

TBAI-catalyzed selective synthesis of sulfonamides and β -aryl sulfonyl Enamines: coupling of arenesulfonyl chlorides and sodium sulfinates with *tert*-amines

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Contents of Supporting Information:

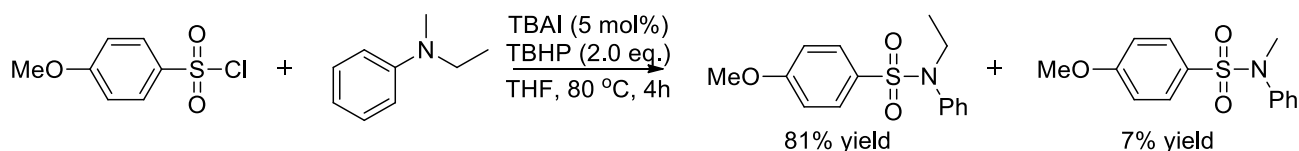
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1. General Information

All reactions were carried out in anhydrous solvent using commercially available reagents that were purchased and used as received. Analytical thin layer chromatography (TLC) was performed on pre-coated 0.25 mm thick silica gel 60-F₂₅₄ plates (*Merck* or *Whatman PE SIL G/UV*); visualized using UV light and by treatment with a KMnO₄, followed by heating. All compounds were purified by flash chromatography using silica gel 100-200 (Greagent G72651J) and gave spectroscopic data consistent with being $\geq 95\%$ the assigned structure. ¹H NMR and ¹³C NMR spectra were recorded on a *Bruker Avance 400* spectrometer in CDCl₃ at ambient temperature; chemical shifts (δ) are given in ppm and calibrated using the signal of residual undeuterated solvent as internal reference ($\delta_{\text{H}} = 7.26$ ppm and $\delta_{\text{C}} = 77.16$ ppm). IR spectra were recorded on an Agilent Technologies Cary 630 FT-IR (ATR) or Perkin-Elmer FT-IR Spectrum 100 (ATR) spectrometer; wavenumbers (ν) are given in cm⁻¹.

The reaction of *N*-methyl-*N*-ethyl aniline with 4-methoxybenzenesulfonyl chloride

Using *N*-methyl-*N*-ethyl aniline as the substrate, we examined the regioselectivity and generality of this reaction. As shown in Scheme S1, the reaction of 4-methoxybenzenesulfonyl chloride with *N*-methyl-*N*-ethyl aniline gave a mixture of sulfonamides in THF.



Scheme S1, The reaction of 4-methoxybenzenesulfonyl chloride with *N*-methyl-*N*-ethyl aniline

2. Spectral Data for the Spectral Data for the sulfonamides 3a-r and 4a-h



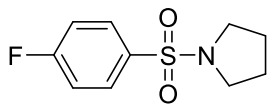
Color and State: Yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, $J = 8.0$ Hz, 2H), 7.60 (d, $J = 8.0$ Hz, 1H), 7.54 (t, $J = 8.0$ Hz, 2H), 3.24 (t, $J = 8.0$ Hz, 4H), 1.74 (t, $J = 4.0$ Hz, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 136.7, 132.6, 129.0, 127.3, 47.9, 25.1.

IR (Neat): 3055, 2850, 1311, 1149, 720 cm⁻¹

MS: m/z C₁₀H₁₃NO₂S 211.3 (M⁺)



1-((4-fluorophenyl)sulfonyl)pyrrolidine (3b)^b

Color and State: White solid. m.p. 67-68 °C

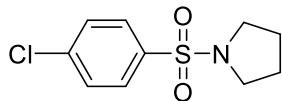
¹H NMR (400 MHz, CDCl₃) δ 7.79-7.76 (m, 2H), 7.14 (t, *J* = 8.0 Hz, 2H), 3.15 (t, *J* = 8.0 Hz, 4H), 1.78 (t, *J* = 4.0 Hz, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 166.3, 163.8, 133.1, 133.0, 130.1, 130.0, 116.3, 116.1, 47.9, 25.2.

¹⁹F NMR (376 MHz, CDCl₃) δ -105.6.

IR (Neat): 2963, 2858, 1347, 1159, 1112, 721 cm⁻¹

MS: m/z C₁₀H₁₂FNO₂S 229.3 (M⁺)



1-((4-chlorophenyl)sulfonyl)pyrrolidine (3c)^c

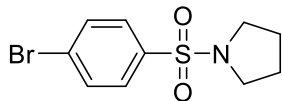
Color and State: Brown solid. m.p. 78-79 °C

¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 3.15 (t, *J* = 4.0 Hz, 4H), 1.69 (s, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 138.9, 135.4, 129.3, 128.8, 47.9, 25.2.

IR (Neat): 2977, 2865, 1454, 1350, 1161, 720 cm⁻¹

MS: m/z C₁₀H₁₂ClNO₂S 245.7 (M⁺)



1-((4-bromophenyl)sulfonyl)pyrrolidine (3d)^c

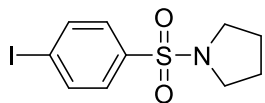
Color and State: White solid. m.p. 102-104 °C

¹H NMR (400 MHz, CDCl₃) δ 7.63-7.58 (m, 4H), 3.15 (t, *J* = 8.0 Hz, 4H), 1.70 (d, *J* = 4.0 Hz, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 136.0, 132.3, 128.9, 127.5, 47.9, 25.2.

IR (Neat): 2982, 1448, 1334, 1162, 761 cm⁻¹

MS: m/z C₁₀H₁₂BrNO₂S 290.2 (M⁺)



1-((4-iodophenyl)sulfonyl)pyrrolidine (3e)^d

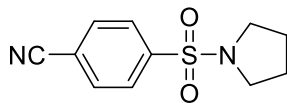
Color and State: Yellow solid. m.p. 141-143 °C

¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 4.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 3.15 (t, *J* = 8.0 Hz, 4H), 1.69 (d, *J* = 8.0 Hz, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 138.2, 136.6, 128.8, 99.9, 47.9, 25.2.

IR (Neat): 2954, 2856, 1472, 13647, 1165, 728 cm⁻¹

MS: m/z C₁₀H₁₂INO₂S 337.2 (M⁺)



4-(pyrrolidin-1-ylsulfonyl)benzonitrile (3f)

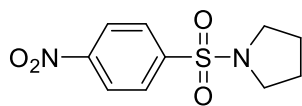
Color and State: White solid. m.p. 111-113 °C

¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 3.28 (s, 4H), 1.8 (d, *J* = 2.0 Hz, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 141.2, 132.9, 127.9, 117.4, 116.1, 48.0, 25.2.

IR (Neat): 2953, 2862, 1488, 1456, 1165, 845 cm⁻¹

HRMS(ESI):Cald for C₁₁H₁₃N₂O₂S[MH]⁺:m/z 237.0692; found: 237.0688.



1-((4-nitrophenyl)sulfonyl)pyrrolidine (3g)^e

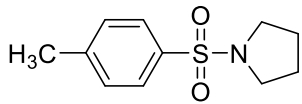
Color and State: White solid. m.p. 131-132 °C

¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, *J* = 12.0 Hz, 2H), 8.04 (d, *J* = 8.0 Hz, 2H), 3.30 (t, *J* = 8.0 Hz, 4H), 1.83 (t, *J* = 8.0 Hz, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 150.1, 143.1, 128.6, 124.4, 48.1, 25.4.

IR (Neat): 2974, 2936, 1600, 1518, 1465, 1349, 1152, 771 cm⁻¹

MS: m/z C₁₀H₁₂N₂O₄S 256.3 (M⁺)



1-tosylpyrrolidine (3h)^a

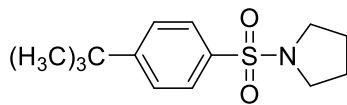
Color and State: White solid. m.p. 133-134 °C

¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.22 (t, *J* = 8.0 Hz, 4H), 2.43 (s, 3H), 1.75 (d, *J* = 4.0 Hz, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 143.3, 133.8, 129.6, 127.5, 47.9, 25.1, 21.4.

IR (Neat): 3010, 2845, 1456, 1327, 729 cm⁻¹

MS: m/z C₁₁H₁₅NO₂S 225.3 (M⁺)



1-((4-(tert-butyl)phenyl)sulfonyl)pyrrolidine (3i)^f

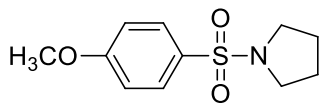
Color and State: White solid. m.p. 138-139 °C

¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 4.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 3.25 (s, 4H), 1.76 (d, *J* = 1.6 Hz, 4H), 1.35 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 156.2, 133.8, 127.4, 126.0, 47.9, 35.1, 31.1, 25.2.

IR (Neat): 3010, 2838, 1448, 1325, 725 cm⁻¹

MS: m/z C₁₄H₂₁NO₂S 267.4 (M⁺)



1-((4-methoxyphenyl)sulfonyl)pyrrolidine (3j)^a

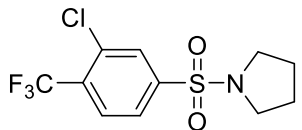
Color and State: White solid. m.p. 165-166 °C

¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 3H), 3.21 (s, 4H), 1.74 (d, *J* = 1.6 Hz, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 162.8, 129.4, 128.2, 114.1, 55.5, 47.8, 25.0.

IR (Neat): 2975, 2853, 1454, 1347, 1162, 719 cm⁻¹

MS: m/z C₁₁H₁₅NO₃S 241.3 (M⁺)



1-((3-chloro-4-(trifluoromethyl)phenyl)sulfonyl)pyrrolidine (3k)

Color and State: Yellow solid. m.p. 87-89 °C

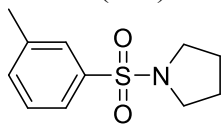
¹H NMR (400 MHz, CDCl₃) δ 8.14 (s, 1H), 1.95 (d, *J* = 8.0 Hz, 1H), 1.71 (d, *J* = 12.0 Hz, 1H), 3.17 (t, *J* = 8.0 Hz, 4H), 1.85 (d, *J* = 4.0 Hz, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 137.1, 136.8, 132.5, 131.6, 129.6, 129.3, 126.7, 126.7, 126.6, 126.6, 123.5, 120.8, 48.1, 25.4.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.0.

IR (Neat): 2929, 1405, 1323, 1134, 711 cm^{-1}

HRMS(ESI):Cald for $\text{C}_{11}\text{H}_{12}\text{ClF}_3\text{NO}_2\text{S}[\text{MH}]^+$:m/z 314.0224; found: 314.0222.



1-(m-tolylsulfonyl)pyrrolidine (3l)

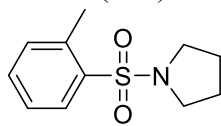
Color and State: Brown solid. m.p. 134-135 $^{\circ}\text{C}$

^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 12.0 Hz, 2H), 3.24 (s, 4H), 2.43 (s, 3H), 1.75 (s, 4H).

^{13}C NMR (101 MHz, CDCl_3) δ 139.14, 136.55, 133.42, 128.87, 127.79, 124.58, 47.92, 25.18, 21.37.

IR (Neat): 2971, 2852, 1451, 1346, 1165, 721 cm^{-1}

HRMS(ESI):Cald for $\text{C}_{11}\text{H}_{16}\text{NO}_2\text{S}[\text{MH}]^+$:m/z 226.0896; found: 226.0892.



1-(o-tolylsulfonyl)pyrrolidine (3m)

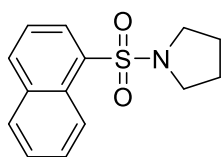
Color and State: Yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, J = 8.0 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.31 (t, J = 4.0 Hz, 2H), 3.30 (t, J = 4.0 Hz, 4H), 2.64 (s, 3H), 1.89 (m, 4H).

^{13}C NMR (101 MHz, CDCl_3) δ 137.8, 137.0, 132.6, 129.4, 127.5, 126.0, 47.3, 25.5, 20.6.

IR (Neat): 2980, 2857, 1455, 1346, 723 cm^{-1}

MS: m/z $\text{C}_{11}\text{H}_{15}\text{NO}_2\text{S}$ 225.3 (M⁺)



1-(naphthalen-1-ylsulfonyl)pyrrolidine (3n)^g

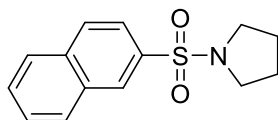
Color and State: White solid. m.p. 79-81 $^{\circ}\text{C}$

^1H NMR (400 MHz, CDCl_3) δ 8.73 (d, J = 12.0 Hz, 1H), 8.09 (d, J = 4.0 Hz, 1H), 1.90 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.51 (t, J = 8.0 Hz, 1H), 7.45-7.37 (m, 2H), 3.21 (t, J = 8.0 Hz, 4H), 1.65 (t, J = 4.0 Hz, 4H).

^{13}C NMR (101 MHz, CDCl_3) δ 134.3, 134.1, 133.8, 129.5, 129.0, 128.8, 127.9, 126.7, 125.2, 124.1, 47.5, 25.4.

IR (Neat): 2970, 2864, 1367, 1151, 726 cm^{-1}

MS: m/z $\text{C}_{14}\text{H}_{15}\text{NO}_2\text{S}$ 261.3 (M⁺)



1-(naphthalen-2-ylsulfonyl)pyrrolidine (3o)^g

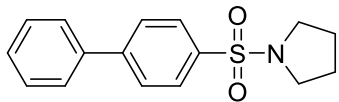
Color and State: White solid. m.p. 106-107 $^{\circ}\text{C}$

^1H NMR (400 MHz, CDCl_3) δ 8.41 (s, 1H), 7.97 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.64-7.58 (m, 2H), 3.30 (s, 4H), 1.71 (s, 4H).

^{13}C NMR (101 MHz, CDCl_3) δ 134.69, 133.85, 132.07, 129.19, 129.09, 128.60, 128.58, 127.82, 127.44, 122.83, 47.96, 25.16.

IR (Neat): 2955, 2860, 1367, 1150, 723 cm^{-1}

MS: m/z $\text{C}_{14}\text{H}_{15}\text{NO}_2\text{S}$ 261.3 (M⁺)



1-([1,1'-biphenyl]-4-ylsulfonyl)pyrrolidine (3p)

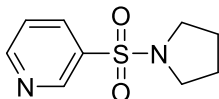
Color and State: White solid. m.p. 139-141 °C

¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 3.27 (t, *J* = 8.0 Hz, 4H), 1.75 (t, *J* = 8.0 Hz, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 145.3, 139.1, 135.4, 129.0, 128.4, 128.0, 127.5, 127.2, 47.9, 25.2.

IR (Neat): 2955, 2846, 1355, 1156, 760 cm⁻¹

HRMS(ESI):Cald for C₁₆H₁₈NO₂S[MH]⁺:m/z 288.1053; found: 288.1048.



3-(pyrrolidin-1-ylsulfonyl)pyridine (3q)^h

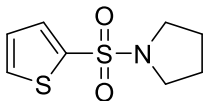
Color and State: Yellow solid. m.p. 75-76 °C

¹H NMR (400 MHz, CDCl₃) δ 8.97 (s, 1H), 8.76 (d, *J* = 4.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 3.20 (t, *J* = 8.0 Hz, 4H), 1.72 (s, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 153.06, 147.86, 134.92, 133.60, 123.78, 47.84, 25.13.

IR (Neat): 3052, 2976, 2839, 1426, 1151, 746 cm⁻¹

MS: m/z C₉H₁₂N₂O₂S 212.3 (M⁺)



1-(thiophen-2-ylsulfonyl)pyrrolidine (3r)

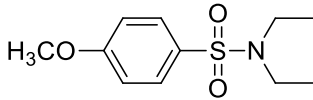
Color and State: Brown solid. m.p. 75-77 °C

¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 4.0 Hz, 1H), 7.59 (d, *J* = 4.0 Hz, 1H), 7.16 (t, *J* = 4.0 Hz, 1H), 3.29 (t, *J* = 8.0 Hz, 4H), 1.77 (t, *J* = 8.0 Hz, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 136.6, 132.0, 131.7, 127.5, 48.2, 25.2.

IR (Neat): 3114, 1964, 1334, 1150 1017, 742 cm⁻¹

HRMS(ESI):Cald for C₈H₁₂NO₂S₂[MH]⁺:m/z 218.0304; found: 218.0300.



***N,N*-diethyl-4-methoxybenzenesulfonamide (4a)^j**

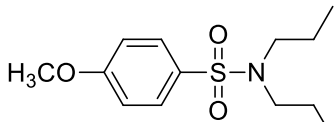
Color and State: Yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 3.86 (s, 3H), 3.24-3.19 (m, 4H), 1.12 (t, *J* = 8.0 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 162.7, 132.1, 129.2, 114.2, 55.7, 42.0, 14.2.

IR (Neat): 2978, 2942, 1498, 1324, 1156, 736 cm⁻¹

MS: m/z C₁₁H₁₇NO₃S 243.3 (M⁺)



4-methoxy-*N,N*-dipropylbenzenesulfonamide (4b)

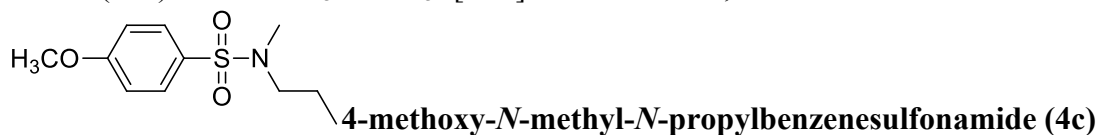
Color and State: Yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 3.86 (s, 3H), 3.05 (t, *J* = 8.0 Hz, 4H), 1.57-1.52 (m, 4H), 0.87 (t, *J* = 8.0 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 162.6, 131.7, 129.1, 114.1, 50.0, 32.9, 22.0, 11.2.

IR (Neat): 2980, 2942, 1495, 1340, 1156, 736 cm⁻¹

HRMS(ESI): Calcd for $C_{13}H_{22}NO_3S[MH]^+$: m/z 272.1315; found: 272.1311.



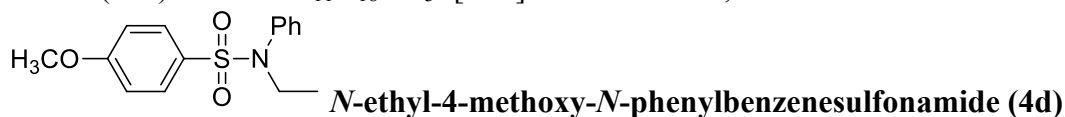
Color and State: Yellow oil.

1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, $J = 8.0$ Hz, 2H), 6.90 (d, $J = 8.0$ Hz, 2H), 3.76 (s, 3H), 2.84 (t, $J = 8.0$ Hz, 2H), 2.59 (s, 3H), 1.49-1.40 (m, 2H), 0.82 (t, $J = 4.0$ Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 129.3, 129.1, 114.1, 55.5, 51.7, 34.5, 20.8, 11.0.

IR (Neat): 2984, 2940, 1498, 1145, 737 cm^{-1}

HRMS(ESI): Calcd for $C_{11}H_{18}NO_3S[MH]^+$: m/z 244.1002; found: 244.1002.



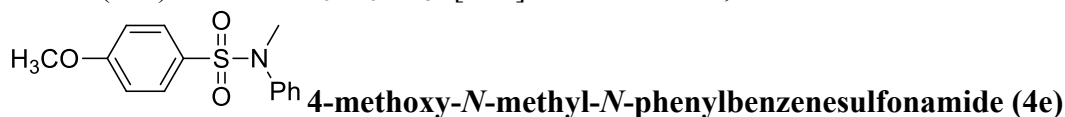
Color and State: Brown oil.

1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 4.0$ Hz, 3H), 7.05 (d, $J = 8.0$ Hz, 2H), 6.91 (d, $J = 8.0$ Hz, 2H), 3.86 (s, 3H), 3.62-3.57 (m, 2H), 1.07 (t, $J = 8.0$ Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 139.1, 130.3, 129.9, 129.1, 129.1, 127.9, 114.0, 55.7, 45.6, 14.1.

IR (Neat): 3025, 1446, 1341, 1166, 741 cm^{-1}

HRMS(ESI): Calcd for $C_{15}H_{18}NO_3S[MH]^+$: m/z 292.1002; found: 292.1000.



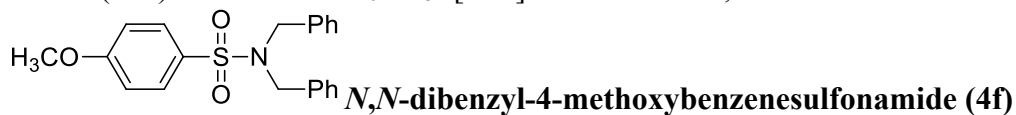
Color and State: Brown oil.

1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, $J = 8.0$ Hz, 2H), 7.24-7.16 (m, 3H), 7.03 (d, $J = 8.0$ Hz, 2H), 6.83 (d, $J = 8.0$ Hz, 2H), 3.78 (s, 3H), 3.08 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 141.8, 130.1, 128.9, 128.3, 127.4, 126.8, 114.0, 55.7, 38.2.

IR (Neat): 3020, 1449, 1340, 1162, 732 cm^{-1}

HRMS(ESI): Calcd for $C_{14}H_{16}NO_3S[MH]^+$: m/z 278.0845; found: 278.0840.



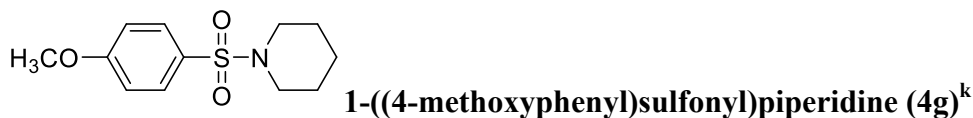
Color and State: Yellow solid. m.p. 63-65 $^{\circ}C$

1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, $J = 8.0$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 1H), 7.27 (d, $J = 8.0$ Hz, 1H), 7.23 (d, $J = 8.0$ Hz, 1H), 7.13 (s, 3H), 6.99 (s, 4H), 6.89 (d, $J = 8.0$ Hz, 2H), 4.23 (s, 4H), 3.80 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 135.9, 132.5, 129.4, 128.7, 128.5, 127.7, 114.3, 55.8, 50.6.

IR (Neat): 2994, 1456, 1346, 1166, 723 cm^{-1}

MS: m/z $C_{21}H_{21}NO_3S$ 367.5 (M⁺)



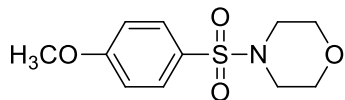
Color and State: Brown solid. m.p. 105-108 $^{\circ}C$

¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 3H), 2.95 (t, *J* = 4.0 Hz, 4H), 1.63 (t, *J* = 4.0 Hz, 4H), 1.42 (d, *J* = 4.0 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 162.8, 129.6, 127.6, 114.1, 55.6, 46.9, 25.1, 23.4.

IR (Neat): 3055, 2855, 1440, 1320, 1050, 763 cm⁻¹

MS: *m/z* C₁₂H₁₇NO₃S 255.3 (M⁺)



4-((4-methoxyphenyl)sulfonyl)morpholine (4h)^k

Color and State: Brown solid. m.p. 155-156 °C

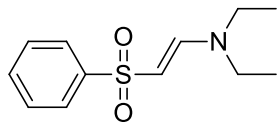
¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 3.88 (s, 3H), 3.73 (s, 4H), 2.97 (s, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 163.2, 129.9, 126.4, 114.3, 66.0, 55.6, 46.0.

IR (Neat): 2921, 2856, 1449, 1350, 1169, 935 cm⁻¹

MS: *m/z* C₁₁H₁₅NO₄S 257.3 (M⁺)

3. Spectral Data for the β-aryl sulfonyl Enamines 5a-o



(E)-N,N-diethyl-2-(phenylsulfonyl)ethenamine (5a)^j

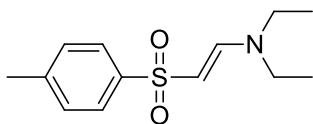
Color and State: white solid. m.p. 45-46 °C

¹H NMR (400 MHz, CDCl₃) δ 7.86-7.85 (m, 2H), 7.47-7.46 (m, 3H), 7.32 (d, *J* = 12.6 Hz, 1H), 4.91 (d, *J* = 12.6 Hz, 1H), 3.24 (broad doublet, 4H), 1.15 (bs, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 149.2, 145.4, 131.6, 128.9, 126.2, 91.3, 50.2, 42.5, 14.6, 11.2.

IR (Neat): 3069, 2977, 2936, 2875, 1614, 1452, 1468 cm⁻¹

MS: *m/z* C₁₂H₁₇NO₂S 239.3 (M⁺)



(E)-N,N-diethyl-2-tosylethen-1-amine (5b)^j

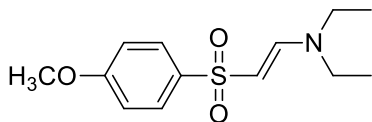
Color and State: Brown oil.

¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.20-7.16 (m, 3H), 4.82 (d, *J* = 12.7 Hz, 1H), 3.08 (broad doublet, 4H), 2.31 (s, 3H), 1.06 (bs, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 148.8, 142.6, 142.1, 129.5, 126.2, 91.8, 50.0, 42.6, 21.5, 14.6, 11.5.

IR (Neat): 3076, 2977, 2935, 2876, 1617, 1493, 1450 cm⁻¹

MS: *m/z* C₁₃H₁₉NO₂S 253.4 (M⁺)



(E)-N,N-diethyl-2-((4-methoxyphenyl)sulfonyl)ethen-1-amine (5c)^j

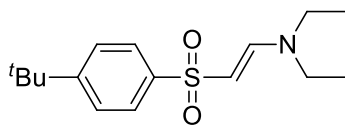
Color and State: Brown oil.

¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 12.7 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.93 (d, *J* = 12.7 Hz, 1H), 3.88 (s, 3H), 3.17 (broad doublet, 4H), 1.18 (bs, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 162.1, 148.6, 137.4, 128.3, 114.0, 92.1, 55.6, 50.1, 42.8, 14.8, 13.8.

IR (Neat): 3069, 2975, 2934, 2872, 1612, 1495, 1460 cm⁻¹

MS: m/z C₁₃H₁₉NO₃S 269.4 (M⁺)



(E)-2-((4-(tert-butyl)phenyl)sulfonyl)-N,N-diethylethen-1-amine (5d)^j

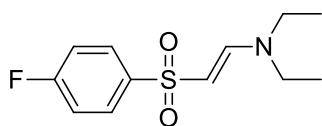
Color and State: Brown oil.

¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 12.7 Hz, 1H), 4.84 (d, *J* = 12.7 Hz, 1H), 3.11 (broad doublet, 4H), 1.26 (s, 9H), 1.08 (bs, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 155.2, 148.9, 142.4, 126.1, 125.9, 91.7, 50.0, 42.8, 35.1, 31.3, 14.8, 11.3.

IR (Neat): 3077, 2982, 2932, 2870, 1613, 1494, 1456 cm⁻¹

MS: m/z C₁₆H₂₅NO₂S 295.4 (M⁺)



(E)-N,N-diethyl-2-((4-fluorophenyl)sulfonyl)ethen-1-amine (5e)^j

Color and State: Brown oil.

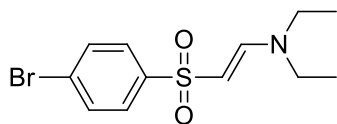
¹H NMR (400 MHz, CDCl₃) δ 7.79-7.76 (dd, *J* = 8.0 Hz, *J* = 4.0 Hz, 2H), 7.24 (d, *J* = 12.6 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 2H), 4.81 (d, *J* = 12.6 Hz, 1H), 3.10 (broad doublet, 4H), 1.13 (bs, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 165.7, 163.2, 149.2, 141.6, 128.2, 128.7, 116.0, 115.8, 91.1, 49.9, 43.0, 14.7, 11.0.

¹⁹F NMR (376 MHz, CDCl₃) δ -107.7.

IR (Neat): 3073, 2979, 2934, 2881, 1615, 1493, 1469 cm⁻¹

MS: m/z C₁₂H₁₆FNO₂S 257.3 (M⁺)



(E)-2-((4-bromophenyl)sulfonyl)-N,N-diethylethen-1-amine (5f)^j

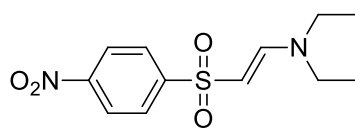
Color and State: Brown solid. m.p. 75-76 °C

¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 12.7 Hz, 1H), 4.80 (d, *J* = 12.7 Hz, 1H), 3.18 (broad doublet, 4H), 1.12 (bs, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 149.4, 144.6, 132.1, 127.9, 126.2, 90.9, 50.2, 42.8, 14.8, 11.2.

