

Diastereoselective Rh-Catalyzed α -Allylation of Chiral Cycloenamines Provides Unusual Linear Regional Selectivity

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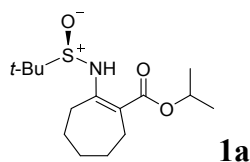
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1. General Information

All reactions were carried out under an argon atmosphere with dry, freshly distilled solvents under anhydrous conditions, unless otherwise noted. Yields refer to chromatographically and spectroscopically (^1H NMR) homogeneous materials, unless otherwise stated. The used solvents were purified and dried according to common procedures. Other chemicals and solvents were commercially available. High-resolution mass spectra (HRMS) were obtained with a FTICR-MS (Ion spec 7.0T) spectrometer. ^1H NMR spectra were obtained by using a Bruker AV 400 or AV 600. Chemical shifts are reported in parts per million (ppm) relative to either a tetramethylsilane internal standard or solvent signals. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants and integration. ^{13}C NMR spectra were recorded using a Bruker AV 400 spectrometer (100 MHz) using CDCl_3 as the solvent. Chemical shifts (δ) are reported in parts per million measured relative to the solvent peak. Melting points (m.p.) were obtained on a Mel-Temp capillary melting point apparatus. Enantiomeric excess (ee) was determined using Agilent HPLC 1260. IR spectra were recorded with a Bio-Rad FTS 6000 Fourier infrared spectrometer.

2. Synthesis of Substrates 1a-1i

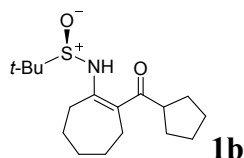


Representative Procedure:

isopropyl (*R*)-2-((*tert*-butylsulfinyl) amino)cyclohept-1-ene-1-carboxylate **1a**:

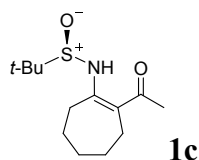
In a round bottom flask, a solution of cyclic sulfinimine (30 mmol) in fresh distilled THF (150mL) was mixed with NaHMDS (30mL, 2M in THF) in a nitrogen atmosphere at $-78\text{ }^\circ\text{C}$. After 1 hour, corresponding isopropyl carbonochloridate (45 mmol) was added dropwise. The mixture was kept stirring at $-78\text{ }^\circ\text{C}$ for 3 h. After the substrate was completely consumed (monitored by TLC analysis), the reaction mixture was quenched with saturated NH_4Cl (100 mL). The mixture was extracted by ethyl acetate (3 x 100mL). The combined organic phase was dried over Na_2SO_4 , and concentrated in *vacuo*. Then the residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to furnish the desired compound **1a** (8.1 g, 90% yield) as yellow oil; $[\alpha]_{\text{D}}^{25} = +2.40$ (c 3.0, CHCl_3). IR (KBr) ν_{max} : 2968, 2928, 2348, 1787, 1687, 1577, 1277, 1145, 870. cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 10.99

(s, 1H), 5.02 (m, 1H), 2.77 (m, 2H), 2.47 (ttd, $J = 15.3, 10.6, 5.4$ Hz, 2H), 1.74 (dd, $J = 14.6, 6.8$ Hz, 2H), 1.68 – 1.39 (m, 4H), 1.32 (s, 9H), 1.24 (dd, $J = 6.3, 1.9$ Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.0, 160.6, 106.6, 67.3, 56.7, 31.8, 30.5, 26.9, 26.1, 24.9, 22.8, 22.2. HRMS (ESI) calculated for $\text{C}_{15}\text{H}_{27}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 324.1604, found 324.1601.



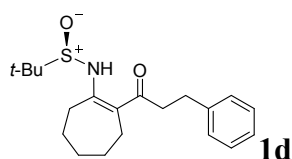
(*R*)-*N*-(2-(cyclopentanecarbonyl)cyclohept-1-en-1-yl)-2-methylpropane-2-sulfinamide
1b:

8.1 g; yield: 87%; yellow oil; $[\alpha]_{20}^{\text{D}} = +19.62$ (c 1.0, CHCl_3). IR (KBr) ν_{max} : 2968, 2920, 2850, 2383, 2360, 1737, 1607, 1260, 800. cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 13.03 (s, 1H), 3.09 – 3.02 (m, 1H), 2.85 – 2.66 (m, 2H), 2.47 (dd, $J = 7.4, 3.5$ Hz, 2H), 1.71 (d, $J = 5.0$ Hz, 2H), 1.68 – 1.45 (m, 11H), 1.32 – 1.22 (m, 9H), 1.17 – 1.15 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.7, 162.7, 113.5, 56.5, 47.5, 31.2, 30.3, 29.7, 27.2, 26.1, 26.1, 24.7, 22.6. HRMS (ESI) calculated for $\text{C}_{17}\text{H}_{29}\text{NNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 334.1811, found 334.1815.



(*R*)-*N*-(2-acetylcyclohept-1-en-1-yl)-2-methylpropane-2-sulfinamide **1c**:

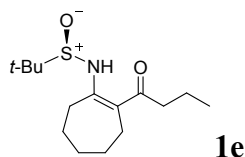
6.3 g; yield: 82%; yellow oil; $[\alpha]_{24}^{\text{D}} = +4.94$ (c 1.1, CHCl_3). IR (KBr) ν_{max} : 2961, 2924, 2854, 1610, 1446, 1395, 1361, 1250, 1210, 1092, 961, 846, 686, 586 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 13.01 (s, 1H), 2.86 – 2.77 (m, 2H), 2.47 (dd, $J = 6.1, 4.8$ Hz, 2H), 2.20 (s, 3H), 1.75 (m, 4H), 1.60 – 1.52 (m, 2H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.2, 163.4, 113.8, 56.9, 31.5, 30.4, 29.2, 28.3, 27.0, 24.9, 22.8. HRMS (ESI) calculated for $\text{C}_{13}\text{H}_{23}\text{NNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 280.1342, found 280.1346.



(*R*)-2-methyl-N-(2-(3-phenylpropanoyl) cyclohept-1-en-1-yl)propane-2-sulfinamide

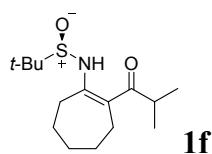
1d:

8.3 g; yield: 80%; yellow oil; $[\alpha]_{22}^D = +18.07$ (c 0.5, CHCl_3). IR (KBr) ν_{max} : 2925, 2854, 1749, 1615, 1507, 1456, 1362, 1091, 750, 699 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 13.04 (s, 1H), 7.29 (d, $J = 6.6$ Hz, 2H), 7.22 – 7.17 (m, 3H), 2.89 (dt, $J = 7.5, 3.4$ Hz, 2H), 2.81 (q, $J = 9.4, 8.9$ Hz, 4H), 2.47 (q, $J = 5.1, 4.1$ Hz, 2H), 1.78 – 1.71 (m, 3H), 1.59 – 1.44 (m, 3H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 201.1, 163.5, 141.7, 128.6, 128.5, 126.1, 113.6, 56.9, 42.7, 31.5, 31.1, 30.5, 27.4, 27.2, 24.9, 22.8. HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{29}\text{NNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 370.1811, found 370.1817.



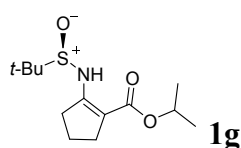
(*R*)-N-(2-butylcyclohept-1-en-1-yl)-2-methylpropane-2-sulfinamide **1e**:

7.0 g; yield: 82%; yellow oil; $[\alpha]_{21}^D = +9.34$ (c 1.2, CHCl_3). IR (KBr) ν_{max} : 2958, 2920, 2349, 1710, 1612, 1458, 1260, 1082, 809. cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 13.08 (s, 1H), 2.81 (d, $J = 9.0$ Hz, 2H), 2.46 (m, 4H), 1.75 (s, 4H), 1.60 – 1.51 (m, 4H), 1.33 (s, 9H), 0.93 (t, $J = 6.4$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 202.5, 163.1, 113.7, 56.8, 42.8, 31.5, 30.4, 27.5, 27.2, 24.9, 22.8, 18.5, 14.1. HRMS (ESI) calculated for $\text{C}_{15}\text{H}_{27}\text{NNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 308.1655, found 308.1652.



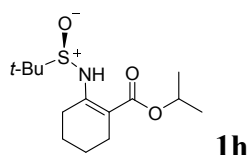
(*R*)-N-(2-isobutyrylcyclohept-1-en-1-yl)-2-methylpropane-2-sulfinamide **1f**:

7.6 g, yield: 89%, yellow oil. $[\alpha]_{22}^D = +7.25$ (c 4.2, CHCl_3). IR (KBr) ν_{max} : 2974, 2928, 2867, 2852, 1596, 1539, 1466, 1448, 1399, 1368, 1232, 1203, 1089, 1014, 969, 840, 827, 799 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 13.13 (s, 1H), 2.95 (q, $J = 6.9$ Hz, 1H), 2.79 (t, $J = 7.7$ Hz, 2H), 2.47 (dt, $J = 6.4, 2.6$ Hz, 2H), 1.71 (q, $J = 8.5, 7.1$ Hz, 3H), 1.52 (td, $J = 15.9, 13.2, 7.7$ Hz, 3H), 1.30 (s, 9H), 1.01 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 206.2, 163.6, 112.9, 56.7, 35.9, 31.3, 30.4, 27.5, 27.2, 24.8, 22.8, 19.2, 19.1. HRMS (ESI) calculated for $\text{C}_{15}\text{H}_{27}\text{NNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 308.1655, found 308.1657.



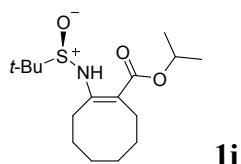
isopropyl (*R*)-2-((*tert*-butylsulfinyl) amino)cyclopent-1-ene-1-carboxylate **1g**:

7.8 g; yield: 95%; yellow oil; $[\alpha]_{24}^D = -26.11$ (c 2.4, CHCl₃). IR (KBr) ν_{\max} : 2964, 2924, 2340, 1680, 1579, 1279, 961, 870. cm⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.20 (s, 1H), 5.03 (m, 1H), 2.93 – 2.84 (m, 1H), 2.64 (ddd, $J = 17.2, 8.3, 5.9$ Hz, 1H), 2.55 – 2.45 (m, 2H), 1.88 (dtd, $J = 16.6, 8.3, 6.2$ Hz, 2H), 1.29 (s, 9H), 1.23 (dd, $J = 6.3, 1.7$ Hz, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 167.5, 157.2, 104.6, 66.9, 56.7, 32.7, 29.34, 22.5, 22.2, 22.2, 20.6. HRMS (ESI) calculated for C₁₃H₂₃NNaO₃S⁺ [M+Na]⁺: 296.1291, found 296.1293.



isopropyl (*R*)-2-((*tert*-butylsulfinyl) amino) cyclohex-1-ene-1-carboxylate **1h**:

6.9 g; yield: 80%; yellow oil; $[\alpha]_{24}^D = -10.78$ (c 0.7, CHCl₃). IR (KBr) ν_{\max} : 2958, 2920, 2360, 1778, 1570, 1276, 877. cm⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 10.78 (s, 1H), 5.02 (dq, $J = 12.5, 6.2$ Hz, 1H), 2.67 (dt, $J = 17.7, 6.3$ Hz, 1H), 2.43 (dt, $J = 17.9, 6.3$ Hz, 1H), 2.24 (dq, $J = 17.4, 11.2, 8.8$ Hz, 2H), 1.67 (ddd, $J = 12.8, 6.1, 3.1$ Hz, 2H), 1.57 (qd, $J = 6.2, 3.2$ Hz, 2H), 1.29 (s, 9H), 1.22 (dd, $J = 6.2, 2.7$ Hz, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 169.9, 153.1, 101.6, 67.1, 56.4, 27.2, 24.0, 22.8, 22.3, 22.1, 22.0. HRMS (ESI) calculated for C₁₄H₂₅NNaO₃S⁺ [M+Na]⁺: 310.1447, found 310.1443.

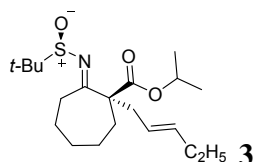


isopropyl (*R, Z*)-2-((*tert*-butylsulfinyl) amino)cyclooct-1-ene-1-carboxylate **1i**:

8.5 g; yield: 90%; yellow oil; $[\alpha]_{24}^D = -10.09$ (c 5.0, CHCl₃). IR (KBr) ν_{\max} : 2955, 2920, 2358, 1770, 1610, 1576, 1268, 872, 601. cm⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 11.04 (s, 1H), 5.02 (m, 1H), 2.75 (dt, $J = 8.6, 4.1$ Hz, 2H), 2.44 (ddd, $J = 14.9, 7.3, 3.1$ Hz, 1H), 2.39 – 2.31 (m, 1H), 1.83 (d, $J = 8.7$ Hz, 1H), 1.68 – 1.43 (m, 7H), 1.31

(s, 9H), 1.22 (dd, $J = 6.4, 3.2$ Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.9, 156.9, 103.7, 67.0, 56.7, 30.3, 29.3, 28.3, 26.8, 26.3, 25.8, 22.8, 22.1, 22.1. HRMS (ESI) calculated for $\text{C}_{16}\text{H}_{29}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 338.1760, found 338.1763.

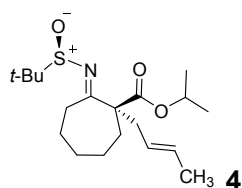
3. Rh-catalyzed Intermolecular Decarboxylative Allylation of β -Sulfinimine Ester



Representative Procedure:

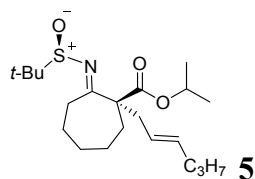
isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl)imino)-1-((*E*)-pent-2-en-1-yl)cycloheptane-1-carboxylate **3**:

In a round bottom flask, a solution of compound **1** (0.30 g, 1.00 mmol) in fresh distilled THF (5 mL) was mixed with NaHMDS (1 mL, 2M in THF) in a nitrogen atmosphere at room temperature. Then add (*E*)-ethyl pent-2-en-1-yl carbonate (0.32 g, 2.00 mmol) and $\text{RhCl}(\text{PPh}_3)_3$ (28 mg, 0.03 mmol). The mixture was kept stirring at room temperature overnight. After the substrate was completely consumed (monitored by TLC analysis), the reaction mixture was quenched with saturated NH_4Cl (30 mL), and extracted by ethyl acetate (3 x 30 mL). The combined organic phase was dried over Na_2SO_4 , and concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate=5:1) to furnish the desired compound **3** (335 mg, 91% yield) as a yellow oil. $[\alpha]_{\text{D}}^{19} = +8.73$ (c 2.2, CHCl_3). IR (KBr) ν_{max} : 2926, 2857, 1730, 1617, 1455, 1386, 1360, 1210, 1190, 1184, 1107, 1082, 969, 801 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 5.49 (dt, $J = 13.7, 6.3$ Hz, 1H), 5.33 (dt, $J = 15.0, 7.3$ Hz, 1H), 4.97 (m, 1H), 2.93 (dt, $J = 11.8, 5.1$ Hz, 1H), 2.75 (dd, $J = 14.0, 6.5$ Hz, 1H), 2.63 (ddd, $J = 13.2, 8.3, 4.7$ Hz, 1H), 2.31 (dd, $J = 14.0, 7.9$ Hz, 1H), 2.11 (dd, $J = 13.1, 8.7$ Hz, 1H), 1.96 (q, $J = 7.2$ Hz, 2H), 1.77 – 1.68 (m, 4H), 1.56 (m, 2H), 1.47 – 1.38 (m, 1H), 1.24 (s, 9H), 1.19 (dd, $J = 6.4, 3.3$ Hz, 6H), 0.93 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.2, 172.5, 136.4, 124.2, 68.6, 61.6, 57.1, 40.0, 34.3, 33.3, 29.6, 27.1, 25.8, 24.0, 22.5, 21.9, 21.8, 13.8. HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{35}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 392.2230, found 392.2232.



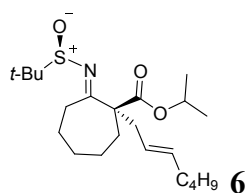
isopropyl (S,E)-1-((E)-but-2-en-1-yl)-2-(((R)-*tert*-butylsulfinyl)imino)cycloheptane-1-carboxylate **4**:

89% yield, yellow oil. $[\alpha]_{18}^D = +18.54$ (c 0.5, CHCl_3). IR (KBr) ν_{max} : 2926, 2856, 1730, 1617, 1456, 1386, 1374, 1361, 1261, 1220, 1193, 1155, 1106, 1083, 969, 802 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 5.52 – 5.40 (m, 1H), 5.40 – 5.23 (m, 1H), 5.02 – 4.96 (m, 1H), 2.93 (ddd, $J = 12.9, 6.8, 4.3$ Hz, 1H), 2.75 (ddt, $J = 13.9, 6.3, 1.4$ Hz, 1H), 2.64 (ddd, $J = 13.1, 8.8, 4.7$ Hz, 1H), 2.35 – 2.26 (m, 1H), 2.17 – 2.06 (m, 1H), 1.81 – 1.68 (m, 5H), 1.64 – 1.63 (m, 1H), 1.62 – 1.39 (m, 4H), 1.25 (s, 9H), 1.19 (dd, $J = 6.2, 3.1$ Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.2, 172.5, 129.2, 126.5, 68.6, 61.6, 57.1, 40.1, 34.2, 33.3, 29.6, 27.0, 24.0, 23.0, 22.5, 21.9, 21.9, 18.2. HRMS (ESI) calculated for $\text{C}_{19}\text{H}_{33}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 378.2073, found 378.2076.



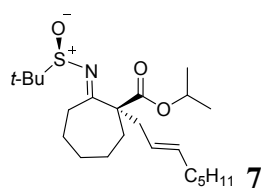
isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl)imino)-1-((*E*)-hex-2-en-1-yl)cycloheptane-1-carboxylate **5**:

76% yield, yellow oil. $[\alpha]_{19}^D = +7.28$ (c 3.3, CHCl_3). IR (KBr) ν_{max} : 2927, 2856, 1730, 1617, 1457, 1386, 1376, 1360, 1210, 1190, 1184, 1107, 1082, 960 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 5.44 (dt, $J = 14.9, 6.5$ Hz, 1H), 5.37 – 5.23 (m, 1H), 4.96 (m, 1H), 2.91 (ddd, $J = 12.7, 6.7, 4.4$ Hz, 1H), 2.74 (dd, $J = 14.0, 6.4$ Hz, 1H), 2.63 (ddd, $J = 13.2, 8.6, 5.0$ Hz, 1H), 2.30 (dd, $J = 14.0, 7.7$ Hz, 1H), 2.10 (dd, $J = 13.3, 8.8$ Hz, 1H), 1.92 (m, 2H), 1.79 – 1.67 (m, 4H), 1.62 – 1.32 (m, 5H), 1.23 (s, 9H), 1.18 (dd, $J = 6.2, 3.1$ Hz, 6H), 0.84 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.1, 172.4, 134.7, 125.3, 68.5, 61.6, 57.1, 40.0, 34.8, 34.2, 33.2, 29.6, 27.0, 23.9, 22.6, 22.5, 21.8, 21.8, 13.7. HRMS (ESI) calculated for $\text{C}_{21}\text{H}_{37}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 406.2386, found 406.2382.



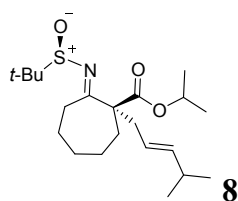
isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl)imino)-1-((*E*)-hept-2-en-1-yl)cycloheptane-1-carboxylate **6**:

86% yield, yellow oil. $[\alpha]_{19}^D = -7.90$ (c 2.3, CHCl_3). IR (KBr) ν_{max} : 2926, 2856, 1731, 1616, 1457, 1386, 1361, 1212, 1189, 1107, 1082, 801 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 5.47 (dt, $J = 14.0, 6.6$ Hz, 1H), 5.35 (dt, $J = 14.9, 7.2$ Hz, 1H), 4.99 (m, 1H), 3.05 – 2.87 (m, 1H), 2.77 (dd, $J = 14.0, 6.4$ Hz, 1H), 2.66 (ddd, $J = 13.2, 8.3, 5.1$ Hz, 1H), 2.33 (dd, $J = 14.0, 7.7$ Hz, 1H), 2.13 (dd, $J = 13.1, 9.0$ Hz, 1H), 1.98 (d, $J = 6.9$ Hz, 2H), 1.76 (m, 5H), 1.64 – 1.38 (m, 4H), 1.33 – 1.31 (m, 2H), 1.26 (s, 9H), 1.21 (dd, $J = 6.3, 3.1$ Hz, 6H), 0.88 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (10m, 0 MHz, Chloroform-*d*) δ 187.2, 172.5, 134.9, 125.1, 68.6, 61.6, 57.1, 40.1, 34.3, 33.2, 32.4, 31.7, 29.6, 27.1, 24.0, 22.5, 22.3, 21.9, 21.8, 14.0. HRMS (ESI) calculated for $\text{C}_{22}\text{H}_{39}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 420.2543, found 420.2548.



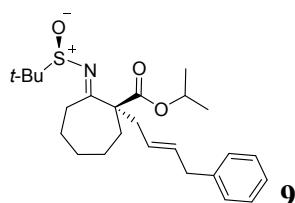
isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl)imino)-1-((*E*)-oct-2-en-1-yl)cycloheptane-1-carboxylate **7**:

72% yield, yellow oil. $[\alpha]_{20}^D = -11.41$ (c 1.1, CHCl_3). IR (KBr) ν_{max} : 2926, 2856, 1730, 1618, 1457, 1386, 1361, 1205, 1182, 1146, 1107, 1082 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 5.46 (dt, $J = 15.2, 6.5$ Hz, 1H), 5.34 (ddd, $J = 14.8, 7.8, 6.4$ Hz, 1H), 4.99 (m, 1H), 2.94 (ddd, $J = 12.8, 6.6, 4.5$ Hz, 1H), 2.77 (dd, $J = 13.9, 6.4$ Hz, 1H), 2.66 (td, $J = 8.2, 7.6, 3.7$ Hz, 1H), 2.32 (dd, $J = 14.0, 7.8$ Hz, 1H), 2.12 (ddd, $J = 12.3, 8.3, 2.9$ Hz, 1H), 1.96 (m, 2H), 1.80 – 1.69 (m, 4H), 1.61 – 1.28 (m, 9H), 1.26 (s, 9H), 1.20 (dd, $J = 6.2, 3.2$ Hz, 6H), 0.87 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.2, 172.5, 135.0, 125.1, 68.6, 61.6, 57.1, 40.0, 34.3, 33.2, 32.7, 31.5, 29.7, 29.2, 27.1, 24.0, 22.6, 22.5, 21.9, 21.8, 14.2. HRMS (ESI) calculated for $\text{C}_{23}\text{H}_{41}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 434.2699, found 434.2698.



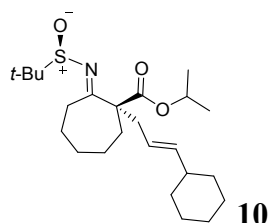
isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl)imino)-1-((*E*)-4-methylpent-2-en-1-yl)cycloheptane-1-carboxylate **8**:

68% yield, yellow oil. $[\alpha]_{20}^D = +16.26$ (c 1.0, CHCl_3). IR (KBr) ν_{max} : 2962, 2872, 1747, 1616, 1261, 1262, 974 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 5.44 (dd, $J = 15.3, 6.6$ Hz, 1H), 5.35 – 5.26 (m, 1H), 4.98 (m, 1H), 2.95 (ddd, $J = 12.8, 6.5, 4.6$ Hz, 1H), 2.76 (dd, $J = 13.9, 6.5$ Hz, 1H), 2.64 (ddd, $J = 13.2, 8.4, 5.3$ Hz, 1H), 2.31 (dd, $J = 13.9, 7.7$ Hz, 1H), 2.22 (dt, $J = 13.5, 6.7$ Hz, 1H), 2.12 (dd, $J = 13.2, 8.8$ Hz, 1H), 1.82 – 1.69 (m, 4H), 1.60 – 1.41 (m, 3H), 1.26 (s, 9H), 1.20 (dd, $J = 6.3, 3.9$ Hz, 6H), 0.94 (dd, $J = 6.7, 1.3$ Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.3, 172.5, 142.0, 122.2, 68.6, 61.7, 57.1, 40.0, 34.3, 33.2, 31.3, 29.7, 27.1, 24.0, 22.7, 22.6, 22.6, 21.9, 21.9. HRMS (ESI) calculated for $\text{C}_{21}\text{H}_{37}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 406.2386, found 406.2389.



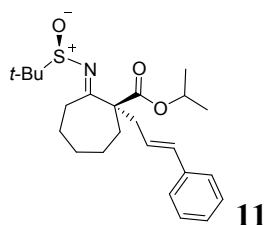
isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl)imino)-1-((*E*)-4-phenylbut-2-en-1-yl)cycloheptane-1-carboxylate **9**:

75% yield, yellow oil. $[\alpha]_{20}^D = +12.43$ (c 0.4, CHCl_3). IR (KBr) ν_{max} : 2926, 2856, 2360, 2342, 1771, 1718, 1616, 1507, 1456, 1210, 1106, 803, 699, 669 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 7.28 (d, $J = 7.7$ Hz, 2H), 7.21 – 7.13 (m, 3H), 5.63 (dt, $J = 14.2, 6.8$ Hz, 1H), 5.47 (dt, $J = 15.0, 7.3$ Hz, 1H), 4.96 (m, 1H), 3.32 (d, $J = 6.8$ Hz, 2H), 2.96 (dt, $J = 12.1, 5.5$ Hz, 1H), 2.82 (dd, $J = 14.0, 6.5$ Hz, 1H), 2.64 (dt, $J = 13.2, 6.7$ Hz, 1H), 2.37 (dd, $J = 14.0, 7.9$ Hz, 1H), 2.15 (dd, $J = 13.3, 8.8$ Hz, 1H), 1.75 (td, $J = 16.2, 13.1, 8.6$ Hz, 5H), 1.49 – 1.40 (m, 2H), 1.25 (s, 9H), 1.16 (dd, $J = 8.0, 6.2$ Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.1, 172.4, 140.6, 133.3, 128.6, 128.5, 126.9, 126.1, 68.7, 61.6, 57.2, 39.9, 39.3, 34.3, 33.3, 29.6, 27.1, 24.0, 22.5, 21.9, 21.8. HRMS (ESI) calculated for $\text{C}_{25}\text{H}_{37}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 454.2386, found 454.2388.



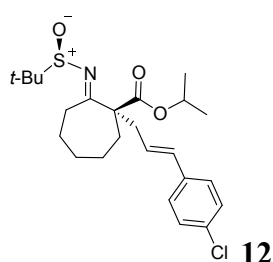
Isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl)imino)-1-((*E*)-3-cyclohexylallyl) cycloheptane-1-carboxylate **10**:

82% yield, yellow oil. $[\alpha]_{20}^D = +18.56$ (c 1.9, CHCl_3). IR (KBr) ν_{max} : 2978, 2925, 2853, 1731, 1617, 1507, 1456, 1387, 1256, 1222, 1182, 1146, 1107, 1081, 972 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 5.41 (dd, $J = 15.4, 6.5$ Hz, 1H), 5.34 – 5.26 (m, 1H), 4.98 (m, 1H), 2.93 (ddd, $J = 12.8, 6.6, 4.5$ Hz, 1H), 2.74 (dd, $J = 13.9, 6.4$ Hz, 1H), 2.63 (ddd, $J = 13.1, 8.5, 5.2$ Hz, 1H), 2.31 (dd, $J = 13.9, 7.6$ Hz, 1H), 2.14 – 2.06 (m, 1H), 1.95 – 1.67 (m, 8H), 1.65 – 1.33 (m, 7H), 1.25 (s, 9H), 1.19 (dd, $J = 6.3, 4.2$ Hz, 6H), 1.13 – 0.98 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.2, 172.5, 140.9, 122.6, 68.6, 61.7, 57.1, 40.9, 40.1, 34.3, 33.2, 33.1, 33.1, 29.6, 27.1, 26.3, 26.1, 24.0, 22.5, 21.9, 21.9. HRMS (ESI) calculated for $\text{C}_{24}\text{H}_{41}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 446.2699, found 446.2697.



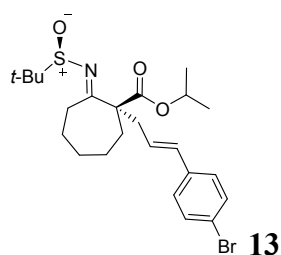
isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl)imino)-1-cinnamylcycloheptane-1-carboxylate **11**:

70% yield, yellow oil. $[\alpha]_{22}^D = +29.52$ (c 0.4, CHCl_3). IR (KBr) ν_{max} : 2928, 2858, 2360, 2342, 2330, 1717, 1699, 1683, 1647, 1616, 1541, 1457, 1105, 1080, 669, 650 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, $J = 7.5$ Hz, 4H), 7.20 (d, $J = 6.8$ Hz, 1H), 6.41 (d, $J = 15.7$ Hz, 1H), 6.19 (dt, $J = 15.5, 7.8$ Hz, 1H), 5.01 (m, 1H), 3.00 (dd, $J = 13.4, 6.5$ Hz, 2H), 2.69 (dt, $J = 13.2, 6.6$ Hz, 1H), 2.55 (dd, $J = 14.1, 8.3$ Hz, 1H), 2.19 (dd, $J = 14.2, 9.0$ Hz, 1H), 1.80 (m, 5H), 1.56 – 1.42 (m, 2H), 1.28 (s, 9H), 1.20 (d, $J = 6.2$ Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.1, 172.4, 137.5, 133.6, 128.6, 127.4, 126.3, 126.0, 68.9, 61.8, 57.2, 40.6, 34.4, 33.7, 29.6, 27.1, 24.1, 22.6, 21.9, 21.9. HRMS (ESI) calculated for $\text{C}_{24}\text{H}_{35}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 440.2230, found 440.2237.



isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl) imino)-1-((*E*)-3-(4-chlorophenyl)allyl)cycloheptane-1-carboxylate **12**:

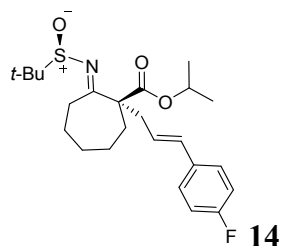
89% yield, yellow oil. $[\alpha]_{22}^D = +30.50$ (c 0.7, CHCl₃). IR (KBr) ν_{\max} : 2977, 2928, 2858, 1729, 1684, 1616, 1506, 1490, 1456, 1235, 1185, 1104, 1080, 1012, 970, 823 cm⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.17 (m, 4H), 6.36 (d, $J = 15.8$ Hz, 1H), 6.17 (ddd, $J = 15.4, 8.1, 6.6$ Hz, 1H), 5.01 (m, 1H), 3.17 – 2.86 (m, 2H), 2.67 (ddd, $J = 13.2, 8.1, 5.5$ Hz, 1H), 2.54 (ddd, $J = 14.0, 8.1, 1.1$ Hz, 1H), 2.18 (dd, $J = 13.7, 8.8$ Hz, 1H), 1.89 – 1.67 (m, 4H), 1.62 – 1.43 (m, 3H), 1.27 (s, 9H), 1.19 (dd, $J = 6.3, 3.7$ Hz, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 187.0, 172.4, 135.9, 132.9, 132.3, 128.8, 127.4, 126.8, 68.9, 61.7, 57.2, 40.6, 34.4, 33.8, 29.6, 27.1, 24.0, 22.5, 21.9, 21.9. HRMS (ESI) calculated for C₂₄H₃₄ClNNaO₃S⁺ [M+Na]⁺: 474.1840, found 474.1847.



isopropyl (*R,E*)-1-((*E*)-3-(4-bromophenyl)allyl)-2-(((*R*)-*tert*-butylsulfinyl)imino)cycloheptane-1-carboxylate **13**:

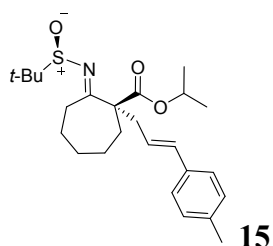
82% yield, $[\alpha]_{21}^D = +29.99$ (c 0.6, CHCl₃). IR (KBr) ν_{\max} : 2970, 2926, 2858, 1730, 1684, 1616, 1506, 1457, 1235, 1180, 1104, 1080, 1012, 970, 801 cm⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.36 (m, 2H), 7.22 – 7.10 (m, 2H), 6.34 (d, $J = 15.8$ Hz, 1H), 6.19 (ddd, $J = 15.7, 8.0, 6.6$ Hz, 1H), 5.00 (m, 1H), 3.14 – 2.86 (m, 2H), 2.67 (ddd, $J = 13.2, 8.0, 5.6$ Hz, 1H), 2.54 (ddd, $J = 13.9, 8.1, 1.1$ Hz, 1H), 2.18 (dd, $J = 13.7, 8.8$ Hz, 1H), 1.77 (ddt, $J = 17.6, 13.4, 7.0$ Hz, 4H), 1.61 – 1.37 (m, 3H), 1.27 (s, 9H), 1.19 (dd, $J = 6.3, 3.9$ Hz, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 187.0, 172.4, 136.3, 132.4, 131.7, 127.8, 126.9, 121.1, 68.9, 61.6, 57.2, 40.6, 34.4, 33.8, 29.6, 27.1, 24.0,

22.5, 21.9, 21.8. HRMS (ESI) calculated for $C_{24}H_{34}BrNNaO_3S^+$ $[M+Na]^+$: 518.1335, found 518.1337.



isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl)imino)-1-((*E*)-3-(4-fluorophenyl)allyl)cycloheptane-1-carboxylate **14**:

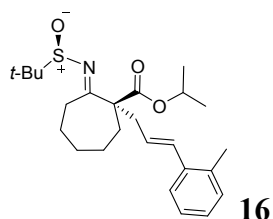
90% yield, yellow oil. $[\alpha]_{23}^D = -10.40$ (c 0.3, $CHCl_3$). IR (KBr) ν_{max} : 2926, 2858, 2361, 2342, 1730, 1718, 1617, 1507, 1457, 1165, 1107, 1081, 1068, 1016, 969 cm^{-1} . 1H NMR (400 MHz, Chloroform-*d*) δ 7.25 (d, $J = 7.5$ Hz, 2H), 6.97 (t, $J = 8.7$ Hz, 2H), 6.37 (d, $J = 15.8$ Hz, 1H), 6.15 – 6.05 (m, 1H), 5.01 (m, 1H), 2.99 (ddd, $J = 13.2, 10.6, 5.9$ Hz, 2H), 2.67 (ddd, $J = 13.2, 8.3, 5.4$ Hz, 1H), 2.53 (dd, $J = 14.1, 8.1$ Hz, 1H), 2.18 (dd, $J = 13.9, 8.8$ Hz, 1H), 1.80 (dd, $J = 14.8, 8.3$ Hz, 4H), 1.59 – 1.40 (m, 3H), 1.27 (s, 9H), 1.20 (dd, $J = 6.3, 3.0$ Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.1, 172.4, 163.4, 161.0, 133.6, 133.6, 132.3, 127.7, 127.6, 125.7, 115.6, 115.4, 68.9, 61.7, 57.2, 40.6, 34.4, 33.8, 29.6, 27.1, 24.0, 22.5, 21.9, 21.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.10 (p, $J = 7.3$ Hz). HRMS (ESI) calculated for $C_{24}H_{34}FNNaO_3S^+$ $[M+Na]^+$: 458.2136, found 458.2137.



isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl)imino)-1-((*E*)-3-(*p*-tolyl)allyl)cycloheptane-1-carboxylate **15**

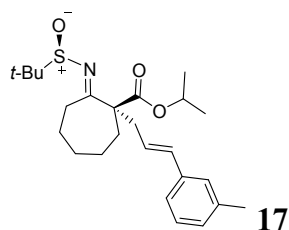
91% yield, yellow oil. $[\alpha]_{21}^D = +12.77$ (c 1.2, $CHCl_3$). IR (KBr) ν_{max} : 2927, 2862, 2360, 2342, 1730, 1616, 1456, 1387, 1361, 1261, 1237, 1106, 1081, 970, 797 cm^{-1} . 1H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.15 (m, 2H), 7.08 (d, $J = 8.0$ Hz, 2H), 6.38 (d, $J = 15.7$ Hz, 1H), 6.12 (ddd, $J = 15.4, 8.2, 6.6$ Hz, 1H), 5.00 (m, 1H), 3.11 – 2.84 (m, 2H), 2.68 (ddd, $J = 13.2, 8.1, 5.4$ Hz, 1H), 2.53 (ddd, $J = 13.9, 8.2, 1.2$ Hz, 1H), 2.31 (s, 3H), 2.21 – 2.12 (m, 1H), 1.77 (m, 5H), 1.57 – 1.42 (m, 2H), 1.28 (s, 9H), 1.20

(dd, $J = 6.3, 1.4$ Hz, 6H). ^{13}C NMR (100 MHz, Chloroform- d) δ 187.1, 172.4, 137.1, 134.7, 133.4, 129.3, 126.1, 124.8, 68.8, 61.8, 57.2, 40.6, 34.4, 33.6, 29.6, 27.1, 24.0, 22.5, 21.9, 21.9, 21.3. HRMS (ESI) calculated for $\text{C}_{25}\text{H}_{37}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 454.2386, found 454.2387.



isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl)imino)-1-((*E*)-3-(*o*-tolyl)allyl)cycloheptane-1-carboxylate **16**:

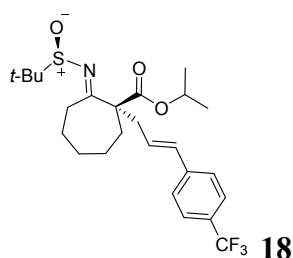
89% yield, yellow oil. $[\alpha]_{23}^{\text{D}} = +16.86$ (c 1.0, CHCl_3). IR (KBr) ν_{max} : 2926, 2868, 2360, 2342, 1731, 1617, 1456, 1386, 1361, 1261, 1237, 1106, 1081, 970, 801 cm^{-1} . ^1H NMR (400 MHz, Chloroform- d) δ 7.38 – 7.32 (m, 1H), 7.12 (q, $J = 3.1$ Hz, 3H), 6.66 – 6.56 (m, 1H), 6.05 (ddd, $J = 15.3, 8.3, 6.5$ Hz, 1H), 5.01 (m, 1H), 3.12 – 2.93 (m, 2H), 2.75 – 2.64 (m, 1H), 2.58 (ddd, $J = 14.0, 8.4, 1.2$ Hz, 1H), 2.31 (s, 3H), 2.23 – 2.15 (m, 1H), 1.82 (dtd, $J = 17.6, 11.4, 10.7, 3.4$ Hz, 4H), 1.63 – 1.45 (m, 3H), 1.28 (s, 9H), 1.20 (dd, $J = 6.3, 1.3$ Hz, 6H). ^{13}C NMR (100 MHz, Chloroform- d) δ 187.0, 172.4, 133.6, 135.1, 131.5, 130.3, 127.3, 126.2, 125.8, 68.8, 61.7, 57.2, 40.8, 34.4, 33.5, 29.6, 27.1, 24.0, 22.5, 21.9, 21.9, 20.0. HRMS (ESI) calculated for $\text{C}_{25}\text{H}_{37}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 454.2386, found 454.2389.



isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl)imino)-1-((*E*)-3-(*m*-tolyl)allyl)cycloheptane-1-carboxylate **17**:

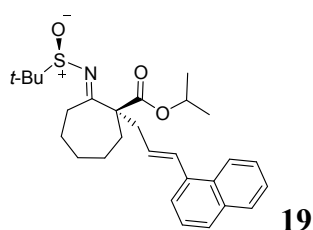
82% yield, yellow oil. $[\alpha]_{24}^{\text{D}} = +15.93$ (c 0.7, CHCl_3). IR (KBr) ν_{max} : 2927, 2862, 2360, 2342, 1731, 1616, 1456, 1387, 1361, 1261, 1237, 1107, 1082, 970, 797 cm^{-1} . ^1H NMR (400 MHz, Chloroform- d) δ 7.20 – 7.09 (m, 3H), 7.02 (d, $J = 7.4$ Hz, 1H), 6.38 (d, $J = 15.7$ Hz, 1H), 6.17 (dt, $J = 15.3, 7.4$ Hz, 1H), 5.01 (m, 1H), 2.99 (dd, $J = 13.8, 6.5$ Hz, 2H), 2.69 (dq, $J = 13.3, 7.0, 6.0$ Hz, 1H), 2.54 (dd, $J = 14.0, 8.2$ Hz, 1H), 2.32

(s, 3H), 2.18 (dd, $J = 14.3, 8.8$ Hz, 1H), 1.82 (dd, $J = 12.2, 7.8$ Hz, 4H), 1.61 – 1.43 (m, 3H), 1.28 (s, 9H), 1.21 (d, $J = 6.2$ Hz, 6H). ^{13}C NMR (100 MHz, Chloroform- d) δ 187.1, 172.4, 138.2, 137.4, 133.7, 128.5, 128.1, 127.0, 125.7, 123.4, 68.8, 61.8, 57.2, 40.6, 34.4, 33.6, 29.6, 27.1, 24.1, 22.6, 21.9, 21.9, 21.5. HRMS (ESI) calculated for $\text{C}_{25}\text{H}_{37}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 454.2386, found 454.2388.



isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl)imino)-1-((*E*)-3-(4-(trifluoromethyl)phenyl)allyl)cycloheptane-1-carboxylate **18**:

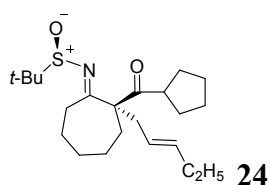
87% yield, yellow oil. $[\alpha]_{24}^{\text{D}} = +31.26$ (c 0.4, CHCl_3). IR (KBr) ν_{max} : 2928, 2857, 2360, 2342, 1732, 1718, 1618, 1507, 1457, 1165, 1123, 1107, 1080, 1068, 1016 cm^{-1} . ^1H NMR (400 MHz, Chloroform- d) δ 7.53 (d, $J = 8.0$ Hz, 2H), 7.39 (d, $J = 8.0$ Hz, 2H), 6.44 (d, $J = 15.8$ Hz, 1H), 6.32 (dt, $J = 15.3, 7.2$ Hz, 1H), 5.07 – 4.96 (m, 1H), 3.01 (dd, $J = 13.2, 6.5$ Hz, 2H), 2.68 (dt, $J = 13.3, 6.7$ Hz, 1H), 2.58 (dd, $J = 14.1, 8.0$ Hz, 1H), 2.19 (dd, $J = 13.7, 8.8$ Hz, 1H), 1.87 – 1.71 (m, 4H), 1.59 (d, $J = 4.9$ Hz, 2H), 1.53 – 1.46 (m, 1H), 1.28 (s, 9H), 1.20 (ddd, $J = 6.0, 4.2, 1.4$ Hz, 6H). ^{13}C NMR (100 MHz, Chloroform- d) δ 186.9, 172.3, 140.9, 132.2, 129.1, 126.4, 125.6, 125.6, 69.0, 61.7, 57.2, 40.6, 34.4, 33.9, 29.6, 27.1, 24.1, 22.5, 22.0, 21.9. ^{19}F NMR (376 MHz, Chloroform- d) δ -62.5. HRMS (ESI) calculated for $\text{C}_{25}\text{H}_{34}\text{F}_3\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 508.2104, found 508.2108.



isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl)imino)-1-((*E*)-3-(naphthalen-1-yl)allyl)cycloheptane-1-carboxylate **19**:

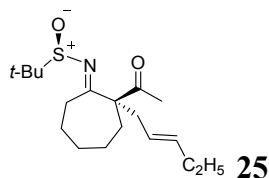
93% yield, yellow oil. $[\alpha]_{24}^{\text{D}} = 28.42$ (c 0.5, CHCl_3). IR (KBr) ν_{max} : 2927, 2857, 2360, 2342, 1732, 1717, 1616, 1507, 1457, 1105, 1079, 815 cm^{-1} . ^1H NMR (400 MHz,

Chloroform-*d*) δ 7.81 – 7.73 (m, 3H), 7.65 (d, $J = 1.6$ Hz, 1H), 7.53 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.47 – 7.39 (m, 2H), 6.58 (d, $J = 15.8$ Hz, 1H), 6.33 (ddd, $J = 15.4, 8.2, 6.6$ Hz, 1H), 5.03 (m, 1H), 3.10 – 2.93 (m, 2H), 2.73 – 2.56 (m, 2H), 2.26 – 2.16 (m, 1H), 1.89 – 1.73 (m, 4H), 1.61 – 1.44 (m, 3H), 1.30 (s, 9H), 1.21 (dd, $J = 6.3, 2.1$ Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.1, 172.5, 134.9, 133.7, 133.6, 132.9, 128.3, 128.0, 127.8, 126.4, 126.3, 125.9, 125.8, 123.6, 68.9, 61.8, 57.2, 40.8, 34.4, 33.8, 29.6, 27.1, 24.0, 22.6, 22.0, 21.9. HRMS (ESI) calculated for $\text{C}_{28}\text{H}_{37}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 490.2386, found 490.2388.



(*R*)-*N*-((*R,E*)-2-(cyclopentanecarbonyl)-2-((*E*)-pent-2-en-1-yl)cycloheptylidene)-2-methylpropane-2-sulfinamide **24**:

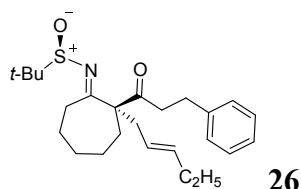
93% yield, yellow oil. $[\alpha]_{20}^{\text{D}} = +376.093$ (c 0.9, CHCl_3). IR (KBr) ν_{max} : 2959, 2929, 2867, 1705, 1609, 1456, 1360, 1261, 1181, 1083, 802 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 5.49 (dt, $J = 15.2, 6.3, 1.3$ Hz, 1H), 5.13 (dddt, $J = 14.9, 8.2, 6.7, 1.6$ Hz, 1H), 3.24 – 3.06 (m, 2H), 3.02 – 2.88 (m, 1H), 2.28 (ddd, $J = 14.6, 7.9, 1.2$ Hz, 1H), 2.18 – 2.04 (m, 2H), 2.01 – 1.85 (m, 4H), 1.79 – 1.65 (m, 7H), 1.64 – 1.35 (m, 5H), 1.31 (s, 9H), 1.21 – 1.12 (m, 1H), 0.92 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 213.8, 187.3, 136.8, 123.7, 68.9, 57.5, 46.3, 37.9, 35.7, 33.0, 31.5, 30.1, 29.6, 29.3, 26.8, 26.6, 25.8, 23.3, 22.9, 13.8. HRMS (ESI) calculated for $\text{C}_{22}\text{H}_{37}\text{NNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 402.2437, found 402.2437.



(*R*)-*N*-((*R,E*)-2-acetyl-2-((*E*)-pent-2-en-1-yl)cycloheptylidene)-2-methylpropane-2-sulfinamide **25**:

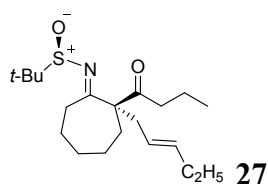
92% yield, yellow oil. $[\alpha]_{24}^{\text{D}} = +222.40$ (c 1.3, CHCl_3). IR (KBr) ν_{max} : 2958, 2927, 2867, 1705, 1609, 1456, 1360, 1261, 1181, 1083, 801 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 5.52 (dt, $J = 14.1, 6.5$ Hz, 1H), 5.20 (dt, $J = 15.0, 7.3$ Hz, 1H), 3.00 (ddd, $J = 12.0, 6.8, 2.8$ Hz, 1H), 2.86 (dd, $J = 14.6, 6.8$ Hz, 1H), 2.36 (ddd, $J = 22.1,$

12.8, 8.0 Hz, 2H), 2.16 – 2.09 (m, 4H), 2.01 – 1.72 (m, 6H), 1.66 – 1.41 (m, 3H), 1.28 (s, 9H), 0.96 – 0.90 (m, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 207.3, 188.0, 136.9, 123.6, 68.4, 57.4, 38.6, 34.7, 30.5, 29.9, 28.6, 26.7, 25.8, 23.7, 22.8, 13.8. HRMS (ESI) calculated for C₁₈H₃₁NNaO₂S⁺ [M+Na]⁺: 348.1968, found 348.1967.



(*R*)-2-methyl-N-((*R,E*)-2-((*E*)-pent-2-en-1-yl)-2-(3-phenylpropanoyl)cycloheptylidene)propane-2-sulfinamide **26**:

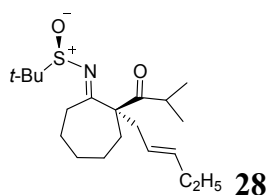
89% yield, yellow oil. [α]₂₃ D= +158.64 (c 0.4, CHCl₃). IR (KBr) ν_{\max} : 2928, 2858, 2360, 1731, 1618, 1456, 1387, 1261, 1237, 1107, 1082, 970, 801 cm⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.27 (m, 1H), 7.25 – 7.05 (m, 4H), 5.48 (dt, *J* = 14.4, 6.6 Hz, 1H), 5.10 (dt, *J* = 15.2, 7.4 Hz, 1H), 2.92 – 2.64 (m, 6H), 2.27 (dd, *J* = 14.8, 7.9 Hz, 1H), 2.10 (q, *J* = 10.8 Hz, 2H), 1.95 (t, *J* = 7.4 Hz, 2H), 1.73 (dt, *J* = 58.6, 10.2 Hz, 5H), 1.36 – 1.23 (m, 11H), 0.92 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 208.4, 187.4, 141.1, 136.9, 128.6, 128.6, 126.3, 123.7, 68.4, 57.5, 40.2, 38.3, 34.7, 30.1, 30.0, 29.9, 29.1, 25.8, 23.5, 22.8, 13.9. HRMS (ESI) calculated for C₂₅H₃₇NNaO₂S⁺ [M+Na]⁺: 438.2437, found 438.2433.



(*R*)-N-((*R,E*)-2-butyl-2-((*E*)-pent-2-en-1-yl)cycloheptylidene)-2-methylpropane-2-sulfinamide **27**:

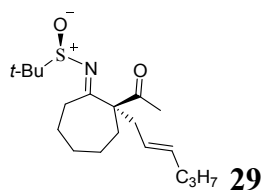
97% yield, yellow oil. [α]₂₁ D= 222.65 (c 1.1, CHCl₃). IR (KBr) ν_{\max} : 2926, 2857, 1731, 1616, 1457, 1386, 1368, 1205, 1182, 1146, 1107, 1082, 801 cm⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 5.50 (dt, *J* = 14.8, 6.4 Hz, 1H), 5.17 (dt, *J* = 15.0, 7.3 Hz, 1H), 3.05 (ddd, *J* = 11.9, 6.7, 2.7 Hz, 1H), 2.89 (dd, *J* = 14.6, 6.7 Hz, 1H), 2.38 (t, *J* = 7.2 Hz, 2H), 2.33 – 2.20 (m, 2H), 2.11 (dd, *J* = 15.1, 10.2 Hz, 1H), 2.01 – 1.53 (m, 9H), 1.30 (m, 11H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 209.3, 187.8, 136.8, 123.8, 68.3, 57.4, 40.3, 38.4, 35.0, 30.1, 30.0,

29.1, 25.8, 23.5, 22.8, 17.4, 13.9, 13.9. HRMS (ESI) calculated for $C_{20}H_{35}NNaO_2S^+$ $[M+Na]^+$: 376.2281, found 376.2283.



