Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

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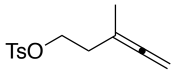
1. General

New compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, IR, MS, and HRMS. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a JEOL JMTC-400/54/SS spectrometer (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz, ^{19}F NMR, 377 MHz). ^{1}H NMR chemical shifts were determined relative to Me_4Si (0.0 ppm) as an internal standard. ^{13}C NMR chemical shifts were determined relative to $CDCl_3$ (77.0 ppm). ^{19}F NMR chemical shifts were determined relative to C_6F_6 (−164.9 ppm) as an external standard. Infrared spectra were recorded on a SHIMADZU IRAffinity-1 FT-IR Spectrometer. Mass spectra were obtained on a SHIMADZU GCMS-QP2010 mass spectrometer. High-resolution mass spectra were obtained on a JEOL JMS-700 mass spectrometer (magnetic sector type mass spectrometer). Melting points were determined on a Stanford Research Systems MPA100 OptiMelt Automated Melting Point System. Chiral-phase high-performance liquid chromatography (HPLC) was performed on a Waters Alliance 2695 Separations Module equipped with chiral columns. Optical rotations were measured in a thermostated conventional 10 cm cell on a JASCO DIP-1000 polarimeter using the sodium-D line (589 nm). All reactions were carried out under nitrogen. Products were purified by chromatography on silica gel BW-300 (Fuji Silysia Chemical Ltd.) or Chromatorex NH (Fuji Silysia Chemical Ltd.). Analytical thin-layer chromatography (TLC) was performed on pre-coated silica gel glass plates (Merck silica gel 60 F_{254} and Fuji Silysia Chromatorex NH, 0.25 mm thickness). Compounds were visualized with UV lamp or treatment with an ethanolic solution of phosphomolybdic acid followed by heating.

2. Materials

Dehydrated tetrahydrofurane (super dehydrated, stabilizer free) was purchased from FUJIFILM Wako Pure Chemical Corporation and used as obtained. Allenes **1a**,[1] **1c**,[2] **1d**,[3] **1e**,[3] **1k**,[4] **1l**,[5] **1m**,[5] **1o**,[5] **1p**,[5] **1r**,[5] **1s**,[5] **1t**,[5] **1u**,[6] **1v**,[5] **1w**,[5] **1x**,[5] **1y**,[7] and **1z**[2] were prepared by known methods. Allene **1b** was prepared according to the reported procedure,[8] and the analytical data were in excellent agreement with reported data.[9] 9-Borabicyclo-[3.3.1]nonane (9-BBN) dimer was purchased and used as obtained. Dicyclohexylborane[10] and diisopinocampheylborane [(−)-$(Ipc)_2BH$][11] were prepared by known method. *N*-Cyano-*N*-phenyl-*p*-toluenesulfonamide (NCTS) was prepared by known method.[12] *p*-Toluenesulfonyl cyanide (TsCN) was purchased and used as obtained. All other solvents and reagents were purchased and used as obtained.



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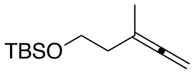

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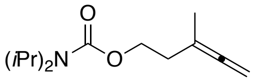

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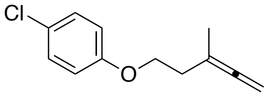

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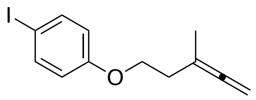

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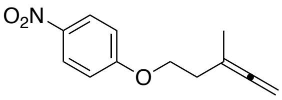

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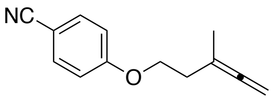

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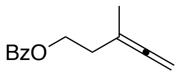

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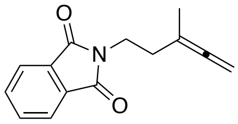

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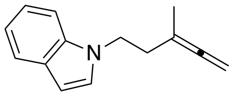

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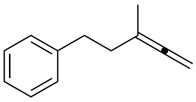

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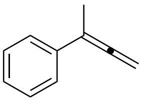

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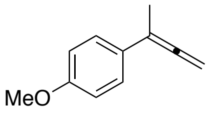

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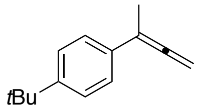

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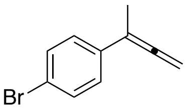

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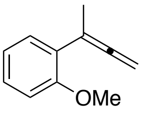

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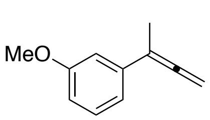

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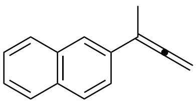

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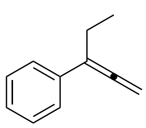

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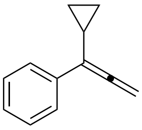

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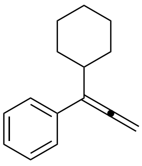

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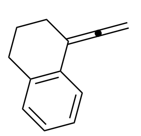

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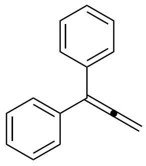

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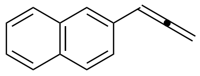

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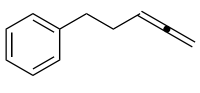

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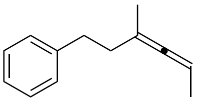

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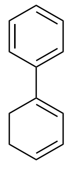

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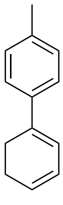

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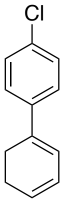

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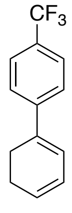

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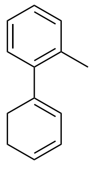

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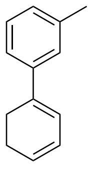

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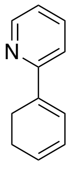

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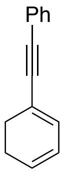

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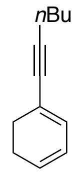

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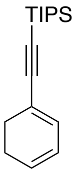

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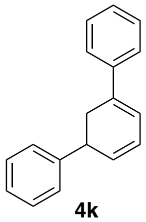

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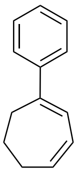


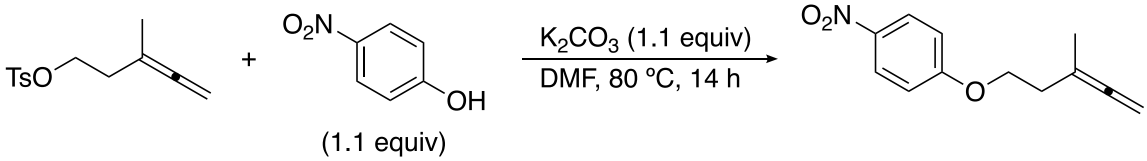
4l

Figure S1. List of substrates

3. Preparation of starting materials

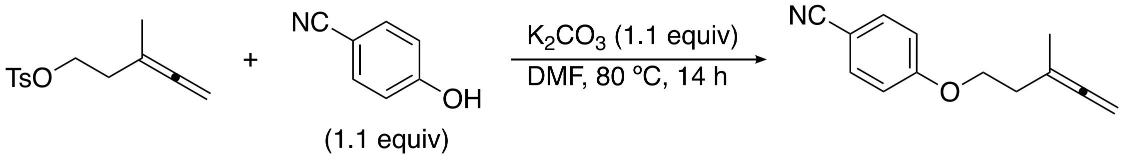
Preparation of allenes

1-((3-methylpenta-3,4-dien-1-yl)oxy)-4-nitrobenzene (1f)



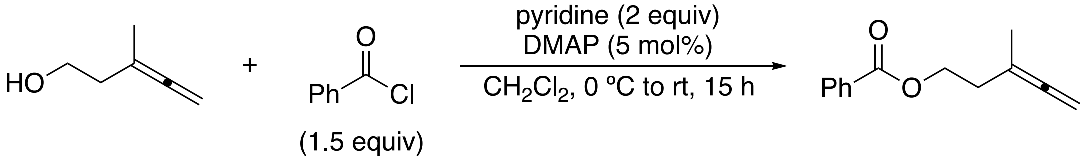
According to the reported procedure,[3] the reaction using DMF (3.8 mL), 4-nitrophenol (770 mg, 5.5 mmol), 3-methylpenta-3,4-dien-1-yl 4-methylbenzenesulfonate (1.24 g, 5.0 mmol), and K_2CO_3 (750 mg, 5.5 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane/EtOAc = 95:5) gave the product as a pale yellow solid (945.7 mg, 86% yield). mp: 44.7–45.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.16 (m, 2H), 6.98–6.90 (m, 2H), 4.66 (tq, J = 3.2, 3.2 Hz, 2H), 4.16 (t, J = 6.4 Hz, 2H), 2.46 (tt, J = 6.4, 3.2 Hz, 2H), 1.78 (t, J = 3.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 164.0, 141.4, 125.9, 114.4, 94.7, 75.2, 67.0, 32.5, 19.1; IR (ATR) 2943, 2911, 1964, 1591, 1497 cm^{-1}; MS (EI) *m/z* 219 (M^+, 5), 81 (95), 80 (21), 79 (100), 77 (24), 65 (30), 63 (24), 55 (21), 53 (93), 51 (22), 50 (20); HRMS: (EI) calcd for ($C_{12}H_{13}NO_3$) 219.0895 (M^+), found *m/z* 219.0896

4-((3-methylpenta-3,4-dien-1-yl)oxy)benzonitrile (1g)



According to the reported procedure,[3] the reaction using DMF (3.0 mL), 4-cyanophenol (540 mg, 4.5 mmol), 3-methylpenta-3,4-dien-1-yl 4-methylbenzenesulfonate (1.03 g, 4.1 mmol), and K_2CO_3 (619 mg, 4.5 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane/EtOAc = 95:5) gave the product as a white solid (671.2 mg, 82% yield). mp: 45.7–46.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.54 (m, 2H), 6.98–6.90 (m, 2H), 4.65 (tq, J = 3.2, 3.2 Hz, 2H), 4.11 (t, J = 6.4 Hz, 2H), 2.43 (tt, J = 6.4, 3.2 Hz, 2H), 1.77 (t, J = 3.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 162.2, 133.9, 119.3, 115.2, 103.8, 94.7, 75.2, 66.5, 32.5, 19.1; IR (ATR) 2947, 2909, 2222, 1960, 1605, 1508 cm^{-1}; MS (EI) *m/z* 199 (M^+, 10), 81 (70), 79 (100), 53 (58); HRMS: (EI) calcd for ($C_{13}H_{13}NO$) 199.0997 (M^+), found *m/z* 199.0997

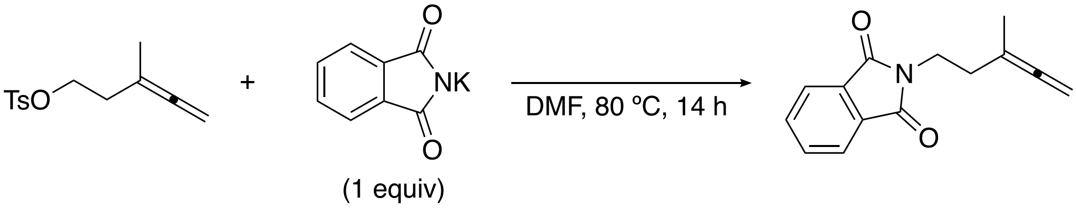
3-methylpenta-3,4-dien-1-yl benzoate (1h)



According to the reported procedure,[3] the reaction using 3-methylpenta-3,4-dien-1-ol (2.27 g, 23.1

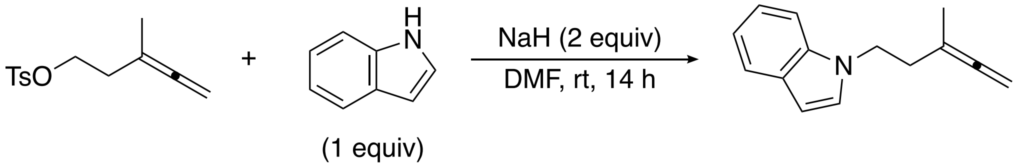
mmol), DMAP (116.3 mg), pyridine (3.1 mL, 46.2 mmol), CH_2Cl_2 (60 mL), and benzoyl chloride (4.89 g, 34.7 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane/EtOAc = 95:5) gave the product as a colorless liquid (3.93 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 4.63 (tq, *J* = 3.2, 3.2 Hz, 2H), 4.43 (t, *J* = 6.4 Hz, 2H), 2.41 (tt, *J* = 6.4, 3.2 Hz, 2H), 1.77 (t, *J* = 3.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3, 166.4, 132.7, 130.3, 129.4, 128.2, 94.6, 74.7, 62.9, 32.5, 18.8; IR (ATR) 2982, 2901, 1962, 1717 cm^{-1}; MS (EI) *m/z* 202 (M$^+$, 1), 105 (100), 79 (47), 77 (85), 51 (32); HRMS: (EI) calcd for ($C_{13}H_{14}O_2$) 202.0994 (M$^+$), found *m/z* 202.0990

2-(3-methylpenta-3,4-dien-1-yl)isoindoline-1,3-dione (1i)



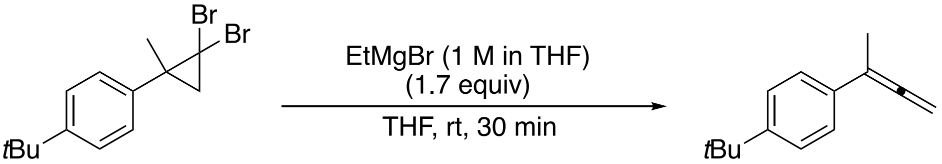
According to the reported procedure,[13] the reaction using 3-methylpenta-3,4-dien-1-yl 4-methylbenzenesulfonate (1.25 g, 5.0 mmol), DMF (6.7 mL), and potassium phtalimide (927 mg, 5.0 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane/EtOAc = 90:10) and recrystallization from hexane/EtOAc gave the product as a white solid (782.3 mg, 69% yield). mp: 89.0–89.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.81 (m, 2H), 7.75–7.68 (m, 2H), 4.52 (tq, *J* = 3.2, 3.2 Hz, 2H), 3.80 (t, *J* = 6.4 Hz, 2H), 2.31 (tt, *J* = 6.4, 3.2 Hz 2H), 1.74 (t, *J* = 3.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 168.3, 133.9, 132.1, 123.2, 95.0, 74.6, 36.1, 32.0, 18.6; IR (ATR) 2951, 2913, 1956, 1767, 1713 cm^{-1}; MS (EI) *m/z* 227 (M$^+$, 42), 226 (39), 160 (100), 148 (21), 133 (33), 130 (47), 105 (49), 104 (41), 80 (56), 79 (42), 77 (70), 76 (49), 51 (26), 50 (28); HRMS: (EI) calcd for ($C_{14}H_{13}NO_2$) 227.0946 (M$^+$), found *m/z* 227.0948

1-(3-methylpenta-3,4-dien-1-yl)-1*H*-indole (1j)



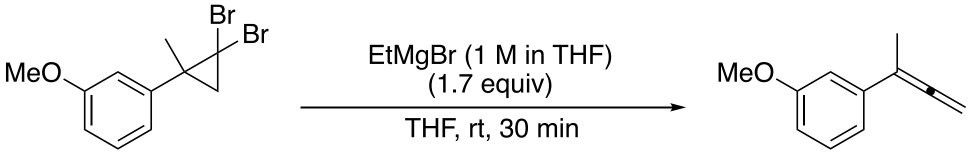
According to the reported procedure,[13] the reaction using indole (589 mg, 5.0 mmol), DMF (3.8 mL), NaH (Assay 50–72%, 360 mg), and 3-methylpenta-3,4-dien-1-yl 4-methylbenzenesulfonate (1.26 g, 5.0 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane/EtOAc = 95:5) gave the product as a pale yellow liquid (760.5 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.13–7.06 (m, 2H), 6.48 (d, *J* = 3.2 Hz, 1H), 4.66 (tq, *J* = 3.2, 3.2 Hz, 2H), 4.23 (t, *J* = 6.4 Hz, 2H), 2.43 (tt, *J* = 6.4, 3.2 Hz, 2H), 1.71 (t, *J* = 3.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 135.9, 128.6, 127.7, 121.3, 120.9, 119.2, 109.2, 101.0, 95.5, 75.3, 44.6, 33.7, 19.0; IR (ATR) 3051, 2978, 2936, 1960, 1462 cm^{-1}; MS (EI) *m/z* 197 (M$^+$, 40), 196 (21), 182 (39), 130 (100), 103 (23), 77 (33); HRMS: (EI) calcd for ($C_{14}H_{15}N$) 197.1204 (M$^+$), found *m/z* 197.1207

1-(buta-2,3-dien-2-yl)-4-*tert*-butylbenzene (1n)



According to the reported procedure,[5] the reaction using 4-(2,2-dibromo-1-methylcyclopropyl)-1-(*tert*-butyl)benzene (4.87 g, 13.2 mmol), THF (30 mL), and EtMgBr (1 M in THF, 23.5 mL, 23.5 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane) gave the product as a colorless liquid (2.21 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.32 (m, 4H), 5.00 (q, *J* = 3.2 Hz, 2H), 2.09 (t, *J* = 3.2 Hz, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.9, 149.5, 133.7, 125.4, 125.2, 99.5, 76.7, 34.4, 31.3, 16.7; IR (ATR) 2963, 2903, 1944, 1512 cm^{-1}; MS (EI) *m/z* 186 (M$^+$, 38), 171 (100), 129 (21), 128 (43), 115 (28), 53 (20); HRMS: (EI) calcd for ($C_{14}H_{18}$) 186.1409 (M$^+$), found *m/z* 186.1410

1-(buta-2,3-dien-2-yl)-3-methoxybenzene (1q)



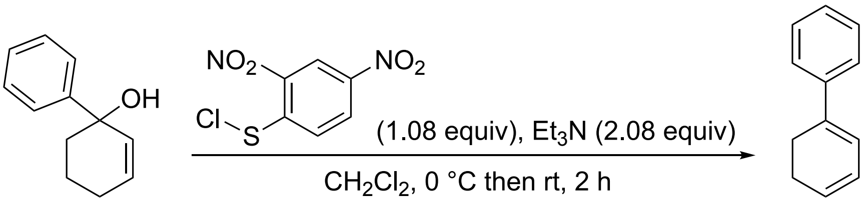
According to the reported procedure,[5] the reaction using 1-(2,2-dibromo-1-methylcyclopropyl)-3-methoxybenzene (2.44 g, 7.6 mmol), THF (20 mL), and EtMgBr (1 M in THF, 13.0 mL, 13.0 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane/EtOAc = 96:4) gave the product as a yellow liquid (1.06 g, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.96 (s, 1H), 6.75 (dd, *J* = 8.0, 2.4 Hz, 1H), 5.02 (q, *J* = 3.2 Hz, 2H), 3.81 (s, 3H), 2.08 (t, *J* = 3.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.0, 159.7, 138.3, 129.2, 118.2, 111.9, 111.5, 99.7, 76.9, 55.1, 16.7; IR (ATR) 2949, 2833, 1942, 1597, 1580, 1487 cm^{-1}; MS (EI) *m/z* 160 (M$^+$, 75), 145 (47), 129 (22), 128 (26), 117 (45), 116 (27), 115 (100), 102 (28), 91 (37), 63 (31), 51 (26); HRMS: (EI) calcd for ($C_{11}H_{12}O$) 160.0888 (M$^+$), found *m/z* 160.0887

Preparation of dienes

Typical procedure[14]**:** A flame dried round-bottom flask containing a magnetic stir bar was charged with alcohol, CH_2Cl_2, and triethylamine, and cooled in an ice bath. To this solution, 2,4-dinitrobenzenesulfenyl chloride was added. The ice bath was removed, and the mixture was stirred at room temperature for 2 h. Then, hexane was added to the reaction mixture. The precipitate was filtered out (celite), and the solution was washed with H_2O and brine and dried over Na_2SO_4.

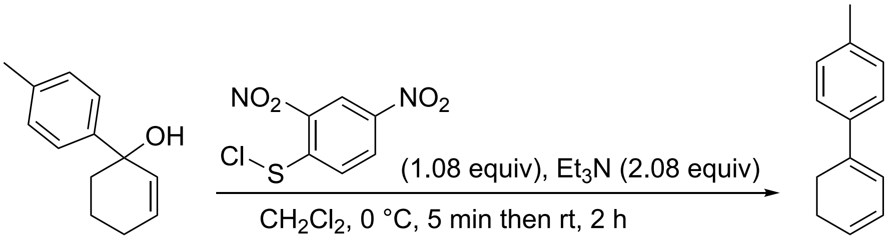
The solvent was removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane) gave the product.

1-phenylcyclohexa-1,3-diene (4a)



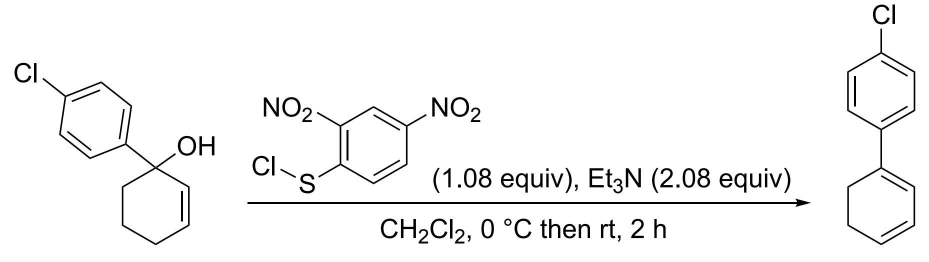
According to the typical procedure, the reaction using 1-phenylcyclohex-2-en-1-ol (1.70 g, 9.76 mmol), CH_2Cl_2 (30 mL), triethylamine (2.90 mL, 20.8 mmol), and 2,4-dinitrobenzenesulfenyl chloride (2.53 g, 10.8 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane) gave the product as a white solid (885 mg, 58% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.52–7.40 (m, 2H), 7.40–7.30 (m, 2H), 7.30–7.17 (m, 1H), 6.33 (d, J = 5.2 Hz, 1H), 6.16–6.03 (m, 1H), 5.97–5.85 (m, 1H), 2.61 (t, J = 9.6 Hz, 2H), 2.44–2.25 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 141.2, 136.3, 128.3, 126.9, 126.0, 125.1, 124.9, 120.8, 25.2, 23.1
The analytical data for this compound were in excellent agreement with the reported data.[14]

1-(4-methylphenyl)cyclohexa-1,3-diene (4b)



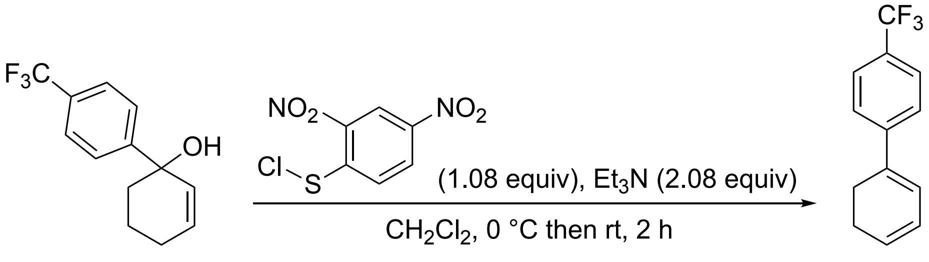
According to the typical procedure, the reaction using 1-(4-methylphenyl)cyclohex-2-en-1-ol (1.81 g, 9.61 mmol), CH_2Cl_2 (30 mL), triethylamine (2.90 mL, 20.8 mmol), and 2,4-dinitrobenzenesulfenyl chloride (2.53 g, 10.8 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane) gave the product as a white solid (1.19 g, 72% yield). mp: 31.2–31.7 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.29 (d, J = 5.2 Hz, 1H), 6.12–6.03 (m, 1H), 5.92–5.81 (m, 1H), 2.58 (t, J = 9.6 Hz, 2H), 2.38–2.27 (m, 5H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 138.3, 136.7, 136.3, 129.0, 125.6, 125.2, 124.8, 120.0, 25.2, 23.1, 21.1; IR: (ATR) 3036, 2920, 2874, 2824, 1512 cm^{-1}; MS: (EI) m/z 170 (M$^+$, 100), 155 (97), 154 (27), 153 (29), 129 (26), 128 (31), 115 (35), 105 (37), 91 (23), 77 (20); HRMS: (EI) calcd for ($C_{13}H_{14}$) 170.1096 (M$^+$), found m/z 170.1095

1-(4-chlorophenyl)cyclohexa-1,3-diene (4c)



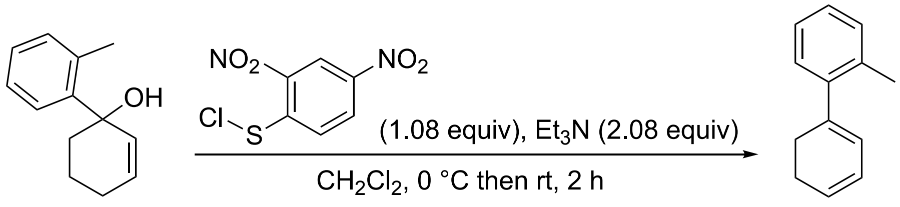
According to the typical procedure, the reaction using 1-(4-chlorophenyl)cyclohex-2-en-1-ol (2.08 g, 9.97 mmol), CH_2Cl_2 (30 mL), triethylamine (2.90 mL, 20.8 mmol), and 2,4-dinitrobenzenesulfenyl chloride (2.53 g, 10.8 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane) gave the product as a yellow solid (1.18 g, 62% yield). mp: 48.5–50.5 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.44–7.33 (m, 2H), 7.33–7.23 (m, 2H), 6.30 (d, *J* = 5.6 Hz, 1H), 6.15–6.03 (m, 1H), 5.97–5.86 (m, 1H), 2.56 (t, *J* = 10.4 Hz, 2H), 2.42–2.27 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 139.6, 135.1, 132.5, 128.4, 126.4, 126.1, 124.9, 121.2, 25.1, 23.1; IR: (ATR) 3038, 2934, 2878, 2830, 1904, 1487 cm^{-1}; MS: (EI) *m/z* 192 ([M+2]$^+$, 28), 190 (M$^+$, 98), 155 (100), 154 (30), 153 (52), 152 (45), 128 (20), 127 (34), 125 (43), 115 (23), 77 (34), 76 (51), 75 (23), 63 (24), 51 (28); HRMS: (EI) calcd for ($C_{12}H_{11}Cl$) 190.0549 (M$^+$), found *m/z* 190.0548

1-(4-trifluoromethylphenyl)cyclohexa-1,3-diene (4d)



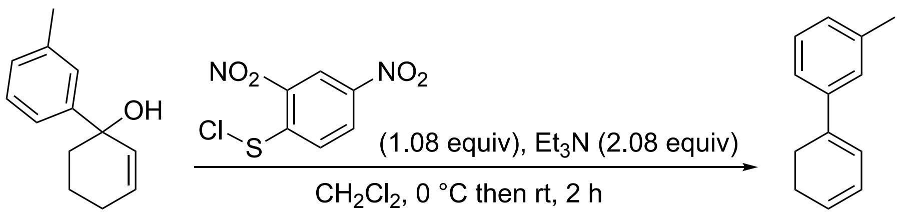
According to the typical procedure, the reaction using 1-(4-trifluoromethylphenyl)cyclohex-2-en-1-ol (1.68 g, 6.94 mmol), CH_2Cl_2 (20 mL), triethylamine (2.00 mL, 14.4 mmol), and 2,4-dinitrobenzenesulfenyl chloride (1.75 g, 7.46 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane) gave the product as a white solid (1.08 g, 70% yield). mp: 31.9–33.0 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 6.40 (d, *J* = 5.2 Hz, 1H), 6.18–6.05 (m, 1H), 6.02–5.90 (m, 1H), 2.61 (t, *J* = 10.0 Hz, 2H), 2.45–2.26 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 144.7, 134.9, 128.6 (q, J_{CF} = 32.1 Hz), 127.3, 125.3 (q, J_{CF} = 4.1 Hz), 125.0, 124.9, 124.3 (q, J_{CF} = 270.0 Hz), 122.8, 25.0, 23.0; ^{19}F NMR: (377 MHz, $CDCl_3$) δ −65.0; IR: (ATR) 3040, 2940, 2878, 2832, 1923, 1612, 1323 cm^{-1}; MS: (EI) *m/z* 224 (M$^+$, 100), 209 (21), 183 (33), 159 (22), 155 (74), 153 (24), 78 (32), 77 (26), 51 (20); HRMS: (EI) calcd for ($C_{13}H_{11}F_3$) 224.0813 (M$^+$), found *m/z* 224.0810

1-(2-methylphenyl)cyclohexa-1,3-diene (4e)



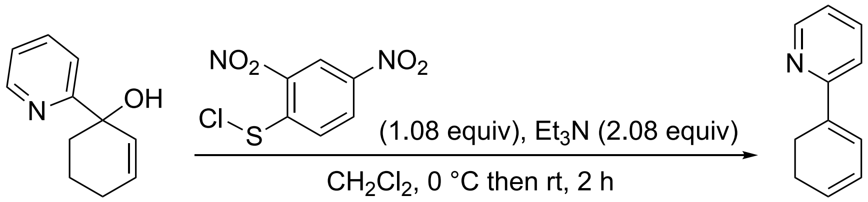
According to the typical procedure, the reaction using 1-(2-methylphenyl)cyclohex-2-en-1-ol (1.13 g, 6.02 mmol), CH$_2$Cl$_2$ (20 mL), triethylamine (1.75 mL, 12.5 mmol), and 2,4-dinitrobenzenesulfenyl chloride (1.53 g, 6.52 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane) gave the product as a colorless liquid (729 mg, 71% yield). ^{1}H NMR: (400 MHz, CDCl$_3$) δ 7.24–7.09 (m, 4H), 6.12–6.02 (m, 1H), 5.92–5.81 (m, 2H), 2.50–2.24 (m, 4H), 2.36 (s, 3H); ^{13}C NMR: (100 MHz, CDCl$_3$) δ 143.1, 138.7, 134.9, 130.2, 128.1, 126.8, 125.6, 125.3, 125.0, 123.0, 27.9, 23.1, 20.5; IR: (ATR) 3038, 2930, 2870, 2822, 1483 cm^{-1}; MS: (EI) *m*/*z* 170 (M$^+$, 100), 155 (94), 154 (25), 153 (32), 142 (38), 141 (46), 129 (48), 128 (65), 127 (20), 115 (63), 105 (32), 91 (26), 77 (27), 51 (22); HRMS: (EI) calcd for (C$_{13}$H$_{14}$) 170.1096 (M$^+$), found *m*/*z* 170.1097

1-(3-methylphenyl)cyclohexa-1,3-diene (4f)



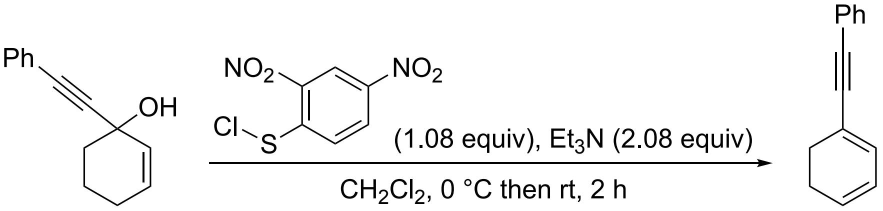
According to the typical procedure, the reaction using 1-(3-methylphenyl)cyclohex-2-en-1-ol (1.87 g, 9.93 mmol), CH$_2$Cl$_2$ (30 mL), triethylamine (2.90 mL, 20.8 mmol), and 2,4-dinitrobenzenesulfenyl chloride (2.53 g, 10.8 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane) gave the product as a colorless liquid (836 mg, 49% yield). ^{1}H NMR: (400 MHz, CDCl$_3$) δ 7.36–7.15 (m, 3H), 7.05 (d, J = 6.8 Hz, 1H), 6.31 (d, J = 5.6 Hz, 1H), 6.14–6.02 (m, 1H), 5.96–5.77 (m, 1H), 2.59 (t, J = 10.0 Hz, 2H), 2.42–2.24 (m, 2H), 2.36 (s, 3H); ^{13}C NMR: (100 MHz, CDCl$_3$) δ 141.3, 137.8, 136.5, 128.3, 127.7, 125.9, 125.7, 125.2, 122.1, 120.7, 25.3, 23.2, 21.5; IR: (ATR) 3034, 2934, 2870, 2822, 1603 cm^{-1}; MS: (EI) *m*/*z* 170 (M$^+$, 100), 169 (24), 155 (96), 154 (34), 153 (33), 152 (21), 141 (20), 129 (34), 128 (38), 115 (40), 105 (38), 91 (26), 77 (22); HRMS: (EI) calcd for (C$_{13}$H$_{14}$) 170.1096 (M$^+$), found *m*/*z* 170.1095

1-(pyridin-2-yl)cyclohexa-1,3-diene (4g)



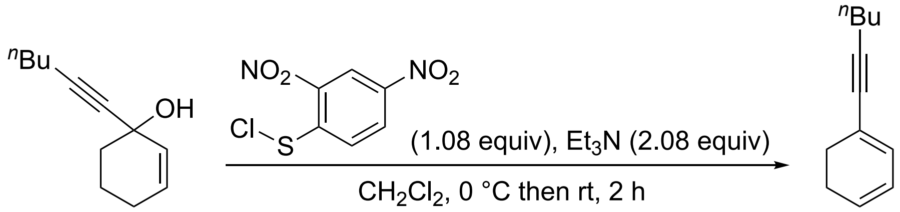
According to the typical procedure, the reaction using 1-(pyridin-2-yl)cyclohex-2-en-1-ol (1.16 g, 6.61 mmol), CH_2Cl_2 (20 mL), triethylamine (1.85 mL, 13.7 mmol), and 2,4-dinitrobenzenesulfenyl chloride (1.67 g, 7.13 mmol) was carried out. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 97:3) gave the product as a yellow liquid (620 mg, 57% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.64–8.53 (m, 1H), 7.70–7.56 (m, 1H), 7.53–7.42 (m, 1H) 7.17–7.05 (m, 1H), 6.80 (d, J = 5.2 Hz, 1H), 6.22–6.10 (m, 1H), 6.08–5.96 (m, 1H), 2.85–2.63 (m, 2H), 2.45–2.25 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 157.9, 149.0, 136.1, 135.8, 128.4, 124.9, 123.7, 121.4, 119.2, 23.12, 23.08; IR: (ATR) 3038, 2999, 2936, 2872, 2824, 1578, 1560, 1464, 1435, 1425 cm^{-1}; MS: (EI) *m*/*z* 157 (M$^+$, 31), 156 (100), 78 (39), 77 (19), 51 (26); HRMS: (FAB+) calcd for ($C_{11}H_{12}N$) 158.0970 ([M+H]$^+$), found *m*/*z* 158.0972

(cyclohexa-1,3-dien-1-ylethynyl)benzene (4h)



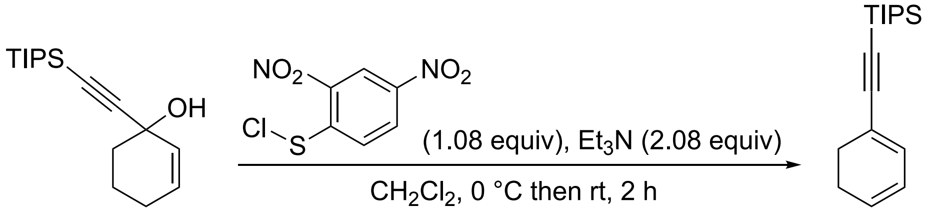
According to the typical procedure, the reaction using 1-(phenylethynyl)cyclohex-2-en-1-ol (0.86 g, 4.34 mmol), CH_2Cl_2 (20 mL), triethylamine (1.26 mL, 9.03 mmol), and 2,4-dinitrobenzenesulfenyl chloride (1.10 g, 4.68 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane) gave the product as a colorless liquid (549 mg, 70% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.53–7.38 (m, 2H), 7.38–7.22 (m, 3H), 6.33 (d, J = 5.2 Hz, 1H), 6.08–5.97 (m, 1H), 5.97–5.85 (m, 1H), 2.48–2.35 (m, 2H), 2.35–2.20 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 131.4, 130.1, 128.2, 127.9, 127.7, 124.6, 123.5, 118.8, 91.3, 91.1, 26.5, 22.4; IR: (ATR) 3036, 2941, 2880, 2824, 2197, 1626, 1597, 1487 cm^{-1}; MS: (EI) *m*/*z* 180 (M$^+$, 100), 179 (98), 178 (99), 165 (95), 152 (33), 126 (24), 115 (26), 102 (46), 89 (43), 77 (26), 76 (43), 63 (25), 51 (31); HRMS: (EI) calcd for ($C_{14}H_{12}$) 180.0939 (M$^+$), found *m*/*z* 180.0936

1-(hex-1-ynyl)cyclohexa-1,3-diene (4i)



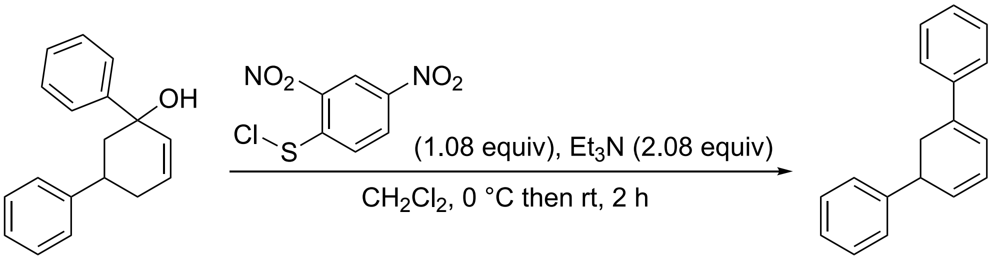
According to the typical procedure, the reaction using 1-(hex-1-ynyl)cyclohex-2-en-1-ol (1.71 g, 9.58 mmol), CH_2Cl_2 (30 mL), triethylamine (2.90 mL, 20.8 mmol), and 2,4-dinitrobenzenesulfenyl chloride (2.53 g, 10.8 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane) gave the product as a colorless liquid (1.13 g, 73% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 6.14 (d, J = 5.2 Hz, 1H), 6.02–5.89 (m, 1H), 5.89–5.77 (m, 1H), 2.35 (t, J = 7.2 Hz, 2H), 2.33–2.13 (m, 4H), 1.68–1.48 (m, 2H), 1.48–1.32 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 128.6, 126.5, 124.5, 119.6, 92.4, 82.2, 30.9, 27.0, 22.4, 22.0, 19.3, 13.6 ; IR: (ATR) 3038, 2957, 2932, 2872, 2828, 2214, 1628, 1562 cm^{-1}; MS: (EI) *m*/*z* 160 (M$^+$, 72), 145 (28), 131 (37), 129 (20), 118 (26), 117 (99), 116 (43), 115 (100), 105 (27), 104 (27), 103 (26), 91 (100), 79 (26), 78 (28), 77 (31), 65 (26), 63 (23), 51 (27); HRMS: (EI) calcd for ($C_{12}H_{16}$) 160.1252 (M$^+$), found *m*/*z* 160.1251

1-triisopropylsilylethynyl-cyclohexa-1,3-diene (4j)



According to the typical procedure, the reaction using 1-triisopropylsilylethynyl-cyclohex-2-en-1-ol (2.76 g, 9.91 mmol), CH_2Cl_2 (30 mL), triethylamine (2.90 mL, 20.8 mmol), and 2,4-dinitrobenzenesulfenyl chloride (2.53 g, 10.8 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane) gave the product as a pale yellow liquid (1.98 g, 77% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 6.27 (d, J = 4.4 Hz, 1H), 5.99–5.92 (m, 1H), 5.92–5.84 (m, 1H), 2.35–2.27 (m, 2H), 2.27–2.16 (m, 2H), 1.13–1.00 (m, 21H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 130.5, 127.6, 124.4, 119.1, 108.8, 92.2, 26.6, 22.3, 18.6, 11.3; IR: (ATR) 3040, 2941, 2864, 2133, 1462, 1244 cm^{-1}; MS: (EI) *m*/*z* 260 (M$^+$, 32), 218 (22), 217 (100), 189 (22), 175 (41), 161 (26), 147 (68), 145 (21), 131 (26), 121 (23), 105 (30), 83 (23), 80 (20), 69 (20), 59 (36), HRMS: (EI) calcd for ($C_{17}H_{28}Si$) 260.1960 (M$^+$), found *m*/*z* 260.1962

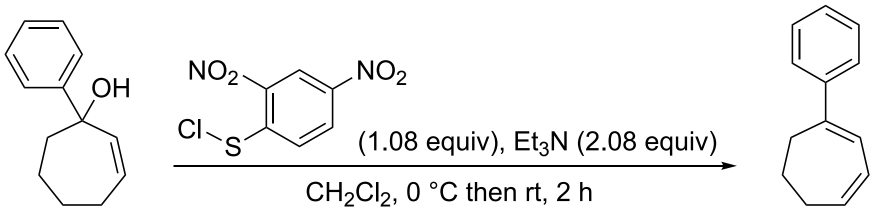
1,5-diphenylcyclohexa-1,3-diene (4k)



According to the typical procedure, the reaction using 1,5-diphenylcyclohexa-2-en-1-ol (0.94 g, 3.76 mmol), CH_2Cl_2 (15 mL), triethylamine (1.04 mL, 7.45 mmol), and 2,4-dinitrobenzenesulfenyl chloride (0.92 g, 3.90 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane) gave the product as a white solid (455 mg, 52% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.49–7.38 (m, 2H), 7.38–7.27 (m, 6H), 7.27–7.17 (m, 2H), 6.38 (d, *J* = 5.2 Hz, 1H), 6.27–6.18 (m, 1H), 5.93 (dd, *J* = 9.2, 3.2 Hz, 1H), 3.88–3.69 (m, 1H), 3.01–2.86 (m, 1H), 2.86–2.70 (m, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 145.3, 140.8, 135.7, 129.6, 128.5, 128.4, 127.6, 127.2, 126.5, 125.4, 125.0, 120.3, 41.0, 34.8

The analytical data for this compound were in excellent agreement with the reported data.[15]

1-phenylcyclohepta-1,3-diene (4l)



According to the typical procedure, the reaction using 1-phenylcyclohepta-2-en-1-ol (0.74 g, 3.92 mmol), CH_2Cl_2 (20 mL), triethylamine (1.15 mL, 8.15 mmol), and 2,4-dinitrobenzenesulfenyl chloride (0.99 g, 4.23 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane) gave the product as a colorless liquid (425 mg, 64% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.44–7.34 (m, 2H), 7.34–7.26 (m, 2H), 7.26–7.15 (m, 1H), 6.06 (d, *J* = 6.4 Hz, 1H), 5.97–5.80 (m, 2H), 2.81–2.65 (m, 2H), 2.50–2.30 (m, 2H), 2.06–1.90 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 144.7, 144.6, 133.9, 128.2, 126.6, 125.9, 125.2, 123.5, 34.2, 32.5, 26.4

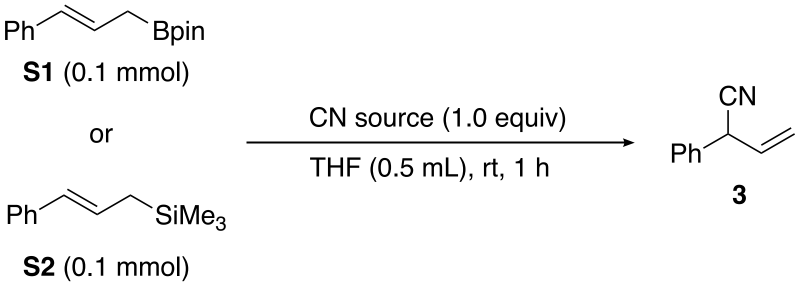
The analytical data for this compound were in excellent agreement with the reported data.[14]

4. Reactions using cinnamyl boronic acid pinacol ester and cinnamyltrimethylsilane

An oven dried 10 mL reaction flask containing a magnetic stir bar was charged with **S1** or **S2** (0.1 mmol), THF (0.5 mL), and NCTS (0.1 mmol). The mixture was stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product, which was analyzed by ^{1}H NMR spectroscopy.

The results are summarized in Table S1. Neither cinnamyl boronic acid pinacol ester (**S1**) nor cinnamyltrimethylsilane (**S2**) underwent electrophilic cynation, and only starting materials were recovered.

Table S1

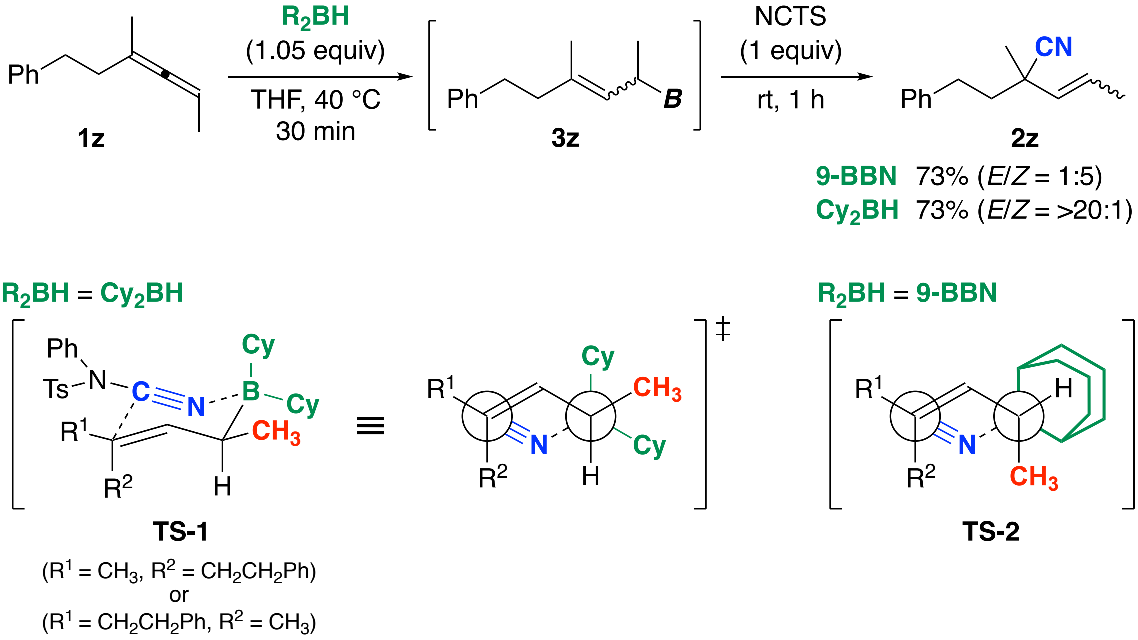


Entry	Nucleophile	CN source	Yield of **3** (%)[a]
1	**S1**	NCTS	0
2	**S1**	TsCN	0
3	**S2**	NCTS	0
4	**S2**	TsCN	0

[a] Determined by ^{1}H NMR.

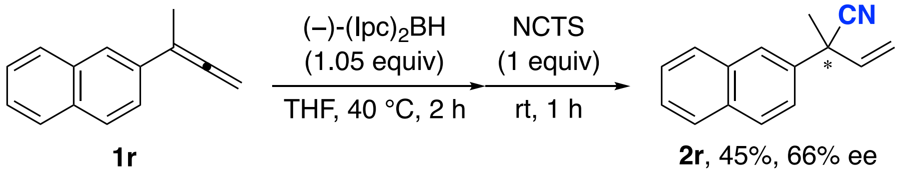
5. Reaction using a trisubstituted allene 1z

When the allene **1z** was subjected to the standard reaction conditions using 9-BBN, the corresponding product **2z** was obtained as a mixture of geometric isomers (*E*/*Z* = 1:5). Meanwhile, the use of Cy_2BH instead of 9-BBN led to (*E*)-**2z** being produced as a single isomer. These stereoselectivities can be explained by the formation of a chair-like six-membered ring transition state in the cyanation step. The reaction using Cy_2BH would proceed through **TS-1**, in which a methyl group at the α-position of the allylic borane **3z** adopts an equatorial position, leading to the formation of the (*E*)-isomer, while the methyl group would be expected to adopt an axial position to minimize steric repulsion between the methyl group and the 9-BBN backbone (**TS-2**, leading to the formation of the (*Z*)-isomer) when 9-BBN is employed.



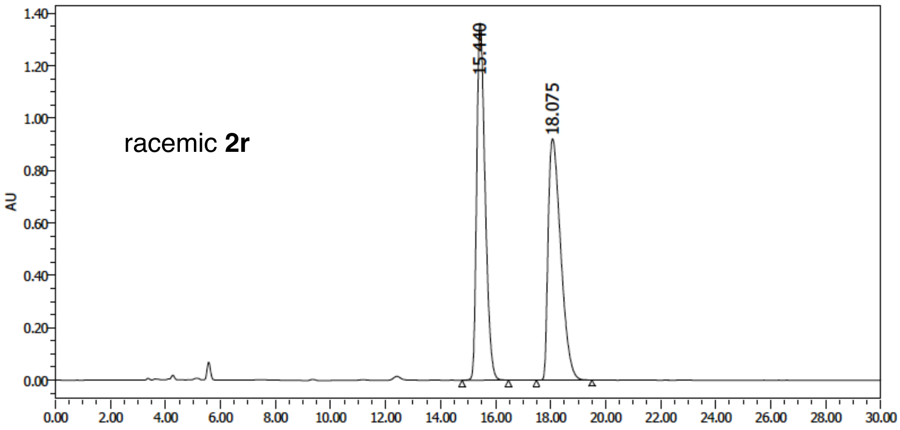
6. Enantioselective cyanation

The reaction of allene 1r

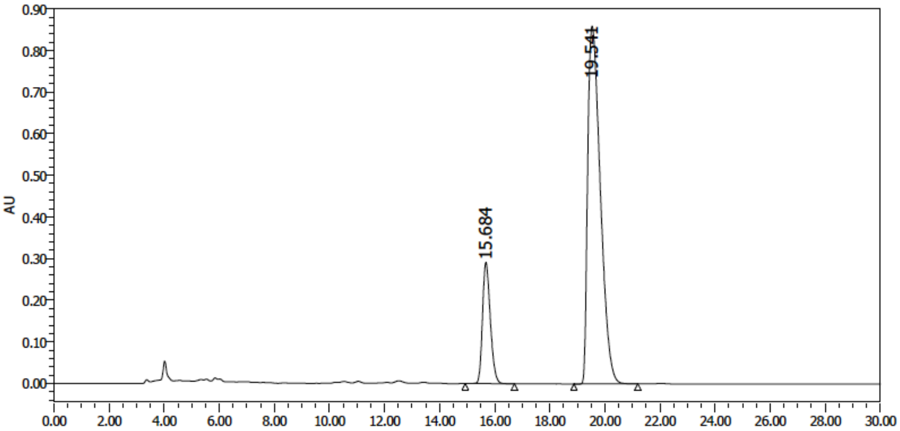


In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with (−)-Ipc_2BH (180.4 mg, 0.63 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 2-(buta-2,3-dien-2-yl)naphthalene (108.1 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 ºC for 2 h before NCTS (163.5 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 95:5) gave the product as a pale yellow liquid (56.2 mg, 45% yield, 66% ee). HPLC analysis (Chiralcel AD-H; 1.0 mL/min; *i*-PrOH/*n*-hexane 0.5:99.5; λ = 209 nm): t_R major = 19.5 min., t_R minor = 15.7 min.; Optical rotation $[\alpha]_D^{20} = -47.7$ (c = 1.01, $CHCl_3$)

The absolute configuration of a major isomer of **2r** was determined to be (*S*) by the optical rotation.[16]

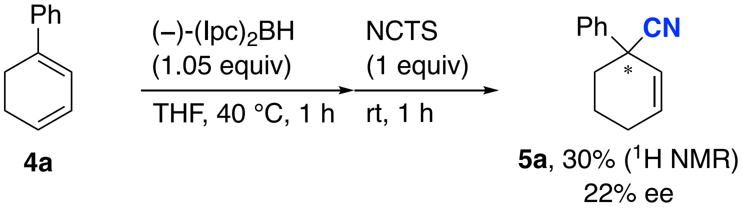


#	retention time	area	area%
1	15.440	29081383	49.98
2	18.075	29110061	50.02

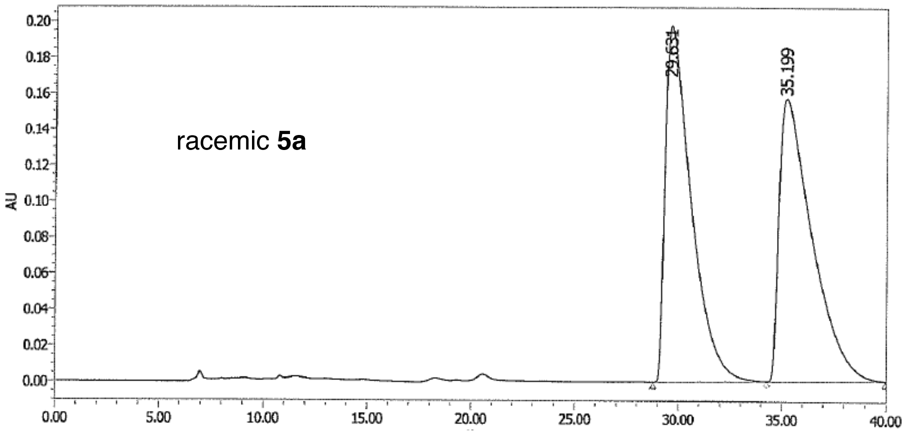


#	retention time	area	area%
1	15.684	5727270	17.34
2	19.541	27298896	82.66

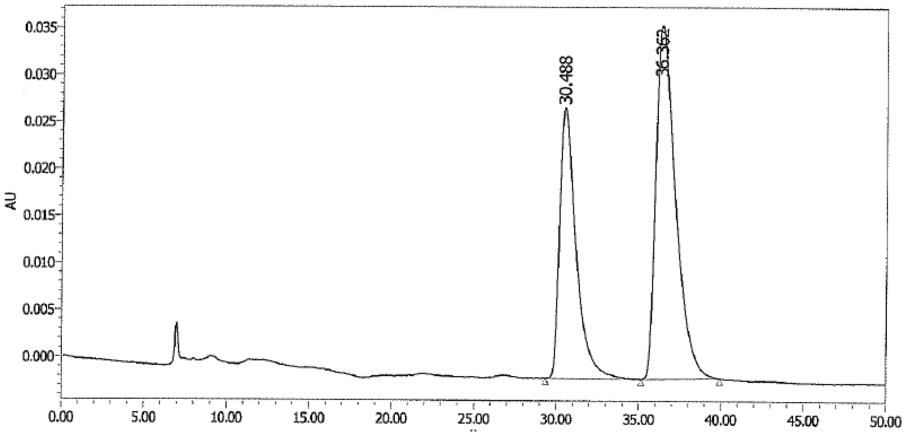
The reaction of cyclic 1,3-diene 4a



In a glove box, an oven dried reaction flask containing a magnetic stir bar was charged with (−)-Ipc$_2$BH (60.6 mg, 0.21 mmol) and THF (1 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-phenylcyclohexa-1,3-diene (31.2 mg, 0.20 mmol) was added to the flask. The mixture was stirred at 40 °C for 1 h before NCTS (54.9 mg, 0.20 mmol) was added and further stirred at room temperature for 1 h. The solution was then concentrated under reduced pressure to give the crude product, which was analyzed by ^{1}H NMR spectroscopy using methyl *tert*-butyl ether (MTBE) as an internal standard. Purification by flash column chromatography on NH silica gel (hexane) gave the product (22% ee). HPLC analysis (CHIRALPAK OB column; 0.5 mL/min; *i*-PrOH/*n*-hexane 0.3:99.7; λ = 220 nm): t_R major = 36.4 min., t_R minor = 30.5 min.



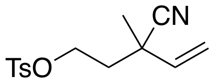
#	retention time	area	area%
1	29.631	17334114	49.90
2	35.199	17402748	50.10



#	retention time	area	area%
1	30.488	2006405	38.91
2	36.362	3150071	61.09

7. Cyanation of allylic boranes: experimental procedure and product data

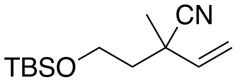
3-cyano-3-methylpent-4-en-1-yl 4-methylbenzenesulfonate (2a)



In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.3 mg, 0.315 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 3-methylpenta-3,4-dien-1-yl 4-methylbenzenesulfonate (151.9 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 ºC for 30 min before TsCN (108.8 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 75:25) gave the product as a colorless liquid (159.2 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, 2H), 7.36 (d, 2H), 5.56 (dd, J = 17.2, 10.0 Hz, 1H), 5.42 (d, J = 17.2 Hz, 1H), 5.23 (d, J = 10.0 Hz, 1H), 4.23–4.05 (m, 2H), 2.46 (s, 3H), 2.11 (ddd, J = 14.0, 7.2, 7.2 Hz, 1H), 1.98 (ddd, J = 14.0, 7.2, 7.2 Hz, 1H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 136.6, 132.5, 129.9, 127.9, 120.9, 116.7, 66.2, 38.5, 38.2, 26.1, 21.6; IR (ATR) 2982, 2926, 2239, 1597 cm^{-1}; MS (EI) m/z 279 (M^+, 5), 155 (32), 92 (20), 91 (100), 65 (41), 53 (21); HRMS: (EI) calcd for ($C_{14}H_{17}NO_3S$) 279.0929 (M^+), found m/z 279.0927

Experimental procedure for gram-scale synthesis of 2a: In a glove box, an oven dried 50 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (770 mg, 3.15 mmol) and THF (20 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 3-methylpenta-3,4-dien-1-yl 4-methylbenzenesulfonate (1.51 g, 6.0 mmol) was added to the flask. The mixture was stirred at 40 ºC for 30 min before TsCN (1.09 g, 6.0 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 75:25 and CH_2Cl_2) gave the product as a colorless liquid (1.60 g, 93% yield).

