Electronic Supplementary Material (ESI) for Organic .
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Supplementary Information

Highly Diastereoselective Addition of Alkoxyethynyl Aluminium Reagents to *N-t*Butylsulfinyl Aldimines

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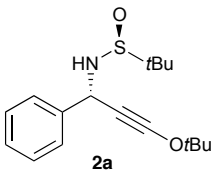
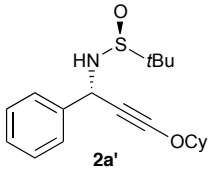
Reactions were generally carried out under argon in oven-dried glassware. Standard inert atmosphere techniques were used in handling all air and moisture sensitive reagents. Dry THF was obtained by filtration through activated molecular sieves and dry CH_2Cl_2 by filtration through activated aluminium oxide. Thin-layer chromatography was performed on (0.2 mm) silica sheets, which were visualized under ultraviolet light and by heating the plate after treatment with phosphomolybdic acid in ethanol, a p-anisaldehyde staining solution (80 mL of 95% ethanol, 2.9 mL of sulfuric acid, 0.86 mL of acetic acid, 2.1 mL of p-anisaldehyde), ninhydrin in ethanol, ceric ammonium molybdate in ethanol, or basic, aqueous $KMnO_4$. Silica gel (0.040-0.063 mm) was employed for flash column chromatography. A Fourier transform infrared spectrometer was used to record IR spectra. ^{1}H NMR and ^{13}C NMR spectra were recorded on either an AV 300, 400, or 500 MHz apparatus. All shifts for ^{1}H spectra were referenced to the residual solvent peak and are reported in ppm. When ambiguous, proton and carbon assignments were established through COSY, HMQC, and/or DEPT experiments. Mass spectra were recorded using either DCI (ammonia/isobutane 63/37), EI, or ESI techniques. HRMS were recorded on an Orbitrap apparatus (ESI). Microanalyses were performed by the microanalysis service of the DCM.

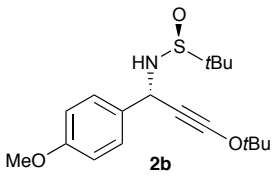
General procedure: To a solution of dichloroenol ether (4 eq) in dry THF (0.3 M) at –80 °C was added dropwise a solution of *n*-BuLi (2.5 M/hexane, 7.8 eq). The reaction mixture was allowed to warm to –20 °C over 45 min and cooled to –80 °C. A solution of Me_2AlCl (0.9 M in heptane, 4 eq) was then added dropwise and the solution stirred for 30 minutes at –80 °C. A solution of sulfinylimine (**1a-i**, 1 eq) in dry THF (0.3 M) was then added dropwise via a cannula, and the flask containing the imine was washed twice with dry THF. The reaction mixture was placed at 0 °C for 3-6 h. After complete disappearance of the starting material (TLC: pentane/EtOAc, 65:35), the reaction was cooled to –80 °C and quenched with $NaHCO_3$ and diluted with EtOAc. The organic phase was washed several times with Rochelle salt, water and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure (bath temperature kept below 30 °C). The residue was purified by flash chromatography (SiO_2/2.5% Et_3N) to afford the *N-tert*butanesulfinamides (**2a-i**).



(S_S^*,S^*)-*N*-(3-(*tert*-Butoxy)-1-phenylprop-2-yn-1-yl)-2-methylpropane-2-sulfinamide (**2a**). Sulfinylimine **1a** (63 mg, 0.3 mmol) and *O-tert*butyl-1,2-dichloroenolether (201 mg, 1.2 mmol) afforded 85 mg (92%, dr > 98:2) of sulfinamide **2a** as a white solid: m.p. 84-86 °C (decomp); IR (neat) 2254, 3034 cm^{-1}; ^1H NMR(400 MHz, $CDCl_3$) δ (ppm) 7.50-7.47 (m, 2H), 7.37-7.23 (m, 3H), 5.25 (d, J = 6.1 Hz, 1H), 3.50 (d, J = 6.1 Hz, 1H), 1.42 (s, 9H), 1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 141.1, 128.7, 128.2, 127.9, 92.4, 87.2, 56.4, 51.5, 40.8, 27.5, 22.9; MS (ESI) *m/z* $[M+H]^+$ 308.1; HRMS (FT, ESI) calcd for $C_{17}H_{25}NNaO_2S$: 330.14982. Found: 330.15012.

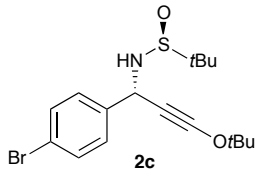


(S_S,S)-*N*-(3-(Cyclohexyloxy)-1-phenylprop-2-yn-1-yl)-2-methylpropane-2-sulfinamide (**2a'**). Sulfinylimine **1a** (720 mg, 3.44 mol) and *O*-cyclohexyl-1,2-dichloroenolether (0.653g, 13.6 mmol) afforded 1.02g (89%, dr > 98:2) of sulfinamide **2a'**: m.p. 89-91 °C (decomp); $[\alpha]^{20}_D$ +28.0 (c = 1, $CHCl_3$); IR (neat) 2272, 3212 cm^{-1}; ^1H NMR(400 MHz, $CDCl_3$) δ (ppm) 7.52-7.46 (m, 2H), 7.38-7.24 (m, 3H), 5.24 (d, J = 5.7 Hz, 1H), 5.00-4.20 (m, 1H), 3.52 (d, J = 5.7 Hz, 1H), 2.02-1.90 (m, 2H), 1.81-1.68 (m, 2H), 1.68-1.55 (m, 2H), 1.55-1.44 (m, 1H), 1.39-1.22 (m, 3H), 1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 141.0, 128.8, 128.2, 128.0, 94.4, 87.0, 56.4, 51.2, 38.9, 22.9, 31.3, 25.4, 23.4; MS (ESI) *m/z* $[M+H]^+$ 334.2; HRMS (FT, ESI) calcd for $C_{19}H_{27}NNaO_2S$: 356.16547. Found: 356.16589.

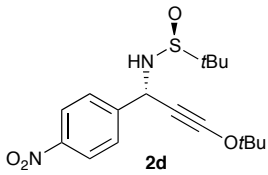


(S_S^*,S^*)-*N*-(3-(*tert*-Butoxy)-1-(4-methoxyphenyl)prop-2-yn-1-yl)-2-methylpropane-2-sulfinamide (**2b**). Sulfinylimine **1b** (68 mg, 0.28 mmol) and *O-tert*butyl-1,2-dichloroenolether (201 mg, 1.2 mmol) afforded 74 mg (77%, dr > 98:2) of sulfinamide **2b** isolated as a white solid: m.p. 82-84 °C (decomp); IR (neat) 2257, 3197 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.39 (d, J = 8.7, 2H), 6.83 (d, J = 8.7, 2H), 5.18 (d, J = 5.9 Hz, 1H), 3.77 (s, 3H), 3.47 (d, J = 5.9 Hz, 1H), 1.39 (s, 9H), 1.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ (ppm) 159.5, 133.2, 129.1, 114.0, 92.1, 87.0, 56.3,

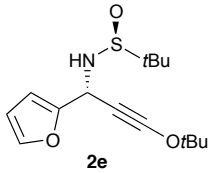
55.5, 50.8, 40.9, 27.4, 22.8; MS (ESI) *m/z* $[M+H]^+$ 338.2; HRMS (FT, ESI) calcd for $C_{18}H_{27}NNaO_3S$: 360.16039. Found: 360.16092.



(S_S^*,S^*)-*N*-(1-(4-Bromophenyl)-3-(*tert*-butoxy)prop-2-yn-1-yl)-2-methylpropane-2-sulfinamide (**2c**). Sulfinylimine **1c** (86.6 mg, 0.3 mmol) and *O-tert*butyl-1,2-dichloroenolether (219 mg, 1.3 mmol) afforded 106 mg (91%, dr = 96:4) of sulfinamide **2c** as a yellow pale solid: m.p. 86-88 °C (decomp); IR (neat) 2264, 3141 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.46 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 5.20 (d, J = 5.7 Hz, 1H), 3.50 (d, J = 5.7 Hz, 1H), 1.40 (s, 9H), 1.19 (s, 9H); ^{13}C NMR (100 MHz, *$CDCl_3$*) δ (ppm) 140.3, 131.9, 129.7, 122.2, 92.6, 87.5, 56.5, 50.8, 40.4, 27.4, 22.9; MS (ESI) *m/z* $[M-H]^-$ 385.9; HRMS (FT, ESI) calcd for $C_{17}H_{24}BrNNaO_2S$: 408.06033. Found: 408.06138.

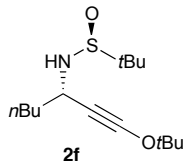


(S_S^*,S^*)-*N*-(3-(*tert*-Butoxy)-1-(4-nitrophenyl)prop-2-yn-1-yl)-2-methylpropane-2-sulfinamide (**2d**): Sulfinylimine **1d** (88.2 mg, 0.34 mmol) and *O-tert*butyl-1,2-dichloroenolether (222.9 mg, 1.33 mmol) afforded 110 mg (90 %, dr = 97:3) of sulfinamide **2d** as a yellow pale solid: m.p. 83-85 °C (decomp); IR (neat) 2261, 3122 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.17-8.14 (m, 2H), 7.67-7.62 (m, 2H), 5.32 (d, J = 5.5 Hz, 1H), 3.62 (d, J = 5.5 Hz, 1H), 1.38 (s, 9H), 1.18 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 148.3, 147.8, 128.8, 124.0, 93.3, 87.9, 56.6, 50.7, 39.8, 27.4, 22.8; MS (ESI) *m/z* $[M+H]^+$ 353.2; HRMS (FT, ESI) calcd for $C_{17}H_{24}N_2NaO_4S$: 375.13490. Found: 375.13522.

