Supporting Information

Simple and Versatile Catalytic System for N-Alkylation of Sulfonamides with Various Alcohols

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Experimental Section:

General: All reactions and manipulations were carried out under an atmosphere of argon by means of standard Schlenk techniques. ^{1}H and ^{13}C NMR spectra were recorded on JEOL A-500 and EX-270 spectrometers. Gas chromatography (GC) analysis was performed on a GL-Sciences GC353B gas chromatograph with a capillary column (GL-Sciences TC-17). Column chromatography was carried out by using Wako-gel C-200. Elemental analyses were carried out at the Microanalysis Center of Kyoto University. Melting points were measured using a Yanagimoto micro melting point apparatus. Solvents were dried by standard procedures and distilled prior to use. N-Benzylidene-*p*-toluenesulfonamide (**13**)[1] and $[Cp^*IrCl_2]_2$[2] were prepared according to the literature method. All other reagents are commercially available and were used as received.

Procedure for the N-alkylation of *p*-toluenesulfonamide with benzyl alcohol shown in Table 1: To an oven-dried, argon purged 30 mL-two-necked round bottom flask were added *p*-toluenesulfonamide (2.0 mmol), benzyl alcohol (2.2 mmol), $[Cp^*IrCl_2]_2$ (0.0010 mmol, 0.050 mol%), base (0.020 mmol, 1.0 mol%), and toluene (1 mL). The mixture was heated under reflux in an oil bath for 17 h. Then, the mixture was allowed to cool to room temperature. Toluene was removed in vacuo and 1,3,5-trimethoxybenzene was added as an internal standard for NMR analysis. The yield of N-benzyl-*p*-toluenesulfonamide was calculated by the integration in ^{1}H-NMR analysis in chloroform-d.

Procedure for the N-alkylation of *p*-toluenesulfonamide with various primary alcohols shown in Table 2: To an oven-dried, Argon purged 30 mL-two-necked round bottom flask were added *p*-toluenesulfonamide

(2.0 mmol), primary alcohol (2.2 mmol), $[Cp^*IrCl_2]_2$ (0.0010-0.030 mmol, 0.050-1.5 mol%), *t*-BuOK (0.020-0.60 mmol, 1.0-30 mol%), and toluene (1 mL). The mixture was heated under reflux in an oil bath for 17 h. Then, the mixture was allowed to cool to room temperature. The products were isolated by column chromatography (eluenet = ethyl acetate/hexane).

N-benzyl-4-methybenzenesulfonamide (3a)[3] (Table 2, Entry 1):
^{1}H NMR (270 MHz, $CDCl_3$): δ 2.42 (s, 3H, CH_3), 4.10 (d, 2H, *J* = 6 Hz, CH_2), 4.94 (br, 1H, NH), 7.17-7.30 (m, 7H, Ar), 7.75 (d, 2H, *J* = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 47.2, 127.1, 127.79, 127.82, 128.6, 129.7, 136.3, 136.9, 143.4.

N-(4-methylbenzyl)-4-methybenzenesulfonamide (3b)[3] (Table 2, Entry 2):
^{1}H NMR (270 MHz, $CDCl_3$): δ 2.31 (s, 3H, $CH_2C_6H_4C\mathit{H_3}$), 2.44 (s, 3H, $SO_2C_6H_4C\mathit{H_3}$), 4.07 (d, 2H, *J* = 6 Hz, CH_2), 4.51 (br, 1H, NH), 7.08 (s, 4H, Ar), 7.32 (d, 2H, *J* = 8 Hz, Ar), 7.77 (d, 2H, *J* = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.0, 21.5, 47.0, 127.2. 127.8, 129.3, 129.7, 133.2, 137.0, 137.7, 143.4.

N-(4-methoxybenzyl)-4-methybenzenesulfonamide (3c)[4,5] (Table 2, Entry 3):
^{1}H NMR (270 MHz, $CDCl_3$): δ 2.43(s, 3H, CH_3), 3.77 (s, 3H, OCH_3), 4.04 (d, 2H, *J* = 6 Hz, CH_2), 4.65 (br, 1H, NH), 6.79 (d, 2H, *J* = 8 Hz, Ar), 7.10 (d, 2H, *J* = 8 Hz, Ar), 7.30 (d, 2H, *J* = 8 Hz, Ar), 7.75 (d, 2H, *J* = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 46.8, 55.3, 114.0, 127.2, 128.3, 129.2, 129.7, 136.9, 143.4, 159.3.

N-(4-phenylbenzyl)-4-methybenzenesulfonamide (3d)[6] (Table 2, Entry 4):
^{1}H NMR (270 MHz, $CDCl_3$): δ 2.44 (s, 3H, CH_3), 4.18 (d, 2H, *J* = 6 Hz, CH_2), 4.60 (t, 1H, *J* = 7 Hz, NH), 7.26-7.53 (m, 11H, Ar), 7.78 (d, 2H, *J* = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.4, 46.9, 127.0. 127.1, 127.3, 127.4, 128.3, 128.7, 129.7, 135.2, 136.9, 140.5, 140.7, 143.4.

N-(2-chlorobenzyl)-4-methybenzenesulfonamide (3e)[3] (Table 2, Entry 5):
^{1}H NMR (270 MHz, $CDCl_3$): δ 2.41 (s, 3H, CH_3), 4.25 (d, 2H, *J* = 6 Hz, CH_2), 4.84 (t, 1H, *J* = 6 Hz, NH), 7.16-7.32 (m, 6H, Ar), 7.72 (d, 2H, *J* = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.4, 44.9, 126.96, 127.02, 129.1, 129.4, 129.6, 130.1, 133.2, 134.0, 136.9, 143.4.

N-(3-chlorobenzyl)-4-methybenzenesulfonamide (3f)[7] (Table 2, Entry 6):
^{1}H NMR (270 MHz, $CDCl_3$): δ 2.42 (s, 3H, CH_3), 4.08 (d, 2H, *J* = 6 Hz, CH_2), 5.14 (br, 1H, NH), 7.08-7.29 (m, 6H, Ar), 7.72 (d, 2H, *J* = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 46.5, 125.9, 127.1, 127.9, 129.7, 129.8, 134.4, 134.4, 136.7, 138.4, 143.6.

N-(4-chlorobenzyl)-4-methybenzenesulfonamide (3g)[3] (Table 2, Entry 7):
^{1}H NMR (270 MHz, $CDCl_3$): δ 2.44 (s, 3H, CH_3), 4.10 (d, 2H, *J* = 6 Hz, CH_2), 4.62 (t, 1H, *J* = 6 Hz, NH), 7.14 (d, 2H, *J* = 8 Hz, Ar), 7.23-7.33 (m, 4H, Ar), 7.74 (d, 2H, *J* = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 46.5, 127.1, 128.7, 129.2, 129.7, 133.6, 134.9, 136.8, 143.6.

N-(2-bromobenzyl)-4-methybenzenesulfonamide (3h)[4,8] (Table 2, Entry 8):
^{1}H NMR (270 MHz, $CDCl_3$): δ 2.40 (s, 3H, CH_3), 4.22 (d, 2H, *J* = 6 Hz, CH_2), 5.04 (br, 1H, NH), 7.11 (d, 1H, *J* = 8 Hz, Ar), 7.18-7. 32 (m, 4H, Ar), 7.45 (d, 1H, *J* = 8 Hz, Ar), 7.71 (d, 1H, *J* = 8 Hz, Ar). ^{13}C NMR (67.8

MHz, $CDCl_3$): δ 21.4, 47.3, 123.3, 127.0, 127.6, 129.4, 129.5, 130.3, 132.6, 135.5, 136.9, 143.4.

N-(3-bromobenzyl)-4-methybenzenesulfonamide (3i) (Table 2, Entry 9):
^{1}H NMR (270 MHz, $CDCl_3$): δ 2.44 (s, 3H, CH_3), 4.11 (d, 2H, J = 6 Hz, CH_2), 4.66 (br, 1H, NH), 7.15 (d, 2H, J = 6 Hz, Ar), 7.26-7.37 (m, 4H, Ar), 7.74 (d, 2H, J = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 46.5 122.6, 126.4, 127.1, 129.8, 130.1, 130.79, 130.84, 136.8, 138.7, 143.7. White powder, mp: 84.4-84.8 °C. Anal. Calcd for $C_{14}H_{14}BrNO_2S$: C, 49.42; H, 4.15; N, 4.12. Found: C, 49.28; H, 3.96; N, 4.09.

N-(4-bromobenzyl)-4-methybenzenesulfonamide (3j)[9] (Table 2, Entry 10):
^{1}H NMR (270 MHz, $CDCl_3$): δ 2.44 (s, 3H, CH_3), 4.09 (d, 2H, J = 6 Hz, CH_2), 4.65 (t, 1H, J = 6 Hz, NH), 7.08 (d, 2H, J = 8 Hz, Ar), 7.31 (d, 2H, J = 8 Hz, Ar), 7.40 (d, 2H, J = 8 Hz, Ar), 7.74 (d, 2H, J = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 46.5, 121.7, 127.1, 129.5, 127.7, 131.6, 135.4, 136.8, 143.6.

N-(4-trifluoromethylbenzyl)-4-methybenzenesulfonamide (3k)[3] (Table 2, Entry 11):
^{1}H NMR (500 MHz, $CDCl_3$): δ 2.40 (s, 3H, CH_3), 4.16 (d, 2H, J = 6 Hz, CH_2), 5.55 (br, 1H, NH), 7.23 (d, 2H, J = 8 Hz, Ar), 7.30 (d, 2H, J = 8 Hz, Ar), 7.46 (d, 2H, J = 8 Hz, Ar), 7.68 (d, 2H, J = 8 Hz, Ar). ^{13}C NMR (125.6 MHz, $CDCl_3$): δ 21.4, 46.6, 124.0 (q, $J_{C\text{-}F}$ = 271 Hz), 125.5(q, $J_{C\text{-}F}$ = 3 Hz), 127.1, 128.1, 129.5, 129.9 (q, $J_{C\text{-}F}$ = 33 Hz), 136.8, 140.6, 143.8.

N-(4-methoxycarbonylbenzyl)-4-methybenzenesulfonamide (3l)[10] (Table 2, Entry 12):
^{1}H NMR (270 MHz, $CDCl_3$): δ 2.43 (s, 3H, CH_3), 3.90 (s, 3H, $COOCH_3$), 4.18 (d, 2H, J = 6 Hz, CH_2), 4.98 (br, 1H, NH), 7.26-7.31 (m, 4H, Ar), 7.74 (d, 2H, J = 8 Hz, Ar), 7.93 (d, 2H, J = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 46.8, 52.1, 127.1. 127.6, 129.6, 129.7, 129.9, 136.8, 141.6, 143.7, 166.7.

N-(naphthalen-2-ylmethyl)-4-methylbenzenesulfonamide (3m)[3] (Table 2, Entry 13):
^{1}H NMR (270 MHz, $CDCl_3$): δ 2.41 (s, 3H, CH_3), 4.29 (d, 2H, J = 5 Hz, CH_2), 4.75 (br, 1H, NH), 7.29-7.31 (m, 4H, Ar), 7.45-7.48 (m, 2H, Ar), 7.60 (s, 1H, Ar), 7.71-7.81 (m, 4H, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.4, 47.3, 125.6, 126.0, 126.2, 126.6, 127.1, 127.6, 127.7, 128.4, 129.6, 132.8, 133.1, 133.7, 136.9, 142.4.

N-(pyridin-4-ylmethyl) -4-methylbenzenesulfonamide (3n) (Table 2, Entry 14):
^{1}H NMR (270 MHz, $CDCl_3$): δ 2.44 (s, 3H, CH_3), 4.17 (d, 2H, J = 6 Hz, CH_2), 5.02 (t, 1H, J = 6 Hz, NH), 7.16 (d, 2H, J = 6 Hz, Ar), 7.32 (d, 2H, J = 8 Hz, Ar), 7.75 (d, 2H, J = 8 Hz, Ar), 8.51 (d, 2H, J = 6 Hz, Ar). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 21.5, 45.9, 122.3, 127.1, 129.8, 136.8, 143.9, 145.7, 150.0. Yellow powder, mp 164.4-164.8 °C. Anal. Calcd for $C_{13}H_{14}N_2O_2S$: C, 59.52; H, 5.38; N, 10.68. Found: C, 59.56; H, 5.35; N, 10.39.

N-hexyl-4-methylbenzenesulfonamide (3o)[11] (Table 2, Entry 15):
^{1}H NMR (270 MHz, $CDCl_3$): δ 0.84 (t, 3H, J = 7 Hz, $CH_2(CH_2)_4CH_3$), 1.20-1.47 (m, 8H, $CH_2(CH_2)_4CH_3$), 2.43 (s, 3H, $C_6H_4CH_3$), 2.92 (q, 2H, J = 7 Hz, $NHCH_2$), 4.71 (br, 1H, NH), 7.31 (d, 2H, J = 8 Hz, Ar), 7.76 (d, 2H, J = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 13.9, 21.5, 22.4, 26.1, 29.5, 31.2, 43.2, 127.1, 129.6, 137.0, 143.2.

N-octyl-4-methylbenzenesulfonamide (3p)[12] (Table 2, Entry 16):
^{1}H NMR (270 MHz, $CDCl_3$): δ 0.87 (t, 3H, J = 7 Hz, $CH_2(CH_2)_6CH_3$), 1.21-1.47 (m, 12H, $CH_2(CH_2)_6CH_3$),

2.43 (s, 3H, $C_6H_4CH_3$), 2.93 (q, 2H, J = 7 Hz, $CH_2(CH_2)_6CH_3$), 4.41 (br, 1H, NH), 7.31 (d, 2H, J = 8 Hz, Ar), 7.76 (d, 2H, J = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 14.0, 21.5, 22.6, 26.5, 28.96, 29.03, 29.5, 31.7, 43.2, 127.1, 129.6, 137.0, 143.2.

N-(4-methypentyl)-4-methylbenzenesulfonamide (3q) (Table 2, Entry 17):
^{1}H NMR (270 MHz, $CDCl_3$): δ 0.82 (d, 6H, J = 7 Hz, $(CH_3)_2CH$), 1.09-1.16 (m, 2H, $NHCH_2CH_2CH_2CH(CH_3)_2$), 1.41-1.46 (m, 3H, $NHCH_2CH_2CH_2CH(CH_3)_2$), 2.43 (s, 3H, $C_6H_4CH_3$), 2.92 (q, 2H, J = 7 Hz, $NHCH_2$), 4.52 (br, 1H, NH), 7.31 (d, 2H, J = 8 Hz, Ar), 7.76 (d, 2H, J = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.4, 22.3, 27.4, 27.5, 35.6, 43.4, 127.0, 129.6, 137.0, 143.2. Yellow liquid. Anal. Calcd for $C_{13}H_{21}NO_2S$: C, 61.14; H, 8.29; N, 5.48. Found: C, 61.08; H, 8.22; N, 5.34.

N-(3,3-dimethylbutyl)-4-methylbenzenesulfonamide (3r) (Table 2, Entry 18):
^{1}H NMR (270 MHz, $CDCl_3$): δ 0.85 (s, 9H, $C(CH_3)_3$), 1.33-1.39 (t, 2H, J = 8 Hz, $NHCH_2CH_2$), 2.44 (s, 3H, $C_6H_4CH_3$), 2.96 (q, 2H, J = 8 Hz, $NHCH_2$), 4.14 (br, 1H, NH), 7.33 (d, 2H, J = 8 Hz, Ar), 7.76 (d, 2H, J = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.4, 29.2, 29.6, 39.8, 43.1, 127.0, 129.5, 136.9, 143.1. White powder, mp 75.0-75.8 °C. Anal. Calcd for $C_{13}H_{21}NO_2S$: C, 61.14; H, 8.29; N, 5.48. Found: C, 61.03; H, 8.23; N, 5.38.

