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Supporting Information

Light-Driven Alkyne *gem*-Hydrogenation: An Intramolecular Approach to *Hoveyda–Grubbs* Catalysts

Tomas J. Saiegh, Tobias Biberger, Raphael J. Zachmann, and Alois Fürstner*

SUPPORTING INFORMATION

Light-Driven Alkyne *gem*-Hydrogenation: An Intramolecular Approach to Hoveyda-Grubbs Catalysts

Tomas J. Saiegh, Tobias Biberger, Raphael J. Zachmann, and Alois Fürstner*

Max-Planck-Institut für Kohlenforschung, 45470 Mülheim/Ruhr, Germany

Email: fuerstner@kofo.mpg.de

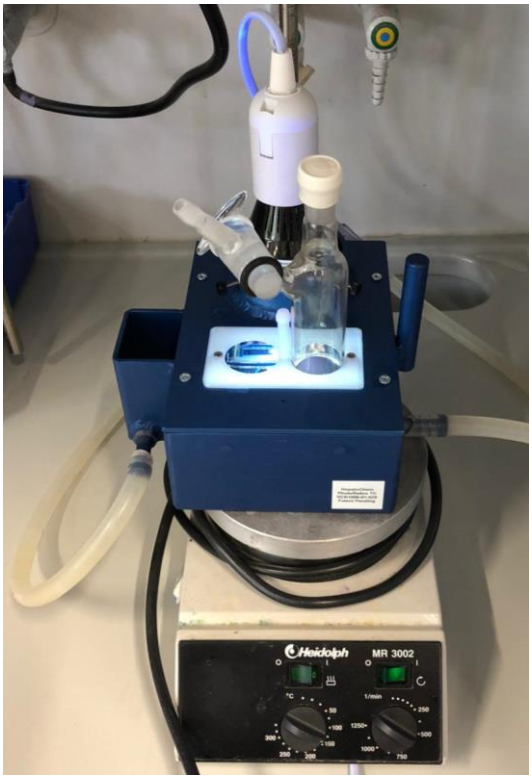
General

Unless stated otherwise, all reactions were carried out under argon in flame-dried Schlenk glassware, ensuring rigorously inert conditions. The solvents were purified by distillation over the indicated drying agents and were stored and handled under argon: CH_2Cl_2 (CaH_2), pentane (Na/K alloy), THF (Na/K alloy), toluene (CaH_2). Benzene and *n*-hexane were degassed via freeze-pump-thaw cycles (3 x) and stored over molecular sieves 3Å. Flash chromatography: Merck Geduran silica gel 60 (40 – 63 µm).

NMR spectra were recorded on Bruker AV 400 or AV III 600 spectrometers in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references[1] and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_C = 77.16 ppm; residual $CHCl_3$: δ_H = 7.26 ppm; CD_2Cl_2: δ_C = 53.84 ppm; residual $CHDCl_2$: δ_H = 5.32 ppm).

IR: Alpha Platinum ATR spectrometer (Bruker), wavenumbers ($\tilde{\nu}$) in cm^{-1}.

MS (EI): Finnigan MAT 8200 (70 eV), DI-MS (EI): Finnigan MAT SSQ 7000, ESI-MS: ESQ 3000 (Bruker), Thermo Scientific LTQ-FT, or Thermo Scientific Exactive spectrometer. HRMS: Bruker APEX III FT-MS (7 T magnet), MAT 95 (Finnigan), Thermo Scientific LTQ-FT, Thermo Scientific Exactive instrument. GC-MS: Shimadzu GCMS-QP2010 Ultra instrument.



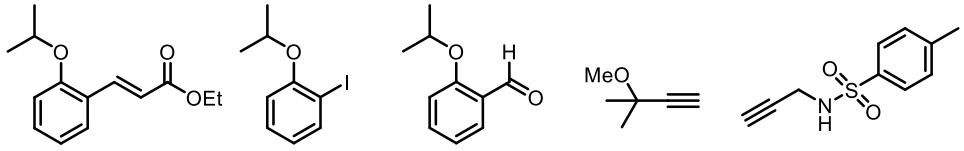
Hydrogen gas (N50, ≥99.999 Vol.%) was purchased from AirLiquide and was used without further purification.

Unless stated otherwise, all commercially available compounds (abcr, Acros, TCI, Aldrich, Alfa Aesar) were used as received.

Photolysis experiments were performed in the PhotoRedOxBox TC from HepatoChem equipped with an EvoluChem™ LED (365 nm, 18 W). When the cooling function was used, water served as the cooling agent (23°C).

Figure S1. PhotoRedOxBox TC from Hepatochem.

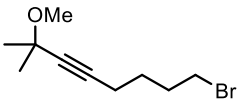
Synthesis of Substrates



8a **9** **S1a** **S2** **S3**

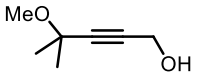
The compounds **8a**,[4] **9**,[2] **S1a**,[3] **S2**[5] and **S3**[6] were prepared according to literature procedures.

8-Bromo-2-methoxy-2-methyloct-3-yne (S4). *n*-BuLi (1.6 M in hexanes, 8 mL, 12.8 mmol) was added dropwise to a solution of 3-methoxy-3-methylbut-1-yne (**S2**, 1.14 g, 11.6 mmol) in THF (100 mL) at 0 °C and stirring was continued for 30 min. 1,4-Dibromobutane (2.00 mL, 16.7 mmol) was added in one portion and the mixture was stirred at reflux temperature overnight. After reaching ambient temperature, sat. aq. NH_4Cl (50 mL) was added and the mixture was extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, pentane/diethyl ether 30:1) to provide a colorless oil (1.40 g, 52%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.46 (t, *J* = 6.7 Hz, 2H), 3.29 (s, 3H), 2.25 (t, *J* = 7.0 Hz, 2H), 2.03 – 1.91 (m, 2H), 1.71 – 1.59 (m, 2H), 1.38 (s, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 83.9, 83.1, 70.8, 51.5, 33.9, 32.2, 28.8, 27.6, 18.1. IR (film) ṽ 2982, 2935, 1453, 1434, 1377, 1360, 1252, 1210, 1171, 1150, 1076, 819 cm^{-1}. HRMS (GC-CI isobutane) calcd for $C_{10}H_{18}OBr$ $[M+H]^+$: 233.05357; found: 233.05357.



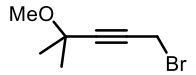
$C_{10}H_{17}BrO$
M = 233,15

4-Methoxy-4-methylpent-2-yn-1-ol (S5). *n*-BuLi (1.6 M in hexanes, 3.16 mL, 5.06 mmol) was added slowly to a solution of alkyne **S2** (452 mg, 4.6 mmol) in THF (20 mL) at −78 °C. The solution was stirred for 1 h at −78 °C before powdered paraformaldehyde (180 mg, 6.0 mmol) was introduced. The mixture was warmed to room temperature and stirring was continued for 1 h before a sat. NH_4Cl solution (10 mL) and EtOAc (10 mL) were added, the layers were separated and the aqueous phase was extracted with EtOAc (2 x 15 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 60:40) to give the title compound as colorless oil (503 mg, 85%). IR (film) ṽ 3395 (br), 2985, 2937, 2827, 1465, 1362, 1251, 1172, 1150, 1060, 1004, 913, 818 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 4.31 (s, 2H), 3.35 (s, 3H), 1.45 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 87.7, 82.4, 70.6, 51.7, 51.3, 28.3. HRMS (ESI) calcd for $C_7H_{12}O_2Na$ $[M+Na]^+$: 151.0729; found: 151.0730. The spectral data are consistent with those reported in the literature.[7]



$C_7H_{12}O_2$
M =128.17 g/mol

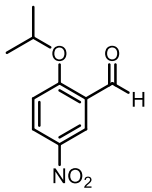
1-Bromo-4-methoxy-4-methylpent-2-yne (13). A solution of alcohol **S5** (100 mg, 0.78 mmol) and CBr_4 (312 mg, 0.94 mmol) in CH_2Cl_2 (3 mL) was cooled to 0 °C before PPh_3 (247 mg, 0.94 mmol) was slowly added. Once the addition was complete, stirring was continued for another 1 h at 0 °C. The mixture was concentrated under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 90:10) to give the title



$C_7H_{11}BrO$
M = 191.07 g/mol

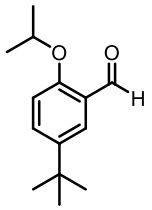
compound as colorless oil (128 mg, 86%). IR (film) ṽ 2985, 2935, 2826, 1378, 1361, 1255, 1211, 1172, 1151, 1074, 918, 822 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 3.95 (s, 2H), 3.35 (s, 3H), 1.44 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 88.9, 79.5, 70.6, 51.9, 28.2, 14.5. HRMS (CI) calcd for $C_7H_{12}BrO$ $[M+H]^+$: 191.0066; found: 191.0067.

2-Isopropoxy-5-nitrobenzaldehyde (S1j). *i*PrBr (2.22 mL, 23.6 mmol) and K_2CO_3 (3.26 g, 23.6 mmol) were successively added to a solution of 2-hydroxy-5-nitrobenzaldehyde (1.97 g, 11.8 mmol) in DMF (20 mL) at room temperature. After stirring at 50 °C for 5 h the reaction was cooled to room temperature, water (20 mL) and EtOAc (20 mL) were introduced, and the phases were separated. The aqueous phase was extracted with EtOAc (2 x 10 mL), the combined organic layers were washed with brine and dried over $MgSO_4$, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 60:40) to give the title compound as a light yellow solid (1.09 g, 44%). IR (film) ṽ 1678, 1607, 1589, 1524, 1480, 1340, 1278, 1109, 1075, 950, 831, 748, 667 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 10.46 (s, 1H), 8.70 (d, *J* = 3.0 Hz, 1H), 8.40 (dd, *J* = 9.3, 2.9 Hz, 1H), 7.09 (d, *J* = 9.6 Hz, 1H), 4.84 (hept, *J* = 6.1 Hz, 1H), 1.48 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 164.5, 141.3, 130.6, 125.2, 124.9, 113.8, 72.8, 22.0. HRMS (ESI) calcd for $C_{10}H_{11}NO_4Na$ $[M+Na]^+$: 232.0580; found: 232.0581. The spectral data are consistent with those reported in the literature.[8]



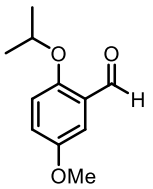
$C_{10}H_{11}NO_4$
M = 209.20 g/mol

5-(*tert*-Butyl)-2-isopropoxybenzaldehyde (S1f). Prepared analogously from 5-(*tert*-butyl)-2-hydroxybenzaldehyde as a colorless oil (1.07 g, 90%). IR (film) ṽ 2964, 2867, 1682, 1606, 1494, 1385, 1365, 1263, 1245, 1191, 1137, 1111, 954 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.84 (d, *J* = 2.7 Hz, 1H), 7.55 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 1H), 4.65 (hept, *J* = 6.0 Hz, 1H), 1.39 (d, *J* = 6.1 Hz, 6H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 158.8, 143.4, 133.2, 125.2, 124.8, 114.0, 71.3, 34.4, 31.4, 22.2. HRMS (EI) calcd for $C_{14}H_{20}O_2$ $[M]^{+\bullet}$: 220.1458; found: 220.1458.



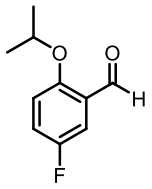
$C_{14}H_{20}O_2$
M = 220.31 g/mol

2-Isopropoxy-5-methoxybenzaldehyde (S1g). Prepared analogously from 2-hydroxy-5-methoxybenzaldehyde as a pale yellow oil (1.75 g, 88%). IR (film) ṽ 2978, 1682, 1490, 1423, 1386, 1275, 1217, 1158, 1038, 952, 820 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.31 (d, *J* = 3.3 Hz, 1H), 7.11 (dd, *J* = 9.0, 3.3 Hz, 1H), 6.96 (d, *J* = 9.0 Hz, 1H), 4.57 (hept, *J* = 6.1 Hz, 1H), 3.80 (s, 3H), 1.37 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 155.5, 153.8, 126.5, 123.9, 116.9, 109.9, 72.4, 55.9, 22.2. HRMS (EI) calcd for $C_{11}H_{14}O_3$ $[M]^{+\bullet}$: 194.0937; found: 194.09938. The spectral data are consistent with those reported in the literature.[8]



$C_{11}H_{14}O_3$
M = 194.23 g/mol

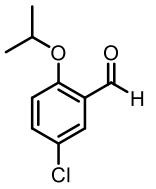
5-Fluoro-2-isopropoxybenzaldehyde (S1h). Prepared analogously from 5-fluoro-2-hydroxybenzaldehyde as a colorless oil (812 mg, 92%). IR (film) ṽ 2980, 2868, 1682, 1613, 1483, 1426, 1386, 1257, 1200, 1138, 1111, 1088, 948, 729 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 10.43 (d, *J* = 3.3 Hz, 1H), 7.49 (dd, *J* = 8.4, 3.3 Hz, 1H), 7.23 (ddd, *J* = 9.1, 7.7, 3.4 Hz, 1H), 6.96 (dd, *J* = 9.1, 3.9 Hz, 1H), 4.61 (hept, *J* = 6.1 Hz, 1H), 1.39 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.3 (d, *J* = 2.0 Hz), 157.02 (d, *J* = 2.5 Hz), 159.9 (d, *J* = 241.9 Hz), 126.8 (d, *J* = 6.0 Hz), 122.6 (d, *J* = 24.1 Hz),



$C_{10}H_{11}FO_2$
M = 182.19 g/mol

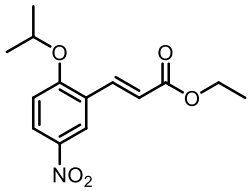
116.2 (d, *J* = 7.0 Hz), 114.0 (d, *J* = 23.1 Hz), 72.3, 22.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ −122.6. HRMS (EI) calcd for $C_{10}H_{11}FO_2$ $[M]^{+\bullet}$: 182.0738; found: 182.0738.

5-Chloro-2-isopropoxybenzaldehyde (S1i). Prepared analogously from 5-chloro-2-hydroxybenzaldehyde as a colorless oil (1.78 g, 86%). IR (film) ṽ 2980, 2870, 1684, 1595, 1476, 1387, 1269, 1238, 1128, 1107, 950, 901 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 7.78 (d, *J* = 2.8 Hz, 1H), 7.45 (dd, *J* = 8.9, 2.8 Hz, 1H), 6.94 (d, *J* = 9.0 Hz, 1H), 4.65 (hept, *J* = 6.0 Hz, 1H), 1.40 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.0, 159.1, 135.4, 128.0, 126.7, 126.2, 115.8, 71.9, 22.0. HRMS (EI) calcd for $C_{10}H_{11}ClO_2$ $[M]^{+\bullet}$: 198.0442; found: 198.0442.



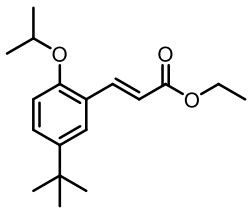
$C_{10}H_{11}ClO_2$
M = 198.65 g/mol

Ethyl (*E*)-3-(2-isopropoxy-5-nitrophenyl)acrylate (8j). LiBr (368 mg, 4.24 mmol) was added to a solution of triethyl phosphonoacetate (0.68 mL, 3.43 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.51 mL, 3.41 mmol) in MeCN (20 mL) at room temperature. The mixture was stirred for 30 min before a solution of aldehyde **S1j** (593 mg, 2.83 mmol) in MeCN (5 mL) was added dropwise. Stirring was continued at room temperature for 16 h before water (20 mL) and *tert*-butyl methyl ether (20 mL) were introduced and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 10 mL), the combined organic layers were washed with brine and dried over $MgSO_4$, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 70:30) to give the title compound as a pale yellow solid (673 mg, 85%). IR (film) ṽ 2982, 2937, 1712, 1636, 1608, 1584, 1517, 1483, 1342, 1275, 1179, 1104, 955, 824, 742 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 2.9 Hz, 1H), 8.21 (dd, *J* = 9.3, 2.8 Hz, 1H), 7.94 (d, *J* = 16.5 Hz, 1H), 6.97 (d, *J* = 9.3 Hz, 1H), 6.60 (d, *J* = 16.2 Hz, 1H), 4.76 (hept, *J* = 6.0 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 1.45 (d, *J* = 6.1 Hz, 6H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 161.3, 141.1, 138.0, 126.7, 124.9, 124.5, 121.4, 112.7, 72.3, 60.8, 22.0, 14.4. HRMS (ESI) calcd for $C_{14}H_{17}NO_5Na$ $[M+Na]^+$: 302.0999; found: 302.0999.



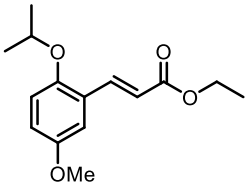
$C_{14}H_{17}NO_5$
M = 279.29 g/mol

Ethyl *(E)*-3-{5-(tert-butyl)-2-isopropoxyphenyl}acrylate (8f). Prepared analogously from aldehyde **S1f** as a colorless oil (1.21 g, 87%). IR (film) ṽ 2963, 1709, 1630, 1492, 1365, 1317, 1272, 1248, 1164, 1112, 1039, 990 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 16.2 Hz, 1H), 7.51 (d, *J* = 2.7 Hz, 1H), 7.33 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.85 (d, *J* = 8.9 Hz, 1H), 6.53 (d, *J* = 16.1 Hz, 1H), 4.57 (hept, *J* = 6.1 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 1.37 (d, *J* = 6.1 Hz, 6H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 154.9, 143.2, 141.2, 128.5, 126.0, 123.7, 118.2, 113.6, 71.0, 60.4, 34.2, 31.5, 22.3, 14.5. HRMS (EI) calcd for $C_{18}H_{26}O_3$ $[M]^{+\bullet}$: 290.1876; found: 290.1877.



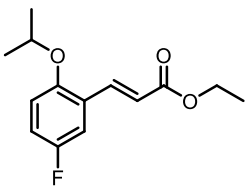
$C_{18}H_{26}O_3$
M = 290.40 g/mol

Ethyl (*E*)-3-(2-isopropoxy-5-methoxyphenyl)acrylate (8g). Prepared analogously from aldehyde **S1g** as a pale yellow oil (2.14 g, 90%). IR (film) ṽ 2978, 1709, 1631, 1492, 1368, 1286, 1215, 1175, 1041, 989, 852 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 16.1 Hz, 1H), 7.07–7.01 (m, 1H), 6.93–6.83 (m, 2H), 6.47 (d, J = 16.2 Hz, 1H), 4.46 (hept, J = 6.1 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 3.79 (s, 3H), 1.38–1.28 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 153.7, 151.3, 140.2, 125.7, 118.7, 117.6, 116.6, 112.6, 72.4, 60.5, 55.9, 22.3, 14.5. HRMS (EI) calcd for $C_{15}H_{20}O_4$ $[M]^{+\bullet}$: 264.1356; found: 264.1356.



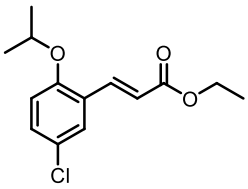
$C_{15}H_{20}O_4$
M = 264.32 g/mol

Ethyl (*E*)-3-(5-fluoro-2-isopropoxyphenyl)acrylate (8h). Prepared analogously from aldehyde **S1h** as a colorless oil (1.02 g, 91%). IR (film) ṽ 2980, 2938, 1711, 1633, 1487, 1368, 1320, 1253, 1177, 1116, 1037, 988, 948 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 16.2, 1.7 Hz, 1H), 7.21 (dd, J = 9.3, 3.2 Hz, 1H), 7.01 (ddd, J = 9.1, 7.7, 3.2 Hz, 1H), 6.86 (dd, J = 9.1, 4.6 Hz, 1H), 6.45 (d, J = 16.2 Hz, 1H), 4.51 (hept, J = 6.1 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 1.36 (d, J = 6.1 Hz, 6H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 156.9 (d, J = 239.4 Hz), 153.1 (d, J = 2.5 Hz), 139.2 (d, J = 2.5 Hz), 126.1 (d, J = 7.0 Hz), 119.6, 117.7 (d, J = 23.6 Hz), 115.8 (d, J = 8.0 Hz), 114.4 (d, J = 23.1 Hz), 72.2, 60.6, 22.2, 14.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ −123.3. HRMS (EI) calcd for $C_{14}H_{17}FO_3$ $[M]^{+\bullet}$: 252.1162; found: 252.1157.



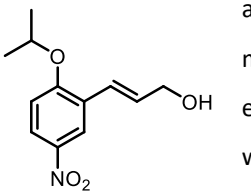
$C_{14}H_{17}FO_3$
M = 252.29 g/mol

Ethyl (*E*)-3-(5-chloro-2-isopropoxyphenyl)acrylate (8i). Prepared analogously from aldehyde **S1i** as a colorless oil (2.00 g, 85%). IR (film) ṽ 2979, 2935, 1711, 1633, 1480, 1367, 1315, 1269, 1249, 1175, 1129, 1108, 1038, 987 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 16.2 Hz, 1H), 7.47 (d, J = 2.8 Hz, 1H), 7.25 (dd, J = 8.8, 2.6 Hz, 1H), 6.84 (d, J = 9.3 Hz, 1H), 6.48 (d, J = 16.1 Hz, 1H), 4.56 (hept, J = 6.1 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 1.37 (d, J = 6.1 Hz, 6H), 1.33 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 155.4, 139.0, 130.8, 128.3, 126.1, 125.7, 119.8, 115.3, 71.6, 60.6, 22.1, 14.5. HRMS (ESI) calcd for $C_{14}H_{17}ClO_3$ $[M]^{+\bullet}$: 268.0866; found: 268.0862.



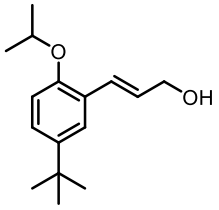
$C_{14}H_{17}ClO_3$
M = 268.74 g/mol

(*E*)-3-(2-Isopropoxy-5-nitrophenyl)prop-2-en-1-ol (10j). DIBAL-H (25 wt. % in toluene, 4.18 mL, 5.88 mmol) was added slowly to a solution of ester **8j** (656 mg, 2.35 mmol) in CH_2Cl_2 (20 mL) at −78 °C. The mixture was warmed to −30 °C and stirring was continued for 3 h before *tert*-butyl methyl ether (20 mL) and a sat. Rochelle salt solution (20 mL) were introduced. The mixture was warmed to room temperature and vigorously stirred for 2 h until clean separation of the layers was reached. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 15 mL), the combined organic layers were washed with brine and dried over $MgSO_4$, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography (silica, hexanes/EtOAc 60:40) to give the title compound as an orange solid (513 mg, 92%). IR (film) ṽ 3380 (br), 2981, 2933, 1582, 1512, 1484, 1339, 1260, 1106, 972, 949, 816, 748 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 2.8 Hz, 1H), 8.10 (dd, J = 9.1, 2.8 Hz, 1H), 6.96–6.85 (m, 2H), 6.50 (dt, J = 16.0, 5.4 Hz, 1H), 4.76–4.66 (m, 1H), 4.38 (br s, 2H), 1.42 (d, J = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 141.1, 131.8, 127.4, 124.5, 124.2, 122.9, 112.3, 71.7, 63.9, 22.1. HRMS (ESI) calcd for $C_{12}H_{15}NO_4Na$ $[M+Na]^+$: 260.0893; found: 260.0864.



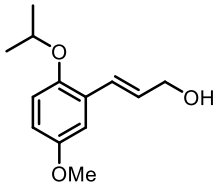
$C_{12}H_{15}NO_4$
M = 237.26 g/mol

***(E)*-3-[5-(tert-Butyl)-2-isopropoxyphenyl]prop-2-en-1-ol (10f).** Prepared analogously from ester **8f** as a colorless oil (351 mg, 94%). IR (film) ṽ 3407 (br), 2694, 1605, 1493, 1363, 1243, 1137, 1113, 972, 959, 908, 732 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 2.5 Hz, 1H), 7.21 (dd, J = 8.6, 2.5 Hz, 1H), 6.93 (dt, J = 16.3, 1.6 Hz, 1H), 6.81 (d, J = 8.7 Hz, 1H), 6.40 (dt, J = 16.1, 6.1 Hz, 1H), 4.51 (hept, J = 6.0 Hz, 1H), 4.33 (dd, J = 6.1, 1.5 Hz, 2H), 1.35 (d, J = 6.1 Hz, 6H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 143.3, 128.4, 127.4, 126.0, 125.7, 124.1, 113.7, 70.9, 64.6, 34.2, 31.6, 22.4. HRMS (EI) calcd for $C_{16}H_{24}O_2$ $[M]^{+\bullet}$: 248.1771; found: 248.1775.



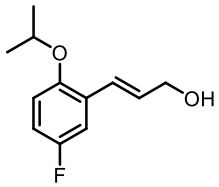
$C_{16}H_{24}O_2$
M = 248.37 g/mol

(*E*)-3-(2-Isopropoxy-5-methoxyphenyl)prop-2-en-1-ol (10g). Prepared analogously from ester **8g** as a colorless oil (562 mg, 92%). IR (film) ṽ 3385 (br), 2976, 2935, 1492, 1427, 1372, 1286, 1214, 1110, 1041, 974 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, J = 3.0 Hz, 1H), 6.92 (d, J = 16.1 Hz, 1H), 6.84 (d, J = 8.9 Hz, 1H), 6.76 (dd, J = 9.0, 3.0 Hz, 1H), 6.36 (dt, J = 16.0, 6.0 Hz, 1H), 4.40 (hept, J = 6.1 Hz, 1H), 4.33 (t, J = 6.0 Hz, 2H), 3.78 (s, 3H), 1.41 (t, J = 6.0 Hz, 1H, OH), 1.32 (d, J = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 149.6, 129.1, 128.3, 126.6, 116.9, 114.3, 111.7, 72.3, 64.4, 55.8, 22.4. HRMS (EI) calcd for $C_{13}H_{18}O_3$ $[M]^{+\bullet}$: 222.1250; found: 222.1252.



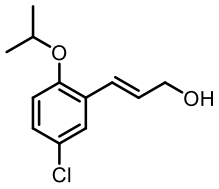
$C_{13}H_{18}O_3$
M = 222.28 g/mol

(*E*)-3-(5-Fluoro-2-isopropoxyphenyl)prop-2-en-1-ol (10h). Prepared analogously from ester **8h** as a colorless oil (546 mg, 97%). IR (film) ṽ 3360 (br), 2978, 2933, 1487, 1428, 1384, 1373, 1246, 1114, 973, 951 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 (dd, J = 9.5, 3.0 Hz, 1H), 6.94–6.78 (m, 3H), 6.35 (dt, J = 16.1, 5.8 Hz, 1H), 4.45 (hept, J = 6.0 Hz, 1H), 4.34 (dd, J = 5.7, 1.6 Hz, 2H), 1.33 (d, J = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3 (d, J = 238.4 Hz), 151.4 (d, J = 2.0 Hz), 130.0, 128.7 (d, J = 7.5 Hz), 125.6 (d, J = 2.0 Hz,), 116.1 (d, J = 8.5 Hz,), 114.9 (d, J = 23.6 Hz), 113.0 (d, J = 23.6 Hz), 72.1, 64.1, 22.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ −123.4. HRMS (ESI) calcd for $C_{12}H_{15}FO_2Na$ $[M+Na]^+$: 233.0948; found: 233.0950.



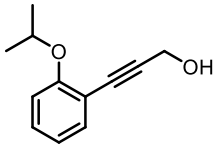
$C_{12}H_{15}FO_2$
M = 210.25 g/mol

(*E*)-3-(5-Chloro-2-isopropoxyphenyl)prop-2-en-1-ol (10i). Prepared analogously from ester **8i** as a white solid (628 mg, 94%). IR (film) ṽ 3349 (br), 2978, 2931, 1479, 1385, 1373, 1244, 1129, 1109, 972, 954 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 2.7 Hz, 1H), 7.13 (dd, J = 8.9, 2.7 Hz, 1H), 6.86 (d, J = 16.1 Hz, 1H), 6.80 (d, J = 9.3 Hz, 1H), 6.36 (dt, J = 16.0, 5.7 Hz, 1H), 4.50 (hept, J = 6.1 Hz, 1H), 4.34 (d, J = 4.2 Hz, 2H), 1.34 (d, J = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 130.1, 128.6, 128.3, 126.8, 125.7, 125.3, 115.4, 71.4, 64.2, 22.2. HRMS (ESI) calcd for $C_{12}H_{15}ClO_2Na$ $[M+Na]^+$: 249.0653; found: 249.0654.



$C_{12}H_{15}ClO_2$
M = 226.70 g/mol

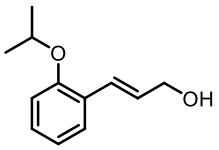
3-(2-Isopropoxyphenyl)prop-2-yn-1-ol (11). 2-Propyn-1-ol (0.187 mL, 3.22 mmol) and iodide **9** (805 mg, 3.07 mmol) were added to a solution of $PdCl_2(PPh_3)_2$ (43.1 mg, 61.4 μmol) and CuI (23.4 mg, 123 μmol) in Et_3N (15 mL). After stirring at room temperature for 5 h, the mixture was filtered through a pad of Celite and the filter cake was washed with EtOAc (20 mL). The combined filtrates were evaporated under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 60:40) to give the title compound as an



$C_{12}H_{14}O_2$
M = 190.24 g/mol

orange oil (497 mg, 85%). IR (film) ṽ 3361 (br), 2978, 2932, 2871, 1564, 1488, 1446, 1384, 1261, 1122, 1024, 960, 753 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, J = 7.8, 1.7 Hz, 1H), 7.28–7.22 (m, 1H), 6.92–6.85 (m, 2H), 4.57 (hept, J = 6.0 Hz, 1H), 4.53 (s, 2H), 1.37 (d, J = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 133.9, 129.9, 120.8, 115.0, 113.7, 91.1, 82.6, 72.0, 52.1, 22.3. HRMS (ESI) calcd for $C_{12}H_{14}O_2Na$ $[M+Na]^+$: 213.0886; found: 213.0886.

(*E*)-3-(2-Isopropoxyphenyl)prop-2-en-1-ol (10a). A solution of alcohol **11** (455 mg, 2.4 mmol) in THF (5 mL) was slowly added to a suspension of $LiAlH_4$ (272 mg, 7.2 mmol) in THF (15 mL) at 0 °C. The mixture was warmed to room temperature and stirring was continued for 3 h before water (2 mL) and NaOH (2 mL, 15% in water) were carefully added. The mixture was stirred for 15 min at room temperature before more water (5 mL) was added. After stirring for additional 15 min, the suspension was filtrated through a pad of Celite, the residue was washed with EtOAc (20 mL) and the combined filtrates were dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 60:40) to give the title compound as a yellow oil (425 mg, 92%). IR (film) ṽ 3344 (br), 2976, 1597, 1484, 1452, 1372, 1238, 1117, 974, 955, 749 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J = 7.6, 1.7 Hz, 1H), 7.20 (ddd, J = 8.2, 7.4, 1.8 Hz, 1H), 6.98–6.86 (m, 3H), 6.38 (dt, J = 16.0, 6.0 Hz, 1H), 4.60–4.51 (m, 1H), 4.33 (dd, J = 6.0, 1.5 Hz, 2H), 1.52 (br s, 1H, OH), 1.36 (d, J = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 128.79, 128.76, 127.2, 126.9, 126.8, 120.7, 114.1, 70.9, 64.5, 22.3. HRMS (ESI) calcd for $C_{12}H_{16}O_2Na$ $[M+Na]^+$: 215.1042; found: 215.1043.

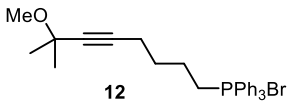


$C_{12}H_{16}O_2$
M = 192.26 g/mol

(*Z*)-3-(2-Isopropoxyphenyl)prop-2-en-1-ol (S6). Lindlar's catalyst (80 mg) and quinoline (3 drops) were added to a solution of alcohol **11** (370 mg, 1.94 mmol) in MeOH (10 mL) at room temperature. The reaction was purged with H_2 for 2 min and then stirred at room temperature for 16 h under hydrogen atmosphere. The suspension was filtered through a pad of Celite and the filter cake was washed with EtOAc (20 mL). The combined filtrates were evaporated under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 60:40) to give the title compound as a pale yellow oil (358 mg, 96%). IR (film) ṽ 3326 (br), 2976, 2932, 1596, 1484, 1450, 1383, 1373, 1287, 1240, 1117, 1015, 954, 751 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.25–7.20 (m, 1H), 7.11 (dd, J = 7.4, 1.7 Hz, 1H), 6.94–6.88 (m, 2H), 6.68 (d, J = 11.7 Hz, 1H), 5.89 (dt, J = 11.6, 6.7 Hz, 1H), 4.58–4.47 (m, 1H), 4.32 (br s, 2H), 1.62 (br s, 1H, OH), 1.34 (d, J = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 130.6, 130.5, 128.8, 127.4, 126.9, 120.4, 114.2, 71.1, 60.1, 22.3. HRMS (EI) calcd for $C_{12}H_{16}O_2$ $[M]^{+\bullet}$: 192.1145; found: 192.1142.

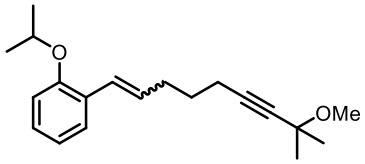
$C_{12}H_{16}O_2$
M = 192.26 g/mol

1-Isopropoxy-2-(8-methoxy-8-methylnon-1-en-6-yn-1-yl)-benzene (6a). A pressure Schlenk flask was charged with a solution of bromide **S4** (337 mg, 1.45 mmol) in toluene (6 mL). PPh_3 (417 mg, 1.59 mmol) was added and the mixture was stirred at 110 °C (bath temperature) for 4 d. The mixture was cooled to 0 °C, causing the precipitation of a white solid. The supernatant was removed with the aid of a filter canula, and the residue was washed with diethyl ether (3 × 10 mL) and dried in high vacuum to afford the corresponding phosphonium salt **12** as a white powder, which was used in the next step without further purification (650 mg, 91%).



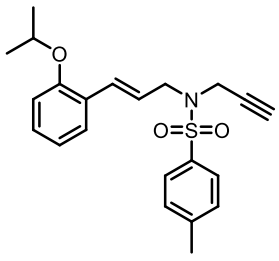
12

A pressure Schlenk flask was charged with the crude phosphonium salt (300 mg, 606 µmol) and K_2CO_3 (200 mg, 1.45 mmol). A solution of 2-isopropoxybenzaldehyde (**S1a**, 50 mg, 305 µmol) in toluene (2.5 mL) was added and the mixture was stirred at 110 °C for 2 d. After reaching ambient temperature, the mixture was filtered through a short silica plug, which was rinsed with pentane/*tert*-butyl methyl ether (20:1, 40 mL). The combined filtrate was evaporated under reduced pressure to provide a colorless oil, which was re-dissolved in MeOH (5 mL). Sat. aq. $NaHSO_3$ (1.5 mL) was added and the mixture was vigorously stirred for 1 min, before H_2O (25 mL) and hexanes/EtOAc (10:1, 25 mL) were added. The phases were separated, the organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/*tert*-butyl methyl ether 40:1) to provide the title compound as an inseparable mixture of double bond isomers (46 mg, 50%, *E:Z* ≈ 2:5). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.41 (dd, *J* = 7.9, 2.0 Hz, 1H, minor isomer), 7.24 (ddd, *J* = 7.7, 1.8, 0.6 Hz, 1H, major isomer), 7.21 – 7.11 (m, 1H, both isomers), 6.95 – 6.84 (m, 2H, both isomers), 6.73 (dt, *J* = 16.0, 1.5 Hz, 1H, minor isomer), 6.54 (dt, *J* = 11.9, 2.1 Hz, 1H, major isomer), 6.19 (dt, *J* = 16.0, 7.0 Hz, 1H, minor isomer), 5.65 (dt, *J* = 11.7, 7.3 Hz, 1H, major isomer), 4.52 (pdd, *J* = 6.1, 4.0, 0.5 Hz, 1H, both isomers), 3.31 (s, 3H, minor isomer), 3.22 (s, 3H, major isomer), 2.48 – 2.17 (m, 4H, both isomers), 1.73 – 1.59 (m, 2H, both isomers), 1.43 – 1.28 (m, 12H, both isomers). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 156.0, 155.2, 131.5, 130.5, 130.4, 128.4, 128.3, 128.2, 128.1, 126.7, 125.9, 125.8, 121.0, 120.4, 114.8, 114.4, 84.6, 84.4, 82.8, 82.7, 71.3, 71.1, 70.8, 70.8, 51.5, 51.4, 32.8, 29.5, 29.0, 28.9, 28.8, 28.2, 22.3, 18.6, 18.3. IR (film) ṽ 2979, 2933, 1484, 1451, 1236, 1171, 1149, 1137, 1119, 1077, 956, 750 cm^{-1}. HRMS (ESI$^+$) calcd for $C_{20}H_{28}O_2$ [M+Na]$^+$: 323.19815; found: 323.19786.



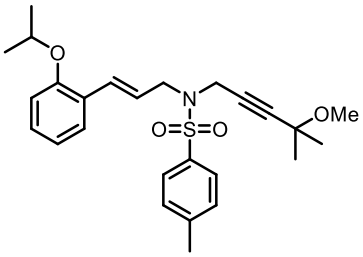
$C_{20}H_{28}O_2$
M = 300,44

***(E)*-*N*-[3-(2-Isopropoxyphenyl)allyl]-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (S7).** *N*-Tosyl-*N*-propargyl amine **S3** (440 mg, 2.10 mmol) and PPh_3 (881 mg, 3.36 mmol) were added to a solution of allylic alcohol **10a** (404 mg, 2.10 mmol) in THF (10 mL). The mixture was cooled to 0 °C before diisopropyl azodicarboxylate (0.62 mL, 3.15 mmol) was added dropwise. Stirring was continued at room temperature for 19 h before the solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 80:20) to give the title compound as colorless oil (645 mg, 80%). IR (film) ṽ 3282, 2976, 2932, 2871, 1597, 1485, 1454, 1348, 1241, 1118, 1094, 898, 749, 659 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.77 (m, app. br d, *J* = 8.3 Hz, 2H), 7.36 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.30 (m, app. br d, *J* = 7.8 Hz, 2H), 7.20 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H), 6.94–6.84 (m, 3H), 6.06 (dt, *J* = 16.0, 7.0 Hz, 1H), 4.55–4.48 (m, 1H), 4.14 (d, *J* = 2.5 Hz, 2H), 4.00 (dd, *J* = 7.0, 1.3 Hz, 2H), 2.43 (s, 3H), 2.03 (t, *J* = 2.5 Hz, 1H), 1.32 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 155.4, 143.6, 136.3, 130.8, 129.6, 129.1, 128.0, 127.3, 126.6, 123.0, 120.8, 114.4, 73.8, 72.4, 71.1, 49.3, 35.9, 22.3, 21.7. HRMS (ESI) calcd for $C_{22}H_{25}NO_3SNa$ [M+Na]$^+$: 406.1447; found: 406.1446.



$C_{22}H_{25}NO_3S$
M = 383.51 g/mol

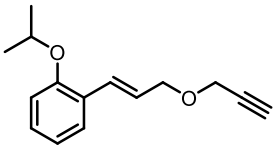
***(E)*-*N*-[3-(2-Isopropoxyphenyl)allyl]-*N*-(4-methoxy-4-methylpent-2-yn-1-yl)-4-methylbenzenesulfonamide**



$C_{26}H_{33}NO_4S$
M = 455.61 g/mol

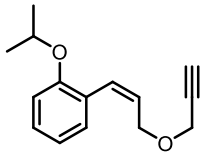
(6b). *n*-BuLi (1.6 M in hexanes, 0.80 mL, 1.28 mmol) was added slowly to a solution of alkyne **S7** (406 mg, 1.06 mmol) in THF (10 mL) at 0 °C. The solution was stirred for 30 min at 0 °C before acetone (0.10 mL, 1.40 mmol) was introduced and stirring was continued for 30 min. For work-up, sat. NH_4Cl solution (5 mL) and EtOAc (10 mL) were added, the layers were separated and the aqueous phase was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was dissolved in THF (10 mL). NaH (50 mg, 2.10 mmol) was added to the solution at 0 °C and the resulting mixture was stirred for 10 min before MeI (0.33 mL, 5.30 mmol) was carefully added at 0 °C. After stirring for another 2 h at room temperature, water (2 mL) and *tert*-butyl methyl ether (10 mL) were introduced and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 10 mL), the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 80:20) to give the title compound as a yellow oil (116 mg, 24%). IR (film) ṽ 2980, 2934, 1710, 1597, 1485, 1454, 1349, 1242, 1161, 1117, 902, 817, 748 cm^{-1}- ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (m, app. br d, *J* = 8.3 Hz, 2H), 7.38 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.31 (m, app. br d, *J* = 8.0 Hz, 2H), 7.20 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 6.94–6.83 (m, 3H), 6.10 (dt, *J* = 15.9, 7.0 Hz, 1H), 4.58–4.49 (m, 1H), 4.19 (s, 2H), 4.01 (dd, *J* = 7.0, 1.3 Hz, 2H), 3.14 (s, 3H), 2.42 (s, 3H), 1.32 (d, *J* = 6.0 Hz, 6H), 1.22 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 143.5, 136.5, 130.3, 129.7, 129.1, 127.9, 127.2, 126.3, 123.1, 120.7, 114.1, 87.7, 77.0, 70.8, 70.3, 51.7, 49.2, 36.1, 28.2, 22.3, 21.6. HRMS (ESI) calcd for $C_{26}H_{33}NO_4SNa$ $[M+Na]^+$: 478.2022; found: 478.2021.

***(E)*-1-Isopropoxy-2-[3-(prop-2-yn-1-yloxy)prop-1-en-1-yl]benzene (S8).** NaH (53 mg, 2.21 mmol) was added to a solution of alcohol **10a** (354 mg, 1.84 mmol) in DMF (4 mL) at 0 °C. The suspension was stirred for 20 min before propargyl bromide (0.196 mL, 2.21 mmol) was added and stirring was continued at room temperature for 16 h. Water (10 mL) was introduced and the mixture was extracted with *tert*-butyl methyl ether (3 × 10 mL). The combined organic phases were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 90:10) to give the title compound as an orange oil (378 mg, 89%). IR (film) ṽ 3293, 2977, 2933, 2852, 1597, 1485, 1453, 1384, 1240, 1117, 1081, 954, 751 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.20 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H), 6.97 (d, *J* = 16.1 Hz, 1H), 6.93–6.85 (m, 2H), 6.28 (dt, *J* = 16.1, 6.4 Hz, 1H), 4.55 (hept, *J* = 6.1 Hz, 1H), 4.26 (dd, *J* = 6.5, 1.4 Hz, 2H), 4.20 (d, *J* = 2.4 Hz, 2H), 2.45 (t, *J* = 2.4 Hz, 1H), 1.36 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 129.2, 128.9, 127.3, 126.8, 125.2, 120.7, 114.3, 80.0, 74.5, 71.04, 70.97, 57.0, 22.3. HRMS (EI) calcd for $C_{15}H_{18}O_2$ $[M]^{+\bullet}$: 230.1301; found: 230.1300.



$C_{15}H_{18}O_2$
M = 230.31 g/mol

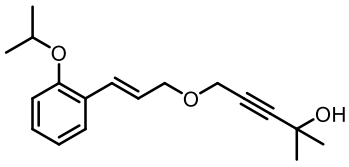
(*Z*)-1-Isopropoxy-2-[3-(prop-2-yn-1-yloxy)prop-1-en-1-yl]benzene (S9). Prepared analogously from alcohol **S6** as



$C_{15}H_{18}O_2$
M = 230.31 g/mol

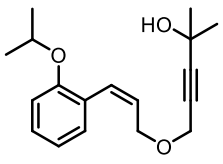
an orange oil (374 mg, 91%). IR (film) ṽ 3292, 2977, 2933, 1597, 1485, 1451, 1373, 1287, 1243, 1117, 1093, 954, 753 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.25–7.20 (m, 1H), 7.17 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.94–6.86 (m, 2H), 6.79 (d, *J* = 11.7 Hz, 1H), 5.83 (dt, *J* = 11.8, 6.6 Hz, 1H), 4.58–4.47 (m, 1H), 4.27 (dd, *J* = 6.6, 1.6 Hz, 2H), 4.16 (d, *J* = 2.4 Hz, 2H), 2.39 (t, *J* = 2.4 Hz, 1H), 1.33 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7 , 130.5, 128.9, 128.8, 127.1, 126.8, 120.2, 113.9, 79.9, 74.5, 70.9, 67.1, 57.6, 22.3. HRMS (ESI) calcd for $C_{15}H_{18}O_2Na$ $[M+Na]^+$: 253.1199; found: 253.1199.

***(E)*-5-{[3-(2-Isopropoxyphenyl)allyl]oxy}-2-methylpent-3-yn-2-ol (S10).** *n*-BuLi (1.6 M in hexanes, 1.2 mL, 1.92 mmol) was slowly added to a solution of alkyne **S8** (369 mg, 1.6 mmol) in THF (10 mL) at 0 °C. The solution was stirred for 30 min at 0 °C before acetone (0.15 mL, 2.04 mmol) was introduced and stirring was continued for 30 min. For work up, sat. NH_4Cl solution (5 mL) and EtOAc (10 mL) were introduced, the layers were separated and the aqueous phase was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 70:30) to give the title compound as yellow oil (304 mg, 66%). IR (film) ṽ 3412 (br), 2978, 2932, 2852, 1597, 1485, 1453, 1372, 1239, 1168, 1117, 953, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.19 (ddd, *J* = 8.1, 7.4, 1.7 Hz, 1H), 6.96 (dt, *J* = 16.0, 1.5 Hz, 1H), 6.93–6.86 (m, 2H), 6.28 (dt, *J* = 16.0, 6.5 Hz, 1H), 4.55 (hept, *J* = 6.0 Hz, 1H), 4.23 (dd, *J* = 6.5, 1.4 Hz, 2H), 4.21 (s, 2H), 1.95 (br s, 1H, OH), 1.54 (s, 6H), 1.36 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 129.0, 128.9, 127.2, 126.8, 125.3, 120.7, 114.3, 91.2, 78.3, 71.1, 71.0, 65.3, 57.3, 31.5, 22.4. HRMS (ESI) calcd for $C_{18}H_{24}O_3Na$ $[M+Na]^+$: 311.1618; found: 311.1620.



$C_{18}H_{24}O_3$
M = 288.39 g/mol

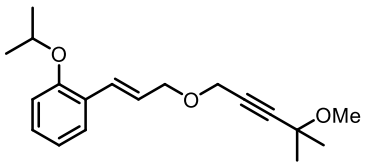
(*Z*)-5-{[3-(2-Isopropoxyphenyl)allyl]oxy}-2-methylpent-3-yn-2-ol (S11). Prepared analogously from alkyne **S9** as



$C_{18}H_{24}O_3$
M = 288.39 g/mol

a yellow oil (244 mg, 66%). IR (film) ṽ 3405 (br), 2978, 2933, 1597, 1485, 1451, 1373, 1242, 1169, 1118, 1090, 953, 754 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.27–7.18 (m, 1H), 7.15 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.96–6.85 (m, 2H), 6.78 (d, *J* = 11.3 Hz, 1H), 5.82 (dt, *J* = 11.7, 6.6 Hz, 1H), 4.52 (h, *J* = 6.0 Hz, 1H), 4.26 (dd, *J* = 6.7, 1.6 Hz, 2H), 4.16 (s, 2H), 1.45 (s, 6H), 1.33 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 130.6, 129.1, 128.8, 127.3, 126.9, 120.2, 113.9, 91.2, 78.1, 70.9, 66.6, 65.2, 57.5, 31.4, 22.3. HRMS (ESI) calcd for $C_{18}H_{24}O_3Na$ $[M+Na]^+$: 311.1618; found: 311.1617.

***(E)*-1-Isopropoxy-2-{3-[(4-methoxy-4-methylpent-2-yn-1-yl)oxy]prop-1-en-1-yl}benzene (*trans*-6c).** NaH (49 mg, 2.04 mmol) was added to a solution of alcohol **S10** (295 mg, 1.02 mmol) in THF (10 mL) at 0 °C. The mixture was stirred for 10 min before MeI (0.32 mL, 5.14 mmol) was carefully added at 0 °C. After stirring for another 2 h at room temperature, water (2 mL) and *tert*-butyl methyl ether (10 mL) were introduced and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 10 mL), the combined organic layers were



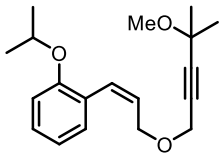
$C_{19}H_{26}O_3$
M = 302.41 g/mol

washed with brine and dried over $MgSO_4$, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 80:20) to give the title compound as a yellow oil (290 mg, 94%).

Alternatively, enyne *trans*-**6c** (768 mg, 65%) was made by direct O-alkylation of compound **10a** with bromide **13** under the conditions described below for product **6j** (NaH, DMF, 0°C).

