

# Supplementary Information

## **“Allylic Amines *via* Iridium Catalyzed C-C Bond Forming Hydrogenation: Imine Vinylation in the Absence of Stoichiometric Metallic Reagents or Byproducts”**

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### Table of Contents

|   |          |
|---|----------|
| I. Experimental Section   |          |
| General -----   | S2       |
| General Procedures for the Reductive Coupling -----                   | S2       |
| Experimental Apparatus -----  | S3       |
| Detailed Procedure for the Reductive Coupling and Spectral Data ----- | S5 – S43 |
| Desulfonylation-Cbz-protection of <b>9b</b> -----                     | S44      |

## I. Experimental Section

**General.** All reactions were run under an atmosphere of argon, unless otherwise indicated. Anhydrous solvents were transferred by an oven-dried syringe. Reaction vessels (18 mm x 150 mm test tube) were oven-dried overnight and cooled under a stream of nitrogen. Toluene was distilled from sodium/benzophenone. Ir(cod)<sub>2</sub>BARF was used as received from Umicore. BIPHEP was used as received from Strem Chemicals. Triphenylacetic acid was purchased from Aldrich and recrystallized from hot methanol before used. Imines (**1a-8a**, **13a**) derived from aryl and  $\alpha,\beta$ -unsaturated aldehydes were prepared according to the literature procedures reported by Stalick.<sup>1</sup> Imines (**9a-12a**) derived from aliphatic aldehydes were prepared according to the literature procedures reported by ChemLa.<sup>2</sup> Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (DC-Fertigplatten Kieselgel 60 F<sub>254</sub>). Preparative column chromatography employing silica gel was performed according to the method of Still.<sup>3</sup> Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion (M+1, M or M-1) or a suitable fragment ion. Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were recorded with a Varian Gemini (400 MHz) spectrometer. Chemical shifts are reported in delta ( $\delta$ ) units, parts per million (ppm) downfield from trimethylsilane. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (<sup>13</sup>C-NMR) spectra were recorded with a Varian Gemini 400 (100 MHz) spectrometer. Chemical shifts are reported in delta ( $\delta$ ) units, ppm relative to the center of the triplet at 77.0 ppm for deuteriochloroform. <sup>13</sup>C NMR spectra were routinely run with broadband decoupling.

**General Procedure for the Coupling of 2-Butyne and *N*-arylsulfonyl aldimines:** To a 18 mm x 150 mm test tube charged with Ir(cod)<sub>2</sub>BARF (5 mol%), BIPHEP (5 mol%), triphenylacetic acid (5 mol%), Na<sub>2</sub>SO<sub>4</sub> (200 mol%), and imine (0.2 mmol, 100 mol%) was added toluene (4.0 mL, 0.05 M). The system was purged with argon gas followed by hydrogen gas. A 1 mL vial was charged with 2-butyne (0.2 mL, excess) and equipped with a balloon containing hydrogen gas (1 atm). The mixture of 2-butyne and hydrogen gas (1 atm) was introduced into the reaction vessel as a vapor *via* cannula (i.e. needle above the level of the liquid). The reaction mixture was stirred at 60 °C under one atmosphere of the hydrogen/2-butyne gas mixture for 24 hours. The reaction mixture was evaporated onto silica gel and the title compound was isolated by flash column chromatography (SiO<sub>2</sub>).

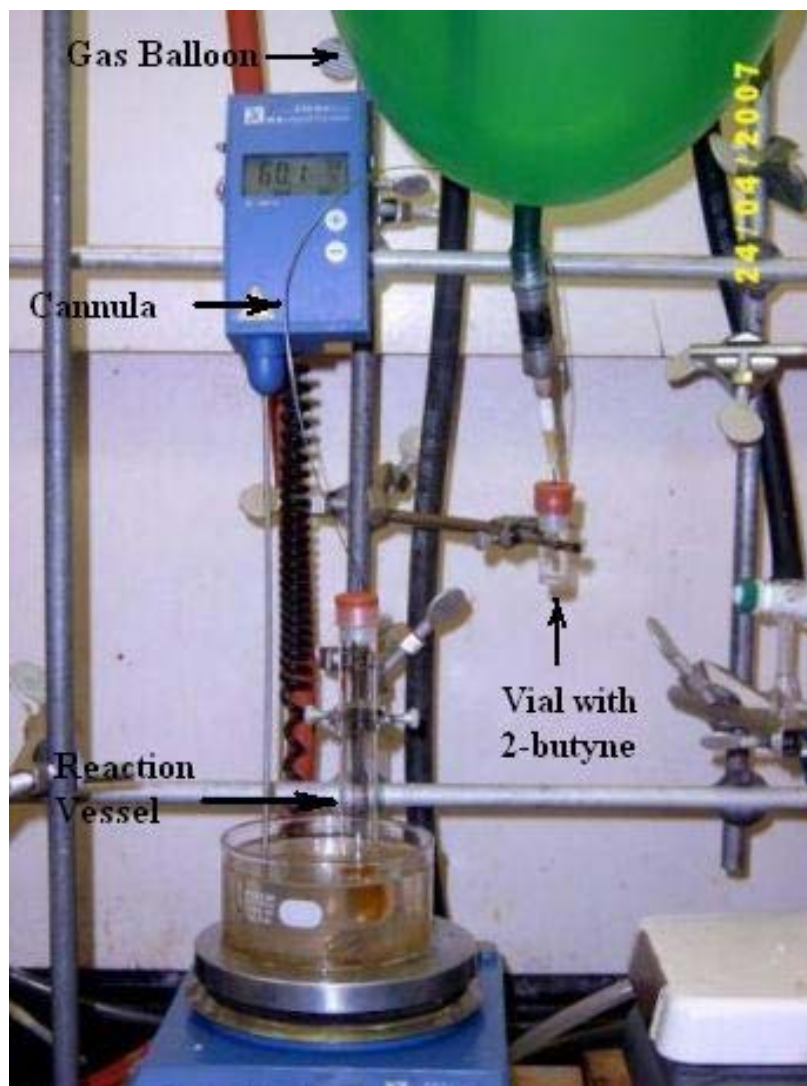
**General Procedure for the Coupling non-volatile Alkynes (b.p. > 60°C) and *N*-arylsulfonyl aldimines:** To a 18 mm x 150 mm test tube containing a solution of Ir(cod)<sub>2</sub>BARF (5 mol%), BIPHEP (5 mol%), triphenylacetic acid (5 mol%), Na<sub>2</sub>SO<sub>4</sub> (200 mol%) and imine (0.2 mmol, 100mol%) in toluene (4.0 mL, 0.05 M or 0.1M) was added alkyne (300 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction mixture was stirred at 60 °C or 80 °C under one atmosphere of the hydrogen/2-butyne gas mixture until complete consumption of starting materials was observed by TLC. The reaction mixture was evaporated onto silica gel and the title compound was isolated by flash column chromatography (SiO<sub>2</sub>).

<sup>1</sup> Wynne, H. J.; Price, E. S.; Rorer, R. J.; Stalick, M. W. *Synth. Comm.* **2003**, 33, 341

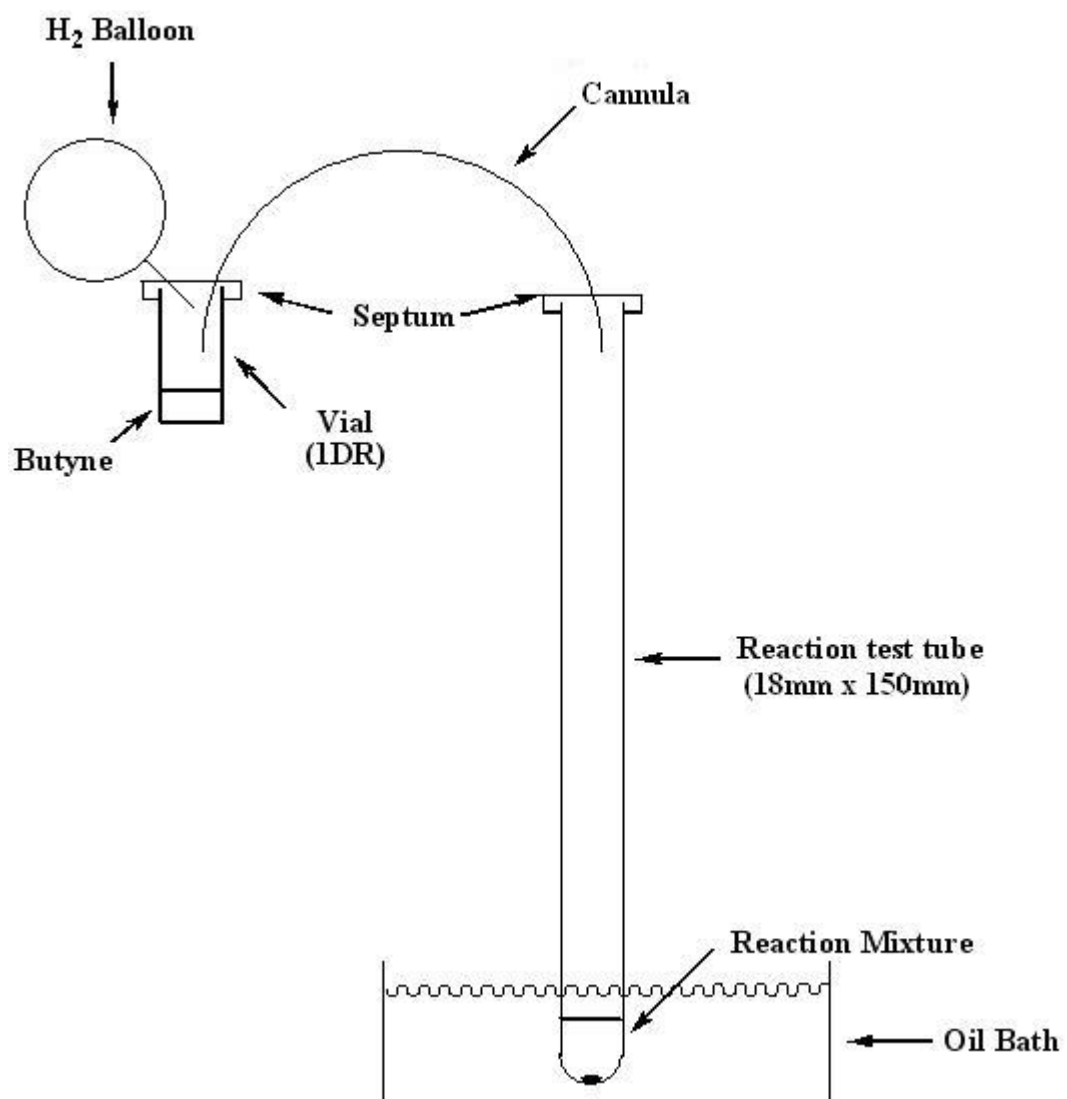
<sup>2</sup> Chelma, F.; Hebbe, V.; Normant, J. F. *Synthesis* **2000**, 75

<sup>3</sup> Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, 43, 2923.

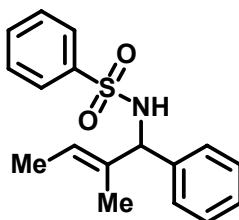
## Experimental Apparatus



- 1) Reaction Vessel: 18 mm (Diameter) \* 150 mm (Length)
- 2) Cannula (Double-Tipped Needle): 24 in. (Length) – 20 (Gauge)
- 3) Vial with 2-Butyne
- 4) Gas Balloon, 9 inches (Sigma-Aldrich)



**(E)-N-(2-Methyl-1-phenyl-but-2-enyl)-benzenesulfonamide (1b).**



**1b**

To a solution of Ir(cod)<sub>2</sub>BARF (12.7 mg, 0.01 mmol, 5 mol%), BIPHEP (5.2 mg, 0.01 mmol, 5 mol%), triphenylacetic acid (2.9 mg, 0.01 mmol, 5 mol%) and Na<sub>2</sub>SO<sub>4</sub> (57 mg, 200 mol%) in toluene (4 mL, 0.05 M) was added N-benzylidene-benzenesulfonamide (**1a**) (49 mg, 0.2 mmol, 100 mol%). The system was purged with argon gas followed by hydrogen gas. A 1 mL vial was charged with 2-butyne (0.2 mL, excess) and equipped with a gas balloon containing hydrogen gas (1 atm). The mixture of 2-butyne and hydrogen gas (1 atm) was introduced into the reaction vessel *via* cannula. The reaction was allowed to stir at 60 °C under 1 atm of hydrogen and 2-butyne gas mixture for 24 hours. Flash column chromatography (SiO<sub>2</sub>, 80% Petroleum Ether, 16% CHCl<sub>3</sub>, 4% EtOAc) provides the title compound (41.0 mg) as white crystals (68% yield).

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.44, 60% Petroleum Ether, 30% CHCl<sub>3</sub>, 10% EtOAc.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.76 (d, *J* = 7.2 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.16-7.24 (m, 3H), 7.10 (dd, *J* = 2.4 Hz, *J* = 8.0 Hz, 2H), 5.40 (q, *J* = 6.8 Hz, 1H), 4.90 (d, *J* = 7.6 Hz, 1H)\*, 4.85 (d, *J* = 7.6 Hz, 1H)\*, 1.48 (d, *J* = 6.8 Hz, 3H), 1.33 (s, 3H).

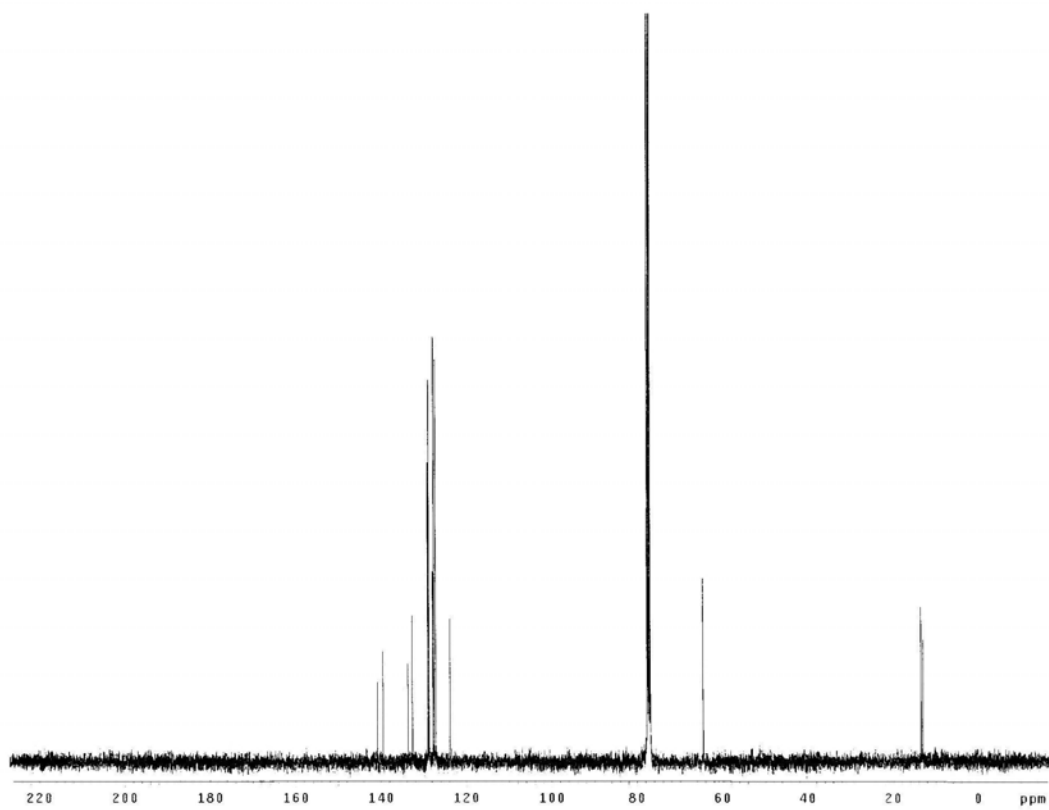
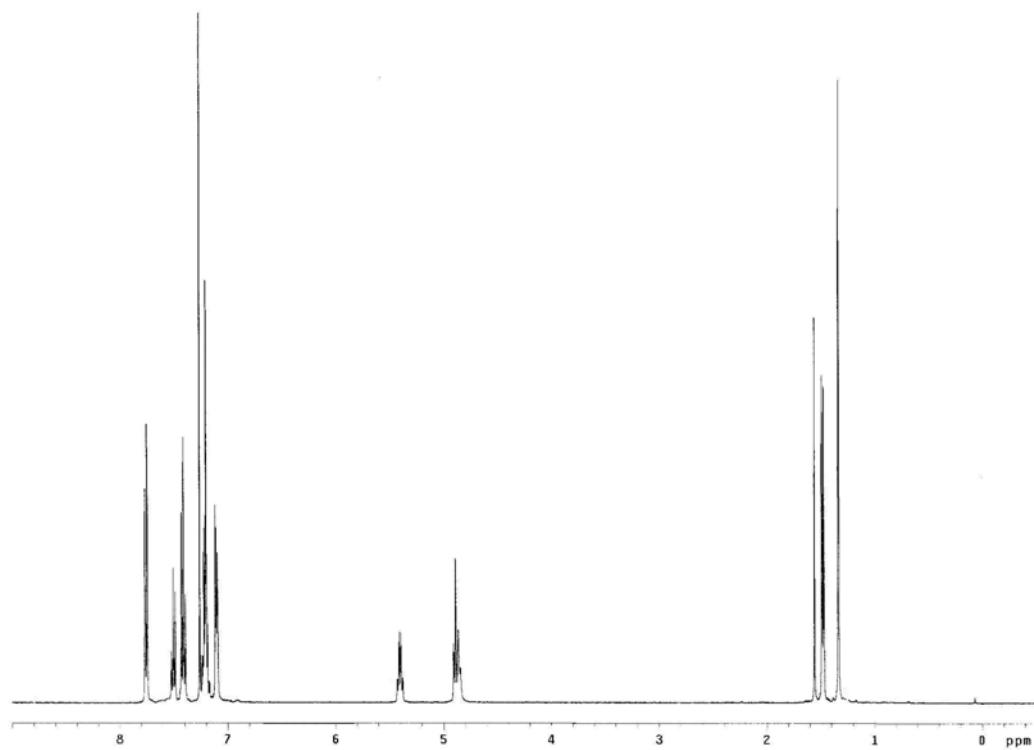
\* signals overlap.

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 140.82, 139.47, 133.61, 132.58, 128.89, 128.66, 127.72, 127.48, 127.05, 123.78, 64.55, 13.44, 13.02.

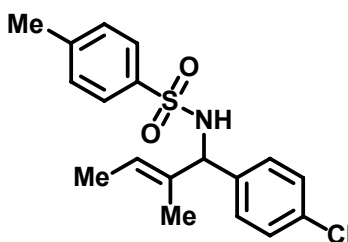
**HRMS** Calcd. for C<sub>17</sub>H<sub>20</sub>NO<sub>2</sub>S (M+1): 302.1215, Found: 302.1216.

**FTIR**(neat): 3263, 3023, 2917, 2360, 1492, 1448, 1432, 1319, 1216, 1162, 1093, 1044, 1030, 938, 913, 809, 757, 740, 722, 687, 602, 562, 584 cm<sup>-1</sup>

**M.P.** 147~148 °C



**(E)-N-[1-(4-Chloro-phenyl)-2-methyl-but-2-enyl]-4-methyl-benzenesulfonamide (2b).**



**2b**

To a solution of Ir(cod)<sub>2</sub>BARF (12.7 mg, 0.01 mmol, 5 mol%), BIPHEP (5.2 mg, 0.01 mmol, 5 mol%), triphenylacetic acid (2.9 mg, 0.01 mmol, 5 mol%) and Na<sub>2</sub>SO<sub>4</sub> (57 mg, 200 mol%) in toluene (4 mL, 0.05 M) was added N-(4-chloro-benzylidene)-4-methyl-benzenesulfonamide (**2a**) (58.7 mg, 0.2 mmol, 100 mol%). The system was purged with argon gas followed by hydrogen gas. A 1 mL vial was charged with 2-butyne (0.2 mL, excess) and equipped with a gas balloon containing hydrogen gas (1 atm). The mixture of 2-butyne and hydrogen gas (1 atm) was introduced into the reaction vessel *via* cannula. The reaction was allowed to stir at 60 °C under 1 atm of hydrogen and 2-butyne gas mixture for 24 hours. Flash column chromatography (SiO<sub>2</sub>, 80% Petroleum Ether, 16% CHCl<sub>3</sub>, 4% EtOAc) provides the title compound (51.1 mg) as white crystals (73% yield).

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.5, 60% Petroleum Ether, 30% CHCl<sub>3</sub>, 10% EtOAc.