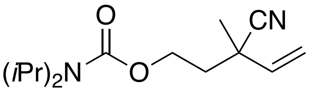
2-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-2-methylbut-3-enenitrile (2b)



In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (38.7 mg, 0.158 mmol) and THF (1 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, *tert*-butyldimethyl((3-methylpenta-3,4-dien-1-yl)oxy)silane (64.0 mg, 0.30 mmol) was added to the flask. The mixture was stirred at 40 ºC for 30 min before NCTS (82.3 mg, 0.30 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 90:10) gave the product as a colorless liquid (61.0 mg, 85% yield). ^{1}H NMR (400

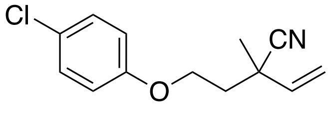
MHz, $CDCl_3$) δ 5.65 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.46 (d, *J* = 17.2 Hz, 1H), 5.21 (d, *J* = 10.4 Hz, 1H), 3.83–3.68 (m, 2H), 1.93 (ddd, *J* = 13.6, 6.8, 6.8 Hz, 1H), 1.82 (ddd, *J* = 13.6, 7.6, 6.0 Hz, 1H), 1.47 (s, 3H), 0.89 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 122.0, 115.4, 59.6, 42.1, 38.7, 26.3, 25.8, 18.2, −5.5; IR (ATR) 2955, 2930, 2857, 2239, 1641 cm^{-1}; HRMS: (CI) calcd for ($C_{13}H_{26}NOSi$) 240.1784 (M^+), found *m*/*z* 240.1785

3-cyano-3-methylpent-4-en-1-yl diisopropylcarbamate (2c)



In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (76.9 mg, 0.315 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 3-methylpenta-3,4-dien-1-yl diisopropylcarbamate (135.2 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 ºC for 30 min before TsCN (108.8 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 90:10 and CH_2Cl_2) gave the product as a colorless liquid (121.4 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 (dd, *J* = 16.4, 10.0 Hz, 1H), 5.51 (d, *J* = 16.4 Hz, 1H), 5.26 (d, *J* = 10.0 Hz, 1H), 4.28–4.13 (m, 2H), 3.90 (sep, *J* = 6.0 Hz, 2H), 2.07 (ddd, *J* = 14.4, 7.2, 7.2 Hz, 1H), 1.97 (ddd, *J* = 14.4, 7.2, 7.2 Hz, 1H), 1.49 (s, 3H), 1.21 (d, *J* = 6.0 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 137.4, 121.7, 116.2, 60.7, 45.9, 38.7, 38.5, 26.1, 20.8 (br); IR (ATR) 2970, 2936, 2239, 1692, 1435, 1310 cm^{-1}; MS (EI) *m*/*z* 252 (M^+, 2), 237 (34), 152 (100); HRMS: (EI) calcd for ($C_{14}H_{24}N_2O_2$) 252.1838 (M^+), found *m*/*z* 252.1837

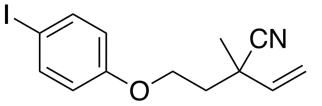
2-(2-(4-chlorophenoxy)ethyl)-2-methylbut-3-enenitrile (2d)



In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.1 mg, 0.315 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-chloro-4-((3-methylpenta-3,4-dien-1-yl)oxy)benzene (125.3 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 ºC for 30 min before TsCN (108.8 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 94:6 and CH_2Cl_2) gave the product as a colorless liquid (127.5 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.20 (m, 2H), 6.85–6.79 (m, 2H), 5.68 (dd, *J* = 16.8, 10.4 Hz, 1H), 5.52 (d, *J* = 16.8 Hz, 1H), 5.27 (d, *J* = 10.4 Hz, 1H), 4.14–4.01 (m, 2H), 2.21 (ddd, *J* = 13.6, 6.8, 6.8 Hz, 1H), 2.06 (ddd, *J* = 13.6, 6.8, 6.8 Hz, 1H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

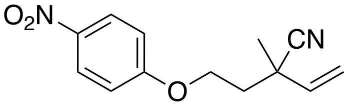
156.9, 137.4, 129.4, 125.9, 121.6, 116.3, 115.7, 64.5, 38.8, 38.6, 26.3; IR (ATR) 2984, 2934, 2880, 2239, 1597 cm^{-1}; MS (EI) *m*/*z* 237 ([M+2]$^+$, 8), 235 (M$^+$, 25), 130 (38), 128 (100), 99 (22), 53 (34); HRMS: (EI) calcd for ($C_{13}H_{14}ClNO$) 235.0764 (M$^+$), found *m*/*z* 235.0765

2-(2-(4-iodophenoxy)ethyl)-2-methylbut-3-enenitrile (2e)



In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.1 mg, 0.315 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-iodo-4-((3-methylpenta-3,4-dien-1-yl)oxy)benzene (181.5 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 ºC for 30 min before NCTS (164.7 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 94:6 and CH_2Cl_2) gave the product as a colorless liquid (170.9 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.53 (m, 2H), 6.70–6.64 (m, 2H), 5.67 (dd, *J* = 17.2, 10.0 Hz, 1H), 5.51 (d, *J* = 17.2 Hz, 1H), 5.27 (d, *J* = 10.0 Hz, 1H), 4.14–3.98 (m, 2H), 2.21 (ddd, *J* = 13.6, 6.8, 6.8 Hz, 1H), 2.05 (ddd, *J* = 13.6, 6.8, 6.8 Hz, 1H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 138.3, 137.3, 121.6, 116.8, 116.3, 83.2, 64.3, 38.8, 38.6, 26.3; IR (ATR) 2955, 2916, 2876, 2237, 1587 cm^{-1}; MS (EI) *m*/*z* 327 (M$^+$, 69), 220 (100), 93 (36), 81 (21), 76 (26), 65 (38), 64 (35), 63 (33), 53 (47); HRMS: (EI) calcd for ($C_{13}H_{14}NOI$) 327.0120 (M$^+$), found *m*/*z* 327.0116

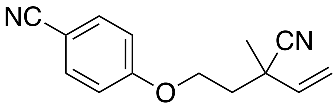
2-methyl-2-(2-(4-nitrophenoxy)ethyl)but-3-enenitrile (2f)



In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.2 mg, 0.315 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-((3-methylpenta-3,4-dien-1-yl)oxy)-4-nitrobenzene (131.9 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 ºC for 30 min before TsCN (108.7 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 90:10) gave the product as a pale yellow liquid (113.2 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24–8.18 (m, 2H), 6.98–6.93 (m, 2H), 5.68 (dd, *J* = 16.8, 10.4 Hz, 1H), 5.54 (d, *J* = 16.8 Hz, 1H), 5.30 (d, *J* = 10.4 Hz, 1H), 4.27–4.13 (m, 2H), 2.28 (ddd, *J* = 13.6, 6.8, 6.8 Hz, 1H), 2.11 (ddd, *J* = 13.6, 6.8, 6.8 Hz, 1H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 141.8, 137.1, 126.0, 121.4, 116.6, 114.4, 65.0, 38.8, 38.4, 26.5; IR (ATR) 2934, 2239, 1593, 1512 cm^{-1}; MS (EI) *m*/*z*

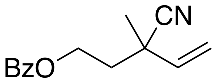
246 (M^+, 39), 139 (34), 109 (60), 108 (20), 93 (32), 91 (27), 81 (100), 80 (44), 79 (29), 65 (32), 64 (26), 63 (29), 53 (80); HRMS: (EI) calcd for ($C_{13}H_{14}N_2O_3$) 246.1004 (M^+), found *m*/*z* 246.1005

4-((3-cyano-3-methylpent-4-en-1-yl)oxy)benzonitrile (2g)



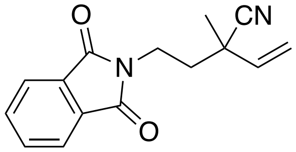
In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.5 mg, 0.315 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, NCTS (164.1 mg, 0.60 mmol) and 4-((3-methylpenta-3,4-dien-1-yl)oxy)benzonitrile (120.2 mg, 0.60 mmol) were added to the flask, and the solution was stirred at 40 ºC for 1.5 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 85:15 and CH_2Cl_2) gave the product as a colorless liquid (118.2 mg, 87% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.63–7.57 (m, 2H), 6.98–6.91 (m, 2H), 5.68 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.53 (d, *J* = 17.2 Hz, 1H), 5.29 (d, *J* = 10.4 Hz, 1H), 4.24–4.08 (m, 2H), 2.25 (ddd, *J* = 13.6, 6.8, 6.8 Hz, 1H), 2.09 (ddd, *J* = 13.6, 6.8, 6.8 Hz, 1H), 1.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 137.1, 134.0, 121.4, 119.1, 116.5, 115.1, 104.4, 64.5, 38.7, 38.4, 26.4; IR (ATR) 2926, 2224, 1605, 1508 cm^{-1}; MS (EI) *m*/*z* 226 (M^+, 33), 119 (100), 102 (29), 91 (25), 90 (20), 81 (57), 80 (27), 53 (52); HRMS: (EI) calcd for ($C_{14}H_{14}N_2O$) 226.1106 (M^+), found *m*/*z* 226.1103

3-cyano-3-methylpent-4-en-1-yl benzoate (2h)



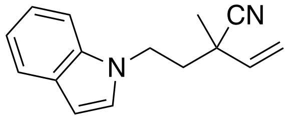
In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.0 mg, 0.315 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, NCTS (163.8 mg, 0.60 mmol) and 3-methylpenta-3,4-dien-1-yl benzoate (121.0 mg, 0.60 mmol) were added to the flask, and the solution was stirred at 40 ºC for 1.5 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 85:15) gave the product as a colorless liquid (119.9 mg, 87% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 5.68 (dd, *J* = 16.8, 10.0 Hz, 1H), 5.55 (d, *J* = 16.8 Hz, 1H), 5.30 (d, *J* = 10.0 Hz, 1H), 4.54–4.48 (m, 2H), 2.22 (ddd, *J* = 13,6, 6.8, 6.8 Hz, 1H), 2.07 (ddd, *J* = 13.6, 6.8, 6.8 Hz, 1H), 1.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 137.1, 133.1, 129.8, 129.7, 128.4, 121.6, 116.5, 61.1, 38.7, 38.4, 26.3; IR (ATR) 3071, 2982, 2934, 2239, 1721, 1603 cm^{-1}; MS (EI) *m*/*z* 229 (M^+, 1), 105 (100), 77 (35); HRMS: (EI) calcd for ($C_{14}H_{15}NO_2$) 229.1103 (M^+), found *m*/*z* 229.1105

2-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-2-methylbut-3-enenitrile (2i)



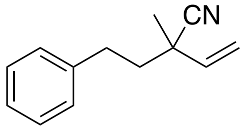
In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.1 mg, 0.315 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, NCTS (163.2 mg, 0.60 mmol) and 2-(3-methylpenta-3,4-dien-1-yl)isoindoline-1,3-dione (136.3 mg, 0.60 mmol) were added to the flask, and the solution was stirred at 40 ºC for 1.5 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product as a white solid (118.9 mg, 78% yield). mp: 69.6–70.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.82 (m, 2H), 7.75–7.69 (m, 2H), 5.67 (dd, J = 17.2, 9.6 Hz, 1H), 5.55 (d, J = 17.2 Hz, 1H), 5.32 (d, J = 9.6 Hz, 1H), 3.92–3.73 (m, 2H), 2.12 (ddd, J = 15.6, 8.4, 5.2 Hz, 1H), 1.97 (ddd, J = 15.6, 9.6, 5.2 Hz, 1H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 136.8, 134.1, 132.0, 123.3, 121.1, 116.9, 38.7, 37.2, 34.2, 26.0; IR (ATR) 3458, 2926, 2876, 2241, 1771, 1705 cm^{-1}; MS (EI) *m*/*z* 254 (M^+, 8), 173 (39), 161 (49), 160 (100), 133 (28), 130 (44), 105 (26), 104 (42), 80 (31), 77 (53), 76 (66), 53 (54), 52 (20), 51 (23), 50 (31); HRMS: (EI) calcd for ($C_{15}H_{14}N_2O_2$) 254.1055 (M^+), found *m*/*z* 254.1054

2-(2-(1*H*-indol-1-yl)ethyl)-2-methylbut-3-enenitrile (2j)



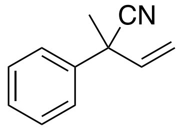
In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (76.9 mg, 0.315 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-(3-methylpenta-3,4-dien-1-yl)-1*H*-indole (119.3 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 ºC for 30 min before NCTS (163.8 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 87:13) gave the product as a pale yellow liquid (114.7 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.6 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 7.07 (d, J = 2.8 Hz, 1H), 6.50 (d, J = 2.8 Hz, 1H), 5.70–5.52 (m, 2H), 5.33 (d, J = 7.2 Hz, 1H), 4.38–4.18 (m, 2H), 2.20 (ddd, J = 16.4, 9.2, 5.6 Hz, 1H), 2.05 (ddd, J = 16.4, 10.8, 5.6 Hz, 1H), 1.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 135.6, 128.7, 127.5, 121.7, 121.2, 121.1, 119.6, 116.9, 109.0, 101.7, 42.8, 39.5, 39.2, 26.2; IR (ATR) 3055, 2980, 2932, 2237, 1464 cm^{-1}; MS (EI) *m*/*z* 224 (M^+, 27), 157 (20), 130 (100), 116 (21), 89 (24), 77 (23), 53 (33); HRMS: (EI) calcd for ($C_{15}H_{16}N_2$) 224.1313 (M^+), found *m*/*z* 224.1310

2-methyl-2-phenethylbut-3-enenitrile (2k)



In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.2 mg, 0.315 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, (3-methylpenta-3,4-dien-1-yl)benzene (95.4 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 ºC for 30 min before TsCN (109.6 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 95:5) gave the product as a colorless liquid (93.3 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.2 Hz, 2H), 7.23–7.15 (m, 3H), 5.65 (dd, *J* = 17.2, 9.6 Hz, 1H), 5.53 (d, *J* = 17.2 Hz, 1H), 5.29 (d, *J* = 9.6 Hz, 1H), 2.83–2.65 (m, 2H), 2.05–1.90 (m, 1H), 1.88–1.75 (m, 1H), 1.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 137.8, 128.5, 128.3, 126.2, 121.9, 116.2, 41.8, 40.7, 31.7, 26.0; IR (ATR) 3028, 2982, 2237, 1454 cm^{-1}; MS (EI) *m/z* 185 (M^+, 3), 105 (100), 104 (57), 91 (52), 79 (21), 77 (24), 65 (22); HRMS: (EI) calcd for ($C_{13}H_{15}N$) 185.1204 (M^+), found *m/z* 185.1203

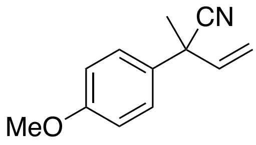
2-methyl-2-phenylbut-3-enenitrile (2l)



In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.0 mg, 0.63 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, buta-2,3-dien-2-ylbenzene (77.8 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 ºC for 2 h before TsCN (109.2 mg, 0.60 mmol) was added and further stirred at room tempareture for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 95:5) gave the product as a colorless liquid (71.8 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.43 (m, 2H), 7.43–7.36 (m, 2H), 7.36–7.29 (m, 1H), 5.96 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.54 (d, *J* = 17.2 Hz, 1H), 5.33 (d, *J* = 10.4 Hz, 1H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 138.2, 128.9, 127.9, 125.8, 121.7, 115.6, 44.3, 26.6

The analytical data for this compound were in excellent agreement with the reported data.[17]

2-(4-methoxyphenyl)-2-methylbut-3-enenitrile (2m)

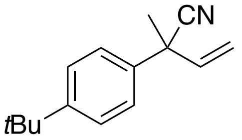


In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with

9-BBN dimer (77.1 mg, 0.63 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-(buta-2,3-dien-2-yl)-4-methoxybenzene (96.0 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 ºC for 2 h before TsCN (108.7 mg, 0.60 mmol) was added and further stirred at room tempareture for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 95:5 and CH_2Cl_2) gave the product as a colorless liquid (82.1 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.32 (m, 2H), 6.93–6.88 (m, 2H), 5.91 (dd, J = 16.8, 10.4 Hz, 1H), 5.51 (d, J = 16.8 Hz, 1H), 5.30 (d, J = 10.4 Hz, 1H), 3.81 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 138.6, 131.4, 127.1, 122.0, 115.3, 114.2, 55.3, 43.7, 26.7

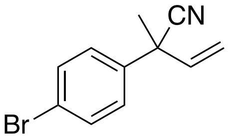
The analytical data for this compound were in excellent agreement with the reported data.[17]

2-(4-*tert*-butylphenyl)-2-methylbut-3-enenitrile (2n)



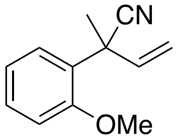
In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.1 mg, 0.315 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-(buta-2,3-dien-2-yl)-4-*tert*-butylbenzene (112.1 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 ºC for 2 h before NCTS (163.5 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 94:6) gave the product as a colorless liquid (106.1 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.32 (m, 4H), 5.94 (dd, J = 17.2, 10.0 Hz, 1H), 5.53 (d, J = 17.2 Hz, 1H), 5.30 (d, J = 10.0 Hz, 1H), 1.81 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 138.5, 136.4, 125.9, 125.6, 121.9, 115.4, 44.1, 34.5, 31.2, 26.6; IR (ATR) 2963, 2905, 2237, 1638 cm^{-1}; MS (EI) m/z 213 (M^+, 14), 198 (100), 115 (23); HRMS: (EI) calcd for ($C_{15}H_{19}N$) 213.1517 (M^+), found m/z 213.1514

2-(4-bromophenyl)-2-methylbut-3-enenitrile (2o)



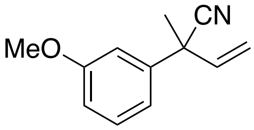
n a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.0 mg, 0.315 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-bromo-4-(buta-2,3-dien-2-yl)benzene (125.8 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 ºC for 2 h before TsCN (108.9 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 94:6) gave the product as a colorless liquid (117.1 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.49 (m, 2H), 7.35–7.29 (m, 2H), 5.91 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.53 (d, *J* = 17.2 Hz, 1H), 5.35 (d, *J* = 10.4 Hz, 1H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 137.7, 132.1, 127.7, 122.2, 121.3, 116.3, 44.1, 26.6; IR (ATR) 3092, 2988, 2938, 2237, 1638, 1489 cm^{-1}; MS (EI) *m*/*z* 237 ($[M+2]^+$, 12), 235 (M^+, 13) 141 (100), 140 (29), 129 (33), 128 (20), 51 (20), 50 (21); HRMS: (EI) calcd for ($C_{11}H_{10}BrN$) 234.9997 (M^+), found *m*/*z* 234.9999

2-(2-methoxyphenyl)-2-methylbut-3-enenitrile (2p)



In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.4 mg, 0.315 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-(buta-2,3-dien-2-yl)-2-methoxybenzene (96.5 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 °C for 2 h before TsCN (109.1 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 95:5) gave the product as a colorless liquid (93.6 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.29 (m, 2H), 7.00–6.91 (m, 2H), 6.09 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.50 (d, *J* = 17.2 Hz, 1H), 5.30 (d, *J* = 10.4 Hz, 1H), 3.90 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 137.6, 129.6, 127.2, 126.7, 121.9, 120.7, 115.4, 112.1, 55.5, 42.1, 25.3; IR (ATR) 2982, 2940, 2839, 2237, 1491 cm^{-1}; MS (EI) *m*/*z* 187 (M^+, 56), 172 (100), 145 (32), 144 (29), 117 (20), 116 (25), 115 (49), 105 (25), 91 (26), 89 (22), 77 (33), 63 (23), 51 (27); HRMS: (EI) calcd for ($C_{12}H_{13}NO$) 187.0997 (M^+), found *m*/*z* 187.1000

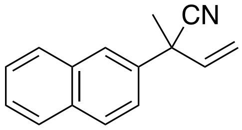
2-(3-methoxyphenyl)-2-methylbut-3-enenitrile (2q)



In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.4 mg, 0.315 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-(buta-2,3-dien-2-yl)-3-methoxybenzene (96.9 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 °C for 2 h before TsCN (109.1 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 95:5) gave the product as a colorless liquid (88.5 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 8.0 Hz, 1H), 7.06–6.99 (m, 1H), 6.99–6.93 (m, 1H), 6.89–6.82 (m, 1H), 5.94 (dd, *J* = 17.2, 10.0 Hz, 1H), 5.54 (d, *J* = 17.2 Hz, 1H), 5.32

(d, *J* = 10.0 Hz, 1H), 3.83 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 141.0, 138.1, 130.0, 121.7, 118.1, 115.7, 113.1, 112.2, 55.3, 44.4, 26.6; IR (ATR) 2986, 2837, 2237, 1601 cm^{-1}; MS (EI) *m/z* 187 (M$^+$, 62), 172 (100), 145 (37), 144 (38), 129 (22), 128 (22), 117 (25), 116 (28), 115 (54), 103 (21), 102 (23), 91 (23), 89 (22), 77 (30), 64 (21), 63 (31), 51 (23); HRMS: (EI) calcd for ($C_{12}H_{13}NO$) 187.0997 (M$^+$), found *m/z* 187.0998

2-methyl-2-(naphthalene-2-yl)but-3-enenitrile (2r)

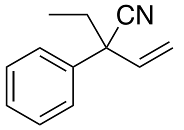


In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.2 mg, 0.315 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 2-(buta-2,3-dien-2-yl)naphthalene (107.9 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 ºC for 2 h before TsCN (108.7 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 95:5) gave the product as a pale yellow liquid (111.4 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.83 (m, 4H), 7.55–7.49 (m, 3H), 6.04 (dd, *J* = 16.8, 10.4 Hz, 1H), 5.59 (d, *J* = 16.8 Hz, 1H), 5.38 (d, *J* = 10.4 Hz, 1H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 136.6, 133.1, 132.7, 128.9, 128.1, 127.5, 126.7, 126.6, 124.7, 123.7, 121.8, 116.0, 44.5, 26.6

The analytical data for this compound were in excellent agreement with the reported data.[16]

Experimental procedure for gram-scale synthesis of 2r: In a glove box, an oven dried 100 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (1.28 g, 5.25 mmol) and THF (33 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 2-(buta-2,3-dien-2-yl)naphthalene (1.8 g, 10 mmol) was added to the flask. The mixture was stirred at 40 ºC for 2 h before TsCN (1.81 g, 10 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 96:4) gave the product as a pale yellow liquid (1.85 g, 89% yield).

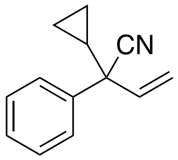
2-ethyl-2-phenylbut-3-enenitrile (2s)



In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (76.7 mg, 0.63 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, penta-1,2-dien-3-ylbenzene (86.1 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 ºC for 2 h before TsCN (108.8 mg, 0.60 mmol) was added and further stirred at room tempareture for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 95:5) gave the product as a colorless liquid (79.9 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.27 (m, 5H), 5.92 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.55 (d, *J* = 17.2 Hz, 1H), 5.33 (d, *J* = 10.4 Hz, 1H), 2.17–1.98 (m, 2H), 1.03 (dd, *J* = 7.6, 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 137.3, 128.9, 127.9, 126.1, 120.5, 116.5, 51.1, 33.0, 9.6

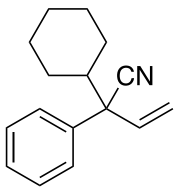
The analytical data for this compound were in excellent agreement with the reported data.[18]

2-cyclopropyl-2-phenylbut-3-enenitrile (2t)



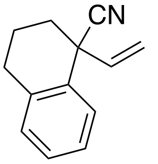
In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.1 mg, 0.315 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, (1-cyclopropylpropa-1,2-dien-1-yl)benzene (93.5 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 ºC for 2 h before TsCN (108.9 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 96:4 and CH_2Cl_2) gave the product as a colorless liquid (61.4 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 5.90 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.58 (d, *J* = 17.2 Hz, 1H), 5.36 (d, *J* = 10.4 Hz, 1H), 1.46–1.35 (m, 1H), 0.80–0.69 (m, 2H), 0.69–0.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 136.3, 128.8, 128.1, 126.7, 119.2, 116.7, 51.4, 18.5, 2.9, 2.7; IR (ATR) 3086, 3011, 2239, 1636 cm^{-1}; MS (EI) *m*/*z* 183 (M^+, 2), 155 (53), 154 (51), 140 (34), 129 (20), 128 (39), 127 (27), 116 (24), 115 (100), 104 (60), 91 (39), 77 (26), 51 (34); HRMS: (EI) calcd for ($C_{13}H_{13}N$) 183.1048 (M^+), found *m*/*z* 183.1045

2-cyclohexyl-2-phenylbut-3-enenitrile (2u)



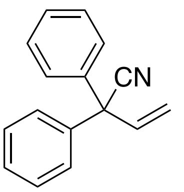
In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.1 mg, 0.315 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, (1-cyclohexylpropa-1,2-dien-1-yl)benzene (118.1 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 ºC for 2 h before TsCN (109.1 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 95:5) gave the product as a colorless liquid (118.7 mg, 88% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45–7.34 (m, 4H), 7.30 (t, *J* = 7.2 Hz, 1H), 5.97 (dd, *J* = 16.4, 10.4 Hz, 1H), 5.57 (d, *J* = 16.4 Hz, 1H), 5.30 (d, *J* = 10.4 Hz, 1H), 1.94–1.78 (m, 3H), 1.73–1.62 (m, 2H), 1.46–1.36 (m, 1H), 1.30–1.05 (m, 5H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.7, 136.7, 128.9, 127.7, 126.1, 119.5, 116.5, 56.6, 46.2, 28.6, 28.3, 26.3, 26.2, 25.9; IR (ATR) 2930, 2855, 2239, 1638 cm^{-1}; MS (EI) *m*/*z* 225 (M$^+$, 1), 143 (100), 116 (21), 115 (47), 55 (56); HRMS: (EI) calcd for ($C_{16}H_{19}N$) 225.1517 (M$^+$), found *m*/*z* 225.1517

1-vinyl-1,2,3,4-tetrahydronaphthalene-1-carbonitrile (2v)



In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.1 mg, 0.315 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-vinylidene-1,2,3,4-tetrahydronaphthalene (93.0 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 °C for 2 h before TsCN (108.9 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 95:5) gave the product as a colorless liquid (90.5 mg, 83% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35–7.29 (m, 1H), 7.25–7.17 (m, 2H), 7.16–7.10 (m, 1H), 5.81 (dd, *J* = 17.2, 10.0 Hz, 1H), 5.58 (d, *J* = 17.2 Hz, 1H), 5.37 (d, *J* = 10.0 Hz, 1H), 2.94–2.76 (m, 2H), 2.33–2.23 (m, 1H), 2.10–1.92 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.5, 136.3, 132.9, 129.8, 129.3, 128.2, 126.6, 122.0, 116.5, 44.5, 35.3, 28.8, 19.3; IR (ATR) 2943, 2866, 2234, 1638, 1489 cm^{-1}; MS (EI) *m*/*z* 183 (M$^+$, 51), 156 (32), 155 (100), 154 (88), 153 (24), 141 (39), 140 (26), 129 (62), 128 (57), 127 (39), 115 (49), 104 (20); HRMS: (EI) calcd for ($C_{13}H_{13}N$) 183.1048 (M$^+$), found *m*/*z* 183.1044

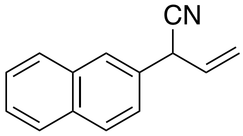
2,2-diphenylbut-3-enenitrile (2w)



In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.1 mg, 0.63 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, propa-1,2-diene-1,1-diyldibenzene (115.6 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 °C for 2 h before TsCN (108.8 mg, 0.60 mmol) was added and further stirred at room tempareture for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 96:4) gave the product as a pale yellow liquid (109.6 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.28 (m, 10H), 6.28 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.53 (d, *J* = 16.8 Hz, 1H), 5.48 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 137.0, 128.9, 128.2, 127.7, 120.6, 117.6, 54.8

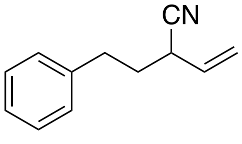
The analytical data for this compound were in excellent agreement with the reported data.[17]

2-(naphthalene-2-yl)but-3-enenitrile (2x)



In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.1 mg, 0.315 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, NCTS (163.4 mg, 0.60 mmol) and 2-(propa-1,2-dien-1-yl)naphthalene (100.0 mg, 0.60 mmol) was added to the flask, and the solution was stirred at 40 ºC for 2.5 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 95:5) gave the product as a colorless liquid (60.2 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.80 (m, 4H), 7.57–7.48 (m, 2H), 7.40 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.97 (ddd, *J* = 17.2, 10.0, 6.0 Hz, 1H), 5.59 (dd, *J* = 17.2, 2.0 Hz, 1H), 5.41 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.71 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.3, 132.9, 132.1, 131.4, 129.2, 127.9, 127.7, 126.8, 126.7, 126.6, 124.9, 118.7, 118.5, 40.8; IR (ATR) 3059, 2928, 2245, 1601 cm^{-1}; MS (EI) *m/z* 193 (M^+, 100), 192 (44), 178 (21), 166 (28), 165 (69); HRMS: (EI) calcd for ($C_{14}H_{11}N$) 193.0891 (M^+), found *m/z* 193.0889

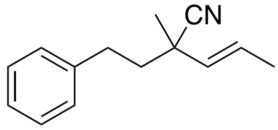
2-phenethylbut-3-enenitrile (2y)



In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.0 mg, 0.315 mmol) and THF (2 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, NCTS (163.8 mg, 0.60 mmol) and penta-3,4-dien-1-ylbenzene (86.5 mg, 0.60 mmol) was added to the flask, and the solution was stirred at 40 ºC for 1.5 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 95:5) gave the product as a colorless liquid (70.9 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 8.0 Hz, 2H), 7.25–7.17 (m, 3H), 5.73 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.45 (d, *J* = 17.2 Hz, 1H), 5.31 (d, *J* = 10.4 Hz, 1H), 3.24 (ddd, *J* = 6.8, 6.8, 6.8 Hz, 1H), 2.92–2.72 (m, 2H), 2.18–1.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 131.7, 128.7, 128.4, 126.5, 119.6, 118.7, 34.4, 34.3, 32.8; IR

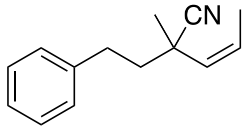
(ATR) 3028, 2928, 2241, 1643 cm^{-1}; MS (EI) *m/z* 171 (M$^+$, 20), 105 (48), 104 (35), 92 (78), 91 (100), 80 (36), 77 (25), 65 (27); HRMS: (EI) calcd for ($C_{12}H_{13}N$) 171.1048 (M$^+$), found *m/z* 171.1047

(*E*)-2-methyl-2-phenethylpent-3-enenitrile ((*E*)-2z)



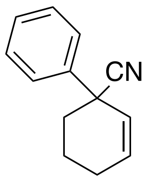
In a glove box, an oven dried 10 mL reaction flask containing a magnetic stir bar was charged with dicyclohexylborane (56.2 mg, 0.315 mmol) and THF (1 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, (3-methylhexa-3,4-dien-1-yl)benzene (52.2 mg, 0.30 mmol) was added to the flask. The mixture was stirred at 40 ºC for 30 min before NCTS (81.6 mg, 0.30 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 95:5 and CH_2Cl_2) gave the product as a colorless liquid (44.5 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.25 (m, 2H), 7.23–7.14 (m, 3H), 5.94 (dq, *J* = 16.4, 10.0 Hz, 1H), 5.27 (dq, *J* = 16.4 Hz, 1.6 Hz, 1H), 2.81–2.65 (m, 2H), 1.98–1.88 (m, 1H), 1.85–1.76 (m, 1H), 1.76 (dd, *J* = 10.0, 1.6 Hz, 3H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 130.9, 128.5, 128.3, 127.1, 126.1, 122.7, 42.3, 39.6, 31.8, 26.4, 17.5; IR (ATR) 3028, 2978, 2934, 2236, 1603, 1497, 1454, 966 cm^{-1}; MS (EI) *m/z* 199 (M$^+$, 8), 105 (100), 104 (25), 91 (26); HRMS: (EI) calcd for ($C_{14}H_{17}N$) 199.1361 (M$^+$), found *m/z* 199.1363

(*Z*)-2-methyl-2-phenethylpent-3-enenitrile ((*Z*)-2z)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.12 (m, 5H), 5.70 (dq, *J* = 11.6, 7.2 Hz, 1H), 5.21–5.15 (m, 1H), 2.89–2.72 (m, 2H), 2.02–1.86 (m, 5H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 129.8, 129.1, 128.6, 128.3, 126.2, 123.4, 43.4, 35.5, 31.6, 26.7, 13.6

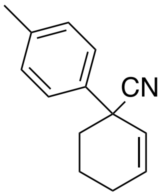
1-phenylcyclohex-2-ene-1-carbonitrile (5a)



In a glove box, an oven dried reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (76.9 mg, 0.375 mmol) and THF (3 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-phenylcyclohexa-1,3-diene (93.2 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 °C for 1 h before NCTS (163.0 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 97:3) gave the product as a colorless liquid (88.1 mg, 81% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.55–7.43 (m, 2H), 7.43–7.35 (m, 2H), 7.35–7.28 (m, 1H), 6.17 (ddd, *J* = 10.0, 3.6, 3.6 Hz, 1H), 5.80–5.70 (m, 1H), 2.39–2.27 (m, 1H), 2.27–2.05 (m, 2H), 2.03–1.65 (m, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 140.8, 132.4, 128.8, 127.8, 126.2, 125.8, 122.5, 42.5, 38.0, 24.2, 19.3; IR: (ATR) 2934, 2232, 1491, 1449 cm^{-1}; MS: (EI) *m*/*z* 183 (M^+, 63), 182 (26), 156 (29), 155 (100), 154 (75), 142 (22), 140 (31), 129 (42), 128 (42), 127 (33), 115 (83), 105 (63), 78 (23), 77 (36), 51 (34); HRMS: (EI) calcd for ($C_{13}H_{13}N$) 183.1048 (M^+), found *m*/*z* 183.1045

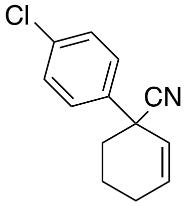
Experimental procedure for gram-scale synthesis of 5a: In a glove box, an oven dried reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (1.28 g, 5.25 mmol) and THF (50 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-phenylcyclohexa-1,3-diene (1.56 g, 10.0 mmol) was added to the flask. The mixture was stirred at 40 °C for 1 h before NCTS (2.72 g, 10.0 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 97:3) gave the product as a colorless liquid (1.56 g, 85% yield).

1-(4-methylphenyl)cyclohex-2-ene-1-carbonitrile (5b)



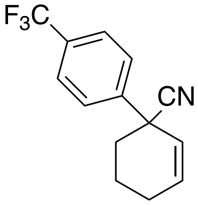
In a glove box, an oven dried reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (76.6 mg, 0.315 mmol) and THF (3 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-(4-methylphenyl)cyclohexa-1,3-diene (102.2 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 °C for 1 h before NCTS (164.0 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 97:3) gave the product as a colorless liquid (103.5 mg, 87% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.15 (ddd, *J* = 10.0, 3.6, 3.6 Hz, 1H), 5.75 (d, *J* = 10.0 Hz, 1H), 2.43–2.26 (m, 1H), 2.36 (s, 3H), 2.26–2.04 (m, 2H), 2.00–1.65 (m, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 137.8, 137.6, 132.2, 129.4, 126.1, 125.9, 122.6, 42.1, 38.0, 24.2, 20.9, 19.3; IR: (ATR) 3030, 2932, 2864, 2835, 2232, 1512, 1445 cm^{-1}; MS: (EI) *m*/*z* 197 (M^+, 37), 169 (42), 168 (21), 155 (20), 154 (100), 129 (25), 128 (22), 127 (27), 115 (30), 105 (29), 92 (48), 91 (30), 77 (23); HRMS: (EI) calcd for ($C_{14}H_{15}N$) 197.1204 (M^+), found *m*/*z* 197.1207

1-(4-chlorophenyl)cyclohex-2-ene-1-carbonitrile (5c)



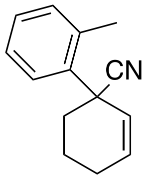
In a glove box, an oven dried reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.1 mg, 0.315 mmol) and THF (3 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-(4-chlorophenyl)cyclohexa-1,3-diene (114.8 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 °C for 1 h before NCTS (163.4 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 97:3) gave the product as a pale yellow liquid (113.2 mg, 86% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.47–7.29 (m, 4H), 6.18 (ddd, J = 9.2, 3.6, 3.6 Hz, 1H), 5.79–5.65 (m, 1H), 2.36–2.05 (m, 3H), 2.01–1.86 (m, 1H), 1.86–1.67 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 139.3, 133.8, 132.9, 128.9, 127.6, 125.2, 122.1, 42.0, 37.9, 24.1, 19.1; IR: (ATR) 2934, 2359, 2234, 1493 cm^{-1}; MS: (EI) *m*/*z* 219 ($[M+2]^+$, 8), 217 (M^+, 20), 154 (100), 127 (25), 105 (21); HRMS: (EI) calcd for ($C_{13}H_{12}ClN$) 217.0658 (M^+), found *m*/*z* 217.0660

1-(4-trifluoromethylphenyl)cyclohex-2-ene-1-carbonitrile (5d)



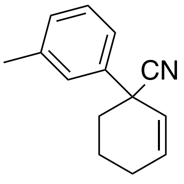
In a glove box, an oven dried reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.4 mg, 0.315 mmol) and THF (3 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-(4-trifluoromethylphenyl)cyclohexa-1,3-diene (134.4 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 °C for 1 h before NCTS (163.7 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 97:3) gave the product as a colorless liquid (126.5 mg, 84% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 6.23 (ddd, J = 9.6, 4.4, 3.6 Hz 1H), 5.80–5.71 (m, 1H), 2.40–2.09 (m, 3H), 2.04–1.89 (m, 1H), 1.89–1.69 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 144.7, 133.3, 130.2 (q, J_{CF} = 32.1 Hz), 126.7, 125.8 (q, J_{CF} = 4.1 Hz), 124.9, 123.8 (q, J_{CF} = 270.5 Hz), 121.8, 42.5, 37.9, 24.1, 19.2; ^{19}F NMR: (377 MHz, $CDCl_3$) δ −65.2; IR: (ATR) 2936, 2234, 1618, 1414, 1325 cm^{-1}; MS: (EI) *m*/*z* 251 (M^+, 31), 223 (32), 154 (100), 127 (28), 54 (76); HRMS: (EI) calcd for ($C_{14}H_{12}F_3N$) 251.0922 (M^+), found *m*/*z* 251.0918

1-(2-methylphenyl)cyclohex-2-ene-1-carbonitrile (5e)



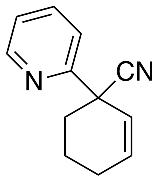
In a glove box, an oven dried reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (76.8 mg, 0.315 mmol) and THF (3 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-(2-methylphenyl)cyclohexa-1,3-diene (99.9 mg, 0.59 mmol) was added to the flask. The mixture was stirred at 40 °C for 1 h before NCTS (163.6 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 97:3) gave the product as a colorless liquid (99.5 mg, 86% yield). ^{1}H NMR: (400 MHz, CDCl$_3$) δ 7.50–7.37 (m, 1H), 7.29–7.15 (m, 3H), 6.16 (ddd, *J* = 9.6, 4.0, 4.0 Hz, 1H), 5.86 (d, *J* = 9.6 Hz, 1H), 2.58 (s, 3H), 2.40–2.28 (m, 1H), 2.28–2.07 (m, 2H), 2.07–1.98 (m, 1H), 1.98–1.81 (m, 1H), 1.78–1.60 (m, 1H); ^{13}C NMR: (100 MHz, CDCl$_3$) δ 137.0, 135.7, 132.7, 131.6, 127.9, 127.6, 126.6, 126.1, 122.4, 41.5, 33.9, 24.1, 20.7, 18.9; IR: (ATR) 2932, 2228, 1487, 1454 cm^{-1}; MS: (EI) *m*/*z* 197 (M$^+$, 37), 169 (26), 168 (29), 155 (24), 154 (100), 141 (22), 129 (34), 128 (32), 127 (34), 115 (48), 105 (55), 92 (68), 91 (33), 77 (28), 65 (27), 51 (21); HRMS: (EI) calcd for ($C_{14}H_{15}N$) 197.1204 (M$^+$), found *m*/*z* 197.1204

1-(3-methylphenyl)cyclohex-2-ene-1-carbonitrile (5f)



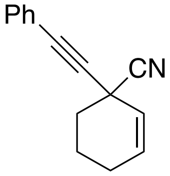
In a glove box, an oven dried reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.2 mg, 0.315 mmol) and THF (3 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-(3-methylphenyl)cyclohexa-1,3-diene (109.2 mg, 0.64 mmol) was added to the flask. The mixture was stirred at 40 °C for 1 h before NCTS (163.8 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 97:3) gave the product as a colorless liquid (102.1 mg, 81% yield). ^{1}H NMR: (400 MHz, CDCl$_3$) δ 7.39–7.20 (m, 3H), 7.12 (d, *J* = 6.4 Hz, 1H), 6.15 (ddd, *J* = 9.6, 4.0, 4.0 Hz, 1H), 5.81–5.69 (m, 1H), 2.37 (s, 3H), 2.32–2.25 (m, 1H), 2.25–2.05 (m, 2H) 2.03–1.68 (m, 3H); ^{13}C NMR: (100 MHz, CDCl$_3$) δ 140.6, 138.4, 132.1, 128.5, 128.4, 126.7, 125.8, 123.1, 122.4, 42.3, 37.9, 24.1, 21.3, 19.2; IR: (ATR) 3032, 2938, 2864, 2835, 2232, 1607 cm^{-1}; MS: (EI) *m*/*z* 197 (M$^+$, 55), 196 (26), 169 (25), 168 (29), 155 (23), 154 (100), 143 (27), 129 (30), 128 (27), 127 (34), 115 (38), 105 (65), 92 (93), 91 (38), 77 (29), 65 (25), 51 (21); HRMS: (EI) calcd for ($C_{14}H_{15}N$) 197.1204 (M$^+$), found *m*/*z* 197.1206

1-(pyridine-2-yl)cyclohex-2-ene-1-carbonitrile (5g)



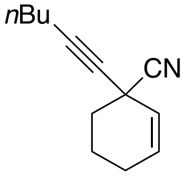
In a glove box, an oven dried reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.1 mg, 0.375 mmol) and THF (3 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-(pyridine-2-yl)cyclohexa-1,3-diene (89.9 mg, 0.57 mmol) was added to the flask. The mixture was stirred at 40 °C for 1 h before NCTS (163.7 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. T Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 97:3) gave the product as a yellow liquid (61.1 mg, 58% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.72–8.60 (m, 1H), 7.81–7.69 (m, 1H), 7.61–7.48 (m, 1H), 7.35–7.19 (m, 1H), 6.19 (ddd, J = 9.6, 4.0, 4.0 Hz, 1H), 5.92–5.80 (m, 1H), 2.44–2.30 (m, 1H), 2.30–2.17 (m, 2H), 2.17–2.06 (m, 1H), 2.06–1.90 (m, 1H), 1.90–1.75 (m, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 159.0 150.0, 137.1, 132.4, 124.8, 122.7, 122.0, 121.0, 44.7, 35.5, 24.1, 19.1
The analytical data for this compound were in excellent agreement with the reported data.[19]

1-(phenylethynyl)cyclohex-2-ene-1-carbonitrile (5h)



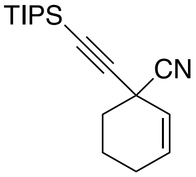
In a glove box, an oven dried reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (128.6 mg, 0.525 mmol) and THF (5 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, NCTS (271.9 mg, 1.00 mmol) and (cyclohexa-1,3-dien-1-ylethynyl)benzene (186.2 mg, 1.03 mmol) was added to the flask. The mixture was stirred at 40 °C for 2 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 97:3) gave the product as a yellow liquid (98.0 mg, 46% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.48–7.37 (m, 2H), 7.37–7.26 (m, 3H), 5.98 (ddd, J = 9.6, 4.0, 4.0 Hz, 1H), 5.78 (ddd, J = 9.6, 2.0, 2.0 Hz, 1H), 2.36–2.24 (m, 1H), 2.22–2.15 (m, 1H), 2.15–2.03 (m, 2H), 1.98–1.77 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 131.7, 131.2, 128.7, 128.2, 123.6, 121.7, 119.8, 85.5, 83.1, 34.7, 31.4, 23.8, 18.5; IR: (ATR) 3036, 2934, 2866, 2835, 2237, 1651, 1599, 1491, 1445 cm^{-1}; MS: (EI) m/z 207 (M^+, 14), 179 (76), 178 (27), 152 (21), 126 (26), 115 (26), 105 (52), 103 (23), 102 (100), 77 (24), 63 (21), 51 (25); HRMS: (EI) calcd for ($C_{15}H_{13}N$) 207.1048 (M^+), found m/z 207.1050

1-(hex-1-ynyl)cyclohex-2-ene-1-carbonitrile (5i)



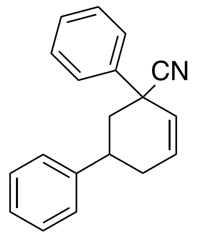
In a glove box, an oven dried reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (128.5 mg, 0.525 mmol) and THF (5 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, NCTS (272.4 mg, 1.00 mmol) and 1-(hex-1-ynyl)cyclohexa-1,3-diene (156.4 mg, 0.98 mmol) was added to the flask. The mixture was stirred at 40 °C for 2 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 97:3) gave the product as a yellow liquid (52.8 mg, 29% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 5.91 (ddd, J = 9.6, 4.0, 4.0 Hz, 1H), 5.68 (ddd, J = 9.6, 2.0, 2.0 Hz, 1H), 2.28–2.14 (m, 3H), 2.13–1.95 (m, 3H), 1.91–1.68 (m, 2H), 1.55–1.43 (m, 2H), 1.43–1.30 (m, 2H), 0.91 (t, 7.6 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 130.5, 124.5, 120.4, 84.0, 76.9, 35.0, 30.9, 30.4, 23.9, 21.8, 18.6, 18.2, 13.5; IR: (ATR) 3036, 2957, 2932, 2864, 2237, 1653, 1456, 1447 cm^{-1}; MS: (EI) m/z 187 (M^+, 1), 130 (29), 117 (59), 116 (37), 115 (27), 105 (100), 104 (25), 103 (27), 91 (39), 89 (23), 79 (23), 77 (38), 65 (22), 63 (22), 51 (26); HRMS: (EI) calcd for ($C_{13}H_{17}N$) 187.1361 (M^+), found m/z 187.1361

1-((triisopropylsilyl)ethynyl)cyclohex-2-ene-1-carbonitrile (5j)



In a glove box, an oven dried reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (76.9 mg, 0.315 mmol) and THF (3 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-((triisopropylsilyl)ethynyl)cyclohexa-1,3-diene (152.4 mg, 0.59 mmol) was added to the flask. The mixture was stirred at 40 °C for 1 h before NCTS (163.6 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 97:3) gave the product as a pale yellow liquid (139.5 mg, 83% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 5.93 (ddd, J = 9.6, 3.6, 3.6 Hz, 1H), 5.78–5.66 (m, 1H), 2.35–2.19 (m, 1H), 2.19–1.96 (m, 3H), 1.96–1.71 (m, 2H), 1.28–0.90 (m, 21H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 130.8, 123.9, 119.8, 103.4, 84.6, 34.9, 31.6, 23.8, 18.43, 18.40, 11.0; IR: (ATR) 3038, 2943, 2891, 2866, 2237, 2168, 1651, 1462 cm^{-1}; MS: (EI) m/z 287 (M^+, 6), 245 (22), 244 (100), 217 (78), 189 (52), 175 (35), 161 (52), 147 (58), 145 (23), 131 (21), 121 (25), 109 (30), 105 (25), 83 (26), 79 (23), 69 (26), 59 (48), 53 (21); HRMS: (EI) calcd for ($C_{18}H_{29}NSi$) 287.2069 (M^+), found m/z 287.2065

1,5-diphenylcyclohex-2-enecarbonitrile (5k)

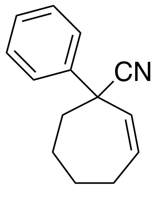


In a glove box, an oven dried reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (76.9 mg, 0.375 mmol) and THF (3 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1,5-diphenylcyclohexa-1,3-diene (138.9 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 °C for 4 h before NCTS (163.3 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product (*dr* = 57:43), which was analyzed by ^{1}H NMR spectroscopy. Purification by flash column chromatography on silica gel (hexane/EtOAc = 95:5) gave the product as a colorless viscous liquid (121.1 mg, 78% combined yield of diastereomers) Further purification by flash column chromatography on silica gel was performed to separate those isomers.

isomer 1: ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.65–7.46 (m, 2H), 7.46–7.37 (m, 2H), 7.37–7.32 (m, 1H), 7.32–7.23 (m, 2H), 7.23–7.15 (m, 1H), 7.15–7.01 (m, 2H), 6.32 (ddd, *J* = 10.0, 5.2, 2.0 Hz, 1H), 5.91 (d, *J* = 10.0 Hz, 1H), 2.73–2.52 (m, 2H), 2.52–2.35 (m, 2H), 2.35–2.15 (m, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 144.1, 139.5, 132.0, 128.8, 128.6, 128.1, 127.3, 126.78, 126.75, 124.1, 123.5, 43.0, 42.9, 34.1, 32.9; IR: (ATR) 3028, 2922, 2234, 1653, 1599, 1491, 1449 cm^{-1}; MS: (EI) *m/z* 259 (M^+, 18), 155 (41), 130 (24), 115 (29), 104 (100), 91 (55); HRMS: (EI) calcd for ($C_{19}H_{17}N$) 259.1361 (M^+), found *m/z* 259.1364

isomer 2: ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.57–7.45 (m, 2H), 7.45–7.36 (m, 2H), 7.36–7.28 (m, 3H), 7.28–7.11 (m, 3H), 6.25 (ddd, *J* = 9.6, 5.2, 2.0 Hz, 1H), 5.89–5.81 (m, 1H), 3.45–3.32 (m, 1H), 2.60–2.42 (m, 2H), 2.37–2.25 (m, 1H), 2.00 (dd, *J* =13.2, 13.2 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 144.2, 140.6, 132.3, 129.0, 128.7, 128.0, 126.8, 126.1, 125.8, 121.8, 45.1, 44.3, 38.4, 32.9 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 3028, 2922, 2230, 1599, 1491, 1449 cm^{-1}; MS: (EI) *m/z* 259 (M^+, 27), 155 (46), 115 (26), 104 (100), 91 (55); HRMS: (EI) calcd for ($C_{19}H_{17}N$) 259.1361 (M^+), found *m/z* 259.1356

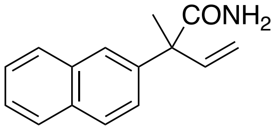
1-phenylcyclohept-2-ene-1-carbonitrile (5l)



n a glove box, an oven dried reaction flask containing a magnetic stir bar was charged with 9-BBN dimer (77.1 mg, 0.375 mmol) and THF (3 mL). The reaction flask was capped, removed from the glove box, and put under nitrogen. Then, 1-phenylcyclohepta-1,3-diene (101.6 mg, 0.60 mmol) was added to the flask. The mixture was stirred at 40 °C for 4 h before NCTS (164.0 mg, 0.60 mmol) was added and further stirred at room temperature for 1 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 97:3) gave the product as a colorless liquid (70.6 mg, 60% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.55–7.45 (m, 2H), 7.45–7.34 (m, 2H), 7.34–7.26 (m, 1H), 6.15–6.05 (m, 1H), 5.77–5.69 (m, 1H), 2.48–2.26 (m, 2H), 2.17–1.98 (m, 3H), 1.98–1.79 (m, 2H), 1.63–1.46 (m, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 142.2, 136.4, 131.6, 128.8, 127.6, 125.5, 121.0, 48.0, 40.9, 27.6, 26.7, 26.4; IR: (ATR) 3061, 3026, 2932, 2859, 2232, 1493, 1449 cm^{-1}; MS: (EI) *m*/*z* 197 (M^+, 27), 196 (29), 168 (22), 155 (47), 154 (67), 141 (29), 140 (30), 130 (100), 129 (84), 128 (49), 127 (36), 116 (26), 115 (86), 103 (39), 102 (26), 91 (30), 89 (20), 78 (22), 77 (43), 68 (74), 67 (36), 65 (21), 63 (20), 55 (20), 51 (44); HRMS: (EI) calcd for ($C_{14}H_{15}N$) 197.1204 (M^+), found *m*/*z* 197.1207

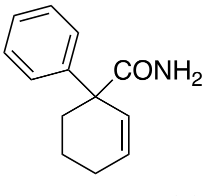
8. Functional group interconversions of β,γ-unsaturated nitrile products

2-methyl-2-(naphthalen-2-yl)but-3-enamide (7)



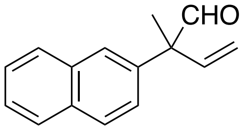
An oven dried reaction flask containing a magnetic stir bar was charged with 2-methyl-2-(naphthalene-2-yl)but-3-enenitrile (52.0 mg, 0.25 mmol) and DMSO (0.5 mL). The mixture was cooled to 0 ºC before NaOH aq. (0.5 M, 150 µL) and H_2O_2 aq. (30 wt% in water, 56 µL) were added and stirred at room temperature for 5 h. The reaction was quenched by the addition of water and extracted with ethyl acetate (3 x 20 mL). The organic layers were combined, dried (anhyd. Na_2SO_4), filtered and concentrated *in vacuo* to afford the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 60:40) gave the product as a white solid (51.7 mg, 92% yield). mp: 78.5–79.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.75 (m, 4H), 7.52–7.39 (m, 3H), 6.44 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.58 (brs, 1H), 5.45 (brs, 1H), 5.36 (d, *J* = 10.8 Hz, 1H), 5.17 (d, *J* = 17.2 Hz, 1H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 141.7, 140.6, 133.2, 132.4, 128.4, 128.0, 127.5, 126.3, 126.2, 125.8, 125.6, 116.1, 54.5, 24.4; IR (ATR) 3410, 3183, 3055, 1649, 1618, 1371 cm^{-1}; MS (EI) *m*/*z* 225 (M^+, 24), 182 (35), 181 (100), 167 (29), 166 (47), 165 (60); HRMS: (EI) calcd for ($C_{15}H_{15}NO$) 225.1154 (M^+), found *m*/*z* 225.1158

1-phenylcyclohex-2-en-1-amide (8)



An oven dried reaction flask containing a magnetic stir bar was charged with 1-phenylcyclohex-2-ene-1-carbonitrile (45.0 mg, 0.25 mmol) and DMSO (0.5 mL). The mixture was cooled to 0 ºC before K_2CO_3 (5.5 mg, 0.04 mmol) and H_2O_2 aq. (30 wt% in water, 56 μL) were added and stirred at room temperature for 16 h. The reaction was quenched by the addition of water and extracted with ethyl acetate (3 x 20 mL). The organic layers were combined, dried (anhyd. Na_2SO_4), filtered and concentrated *in vacuo* to afford the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 50:50) gave the product as a white solid (41.5 mg, 84% yield). mp: 74.9–75.5 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.50–7.38 (m, 2H), 7.38–7.32 (m, 2H), 7.32–7.18 (m, 1H), 6.10 (ddd, *J* = 10.4, 3.6, 3.6 Hz, 1H), 5.97 (d, *J* = 3.6 Hz, 1H), 5.67–5.33 (brs, 2H), 2.69–2.49 (m, 1H), 2.28–2.00 (m, 2H), 1.95–1.79 (m, 1H), 1.79–1.65 (m, 1H), 1.65–1.50 (m, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 177.9, 144.4, 131.4, 129.0, 128.4, 126.82, 126.77, 52.4, 33.7, 24.9, 19.2; IR: (ATR) 3410, 3177, 2940, 1638, 1491, 1373 cm^{-1}; MS: (EI) *m*/*z* 201 (M$^+$, 3), 157 (62), 129 (41), 128 (33), 115 (49), 91 (100), 79 (21), 77 (34), 51 (25); HRMS: (EI) calcd for ($C_{13}H_{15}NO$) 201.1154 (M$^+$), found *m*/*z* 201.1153

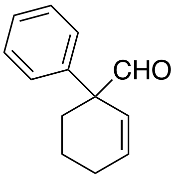
2-methyl-2-(naphthalen-2-yl)but-3-enal (9)



According to the reported procedure,[20] the reaction using 2-methyl-2-(naphthalene-2-yl)but-3-enenitrile (52.0 mg, 0.25 mmol), toluene (1.25 mL), and diisobutylaluminium hydride (1 M solution in hexanes, 0.31 mL, 0.31 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane/EtOAc = 95:5) gave the product as a colorless liquid (44.4 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.88–7.80 (m, 3H), 7.71 (d, *J* = 2.0 Hz, 1H), 7.52–7.46 (m, 2H), 7.34 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.32 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.47 (d, *J* = 10.8 Hz, 1H), 5.23 (d, *J* = 17.6 Hz, 1H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 138.3, 137.4, 133.4, 132.5, 128.6, 128.0, 127.6, 126.44, 126.39, 126.3, 125.4, 117.7, 58.0, 20.2

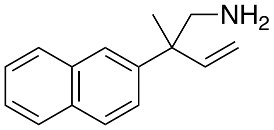
The analytical data for this compound were in excellent agreement with the reported data.[16]

1-phenylcyclohex-2-en-1-carbaldehyde (10)



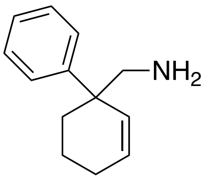
According to the reported procedure,[20] the reaction using 1-phenylcyclohex-2-ene-1-carbonitrile (44.3 mg, 0.24 mmol), toluene (0.5 mL), and diisobutylaluminium hydride (1 M solution in hexanes, 0.30 mL, 0.30 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane/EtOAc = 95:5) gave the product as a colorless liquid (37.0 mg, 82% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 9.45 (s, 1H) 7.44–7.31 (m, 2H), 7.31–7.15 (m, 3H), 6.24 (ddd, *J* = 10.0, 4.0, 4.0 Hz, 1H), 5.92 (ddd, *J* = 10.0, 2.4, 2.4 Hz, 1H), 2.39–2.25 (m, 1H), 2.15–1.98 (m, 2H), 1.84–1.73 (m, 1H), 1.70–1.58 (m, 1H), 1.58–1.45 (m, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 199.1, 140.7, 133.4, 128.8, 127.7, 127.2, 124.2, 56.6, 30.9, 25.0, 18.6; IR: (ATR) 3021, 2936, 2835, 2708, 1724, 1493, 1447 cm^{-1}; MS: (EI) *m/z* 186 (M$^+$, 0.3), 157 (71), 129 (32), 115 (28), 91 (100), 77 (21); HRMS: (EI) calcd for ($C_{13}H_{14}O$) 186.1045 (M$^+$), found *m/z* 186.1047

2-methyl-2-(naphthalen-2-yl)but-3-en-1-amine (11)



According to the reported procedure,[21] the reaction using $LiAlH_4$ (9.6 mg, 0.25 mmol), Et_2O (1.25 mL), and 2-methyl-2-(naphthalene-2-yl)but-3-enenitrile (52.0 mg, 0.25 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane/EtOAc = 80:20) gave the product as a colorless liquid (32.0 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.78 (m, 3H), 7.74 (d, *J* = 2.0 Hz, 1H), 7.50–7.42 (m, 3H), 6.15 (dd, *J* = 16.4, 10.0 Hz, 1H), 5.27 (dd, *J* = 10.8, 1.2 Hz, 1H), 5.14 (dd, *J* = 16.4, 1.2 Hz, 1H), 3.11 (d, *J* = 13.2 Hz, 1H), 3.04 (d, *J* = 13.2 Hz, 1H), 1.49 (s, 3H), 1.34 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 142.9, 133.3, 132.0, 128.0, 127.9, 127.4, 126.0, 125.6, 125.42, 125.38, 113.9, 51.6, 46.9, 23.2; IR (ATR) 3385, 3055, 2967, 2930, 2870, 1630, 1599, 1504 cm^{-1}; MS (EI) *m/z* 211 (M$^+$, 3), 182 (100), 181 (30), 167 (36), 166 (38), 165 (63); HRMS: (EI) calcd for ($C_{15}H_{17}N$) 211.1361 (M$^+$), found *m/z* 211.1364

1-phenylcyclohex-2-en-1-methanamine (12)



According to the reported procedure,[21] the reaction using $LiAlH_4$ (37.8 mg, 0.99 mmol), Et_2O (2.5 mL), and 1-phenylcyclohex-2-ene-1-carbonitrile (89.9 mg, 0.49 mmol) was conducted. The reaction was quenched by the addition of water (38 μL), a 2M NaOH solution (76 μL), and water (114 μL), and stirred for 1 hour at room temperature. The mixture was then filtered through Celite, dried (anhyd. $MgSO_4$), filtered and concentrated under reduced pressure to give the product as a colorless liquid (71.3 mg, 78% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.41–7.29 (m, 4H), 7.25–7.16 (m, 1H), 6.01 (ddd, *J* = 10.0, 3.6, 3.6 Hz, 1H), 5.94–5.87 (m, 1H), 3.01 (d, *J* = 13.4 Hz, 1H), 2.82 (d, *J* = 13.4 Hz, 1H), 2.12–1.99 (m, 2H), 1.95–1.84 (m, 1H), 1.79–1.65 (m, 1H), 1.65–1.53 (m, 1H), 1.45–1.30 (m, 1H), 1.20 (brs, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 146.2, 131.1, 129.5, 128.2, 127.3, 125.9, 52.7, 45.3, 34.0, 25.5, 18.6; IR: (ATR) 3055, 3021, 2928, 2862, 2835, 1597, 1493, 1447 cm^{-1}; MS: (EI) *m/z* 187 (M$^+$, 0.9), 158 (32), 157 (28), 129 (34), 128 (22), 115 (34), 91 (100), 77 (21); HRMS: (EI) calcd for ($C_{13}H_{17}N$) 187.1361 (M$^+$), found *m/z* 187.1359

9. References

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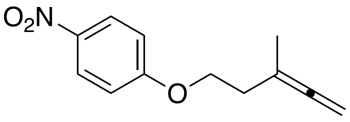
10. NMR spectra



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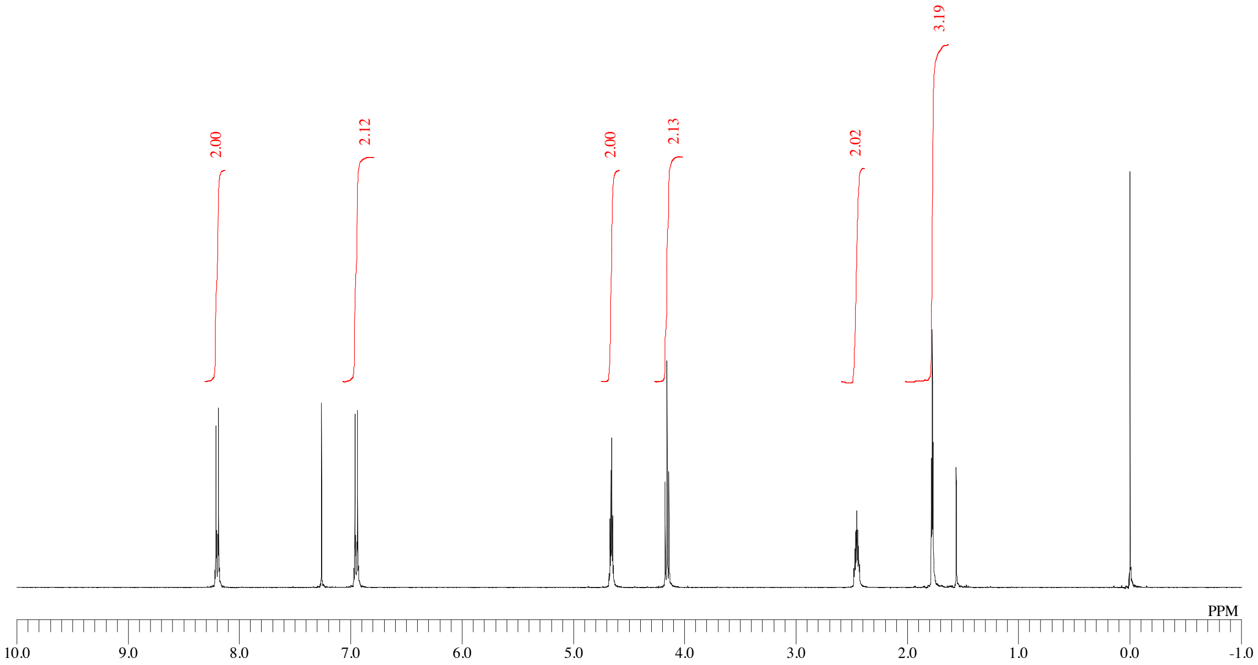