N-(2-methylbutyl)-4-methylbenzenesulfonamide (3s)[13] (Table 2, Entry 19):
^{1}H NMR (270 MHz, $CDCl_3$): δ 0.79-0.86 (m, 6H, $CH_3CH_2CHCH_3CH_2NH$), 1.02-1.18 (m, 1H, $CH_3CH_2CHCH_3CH_2NH$), 1.27-1.75 (m, 2H, $CH_3CH_2CHCH_3CH_2NH$), 2.42 (s, 3H, $C_6H_4CH_3$), 2.67-2.88 (m, 2H, $CH_3CH_2CHCH_3CH_2NH$), 4.85 (br, 1H, NH), 7.30 (d, 2H, J = 8 Hz, Ar), 7.76 (d, 2H, J = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 11.0, 16.9, 21.4, 26.6, 34.6, 48.7, 127.0, 129.6, 137.0, 143.2.

N-(cyclohexylmethyl)-4-methylbenzenesulfonamide (3t)[14] (Table 2, Entry 20):
^{1}H NMR (270 MHz, $CDCl_3$): δ 0.82-1.69 (m, 11H, $(CH_2)_5$), 2.43 (s, 3H, $C_6H_4CH_3$), 2.77 (t, 2H, J = 7 Hz, CH_2), 4.34 (t, 1H, J = 7 Hz, NH), 7.31 (d, 2H, J = 8 Hz, Ar), 7.74 (d, 2H, J = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 25.6, 26.2, 30.5, 37.7, 49.3, 127.0, 129.6, 137.1, 143.2.

N-(3-phenylpropyl)-4-methylbenzenesulfonamide (3u) (Table 2, Entry 21):
^{1}H NMR (500 MHz, $CDCl_3$): δ 1.65-1.80 (m, 2H, $NHCH_2CH_2CH_2Ph$), 2.42 (s, 3H, $C_6H_4CH_3$), 2.59 (t, 2H, J = 7 Hz, $NHCH_2CH_2CH_2Ph$), 2.95 (q, 2H, J = 7 Hz, $NHCH_2CH_2CH_2Ph$), 4.73 (t, 1H, J = 7 Hz, NH), 7.07 (d, 2H, J = 7 Hz, Ar), 7.17 (t, 1H, J = 7 Hz, Ar), 7.24 (t, 2H, J = 7 Hz, Ar), 7.29 (d, 2H, J = 8 Hz, Ar), 7.74 (d, 2H, J = 8 Hz, Ar). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 21.4, 31.0, 32.6, 42.5, 125.9, 127.0, 128.3, 128.3, 129.6, 136. 9, 140.9, 143.2. Yellow liquid. Anal. Calcd for $C_{16}H_{19}NO_2S$: C, 66.41; H, 6.62; N, 4.84. Found: C, 66.44; H, 6.32; N,4.73.

Procedure for the N-alkylation of *p*-toluenesulfonamide with various secondary alcohols shown in Table 3: To an oven-dried, argon purged 30 mL-two-necked round bottom flask were added *p*-toluenesulfonamide (1.0 mmol), secondary alcohol (1.5 mmol), $[Cp^*IrCl_2]_2$ (0.0050 mmol, 0.50 mol%), *t*-BuOK (10 mol%) and *p*-xylene (1 mL). The mixture was heated under reflux in an oil bath for 17 h. Then, the mixture was allowed to cool to room temperature. The products were isolated by column chromatography (eluenet = ethyl acetate/hexane).

N-cyclopentyl-4-methylbenzenesulfonamide (5a)[15] (Table 3, Entry 1):
^{1}H NMR (270 MHz, $CDCl_3$): δ 1.33-1.85 (m, 8H, $(CH_2)_4$), 2.43 (s, 3H, CH_3), 3.50-3.63 (m, 1H, CH), 5.09 (d, 1H, *J* = 7 Hz, NH), 7.30 (d, 2H, *J* = 8 Hz, Ar), 7.79 (d, 2H, *J* = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ (ppm) 21.4, 23.0, 33.3, 55.1, 127.0, 129.5, 137.8, 143.1.

N-cyclohexyl-4-methylbenzenesulfonamide (5b)[15] (Table 3, Entry 2):
^{1}H NMR (270 MHz, $CDCl_3$): δ 1.13-1.78 (m, 10H, $(CH_2)_5$), 2.42 (s, 3H, CH_3), 3.11 (br, 1H, CH), 4.60 (br, 1H, NH), 7.29 (d, 2H, *J* = 8 Hz, Ar), 7.78 (d, 2H, *J* = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.4, 24.6, 25.1, 33.8, 52.5, 126.9, 129.5, 138.5, 143.0.

N-cycloheptyl-4-methylbenzenesulfonamide (5c)[16] (Table 3, Entry 3):
^{1}H NMR (270 MHz, $CDCl_3$): δ 1.29-1.82 (m, 12H, $(CH_2)_6$), 2.44 (s, 3H, CH_3), 3.27-3.40 (m, 1H, CH), 4.80 (d, 1H, *J* = 8 Hz, NH), 7.31 (d, 2H, *J* = 8 Hz, Ar), 7.79 (d, 2H, *J* = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.5, 23.5, 27.9, 35.8, 54.7, 127.0, 129.6, 138.2, 143.0.

N-(1-phenylethyl)-4-methylbenzenesulfonamide (5d)[17,18] (Table 3, Entry 4):
^{1}H NMR (270 MHz, $CDCl_3$): δ 1.38 (d, *J* = 7 Hz, 3H, $CHCH_3$), 2.34 (s, 3H, $C_6H_4CH_3$), 4.39-4.50 (m, 1H, $CHCH_3$), 5.73 (d, 1H, *J* = 7 Hz, NH), 7.13 (m, 7H, Ar), 7.63 (d, 2H, *J* = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.3, 23.4, 53.5, 126.0, 126.9, 127.1, 128.3, 129.2, 137.6, 142.1, 142.8.

Procedure for the N-Alkylation of various sulfonamides with benzylalcohol Shown in Table 4: To an oven-dried, argon purged 30 mL-two-necked round bottom flask were added sulfonamide (2.0 mmol), benzyl alcohol (2.2 mmol), $[Cp^*IrCl_2]_2$ (0.0010-0.020 mmol, 0.050-1.0 mol%), *t*-BuOK (0.020-0.40 mmol, 1.0-20 mol%), and toluene (1 mL). The mixture was heated to reflux in an oil bath for 17 h. Then, the mixture was allowed to cool to room temperature. The products were isolated by column chromatography (eluenet = ethyl acetate/hexane).

N-benzyl-benzenesulfonamide (7)[7] (Table 4, Entry 1):
^{1}H NMR (270 MHz, $CDCl_3$): δ 4.16 (d, 2H, *J* = 6 Hz, CH_2), 4.68 (br, 1H, NH), 7.20-7.26 (m, 5H, Ar), 7.51-7.59 (m, 3H, Ar), 7.88 (d, 2H, *J* = 7 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 47.2, 127.1, 127.8, 127.9, 128.7, 129.1, 132.6, 136.2, 139.9.

N-benzyl-4-methoxybenzenesulfonamide (8)[14] (Table 4, Entry 2):
^{1}H NMR (270 MHz, $CDCl_3$): δ 3.89 (s, 3H, OCH_3), 4.13 (d, 2H, *J* = 6 Hz, CH_2), 4.55 (br, 1H, NH), 6.98 (d, 2H, *J* = 9 Hz, Ar), 7.21-7.26 (m, 5H, Ar), 7.82 (d, 2H, *J* = 9 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 47.1, 55.5, 114.2, 127.7, 127.8, 128.5, 129.2, 131.4, 136.3, 162.8.

N-benzyl-4-chlorobenzenesulfonamide (9)[14] (Table 4, Entry 3):
^{1}H NMR (270 MHz, $CDCl_3$): δ 4.16 (d, 2H, *J* = 6 Hz, CH_2), 4.69 (br, 1H, NH), 7.18-7.30 (m, 5H, Ar), 7.48 (d, 2H, *J* = 8 Hz, Ar), 7.80 (d, 2H, *J* = 7 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 47.2, 127.8, 128.0, 128.5, 128.7, 129.3, 135.9, 138.5, 139.1.

N-benzyl-4-nitrobenzenesulfonamide (10)[14] (Table 4, Entry 4):
^{1}H NMR (270 MHz, $CDCl_3$): δ 4.24 (d, 2H, *J* = 6 Hz, CH_2), 4.91 (br, 1H, NH), 7.17-7.26 (m, 5H, Ar), 8.00 (d, 2H, *J* = 8 Hz, Ar), 8.31 (d, 2H, *J* = 8 Hz, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 47.3, 124.3, 127.9, 128.2, 128.3, 128.8, 135.5, 146.0, 149.9.

N-benzylmethanesulfonamide (11)[7] (Table 4, Entry 5):
^{1}H NMR (270 MHz, $CDCl_3$): δ (ppm) 2.87 (s, 3H, CH_3), 4.32 (s, 2H, CH_2), 4.70 (br, 1H, NH), 7.34-7.37 (m, 5H, Ar). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 40.9, 47.0, 127.8, 127.9, 128.8, 136.9.

Procedure for the preparation of the sulfonylimido-bridged unsaturated dinuclear iridium complex 12[19] shown in eq 1: To an oven-dried, argon purged 50 mL-two-necked round bottom flask were added $[Cp^*IrCl_2]_2$ (383.3 mg, 0.50 mmol), *p*-toluenesulfonamide (171.4 mg, 1.0 mmol), *t*-BuOK (112.3 mg, 1.0 mmol), and toluene (1 mL). Then, the mixture was stirred at room temperature for 1 h. Toluene was removed in vacuo and the residue was extracted with dichloromethane (10 mL) and filtered through a pad of Celite. The dinuclear iridium complex **12** was obtained in 74% yield after evaporation of the solvent followed by washing with Et_2O (10 mL). ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.66 (s, 30H, Cp*), 2.39 (s, 6H, CH_3), 7.16 (d, 4H, *J* = 8 Hz, Ar), 7.77 (d, 4H, *J* = 8 Hz, Ar). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 10.1, 21.4, 89.3, 126.9, 128.4, 140.4, 143.1.

Procedure for the the N-Alkylation of *p*-toluenesulfonamide with benzyl alcohol catalyzed by 12 shown in eq 2: To an oven-dried, argon purged 30 mL-two-necked round bottom flask were added *p*-toluenesulfonamide (341.2 mg, 2.0 mmol), benzyl alcohol (241.1 mg, 2.2 mmol), **12** (0.0010 mmol, 0.050 mol%), *t*-BuOK (0.020 mmol, 1.0 mol%), and toluene (1 mL). The mixture was heated under reflux in an oil bath for 17 h. Then, the mixture was allowed to cool to room temperature. Toluene was removed in vacuo and 1,3,5-trimethoxybenzene was added as an internal standard for NMR analysis. The yield of N-benzyl-*p*-toluenesulfonamide was calculated by the integration in ^{1}H-NMR analysis in Chloroform-d.

Procedure for the substoichiometric reaction of *p*-toluenesulfonamide with benzyl alcohol and NMR monitoring shown in eq 3: In an oven-dried, argon purged NMR tube, *p*-toluenesulfonamide (34.6 mg, 0.20 mmol), benzyl alcohol (22.5 mg, 0.21 mmol), $[Cp^*IrCl_2]_2$ (0.020 mmol, 10 mol%), *t*-BuOK (0.08 mmol, 40 mol%), and toluene-d_8 (0.8 mL) were placed. The mixture was heated at 100 °C in the NMR probe for 12 h. The reaction was monitored by ^{1}H NMR. The results are shown in Figure S1.

Procedure for the reaction of 13 with 2a shown in eq 4.: To an oven-dried, argon purged 30 mL-two-necked round bottom flask were added **13** (518.4 mg, 2.0 mmol), benzyl alcohol (241.1 mg, 2.2 mmol), **12** (0.0010 mmol, 0.050 mol%), *t*-BuOK (0.020 mmol, 1.0 mol%), and toluene (1 mL). The mixture was heated under reflux in an oil bath for 17 h. Then, the mixture was allowed to cool to room temperature. Toluene was removed in vacuo and 1,3,5-trimethoxybenzene was added as an internal standard for GC and NMR analysis. The yield of N-benzyl-*p*-toluenesulfonamide was calculated by the integration in ^{1}H-NMR analysis in Chloroform-d. The yield of benzaldehyde was determined by GC analysis.

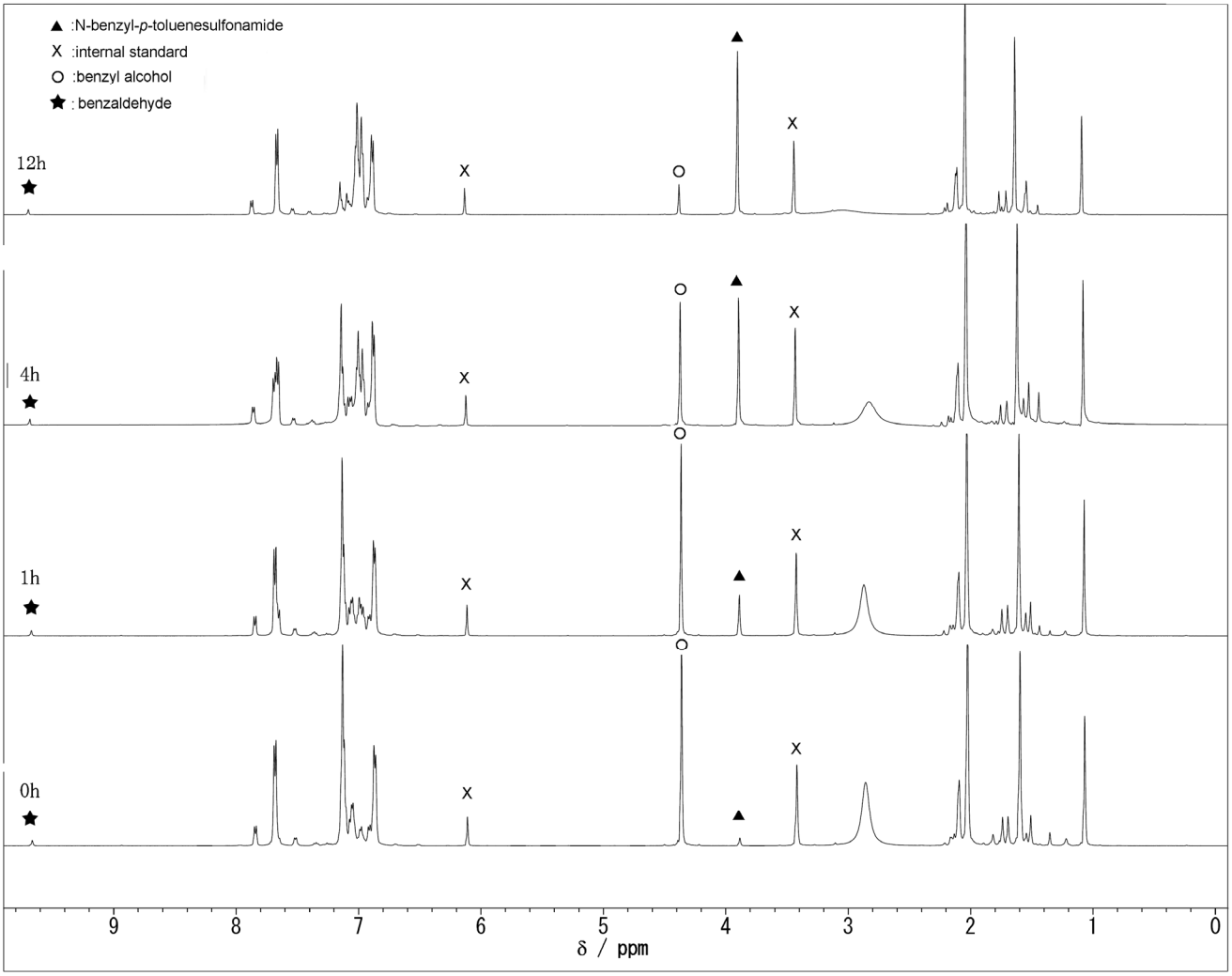

Figure S1. Result of the ^{1}H NMR Monitoring of the Reaction of *p*-Toluenesulfonamide with Benzyl Alcohol Shown in eq 3