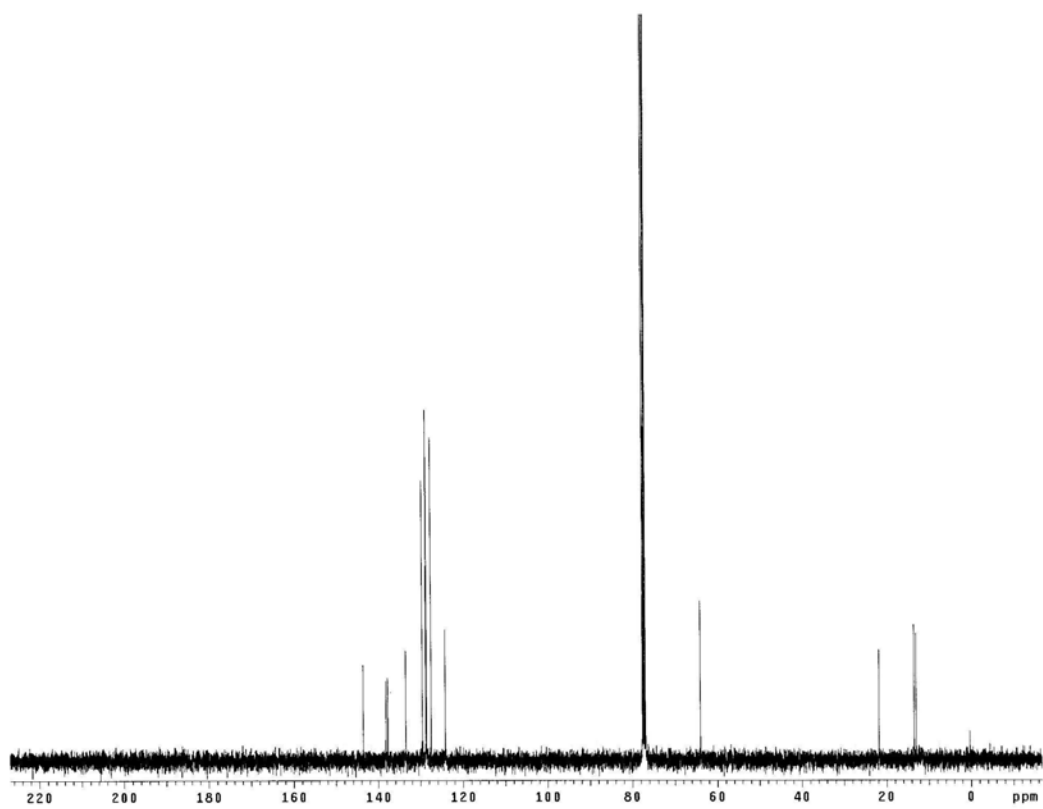
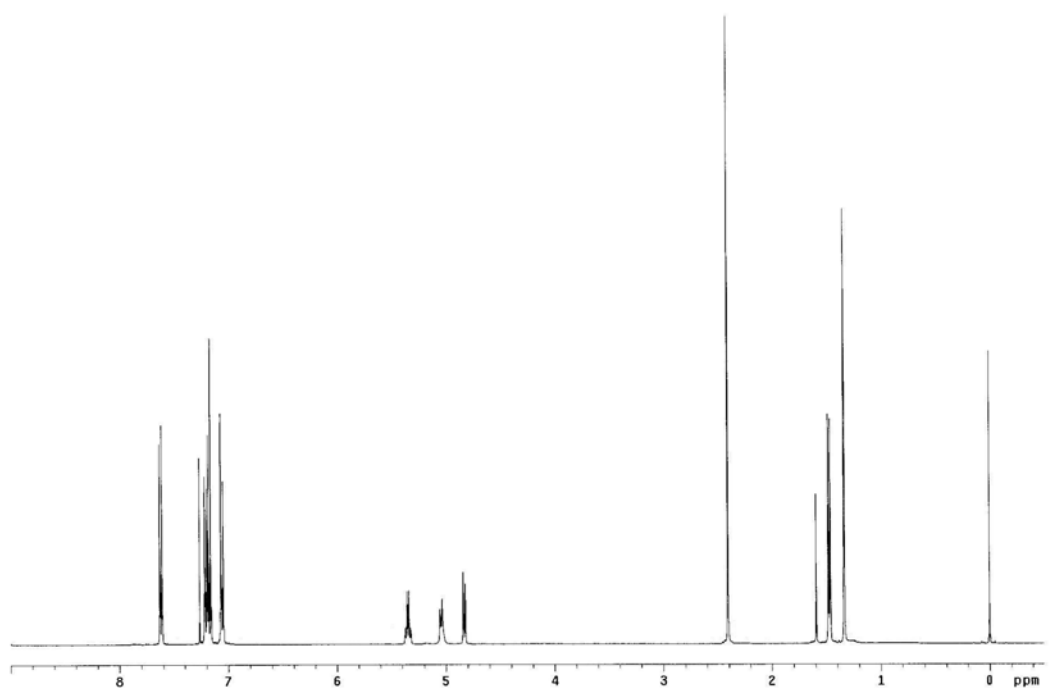
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.62 (d, *J* = 8.4 Hz, 2H), 7.15-7.22 (m, 4H), 7.06 (d, *J* = 8.4 Hz, 2H), 5.35 (q, *J* = 6.8 Hz, 1H), 5.04 (d, *J* = 8.0 Hz, 1H), 4.83 (d, *J* = 8.0 Hz, 1H), 2.41 (s, 3H), 1.47 (d, *J* = 6.8 Hz, 3H), 1.34 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 143.53, 138.18, 137.70, 133.44, 129.54, 128.68, 128.56, 127.50, 124.16, 63.97, 21.73, 13.45, 12.99.

**HRMS** Calcd. for C<sub>18</sub>H<sub>21</sub>NO<sub>2</sub>SCl (M+1): 350.0982, Found: 350.0977.

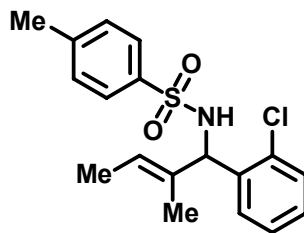
**FTIR**(neat): 3275, 2919, 1598, 1490, 1435, 1328, 1160, 1090, 1043, 1014, 923, 813, 706, 666, 572 cm<sup>-1</sup>

**M.P.** 126~127 °C





**(E)-N-[1-(2-Chloro-phenyl)-2-methyl-but-2-enyl]-4-methyl-benzenesulfonamide (3b).**



**3b**

To a solution of Ir(cod)<sub>2</sub>BARF (12.7 mg, 0.01 mmol, 5 mol%), BIPHEP (5.2 mg, 0.01 mmol, 5 mol%), triphenylacetic acid (2.9 mg, 0.01 mmol, 5 mol%) and Na<sub>2</sub>SO<sub>4</sub> (57 mg, 200 mol%) in toluene (4 mL, 0.05 M) was added N-(2-chloro-benzylidene)-4-methyl-benzenesulfonamide (**3a**) (58.7 mg, 0.2 mmol, 100 mol%). The system was purged with argon gas followed by hydrogen gas. A 1 mL vial was charged with 2-butyne (0.2 mL, excess) and equipped with a gas balloon containing hydrogen gas (1 atm). The mixture of 2-butyne and hydrogen gas (1 atm) was introduced into the reaction vessel *via* cannula. The reaction was allowed to stir at 60 °C under 1 atm of hydrogen and 2-butyne gas mixture for 24 hours. Flash column chromatography (SiO<sub>2</sub>, 80% Petroleum Ether, 16% CHCl<sub>3</sub>, 4% EtOAc) provides the title compound (42.0 mg) as white crystals (60% yield).

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.4, 60% Petroleum Ether, 30% CHCl<sub>3</sub>, 10% EtOAc.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.61 (d, *J* = 8.0 Hz, 2H), 7.06-7.24 (m, 6H), 5.19 (d, *J* = 7.6 Hz, 2H), 4.98 (d, *J* = 7.6 Hz, 1H), 2.36 (s, 3H), 1.51 (s, 3H),\* 1.50 (d, *J* = 6.8 Hz, 3H).\*

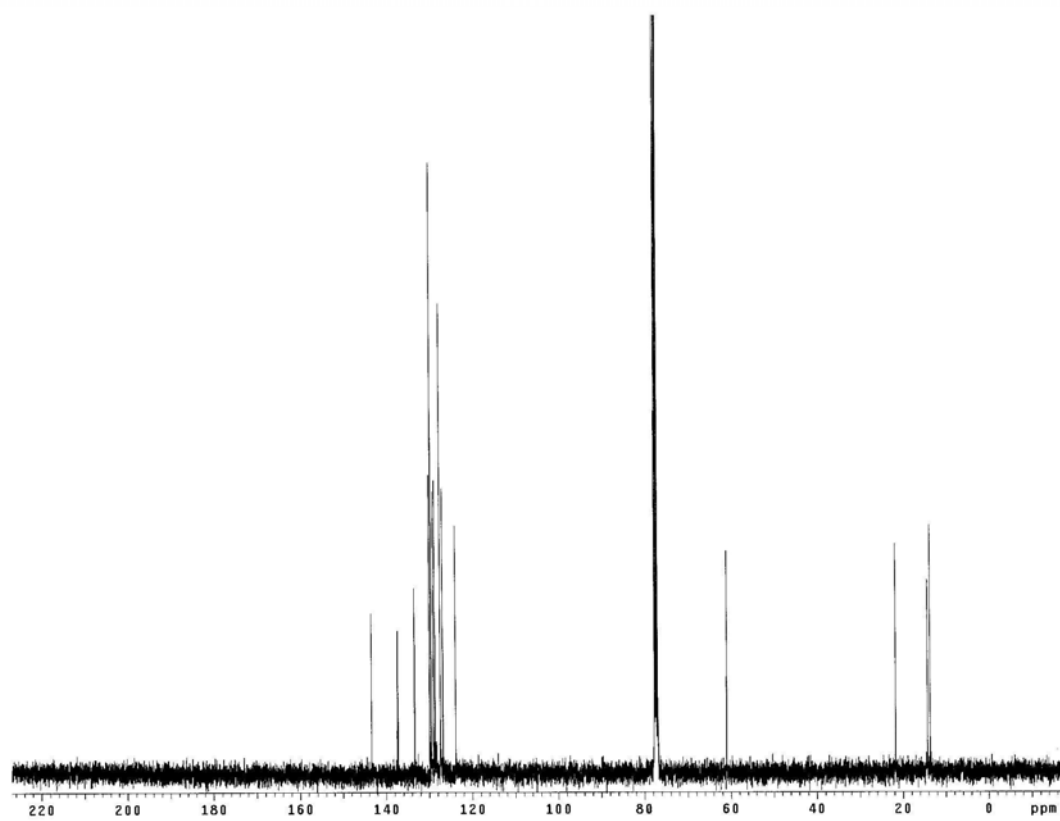
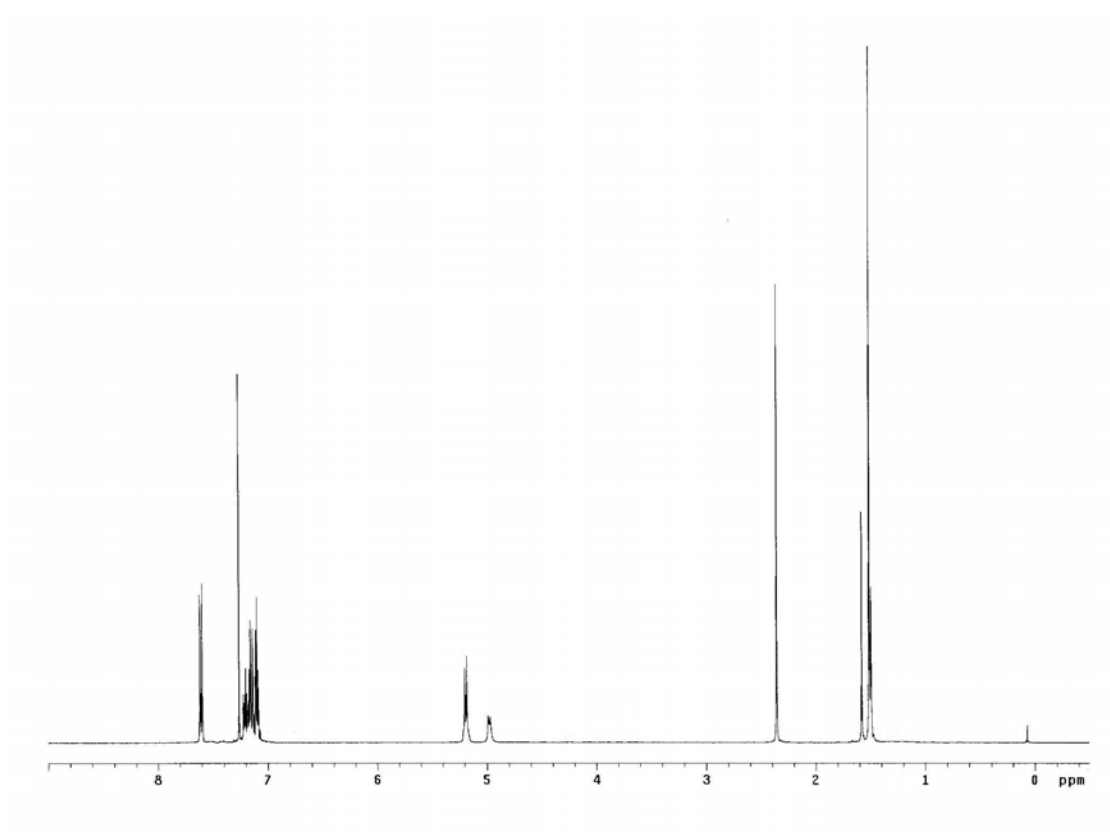
\* signals overlap.

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 143.38, 137.37, 137.21, 133.36, 133.27, 129.87, 129.52, 128.99, 128.61, 127.40, 126.79, 123.86, 60.97, 21.69, 14.24, 13.62.

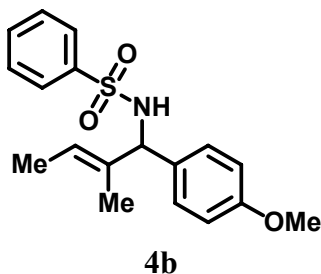
**HRMS** Calcd. for C<sub>18</sub>H<sub>21</sub>NO<sub>2</sub>SClNa (M+23): 372.0800, Found: 372.0796.

**FTIR**(neat): 3276, 2920, 1597, 1558, 1507, 1472, 1443, 1329, 1160, 1092, 1034, 922, 813, 754, 707, 667, 573 cm<sup>-1</sup>

**M.P.** 105~106 °C



**(E)-N-[1-(4-Methoxy-phenyl)-2-methyl-but-2-enyl]-benzenesulfonamide (4b).**



To a solution of Ir(cod)<sub>2</sub>BARF (12.7 mg, 0.01 mmol, 5 mol%), BIPHEP (5.2 mg, 0.01 mmol, 5 mol%), triphenylacetic acid (2.9 mg, 0.01 mmol, 5 mol%) and Na<sub>2</sub>SO<sub>4</sub> (57 mg, 200 mol%) in toluene (4 mL, 0.05 M) was added N-(4-methoxy-benzylidene)-benzenesulfonamide (**4a**) (55.1 mg, 0.2 mmol, 100 mol%). The system was purged with argon gas followed by hydrogen gas. A 1 mL vial was charged with 2-butyne (0.2 mL, excess) and equipped with a gas balloon containing hydrogen gas (1 atm). The mixture of 2-butyne and hydrogen gas (1 atm) was introduced into the reaction vessel *via* cannula. The reaction was allowed to stir at 60 °C under 1 atm of hydrogen and 2-butyne gas mixture for 24 hours. Flash column chromatography (SiO<sub>2</sub>, 80% Petroleum Ether, 16% CHCl<sub>3</sub>, 4% EtOAc) provides the title compound (46.5 mg) as white crystals (70% yield).

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.3, 60% Petroleum Ether, 30% CHCl<sub>3</sub>, 10% EtOAc.

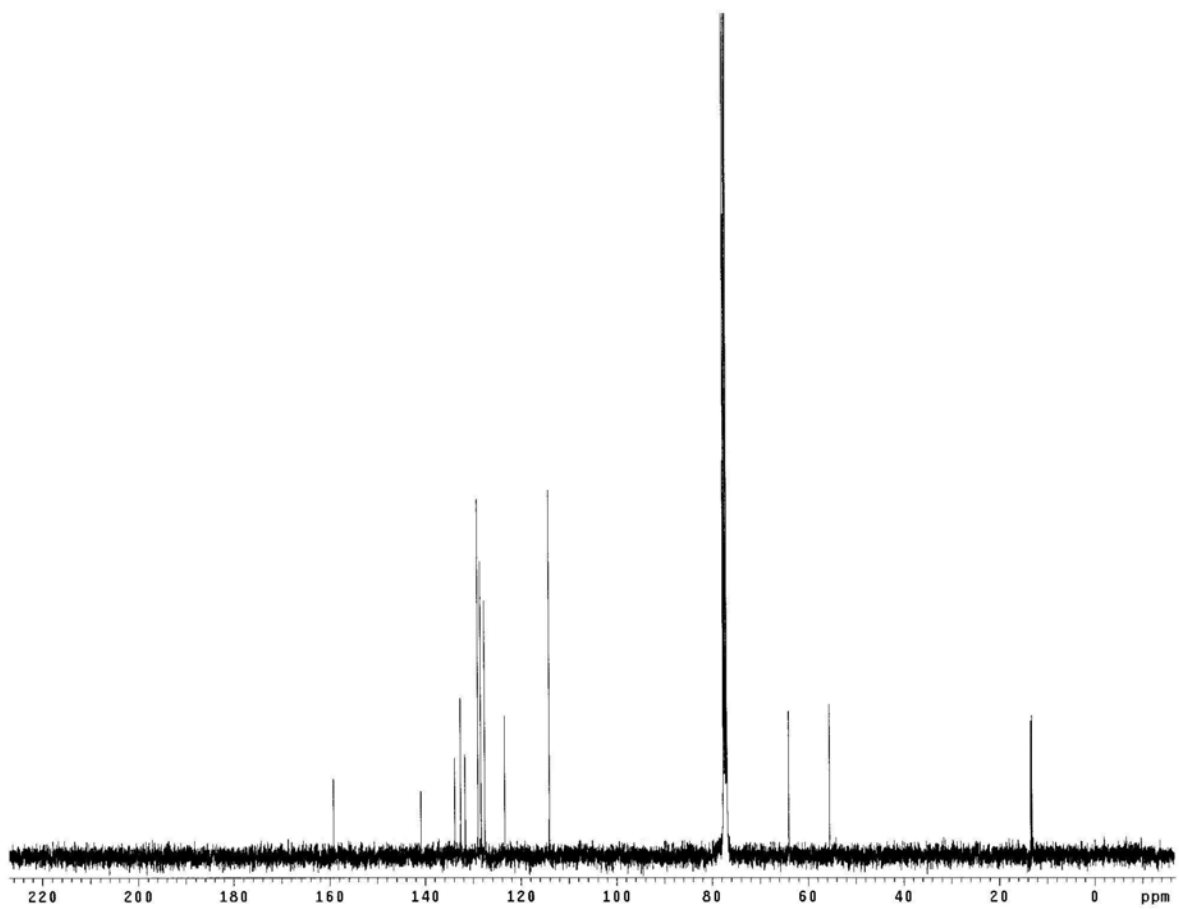
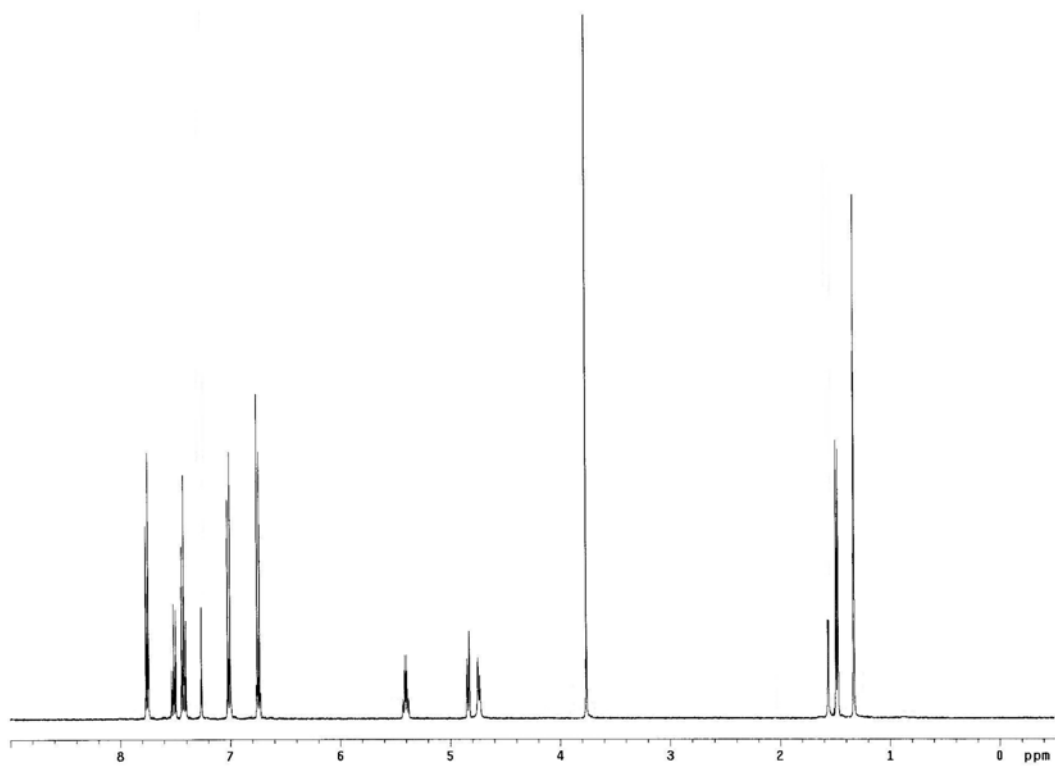
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.75 (d, *J* = 7.4 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.74 (d, *J* = 8.2 Hz, 2H), 5.40 (q, *J* = 6.8 Hz, 1H), 4.83 (d, *J* = 7.6 Hz, 1H), 4.74 (d, *J* = 7.6 Hz, 1H), 3.76 (s, 3H), 1.48 (d, *J* = 6.8 Hz, 3H), 1.33 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 159.17, 140.87, 133.75, 132.55, 131.58, 128.88, 128.27, 127.50, 123.34, 114.03, 63.99, 55.49, 13.43, 13.12.

