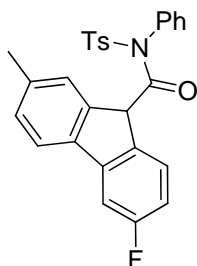
2-fluoro-7-methyl-N-phenyl-N-tosyl-9H-fluorene-9-carboxamide (2b)



2b

Compound **2b** was prepared in 75% yield according to the general procedure (Table 2, entry 2). ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, 2H, $J = 8.4$ Hz), 7.37 – 7.17 (m, 6H), 7.14 – 7.01 (m, 4H), 7.00 – 6.93 (m, 1H), 6.80 (d, 2H, $J = 7.6$ Hz), 4.75 (s, 1H), 2.47 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.9, 162.1 (d, $J = 244.8$ Hz), 145.1, 142.6 (d, $J = 8.4$ Hz), 141.1, 138.0, 137.7 (d, $J = 1.7$ Hz), 137.1, 135.6, 133.8, 130.7, 129.4, 129.4, 129.3, 129.1, 128.7, 124.8, 120.8 (d, $J = 8.7$ Hz), 119.7, 115.1 (d, $J = 22.8$ Hz), 111.6 (d, $J = 23.3$ Hz), 56.0, 21.6, 21.5; IR (neat): 2919, 2850, 1698, 1464, 1367, 1172, 810, 701, 573; MS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{22}\text{FNNaO}_3\text{S}]^+$: 494.1; Found: 494.1; HRMS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{22}\text{FNNaO}_3\text{S}]^+$: 494.1197; Found: 494.1207.

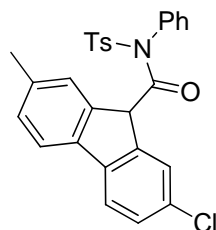
6-fluoro-2-methyl-N-phenyl-N-tosyl-9H-fluorene-9-carboxamide (2c)



2c

Compound **2c** was prepared in 56% yield according to the general procedure (Table 2, entry 3). ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, 2H, $J = 8.0$ Hz), 7.34 – 7.24 (m, 4H), 7.22 – 7.17 (m, 2H), 7.11 (d, 1H, $J = 7.6$ Hz), 7.08 – 7.00 (m, 3H), 6.89 (td, 1H, $J = 8.8$ Hz, $J = 2.4$ Hz), 6.73 (d, 2H, $J = 7.6$ Hz), 4.73 (s, 1H), 2.45 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.2, 163.2 (d, $J = 244.0$ Hz), 145.0, 143.8 (d, $J = 9.2$ Hz), 142.1, 138.2, 138.0 (d, $J = 3.0$ Hz), 136.2 (d, $J = 2.5$ Hz), 135.6, 133.7, 130.7, 129.4, 129.3(2), 129.2(9), 129.1, 128.6, 125.2 (d, $J = 9.3$ Hz), 124.9, 120.2, 113.6 (d, $J = 23.2$ Hz), 107.0 (d, $J = 23.2$ Hz), 55.6, 21.7, 21.6; IR (neat): 2921, 2851, 1691, 1594, 1487, 1364, 1171, 813, 694, 565; MS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{22}\text{FNNaO}_3\text{S}]^+$: 494.1; Found: 494.1; HRMS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{22}\text{FNNaO}_3\text{S}]^+$: 494.1197; Found: 494.1206.

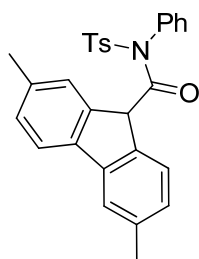
2-chloro-7-methyl-N-phenyl-N-tosyl-9H-fluorene-9-carboxamide (2d)



2d

Compound **2d** was prepared in 67% yield according to the general procedure (Table 2, entry 4). ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, 2H, $J = 8.0$ Hz), 7.35 (d, 2H, $J = 8.0$ Hz), 7.30 (d, 2H, $J = 7.6$ Hz), 7.25 (d, 2H, $J = 6.0$ Hz), 7.21 (d, 2H, $J = 8.8$ Hz), 7.10 (t, 3H, $J = 7.6$ Hz), 6.83 (d, 2H, $J = 7.6$ Hz), 4.74 (s, 1H), 2.47 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.8, 145.1, 142.4, 141.2, 140.3, 137.9, 137.8, 135.6, 133.9, 132.4, 130.8, 129.5, 129.4, 129.3, 129.2, 128.8, 128.3, 124.9, 124.5, 120.8, 120.0, 55.8, 21.7, 21.6; IR (neat): 2920, 2851, 1679, 1594, 1459, 1363, 1166, 814, 694, 568; MS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{22}\text{ClINNaO}_3\text{S}]^+$: 510.1; Found: 510.1; HRMS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{22}\text{ClINNaO}_3\text{S}]^+$: 510.0901; Found: 510.0910.

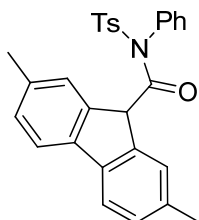
2,6-dimethyl-N-phenyl-N-tosyl-9H-fluorene-9-carboxamide (2e)



2e

Compound **2e** was prepared in 58% yield according to the general procedure (Table 2, entry 5). ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, 2H, $J = 8.0$ Hz), 7.34 – 6.99 (m, 11H), 6.80 (d, 2H, $J = 7.6$ Hz), 4.71 (s, 1H), 2.44 (s, 3H), 2.37 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.7, 144.8, 141.8, 141.6, 139.0, 138.0, 137.9, 137.2, 135.8, 134.0, 130.8, 129.3, 129.2, 128.8, 128.6, 127.7, 124.8, 123.8, 120.5, 119.8, 55.7, 21.6, 21.5, 21.4; IR (neat): 2921, 2852, 1697, 1596, 1488, 1364, 1171, 801, 694, 573; MS (ES^+) Calculated for $[\text{C}_{29}\text{H}_{25}\text{NNaO}_3\text{S}]^+$: 490.1; Found: 490.1; HRMS (ES^+) Calculated for $[\text{C}_{29}\text{H}_{25}\text{NNaO}_3\text{S}]^+$: 490.1447; Found: 490.1456.

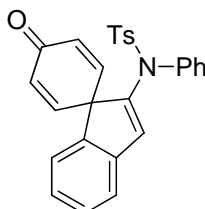
2,7-dimethyl-N-phenyl-N-tosyl-9H-fluorene-9-carboxamide (2f)



2f

Compound **2f** was prepared in 64% yield according to the general procedure (Table 2, entry 6). ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, 2H, $J = 8.4$ Hz), 7.35 – 7.06 (m, 11H), 6.82 (d, 2H, $J = 7.6$ Hz), 4.72 (s, 1H), 2.46 (s, 3H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.7, 144.8, 141.1, 139.0, 136.8, 135.8, 134.0, 130.8, 129.3, 129.3, 128.8, 128.6, 124.7, 119.7, 55.9, 21.7, 21.5; IR (neat): 2923, 2853, 1703, 1596, 1487, 1469, 1361, 1171, 808, 695, 565; MS (ES^+) Calculated for $[\text{C}_{29}\text{H}_{25}\text{NNaO}_3\text{S}]^+$: 490.1; Found: 490.1; HRMS (ES^+) Calculated for $[\text{C}_{29}\text{H}_{25}\text{NNaO}_3\text{S}]^+$: 490.1447; Found: 490.1455.

4-methyl-N-(4-oxospiro[cyclohexa[2,5]diene-1,1'-inden]-2'-yl)-N-phenylbenzenesulfonamide (2g')

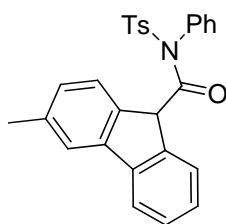


2g'

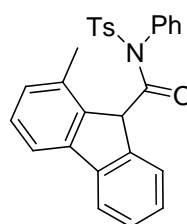
Compound **2g'** was prepared in 86% yield according to the general procedure (Table 2, entry 7). ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, 2H, $J = 8.4$ Hz), 7.39 (d, 1H, $J = 7.6$ Hz), 7.37 – 7.23 (m, 6H), 7.21 – 7.15 (m, 3H), 7.13 (s, 1H), 6.90 (d, 1H, $J = 7.6$ Hz), 6.08 (d, 2H, $J = 10.0$ Hz), 6.00 (d, 2H, $J = 10.0$ Hz), 2.47 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 185.8, 146.5, 145.3, 144.4, 142.0, 139.1, 138.2, 136.2, 130.0, 129.9, 129.6, 128.9, 128.8, 128.3, 126.8, 126.6, 123.3, 122.1, 59.8, 21.6; IR (neat): 3062, 2921, 2236, 1594, 1490, 1454, 1373, 1176; MS (ES^+) Calculated for $[\text{C}_{27}\text{H}_{21}\text{NNaO}_3\text{S}]^+$: 462.1; Found: 462.1; HRMS (ES^+) Calculated for $[\text{C}_{27}\text{H}_{21}\text{NNaO}_3\text{S}]^+$: 462.1134; Found: 462.1131.

3-methyl-N-phenyl-N-tosyl-9H-fluorene-9-carboxamide (2h)

1-methyl-N-phenyl-N-tosyl-9H-fluorene-9-carboxamide (2h')



2h

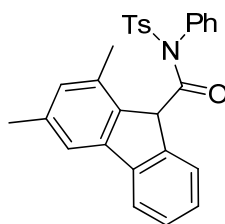


2h'

Compound **2h** and **2h'** (**2h/2h'** = 3/1) were prepared in 72% yield according to the general procedure (Table 2, entry 8). Compound **2h**: ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, 2H, $J = 8.0$ Hz), 7.38 (d, 2H, $J = 7.6$ Hz), 7.36 – 7.12 (m, 7H), 7.12 – 6.94 (m, 3H),

6.73 (d, 2H, $J = 7.6$ Hz), 4.76 (s, 1H), 2.43 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.6, 144.8, 141.6, 141.5, 141.3, 138.1, 137.9, 135.7, 133.8, 130.7, 129.3, 129.2, 129.1, 128.4, 128.2, 128.0, 127.2, 124.2, 123.8, 120.8, 120.1, 56.0, 21.6, 21.4; IR (neat): 3039, 2923, 2855, 1716, 1698, 1596, 1488, 1450, 1365, 1171; MS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{23}\text{NNaO}_3\text{S}]^+$: 476.1; Found: 476.1; HRMS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{23}\text{NNaO}_3\text{S}]^+$: 476.1291; Found: 476.1294. Mixtures of compound **2h** and compound **2h'**: ^1H NMR (400 MHz, CDCl_3) δ 7.91 – 7.86 (m, 2H), 7.44 – 7.15 (m, 8H), 7.07 – 6.98 (m, 3H), 6.88 – 6.78 (m, 1H), 6.74 – 6.70 (m, 1H), 6.54 – 6.43 (m, 1H), 4.79 (s, 0.5H), 4.77 (s, 0.5H), 2.47 (s, 1.5H), 2.46 (s, 1.5H), 2.38 (s, 1.5H), 2.33 (s, 1.5H).

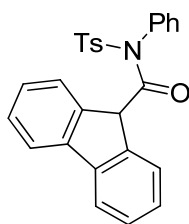
1,3-dimethyl-N-phenyl-N-tosyl-9H-fluorene-9-carboxamide (**2i**)



2i

Compound **2i** was prepared in 88% yield according to the general procedure (Table 2, entry 9). ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, 2H, $J = 8.4$ Hz), 7.41 (d, 1H, $J = 7.2$ Hz), 7.32 (d, 3H, $J = 8.0$ Hz), 7.25 – 7.18 (m, 2H), 7.09 (t, 1H, $J = 7.2$ Hz), 6.99 (s, 1H), 6.86 (s, 3H), 6.54 (s, 2H), 4.73 (s, 1H), 2.46 (s, 3H), 2.33 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.2, 144.8, 141.8, 141.5, 140.9, 138.0, 136.7, 136.0, 134.1, 133.2, 130.4, 129.6, 129.3, 129.2, 129.0, 127.9, 126.9, 123.8, 120.2, 118.3, 56.2, 21.6, 21.2, 18.8; IR (neat): 2921, 2852, 1688, 1595, 1487, 1363, 1170, 694, 563; MS (ES^+) Calculated for $[\text{C}_{29}\text{H}_{25}\text{NNaO}_3\text{S}]^+$: 490.1; Found: 490.1; HRMS (ES^+) Calculated for $[\text{C}_{29}\text{H}_{25}\text{NNaO}_3\text{S}]^+$: 490.1447; Found: 490.1454.

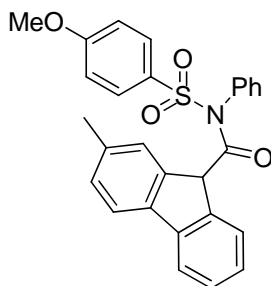
N-phenyl-N-tosyl-9H-fluorene-9-carboxamide (**2j**)



2j

Compound **2j** was prepared in 54% yield according to the general procedure (Table 2, entry 10). ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, 2H, $J = 8.4$ Hz), 7.40 (d, 4H, $J = 7.6$ Hz), 7.33 – 7.19 (m, 6H), 7.13 (t, 1H, $J = 7.6$ Hz), 6.96 (t, 2H, $J = 7.6$ Hz), 6.68 (d, 2H, $J = 7.6$ Hz), 4.81 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.4, 144.9, 141.4, 140.8, 135.7, 133.5, 130.8, 129.3, 129.2, 129.2, 128.4, 128.0, 127.3, 124.2, 120.2, 56.5, 21.6; IR (neat): 2924, 2853, 1693, 1595, 1449, 1359, 1172, 742, 681, 570; MS (ES^+) Calculated for $[\text{C}_{27}\text{H}_{21}\text{NNaO}_3\text{S}]^+$: 462.1; Found: 462.1; HRMS (ES^+) Calculated for $[\text{C}_{27}\text{H}_{21}\text{NNaO}_3\text{S}]^+$: 462.1134; Found: 462.1145.

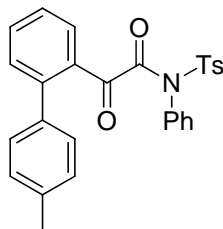
N-((4-methoxyphenyl)sulfonyl)-2-methyl-N-phenyl-9H-fluorene-9-carboxamide (2m)



2m

Compound **2m** was prepared in 71% yield according to the general procedure (Table 2, entry 13). ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, 2H, $J = 8.8$ Hz), 7.45 – 7.14 (m, 7H), 7.10 (d, 1H, $J = 8.0$ Hz), 7.08 – 6.93 (m, 4H), 6.76 (d, 2H, $J = 7.6$ Hz), 4.76 (s, 1H), 3.88 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.6, 163.8, 141.6, 141.2, 140.8, 138.9, 137.4, 134.0, 131.6, 130.8, 130.0, 129.2, 128.9, 128.6, 128.0, 126.8, 124.8, 124.1, 120.0, 119.9, 113.8, 56.1, 55.6, 21.6; IR (neat): 2921, 2951, 1697, 1592, 1488, 1346, 1133, 696, 568; MS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{23}\text{NNaO}_4\text{S}]^+$: 492.1; Found: 492.1; HRMS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{23}\text{NNaO}_4\text{S}]^+$: 492.1240; Found: 492.1246.

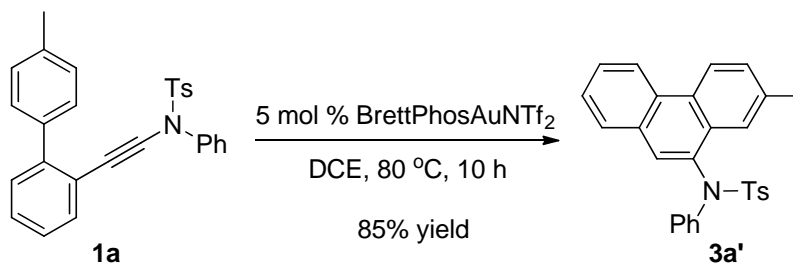
2-(4'-methyl-[1,1'-biphenyl]-2-yl)-2-oxo-N-phenyl-N-tosylacetamide (3a)



3a

^1H NMR (500 MHz, CDCl_3) 7.96 (d, 1H, $J = 7.5$ Hz), 7.66 (d, 2H, $J = 8.3$ Hz), 7.55 (td, 1H, $J = 7.5$ Hz, 1.0 Hz), 7.44 (t, 1H, $J = 7.5$ Hz), 7.38 – 7.16 (m, 10H), 6.83 (d, 2H, $J = 7.5$ Hz), 2.44 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 187.9, 166.0, 145.4, 144.3, 137.4, 136.9, 134.1, 133.5, 133.1, 132.0, 131.3, 131.2, 130.5, 129.8, 129.5, 129.4, 129.1, 129.0, 128.8, 127.2, 21.6, 21.2; IR (neat): 2958, 2931, 2872, 1737(s), 1713(s), 1642, 1489, 1408, 1306, 1173, 1049, 1012, 913, 743; MS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{23}\text{NNaO}_4\text{S}]^+$: 492.1; Found: 492.1; HRMS (ES^+) Calculated for $[\text{C}_{28}\text{H}_{23}\text{NNaO}_4\text{S}]^+$: 492.1240; Found: 492.1248.

4-methyl-N-(7-methylphenanthren-9-yl)-N-phenylbenzenesulfonamide (3a')

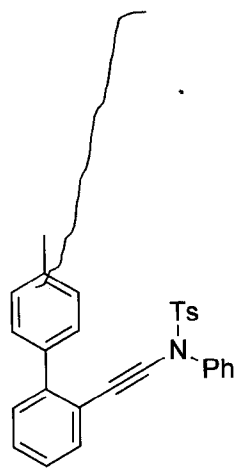


^1H NMR (400 MHz, CDCl_3) δ 8.55 (d, 1H, $J = 8.4$ Hz), 8.49 (d, 1H, $J = 8.4$ Hz), 8.13 (s, 1H), 7.75 – 7.47 (m, 8H), 7.42 (d, 1H, $J = 8.0$ Hz), 7.31 – 7.10 (m, 5H), 2.49 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.7, 141.3, 137.2, 137.1, 135.6, 130.8, 130.6, 130.4, 129.6, 129.4, 129.0, 128.9, 128.7, 128.5, 128.0, 127.5, 126.6, 126.4, 124.2, 122.7, 122.4, 21.8, 21.50; IR (neat): 2919, 2850, 1640, 1630, 1485, 1353, 1164, 749, 692, 571;

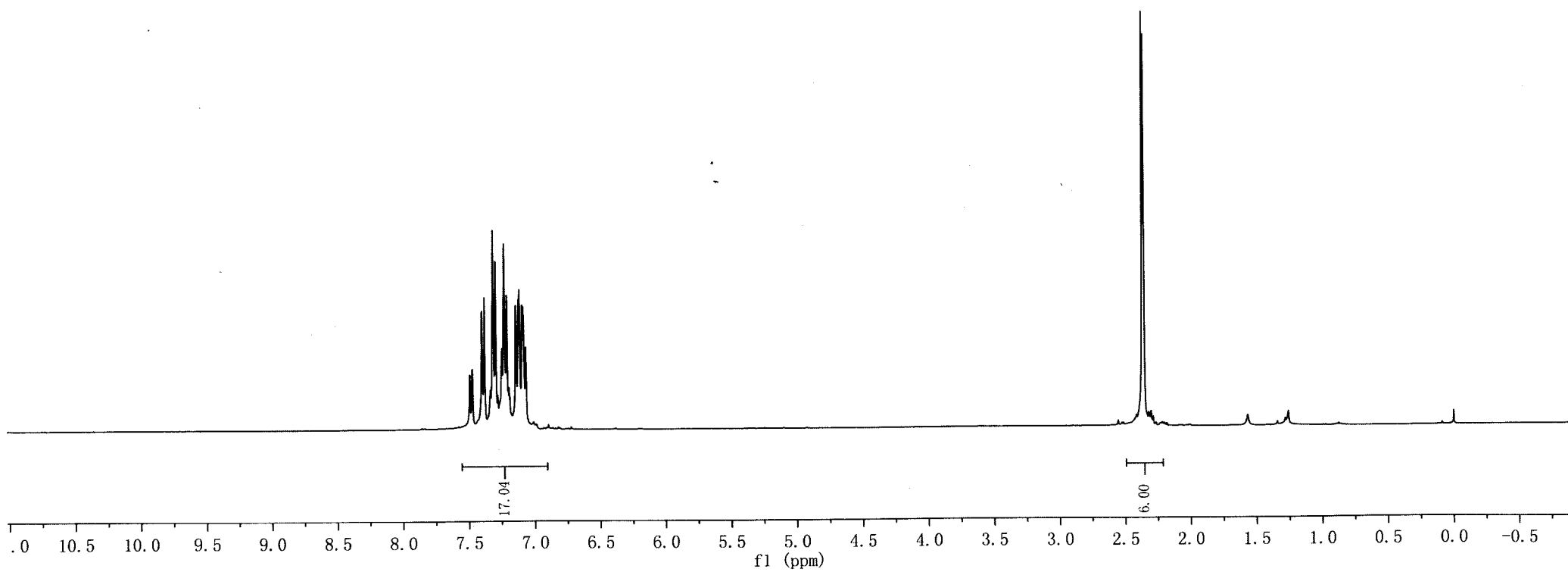
MS (ES⁺) Calculated for [C₂₈H₂₃NNaO₂S]⁺: 460.1; Found: 460.1; HRMS (ES⁺)
Calculated for [C₂₈H₂₃NNaO₂S]⁺: 460.1342; Found: 460.1352.

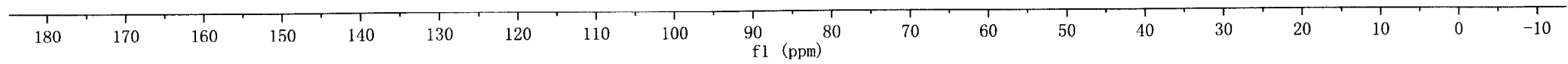
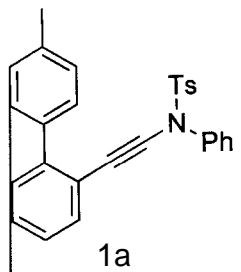
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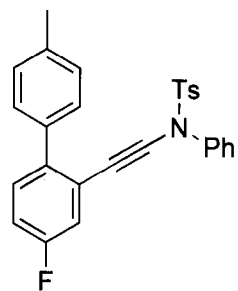
1. a) D. Hojo, K. Tanaka, *Org. Lett.* **2012**, *14*, 1492; b) P.-Y. Yao, Y. Zhang, R. P. Hsung, K. Zhao, *Org. Lett.* **2008**, *10*, 4275; c) Natalia Chernyak, Vladimir Gevorgyan, *Adv. Synth. Catal.* **2009**, *351*, 1101.