IR (Neat): 3069, 2969, 2920, 2850, 1610, 1569 cm⁻¹

MS: m/z C₁₂H₁₆BrNO₂S 318.2 (M⁺)



(E)-N,N-diethyl-2-((4-nitrophenyl)sulfonyl)ethen-1-amine (5g)^l

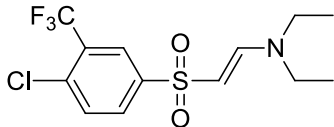
Color and State: Yellow solid. m.p. 111-112 °C

¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 8.0 Hz, 2H), 7.95, (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 12.7 Hz, 1H), 4.82 (d, *J* = 12.7 Hz, 1H), 3.15 (broad doublet, 4H), 1.13 (bs, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 151.4, 150.4, 149.4, 127.4, 124.3, 89.8, 50.5, 43.0, 14.8, 11.2.

IR (Neat): 3364, 2920, 1535, 1348, 1147 cm⁻¹

MS: *m/z* C₁₂H₁₆N₂O₄S 284.3 (M⁺)



(E)-2-((4-chloro-3-(trifluoromethyl)phenyl)sulfonyl)-N,N-

diethylethen-1-amine (5h)

Color and State: Brown solid. m.p. 90-91 °C

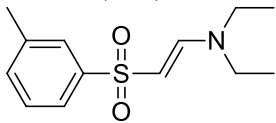
¹H NMR (400 MHz, CDCl₃) δ 8.09 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.54-7.51 (m, 1H), 7.25 (d, *J* = 12.6 Hz, 1H), 4.80 (d, *J* = 12.6 Hz, 1H), 3.14 (broad doublet, 4H), 1.10 (bs, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 150.1, 144.9, 132.2, 130.5, 125.8, 125.7, 123.7, 121.0, 90.0, 50.4, 43.0, 14.8, 11.2.

¹⁹F NMR (376 MHz, CDCl₃) δ -62.9.

IR (Neat): 3064, 2976, 2935, 2872, 1615, 1468 cm⁻¹

HRMS(ESI): Calcd for C₁₃H₁₆ClF₃NO₃S[MH]⁺: *m/z* 342.0537; found: 342.0532.



(E)-N,N-diethyl-2-(m-tolylsulfonyl)ethen-1-amine (5i)^j

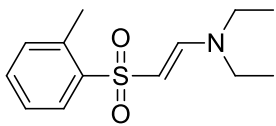
Color and State: Brown oil.

¹H NMR (400 MHz, CDCl₃) δ 7.70-7.63 (m, 2H), 7.36-7.29 (m, 3H), 4.90 (d, *J* = 12.7 Hz, 1H), 3.18 (broad doublet, 4H), 2.40 (s, 3H), 1.14 (bs, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 149.0, 145.2, 139.0, 132.4, 128.8, 126.6, 123.3, 91.5, 50.2, 42.7, 21.5, 15.0, 11.1.

IR (Neat): 3080, 2935, 2876, 1615, 1490, 1455 cm⁻¹

MS: *m/z* C₁₃H₁₉NO₂S 253.4 (M⁺)



(E)-N,N-diethyl-2-(o-tolylsulfonyl)ethen-1-amine (5j)^j

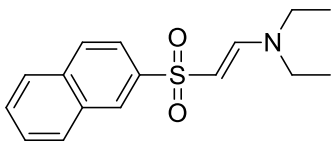
Color and State: Brown oil.

¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.41-7.37 (m, 1H), 7.31-7.25 (m, 3H), 4.92 (d, *J* = 12.7 Hz, 1H), 4.18 (broad doublet, 4H), 2.62 (s, 3H), 1.16 (bs, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 149.6, 142.8, 132.3, 131.9, 129.5, 127.8, 126.2, 90.6, 50.1, 42.9, 20.3, 14.9, 11.2.

IR (Neat): 3066, 2976, 2922, 2871, 1613, 1493, 1468 cm⁻¹

MS: *m/z* C₁₃H₁₉NO₂S 253.4 (M⁺)



(E)-N,N-diethyl-2-(naphthalen-2-ylsulfonyl)ethen-1-amine (5k)

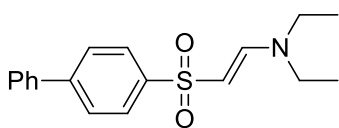
Color and State: Yellow solid. m.p. 124-125 °C

¹H NMR (400 MHz, CDCl₃) δ 8.35 (s, 1H), 7.85-7.82 (m, 2H), 7.80-7.73 (m, 2H), 7.53-7.45 (m, 2H), 7.29 (d, *J* = 12.7 Hz, 1H), 4.89 (d, *J* = 12.7 Hz, 1H), 3.11 (broad doublet, 4H), 1.07 (bs, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 149.2, 142.3, 134.5, 132.5, 129.3, 129.2, 128.3, 127.9, 127.3, 126.6, 122.5, 50.2, 42.8, 14.9, 11.2.

IR (Neat): 3070, 2975, 2930, 2872, 1612, 1495, 1465 cm⁻¹

HRMS(ESI): Calcd for C₁₆H₂₀NO₂S[MH]⁺: m/z 290.1209; found: 290.1205.



(E)-2-([1,1'-biphenyl]-4-ylsulfonyl)-N,N-diethylethen-1-amine (5l)

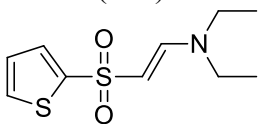
Color and State: Yellow solid. m.p. 102-104 °C

¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 12.7 Hz, 1H), 4.88 (d, *J* = 12.7 Hz, 1H), 3.11 (broad doublet, 4H), 1.09 (bs, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 149.2, 144.5, 144.1, 139.9, 129.1, 128.3, 127.6, 127.4, 126.8, 91.6, 50.2, 42.8, 14.9, 11.3.

IR (Neat): 3071, 2976, 2922, 2871, 1613, 1493, 1468 cm⁻¹

HRMS(ESI): Calcd for C₁₈H₂₁NO₂S[MH]⁺: m/z 316.1366; found: 316.1362.



(E)-N,N-diethyl-2-(thiophen-2-ylsulfonyl)ethen-1-amine (5m)^m

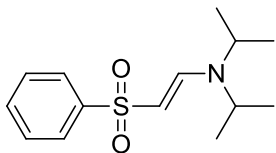
Color and State: Brown oil

¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 4.0 Hz, 1H), 7.41 (d, *J* = 4.0 Hz, 1H), 7.27 (d, *J* = 12.6 Hz, 1H), 6.94 (t, *J* = 4.0 Hz, 1H), 4.96 (d, *J* = 12.6 Hz, 1H), 3.12 (broad doublet, 4H), 1.10 (bs, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 149.3, 148.3, 130.6, 130.0, 127.2, 92.5, 50.2, 43.0, 14.9, 11.3.

IR (Neat): 3078, 2976, 2934, 2875, 1613, 1507 cm⁻¹

MS: m/z C₁₀H₁₅NO₂S₂ 245.4 (M⁺)



(E)-N-isopropyl-N-(2-(phenylsulfonyl)vinyl)propan-2-amine (5n)^l

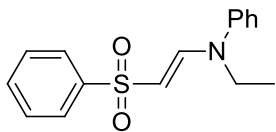
Color and State: Brown oil.

¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.40-7.38 (m, 3H), 7.33 (d, *J* = 12.8 Hz, 1H), 4.90 (d, *J* = 12.8 Hz, 1H), 3.53 (broad doublet, 2H), 1.14 (bs, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 145.6, 145.4, 131.5, 128.9, 126.2, 92.4, 49.4, 47.7, 23.6, 19.8.

IR (Neat): 3074, 2976, 2925, 2869, 1607, 1542 cm⁻¹

MS: m/z C₁₄H₂₁NO₂S 267.4 (M⁺)



(E)-N-ethyl-N-(2-(phenylsulfonyl)vinyl)aniline (5o)

Color and State: Brown oil.

¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 12.2 Hz, 1H), 7.53-7.46 (m, 3H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.27 (d, *J* = 12.2 Hz, 1H), 3.67-3.61 (m, 2H), 1.20 (t, *J* = 8.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 144.5, 132.0, 129.8, 129.7, 129.0, 127.0, 126.4, 125.8, 124.3, 97.5, 40.2, 13.1.

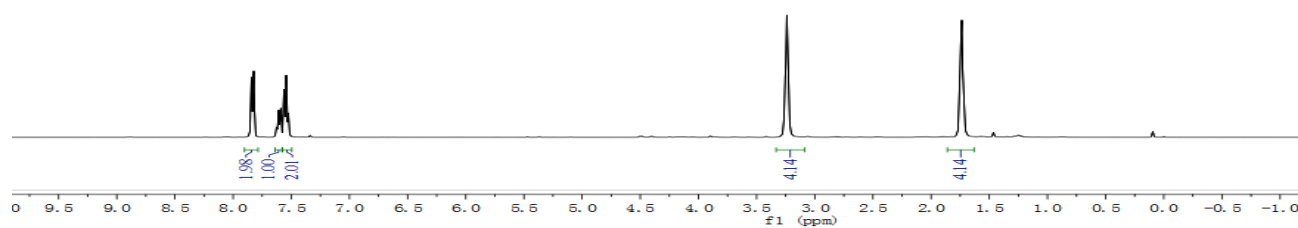
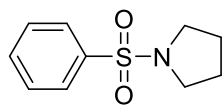
IR (Neat): 3068, 2970, 2903, 2852, 1610, 1492, 1467 cm⁻¹

HRMS(ESI): Calcd for C₁₆H₁₈NO₂S[MH]⁺: m/z 288.1053; found: 288.1051.

4. References

- (a) S. Yotphan, L. Sumunnee, D. Beukeaw, C. Buathongjan, V. Reutrakul, *Org. Biomol. Chem.* **2016**, *14*, 590; (b) M. K. Narayanam, G. Ma, P. A. Champagne, K. N. Houk, J. M. Murphy, *Angew. Chem. Int. Ed.* **2017**, *56*, 13006; (c) X. Tang, L. Huang, C. Qi, W. Wu, H. Jiang, *Chem. Commun.* **2013**, *49*, 6102; (d) G. Cheng, S. Muench, Y. Zhou, G. A. Afanador, E. J. Mui, A. Fomovska, B. S. Lai, S. T. Prigge, C. W. Roberts, M. R. Hickman, P. J. Lee, S. E. Leed, J. M. Auschwitz, D. W. Rice, R. Meleod, *Bio. Med. Chem. Lett.* **2013**, *23*, 2035; (e) T.-Y. Xu, S.-L. Zhang, G.-Q. Dong, X.-Z. Liu, X. Wang, X.-Q. Lv, Q.-J. Qian, R.-Y. Zhang, C.-Q. Sheng, C.-Y. Miao, *Scientific Reports*, **2015**, *5*, 10043; (f) H. Zhu, Y. Shen, Q. Deng, C. Huang, T. Tu, *Chem. Asian J.* **2017**, *12*, 706; (g) V. Hojat, *Bulletin Korean Chem. Society*, **2012**, *33*, 383; (h) H. Wollven, C. González-Rodríguez, I. Marco, A. L. Thompson, M. C. Wills, *Org. Lett.* **2011**, *13*, 4876; (j) J. Lai, L. Chang, G. Yuan, *Org. Lett.* **2016**, *18*, 3194; (k) S. K. R. Parumala, R. K. Peddinti, *Tetrahedron Lett.* **2016**, *57*, 1232; (l) Y. Cai, R. Zhang, D. Sun, S. Xu, Q. Zhou, *Synlett*, **2017**, *28*, 1630; (m) M. Chen, Z.-T. Huang, Q.-Y. Zheng, *Org. Biomol. Chem.* **2014**, *12*, 9337.

5. Proton and Carbon NMR Spectra

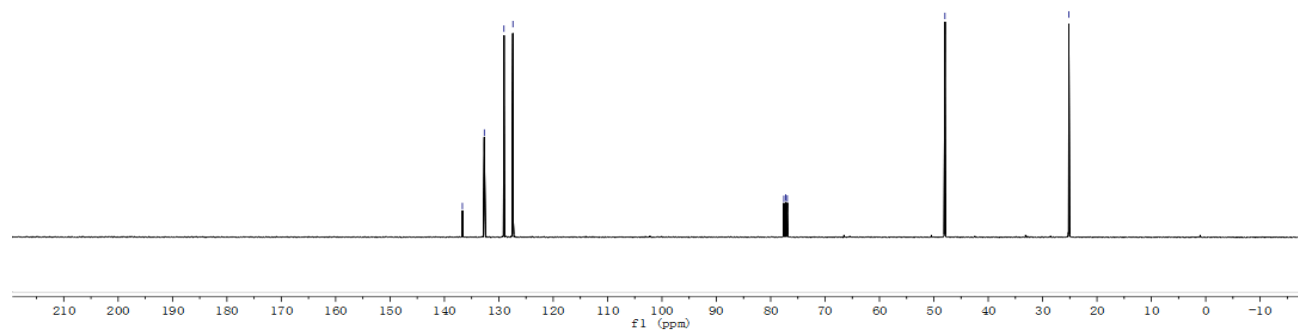
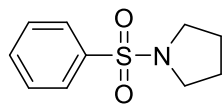


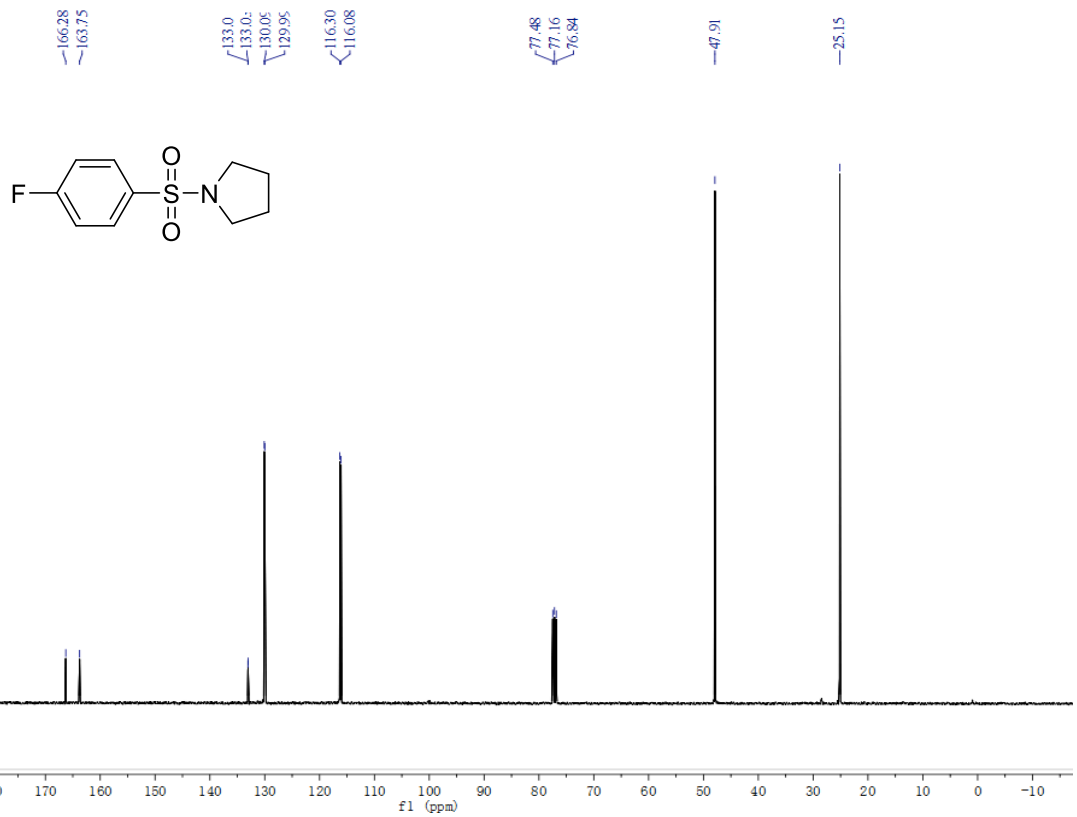
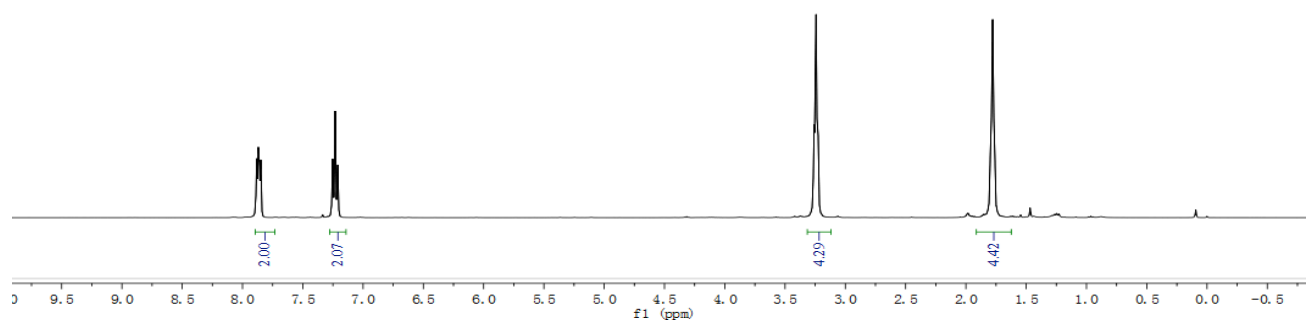
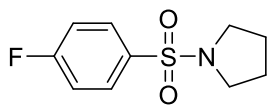
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127.40

77.59
77.27
76.95

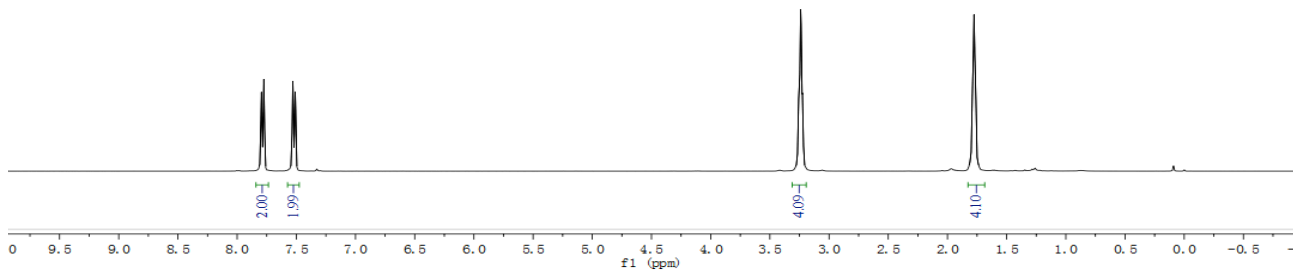
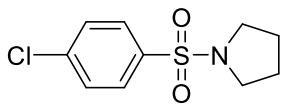
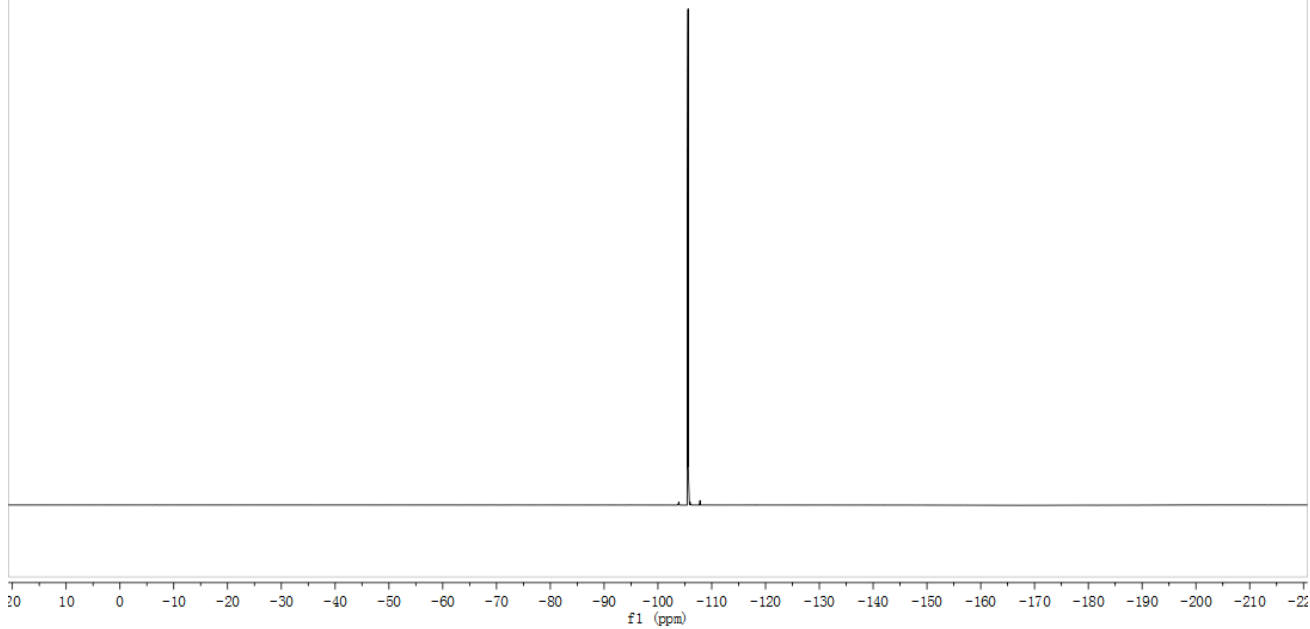
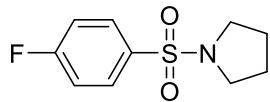
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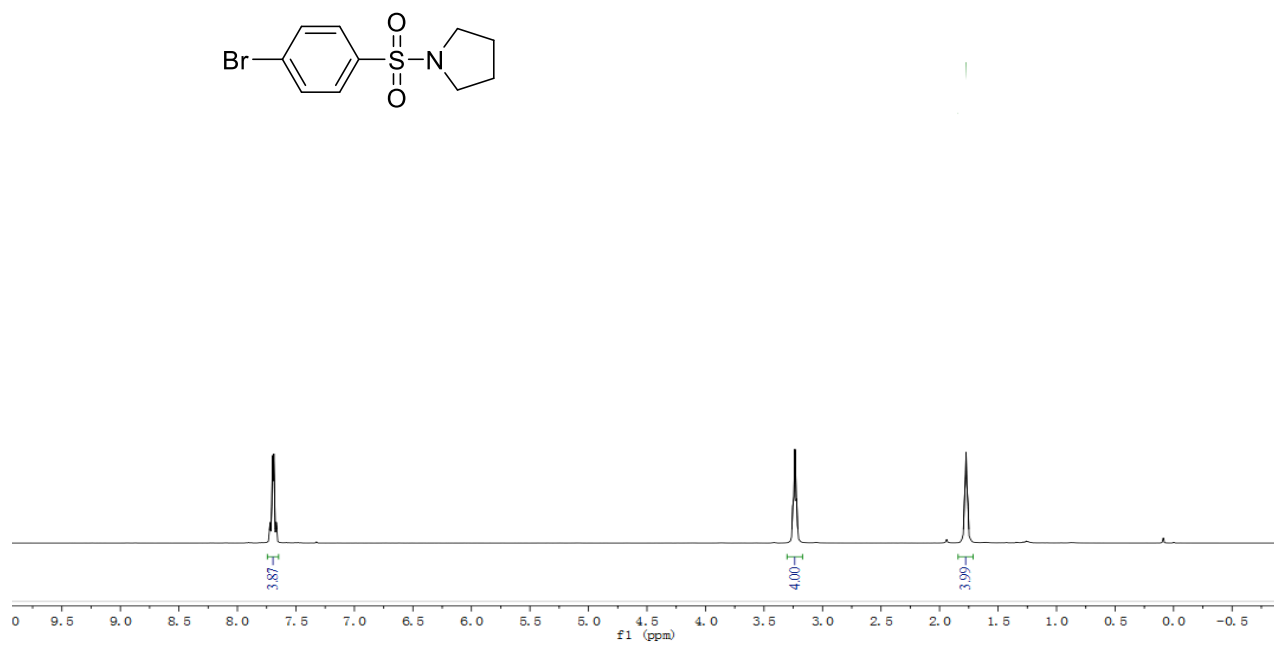
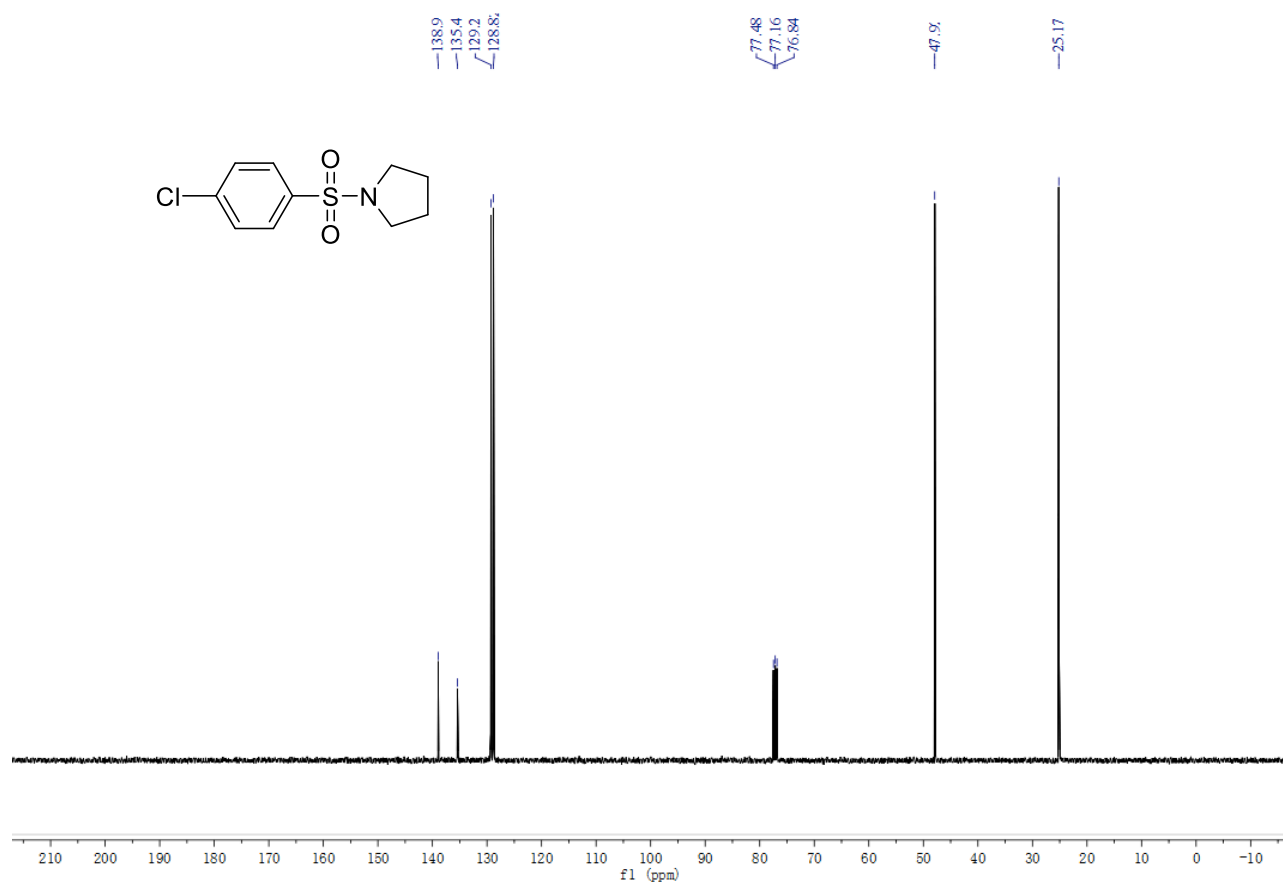
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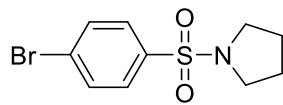