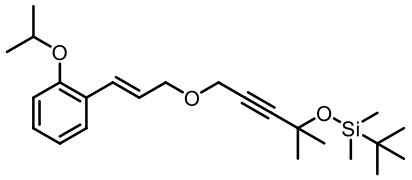
IR (film) ṽ 2980, 2935, 1597, 1485, 1453, 1375, 1359, 1240, 1173, 1117, 1076, 955, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, J = 7.6, 1.7 Hz, 1H), 7.19 (ddd, J = 8.2, 7.4, 1.7 Hz, 1H), 6.96 (d, J = 16.1 Hz, 1H), 6.93–6.85 (m, 2H), 6.28 (dt, J = 16.1, 6.5 Hz, 1H), 4.55 (hept, J = 6.1 Hz, 1H), 4.27–4.22 (m, 4H), 3.38 (s, 3H), 1.47 (s, 6H), 1.35 (d, J = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 129.0, 128.9, 127.2, 126.8, 125.3, 120.7, 114.2, 88.3, 80.3, 70.92, 70.87, 70.7, 57.2, 51.8, 28.5, 22.3. HRMS (ESI) calcd for $C_{19}H_{26}O_3Na$ $[M+Na]^+$: 325.1774; found: 325.1778.

(*Z*)-1-Isopropoxy-2-{3-[(4-methoxy-4-methylpent-2-yn-1-yl)oxy]prop-1-en-1-yl}benzene (*cis*-6c). Prepared analogously from alcohol **S11** as a pale yellow oil (215 mg, 89%). IR (film) ṽ 2980, 2935, 1597, 1485, 1451, 1376, 1244, 1173, 1118, 1077, 955, 753 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.25–7.18 (m, 1H), 7.15 (dd, J = 7.5, 1.8 Hz, 1H), 6.93–6.86 (m, 2H), 6.78 (d, J = 11.3 Hz, 1H), 5.83 (dt, J = 11.7, 6.6 Hz, 1H), 4.57–4.47 (m, 1H), 4.27 (dd, J = 6.6, 1.6 Hz, 2H), 4.19 (s, 2H), 3.27 (s, 3H), 1.39 (s, 6H), 1.33 (d, J = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 130.5, 128.9, 128.8, 127.4, 126.8, 120.2, 113.9, 88.2, 80.2, 70.9, 70.6, 66.7, 57.7, 51.7, 28.4, 22.3. HRMS (ESI) calcd for $C_{19}H_{26}O_3Na$ $[M+Na]^+$: 325.1774; found: 325.1776.



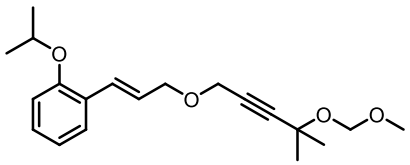
$C_{19}H_{26}O_3$
M = 302.41 g/mol

***(E)-tert*-Butyl[(5-{[3-(2-isopropoxyphenyl)allyl]oxy}-2-methylpent-3-yn-2-yl)oxy]dimethylsilane (6d).** 2,6-Lutidine (0.09 mL, 0.77 mmol) and TBSOTf (0.09 mL, 0.39 mmol) were successively added to a solution of alcohol **S10** (100 mg, 0.35 mmol) in CH_2Cl_2 (4 mL) at 0 °C. The mixture was warmed to room temperature and stirring was continued for 2 h before water (4 mL) and EtOAc (10 mL) were introduced. The layers were separated and the aqueous phase was extracted with EtOAc (2 x 5 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 90:10) to give the title compound as pale yellow oil (128 mg, 91%). IR (film) ṽ 2930, 2856, 1598, 1485, 1359, 1241, 1161, 1118, 1092, 1036, 837, 777 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, J = 7.7, 1.7 Hz, 1H), 7.19 (ddd, J = 8.2, 7.4, 1.8 Hz, 1H), 6.96 (d, J = 16.1 Hz, 1H), 6.93–6.85 (m, 2H), 6.28 (dt, J = 16.1, 6.5 Hz, 1H), 4.55 (hept, J = 6.1 Hz, 1H), 4.23 (dd, J = 6.5, 1.4 Hz, 2H), 4.21 (s, 2H), 1.48 (s, 6H), 1.35 (d, J = 6.1 Hz, 6H), 0.87 (s, 9H), 0.18 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 128.9, 128.8, 127.2, 126.9, 125.5, 120.7, 114.2, 91.8, 78.6, 70.9, 70.8, 66.4, 57.3, 33.1, 25.9, 22.3, 18.1, −2.8. HRMS (ESI) calcd for $C_{24}H_{38}O_3SiNa$ $[M+Na]^+$: 425.2482; found: 425.2482.



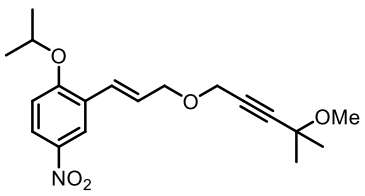
$C_{24}H_{38}O_3Si$
M = 402.65 g/mol

***(E)*-1-Isopropoxy-2-(3-{[4-(methoxymethoxy)-4-methylpent-2-yn-1-yl]oxy}prop-1-en-1-yl)benzene (6e).** *N*,*N*-Diisopropylethylamine (0.3 mL, 1.7 mmol) and MOMCl (0.08 mL, 1.05 mmol) were successively added to a solution of alcohol **S10** (99 mg, 0.34 mmol) in CH_2Cl_2 (4 mL) at 0 °C. The mixture was warmed to room temperature and stirring was continued for 16 h before water (4 mL) and EtOAc (10 mL) were introduced. The layers were separated and the aqueous phase was extracted with EtOAc (2 x 5 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 80:20) to give the title compound as colorless oil (84 mg, 74%). IR (film) ṽ 2980, 2934, 1597, 1485, 1453, 1382, 1241, 1145, 1118, 1090, 1035, 924, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, J = 7.6, 1.8 Hz, 1H), 7.19 (ddd, J = 8.2, 7.4, 1.8 Hz, 1H), 6.95 (d, J = 16.0 Hz, 1H), 6.93–6.84 (m, 2H), 6.28 (dt, J = 16.1, 6.5 Hz, 1H), 4.91 (s, 2H), 4.55 (hept, J = 6.3 Hz, 1H), 4.28–4.20 (m, 4H), 3.39 (s, 3H), 1.54 (s, 6H), 1.35 (d, J = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 129.1, 128.9, 127.2, 126.8, 125.3, 120.7, 114.2, 93.3, 88.3, 80.8, 71.2, 70.9, 57.2, 55.6, 30.3, 22.3. HRMS (ESI) calcd for $C_{20}H_{28}O_4Na$ $[M+Na]^+$: 355.1880; found: 355.1878.



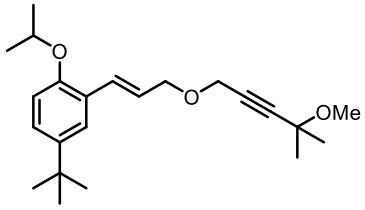
$C_{20}H_{28}O_4$
M = 332.44 g/mol

(*E*)-1-Isopropoxy-2-{3-[(4-methoxy-4-methylpent-2-yn-1-yl)oxy]prop-1-en-1-yl}-4-nitrobenzene (6j). NaH (7.2 mg, 0.30 mmol) was added to a solution of alcohol **10j** (59 mg, 0.25 mmol) in DMF (2 mL) at 0 °C. The mixture was stirred for 20 min before bromide **13** (50 mg, 0.26 mmol) was carefully added at 0 °C. After stirring for another 16 h at room temperature, water (2 mL) and *tert*-butyl methyl ether (5 mL) were introduced and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 5 mL), the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 70:30) to give the title compound as a yellow oil (52 mg, 60%). IR (film) ṽ 2982, 2935, 1583, 1516, 1484, 1341, 1259, 1173, 1106, 1078, 951, 818, 748 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 2.9 Hz, 1H), 8.11 (dd, J = 9.1, 2.8 Hz, 1H), 6.96–6.86 (m, 2H), 6.43 (dt, J = 16.1, 6.1 Hz, 1H), 4.71 (hept, J = 6.3 Hz, 1H), 4.31–4.22 (m, 4H), 3.38 (s, 3H), 1.47 (s, 6H), 1.42 (d, J = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 141.1, 128.6, 127.2, 126.3, 124.7, 123.0, 112.3, 88.6, 80.0, 71.7, 70.7, 70.2, 57.7, 51.8, 28.4, 22.1. HRMS (ESI) calcd for $C_{19}H_{25}NO_5Na$ $[M+Na]^+$: 370.1625; found: 370.1624.



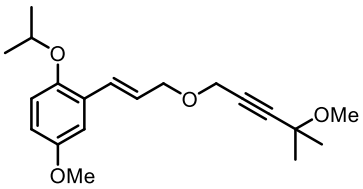
$C_{19}H_{25}NO_5$
M = 347.41 g/mol

***(E)*-4-(*tert*-Butyl)-1-isopropoxy-2-{3-[(4-methoxy-4-methylpent-2-yn-1-yl)oxy]prop-1-en-1-yl}benzene (6f).** Prepared analogously from alcohol **10f** as a yellow oil (144 mg, 65%). IR (film) ṽ 2966, 1496, 1465, 1361, 1246, 1173, 1077, 973, 958, 914 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 2.5 Hz, 1H), 7.21 (dd, J = 8.6, 2.5 Hz, 1H), 6.95 (d, J = 16.1 Hz, 1H), 6.81 (d, J = 8.9 Hz, 1H), 6.30 (dt, J = 16.1, 6.5 Hz, 1H), 4.50 (hept, J = 6.1 Hz, 1H), 4.28–4.22 (m, 4H), 3.38 (s, 3H), 1.47 (s, 6H), 1.34 (d, J = 6.1 Hz, 6H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 143.3, 129.6, 125.9, 125.8, 125.0, 124.1, 113.8, 88.2, 80.3, 71.0, 70.7, 57.2, 51.8, 34.3, 31.6, 28.5, 22.4. HRMS (EI) calcd for $C_{23}H_{34}O_3$ $[M]^{+\bullet}$: 358.2502; found: 358.0205.



$C_{23}H_{34}O_3$
M = 358.52 g/mol

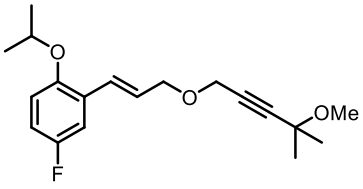
(*E*)-1-Isopropoxy-4-methoxy-2-{3-[(4-methoxy-4-methylpent-2-yn-1-yl)oxy]prop-1-en-1-yl}benzene (6g).



$C_{20}H_{28}O_4$
M = 332.44 g/mol

Prepared analogously from alcohol **10g** as a pale yellow oil (105 mg, 63%). IR (film) ṽ 2980, 2936, 2834, 1492, 1467, 1380, 1359, 1286, 1248, 1211, 1173, 1113, 1076, 1042, 975 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, J = 3.2 Hz, 1H), 6.94 (d, J = 16.3 Hz, 1H), 6.83 (d, J = 8.9 Hz, 1H), 6.76 (dd, J = 9.0, 3.0 Hz, 1H), 6.26 (dt, J = 16.1, 6.5 Hz, 1H), 4.38 (hept, J = 6.1 Hz, 1H), 4.31–4.21 (m, 4H), 3.78 (s, 3H), 3.37 (s, 3H), 1.47 (s, 6H), 1.31 (d, J = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 149.7, 128.8, 128.2, 125.6, 117.0, 114.5, 111.6, 88.3, 80.2, 72.4, 70.72, 70.66, 57.3, 55.8, 51.8, 28.5, 22.4. HRMS (EI) calcd for $C_{20}H_{28}O_4$ $[M]^{+\bullet}$: 332.1982; found: 332.1983.

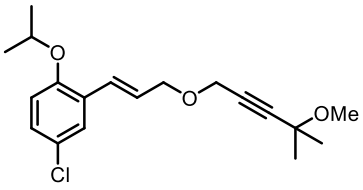
(*E*)-4-Fluoro-1-isopropoxy-2-{3-[(4-methoxy-4-methylpent-2-yn-1-yl)oxy]prop-1-en-1-yl}benzene (6h).



$C_{19}H_{25}FO_3$
M = 320.40 g/mol

Prepared analogously from alcohol **10h** as a yellow oil (189 mg, 43%). IR (film) ṽ 2981, 2936, 1488, 1376, 1359, 1249, 1174, 1116, 1077, 973, 949 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 (dd, J = 9.6, 3.0 Hz, 1H), 6.96–6.77 (m, 3H), 6.26 (dt, J = 16.1, 6.3 Hz, 1H), 4.45 (hept, J = 6.0 Hz, 1H), 4.31–4.18 (m, 4H), 3.37 (s, 3H), 1.47 (s, 6H), 1.33 (d, J = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3 (d, J = 238.9 Hz), 151.4 (d, J = 2.0 Hz), 128.6 (d, J = 7.0 Hz), 127.8 (d, J = 2.5 Hz), 126.6, 116.2 (d, J = 8.0 Hz), 115.0 (d, J = 23.1 Hz), 113.1 (d, J = 23.6 Hz), 88.4, 80.2, 72.2, 70.7, 70.5, 57.4, 51.8, 28.4, 22.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ −123.4. HRMS (ESI) calcd for $C_{19}H_{25}FO_3Na$ $[M+Na]^+$: 343.1680; found: 343.1684.

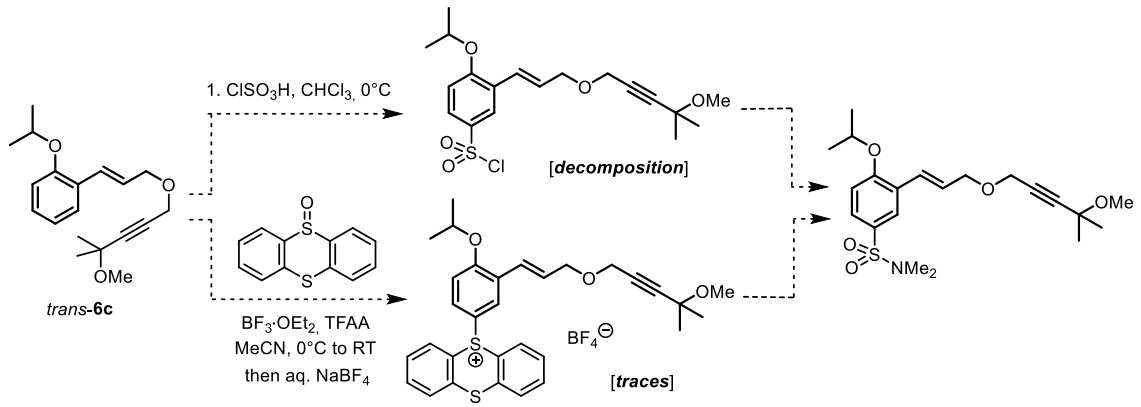
(*E*)-4-Chloro-1-isopropoxy-2-{3-[(4-methoxy-4-methylpent-2-yn-1-yl)oxy]prop-1-en-1-yl}benzene (6i).



$C_{19}H_{25}ClO_3$
M = 336.86 g/mol

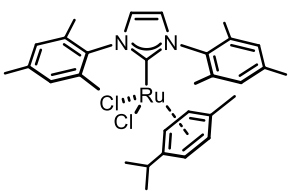
Prepared analogously from alcohol **10i** as a pale yellow oil (281 mg, 62%). IR (film) ṽ 2981, 2936, 1480, 1359, 1245, 1173, 1111, 1077, 973, 954 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 2.7 Hz, 1H), 7.13 (dd, J = 8.7, 2.7 Hz, 1H), 6.88 (d, J = 16.2 Hz, 1H), 6.80 (d, J = 9.0 Hz, 1H), 6.27 (dt, J = 16.1, 6.3 Hz, 1H), 4.50 (hept, J = 6.0 Hz, 1H), 4.27–4.20 (m, 4H), 3.37 (s, 3H), 1.47 (s, 6H), 1.34 (d, J = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 128.5, 128.4, 127.5, 126.9, 126.8, 125.8, 115.5, 88.4, 80.2, 71.5, 70.7, 70.5, 57.4, 51.8, 28.4, 22.2. HRMS (EI) calcd for $C_{19}H_{25}ClO_3$ $[M]^{+\bullet}$: 336.1487; found: 336.1487.

Attempted Preparation of a Sulfonamide Derivative by Late-Stage Functionalization of *trans*-6c.[12,13]

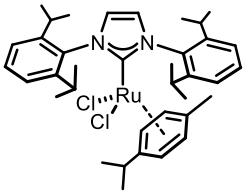


Light-driven Hydrogenative Metathesis Reactions

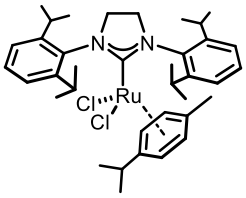
Synthesis of Precatalysts



1a



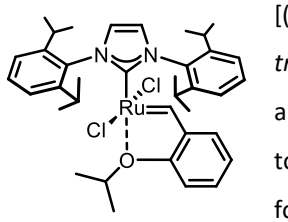
1b



1c

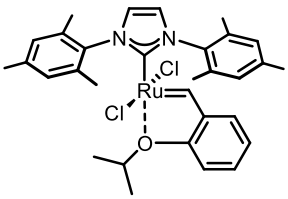
The compounds **1a,b**[9] and **1c**[11] were prepared according to literature procedures.

Representative procedure. Preparation of Ruthenium Carbene Complex 3b. In a flame-dried Schlenk tube, [(IPr)Ru(*p*-cymene)Cl_2] **1b** (70 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (5 mL). Alkyne *trans*-**6c** (31 mg, 0.10 mmol) was added, the Schlenk tube was closed with a septum and then transferred into the photolysis apparatus. A hydrogen-filled balloon attached to a needle was pierced through the septum and the tube was flushed with hydrogen for 2 min through an outlet cannula. After the first 10 seconds of flushing with hydrogen, the light source was switched on and the reaction mixture was stirred for 3 h at room temperature under a hydrogen atmosphere with a constant irradiation by the blue LED (λ = 365 nm). The reaction mixture was then diluted with pentane (5 mL) and the resulting solution was flushed through a short silica pad (pentane/*tert*-butyl methyl ether gradient, 10:1 to 1:1). A dark brown band was collected and the solvent was removed under reduced pressure to give the title compound as a dark brown solid material (48 mg, 68%). IR (film) ṽ 2965, 2928, 2867, 1590, 1576, 1474, 1454, 1385, 1308, 1217, 1114, 935, 801 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2) δ 16.50 (s, 1H), 7.63 (t, *J* = 7.8 Hz, 2H), 7.56–7.48 (m, 1H), 7.43 (d, *J* = 7.8 Hz, 4H), 7.19 (s, 2H), 6.97 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.92–6.83 (m, 2H), 4.92 (hept, *J* = 6.2 Hz, 1H), 3.08 (hept, *J* = 6.9 Hz, 4H), 1.37 (d, *J* = 6.2 Hz, 6H), 1.19 (d, *J* = 6.8 Hz, 12H), 1.14 (d, *J* = 7.0 Hz, 12H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 286.9, 177.6, 152.7, 148.6, 145.0, 136.6, 130.8, 129.1, 126.6, 124.2, 122.8, 121.9, 113.4, 75.6, 29.2, 26.5, 22.8, 21.8. HRMS (ESI) calcd for $C_{37}H_{48}ClN_2ORu$ $[M\text{-}Cl]^+$: 673.2493; found: 673.2487. The spectral data are consistent with those reported in the literature.[10]



$C_{37}H_{48}Cl_2N_2ORu$
M = 708.77 g/mol

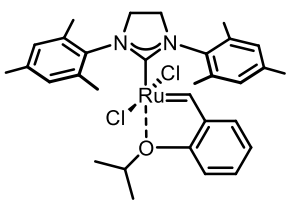
Complex 3c. Prepared analogously from [Ru(IMes)(*p*-cymene)Cl_2] **1a** (61 mg, 0.10 mmol) and alkyne *trans*-**6c** (31 mg, 0.10 mmol). The crude material was flushed through a short silica pad (pentane/*tert*-butyl methyl ether gradient, 5:1 to 2:1). A dark green band was collected and the solvent was removed under reduced pressure. The residue was triturated with pentane at 0 °C, the supernatant was filtered off and the product was dried under reduced pressure to give the title compound as a dark green solid material (32 mg, 51%). IR (film) ṽ 2977, 2919, 1590, 1475, 1453, 1384, 1320, 1261, 1113, 1036, 913, 731 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2) δ 16.66 (s, 1H), 7.56 (ddd, *J* = 8.8, 7.4, 1.7 Hz, 1H), 7.15 (s, 2H), 7.13 (s, 4H), 7.05 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 4.92 (hept, *J* = 6.2 Hz, 1H), 2.46 (s, 6H), 2.24 (s, 12H), 1.31 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 291.9, 175.5, 152.6, 145.7,



$C_{31}H_{36}Cl_2N_2ORu$
M = 624.61 g/mol

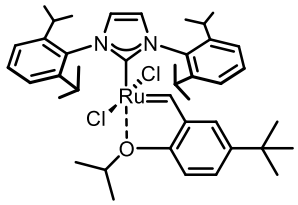
140.1, 138.4, 136.3, 129.4, 129.3, 125.3, 122.9, 122.1, 113.4, 75.7, 21.35, 21.30, 19.2. HRMS (ESI) calcd for $C_{31}H_{36}ClN_2ORu$ $[M\text{-}Cl]^+$: 589.1554; found: 589.1555. The spectral data are consistent with those reported in the literature.[10]

Complex 3d. Prepared analogously from [Ru(H$_2$IMes)(*p*-cymene)Cl$_2$] **1c** (28 mg, 0.046 mmol) and alkyne *trans*-**6c** (15 mg, 0.050 mmol). After 16 h, the crude material was flushed through a short silica pad (pentane/*tert*-butyl methyl ether gradient, 10:1 to 1:1). A dark green band was collected and the solvent was removed under reduced pressure to provide a solid material that was triturated with pentane at −78 °C. The supernatant was filtered off and the residue was dried under reduced pressure to give the title compound as a dark green solid material (5 mg, 17%). IR (film) ṽ 2977, 2917, 1589, 1477, 1452, 1420, 1259, 1113, 912, 730 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.51 (d, J = 1.0 Hz, 1H), 7.55 (ddd, J = 8.8, 7.2, 1.8 Hz, 1H), 7.07 (s, 4H), 6.96 (dd, J = 7.5, 1.8 Hz, 1H), 6.90 (td, J = 7.3, 1.0 Hz, 1H), 6.84 (d, J = 8.6 Hz, 1H), 4.88 (hept, J = 6.1 Hz, 1H), 4.16 (s, 4H), 2.44 (s, 12H), 2.41 (s, 6H), 1.23 (d, J = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 296.0, 211.2, 152.4, 145.6, 139.3, 129.8, 129.6, 122.7, 122.6, 113.3, 75.5, 51.9, 21.3, 21.2. HRMS (ESI) calcd for $C_{31}H_{38}Cl_2N_2ORu$ $[M]^{+\bullet}$: 626.1399; found: 626.1395. The spectral data are consistent with those of a commercially available sample.



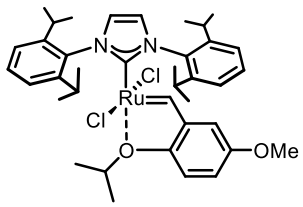
$C_{31}H_{38}Cl_2N_2ORu$
M = 626.63 g/mol

Complex 3e. Prepared analogously from [Ru(IPr)(*p*-cymene)Cl$_2$] **1b** (37 mg, 0.05 mmol) and alkyne **6f** (19 mg, 0.05 mmol). After 16 h the crude material was flushed through a short silica pad (pentane/*tert*-butyl methyl ether gradient, 10:1 to 5:1). A brown band was collected and the solvent was removed under reduced pressure. The residue was triturated with pentane at −78 °C, the supernatant was filtered off, and the product was dried under reduced pressure give the title compound as a dark red solid material (25 mg, 61%). IR (film) ṽ 2965, 2868, 1489, 1464, 1384, 1309, 1271, 1138, 1106, 842 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.46 (s, 1H), 7.63 (t, J = 7.7 Hz, 2H), 7.57 (dd, J = 8.7, 2.5 Hz, 1H), 7.44 (d, J = 7.8 Hz, 4H), 7.19 (s, 2H), 6.94 (d, J = 2.3 Hz, 1H), 6.78 (d, J = 8.8 Hz, 1H), 4.88 (hept, J = 6.1 Hz, 1H), 3.08 (hept, J = 7.2 Hz, 4H), 1.35 (d, J = 6.0 Hz, 6H), 1.28 (s, 9H), 1.20 (d, J = 6.8 Hz, 12H), 1.14 (d, J = 6.8 Hz, 12H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 288.1, 178.0, 150.7, 148.6, 145.7, 144.6, 136.6, 130.7, 126.6, 126.2, 124.2, 118.9, 112.7, 75.3, 34.1, 31.6, 29.2, 26.5, 22.8, 21.8. HRMS (ESI) calcd for $C_{41}H_{56}Cl_2N_2ORuNa$ $[M+Na]^+$: 787.2705; found: 787.2700.



$C_{41}H_{56}Cl_2N_2ORu$
M = 764.88 g/mol

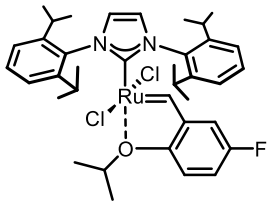
Complex 3f. Prepared analogously from [Ru(IPr)(*p*-cymene)Cl$_2$] **1b** (37 mg, 0.05 mmol) and alkyne **6g** (18 mg, 0.05 mmol). After 16 h the crude material was flushed through a short silica pad (pentane/*tert*-butyl methyl ether gradient, 10:1 to 2:1). A brown band was collected and the solvent was removed under reduced pressure. The residue was triturated with pentane at −78 °C, the supernatant was filtered off, and the product was dried under reduced pressure to give the title compound as a dark brown solid material (26 mg, 66%). IR (film) ṽ 2966, 2930, 2868, 1471, 1399, 1385, 1317, 1274, 1212, 1131, 1103, 936, 906 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.43 (s, 1H), 7.62 (t, J = 7.8 Hz, 2H),



$C_{38}H_{50}Cl_2N_2O_2Ru$
M = 738.80 g/mol

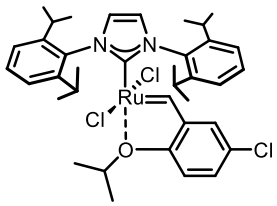
7.43 (d, *J* = 7.5 Hz, 4H), 7.18 (s, 2H), 7.10 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 6.49 (d, *J* = 2.9 Hz, 1H), 4.83 (hept, *J* = 6.4 Hz, 1H), 3.75 (s, 3H), 3.07 (hept, *J* = 6.8 Hz, 4H), 1.34 (d, *J* = 6.2 Hz, 6H), 1.20 (d, *J* = 6.8 Hz, 12H), 1.14 (d, *J* = 7.0 Hz, 12H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 285.8, 177.3, 155.6, 148.6, 146.8, 145.3, 136.5, 130.8, 126.6, 124.3, 113.4, 113.4, 106.9, 75.4, 56.3, 29.2, 26.5, 22.8, 21.8. HRMS (ESI) calcd for $C_{38}H_{50}Cl_2N_2O_2RuNa$ $[M+Na]^+$: 761.2185; found: 761.2176.

Complex 3g. Prepared analogously from [Ru(IPr)(*p*-cymene)Cl_2] **1b** (34 mg, 0.05 mmol) and alkyne **6h** (16 mg, 0.05 mmol). After 16 h the crude material was flushed through a short silica pad (pentane/*tert*-butyl methyl ether gradient, 10:1 to 5:1). A brown band was collected and the solvent was removed under reduced pressure. The residue was triturated with pentane at −78 °C, the supernatant was filtered off, and the product was dried under reduced pressure to give the title compound as a light brown solid material (16 mg, 45%). IR (film) ṽ 2966, 2868, 1482, 1385, 1317, 1308, 1272, 1212, 1134, 1116, 1102, 933, 803 cm^{-1}. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 16.38 (d, *J* = 1.1 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 4H), 7.26 (ddd, *J* = 9.1, 8.1, 3.1 Hz, 1H), 7.19 (s, 2H), 6.78 (dd, *J* = 8.8, 3.9 Hz, 1H), 6.67 (dd, *J* = 8.0, 3.1 Hz, 1H), 4.86 (hept, *J* = 5.8 Hz, 1H), 3.05 (hept, *J* = 6.8 Hz, 4H), 1.35 (d, *J* = 6.2 Hz, 6H), 1.19 (d, *J* = 6.7 Hz, 12H), 1.13 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 283.1, 176.0, 159.1 (d, *J* = 240.9 Hz), 148.6, 148.5 (d, *J* = 1.8 Hz), 145.3 (d, *J* = 6.4 Hz), 136.4, 130.9, 126.7, 124.3, 114.1 (d, *J* = 24.7 Hz), 113.7 (d, *J* = 8.4 Hz), 107.3 (d, *J* = 22.3 Hz), 76.1, 29.2, 26.5, 22.8, 21.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ −124.6. HRMS (ESI) calcd for $C_{37}H_{47}Cl_2FN_2ORuNa$ $[M+Na]^+$: 749.1985; found: 749.1985.



$C_{37}H_{47}Cl_2FN_2ORu$
M = 726.76 g/mol

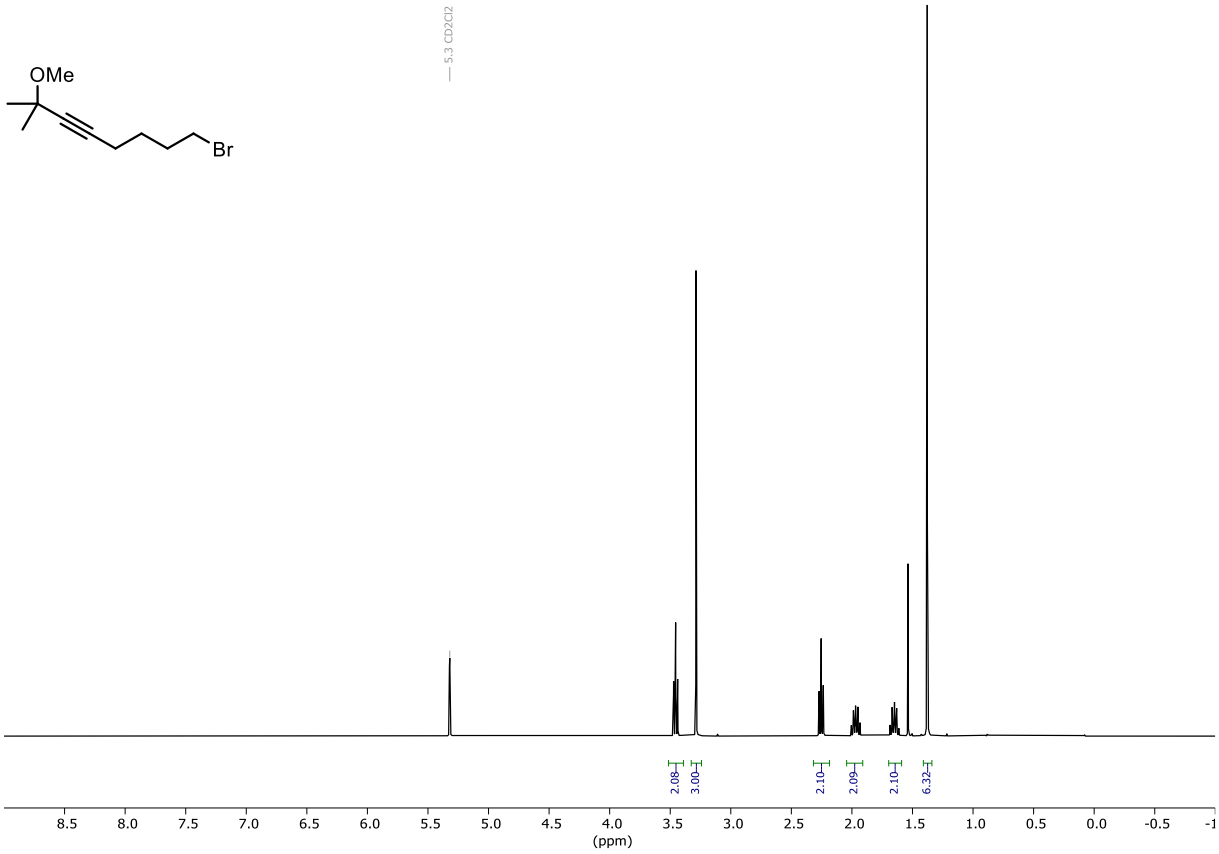
Complex 3h. Prepared analogously from [Ru(IPr)(*p*-cymene)Cl_2] **1b** (41 mg, 0.06 mmol) and alkyne **6i** (20 mg, 0.06 mmol). After 16 h the crude material was flushed through a short silica pad (pentane/*tert*-butyl methyl ether gradient, 10:1 to 2:1). A brown band was collected and the solvent was removed. The residue was triturated with pentane at −78 °C, the supernatant was filtered off, and the product was dried under reduced pressure to give the title compound as a brown solid material (22 mg, 50%). IR (film) ṽ 2966, 2930, 2868, 1471, 1399, 1385, 1317, 1274, 1212, 1131, 1103, 936, 906 cm^{-1}. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 16.38 (s, 1H), 7.64 (t, *J* = 7.8 Hz, 2H), 7.49 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 4H), 7.19 (s, 2H), 6.94 (d, *J* = 2.4 Hz, 1H), 6.80 (d, *J* = 8.5 Hz, 1H), 4.88 (hept, *J* = 6.3 Hz, 1H), 3.05 (hept, *J* = 6.7 Hz, 4H), 1.35 (d, *J* = 6.2 Hz, 6H), 1.19 (d, *J* = 6.5 Hz, 12H), 1.13 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 282.7, 175.8, 151.1, 148.6, 145.7, 136.4, 130.9, 128.2, 127.6, 126.7, 124.3, 120.8, 114.4, 76.4, 29.2, 26.5, 22.8, 21.7. HRMS (ESI) calcd for $C_{37}H_{47}Cl_3N_2ORuNa$ $[M+Na]^+$: 765.1690; found: 765.7690.



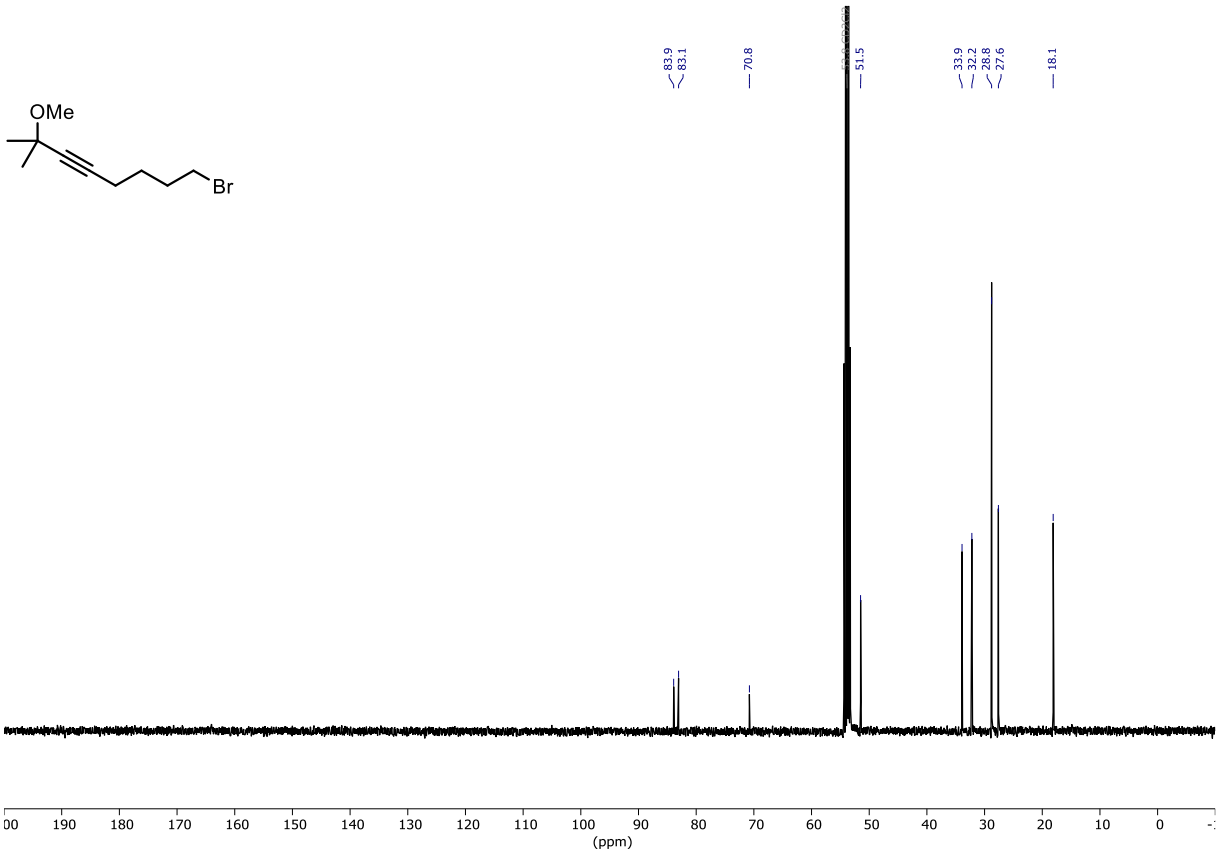
$C_{37}H_{47}Cl_3N_2ORu$
M = 743.22 g/mol

Copies of Spectra

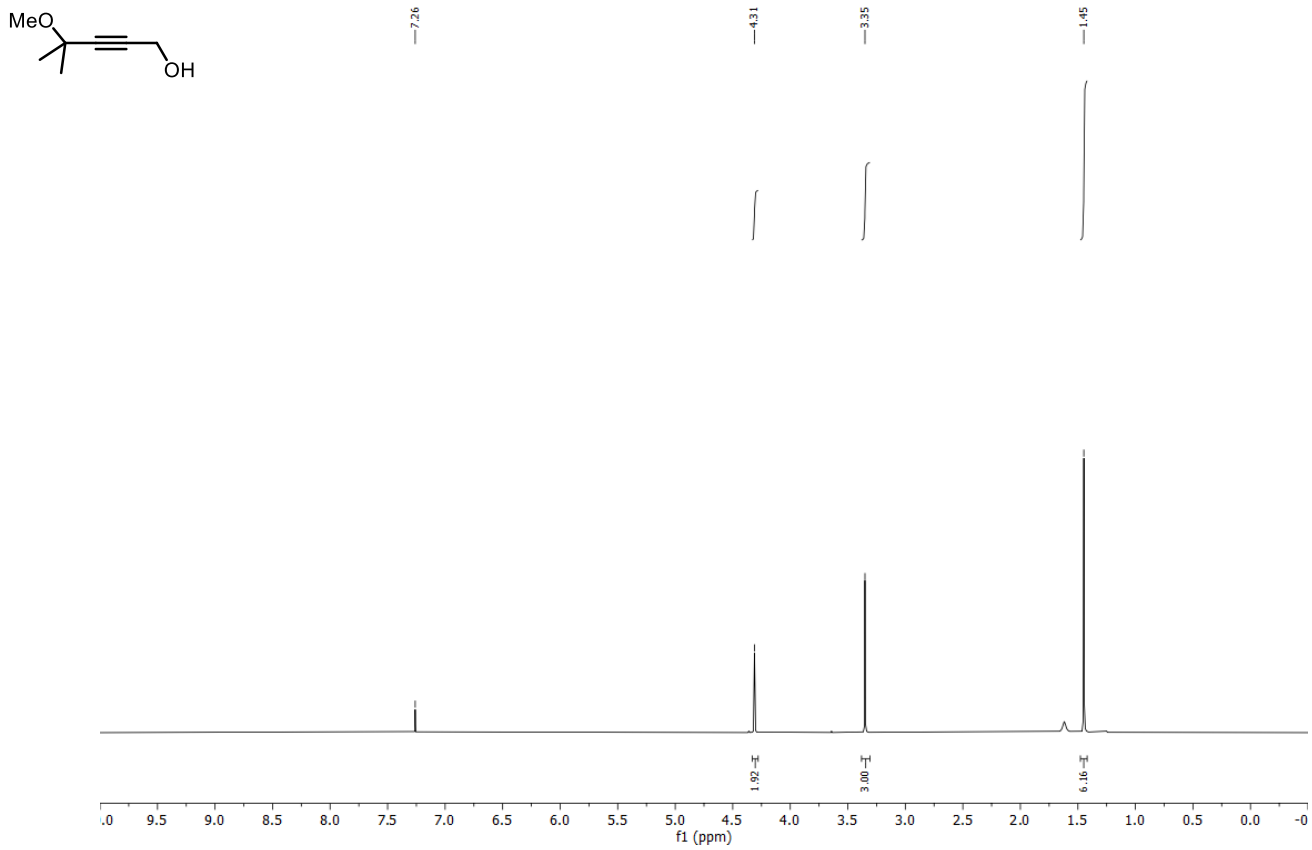
^{1}H NMR (400 MHz, CD_2Cl_2)



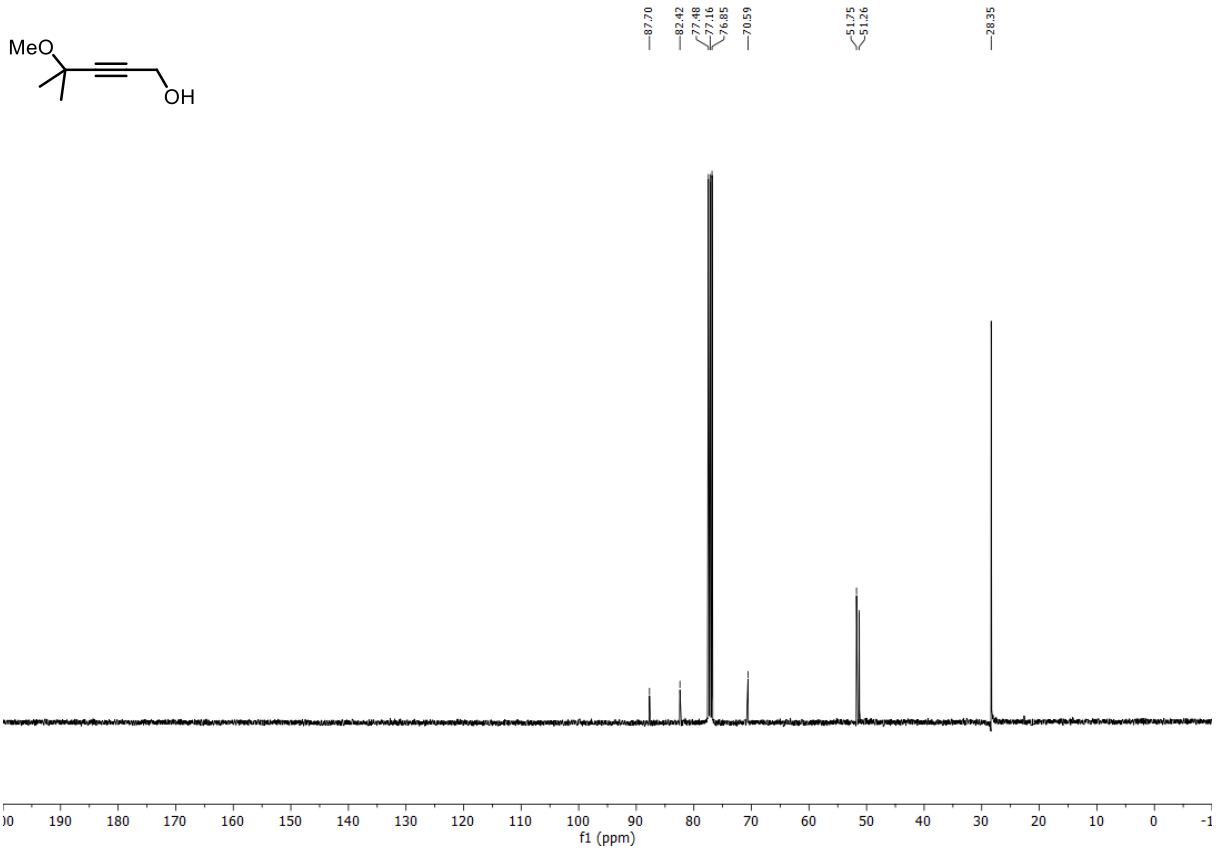
^{13}C NMR (101 MHz, CD_2Cl_2)



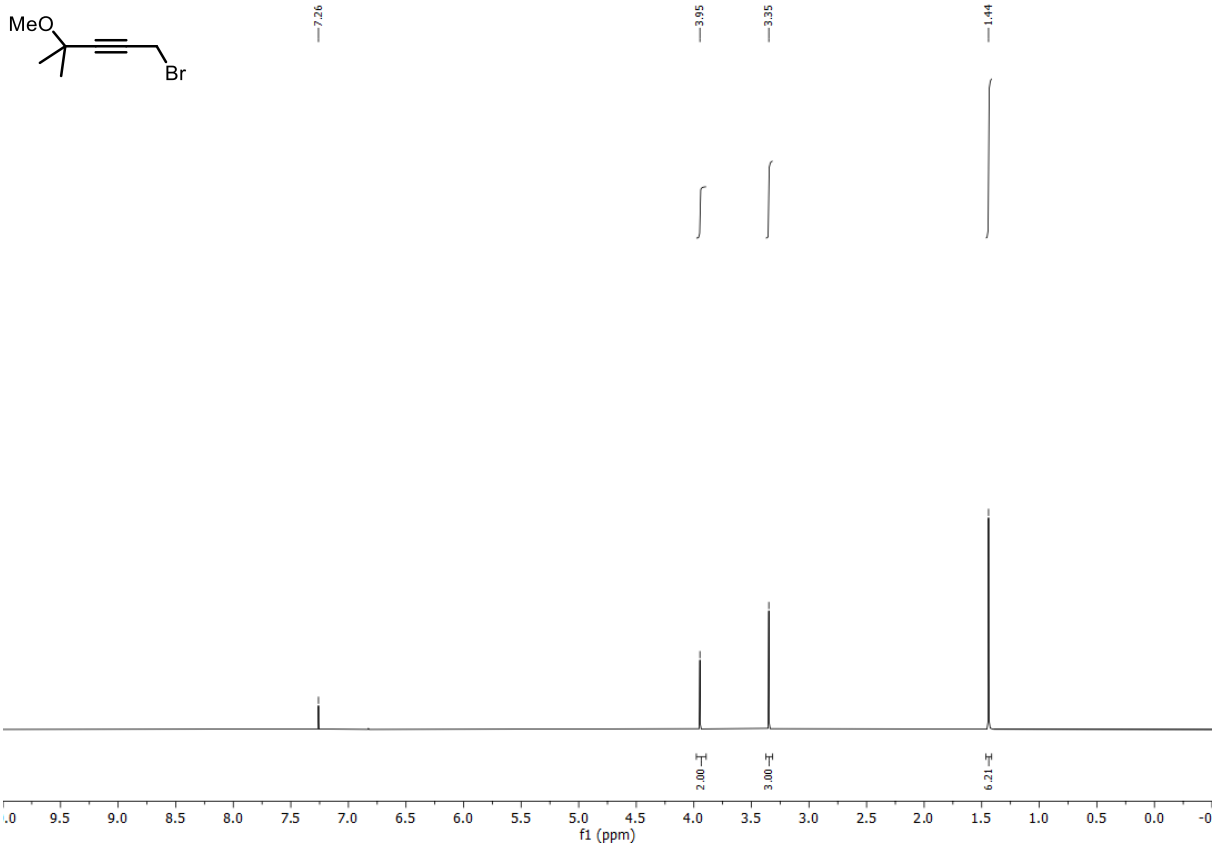
^{1}H NMR (400 MHz, $CDCl_3$)