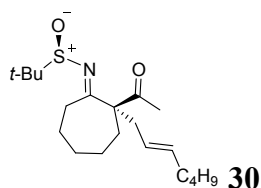
(R)-*N*-((*R,E*)-2-isobutyryl-2-((*E*)-pent-2-en-1-yl)cycloheptylidene)-2-methylpropane-2-sulfinamide **28**:

95% yield, yellow oil. $[\alpha]_{21}^D = +255.45$ (c 0.6, $CHCl_3$). IR (KBr) ν_{max} : 2927, 2860, 1731, 1616, 1458, 1386, 1374, 1361, 1261, 1206, 1155, 1106, 1083, 969, 802 cm^{-1} . 1H NMR (400 MHz, Chloroform-*d*) δ 5.55 – 5.45 (m, 1H), 5.13 (m, 1H), 3.24 – 3.01 (m, 2H), 2.98 – 2.87 (m, 1H), 2.32 (ddd, $J = 14.7, 8.0, 1.2$ Hz, 1H), 2.18 – 1.90 (m, 6H), 1.80 – 1.63 (m, 3H), 1.32 (m, 11H), 1.03 (d, $J = 6.6$ Hz, 3H), 0.93 (t, $J = 7.5$ Hz, 3H), 0.89 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 213.9, 187.2, 136.8, 123.8, 69.0, 57.5, 37.8, 35.8, 34.9, 30.1, 29.9, 28.8, 25.8, 23.2, 22.9, 20.8, 19.8, 13.8. HRMS (ESI) calculated for $C_{20}H_{35}NNaO_2S^+$ $[M+Na]^+$: 376.2281, found 376.2284.



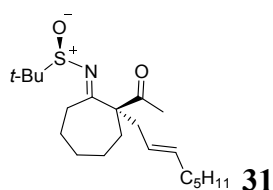
(R)-*N*-((*R,E*)-2-acetyl-2-((*E*)-hex-2-en-1-yl)cycloheptylidene)-2-methylpropane-2-sulfinamide **29**:

83% yield, yellow oil. $[\alpha]_{24}^D = +210.65$ (c 1.3, $CHCl_3$). IR (KBr) ν_{max} : 2956, 2927, 2860, 1710, 1610, 1457, 1359, 1166, 1148, 1082, 970 cm^{-1} . 1H NMR (400 MHz, Chloroform-*d*) δ 5.48 (dt, $J = 15.0, 6.8, 1.3$ Hz, 1H), 5.24 – 5.16 (m, 1H), 3.01 (ddd, $J = 12.0, 7.0, 3.1$ Hz, 1H), 2.88 (ddt, $J = 14.5, 6.7, 1.2$ Hz, 1H), 2.42 – 2.30 (m, 2H), 2.10 (s, 4H), 1.99 – 1.74 (m, 5H), 1.69 – 1.63 (m, 2H), 1.56 – 1.33 (m, 4H), 1.28 (s, 9H), 0.85 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 207.3, 188.0, 135.2, 124.7, 68.3, 57.4, 38.6, 34.8, 34.7, 30.4, 29.9, 28.6, 26.7, 23.7, 22.7, 22.6, 13.7. HRMS (ESI) calculated for $C_{19}H_{33}NNaO_2S^+$ $[M+Na]^+$: 362.2124, found 362.2127.



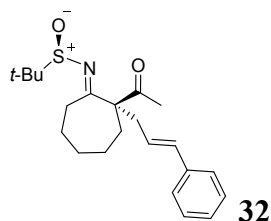
(*R*)-*N*-((*R,E*)-2-acetyl-2-((*E*)-hept-2-en-1-yl)cycloheptylidene)-2-methylpropane-2-sulfonamide **30**:

80% yield, yellow oil. $[\alpha]_{24}^D = +219.67$ (c 1.8, CHCl_3). IR (KBr) ν_{max} : 2958, 2928, 2858, 1711, 1616, 1458, 1359, 1205, 1148, 1082, 979 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 5.53 – 5.43 (m, 1H), 5.23 – 5.15 (m, 1H), 3.00 (ddd, $J = 12.0, 7.0, 3.1$ Hz, 1H), 2.86 (dd, $J = 14.6, 6.7$ Hz, 1H), 2.41 – 2.29 (m, 2H), 2.09 (s, 4H), 2.03 – 1.67 (m, 7H), 1.66 – 1.29 (m, 6H), 1.27 (s, 9H), 0.85 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 207.3, 188.0, 135.4, 124.5, 68.3, 57.3, 38.6, 34.7, 32.4, 31.6, 30.4, 29.9, 28.5, 26.7, 23.7, 22.7, 22.3, 14.0. HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{35}\text{NNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 376.2281, found 376.2287.



(*R*)-*N*-((*R,E*)-2-acetyl-2-((*E*)-oct-2-en-1-yl)cycloheptylidene)-2-methylpropane-2-sulfonamide **31**:

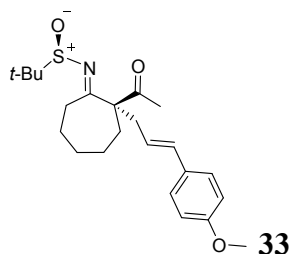
81% yield, yellow oil. $[\alpha]_{22}^D = +251.97$ (c 0.8, CHCl_3). IR (KBr) ν_{max} : 2959, 2927, 2860, 1716, 1617, 1458, 1359, 1205, 1150, 1082, 979 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 5.49 (dt, $J = 14.9, 6.7, 1.3$ Hz, 1H), 5.26 – 5.12 (m, 1H), 3.01 (ddd, $J = 12.0, 6.9, 3.1$ Hz, 1H), 2.88 (dd, $J = 14.5, 6.7$ Hz, 1H), 2.43 – 2.30 (m, 2H), 2.10 (s, 4H), 2.02 – 1.64 (m, 8H), 1.55 – 1.33 (m, 3H), 1.29 (s, 9H), 1.26 – 1.19 (m, 4H), 0.87 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 207.4, 188.0, 135.5, 124.5, 68.4, 57.4, 38.6, 34.7, 32.7, 31.5, 30.4, 29.9, 29.2, 28.6, 26.7, 23.7, 22.8, 22.6, 14.2. HRMS (ESI) calculated for $\text{C}_{21}\text{H}_{37}\text{NNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 390.2437, found 390.2433.



(*R*)-*N*-((*R,E*)-2-acetyl-2-cinnamylcycloheptylidene)-2-methylpropane-2-sulfinamide

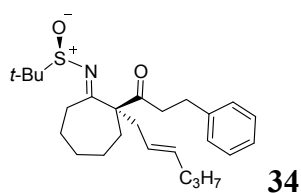
32:

90% yield, yellow oil. $[\alpha]_{24}^D = +165.74$ (c 1.1, CHCl_3). IR (KBr) ν_{max} : 2927, 2857, 1707, 1610, 1496, 1456, 1360, 1079, 967, 746, 694 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 4H), 7.21 (td, $J = 5.8, 2.6$ Hz, 1H), 6.44 (d, $J = 15.7$ Hz, 1H), 6.02 (dt, $J = 15.3, 7.4$ Hz, 1H), 3.11 – 3.01 (m, 2H), 2.63 – 2.55 (m, 1H), 2.45 (td, $J = 11.4, 3.2$ Hz, 1H), 2.17 (s, 4H), 1.92 – 1.67 (m, 5H), 1.56 – 1.37 (m, 2H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 207.2, 187.8, 137.1, 134.0, 128.7, 127.6, 126.3, 125.1, 68.3, 57.4, 39.3, 34.8, 31.0, 30.0, 28.5, 26.8, 23.9, 22.8. HRMS (ESI) calculated for $\text{C}_{22}\text{H}_{31}\text{NNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 396.1968, found 396.1963.



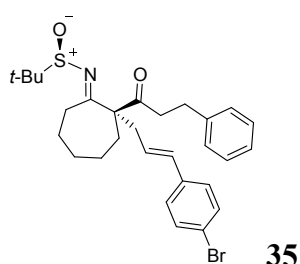
(*R*)-*N*-((*R,E*)-2-acetyl-2-((*E*)-3-(4-methoxyphenyl)allyl)cycloheptylidene)-2-methylpropane-2-sulfinamide **33**:

91% yield, yellow oil. $[\alpha]_{24}^D = +141.90$ (c 0.8, CHCl_3). IR (KBr) ν_{max} : 2927, 2856, 2342, 1706, 1635, 1608, 1457, 1109, 1034, 968, 834, 802, 754 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, $J = 8.6$ Hz, 2H), 6.82 (d, $J = 8.4$ Hz, 2H), 6.37 (d, $J = 15.7$ Hz, 1H), 5.86 (dt, $J = 15.3, 7.4$ Hz, 1H), 3.79 (s, 3H), 3.11 – 2.99 (m, 2H), 2.56 (dd, $J = 14.6, 7.9$ Hz, 1H), 2.44 (td, $J = 11.5, 3.2$ Hz, 1H), 2.16 (s, 4H), 1.92 – 1.68 (m, 5H), 1.59 – 1.39 (m, 2H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 207.3, 187.9, 159.3, 133.3, 130.0, 127.4, 122.8, 114.1, 68.4, 57.4, 55.4, 39.3, 34.8, 31.0, 30.0, 28.5, 26.8, 23.9, 22.8. HRMS (ESI) calculated for $\text{C}_{23}\text{H}_{33}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 426.2073, found 426.2074.



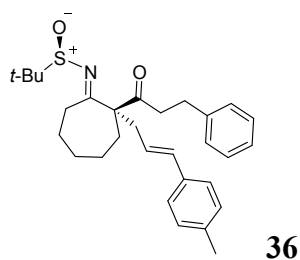
(*R*)-*N*-((*R,E*)-2-((*E*)-hex-2-en-1-yl)-2-(3-phenylpropanoyl)cycloheptylidene)-2-methylpropane-2-sulfinamide **34**:

89% yield, yellow oil. $[\alpha]_{22}^D = +176.25$ (c 0.8, CHCl_3). IR (KBr) ν_{max} : 2928, 2857, 1709, 1616, 1496, 1456, 1367, 1078, 967, 746, 694 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.11 (m, 5H), 5.43 (dt, $J = 15.0, 7.3$ Hz, 1H), 5.09 (dt, $J = 15.3, 7.4$ Hz, 1H), 2.93 – 2.60 (m, 6H), 2.26 (dd, $J = 15.1, 8.0$ Hz, 1H), 2.09 (q, $J = 10.8$ Hz, 2H), 1.85 (dt, $J = 40.9, 11.4$ Hz, 4H), 1.66 (d, $J = 9.9$ Hz, 2H), 1.43 – 1.18 (m, 14H), 0.85 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 208.3, 187.4, 141.1, 135.2, 128.6, 128.6, 126.3, 124.8, 68.3, 57.5, 40.2, 38.3, 34.8, 34.7, 30.1, 29.9, 29.0, 23.5, 22.8, 22.6, 13.8. HRMS (ESI) calculated for $\text{C}_{26}\text{H}_{39}\text{NNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 452.2594, found 452.2595.



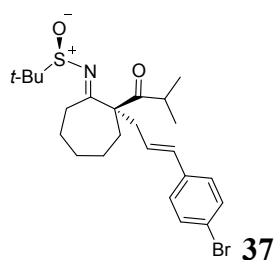
(*R*)-*N*-((*R,E*)-2-((*E*)-3-(4-bromophenyl)allyl)-2-(3-phenylpropanoyl)cycloheptylidene)-2-methylpropane-2-sulfinamide **35**:

89% yield, yellow oil. $[\alpha]_{22}^D = +121.58$ (c 1.2, CHCl_3). IR (KBr) ν_{max} : 2958, 2925, 2858, 2360, 2341, 1706, 1609, 1506, 1455, 1261, 1705, 1009, 800, 750, 699 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 (dd, $J = 8.4, 2.0$ Hz, 2H), 7.26 – 7.22 (m, 2H), 7.21 – 7.06 (m, 5H), 6.30 (d, $J = 15.5$ Hz, 1H), 5.85 (dt, $J = 15.8, 7.6$ Hz, 1H), 3.02 (dd, $J = 14.9, 6.7$ Hz, 1H), 2.84 (m, 5H), 2.48 (dd, $J = 14.8, 8.1$ Hz, 1H), 2.23 – 2.03 (m, 2H), 1.83 (dd, $J = 15.3, 8.6$ Hz, 2H), 1.77 – 1.64 (m, 3H), 1.47 – 1.39 (m, 1H), 1.30 (s, 9H), 1.27 – 1.24 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 208.1, 187.2, 140.9, 135.9, 132.7, 131.7, 128.7, 128.6, 127.8, 126.4, 126.1, 121.3, 68.2, 57.5, 40.3, 39.0, 34.7, 30.6, 30.0, 30.0, 28.9, 23.6, 22.8. HRMS (ESI) calculated for $\text{C}_{29}\text{H}_{36}\text{BrNNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 564.1542, found 564.1545.



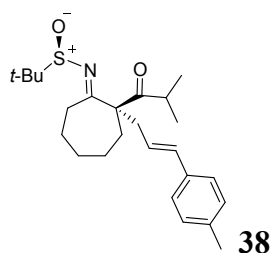
(*R*)-2-methyl-N-((*R,E*)-2-(3-phenylpropanoyl)-2-((*E*)-3-(*p*-tolyl)allyl) cycloheptylidene) propane-2-sulfinamide **36**:

85% yield, yellow oil. $[\alpha]_{22}^D = +136.80$ (c 1.6, CHCl_3). IR (KBr) ν_{max} : 2960, 2925, 2858, 2360, 2342, 1709, 1611, 1509, 1262, 1009, 801, 750, 699 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 7.28 (d, $J = 7.1$ Hz, 1H), 7.25 (d, $J = 1.7$ Hz, 1H), 7.21 – 7.08 (m, 7H), 6.36 (d, $J = 15.6$ Hz, 1H), 5.84 (ddd, $J = 15.3, 8.1, 6.7$ Hz, 1H), 3.05 (dd, $J = 14.7, 6.7$ Hz, 1H), 2.92 – 2.74 (m, 5H), 2.50 (ddd, $J = 14.7, 8.1, 1.3$ Hz, 1H), 2.33 (s, 3H), 2.19 – 2.08 (m, 2H), 1.87 (dd, $J = 15.1, 8.6$ Hz, 2H), 1.74 – 1.65 (m, 3H), 1.47 – 1.38 (m, 1H), 1.31 (s, 9H), 1.28 – 1.25 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 208.2, 187.3, 141.0, 137.4, 134.3, 133.8, 129.3, 128.6, 128.6, 126.3, 126.2, 124.0, 68.4, 57.5, 40.3, 39.0, 34.7, 30.4, 30.1, 30.0, 29.0, 23.6, 22.8, 21.3. HRMS (ESI) calculated for $\text{C}_{30}\text{H}_{39}\text{NNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 500.2594, found 500.2595.



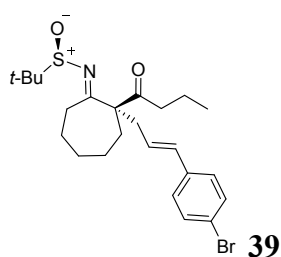
(*R*)-N-((*R,E*)-2-((*E*)-3-(4-bromophenyl)allyl)-2-isobutyrylcycloheptylidene)-2-methylpropane-2-sulfinamide **37**:

91% yield, yellow oil. $[\alpha]_{21}^D = +180.30$ (c 2.3, CHCl_3). IR (KBr) ν_{max} : 2970, 2926, 2858, 1733, 1617, 1506, 1457, 1235, 1180, 1104, 1080, 1016, 977, 801 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, $J = 8.4$ Hz, 2H), 7.13 (d, $J = 8.4$ Hz, 2H), 6.35 (d, $J = 15.7$ Hz, 1H), 5.93 (ddd, $J = 15.3, 8.0, 6.7$ Hz, 1H), 3.37 – 2.95 (m, 3H), 2.56 (ddd, $J = 14.8, 8.1, 1.3$ Hz, 1H), 2.16 (ddd, $J = 25.8, 13.6, 9.7$ Hz, 2H), 1.96 (m, 2H), 1.80 – 1.64 (m, 3H), 1.33 (m, 11H), 1.05 (d, $J = 6.6$ Hz, 3H), 0.93 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 213.7, 187.0, 136.0, 132.7, 131.8, 127.7, 126.3, 121.2, 68.9, 57.5, 38.4, 35.8, 35.2, 30.1, 29.7, 29.5, 23.3, 22.8, 20.7, 20.0. HRMS (ESI) calculated for $\text{C}_{24}\text{H}_{34}\text{BrNNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 502.1386, found 502.1384.



(R)-N-((*R,E*)-2-isobutyryl-2-((*E*)-3-(*p*-tolyl)allyl)cycloheptylidene)-2-methylpropane-2-sulfinamide **38**:

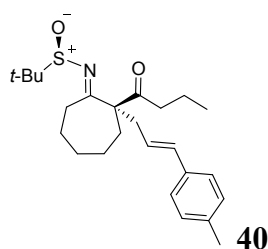
83% yield, yellow oil. $[\alpha]_{21}^D = +284.78$ (c 1.4, CHCl_3). IR (KBr) ν_{max} : 2971, 2927, 2860, 1733, 1614, 1505, 1456, 1180, 1101, 1089, 1016, 977, 801 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 7.18 (d, $J = 8.0$ Hz, 2H), 7.09 (d, $J = 7.9$ Hz, 2H), 6.38 (d, $J = 15.7$ Hz, 1H), 5.88 (ddd, $J = 15.3, 8.0, 6.7$ Hz, 1H), 3.24 – 3.04 (m, 3H), 2.57 (ddd, $J = 14.8, 8.0, 1.3$ Hz, 1H), 2.31 (s, 3H), 2.16 (ddd, $J = 24.9, 13.6, 9.7$ Hz, 2H), 1.98 (dd, $J = 15.4, 8.3$ Hz, 2H), 1.82 – 1.67 (m, 3H), 1.40 (dd, $J = 11.4, 6.1$ Hz, 1H), 1.35 (s, 9H), 1.24 – 1.17 (m, 1H), 1.06 (d, $J = 6.6$ Hz, 3H), 0.93 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 213.8, 187.1, 137.3, 134.3, 133.7, 129.4, 126.1, 124.2, 69.1, 57.6, 38.4, 35.8, 35.2, 30.2, 29.8, 29.4, 23.3, 22.9, 21.3, 20.8, 19.9. HRMS (ESI) calculated for $\text{C}_{25}\text{H}_{37}\text{NNaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 438.2437, found 438.2436.



(R)-N-((*R,E*)-2-((*E*)-3-(4-bromophenyl)allyl)-2-butyl)cycloheptylidene)-2-methylpropane-2-sulfinamide **39**:

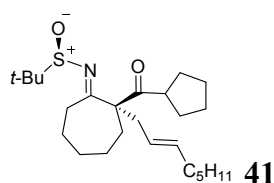
80% yield, yellow oil. $[\alpha]_{21}^D = +114.60$ (c 2.1, CHCl_3). IR (KBr) ν_{max} : 2958, 2927, 2360, 2341, 1707, 1611, 1507, 1458, 1261, 1009, 801, 750. cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, $J = 8.1$ Hz, 2H), 7.14 (d, $J = 8.1$ Hz, 2H), 6.34 (d, $J = 15.7$ Hz, 1H), 5.99 (dt, $J = 15.4, 7.4$ Hz, 1H), 3.21 – 2.93 (m, 2H), 2.53 (dd, $J = 14.7, 8.0$ Hz, 1H), 2.43 (td, $J = 7.2, 3.4$ Hz, 2H), 2.30 (td, $J = 11.7, 3.1$ Hz, 1H), 2.15 (dd, $J = 15.2, 10.1$ Hz, 1H), 1.95 – 1.83 (m, 2H), 1.79 – 1.55 (m, 5H), 1.49 – 1.42 (m, 1H), 1.31 (m, 10H), 0.85 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 209.1, 187.5, 136.0, 132.6, 131.7, 127.7, 126.3, 121.2, 68.2, 57.4, 40.4, 39.0, 35.0, 30.8, 30.0, 28.9,

23.63, 22.8, 17.4, 13.9. HRMS (ESI) calculated for $C_{24}H_{34}BrNNaO_2S^+$ $[M+Na]^+$: 502.1386, found 502.1385.



(*R*)-*N*-((*R,E*)-2-butryl-2-((*E*)-3-(*p*-tolyl)allyl)cycloheptylidene)-2-methylpropane-2-sulfinamide **40**:

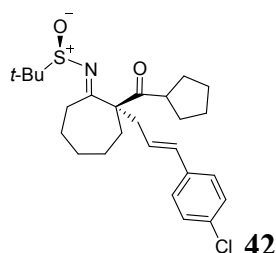
90% yield, yellow oil. $[\alpha]_{22}^D = +181.36$ (c 2.3, $CHCl_3$). IR (KBr) ν_{max} : 2960, 2928, 2358, 2341, 1709, 1616, 1507, 1458, 1260, 1011, 801, 750. cm^{-1} . 1H NMR (400 MHz, Chloroform-*d*) δ 7.18 (d, $J = 8.1$ Hz, 2H), 7.08 (d, $J = 7.9$ Hz, 2H), 6.38 (d, $J = 15.7$ Hz, 1H), 5.93 (ddd, $J = 15.3, 8.0, 6.7$ Hz, 1H), 3.23 – 2.93 (m, 2H), 2.54 (ddd, $J = 14.6, 8.0, 1.3$ Hz, 1H), 2.44 (td, $J = 7.1, 1.7$ Hz, 2H), 2.31 (m, 4H), 2.16 (dd, $J = 15.2, 10.1$ Hz, 1H), 1.91 (m, 2H), 1.79 – 1.55 (m, 5H), 1.49 – 1.42 (m, 1H), 1.31 (m, 10H), 0.85 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 209.2, 187.7, 137.3, 134.3, 133.6, 129.3, 126.1, 124.2, 68.3, 57.4, 40.3, 39.0, 35.0, 30.6, 30.0, 29.0, 23.6, 22.8, 21.3, 17.4, 13.9. HRMS (ESI) calculated for $C_{25}H_{37}NNaO_2S^+$ $[M+Na]^+$: 438.2437, found 438.2435.



(*R*)-*N*-((*R,E*)-2-isobutyryl-2-((*E*)-oct-2-en-1-yl)cycloheptylidene)-2-methylpropane-2-sulfinamide **41**:

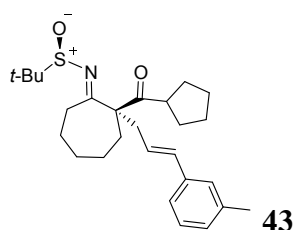
89% yield, yellow oil. $[\alpha]_{21}^D = +261.01$ (c 1.1, $CHCl_3$). IR (KBr) ν_{max} : 2960, 2929, 2867, 1706, 1610, 1457, 1362, 1262, 1182, 1080, 801 cm^{-1} . 1H NMR (400 MHz, Chloroform-*d*) δ 5.44 (dt, $J = 14.2, 6.7$ Hz, 1H), 5.16 – 5.08 (m, 1H), 3.29 – 3.03 (m, 2H), 2.95 (dd, $J = 14.7, 6.6$ Hz, 1H), 2.28 (dd, $J = 14.6, 8.0$ Hz, 1H), 2.11 (ddd, $J = 24.0, 15.0, 11.0$ Hz, 2H), 1.92 (m, 4H), 1.77 – 1.67 (m, 6H), 1.62 – 1.47 (m, 3H), 1.42 – 1.15 (m, 19H), 0.86 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 213.8, 187.3, 135.4, 124.6, 68.9, 57.5, 46.2, 38.0, 35.6, 33.0, 32.7, 31.5, 31.5, 30.1, 29.6, 29.2,

29.1, 26.8, 26.6, 23.3, 22.9, 22.6, 14.2. HRMS (ESI) calculated for $C_{23}H_{41}NNaO_2S^+$ $[M+Na]^+$: 444.2907, found 444.2903.



(*R*)-*N*-((*R,E*)-2-((*E*)-3-(4-chlorophenyl)allyl)-2-(cyclopentanecarbonyl) cycloheptylidene)-2-methylpropane-2-sulfinamide **42**:

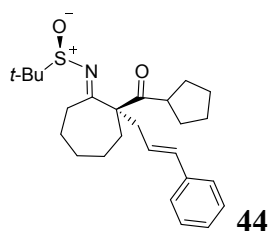
93% yield, yellow oil. $[\alpha]_{20}^D = +652.80$ (c 0.4, $CHCl_3$). IR (KBr) ν_{max} : 2958, 2864, 2358, 2340, 1707, 1609, 1509, 1457, 1260, 1082, 964, 800, 775. cm^{-1} . 1H NMR (400 MHz, Chloroform-*d*) δ 7.24 (d, $J = 8.6$ Hz, 2H), 7.21 – 7.15 (m, 2H), 6.35 (d, $J = 15.7$ Hz, 1H), 5.92 (ddd, $J = 15.4, 8.1, 6.8$ Hz, 1H), 3.31 – 2.98 (m, 3H), 2.52 (ddd, $J = 14.7, 8.1, 1.3$ Hz, 1H), 2.25 – 2.06 (m, 2H), 1.93 (td, $J = 15.1, 14.4, 8.3$ Hz, 2H), 1.83 – 1.36 (m, 13H), 1.33 (s, 9H), 1.25 – 1.20 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 213.7, 181.7, 135.6, 133.1, 132.6, 128.8, 127.4, 126.1, 68.8, 57.5, 46.5, 38.5, 35.6, 33.0, 31.7, 30.1, 30.0, 29.4, 26.8, 26.7, 23.4, 22.8. HRMS (ESI) calculated for $C_{26}H_{36}ClNNaO_2S^+$ $[M+Na]^+$: 484.2047, found 484.2046.



(*R*)-*N*-((*R,E*)-2-(cyclopentanecarbonyl)-2-((*E*)-3-(*m*-tolyl)allyl)cycloheptylidene)-2-methylpropane-2-sulfinamide **43**:

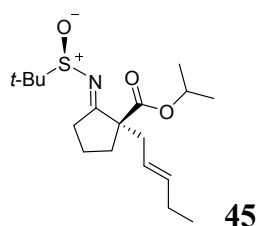
81% yield, yellow oil. $[\alpha]_{21}^D = +199.30$ (c 0.8, $CHCl_3$). IR (KBr) ν_{max} : 2953, 2864, 2360, 2342, 1703, 1606, 1507, 1456, 1261, 1082, 964, 800, 775, 692 cm^{-1} . 1H NMR (400 MHz, Chloroform-*d*) δ 7.17 (t, $J = 7.6$ Hz, 1H), 7.11 – 7.01 (m, 3H), 6.37 (d, $J = 15.7$ Hz, 1H), 5.93 (ddd, $J = 15.3, 8.1, 6.8$ Hz, 1H), 3.37 – 3.04 (m, 3H), 2.53 (ddd, $J = 14.6, 8.1, 1.3$ Hz, 1H), 2.32 (s, 4H), 2.17 (ddd, $J = 19.6, 15.3, 11.1$ Hz, 2H), 2.02 – 1.90 (m, 2H), 1.74 (m, 8H), 1.57 – 1.40 (m, 4H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 213.8, 187.2, 138.2, 137.1, 133.9, 128.5, 128.3, 126.9, 125.0, 123.4,

69.0, 57.5, 46.4, 38.6, 35.6, 33.0, 31.7, 30.1, 29.8, 29.5, 26.8, 26.7, 23.4, 22.7, 21.5.
HRMS (ESI) calculated for $C_{27}H_{39}NNaO_2S^+$ $[M+Na]^+$: 464.2594, found 464.2596.



N-((*R,E*)-2-cinnamyl-2-(cyclopentanecarbonyl)cycloheptylidene)-2-methylpropane-2-sulfinamide **44**:

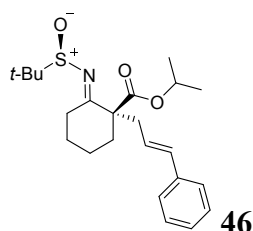
79% yield, yellow oil. $[\alpha]_{23}^D = +201.61$ (c 0.9, $CHCl_3$). IR (KBr) ν_{max} : 2952, 2860, 2361, 2344, 1709, 1603, 1501, 1453, 1263, 1091, 959, 803, 769 cm^{-1} . 1H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.28 (m, 2H), 7.27 – 7.11 (m, 3H), 6.41 (d, $J = 15.6$ Hz, 1H), 5.96 (dt, $J = 15.4, 7.5$ Hz, 1H), 3.18 (ddd, $J = 27.9, 15.8, 7.1$ Hz, 3H), 2.55 (dd, $J = 14.8, 8.1$ Hz, 1H), 2.26 – 2.07 (m, 2H), 1.94 (dd, $J = 15.3, 8.7$ Hz, 2H), 1.77 – 1.63 (m, 7H), 1.55 (q, $J = 7.9, 7.4$ Hz, 2H), 1.43 (q, $J = 5.7, 5.0$ Hz, 2H), 1.34 (d, $J = 2.0$ Hz, 9H), 1.29 – 1.18 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 213.6, 187.1, 137.1, 133.8, 128.5, 127.4, 126.1, 125.3, 68.8, 57.4, 46.4, 38.5, 35.5, 32.9, 31.6, 30.0, 29.8, 29.3, 26.7, 26.6, 23.4, 22.8. HRMS (ESI) calculated for $C_{26}H_{37}NNaO_2S^+$ $[M+Na]^+$: 450.2437, found 450.2433.



isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl)imino)-1-((*E*)-pent-2-en-1-yl)cyclopentane-1-carboxylate **45**:

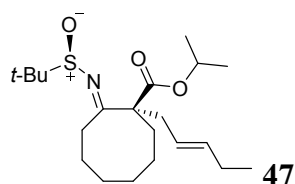
66% yield, yellow oil. $[\alpha]_{26}^D = +151.61$ (c 0.7, $CHCl_3$). IR (KBr) ν_{max} : 2962, 2927, 1731, 1637, 1458, 1106, 1085, 789 cm^{-1} . 1H NMR (400 MHz, Chloroform-*d*) δ 5.54 (dt, $J = 15.2, 6.2, 1.2$ Hz, 1H), 5.41 – 5.25 (m, 1H), 4.99 (m, 1H), 3.01 – 2.85 (m, 1H), 2.75 – 2.64 (m, 2H), 2.33 – 2.27 (m, 1H), 2.26 – 2.19 (m, 1H), 1.99 (tt, $J = 7.6, 1.3$ Hz, 2H), 1.94 – 1.79 (m, 3H), 1.24 (s, 9H), 1.22 – 1.18 (m, 6H), 0.94 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.6, 172.0, 136.8, 123.8, 68.7, 61.4, 57.3, 38.8,

33.9, 32.4, 25.8, 22.7, 22.4, 21.8, 13.9. HRMS (ESI) calculated for $C_{18}H_{31}NNaO_3S^+$ $[M+Na]^+$: 364.1917, found 364.1919.



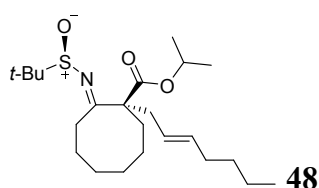
Isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl) imino) -1-cinnamyl cyclohexane-1-carboxylate **46**:

79% yield, yellow oil. $[\alpha]_{26}^D = +62.61$ (c 3.0, $CHCl_3$). IR (KBr) ν_{max} : 2979, 2935, 2866, 1730, 1629, 1257, 1103, 1079, 966, 743, 789 cm^{-1} . 1H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 4H), 7.19 (td, $J = 5.9, 2.6$ Hz, 1H), 6.37 (d, $J = 15.7$ Hz, 1H), 6.17 (dt, $J = 15.4, 7.4$ Hz, 1H), 5.03 (m, 1H), 3.77 (dt, $J = 14.1, 3.9$ Hz, 1H), 2.76 (ddd, $J = 14.0, 7.1, 1.3$ Hz, 1H), 2.59 – 2.44 (m, 2H), 2.22 (ddd, $J = 14.3, 12.6, 5.1$ Hz, 1H), 1.92 – 1.83 (m, 1H), 1.71 – 1.45 (m, 4H), 1.31 (s, 9H), 1.20 (dd, $J = 11.9, 6.3$ Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 183.6, 171.8, 137.4, 133.3, 128.6, 127.3, 126.2, 125.4, 68.9, 59.4, 58.1, 40.1, 36.12, 32.2, 27.2, 22.9, 22.5, 21.9, 21.8. HRMS (ESI) calculated for $C_{23}H_{33}NNaO_3S^+$ $[M+Na]^+$: 426.2073, found 426.2079.



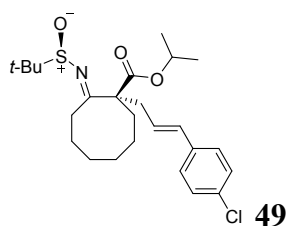
isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl)imino)-1-((*E*)-pent-2-en-1-yl)cyclooctane-1-carboxylate **47**:

59% yield, yellow oil. $[\alpha]_{26}^D = +189.09$ (c 0.1, $CHCl_3$). IR (KBr) ν_{max} : 2959, 2925, 2856, 1730, 1609, 1464, 1104, 1089, 801. cm^{-1} . 1H NMR (400 MHz, Chloroform-*d*) δ 5.52 (dt, $J = 13.5, 6.3$ Hz, 1H), 5.30 (dt, $J = 14.9, 7.5$ Hz, 1H), 4.98 (p, $J = 6.3$ Hz, 1H), 2.85 (dt, $J = 12.5, 4.7$ Hz, 2H), 2.49 – 2.36 (m, 2H), 2.35 – 2.26 (m, 1H), 2.13 – 1.84 (m, 5H), 1.79 – 1.59 (m, 3H), 1.57 – 1.35 (m, 3H), 1.26 (s, 9H), 1.18 (dd, $J = 12.8, 6.3$ Hz, 6H), 0.94 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.6, 171.9, 136.1, 124.2, 68.8, 61.5, 56.8, 36.3, 33.6, 30.5, 27.7, 25.8, 25.2, 24.8, 23.1, 22.3, 21.9, 21.8, 13.9. HRMS (ESI) calculated for $C_{21}H_{37}NNaO_3S^+$ $[M+Na]^+$: 406.2386, found 406.2389.



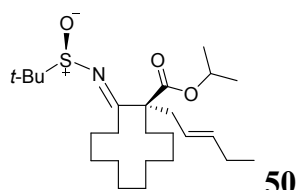
isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl)imino)-1-((*E*)-hept-2-en-1-yl)cyclooctane-1-carboxylate **48**:

62% yield, yellow oil. $[\alpha]_{26}^D = +99.69$ (c 0.6, CHCl_3). IR (KBr) ν_{max} : 2958, 2926, 2850, 2359, 1730, 1608, 1466, 1260, 1104, 804. cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 5.47 (dt, $J = 14.1, 6.7$ Hz, 1H), 5.33 – 5.26 (m, 1H), 4.97 (p, $J = 6.3$ Hz, 1H), 2.84 (dt, $J = 12.5, 4.8$ Hz, 2H), 2.42 (ddd, $J = 13.7, 10.2, 5.0$ Hz, 2H), 2.30 (ddd, $J = 15.4, 11.5, 3.7$ Hz, 1H), 2.08 – 1.89 (m, 5H), 1.80 – 1.62 (m, 3H), 1.58 – 1.36 (m, 4H), 1.26 (s, 12H), 1.17 (dd, $J = 13.0, 6.2$ Hz, 6H), 0.91 – 0.84 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.6, 171.9, 134.6, 125.2, 68.8, 61.4, 56.8, 36.3, 33.5, 32.5, 31.7, 30.5, 27.6, 25.2, 24.8, 23.1, 22.3, 22.3, 21.9, 21.8, 14.1. HRMS (ESI) calculated for $\text{C}_{23}\text{H}_{41}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 434.2699, found 434.2697.



isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl)imino)-1-((*E*)-3-(4-chlorophenyl)allyl)cyclooctane-1-carboxylate **49**:

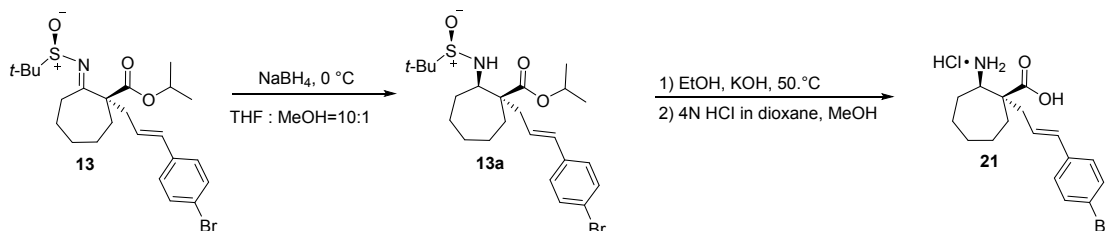
80% yield, yellow oil. $[\alpha]_{26}^D = +142.69$ (c 0.7, CHCl_3). IR (KBr) ν_{max} : 2979, 2931, 2862, 2362, 1730, 1608, 1491, 1191, 1089, 967. cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.15 (m, 4H), 6.37 (d, $J = 15.7$ Hz, 1H), 6.13 (ddd, $J = 15.4, 8.5, 6.3$ Hz, 1H), 4.99 (m, 1H), 3.07 (dd, $J = 14.5, 6.4$ Hz, 1H), 2.89 (dt, $J = 13.1, 4.9$ Hz, 1H), 2.60 (dd, $J = 14.5, 8.6$ Hz, 1H), 2.52 – 2.28 (m, 2H), 2.18 – 1.85 (m, 3H), 1.82 – 1.63 (m, 3H), 1.62 – 1.36 (m, 3H), 1.28 (s, 9H), 1.16 (dd, $J = 6.3, 4.0$ Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.4, 171.8, 135.9, 132.9, 132.1, 128.8, 127.4, 126.9, 69.1, 61.5, 56.9, 37.0, 33.6, 30.5, 28.4, 25.2, 24.8, 23.3, 22.3, 21.9, 21.8. HRMS (ESI) calculated for $\text{C}_{25}\text{H}_{36}\text{ClNNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 488.1997, found 488.1998.



isopropyl (*R,E*)-2-(((*R*)-*tert*-butylsulfinyl)imino)-1-((*E*)-pent-2-en-1-yl)cyclododecane-1-carboxylate **50**:

42% yield, yellow oil. $[\alpha]_{26}^D = +78.12$ (c 0.5, CHCl_3). IR (KBr) ν_{max} : 2962, 2931, 2361, 1734, 1637, 1458, 1192, 913. cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 5.50 (dt, $J = 13.9, 6.5$ Hz, 1H), 5.19 (dt, $J = 15.1, 7.5$ Hz, 1H), 4.99 (m, 1H), 3.33 (ddd, $J = 13.6, 9.9, 7.2$ Hz, 1H), 2.59 – 2.37 (m, 2H), 2.14 (dt, $J = 12.9, 5.8$ Hz, 1H), 2.07 – 1.76 (m, 5H), 1.67 (dd, $J = 13.7, 6.5$ Hz, 3H), 1.58 – 1.34 (m, 10H), 1.31 (s, 11H), 1.19 (t, $J = 6.0$ Hz, 6H), 0.94 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 183.2, 172.5, 136.3, 123.7, 68.7, 36.1, 30.6, 29.8, 26.8, 26.0, 25.9, 25.4, 25.1, 24.4, 23.9, 23.7, 23.1, 21.9, 21.6, 20.0, 14.0. HRMS (ESI) calculated for $\text{C}_{25}\text{H}_{45}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 462.3021, found 462.3027.

4. Preparation β -amino acid **21** from product **13**



isopropyl (1*R*,2*R*)-1-((*E*)-3-(4-bromophenyl)allyl)-2-(((*R*)-*tert*-butylsulfinyl)amino)cyclo heptane-1-carboxylate **13a**:

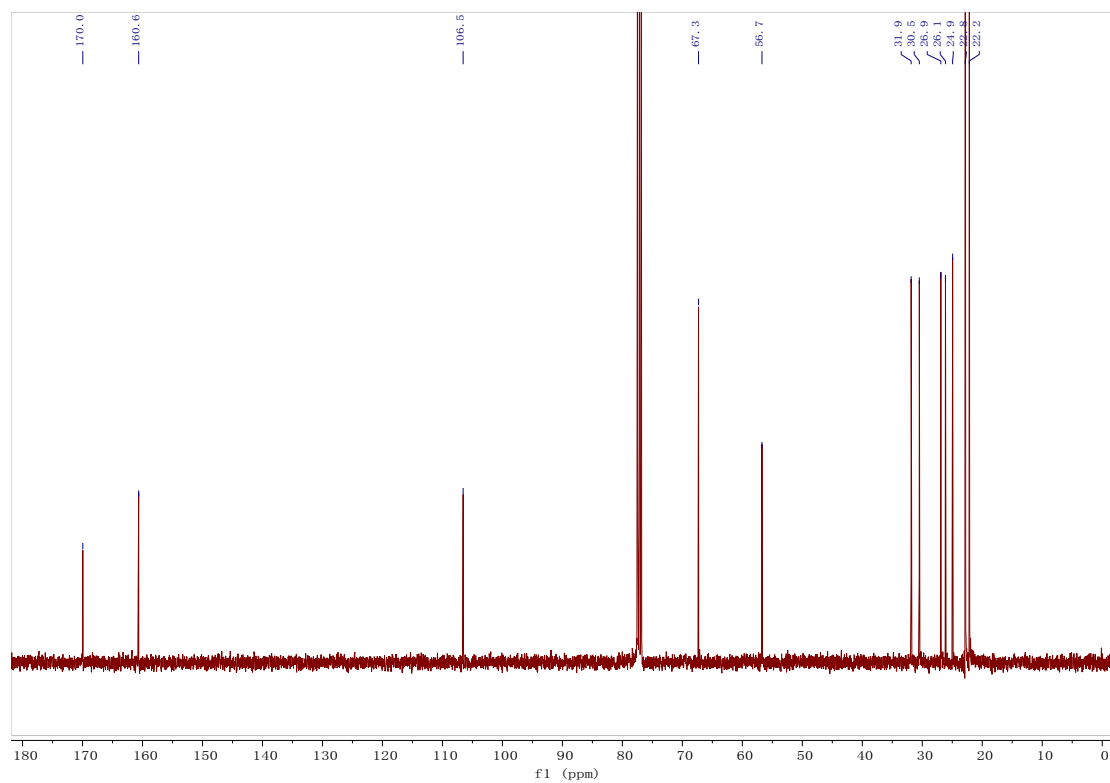
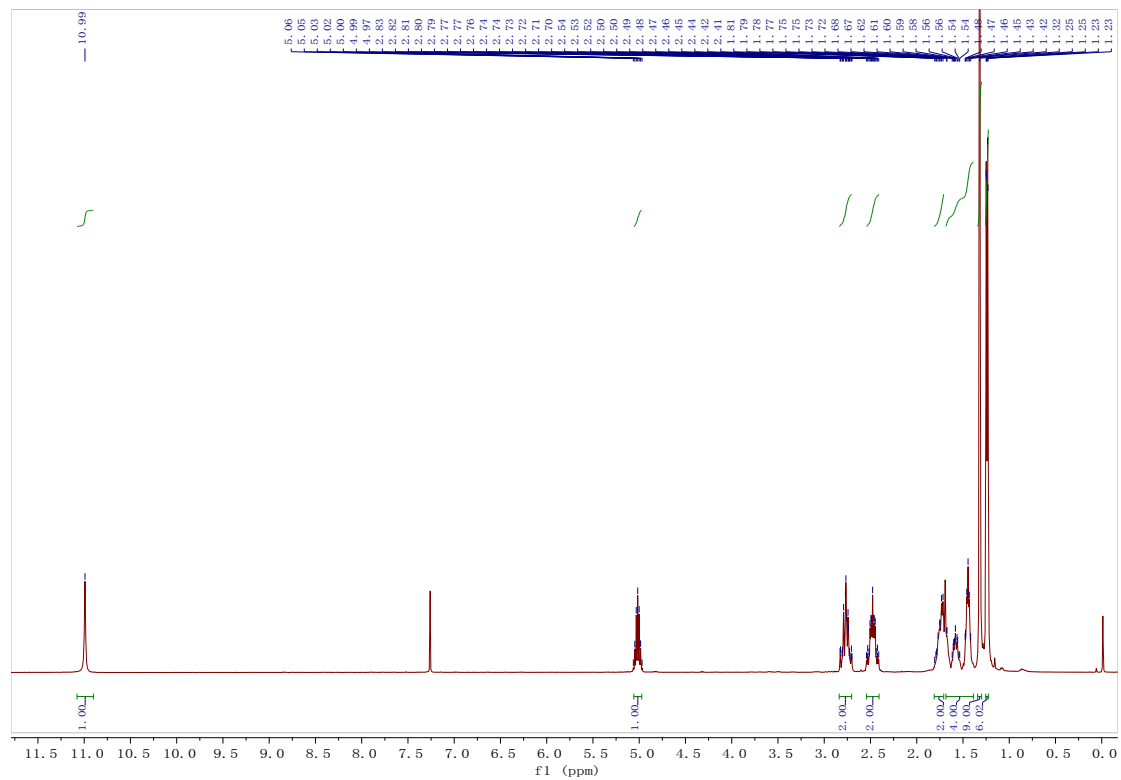
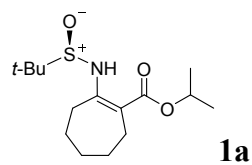
In a round bottom flask, a solution of compound **13** (0.6 g, 1.2 mmol) in fresh distilled THF (12 mL) and MeOH (1.2 mL) was mixed with NaBH_4 (136mg, 3.6mmol) in a nitrogen atmosphere at 0°C. After the substrate was completely consumed (monitored by TLC analysis), the reaction mixture was quenched with H_2O (10 mL), and extracted by ethyl acetate (3 x 20 mL). The combined organic phase was dried over Na_2SO_4 , and concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate=4:1) to furnish the desired compound **13a** (542 mg, 91% yield) as a colorless oil. $[\alpha]_{24}^D = -43.32$ (c 1.8, CHCl_3). IR (KBr) ν_{max} : 2930, 2863, 2360, 2342, 1716, 1684, 1507, 1457, 1174, 1105, 1009, 968, 800 cm^{-1} . ^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.36 (m, 2H), 7.25 – 7.16 (m, 2H), 6.48 (d, $J = 15.7$ Hz, 1H), 6.22 (dt, $J = 15.5, 7.6$ Hz, 1H), 5.03 (m, 1H), 4.61 (d, $J = 7.1$ Hz, 1H), 3.26

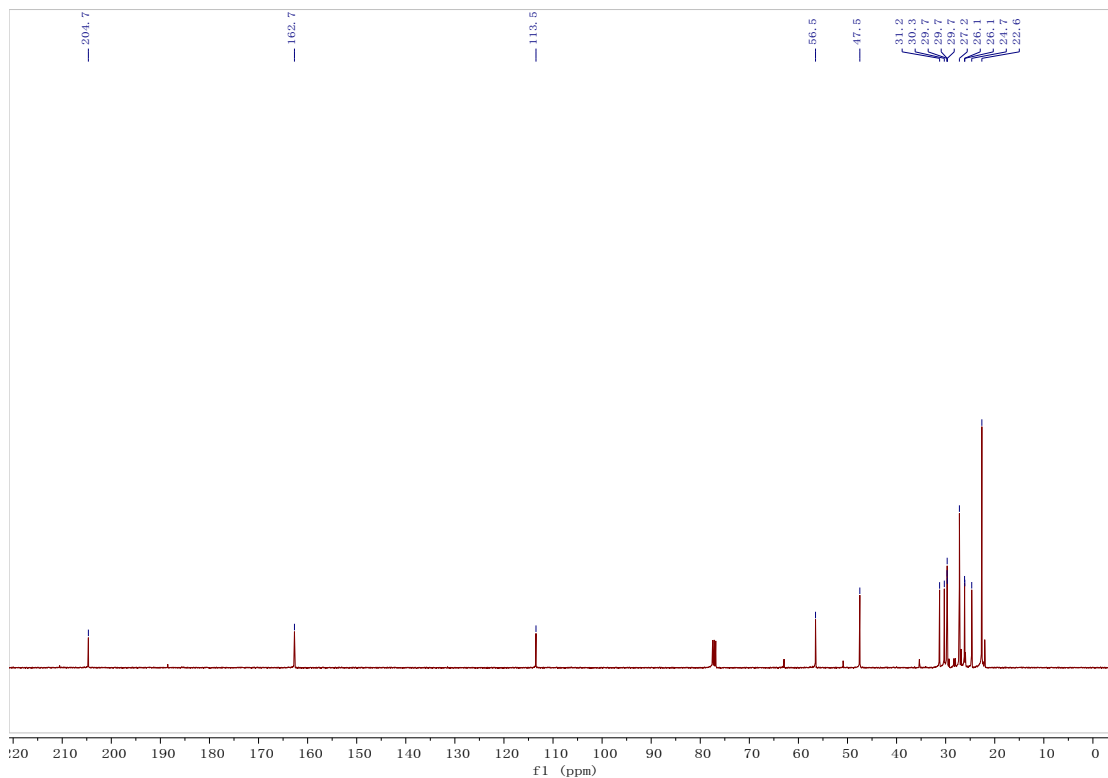
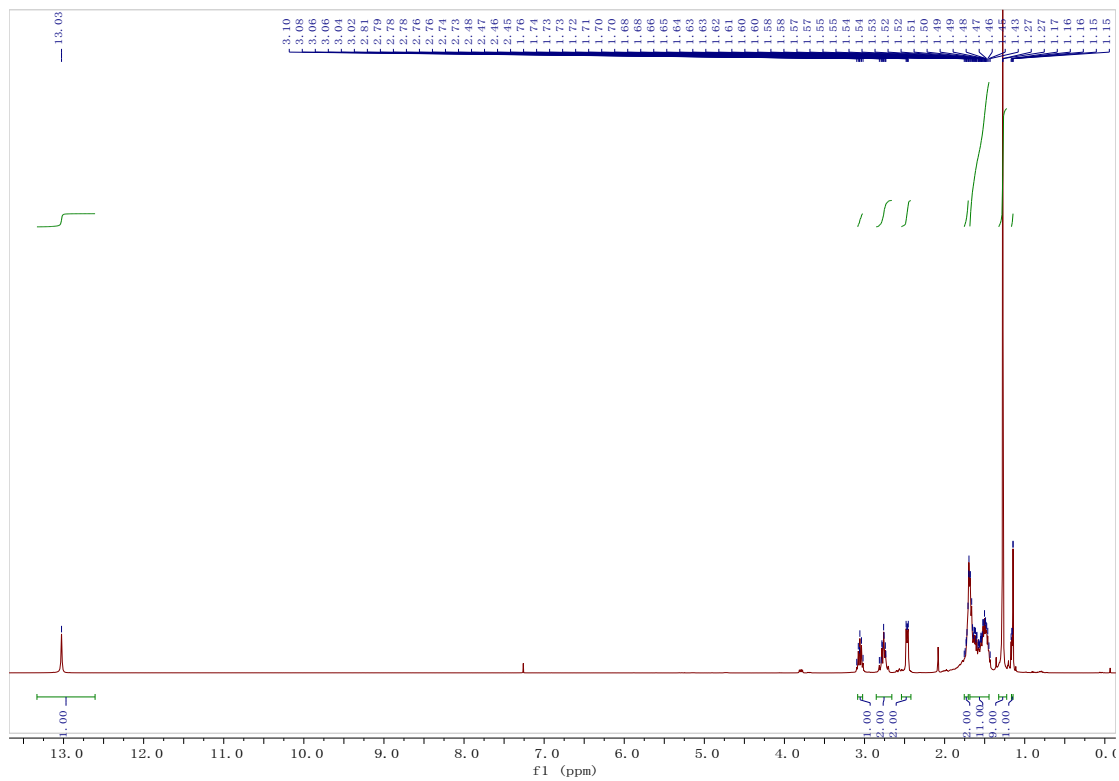
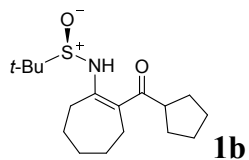
(ddd, $J = 9.8, 7.1, 2.6$ Hz, 1H), 2.77 – 2.60 (m, 2H), 2.10 – 1.63 (m, 6H), 1.60 – 1.35 (m, 4H), 1.24 (d, $J = 6.3$ Hz, 6H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, Chloroform- d) δ 175.3, 136.5, 132.9, 131.6, 127.8, 126.2, 120.9, 68.5, 62.7, 55.8, 53.7, 41.1, 34.0, 32.5, 27.4, 24.9, 22.9, 22.6, 22.0, 21.9. HRMS (ESI) calculated for $\text{C}_{24}\text{H}_{36}\text{BrNNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 520.1491, found 520.1493.