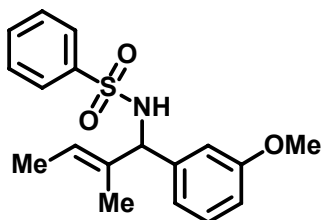
**HRMS** Calcd. for C<sub>18</sub>H<sub>22</sub>NO<sub>3</sub>S (M+1): 332.1320, Found: 332.1321.

**FTIR**(neat): 3276, 2917, 2850, 2361, 1610, 1510, 1447, 1323, 1248, 1160, 1092, 1032, 921, 832, 797, 720, 689, 591, 557 cm<sup>-1</sup>

**M.P.** 119~120 °C



**(E)-N-[1-(3-Methoxy-phenyl)-2-methyl-but-2-enyl]-benzenesulfonamide (5b).**



**5b**

To a solution of Ir(cod)<sub>2</sub>BARF (12.7 mg, 0.01 mmol, 5 mol%), BIPHEP (5.2 mg, 0.01 mmol, 5 mol%), triphenylacetic acid (2.9 mg, 0.01 mmol, 5 mol%) and Na<sub>2</sub>SO<sub>4</sub> (57 mg, 200 mol%) in toluene (4 mL, 0.05 M) was added N-(3-methoxy-benzylidene)-benzenesulfonamide (**5a**) (55.1 mg, 0.2 mmol, 100 mol%). The system was purged with argon gas followed by hydrogen gas. A 1 mL vial was charged with 2-butyne (0.2 mL, excess) and equipped with a gas balloon containing hydrogen gas (1 atm). The mixture of 2-butyne and hydrogen gas (1 atm) was introduced into the reaction vessel *via* cannula. The reaction was allowed to stir at 60 °C under 1 atm of hydrogen and 2-butyne gas mixture for 24 hours. Flash column chromatography (SiO<sub>2</sub>, 80% Petroleum Ether, 16% CHCl<sub>3</sub>, 4% EtOAc) provides the title compound (49.0 mg) as white crystals (74% yield).

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.34, 60% Petroleum Ether, 30% CHCl<sub>3</sub>, 10% EtOAc.

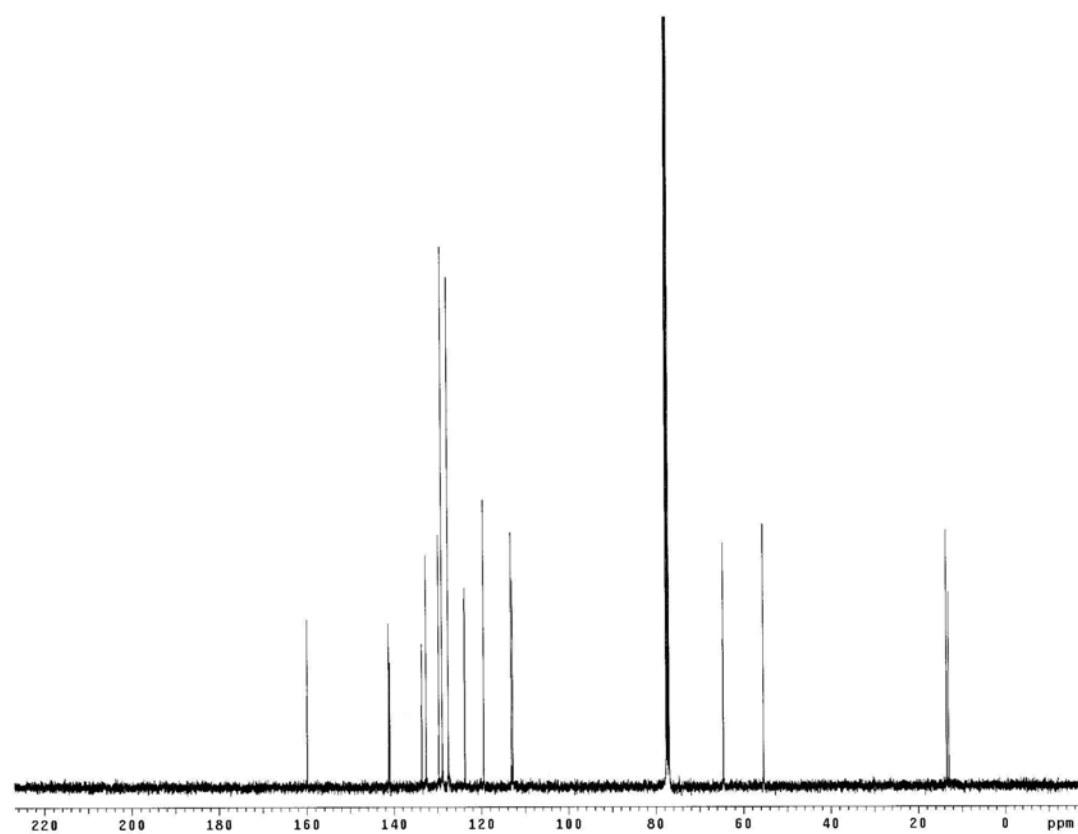
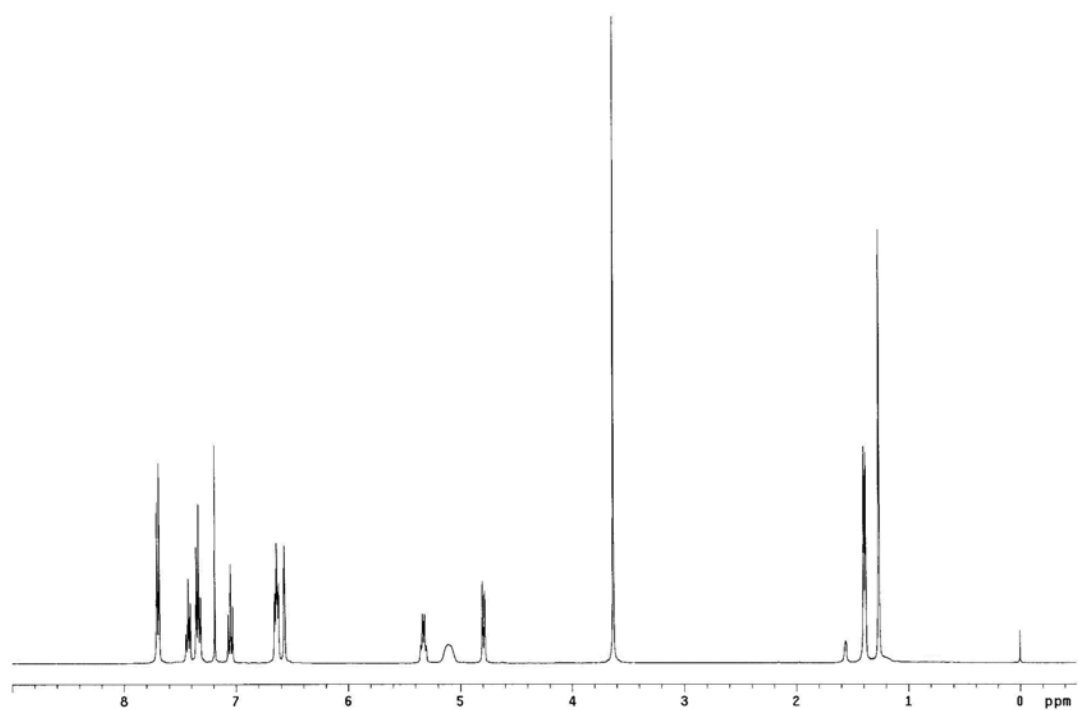
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.70 (d, *J* = 7.2 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.60-6.68 (m, 2H), 6.57 (s, 1H), 5.33 (q, *J* = 6.4 Hz, 1H), 5.11 (br. s 1H), 4.79 (d, *J* = 8.0 Hz, 1H), 3.63 (s, 3H), 1.39 (d, *J* = 6.4 Hz, 3H), 1.26 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 159.85, 141.16, 140.87, 132.54, 129.66, 128.88, 127.48, 123.72, 119.41, 113.09, 112.76, 64.53, 55.39, 13.44, 12.96.

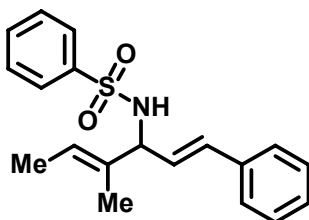
**HRMS** Calcd. for C<sub>18</sub>H<sub>22</sub>NO<sub>3</sub>S (M+1): 332.1320, Found: 332.1324.

**FTIR**(neat): 3279, 3064, 2919, 2860, 1600, 1488, 1448, 1327, 1287, 1265, 1161, 1092, 1039, 917, 808, 781, 756, 720, 689, 596 cm<sup>-1</sup>

**M.P.** 78~79 °C



**(E)-N-(2-Methyl-1-styryl-but-2-enyl)-benzenesulfonamide (6b).**



**6b**

To a solution of Ir(cod)<sub>2</sub>BARF (12.7 mg, 0.01 mmol, 5 mol%), BIPHEP (5.2 mg, 0.01 mmol, 5 mol%), triphenylacetic acid (2.9 mg, 0.01 mmol, 5 mol%) and Na<sub>2</sub>SO<sub>4</sub> (57 mg, 200 mol%) in toluene (4 mL, 0.05 M) was added N-(3-phenyl-allylidene)-benzenesulfonamide (**6a**) (54.3 mg, 0.2 mmol, 100 mol%). The system was purged with argon gas followed by hydrogen gas. A 1 mL vial was charged with 2-butyne (0.2 mL, excess) and equipped with a gas balloon containing hydrogen gas (1 atm). The mixture of 2-butyne and hydrogen gas (1 atm) was introduced into the reaction vessel *via* cannula. The reaction was allowed to stir at 60 °C under 1 atm of hydrogen and 2-butyne gas mixture for 24 hours. Flash column chromatography (SiO<sub>2</sub>, 80% Petroleum Ether, 16% CHCl<sub>3</sub>, 4% EtOAc) provides the title compound (55.7 mg) as white crystals (85% yield).

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.44, 60% Petroleum Ether, 30% CHCl<sub>3</sub>, 10% EtOAc.

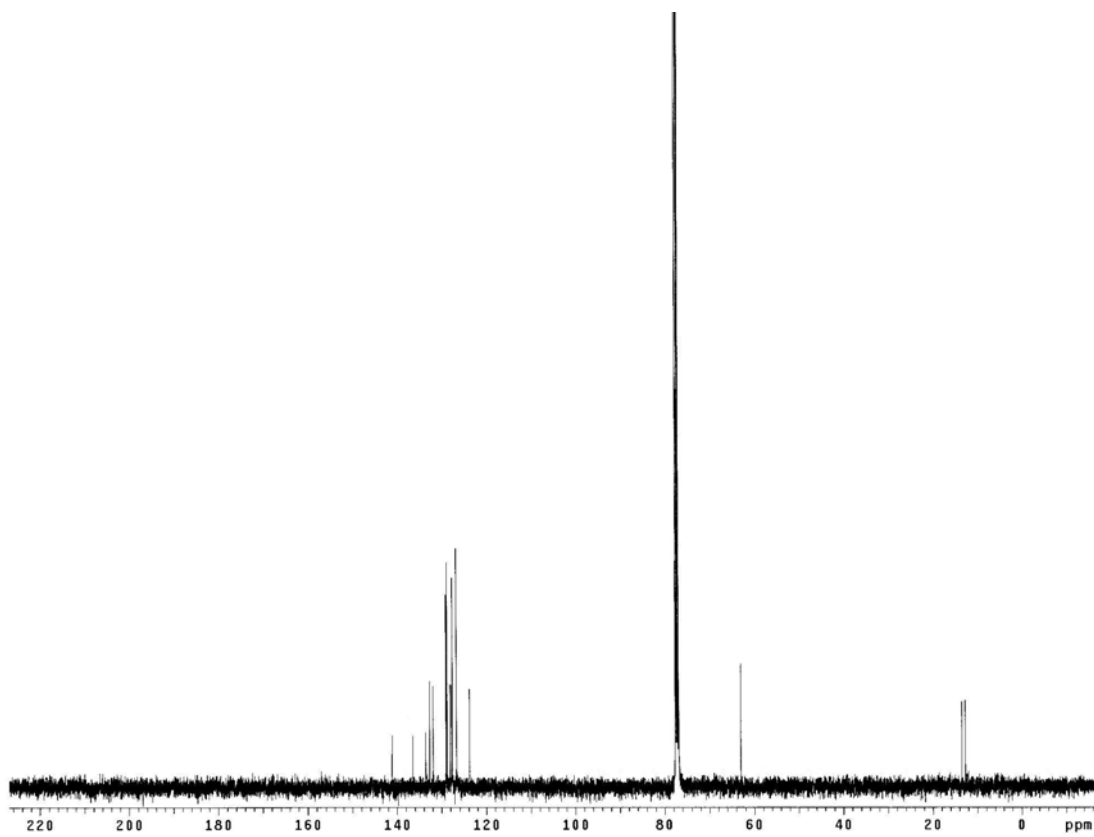
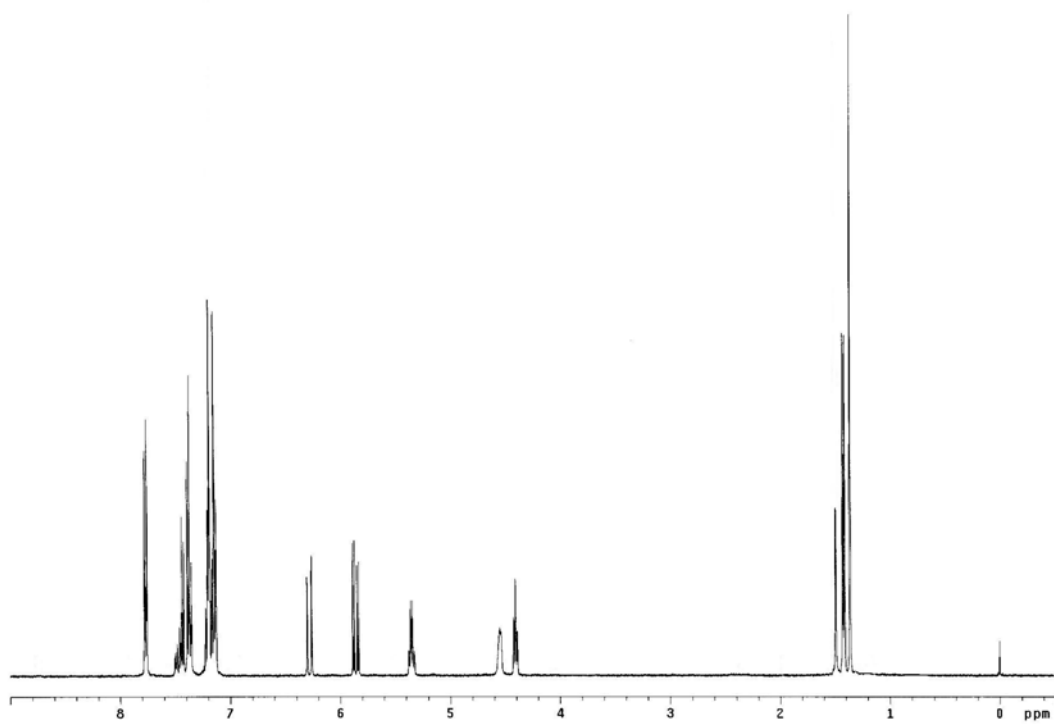
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.77 (d, *J* = 7.6 Hz, 2H), 7.34-7.45 (m, 3H), 7.12-7.24 (m, 5H), 6.28 (d, *J* = 16 Hz, 1H), 5.86 (dd, *J* = 16 Hz, *J* = 6.4 Hz, 1H), 5.35 (q, *J* = 6.8 Hz, 1H), 4.55 (br. s, 1H), 4.41 (dd, *J* = 6.4 Hz, *J* = 6.4, 1H), 1.42 (d, *J* = 6.8 Hz, 3H), 1.36 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 141.09, 136.41, 133.50, 132.64, 131.89, 128.96, 128.74, 128.06, 127.75, 127.60, 126.65, 123.76, 63.01, 13.46, 12.70.

**HRMS** Calcd. for C<sub>19</sub>H<sub>22</sub>NO<sub>2</sub>S (M+1): 328.1371, Found: 328.1372.

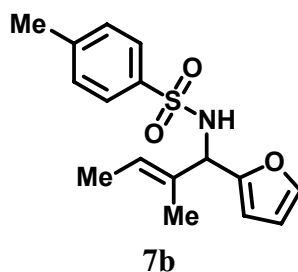
**FTIR**(neat): 3273, 3027, 2918, 2361, 1578, 1496, 1447, 1324, 1160, 1092, 1070, 1027, 967, 922, 786, 721, 689, 586, 555 cm<sup>-1</sup>

**M.P.** 97~98 °C





**(E)-N-(1-Furan-2-yl-2-methyl-but-2-enyl)-4-methyl-benzenesulfonamide (7b).**



To a solution of Ir(cod)<sub>2</sub>BARF (12.7 mg, 0.01 mmol, 5 mol%), BIPHEP (5.2 mg, 0.01 mmol, 5 mol%), triphenylacetic acid (2.9 mg, 0.01 mmol, 5 mol%) and Na<sub>2</sub>SO<sub>4</sub> (57 mg, 200 mol%) in toluene (4 mL, 0.05 M) was added N-furan-2-ylmethylene-4-methyl-benzenesulfonamide (**7a**) (49.9 mg, 0.2 mmol, 100 mol%). The system was purged with argon gas followed by hydrogen gas. A 1 mL vial was charged with 2-butyne (0.2 mL, excess) and equipped with a gas balloon containing hydrogen gas (1 atm). The mixture of 2-butyne and hydrogen gas (1 atm) was introduced into the reaction vessel *via* cannula. The reaction was allowed to stir at 60 °C under 1 atm of hydrogen and 2-butyne gas mixture for 24 hours. Flash column chromatography (SiO<sub>2</sub>, 80% Petroleum Ether, 16% CHCl<sub>3</sub>, 4% EtOAc) provides the title compound (50.1 mg) as white crystals (82% yield).

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.42, 60% Petroleum Ether, 30% CHCl<sub>3</sub>, 10% EtOAc.