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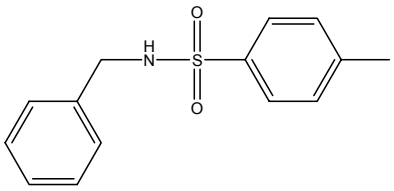
Table 2, Entry 1
^{1}H NMR



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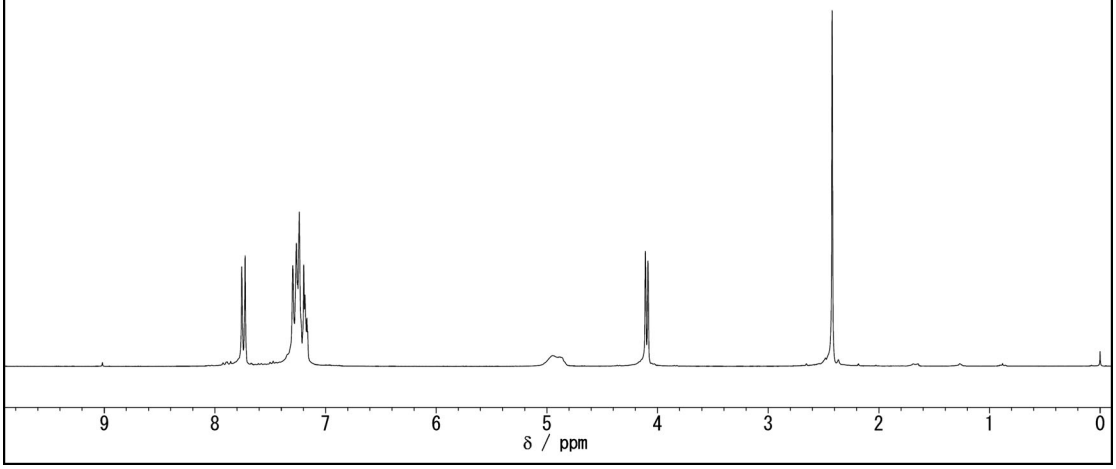

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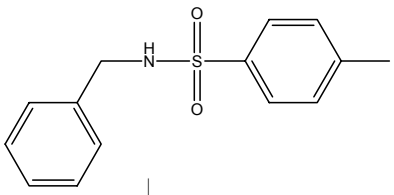

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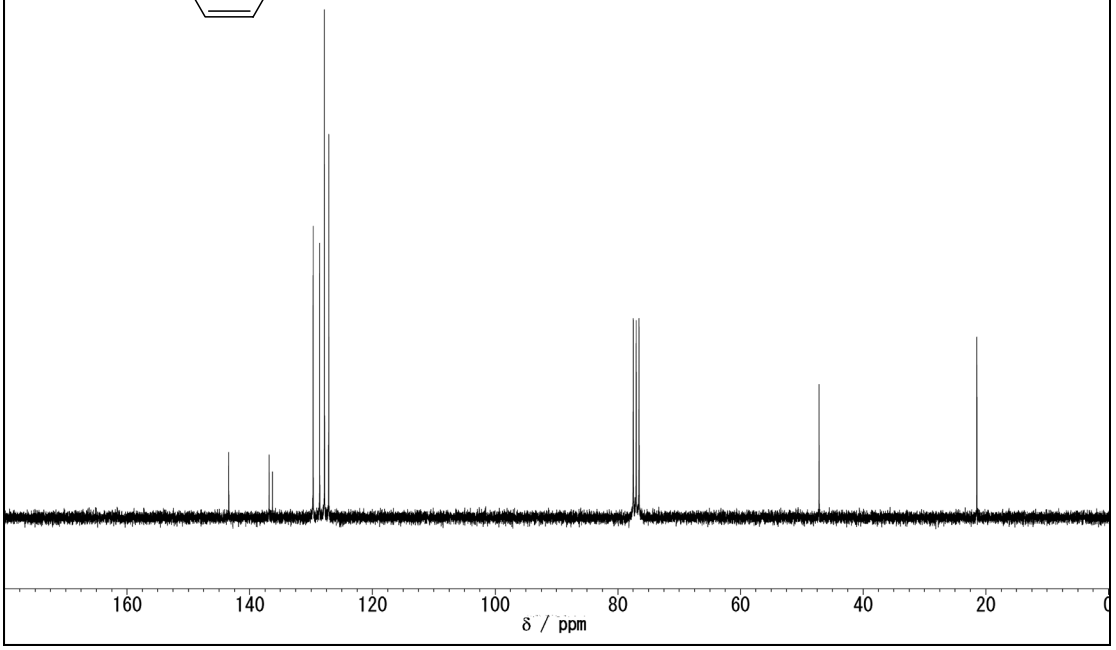

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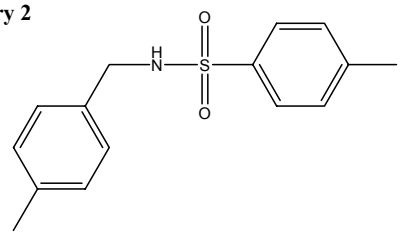

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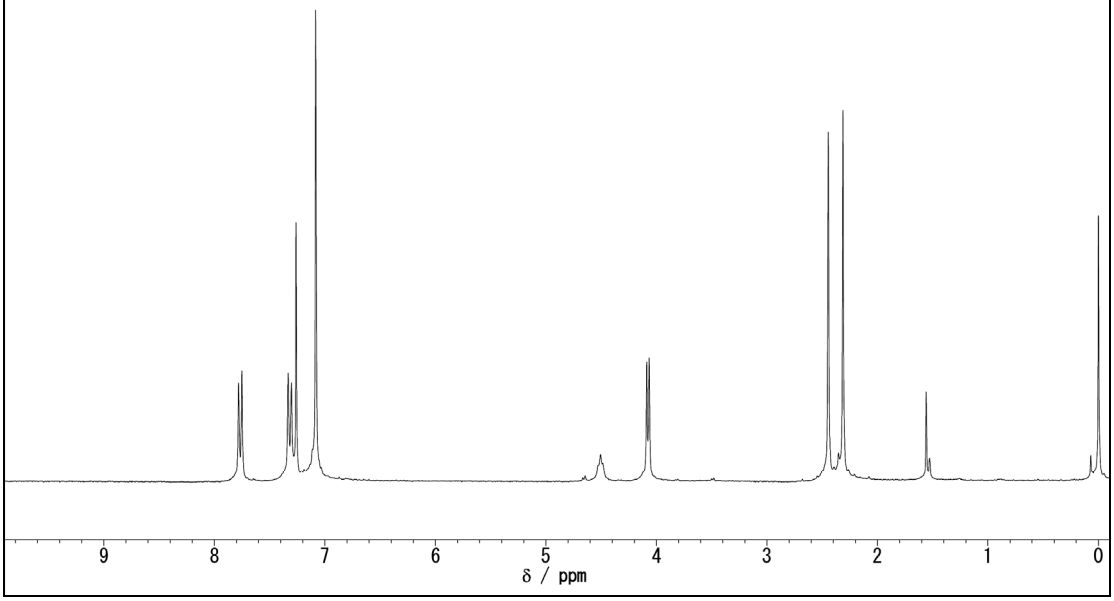

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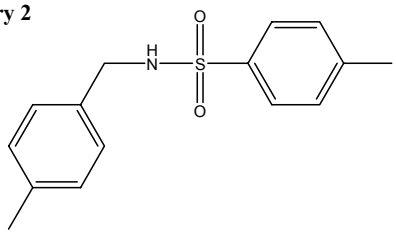

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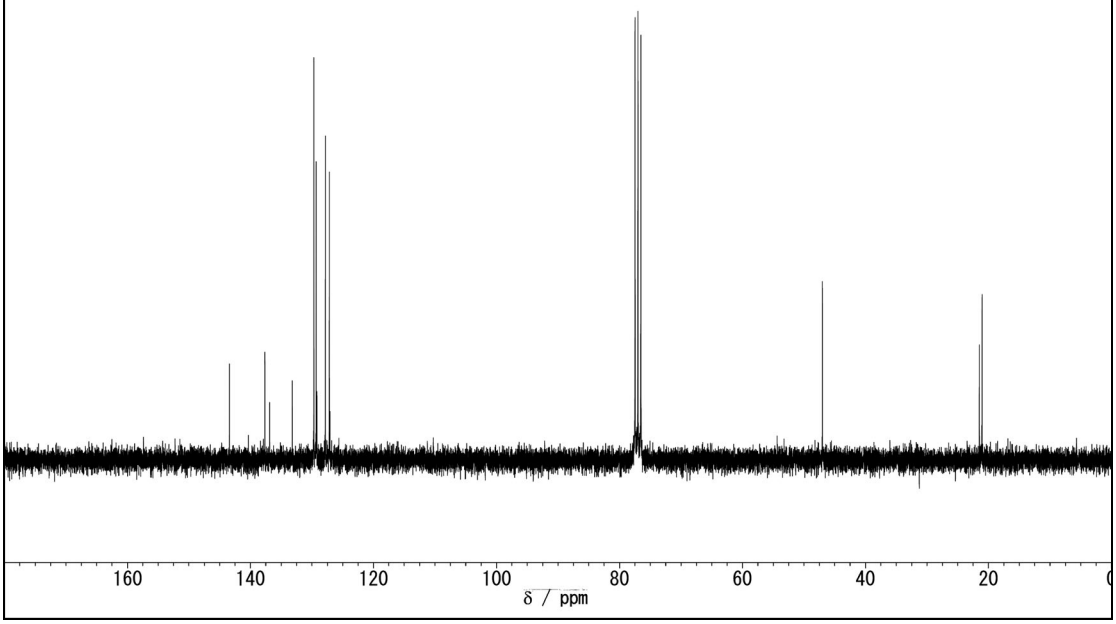

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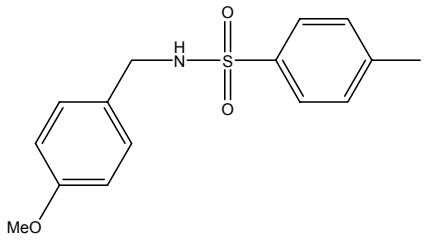

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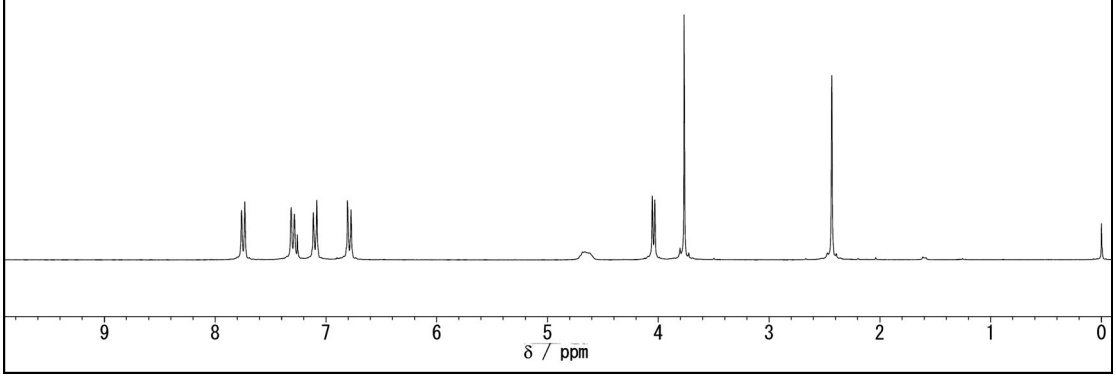

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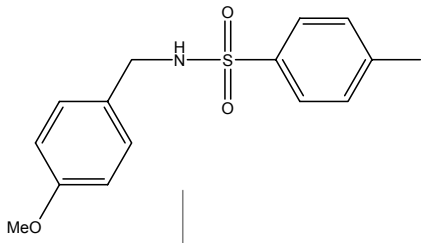

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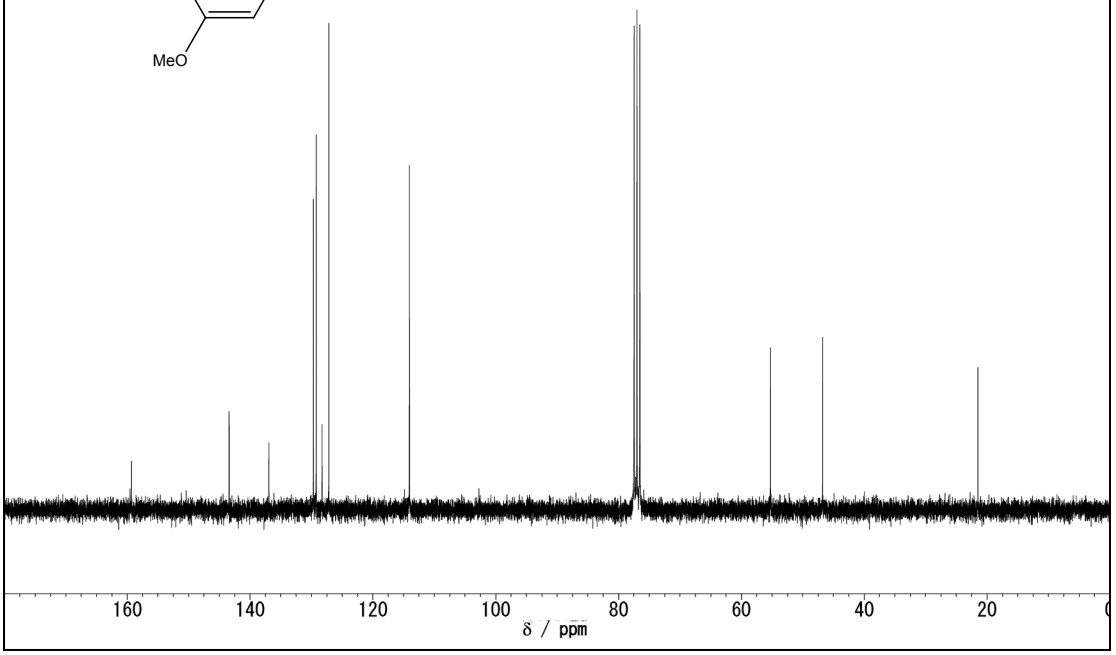

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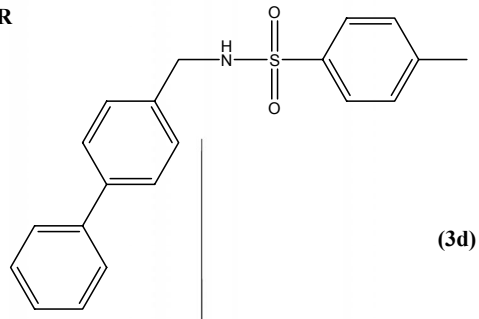

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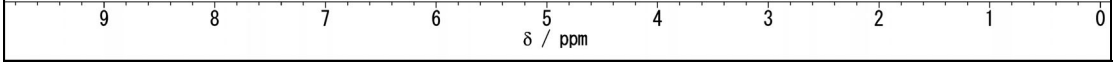

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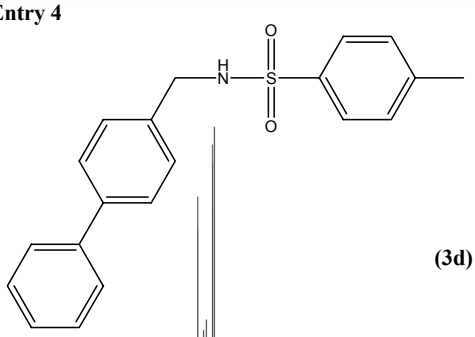

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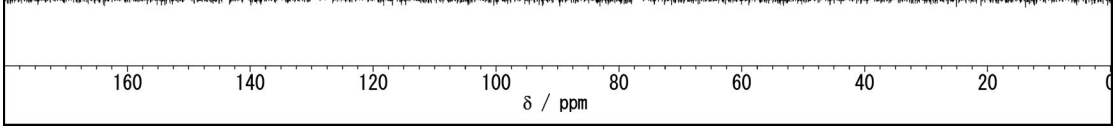