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19F





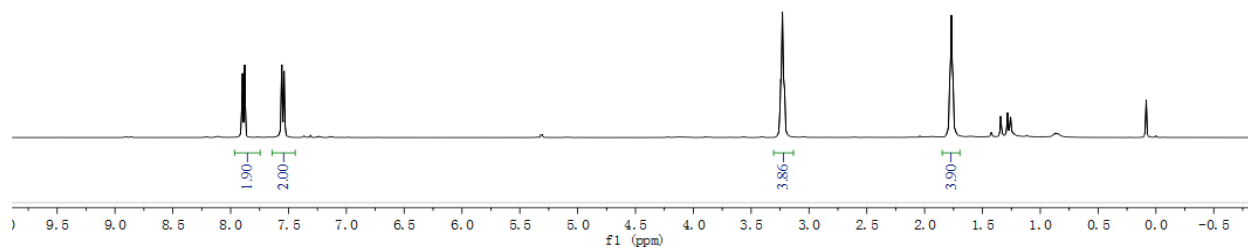
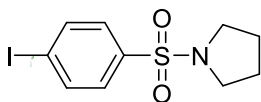
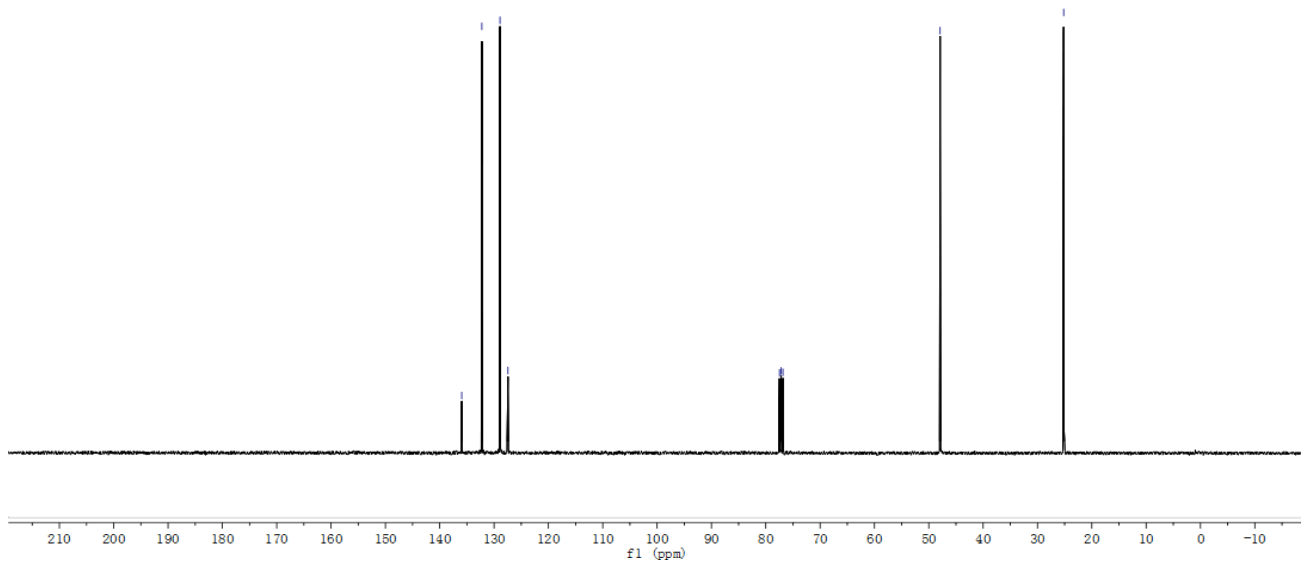


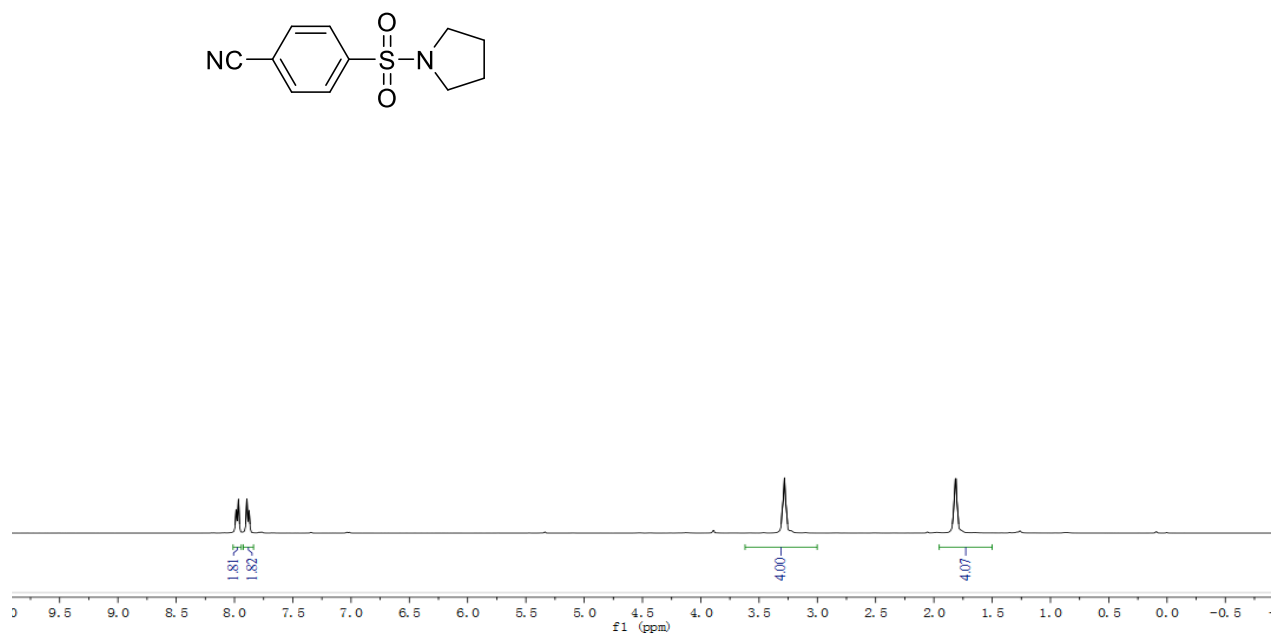
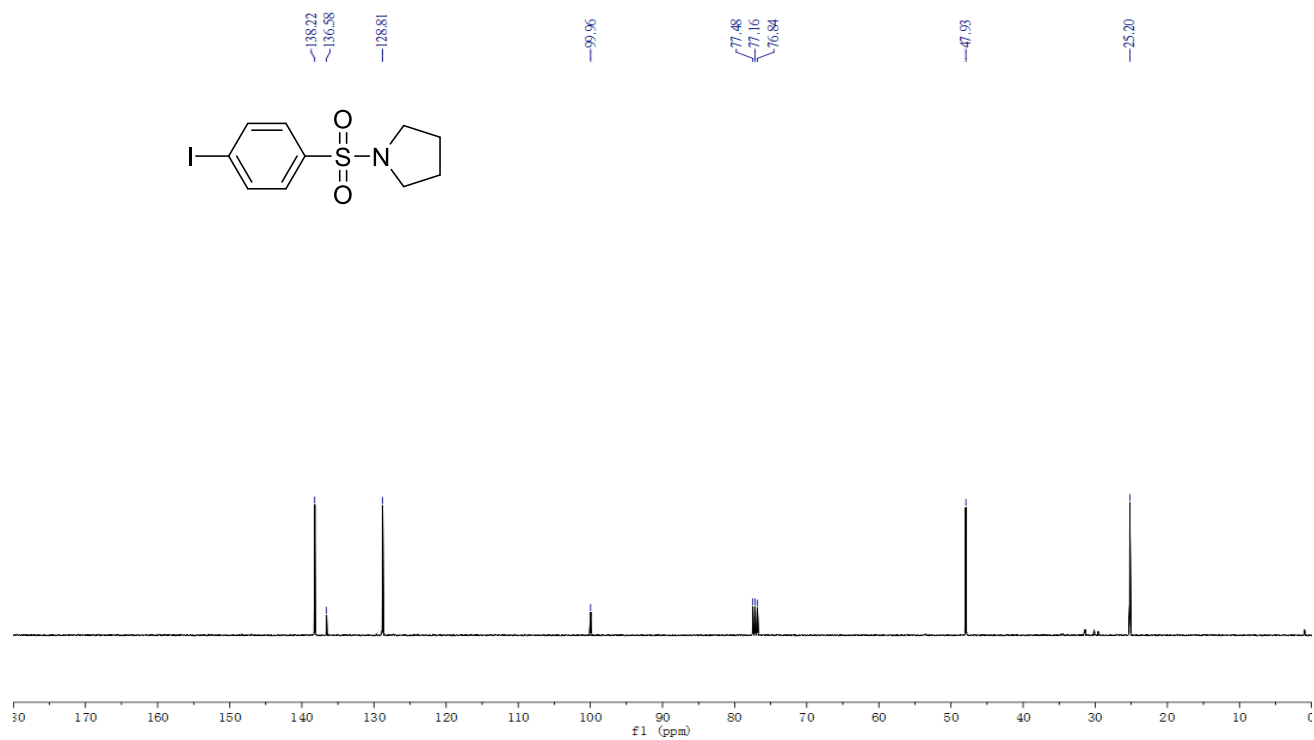
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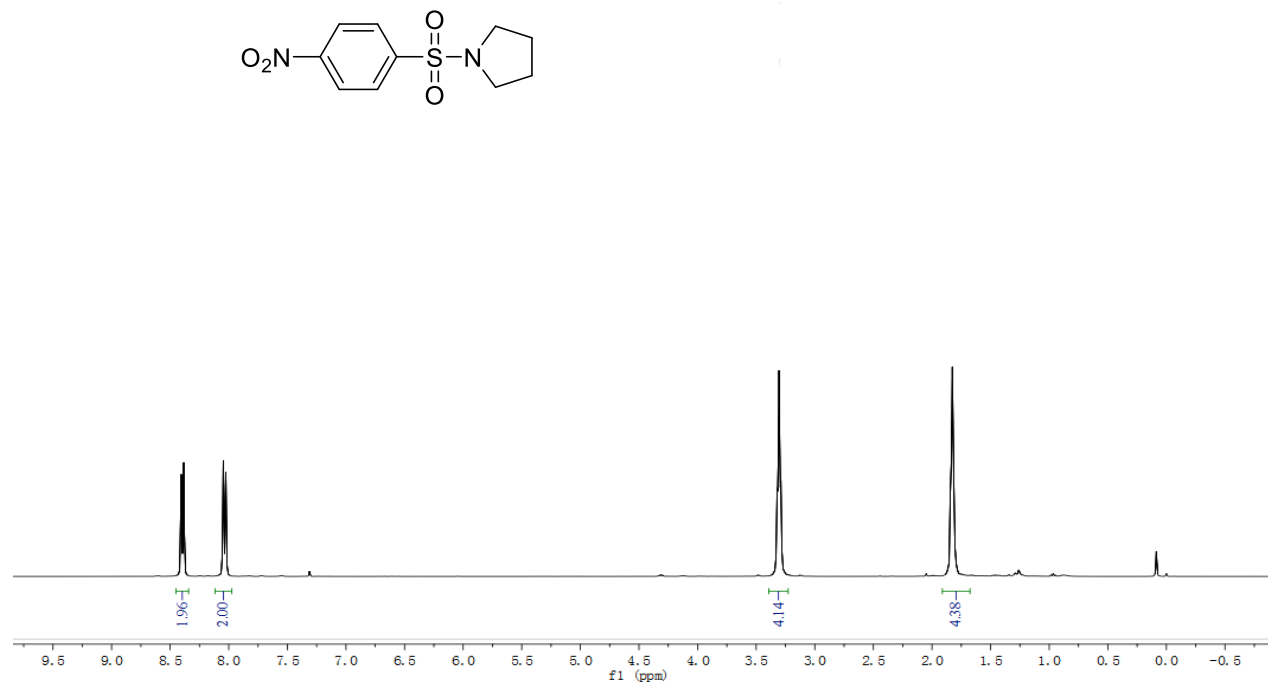
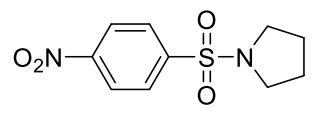
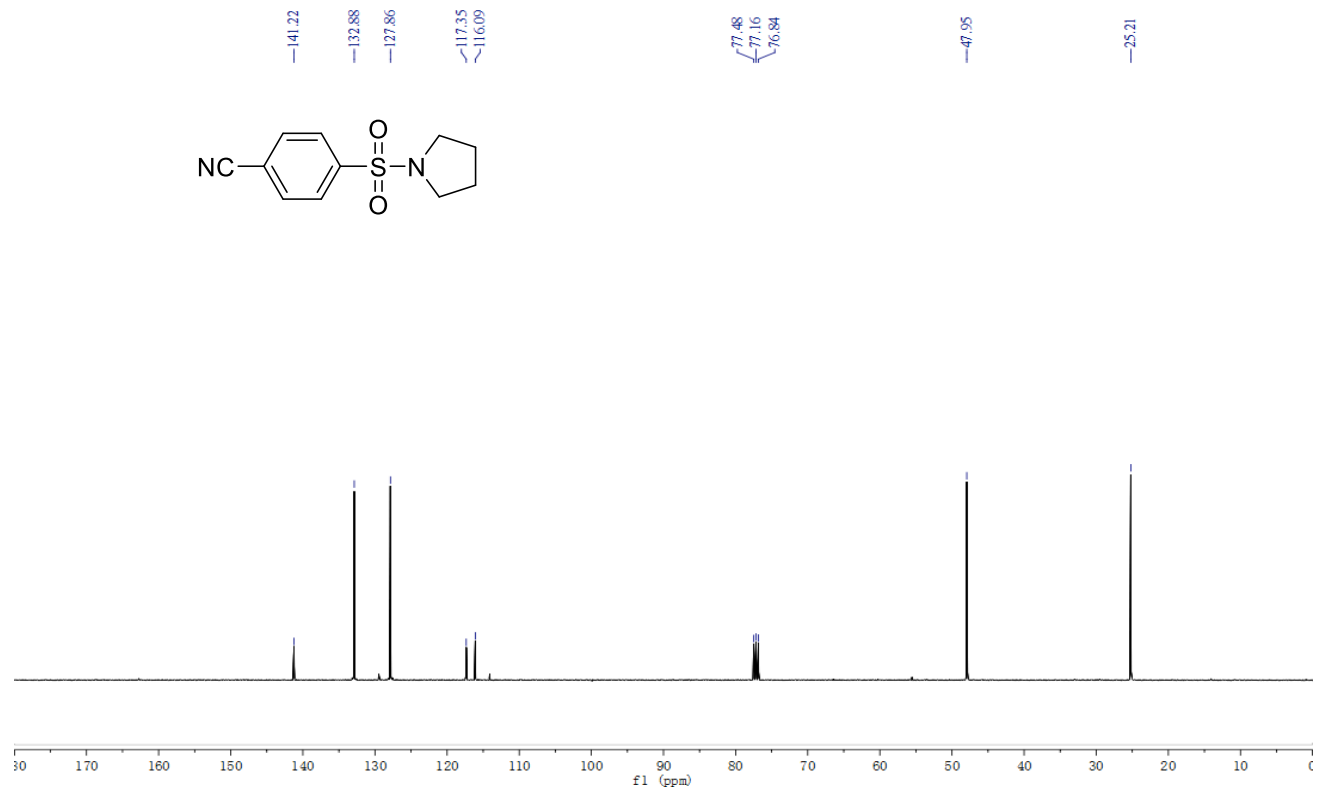
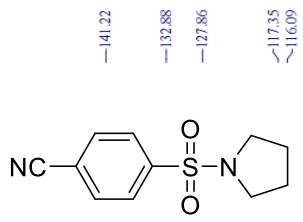
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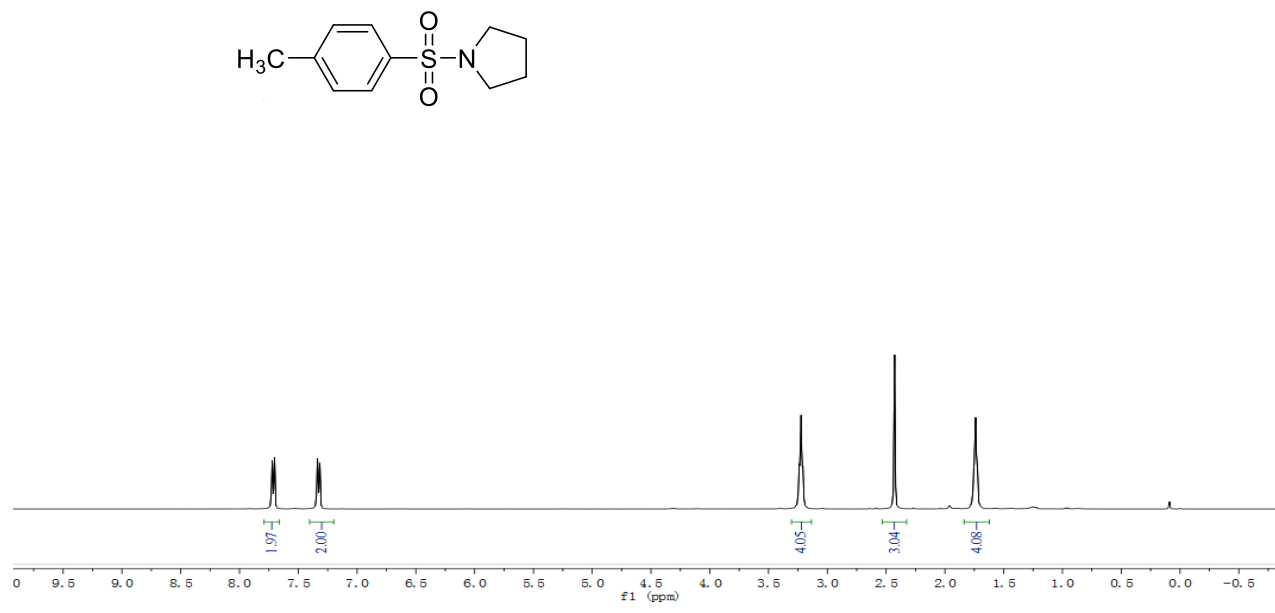
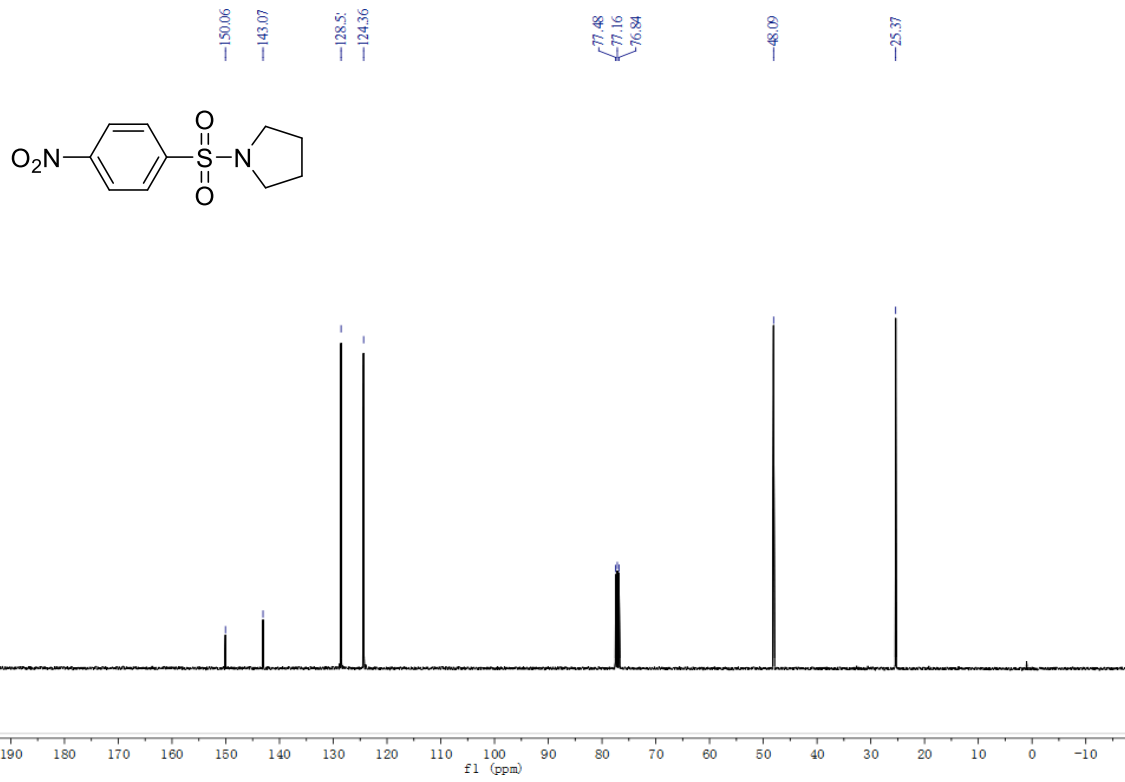
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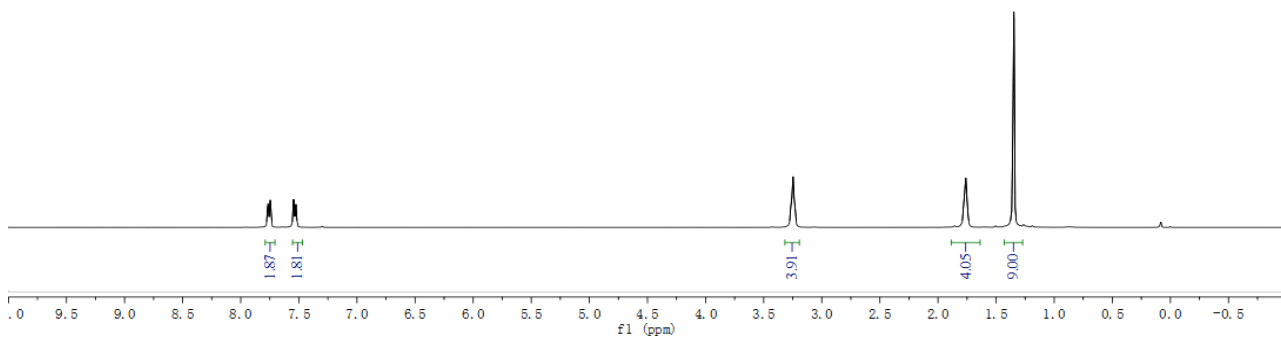
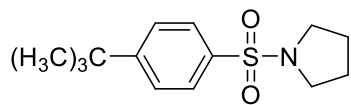
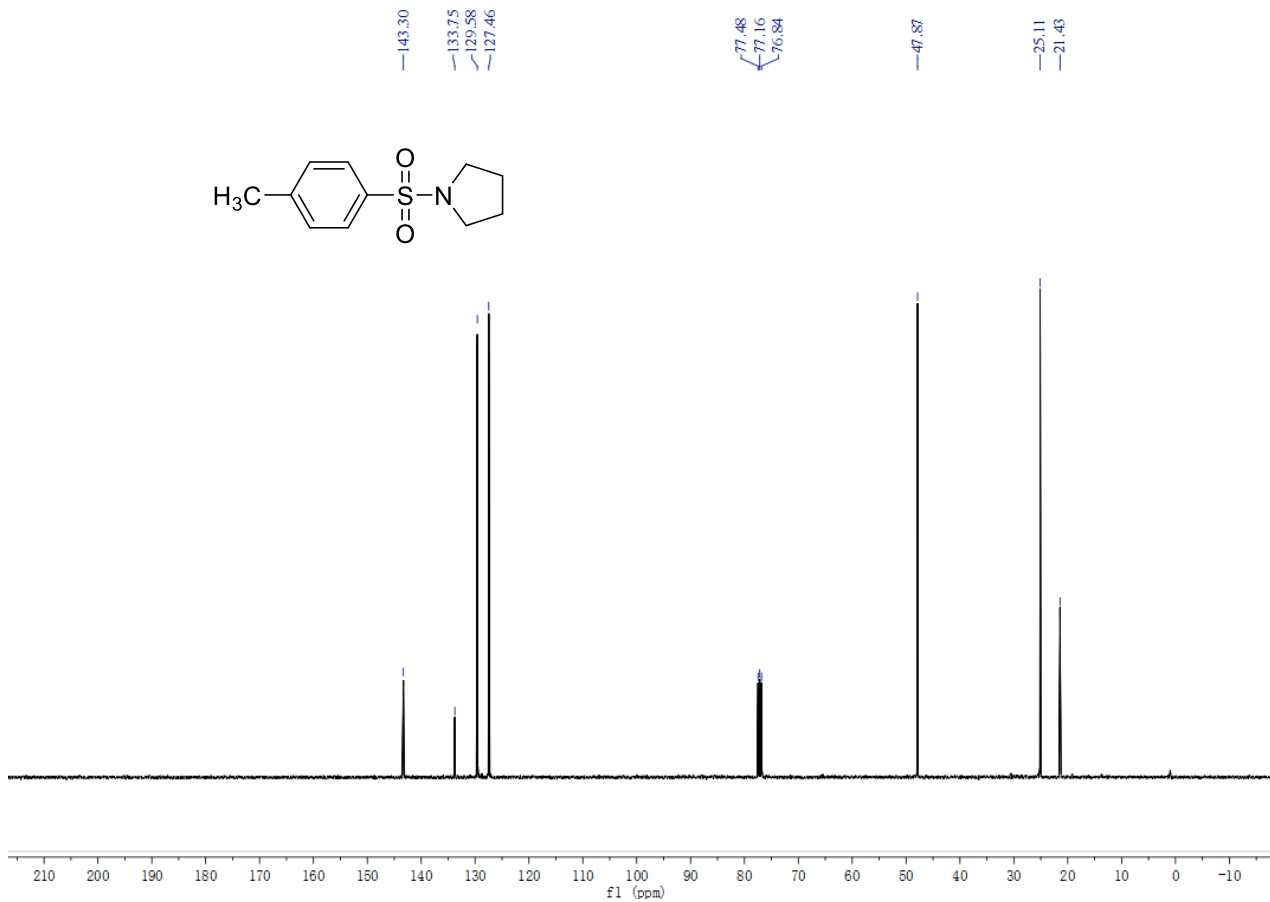
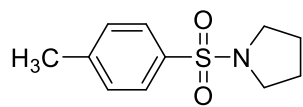
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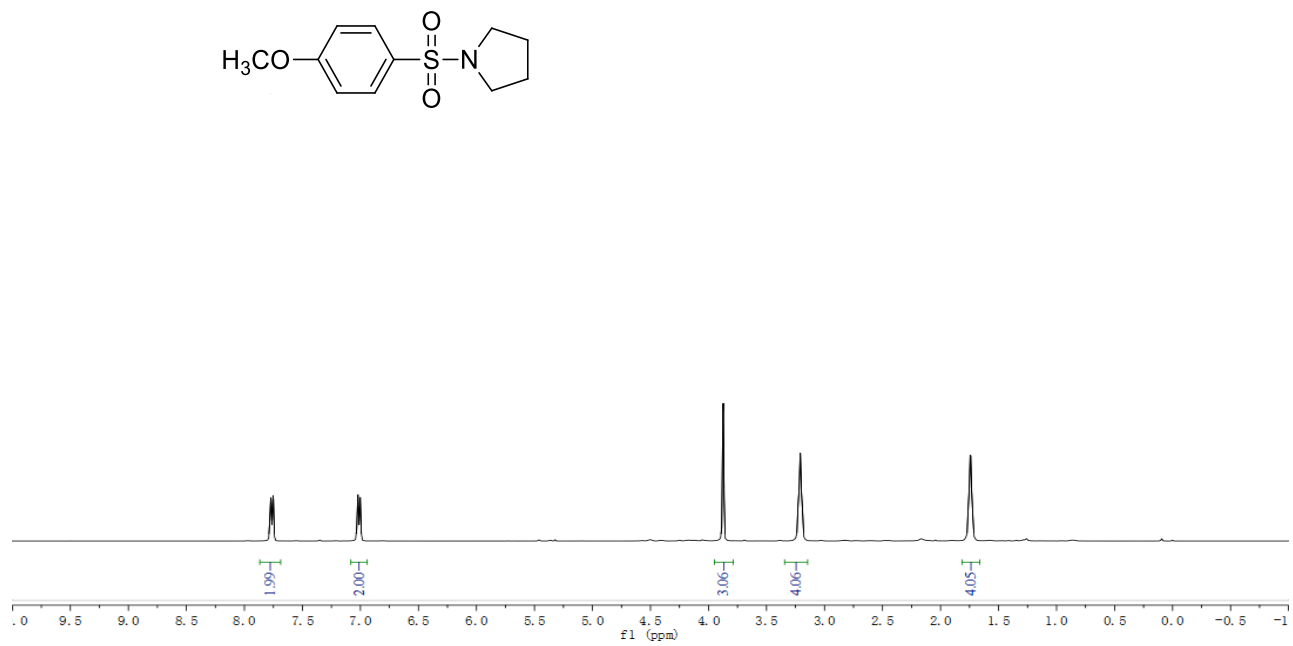
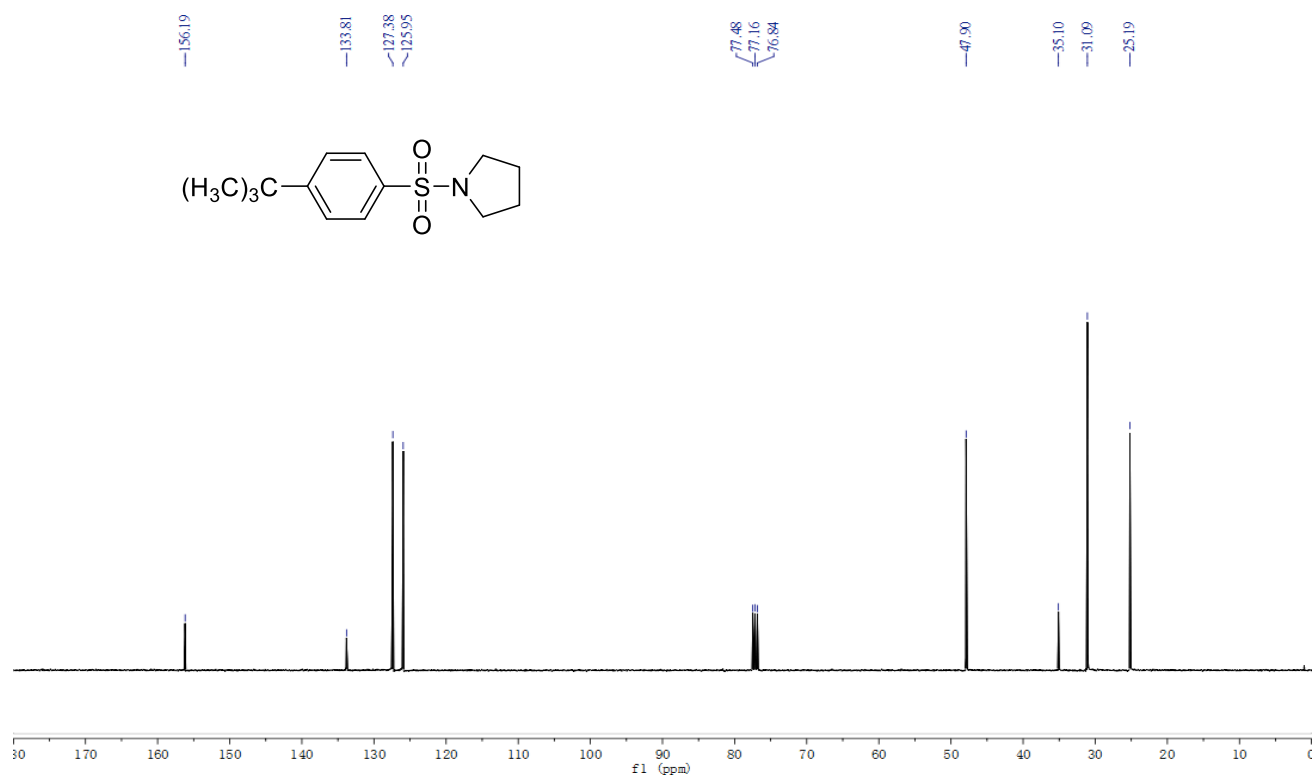


