

Supporting Information for:

Silver-Promoted Synthesis of Vinyl Sulfones from Vinyl Bromides and Sulfonyl Hydrazides in Water

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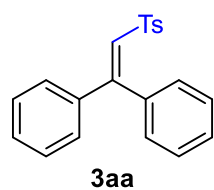
1. General Information

All commercially available chemical resources were used as received. Chromatographic purification of products was accomplished using forced flow chromatography on silica gel 60 (300~400 μm). Thin layer chromatography was performed on silica gel (200~300 μm). Nuclear Magnetic Resonance (NMR) spectras were acquired on a Varian Mercury 400 operating at 400, 100 and 376 MHz for ^1H , ^{13}C , ^{19}F respectively. Chemical shifts were reported in δ ppm referenced to an internal SiMe_4 standard for ^1H NMR, chloroform- d (δ 77.16) for ^{13}C NMR. Multiplicities were reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiple, br = broad resonance. 2,2-Diarylvinyl bromides **1a-1q** and **1a'** were prepared according to the reported procedures,^[1, 2] and **1r-1u** were obtained from commercial resources. Sulfonyl hydrazides **2d-2f**, **2i-2m** and **2p** were prepared according to the reported procedures,^[3-6] and **2a-2c**, **2g**, **2n** and **2o** were obtained from commercial resources.

2. Synthesis of Vinyl Sulfones **3**

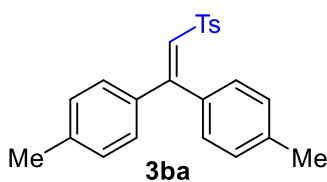
General Procedure: To a 25 mL Schlenk tube charged with a stir bar, vinyl bromides **1** (0.2 mmol), sulfonyl hydrazides **2** (0.3 mmol), AgF (50.8 mg, 0.4 mmol), and DPPH (13.6 mg, 0.03 mmol) were added. After filled with argon, water (5 mL) was added via a syringe. After stirred at 80 $^\circ\text{C}$ for 10 h, the reaction mixture was cooled down to room temperature, washed with brine (15 mL) and extracted with EtOAc (3 \times 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (PE/EA = 5:1~2:1) to afford pure products **3**.

(2-tosylethene-1,1-diyl)dibenzene (**3aa**)



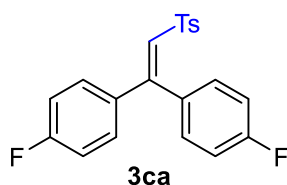
White solid; ^1H NMR (400 MHz, CDCl_3): δ 7.47 (d, J = 8.0 Hz, 2H), 7.41-7.24 (m, 6H), 7.23-7.07 (m, 6H), 6.99 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 154.81, 143.86, 139.32, 138.69, 135.67, 130.34, 129.87, 129.44, 129.06, 128.94, 128.67, 128.31, 127.91, 127.79, 21.68; EI-MS (m/z , %): 334 (M^+ , 2.09), 84 (100), 86 (62.74), 57 (34.83); HRMS (EI): m/z calcd for: $\text{C}_{21}\text{H}_{18}\text{O}_2\text{S}$, 334.1028 [M] $^+$; found: 334.1034.

4,4'-(2-tosylethene-1,1-diyl)bis(methylbenzene) (**3ba**)



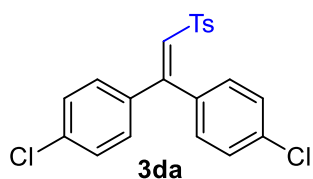
White solid; ^1H NMR (400 MHz, CDCl_3): δ 7.50 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.12-7.07 (m, 6H), 6.99 (d, J = 8.0 Hz, 2H), 6.90 (s, 1H), 2.39 (s, 3H), 2.38 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 154.99, 143.72, 140.71, 139.03, 138.94, 136.80, 132.99, 129.91, 129.35, 129.35, 128.55, 128.37, 127.80, 127.66, 21.69, 21.56, 21.39. EI-MS (m/z , %): 362 (M^+ , 34.15), 91 (100), 119 (58.6), 148 (38.35); HRMS (EI): m/z calcd for: $\text{C}_{23}\text{H}_{22}\text{O}_2\text{S}$, 362.1341 [M] $^+$; found: 362.1342.

4,4'-(2-tosylethene-1,1-diyl)bis(fluorobenzene) (3ca)



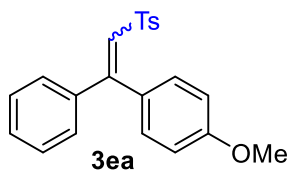
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.50 (d, $J = 8.3$ Hz, 2H), 7.23-7.14 (m, 4H), 7.14-7.07 (m, 2H), 7.05-6.97 (m, 4H), 6.93 (s, 1H), 2.39 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 164.14 (d, $J = 248.1$ Hz), 163.30 (d, $J = 248.1$ Hz), 152.53, 144.21, 138.52, 135.34 (d, $J = 3.3$ Hz), 131.92 (d, $J = 8.4$ Hz), 131.45 (d, $J = 3.4$ Hz), 130.33 (d, $J = 8.6$ Hz), 129.57, 129.22, 127.74, 115.90 (d, $J = 21.8$ Hz), 115.189 (d, $J = 21.6$ Hz), 21.69. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -109.76, -111.61; **EI-MS** (m/z, %): 370 (M^+ , 0.6), 91 (100), 119 (54.67), 84 (45.21); **HRMS** (EI): m/z calcd for: $\text{C}_{21}\text{H}_{16}\text{O}_2\text{F}_2\text{S}$, 370.0839 [M] $^+$; found: 370.0834.

4,4'-(2-tosylethene-1,1-diyl)bis(chlorobenzene) (3da)



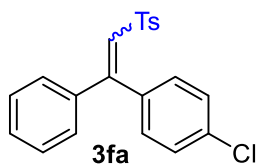
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.51 (d, $J = 8.3$ Hz, 2H), 7.32-7.25 (m, 4H), 7.21 (d, $J = 8.1$ Hz, 2H), 7.11 (d, $J = 8.5$ Hz, 2H), 7.05 (d, $J = 8.5$ Hz, 2H), 6.95 (s, 1H), 2.41 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 152.01, 144.41, 139.18, 137.37, 136.88, 135.54, 133.73, 131.27, 129.84, 129.66, 129.55, 129.10, 128.41, 127.85, 21.76. **EI-MS** (m/z, %): 402 (M^+ , 74.12), 212 (100), 91 (97.2), 176 (86.32); **HRMS** (EI): m/z calcd for: $\text{C}_{21}\text{H}_{16}\text{O}_2\text{SCl}_2$, 402.0248 [M] $^+$; found: 402.0243.

1-methoxy-4-(1-phenyl-2-tosylvinyl)benzene (1:1) (3ea)



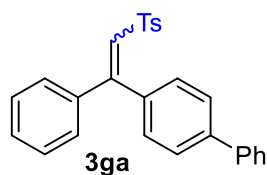
(Isomer ratio = 1:1); White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.45 (d, $J = 8.3$ Hz, 1H), 7.37 (d, $J = 8.3$ Hz, 1H), 7.28 (d, $J = 7.3$ Hz, 1H), 7.24-7.18 (m, 2H), 7.14-7.09 (m, 1.5H), 7.09-7.03 (m, 2.5H), 7.01-6.97 (m, 2H), 6.86 (s, 0.5H), 6.81 (s, 0.5H), 6.76-6.70 (m, 2H), 3.77 (s, 1.5H), 3.71 (s, 1.5H), 2.30 (s, 1.5H), 2.29 (s, 1.5H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 161.48, 160.39, 154.81, 154.42, 143.77, 143.62, 139.90, 138.98, 138.82, 135.84, 135.81, 131.68, 131.45, 130.24, 129.83, 129.38, 129.34, 128.79, 128.58, 128.54, 128.36, 127.98, 127.82, 127.69, 127.68, 126.78, 114.03, 113.28, 55.47, 55.38, 21.65, 21.63. **EI-MS** (m/z, %): 364 (M^+ , 4.79), 191 (100), 84 (80.93), 86 (50.26); **HRMS** (EI): m/z calcd for: $\text{C}_{22}\text{H}_{20}\text{O}_3\text{S}$, 364.1133 [M] $^+$; found: 364.1143.

1-chloro-4-(1-phenyl-2-tosylvinyl)benzene (3fa)



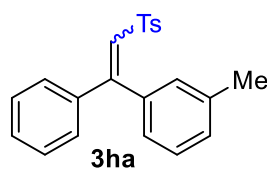
(Isomer ratio = 1:1); White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.51 (d, $J = 8.0$ Hz, 1H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.41-7.22 (m, 5H), 7.21-7.02 (m, 6H), 6.97 (s, 1H), 2.39 (s, 1.5H), 2.36 (s, 1.5H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 153.41, 153.29, 144.20, 144.00, 138.80, 138.45, 138.39, 137.73, 136.52, 135.20, 135.17, 134.10, 131.26, 130.53, 129.79, 129.77, 129.54, 129.46, 129.37, 129.35, 129.13, 128.89, 128.76, 128.24, 128.17, 128.01, 127.77, 127.72, 21.68, 21.65. **EI-MS** (m/z, %): 368 (M^+ , 41.53), 178 (100), 212 (57.73), 176 (55.52); **HRMS** (EI): m/z calcd for: $\text{C}_{21}\text{H}_{17}\text{O}_2\text{SCl}$, 368.0638 [M] $^+$; found: 368.0646.

4-(1-phenyl-2-tosylvinyl)-1,1'-biphenyl (3ga)



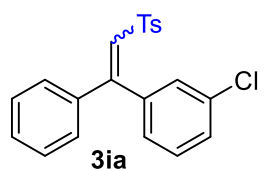
(Isomer ratio = 5:2); White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.56-7.157(m, 14H), 7.13-7.03 (m, 4H), 6.95 (m, 1H), 2.31 (m, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 154.37, 143.88, 143.22, 140.00, 139.38, 138.11, 135.64, 130.52, 130.40, 129.92, 129.47, 129.41, 129.03, 128.80, 128.74, 128.45, 128.07, 127.99, 127.91, 127.85, 127.33, 127.23, 127.19, 126.56, 21.70. **EI-MS** (m/z, %): 410 (M^+ , 3.03), 191 (100), 84 (52.13), 57 (37.56); **HRMS** (EI): m/z calcd for: $\text{C}_{27}\text{H}_{22}\text{O}_2\text{S}$, 410.1341 [M] $^+$; found: 410.1337.

1-methyl-3-(1-phenyl-2-tosylvinyl)benzene (3ha)



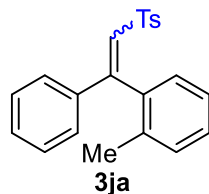
(Isomer ratio = 1:1); White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.46 (dd, J = 8.1, 6.3 Hz, 2H), 7.39-7.33 (m, 1H), 7.32-7.27 (m, 2H), 7.23-7.07 (m, 6H), 7.03 (s, 0.5H), 6.99-6.92 (m, 2H), 6.73 (s, 0.5H), 2.38 (m, 3H), 2.29 (s, 1.5H), 2.25 (s, 1.5H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 155.07, 143.80, 143.71, 139.36, 139.28, 138.77, 138.43, 137.51, 135.77, 135.53, 131.14, 130.30, 130.12, 129.86, 129.86, 129.62, 129.41, 129.31, 129.09, 128.90, 128.79, 128.66, 128.55, 128.28, 128.28, 127.86, 127.86, 127.79, 127.12, 125.64, 21.68, 21.65, 21.45, 21.40. **EI-MS** (m/z, %): 348 (M^+ , 66.65), 192 (100), 178 (80.87), 193 (55.08); **HRMS** (EI): m/z calcd for: $\text{C}_{22}\text{H}_{20}\text{O}_2\text{S}$, 348.1184 [M] $^+$; found: 348.1196.

1-chloro-3-(1-phenyl-2-tosylvinyl)benzene (3ia)



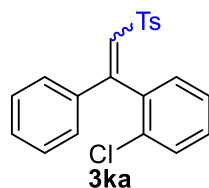
(Isomer ratio = 1:1); White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.47 (d, J = 8.0 Hz, 2H), 7.43-7.35 (m, 1H), 7.36-7.27 (m, 3.5H), 7.27-7.03 (m, 6.5H), 6.97 (s, 0.5H), 6.83 (s, 0.5H), 2.40 (s, 1.5H), 2.38 (s, 1.5H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 153.23, 152.97, 144.29, 144.11, 141.22, 138.39, 138.33, 137.26, 135.03, 134.77, 134.04, 130.61, 130.23, 130.23, 129.99, 129.92, 129.80, 129.56, 129.52, 129.32, 129.24, 128.96, 128.84, 128.34, 128.22, 128.14, 128.08, 127.83, 127.78, 126.51, 21.69, 21.69. **EI-MS** (m/z, %): 368 (M^+ , 41.53), 178 (100), 212 (57.73), 176 (55.52); **HRMS** (EI): m/z calcd for: $\text{C}_{21}\text{H}_{17}\text{O}_2\text{SCl}$, 368.0638 [M] $^+$; found: 368.0646.

1-methyl-2-(1-phenyl-2-tosylvinyl)benzene (3ja)



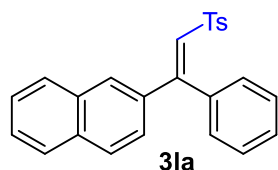
(Isomer ratio = 1:1); White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.58 (d, J = 8.2 Hz, 0.33H), 7.41-7.16 (m, 9.16H), 7.16-7.10 (m, 2.66H), 7.08-7.03 (m, 1.66H), 6.59 (s, 0.16H), 2.38 (s, 3H), 2.04 (s, 0.5H), 1.69 (s, 2.5H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 154.48, 143.92, 138.33, 137.74, 136.34, 134.55, 131.37, 131.02, 130.39, 130.09, 130.08, 129.94, 129.51, 129.47, 129.33, 129.15, 128.93, 128.86, 127.99, 127.78, 127.67, 127.37, 125.92, 125.29, 21.68, 20.35, 19.59, 17.79. **EI-MS** (m/z, %): 348 (M^+ , 8.61), 193 (100), 192 (93.17), 115 (55.66); **HRMS** (EI): m/z calcd for: $\text{C}_{21}\text{H}_{18}\text{O}_3\text{S}$, 348.1184 [M] $^+$; found: 348.1188.

1-chloro-2-(1-phenyl-2-tosylvinyl)benzene (3ka)



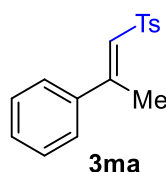
(Isomer ratio = 5:1); White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.57 (d, $J = 8.3$ Hz, 0.33H), 7.51 (d, $J = 8.3$ Hz, 1.66H), 7.39-7.14 (m, 11H), 7.07 (s, 0.83H), 6.71 (s, 0.16H), 2.39 (s, 2.5H), 2.37 (s, 0.5H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 151.24, 144.26, 137.87, 137.15, 134.24, 133.23, 133.09, 131.94, 130.94, 130.44, 130.22, 129.83, 129.75, 129.58, 129.56, 129.49, 129.37, 128.86, 127.98, 127.83, 127.80, 127.40, 126.90, 126.38, 21.73, 21.70. **EI-MS** (m/z, %): 368 (M^+ , 0.16), 333 (100), 334 (46.13), 178 (37.18); **HRMS** (EI): m/z calcd for: $\text{C}_{21}\text{H}_{17}\text{O}_2\text{SCl}$, 368.0638 [M] $^+$; found: 368.0641.

(E)-2-(1-phenyl-2-tosylvinyl)naphthalene (3la)



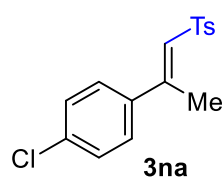
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.85 (d, $J = 8.2$ Hz, 1H), 7.72 (d, $J = 8.2$ Hz, 1H), 7.55-7.50 (m, 1H), 7.46 (d, $J = 6.9$ Hz, 1H), 7.36 (s, 1H), 7.34-7.24 (m, 6H), 7.11 (d, $J = 8.1$ Hz, 2H), 7.03 (dd, $J = 12.1, 7.8$ Hz, 2H), 6.70 (d, $J = 8.1$ Hz, 2H), 2.11 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 153.14, 143.35, 138.23, 133.41, 132.12, 131.61, 130.75, 130.71, 130.46, 129.51, 129.46, 128.93, 128.81, 128.15, 127.68, 127.38, 126.08, 125.70, 125.68, 124.99, 21.39. **EI-MS** (m/z, %): 384 (M^+ , 1.02), 229 (100), 228 (93.13), 230 (26.32); **HRMS** (EI): m/z calcd for: $\text{C}_{25}\text{H}_{20}\text{O}_2\text{S}$, 384.1184 [M] $^+$; found: 384.1190. The geometry was tentatively assigned according to the proposed mechanism.

(E)-1-methyl-4-((2-phenylprop-1-en-1-yl)sulfonyl)benzene (3ma)



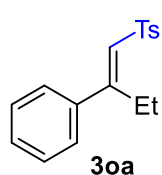
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.85 (d, $J = 8.3$ Hz, 2H), 7.42-7.32 (m, 7H), 6.60 (d, $J = 1.2$ Hz, 1H), 2.52 (d, $J = 1.2$ Hz, 3H), 2.44 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 144.28, 140.41, 134.77, 129.99, 129.94, 128.85, 128.02, 127.97, 127.45, 126.45, 21.75, 17.31. **EI-MS** (m/z, %): 272 (M^+ , 79.22), 115 (100), 206 (87.43), 105 (74.64); **HRMS** (EI): m/z calcd for: $\text{C}_{16}\text{H}_{16}\text{O}_2\text{S}$, 272.0871 [M] $^+$; found: 272.0870. The data is consistent with the reported literature.^[7]

(E)-1-chloro-4-(1-tosylprop-1-en-2-yl)benzene (3na)



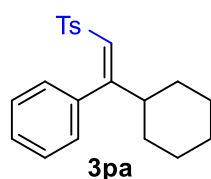
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.85 (d, $J = 8.3$ Hz, 2H), 7.38-7.30 (m, 6H), 6.59 (d, $J = 1.2$ Hz, 1H), 2.50 (d, $J = 1.2$ Hz, 3H), 2.44 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 151.56, 144.42, 139.05, 138.60, 135.95, 130.00, 128.99, 128.24, 127.72, 127.39, 21.72, 17.13. **EI-MS** (m/z, %): 306 (M^+ , 75.04), 115 (100), 139 (85.18), 240 (66.46); **HRMS** (EI): m/z calcd for: $\text{C}_{16}\text{H}_{15}\text{O}_2\text{ClS}$, 306.0481 [M] $^+$; found: 306.0487. The geometry was determined by NOE analysis.

(E)-1-methyl-4-((2-phenylbut-1-en-1-yl)sulfonyl)benzene (3oa)



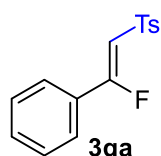
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.86 (d, $J = 8.2$ Hz, 2H), 7.35 (d, $J = 7.4$ Hz, 7H), 6.47 (s, 1H), 3.06 (q, $J = 7.4$ Hz, 2H), 2.44 (s, 3H), 0.97 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 159.32, 144.25, 139.54, 139.02, 129.99, 129.76, 128.86, 127.56, 127.40, 126.91, 23.78, 21.77, 13.24. **EI-MS** (m/z, %): 286 (M^+ , 60.79), 220 (100), 91 (79.69), 251 (62.09); **HRMS** (EI): m/z calcd for: $\text{C}_{17}\text{H}_{18}\text{O}_2\text{S}$, 286.1028 [M] $^+$; found: 286.1032. The geometry was determined by NOE analysis.

(Z)-1-((2-cyclohexyl-2-phenylvinyl)sulfonyl)-4-methylbenzene (3pa)



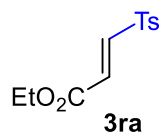
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.27 (ddd, $J = 22.9, 14.3, 7.5$ Hz, 5H), 7.09 (d, $J = 8.0$ Hz, 2H), 6.91 (d, $J = 7.0$ Hz, 2H), 6.46 (s, 1H), 2.36 (s, 3H), 2.14 (t, $J = 11.0$ Hz, 1H), 1.73 (d, $J = 10.2$ Hz, 4H), 1.63 (d, $J = 12.9$ Hz, 1H), 1.14 (ddd, $J = 23.7, 18.4, 7.0$ Hz, 5H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 162.92, 143.51, 138.87, 136.53, 129.26, 128.41, 128.01, 127.96, 127.63, 127.59, 47.85, 31.31, 26.29, 25.88, 21.65. **EI-MS** (m/z, %): 340 (M^+ , 59.22), 84 (100), 86 (78.18), 141 (23.8); **HRMS** (EI): m/z calcd for: $\text{C}_{21}\text{H}_{24}\text{O}_2\text{S}$, 340.1497 [M] $^+$; found: 340.1505. The geometry was determined by NOE analysis.

(E)-1-((2-fluoro-2-phenylvinyl)sulfonyl)-4-methylbenzene (3qa)



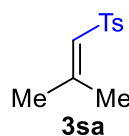
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.94 (d, $J = 8.0$ Hz, 2H), 7.59-7.32 (m, 7H), 6.56 (d, $J = 32.3$ Hz, 1H), 2.45 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 162.76, 144.73, 132.51, 129.94, 129.13 (d, $J = 1.5$ Hz), 127.81 (d, $J = 1.3$ Hz), 126.02 (d, $J = 7.8$ Hz), 109.93 (d, $J = 12.5$ Hz), 21.79. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) $\delta = -93.48$ (d, 32.3 Hz); **EI-MS** (m/z, %): 276 (M^+ , 1.33), 84 (100), 86 (65.01), 47 (15.51); **HRMS** (EI): m/z calcd for: $\text{C}_{15}\text{H}_{13}\text{O}_2\text{FS}$, 276.0620 [M] $^+$; found: 276.0630. The geometry was determined by NOE analysis.

ethyl (E)-3-tosylacrylate (3ra)



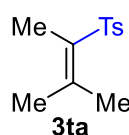
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.80 (d, $J = 8.1$ Hz, 2H), 7.44-7.24 (m, 3H), 6.80 (d, $J = 15.2$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 2.47 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 163.66, 145.79, 143.54, 135.50, 130.61, 130.40, 128.52, 62.14, 21.88, 14.17. **EI-MS** (m/z, %): 254 (M^+ , 24), 139 (100), 91 (28.18), 145 (14.74); **HRMS** (EI): m/z calcd for: $\text{C}_{12}\text{H}_{14}\text{O}_4\text{S}$, 254.0613 [M] $^+$; found: 254.0618. The data is consistent with the reported literature.^[8]

1-methyl-4-((2-methylprop-1-en-1-yl)sulfonyl)benzene (3sa)



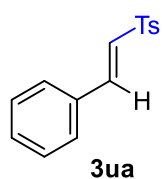
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.78 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 8.2$ Hz, 2H), 6.18 (s, 1H), 2.43 (s, 3H), 2.14 (s, 3H), 1.88 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 153.75, 143.95, 139.57, 129.81, 127.19, 126.62, 27.13, 21.64, 19.23. **EI-MS** (m/z, %): 210 (M^+ , 63.75), 144 (100), 143 (89.75), 139 (69.06); **HRMS** (EI): m/z calcd for: $\text{C}_{11}\text{H}_{14}\text{O}_2\text{S}$, 210.0715 [M] $^+$; found: 210.0716.

1-methyl-4-((3-methylbut-2-en-2-yl)sulfonyl)benzene (3ta)



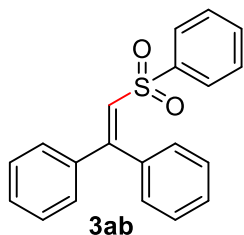
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.74 (d, $J = 8.2$ Hz, 2H), 7.31 (d, $J = 8.2$ Hz, 2H), 2.43 (s, 3H), 2.21 (d, $J = 1.2$ Hz, 3H), 2.00 (s, 3H), 1.86 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 146.84, 143.71, 139.19, 131.36, 129.72, 127.15, 103.58, 24.57, 22.22, 21.70, 16.03. **EI-MS** (m/z, %): 224 (M^+ , 47.43), 158 (100), 159 (62.86), 139 (57.09); **HRMS** (EI): m/z calcd for: $\text{C}_{12}\text{H}_{16}\text{O}_2\text{S}$, 224.0871 [M] $^+$; found: 224.0873.

(E)-1-methyl-4-(styrylsulfonyl)benzene (3ua)



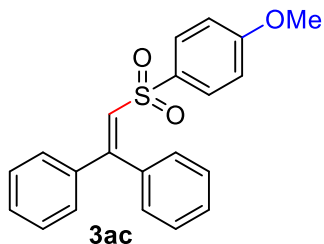
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.83 (d, $J = 8.3$ Hz, 2H), 7.66 (d, $J = 15.4$ Hz, 1H), 7.51-7.45 (m, 2H), 7.36 (dd, $J = 18.2, 7.6$ Hz, 5H), 6.85 (d, $J = 15.4$ Hz, 1H), 2.43 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 144.50, 142.04, 137.84, 132.55, 131.21, 130.07, 129.16, 128.62, 127.81, 127.73, 21.73. **EI-MS** (m/z, %): 258 (M^+ , 53.86), 91 (100), 139 (78.84), 77 (39.22); **HRMS** (EI): m/z calcd for: $\text{C}_{15}\text{H}_{14}\text{O}_2\text{S}$, 258.0715 [M] $^+$; found: 258.0724.

(2-(phenylsulfonyl)ethene-1,1-diyl)dibenzene (3ab)



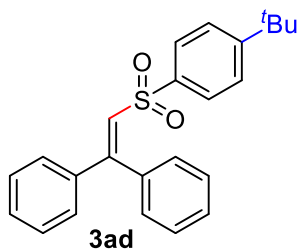
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.50 (d, $J = 7.3$ Hz, 2H), 7.40 (t, $J = 7.4$ Hz, 1H), 7.32-7.16 (m, 8H), 7.13 (d, $J = 7.3$ Hz, 2H), 7.00 (d, $J = 7.1$ Hz, 2H), 6.95 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 155.31, 141.53, 139.16, 135.54, 132.94, 130.44, 129.84, 128.97, 128.83, 128.77, 128.69, 128.30, 127.95, 127.71. **EI-MS** (m/z, %): 320 (M^+ , 14.3), 191 (100), 178 (31.18), 57 (28.6); **HRMS** (EI): m/z calcd for: $\text{C}_{20}\text{H}_{16}\text{O}_2\text{S}$, 320.0871 [M] $^+$; found: 320.0878.

(2-((4-methoxyphenyl)sulfonyl)ethene-1,1-diyl)dibenzene (3ac)



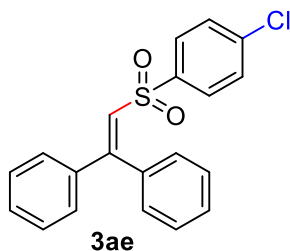
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.42 (d, $J = 8.9$ Hz, 2H), 7.32-7.26 (m, 1H), 7.26-7.19 (m, 4H), 7.15-7.10 (m, 2H), 7.05-7.00 (m, 2H), 6.93 (s, 1H), 6.73 (d, $J = 8.9$ Hz, 2H), 3.75 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 163.22, 154.40, 139.32, 135.70, 133.20, 130.29, 129.95, 129.89, 129.45, 128.92, 128.67, 128.27, 127.95, 114.01, 55.73. **EI-MS** (m/z, %): 350 (M^+ , 34.15), 178 (100), 286 (58.18), 179 (35.4); **HRMS** (EI): m/z calcd for: $\text{C}_{21}\text{H}_{18}\text{O}_3\text{S}$, 350.0977 [M] $^+$; found: 350.0985.

(2-((4-tert-butyl)phenyl)sulfonyl)ethene-1,1-diyl)dibenzene (3ad)



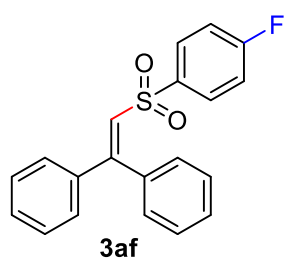
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.50 (d, $J = 8.6$ Hz, 2H), 7.40-7.24 (m, 8H), 7.23-7.19 (m, 2H), 7.11-7.05 (m, 2H), 7.02 (s, 1H), 1.30 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 156.72, 154.62, 139.28, 138.35, 135.69, 130.32, 129.86, 129.22, 128.85, 128.66, 128.30, 127.91, 127.62, 125.76, 35.20, 31.14. **EI-MS** (m/z, %): 376 (M^+ , 32.15), 178 (100), 167 (50), 179 (41.89); **HRMS** (EI): m/z calcd for: $\text{C}_{24}\text{H}_{24}\text{O}_2\text{S}$, 376.1497 [M] $^+$; found: 376.1500.

(2-((4-chlorophenyl)sulfonyl)ethene-1,1-diyl)dibenzene (3ae)



White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.46 (d, $J = 8.6$ Hz, 2H), 7.37 (dt, $J = 4.9, 4.0$ Hz, 2H), 7.34-7.26 (m, 6H), 7.23-7.18 (m, 2H), 7.08-7.04 (m, 2H), 7.02 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 155.70, 139.89, 139.46, 138.82, 135.36, 130.58, 129.79, 129.16, 129.08, 128.93, 128.69, 128.55, 128.25, 127.96. **EI-MS** (m/z, %): 354 (M^+ , 25.72), 178 (100), 179 (42.76), 115 (40.19); **HRMS** (EI): m/z calcd for: $\text{C}_{20}\text{H}_{15}\text{O}_2\text{S}\text{Cl}$, 354.0481 [M] $^+$; found: 354.0476.

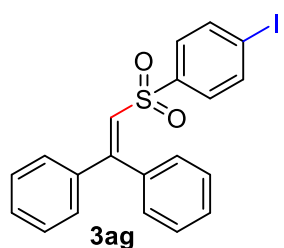
(2-((4-fluorophenyl)sulfonyl)ethene-1,1-diyl)dibenzene (3af)



338.0777 [M]⁺; found: 338.0772.

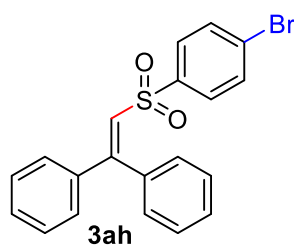
White solid; ¹H NMR (400 MHz, CDCl₃): δ 7.57-7.51 (m, 2H), 7.41-7.35 (m, 2H), 7.34-7.27 (m, 4H), 7.23-7.18 (m, 2H), 7.09-7.05 (m, 2H), 7.04 (s, 1H), 6.99 (t, *J* = 8.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 165.29 (d, *J* = 257.9 Hz), 155.49, 138.95, 135.46, 130.58, 130.57 (d, *J* = 9.5 Hz), 129.86, 129.10, 128.89, 128.74, 128.29, 128.03, 115.94 (d, *J* = 22.5 Hz). **EI-MS** (*m/z*, %): 338 (M⁺, 40.83), 178 (100), 179 (45.29), 167 (34.39); **HRMS** (EI): *m/z* calcd for: C₂₀H₁₅O₂FS, 338.0777 [M]⁺; found: 338.0772.

(2-((4-iodophenyl)sulfonyl)ethene-1,1-diyl)dibenzene (3ag)



White solid; ¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.42-7.17 (m, 10H), 7.05 (d, *J* = 7.2 Hz, 2H), 7.01 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 155.78, 141.14, 138.90, 137.95, 135.42, 130.63, 129.85, 129.14, 129.12, 128.75, 128.53, 128.31, 128.02, 100.72. **EI-MS** (*m/z*, %): 446 (M⁺, 24.29), 57 (100), 71 (82.35), 178 (76.66); **HRMS** (EI): *m/z* calcd for: C₂₀H₁₅O₂IS, 445.9838 [M]⁺; found: 445.9840.

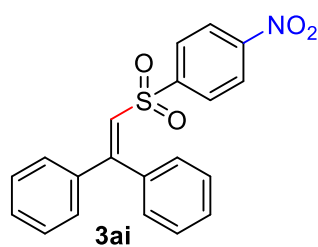
(2-((4-bromophenyl)sulfonyl)ethene-1,1-diyl)dibenzene (3ah)



397.9977.

White solid; ¹H NMR (400 MHz, CDCl₃): δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.41-7.35 (m, 4H), 7.30 (td, *J* = 7.6, 2.2 Hz, 4H), 7.20 (d, *J* = 7.4 Hz, 2H), 7.06 (d, *J* = 7.4 Hz, 2H), 7.02 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 155.77, 140.45, 138.85, 135.39, 131.94, 130.61, 129.82, 129.27, 129.12, 128.86, 128.73, 128.53, 128.10, 128.00. **EI-MS** (*m/z*, %): 398 (M⁺, 17.76), 178 (100), 179 (42.98), 167 (31.61); **HRMS** (EI): *m/z* calcd for: C₂₀H₁₅O₂SBr, 397.9976 [M]⁺; found: 397.9977.

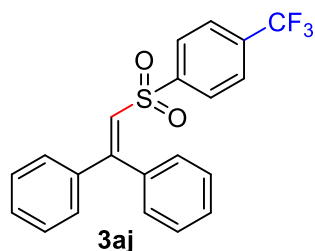
(2-((4-nitrophenyl)sulfonyl)ethene-1,1-diyl)dibenzene (3ai)



365.0722 [M]⁺; found: 365.0729.

White solid; ¹H NMR (400 MHz, CDCl₃): δ 8.13 (d, *J* = 8.7 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.41 (dd, *J* = 12.7, 7.2 Hz, 2H), 7.36-7.25 (m, 4H), 7.22 (d, *J* = 7.7 Hz, 2H), 7.07 (s, 1H), 7.03 (d, *J* = 7.5 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 157.21, 150.07, 147.04, 138.47, 135.18, 131.03, 129.90, 129.46, 129.08, 128.85, 128.38, 128.13, 127.77, 123.76. **EI-MS** (*m/z*, %): 365 (M⁺, 32.24), 178 (100), 179 (45.28), 167 (19.85); **HRMS** (EI): *m/z* calcd for: C₂₀H₁₅NO₄S, 365.0722 [M]⁺; found: 365.0729.

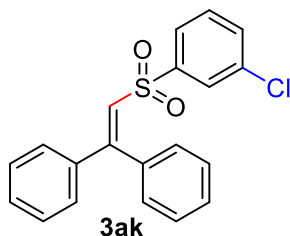
(2-((4-(trifluoromethyl)phenyl)sulfonyl)ethene-1,1-diyl)dibenzene (3aj)



White solid; ¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.44-7.18 (m, 8H), 7.06 (s, 1H), 7.02 (d, *J* = 7.3 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 156.47, 144.83, 138.68, 135.31, 134.59, 134.27, 130.85, 129.87, 129.26, 128.82, 128.37, 128.33, 128.25, 128.09, 125.77 (q, *J* = 3.7 Hz). ¹⁹F NMR (376 MHz,

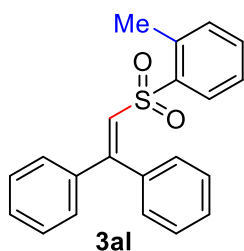
CDCl₃) δ -63.25; **EI-MS** (m/z, %): 388 (M⁺, 5.4), 84 (100), 86 (69.93), 191 (28.22); **HRMS** (EI): m/z calcd for: C₂₁H₁₅F₃O₂S, 388.0745 [M]⁺; found: 388.0752.

(2-((3-chlorophenyl)sulfonyl)ethene-1,1-diyl)dibenzene (3ak)



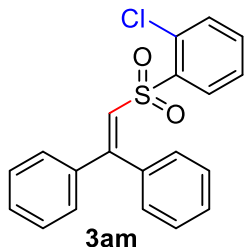
White solid; **¹H NMR** (400 MHz, CDCl₃): δ 7.49-7.37 (m, 5H), 7.31 (dd, J = 14.8, 7.8 Hz, 5H), 7.24-7.20 (m, 2H), 7.06 (s, 1H), 7.04 (s, 2H). **¹³C NMR** (100 MHz, CDCl₃): δ 156.19, 143.17, 138.83, 135.20, 134.91, 133.07, 130.73, 130.05, 129.84, 129.35, 128.80, 128.53, 128.35, 128.17, 128.06, 125.87. **EI-MS** (m/z, %): 354 (M⁺, 32.79), 178 (100), 179 (48.67), 167 (31.3); **HRMS** (EI): m/z calcd for: C₂₀H₁₅O₂SCl, 354.0481 [M]⁺; found: 354.0885.

(2-(o-tolylsulfonyl)ethene-1,1-diyl)dibenzene (3al)



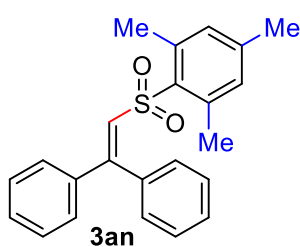
White solid; **¹H NMR** (400 MHz, CDCl₃): δ 7.45-7.36 (m, 2H), 7.31 (dd, J = 14.3, 7.4 Hz, 3H), 7.27-7.21 (m, 4H), 7.17 (t, J = 7.4 Hz, 3H), 7.06 (s, 1H), 7.03-6.96 (m, 3H), 2.65 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃): δ 153.96, 138.23, 136.23, 134.37, 131.89, 130.97, 129.47, 128.67, 128.50, 127.96, 127.87, 127.80, 127.31, 126.87, 125.01, 19.70. **EI-MS** (m/z, %): 334 (M⁺, 11.13), 178 (100), 57 (67.38), 191 (53.13); **HRMS** (EI): m/z calcd for: C₂₁H₁₈O₂S, 334.1028 [M]⁺; found: 334.1037.

