

Supporting Information for:

Facile Preparation of 1,2-Dihydroisoquinolines from *N*-Benzylsulfonamides and Bromoacetylenes

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General. ^1H and ^{13}C NMR spectra were taken on an Agilent 400-MR spectrometer at 400 and 100 MHz. CDCl_3 was used as the solvent unless otherwise noted. Chemical shifts are reported in parts per million shift (δ value) from Me_4Si (δ 0 ppm for ^1H) or based on the middle peak of the solvent (CDCl_3) (δ 77.00 ppm for ^{13}C) as an internal standard. Signal patterns are indicated as br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants (J) are given in Hertz. When yields were determined by ^1H NMR spectroscopy, a known amount of trichloroethylene was added as an internal standard. Infrared (IR) spectra were recorded on a JASCO A-100 spectrometer and are reported in wave numbers (cm^{-1}). High resolution mass spectra (HRMS) were obtained on a Bruker micrOTOF II by the positive electrospray ionization (ESI) method calibrated with sodium formate or on a JEOL JMS-700 by the fast atom bombardment (FAB) method (matrix: *m*-nitrobenzyl alcohol (NBA)) calibrated with perfluoropolyether or by the electron ionization (EI) method calibrated with perfluorokerosene at the Suzukake-dai Material Analysis Center, Technical Department, Tokyo Institute of Technology. Column chromatography was performed with silica gel [Wakogel® R-200, size 100-200 mesh (75-150 μm), Cat. No. 233-00077, Wako Pure Chemical Industries, Ltd. (Japan)]. Dry solvents (THF, CH_2Cl_2 , and DMF) were purchased from Kanto Chemicals Co. (Japan). K_3PO_4 was purchased from Koso Chemical Co. (Japan). Chemicals were purified or dried in a standard manner, if necessary.

1-Chloro-1-octyne (1). Starting haloacetylene for 8.

This is a known compound [Salvi, L.; Jeon, S.-J.; Fisher, E. L.; Carroll, P. J.; Walsh, P. J. *J. Am. Chem. Soc.* **2007**, *129*, 16119-16125].

^1H NMR δ 0.89 (t, J = 7.0 Hz, 3H), 1.22-1.41 (m, 6H), 1.50 (quintet, J = 7.2 Hz, 2H), 2.16 (t, J = 7.2 Hz, 2H).

^{13}C NMR δ 14.00, 18.75, 22.53, 28.36, 28.48, 31.31, 56.91 ($\text{C}\equiv\text{CCl}$), 69.73 ($\text{C}\equiv\text{CCl}$).

The ^{13}C NMR shifts assigned to acetylenic carbons were in good agreement with those reported in the following literature [Stothers, J. B. In *Organic Chemistry*; Blomquist, A. T., Wasserman, H., Eds.; Academic Press: New York, 1972; Vol. 24, p 195].

IR (neat) 2959, 2928, 2857, 2240 (C≡C), 1460, 1377, 1089, 728 cm⁻¹.

HRMS (EI) Calcd for C₈H₁₃³⁵Cl [M]⁺: 144.0705. Found: 144.0706.

1-Bromo-1-octyne (2). This is a known compound [Correia, J. *J. Org. Chem.* **1992**, *57*, 4555-4557] and was prepared according to a literature method [Tobe, Y.; Utsumi, N.; Kawabata, K.; Nagano, A.; Adachi, K.; Araki, S.; Sonoda, M.; Hirose, K.; Naemura, K. *J. Am. Chem. Soc.* **2002**, *124*, 5350-5363].

¹H NMR δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.22-1.42 (m, 6H), 1.51 (m, 2H), 2.20 (t, *J* = 7.2 Hz, 2H).

¹³C NMR δ 13.99, 19.66, 22.51, 28.28, 28.47, 31.29, 37.39 (C≡CBr), 80.42 (C≡CBr).

The ¹³C NMR shifts assigned to acetylenic carbons were in good agreement with those reported in the following literature [Stothers, J. B. In *Organic Chemistry*; Blomquist, A. T., Wasserman, H., Eds.; Academic Press: New York, 1972; Vol. 24, p 195].

IR (neat) 2930, 2903, 2859, 2209 (C≡C), 1466, 1378, 1327, 1111, 725 cm⁻¹.

These spectral properties were in good agreement with those reported in the above literature.

1-Iodo-1-octyne (3). Starting haloacetylene for 10. This is a known compound [Reddy, K. R.; Venkateshwar, M.; Maheswari, C. U.; Kumar, P. S. *Tetrahedron Lett.* **2010**, *51*, 2170-2173].

¹H NMR δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.22-1.41 (m, 6H), 1.51 (m, 2H), 2.35 (t, *J* = 7.0 Hz, 2H).

¹³C NMR δ -7.67 (C≡CI), 14.02, 20.80, 22.49, 28.44 (2 carbons), 31.25, 94.83 (C≡CI).

The ¹³C NMR shifts assigned to acetylenic carbons were in good agreement with those reported in the following literature [Stothers, J. B. In *Organic Chemistry*; Blomquist, A. T., Wasserman, H., Eds.; Academic Press: New York, 1972; Vol. 24, p 195].

IR (neat) 2952, 2926, 2857, 2188 (C≡C), 1468, 1379, 1101, 722 cm⁻¹.

N-Benzylethanesulfonamide (4).

¹H NMR δ 1.31 (t, *J* = 7.4 Hz, 3H), 2.95 (q, *J* = 7.4 Hz, 2H), 4.29 (d, *J* = 6.0 Hz, 2H), 4.62 (br s, 1H), 7.29-7.33 (m, 5H).

¹³C NMR δ 8.16, 47.08, 47.49, 127.83 (2 carbons), 127.96, 128.78 (2 carbons), 136.98.

IR (KBr) 3289 (N-H), 3038, 2974, 1497, 1433, 1317, 1141, 1060, 866, 706 cm⁻¹.

HRMS (ESI) Calcd for C₉H₁₃NO₂SNa [M+Na]⁺: 222.0559. Found: 222.0554.

M.p. 65-67 °C.

N-Benzylmethanesulfonamide (5). Starting sulfonamide for 11.

¹H NMR δ 2.84 (s, 3H), 4.30 (d, *J* = 6.0 Hz, 2H), 4.95 (br s, 1H), 7.28-7.39 (m, 5H).

¹³C NMR δ 41.00, 47.11, 127.87 (2 carbons), 128.04, 128.84 (2 carbons), 136.66.

IR (KBr) 3229 (N-H), 3020, 2932, 1456, 1310, 1136, 1062, 878, 739 cm⁻¹.

HRMS (ESI) Calcd for C₈H₁₁NO₂SNa [M+Na]⁺: 208.0403. Found: 208.0397.

M.p. 65-67 °C.

***N*-Benzyl-1-butanesulfonamide (6). Starting sulfonamide for 12.**

¹H NMR δ 0.89 (t, *J* = 7.6 Hz, 3H), 1.37 (sextet, *J* = 7.6 Hz, 2H), 1.73 (m, 2H), 2.92 (m, 2H), 4.30 (d, *J* = 6.0 Hz, 2H), 4.56 (br s, 1H), 7.28-7.40 (m, 5H).

¹³C NMR δ 13.50, 21.43, 25.56, 47.21, 53.05, 127.90 (2 carbons), 128.07, 128.86 (2 carbons), 136.89.

IR (KBr) 3277 (N-H), 3034, 2958, 1496, 1456, 1313, 1134, 1064, 868, 697 cm⁻¹.

HRMS (ESI) Calcd for C₁₁H₁₇NO₂SNa [M+Na]⁺: 250.0872. Found: 250.0868.

M.p. 63-65 °C.

***N*-Benzyl-2-propanesulfonamide (7). Starting sulfonamide for 13.**

¹H NMR δ 1.35 (d, *J* = 6.8 Hz, 6H), 3.09 (septet, *J* = 6.8 Hz, 1H), 4.31 (d, *J* = 6.0 Hz, 2H), 4.51 (br s, 1H), 7.27-7.39 (m, 5H).

¹³C NMR δ 16.55 (2 carbons), 47.55, 53.83, 127.81 (2 carbons), 127.94, 128.79 (2 carbons), 137.30.

IR (KBr) 3294 (N-H), 3061, 2980, 1497, 1425, 1311, 1147, 1061, 838, 748, 689 cm⁻¹.

HRMS (ESI) Calcd for C₁₀H₁₅NO₂SNa [M+Na]⁺: 236.0716. Found: 236.0718.

M.p. 95-97 °C.

***(Z)*-*N*-Benzyl-*N*-(1-chloro-1-octen-2-yl)ethanesulfonamide (8).**

A mixture of 1-chloro-1-octyne (**1**) (30.2 mg, 0.209 mmol), *N*-benzylethanesulfonamide (**4**) (121 mg, 0.605 mmol), and K₃PO₄ (63.0 mg, 0.297 mmol) in DMF (0.20 mL) was stirred in an oil bath maintained at 120 °C for 2 h under argon. After being cooled to room temperature, the reaction mixture was diluted with water (3 mL) and extracted with ethyl acetate (3 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude product, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (45.3 mg, 63%) as an oil and as a single isomer.

¹H NMR δ 0.82 (t, *J* = 7.2 Hz, 3H), 1.04-1.24 (m, 8H), 1.45 (t, *J* = 7.6 Hz, 3H), 2.02 (br s, 2H), 3.17 (q, *J* = 7.6 Hz, 2H), 4.65 (s, 2H), 5.95 (t, *J* = 1.6 Hz, 1H), 7.27-7.35 (m, 3H), 7.38 (m, 2H).

NOESY experiments showed correlation between the peaks at δ 2.02 ppm (br s, 2H, CH₂C=CCl) and at δ 5.95 ppm (t, *J* = 1.6 Hz, 1H, CHCl). Thus, the stereochemistry of the olefinic bond has been confirmed.

¹³C NMR δ 8.15, 13.96, 22.37, 26.43, 28.57, 31.35, 36.38, 48.71, 52.32, 116.14, 128.11, 128.41 (2 carbons), 129.26 (2 carbons), 136.06, 141.88.

IR (neat) 3032, 2929, 2858, 1621, 1456, 1341, 1148, 1042, 859, 731, 702 cm⁻¹.

HRMS (ESI) Calcd for C₁₇H₂₆³⁵ClNO₂SNa [M+Na]⁺: 366.1265. Found: 366.1256.

***(Z)*-*N*-Benzyl-*N*-(1-bromo-1-octen-2-yl)ethanesulfonamide (9).**

With 2 equiv of sulfonamide 4.

A mixture of 1-bromo-1-octyne (**2**) (37.9 mg, 0.200 mmol), *N*-benzylethanesulfonamide (**4**) (79.4

mg, 0.399 mmol), and K_3PO_4 (63.5 mg, 0.299 mmol) in DMF (0.20 mL) was stirred in an oil bath maintained at 120 °C for 3 h under argon. After being cooled to room temperature, the reaction mixture was diluted with water (3 mL) and extracted with ethyl acetate (3 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, 1H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (48.9 mg, 63%) as an oil and as a single isomer.

1H NMR δ 0.83 (t, $J = 7.2$ Hz, 3H), 1.04-1.30 (m, 8H), 1.46 (t, $J = 7.4$ Hz, 3H), 2.01 (br s, 2H), 3.20 (q, $J = 7.4$ Hz, 2H), 4.66 (s, 2H), 6.10 (t, $J = 1.4$ Hz, 1H), 7.28-7.36 (m, 3H), 7.39 (m, 2H).

NOESY experiments showed correlation between the peaks at δ 2.01 ppm (br s, 2H, $CH_2C=CBr$) and at δ 6.10 ppm (t, $J = 1.4$ Hz, 1H, $CHBr$). Thus, the stereochemistry of the olefinic bond has been confirmed.

^{13}C NMR δ 8.25, 13.97, 22.40, 26.64, 28.58, 31.38, 37.70, 49.26, 52.44, 105.34, 128.18, 128.46 (2 carbons), 129.42 (2 carbons), 136.03, 144.64.

IR (neat) 3032, 2928, 2856, 1617, 1457, 1340, 1147, 1041, 882, 759, 701 cm^{-1} .

HRMS (ESI) Calcd for $C_{17}H_{26}^{79}BrNO_2SNa$ $[M+Na]^+$: 410.0765. Found: 410.0775.

With 3 equiv of sulfonamide 4.

A mixture of 1-bromo-1-octyne (**2**) (38.8 mg, 0.205 mmol), *N*-benzylethanesulfonamide (**4**) (120 mg, 0.600 mmol), and K_3PO_4 (63.7 mg, 0.300 mmol) in DMF (0.20 mL) was stirred in an oil bath maintained at 120 °C for 2 h under argon. After being cooled to room temperature, the reaction mixture was diluted with water (3 mL) and extracted with ethyl acetate (3 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude product, 1H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (55.2 mg, 69%) as an oil and as a single isomer.

The spectroscopic data are shown above.

Recovery of the starting sulfonamide 4.

A mixture of 1-bromo-1-octyne (**2**) (38.5 mg, 0.204 mmol), *N*-benzylethanesulfonamide (**4**) (120 mg, 0.601 mmol), and K_3PO_4 (64.3 mg, 0.303 mmol) in DMF (0.20 mL) was stirred in an oil bath maintained at 120 °C for 2 h under argon. After being cooled to room temperature, the reaction mixture was diluted with water (3 mL) and extracted with ethyl acetate (3 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude product, 1H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (48.9 mg, 62% yield based on **2**) as an oil and as a single isomer, and the recovered starting material **4** (86.3 mg, 91% yield based on unreacted **4**) as a solid, which may be recycled in another run; or the yield of **9** based on the consumed sulfonamide **4** was calculated to be 76%.

The spectroscopic data are shown above.

(Z)-N-Benzyl-N-(1-iodo-1-octen-2-yl)ethanesulfonamide (10).

A mixture of 1-iodo-1-octyne (**3**) (48.4 mg, 0.205 mmol), *N*-benzylethanesulfonamide (**4**) (120 mg, 0.600 mmol), and K_3PO_4 (63.0 mg, 0.297 mmol) in DMF (0.20 mL) was stirred in an oil bath maintained at 120 °C for 2 h under argon. After being cooled to room temperature, the reaction mixture was diluted with water (3 mL) and extracted with ethyl acetate (3 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude solid, 1H NMR analysis of which revealed the absence of the title compound.

(Z)-N-Benzyl-N-(1-bromo-1-octen-2-yl)methanesulfonamide (11).

A mixture of 1-bromo-1-octyne (**2**) (37.9 mg, 0.200 mmol), *N*-benzylmethanesulfonamide (**5**) (111 mg, 0.600 mmol), and K_3PO_4 (62.9 mg, 0.296 mmol) in DMF (0.20 mL) was stirred in an oil bath maintained at 120 °C for 2 h under argon. After being cooled to room temperature, the reaction mixture was diluted with water (3 mL) and extracted with ethyl acetate (3 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude product, 1H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (49.9 mg, 67%) as an oil and as a single isomer.

1H NMR δ 0.83 (t, $J = 7.2$ Hz, 3H), 1.06-1.26 (m, 8H), 2.05 (br s, 2H), 3.06 (s, 3H), 4.64 (s, 2H), 6.12 (s, 1H), 7.28-7.37 (m, 3H), 7.40 (m, 2H).

^{13}C NMR δ 13.98, 22.40, 26.51, 28.57, 31.37, 37.41, 42.02, 52.22, 105.39, 128.22, 128.50 (2 carbons), 129.35 (2 carbons), 135.76, 144.50.

IR (neat) 3031, 2929, 2857, 1619, 1456, 1341, 1152, 1050, 961, 883, 702, 516 cm^{-1} .

HRMS (ESI) Calcd for $C_{16}H_{24}^{79}BrNO_2SNa$ $[M+Na]^+$: 396.0594. Found: 396.0603

(Z)-N-Benzyl-N-(1-bromo-1-octen-2-yl)-1-butanesulfonamide (12).

A mixture of 1-bromo-1-octyne (**2**) (75.5 mg, 0.399 mmol), *N*-benzyl-1-butanesulfonamide (**6**) (273 mg, 1.20 mmol), and K_3PO_4 (127 mg, 0.597 mmol) in DMF (0.40 mL) was stirred in an oil bath maintained at 120 °C for 2 h under argon. After being cooled to room temperature, the reaction mixture was diluted with water (3 mL) and extracted with ethyl acetate (3 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude product, 1H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (111 mg, 67%) as an oil and as a single isomer.

1H NMR δ 0.82 (t, $J = 7.2$ Hz, 3H), 0.95 (t, $J = 7.6$ Hz, 3H), 1.04-1.24 (m, 8H), 1.46 (sextet, $J = 7.6$ Hz, 2H), 1.90 (m, 2H), 2.01 (br s, 2H), 3.16 (m, 2H), 4.65 (s, 2H), 6.09 (t, $J = 1.6$ Hz, 1H), 7.27-7.36 (m, 3H), 7.39 (m, 2H).

^{13}C NMR δ 13.58, 13.98, 21.70, 22.40, 25.43, 26.62, 28.58, 31.38, 37.73, 52.35, 54.67, 105.23, 128.16, 128.45 (2 carbons), 129.41 (2 carbons), 136.04, 144.68.

IR (neat) 3032, 2929, 2859, 1618, 1457, 1341, 1147, 1048, 882, 701 cm^{-1} .

HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{30}^{79}\text{BrNO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 438.1073. Found: 438.1083.

(Z)-N-Benzyl-N-(1-bromo-1-octen-2-yl)-2-propanesulfonamide (13).

A mixture of 1-bromo-1-octyne (**2**) (37.4 mg, 0.198 mmol), *N*-benzyl-2-propanesulfonamide (**7**) (128 mg, 0.601 mmol), and K_3PO_4 (63.9 mg, 0.301 mmol) in DMF (0.20 mL) was stirred in an oil bath maintained at 120 °C for 2 h under argon. After being cooled to room temperature, the reaction mixture was diluted with water (3 mL) and extracted with ethyl acetate (3 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude product, ^1H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (48.8 mg, 61%) as an oil and as a single isomer.

^1H NMR δ 0.81 (t, $J = 7.2$ Hz, 3H), 1.00-1.20 (m, 8H), 1.48 (d, $J = 6.8$ Hz, 6H), 1.94 (br s, 2H), 3.40 (septet, $J = 6.8$ Hz, 1H), 4.70 (s, 2H), 6.06 (t, $J = 1.6$ Hz, 1H), 7.27-7.35 (m, 3H), 7.39 (m, 2H).

^{13}C NMR δ 13.96, 17.19 (2 carbons), 22.37, 26.83, 28.58, 31.35, 38.06, 53.20, 55.85, 105.20, 128.16, 128.40 (2 carbons), 129.56 (2 carbons), 136.18, 145.06.

IR (neat) 3031, 2928, 2857, 1605, 1457, 1336, 1142, 1044, 880, 699, 612 cm^{-1} .

HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{28}^{79}\text{BrNO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 424.0916. Found: 424.0904.

3-Hexyl-2-methanesulfonyl-1,2-dihydroisoquinoline (14) (Table 2, entry 10).

A mixture of *N*-(bromoalkenyl)sulfonamide **11** (93.6 mg, 0.250 mmol), triphenylphosphine (19.7 mg, 0.075 mmol), KOAc (49.7 mg, 0.506 mmol), and palladium acetate (5.6 mg, 0.025 mmol) in DMF (0.75 mL) was stirred in an oil bath maintained at 120 °C for 45 min under argon. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate (3 mL) and filtered through Celite with the aid of ethyl acetate. The combined filtrates were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, in which the aromatized product was not detected by ^1H NMR analysis. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (44.3 mg, 60%) as an oil.

^1H NMR δ 0.89 (t, $J = 7.0$ Hz, 3H), 1.22-1.44 (m, 6H), 1.67 (quintet, $J = 7.4$ Hz, 2H), 2.42 (s, 3H), 2.62 (t, $J = 7.4$ Hz, 2H), 4.68 (s, 2H), 6.40 (s, 1H), 7.12 (d, $J = 7.2$ Hz, 1H), 7.18 (d, $J = 7.2$ Hz, 1H), 7.23 (t, $J = 7.2$ Hz, 1H), 7.27 (t, $J = 7.2$ Hz, 1H).

^{13}C NMR δ 14.06, 22.59, 28.36, 28.82, 31.60, 35.56, 37.91, 50.47, 119.08, 124.74, 125.09, 127.88, 128.28, 129.65, 131.44, 142.72.

IR (neat) 3021, 2926, 2855, 1631, 1455, 1346, 1154, 1023, 961, 769, 608 cm^{-1} .

HRMS (FAB, NBA) Calcd for $\text{C}_{16}\text{H}_{23}\text{NO}_2\text{S}$ $[\text{M}]^+$: 293.1450. Found: 293.1453.

2-Ethanesulfonyl-3-hexyl-1,2-dihydroisoquinoline (15).

With 2 equiv of KOAc (Table 2, entry 11).

A mixture of *N*-(bromoalkenyl)sulfonamide **9** (56.8 mg, 0.146 mmol), triphenylphosphine (11.5 mg, 0.044 mmol), KOAc (28.7 mg, 0.292 mmol), and palladium acetate (3.3 mg, 0.015 mmol) in DMF (0.44 mL) was stirred in an oil bath maintained at 120 °C for 45 min under argon. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate (3 mL) and filtered through Celite with the aid of ethyl acetate. The combined filtrates were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, in which the aromatized product was not detected by ¹H NMR analysis. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (32.9 mg, 73%) as an oil.

¹H NMR δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.4 Hz, 3H), 1.24-1.44 (m, 6H), 1.67 (quintet, *J* = 7.4 Hz, 2H), 2.62 (q, *J* = 7.4 Hz, 2H), 2.62 (t, *J* = 7.4 Hz, 2H), 4.67 (s, 2H), 6.33 (s, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H).

¹³C NMR δ 7.51, 14.06, 22.58, 28.41, 28.82, 31.59, 35.48, 46.35, 50.36, 118.19, 124.54, 124.58, 127.66, 128.14, 130.03, 131.65, 142.54.

IR (neat) 3022, 2928, 2856, 1630, 1455, 1344, 1150, 1040, 911, 758, 630 cm⁻¹.

HRMS (FAB, NBA) Calcd for C₁₇H₂₅NO₂SNa [M+Na]⁺: 330.1504. Found: 330.1508.

With 3 equiv of KOAc (Table 2, entry 14).

A mixture of *N*-(bromoalkenyl)sulfonamide **9** (53.3 mg, 0.137 mmol), triphenylphosphine (10.9 mg, 0.042 mmol), KOAc (40.4 mg, 0.412 mmol), and palladium acetate (3.1 mg, 0.014 mmol) in DMF (0.40 mL) was stirred in an oil bath maintained at 120 °C for 45 min under argon. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate (3 mL) and filtered through Celite with the aid of ethyl acetate. The combined filtrates were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, in which the aromatized product was not detected by ¹H NMR analysis. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (33.6 mg, 80%) as an oil.

The spectroscopic data are shown above.

2-(1-Butanesulfonyl)-3-hexyl-1,2-dihydroisoquinoline (16).

A mixture of *N*-(bromoalkenyl)sulfonamide **12** (58.6 mg, 0.141 mmol), triphenylphosphine (11.1 mg, 0.042 mmol), KOAc (27.7 mg, 0.282 mmol), and palladium acetate (3.2 mg, 0.014 mmol) in DMF (0.42 mL) was stirred in an oil bath maintained at 120 °C for 45 min under argon. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate (3 mL) and filtered through Celite with the aid of ethyl acetate. The combined filtrates were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, in which the aromatized product was not detected by ¹H NMR analysis. The crude sample was

chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (32.3 mg, 68%) as an oil.

^1H NMR δ 0.68 (t, $J = 7.4$ Hz, 3H), 0.89 (t, $J = 7.2$ Hz, 3H), 1.13 (sextet, $J = 7.4$ Hz, 2H), 1.25-1.42 (m, 6H), 1.50 (m, 2H), 1.67 (quintet, $J = 7.4$ Hz, 2H), 2.58 (m, 2H), 2.63 (t, $J = 7.4$ Hz, 2H), 4.66 (s, 2H), 6.33 (s, 1H), 7.10 (d, $J = 7.6$ Hz, 1H), 7.15 (d, $J = 7.6$ Hz, 1H), 7.22 (t, $J = 7.6$ Hz, 1H), 7.26 (t, $J = 7.6$ Hz, 1H).

^{13}C NMR δ 13.22, 14.06, 21.41, 22.59, 24.90, 28.43, 28.83, 31.60, 35.53, 50.38, 51.79, 118.19, 124.48, 124.87, 127.65, 128.15, 130.03, 131.71, 142.69.

IR (neat) 3021, 2927, 2857, 1629, 1456, 1344, 1150, 1057, 913, 757, 630 cm^{-1} .

HRMS (FAB, NBA) Calcd for $\text{C}_{19}\text{H}_{29}\text{NO}_2\text{S}$ $[\text{M}]^+$: 335.1919. Found: 335.1915.

3-Hexyl-2-(2-propanesulfonyl)-1,2-dihydroisoquinoline (17).

A mixture of *N*-(bromoalkenyl)sulfonamide **13** (52.7 mg, 0.131 mmol), triphenylphosphine (10.4 mg, 0.040 mmol), KOAc (25.8 mg, 0.263 mmol), and palladium acetate (2.9 mg, 0.013 mmol) in DMF (0.39 mL) was stirred in an oil bath maintained at 120 °C for 45 min under argon. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate (3 mL) and filtered through Celite with the aid of ethyl acetate. The combined filtrates were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, ^1H NMR analysis of which revealed the presence of **17** and **13** in 59 and 17% yields and the absence of the aromatized product. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford a mixture of **17** and **13** (27.0 mg, **17/13** = 76:24) as an oil. As it was difficult to separate **17** from **13** by routine flash chromatography, a small portion of the mixture was purified by a recycling preparative HPLC [Model LC-9201R/U equipped with a JAIGEL-H column (length: 600 mm x 2 cycles, bore: 20 mm), Japan Analytical Industry Co., Ltd. (Japan); eluent: chloroform (3.5 mL/min)] to afford a pure sample of the title compound.

^1H NMR δ 0.89 (t, $J = 7.2$ Hz, 3H), 1.11 (d, $J = 6.8$ Hz, 6H), 1.22-1.45 (m, 6H), 1.68 (quintet, $J = 7.6$ Hz, 2H), 2.62 (t, $J = 7.6$ Hz, 2H), 2.96 (septet, $J = 6.8$ Hz, 1H), 4.67 (s, 2H), 6.20 (s, 1H), 7.07 (d, $J = 7.2$ Hz, 1H), 7.12 (d, $J = 7.2$ Hz, 1H), 7.20 (t, $J = 7.2$ Hz, 1H), 7.25 (t, $J = 7.2$ Hz, 1H).

^{13}C NMR δ 14.06, 16.75 (2 carbons), 22.61, 28.61, 28.91, 31.63, 35.39, 50.59, 55.69, 116.41, 124.23, 124.74, 127.42, 128.04, 130.06, 132.02, 143.03.

IR (neat) 3021, 2926, 2855, 1627, 1455, 1339, 1145, 1058, 916, 755, 628 cm^{-1} .

HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{27}\text{NO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 344.1655. Found: 344.1654.

Experiment for confirming the structure of 15 by its transformation to 3-hexylisoquinoline (18). This product is a known compound [Hwang, S.; Lee, Y.; Lee, P. H.; Shin, S. *Tetrahedron Lett.* **2009**, *50*, 2305-2308].

After *t*-BuOK (115 mg, 1.03 mmol) was added to a solution of **15** (69.8 mg, 0.227 mmol) in *t*-BuOH (733 mg), it was refluxed for 1 h under argon. After being cooled to room temperature, the solvent was removed under reduced pressure. Ether and water were added to the residue.

The organic layer was separated and the aqueous layer was extracted with ether three times. The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (44.1 mg, 91%) as an oil.

¹H NMR δ 0.86 (t, *J* = 7.0 Hz, 3H), 1.20-1.44 (m, 6H), 1.79 (quintet, *J* = 7.6 Hz, 2H), 2.91 (t, *J* = 7.6 Hz, 2H), 7.44 (s, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 9.18 (s, 1H).

¹³C NMR δ 14.05, 22.57, 29.07, 29.97, 31.73, 38.13, 117.85, 126.04, 126.20, 127.02, 127.44, 130.13, 136.50, 152.01, 155.86.

IR (neat) 3055, 2926, 2855, 1630, 1591, 1456, 1276, 1168, 949, 878, 747 cm⁻¹.

HRMS (ESI) Calcd for C₁₅H₂₀N [M+H]⁺: 214.1519. Found: 214.1519.

These spectral properties were in good agreement with those reported in the above literature.

5-(Benzyloxy)-1-bromo-1-pentyne (23). Starting bromoacetylene for 37. This is a known compound [Yamagishi, M.; Nishigai, K.; Hata, T.; Urabe, H. *Org. Lett.* **2011**, *13*, 4873-4875].

¹H NMR δ 1.81 (m, 2H), 2.34 (t, *J* = 7.2 Hz, 2H), 3.55 (t, *J* = 6.0 Hz, 2H), 4.51 (s, 2H), 7.24-7.37 (m, 5H).

¹³C NMR δ 16.56, 28.45, 37.94 (C≡C), 68.54, 72.96, 79.70 (C≡C), 127.55, 127.58 (2 carbons), 128.36 (2 carbons), 138.38.

IR (neat) 3063, 3030, 2927, 2857, 2209 (C≡C), 1453, 1364, 1105, 736, 697 cm⁻¹.

Anal. Calcd for C₁₂H₁₃BrO: C, 56.94; H, 5.18. Found: C, 56.71; H, 5.21.

1-Bromo-3-methoxy-1-octyne (24). Starting bromoacetylene for 38. This is a known compound [Yamagishi, M.; Nishigai, K.; Hata, T.; Urabe, H. *Org. Lett.* **2011**, *13*, 4873-4875].

¹H NMR δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.19-1.38 (m, 4H), 1.43 (m, 2H), 1.70 (m, 2H), 3.40 (s, 3H), 3.95 (t, *J* = 6.4 Hz, 1H).

¹³C NMR δ 14.00, 22.52, 24.81, 31.47, 35.44, 45.06 (C≡C), 56.62, 72.22 (C≡C), 79.31.

IR (neat) 2931, 2861, 2200 (C≡C), 1466, 1341, 1098, 898 cm⁻¹.

Anal. Calcd for C₉H₁₅BrO: C, 49.33; H, 6.90. Found: C, 49.48; H, 6.57.

11-Bromo-10-undecyn-1-ol (25). Starting bromoacetylene for 39. This is a known compound [Yamagishi, M.; Nishigai, K.; Hata, T.; Urabe, H. *Org. Lett.* **2011**, *13*, 4873-4875].

¹H NMR δ 1.25-1.61 (m, 15H), 2.20 (t, *J* = 7.0 Hz, 2H), 3.64 (t, *J* = 6.6 Hz, 2H).

¹³C NMR δ 19.64, 25.68, 28.24, 28.71, 28.96, 29.32, 29.39, 32.76, 37.43 (C≡C), 63.04, 80.44 (C≡C).

IR (neat) 3344 (O-H), 2929, 2856, 2218 (C≡C), 1464, 1214, 1057, 758 cm⁻¹.

Anal. Calcd for C₁₁H₁₉BrO: C, 53.45; H, 7.75. Found: C, 53.62; H, 7.63.

1-Bromo-1-octyn-3-ol (26). Starting bromoacetylene for 40. This is a known compound

[Yamagishi, M.; Nishigai, K.; Hata, T.; Urabe, H. *Org. Lett.* **2011**, *13*, 4873-4875].

^1H NMR δ 0.90 (t, $J = 6.8$ Hz, 3H), 1.24-1.50 (m, 6H), 1.70 (m, 2H), 2.01 (br s, 1H), 4.39 (t, $J = 6.6$ Hz, 1H).

^{13}C NMR δ 13.95, 22.50, 24.67, 31.36, 37.59, 44.86 (C \equiv C), 63.43, 81.22 (C \equiv C).

IR (neat) 3340 (O-H), 2951, 2934, 2861, 2219 (C \equiv C), 1477, 1341, 1133, 1034, 735 cm^{-1} .

Anal. Calcd for $\text{C}_8\text{H}_{13}\text{BrO}$: C, 46.85; H, 6.39. Found: C, 46.84; H, 6.16.

***N*-(4-Methylphenyl)methyl]ethanesulfonamide (27). Starting sulfonamide for 32.**

^1H NMR δ 1.29 (t, $J = 7.6$ Hz, 3H), 2.34 (s, 3H), 2.92 (q, $J = 7.6$ Hz, 2H), 4.24 (d, $J = 6.0$ Hz, 2H), 4.75 (br s, 1H), 7.15 (d, $J = 8.0$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 2H).

^{13}C NMR δ 8.17, 21.06, 46.87, 47.45, 127.81 (2 carbons), 129.44 (2 carbons), 133.90, 137.73.

IR (KBr) 3287 (N-H), 3009, 2977, 2939, 1517, 1434, 1313, 1139, 1059, 869, 810, 722 cm^{-1} .

HRMS (ESI) Calcd for $\text{C}_{10}\text{H}_{15}\text{NO}_2\text{SNa}$ [M+Na] $^+$: 236.0716. Found: 236.0719.

M.p. 67-69 $^\circ\text{C}$.

***N*-(4-Methoxyphenyl)methyl]ethanesulfonamide (28). Starting sulfonamide for 33.**

^1H NMR δ 1.32 (t, $J = 7.4$ Hz, 3H), 2.94 (q, $J = 7.4$ Hz, 2H), 3.81 (s, 3H), 4.24 (d, $J = 5.6$ Hz, 2H), 4.41 (br t, $J = 5.6$ Hz, 1H), 6.89 (d, $J = 8.8$ Hz, 2H), 7.27 (d, $J = 8.8$ Hz, 2H).

^{13}C NMR δ 8.21, 46.66, 47.51, 55.27, 114.15 (2 carbons), 128.95, 129.27 (2 carbons), 159.33.

IR (KBr) 3281 (N-H), 3034, 2927, 2842, 1514, 1313, 1130, 1030, 849, 723 cm^{-1} .

HRMS (ESI) Calcd for $\text{C}_{10}\text{H}_{15}\text{NO}_3\text{SNa}$ [M+Na] $^+$: 252.0665. Found: 252.0664.

M.p. 75-77 $^\circ\text{C}$.

***N*-(4-Chlorophenyl)methyl]ethanesulfonamide (29). Starting sulfonamide for 34.**

^1H NMR δ 1.31 (t, $J = 7.4$ Hz, 3H), 2.94 (q, $J = 7.4$ Hz, 2H), 4.26 (d, $J = 6.0$ Hz, 2H), 4.87 (br s, 1H), 7.29 (d, $J = 8.4$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H).

^{13}C NMR δ 8.18, 46.38, 47.68, 128.94 (2 carbons), 129.19 (2 carbons), 133.82, 135.59.

IR (KBr) 3284 (N-H), 3034, 2978, 2939, 1492, 1437, 1323, 1140, 1066, 868, 728 cm^{-1} .

HRMS (ESI) Calcd for $\text{C}_9\text{H}_{12}^{35}\text{ClNO}_2\text{SNa}$ [M+Na] $^+$: 256.0169. Found: 256.0169.

M.p. 93-95 $^\circ\text{C}$.

***N*-(2-Methylphenyl)methyl]ethanesulfonamide (30). Starting sulfonamide for 35.**

^1H NMR δ 1.29 (t, $J = 7.4$ Hz, 3H), 2.37 (s, 3H), 2.93 (q, $J = 7.4$ Hz, 2H), 4.27 (d, $J = 6.0$ Hz, 2H), 4.66 (br s, 1H), 7.15-7.24 (m, 3H), 7.30 (d, $J = 6.8$ Hz, 1H).

^{13}C NMR δ 8.11, 18.89, 45.06, 47.24, 126.25, 128.18, 128.67, 130.63, 134.57, 136.36.

IR (KBr) 3277 (N-H), 3023, 2974, 2938, 1317, 1137, 1044, 886, 758 cm^{-1} .

HRMS (ESI) Calcd for $\text{C}_{10}\text{H}_{15}\text{NO}_2\text{SNa}$ [M+Na] $^+$: 236.0716. Found: 236.0711.

M.p. 50-52 $^\circ\text{C}$.

***N*-[(3,5-Dimethylphenyl)methyl]ethanesulfonamide (31). Starting sulfonamide for 36.**

¹H NMR δ 1.33 (t, *J* = 7.4 Hz, 3H), 2.31 (s, 6H), 2.97 (q, *J* = 7.4 Hz, 2H), 4.22 (d, *J* = 6.0 Hz, 2H), 4.47 (br s, 1H), 6.95 (s, 3H).

¹³C NMR δ 8.22, 21.20 (2 carbons), 47.12, 47.38, 125.60 (2 carbons), 129.60 (2 carbons), 136.72, 138.47.

IR (KBr) 3235 (N-H), 3007, 2978, 2939, 1609, 1309, 1131, 1051, 872, 713 cm⁻¹.

HRMS (ESI) Calcd for C₁₁H₁₇NO₂SNa [M+Na]⁺: 250.0872. Found: 250.0868.

M.p. 38-39 °C.

***(Z)*-*N*-(1-Bromo-1-octen-2-yl)-*N*-[(4-methylphenyl)methyl]ethanesulfonamide (32).**

A mixture of 1-bromo-1-octyne (**2**) (37.8 mg, 0.200 mmol), *N*-[(4-methylphenyl)methyl]ethanesulfonamide (**27**) (128 mg, 0.599 mmol), and K₃PO₄ (64.3 mg, 0.303 mmol) in DMF (0.20 mL) was stirred in an oil bath maintained at 120 °C for 2 h under argon. After being cooled to room temperature, the reaction mixture was diluted with water (3 mL) and extracted with ethyl acetate (3 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude product, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (58.1 mg, 72%) as an oil and as a single isomer.

¹H NMR δ 0.81 (t, *J* = 7.4 Hz, 3H), 1.02-1.22 (m, 8H), 1.43 (t, *J* = 7.4 Hz, 3H), 1.99 (br s, 2H), 2.32 (s, 3H), 3.17 (q, *J* = 7.4 Hz, 2H), 4.60 (s, 2H), 6.07 (t, *J* = 1.4 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H).

¹³C NMR δ 8.24, 14.00, 21.14, 22.39, 26.60, 28.58, 31.39, 37.68, 49.23, 52.14, 105.26, 129.10 (2 carbons), 129.35 (2 carbons), 132.93, 137.92, 144.62.

IR (neat) 3093, 2926, 2857, 1615, 1457, 1340, 1148, 1045, 885, 805, 727 cm⁻¹.

HRMS (ESI) Calcd for C₁₈H₂₈⁷⁹BrNO₂SNa [M+Na]⁺: 424.0916. Found: 424.0910.

***(Z)*-*N*-(1-Bromo-1-octen-2-yl)-*N*-[(4-methoxyphenyl)methyl]ethanesulfonamide (33).**

A mixture of 1-bromo-1-octyne (**2**) (39.0 mg, 0.206 mmol), *N*-[(4-methoxyphenyl)methyl]ethanesulfonamide (**28**) (138 mg, 0.601 mmol), and K₃PO₄ (64.1 mg, 0.302 mmol) in DMF (0.20 mL) was stirred in an oil bath maintained at 120 °C for 2 h under argon. After being cooled to room temperature, the reaction mixture was diluted with water (3 mL) and extracted with ethyl acetate (3 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude product, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (54.0 mg, 63%) as an oil and as a single isomer.

¹H NMR δ 0.83 (t, *J* = 7.2 Hz, 3H), 1.06-1.26 (m, 8H), 1.45 (t, *J* = 7.2 Hz, 3H), 2.02 (br s, 2H), 3.17 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 4.61 (s, 2H), 6.09 (t, *J* = 1.6 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H),

7.31 (d, $J = 8.8$ Hz, 2H).

^{13}C NMR δ 8.21, 13.96, 22.37, 26.60, 28.57, 31.39, 37.75, 49.24, 51.84, 55.20, 105.22, 113.73 (2 carbons), 128.04, 130.71 (2 carbons), 144.63, 159.49.

IR (neat) 3083, 2930, 2857, 1612, 1514, 1339, 1248, 1147, 1039, 885, 809, 728 cm^{-1} .

HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{28}^{79}\text{BrNO}_3\text{SNa}$ [$\text{M}+\text{Na}$] $^+$: 440.0865. Found: 440.0857.

(Z)-N-(1-Bromo-1-octen-2-yl)-N-[(4-chlorophenyl)methyl]ethanesulfonamide (34).

A mixture of 1-bromo-1-octyne (**2**) (37.1 mg, 0.196 mmol), *N*-[(4-chlorophenyl)methyl]ethanesulfonamide (**29**) (141 mg, 0.602 mmol), and K_3PO_4 (63.4 mg, 0.299 mmol) in DMF (0.22 mL) was stirred in an oil bath maintained at 120 °C for 2 h under argon. After being cooled to room temperature, the reaction mixture was diluted with water (3 mL) and extracted with ethyl acetate (3 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude product, ^1H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (54.8 mg, 66%) as an oil and as a single isomer.

^1H NMR δ 0.84 (t, $J = 7.2$ Hz, 3H), 1.05-1.26 (m, 8H), 1.46 (t, $J = 7.4$ Hz, 3H), 2.04 (br s, 2H), 3.20 (q, $J = 7.4$ Hz, 2H), 4.63 (s, 2H), 6.11 (s, 1H), 7.30 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H).

^{13}C NMR δ 8.23, 13.98, 22.40, 26.72, 28.56, 31.39, 37.77, 49.23, 51.76, 105.43, 128.65 (2 carbons), 130.75 (2 carbons), 134.17, 134.69, 144.55.

IR (neat) 3091, 2929, 2857, 1621, 1492, 1340, 1147, 1044, 886, 802, 722 cm^{-1} .

HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{25}^{79}\text{Br}^{35}\text{ClNO}_2\text{SNa}$ [$\text{M}+\text{Na}$] $^+$: 444.0370. Found: 444.0376.

(Z)-N-(1-Bromo-1-octen-2-yl)-N-[(2-methylphenyl)methyl]ethanesulfonamide (35).

A mixture of 1-bromo-1-octyne (**2**) (38.7 mg, 0.205 mmol), *N*-[(2-methylphenyl)methyl]ethanesulfonamide (**30**) (130 mg, 0.612 mmol), and K_3PO_4 (65.4 mg, 0.308 mmol) in DMF (0.20 mL) was stirred in an oil bath maintained at 120 °C for 2 h under argon. After being cooled to room temperature, the reaction mixture was diluted with water (3 mL) and extracted with ethyl acetate (3 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude product, ^1H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (50.8 mg, 62%) as an oil and as a single isomer.

^1H NMR δ 0.82 (t, $J = 7.2$ Hz, 3H), 1.01-1.12 (m, 6H), 1.16 (m, 2H), 1.47 (t, $J = 7.2$ Hz, 3H), 1.95 (br s, 2H), 2.43 (s, 3H), 3.21 (q, $J = 7.2$ Hz, 2H), 4.77 (s, 2H), 6.09 (t, $J = 1.6$ Hz, 1H), 7.12-7.23 (m, 3H), 7.34 (m, 1H).

NOESY experiments showed correlation between the peaks at δ 1.95 ppm (br s, 2H, $\text{CH}_2\text{C}=\text{CBr}$) and at δ 6.09 ppm (t, $J = 1.6$ Hz, 1H, CHBr). Thus, the stereochemistry of the olefinic bond has been confirmed.

^{13}C NMR δ 8.22, 13.95, 19.26, 22.34, 26.43, 28.49, 31.34, 37.93, 49.09 (2 carbons), 105.26, 125.88, 128.36, 130.44, 130.80, 133.53, 137.47, 144.44.

IR (neat) 3078, 2929, 2858, 1618, 1459, 1340, 1149, 1037, 888, 743 cm^{-1} .

HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{28}^{79}\text{BrNO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 424.0916. Found: 424.0918.

(Z)-N-(1-Bromo-1-octen-2-yl)-N-[(3,5-dimethylphenyl)methyl]ethanesulfonamide (36).

A mixture of 1-bromo-1-octyne (**2**) (37.9 mg, 0.200 mmol), *N*-[(3,5-dimethylphenyl)methyl]ethanesulfonamide (**31**) (136 mg, 0.598 mmol), and K_3PO_4 (63.7 mg, 0.300 mmol) in DMF (0.20 mL) was stirred in an oil bath maintained at 120 °C for 2 h under argon. After being cooled to room temperature, the reaction mixture was diluted with water (3 mL) and extracted with ethyl acetate (3 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude product, ^1H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (54.5 mg, 65%) as an oil and as a single isomer.

^1H NMR δ 0.83 (t, $J = 7.2$ Hz, 3H), 1.04-1.26 (m, 8H), 1.46 (t, $J = 7.4$ Hz, 3H), 2.02 (br s, 2H), 2.30 (s, 6H), 3.21 (q, $J = 7.4$ Hz, 2H), 4.58 (s, 2H), 6.09 (t, $J = 1.6$ Hz, 1H), 6.93 (s, 1H), 6.99 (s, 2H).

^{13}C NMR δ 8.25, 13.99, 21.18 (2 carbons), 22.40, 26.61, 28.58, 31.42, 37.66, 49.18, 52.31, 105.20, 127.10 (2 carbons), 129.72 (2 carbons), 135.78, 137.95, 144.57.

IR (neat) 3088, 2927, 2857, 1608, 1460, 1341, 1148, 1047, 878, 782, 728, 643 cm^{-1} .

HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{30}^{79}\text{BrNO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 438.1073. Found: 438.1068.

(Z)-N-Benzyl-N-[5-(benzyloxy)-1-bromo-1-penten-2-yl]ethanesulfonamide (37).

A mixture of 5-(benzyloxy)-1-bromo-1-pentyne (**23**) (53.5 mg, 0.211 mmol), *N*-benzylethanesulfonamide (**4**) (120 mg, 0.603 mmol), and K_3PO_4 (64.7 mg, 0.305 mmol) in DMF (0.20 mL) was stirred in an oil bath maintained at 120 °C for 2 h under argon. After being cooled to room temperature, the reaction mixture was diluted with water (3 mL) and extracted with ethyl acetate (3 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude product, ^1H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (62.9 mg, 66%) as an oil and as a single isomer.

^1H NMR δ 1.45 (t, $J = 7.4$ Hz, 3H), 1.49 (m, 2H), 2.16 (br s, 2H), 3.20 (q, $J = 7.4$ Hz, 2H), 3.26 (t, $J = 6.4$ Hz, 2H), 4.39 (s, 2H), 4.66 (s, 2H), 6.11 (s, 1H), 7.24-7.40 (m, 10H).

^{13}C NMR δ 8.19, 26.78, 34.07, 49.18, 52.33, 68.92, 72.68, 105.74, 127.51, 127.56 (2 carbons), 128.20, 128.30 (2 carbons), 128.48 (2 carbons), 129.34 (2 carbons), 135.89, 138.34, 143.75.

IR (neat) 3031, 2919, 2850, 1625, 1455, 1338, 1147, 1042, 880, 737, 700 cm^{-1} .

HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{26}^{79}\text{BrNO}_3\text{SNa}$ $[\text{M}+\text{Na}]^+$: 474.0709. Found: 474.0709.

(Z)-N-Benzyl-N-(1-bromo-3-methoxy-1-octen-2-yl)ethanesulfonamide (38).

A mixture of 1-bromo-3-methoxy-1-octyne (**24**) (45.8 mg, 0.209 mmol), *N*-benzylethanesulfonamide (**4**) (122 mg, 0.614 mmol), and K₃PO₄ (66.2 mg, 0.312 mmol) in DMF (0.20 mL) was stirred in an oil bath maintained at 120 °C for 2 h under argon. After being cooled to room temperature, the reaction mixture was diluted with water (3 mL) and extracted with ethyl acetate (3 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (43.6 mg, 50%) as an oil and as a single isomer.

¹H NMR δ 0.82 (t, *J* = 7.4 Hz, 3H), 0.86-1.34 (m, 8H), 1.45 (t, *J* = 7.4 Hz, 3H), 3.18 (q, *J* = 7.4 Hz, 2H), 3.21 (s, 3H), 3.75 (br m, 1H), 4.68 (d, *J* = 14.8 Hz, 1H), 4.84 (br d, *J* = 14.8 Hz, 1H), 6.51 (d, *J* = 0.8 Hz, 1H), 7.27-7.35 (m, 3H), 7.41 (m, 2H).

¹³C NMR δ 8.20, 13.96, 22.40, 25.06, 31.41, 33.79, 48.85, 53.00, 57.07, 84.55, 107.88, 128.21, 128.51 (2 carbons), 129.39 (2 carbons), 136.50, 144.52.

IR (neat) 3032, 2929, 2858, 1612, 1457, 1343, 1149, 1043, 726, 702 cm⁻¹.

HRMS (ESI) Calcd for C₁₈H₂₈⁷⁹BrNO₃SNa [M+Na]⁺: 440.0865. Found: 440.0852.

(Z)-N-Benzyl-N-(1-bromo-11-hydroxy-1-undecen-2-yl)ethanesulfonamide (39).

A mixture of 11-bromo-10-undecyn-1-ol (**25**) (48.1 mg, 0.195 mmol), *N*-benzylethanesulfonamide (**4**) (117 mg, 0.586 mmol), and K₃PO₄ (62.2 mg, 0.293 mmol) in DMF (0.20 mL) was stirred in an oil bath maintained at 120 °C for 2 h under argon. After being cooled to room temperature, the reaction mixture was diluted with water (3 mL) and extracted with ethyl acetate (3 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford a mixture of the title compound and starting sulfonamide **4** (138 mg) as an oil. This sample was further purified by a recycling preparative HPLC [Model LC-9201R/U equipped with a JAIGEL-H column (length: 600 mm x 2 cycles, bore: 20 mm), Japan Analytical Industry Co., Ltd. (Japan); eluent: chloroform (3.5 mL/min)] to afford the pure title compound (58.2 mg, 67%) as an oil.

¹H NMR δ 1.04-1.43 (m, 13H), 1.46 (t, *J* = 7.6 Hz, 3H), 1.55 (m, 2H), 2.01 (br s, 2H), 3.20 (q, *J* = 7.6 Hz, 2H), 3.63 (t, *J* = 6.4 Hz, 2H), 4.66 (s, 2H), 6.10 (t, *J* = 1.4 Hz, 1H), 7.27-7.36 (m, 3H), 7.39 (m, 2H).

¹³C NMR δ 8.23, 25.63, 26.61, 28.84, 29.06, 29.25, 29.26, 32.73, 37.65, 49.23, 52.40, 63.00, 105.35, 128.17, 128.45 (2 carbons), 129.39 (2 carbons), 136.00, 144.55.

IR (neat) 3447 (O-H), 3031, 2928, 2854, 1620, 1456, 1337, 1185, 1147, 1047, 884, 726, 702 cm⁻¹.

HRMS (ESI) Calcd for C₂₀H₃₂⁷⁹BrNO₃SNa [M+Na]⁺: 468.1178. Found: 468.1168.

(Z)-N-Benzyl-N-(1-bromo-3-hydroxy-1-octen-2-yl)ethanesulfonamide (40).

A mixture of 1-bromo-1-octyn-3-ol (**26**) (41.1 mg, 0.200 mmol), *N*-benzylethanesulfonamide (**4**)

(119 mg, 0.598 mmol), and K_3PO_4 (64.4 mg, 0.303 mmol) in DMF (0.20 mL) was stirred in an oil bath maintained at 120 °C for 2 h under argon. After being cooled to room temperature, the reaction mixture was diluted with water (3 mL) and extracted with ethyl acetate (3 mL x 3). The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude product, 1H NMR analysis of which showed the presence of a single isomer. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (49.4 mg, 61%) as a solid and as a single isomer.

1H NMR δ 0.81 (t, $J = 7.2$ Hz, 3H), 0.88-1.30 (m, 8H), 1.48 (t, $J = 7.4$ Hz, 3H), 3.02 (br s, 1H), 3.23 (q, $J = 7.4$ Hz, 2H), 3.82 (br s, 1H), 4.66 (br s, 1H), 4.82 (br s, 1H), 6.58 (s, 1H), 7.28-7.42 (m, 5H).

^{13}C NMR δ 8.19, 13.93, 22.36, 25.60, 31.32, 35.28, 49.12, 52.60, 75.70, 110.64, 128.42, 128.62 (2 carbons), 129.52 (2 carbons), 136.03, 147.84.

IR (KBr) 3530 (O-H), 3062, 2932, 2866, 1620, 1455, 1336, 1138, 1049, 892, 702, 594 cm^{-1} .

HRMS (ESI) Calcd for $C_{17}H_{26}^{79}BrNO_3SNa$ $[M+Na]^+$: 426.0709. Found: 426.0712.

M.p. 67-69°C.

2-Ethanesulfonyl-3-hexyl-6-methyl-1,2-dihydroisoquinoline (41).

A mixture of *N*-(bromoalkenyl)sulfonamide **32** (57.0 mg, 0.142 mmol), triphenylphosphine (11.2 mg, 0.043 mmol), KOAc (41.7 mg, 0.425 mmol), and palladium acetate (3.2 mg, 0.014 mmol) in DMF (0.42 mL) was stirred in an oil bath maintained at 120 °C for 45 min under argon. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate (3 mL) and filtered through Celite with the aid of ethyl acetate. The combined filtrates were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, in which the aromatized product was not detected by 1H NMR analysis. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (35.9 mg, 79%) as an oil.

1H NMR δ 0.89 (t, $J = 7.4$ Hz, 3H), 1.09 (t, $J = 7.6$ Hz, 3H), 1.26-1.48 (m, 6H), 1.66 (m, 2H), 2.33 (s, 3H), 2.61 (t, $J = 7.6$ Hz, 2H), 2.61 (q, $J = 7.6$ Hz, 2H), 4.62 (s, 2H), 6.28 (s, 1H), 6.91 (s, 1H), 7.03 (s, 2H).

^{13}C NMR δ 7.53, 14.05, 21.20, 22.59, 28.44, 28.82, 31.60, 35.53, 46.31, 50.18, 118.34, 124.71, 125.25, 127.22, 128.30, 131.59, 137.81, 142.45.

IR (neat) 3042, 2927, 2857, 1632, 1458, 1343, 1151, 1039, 907, 736, 605 cm^{-1} .

HRMS (ESI) Calcd for $C_{18}H_{27}NO_2SNa$ $[M+Na]^+$: 344.1655. Found: 344.1651.

2-Ethanesulfonyl-3-hexyl-6-methoxy-1,2-dihydroisoquinoline (42).

A mixture of *N*-(bromoalkenyl)sulfonamide **33** (63.3 mg, 0.151 mmol), triphenylphosphine (12.1 mg, 0.046 mmol), KOAc (45.3 mg, 0.462 mmol), and palladium acetate (3.5 mg, 0.016 mmol) in DMF (0.46 mL) was stirred in an oil bath maintained at 120 °C for 45 min under argon. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate (3 mL) and filtered through Celite with the aid of ethyl acetate. The combined filtrates were washed

successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, in which the aromatized product was not detected by ^1H NMR analysis. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (39.7 mg, 78%) as an oil.

^1H NMR δ 0.89 (t, $J = 7.0$ Hz, 3H), 1.10 (t, $J = 7.6$ Hz, 3H), 1.24-1.41 (m, 6H), 1.66 (quintet, $J = 7.4$ Hz, 2H), 2.61 (t, $J = 7.4$ Hz, 2H), 2.62 (q, $J = 7.6$ Hz, 2H), 3.80 (s, 3H), 4.61 (s, 2H), 6.28 (s, 1H), 6.65 (d, $J = 2.4$ Hz, 1H), 6.75 (dd, $J = 2.4, 8.4$ Hz, 1H), 7.06 (d, $J = 8.4$ Hz, 1H).

^{13}C NMR δ 7.56, 14.06, 22.60, 28.45, 28.84, 31.62, 35.55, 46.45, 49.95, 55.32, 110.13, 112.77, 118.24, 122.48, 125.80, 132.88, 143.13, 159.53.

IR (neat) 3047, 2928, 2856, 1630, 1499, 1343, 1185, 1151, 1040, 903, 737 cm^{-1} .

HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{27}\text{NO}_3\text{SNa}$ $[\text{M}+\text{Na}]^+$: 360.1604. Found: 360.1594.

6-Chloro-2-ethanesulfonyl-3-hexyl-1,2-dihydroisoquinoline (43).

A mixture of *N*-(bromoalkenyl)sulfonamide **34** (54.3 mg, 0.128 mmol), triphenylphosphine (10.1 mg, 0.039 mmol), KOAc (37.0 mg, 0.377 mmol), and palladium acetate (2.9 mg, 0.013 mmol) in DMF (0.39 mL) was stirred in an oil bath maintained at 120 °C for 45 min under argon. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate (3 mL) and filtered through Celite with the aid of ethyl acetate. The combined filtrates were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, in which the aromatized product was not detected by ^1H NMR analysis. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (37.6 mg, 86%) as an oil.

^1H NMR δ 0.89 (t, $J = 7.0$ Hz, 3H), 1.11 (t, $J = 7.6$ Hz, 3H), 1.22-1.46 (m, 6H), 1.66 (quintet, $J = 7.6$ Hz, 2H), 2.62 (t, $J = 7.6$ Hz, 2H), 2.65 (q, $J = 7.6$ Hz, 2H), 4.64 (s, 2H), 6.25 (s, 1H), 7.09 (d, $J = 2.0$ Hz, 1H), 7.09 (d, $J = 8.0$ Hz, 1H), 7.19 (dd, $J = 2.0, 8.0$ Hz, 1H).

^{13}C NMR δ 7.56, 14.03, 22.55, 28.39, 28.81, 31.55, 35.45, 46.76, 49.85, 116.84, 124.38, 126.05, 127.41, 128.22, 133.31, 133.81, 144.09.

IR (neat) 3024, 2927, 2856, 1628, 1485, 1345, 1152, 1040, 910, 737 cm^{-1} .

HRMS (FAB, NBA) Calcd for $\text{C}_{17}\text{H}_{24}^{35}\text{ClNO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 364.1114. Found: 364.1110.

2-Ethanesulfonyl-3-hexyl-8-methyl-1,2-dihydroisoquinoline (44).

A mixture of *N*-(bromoalkenyl)sulfonamide **35** (56.1 mg, 0.139 mmol), triphenylphosphine (11.0 mg, 0.042 mmol), KOAc (41.2 mg, 0.420 mmol), and palladium acetate (3.1 mg, 0.014 mmol) in DMF (0.42 mL) was stirred in an oil bath maintained at 120 °C for 45 min under argon. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate (3 mL) and filtered through Celite with the aid of ethyl acetate. The combined filtrates were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, in which the aromatized product was not detected by ^1H NMR analysis. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (35.5 mg, 79%)

as an oil.

^1H NMR δ 0.89 (t, $J = 7.2$ Hz, 3H), 1.06 (t, $J = 7.4$ Hz, 3H), 1.24-1.42 (m, 6H), 1.67 (quintet, $J = 7.4$ Hz, 2H), 2.33 (s, 3H), 2.60 (q, $J = 7.4$ Hz, 2H), 2.61 (t, $J = 7.4$ Hz, 2H), 4.69 (s, 2H), 6.30 (s, 1H), 6.94 (d, $J = 7.6$ Hz, 1H), 7.06 (d, $J = 7.6$ Hz, 1H), 7.14 (t, $J = 7.6$ Hz, 1H).

^{13}C NMR δ 7.50, 14.06, 18.58, 22.61, 28.39, 28.84, 31.63, 35.33, 46.25, 47.34, 118.72, 122.46, 127.56, 128.76, 129.58, 131.66, 133.19, 142.01.

IR (neat) 3020, 2927, 2856, 1633, 1468, 1345, 1151, 1060, 897, 778, 530 cm^{-1} .

HRMS (FAB, NBA) Calcd for $\text{C}_{18}\text{H}_{27}\text{NO}_2\text{S}$ $[\text{M}]^+$: 321.1763. Found: 321.1758.

2-Ethanesulfonyl-3-hexyl-5,7-dimethyl-1,2-dihydroisoquinoline (45).

A mixture of *N*-(bromoalkenyl)sulfonamide **36** (61.3 mg, 0.147 mmol), triphenylphosphine (11.6 mg, 0.044 mmol), KOAc (43.9 mg, 0.447 mmol), and palladium acetate (3.3 mg, 0.015 mmol) in DMF (0.44 mL) was stirred in an oil bath maintained at 120 °C for 45 min under argon. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate (3 mL) and filtered through Celite with the aid of ethyl acetate. The combined filtrates were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, in which the aromatized product was not detected by ^1H NMR analysis. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (38.4 mg, 78%) as an oil.

^1H NMR δ 0.89 (t, $J = 6.8$ Hz, 3H), 1.11 (t, $J = 7.6$ Hz, 3H), 1.24-1.42 (m, 6H), 1.67 (quintet, $J = 7.2$ Hz, 2H), 2.30 (s, 6H), 2.58 (t, $J = 7.2$ Hz, 2H), 2.61 (q, $J = 7.6$ Hz, 2H), 4.58 (s, 2H), 6.41 (s, 1H), 6.81 (s, 1H), 6.91 (s, 1H).

^{13}C NMR δ 7.54, 14.06, 18.69, 21.16, 22.60, 28.57, 28.85, 31.62, 35.81, 46.25, 50.78, 115.75, 123.38, 127.32, 130.40 (2 carbons), 132.36, 137.30, 141.42.

IR (neat) 3054, 2926, 2856, 1628, 1458, 1344, 1152, 1048, 910, 741, 645 cm^{-1} .

HRMS (FAB, NBA) Calcd for $\text{C}_{19}\text{H}_{29}\text{NO}_2\text{S}$ $[\text{M}]^+$: 335.1919. Found: 335.1919.

3-[3-(Benzyloxy)propyl]-2-ethanesulfonyl-1,2-dihydroisoquinoline (46).

A mixture of *N*-(bromoalkenyl)sulfonamide **37** (63.3 mg, 0.140 mmol), triphenylphosphine (11.0 mg, 0.041 mmol), KOAc (41.2 mg, 0.420 mmol), and palladium acetate (3.1 mg, 0.014 mmol) in DMF (0.41 mL) was stirred in an oil bath maintained at 120 °C for 45 min under argon. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate (3 mL) and filtered through Celite with the aid of ethyl acetate. The combined filtrates were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, in which the aromatized product was not detected by ^1H NMR analysis. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (41.1 mg, 79%) as an oil.

^1H NMR δ 1.07 (t, $J = 7.6$ Hz, 3H), 2.00 (m, 2H), 2.62 (q, $J = 7.6$ Hz, 2H), 2.73 (t, $J = 7.4$ Hz, 2H), 3.55 (t, $J = 6.2$ Hz, 2H), 4.50 (s, 2H), 4.62 (s, 2H), 6.32 (s, 1H), 7.08 (d, $J = 7.2$ Hz, 1H), 7.13 (d, J

= 7.2 Hz, 1H), 7.19-7.36 (m, 7H).

¹³C NMR δ 7.51, 28.45, 32.25, 46.40, 50.32, 69.35, 72.94, 118.71, 124.61, 124.86, 127.51, 127.73 (2 carbons), 127.79, 128.16, 128.31 (2 carbons), 130.03, 131.54, 138.47, 141.59.

IR (neat) 3029, 2938, 2855, 1630, 1454, 1342, 1185, 1150, 1040, 912, 756 cm⁻¹.

HRMS (ESI) Calcd for C₂₁H₂₅NO₃SNa [M+Na]⁺: 394.1447. Found: 394.1441.

2-Ethanesulfonyl-3-(1-methoxyhexyl)-1,2-dihydroisoquinoline (47).

A mixture of *N*-(bromoalkenyl)sulfonamide **38** (62.5 mg, 0.149 mmol), triphenylphosphine (11.8 mg, 0.045 mmol), KOAc (43.9 mg, 0.447 mmol), and palladium acetate (3.4 mg, 0.015 mmol) in DMF (0.45 mL) was stirred in an oil bath maintained at 120 °C for 45 min under argon. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate (3 mL) and filtered through Celite with the aid of ethyl acetate. The combined filtrates were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, in which the aromatized product was not detected by ¹H NMR analysis. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (42.3 mg, 84%) as an oil.

¹H NMR δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.4 Hz, 3H), 1.24-1.56 (m, 6H), 1.64 (m, 1H), 1.83 (m, 1H), 2.49 (qd, *J* = 7.4, 14.4 Hz, 1H), 2.72 (qd, *J* = 7.4, 14.4 Hz, 1H), 3.45 (s, 3H), 4.40 (d, *J* = 16.4 Hz, 1H), 4.42 (t, *J* = 6.4 Hz, 1H), 4.93 (d, *J* = 16.4 Hz, 1H), 6.71 (s, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H).

¹³C NMR δ 7.54, 14.03, 22.58, 25.21, 31.73, 36.42, 46.24, 50.38, 57.50, 81.22, 117.50, 124.97, 125.48, 128.24, 128.35, 130.37, 131.11, 142.78.

IR (neat) 3021, 2930, 2858, 1632, 1455, 1344, 1150, 1039, 914, 761, 639 cm⁻¹.

HRMS (FAB, NBA) Calcd for C₁₈H₂₇NO₃S [M]⁺: 337.1712. Found: 337.1712.

2-Ethanesulfonyl-3-(9-hydroxynonyl)-1,2-dihydroisoquinoline (48).

A mixture of *N*-(bromoalkenyl)sulfonamide **39** (59.3 mg, 0.133 mmol), triphenylphosphine (10.5 mg, 0.040 mmol), KOAc (39.6 mg, 0.404 mmol), and palladium acetate (3.0 mg, 0.013 mmol) in DMF (0.40 mL) was stirred in an oil bath maintained at 120 °C for 45 min under argon. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate (3 mL) and filtered through Celite with the aid of ethyl acetate. The combined filtrates were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, in which the aromatized product was not detected by ¹H NMR analysis. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (38.9 mg, 80%) as an oil.

¹H NMR δ 1.08 (t, *J* = 7.4 Hz, 3H), 1.22-1.46 (m, 11H), 1.56 (quintet, *J* = 7.0 Hz, 2H), 1.67 (m, 2H), 2.61 (t, *J* = 7.4 Hz, 2H), 2.61 (q, *J* = 7.4 Hz, 2H), 3.64 (t, *J* = 7.0 Hz, 2H), 4.67 (s, 2H), 6.33 (s, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H).

^{13}C NMR δ 7.51, 25.66, 28.42, 29.09, 29.26, 29.32, 29.45, 32.74, 35.47, 46.34, 50.36, 63.02, 118.22, 124.54, 124.86, 127.68, 128.15, 130.02, 131.64, 142.51.

IR (neat) 3448 (O-H), 3068, 2930, 2858, 1630, 1455, 1340, 1186, 1149, 1060, 757, 530 cm^{-1} .

HRMS (FAB, NBA) Calcd for $\text{C}_{20}\text{H}_{31}\text{NO}_3\text{S}$ $[\text{M}]^+$: 365.2025. Found: 365.2030.

2-Ethanesulfonyl-3-(1-hydroxyhexyl)-1,2-dihydroisoquinoline (49).

A mixture of *N*-(bromoalkenyl)sulfonamide **40** (47.7 mg, 0.118 mmol), triphenylphosphine (9.3 mg, 0.035 mmol), KOAc (35.2 mg, 0.359 mmol), and palladium acetate (2.6 mg, 0.012 mmol) in DMF (0.35 mL) was stirred in an oil bath maintained at 120 °C for 45 min under argon. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate (3 mL) and filtered through Celite with the aid of ethyl acetate. The combined filtrates were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, in which the aromatized product was not detected by ^1H NMR analysis. The crude sample was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (33.7 mg, 88%) as an oil.

^1H NMR δ 0.90 (t, J = 7.0 Hz, 3H), 1.09 (t, J = 7.4 Hz, 3H), 1.24-1.56 (m, 6H), 1.78 (m, 1H), 1.89 (m, 1H), 2.64 (m, 2H), 2.94 (br s, 1H), 4.60 (t, J = 6.6 Hz, 1H), 4.62 (d, J = 16.4 Hz, 1H), 4.72 (d, J = 16.4 Hz, 1H), 6.72 (s, 1H), 7.16-7.22 (m, 2H), 7.24-7.35 (m, 2H).

^{13}C NMR δ 7.44, 13.99, 22.59, 25.59, 31.66, 36.16, 46.01, 50.53, 72.73, 119.63, 124.97, 125.60, 128.41, 128.54, 130.50, 130.98, 143.67.

IR (neat) 3451 (O-H), 3022, 2929, 2857, 1632, 1455, 1341, 1185, 1150, 1040, 914, 760, 639 cm^{-1} .

HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_3\text{SNa}$ $[\text{M}+\text{Na}]^+$: 346.1447. Found: 346.1447.

2-Ethanesulfonyl-3-hexyl-1,2,3,4-tetrahydroisoquinoline (50).

A mixture of **15** (42.9 mg, 0.140 mmol) and 10%-Pd/C (15.8 mg, 0.015 mmol) in MeOH (0.60 mL) was stirred at room temperature for 24 h under H_2 (1 atm). The solution was filtered through Celite with the aid of MeOH (2 mL x 4). The combined filtrates were concentrated *in vacuo* to give a crude oil, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (39.8 mg, 92%) as an oil.

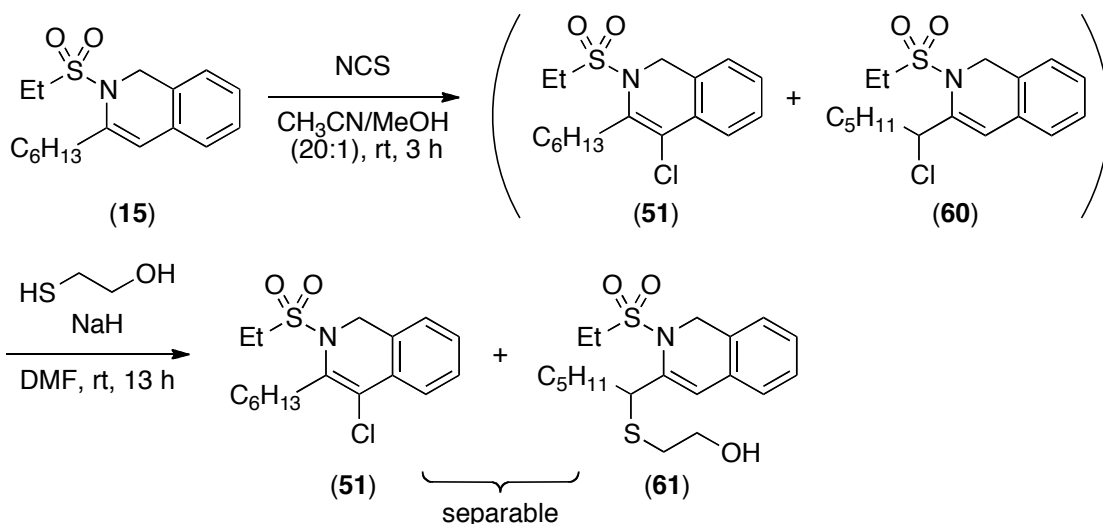
^1H NMR δ 0.86 (t, J = 6.8 Hz, 3H), 1.16-1.32 (m, 6H), 1.28 (t, J = 7.2 Hz, 3H), 1.32-1.50 (m, 3H), 1.61 (m, 1H), 2.67 (d, J = 16.2 Hz, 1H), 2.89 (dq, J = 14.4, 7.2 Hz, 1H), 2.94 (dq, J = 14.4, 7.2 Hz, 1H), 3.14 (dd, J = 6.0, 16.2 Hz, 1H), 4.16 (m, 1H), 4.31 (d, J = 17.0 Hz, 1H), 4.64 (d, J = 17.0 Hz, 1H), 7.08 (m, 1H), 7.12 (m, 1H), 7.16-7.23 (m, 2H).