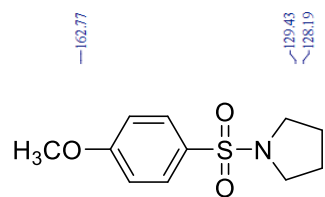












162.77

129.43
128.19

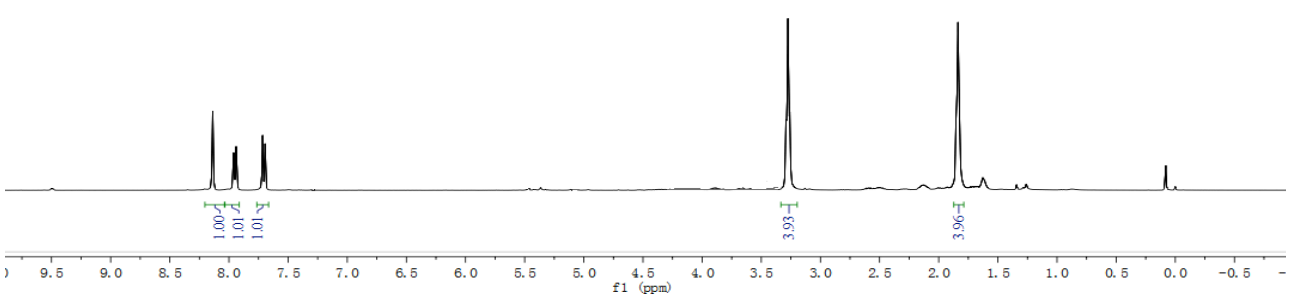
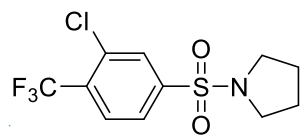
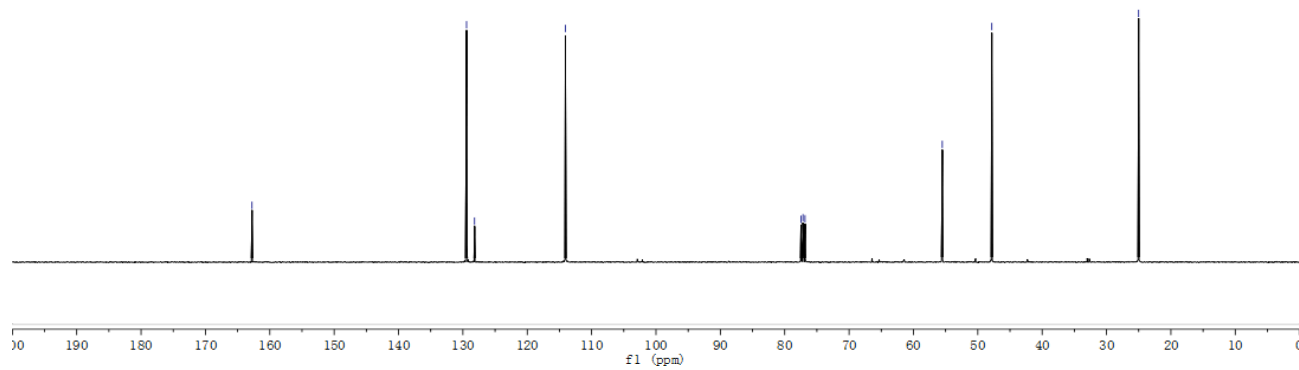
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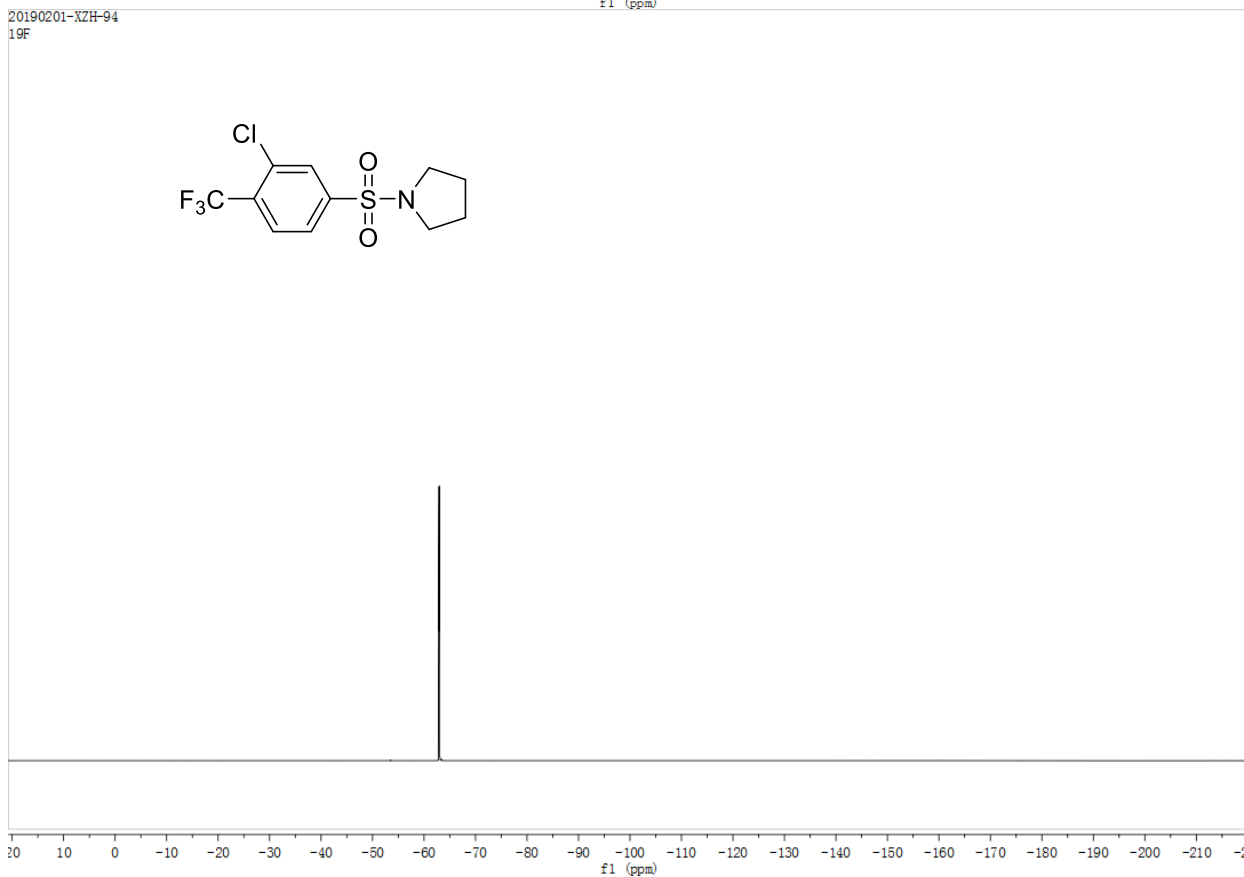
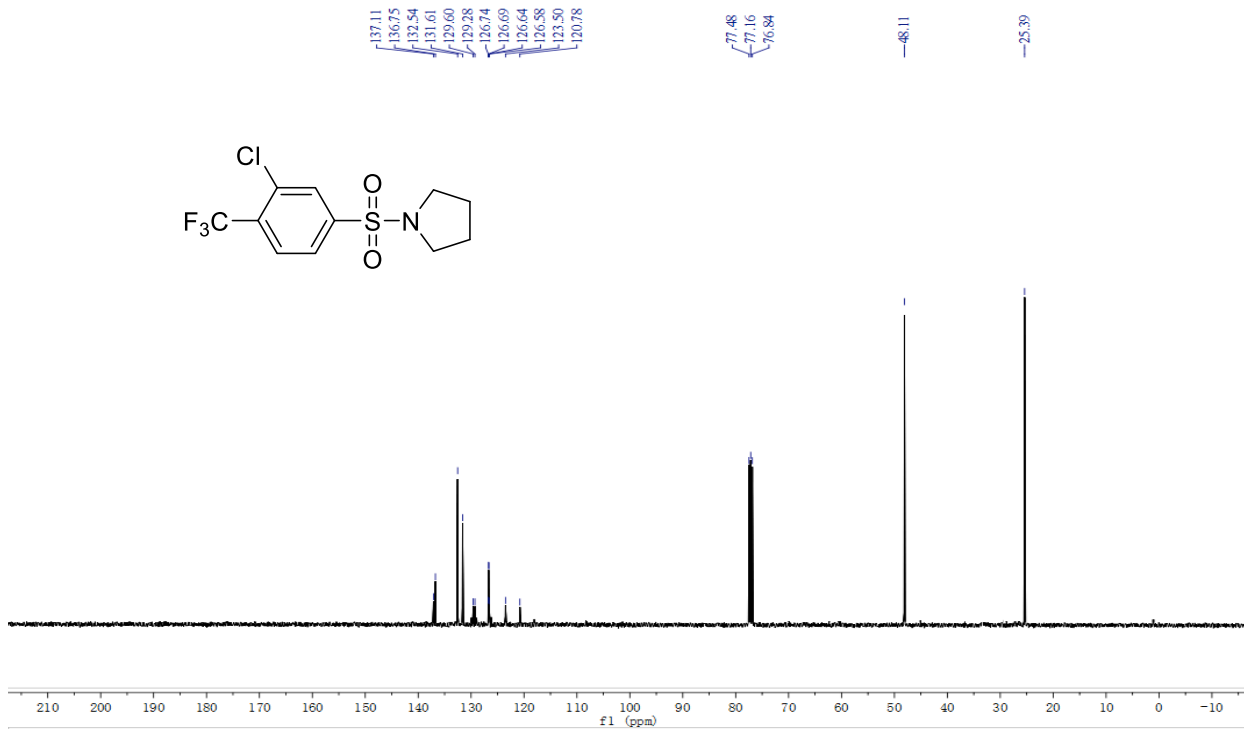
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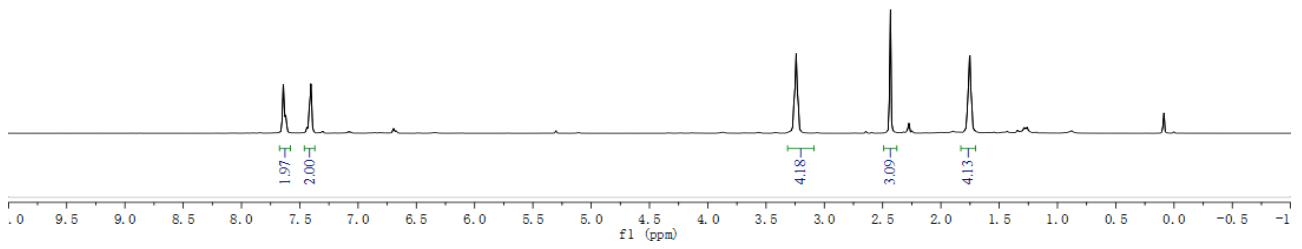
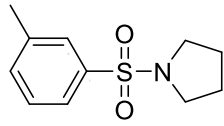
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47.82

25.01





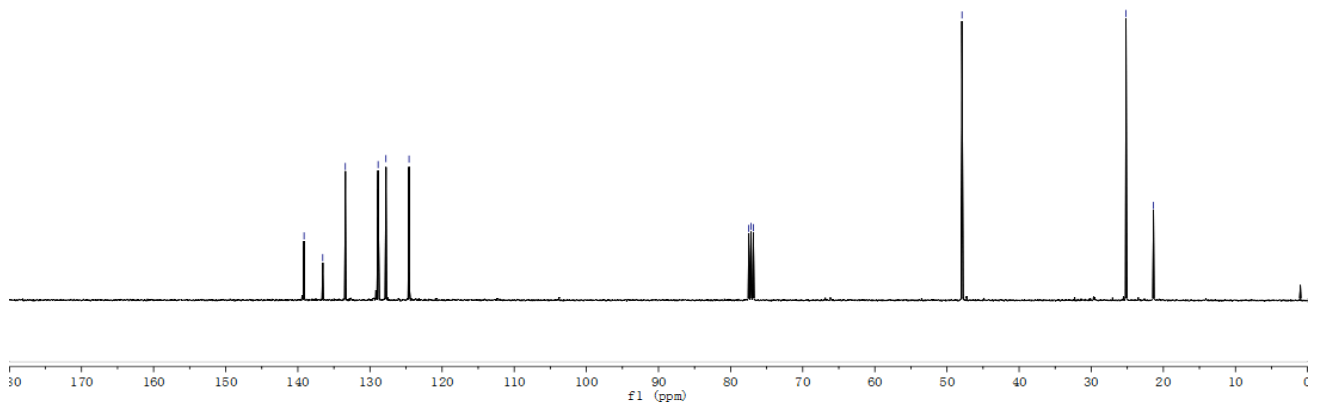
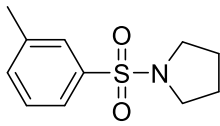


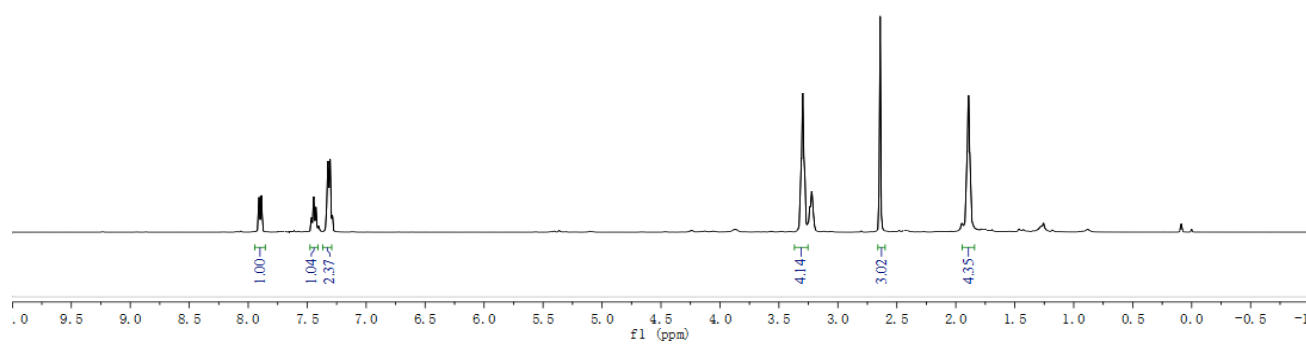
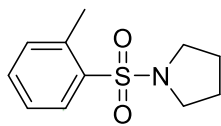
139.14
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128.87
127.79
124.58

77.48
77.16
76.84

-47.92

-25.18
-21.37



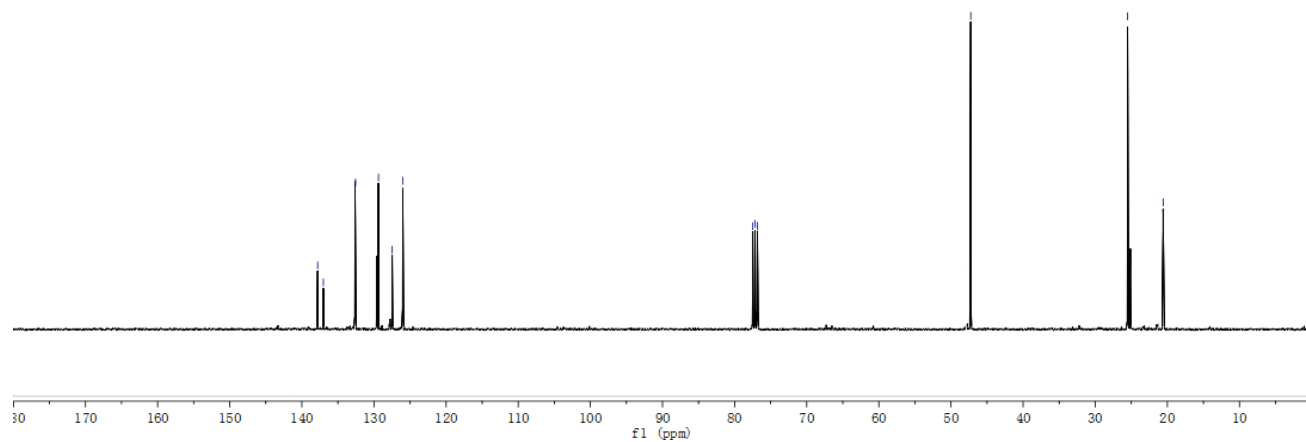
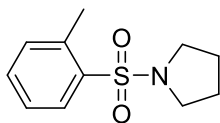


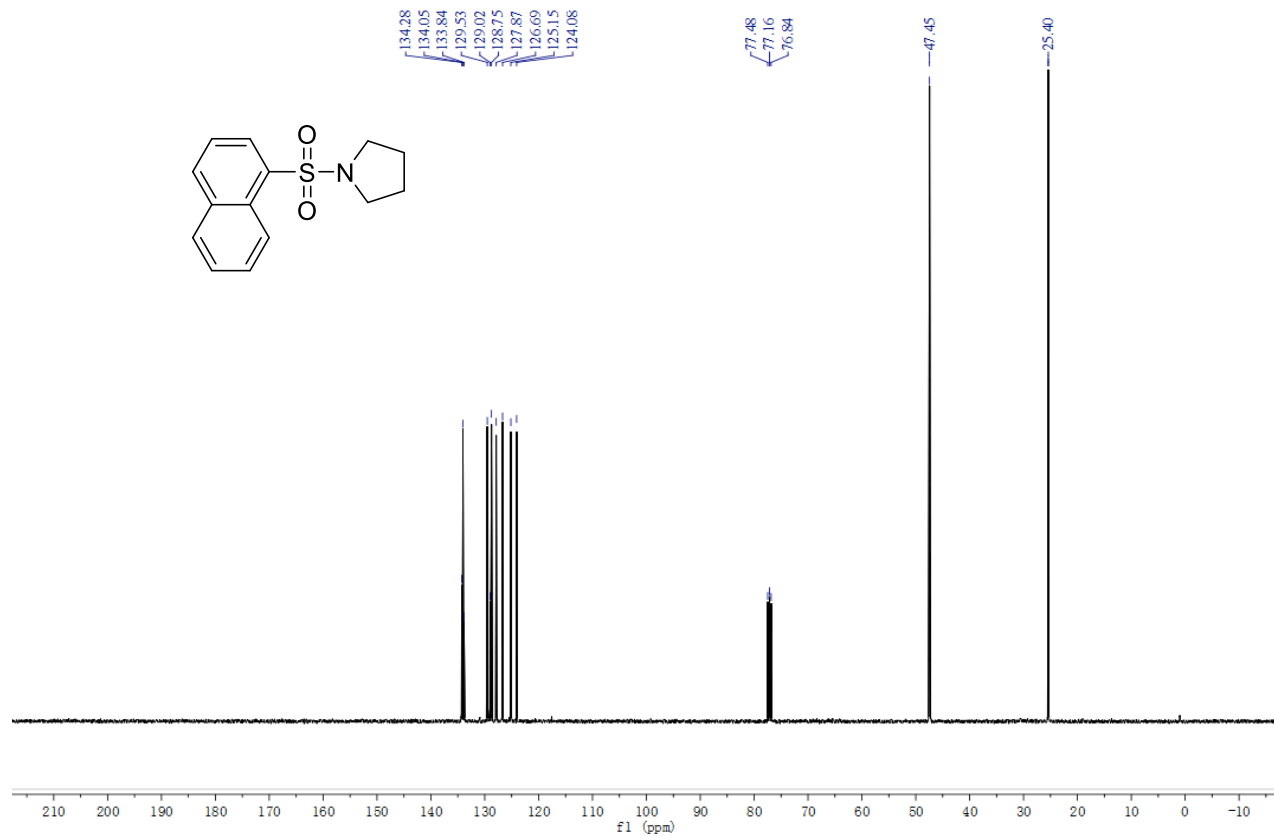
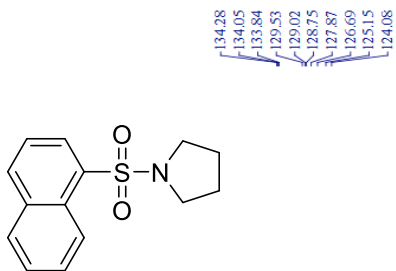
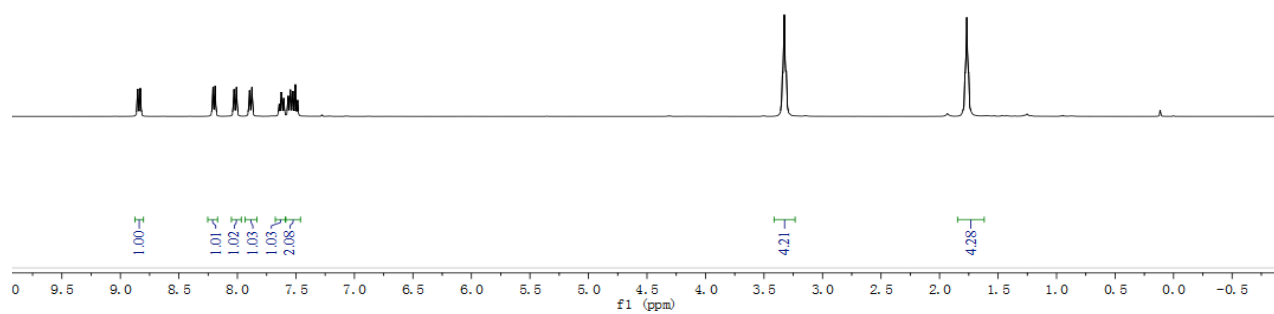
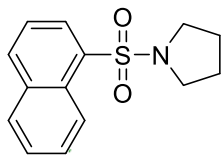
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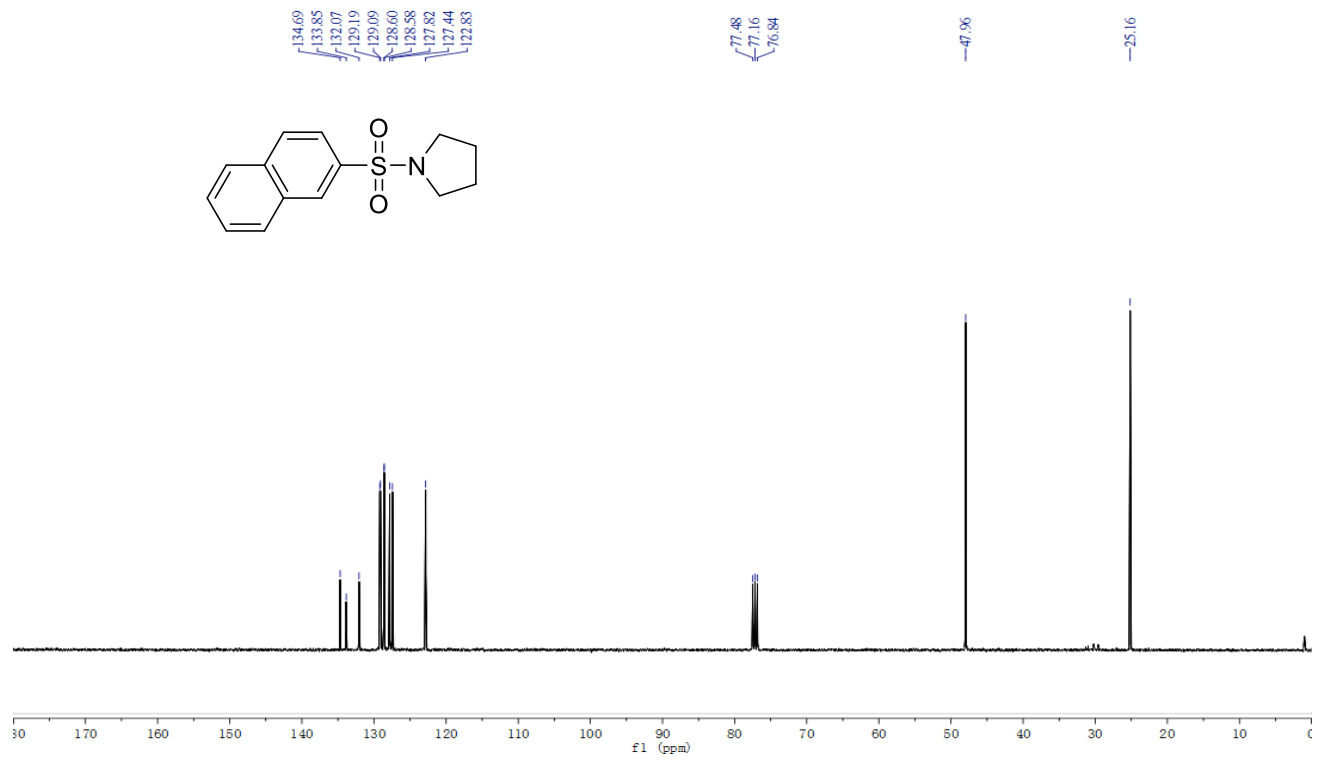
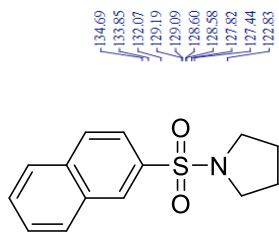
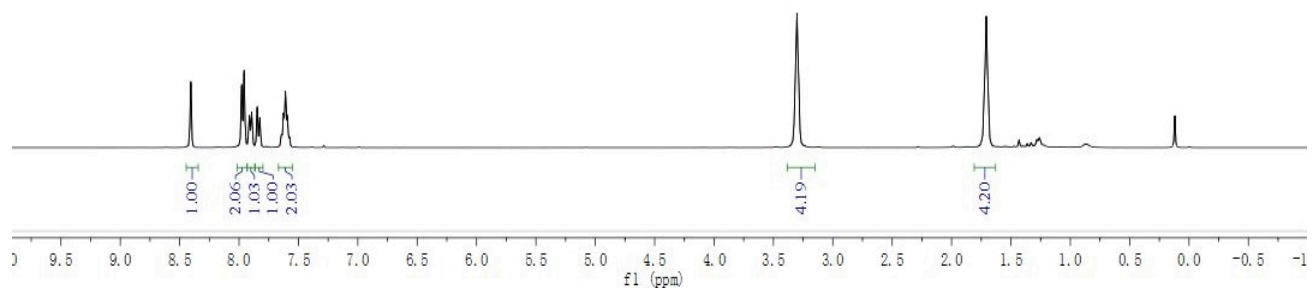
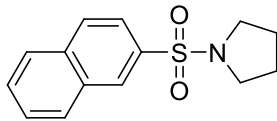
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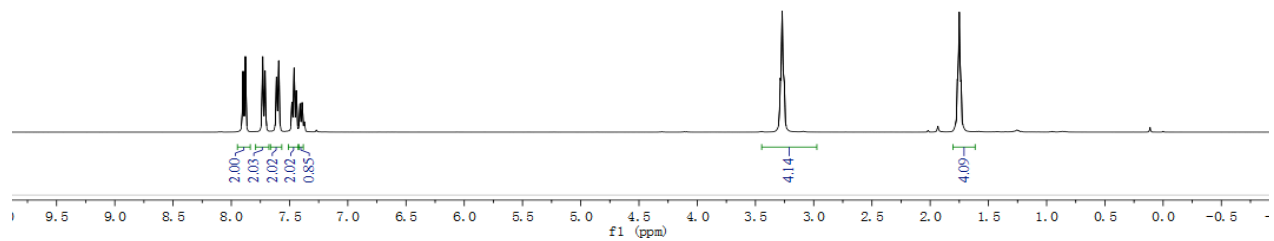
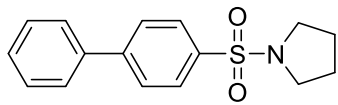
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25.51
20.88