(2-((2-chlorophenyl)sulfonyl)ethene-1,1-diyl)dibenzene (3am)



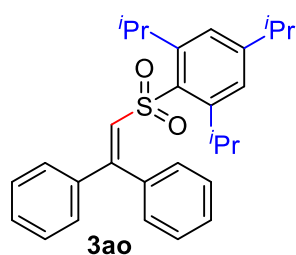
White solid; **¹H NMR** (400 MHz, CDCl₃): δ 7.44 (dd, J = 8.0, 1.3 Hz, 1H), 7.41-7.31 (m, 5H), 7.29-7.20 (m, 3H), 7.18 (s, 1H), 7.13 (t, J = 7.6 Hz, 2H), 7.05 (td, J = 8.1, 1.4 Hz, 1H), 6.99 (d, J = 7.1 Hz, 2H). **¹³C NMR** (100 MHz, CDCl₃): δ 155.41, 139.13, 135.33, 133.75, 132.21, 131.18, 130.97, 130.55, 129.60, 128.96, 128.77, 128.46, 128.24, 127.79, 126.74. **EI-MS** (m/z, %): 354 (M⁺, 29.38), 178 (100), 167 (43.14), 179 (42.59); **HRMS** (EI): m/z calcd for: C₂₀H₁₅O₂SCl, 354.0481 [M]⁺; found: 354.0488.

(2-(mesitylsulfonyl)ethene-1,1-diyl)dibenzene (3an)



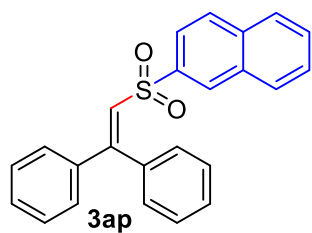
White solid; **¹H NMR** (400 MHz, CDCl₃): δ 7.40-7.24 (m, 4H), 7.24-7.16 (m, 4H), 7.06 (s, 1H), 6.98 (d, J = 7.2 Hz, 2H), 6.75 (m, 2H), 2.44 (s, 6H), 2.24 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃): δ 153.19, 142.60, 139.45, 139.25, 135.58, 135.51, 131.77, 131.28, 130.20, 129.21, 128.74, 128.61, 128.09, 127.89, 22.60, 21.03. **EI-MS** (m/z, %): 362 (M⁺, 4.33), 178 (100), 297 (89.71), 165 (61.43); **HRMS** (EI): m/z calcd for: C₂₃H₂₂O₂S, 362.1341 [M]⁺; found: 364.1343.

2-((2,4,6-triisopropylphenyl)sulfonyl)ethene-1,1-diyl)dibenzene (**3ao**)



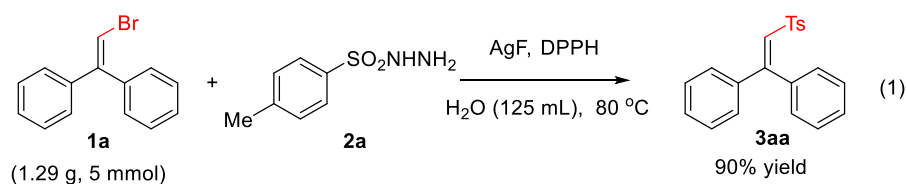
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.31-7.15 (m, 4H), 7.14-7.07 (m, 4H), 7.04 (s, 1H), 6.96 (d, $J = 7.3$ Hz, 2H), 6.91 (s, 2H), 3.93 (dt, $J = 13.4, 6.7$ Hz, 2H), 2.77 (dt, $J = 13.8, 6.9$ Hz, 1H), 1.15 (d, $J = 6.9$ Hz, 6H), 1.10 (d, $J = 6.7$ Hz, 12H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 153.21, 150.37, 139.61, 132.86, 130.04, 129.60, 128.72, 128.58, 128.09, 127.85, 123.26, 123.26, 34.41, 29.88, 24.93, 23.78. **EI-MS** (m/z , %): 446 (M^+ , 1.55), 180 (100), 191 (72.5), 57 (29.85); **HRMS** (EI): m/z calcd for: $\text{C}_{29}\text{H}_{34}\text{O}_2\text{S}$, 446.2280 [M] $^+$; found: 446.2284.

2-((2,2-diphenylvinyl)sulfonyl)naphthalene (**3ap**)



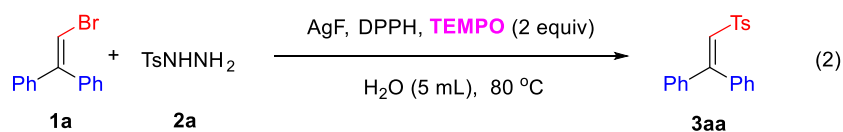
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.97 (s, 1H), 7.90-7.80 (m, 2H), 7.76 (d, $J = 7.9$ Hz, 1H), 7.60 (ddd, $J = 31.2, 15.8, 7.8$ Hz, 3H), 7.39-7.32 (m, 1H), 7.28 (t, $J = 7.3$ Hz, 3H), 7.18 (dd, $J = 13.4, 7.1$ Hz, 4H), 7.10 (s, 1H), 7.03 (d, $J = 7.3$ Hz, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 155.46, 139.08, 138.04, 135.34, 134.91, 131.97, 130.46, 129.81, 129.74, 129.45, 129.10, 129.07, 129.03, 128.84, 128.68, 128.29, 127.87, 127.82, 127.39, 122.61. **EI-MS** (m/z , %): 370 (M^+ , 1.98), 84 (100), 86 (79.14), 47 (26.24); **HRMS** (EI): m/z calcd for: $\text{C}_{24}\text{H}_{18}\text{O}_2\text{S}$, 370.1028 [M] $^+$; found: 370.1034.

3. Gram-Scale Synthesis

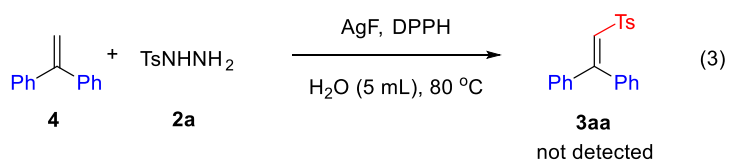


To a 250 mL Schlenk tube charged with a stir bar, 2,2-diphenylethenyl bromide (**1a**) (5 mmol), 4-methylbenzenesulfonylhydrazide (**2a**) (7.5 mmol), AgF (1.27 g, 10 mmol), and DPPH (340 mg, 0.75 mmol) were added. After stirred at 80 °C for 10 h, the reaction mixture was cooled down to room temperature, washed with brine (15 mL) and extracted with EtOAc (3×10 mL). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (PE/EA = 5:1) to afford pure products **3aa** in 90% yield.

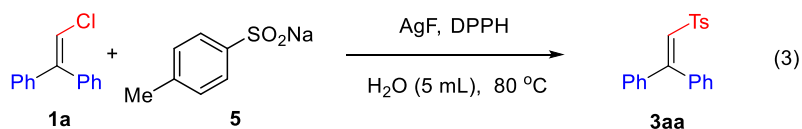
4. Control Experiments



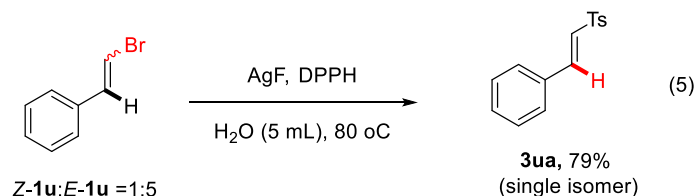
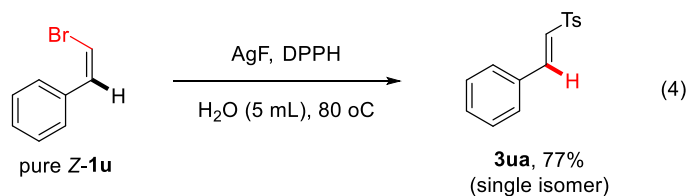
To a 25 mL Schlenk tube charged with a stir bar, 2,2-diphenylethenyl bromide (**1a**) (0.2 mmol), 4-methylbenzenesulfonylhydrazide (**2a**) (0.3 mmol), AgF (50.8 mg, 0.4 mmol), DPPH (13.6 mg, 0.03 mmol) and TEMPO (62.4 mg, 2 equiv) were added. After filled with argon, water (5 mL) was added via a syringe. The mixture was stirred at 80 °C for 10 h. Upon completion, the yield of the product was detected by ¹H NMR with CH₂Br₂ as the internal standard.



To a 25 mL Schlenk tube charged with a stir bar, 1,1-diphenylethene (**1a**) (0.2 mmol), 4-methylbenzenesulfonylhydrazide (**2a**) (0.3 mmol), AgF (50.8 mg, 0.4 mmol), DPPH (13.6 mg, 0.03 mmol) were added. After filled with argon, water (5 mL) was added via a syringe. The mixture was stirred at 80 °C for 10 h. Upon completion, the yield of the product was detected by ¹H NMR with CH₂Br₂ as the internal standard.



To a 25 mL Schlenk tube charged with a stir bar, 2,2-diphenylethenyl bromide (**1a**) (0.2 mmol), sodium *p*-tolylsulfinate (**5**) (0.3 mmol), AgF (50.8 mg, 0.4 mmol), DPPH (13.6 mg, 0.03 mmol) were added. After filled with argon, water (5 mL) was added via a syringe. The mixture was stirred at 80 °C for 10 h. Upon completion, the yield of the product was detected by ¹H NMR with CH₂Br₂ as the internal standard.

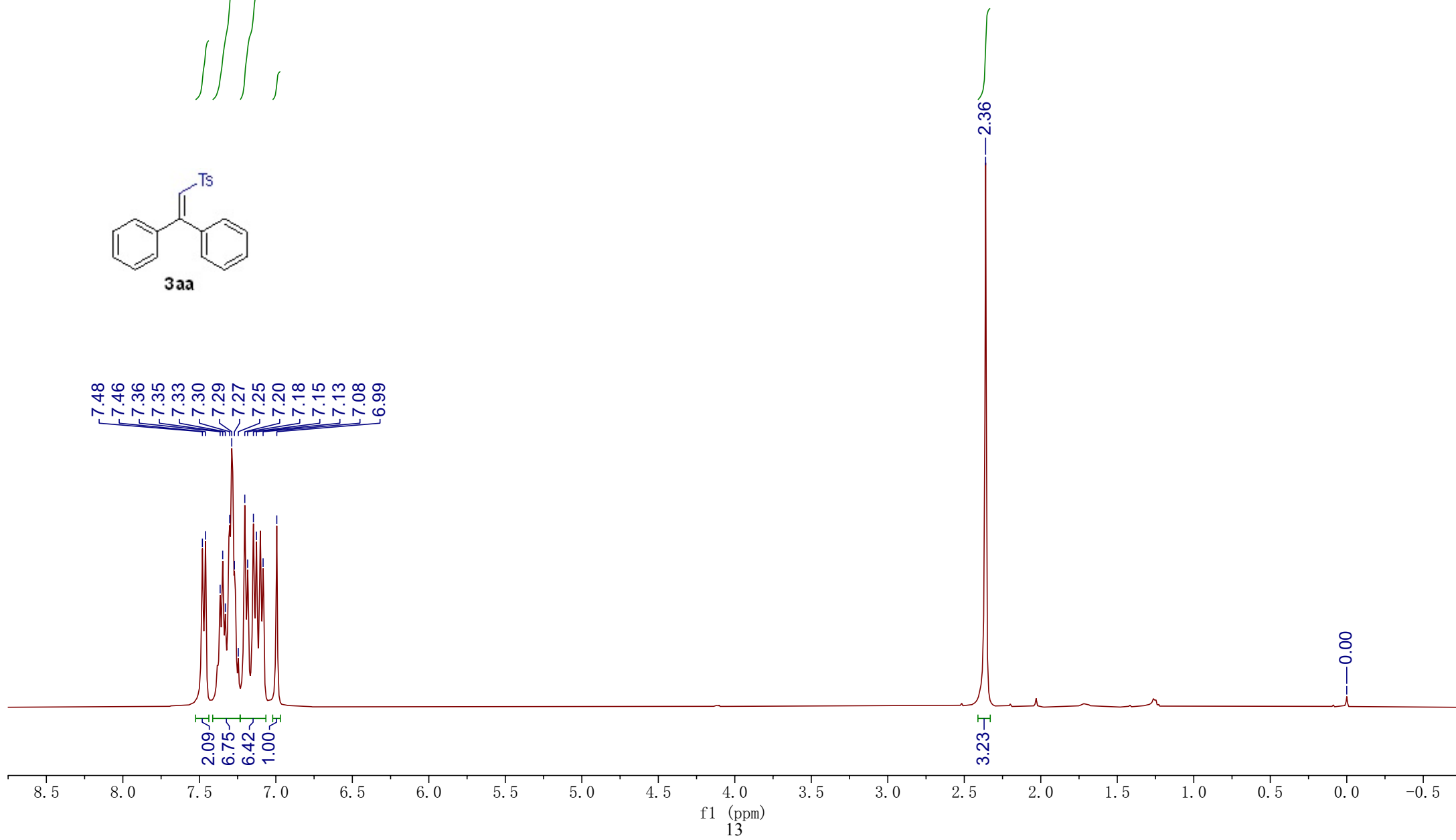
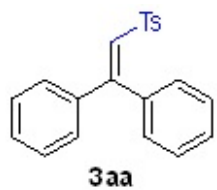
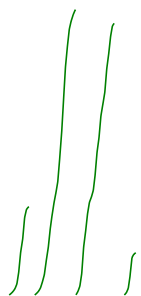


To a 25 mL Schlenk tube charged with a stir bar, *Z*-β-bromostyrene (**Z-1u**) or β-bromostyrene (**Z-1u**:**E-1u** = 1:5) (0.2 mmol), 4-methylbenzenesulfonohydrazide (**2a**) (0.3 mmol), AgF (50.8 mg, 0.4 mmol), DPPH (13.6 mg, 0.03 mmol) were added. After filled with argon, water (5 mL) was added via a syringe. The mixture was stirred at 80 °C for 10 h. Upon completion, the reaction mixture was washed with brine (15 mL) and extracted with EtOAc (3×10 mL). The combined organic phases were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (PE/EA = 5:1) to afford pure products (**3ua**).

5. References

- [1] G. Zhang, R. X. Bai, C. H. Li, C. G. Feng, G. Q. Lin, *Tetrahedron* 2019, **75**, 1658.
- [2] J. J. Molloy, J. B. Metternich, C. G. Daniliuc, A. J. B. Watson, R. Gilmour, *Angew. Chem. Int. Ed.* 2018, **57**, 3168.
- [3] G. L. Backes, D. M. Neumann, B. S. Jursic, *Bioorg. Med. Chem.* 2014, **22**, 4629.
- [4] L. Y. Fu, T. M. Xian, K. T. Shi, *Chem. Eur. J.* 2012, **18**, 1582.
- [5] B. Wang, Z. C. Yan, Y. Y. Liu, J. W. Wang, Z. G. Zha, Z. Y. Wang, *Green Chem.* 2019, **21**, 205.
- [6] X. Zhao, L. P. Zhang, T. J. Li, G. Y. Liu, H. M. Wang, K. Lu, *Chem. Commun.* 2014, **50**, 13121.
- [7] A. O. Terent'ev, O. M. Mulina, D. A. Pirgach, A. I. Ilovaisky, M. A. Syroeshkin, N. I. Kapustina, G. I. Nikishin, *Tetrahedron* 2017, **73**, 6871.
- [8] K. Kiyokawa, T. Nagata, J. Hayakawa, S. Minakata, *Chem. Eur. J.* 2014, **20**, 1.

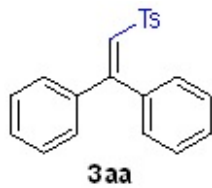
6. Copies of ^1H NMR, ^{13}C NMR and ^{19}F NMR



7.48
7.46
7.36
7.35
7.33
7.30
7.29
7.27
7.25
7.20
7.18
7.15
7.13
7.08
6.99

2.09
6.75
6.42
1.00

f1 (ppm)
13



—154.81

~143.86

~139.32

~138.69

~135.67

~130.34

~129.87

~129.44

~129.06

~128.94

~128.67

~128.31

~127.91

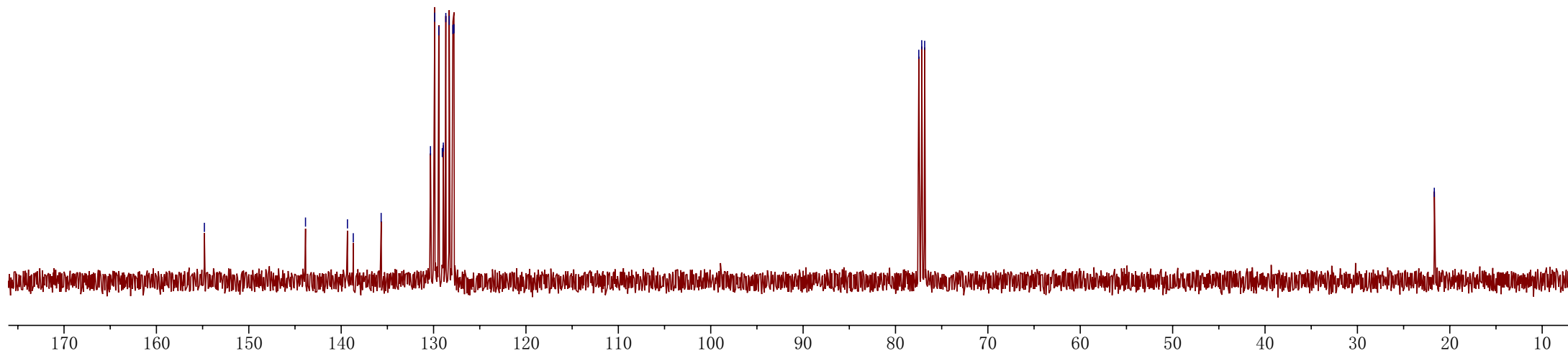
~127.79

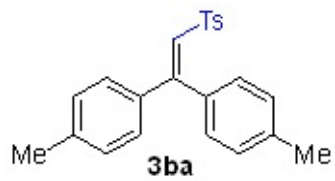
~77.48

~77.16

~76.84

—21.68

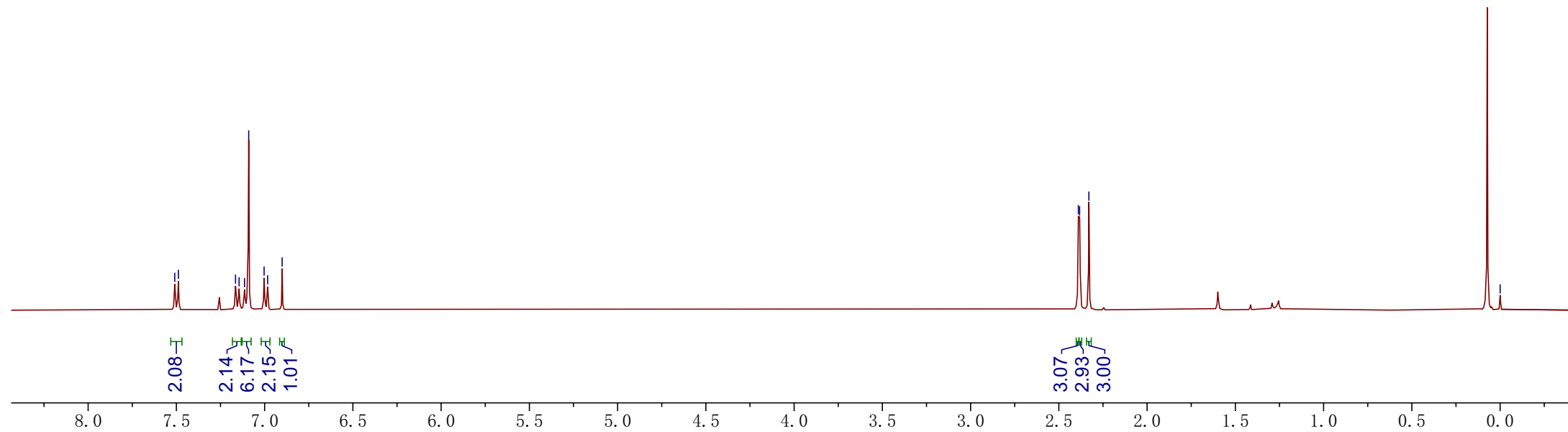




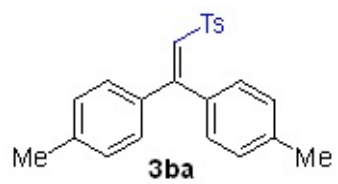
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6.98
6.90

2.39
2.38
2.33

— 0.00



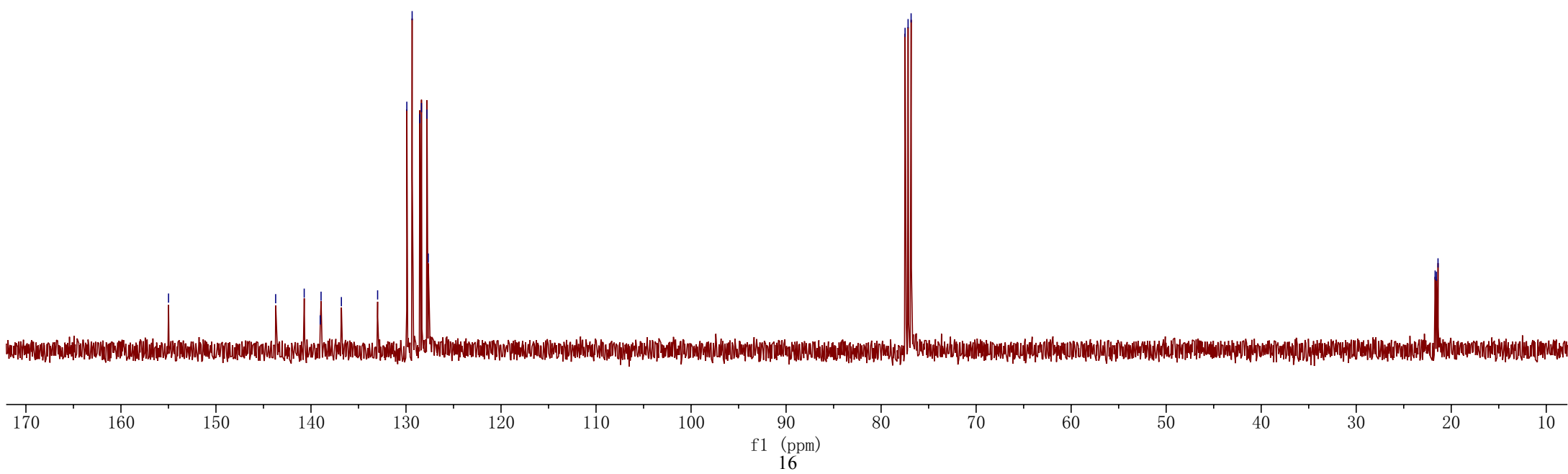
f1 (ppm)
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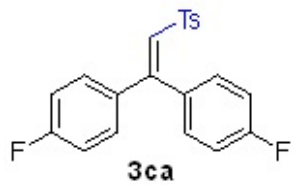


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139.03
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136.80
132.99
129.91
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127.80
127.66

77.48
77.16
76.84

21.69
21.56
21.39

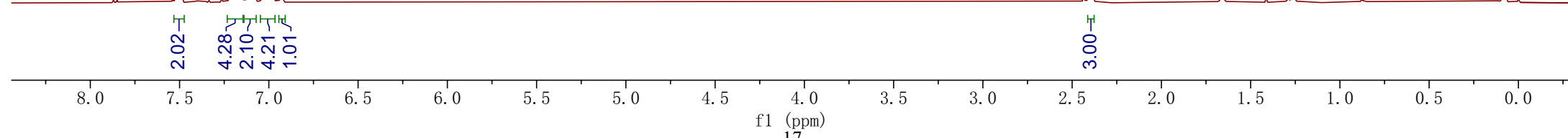


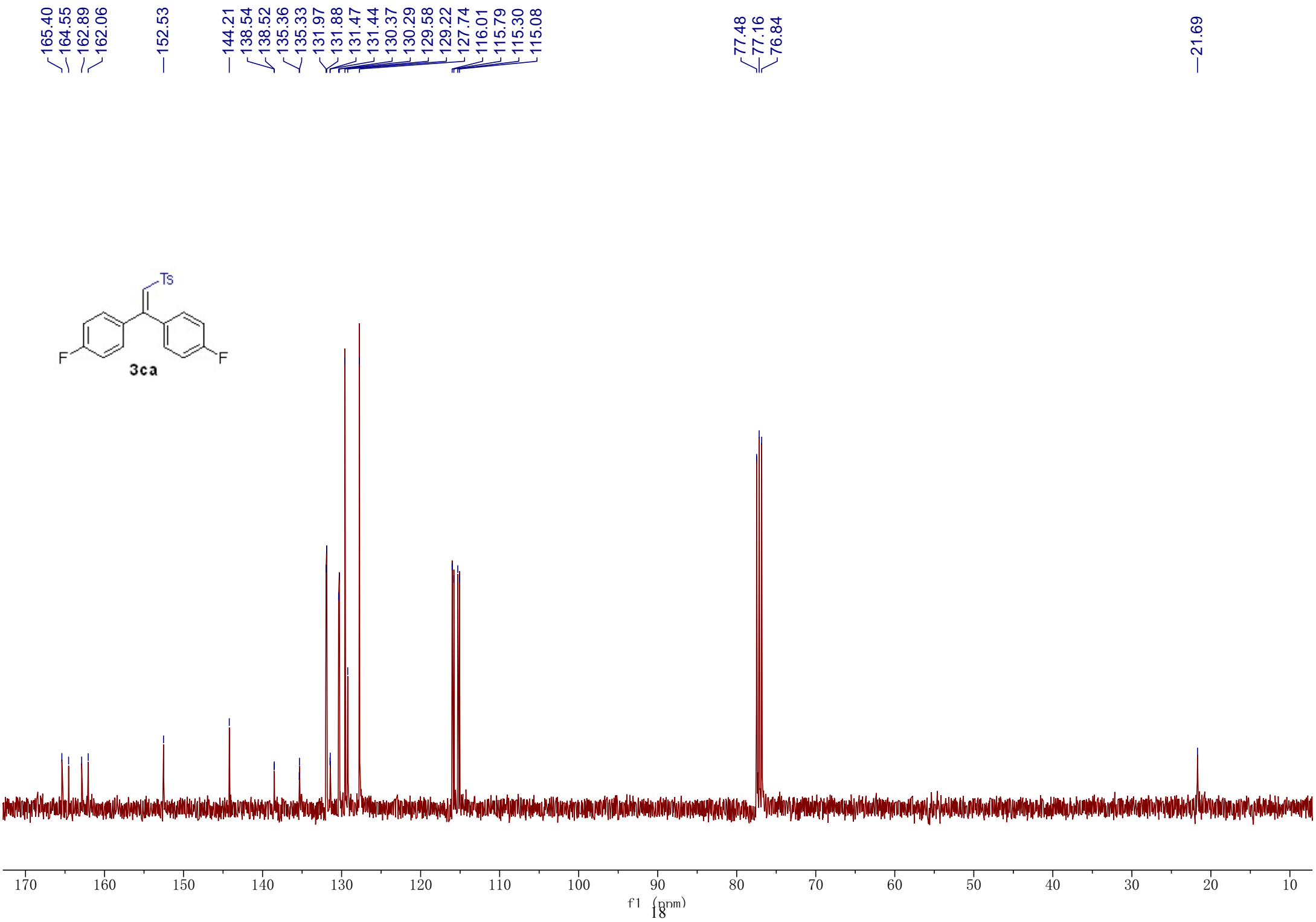
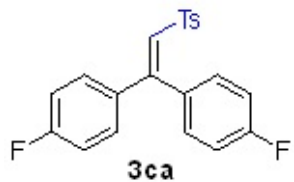


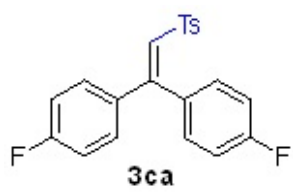
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6.98
6.93

2.39

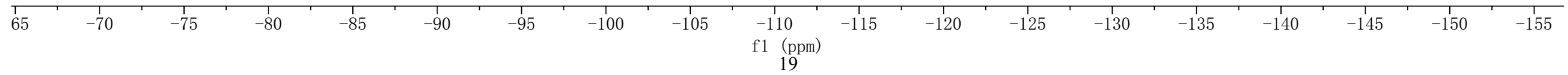
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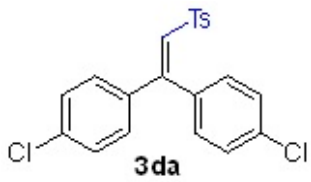
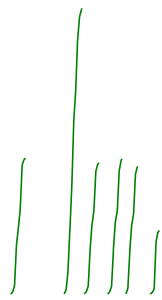




---109.76
---111.61

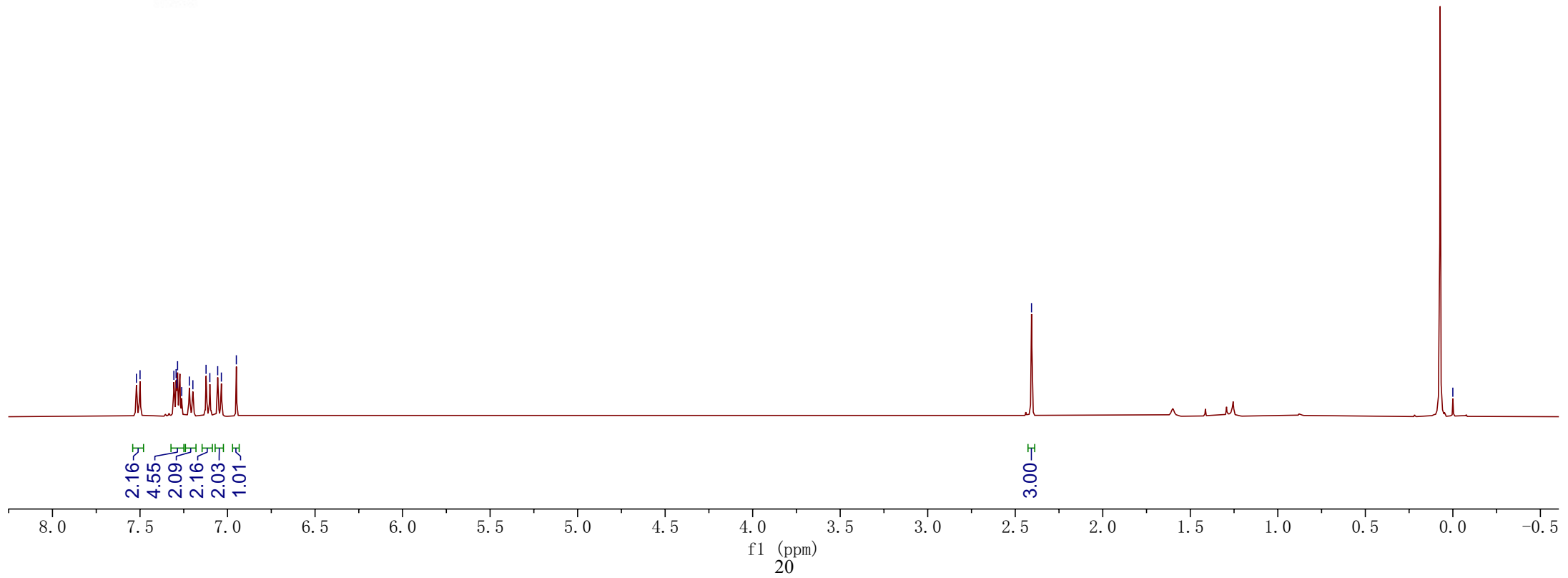


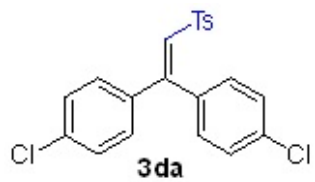
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—2.41

—0.00



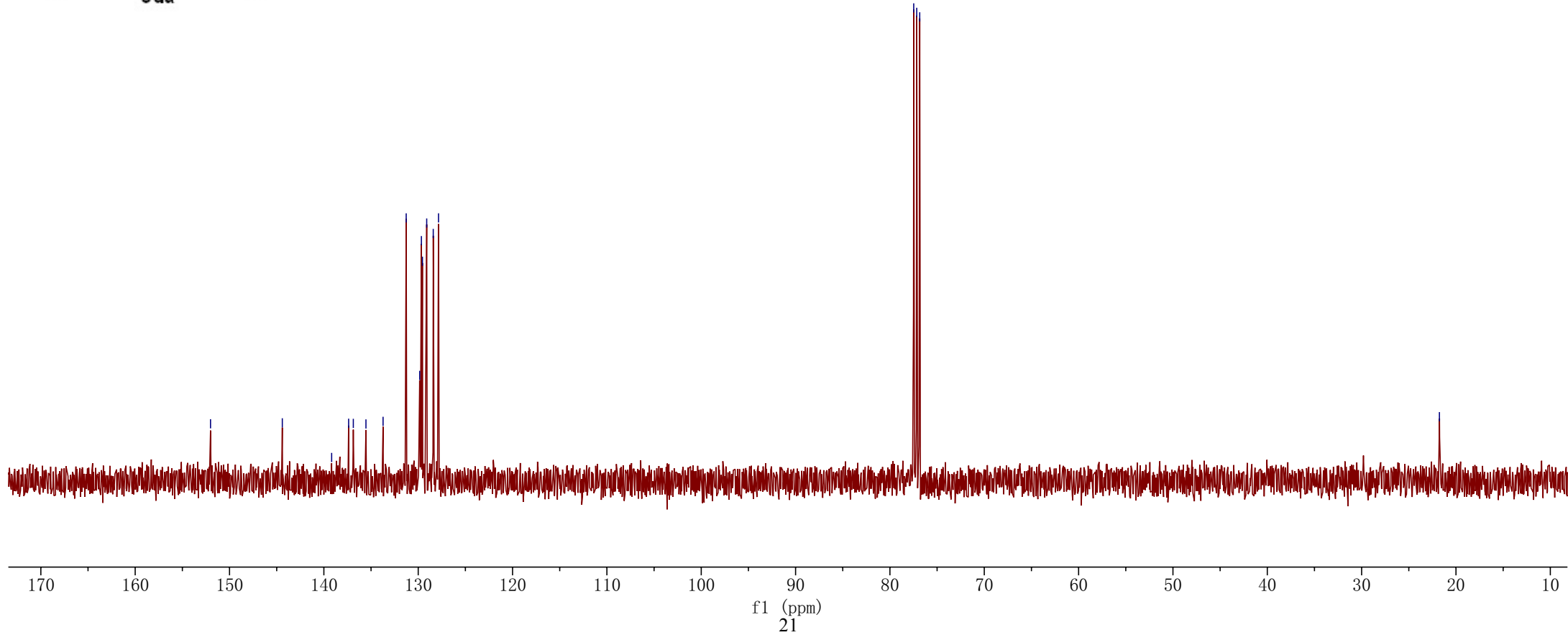
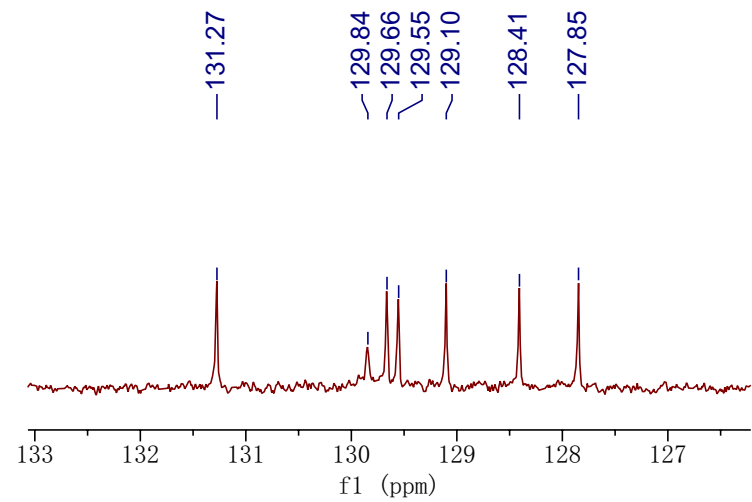