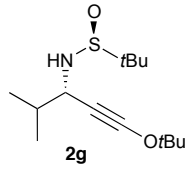


(S_S^*,S^*)-*N*-(3-(*tert*-Butoxy)-1-(furan-2-yl)prop-2-yn-1-yl)-2-methylpropane-2-sulfinamide (**2e**). sulfinylimine **1e** (56.8 mg, 0.29 mmol) and *O-tert*butyl-1,2-dichloroenolether (205 mg, 1.22 mmol) afforded 72 mg (85%, dr = 95:5) of sulfinamide **2e** as a yellow pale solid: m.p. 61-63 °C; IR (neat) 2268, 3151 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.36 (ps t, J = 1.9, 1H), 6.37 (ps d, J = 3.1 Hz, 1H), 6.31 (dd, J = 3.1, 1.9 Hz, 1H), 5.28 (d, J = 6.4 Hz, 1H), 3.49 (d, J = 6.4 Hz, 1H), 1.43 (s,

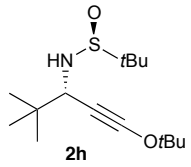
9H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, *CDCl$_3$*) δ (ppm) 153.6, 142.8, 110.5, 107.7, 91.2, 87.4, 56.5, 45.8, 38.4, 27.4, 22.7; MS (ESI) *m/z* [M+H]$^+$ 298.2; HRMS (FT, ESI) calcd for $C_{15}H_{23}NNaO_3S$: 320.12909. Found: 320.12941.



(S_S^*,S^*)-*N*-(3-(*tert*-Butoxy)hept-1-yn-3-yl)-2-methylpropane-2-sulfinamide (2f). sulfinylimine **1f** (56.3 mg, 0.3 mmol) and *O-tert*butyl-1,2-dichloroenolether (204 mg, 1.2 mmol) afforded 70 mg (83%, dr = 93:7) of sulfinamide **2f** as a white solid: m.p. 39-40 °C; IR (neat) 2257, 3027 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 4.02 (td, *J* = 7.2, 5.9 Hz, 1H), 3.14 (d, *J* = 5.9 Hz, 1H), 1.71-1.54 (m, 2H), 1.45-1.23 (m, 4H), 1.37 (s, 9H), 1.18 (s, 9H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 90.4, 86.5, 56.1, 48.1, 41.6, 37.9, 28.2, 27.4, 22.9, 22.6, 14.3; MS (ESI) *m/z* [M+H]$^+$ 288.2; HRMS (FT, ESI) calcd for $C_{15}H_{29}NNaO_2S$: 310.18112. Found: 310.18133.

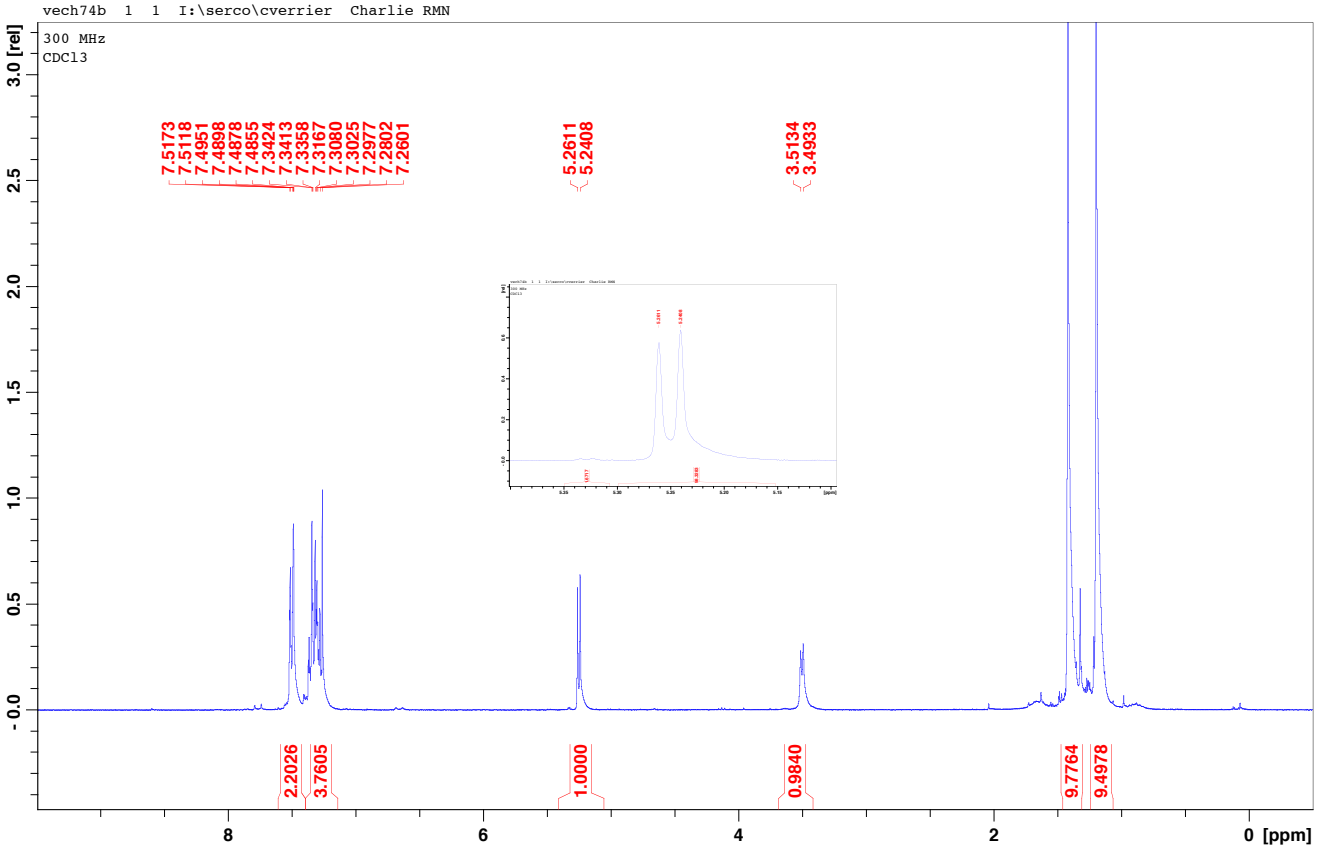


(S_S^*,S^*)-*N*-(3-(*tert*-Butoxy)-4-methylpent-1-yn-3-yl)-2-methylpropane-2-sulfinamide (**2g**). sulfinylimine **1g** (58.5 mg, 0.33 mmol) and *O-tert*butyl-1,2-dichloroenolether (214 mg, 1.27 mmol) afforded 98 mg (83%, dr = 94:6) of sulfinamide **2g** as a colourless oil: IR (neat) 2255, 3200 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm) 3.91 (dd, *J* = 6.1, 4.9 Hz, 1H), 3.11 (d, *J* = 6.4 Hz, 1H), 1.85 (dhept., *J* = 6.7, 4.9 Hz, 1H), 1.36 (s, 9H), 1.17 (s, 9H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm) 91.0, 86.4, 56.2, 54.0, 39.6, 34.2, 27.4, 22.9, 19.4, 17.6; MS (ESI) *m/z* [M+H]$^+$ 274.2; HRMS (FT, ESI) calcd for $C_{14}H_{27}NNaO_2S$: 296.16547. Found: 296.16575.



(S_S^*,S^*)-*N*-(3-(*tert*-Butoxy)-4,4-dimethylpent-1-yn-3-yl)-2-methylpropane-2-sulfinamide (2h). Sulfinylimine **1h** (56.2 mg, 0.3 mmol) and *O-tert*butyl-1,2-dichloroenolether (211 mg, 1.26 mmol) afforded 71 mg (83%, dr = 95:5) of sulfinamide **2h** as a white solid: m.p. 90-92 °C (decomp); IR (neat) 2255, 3207 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 3.67 (d, *J* = 8.9 Hz, 1H), 3.01 (d, *J* = 8.9 Hz, 1H), 1.38 (s, 9H), 1.20 (s, 9H) , 0.95 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 91.2, 86.4,

59.0, 56.7, 40.4, 36.8, 27.5, 26.5, 23.1; MS (ESI) *m/z* $[M+H]^+$ 288.2; HRMS (FT, ESI) calcd for $C_{15}H_{29}NNaO_2S$: 310.18112. Found: 310.18137.