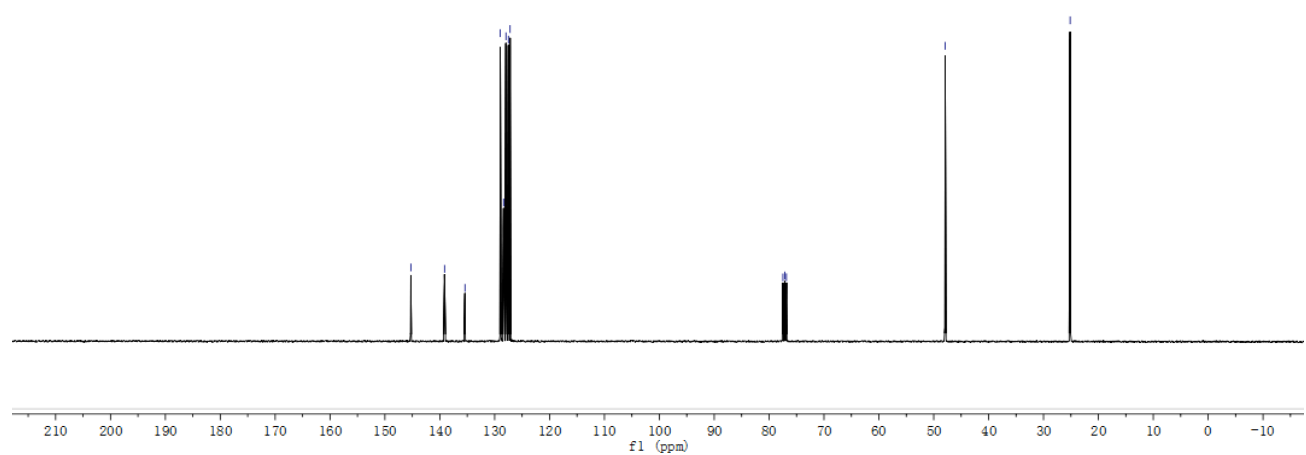
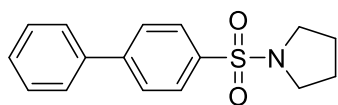


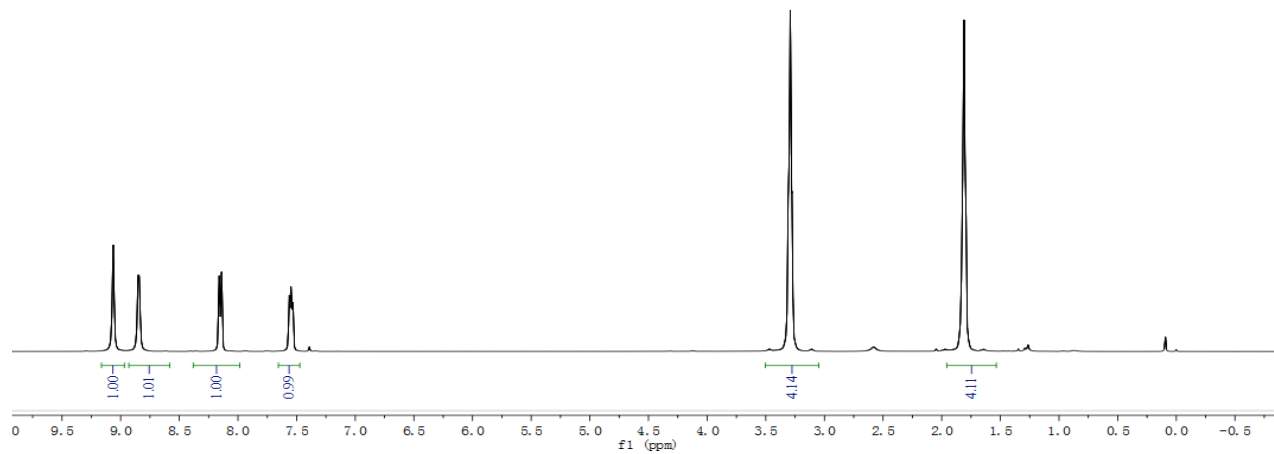
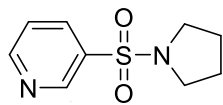
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128.38
127.95
127.50
127.19

77.48
77.16
76.84

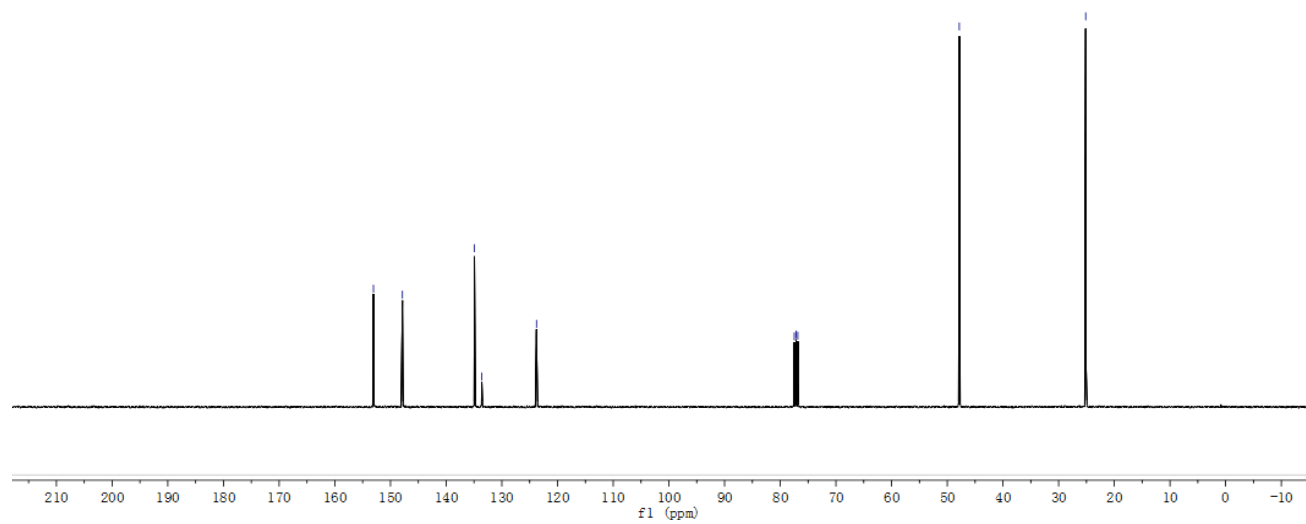
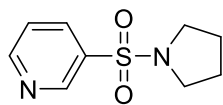
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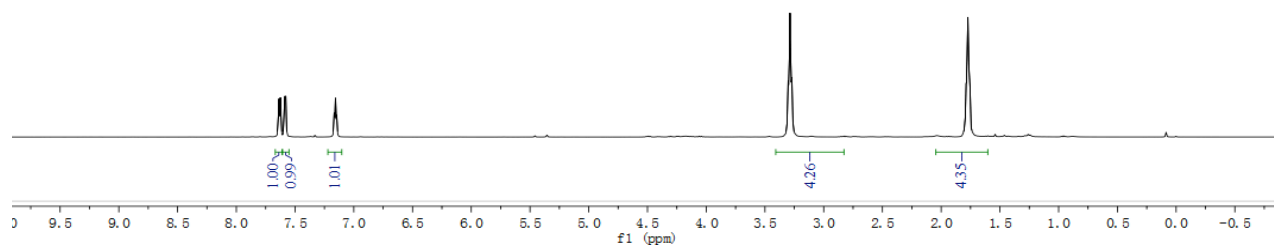
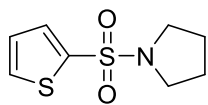
25.15





133.06
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134.92
133.60
123.78
77.48
77.16
76.84
47.84
25.13



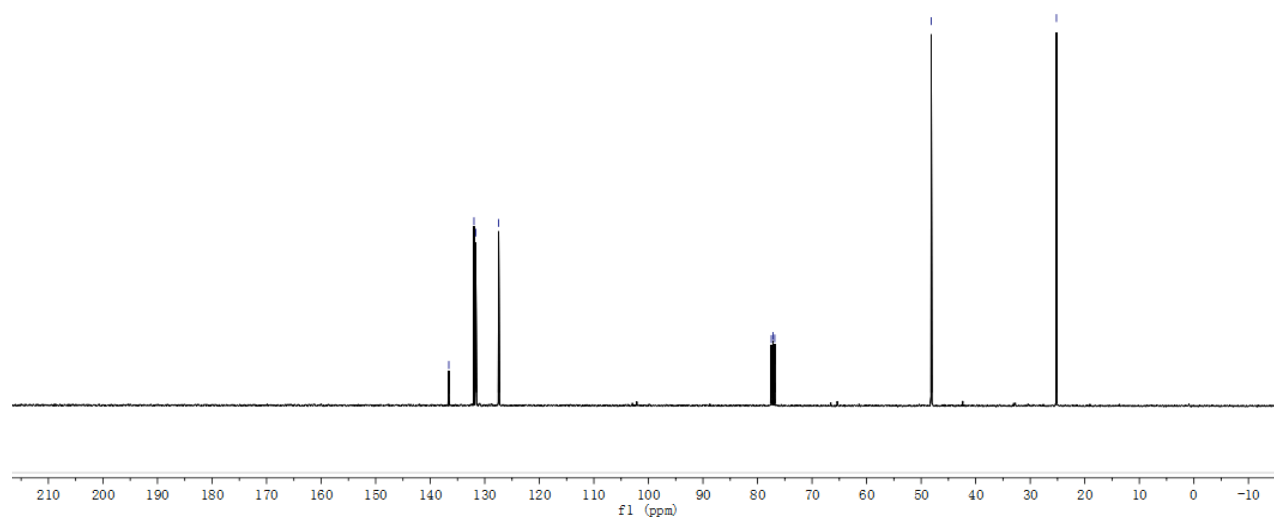
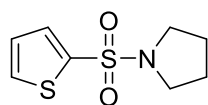


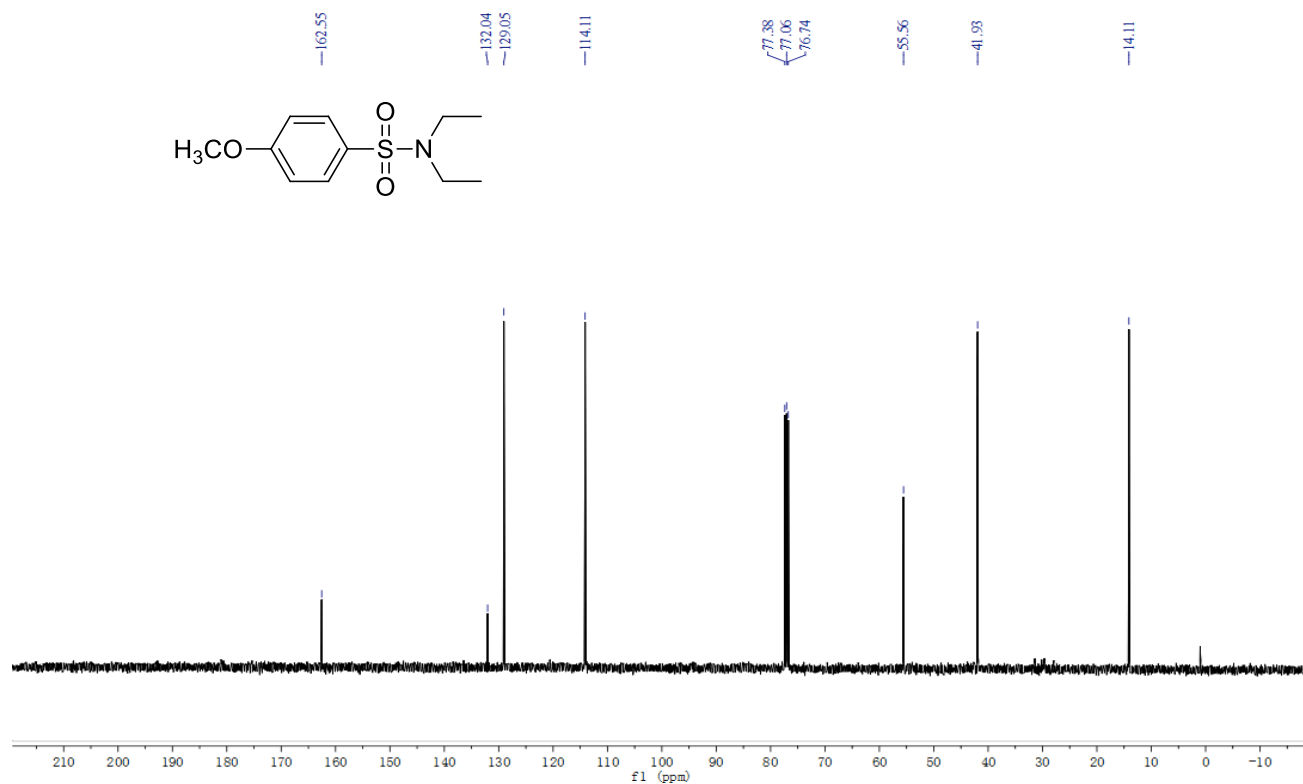
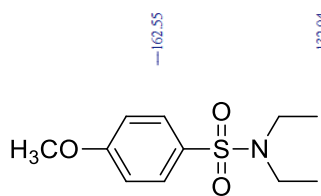
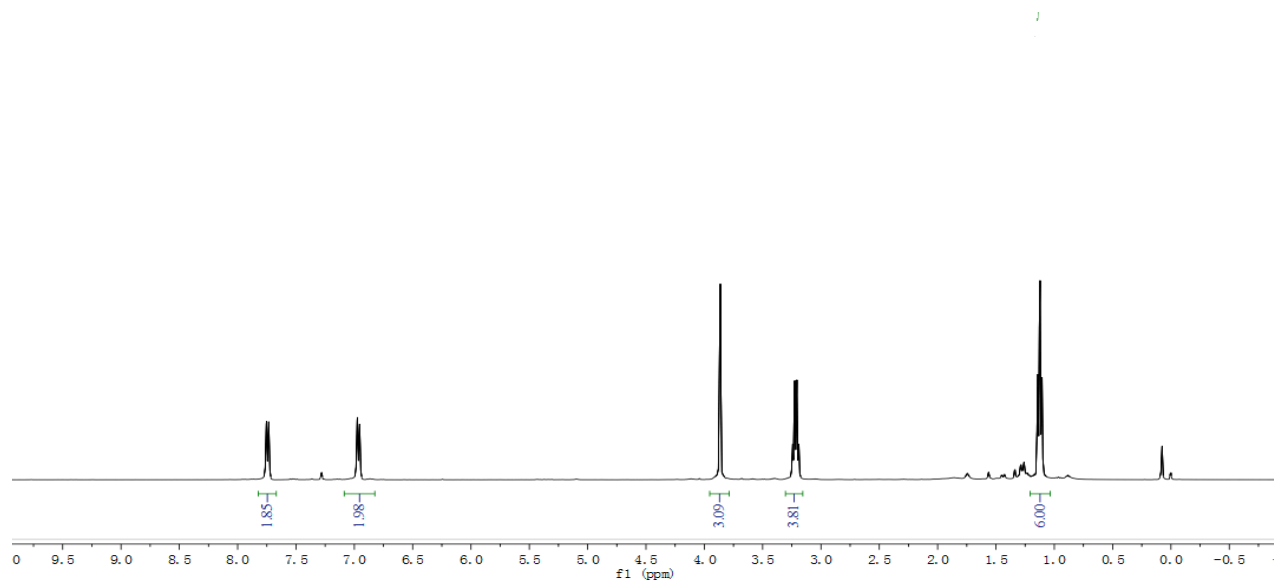
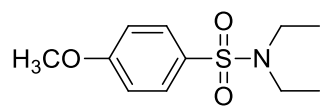
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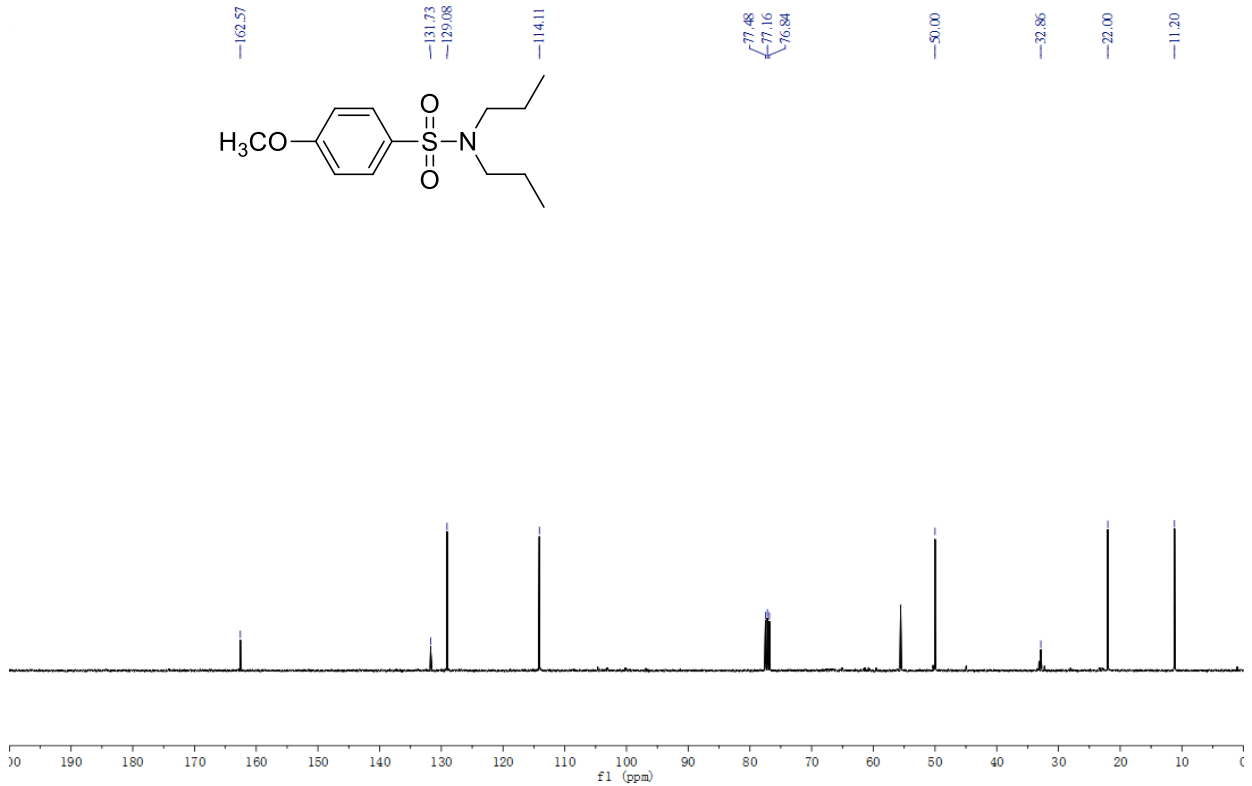
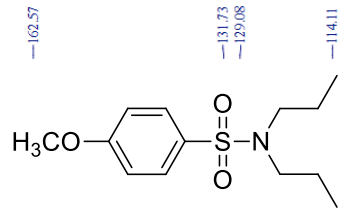
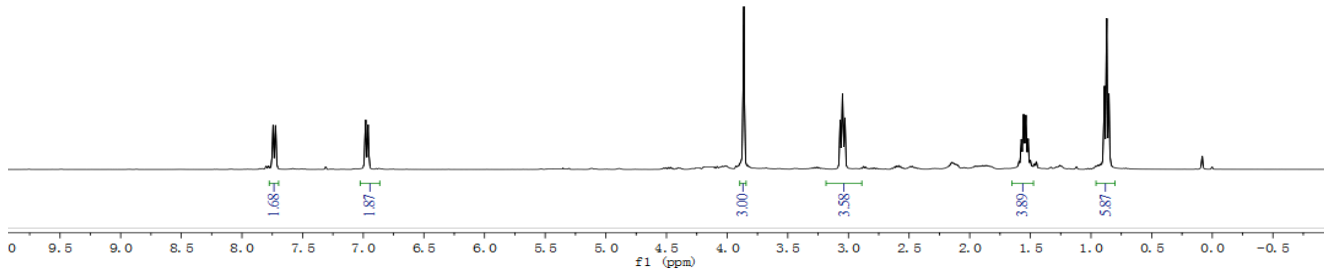
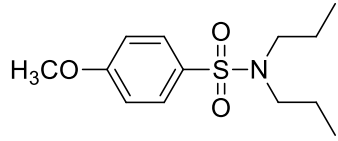
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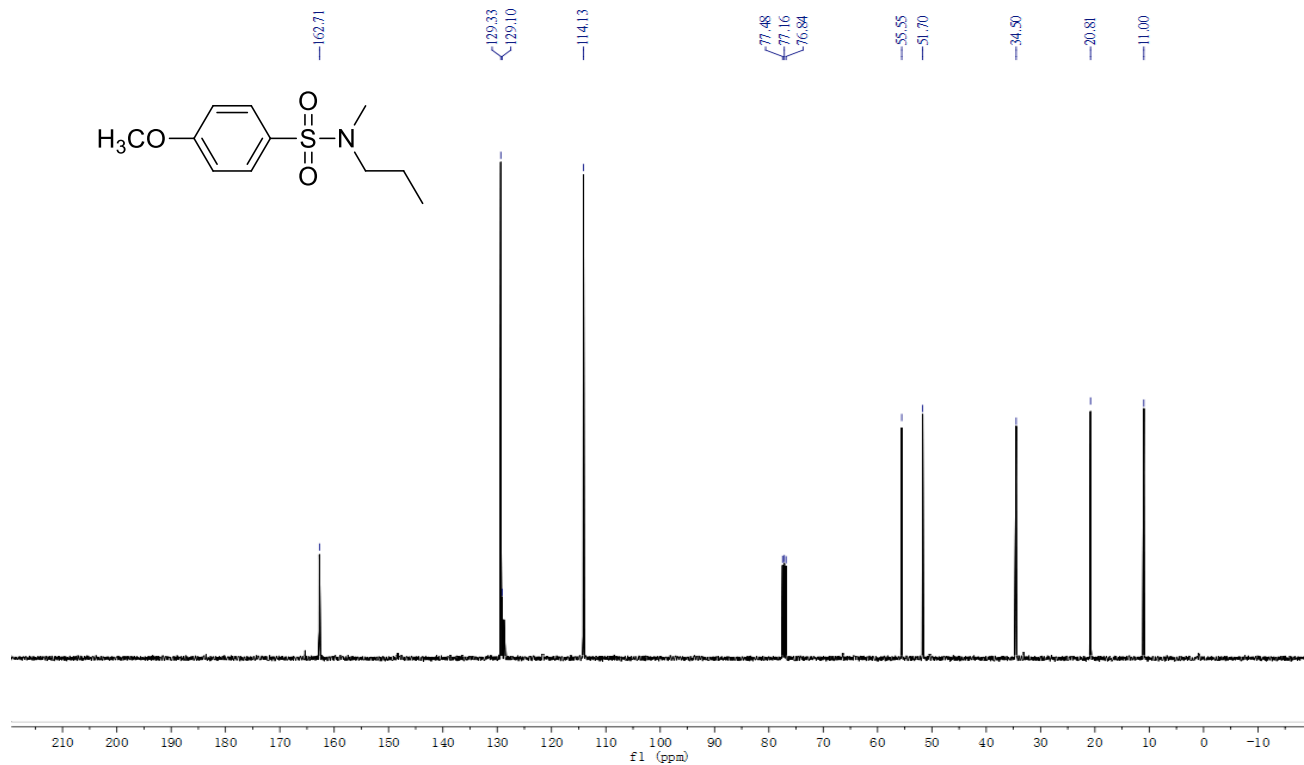
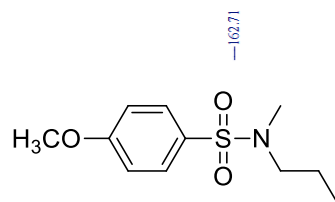
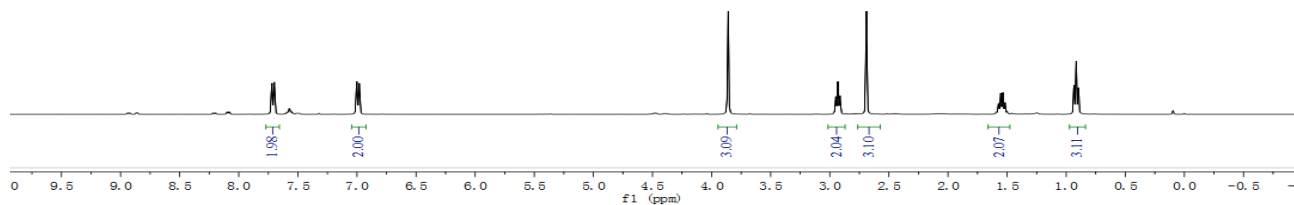
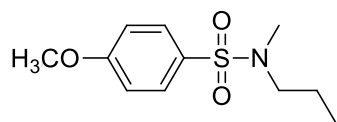
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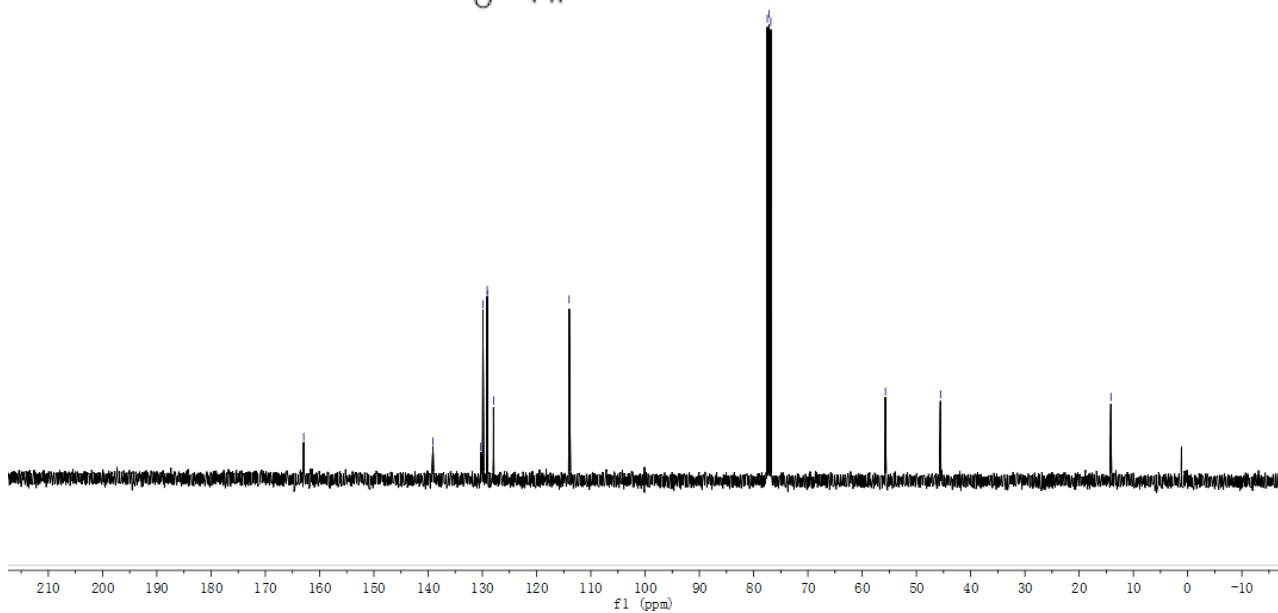
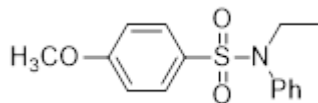
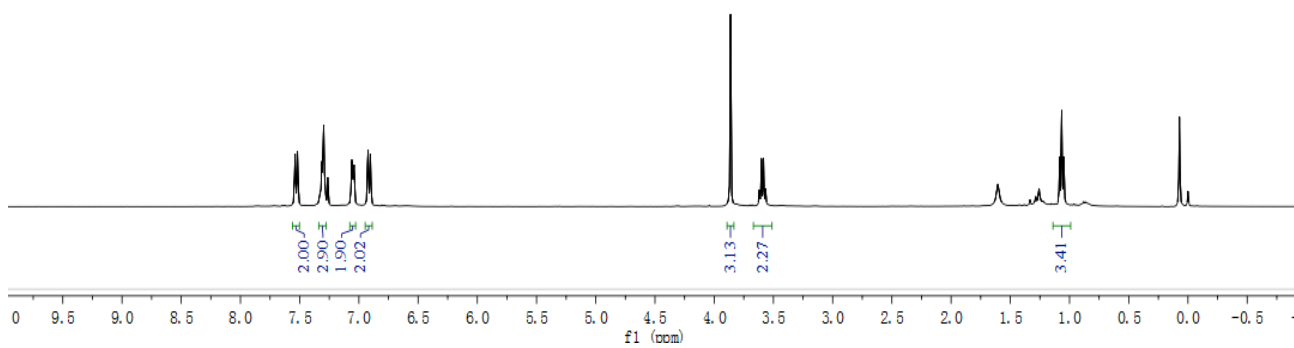
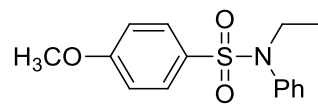
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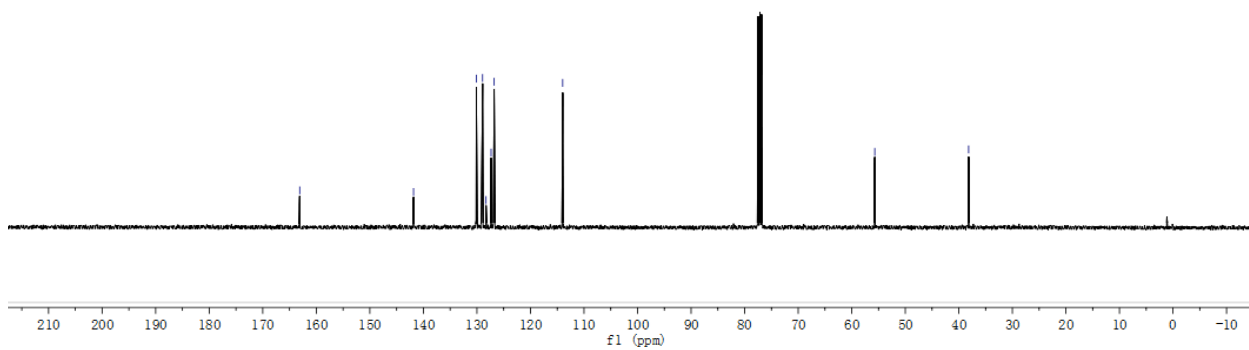
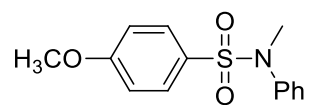
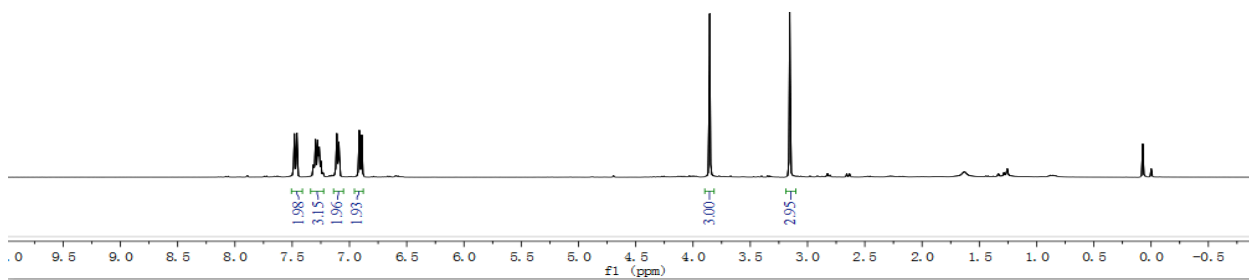
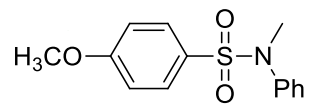