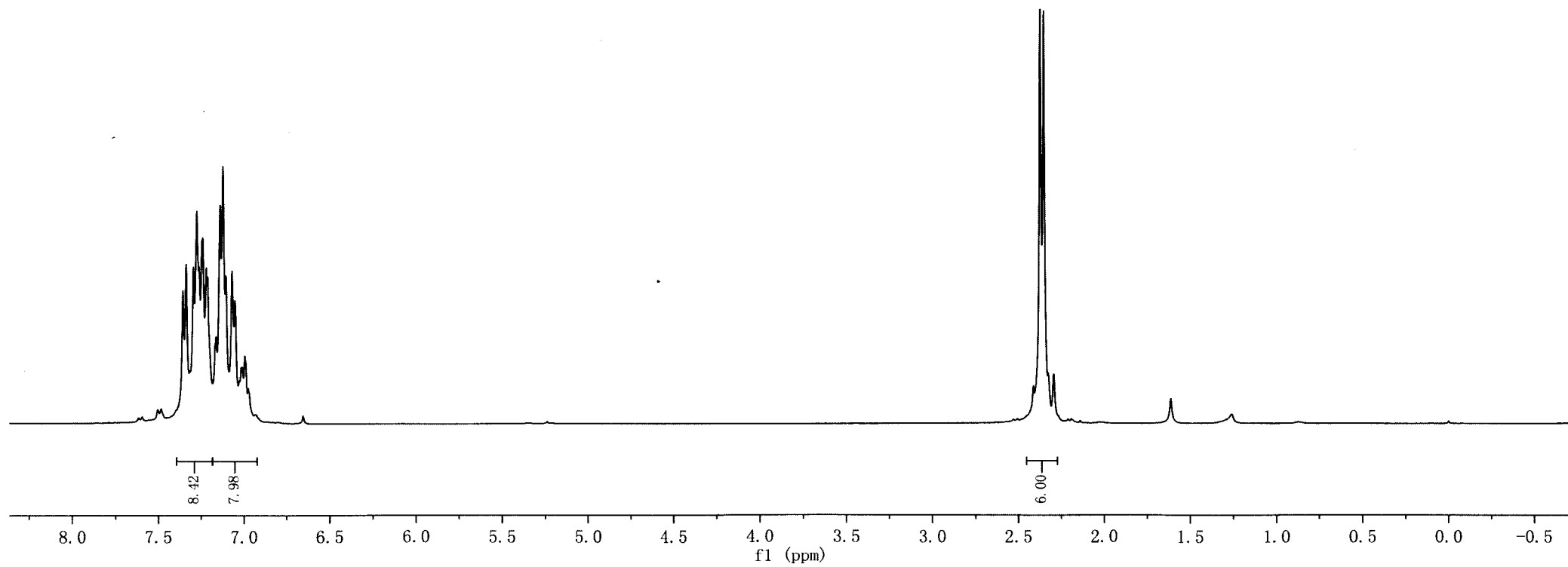
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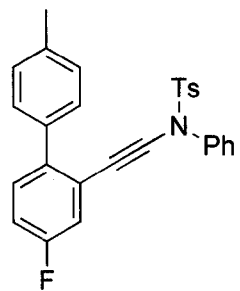




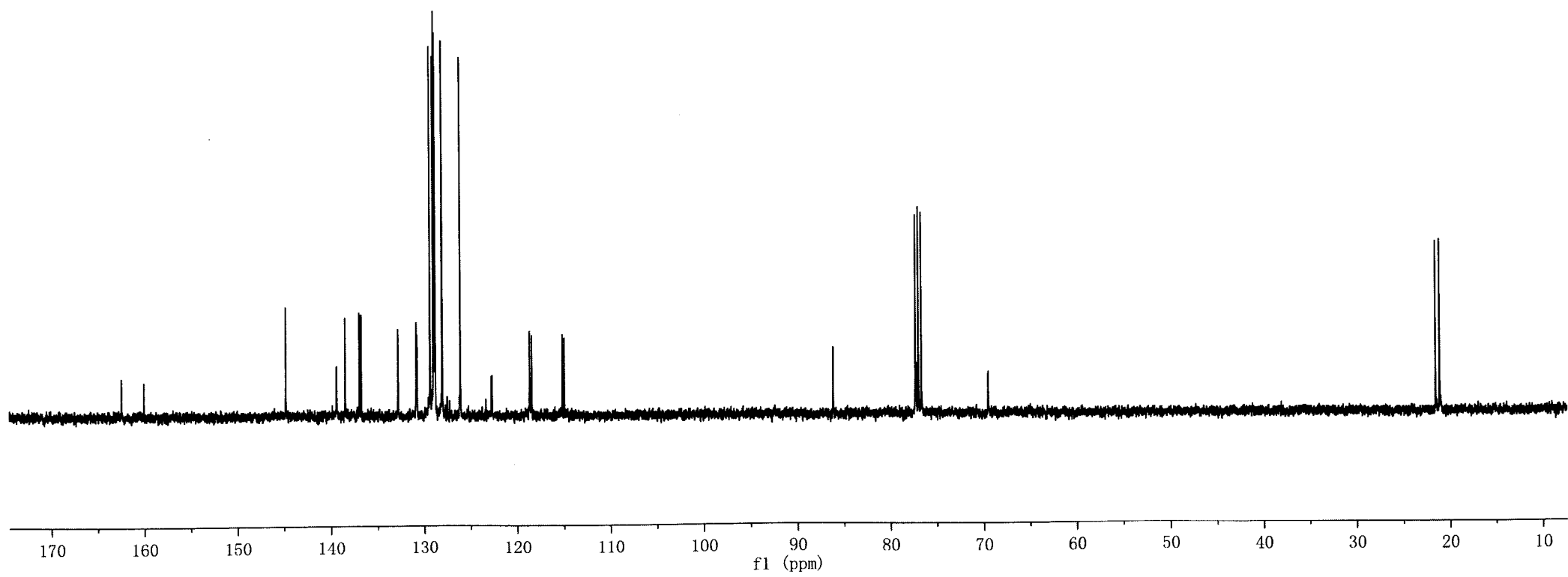


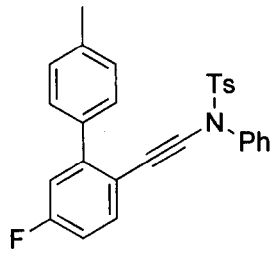
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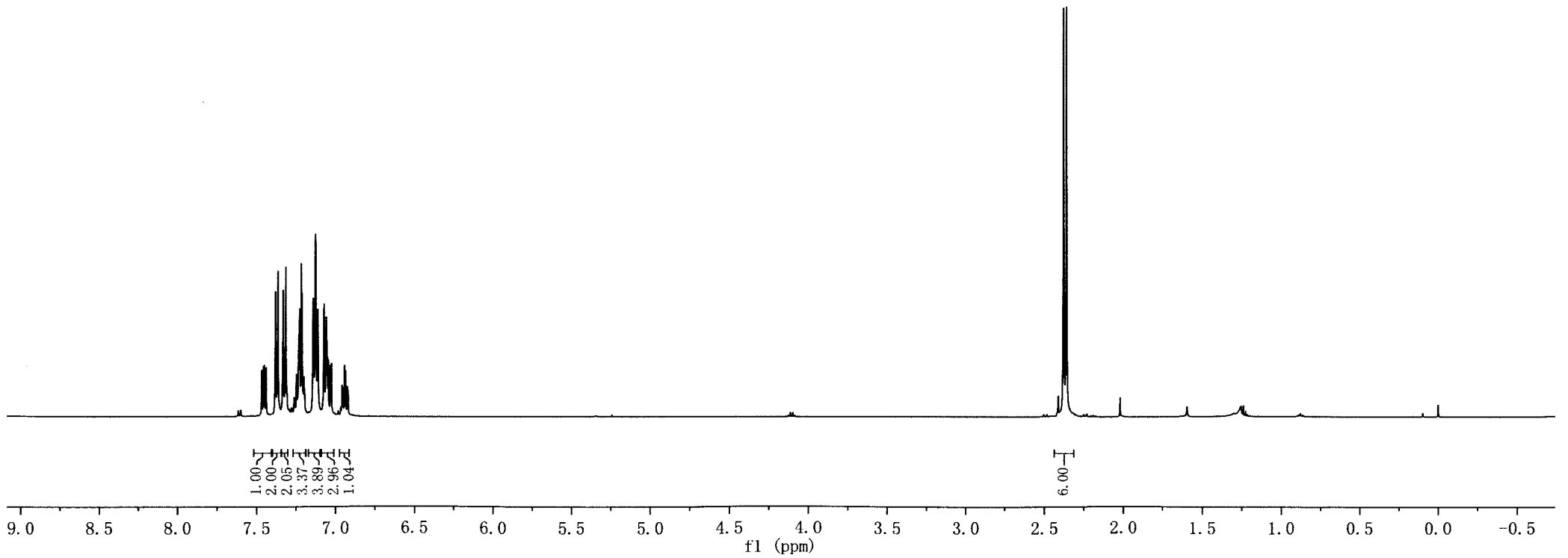


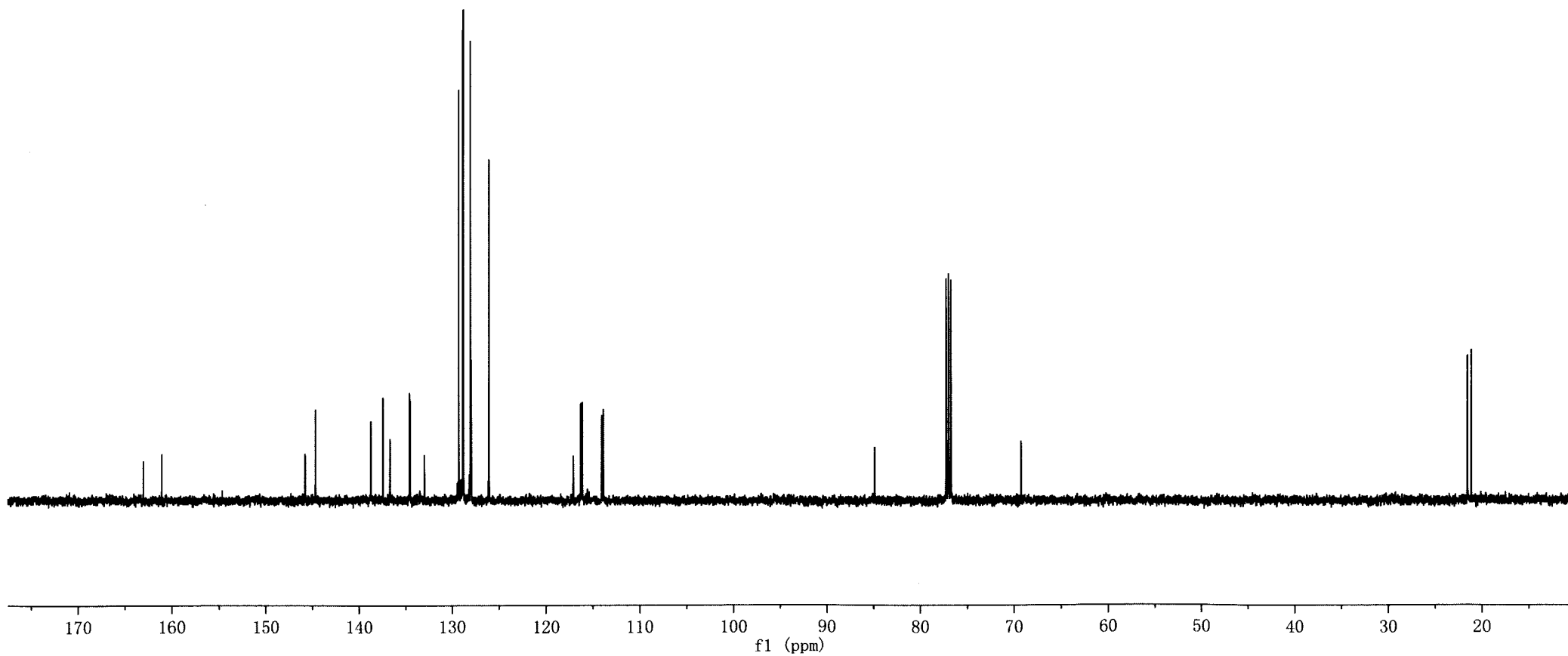
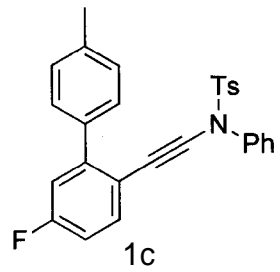
1b

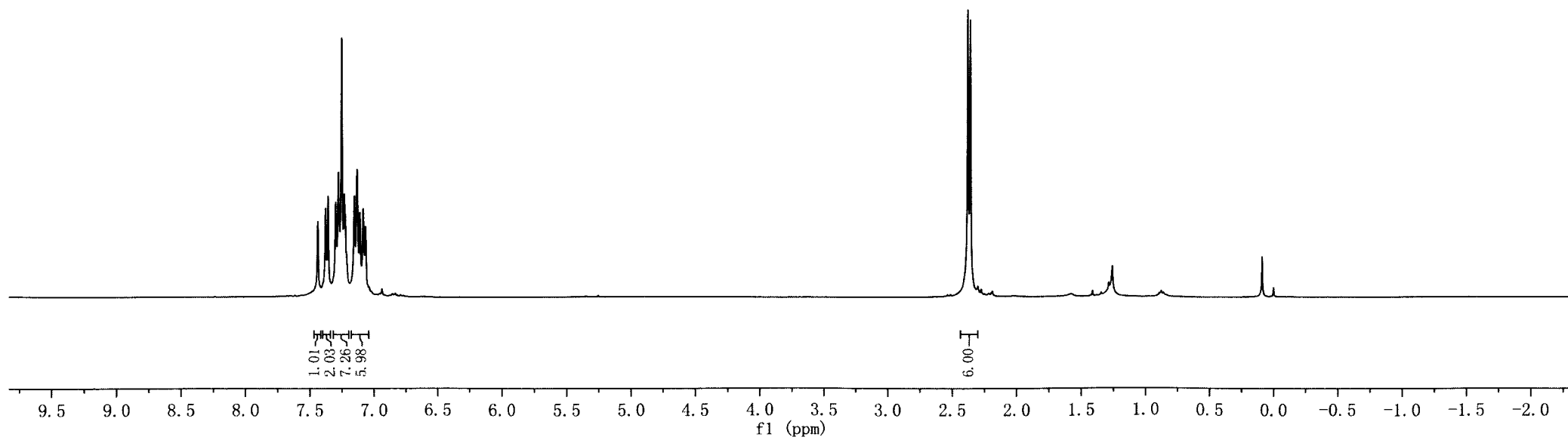
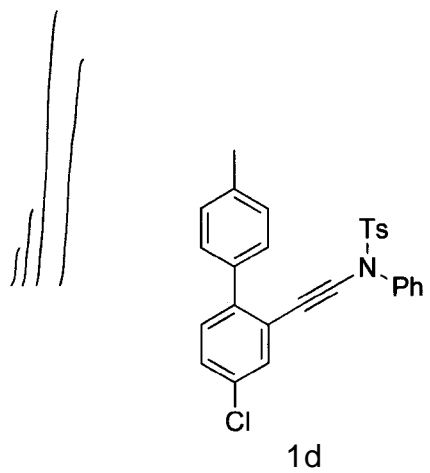