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21.76

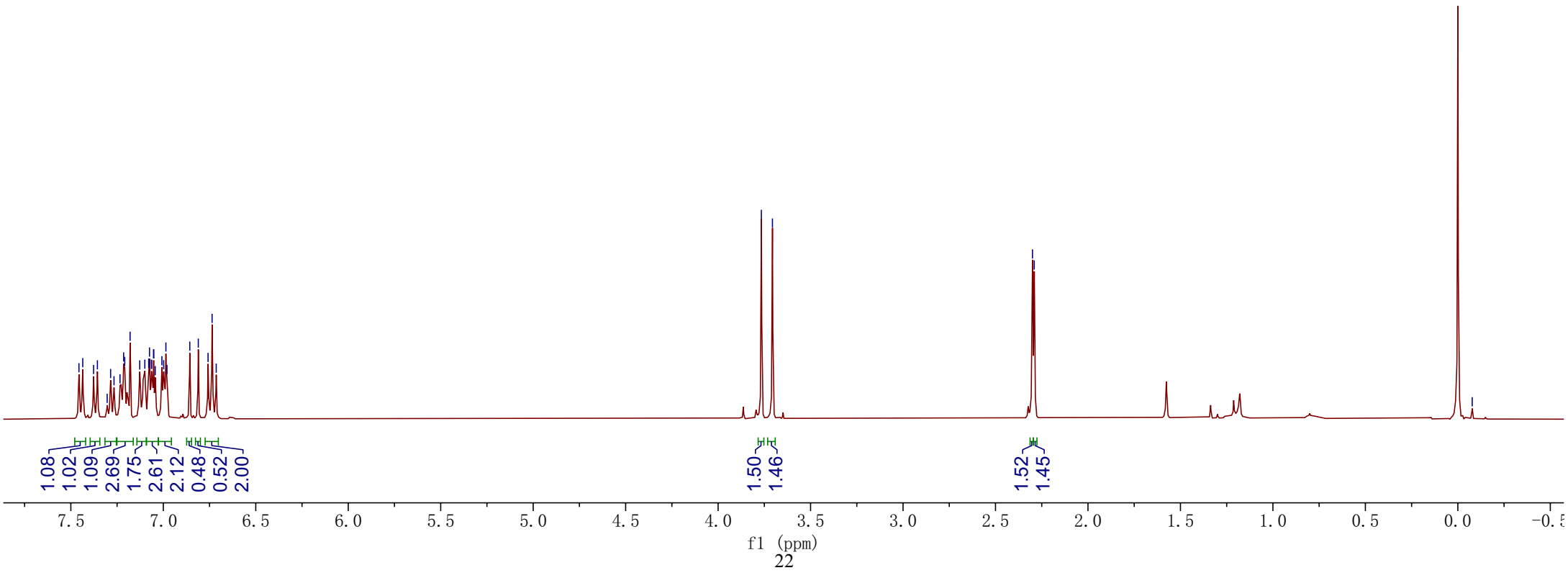
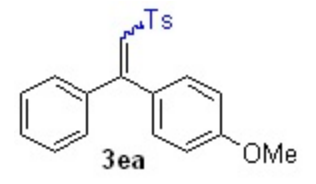
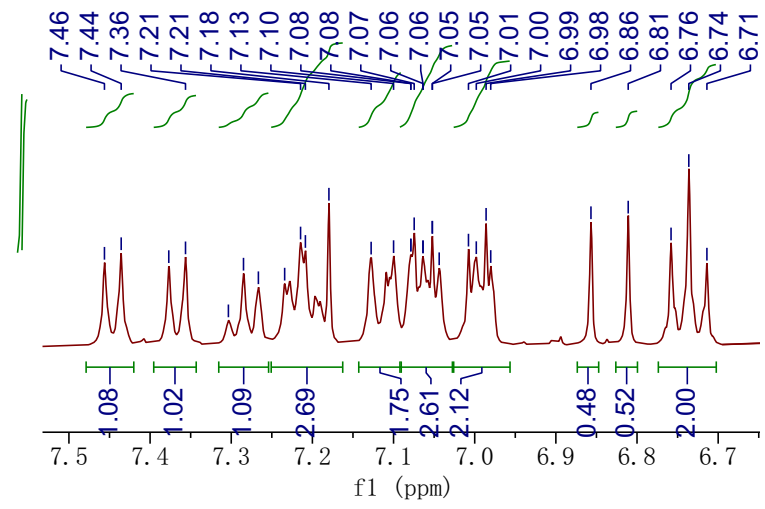
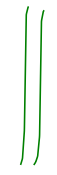
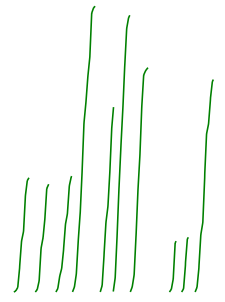


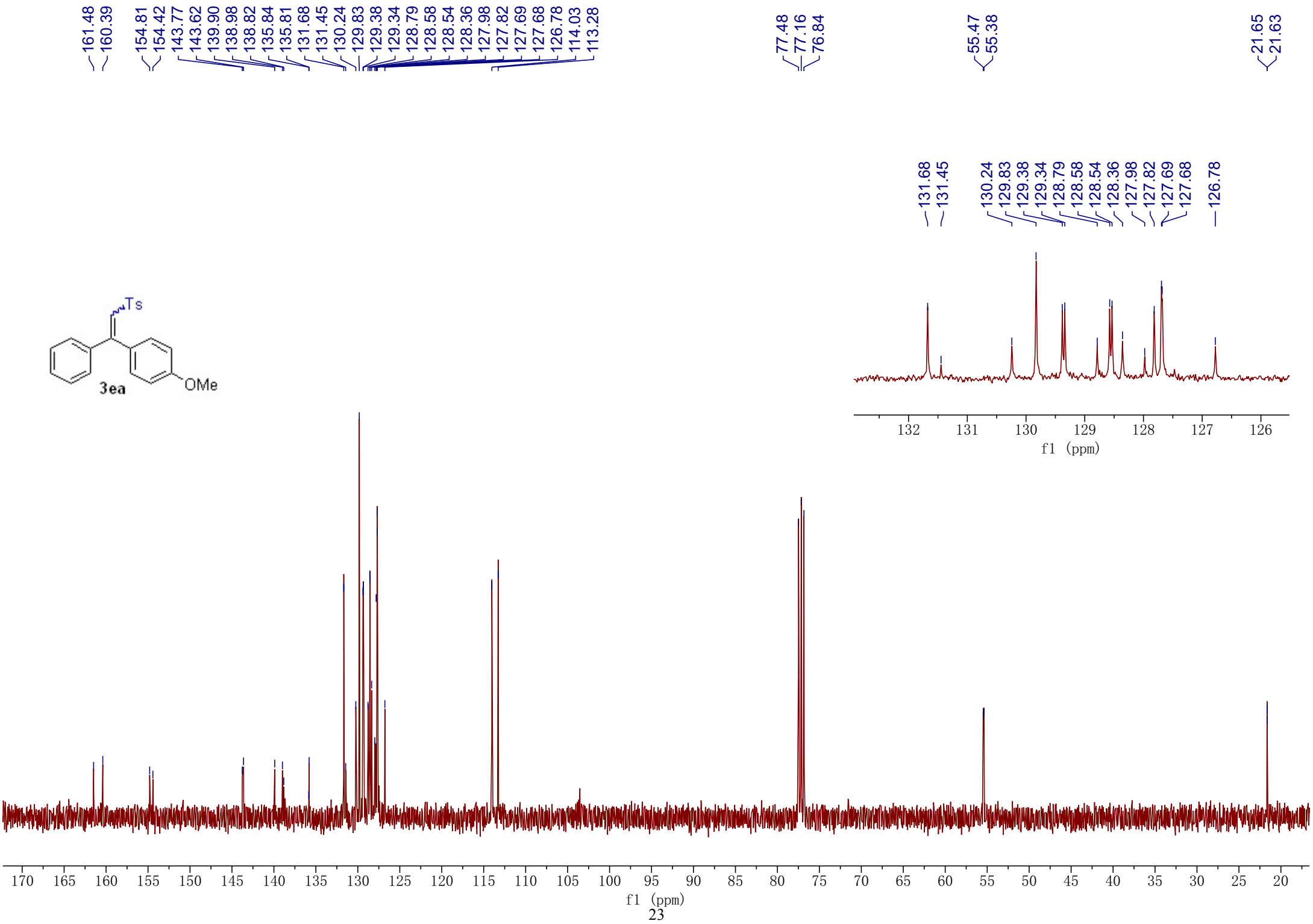
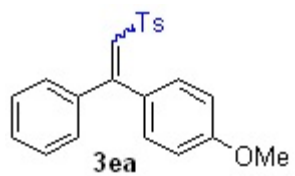
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3.77
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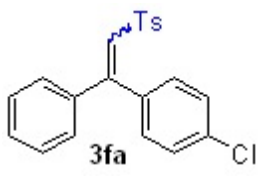
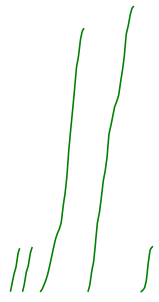
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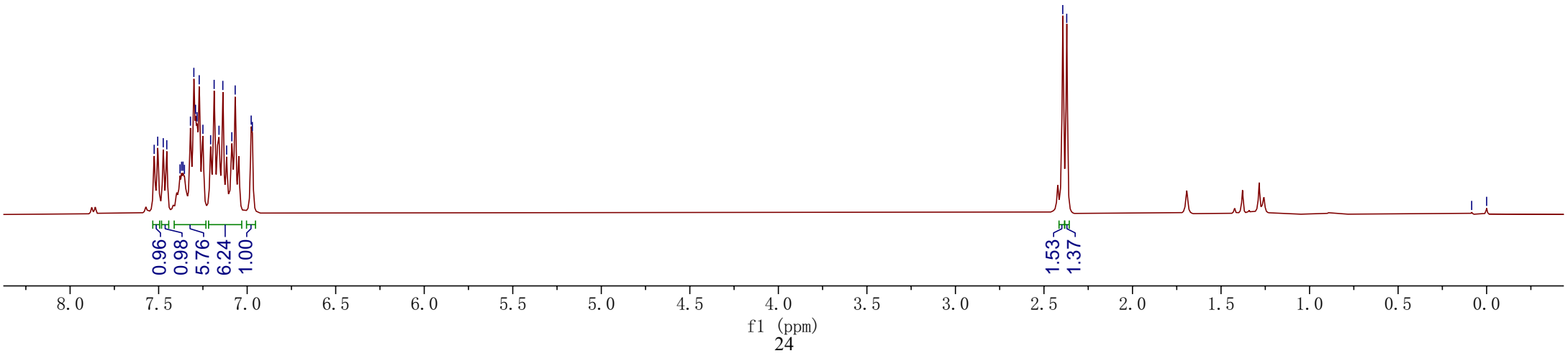
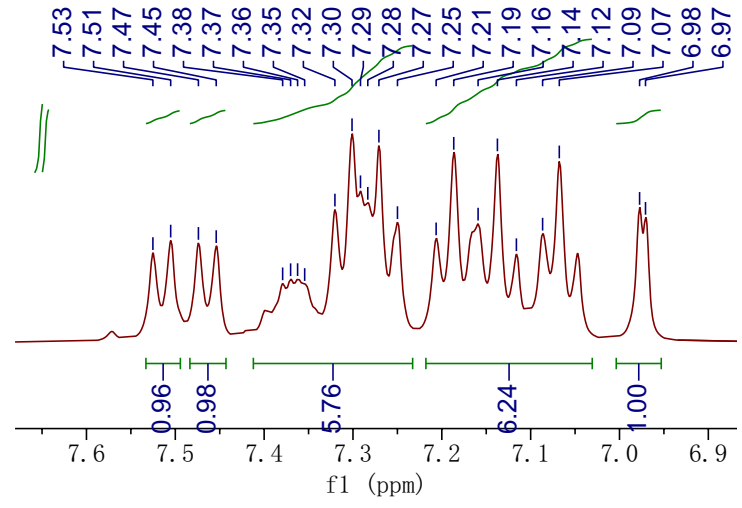




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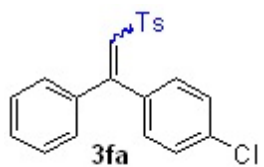
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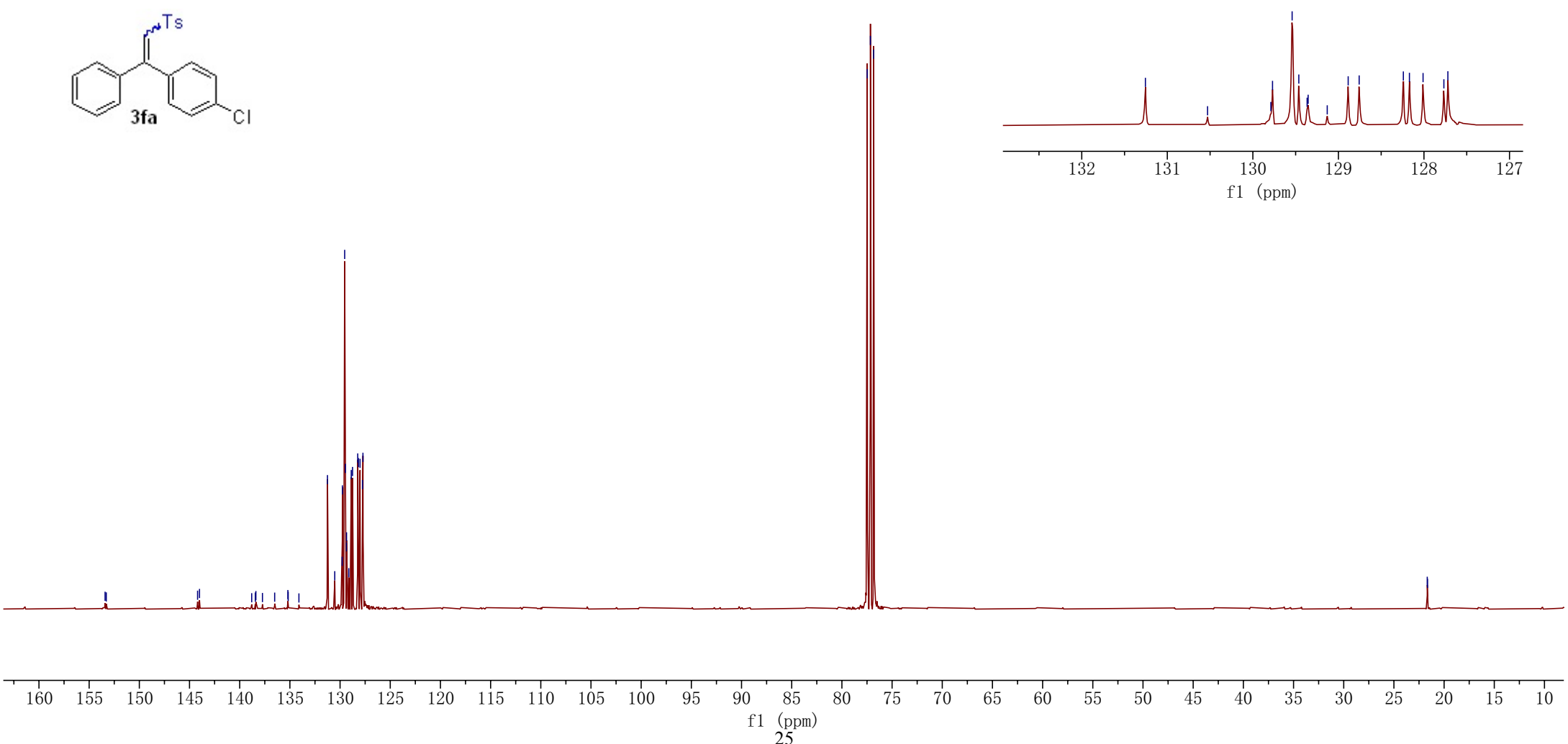
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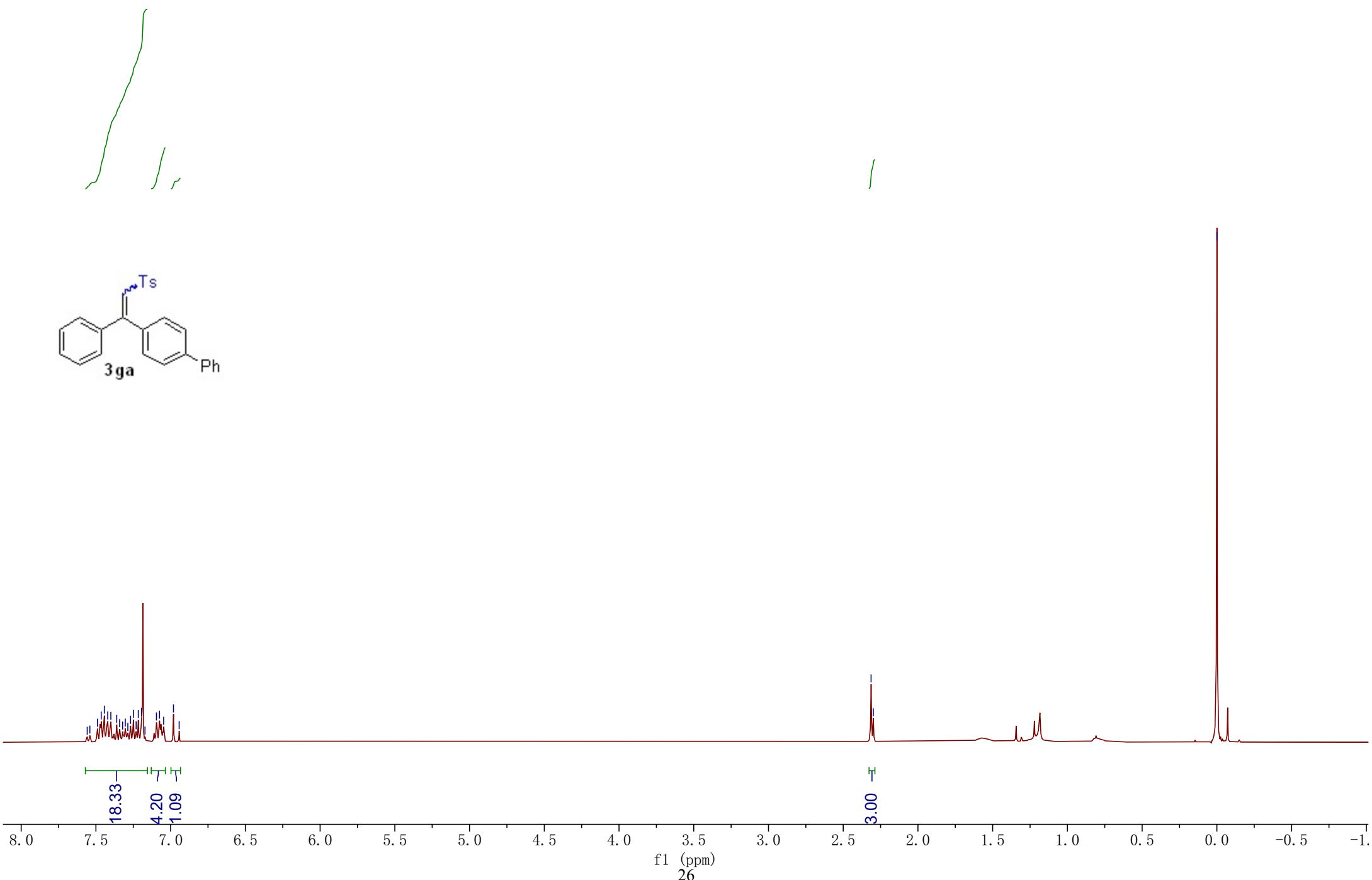
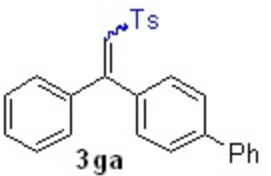
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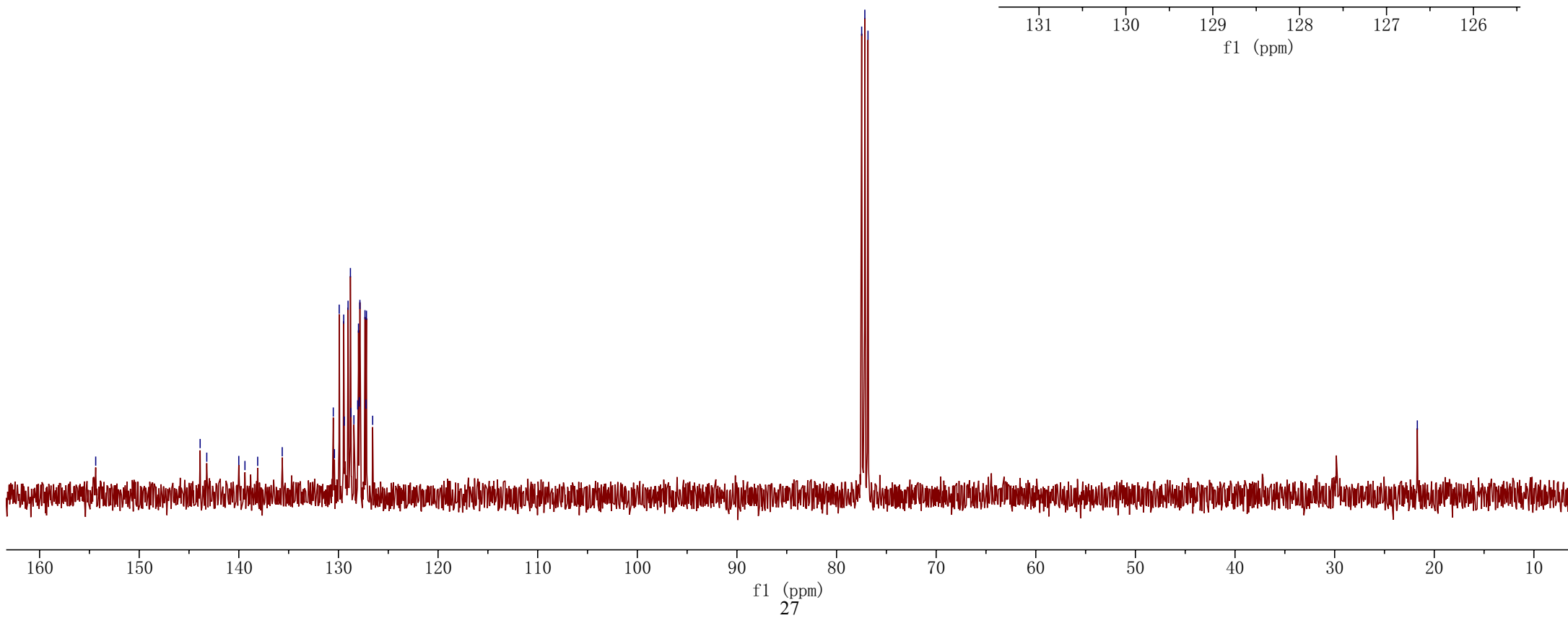
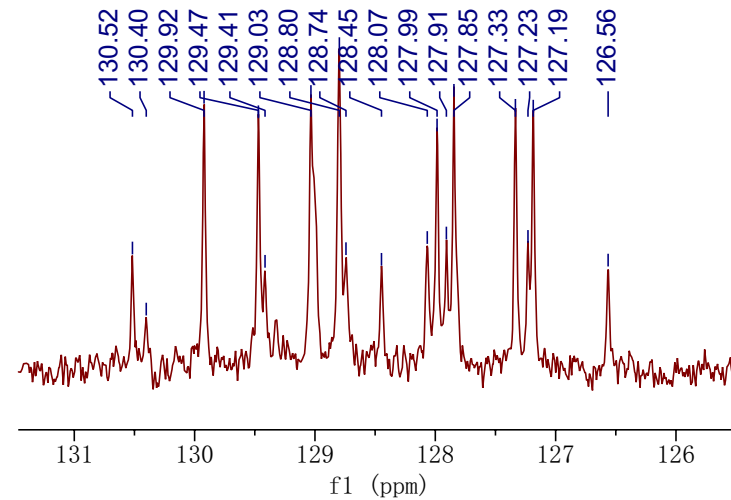
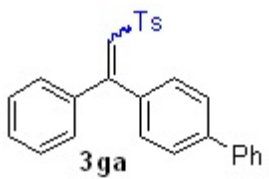
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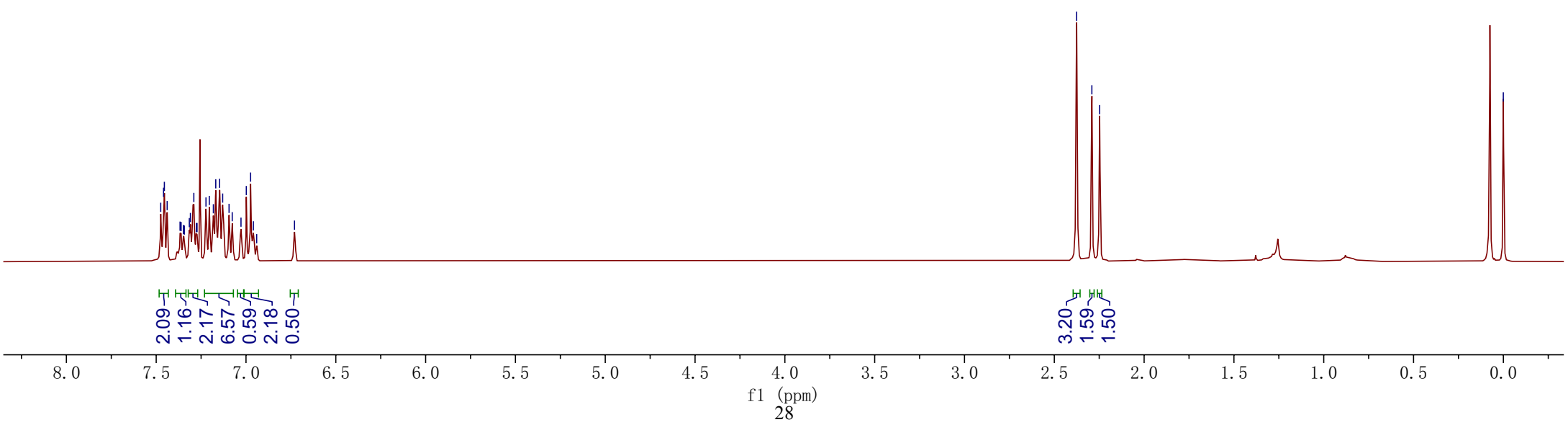
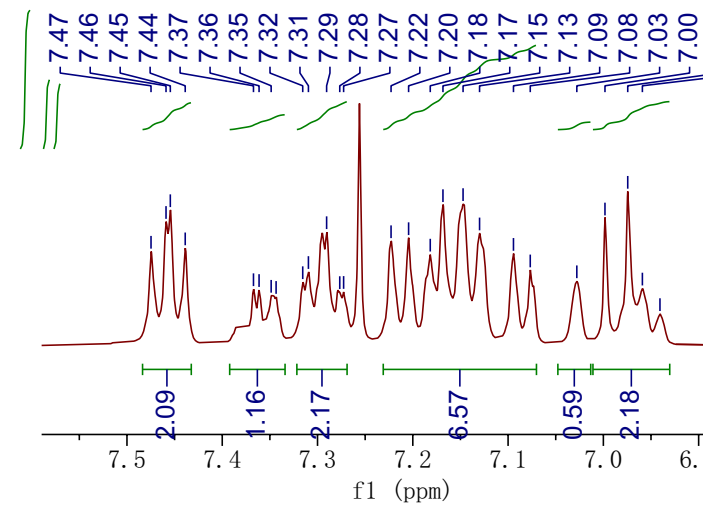
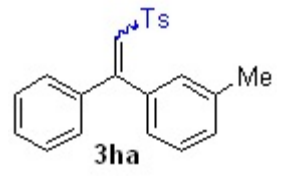
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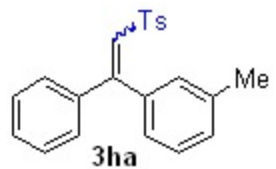
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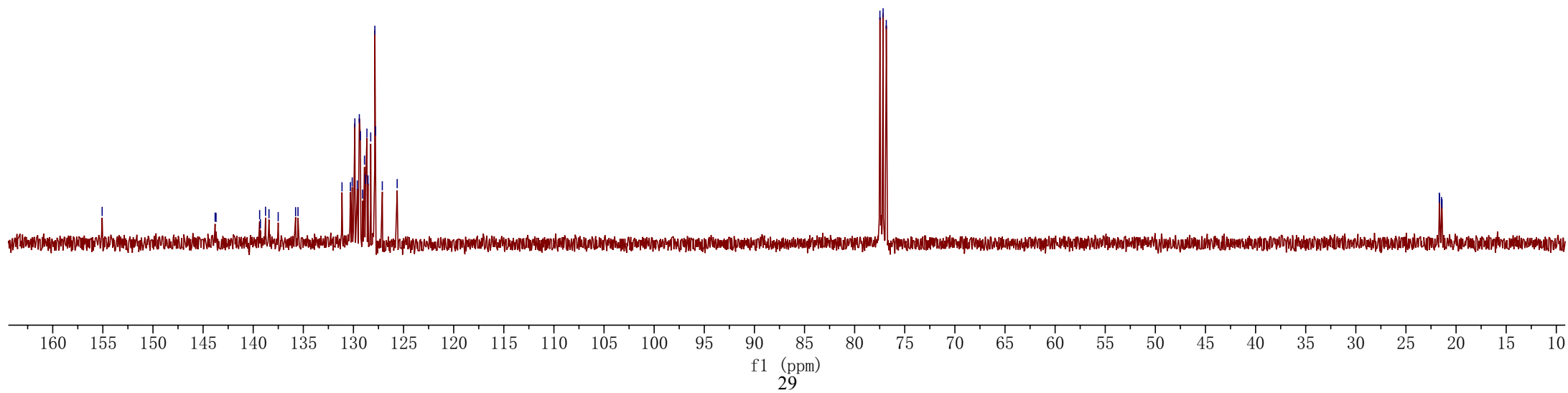
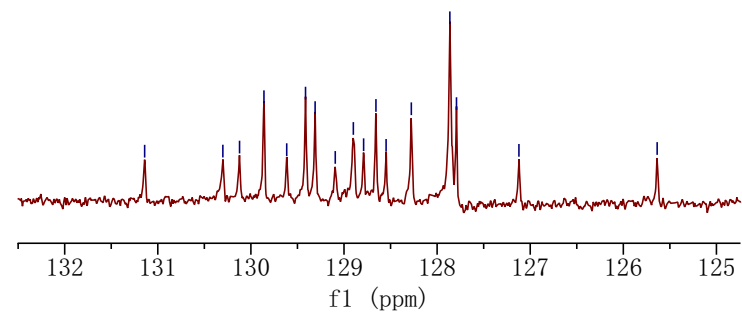
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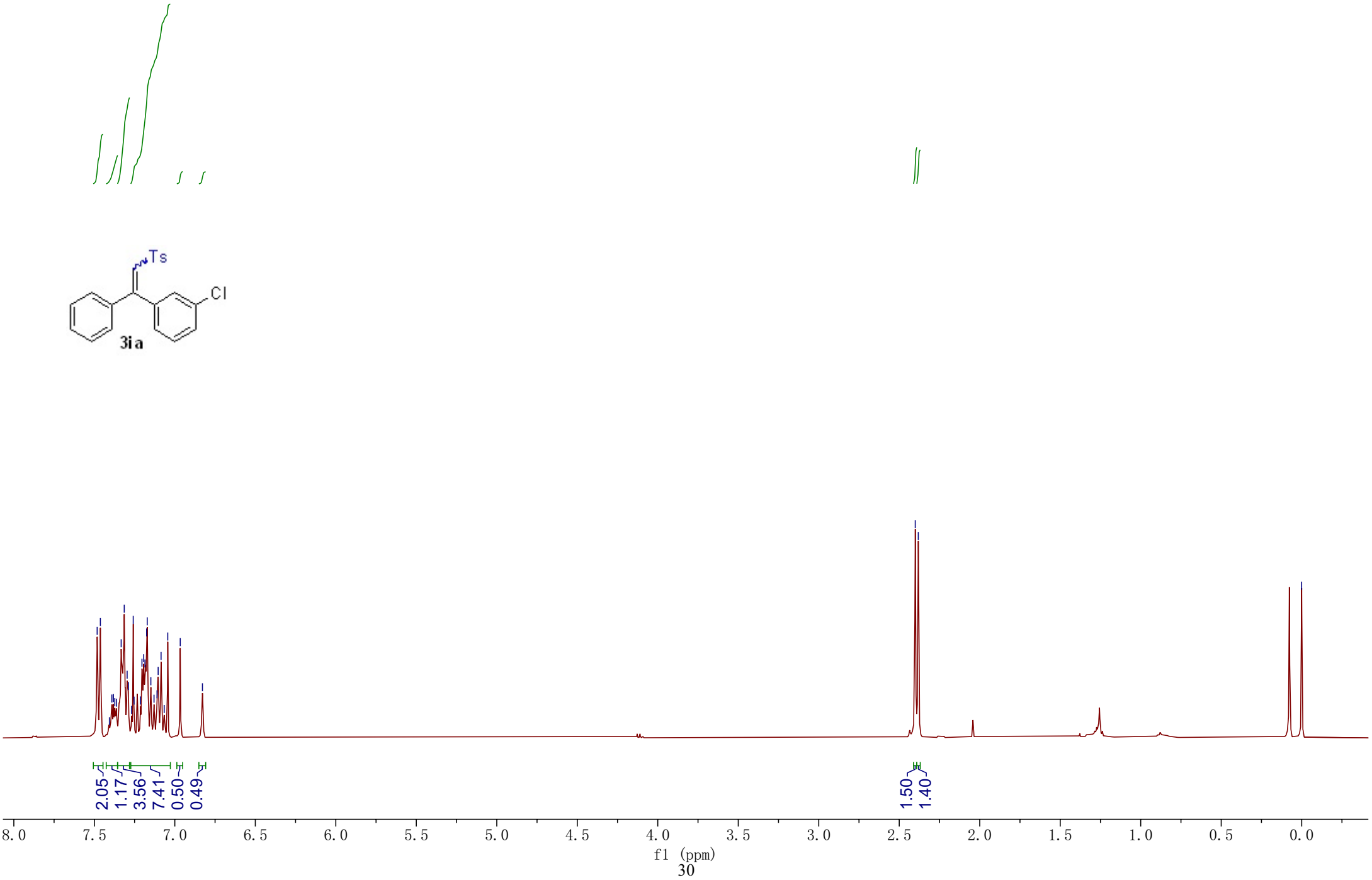
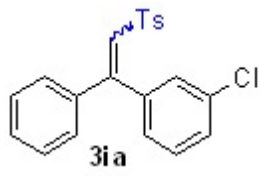
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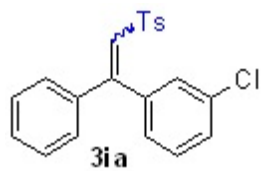