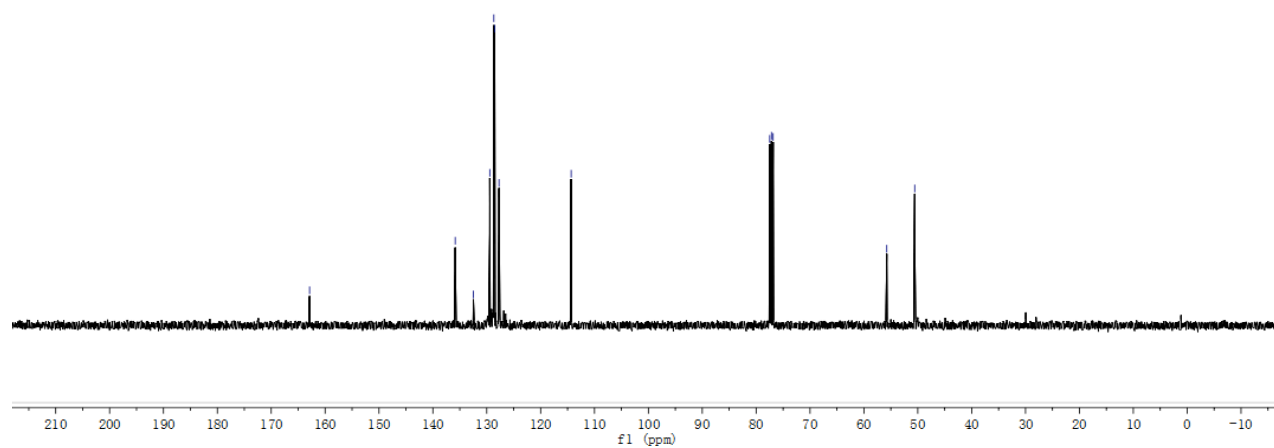
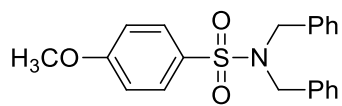
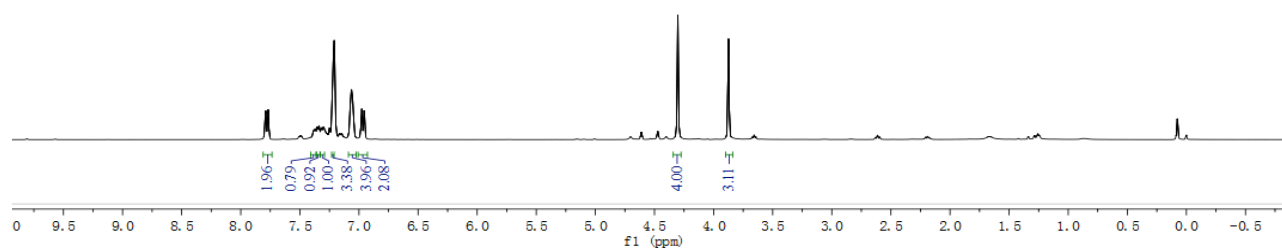
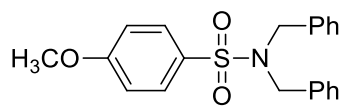


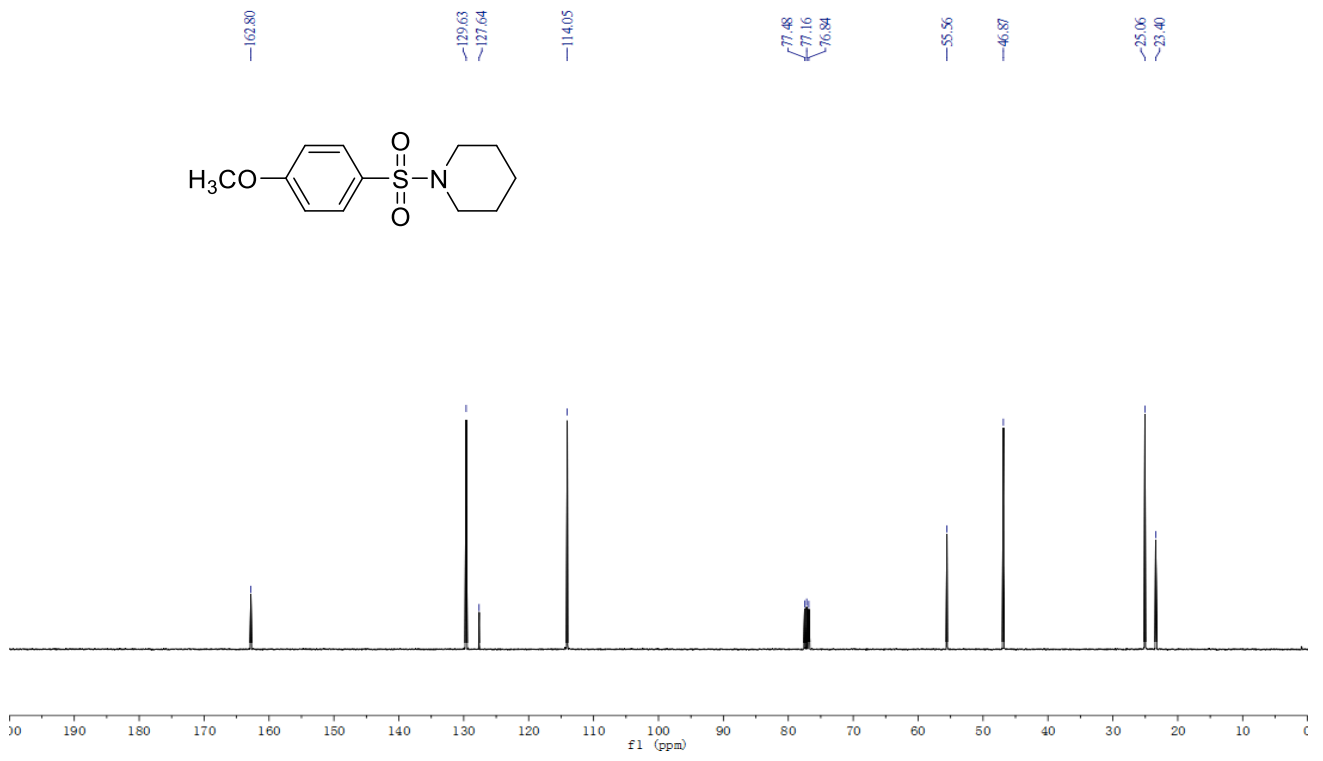
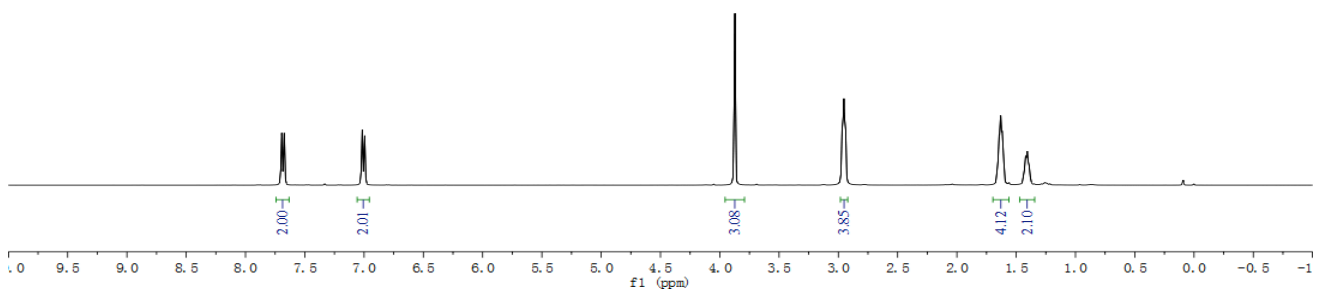
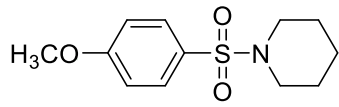


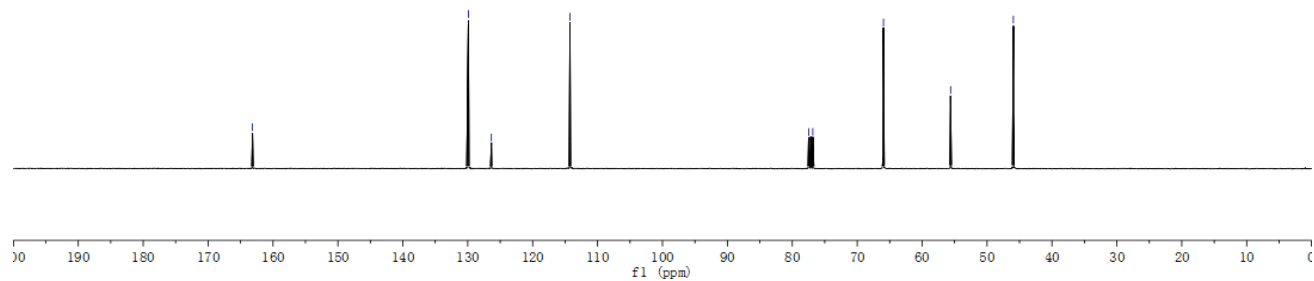
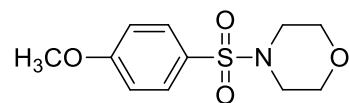
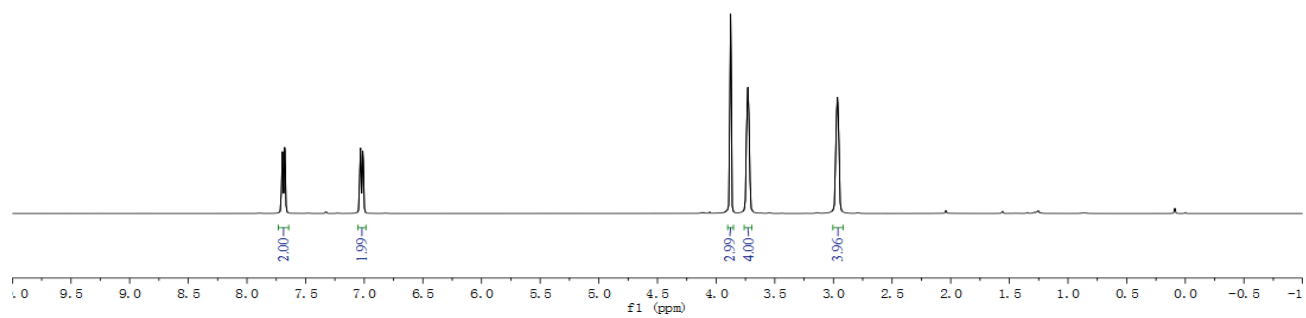
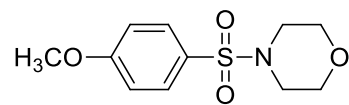


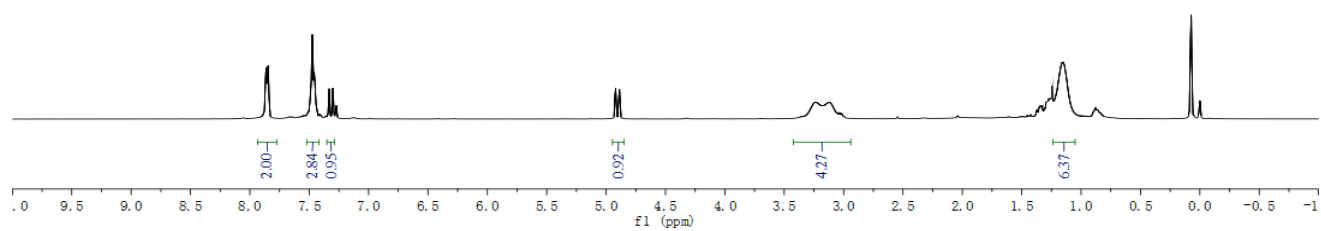
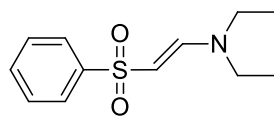




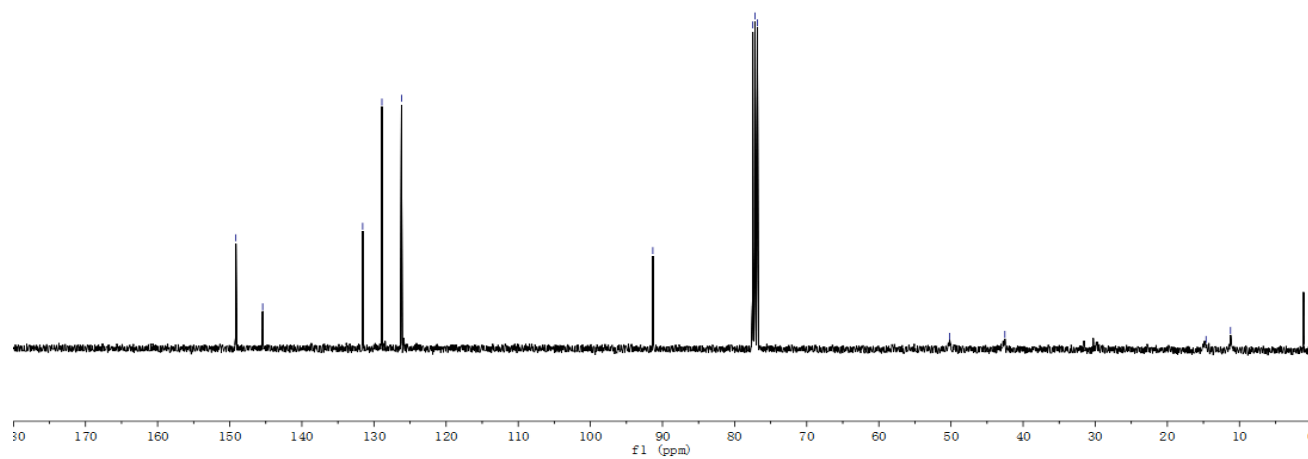
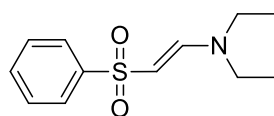


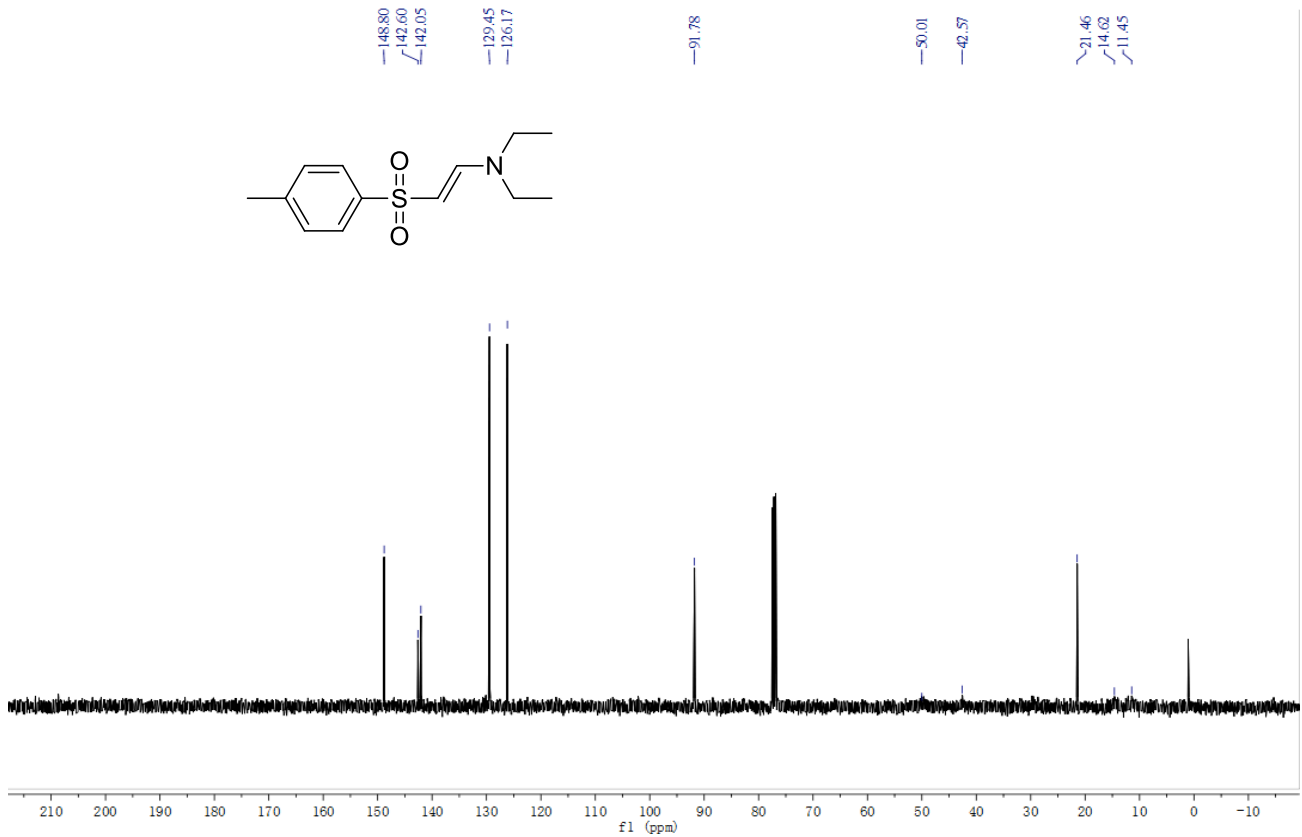
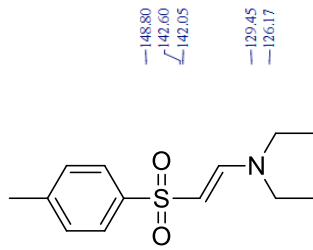
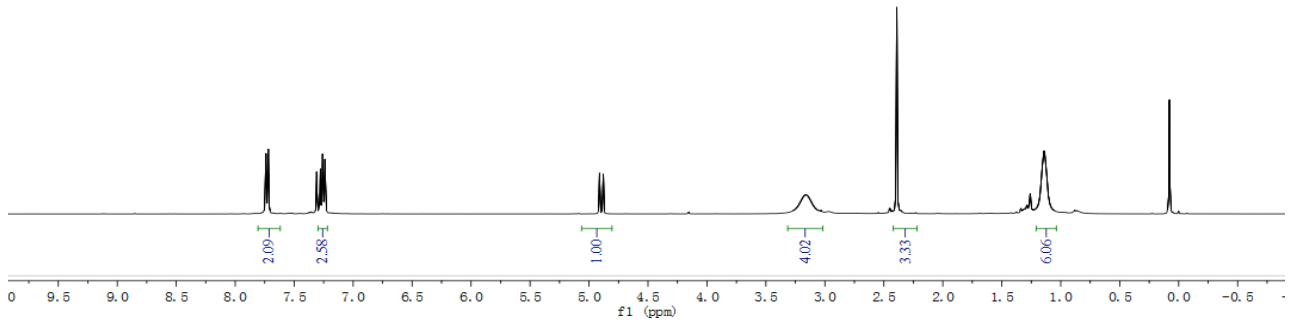
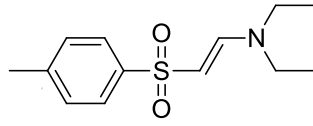


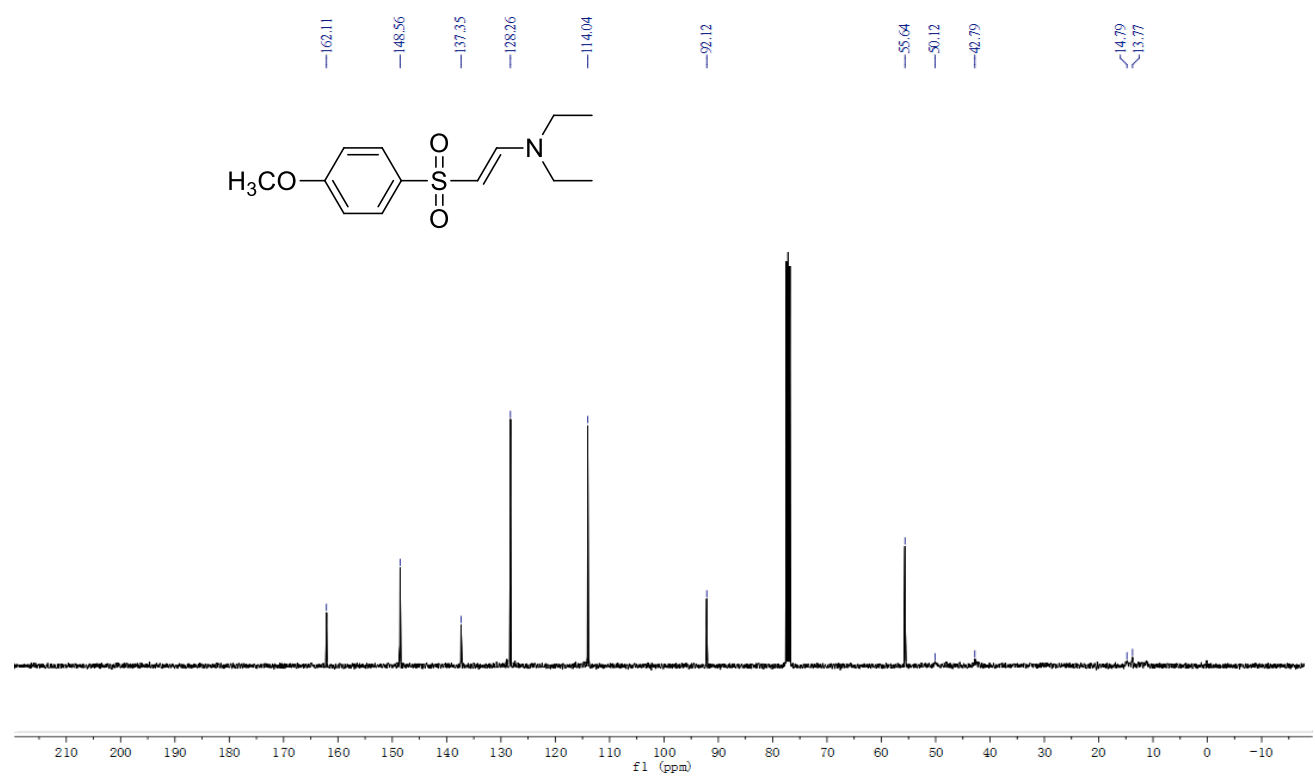
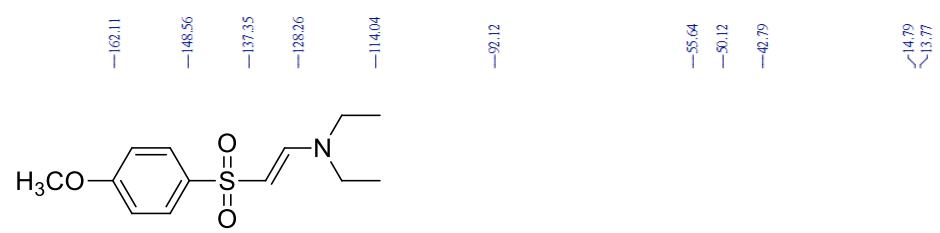
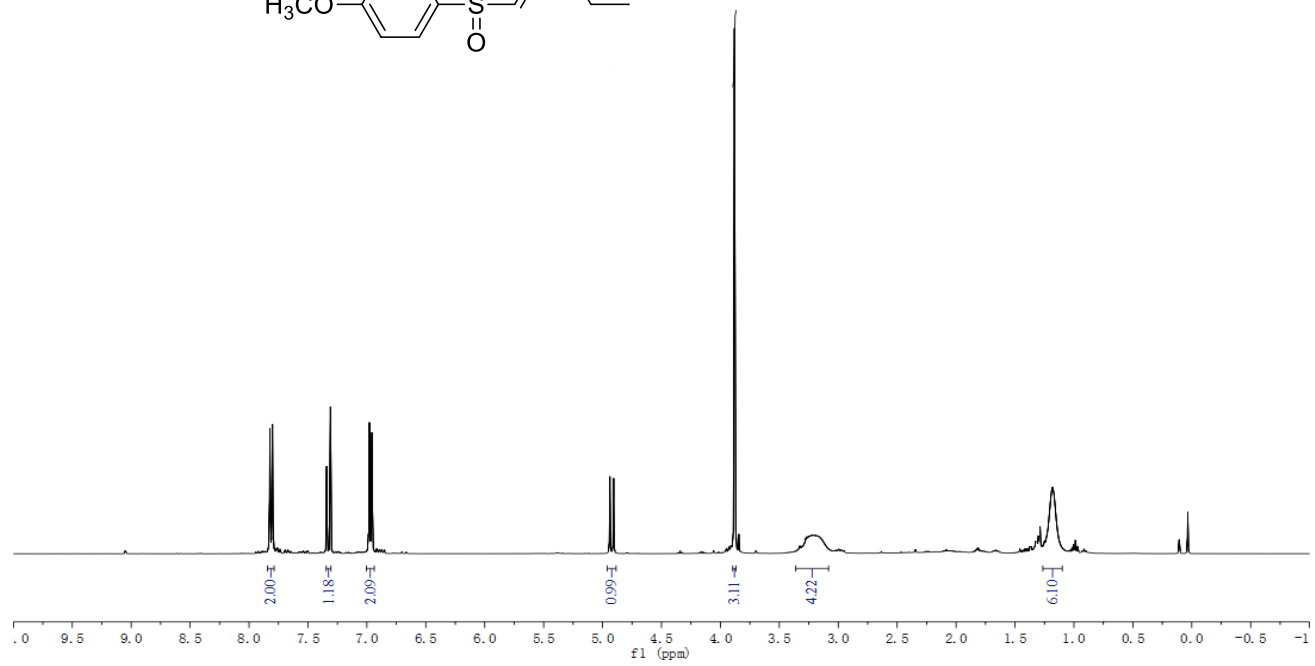
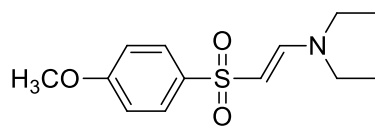