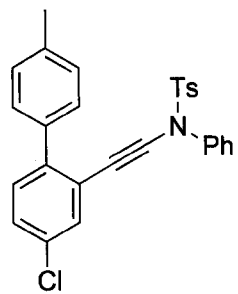


1c

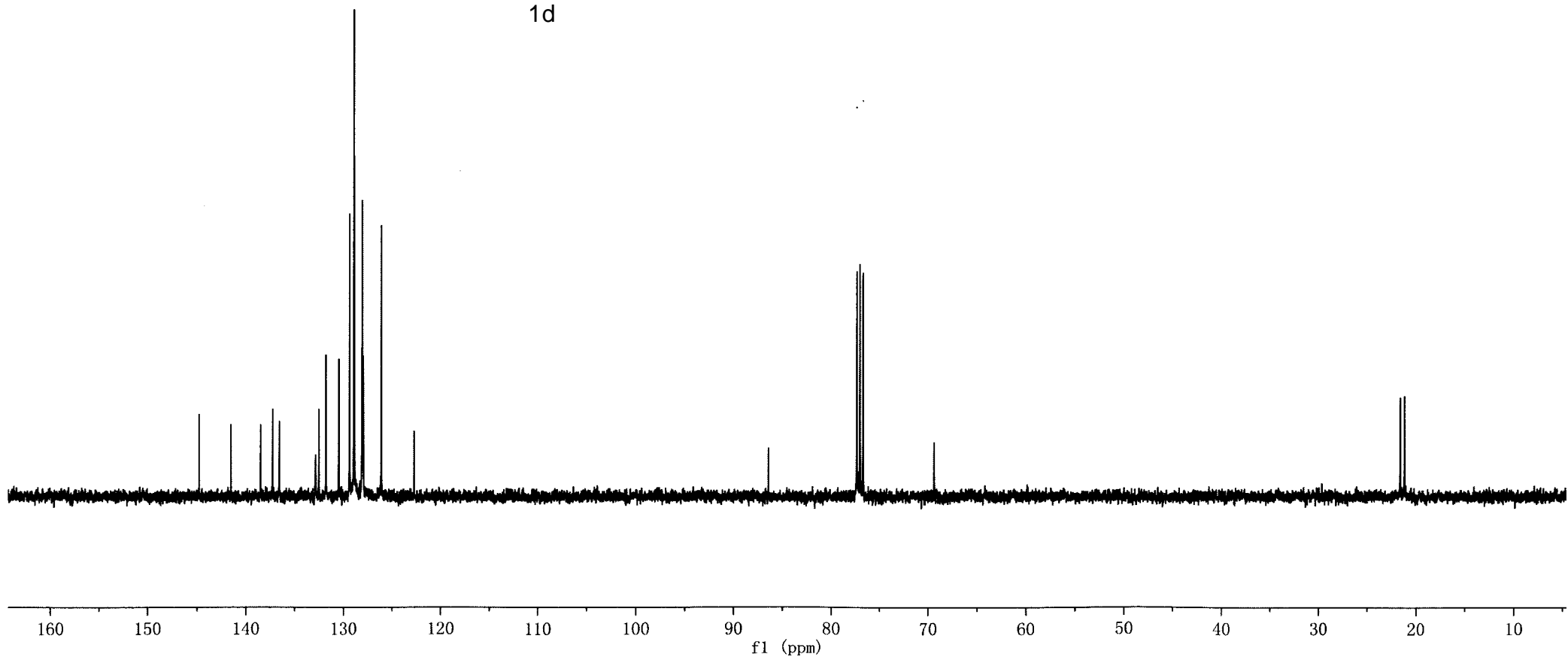


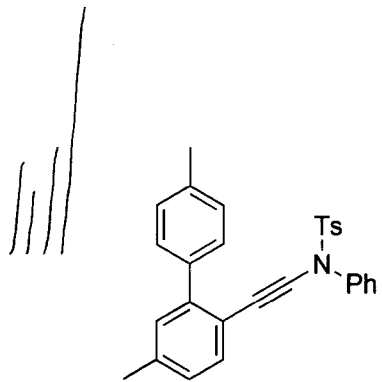




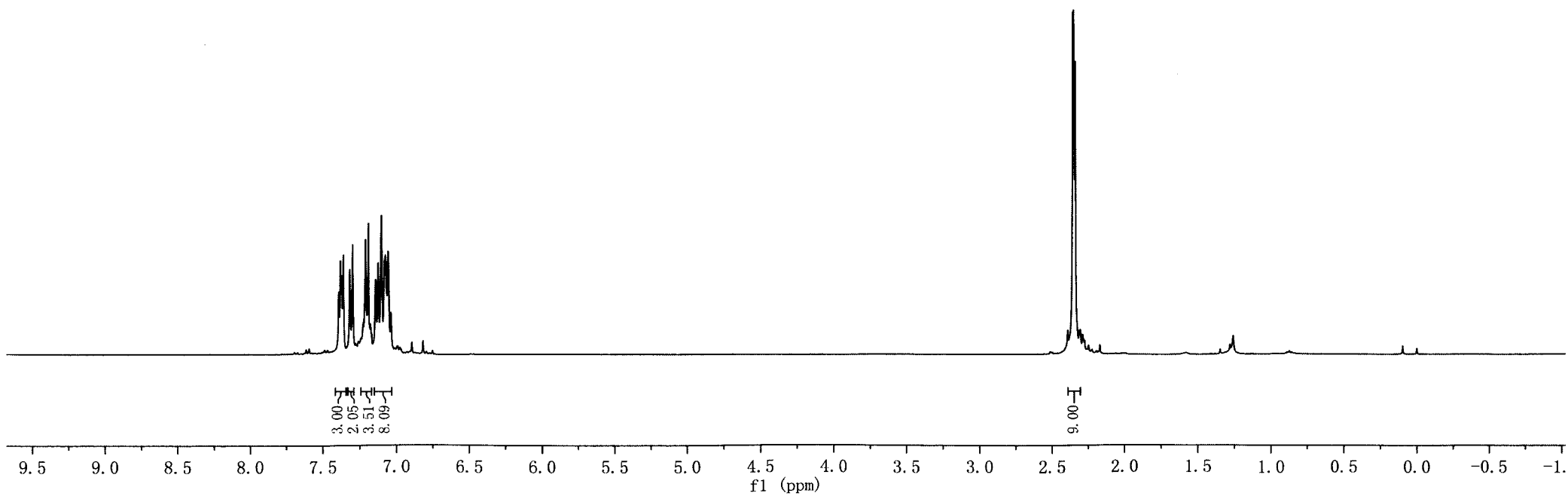


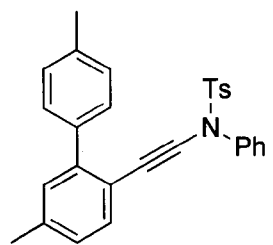
1d



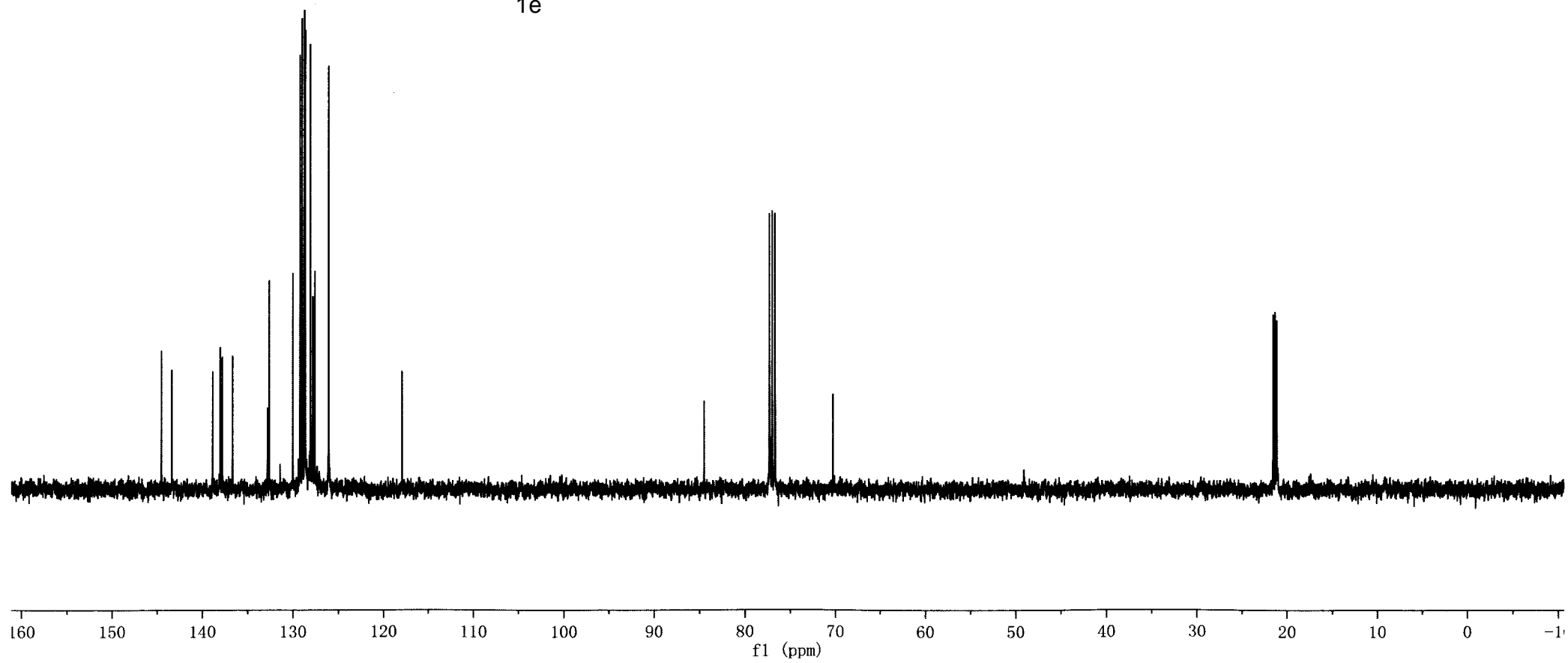


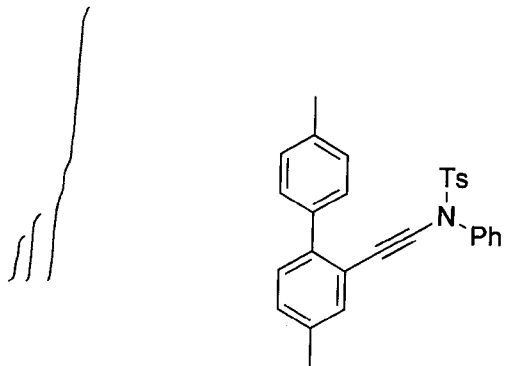
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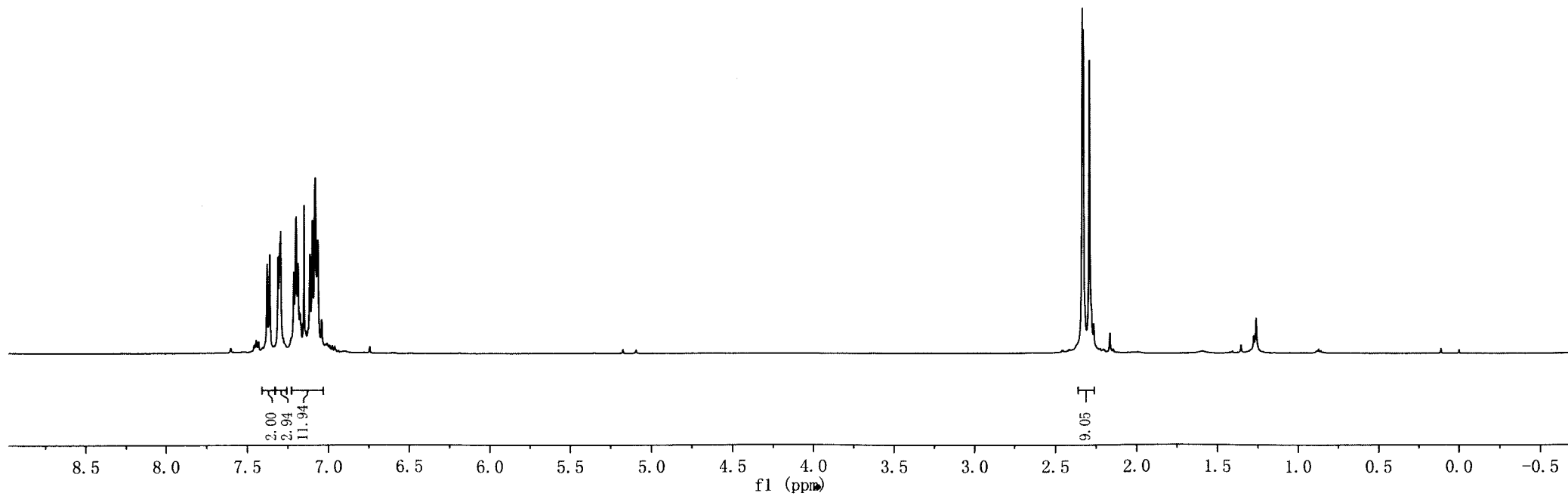


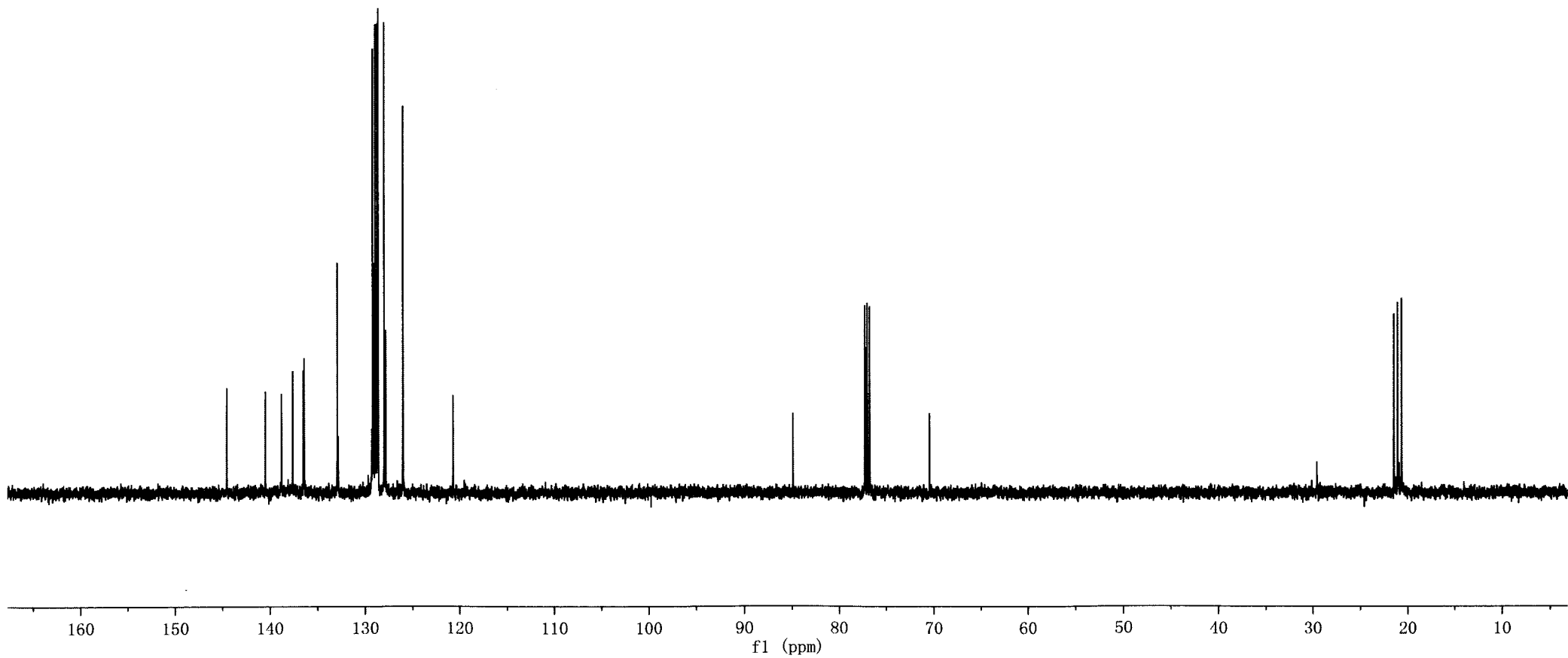
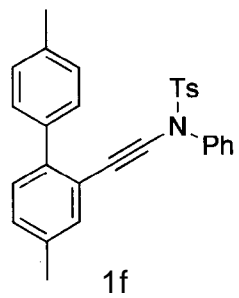
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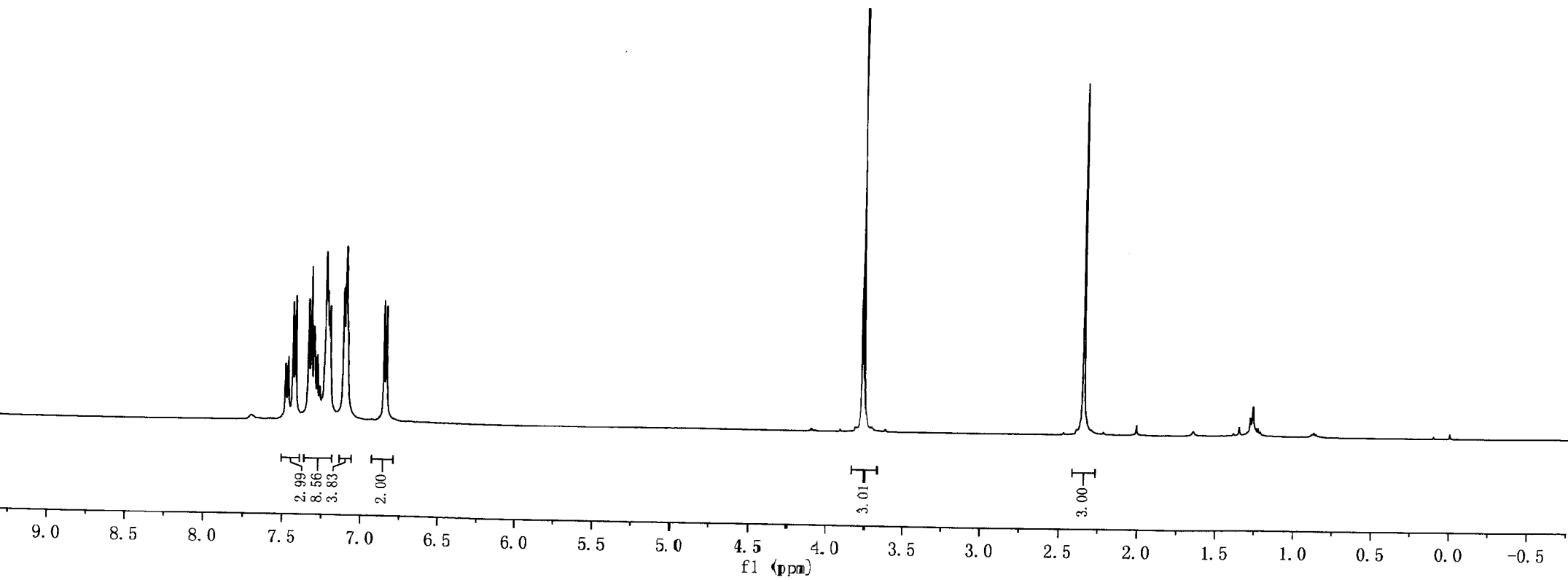
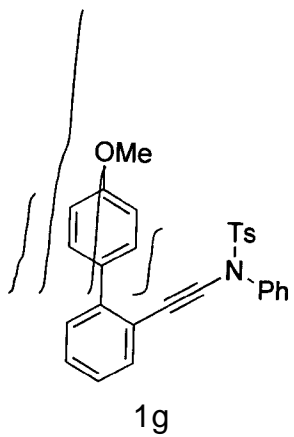


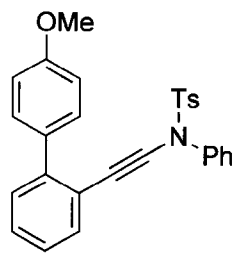


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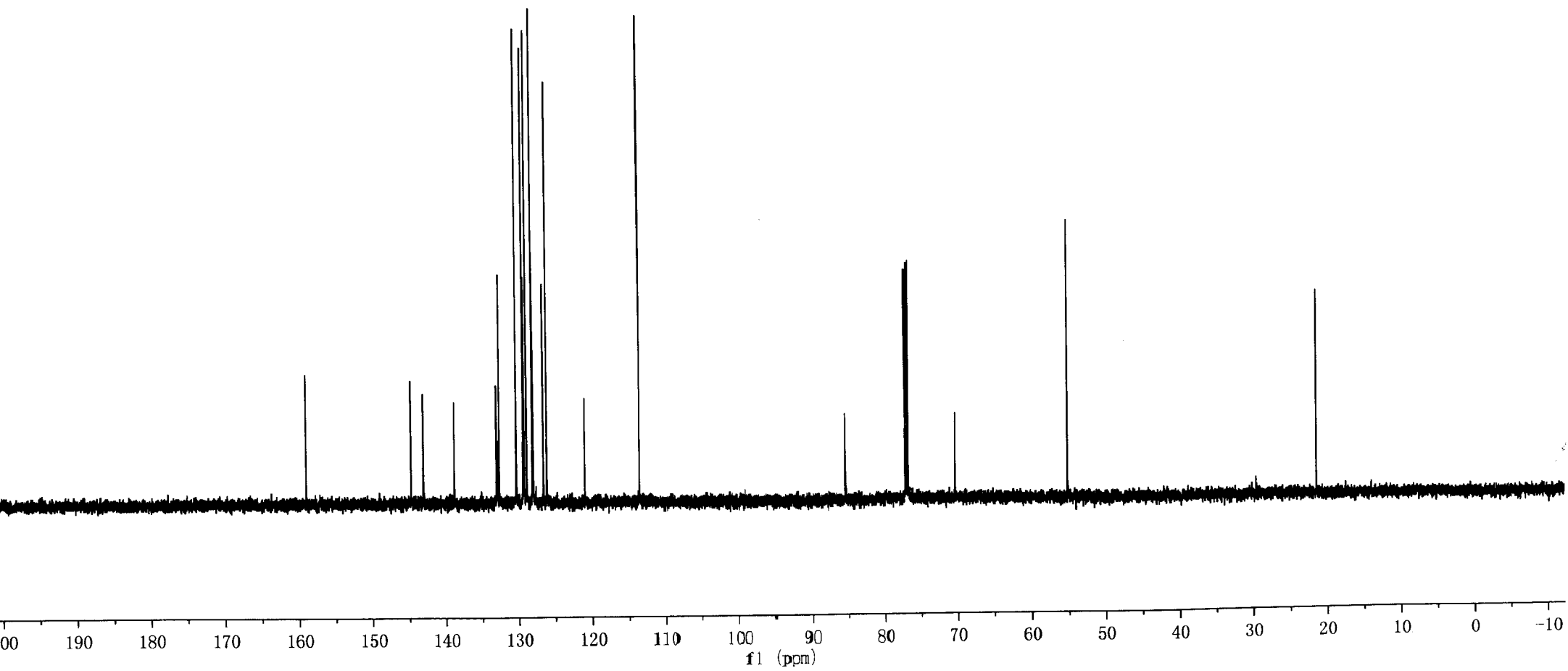


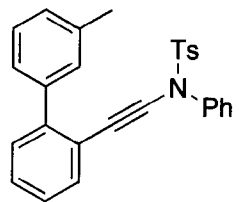




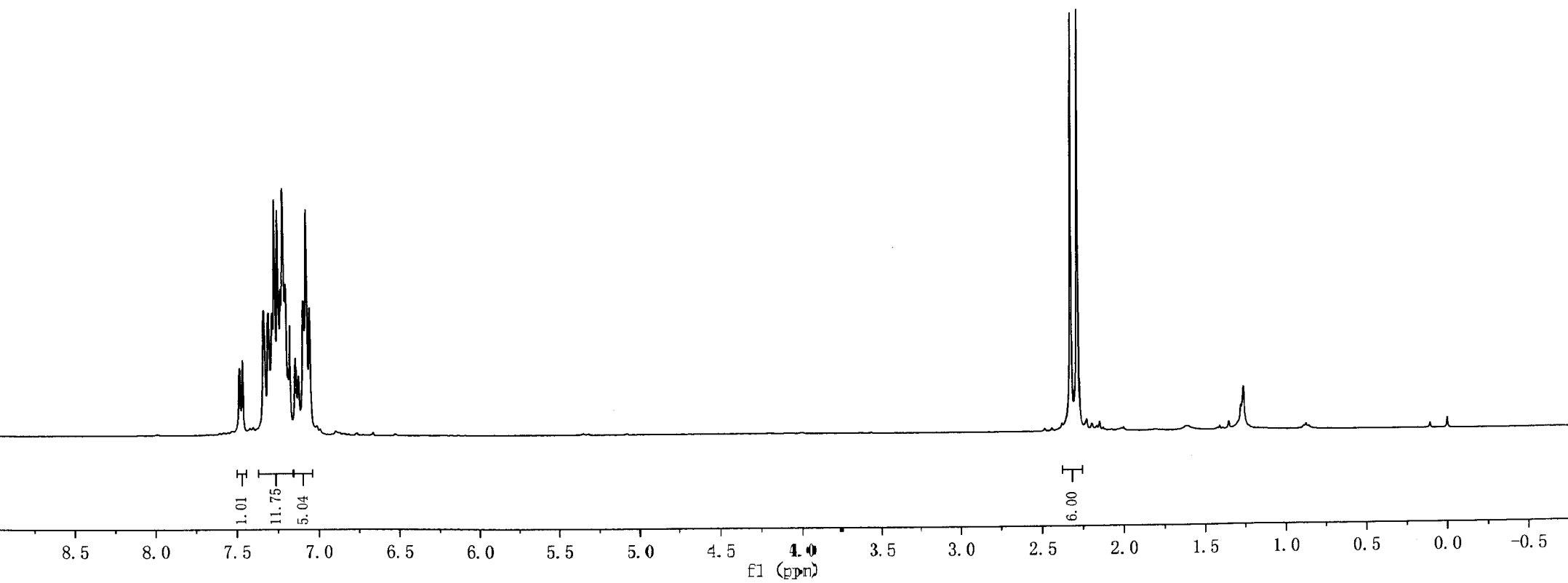


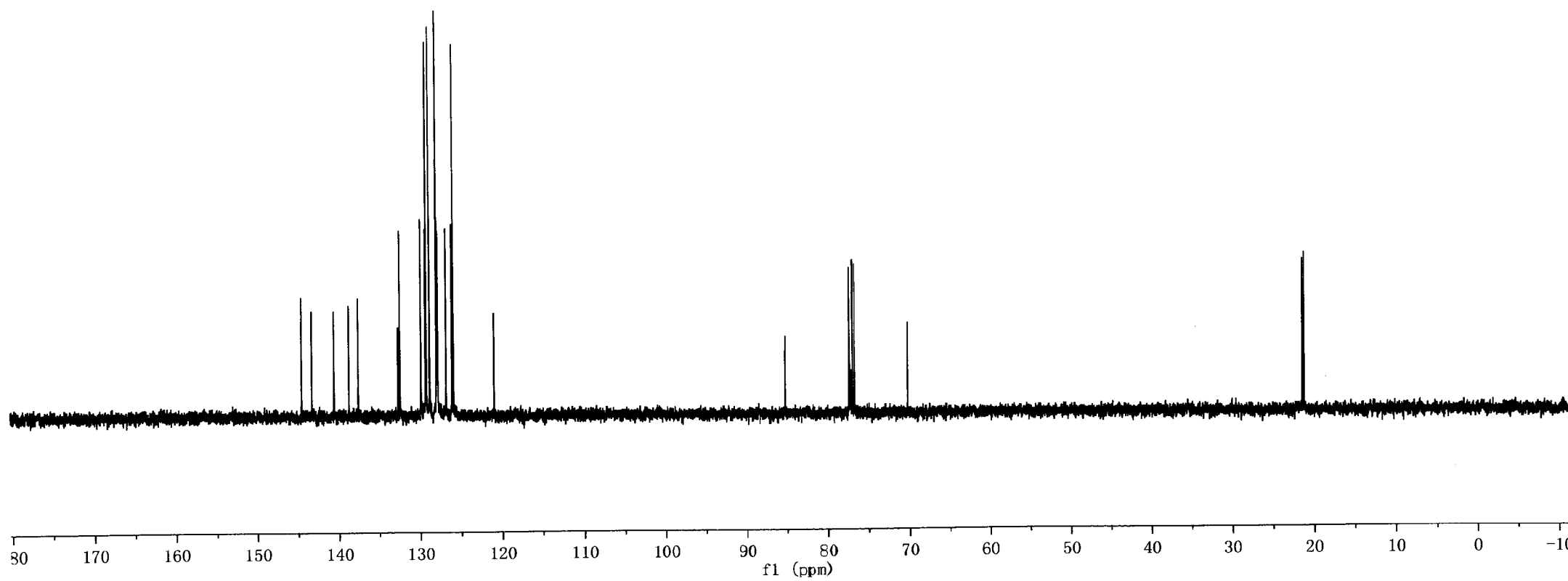
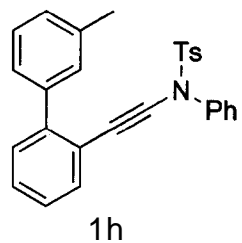
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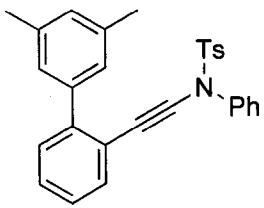




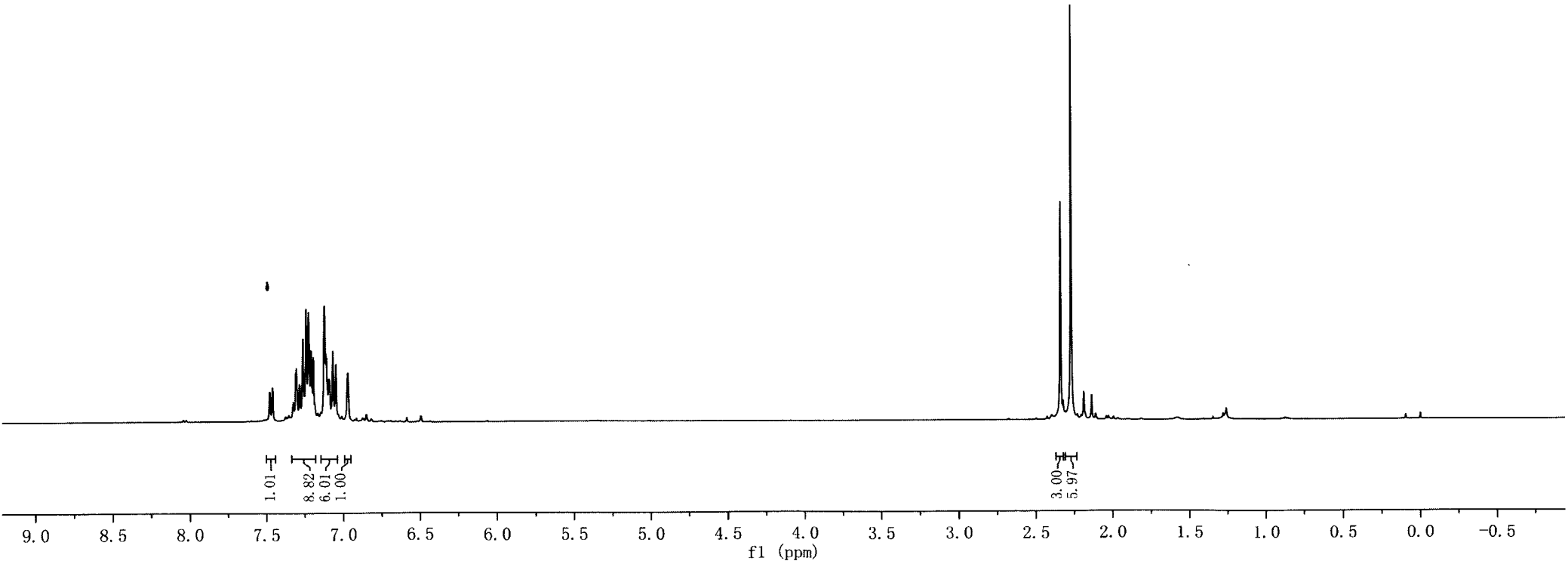
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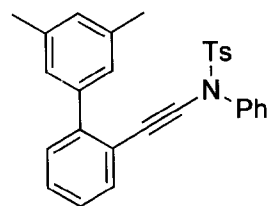




