
Supporting Information for

N-heterocyclic carbene-catalyzed regio- and stereoselective hydrothiolation reaction of alkynes

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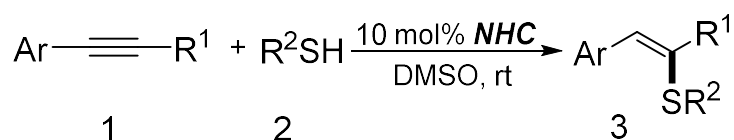
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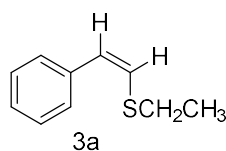
1. Experimental Section

All reactions were conducted under nitrogen atmosphere in oven-dried glassware with magnetic stirring bar. ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3) and ^{19}F NMR (376 MHz, CDCl_3) spectra were recorded using deuterated chloroform as solvent, with tetramethylsilane as an internal standard and reported in ppm (δ). Melting points were measured on a WRS-1B melting point apparatus and were uncorrected. Thiols and other chemicals were obtained from Adamas-beta and used without purification. Anhydrous THF and toluene were distilled from sodium and benzophenone. DMF, CH_2Cl_2 and CH_3CN were distilled from calcium hydride. DMSO was distilled from calcium hydride under vacuum. 1, 2-Dichloroethane was distilled from calcium chloride.

2. General procedure for NHC-catalyzed hydrothiolation reaction of alkynes



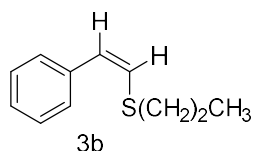
NHC **A** (7.8 mg, 10 mol%) was dissolved in 2.0 mL dry DMSO, followed by the addition of alkyne **1** (0.2 mmol), and thiol **2** (0.3 mmol) at ambient temperature. The reaction mixture was stirred at the same temperature for 10 h. Then, the mixture was diluted with EtOAc (30 mL), washed with water and dried over MgSO_4 . The solvent was removed *in vacuo* and the crude product was purified by flash column chromatography on silica gel (PE) to give the desired product.



(*Z/E*)-Ethyl(styryl)sulfane¹

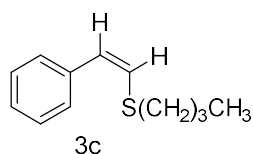
Colorless oil; yield: 87 %; an inseparable 17:1 *Z/E* mixture; Data for *Z*-**3a**: ^1H NMR (400 MHz, CDCl_3) δ 7.450 -7.45 (m, 2H), 7.37-7.32 (m, 2H), 7.26 – 7.15 (m, 1H), 6.45 (d, $J = 10.9$ Hz, 1H), 6.25 (d, $J = 10.9$ Hz, 1H), 2.80 (q, $J = 7.4$ Hz, 2H), 1.35 (t, $J = 7.4$ Hz, 3H). Selected data for *E*-**3a**: ^1H NMR (400 MHz, CDCl_3) δ 6.73 (d, $J =$

15.6 Hz, 1H), 6.47 (d, $J = 16.2$ Hz, 1H). Data for **Z-3a**: ^{13}C NMR (100 MHz, CDCl_3) δ 137.0, 128.6, 128.2, 127.2, 126.6, 125.5, 29.7, 15.4.



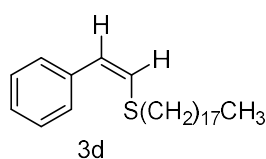
(Z/E)-Propyl(styryl)sulfane²

Colorless oil; yield: 86 % ; an inseparable 17:1 *Z/E* mixture; Data for **Z-3b**: ^1H NMR (400 MHz, CDCl_3) δ 7.53 – 7.47 (m, 2H), 7.40 – 7.30 (m, 2H), 7.24 – 7.14 (m, 1H), 6.42 (d, $J = 10.9$ Hz, 1H), 6.23 (d, $J = 10.9$ Hz, 1H), 2.75 (t, $J = 7.2$ Hz, 2H), 1.74 – 1.68 (m, 2H), 1.02 (t, $J = 7.3$ Hz, 3H). Selected data for **E-3b**: ^1H NMR (400 MHz, CDCl_3) δ 6.72 (d, $J = 15.6$ Hz, 1H), 6.46 (d, $J = 15.6$ Hz, 1H), 2.66 (m, 2H). Data for **Z-3b**: ^{13}C NMR (100 MHz, CDCl_3) δ 137.1, 128.6, 128.2, 127.7, 126.6, 125.3, 37.9, 23.6, 13.2.



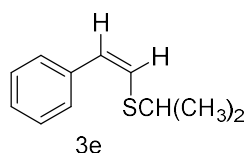
(Z/E)-Butyl(styryl)sulfane³

Colorless oil; yield: 83 %; an inseparable 14:1 *Z/E* mixture; Data for **Z-3c**: ^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.46 (m, 2H), 7.34 (t, $J = 7.8$ Hz, 2H), 7.30 – 7.15 (m, 1H), 6.42 (d, $J = 11.0$ Hz, 1H), 6.24 (d, $J = 10.9$ Hz, 1H), 2.77 (t, $J = 7.4$ Hz, 2H), 1.71–1.63 (m, 2H), 1.45 (dt, $J = 14.8, 7.3$ Hz, 2H), 0.93 (t, $J = 7.4$ Hz, 3H). Selected data for **E-3c**: ^1H NMR (400 MHz, CDCl_3) δ 6.72 (d, $J = 15.6$ Hz, 1H), 6.48 (d, $J = 15.6$ Hz, 1H), 2.68 (m, 2H). Data for **Z-3c**: ^{13}C NMR (100 MHz, CDCl_3) δ 137.1, 128.6, 128.2, 127.7, 126.6, 125.3, 35.6, 32.3, 21.7, 13.7.

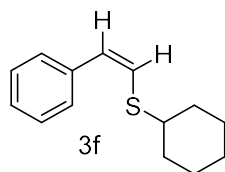


(Z/E)-Octadecyl(styryl)sulfane⁴

White solid; yield: 70 %; an inseparable 6:1 *Z/E* mixture; m.p. 46.3 – 49.2 °C; Data for *Z*-**3d**: ¹H NMR (400 MHz, CDCl₃) δ 7.50-7.46 (m, *J* = 2H), 7.39 – 7.27 (m, 3H), 7.23 – 7.16 (m, 1H), 6.43 (d, *J* = 10.8 Hz, 1H), 6.24 (d, *J* = 10.9 Hz, 1H), 2.78 (t, *J* = 7.4 Hz, 2H), 1.73-1.64 (m, 3H), 1.43 – 1.24(m, 29 H), 0.89 (t, *J* = 7.0 Hz, 3H). Selected data for *E*-**3d**: ¹H NMR (400 MHz, CDCl₃) δ 6.72 (d, *J* = 15.6 Hz, 1H). Data for *Z*-**3d**: ¹³C NMR (100 MHz, CDCl₃) δ 137.1, 128.6, 128.2, 127.7, 126.5, 125.2, 35.9, 32.0, 30.3, 29.72, 29.71, 29.68, 29.66, 29.6, 29.5, 29.4, 29.2, 28.6, 22.7.

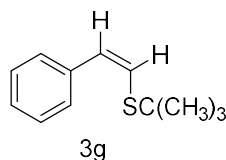
**(Z/E)-Isopropyl(styryl)sulfane⁵**

Colorless oil; yield: 66 %; an inseparable 17:1 *Z/E* mixture; Data for *Z*-**3e**: ¹H NMR (400 MHz, CDCl₃) δ 7.49-7.46(m, 2H), 7.39 – 7.28 (m, 2H), 7.22 – 7.16 (m, 1H), 6.45 (d, *J* = 11.0 Hz, 1H), 6.32 (d, *J* = 11.0 Hz, 1H), 3.15 (hept, *J* = 6.8 Hz, 1H), 1.39 (s, 3H), 1.37 (s, 3H). Selected data for *E*-**3e**: ¹H NMR (400 MHz, CDCl₃) δ 6.76 (d, *J* = 15.6 Hz, 1H), 6.57 (d, *J* = 15.7 Hz, 1H). Data for *Z*-**3e**: ¹³C NMR (100 MHz, CDCl₃) δ 137.1, 128.7, 128.2, 126.6, 125.9, 125.3, 39.2, 23.5.

**(Z/E)-Cyclohexyl(styryl)sulfane⁵**

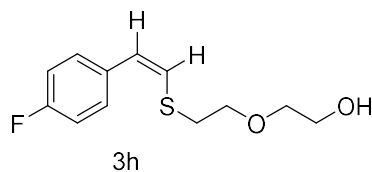
Colorless oil; yield: 95 %; an inseparable 20:1 *Z/E* mixture; Data for *Z*-**3f**: ¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.46 (m, 2H), 7.38 – 7.27 (m, 2H), 7.22 – 7.15 (m, 1H), 6.42 (d, *J* = 11.0 Hz, 1H), 6.32 (d, *J* = 11.0 Hz, 1H), 2.88 (tt, *J* = 10.7, 3.7 Hz, 1H), 2.09 – 2.03 (m, 2H), 1.83-1.76 (m, 2H), 1.65 – 1.59 (m, 1H), 1.51-1.41 (m, 2H), 1.37 – 1.23 (m, 3H). Selected data for *E*-**3f**: ¹H NMR (400 MHz, CDCl₃) δ 6.76 (d, *J* =

15.6 Hz, 1H), 6.56 (d, $J = 15.6$ Hz, 1H). Data for **Z-3f**: ^{13}C NMR (100 MHz, CDCl_3) δ 137.2, 128.6, 128.2, 126.5, 125.9, 125.0, 47.8, 33.7, 26.0, 25.6.



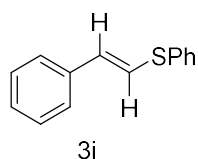
(Z/E)-Tert-butyl(styryl)sulfane⁵

Colorless oil; yield: 92 %; an inseparable 28:1 *Z/E* mixture; Data for **Z-3g**: ^1H NMR (400 MHz, CDCl_3) δ 7.56-7.52 (m, 2H), 7.43 – 7.36 (m, 2H), 7.27 – 7.21 (m, 1H), 6.53 (d, $J = 11.2$ Hz, 1H), 6.49 (d, $J = 11.2$ Hz, 1H), 1.47 (s, 9H). Selected data for **E-3g**: ^1H NMR (400 MHz, CDCl_3) δ 6.87 (d, $J = 15.5$ Hz, 1H), 6.72 (d, $J = 15.5$ Hz, 1H). Data for **Z-3g**: ^{13}C NMR (100 MHz, CDCl_3) δ 128.7, 128.2, 126.6, 125.4, 123.5, 44.5, 30.8.



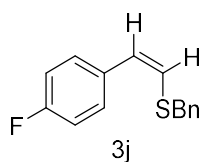
(Z)-2-(2-((4-Fluorostyryl)thio)ethoxy)ethan-1-ol

Colorless oil; yield: 98 %; IR (KBr): 3440, 2926, 2868, 2360, 1601, 1506, 1360, 1230, 1119, 837, 688 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.55 – 7.41 (m, 2H), 7.09 – 7.02 (m, 2H), 6.43 (d, $J = 10.8$ Hz, 1H), 6.26 (d, $J = 10.8$ Hz, 1H), 3.78 – 3.72 (m, 4H), 3.63 – 3.58 (m, 2H), 3.00 (t, $J = 6.5$ Hz, 2H), 2.15 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.4 (d, $J = 247.2$ Hz), 132.9 (d, $J = 3.3$ Hz), 130.3, 126.6 (d, $J = 2.3$ Hz), 124.9, 115.1, 72.2, 70.6, 61.7, 35.2. ^{19}F NMR (376 MHz, CDCl_3) δ -114.61. HRMS (ESI): m/z calcd for $\text{C}_{12}\text{H}_{16}\text{FO}_2\text{S}^+ (\text{M}+\text{H})^+$ 243.0850, found: 243.0846.



(E/Z)-Phenyl(styryl)sulfane⁶

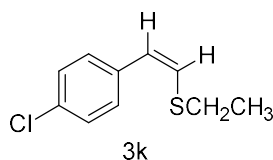
Colorless oil; yield: 52 %; an inseparable 4:1 *E/Z* mixture; Data for *E*-**3h**: ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.39 (m, 2H), 7.35 – 7.26 (m, 7H), 7.25 – 7.22 (m, 1H), 6.88 (d, $J = 15.4$ Hz, 1H), 6.73 (d, $J = 15.5$ Hz, 1H). Selected data for *Z*-**3h**: ^1H NMR (400 MHz, CDCl_3) δ 6.59 (d, $J = 10.7$ Hz, 1H), 6.50 (d, $J = 10.8$ Hz, 1H). Data for *E*-**3h**: ^{13}C NMR (100 MHz, CDCl_3) δ 136.5, 131.8, 129.9, 129.2, 128.7, 127.6, 127.0, 126.0, 123.4.



(Z)-Benzyl(4-fluorostyryl)sulfane⁷

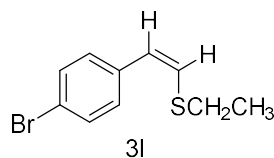
Colorless oil; Yield: 88 %; ^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.44 (m, 2H), 7.42 – 7.30 (m, 5H), 7.13 – 7.00 (m, 2H), 6.42 (d, $J = 10.9$ Hz, 1H), 6.26 (d, $J = 11.0$ Hz, 1H), 4.03 (s, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 161.4 (d, $J = 247.2$ Hz), 137.3, 133.1 (d, $J = 3.3$ Hz), 130.3 (d, $J = 8.8$ Hz), 129.0, 128.7, 127.5, 125.6 (d, $J = 2.2$ Hz), 124.8, 115.2 (d, $J = 21.5$ Hz), 39.4. ^{19}F NMR (376 MHz, CDCl_3) δ -114.66.



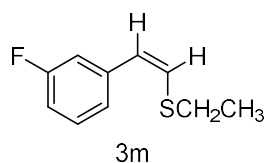
(Z/E)-(4-Chlorostyryl)(ethyl)sulfane⁸

Colorless oil; yield: 93 %; an inseparable 10:1 *Z/E* mixture; Data for *Z*-**3k**: ^1H NMR (400 MHz, CDCl_3) δ 7.47 – 7.41 (m, 2H), 7.37 – 7.32 (m, 2H), 6.42 (d, $J = 10.9$ Hz, 1H), 6.31 (d, $J = 10.9$ Hz, 1H), 2.84 (q, $J = 7.4$ Hz, 2H), 1.39 (t, $J = 7.4$ Hz, 3H). Selected data for *E*-**3k**: ^1H NMR (400 MHz, CDCl_3) δ 6.71 (d, $J = 15.6$ Hz, 1H). Data for *Z*-**3k**: ^{13}C NMR (100 MHz, CDCl_3) δ 135.5, 132.1, 129.8, 128.4, 128.0, 124.3, 29.8, 15.4.



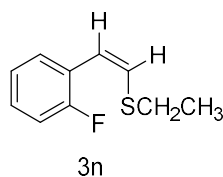
(*Z/E*)-(4-Bromostyryl)(ethyl)sulfane

Colorless oil; yield: 89 %; an inseparable 8:1 *Z/E* mixture; IR (KBr): 3424, 2970, 2925, 2360, 1595, 1384, 1263, 1072, 827 cm^{-1} ; Data for *Z*-**3j**: ^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.47 (m, 2H), 7.40 – 7.35 (m, 2H), 6.40 (d, J = 10.9 Hz, 1H), 6.33 (d, J = 11.0 Hz, 1H), 2.84 (q, J = 7.4 Hz, 2H), 1.39 (t, J = 7.4 Hz, 3H). Selected data for *E*-**3j**: ^1H NMR (400 MHz, CDCl_3) δ 6.73 (d, J = 15.6 Hz, 1H). Data for *Z*-**3j**: ^{13}C NMR (100 MHz, CDCl_3) δ 135.9, 131.3, 130.1, 128.3, 124.3, 120.3, 29.8, 15.4. HRMS (ESI): m/z calcd for $\text{C}_{10}\text{H}_{12}\text{BrS}^+$ ($\text{M}+\text{H}$) $^+$: 242.9838, found: 242.9838.



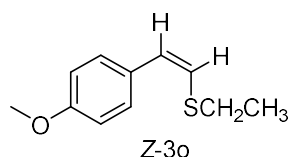
(*Z/E*)-Ethyl(3-fluorostyryl)sulfane

Colorless oil; yield: 81 %; an inseparable 6:1 *Z/E* mixture; IR (KBr): 3442, 2972, 2928, 1609, 1489, 1442, 1364, 1265, 956, 869, 784, 672 cm^{-1} ; Data for *Z*-**3m**: ^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.29 (m, 1H), 7.26 (d, J = 7.4 Hz, 2H), 6.97 – 6.90 (m, 1H), 6.44 (d, J = 11.1 Hz, 1H), 6.36 (d, J = 10.9 Hz, 1H), 2.85 (q, J = 7.4 Hz, 2H), 1.40 (t, J = 7.4 Hz, 3H). Selected data for *E*-**3m**: ^1H NMR (400 MHz, CDCl_3) δ 6.63 (d, J = 15.6 Hz, 1H). Data for *Z*-**3m**: ^{13}C NMR (100 MHz, CDCl_3) δ 162.7 (d, J = 244.6 Hz), 139.2 (d, J = 7.9 Hz), 129.6 (d, J = 8.5 Hz), 128.9, 124.4 (d, J = 2.7 Hz), 124.3 (d, J = 2.6 Hz), 115.1 (d, J = 22.2 Hz), 113.3, 29.8, 15.4. Selected data for *E*-**3m**: ^{13}C NMR (100 MHz, CDCl_3) δ 26.5, 14.5. Data for *Z*-**3m**: ^{19}F NMR (376 MHz, CDCl_3) δ -113.41 (s, 1F). Data for *E*-**3m**: ^{19}F NMR (376 MHz, CDCl_3) δ -113.53 (s, 1F). HRMS (ESI): m/z calcd for $\text{C}_{10}\text{H}_{12}\text{FS}^+$ ($\text{M}+\text{H}$) $^+$: 183.0638, found: 183.0640.