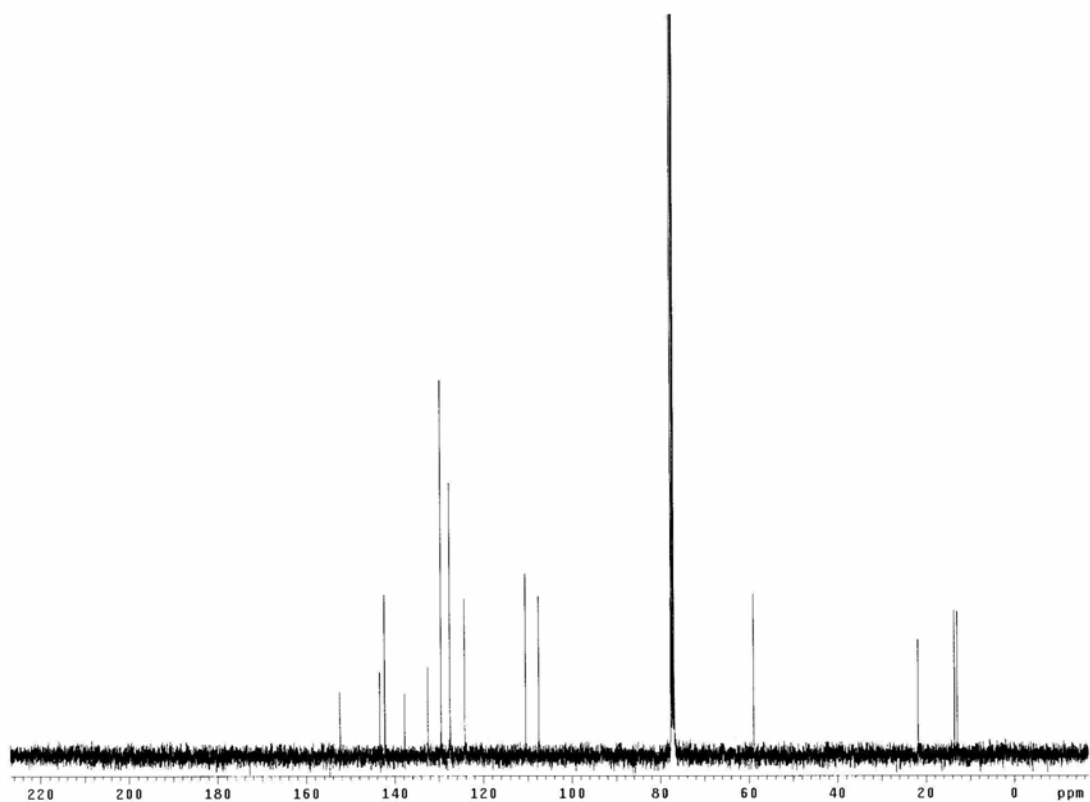
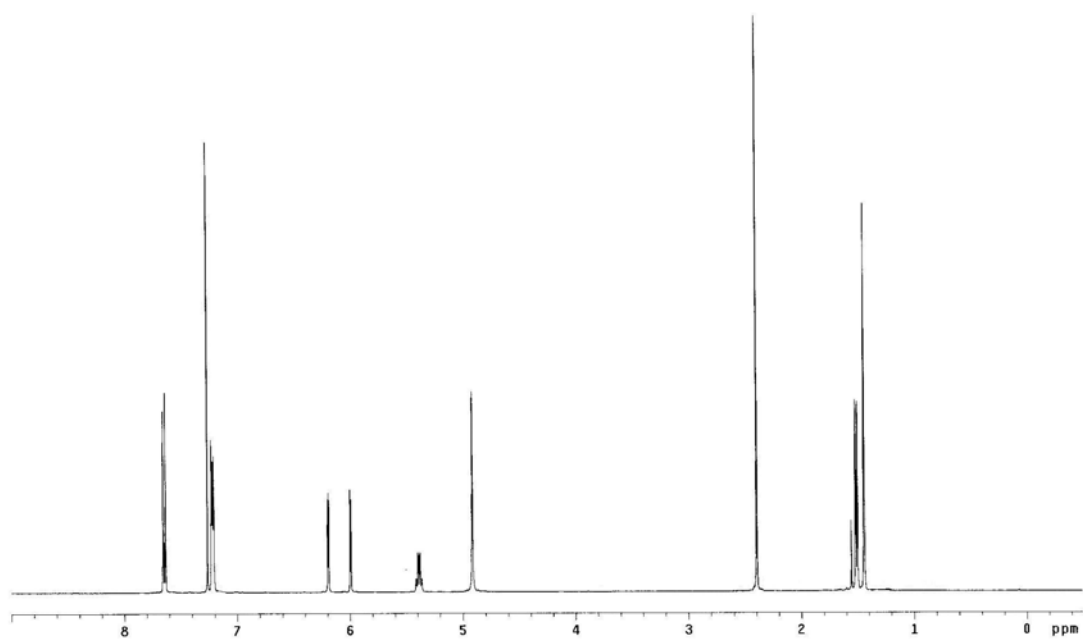
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.64 (d, *J* = 8.0 Hz, 2H), 7.18-7.23 (m, 3H), 6.19 (dd, *J* = 3.4 Hz, *J* = 2.0 Hz, 1H), 5.99 (d, *J* = 3.4 Hz, 1H), 5.39 (q, *J* = 6.8 Hz, 1H), 4.91 (s, 2H), 2.39 (s, 3H), 1.51 (d, *J* = 6.8 Hz, 3H), 1.44 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 152.34, 143.34, 142.25, 137.77, 132.47, 129.49, 127.46, 124.17, 110.45, 107.46, 58.96, 21.72, 13.53, 12.90.

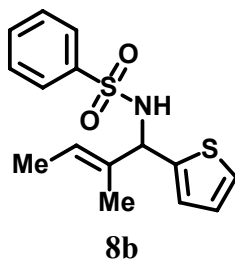
**HRMS** Calcd. for C<sub>16</sub>H<sub>20</sub>NO<sub>3</sub>S (M+1): 306.1164, Found: 306.1168.

**FTIR**(neat): 3276, 2918, 2850, 2360, 1652, 1497, 1436, 1324, 1162, 1093, 1011, 921, 811, 734, 667, 598 cm<sup>-1</sup>

**M.P.** 88~89 °C



**(E)-N-(2-Methyl-1-thiophen-2-yl-but-2-enyl)-benzenesulfonamide (8b).**



To a solution of Ir(cod)<sub>2</sub>BARF (12.7 mg, 0.01 mmol, 5 mol%), BIPHEP (5.2 mg, 0.01 mmol, 5 mol%), triphenylacetic acid (2.9 mg, 0.01 mmol, 5 mol%) and Na<sub>2</sub>SO<sub>4</sub> (57 mg, 200 mol%) in toluene (4 mL, 0.05 M) was added N-thiophen-2-ylmethylene-benzenesulfonamide (**8a**) (50.3 mg, 0.2 mmol, 100 mol%). The system was purged with argon gas followed by hydrogen gas. A 1 mL vial was charged with 2-butyne (0.2 mL, excess) and equipped with a gas balloon containing hydrogen gas (1 atm). The mixture of 2-butyne and hydrogen gas (1 atm) was introduced into the reaction vessel *via* cannula. The reaction was allowed to stir at 60 °C under 1 atm of hydrogen and 2-butyne gas mixture for 24 hours. Flash column chromatography (SiO<sub>2</sub>, 80% Petroleum Ether, 16% CHCl<sub>3</sub>, 4% EtOAc) provides the title compound (50.0 mg) as white crystals (81% yield).

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.42, 60% Petroleum Ether, 30% CHCl<sub>3</sub>, 10% EtOAc

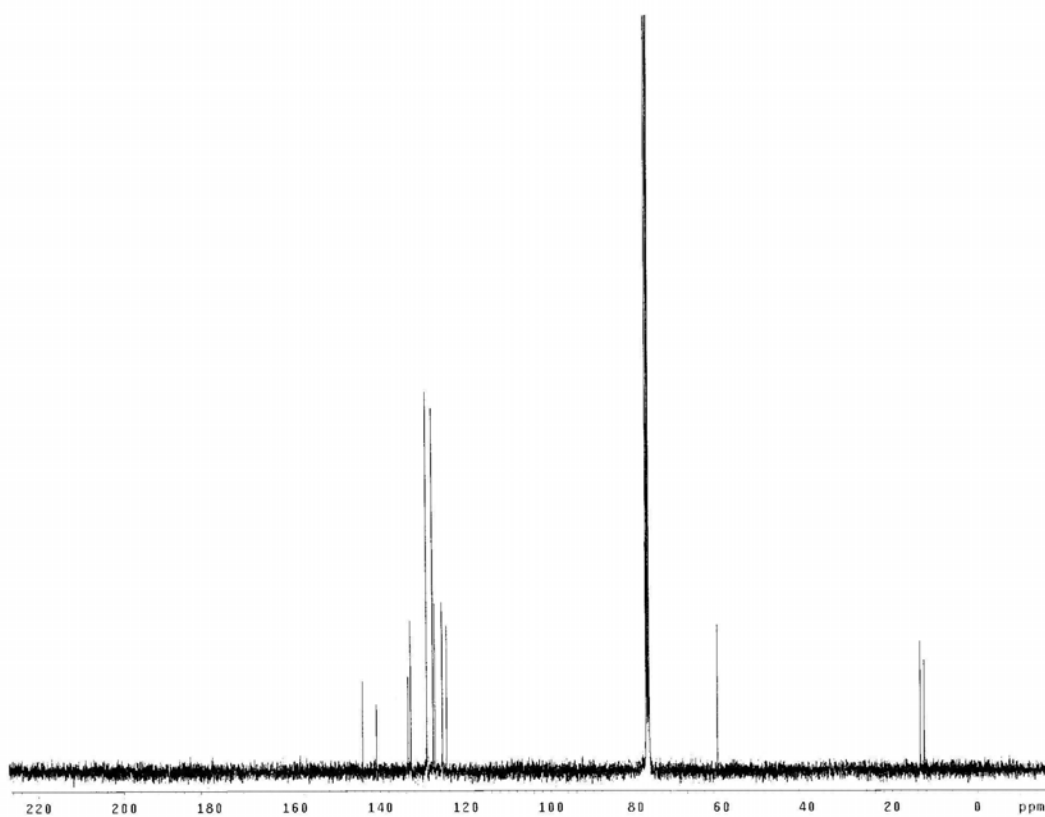
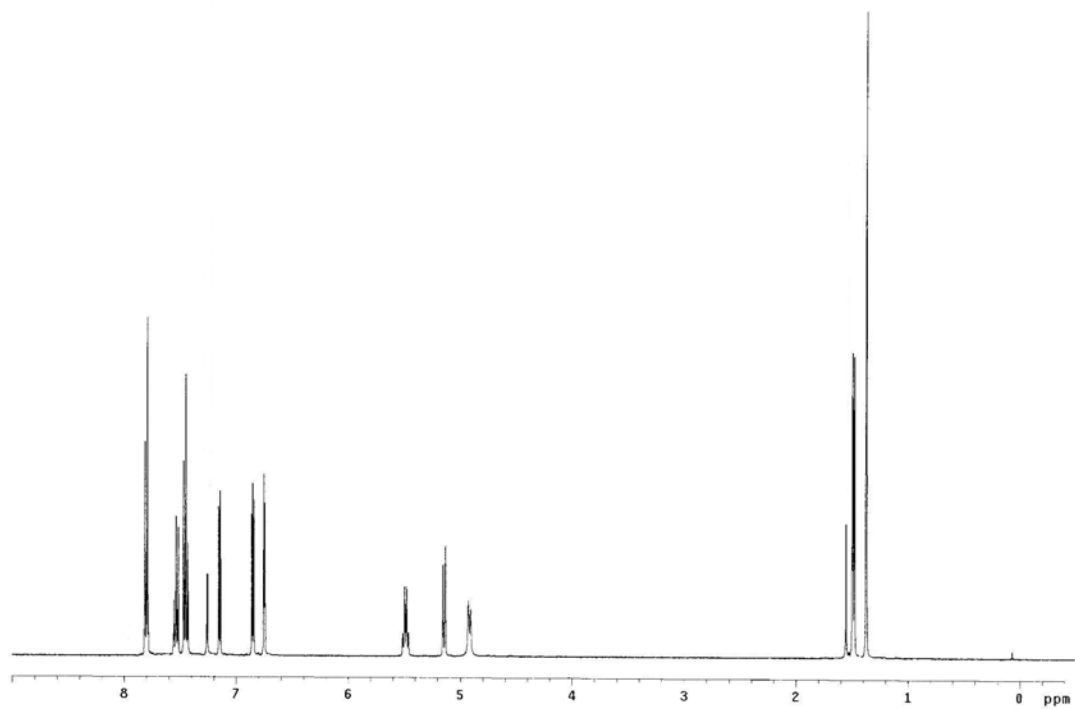
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.80 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.15 (dd, *J* = 1.2 Hz, *J* = 5.2 Hz, 1H), 6.85 (dd, *J* = 3.6 Hz, *J* = 5.2 Hz, 1H), 6.74-6.77 (m, 1H), 5.49 (q, *J* = 7.0 Hz, 1H), 5.14 (d, *J* = 8.0 Hz, 1H), 4.92 (d, *J* = 8.0 Hz, 1H), 1.48 (d, *J* = 7.0 Hz, 3H), 1.37 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 144.04, 140.77, 133.37, 132.74, 128.95, 127.53, 127.08, 125.41, 125.34, 124.35, 60.97, 13.42, 12.46.

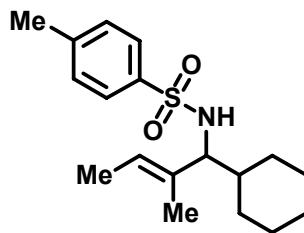
**HRMS** Calcd. for C<sub>15</sub>H<sub>18</sub>NO<sub>2</sub>S<sub>2</sub> (M+1): 308.0779, Found: 308.0775.

**FTIR**(neat): 3261, 2916, 1574, 1478, 1430, 1379, 1321, 1289, 1227, 1161, 1092, 1032, 920, 850, 802, 753, 722, 701, 686, 624, 579, 553 cm<sup>-1</sup>

**M.P.** 137~138 °C



**(E)-N-(1-Cyclohexyl-2-methyl-but-2-enyl)-4-methyl-benzenesulfonamide (9b).**



**9b**

To a solution of Ir(cod)<sub>2</sub>BARF (12.7 mg, 0.01 mmol, 5 mol%), BIPHEP (5.2 mg, 0.01 mmol, 5 mol%), triphenylacetic acid (2.9 mg, 0.01 mmol, 5 mol%) and Na<sub>2</sub>SO<sub>4</sub> (57 mg, 200 mol%) in toluene (4 mL, 0.05 M) was added N-cyclohexylmethylene-4-methyl-benzenesulfonamide (**9a**) (53.1 mg, 0.2 mmol, 100 mol%). The system was purged with argon gas followed by hydrogen gas. A 1 mL vial was charged with 2-butyne (0.2 mL, excess) and equipped with a gas balloon containing hydrogen gas (1 atm). The mixture of 2-butyne and hydrogen gas (1 atm) was introduced into the reaction vessel *via* cannula. The reaction was allowed to stir at 60 °C under 1 atm of hydrogen and 2-butyne gas mixture for 24 hours. Flash column chromatography (SiO<sub>2</sub>, 80% Petroleum Ether, 16% CHCl<sub>3</sub>, 4% EtOAc) provides the title compound (48.5 mg) as white crystals (75% yield).

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.54, 60% Petroleum Ether, 30% CHCl<sub>3</sub>, 10% EtOAc.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.65 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 5.07 (q, *J* = 6.8 Hz, 1H), 4.73 (d, *J* = 8.4 Hz, 1H), 3.39 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 2.40 (s, 3H), 1.97 (d, *J* = 13.6 Hz, 1H), 1.54-1.78 (m, 3H), 1.29 (d, *J* = 6.8 Hz, 3H),\* 1.17 (s, 3H),\* 1.04-1.42 (m, 5H),\* 0.84-0.98 (m, 1H), 0.70-0.80 (m, 1H).

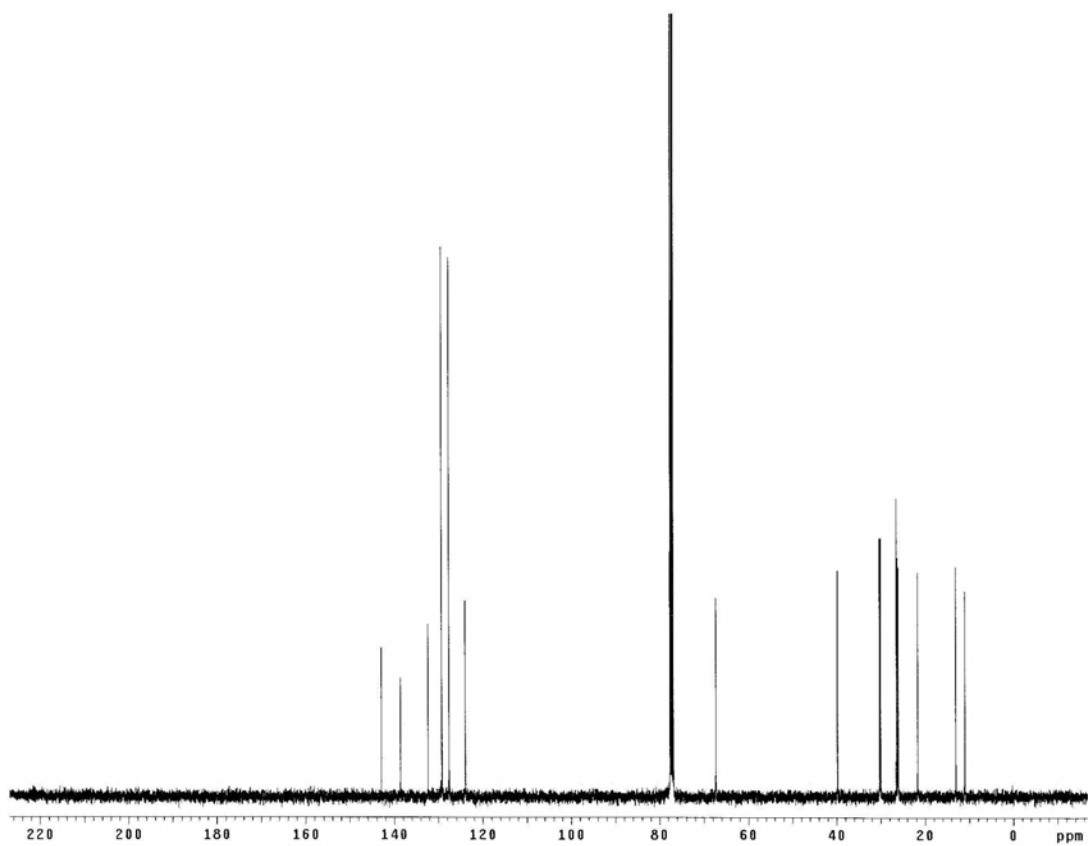
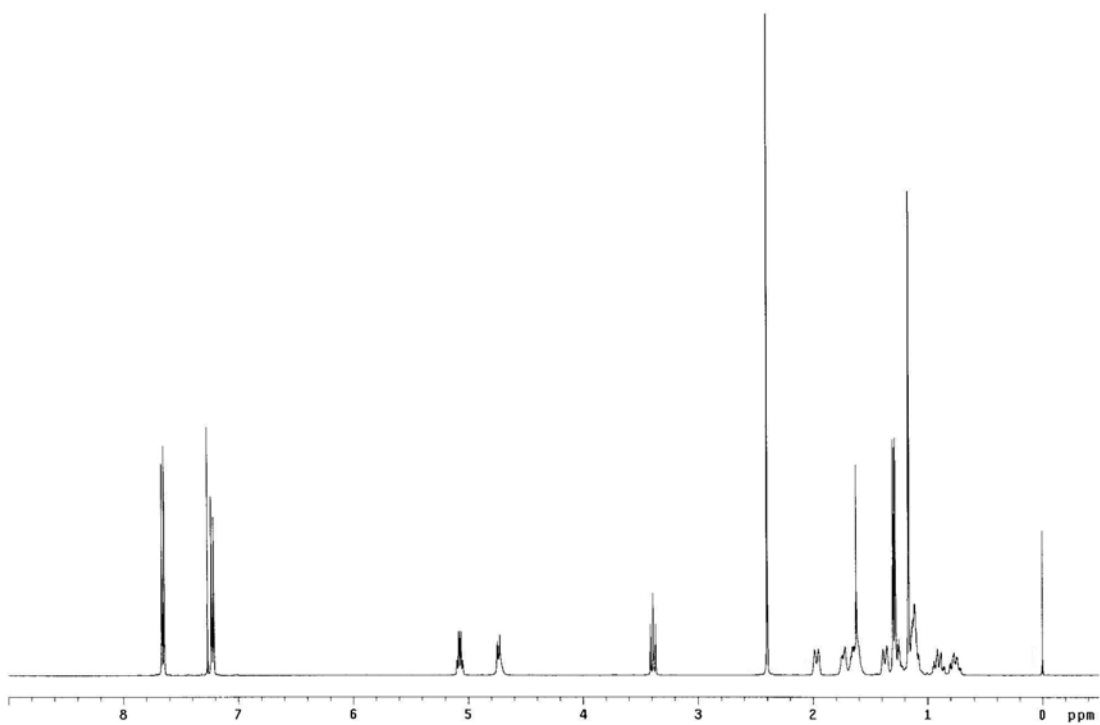
\* signals overlap.