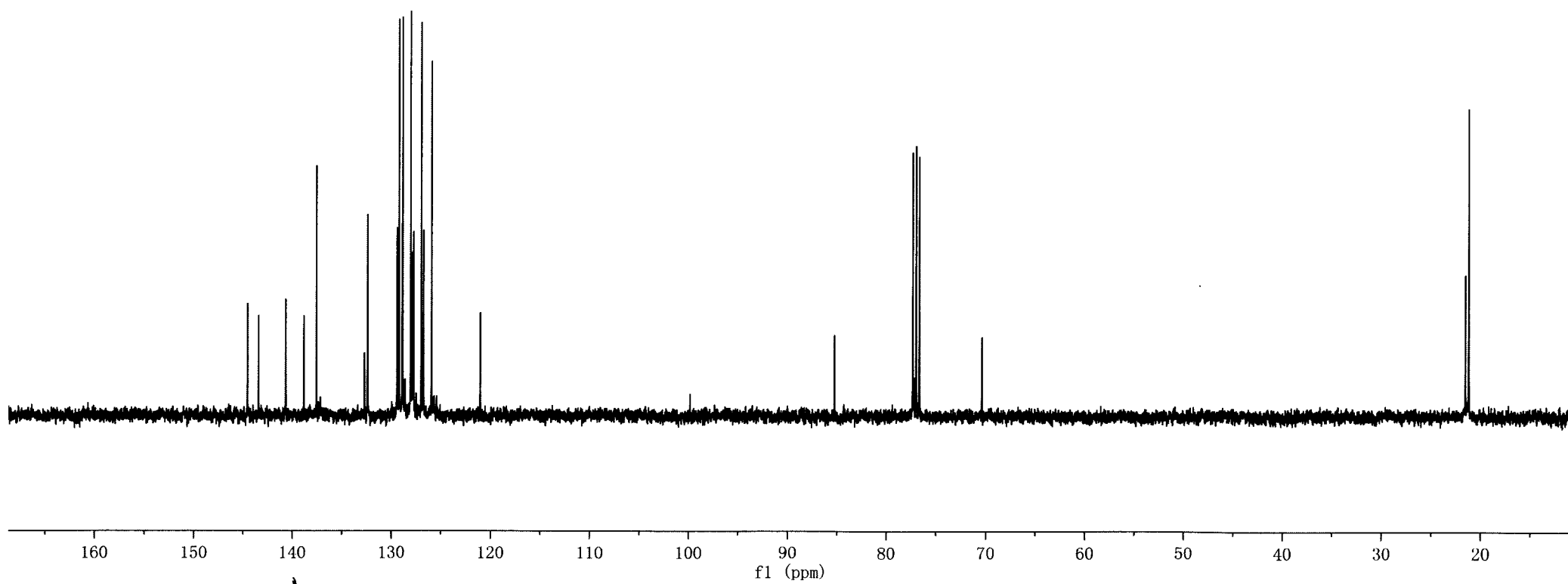


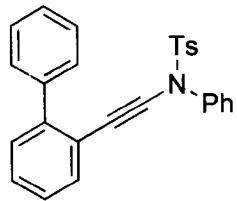
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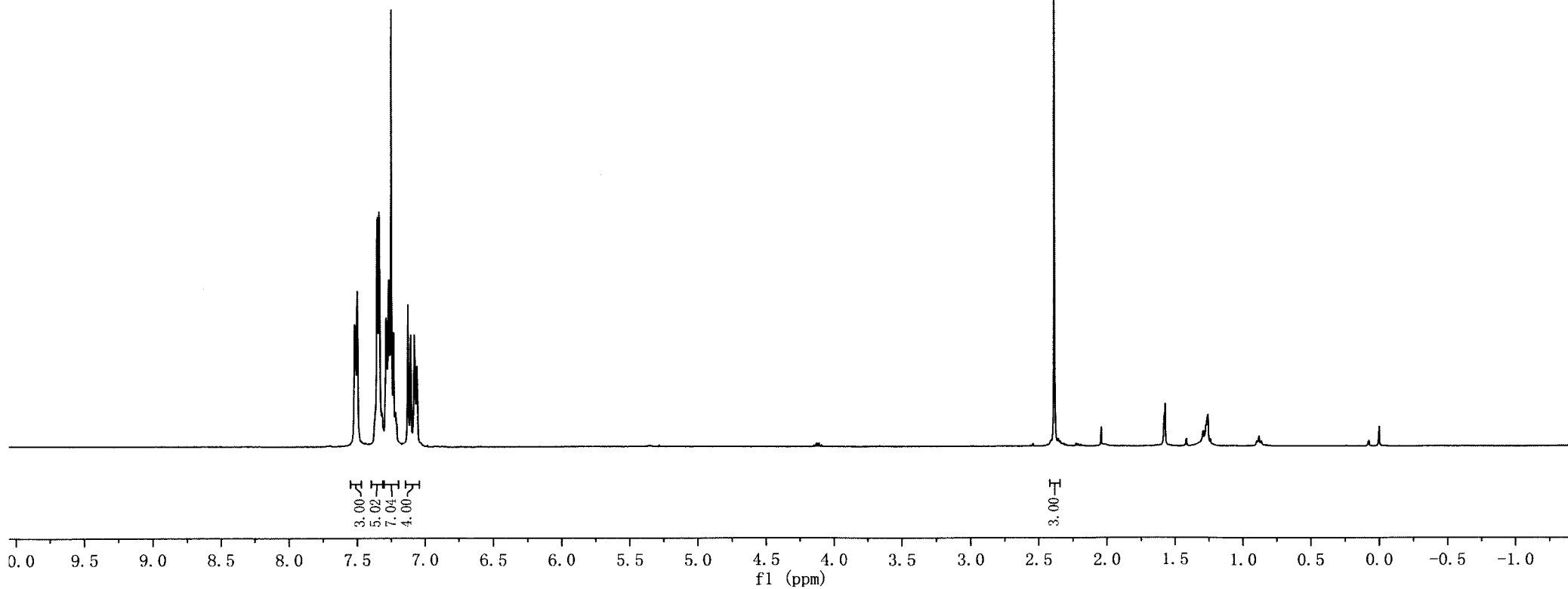


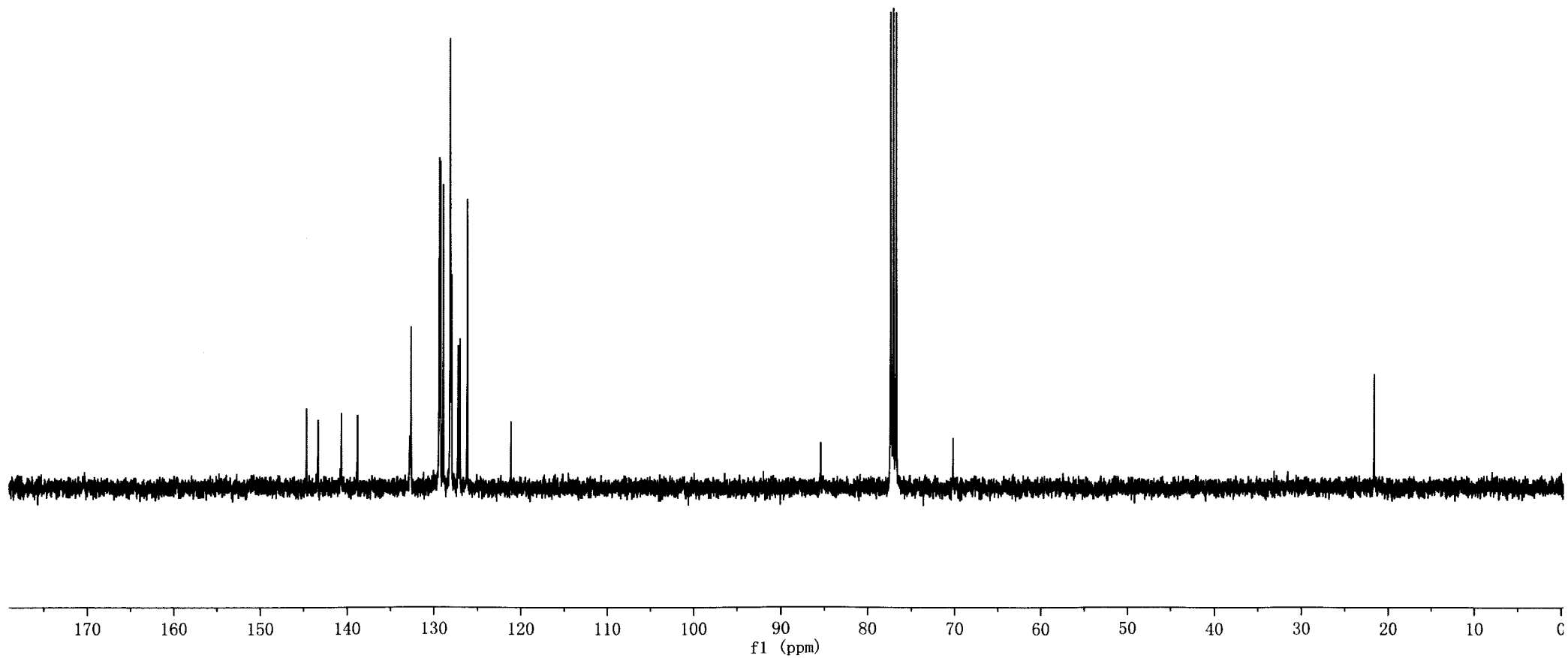
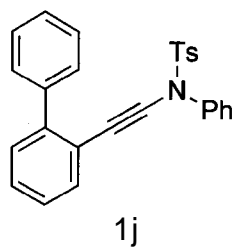
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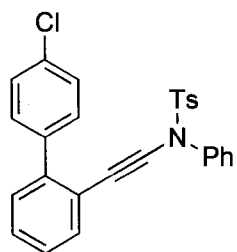


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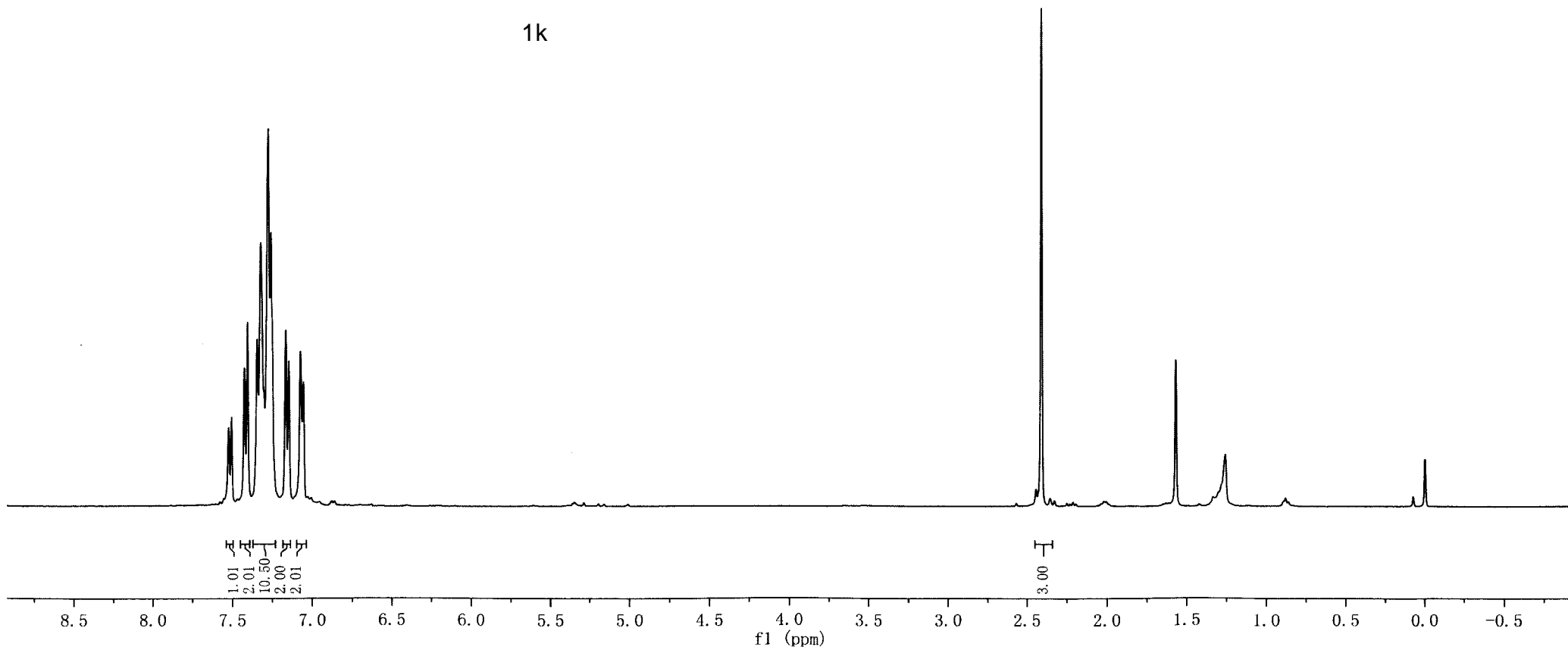


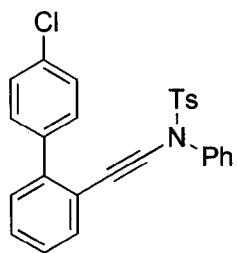
Handwritten integration curve for the aromatic region (7.0-7.5 ppm).



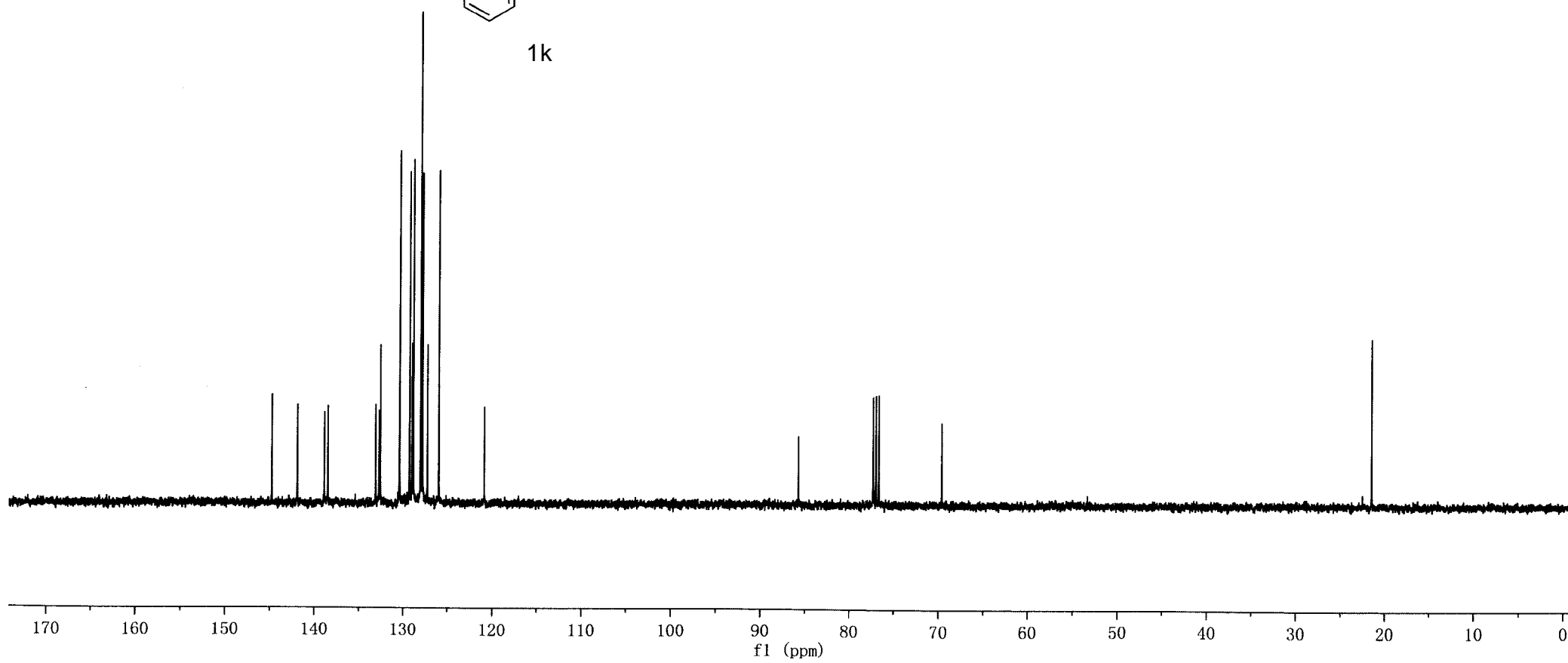
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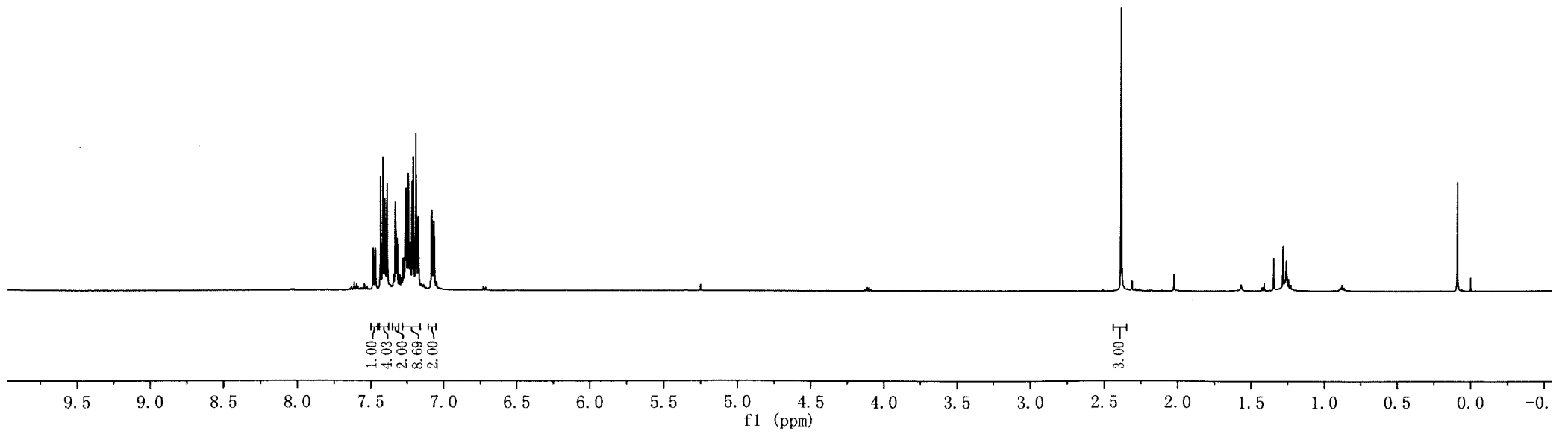
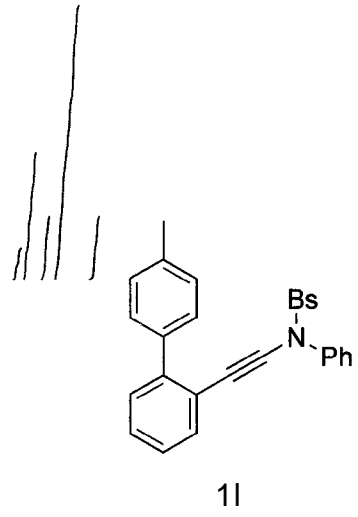
Handwritten integration curve for the aliphatic region (1.0-2.5 ppm).

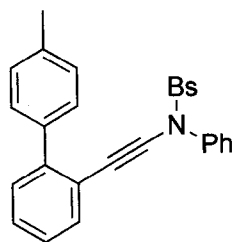




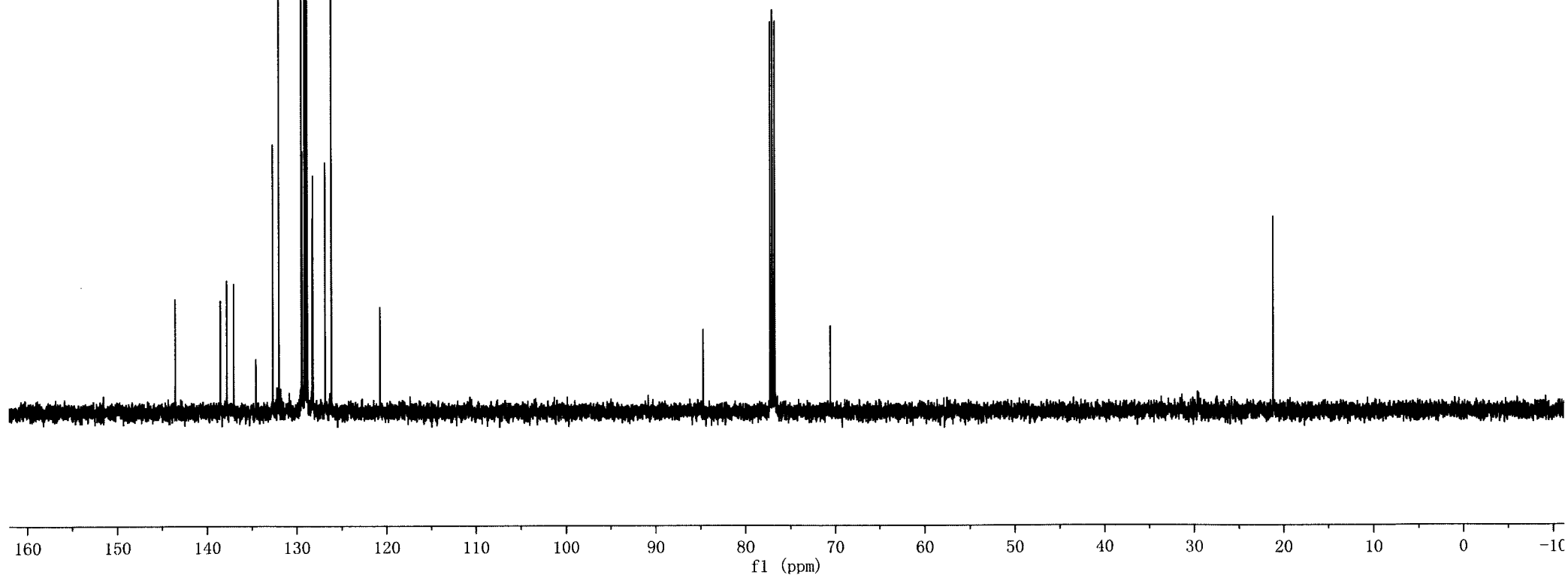
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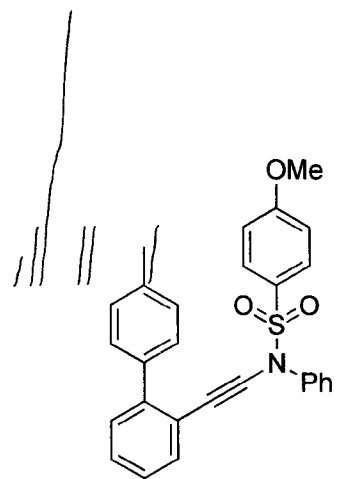