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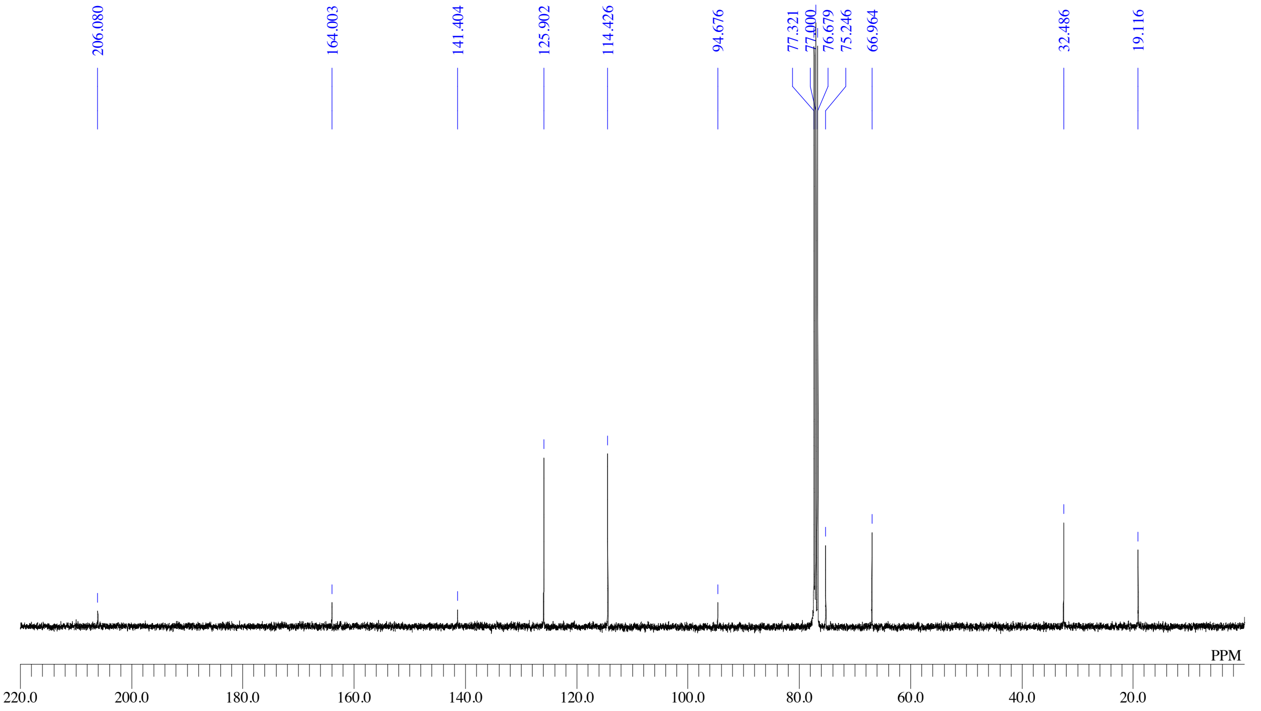

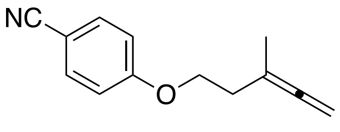

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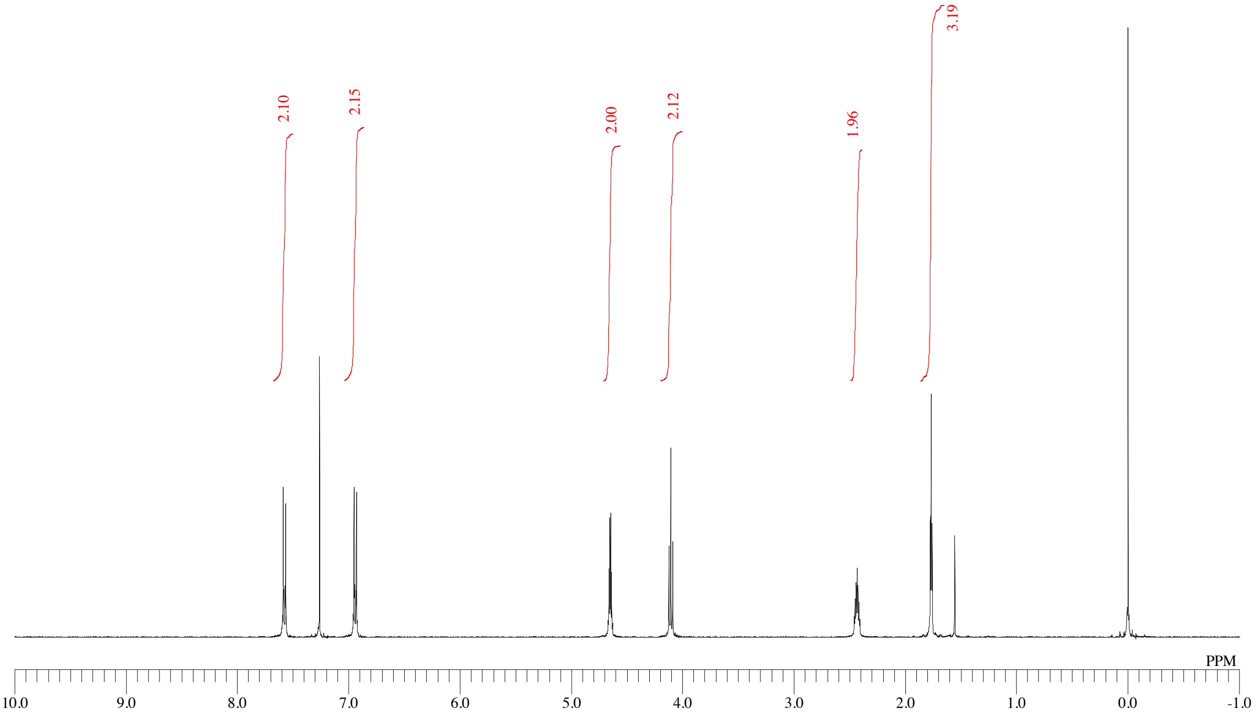

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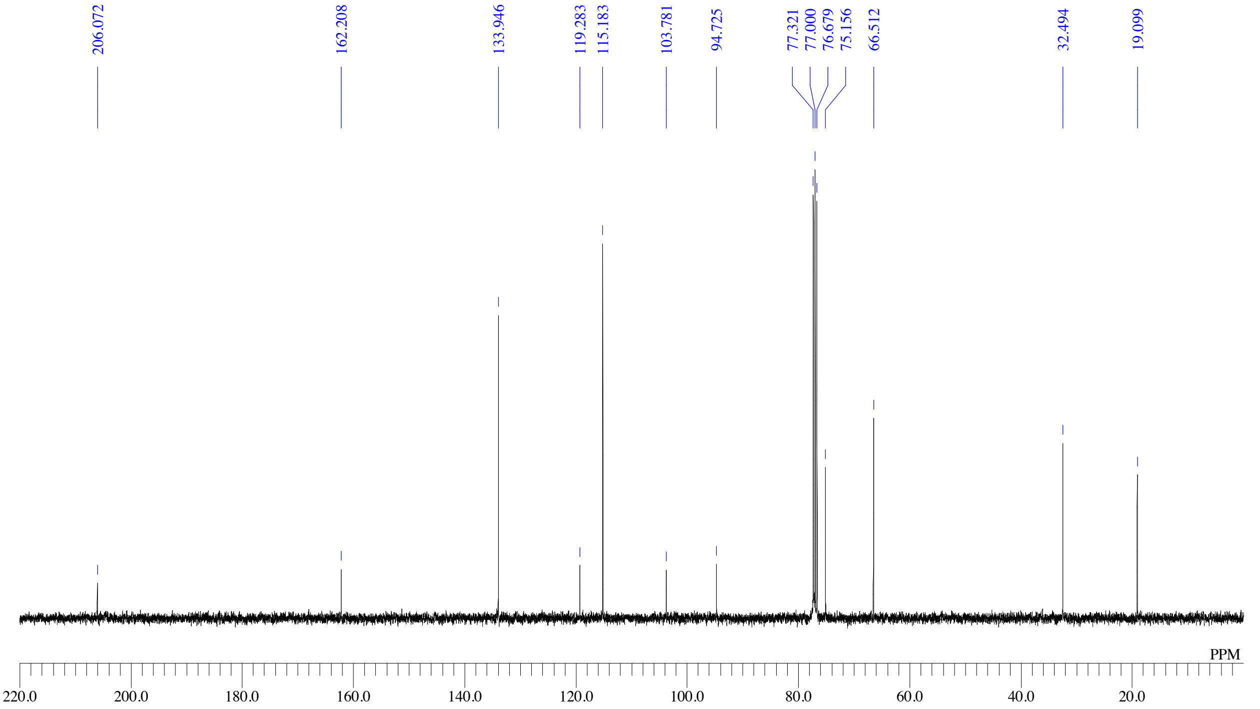

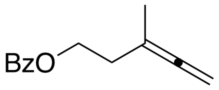

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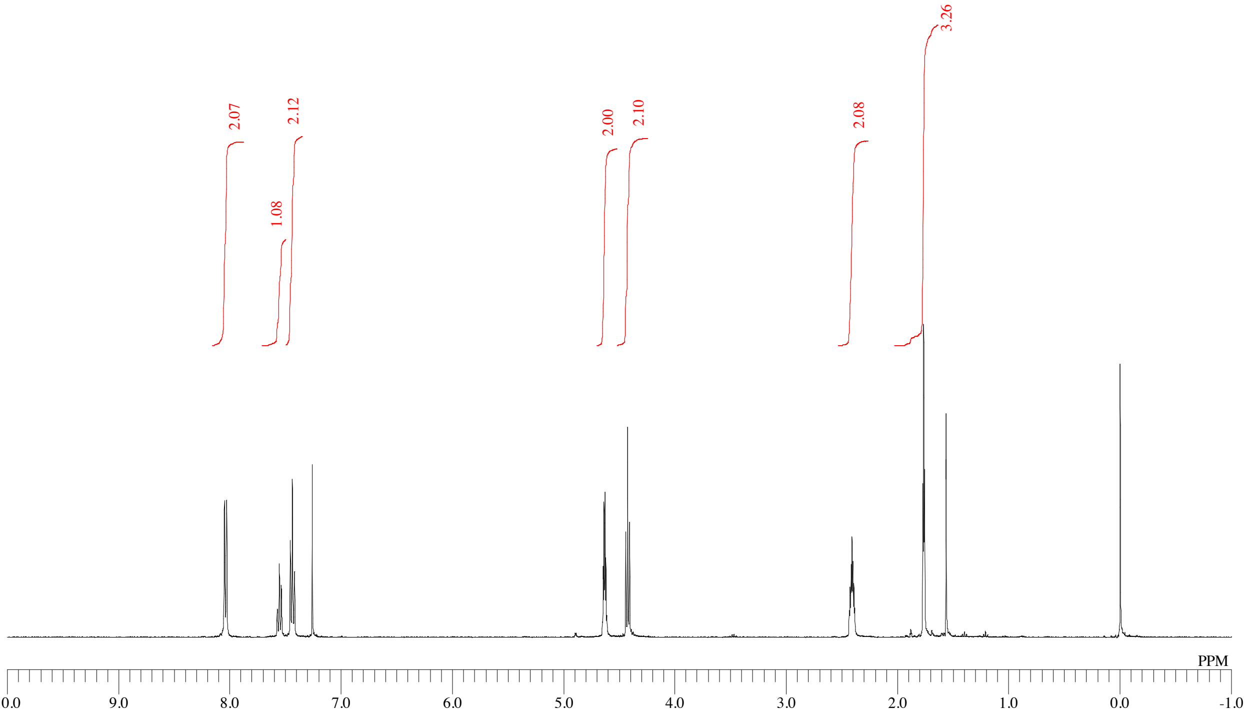

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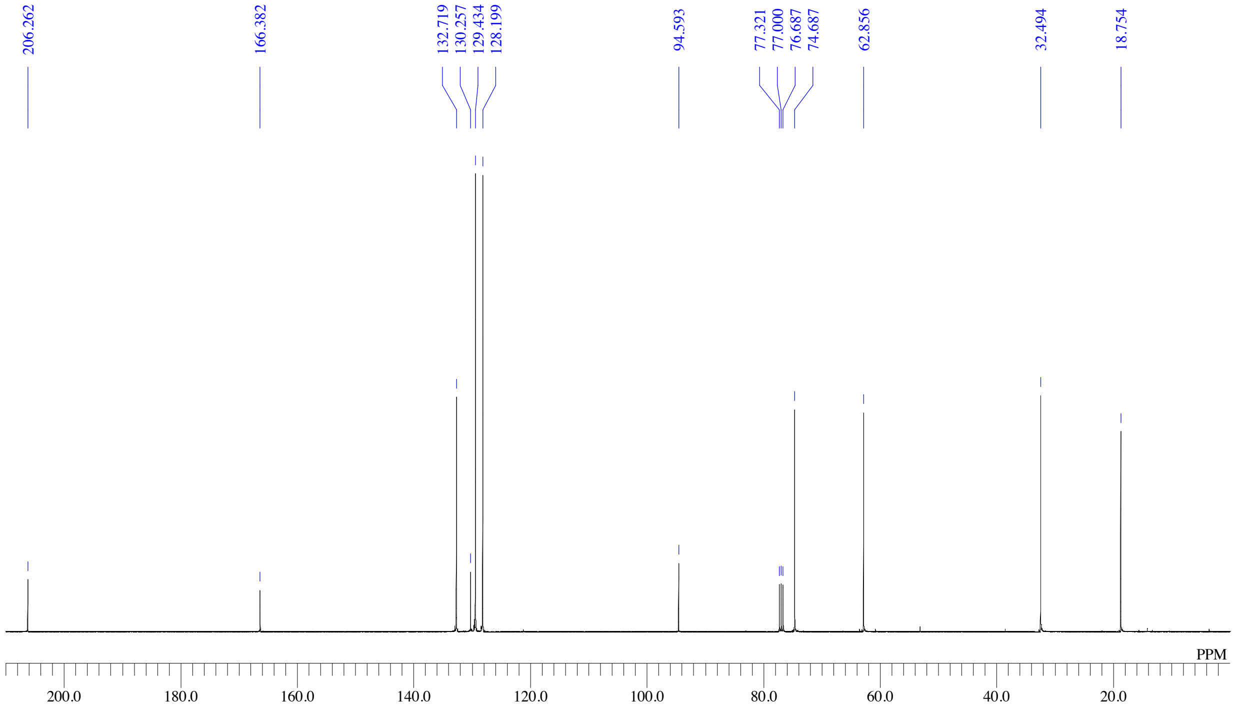

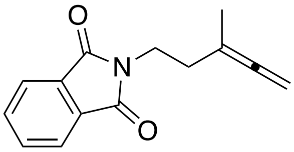

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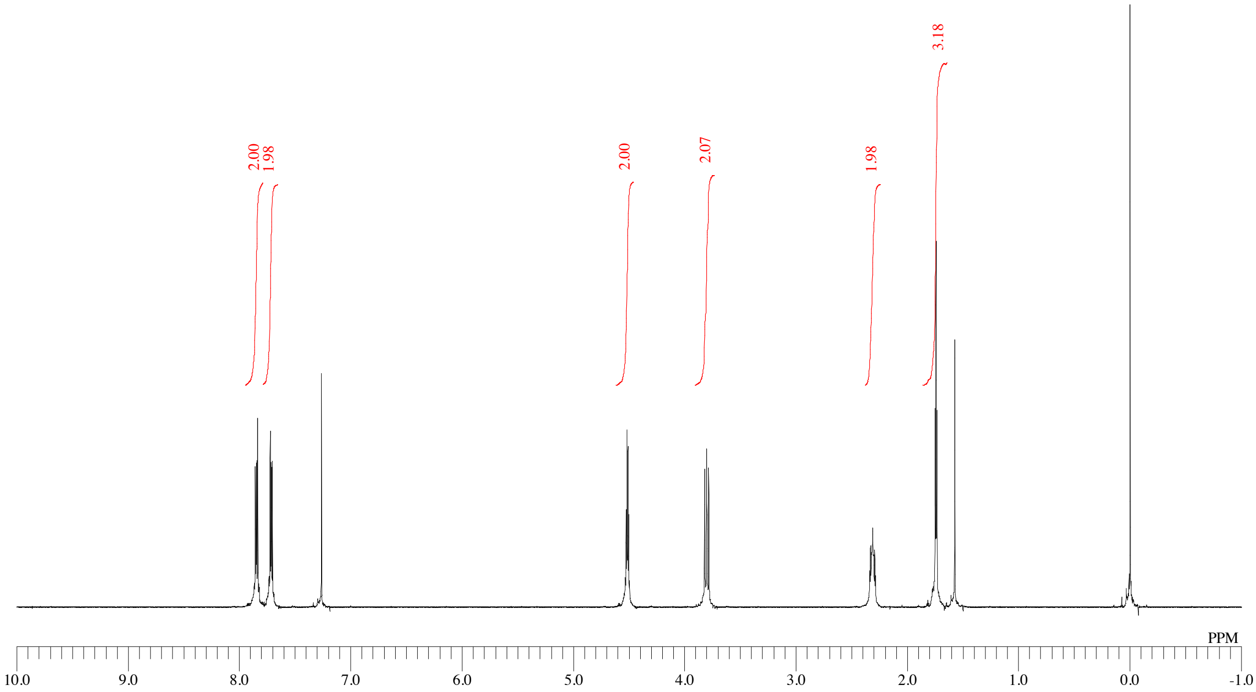

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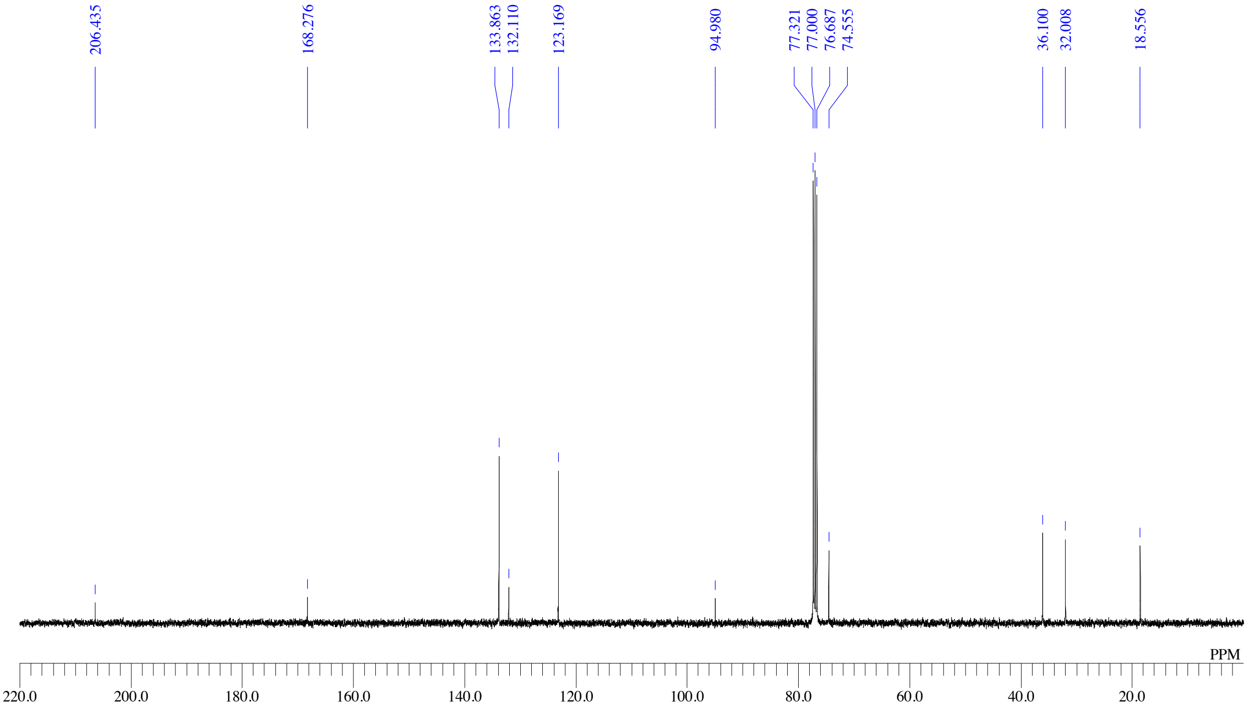

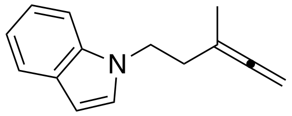

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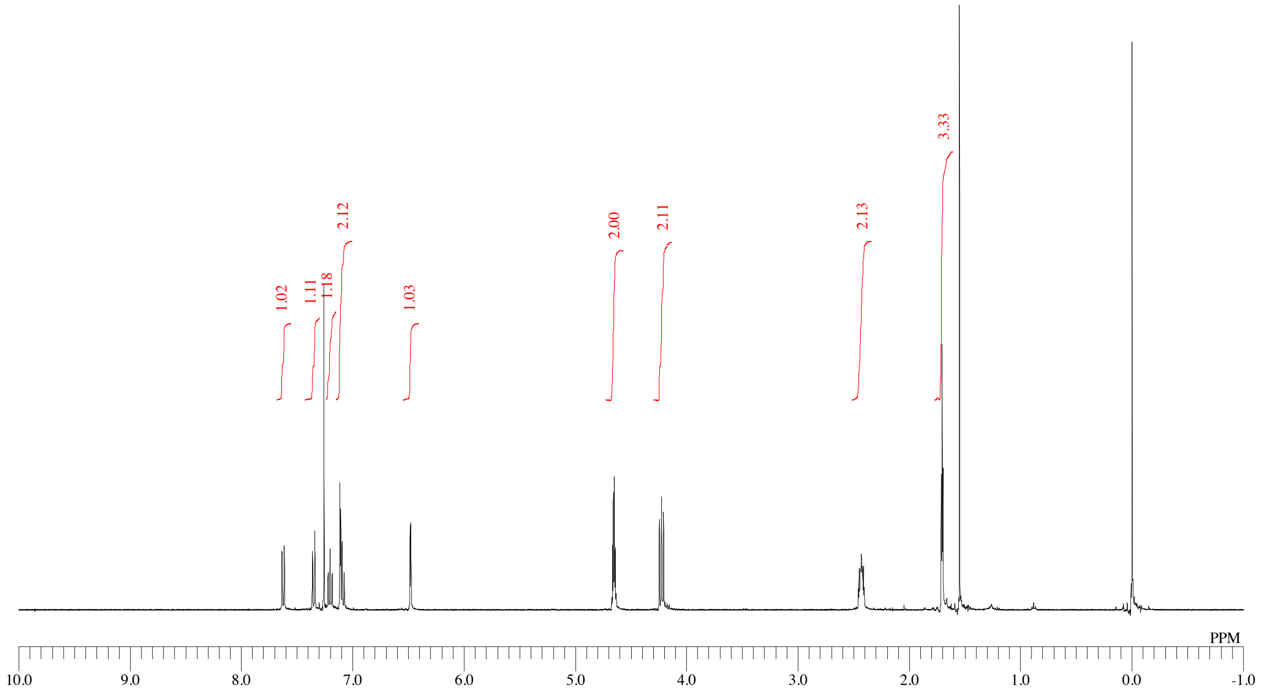

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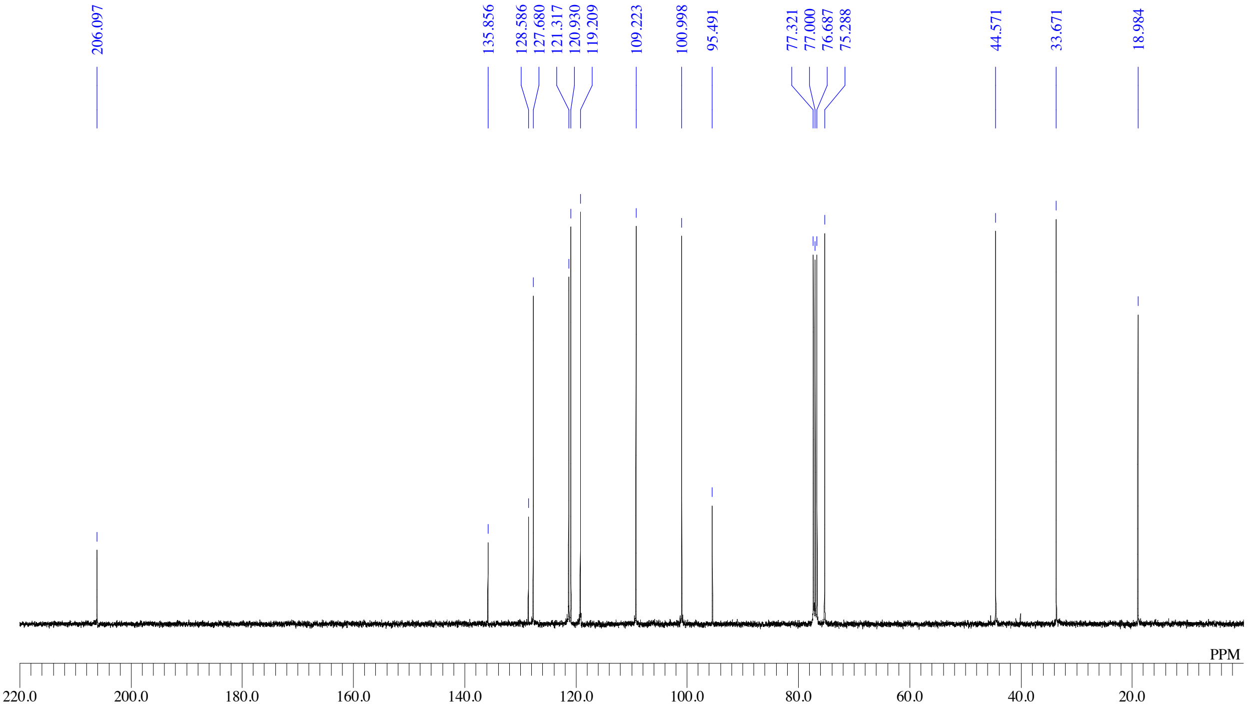

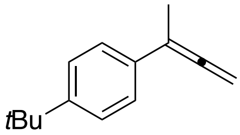

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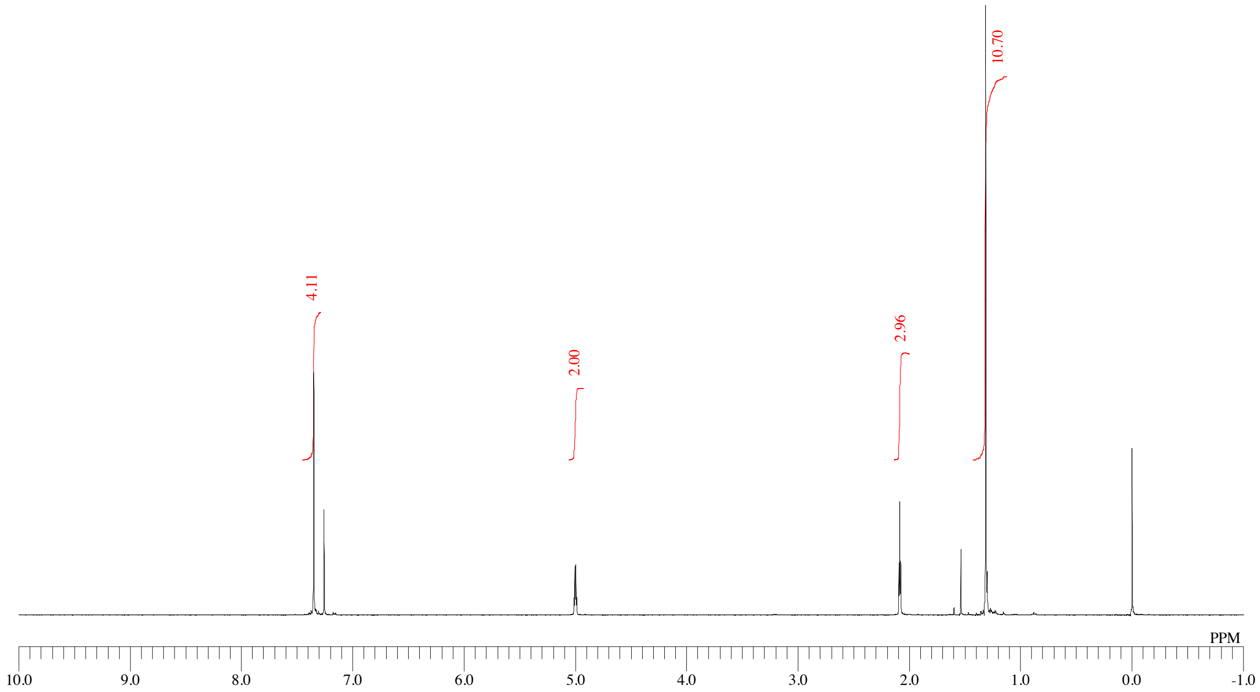

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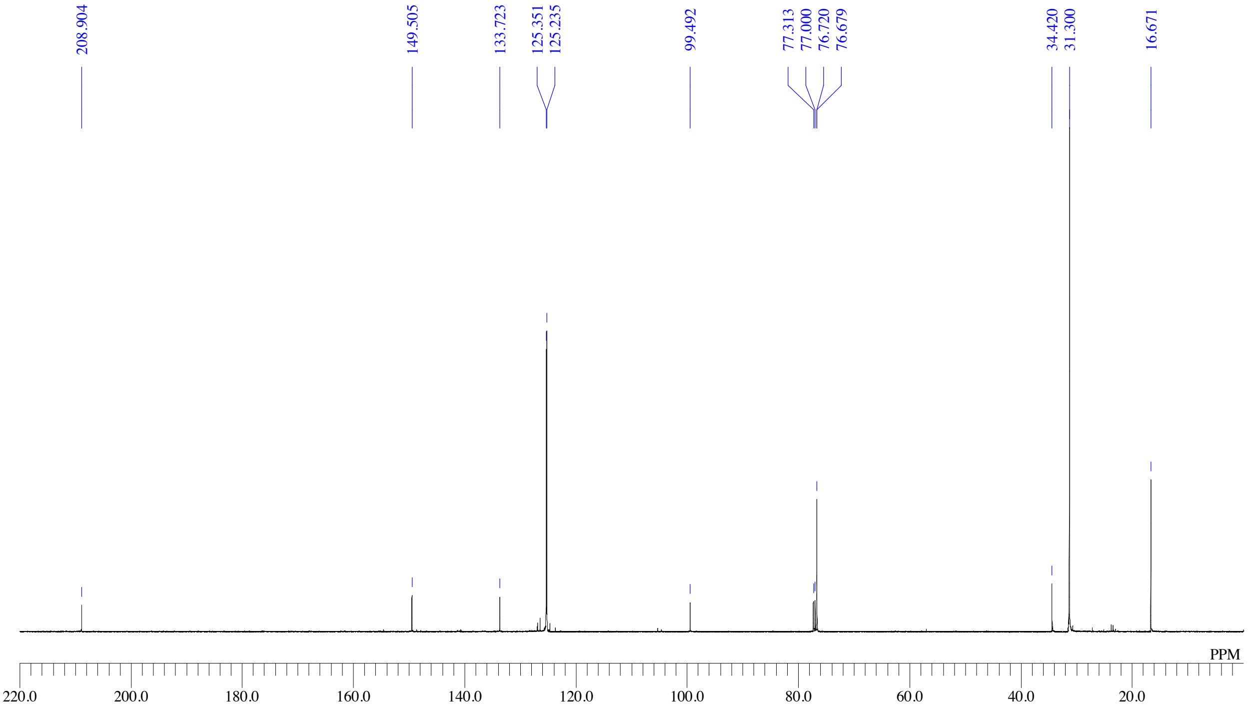

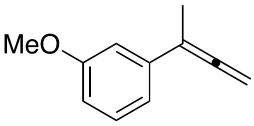

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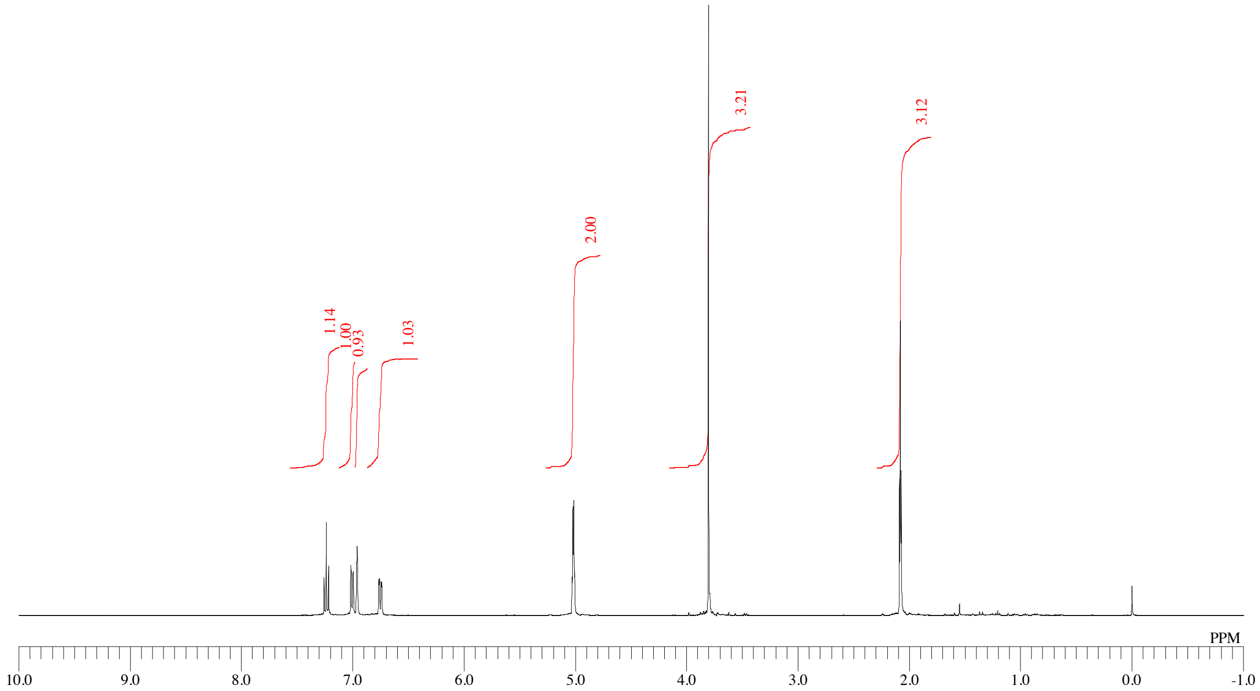

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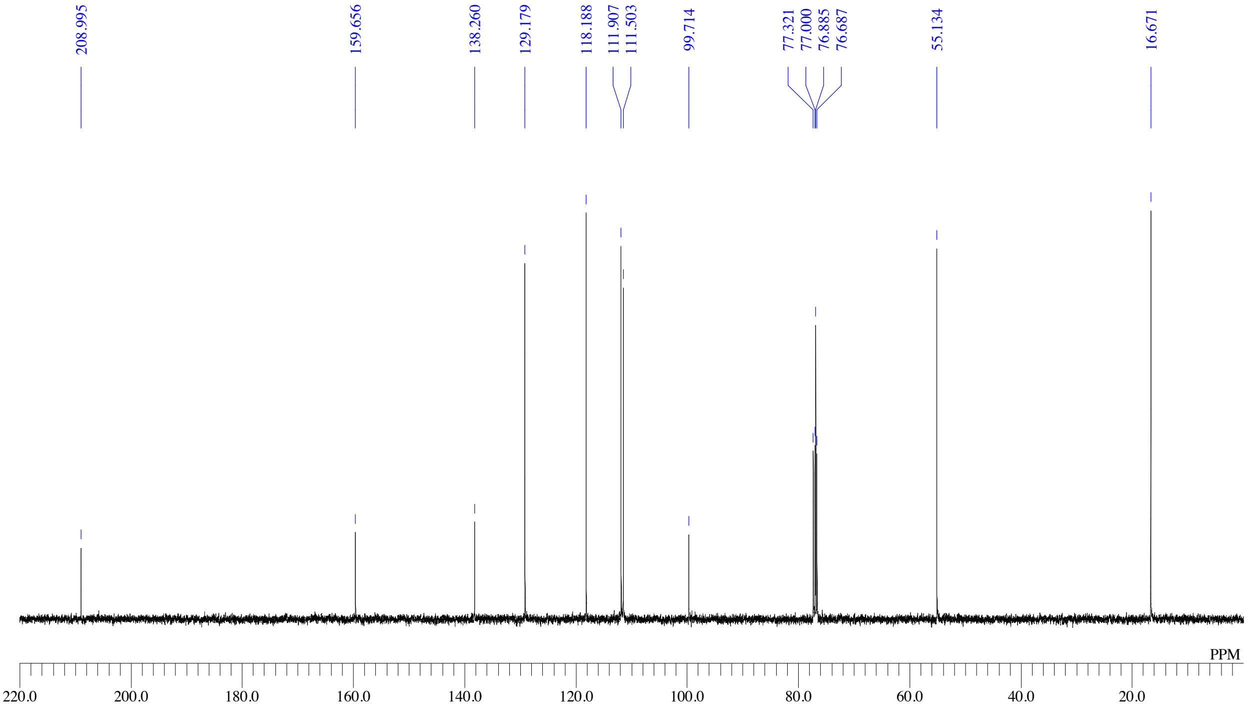

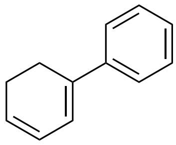

4a

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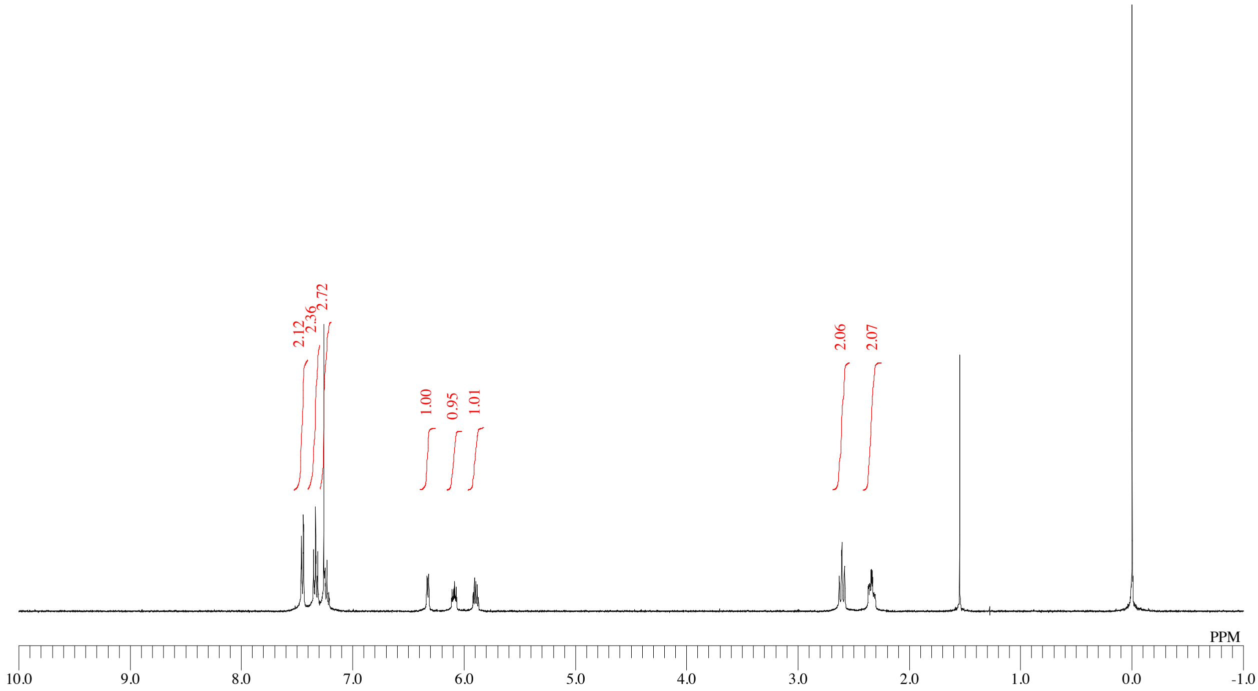

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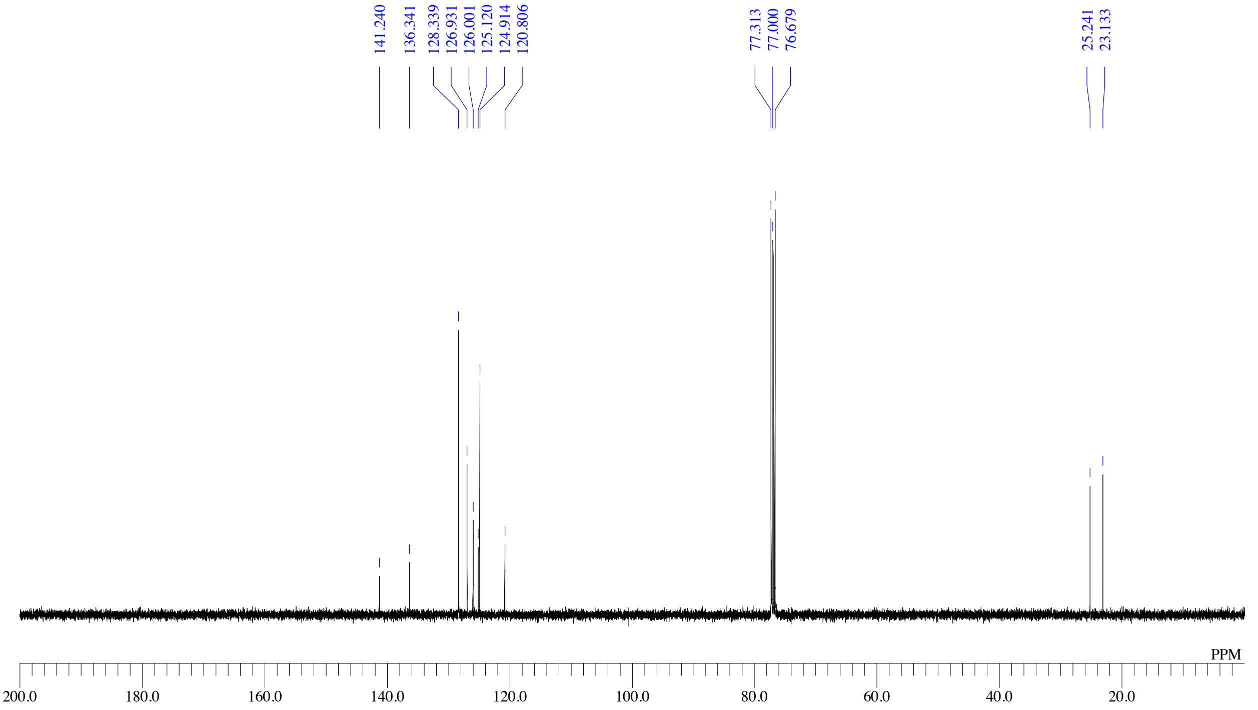

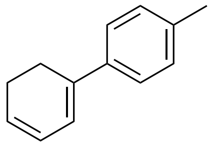

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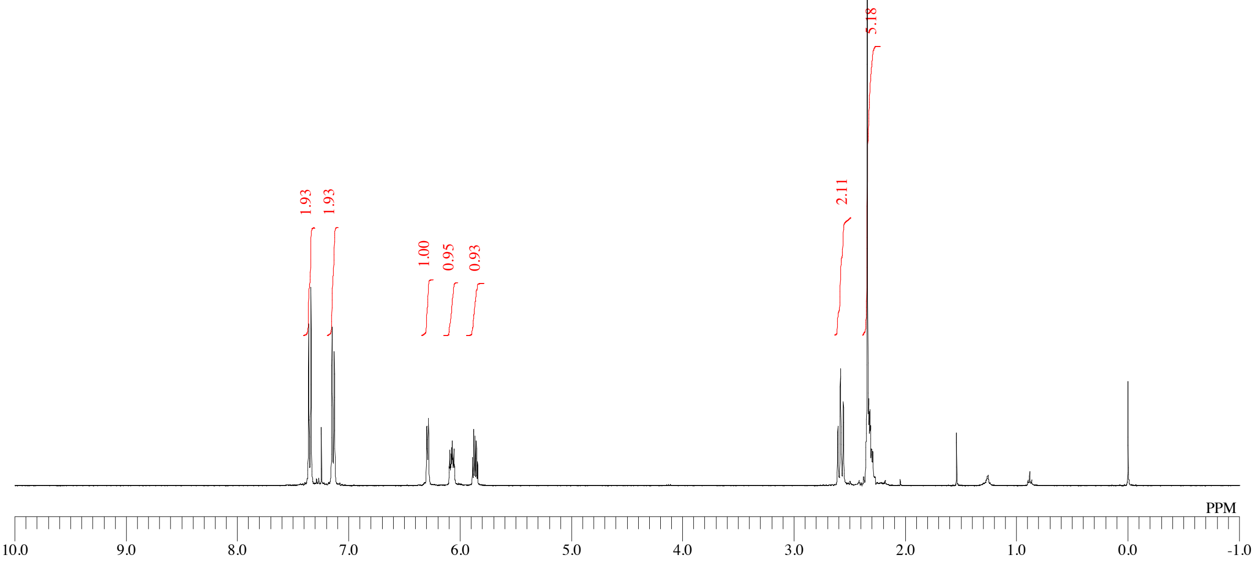

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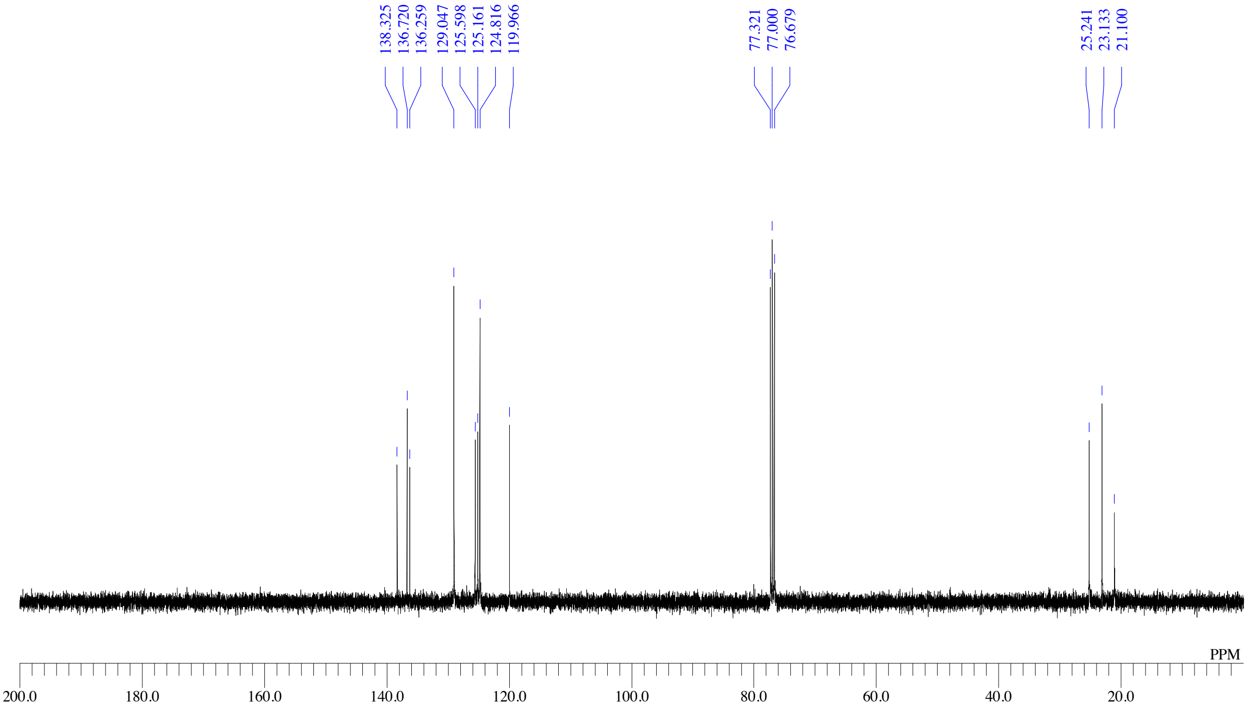

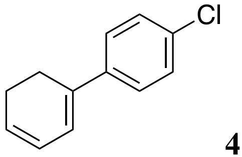

4c

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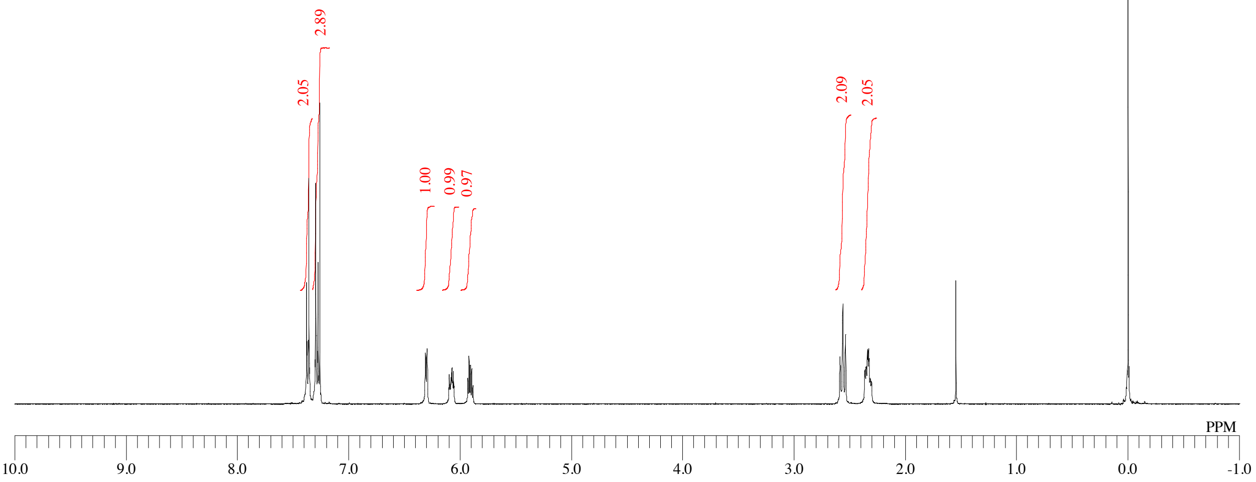

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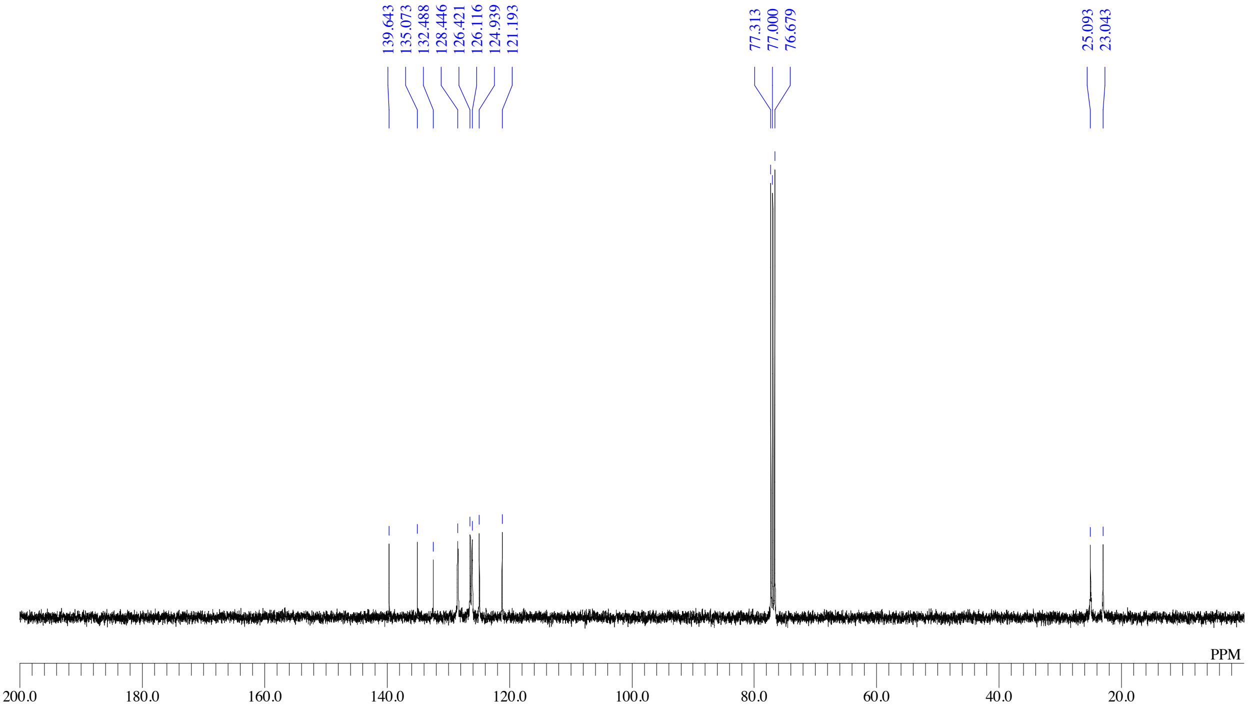

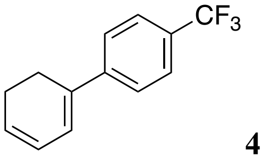

4d

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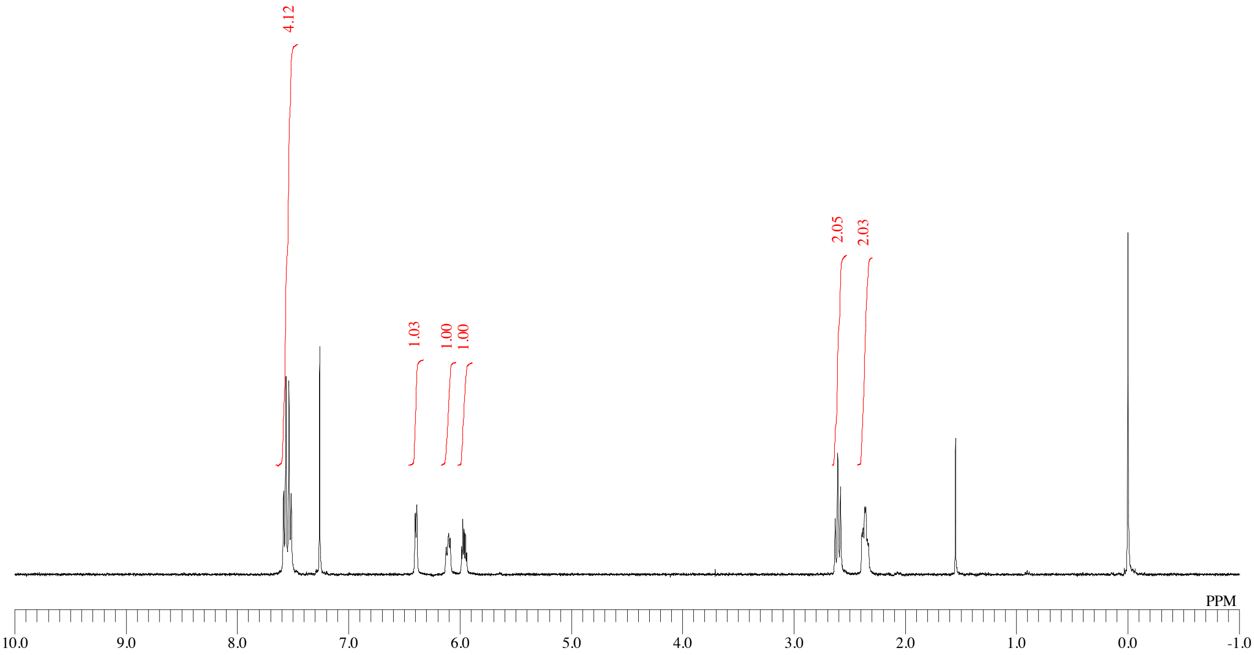

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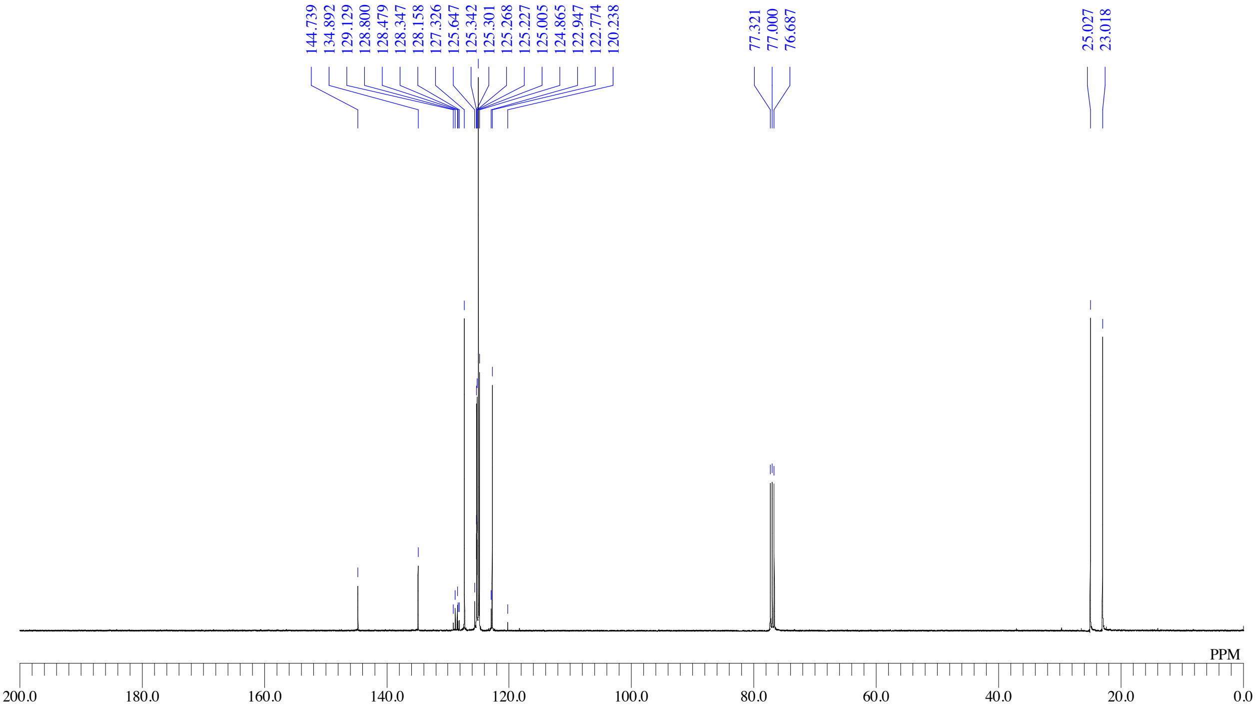