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 142.86, 138.59, 132.28, 129.20, 127.55, 123.91, 67.31, 39.81, 30.23, 30.05, 26.48, 26.19, 26.09, 21.69, 13.05, 11.03.

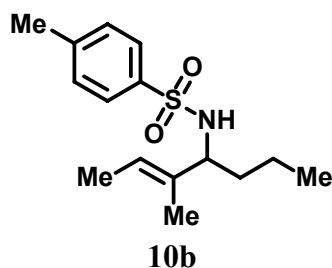
**HRMS** Calcd. for C<sub>18</sub>H<sub>28</sub>NO<sub>2</sub>S (M+1): 322.1841, Found: 322.1840.

**FTIR**(neat): 3431, 2922, 2851, 2360, 1647, 1558, 1507, 1448, 1322, 1158, 1094, 1030, 813, 668, 569 cm<sup>-1</sup>

**M.P.** 140~141 °C



**(E)-4-Methyl-N-(2-methyl-1-propyl-but-2-enyl)-benzenesulfonamide (10b).**



To a solution of Ir(cod)<sub>2</sub>BARF (12.7 mg, 0.01 mmol, 5 mol%), BIPHEP (5.2 mg, 0.01 mmol, 5 mol%), triphenylacetic acid (2.9 mg, 0.01 mmol, 5 mol%) and Na<sub>2</sub>SO<sub>4</sub> (57 mg, 200 mol%) in toluene (4 mL, 0.05 M) was added N-Butylidene-4-methyl-benzenesulfonamide (**10a**) (45 mg, 0.2 mmol, 100 mol%). The system was purged with argon gas followed by hydrogen gas. A 1 mL vial was charged with 2-butyne (0.2 mL, excess) and equipped with a gas balloon containing hydrogen gas (1 atm). The mixture of 2-butyne and hydrogen gas (1 atm) was introduced into the reaction vessel *via* cannula. The reaction was allowed to stir at 60 °C under 1 atm of hydrogen and 2-butyne gas mixture for 24 hours. Flash column chromatography (SiO<sub>2</sub>, 80% Petroleum Ether, 16% CHCl<sub>3</sub>, 4% EtOAc) provides the title compound (38.1 mg) as white crystals (68% yield).

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.48, 60% Petroleum Ether, 30% CHCl<sub>3</sub>, 10% EtOAc.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.59 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.14 (q, *J* = 6.4 Hz, 1H), 4.30 (br. s, 1H), 3.63 (q, *J* = 7.4 Hz, 1H), 2.34 (s, 3H), 1.30 (d, *J* = 6.4 Hz, 3H),<sup>#</sup> 1.28-1.40 (m, 2H),<sup>#</sup> 1.13 (s, 3H),<sup>\*</sup> 1.02-1.21 (m, 2H),<sup>\*</sup> 0.77 (t, *J* = 7.2 Hz, 3H).

<sup>#</sup> signals overlap;

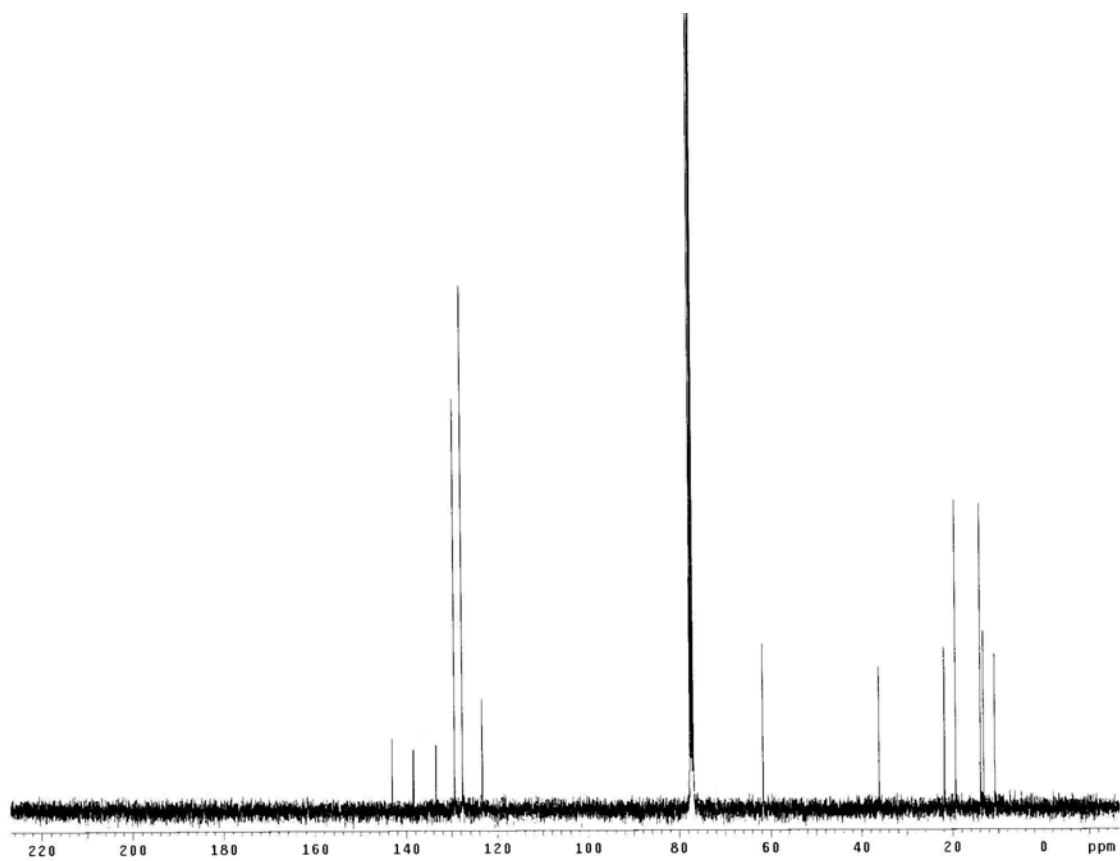
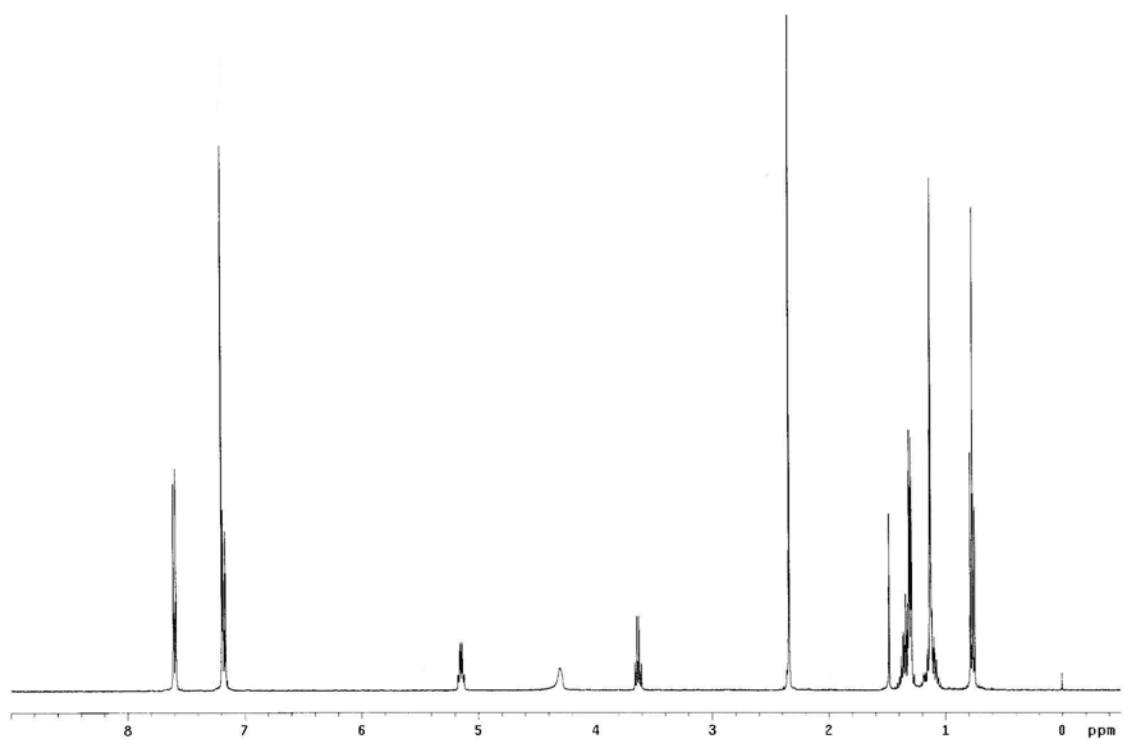
<sup>\*</sup> signals overlap.

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 143.05, 138.36, 133.40, 129.31, 127.59, 123.24, 61.65, 36.13, 21.71, 19.27, 13.84, 13.15, 10.68.

**HRMS** Calcd. for C<sub>15</sub>H<sub>24</sub>NO<sub>2</sub>S (M+1): 282.1518, Found: 282.1522.

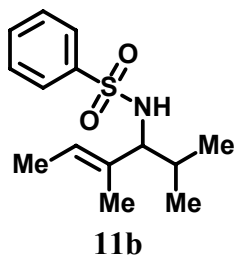
**FTIR**(neat): 3262, 2959, 2930, 2864, 2360, 1652, 1599, 1496, 1455, 1421, 1321, 1288, 1161, 1094, 1022, 926, 812, 668, 563 cm<sup>-1</sup>

**M.P.** 87~88 °C





**(E)-N-(1-Isopropyl-2-methyl-but-2-enyl)-benzenesulfonamide (11b).**



To a solution of Ir(cod)<sub>2</sub>BARF (12.7 mg, 0.01 mmol, 5 mol%), BIPHEP (5.2 mg, 0.01 mmol, 5 mol%), triphenylacetic acid (2.9 mg, 0.01 mmol, 5 mol%) and Na<sub>2</sub>SO<sub>4</sub> (57 mg, 200 mol%) in toluene (4 mL, 0.05 M) was added N-isobutyridene-benzenesulfonamide (**11a**) (42.3 mg, 0.2 mmol, 100 mol%). The system was purged with argon gas followed by hydrogen gas. A 1 mL vial was charged with 2-butyne (0.2 mL, excess) and equipped with a gas balloon containing hydrogen gas (1 atm). The mixture of 2-butyne and hydrogen gas (1 atm) was introduced into the reaction vessel *via* cannula. The reaction was allowed to stir at 60 °C under 1 atm of hydrogen and 2-butyne gas mixture for 24 hours. Flash column chromatography (SiO<sub>2</sub>, 80% Petroleum Ether, 16% CHCl<sub>3</sub>, 4% EtOAc) provides the title compound (38 mg) as white crystals (71% yield).

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.42, 60% Petroleum Ether, 30% CHCl<sub>3</sub>, 10% EtOAc

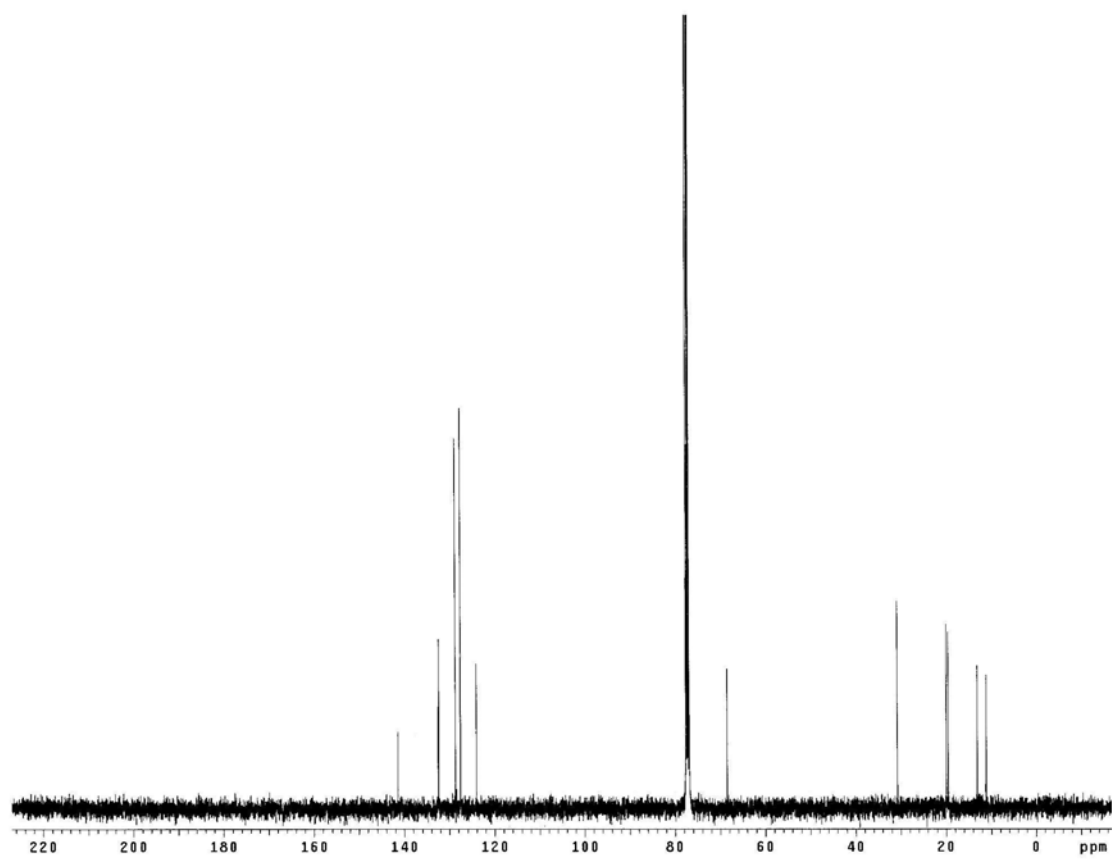
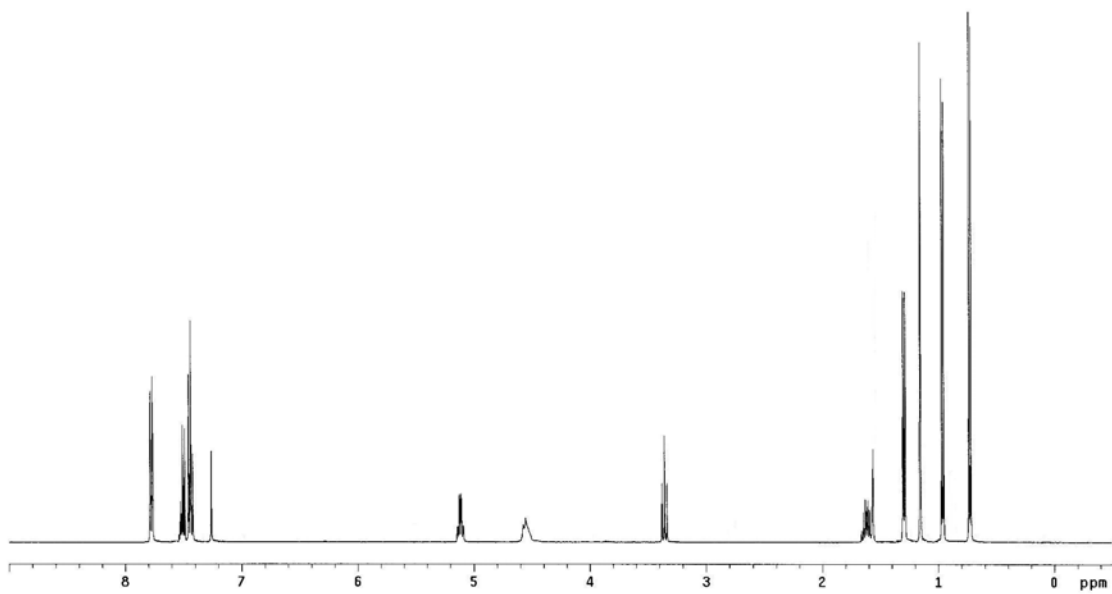
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.77 (d, *J* = 6.8 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 7.42-7.47 (m, 2H), 5.11 (q, *J* = 7.0 Hz, 1H), 4.30 (br. d, *J* = 8.4 Hz, 1H), 3.34 (t, *J* = 8.4 Hz, 1H), 1.58-1.68 (m, 1H), 1.29 (d, *J* = 6.8 Hz, 3H), 1.56 (s, 3H), 0.96 (d, *J* = 6.4 Hz, 3H), 0.73 (d, *J* = 6.4 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 141.35, 132.44, 132.31, 128.66, 127.52, 124.01, 68.46, 30.74, 19.94, 19.52, 13.07, 11.08.

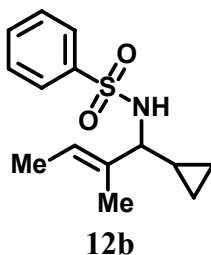
**HRMS** Calcd. for C<sub>14</sub>H<sub>22</sub>NO<sub>2</sub>S (M+1): 268.1371, Found: 268.1375.

**FTIR**(neat): 3264, 2961, 2921, 2871, 1448, 1430, 1381, 1319, 1289, 1162, 1094, 1035, 910, 866, 802, 754, 721, 688, 619, 590, 557 cm<sup>-1</sup>

**M.P.** 116~117 °C



**(E)-N-(1-Cyclopropyl-2-methyl-but-2-enyl)-benzenesulfonamide (12b).**



To a solution of Ir(cod)<sub>2</sub>BARF (12.7 mg, 0.01 mmol, 5 mol%), BIPHEP (5.2 mg, 0.01 mmol, 5 mol%), triphenylacetic acid (2.9 mg, 0.01 mmol, 5 mol%) and Na<sub>2</sub>SO<sub>4</sub> (57 mg, 200 mol%) in toluene (4 mL, 0.05 M) was added N-cyclopropylmethylene-benzenesulfonamide (**12a**) (42 mg, 0.2 mmol, 100 mol%). The system was purged with argon gas followed by hydrogen gas. A 1 mL vial was charged with 2-butyne (0.2 mL, excess) and equipped with a gas balloon containing hydrogen gas (1 atm). The mixture of 2-butyne and hydrogen gas (1 atm) was introduced into the reaction vessel *via* cannula. The reaction was allowed to stir at 60 °C under 1 atm of hydrogen and 2-butyne gas mixture for 24 hours. Flash column chromatography (SiO<sub>2</sub>, 80% Petroleum Ether, 16% CHCl<sub>3</sub>, 4% EtOAc) provides the title compound (46 mg) as white crystals (87% yield).

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.40, 60% Petroleum Ether, 30% CHCl<sub>3</sub>, 10% EtOAc.