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0.00



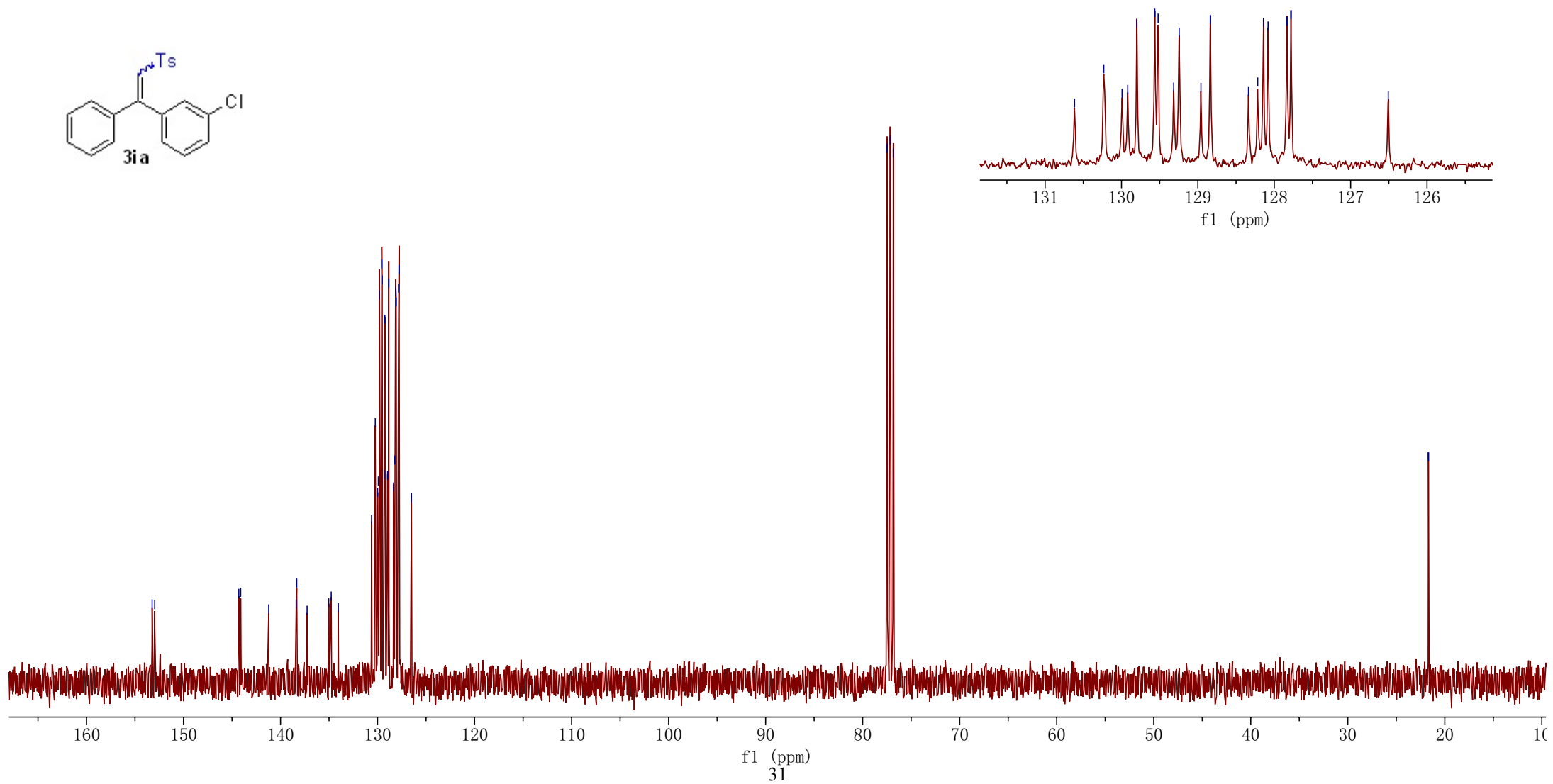


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76.84

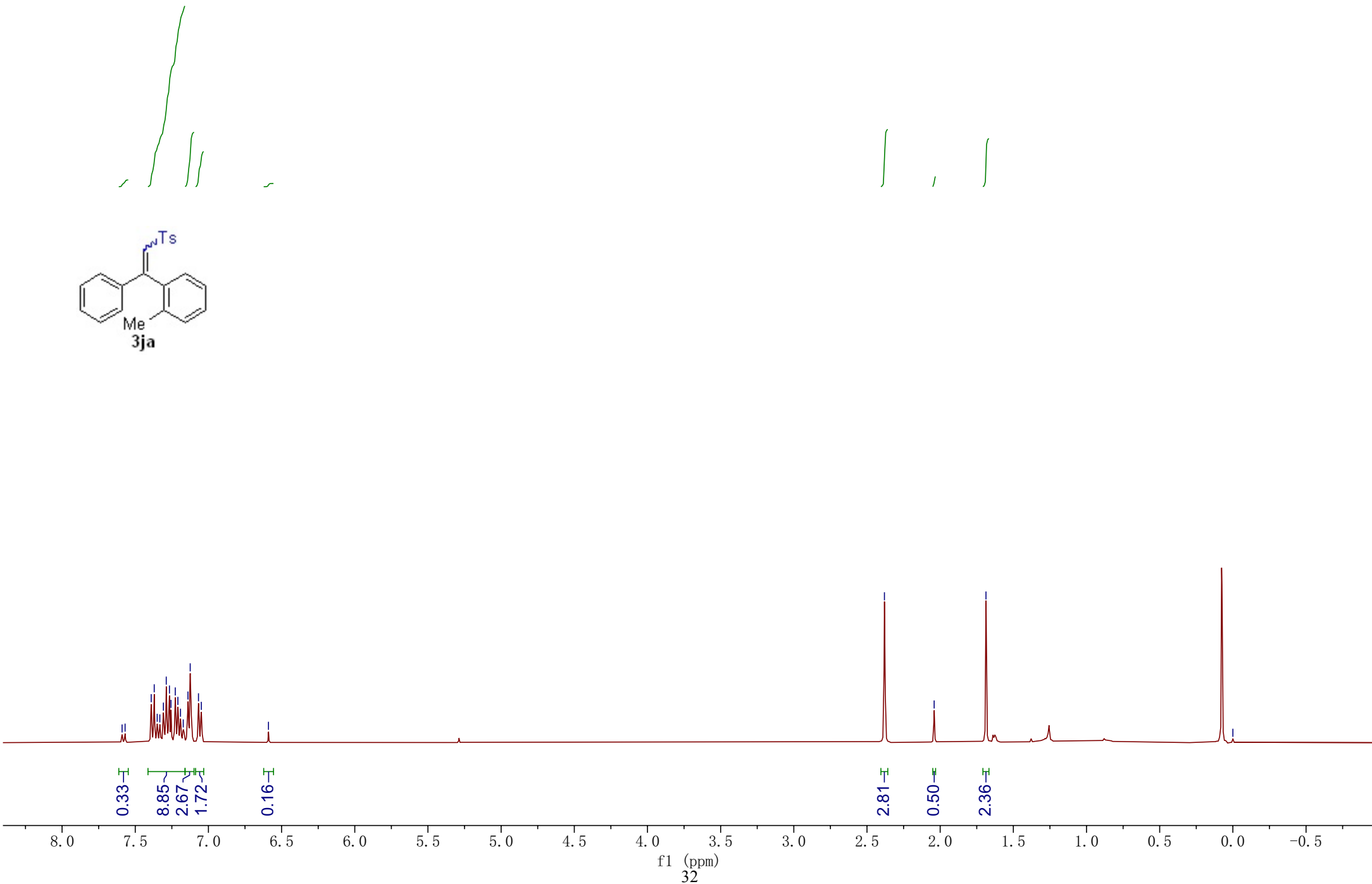
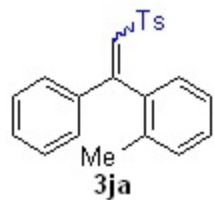
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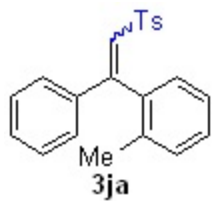
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128.22
128.14
128.08
127.83
127.78
126.51



7.59
7.57
7.39
7.37
7.35
7.33
7.31
7.29
7.27
7.26
7.23
7.21
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7.05
6.59

-2.38
-2.04
-1.69
-0.00

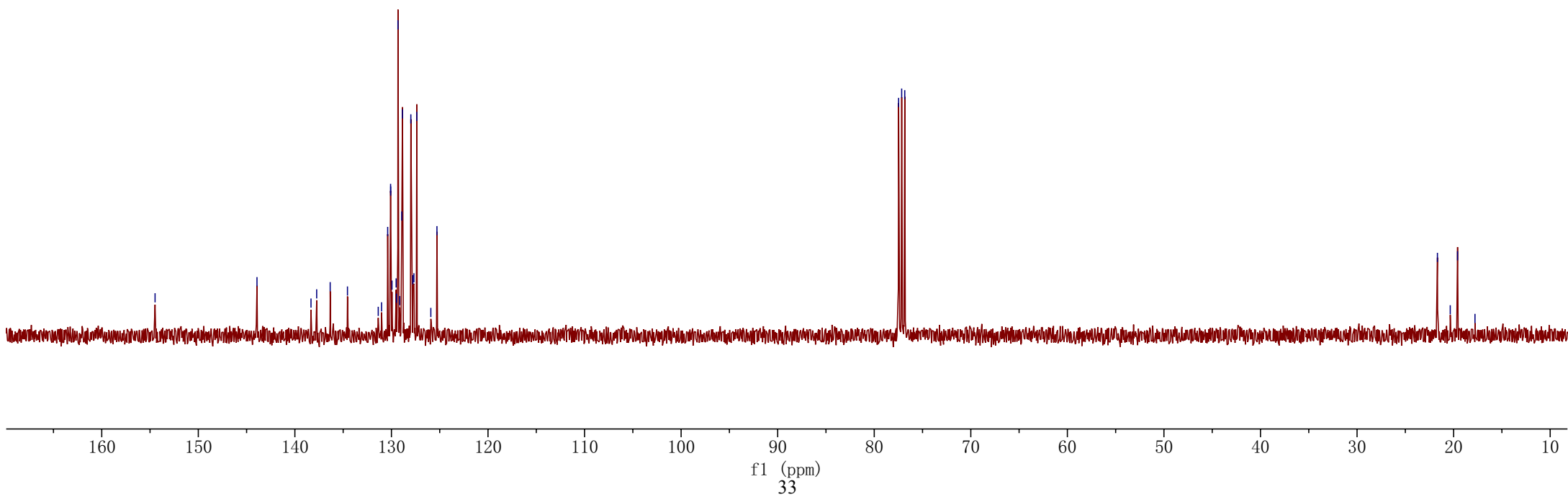
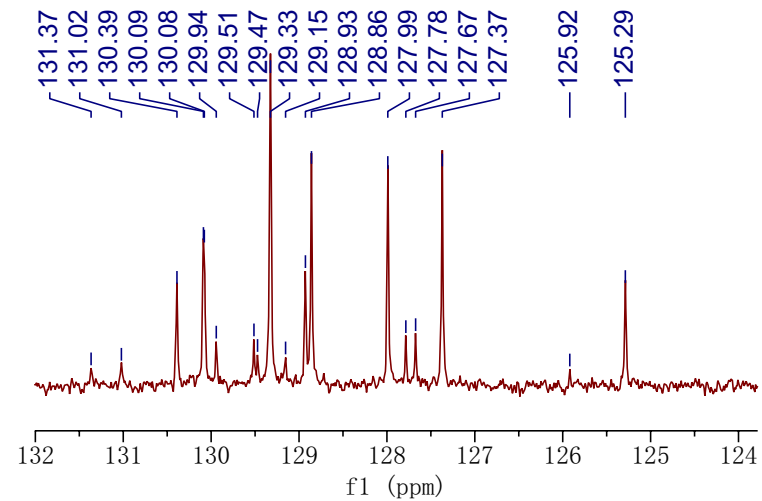




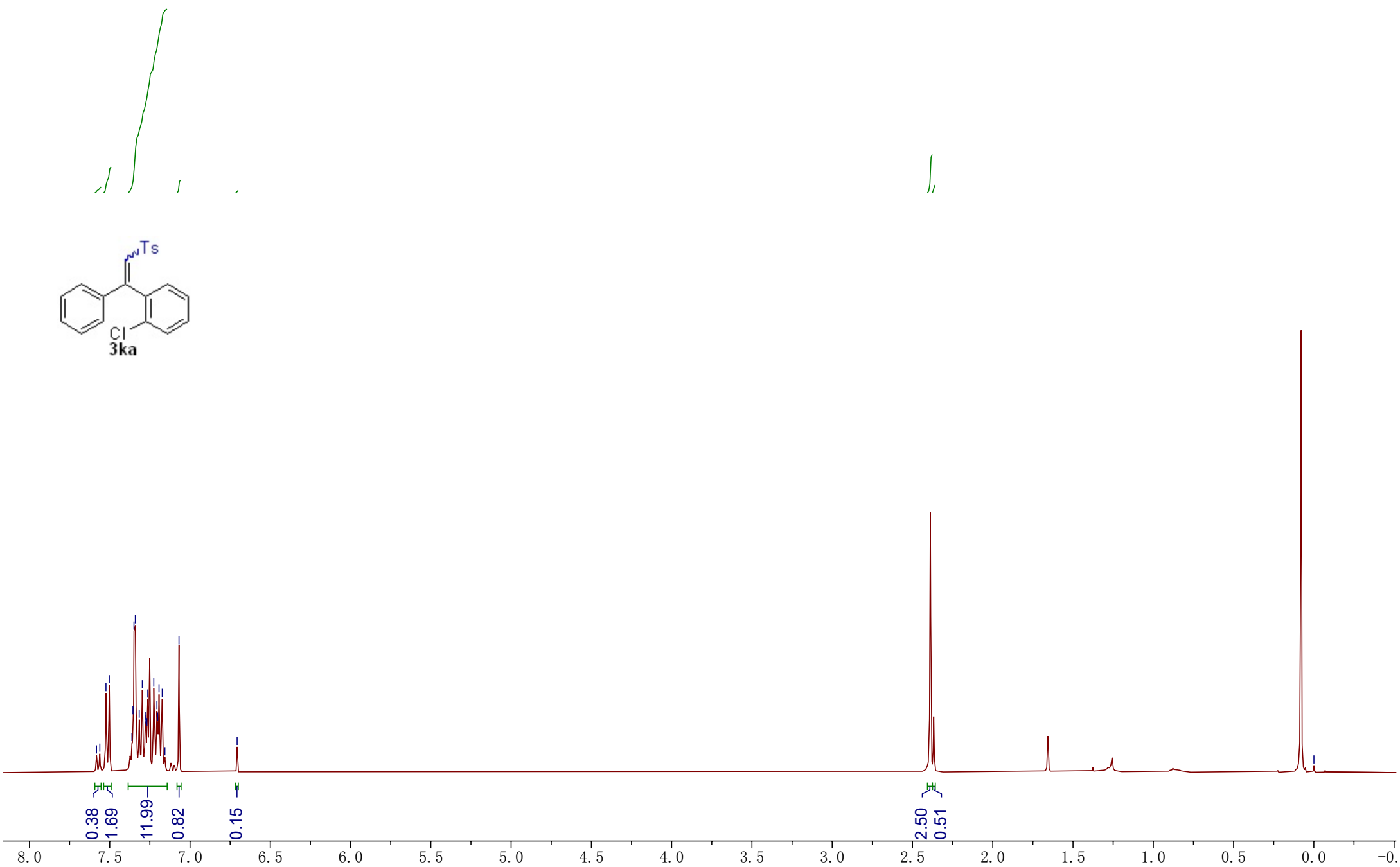
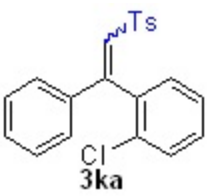
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76.84

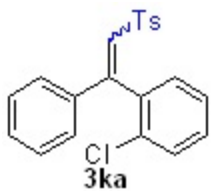
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6.71



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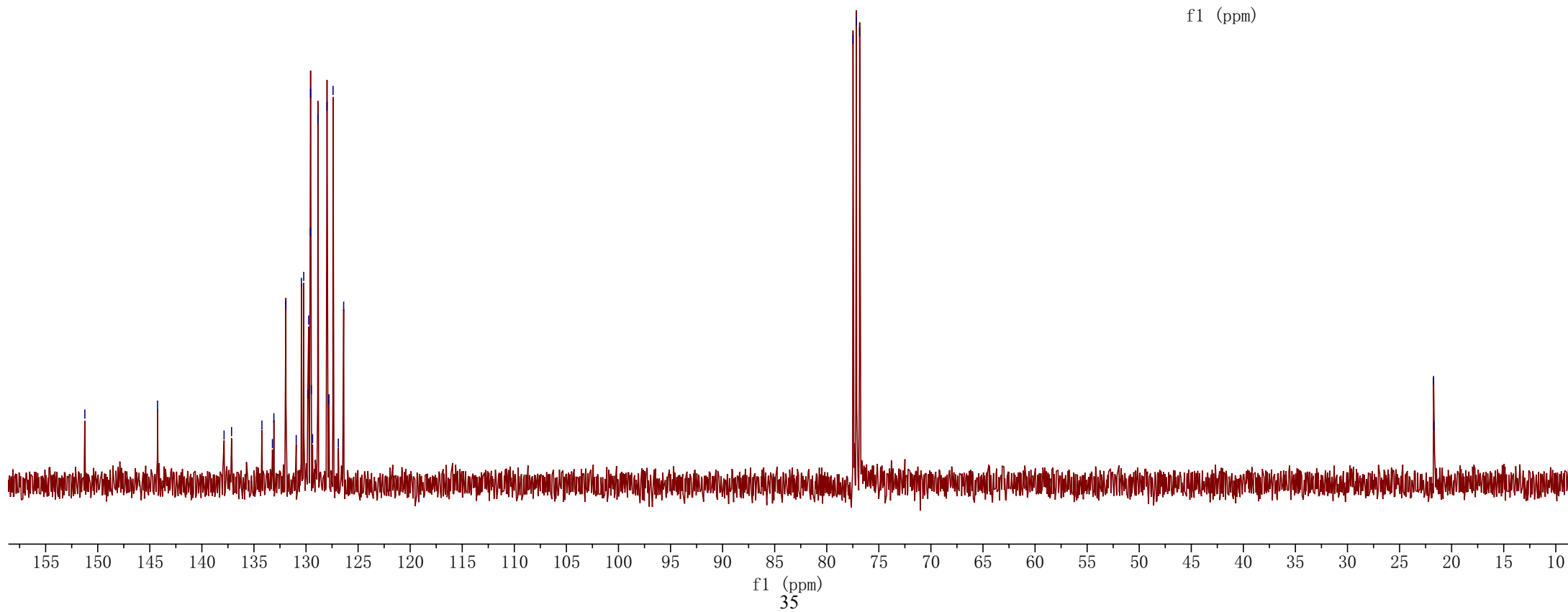
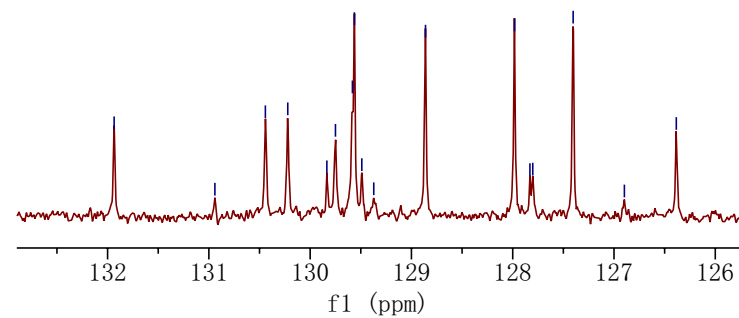


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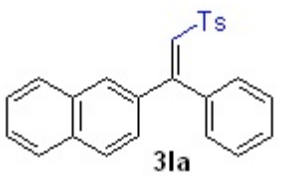
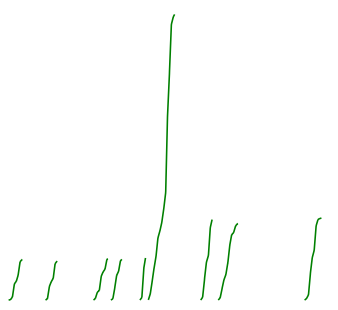
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76.84

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21.70

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127.40
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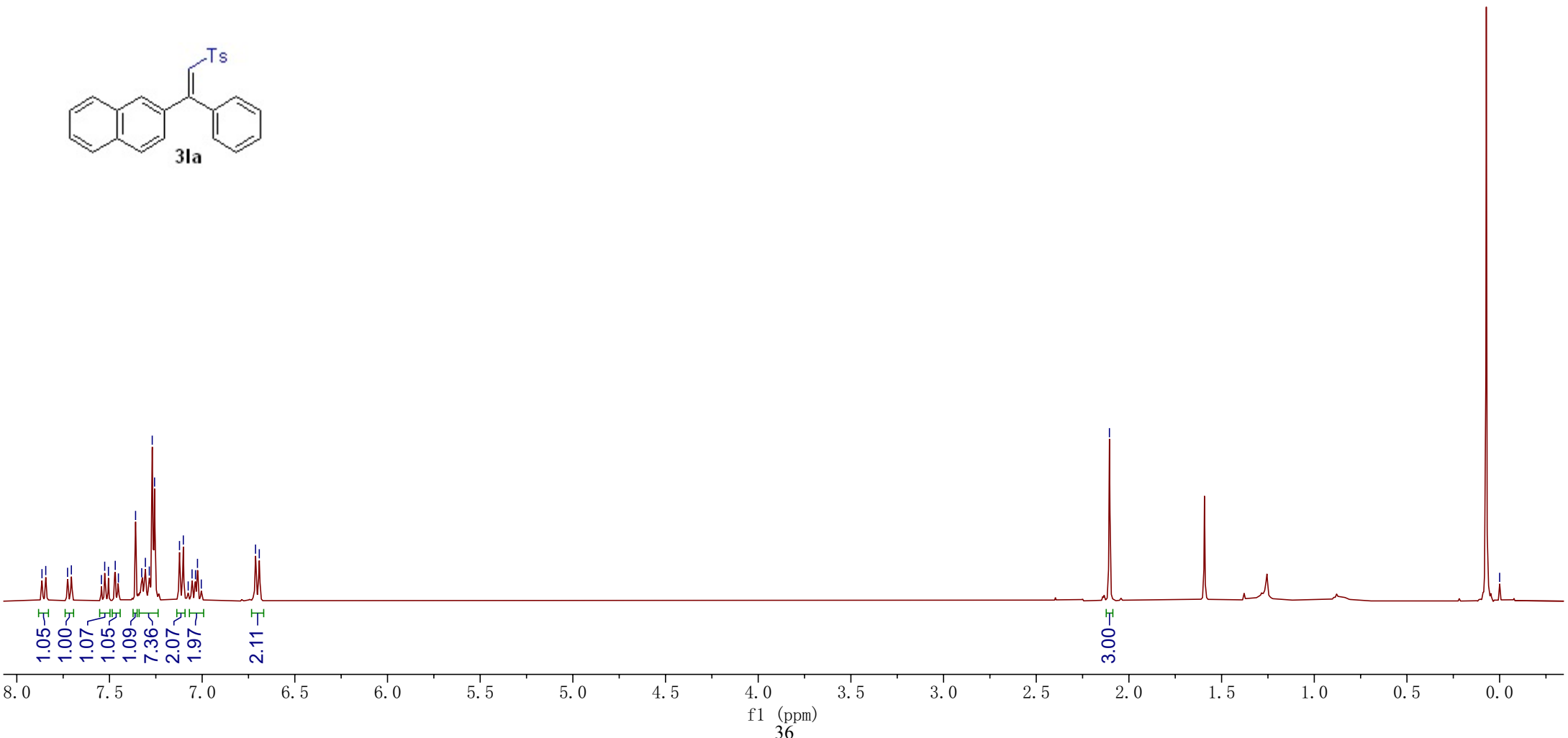


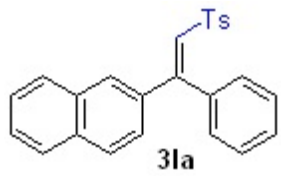
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7.47
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7.29
7.27
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7.05
7.04
7.03
7.00
6.71
6.69



—2.11

—0.00

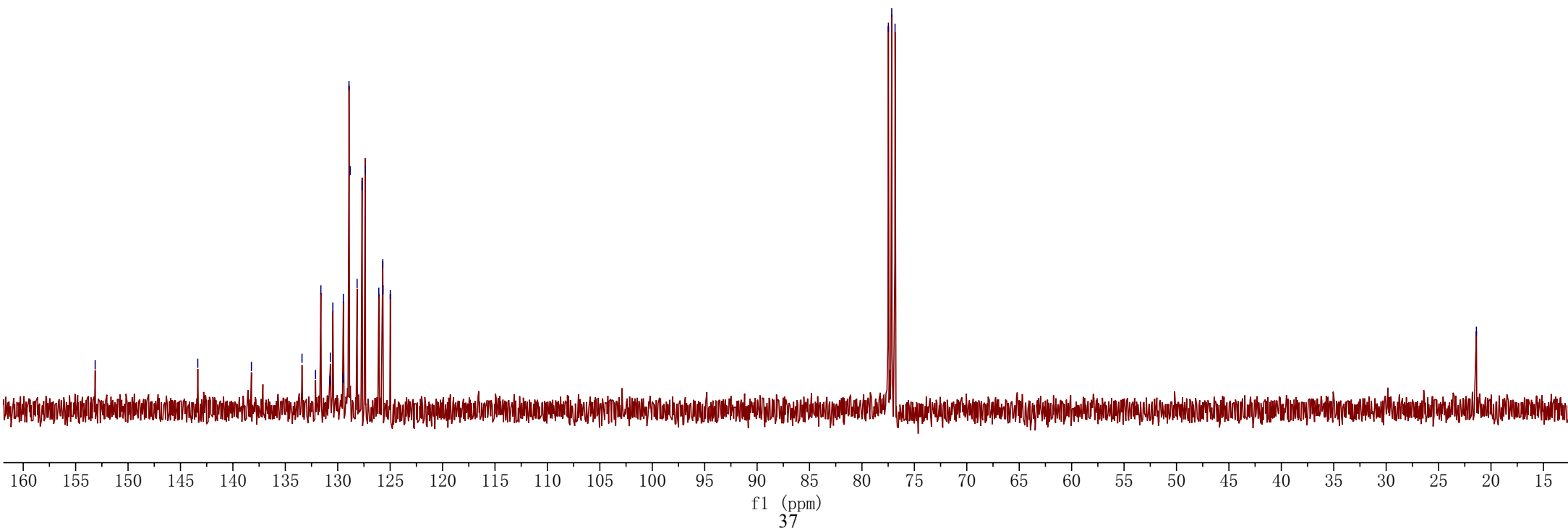
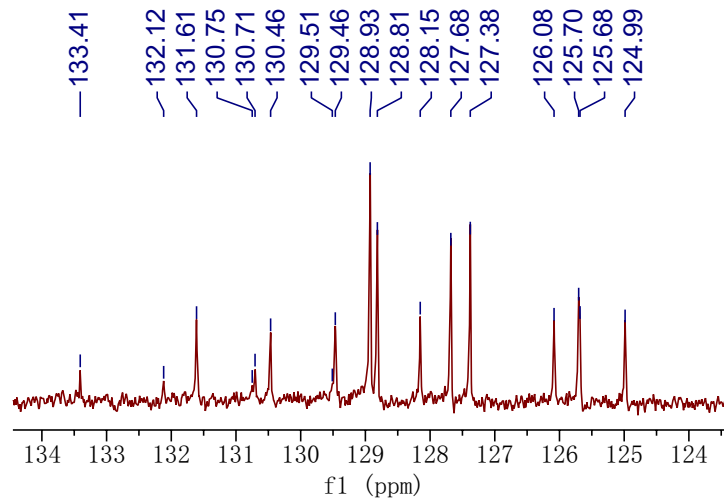




— 153.14
— 143.35
— 138.23
— 133.41
— 132.12
— 131.61
— 130.75
— 130.71
— 130.46
— 129.51
— 129.46
— 128.93
— 128.81
— 128.15
— 127.68
— 127.38
— 126.08
— 125.70
— 125.68
— 124.99

— 77.48
— 77.16
— 76.84

— 21.39

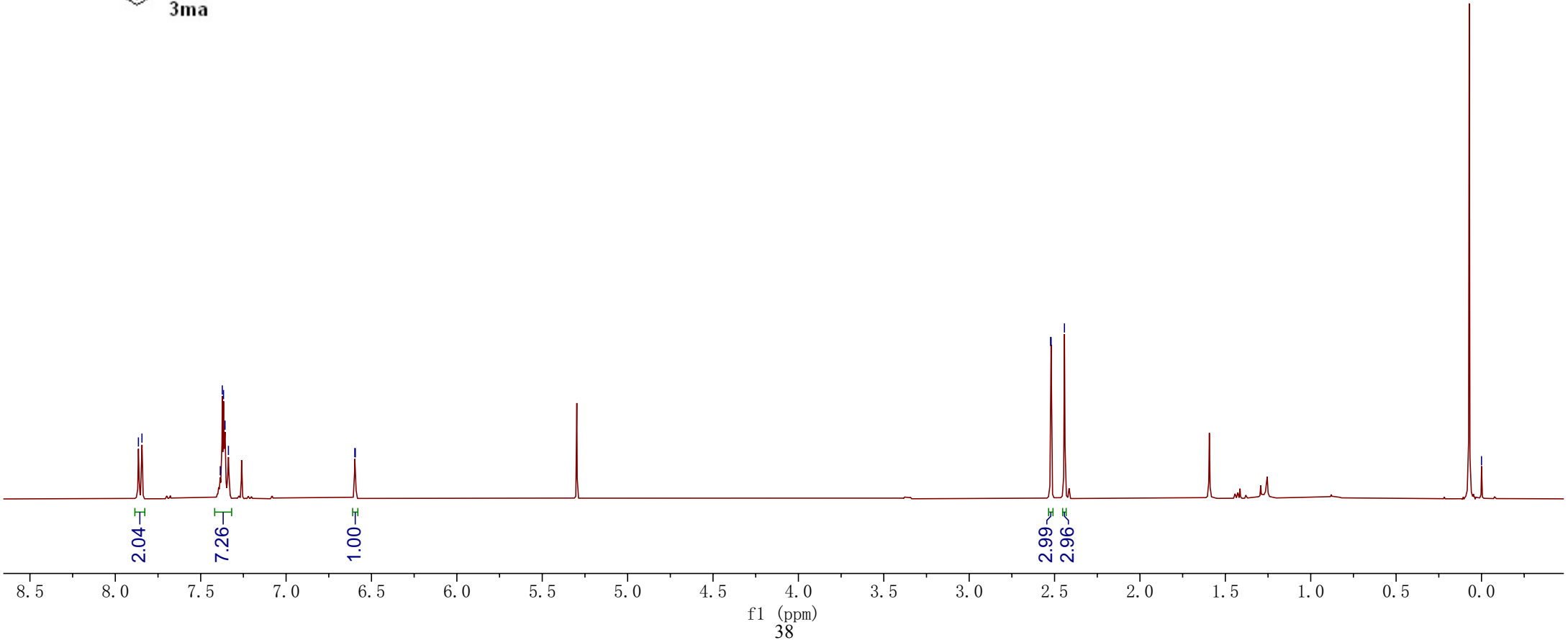
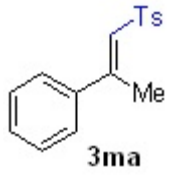


7.86
7.84
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7.37
7.37
7.36
7.34

6.60
6.59

2.52
2.52
2.44

0.00



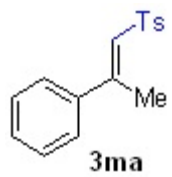
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7.26

1.00

2.99

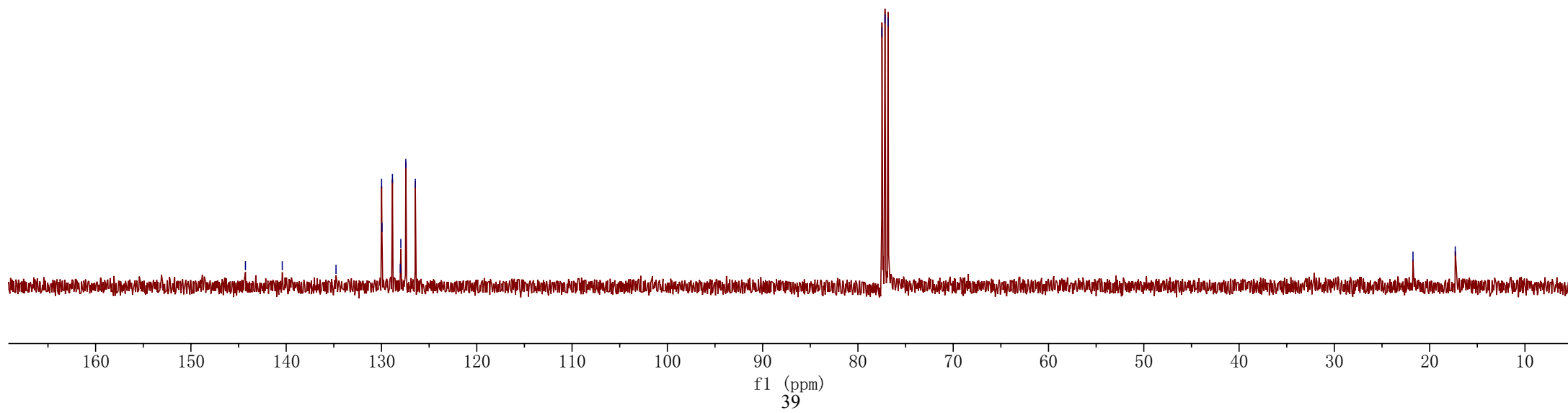
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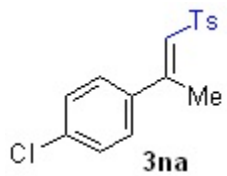


—144.28
—140.41
—134.77
129.99
129.94
128.85
128.02
127.97
127.45
126.45

77.48
77.16
76.84

—21.75
—17.31





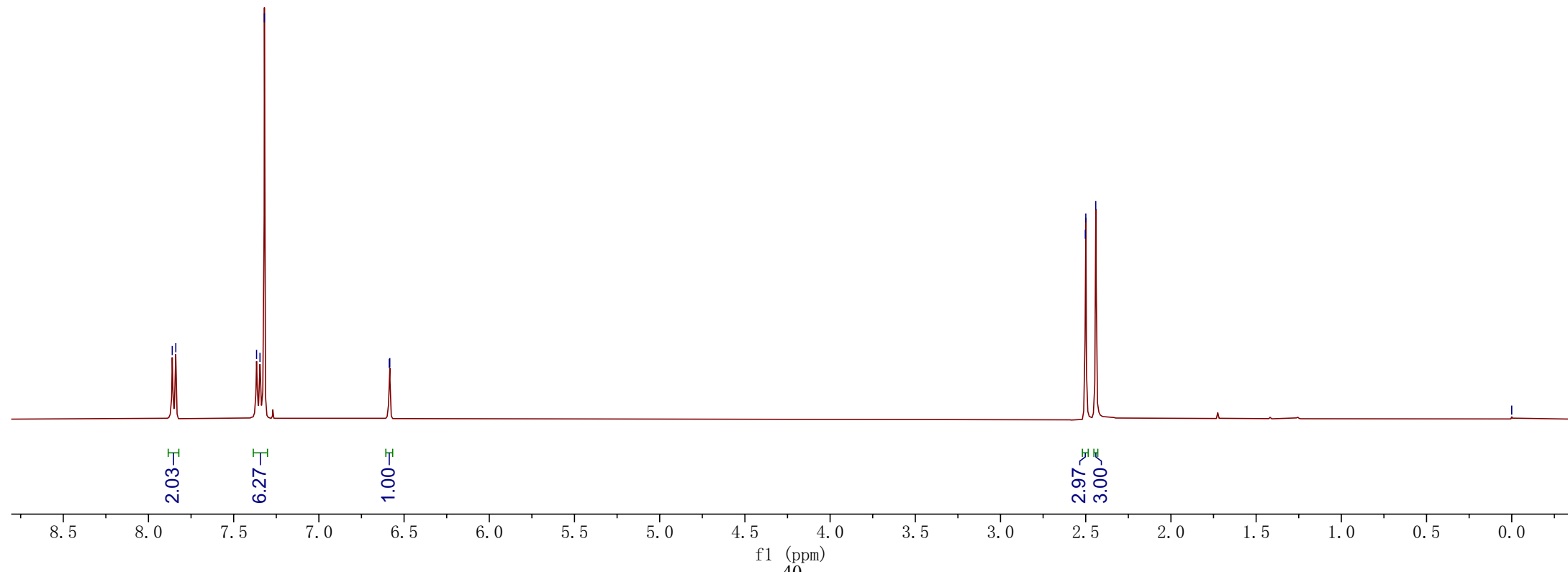
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7.84

7.37
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7.32

6.59
6.58

2.50
2.50
2.44

0.00



2.03

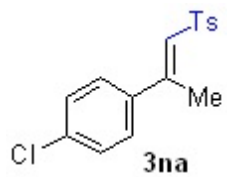
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1.00