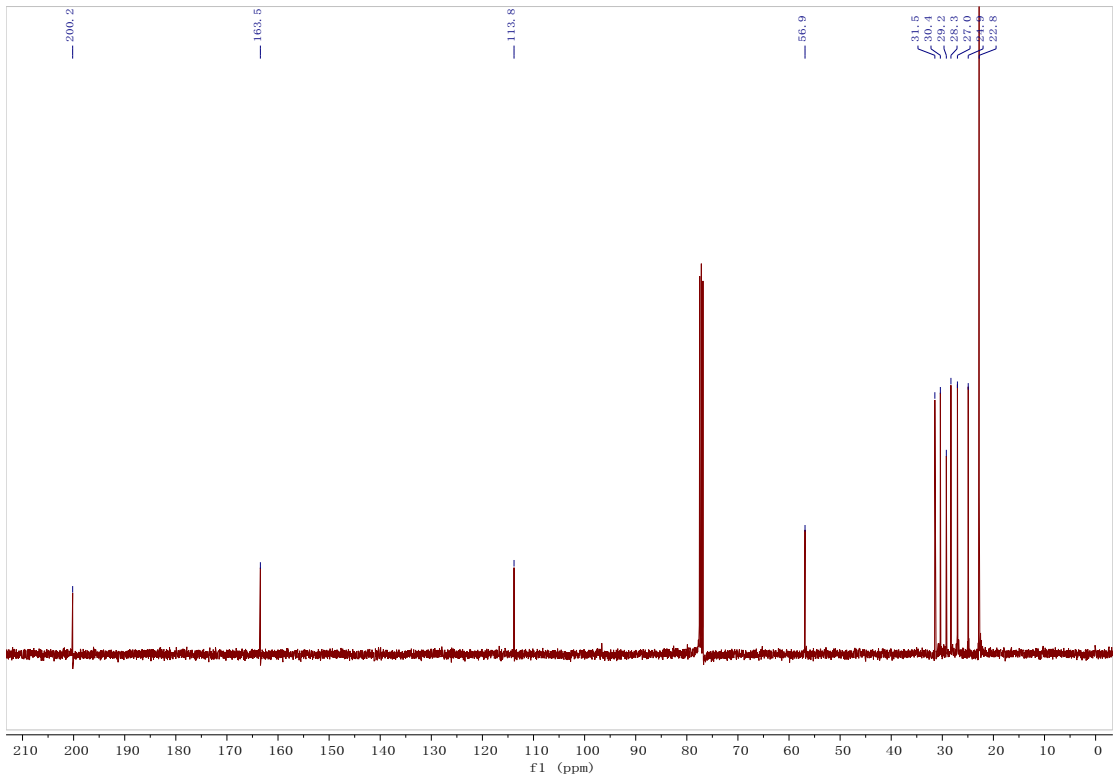
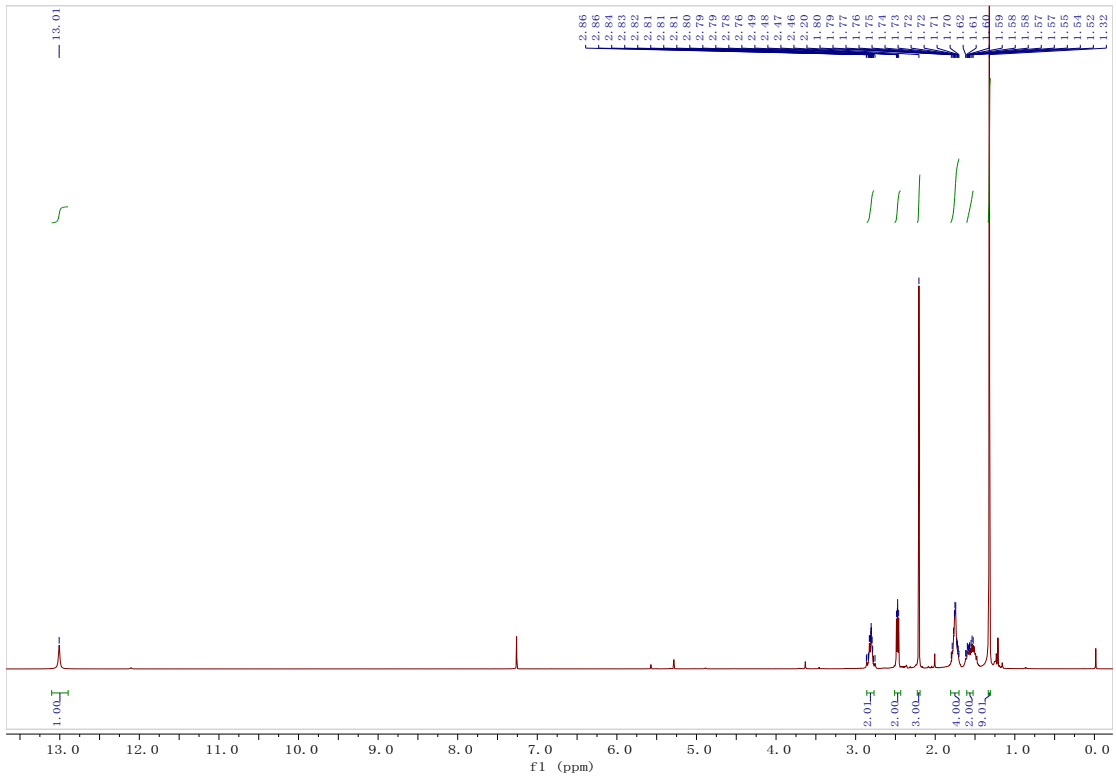
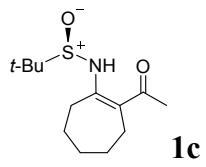
(1*R*,2*R*)-2-amino-1-((*E*)-3-(4-bromophenyl)allyl) cycloheptane-1-carboxylic acid hydro- chloride **21**:

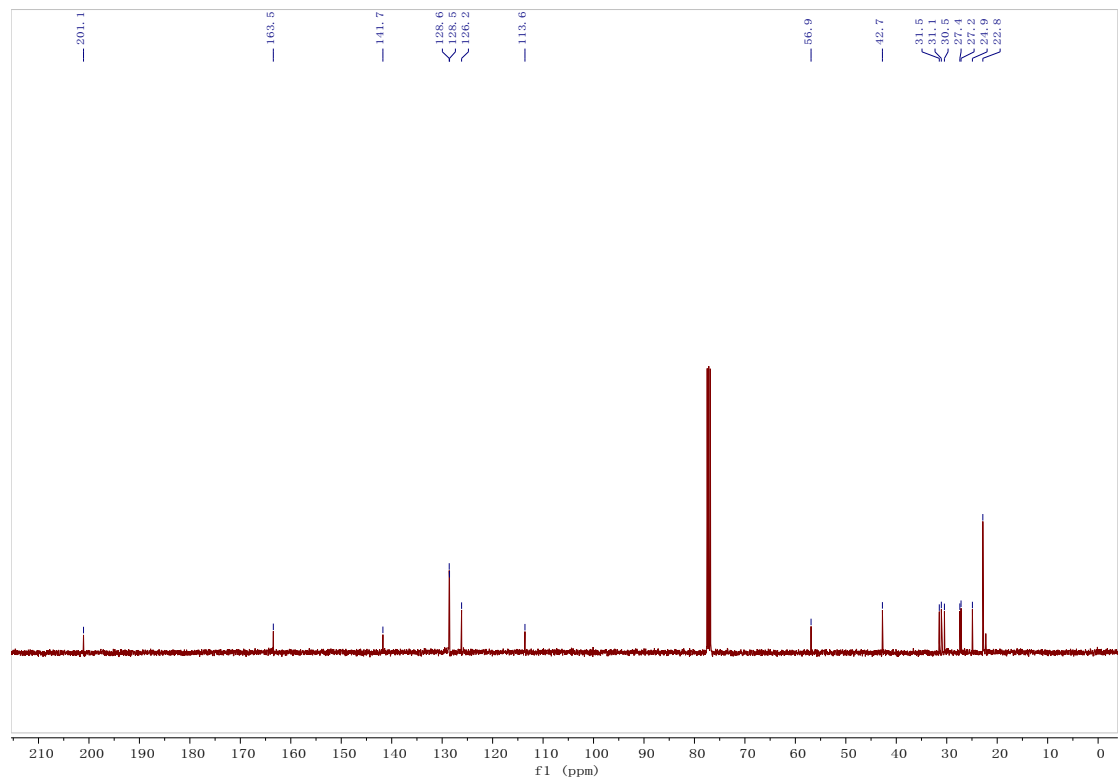
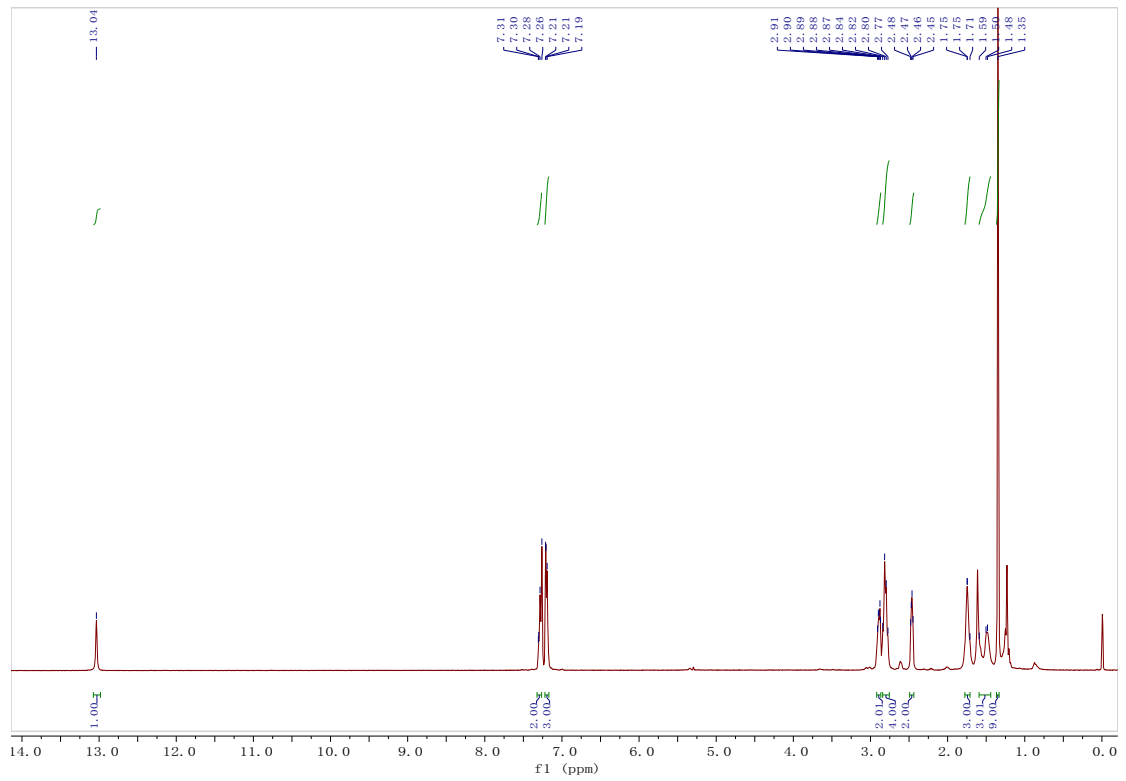
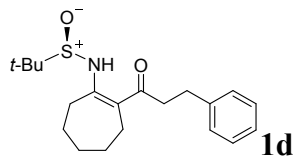
The compound **13a** (330 mg, 0.66 mmol) of methanol (3.3mL) was added 1,4-dioxane (0.66 mL) of 4.0 M HCl. The mixture was stirred at room temperature for 2 hours. The mixture was completely evaporated in *vacuo*. A white solid precipitated and washed with ethyl acetate. Filtered to give product **21** (192 mg, 83% yield) as a white solid. $[\alpha]_{\text{D}}^{22} = +2.61$ (c 0.3, MeOH). m. p. 103.7 °C -105.8 °C. IR (KBr) ν_{max} : 2987, 2360, 2342, 2330, 1792, 1733, 1684, 1541, 1507, 1457 cm^{-1} . ^1H NMR (400 MHz, Methanol- d_4) δ 7.52 – 7.41 (m, 2H), 7.33 (d, $J = 8.5$ Hz, 2H), 6.55 (d, $J = 15.7$ Hz, 1H), 6.30 (dt, $J = 15.4, 7.5$ Hz, 1H), 3.27 (dd, $J = 10.0, 2.5$ Hz, 1H), 2.77 (ddd, $J = 14.1, 7.0, 1.4$ Hz, 1H), 2.61 (dd, $J = 14.1, 8.0$ Hz, 1H), 2.16 – 1.51 (m, 10H). ^{13}C NMR (100 MHz, Methanol- d_4) δ 177.4, 137.5, 134.8, 132.7, 129.1, 125.7, 122.2, 58.4, 52.6, 41.6, 34.1, 31.1, 27.7, 25.3, 23.3. HRMS (ESI) calculated for $\text{C}_{17}\text{H}_{22}\text{BrNNaO}_2^+$ $[\text{M}+\text{Na}]^+$: 374.0726, found 374.0724.

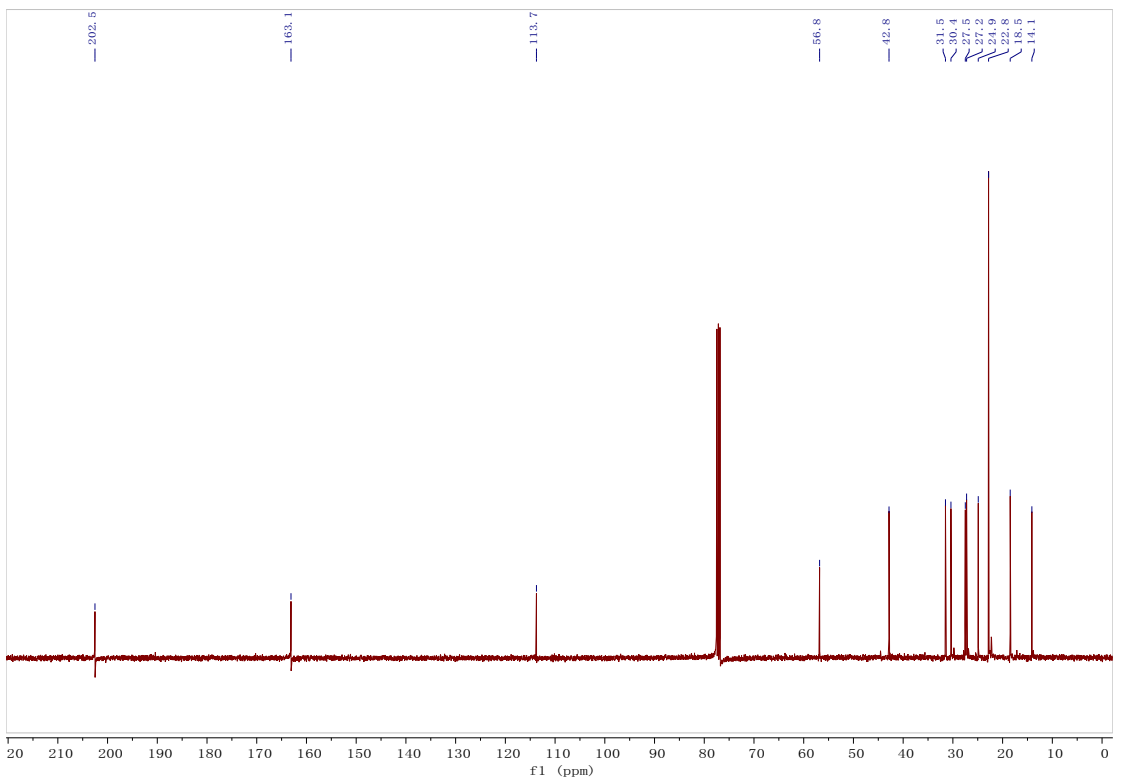
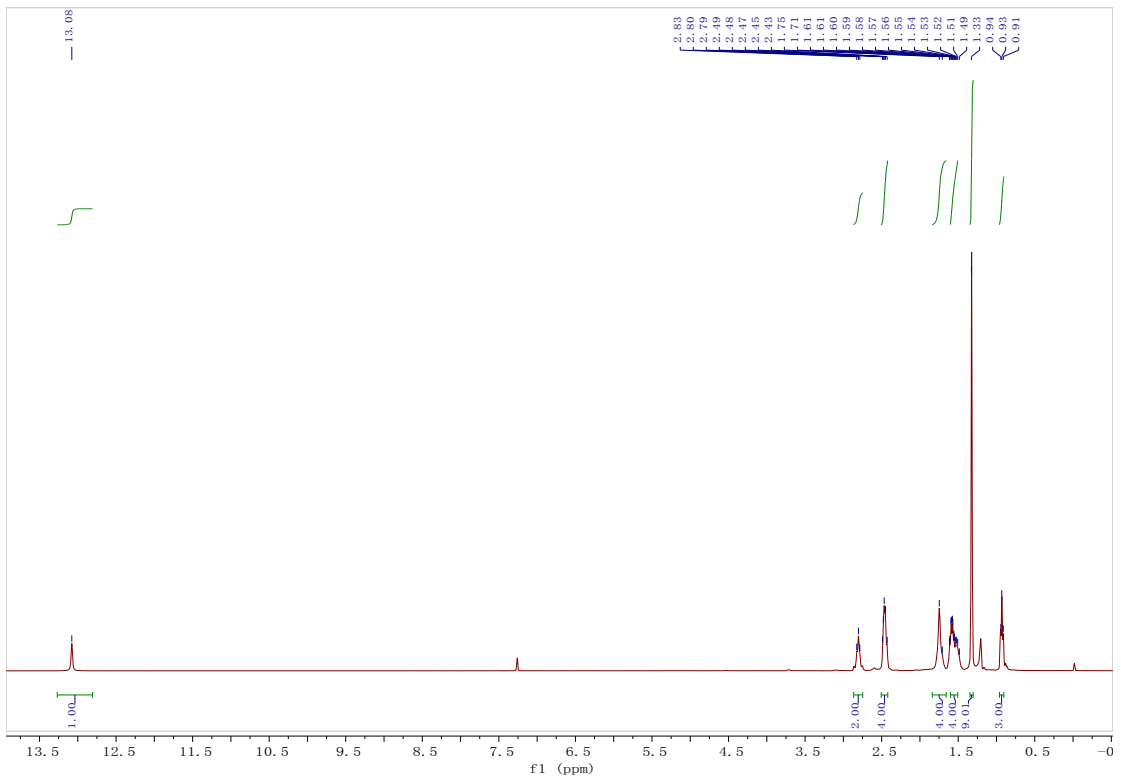
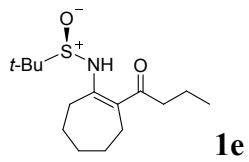
5. NMR Spectrums of Compounds

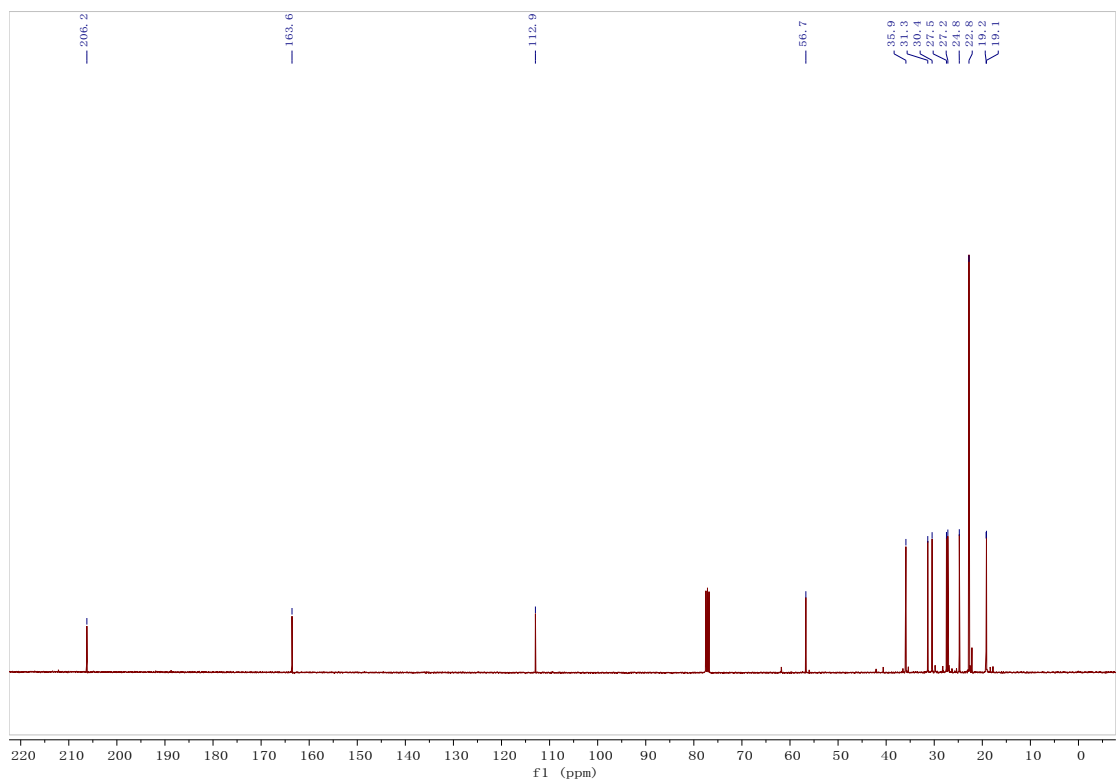
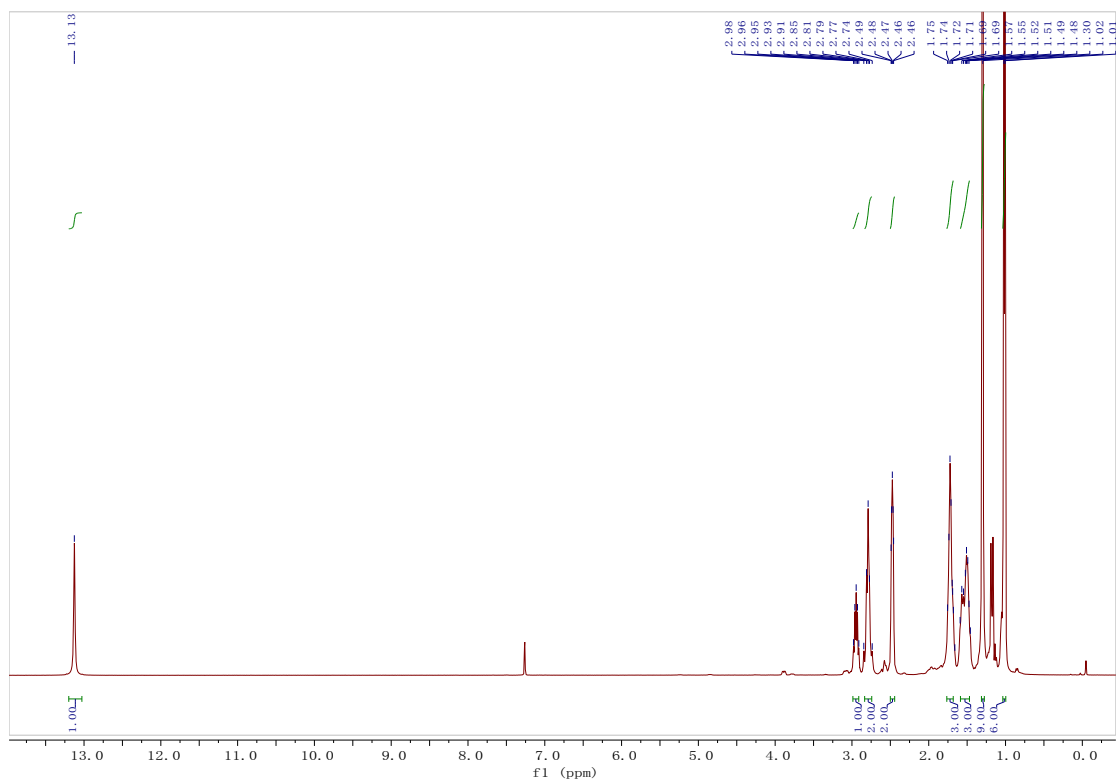
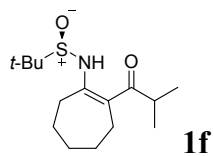


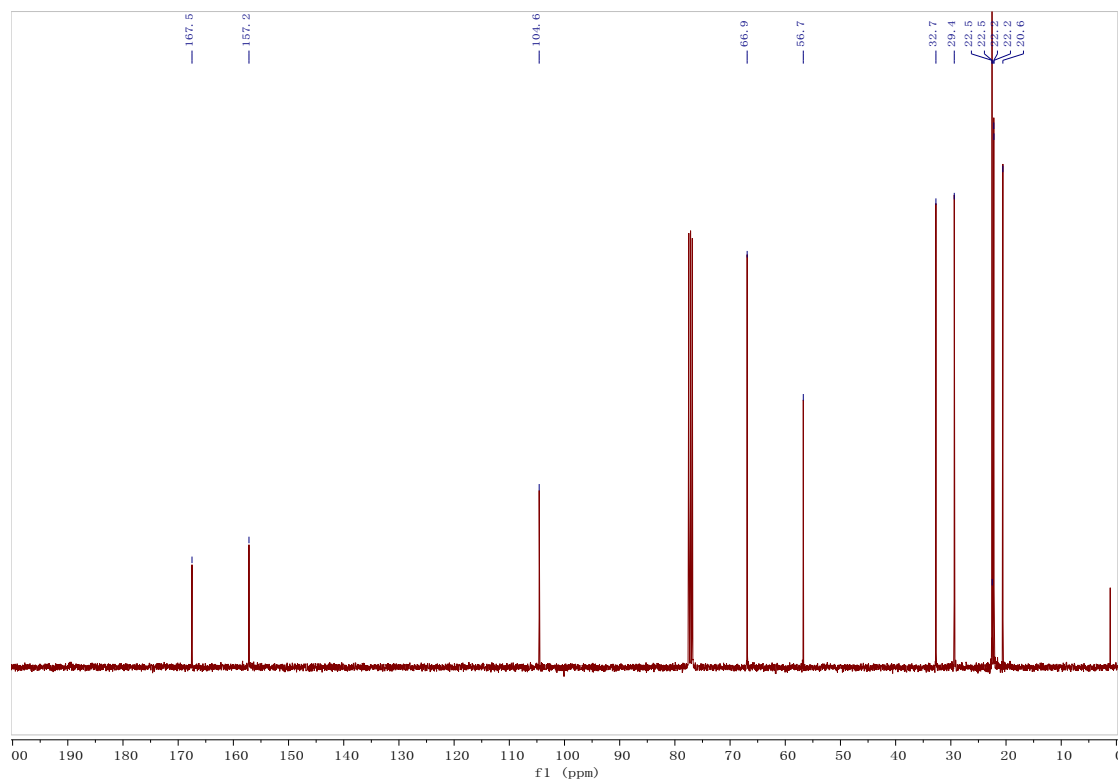
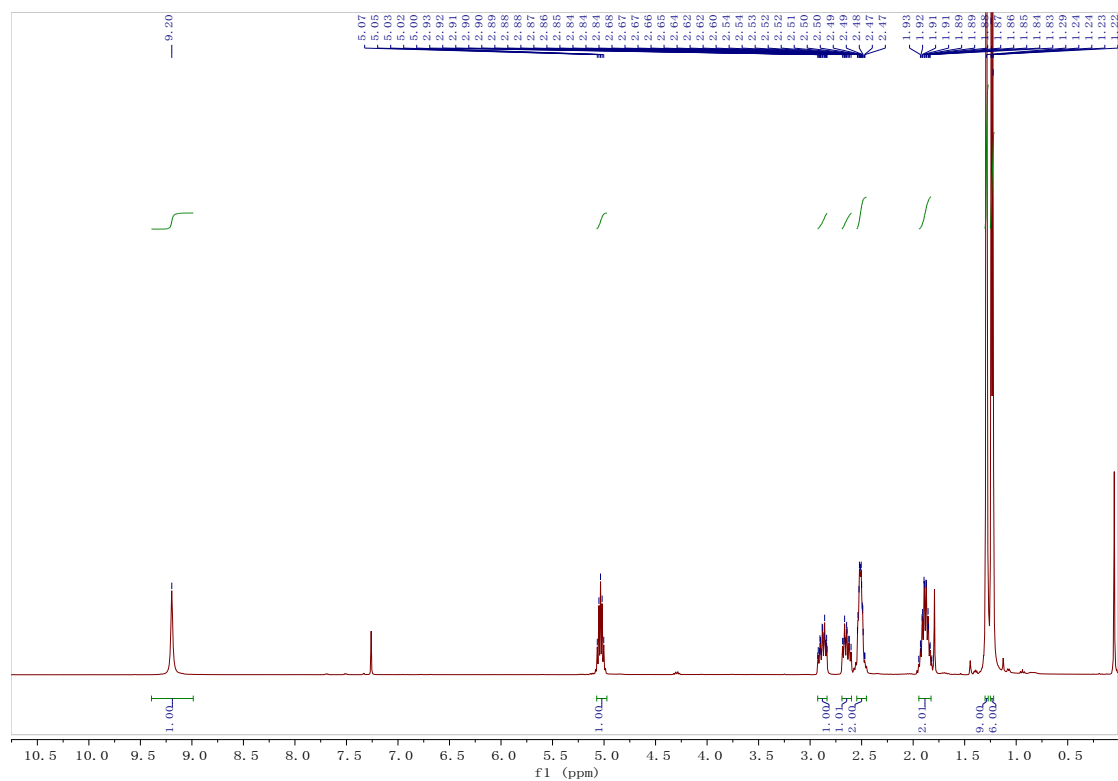
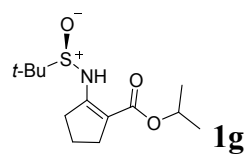


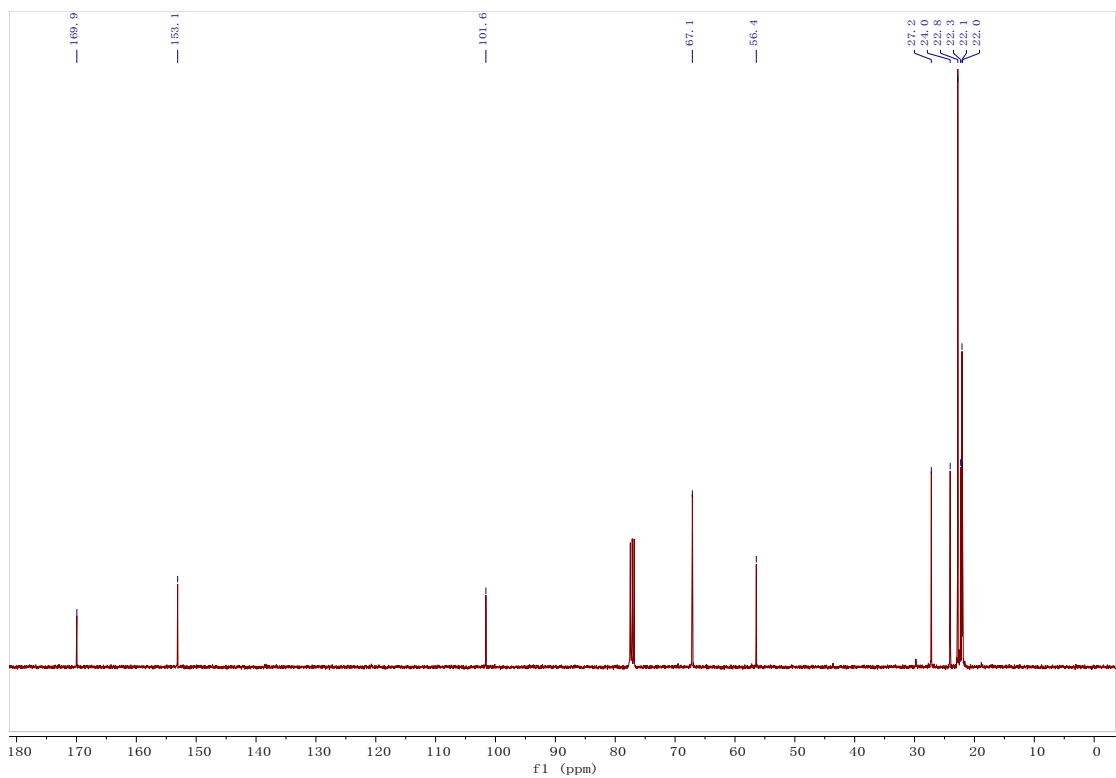
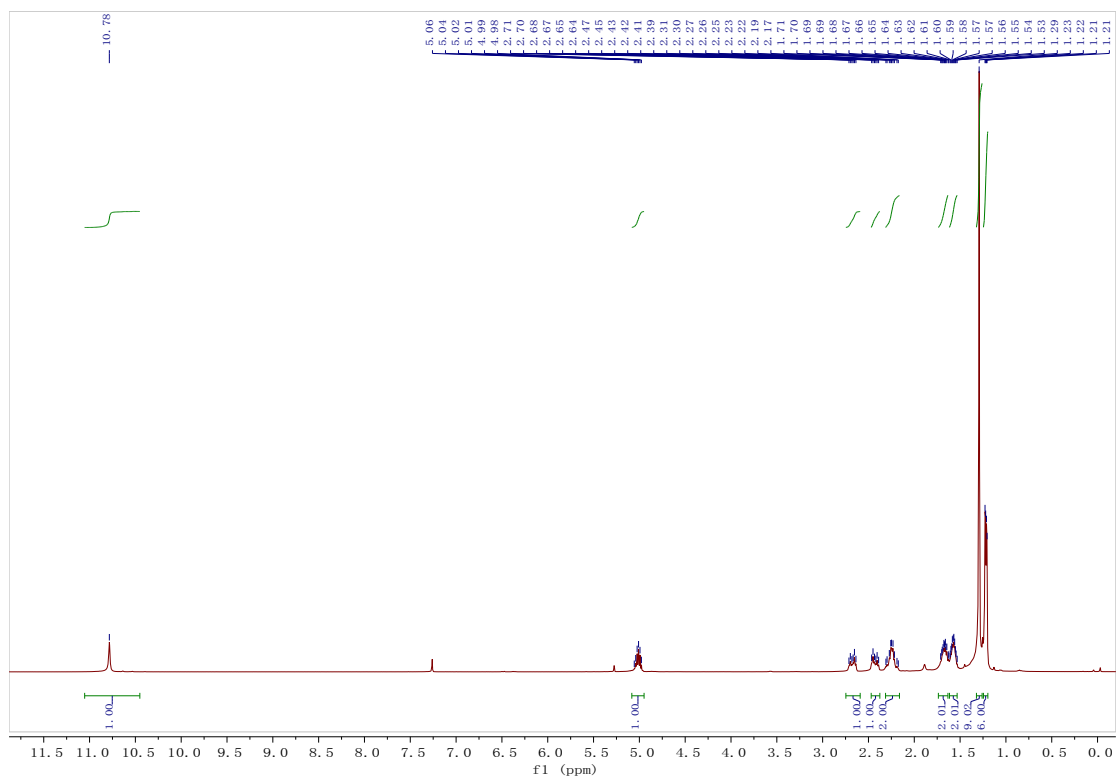
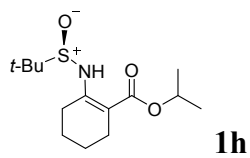


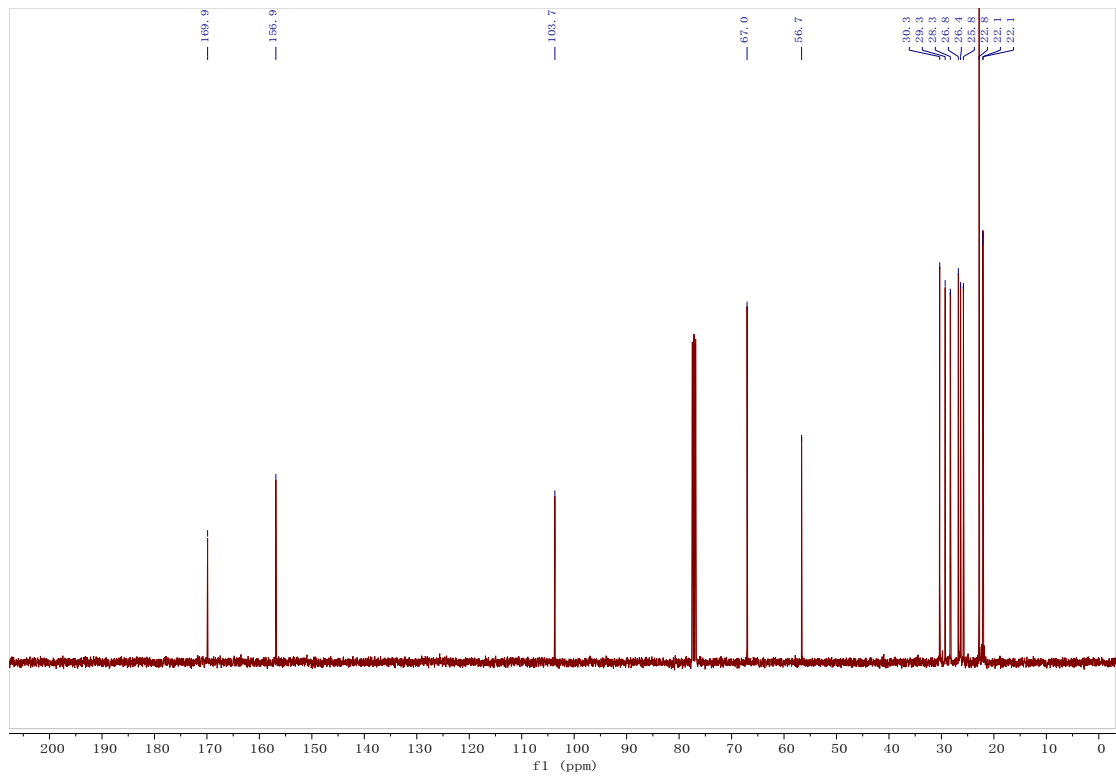
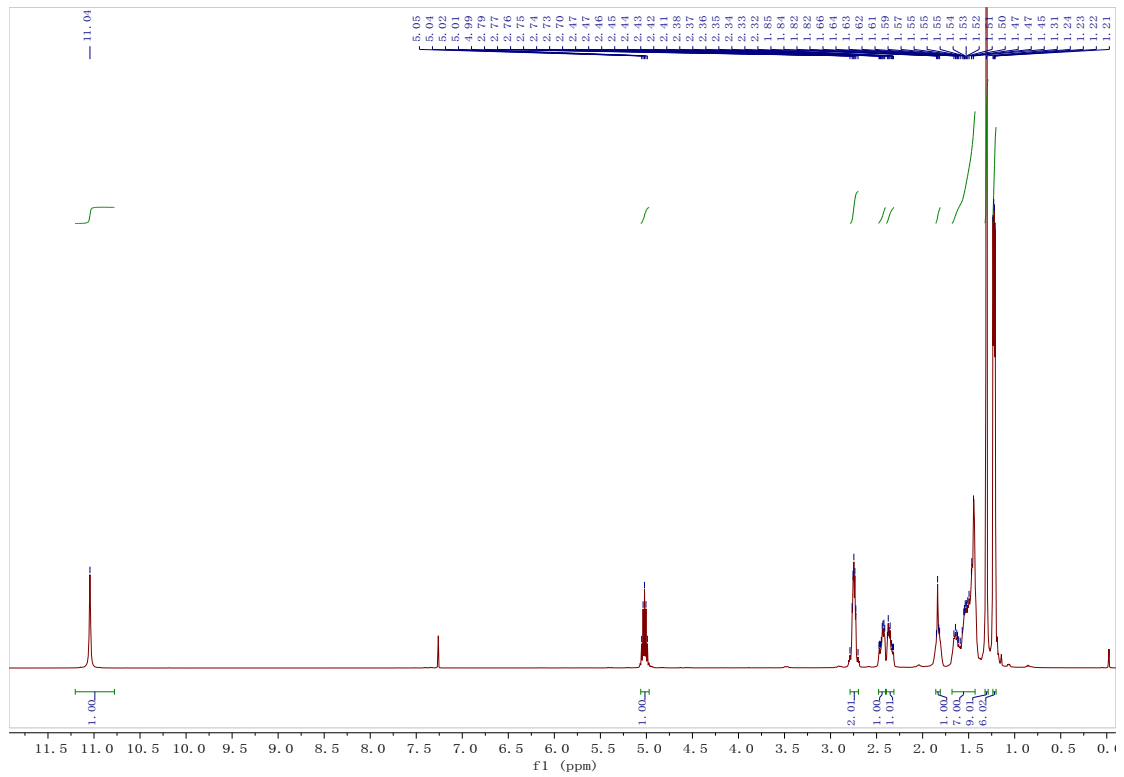
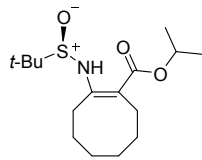


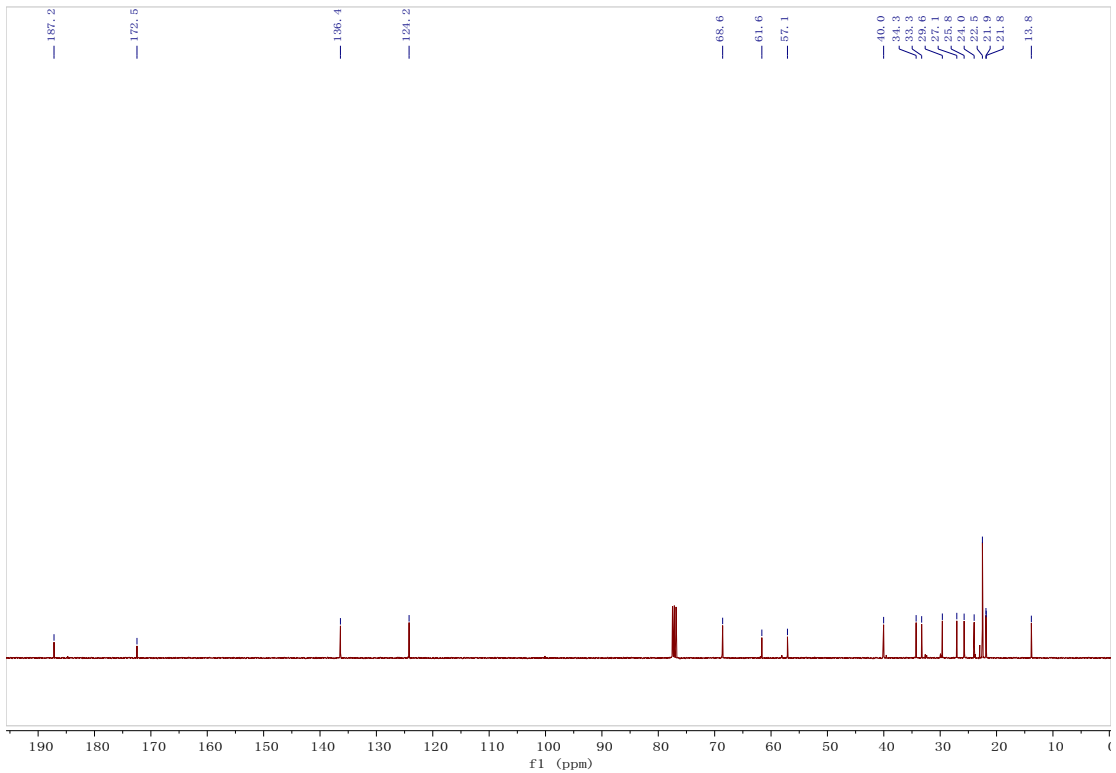
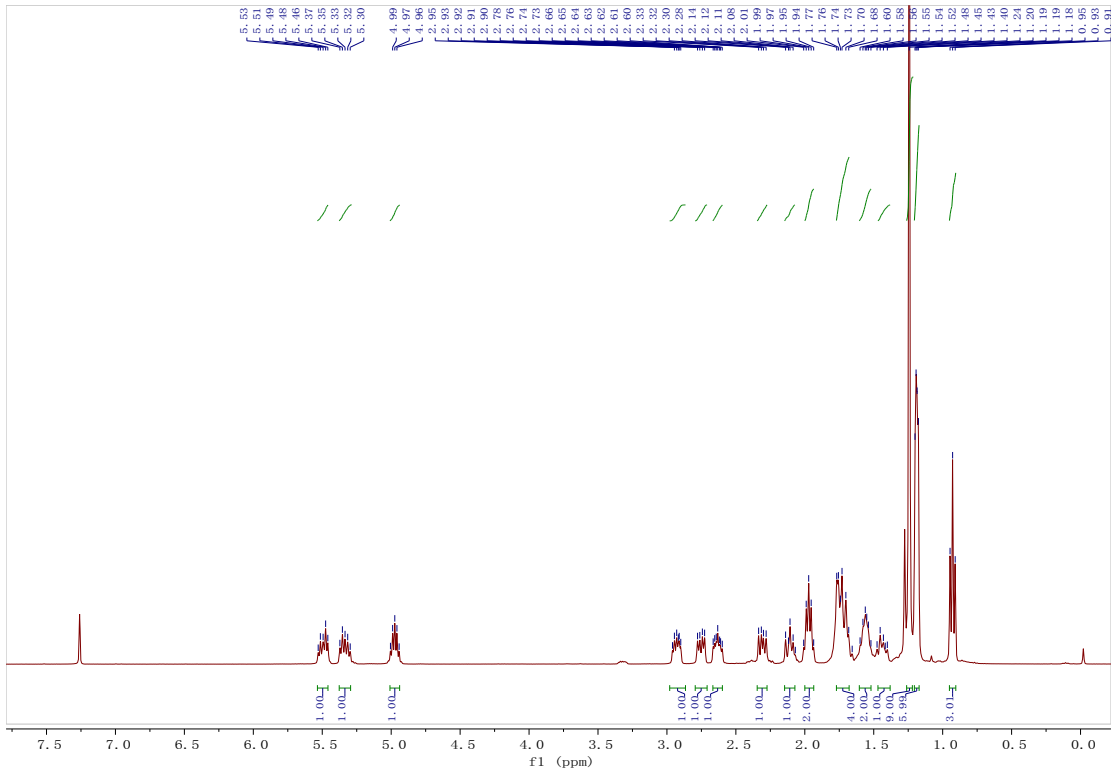
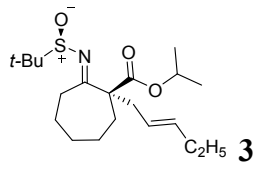