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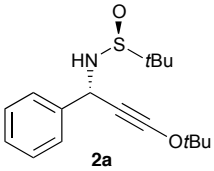

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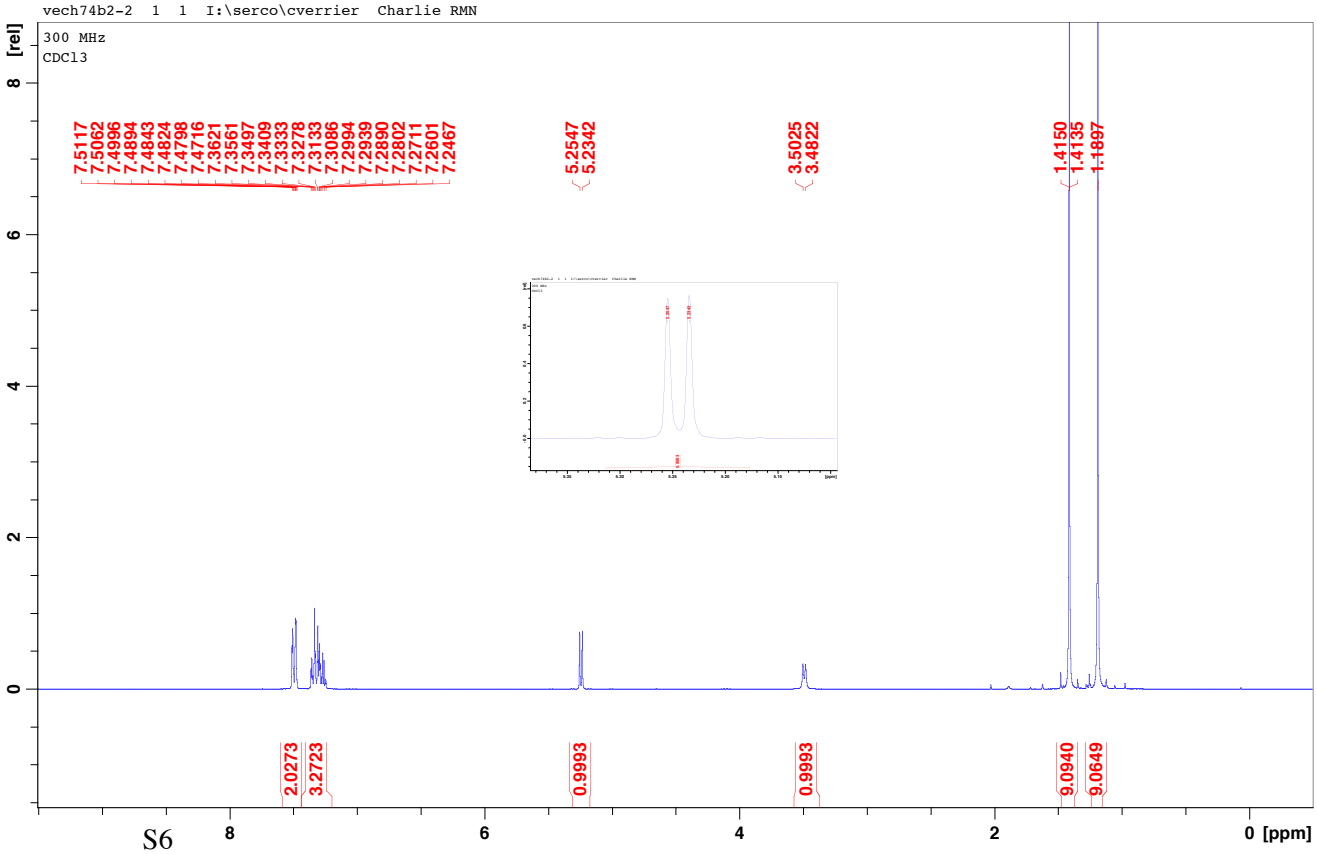

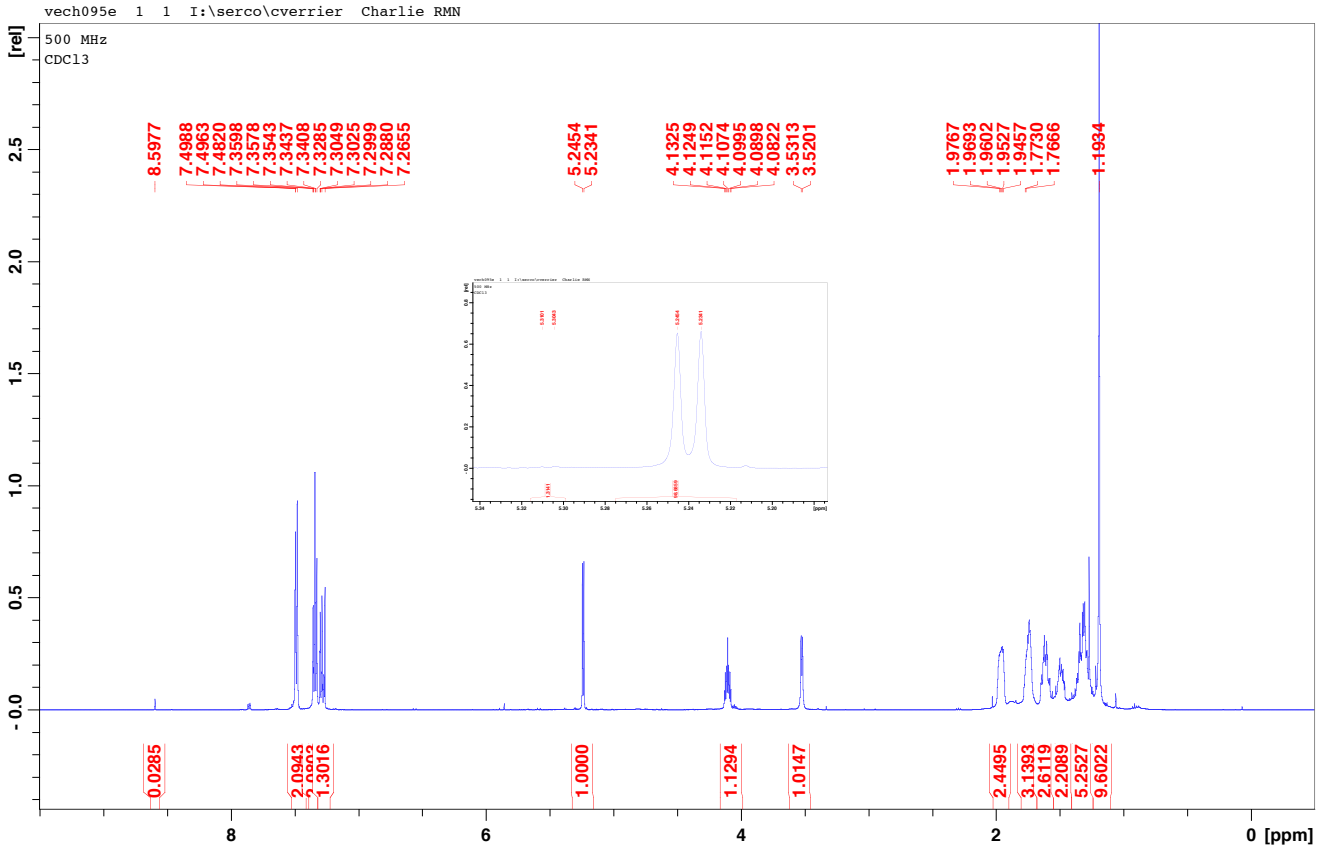

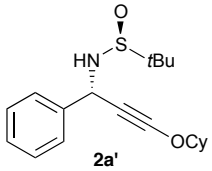

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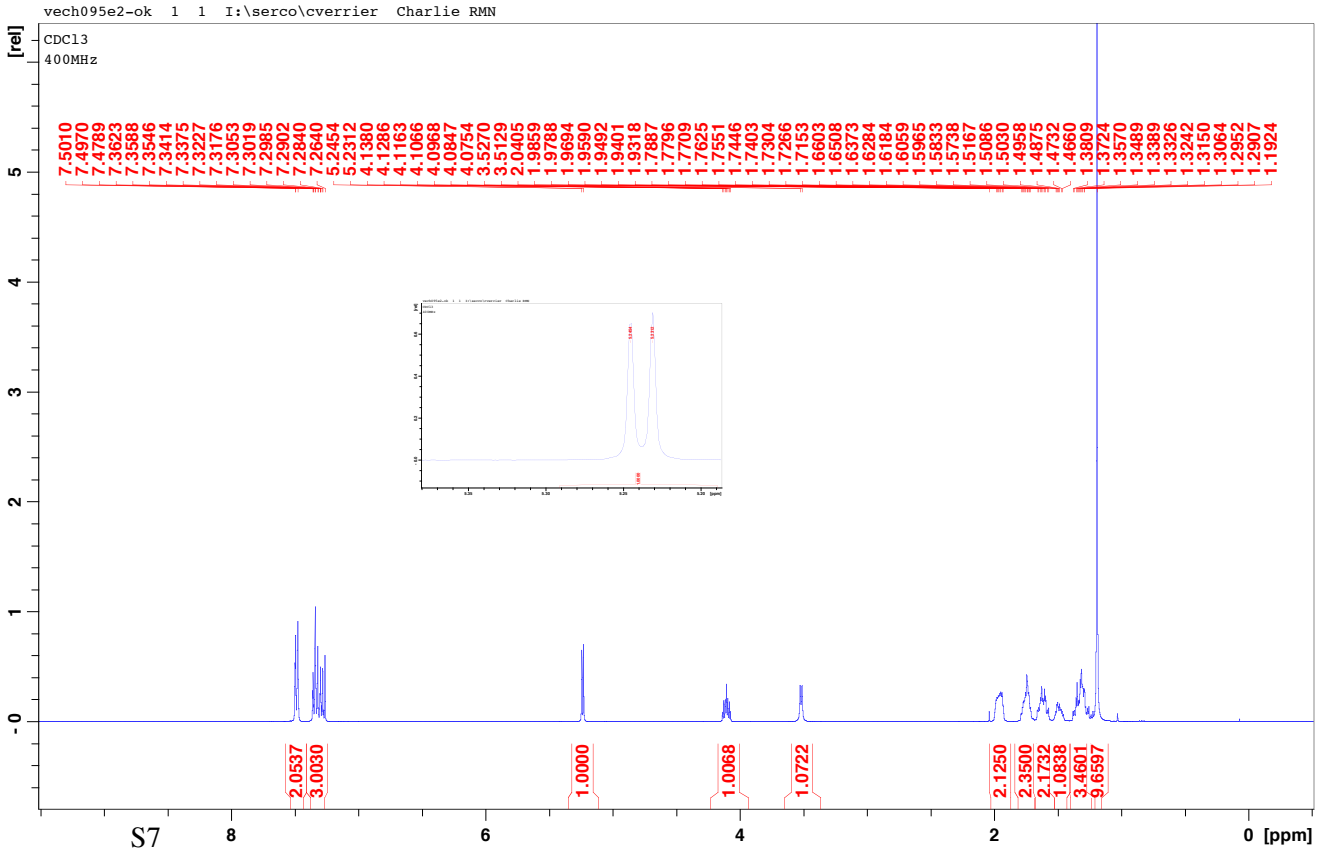