^{13}C NMR δ 8.11, 13.97, 22.52, 26.20, 28.98, 31.68, 32.07, 32.70, 42.91, 46.83, 51.76, 125.78, 126.34, 126.99, 129.69, 131.98, 132.36.

IR (neat) 3023, 2928, 2852, 1453, 1330, 1140, 1040, 959, 722, 509 cm^{-1} .

HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{27}\text{NO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 332.1655. Found: 332.1655.

4-Chloro-2-ethanesulfonyl-3-hexyl-1,2-dihydroisoquinoline (51).



A mixture of **15** (62.2 mg, 0.202 mmol) and *N*-chlorosuccinimide (30.2 mg, 0.226 mmol) in CH₃CN (1.4 mL) and MeOH (0.07 mL) was stirred in a test tube covered with aluminum foil at room temperature for 3 h under argon. The reaction mixture was diluted with ethyl acetate and washed successively with aqueous Na₂S₂O₃ solution, saturated aqueous NaHCO₃ solution, water, and brine. The organic layer was dried over Na₂SO₄ and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which revealed the presence of **51** and 3-(1-chlorohexyl)-2-ethanesulfonyl-1,2-dihydroisoquinoline (**60**) in 86 and 10% yields, respectively. As chloride **51** and **60** could not be separated by silica gel chromatography, pure **51** was isolated as follows. To a stirred suspension of NaH (3.1 mg of a 60 % dispersion in oil, 0.080 mmol) in DMF (0.20 mL) was added 2-mercaptoethanol (6.1 mg, 0.080 mmol) in DMF (0.40 mL) dropwise at 0 °C under argon. After the solution was stirred at 0 °C for 15 min, the above crude mixture of **51** and **60** in DMF (0.40 mL) was added. Then the reaction mixture was warmed to room temperature, stirred for 13 h, diluted with ethyl acetate, and quenched with water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which revealed the presence of **51** and 2-ethanesulfonyl-3-[1-(2-hydroxyethylthio)hexyl]-1,2-dihydroisoquinoline (**61**) in 93 and 3% yields, respectively. The crude oil was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (52.2 mg, 75%) as an oil and as a single regioisomer.

¹H NMR δ 0.90 (t, *J* = 7.0 Hz, 3H), 1.09 (t, *J* = 7.4 Hz, 3H), 1.28-1.46 (m, 6H), 1.71 (quintet, *J* = 7.2 Hz, 2H), 2.53 (q, *J* = 7.4 Hz, 2H), 2.86 (t, *J* = 7.2 Hz, 2H), 4.67 (s, 2H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.59 (d, *J* = 7.2 Hz, 1H).

¹³C NMR δ 7.46, 14.02, 22.56, 28.20, 29.02, 31.59, 32.45, 46.59, 50.01, 124.14, 124.54, 124.94, 128.42, 129.97, 130.95, 131.66, 139.13.

IR (neat) 3070, 2928, 2857, 1606, 1452, 1344, 1154, 1025, 950, 934, 768, 626 cm⁻¹.

HRMS (ESI) Calcd for C₁₇H₂₄³⁵ClNO₂SNa [M+Na]⁺: 364.1108. Found: 364.1101.

3-(1-Chlorohexyl)-2-ethanesulfonyl-1,2-dihydroisoquinoline (60).

¹H NMR (only characteristic peaks are shown) δ 2.02 (m, 1H), 2.16 (m, 1H), 2.69 (dq, $J = 14.8, 7.2$ Hz, 1H), 4.62 (d, $J = 16.4$ Hz, 1H), 4.78 (d, $J = 16.4$ Hz, 1H), 5.17 (dd, $J = 5.0, 8.4$ Hz, 1H), 6.87 (s, 1H).

2-Ethanesulfonyl-3-[1-(2-hydroxyethylthio)hexyl]-1,2-dihydroisoquinoline (61).

¹H NMR (only characteristic peaks are shown) δ 1.92 (m, 1H), 2.19 (br t, $J = 6.0$ Hz, 1H), 2.59 (q, $J = 7.6$ Hz, 2H), 2.82 (t, $J = 6.0$ Hz, 1H), 2.83 (t, $J = 6.0$ Hz, 1H), 3.79 (br q, $J = 6.0$ Hz, 1H), 4.13 (t, $J = 7.2$ Hz, 1H), 4.71 (s, 2H), 6.72 (s, 1H), 7.14-7.22 (m, 2H), 7.24-7.32 (m, 2H).

3-(1-Bromohexyl)-2-ethanesulfonyl-1,2-dihydroisoquinoline (52).

To a solution of **15** (154 mg, 0.500 mmol) in CH₂Cl₂ (1.0 mL) was added Br₂ (88.3 mg, 0.553 mmol) in CH₂Cl₂ (0.50 mL) at 0 °C under argon. The reaction mixture was stirred at the same temperature for 15 min, diluted with CH₂Cl₂, and quenched with aqueous Na₂S₂O₃ solution. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂. The combined organic layers were washed successively with water and brine, dried over Na₂SO₄, and concentrated *in vacuo* to give the spectroscopically pure title compound (190 mg, 98%) as an oil. Attempted purification of the product on silica gel resulted in the considerable decomposition.

As this compound appears to suffer from the inhibition of free rotation of the sulfonamide and bromoalkyl side chains in the NMR time scale due to the steric hindrance between them, its ¹³C NMR spectrum shows an increased number of peaks.

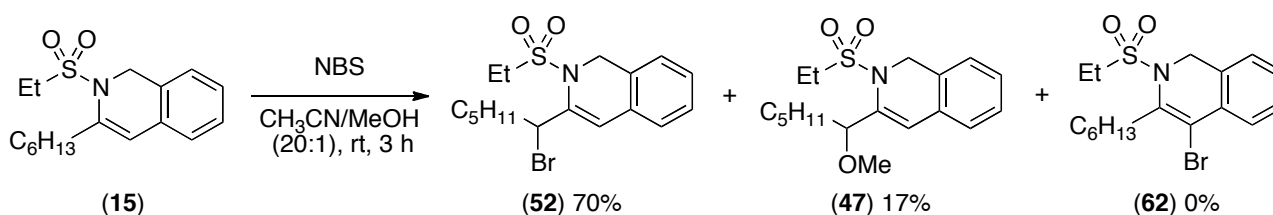
¹H NMR δ 0.92 (t, $J = 6.8$ Hz, 3H), 1.17 (t, $J = 7.2$ Hz, 3H), 1.29-1.43 (m, 4H), 1.50 (m, 1H), 1.64 (m, 1H), 2.10-2.22 (m, 2H), 2.65 (dq, $J = 14.0, 7.2$ Hz, 1H), 2.70 (dq, $J = 14.0, 7.2$ Hz, 1H), 4.63 (d, $J = 16.2$ Hz, 1H), 4.84 (d, $J = 16.2$ Hz, 1H), 5.26 (dd, $J = 6.4, 8.0$ Hz, 1H), 6.84 (s, 1H), 7.14-7.23 (m, 2H), 7.26-7.33 (m, 2H).

¹³C NMR δ 7.26, 13.92, 22.42, 27.54, 31.09, 37.01, 46.79, 50.67, [53.19 (0.50 C), 53.24 (0.50 C)], 120.70, 125.02, 126.02, 128.40, 129.18, 130.66, 130.82, 142.30. The values in square brackets may be attributable to the same carbon for the above reason.

IR (neat) 3069, 2928, 2845, 1624, 1453, 1344, 1149, 1036, 912, 756, 737, 642 cm⁻¹.

HRMS (FAB, NBA) Calcd for C₁₇H₂₄⁷⁹BrNO₂S [M]⁺: 385.0711. Found: 385.0701.

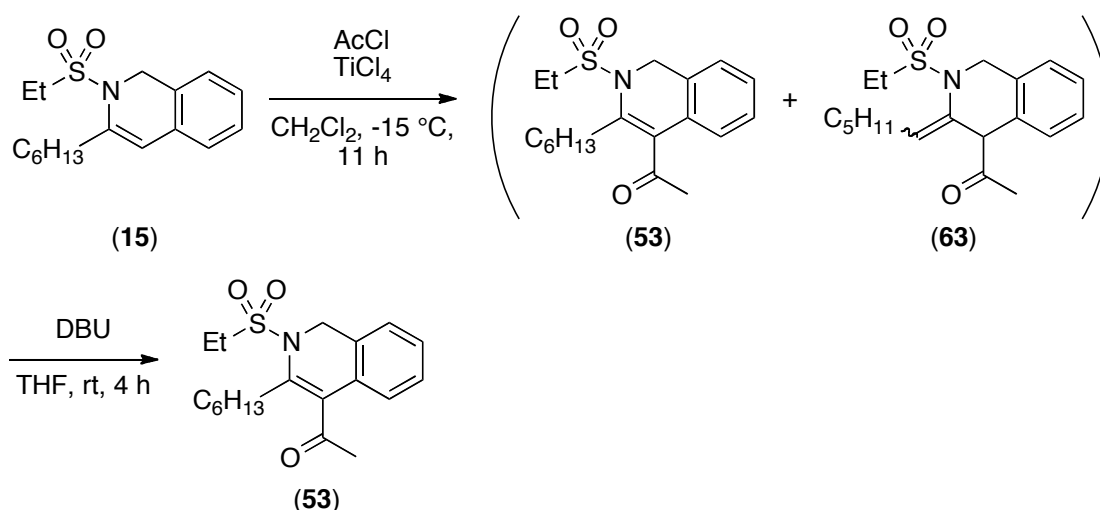
Bromination of **15** with *N*-bromosuccinimide under the same reaction conditions as those of *N*-chlorosuccinimide.



A mixture of **15** (60.9 mg, 0.198 mmol) and *N*-bromosuccinimide (39.0 mg, 0.219 mmol) in CH₃CN (1.4 mL) and MeOH (0.07 mL) was stirred in a test tube covered with aluminum foil at room temperature for 3 h under argon. The reaction mixture was diluted with ethyl acetate and

washed successively with aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution, saturated aqueous NaHCO_3 solution, water, and brine. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give a crude oil, ^1H NMR analysis of which revealed the formation of **52**, 2-ethanesulfonyl-3-(1-methoxyhexyl)-1,2-dihydroisoquinoline (**47**), and 4-bromo-2-ethanesulfonyl-1,2-dihydroisoquinoline (**62**) in 70, 17, and 0% yields, respectively.

4-Acetyl-2-ethanesulfonyl-3-hexyl-1,2-dihydroisoquinoline (**53**).



To a solution of **15** (42.9 mg, 0.140 mmol) in CH_2Cl_2 (1.0 mL) were added dropwise AcCl (0.030 mL, 0.422 mmol) and TiCl_4 (1.0 M in CH_2Cl_2 , 0.420 mL, 0.420 mmol) in this order at -15°C under argon. The reaction mixture was stirred for 11 h and quenched with water at the same temperature. The heterogeneous solution was diluted with CH_2Cl_2 and neutralized with saturated aqueous NaHCO_3 solution. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 . The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, ^1H NMR analysis of which revealed the presence of **53** and 4-acetyl-2-ethanesulfonyl-3-hexylidene-1,2,3,4-tetrahydroisoquinoline (**63**) in 63 and 13% yields, respectively. Minor regioisomer **63** was successfully converted to **53** as follows. To a solution of this crude mixture of **53** and **63** in THF (0.20 mL) was added DBU (2.8 mg, 0.018 mmol) in THF (0.50 mL). The mixture was stirred at room temperature for 4 h under argon and diluted with ethyl acetate. The solution was washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (33.7 mg, 69%) as an oil and as a single regioisomer.

^1H NMR δ 0.89 (t, $J = 7.2$ Hz, 3H), 1.05 (t, $J = 7.6$ Hz, 3H), 1.24-1.40 (m, 6H), 1.69 (quintet, $J = 7.6$ Hz, 2H), 2.42 (s, 3H), 2.54 (q, $J = 7.6$ Hz, 2H), 2.65 (t, $J = 7.6$ Hz, 2H), 4.65 (s, 2H), 7.05 (m, 1H), 7.24 (m, 1H), 7.27-7.34 (m, 2H).

^{13}C NMR δ 7.41, 13.96, 22.51, 29.05, 29.12, 31.52, 31.93, 32.85, 47.01, 50.26, 123.20, 125.40, 128.49, 128.59, 128.99, 130.75, 132.80, 140.26, 203.46 (C=O).

IR (neat) 3070, 2928, 2857, 1695 (C=O), 1609, 1453, 1344, 1149, 1034, 779, 704, 599 cm^{-1} .

HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{27}\text{NO}_3\text{SNa}$ $[\text{M}+\text{Na}]^+$: 372.1604. Found: 372.1593.

4-Acetyl-2-ethanesulfonyl-3-hexylidene-1,2,3,4-tetrahydroisoquinoline (63).

^1H NMR (only characteristic peaks are shown) δ 2.18 (q, $J = 7.6$ Hz, 2H), 2.22 (s, 3H), 2.87 (dq, $J = 14.0, 7.2$ Hz, 1H), 2.95 (dq, $J = 14.0, 7.2$ Hz, 1H), 4.68 (s, 2H), 4.76 (s, 1H), 5.96 (t, $J = 7.6$ Hz, 1H).

2-Ethanesulfonyl-4-heptanoyl-3-hexyl-1,2-dihydroisoquinoline (54).

To a solution of **15** (39.5 mg, 0.128 mmol) in CH_2Cl_2 (0.90 mL) were added dropwise heptanoyl chloride (0.060 mL, 0.389 mmol) and TiCl_4 (1.0 M in CH_2Cl_2 , 0.390 mL, 0.390 mmol) in this order at -15 $^\circ\text{C}$ under argon. The reaction mixture was stirred for 8 h and quenched with water at the same temperature. The heterogeneous solution was diluted with CH_2Cl_2 and neutralized with saturated aqueous NaHCO_3 solution. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 . The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, ^1H NMR analysis of which revealed the clean formation of the α,β -unsaturated ketone without contamination by its β,γ -unsaturated isomer. The crude oil was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (35.8 mg, 67%) as an oil.

^1H NMR δ 0.87 (t, $J = 6.8$ Hz, 3H), 0.88 (t, $J = 6.4$ Hz, 3H), 1.05 (t, $J = 7.6$ Hz, 3H), 1.20-1.40 (m, 12H), 1.60-1.75 (m, 4H), 2.53 (q, $J = 7.6$ Hz, 2H), 2.59 (t, $J = 7.6$ Hz, 2H), 2.65 (t, $J = 7.4$ Hz, 2H), 4.67 (s, 2H), 7.01 (m, 1H), 7.23 (m, 1H), 7.27-7.32 (m, 2H).

^{13}C NMR δ 7.41, 13.93, 13.96, 22.43, 22.53, 23.65, 28.78, 29.13, 29.22, 31.53, 31.56, 33.01, 44.53, 46.93, 50.31, 123.13, 125.39, 128.45, 128.50, 129.27, 130.62, 132.67, 139.97, 206.17 (C=O).

IR (neat) 3066, 2928, 2852, 1695 (C=O), 1606, 1452, 1344, 1144, 1040, 914, 779, 731, 527 cm^{-1} .

HRMS (ESI) Calcd for $\text{C}_{24}\text{H}_{37}\text{NO}_3\text{SNa}$ $[\text{M}+\text{Na}]^+$: 442.2386. Found: 442.2374.

1-Butyl-3-hexyl-4-hydroxyisoquinoline (55). The similar aerial oxidation of 1,2-dihydroisoquinolines has been reported in the following literature [Uno, H.; Okada, S.; Suzuki, H. *J. Heterocyclic. Chem.* **1991**, 28, 341-346].

To a mixture of **15** (56.1 mg, 0.183 mmol) and *t*-BuOK (61.9 mg, 0.552 mmol) in THF (1.3 mL) was added *n*-BuLi (1.60 M in hexane, 0.340 mL, 0.544 mmol) dropwise at -78 $^\circ\text{C}$ under argon. After the solution was stirred at the same temperature for 1.5 h under argon, air dried with CaCl_2 was introduced to the reaction mixture, which was further stirred at -78 $^\circ\text{C}$ for 2 h. The reaction mixture was quenched with water at -78 $^\circ\text{C}$ and extracted ethyl acetate twice. The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (29.7 mg, 57%) as a solid.

^1H NMR δ 0.85 (t, $J = 6.8$ Hz, 3H), 0.94 (t, $J = 7.2$ Hz, 3H), 1.20-1.39 (m, 6H), 1.44 (sextet, $J = 7.2$ Hz, 2H), 1.68-1.82 (m, 4H), 2.90 (t, $J = 7.8$ Hz, 2H), 3.20 (t, $J = 8.0$ Hz, 2H), 3.40 (br s, 1H), 7.51 (t,

$J = 8.0$ Hz, 1H), 7.63 (t, $J = 8.0$ Hz, 1H), 8.05 (d, $J = 8.0$ Hz, 1H), 8.15 (d, $J = 8.0$ Hz, 1H).

^{13}C NMR δ 13.93, 14.02, 22.59, 22.89, 29.16, 29.33, 31.81, 32.15, 32.42, 34.80, 121.14, 125.29, 125.98, 126.32, 128.36, 128.79, 137.52, 142.11, 153.96.

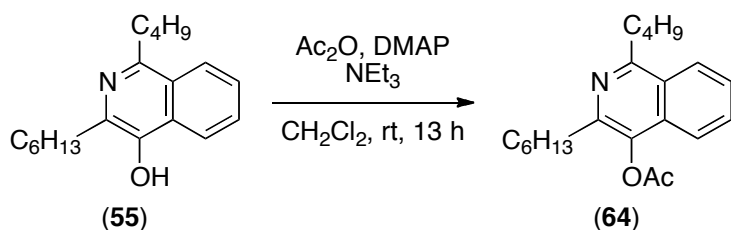
IR (KBr) 3070, 2951, 2918, 2852, 1577, 1463, 1367, 1191, 1106, 774, 647, 490 cm^{-1} .

Obvious absorption of O-H (around 3500 cm^{-1}) was not observed in the IR spectrum (however, see below).

HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{28}\text{NO}$ $[\text{M}+\text{H}]^+$: 286.2165. Found: 286.2165.

M.p. 89-91 $^{\circ}\text{C}$.

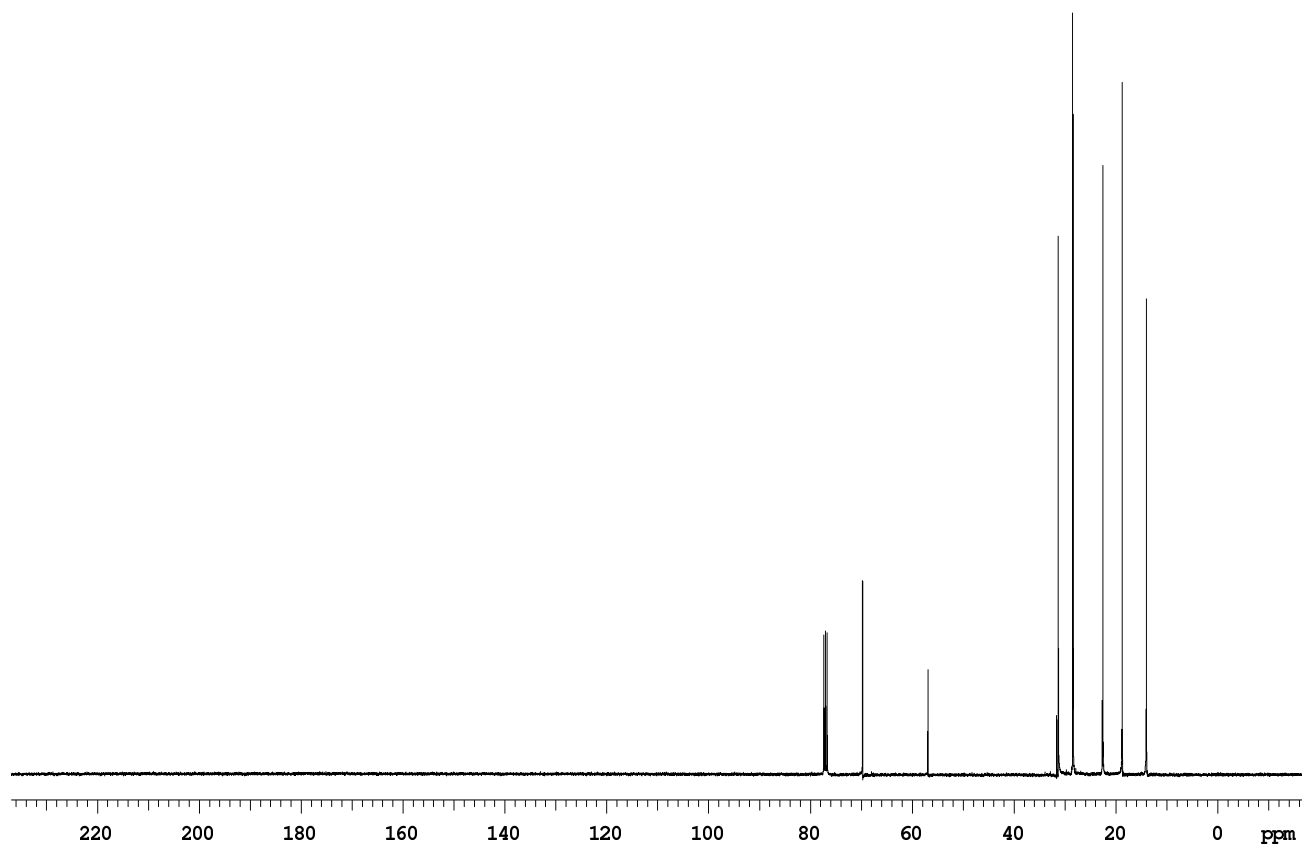
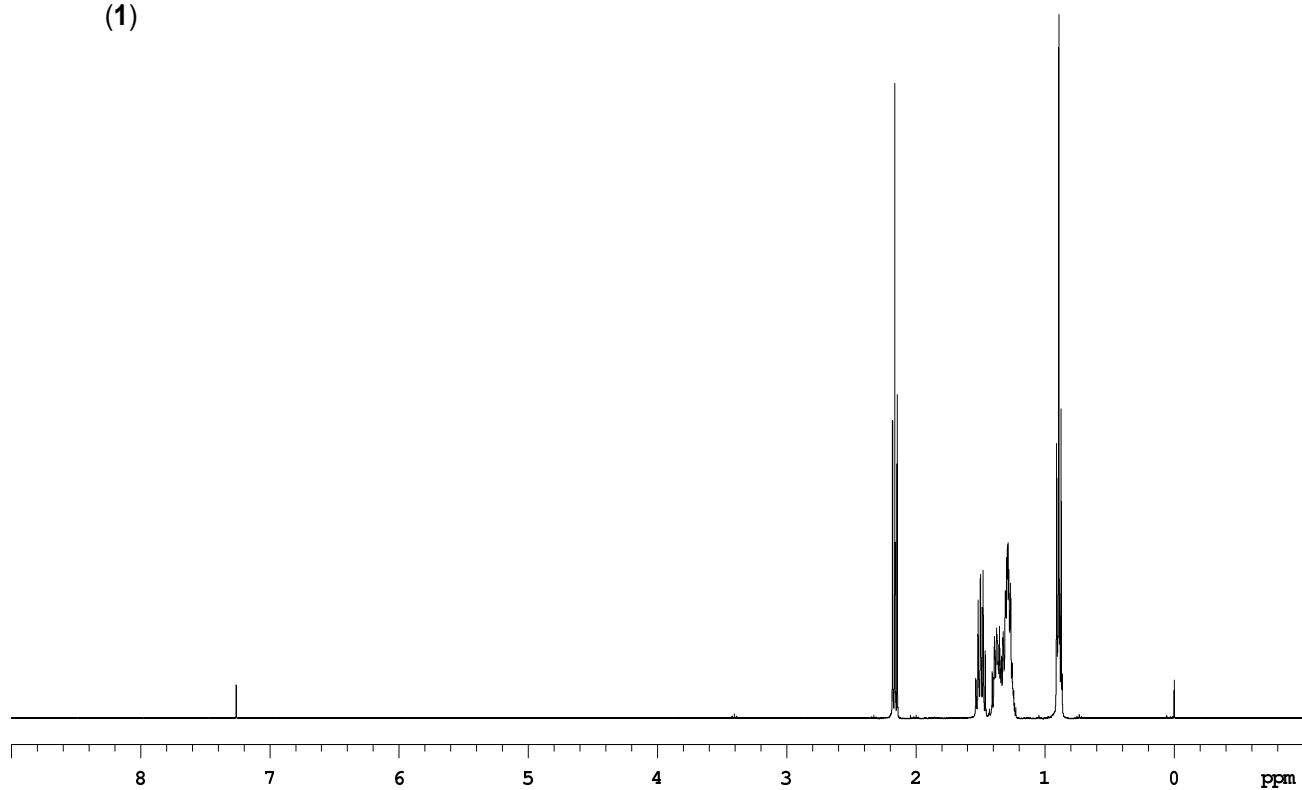
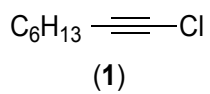
Structural confirmation of **55**. 4-Acetyloxy-1-butyl-3-hexyloquinoline (**64**).

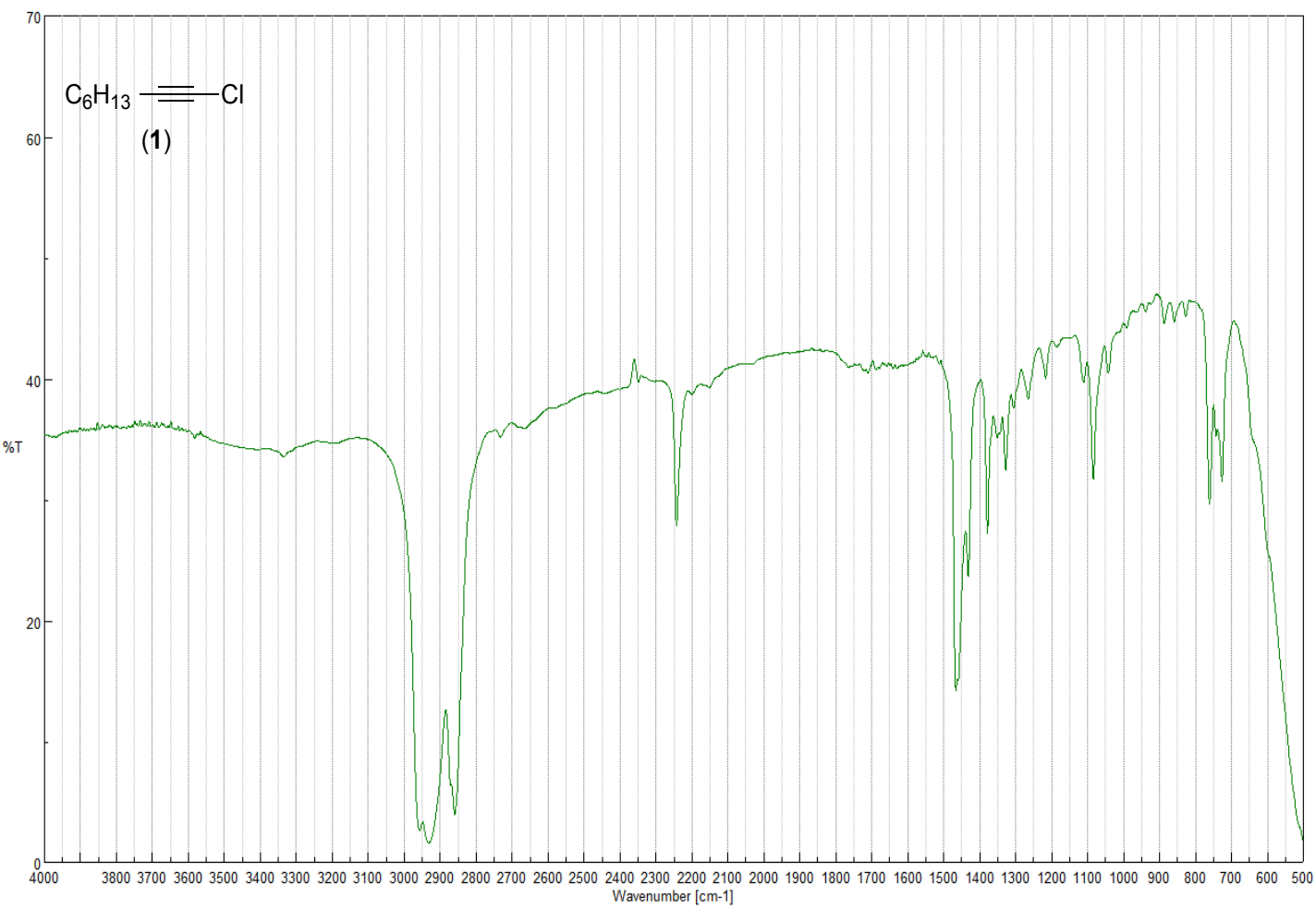
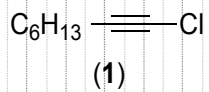


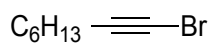
To a solution of **55** (9.4 mg, 0.033 mmol) in CH_2Cl_2 (0.50 mL) were added NEt_3 (0.030 mL, 0.216 mmol), 4-(*N,N*-dimethylamino)pyridine (4.0 mg, 0.033 mmol), and Ac_2O (0.010 mL, 0.106 mmol) in this order at 0 $^{\circ}\text{C}$. After being stirred for 13 h at room temperature, the reaction mixture was quenched with water and diluted with ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed successively with water and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (7.7 mg, 71%) as an oil.

^1H NMR δ 0.88 (t, $J = 6.8$ Hz, 3H), 0.98 (t, $J = 7.6$ Hz, 3H), 1.22-1.44 (m, 6H), 1.48 (sextet, $J = 7.6$ Hz, 2H), 1.75 (quintet, $J = 7.6$ Hz, 2H), 1.83 (quintet, $J = 7.6$ Hz, 2H), 2.48 (s, 3H), 2.78 (t, $J = 7.6$ Hz, 2H), 3.23 (t, $J = 7.6$ Hz, 2H), 7.52 (t, $J = 8.4$ Hz, 1H), 7.61-7.70 (m, 2H), 8.10 (d, $J = 8.4$ Hz, 1H).

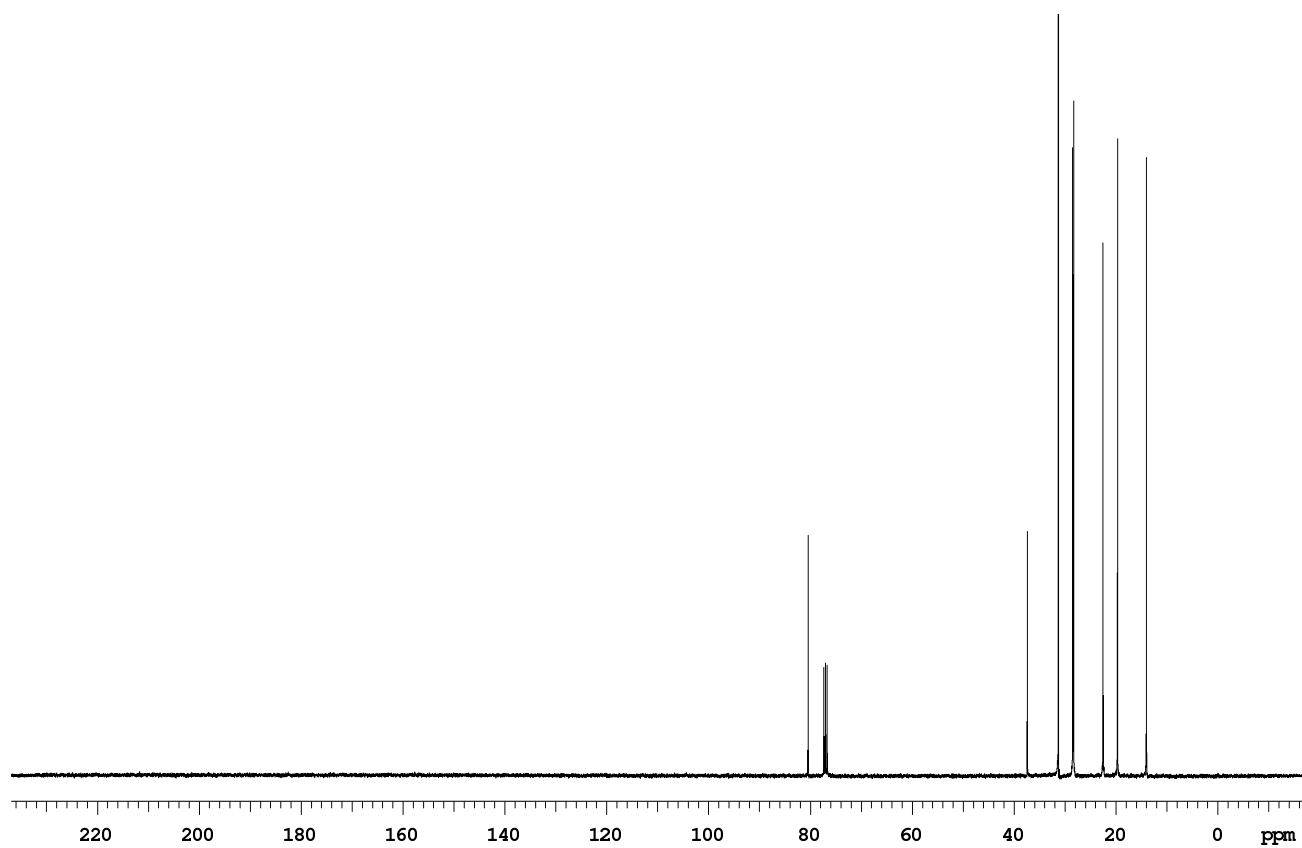
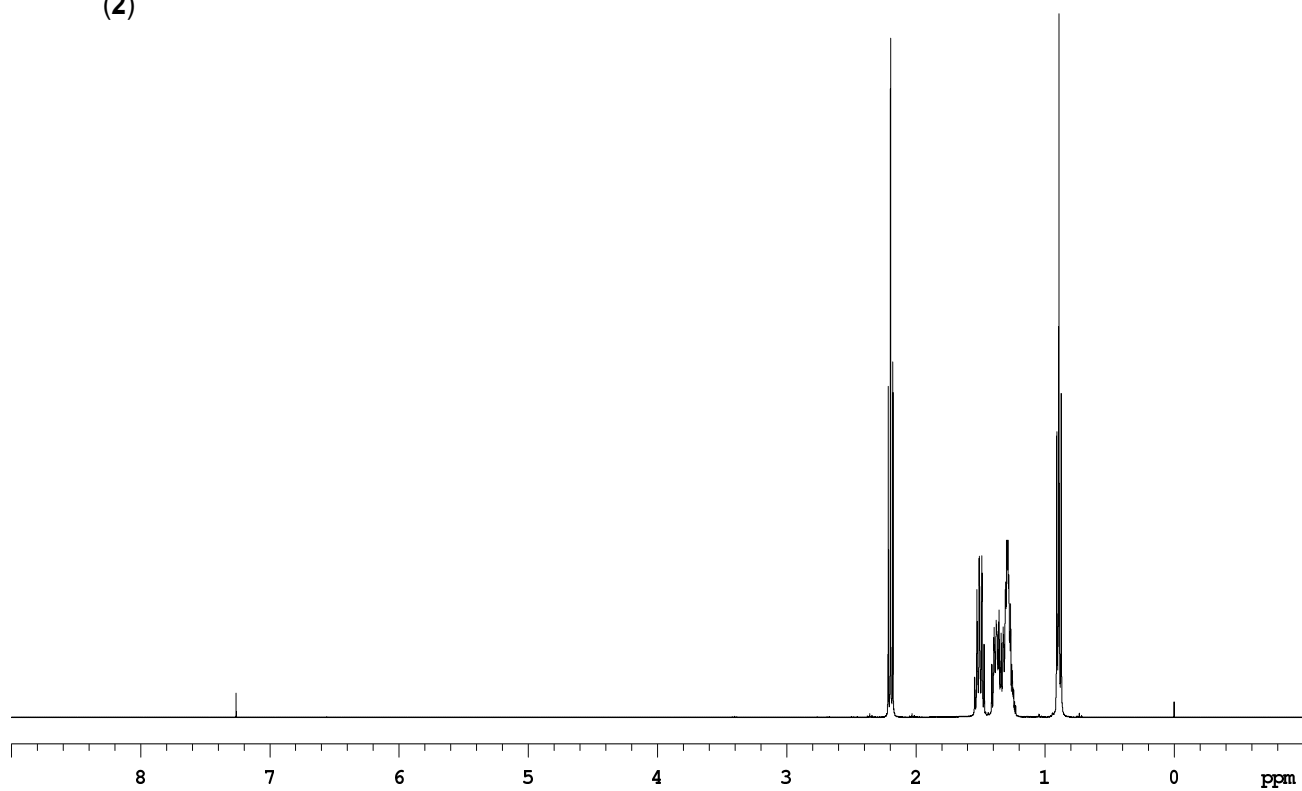
The introduction of an acetyl group indicates the presence of a hydroxyl group in **55**.

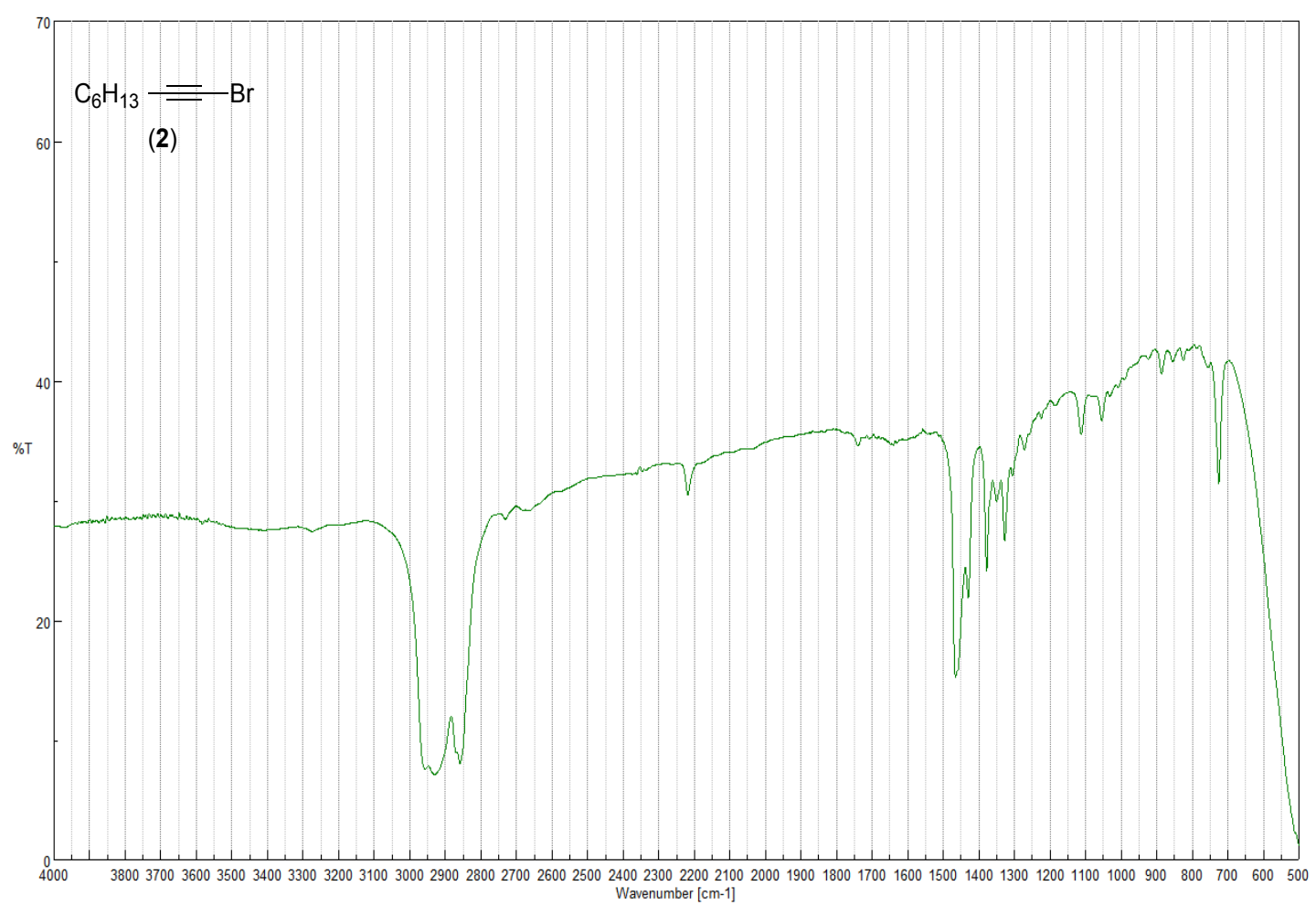
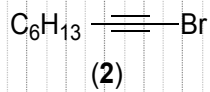


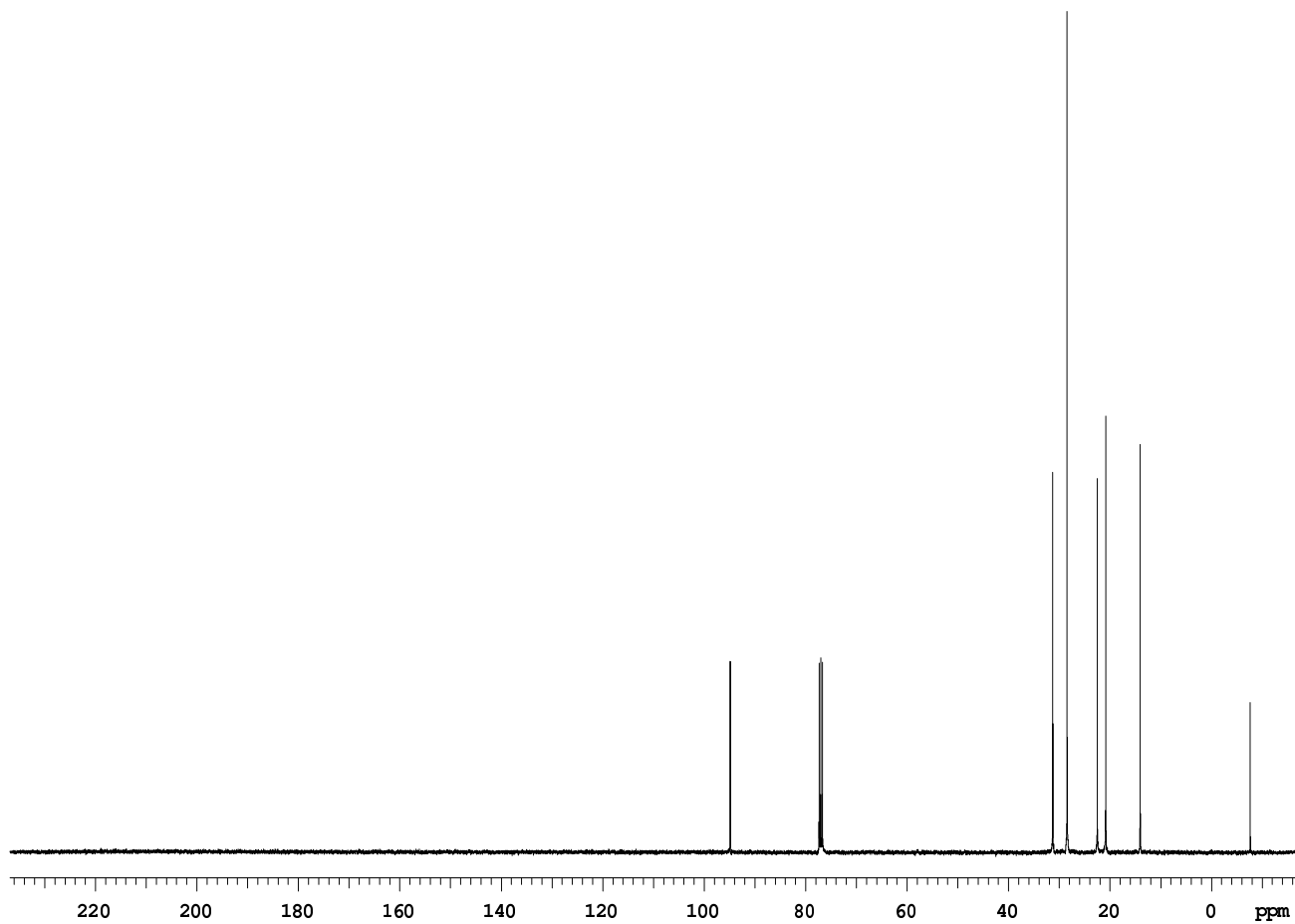
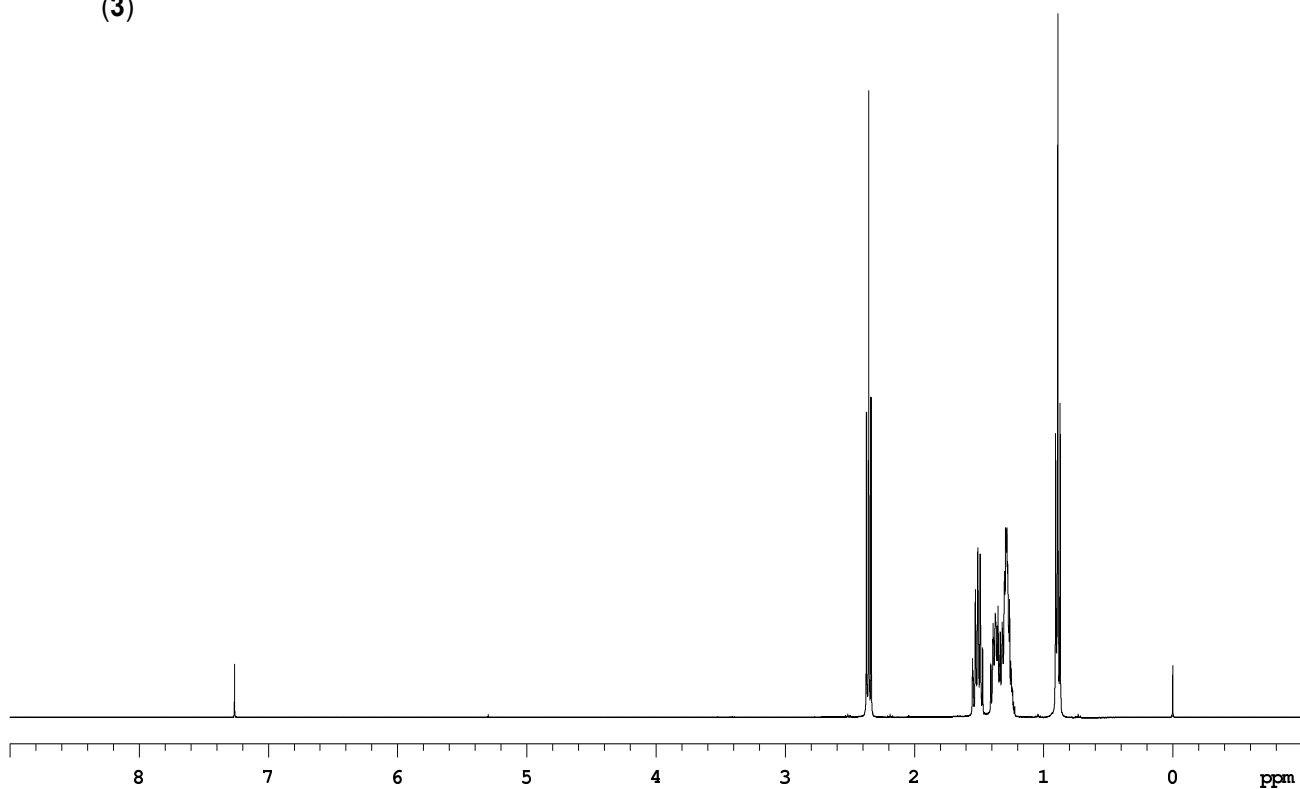
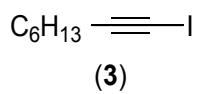


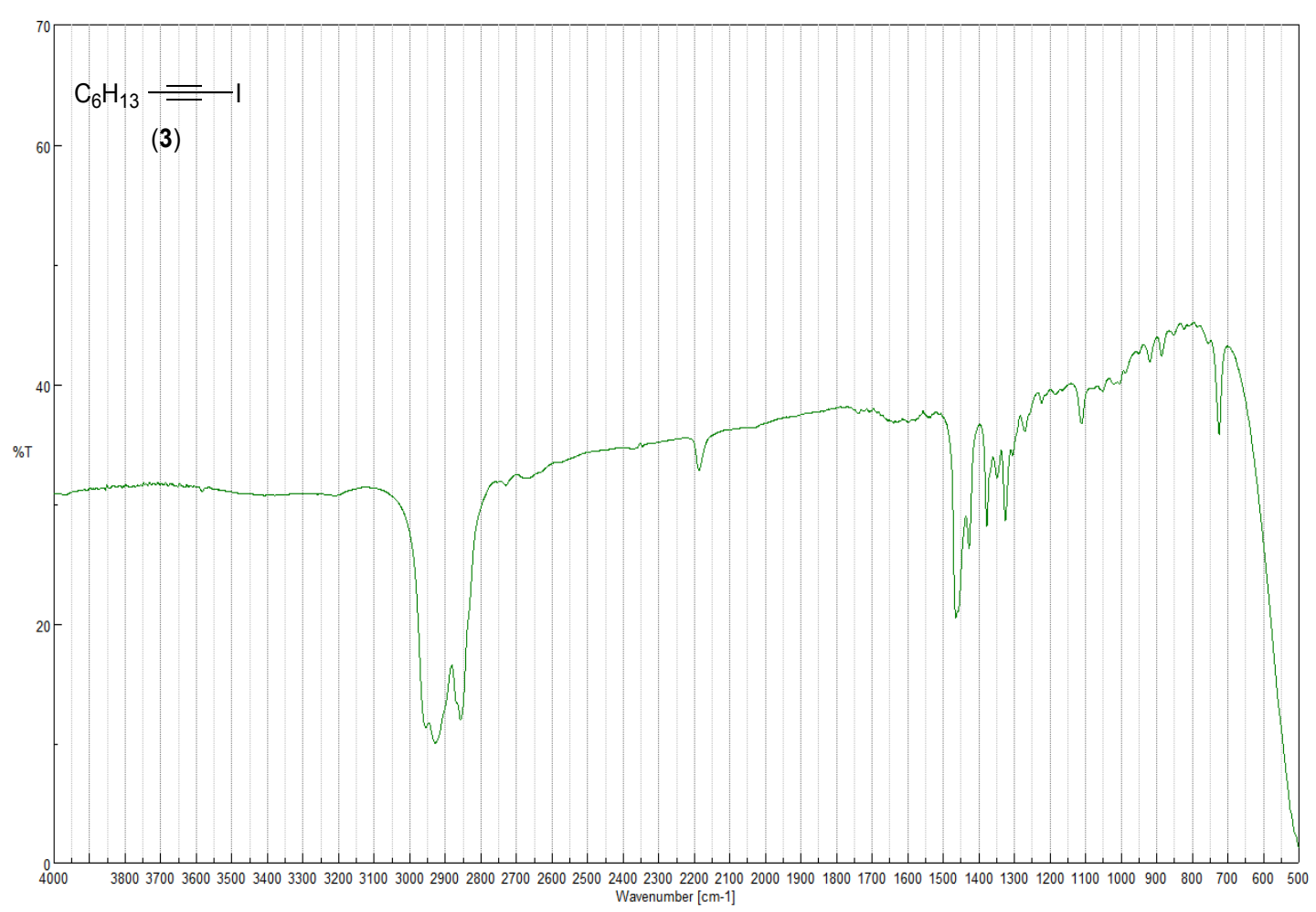
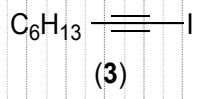


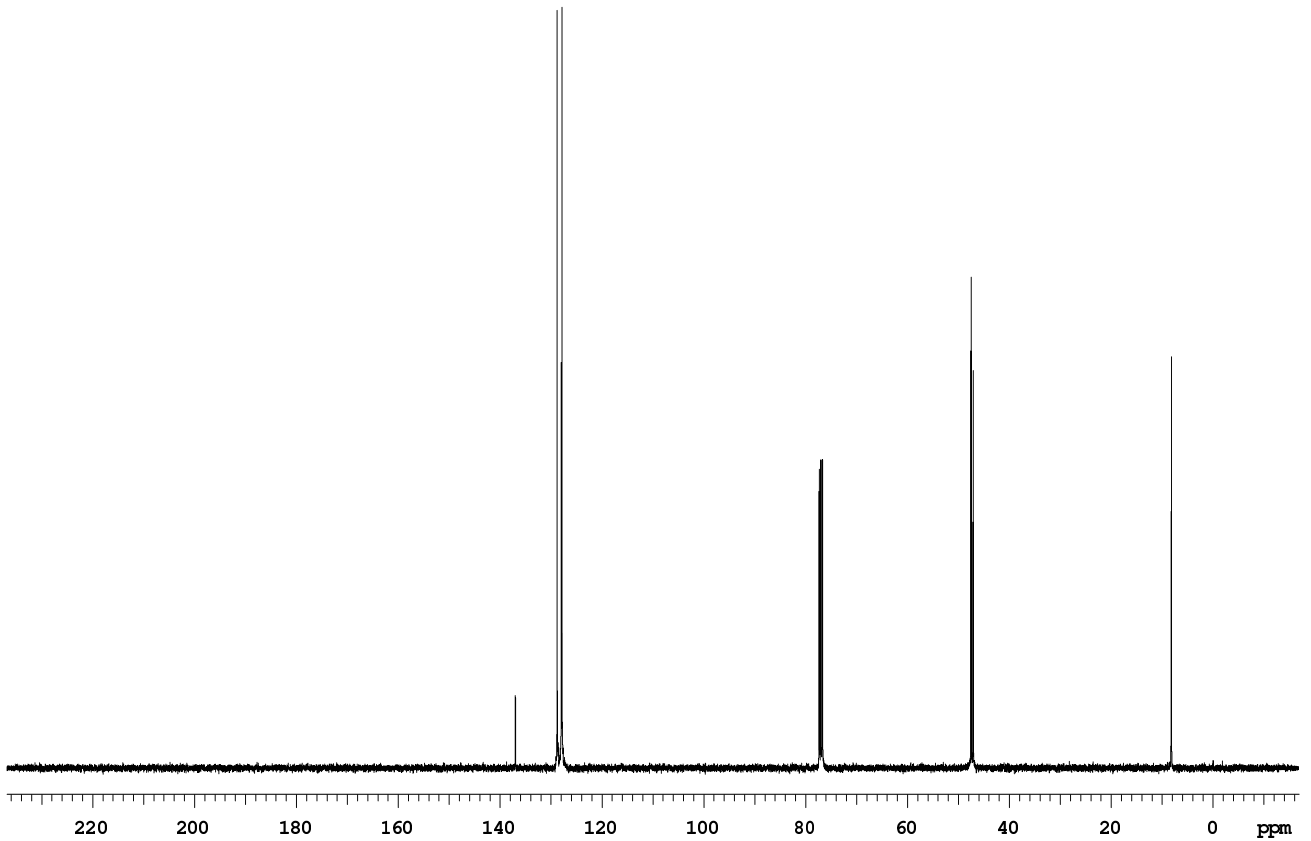
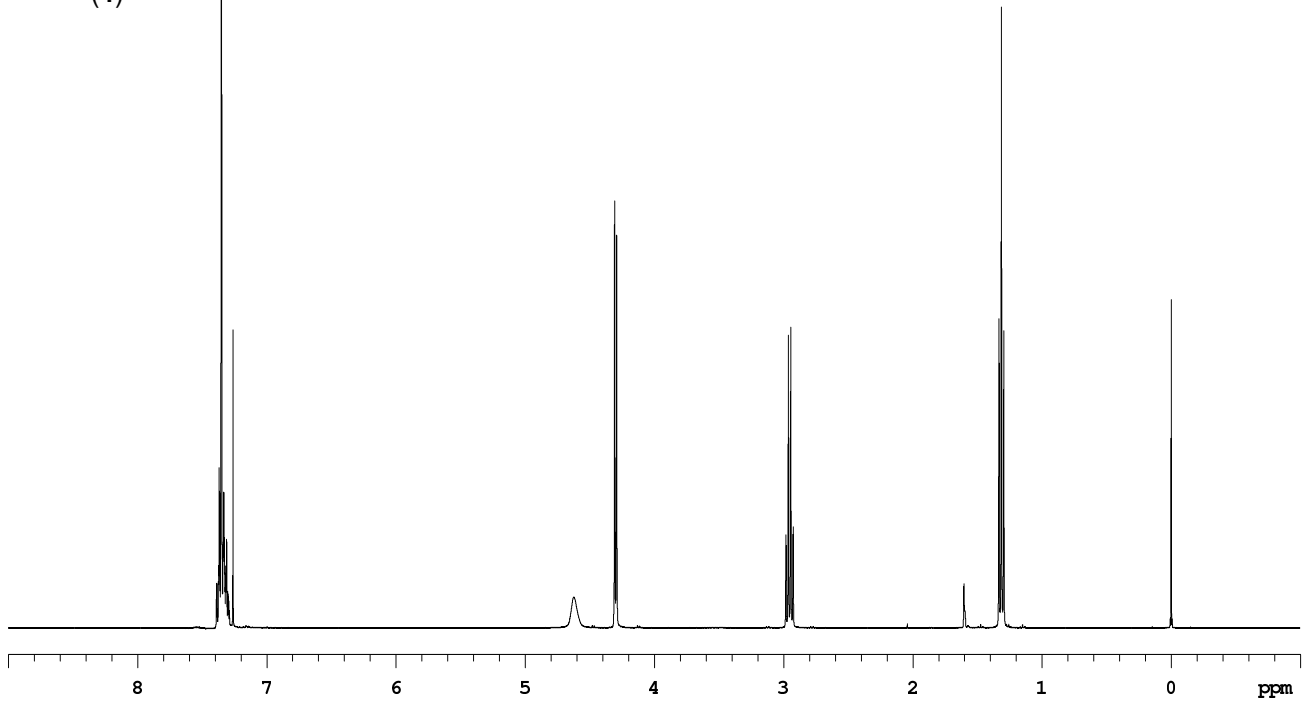
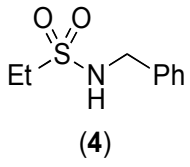
(2)

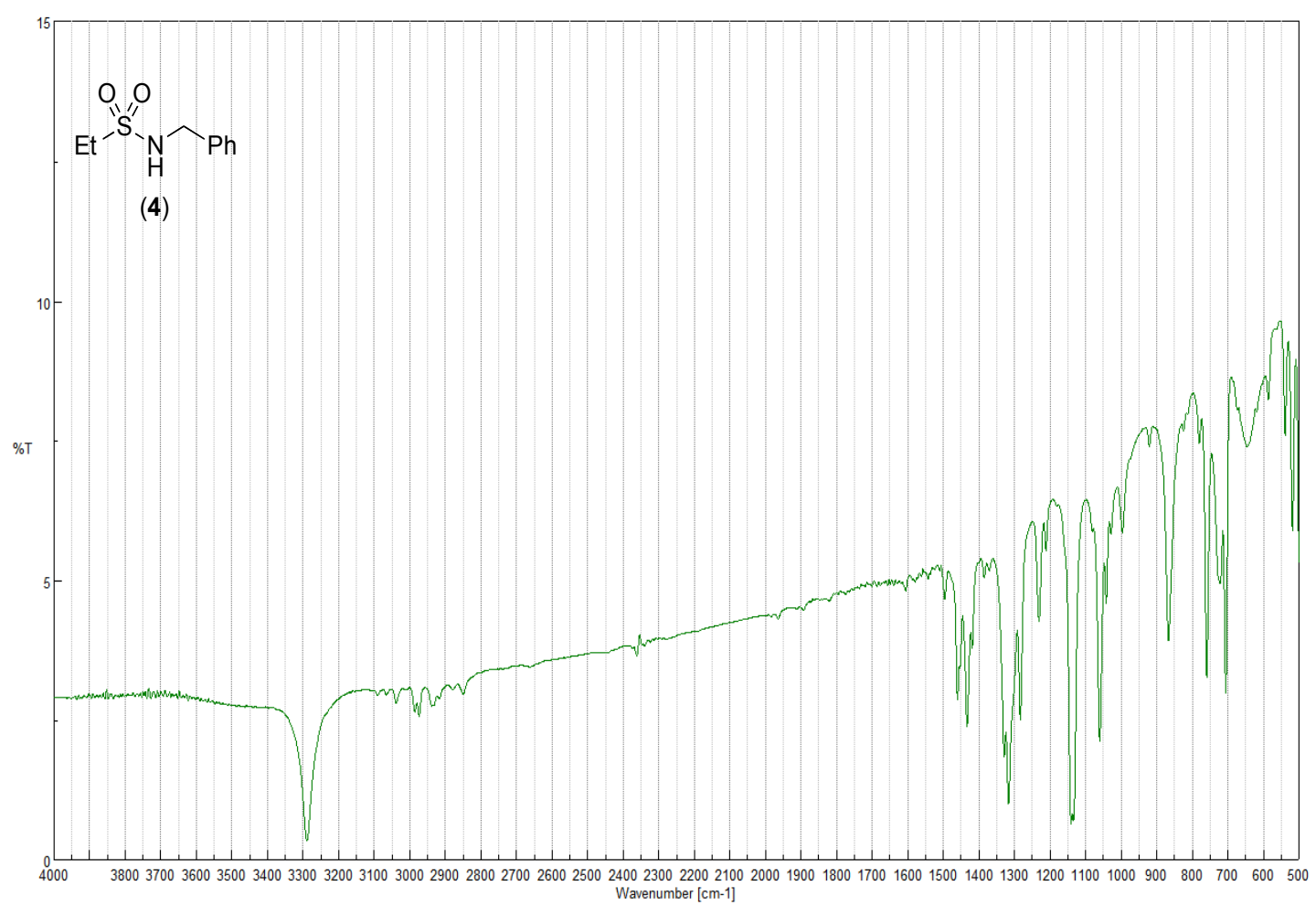
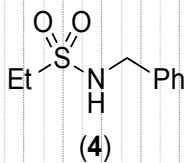


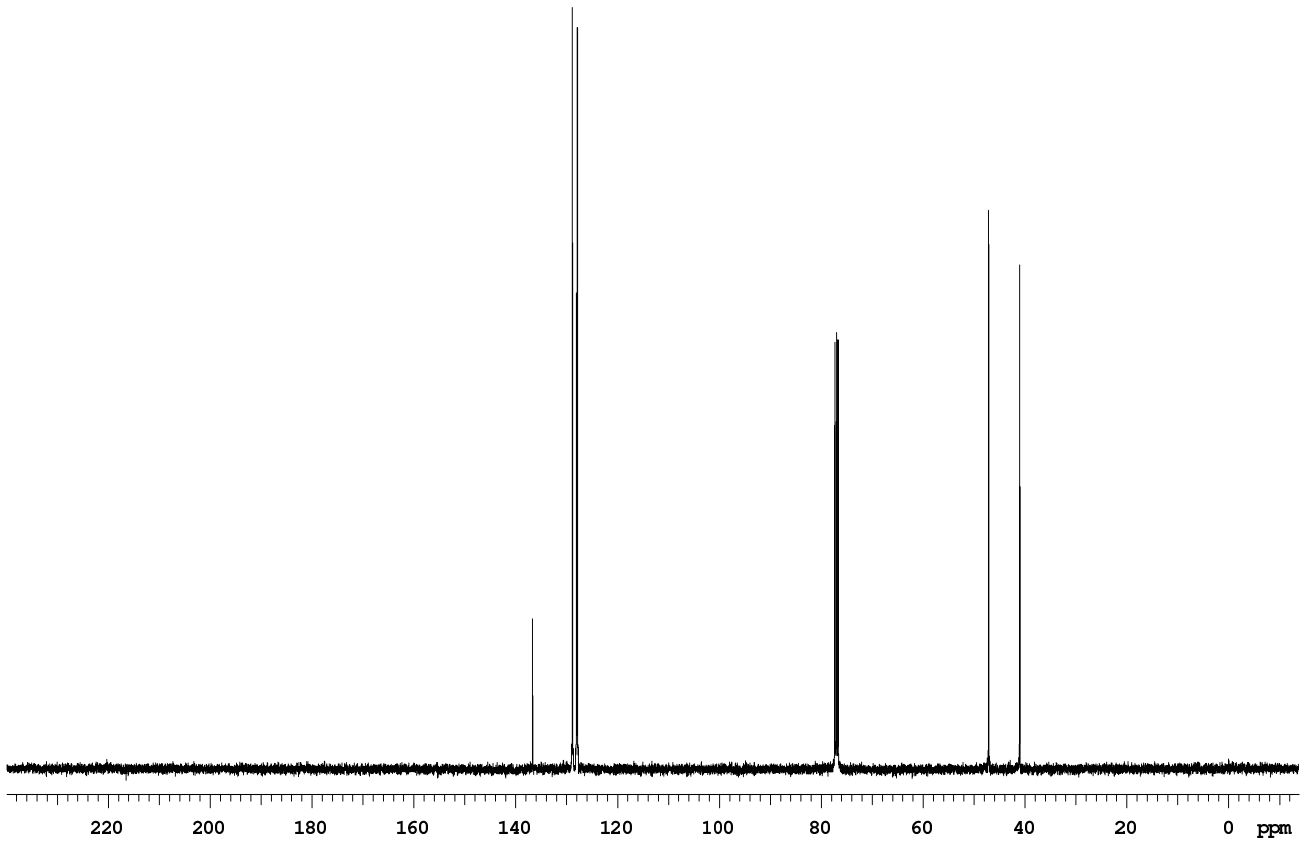
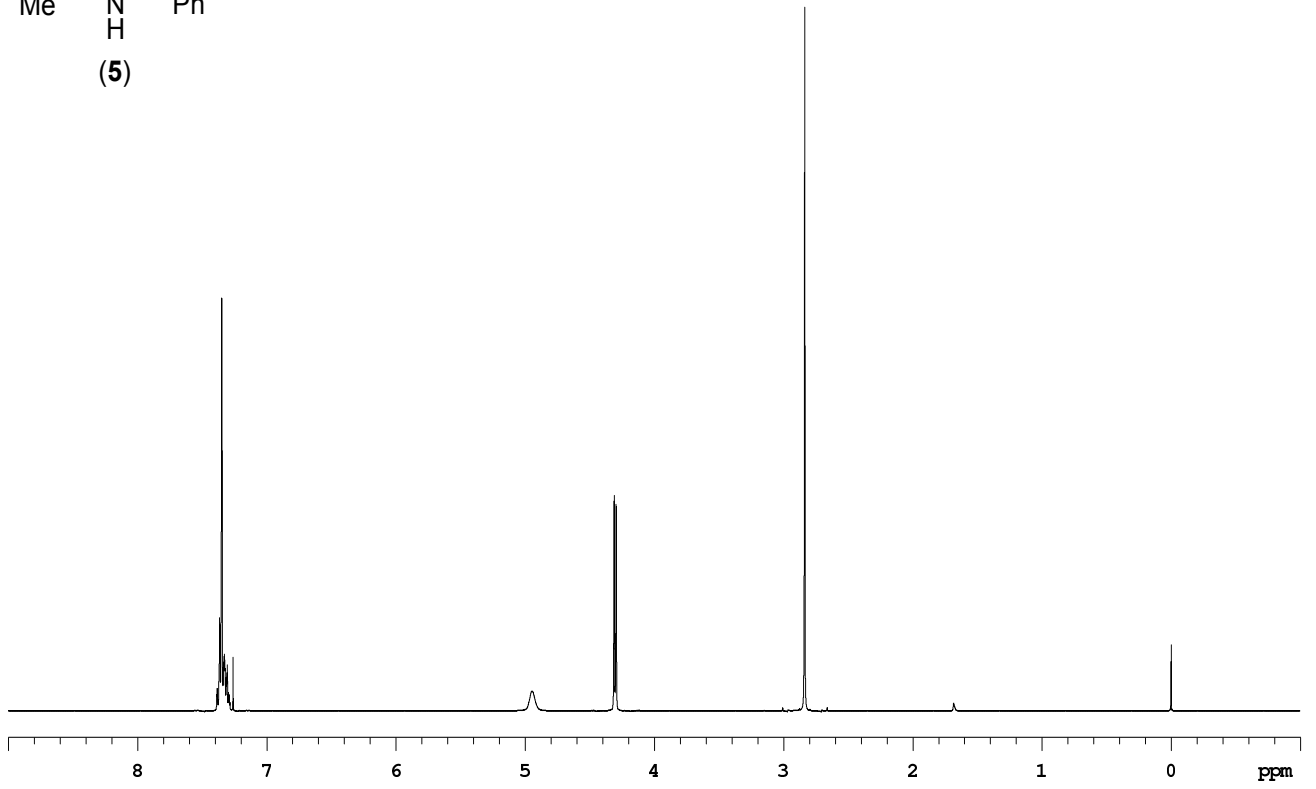
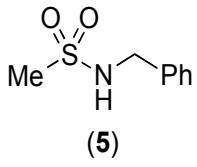


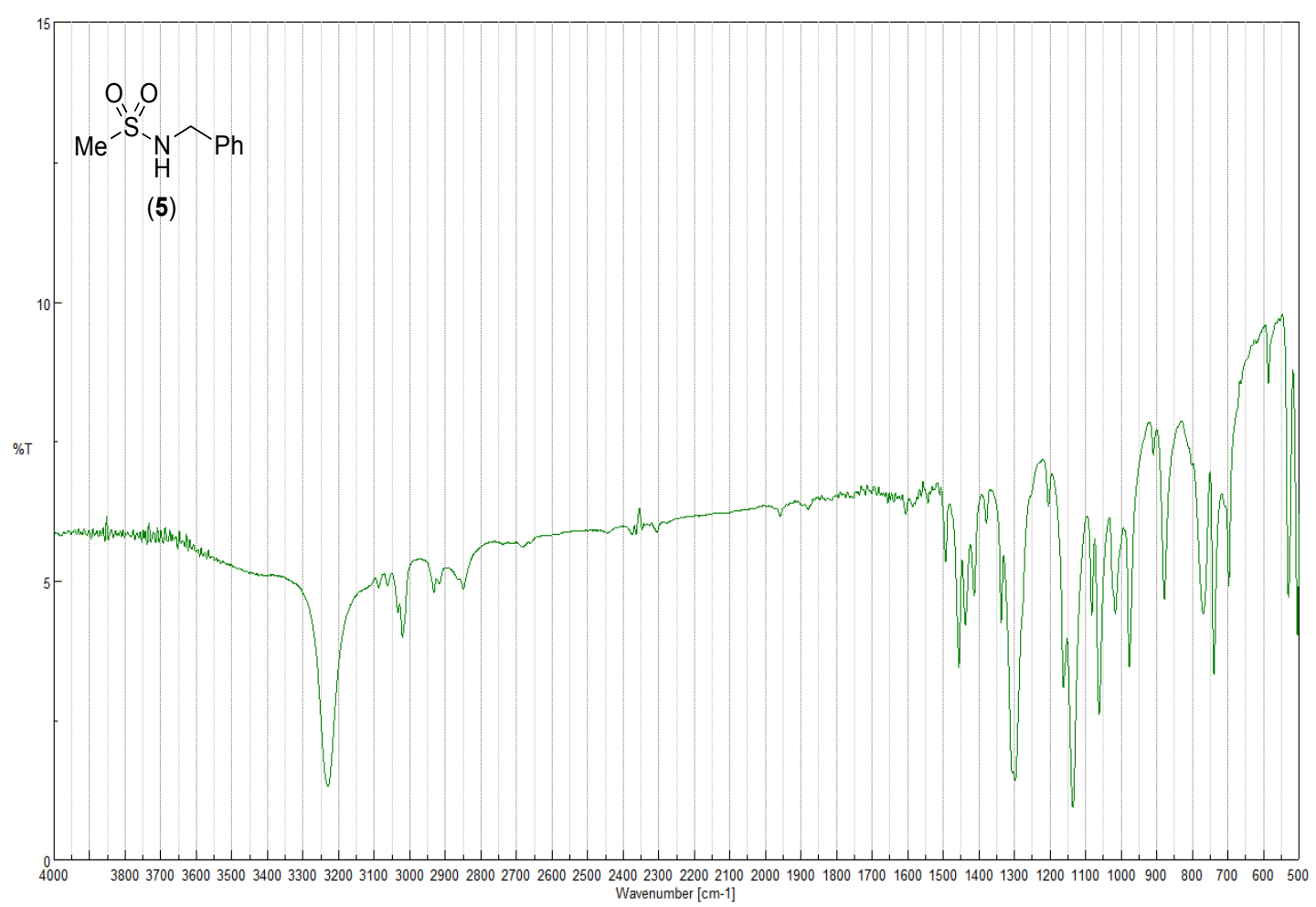
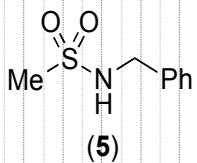