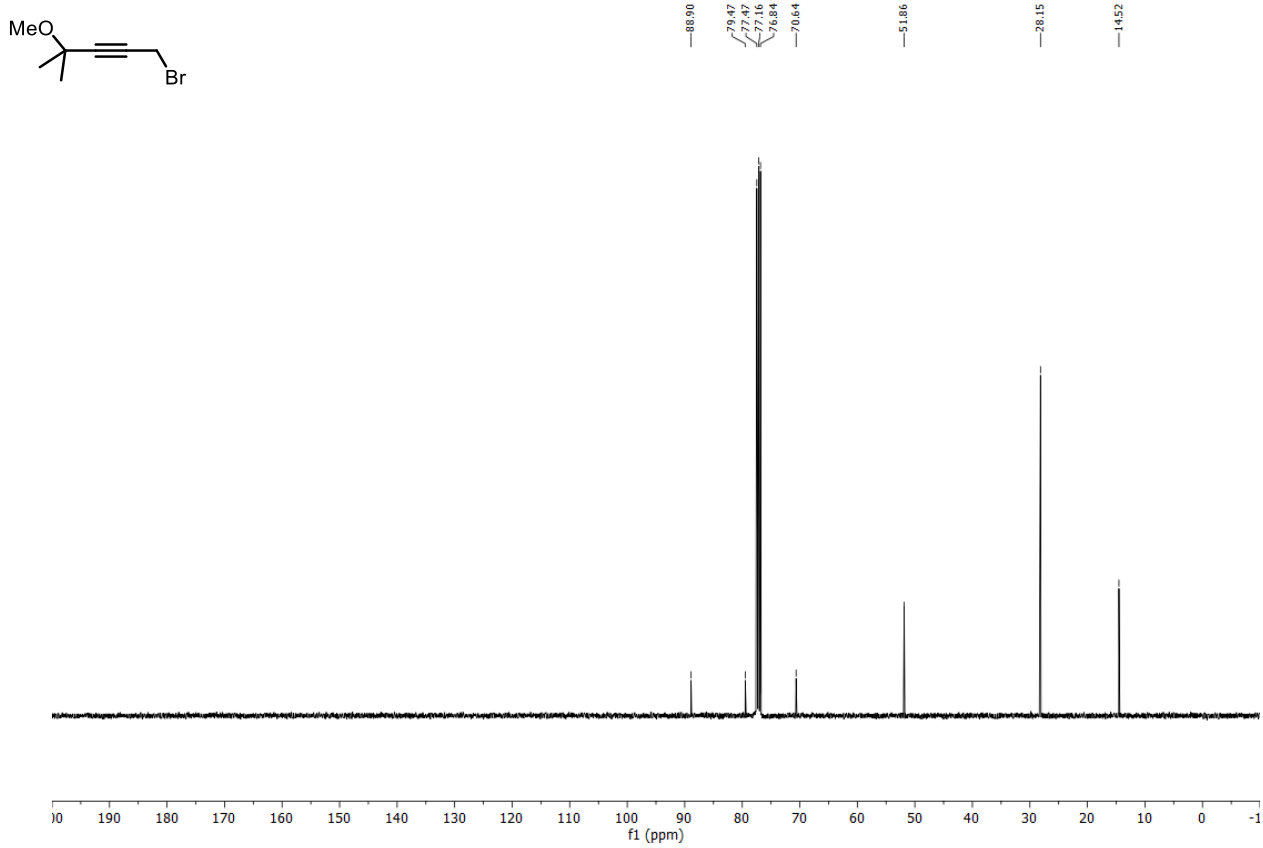
^{13}C NMR (101 MHz, $CDCl_3$)



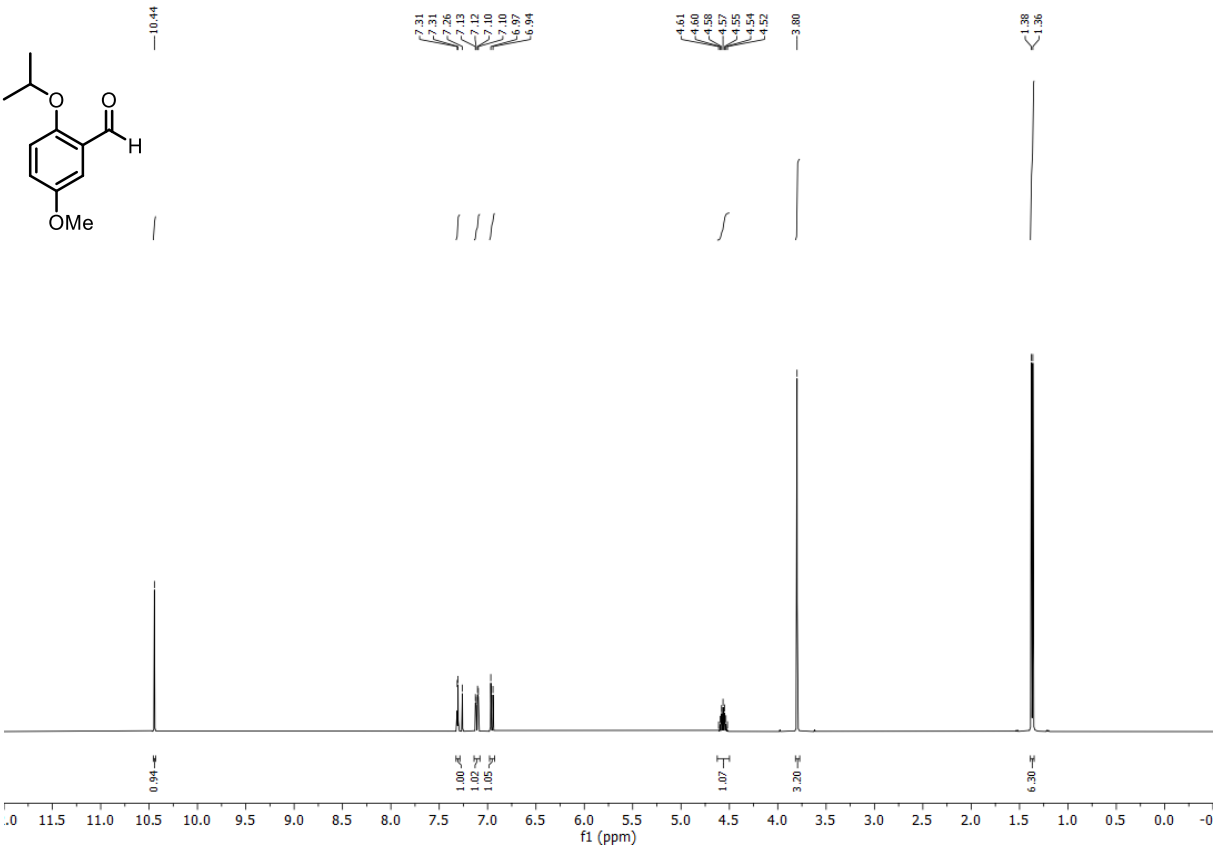
^{1}H NMR (400 MHz, $CDCl_3$)



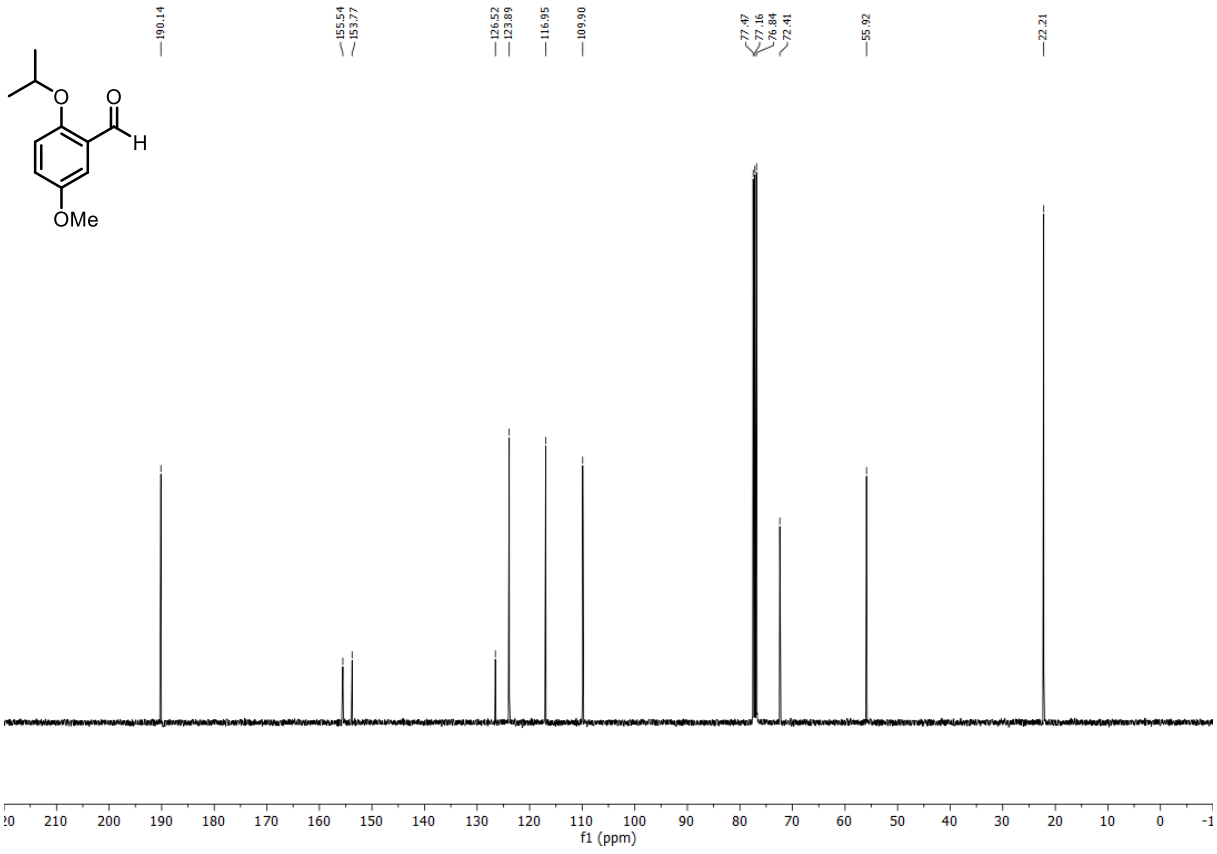
^{13}C NMR (101 MHz, $CDCl_3$)



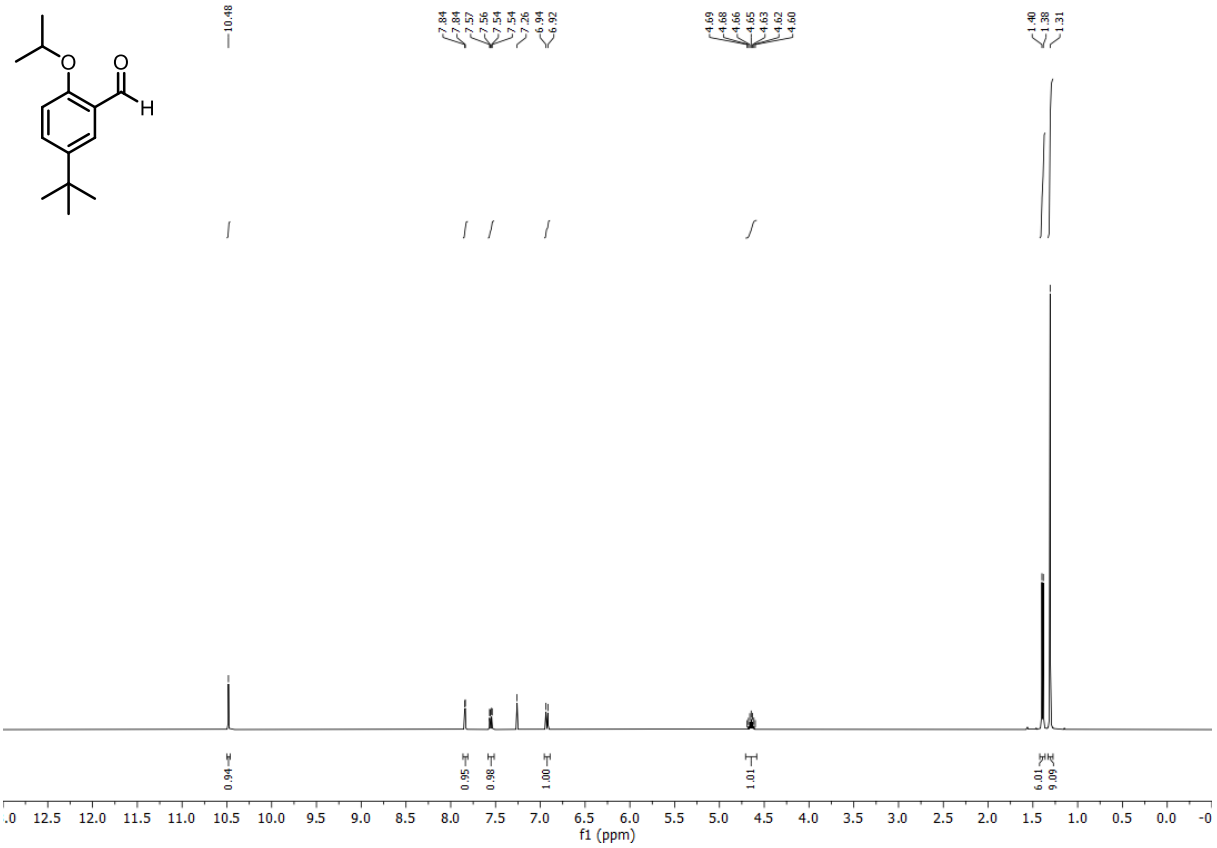
^{1}H NMR (400 MHz, $CDCl_3$)



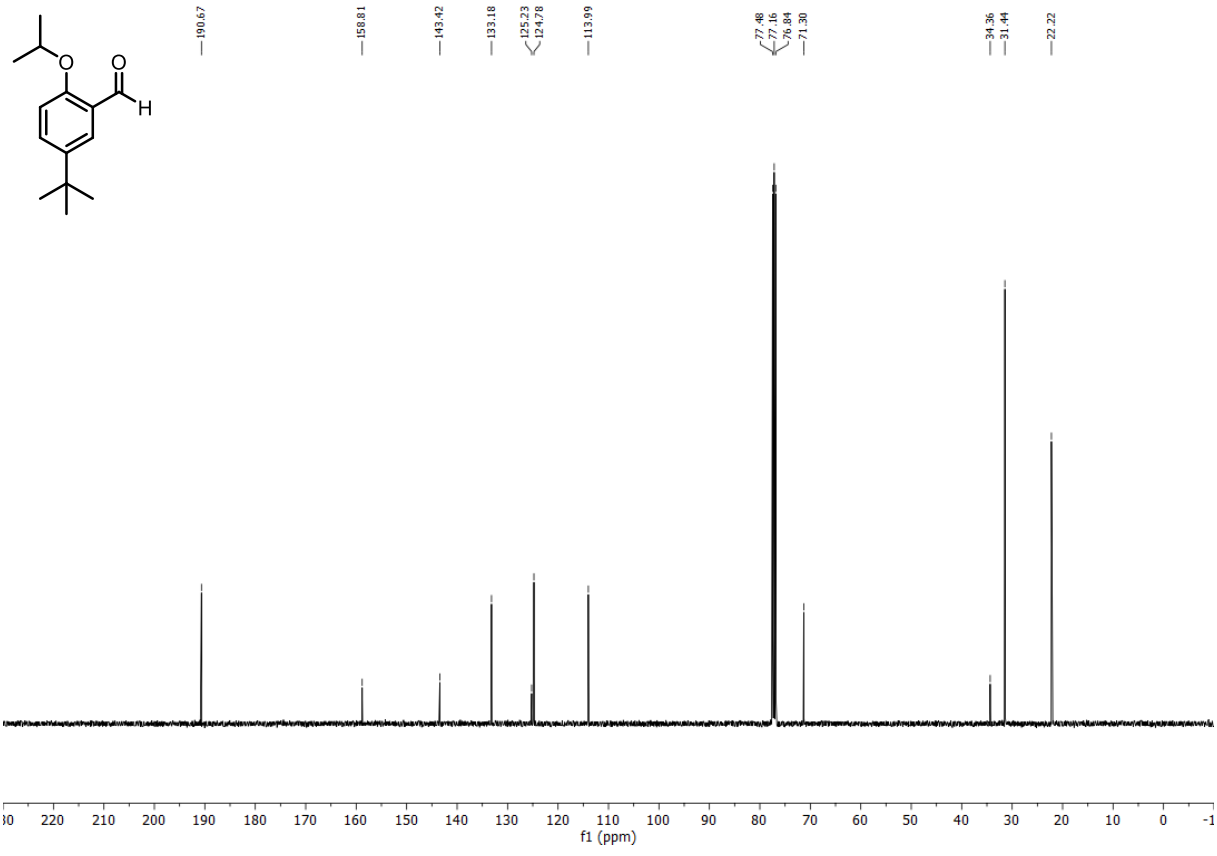
^{13}C NMR (101 MHz, $CDCl_3$)



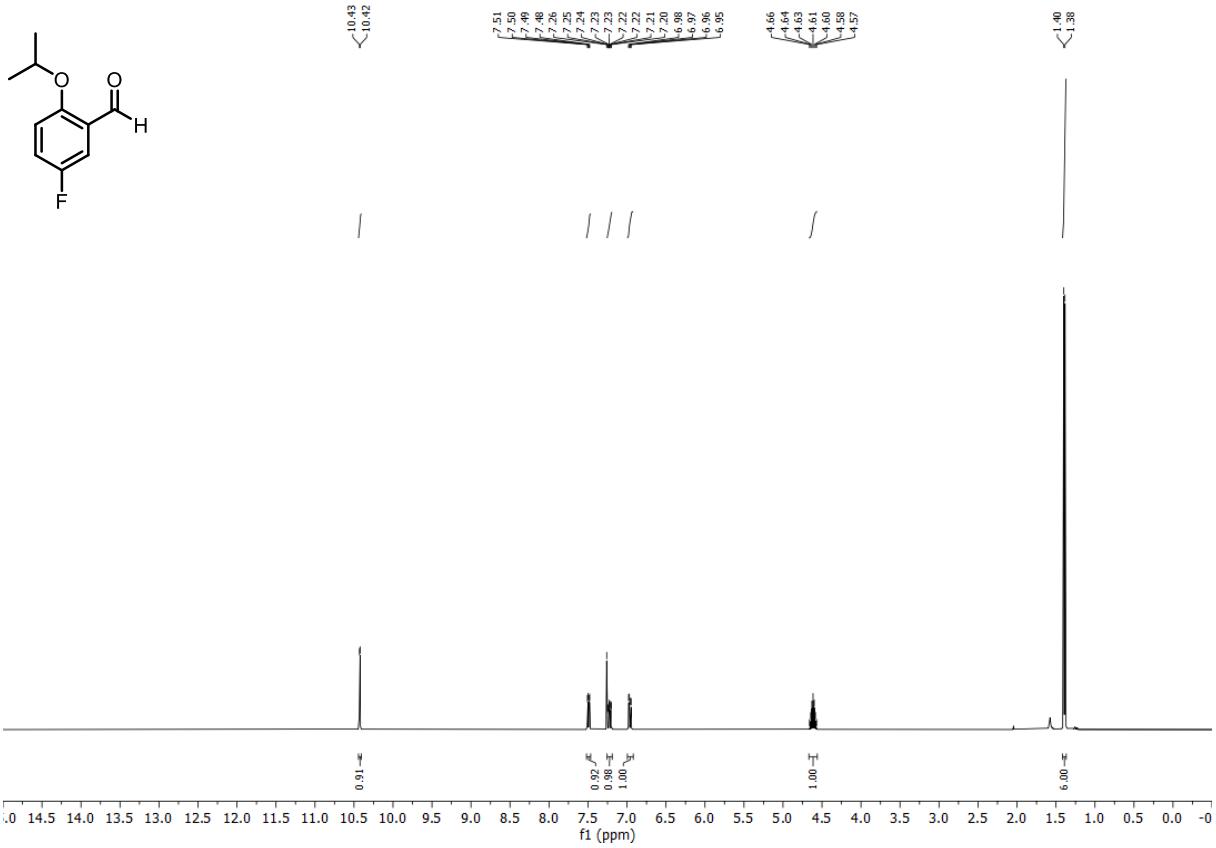
^{1}H NMR (400 MHz, $CDCl_3$)



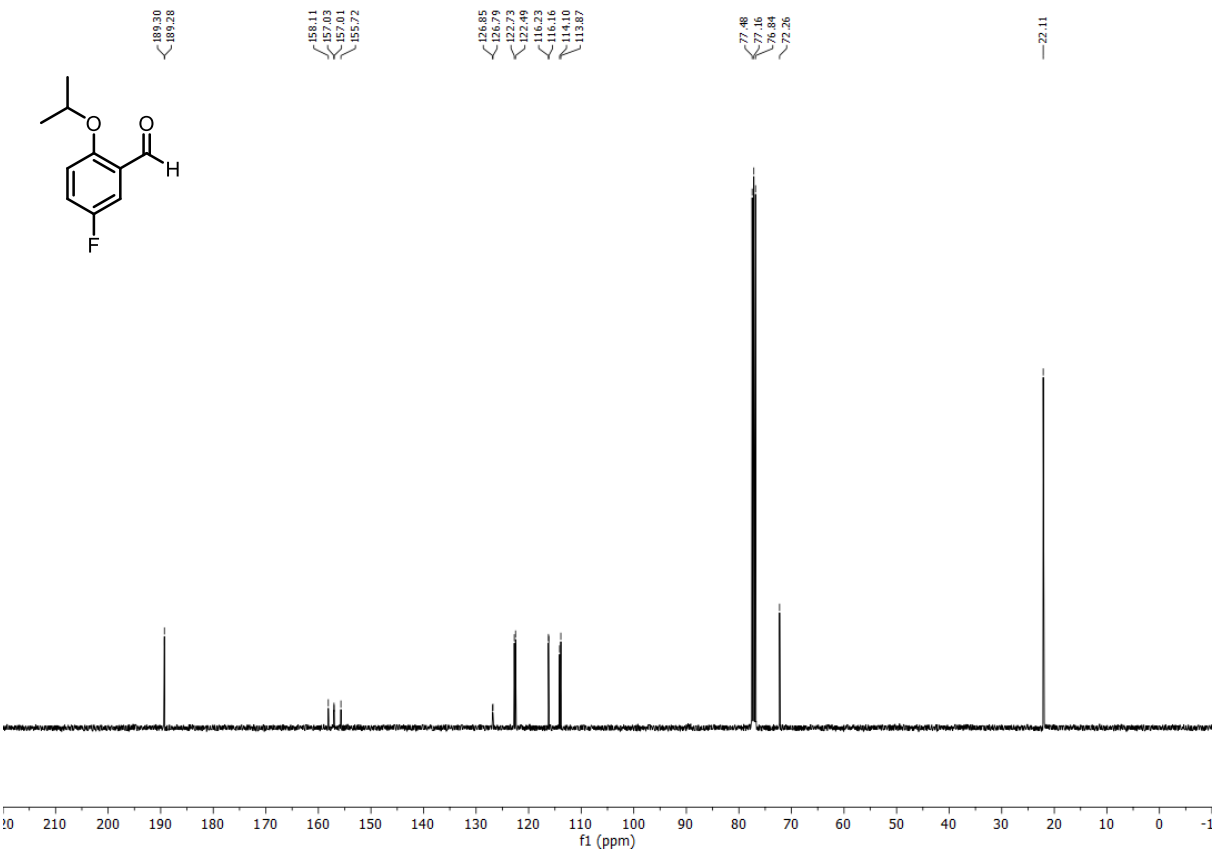
^{13}C NMR (101 MHz, $CDCl_3$)



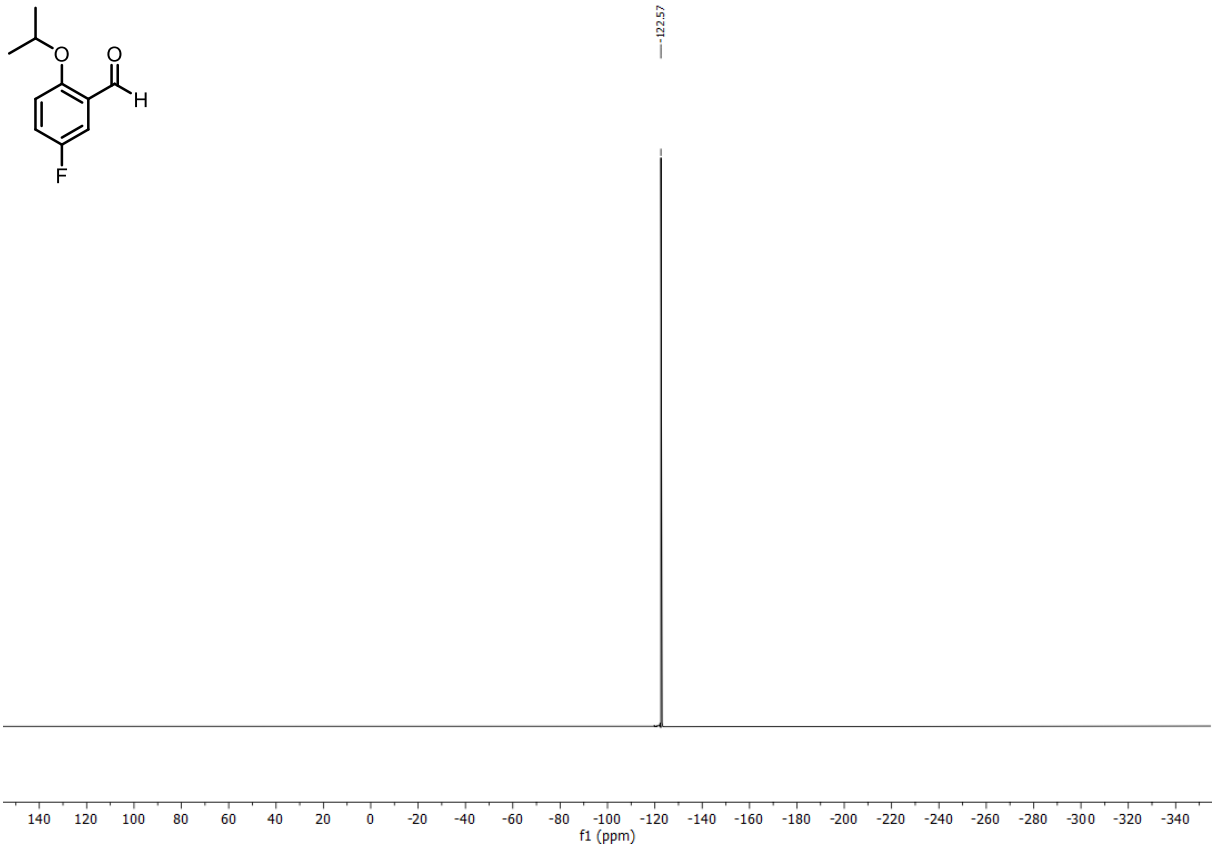
^{1}H NMR (400 MHz, $CDCl_3$)



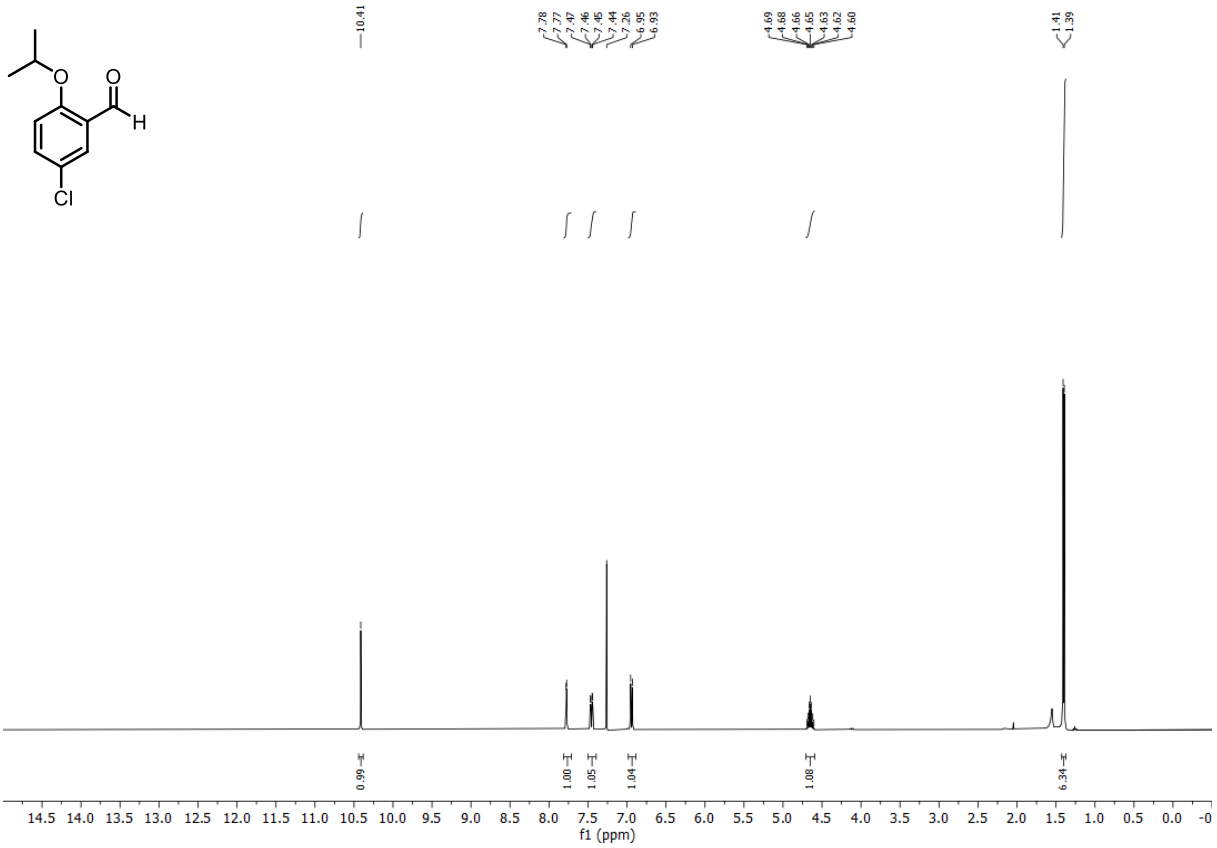
^{13}C NMR (101 MHz, $CDCl_3$)



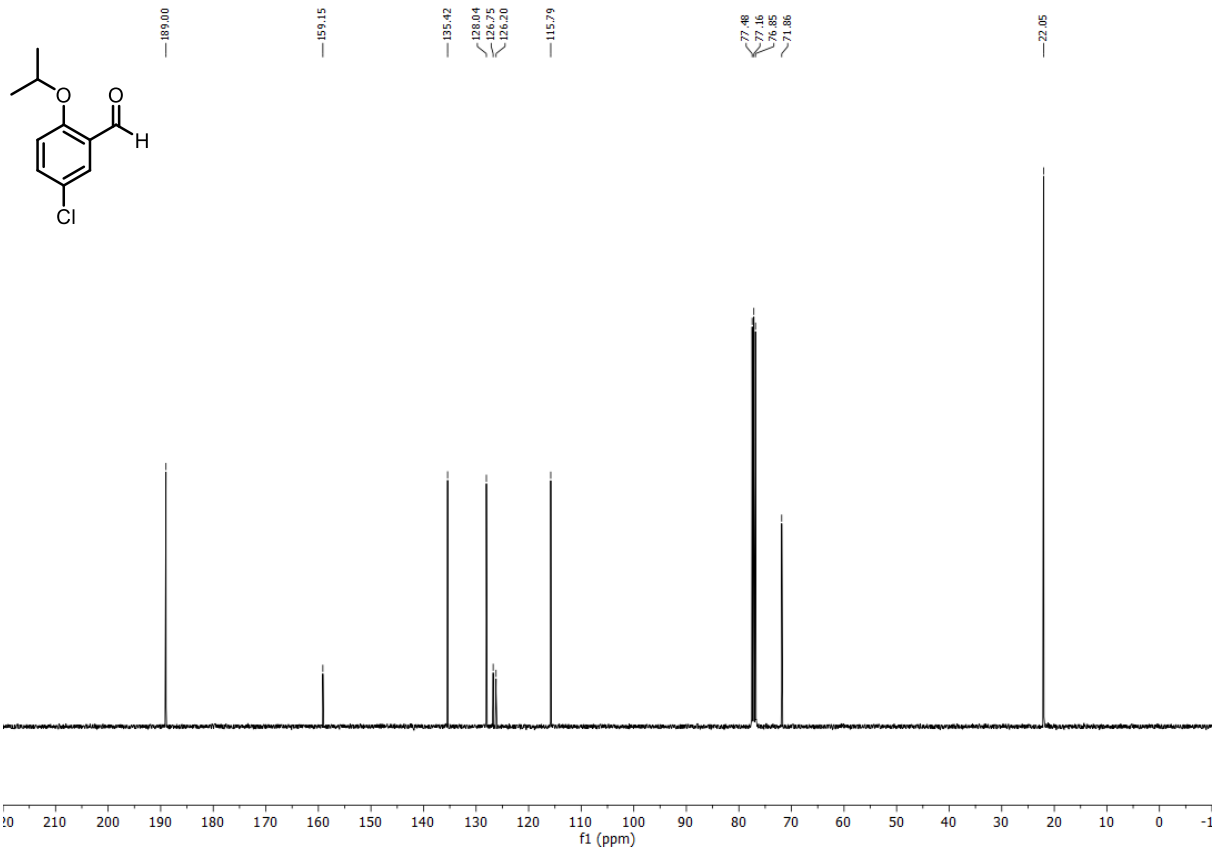
^{19}F NMR (282 MHz, $CDCl_3$)



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



^{13}C NMR (101 MHz, $CDCl_3$)



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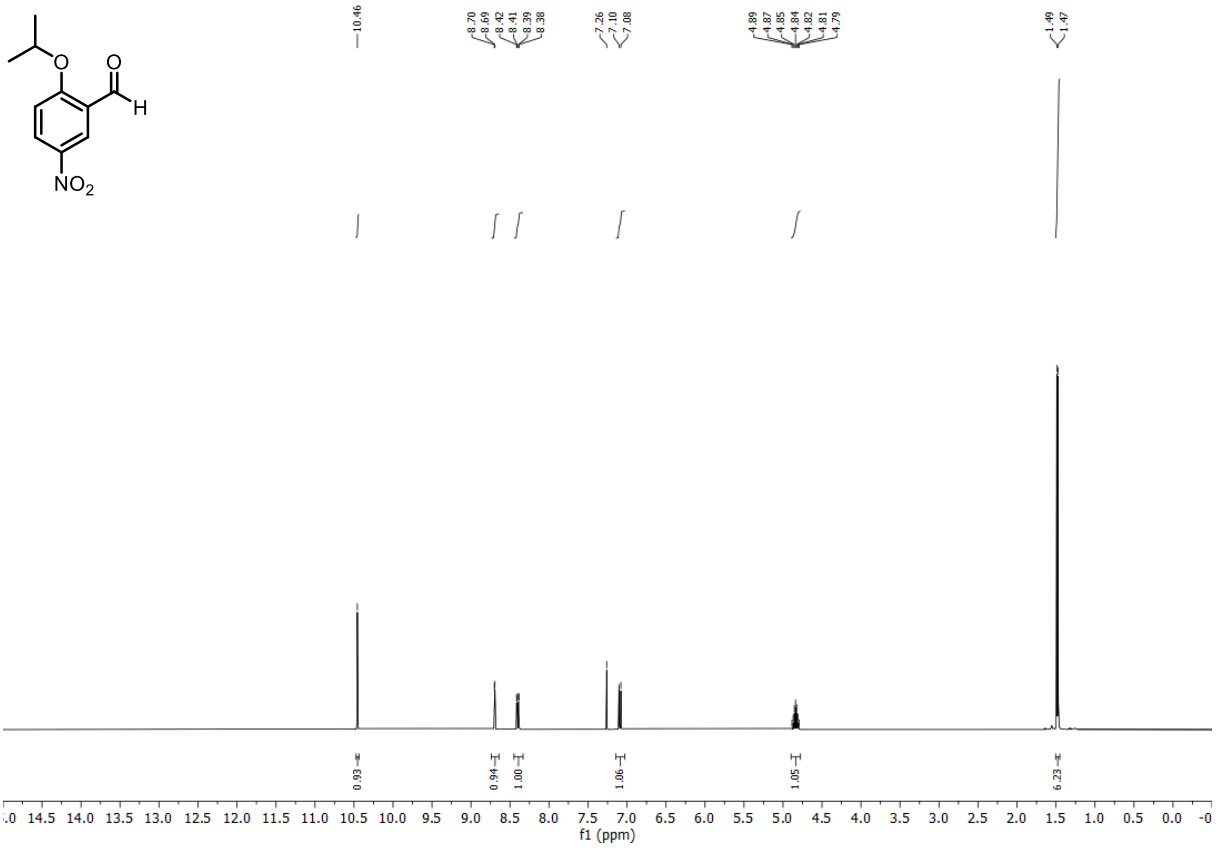
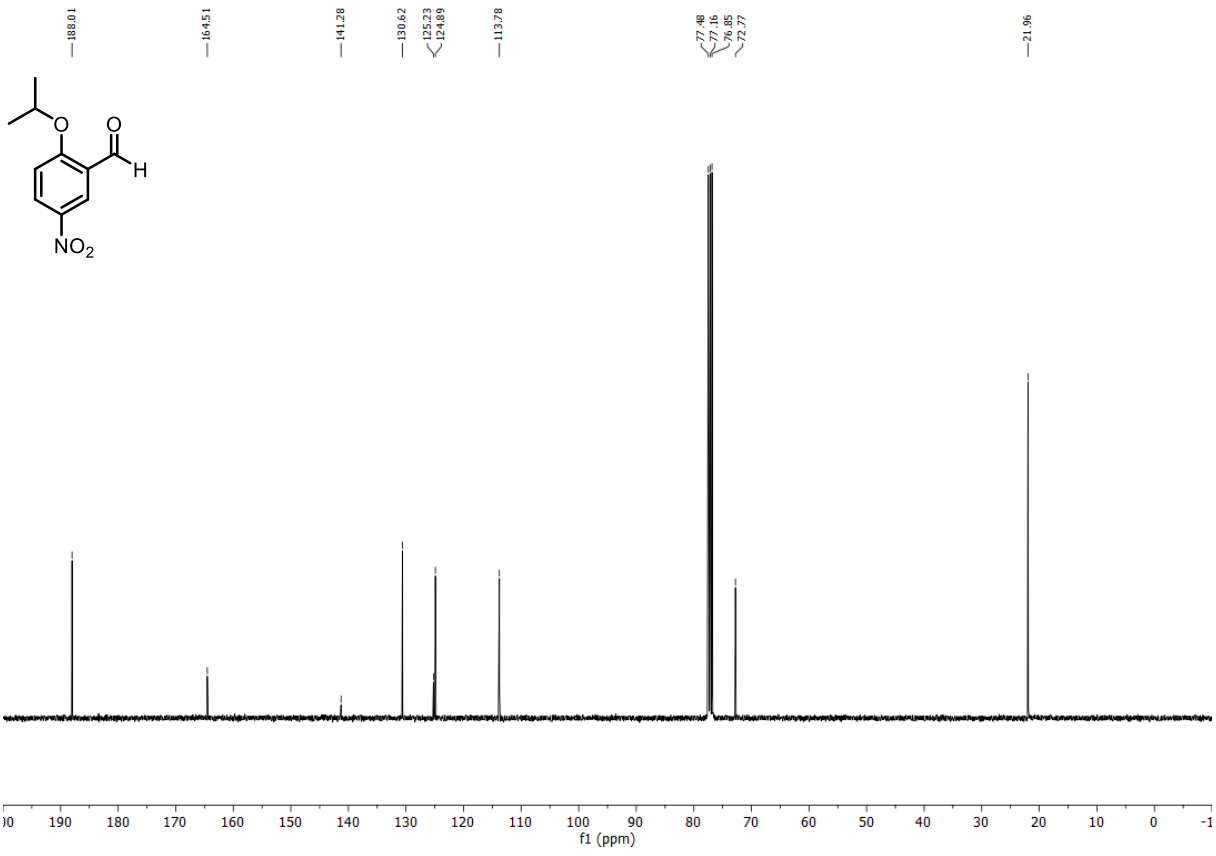
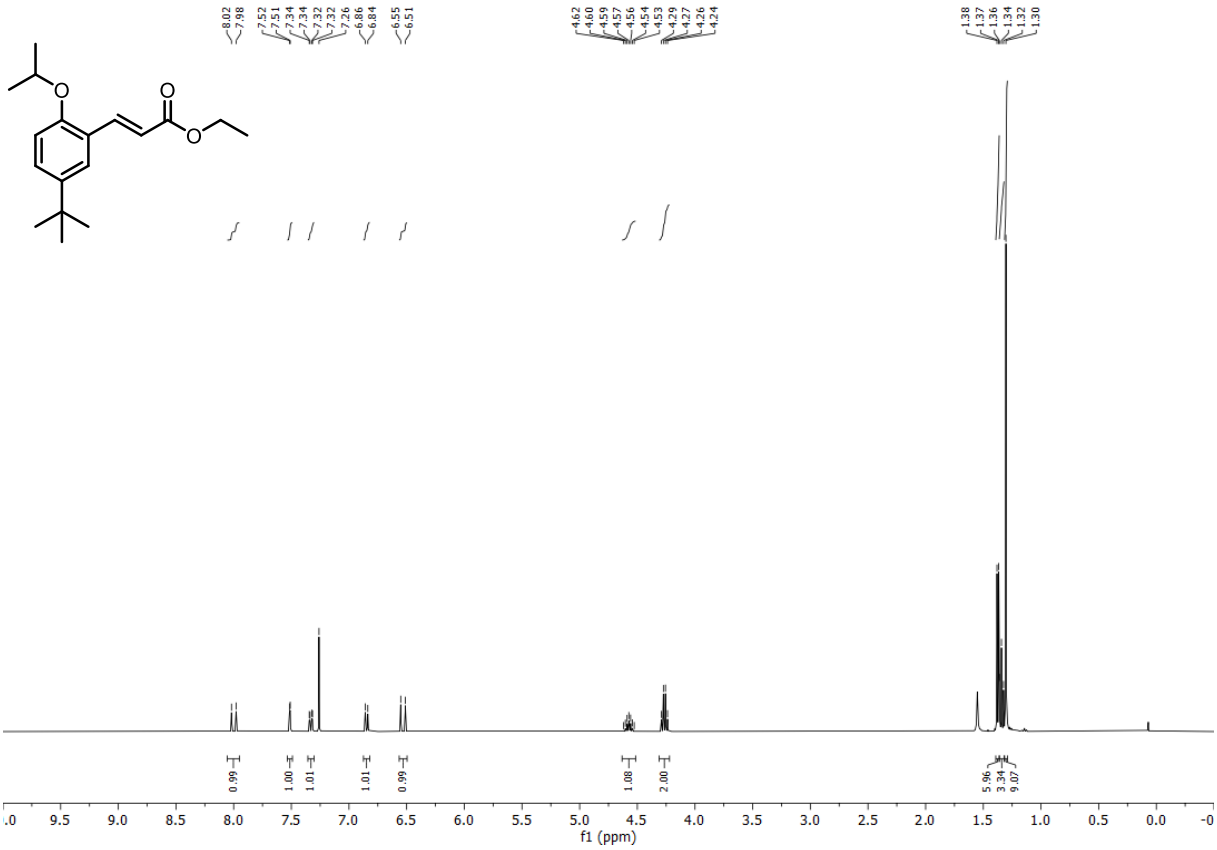


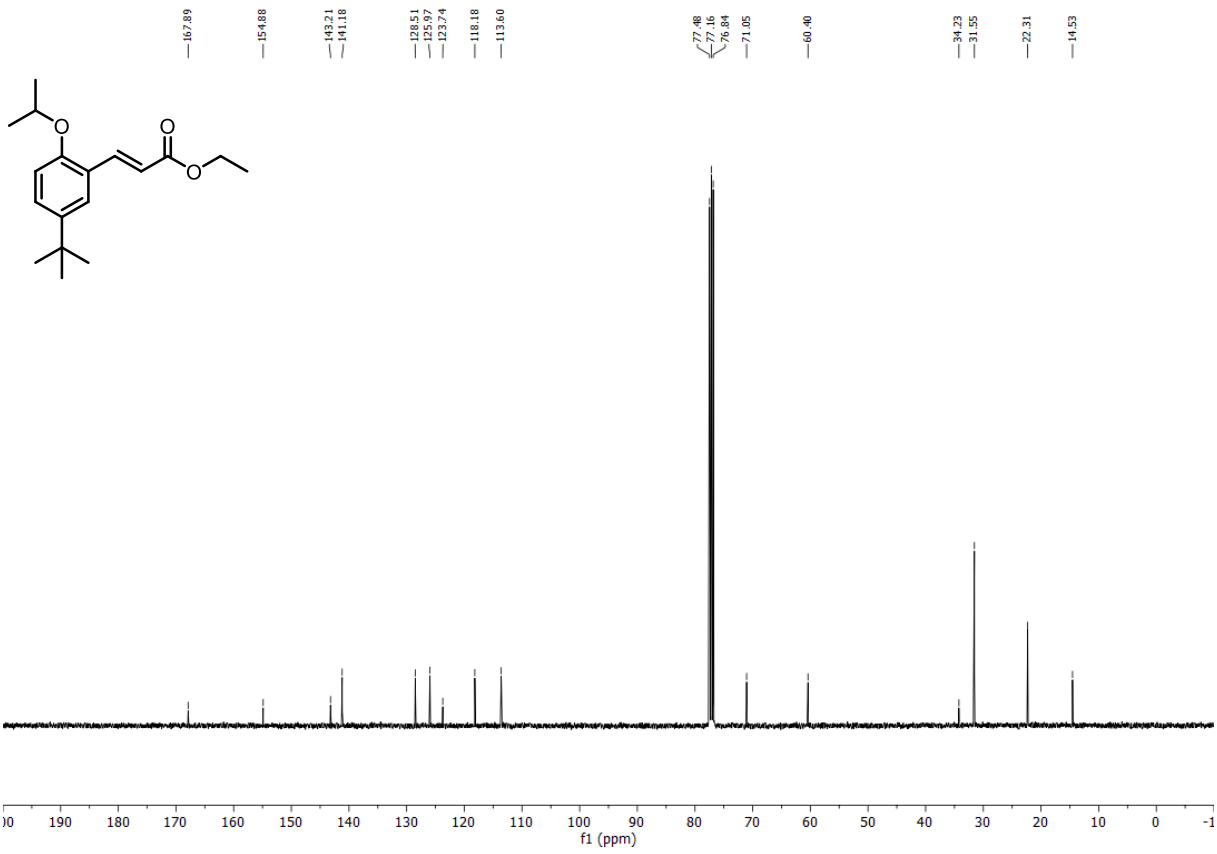
^{13}C NMR (101 MHz, $CDCl_3$)



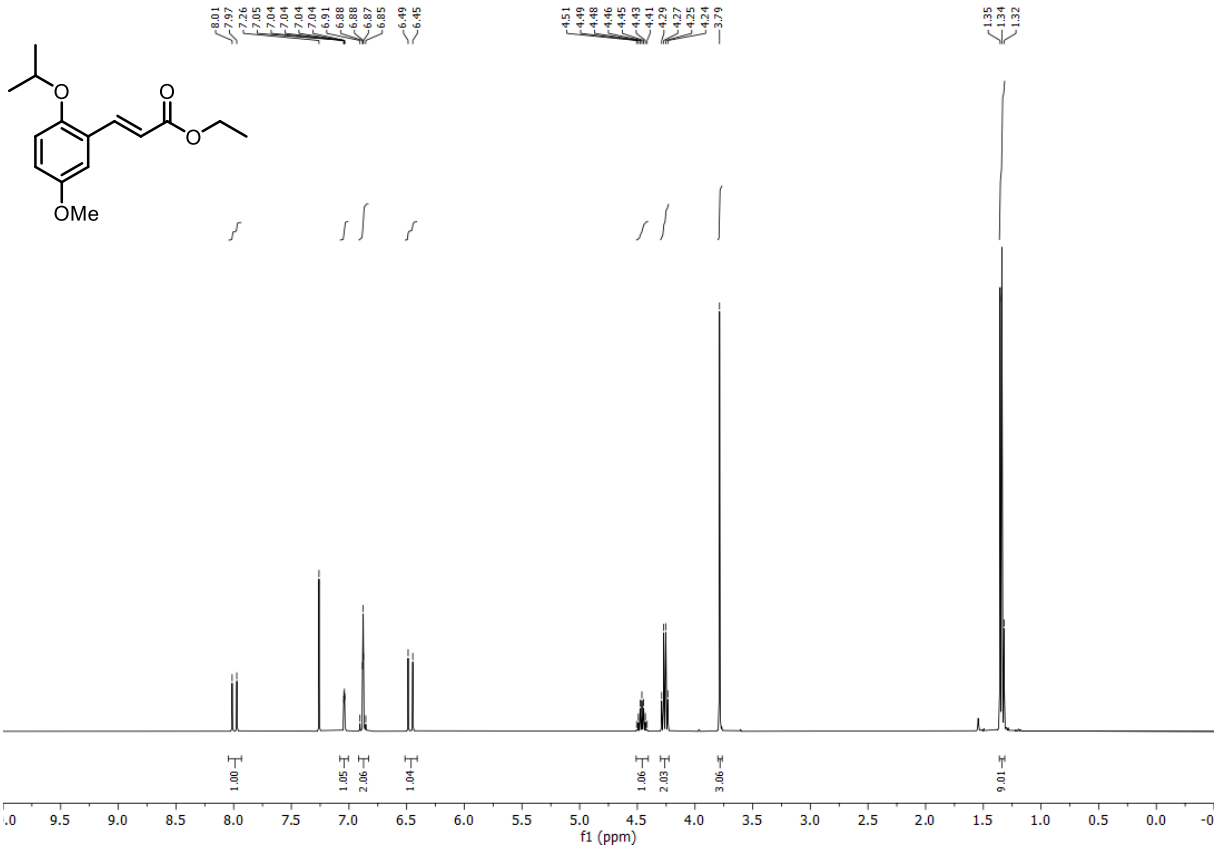
^{1}H NMR (400 MHz, $CDCl_3$)