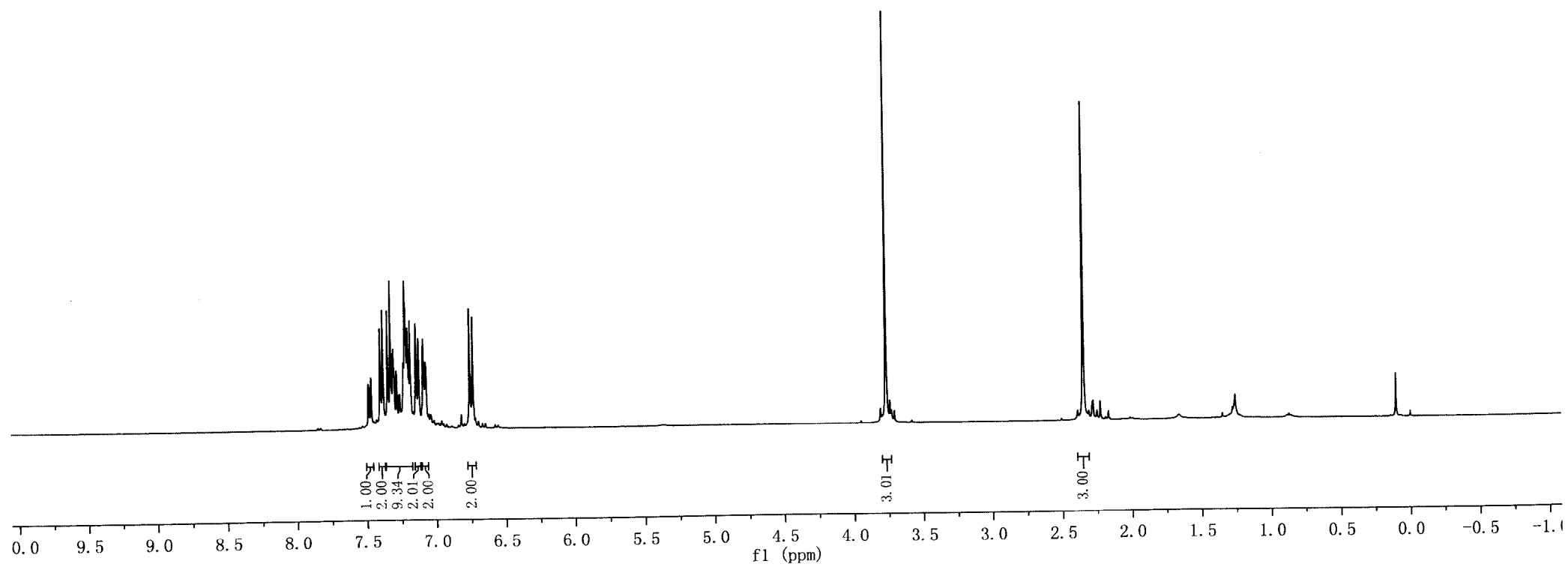


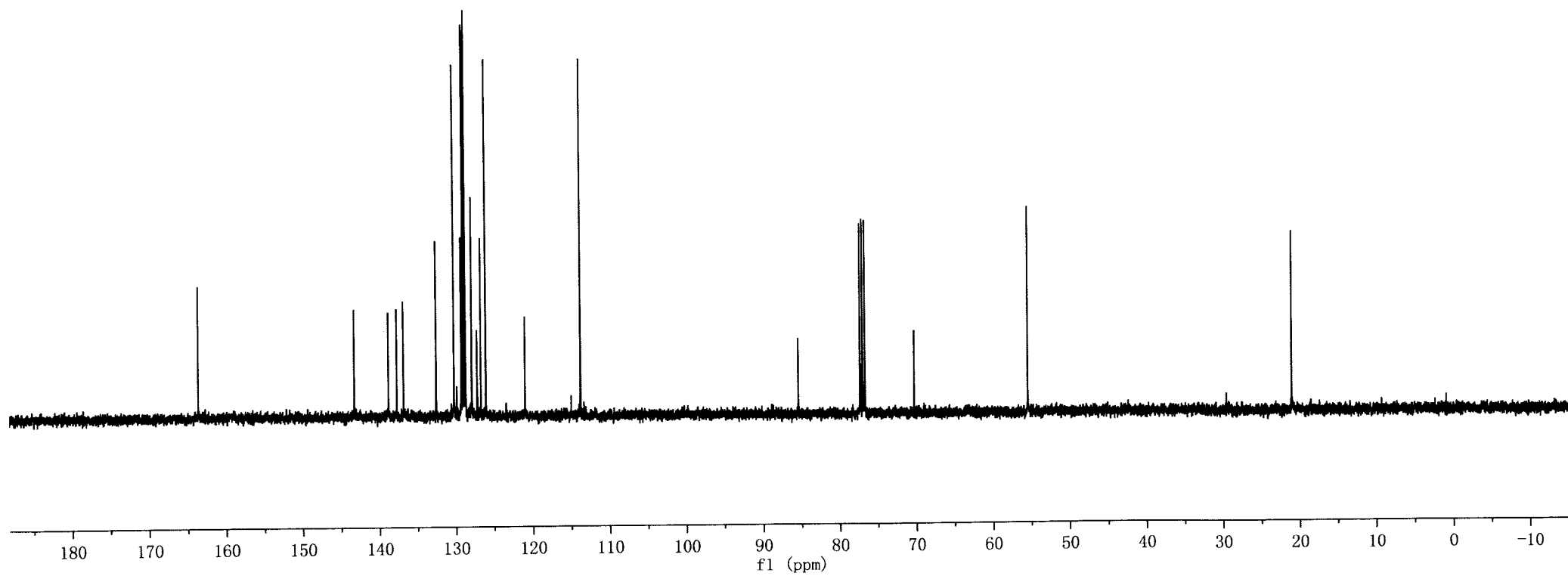
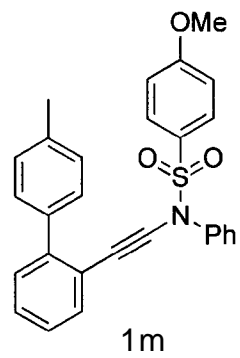
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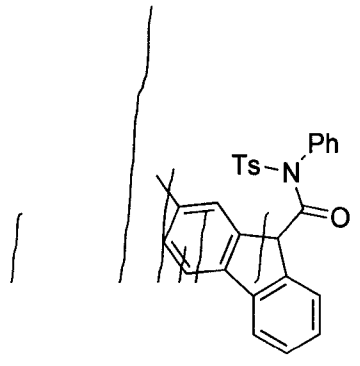




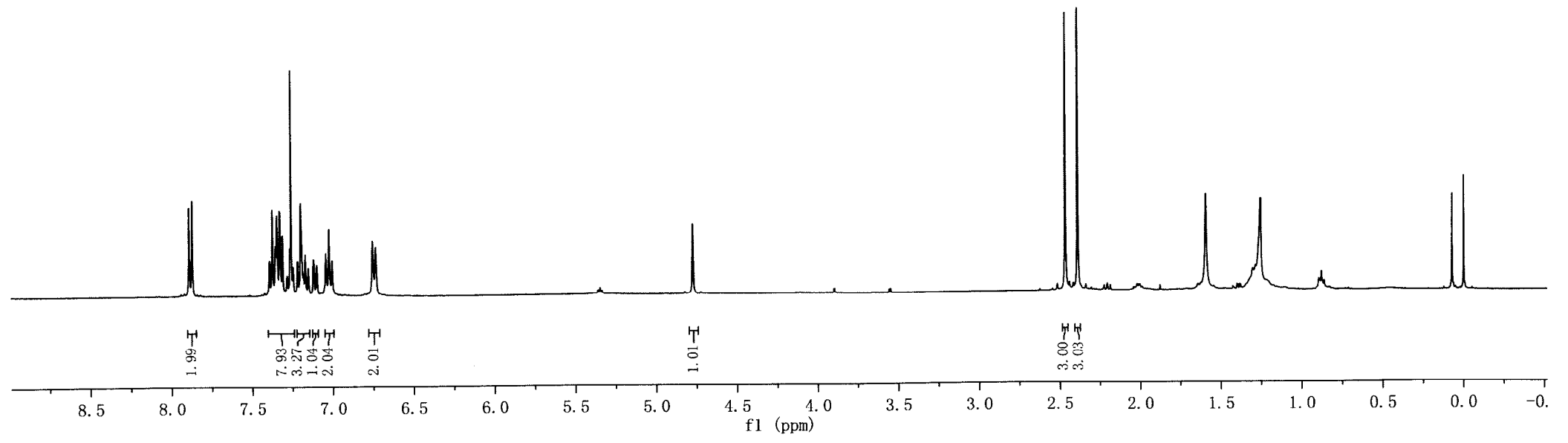
1m

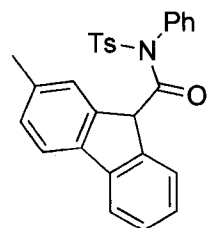




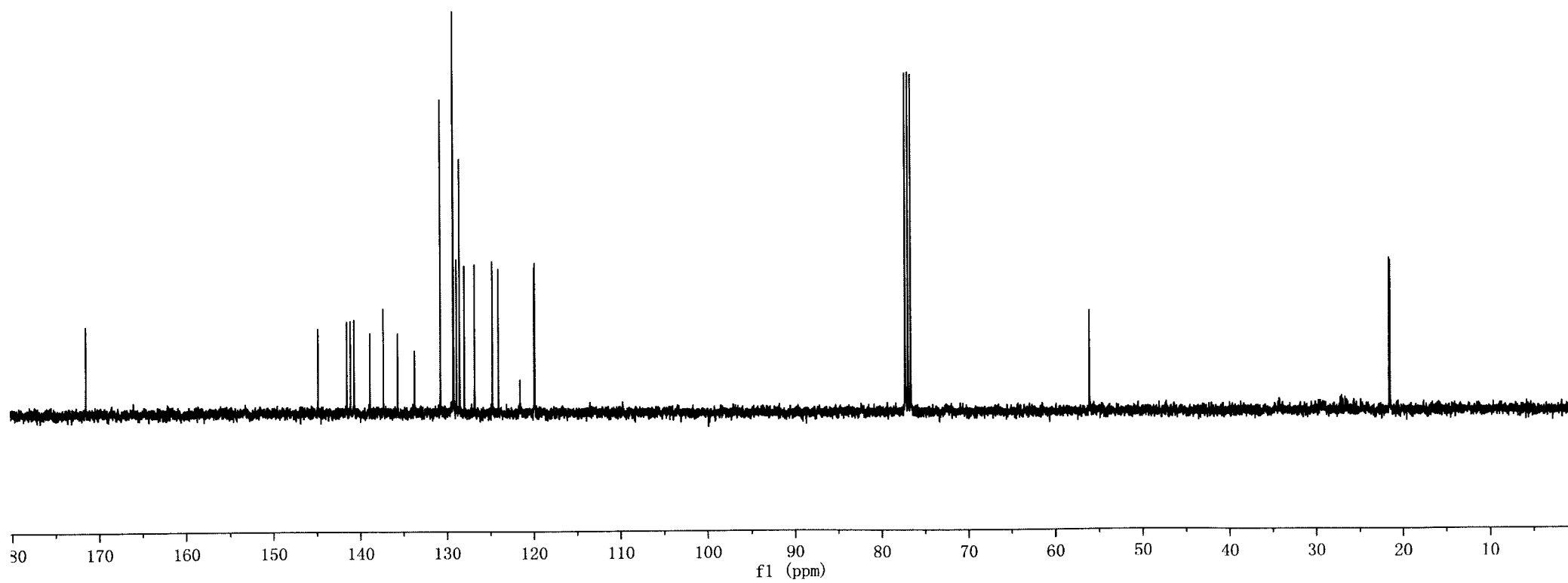


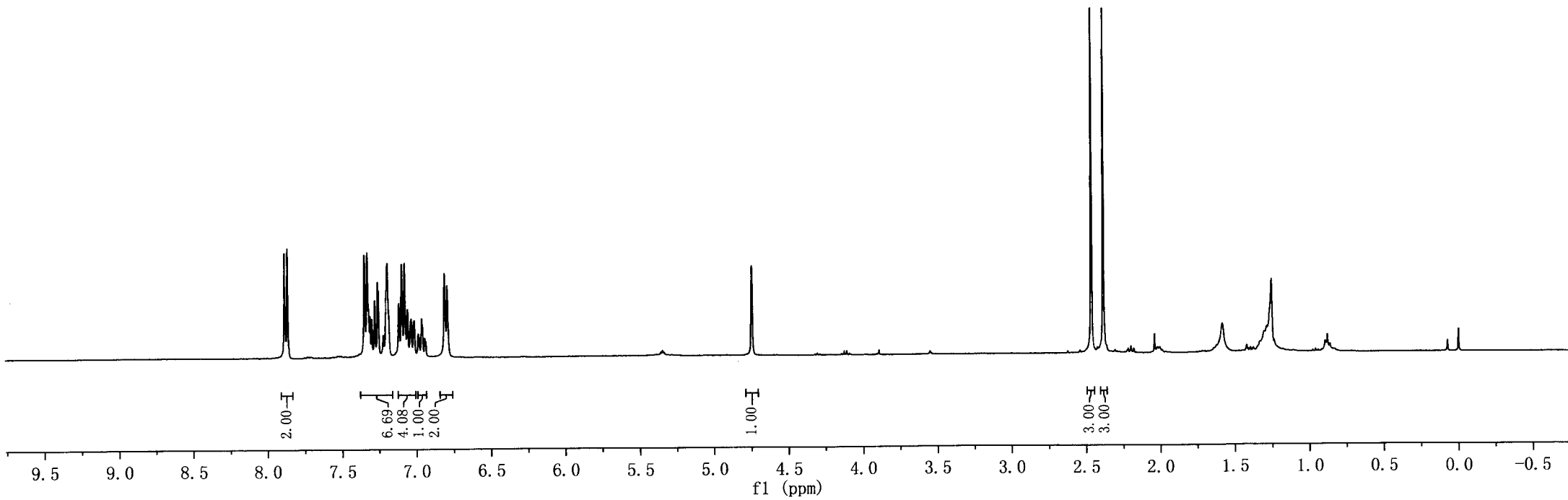
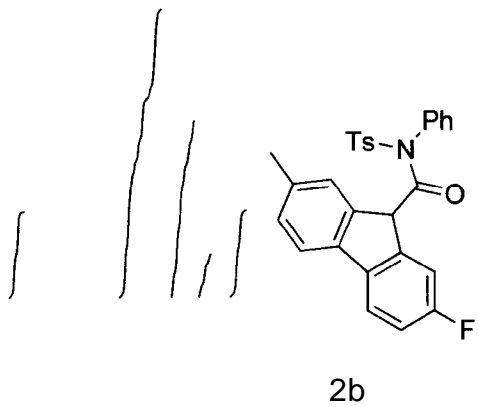
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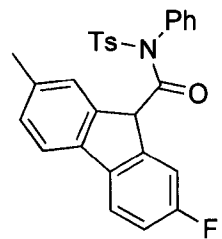




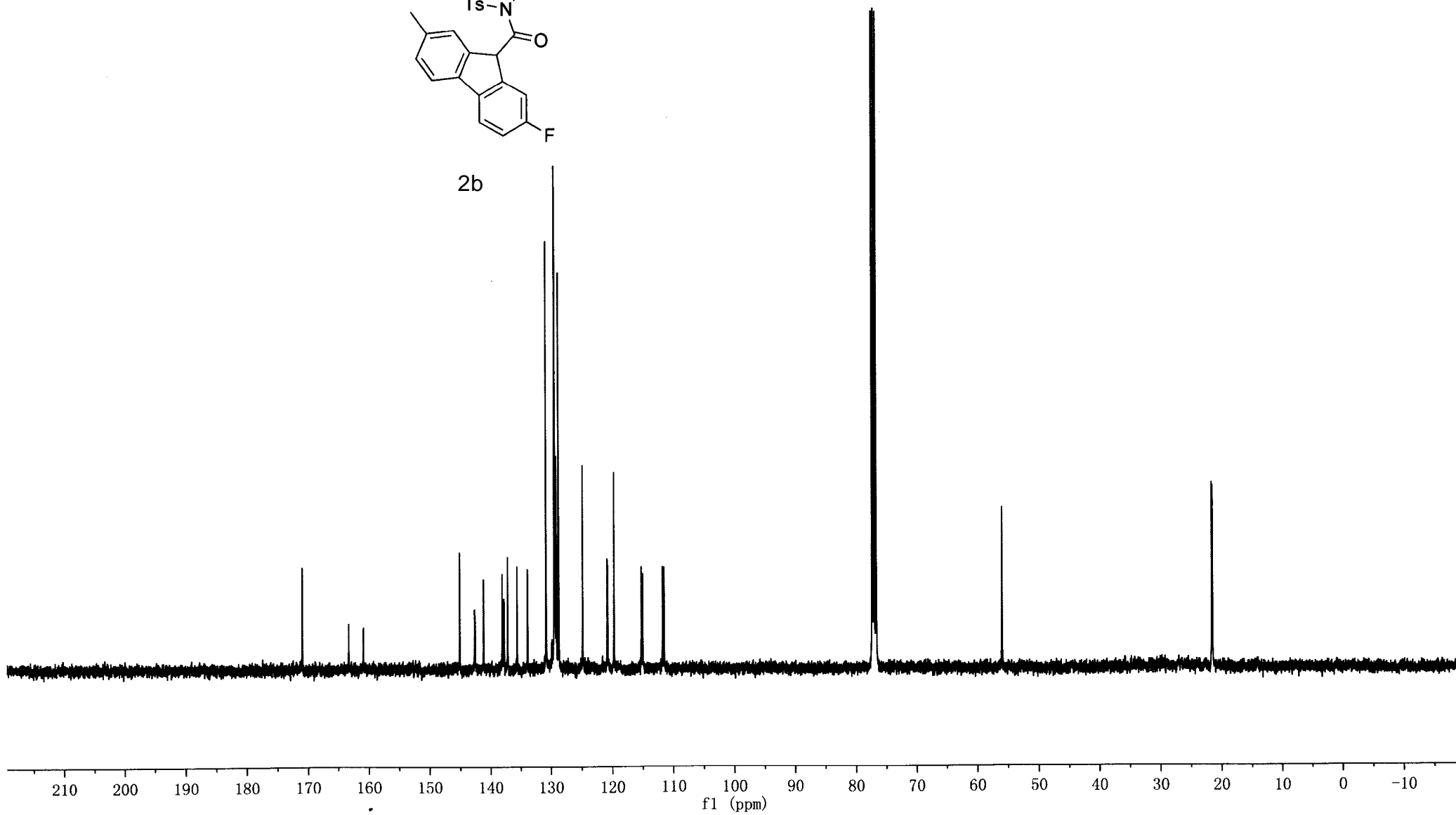
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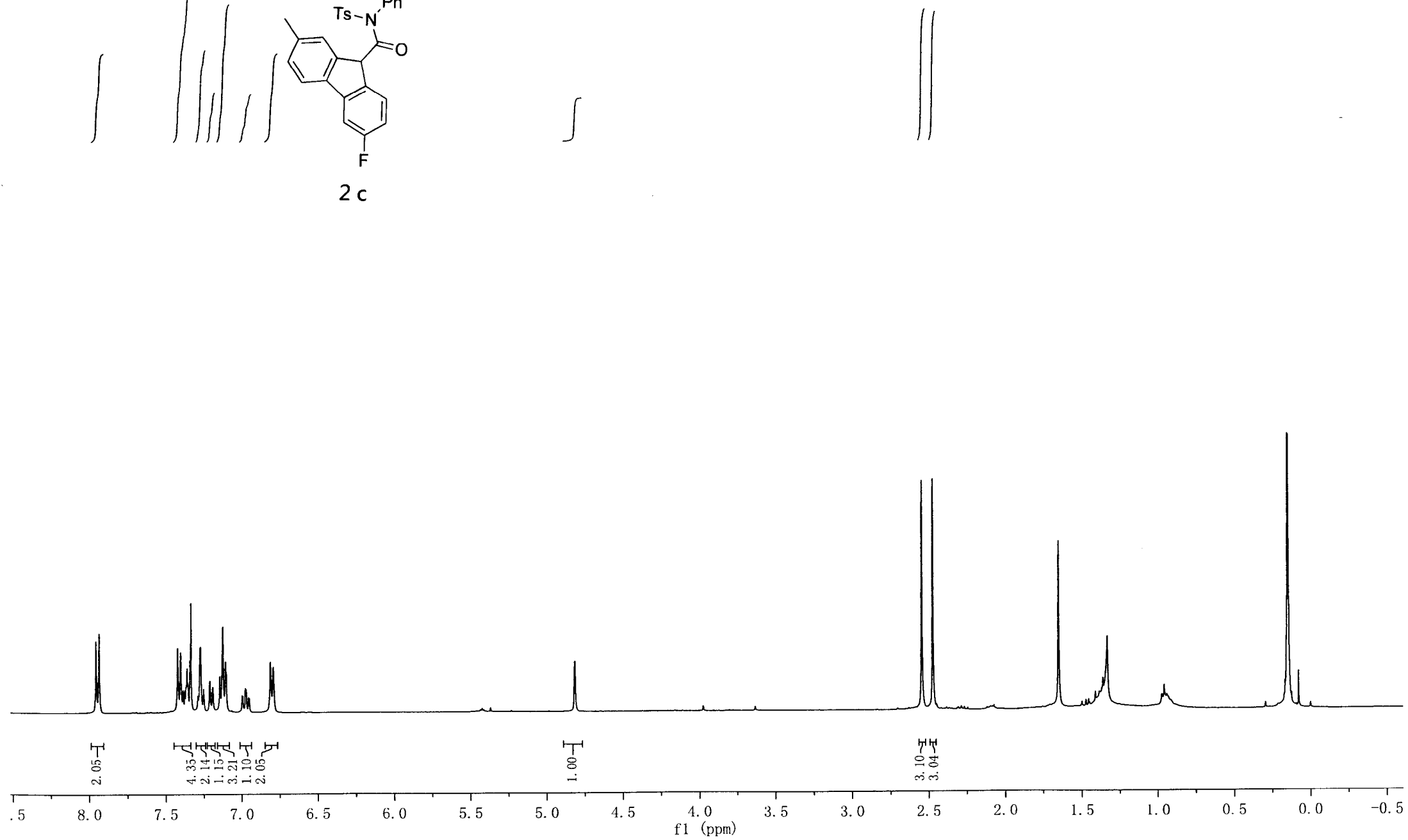
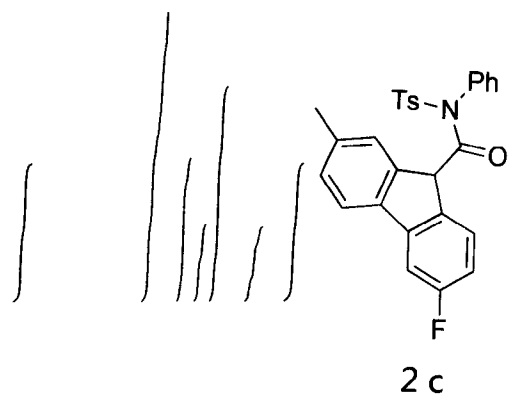