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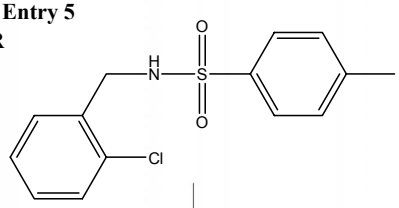

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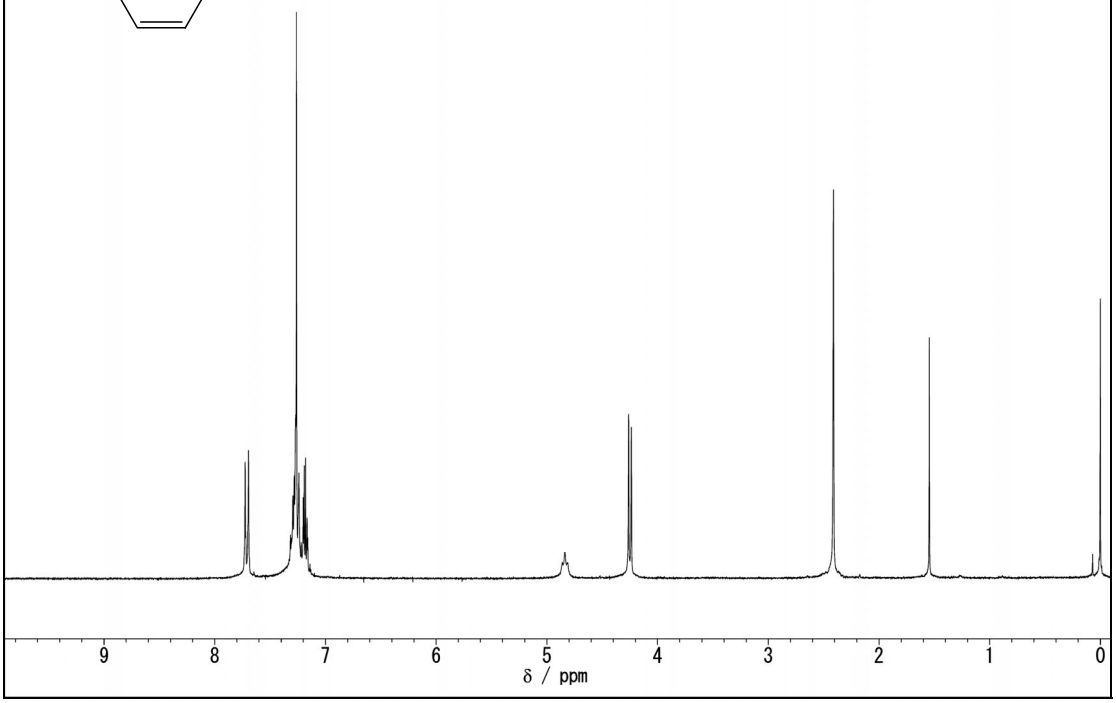

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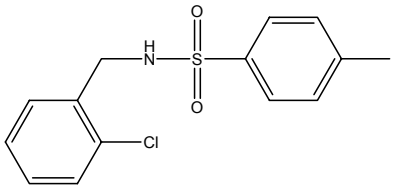

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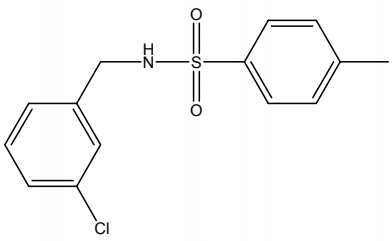

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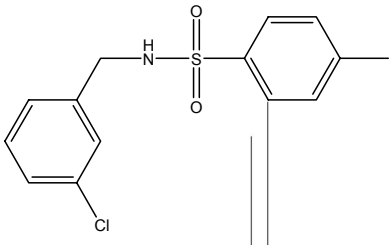

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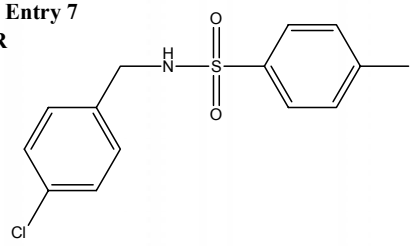

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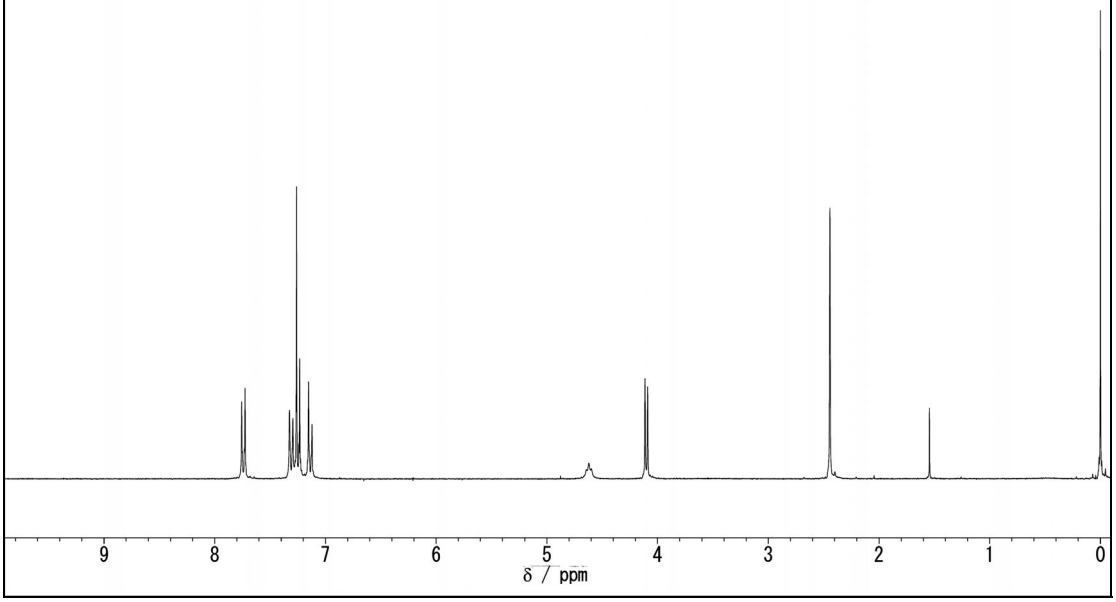

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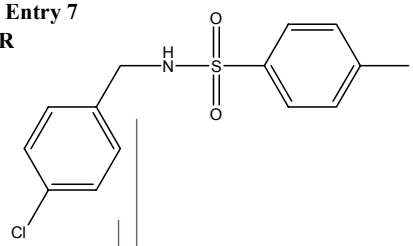

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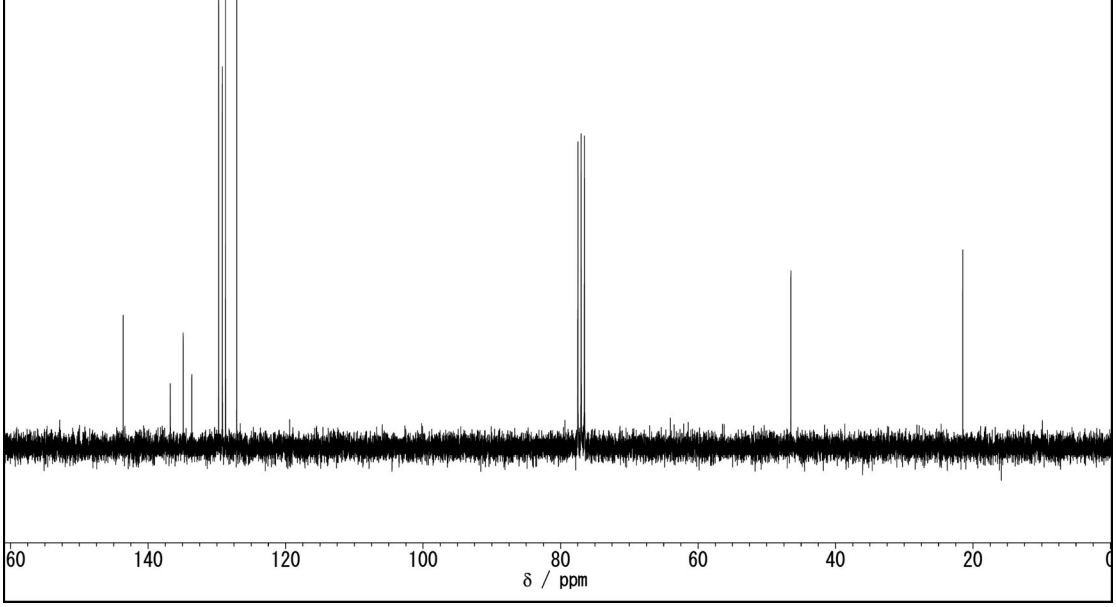

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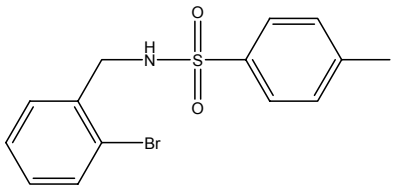

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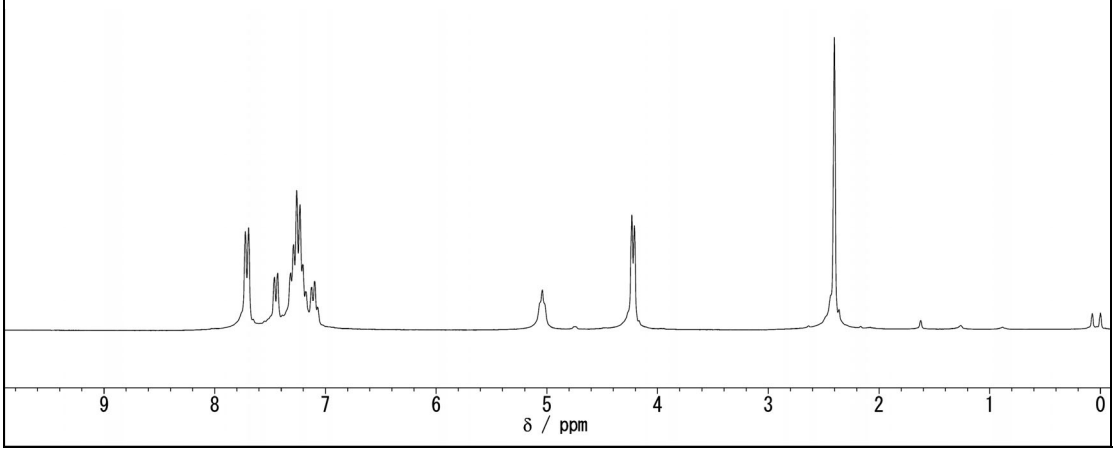

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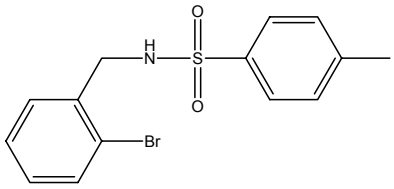

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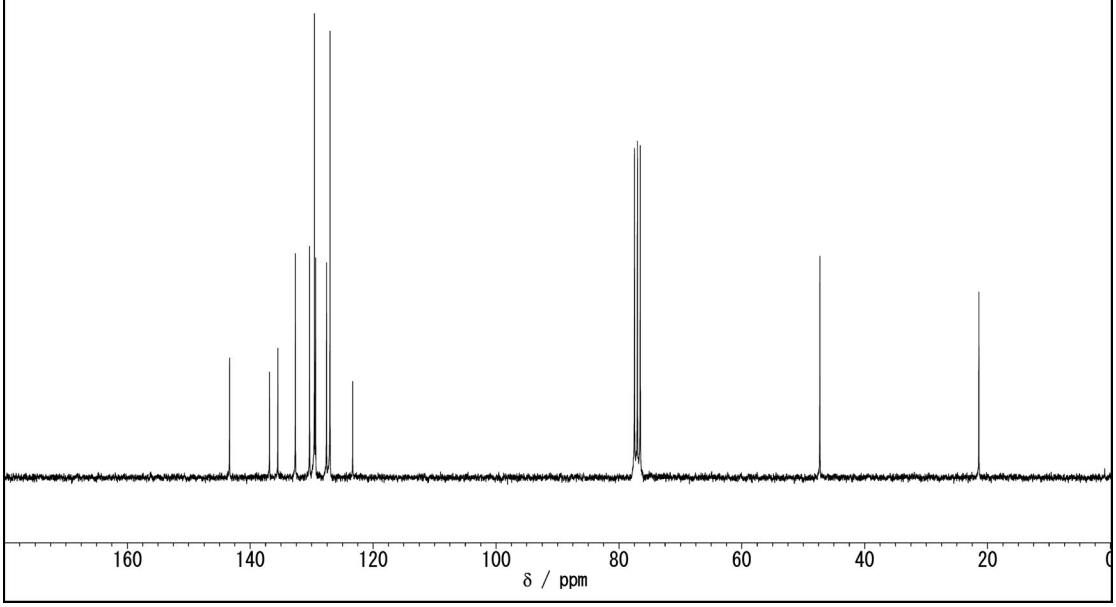

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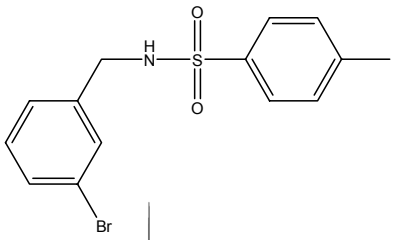

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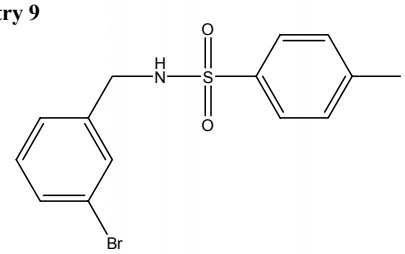

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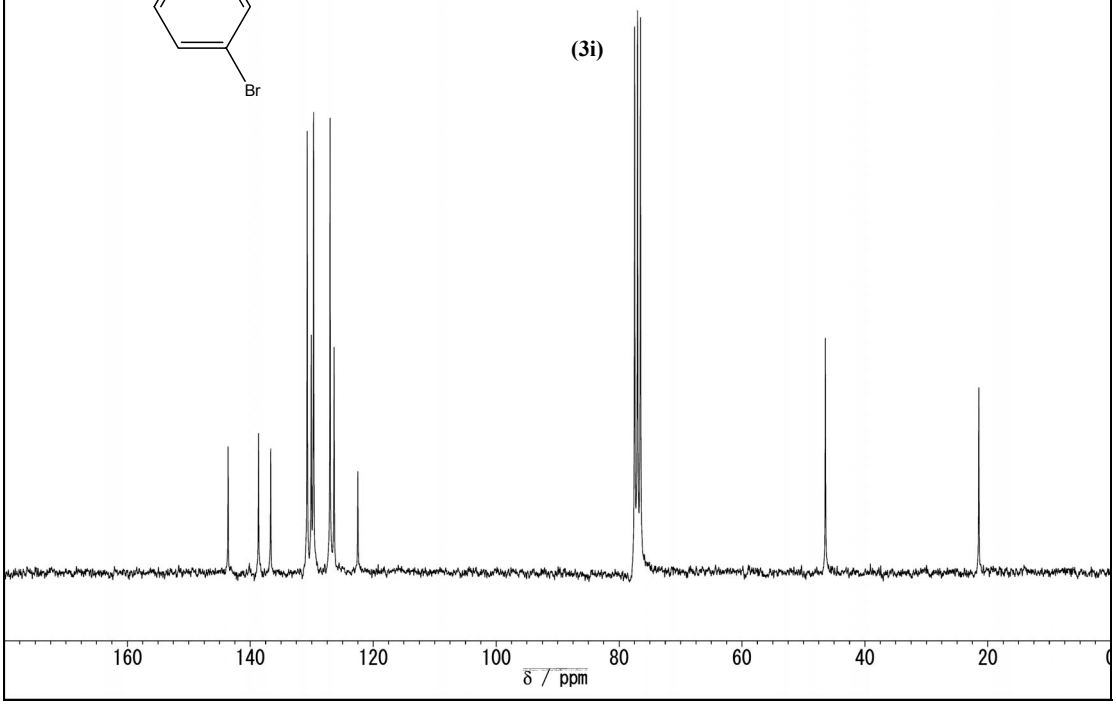