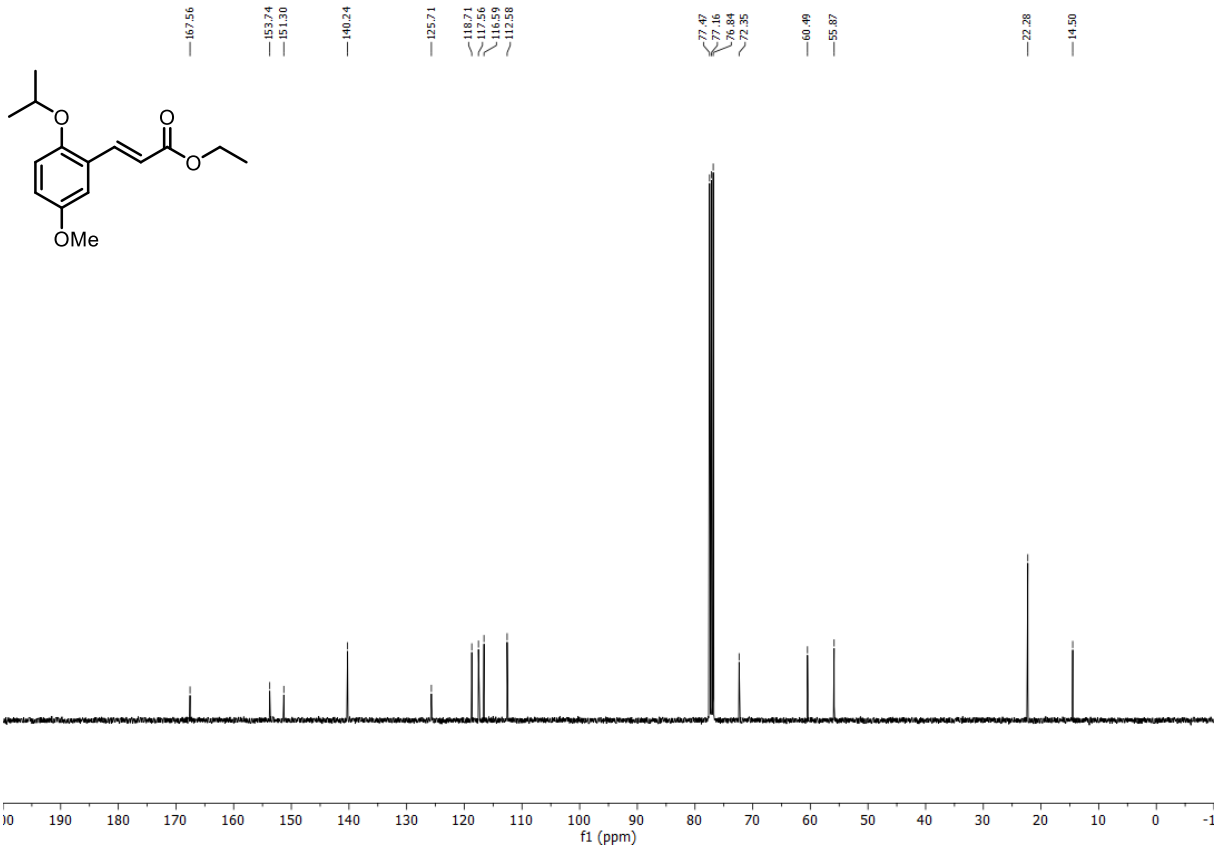
^{13}C NMR (101 MHz, $CDCl_3$)



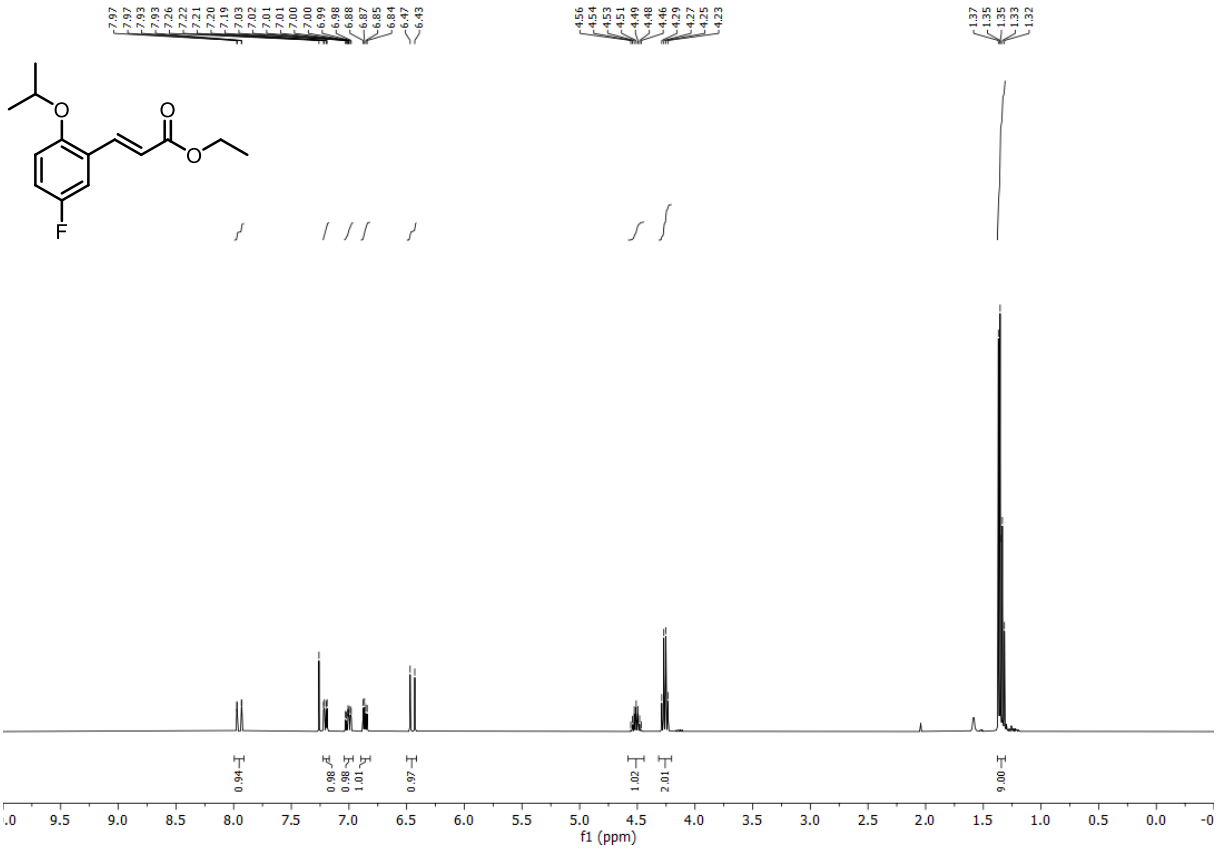
^{1}H NMR (400 MHz, $CDCl_3$)



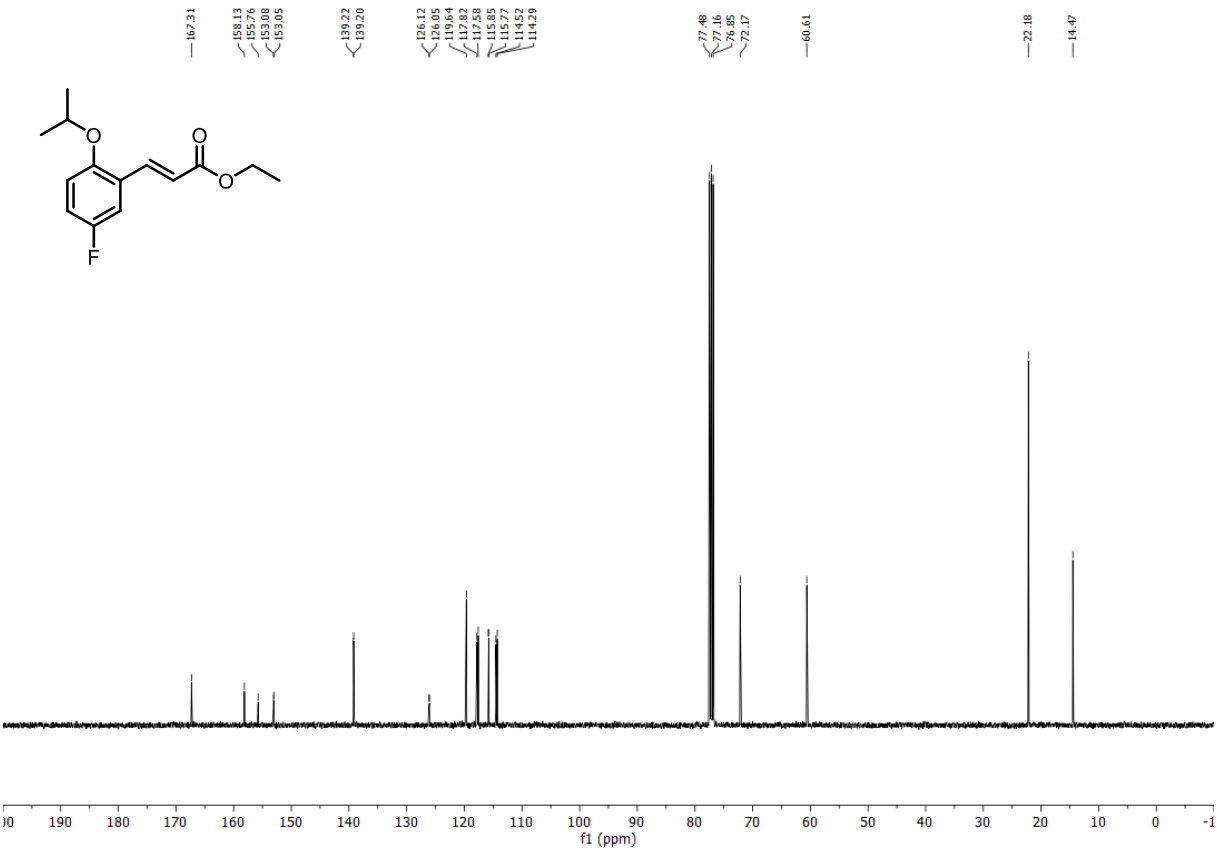
^{13}C NMR (101 MHz, $CDCl_3$)



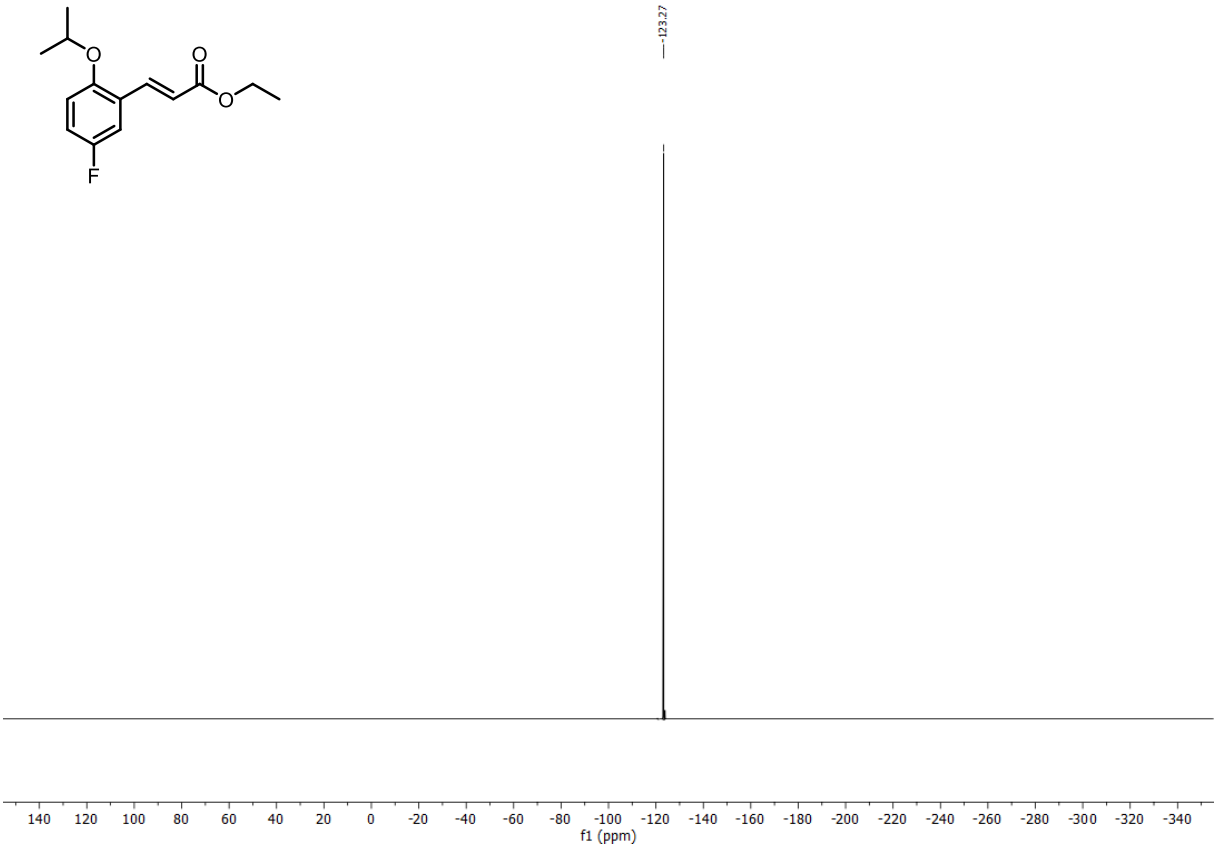
^{1}H NMR (400 MHz, $CDCl_3$)



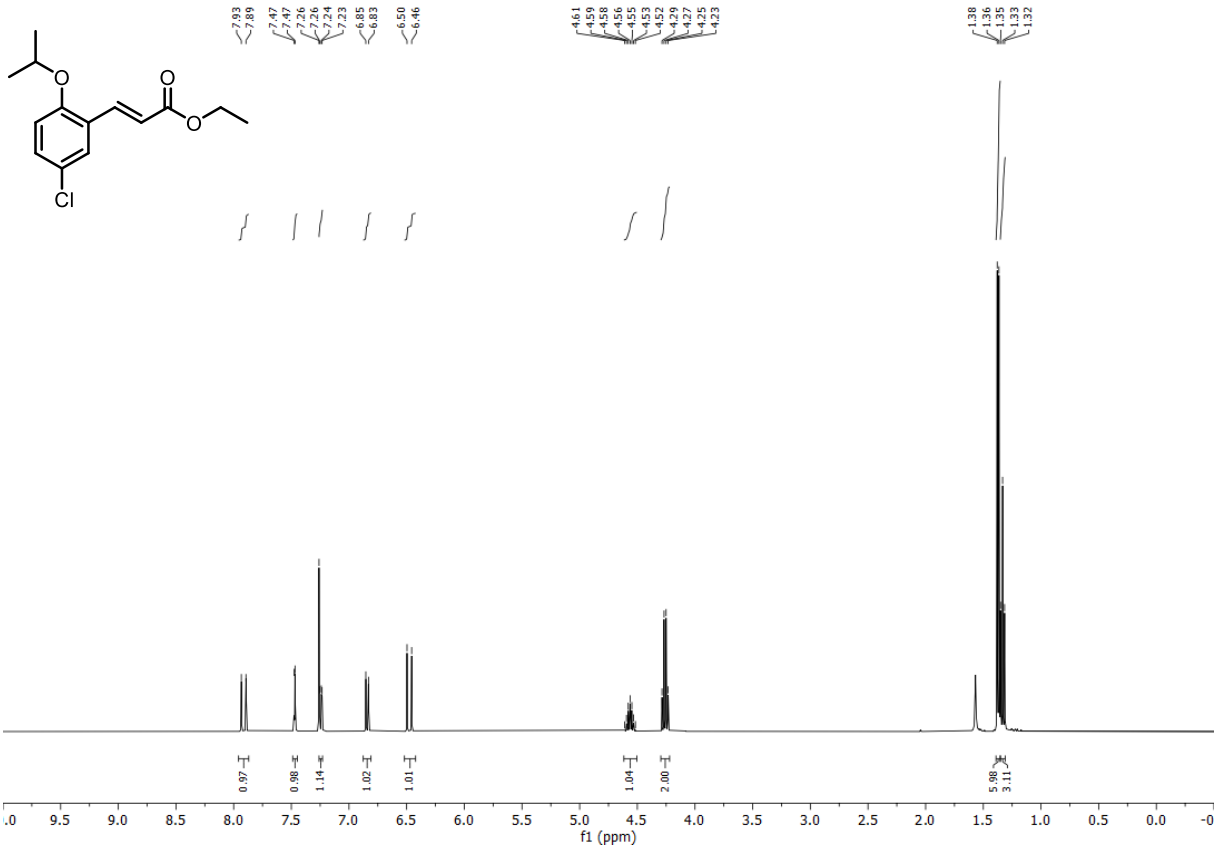
^{13}C NMR (101 MHz, $CDCl_3$)



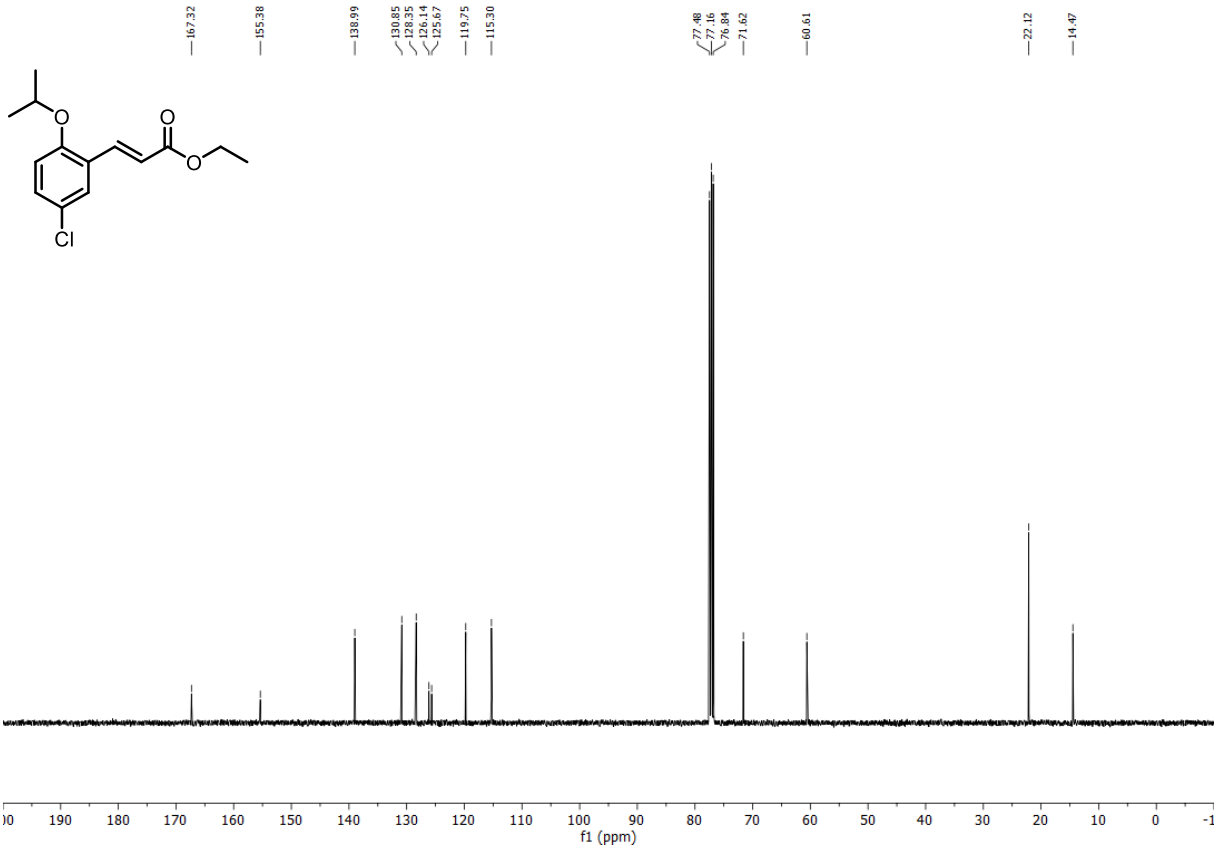
^{19}F NMR (282 MHz, $CDCl_3$)



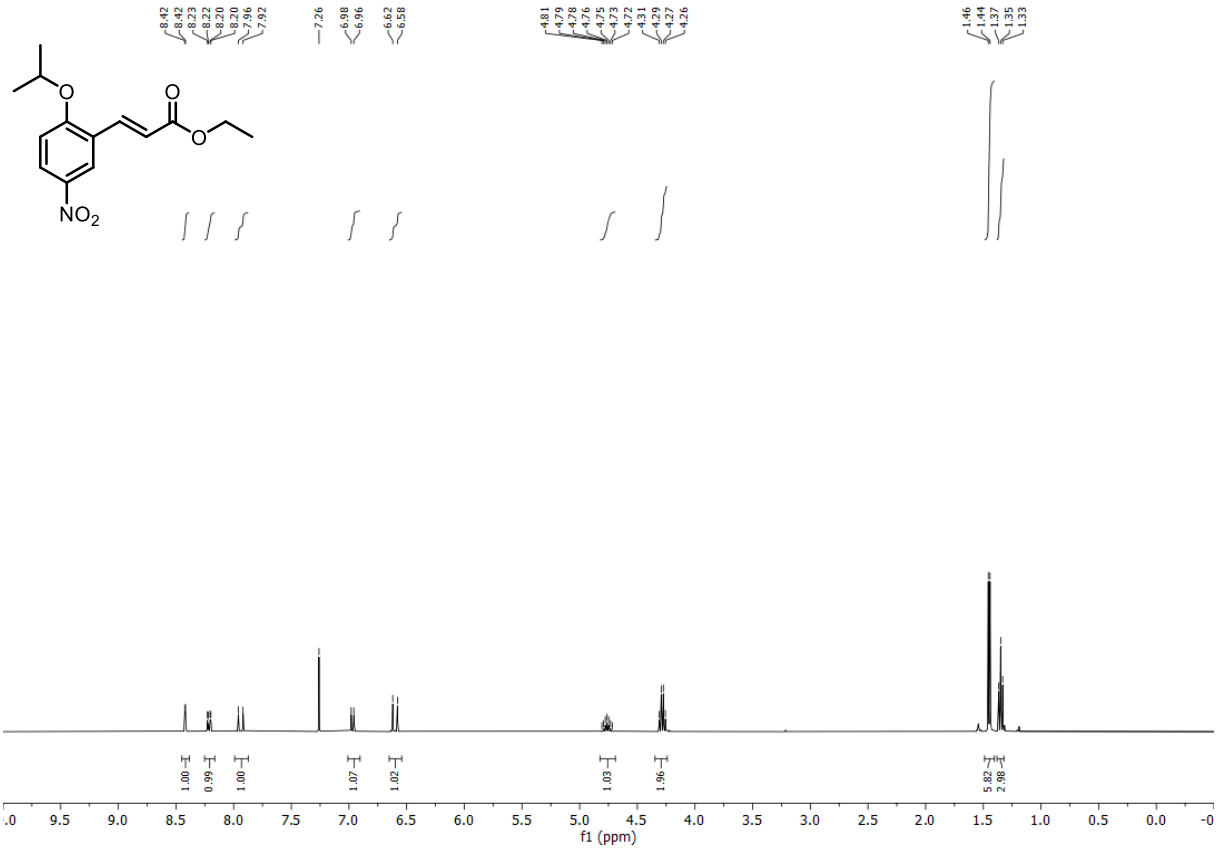
^{1}H NMR (400 MHz, $CDCl_3$)



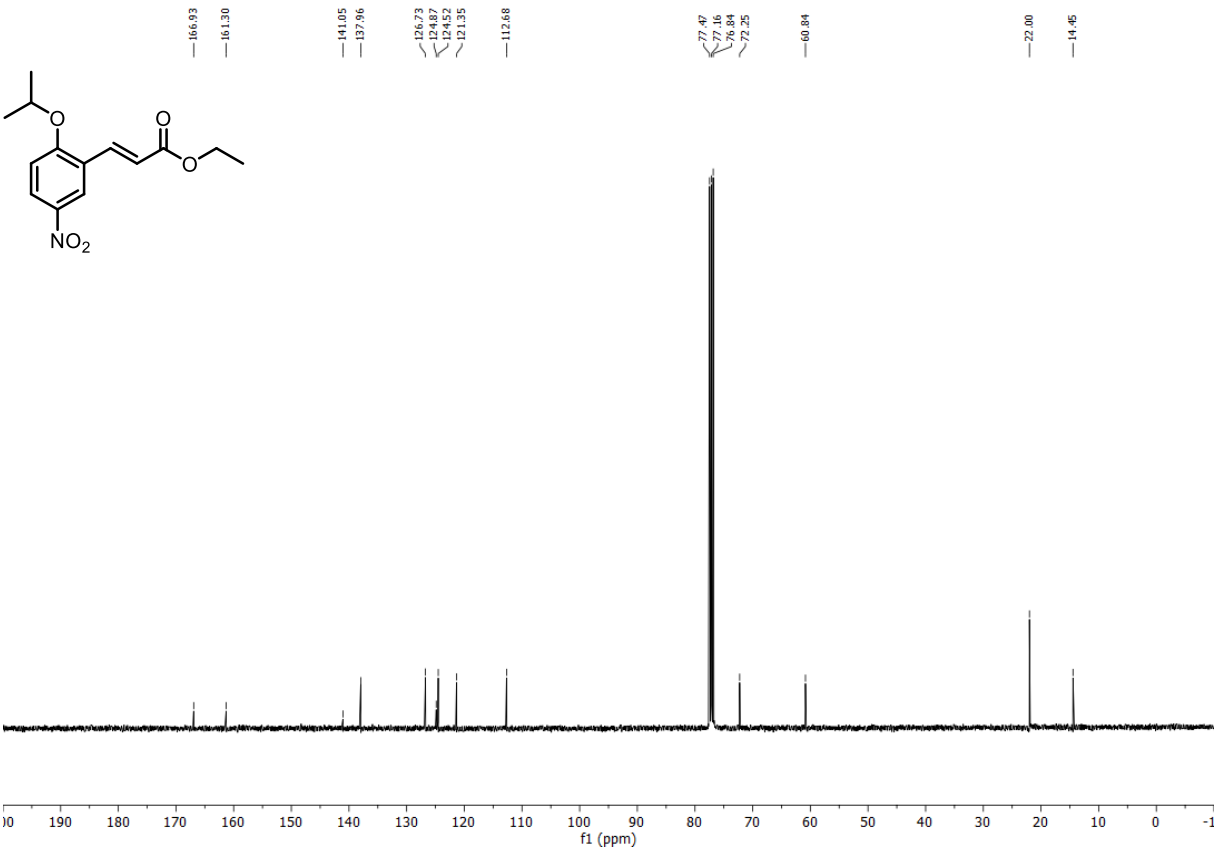
^{13}C NMR (101 MHz, $CDCl_3$)



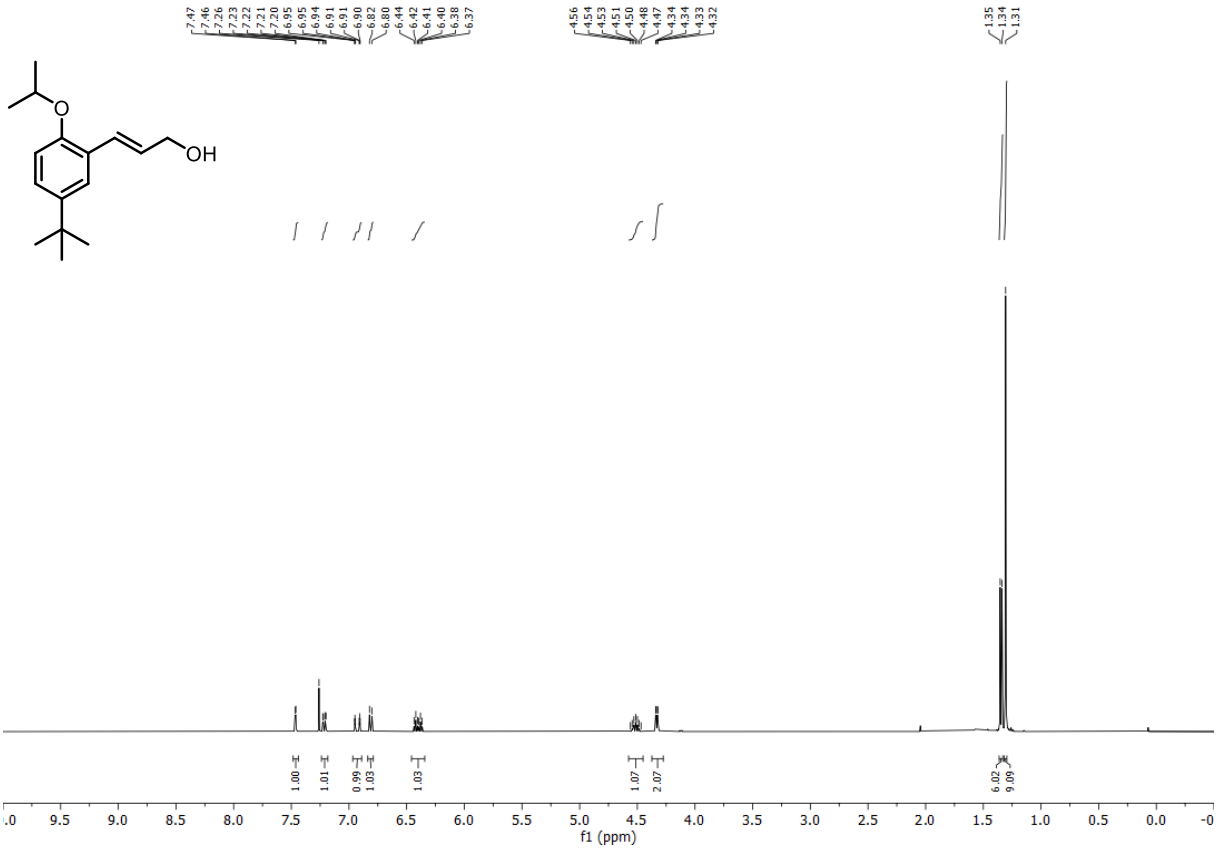
^{1}H NMR (400 MHz, $CDCl_3$)



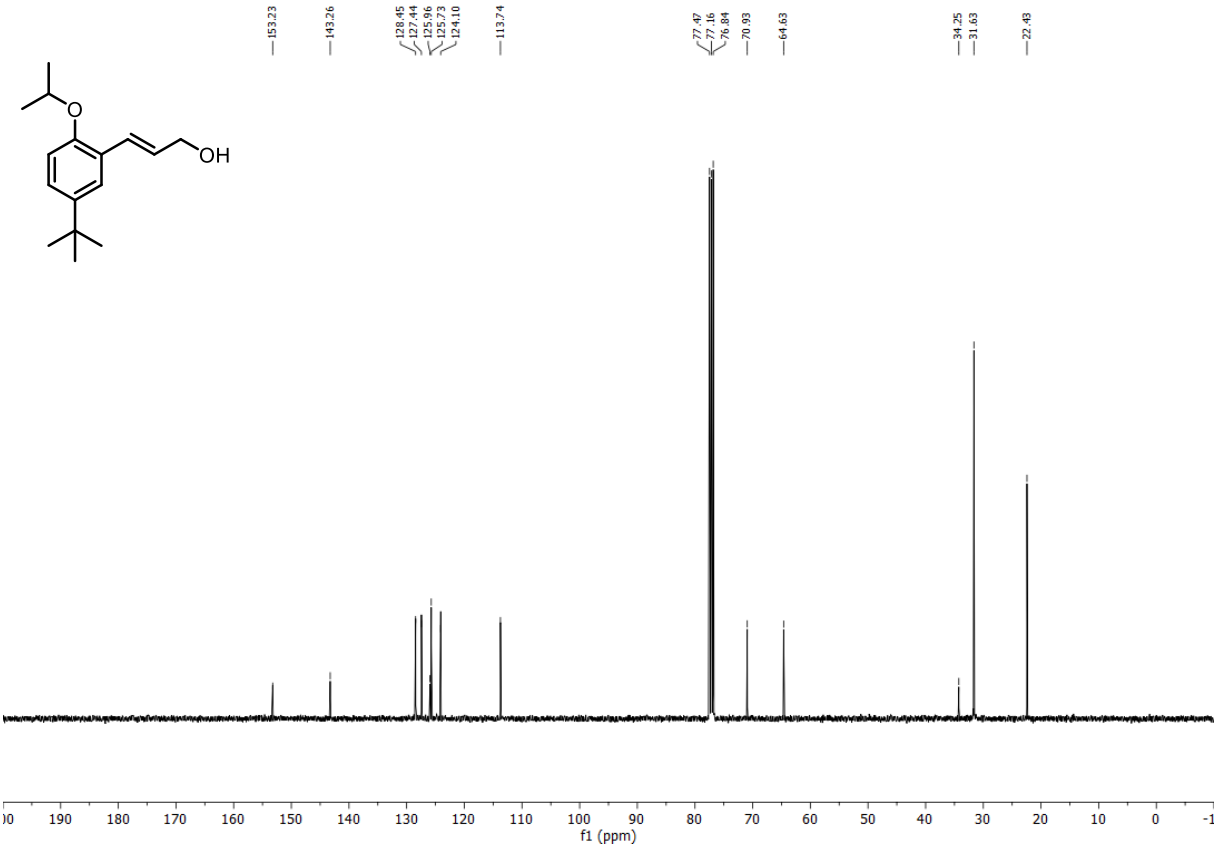
^{13}C NMR (101 MHz, $CDCl_3$)



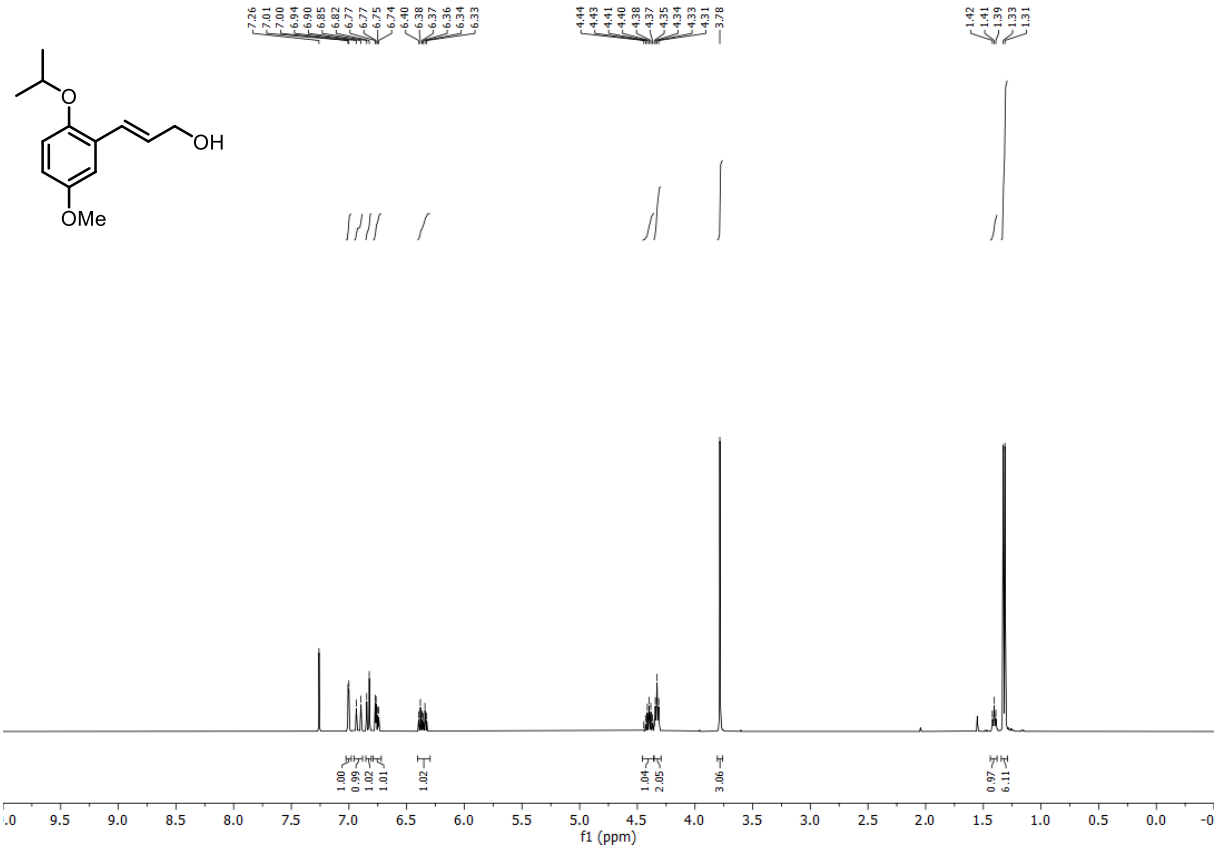
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



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



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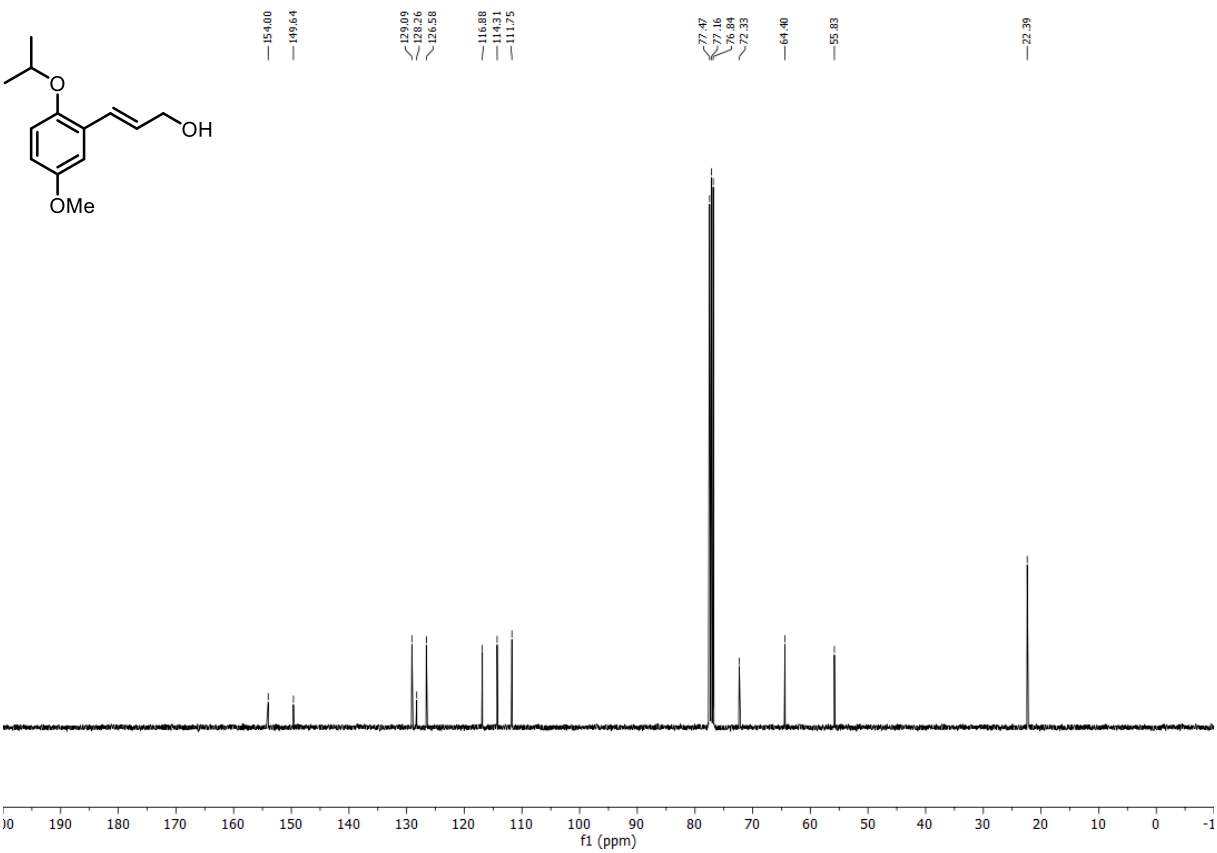

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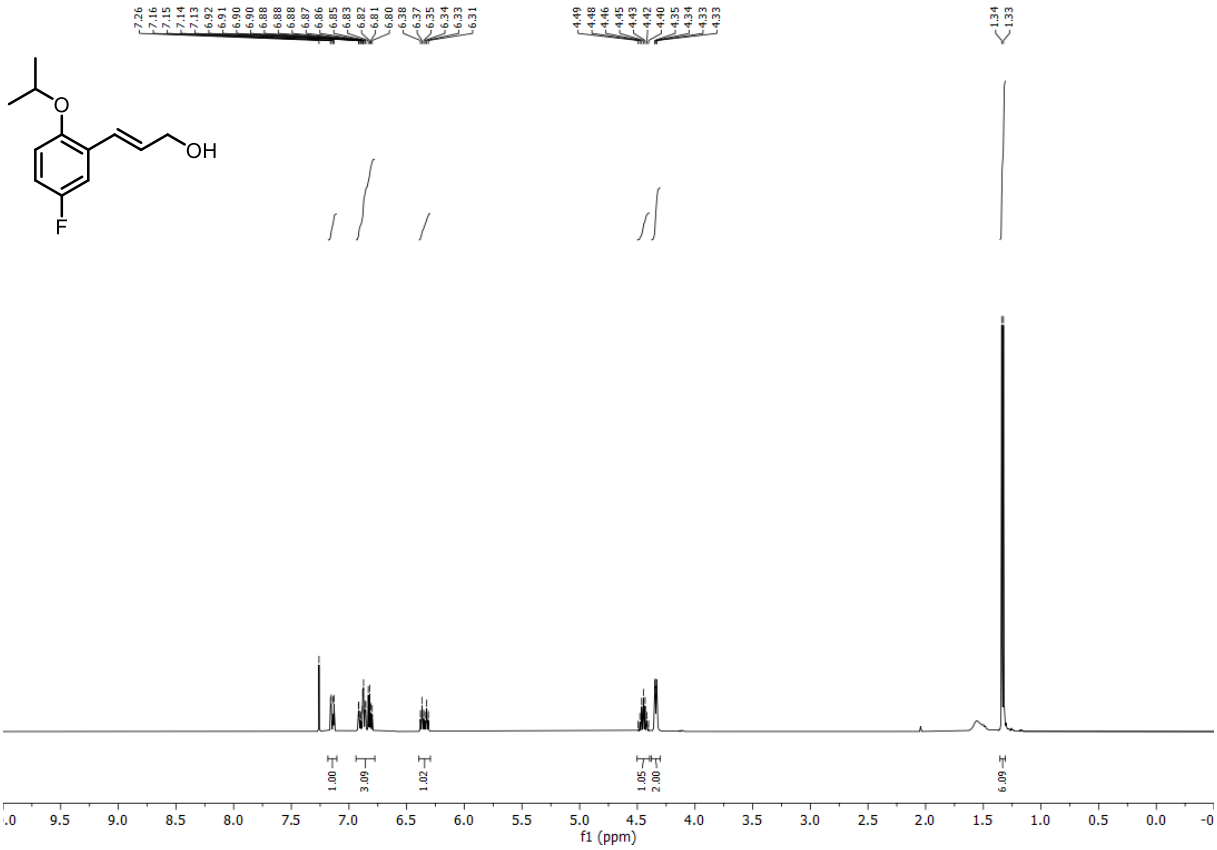

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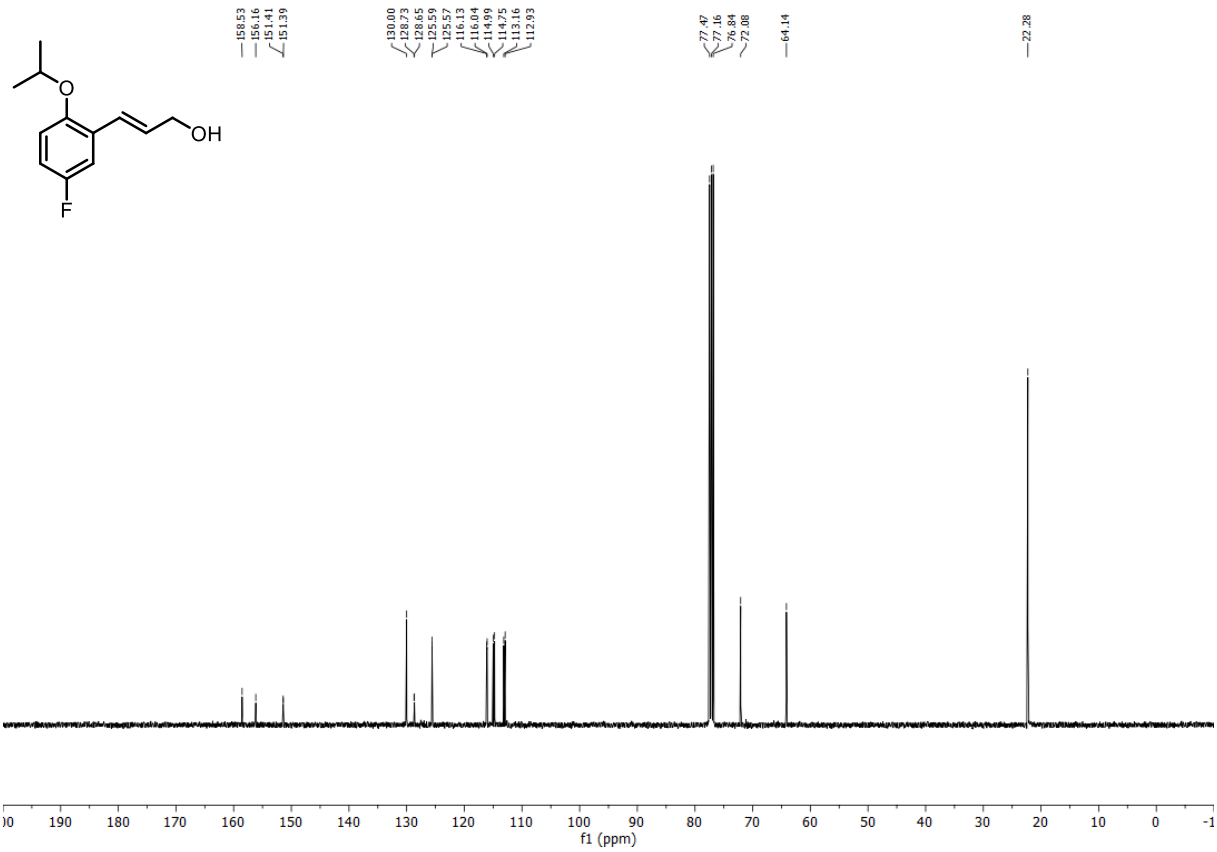
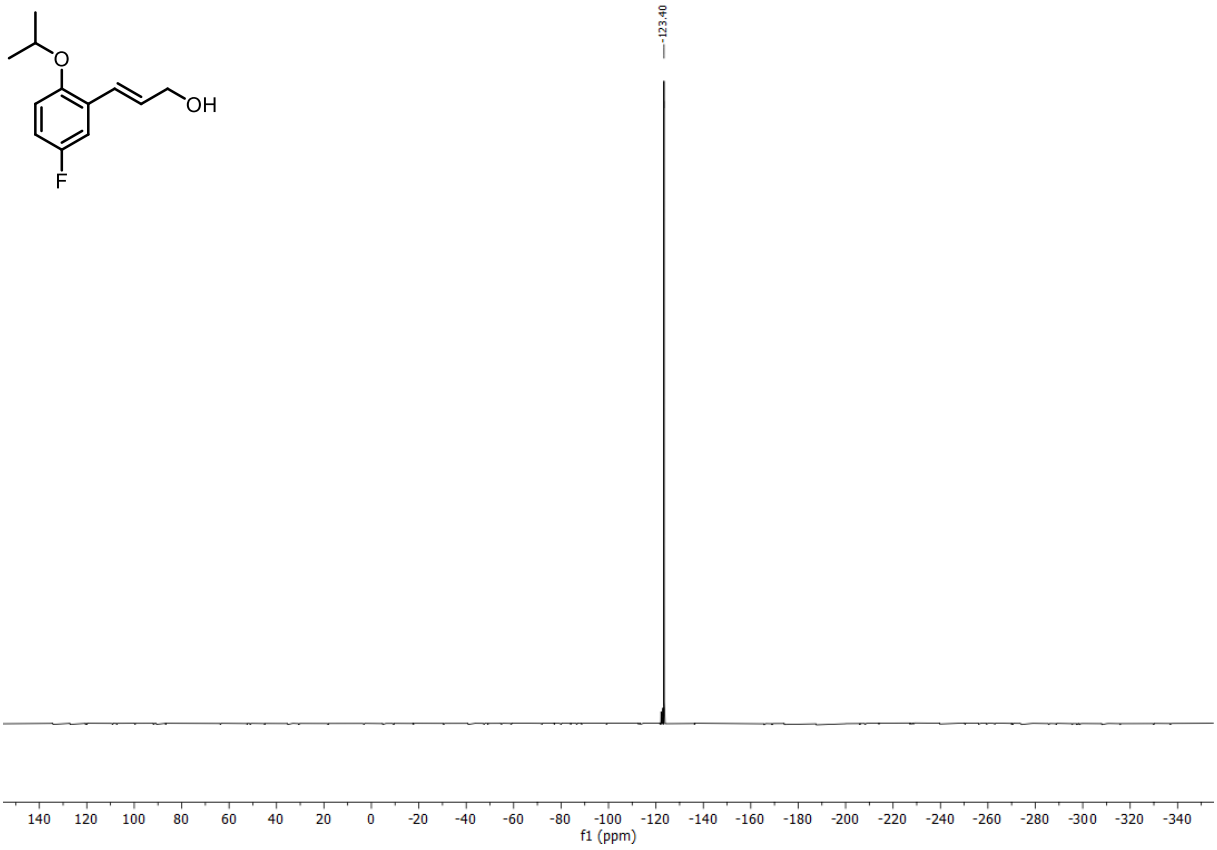
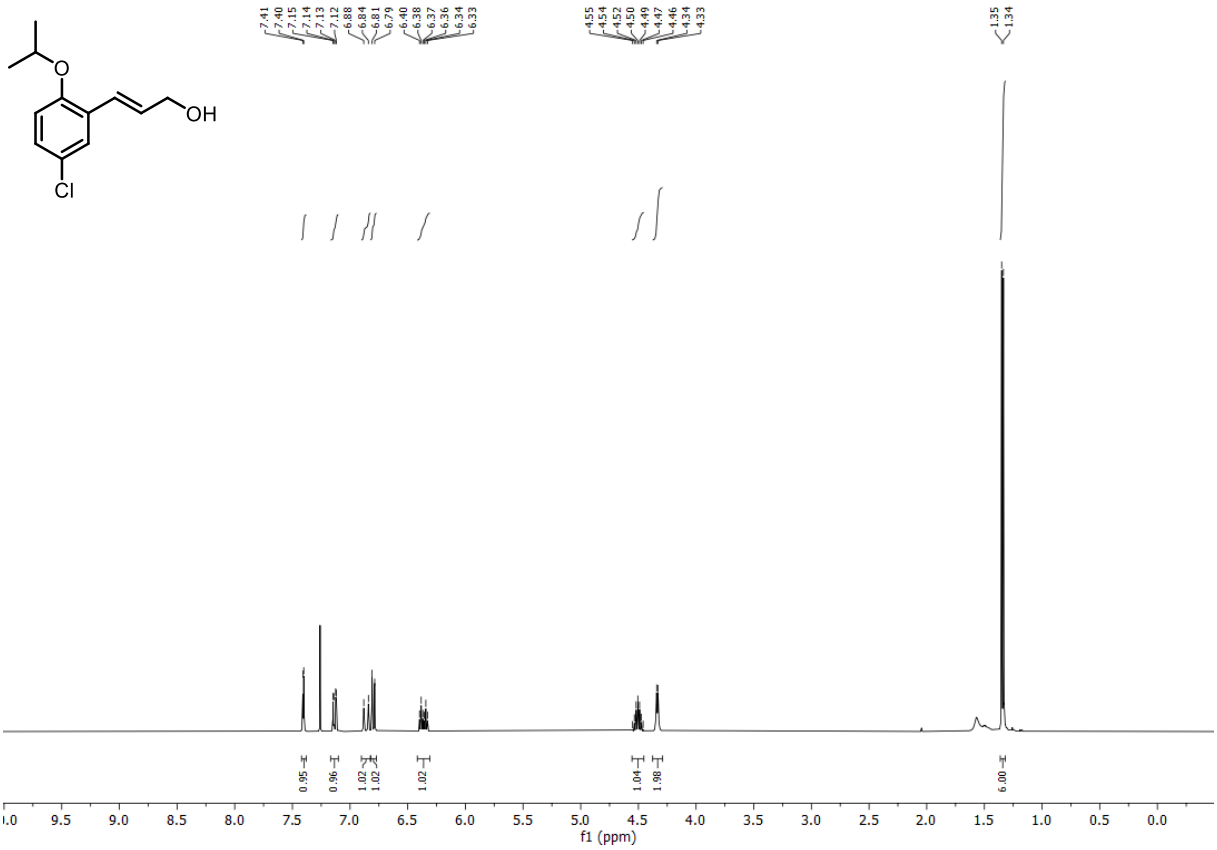