2.97

3.00

f1 (ppm)
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— 151.56

— 144.42

139.05

138.60

135.95

130.00

128.99

128.24

127.72

127.39

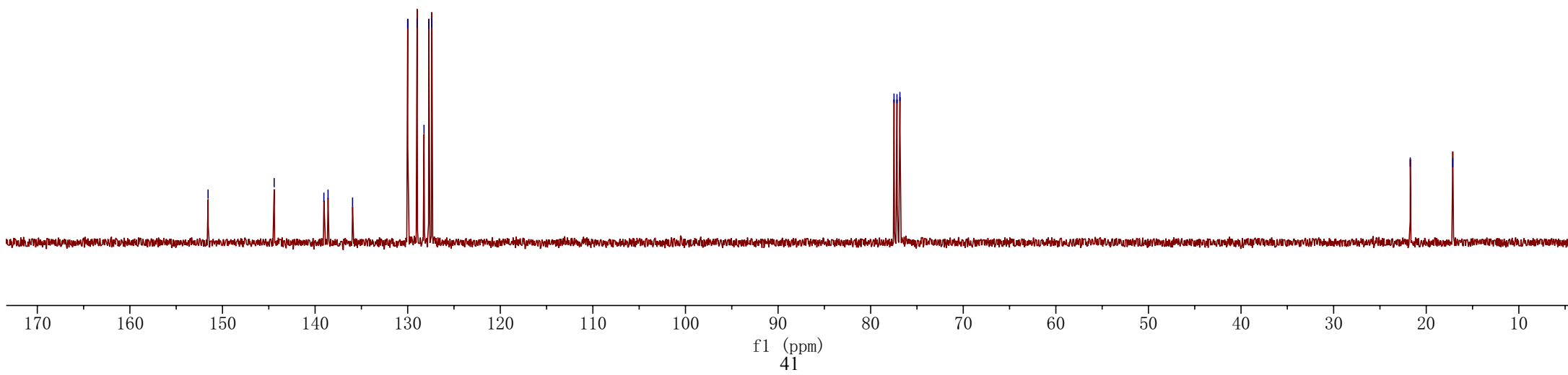
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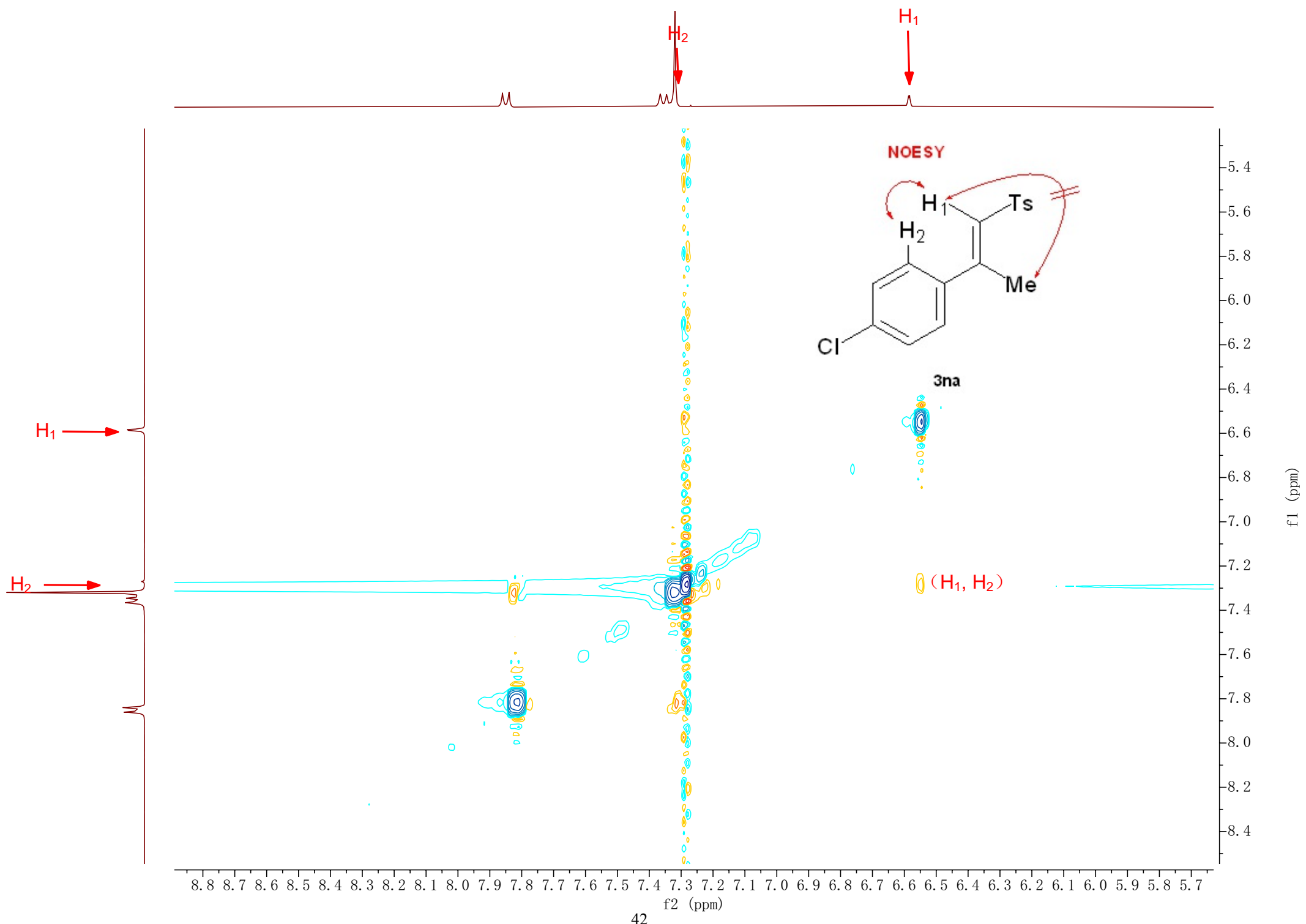
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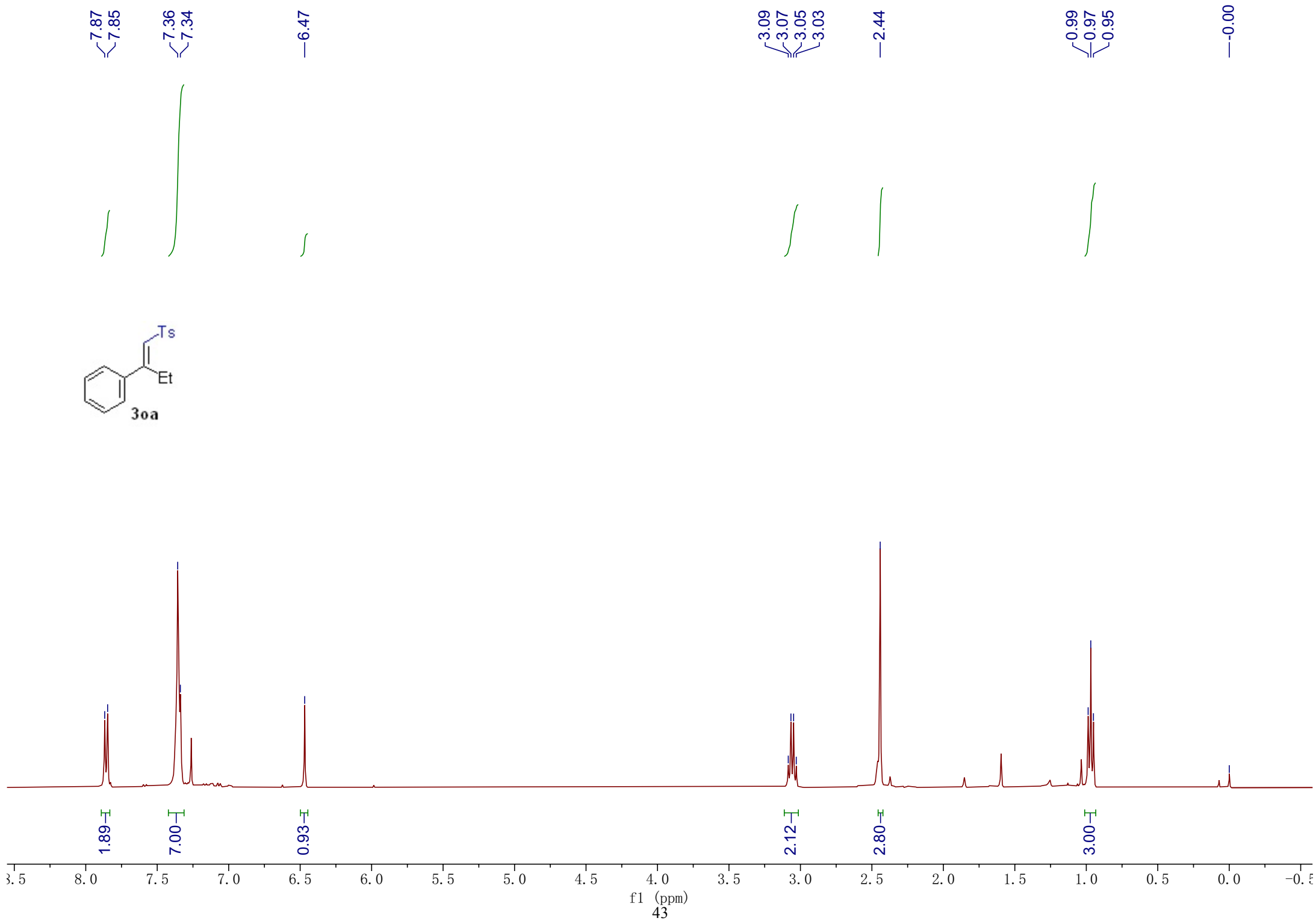
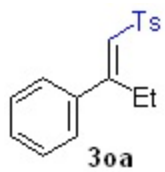
76.84

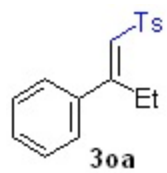
— 21.72

— 17.13









— 159.32

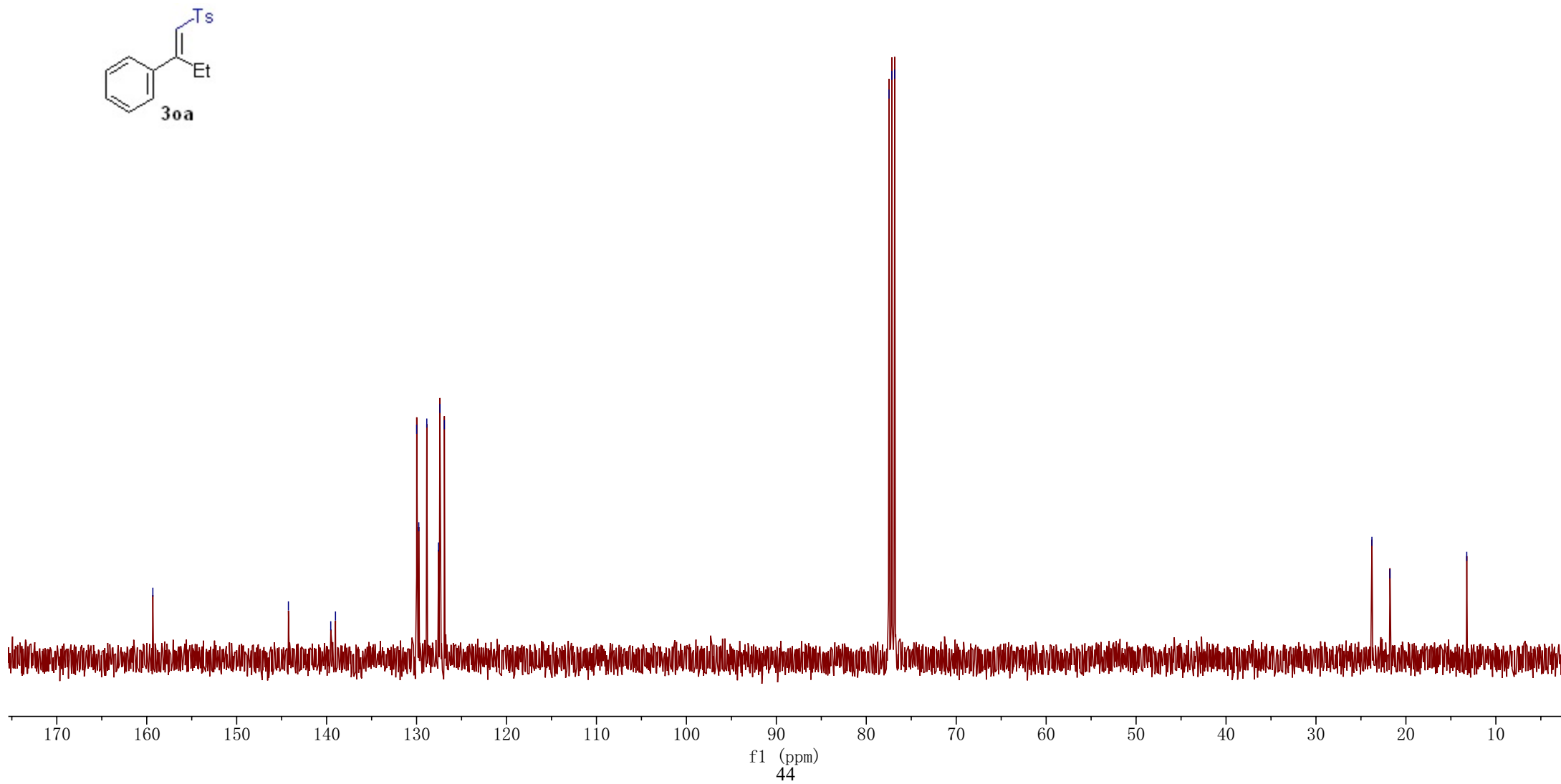
— 144.25
— 139.54
— 139.02

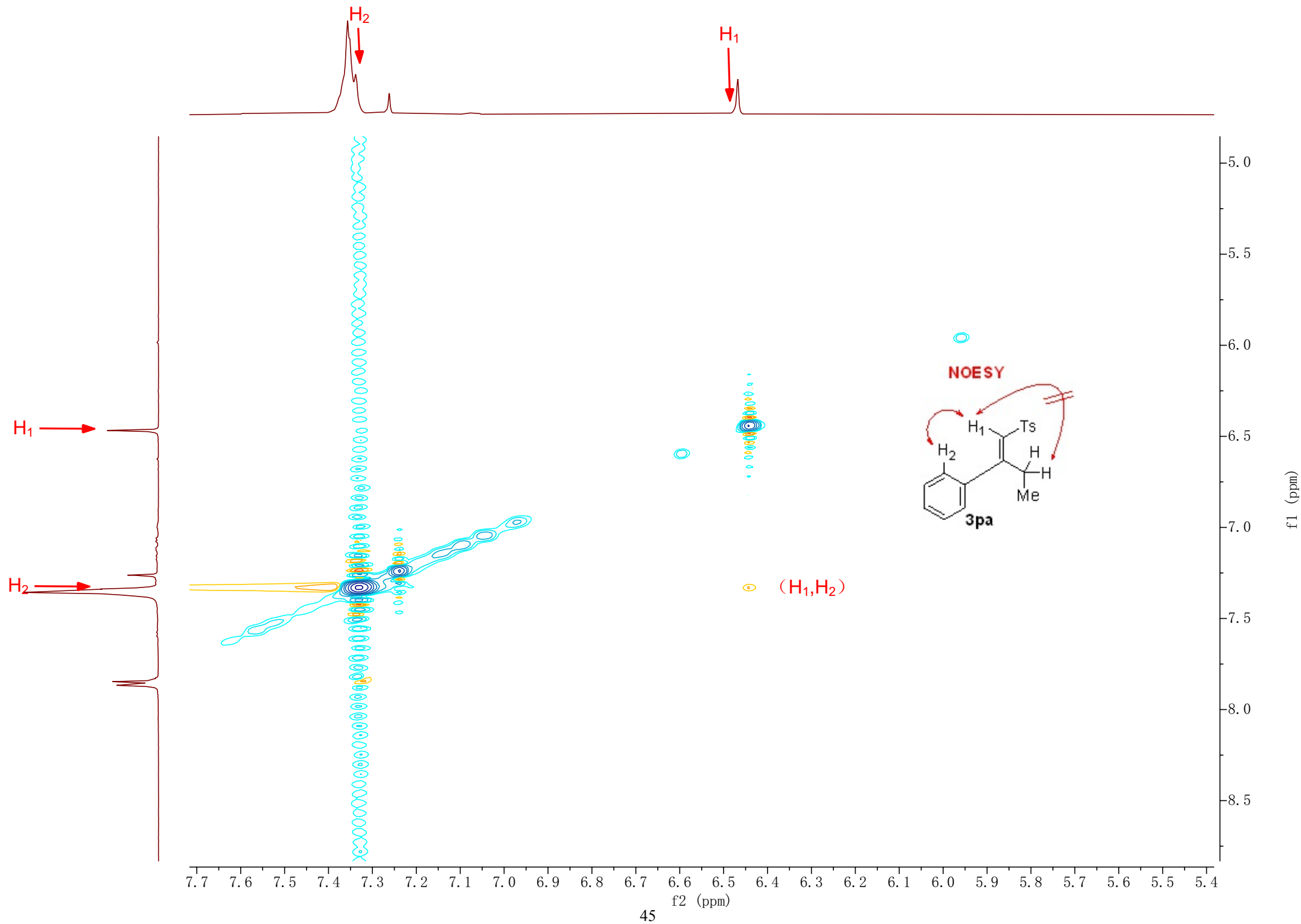
— 129.99
— 129.76
— 128.86
— 127.56
— 127.40
— 126.91

— 77.48
— 77.16
— 76.84

— 23.78
— 21.77

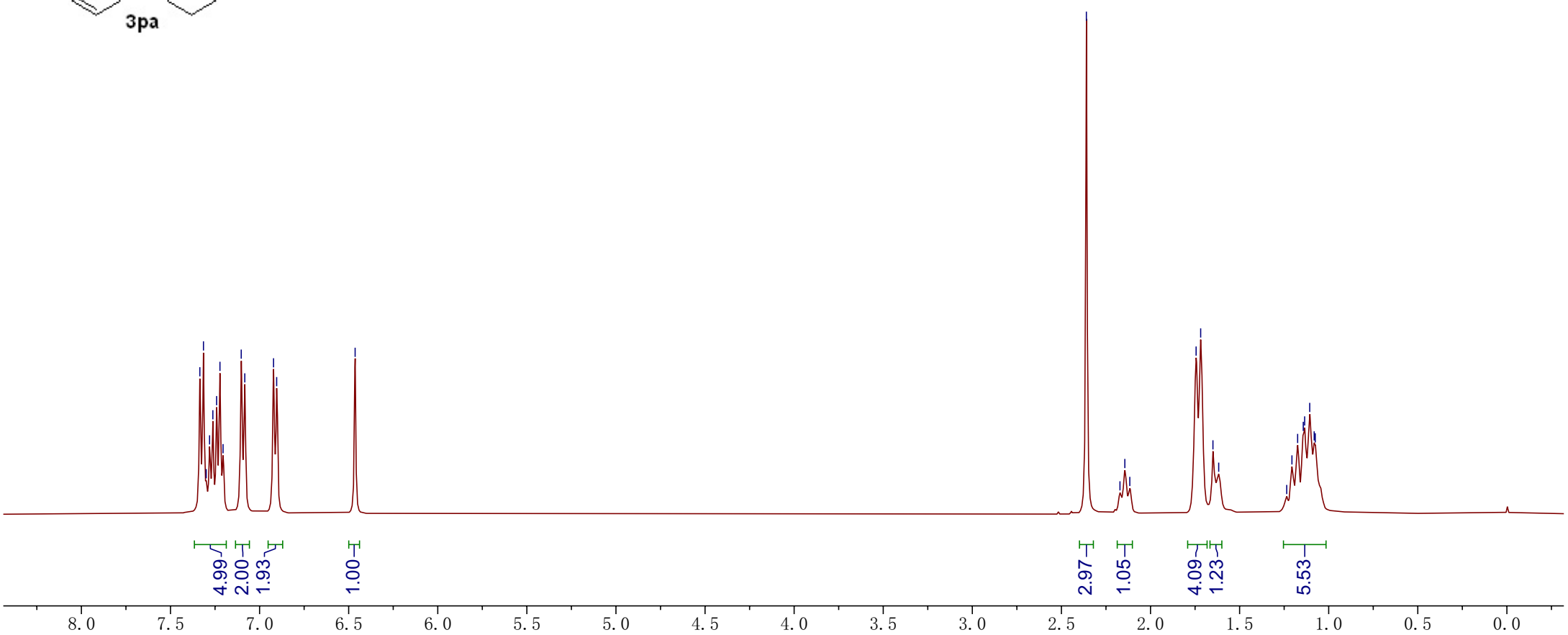
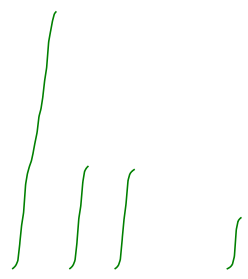
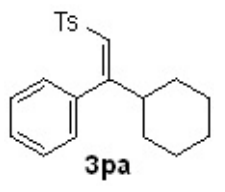
— 13.24

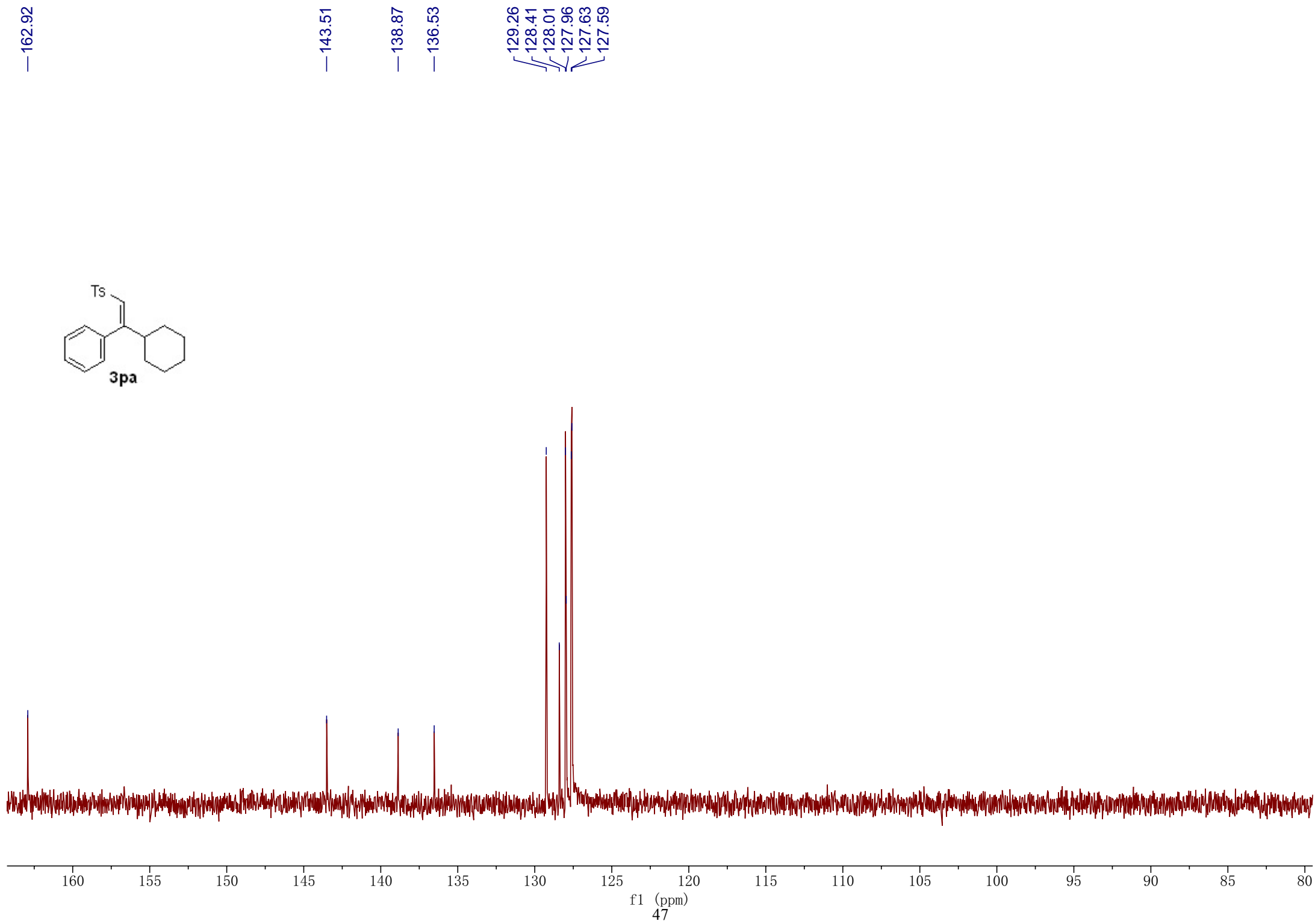
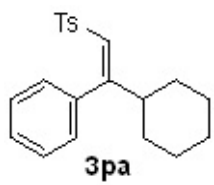


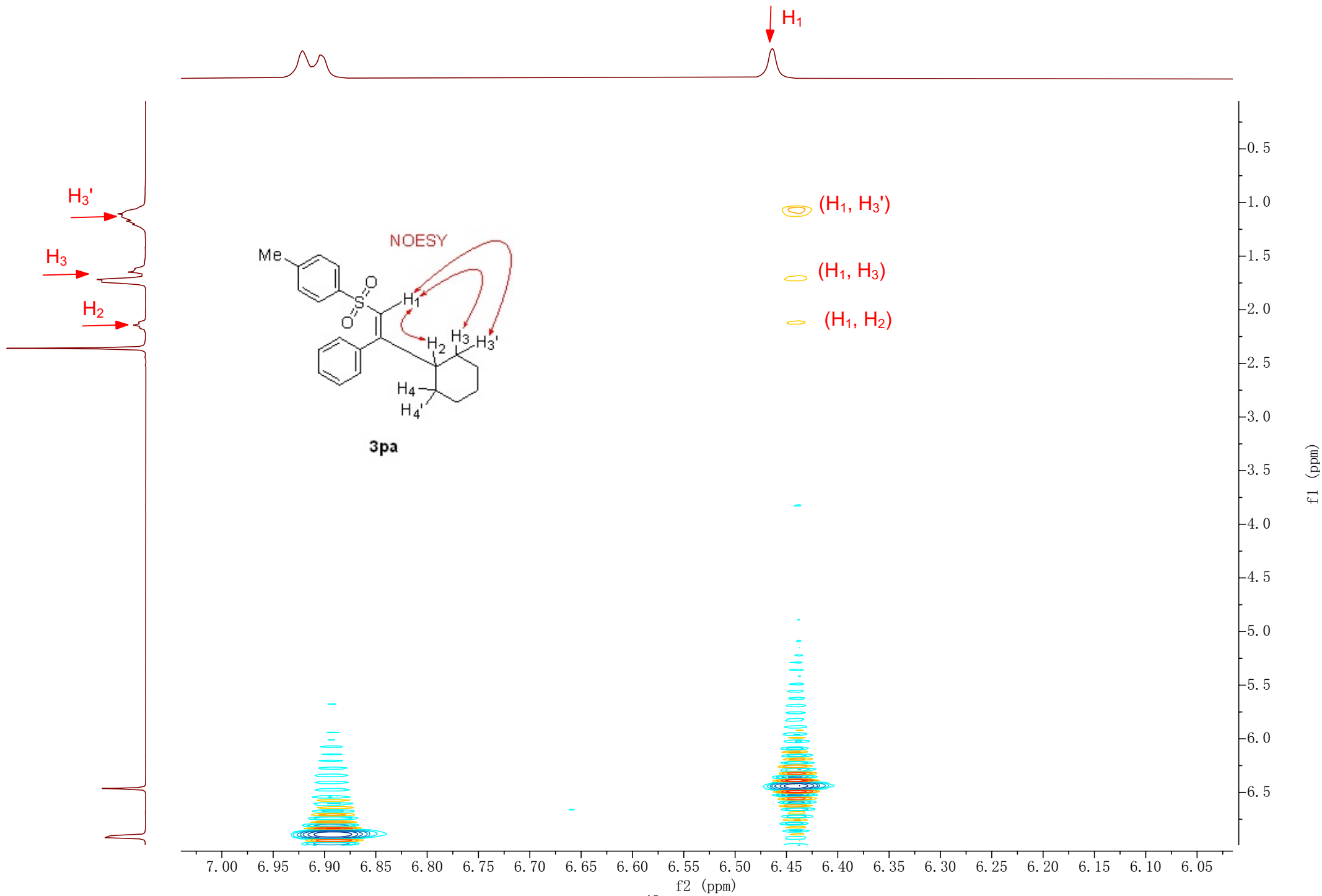


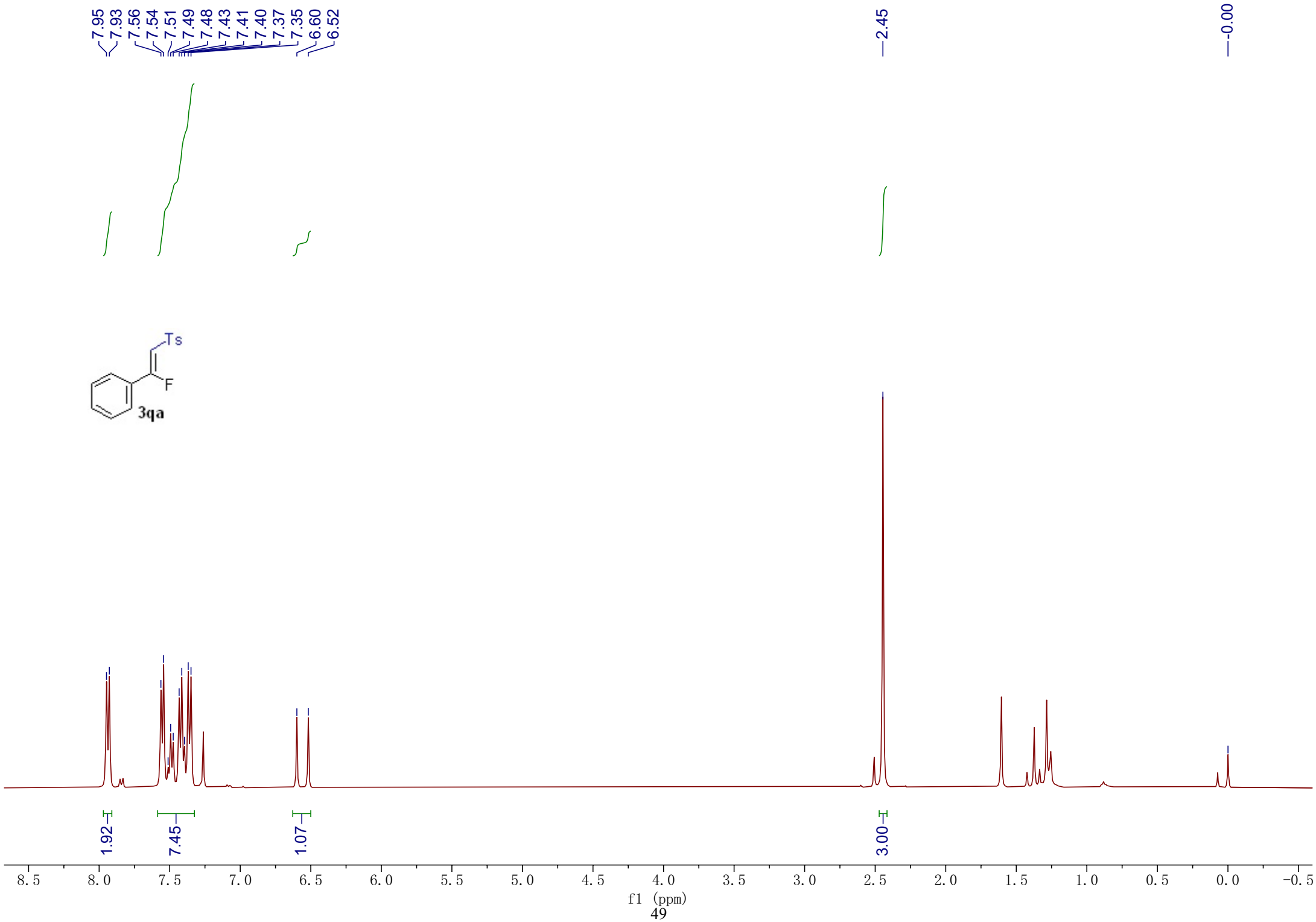
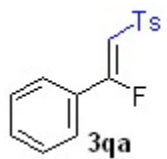
7.34
7.31
7.30
7.28
7.26
7.24
7.22
7.20
7.10
7.08
6.92
6.90
— 6.46

2.36
2.17
2.14
2.12
1.74
1.72
1.65
1.62
1.24
1.21
1.17
1.14
1.13
1.11
1.08
1.08









—162.76

—144.73

132.51

129.94

129.14

129.12

127.82

127.81

126.05

125.98

109.99

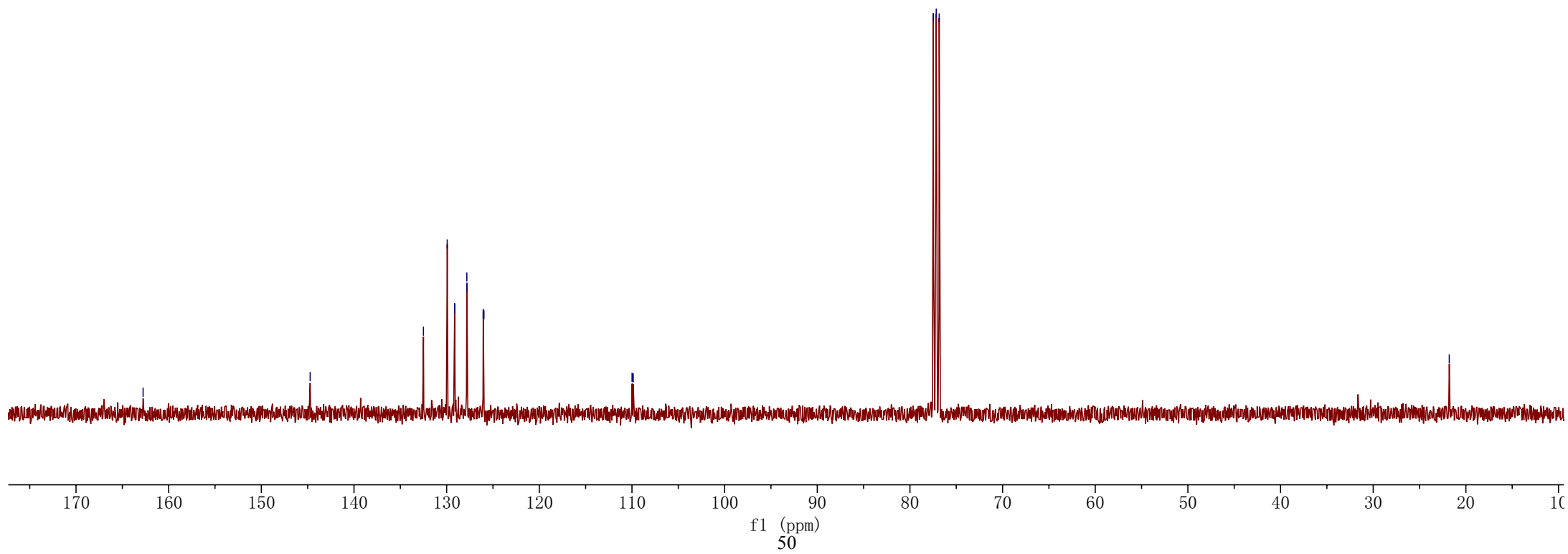
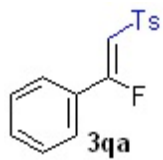
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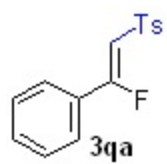
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77.16

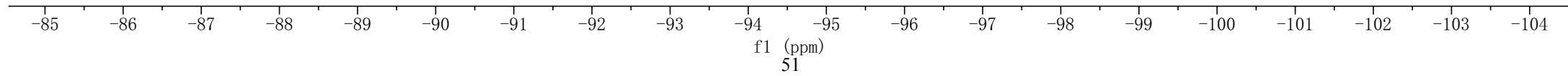
76.84

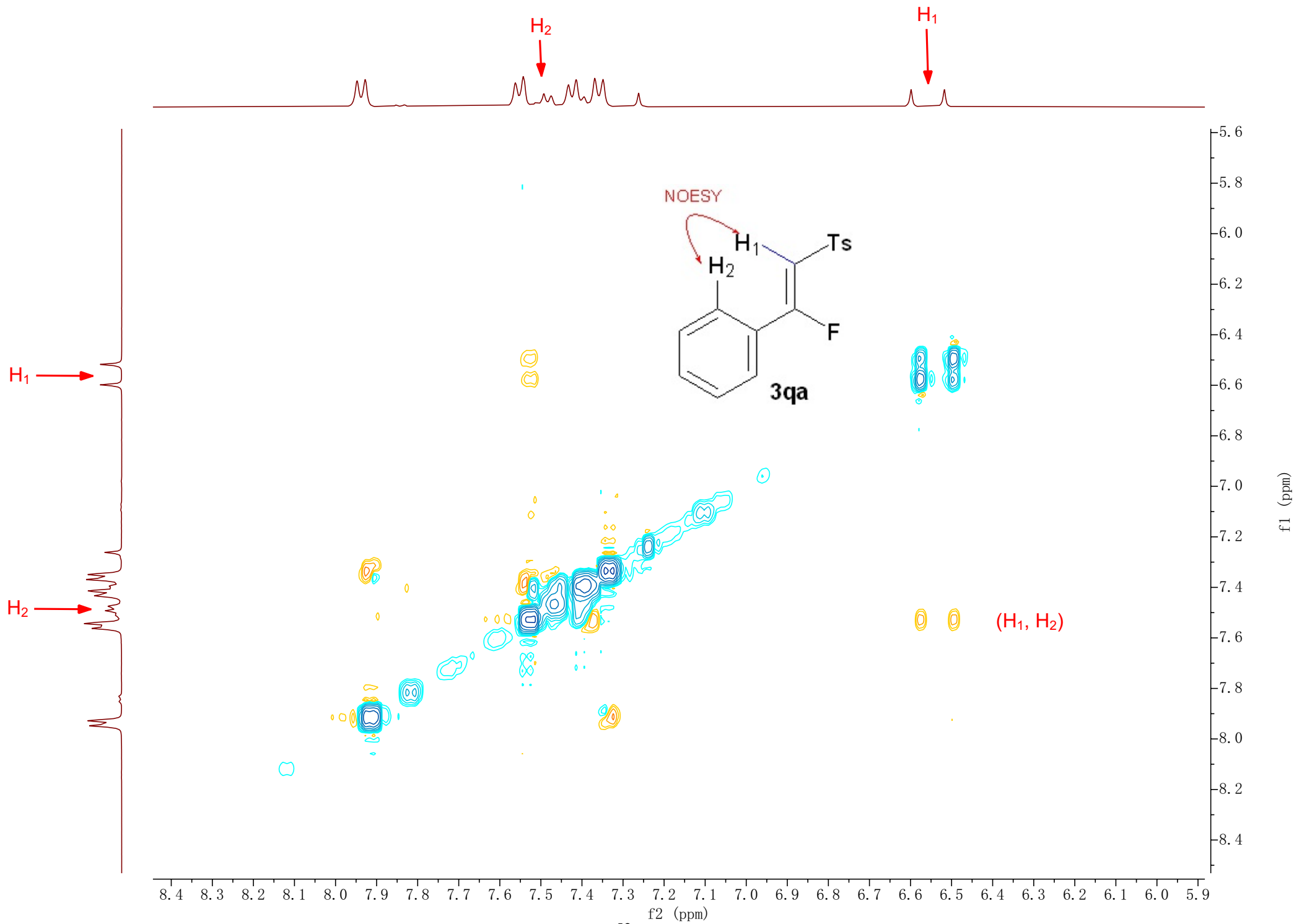
—21.79

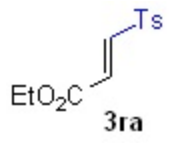




-93.431
-93.517







7.81
7.79
7.40
7.38
7.34
7.30
7.27
6.82
6.78

4.27
4.26
4.24
4.22

2.47

1.32
1.30
1.29

0.00

1.84

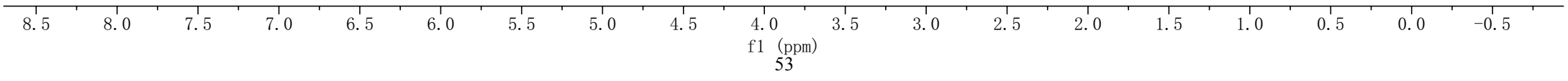
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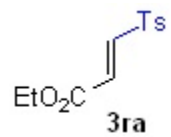
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2.06