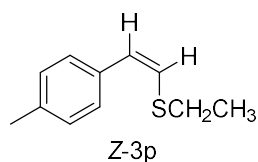
(Z/E)-ethyl(2-fluorostyryl)sulfane

Colorless oil; yield: 99 %; an inseparable 13:1 *Z/E* mixture; IR (KBr): 3441, 2968, 2927, 1568, 1481, 1451, 1235, 1097, 820, 758 cm^{-1} ; Data for *Z*-**3n**: ^1H NMR (400 MHz, CDCl_3) δ 7.73 (td, $J = 7.7, 2.0$ Hz, 1H), 7.23 – 7.11 (m, 2H), 7.06 – 7.00 (m, 1H), 6.64 (d, $J = 11.0$ Hz, 1H), 6.39 (d, $J = 11.0$ Hz, 1H), 2.81 (q, $J = 7.4$ Hz, 2H), 1.36 (t, $J = 7.4$ Hz, 3H). Selected data for *E*-**3n**: ^1H NMR (400 MHz, CDCl_3) δ 6.86 (d, $J = 15.8$ Hz, 1H), 6.55 (d, $J = 15.6$ Hz, 1H). Data for *Z*-**3n**: ^{13}C NMR (100 MHz, CDCl_3) δ 159.8 (d, $J = 248.8$ Hz), 129.3 (d, $J = 1.3$ Hz), 129.2, 128.2 (d, $J = 8.4$ Hz), 124.9 (d, $J = 12.1$ Hz), 123.6 (d, $J = 3.7$ Hz), 117.1 (d, $J = 6.8$ Hz), 115.1 (d, $J = 22.2$ Hz), 29.6, 15.4. Data for *Z*-**3n**: ^{19}F NMR (376 MHz, CDCl_3) δ -117.23 (s, 1F). Data for *E*-**3n**: -118.77 (s, 1F). HRMS (ESI): m/z calcd for $\text{C}_{10}\text{H}_{12}\text{FS}^+$ ($\text{M}+\text{H}$) $^+$ 183.0638, found: 183.0638.



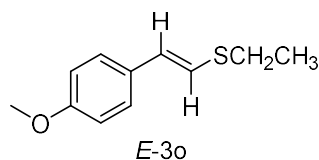
(Z/E)-ethyl(4-methoxystyryl)sulfane

Colorless oil; yield: 64 %; an inseparable 1.3:1 *Z/E* mixture; IR (KBr): 3432, 2967, 2926, 1593, 1471, 1426, 1365, 1265, 1215, 1148, 1095, 867, 826, 743 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.39 (m, 2H), 6.92 – 6.87 (m, 2H), 6.40 (d, $J = 10.8$ Hz, 1H), 6.12 (d, $J = 10.8$ Hz, 1H), 3.81 (s, 3H), 2.79 (m, 2H), 1.34 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.2, 129.9, 126.7, 124.5, 122.1, 113.7, 55.3, 29.6, 15.4. HRMS (ESI): m/z calcd for $\text{C}_{11}\text{H}_{15}\text{OS}^+$ ($\text{M}+\text{H}$) $^+$ 195.0838, found: 195.0838.



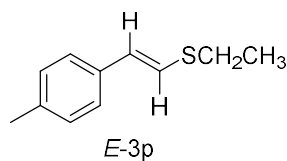
(Z/E)-Ethyl(4-methylstyryl)sulfane⁹

Colorless oil; yield: 41 %; an inseparable 2.5:1 *Z/E* mixture; ¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.17 – 7.14 (m, 2H), 6.42 (d, *J* = 10.7 Hz, 1H), 6.18 (d, *J* = 10.9 Hz, 1H), 2.81 – 2.76 (m, 2H), 2.33 (s, 3H), 1.35 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 136.4, 134.3, 128.9, 128.6, 126.0, 125.5, 29.7, 21.3, 15.4.



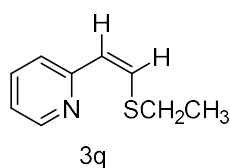
(E/Z)-Ethyl(4-methoxystyryl)sulfane

Colorless oil; yield: 99 %; an inseparable 1.8:1 *E/Z* mixture; IR (KBr): 3441, 2926, 2870, 1606, 1509, 1252, 1174, 1034, 832 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.23 (m, 2H), 6.90 – 6.85 (m, 2H), 6.60 (d, *J* = 15.5 Hz, 1H), 6.50 (d, *J* = 15.6 Hz, 1H), 3.83 (s, 3H), 2.83 (m, 2H), 1.39 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 158.7, 130.0, 127.4, 125.2, 122.1, 114.1, 55.3, 26.8, 14.7. HRMS (ESI): *m/z* calcd for C₁₁H₁₅OS⁺ (*M*+H)⁺ 195.0838, found 195.0838.



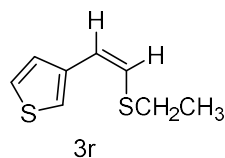
(E/Z)-Ethyl(4-methylstyryl)sulfane⁹

Colorless oil; yield: 99 %; an inseparable 2.5:1 *E/Z* mixture; ¹H NMR (400 MHz, CDCl₃) δ 7.18 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.65 (d, *J* = 15.6 Hz, 1H), 6.45 (d, *J* = 15.3 Hz, 1H), 2.84 – 2.79 (m, 2H), 2.31 (s, 3H), 1.36 (d, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 136.6, 134.4, 129.3, 127.3, 125.4, 123.6, 26.7, 21.2, 14.7.



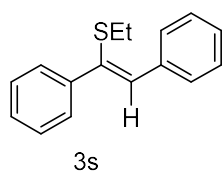
(Z/E)-2-(2-(Ethylthio)vinyl)pyridine

Colorless oil; yield: 99 %; an inseparable 8:1 *Z/E* mixture; IR (KBr): 3436, 2926, 1723, 1686, 1526, 1350, 1187, 785, 741 cm⁻¹; Data for *Z*-**3o**: ¹H NMR (400 MHz, CDCl₃) δ 8.67 (d, *J* = 4.8 Hz, 1H), 7.61 (td, *J* = 7.7, 1.8 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.07 – 7.02 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H), 6.60 (d, *J* = 10.7 Hz, 1H), 6.50 (d, *J* = 10.6 Hz, 1H), 2.78 (q, *J* = 7.4 Hz, 2H), 1.38 (t, *J* = 7.4 Hz, 3H). Selected data for *E*-**3o**: ¹H NMR (400 MHz, CDCl₃) δ 2.88 (q, *J* = 7.4 Hz, 2H). Data for *E*-**3o**: ¹³C NMR (100 MHz, CDCl₃) δ 156.0, 148.8, 135.9, 133.8, 123.4, 122.9, 120.4, 30.2, 15.4. Selected data for *E*-**3o**: ¹³C NMR (100 MHz, CDCl₃) δ 26.3, 14.5. HRMS (ESI): *m/z* calcd for C₉H₁₂NS⁺ (*M*+H)⁺ 166.0685, found: 166.0685.



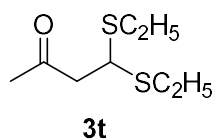
(Z)-3-(2-(Ethylthio)vinyl)thiophene

Colorless oil; yield: 98 %; IR (KBr): 3442, 2966, 2925, 1593, 1384, 1341, 1265, 841, 781, 609 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.44 (m, 1H), 7.33 – 7.26 (m, 2H), 6.53 (d, *J* = 10.6 Hz, 1H), 6.22 (d, *J* = 10.6 Hz, 1H), 2.86 (q, *J* = 7.4 Hz, 2H), 1.40 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 138.4, 128.7, 126.0, 124.8, 123.1, 119.8, 29.3, 15.5. HRMS (ESI): *m/z* calcd for C₈H₁₁S₂⁺ (*M*+H)⁺ 171.0297, found 171.0291.

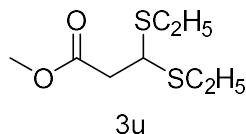


(Z/E)-(1,2-Diphenylvinyl)(ethyl)sulfane¹⁰

Colorless oil; yield: 68 %; an inseparable 17:1 *Z/E* mixture; Data for *Z*-**3s**: ¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.68 (m, 2H), 7.62 – 7.57 (m, 2H), 7.41 – 7.31 (m, 5H), 7.28 – 7.22 (m, 1H), 6.81 (s, 1H), 2.43 (q, *J* = 7.3 Hz, 2H), 1.07 (t, *J* = 7.4 Hz, 3H). Selected data for *E*-**3s**: ¹H NMR (400 MHz, CDCl₃) δ 6.74 (s, 1H), 2.54 (q, *J* = 7.4 Hz, 2H), 1.22 (t, *J* = 7.4 Hz, 3H). Data for *Z*-**3s**: ¹³C NMR (100 MHz, CDCl₃) δ 141.2, 137.2, 132.2, 129.7, 128.4, 128.3, 128.1, 127.9, 127.2, 27.0, 15.0. Selected data for *E*-**3s**: ¹³C NMR (100 MHz, CDCl₃) δ 26.0, 14.4.

**4,4-Bis(ethylthio)butan-2-one**¹¹

colorless oil; Yield: 61 % . ¹H NMR (400 MHz, CDCl₃) δ 4.30 (t, *J* = 7.1 Hz, 1H), 2.92 (d, *J* = 7.1 Hz, 2H), 2.76 – 2.57 (m, 4H), 2.20 (s, 3H), 1.27 (t, *J* = 7.4 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 204.77 , 50.30 , 45.31 , 30.70 , 24.76 , 14.41 .

**Methyl 3,3-bis(ethylthio)propanoate**¹²

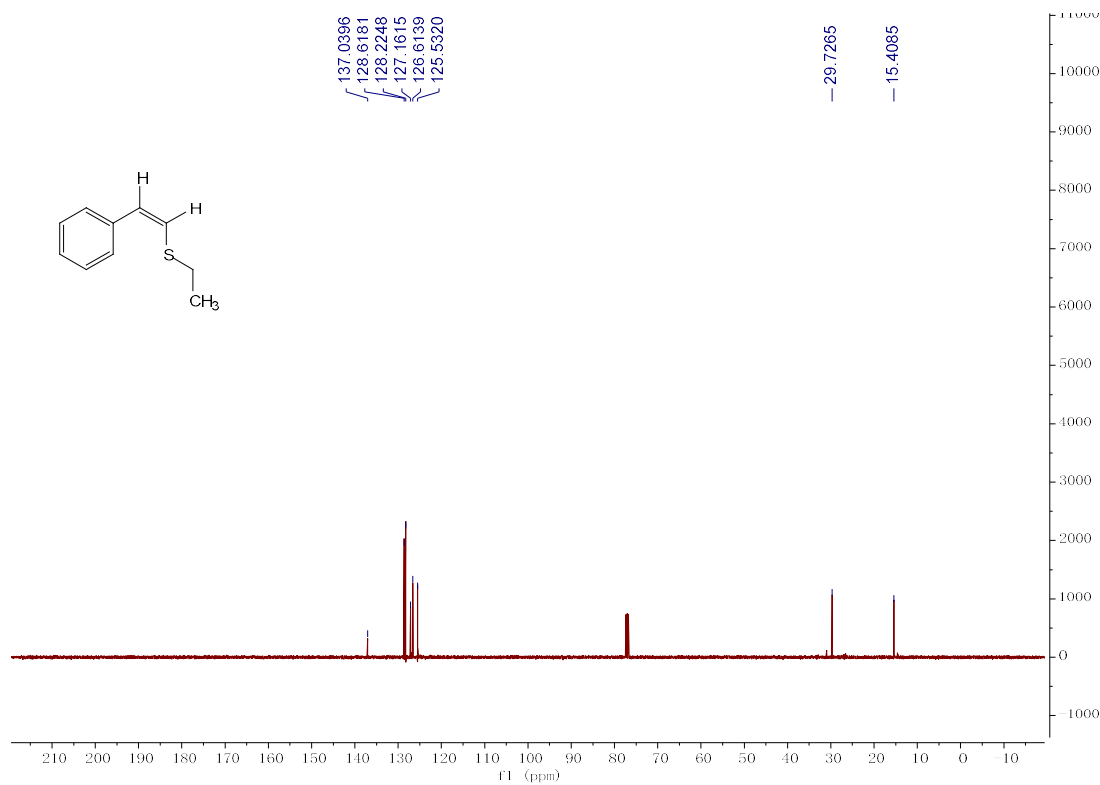
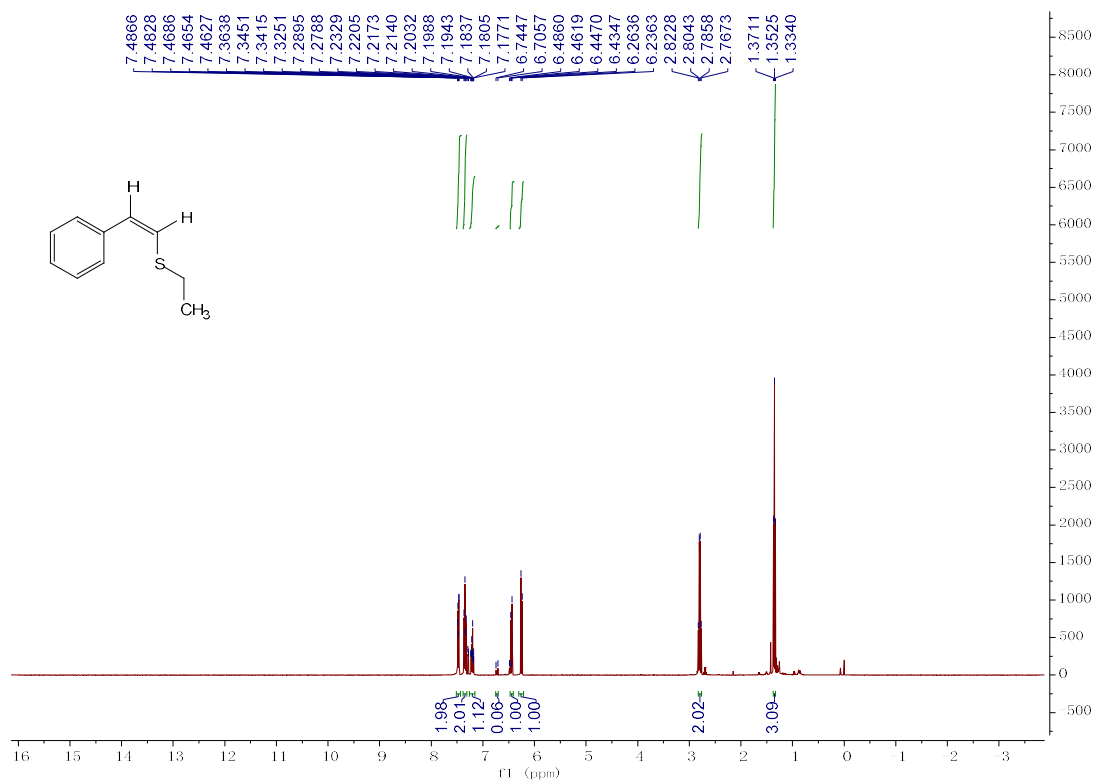
colorless oil; Yield: 82 % . ¹H NMR (400 MHz, CDCl₃) δ 4.25 (t, *J* = 7.6 Hz, 1H), 3.73 (s, 3H), 2.82 (d, *J* = 7.6 Hz, 2H), 2.75 – 2.59 (m, 4H), 1.27 (t, *J* = 7.4 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 170.65 , 51.98 , 46.56 , 41.79 , 24.48 , 14.40 .