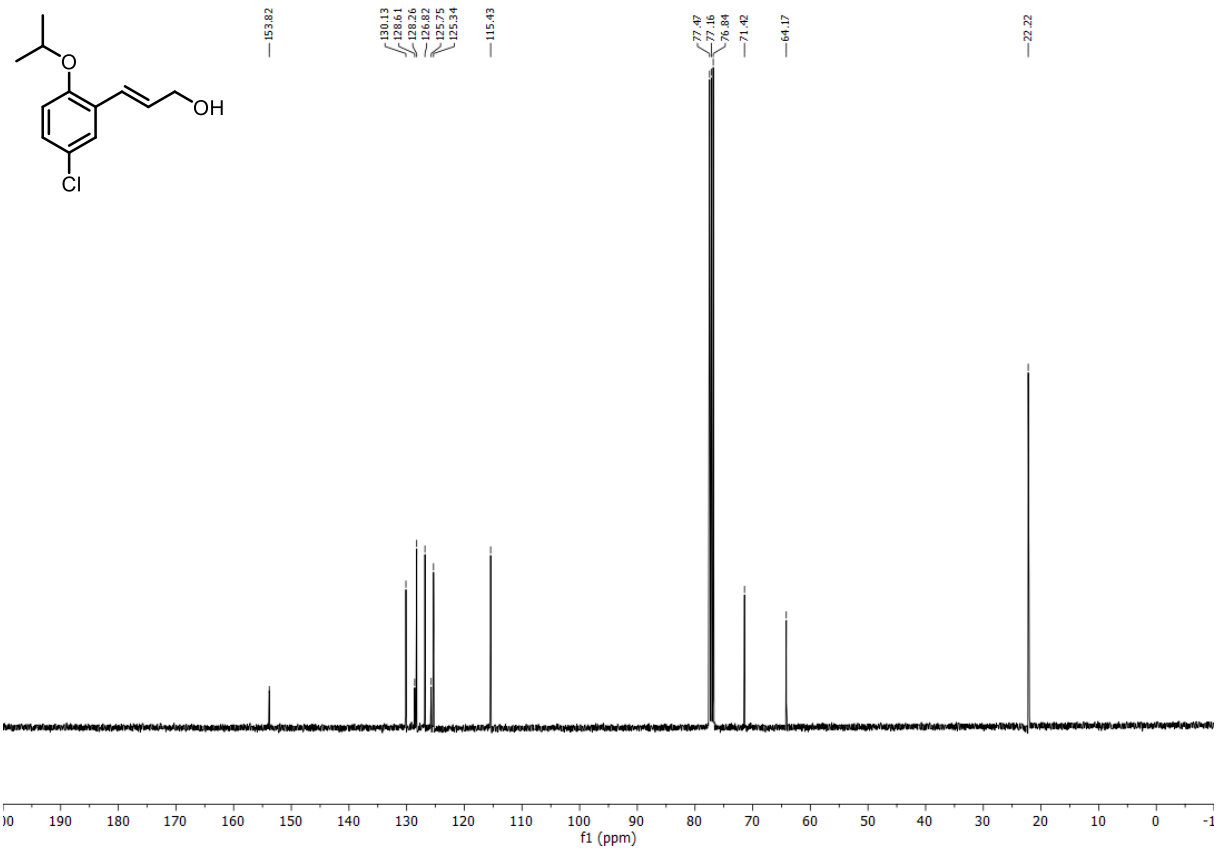
^{19}F NMR (282 MHz, $CDCl_3$)



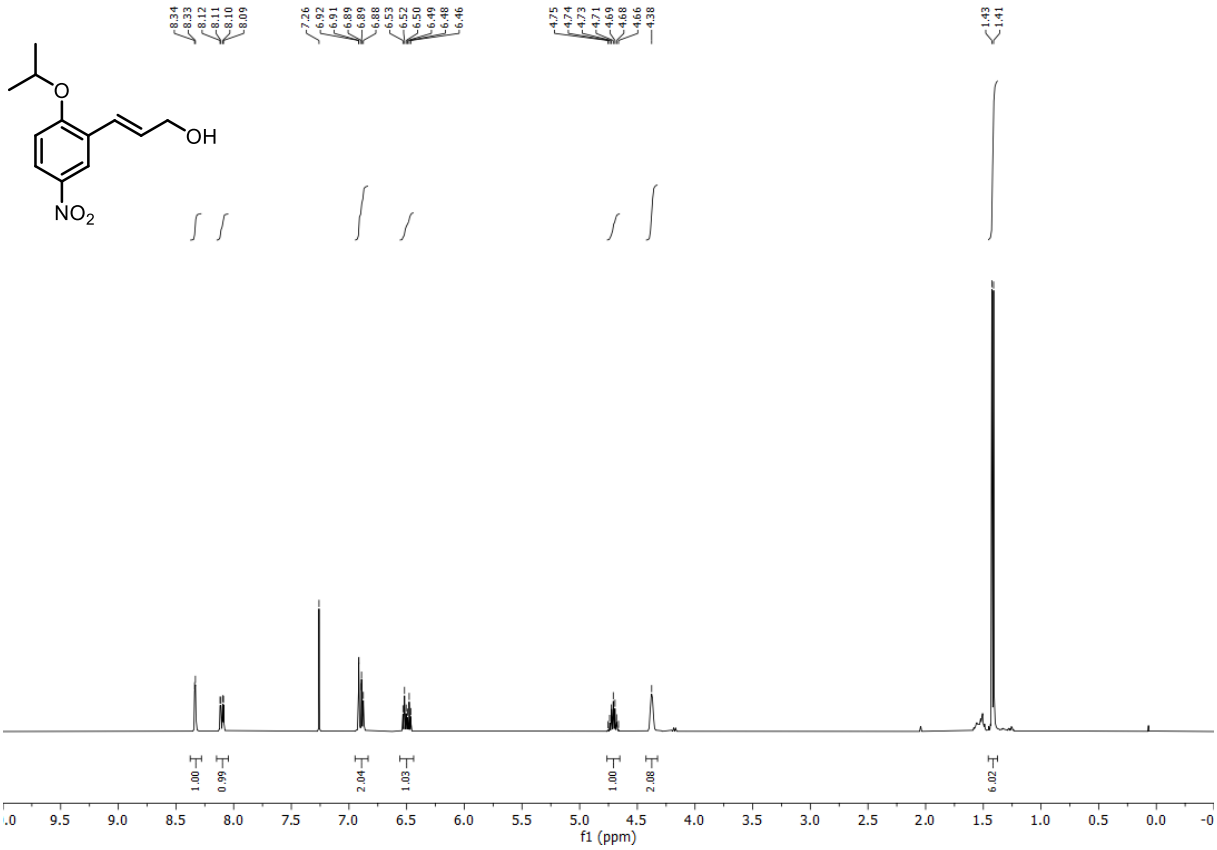
^{1}H NMR (400 MHz, $CDCl_3$)



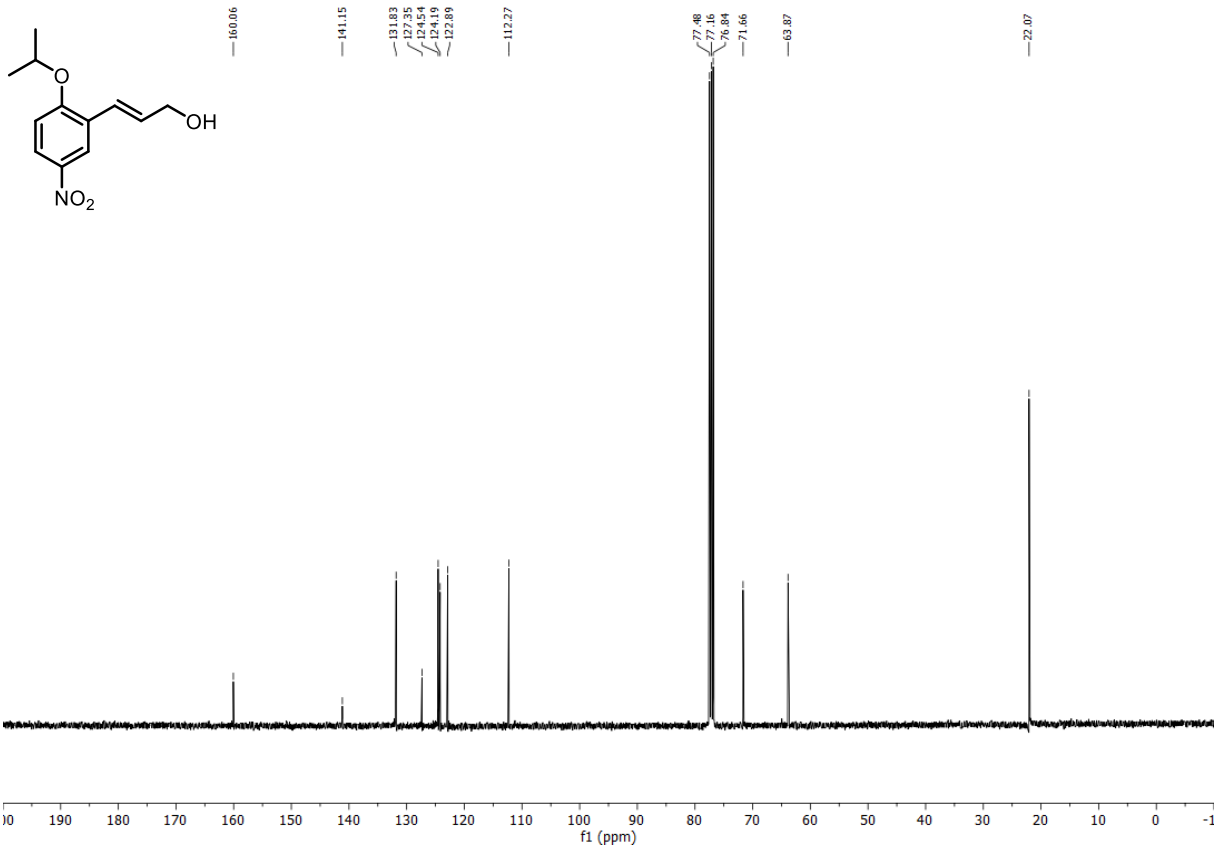
^{13}C NMR (101 MHz, $CDCl_3$)



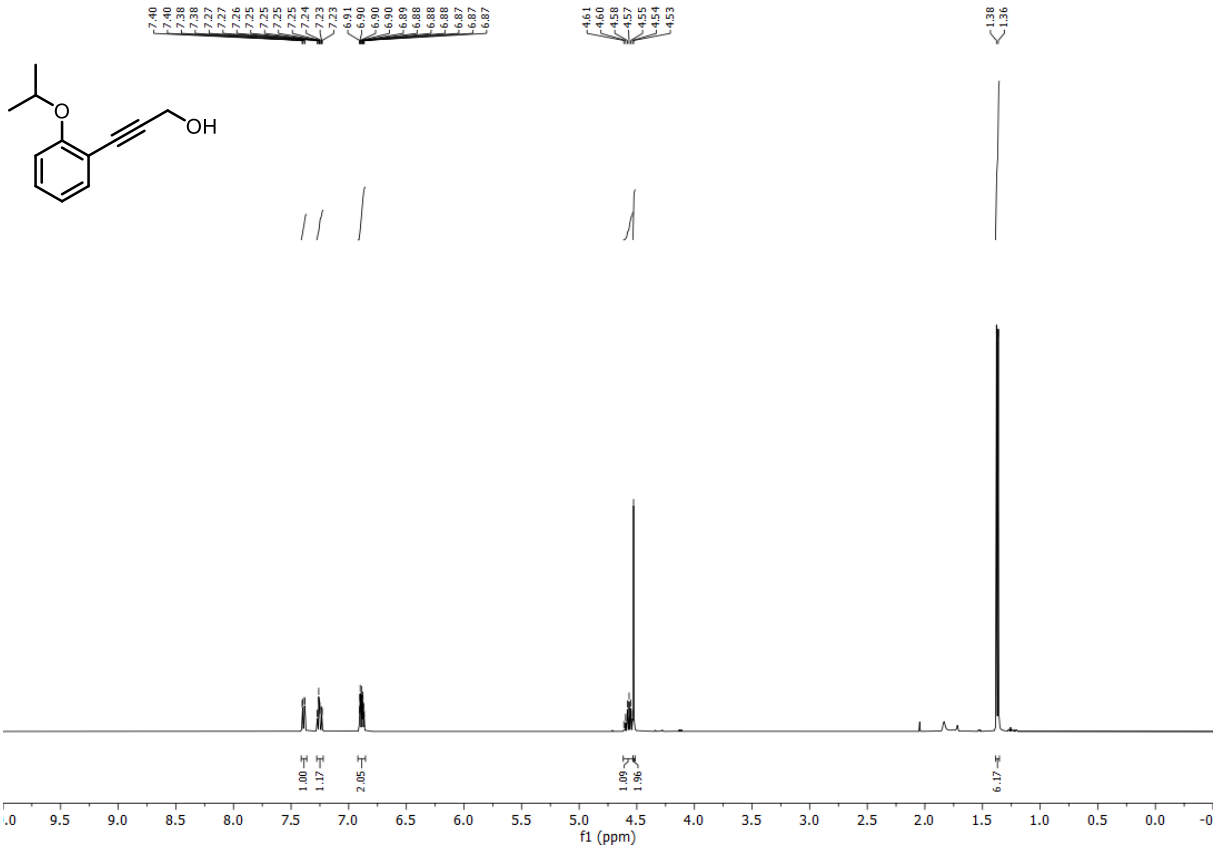
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



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



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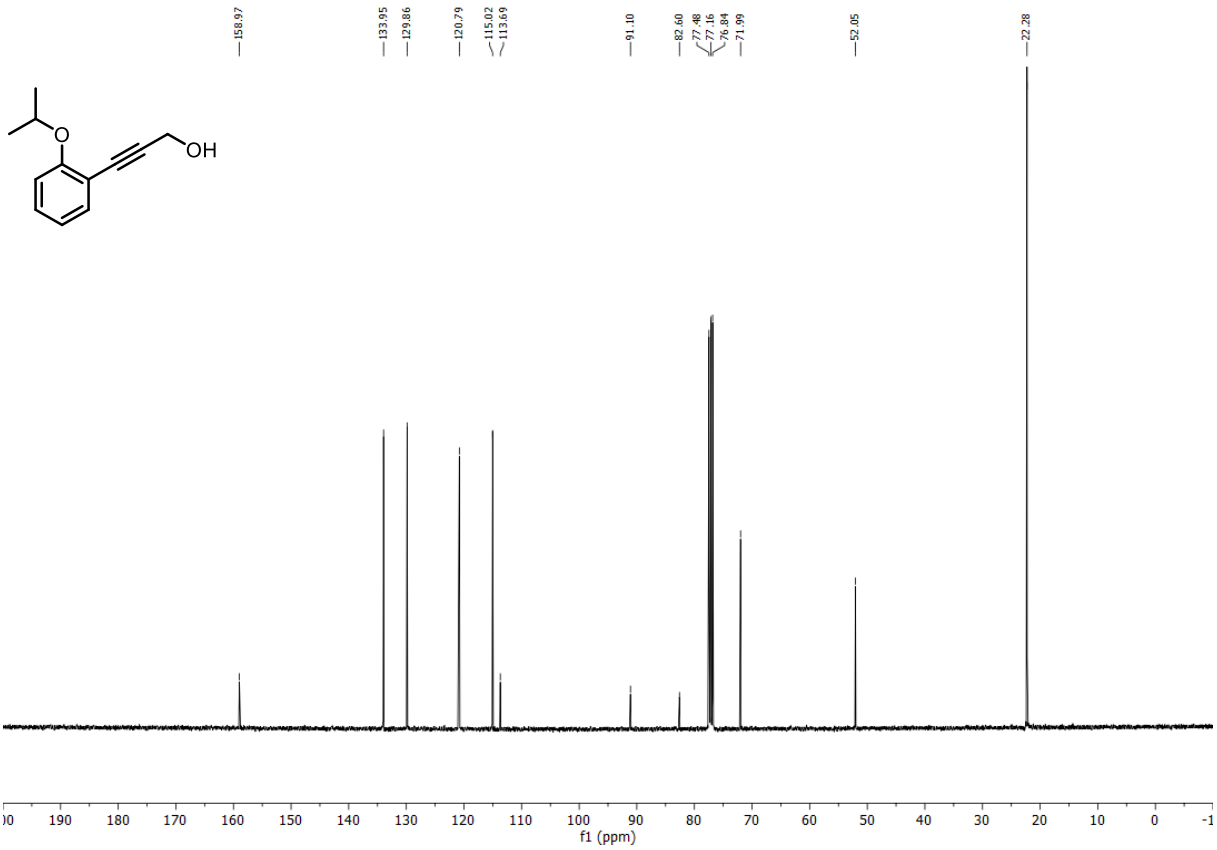

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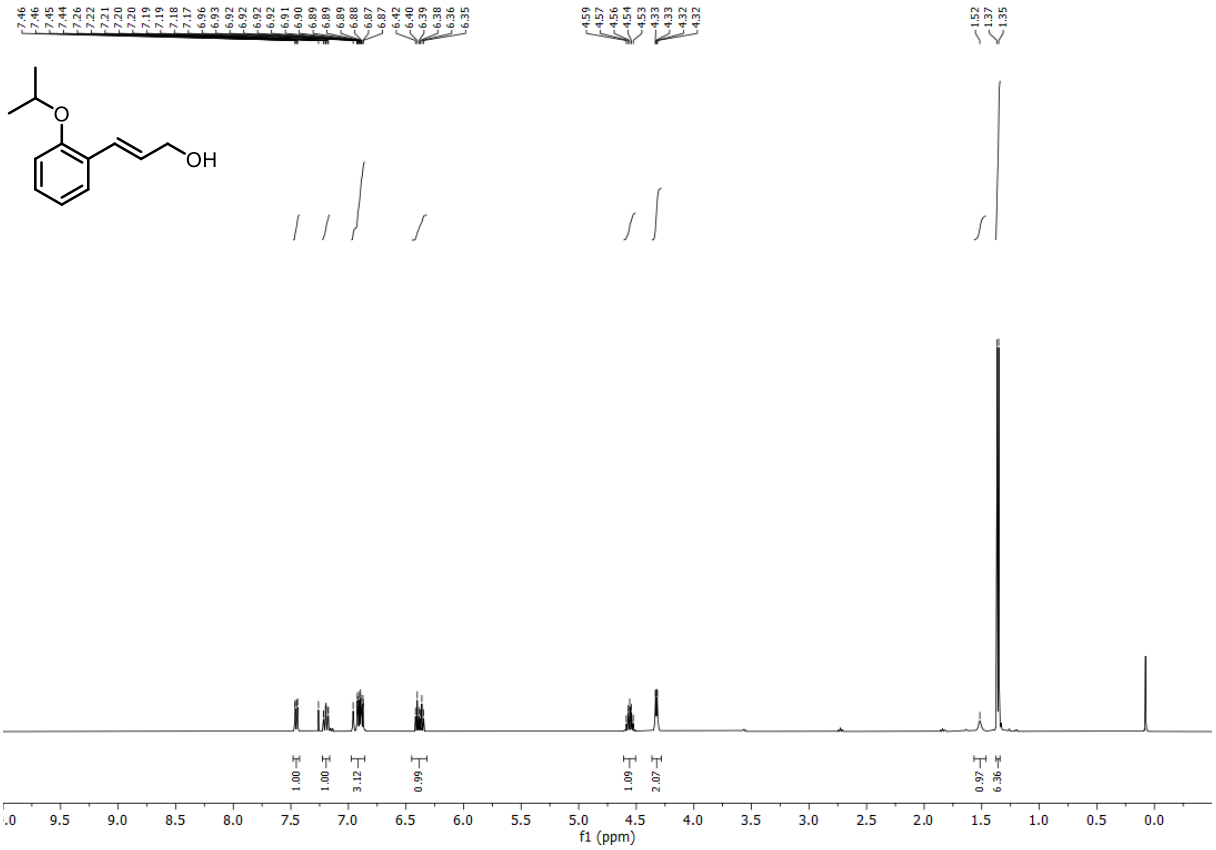
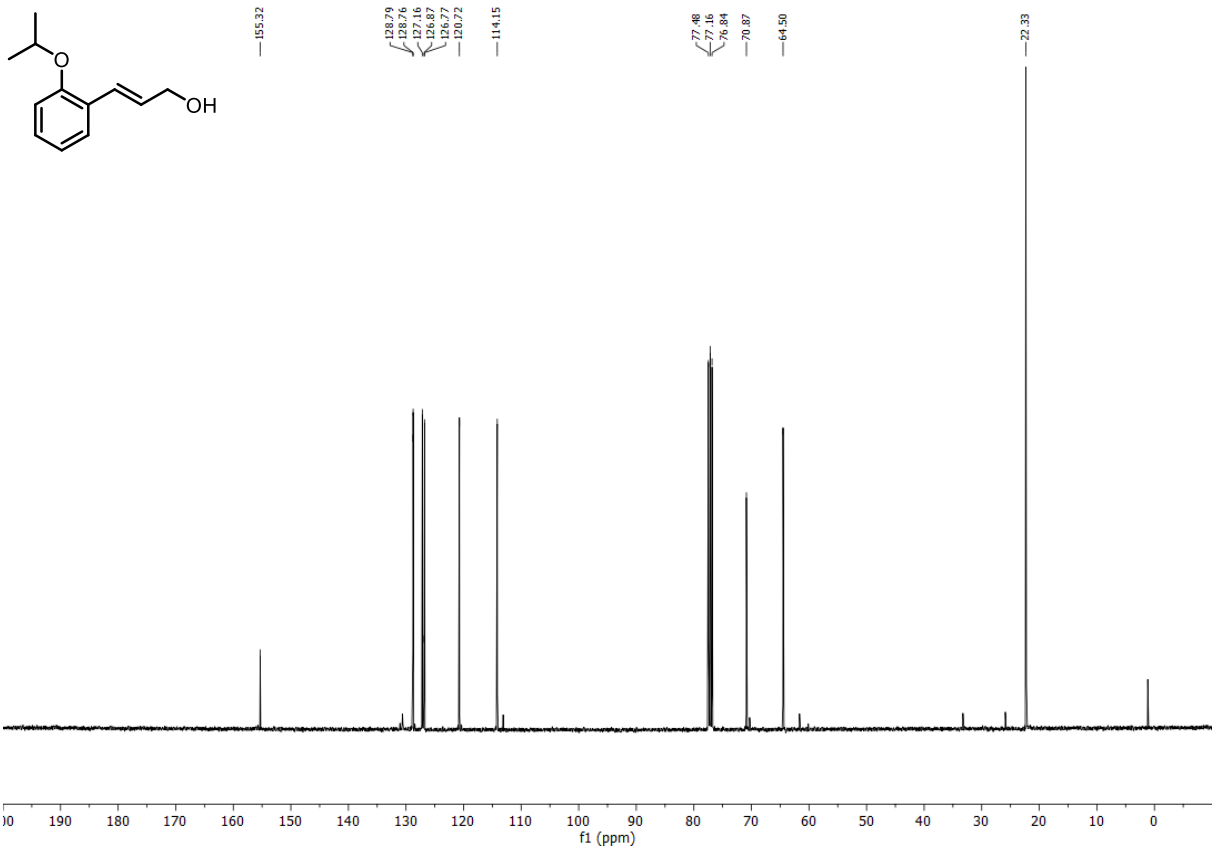
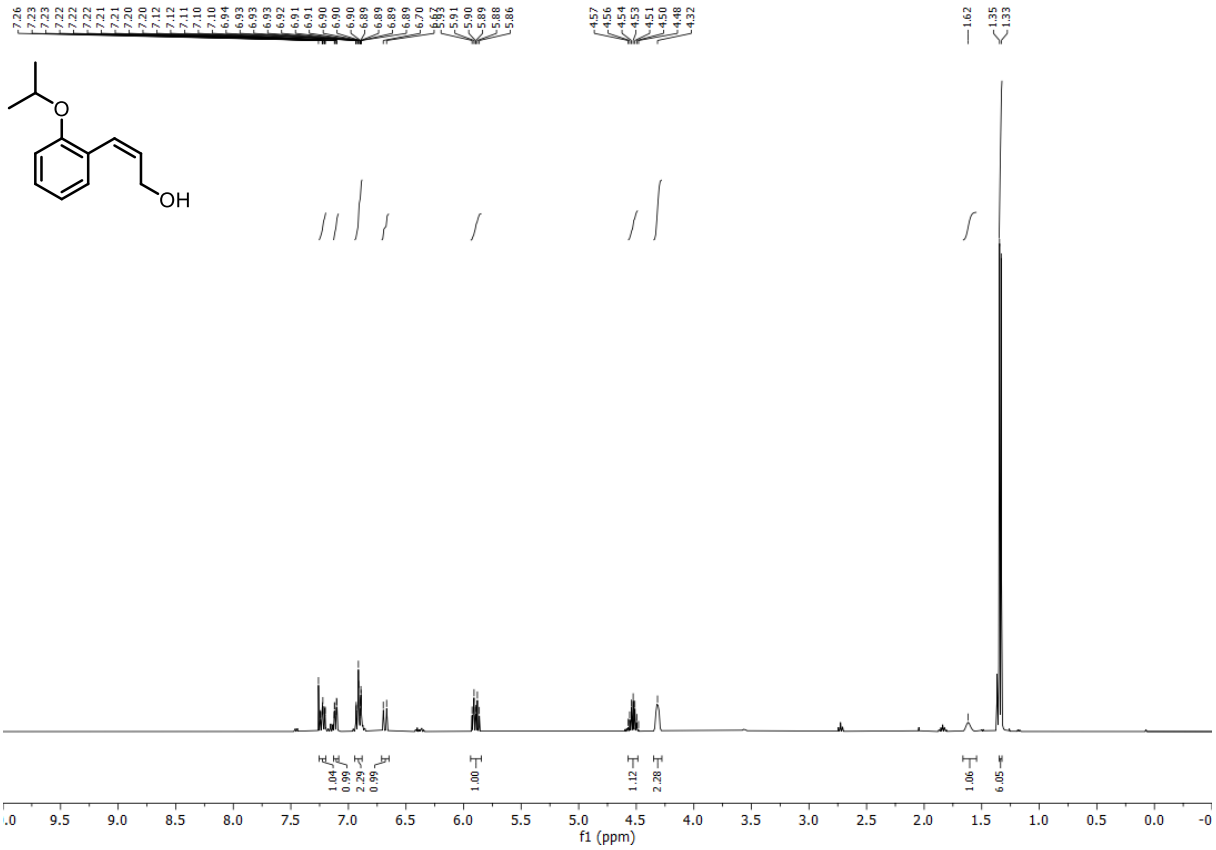


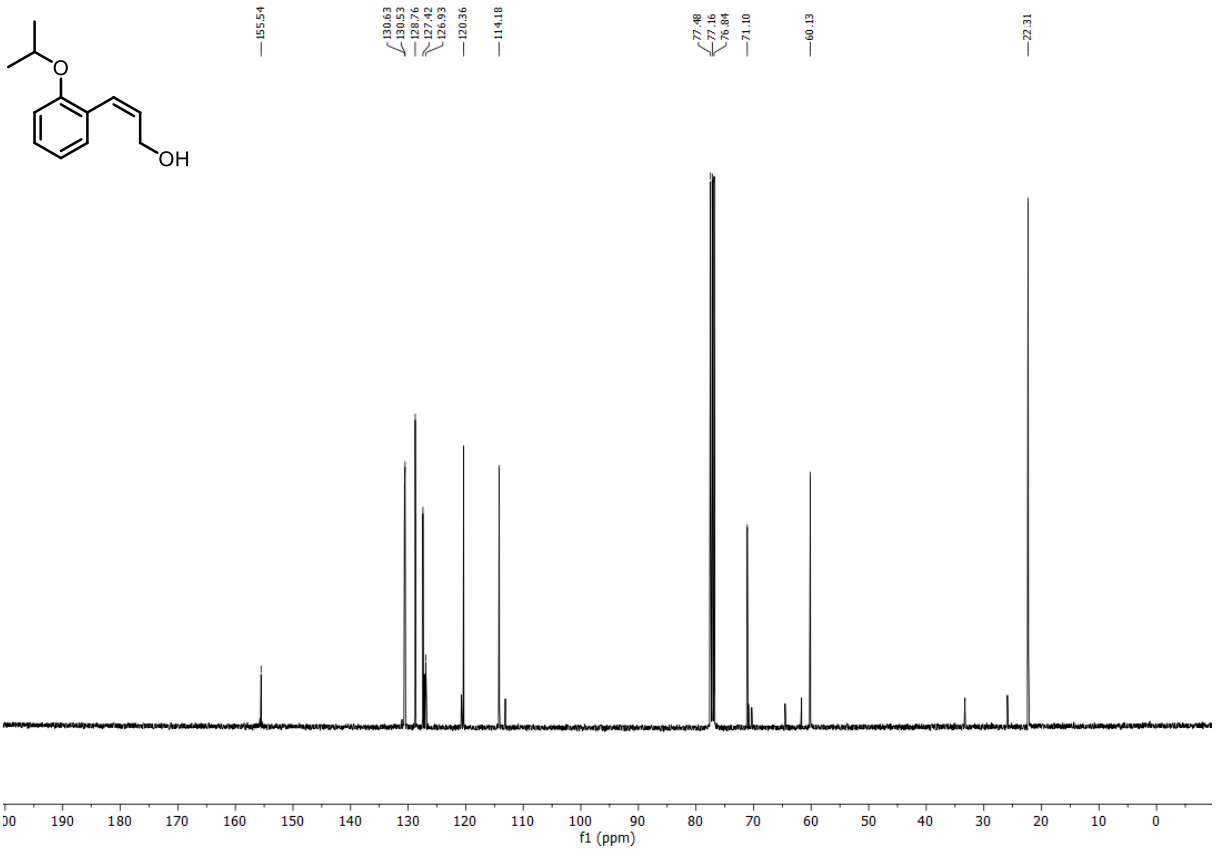
^{13}C NMR (101 MHz, $CDCl_3$)



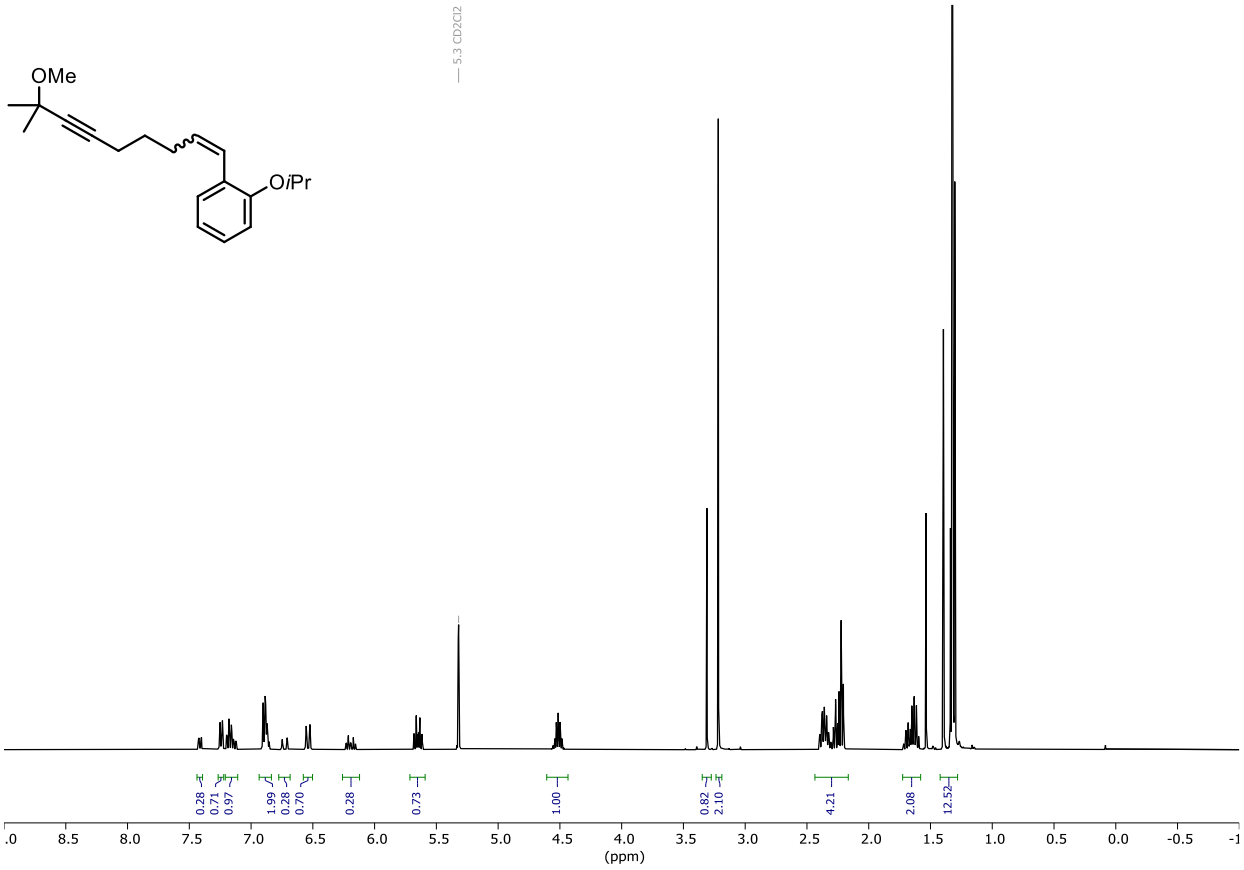
^{1}H NMR (400 MHz, $CDCl_3$)



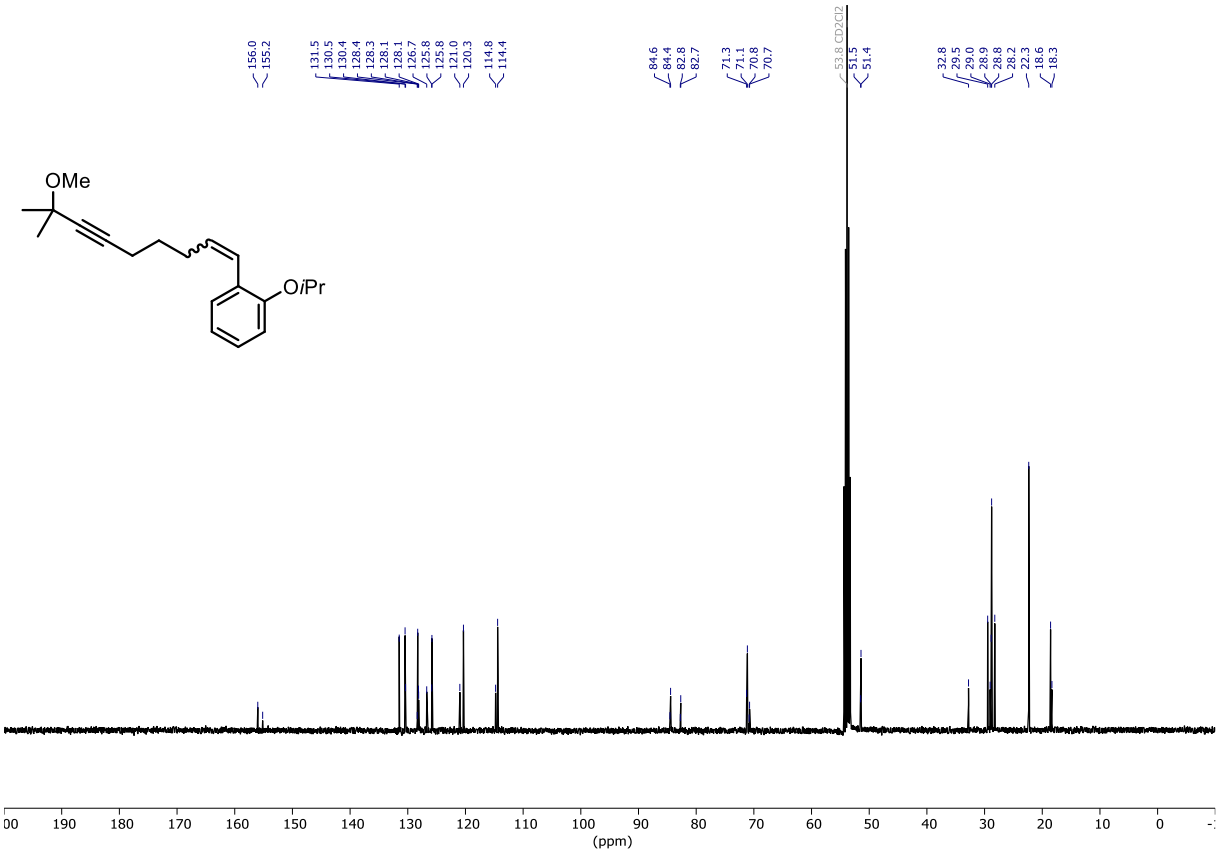
^{13}C NMR (101 MHz, $CDCl_3$)



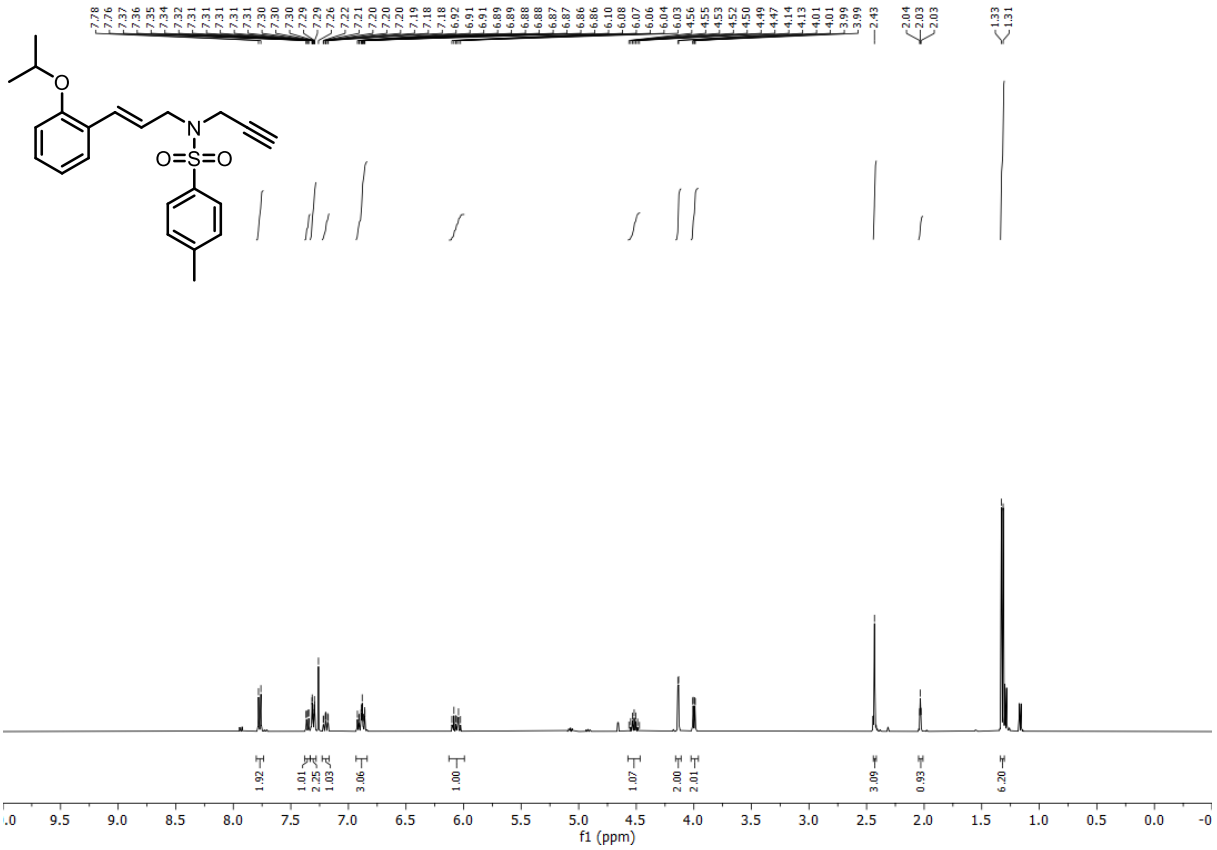
^{1}H NMR (400 MHz, CD_2Cl_2, *E*/*Z* ≈ 2:5)



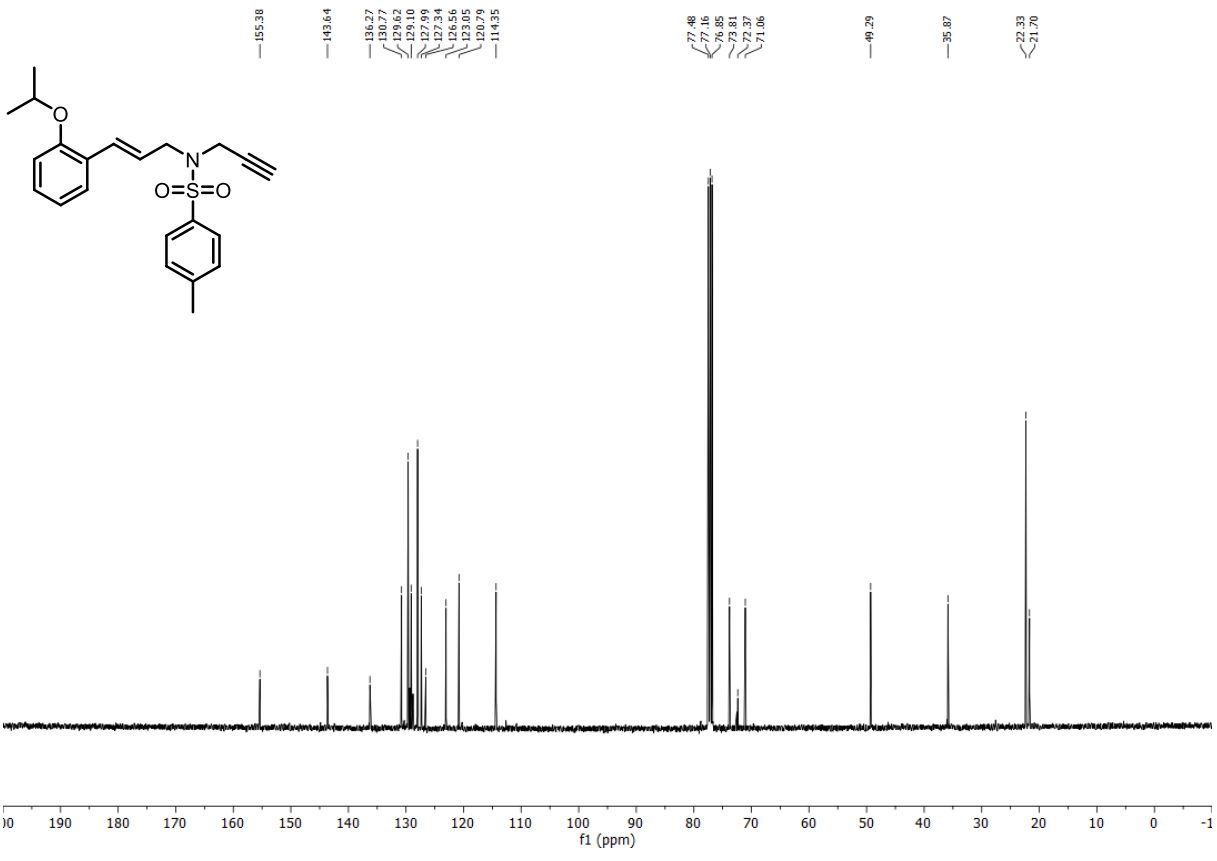
^{13}C NMR (400 MHz, CD_2Cl_2, *E*/*Z* ≈ 2:5)