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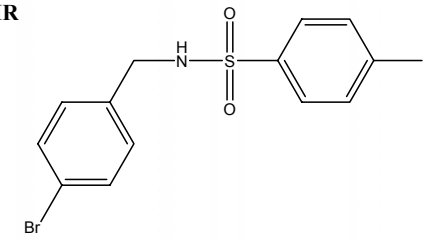

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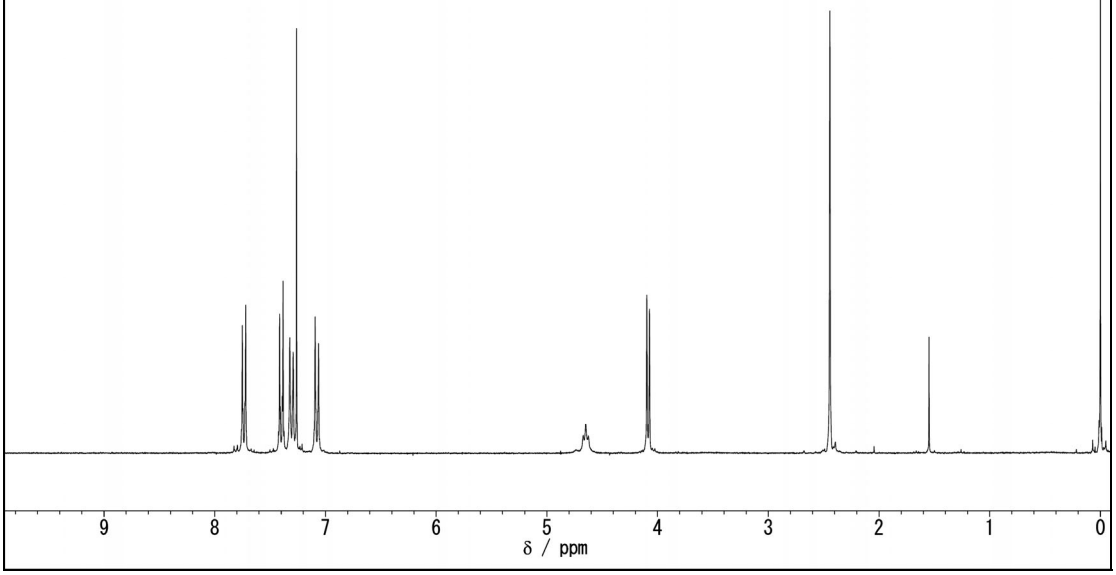

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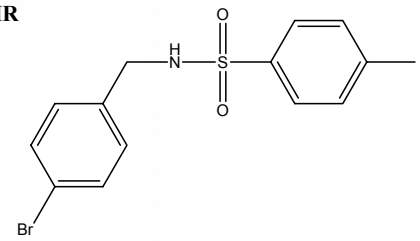

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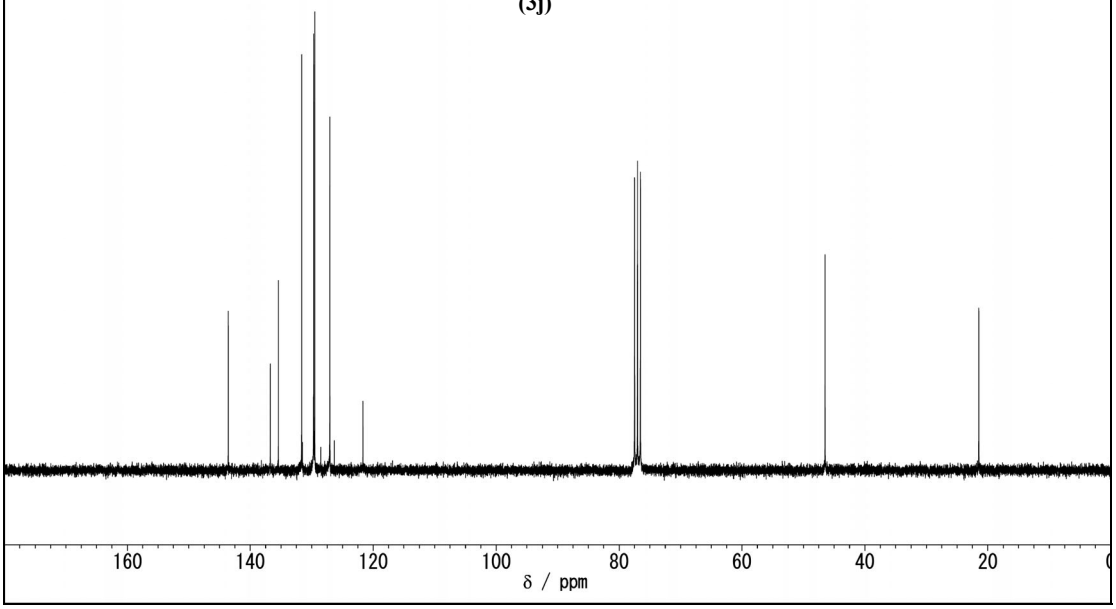

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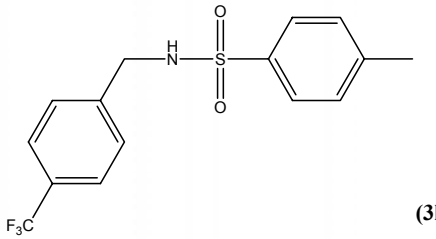

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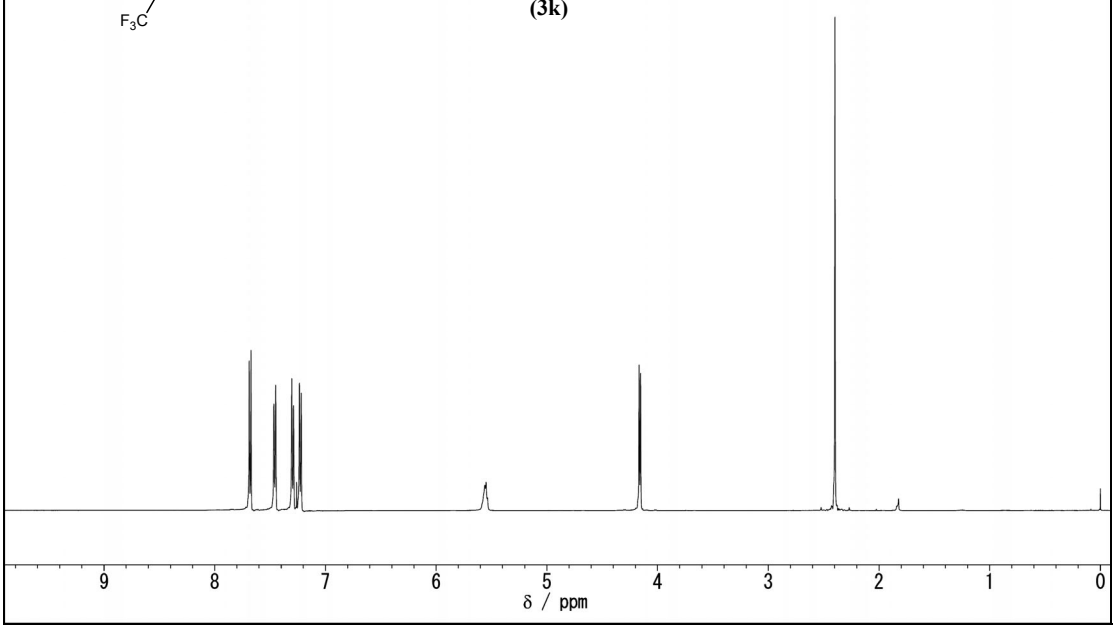

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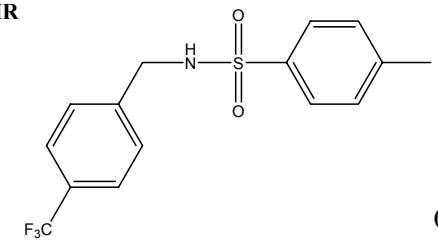

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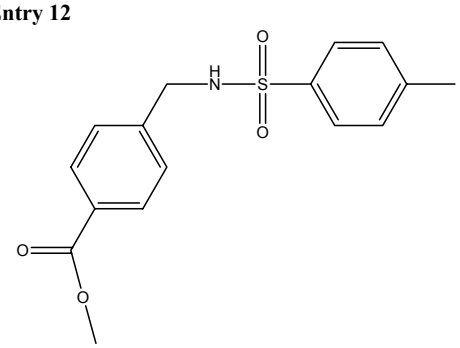

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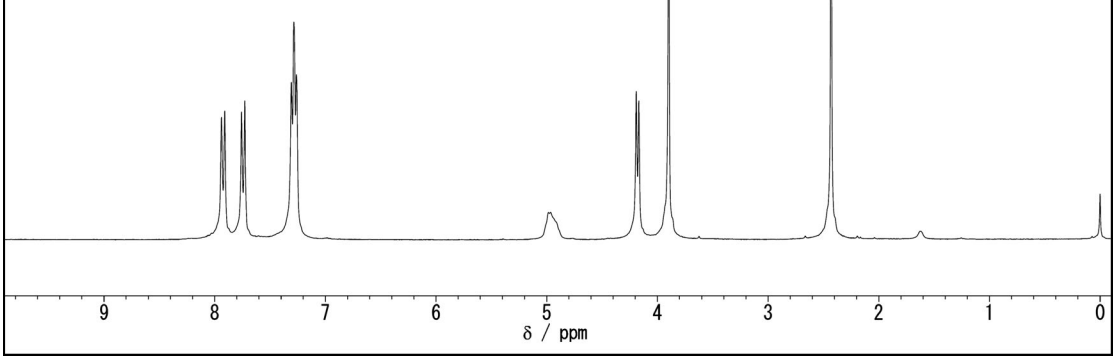

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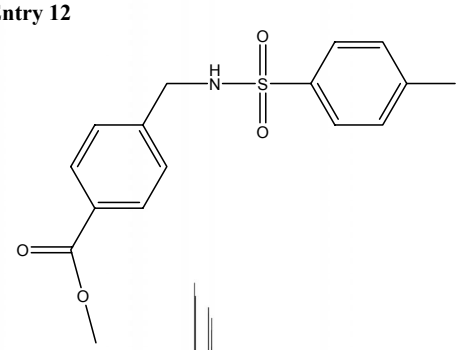


(3l)

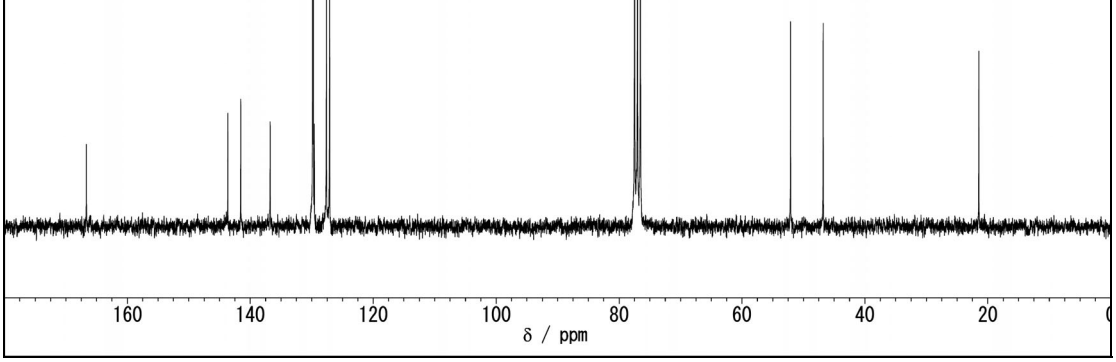
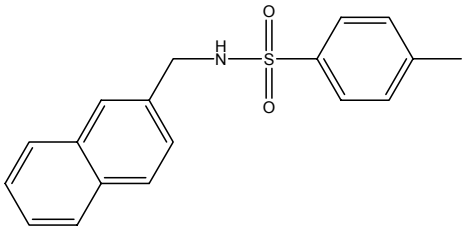


Table 2, Entry 13
^{1}H NMR



(3m)

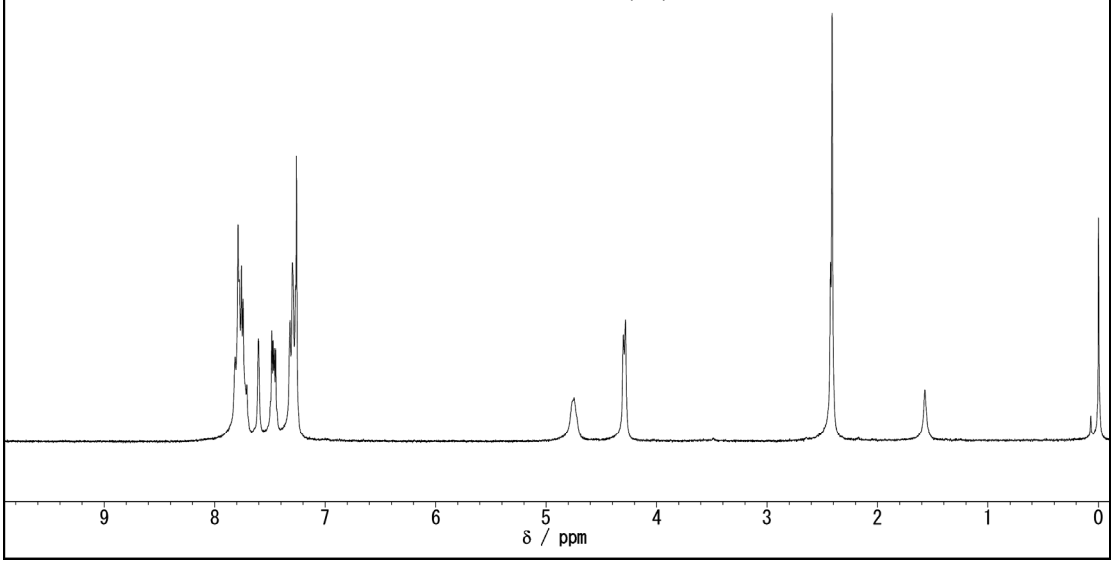
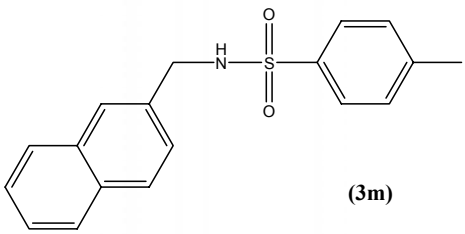
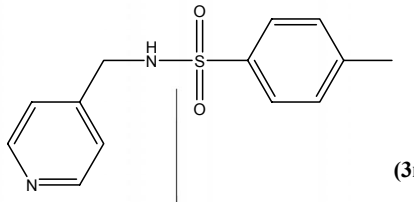


Table 2, Entry 13
^{13}C NMR



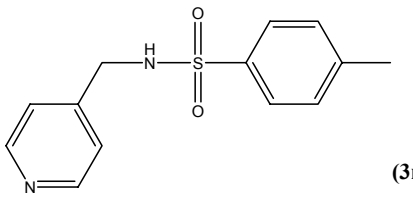
(3m)

Table 2, Entry 14
^{1}H NMR



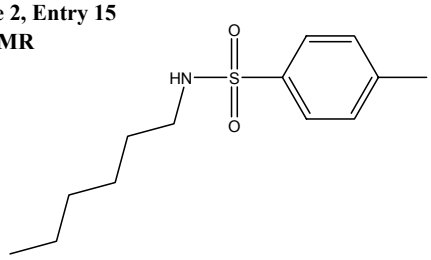
(3n)

Table 2, Entry 14
^{13}C NMR



(3n)

Table 2, Entry 15
^{1}H NMR



(3o)