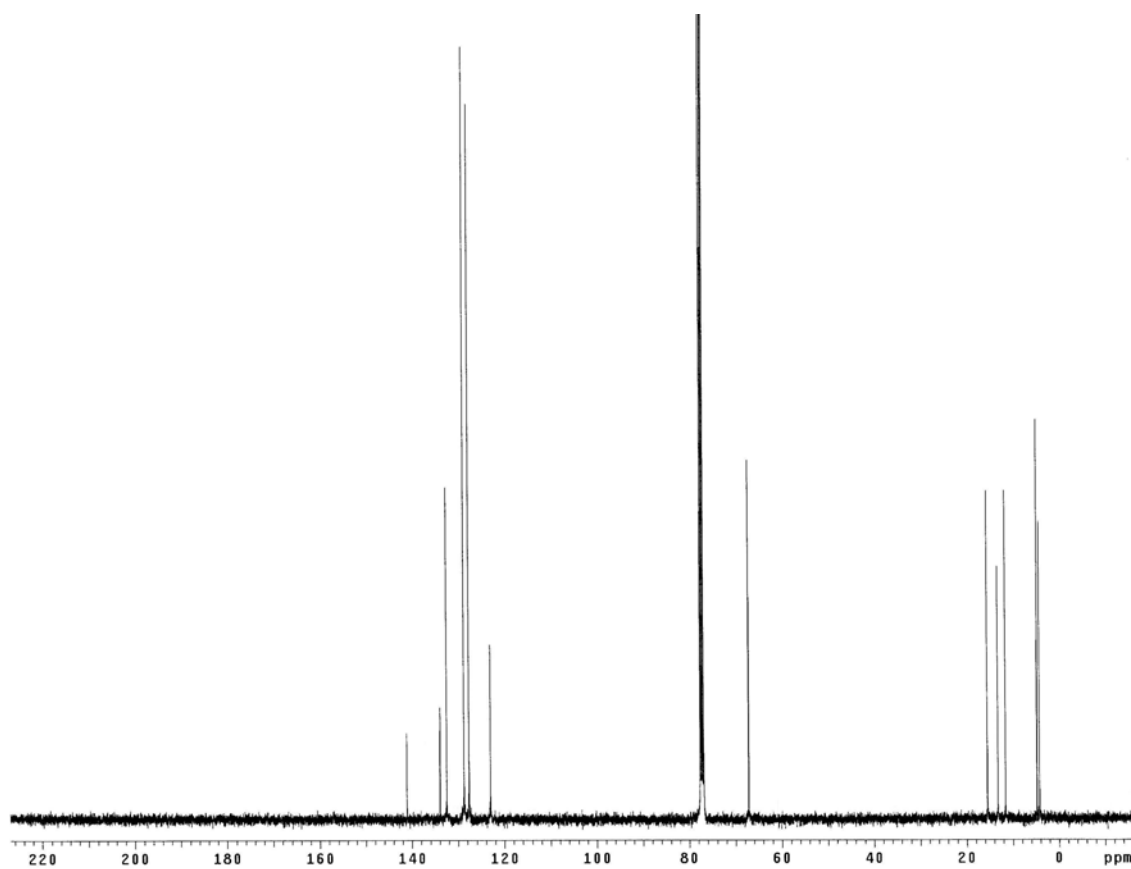
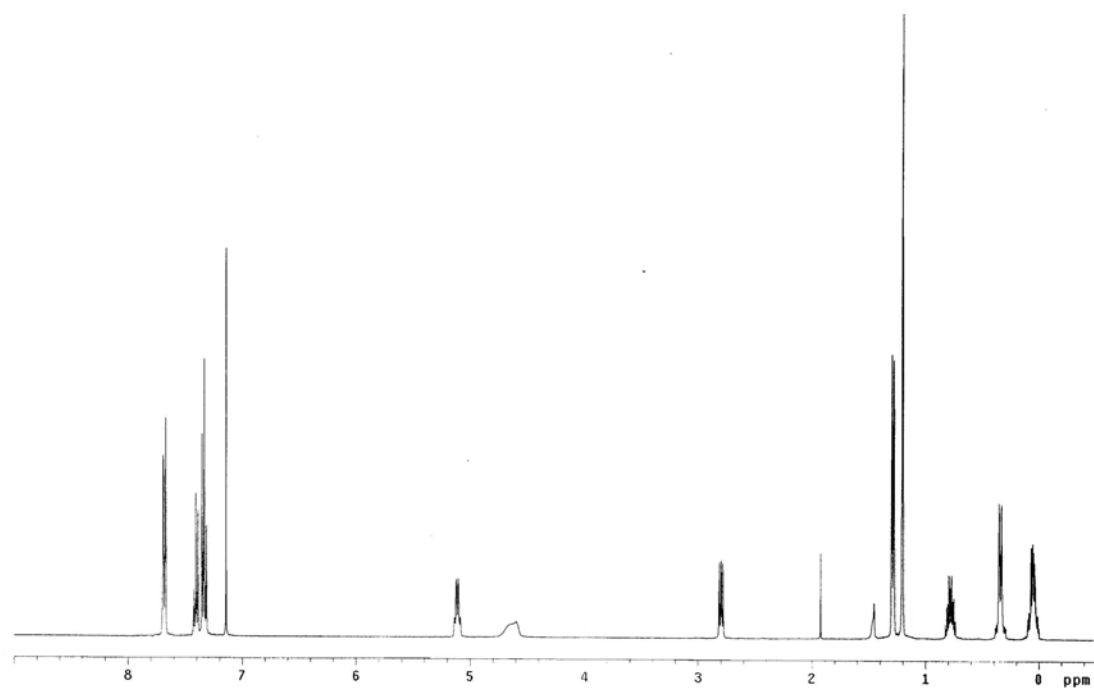
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.68 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.31-7.38 (m, 2H), 5.11 (q, *J* = 6.8 Hz, 1H), 4.59 (br. s, 1H), 2.79 (dd, *J* = 5.6 Hz, *J* = 9.2 Hz, 1H), 1.28 (d, *J* = 6.8 Hz, 3H), 1.20 (s, 3H), 0.72-0.84 (m, 1H), 0.28-0.40 (m, 2H), 0.00-0.12 (m, 2H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 141.11, 133.88, 132.46, 128.73, 127.64, 123.01, 67.18, 15.52, 13.23, 11.57, 4.76, 4.21

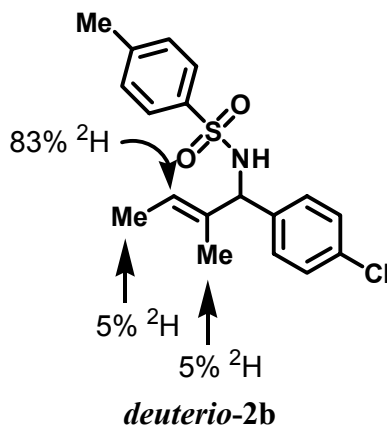
**HRMS** Calcd. for C<sub>14</sub>H<sub>20</sub>NO<sub>2</sub>S (M+1): 266.1215, Found: 266.1216.

**FTIR**(neat): 3273, 3069, 3006, 2919, 2861, 1448, 1432, 1380, 1320, 1288, 1162, 1093, 1032, 950, 901, 864, 831, 800, 754, 720, 688, 617, 587, 558 cm<sup>-1</sup>

**M.P.** 98~99 °C



**(E)-3-deuterio-N-[1-(4-Chloro-phenyl)-2-methyl-but-2-enyl]-4-methyl-benzenesulfonamide (deuterio-2b).**

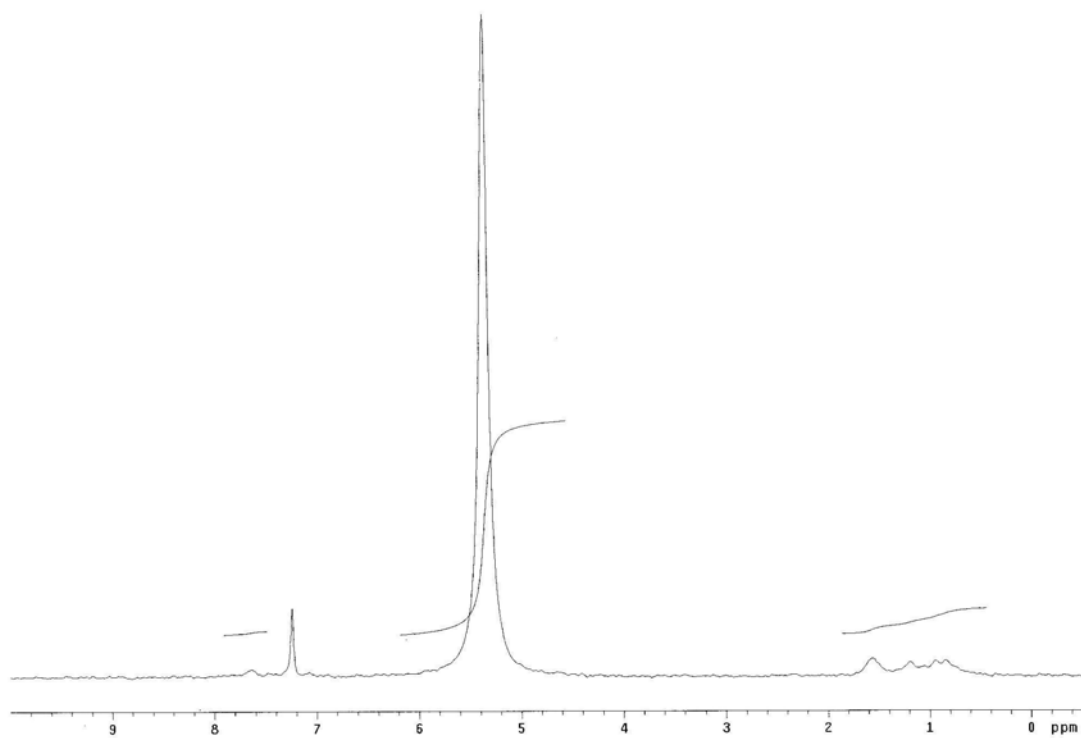
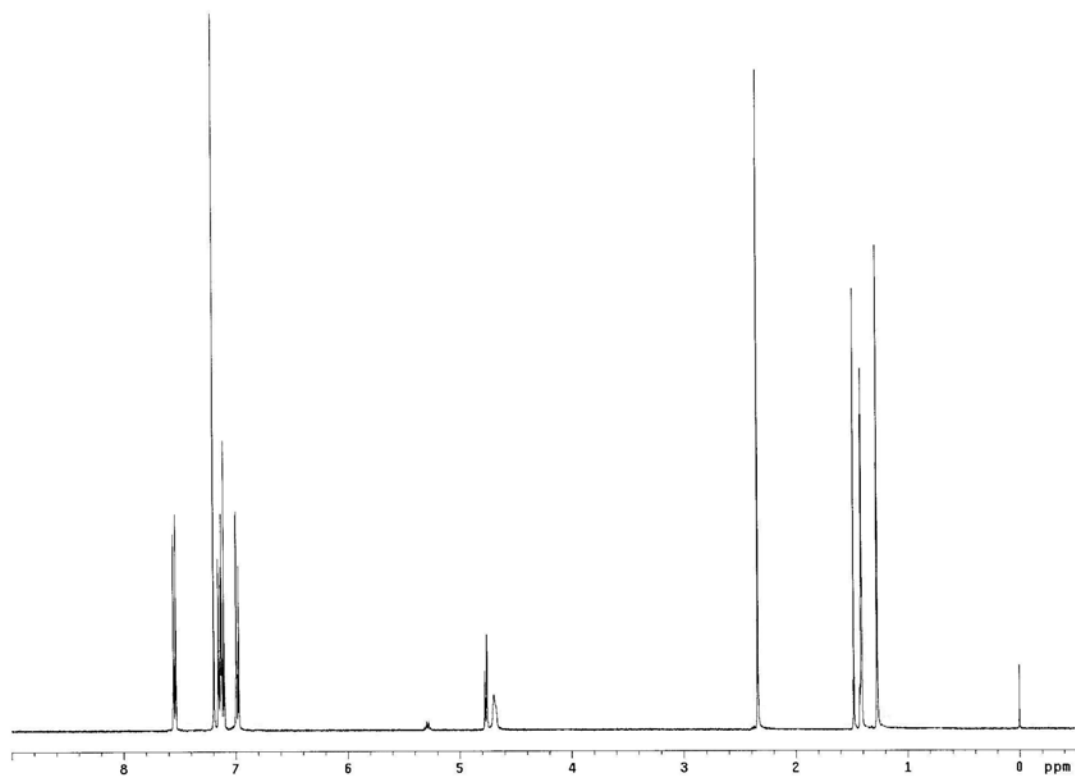


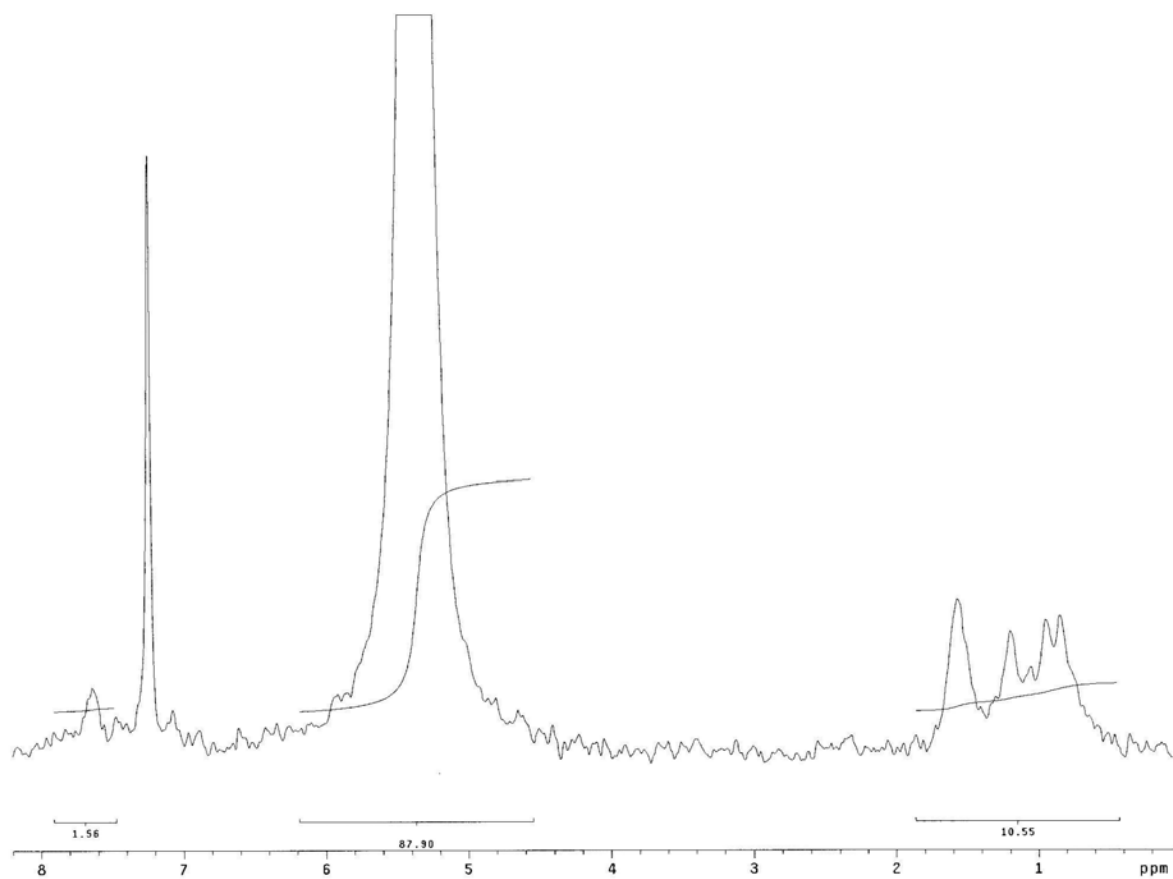
To a solution of Ir(cod)<sub>2</sub>BARF (12.7 mg, 0.01 mmol, 5 mol%), BIPHEP (5.2 mg, 0.01 mmol, 5 mol%), triphenylacetic acid (2.9 mg, 0.01 mmol, 5 mol%) and Na<sub>2</sub>SO<sub>4</sub> (57 mg, 200 mol%) in toluene (4 mL, 0.05 M) was added N-(4-chloro-benzylidene)-4-methyl-benzenesulfonamide (**2a**) (58.7 mg, 0.2 mmol, 100 mol%). The system was purged with argon gas followed by deuterium gas (99.6% D<sub>2</sub>). A 1 mL vial was charged with 2-butyne (0.2 mL, excess) and equipped with a gas balloon containing deuterium gas (99.6% D<sub>2</sub>, 1 atm). The mixture of 2-butyne and deuterium gas (99.6% D<sub>2</sub>, 1 atm) was introduced into the reaction vessel *via* cannula. The reaction was allowed to stir at 60 °C under 1 atm of deuterium (99.6% D<sub>2</sub>) and 2-butyne gas mixture for 24 hours. The title compound (**deuterio-2b**) was purified by flash column chromatography (SiO<sub>2</sub>, 80% Petroleum Ether, 16% CHCl<sub>3</sub>, 4% EtOAc) to furnish the title compound (45.1 mg) as white crystals (64% yield).

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.5, 60% Petroleum Ether, 30% CHCl<sub>3</sub>, 10% EtOAc

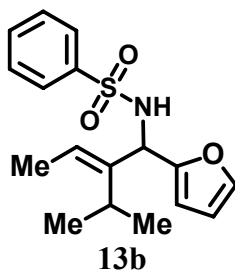
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.54 (d, *J* = 8.4 Hz, 2H), 7.08-7.18 (m, 4H), 6.98 (d, *J* = 8.4 Hz, 2H), 5.35 (q, *J* = 6.8 Hz, 0.17H), 4.76 (d, *J* = 8.0 Hz, 1H), 4.69 (br. s, 1H), 2.34 (s, 3H), 1.41 (s, 3H), 1.27 (s, 3H).

**<sup>2</sup>H NMR** (77 MHz, CHCl<sub>3</sub>): 5.36 (s, 0.87 <sup>2</sup>H), 1.01-1.80 (m, 0.05 <sup>2</sup>H) 0.40-1.00 (m, 0.05 <sup>2</sup>H).





**(E)-N-(1-(furan-2-yl)-2-isopropylbut-2-enyl)benzenesulfonamide (13b)**



To a solution of Ir(cod)<sub>2</sub>BARF (12.7 mg, 0.01 mmol, 5 mol%), BIPHEP (5.2 mg, 0.01 mmol, 5 mol%), triphenylacetic acid (2.9 mg, 0.01 mmol, 5 mol%), Na<sub>2</sub>SO<sub>4</sub> (57 mg, 0.4 mmol, 200 mol%) and (E)-N-(furan-2-ylmethylene)benzenesulfonamide (**13a**) (47.1mg, 0.2 mmol, 100mol%) in toluene (0.05 M, 4 mL) was added 4-methyl-2-pentyne (49.3mg 0.6 mmol, 300 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 60 °C under 1 atm of hydrogen for 6 hours (control by TLC). Flash column chromatography (SiO<sub>2</sub>, 20% EtOAc/hexane) provides the title compound (51 mg) as colorless oil (80% yield).

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.34, 30% EtOAc/hexane

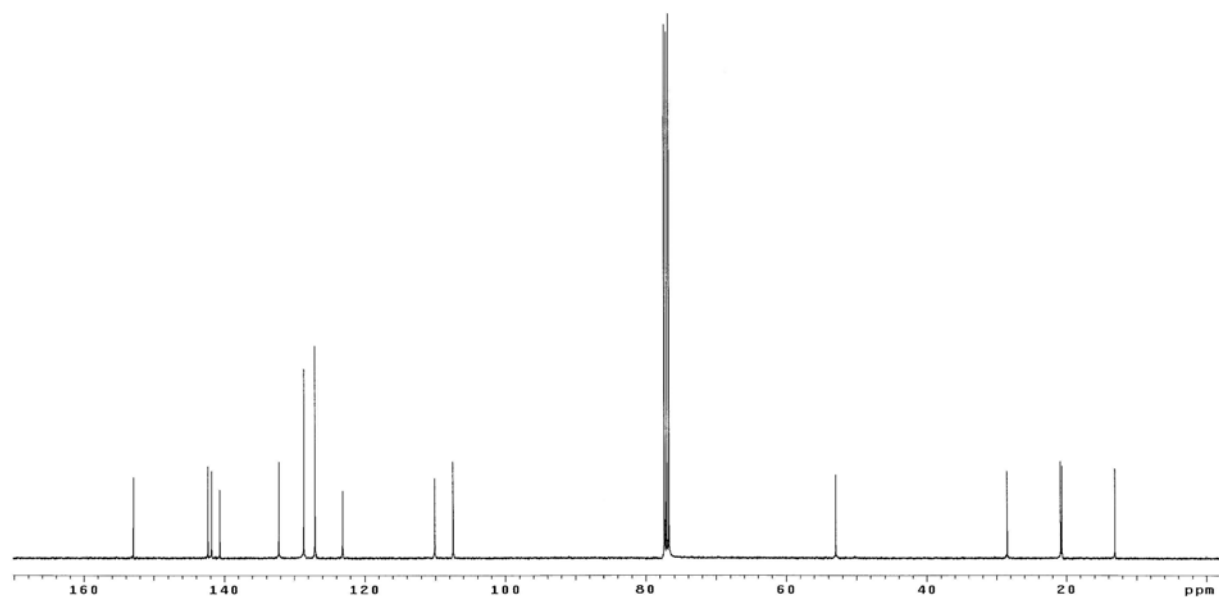
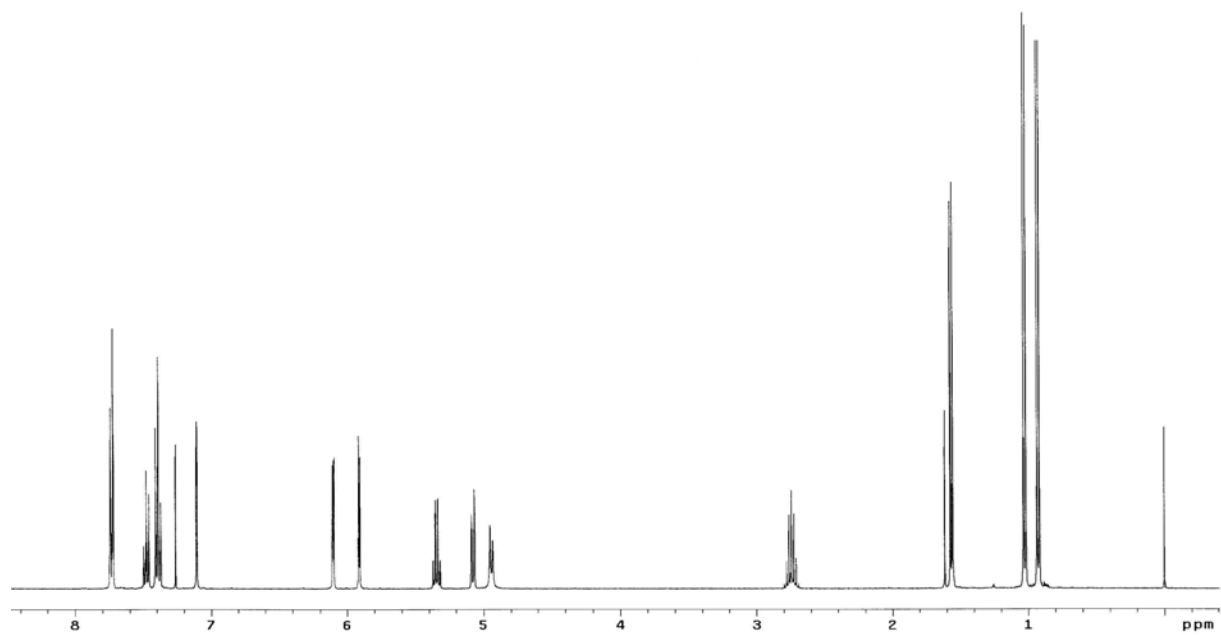
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.74 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.10 (d, *J* = 1.7 Hz, 1H), 6.10 (dd, *J* = 3.6, 1.7 Hz, 1H), 5.91 (d, *J* = 3.6 Hz, 1H), 5.34 (q, *J* = 6.4 Hz, 1H), 5.07 (d, *J* = 8.0 Hz, 1H), 4.94 (d, *J* = 8.0 Hz, 1H), 2.74 (hept, *J* = 7.2 Hz, 1H), 1.56 (d, *J* = 7.2 Hz, 3H), 1.02 (d, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 7.2 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 152.93, 142.34, 141.82, 140.64, 132.21, 128.65, 127.04, 123.10, 110.07, 107.48, 52.94, 28.47, 20.83, 20.64, 13.08