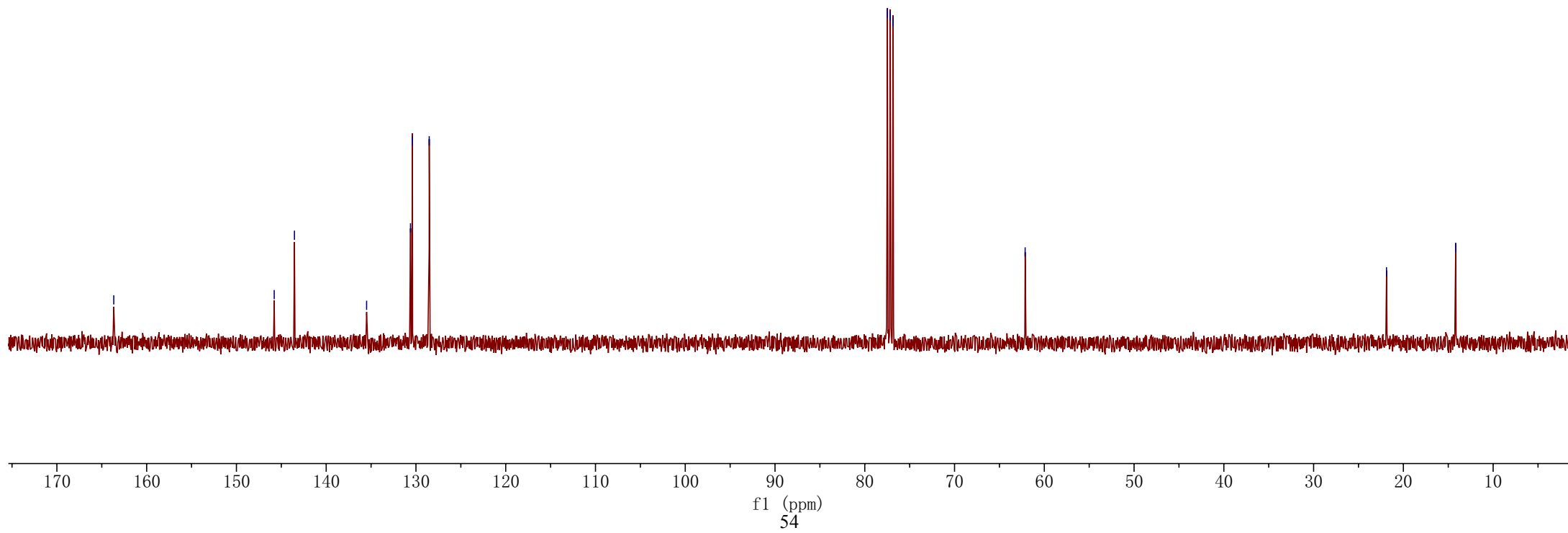
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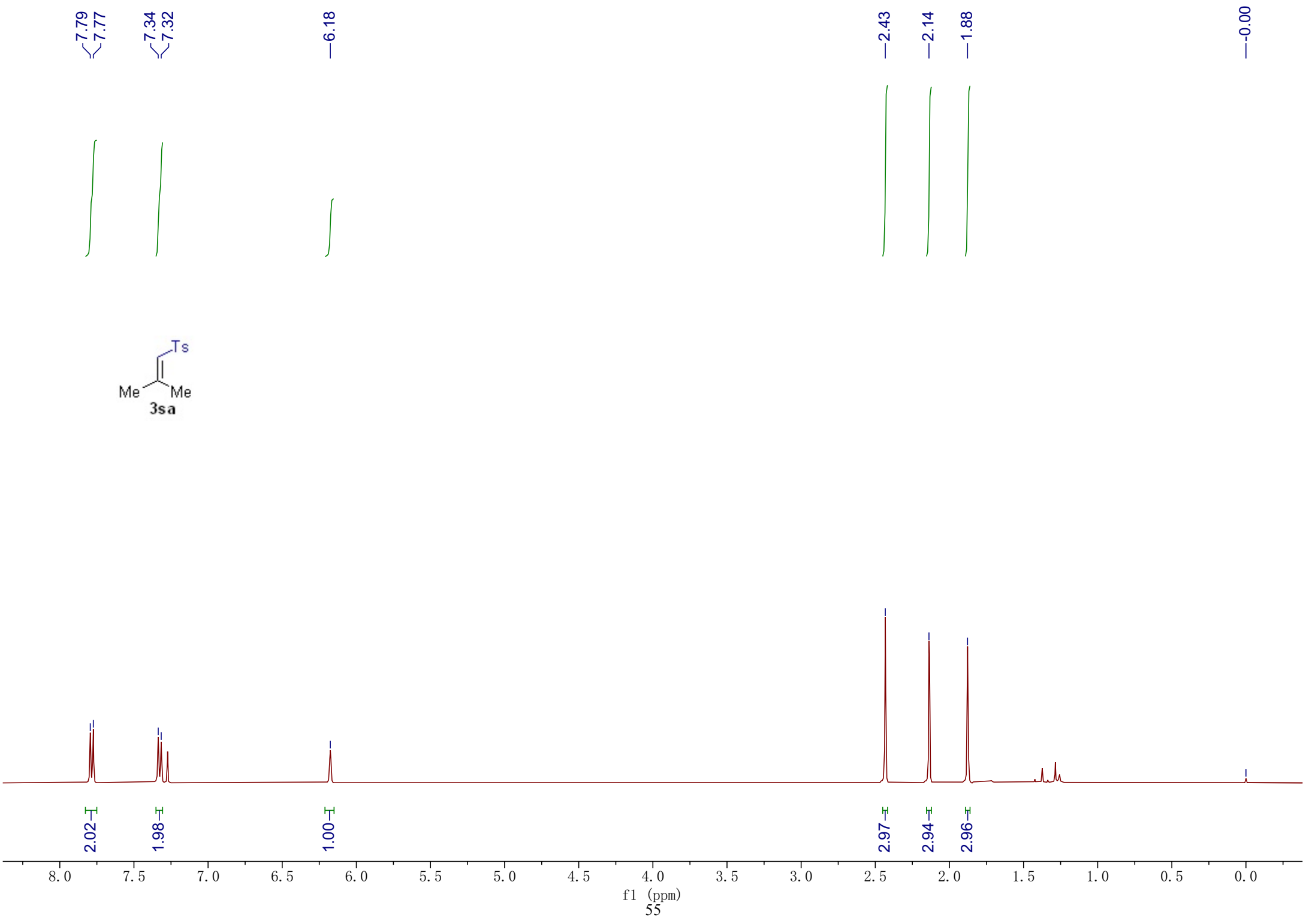
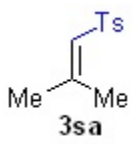
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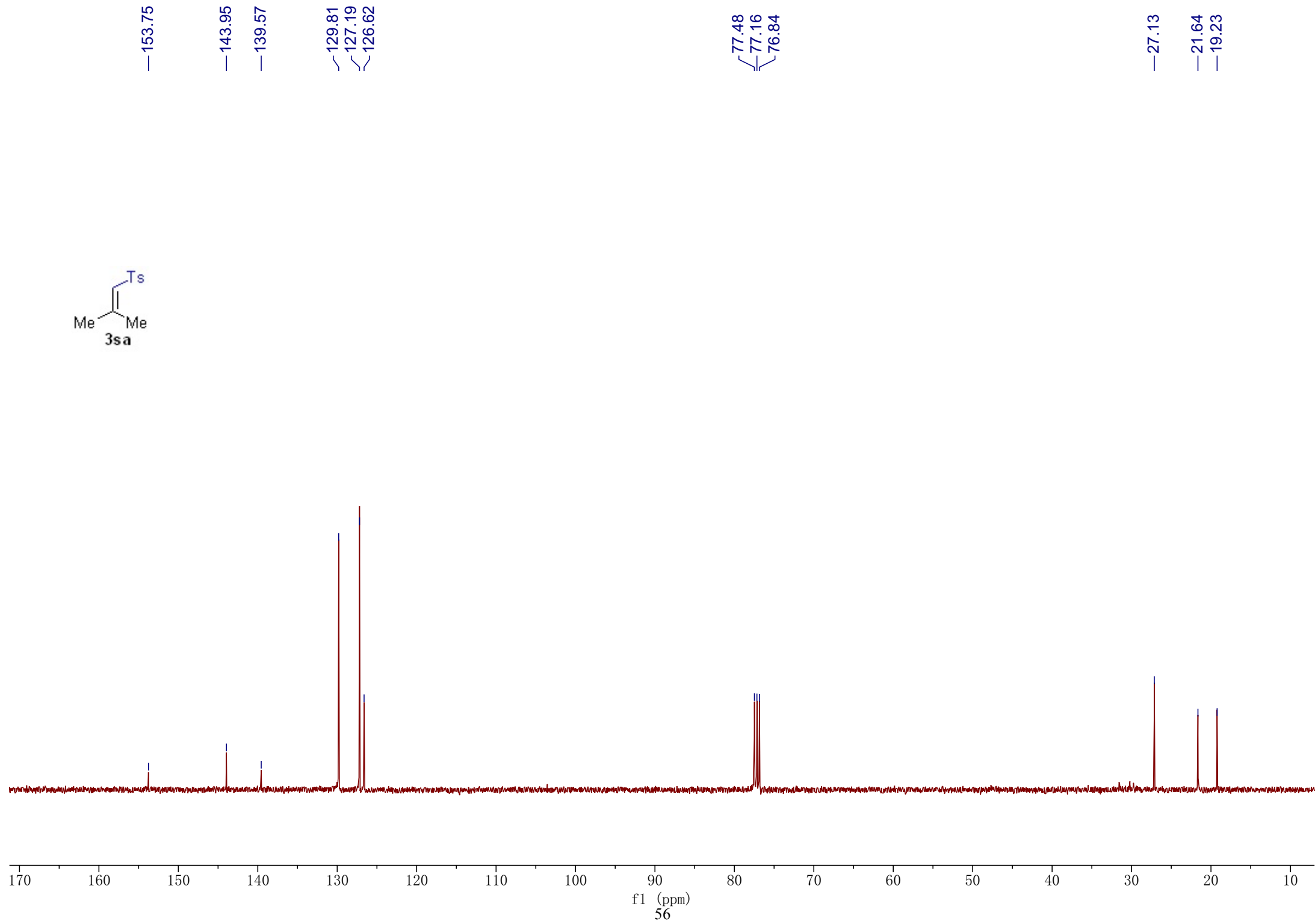
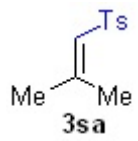




— 163.66 — 145.79 — 143.54 — 135.50 — 130.61 — 130.40 — 128.52 — 77.48 — 77.16 — 76.84 — 62.14 — 21.88 — 14.17



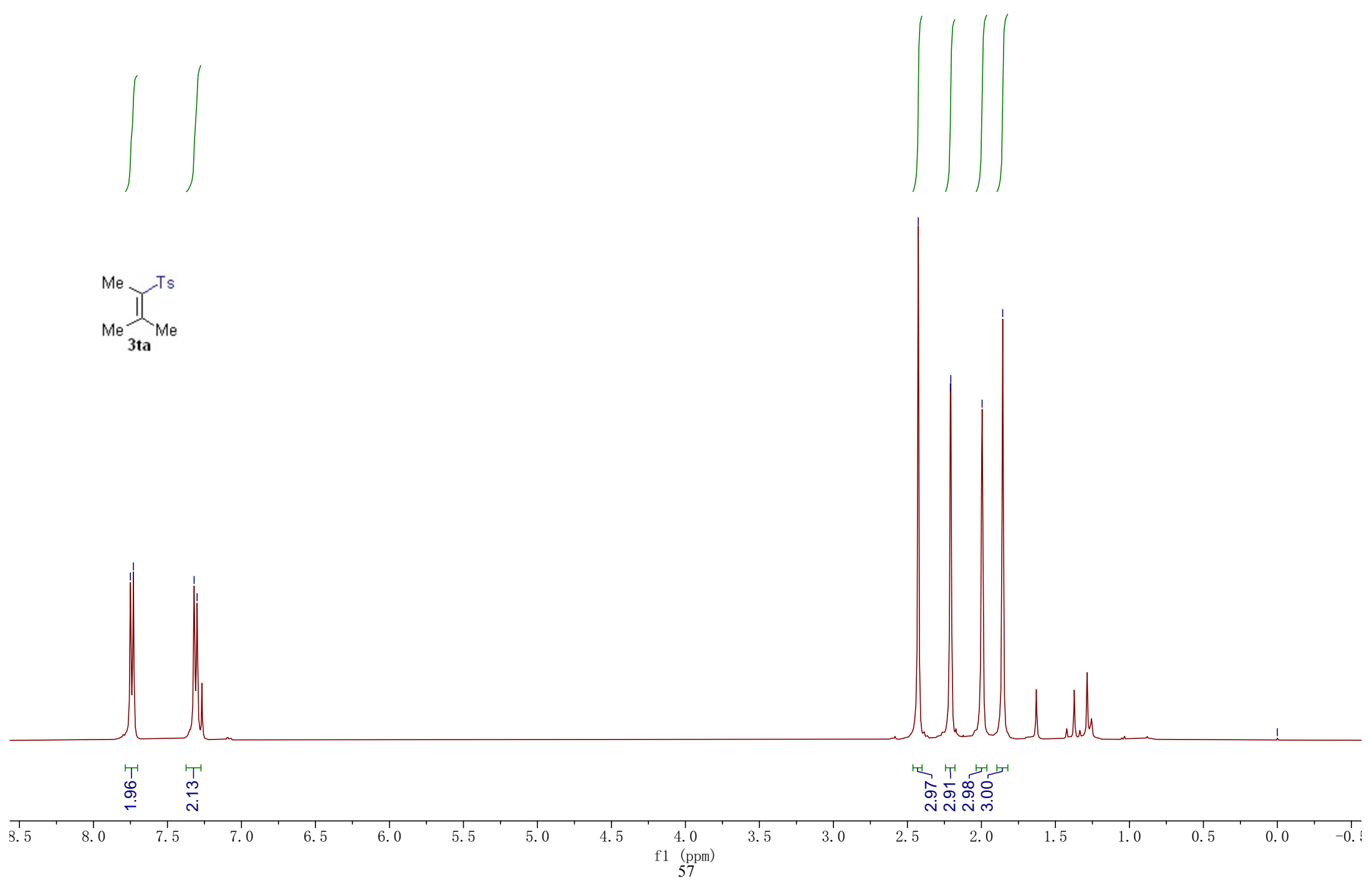
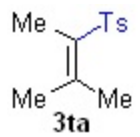




7.75
7.73
7.32
7.30

2.43
2.21
2.21
2.00
1.86

0.00



1.96

2.13

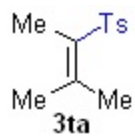
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2.91

2.98

3.00

f1 (ppm)
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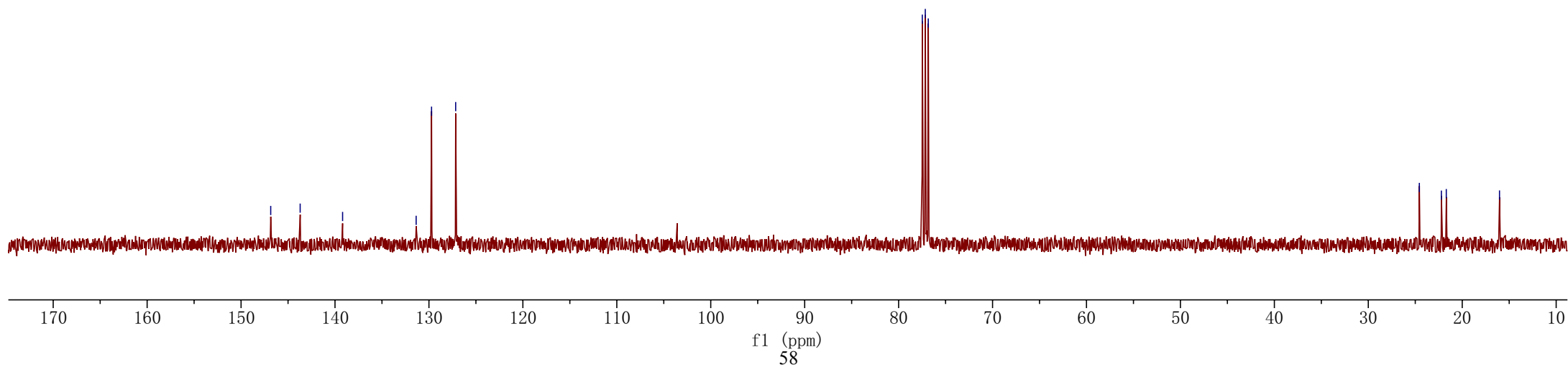


146.84
143.71
139.19

131.36
129.72
127.15

77.48
77.16
76.84

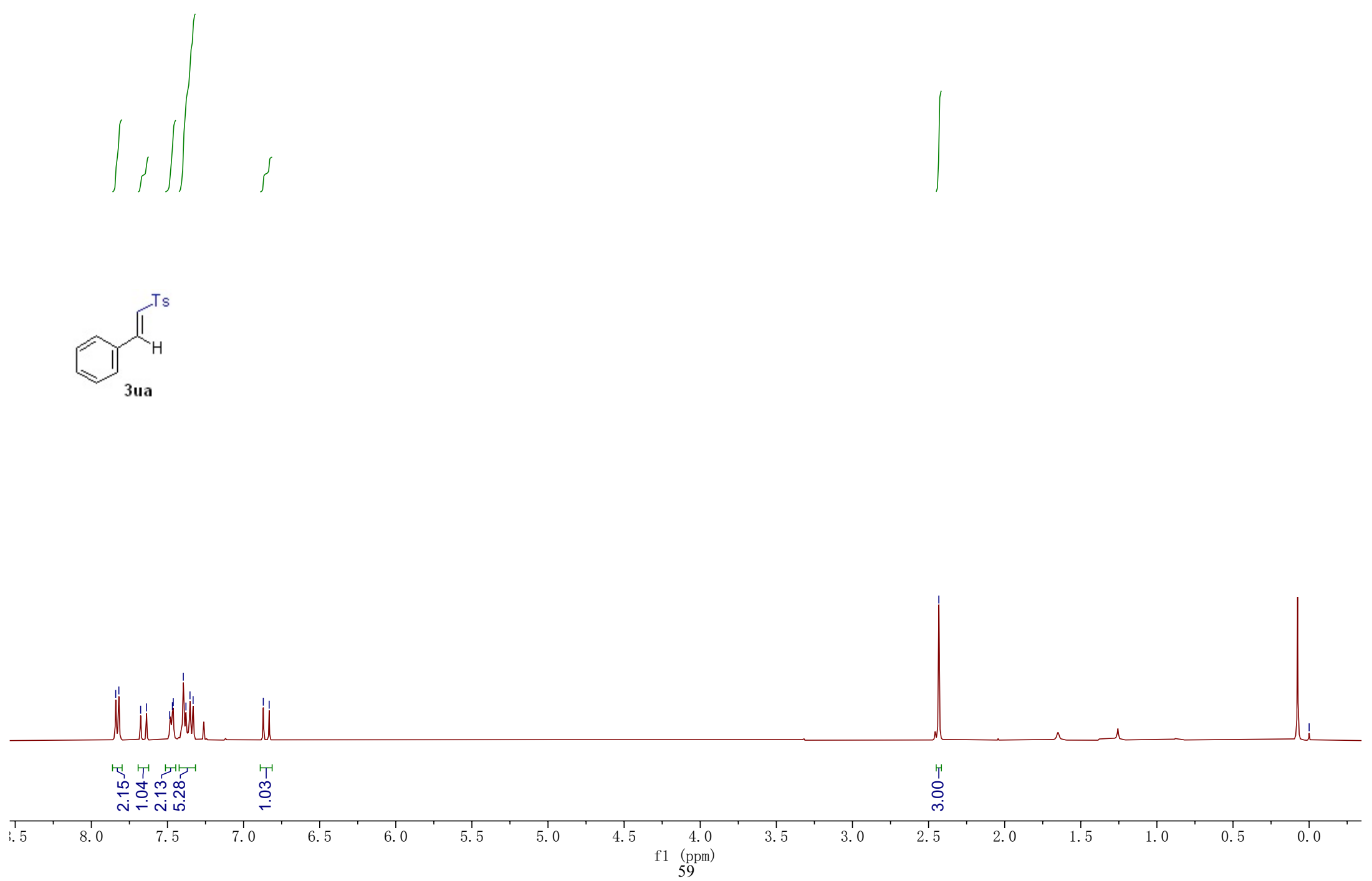
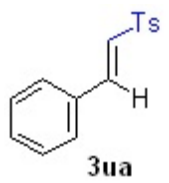
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22.22
21.70
16.03

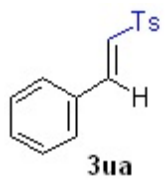


7.84
7.82
7.68
7.64
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7.47
7.46
7.40
7.38
7.35
7.33
6.87
6.83

2.43

0.00

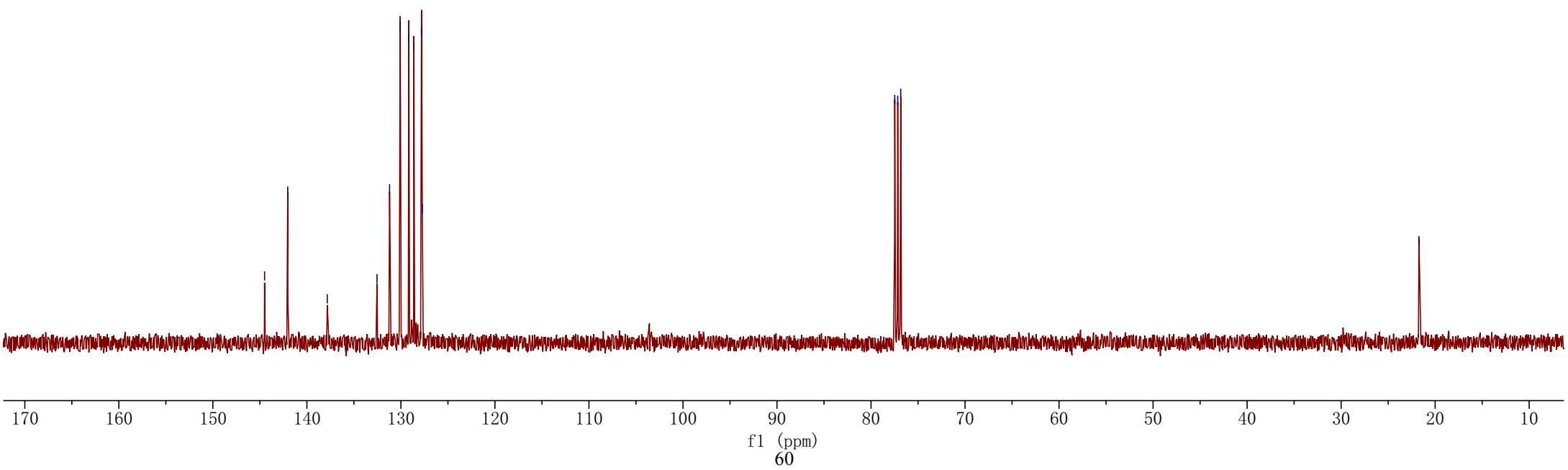




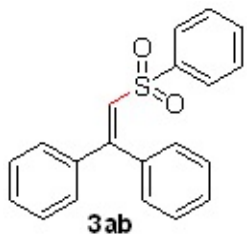
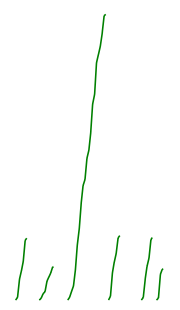
144.50
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130.07
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128.62
127.81
127.73

77.48
77.16
76.84

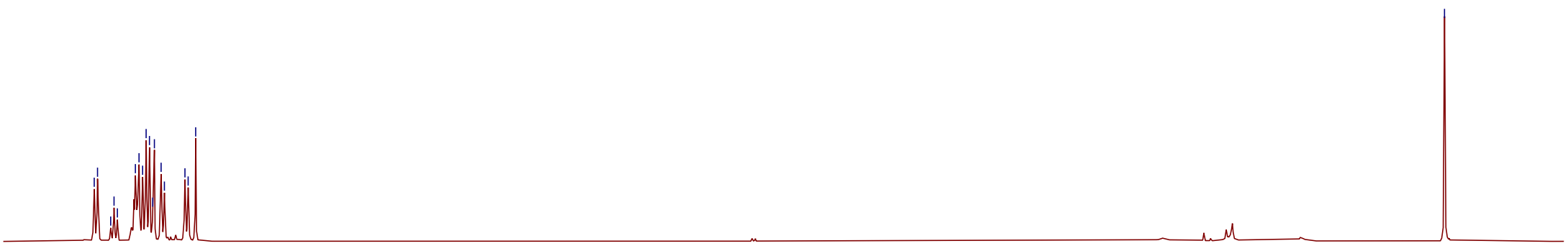
21.73



7.51
7.49
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7.19
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7.01
6.99
6.95



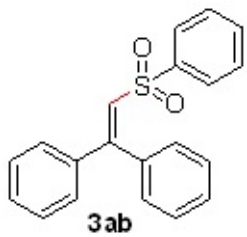
— 0.00



1.98
1.07
9.15
2.07
2.00
1.00

8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.5
2.0
1.5
1.0
0.5
0.0
-0.5

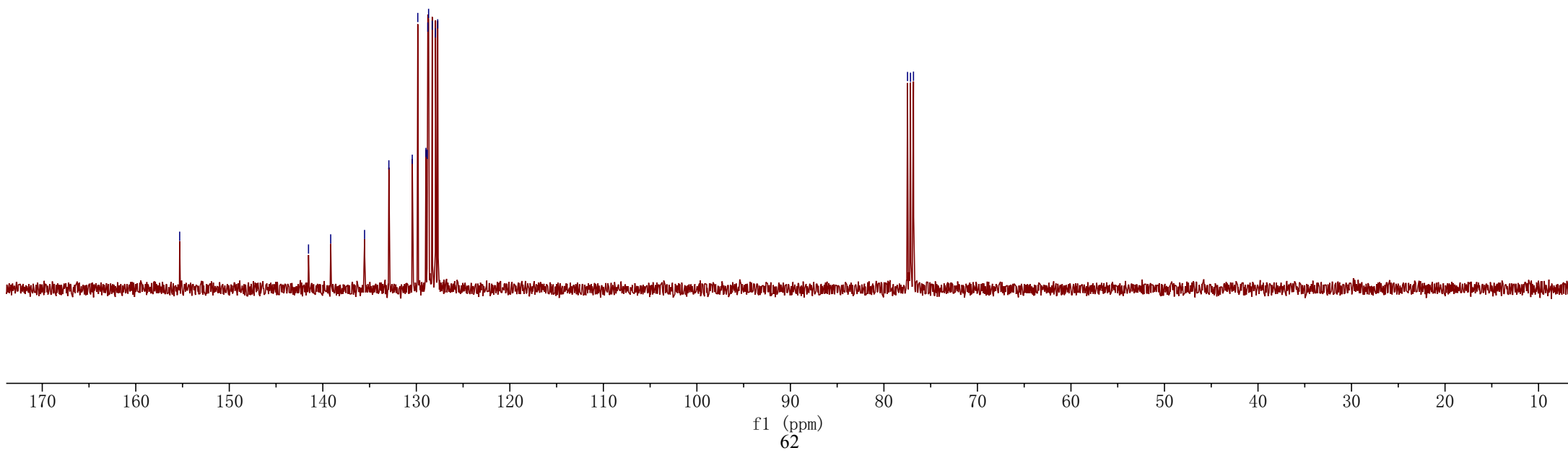
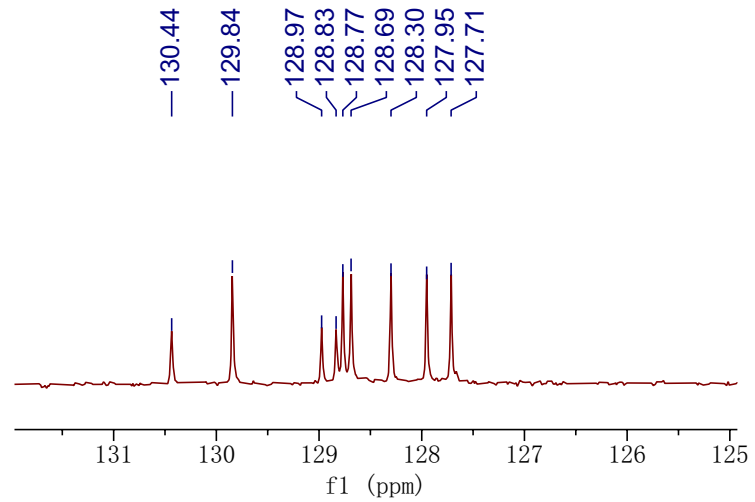
f1 (ppm)
61



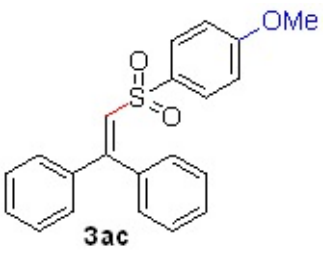
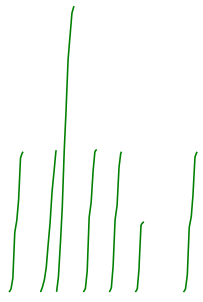
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128.77
128.69
128.30
127.95
127.71

77.48
77.16
76.84

130.44
129.84
128.97
128.83
128.77
128.69
128.30
127.95
127.71



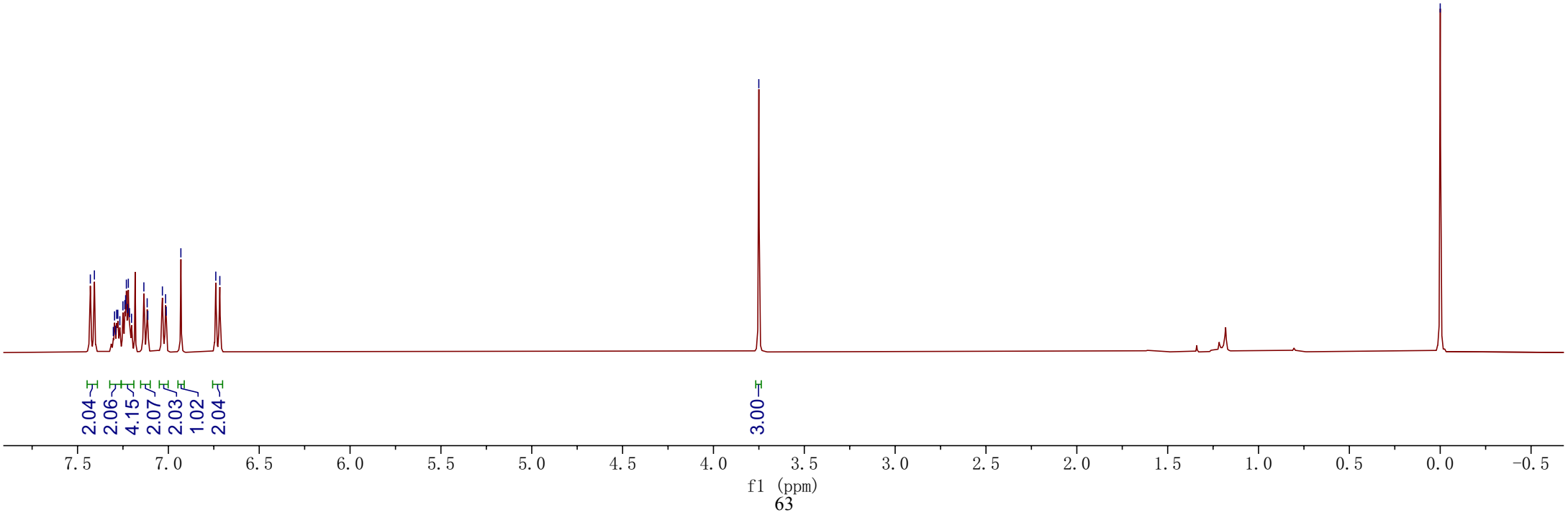
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7.22
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7.02
7.01
6.93
6.74
6.72

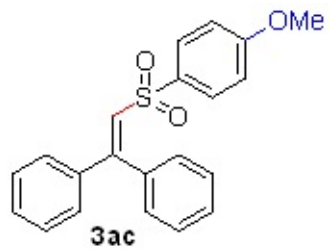


—3.75



—0.00

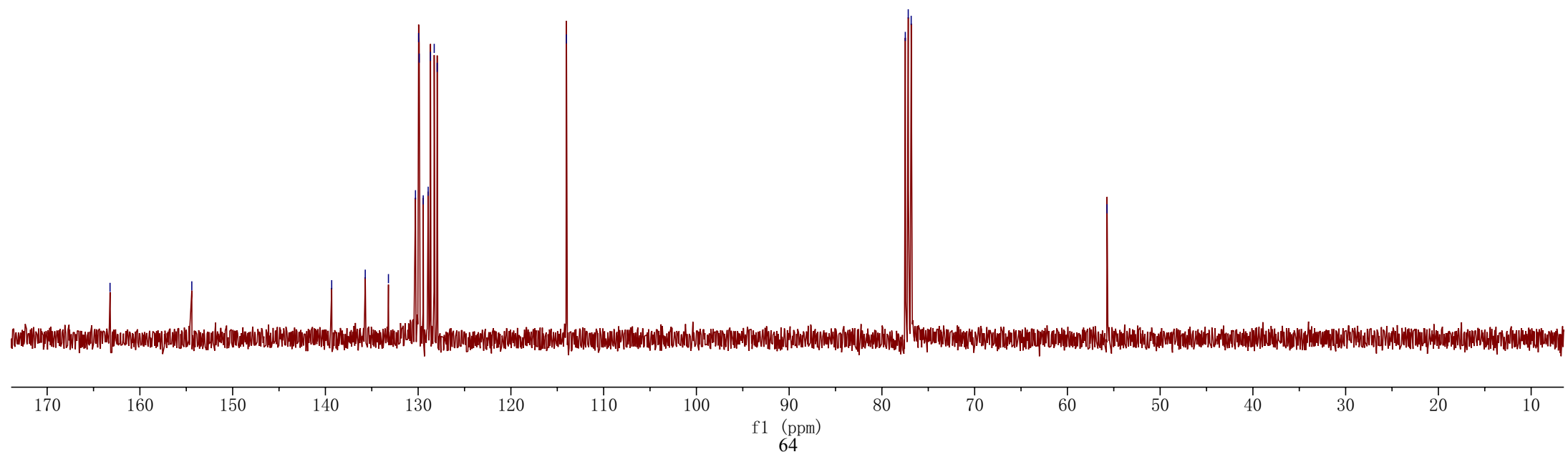
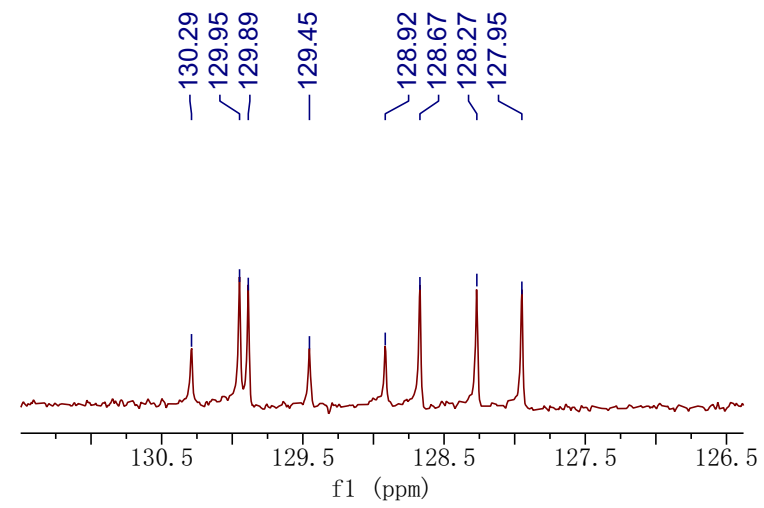




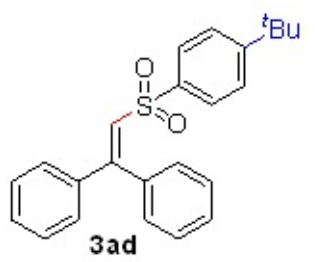
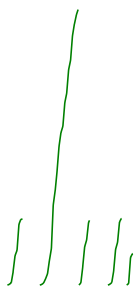
—163.22
—154.40
139.32
135.70
133.20
130.29
129.95
129.89
129.45
128.92
128.67
128.27
127.95
—114.01