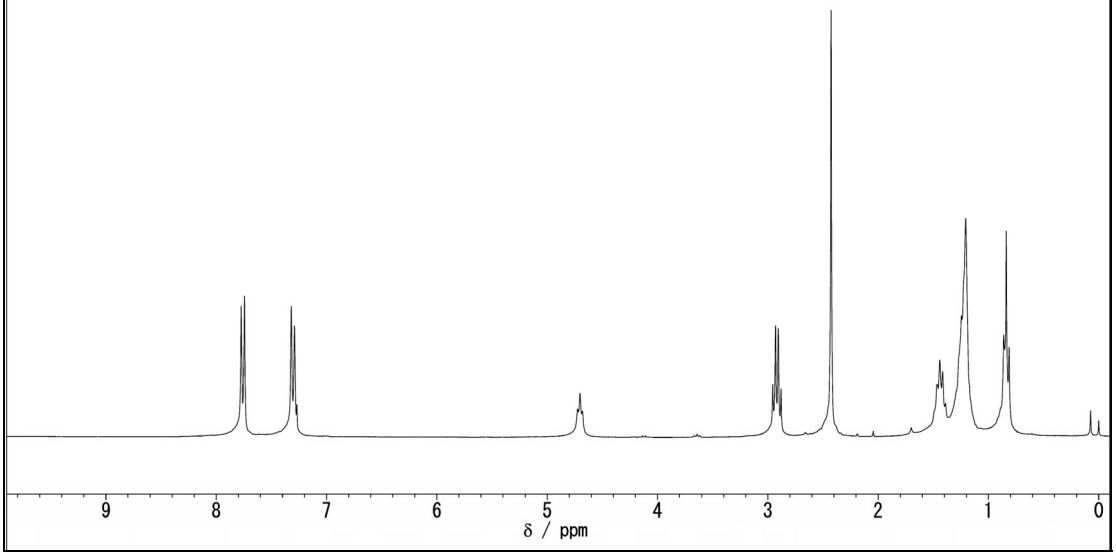
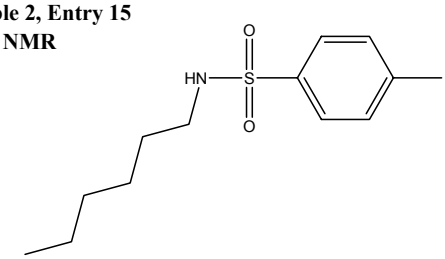


Table 2, Entry 15
^{13}C NMR



(3o)

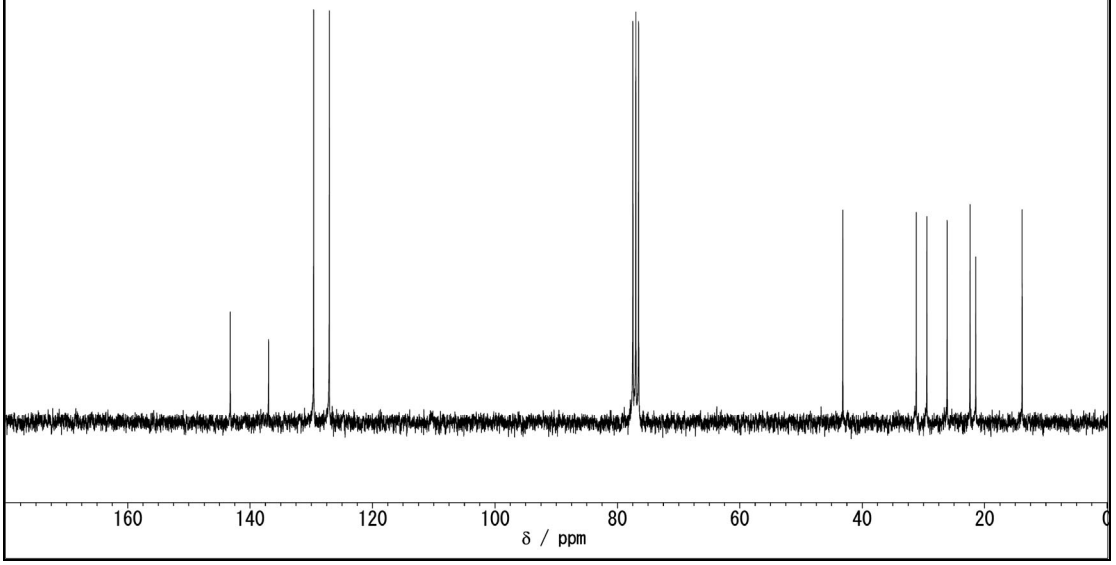
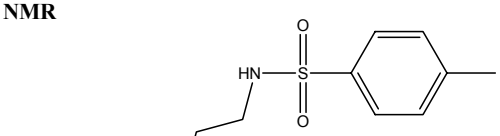


Table 2, Entry 16
^{1}H NMR



(3p)

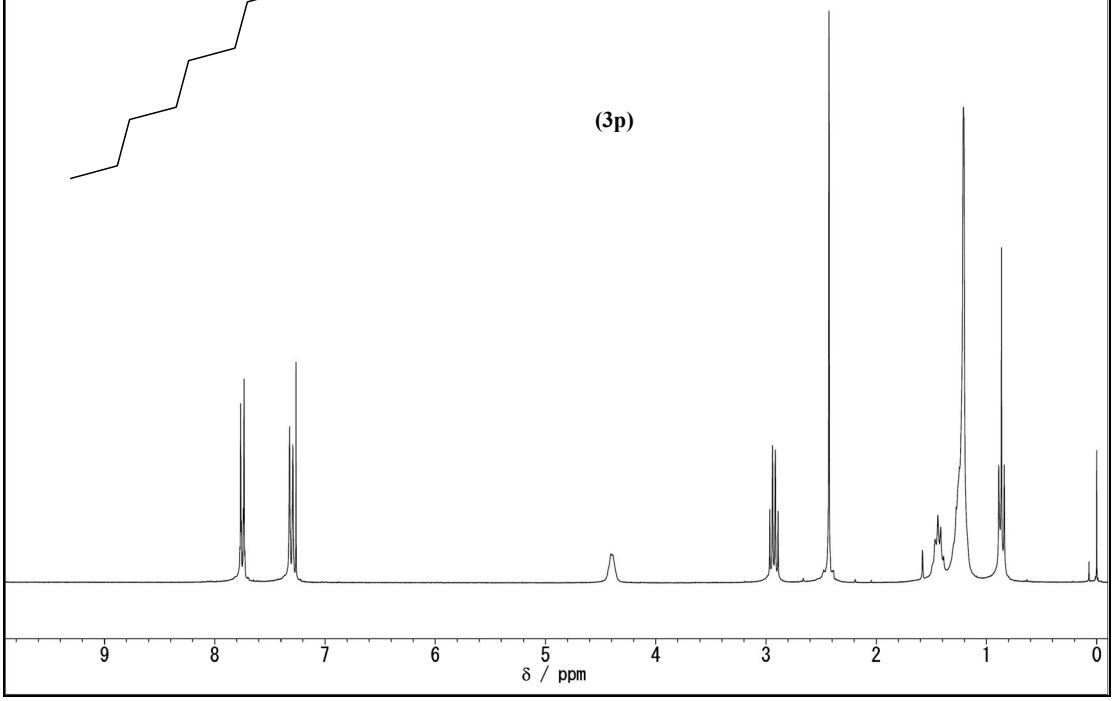
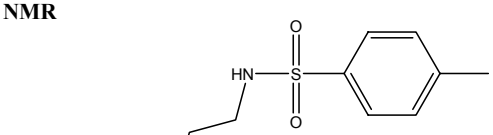


Table 2, Entry 16
^{13}C NMR



(3p)

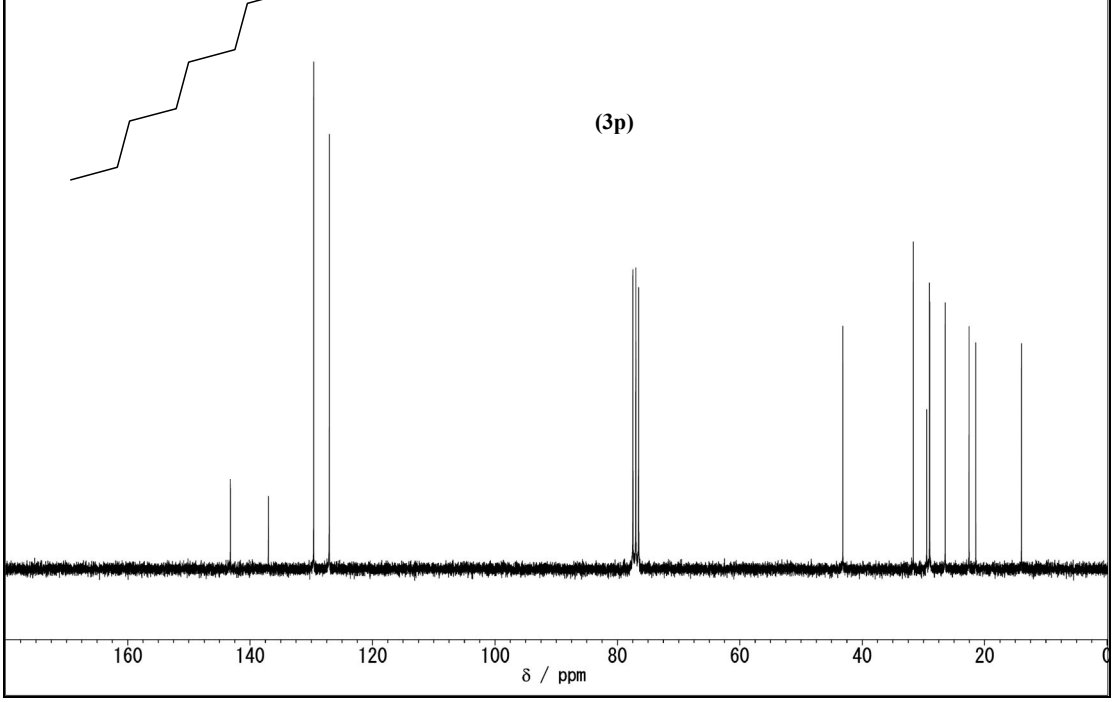
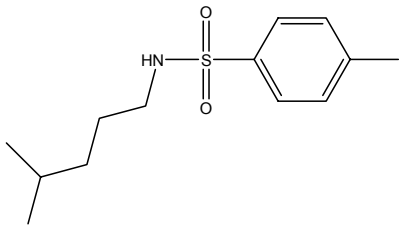
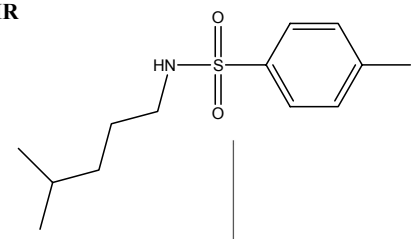


Table 2, Entry 17
^{1}H NMR



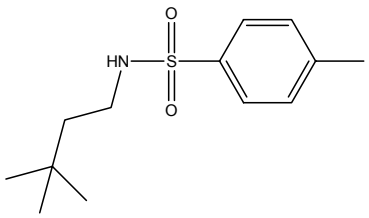
(3q)

Table 2, Entry 17
^{13}C NMR



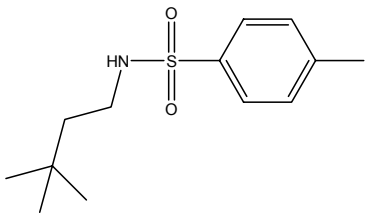
(3q)

Table 2, Entry 18
^{1}H NMR



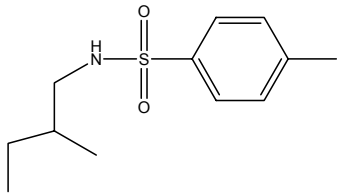
(3r)

Table 2, Entry 18
^{13}C NMR



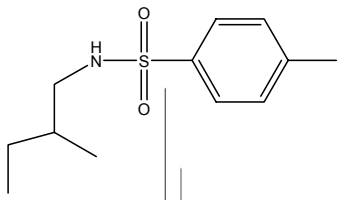
(3r)

Table 2, Entry 19
^{1}H NMR



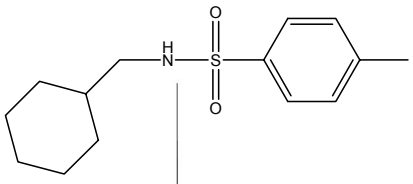
(3s)

Table 2, Entry 19
^{13}C NMR



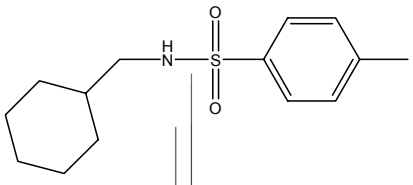
(3s)

Table 2, Entry 20
^{1}H NMR



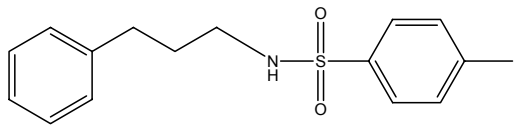
(3t)

Table 2, Entry 20
^{13}C NMR



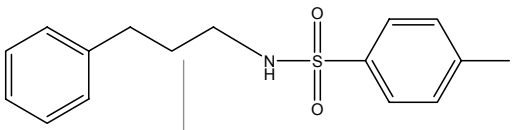
(3t)

Table 2, Entry 21
^{1}H NMR



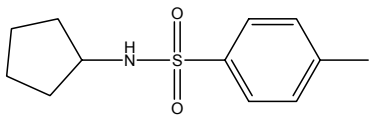
(3u)

Table 2, Entry 21
^{13}C NMR



(3u)

Table 3, Entry1
^{1}H NMR



(5a)

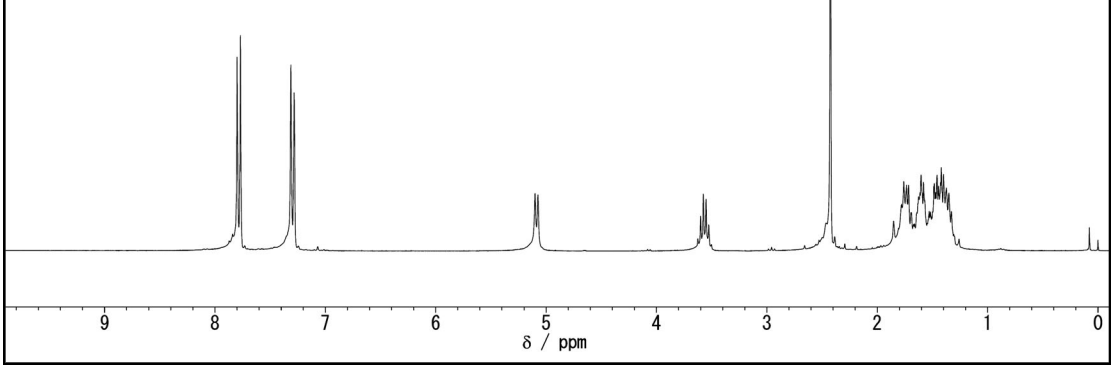
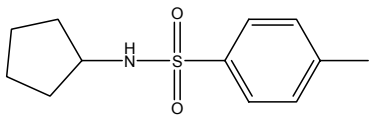
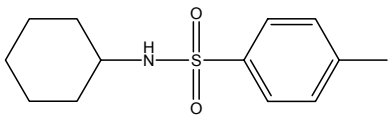


Table 3, Entry1
^{13}C NMR



(5a)

Table 3, Entry 2
^{1}H NMR



(5b)