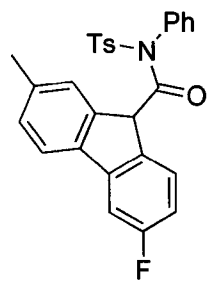




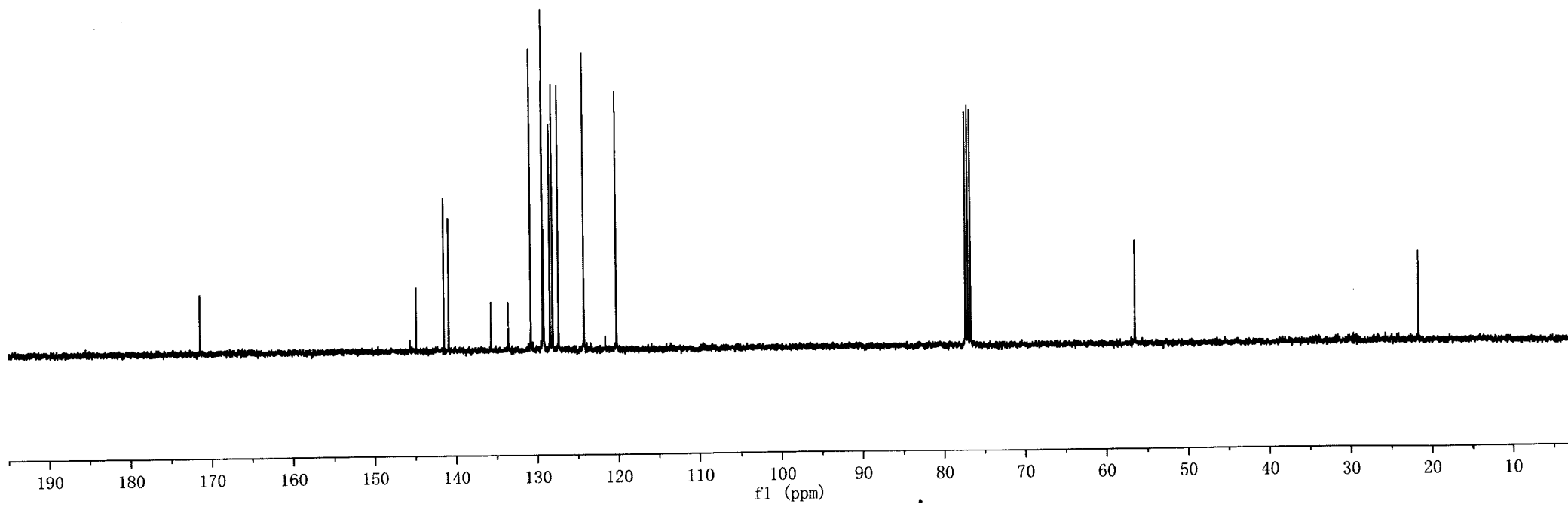
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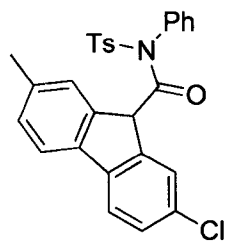
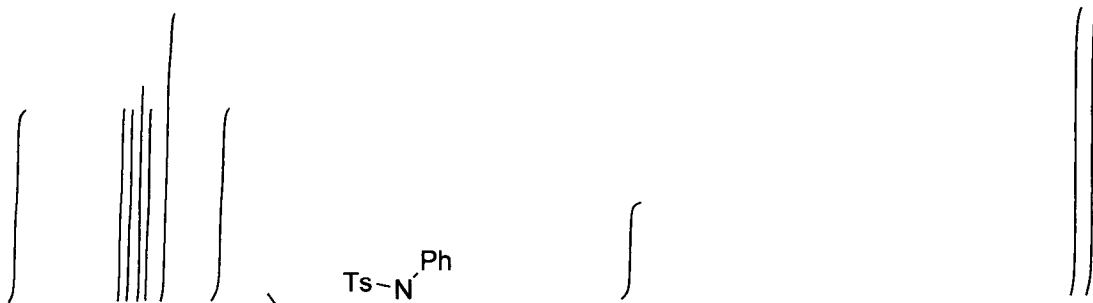




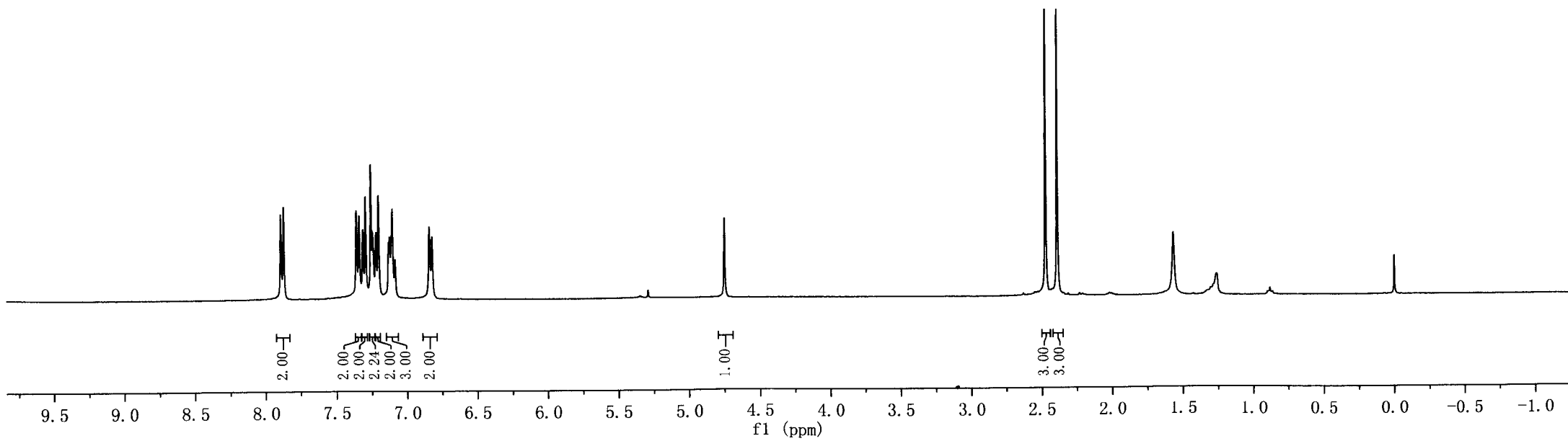


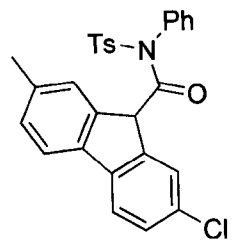
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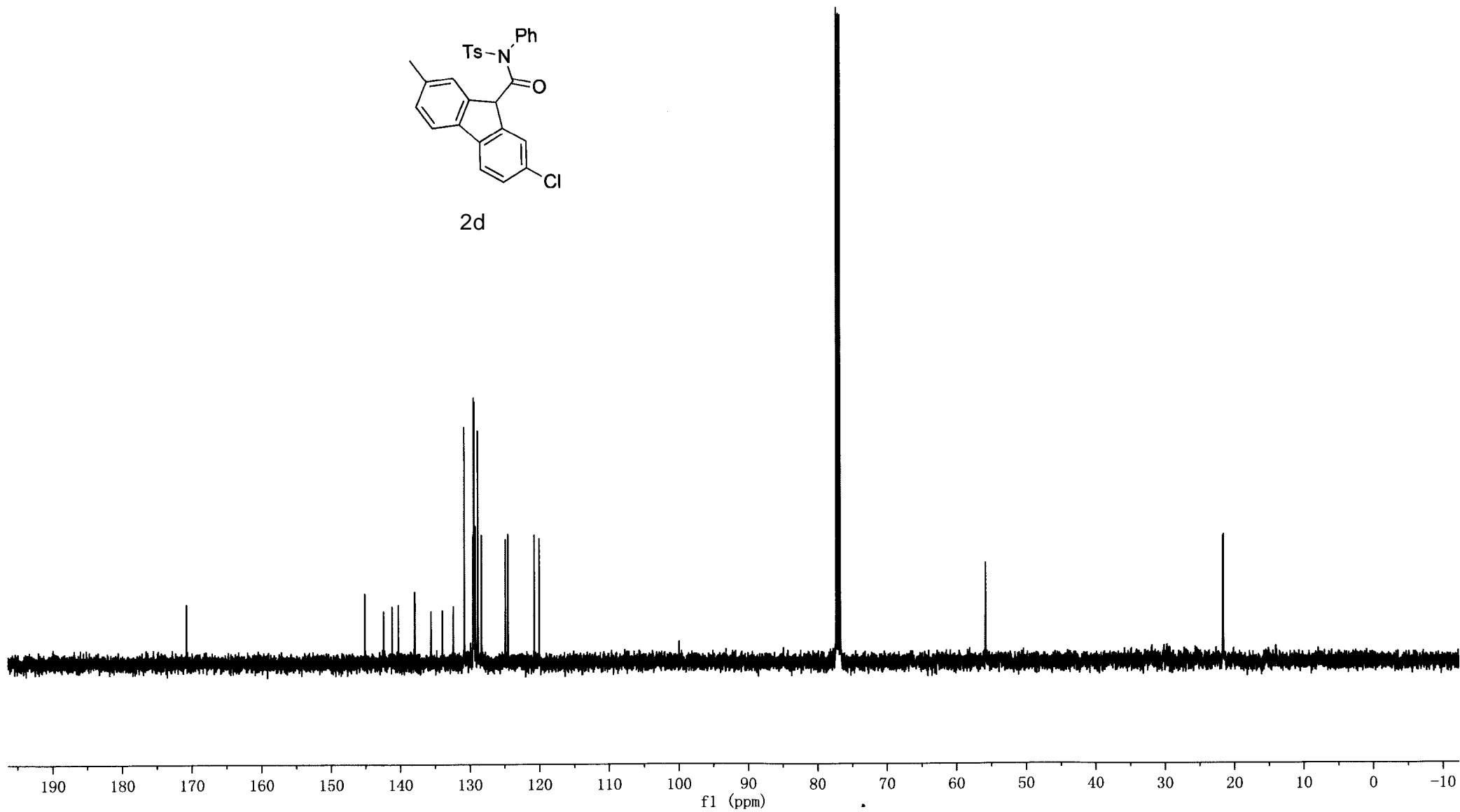


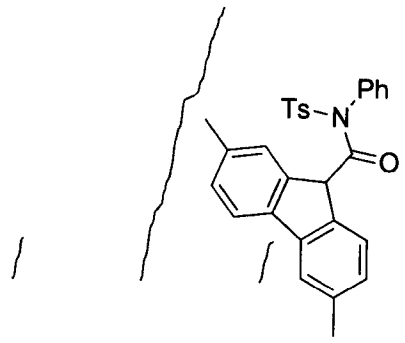
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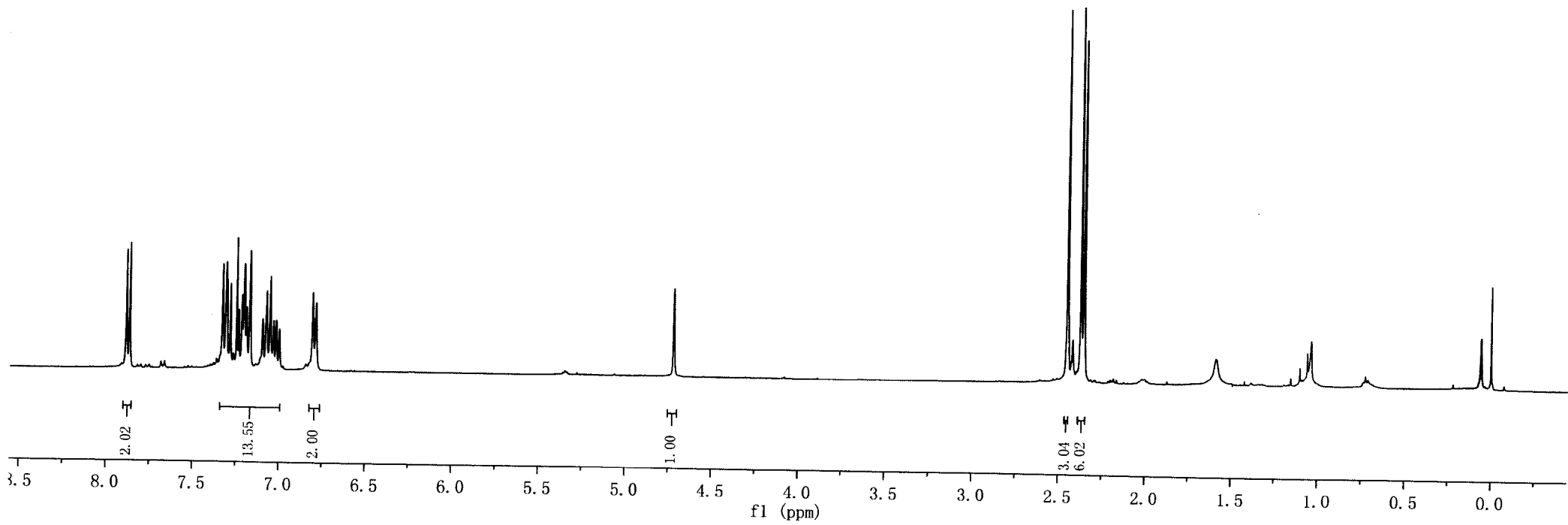


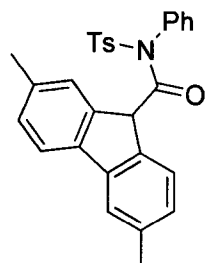
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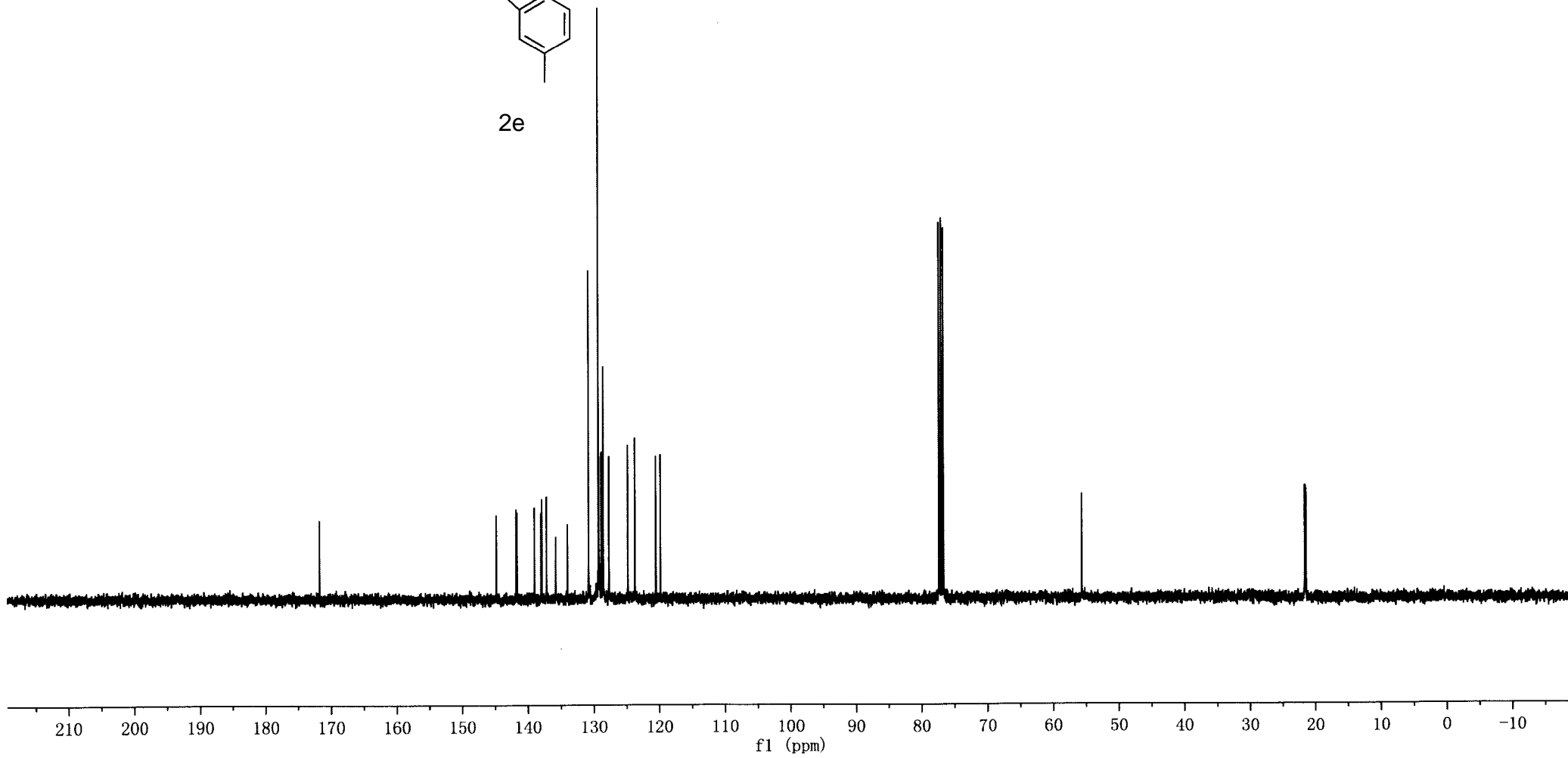


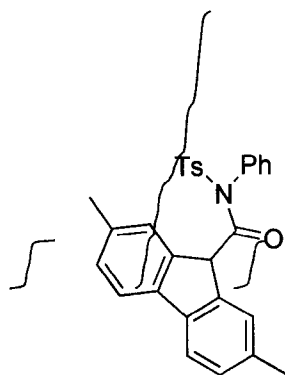
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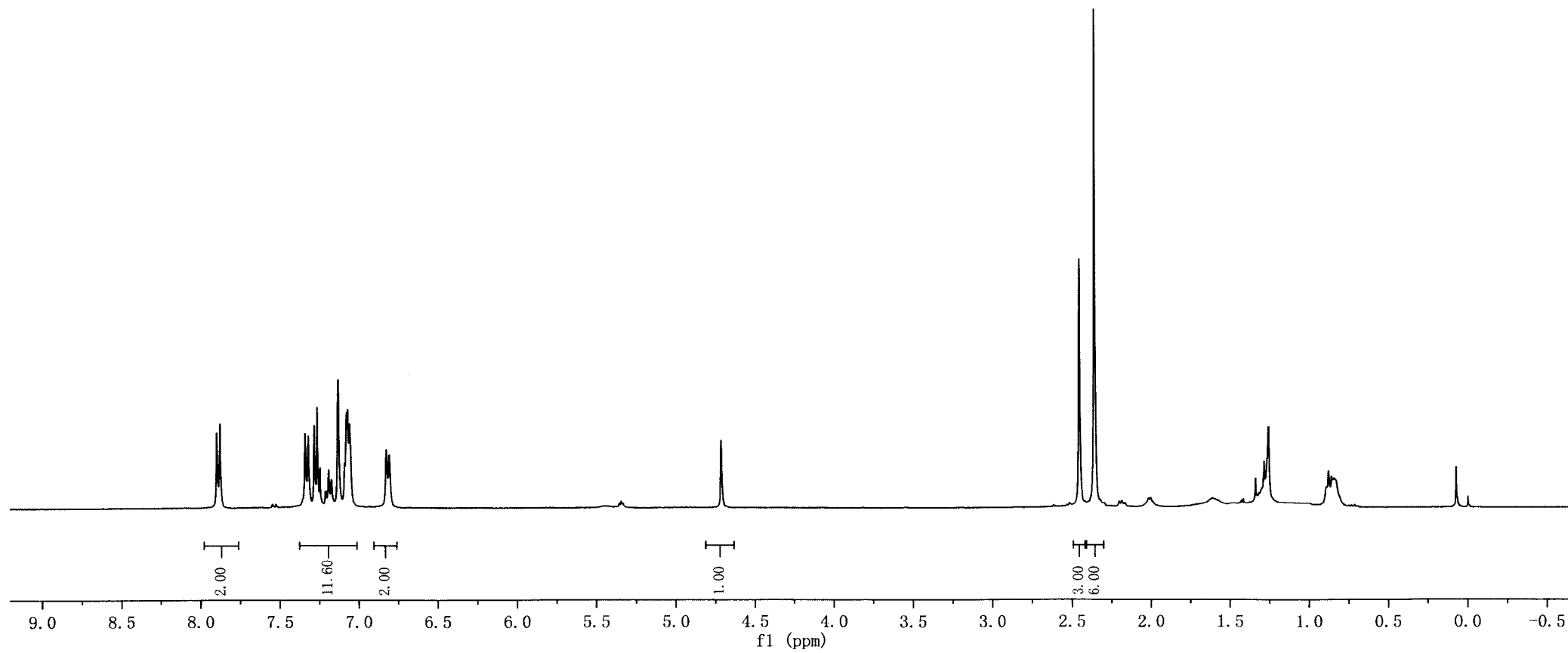


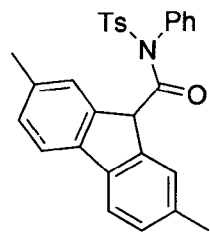
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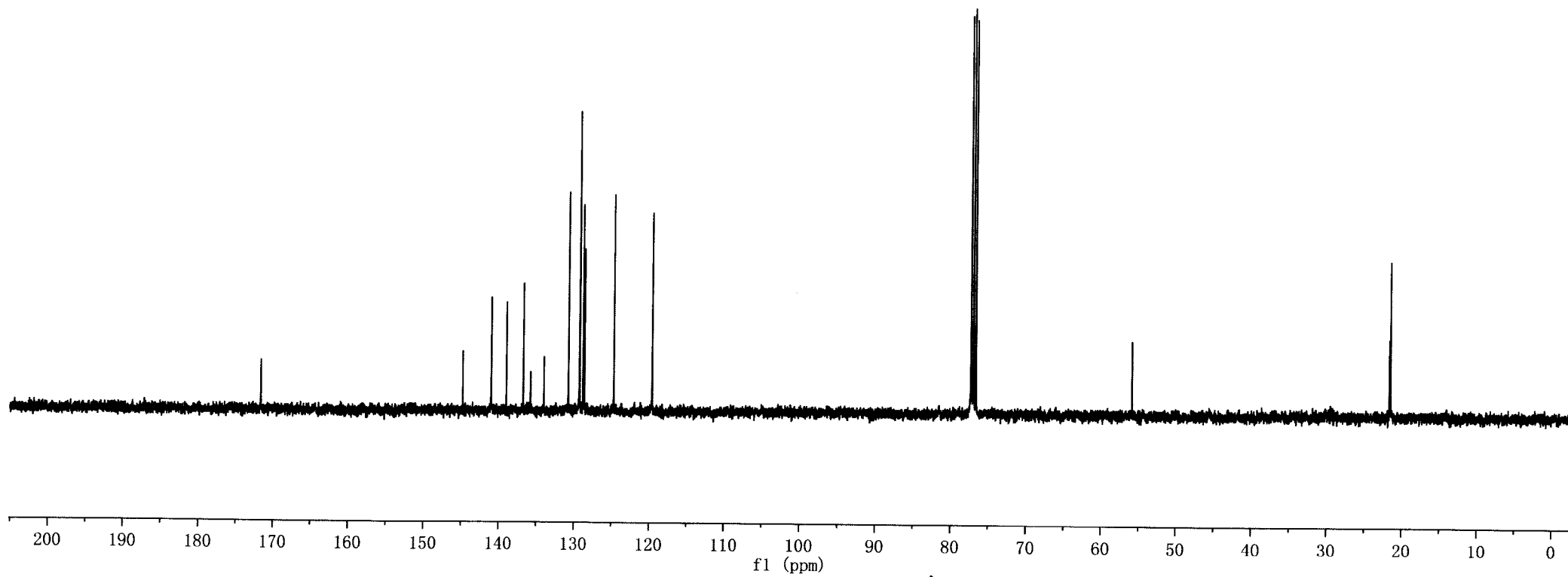