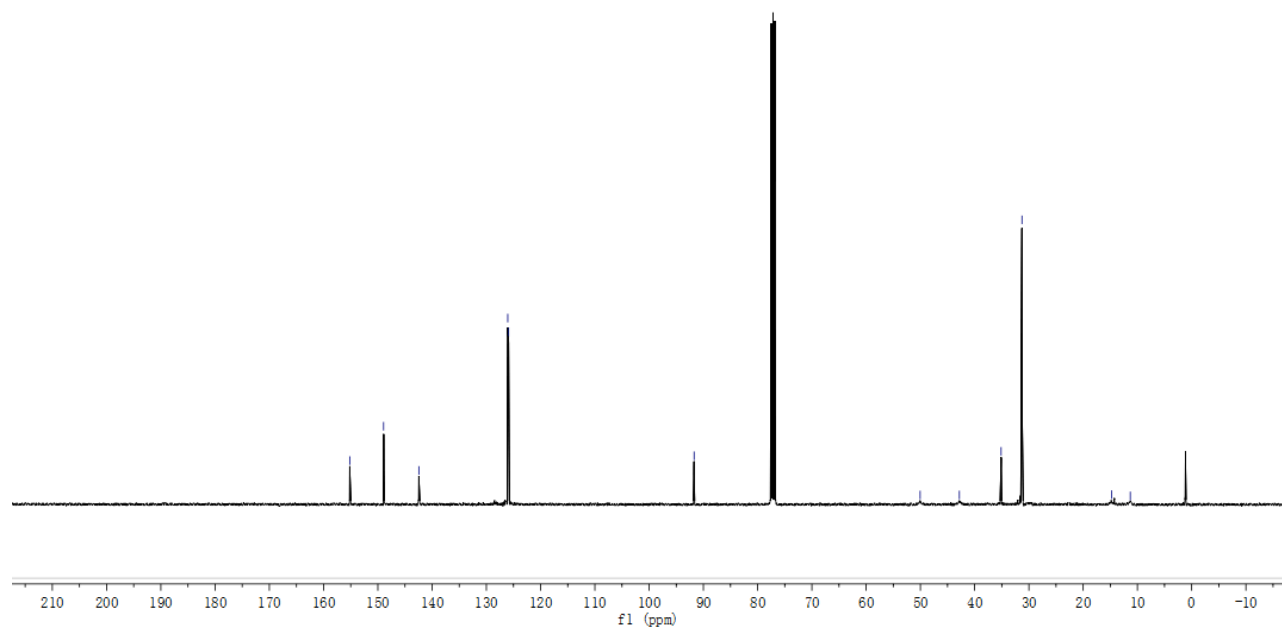
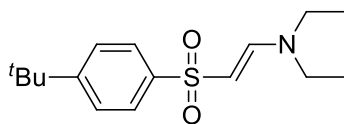
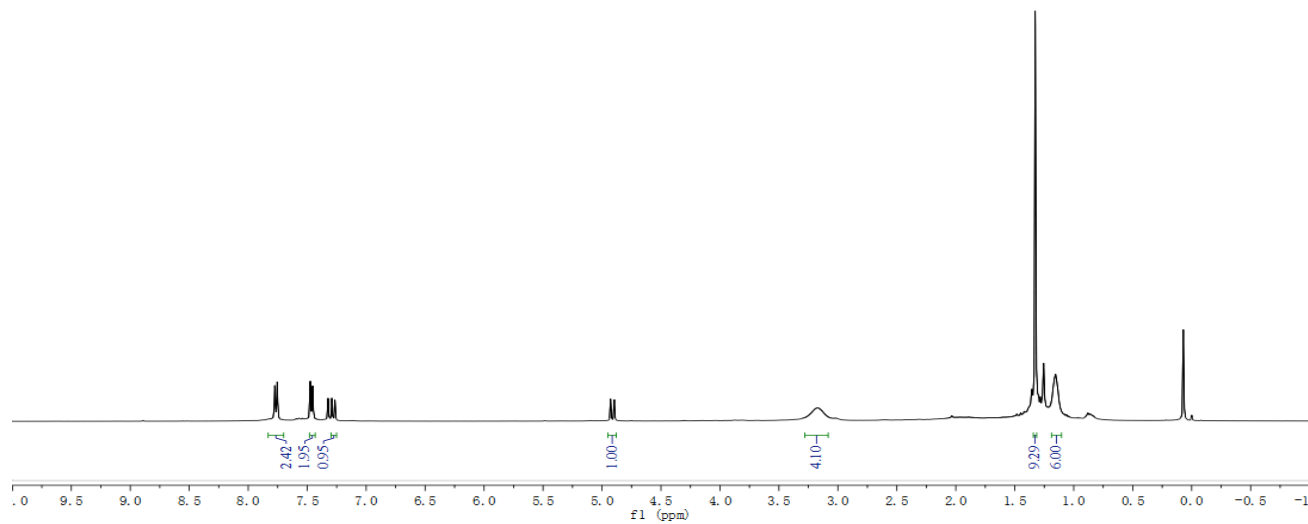
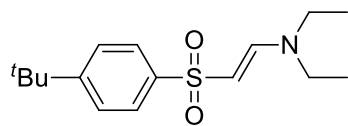


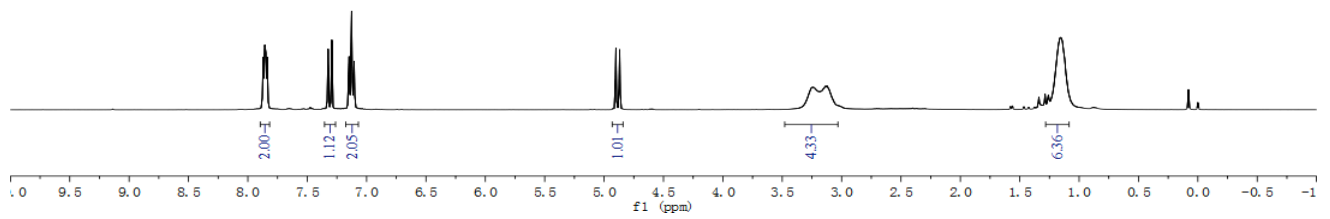
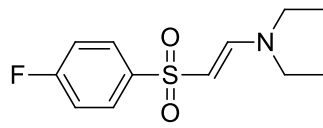
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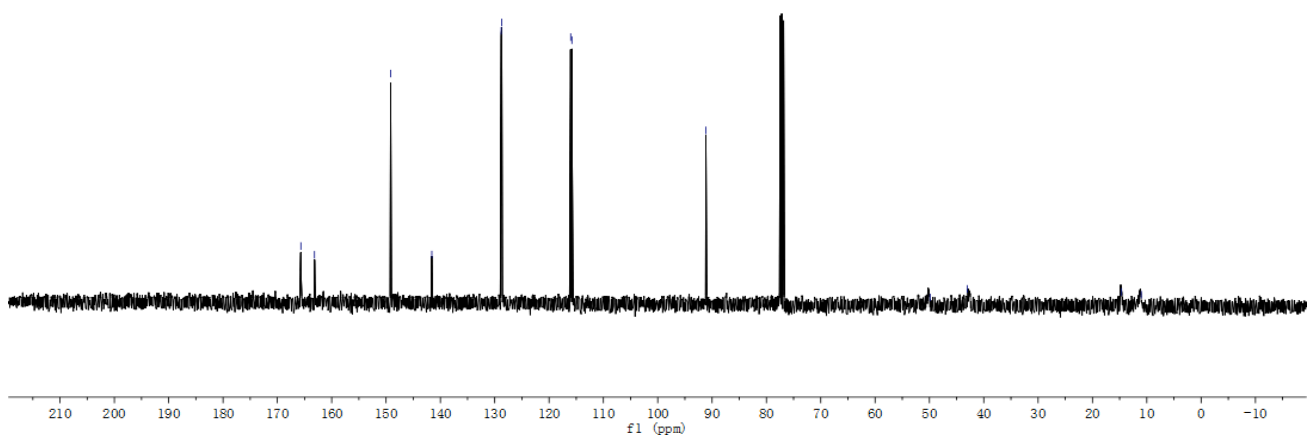
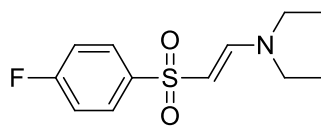




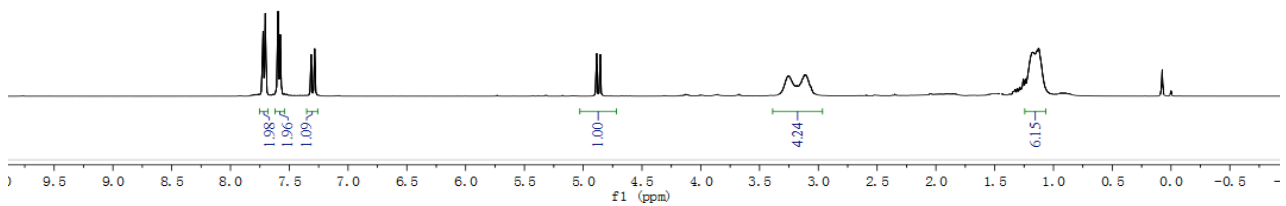
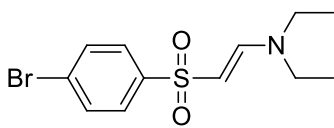
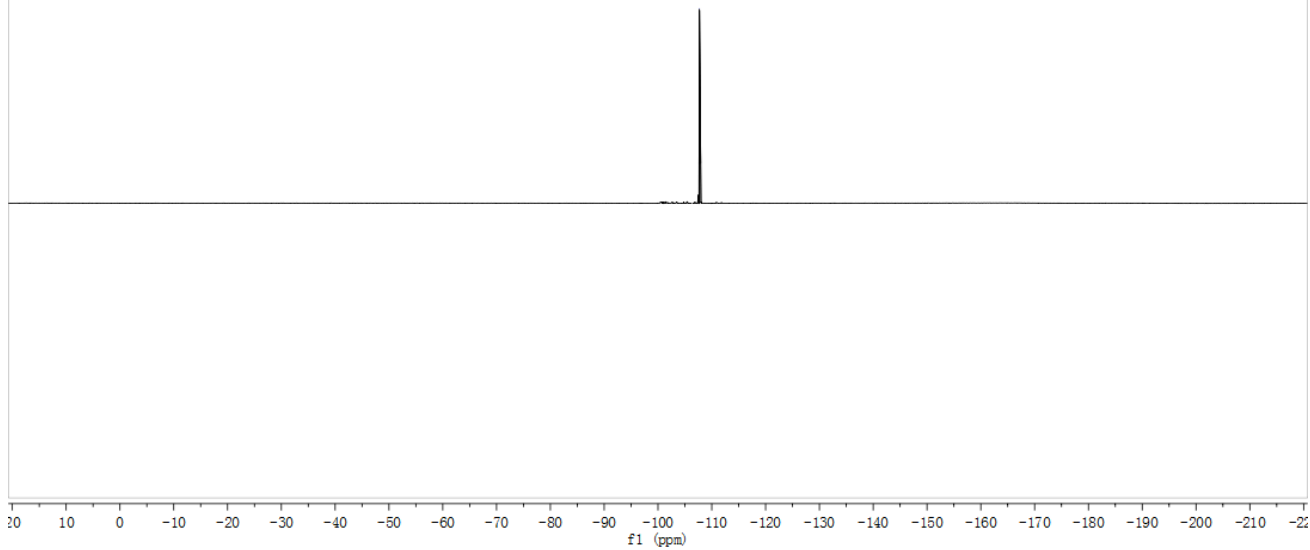
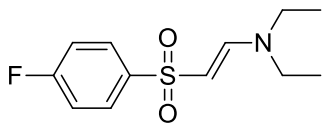


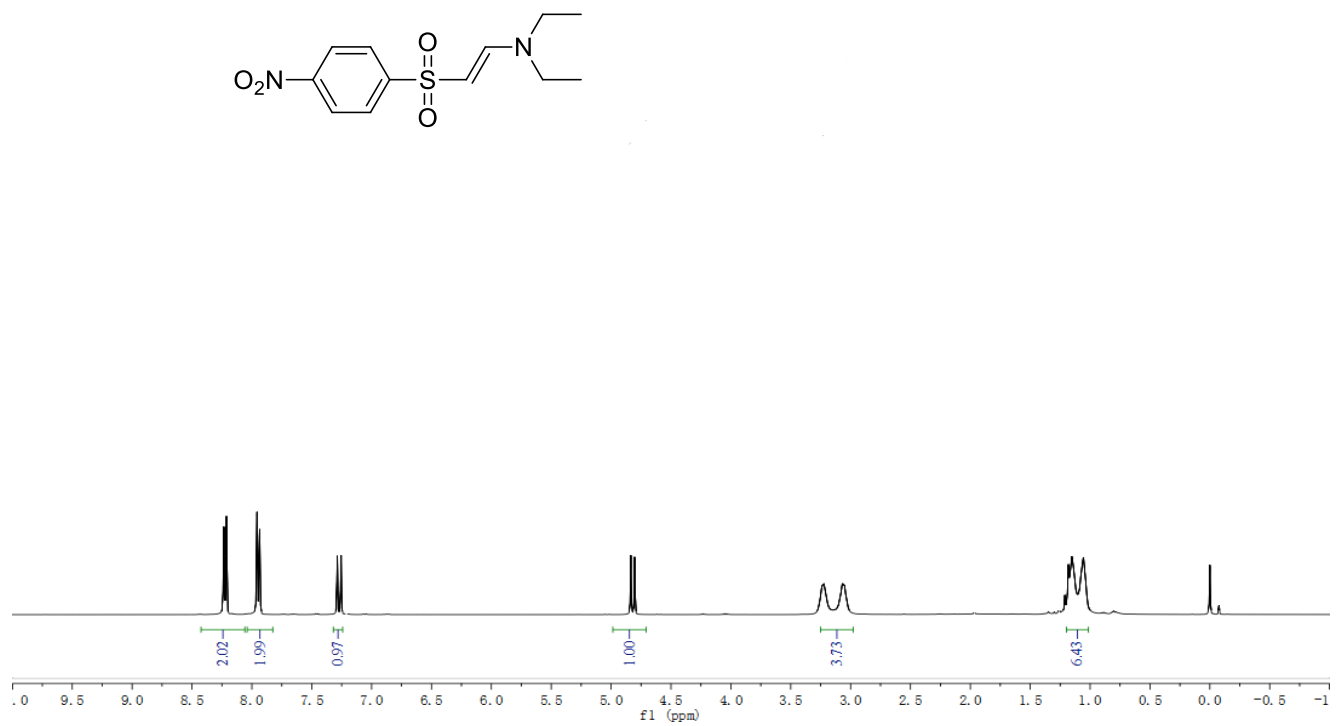
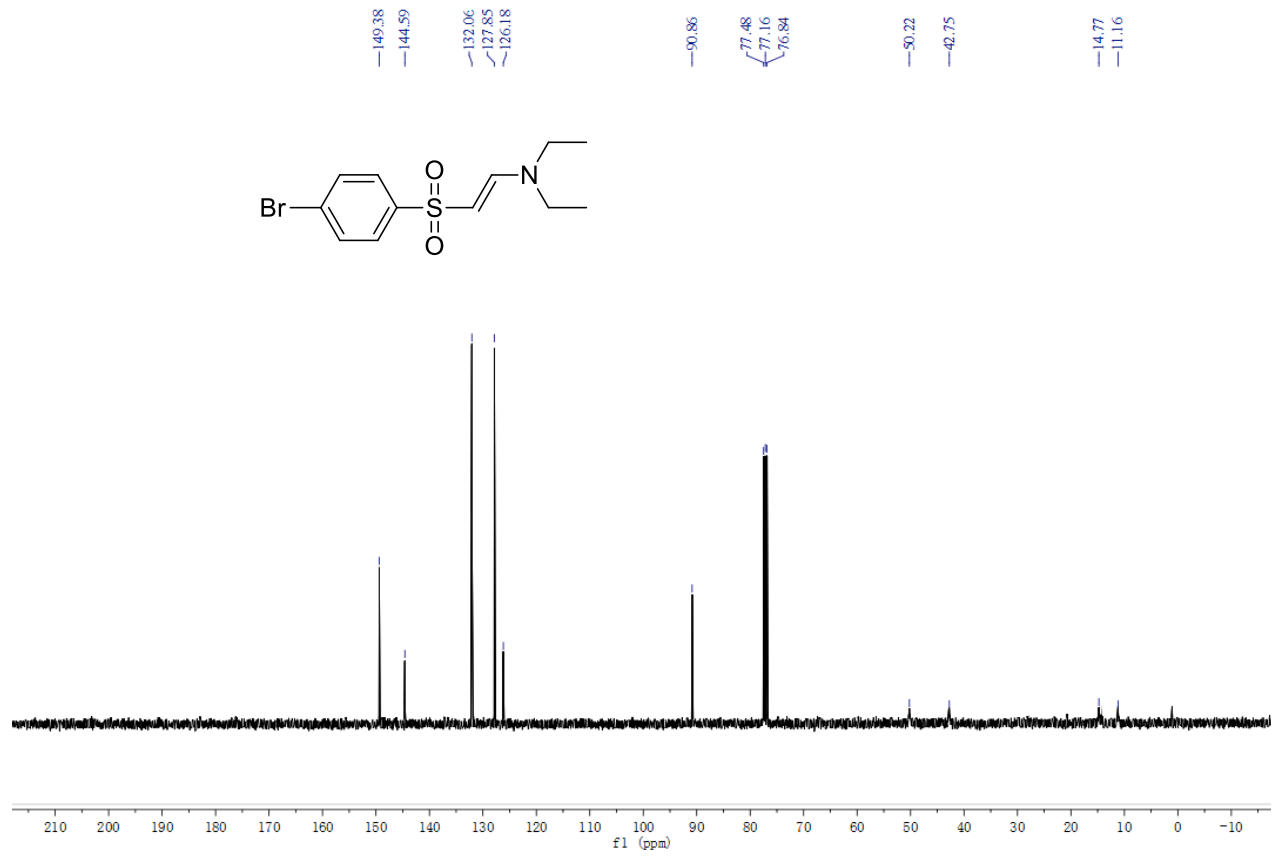


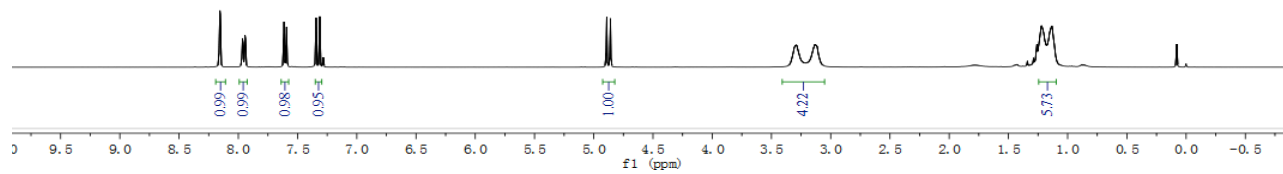
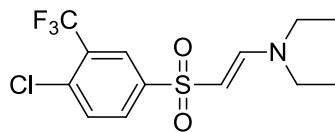
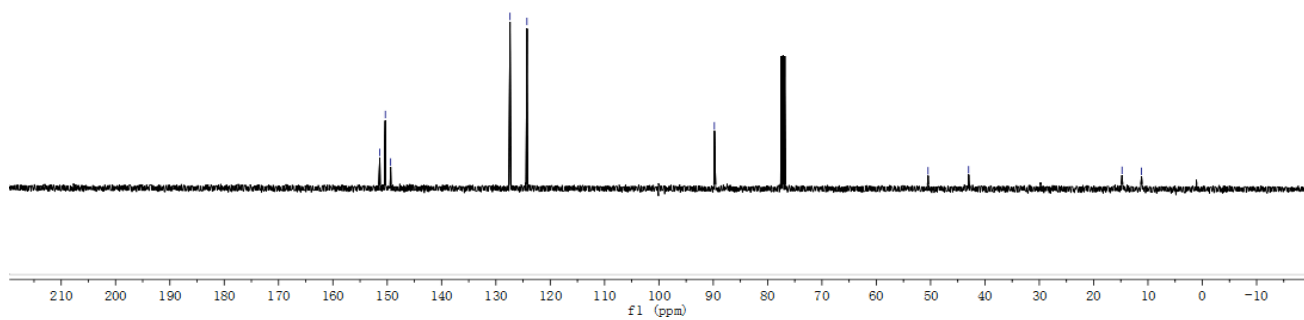
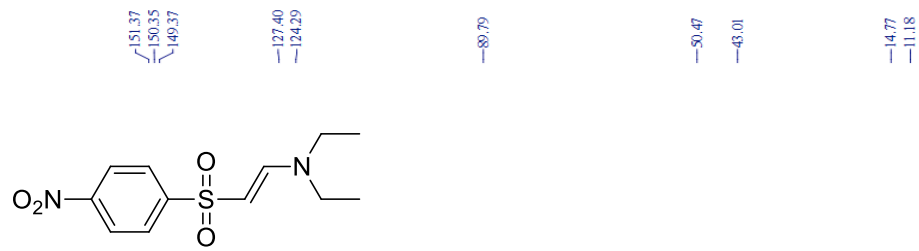
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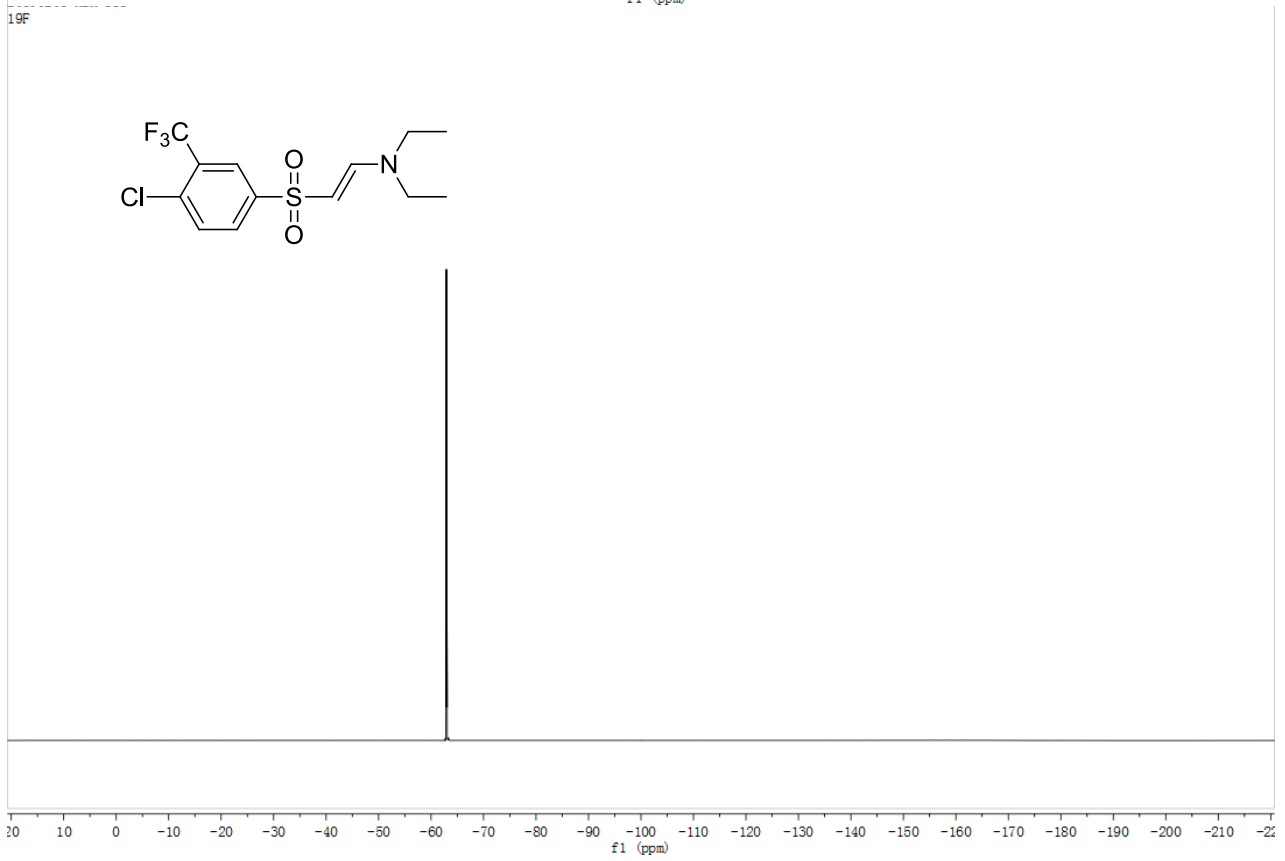
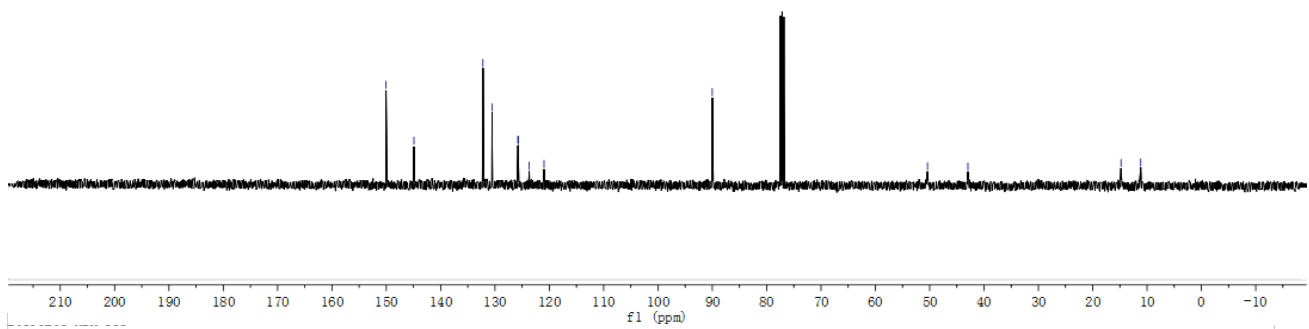
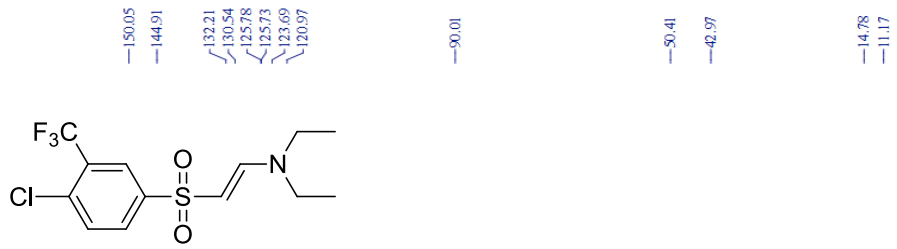