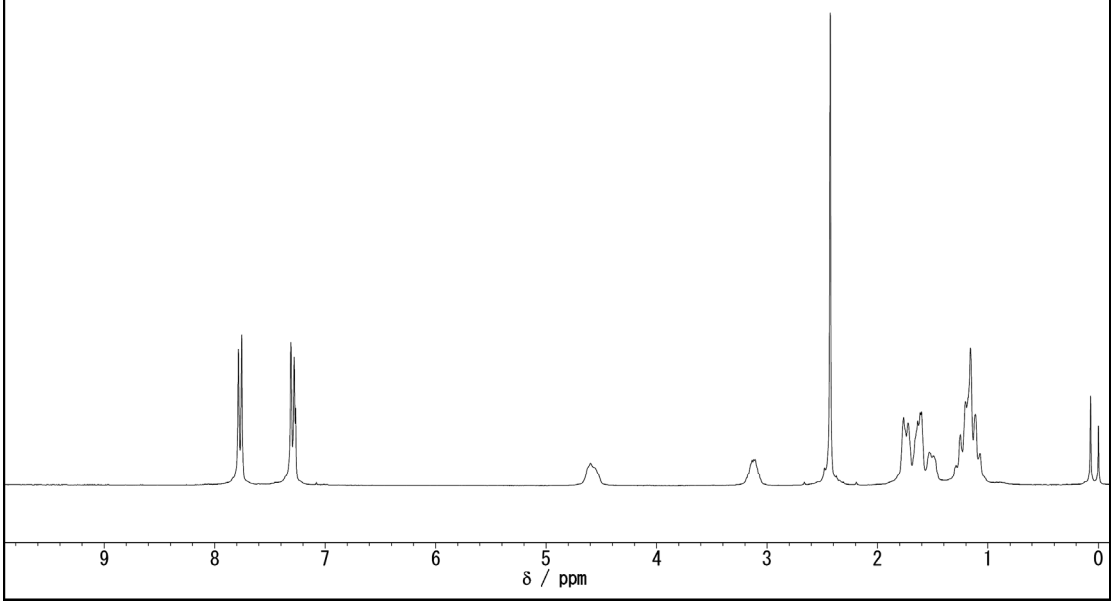
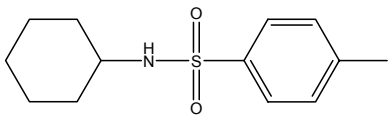
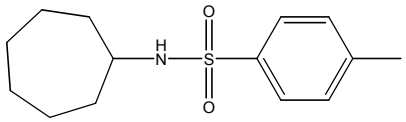


Table 3, Entry 2
^{13}C NMR



(5b)

Table 3, Entry3
^{1}H NMR



(5c)

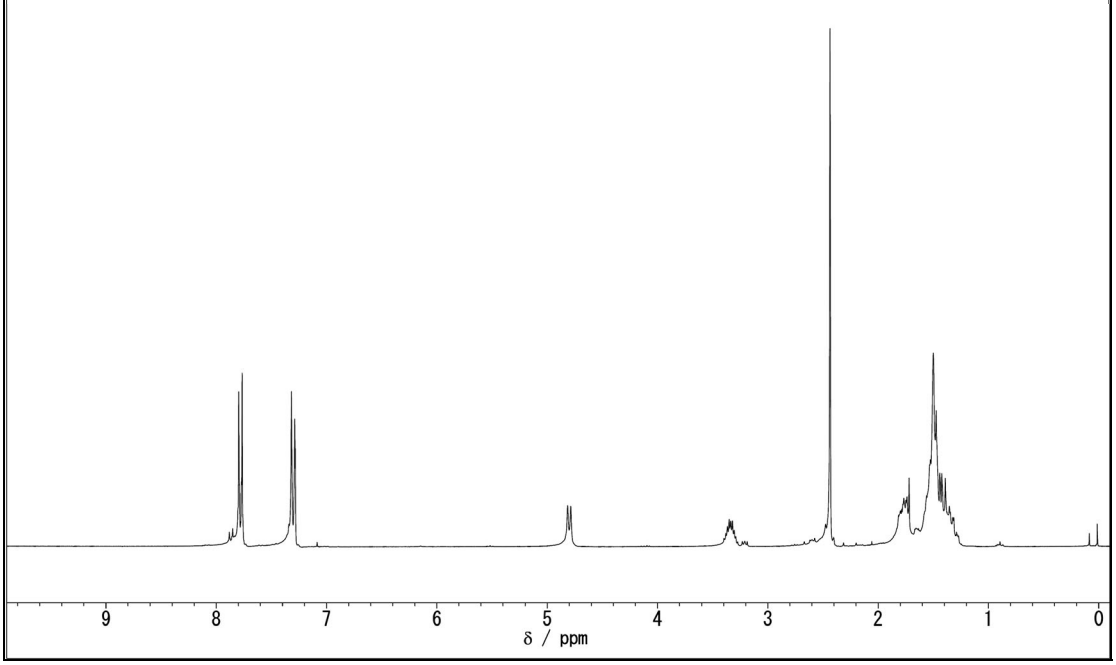
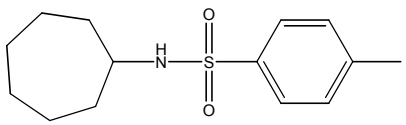
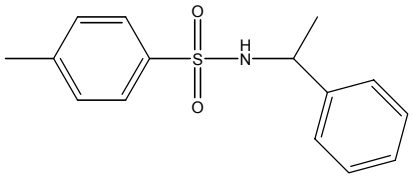


Table 3, Entry3
^{13}C NMR



(5c)

Table 3, Entry 4
^{1}H NMR



(5d)

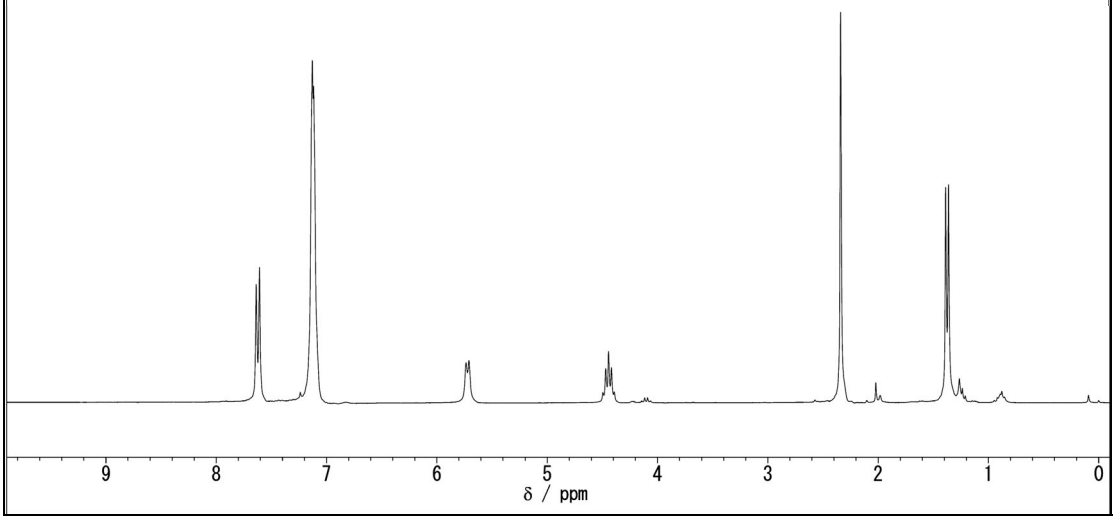
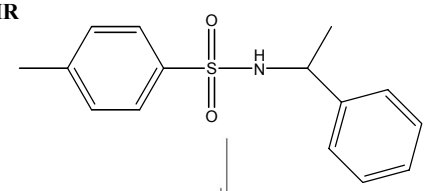


Table 3, Entry 4
^{13}C NMR



(5d)

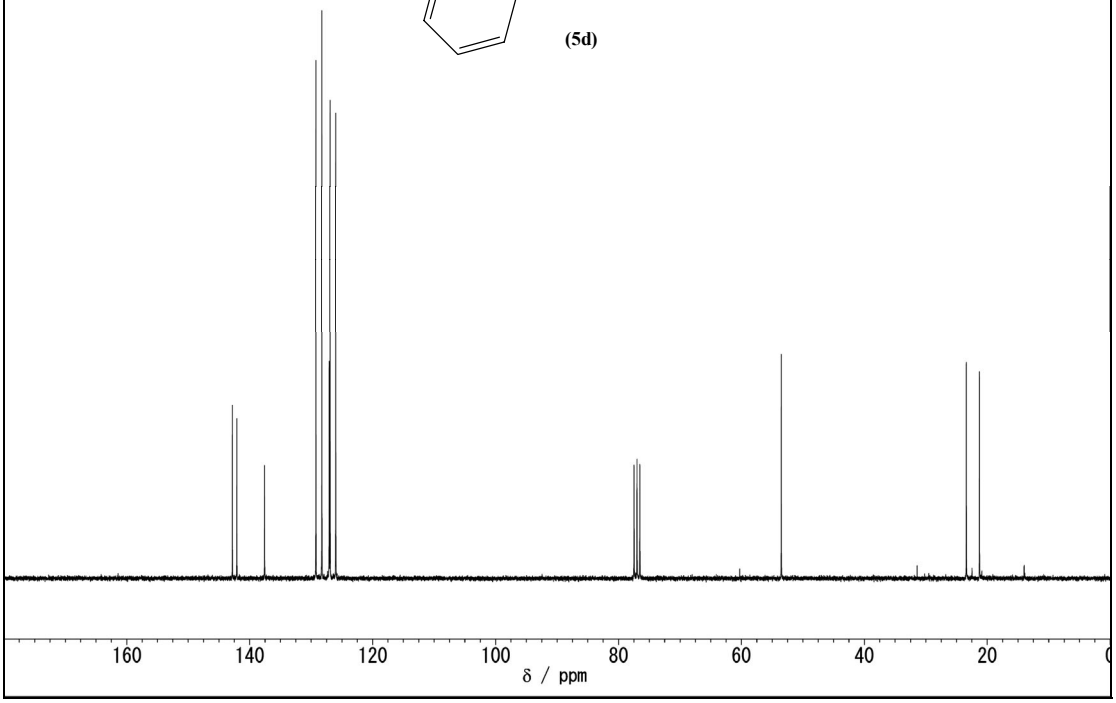
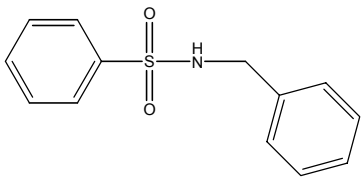


Table 4, Entry 1
^{1}H NMR



(7)

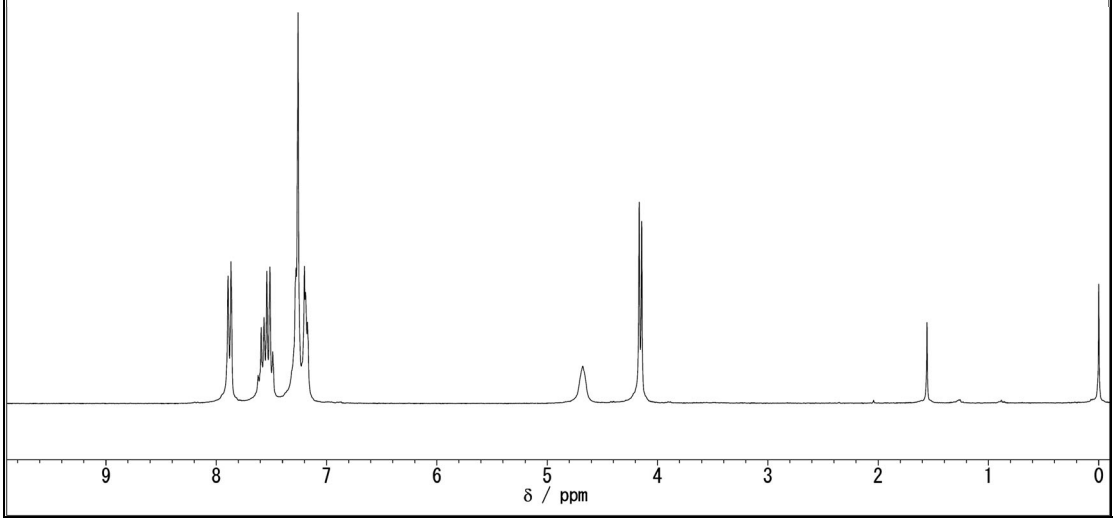
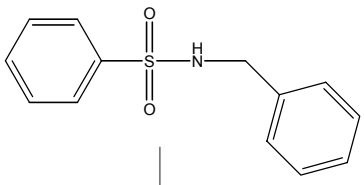


Table 4, Entry 1
^{1}H NMR



(7)

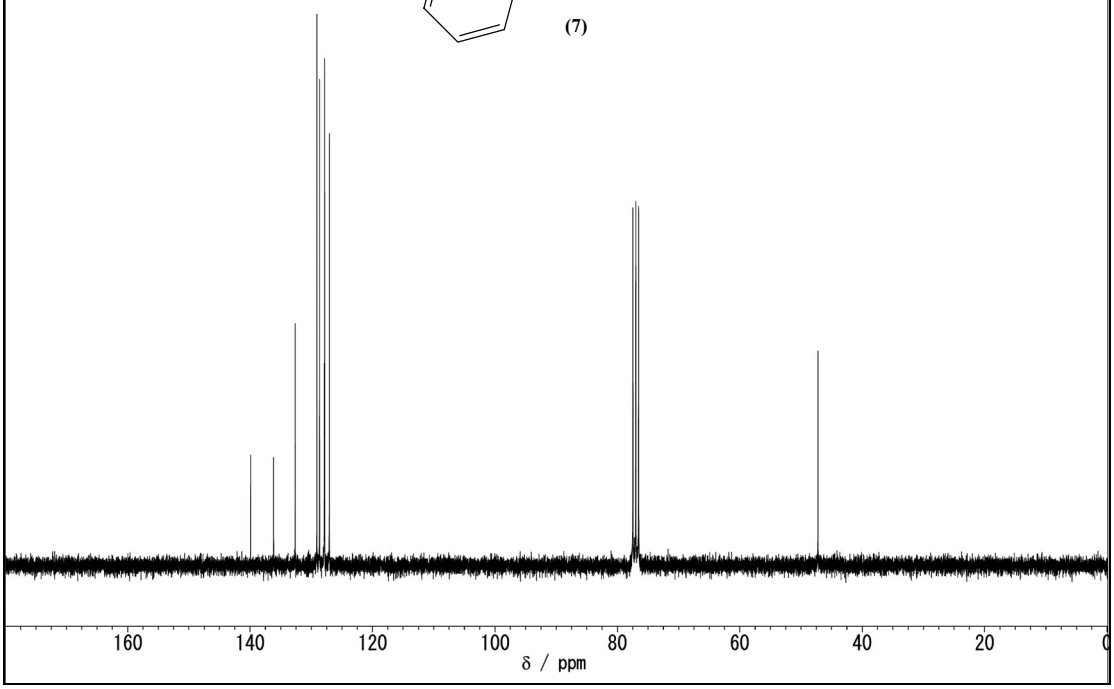
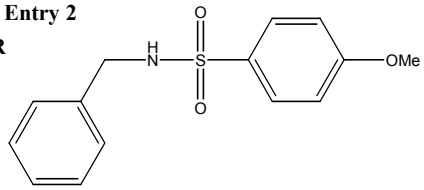


Table 4, Entry 2
^{1}H NMR



(8)