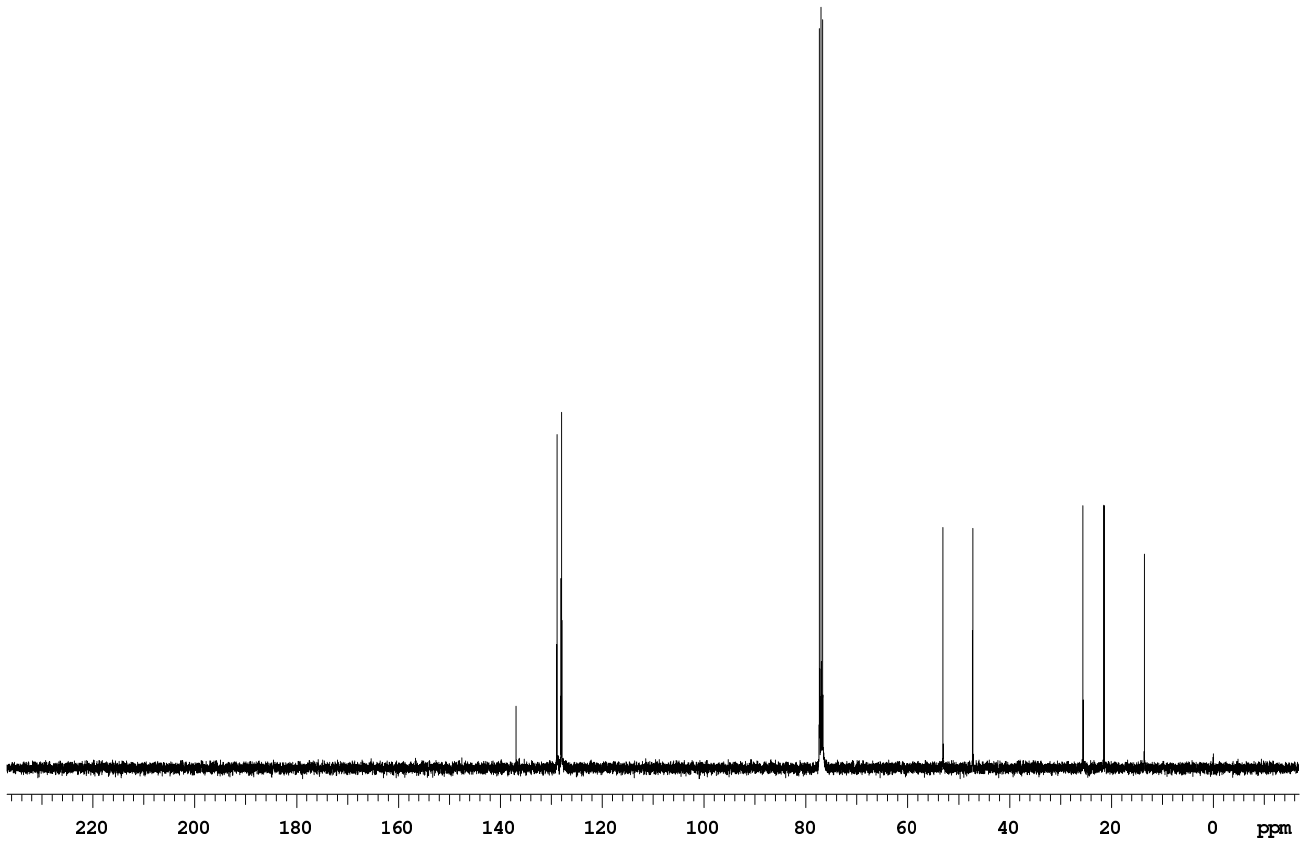
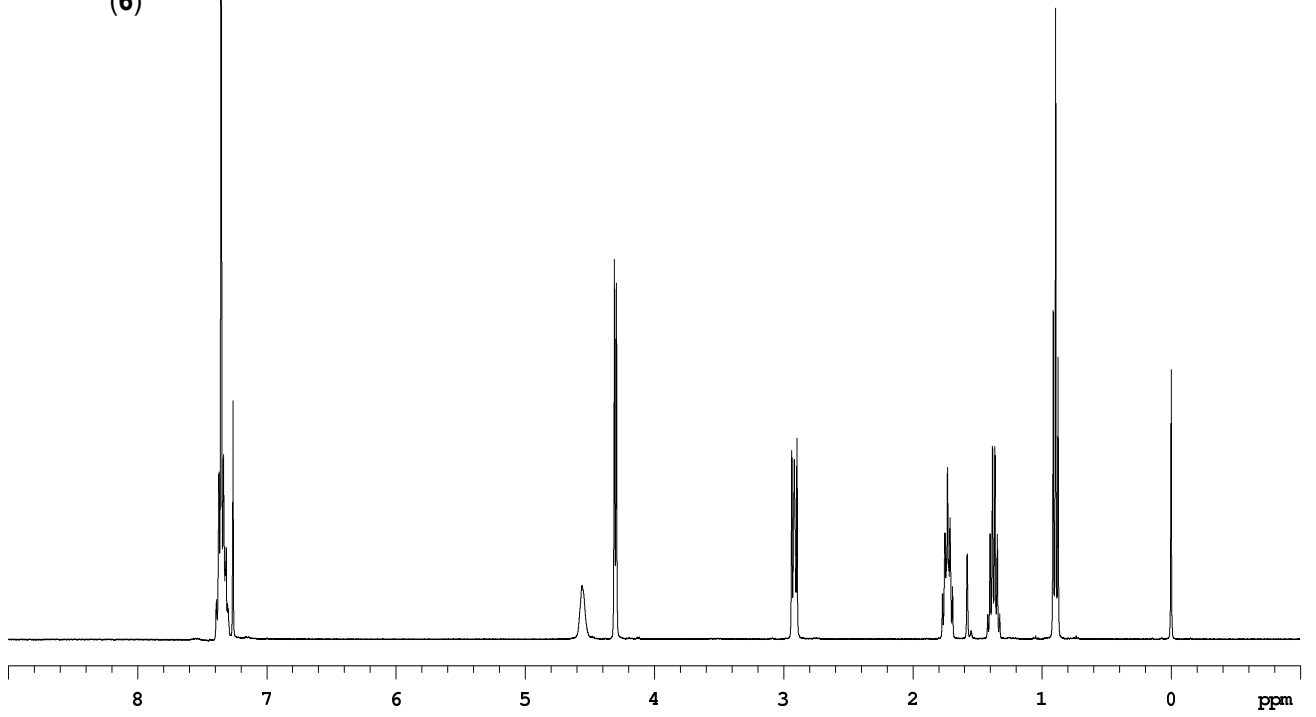
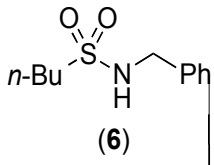


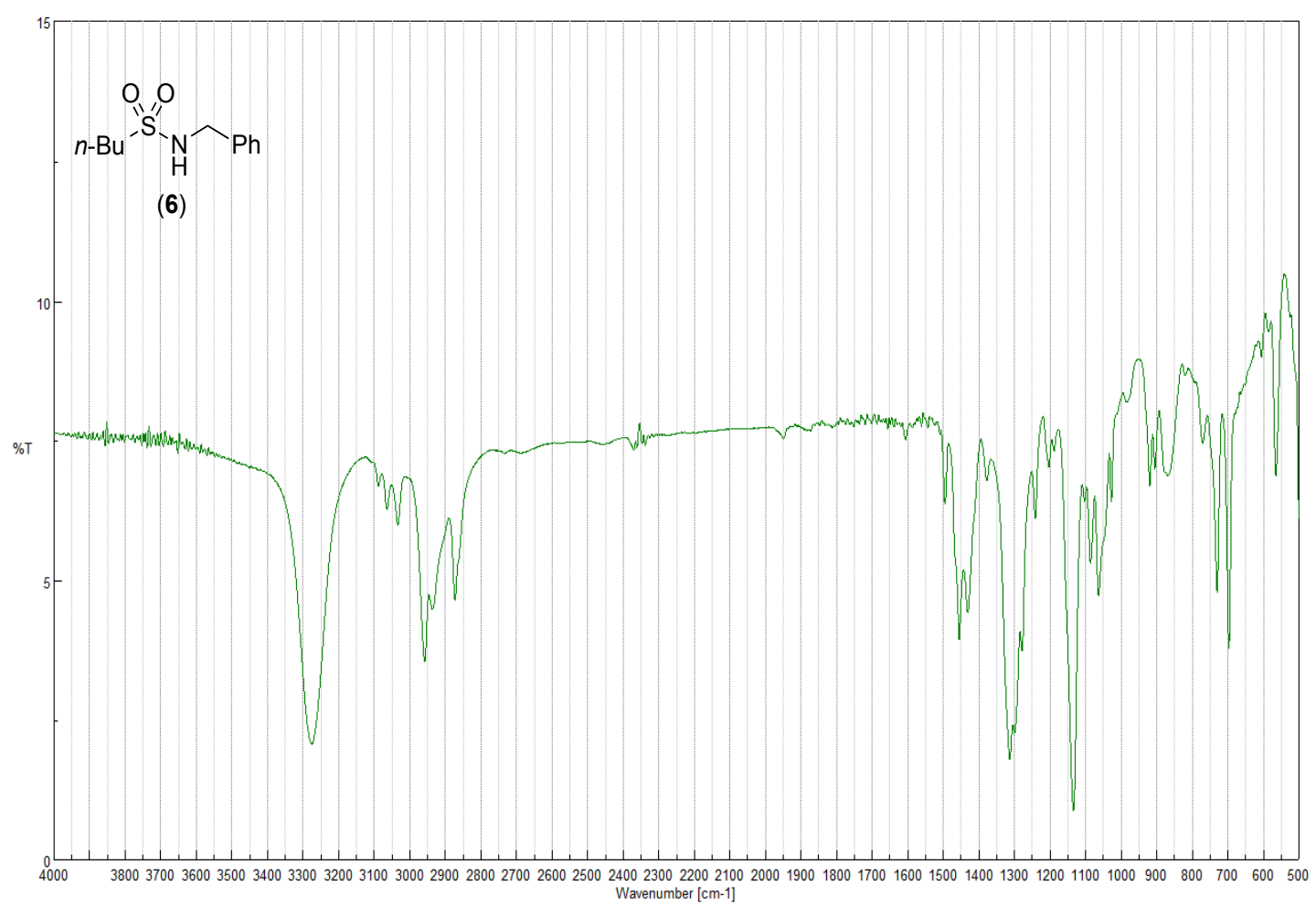
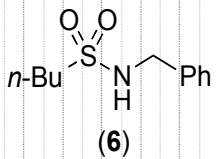


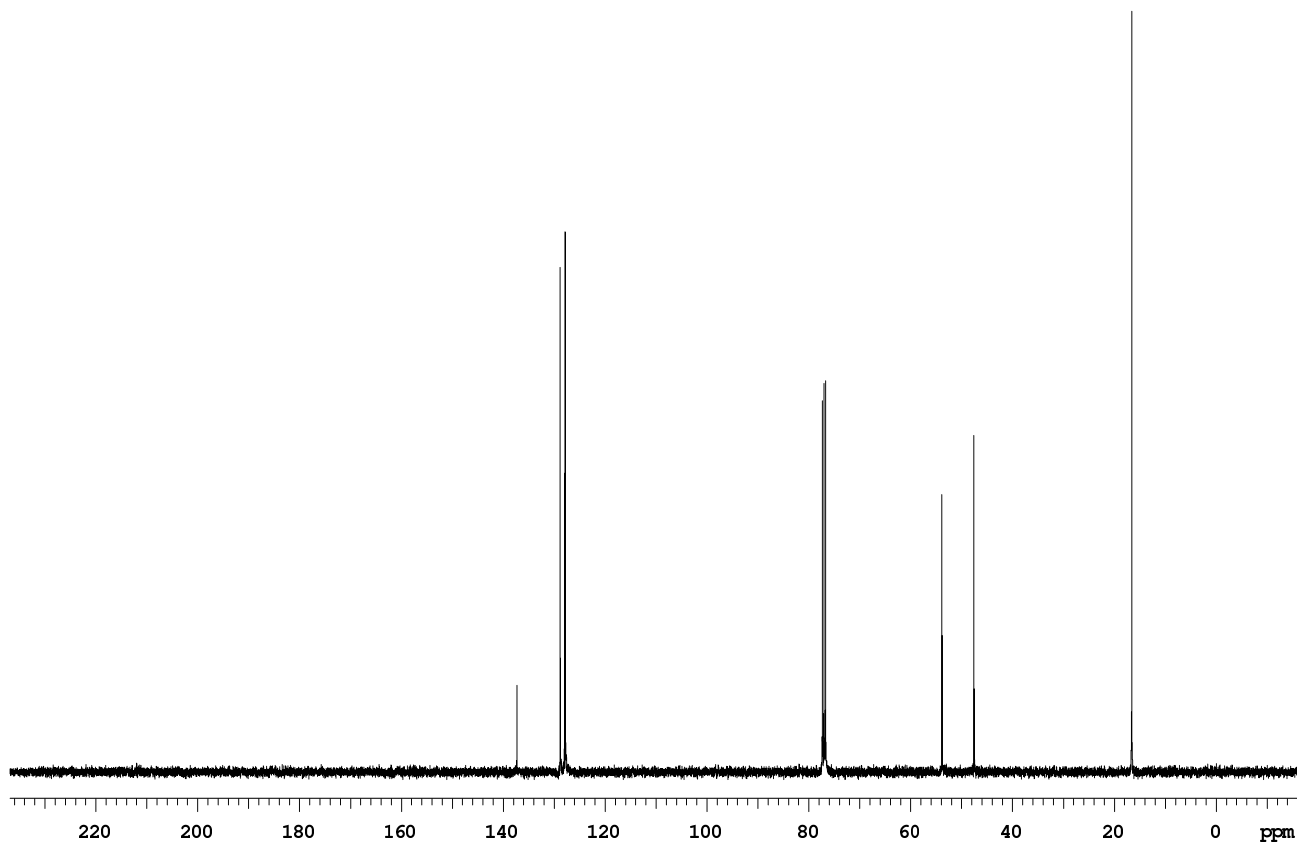
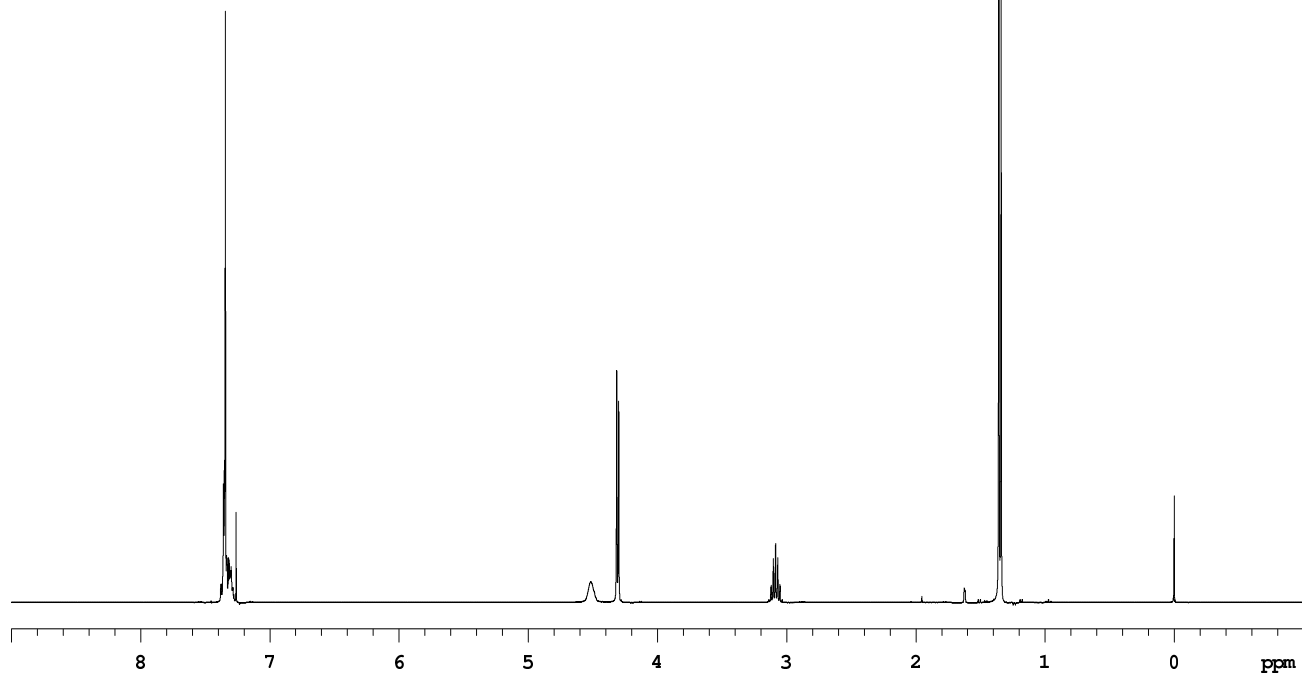
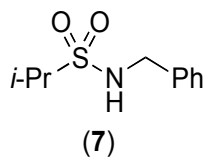


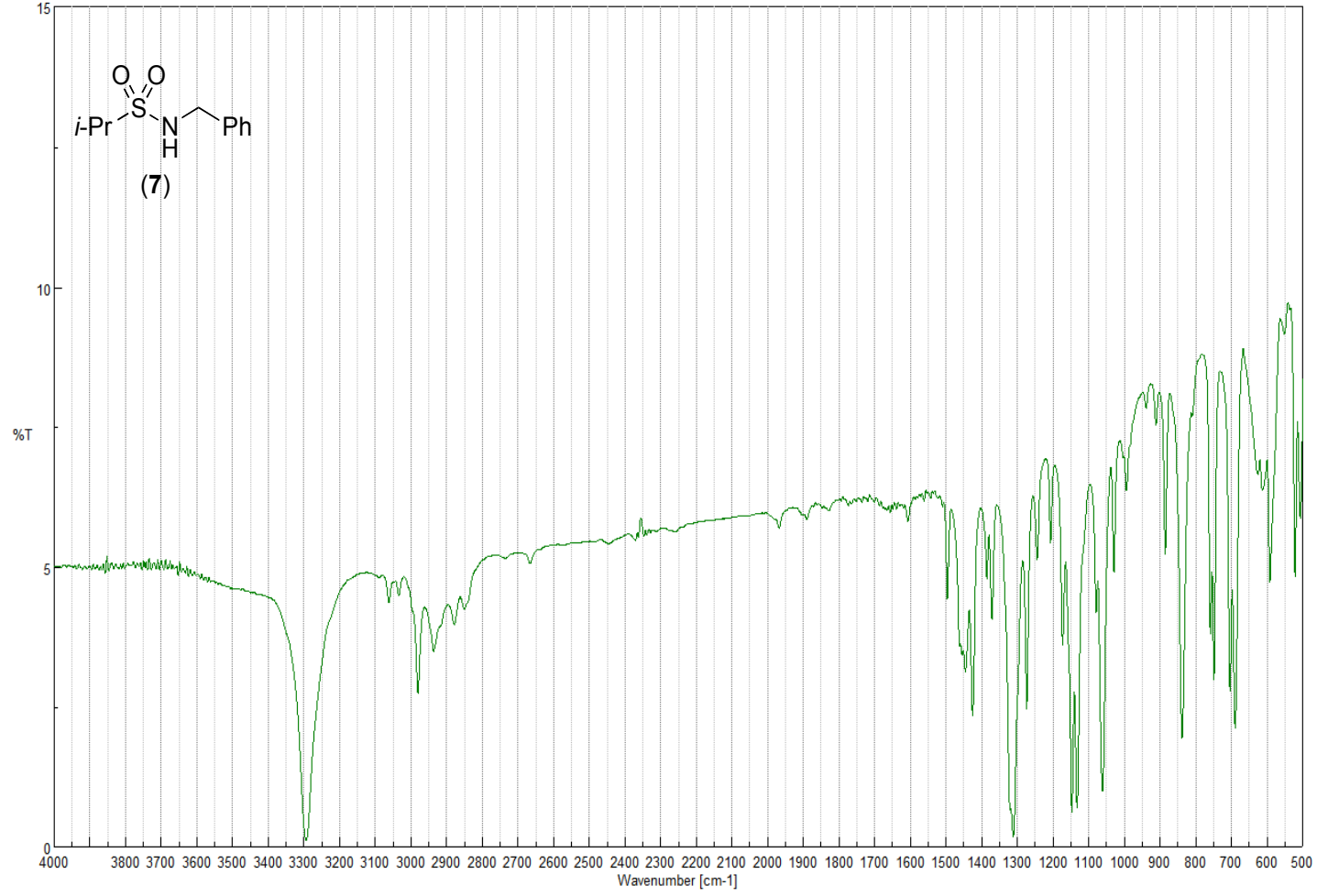
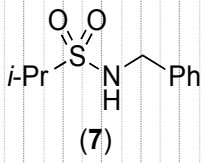


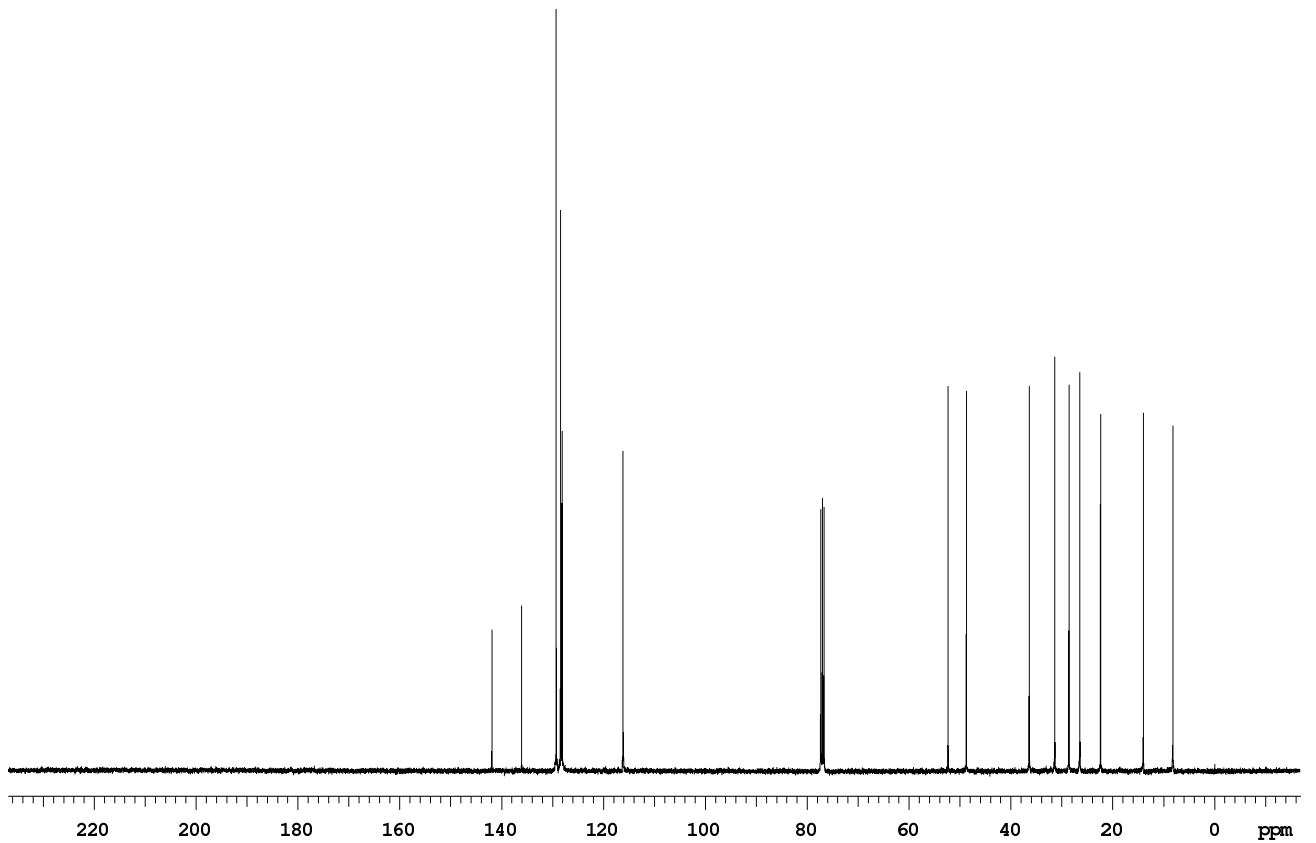
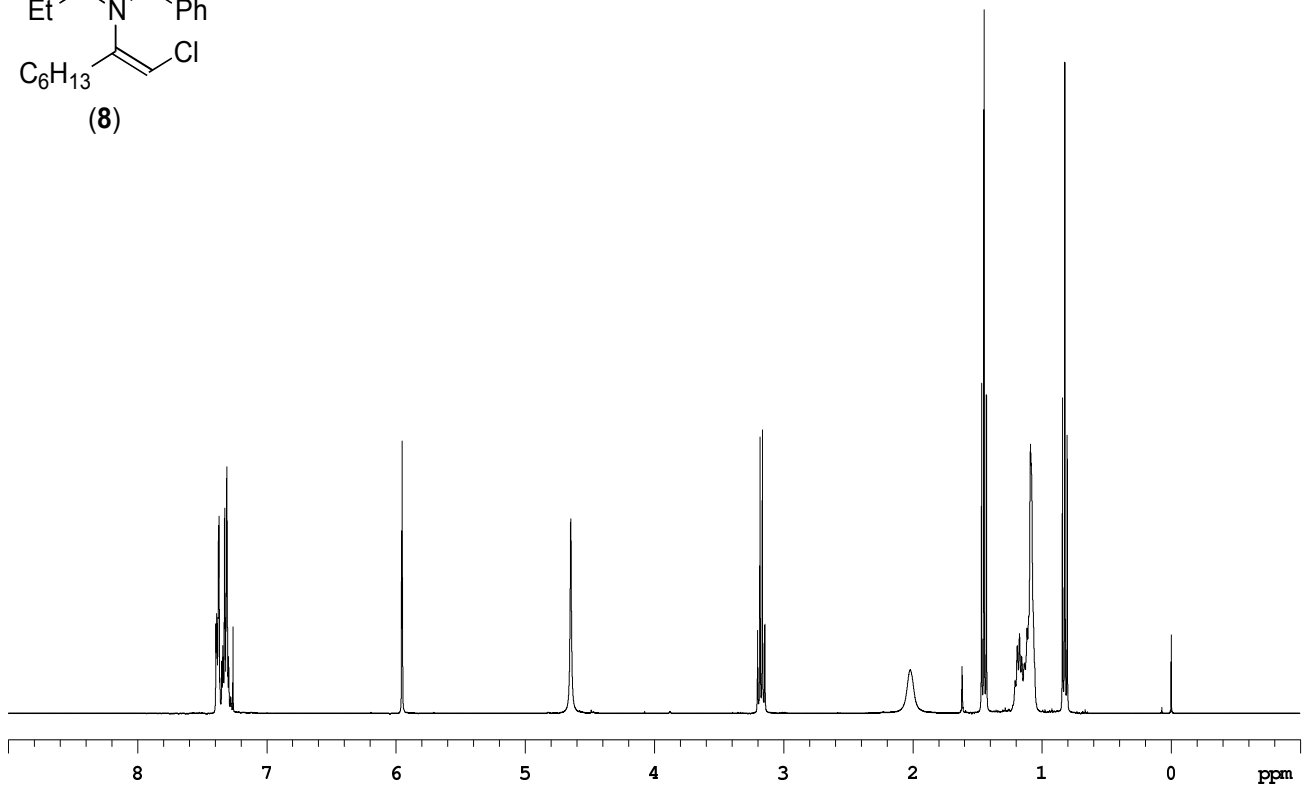
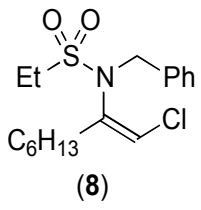


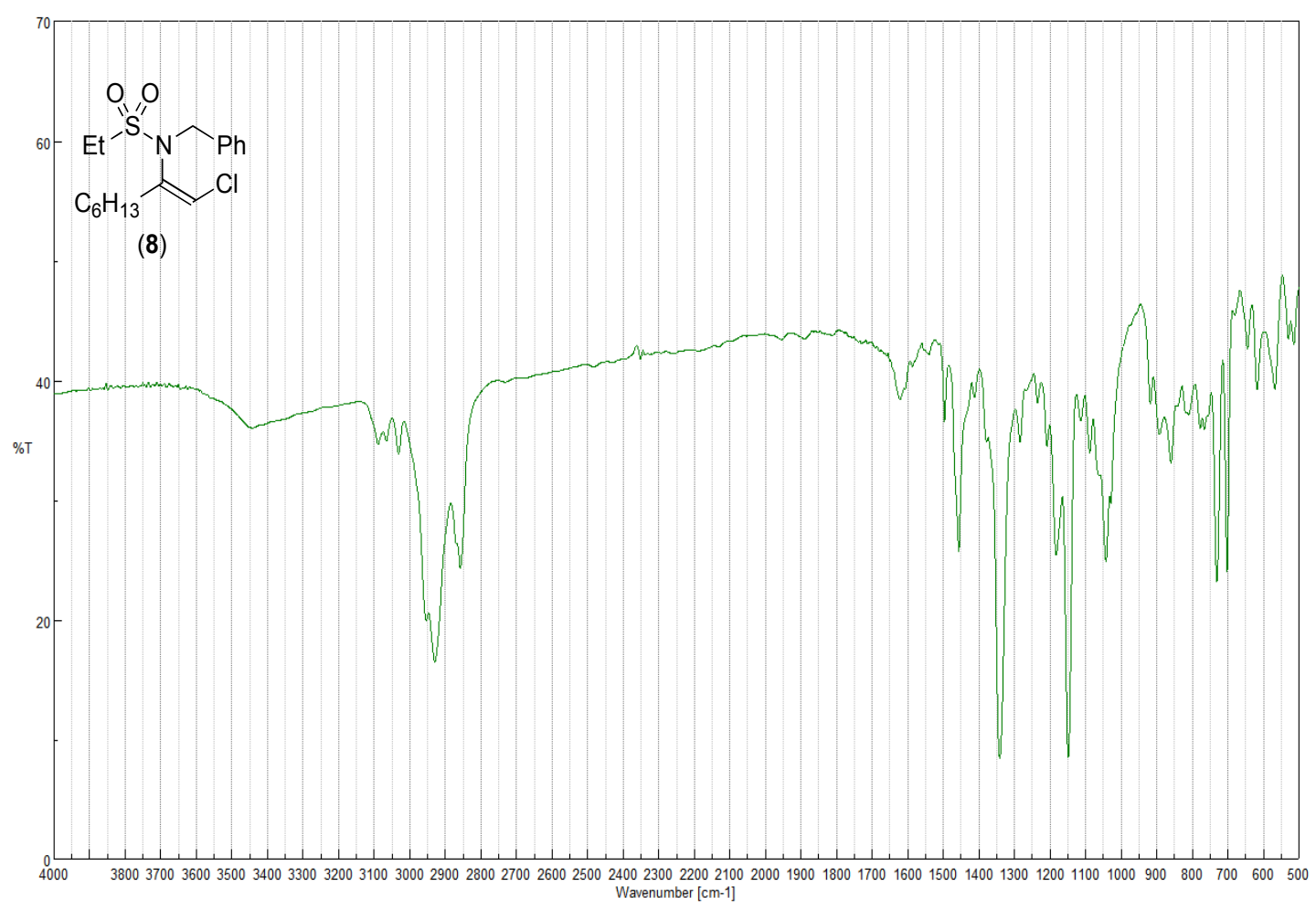
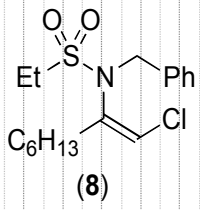


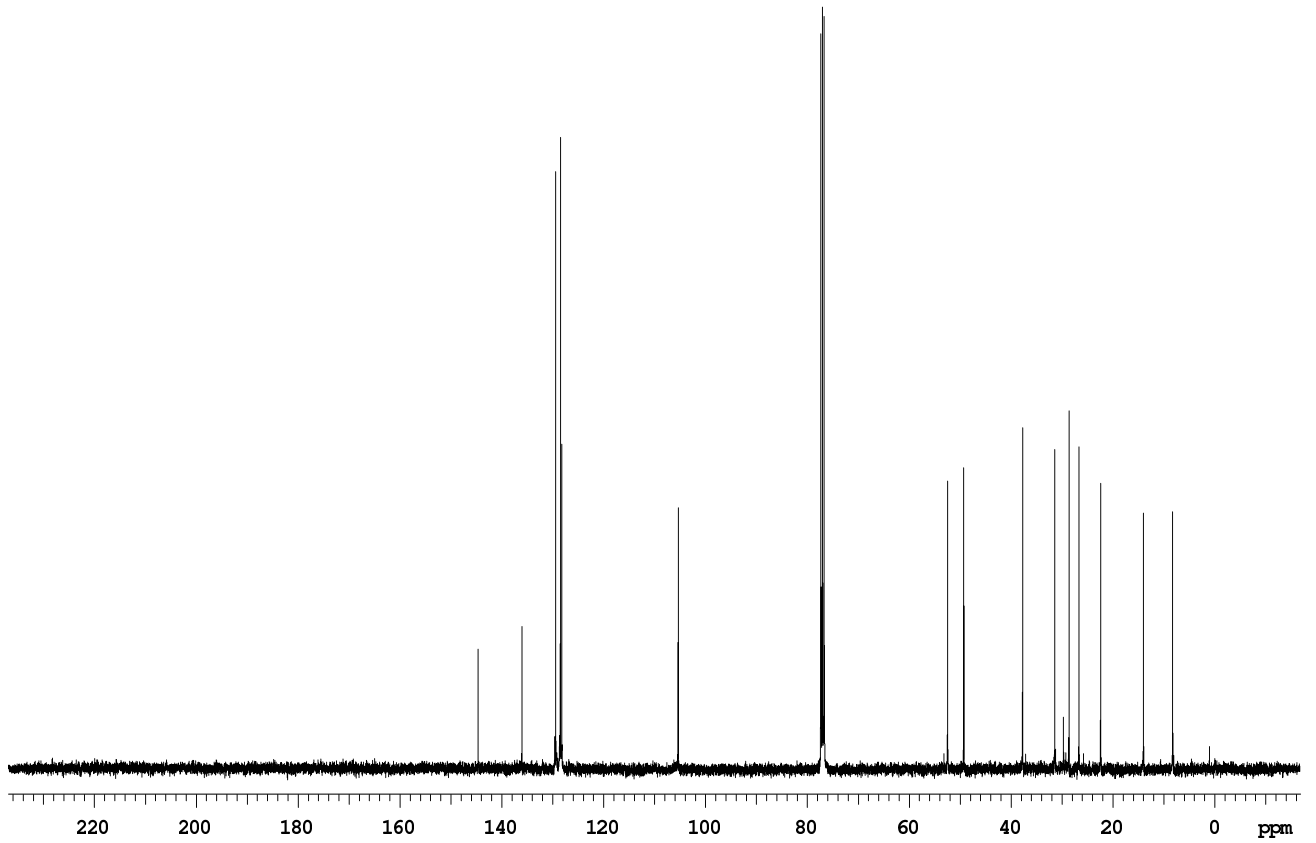
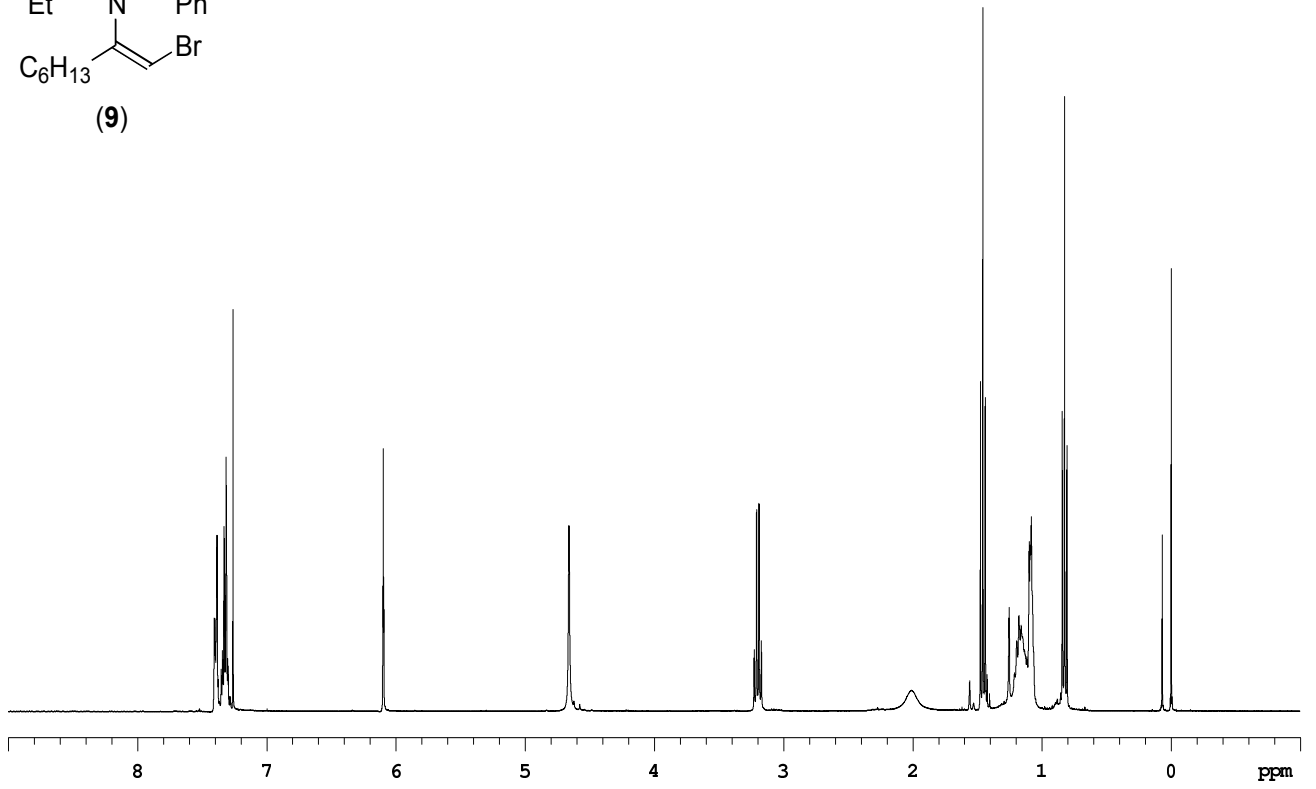
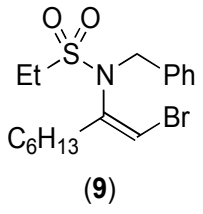


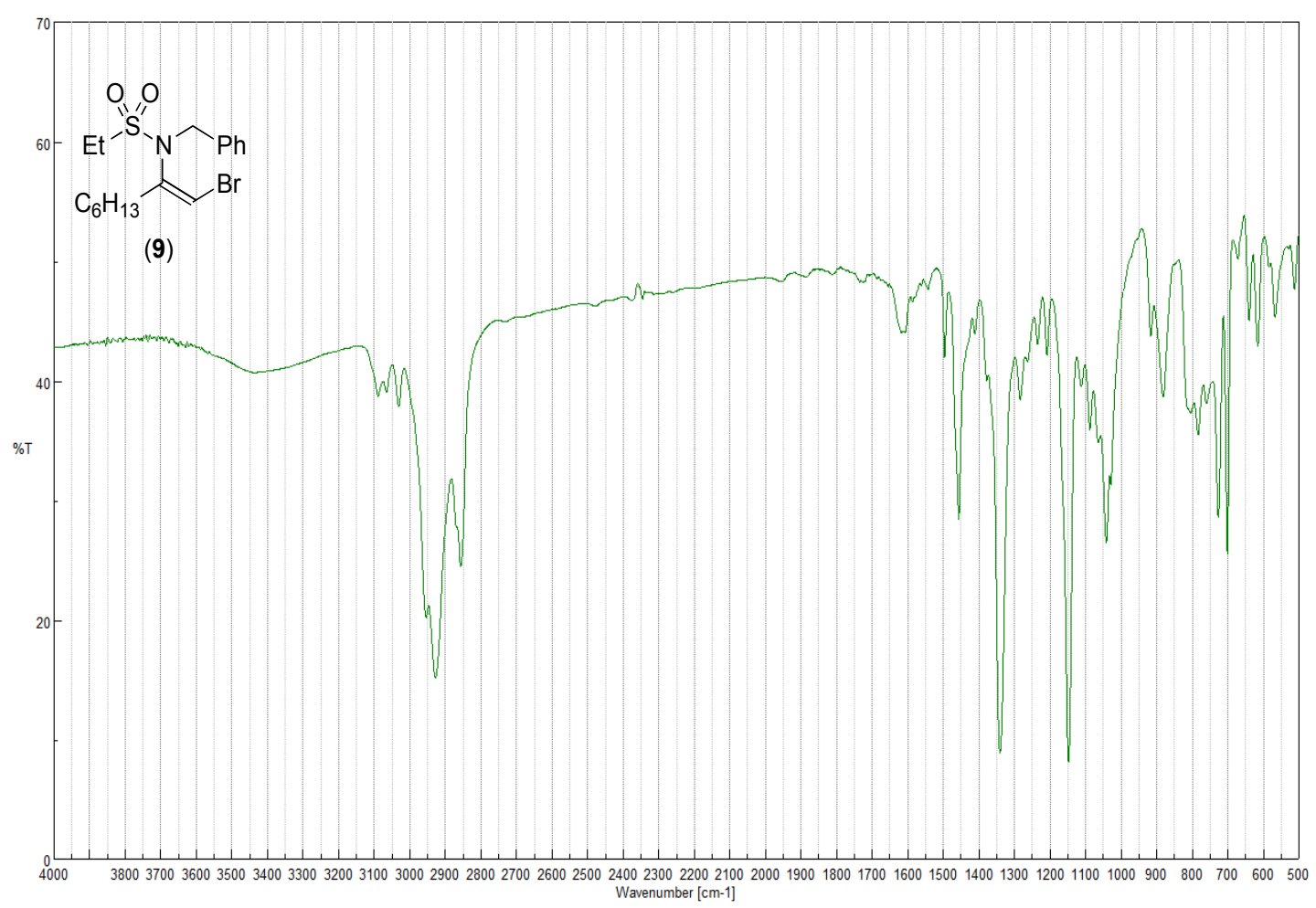
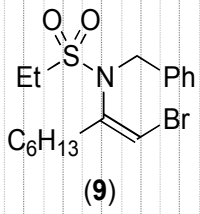


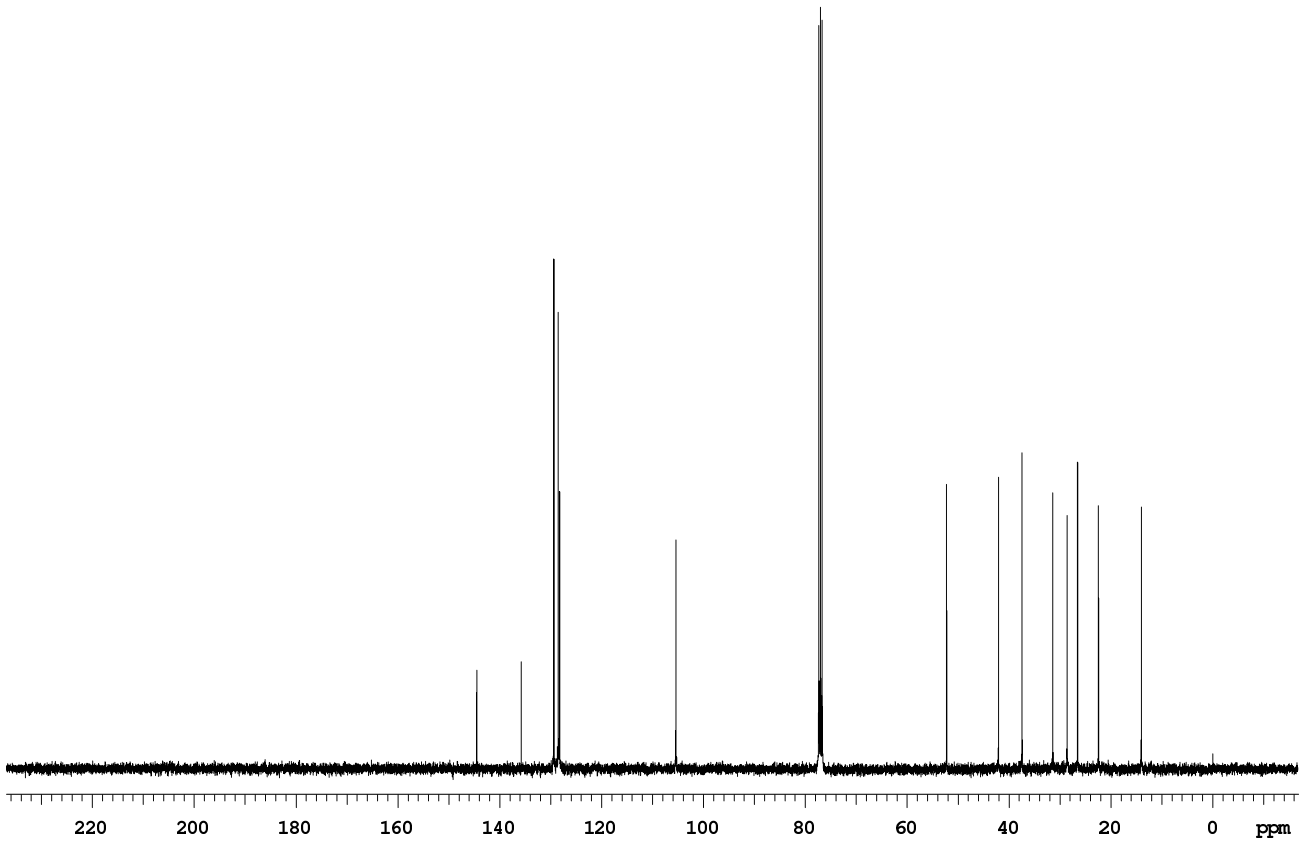
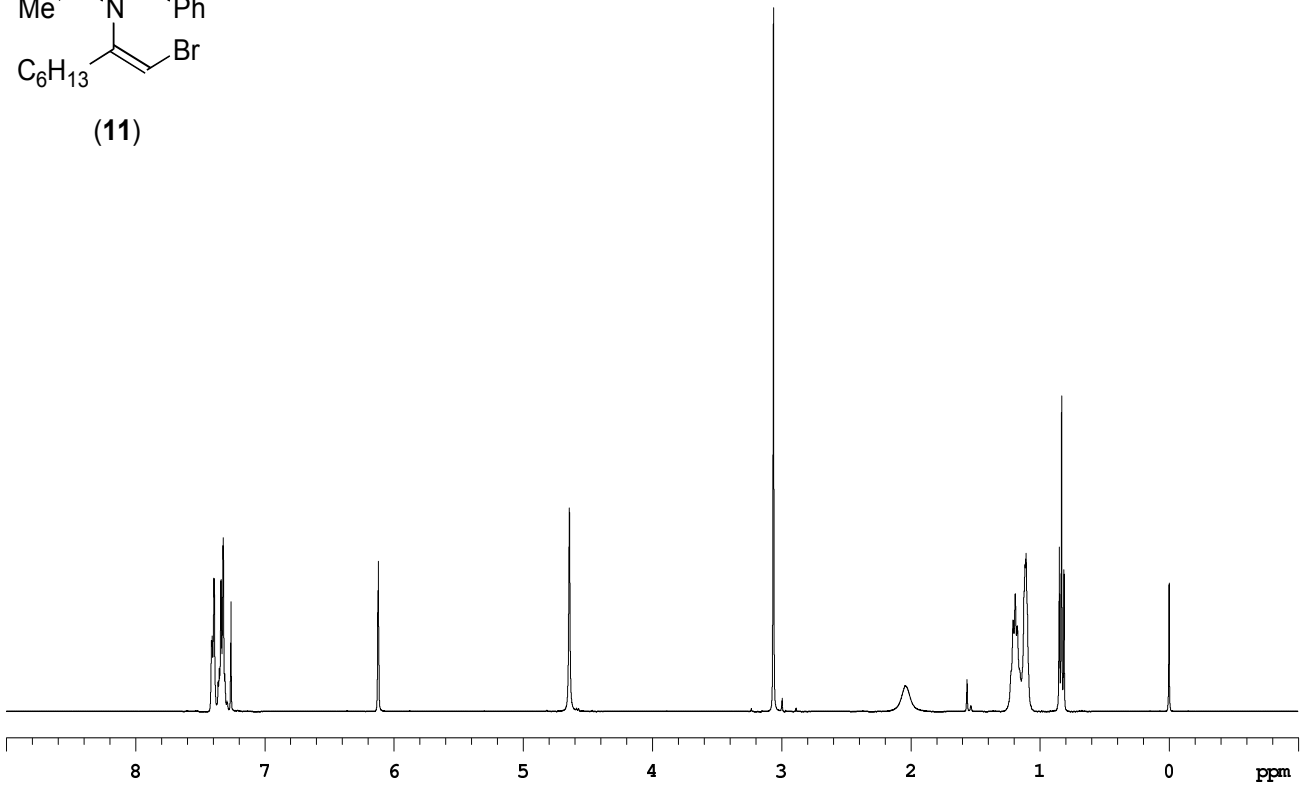
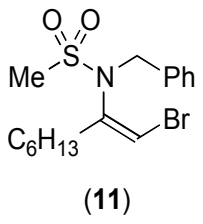


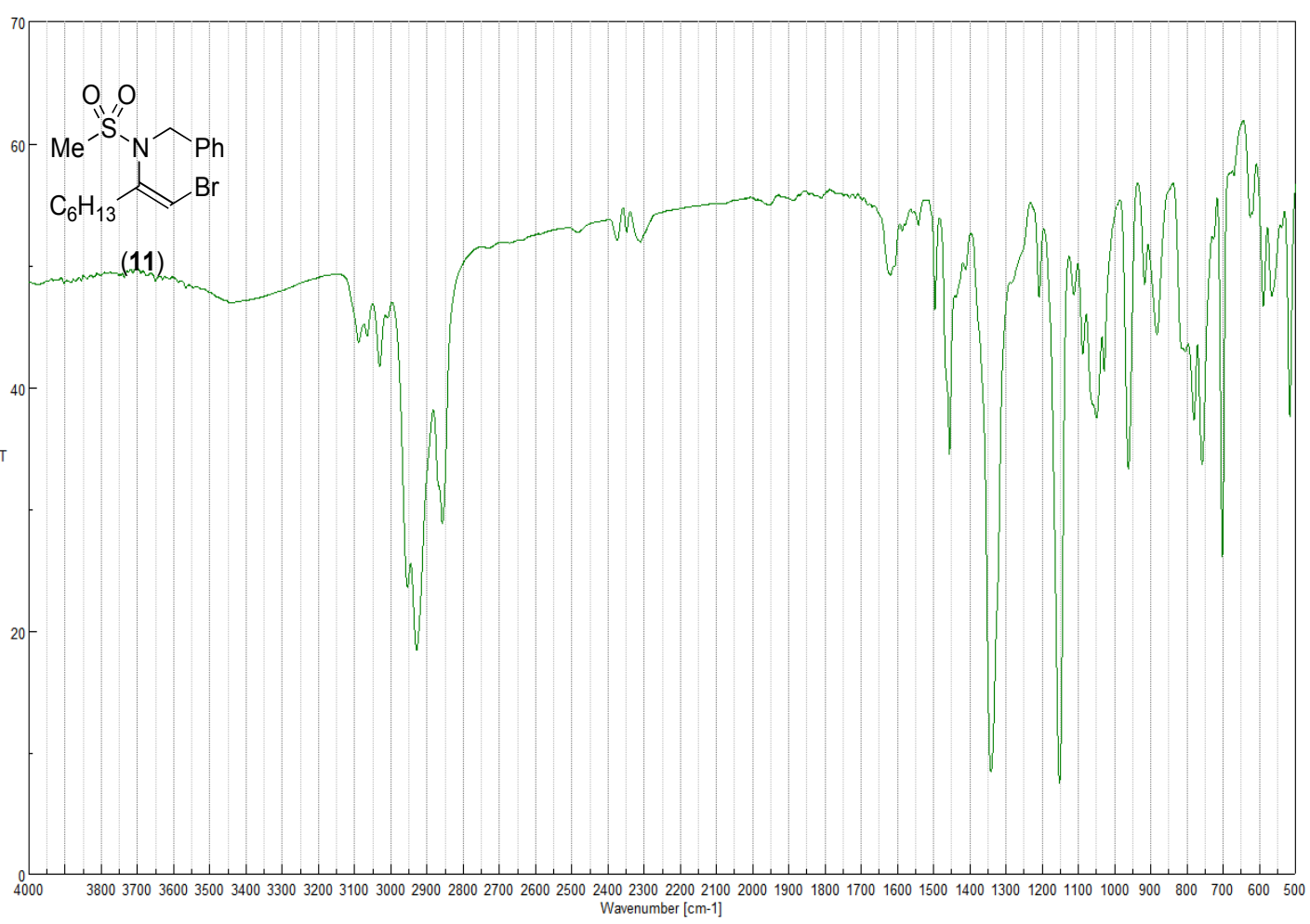


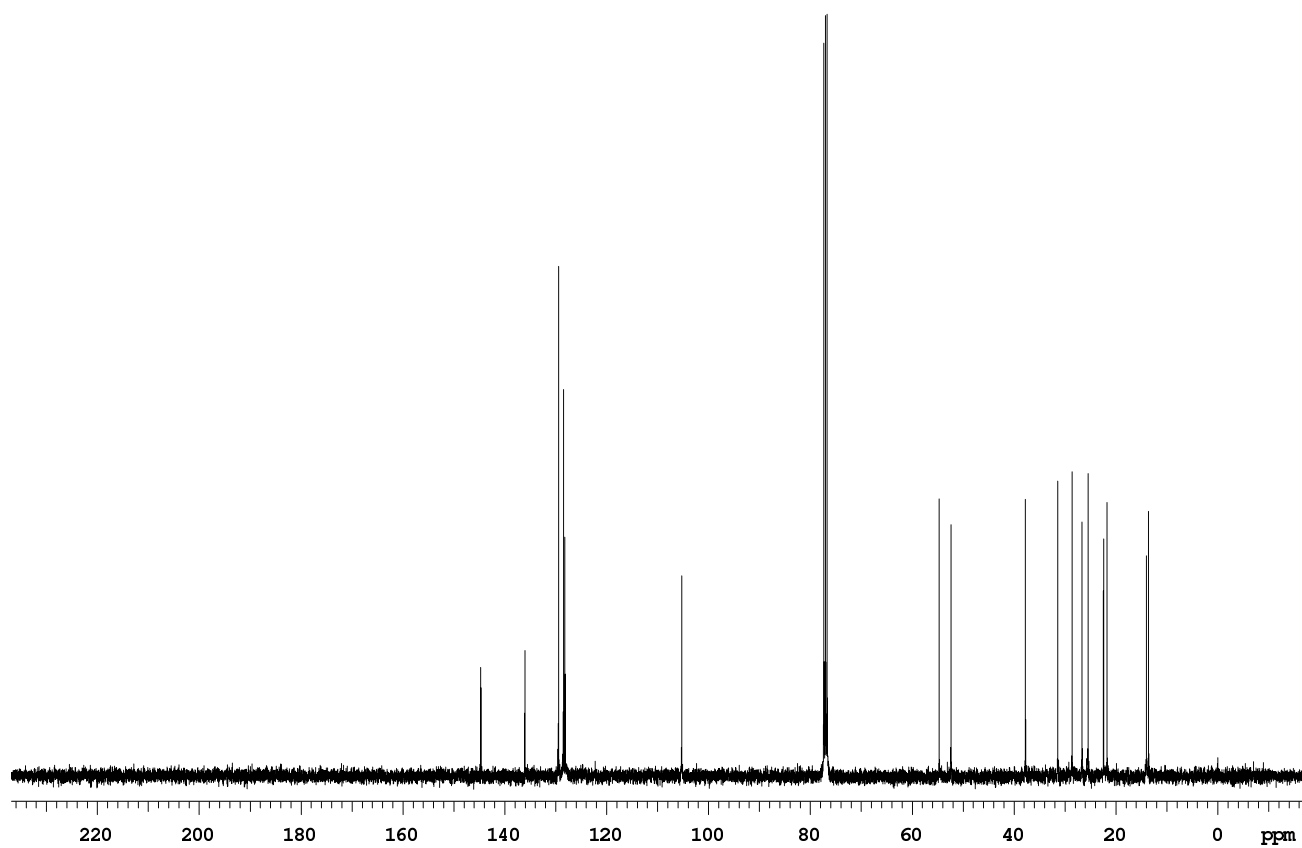
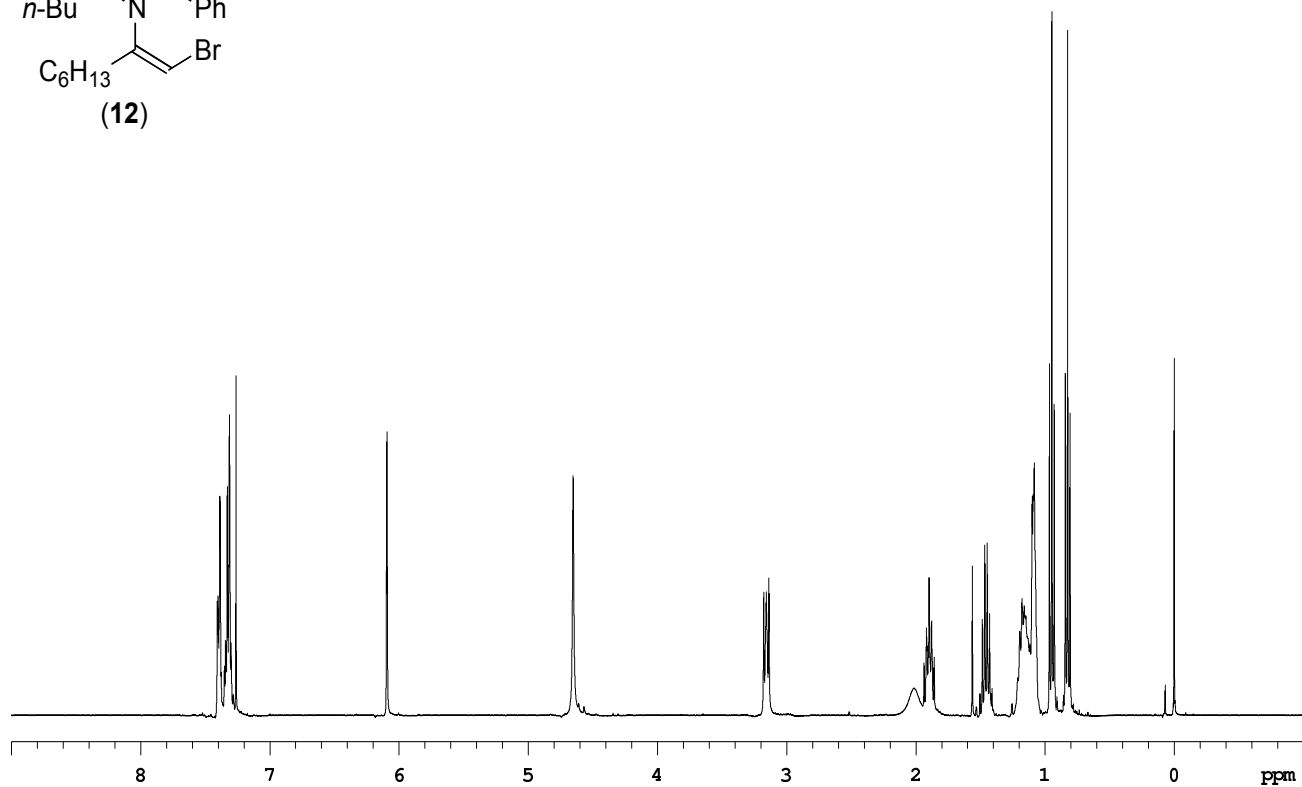
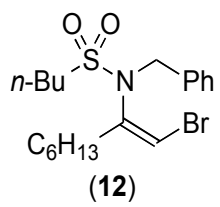


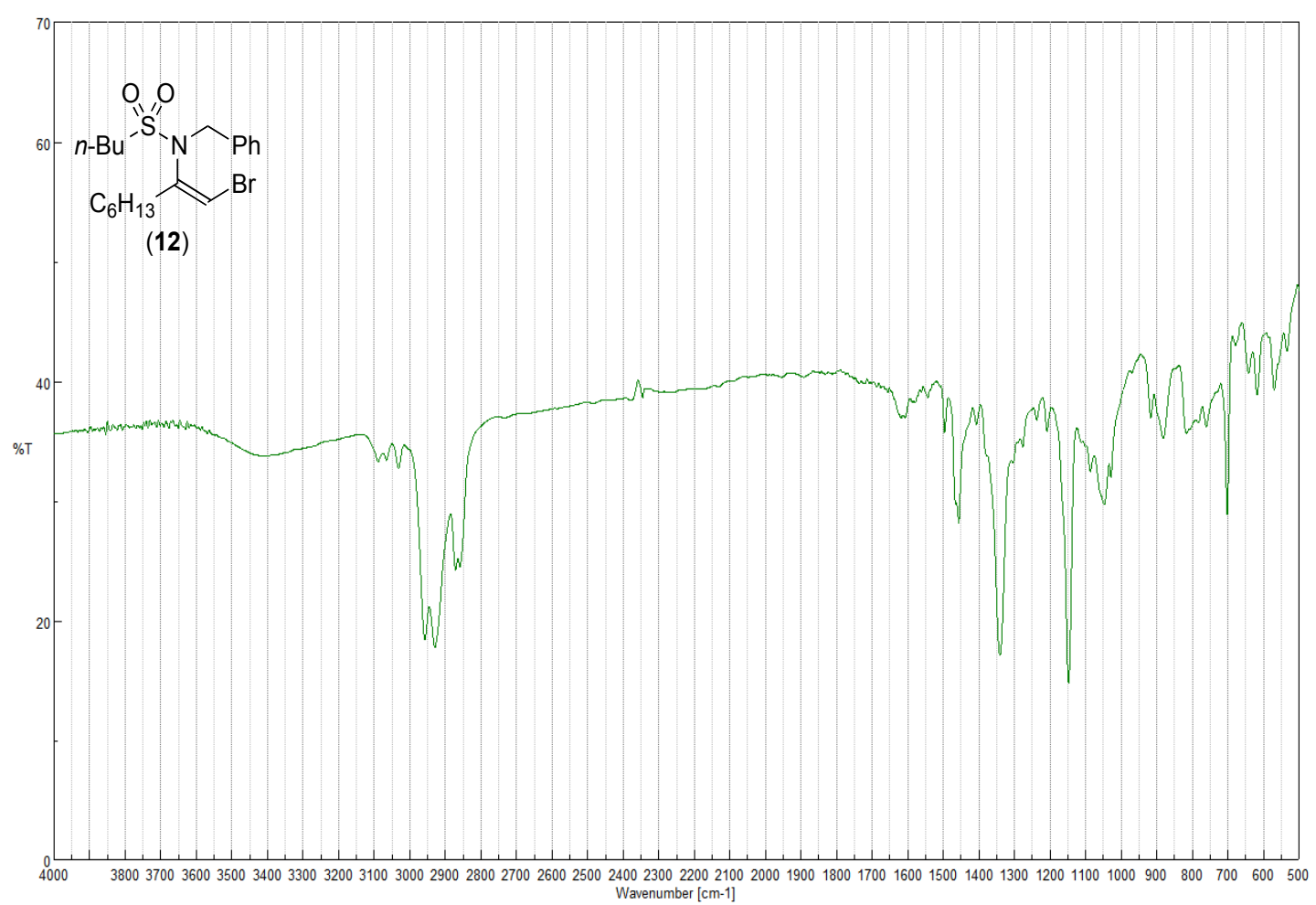
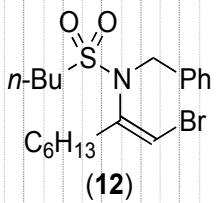


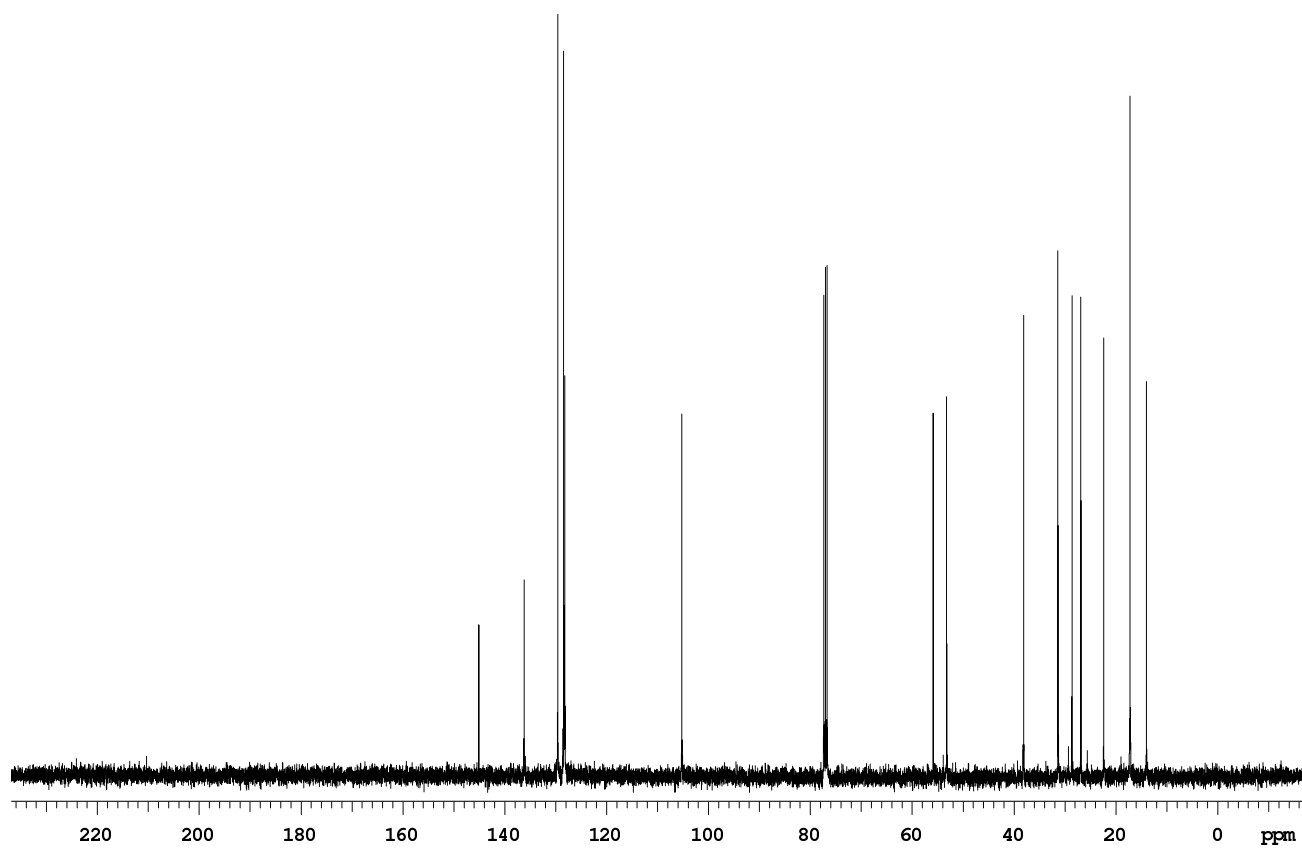
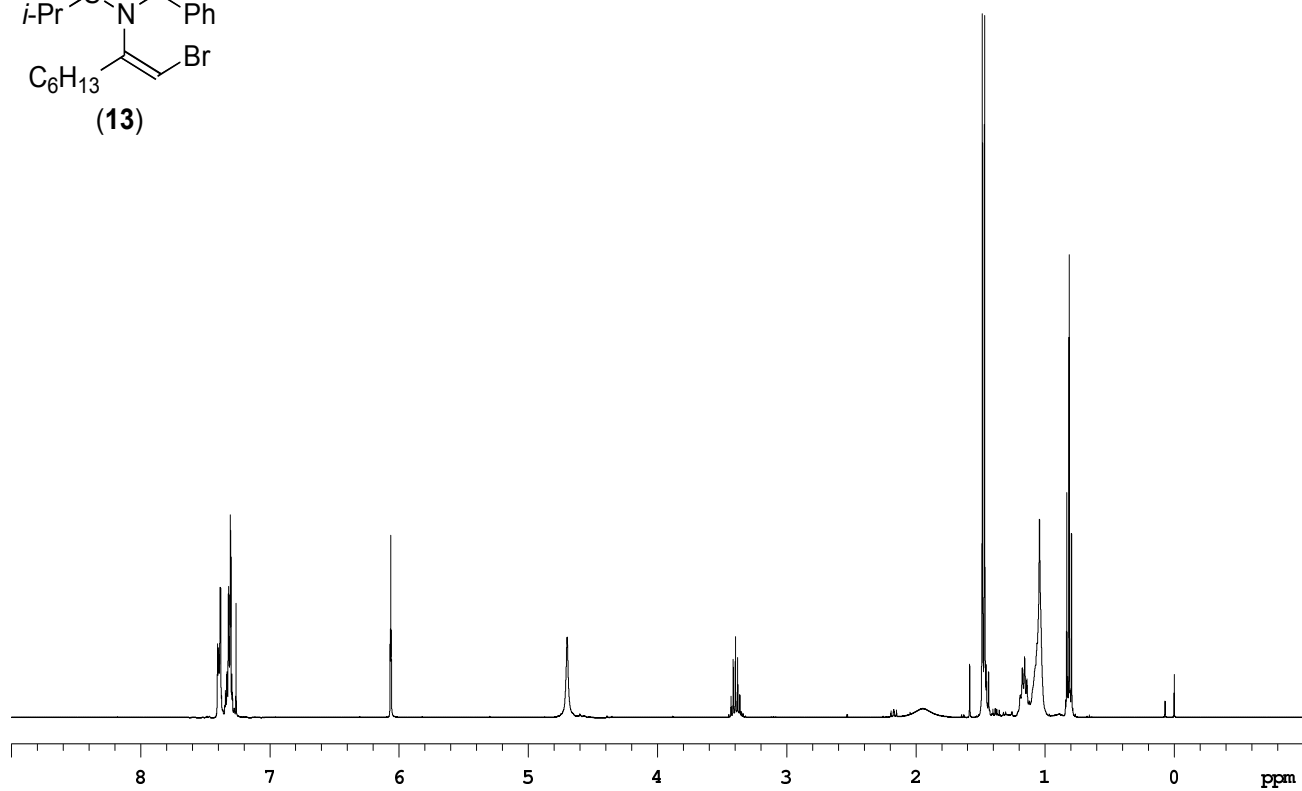
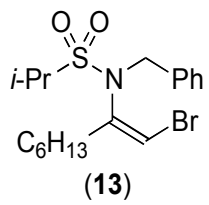