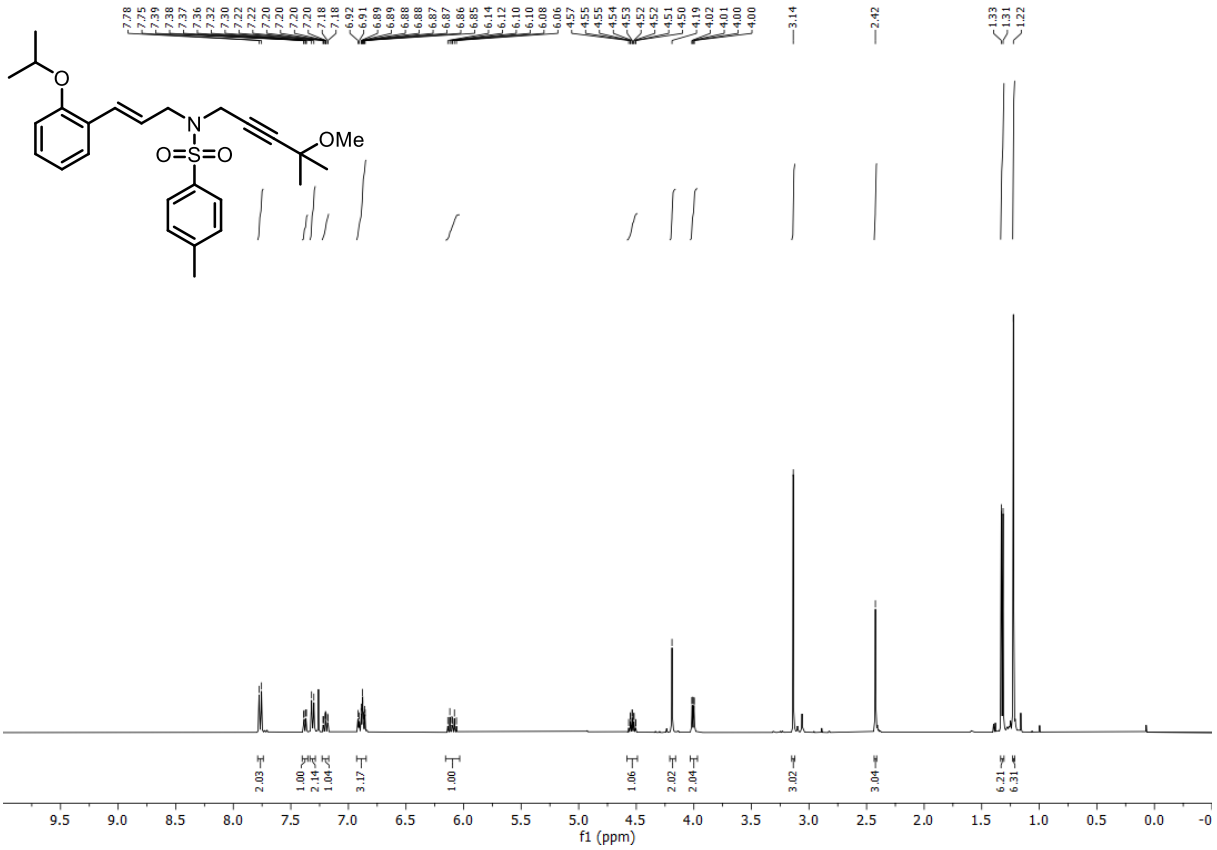
^{1}H NMR (400 MHz, $CDCl_3$)



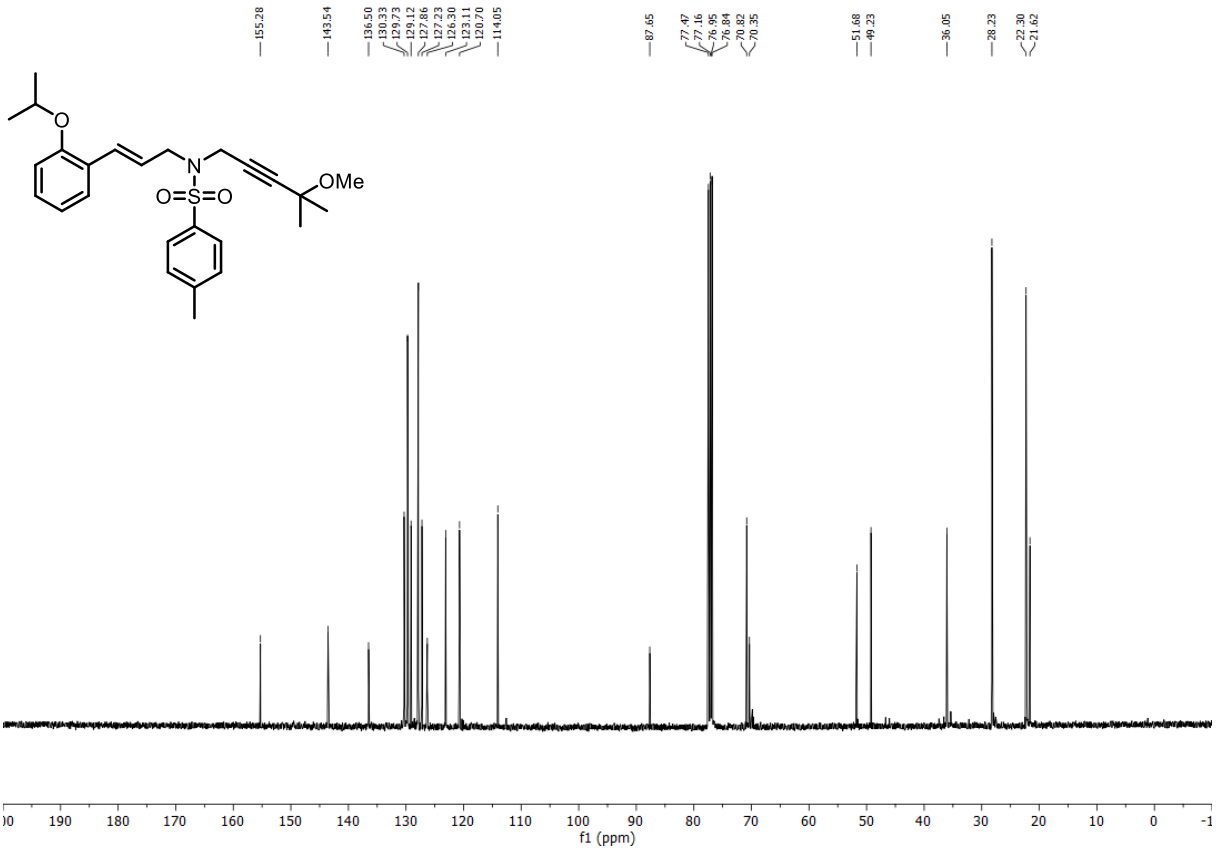
^{13}C NMR (101 MHz, $CDCl_3$)



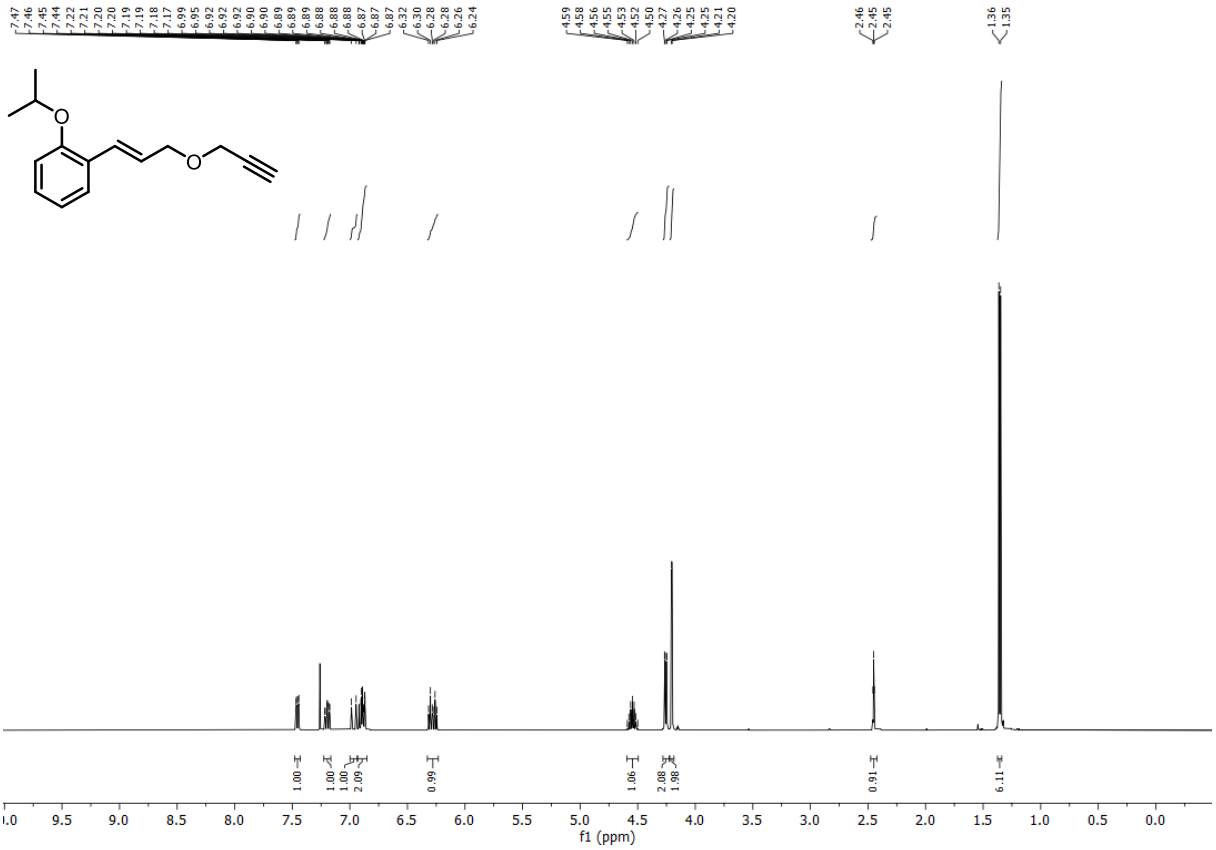
^{1}H NMR (400 MHz, $CDCl_3$)



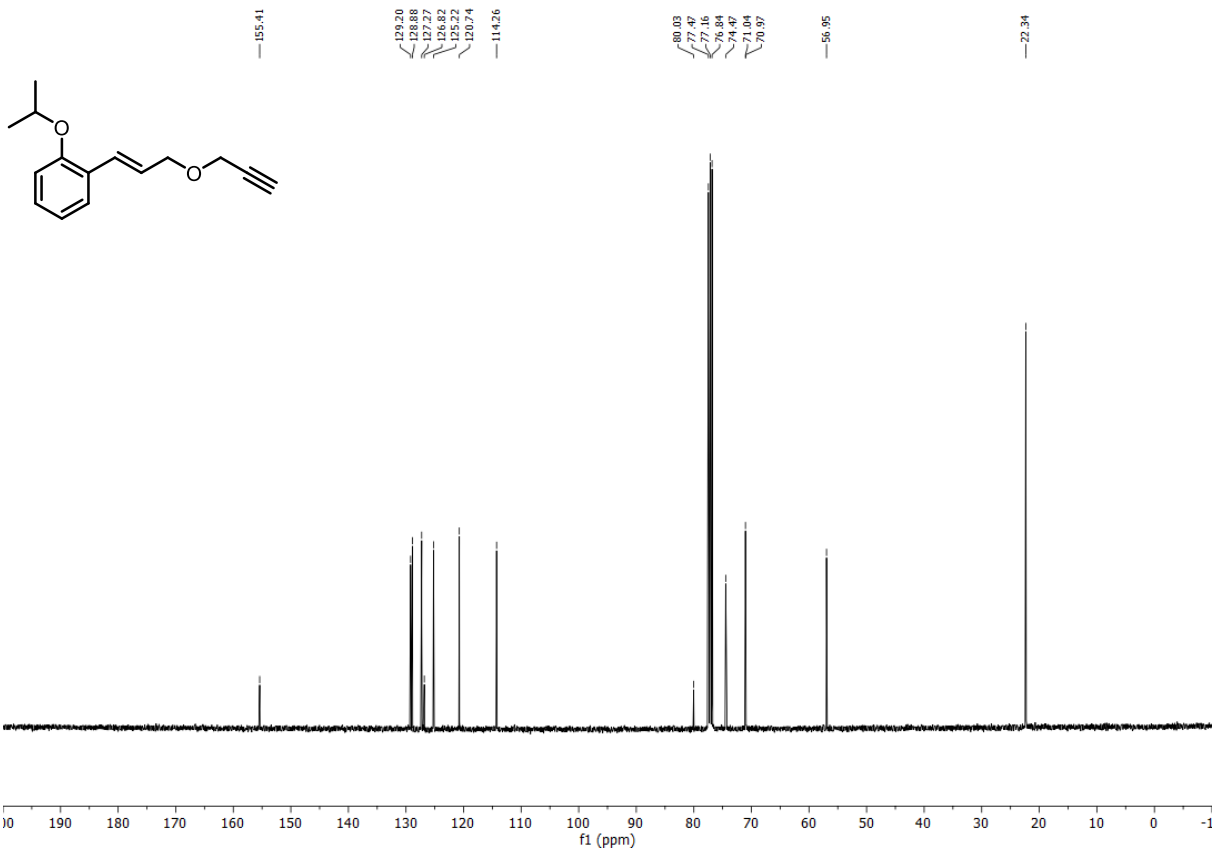
^{13}C NMR (101 MHz, $CDCl_3$)



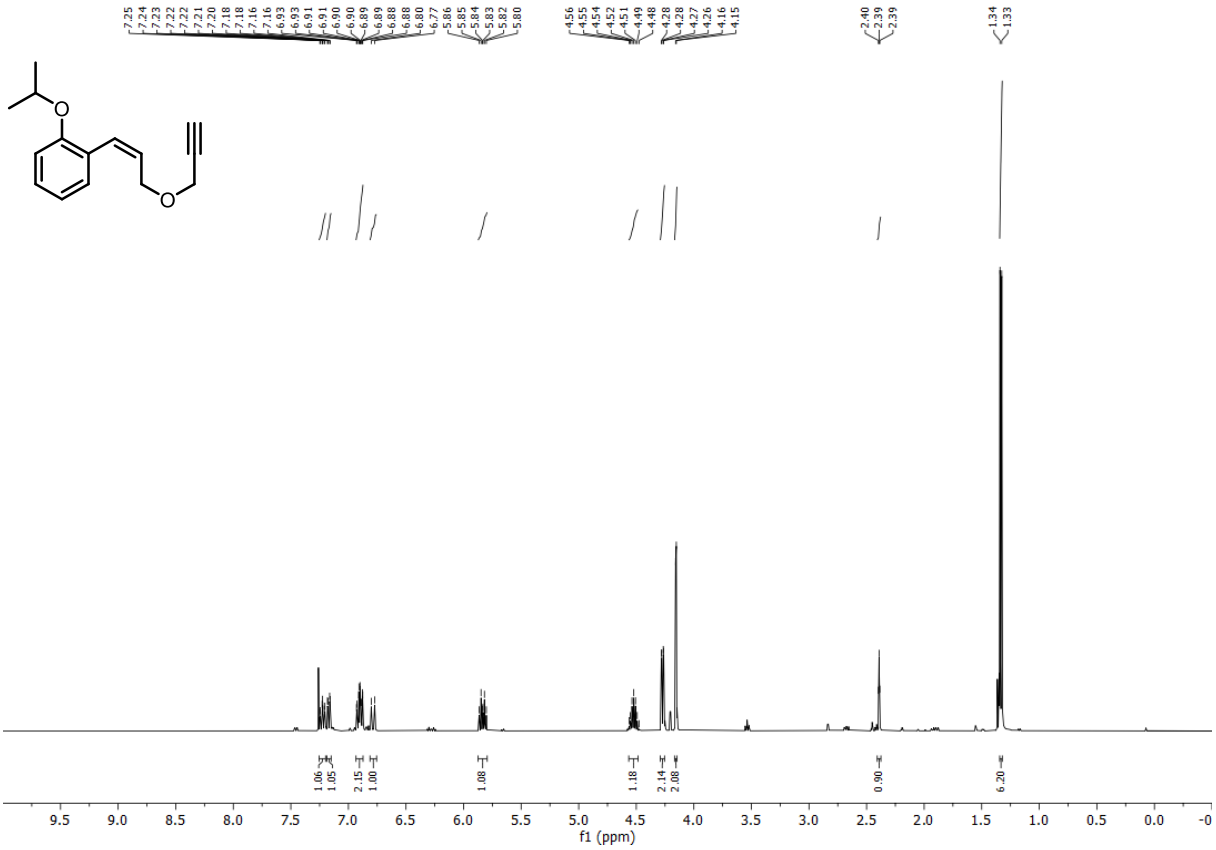
^{1}H NMR (400 MHz, $CDCl_3$)



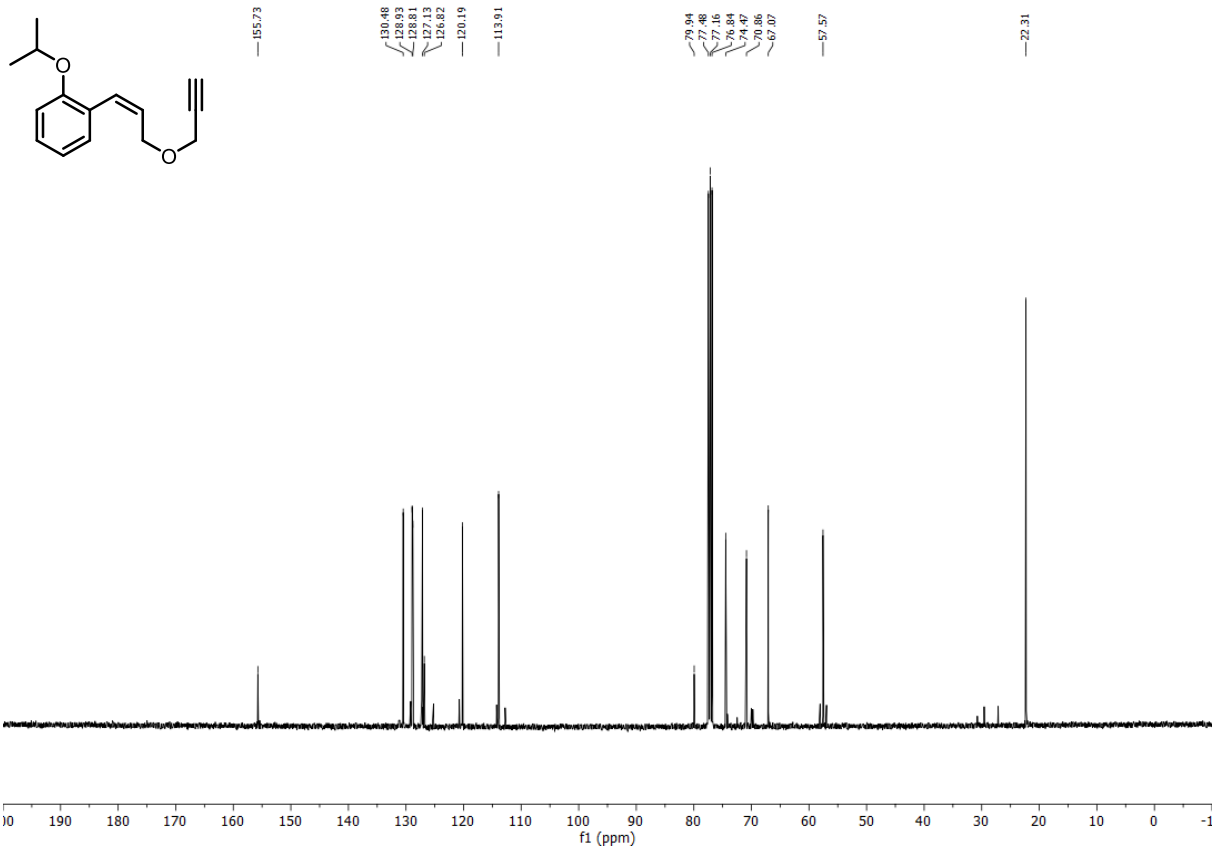
^{13}C NMR (101 MHz, $CDCl_3$)



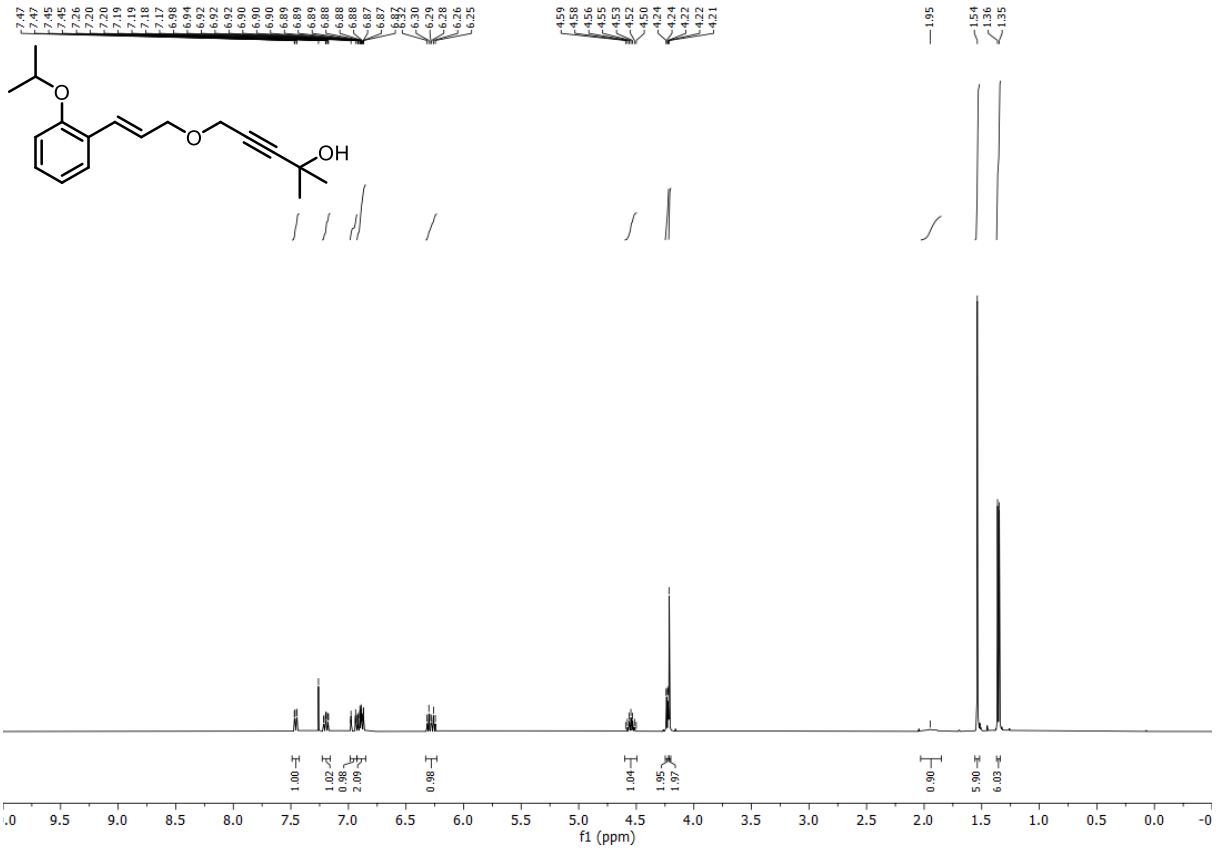
^{1}H NMR (400 MHz, $CDCl_3$)



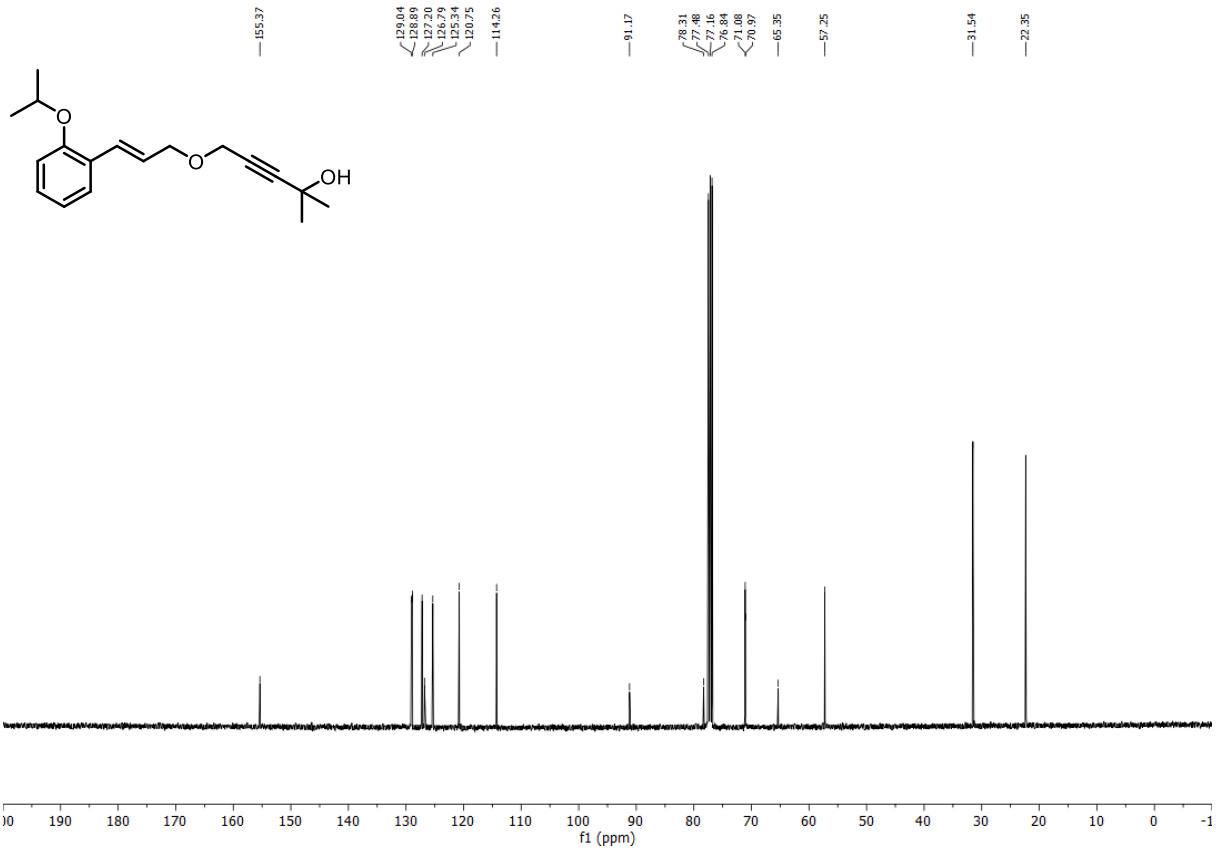
^{13}C NMR (101 MHz, $CDCl_3$)



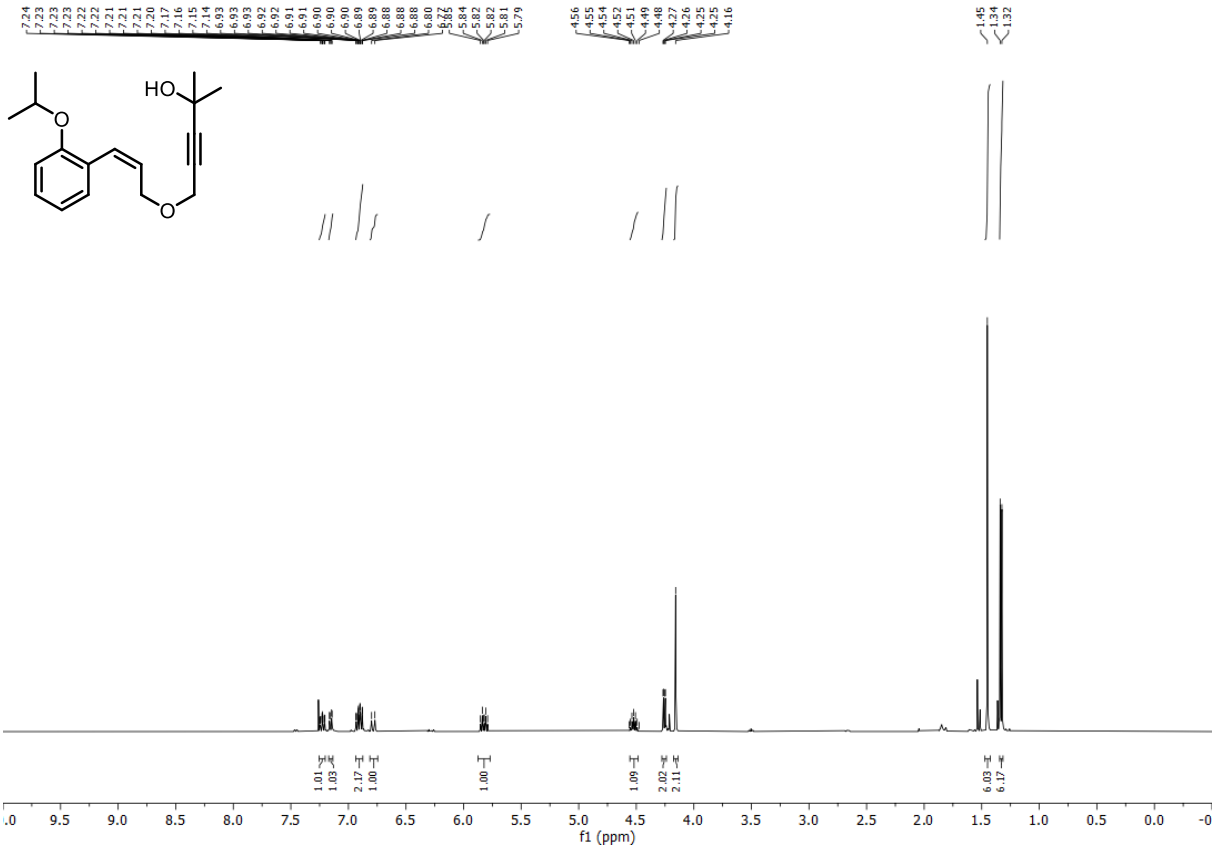
^{1}H NMR (400 MHz, $CDCl_3$)



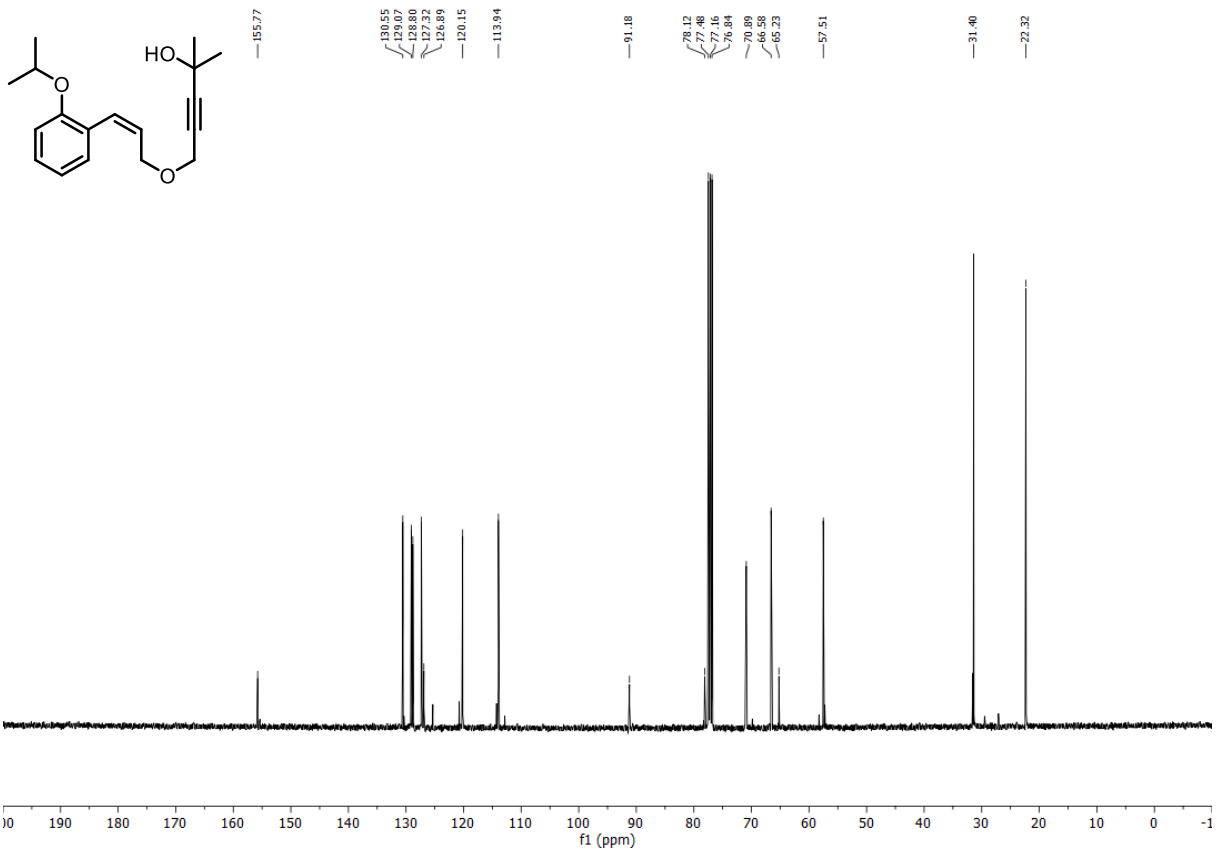
^{13}C NMR (101 MHz, $CDCl_3$)



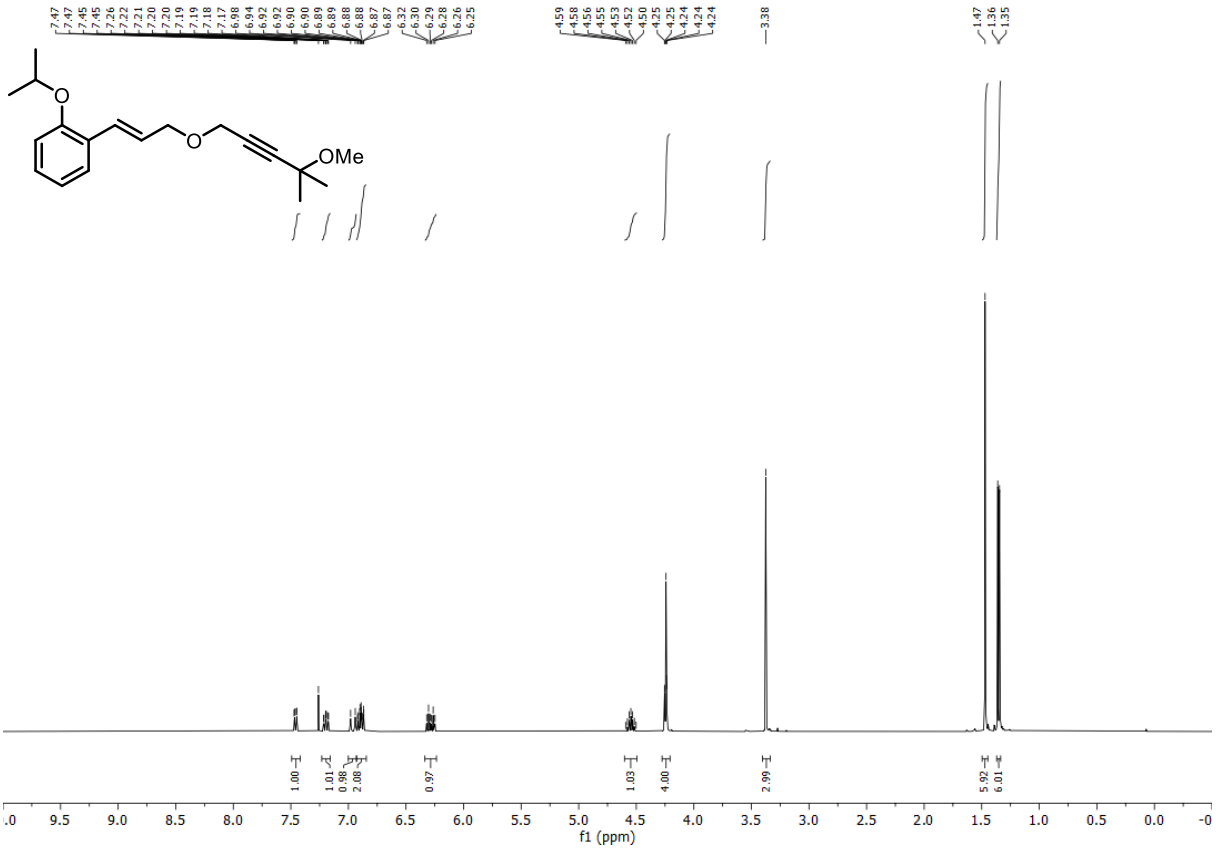
^{1}H NMR (400 MHz, $CDCl_3$)



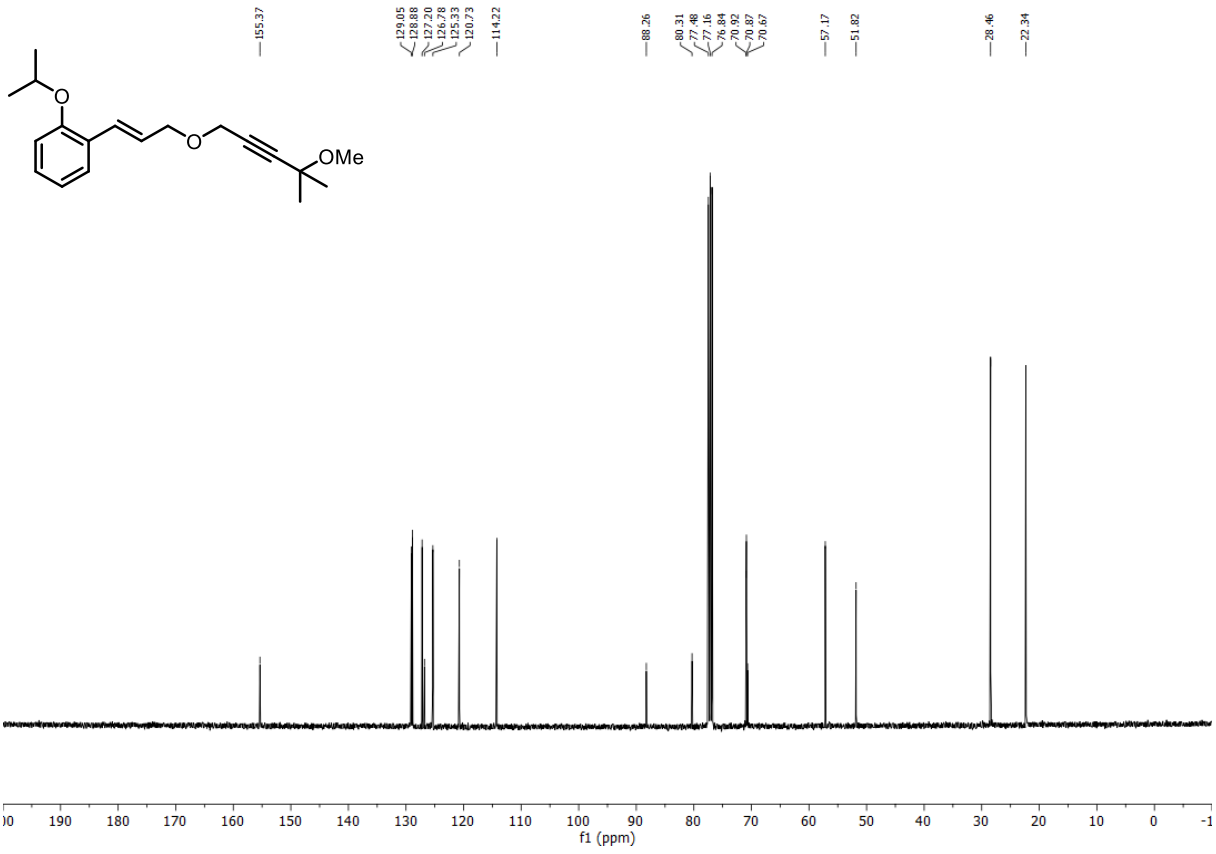
^{13}C NMR (101 MHz, $CDCl_3$)



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



^{13}C NMR (101 MHz, $CDCl_3$)



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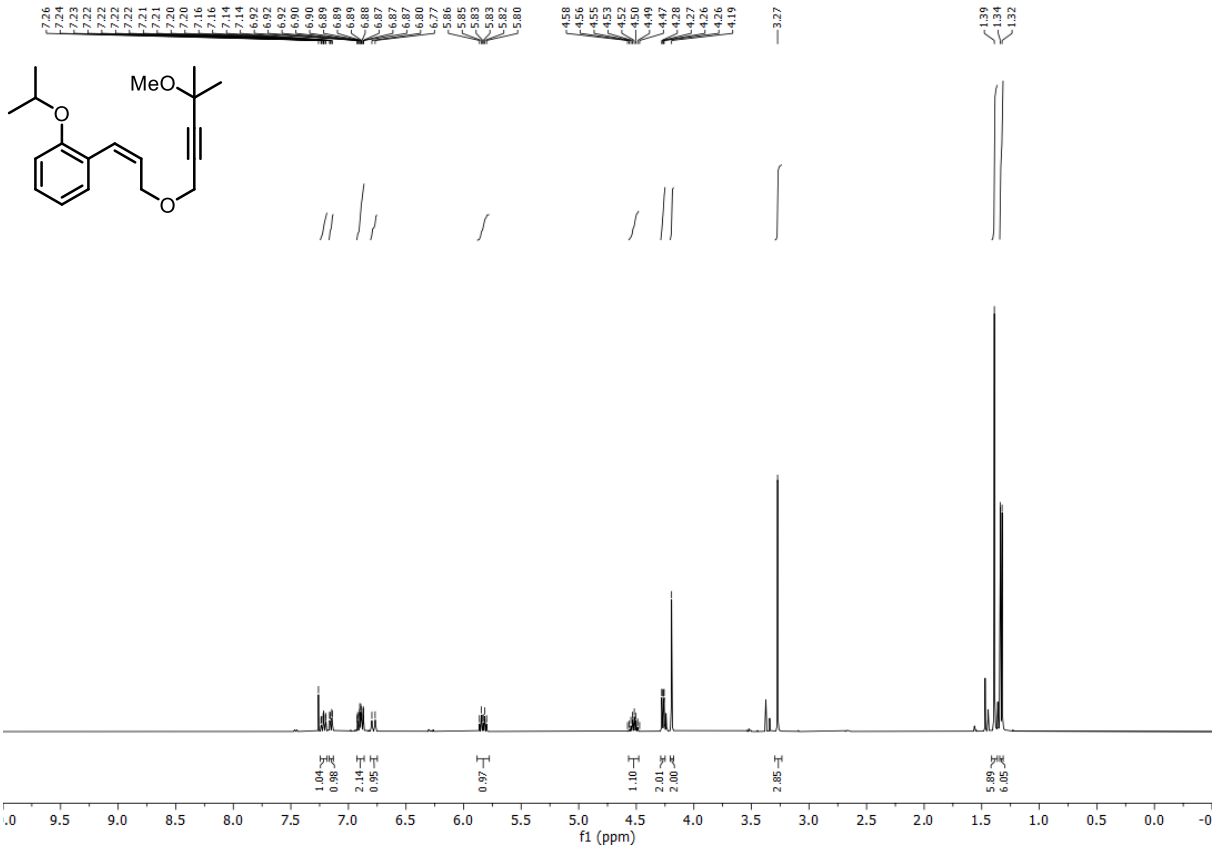

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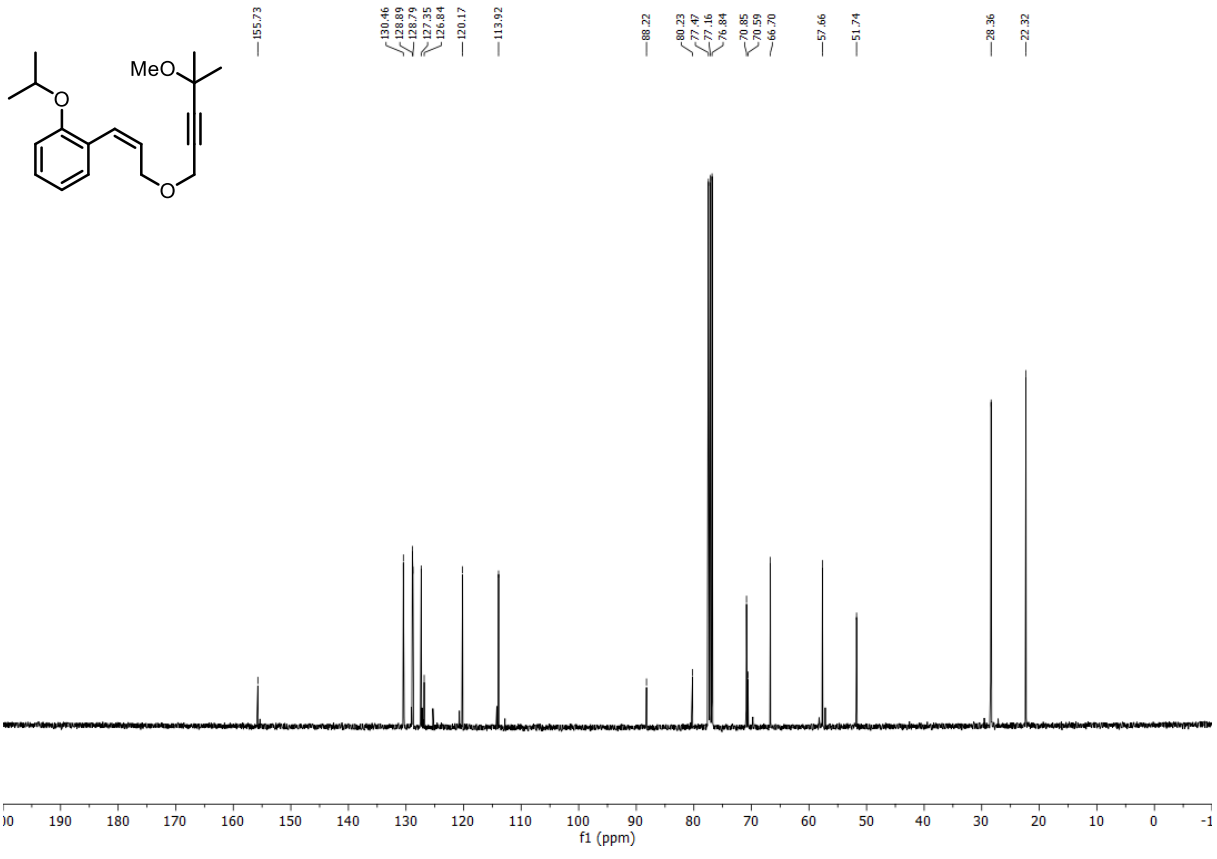

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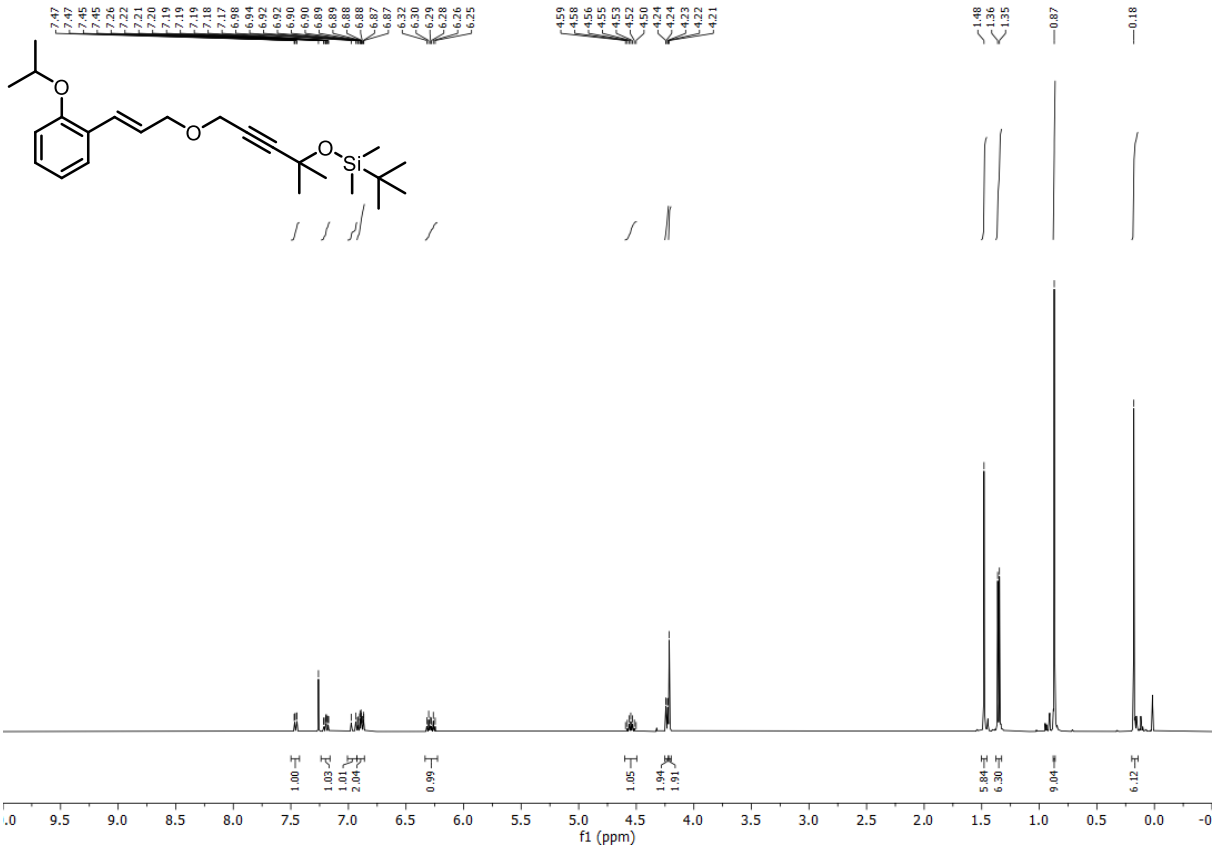