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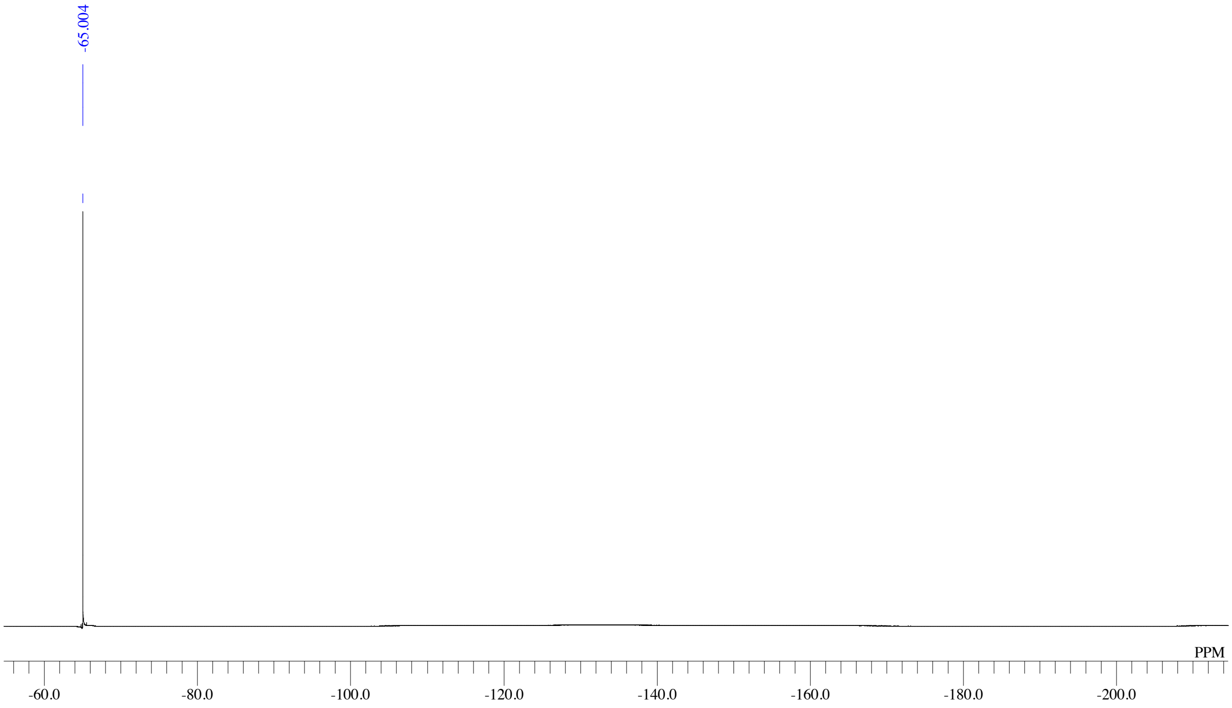

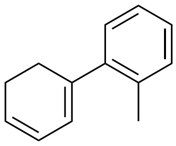

4e

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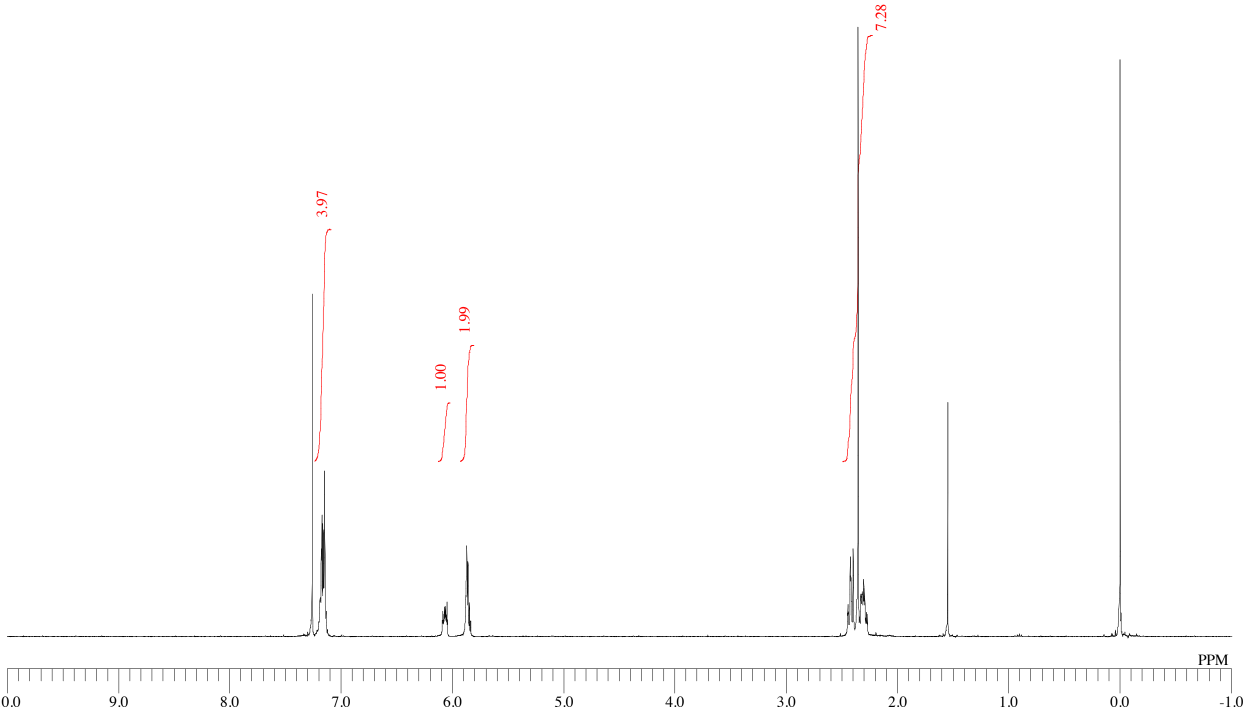

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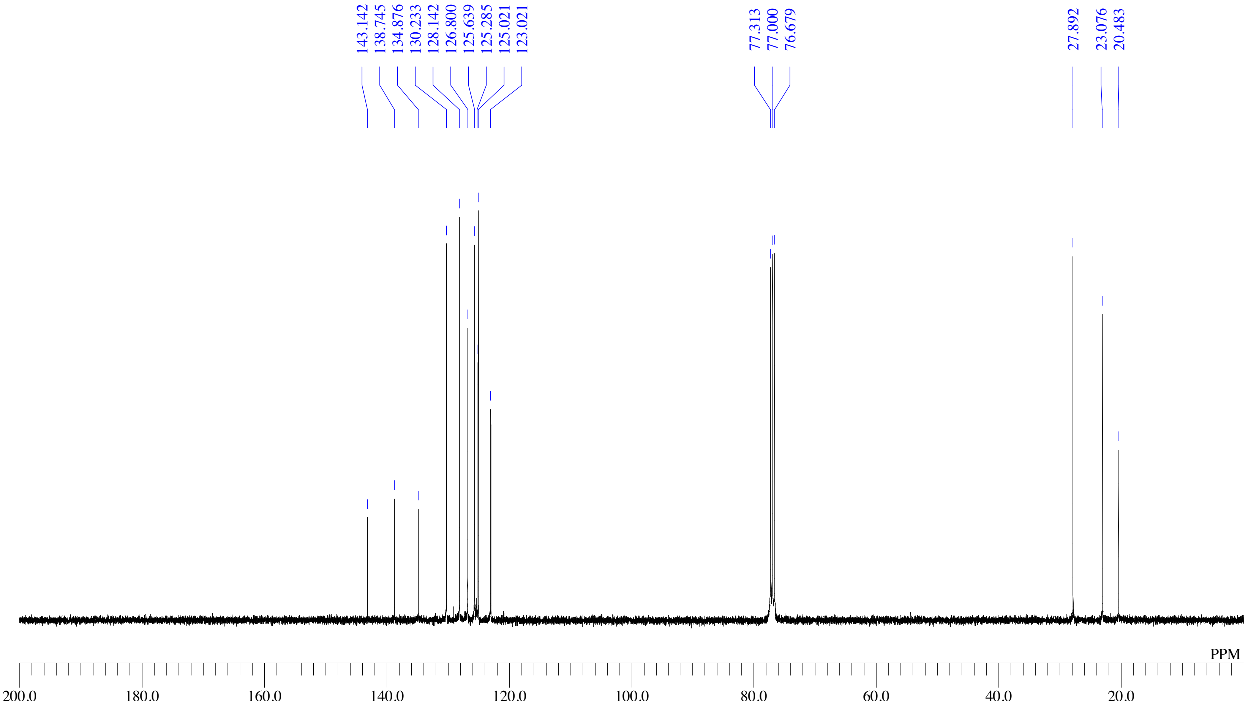

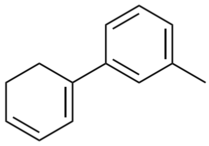

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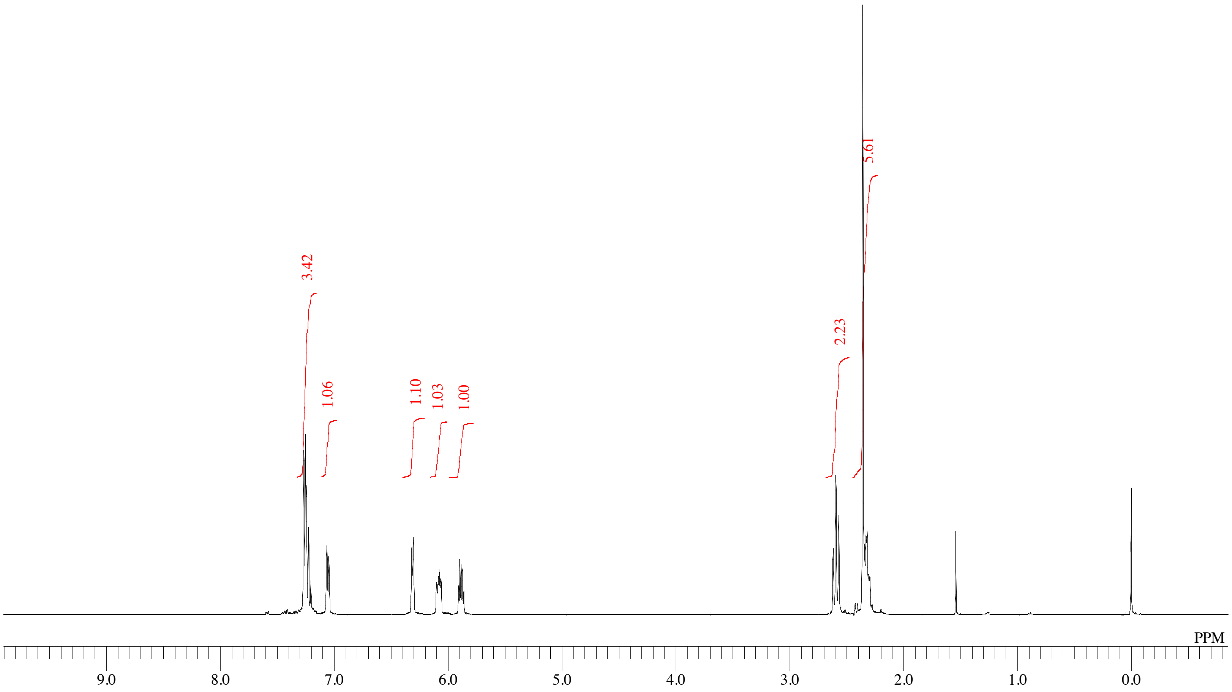

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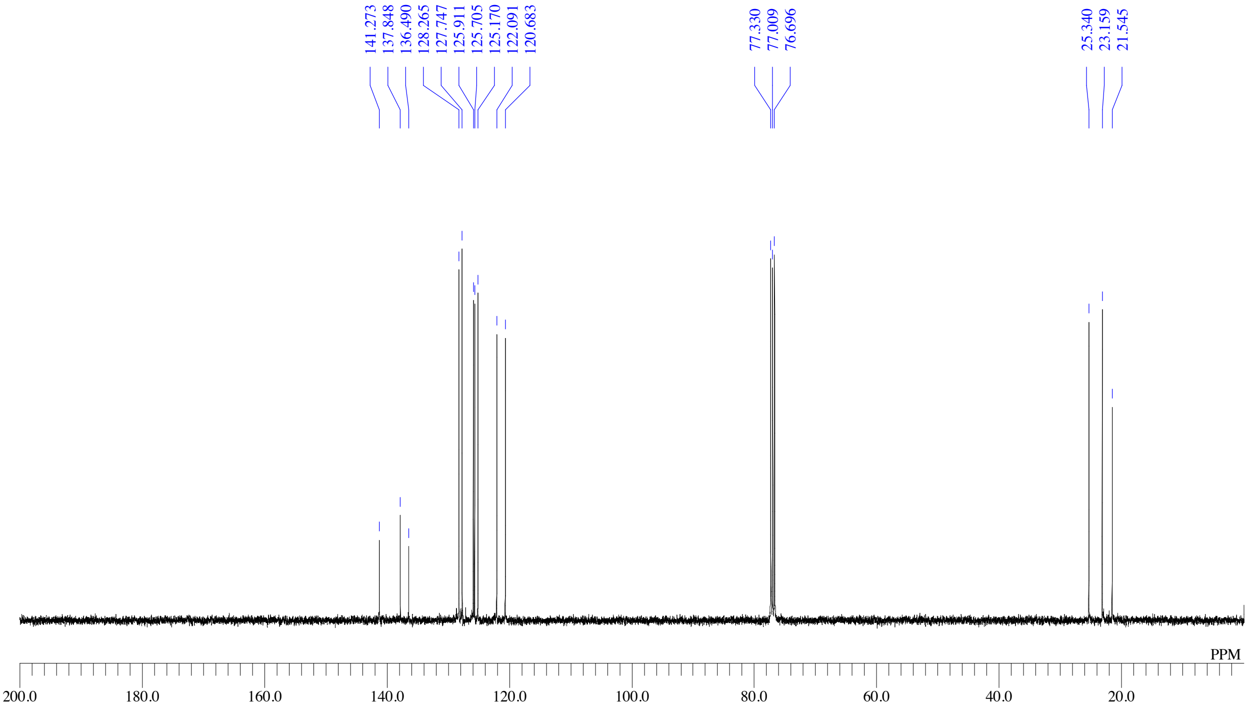

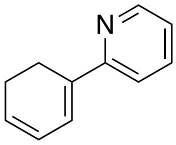

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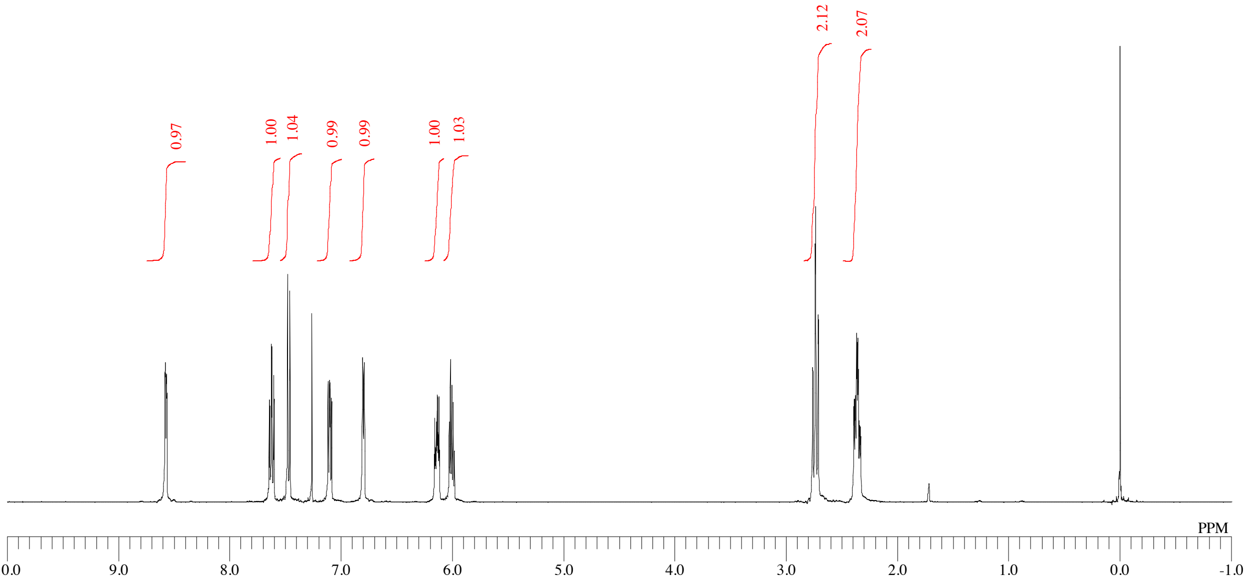

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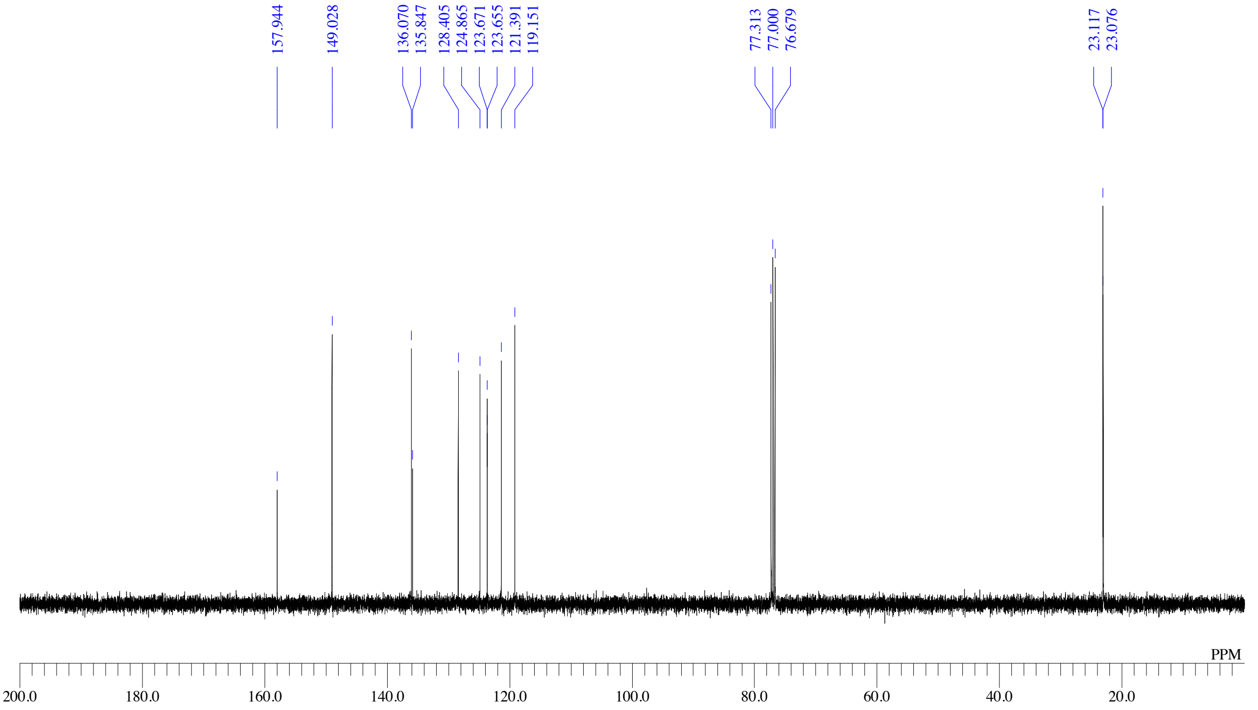

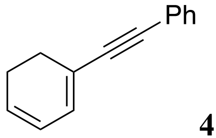

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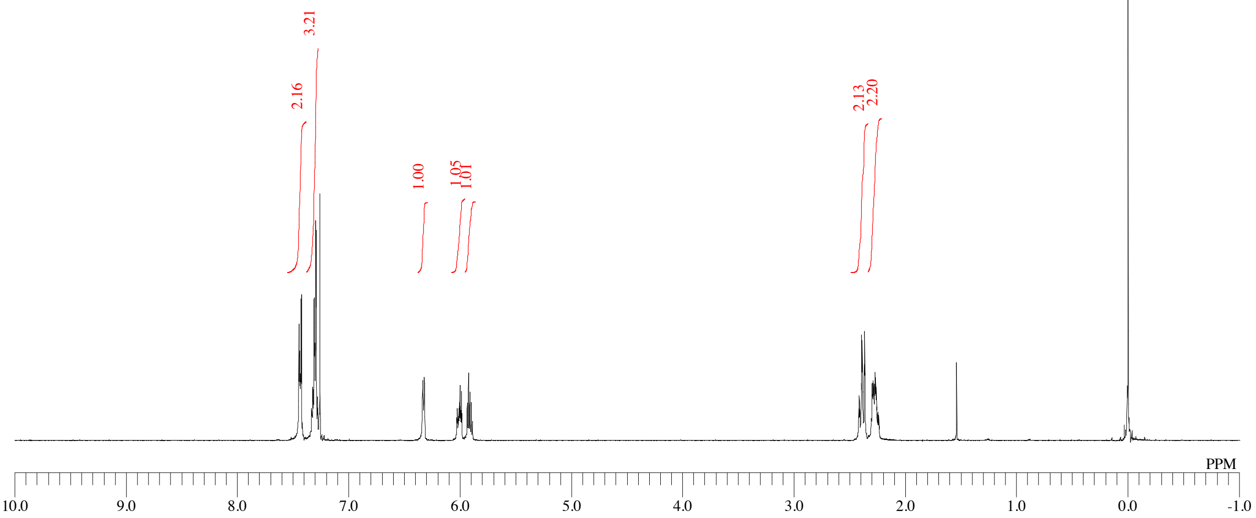

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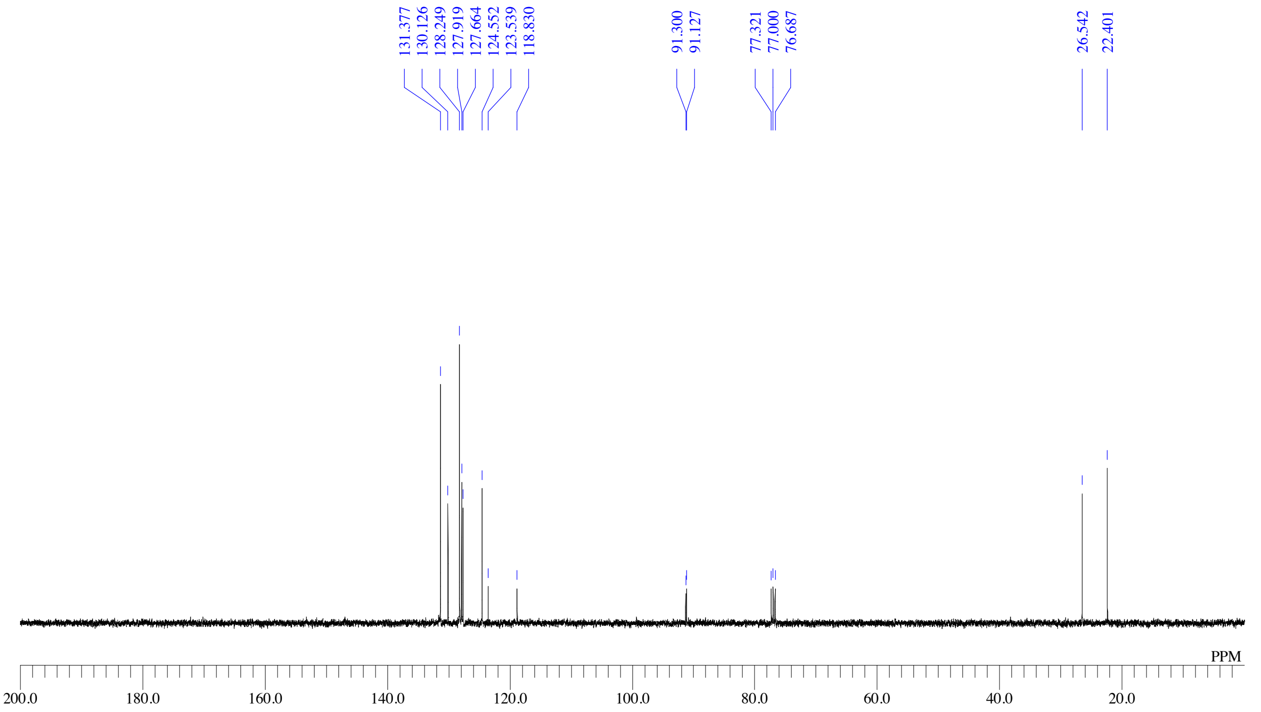

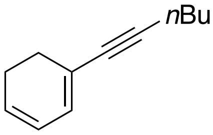

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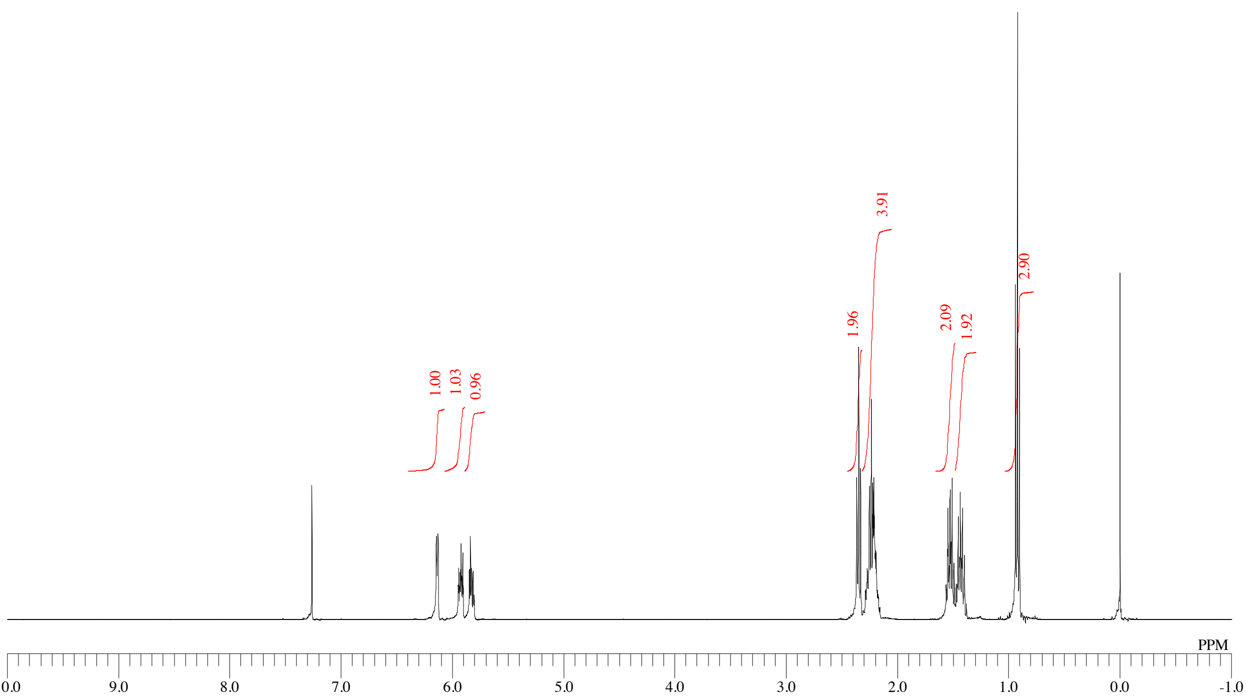

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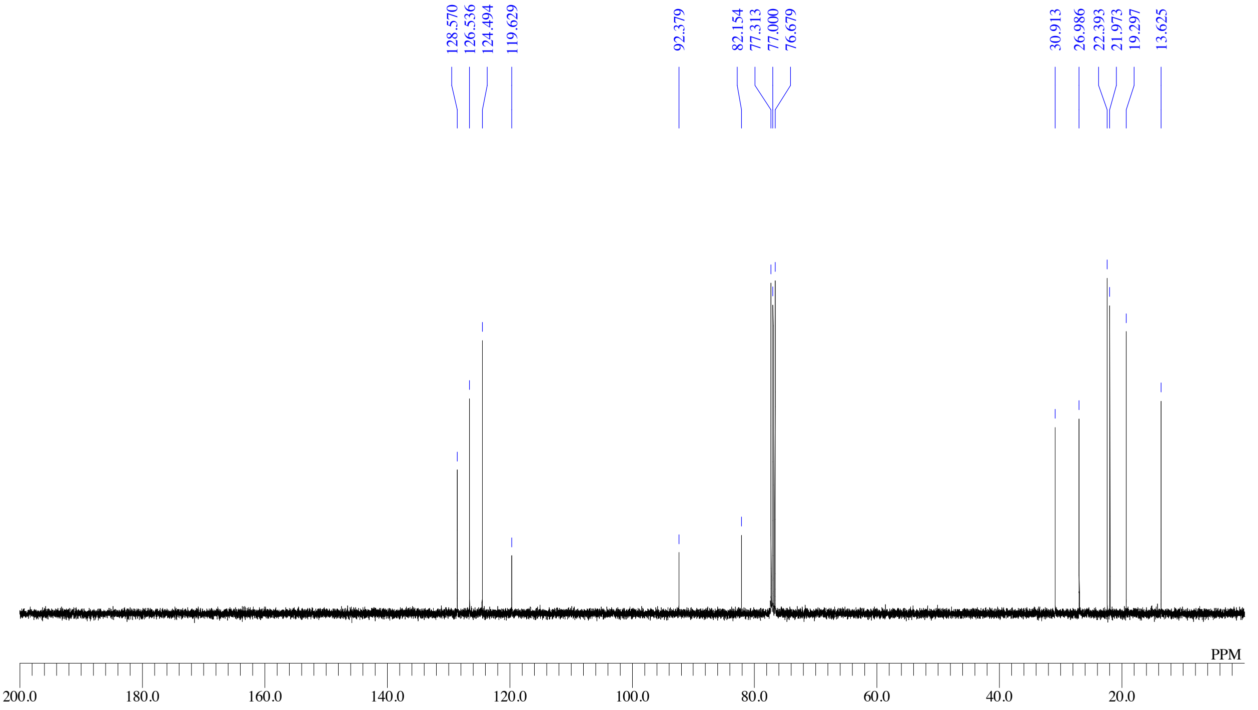

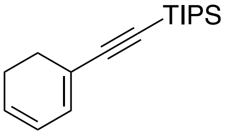

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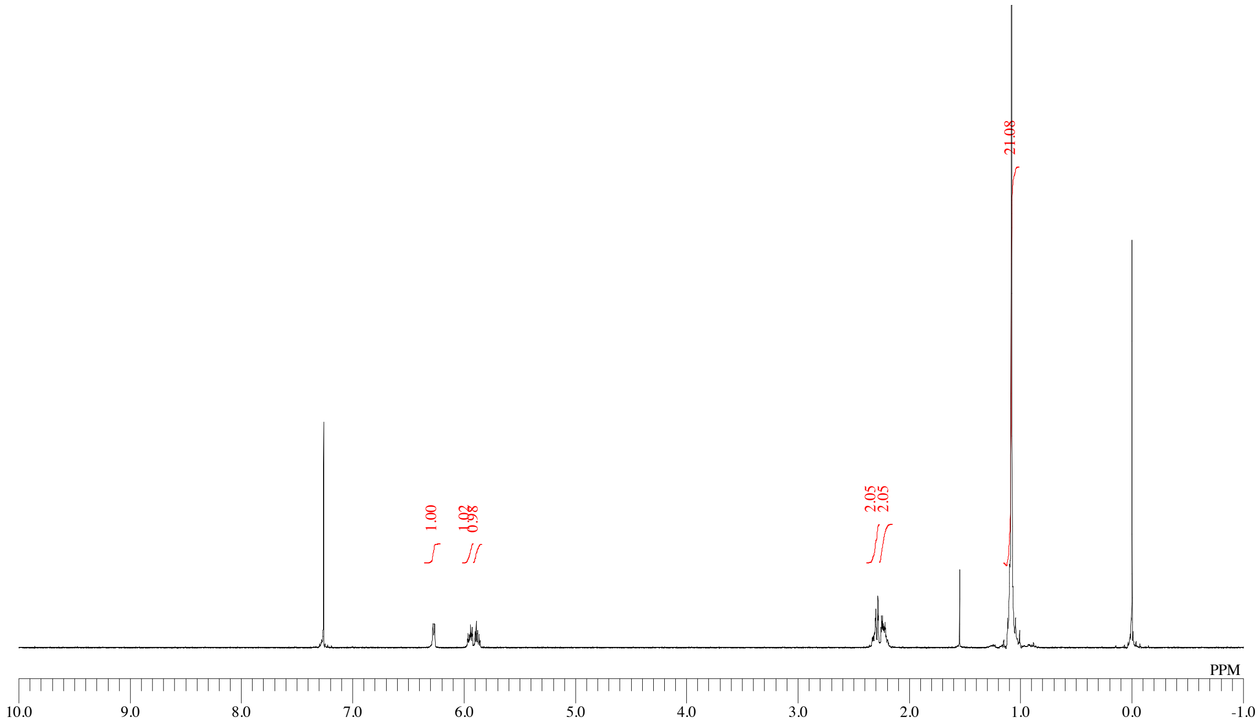

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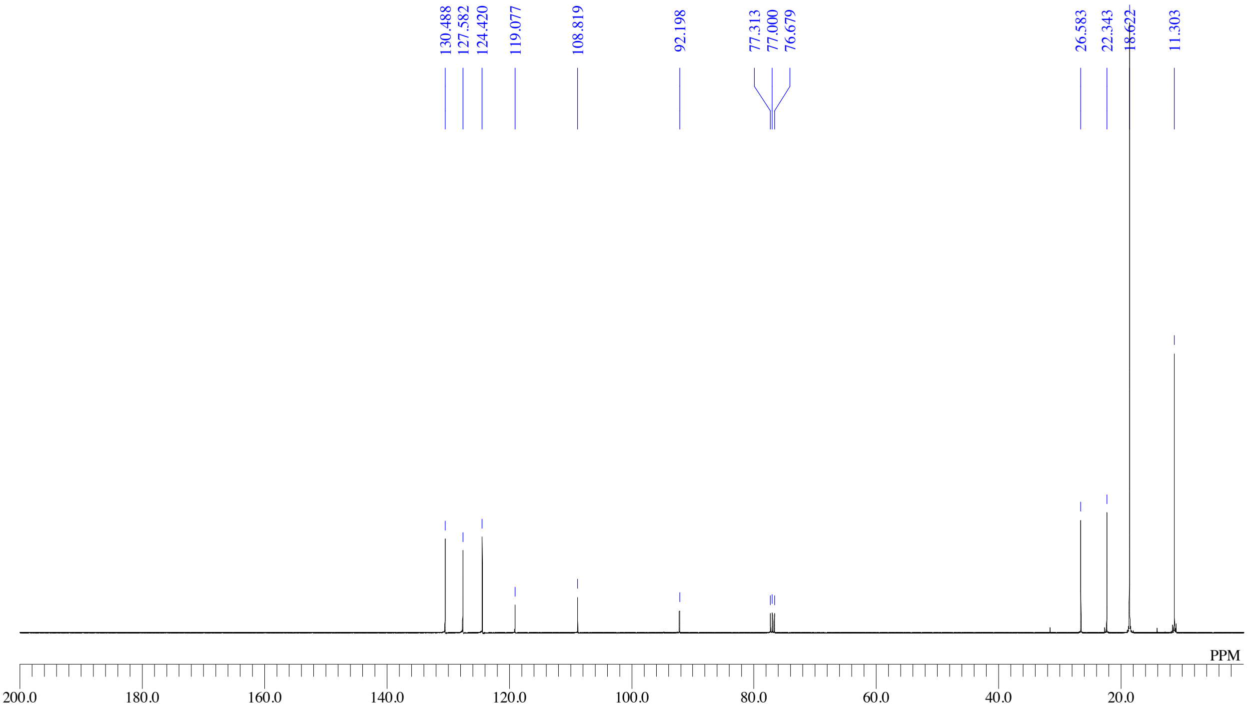

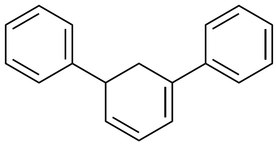

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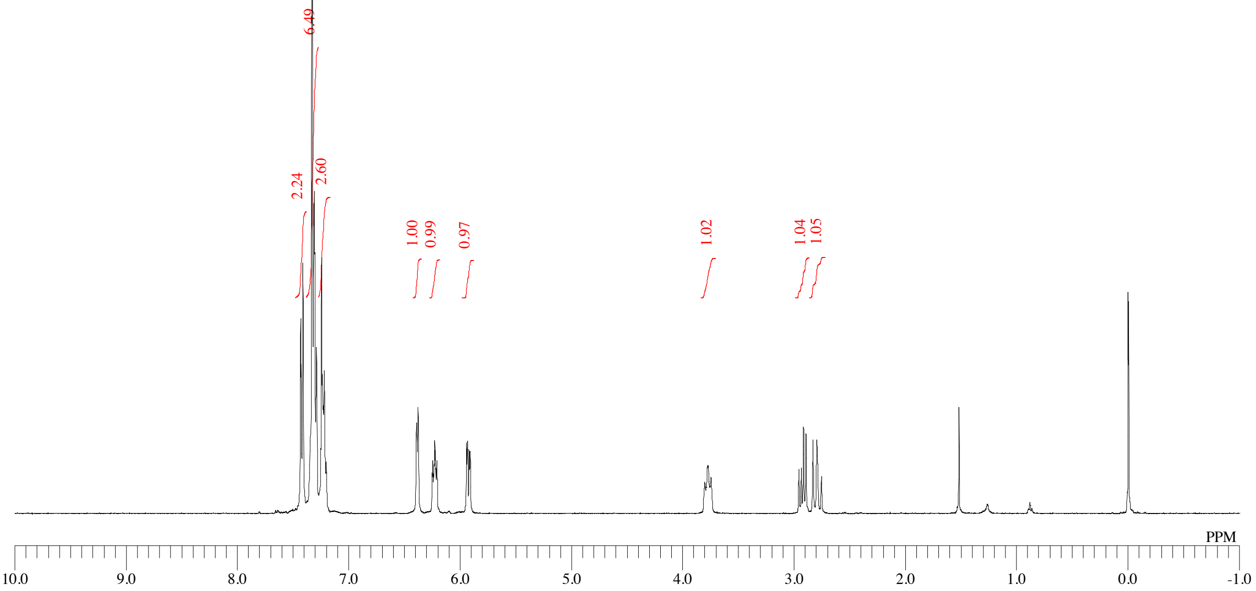

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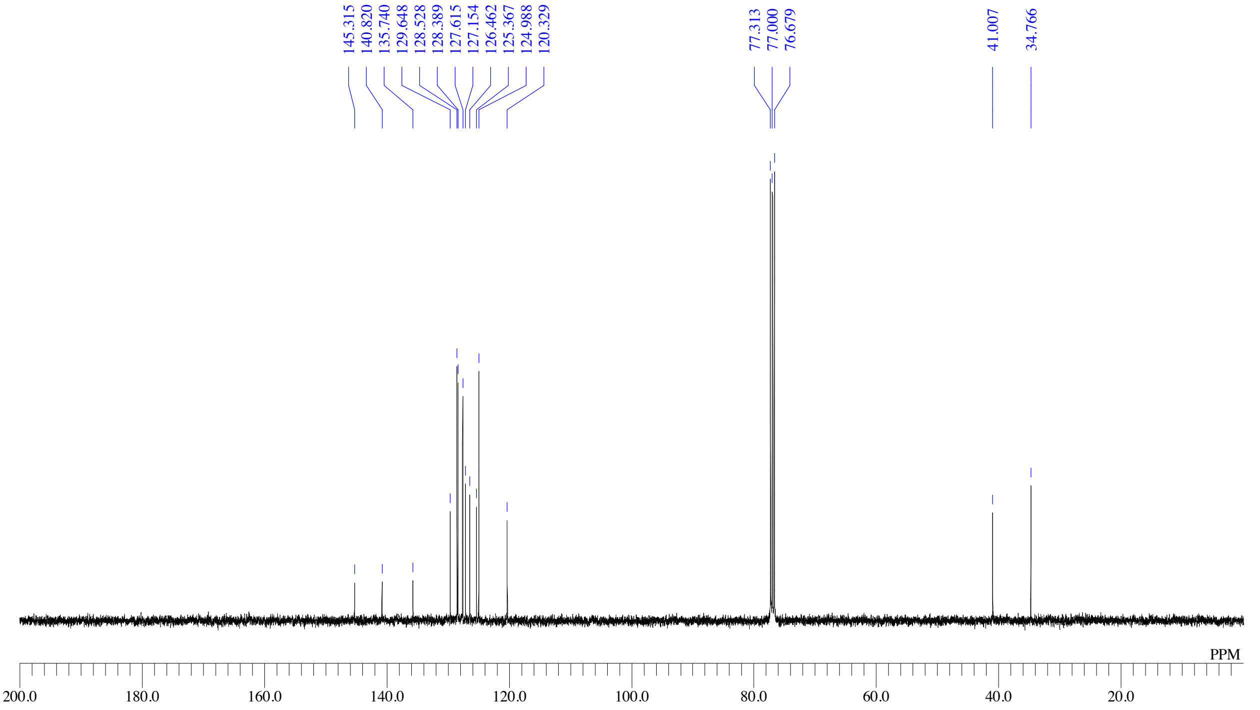

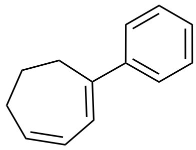

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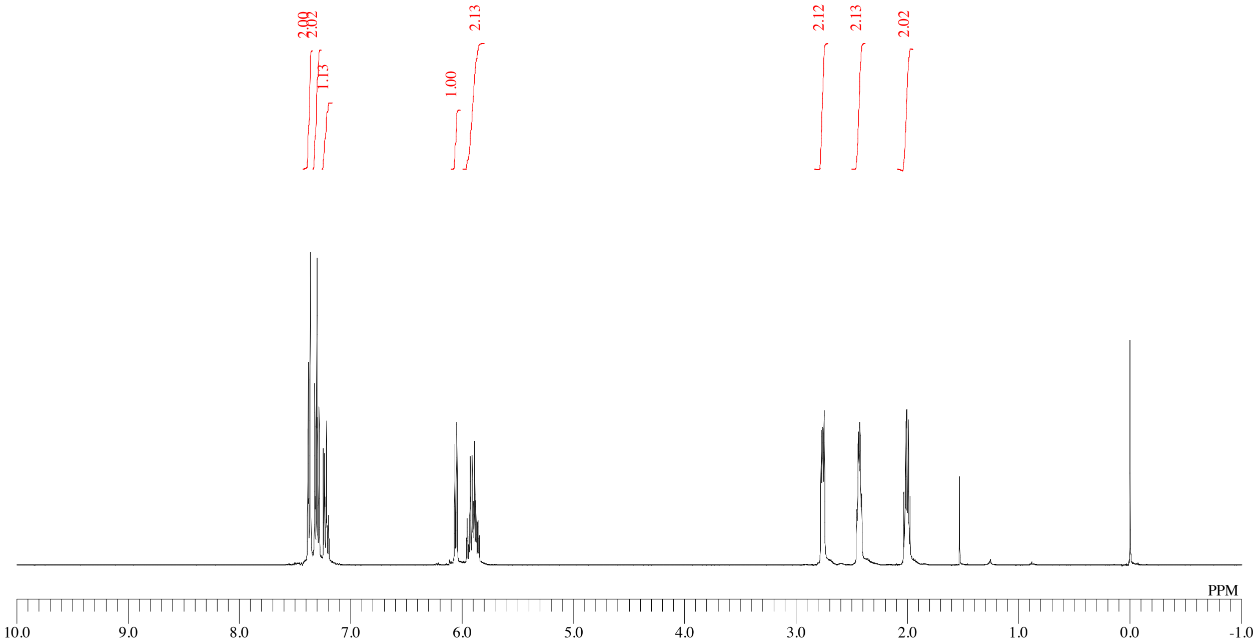

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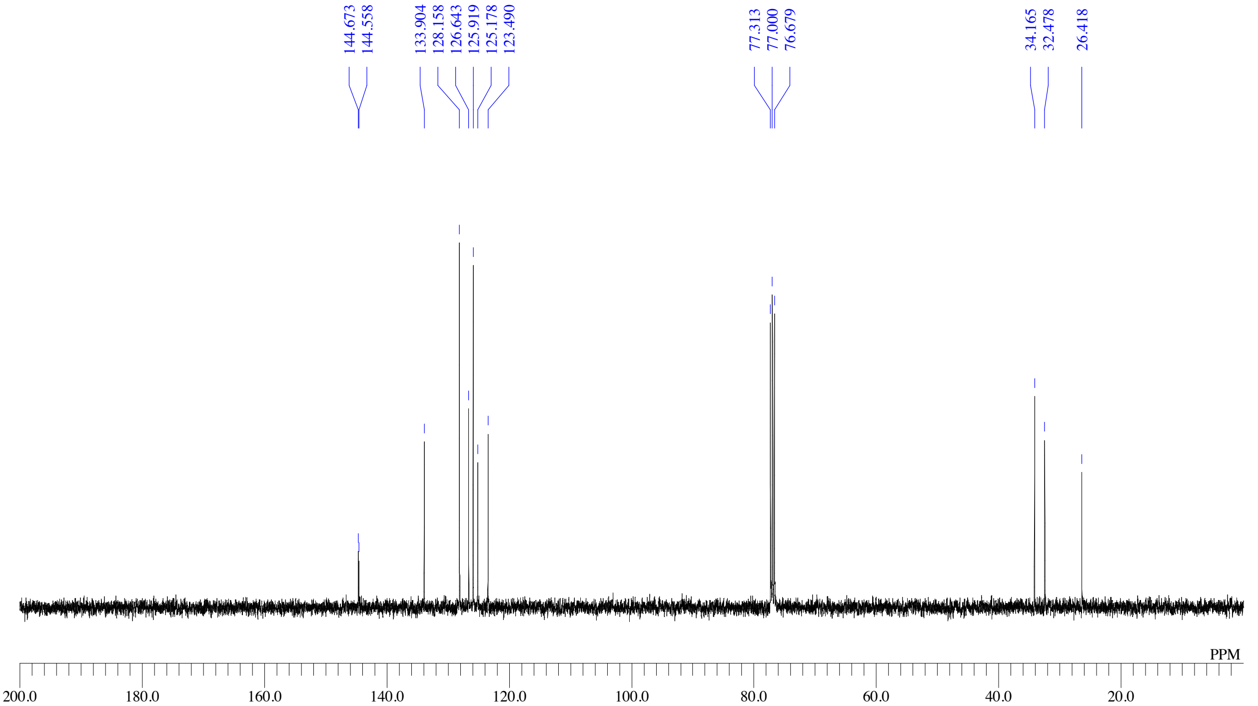

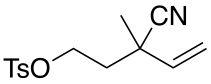

2a

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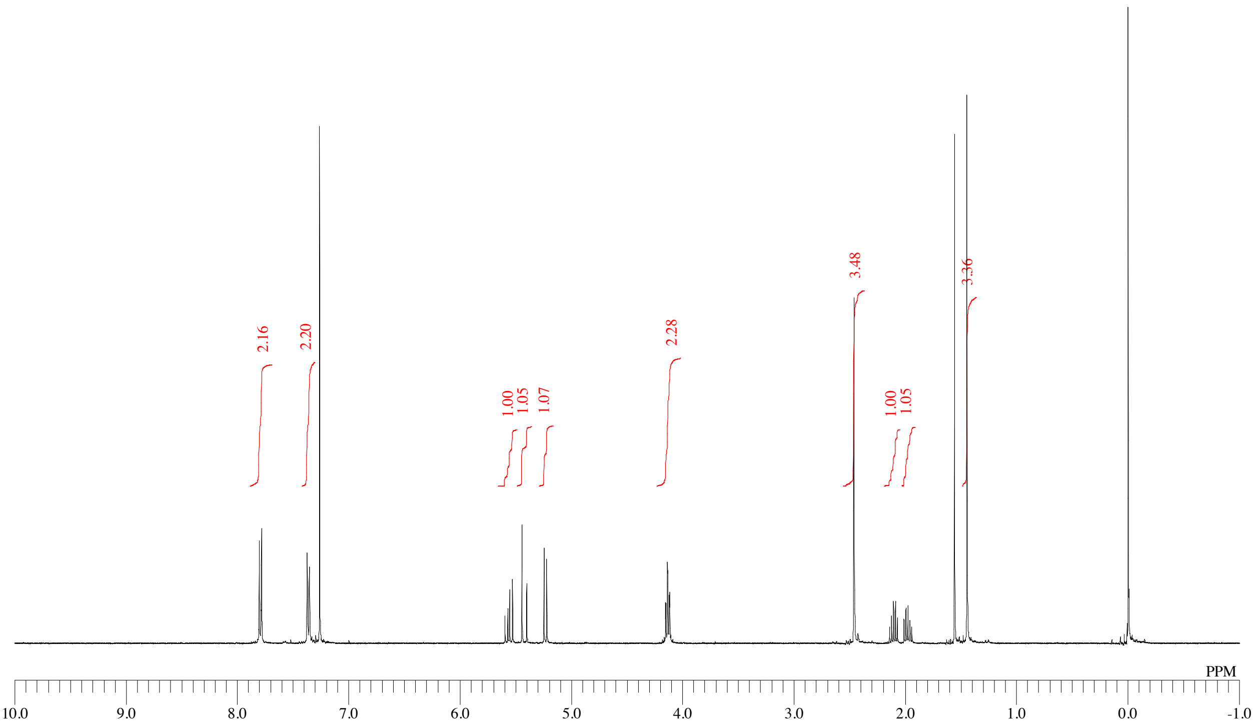
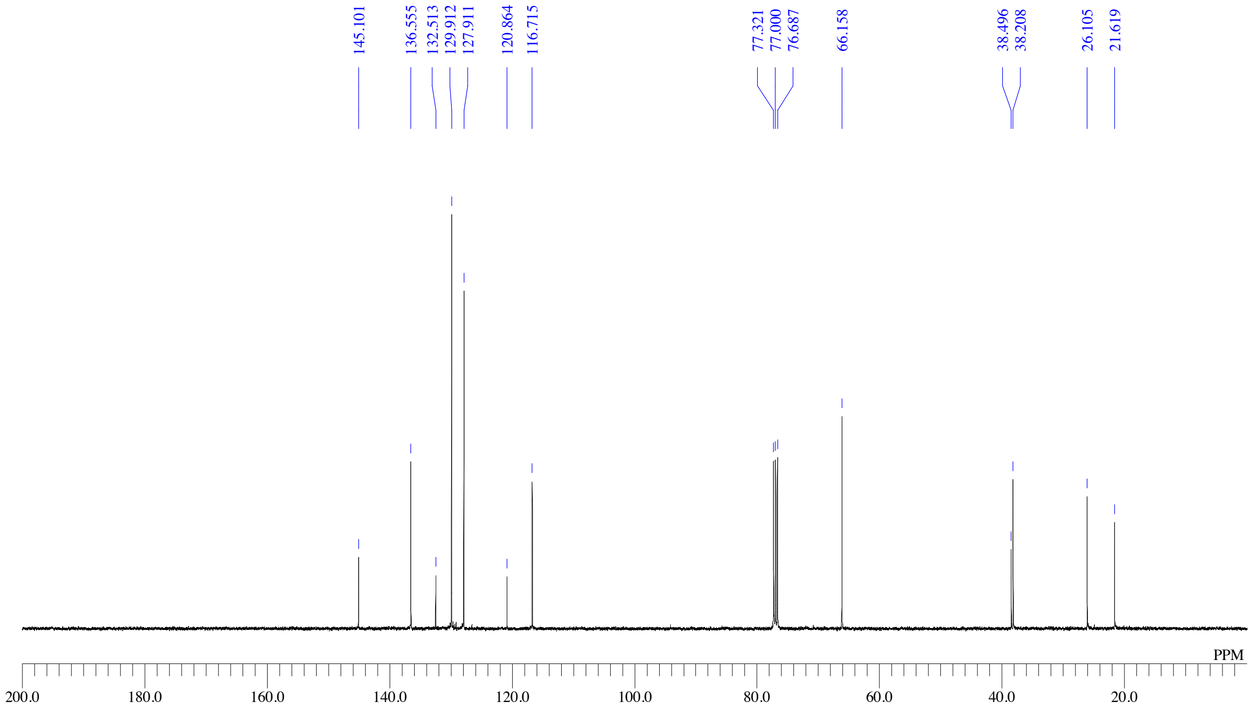
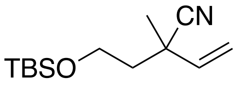


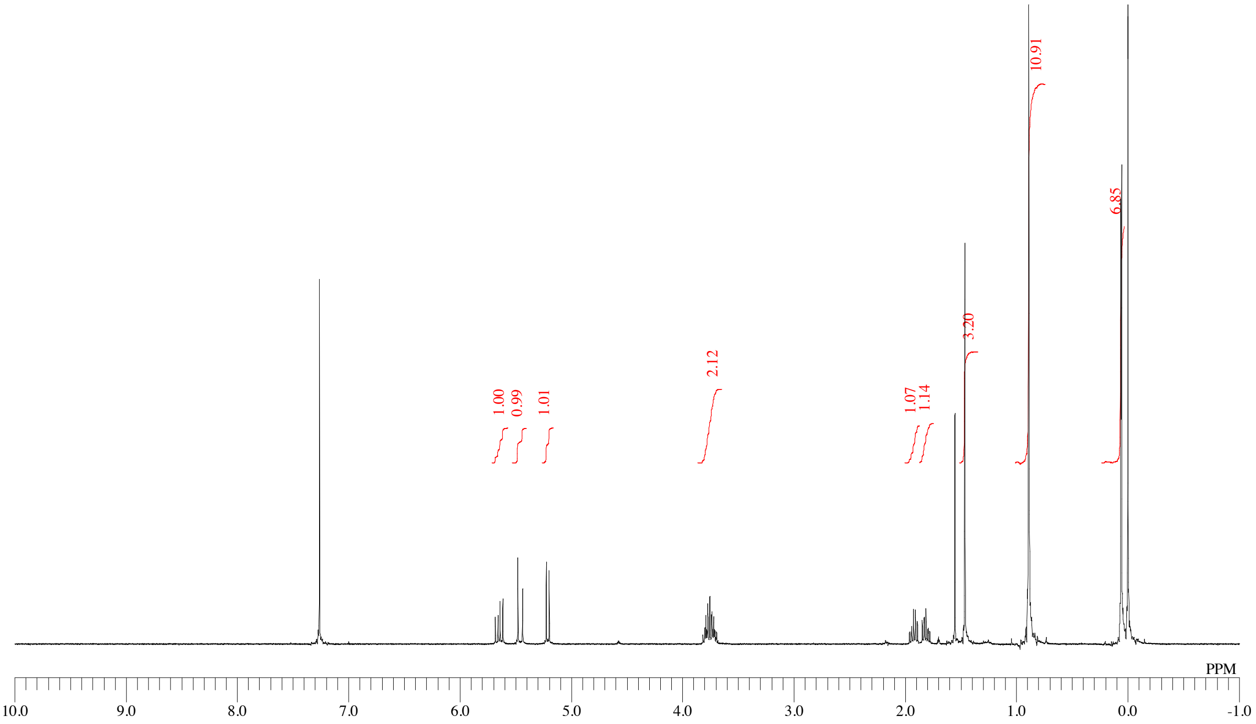
^{13}C NMR: (100 MHz, CDCl$_3$)



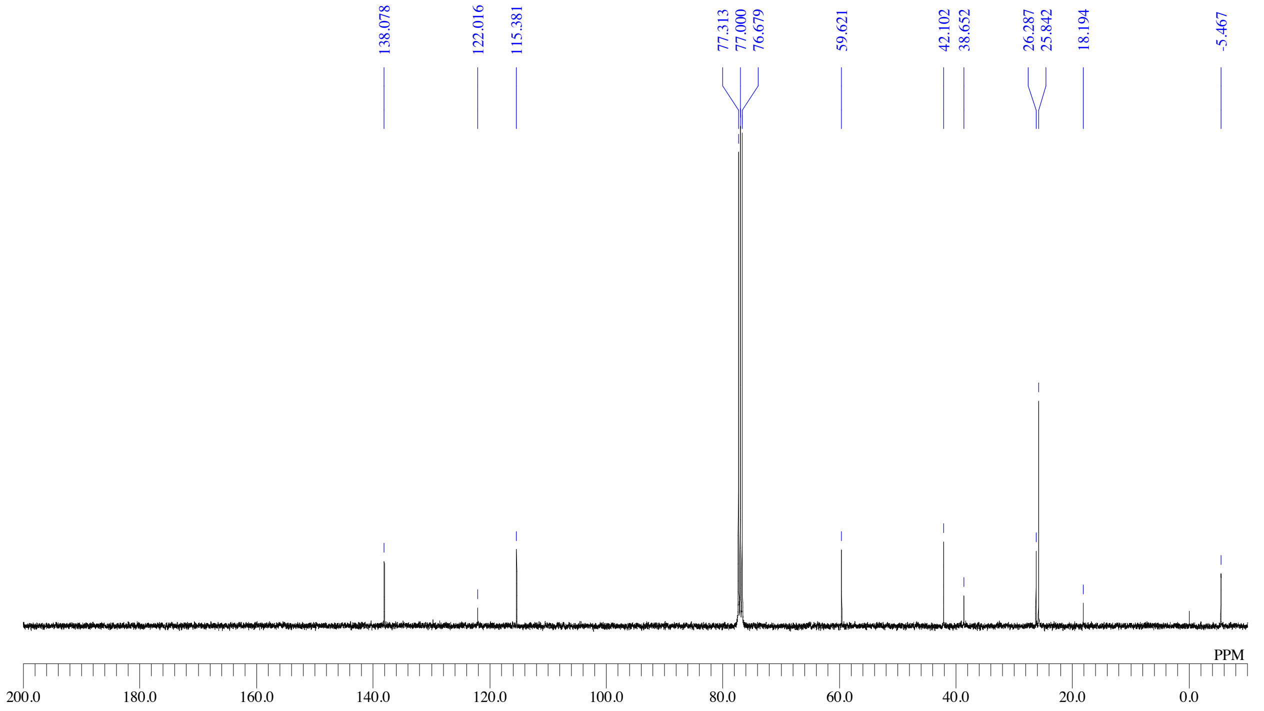


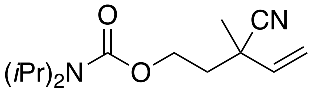
2b

^{1}H NMR: (400 MHz, $CDCl_3$)



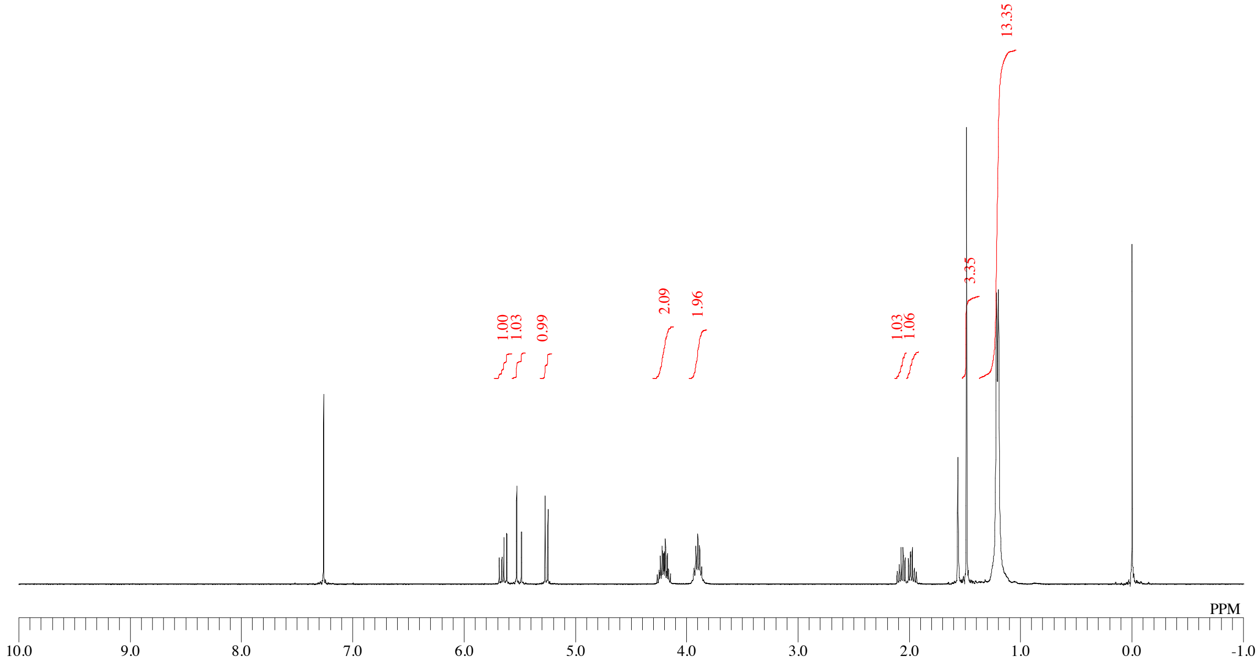
^{13}C NMR: (100 MHz, $CDCl_3$)