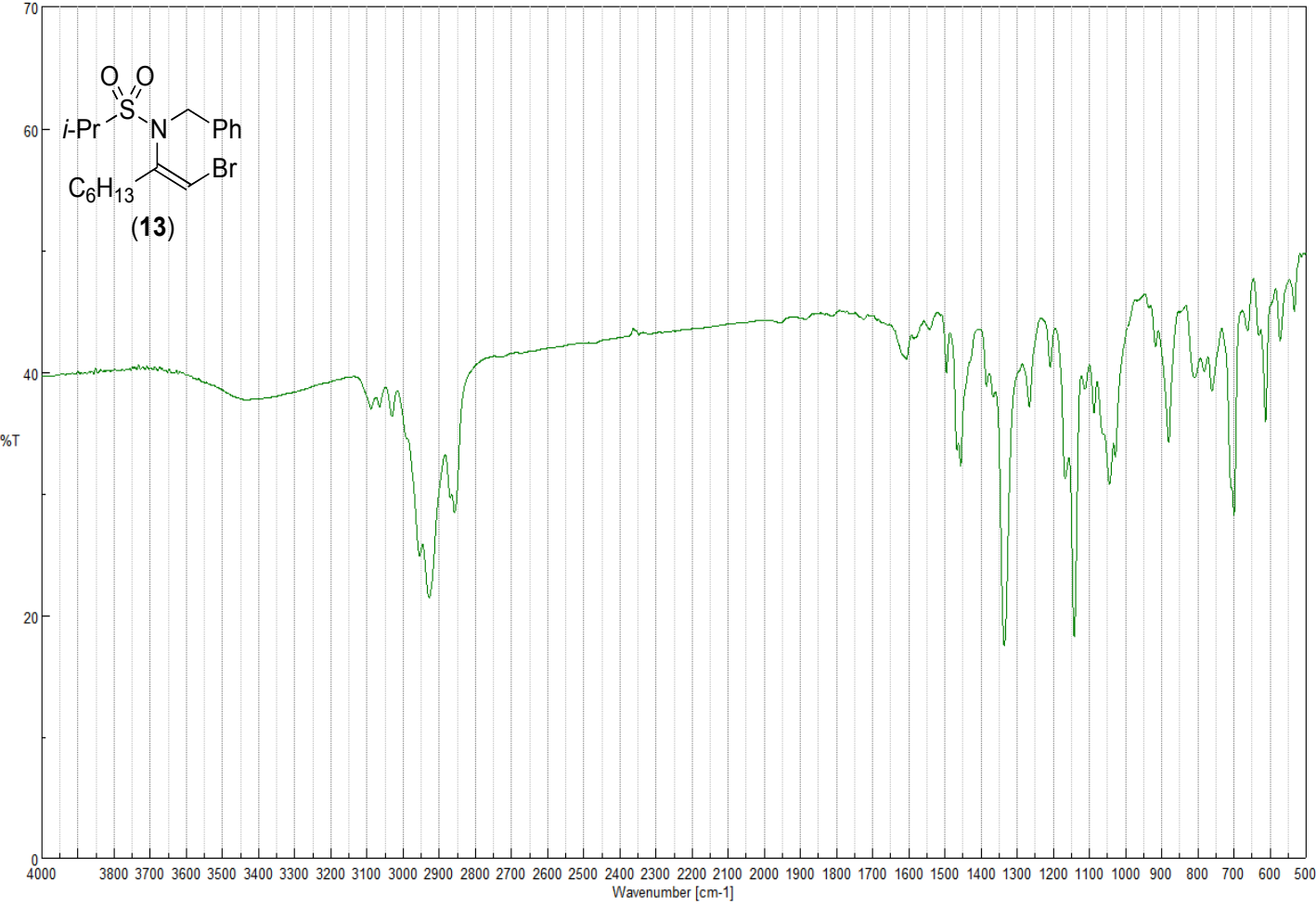
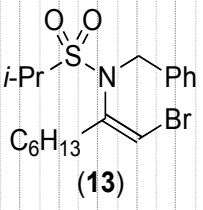


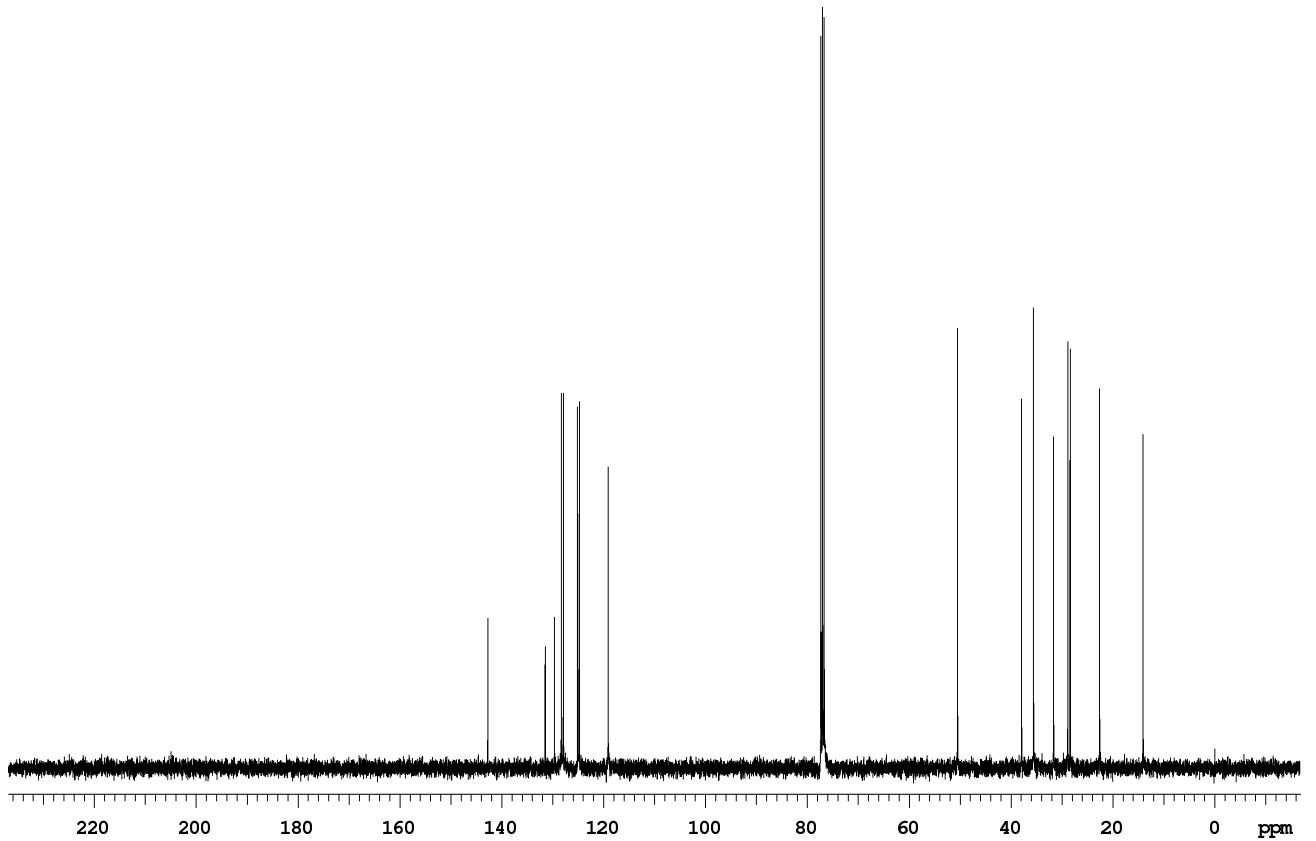
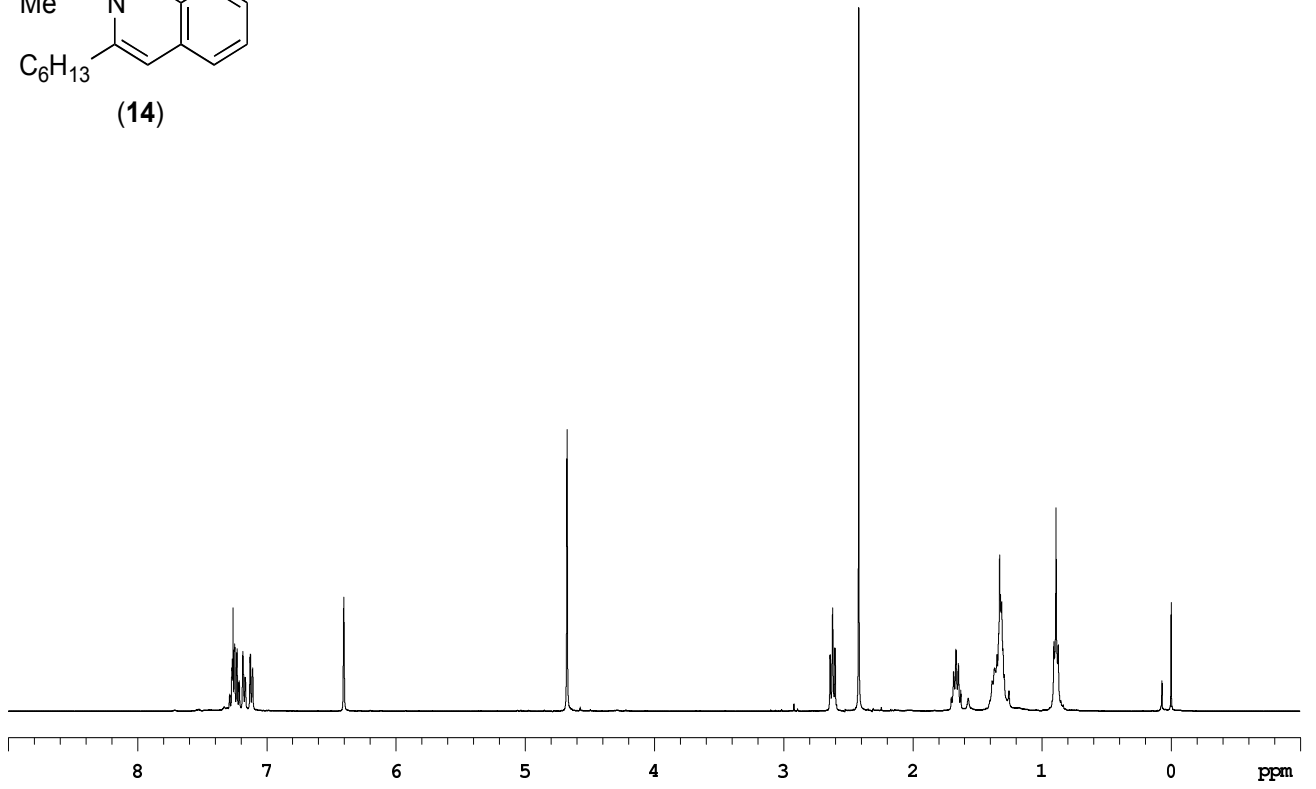
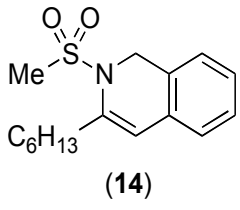


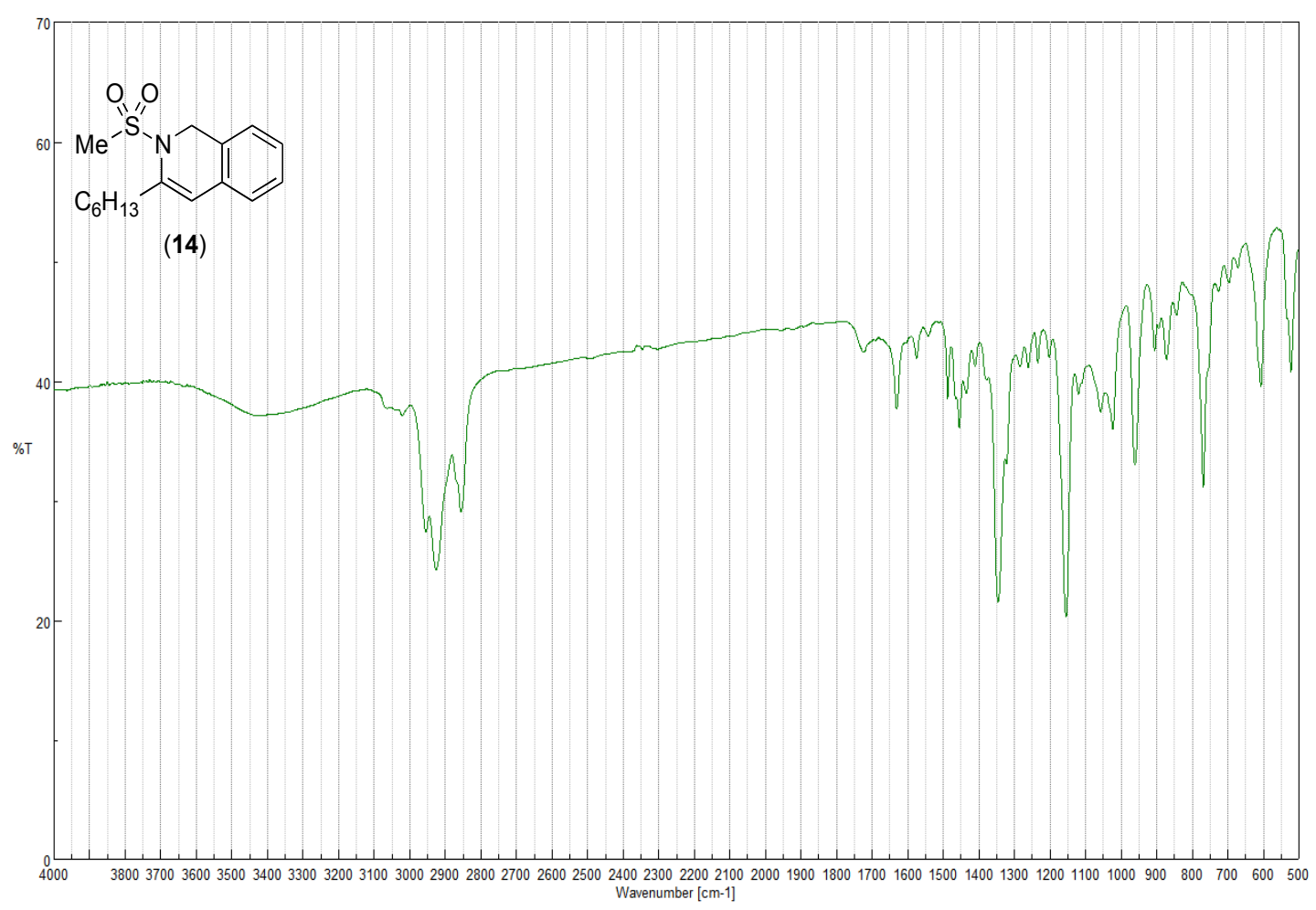
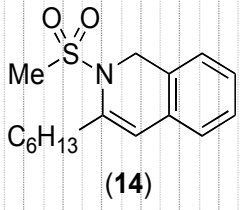


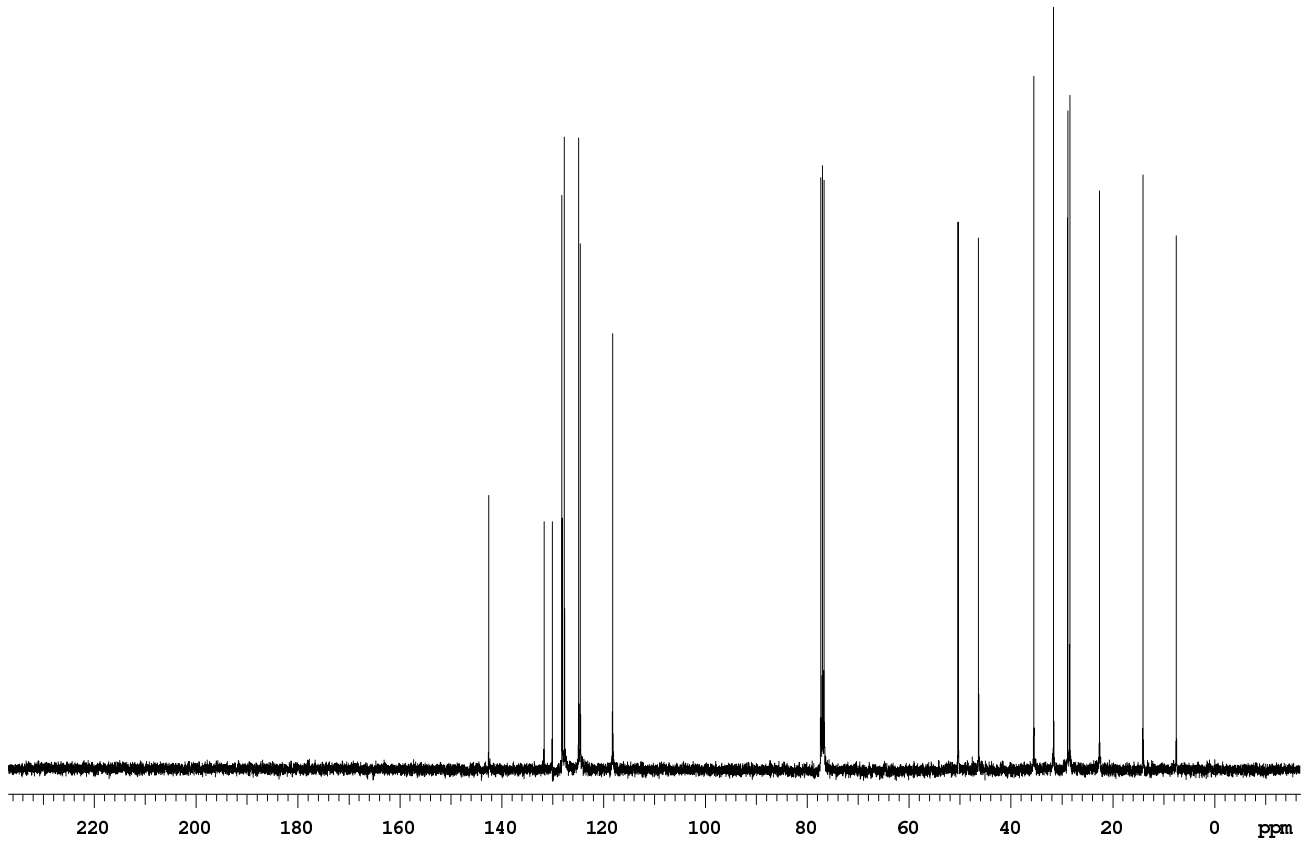
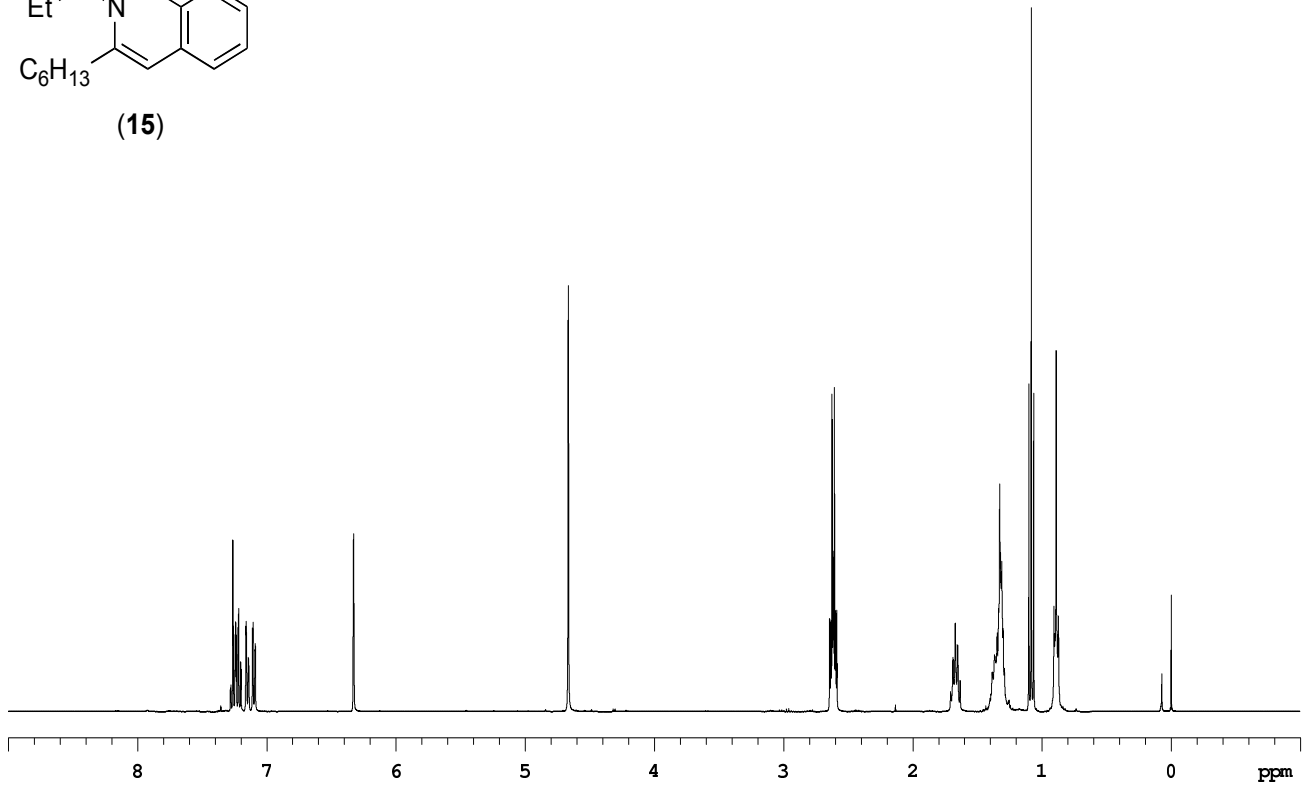
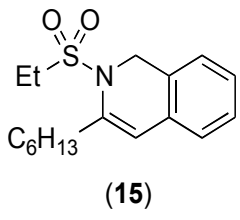


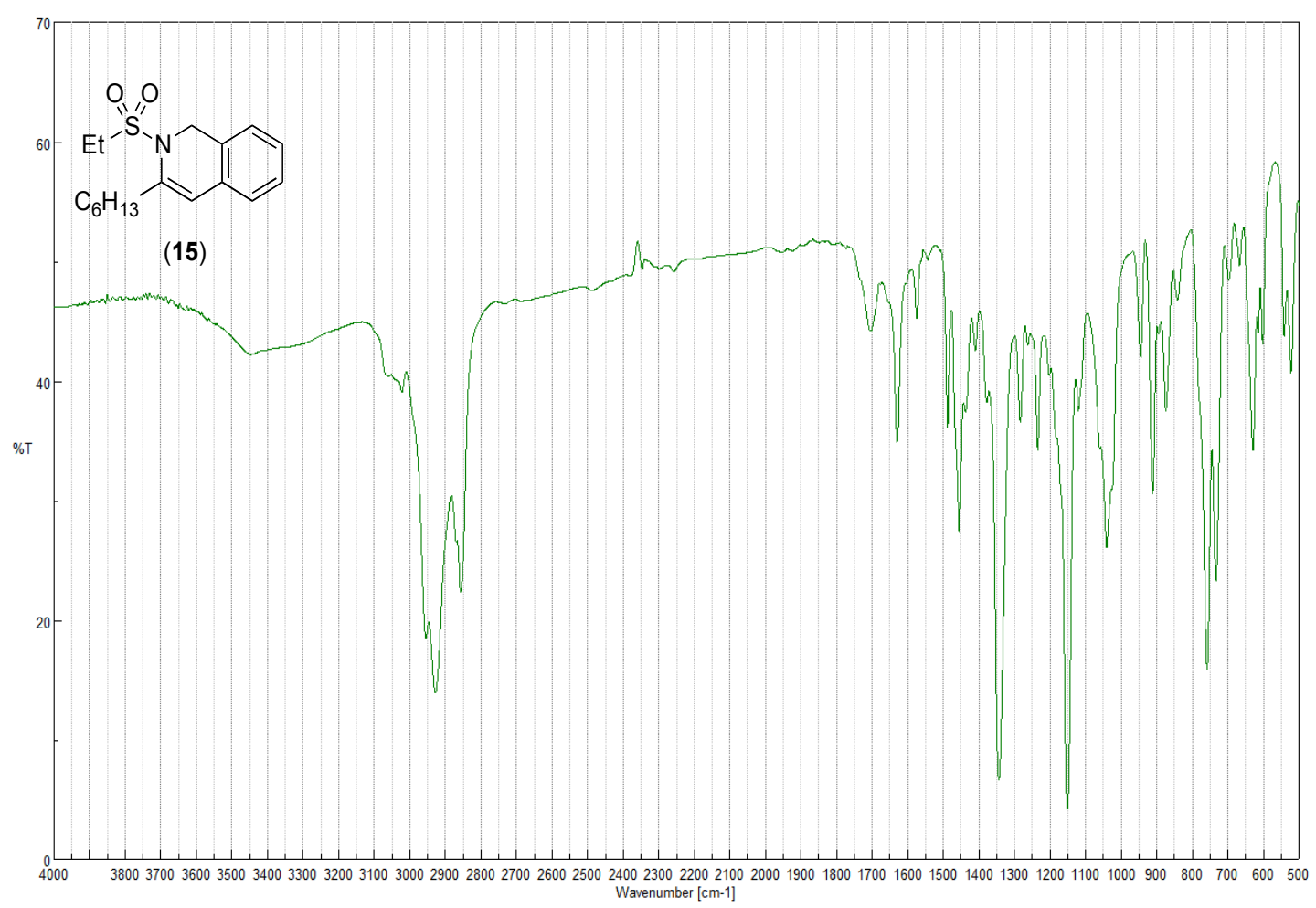
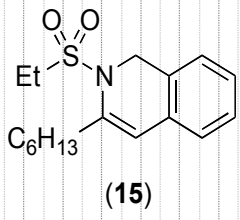


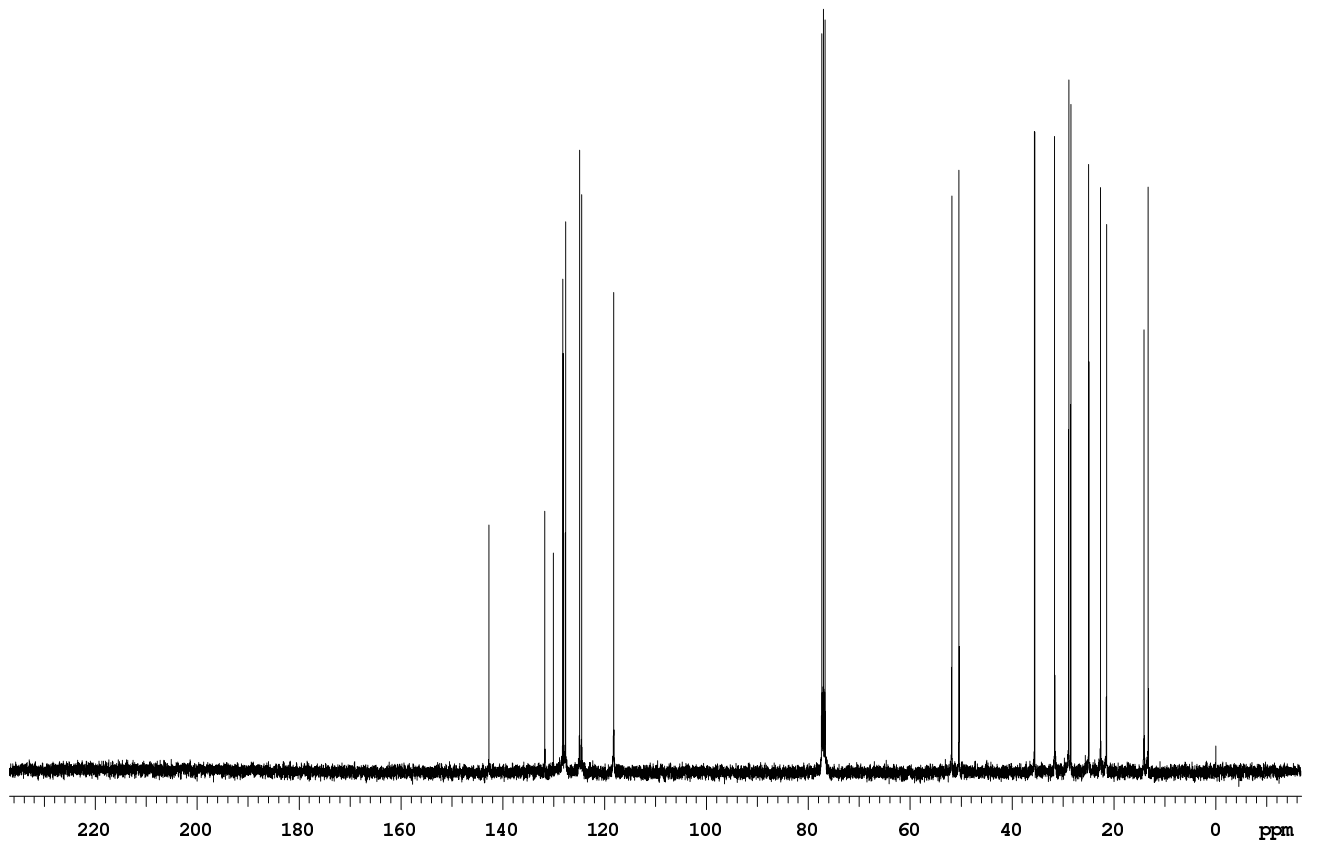
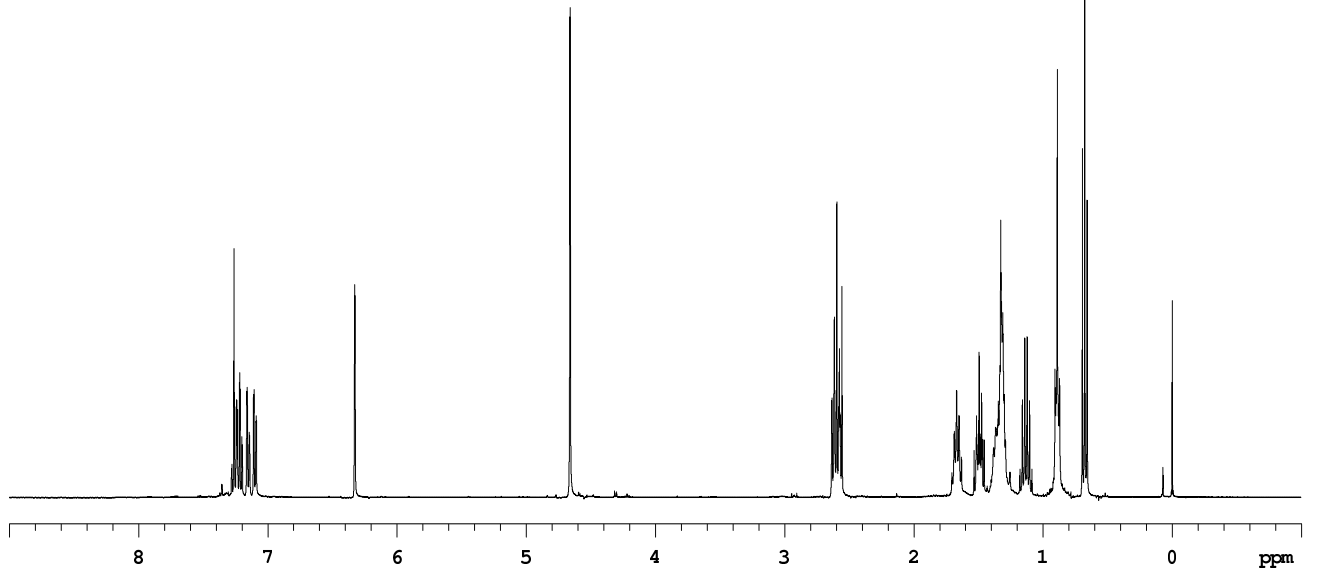
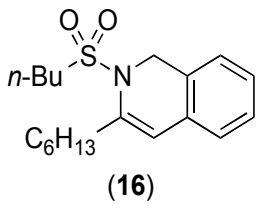


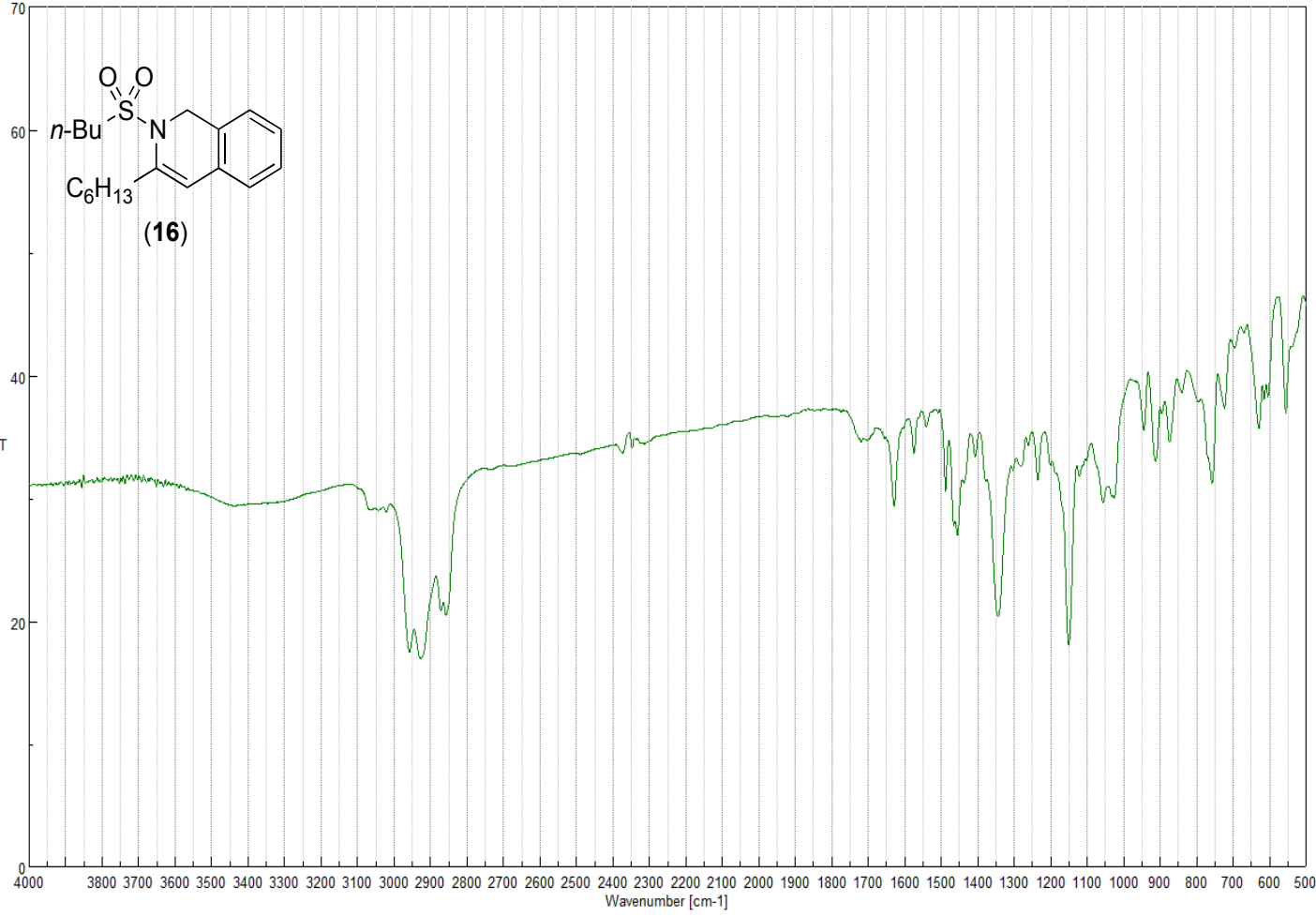


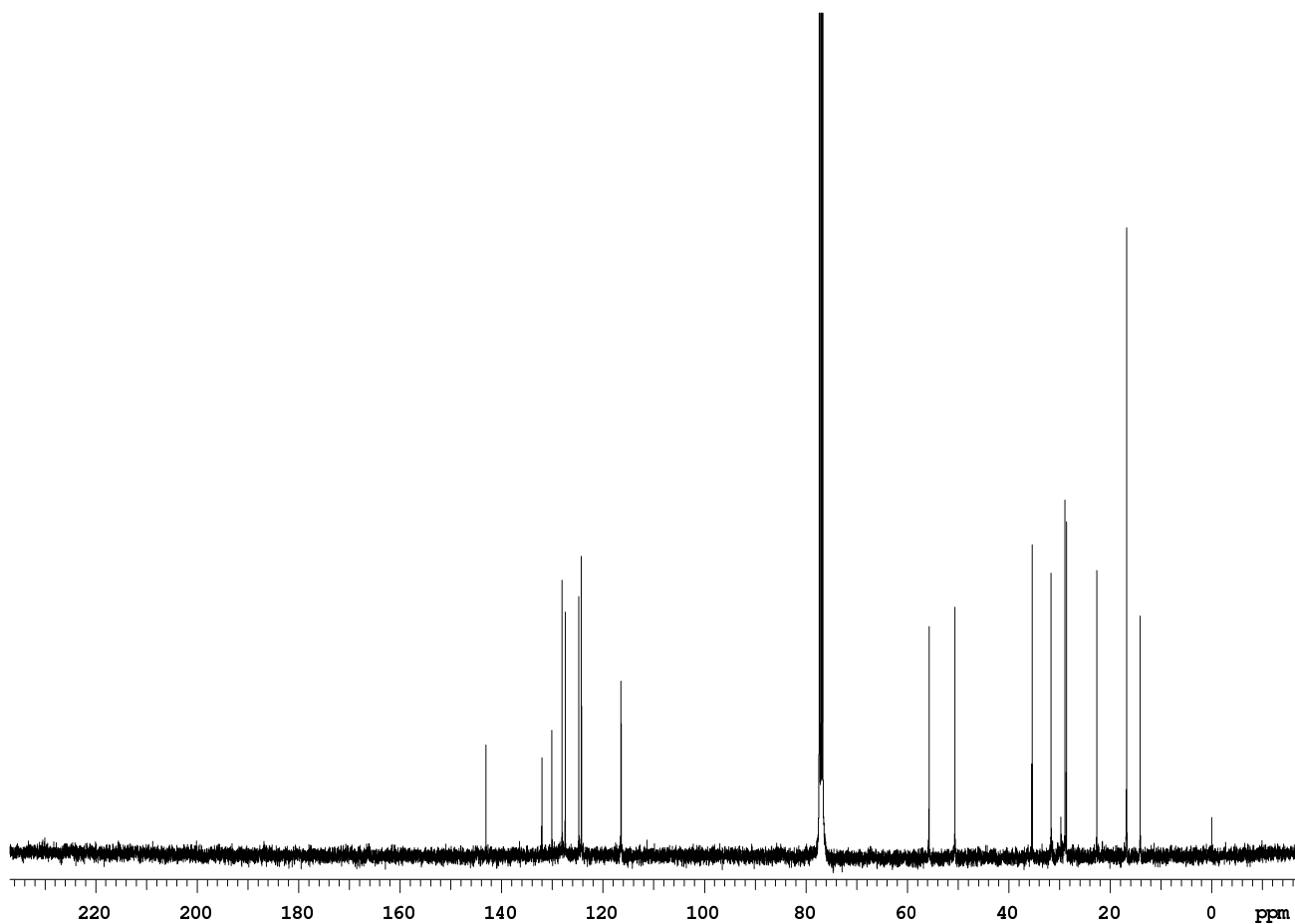
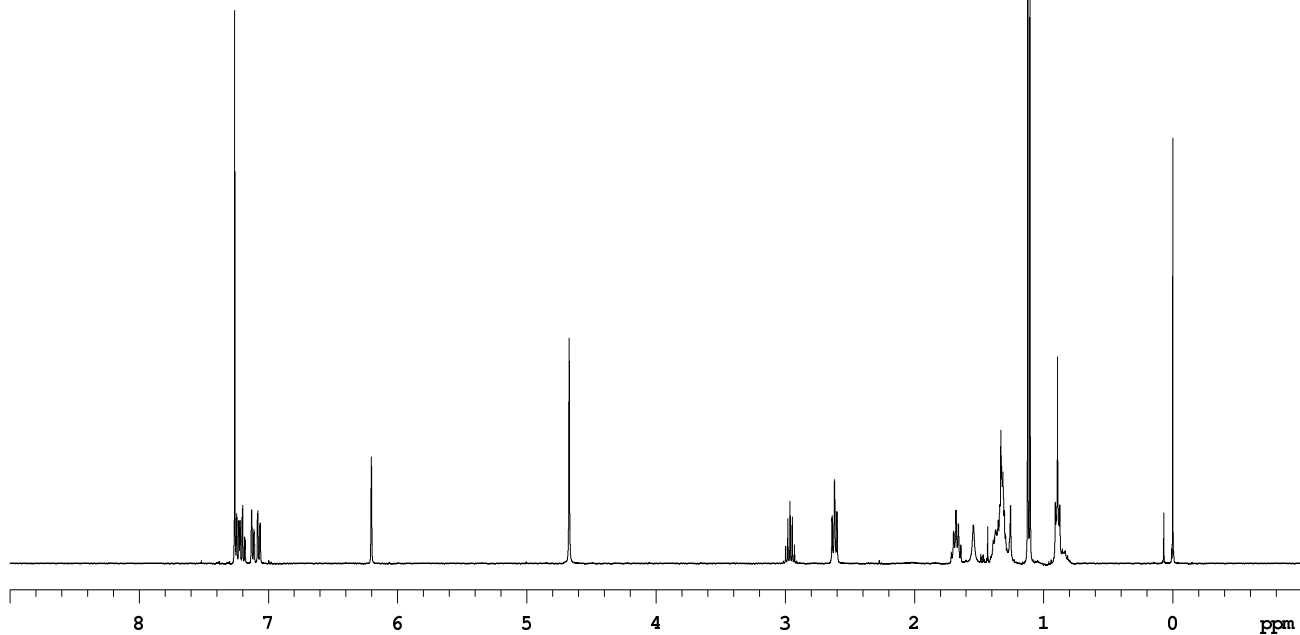
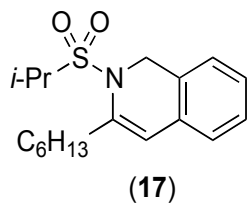


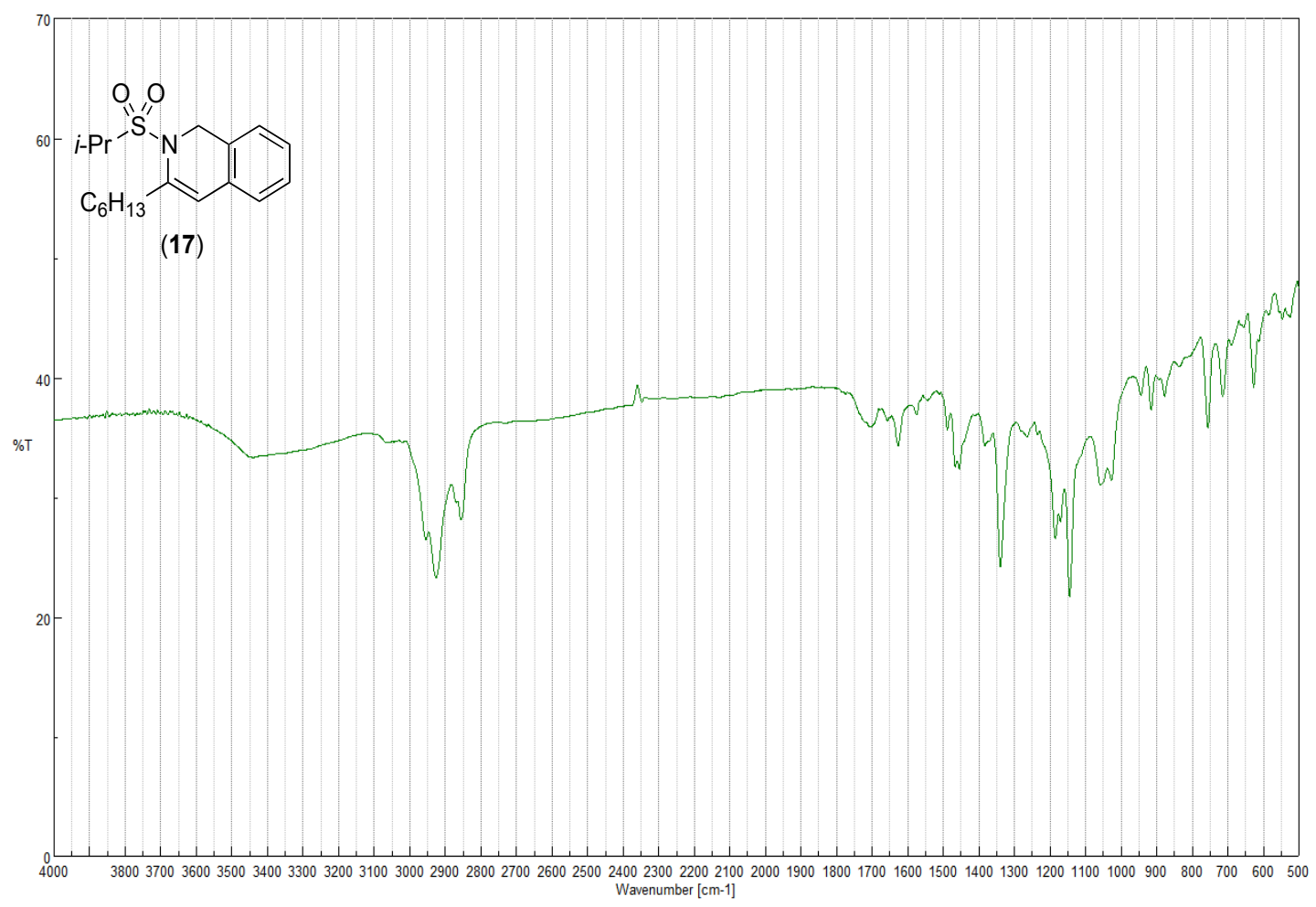
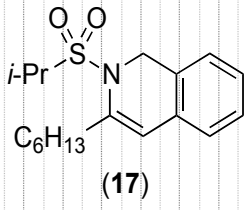


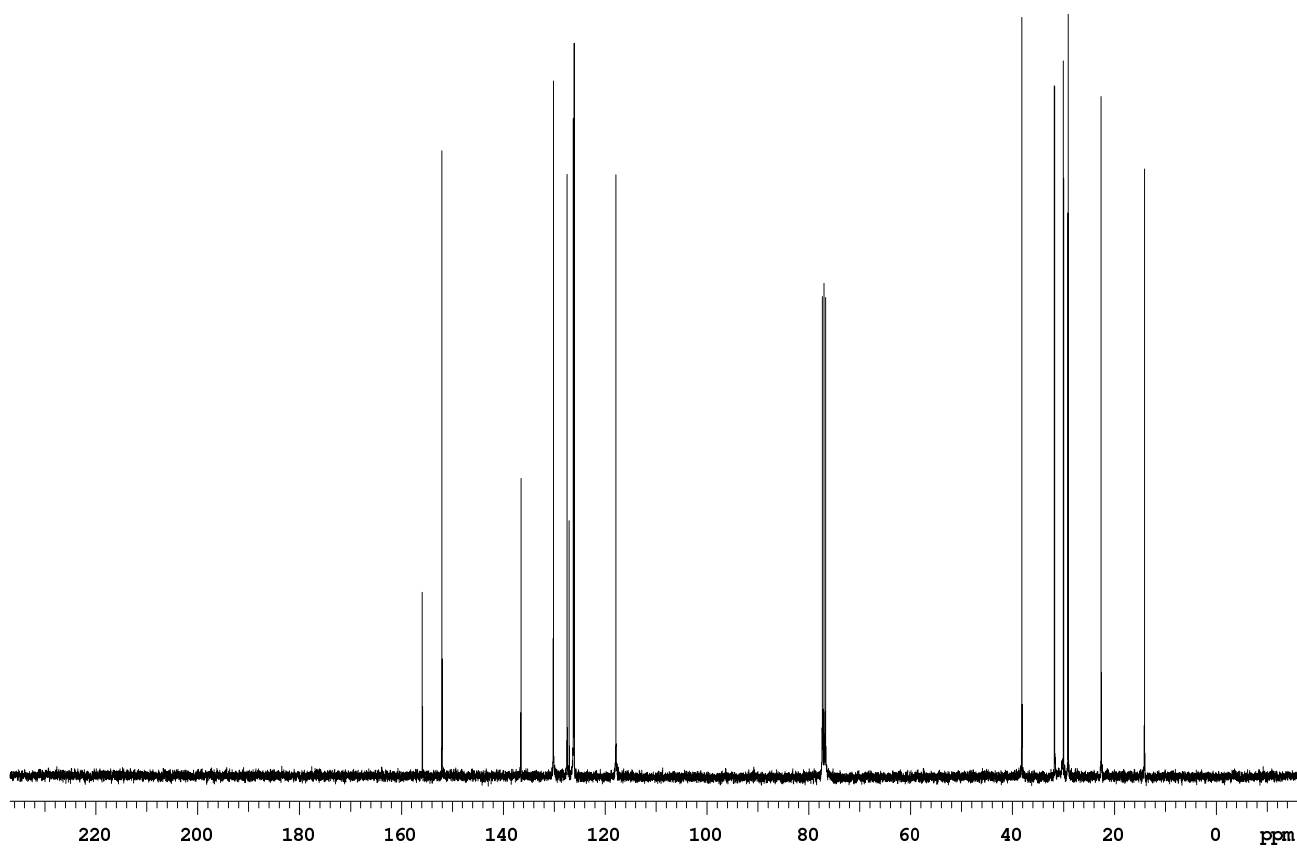
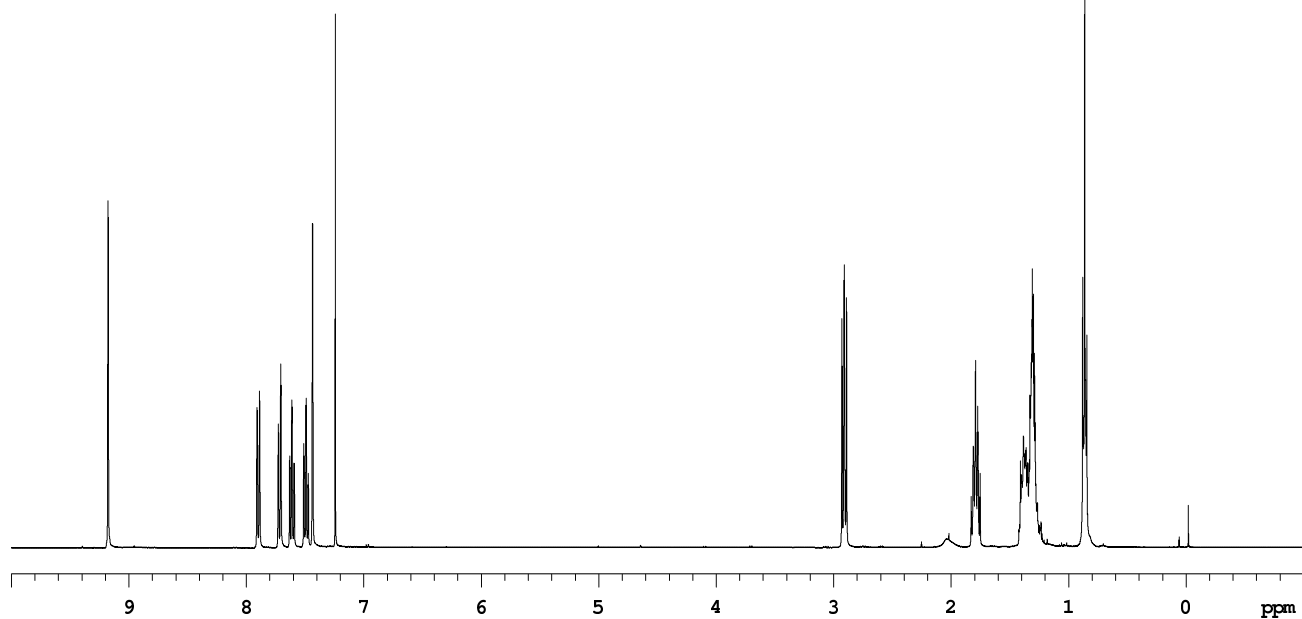
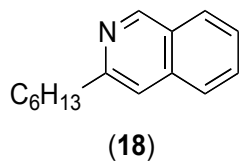


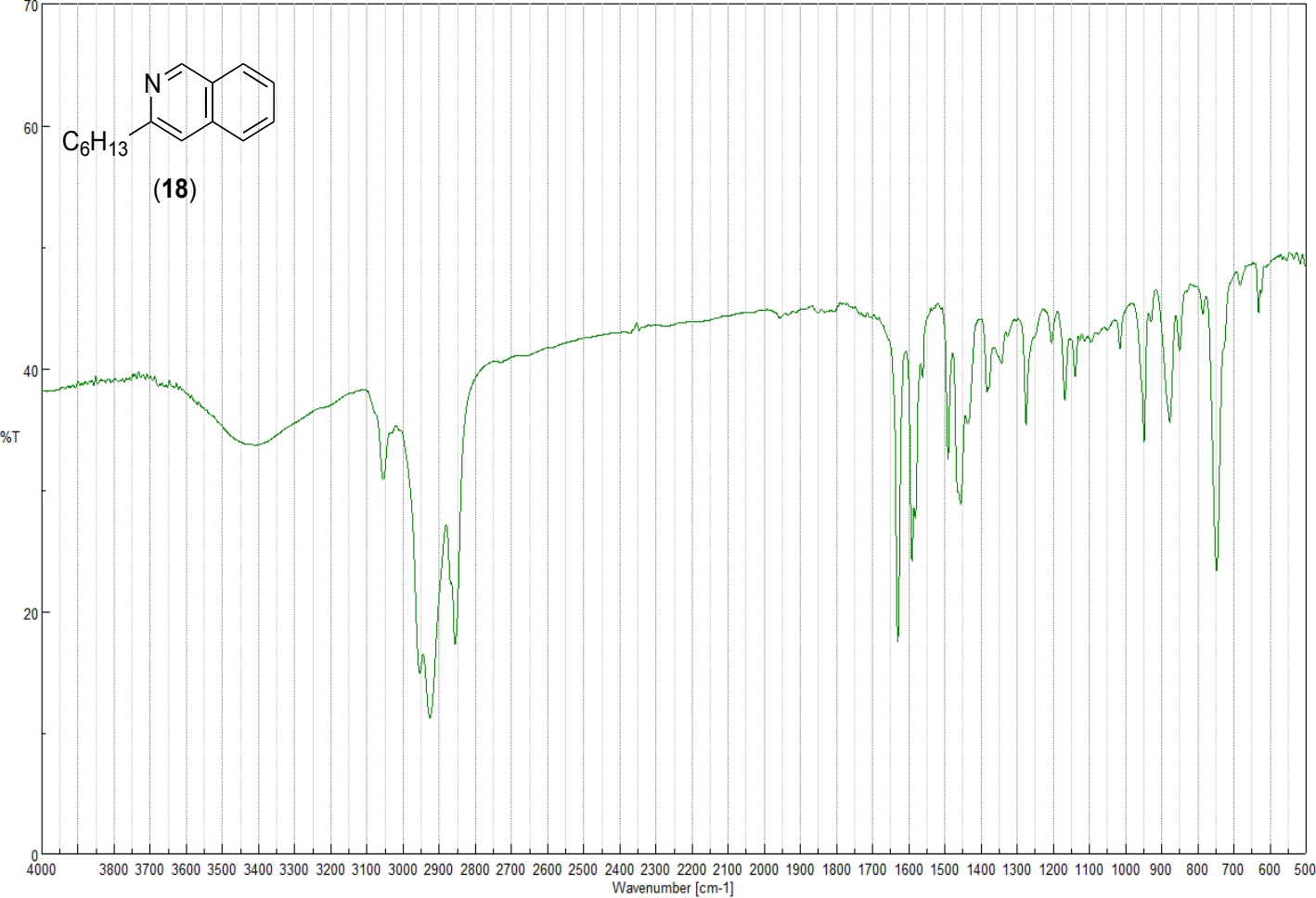
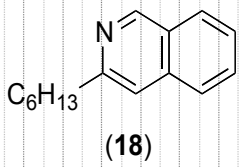


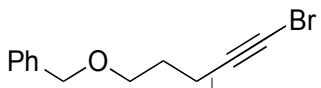




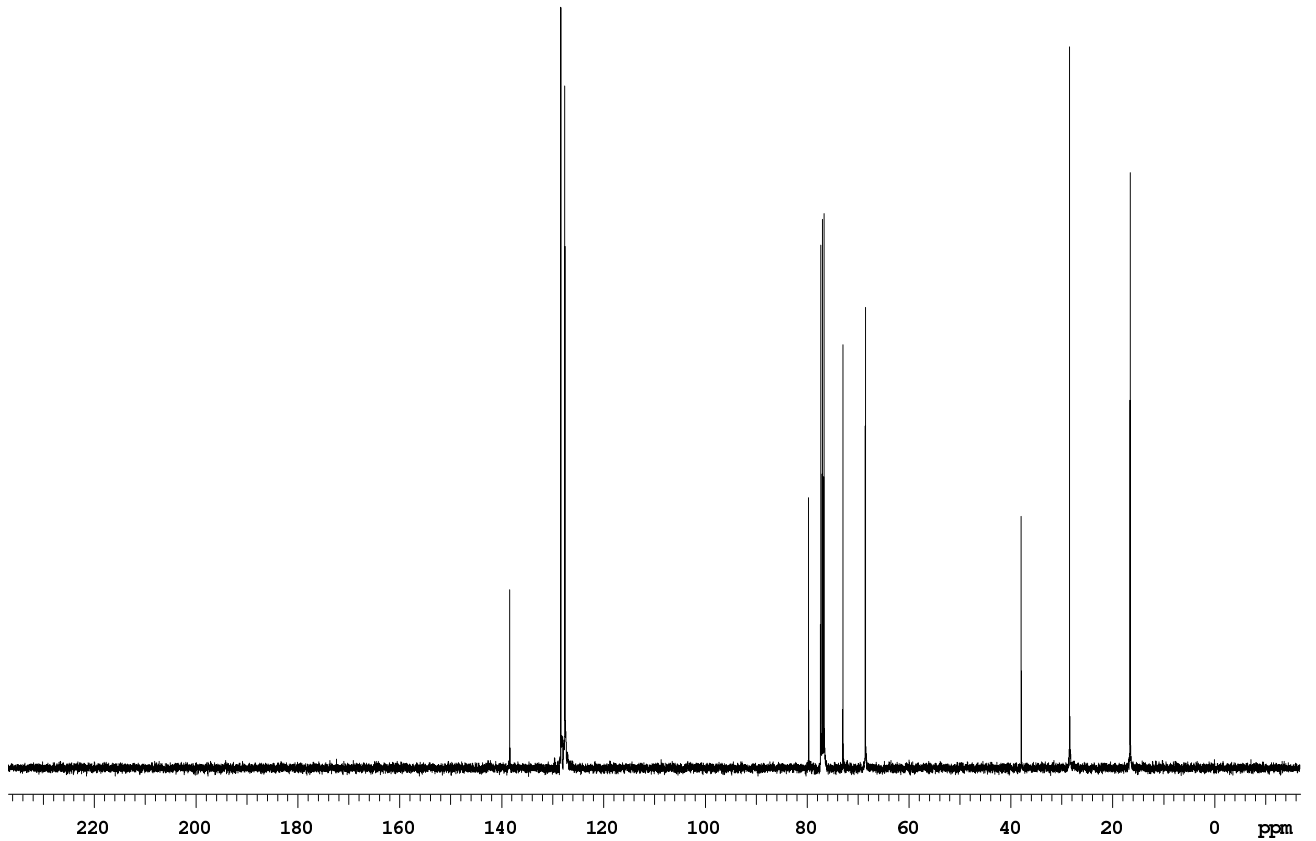
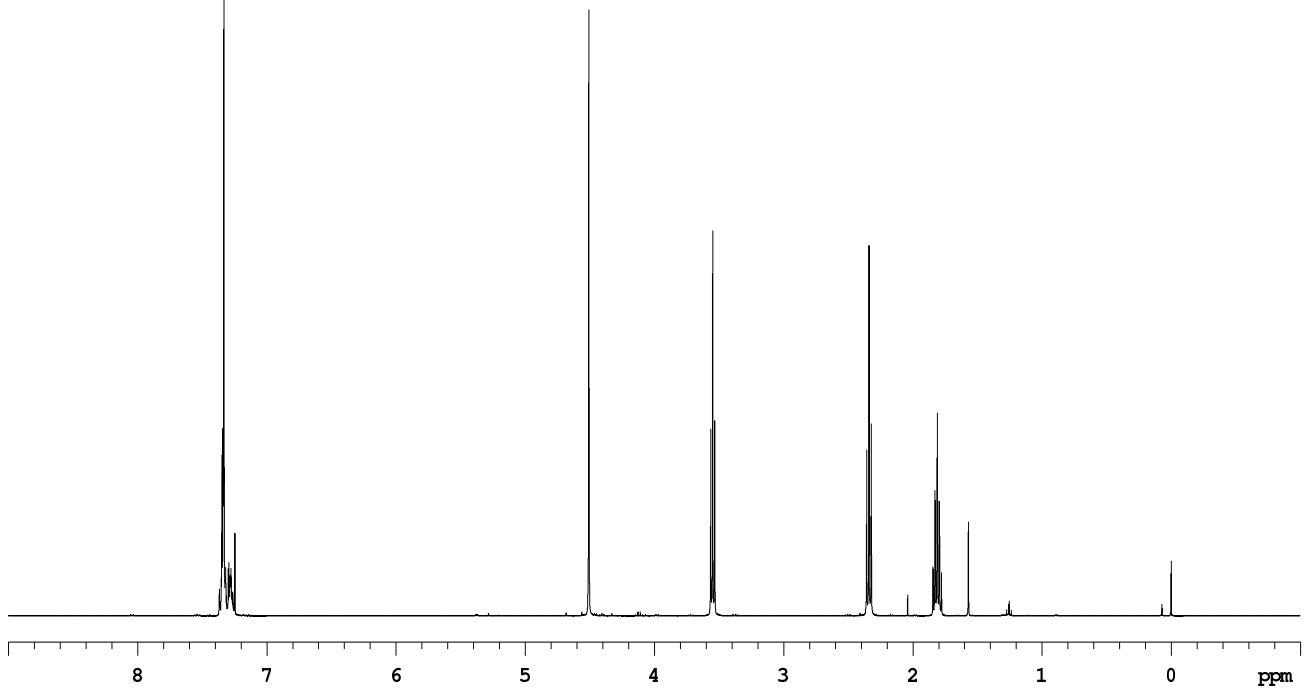


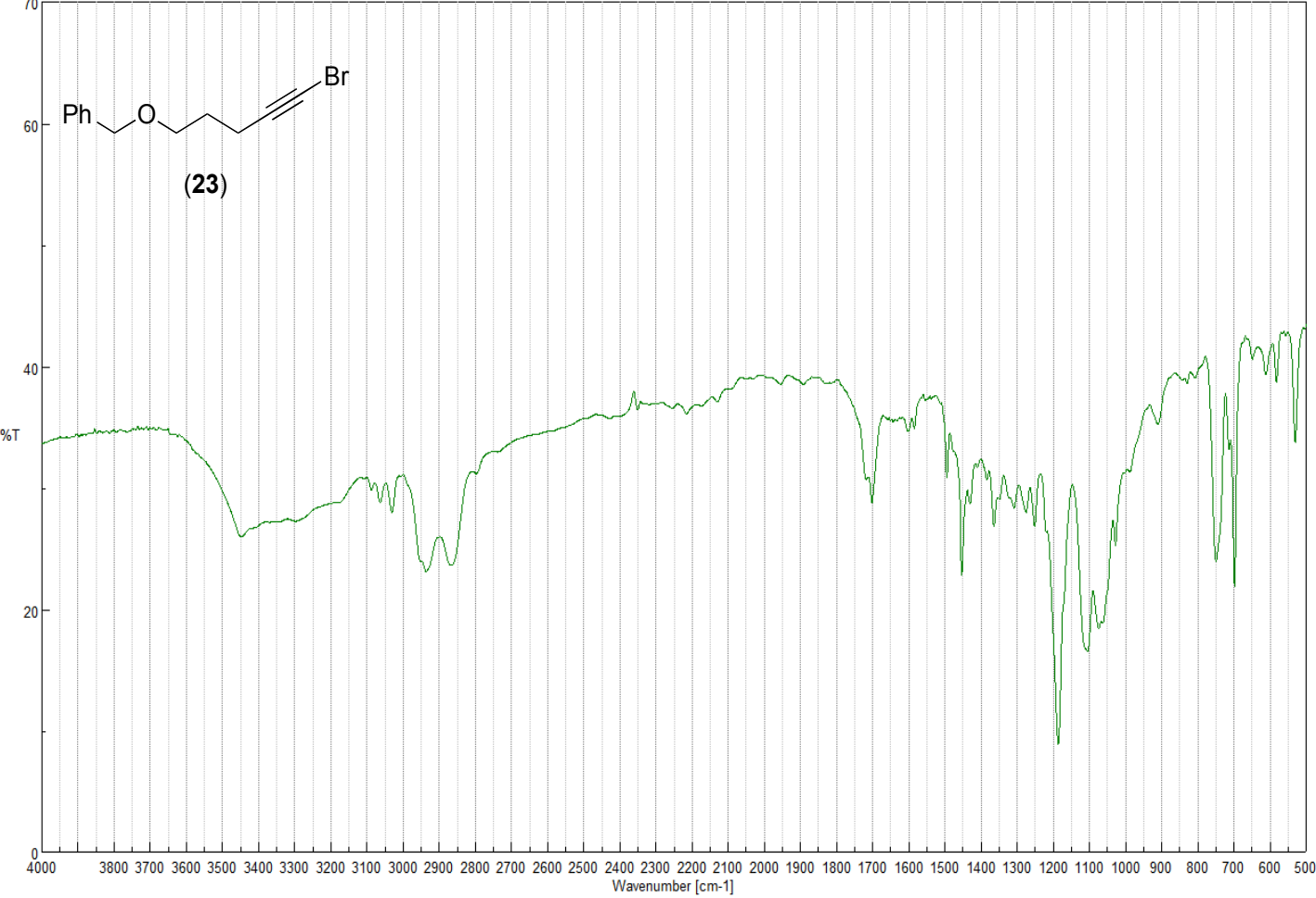
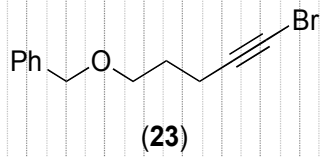


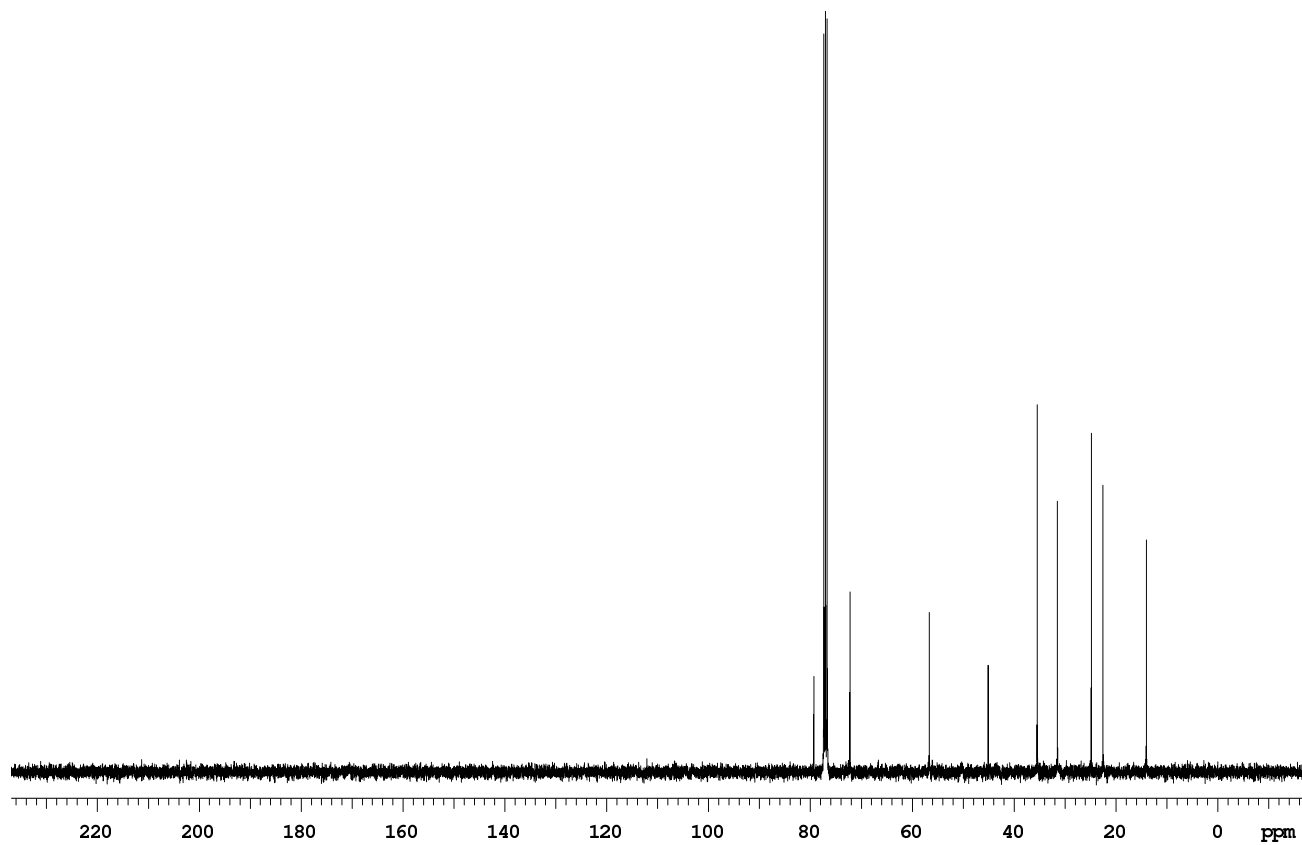
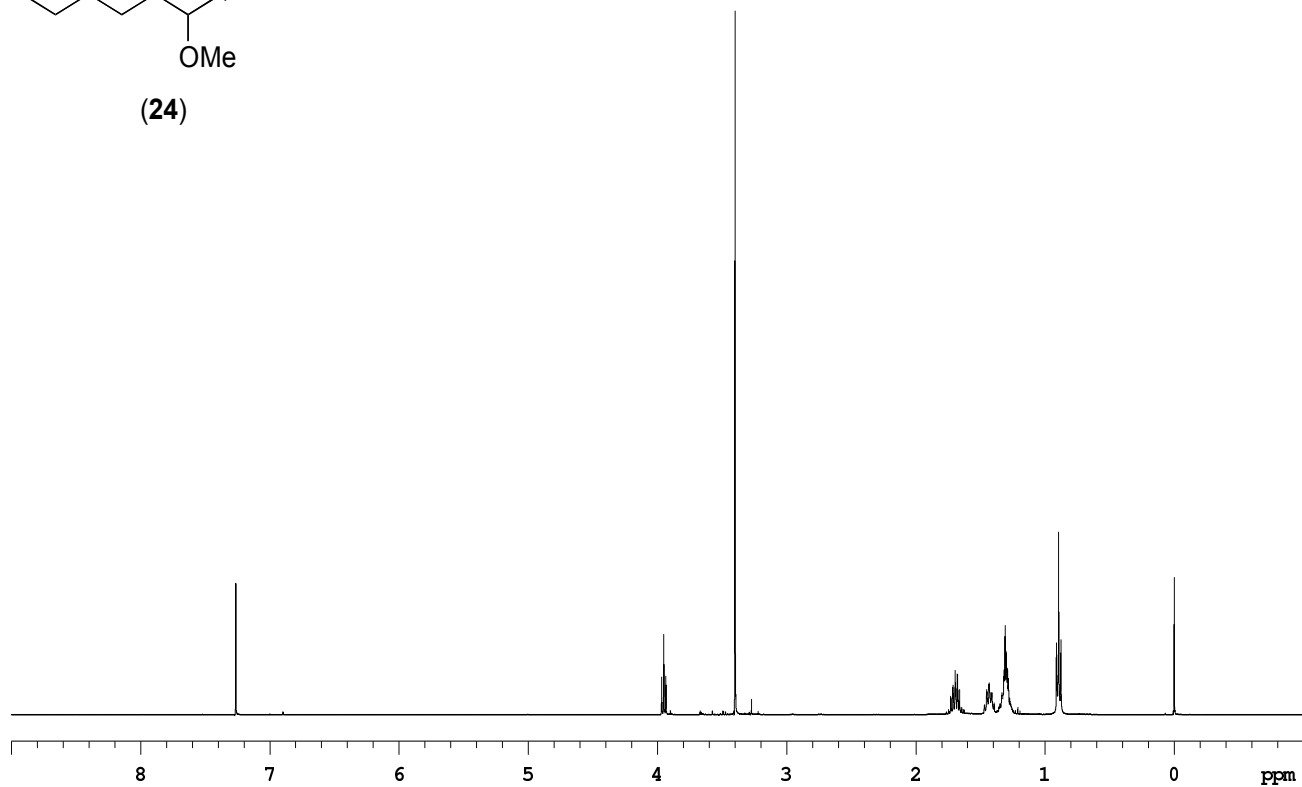
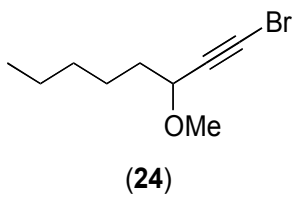