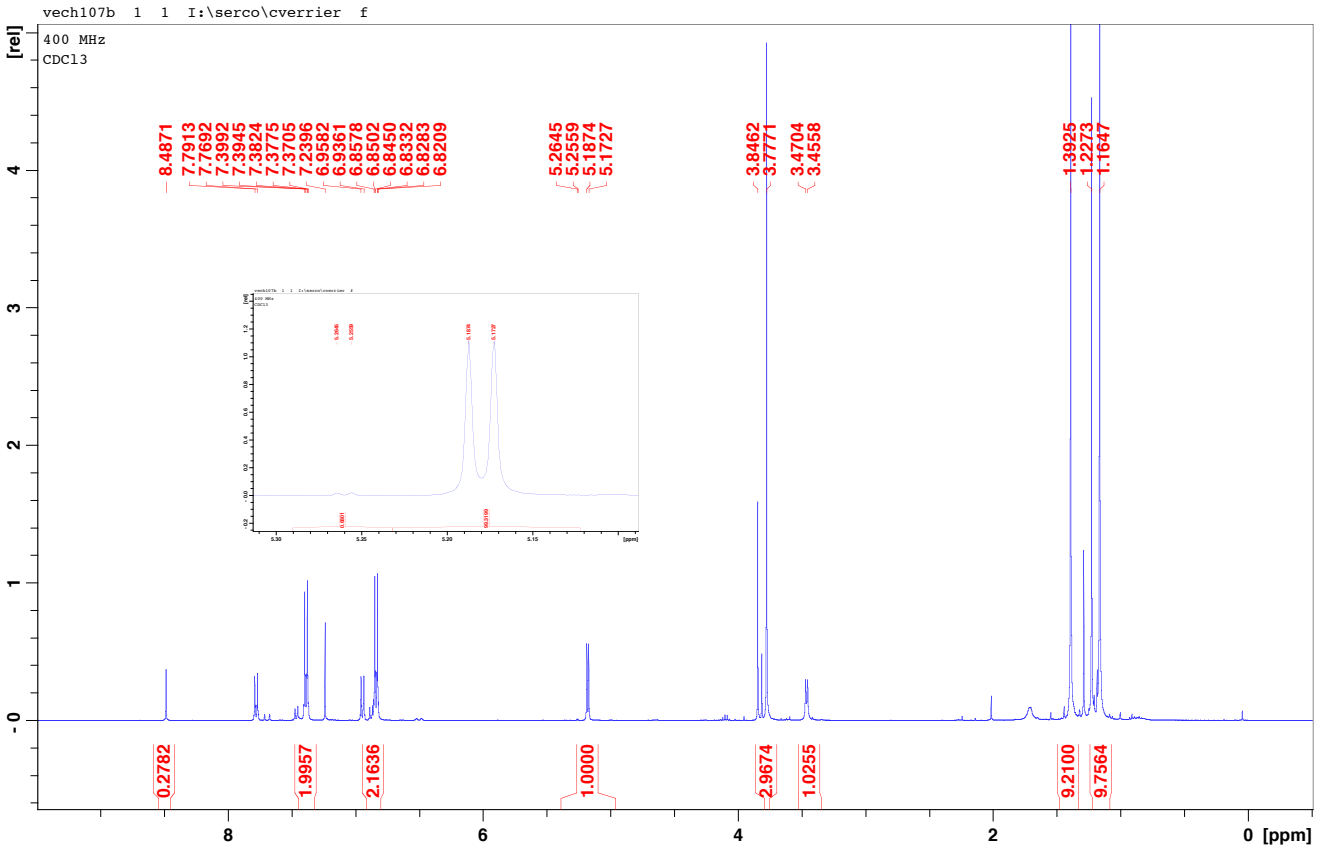

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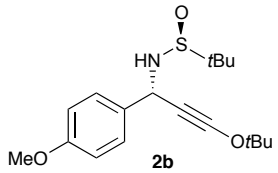

2b

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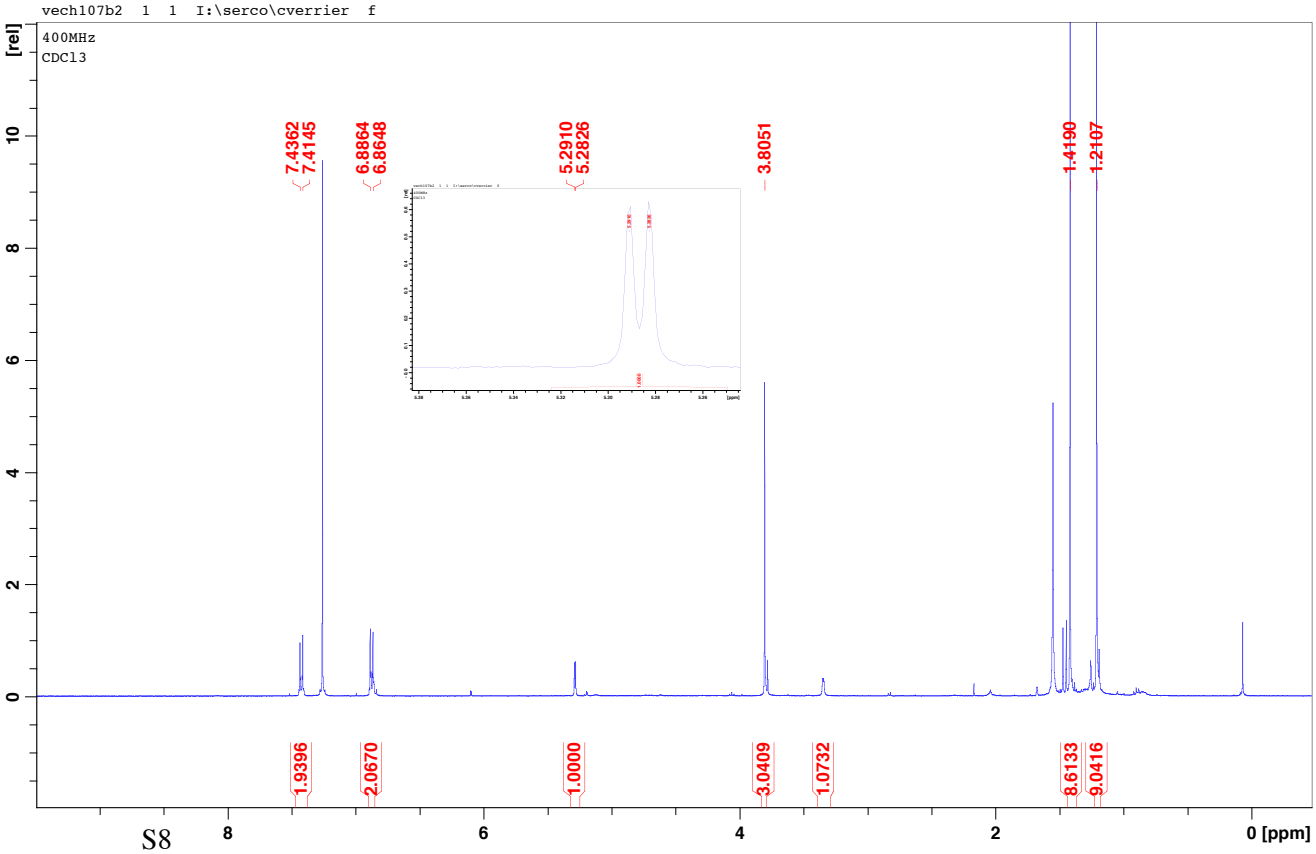