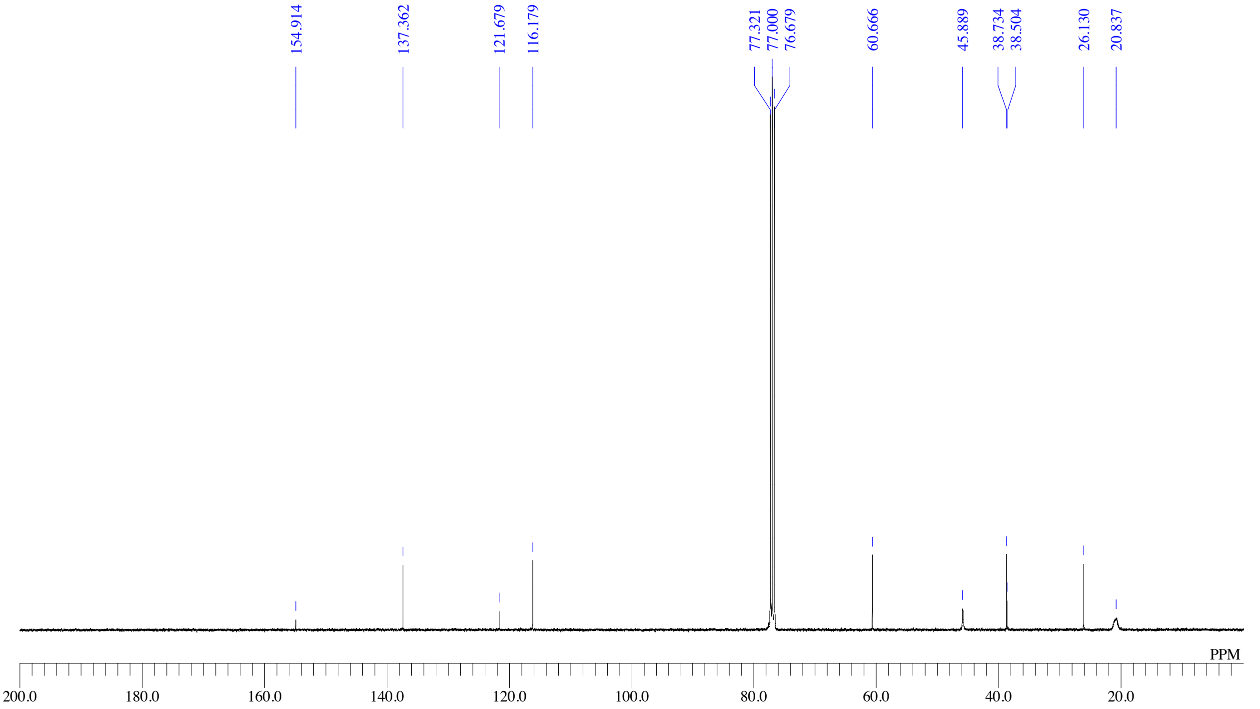


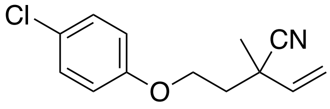
2c

^{1}H NMR: (400 MHz, CDCl$_3$)



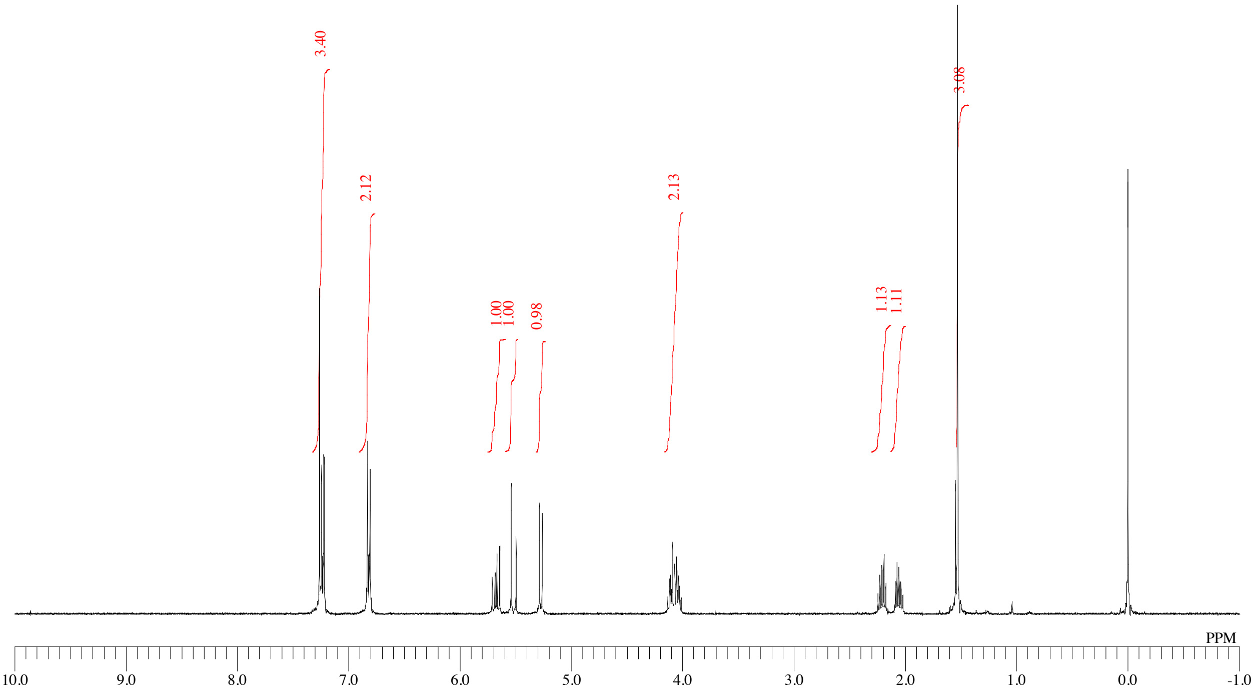
^{13}C NMR: (100 MHz, CDCl$_3$)



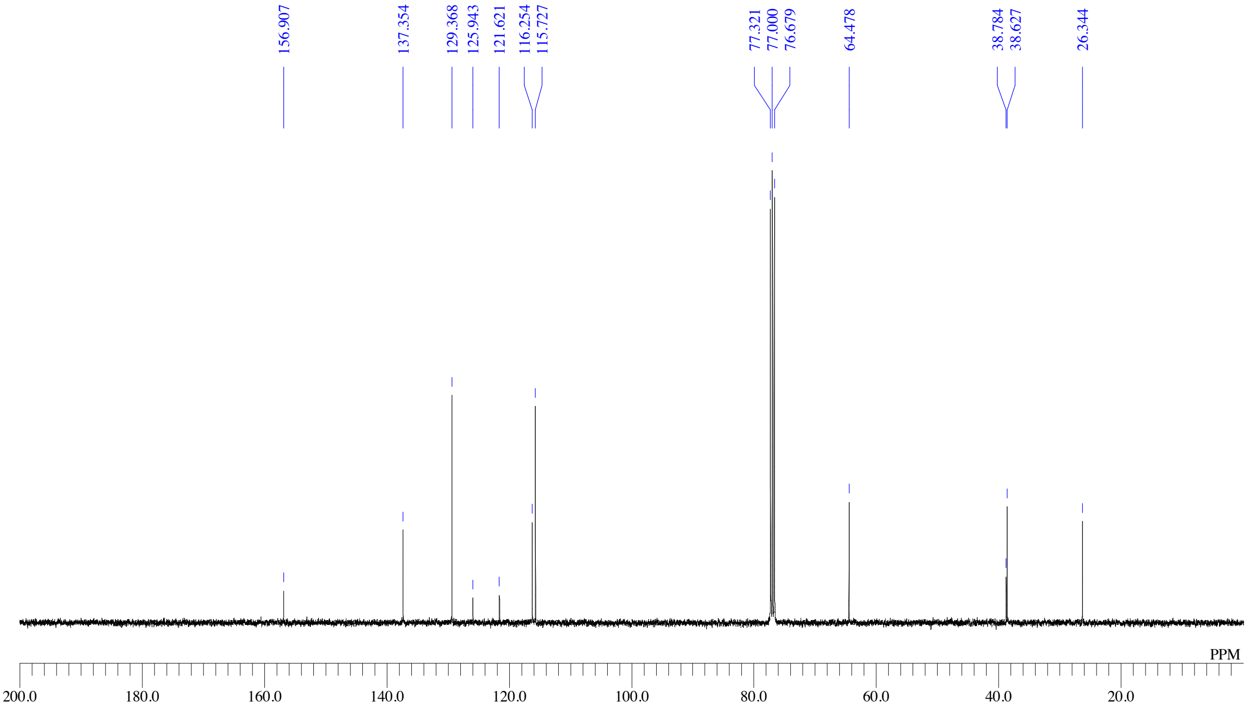


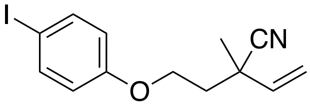
2d

^{1}H NMR: (400 MHz, CDCl$_3$)



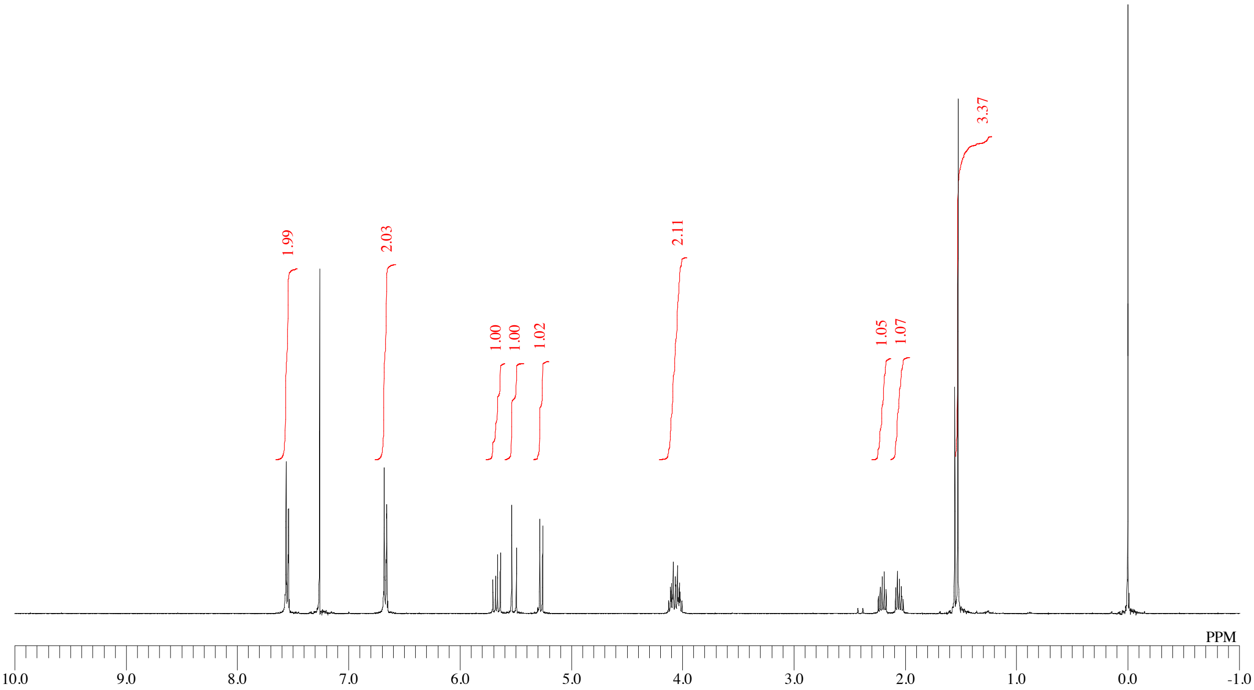
^{13}C NMR: (100 MHz, CDCl$_3$)



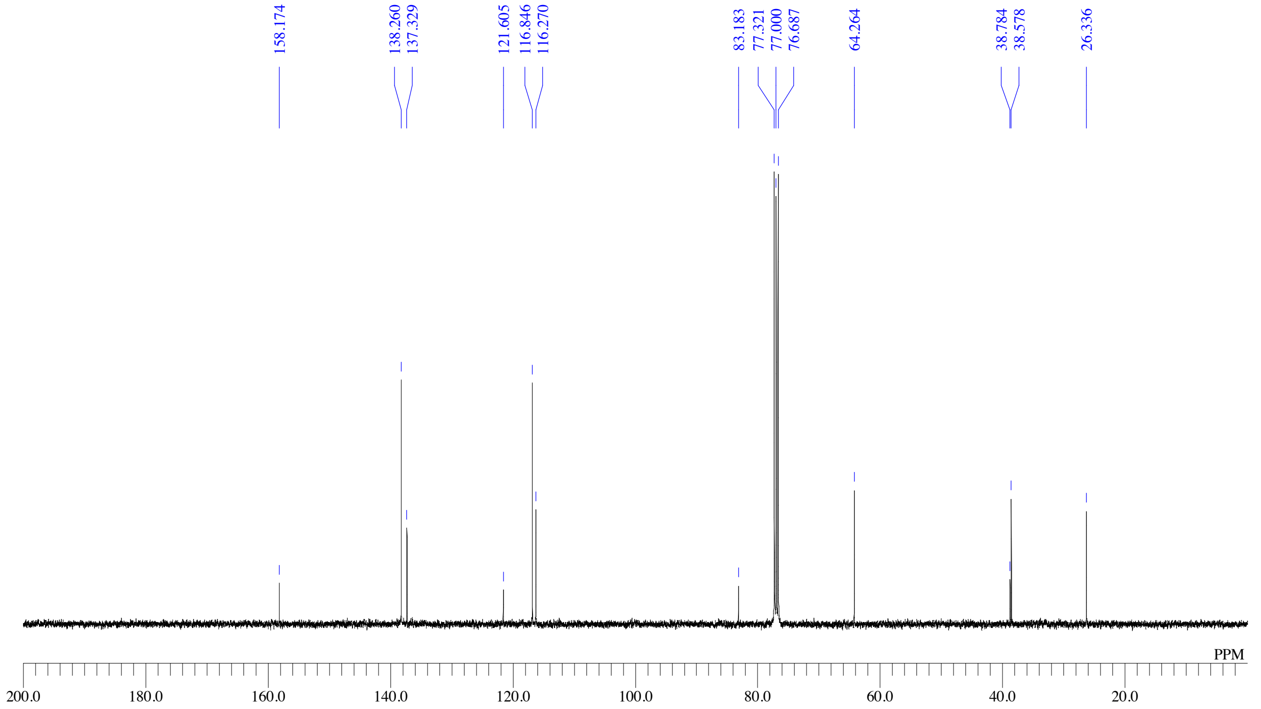


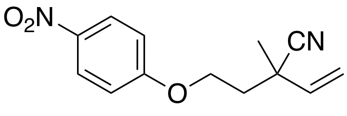
2e

^{1}H NMR: (400 MHz, CDCl$_3$)



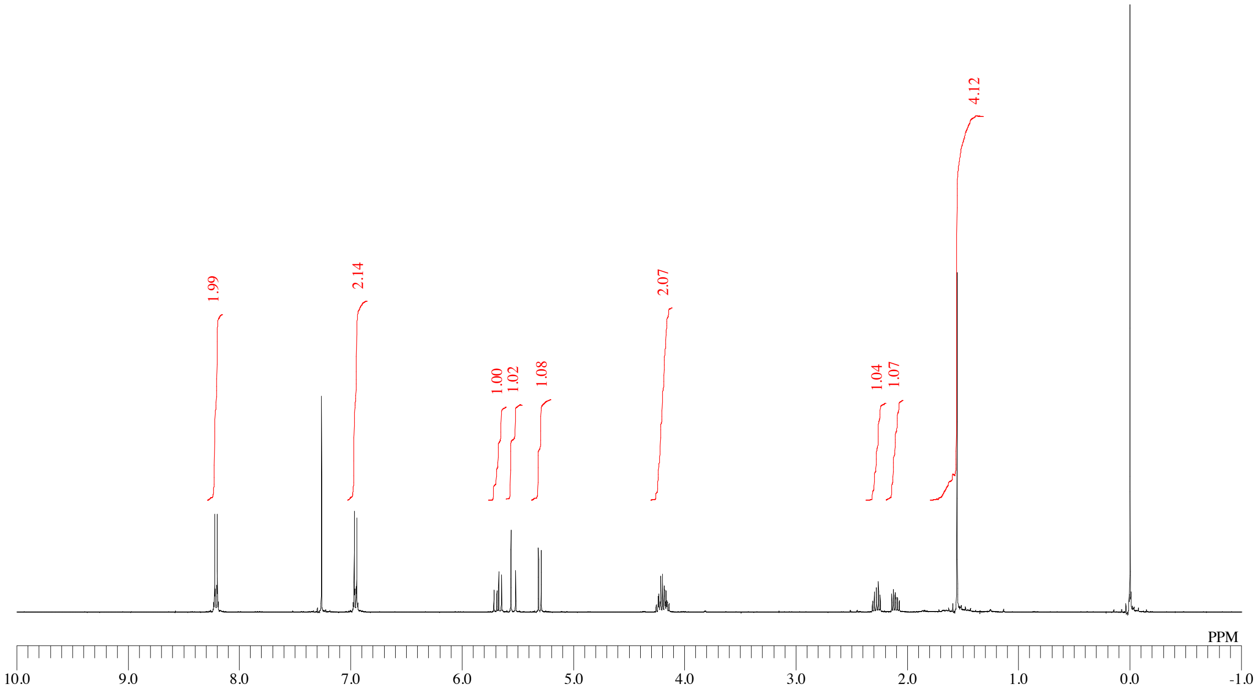
^{13}C NMR: (100 MHz, CDCl$_3$)



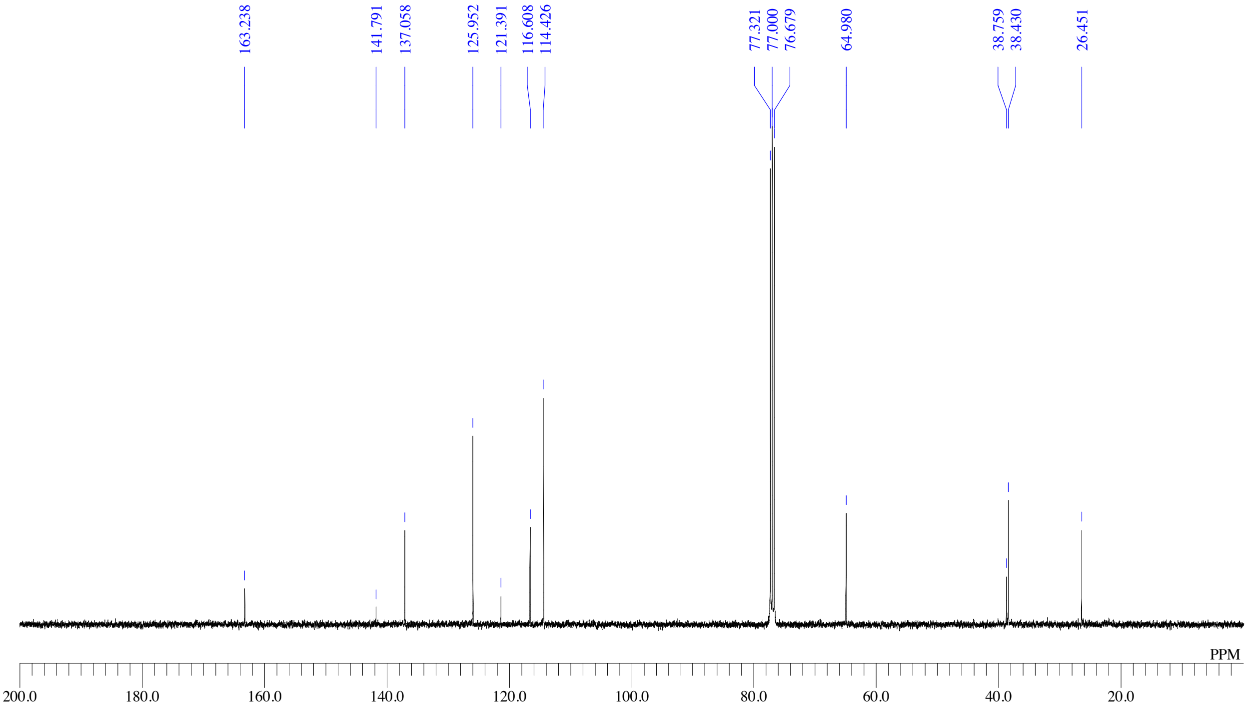


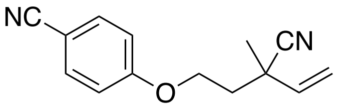
2f

^{1}H NMR: (400 MHz, CDCl$_3$)



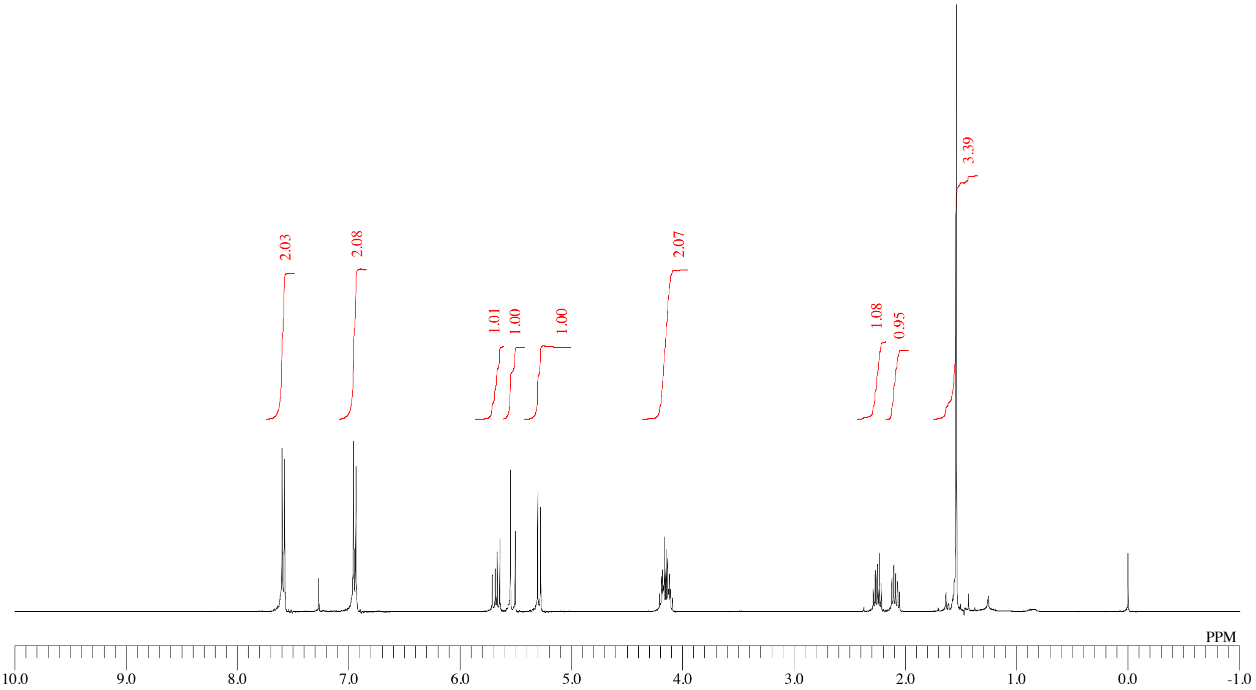
^{13}C NMR: (100 MHz, CDCl$_3$)



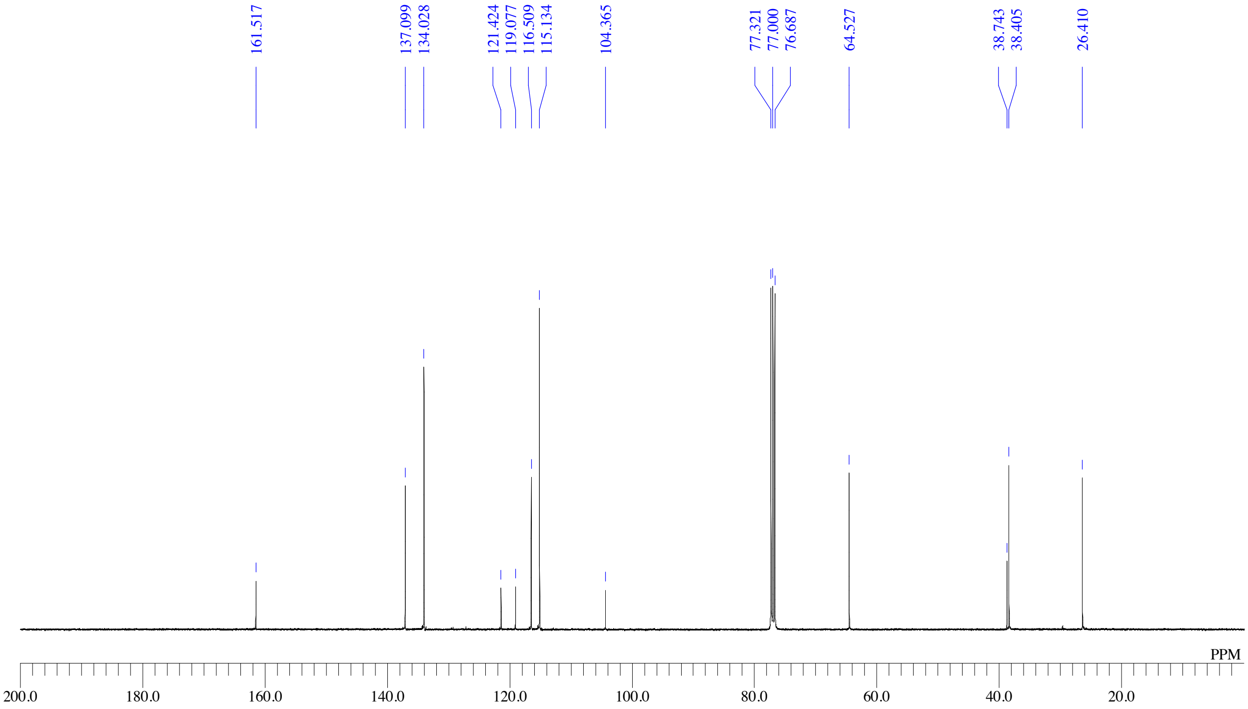


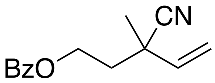
2g

^{1}H NMR: (400 MHz, CDCl$_3$)



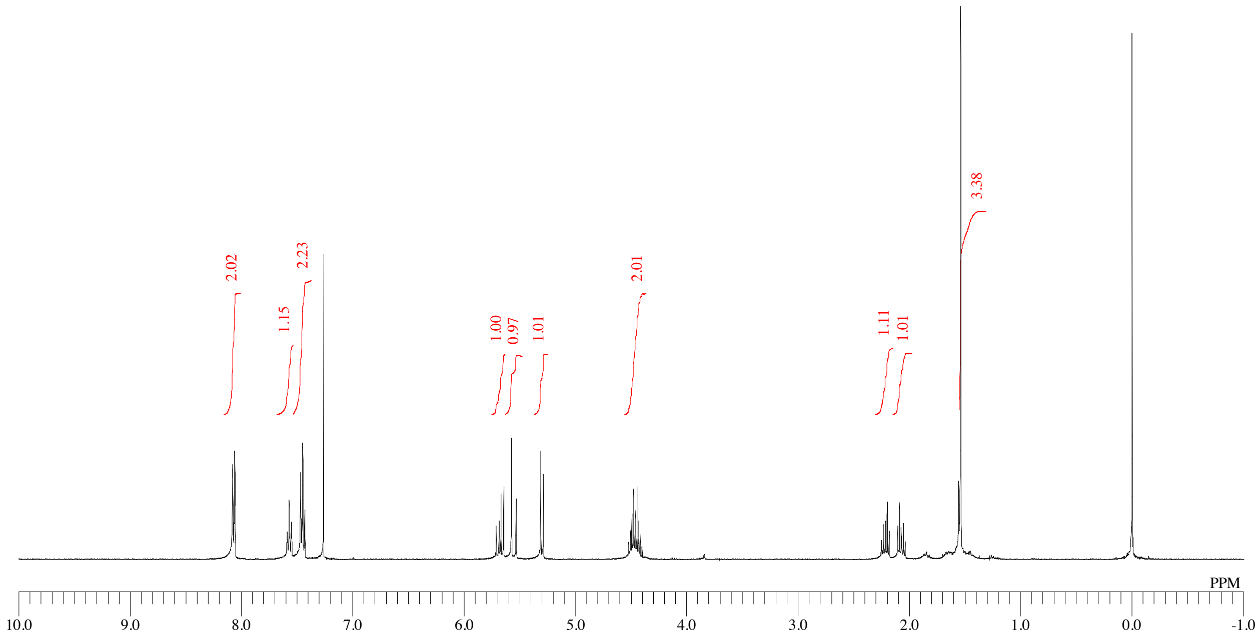
^{13}C NMR: (100 MHz, CDCl$_3$)



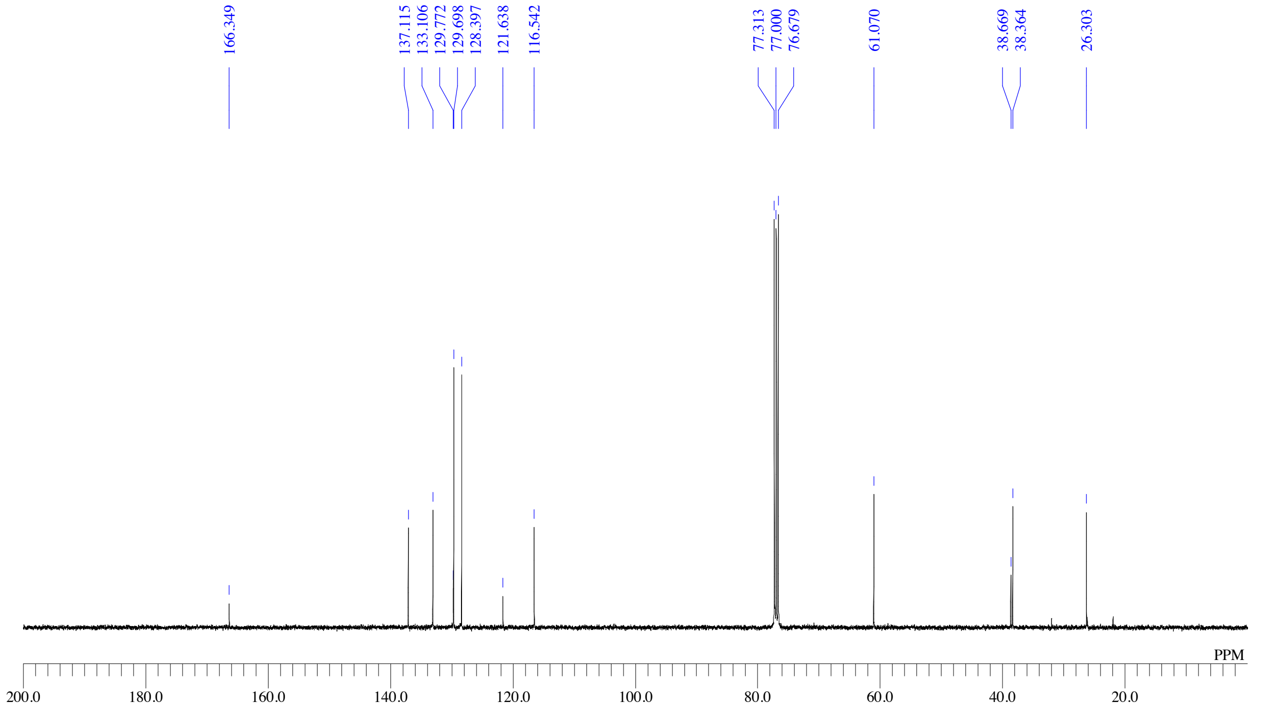


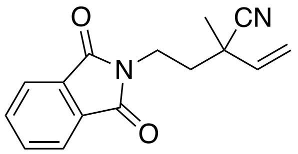
2h

^{1}H NMR: (400 MHz, CDCl$_3$)



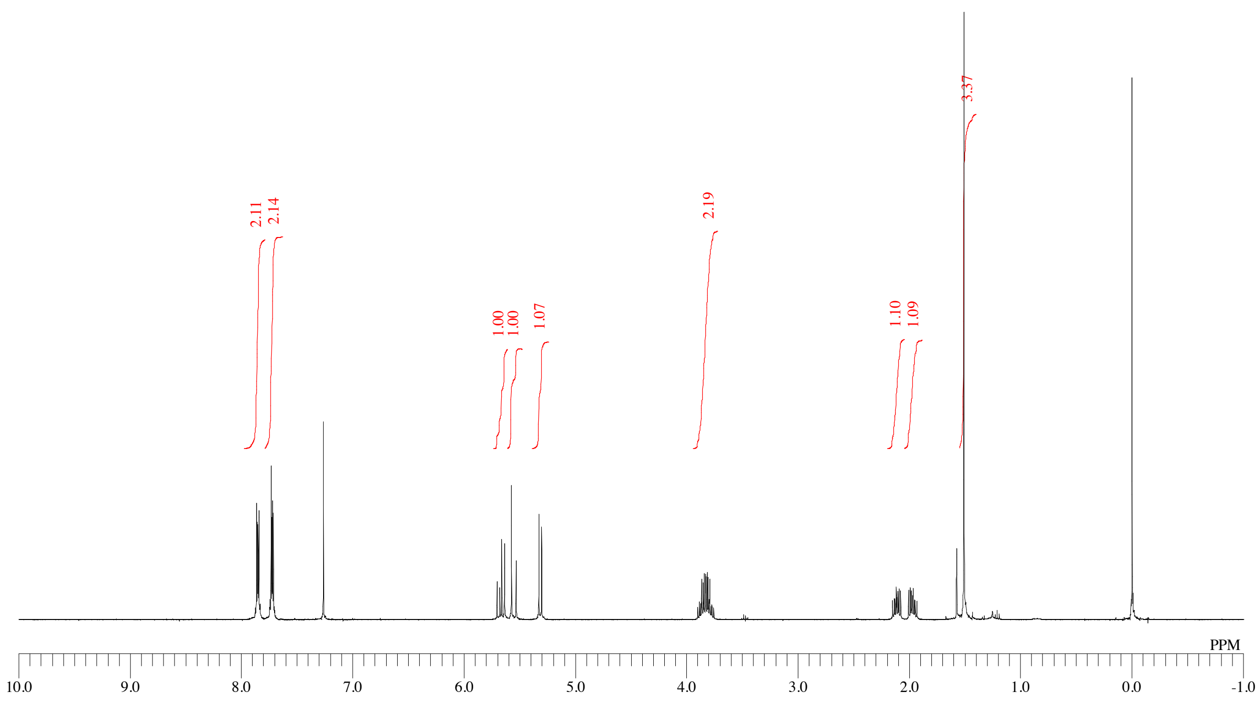
^{13}C NMR: (100 MHz, CDCl$_3$)



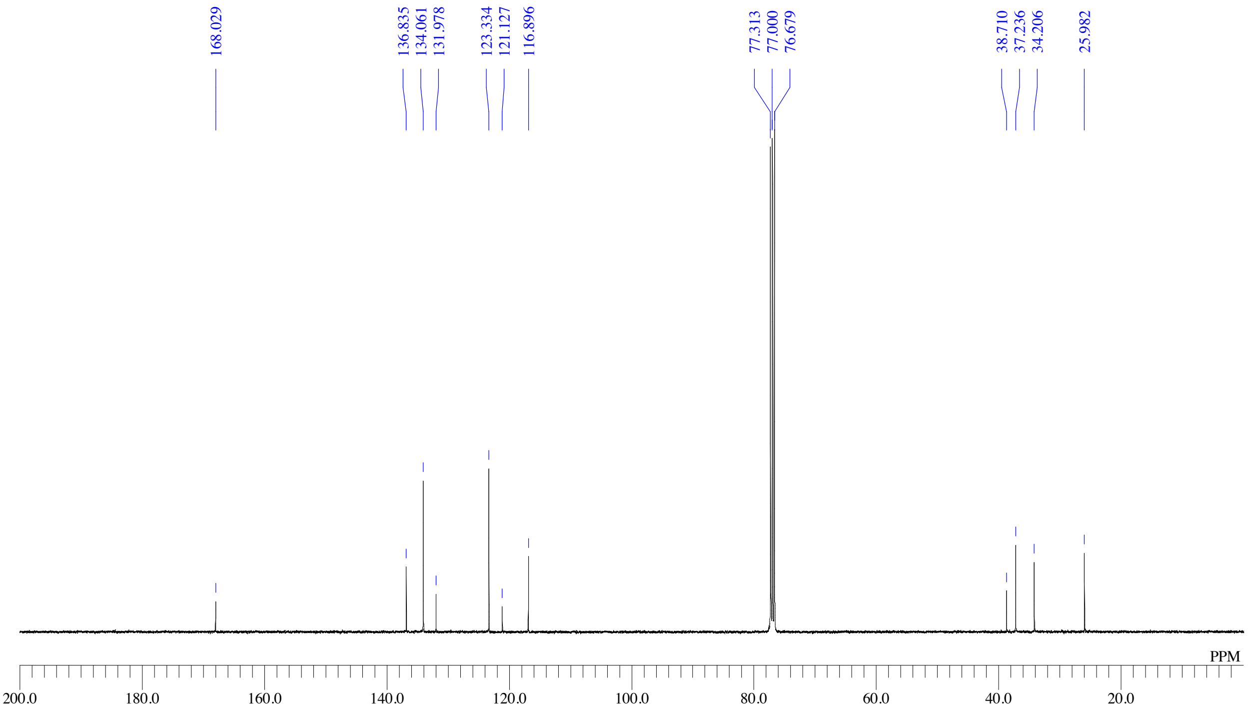


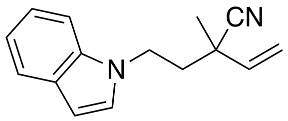
2i

^{1}H NMR: (400 MHz, CDCl$_3$)



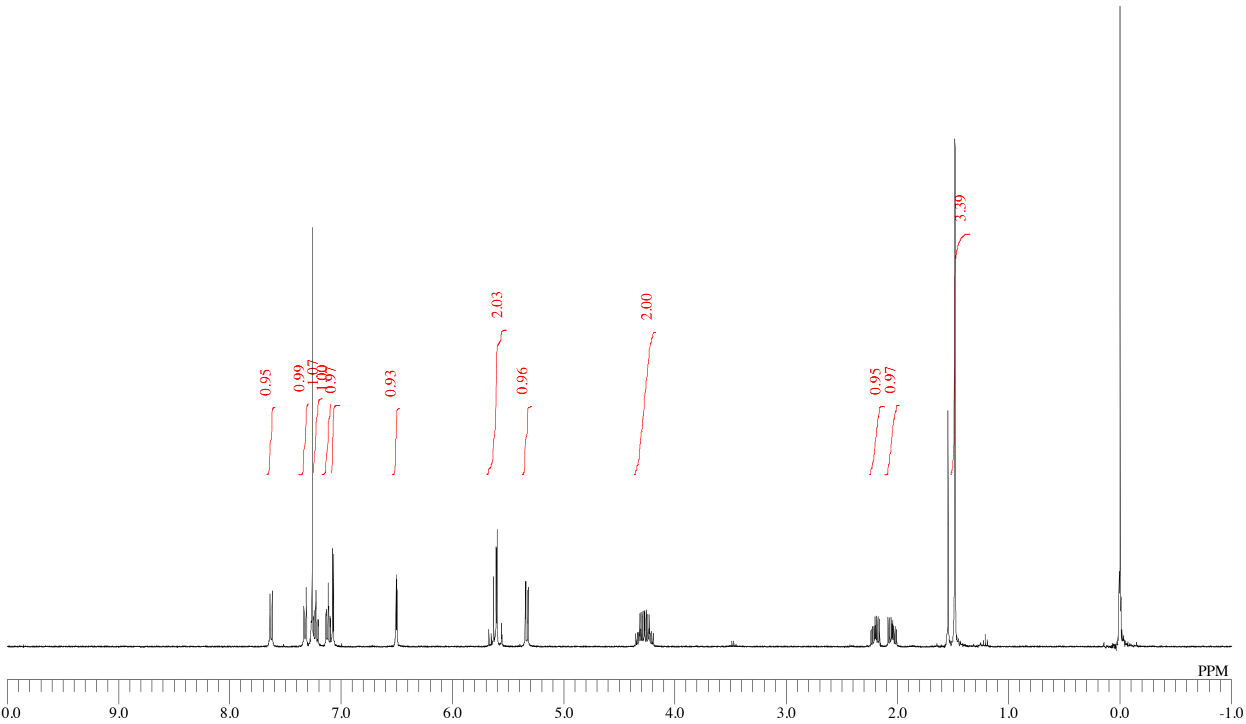
^{13}C NMR: (100 MHz, CDCl$_3$)



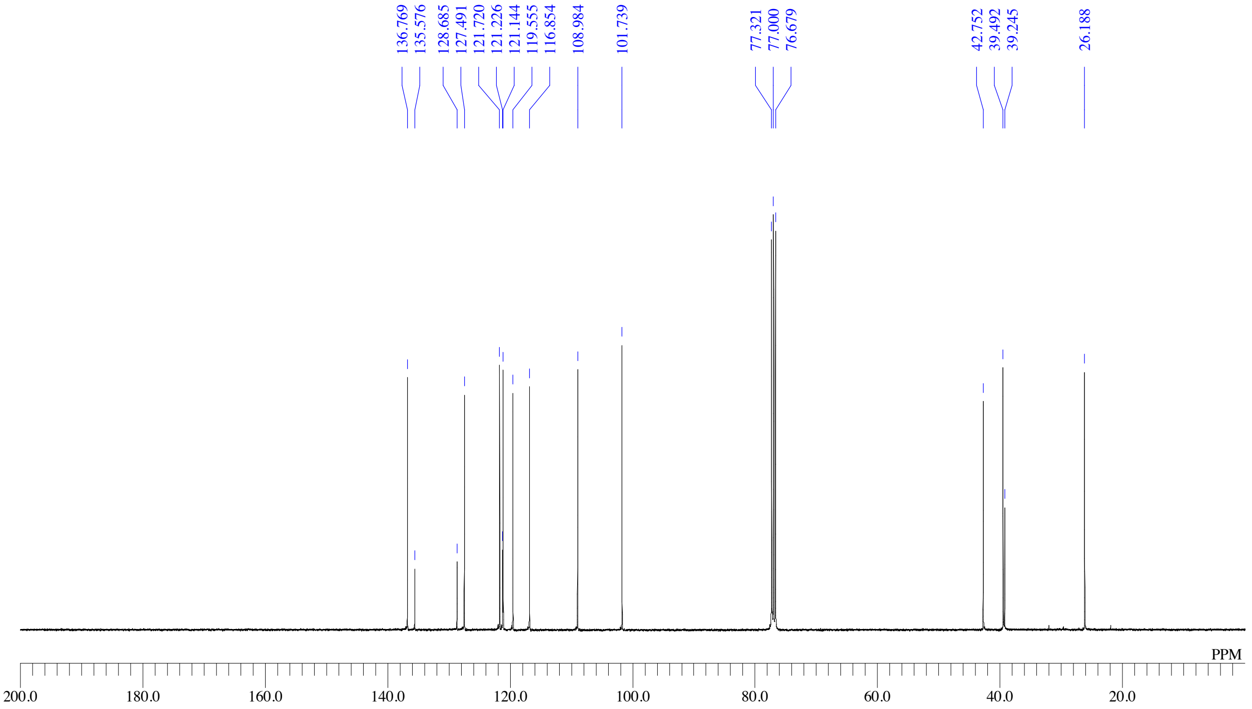


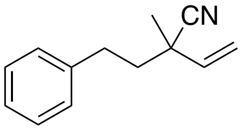
2j

^{1}H NMR: (400 MHz, CDCl$_3$)



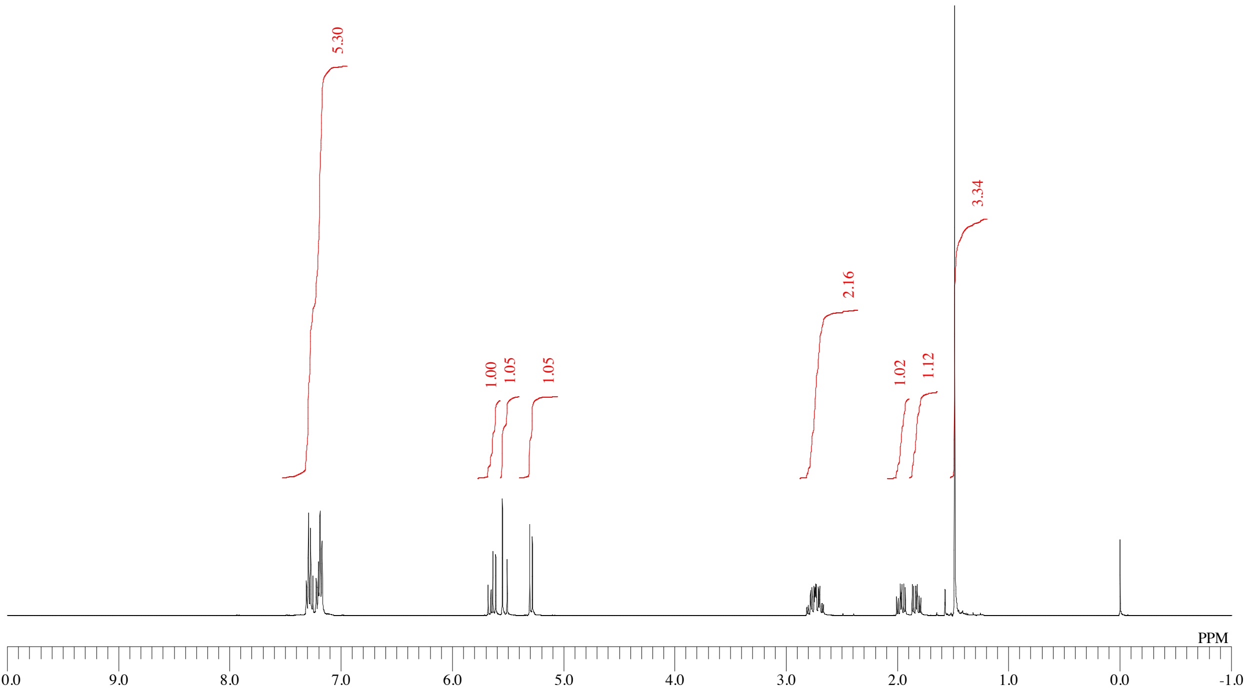
^{13}C NMR: (100 MHz, CDCl$_3$)



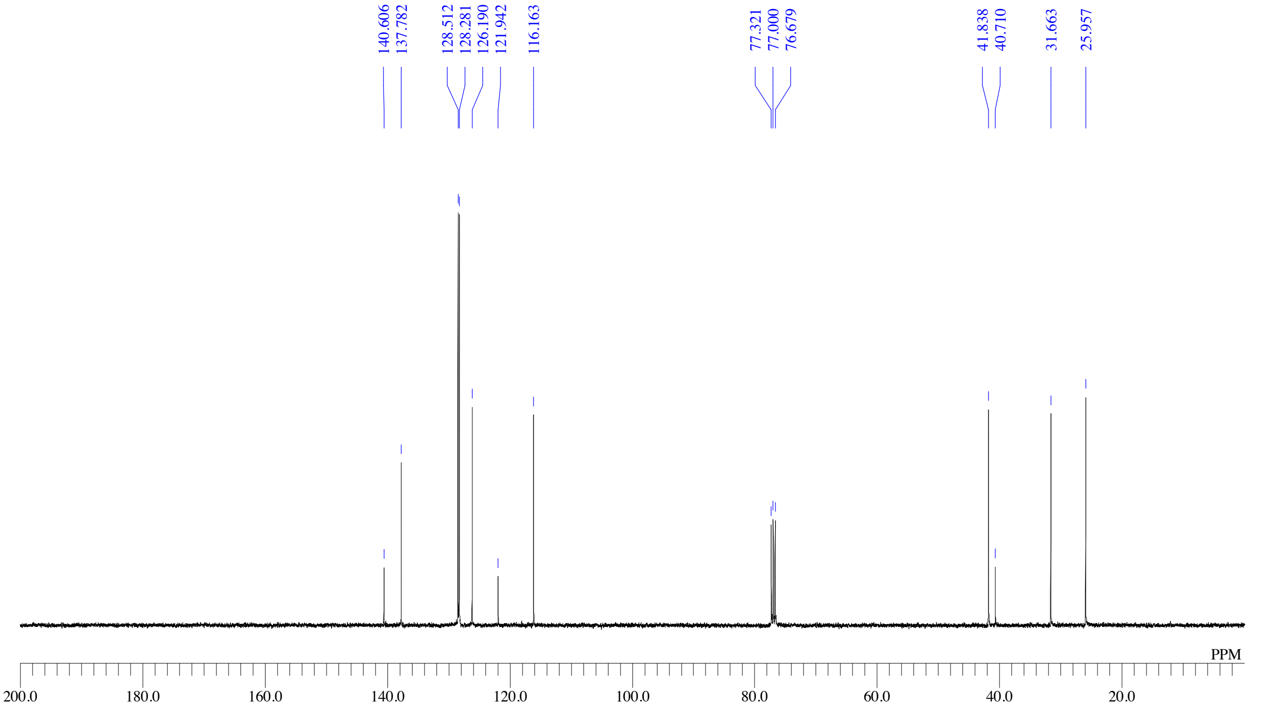


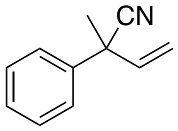
2k

^{1}H NMR: (400 MHz, $CDCl_3$)



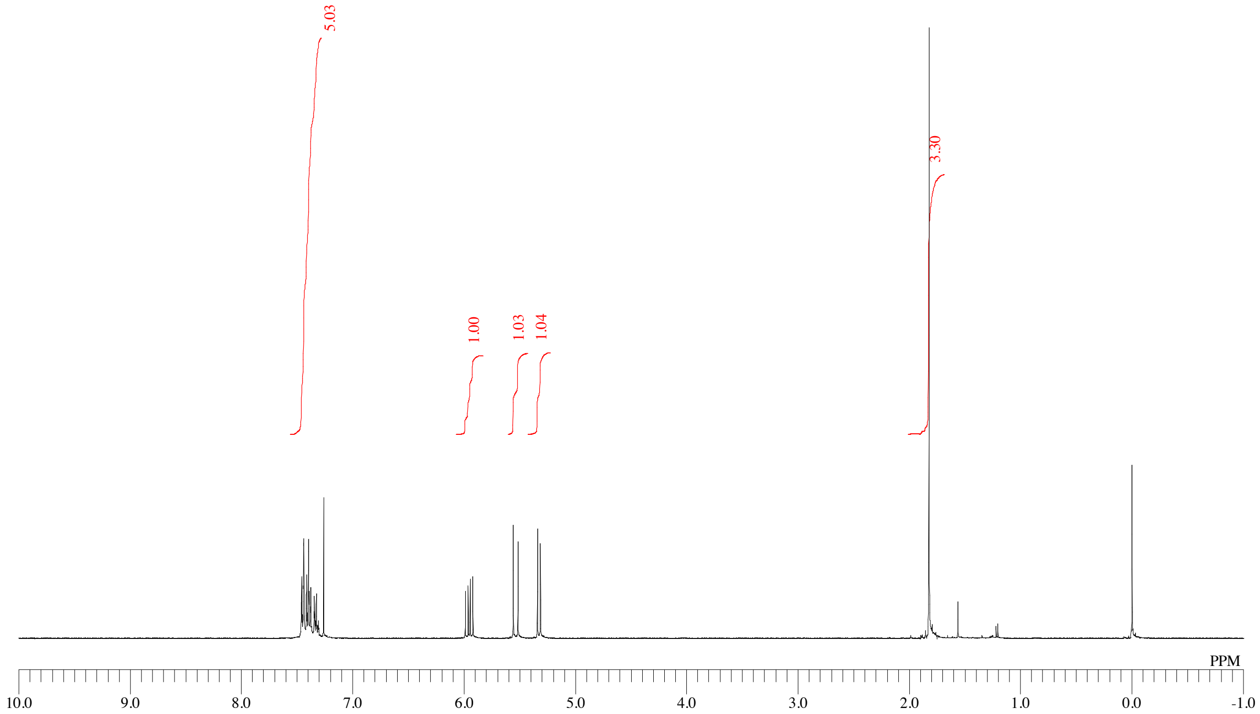
^{13}C NMR: (100 MHz, $CDCl_3$)



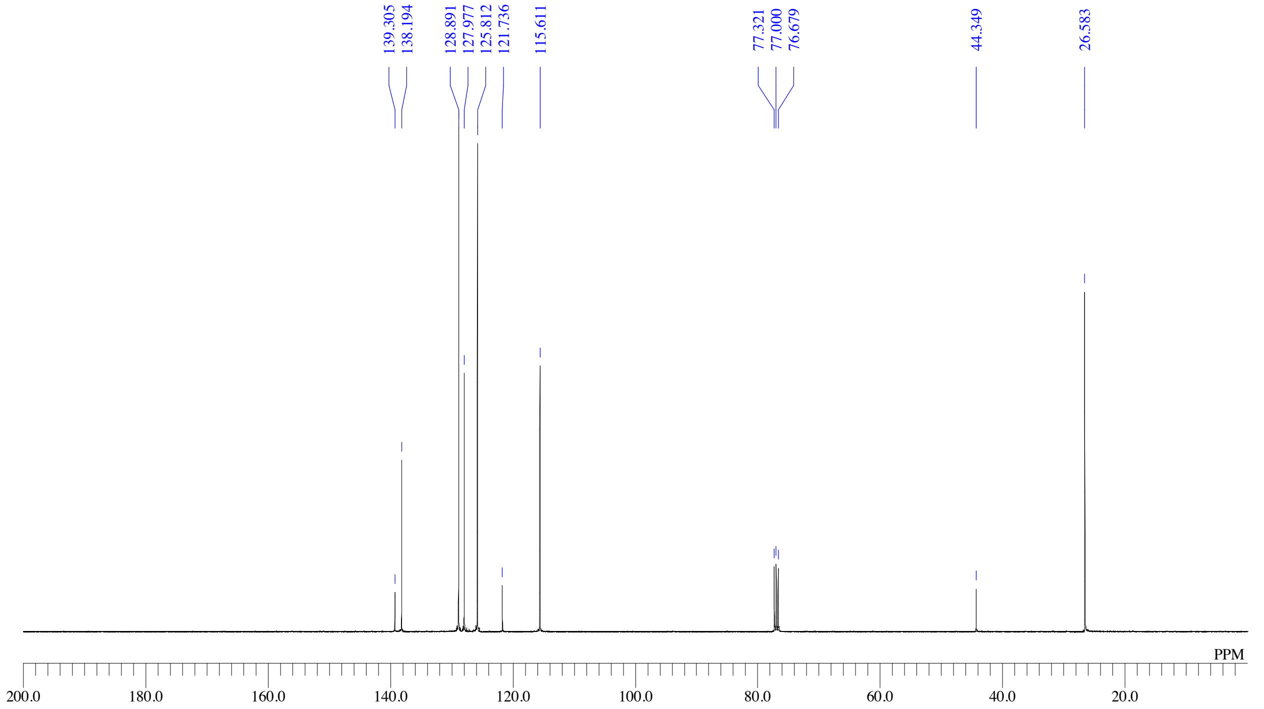


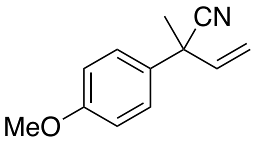
2l

^{1}H NMR: (400 MHz, $CDCl_3$)



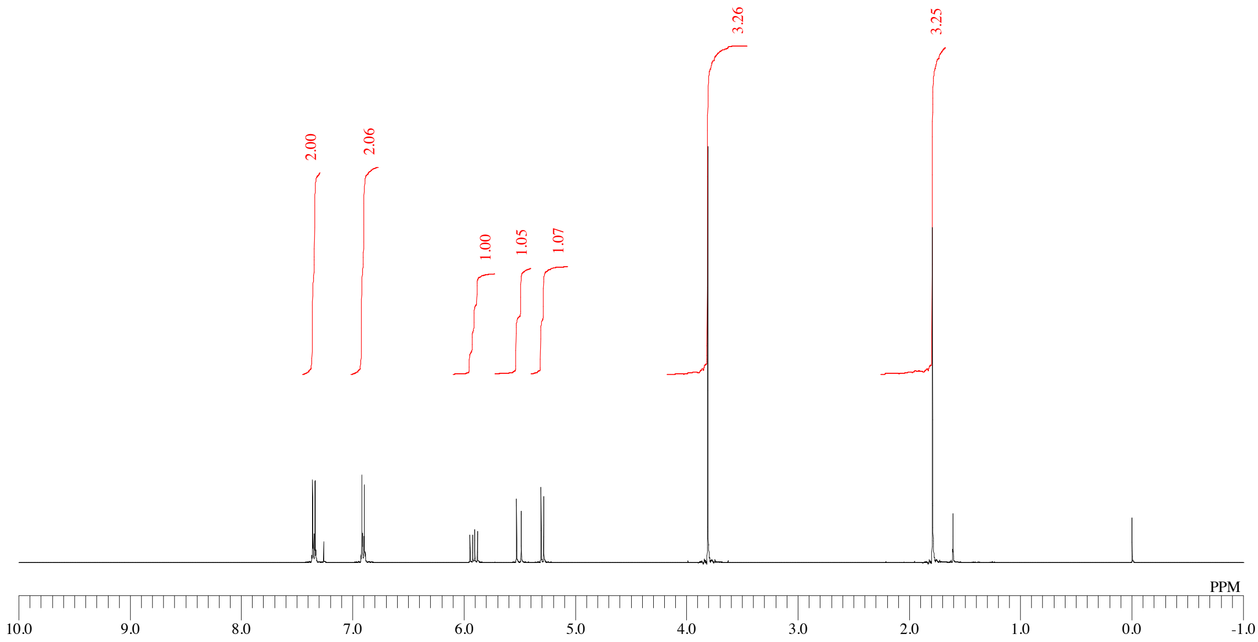
^{13}C NMR: (100 MHz, $CDCl_3$)



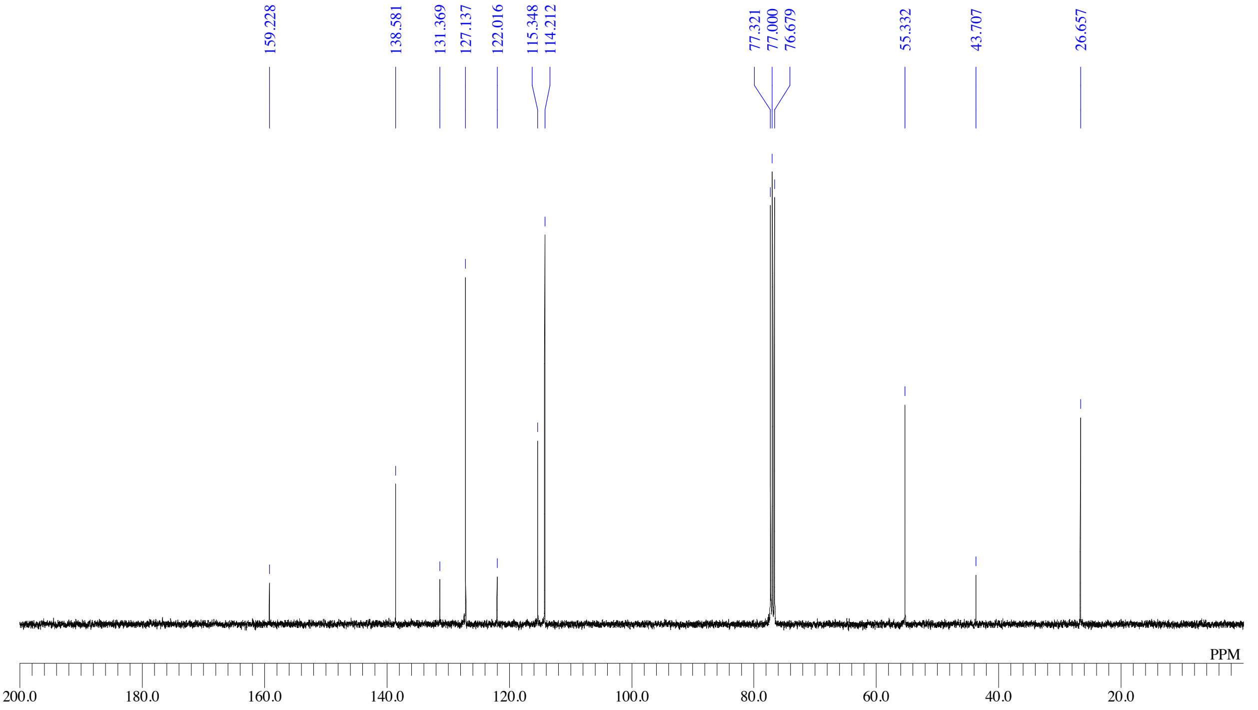


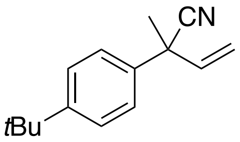
2m

^{1}H NMR: (400 MHz, $CDCl_3$)