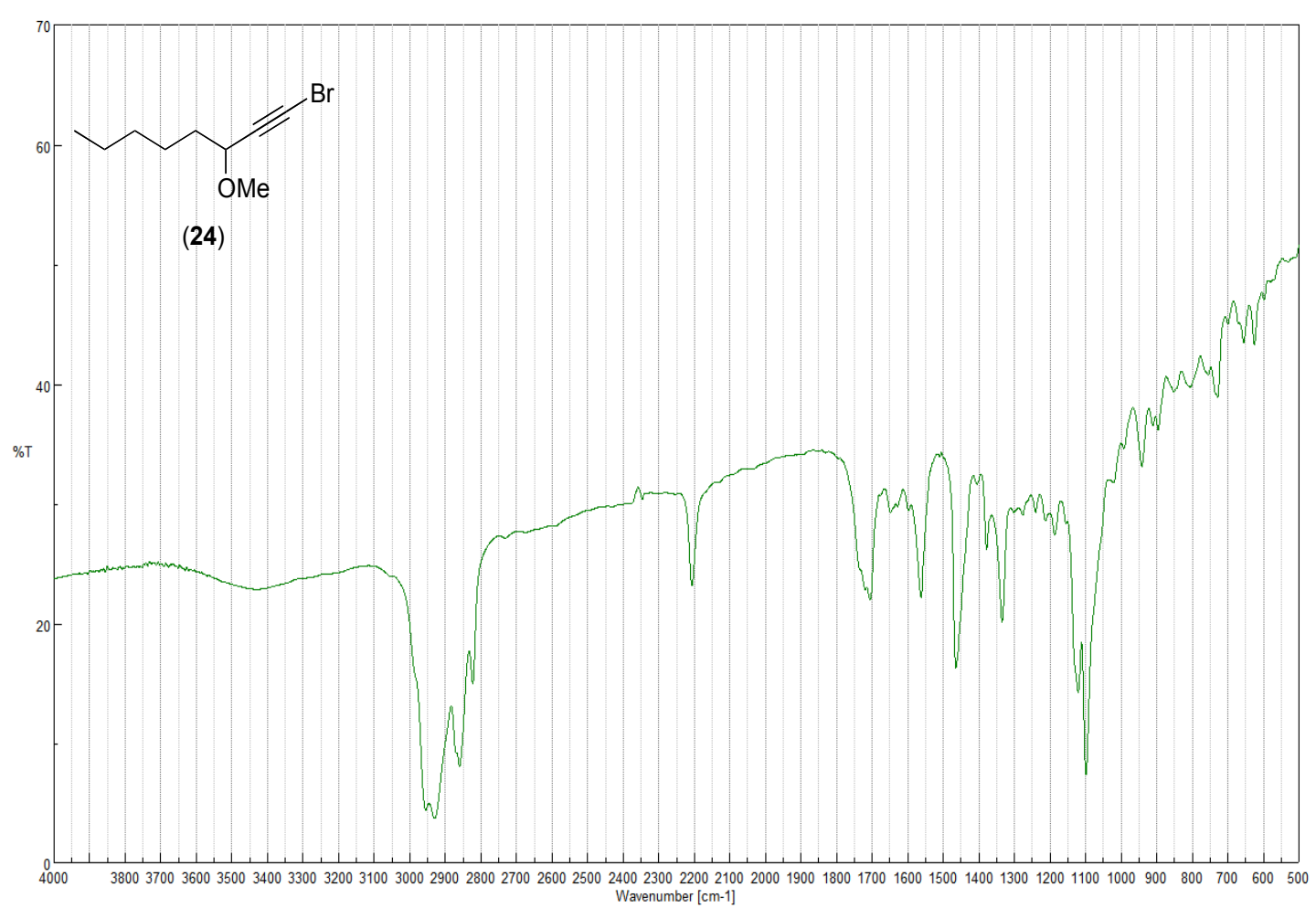
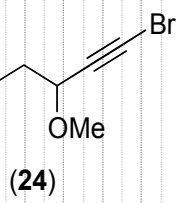


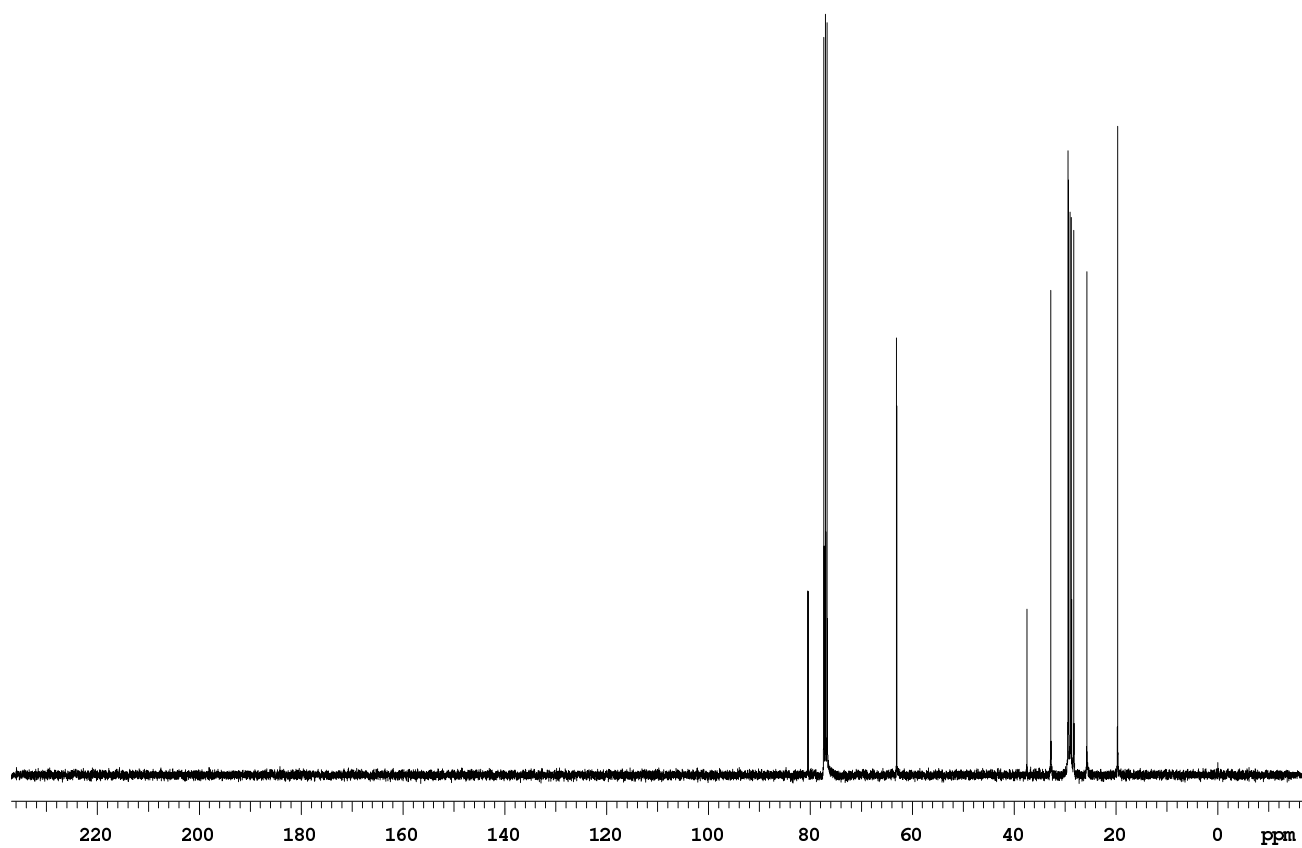
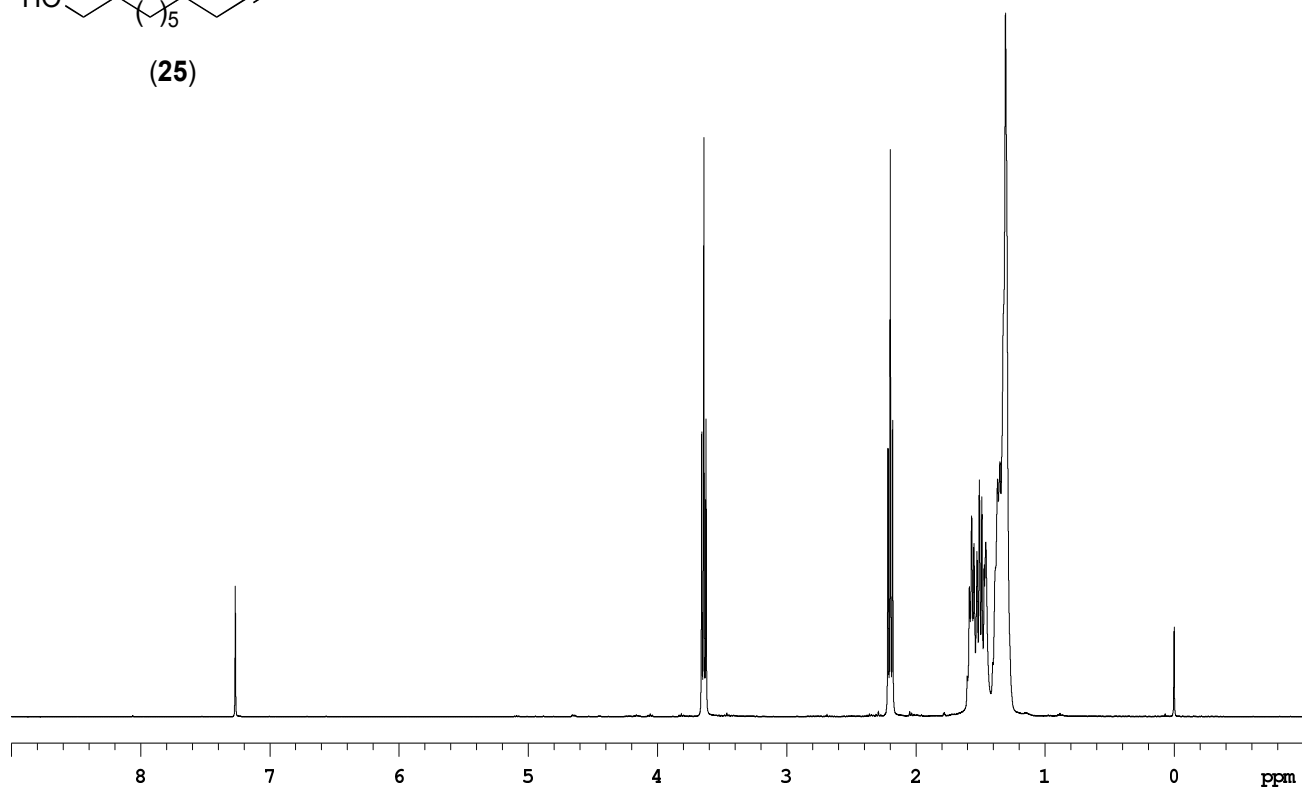
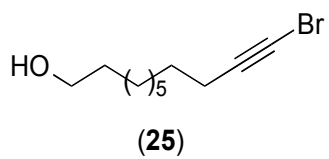
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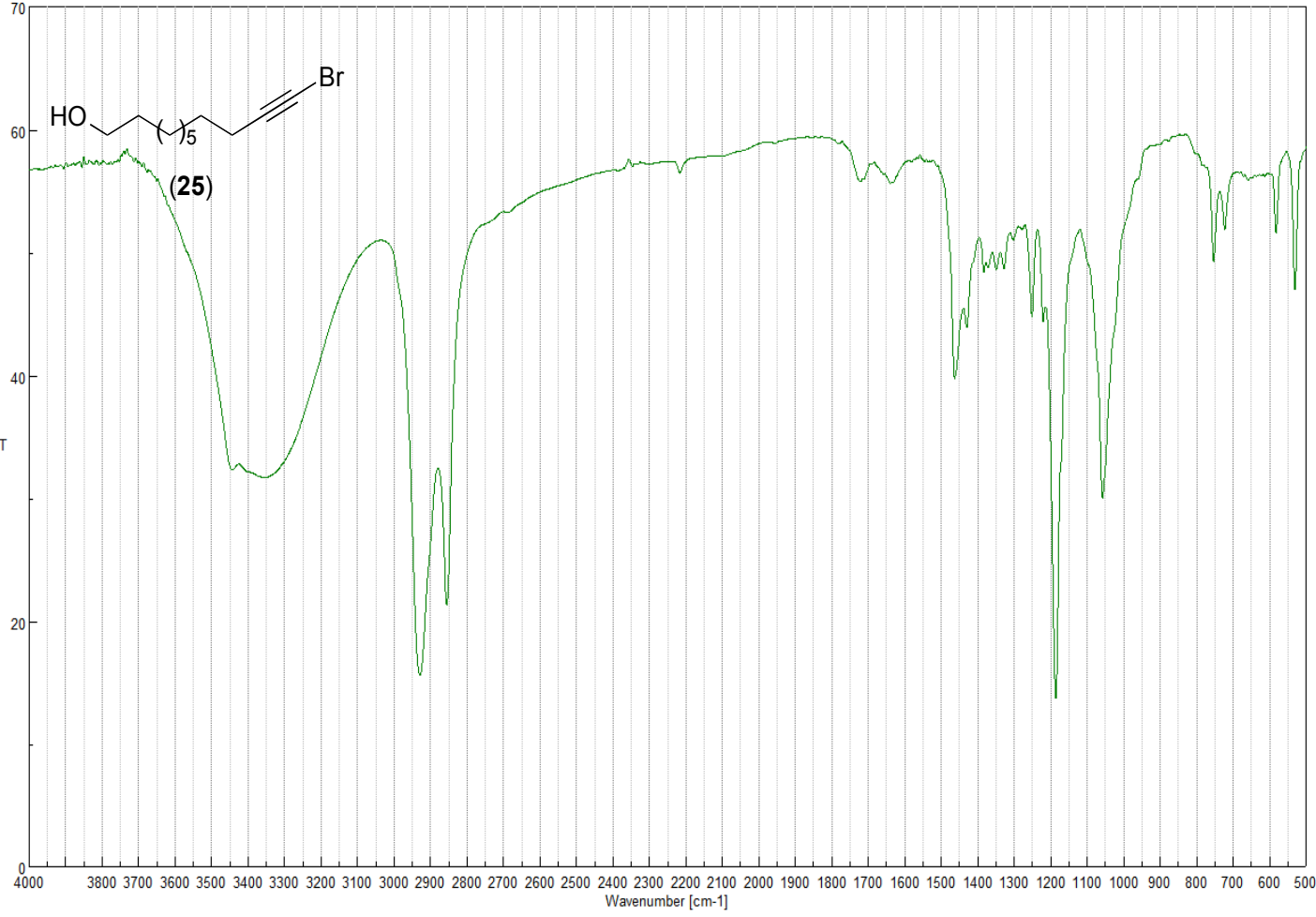


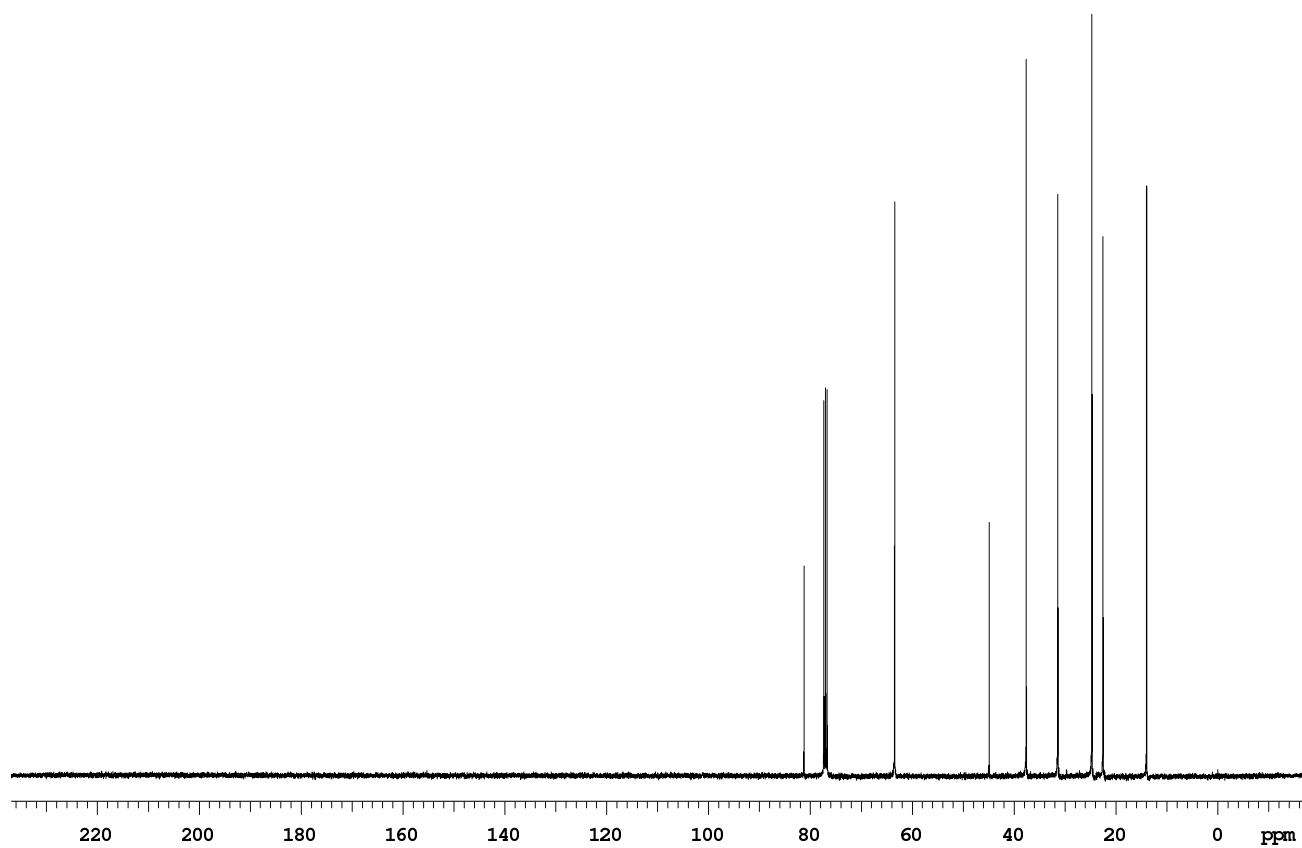
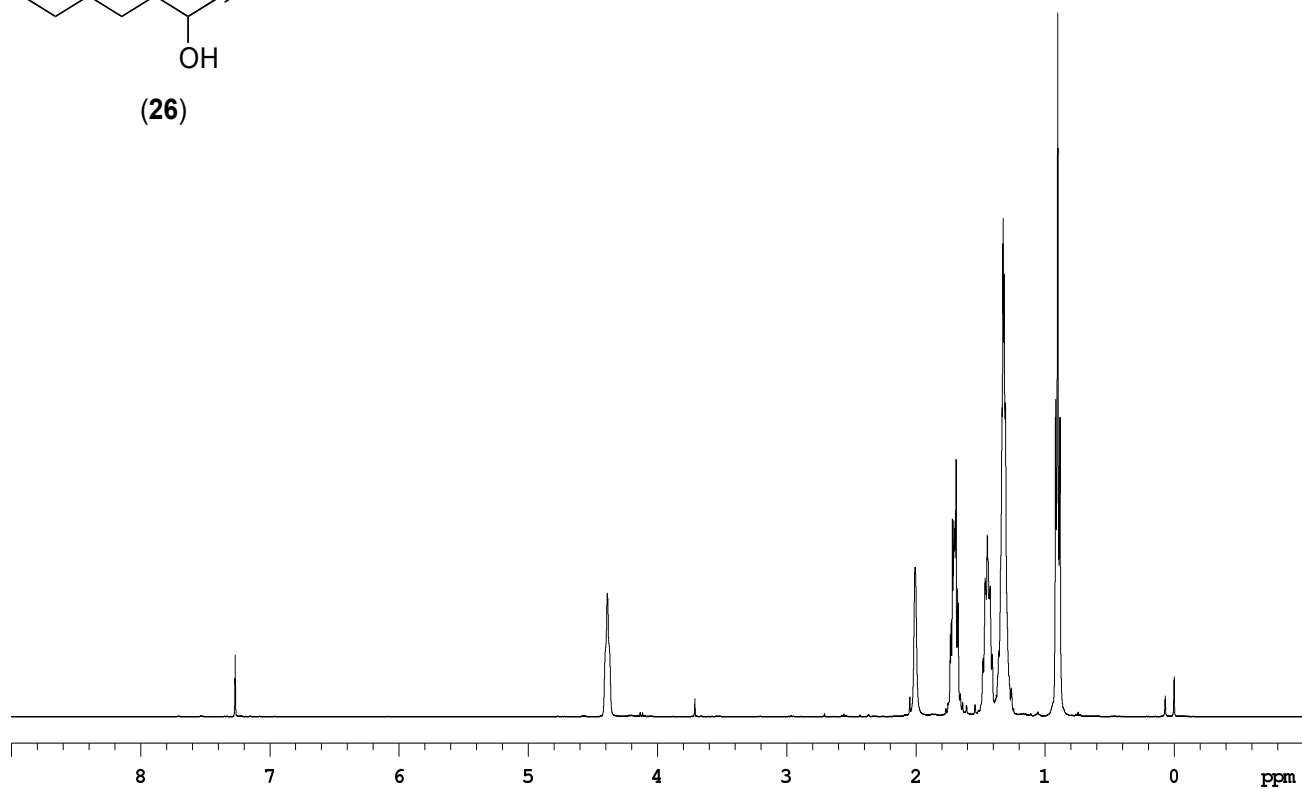
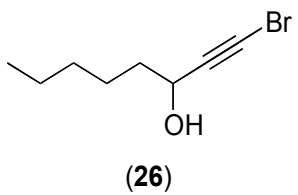


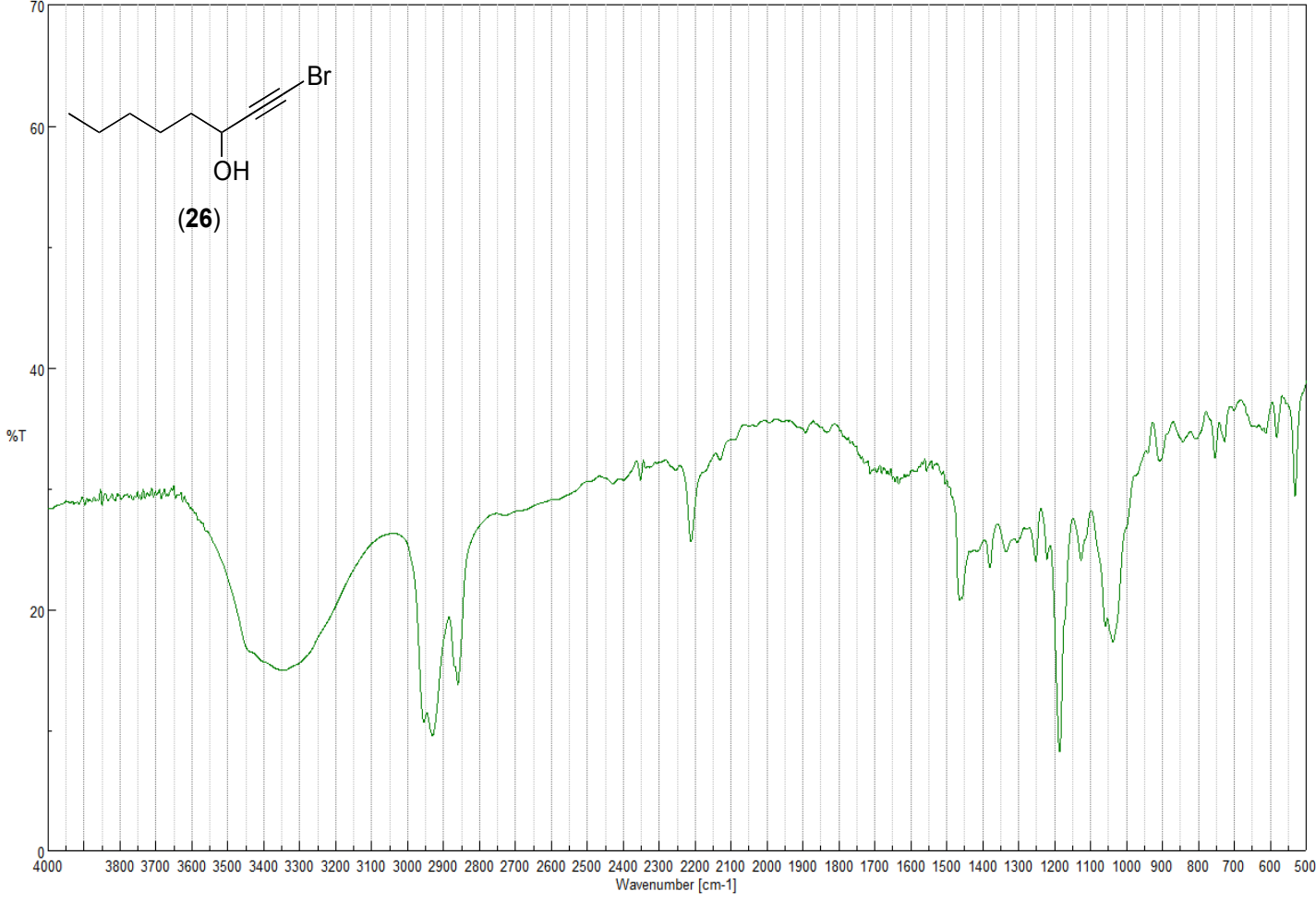
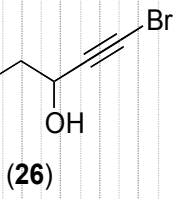


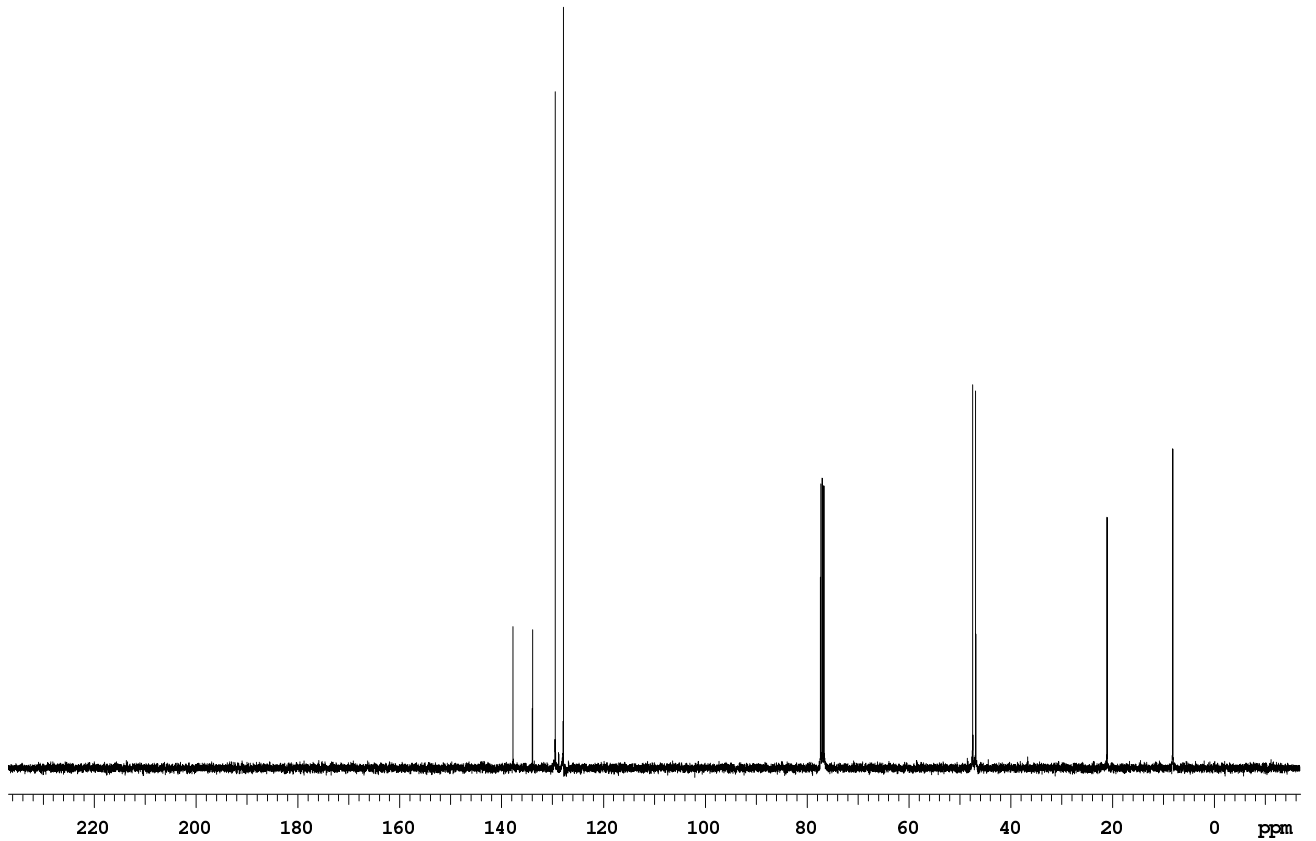
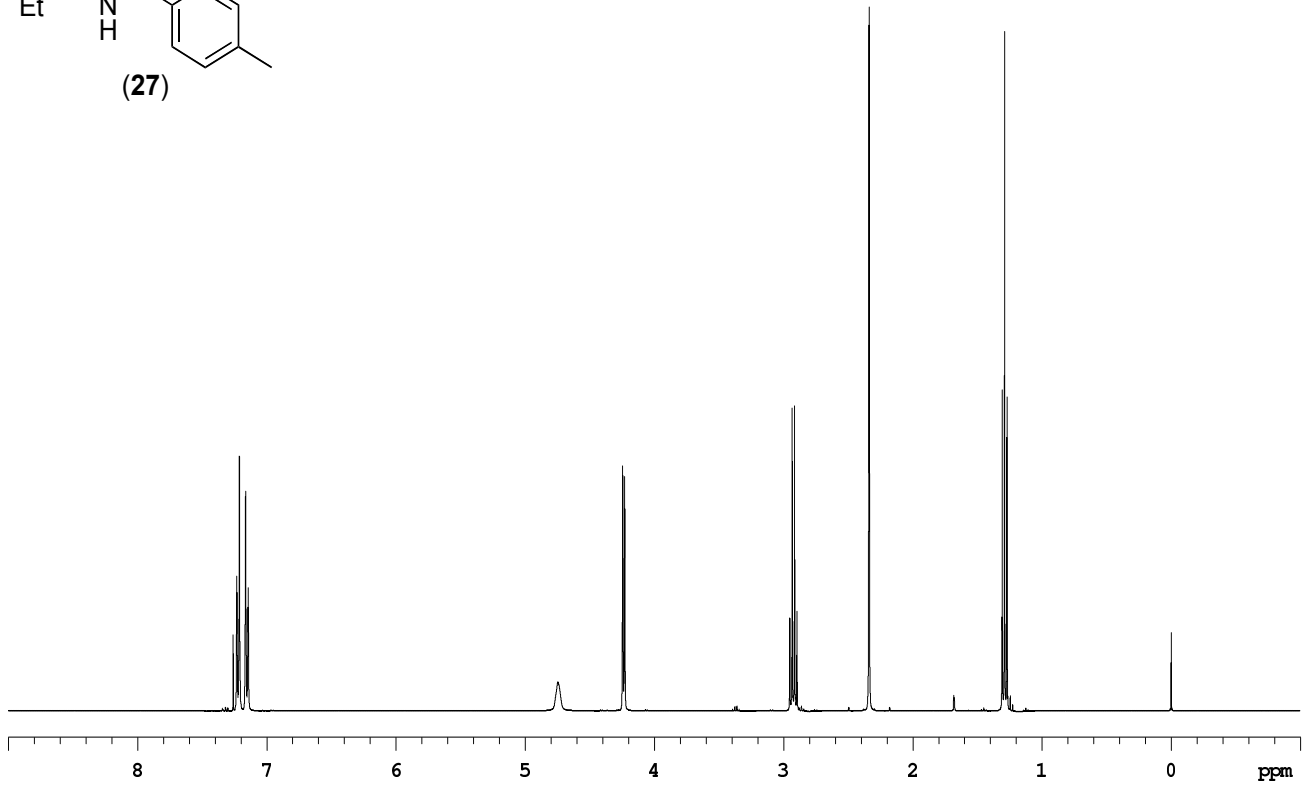
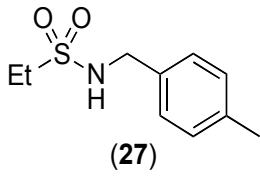


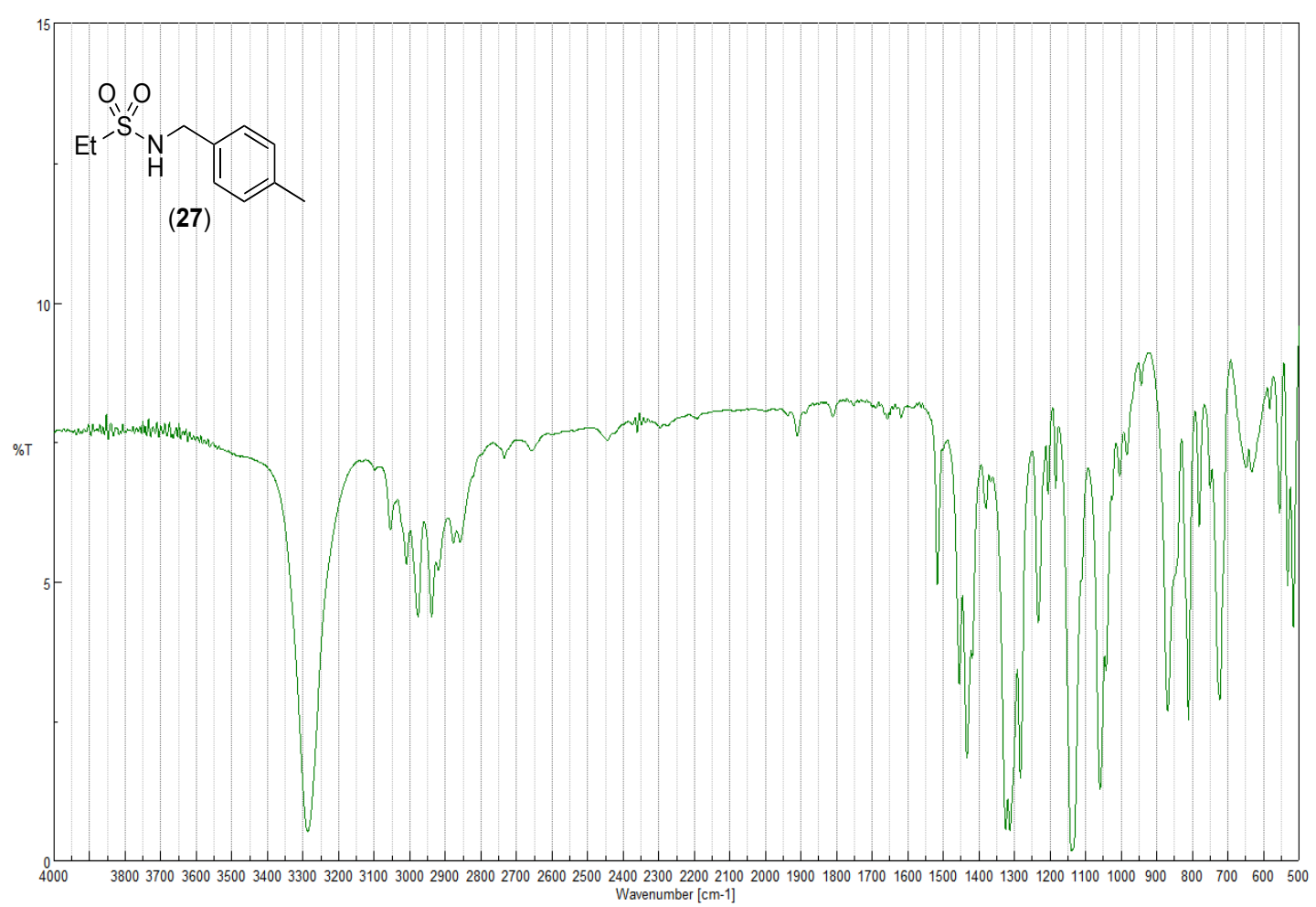
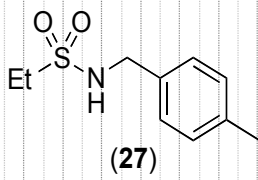


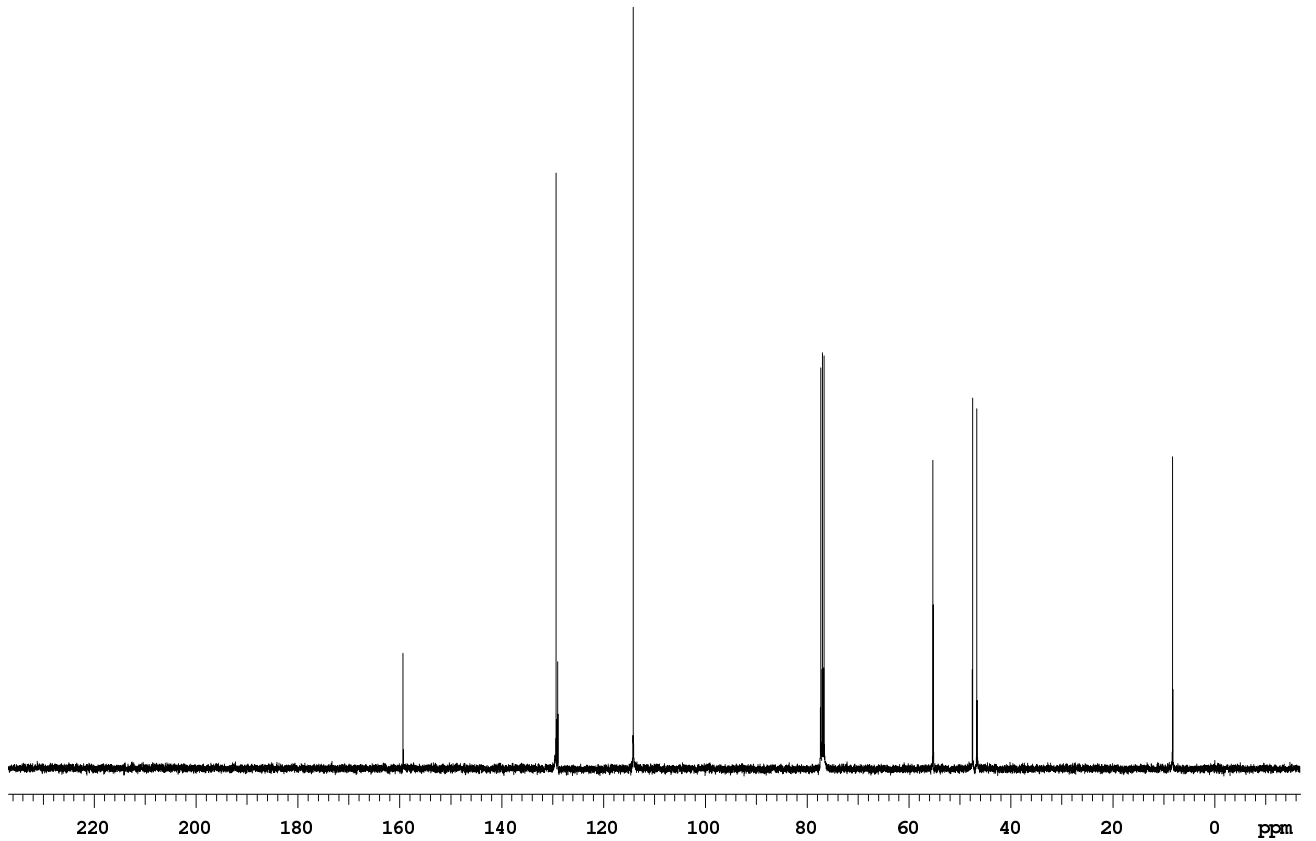
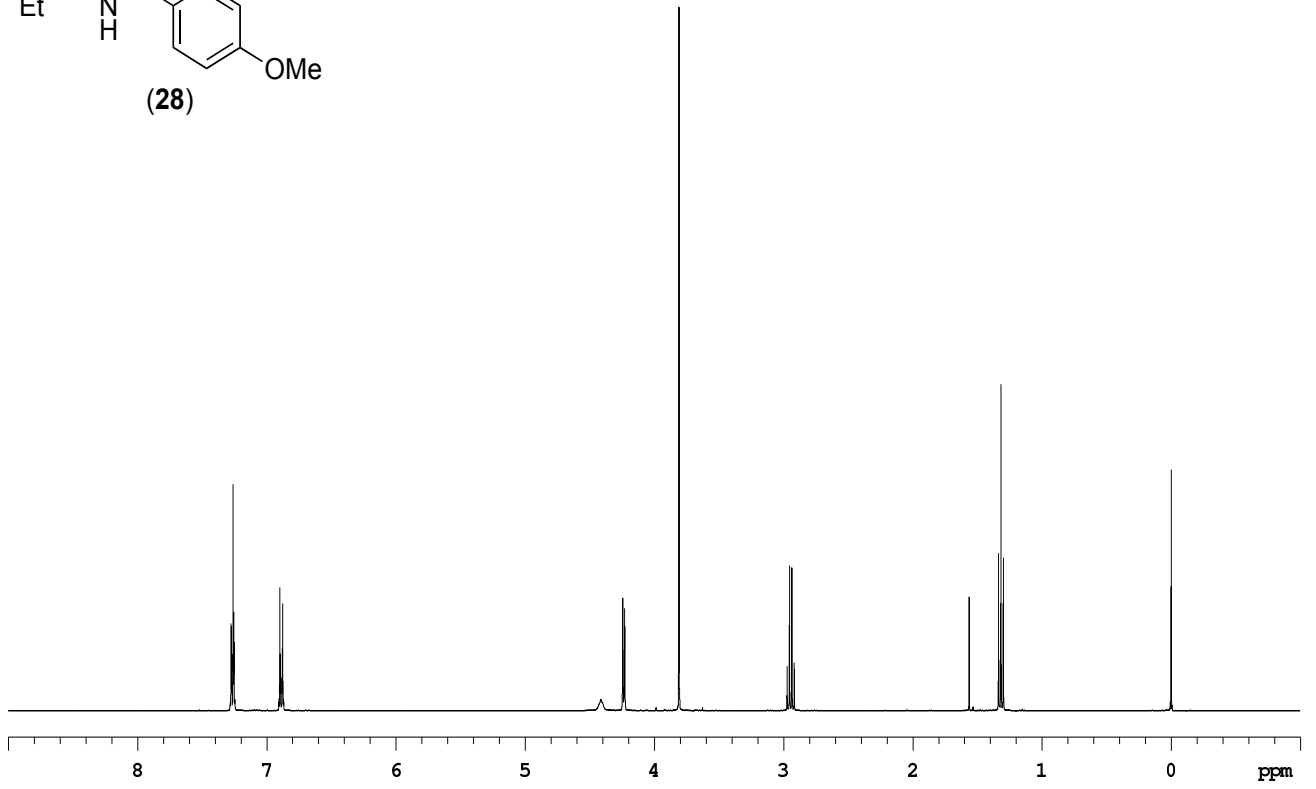
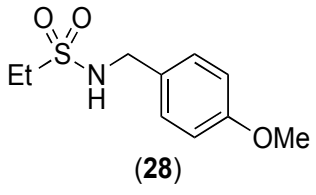


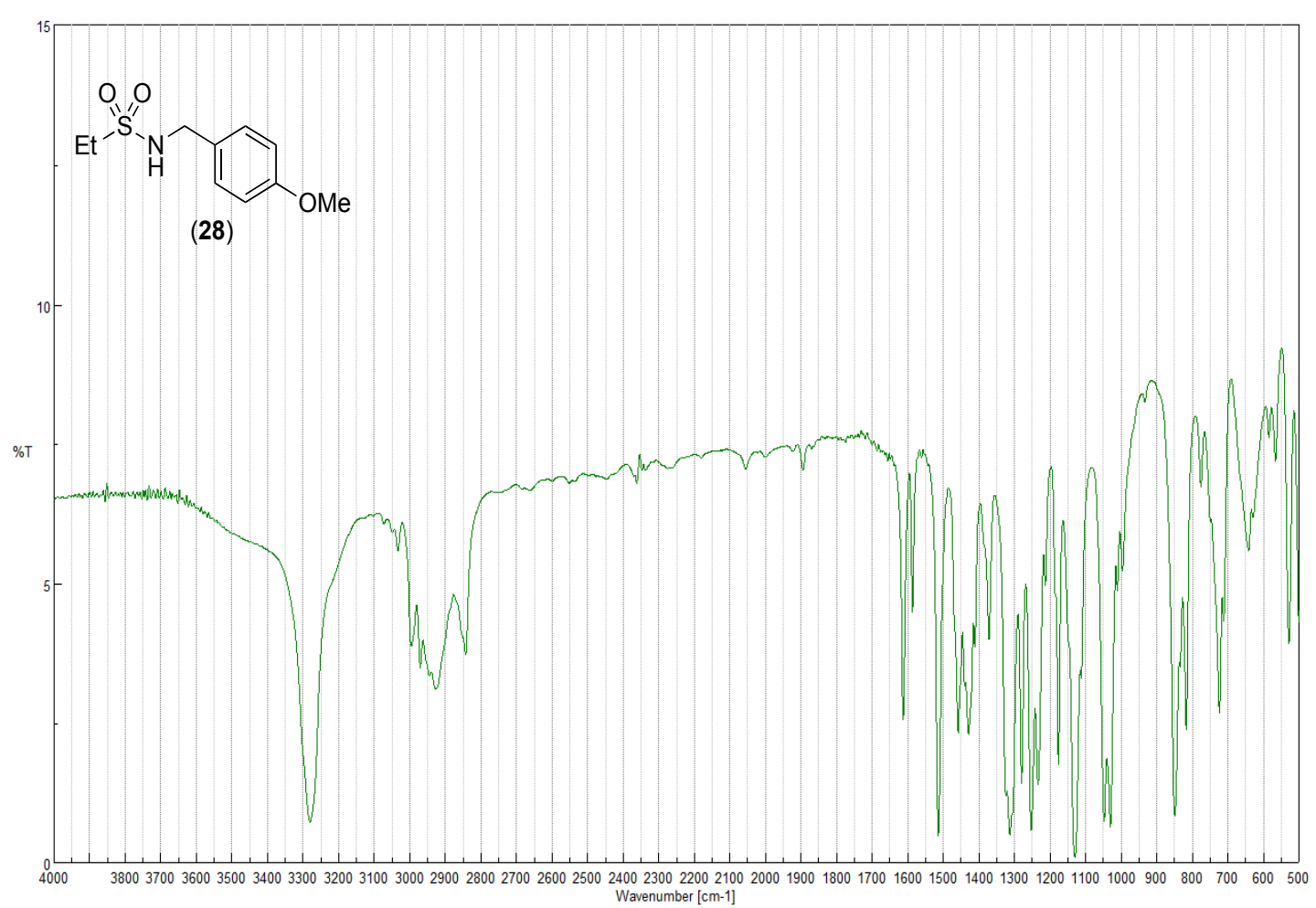
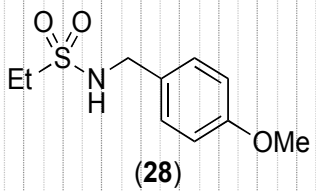


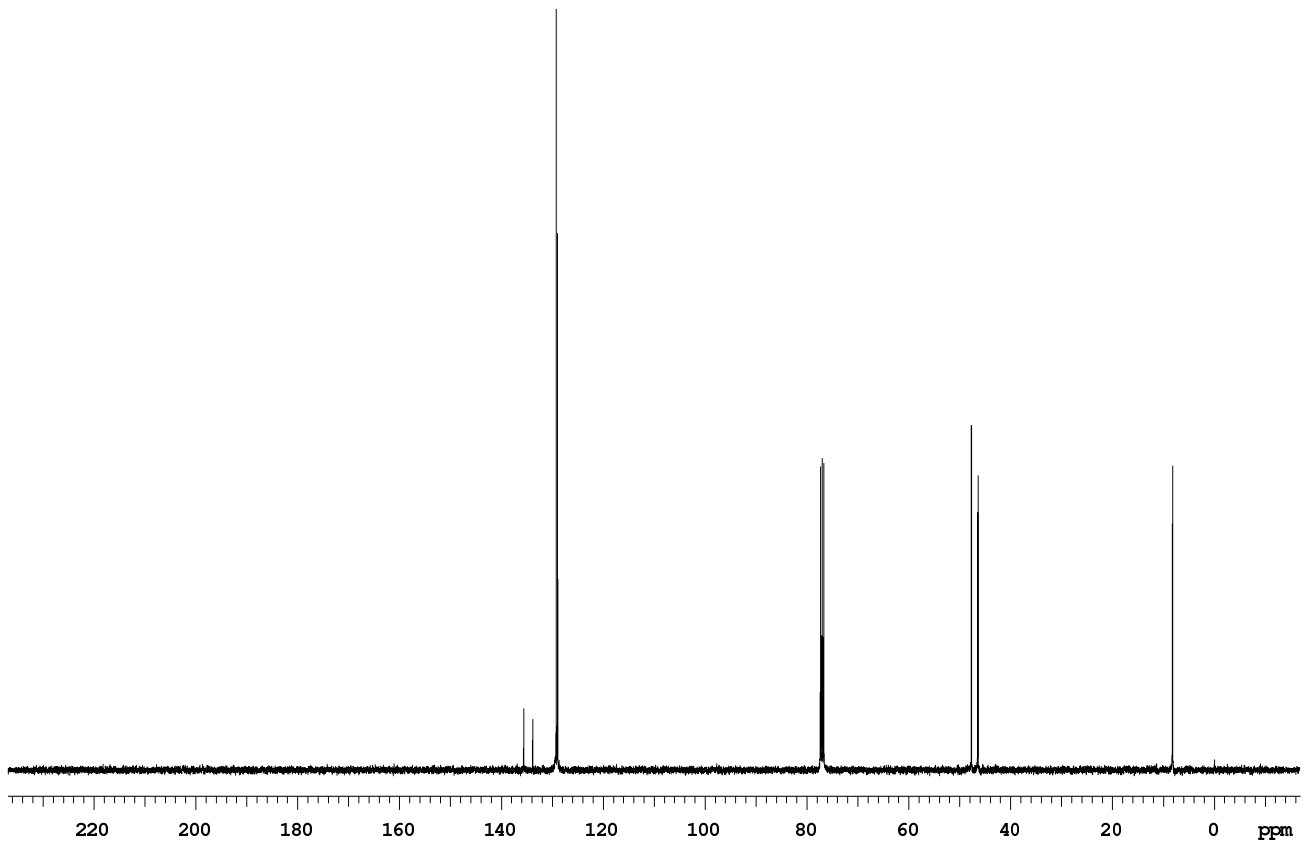
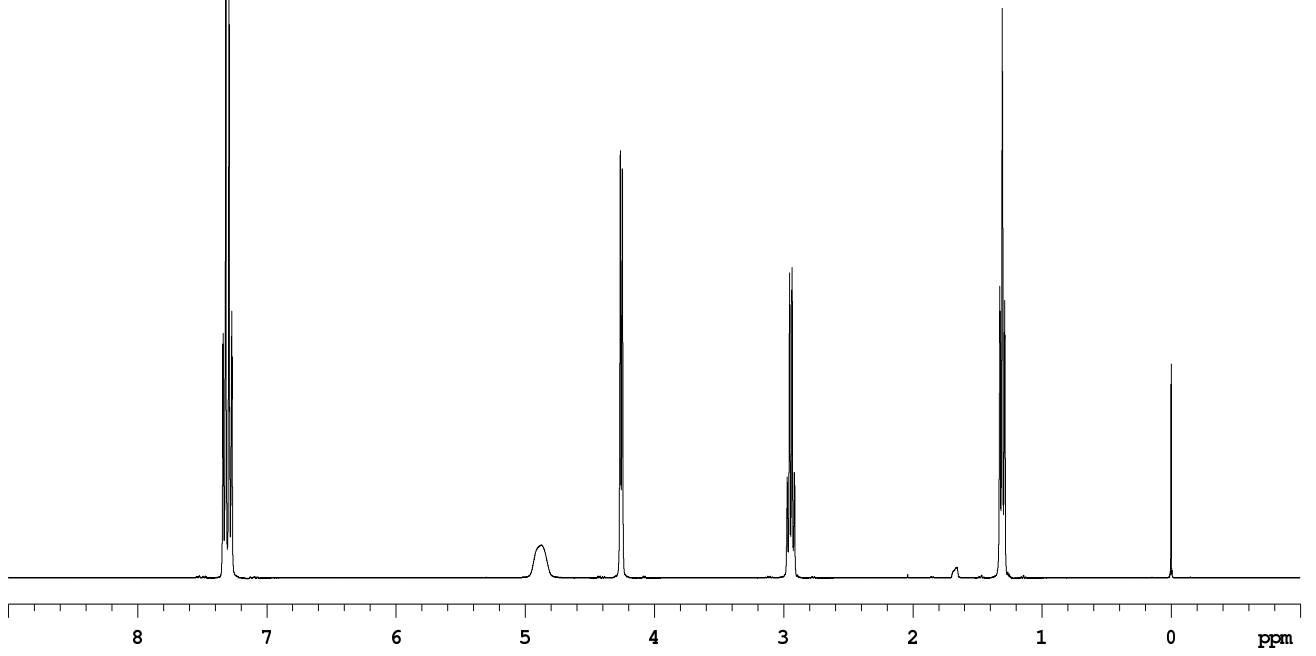
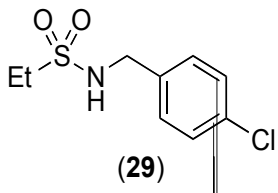


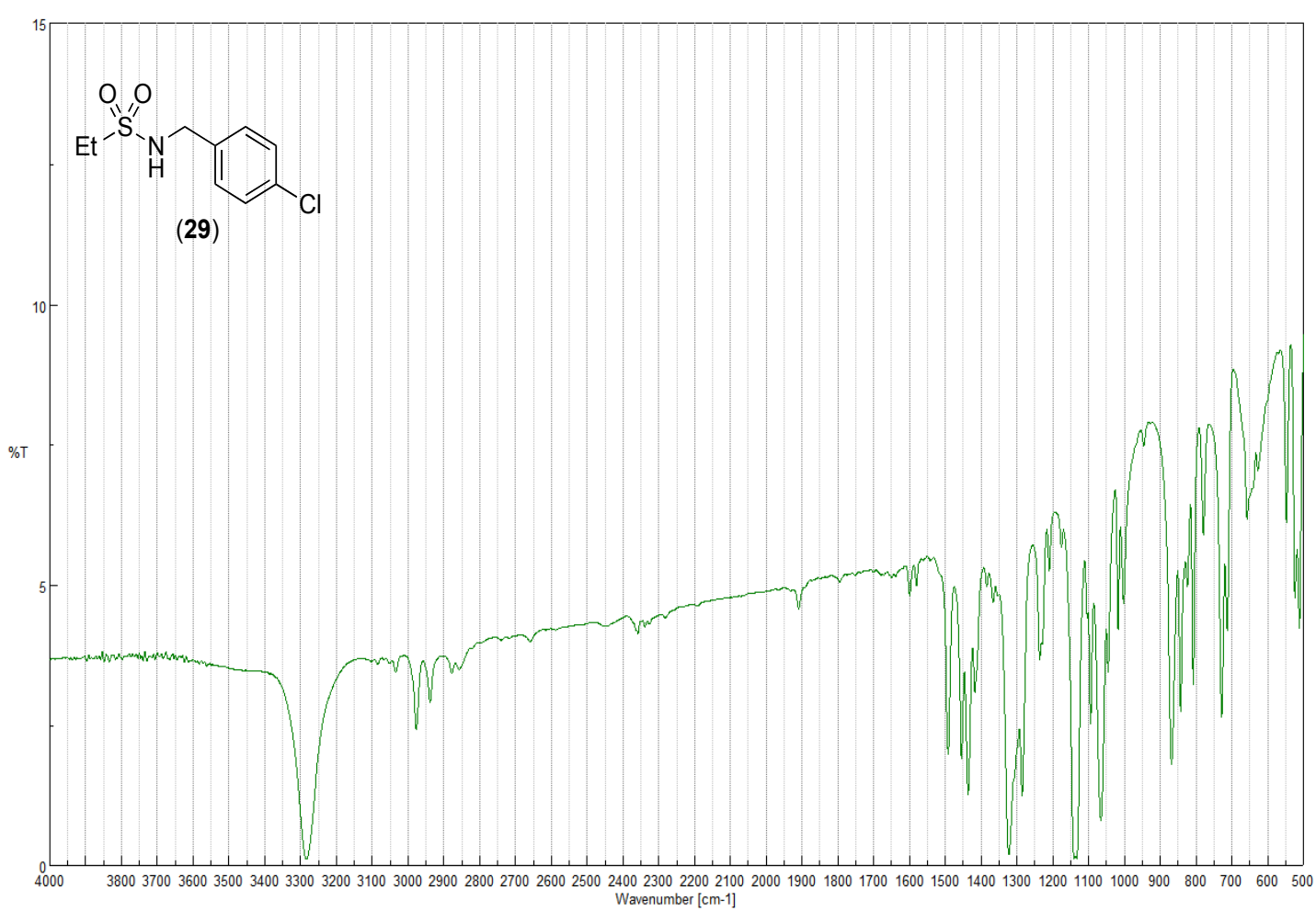
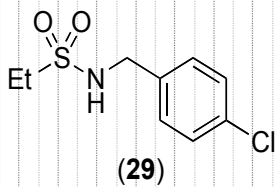


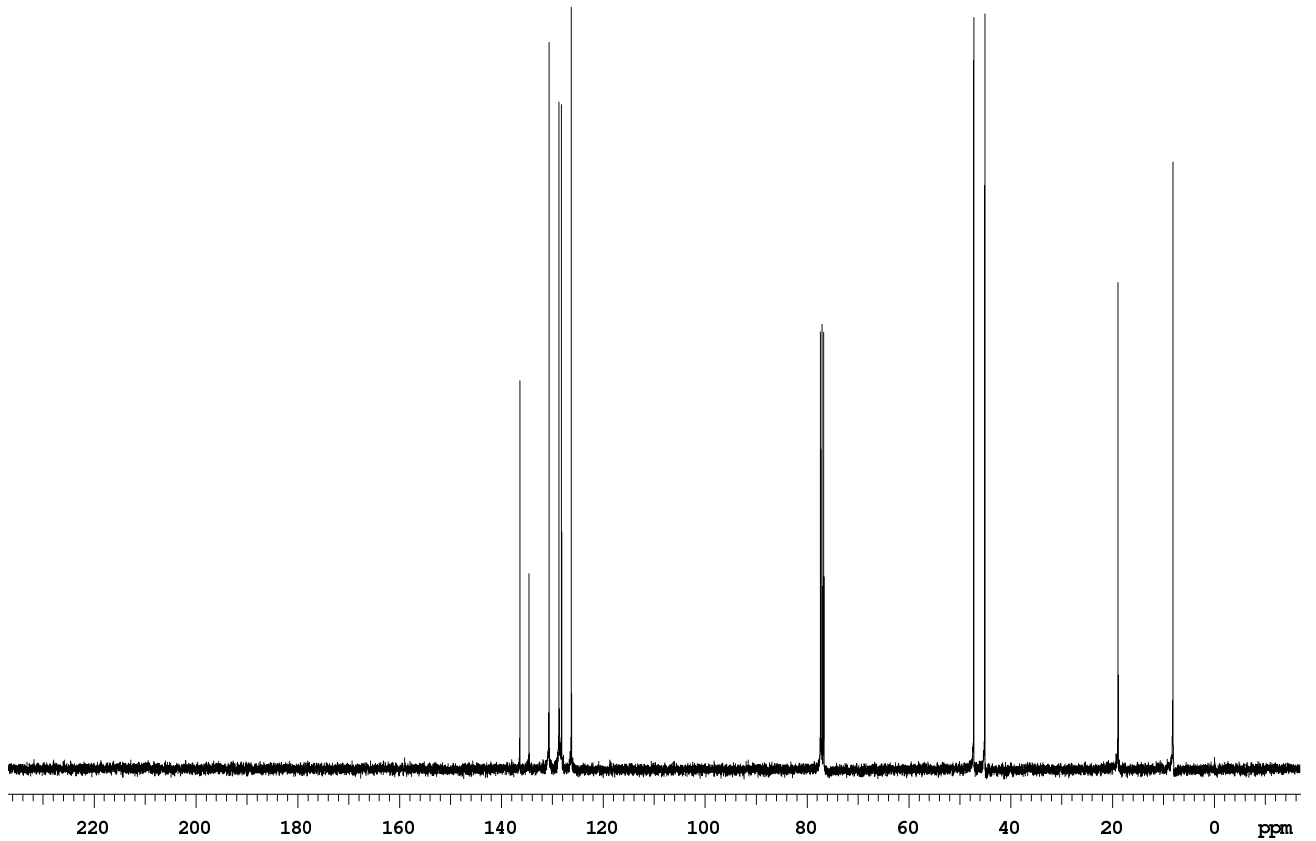
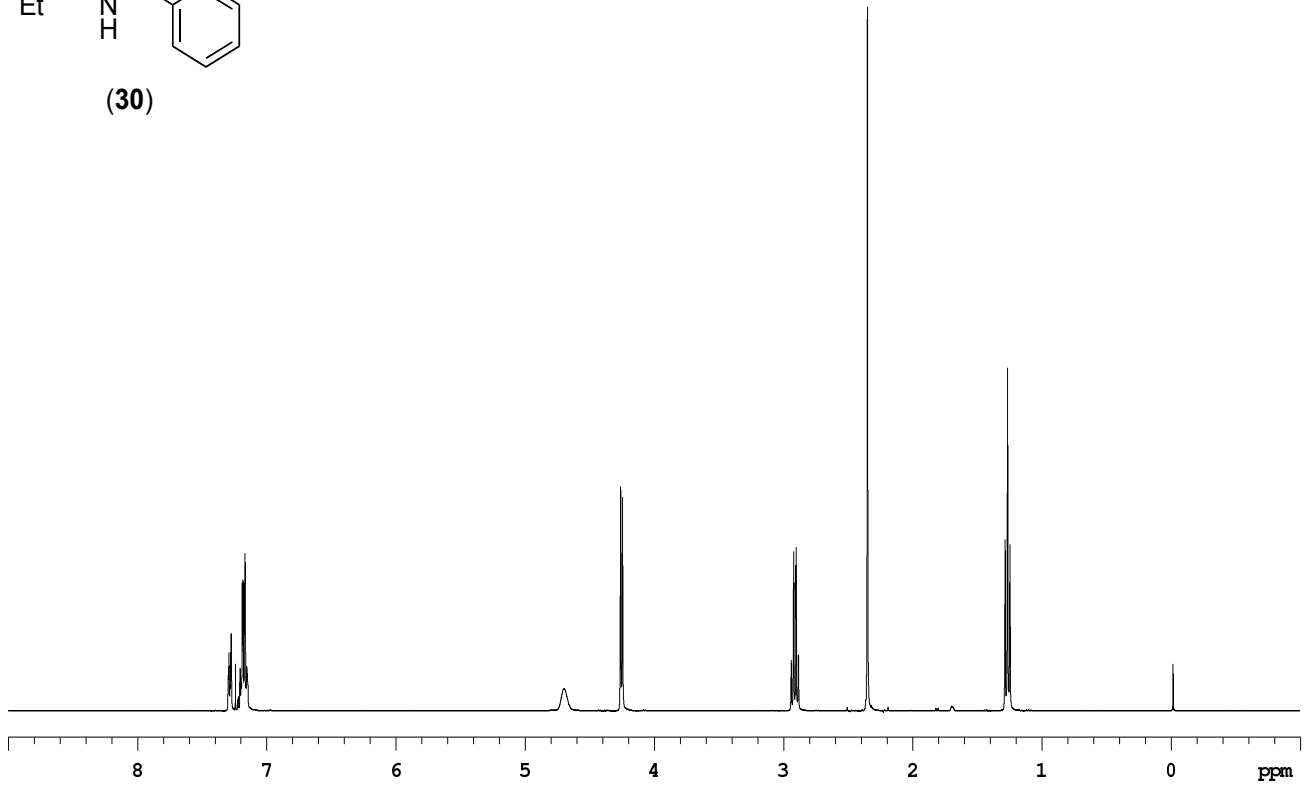
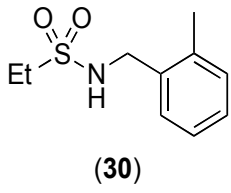


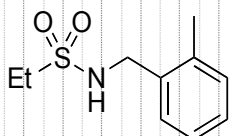




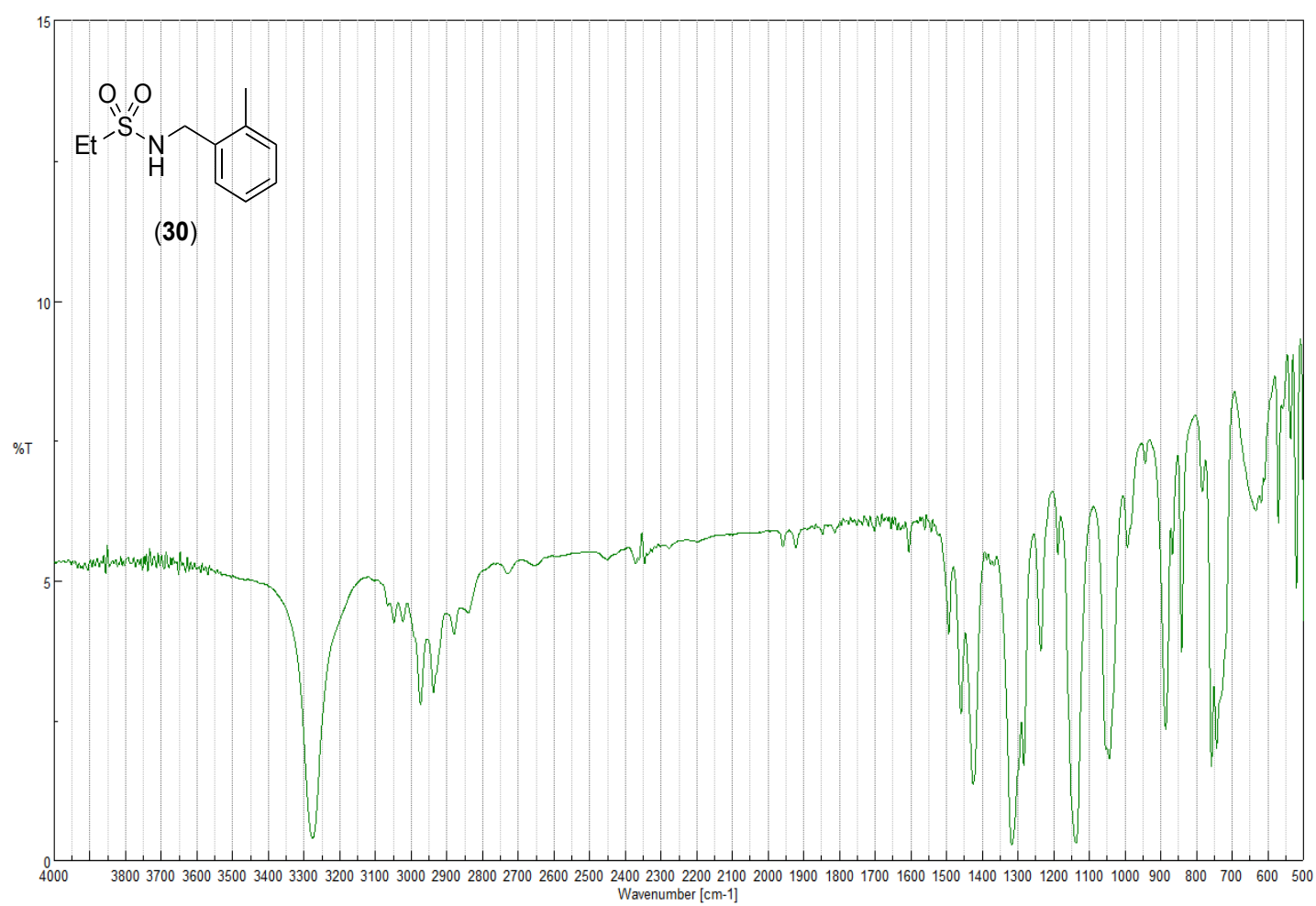


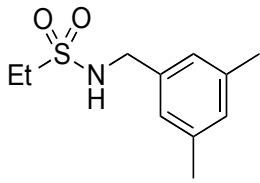




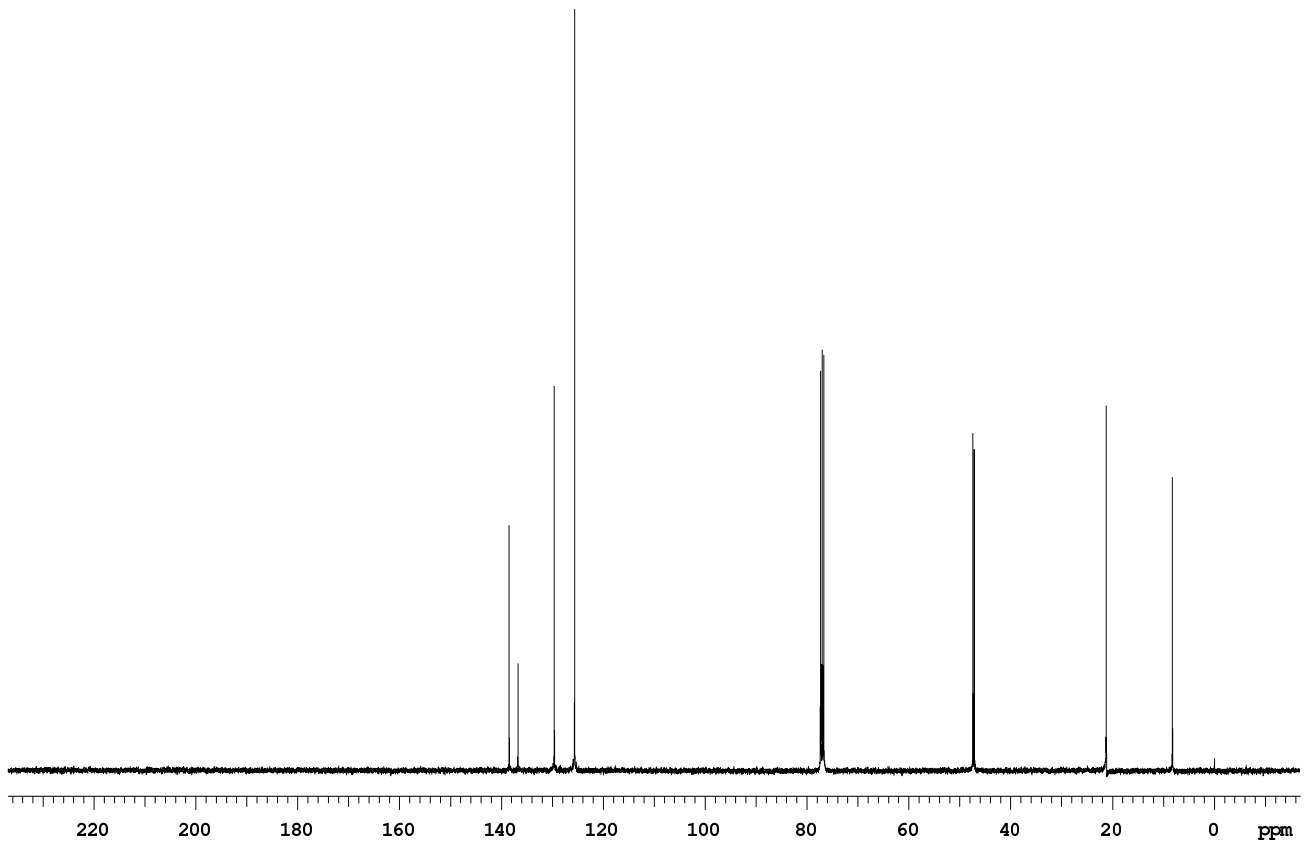
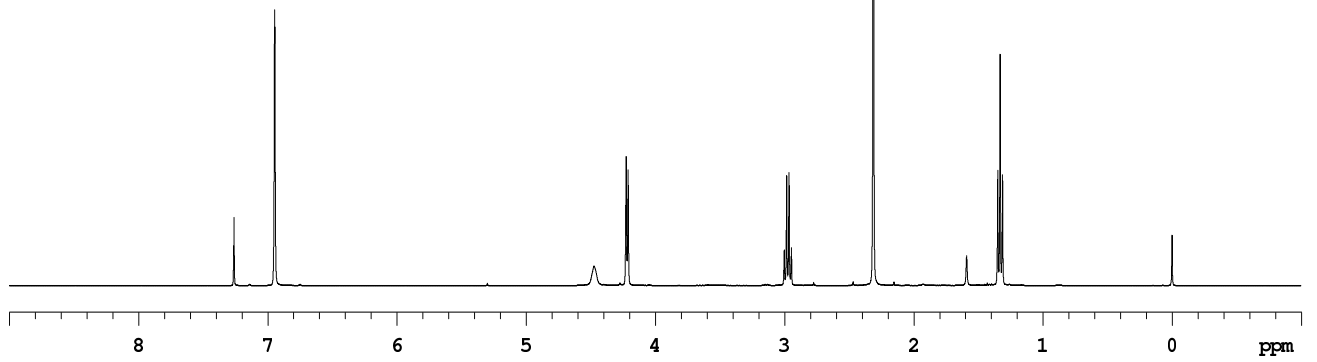