References

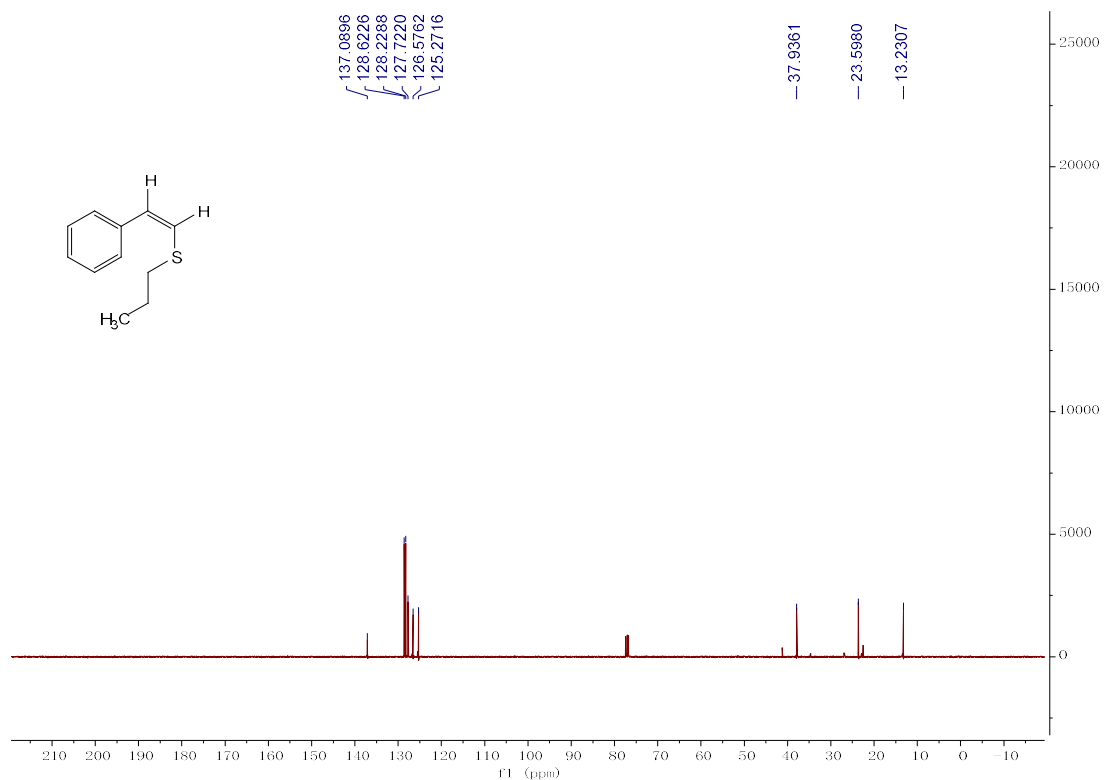
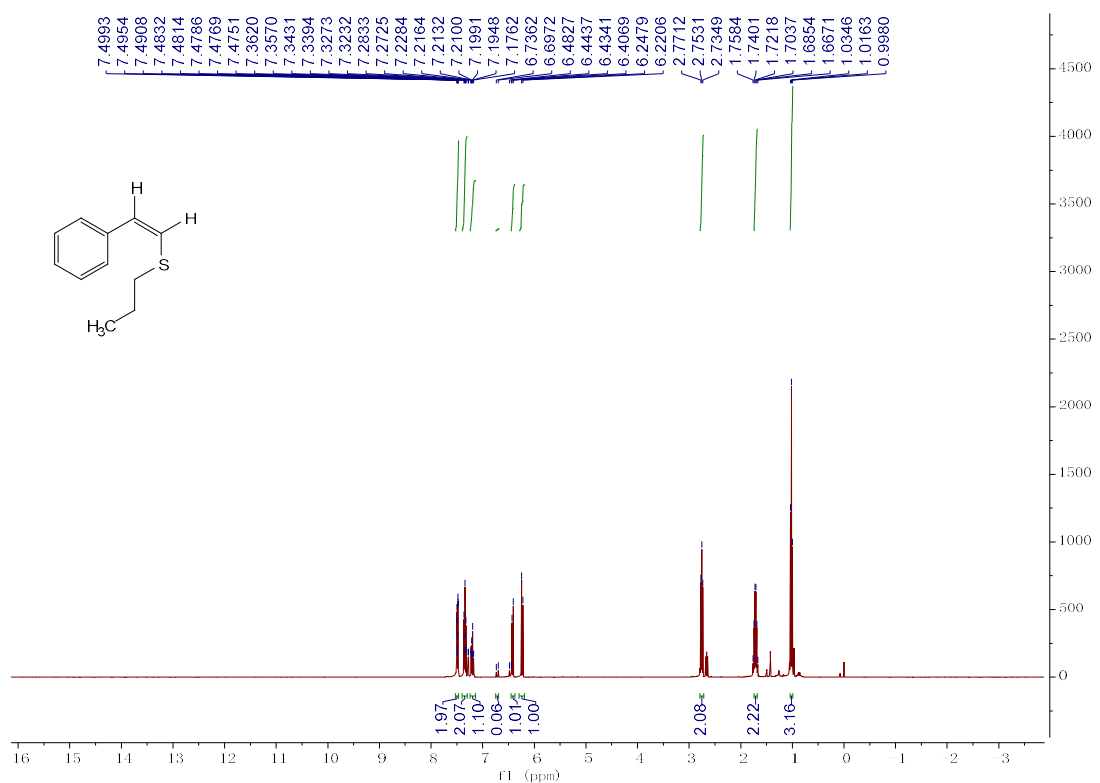
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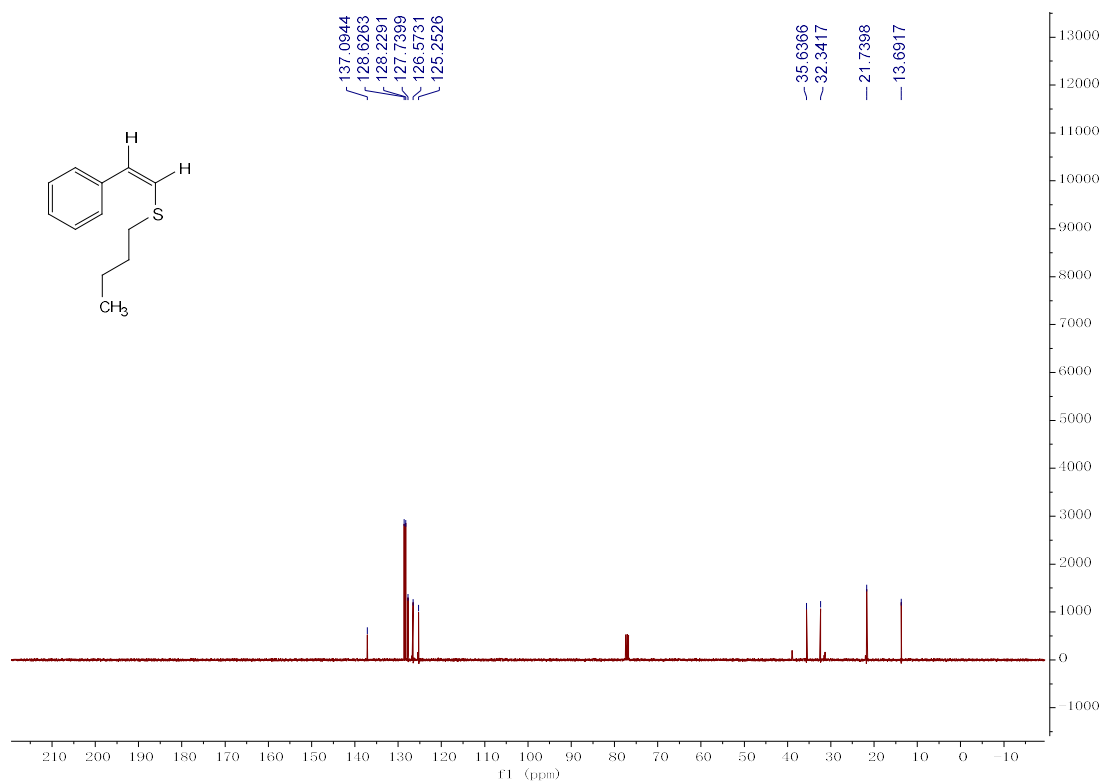
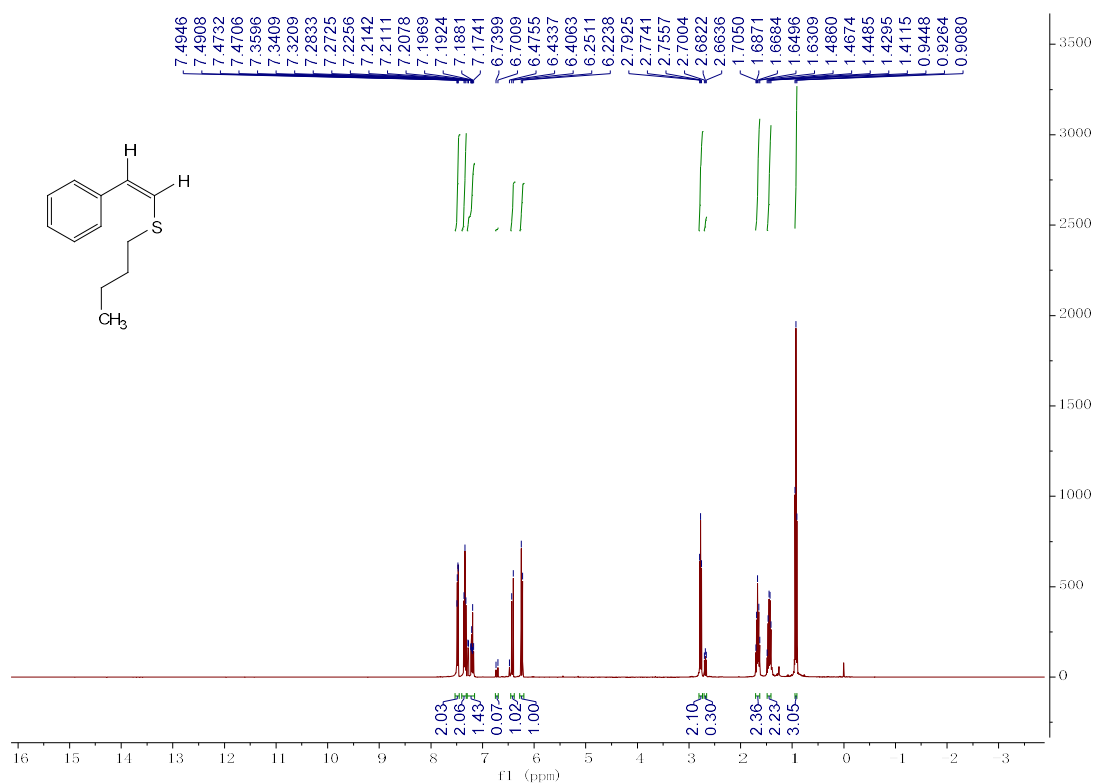
(Z/E)-Ethyl(styryl)sulfane(3a)



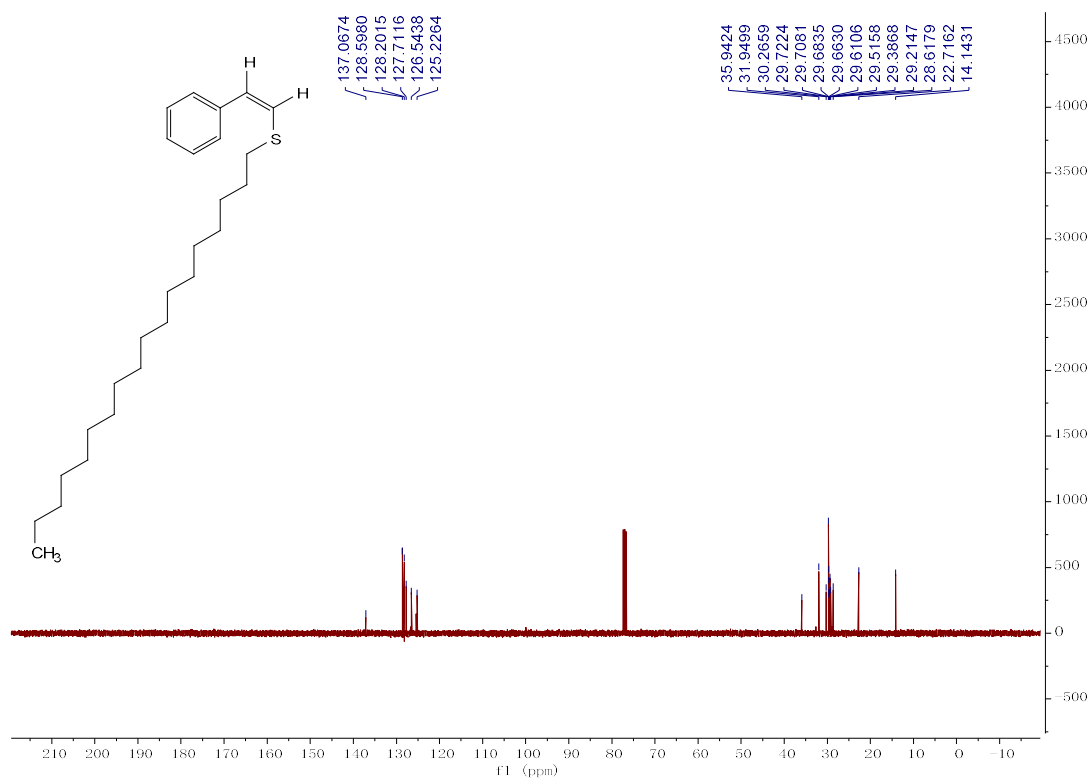
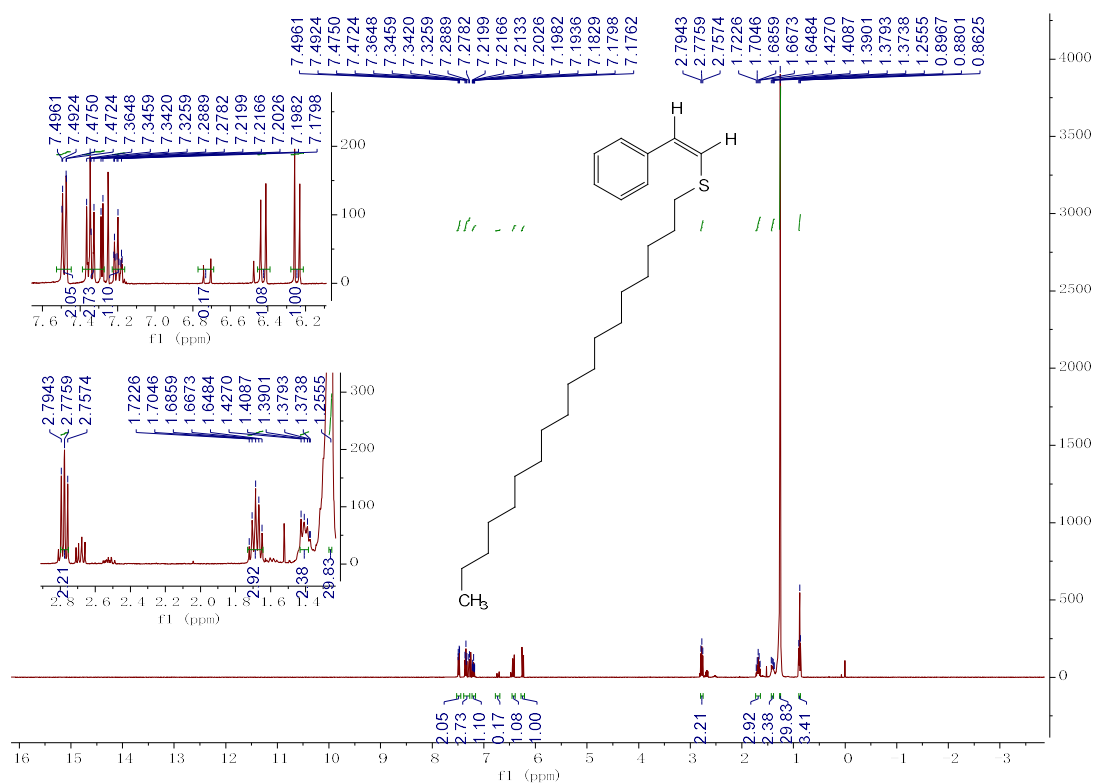
(Z/E)-Propyl(styryl)sulfane(3b)



(Z/E)-Butyl(styryl)sulfane(3c)



(Z/E)-Octadecyl(styryl)sulfane(3d)

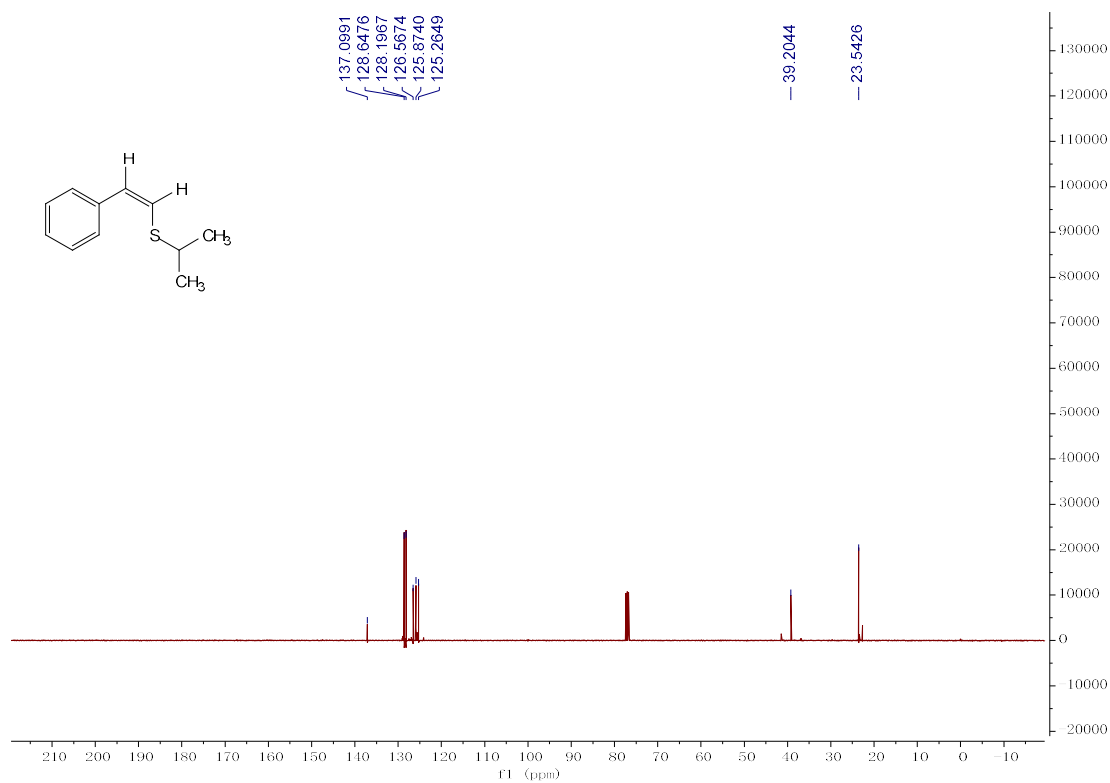


Chemical structure: CC(C)S/C=C/c1ccccc1

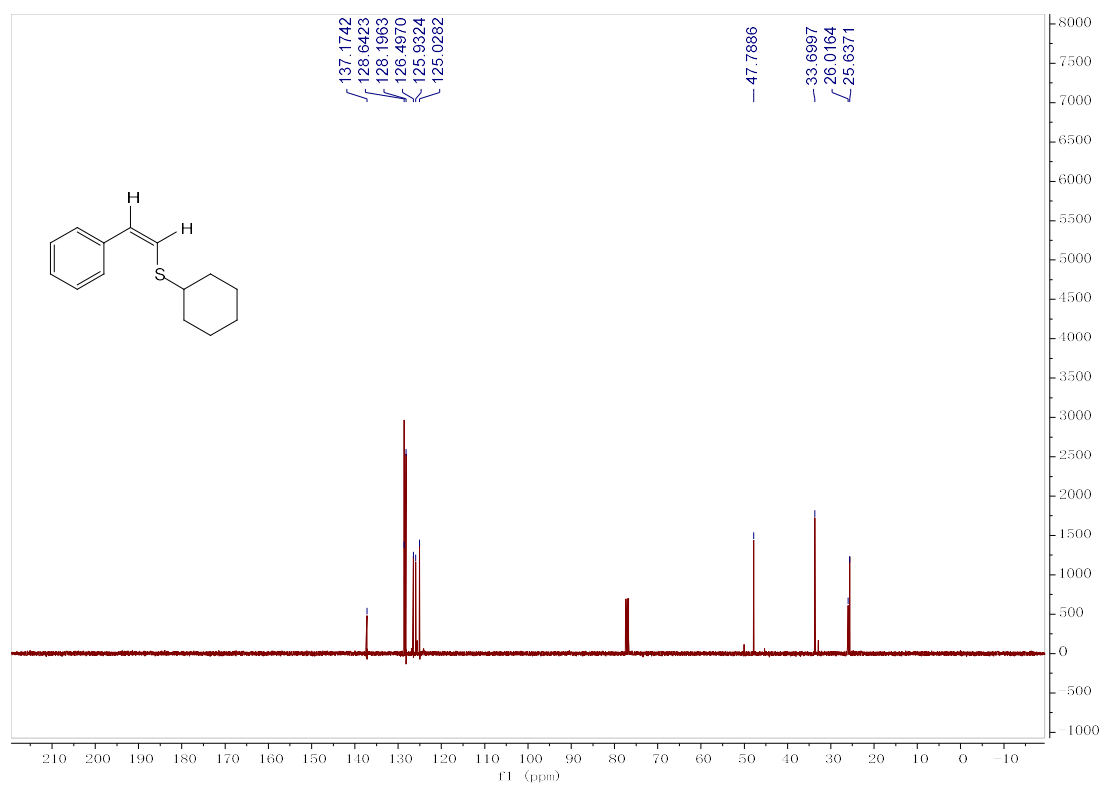
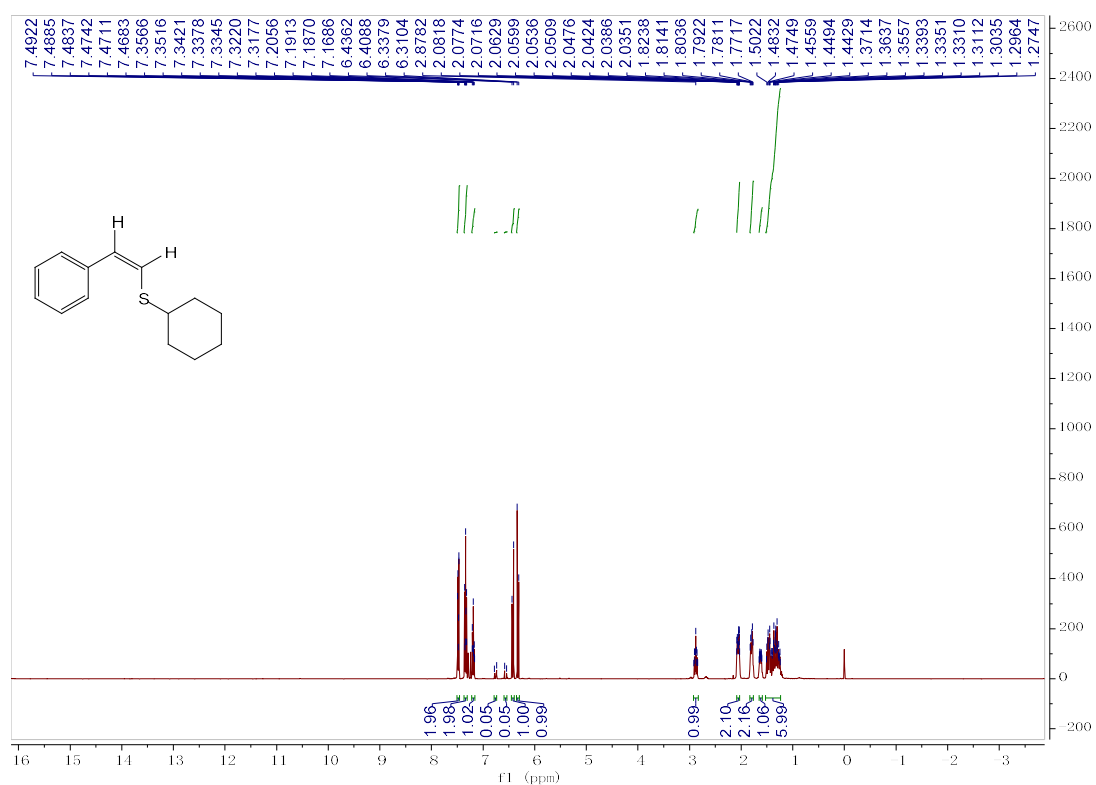
¹H NMR spectrum (ppm):