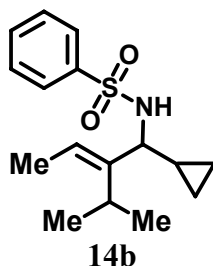
**HRMS** Calcd. for C<sub>17</sub>H<sub>22</sub>NO<sub>3</sub>S (M+1): 320.1320, Found: 320.1323

**FTIR** (neat): 3374, 3281, 3056, 2965, 2933, 2874, 2301, 1448, 1421, 1329, 1266, 1163, 1093, 1070, 1012, 912, 738, 705, 585 cm<sup>-1</sup>





**(E)-N-(1-cyclopropyl-2-isopropylbut-2-enyl)benzenesulfonamide (14b)**



To a solution of Ir(cod)<sub>2</sub>BARF (12.7 mg, 0.01 mmol, 5 mol%), BIPHEP (5.2 mg, 0.01 mmol, 5 mol%), triphenylacetic acid (2.9 mg, 0.01 mmol, 5 mol%), , Na<sub>2</sub>SO<sub>4</sub> (57 mg, 0.4 mmol, 200 mol%) and (E)-N-(cyclopropylmethylene)benzenesulfonamide (**12a**) (41.8mg, 0.2 mmol, 100mol%) in Toluene (0.05 M, 4 mL) was added 4-methyl-2-pentyne (49.3mg 0.6 mmol, 300 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 60 °C under 1 atm of hydrogen for 6 hours (control by TLC). Flash column chromatography (SiO<sub>2</sub>, 20% EtOAc/hexane) provides the title compound (42 mg) as colorless oil (71% yield).

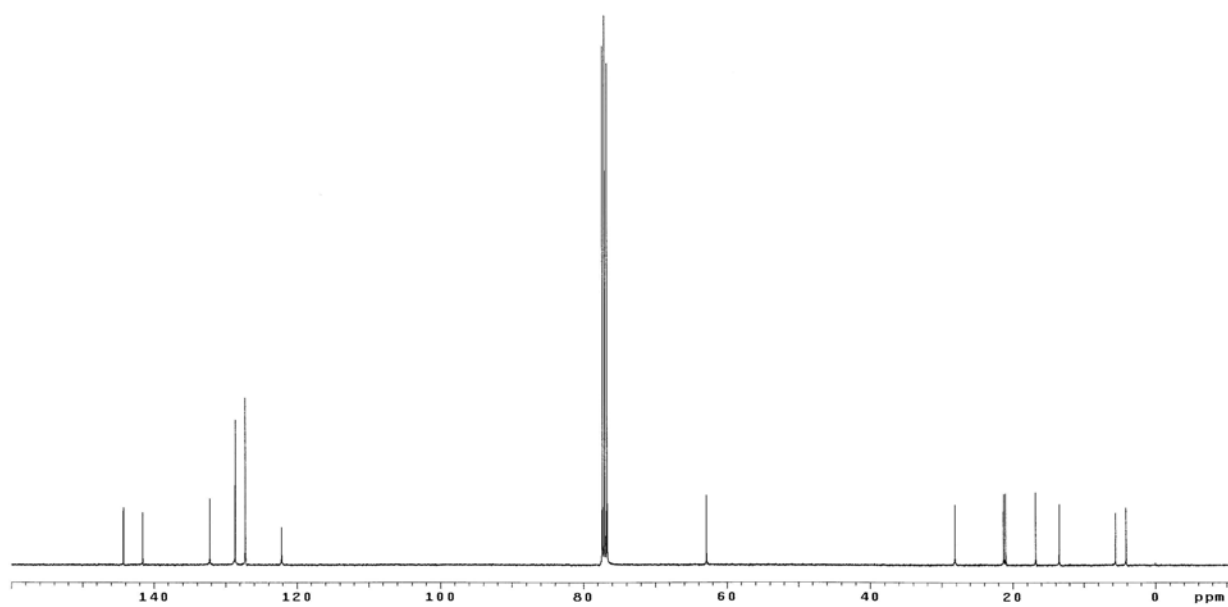
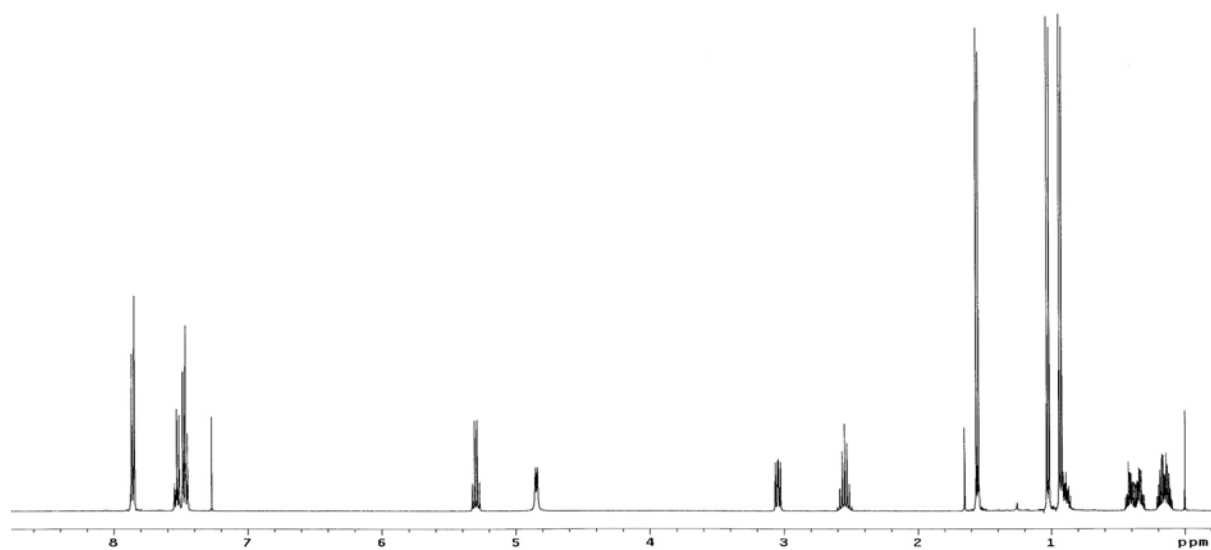
**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.34, 30% EtOAc/hexane.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.86 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 2H), 5.30 (q, *J* = 7.2 Hz, 1H), 4.88 (d, *J* = 6.4 Hz, 1H), 3.04 (dd, *J* = 8.8, 6.4 Hz, 1H), 2.55 (hept, *J* = 7.2 Hz, 1H), 1.55 (d, *J* = 7.2 Hz, 3H), 1.02 (d, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 7.2 Hz, 3H), 0.91 – 0.83 (m, 1H), 0.44 – 0.30 (m, 2H), 0.21 – 0.09 (m, 2H)

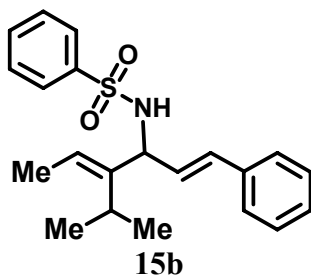
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 144.26, 141.56, 132.21, 128.66, 127.22, 122.14, 62.90, 28.11, 21.26, 20.99, 16.78, 13.44, 5.59, 4.10

**HRMS** Calcd. for C<sub>16</sub>H<sub>24</sub>NO<sub>2</sub>S(M+1): 294.1528, Found: 294.1529

**FTIR** (neat): 3382, 3282, 3062, 3006, 2965, 2933, 2873, 2255, 1448, 1421, 1323, 1266, 1159, 1095, 1072, 1027, 951, 864, 733, 689, 650, 588, 559 cm<sup>-1</sup>



**N-((1E,4E)-4-isopropyl-1-phenylhexa-1,4-dien-3-yl)benzenesulfonamide (15b)**



To a solution of Ir(cod)<sub>2</sub>BARF (12.7 mg, 0.01 mmol, 5 mol%), BIPHEP (5.2 mg, 0.01 mmol, 5 mol%), triphenylacetic acid (2.9 mg, 0.01 mmol, 5 mol%), Na<sub>2</sub>SO<sub>4</sub> (57 mg, 0.4 mmol, 200 mol%) and (E)-N-((E)-3-phenylallylidene)benzenesulfonamide (**6a**) (54.3mg, 0.2 mmol, 100mol%) in Toluene (0.1 M, 2 mL) was added 4-methyl-2-pentyne (49.3mg 0.6 mmol, 300 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 60 °C under 1 atm of hydrogen for 3 hours (control by TLC). Flash column chromatography (SiO<sub>2</sub>, 20% EtOAc/hexane) provides the title compound (45 mg) as colorless oil (62% yield).

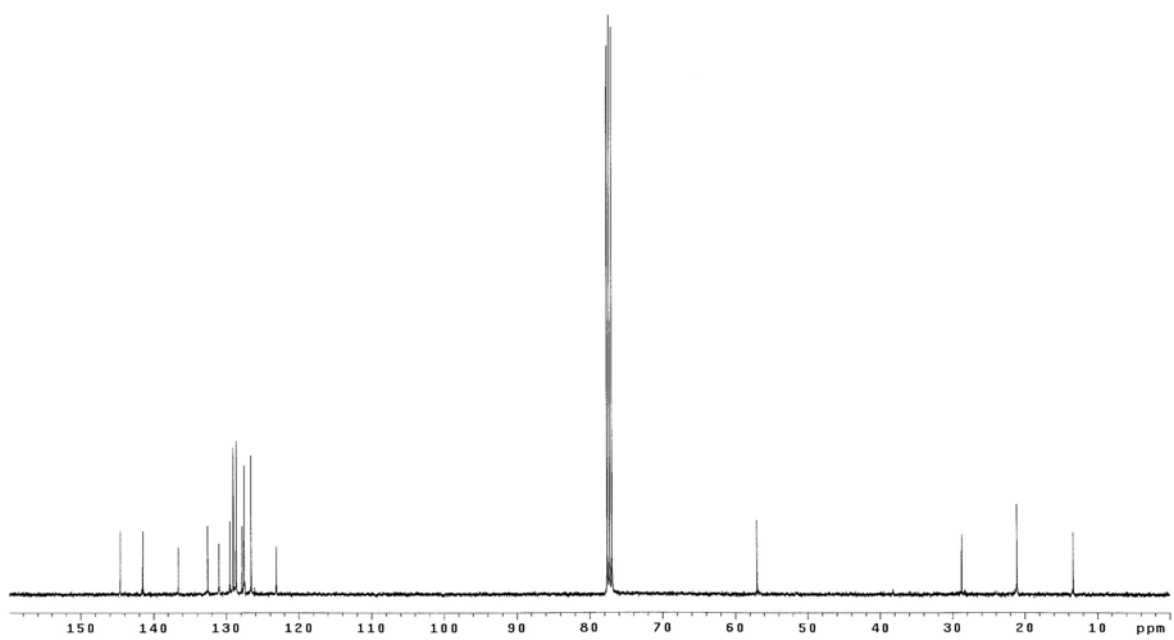
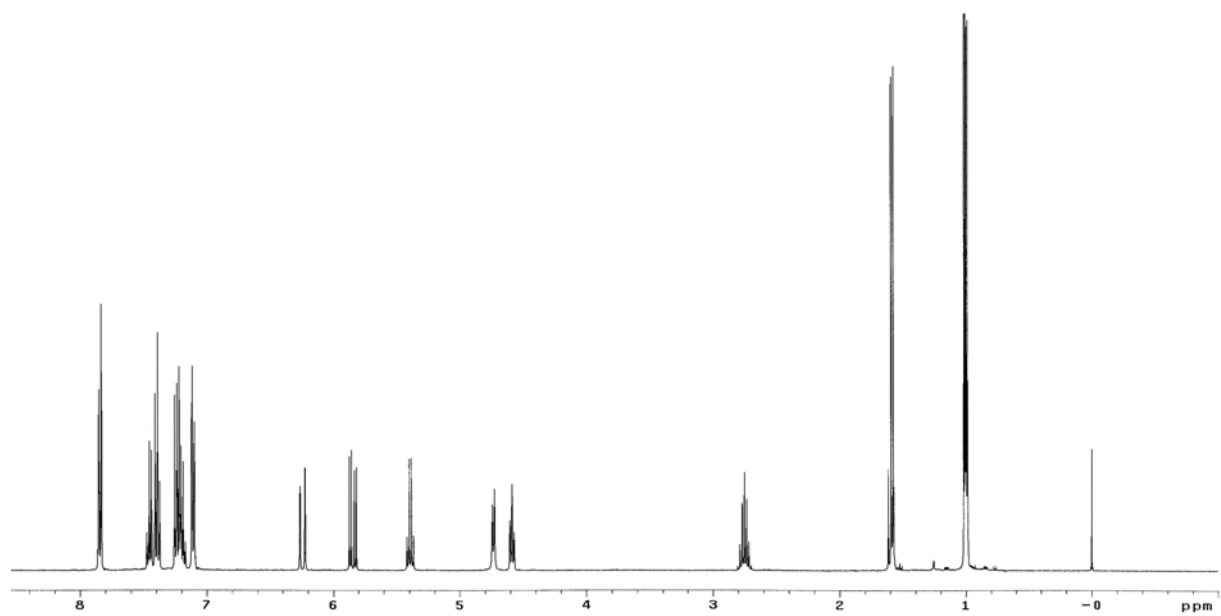
**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.34, 30% EtOAc/hexane.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.84 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.26 – 7.17 (m, 5H), 6.24 (d, *J* = 16 Hz, 1H), 5.84 (dd, *J* = 16, 7.2 Hz, 1H), 5.39 (q, *J* = 7.2 Hz, 1H), 4.73 (q, *J* = 7.2 Hz, 1H), 4.59 (t, *J* = 7.2 Hz, 1H), 2.75 (hept, *J* = 7.2 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H), 1.01 (d, *J* = 7.2 Hz, 3H), 0.99 (d, *J* = 7.2 Hz, 3H)

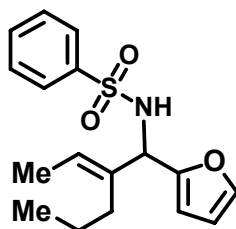
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 144.58, 141.49, 136.60, 132.55, 131.00, 129.49, 129.03, 128.63, 127.83, 127.55, 126.59, 129.123.14, 57.00, 28.73, 21.09, 13.35.

**HRMS** Calcd. for C<sub>21</sub>H<sub>26</sub>NO<sub>2</sub>S (M+1): 356.1684, Found: 356.1687

**FTIR** (neat): 3280, 3061, 2962, 2931, 2871, 2255, 1599, 1496, 1447, 1325, 1161, 1093, 1070, 967, 913, 737, 690, 599 cm<sup>-1</sup>



**(E)-N-(2-ethylidene-1-(furan-2-yl)pentyl)benzenesulfonamide (16b)**



**16b**

**(mixture of two regioisomers)**

To a solution of Ir(cod)<sub>2</sub>BARF (12.7 mg, 0.01 mmol, 5 mol%), BIPHEP (5.2 mg, 0.01 mmol, 5 mol%), triphenylacetic acid (2.9 mg, 0.01 mmol, 5 mol%), Na<sub>2</sub>SO<sub>4</sub> (57 mg, 0.4 mmol, 200 mol%) and (E)-N-(furan-2-ylmethylene)benzenesulfonamide (**13a**) (47mg, 0.2 mmol, 100mol%) in Toluene (0.05 M, 4 mL) was added 2-hexyne (49.3mg 0.6 mmol, 300 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 80 °C under 1 atm of hydrogen for 4 hours (control by TLC). Flash column chromatography (SiO<sub>2</sub>, 20% EtOAc/hexane) provides the title compound (46 mg) as colorless oil. (71% yield, 10:1 r.r.).