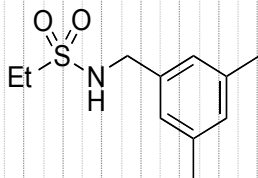
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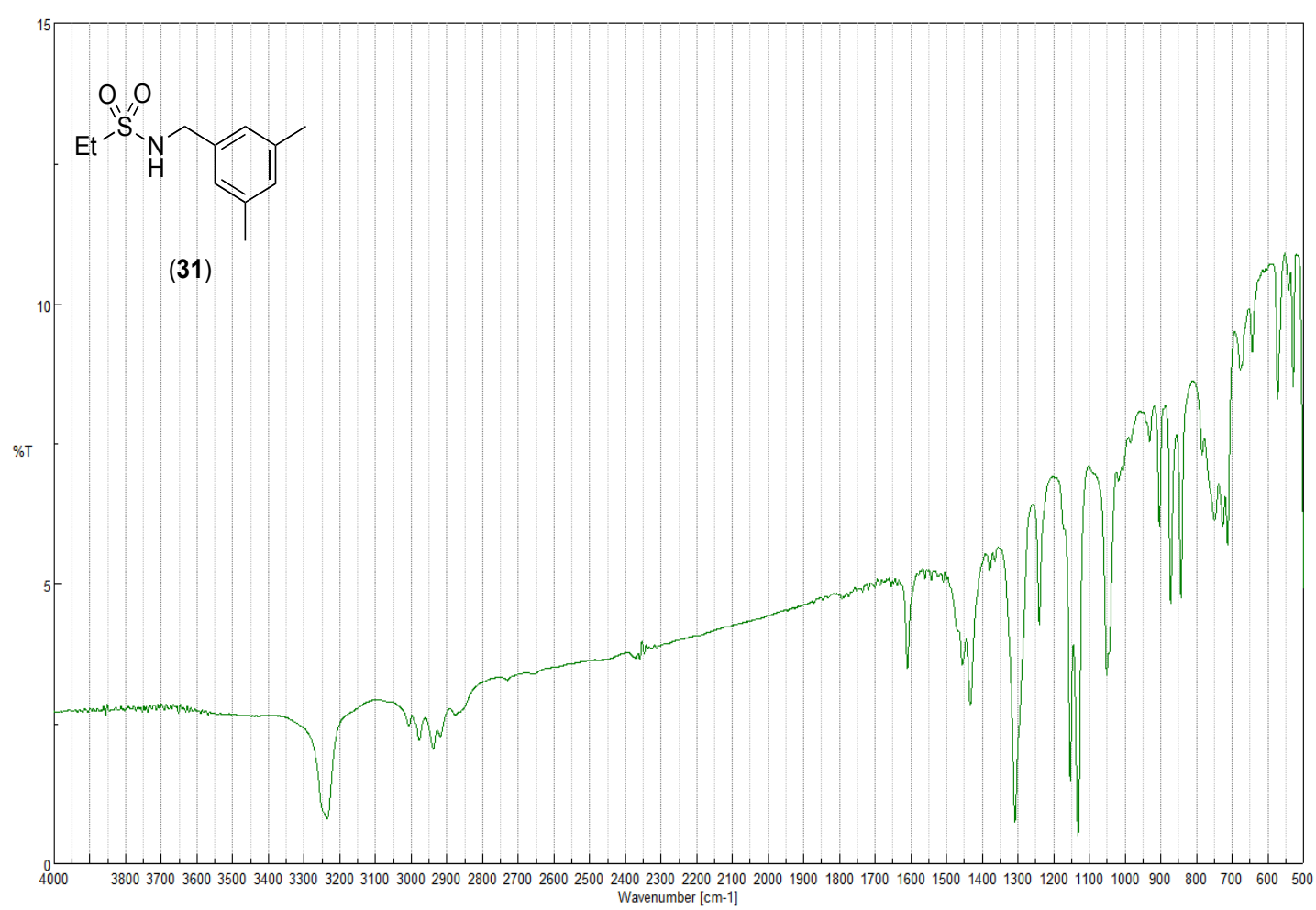


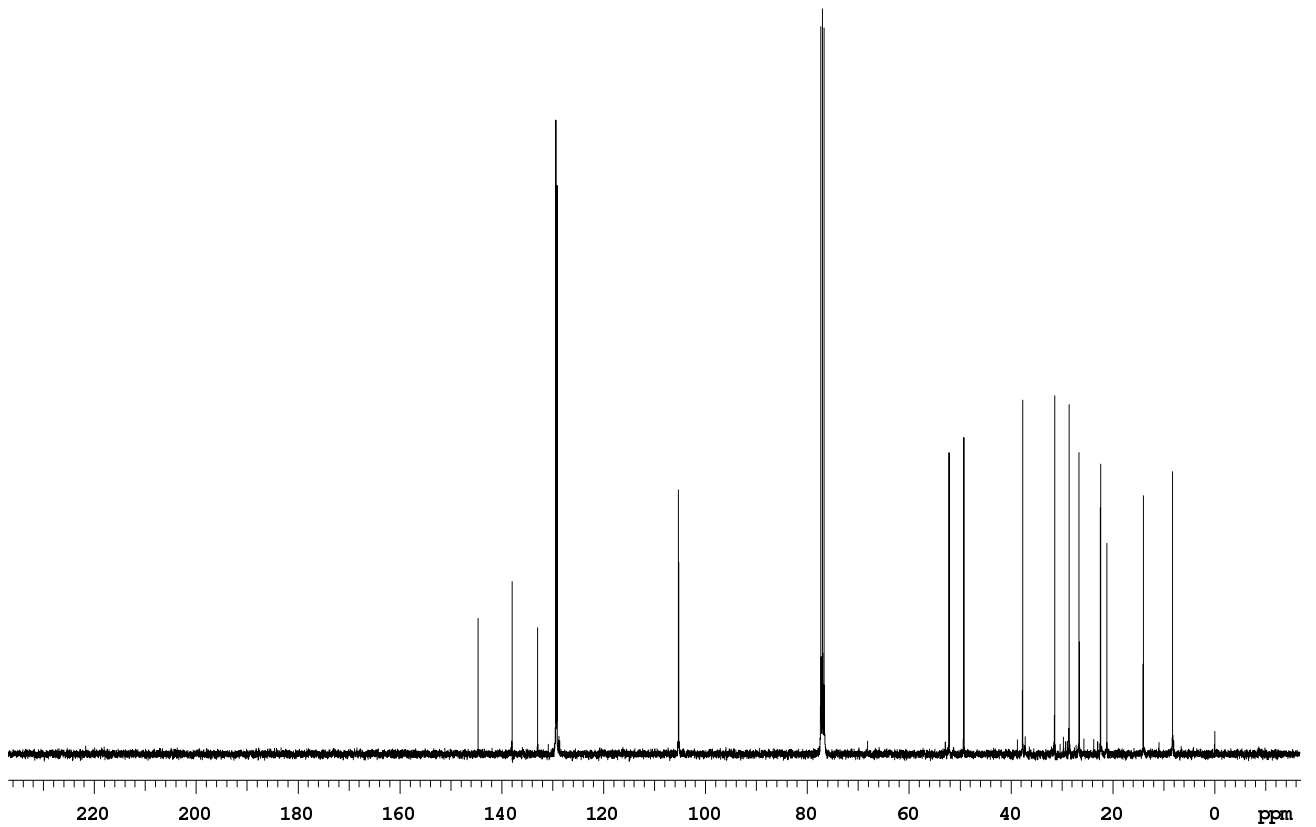
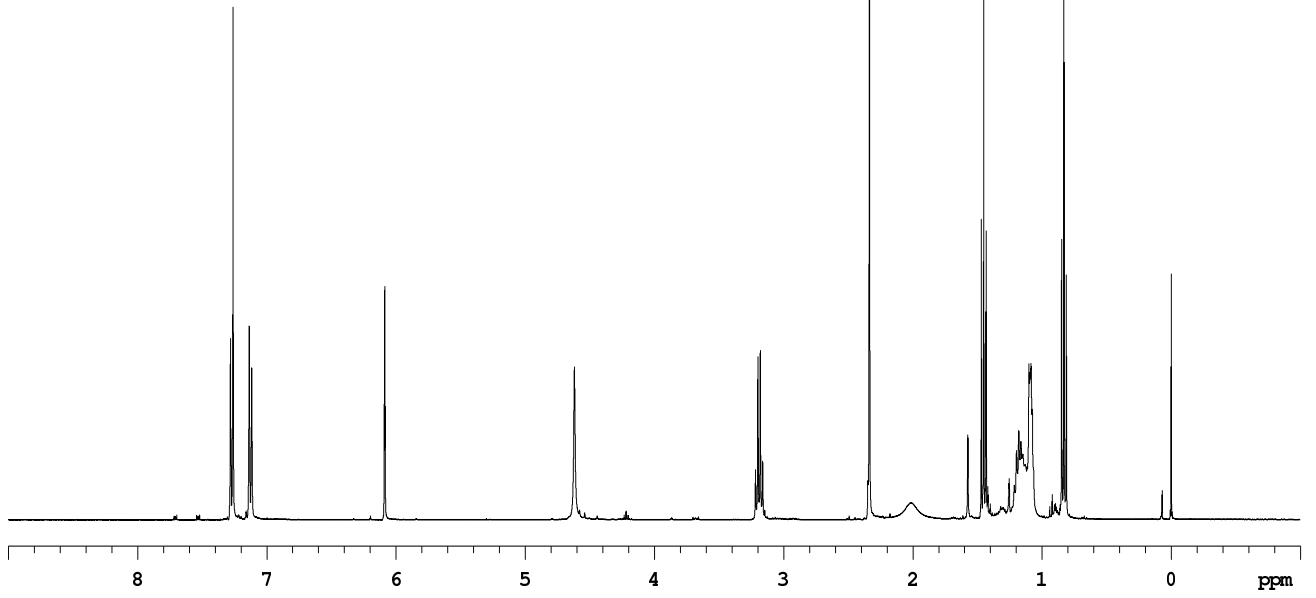
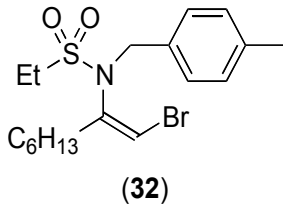
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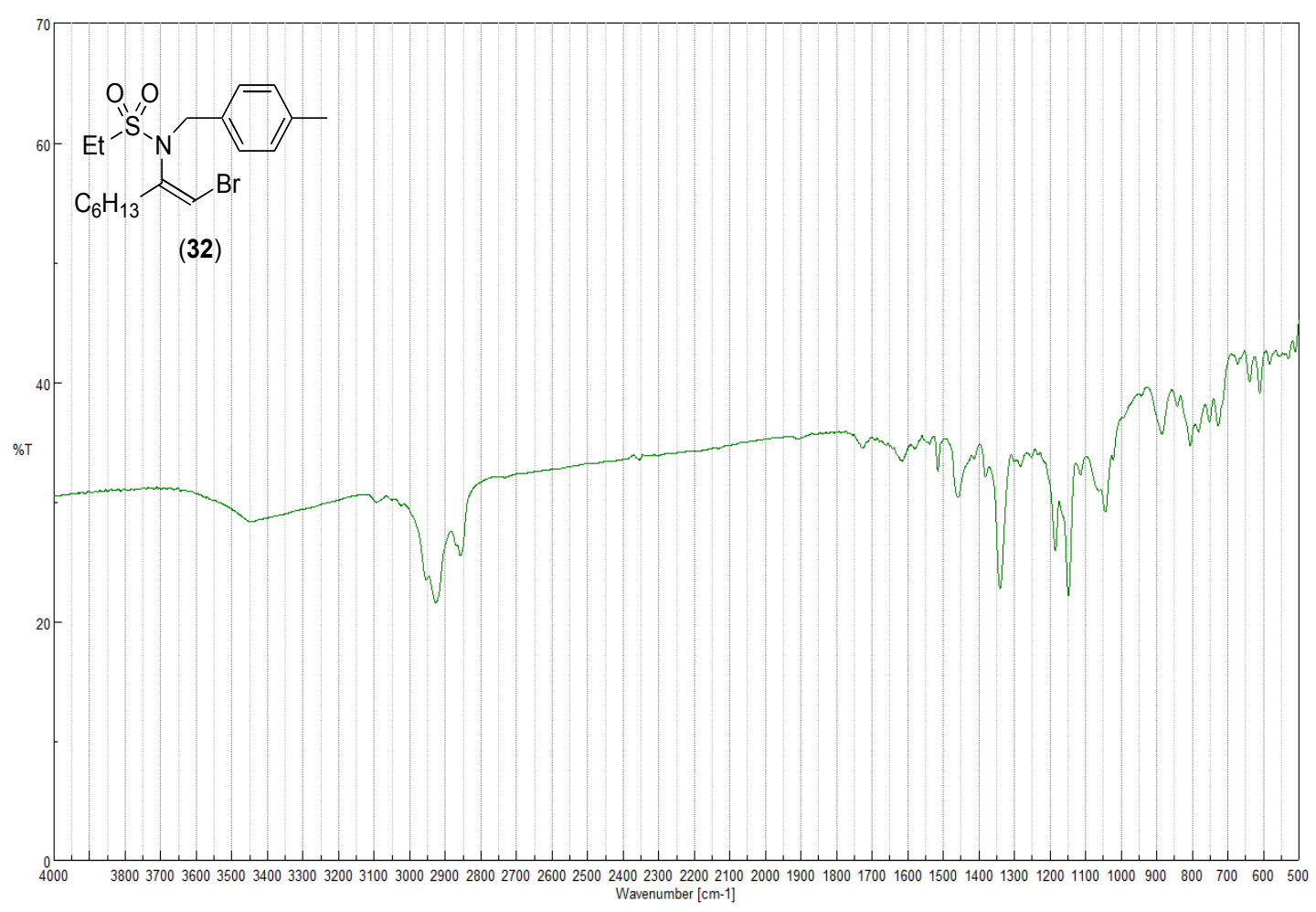
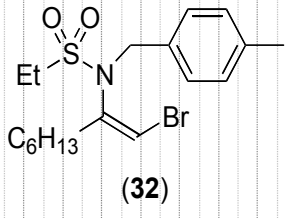


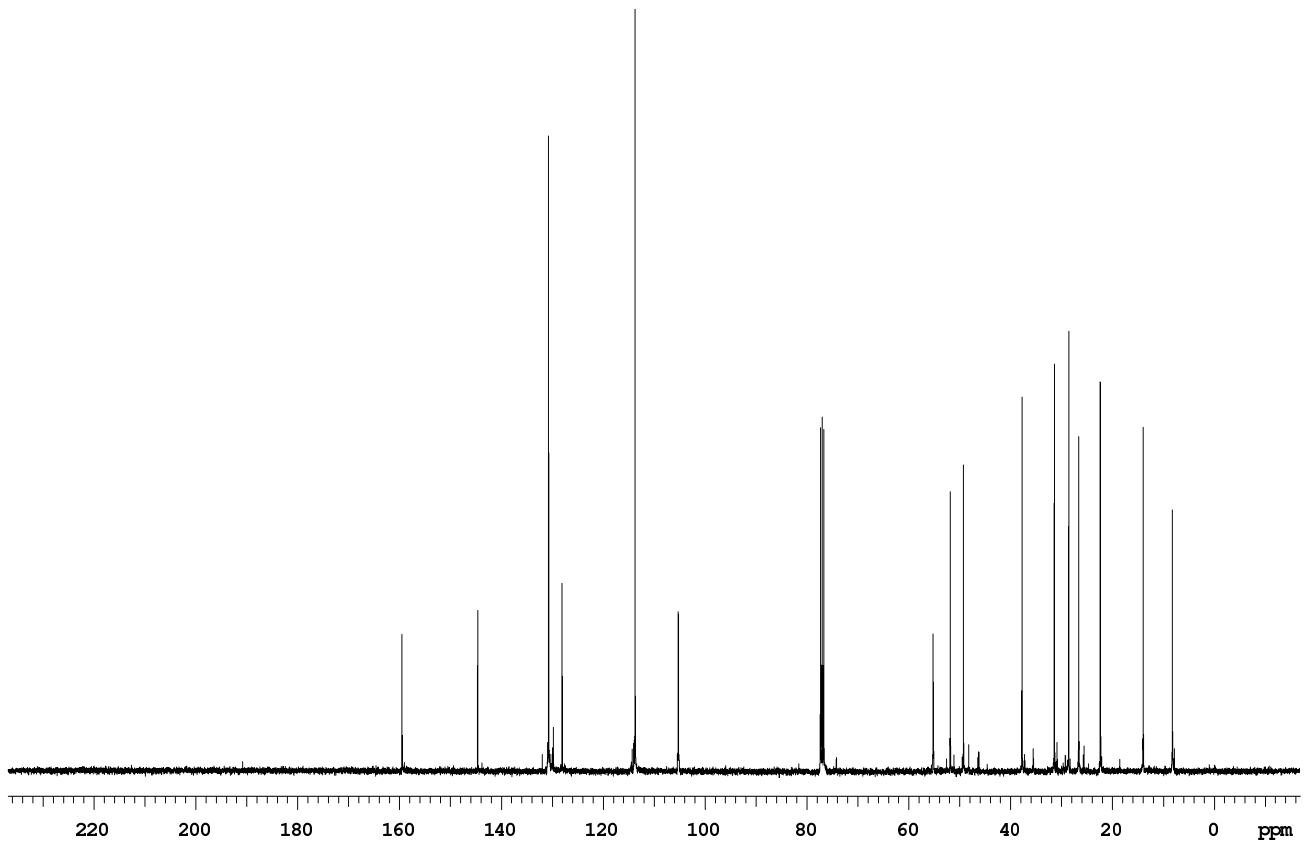
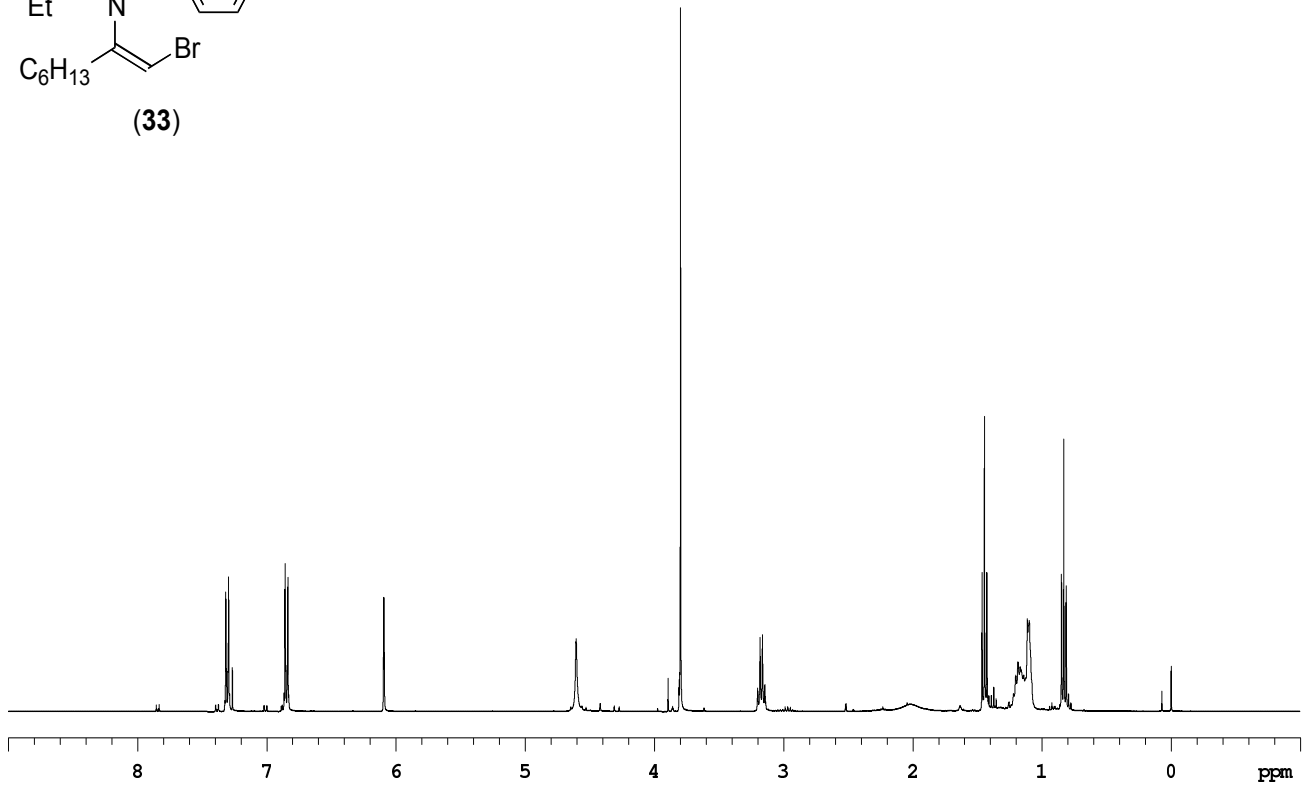
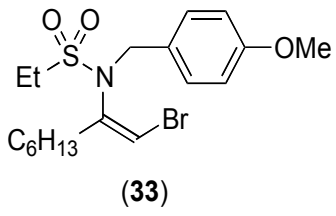


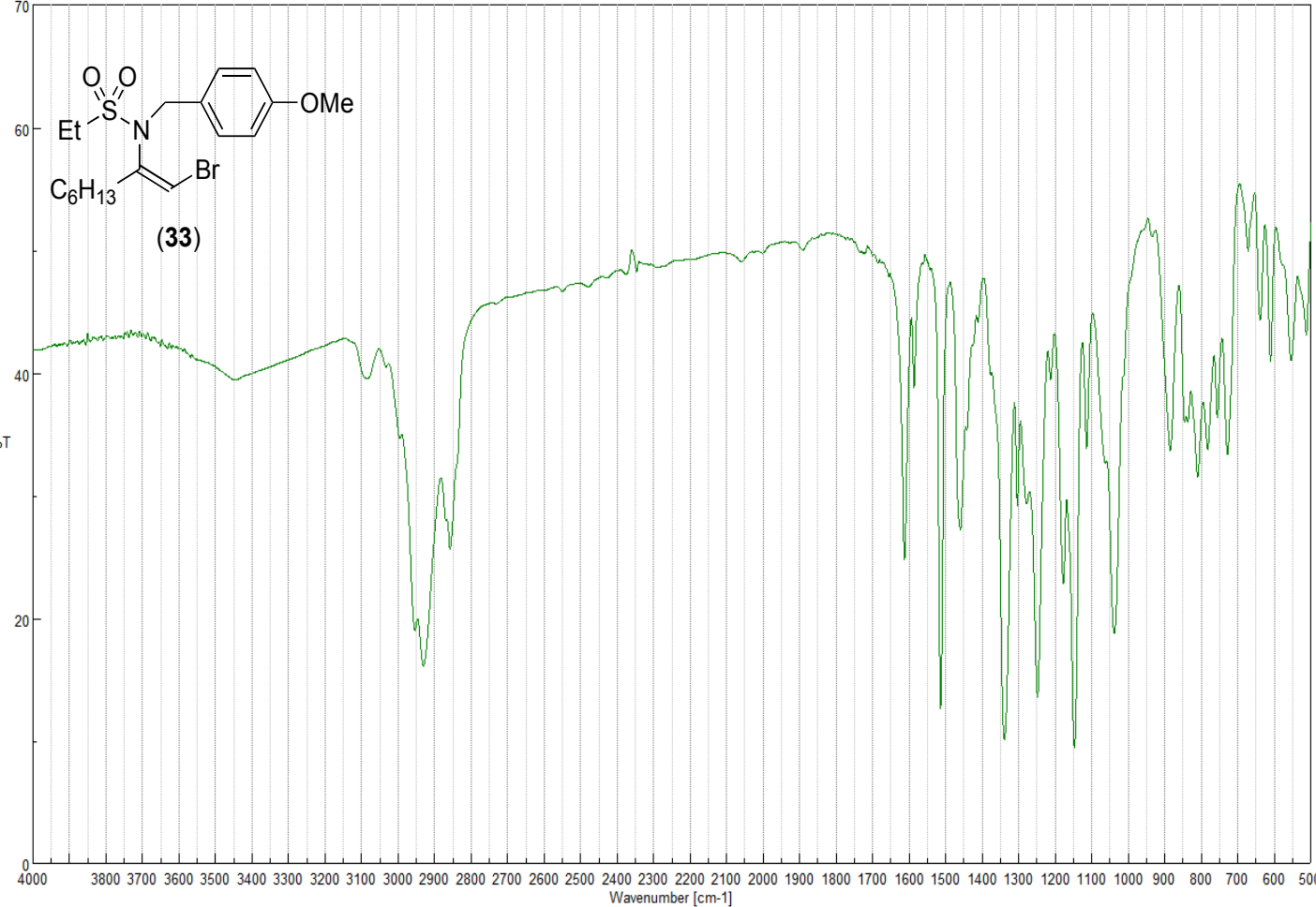
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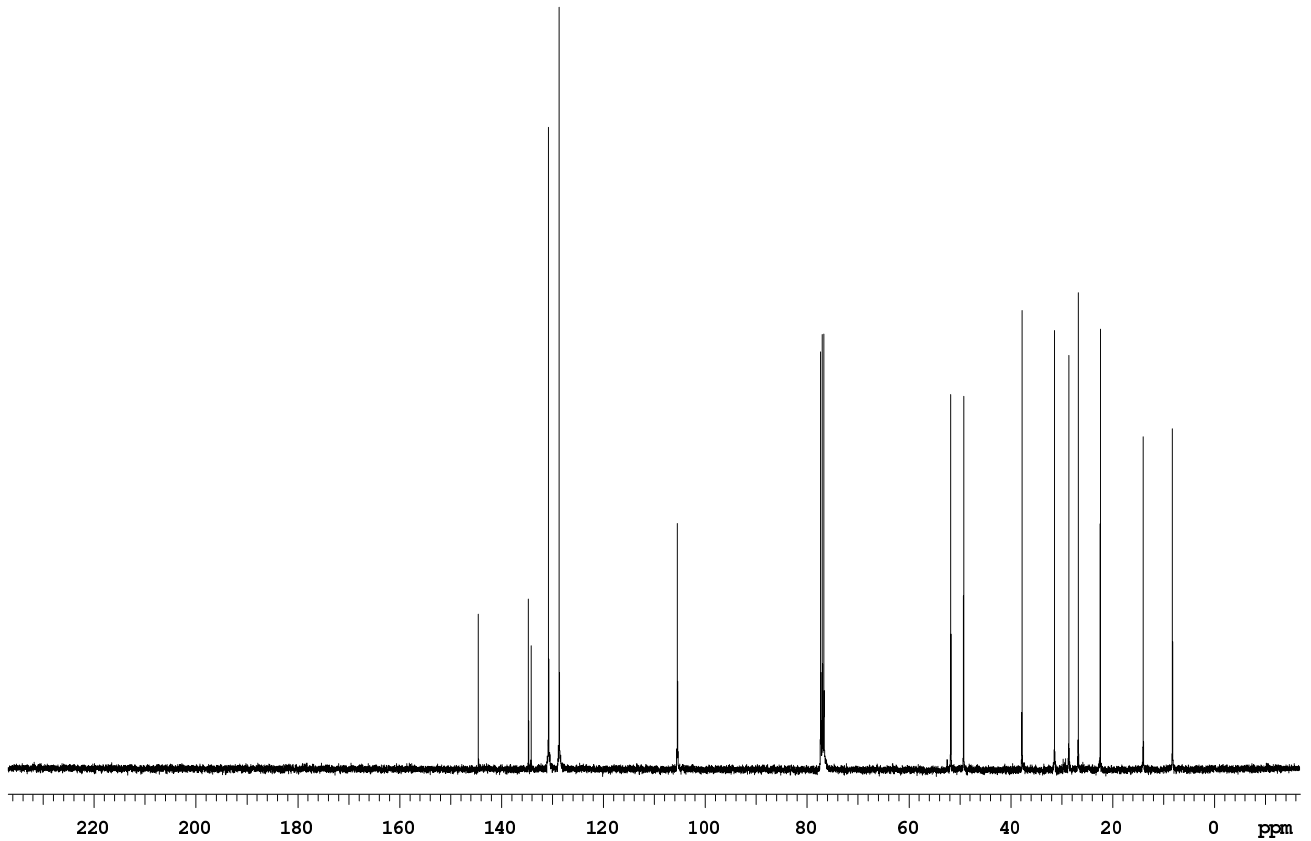
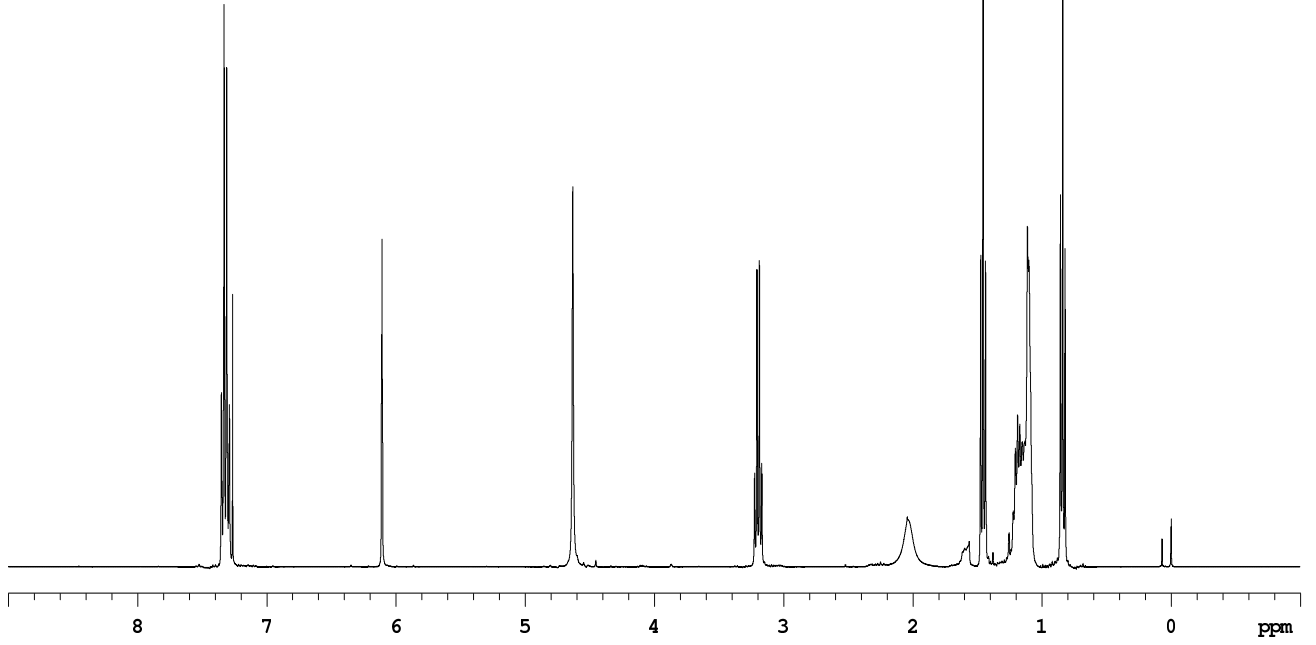
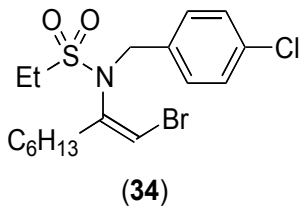


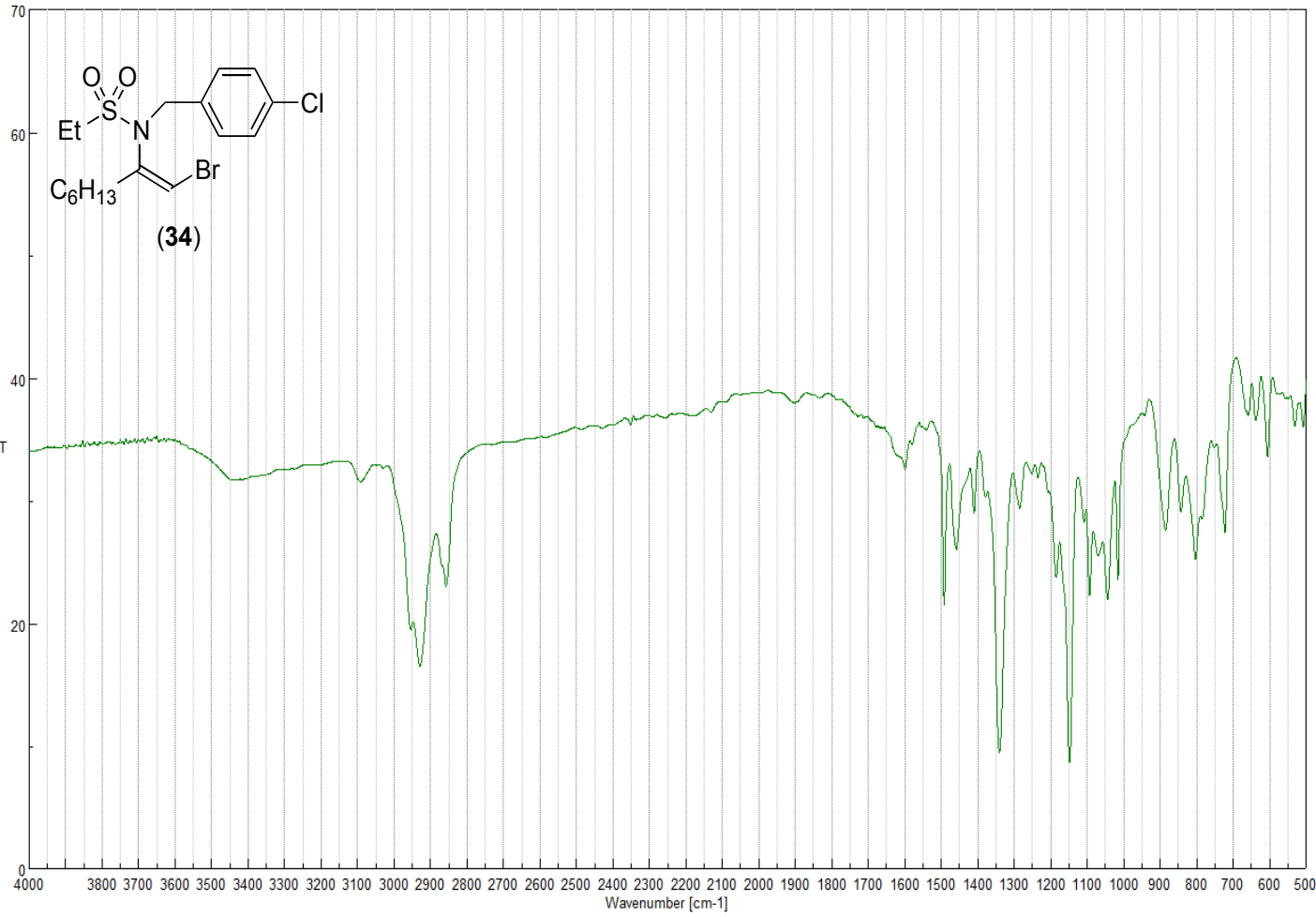


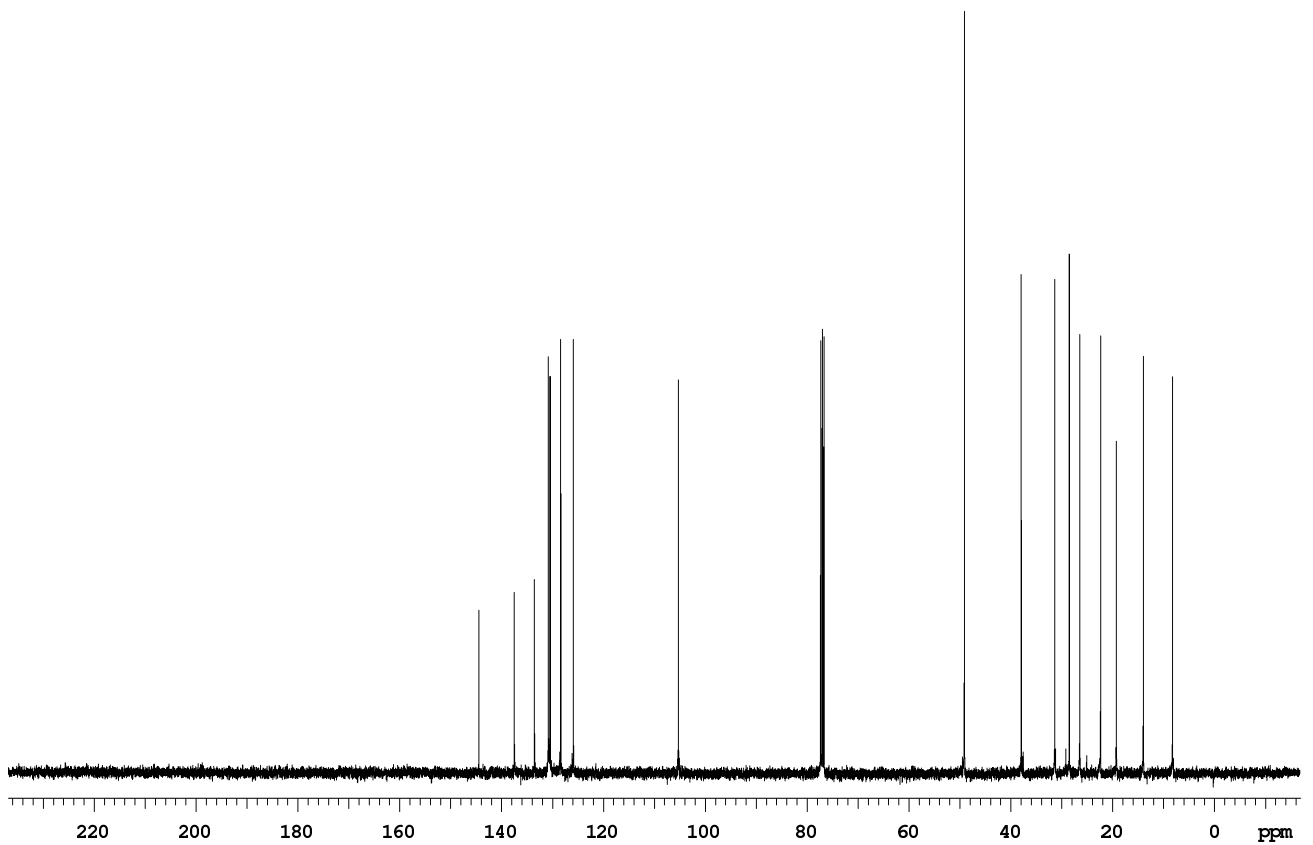
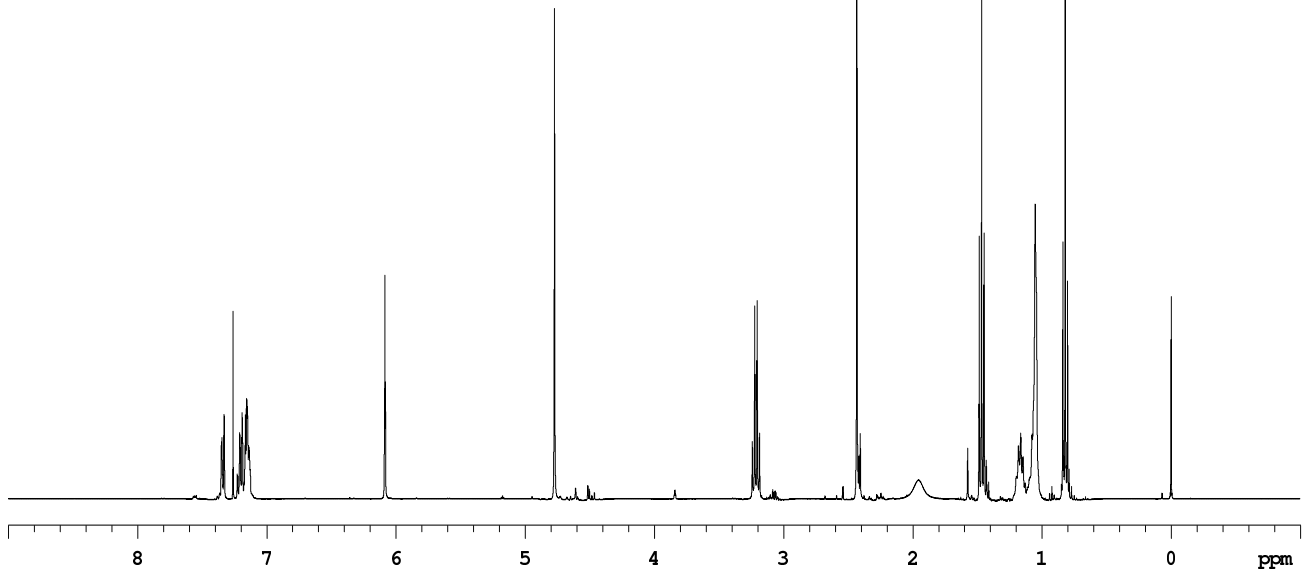
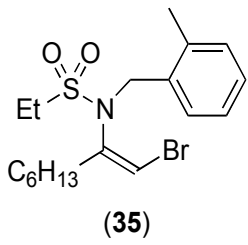


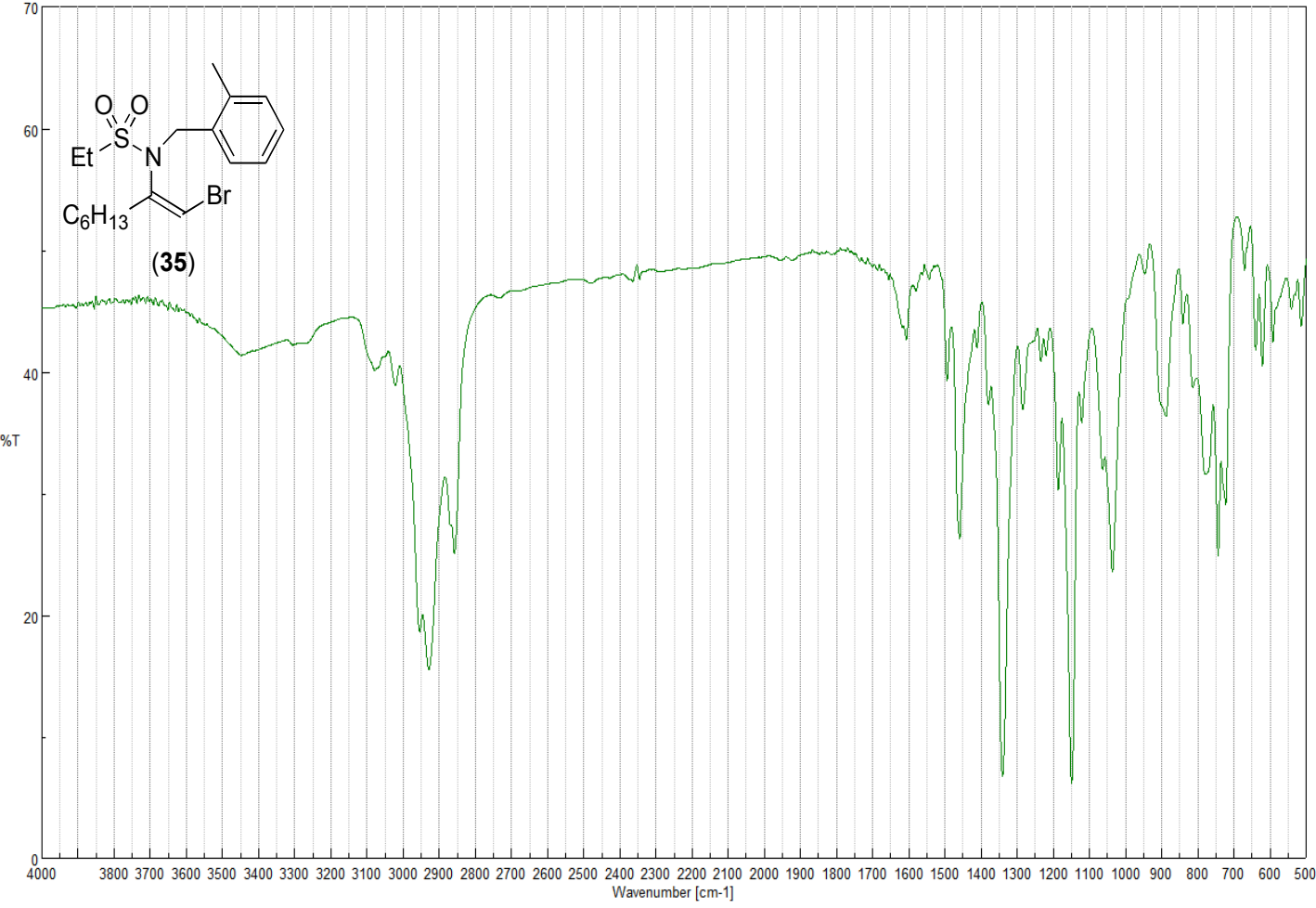
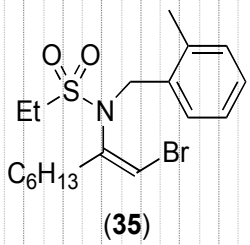


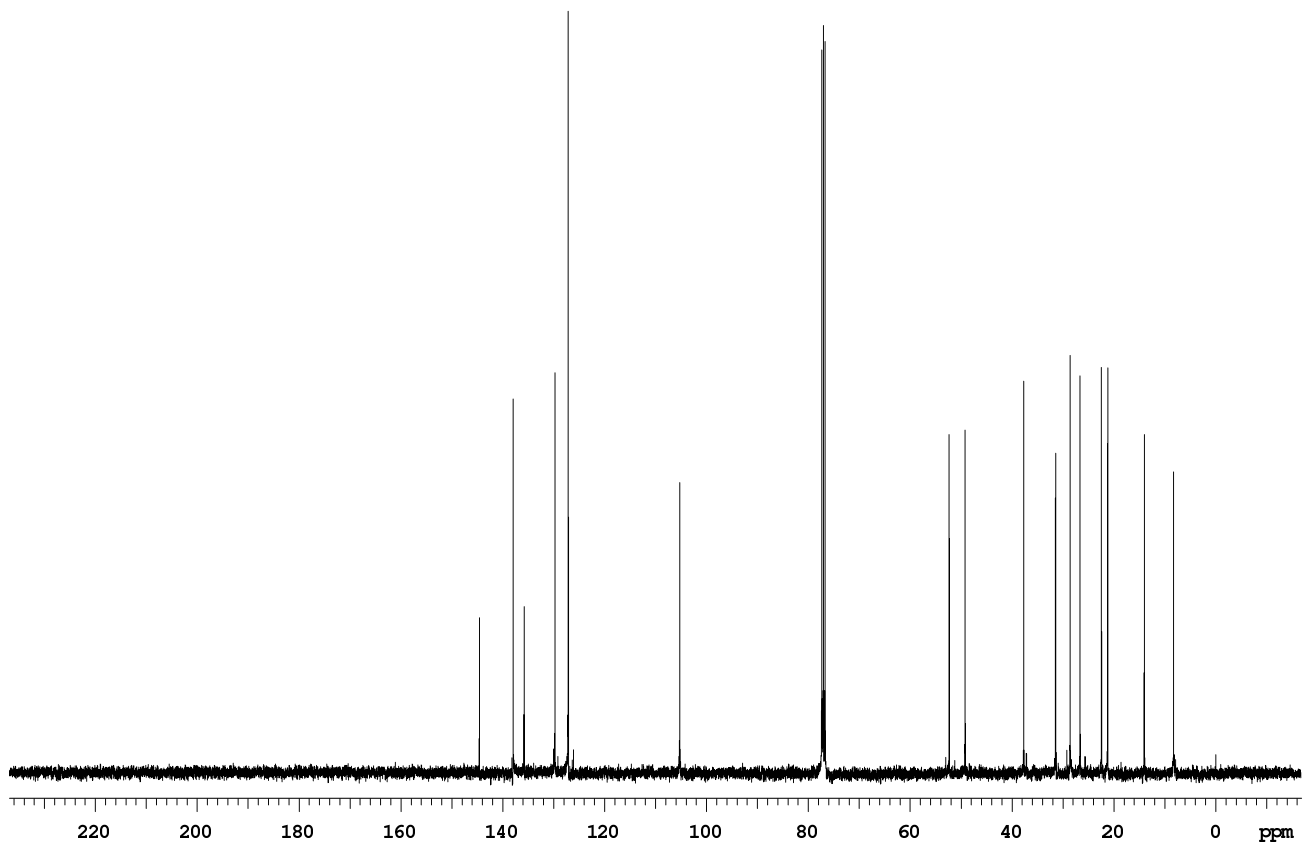
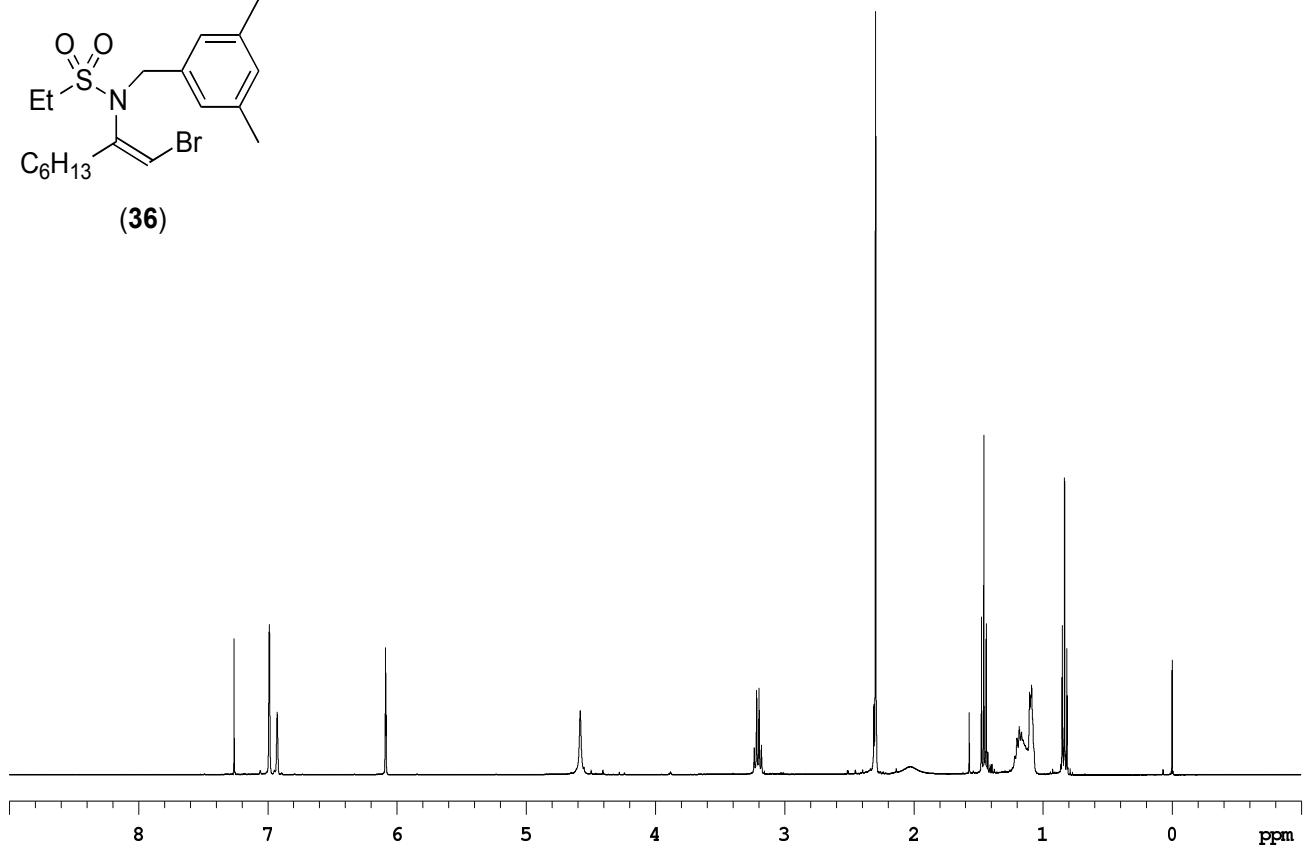
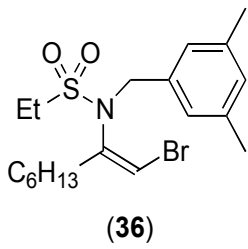


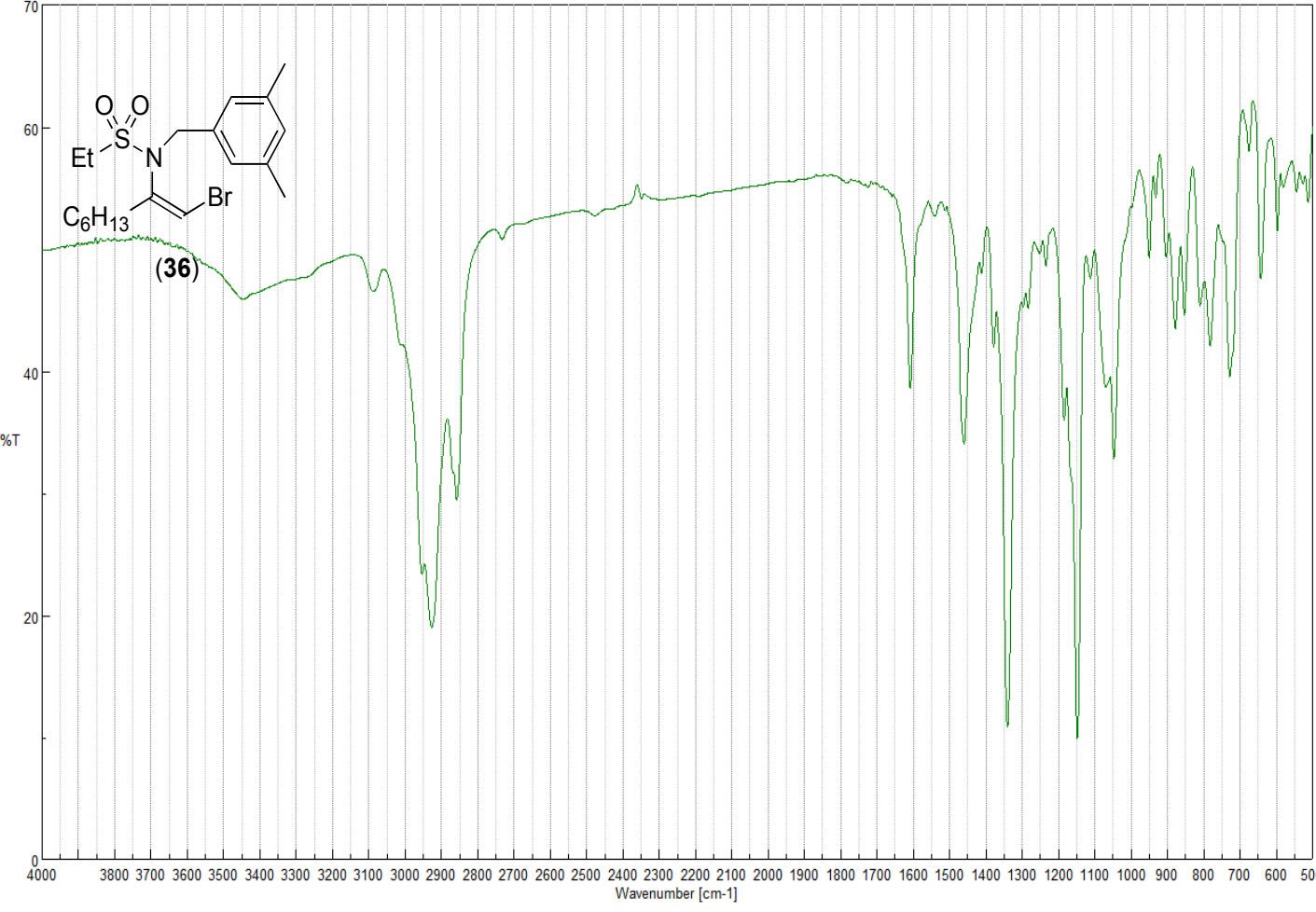


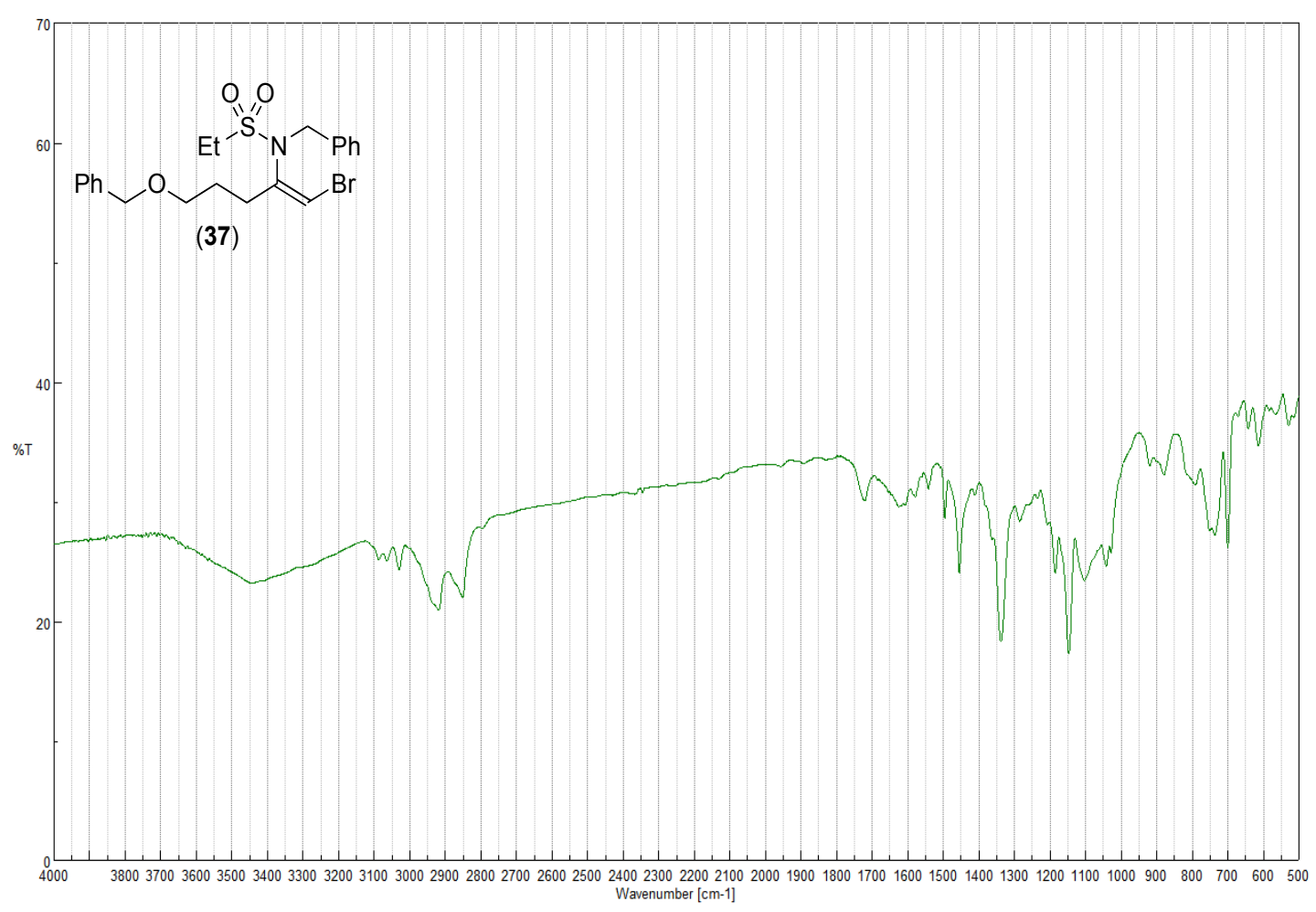
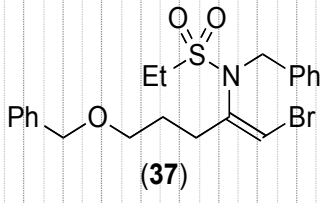


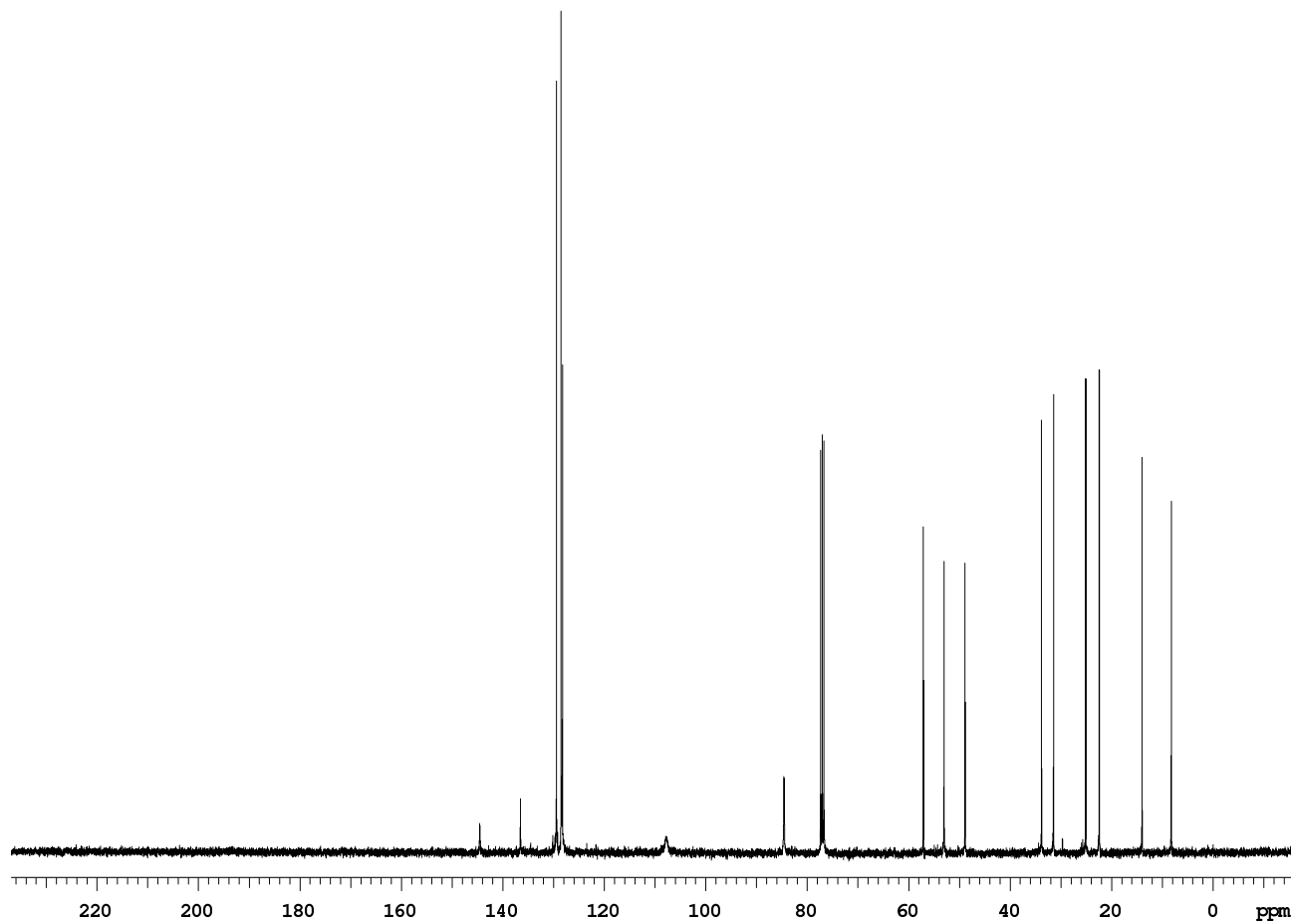
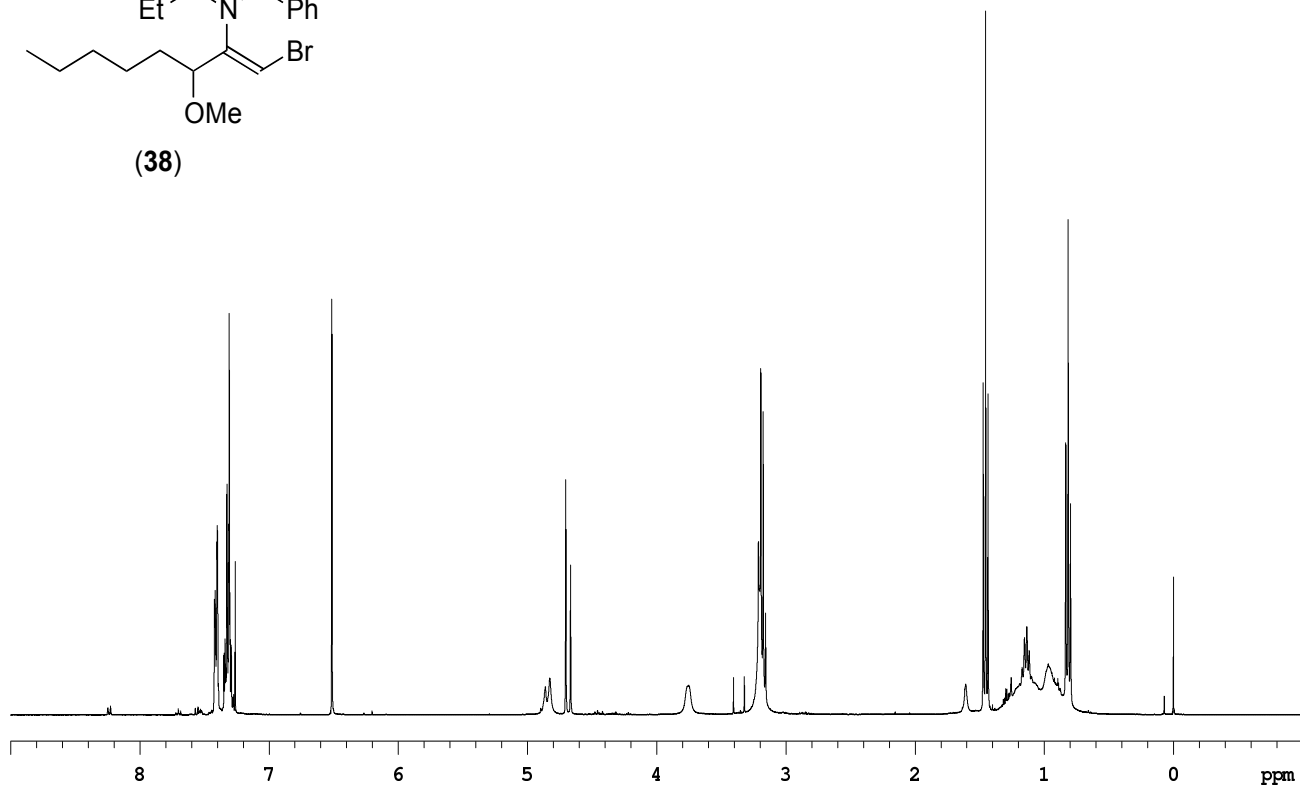
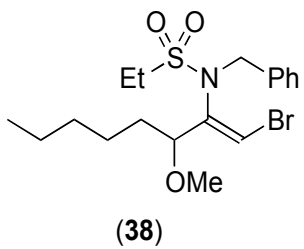