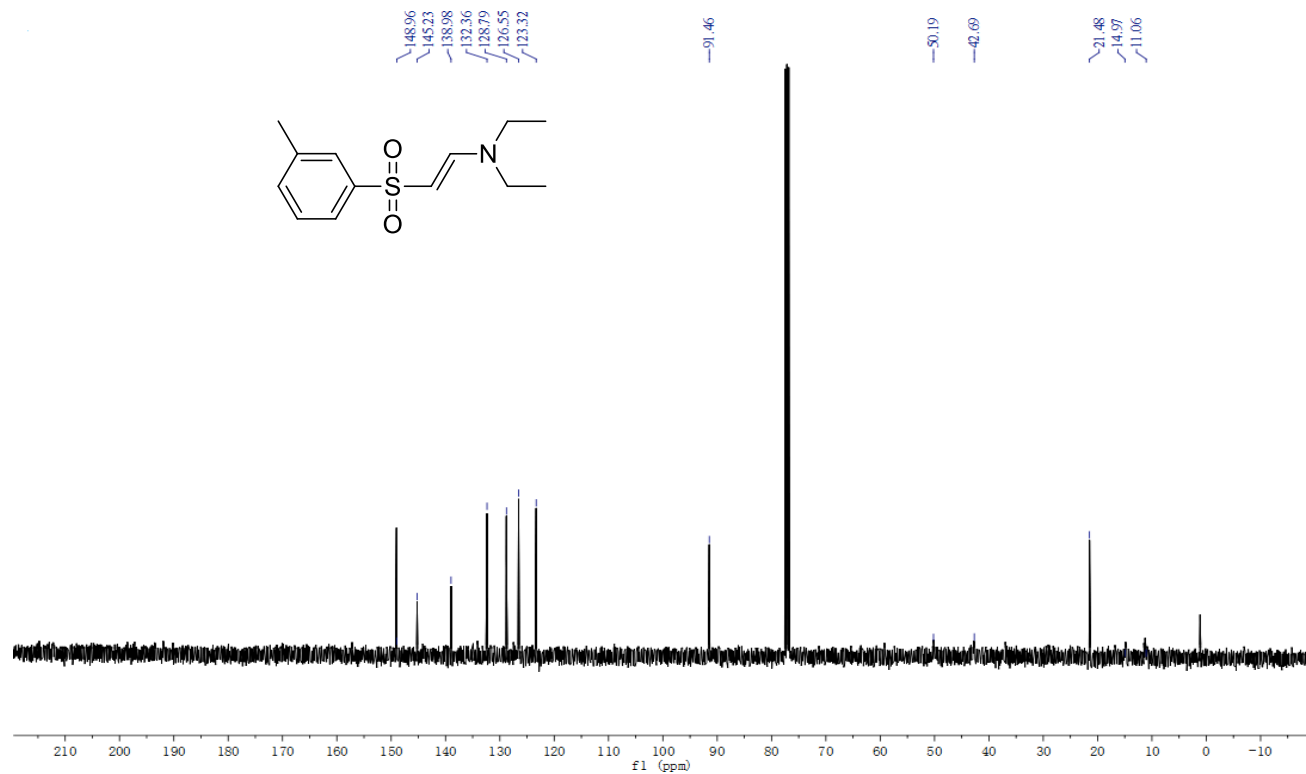
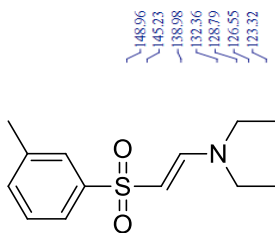
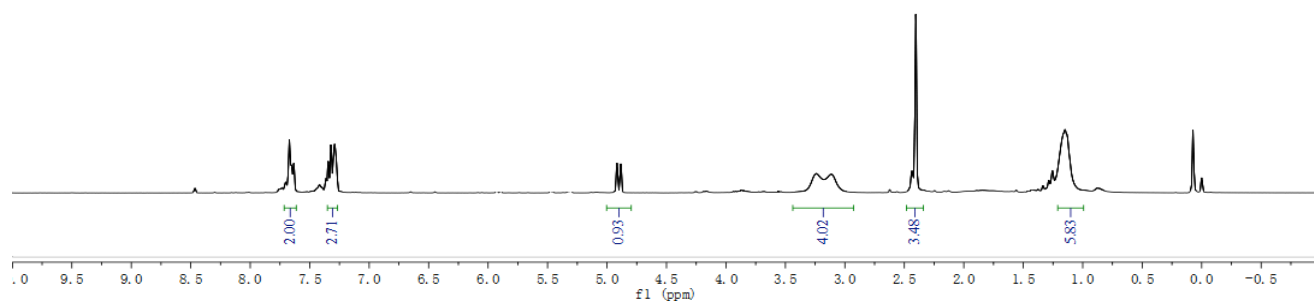
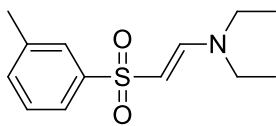
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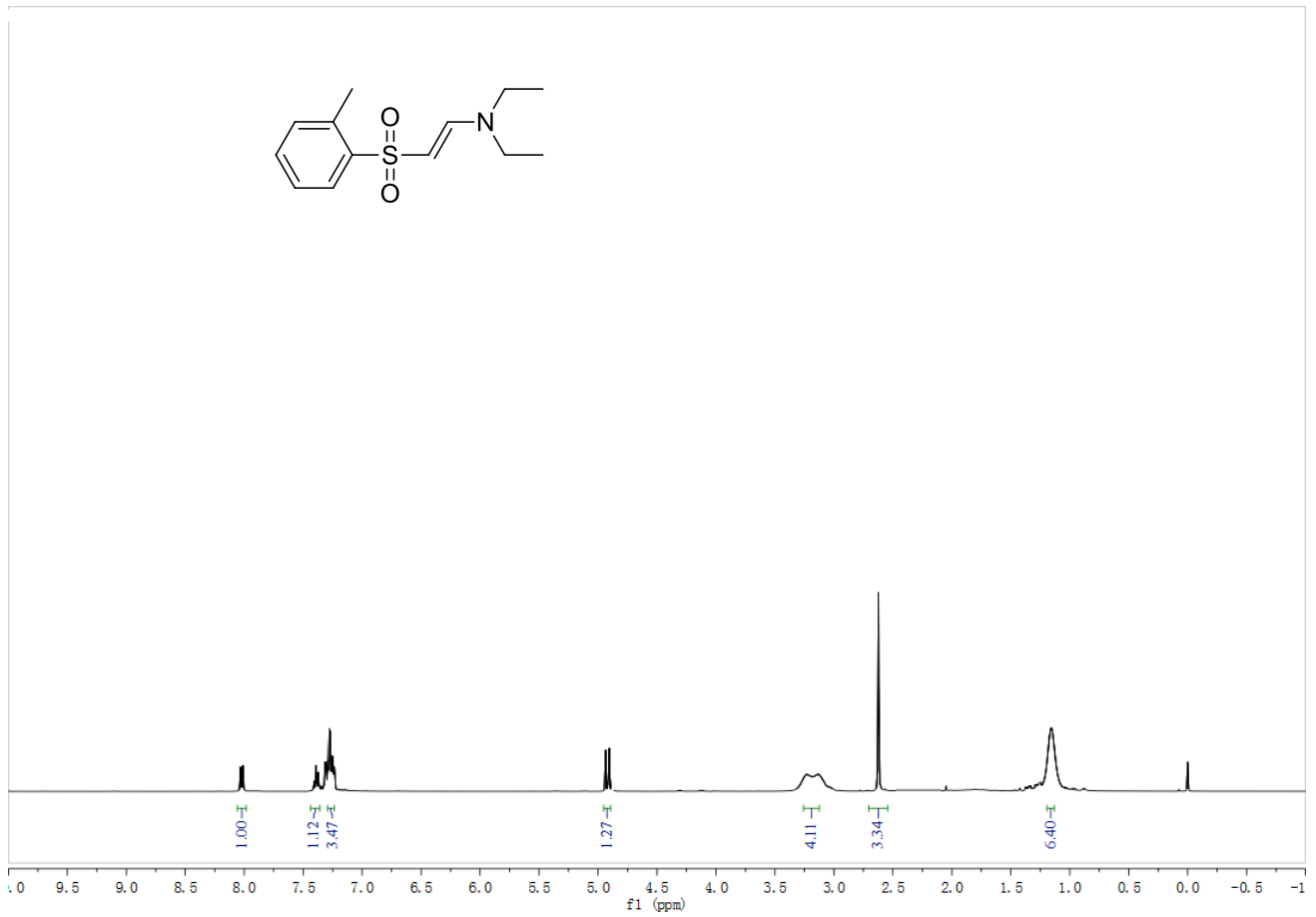
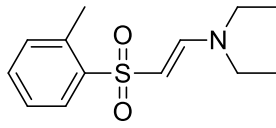




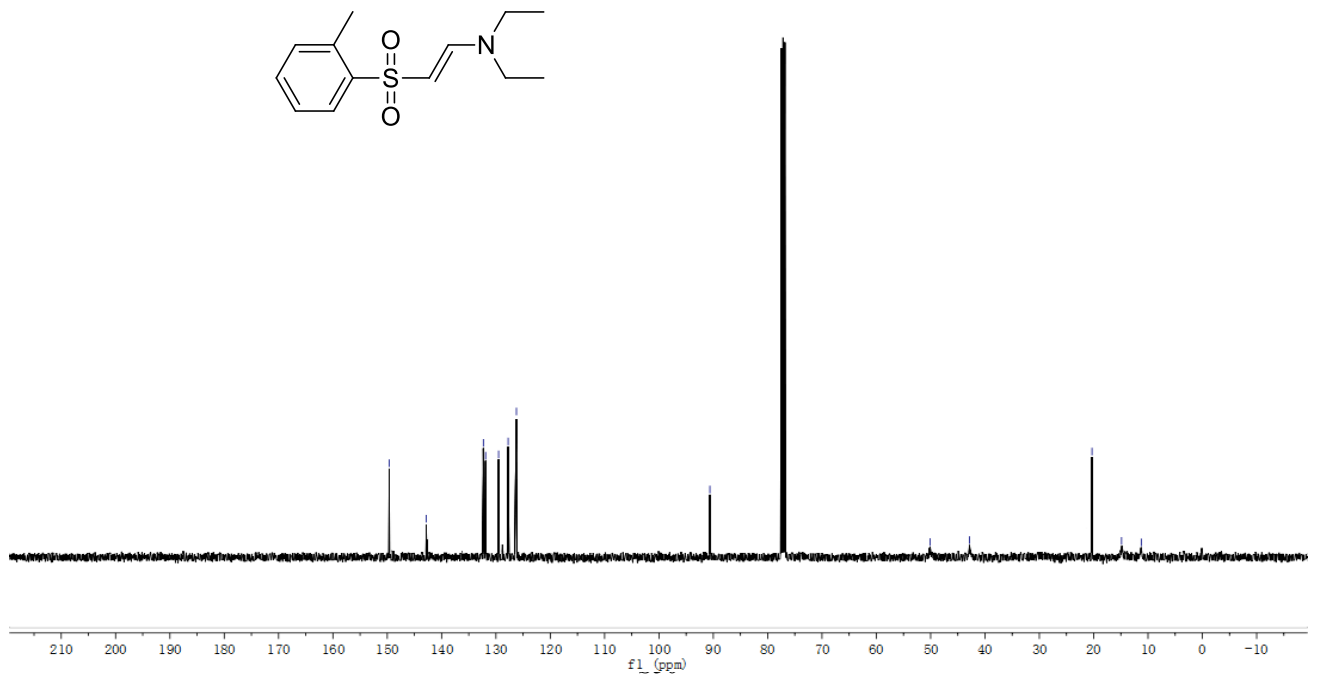
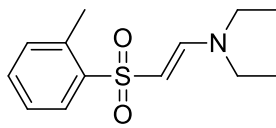


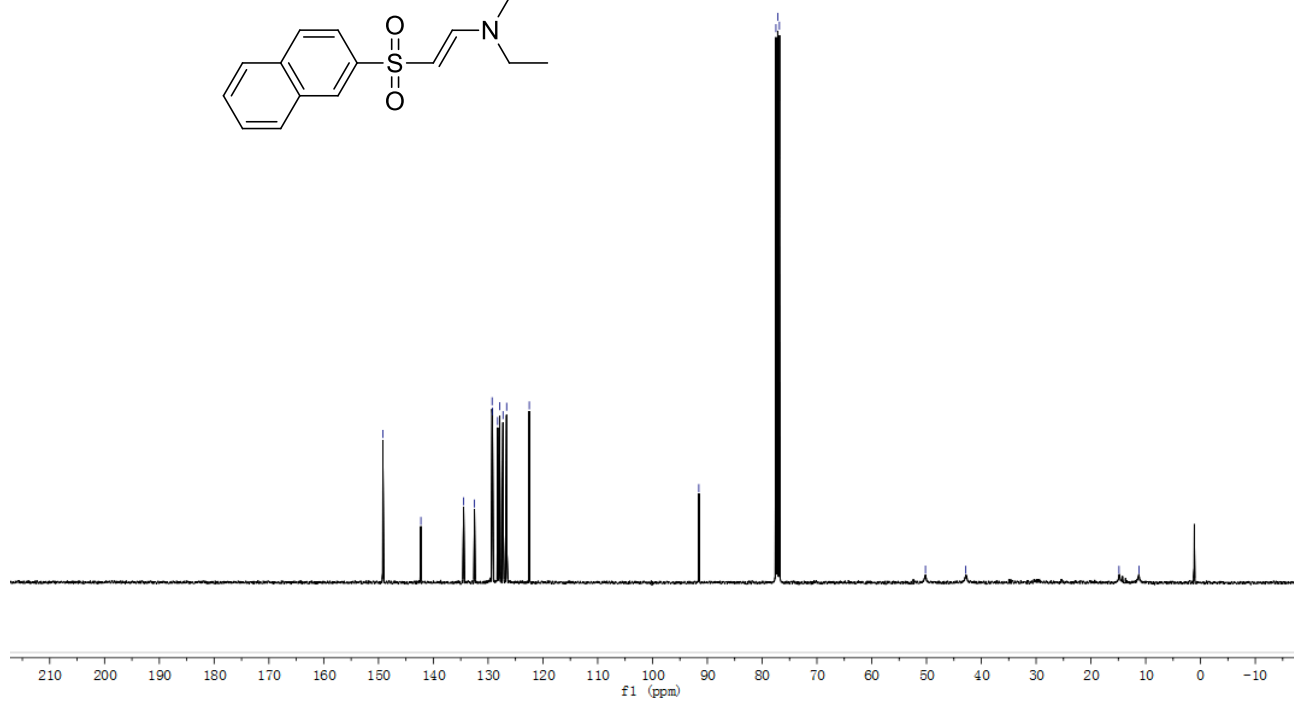
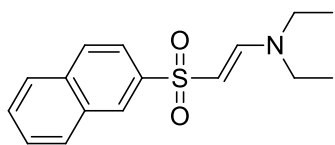
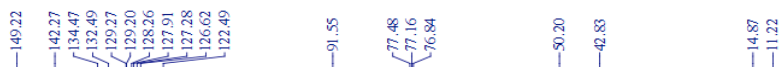
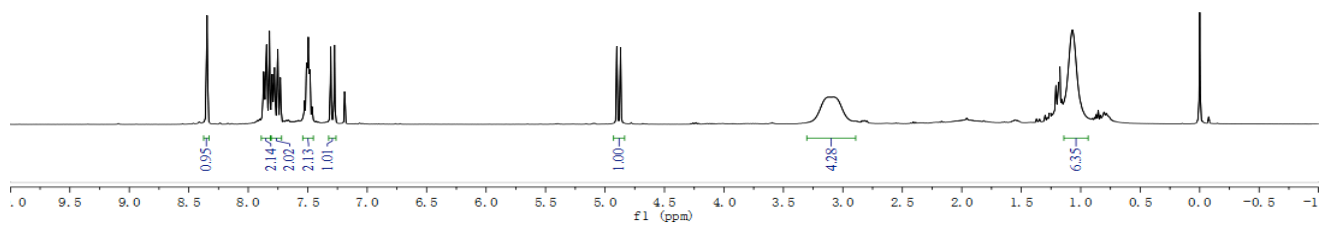
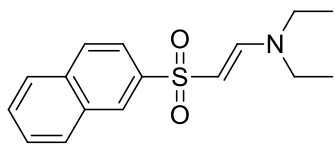


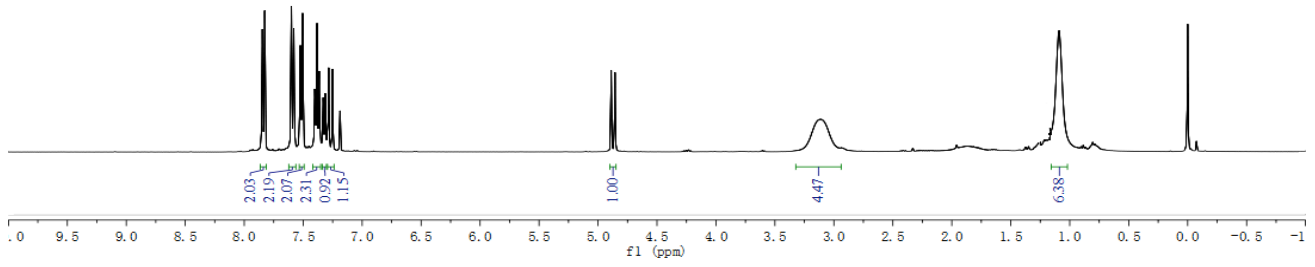
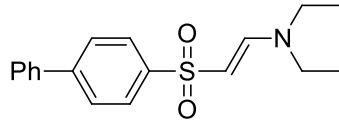




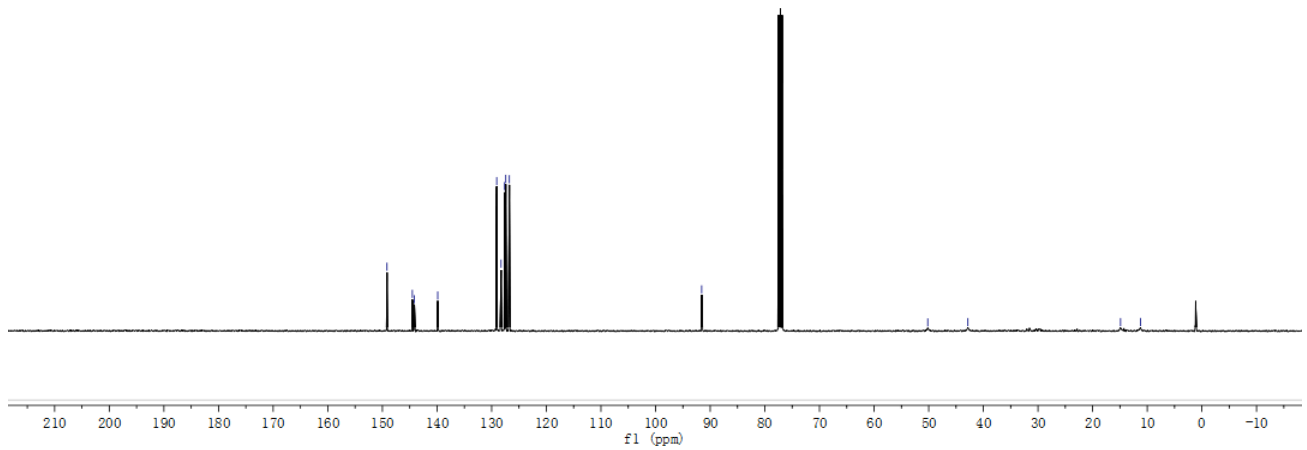
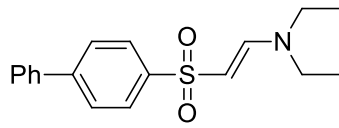
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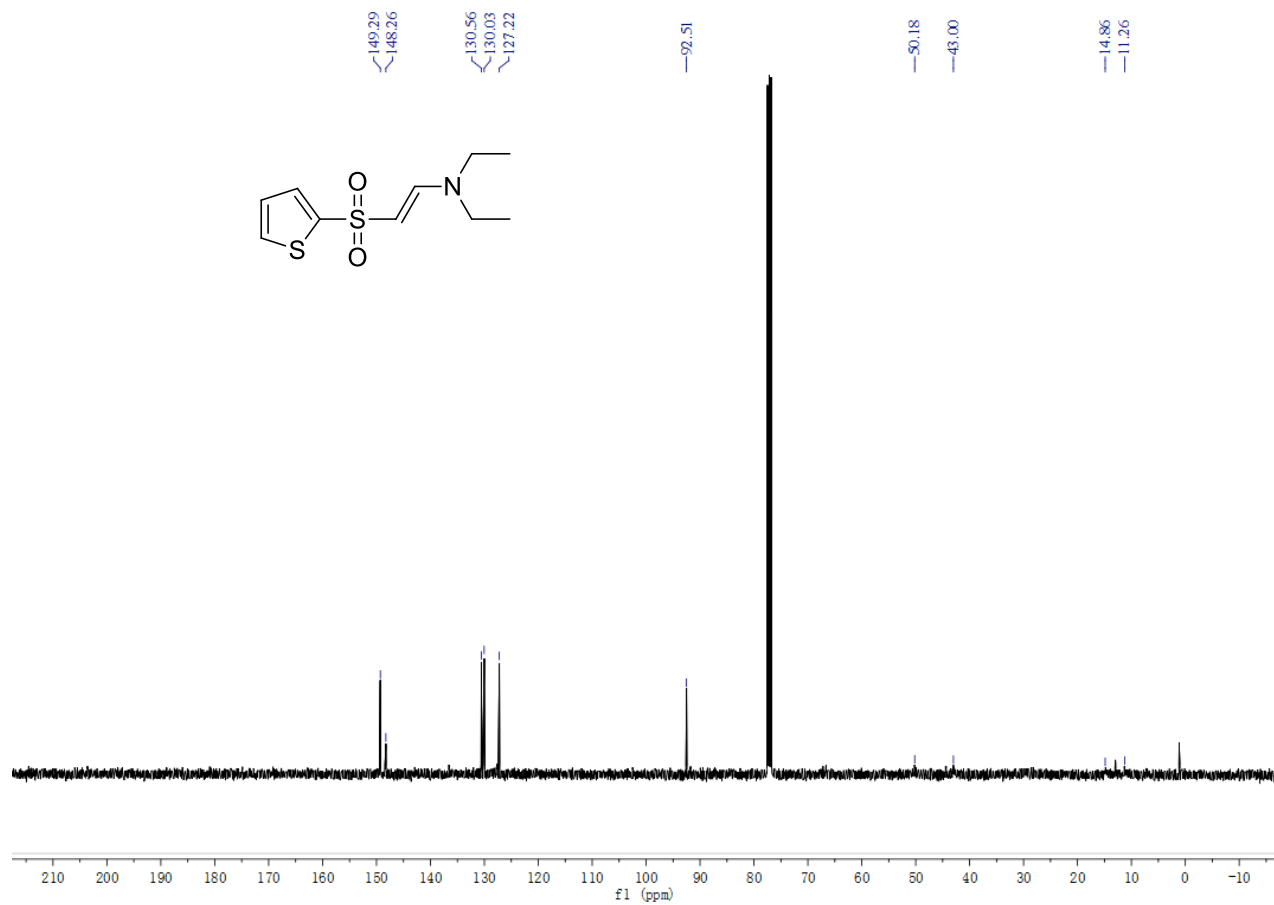
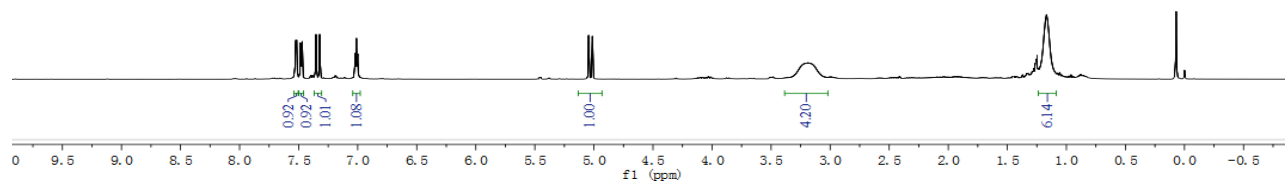
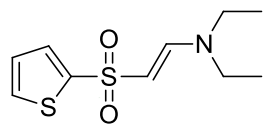


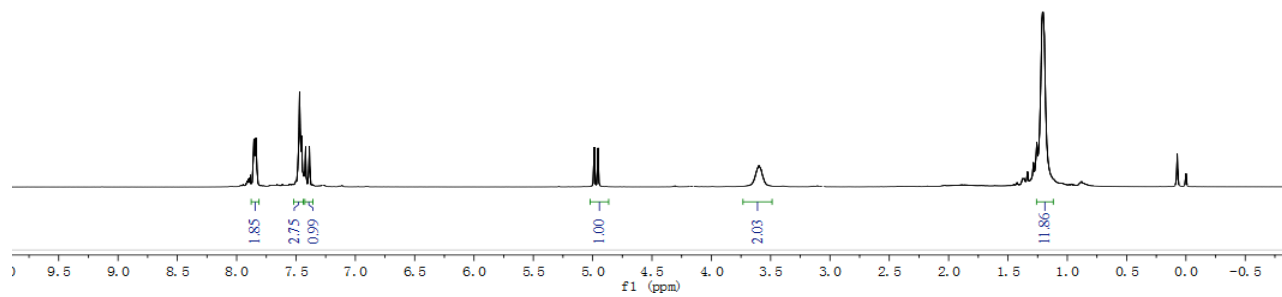
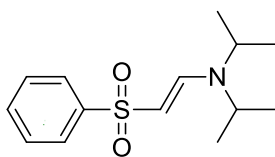




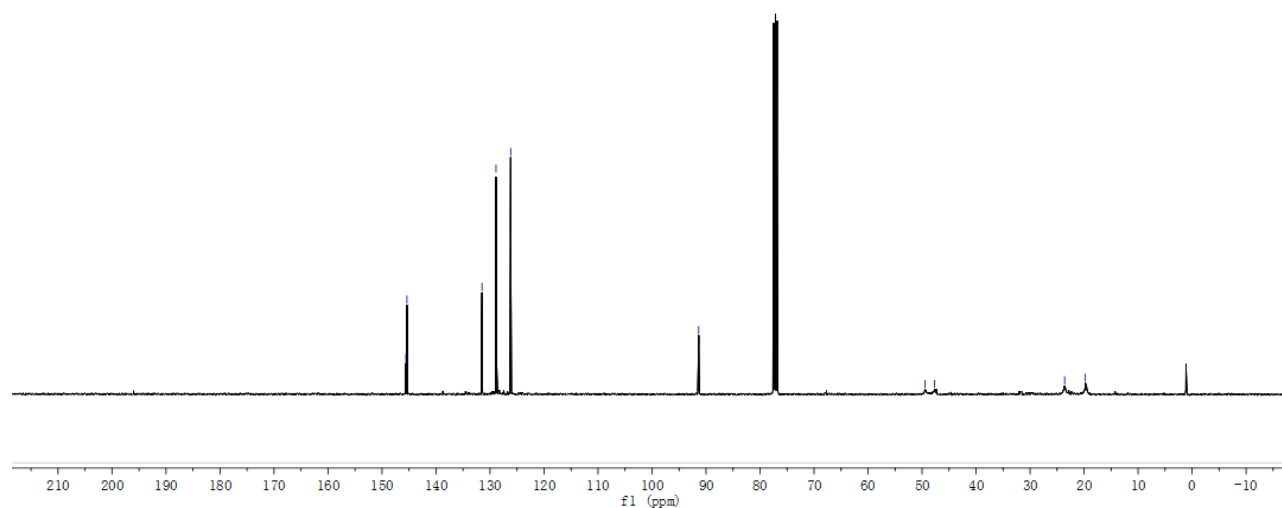
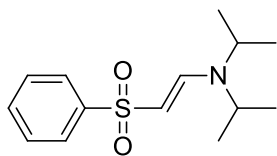
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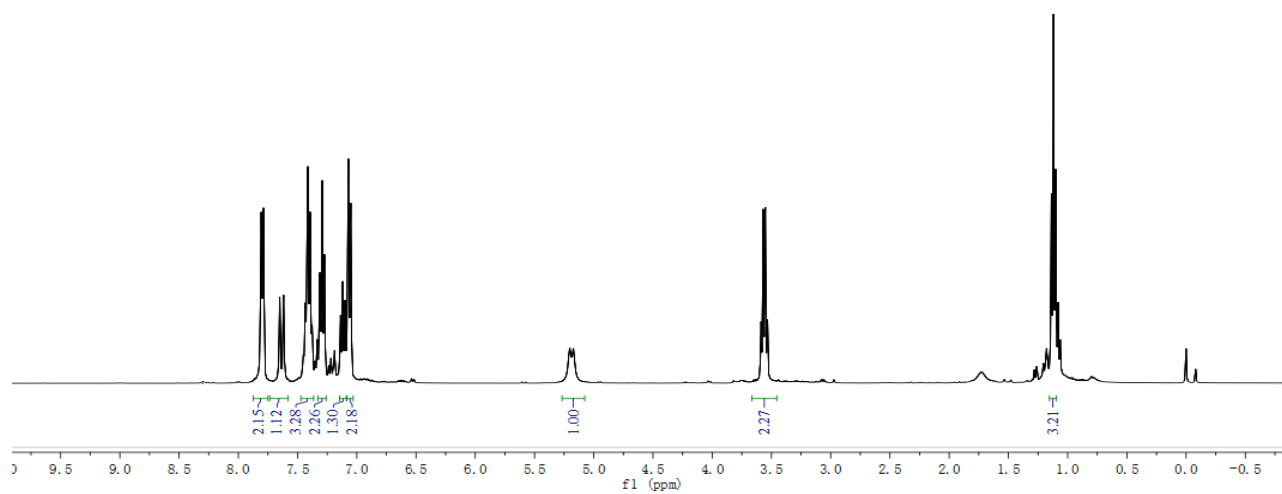
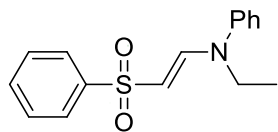






145.58
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128.89
126.18
91.35
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47.66
23.60
19.76





144.52, 131.96, 129.77, 129.71, 129.01, 126.95, 126.42, 125.77, 124.33, -97.52, 77.48, 77.16, 76.84, -40.15, -13.11