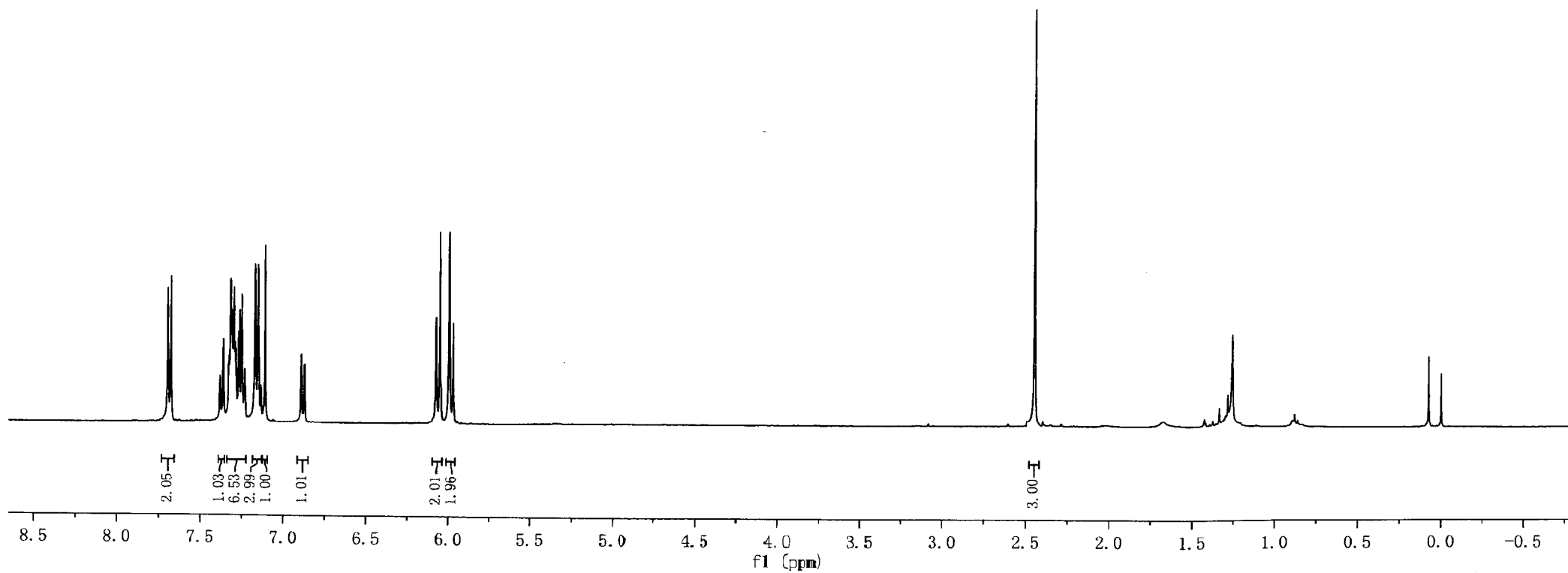
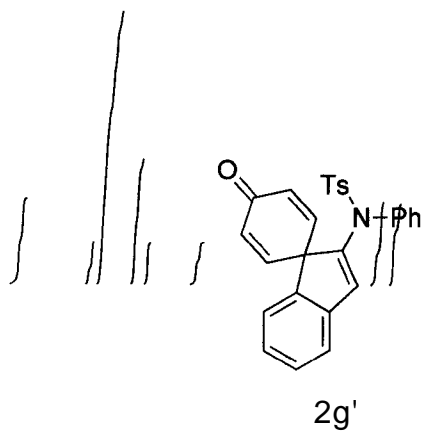
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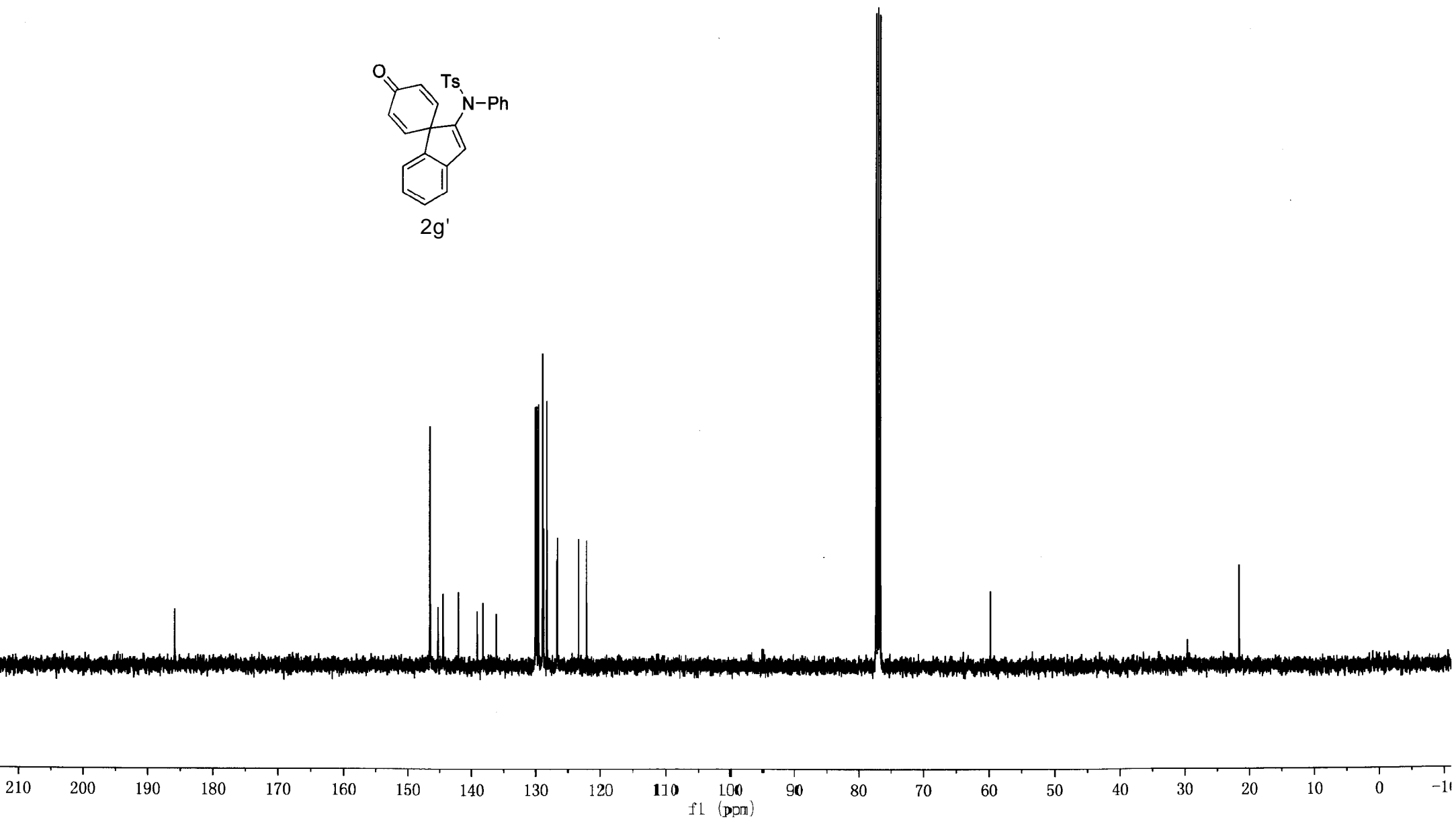
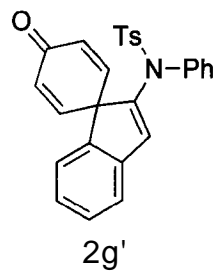


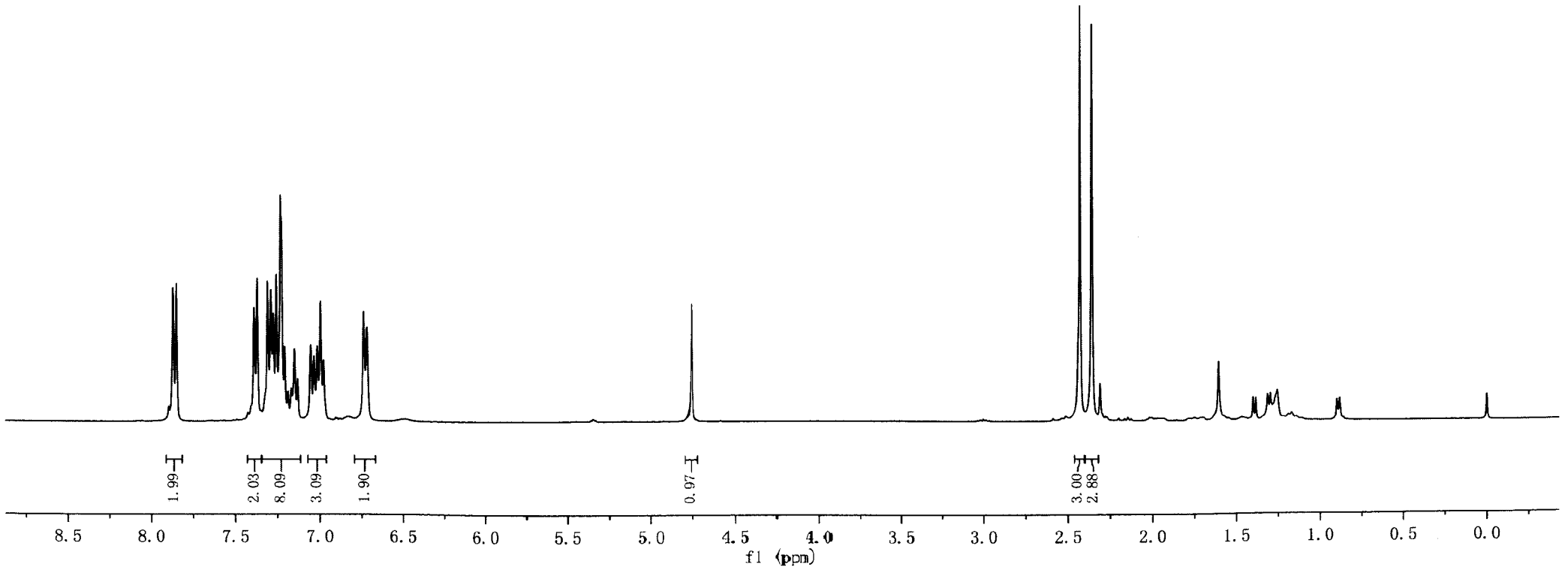
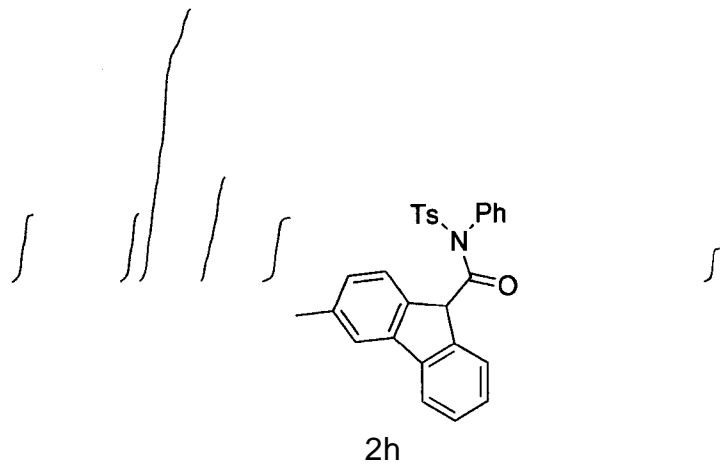


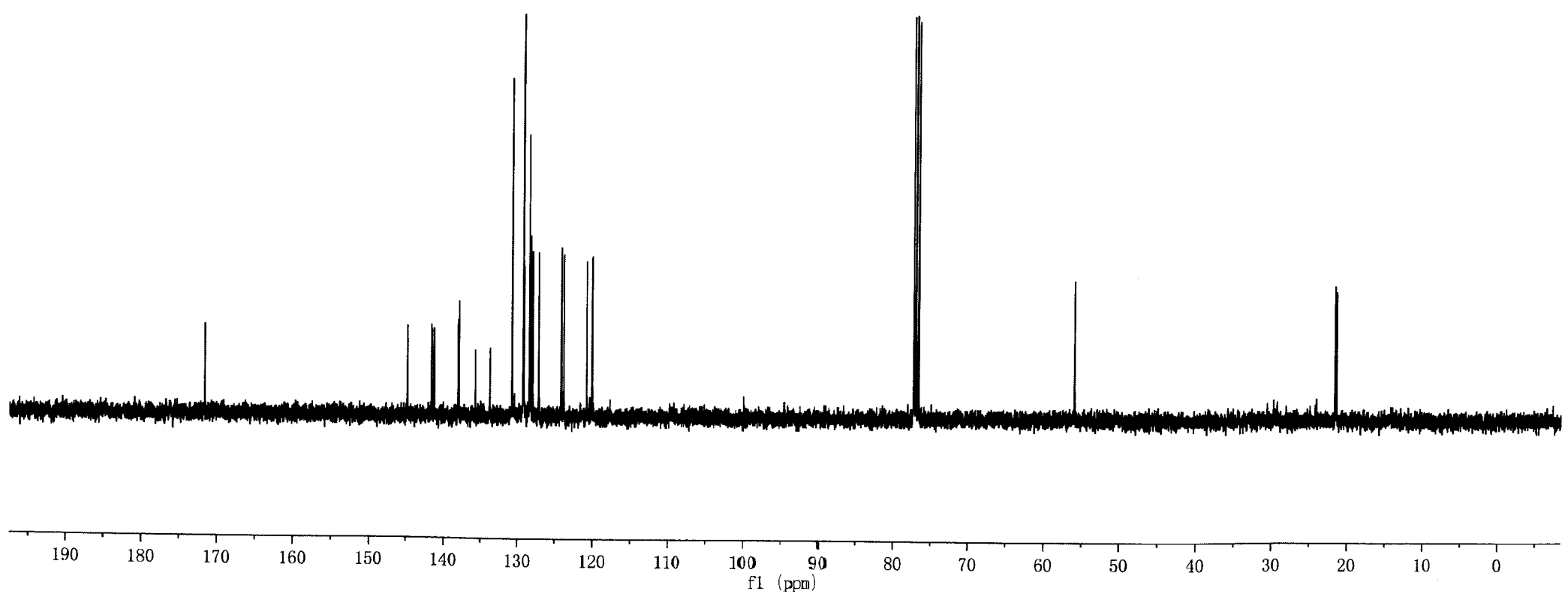
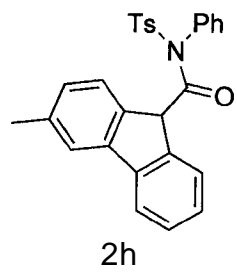
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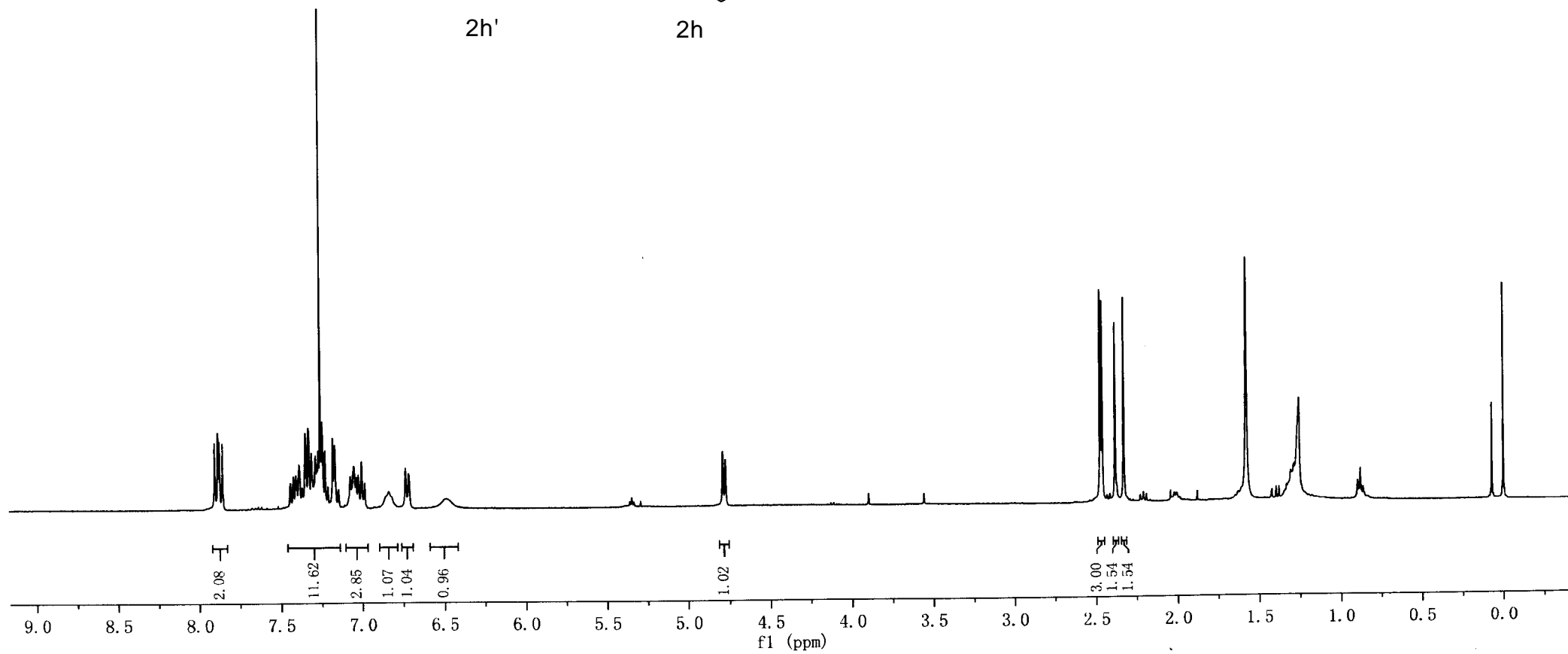
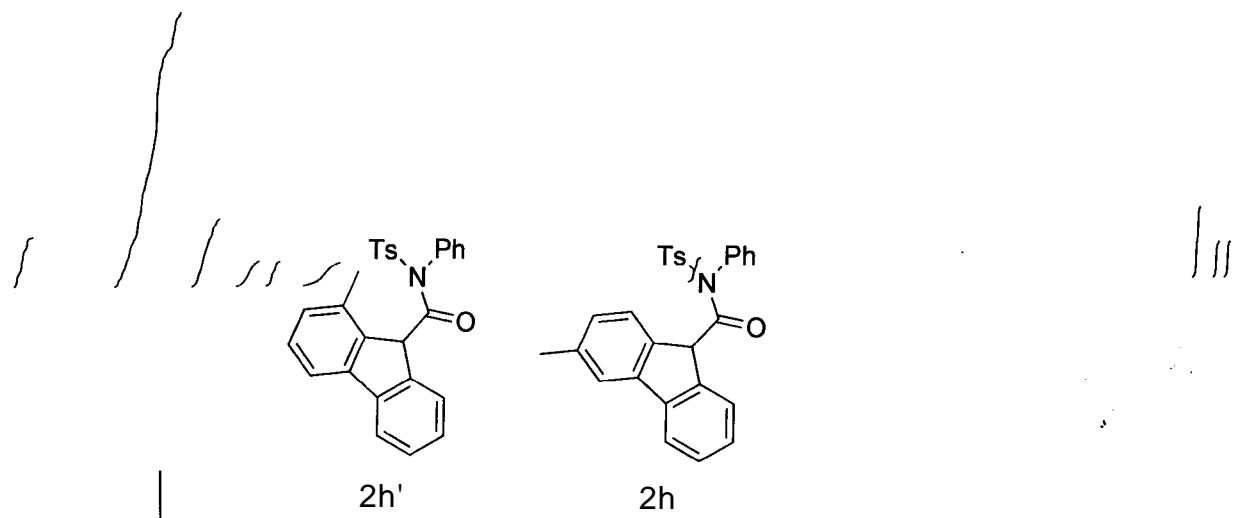


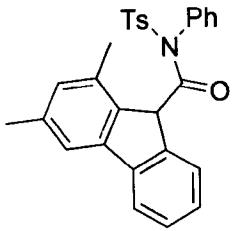
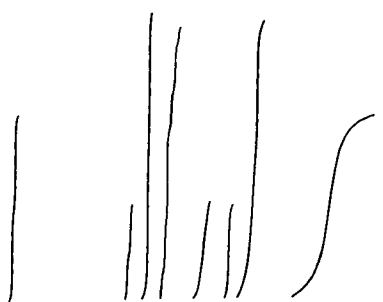