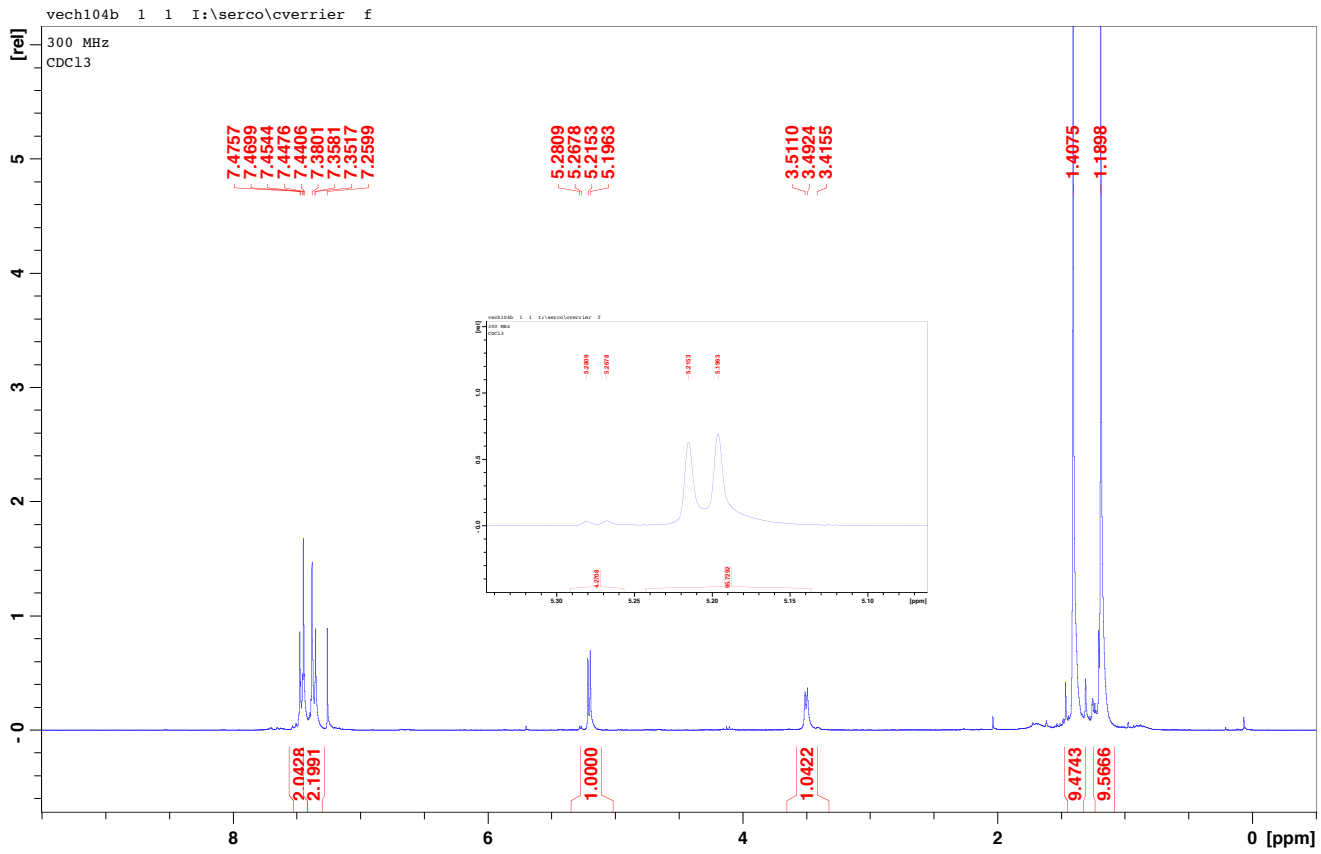

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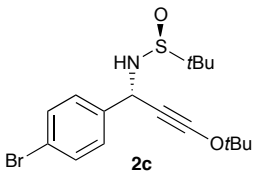

2c

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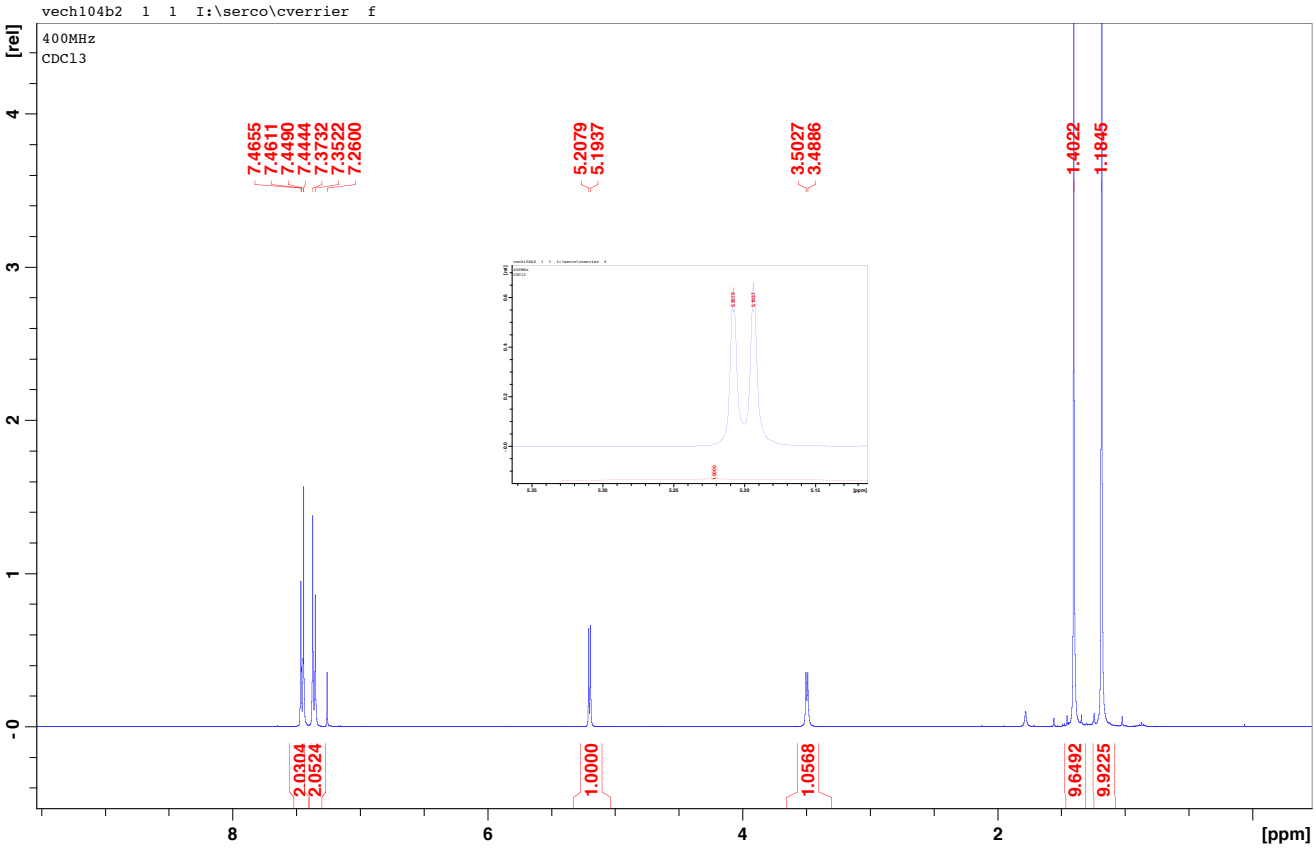