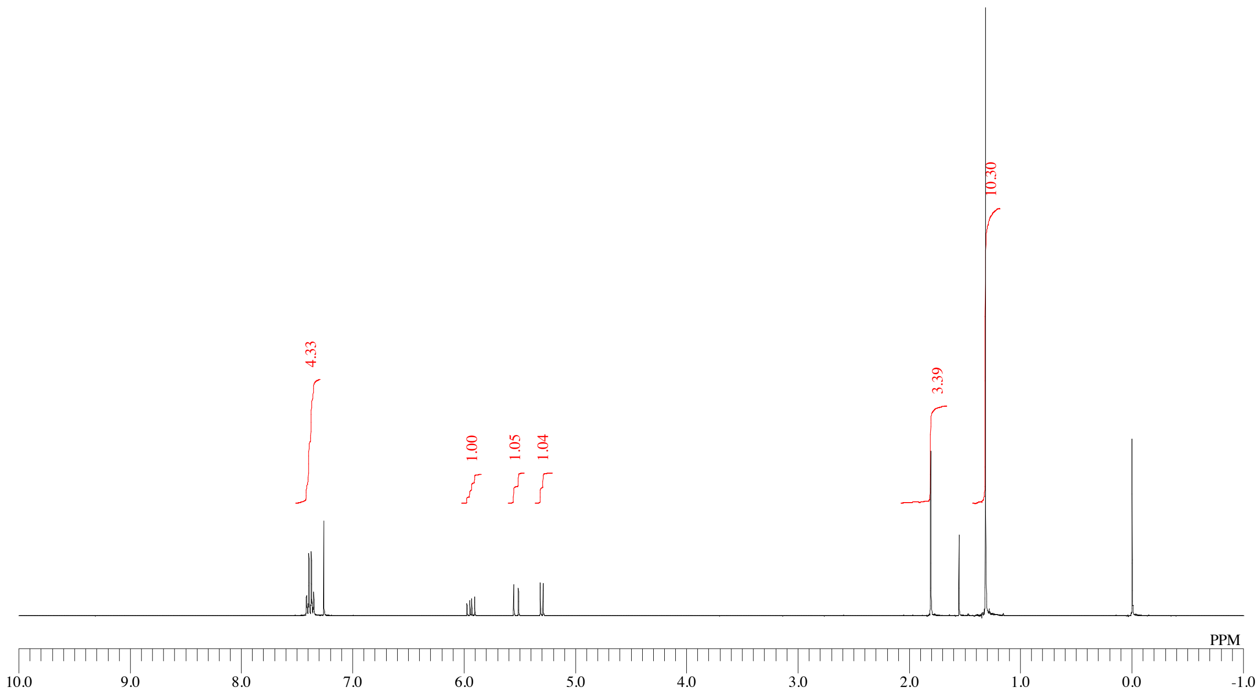
^{13}C NMR: (100 MHz, $CDCl_3$)



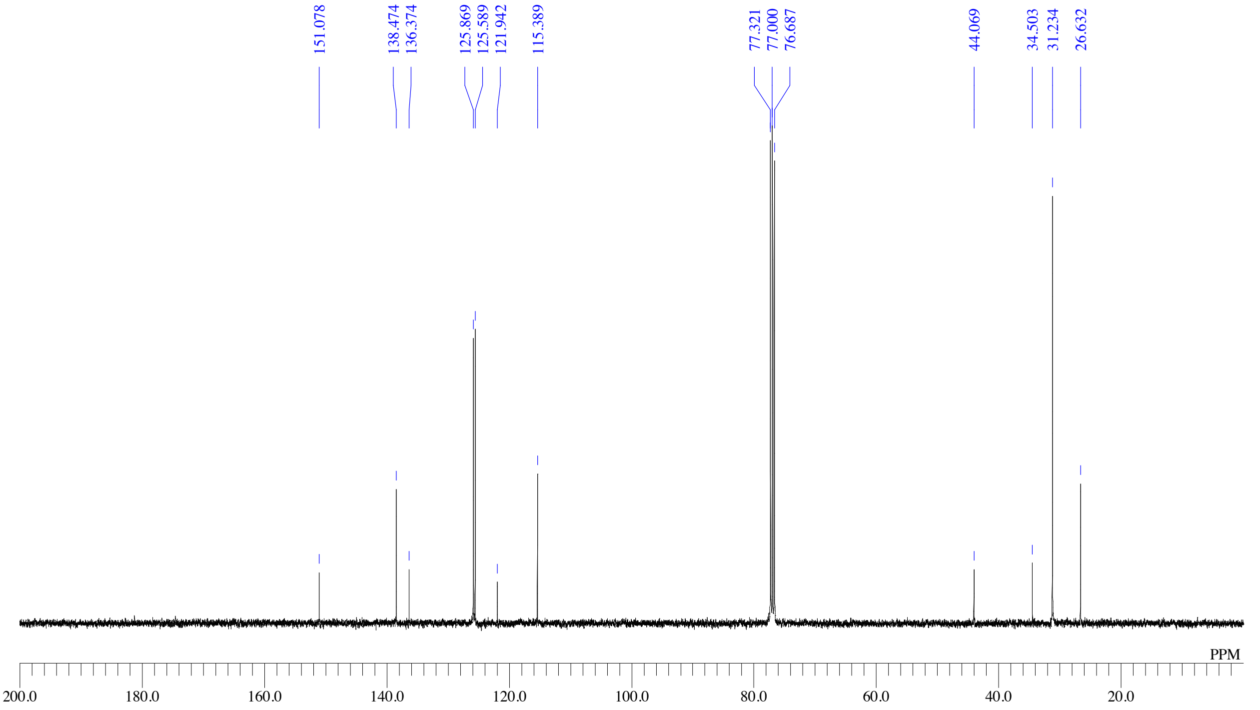


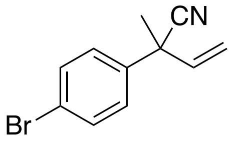
2n

^{1}H NMR: (400 MHz, $CDCl_3$)



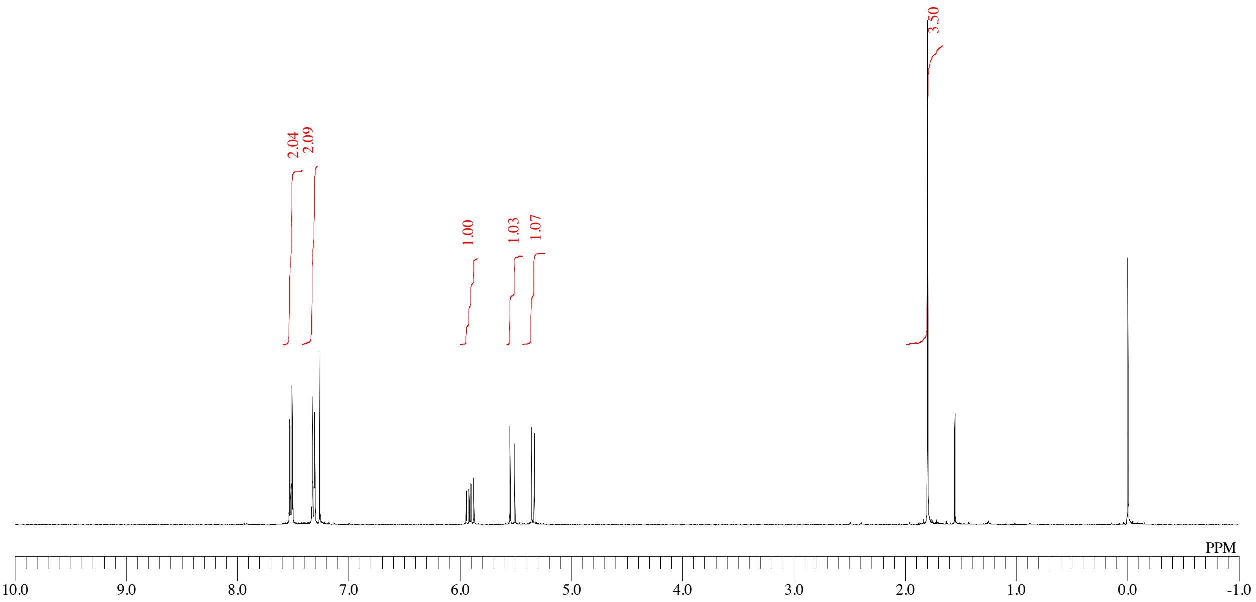
^{13}C NMR: (100 MHz, $CDCl_3$)



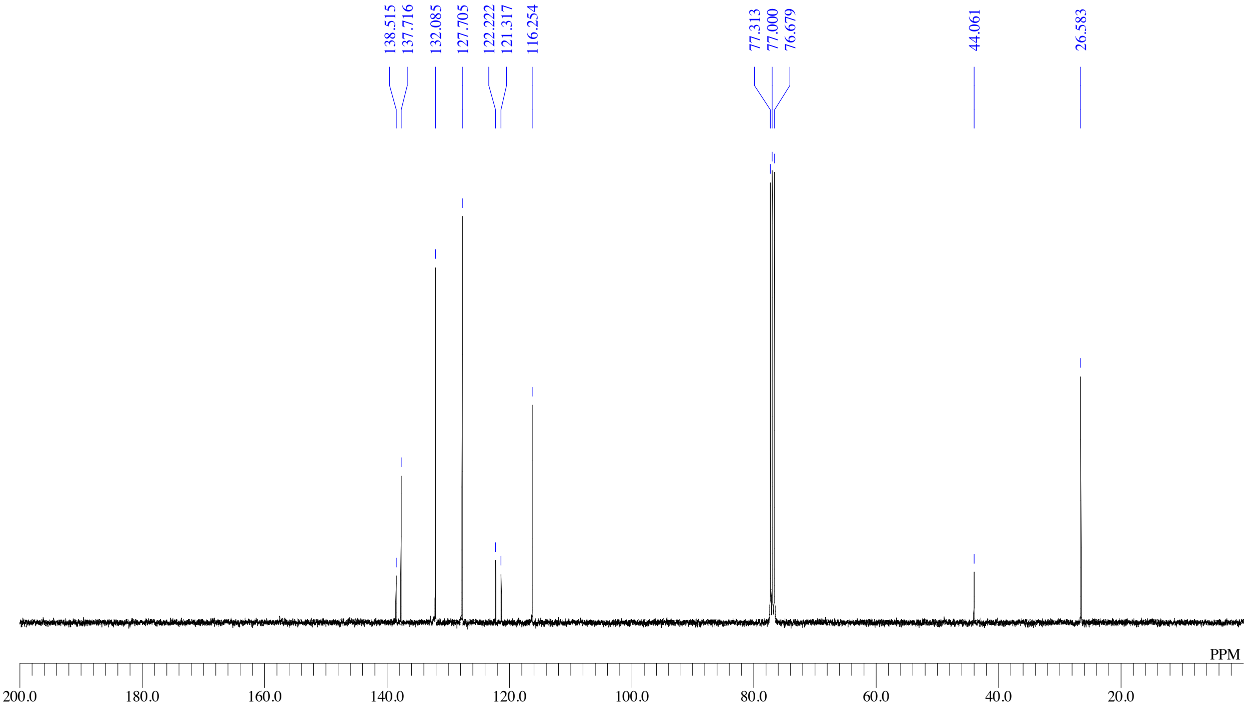


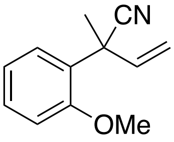
2o

^{1}H NMR: (400 MHz, CDCl$_3$)



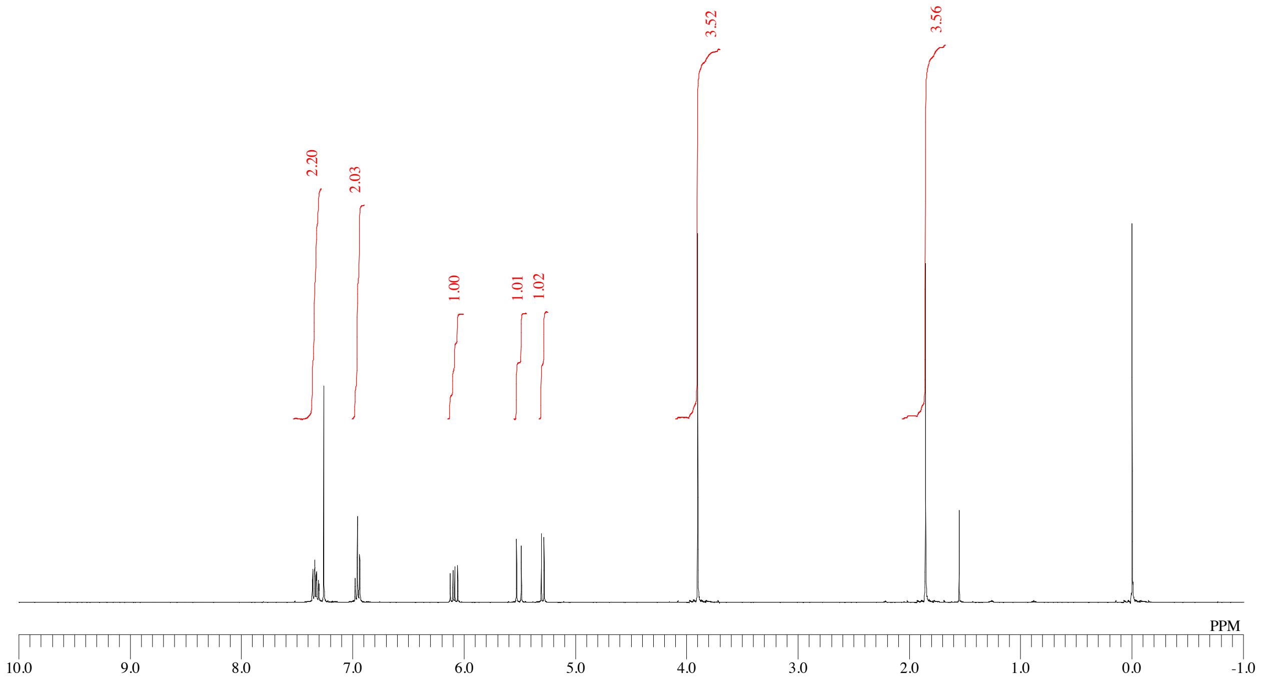
^{13}C NMR: (100 MHz, CDCl$_3$)



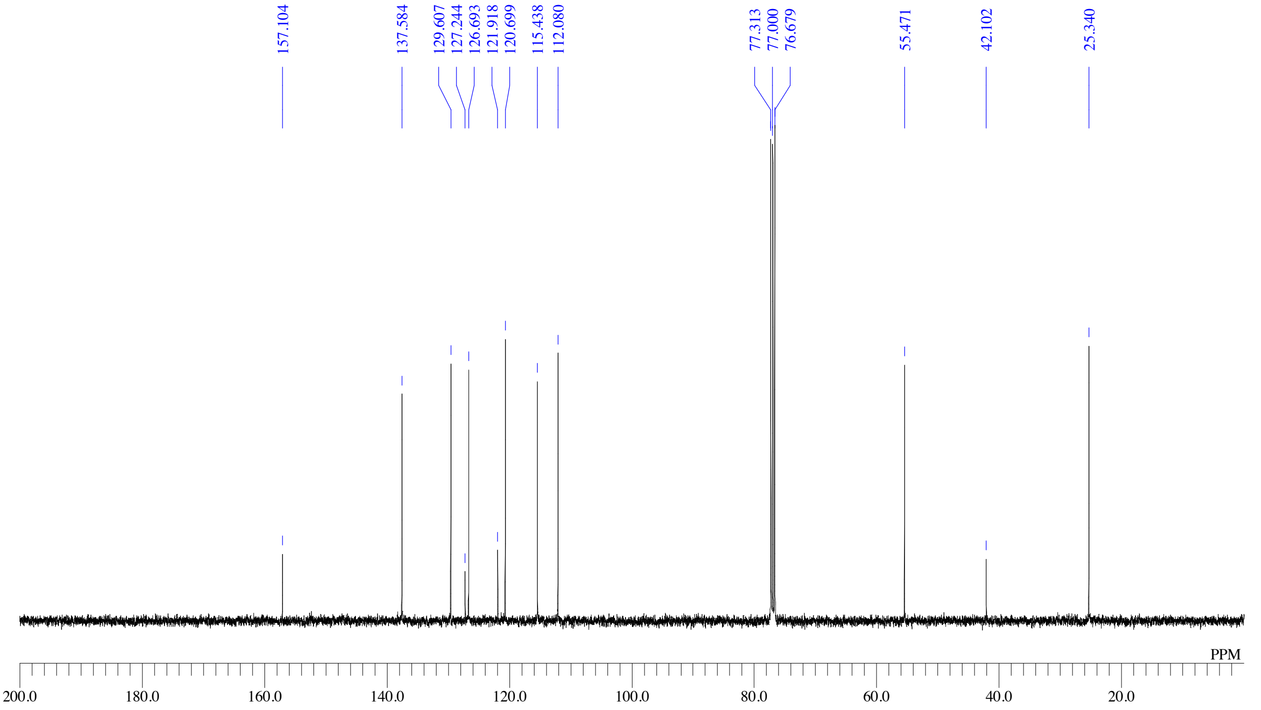


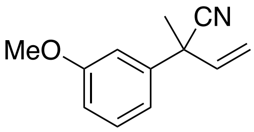
2p

^{1}H NMR: (400 MHz, CDCl$_3$)



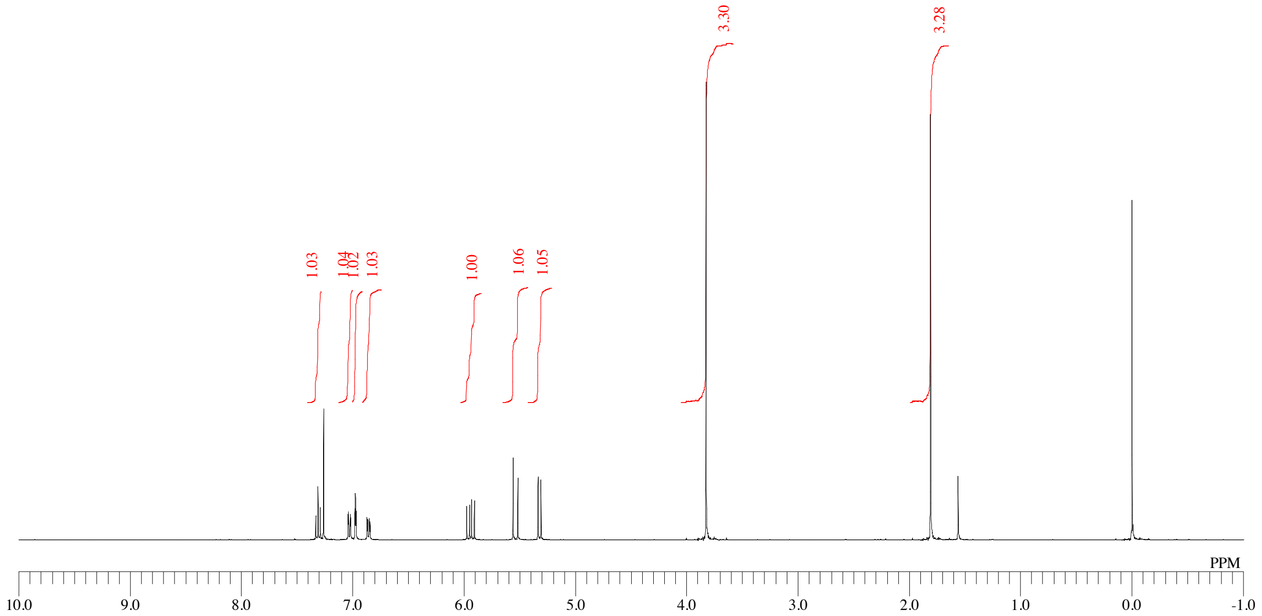
^{13}C NMR: (100 MHz, CDCl$_3$)



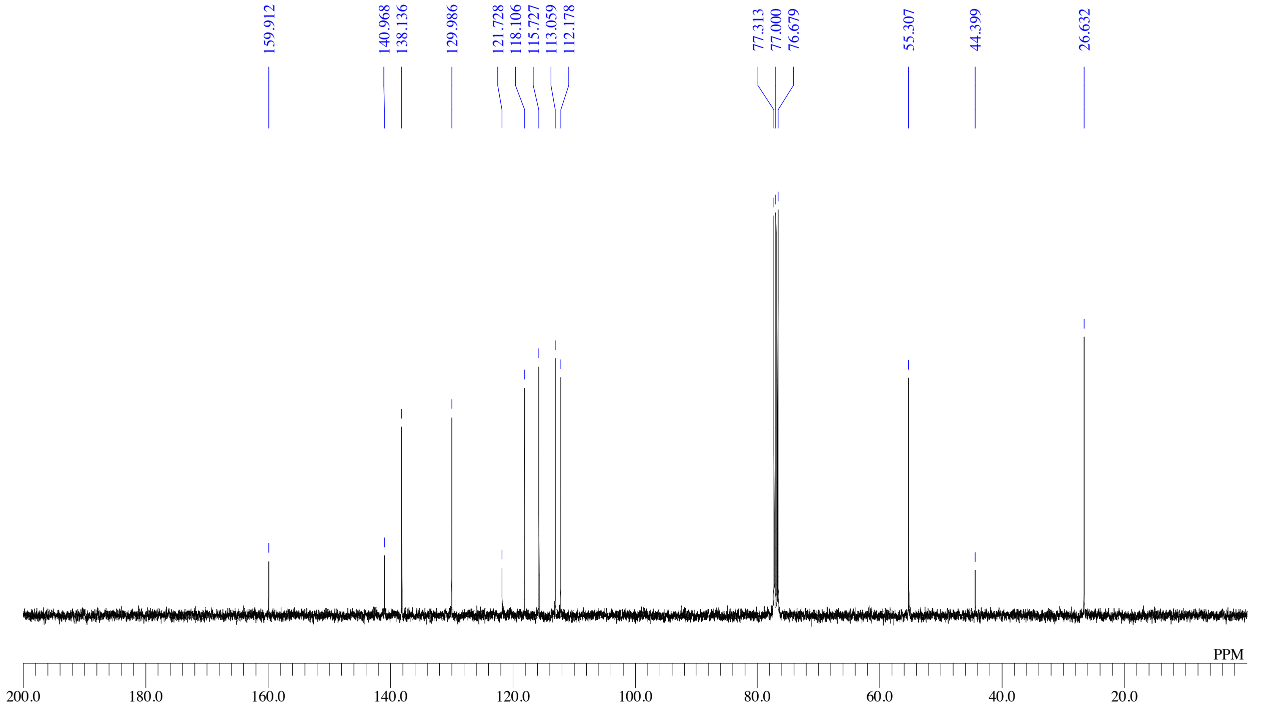


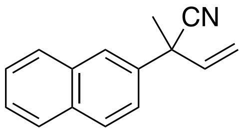
2q

^{1}H NMR: (400 MHz, $CDCl_3$)



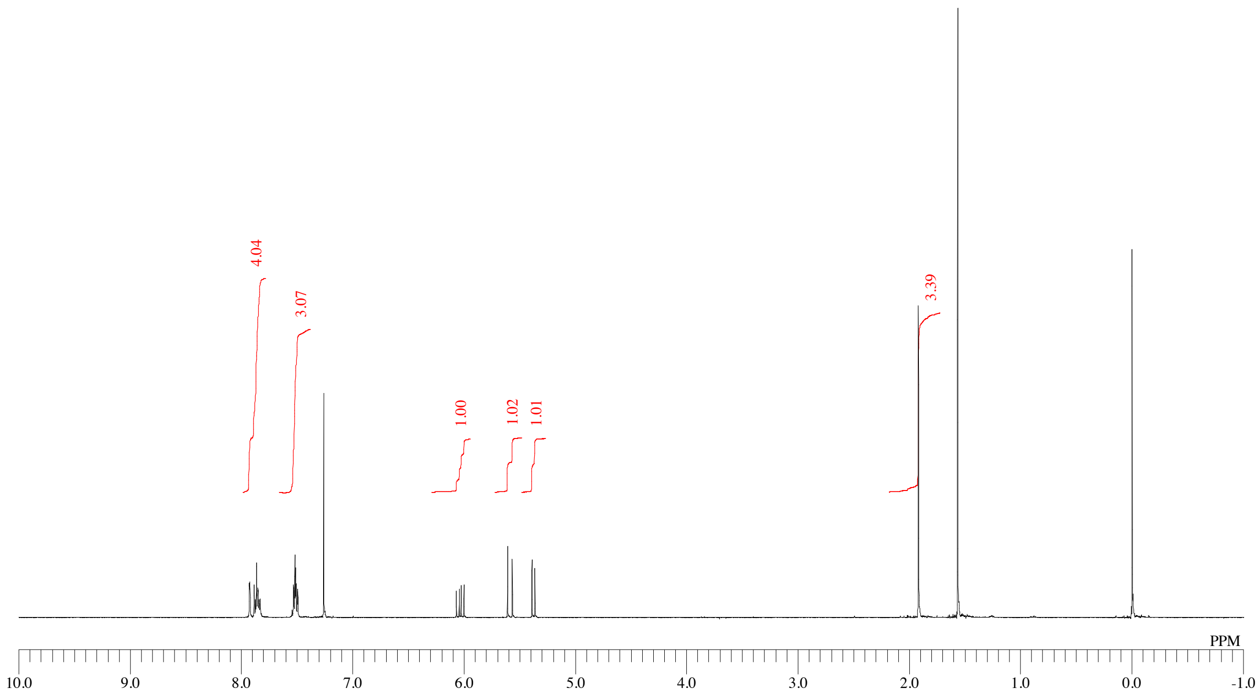
^{13}C NMR: (100 MHz, $CDCl_3$)



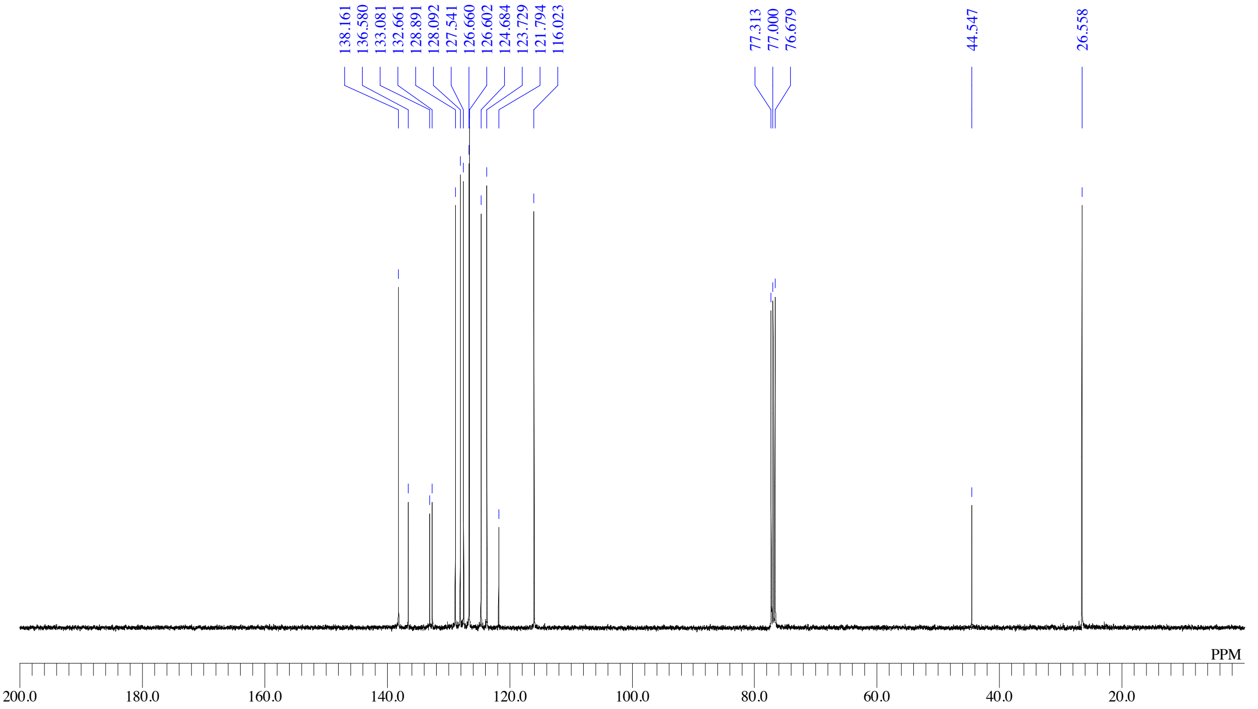


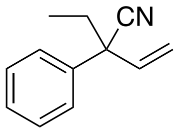
2r

^{1}H NMR: (400 MHz, $CDCl_3$)



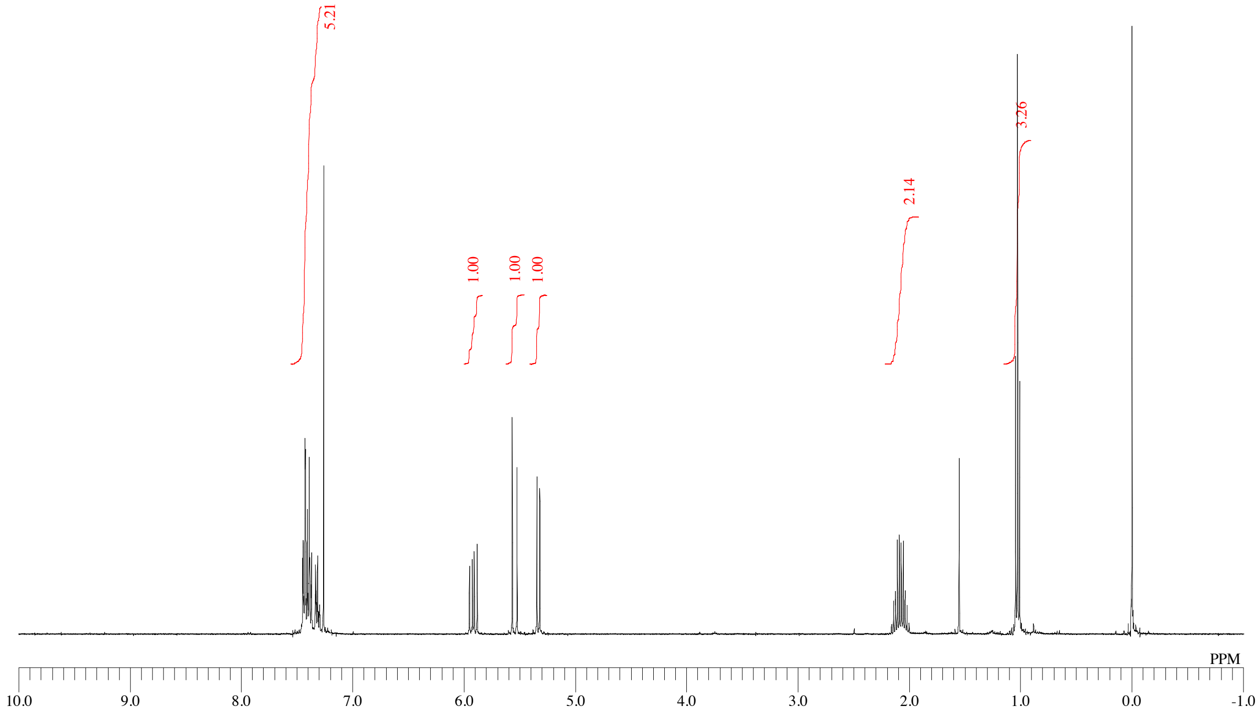
^{13}C NMR: (100 MHz, $CDCl_3$)



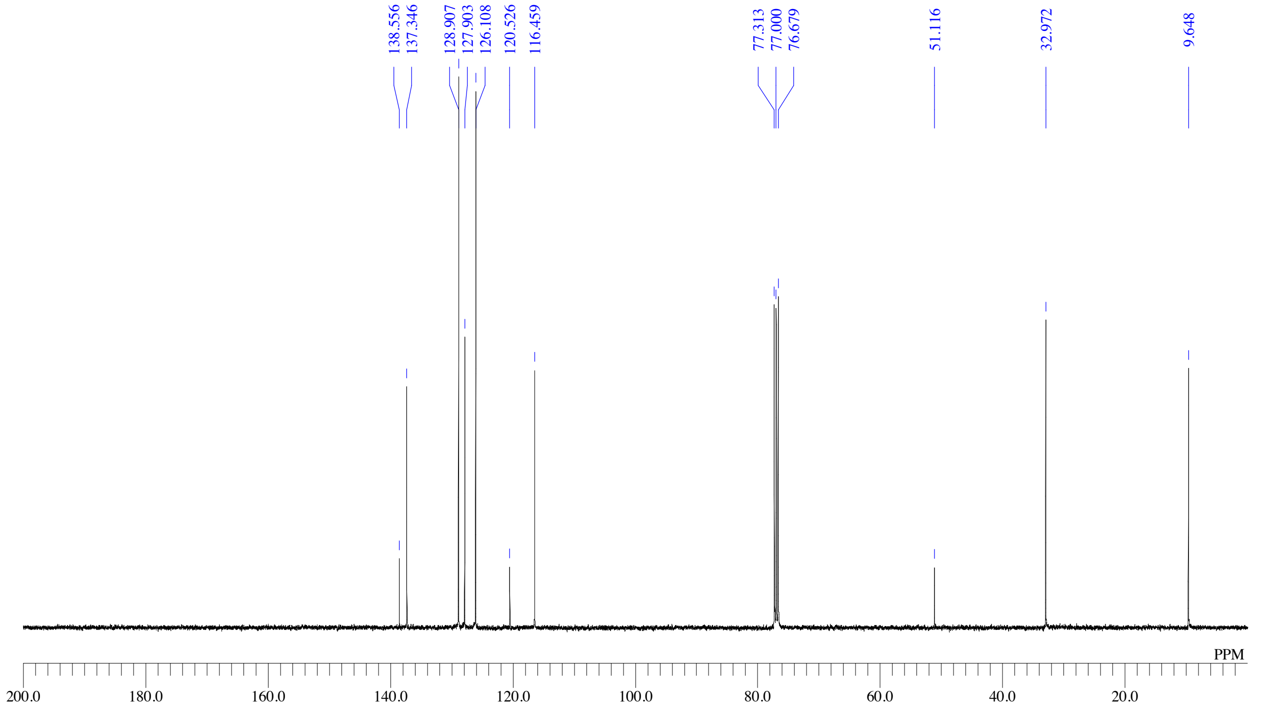


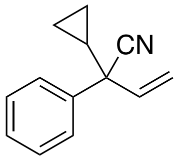
2s

^{1}H NMR: (400 MHz, $CDCl_3$)



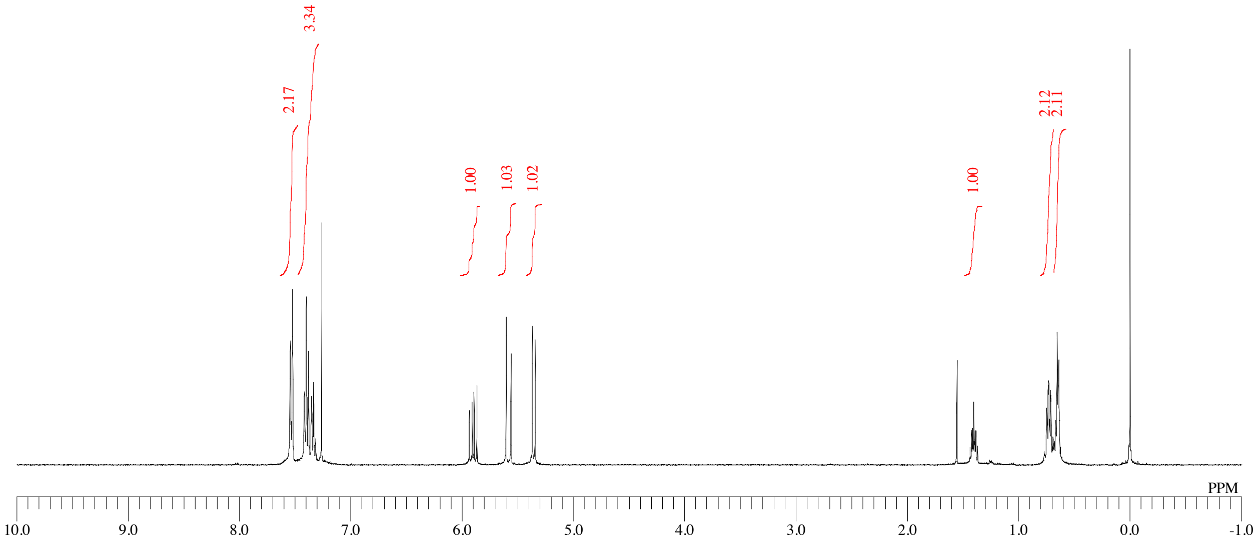
^{13}C NMR: (100 MHz, $CDCl_3$)



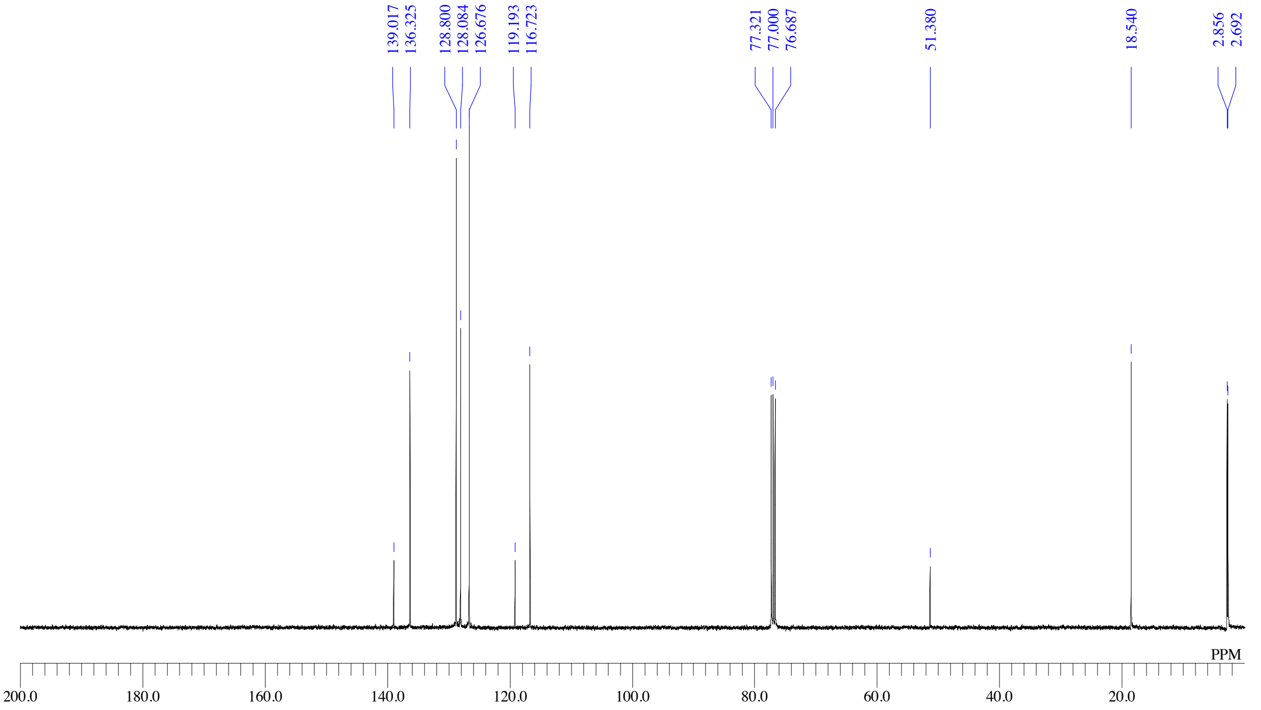


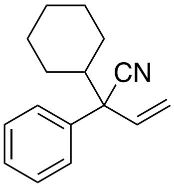
2t

^{1}H NMR: (400 MHz, $CDCl_3$)



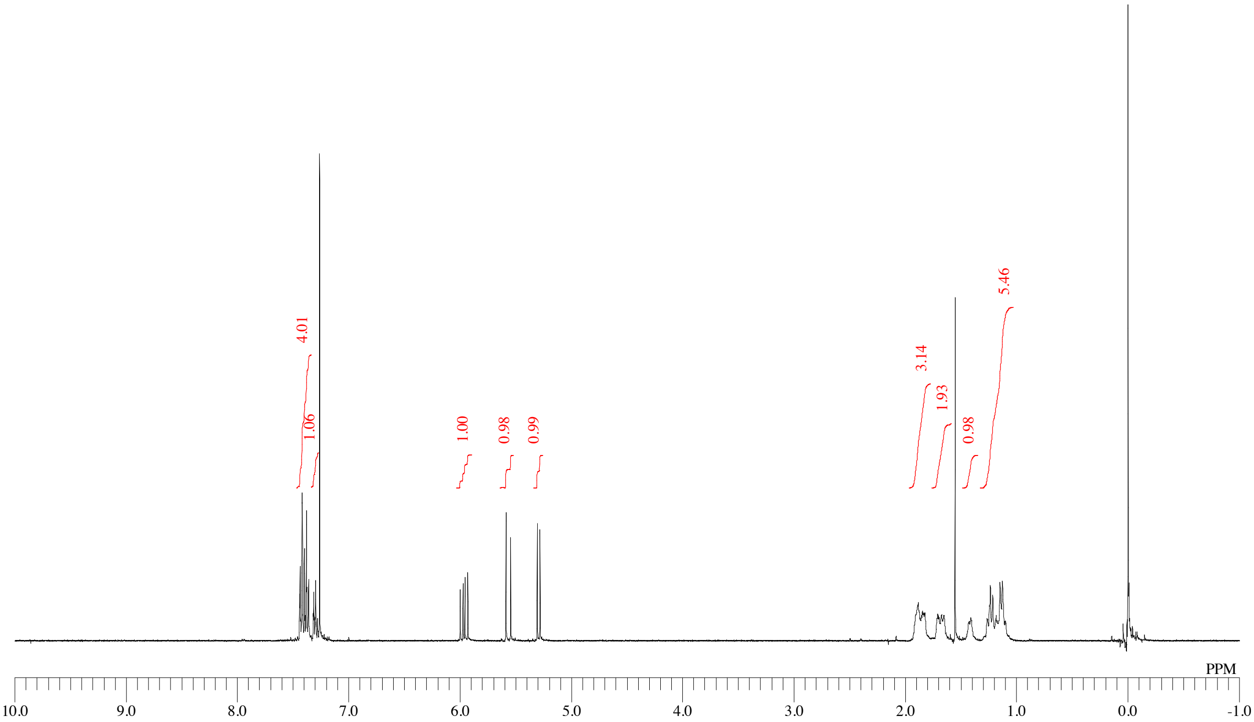
^{13}C NMR: (100 MHz, $CDCl_3$)



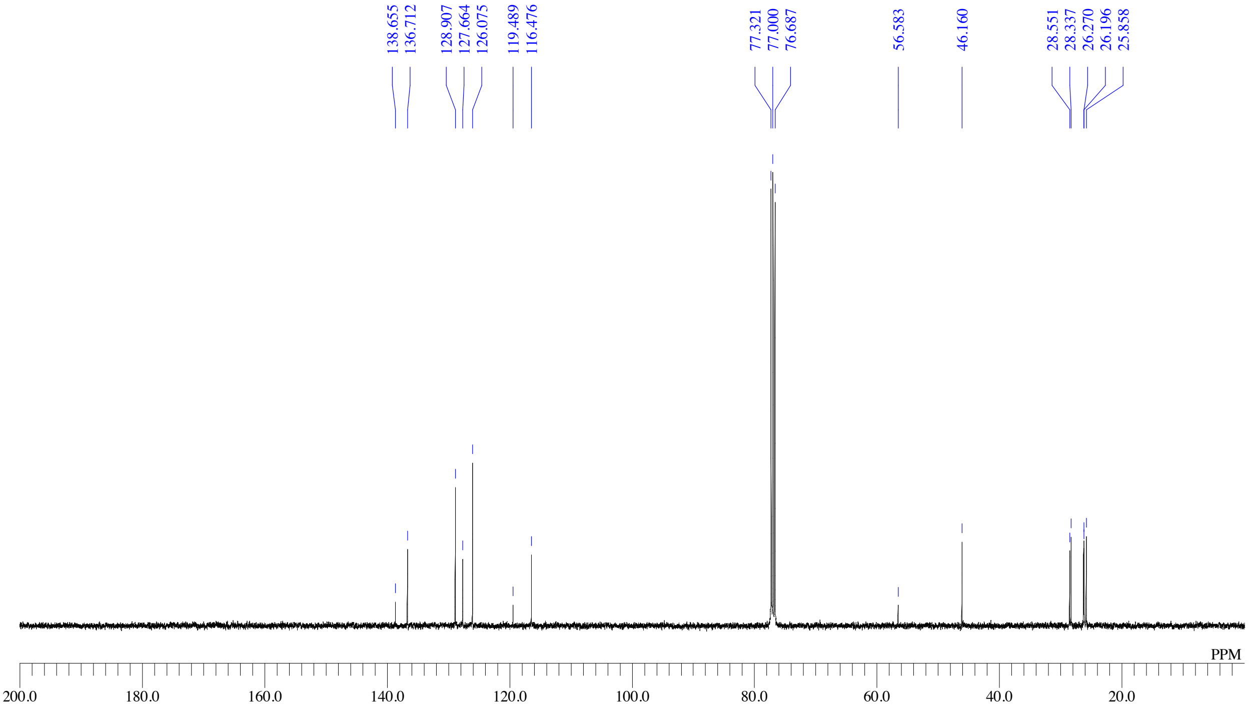


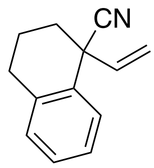
2u

^{1}H NMR: (400 MHz, $CDCl_3$)



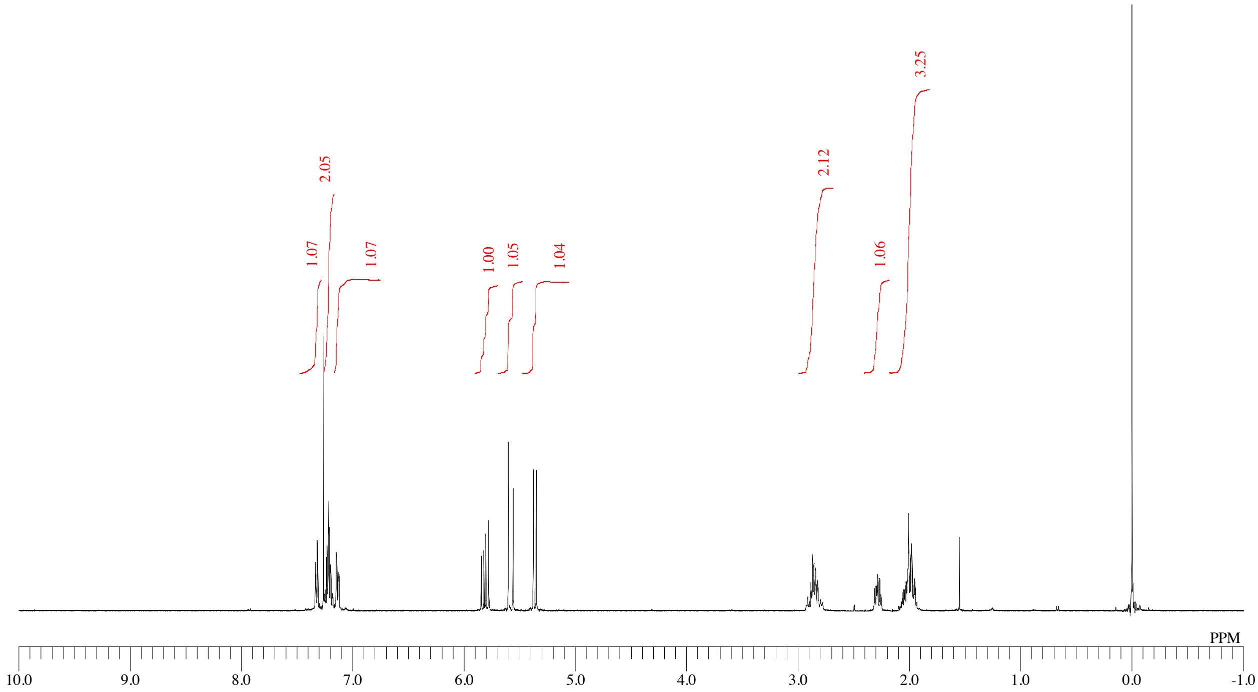
^{13}C NMR: (100 MHz, $CDCl_3$)



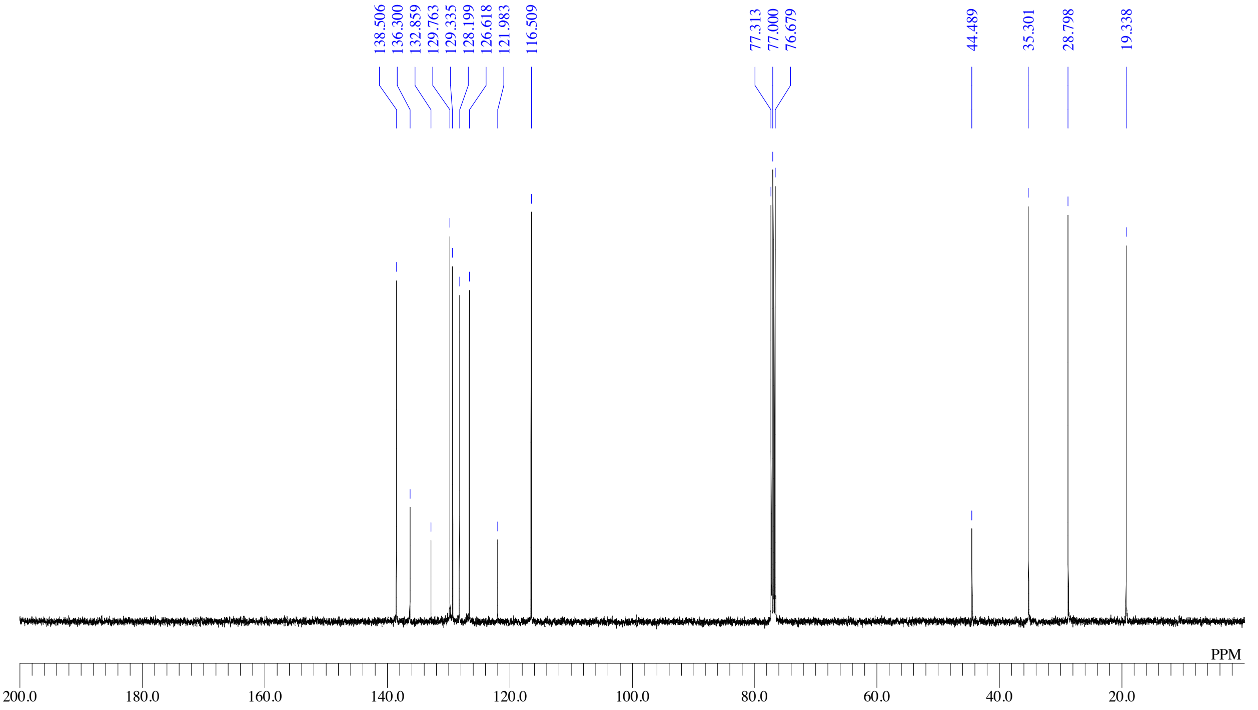


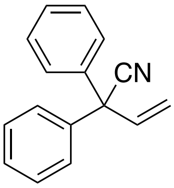
2v

^{1}H NMR: (400 MHz, CDCl$_3$)



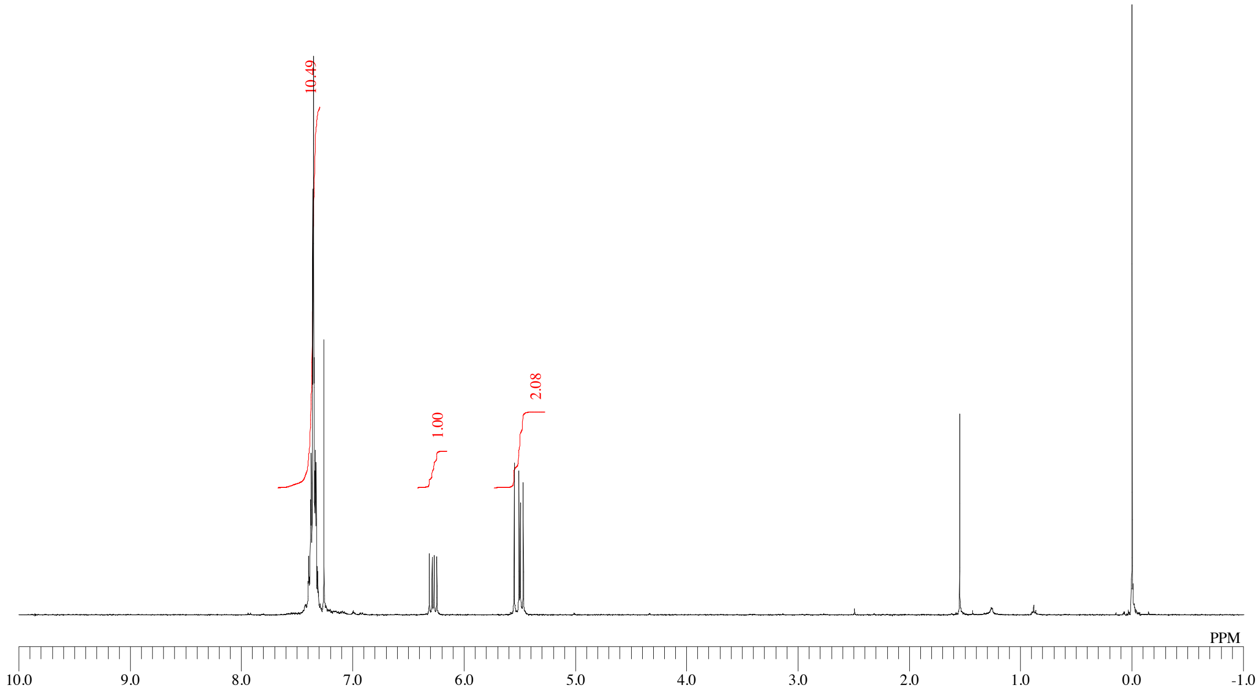
^{13}C NMR: (100 MHz, CDCl$_3$)



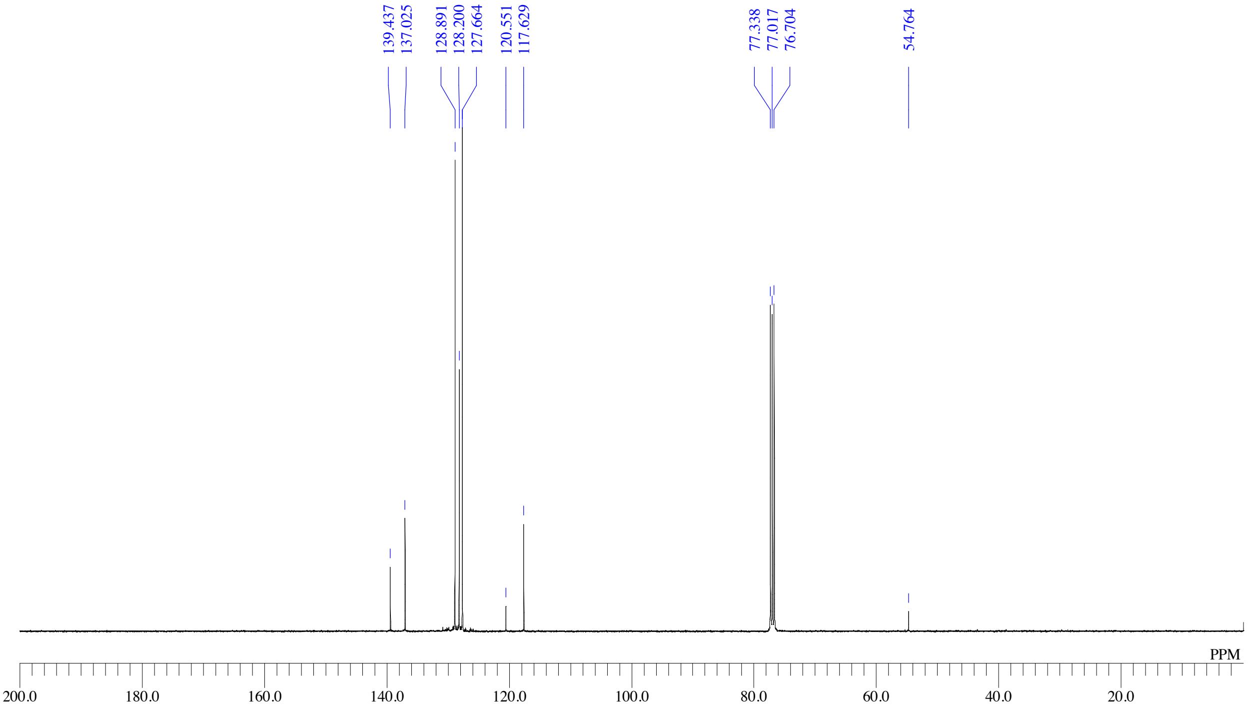


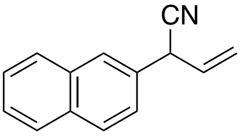
2w

^{1}H NMR: (400 MHz, CDCl$_3$)



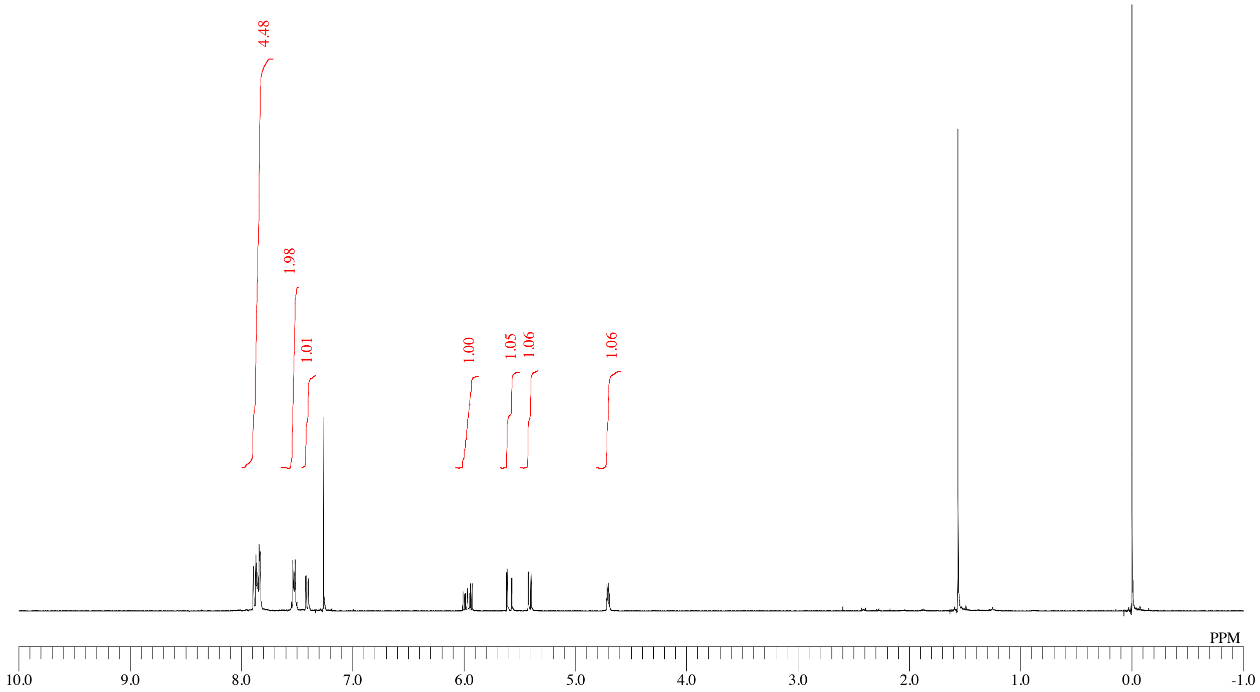
^{13}C NMR: (100 MHz, CDCl$_3$)