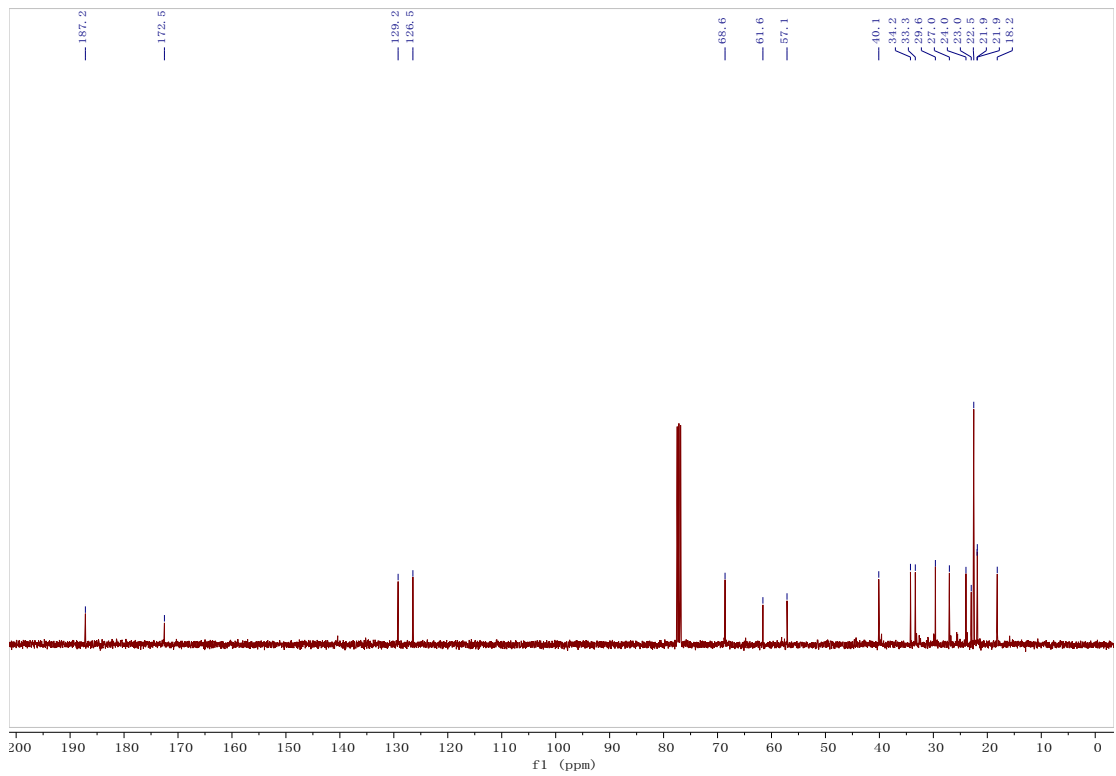
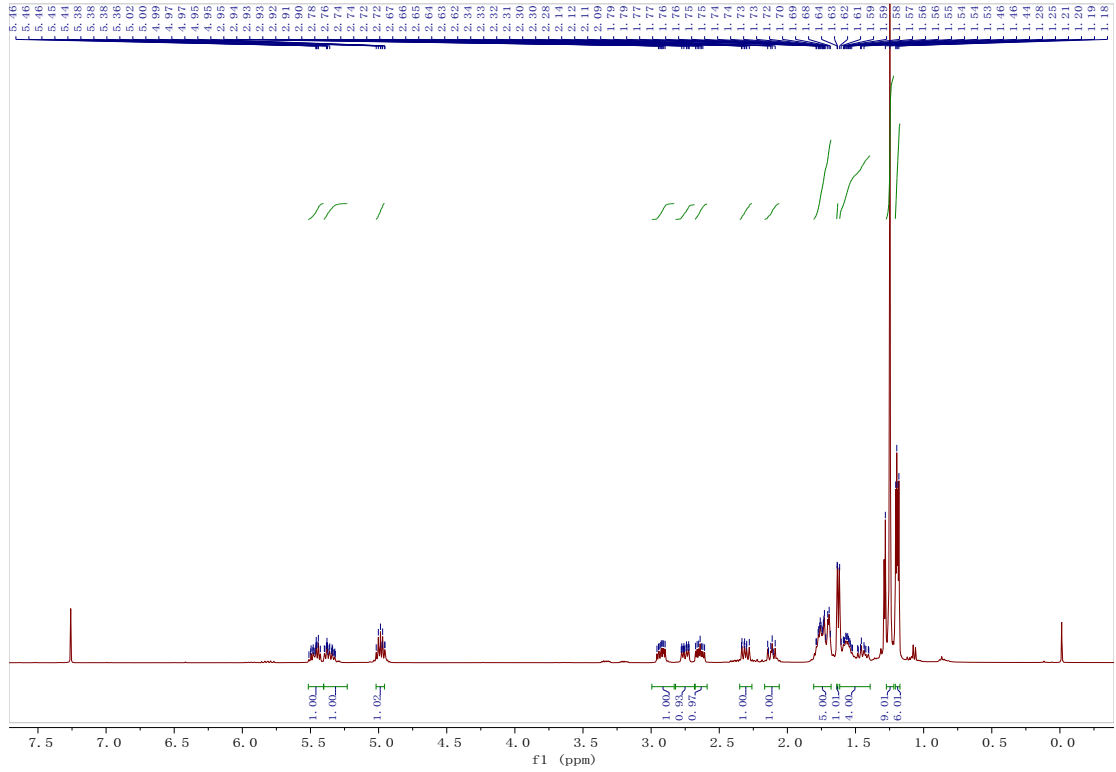
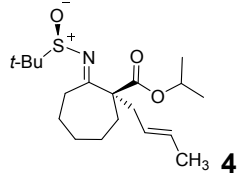


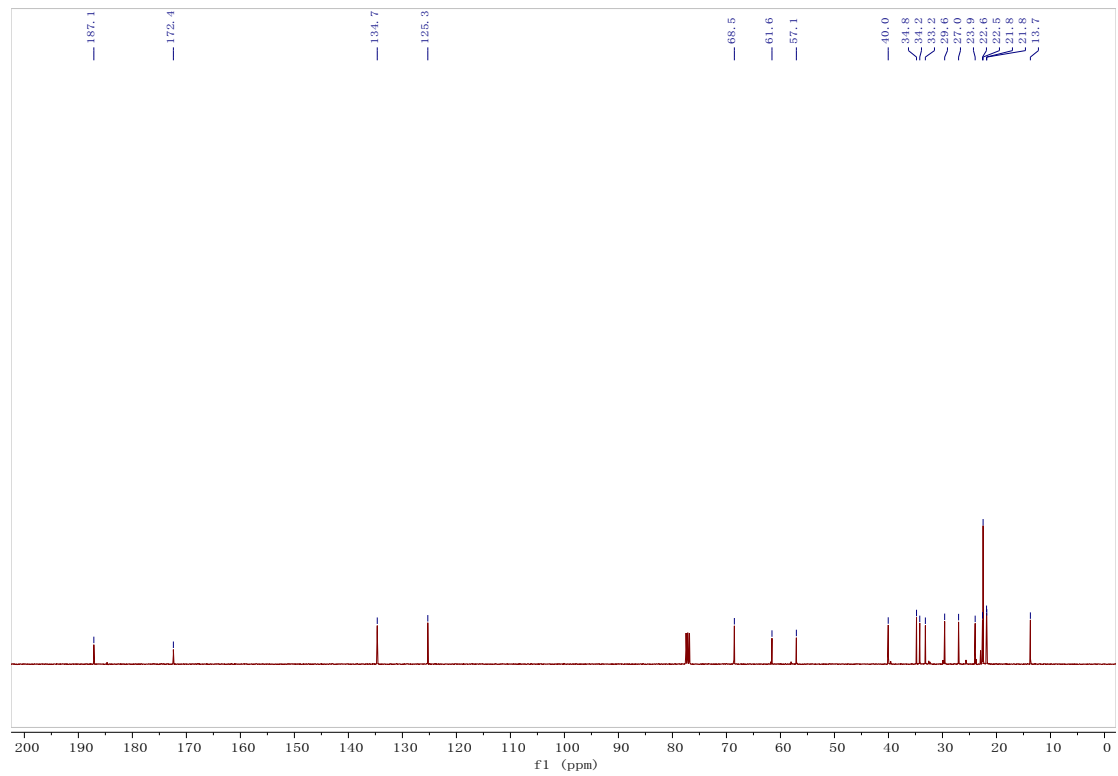
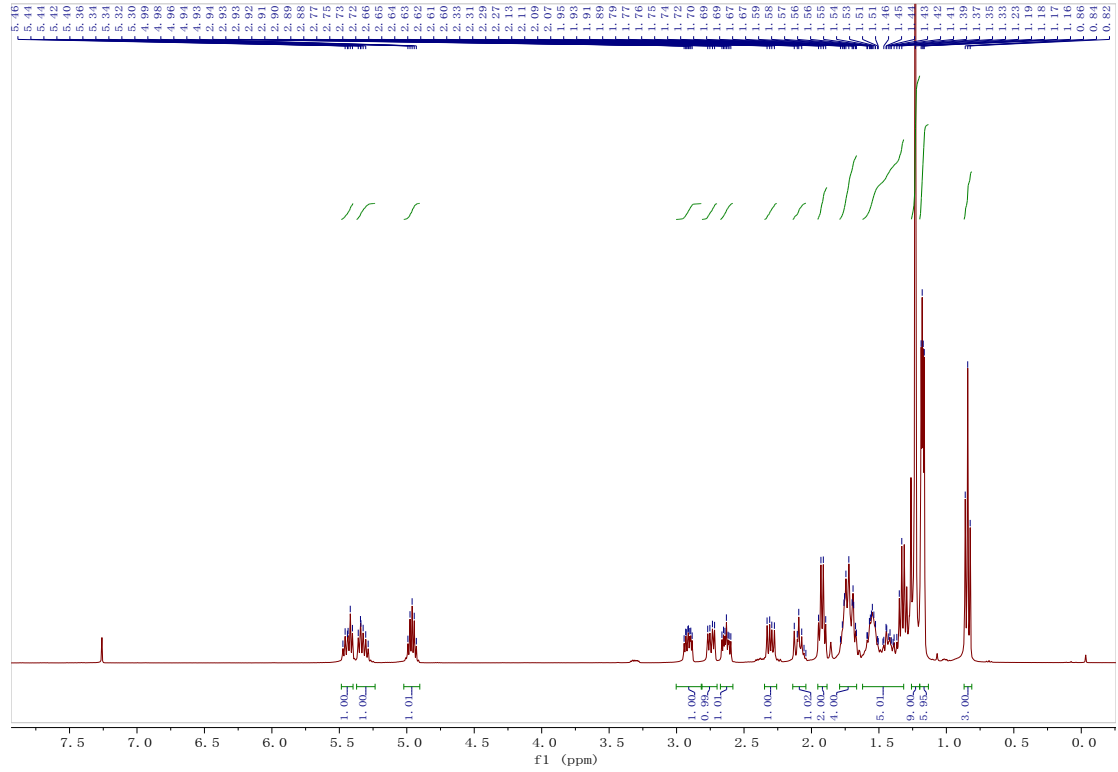
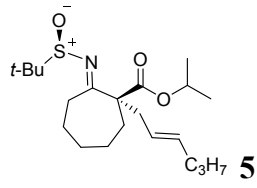


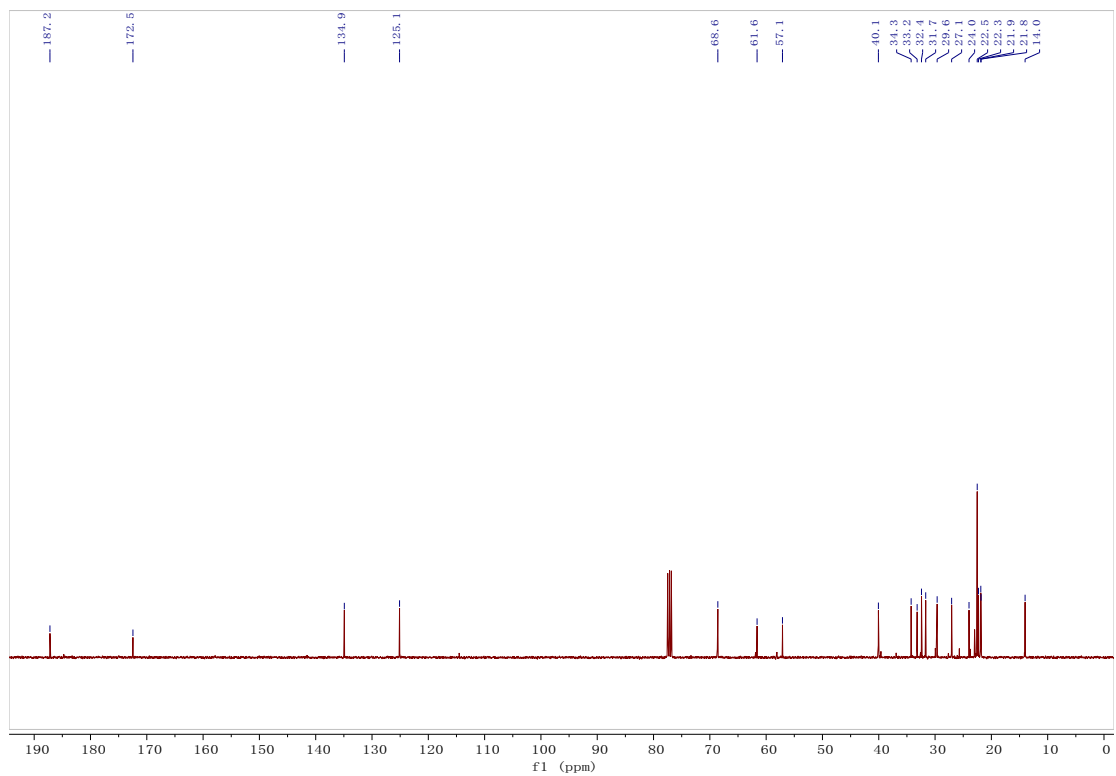
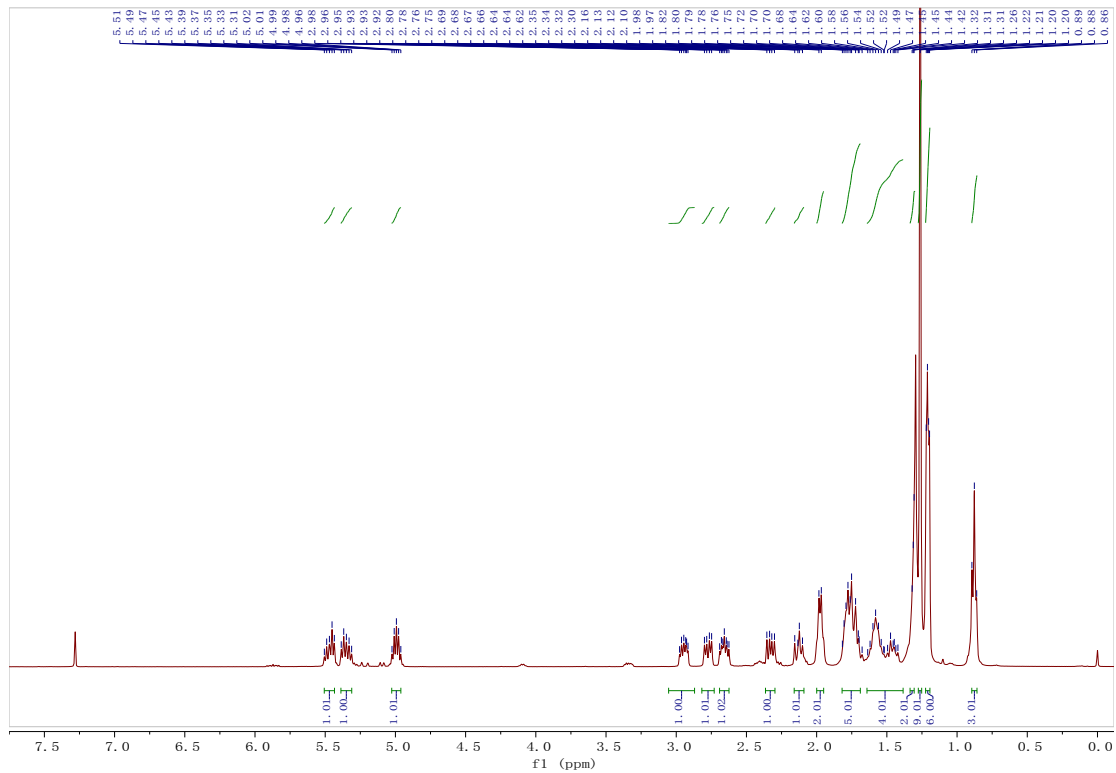
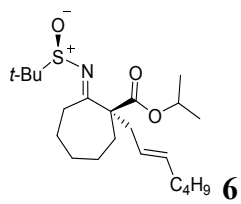


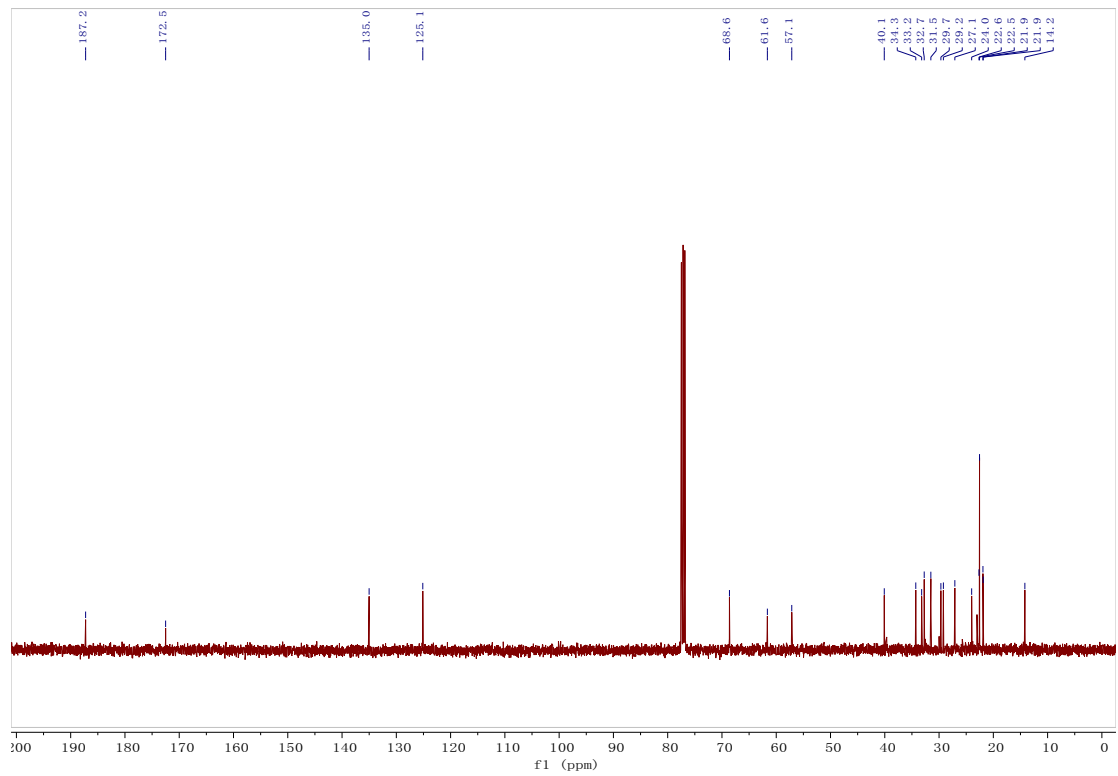
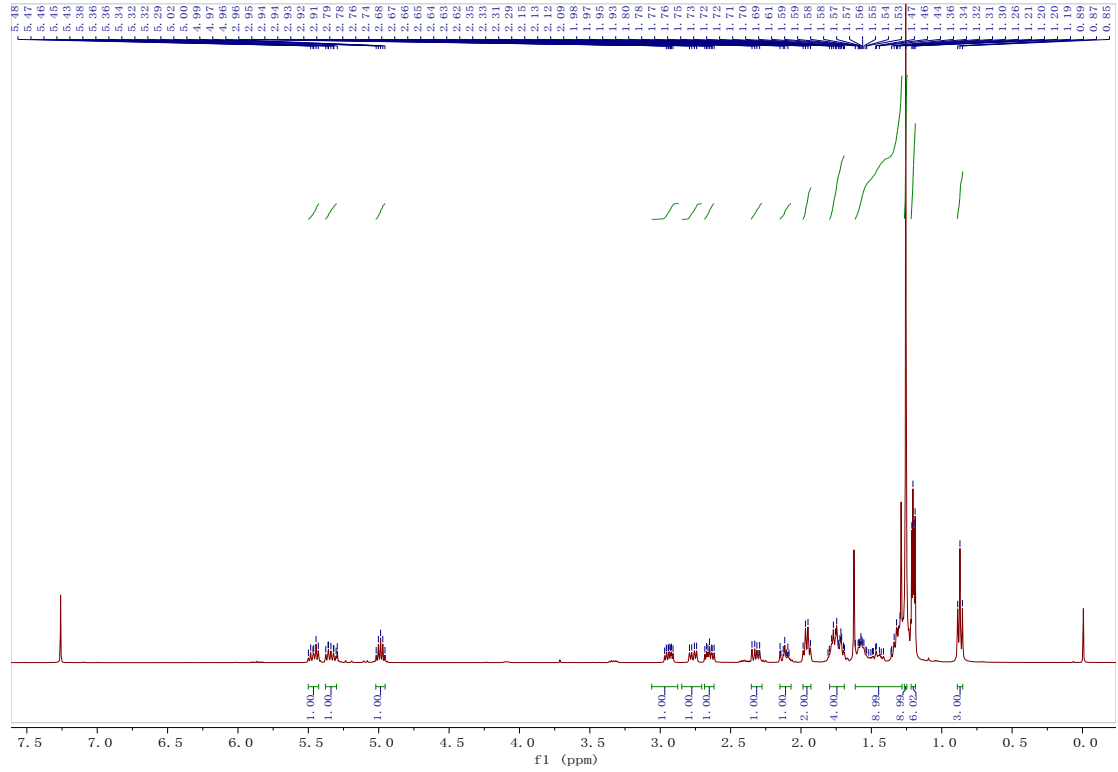
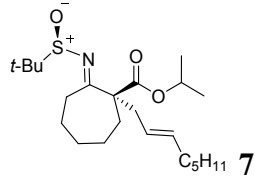


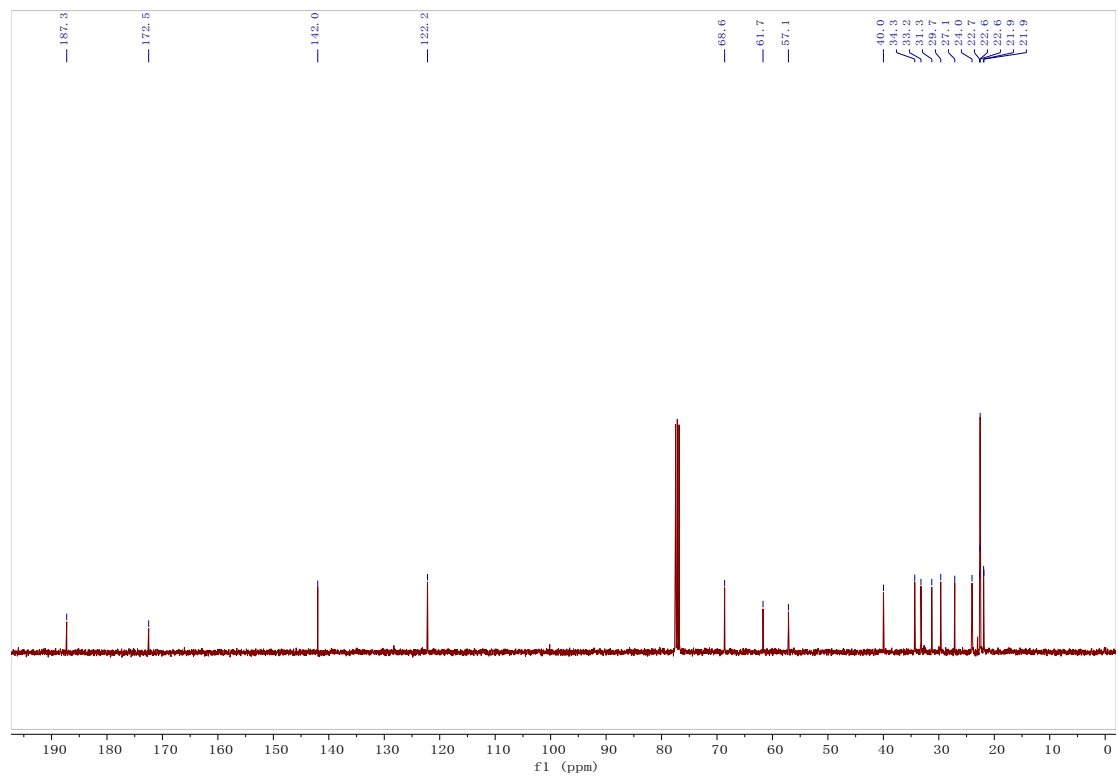
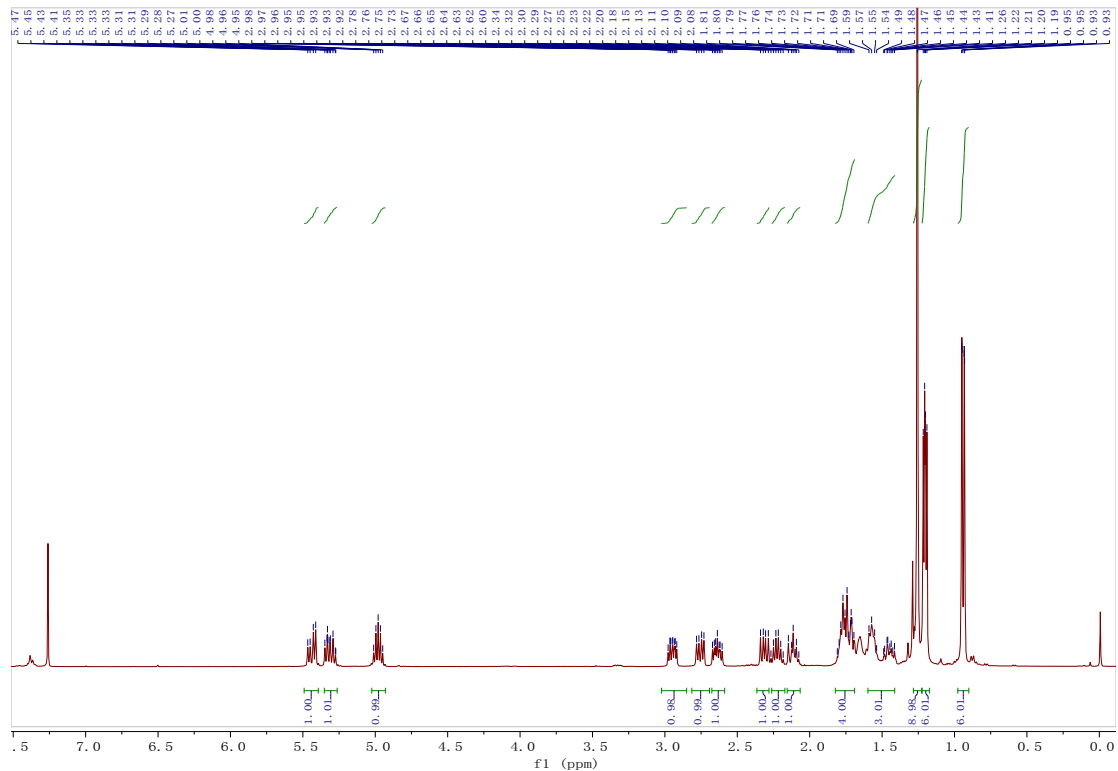
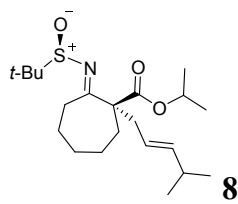


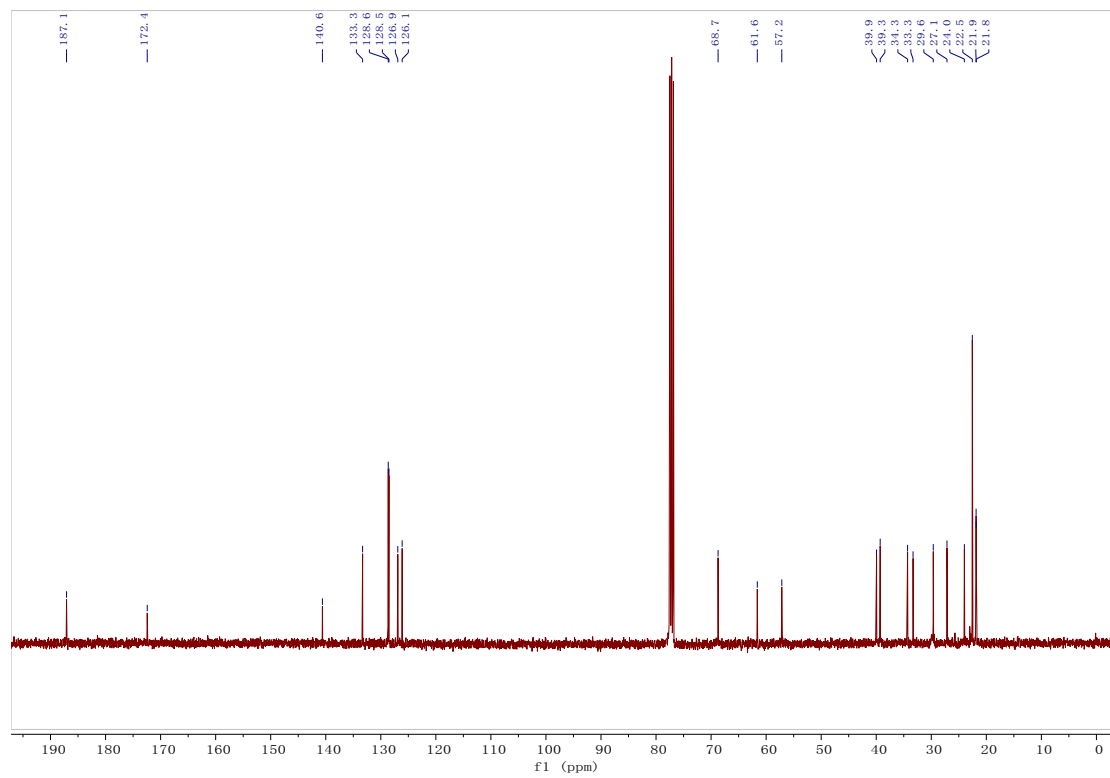
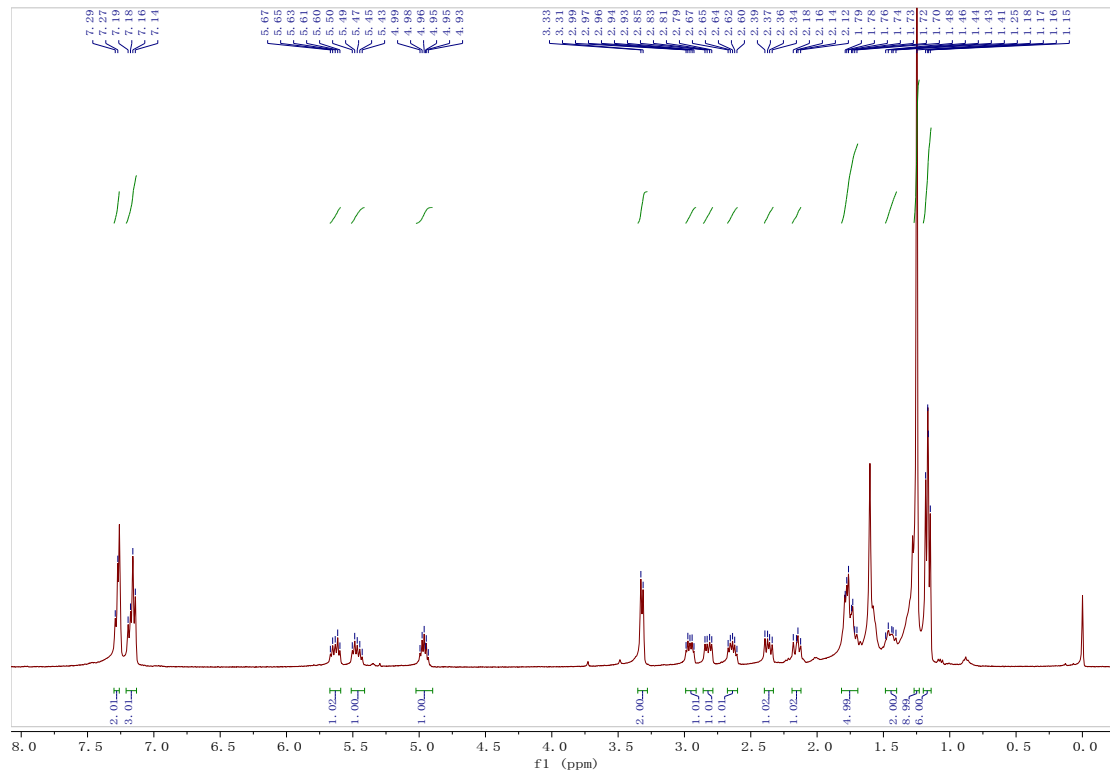
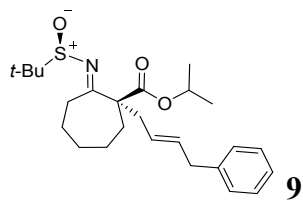


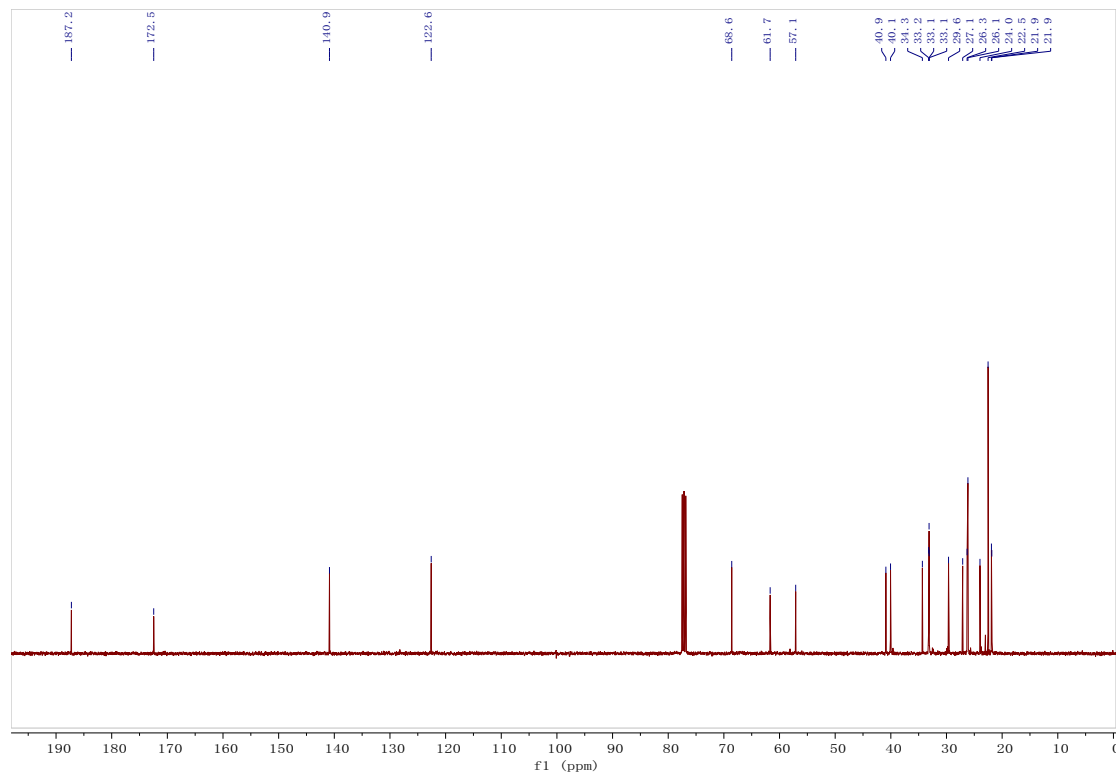
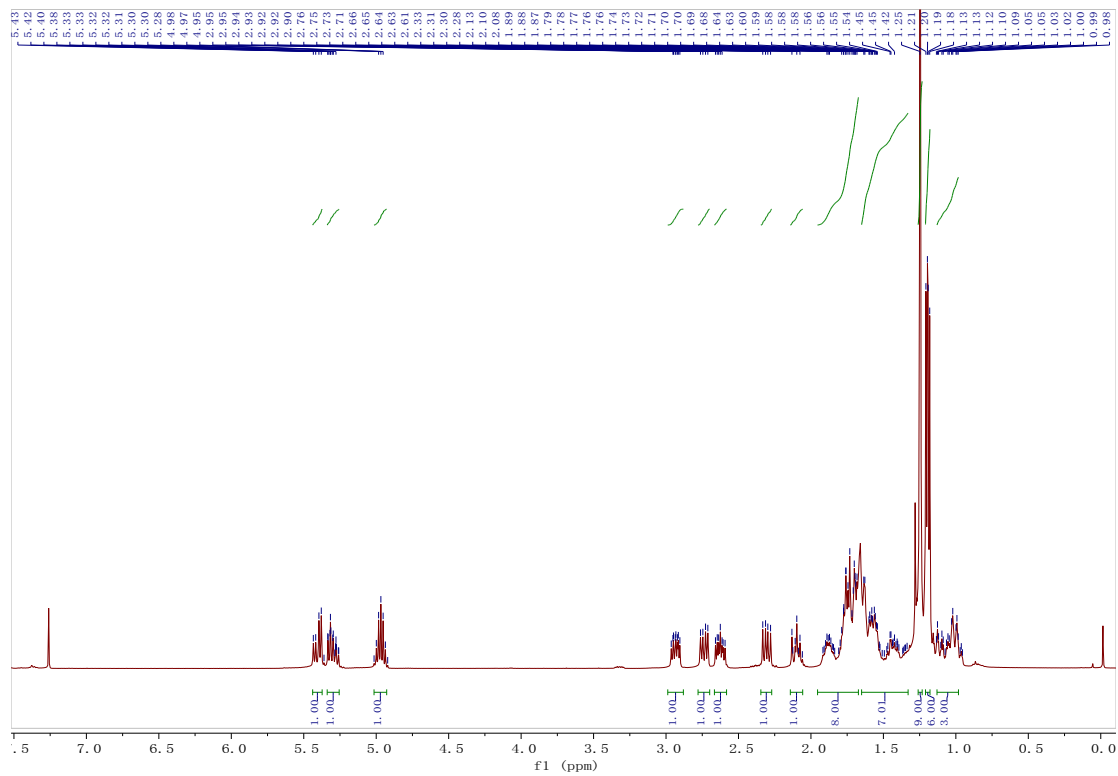
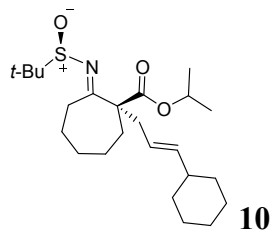


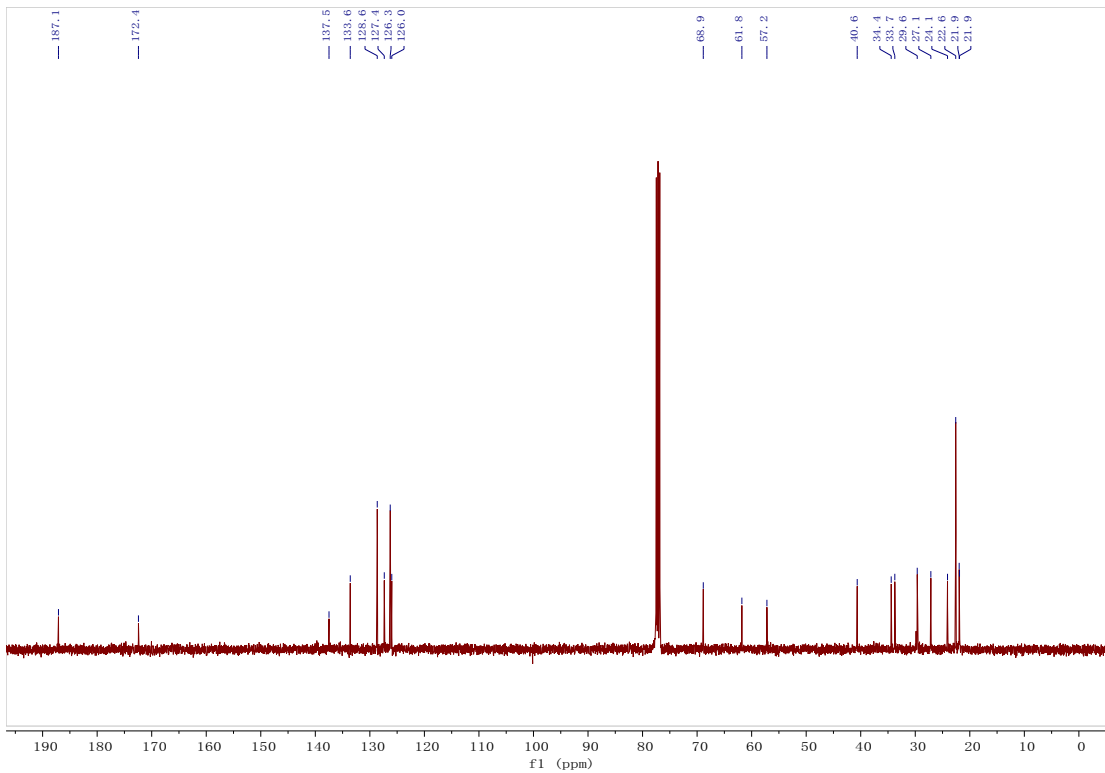
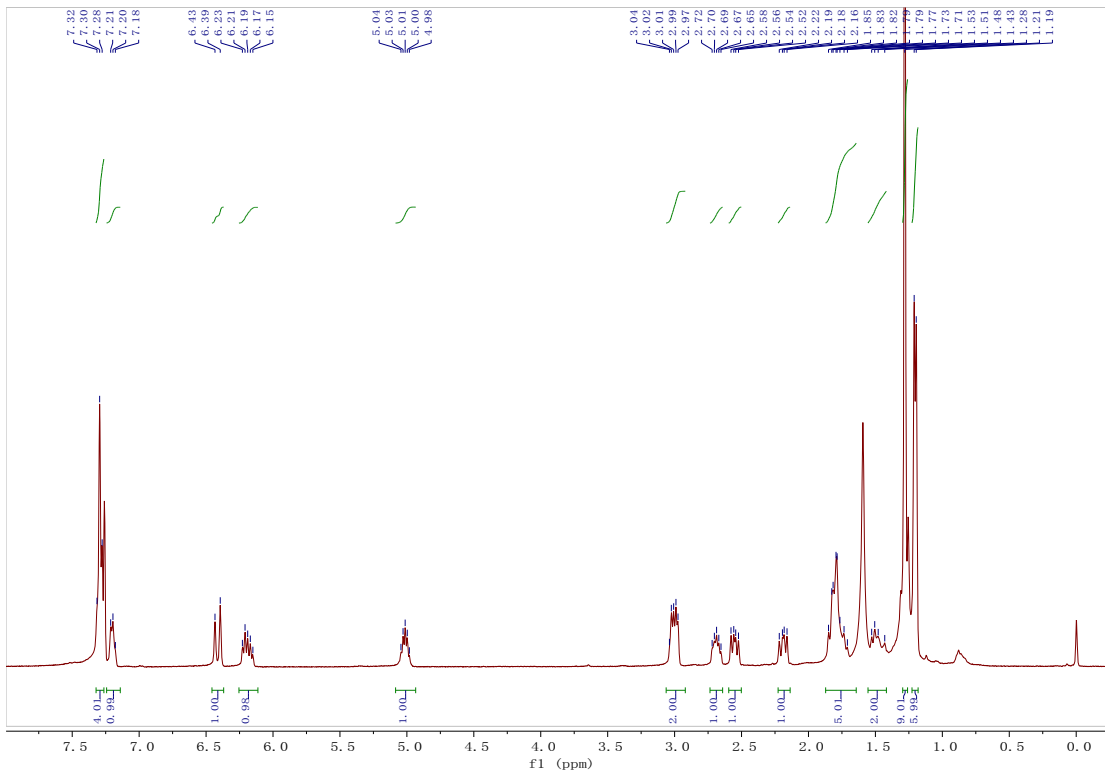
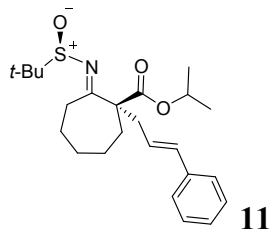


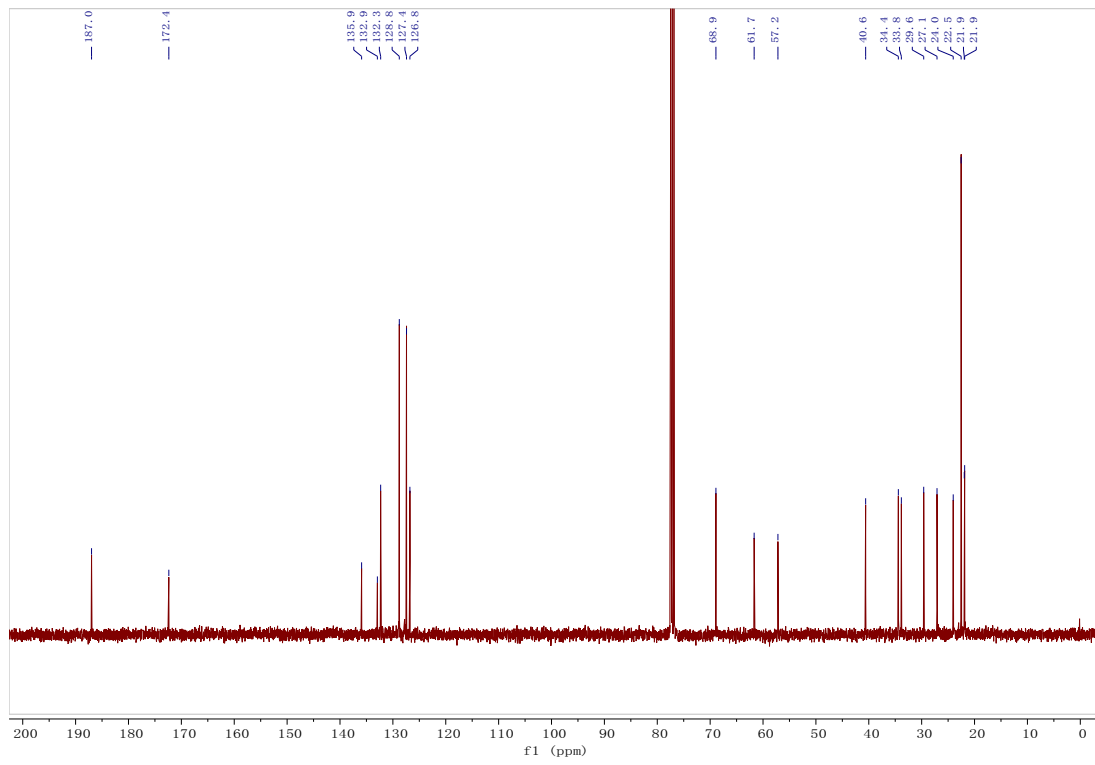
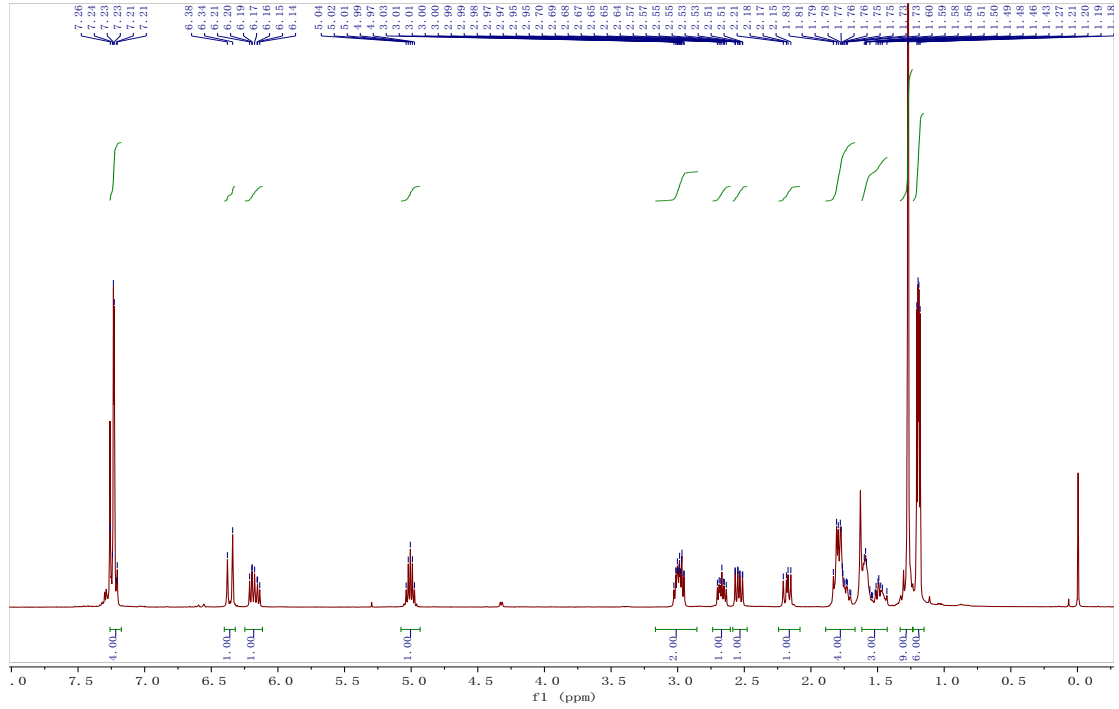
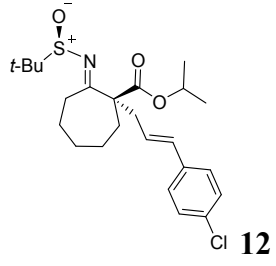


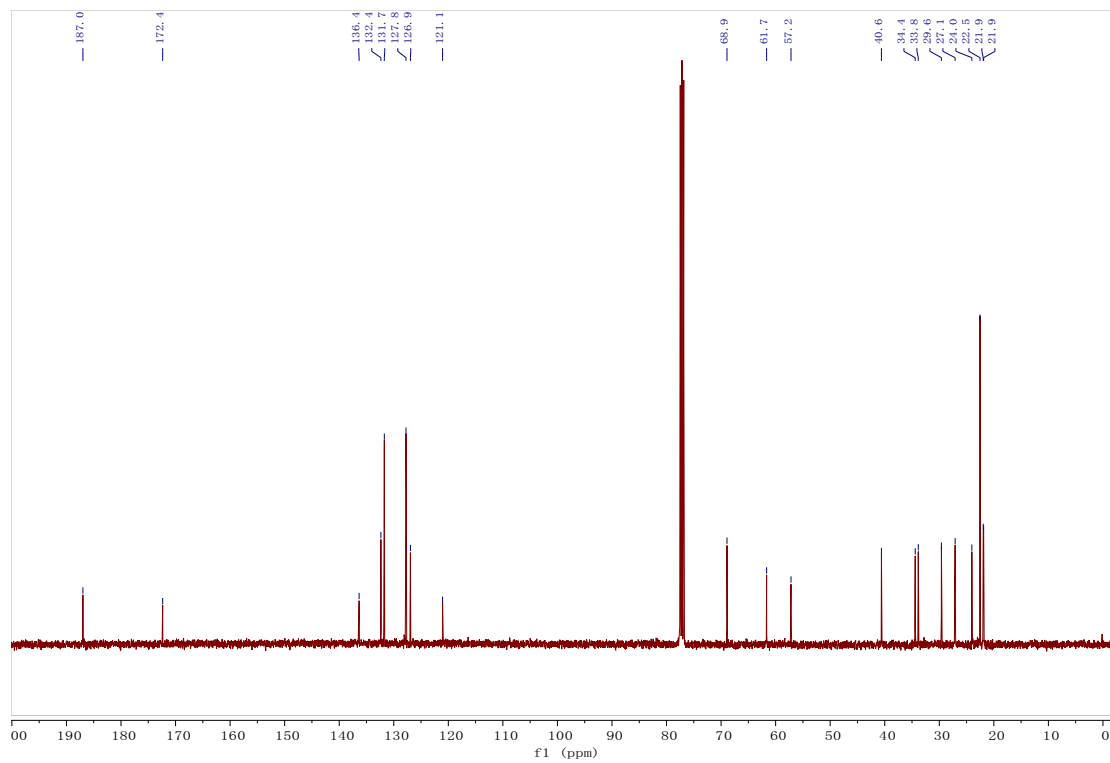
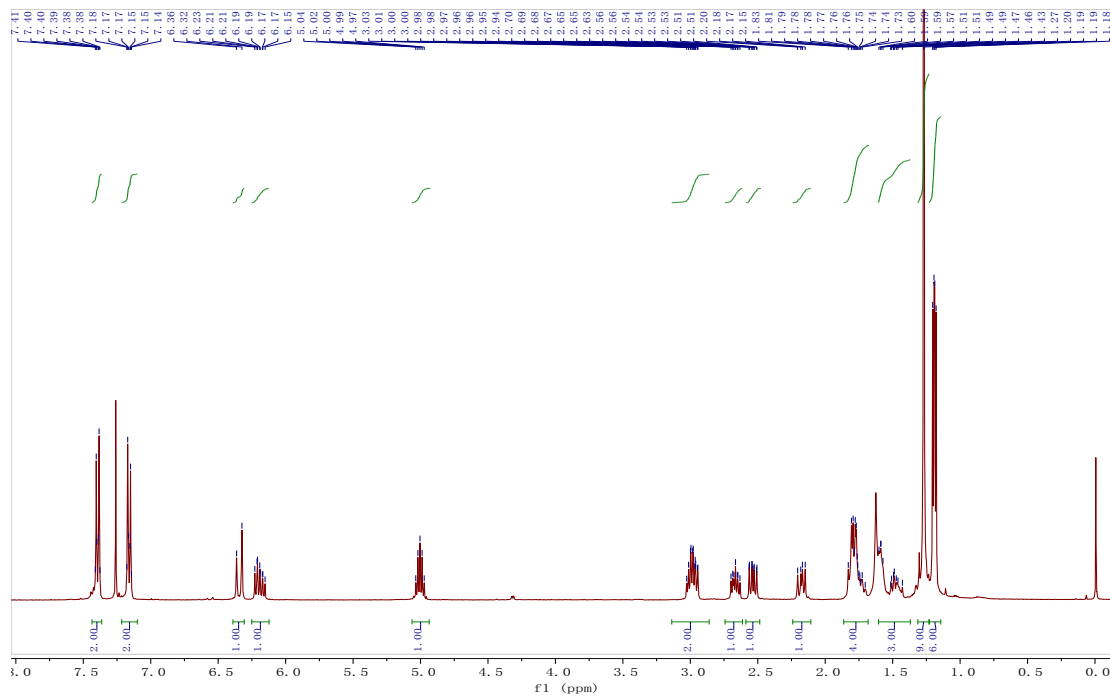
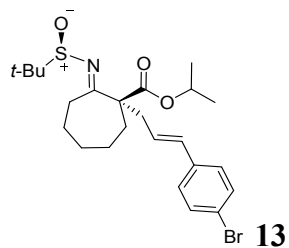