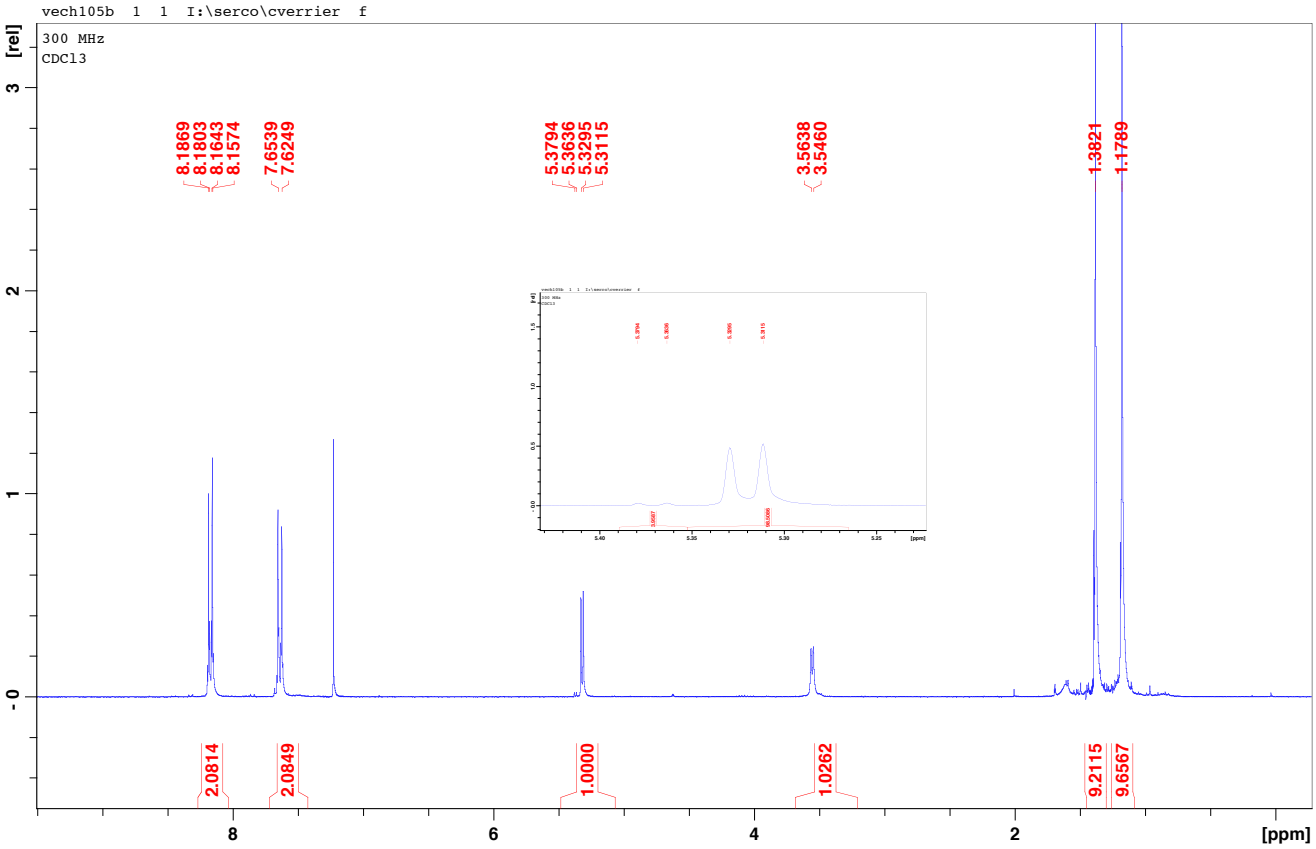

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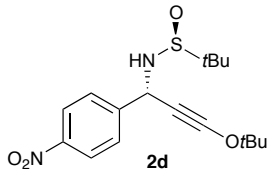

2d

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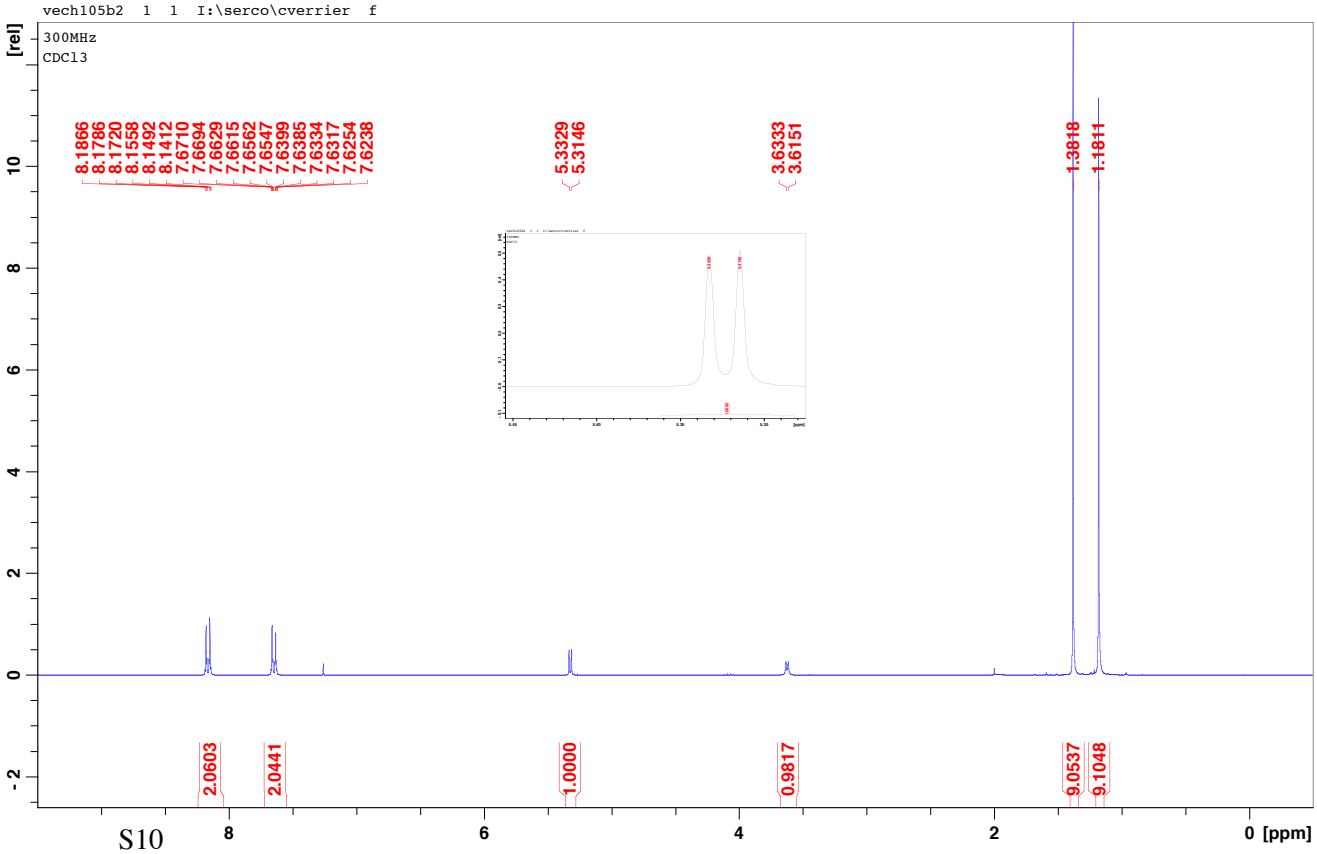

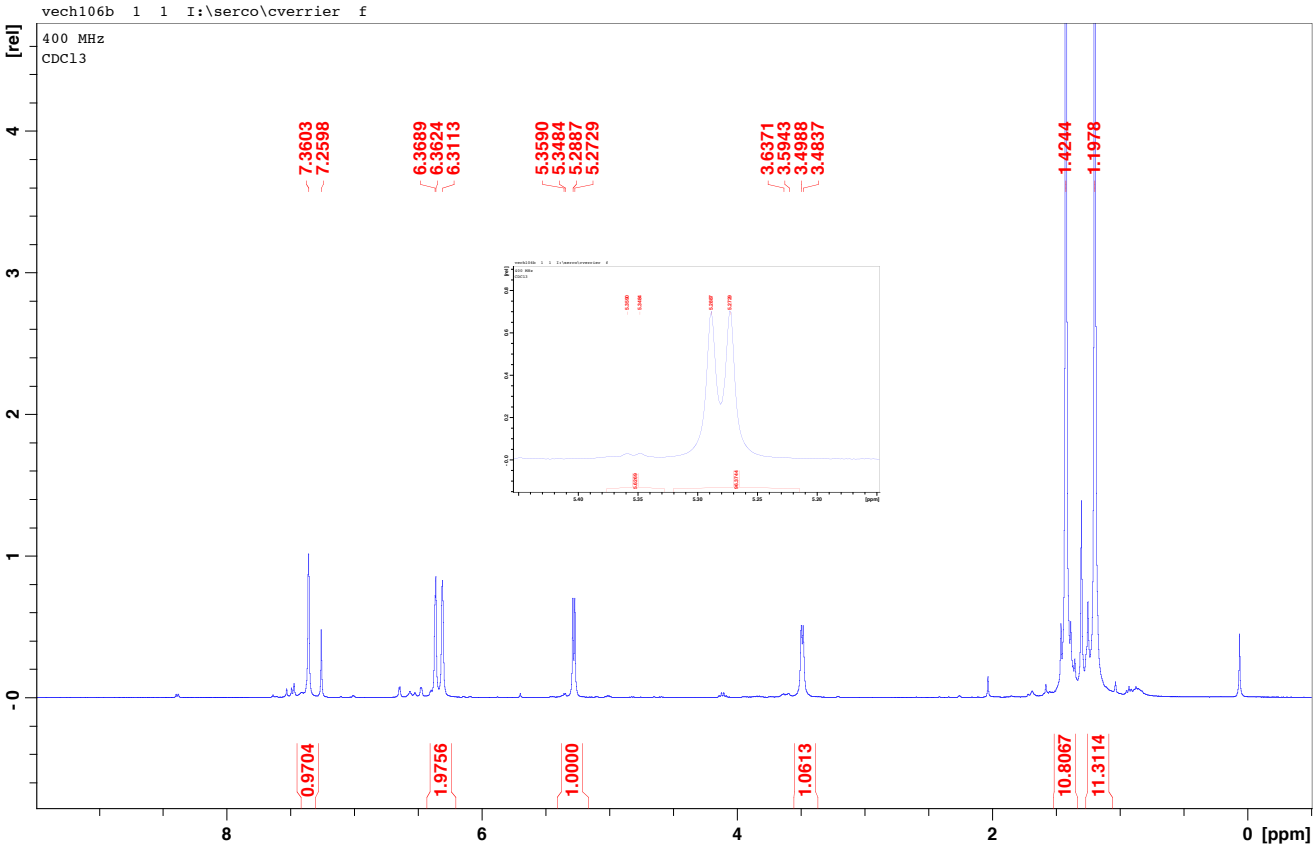

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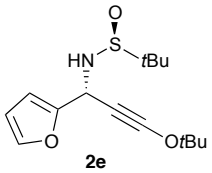