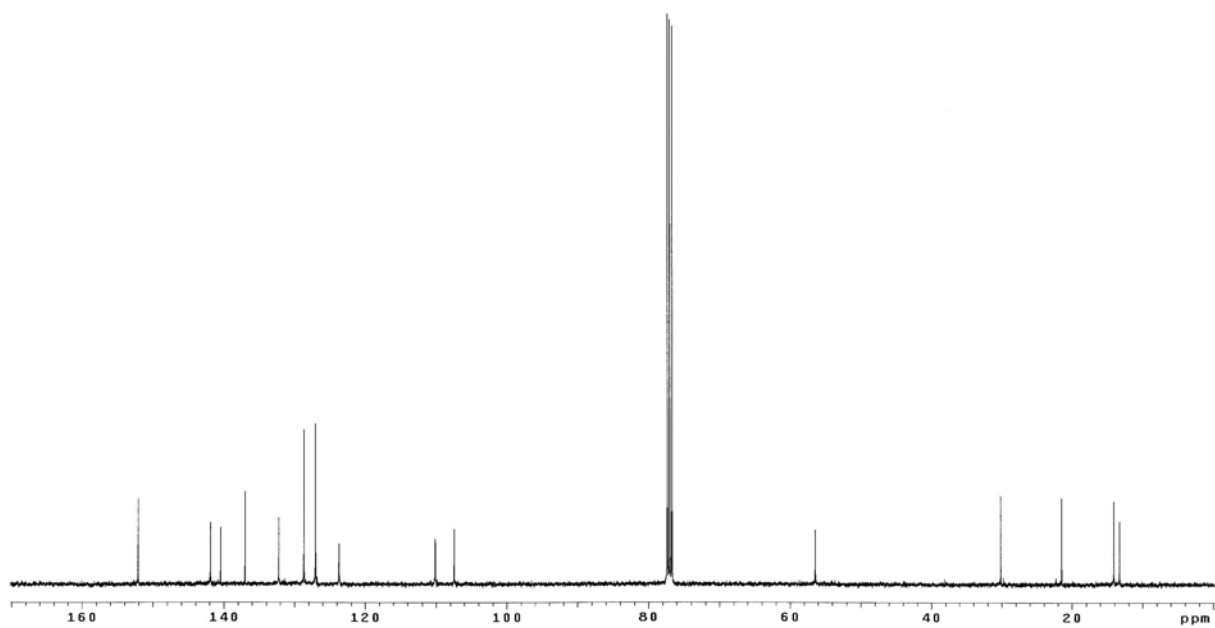
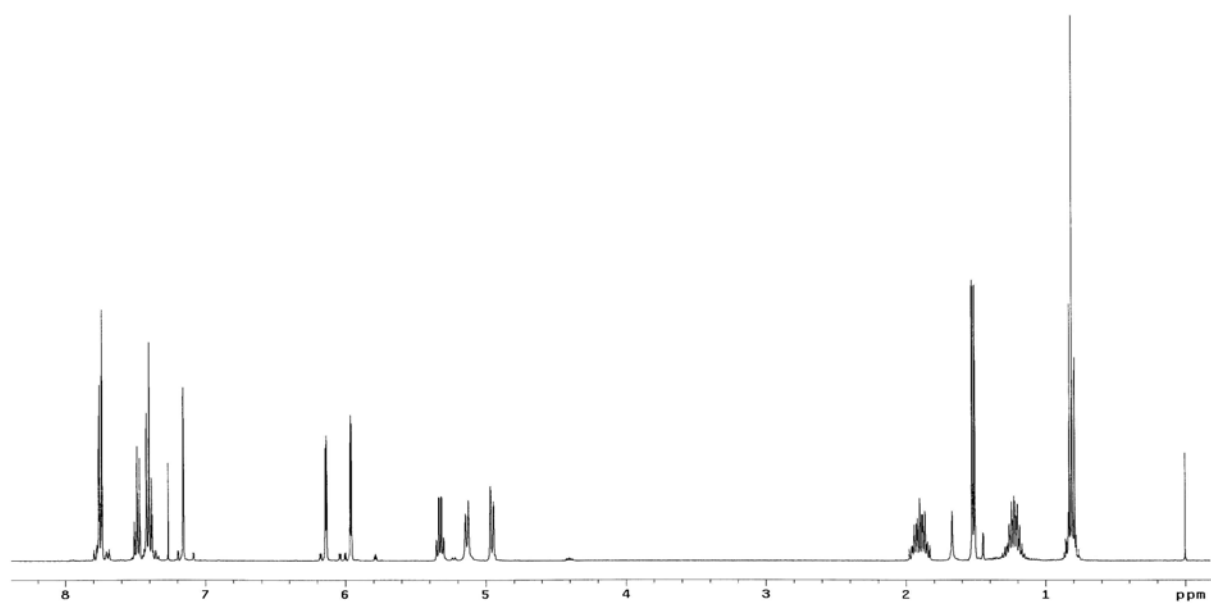
**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.34, 30% EtOAc/hexane.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.78 and 7.50 (minor: d, *J* = 7.2 Hz, 2H; major: d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.19 and 7.16 (minor: d, *J* = 1.6 Hz, 1H; major: d, *J* = 1.6 Hz, 1H), 6.17 and 6.13 (minor: dd, *J* = 3.6, 1.6 Hz, 1H; major: dd, *J* = 3.6, 1.6 Hz, 1H), 6.00 and 5.96 (minor: d, *J* = 3.6 Hz, 1H; major: *J* = 3.6 Hz, 1H), 5.33 (q, *J* = 7.2 Hz, 1H), 5.22 and 5.13 (minor: d, *J* = 8.0 Hz, 1H; major: d, *J* = 8.0 Hz, 1H), 4.95 (d, *J* = 8.0 Hz, 1H), 1.98 – 1.83 (m, 2H), 1.51 and 1.45 (minor: s, 3H; major: d, *J* = 7.2 Hz, 3H), 1.29 – 1.17 (m, 2H), 0.81 (t, *J* = 7.2 Hz, 3H).

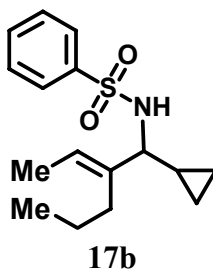
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 152.08, 141.88, 140.45, 136.99, 132.24, 128.65, 127.01, 123.69, 110.12, 107.45, 56.40, 30.14, 21.47, 12.08, 13.29

**HRMS** Calcd. for C<sub>17</sub>H<sub>20</sub>NO<sub>3</sub>S (M-1): 318.1164, Found: 318.1162

**FTIR** (neat): 3380, 3275, 3055, 2962, 2933, 2872, 2254, 1448, 1417, 1329, 1265, 1163, 1094, 1071, 1012, 911, 735, 650, 587 cm<sup>-1</sup>



**(E)-N-(1-cyclopropyl-2-ethylidenepentyl)benzenesulfonamide (17b)**



**(mixture of regioisomers)**

To a solution of Ir(cod)<sub>2</sub>BARF (12.7 mg, 0.01 mmol, 5 mol%), BIPHEP (5.2 mg, 0.01 mmol, 5 mol%), triphenylacetic acid (2.9 mg, 0.01 mmol, 5 mol%), Na<sub>2</sub>SO<sub>4</sub> (57 mg, 0.4 mmol, 200 mol%) and (E)-N-(cyclopropylmethylene)benzenesulfonamide (**12a**) (41.8mg, 0.2 mmol, 100mol%) in Toluene (0.05 M, 4 mL) was added 2-hexyne (49.3mg 0.6 mmol, 300 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 80 °C under 1 atm of hydrogen for 4 hours (control by TLC). Flash column chromatography (SiO<sub>2</sub>, 20% EtOAc/hexane) provides the title compound (38 mg) as colorless oil (64% yield, 10:1 r.r.).

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.34, 30% EtOAc/hexane.

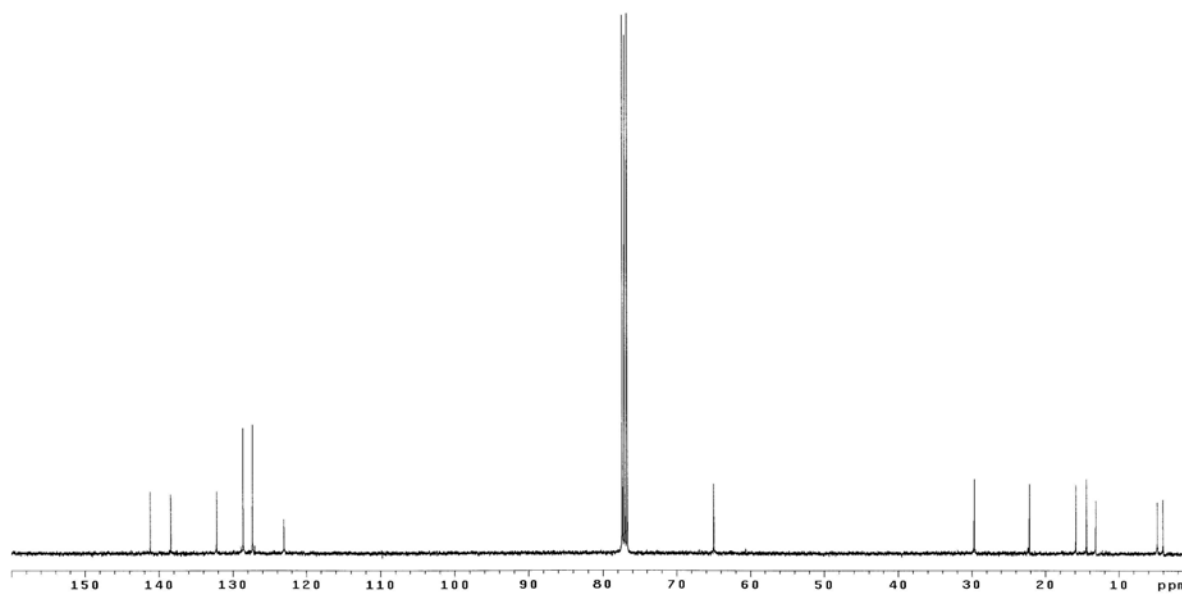
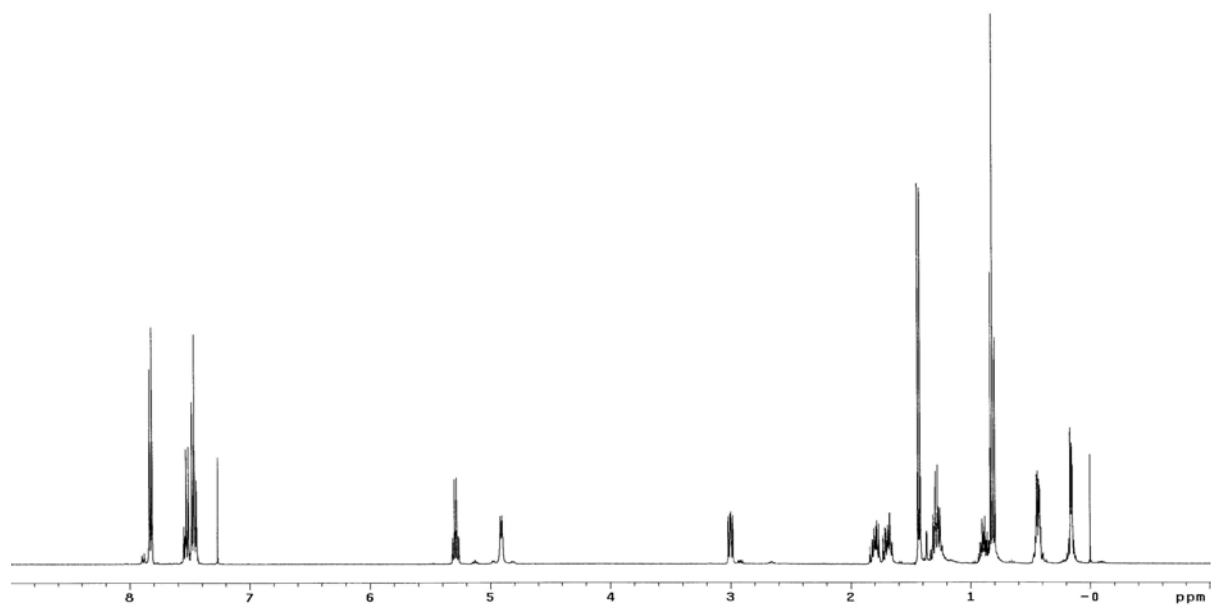
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.88 and 7.82 (minor: d, *J* = 7.2 Hz, 2H; major: d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 5.28 and 5.12 (minor: t, *J* = 7.2 Hz, 1H; major: q, *J* = 7.2 Hz, 1H), 4.97 and 4.90 (minor: d, *J* = 5.6 Hz, 1H; major: d, *J* = 5.6 Hz, 1H), 2.99 and 2.91 (minor: dd, *J* = 8.8, 5.6 Hz, 1H; major: dd, *J* = 8.8, 5.6 Hz, 1H), 1.68 – 1.49 (m, 2H), 1.42 and 1.36 (minor: s, 3H; major: d, *J* = 7.2 Hz, 3H), 1.31 – 1.23 (m, 2H), 0.91 – 0.85 (m, 1H); 0.81 (t, *J* = 7.2 Hz, 3H), 0.45 – 0.41 (m, 2H), 0.15 (d, *J* = 4.8 Hz, 2H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 141.19, 138.41, 132.19, 128.60, 127.33, 123.06, 64.97, 29.64, 22.16, 15.85, 14.41, 13.15, 4.77, 4.01

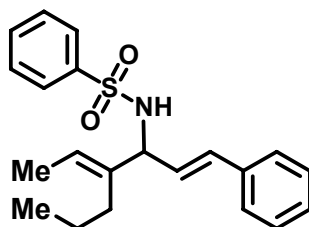
**HRMS** Calcd. for C<sub>16</sub>H<sub>22</sub>NO<sub>2</sub>S (M-1): 292.1371, Found: 292.1373

**FTIR** (neat): 3279, 3067, 3006, 2959, 2932, 2871, 1448, 1379, 1325, 1160, 1095, 1073, 1039, 985, 954, 896, 863, 837, 755, 720, 690, 591, 563 cm<sup>-1</sup>





**N-((1E,4E)-4-ethylidene-1-phenylhept-1-en-3-yl)benzenesulfonamide (18b)**



**18b**

**(mixture of regioisomers)**

To a solution of Ir(cod)<sub>2</sub>BARF (12.7 mg, 0.01 mmol, 5 mol%), BIPHEP (5.2 mg, 0.01 mmol, 5 mol%), triphenylacetic acid (2.9 mg, 0.01 mmol, 5 mol%), Na<sub>2</sub>SO<sub>4</sub> (57 mg, 0.4 mmol, 200 mol%) and (E)-N-((E)-3-phenylallylidene)benzenesulfonamide (**6a**) (54.3mg, 0.2 mmol, 100mol%) in Toluene (0.05 M, 4 mL) was added 2-hexyne (49.3mg 0.6 mmol, 300 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 80 °C under 1 atm of hydrogen for 2 hours (control by TLC). Flash column chromatography (SiO<sub>2</sub>, 20% EtOAc/hexane) provides the title compound (41 mg) as colorless oil (58% yield, 10:1 r.r.).

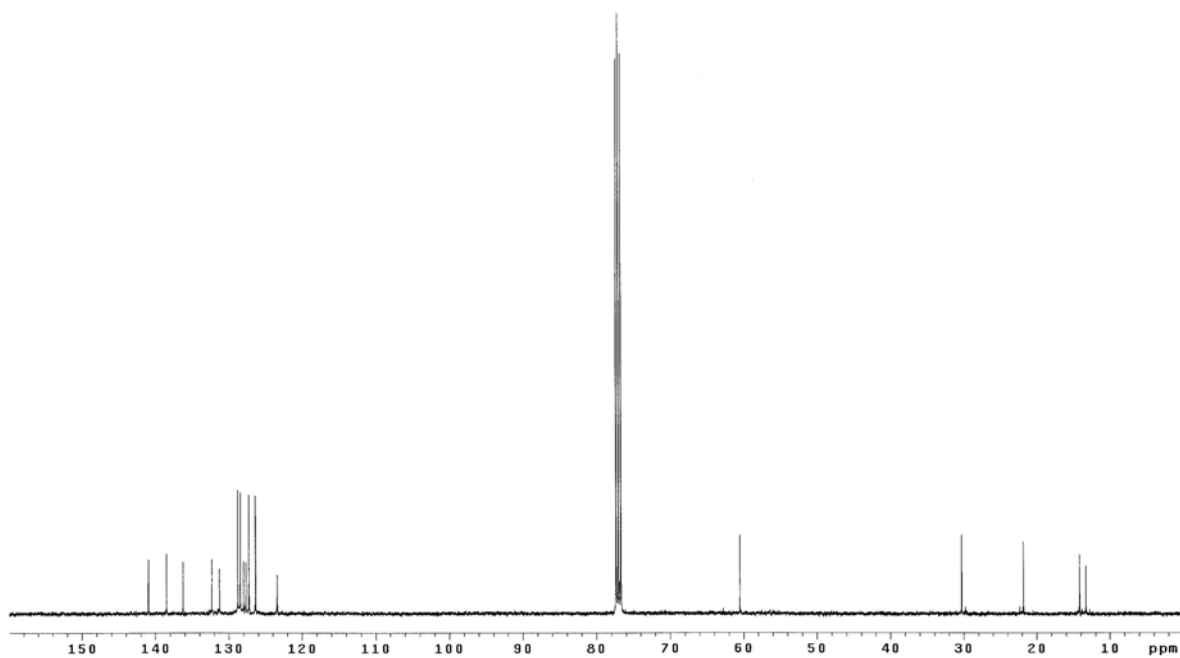
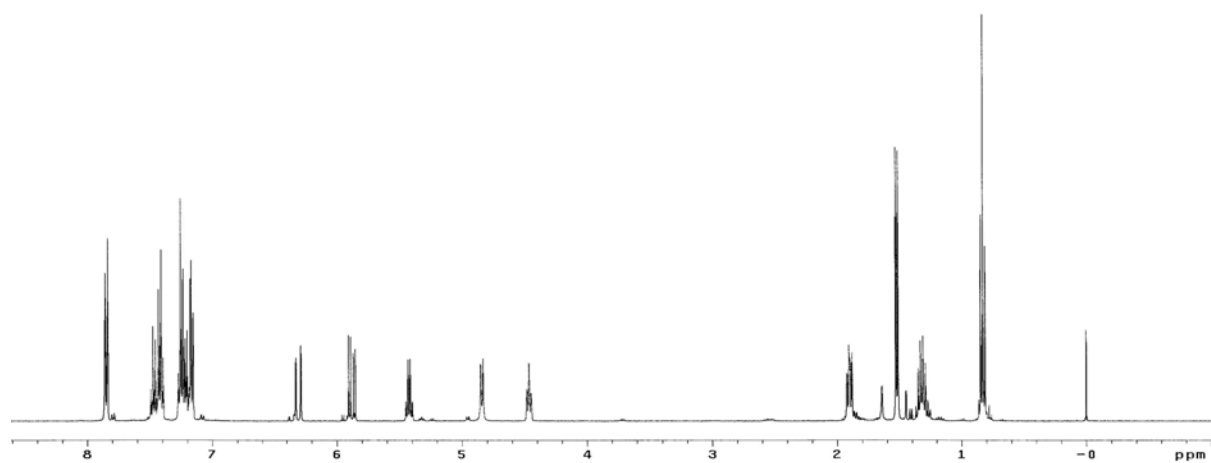
**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.34, 30% EtOAc/hexane.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.85 and 7.79 (minor: d, *J* = 7.2 Hz, 2H; major: d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.28 – 7.15 (m, 5H), 6.36 and 6.30 (minor: d, *J* = 8.0 Hz, 1H; major: d, *J* = 8.0 Hz, 1H), 5.93 and 5.88 (minor: dd, *J* = 16, 6.8 Hz, 1H; major: dd, *J* = 16, 6.8 Hz, 1H), 5.42 and 5.32 (minor: t, *J* = 6.8 Hz, 1H; major: q, *J* = 6.8 Hz, 1H), 4.95 and 4.84 (minor: d, *J* = 7.6 Hz, 1H; major: d, *J* = 7.6 Hz, 1H), 4.46 (t, *J* = 7.2 Hz, 1H), 1.92 – 1.84 (m, 2H), 1.52 and 1.44 (minor: s, 3H; major: d, *J* = 6.8 Hz, 3H), 1.32 (hex, *J* = 8.0 Hz, 2H), 0.83 (t, *J* = 7.2 Hz, 3H).

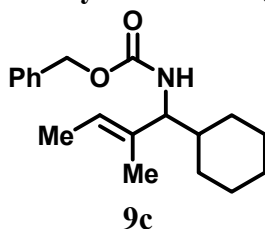
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 140.94, 138.48, 136.25, 132.32, 131.25, 128.75, 128.41, 127.97, 127.64, 127.26, 126.36, 123.41, 60.50, 30.25, 21.80, 14.14, 13.28.

**HRMS** Calcd. for C<sub>21</sub>H<sub>26</sub>NO<sub>2</sub>S(M+1): 356.1684, Found: 356.1687

**FTIR** (neat): 3386, 3276, 3063, 3029, 2961, 2932, 2872, 2255, 1448, 1408, 1326, 1162, 1093, 1071, 967, 909, 733, 691, 650, 589 cm<sup>-1</sup>



**(E)-benzyl 1-cyclohexyl-2-methylbut-2-enylcarbamate (9c)**



To a solution of (E)-N-(1-cyclohexyl-2-methylbut-2-enyl)-4-methylbenzenesulfonamide (**9b**) (50.2 mg, 0.16 mmol, 100 mol%) in dimethoxyethane (0.44 M, 5 mL) was added a 5 mL sodium naphthalenide solution [prepared from naphthalene (1.2 g, 9.36 mmol) and Na (0.20 mg, 8.70 mmol) in 20 mL DME with stirring for 2 hours at room temperature]. The resulting reaction mixture was stirring at room temperature for 1 hour and then quenched with 1 mL water. Solvent was evaporated under reduced pressure to give a crude residue, which was in 10 mL ethyl acetate and 4 mL saturated Na<sub>2</sub>CO<sub>3</sub>. To this solution was added benzyl chloroformate (136 mg, 0.80 mmol, 500 mol%) and the resulting reaction mixture was stirring at room temperature for 2 hours. The aqueous layer was extracted with ethyl acetate (15 mL x 3) and the combined organic layers were concentrated. The crude residue was purified by column chromatography [SiO<sub>2</sub>, 5% EtOAc/Hexane] to furnish the title compound (40 mg) as colorless oil (85% yield).

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.43, 20% EtOAc/Hexane.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.36 – 7.26 (m, 5H), 5.40 (br, q, *J* = 6 Hz, 1H), 5.11 – 5.04 (m, 2H), 4.77 (br, d, *J* = 6 Hz, 1H), 3.79 (br, t, *J* = 8.8 Hz, 1H), 1.74 (br, m, 3H), 1.58 (d, *J* = 6.8 Hz, 3H), 1.52 (s, 3H), 1.64 – 1.50 (br, m, 2H), 1.35 – 0.89 (br, 6H).