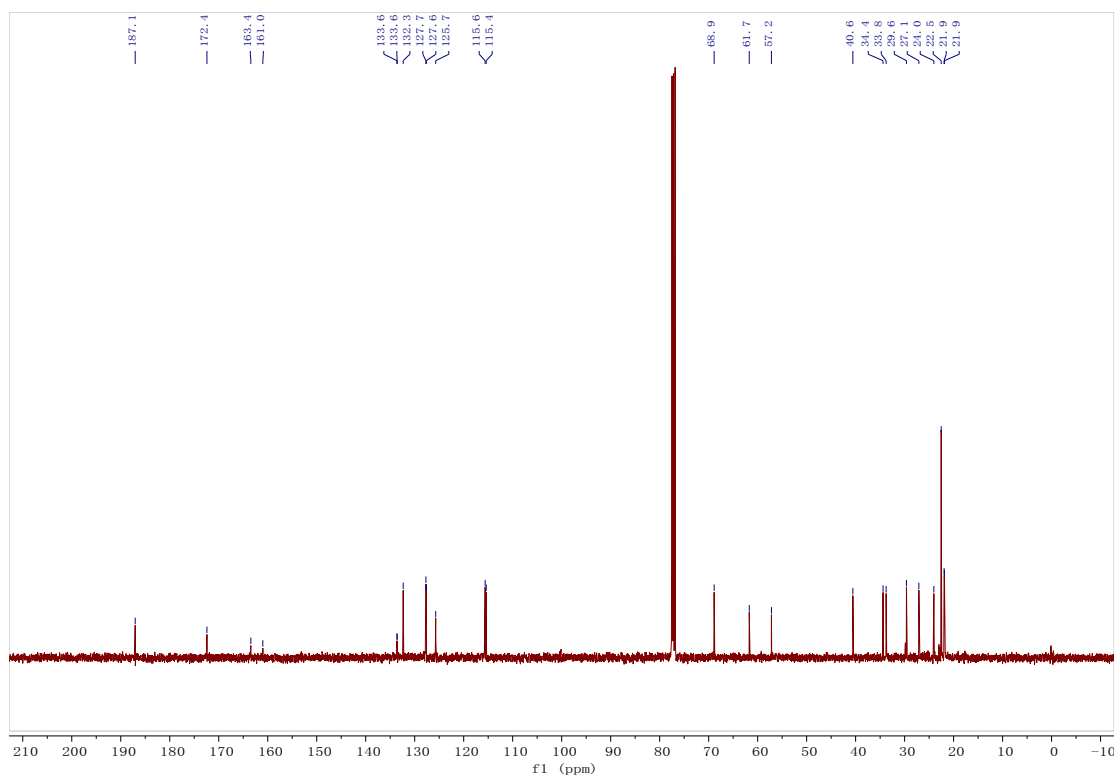
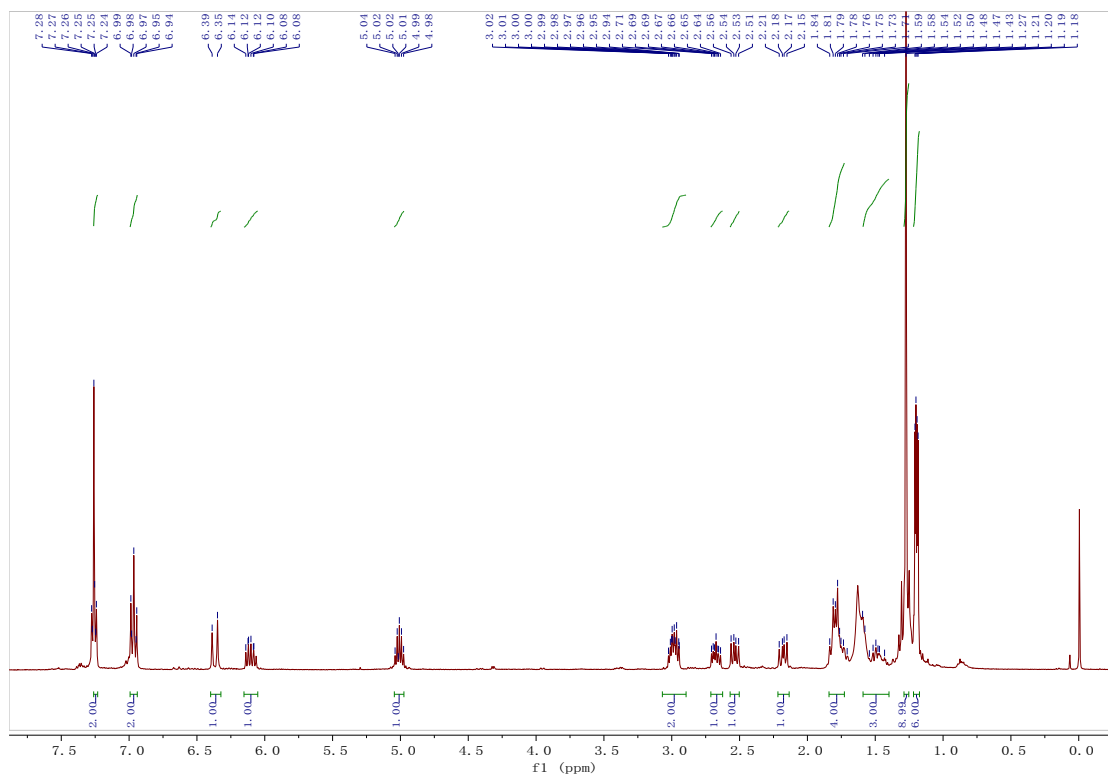
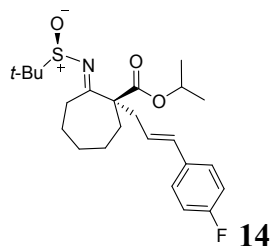


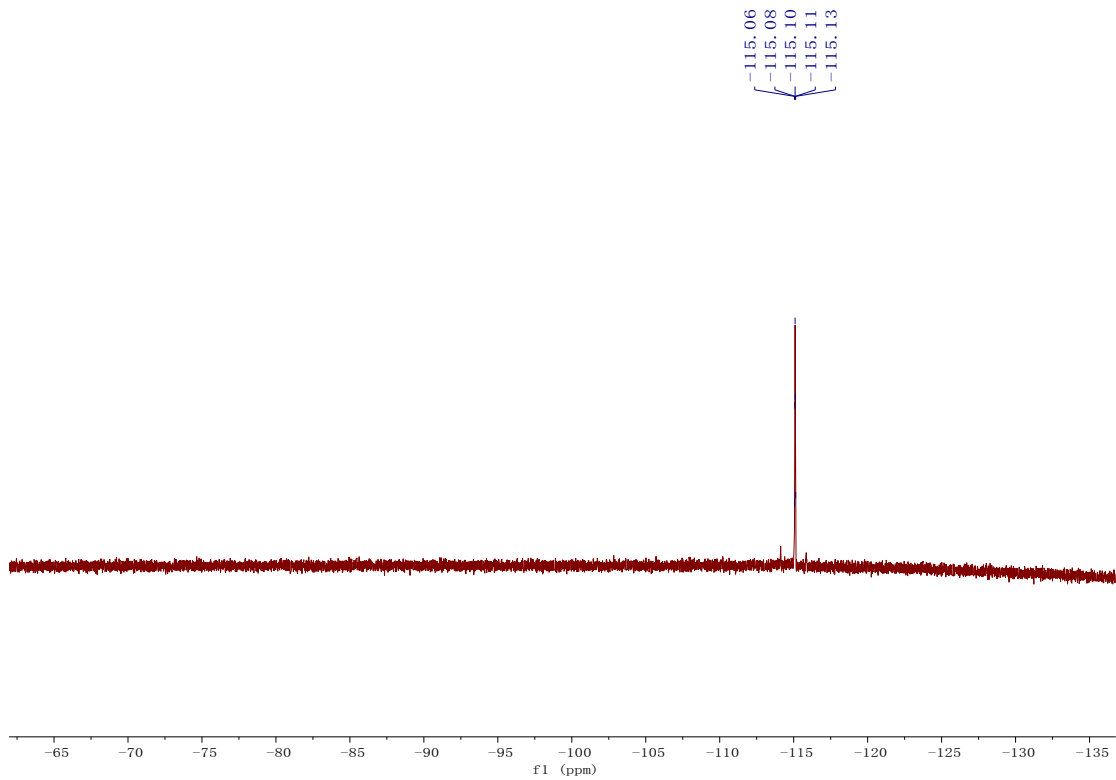
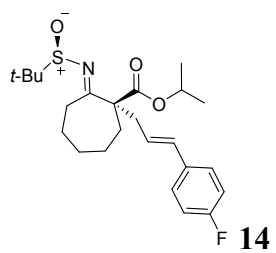


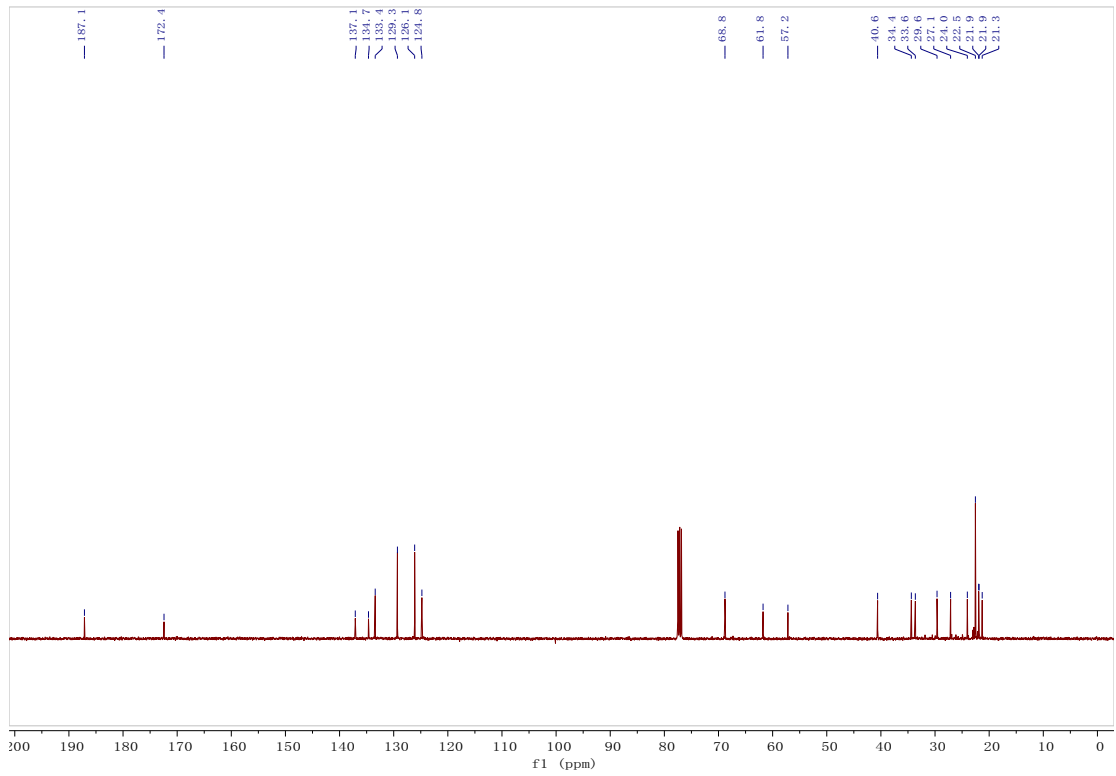
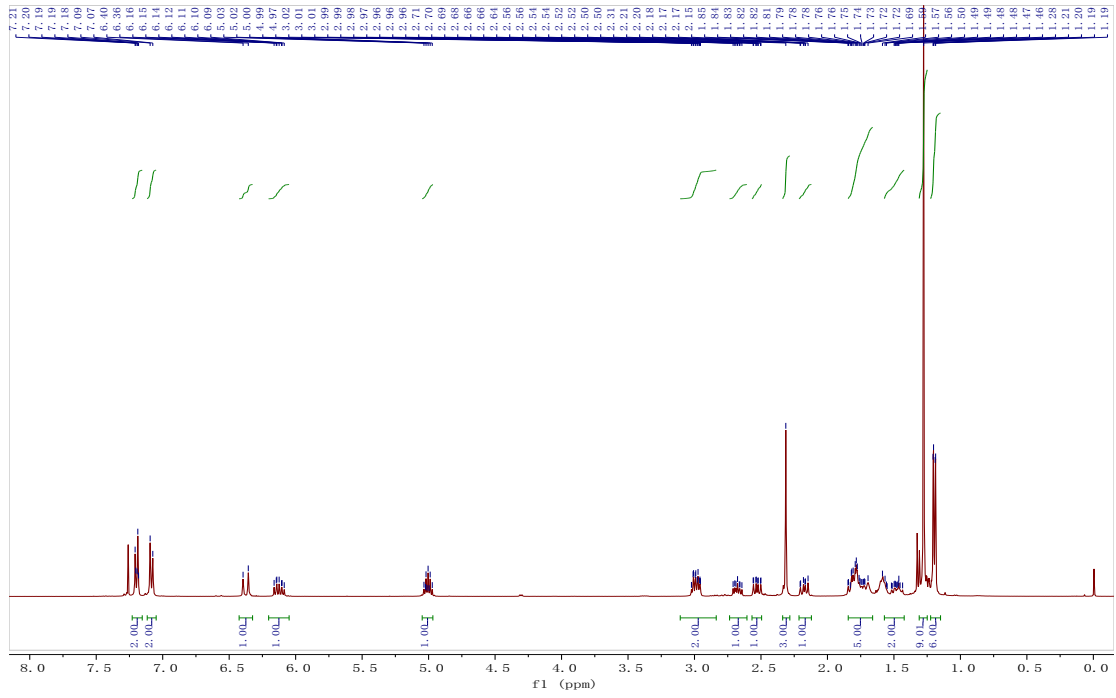
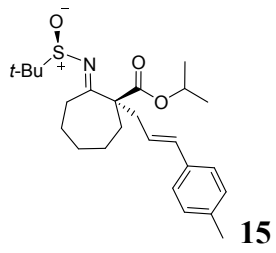


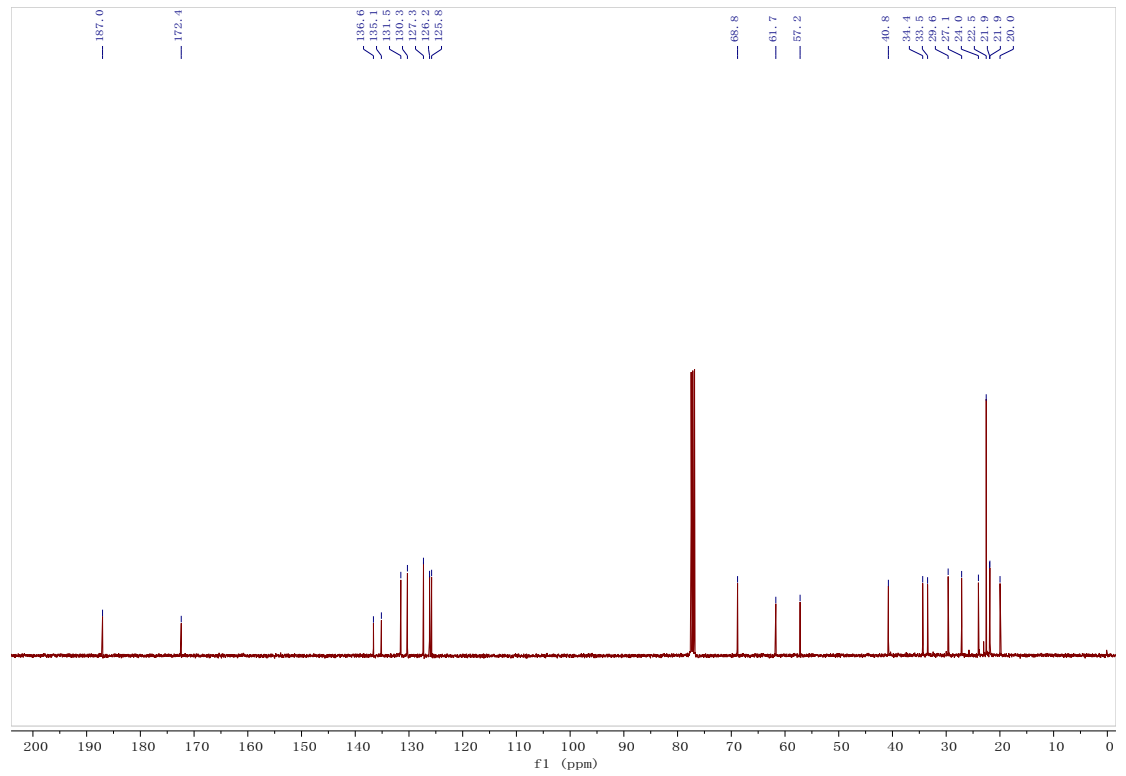
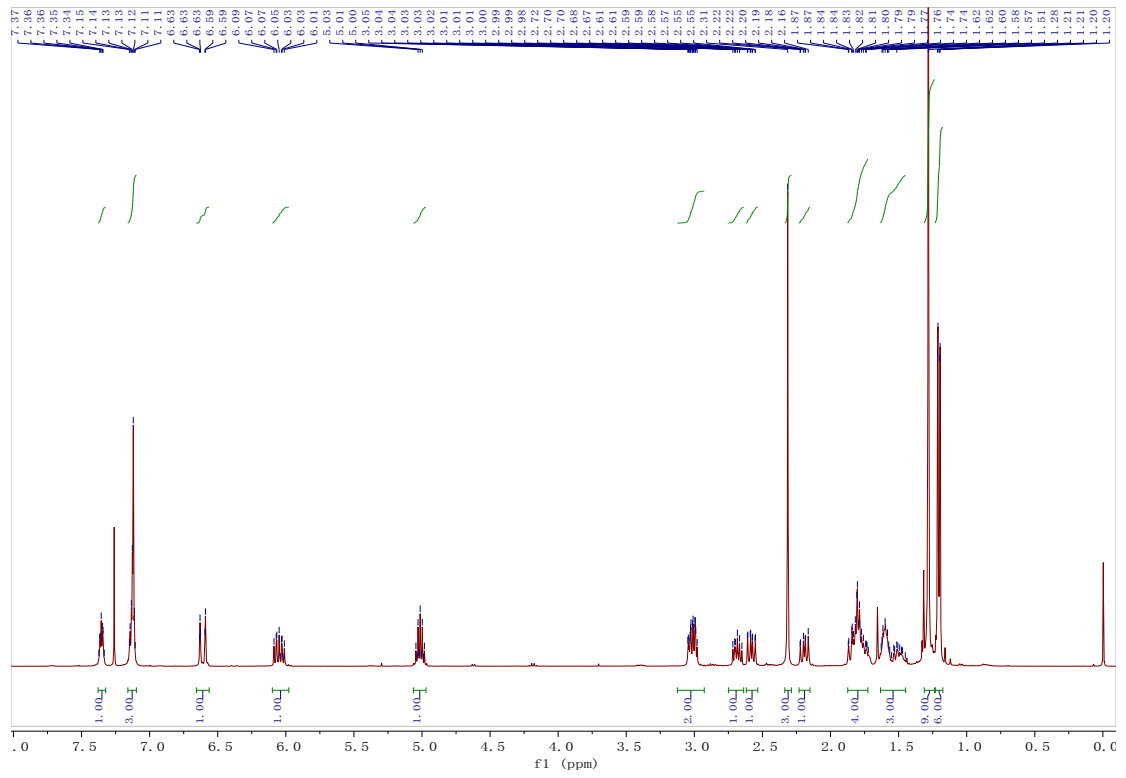
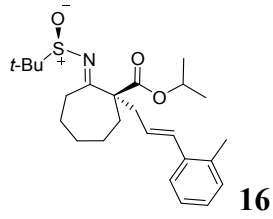


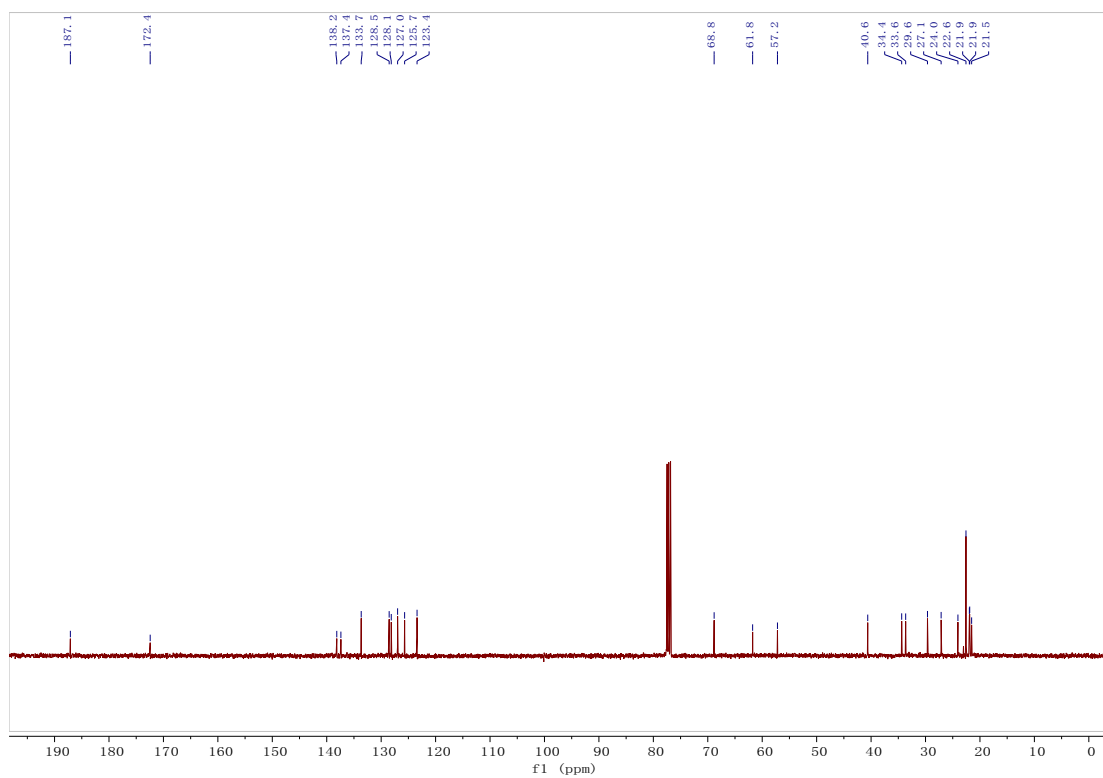
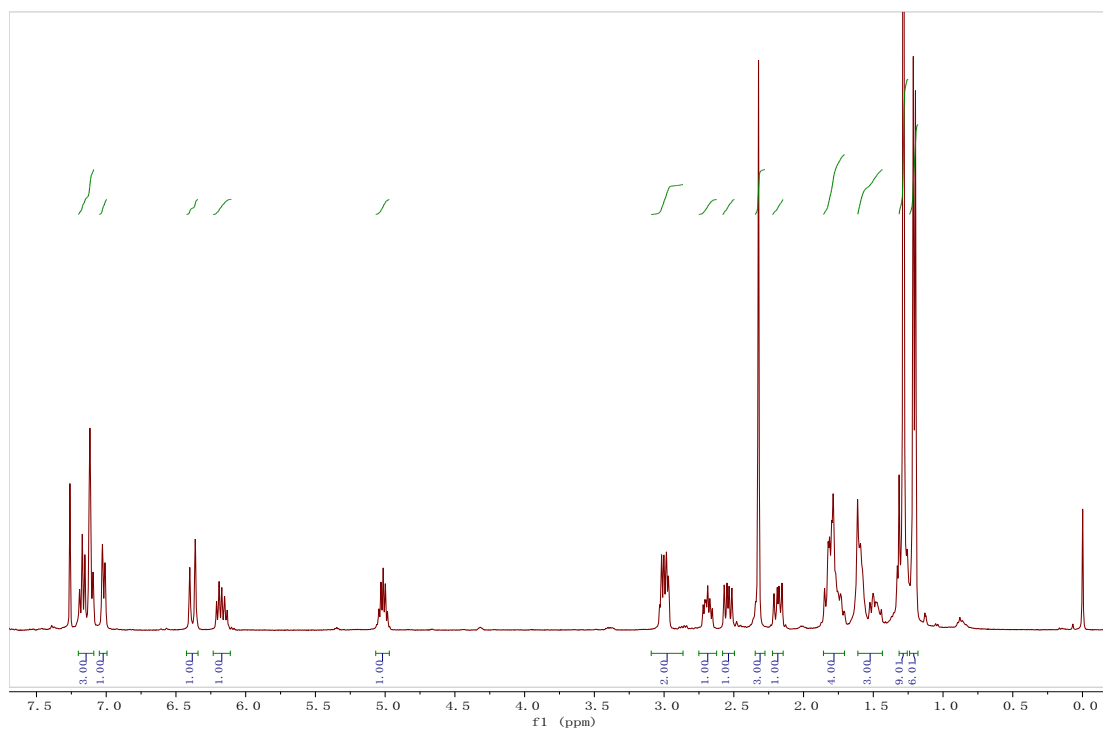
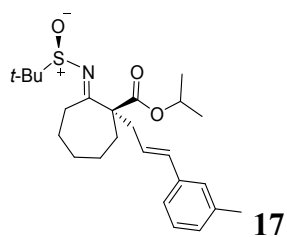


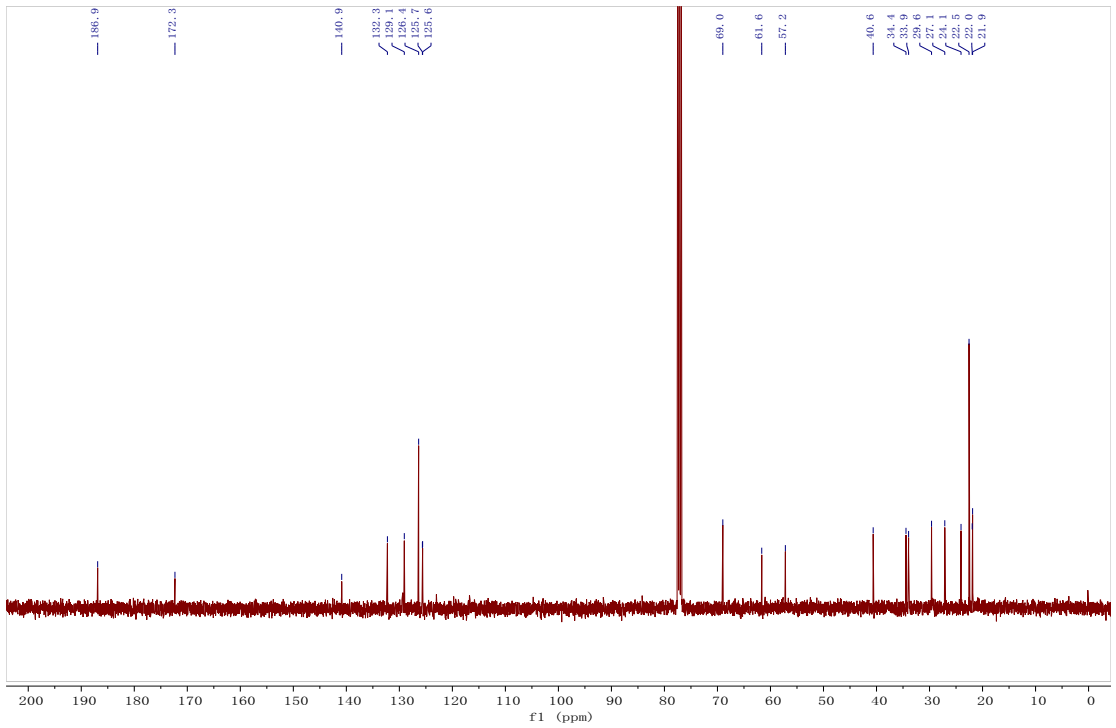
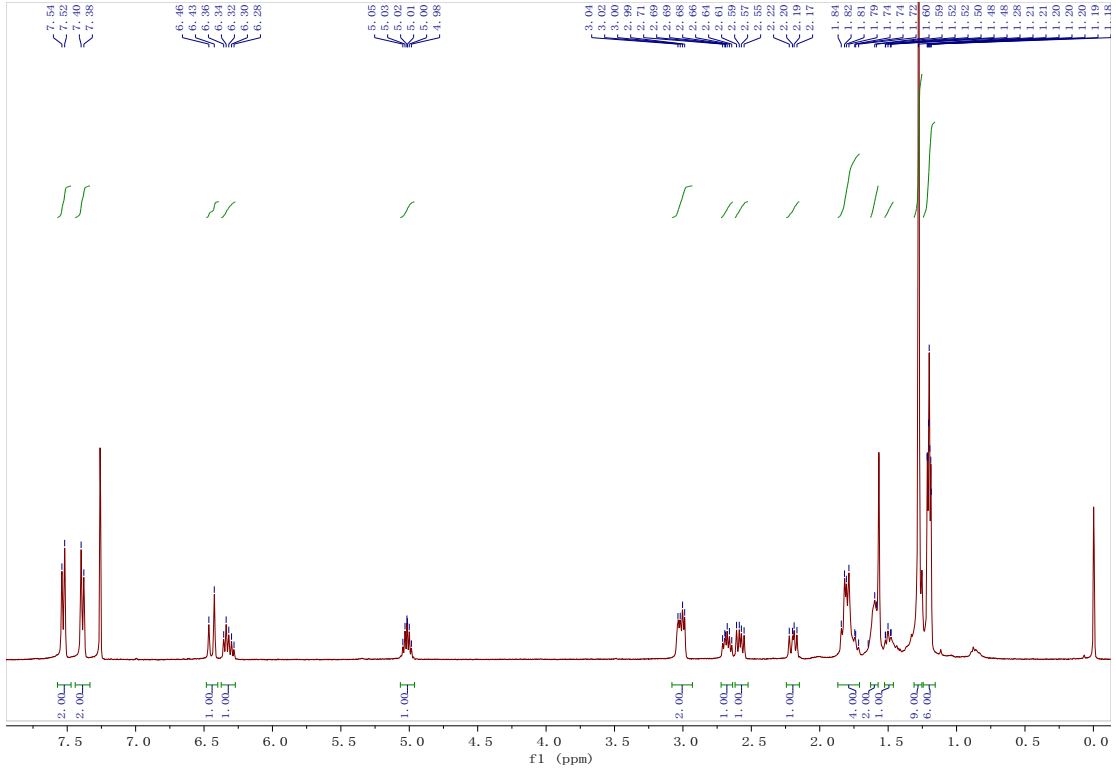
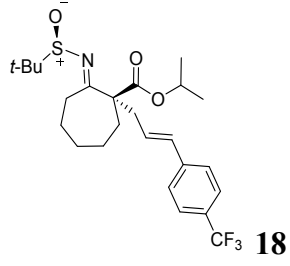


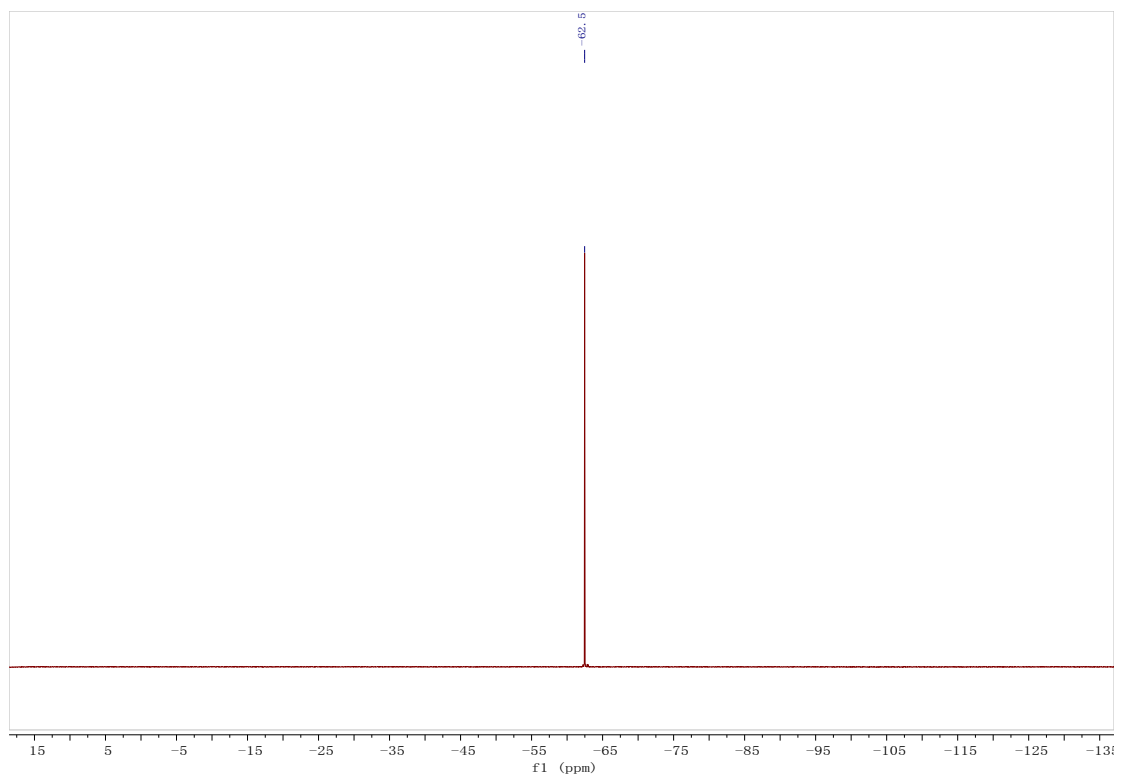
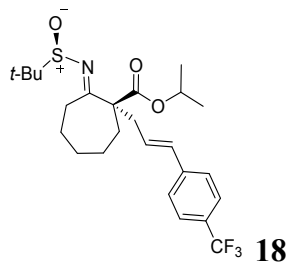


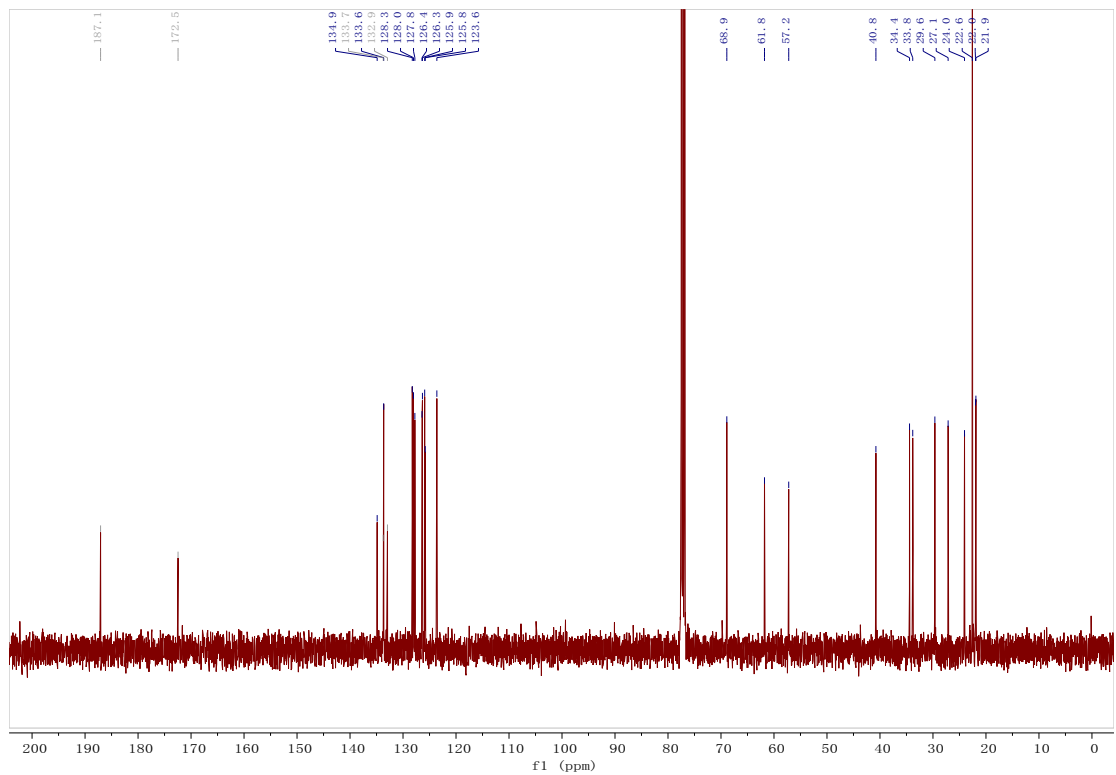
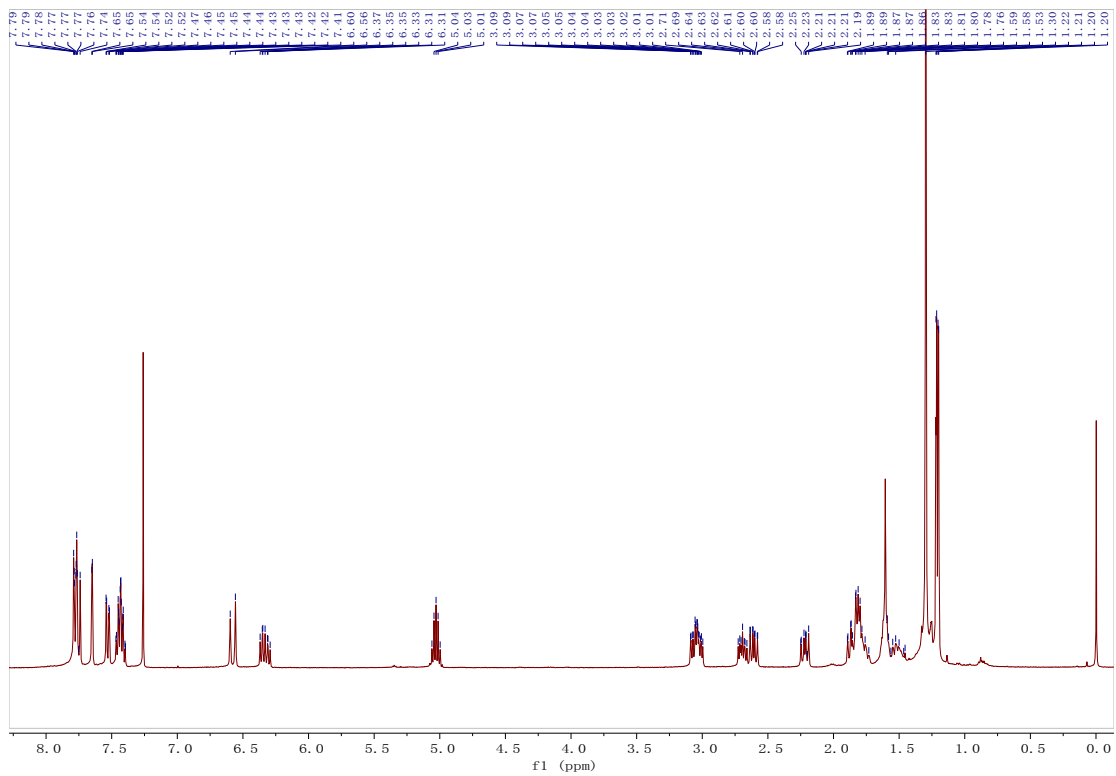
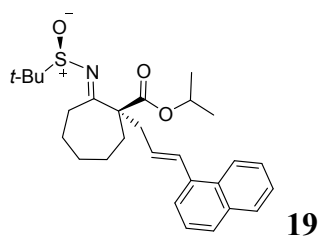


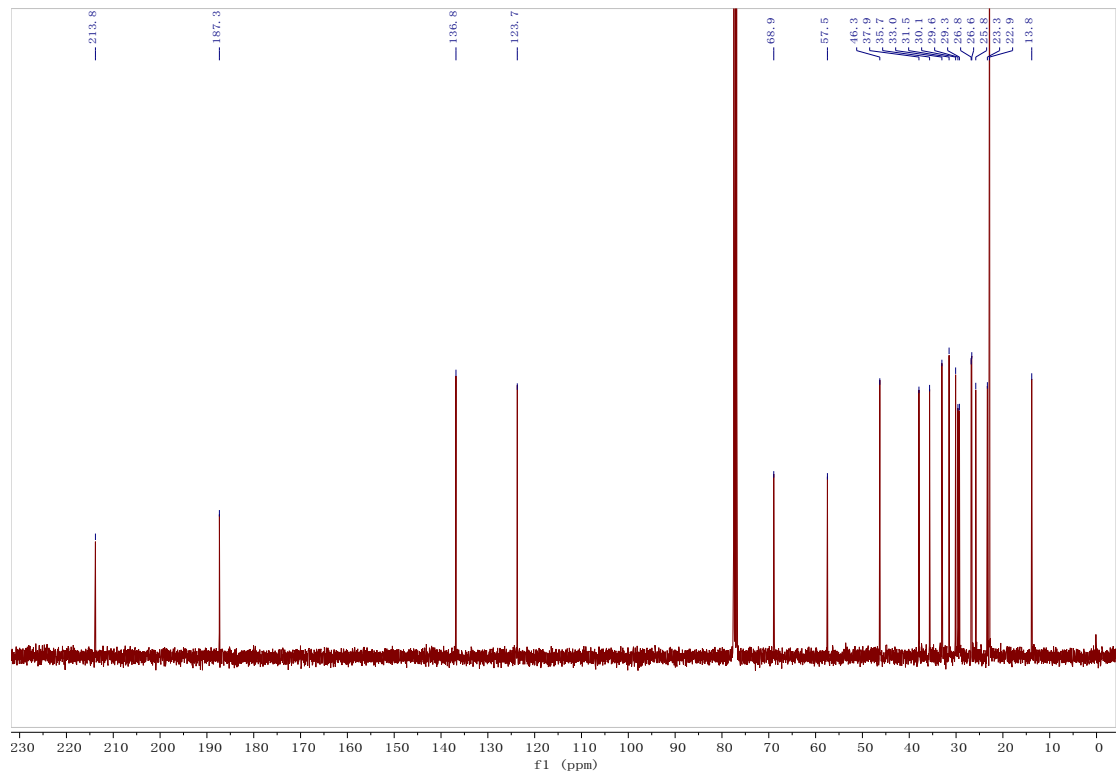
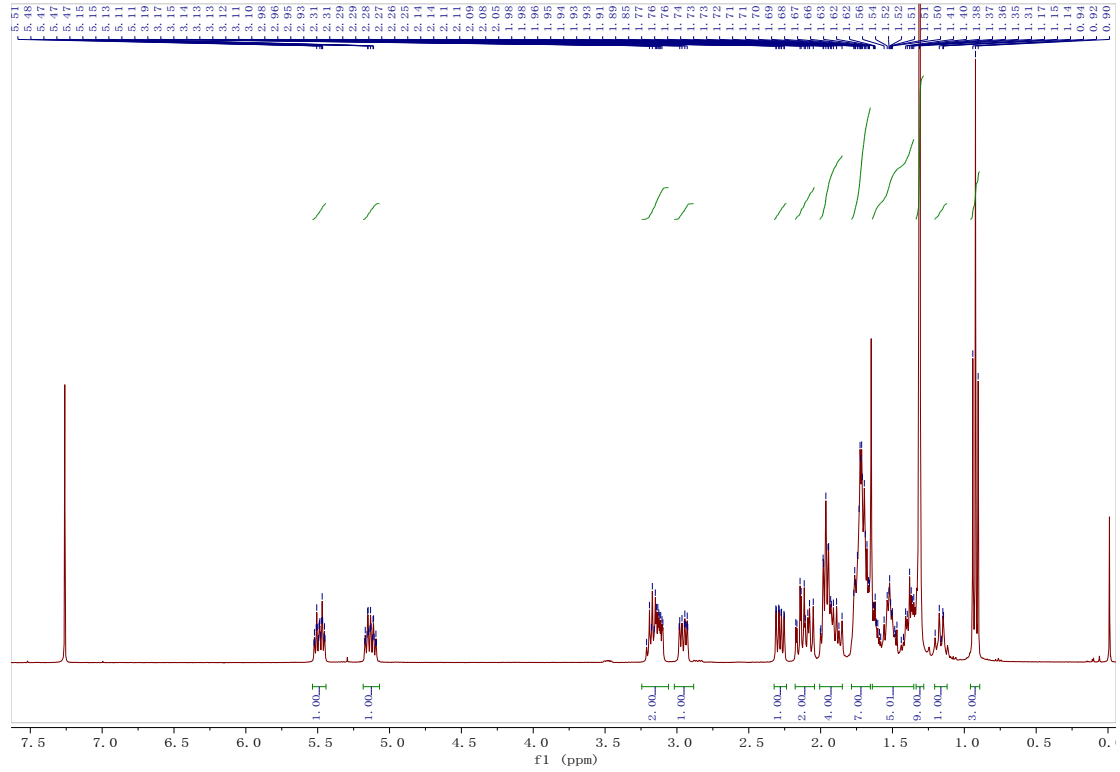
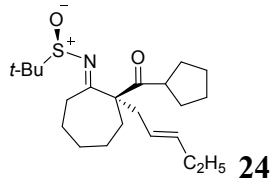


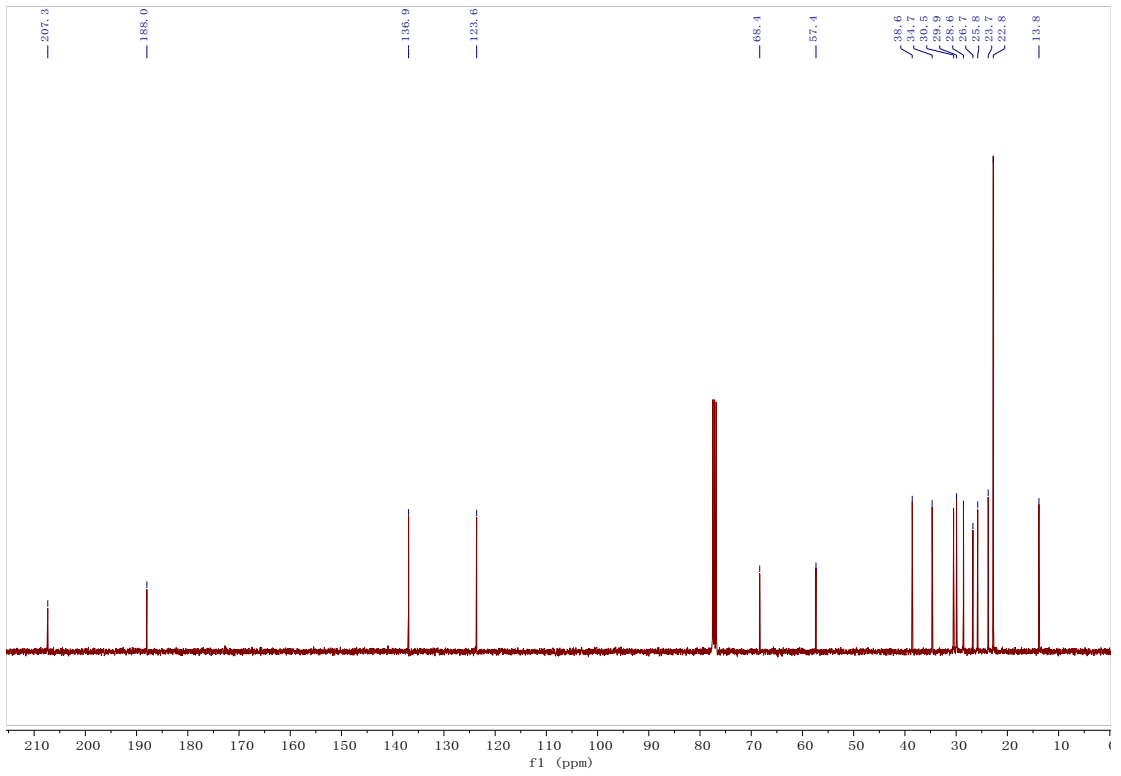
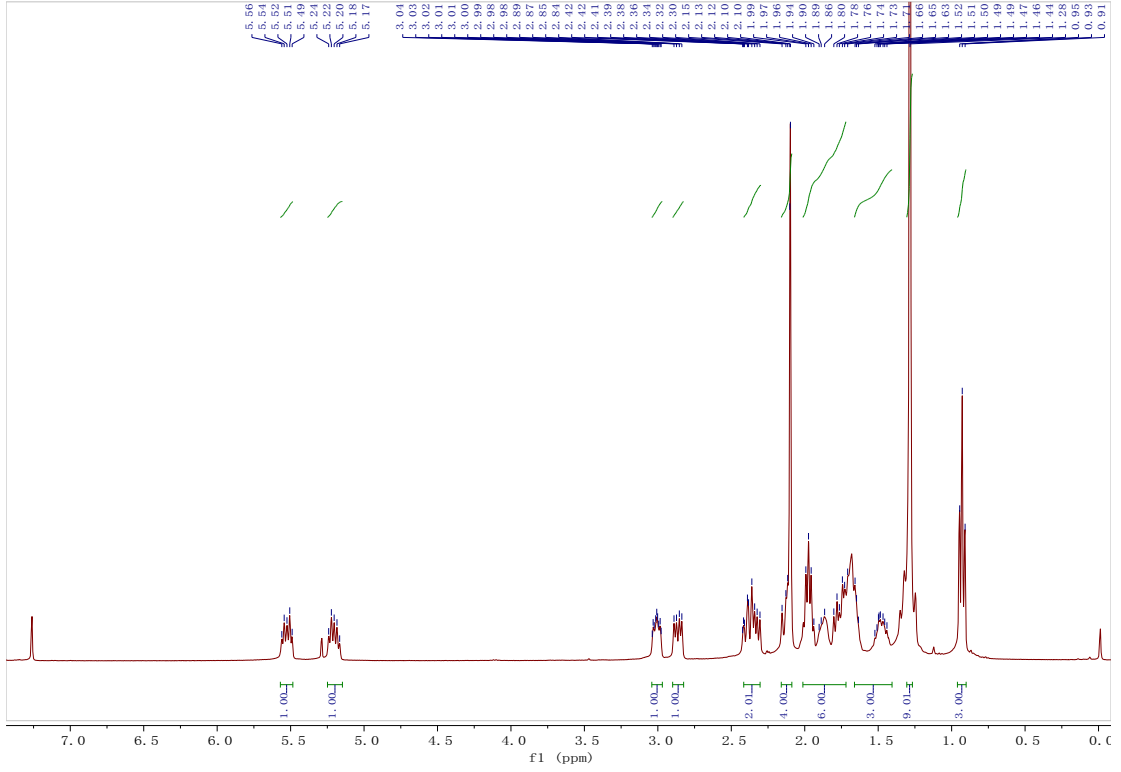
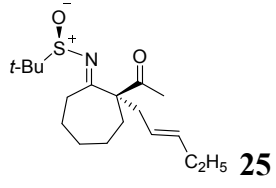