77.48
77.16
76.84
—55.73

130.29
129.95
129.89
—129.45
128.92
128.67
128.27
127.95

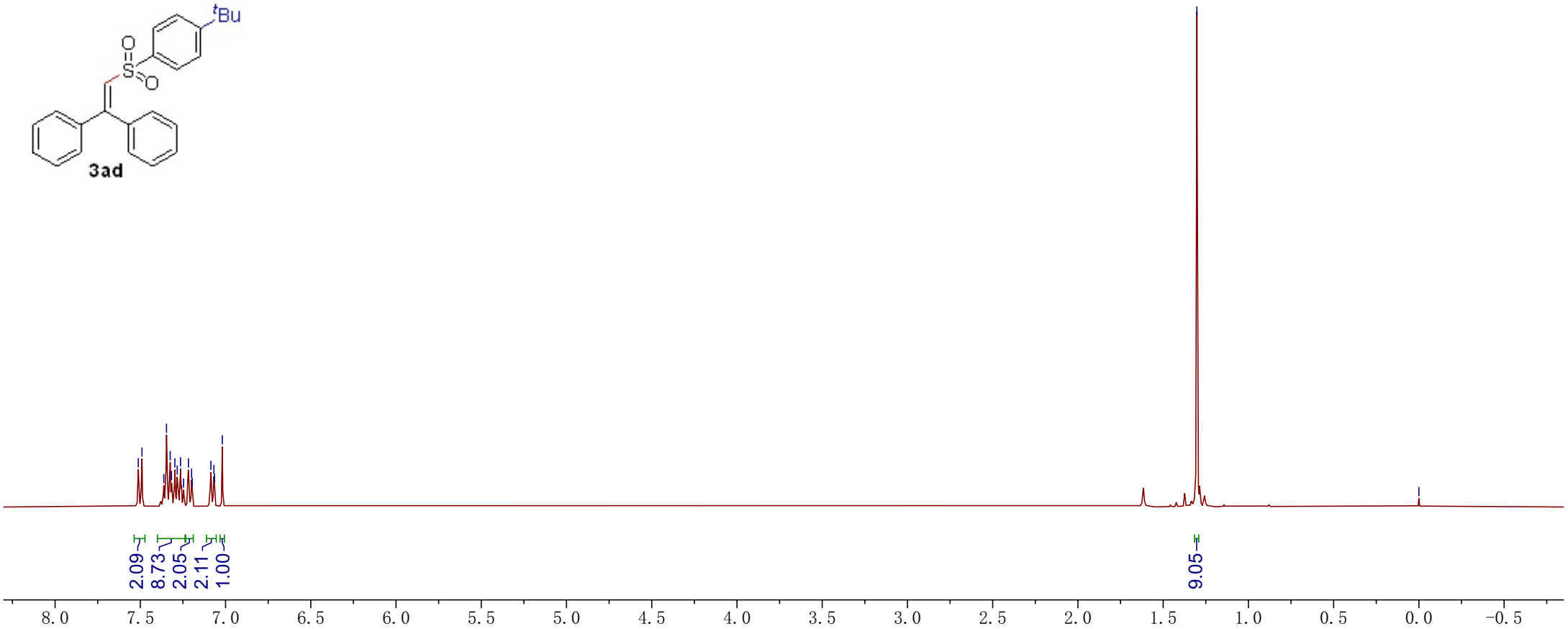


7.51
7.49
7.36
7.35
7.32
7.32
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7.20
7.09
7.07
7.06
7.02



1.30

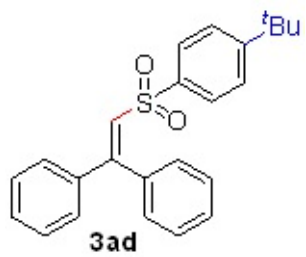
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2.09
8.73
2.05
2.11
1.00

9.05

f1 (ppm)
65

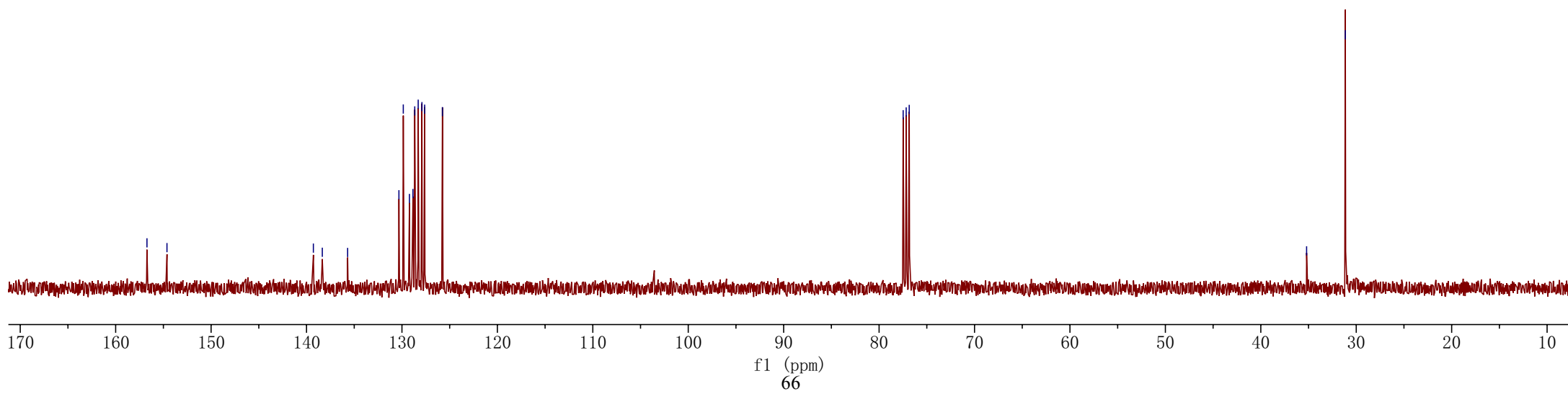


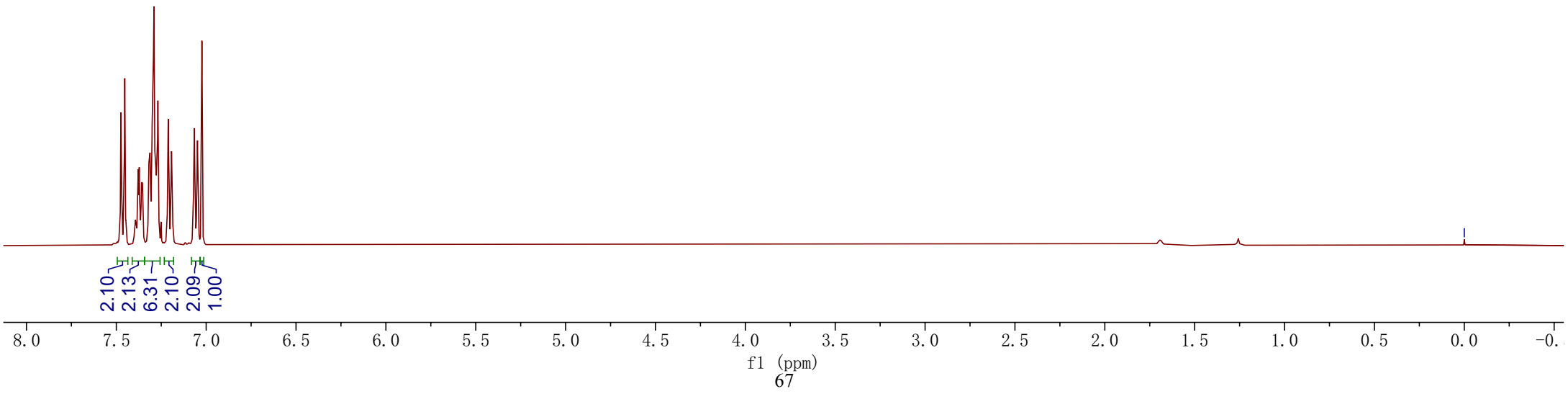
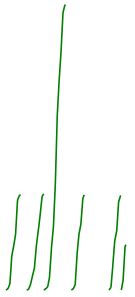
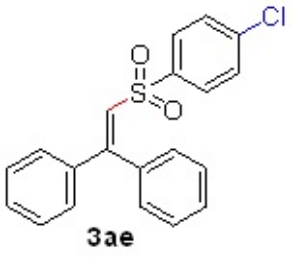
— 156.72
— 154.62

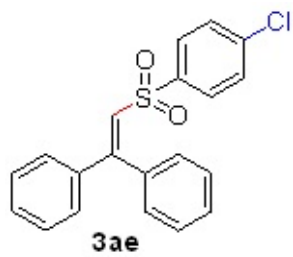
— 139.28
— 138.35
— 135.69
— 130.32
— 129.86
— 129.22
— 128.85
— 128.66
— 128.30
— 127.91
— 127.62
— 125.76

— 77.48
— 77.16
— 76.84

— 35.20
— 31.14







— 155.70

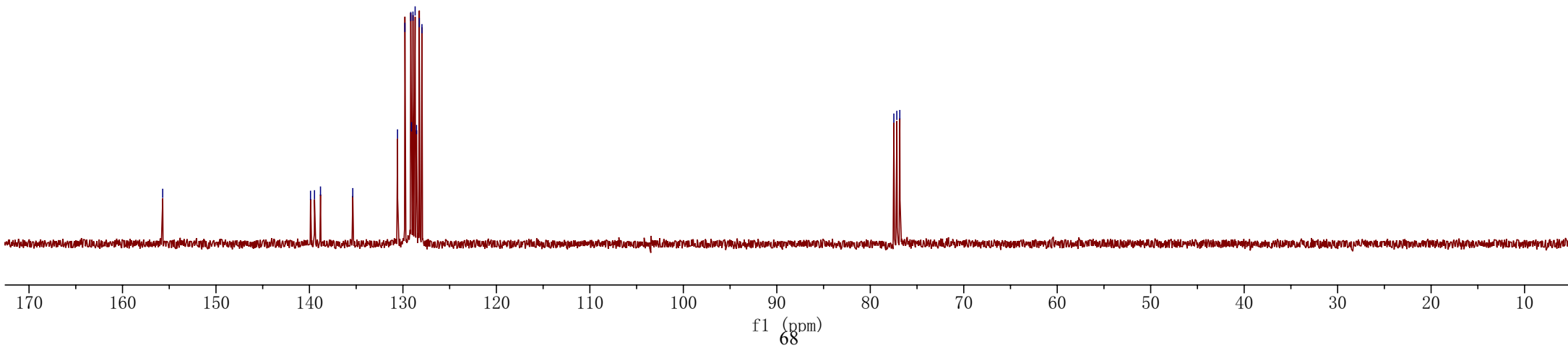
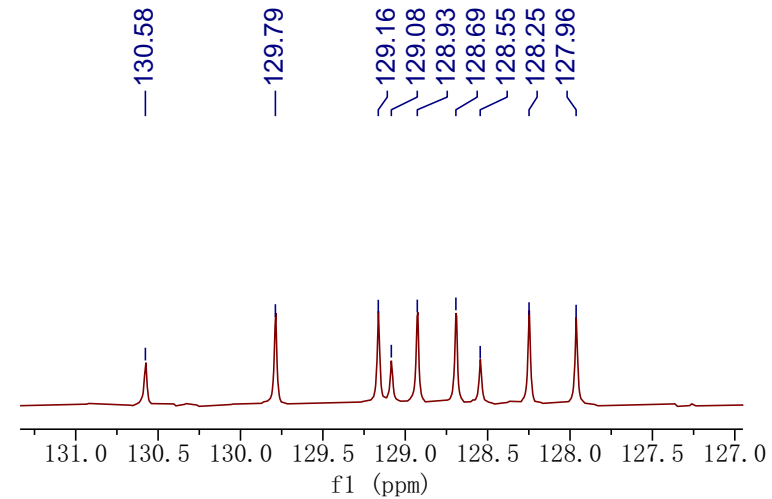
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138.82
135.36
130.58
129.79
129.16
129.08
128.93
128.69
128.55
128.25
127.96

77.48
77.16
76.84

— 130.58

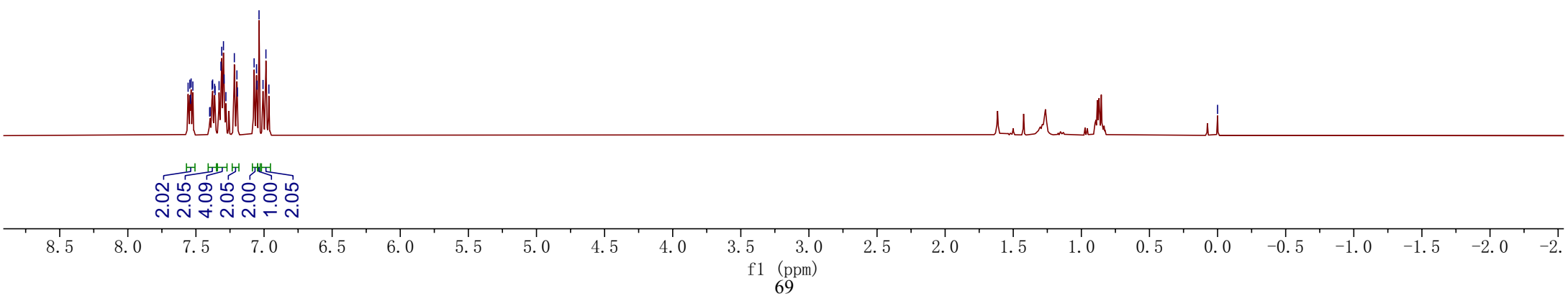
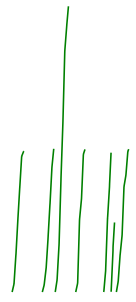
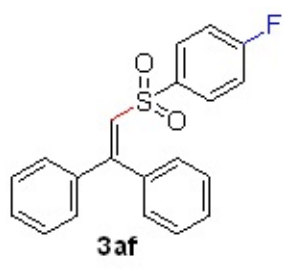
— 129.79

129.16
129.08
128.93
128.69
128.55
128.25
127.96



7.56
7.54
7.54
7.54
7.52
7.40
7.40
7.38
7.38
7.36
7.36
7.33
7.32
7.31
7.30
7.29
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7.07
7.06
7.05
7.04
7.01
6.99
6.96

— 0.00

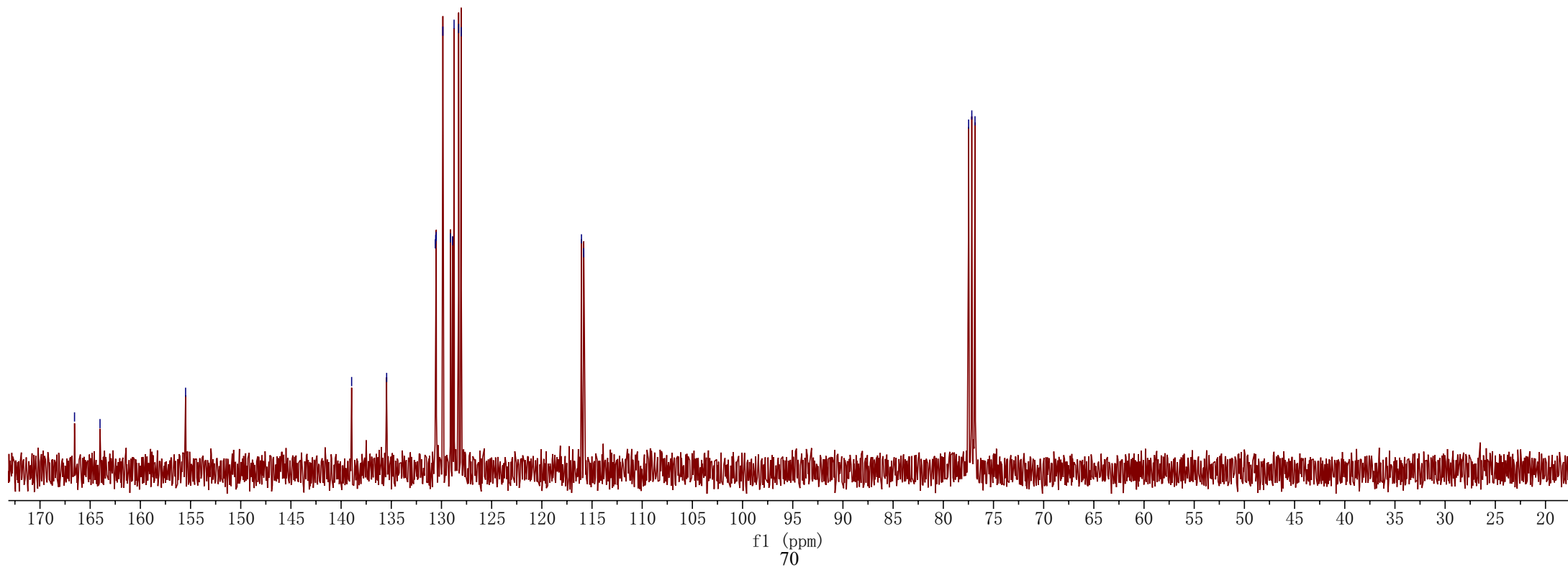
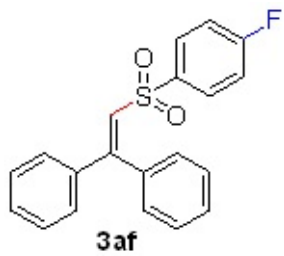


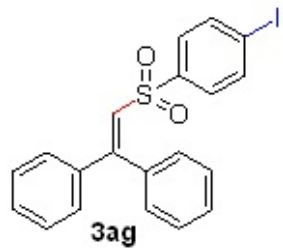
— 166.56
— 164.02

— 155.49

— 138.95
— 135.46
— 130.62
— 130.58
— 130.52
— 129.86
— 129.10
— 128.89
— 128.74
— 128.29
— 128.03
— 116.05
— 115.83

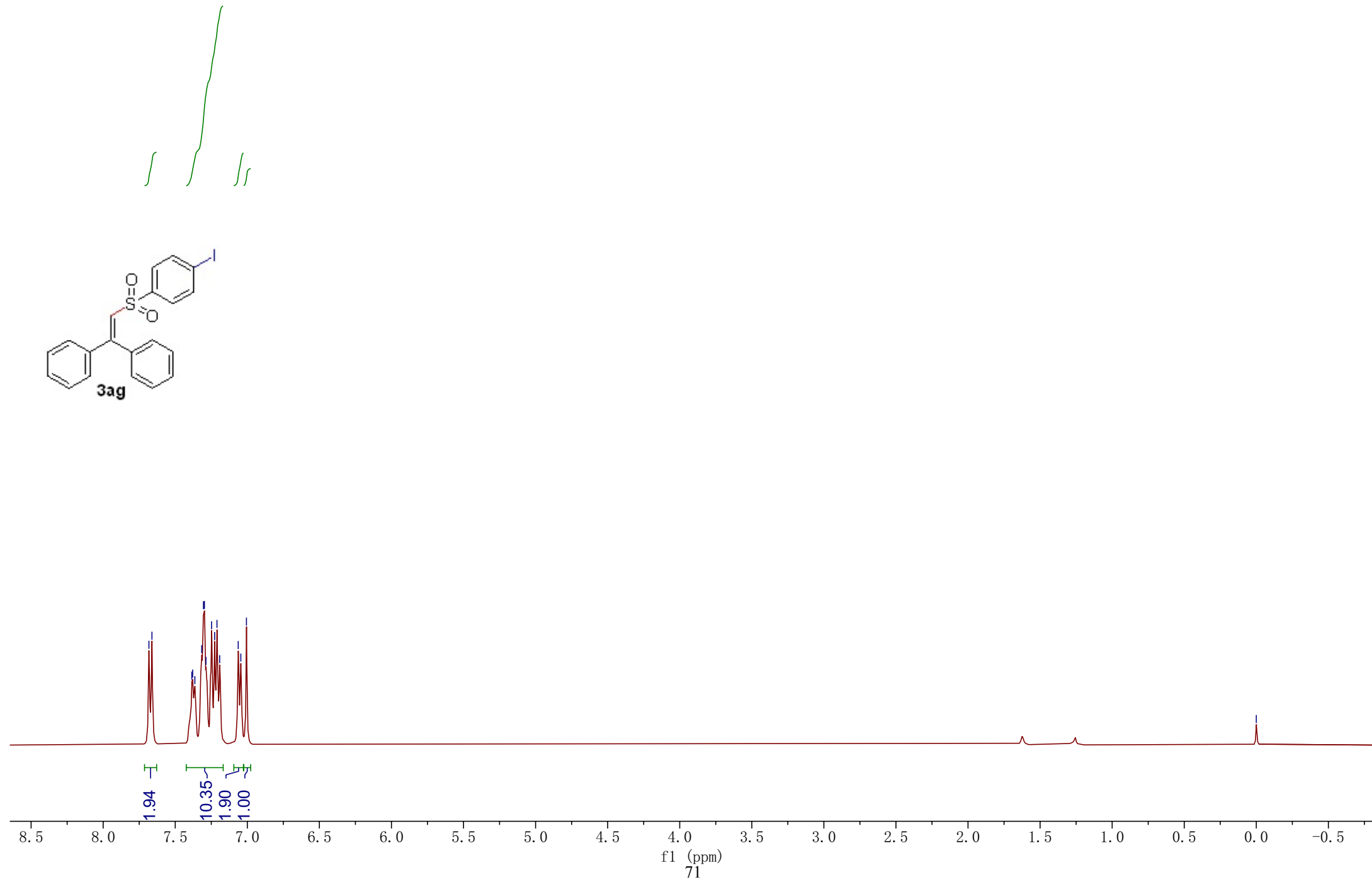
— 77.48
— 77.16
— 76.84

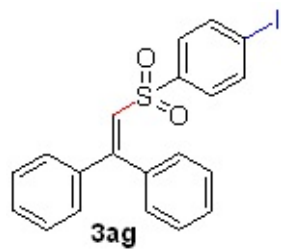




7.68
7.66
7.39
7.38
7.36
7.32
7.30
7.29
7.25
7.23
7.21
7.19
7.06
7.05
7.01

—0.00





— 155.78

— 141.14
— 138.90
— 137.95
— 135.42
— 130.63
— 129.85
— 129.14
— 129.12
— 128.75
— 128.53
— 128.31
— 128.02

— 100.72

— 77.48
— 77.16
— 76.84

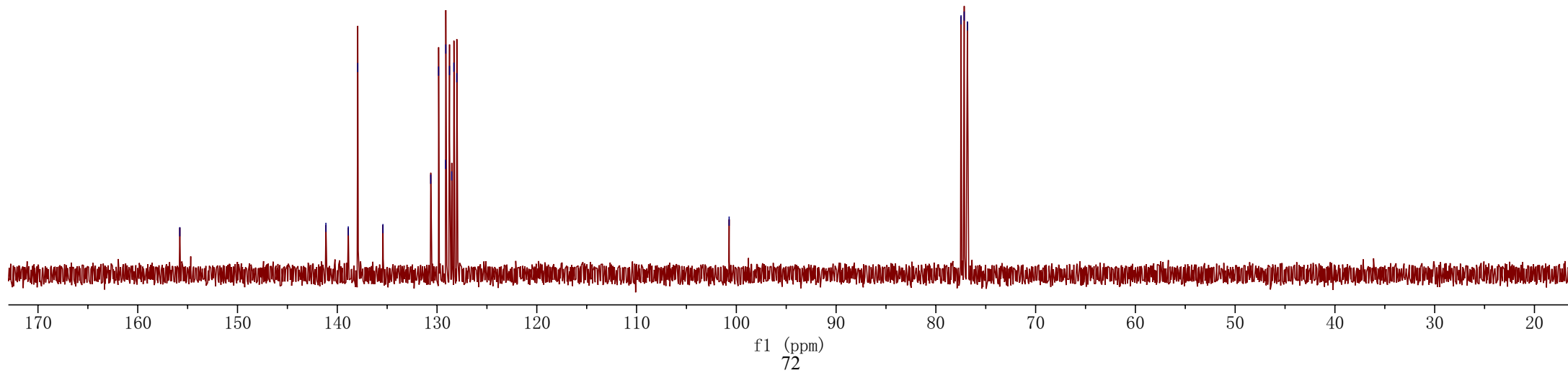
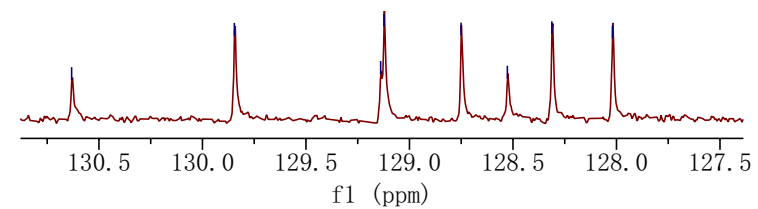
— 130.63

— 129.85

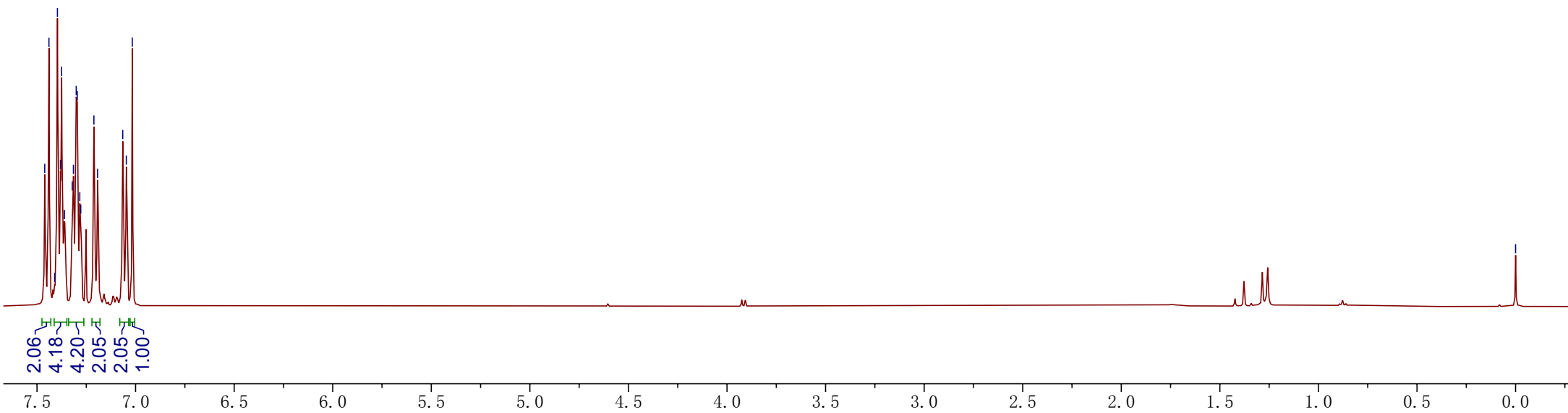
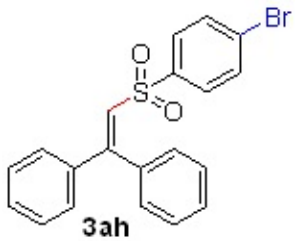
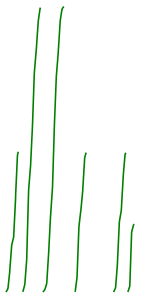
— 129.14
— 129.12

— 128.75
— 128.53
— 128.31

— 128.02

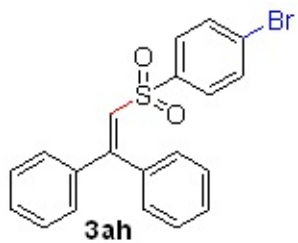


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7.36
7.32
7.32
7.30
7.30
7.28
7.28
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7.19
7.07
7.05
7.02



2.06
4.18
4.20
2.05
2.05
1.00

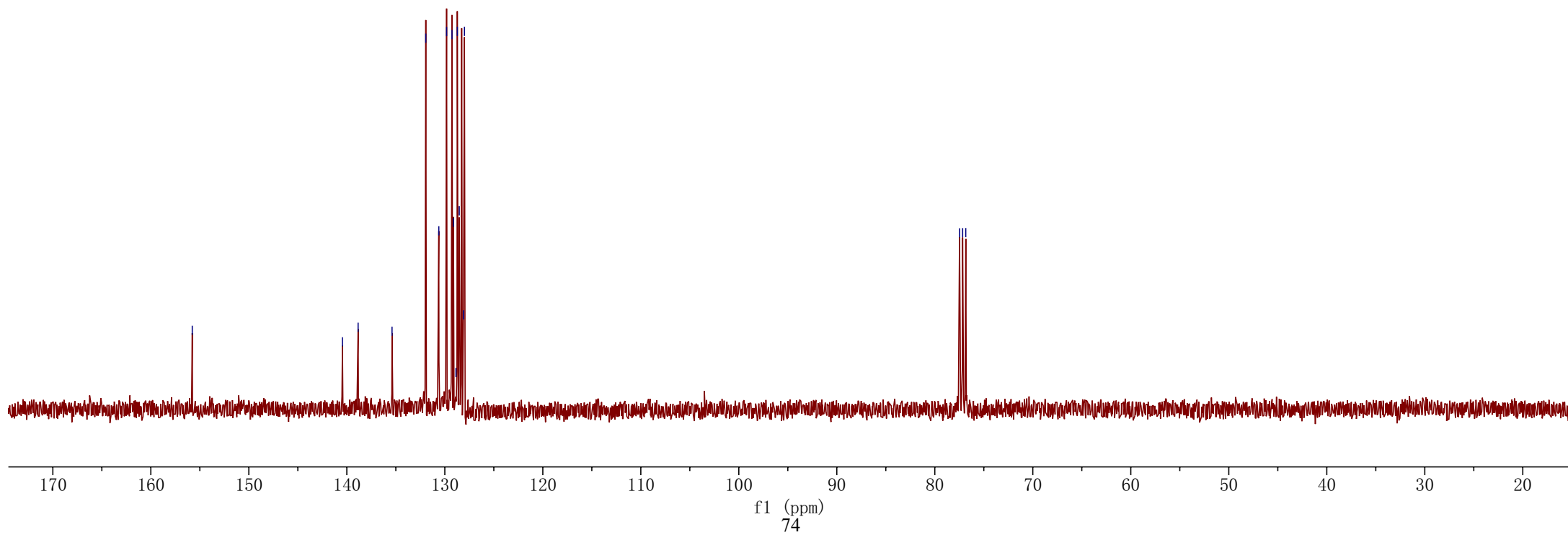
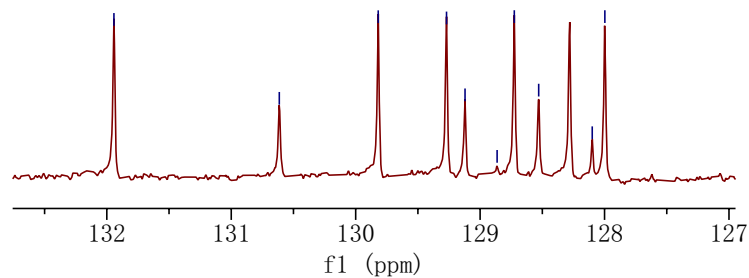
f1 (ppm)
73



155.77
140.45
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130.61
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129.12
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128.73
128.53
128.10
128.00

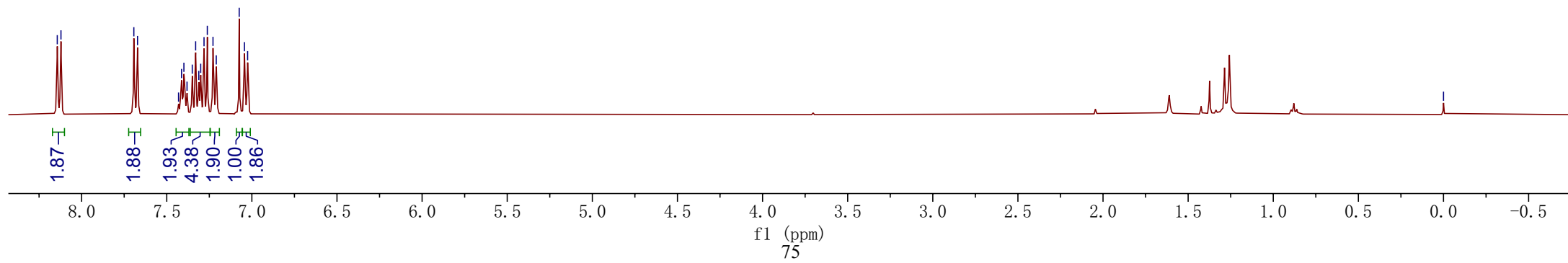
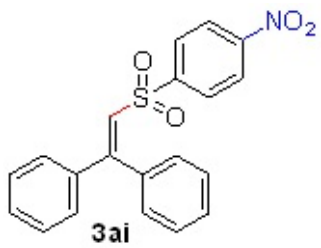
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77.16
76.84

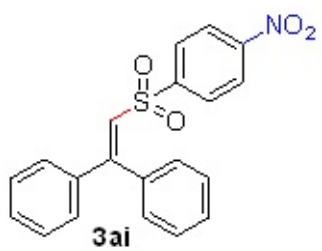
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129.82
129.27
129.12
128.86
128.73
128.53
128.10
128.00



8.14
8.12
7.69
7.67
7.43
7.41
7.40
7.38
7.35
7.33
7.31
7.30
7.28
7.26
7.23
7.21
7.07
7.04
7.02

— 0.00

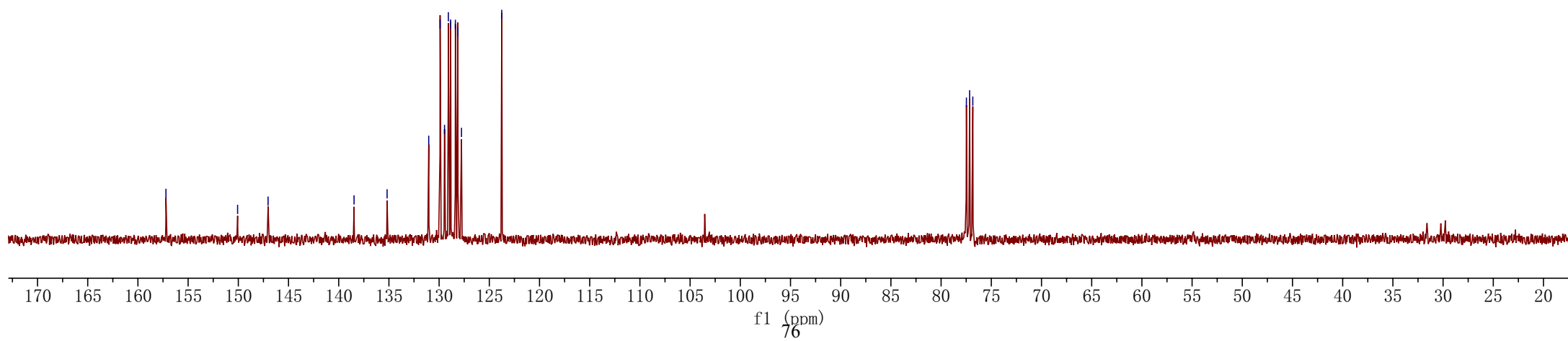
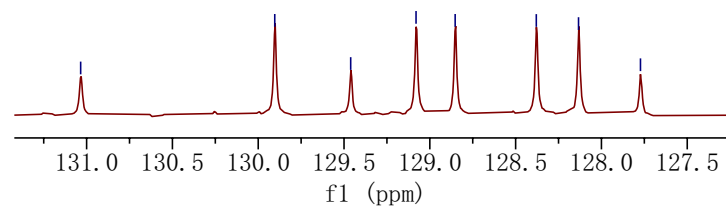




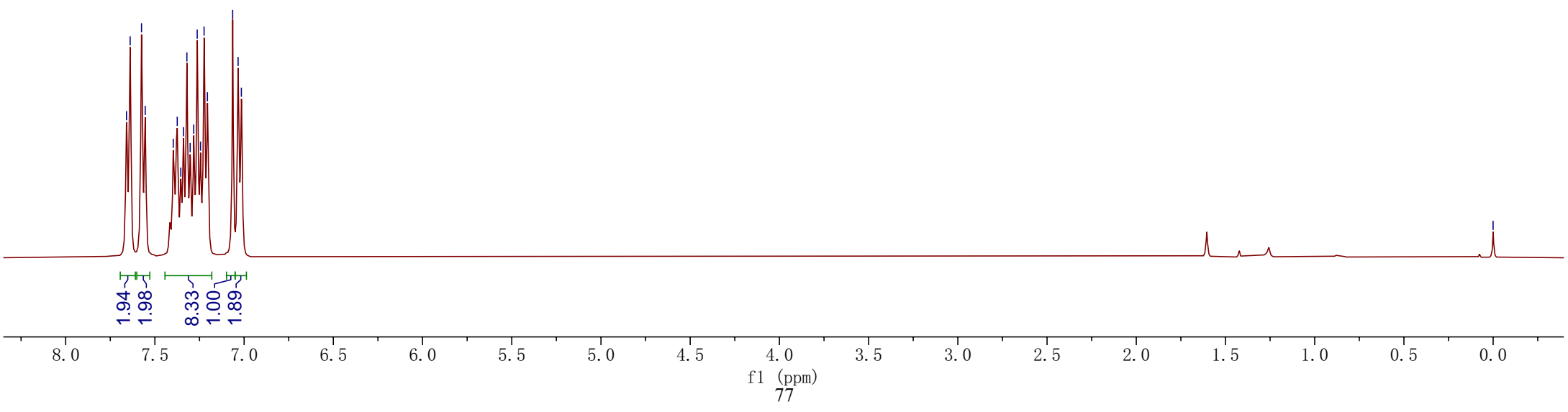
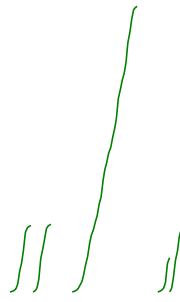
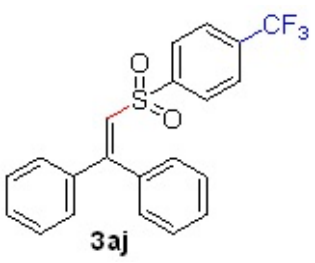
—157.21
—150.07
—147.04
138.47
135.18
131.03
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129.46
129.08
128.85
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128.13
127.77
123.76