- 7.4859, 7.4823, 7.4647, 7.4632, 7.4616, 7.3617, 7.3568, 7.3471, 7.3427, 7.3390, 7.3272, 7.3229, 7.3003, 7.2174, 7.2142, 7.2110, 7.2001, 7.1957, 7.1912, 7.1773, 6.7805, 6.7414, 6.5904, 6.5513, 6.4641, 6.4367, 6.3371, 6.3096, 3.1961, 3.1791, 3.1623, 3.1453, 3.1285, 3.1115, 3.0946, 1.3858, 1.3689

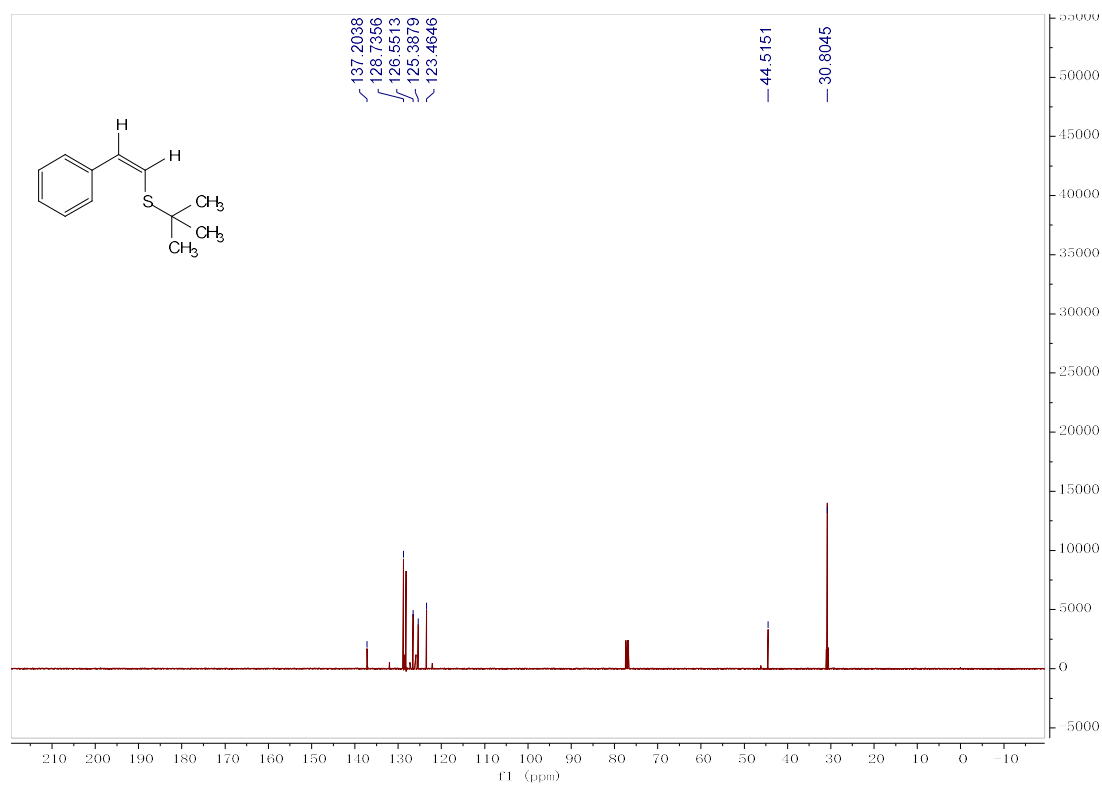
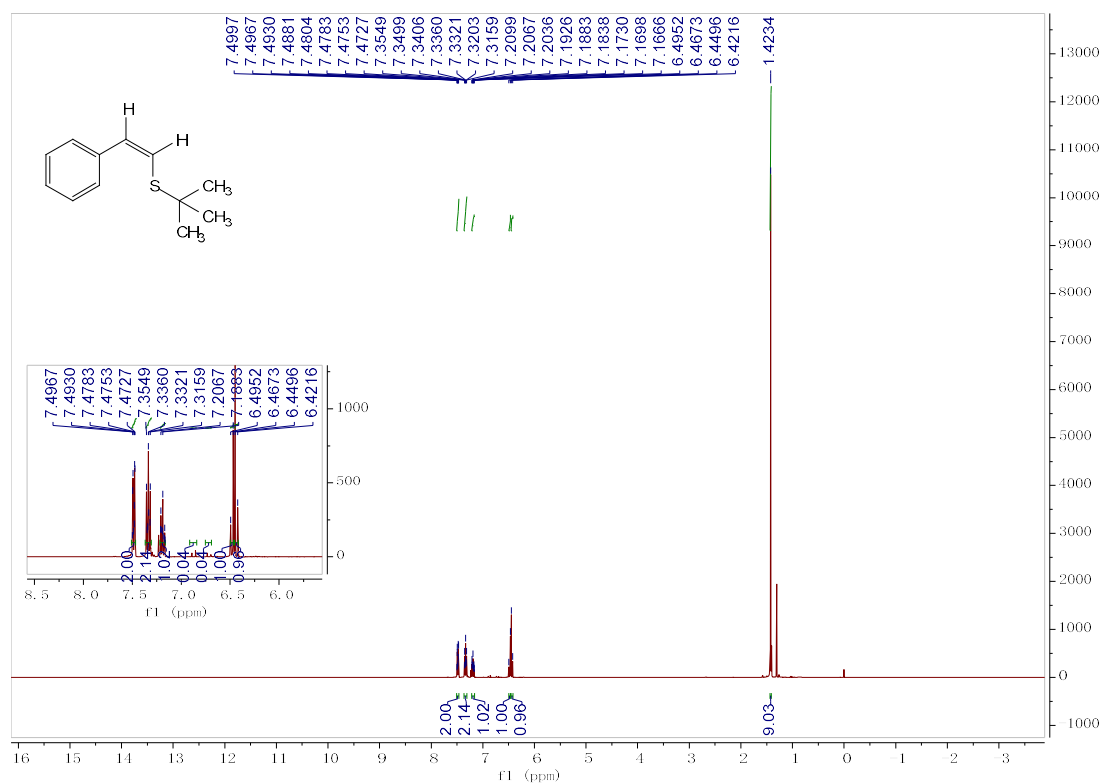
Integration values (from left to right): 1.97, 2.28, 1.05, 0.06, 0.05, 1.01, 1.00, 1.00, 1.00, 1.00, 3.00, 3.00



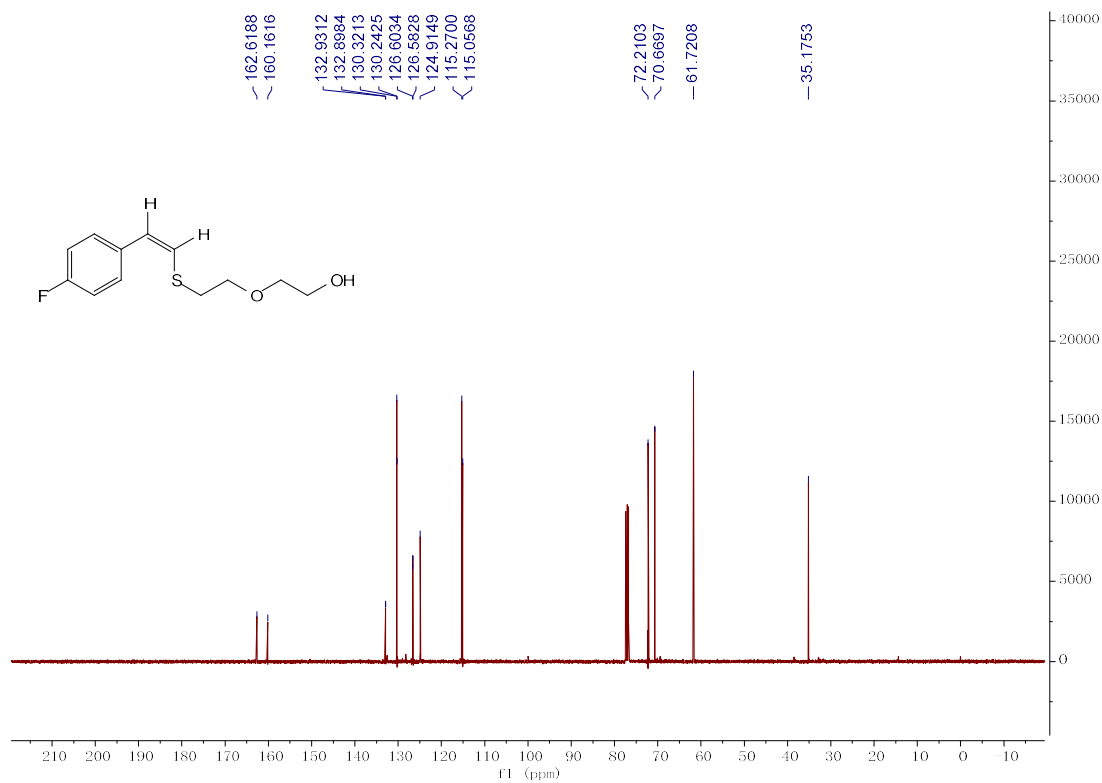
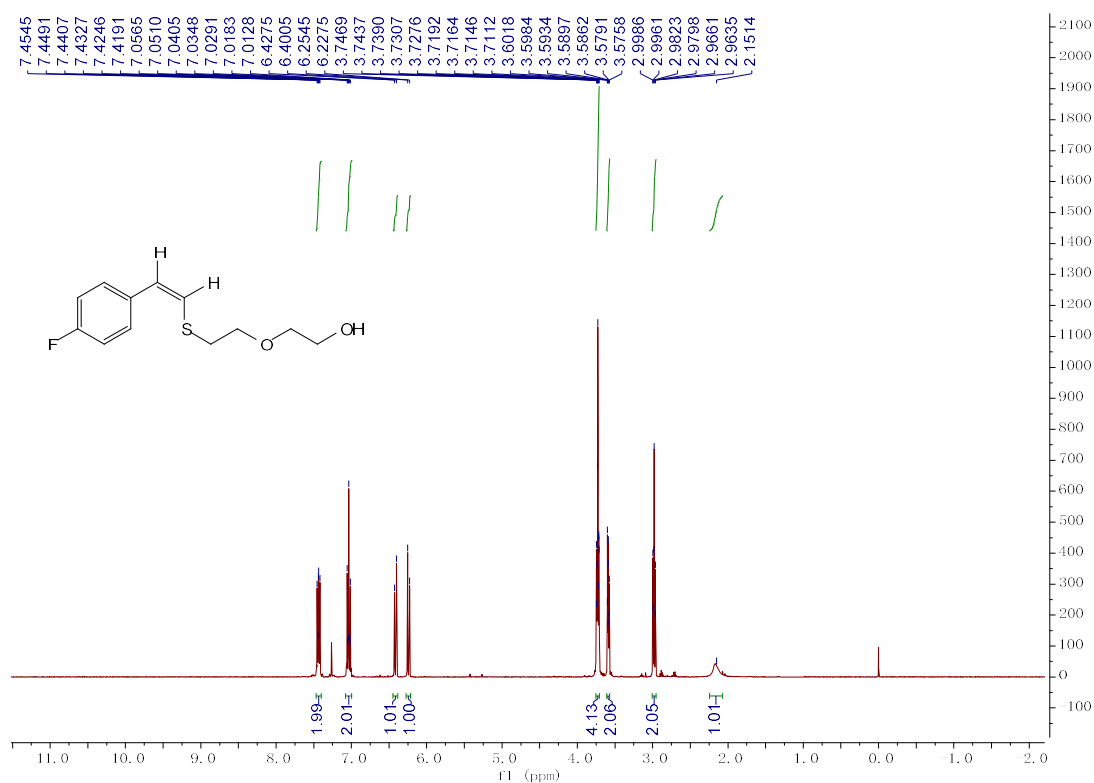
(Z/E)-Cyclohexyl(styryl)sulfane(3f)



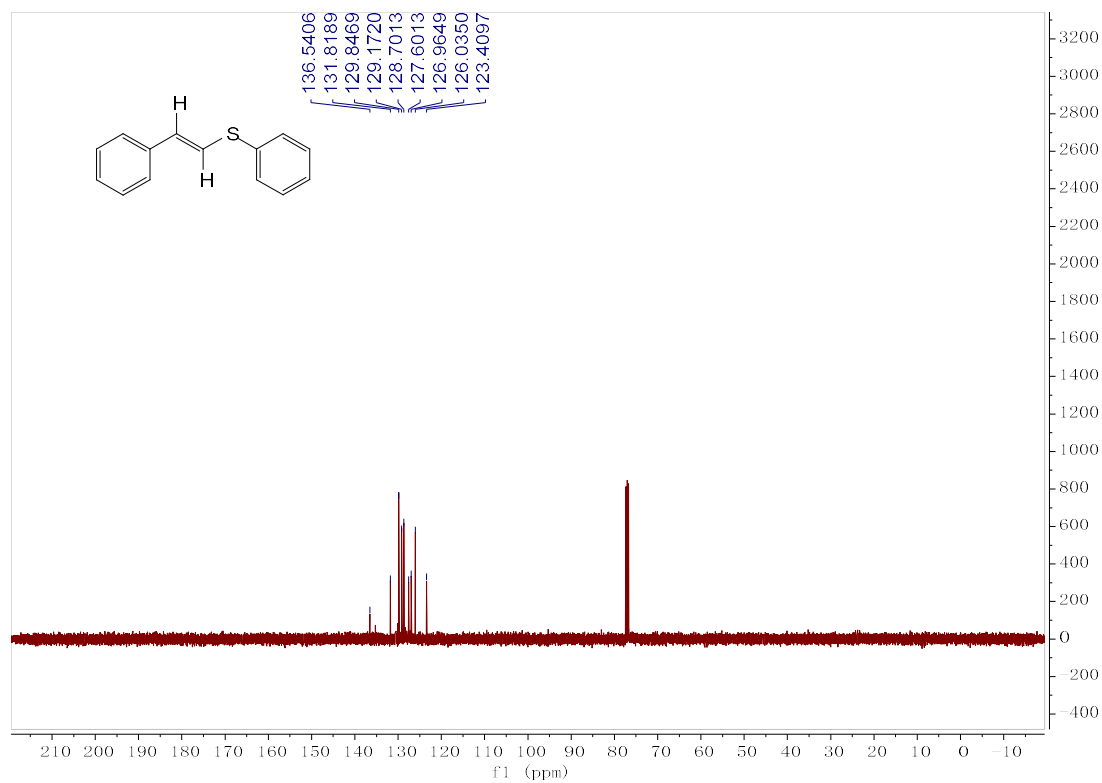
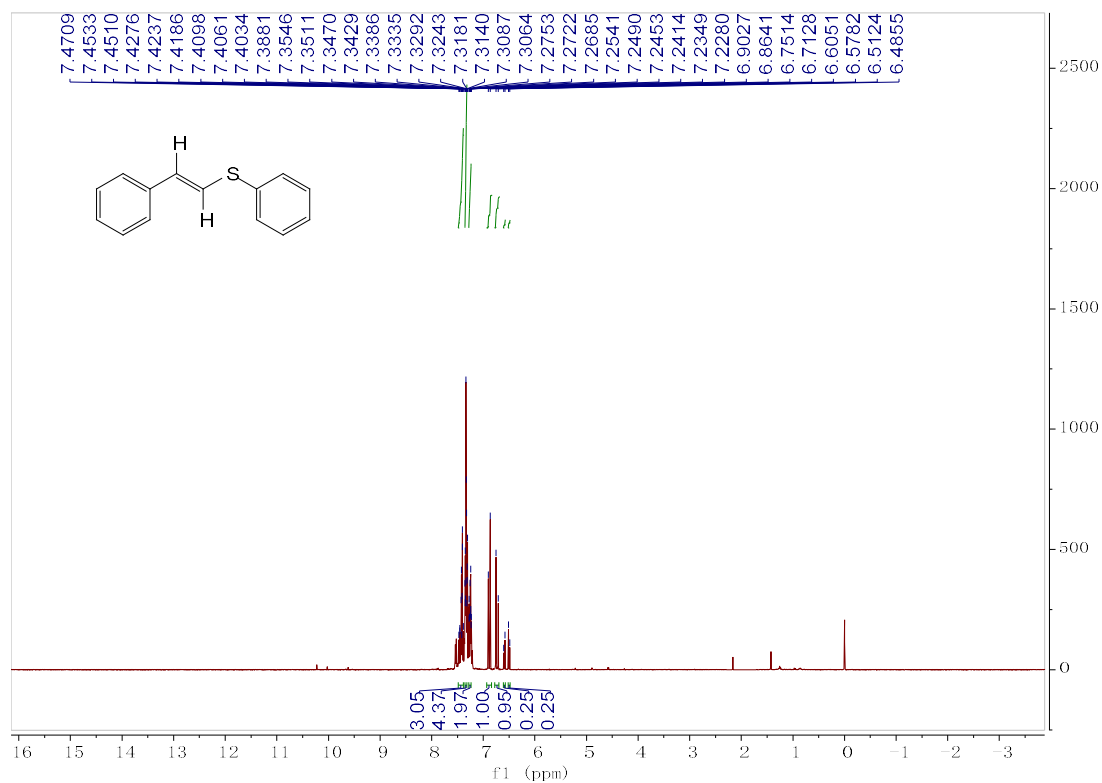
(Z/E)-Tert-butyl(styryl)sulfane(3g)