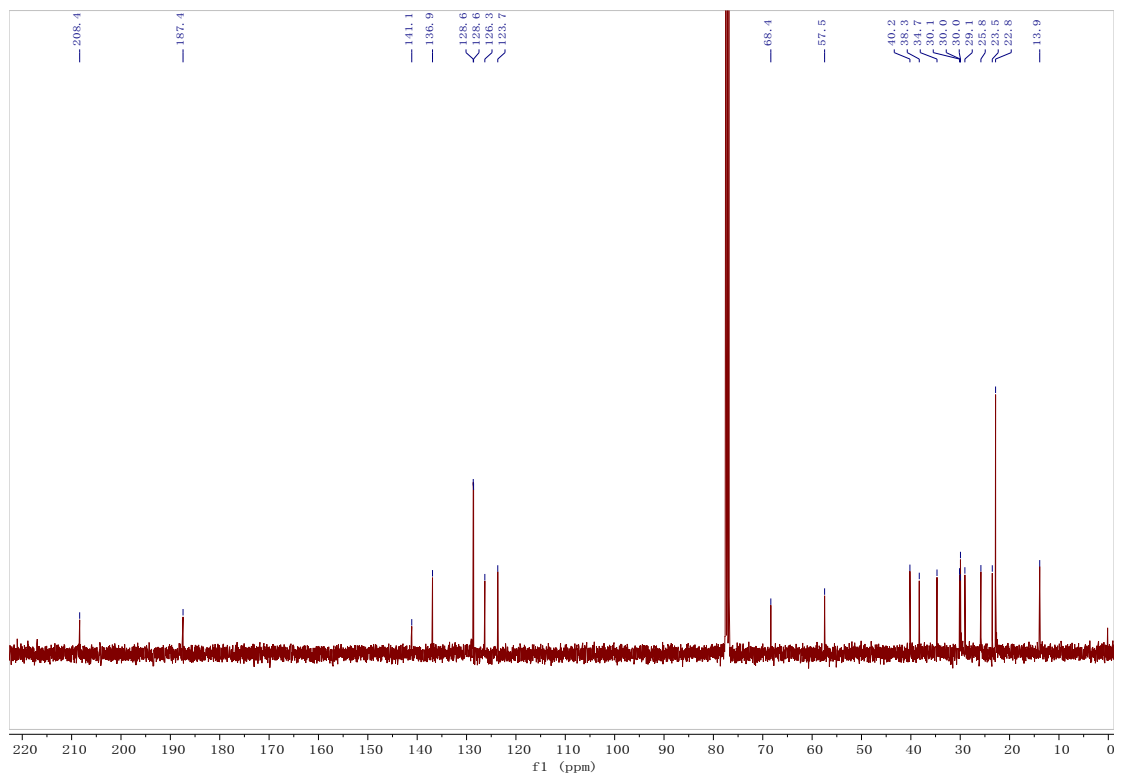
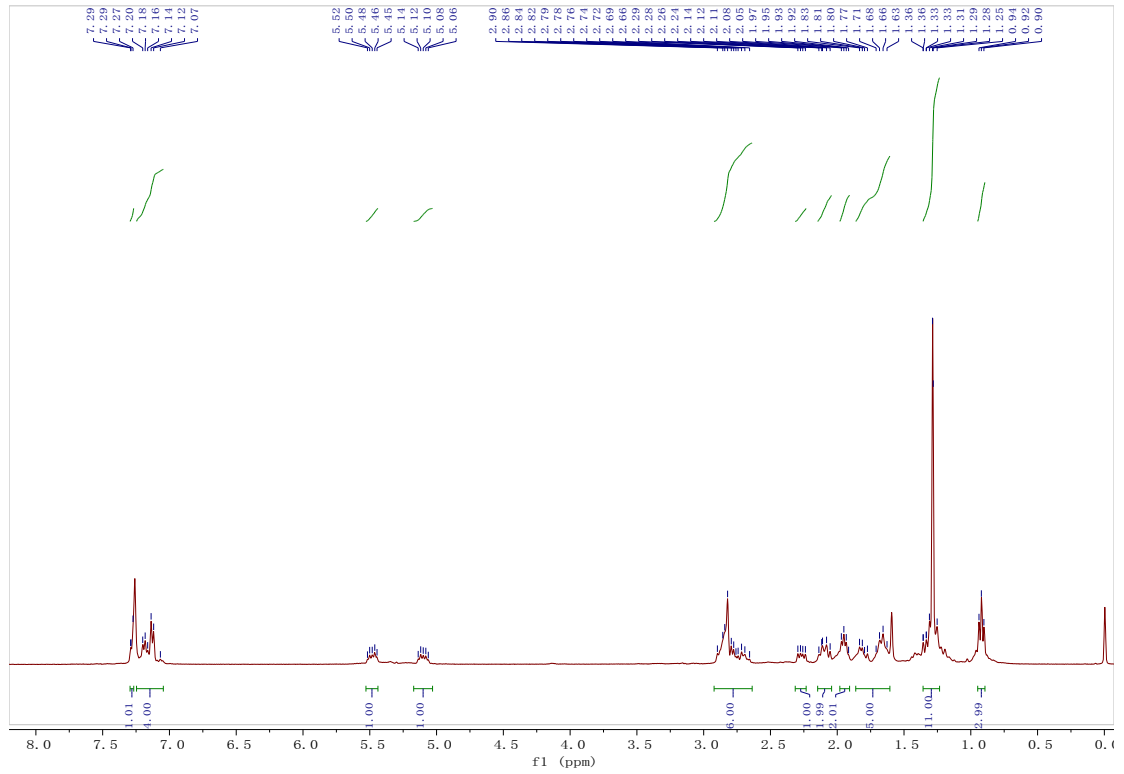
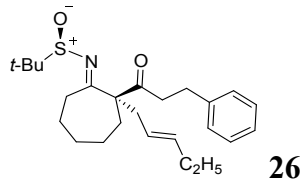


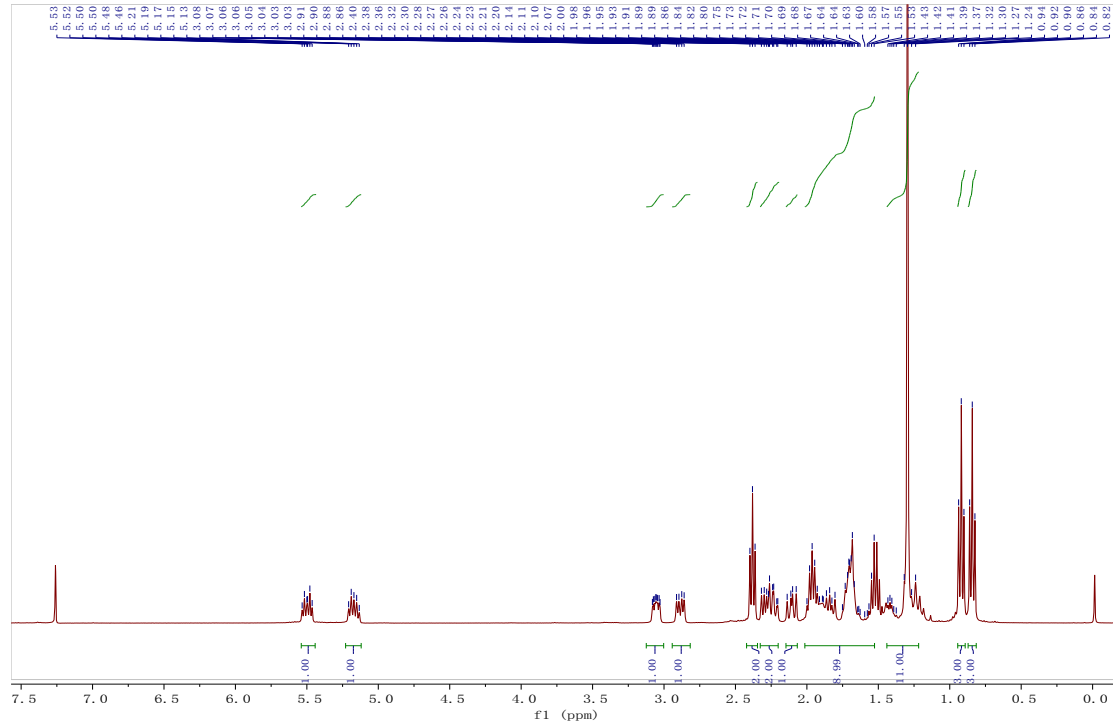
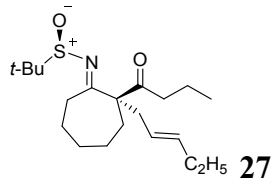












— 209.35

— 187.76

— 136.77

— 123.75

— 68.29

— 57.40

— 40.29

— 38.35

— 35.02

— 30.08

— 30.00

— 29.08

— 25.80

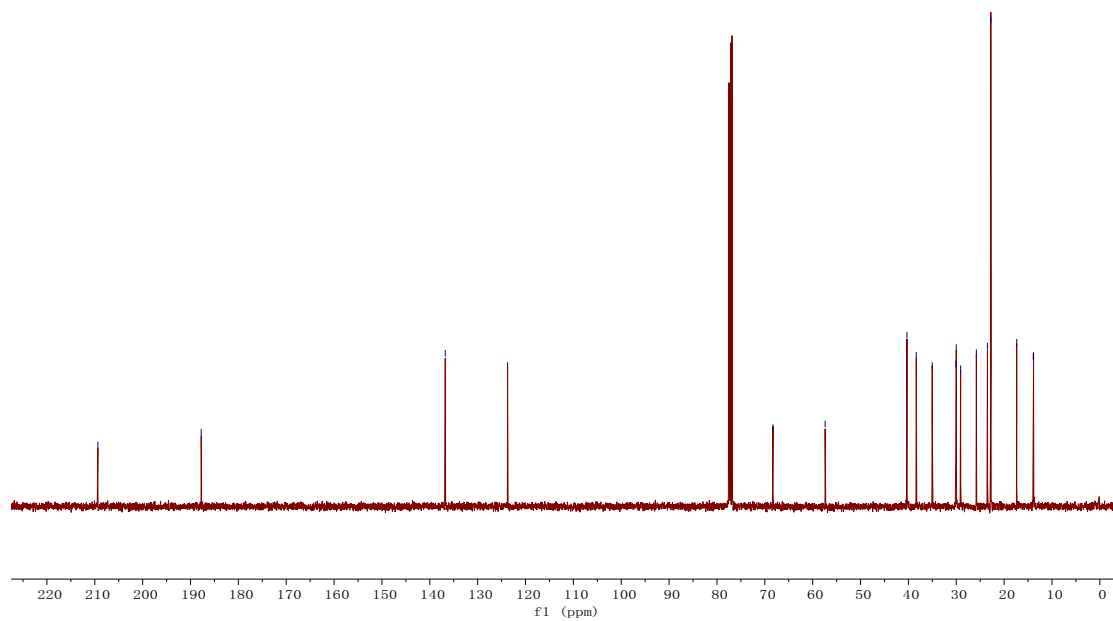
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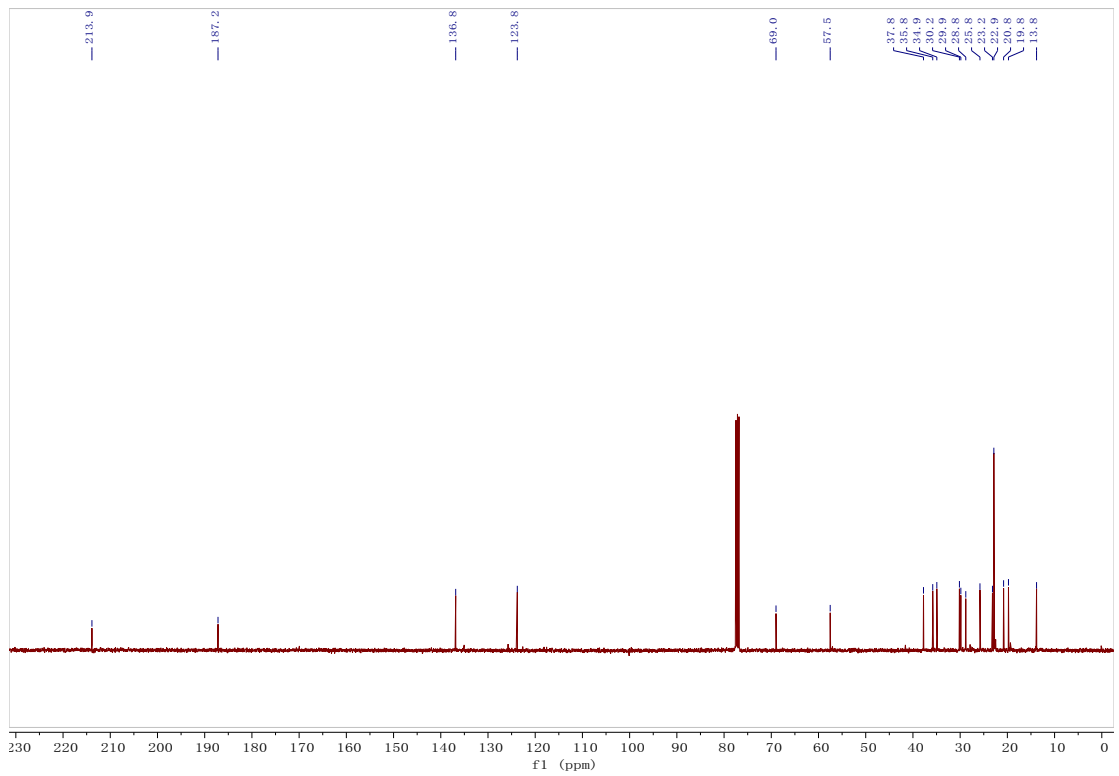
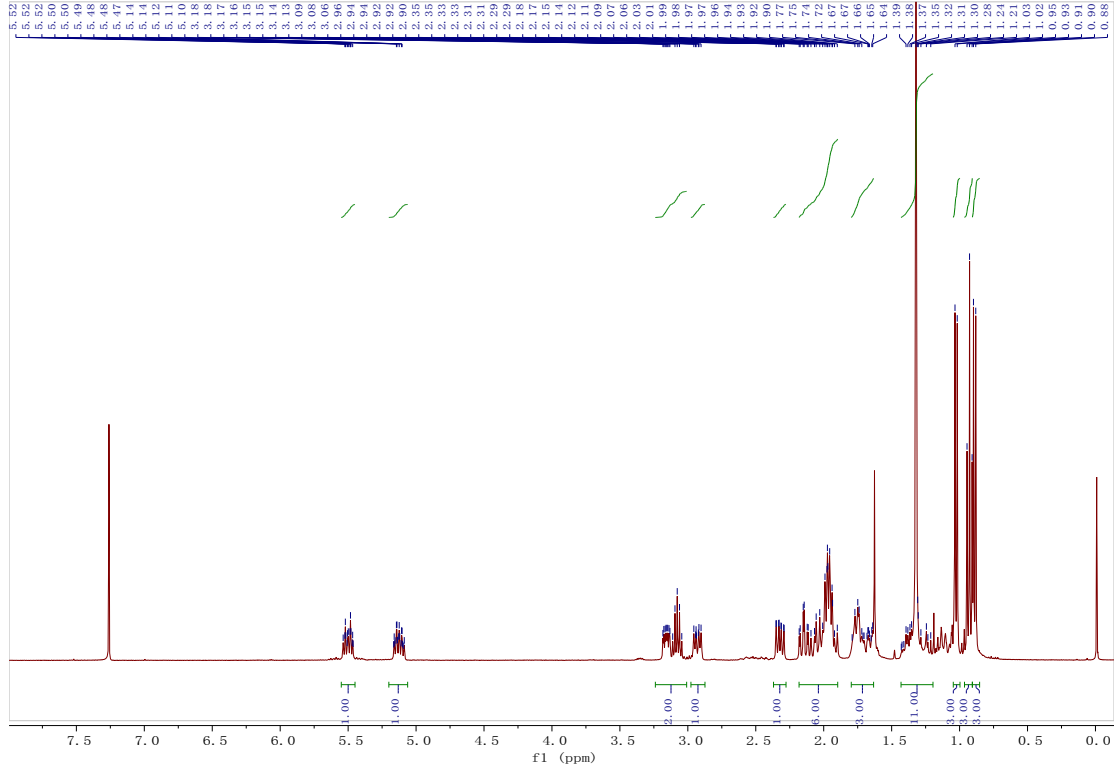
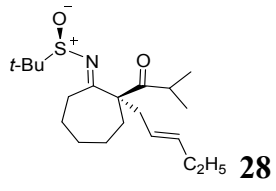
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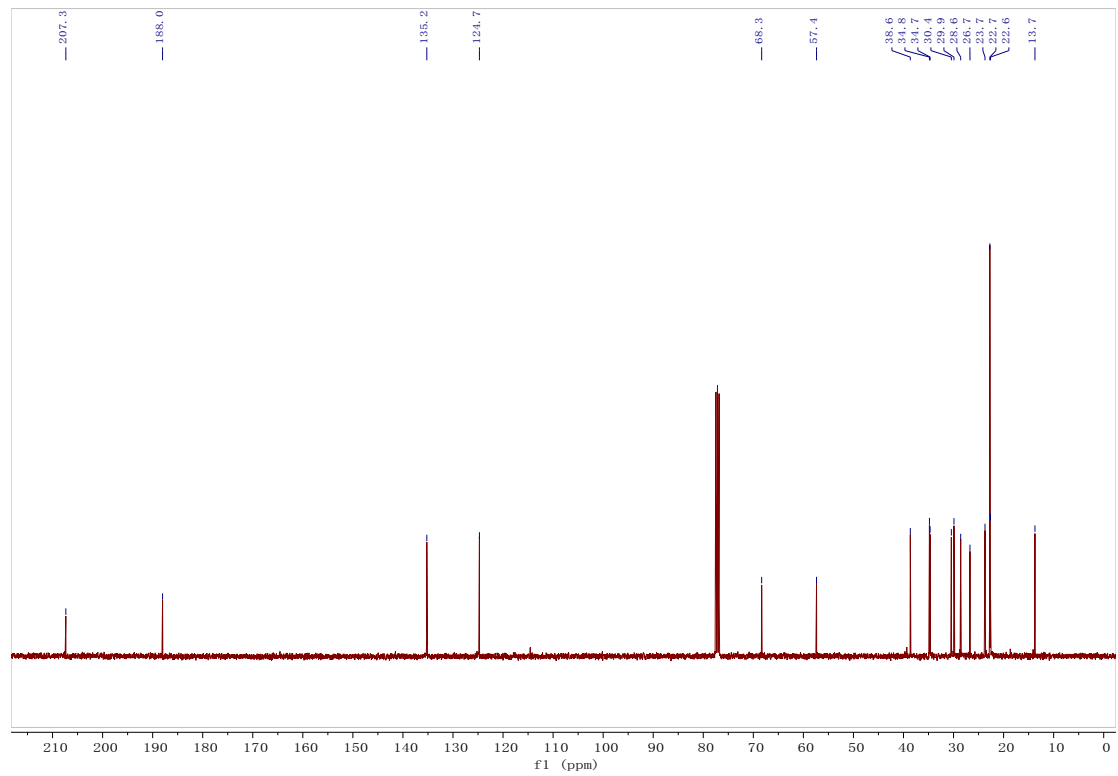
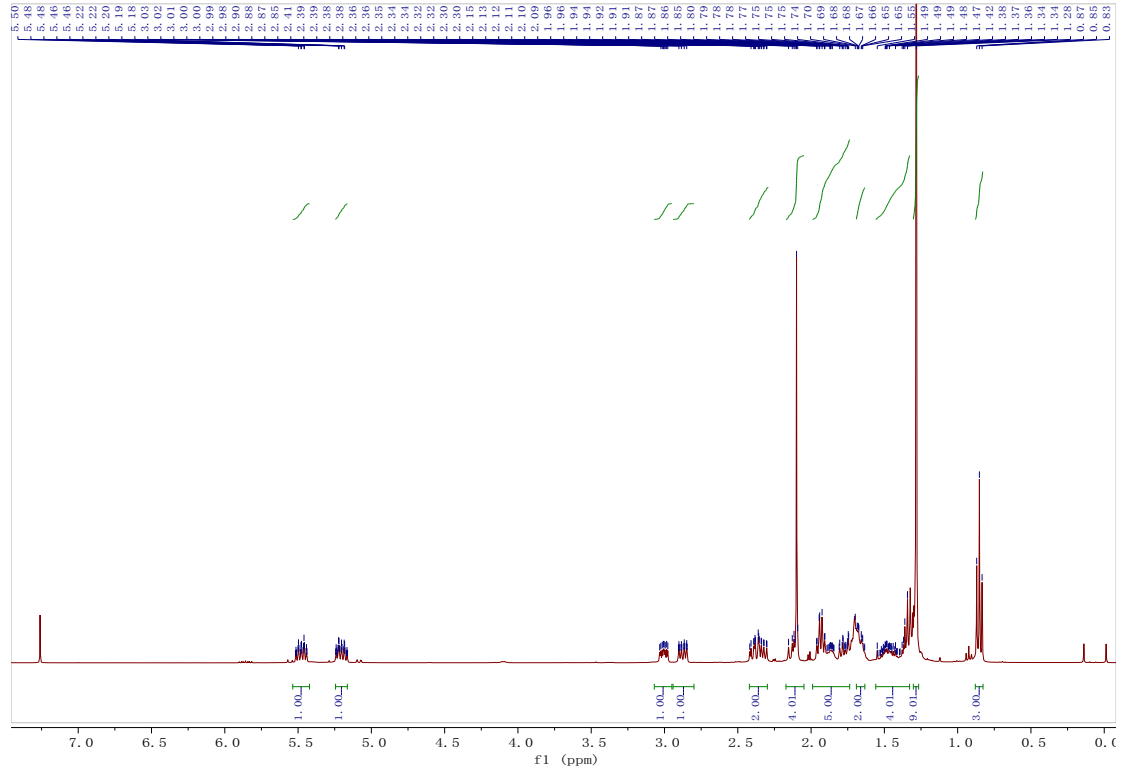
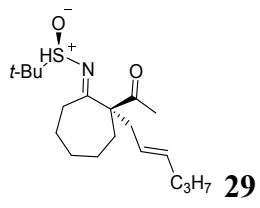
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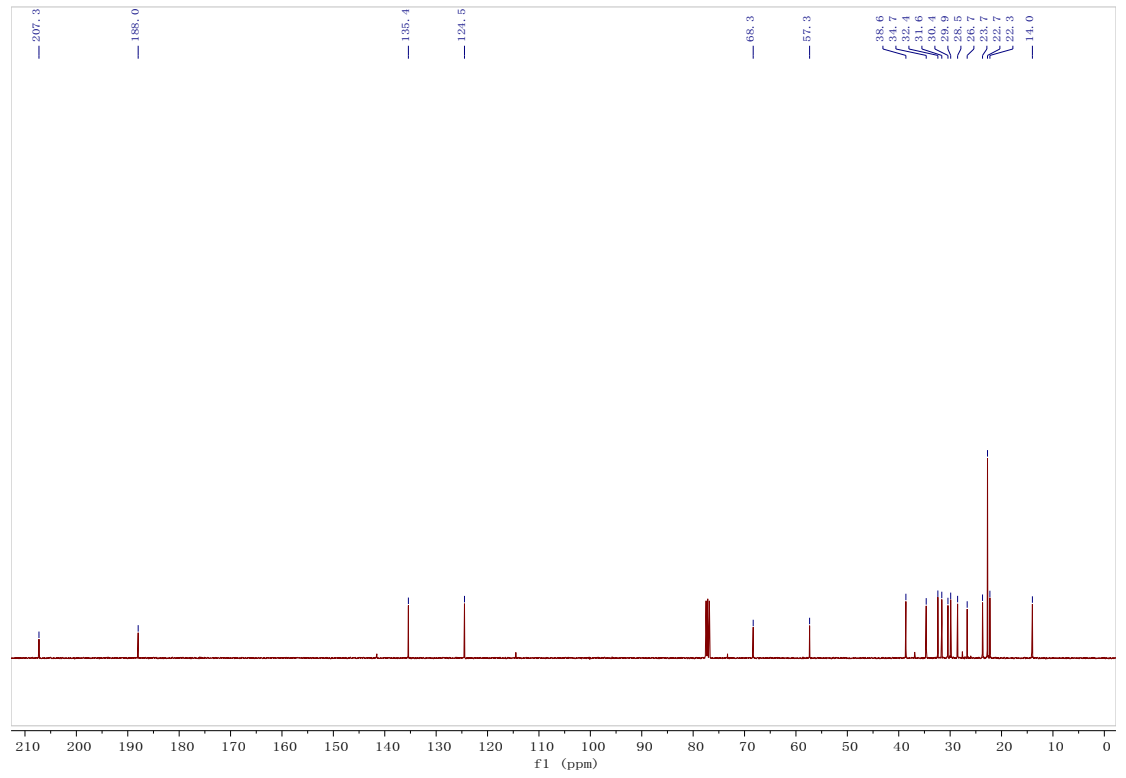
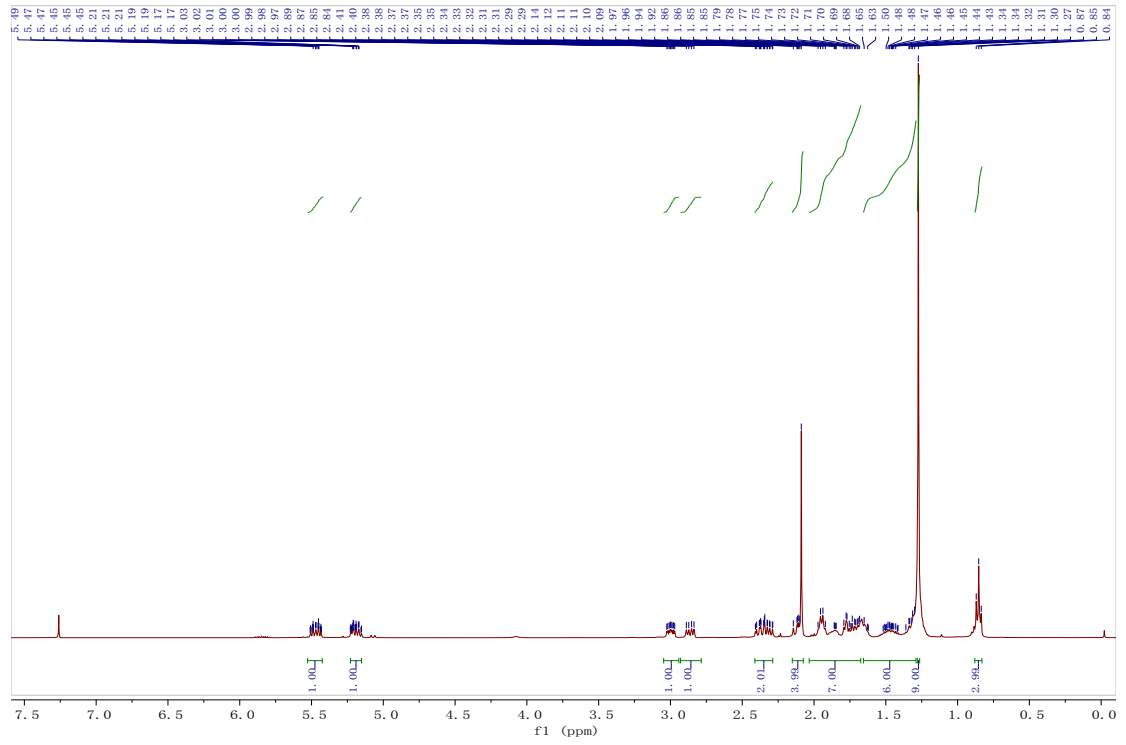
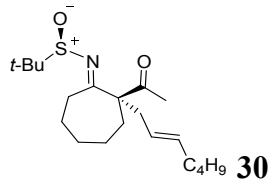
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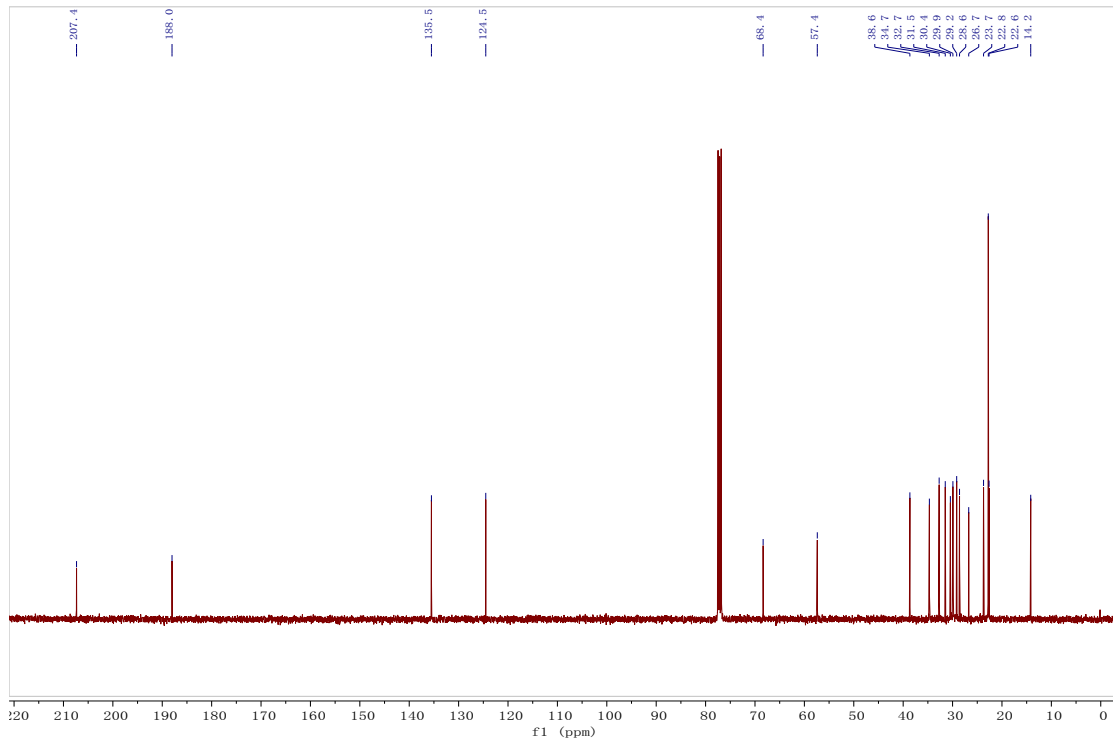
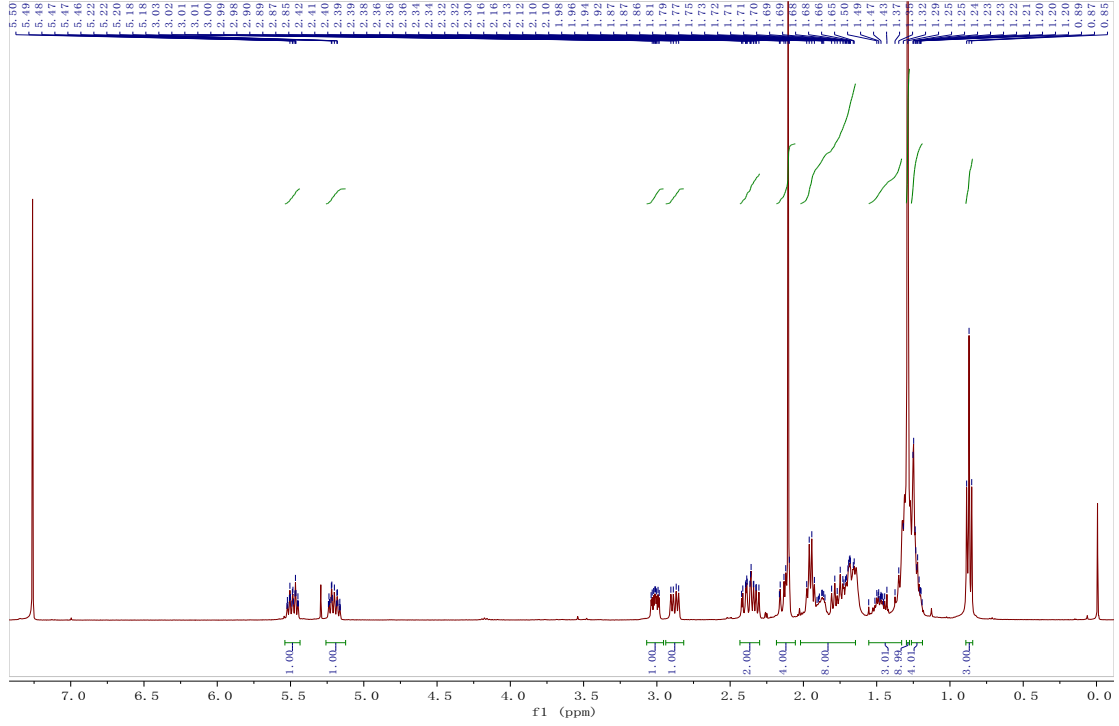
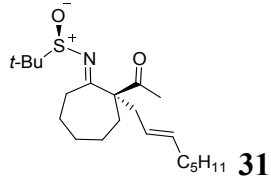
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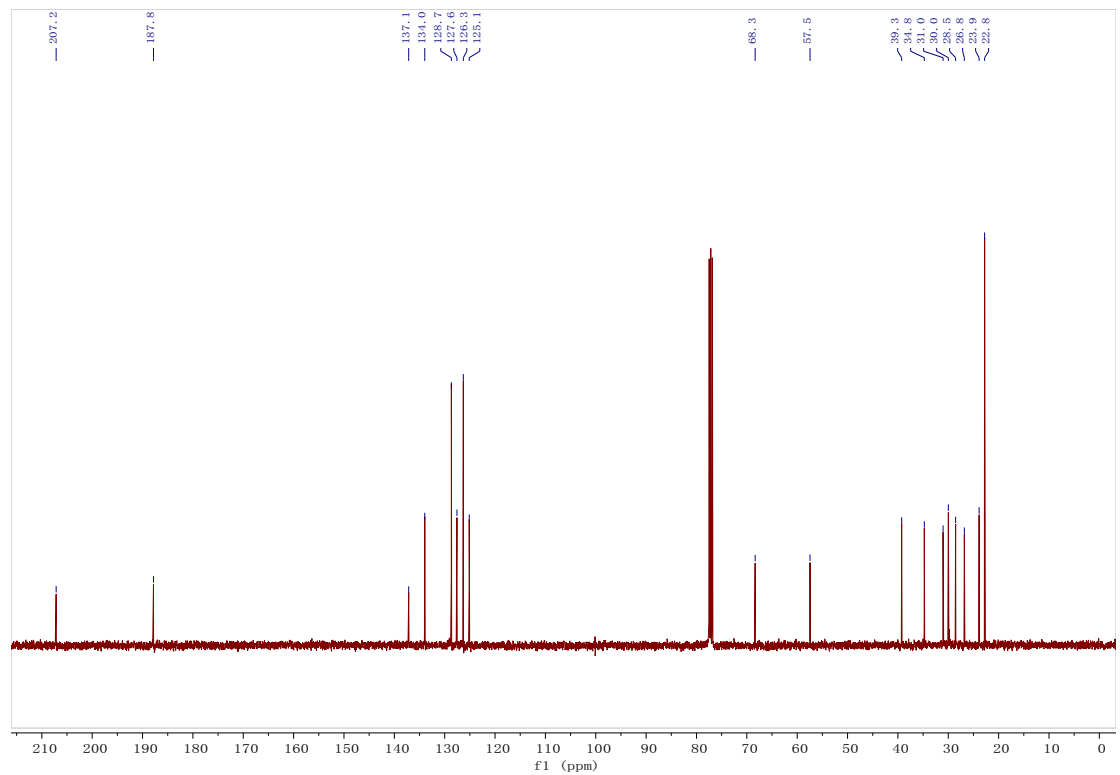
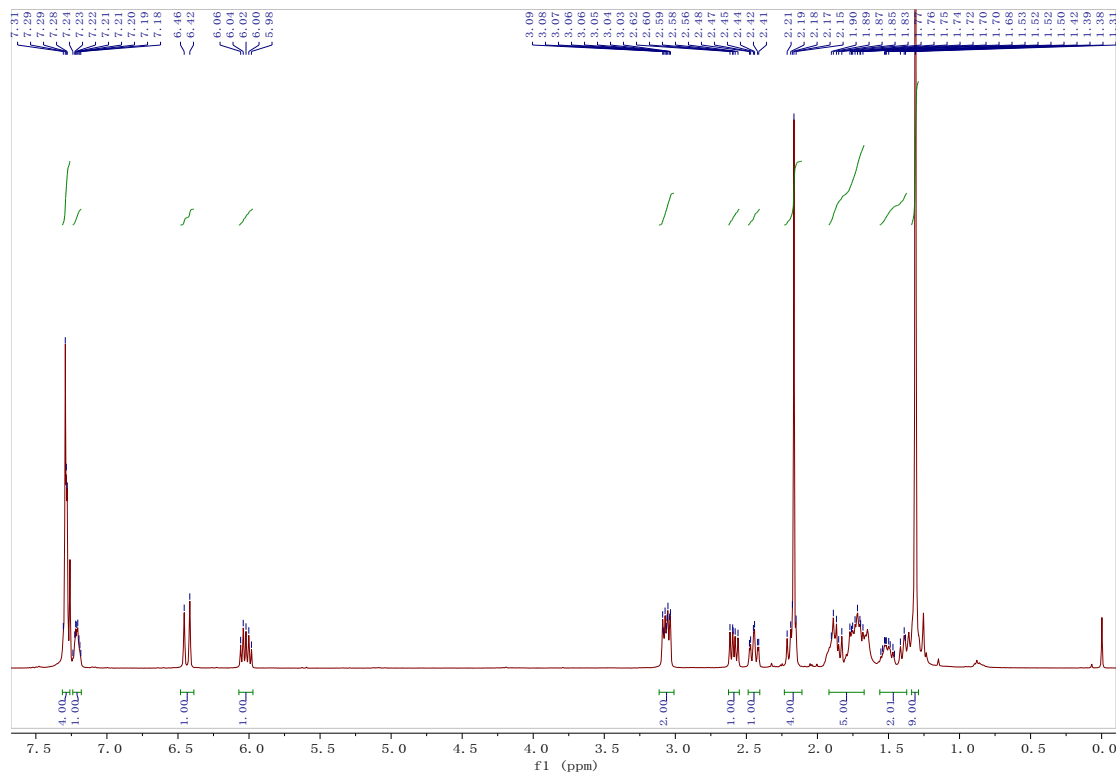
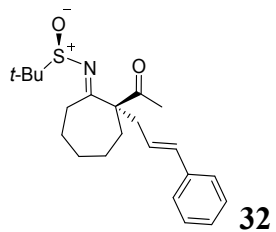


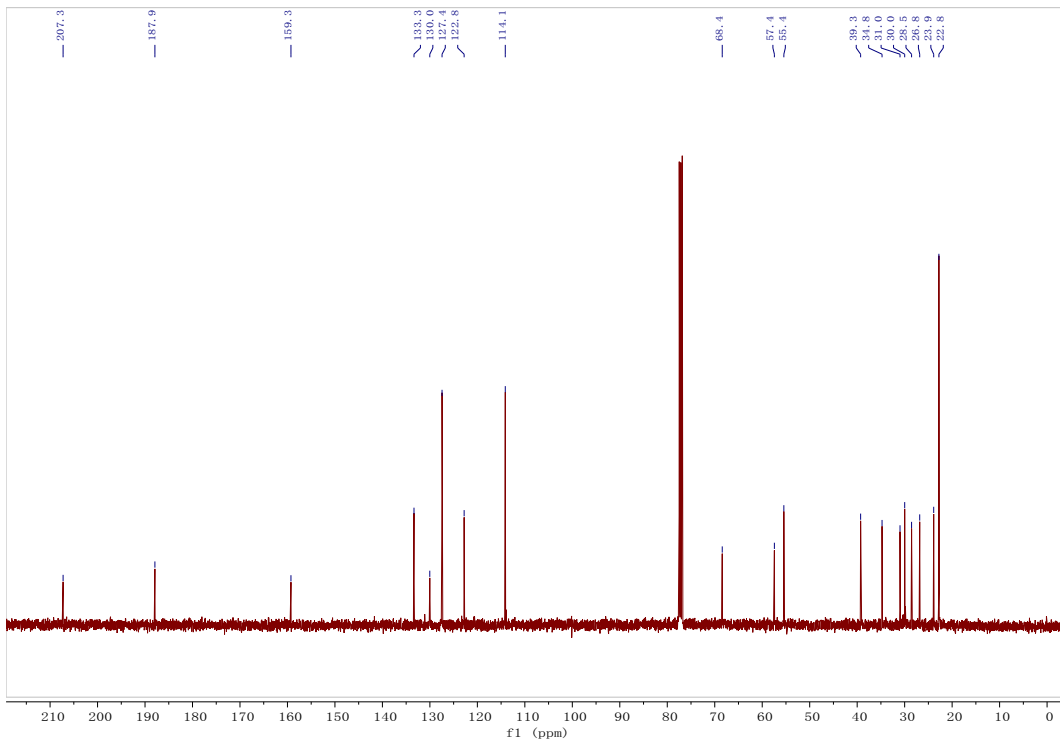
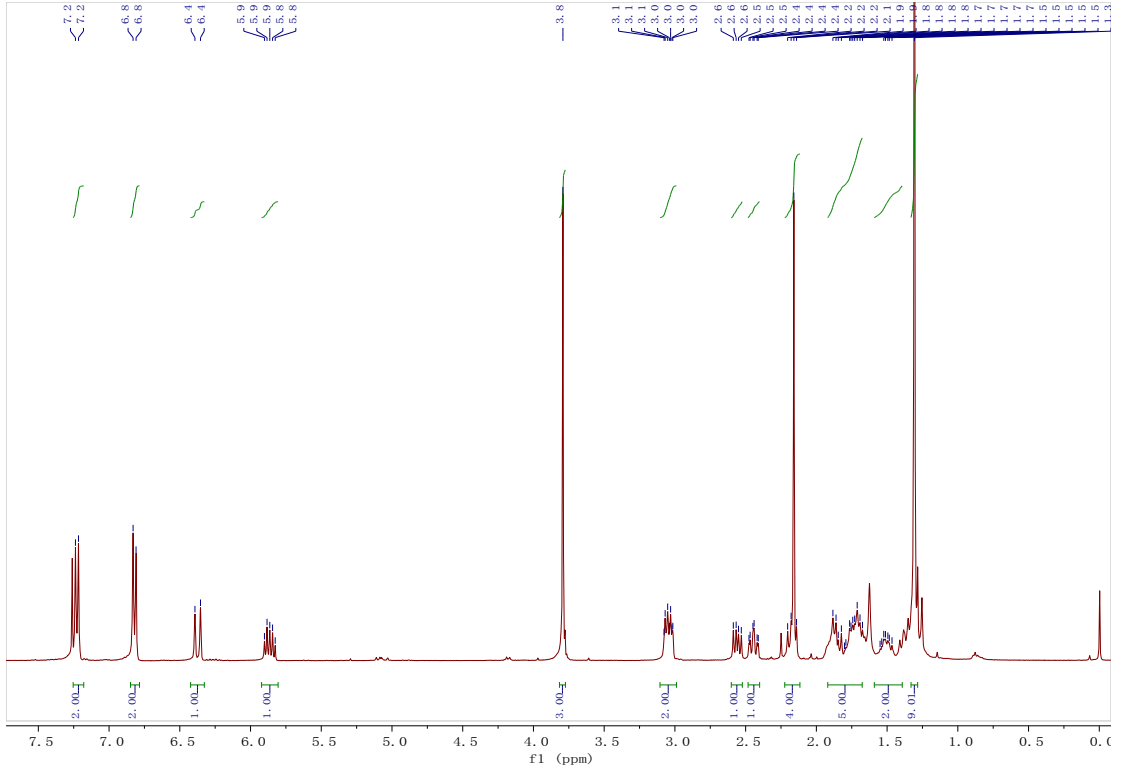
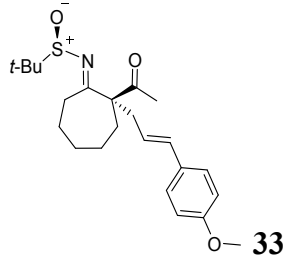


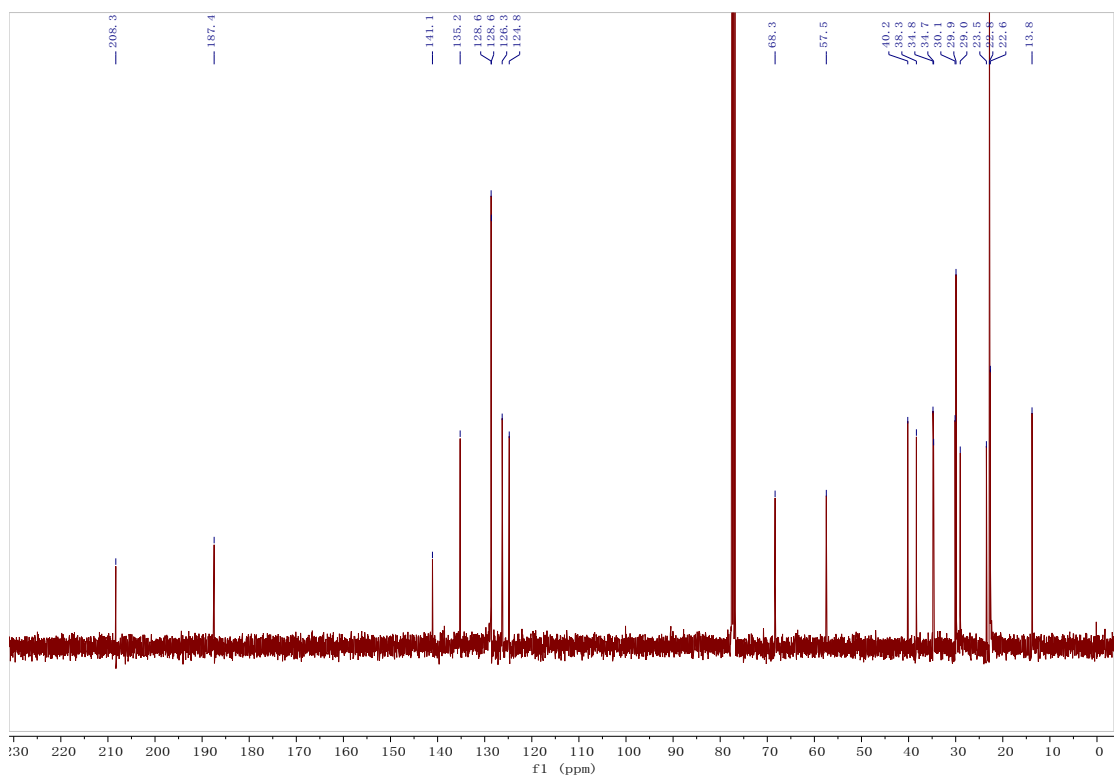
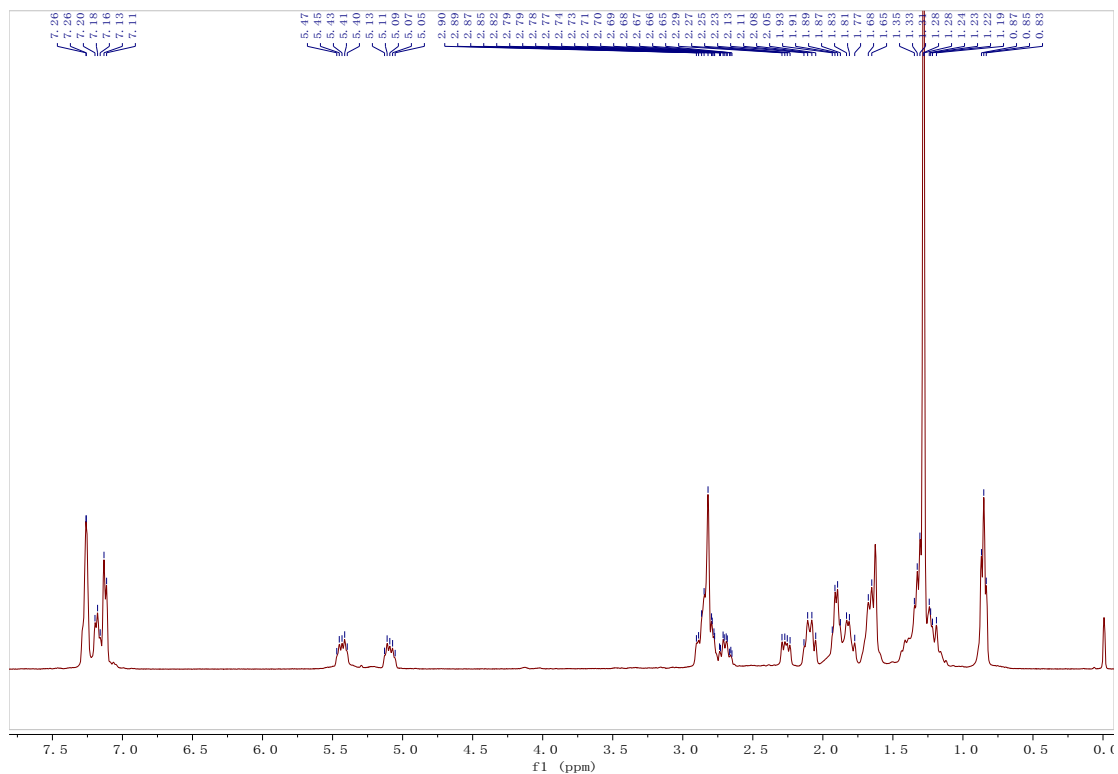
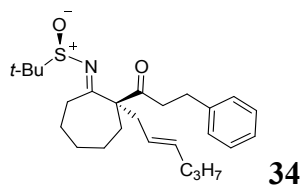