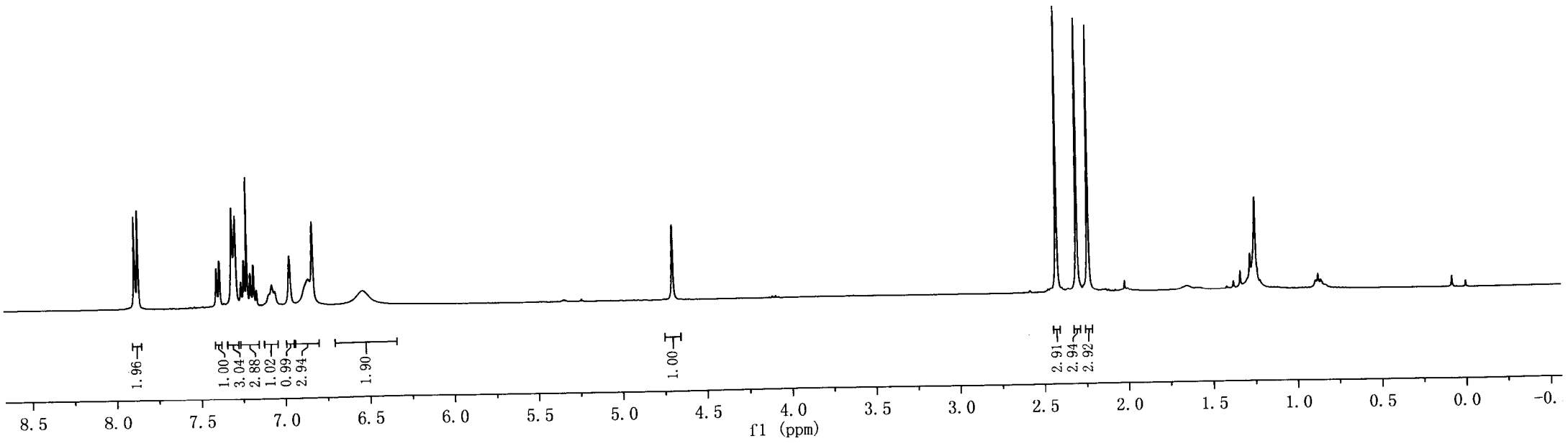


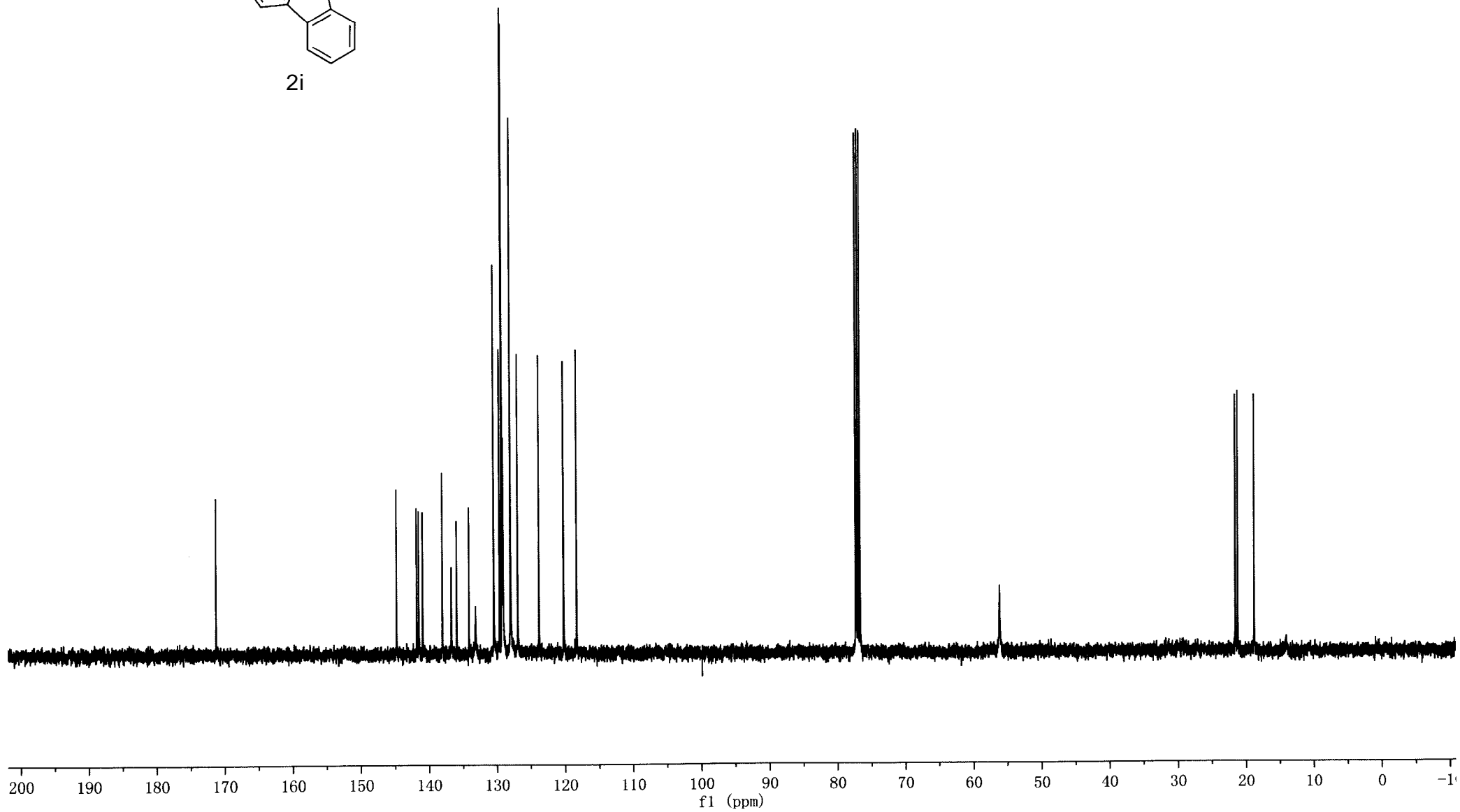
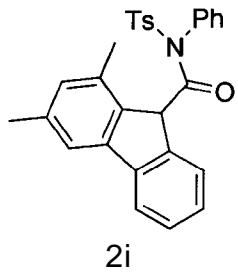


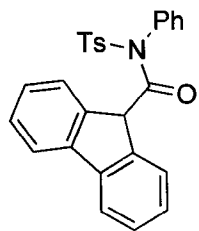




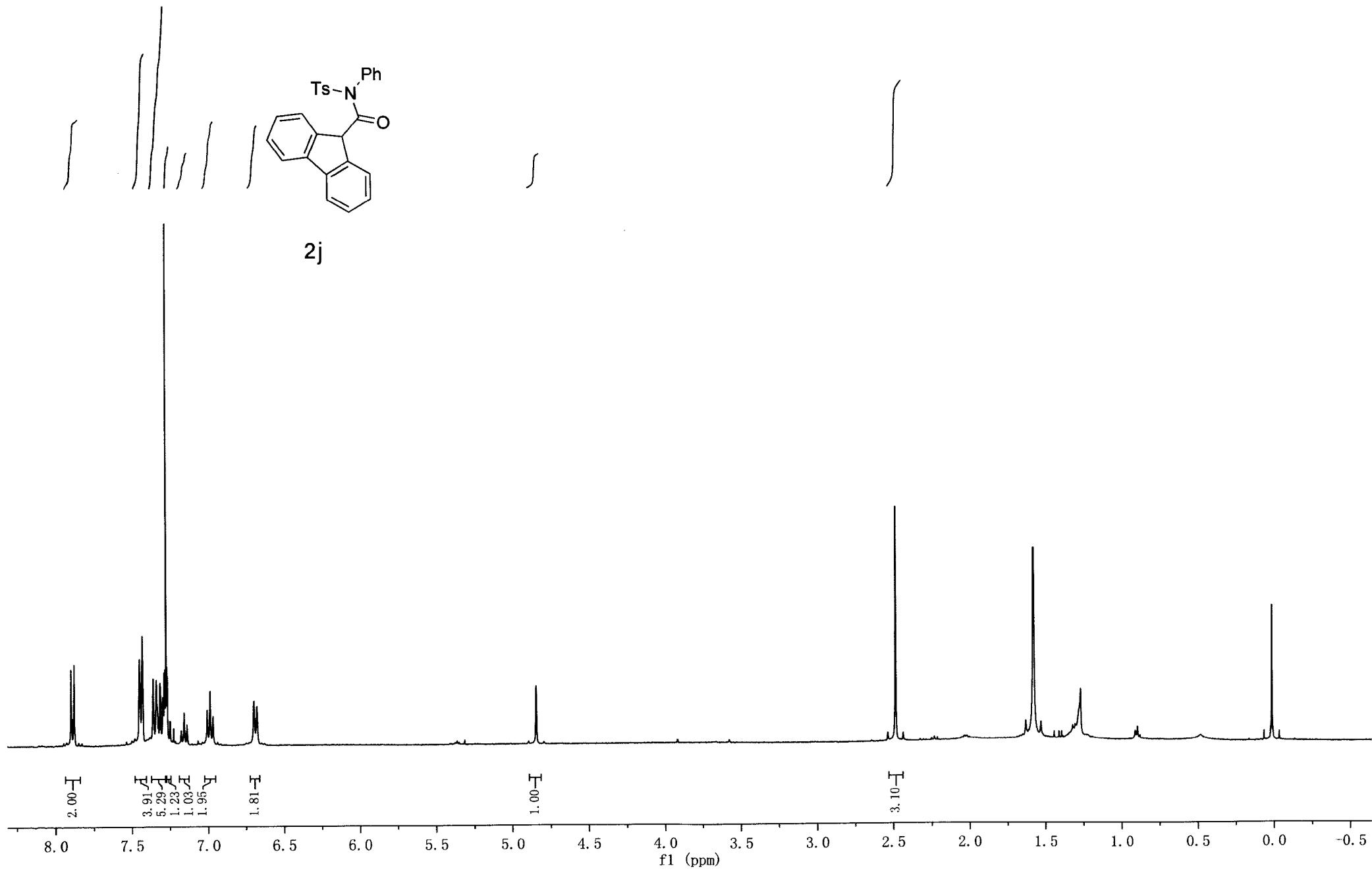
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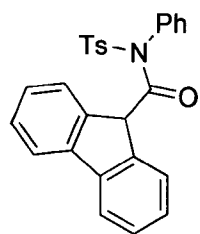




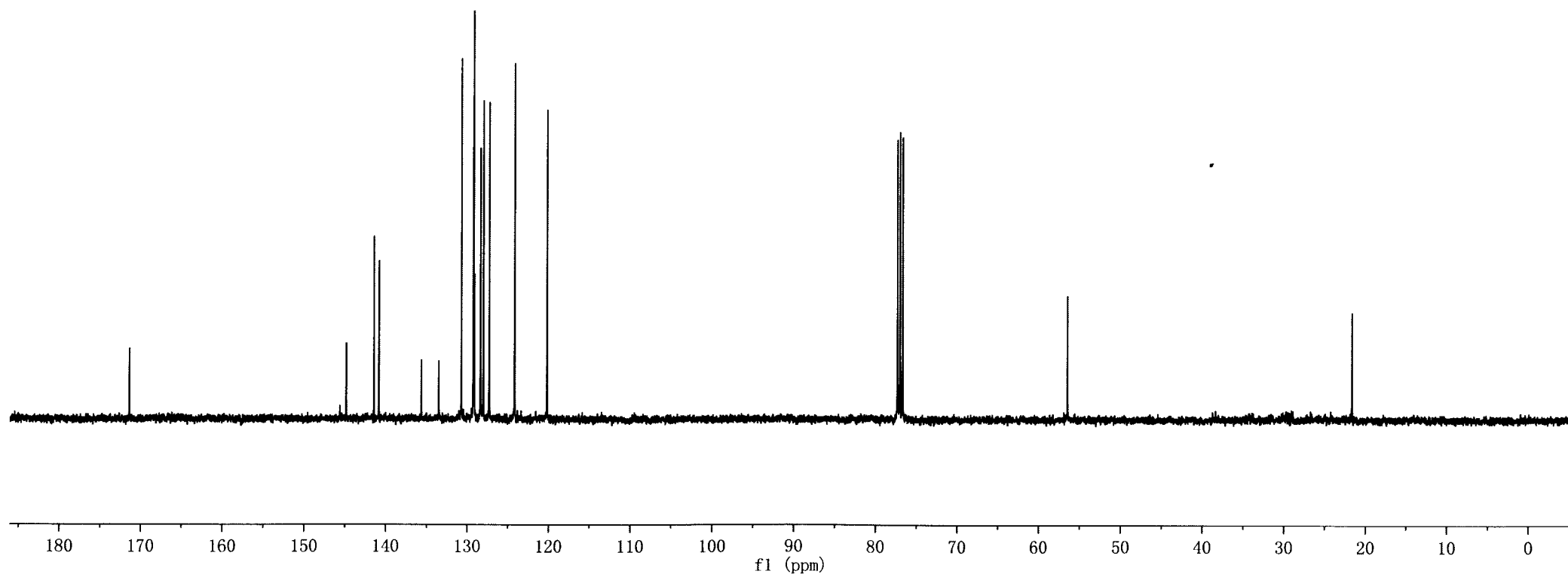


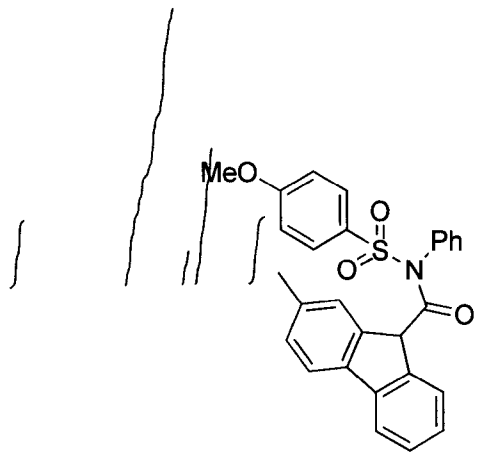
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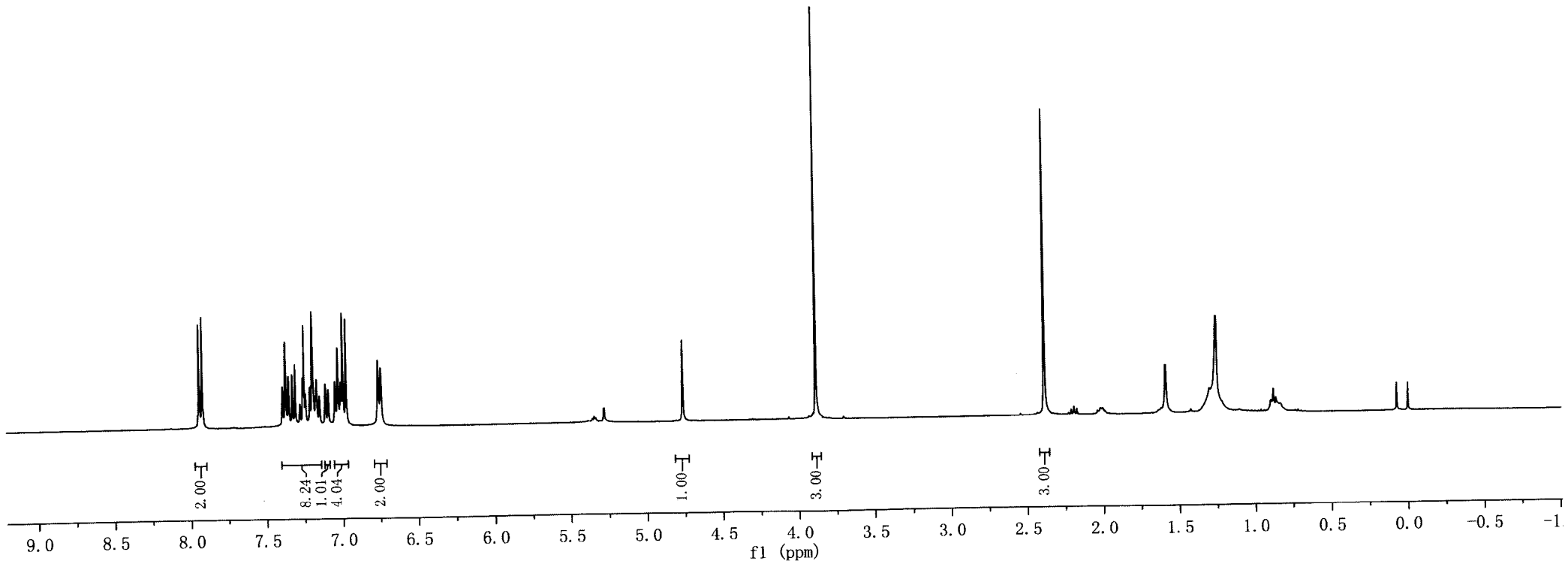


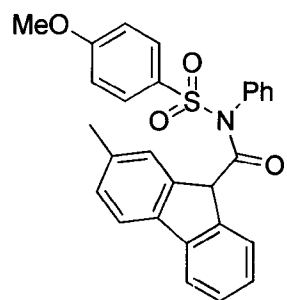
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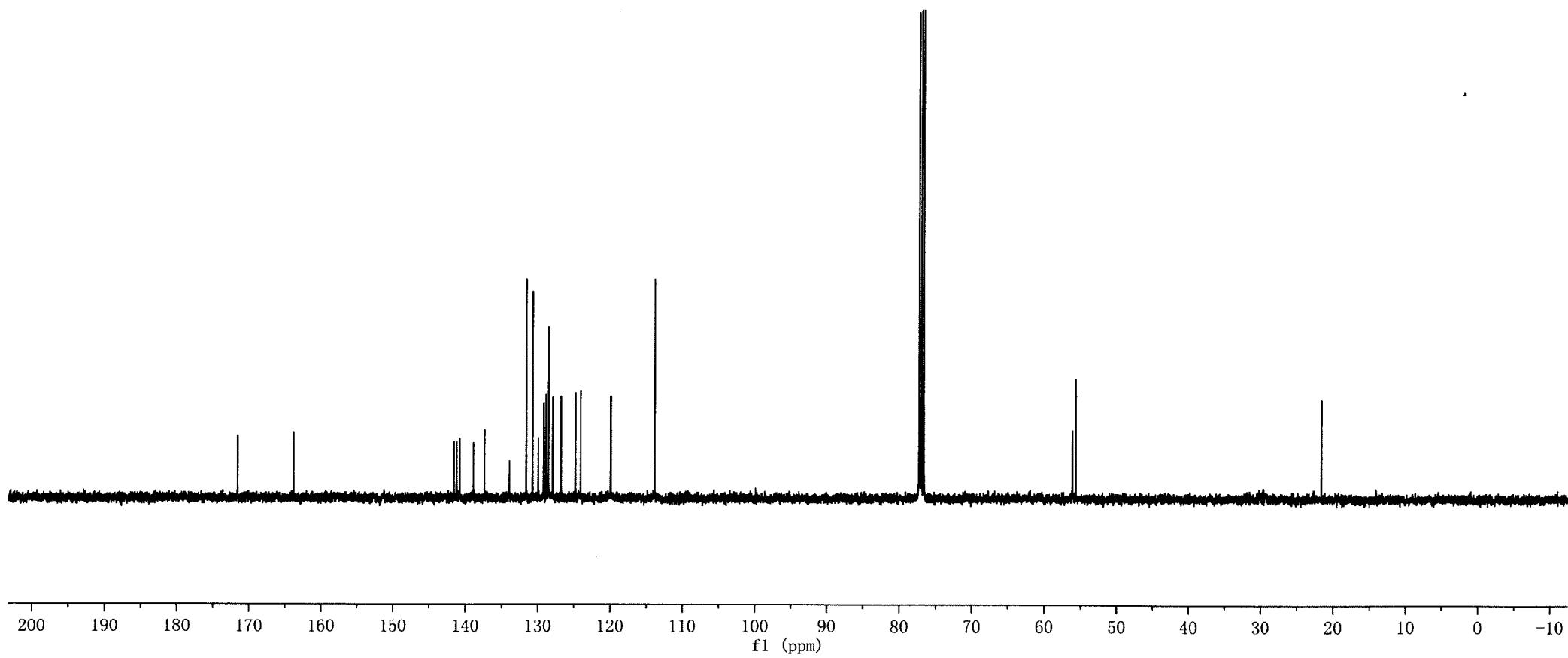


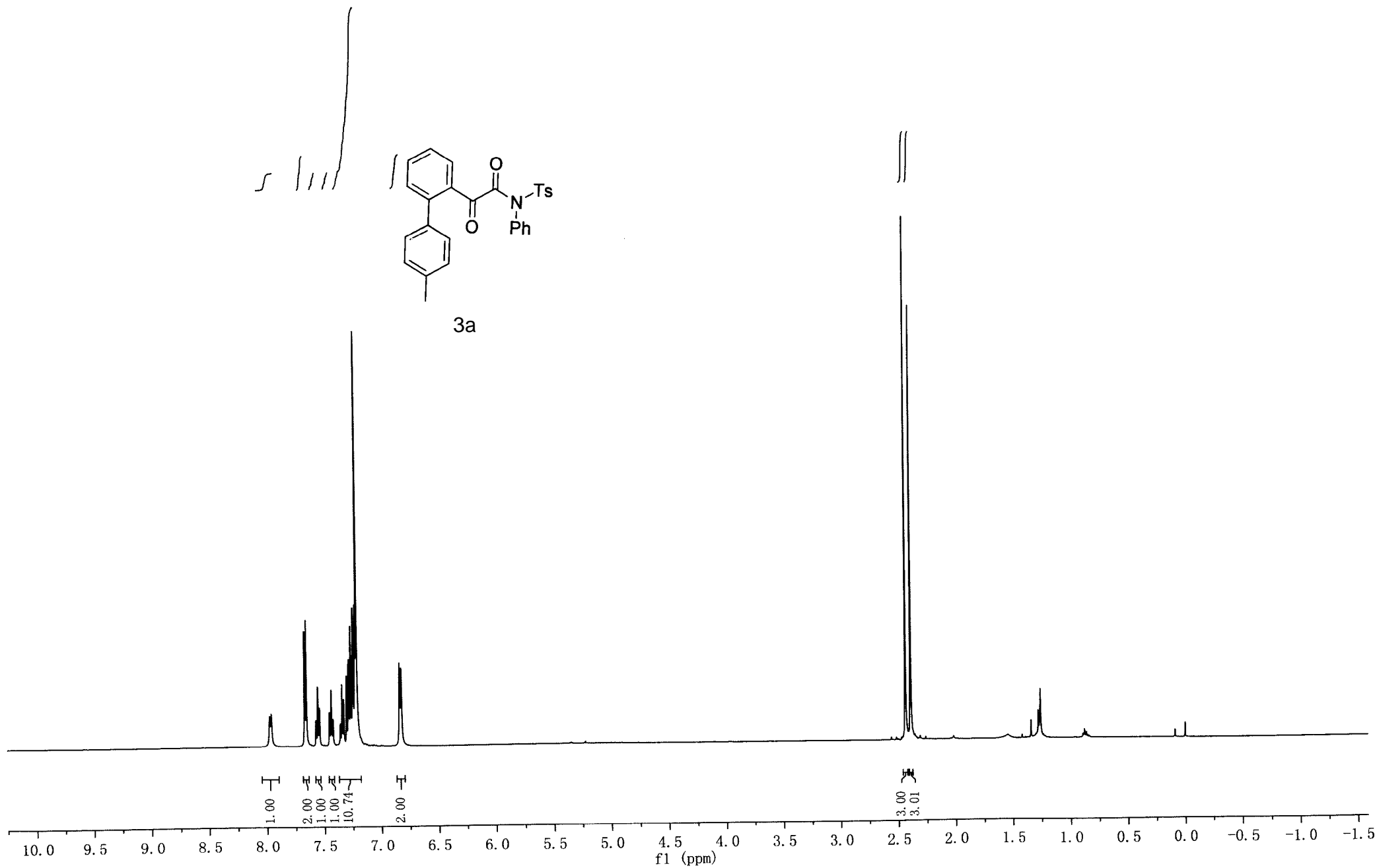
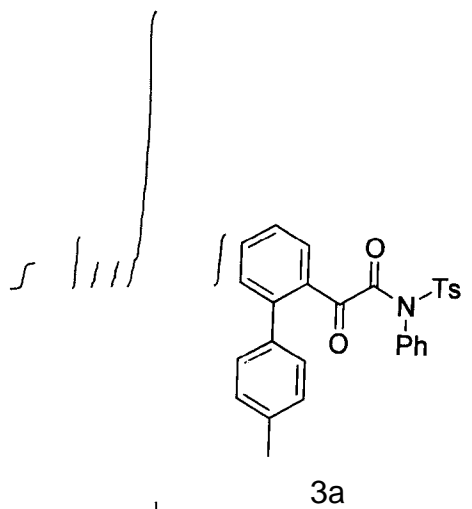
2m

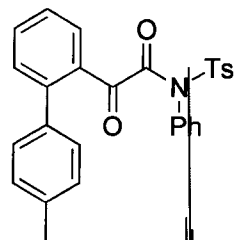




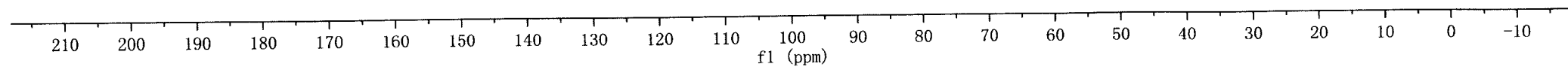
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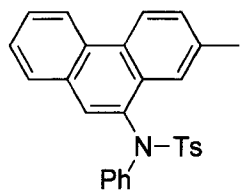
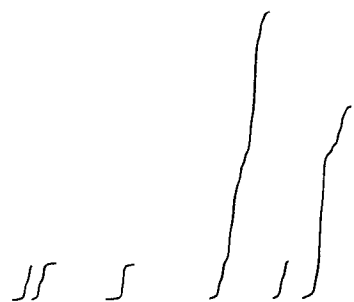






3a





3a'