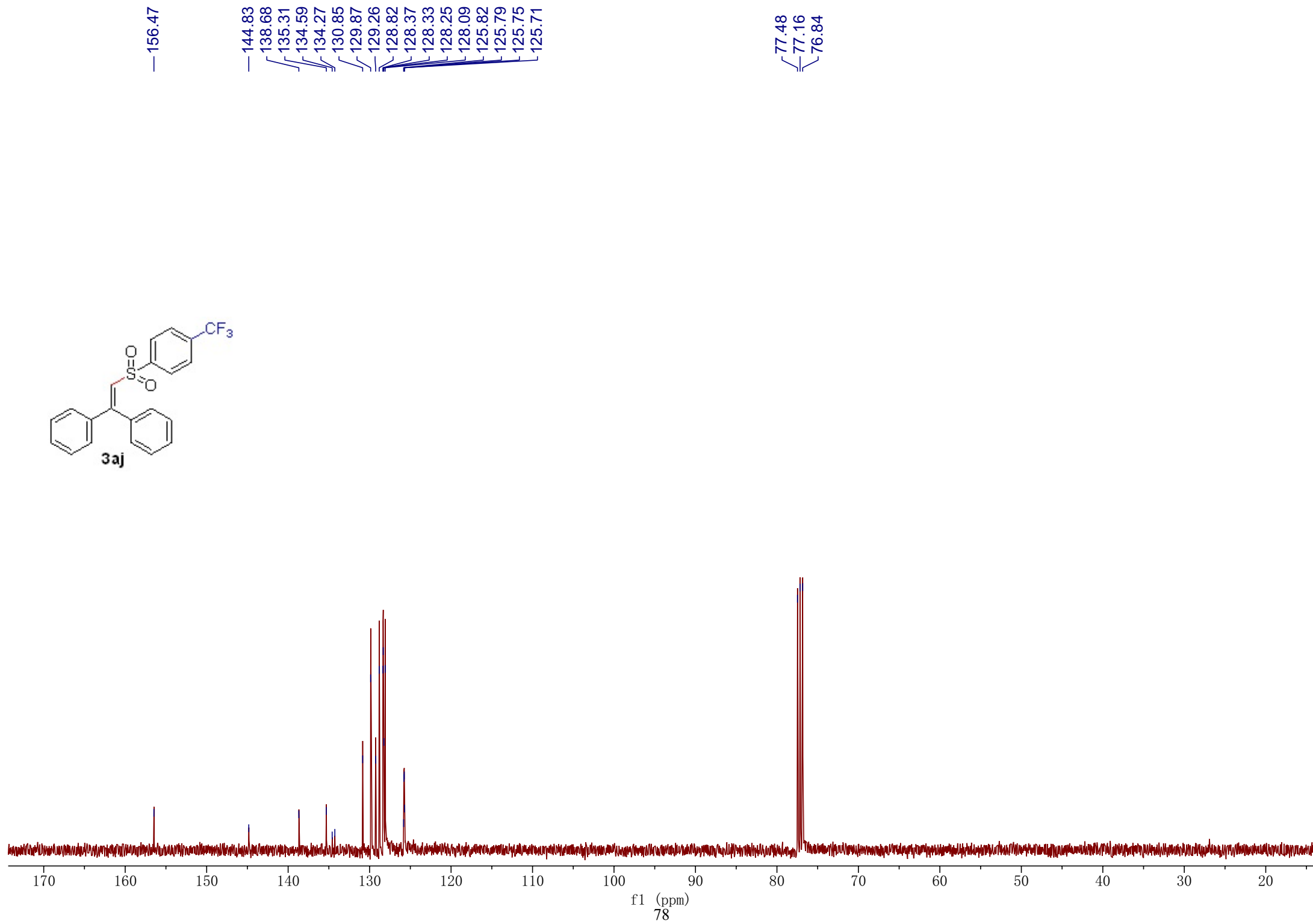
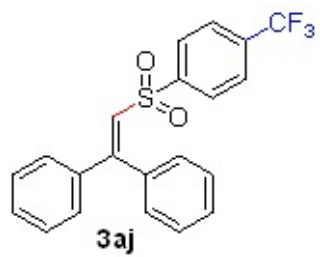
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76.84

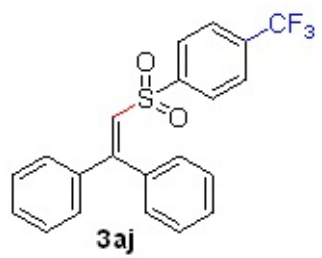
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—129.90
—129.46
—129.08
—128.85
—128.38
—128.13
—127.77



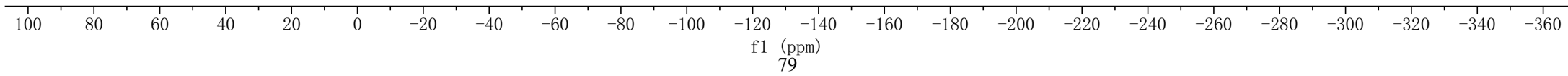
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7.21
7.06
7.03
7.02





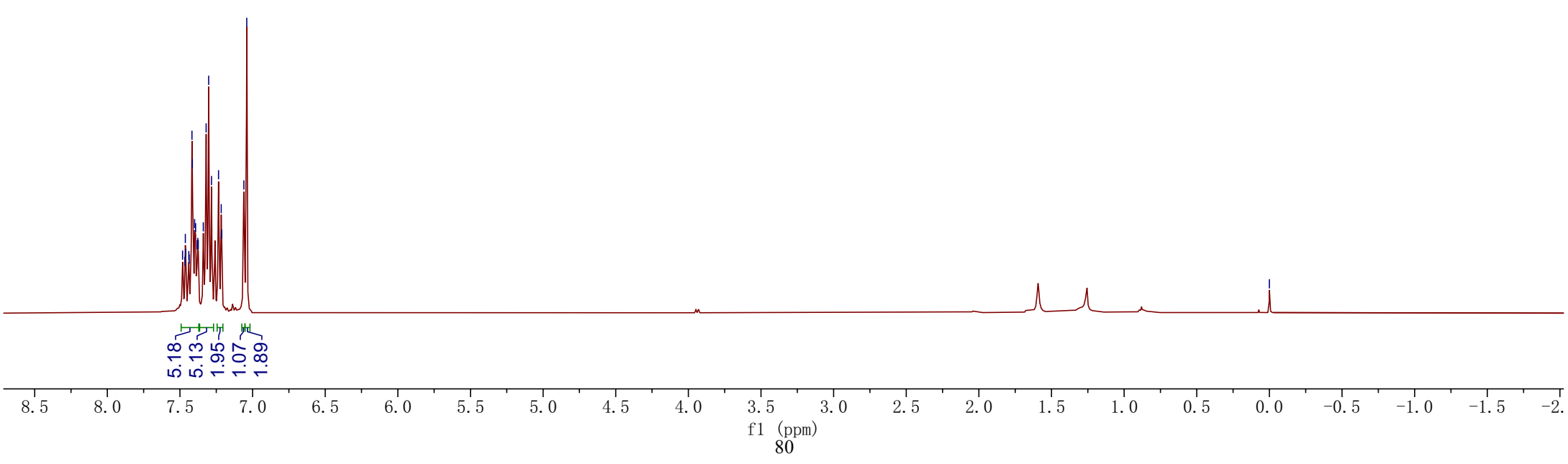
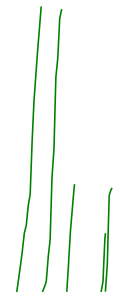
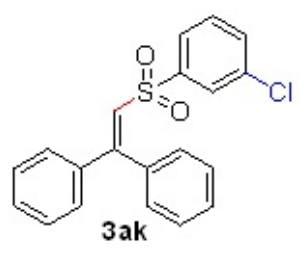


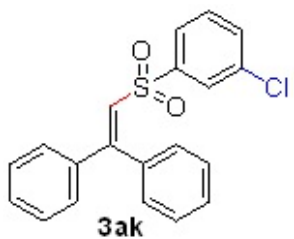
—63.25



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7.47
7.46
7.46
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7.38
7.37
7.34
7.32
7.30
7.28
7.23
7.22
7.21
7.06
7.04

—0.00





— 156.19

— 143.17
— 138.83
— 135.20
— 134.91
— 133.07
— 130.73
— 130.05
— 129.84
— 129.35
— 128.80
— 128.53
— 128.35
— 128.17
— 128.06
— 125.87

— 77.48
— 77.16
— 76.84

— 130.73

— 130.05

— 129.84

— 129.35

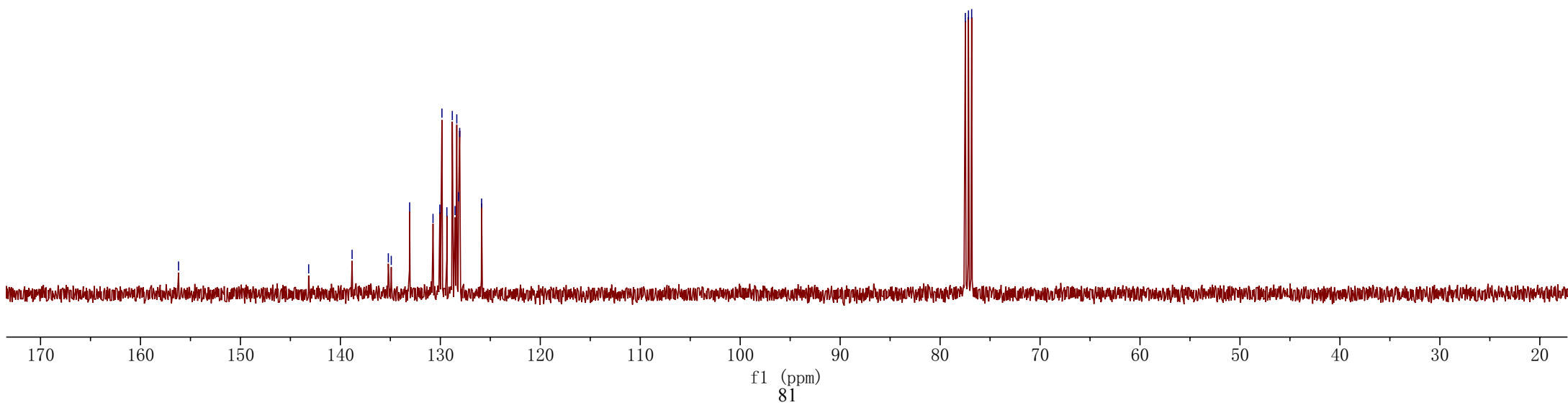
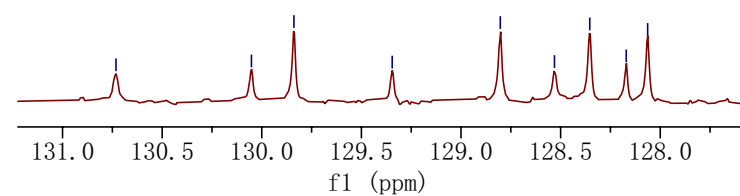
— 128.80

— 128.53

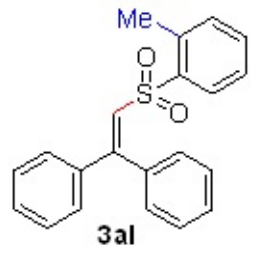
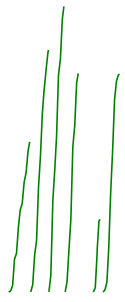
— 128.35

— 128.17

— 128.06

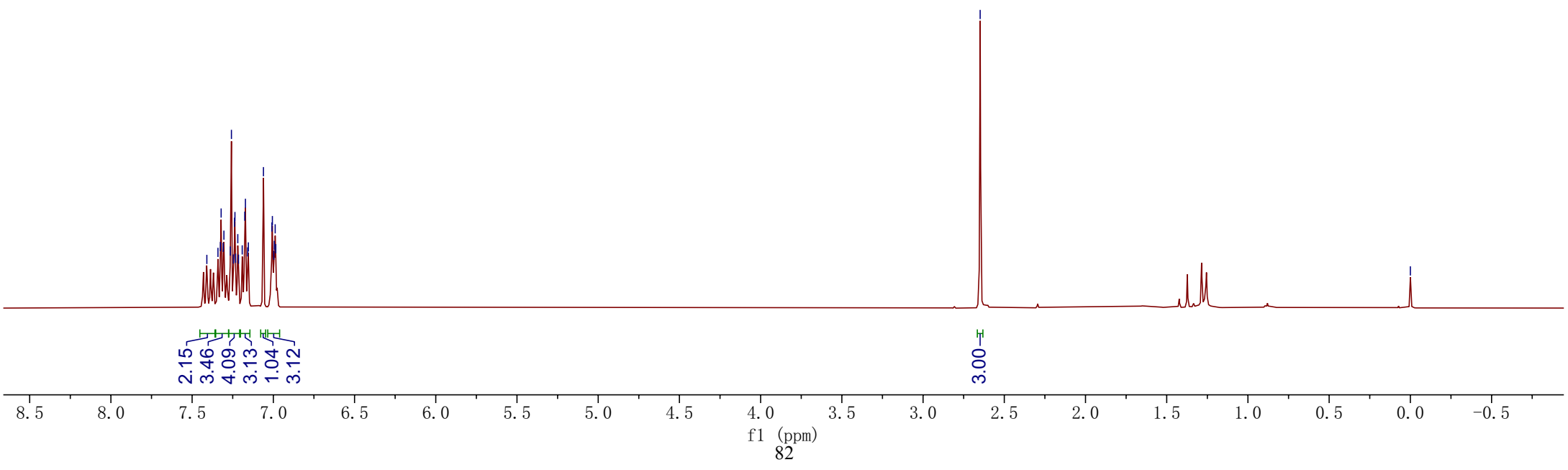


7.41
7.34
7.33
7.32
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7.26
7.26
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7.24
7.24
7.23
7.22
7.21
7.19
7.18
7.17
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7.06
7.01
7.01
7.00
6.99
6.99
6.98



—2.65

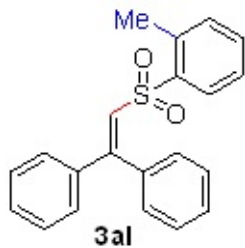
—0.00



2.15
3.46
4.09
3.13
1.04
3.12

3.00

f1 (ppm)
82



139.23
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135.37
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131.97
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129.67
129.50
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127.87
126.01

77.48
77.16
76.84

20.70

130.47

129.67

129.50

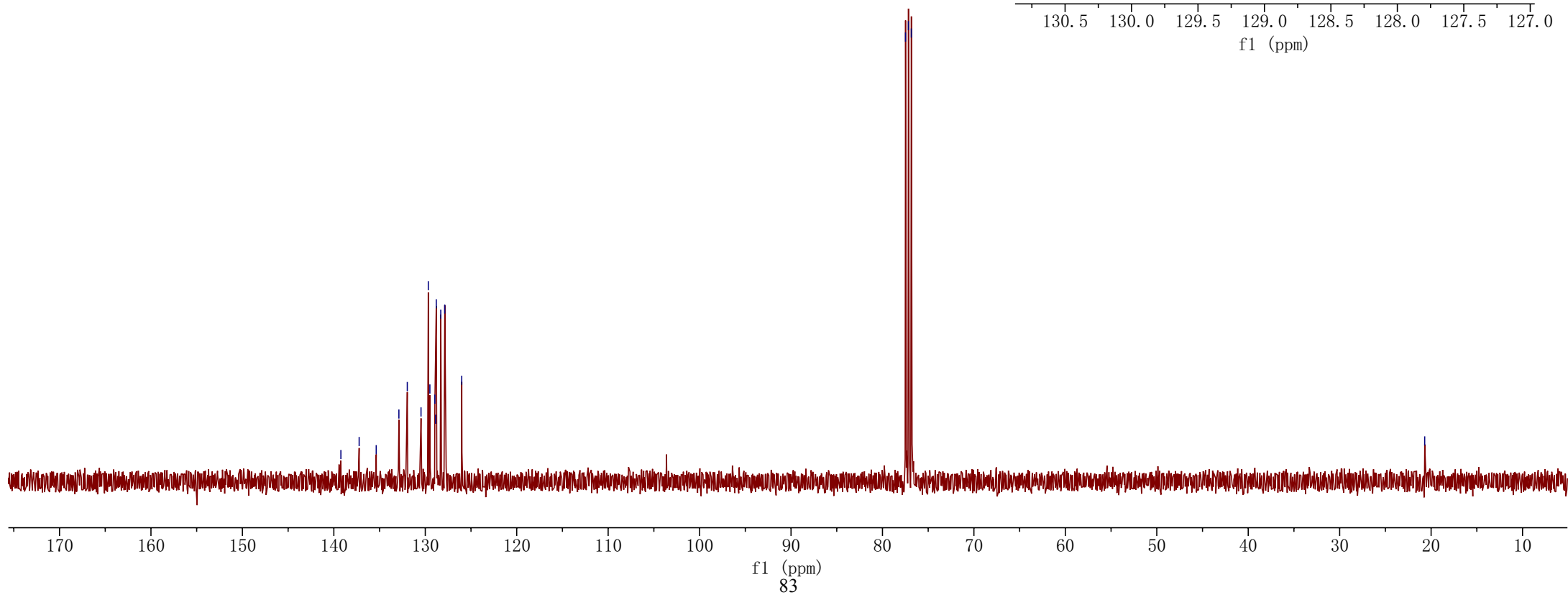
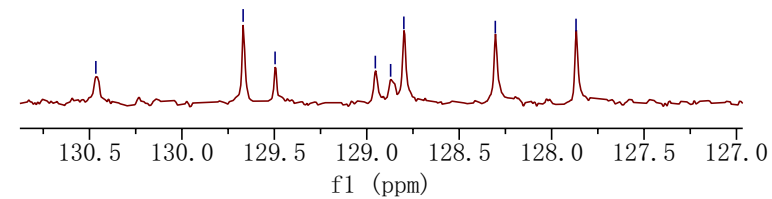
128.95

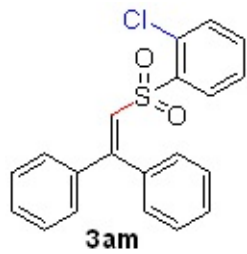
128.87

128.80

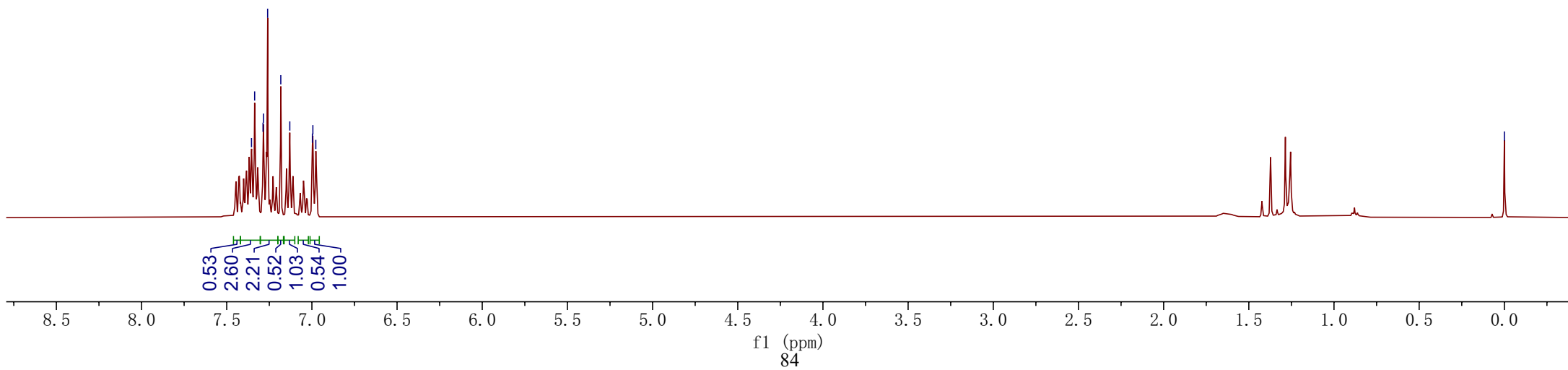
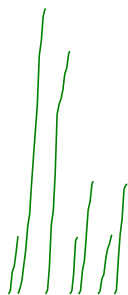
128.30

127.87

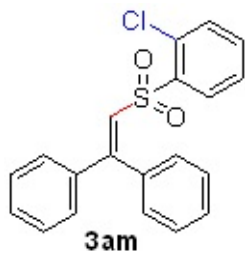




7.35
7.34
7.29
7.28
7.26
7.18
7.13
7.00
6.99
6.98



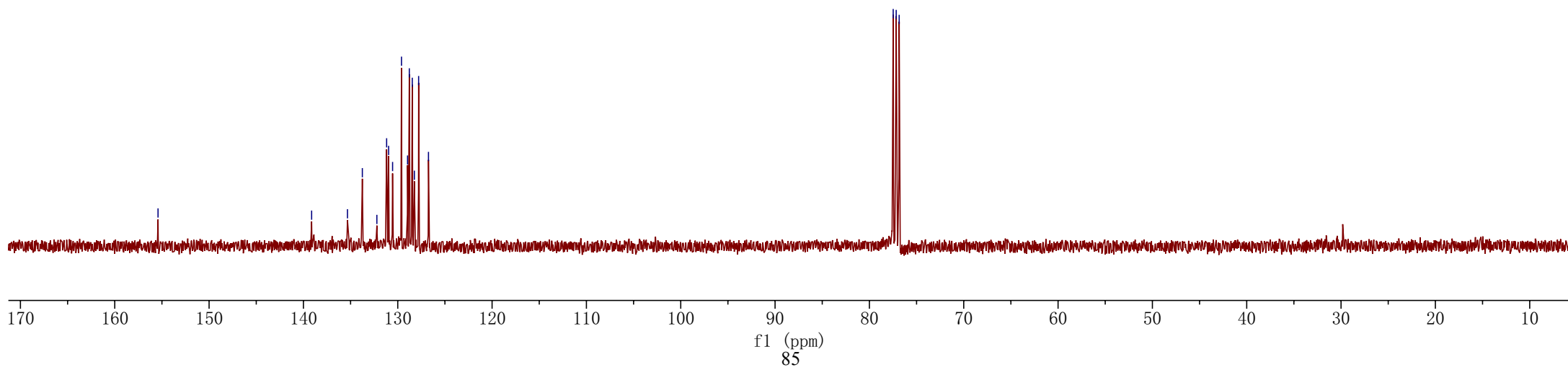
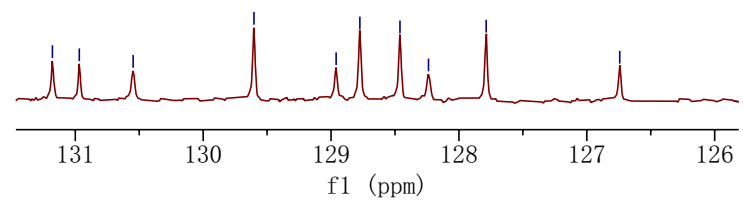
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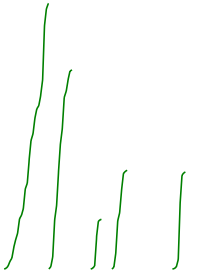
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128.46
128.24
127.79
126.74

77.48
77.16
76.84

131.18
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130.55
129.60
128.96
128.77
128.46
128.24
127.79
126.74



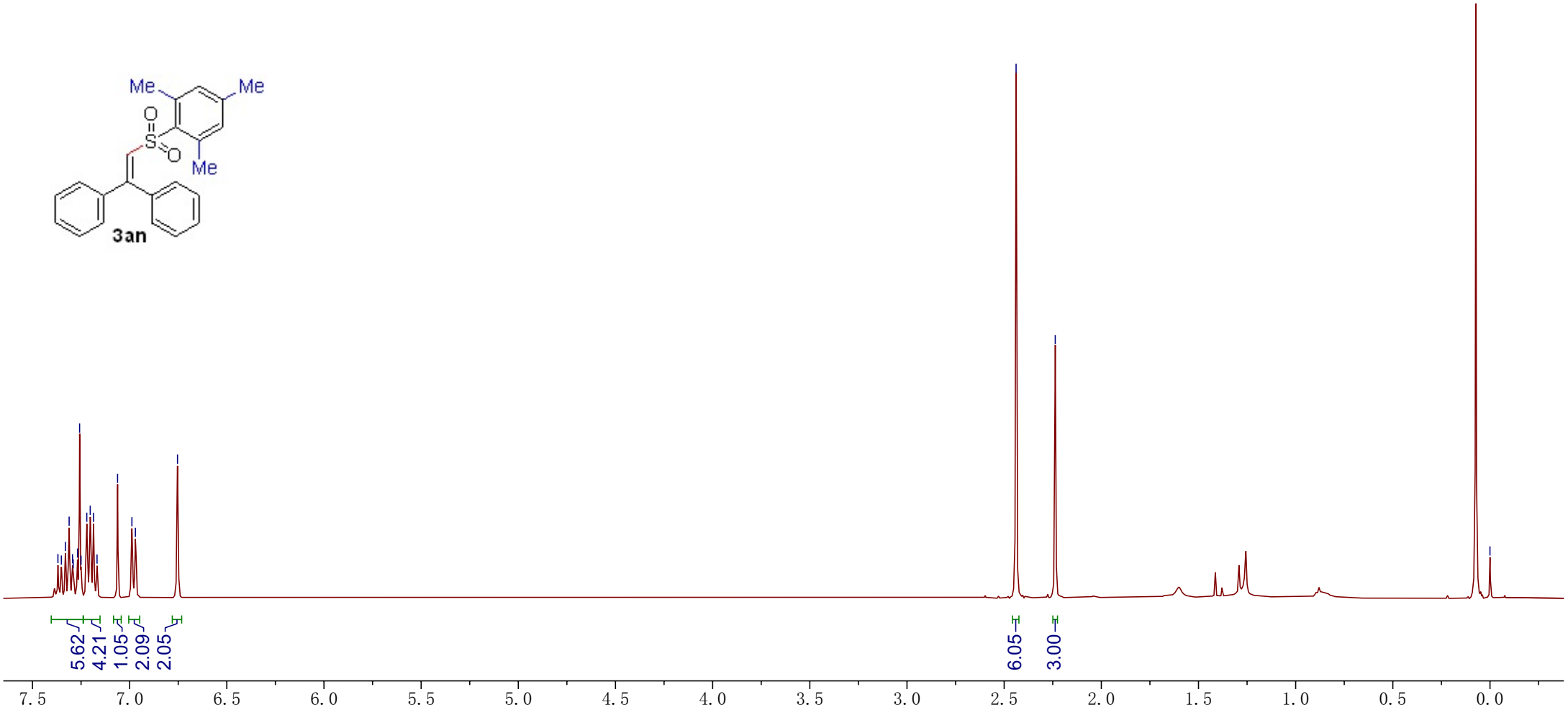
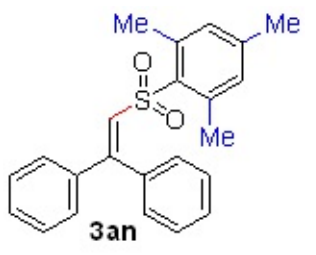
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7.35
7.33
7.31
7.29
7.29
7.27
7.26
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7.22
7.20
7.19
7.17
7.06
6.99
6.97
6.75



-2.44

-2.24

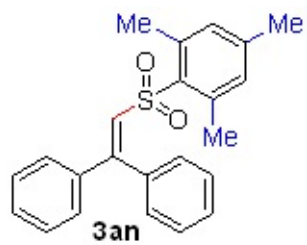
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2.09
2.05

6.05

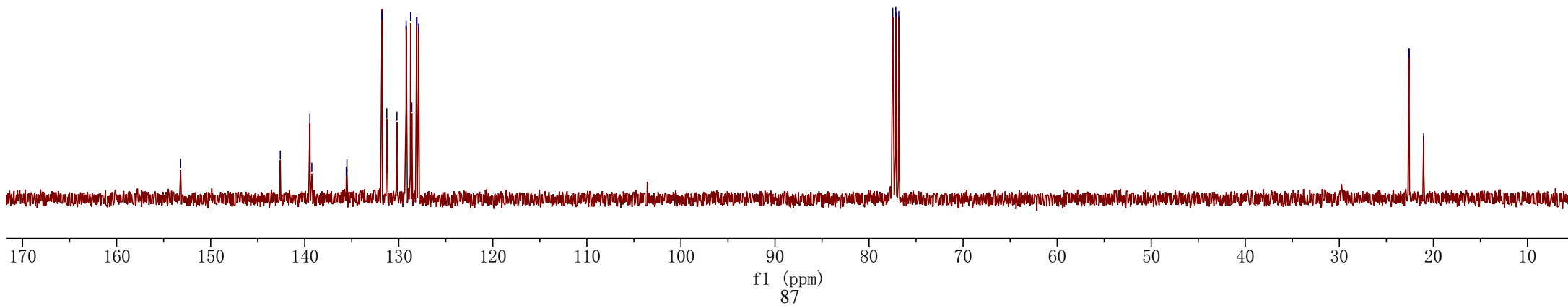
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153.19
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139.45
139.25
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131.77
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128.09
127.89

77.48
77.16
76.84

22.60
21.03



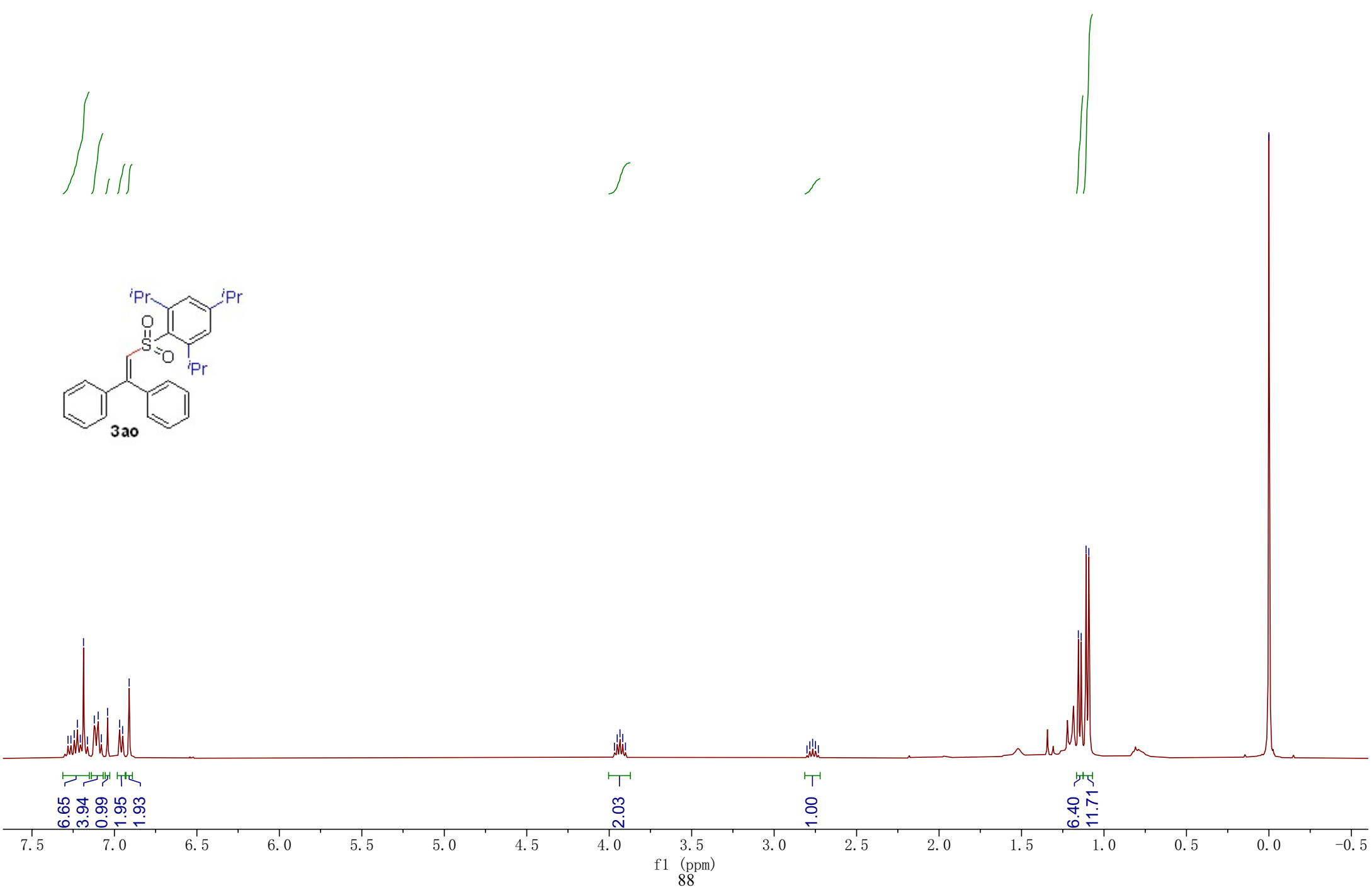
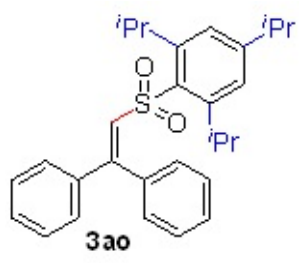
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7.24
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7.21
7.19
7.16
7.12
7.10
7.08
7.04
6.97
6.95
6.91

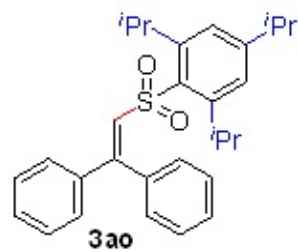
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3.95
3.93
3.92
3.90

2.80
2.78
2.77
2.75
2.73

1.16
1.14
1.11
1.09

-0.00





— 153.21
— 150.37
139.61
132.86
130.04
129.60
128.72
128.58
128.09
127.85
— 123.26

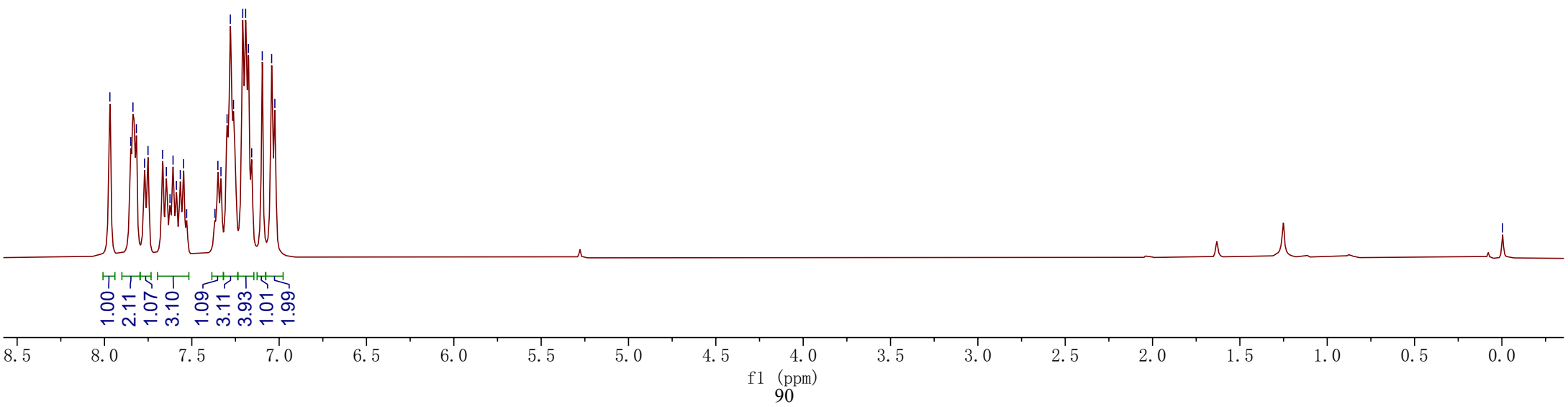
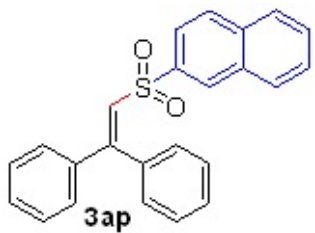
77.48
77.16
76.84

— 34.41
— 29.88
24.93
23.78

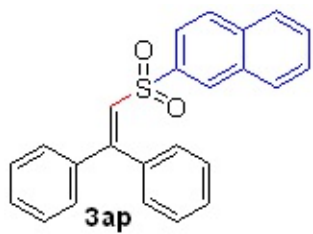
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f1 (ppm)
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7.85
7.84
7.82
7.77
7.75
7.67
7.65
7.62
7.61
7.59
7.57
7.55
7.53
7.37
7.35
7.33
7.30
7.28
7.26
7.21
7.19
7.18
7.16
7.10
7.04
7.02



— 0.00



155.46
139.08
138.04
135.34
134.91
131.97
130.46
129.81
129.74
129.45
129.10
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129.03
128.84
128.68
128.29
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127.82
127.39
122.61

77.48
77.16
76.84

130.46
129.81
129.74
129.45
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129.07
129.03
128.84
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127.87
127.82
127.39