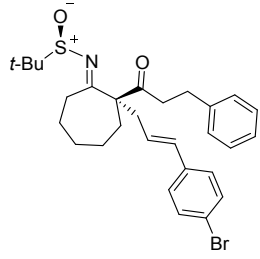




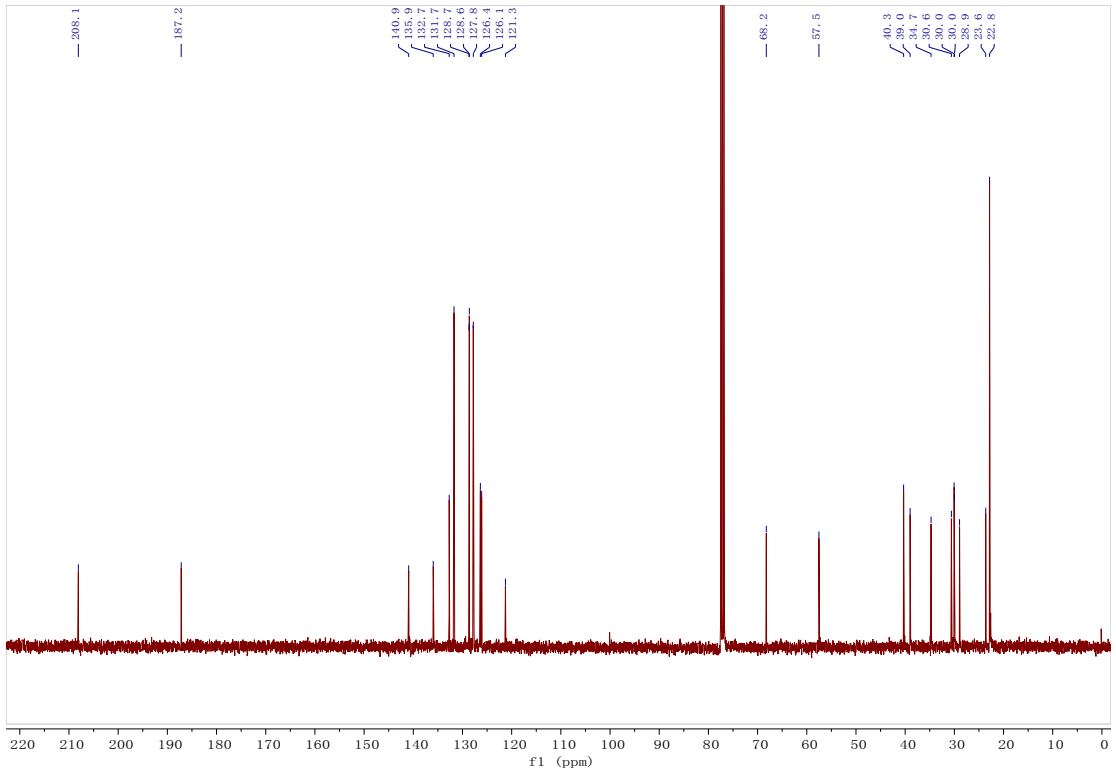
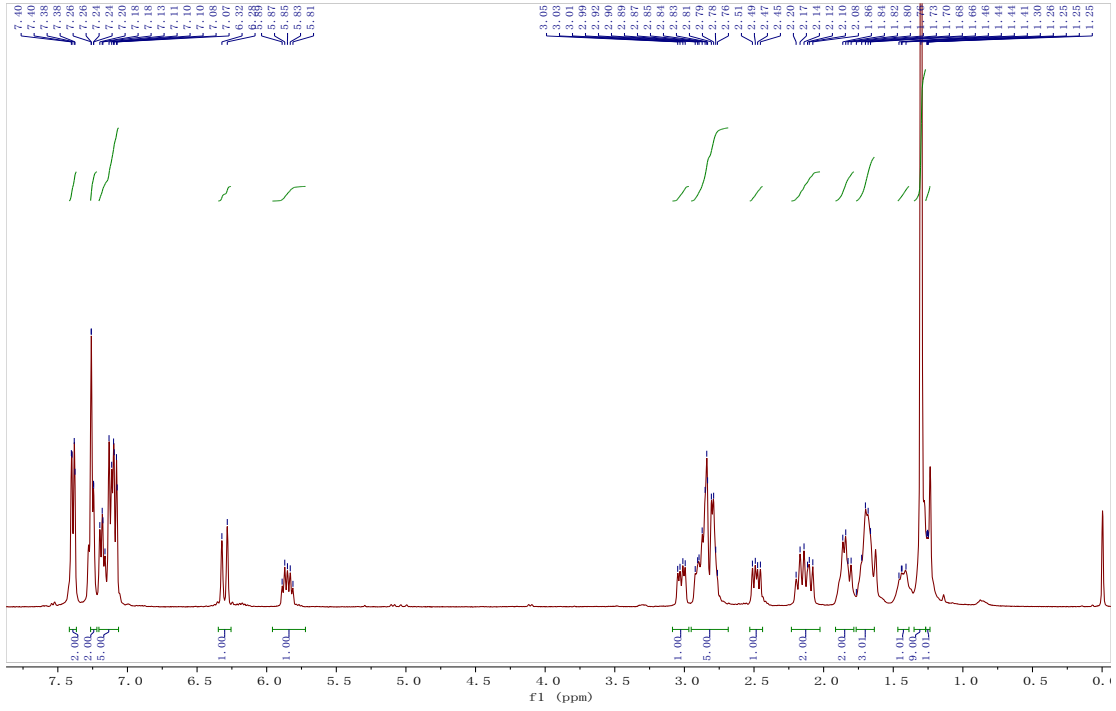


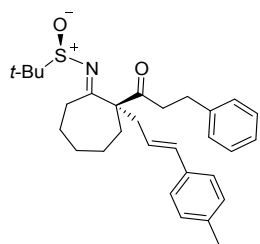




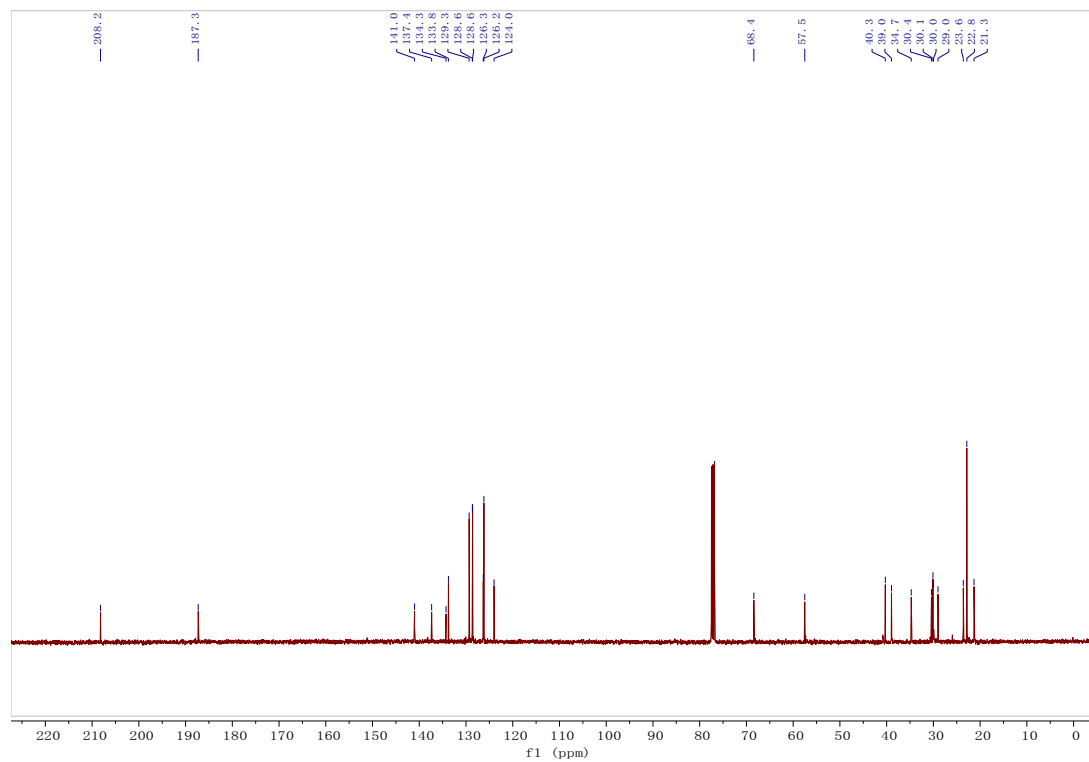
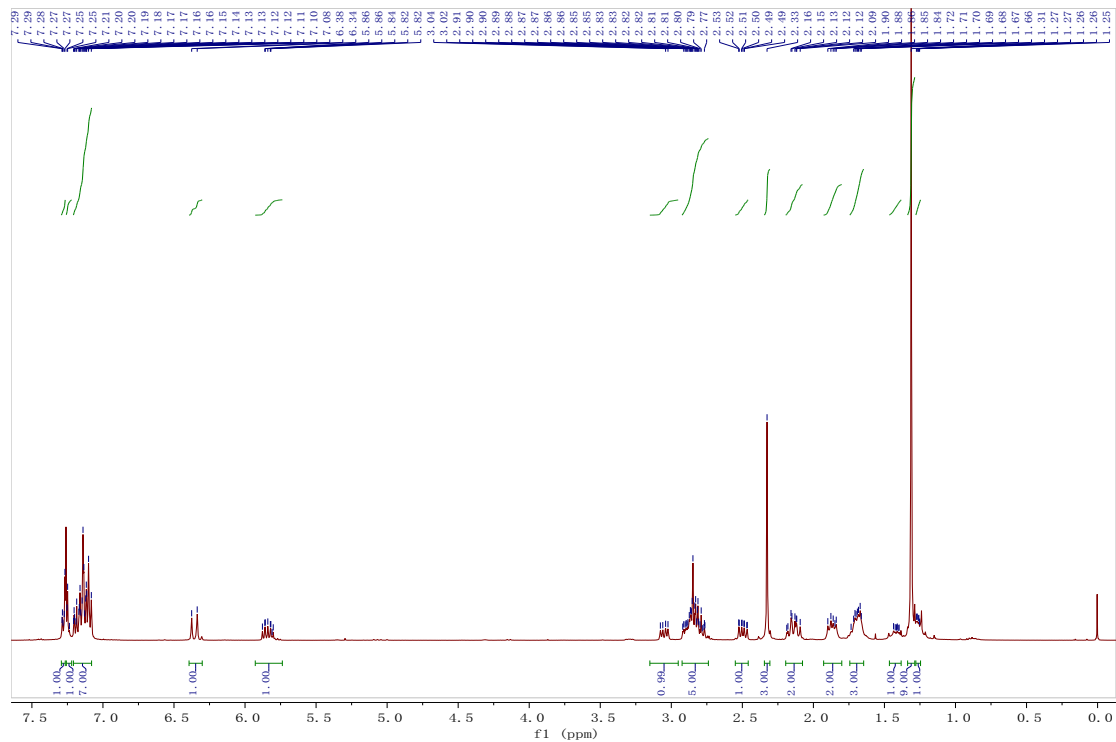


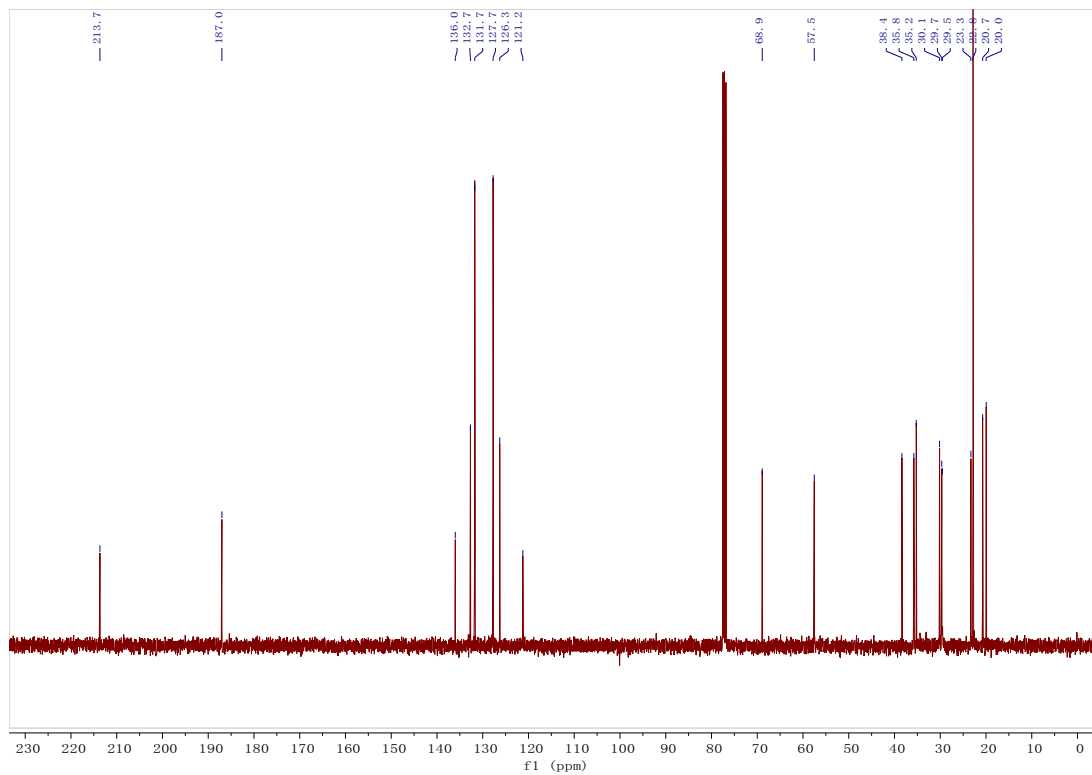
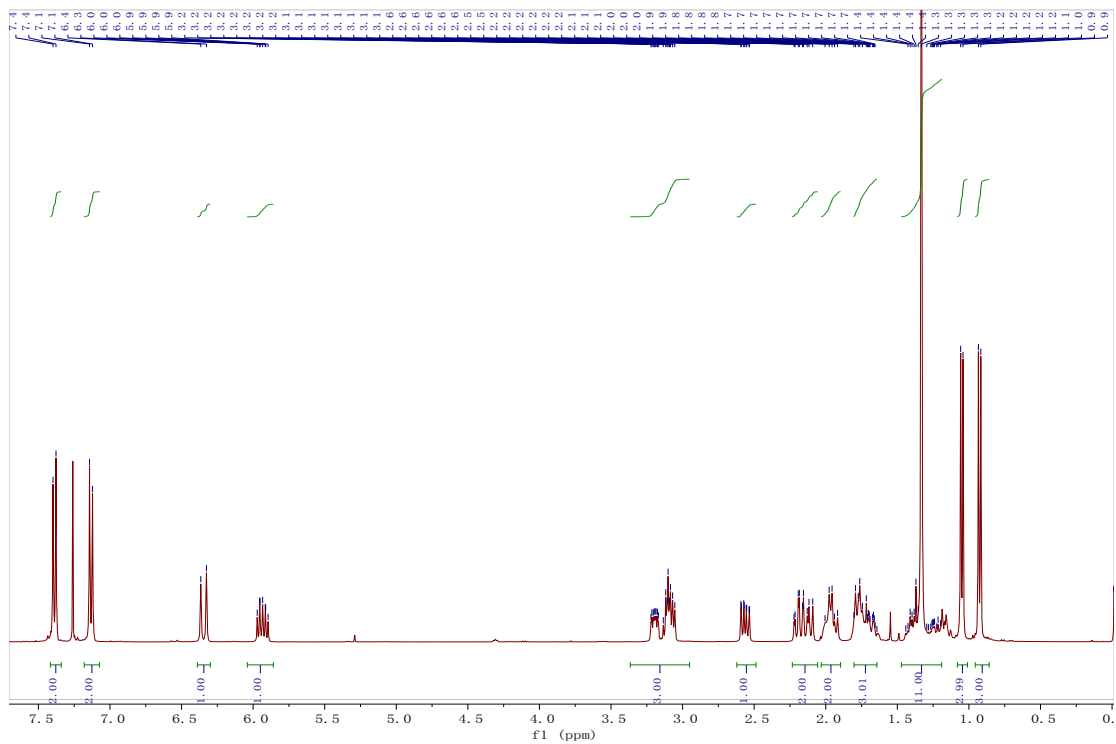
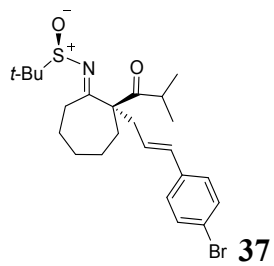
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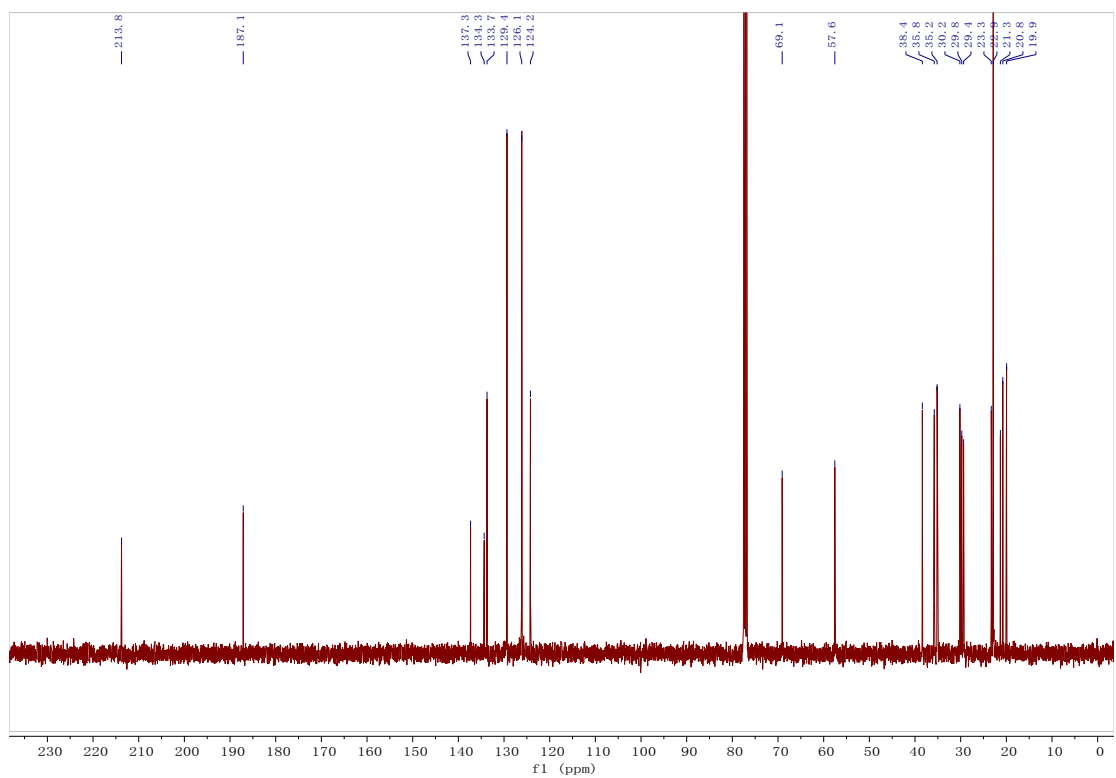
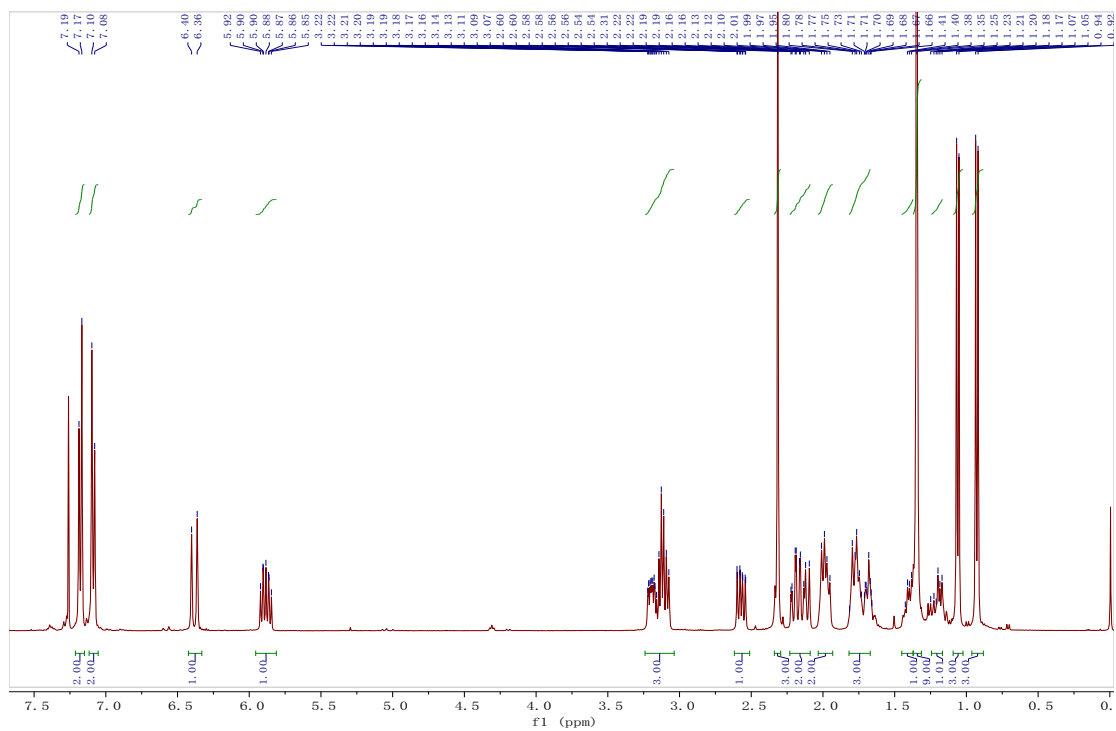
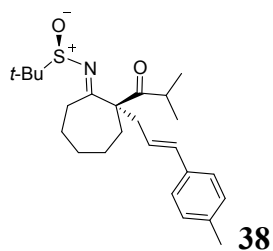


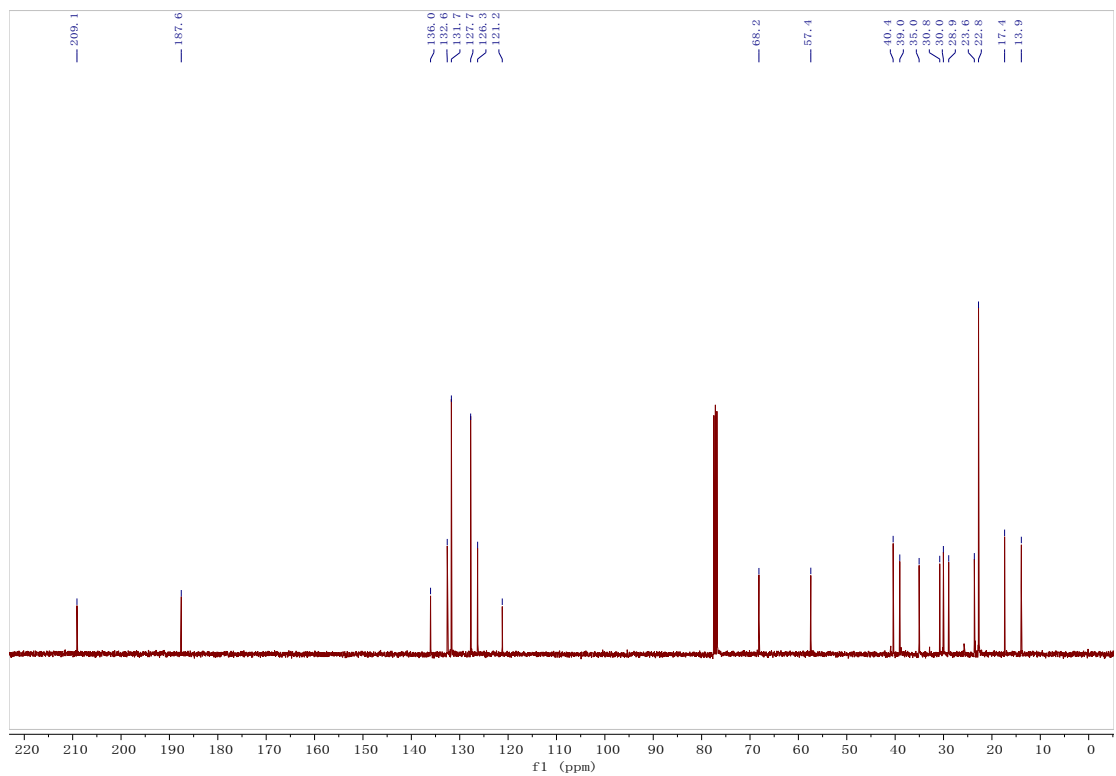
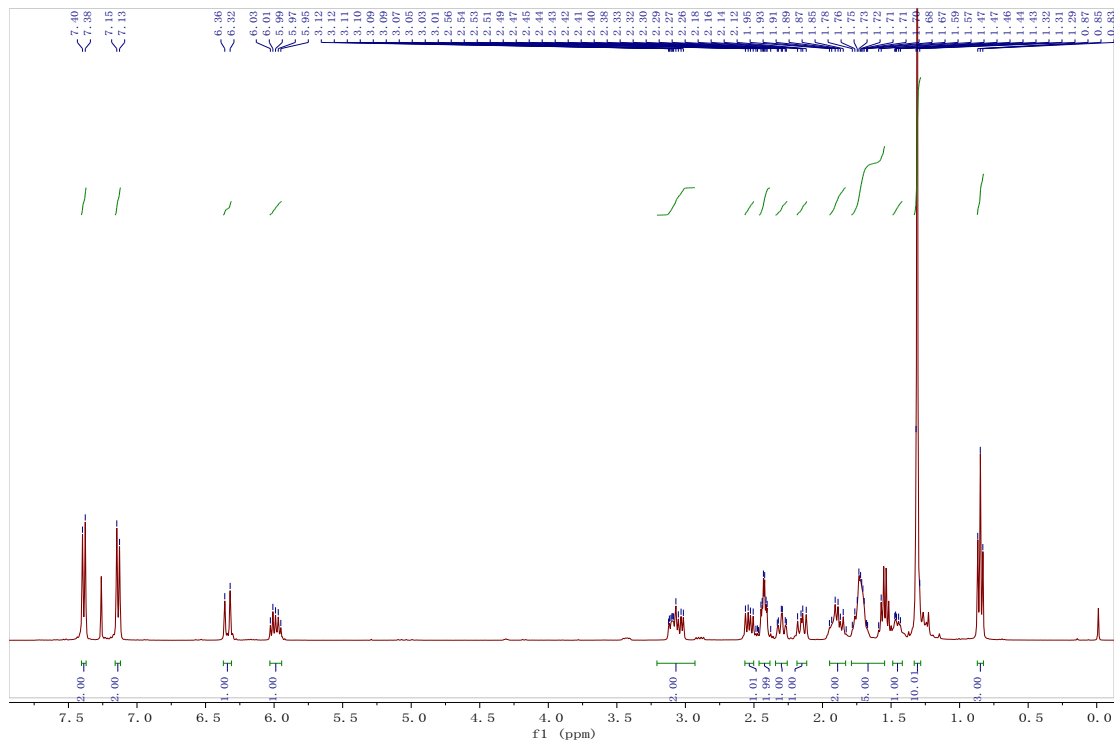
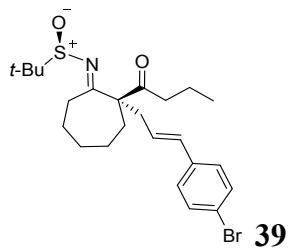


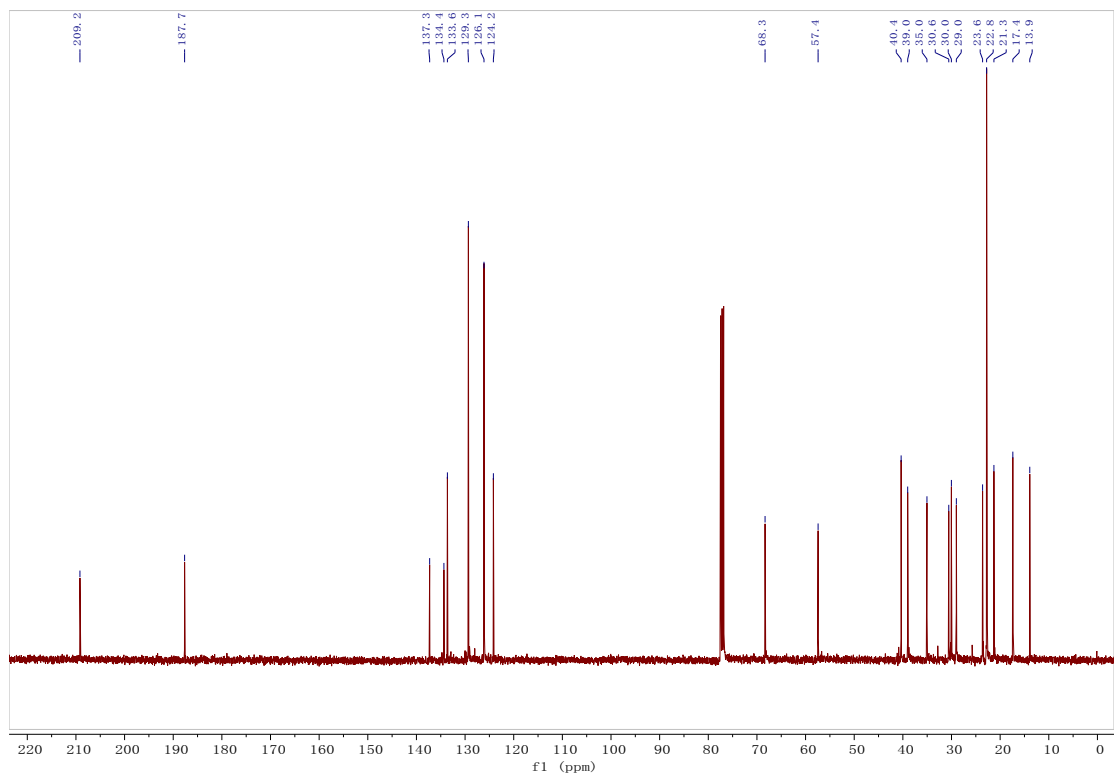
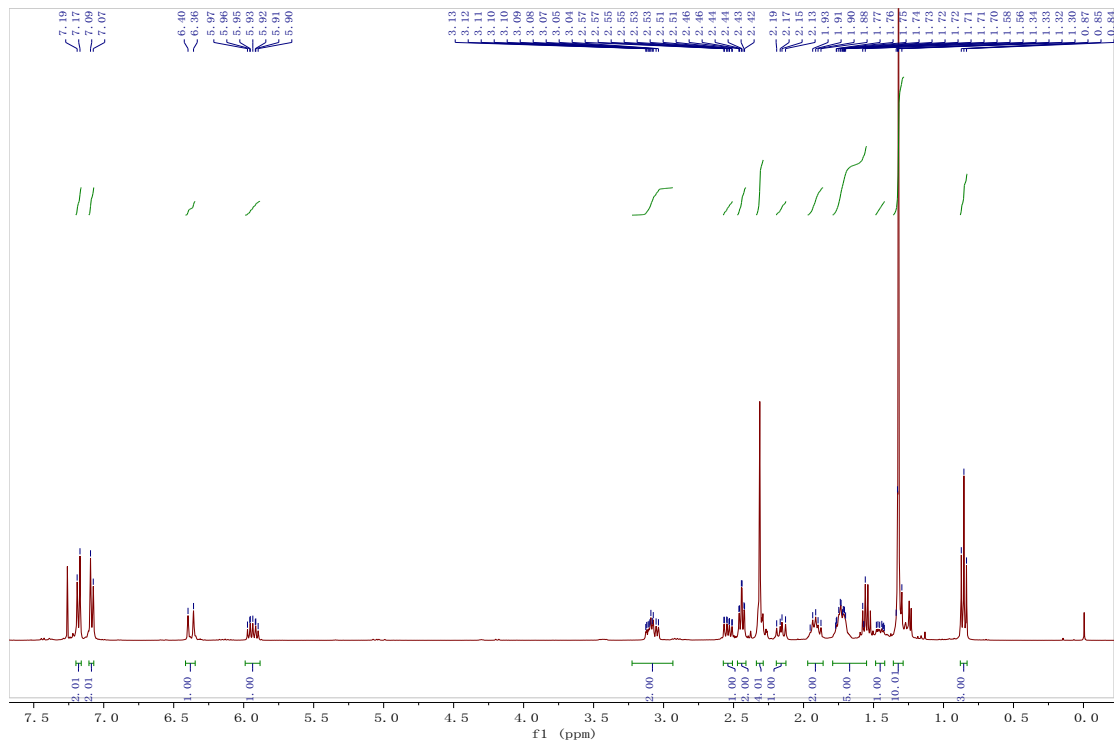
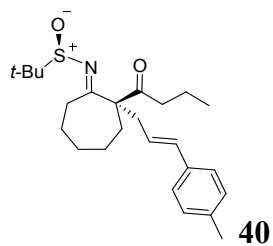
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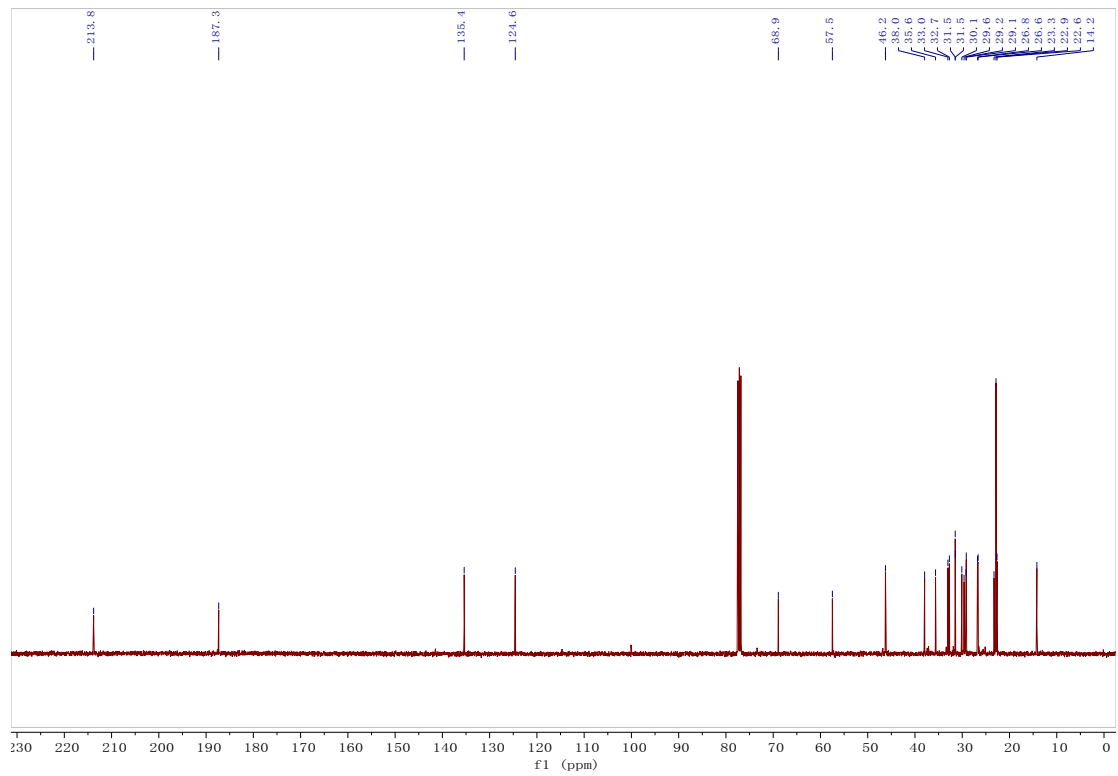
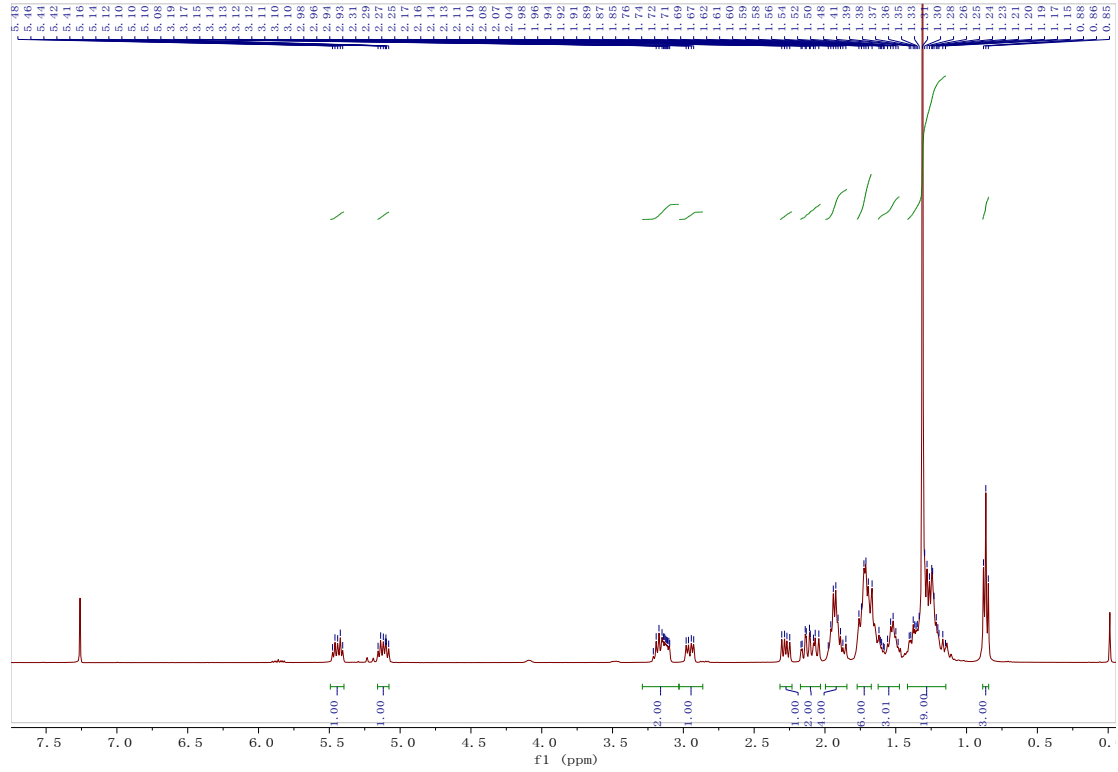
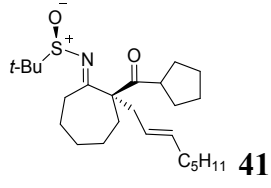


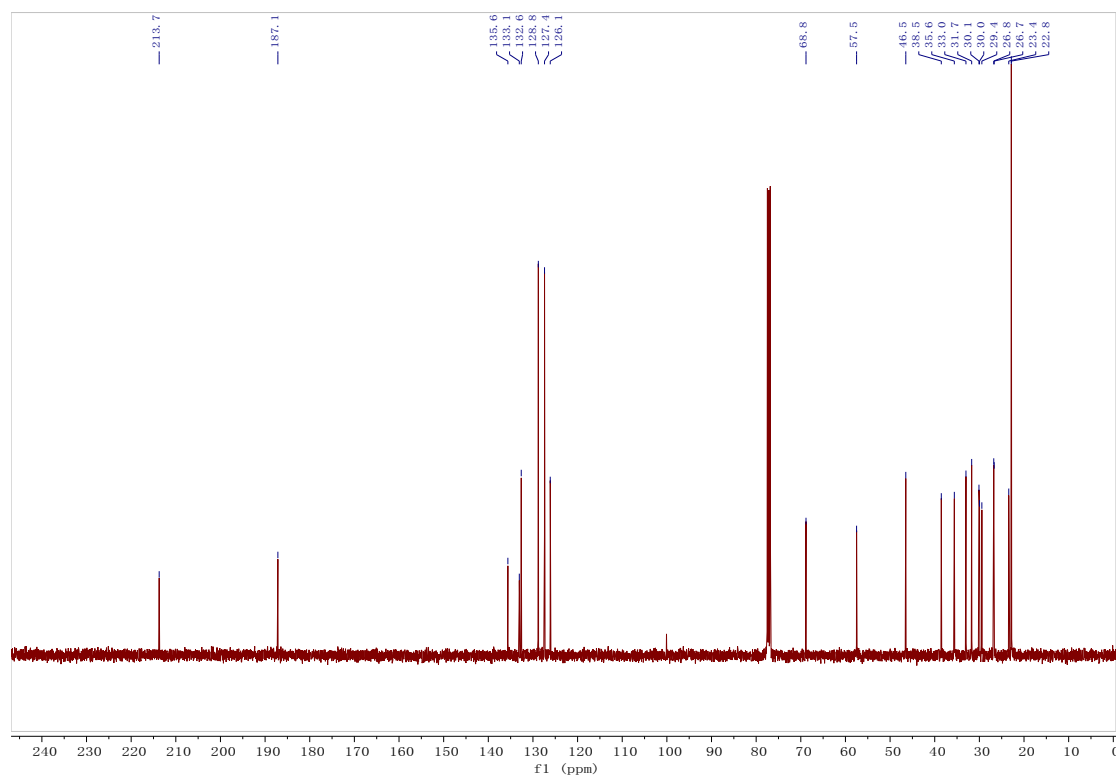
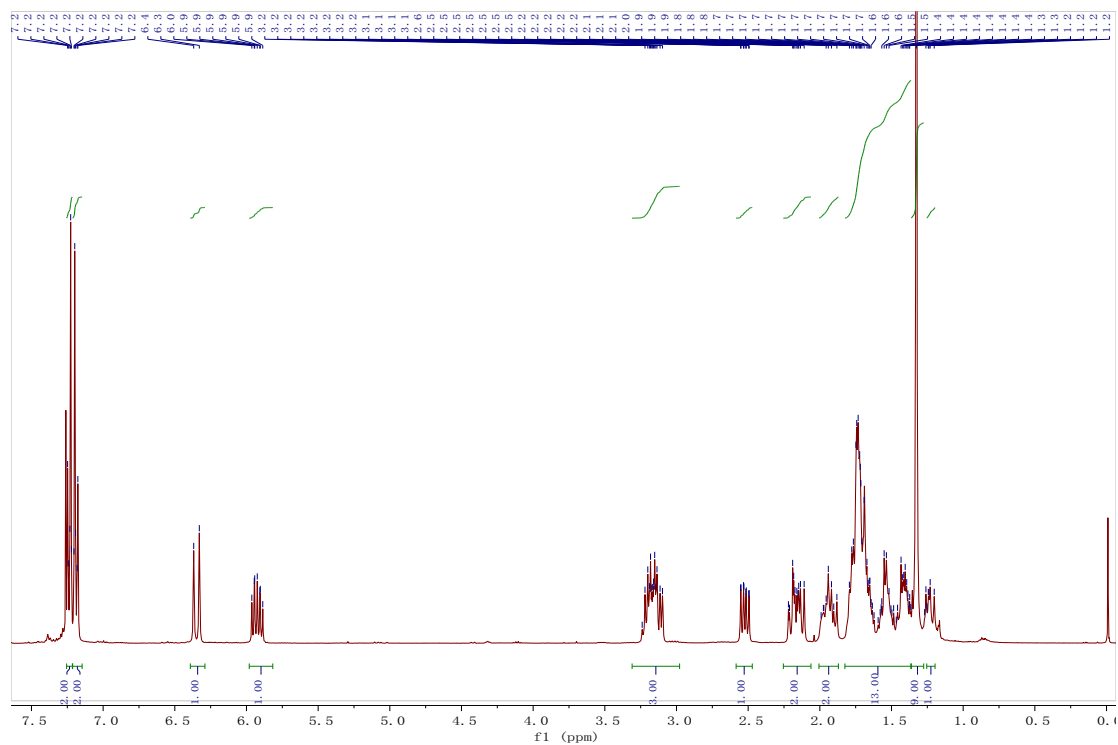
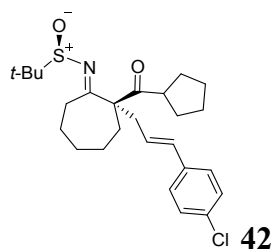


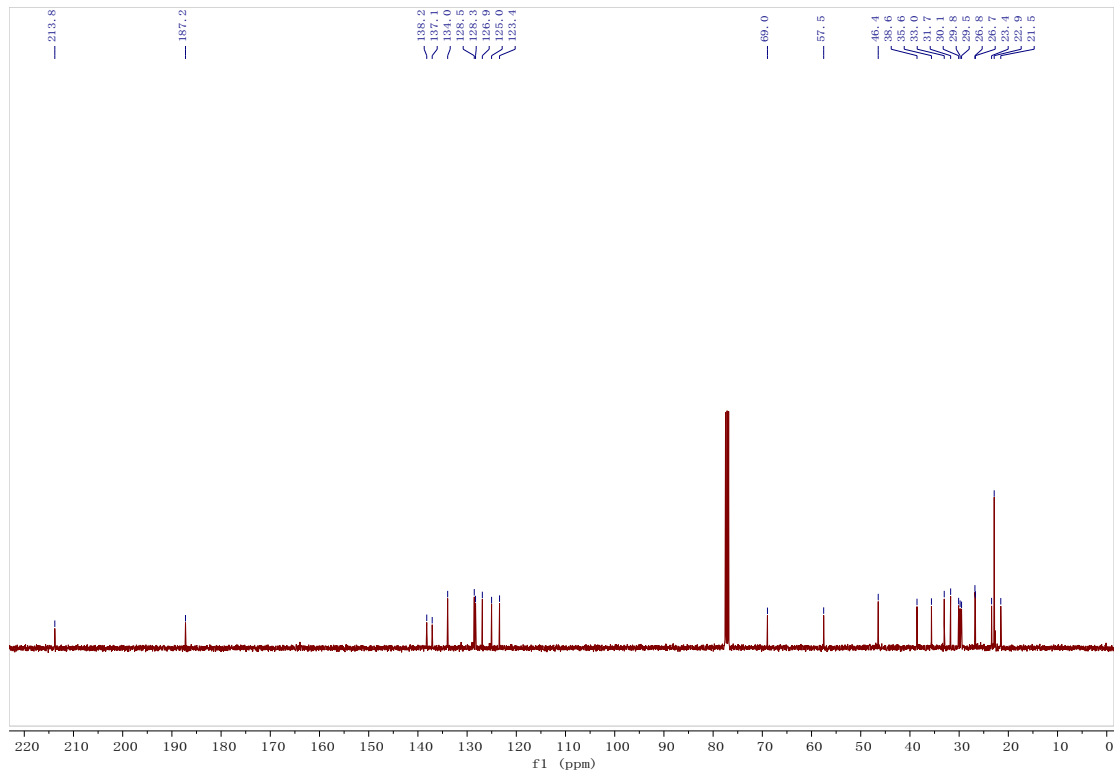
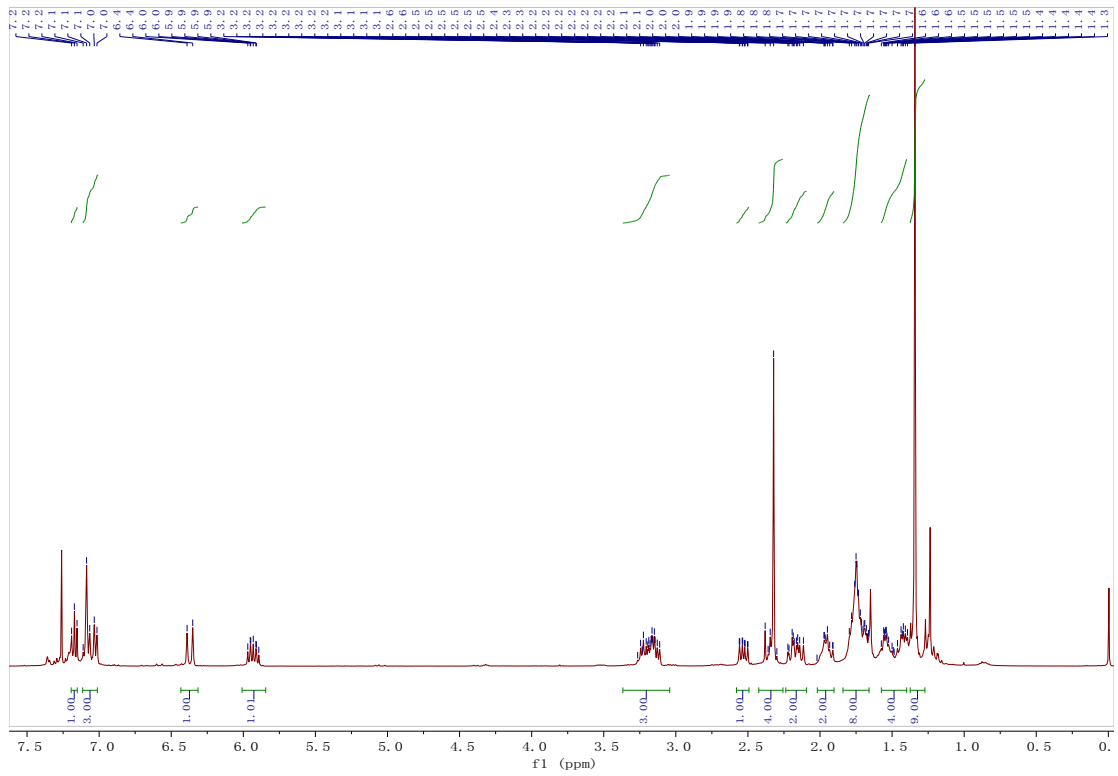
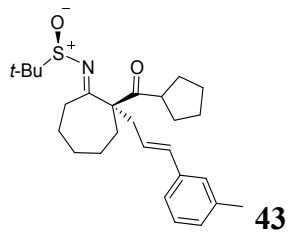