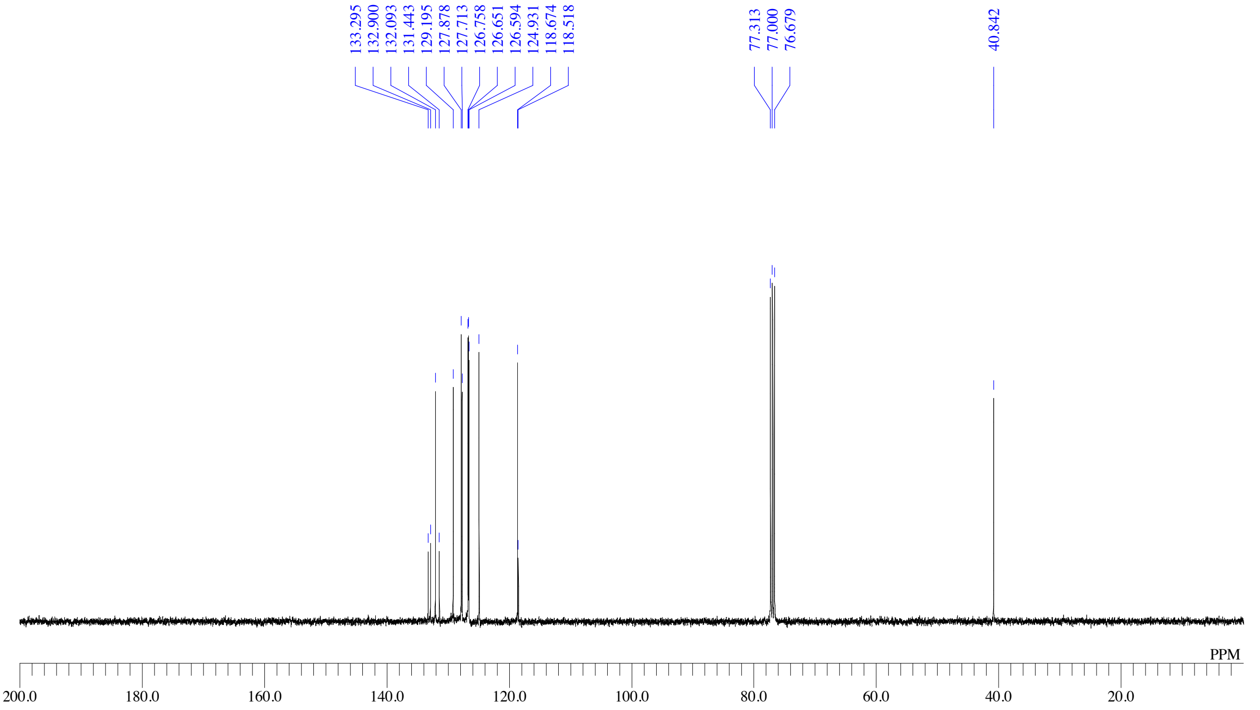


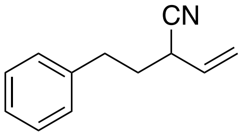
2x

^{1}H NMR: (400 MHz, CDCl$_3$)



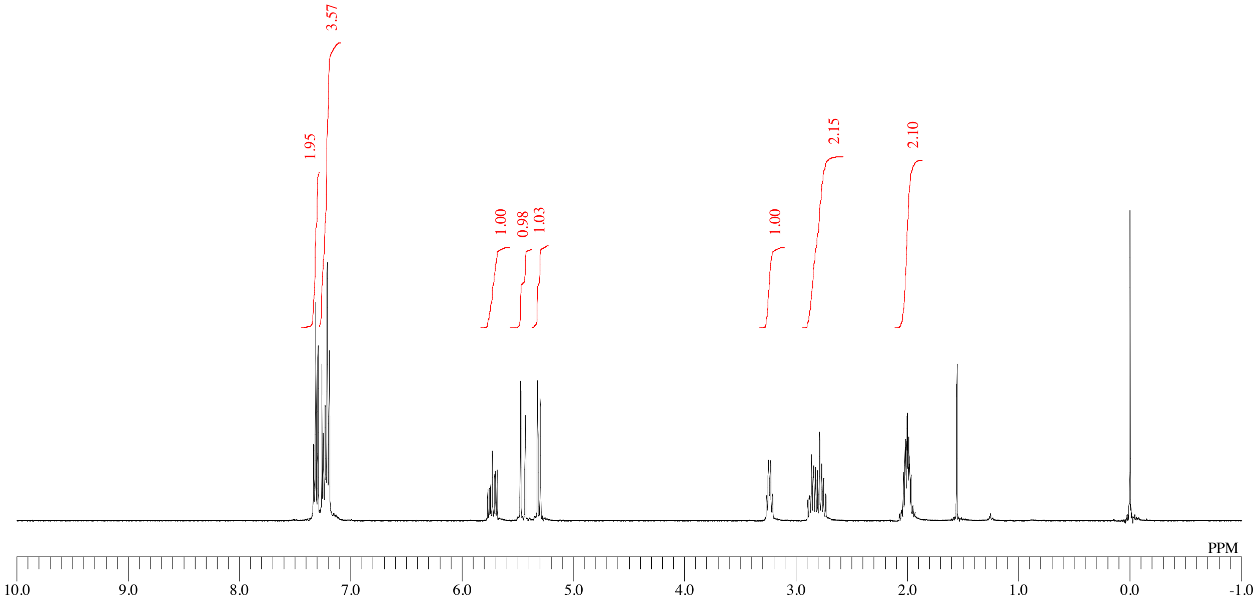
^{13}C NMR: (100 MHz, CDCl$_3$)



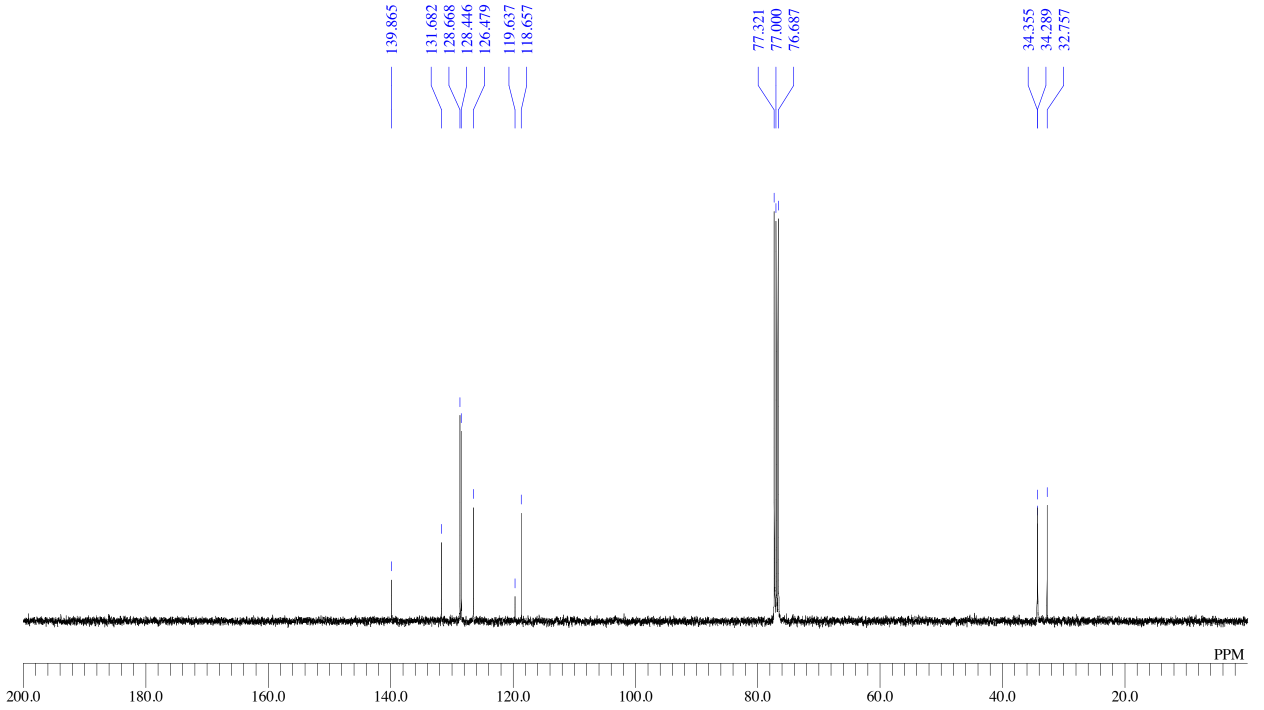


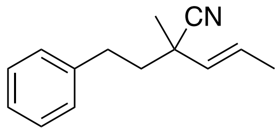
2y

^{1}H NMR: (400 MHz, $CDCl_3$)



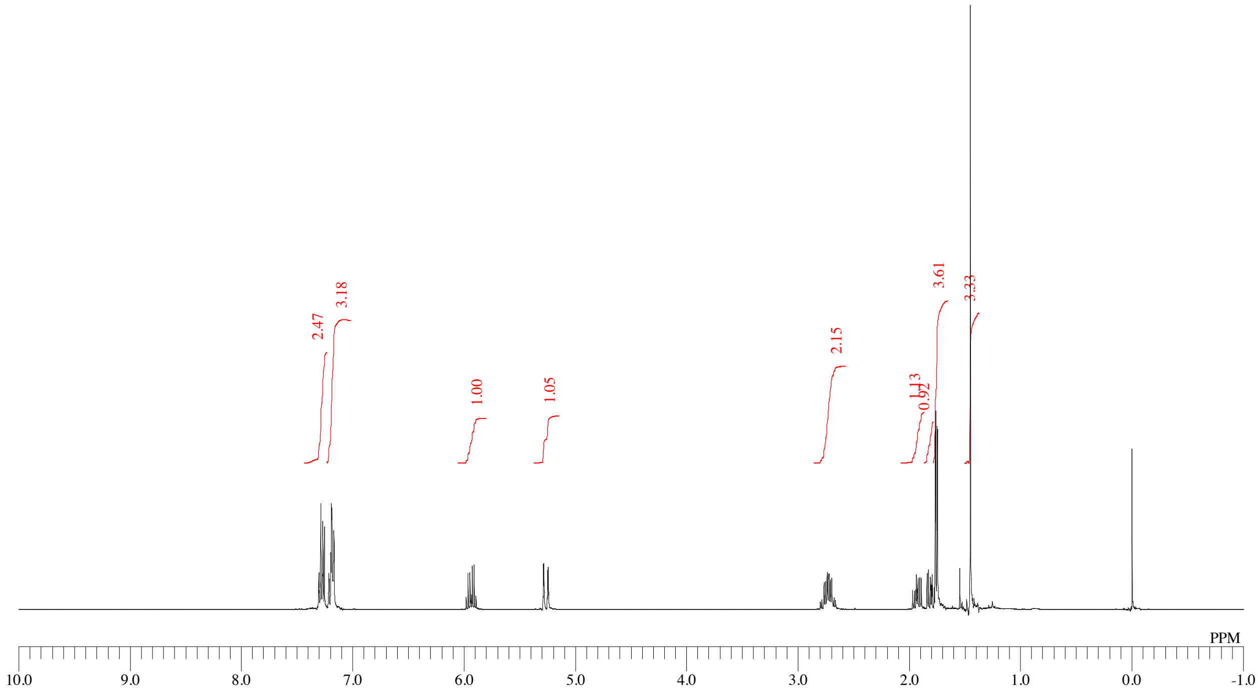
^{13}C NMR: (100 MHz, $CDCl_3$)



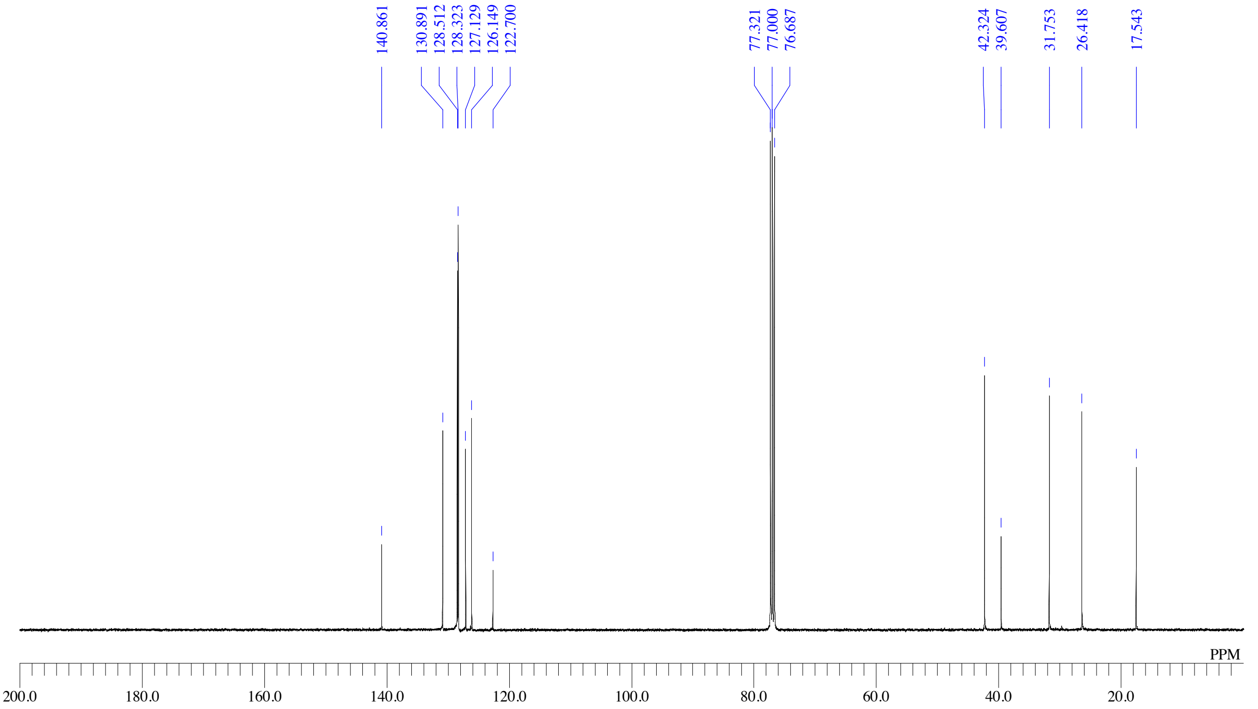


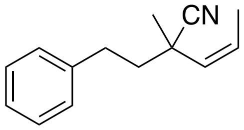
(*E*)-2z

^{1}H NMR: (400 MHz, CDCl$_3$)



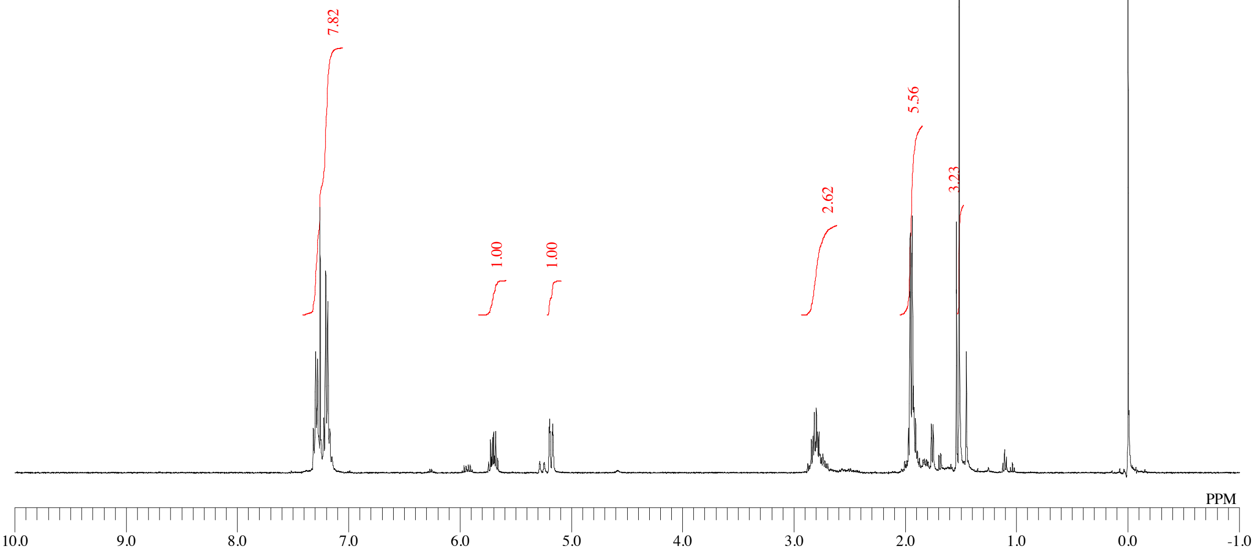
^{13}C NMR: (100 MHz, CDCl$_3$)



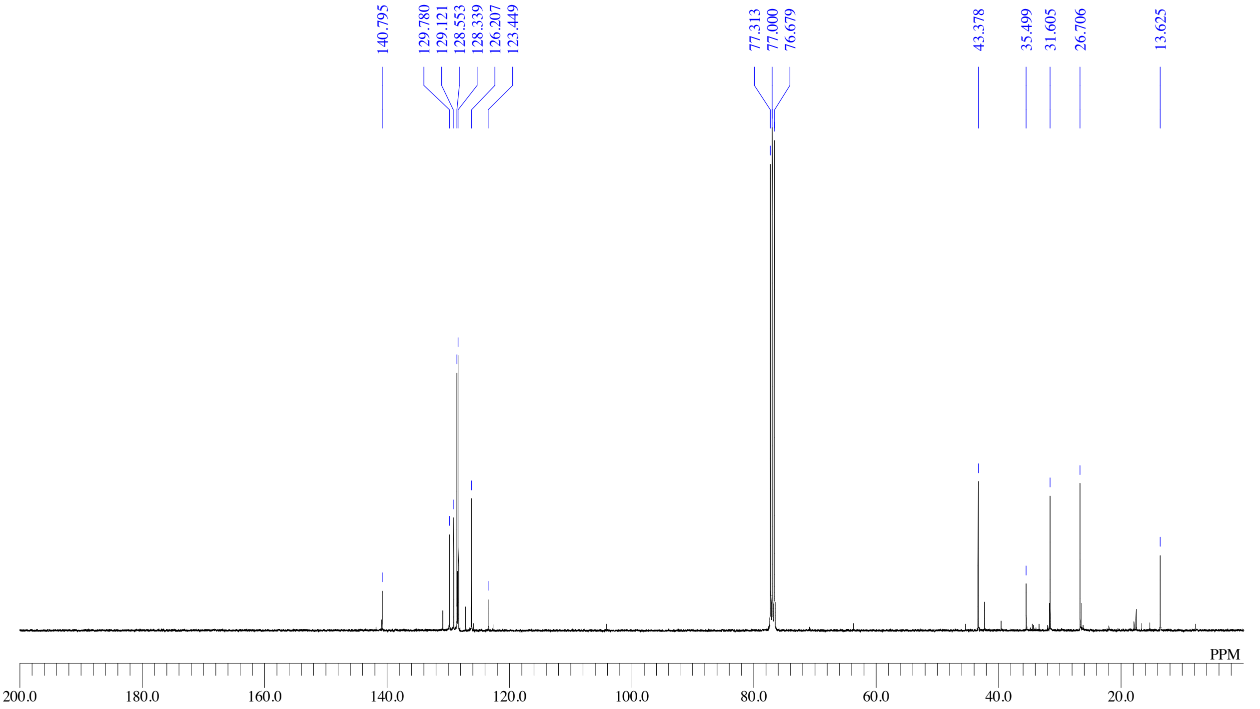


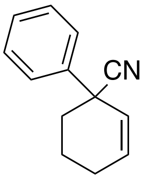
(*Z*)-2z (mixture of *E*/*Z* isomeres)

^{1}H NMR: (400 MHz, $CDCl_3$)



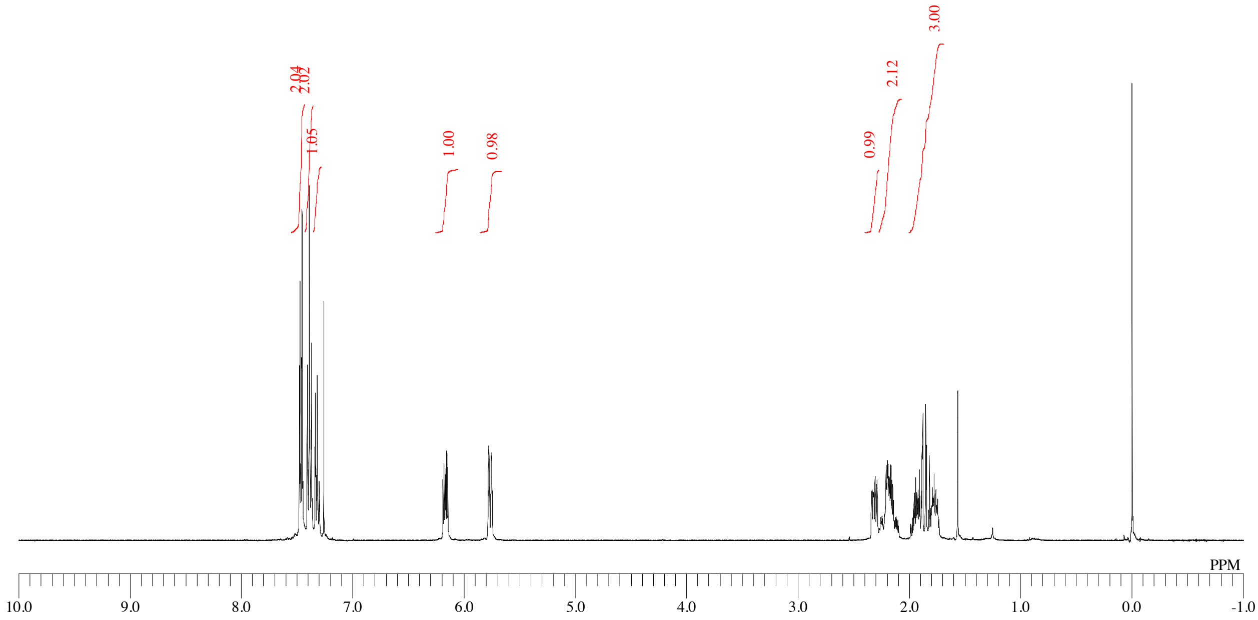
^{13}C NMR: (100 MHz, $CDCl_3$)



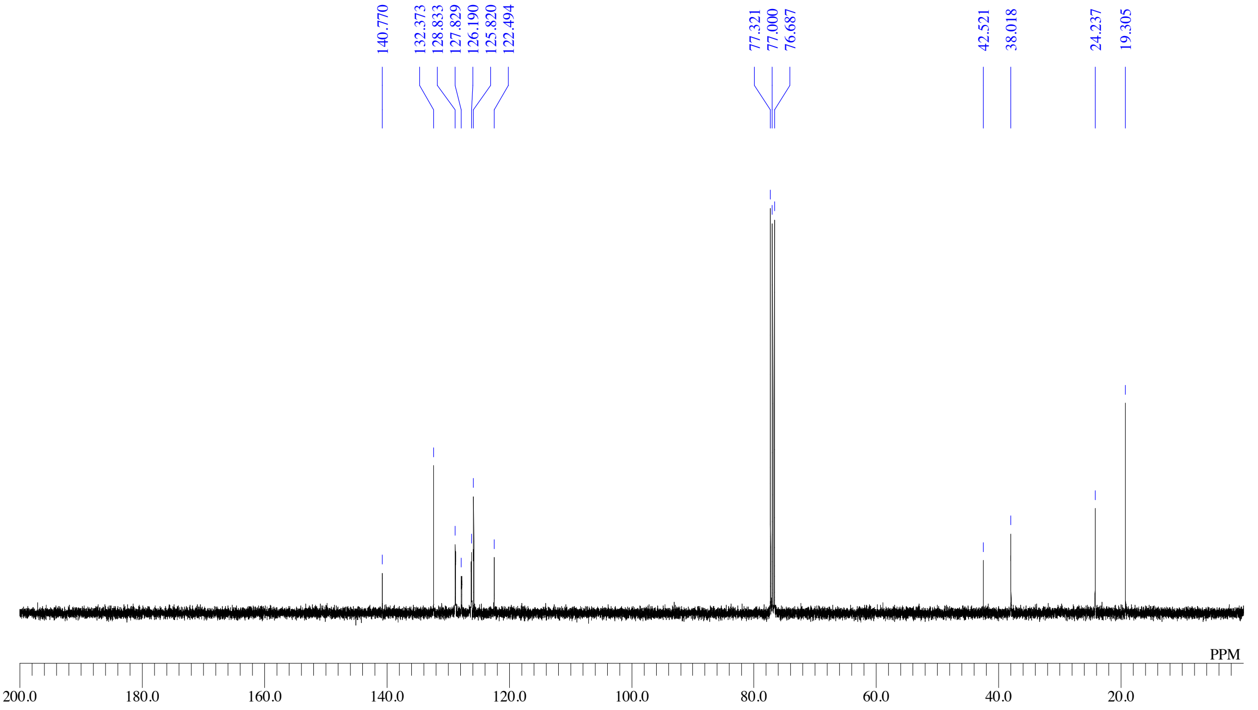


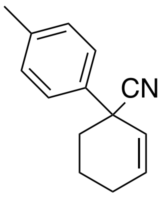
5a

^{1}H NMR: (400 MHz, CDCl$_3$)



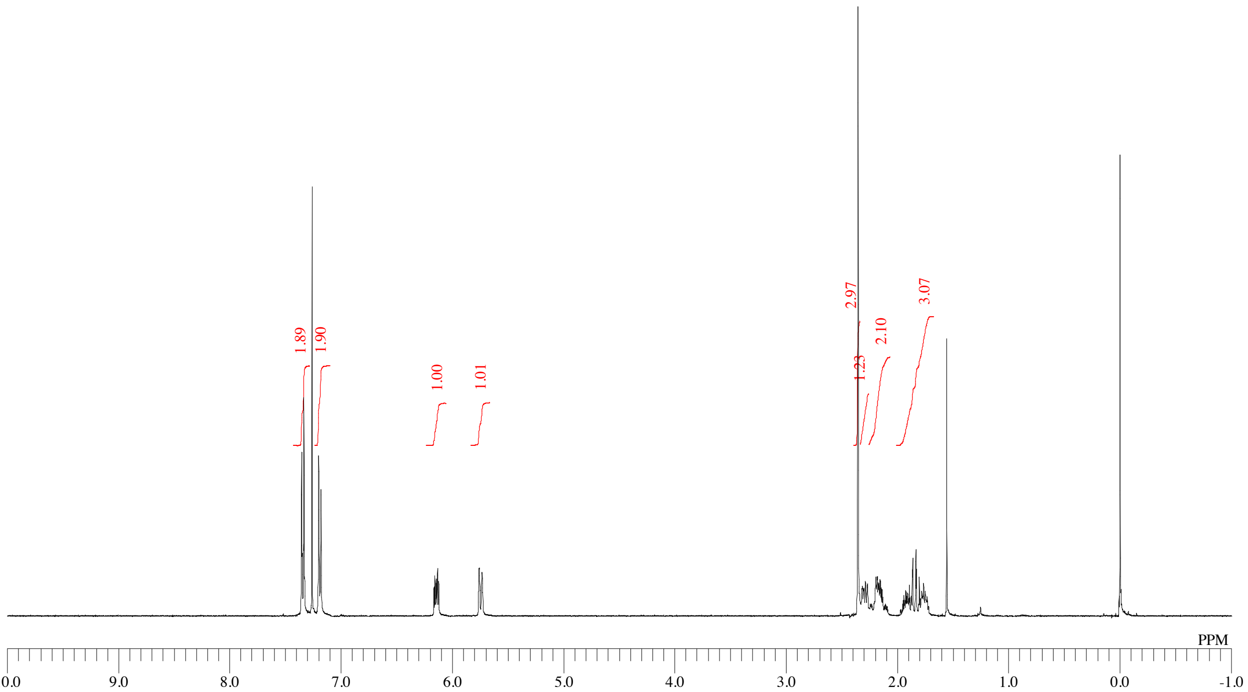
^{13}C NMR: (100 MHz, CDCl$_3$)



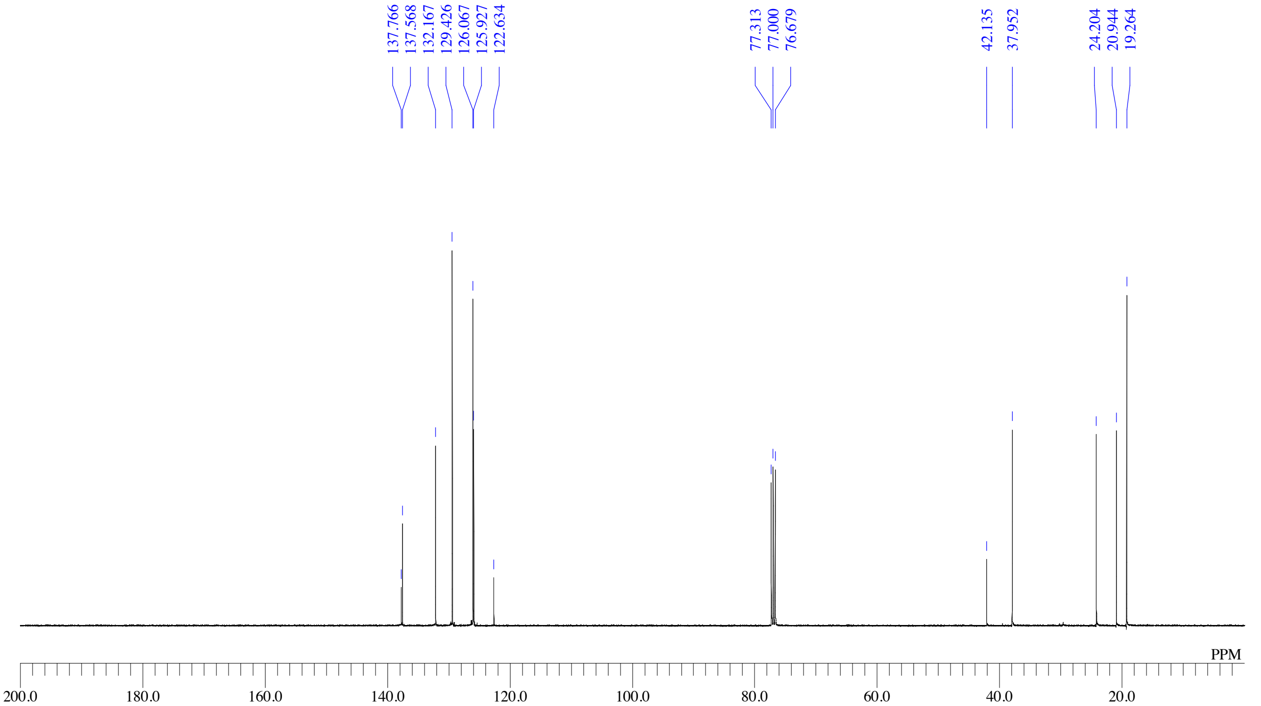


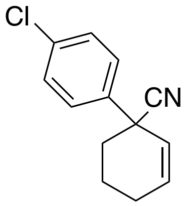
5b

^{1}H NMR: (400 MHz, $CDCl_3$)



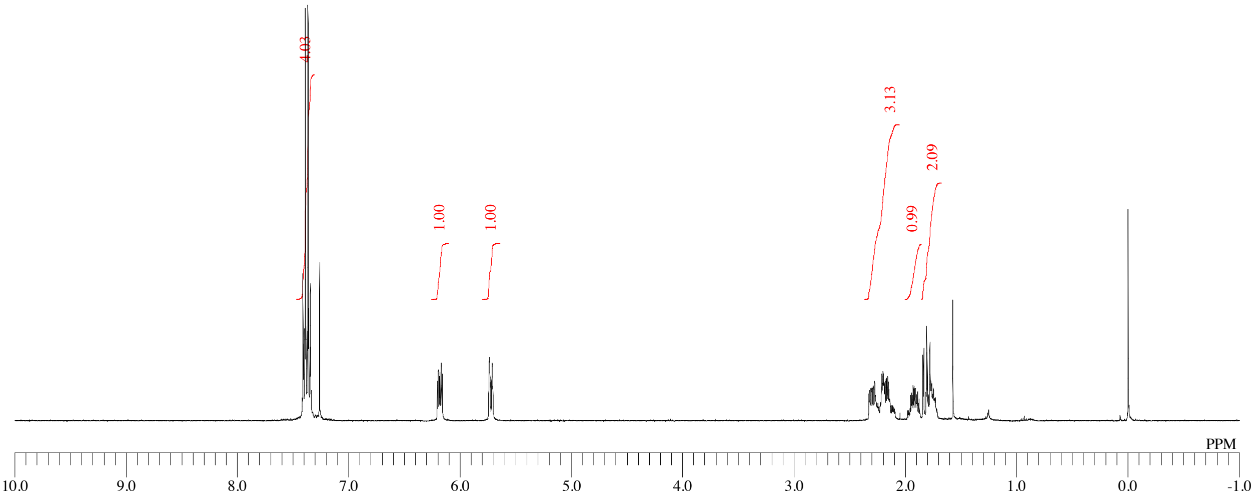
^{13}C NMR: (100 MHz, $CDCl_3$)



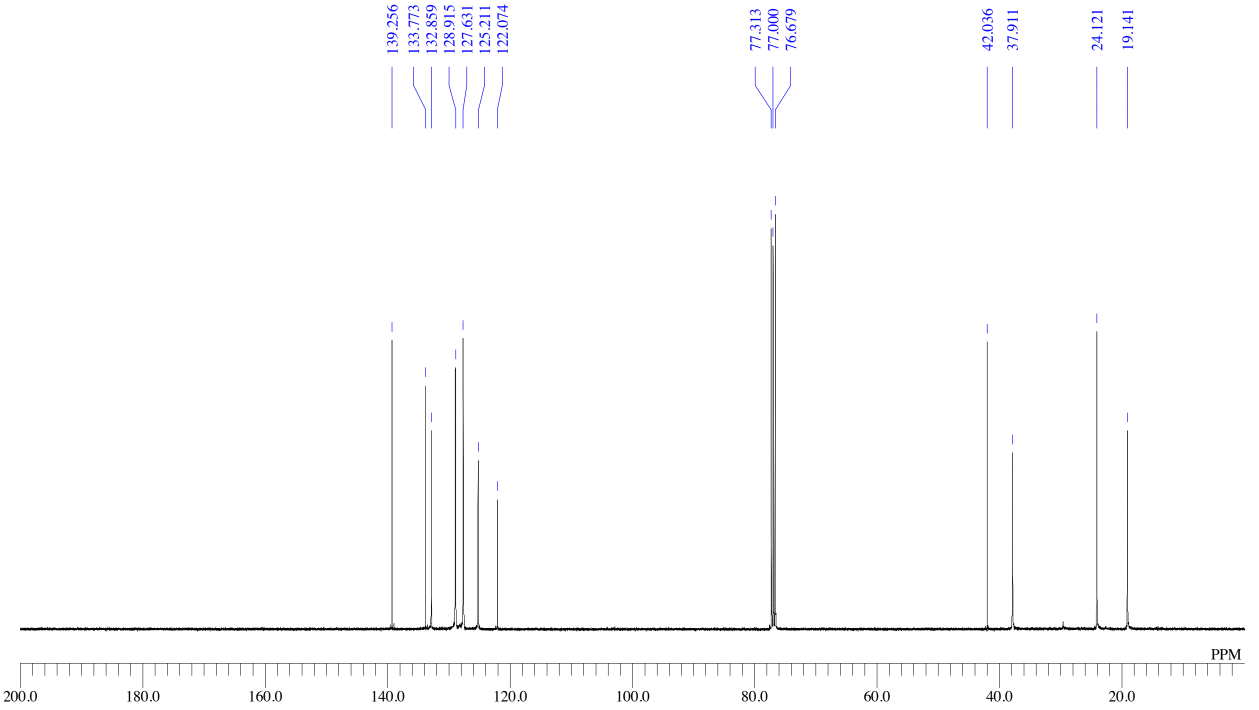


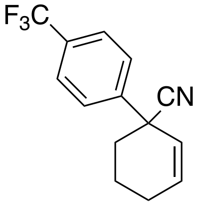
5c

^{1}H NMR: (400 MHz, $CDCl_3$)



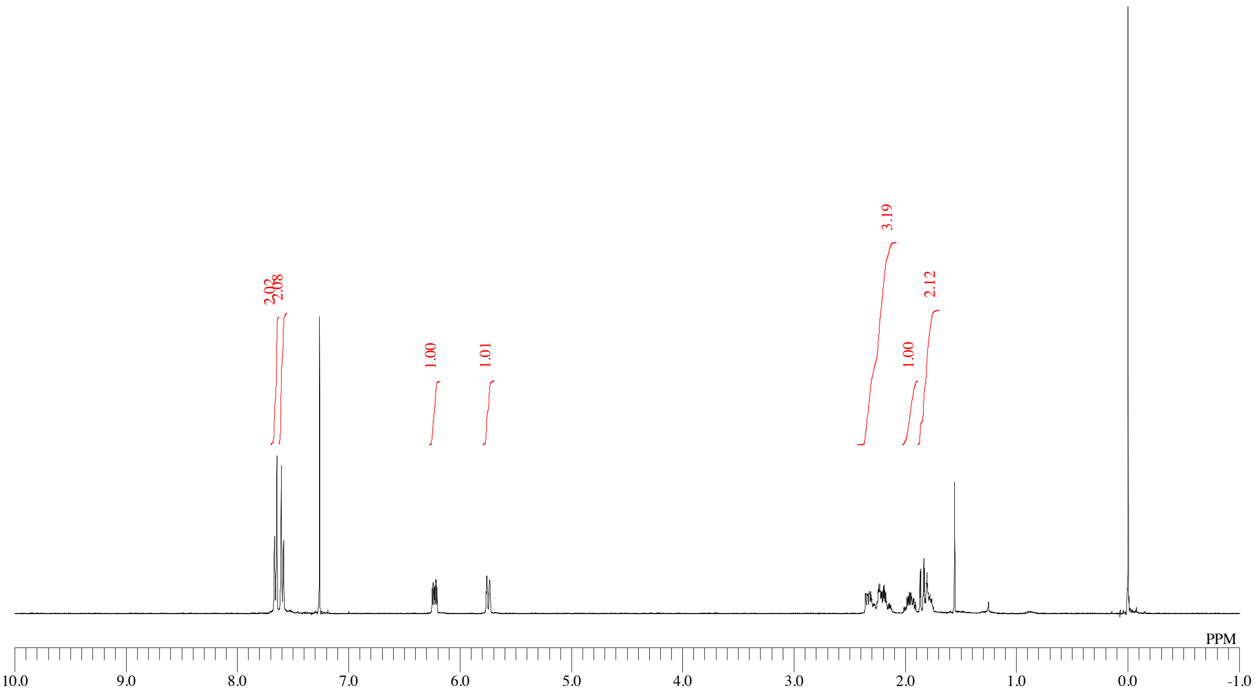
^{13}C NMR: (100 MHz, $CDCl_3$)



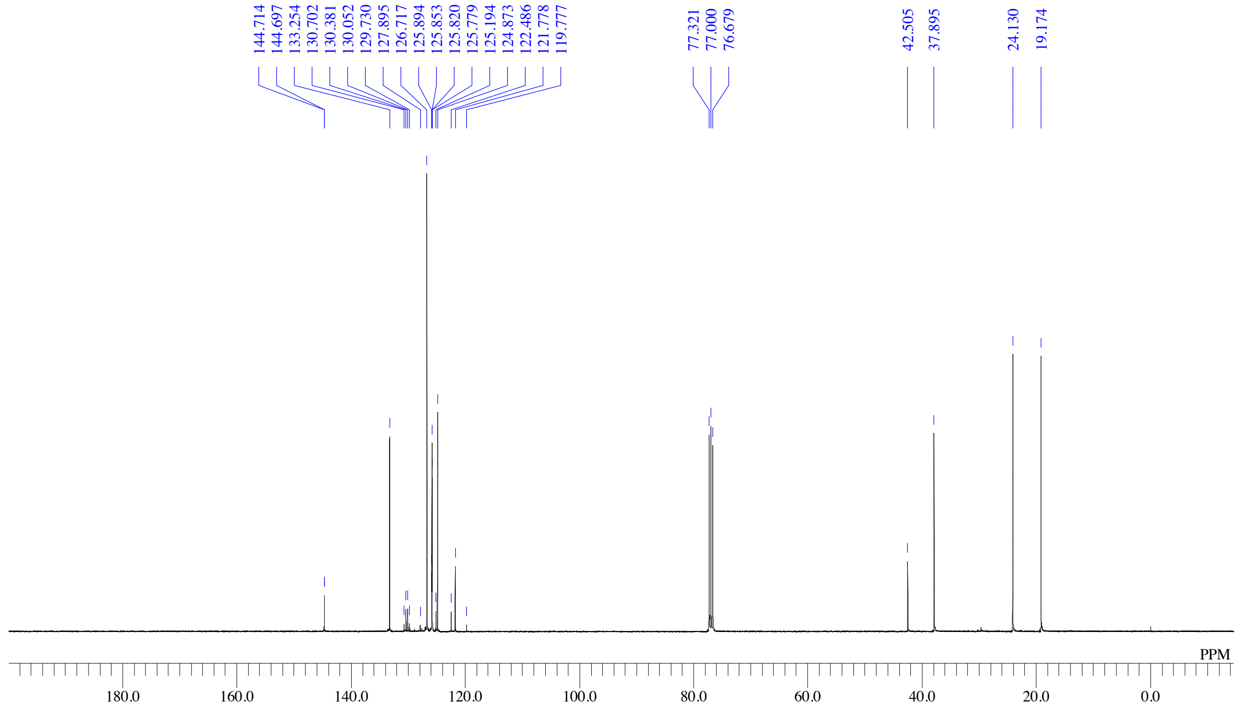


5d

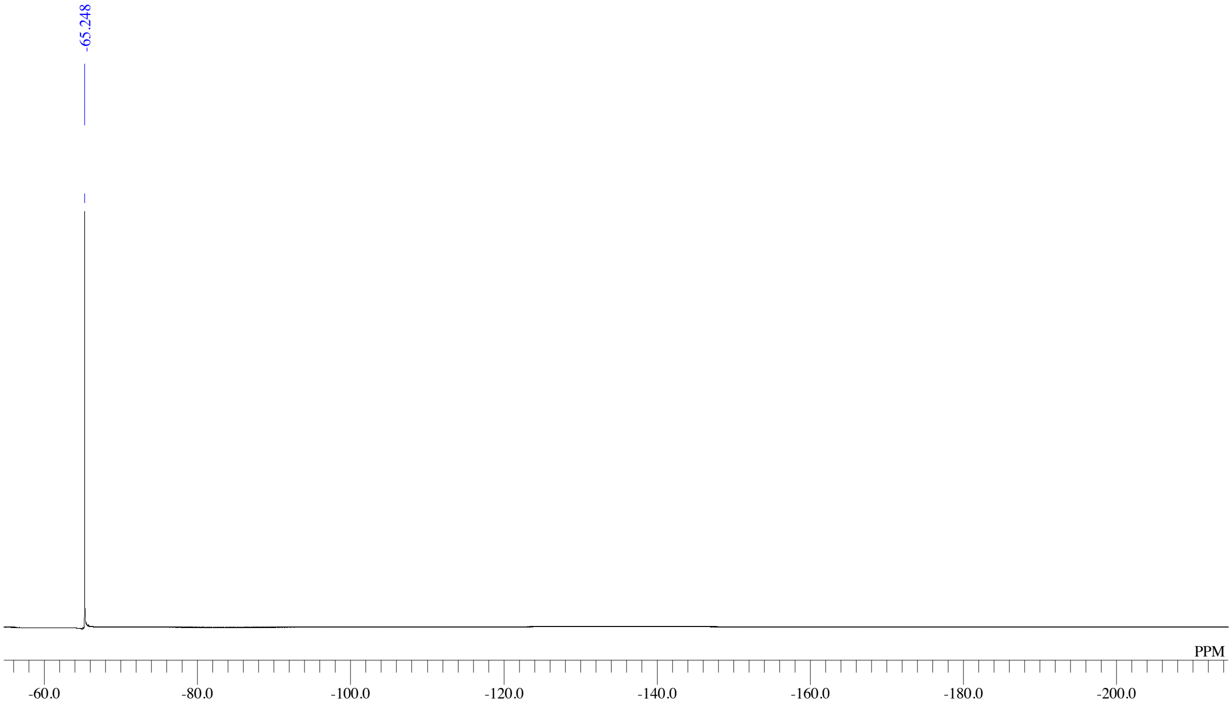
^{1}H NMR: (400 MHz, CDCl$_3$)

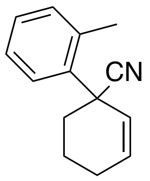


^{13}C NMR: (100 MHz, CDCl$_3$)



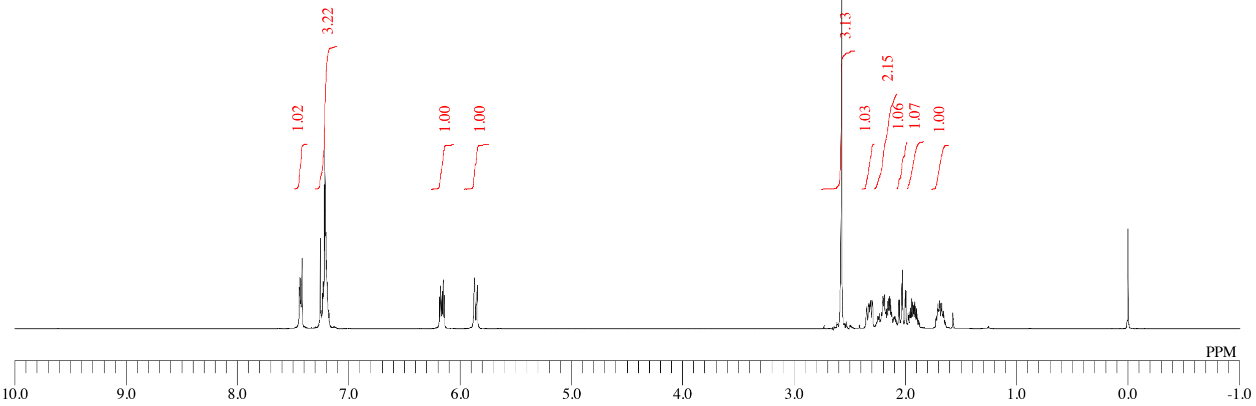
^{19}F NMR: (377 MHz, CDCl$_3$)



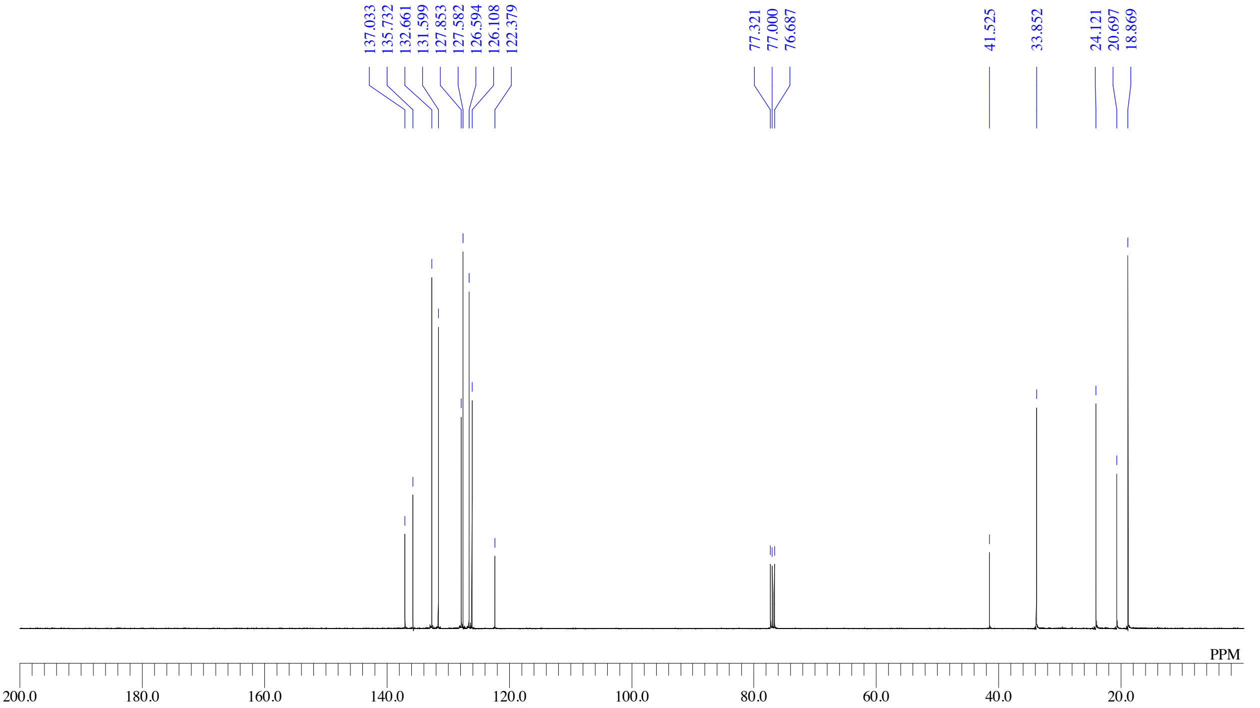


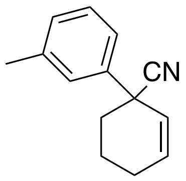
5e

^{1}H NMR: (400 MHz, CDCl$_3$)



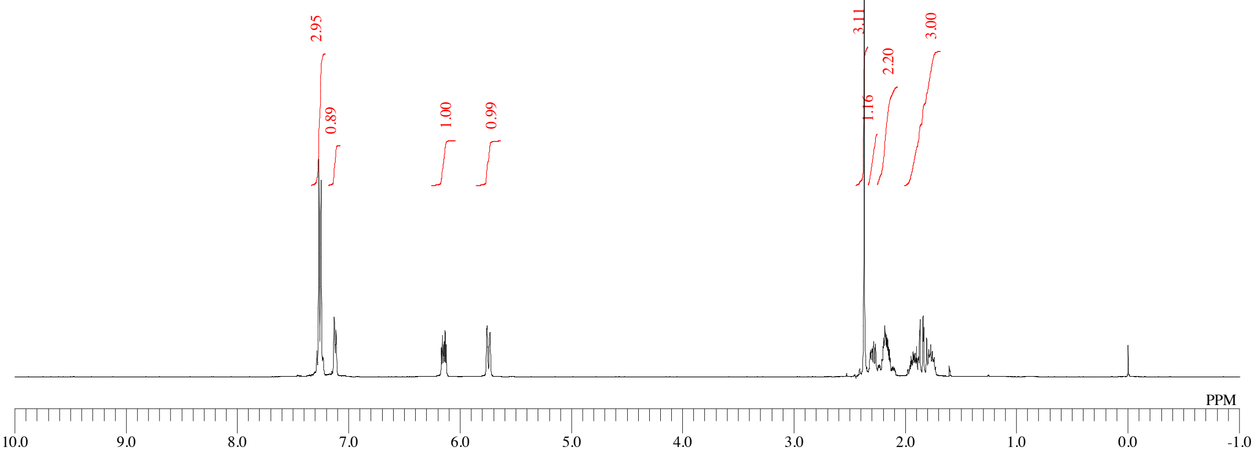
^{13}C NMR: (100 MHz, CDCl$_3$)



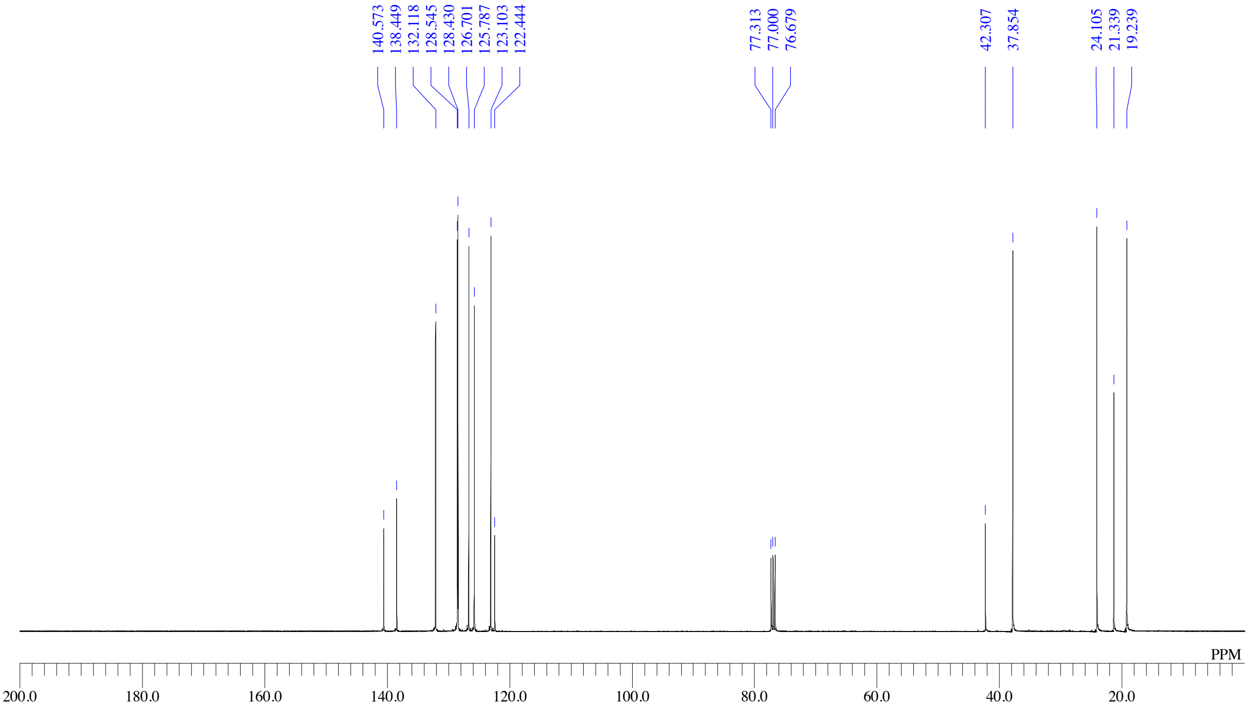


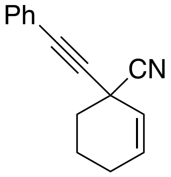
5f

^{1}H NMR: (400 MHz, $CDCl_3$)



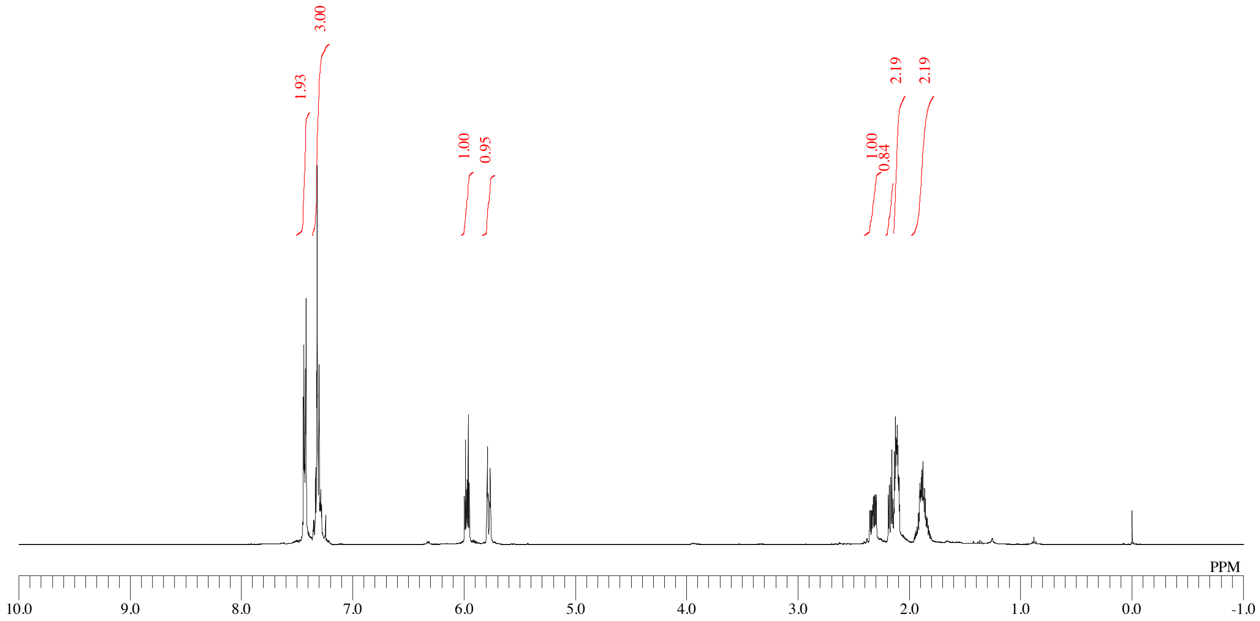
^{13}C NMR: (100 MHz, $CDCl_3$)



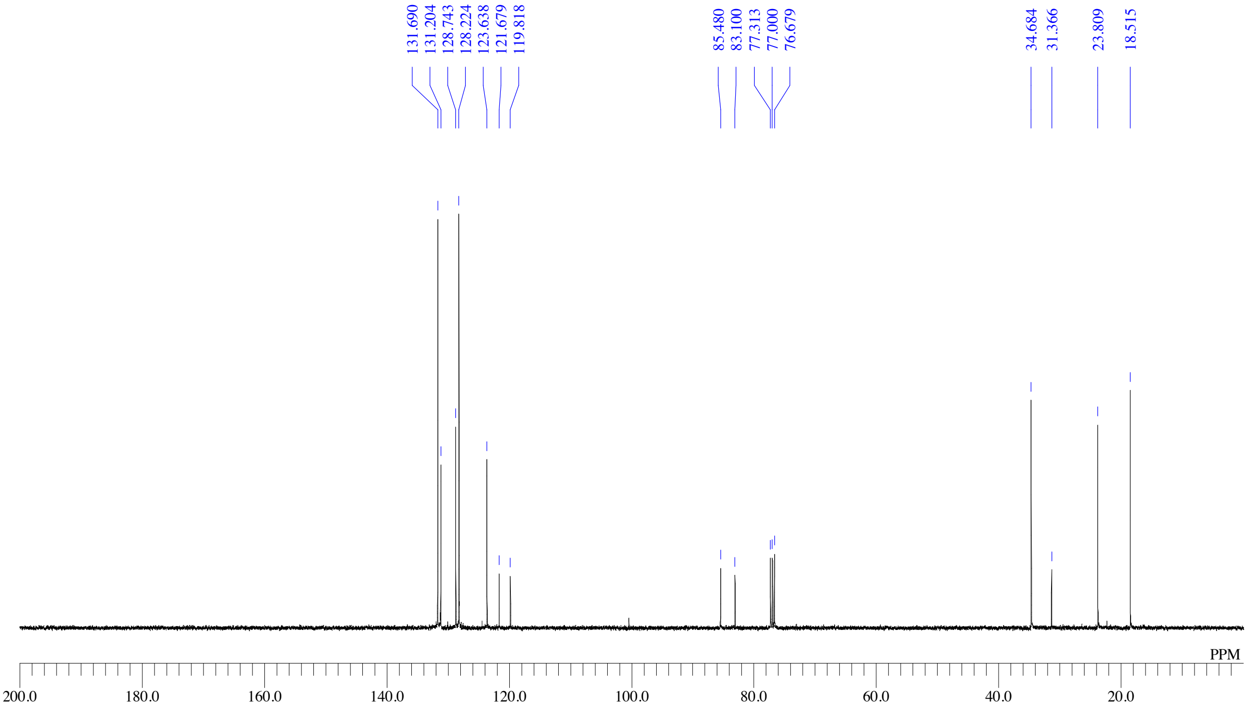


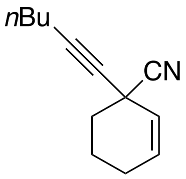
5g

^{1}H NMR: (400 MHz, $CDCl_3$)



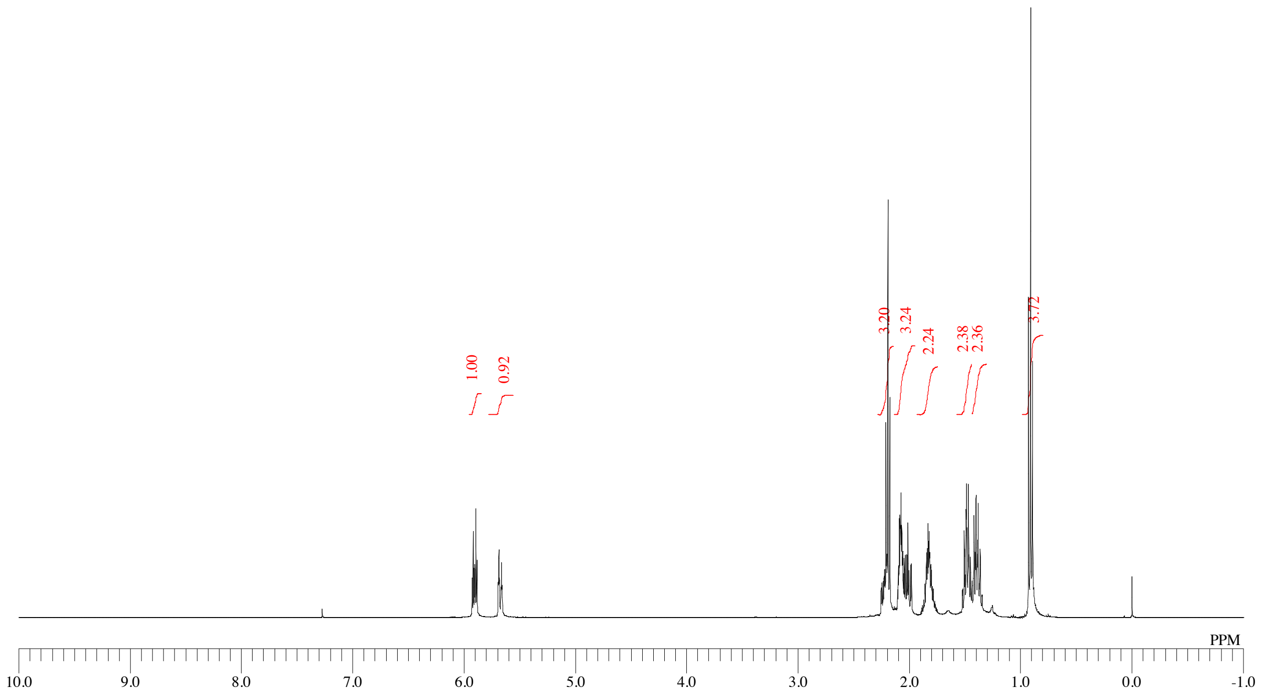
^{13}C NMR: (100 MHz, $CDCl_3$)