2e

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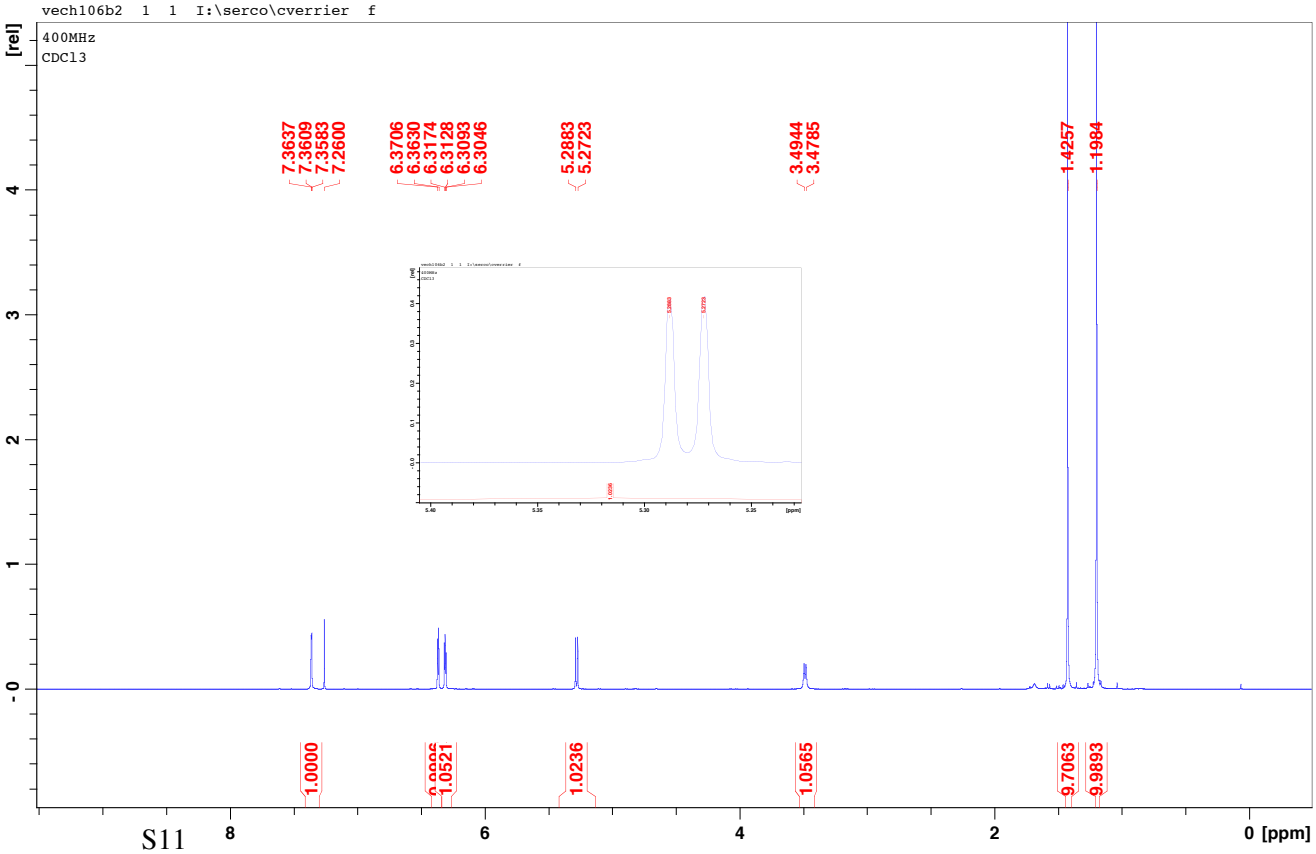

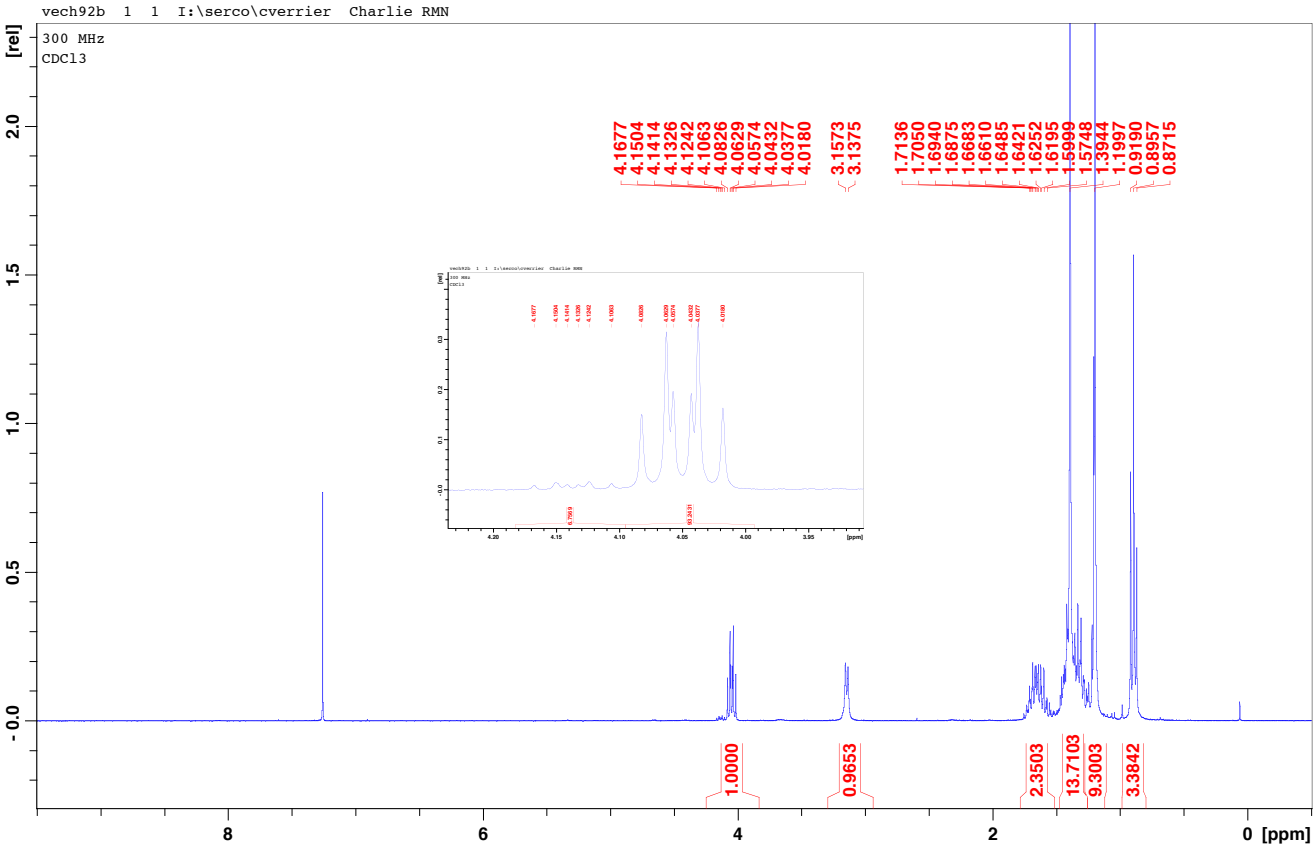

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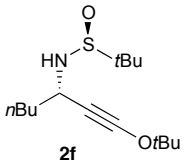