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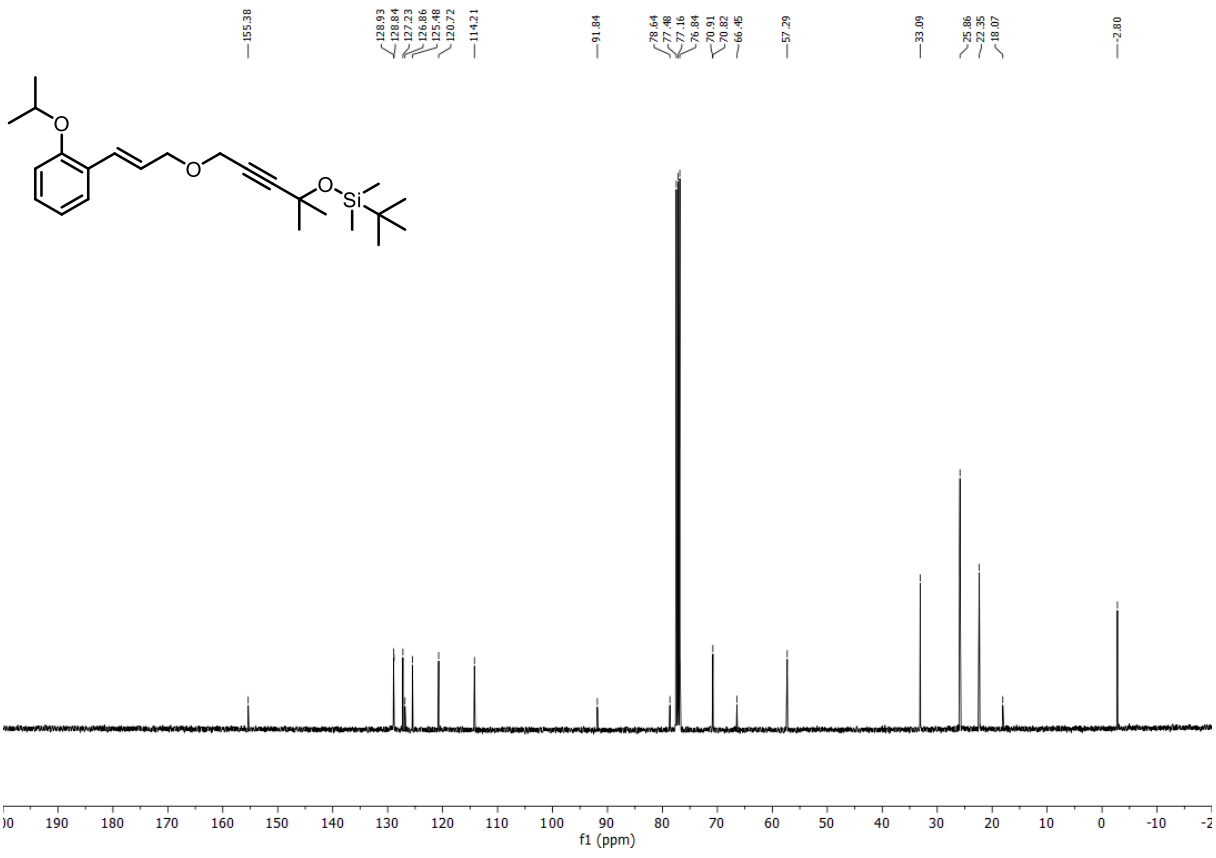
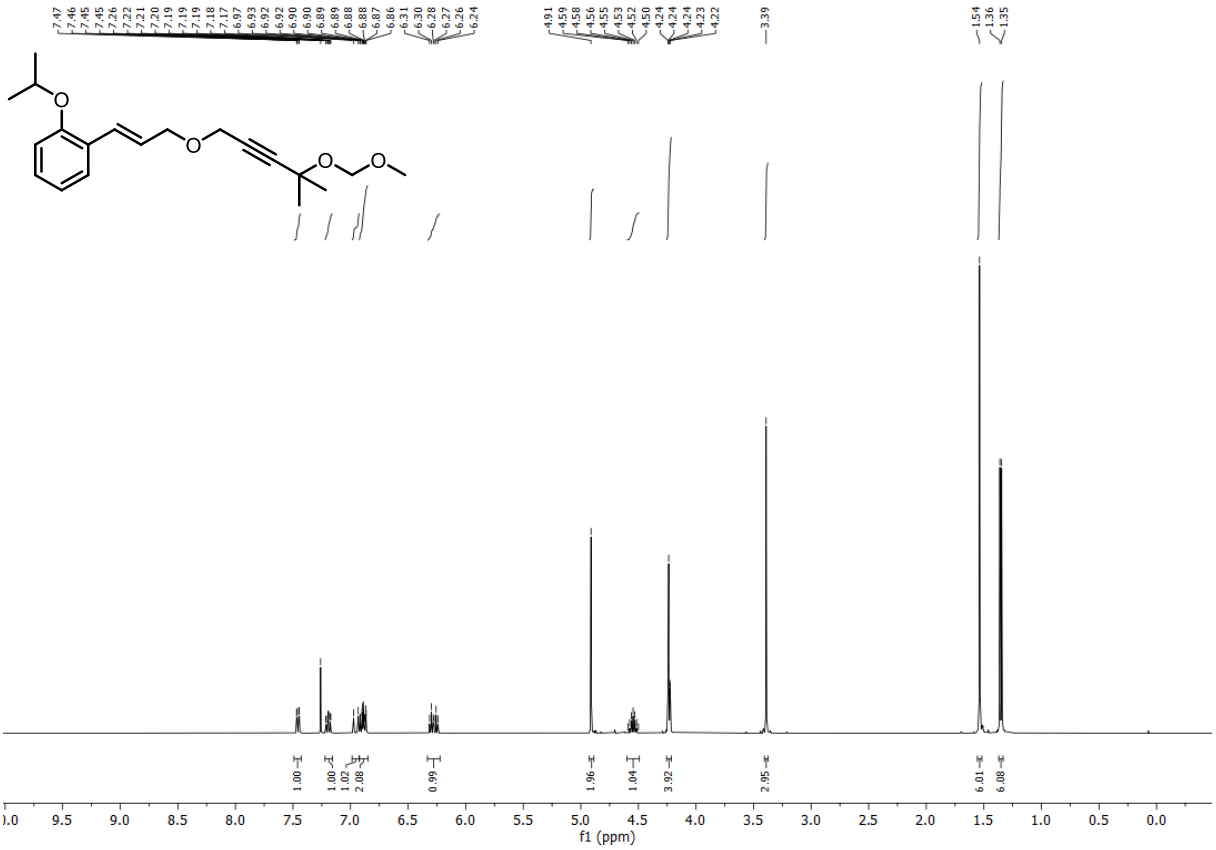
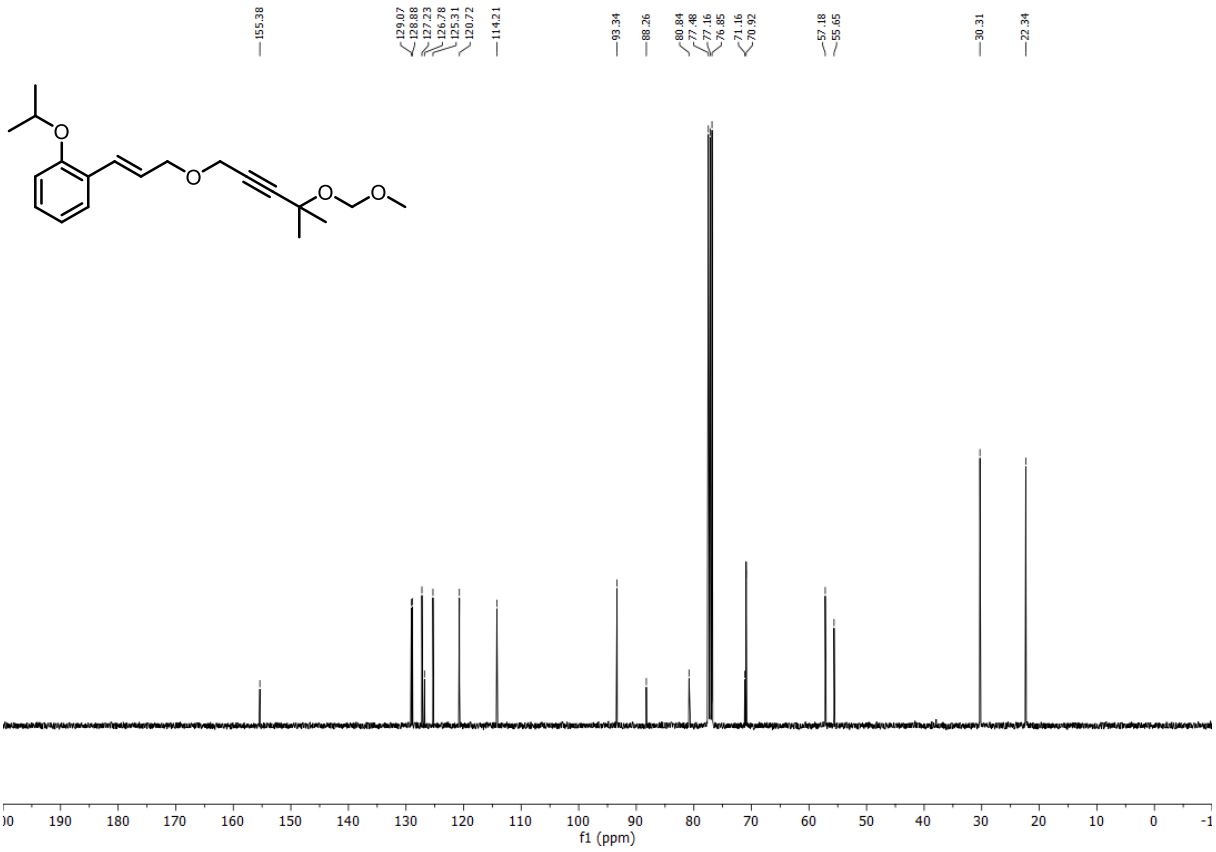


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



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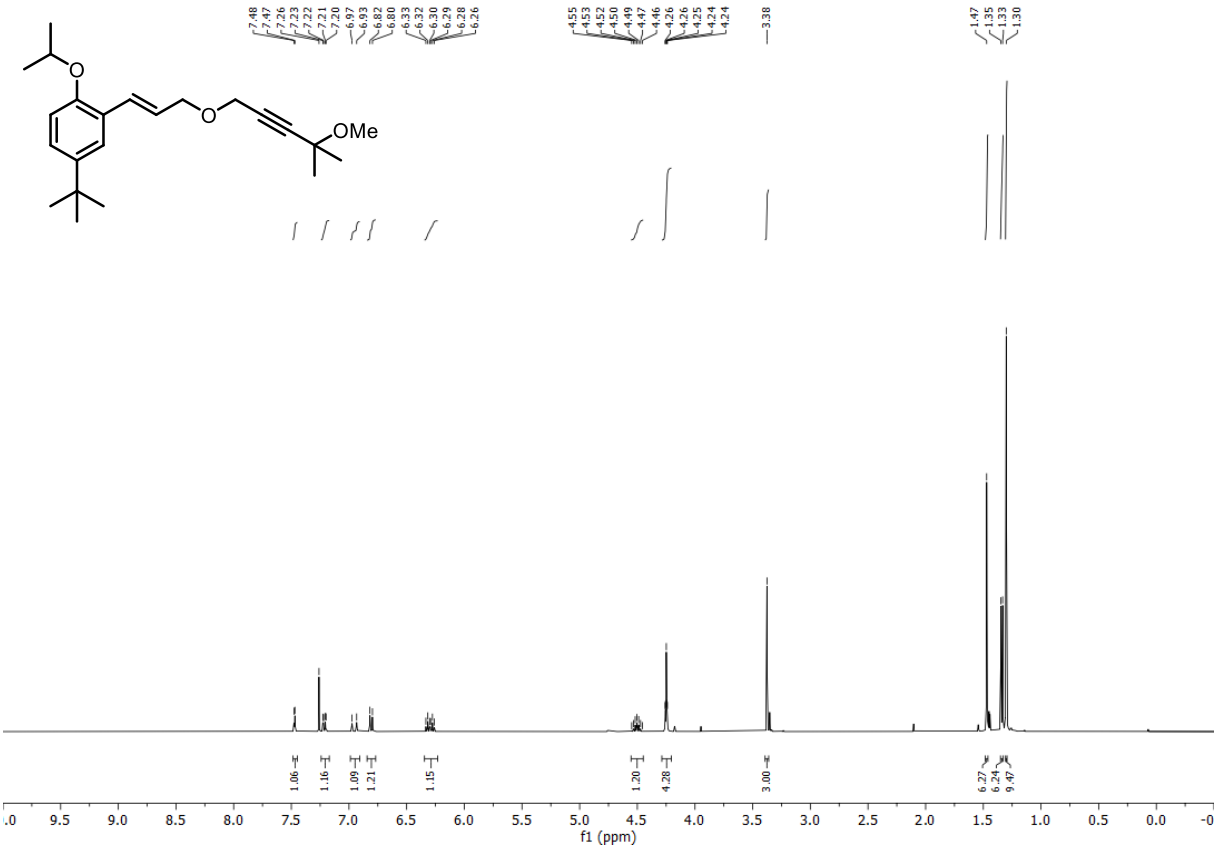
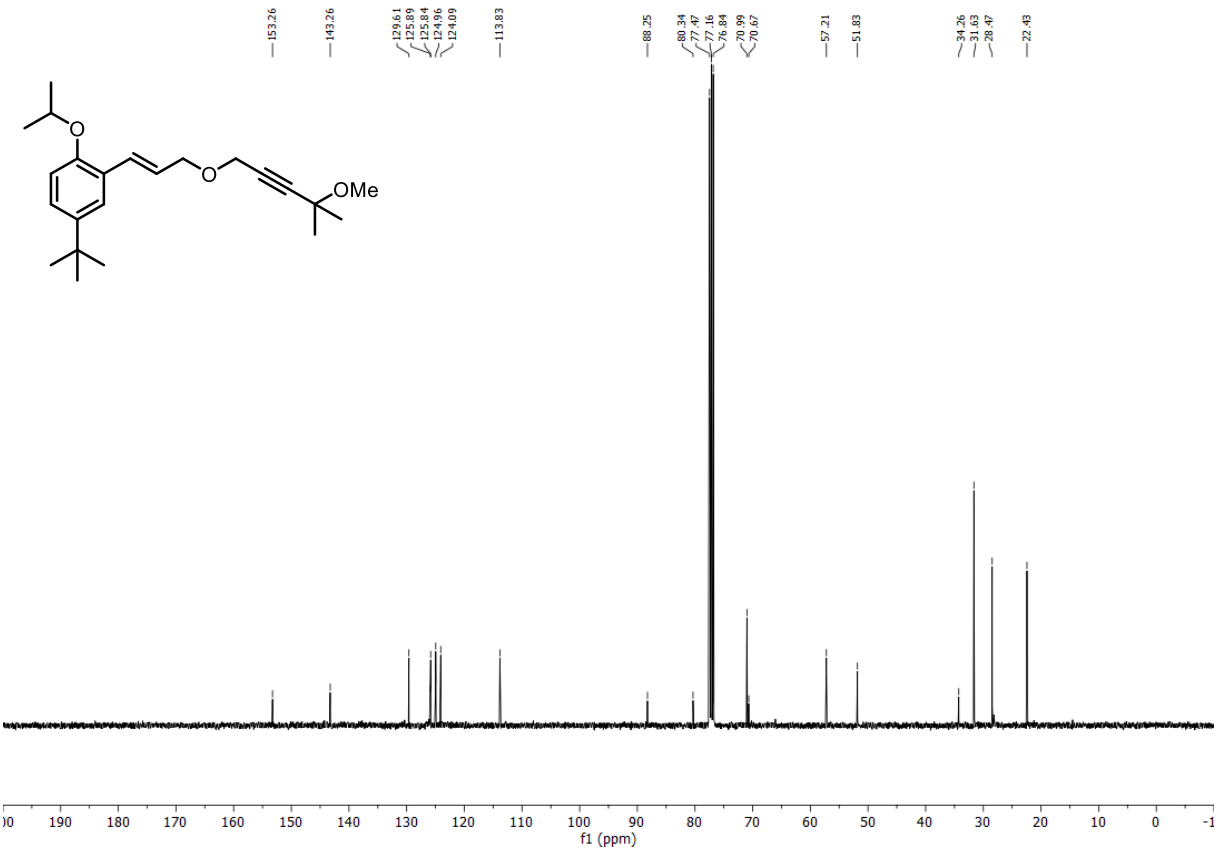


^{13}C NMR (101 MHz, $CDCl_3$)



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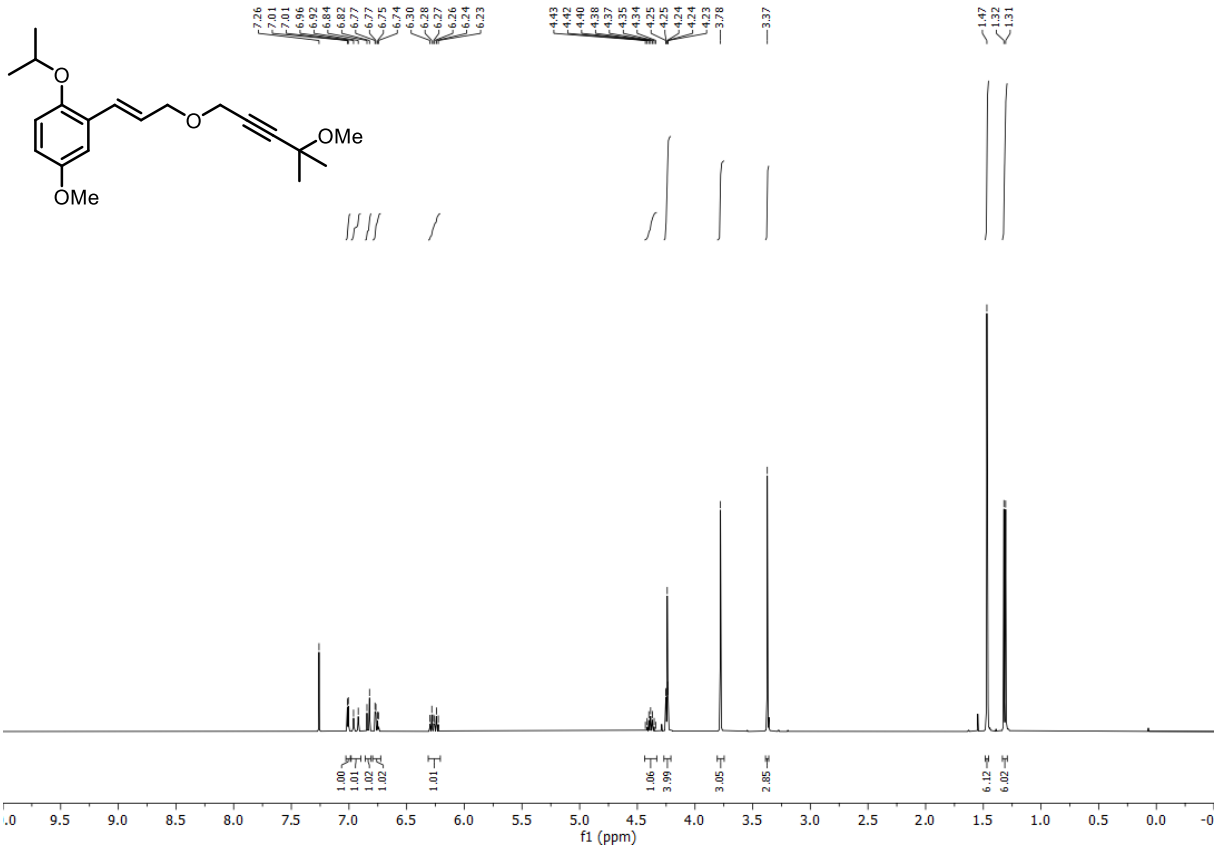

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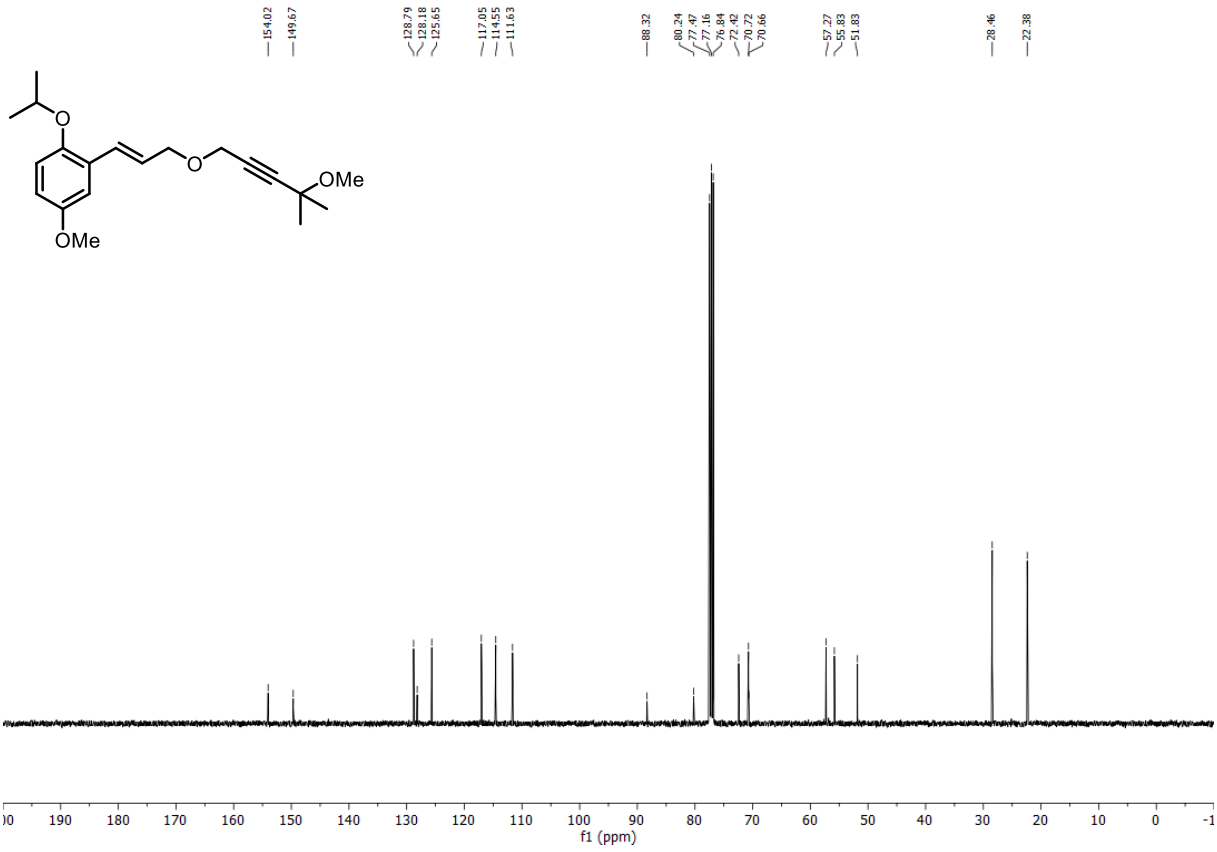

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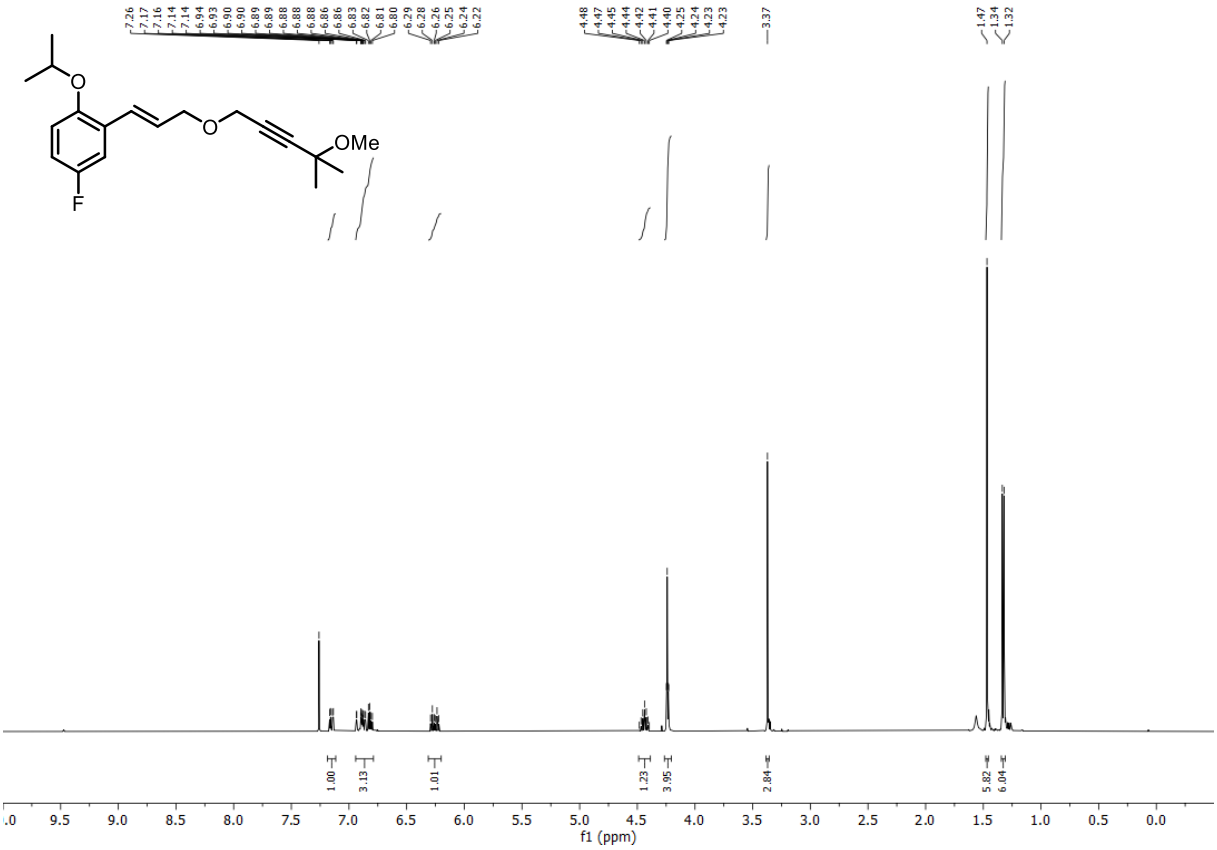

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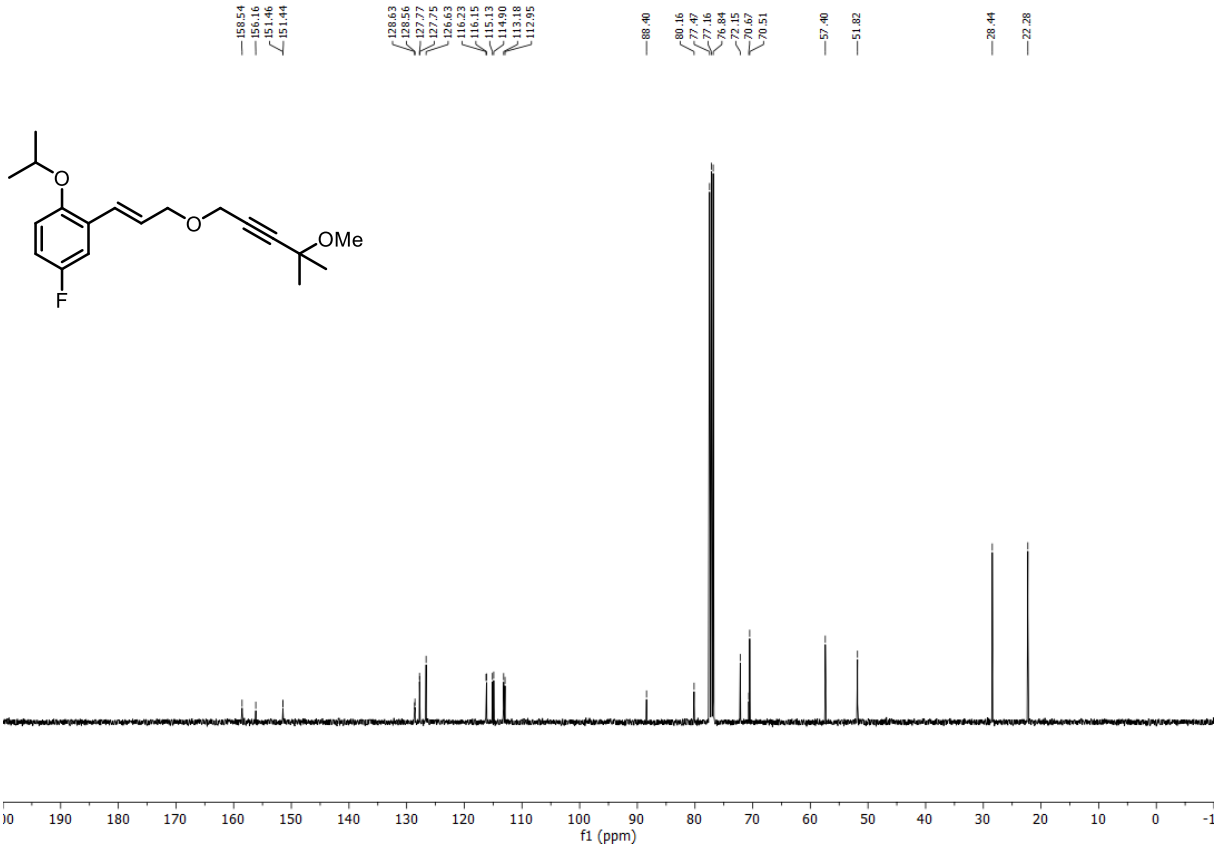
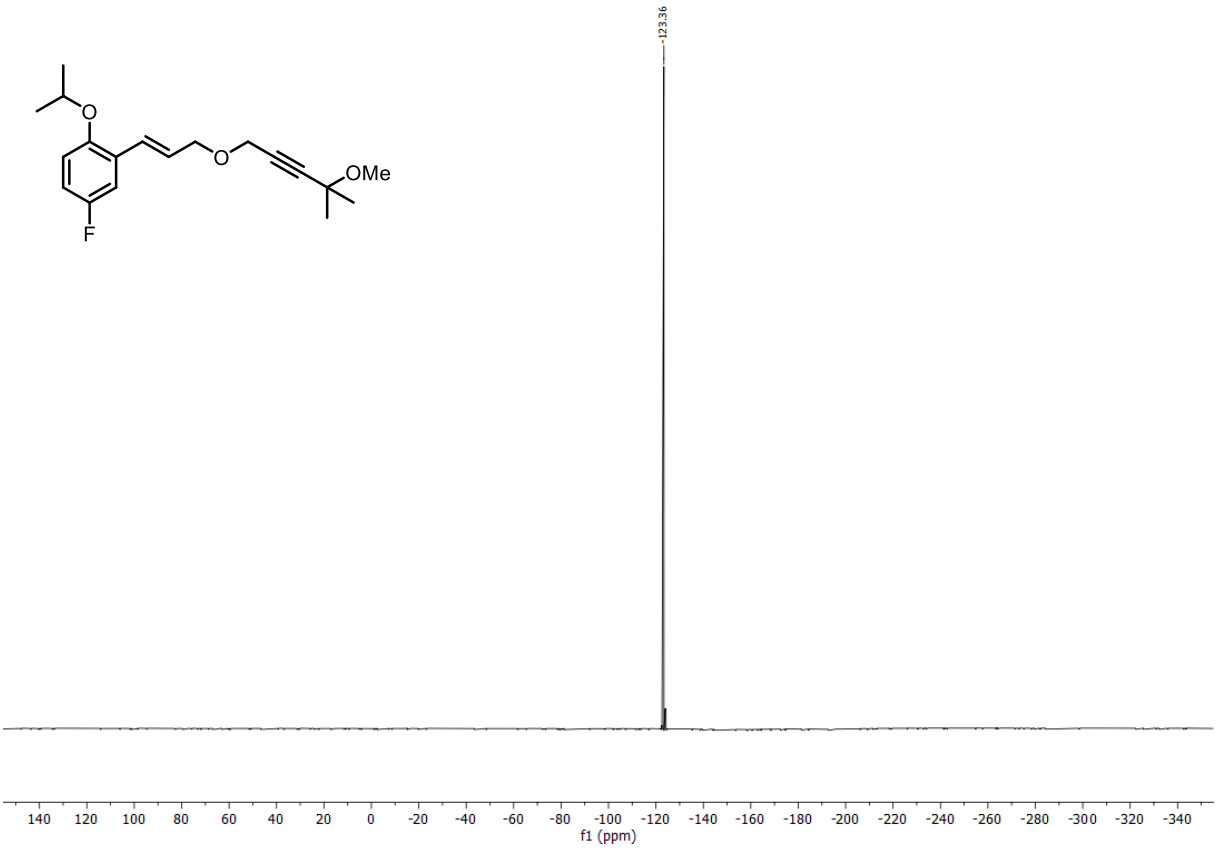
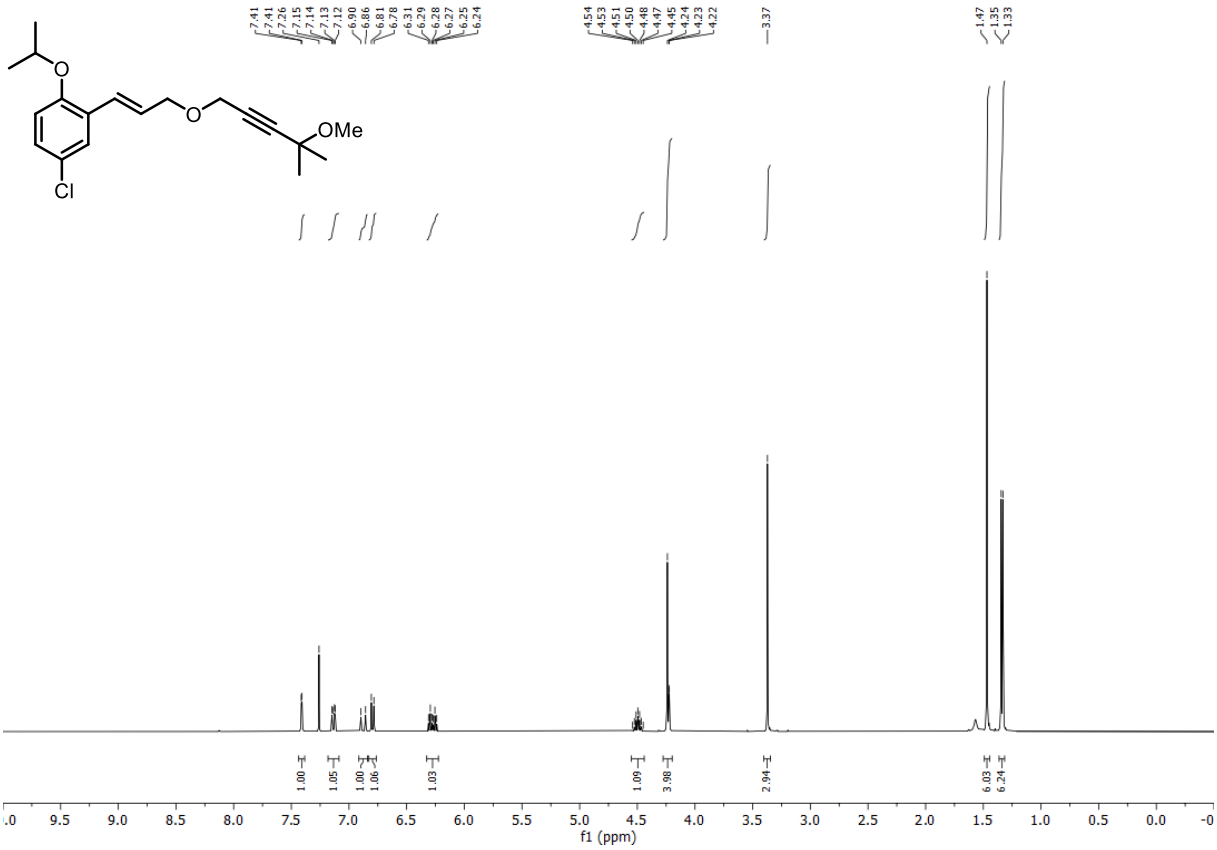


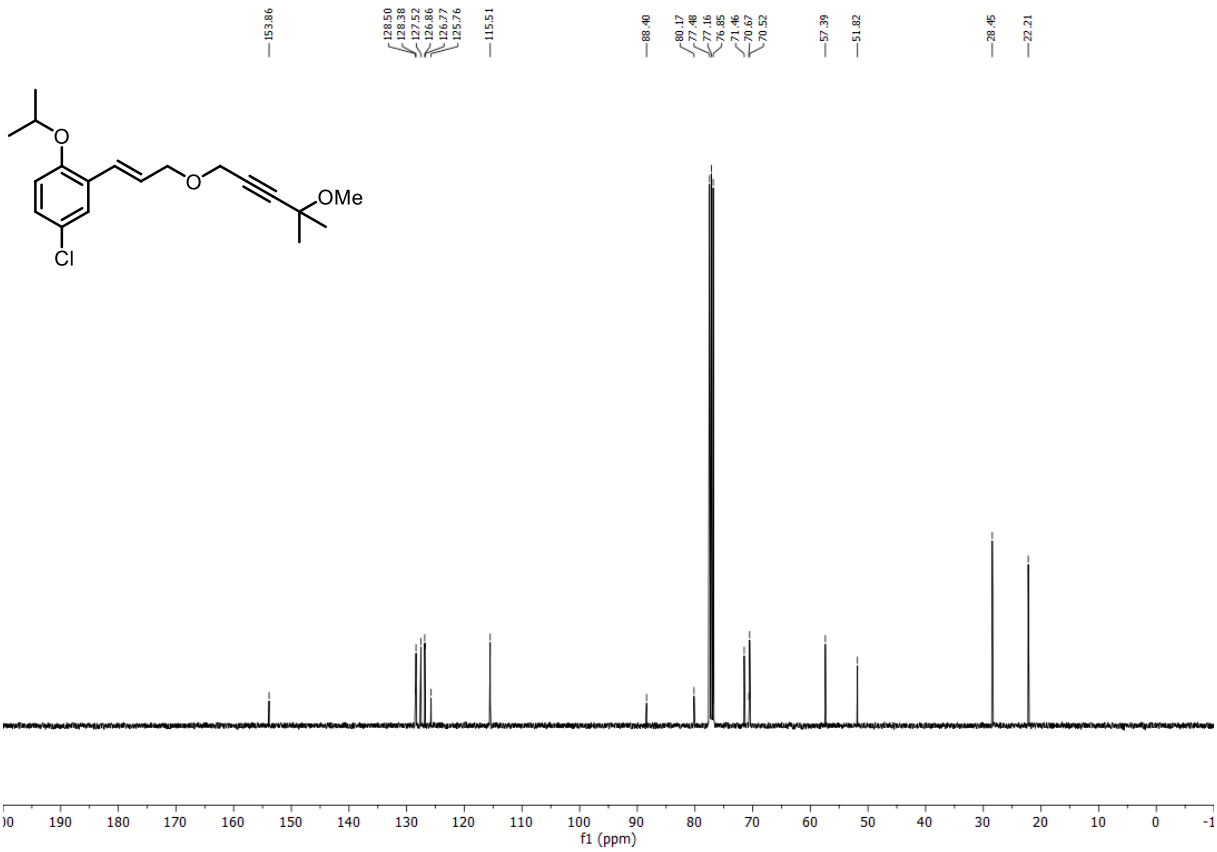
^{19}F NMR (282 MHz, $CDCl_3$)



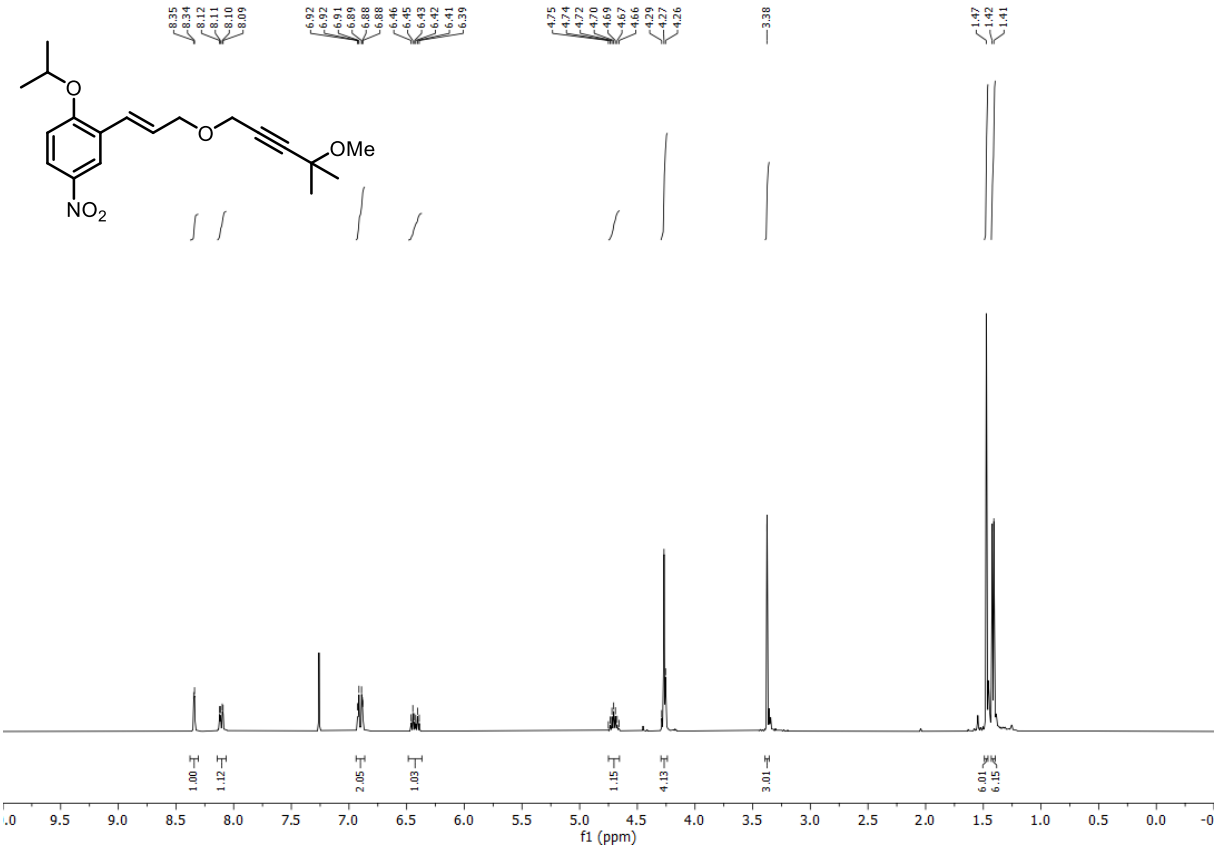
^{1}H NMR (400 MHz, $CDCl_3$)



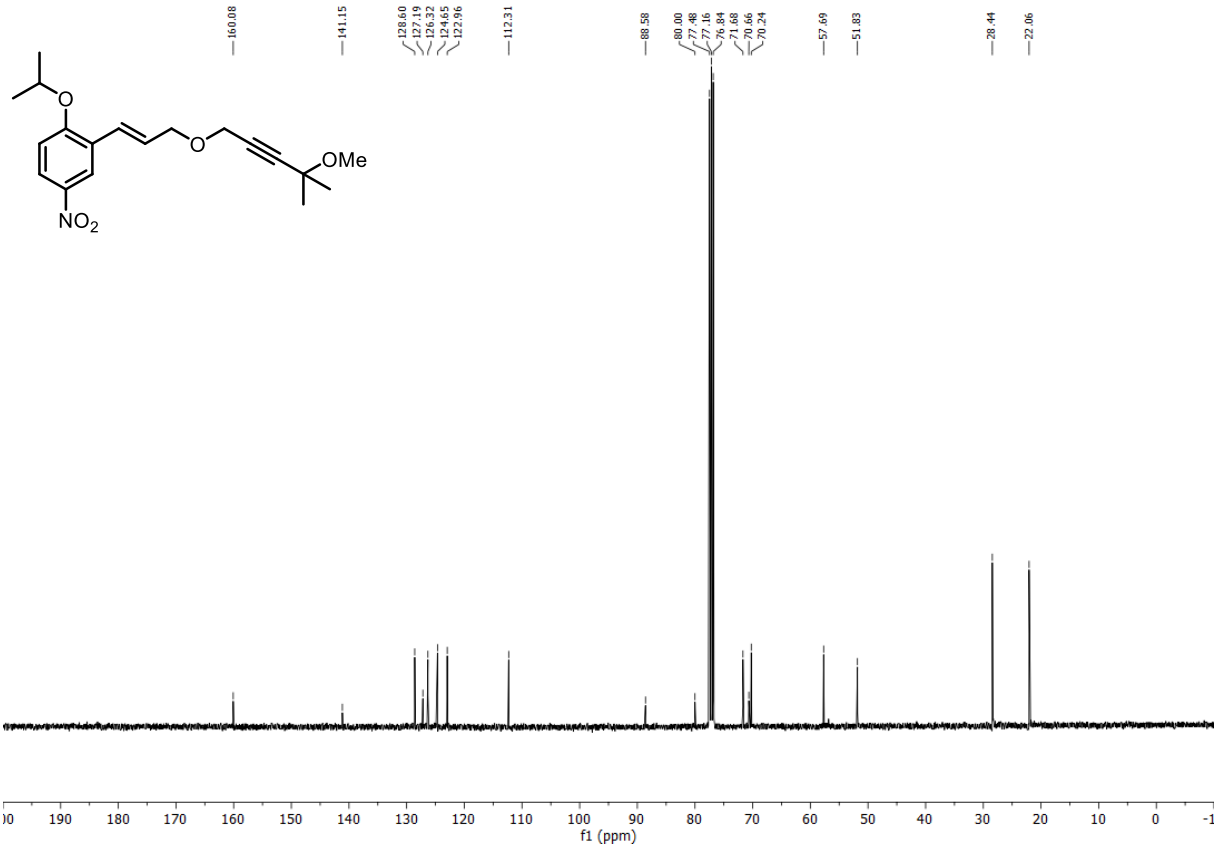
^{13}C NMR (101 MHz, $CDCl_3$)



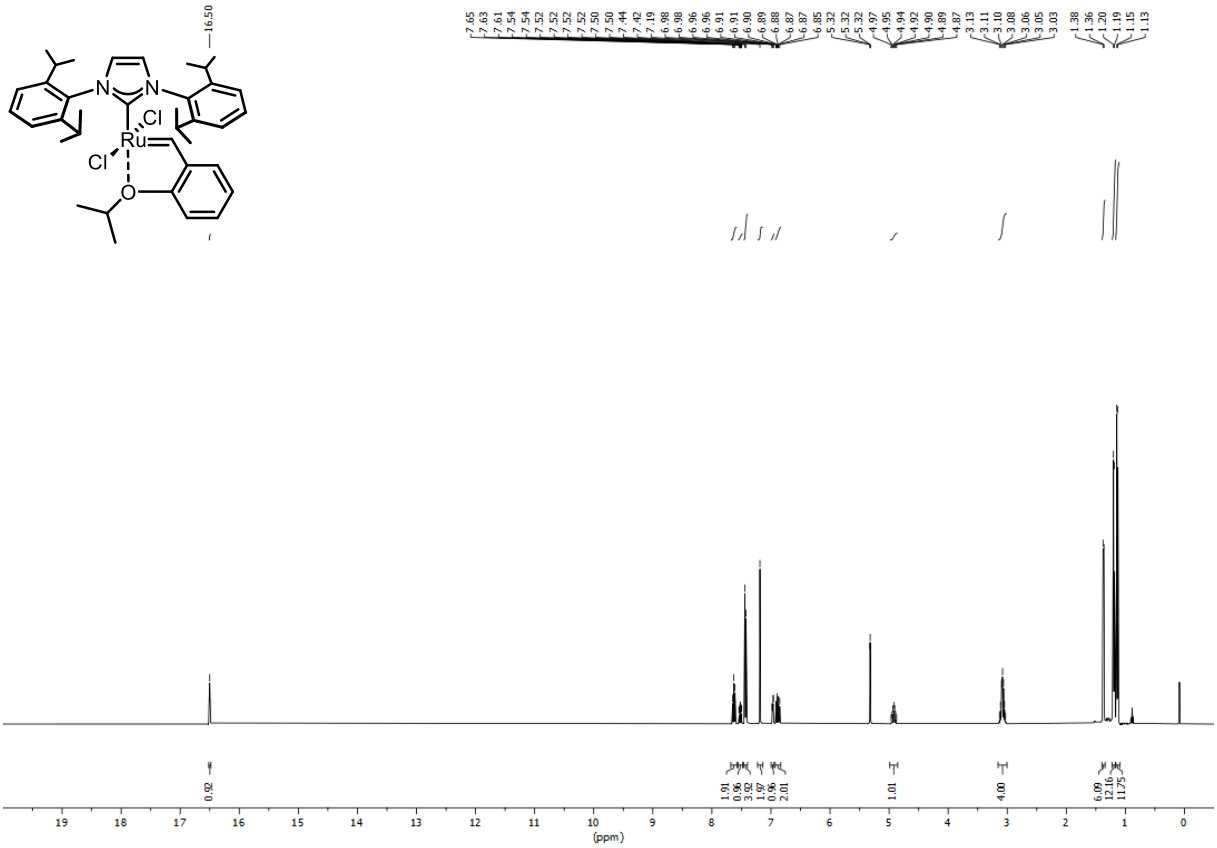
^{1}H NMR (400 MHz, $CDCl_3$)