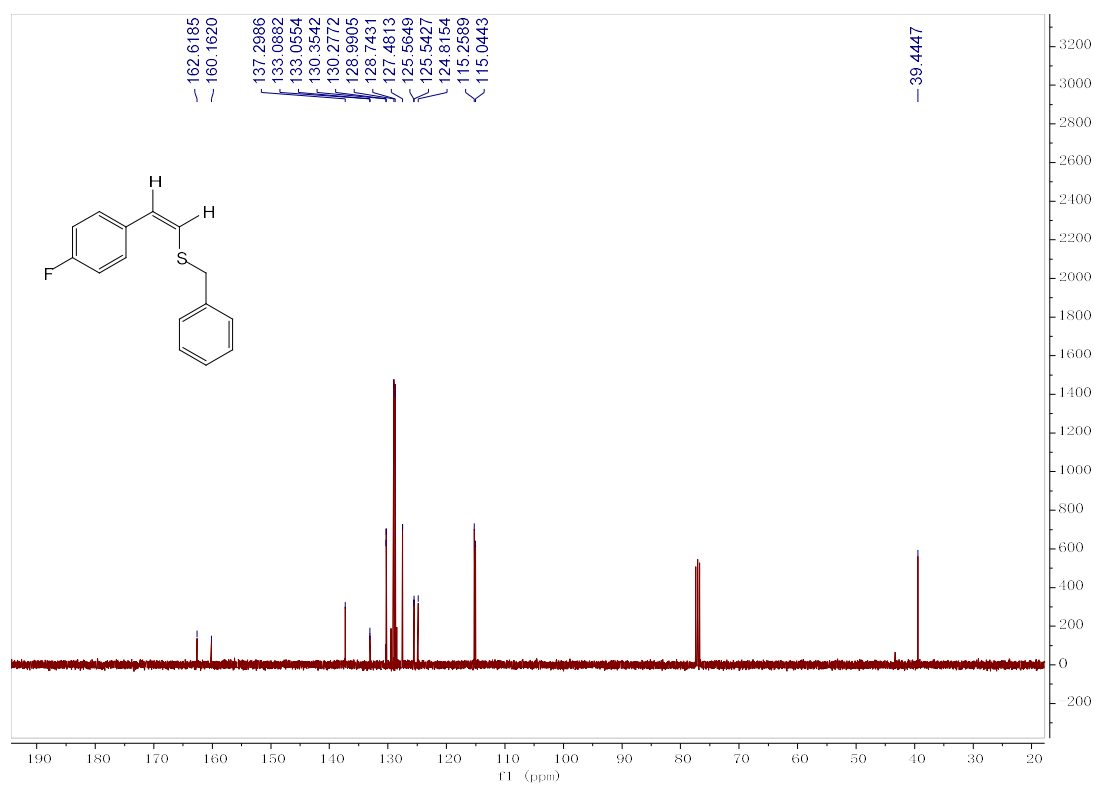
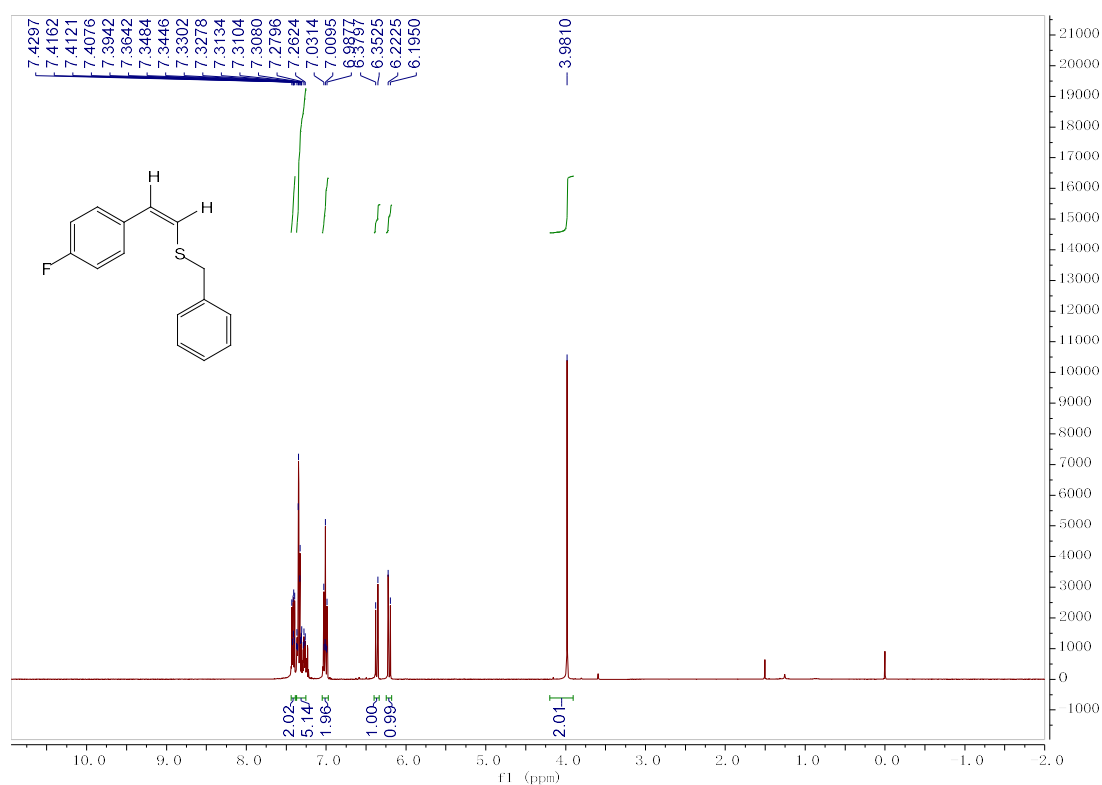
(Z)-2-(2-((4-Fluorostyryl)thio)ethoxy)ethan-1-ol(3h)



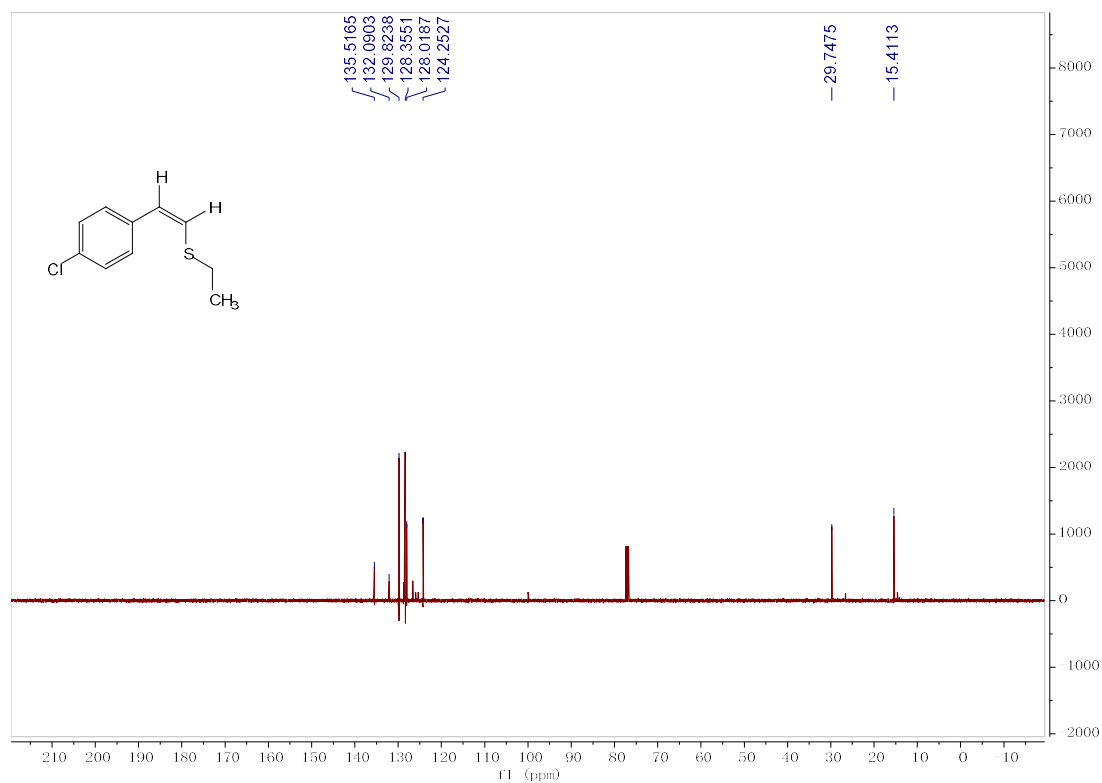
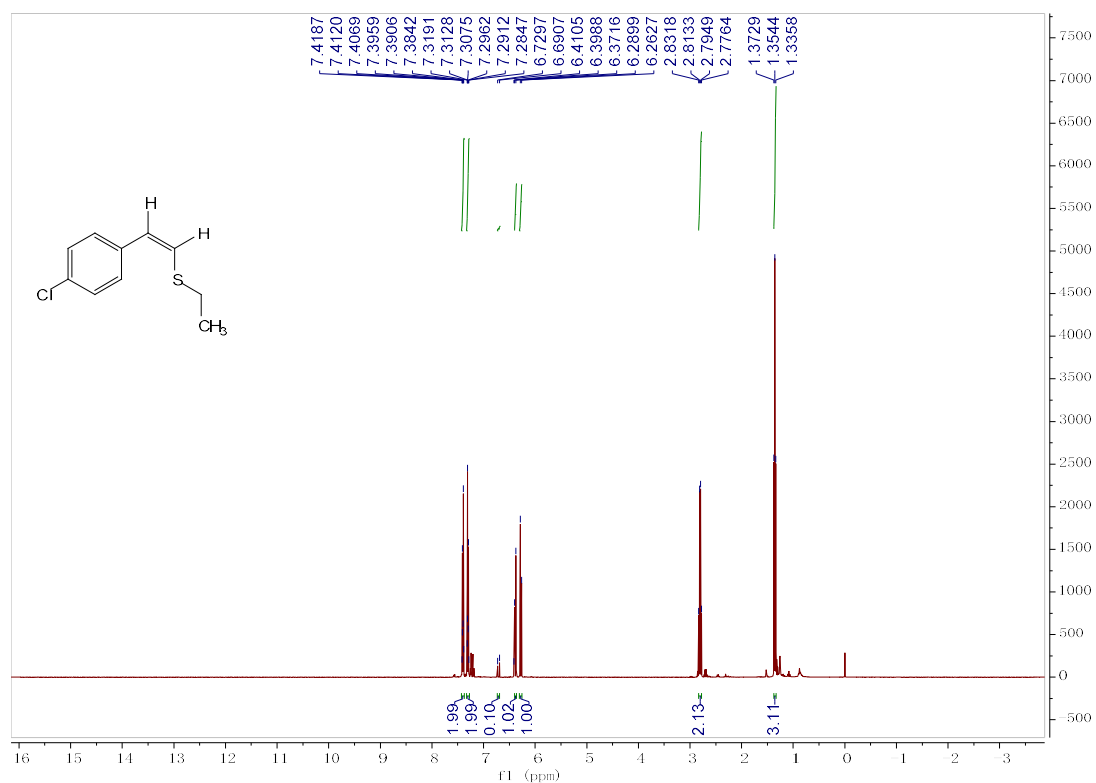
(E/Z)-Phenyl(styryl)sulfane(3i)



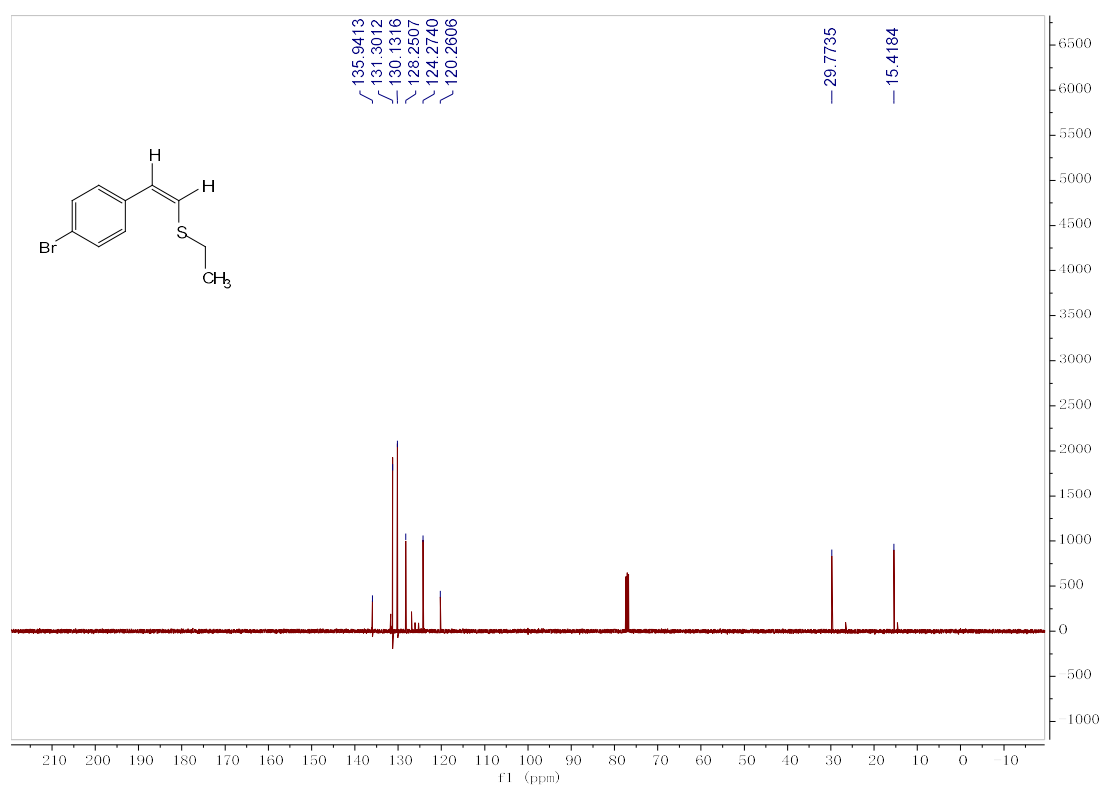
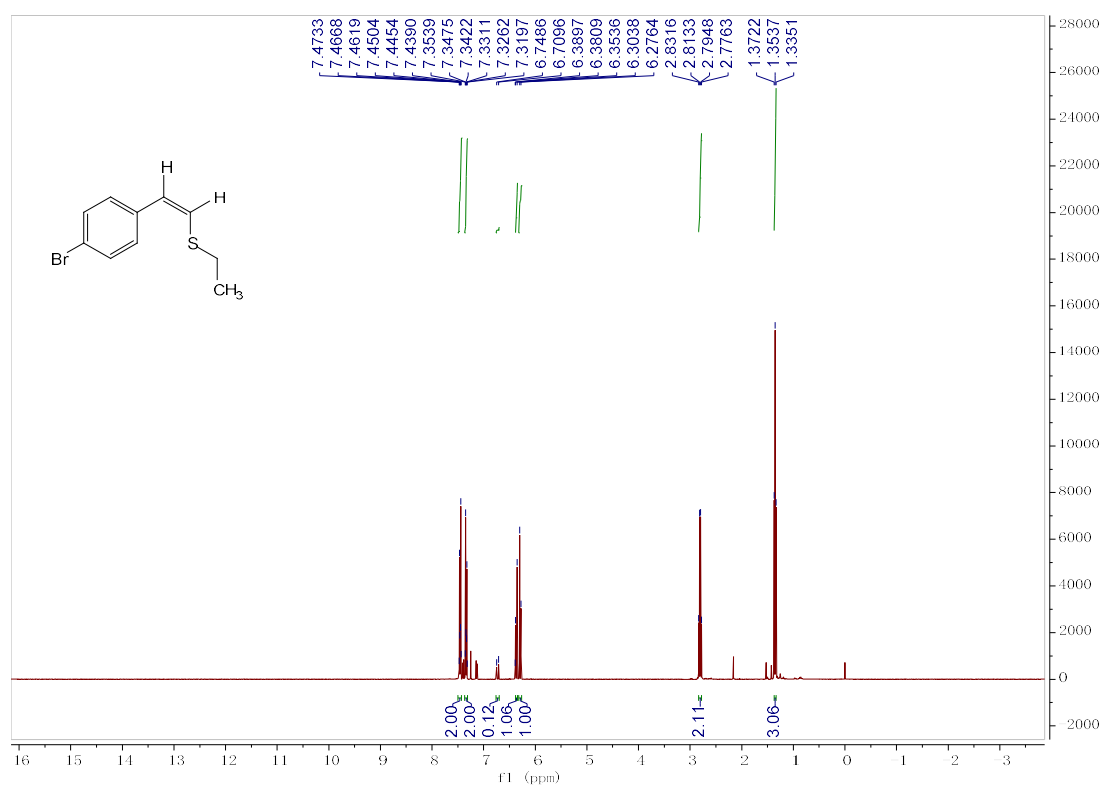
(Z/E)-Benzyl(4-fluorostyryl)sulfane(3j)