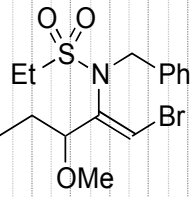




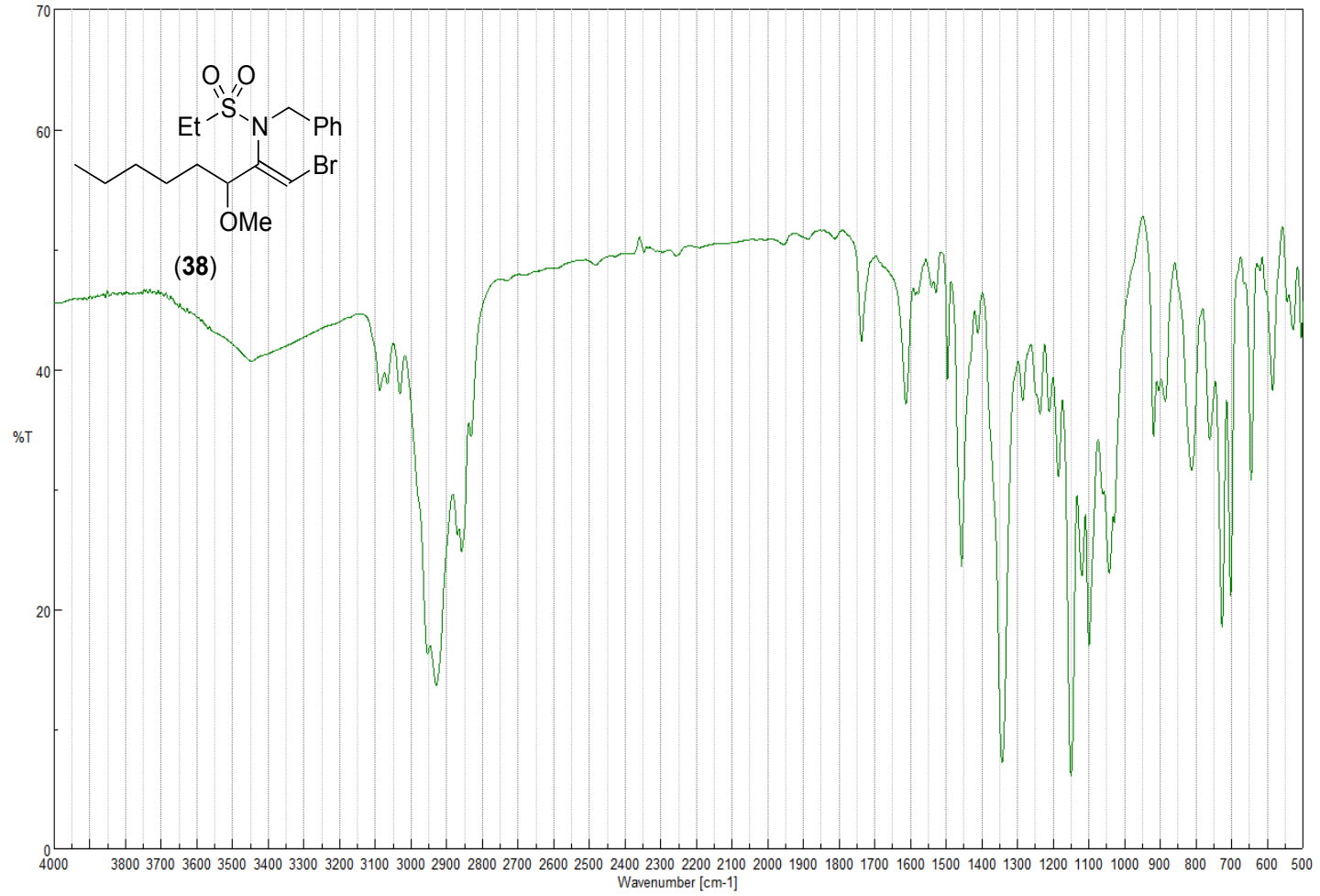


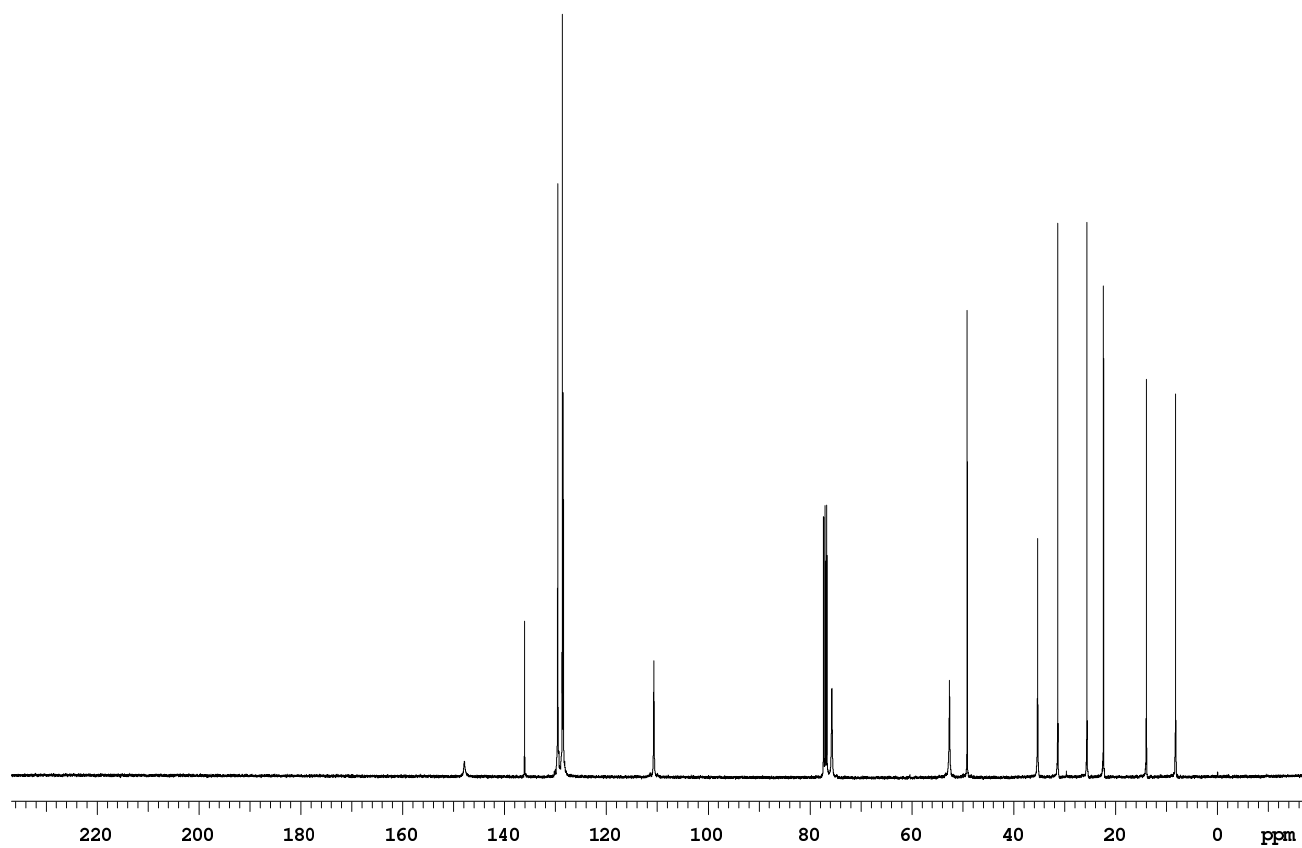
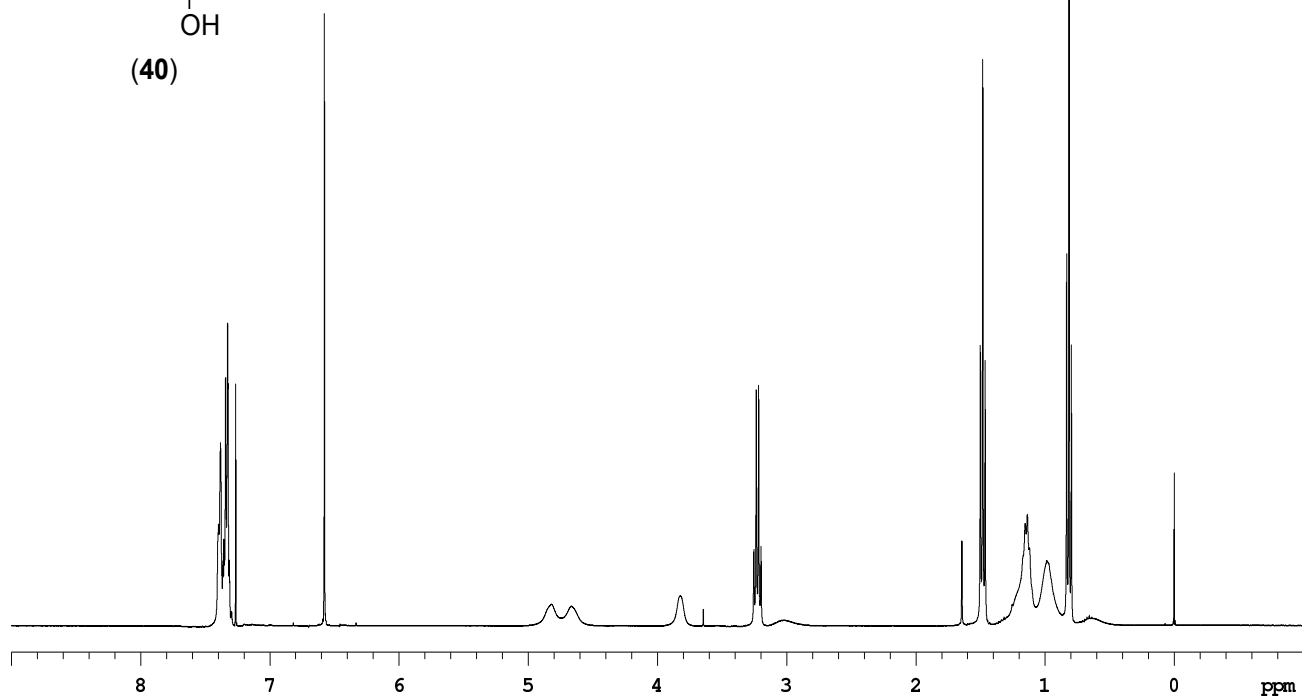
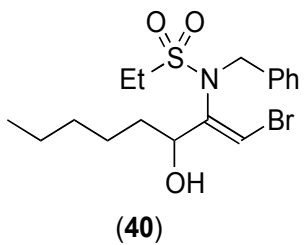


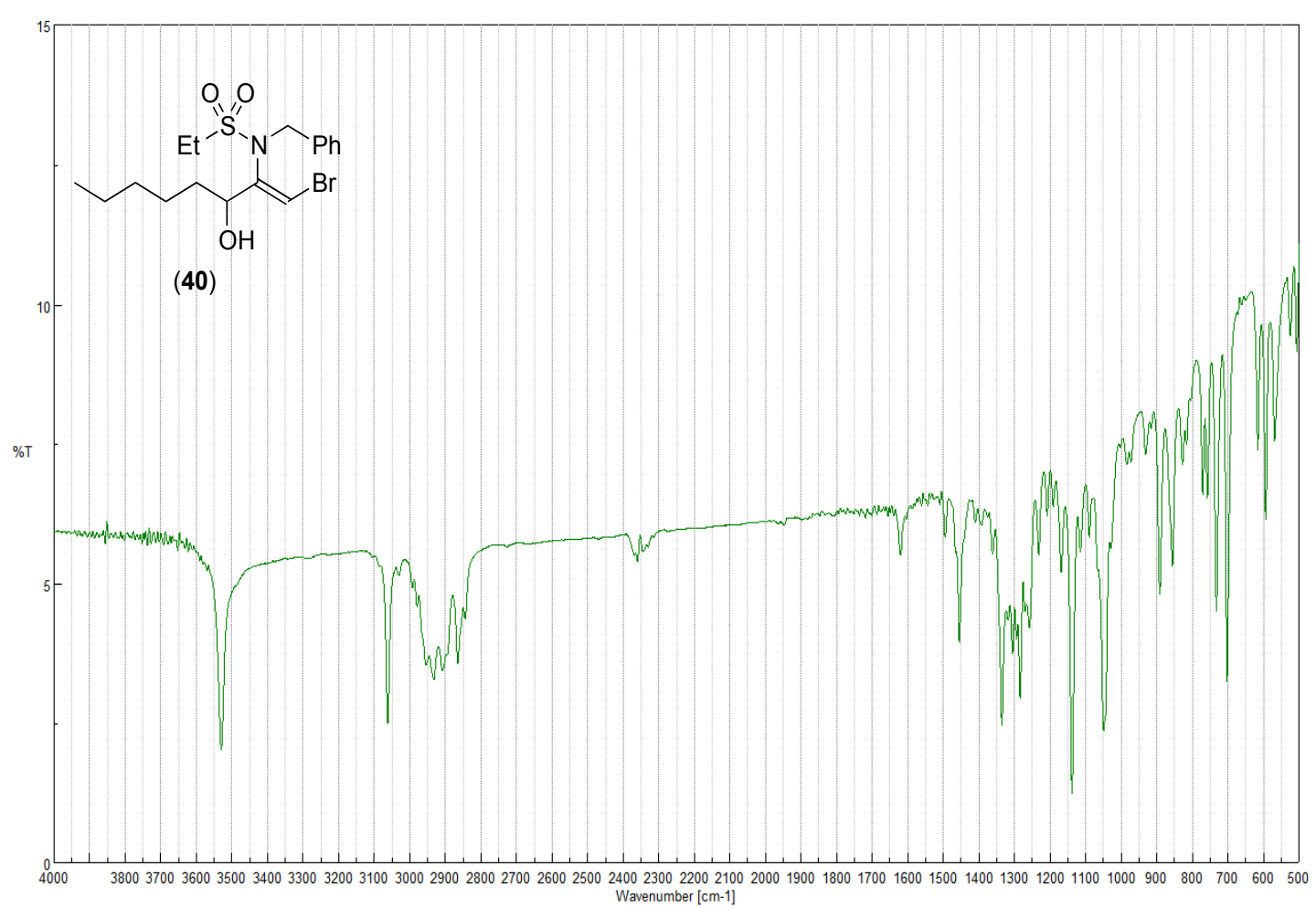
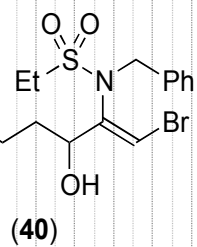


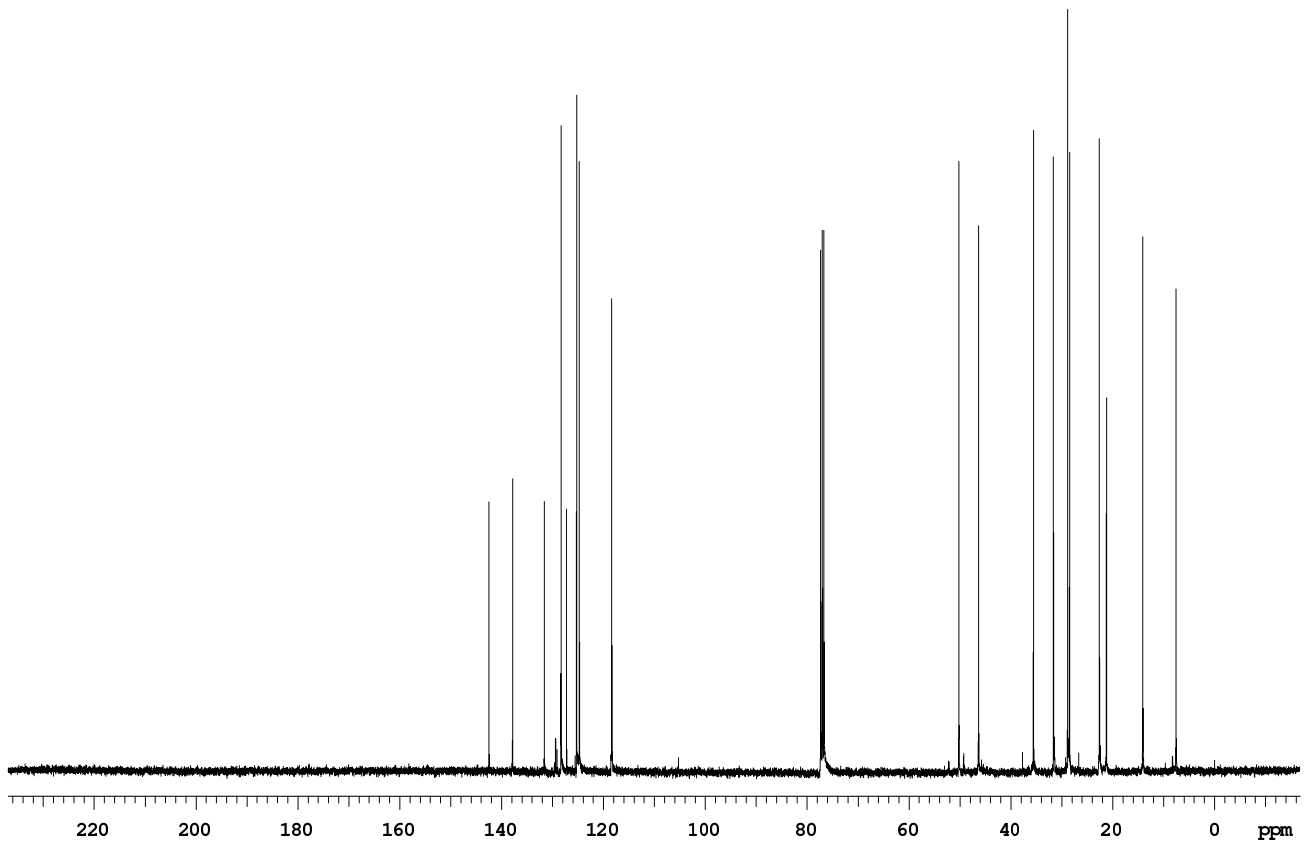
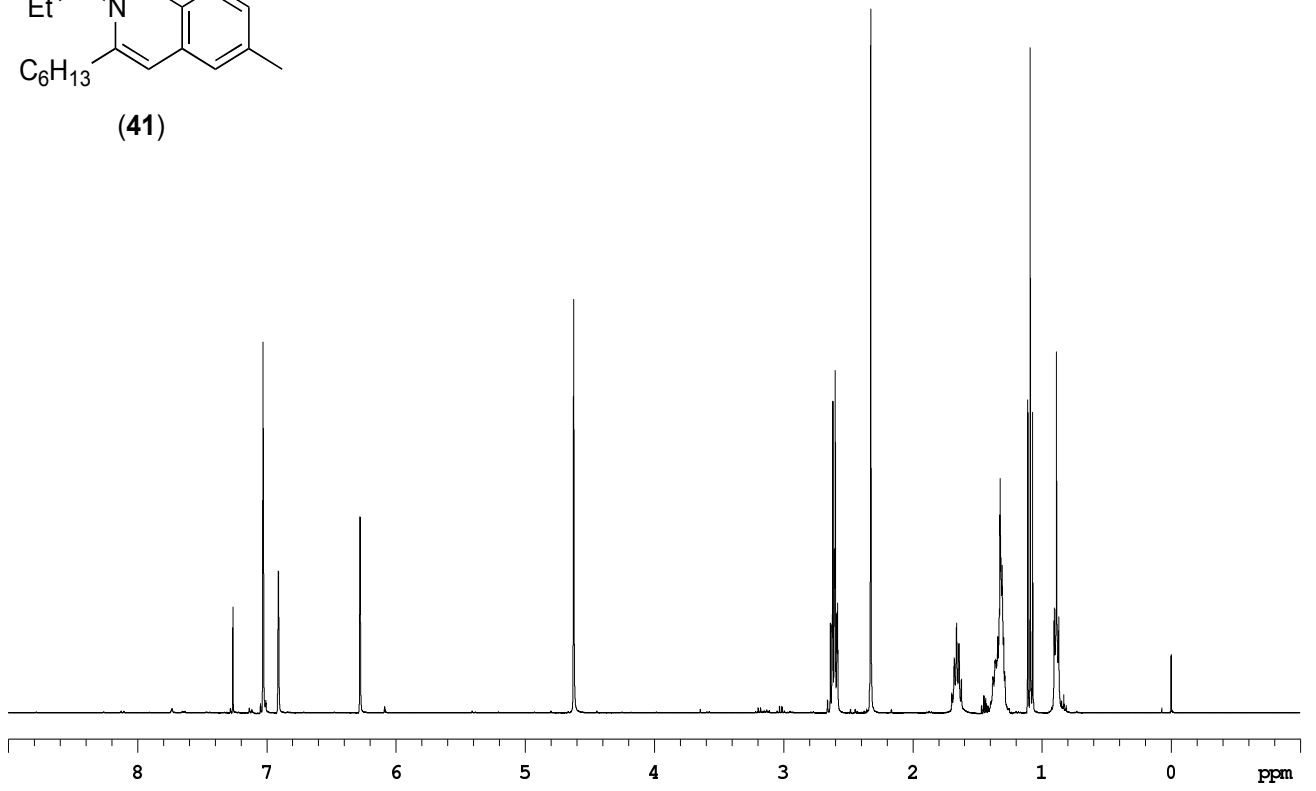
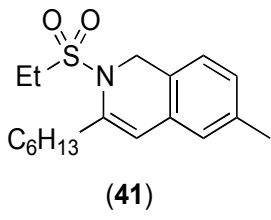


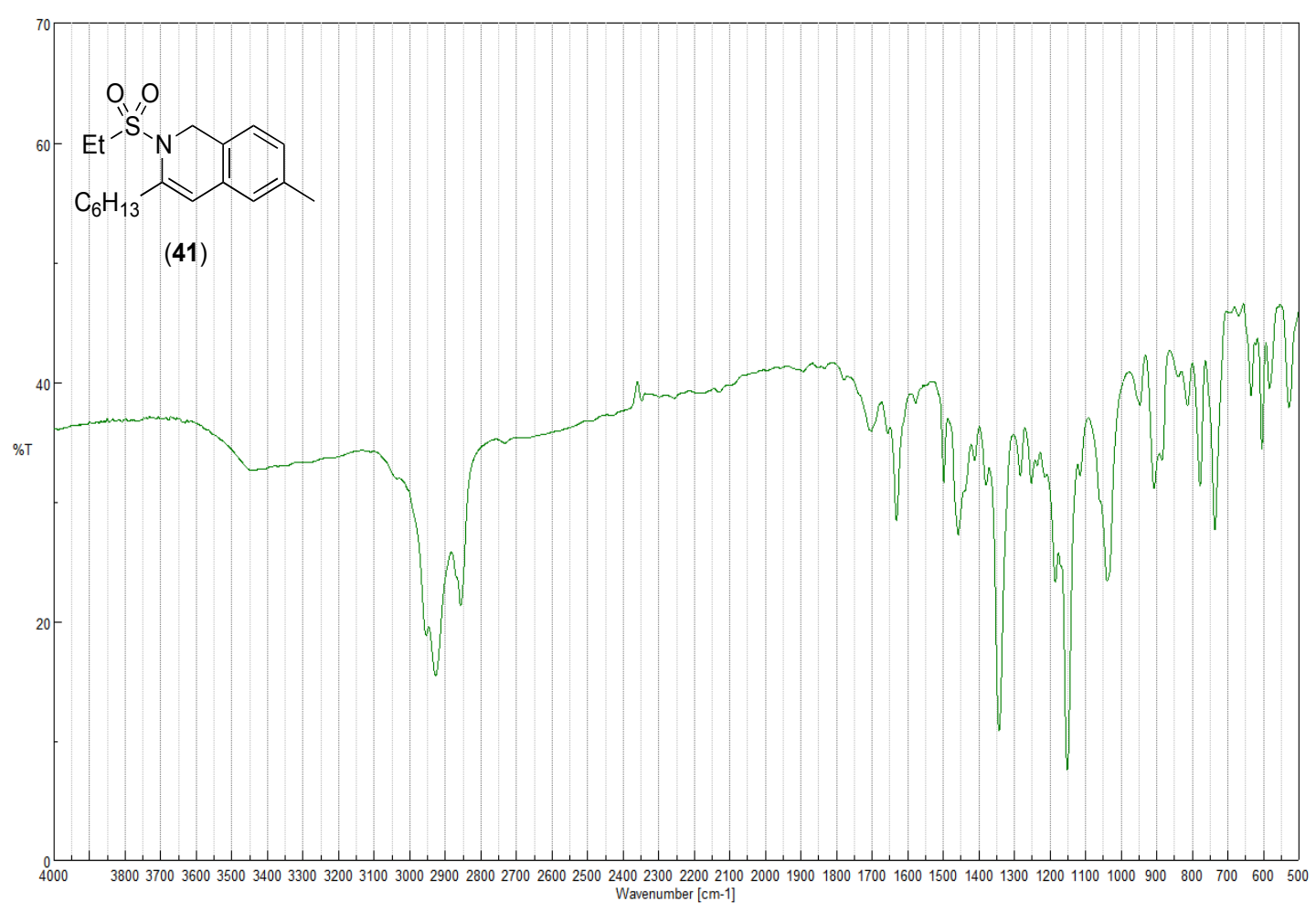
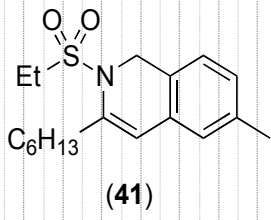
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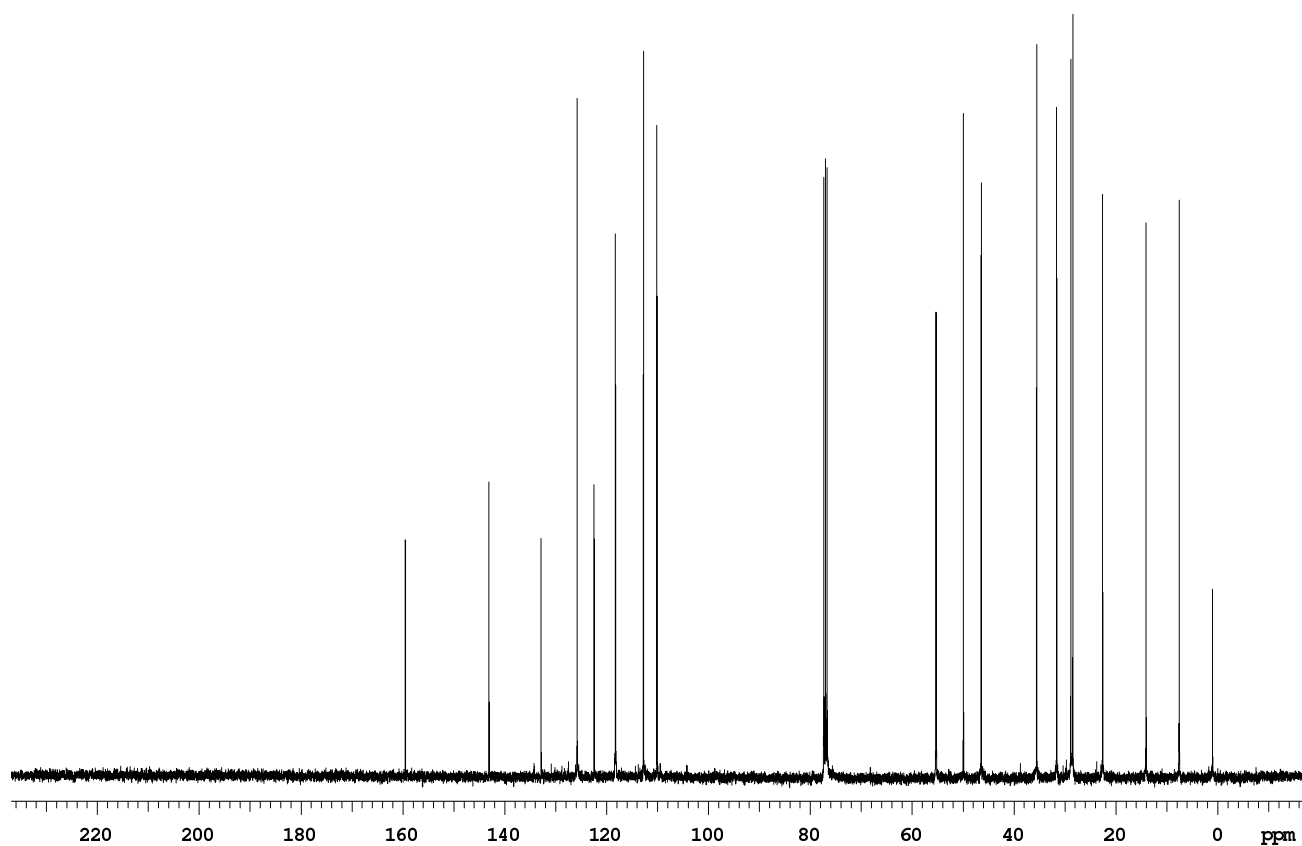
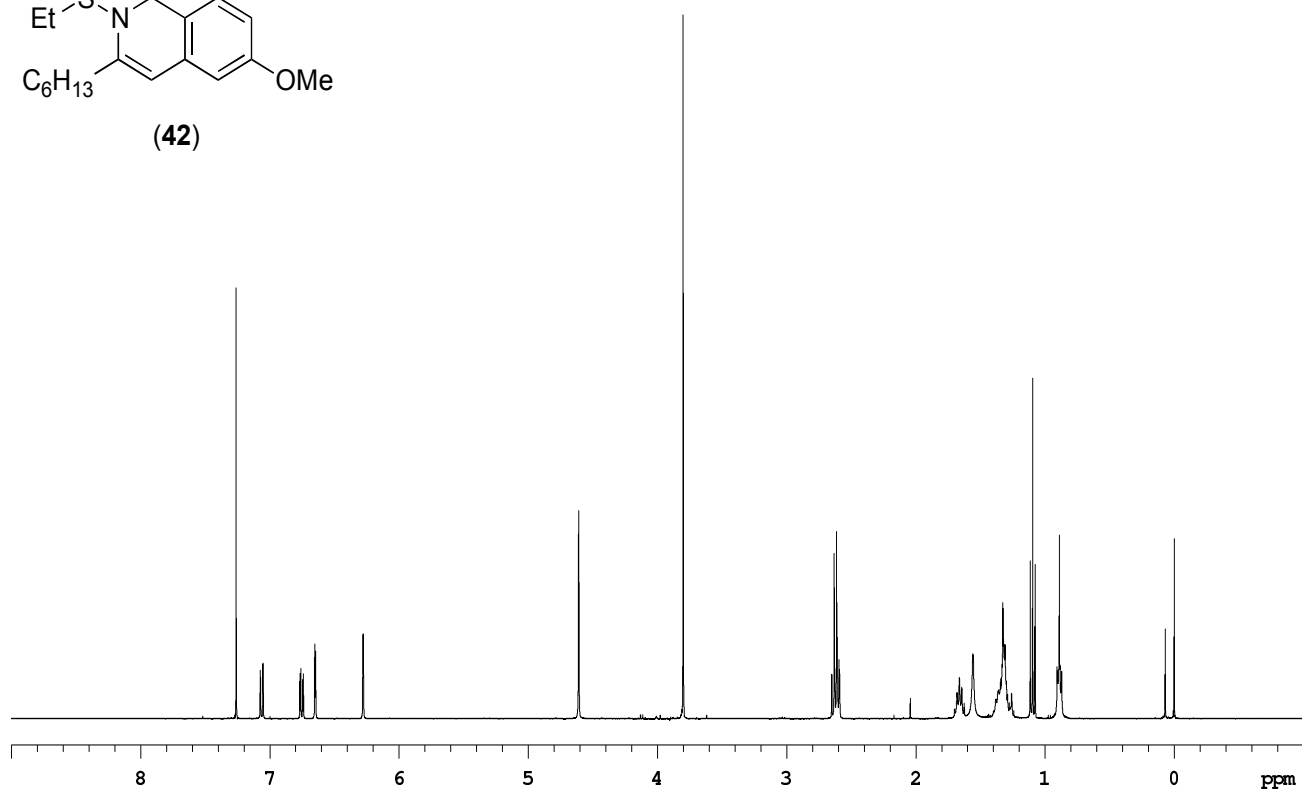
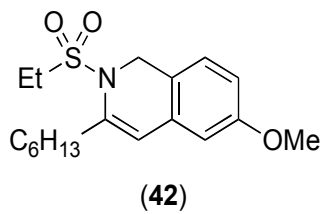


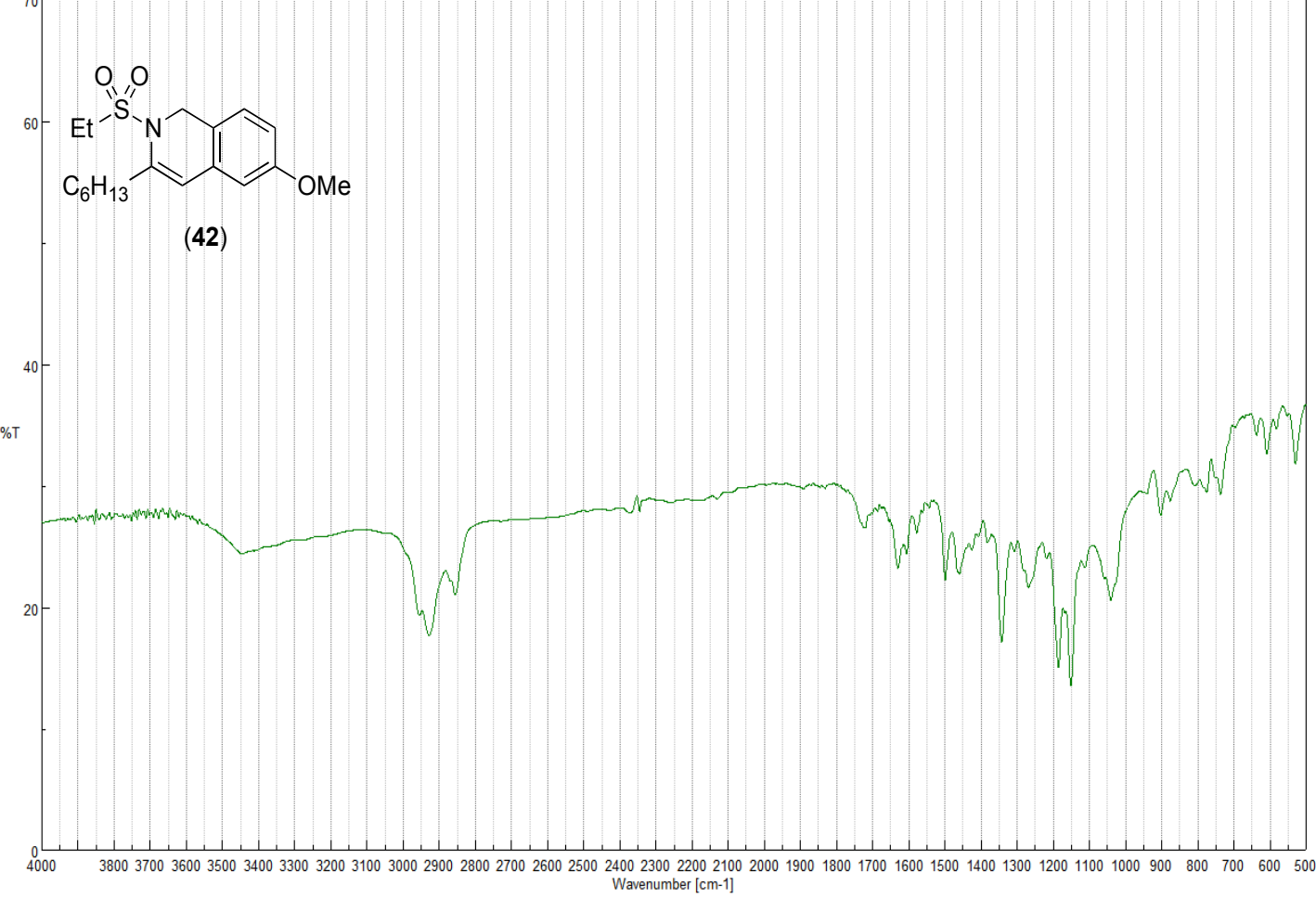
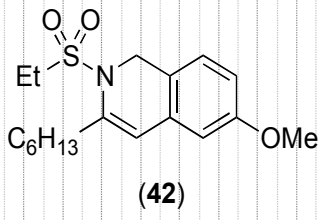


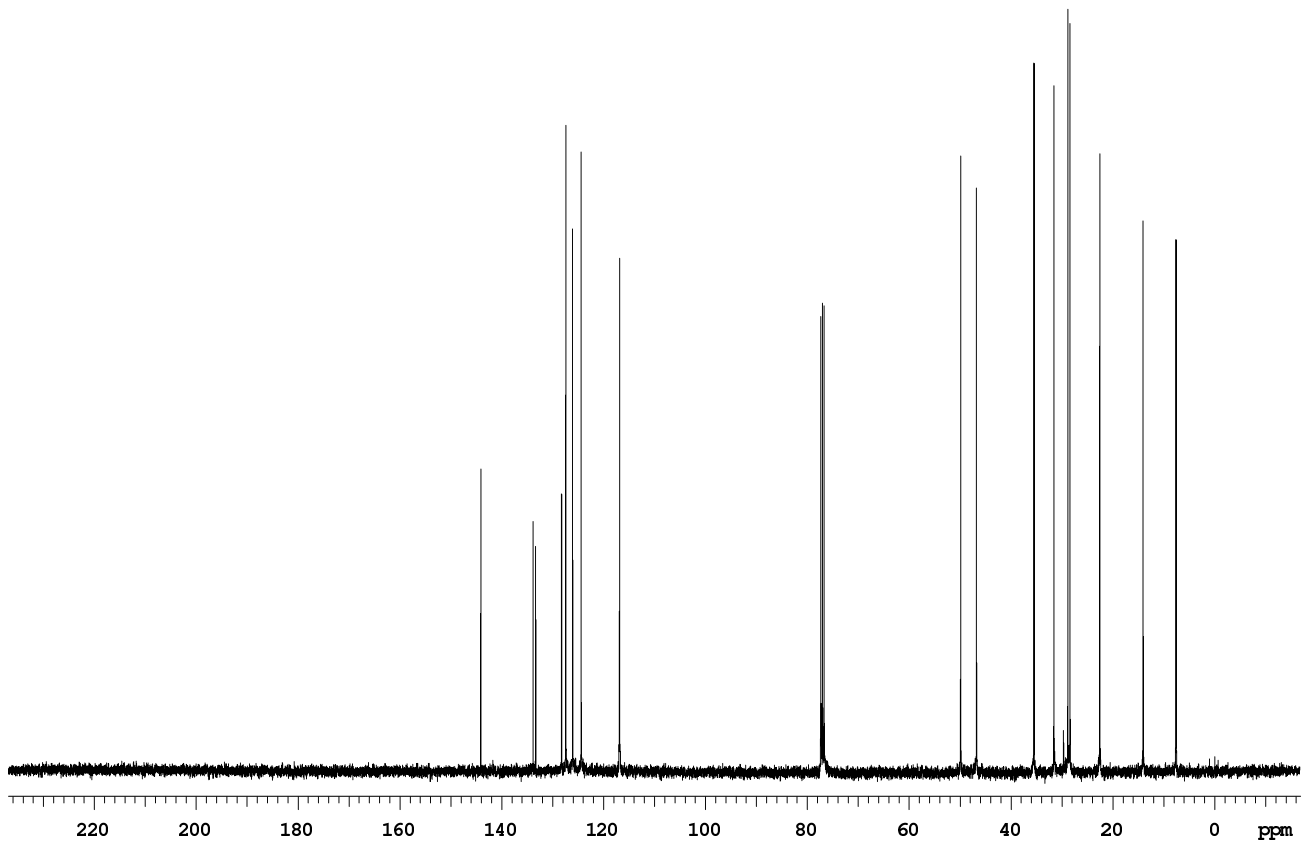
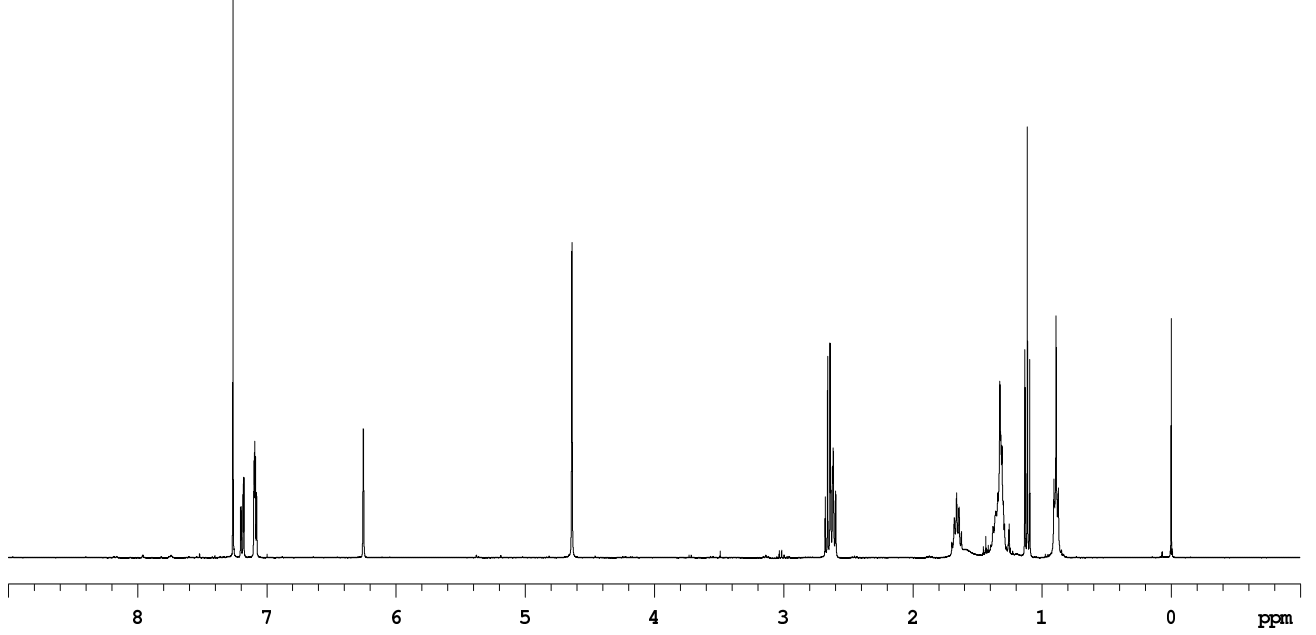
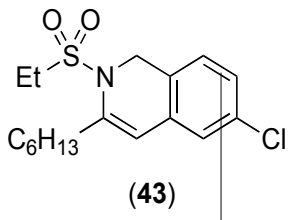


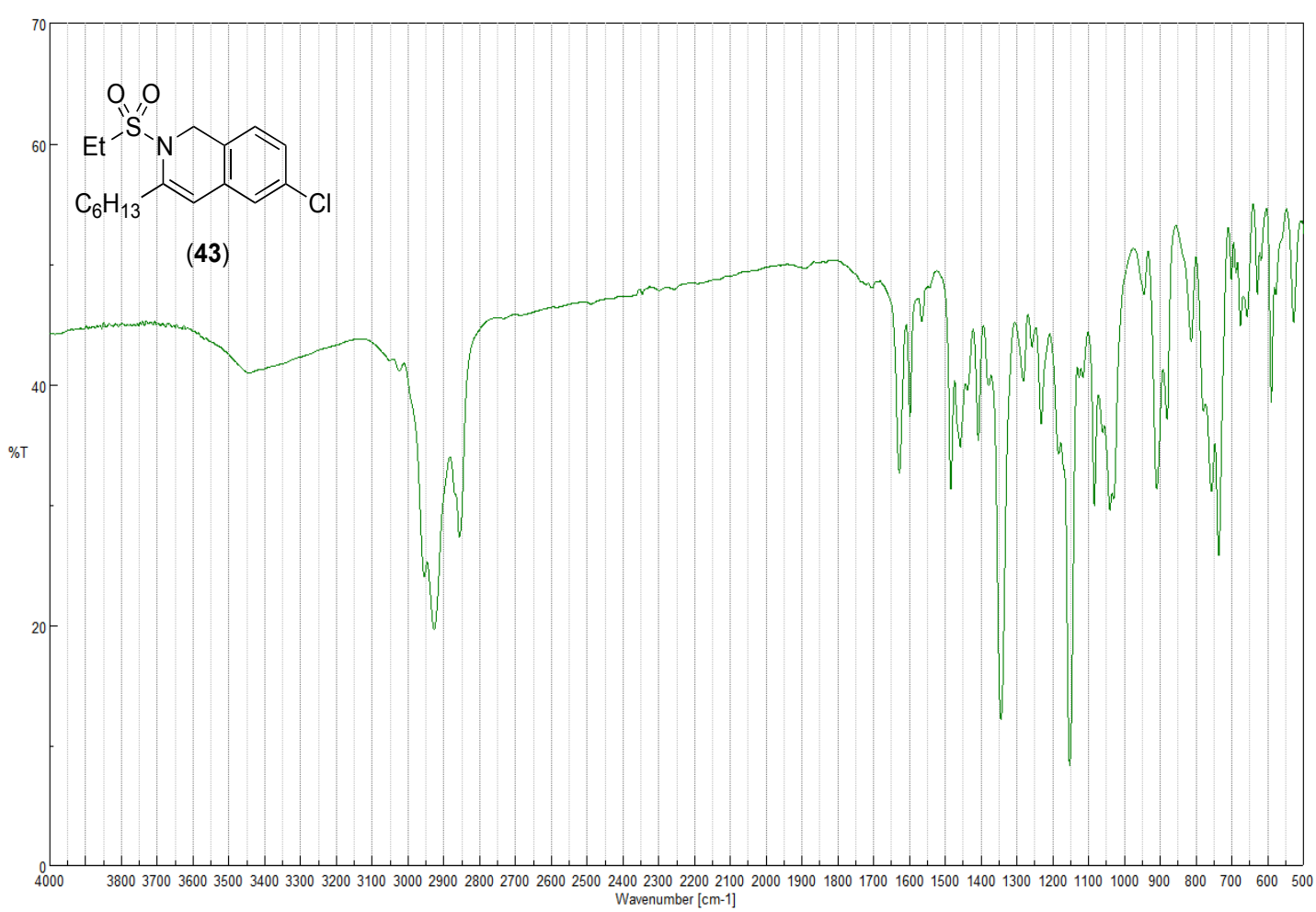
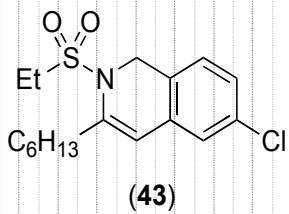


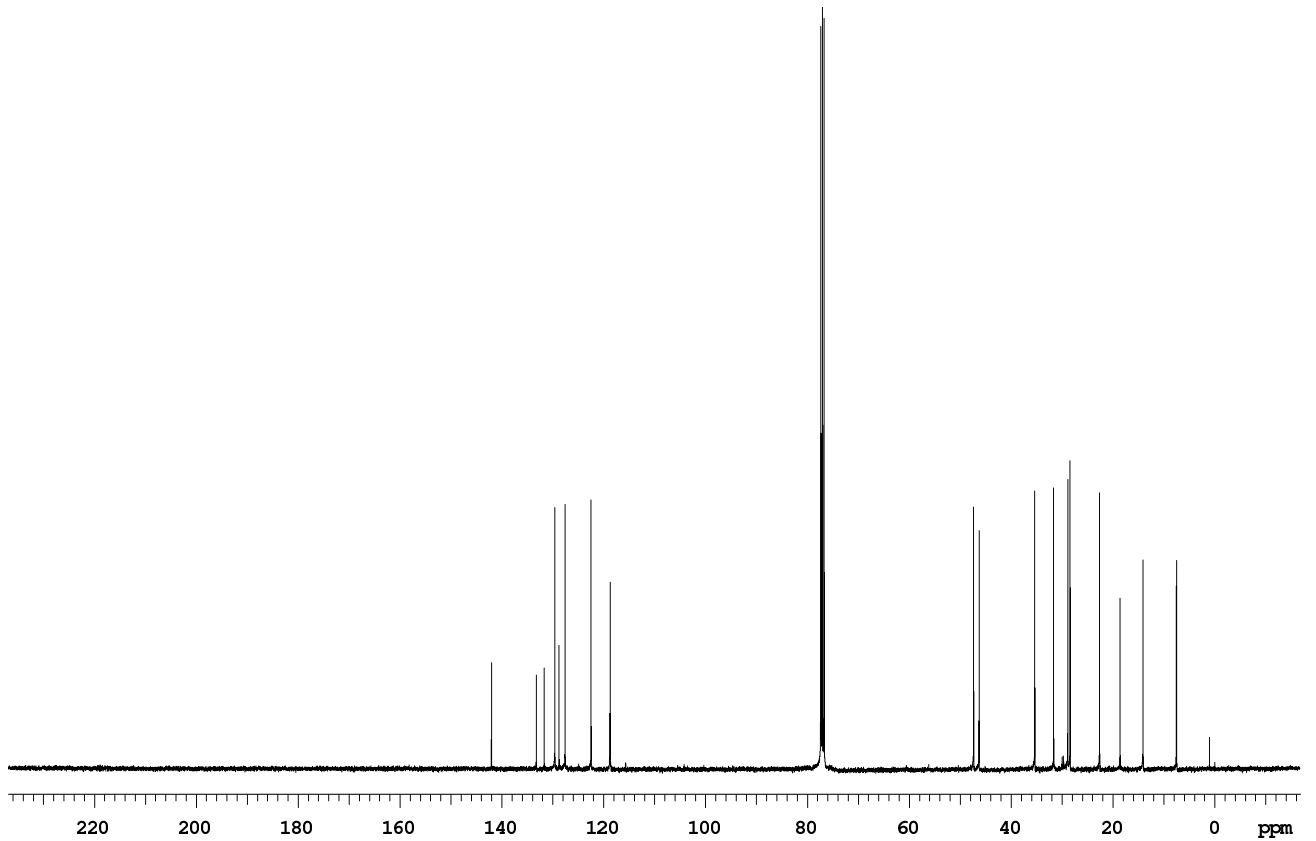
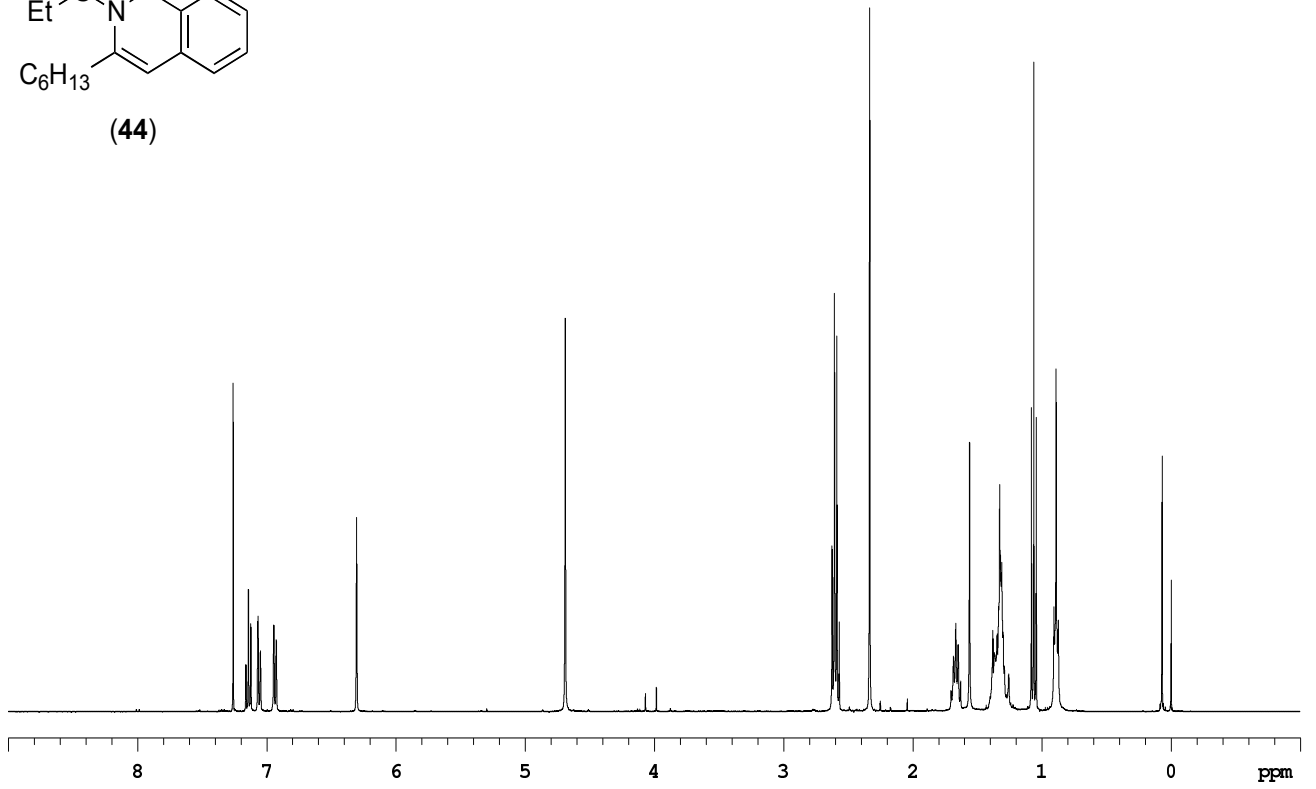
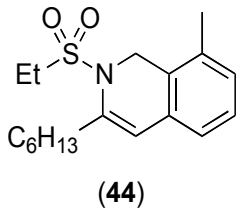


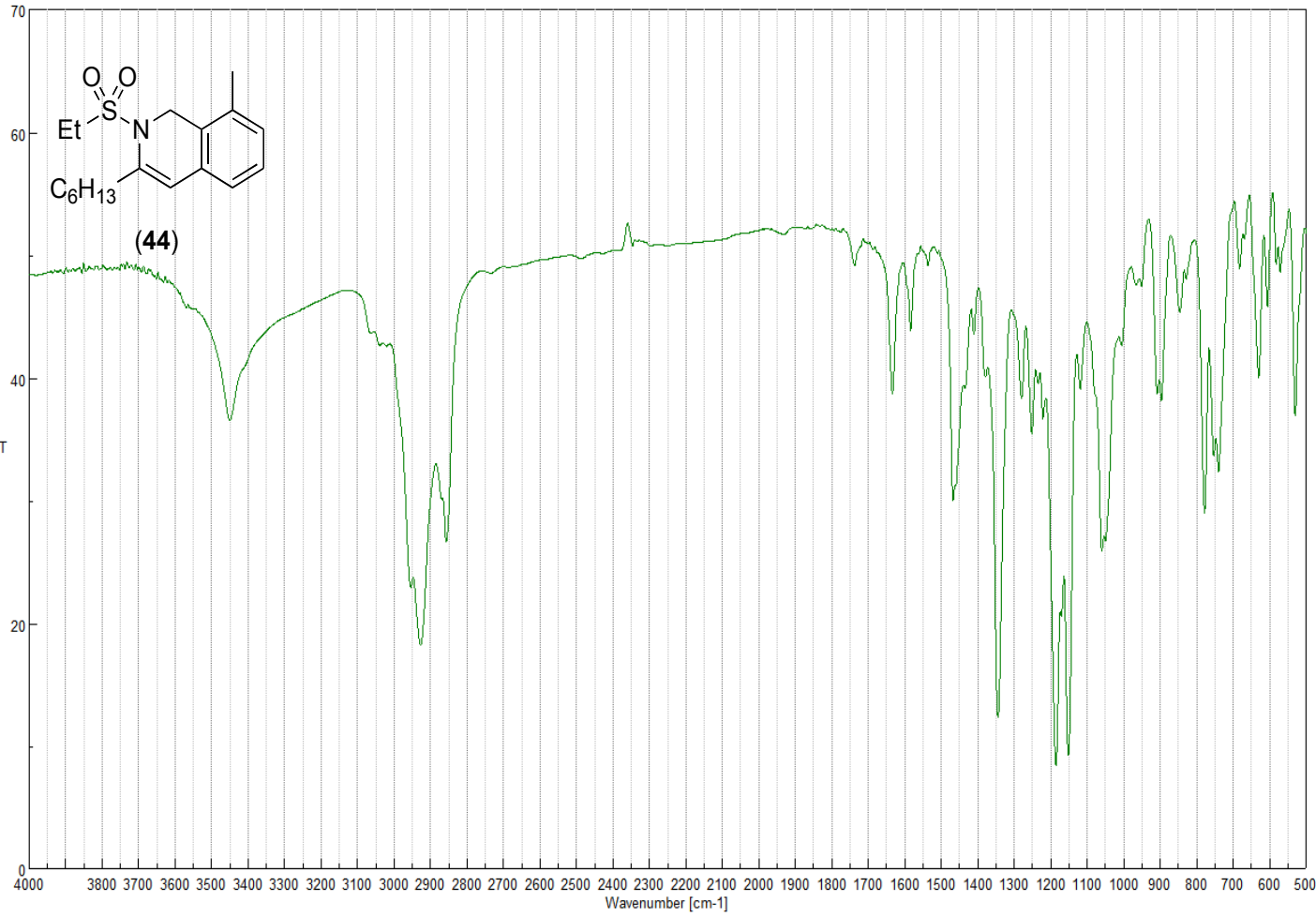


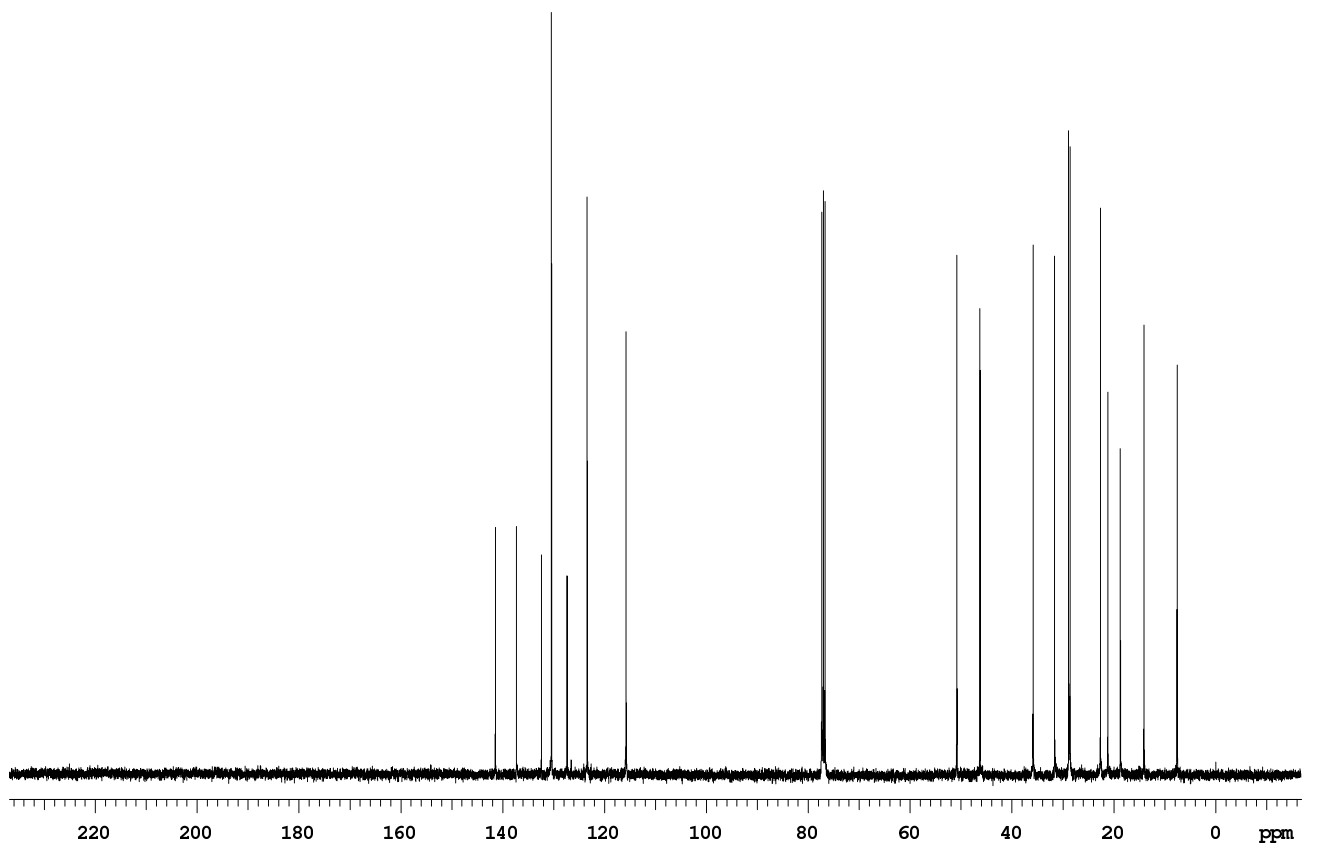
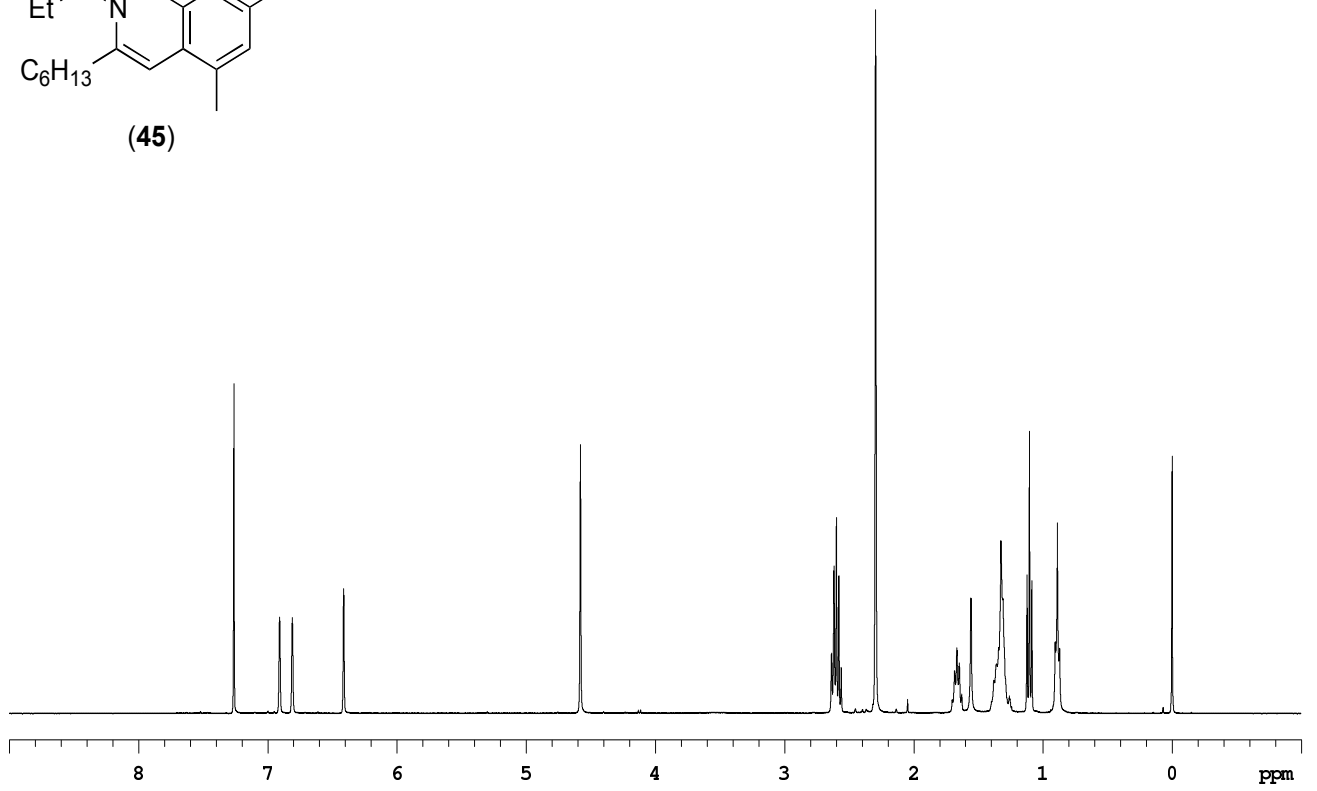
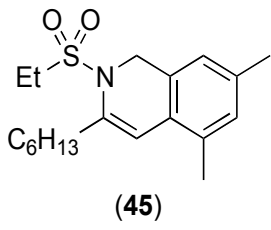


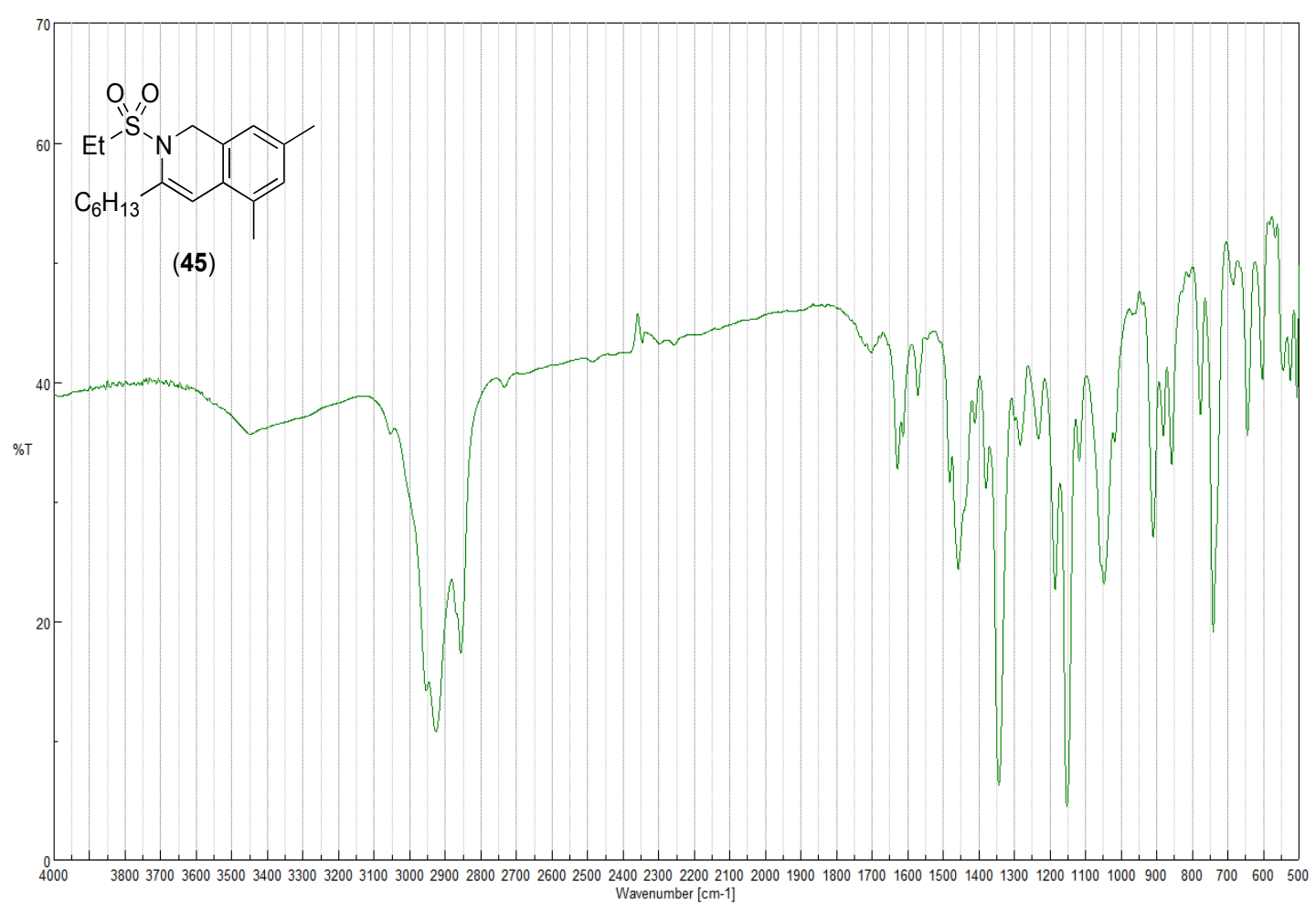
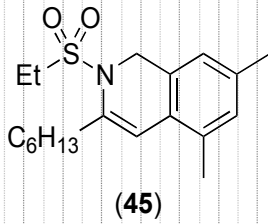


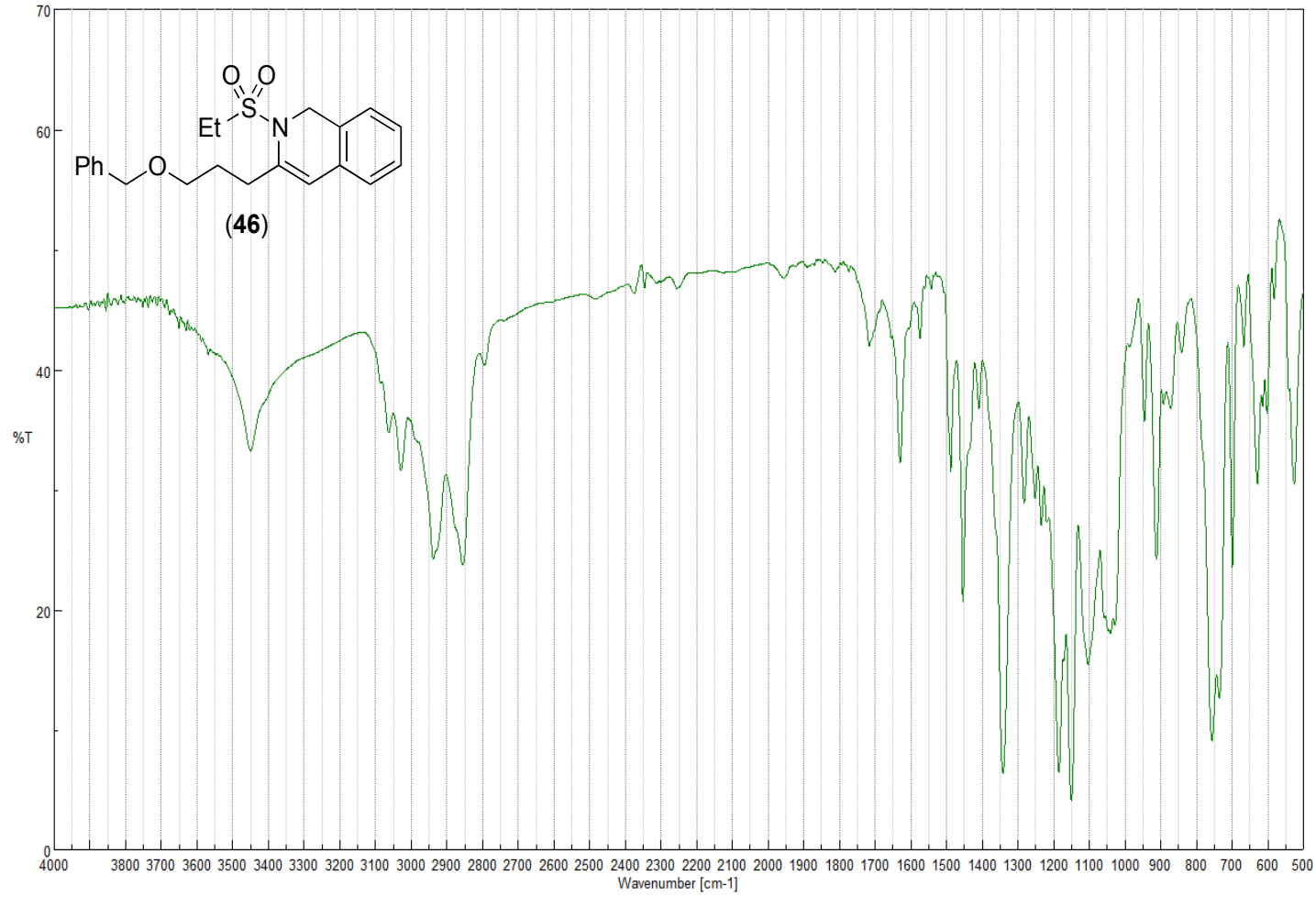
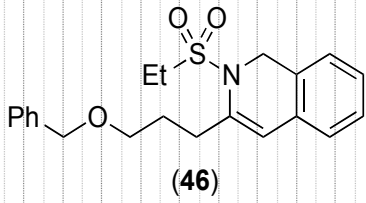