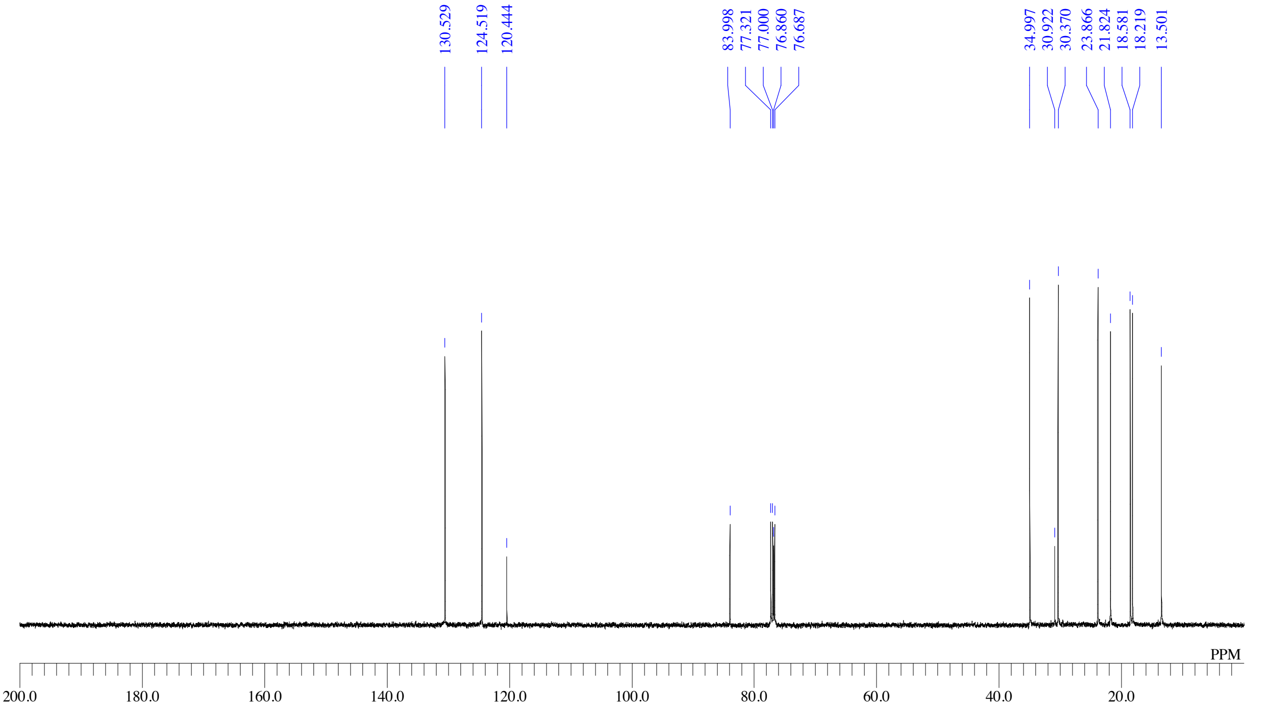


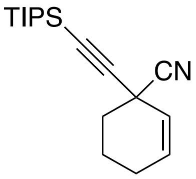
5h

^{1}H NMR: (400 MHz, CDCl$_3$)



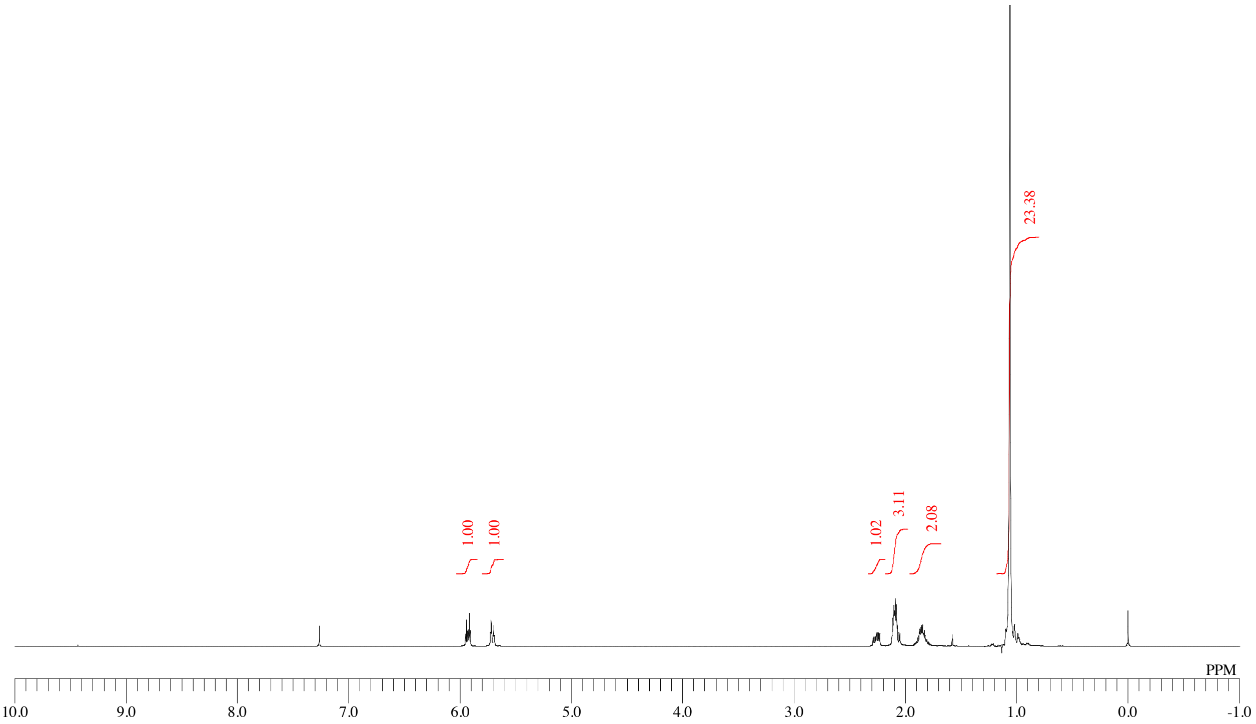
^{13}C NMR: (100 MHz, CDCl$_3$)



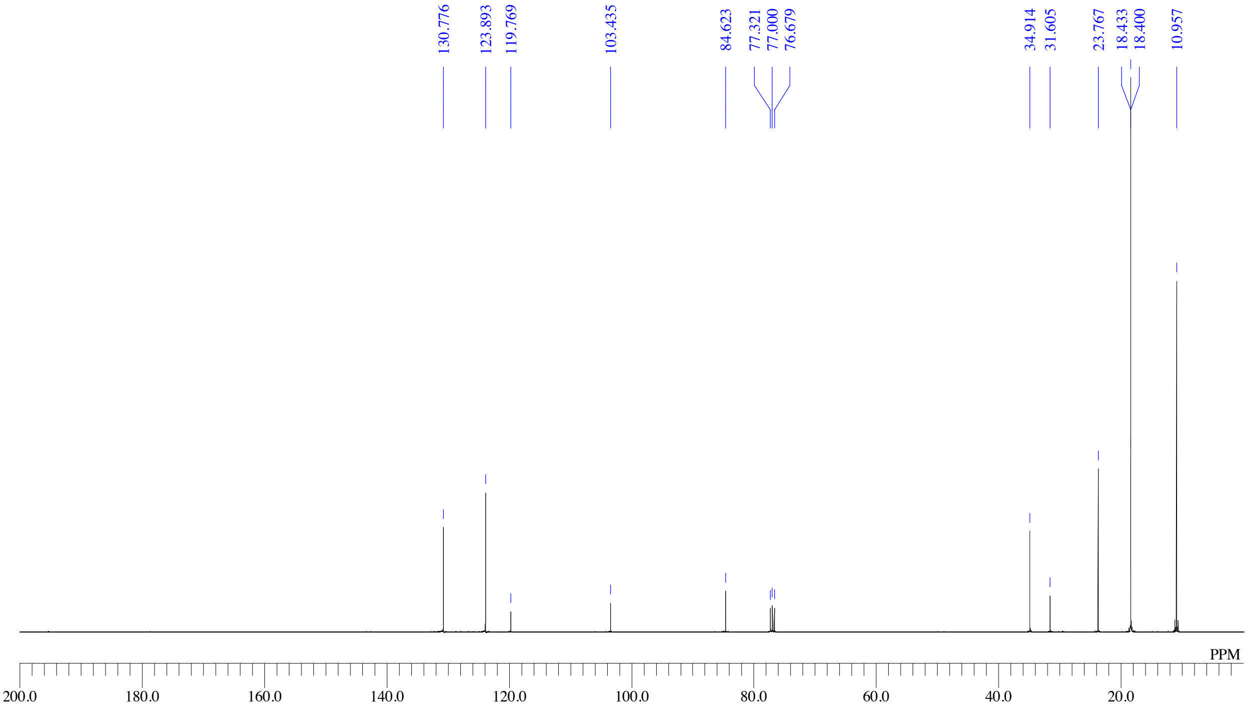


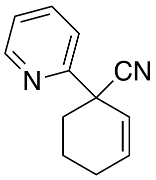
5i

^{1}H NMR: (400 MHz, $CDCl_3$)



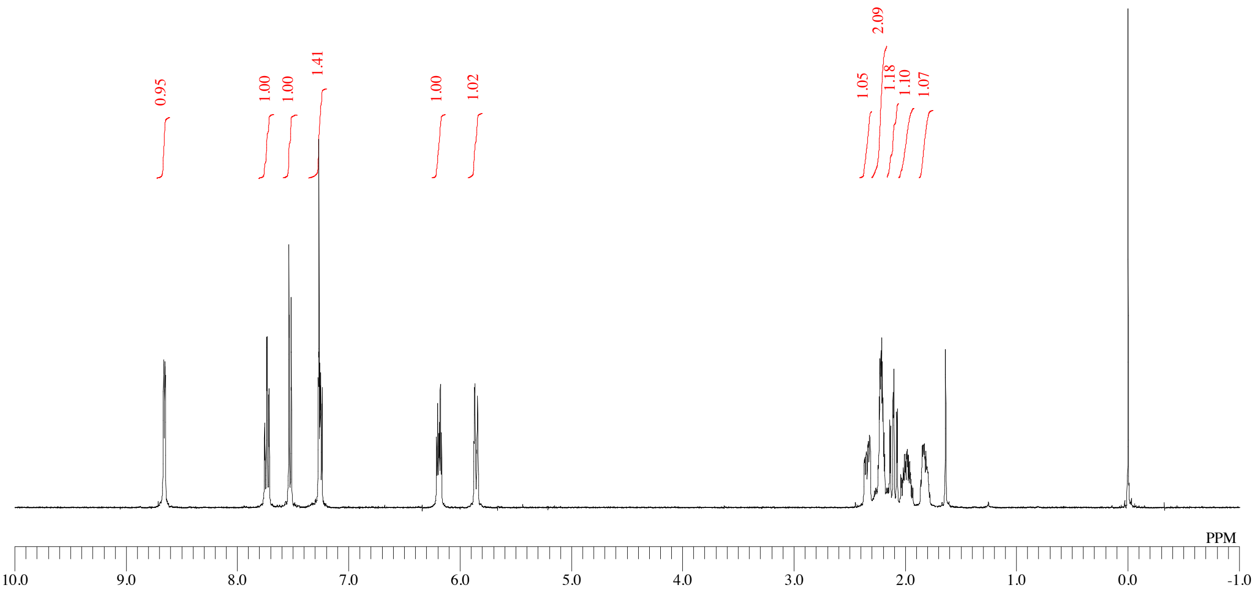
^{13}C NMR: (100 MHz, $CDCl_3$)



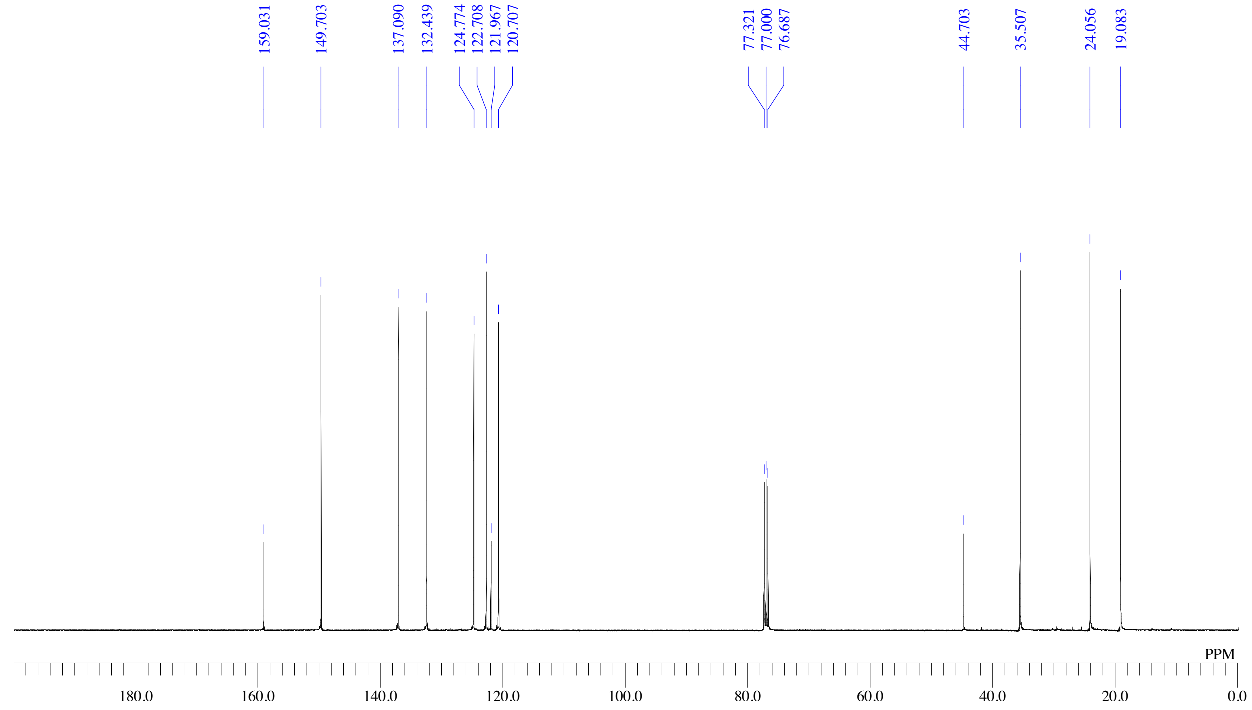


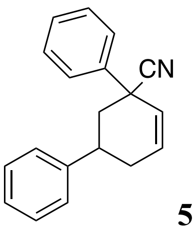
5j

^{1}H NMR: (400 MHz, $CDCl_3$)



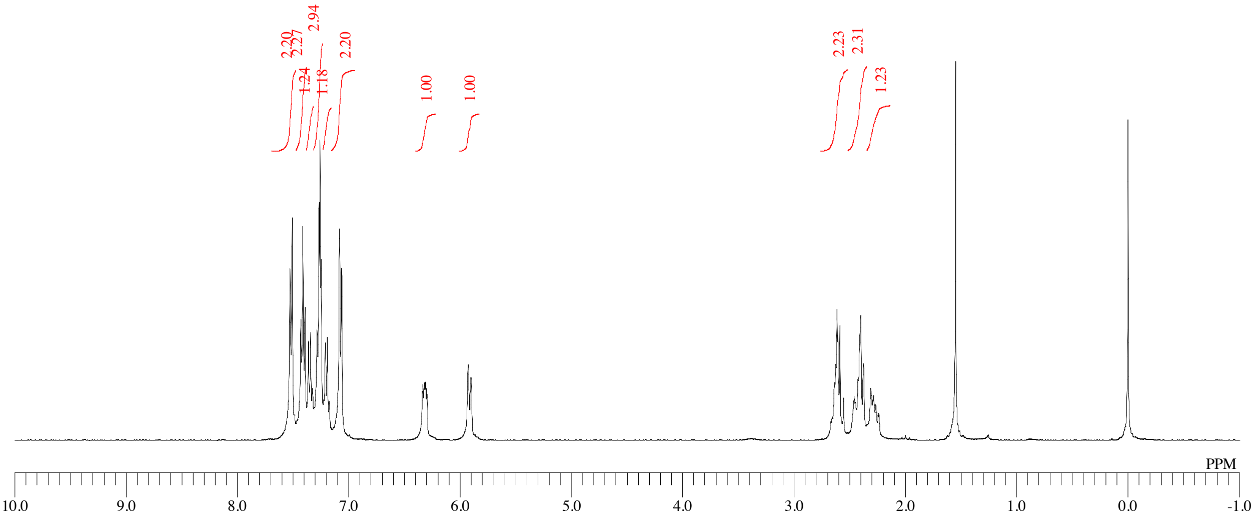
^{13}C NMR: (100 MHz, $CDCl_3$)



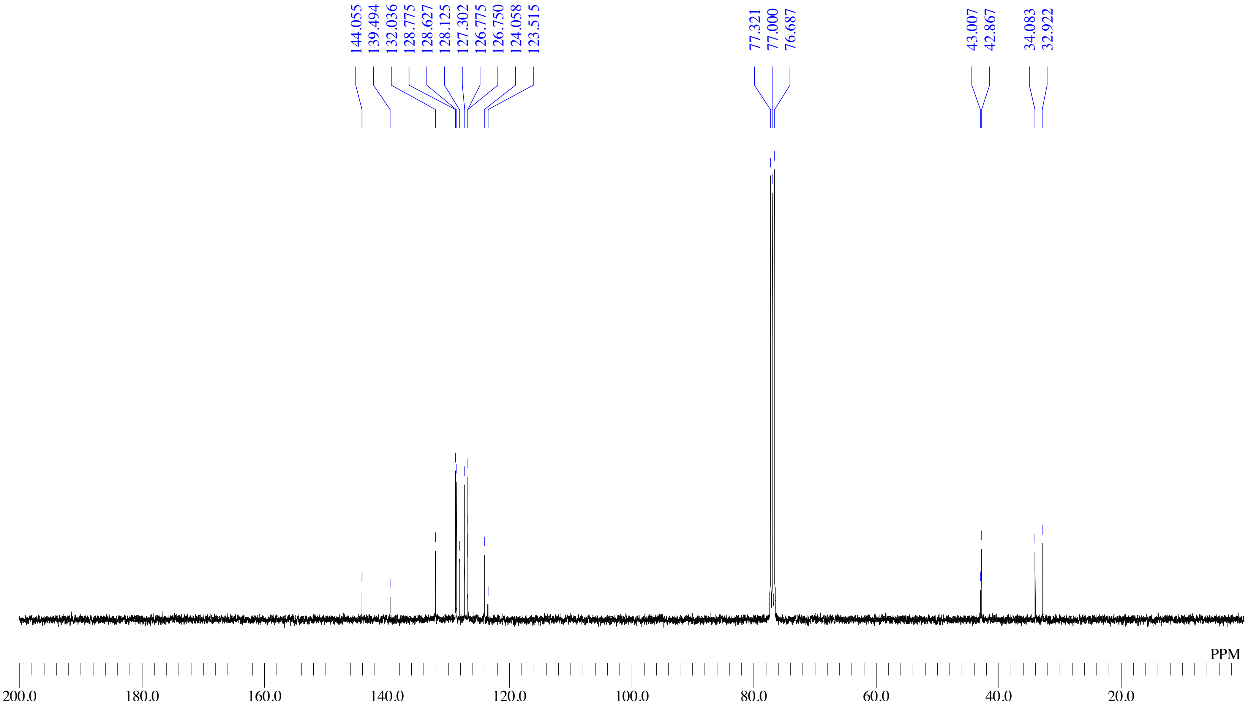


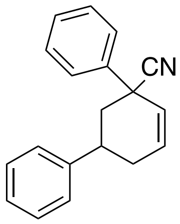
5k (isomer 1)

^{1}H NMR: (400 MHz, CDCl$_3$)



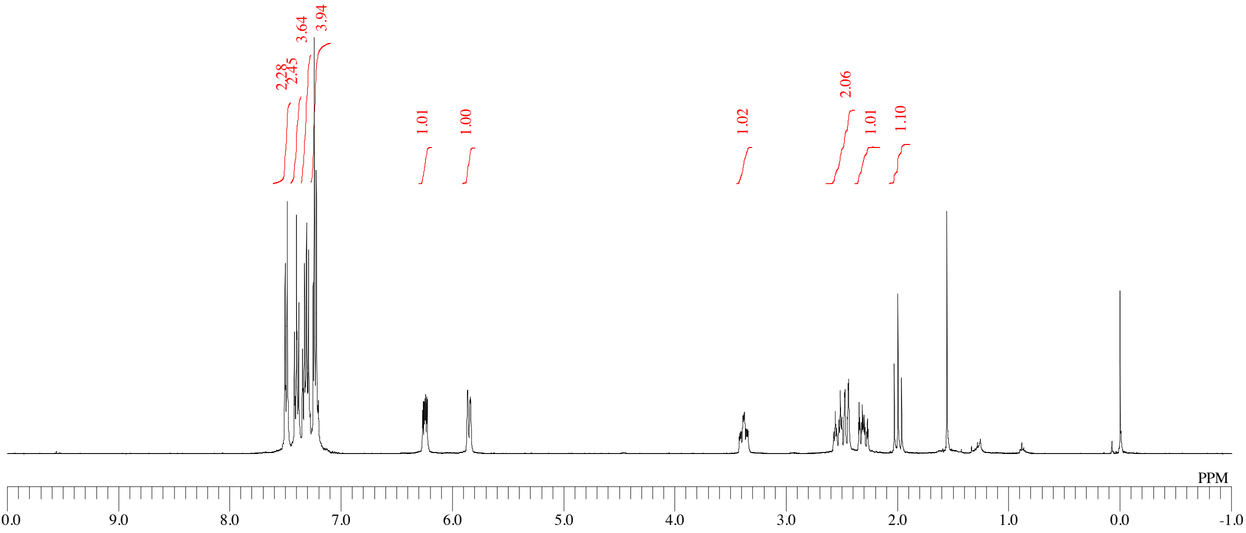
^{13}C NMR: (100 MHz, CDCl$_3$)



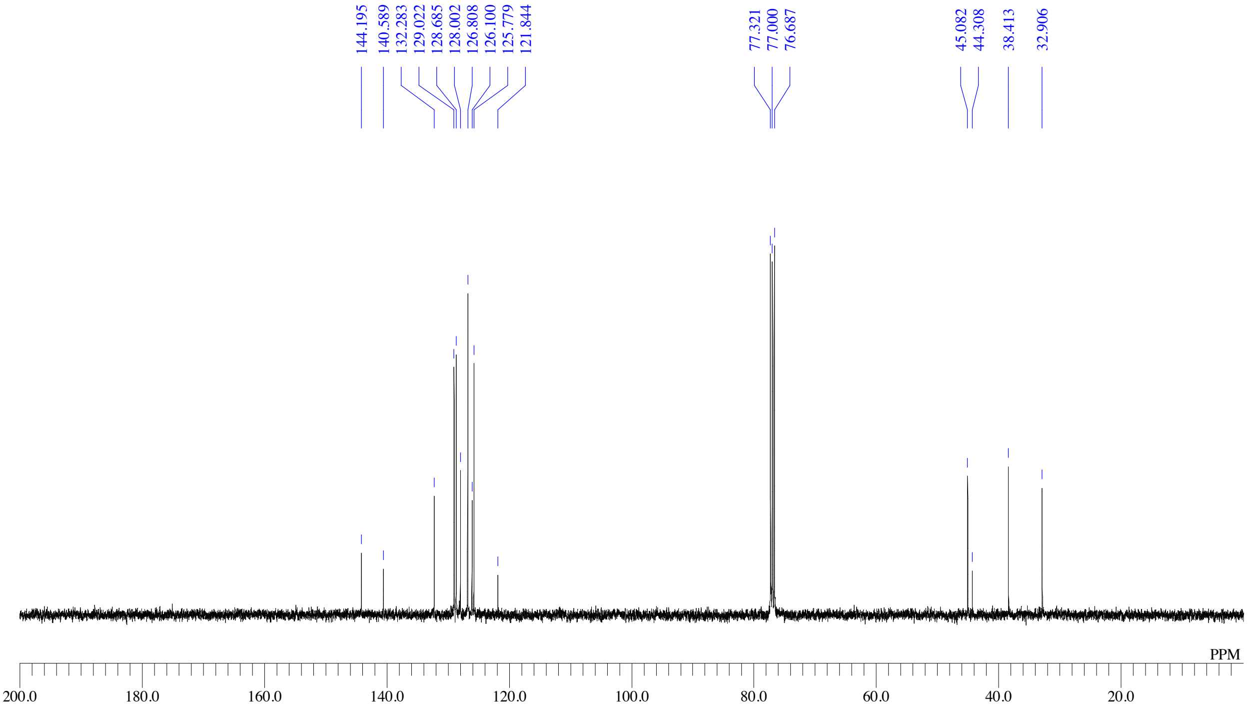


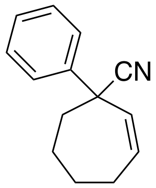
5k (isomer 2)

^{1}H NMR: (400 MHz, CDCl$_3$)



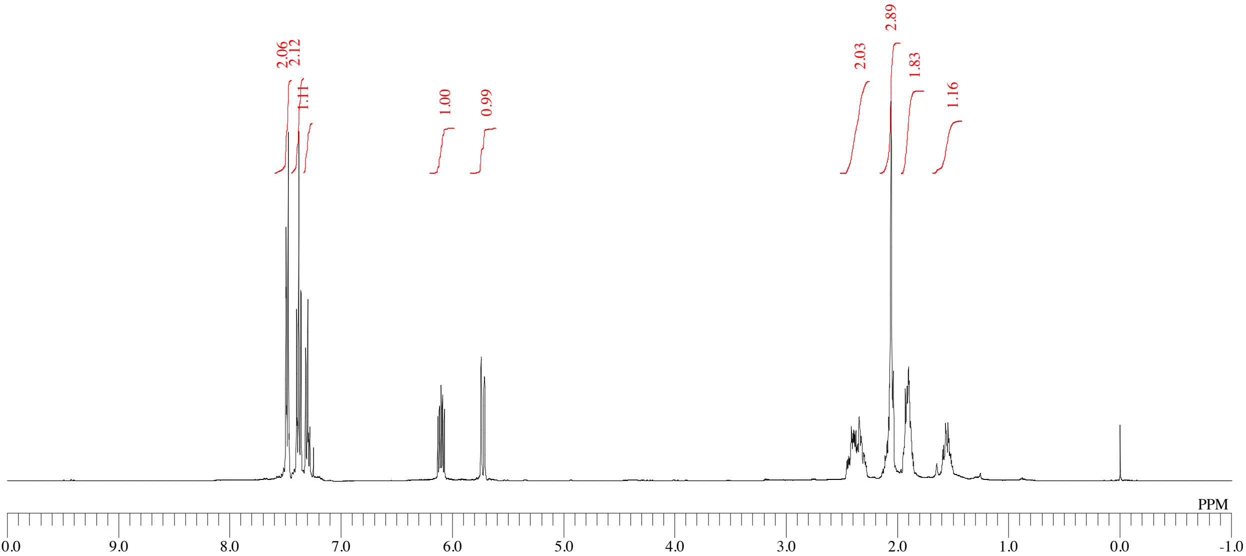
^{13}C NMR: (100 MHz, CDCl$_3$)



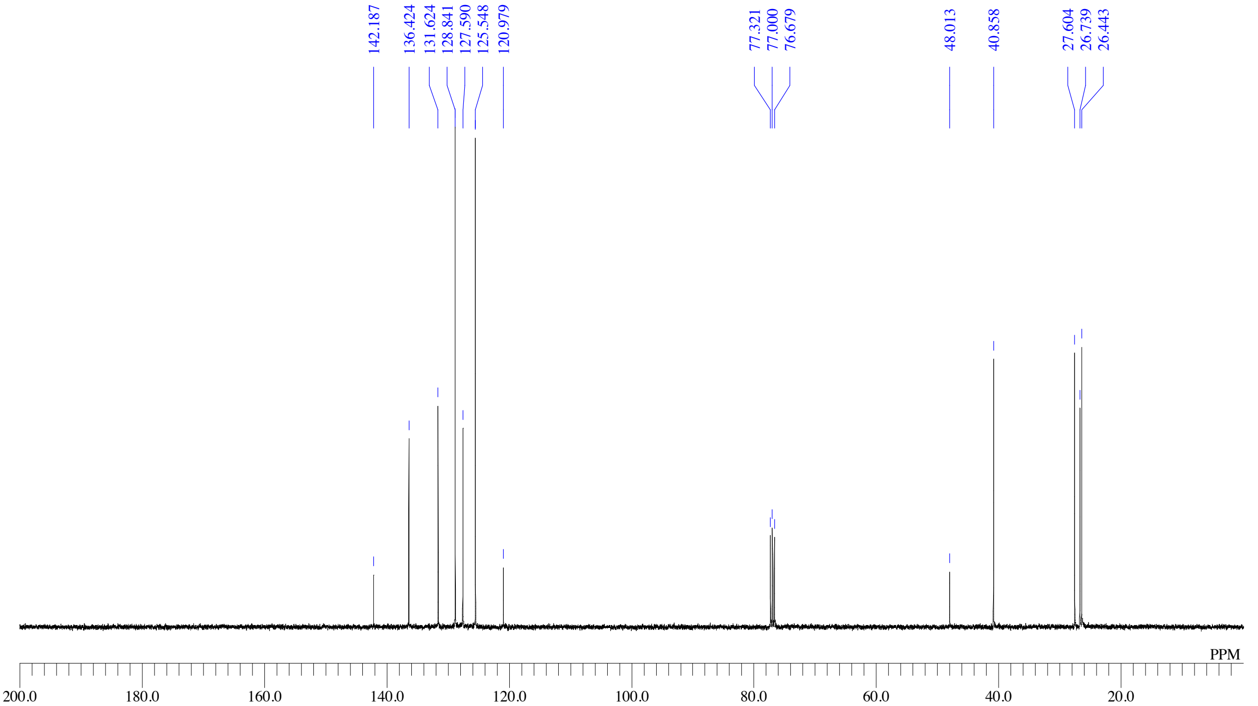


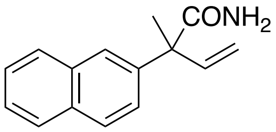
5l

^{1}H NMR: (400 MHz, CDCl$_3$)



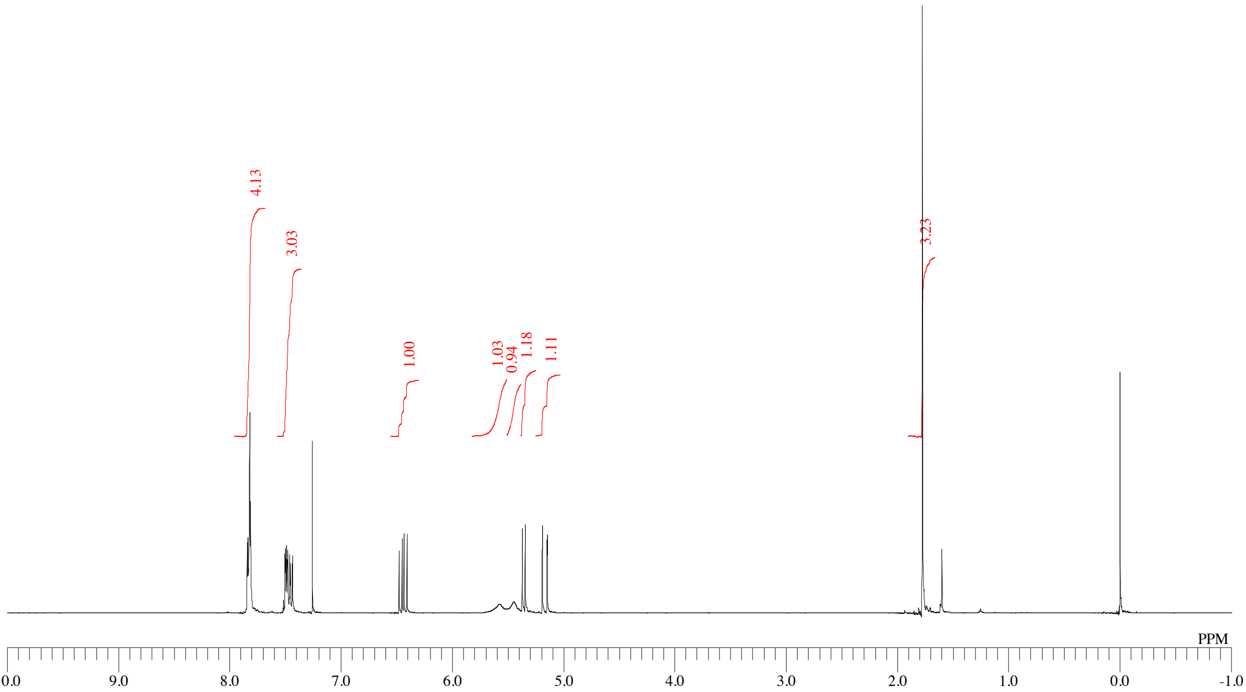
^{13}C NMR: (100 MHz, CDCl$_3$)



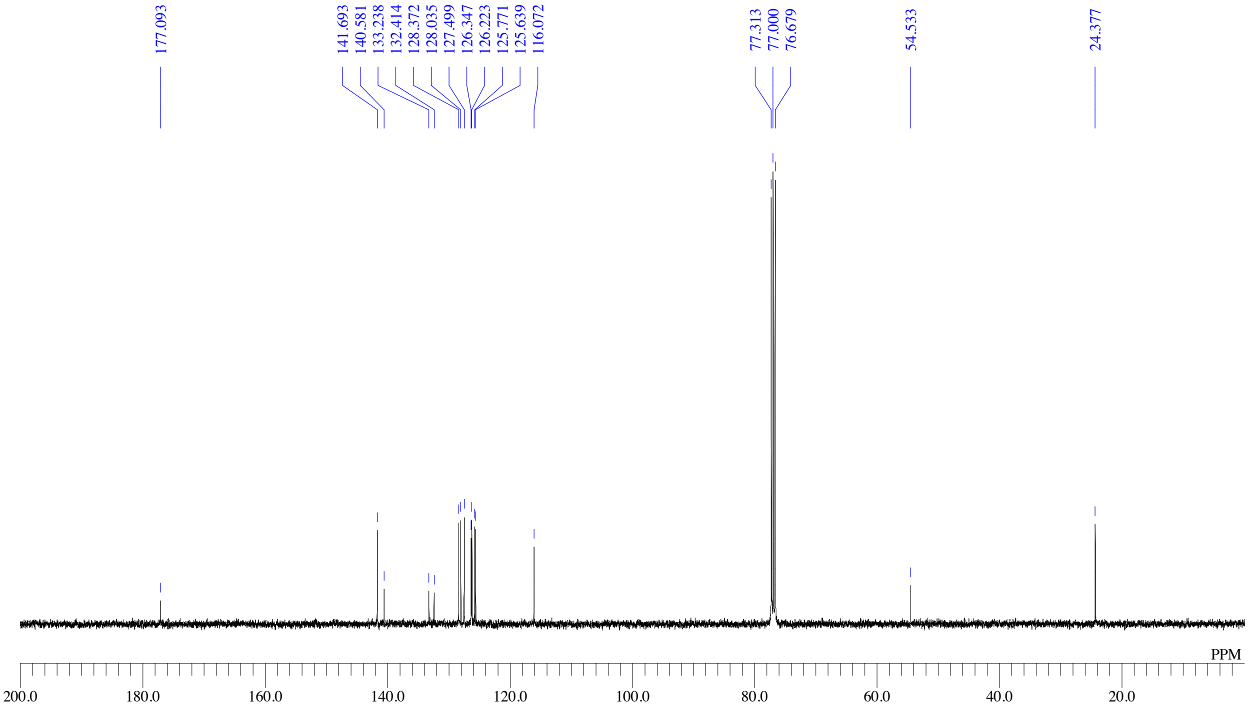


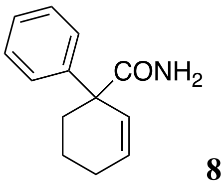
7

^{1}H NMR: (400 MHz, $CDCl_3$)



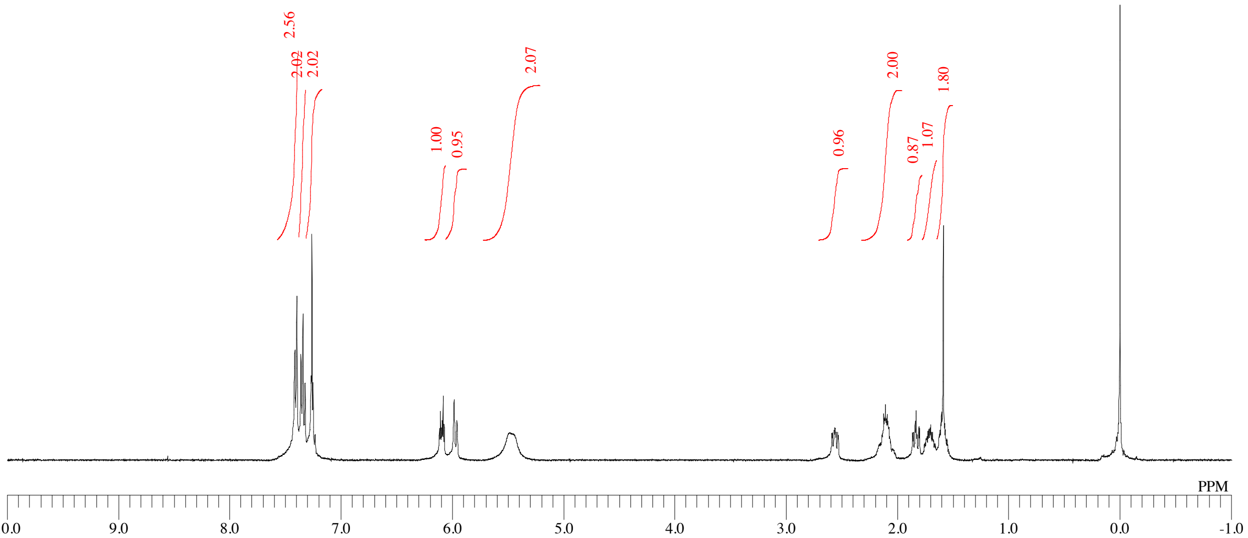
^{13}C NMR: (100 MHz, $CDCl_3$)



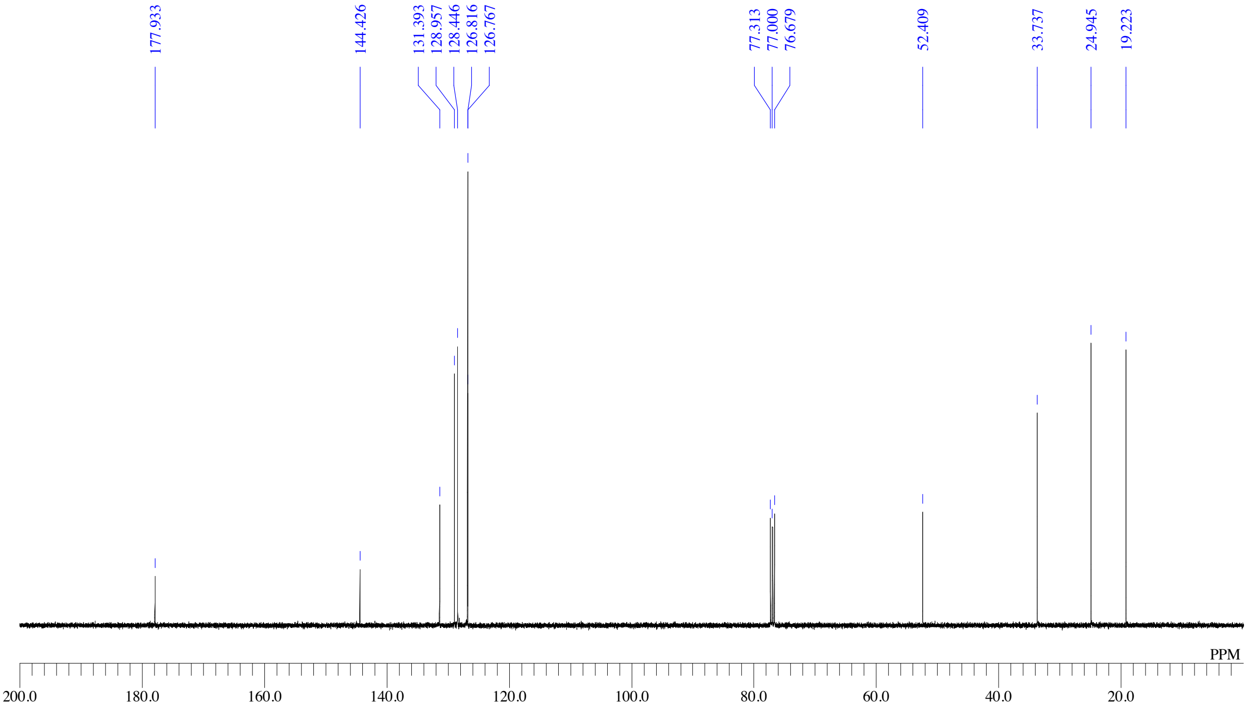


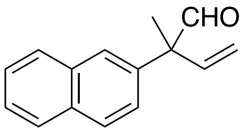
8

^{1}H NMR: (400 MHz, CDCl$_3$)



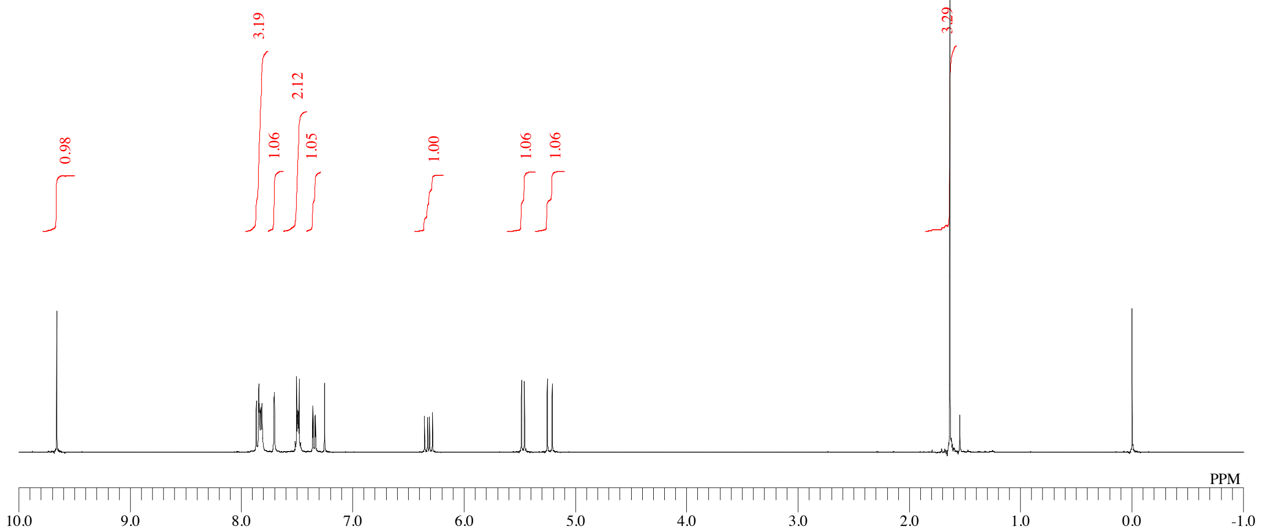
^{13}C NMR: (100 MHz, CDCl$_3$)



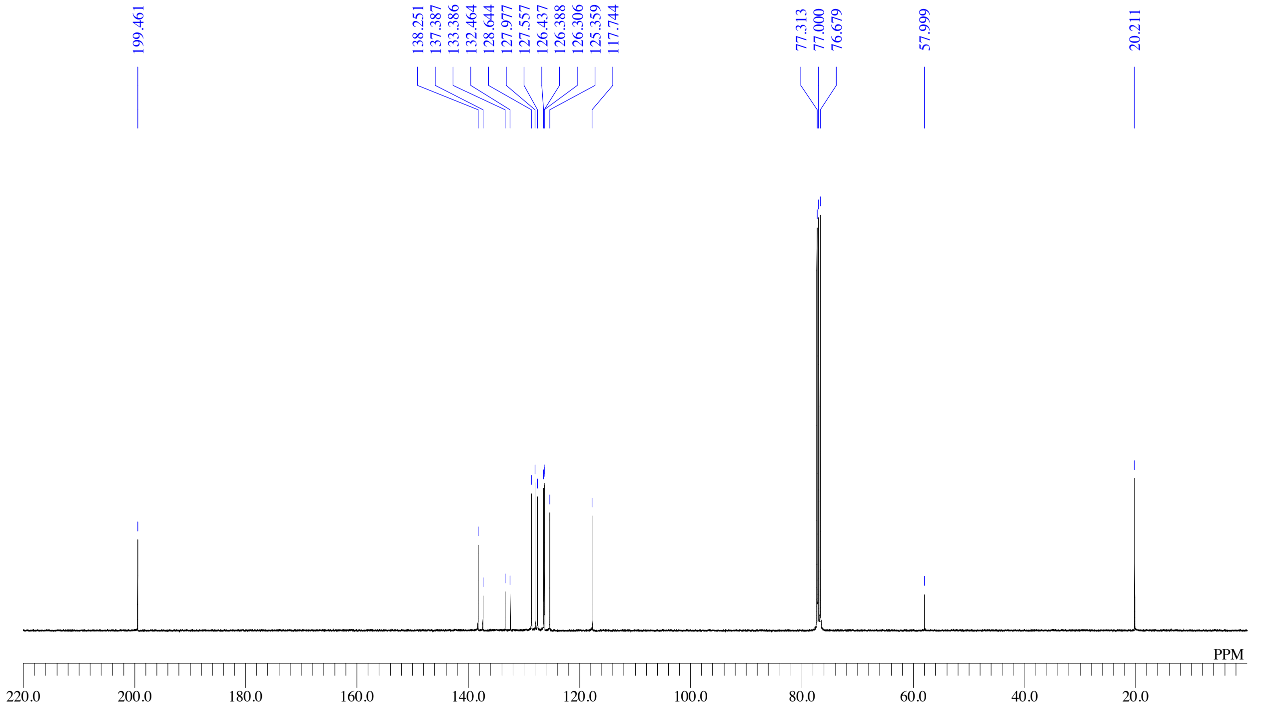


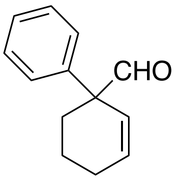
9

^{1}H NMR: (400 MHz, CDCl$_3$)



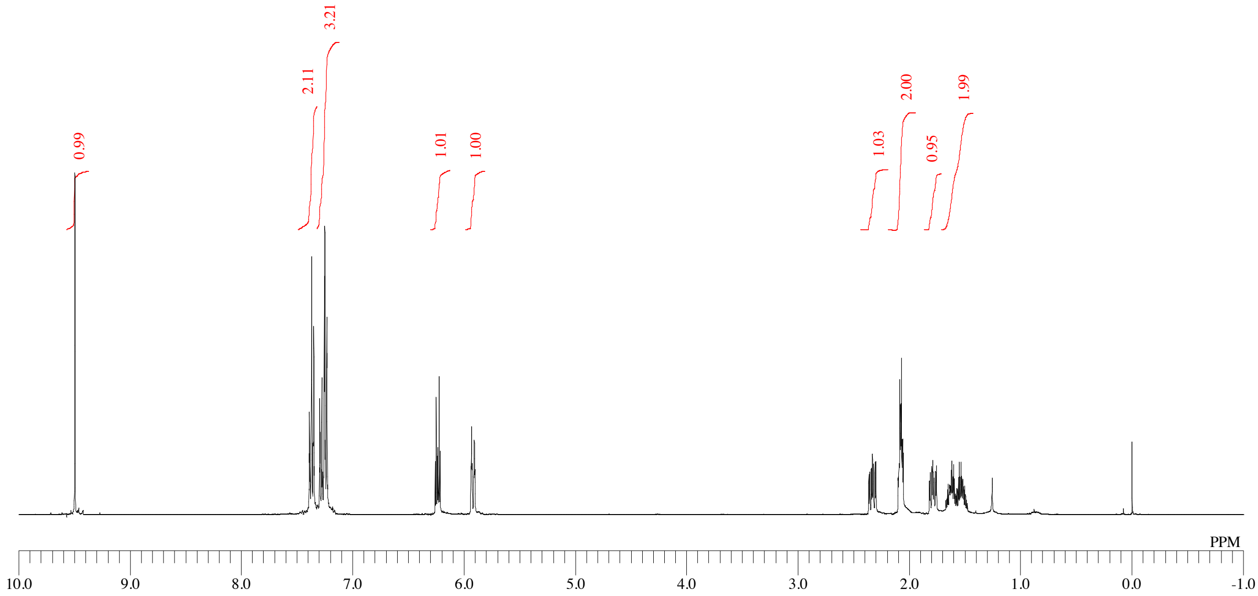
^{13}C NMR: (100 MHz, CDCl$_3$)



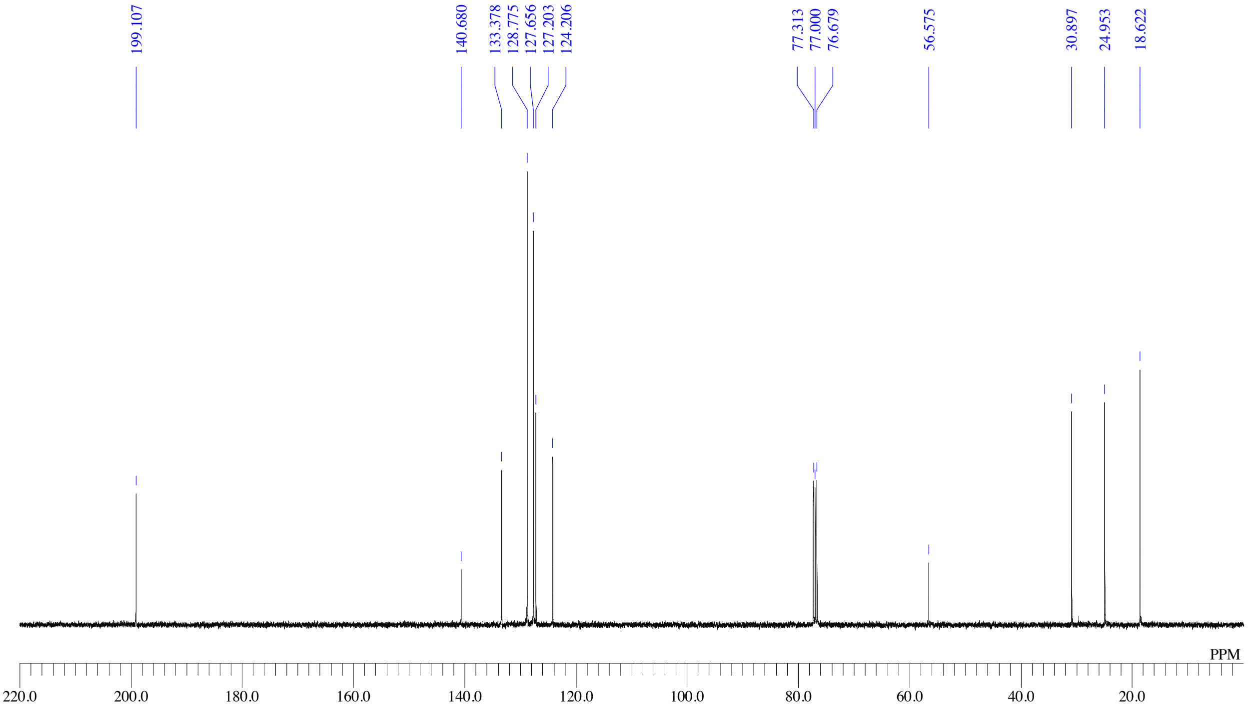


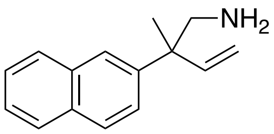
10

^{1}H NMR: (400 MHz, $CDCl_3$)



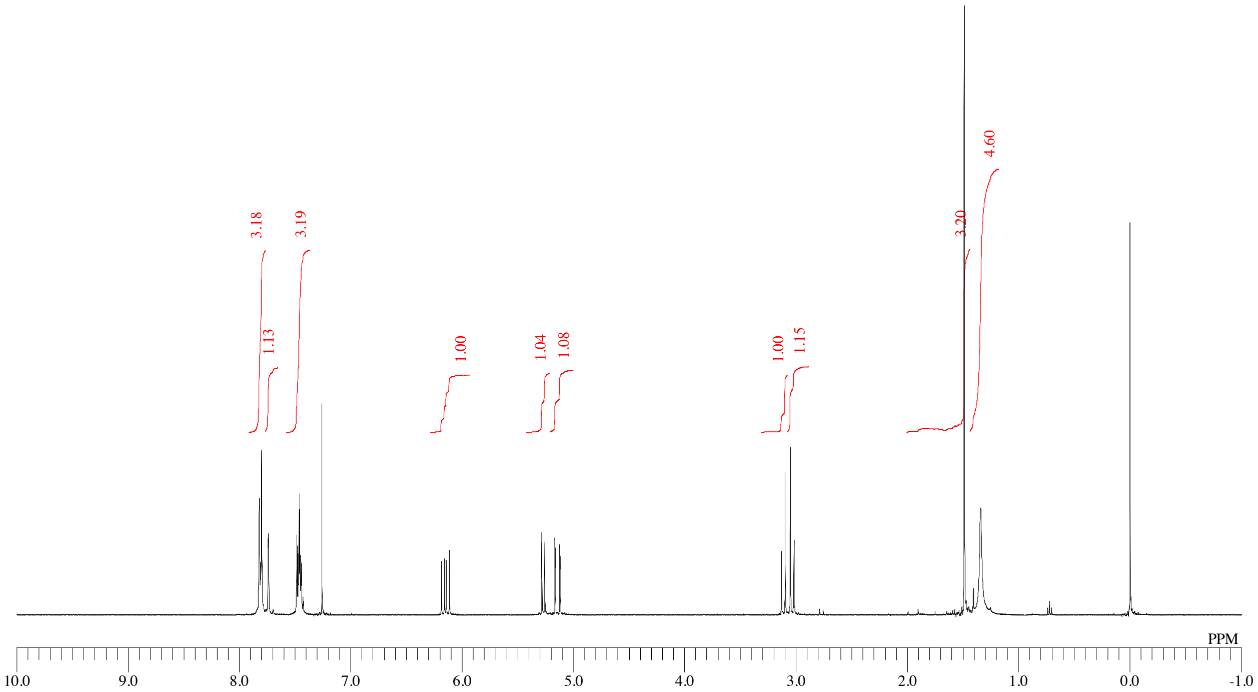
^{13}C NMR: (100 MHz, $CDCl_3$)



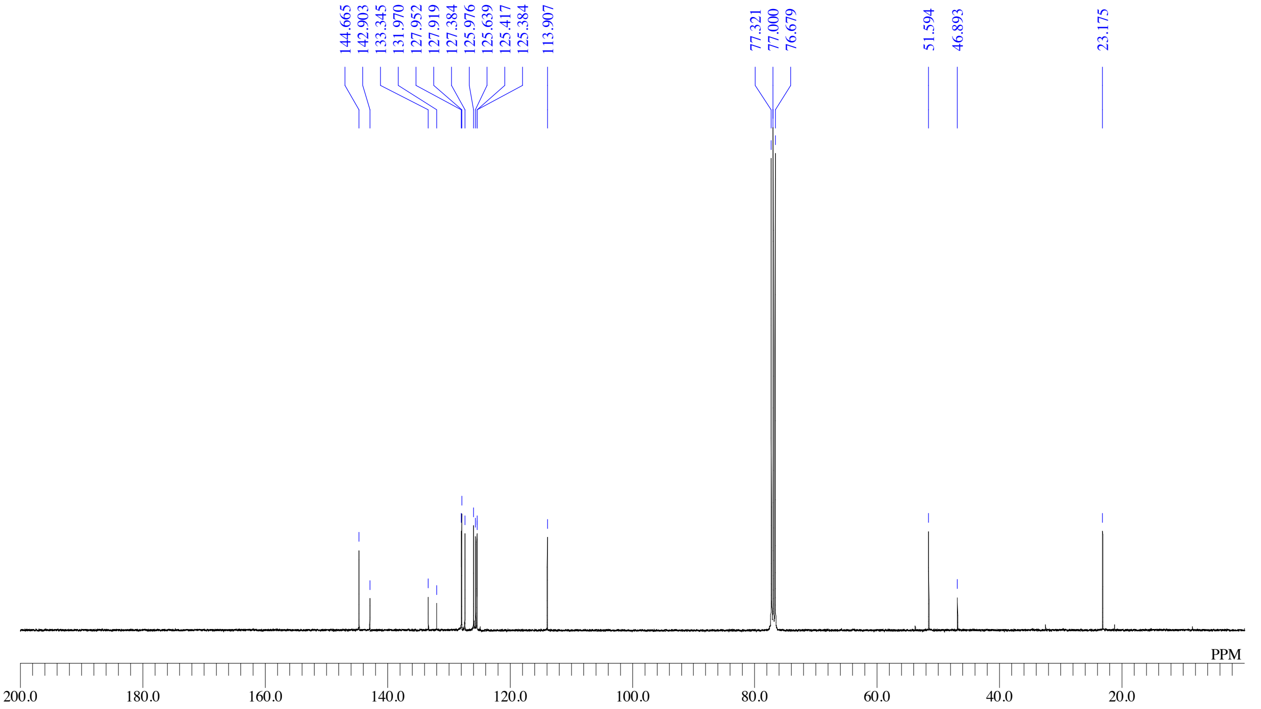


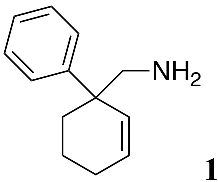
11

^{1}H NMR: (400 MHz, $CDCl_3$)



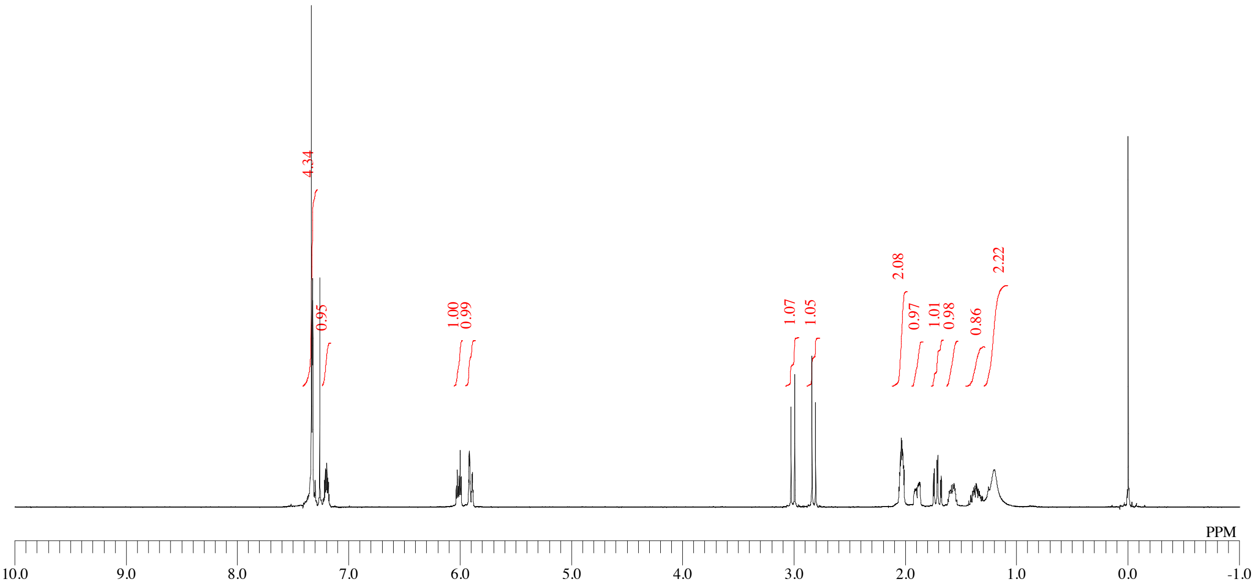
^{13}C NMR: (100 MHz, $CDCl_3$)





12

^{1}H NMR: (400 MHz, CDCl$_3$)



^{13}C NMR: (100 MHz, CDCl$_3$)