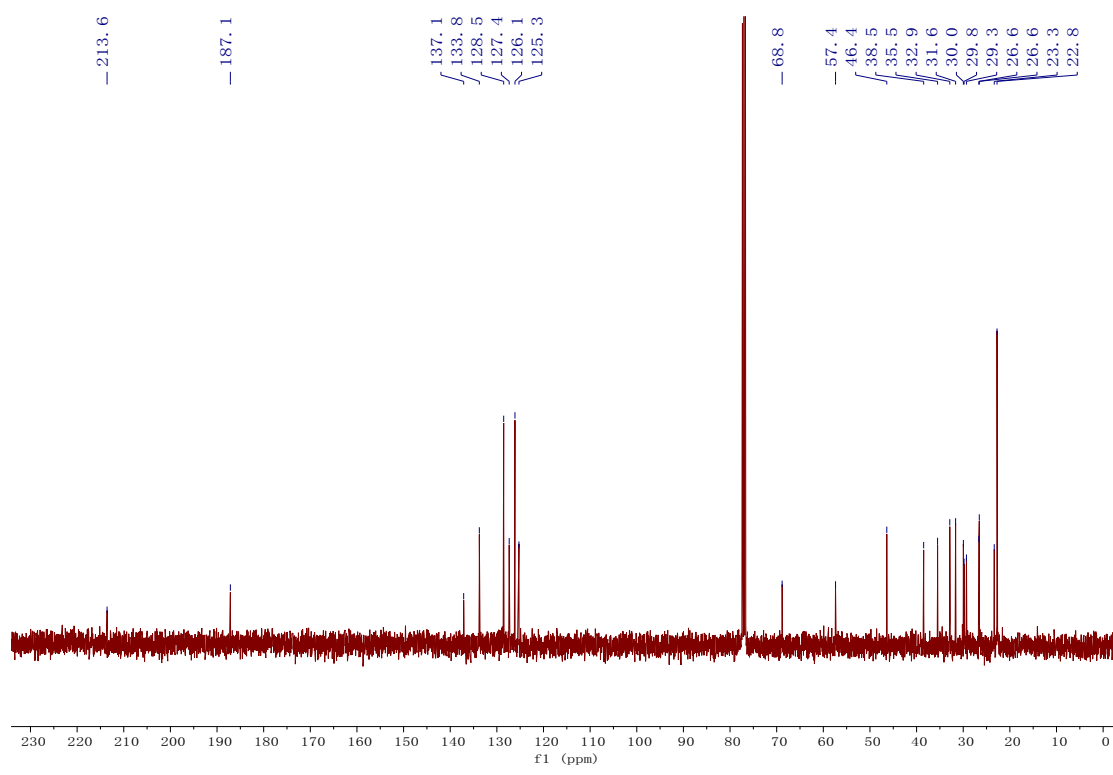
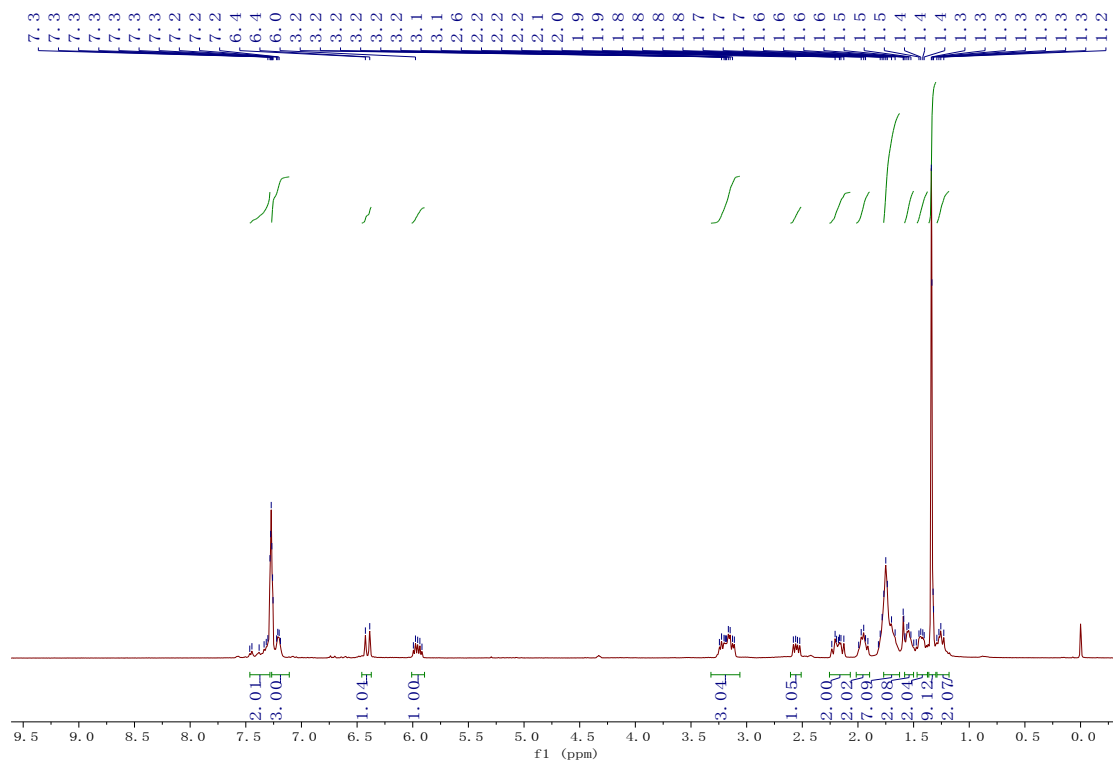
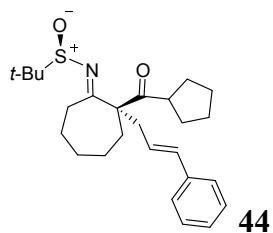


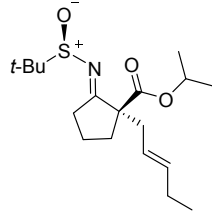




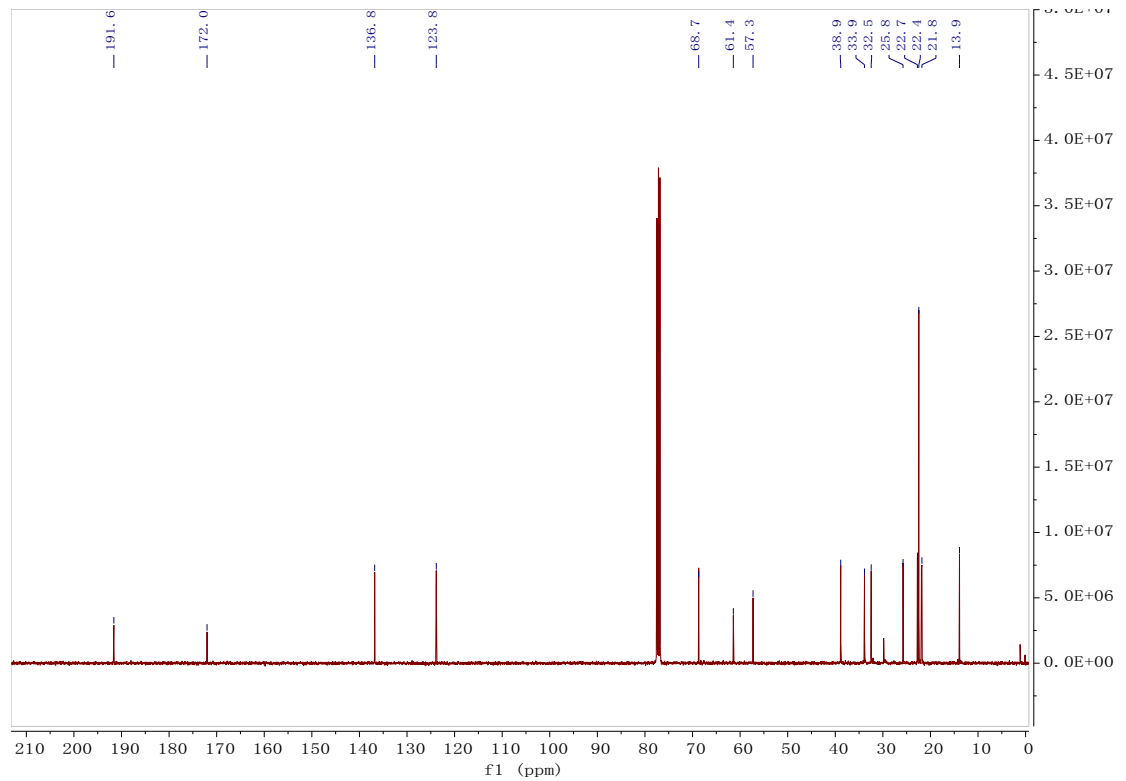
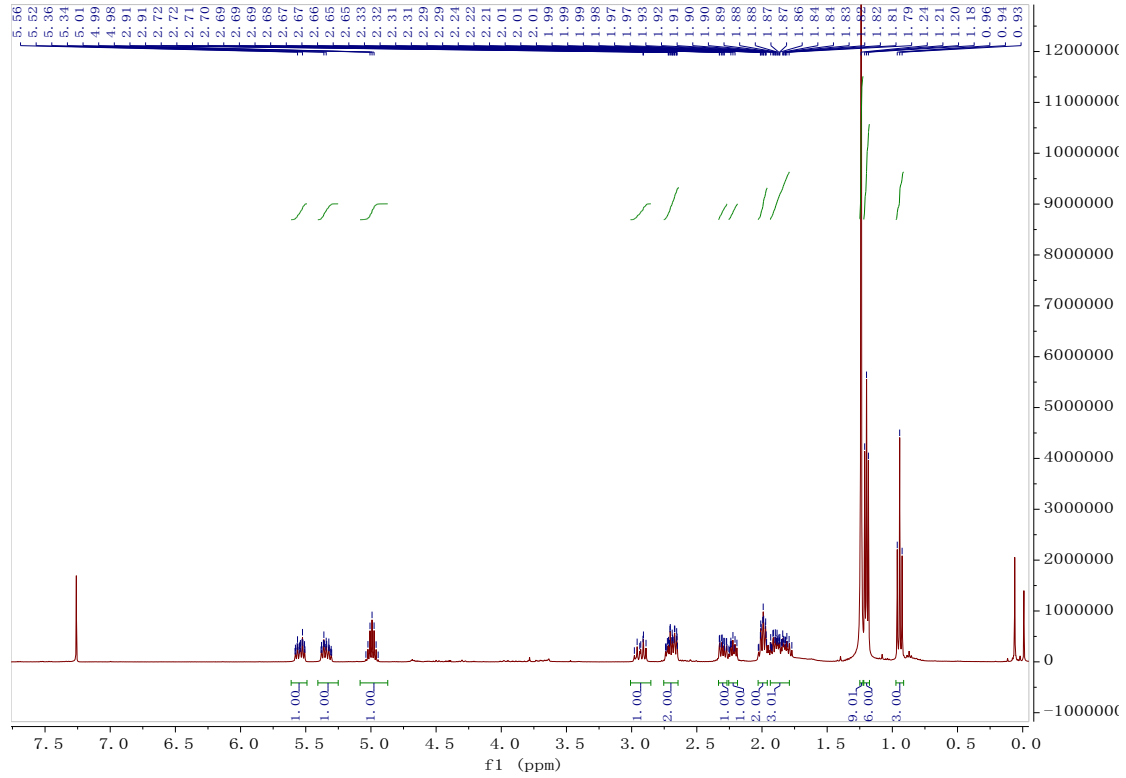


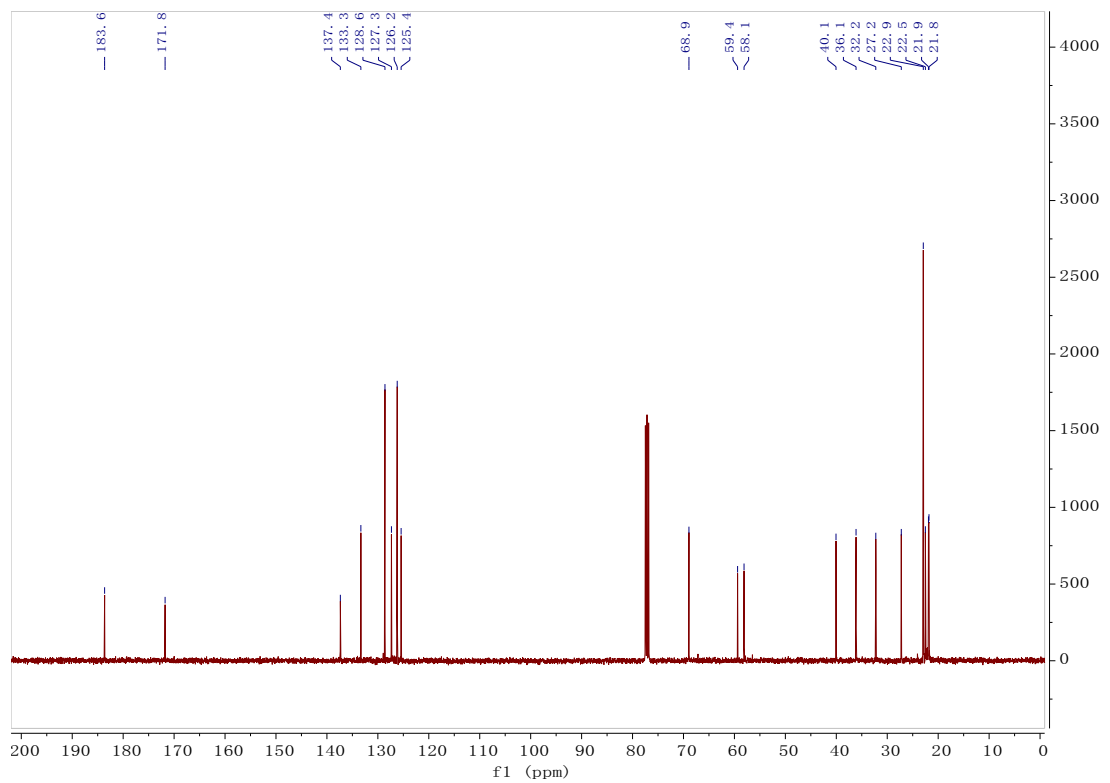
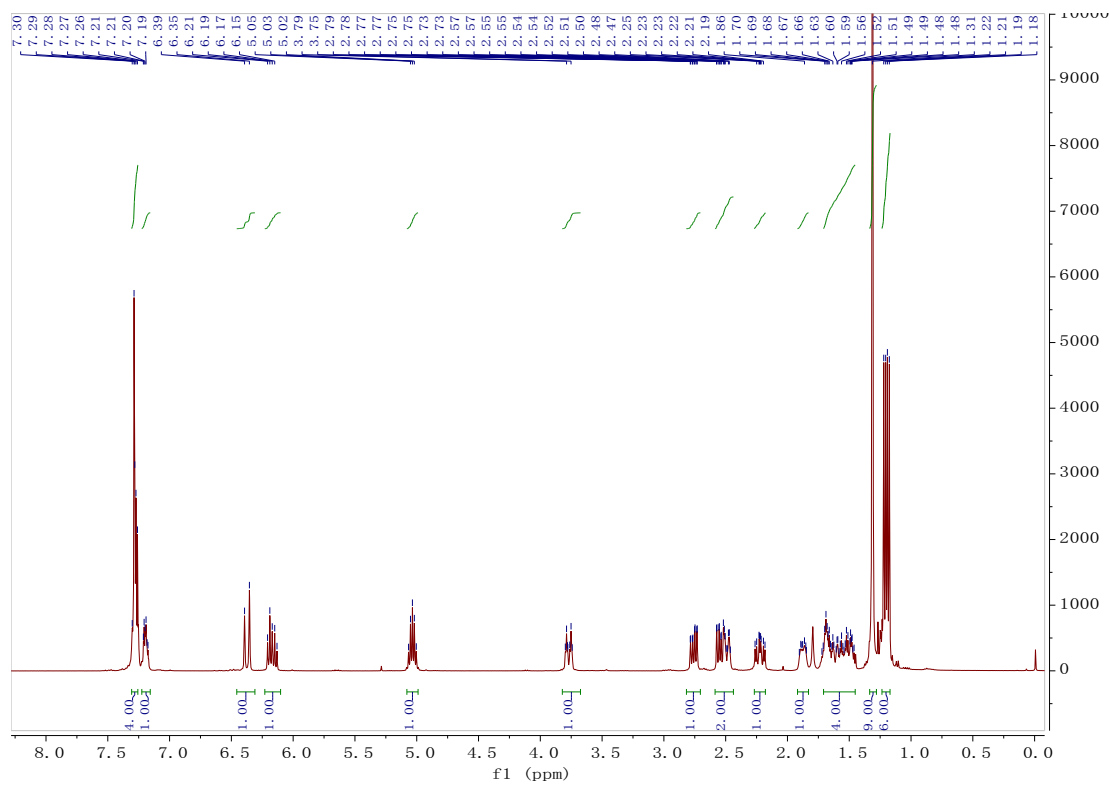
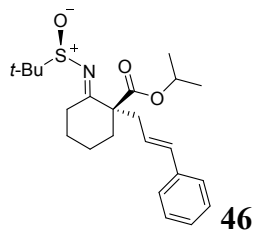


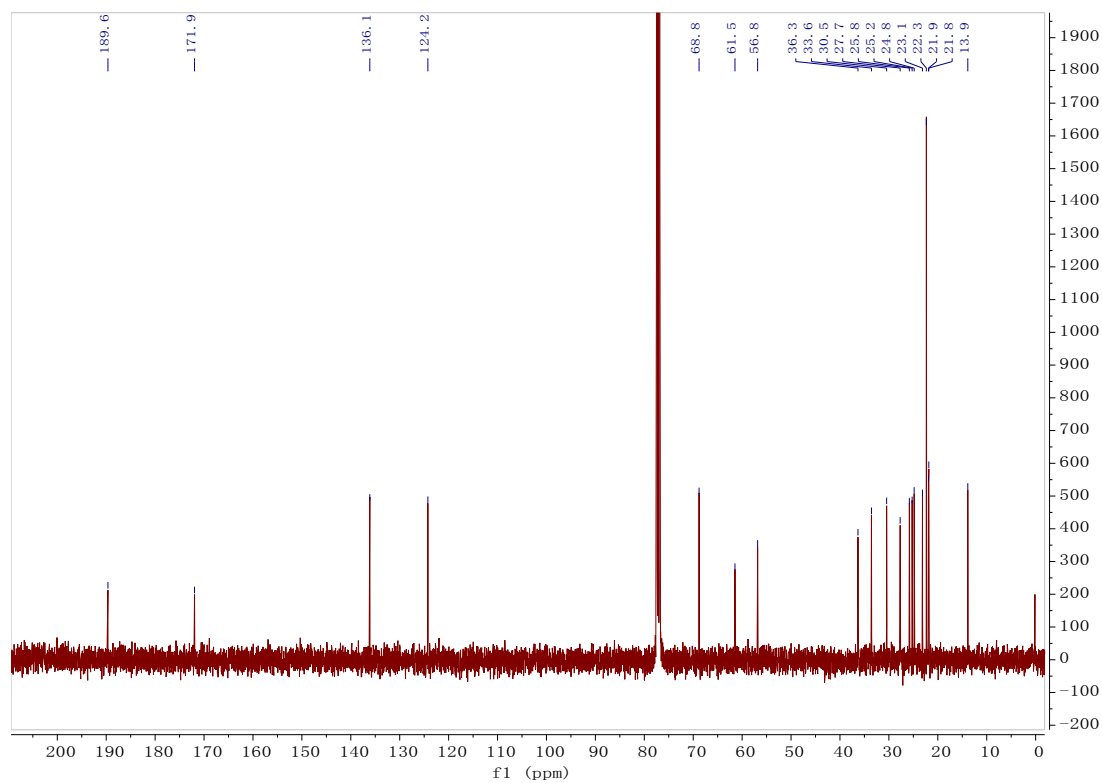
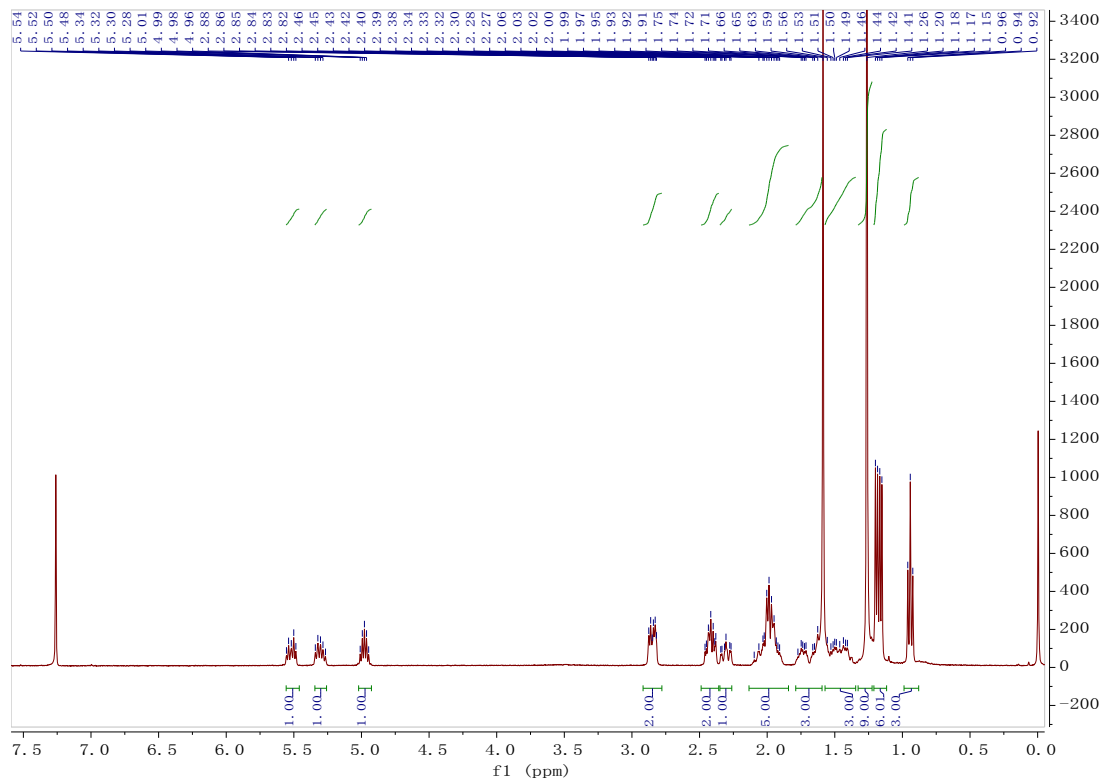
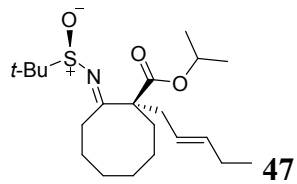


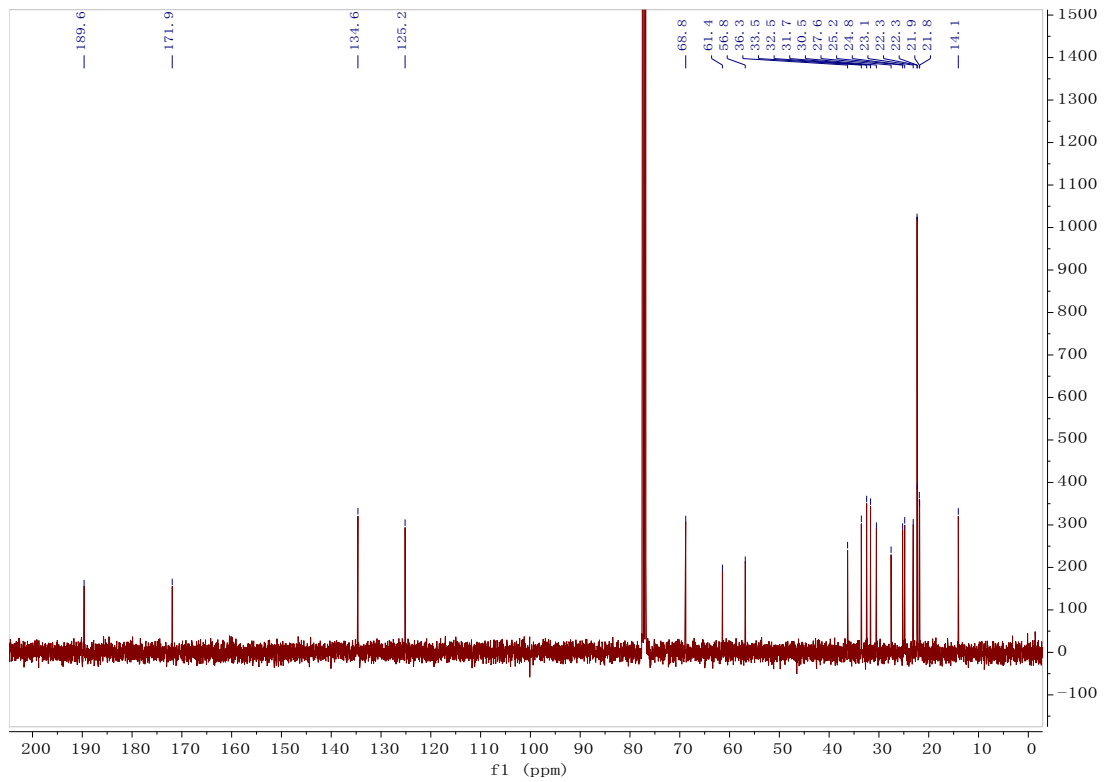
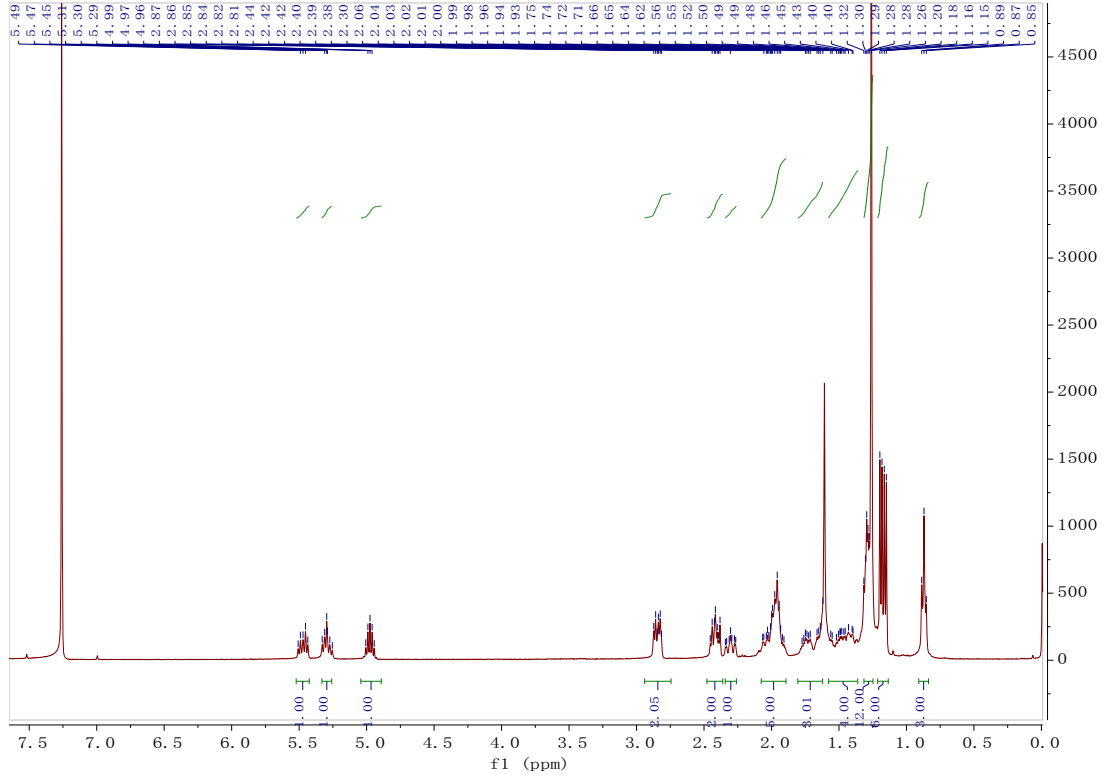
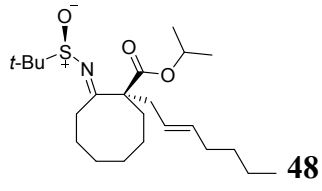


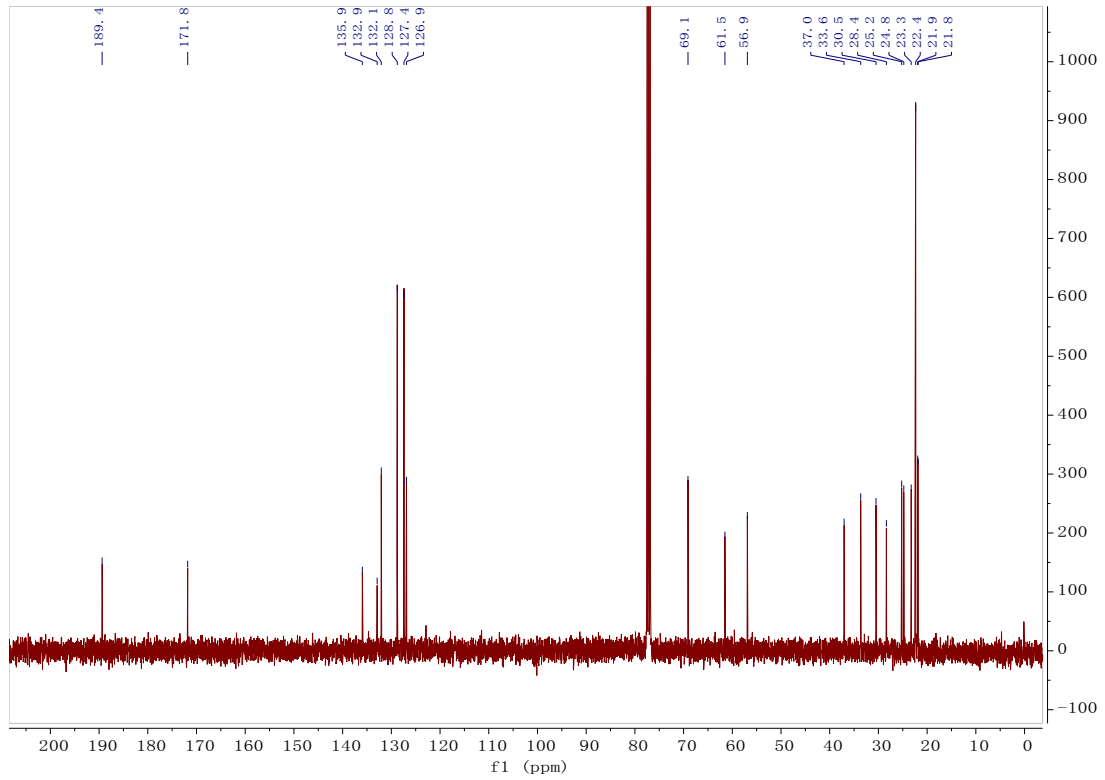
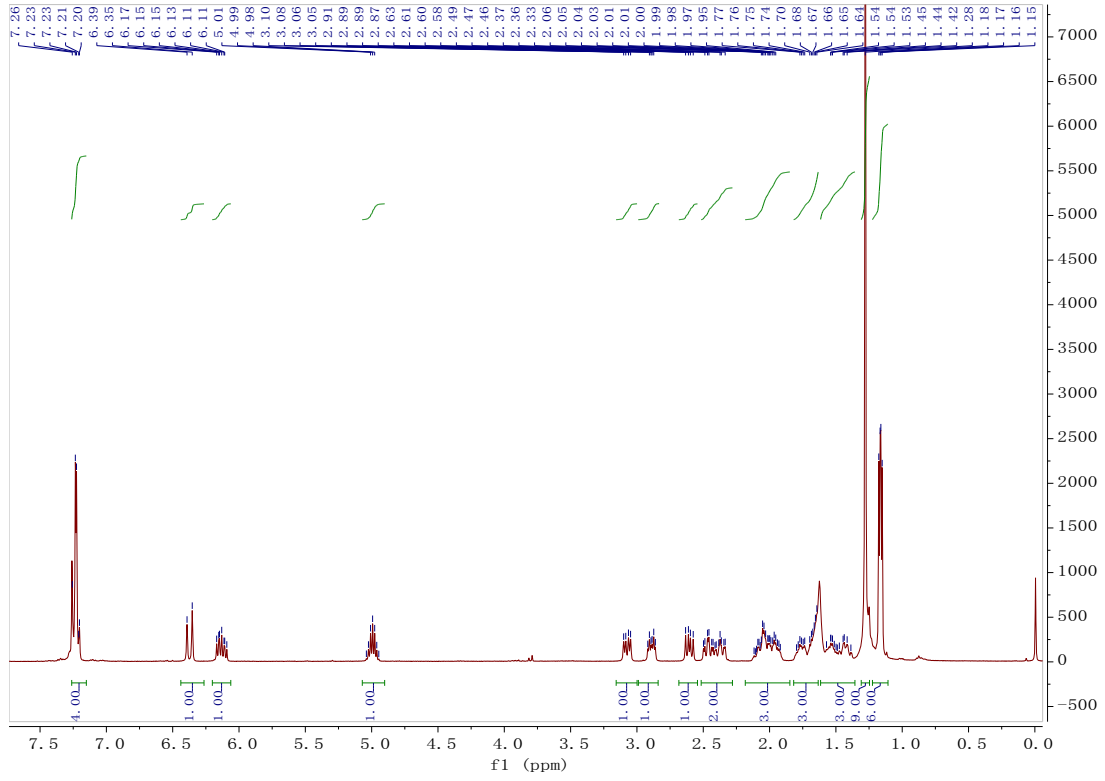
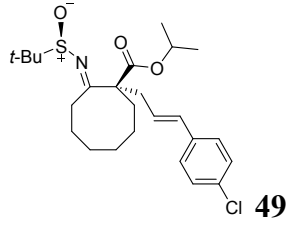
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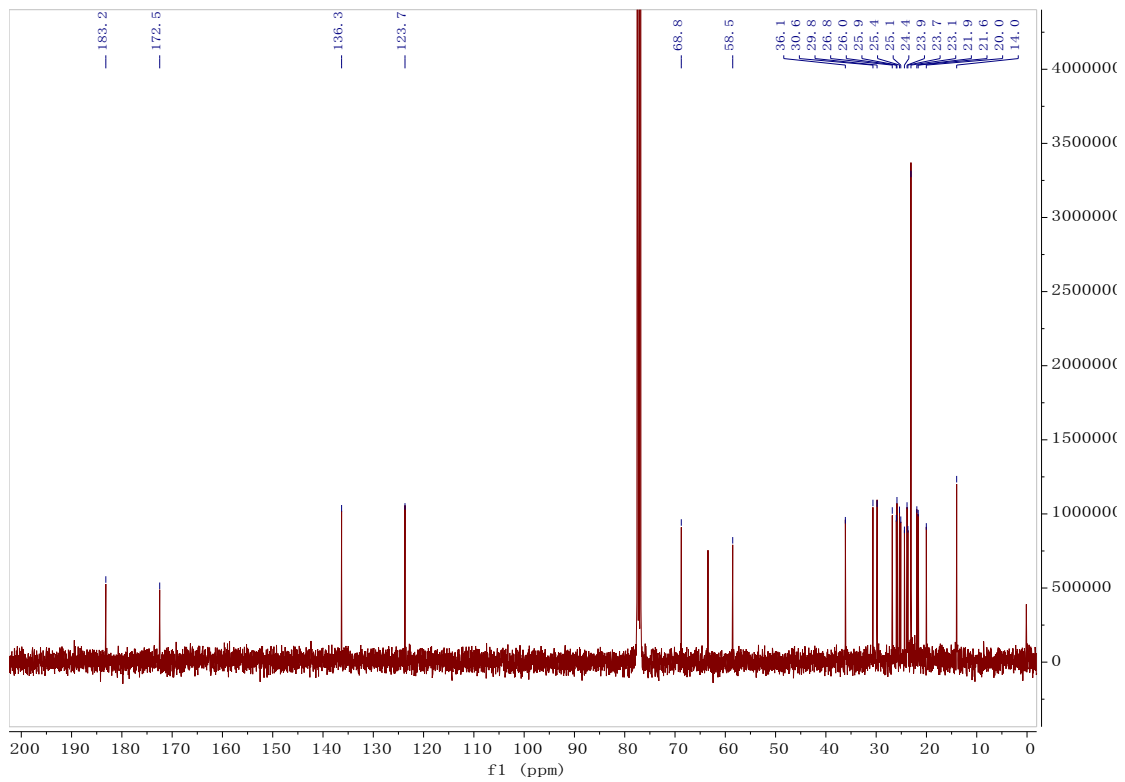
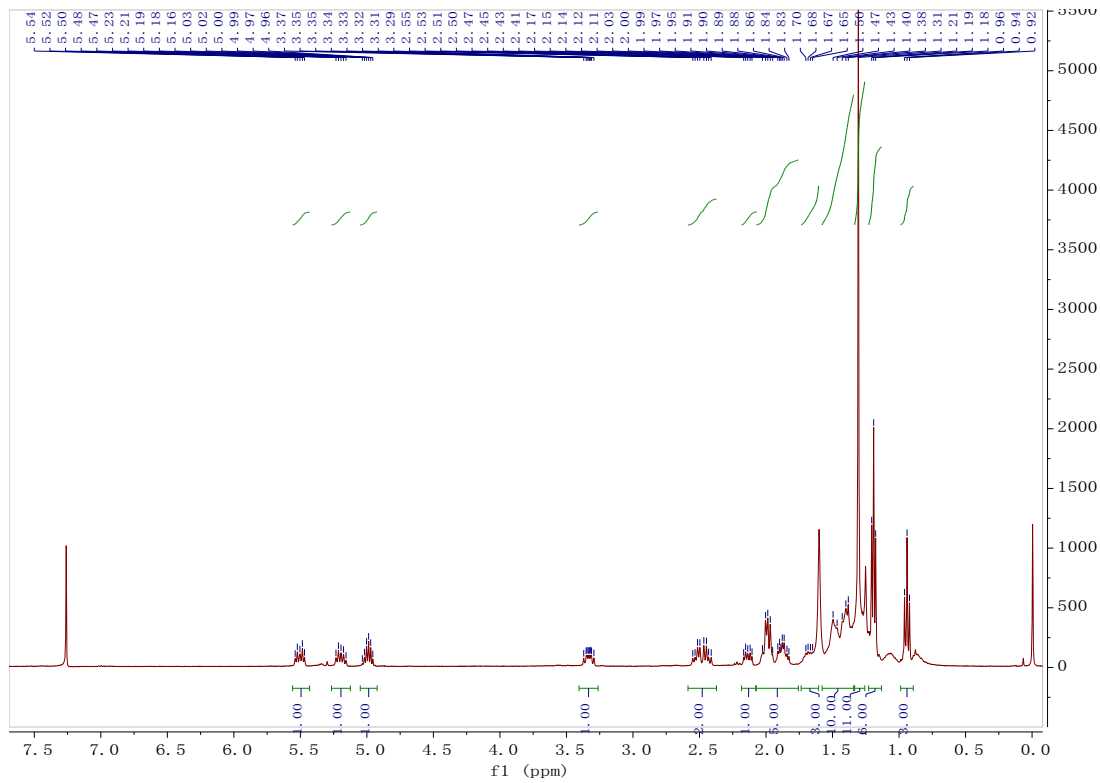
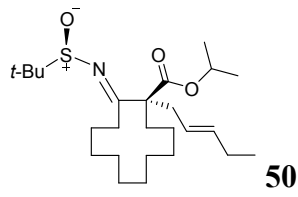


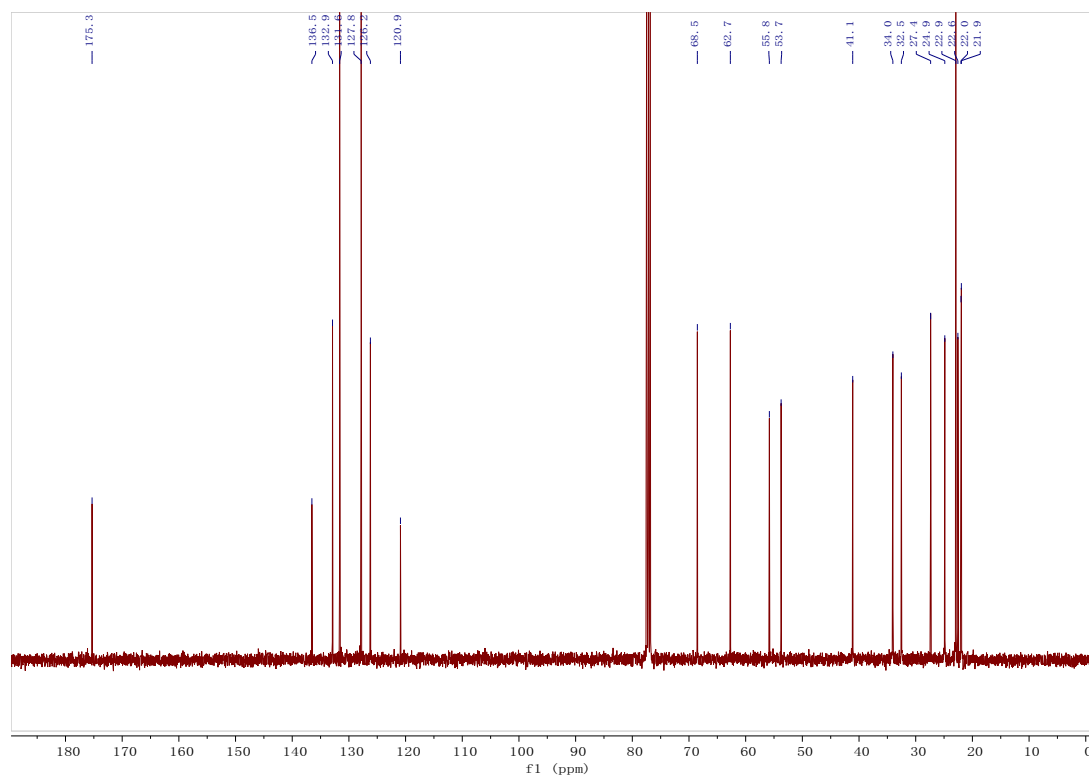
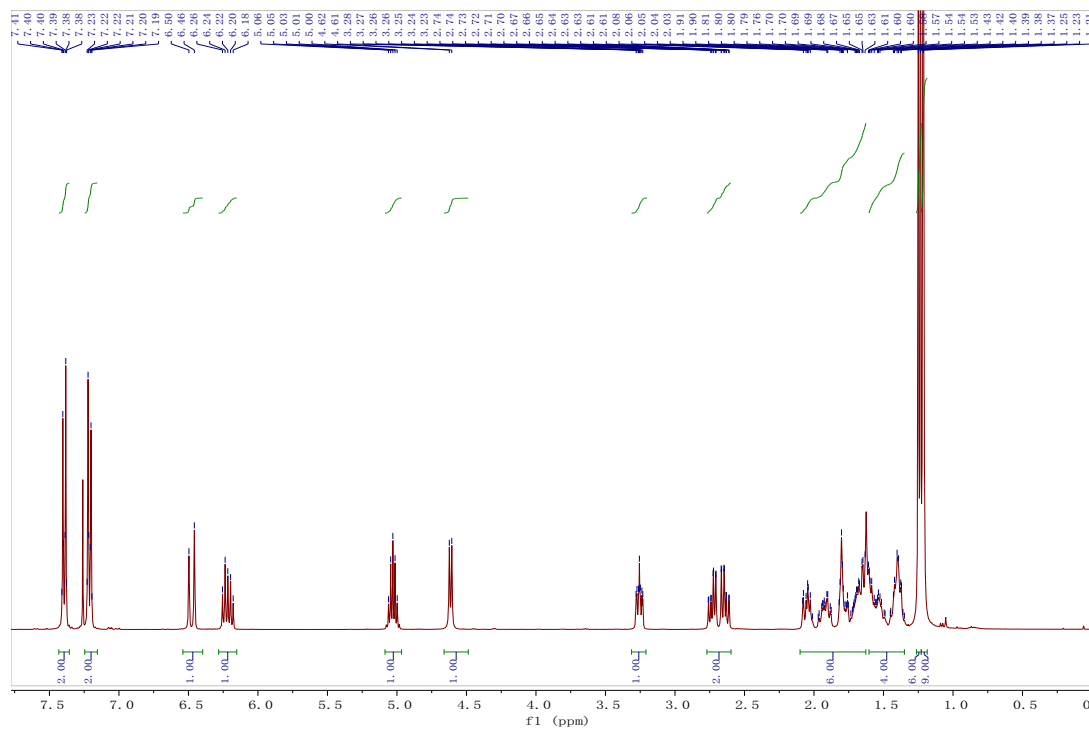
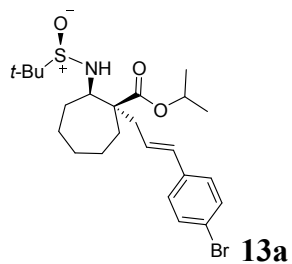


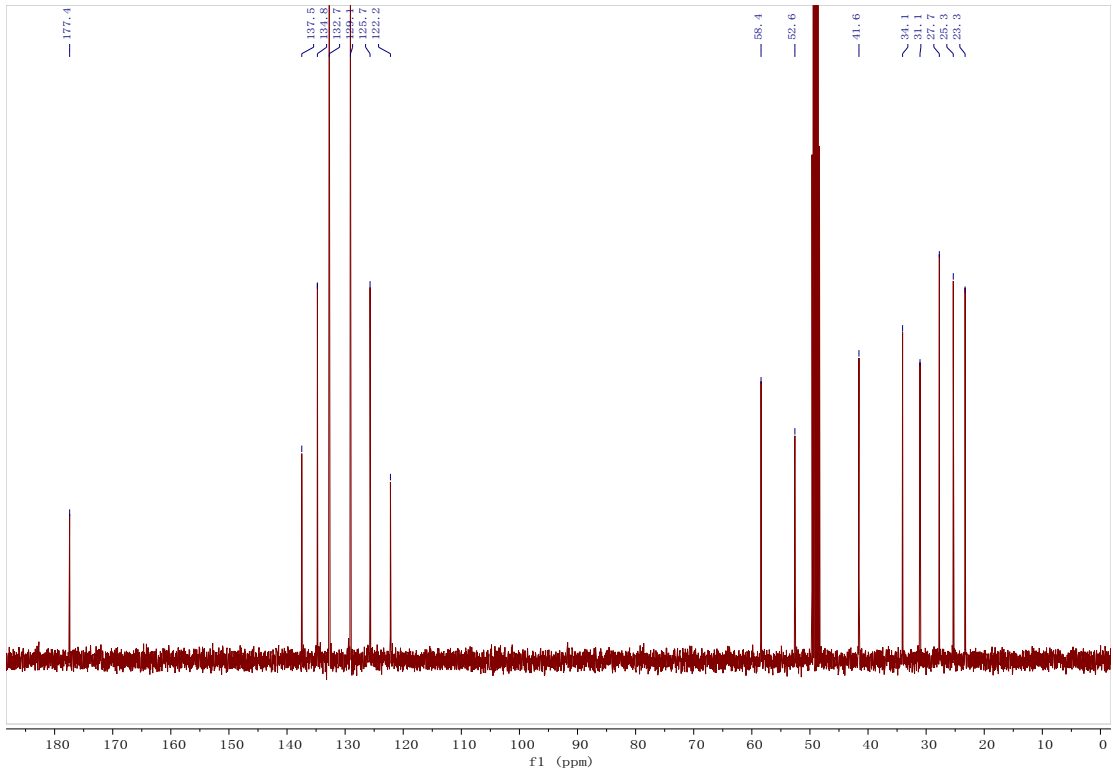
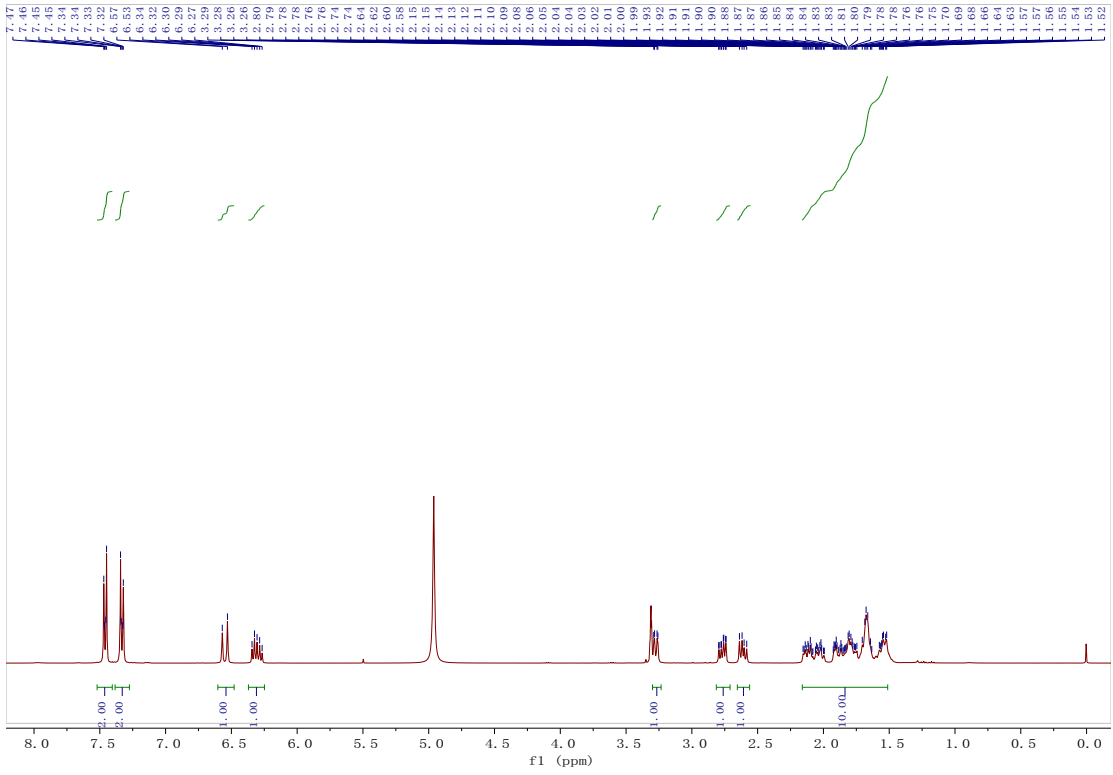
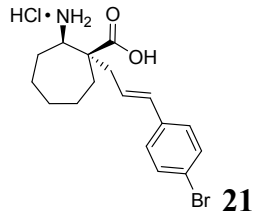




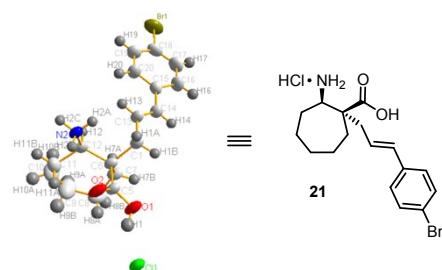








6. Crystal data of Compound 21



Crystal data and structure refinement for 21.

Identification code	21
Empirical formula	C ₁₇ H ₂₃ BrClNO ₂
Formula weight	480.86
Temperature/K	239(70)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	10.6230(3)
b/Å	9.49924(19)
c/Å	13.5627(4)
α /°	90
β /°	103.281(3)
γ /°	90
Volume/Å ³	1332.01(6)
Z	2
$\rho_{\text{calc}}/\text{g/cm}^3$	1.199
μ /mm ⁻¹	3.204
F(000)	504.0
Radiation	CuK α (λ = 1.54184)
2 Θ range for data collection/°	6.696 to 148.466
Index ranges	-13 \leq h \leq 12, -11 \leq k \leq 11, -16 \leq l \leq 16
Reflections collected	25502
Independent reflections	5141 [R _{int} = 0.0508, R _{sigma} = 0.0356]
Data/restraints/parameters	5141/120/256
Goodness-of-fit on F ²	1.034

Final R indexes [$I \geq 2 \sigma(I)$]	$R_1 = 0.0709$, $wR_2 = 0.2039$
Final R indexes [all data]	$R_1 = 0.0764$, $wR_2 = 0.2138$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.91/-0.37
Flack parameter	-0.003(10)