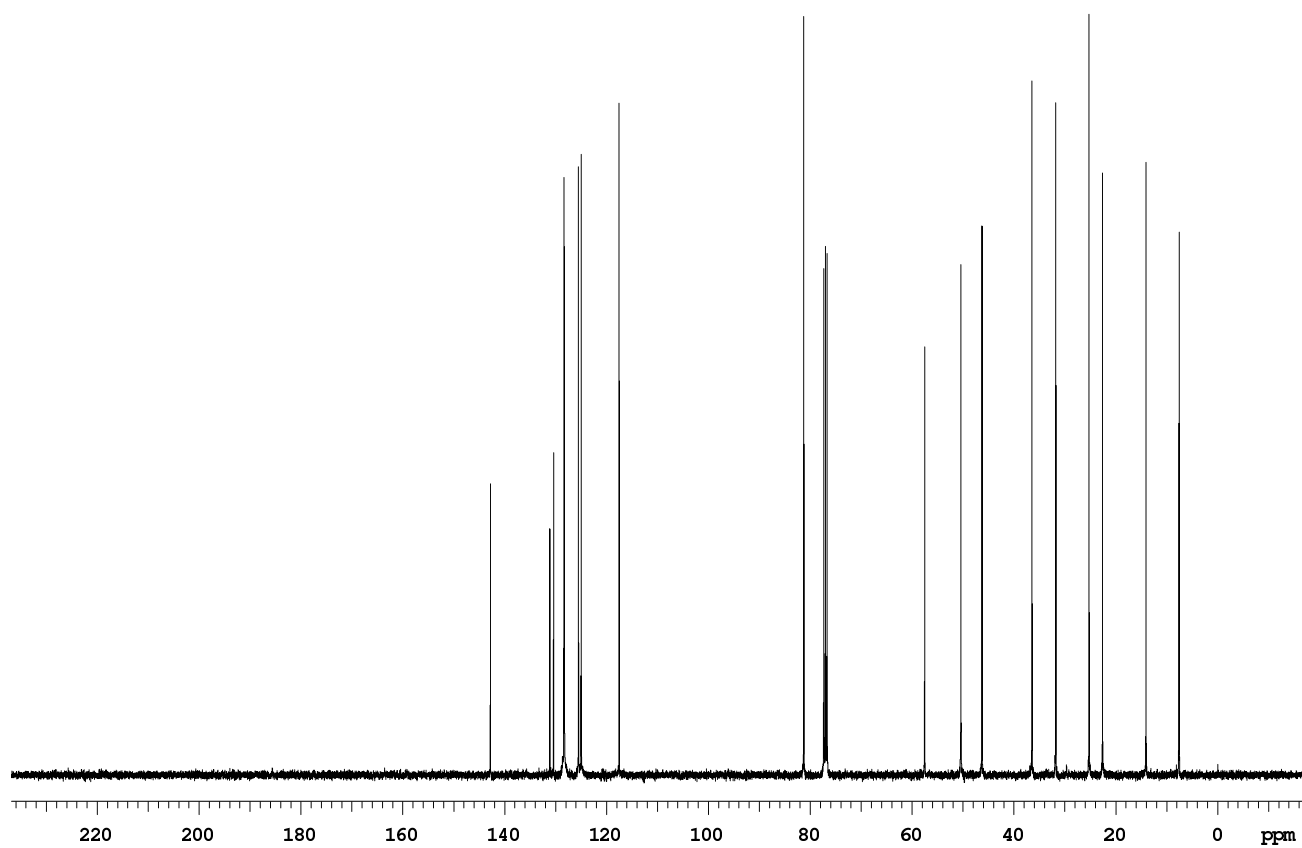
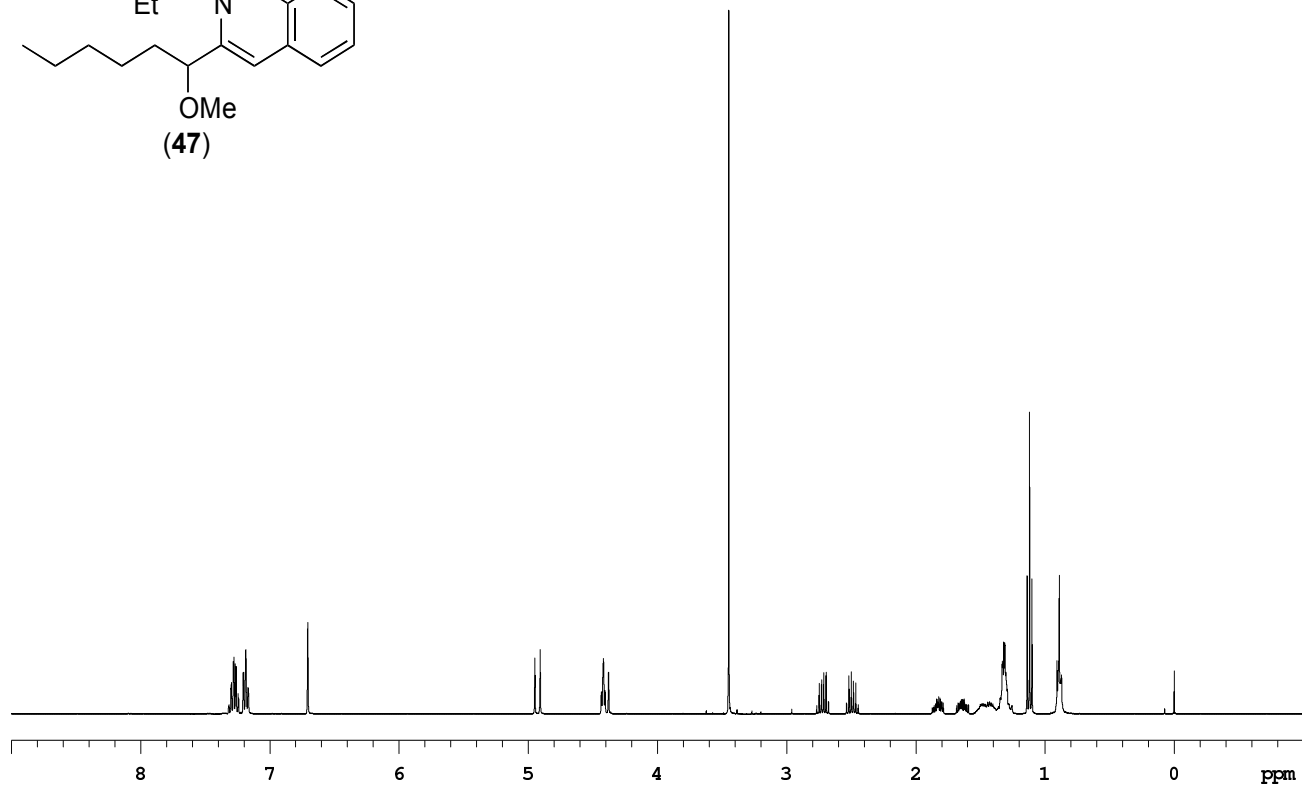
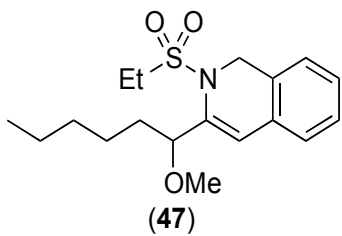


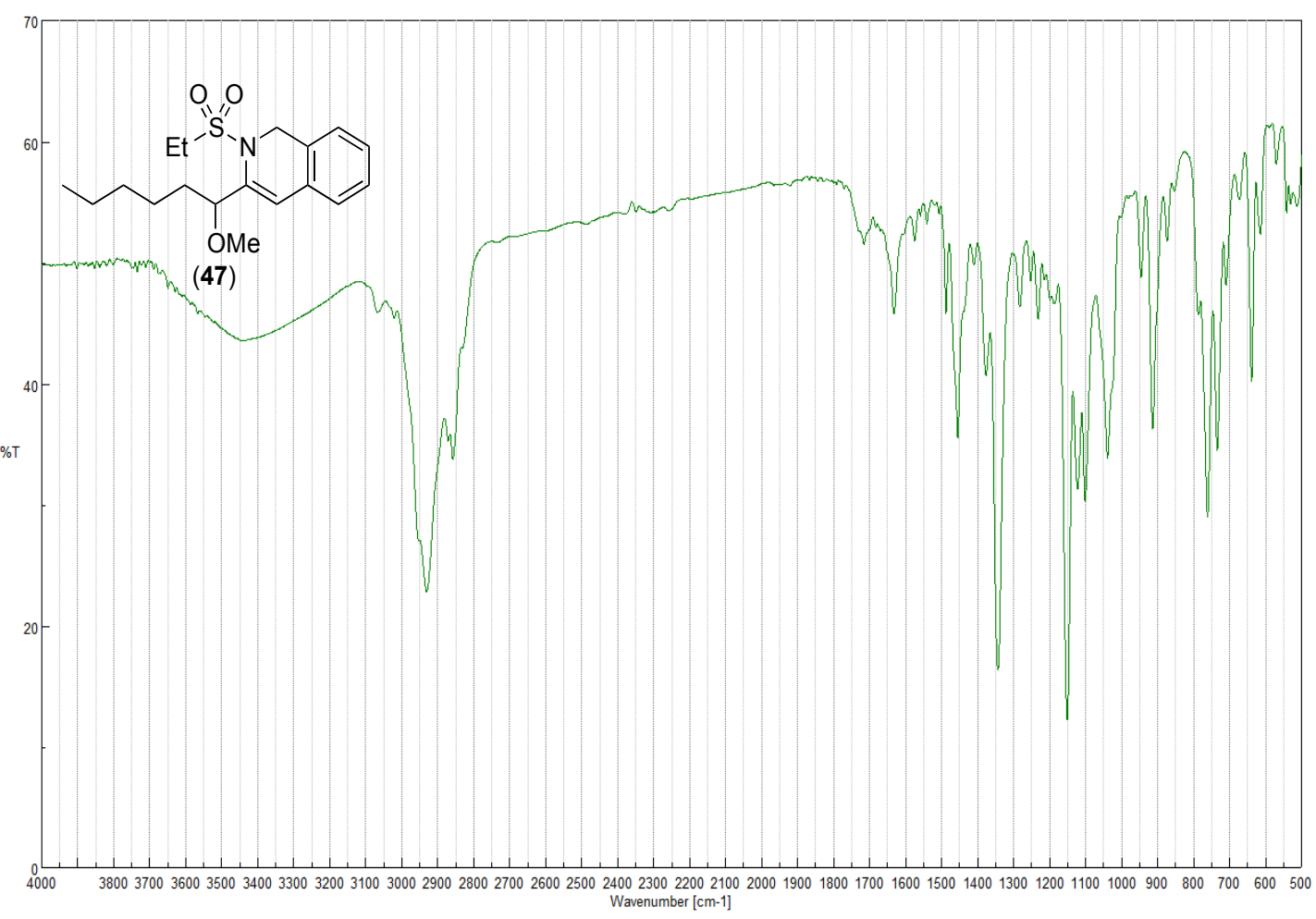


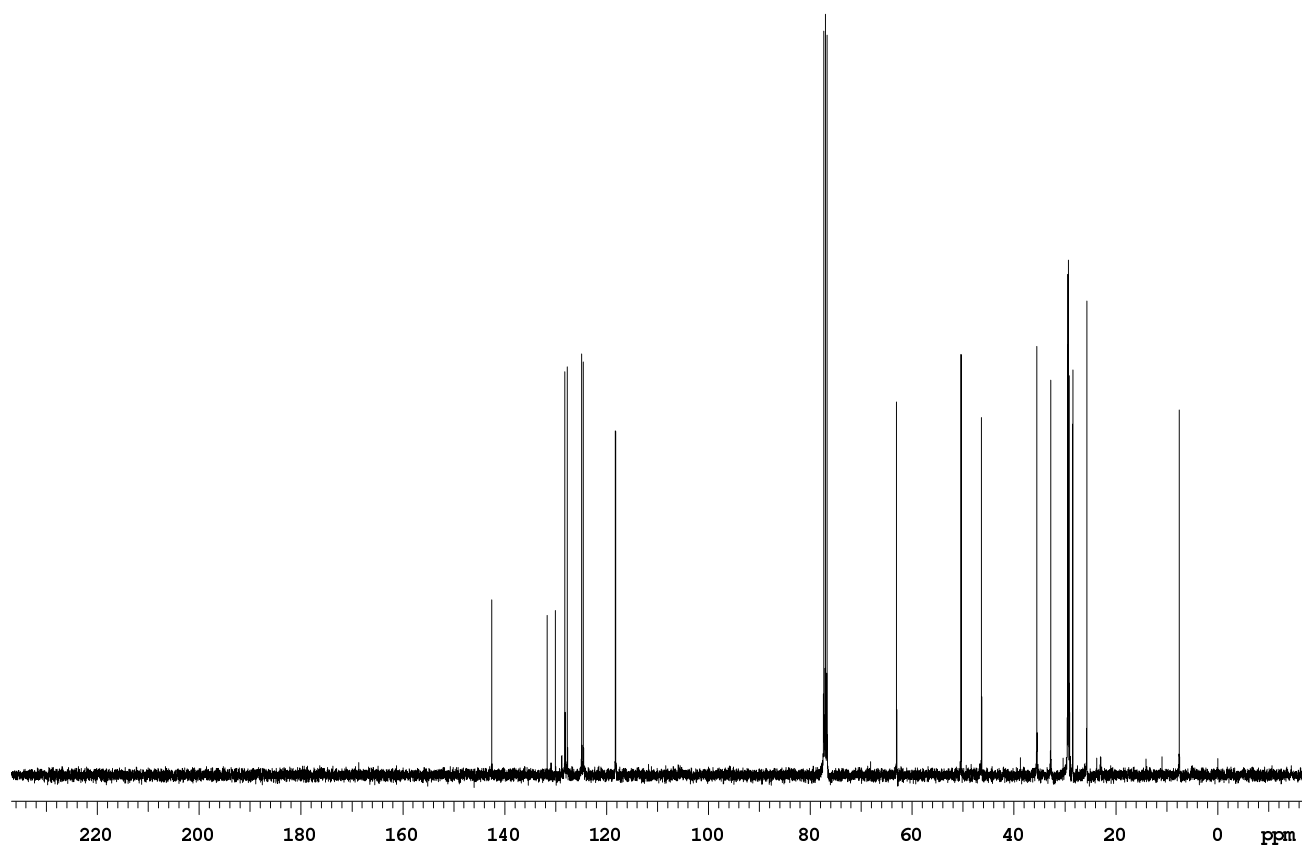
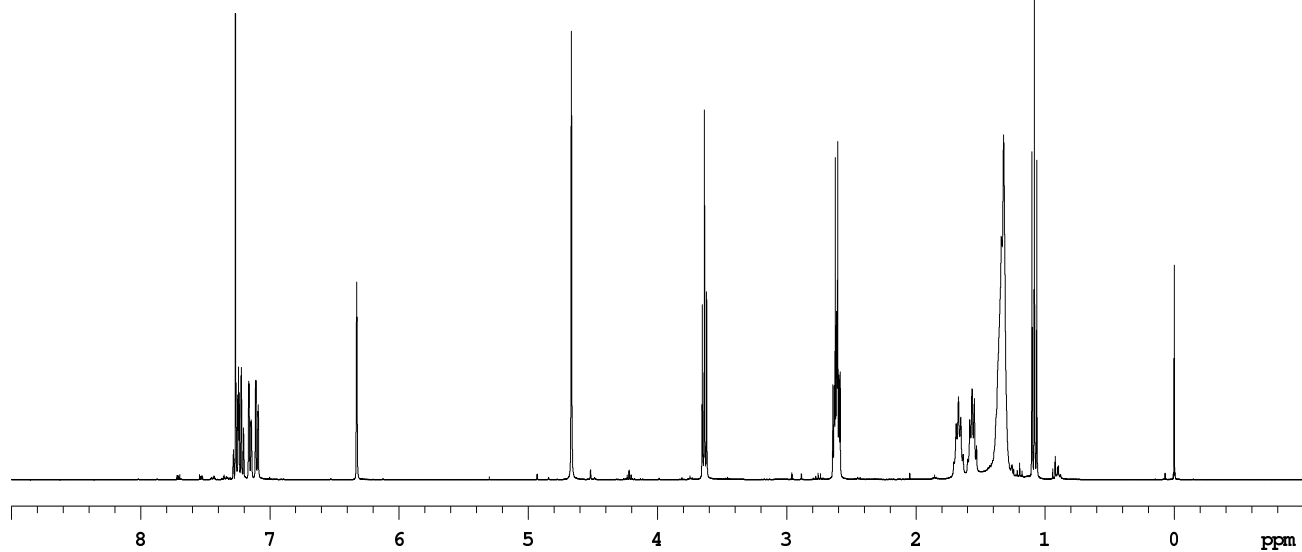
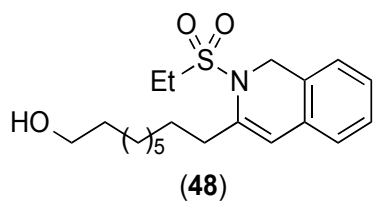


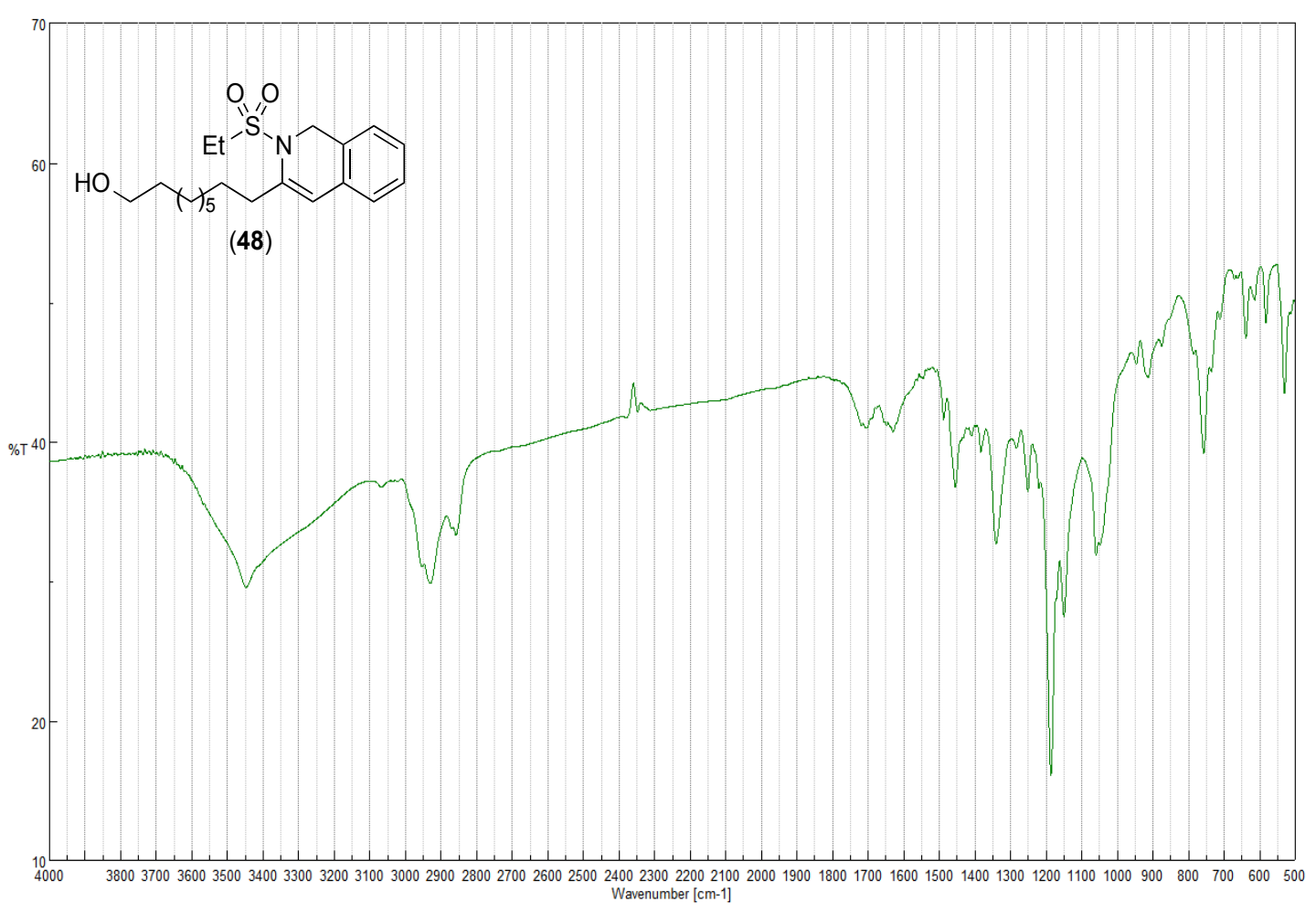
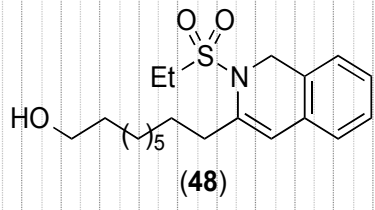


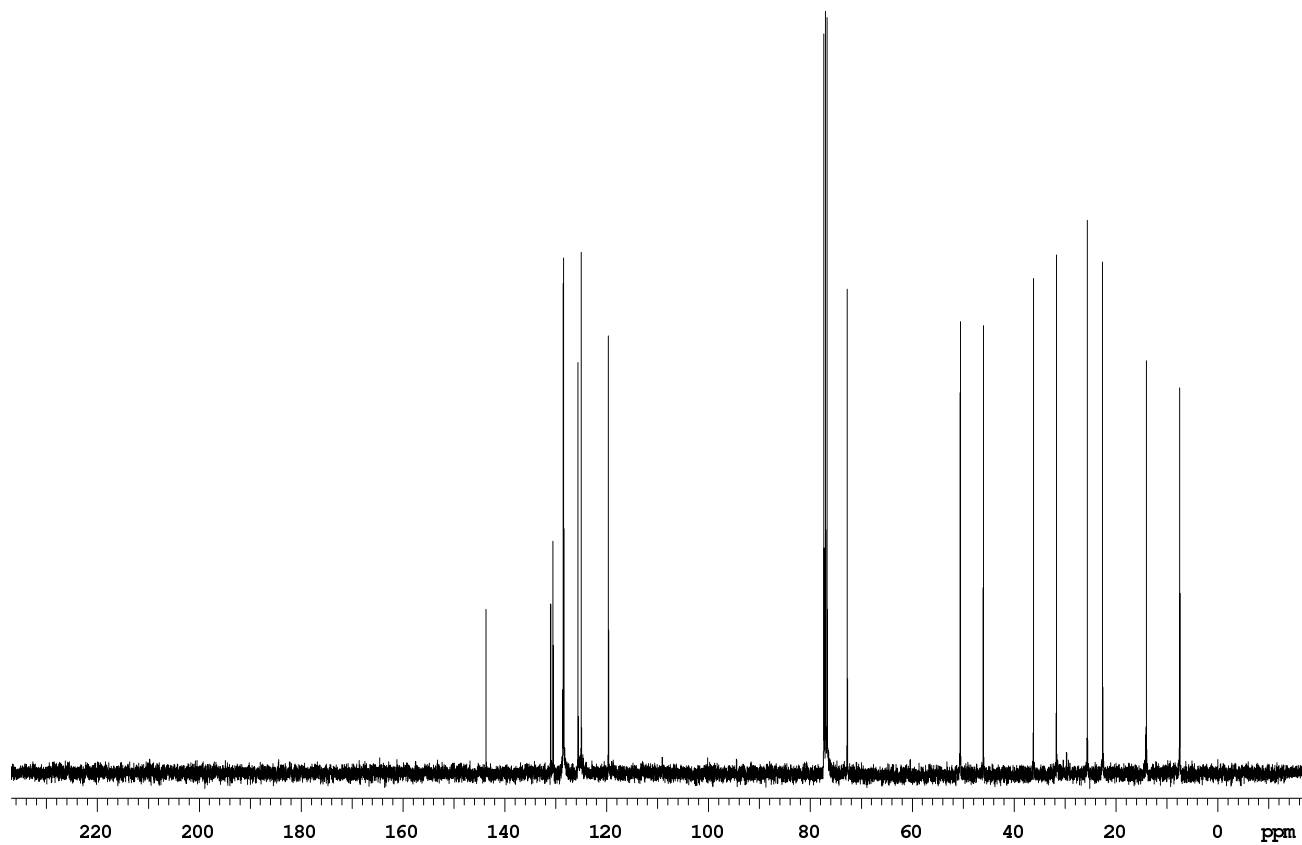
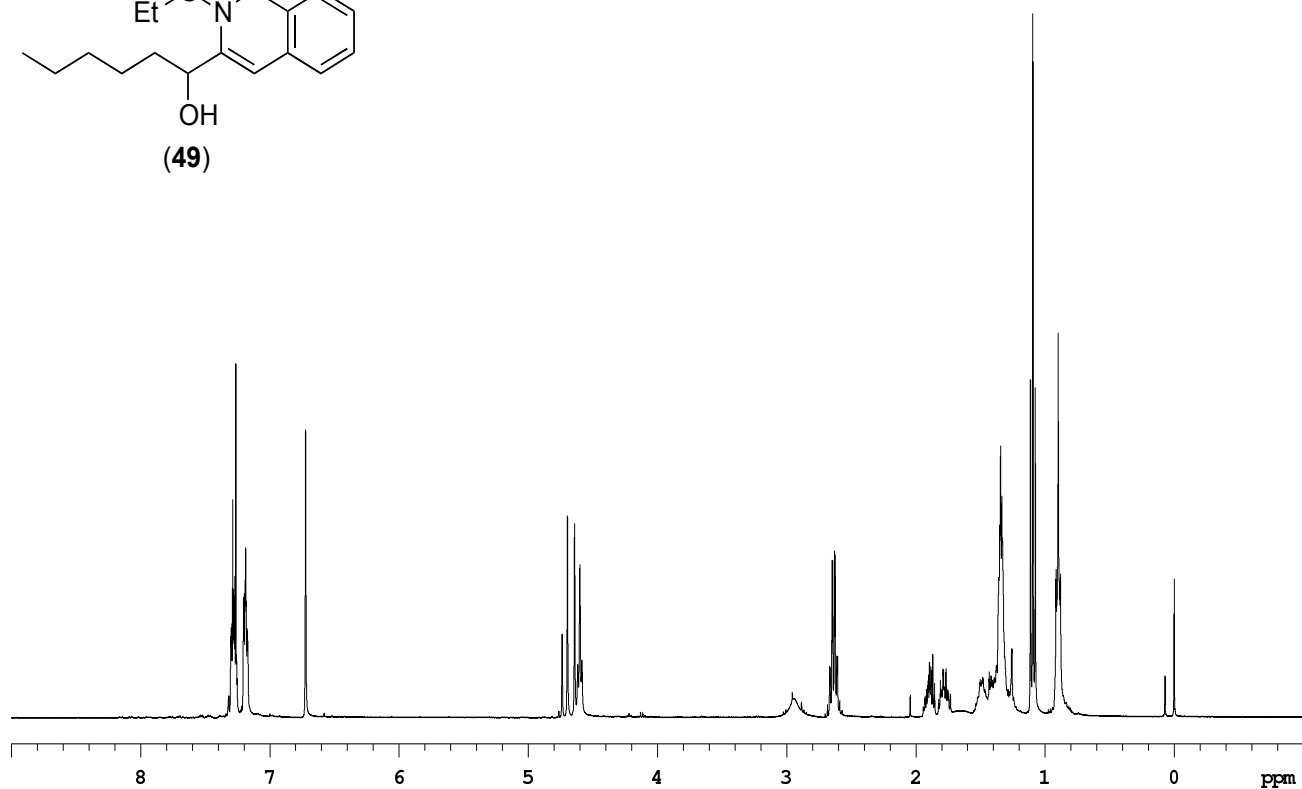
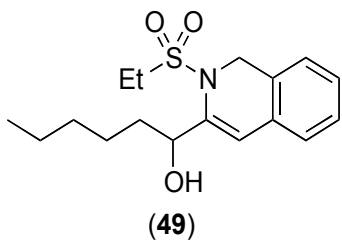


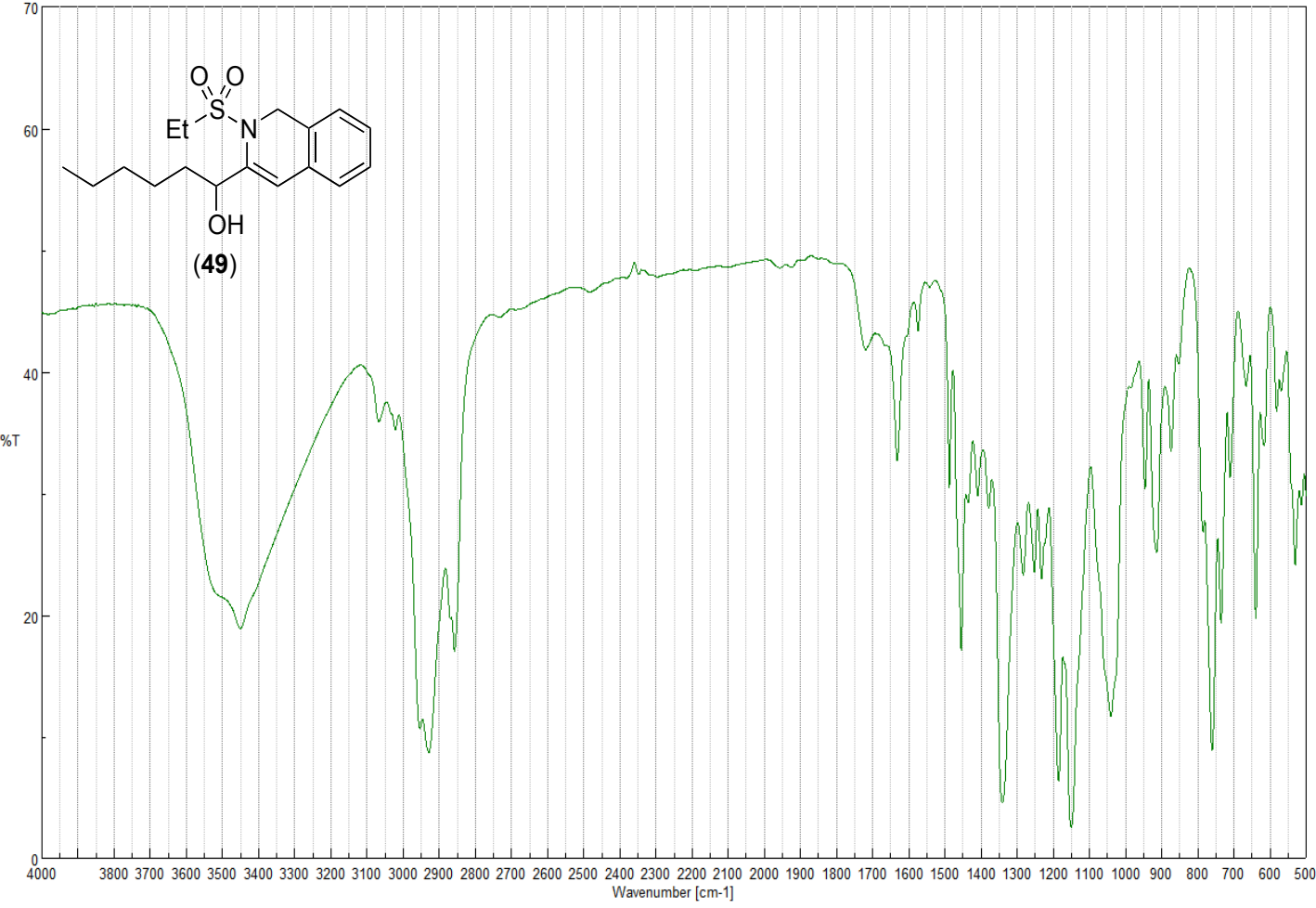
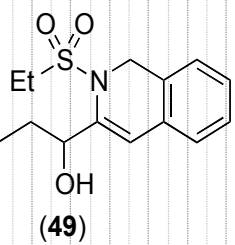


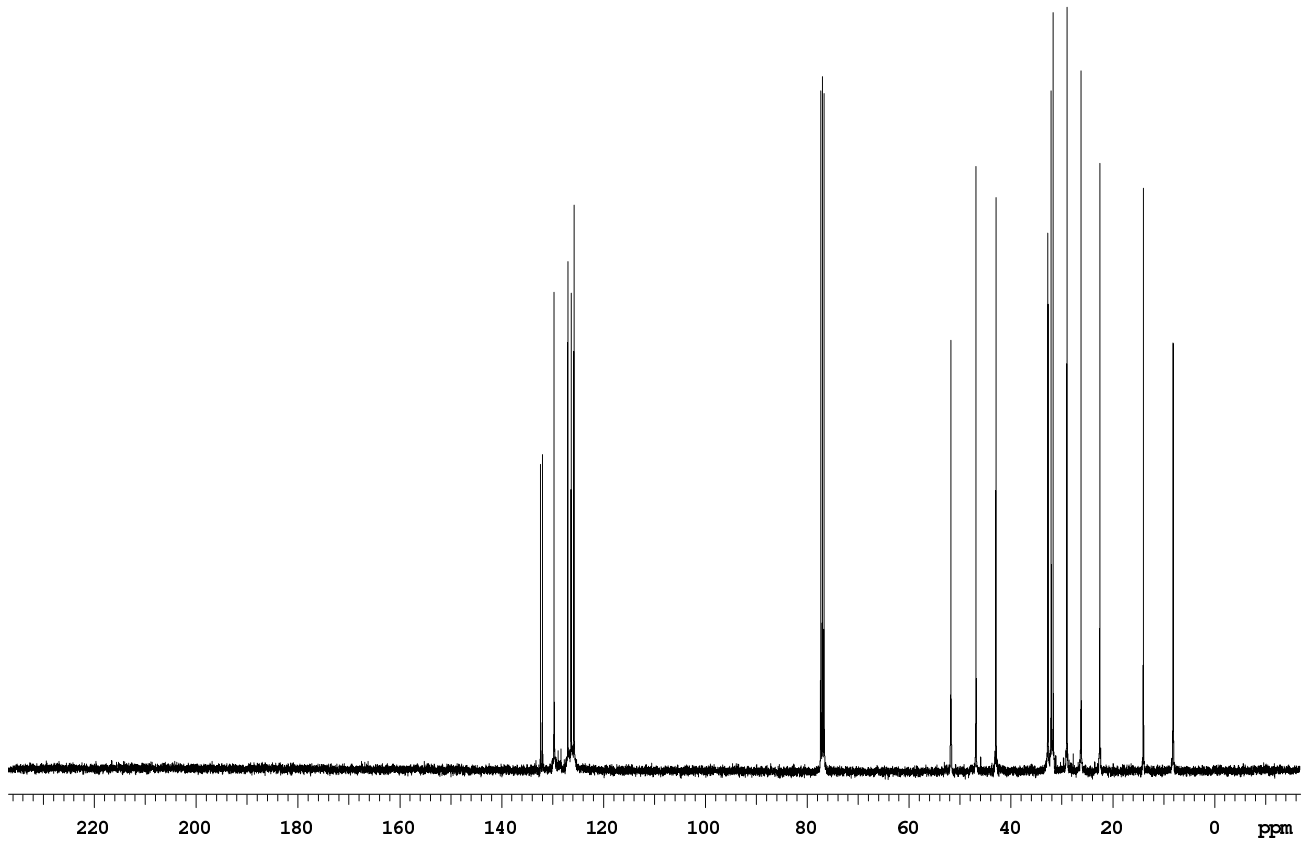
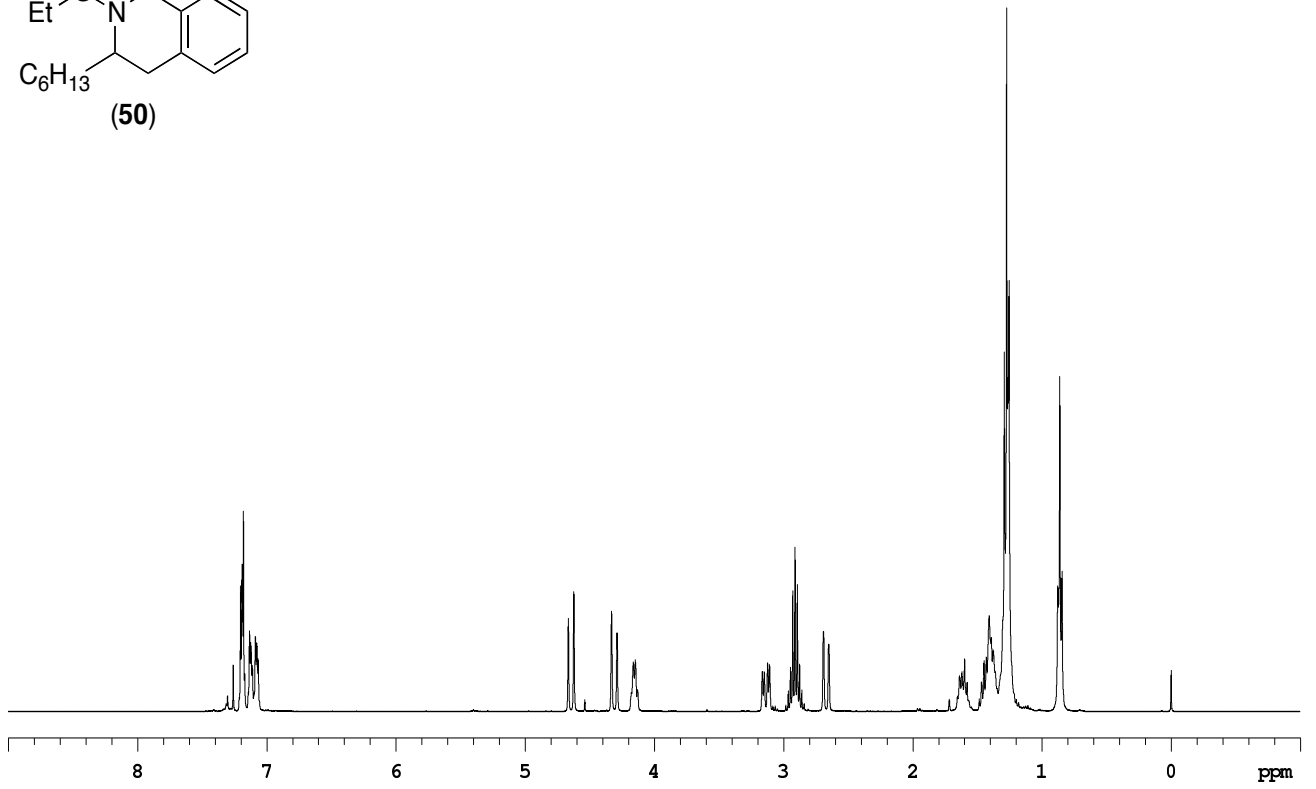
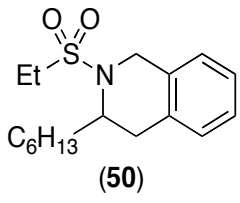


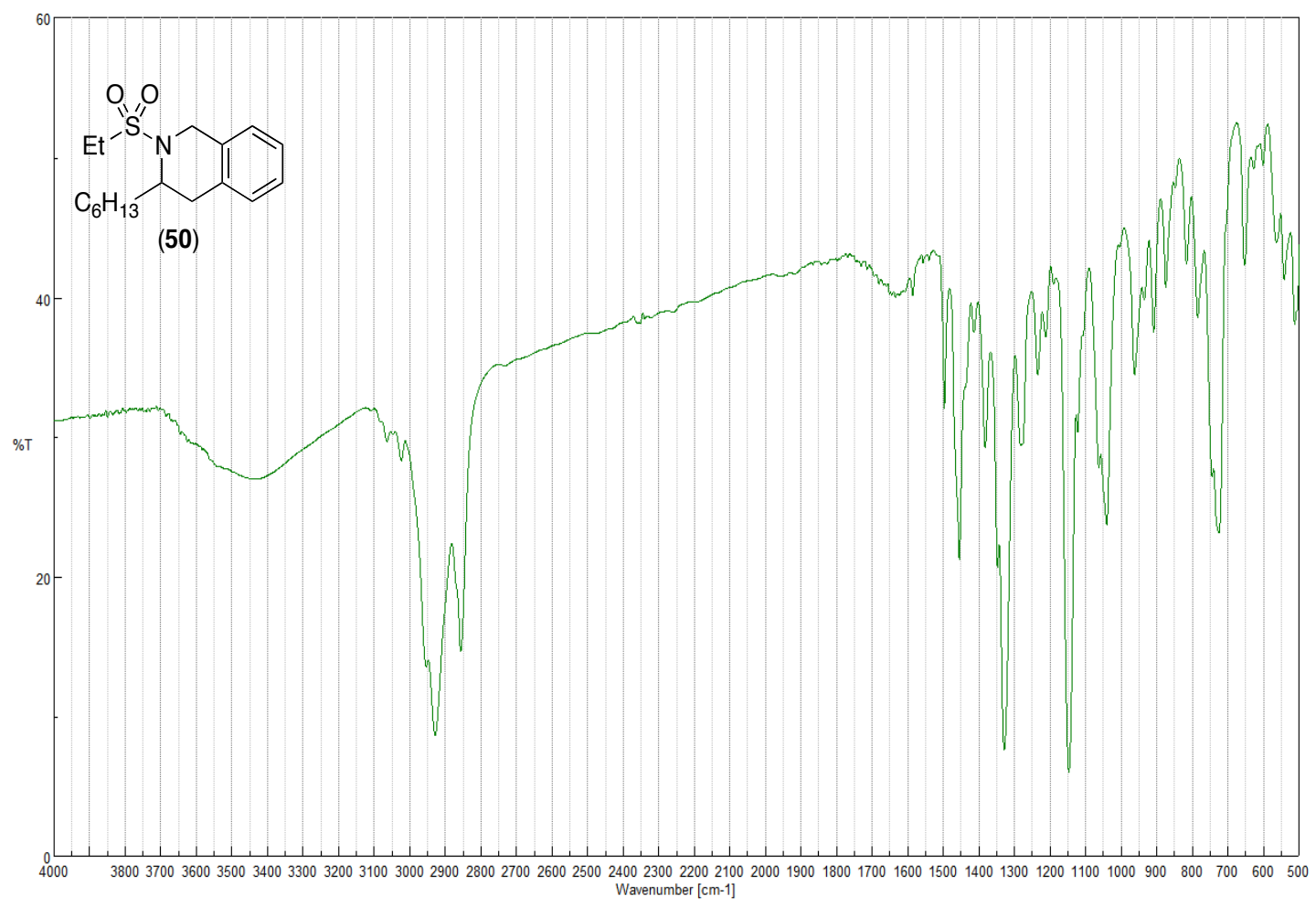
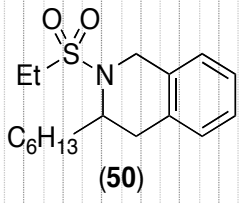


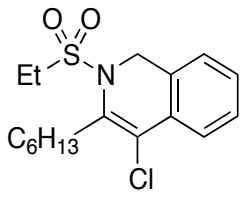




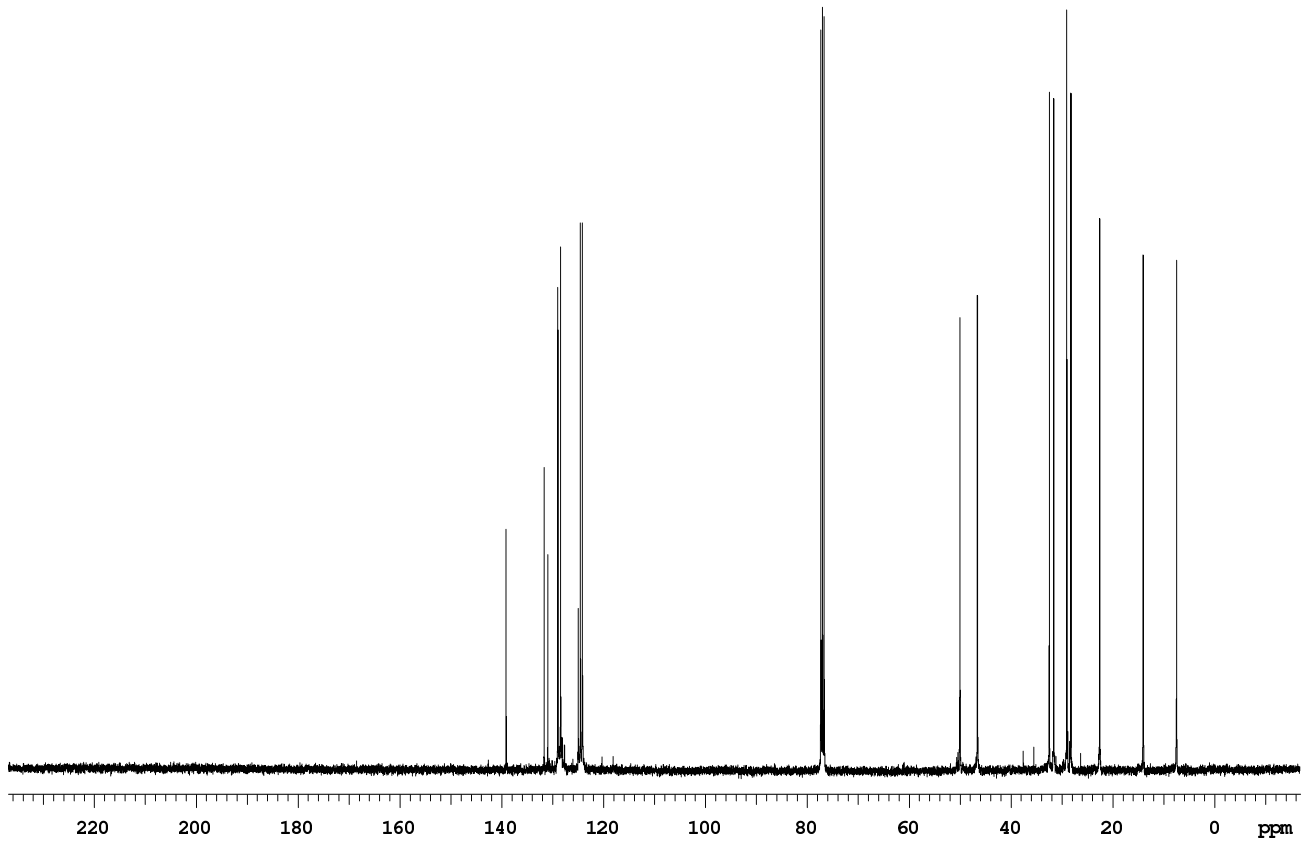
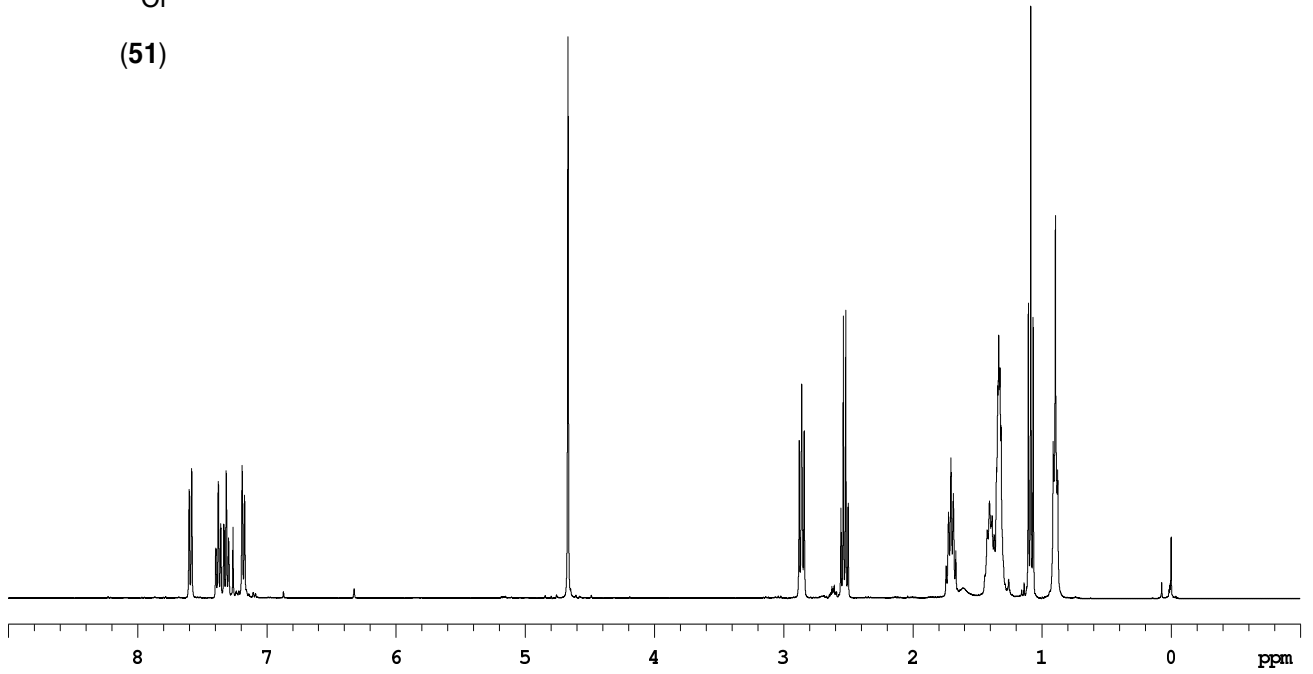


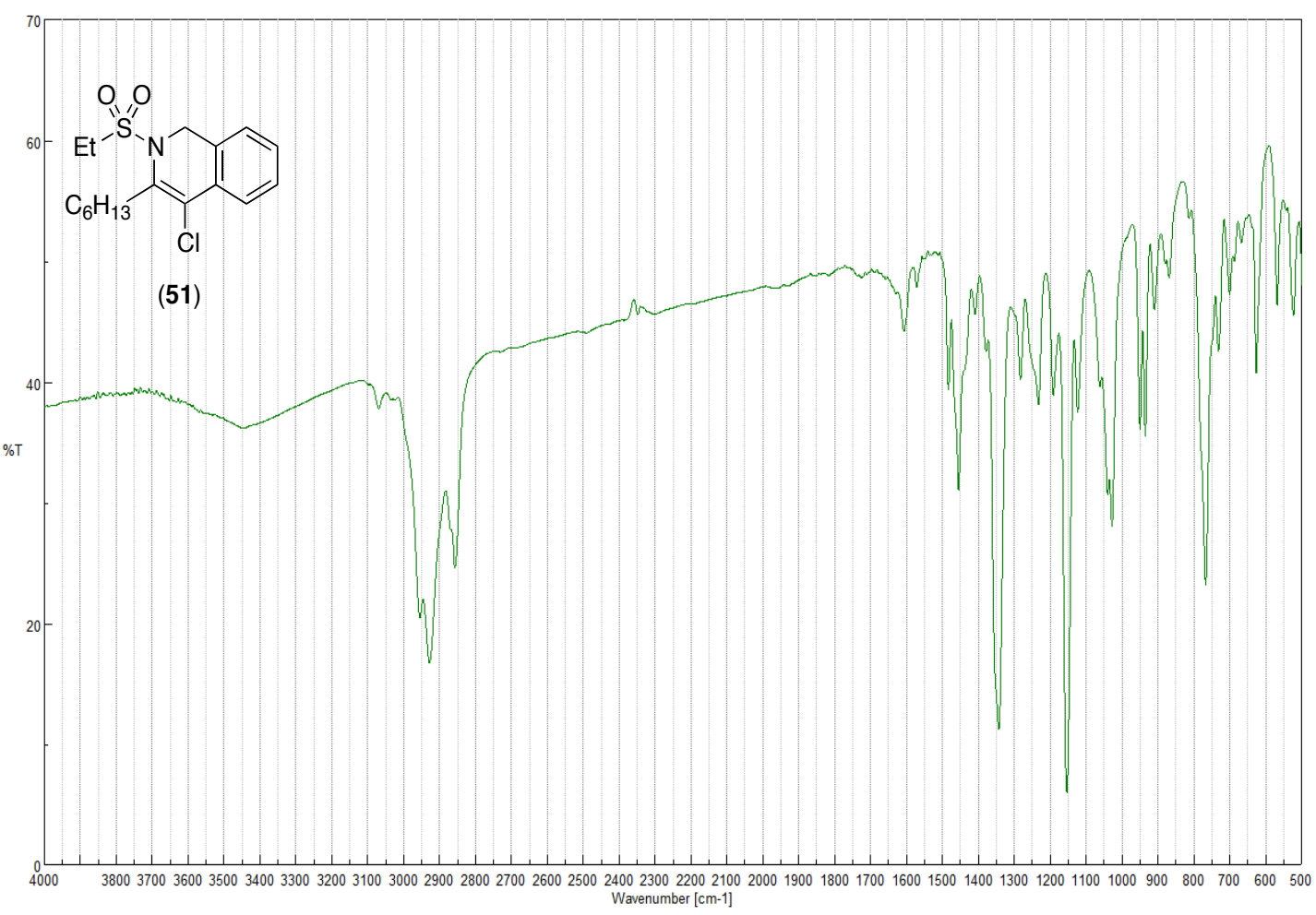
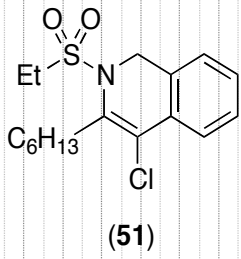


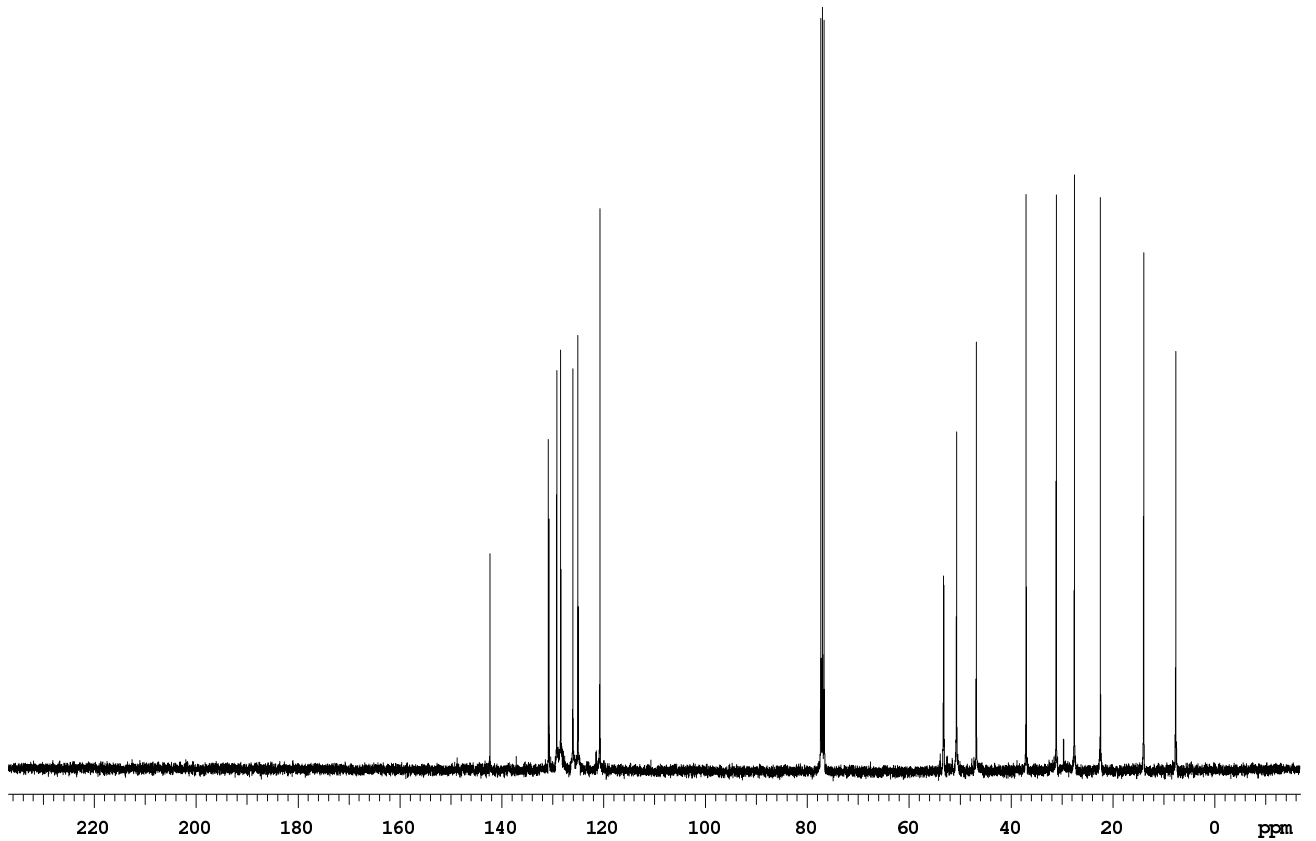
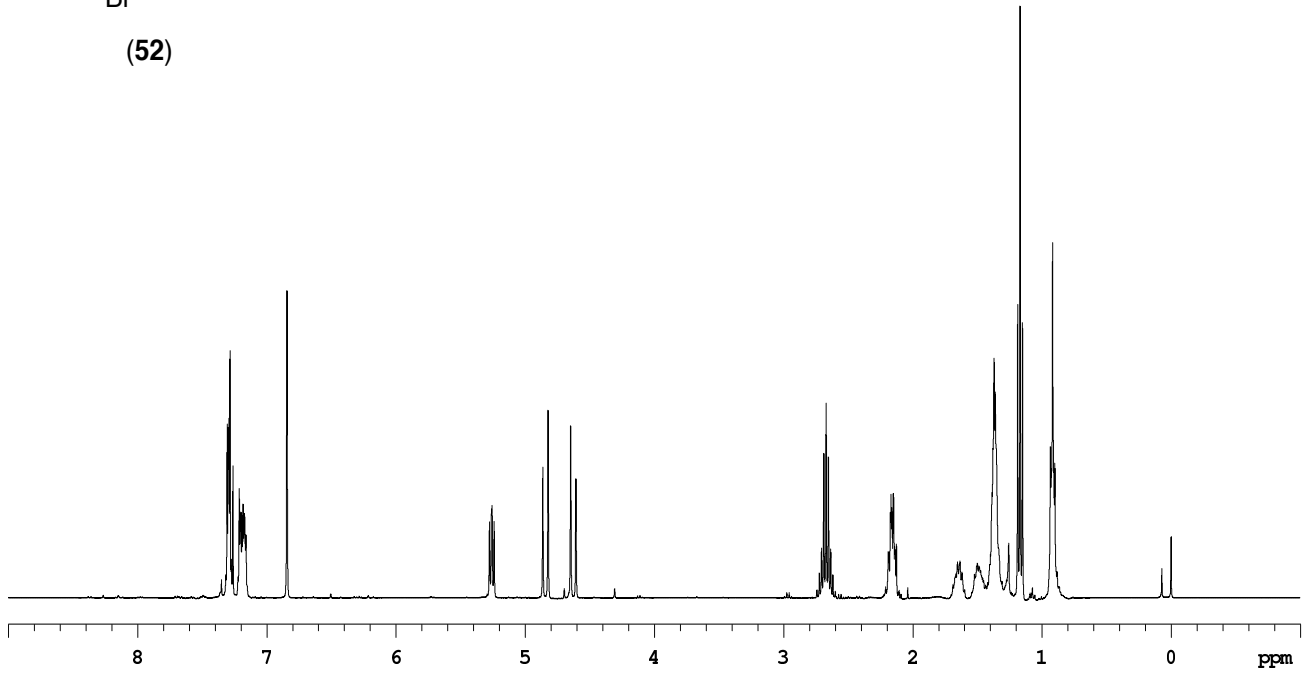
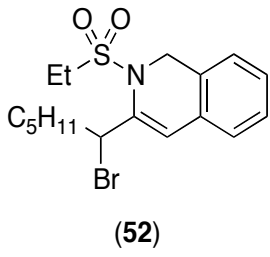


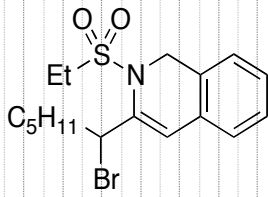


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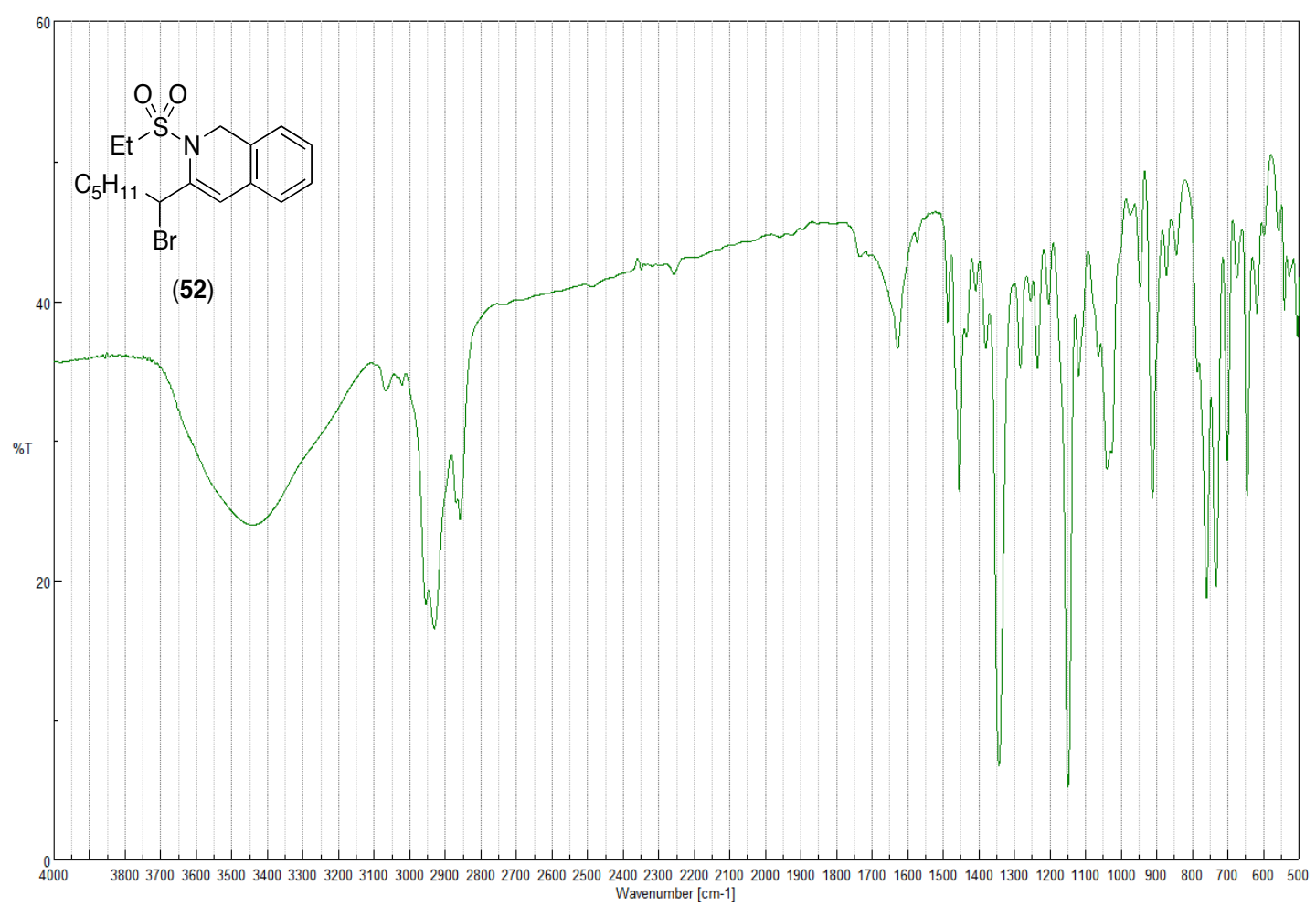


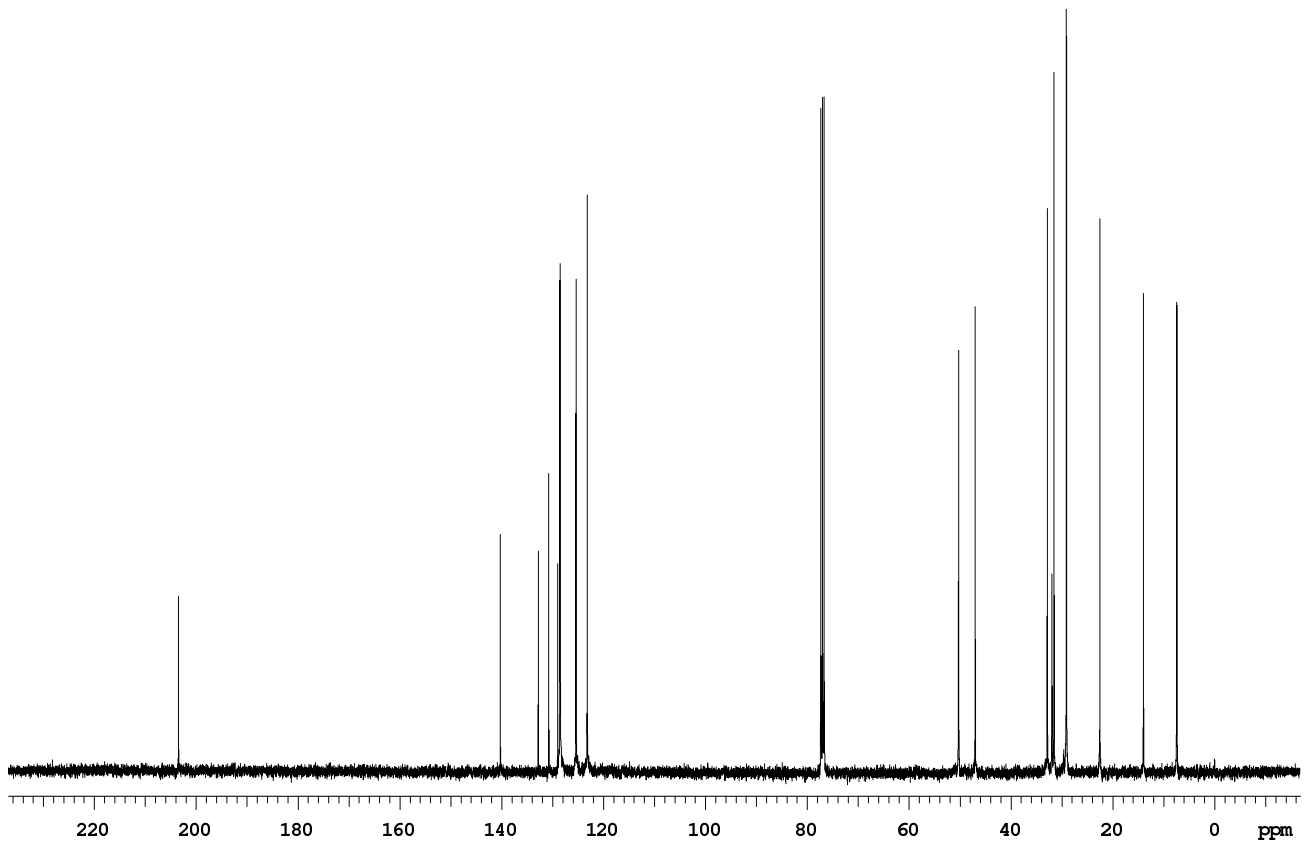
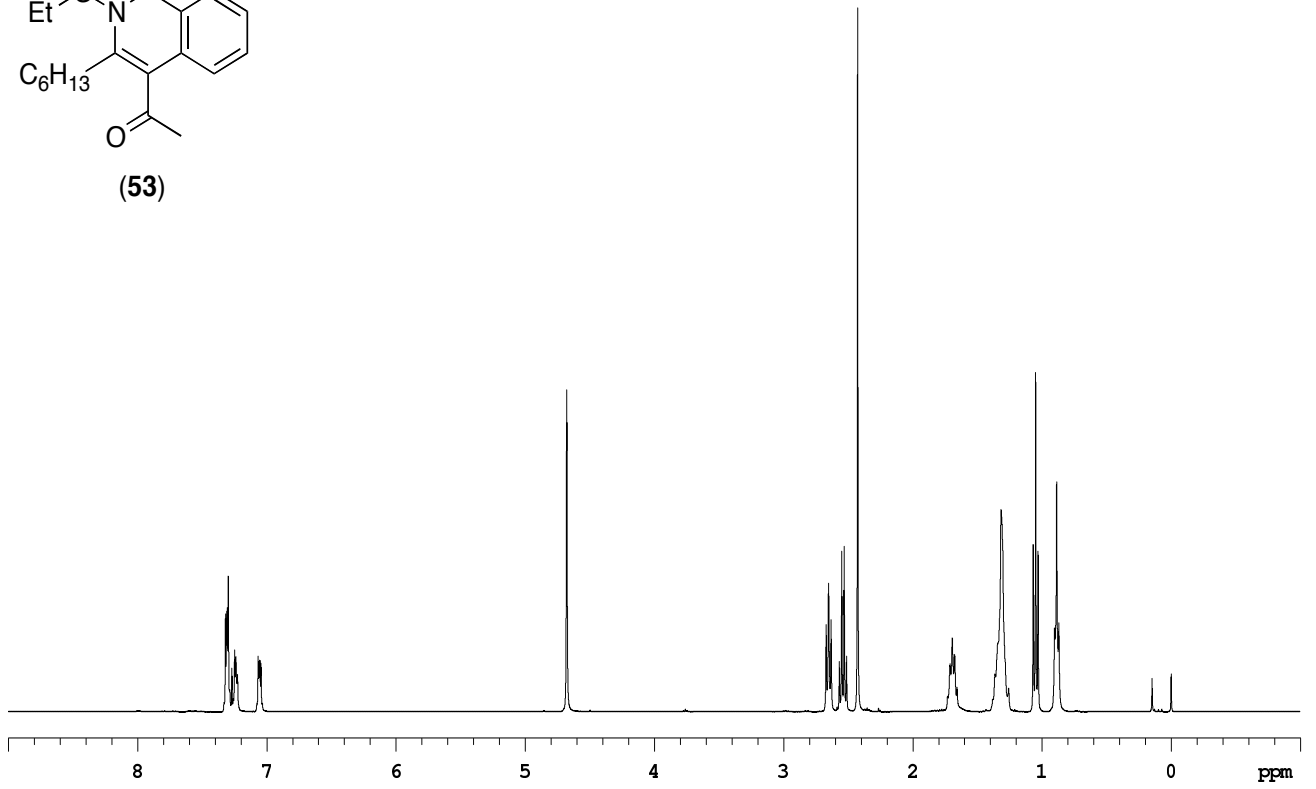
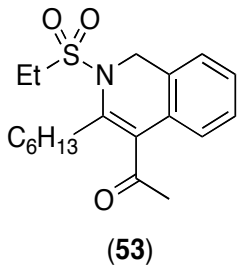


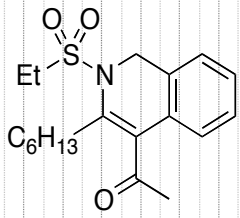




(52)







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