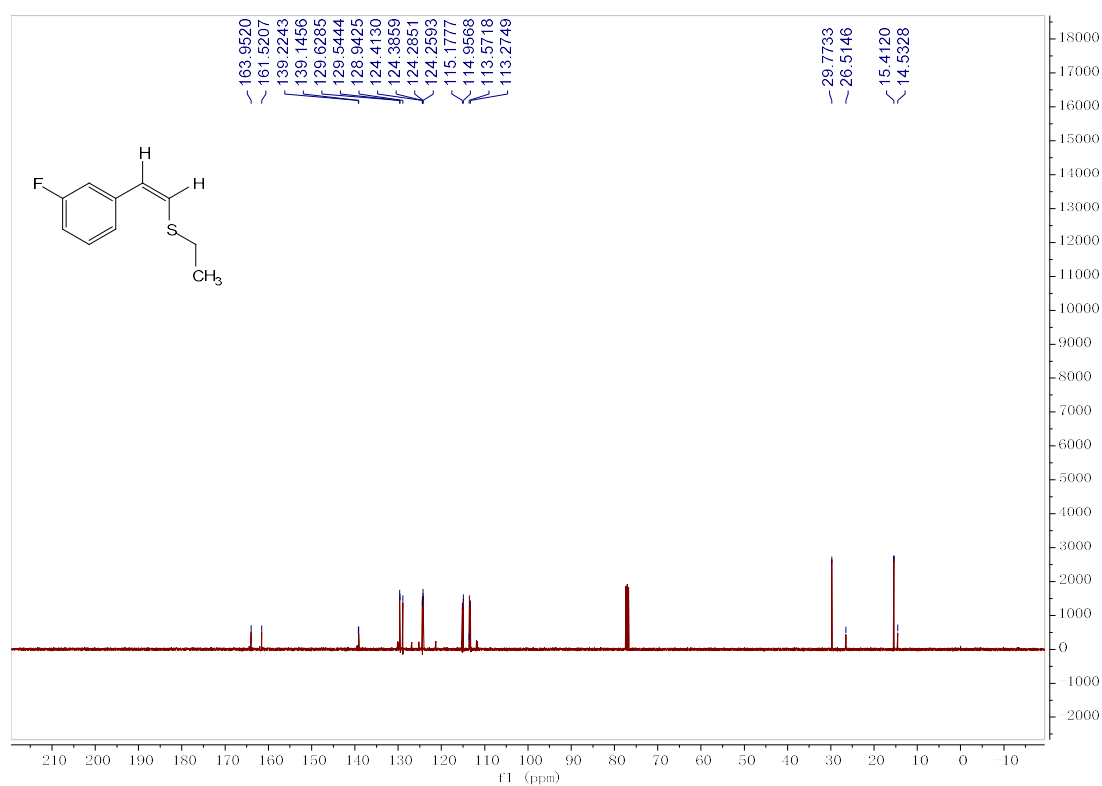
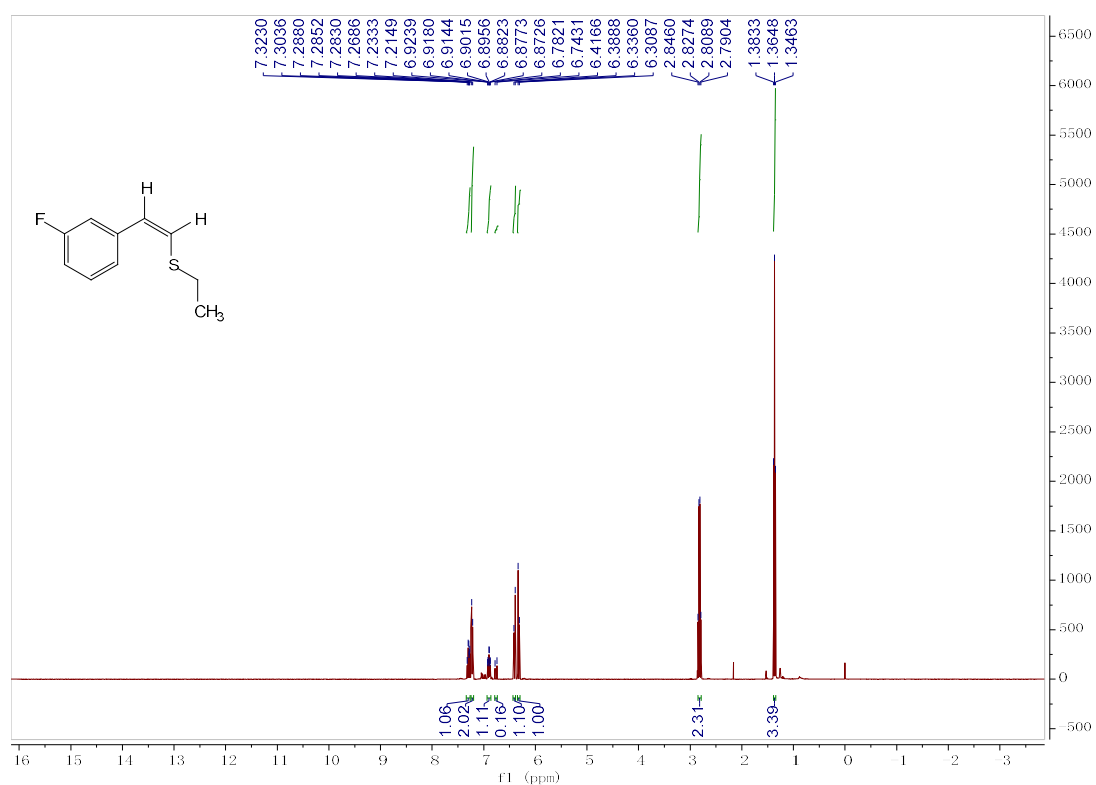
(Z/E)-(4-Chlorostyryl)(ethyl)sulfane(3k)



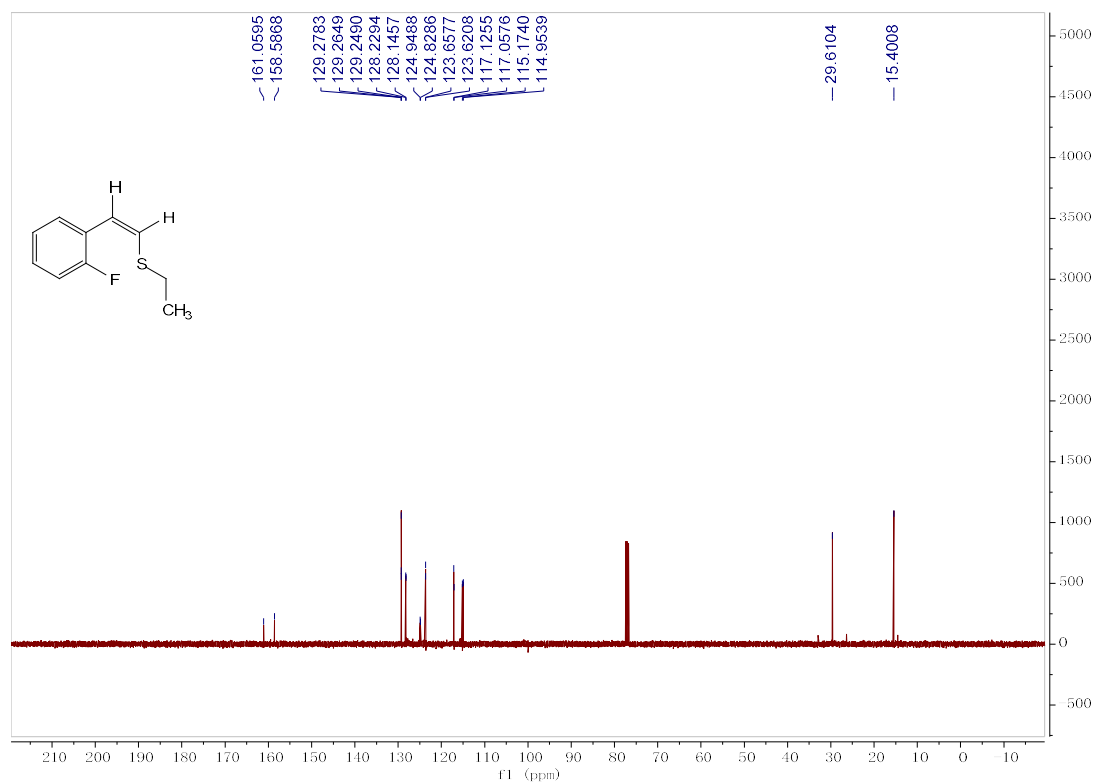
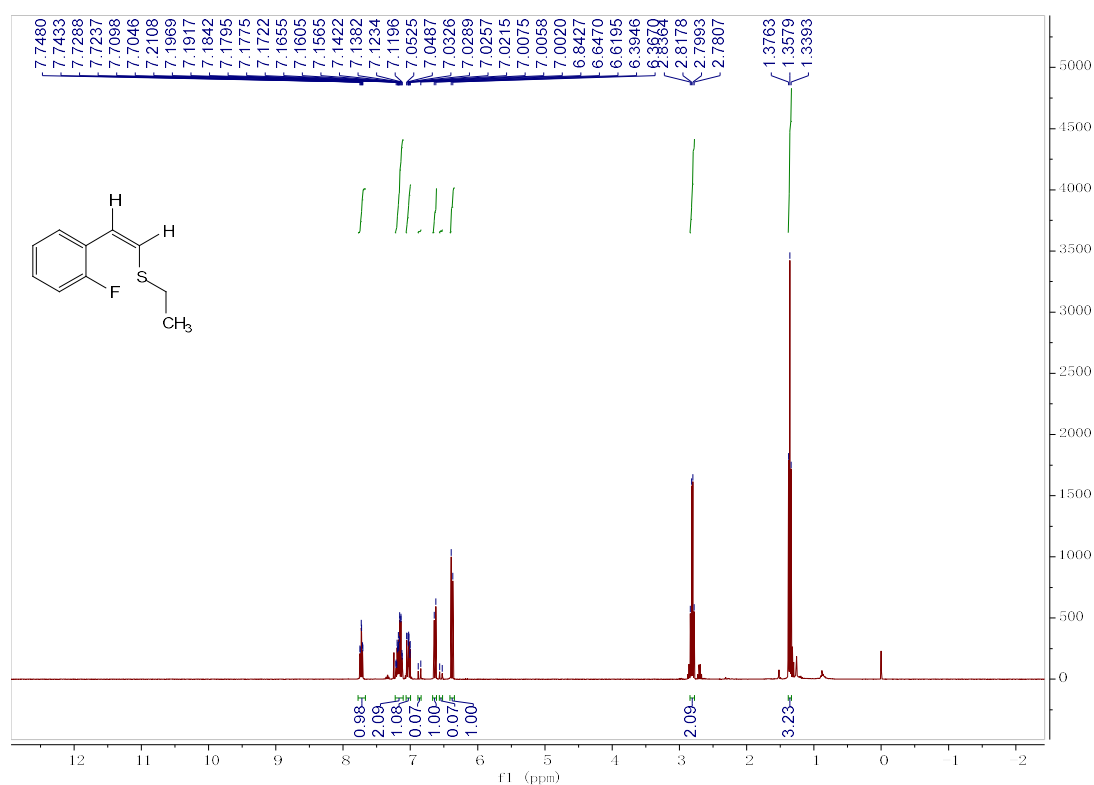
(Z/E)-(4-Bromostyryl)(ethyl)sulfane(3l)



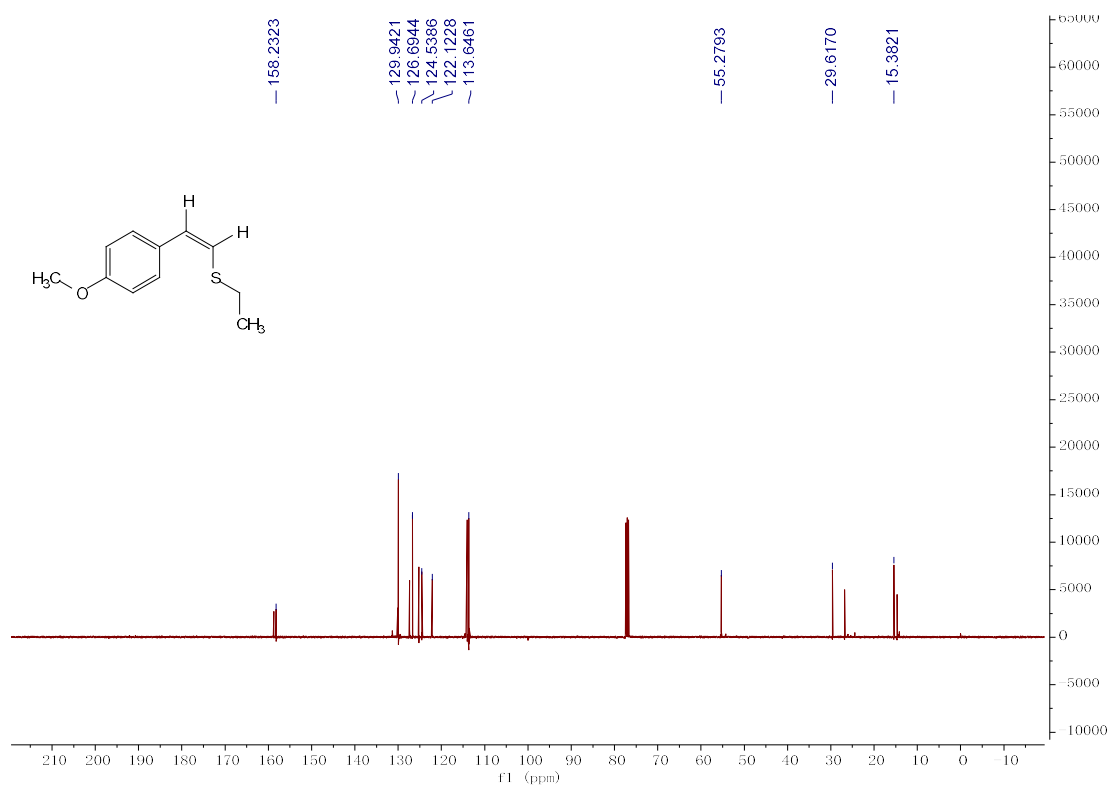
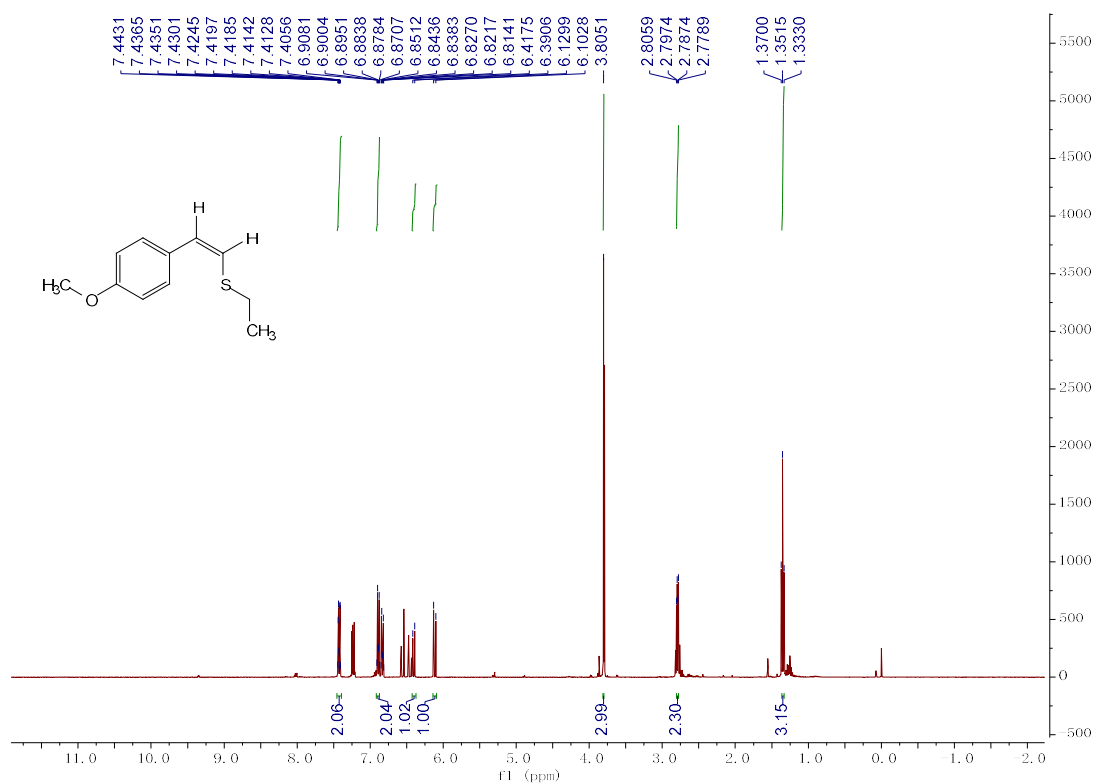
(Z/E)-Ethyl(3-fluorostyryl)sulfane(3m)