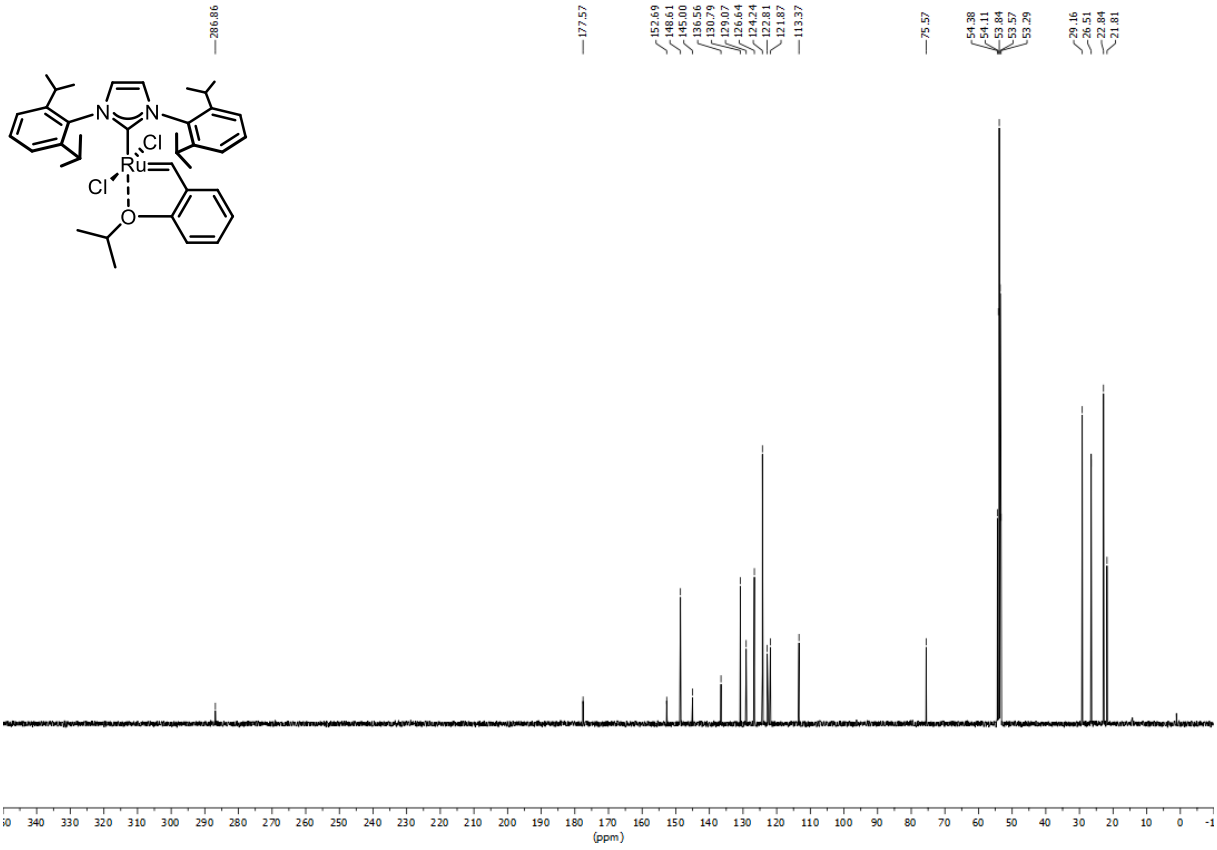
^{13}C NMR (101 MHz, $CDCl_3$)



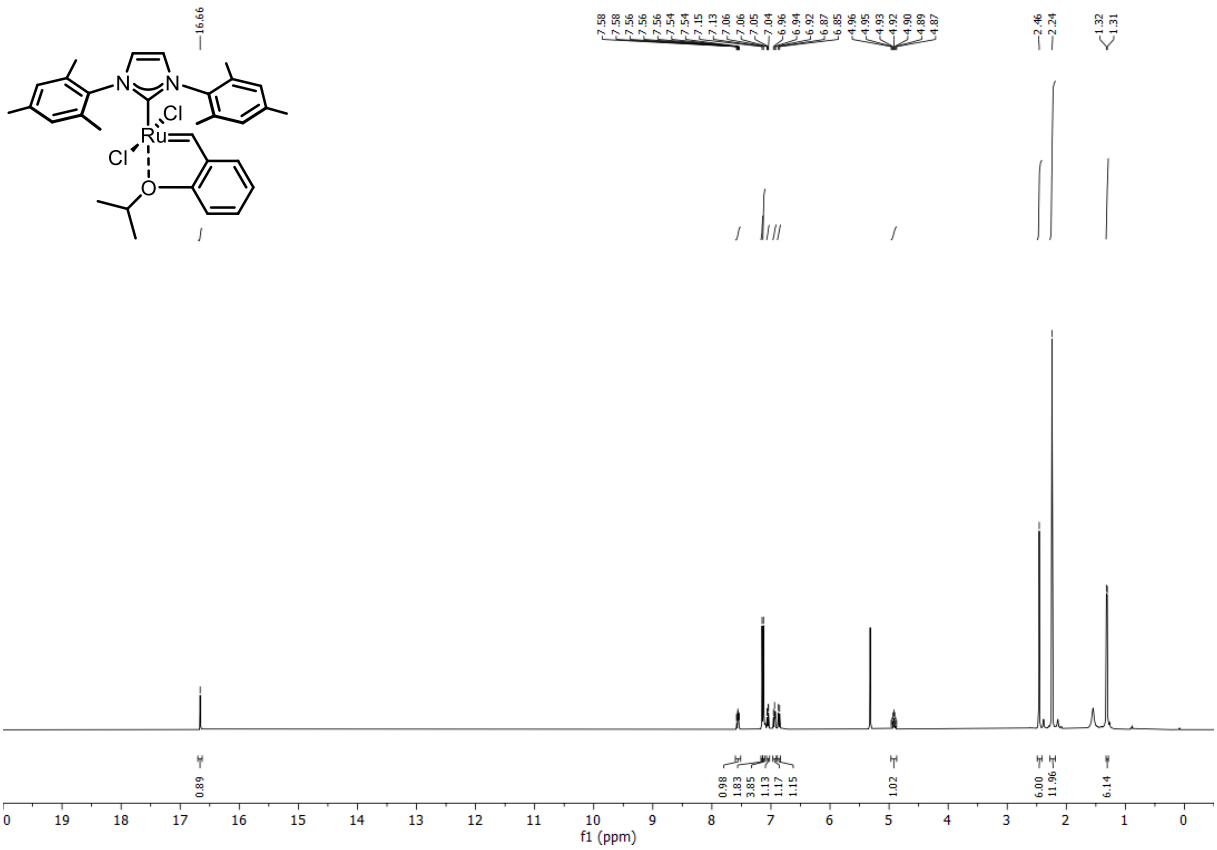
^{1}H NMR (400 MHz, CD_2Cl_2)



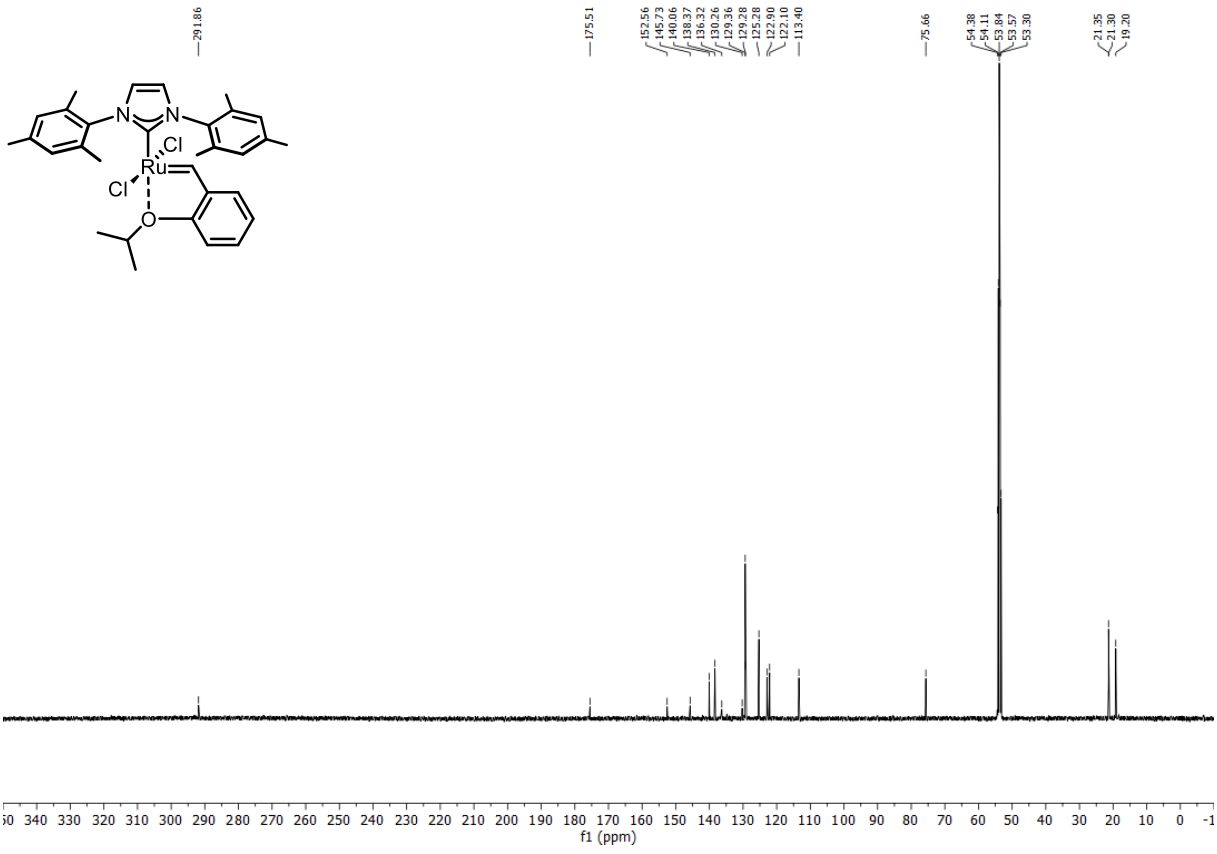
^{13}C NMR (101 MHz, CD_2Cl_2)



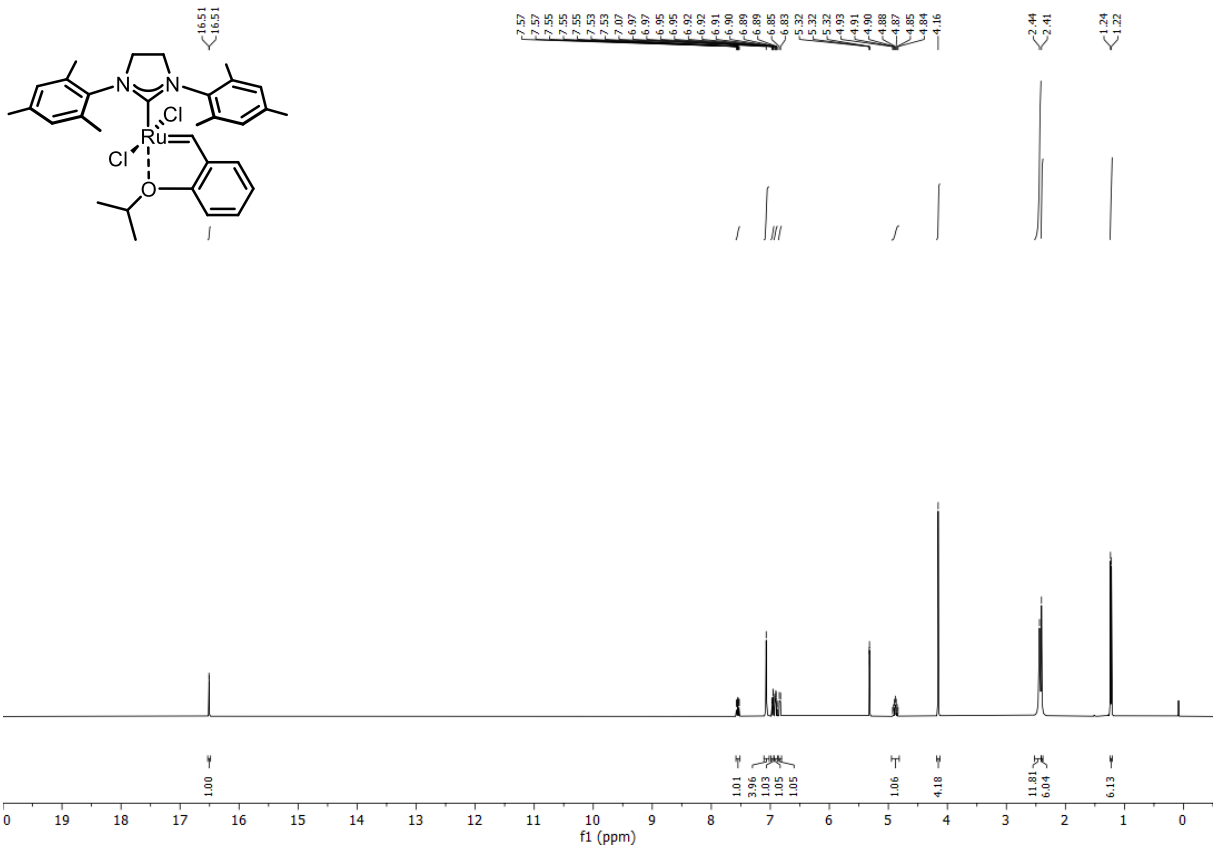
^{1}H NMR (400 MHz, CD_2Cl_2)



^{13}C NMR (101 MHz, CD_2Cl_2)



^{1}H NMR (400 MHz, CD_2Cl_2)



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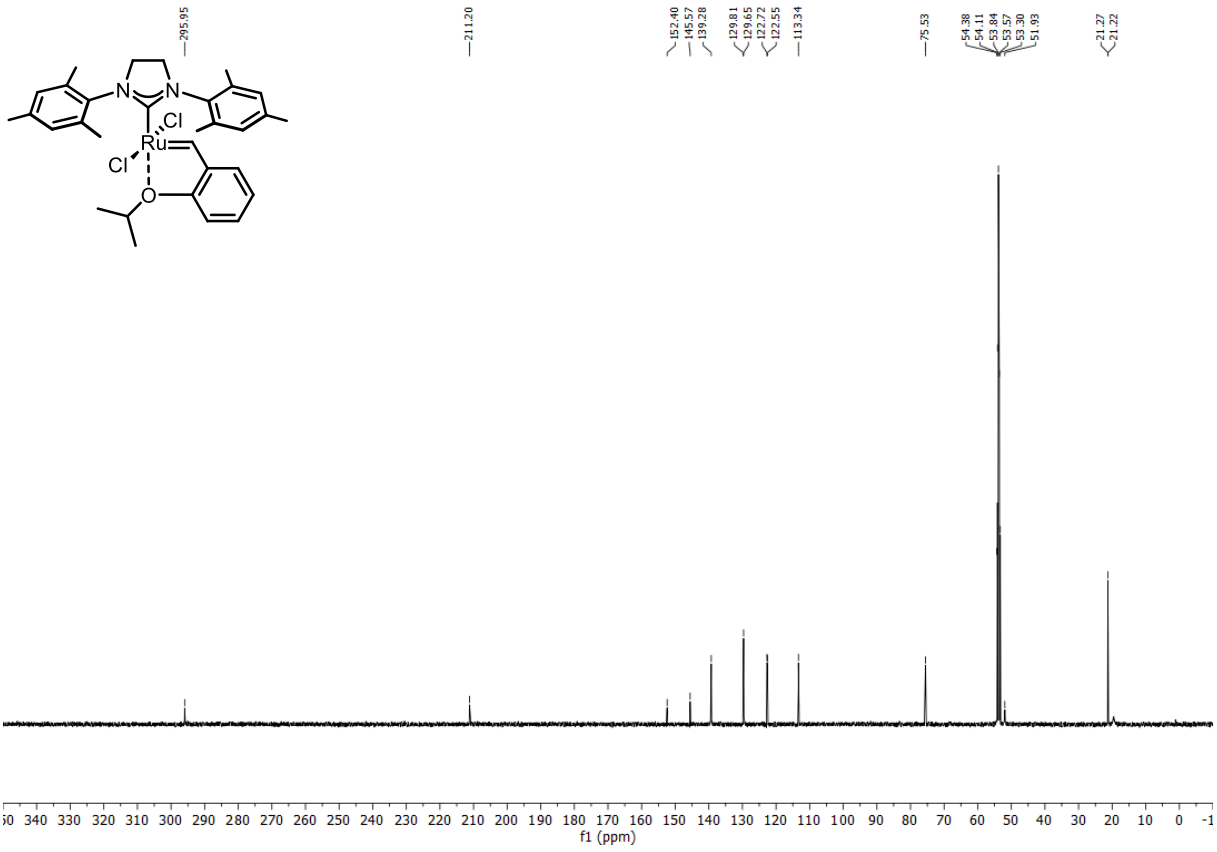
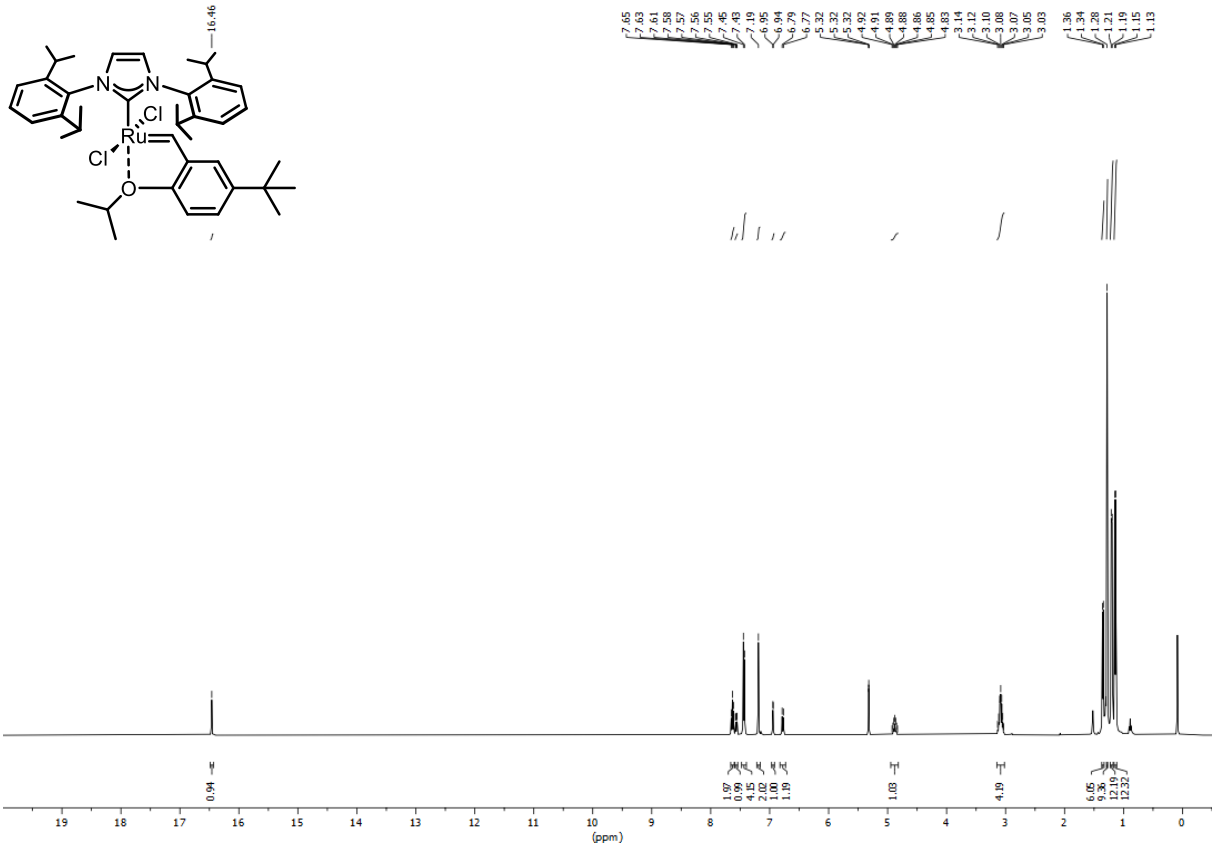
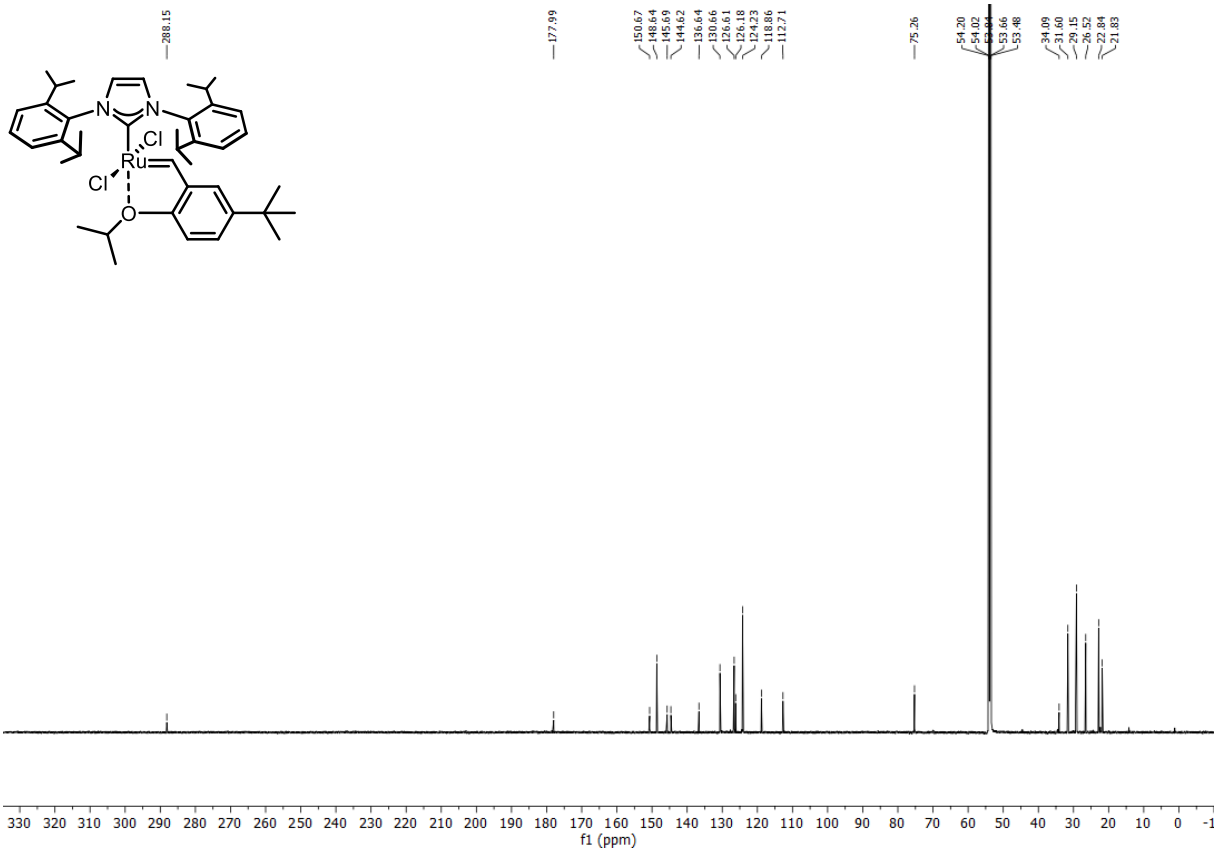


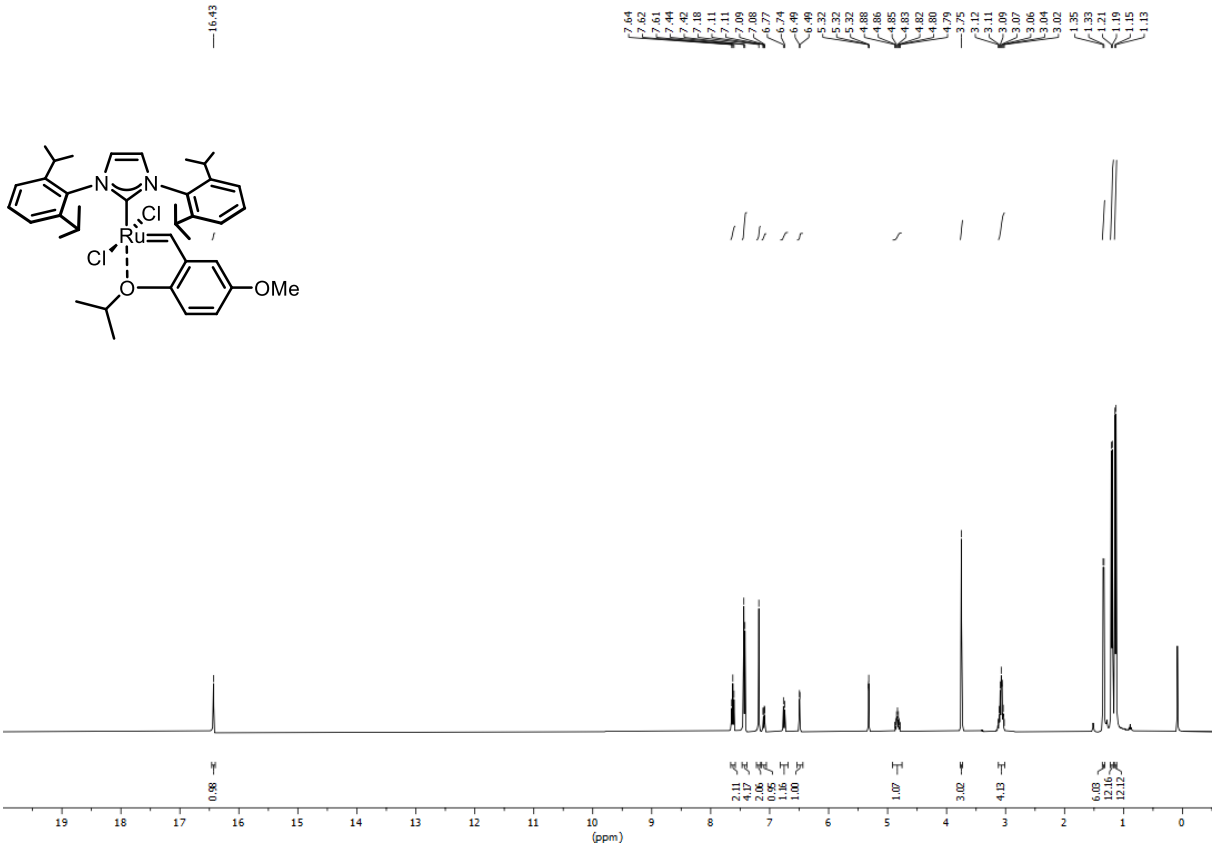
^{1}H NMR (400 MHz, CD_2Cl_2)



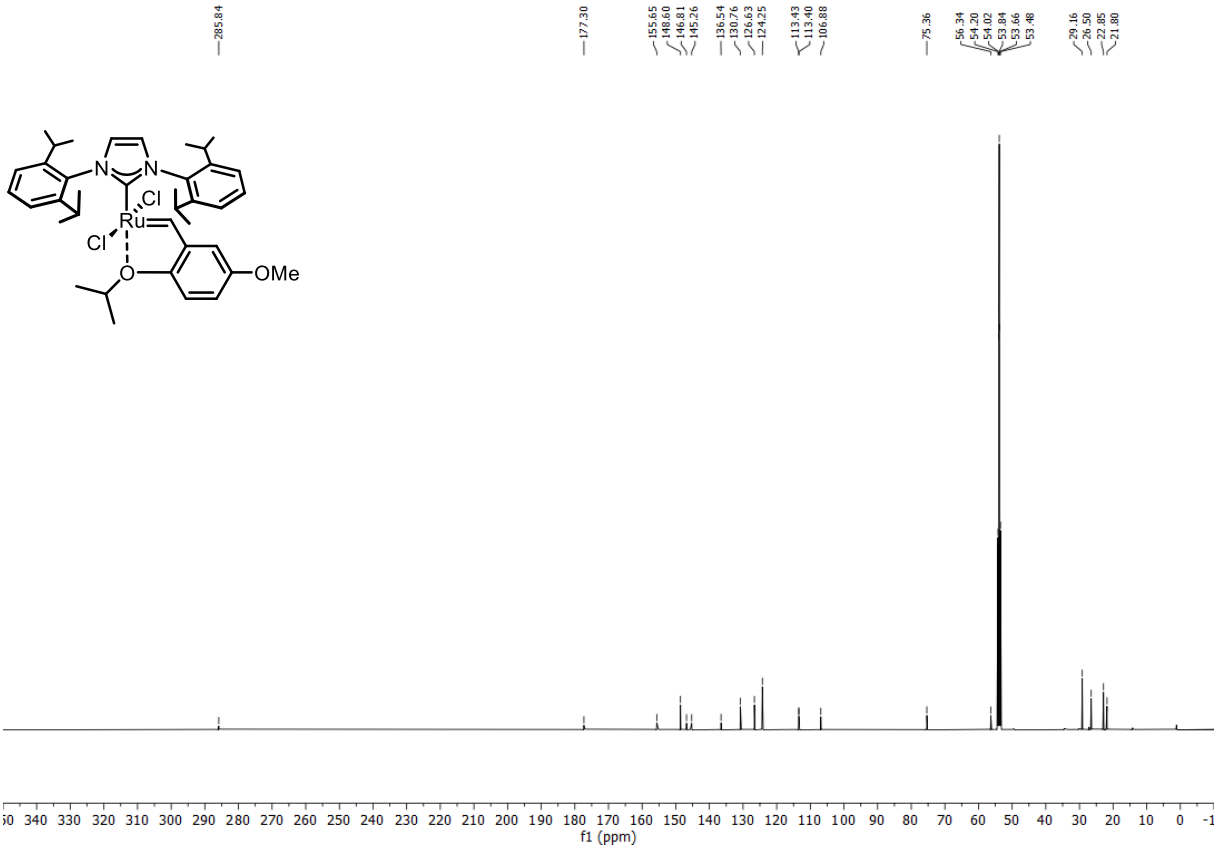
^{13}C NMR (151 MHz, CD_2Cl_2)



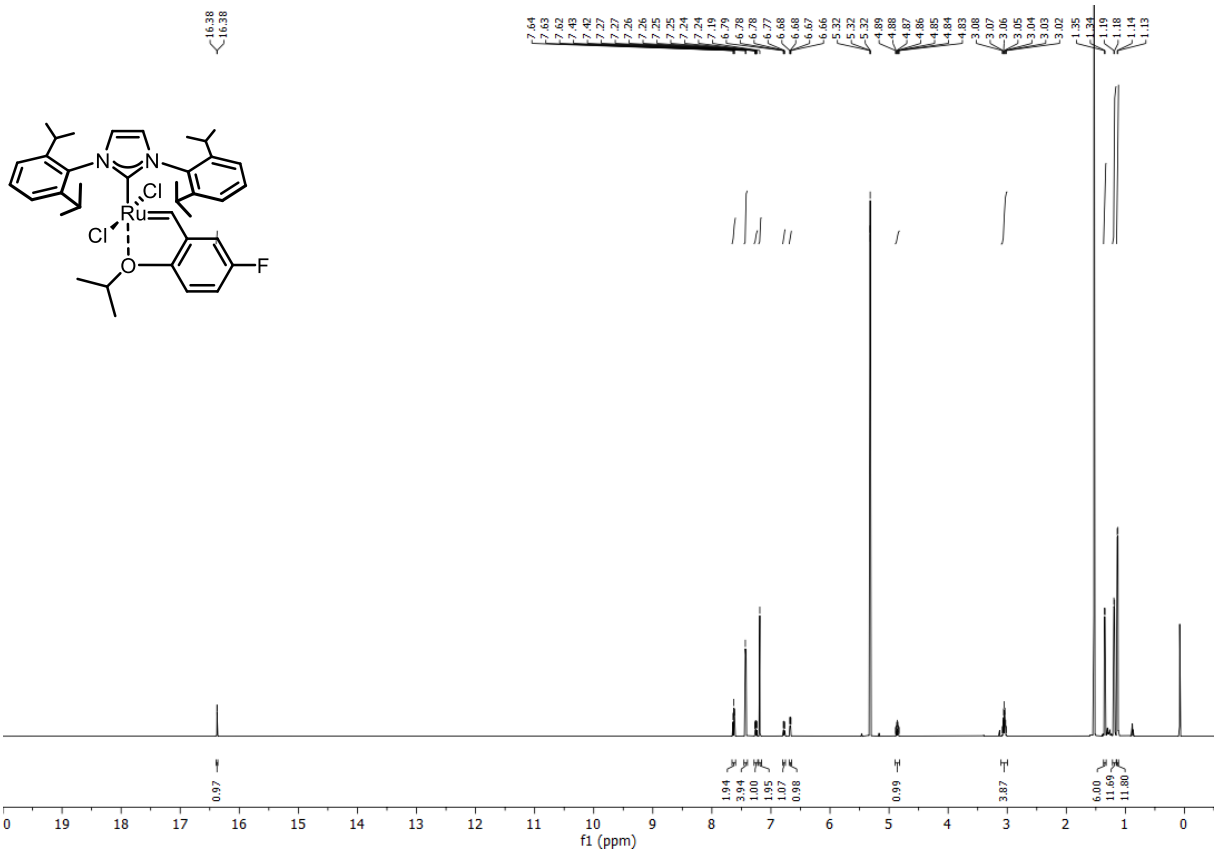
^{1}H NMR (400 MHz, CD_2Cl_2)



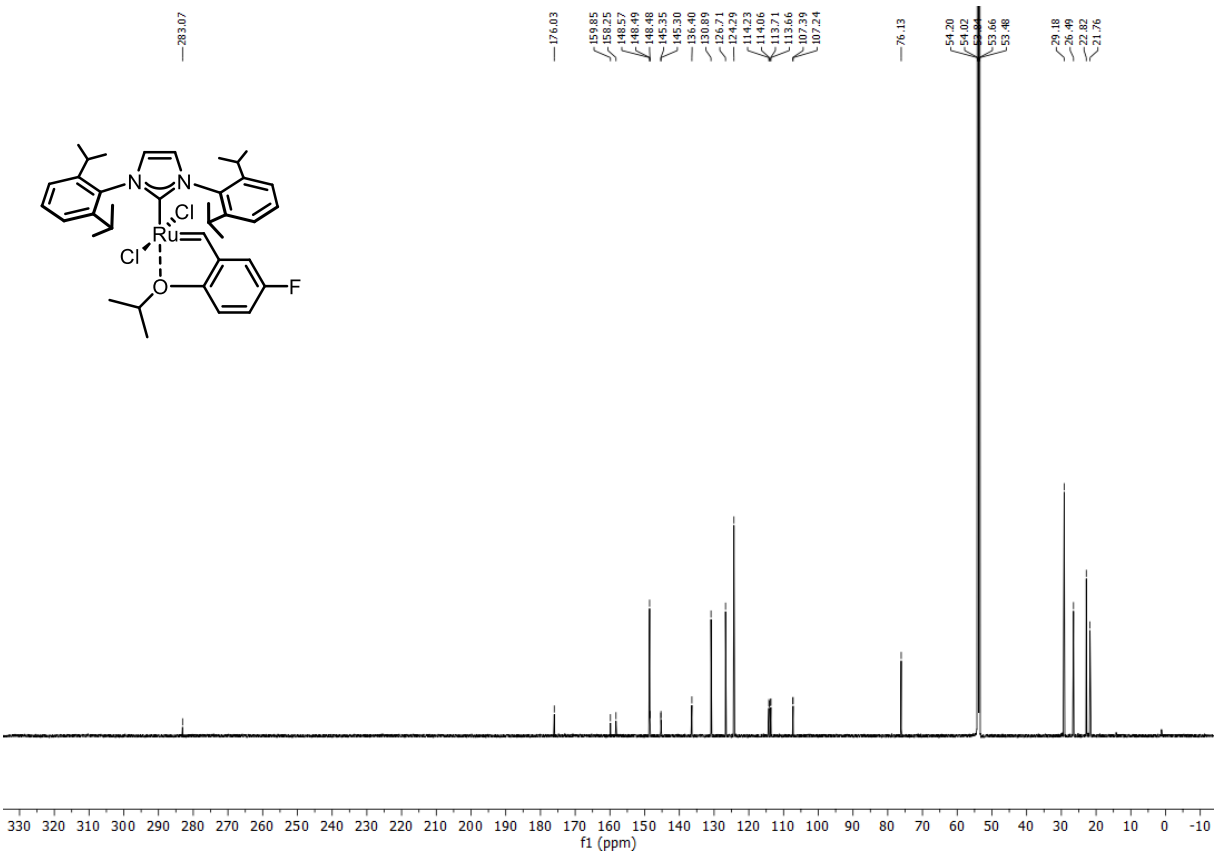
^{13}C NMR (151 MHz, CD_2Cl_2)



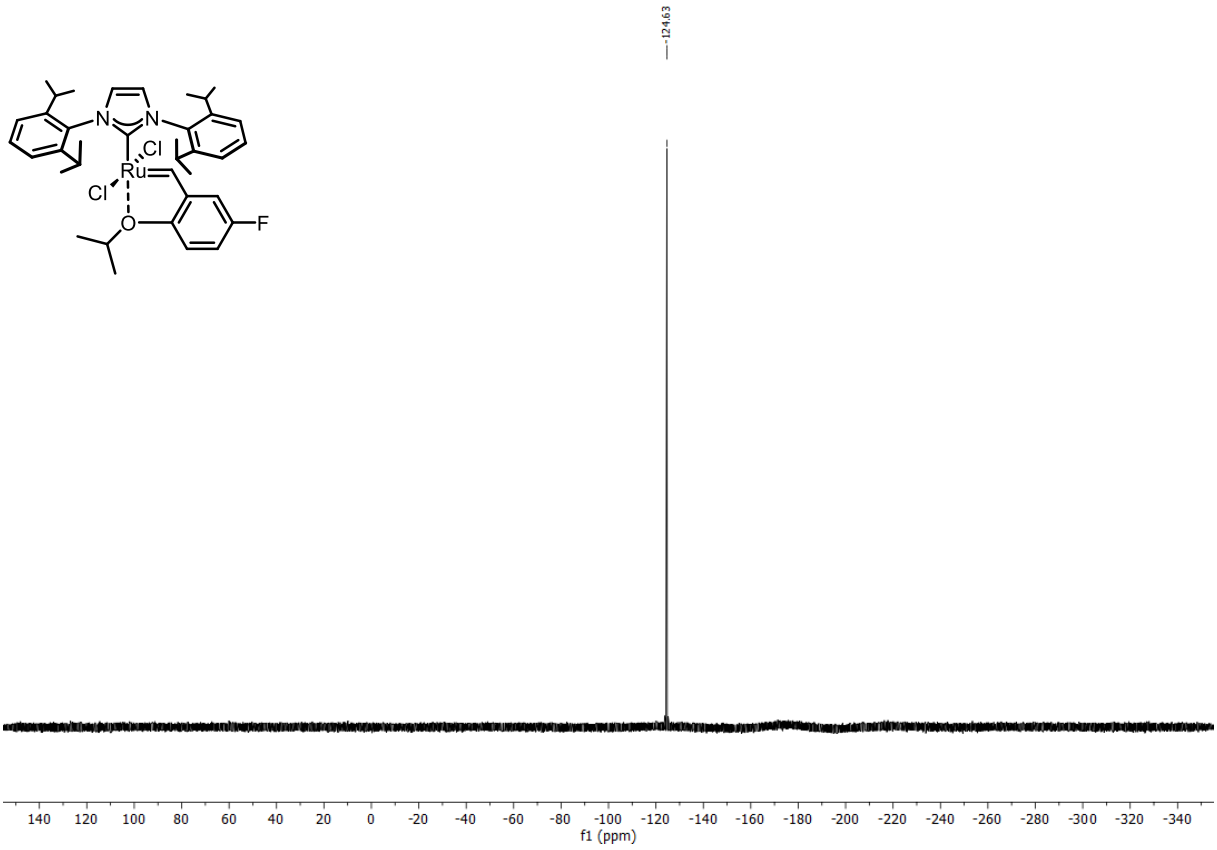
^{1}H NMR (600 MHz, CD_2Cl_2)



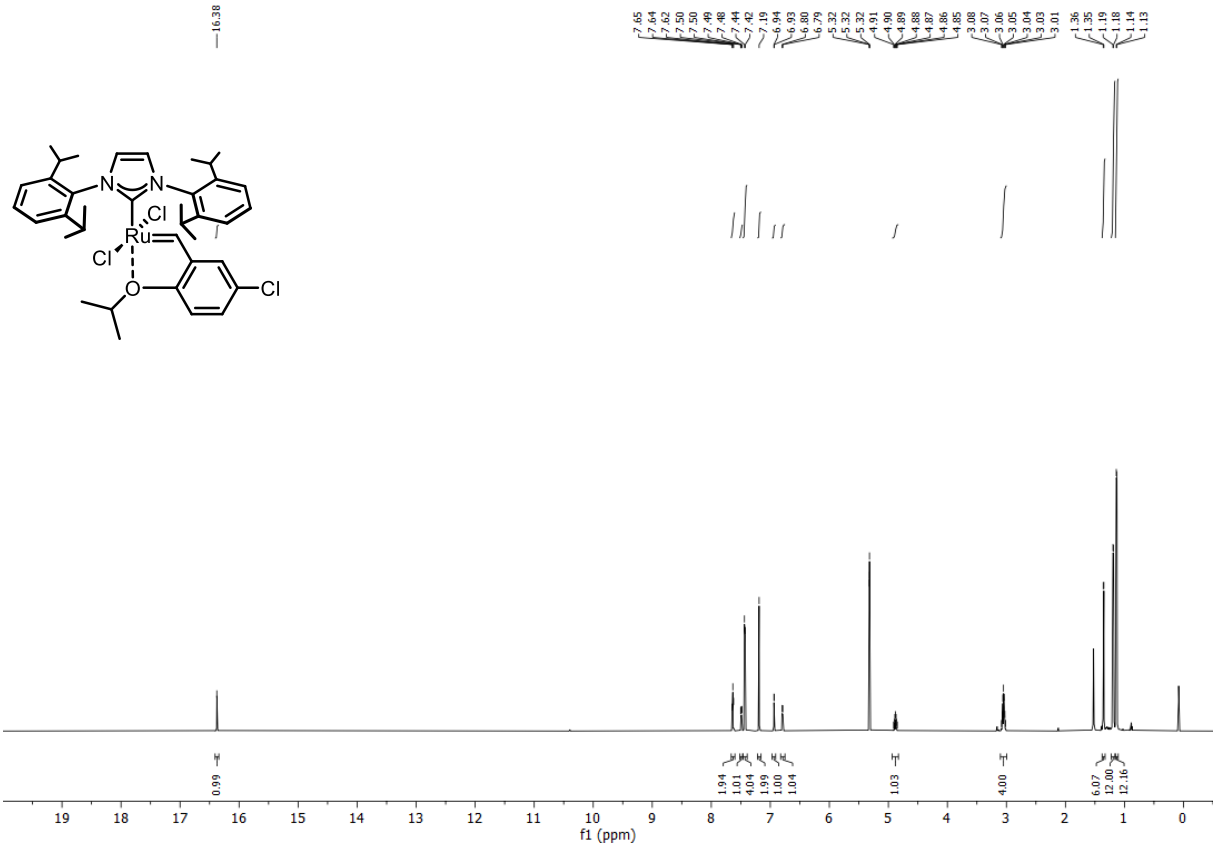
^{13}C NMR (151 MHz, CD_2Cl_2)



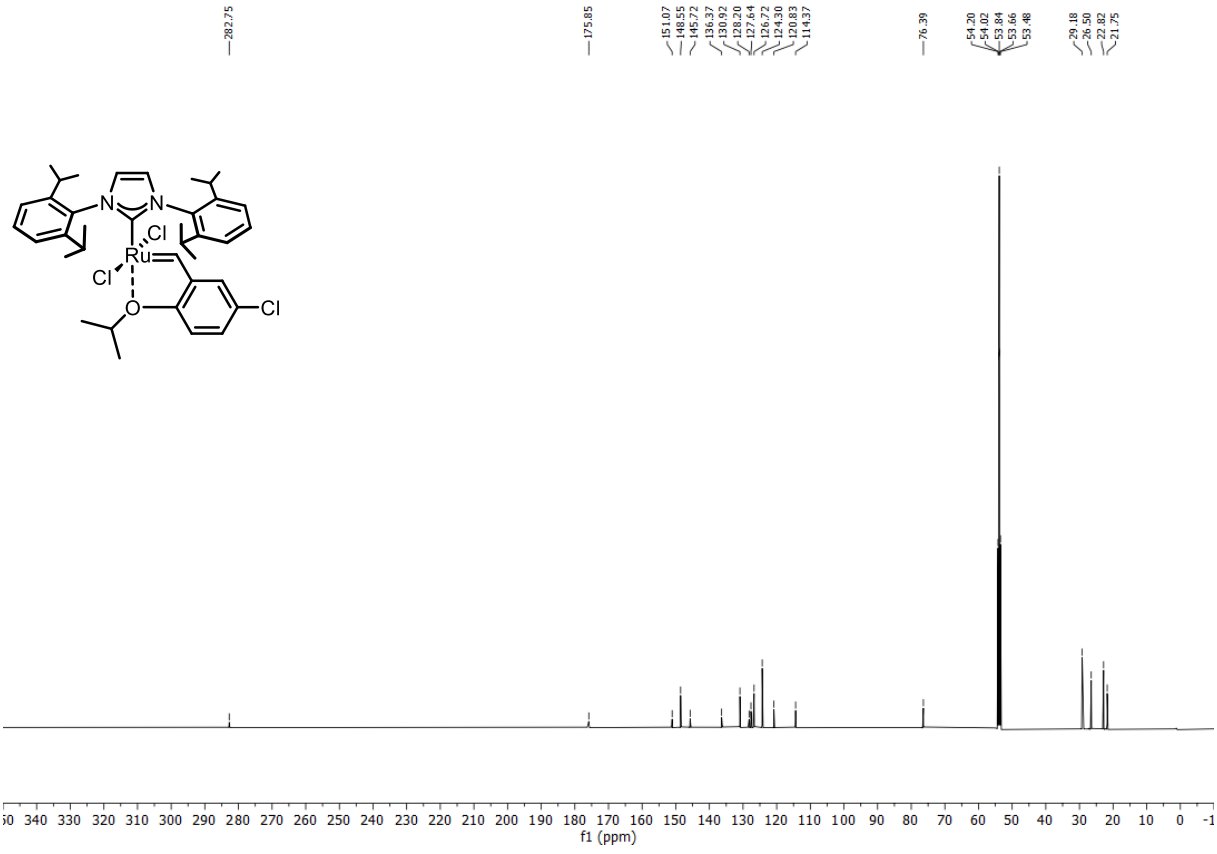
^{19}F NMR (282 MHz, CD_2Cl_2)



^{1}H NMR (600 MHz, CD_2Cl_2)



^{13}C NMR (151 MHz, CD_2Cl_2)



References

1. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179.
2. A. Yoshimura, V. N. Nemykin, V. V. Zhdankin*, Chem. Eur. J.* **2011**, *17*, 10538–10541.
3. M. Rouen, P. Chaumont, G. Barozinno-Consiglio, J. Maddaluno, A. Harrison-Marchand, *Chem. Eur. J.* **2018**, *24*, 9238–9242.
4. T. A. Hamlin, C. B. Kelly, N. E. Leadbeater, *Eur. J. Org. Chem.* **2013**, *18*, 3658–3661
5. R. B. Richard, C. M. Carson, R. J. Ehr, US4215127 *Patent*.
6. L. S. Kocsis, E. Benedetti, K. M. Brummond, *Org. Lett.* **2012**, *14*, 4430–4433.
7. M. O. Duffey, D. B. England, Z. Hu, M. Ito, S. P. Langston, C. McIntyre, H. Mizutani, H. Xu, WO2015002994A2 *Patent*.
8. J. J. Van Veldhuizen, D. G. Gillingham, S. B. Garber, O. Kataoka, A. H. Hoveyda, *J. Am. Chem. Soc.* **2003**, *125*, 12502–12508.
9. T. Biberger, R. J. Zachmann, A. Fürstner, *Angew. Chem. Int. Ed.* **2020**, *59*, 18423–18429.
10. R. J. Zachmann, A Fürstner, *Chem. Eur. J.* **2021**, *27*, 7663–7666.
11. C. S. Day, D. E. Fogg, *Organometallics* **2018**, *37*, 4551−4555.
12. M. S. Morgan, L. H. Cretcher, *J. Am. Chem. Soc.* **1948**, *70*, 375−378.
13. E. M. Alvarez, M. B. Plutschak, F. Berger, T. Ritter, *Org. Lett*. **2020**, *22*, 4593−4596.