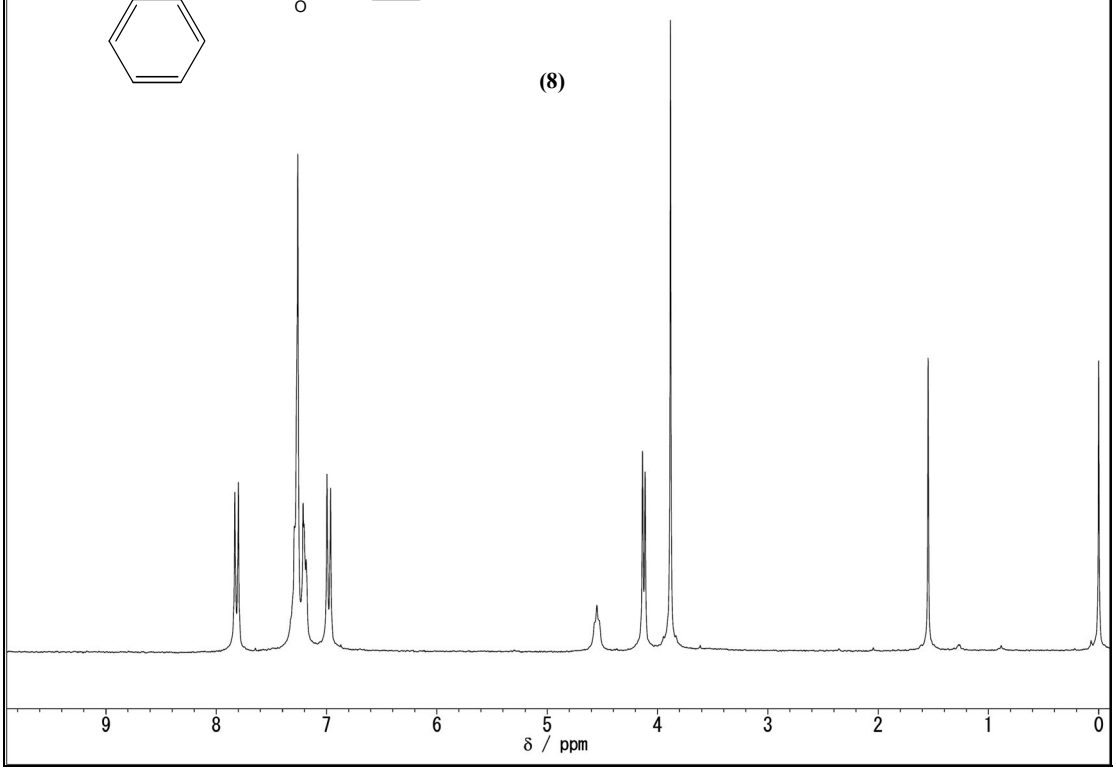
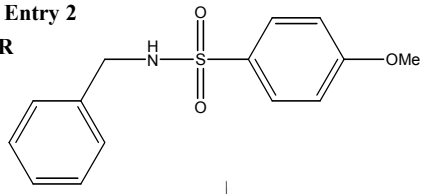
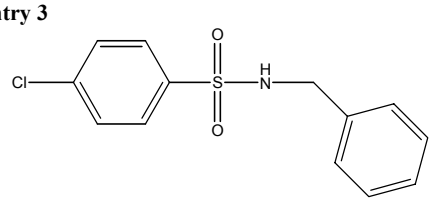


Table 4, Entry 2
^{13}C NMR



(8)

Table 4, Entry 3
^{1}H NMR



(9)

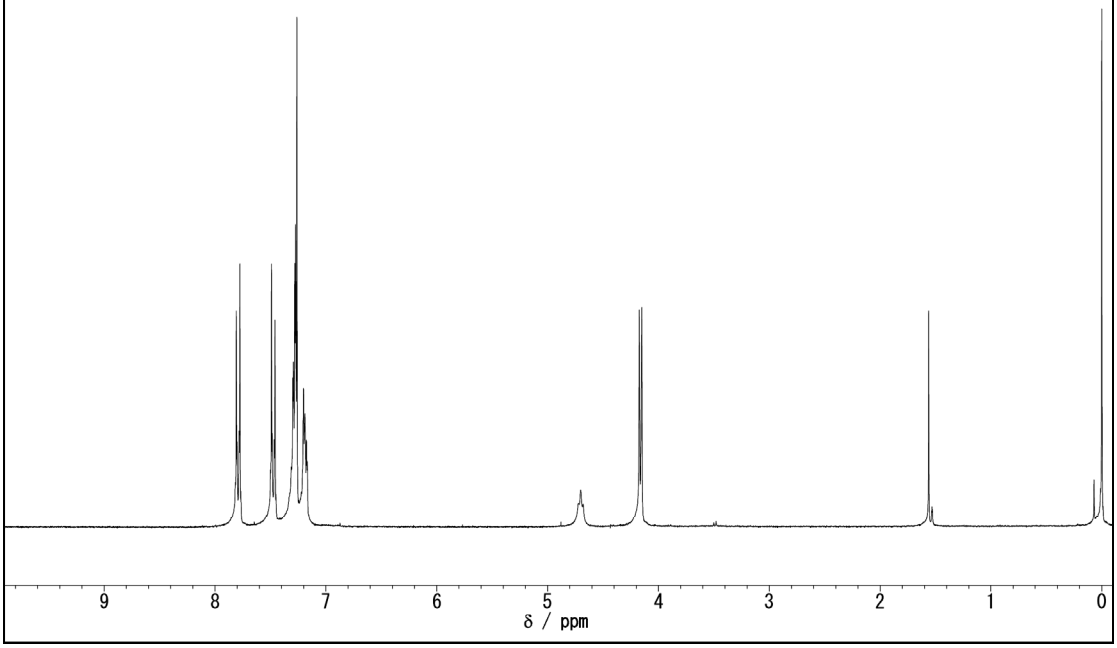
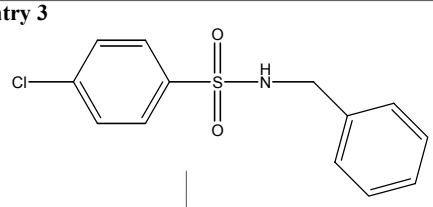


Table 4, Entry 3
^{13}C NMR



(9)

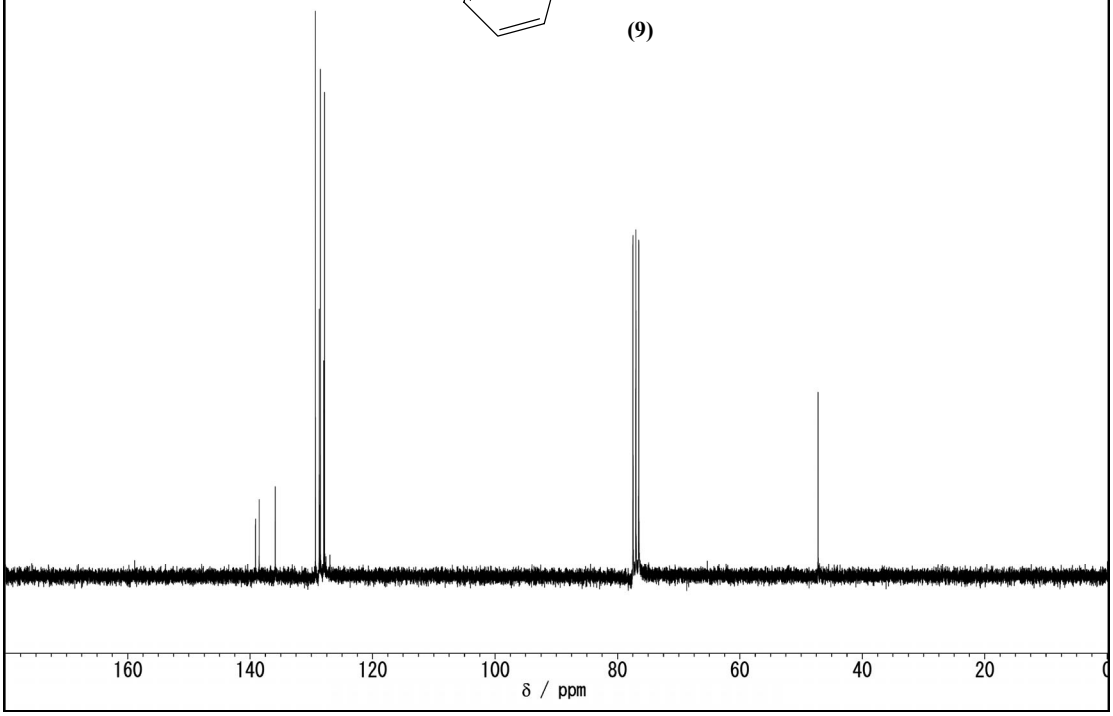
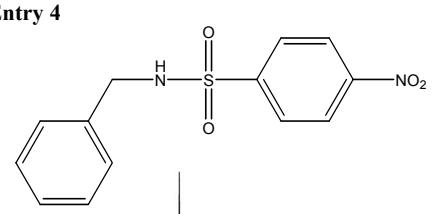


Table 4, Entry 4
^{1}H NMR



(10)

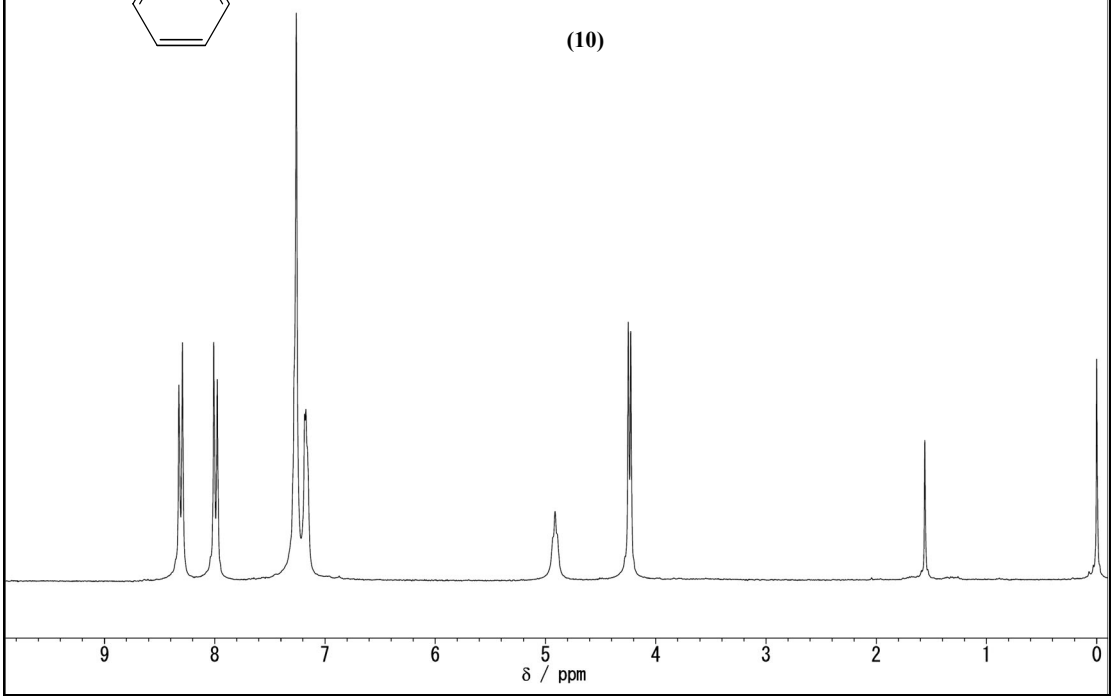
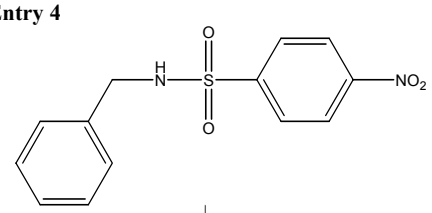


Table 4, Entry 4
^{13}C NMR



(10)

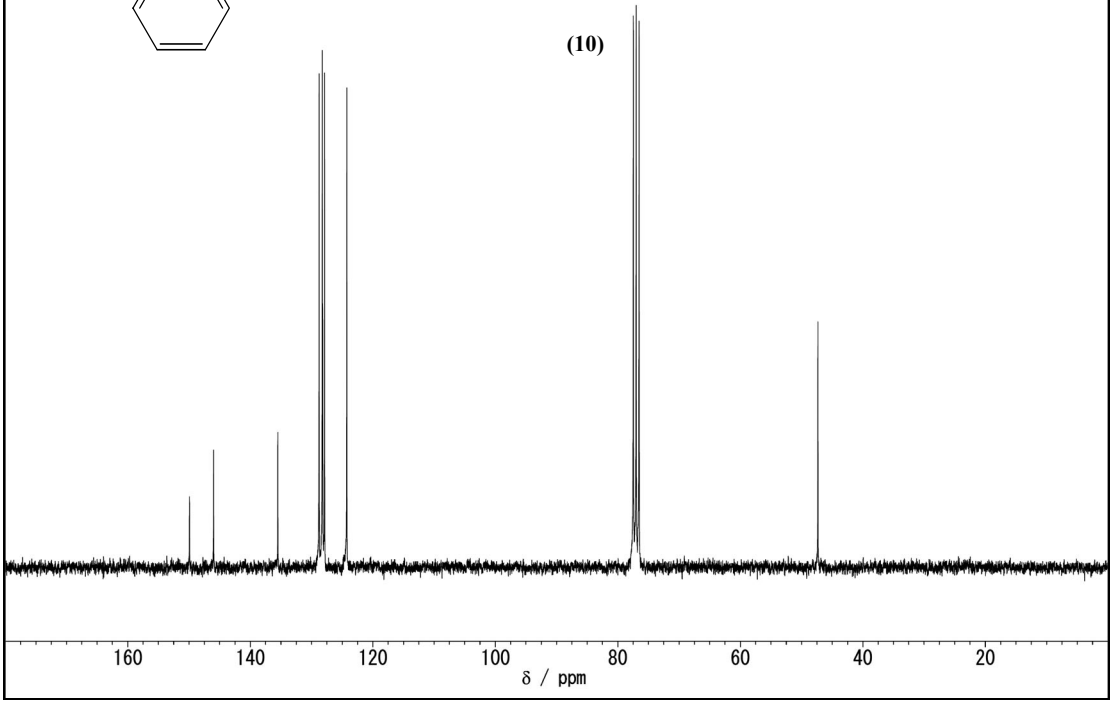
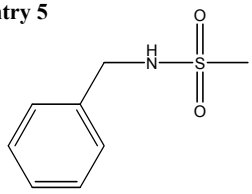


Table 4, Entry 5
^{1}H NMR



(11)

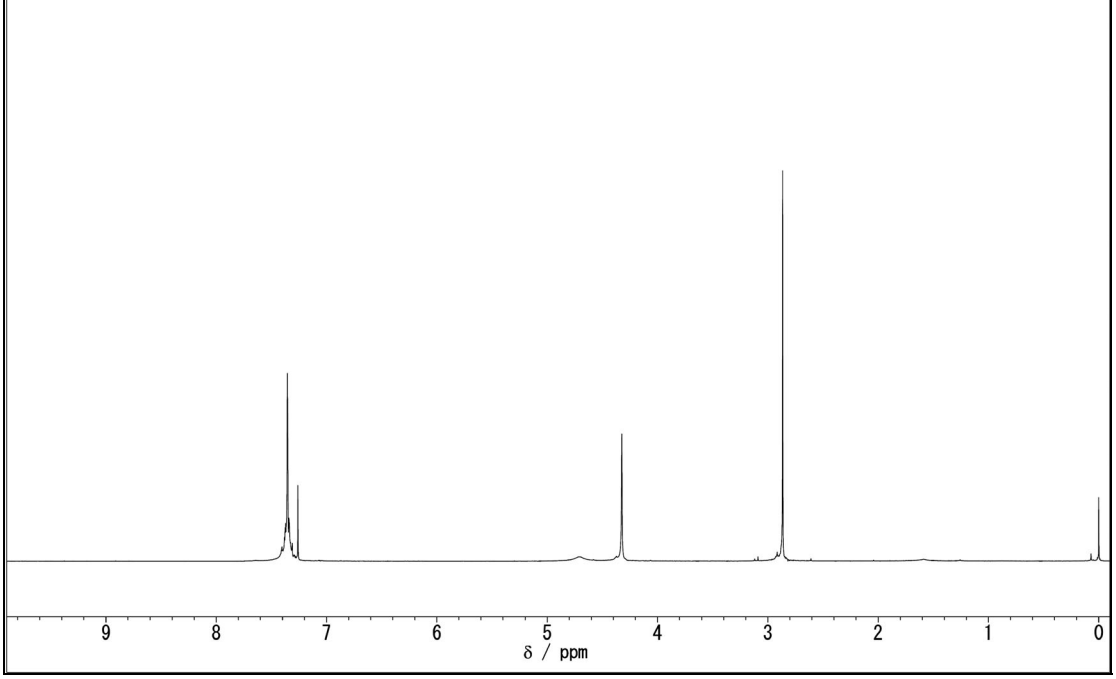
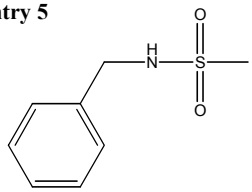


Table 4, Entry 5
^{13}C NMR



(11)