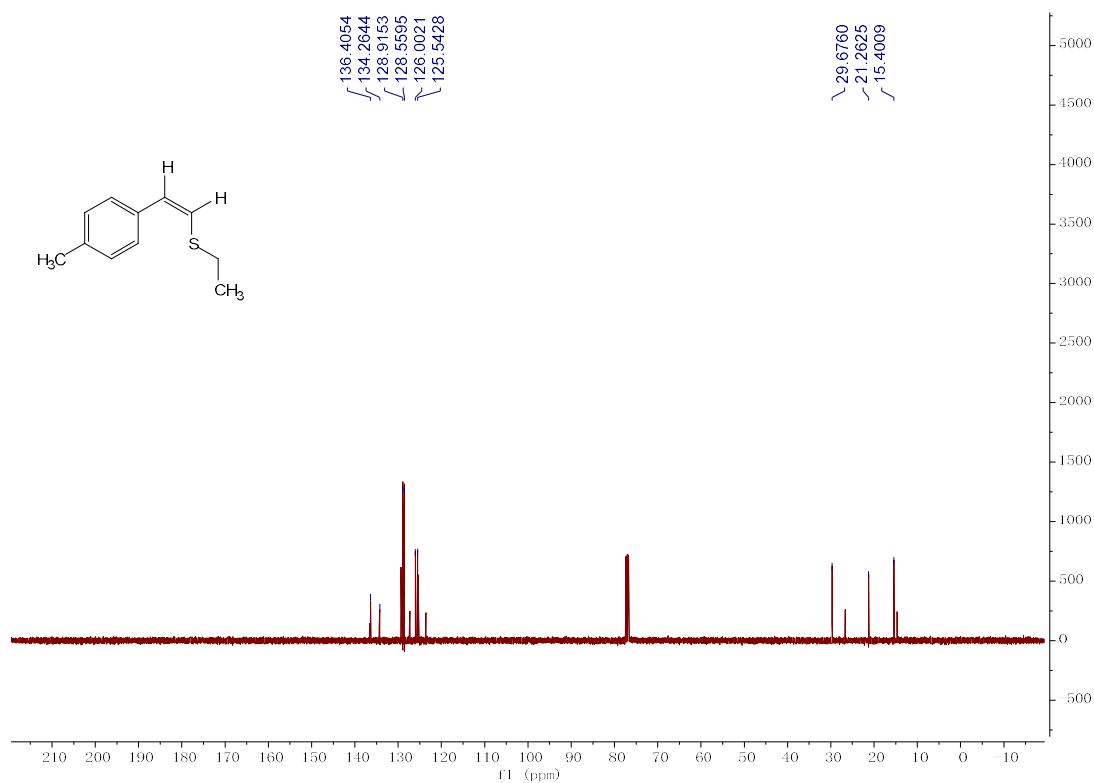
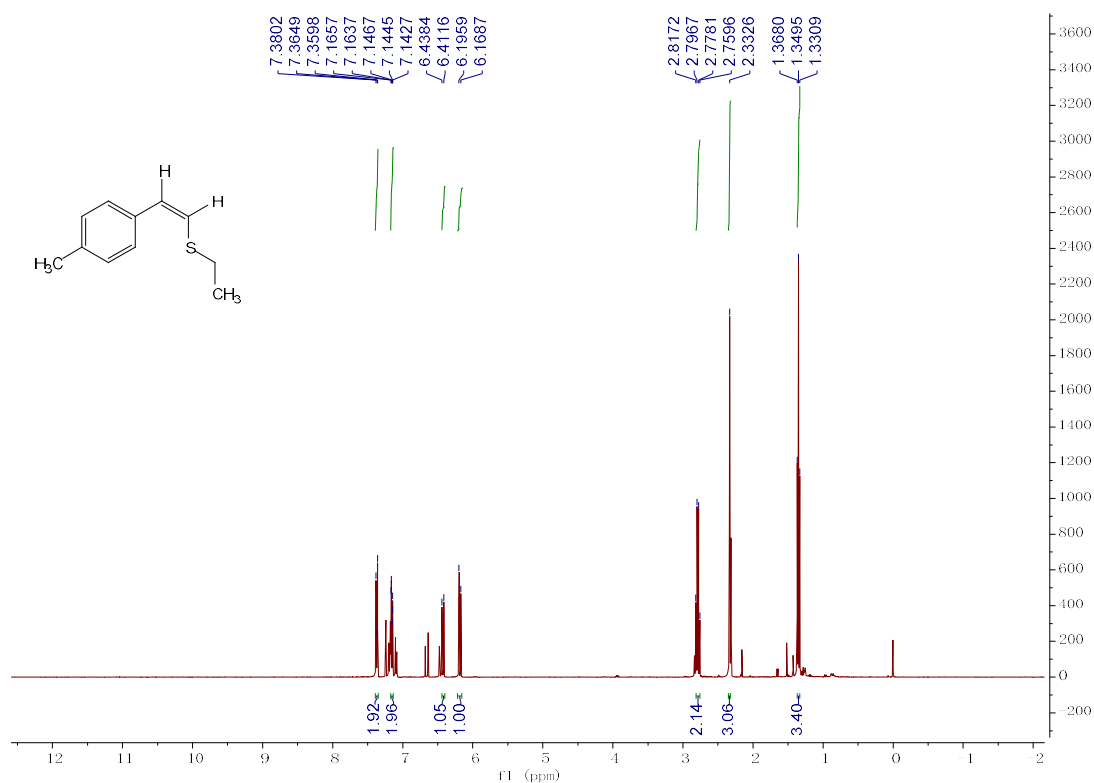
(Z/E)-ethyl(2-fluorostyryl)sulfane(3n)



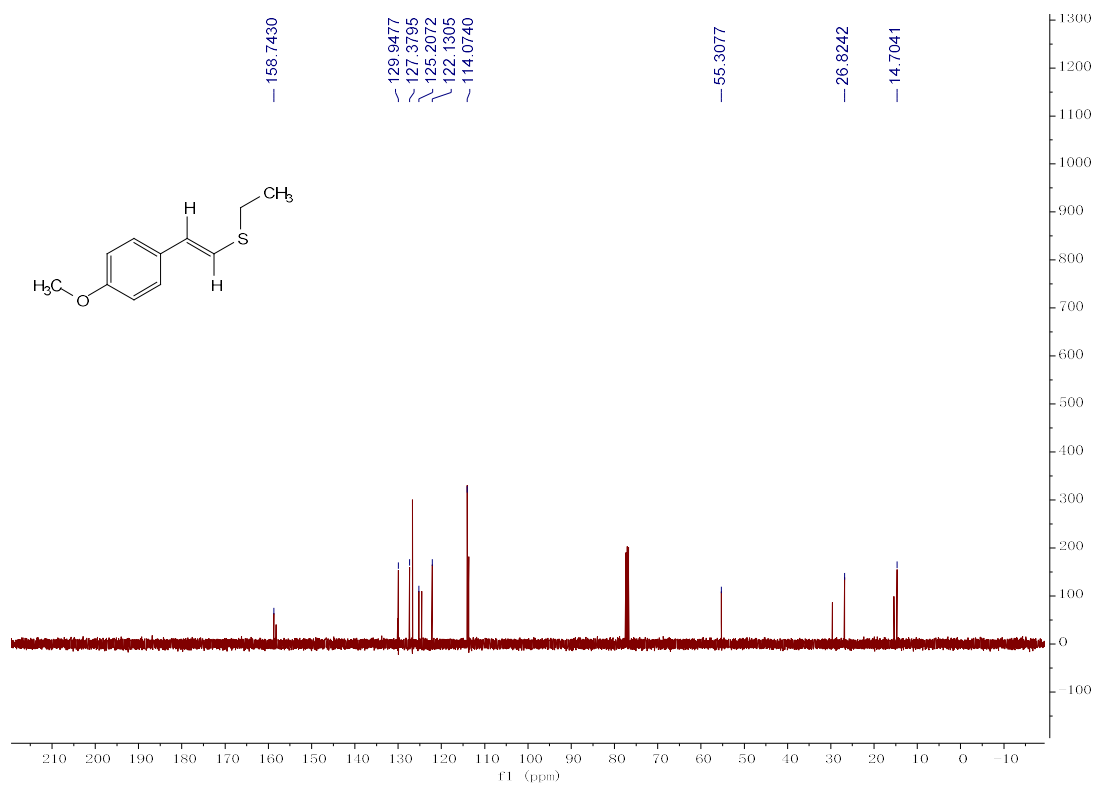
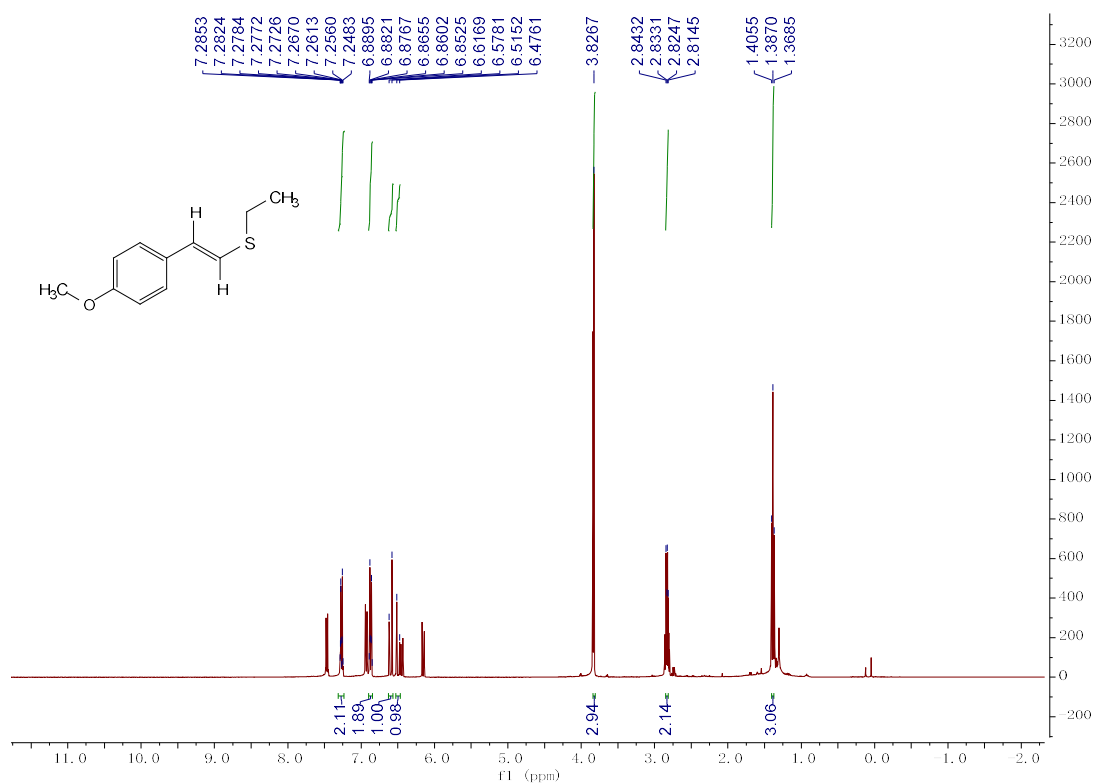
(Z/E)-ethyl(4-methoxystyryl)sulfane(Z-3o)



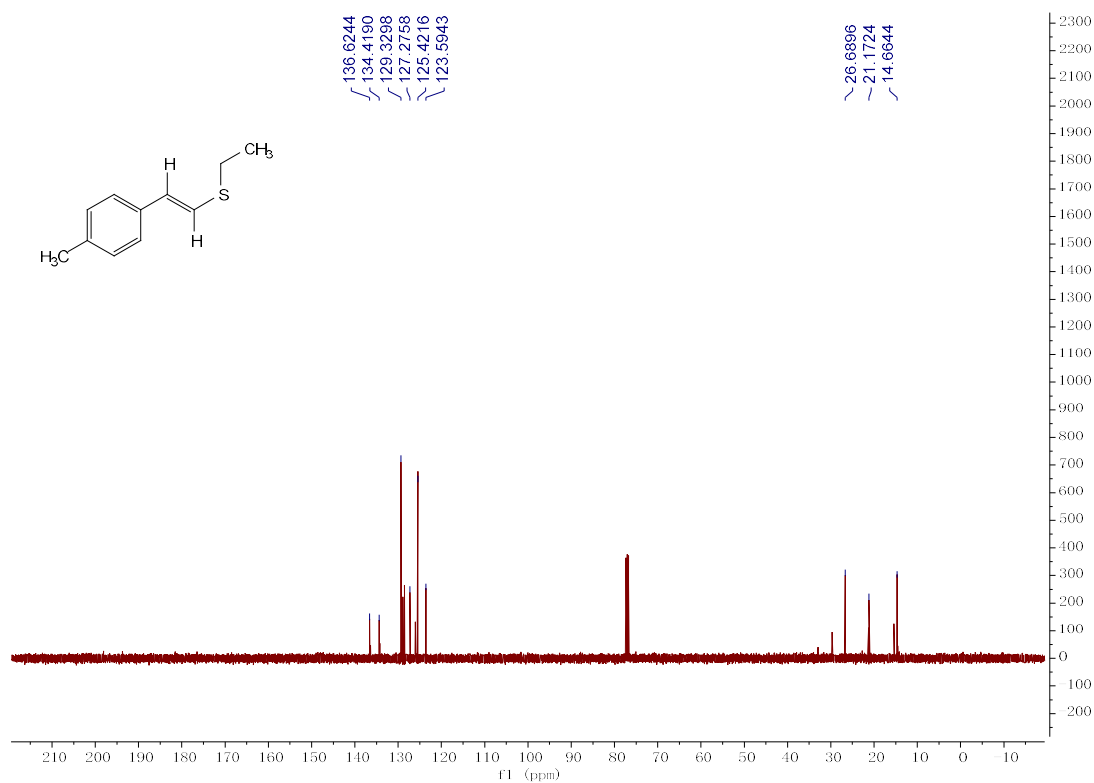
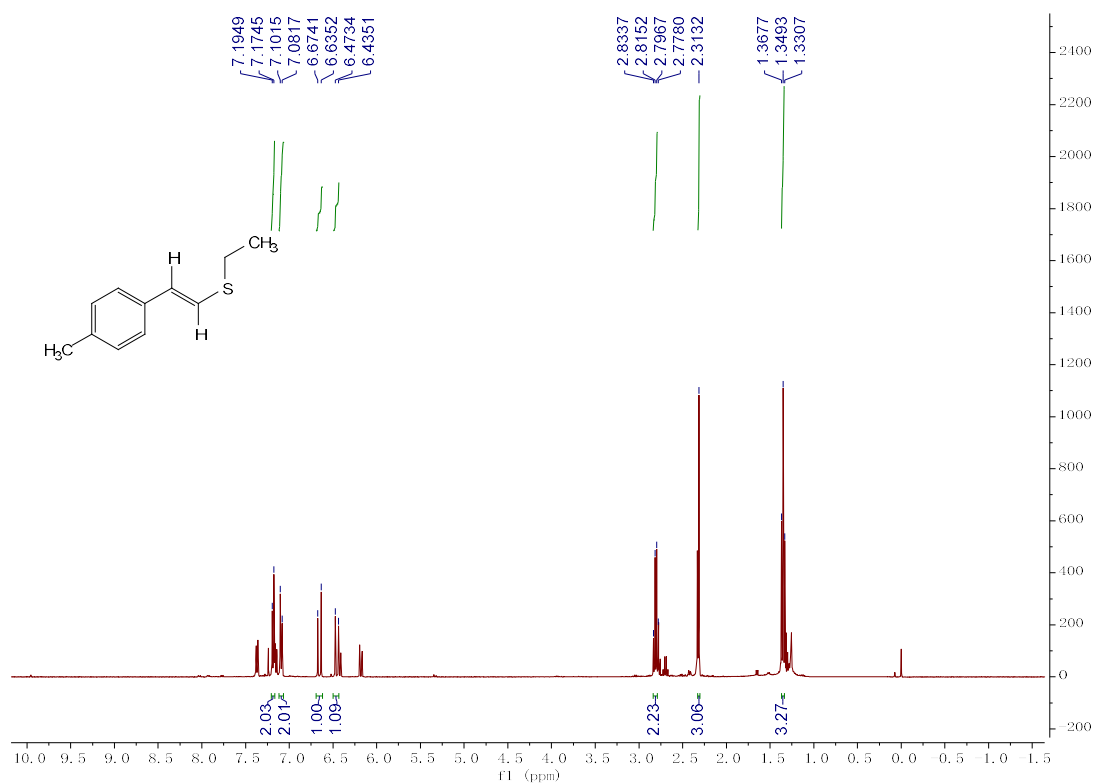
(Z/E)-Ethyl(4-methylstyryl)sulfane(Z-3p)



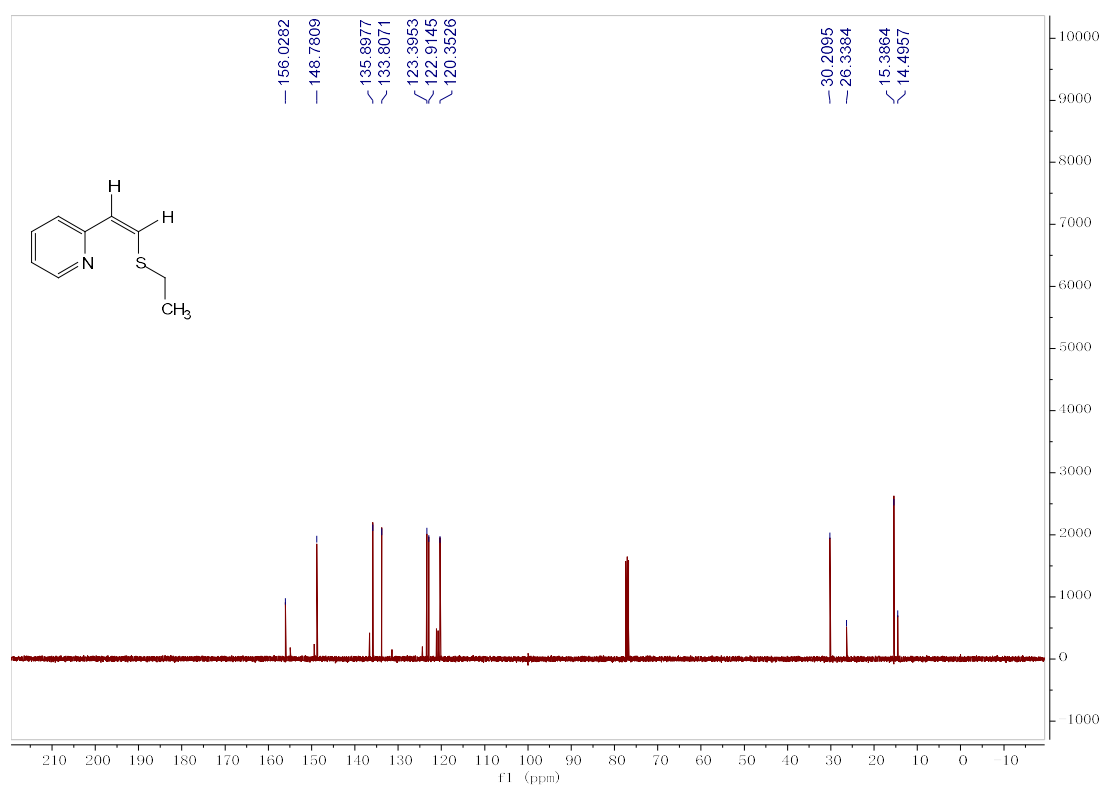
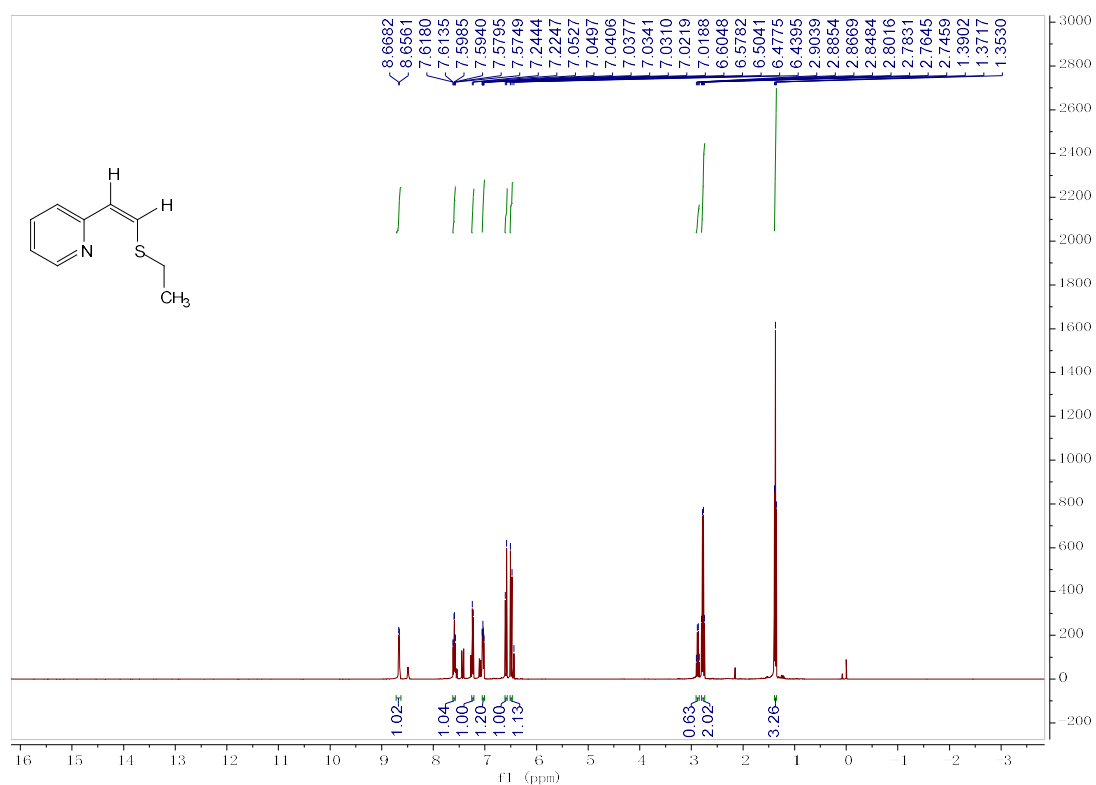
(*E/Z*)-Ethyl(4-methoxystyryl)sulfane(*E*-3o)



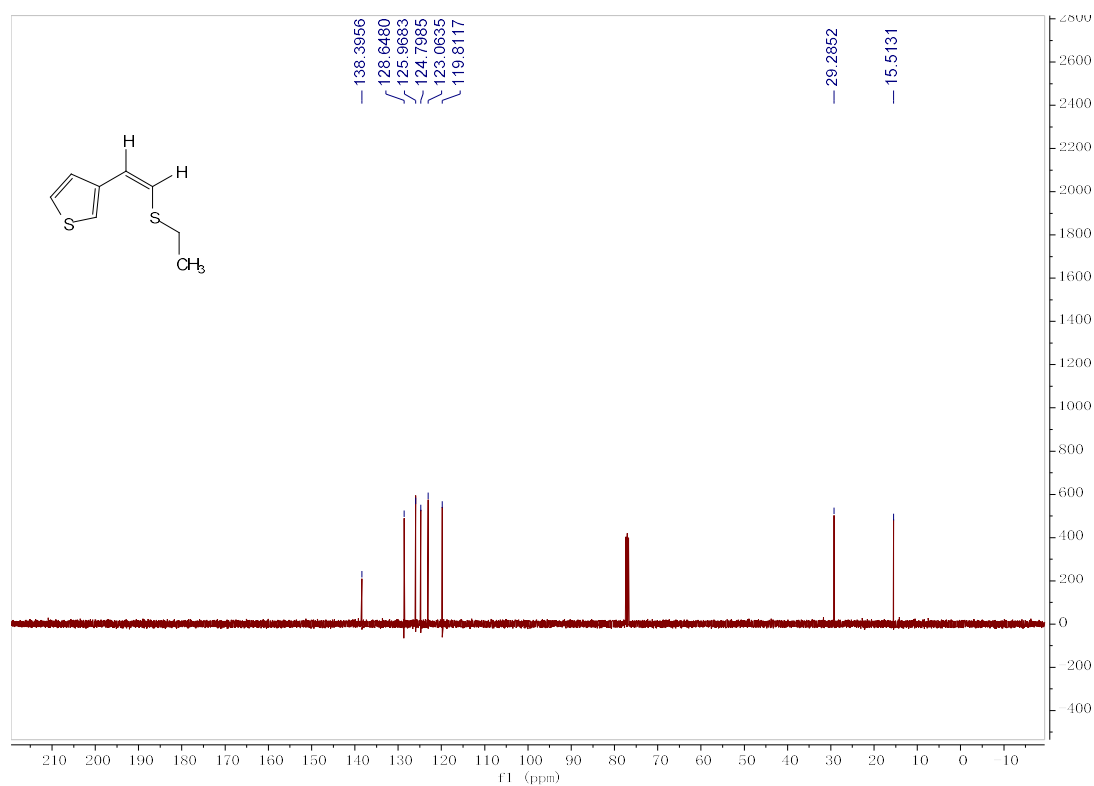
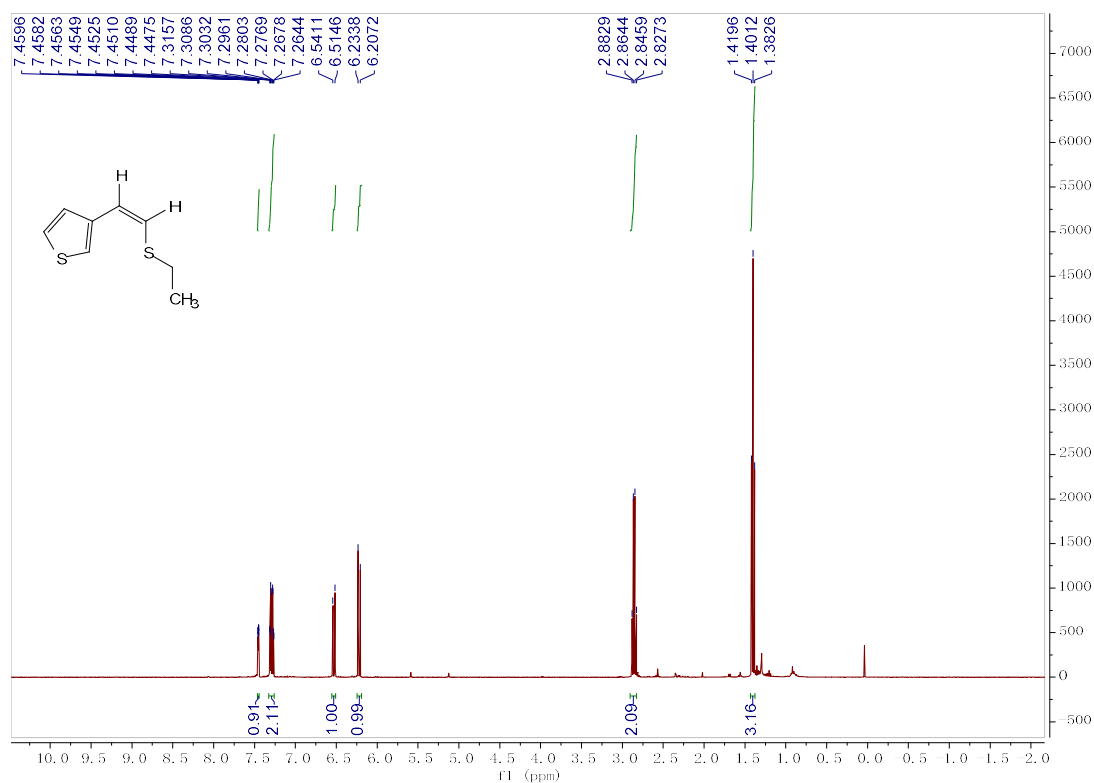
(*E/Z*)-Ethyl(4-methylstyryl)sulfane(*E*-3p)



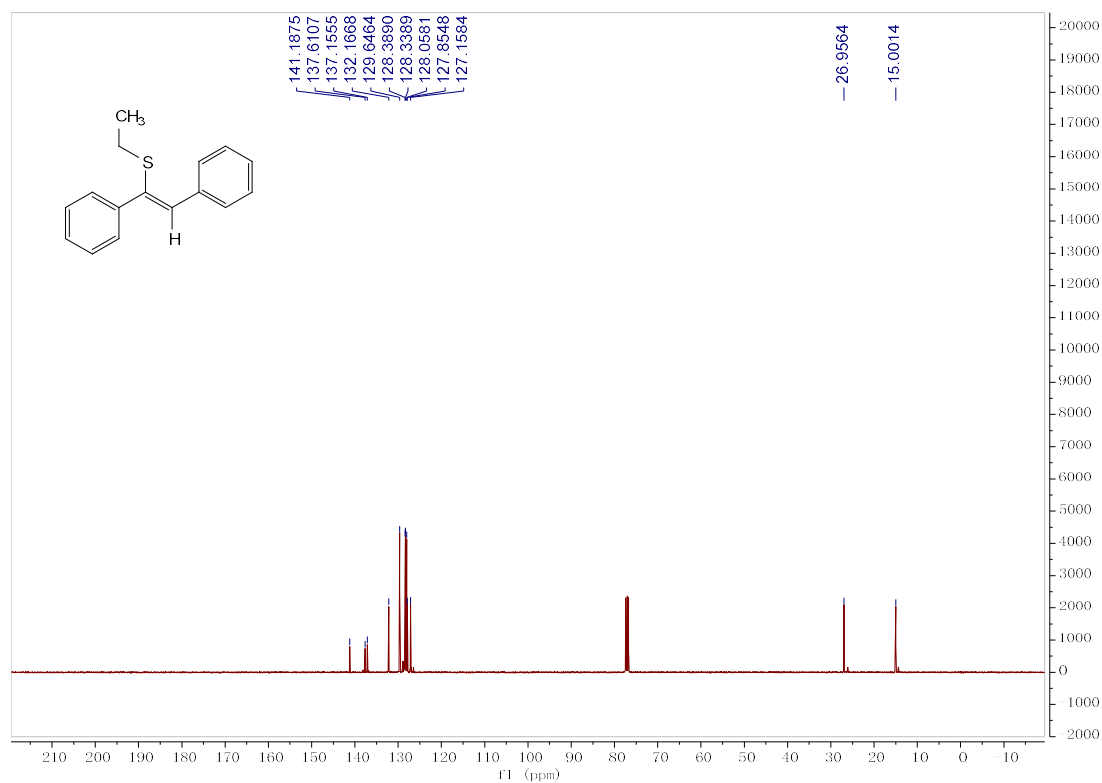
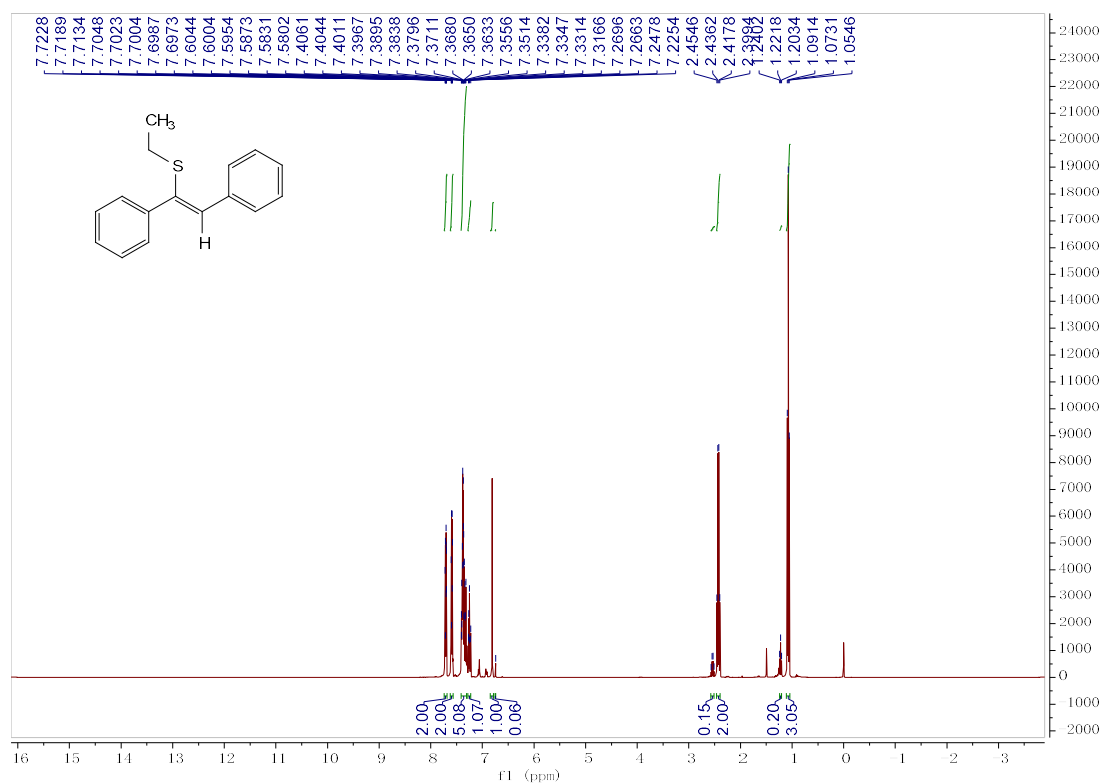
(Z/E)-2-(2-(Ethylthio)vinyl)pyridine(3q)



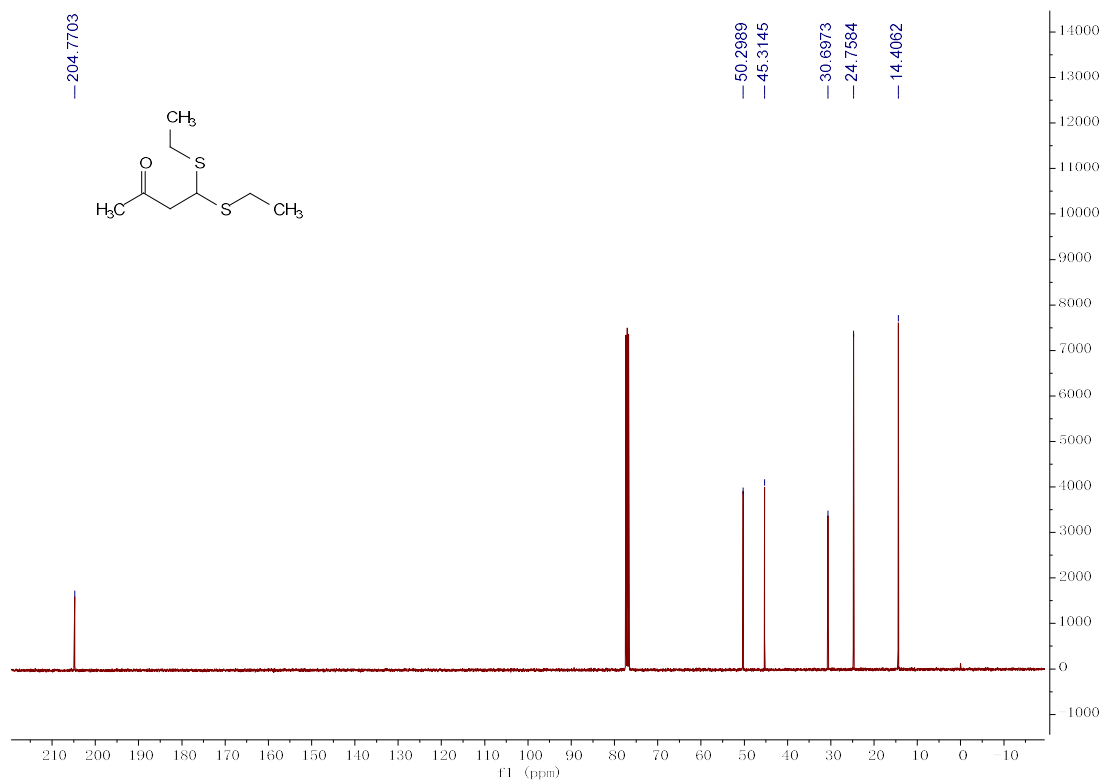
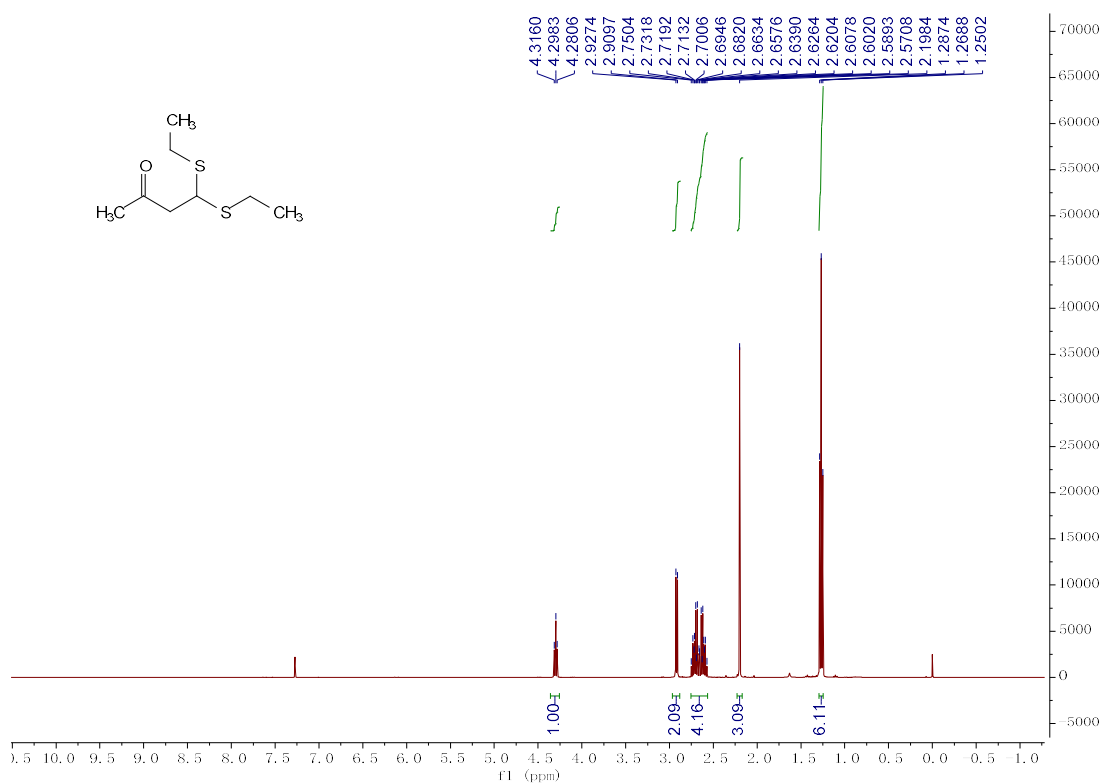
(Z)-3-(2-(Ethylthio)vinyl)thiophene(3r)



(Z/E)-(1,2-Diphenylvinyl)(ethyl)sulfane(3s)



4,4-Bis(ethylthio)butan-2-one (3t)



Methyl 3,3-bis(ethylthio)propanoate (u)