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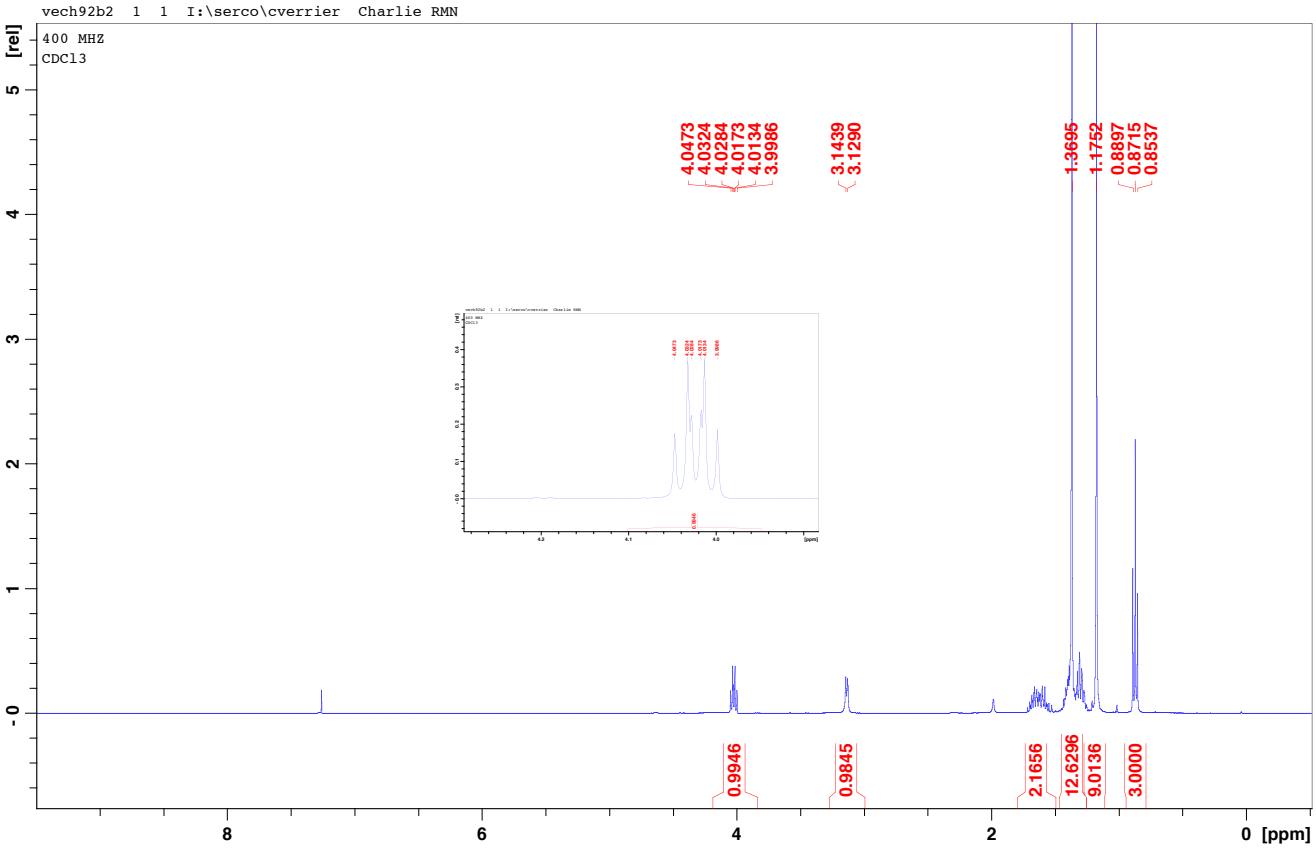

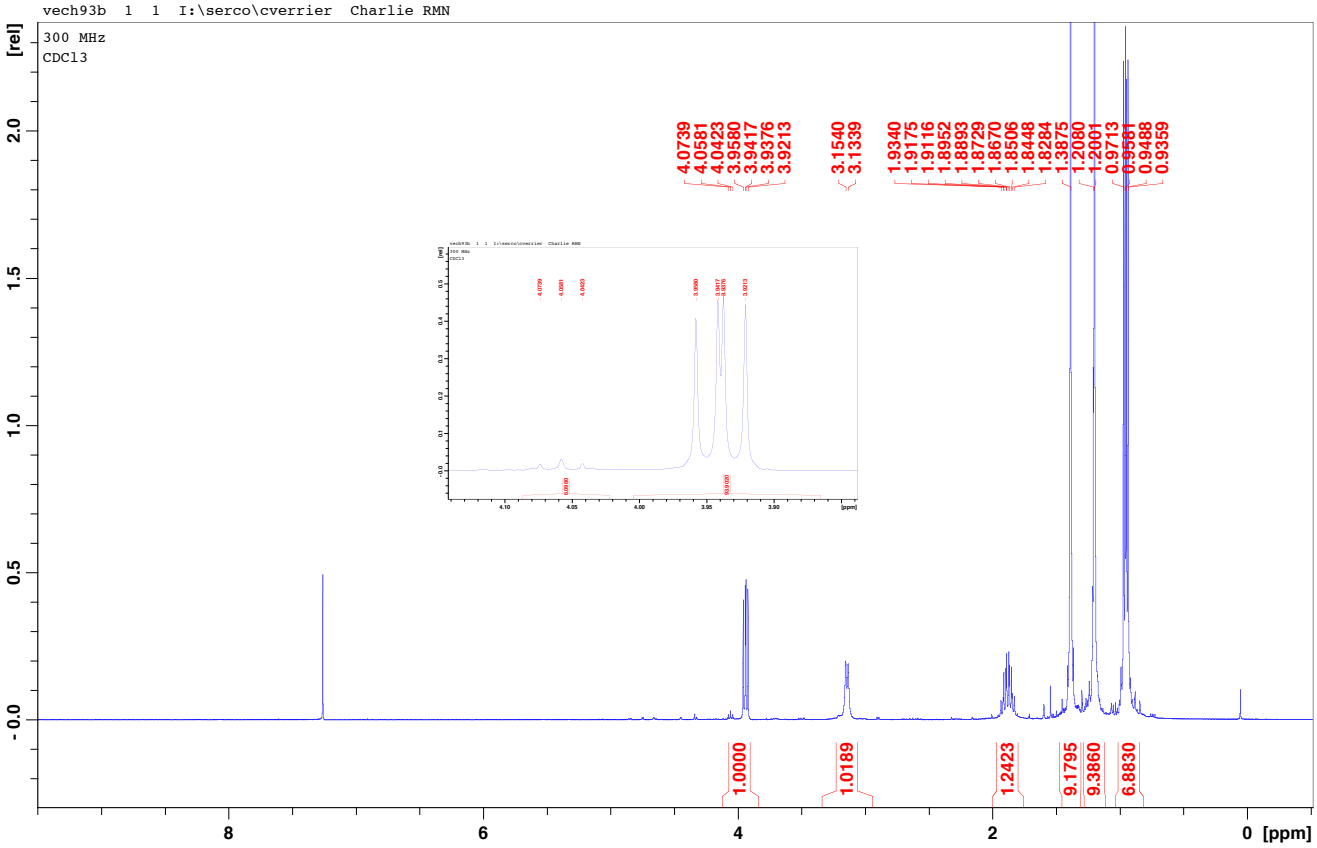

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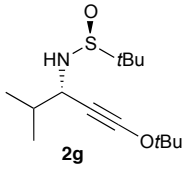

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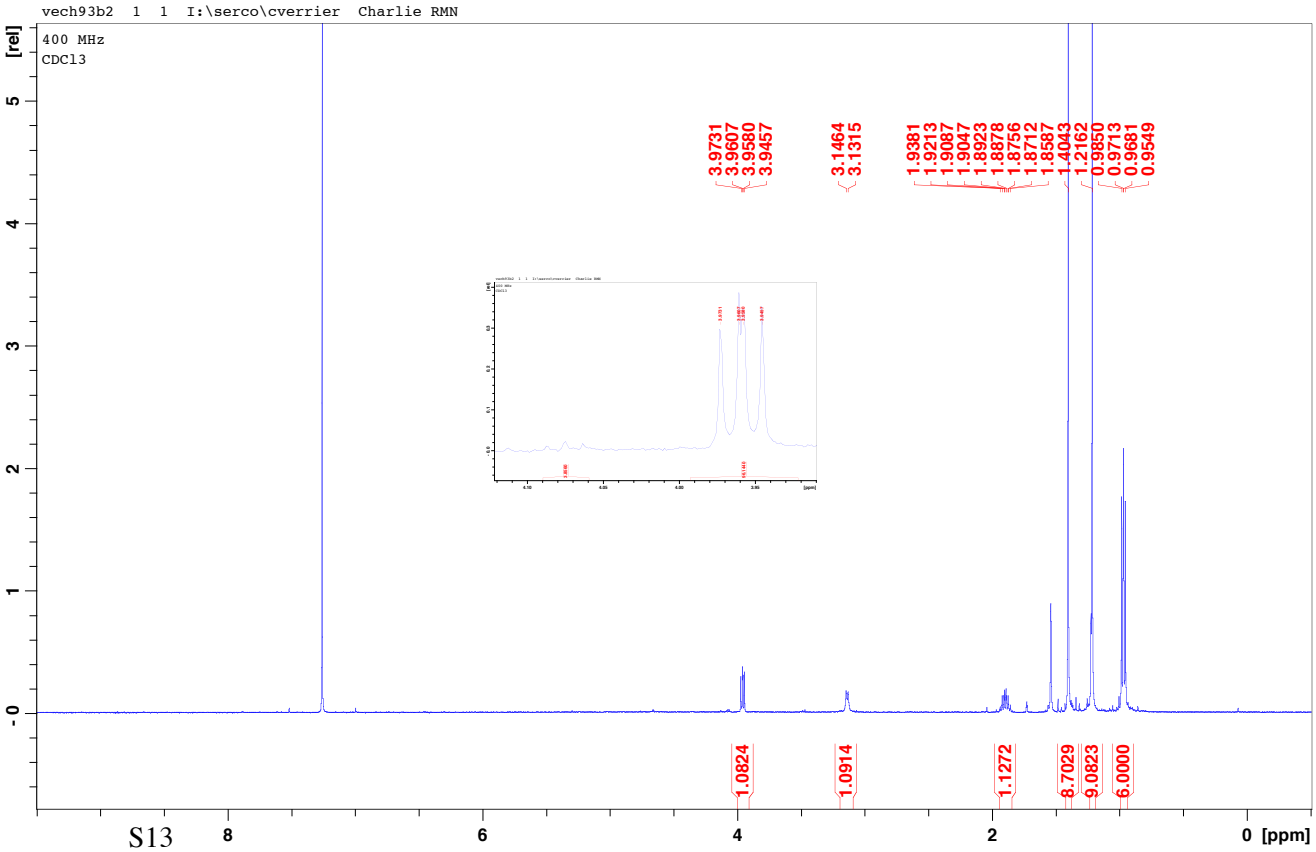

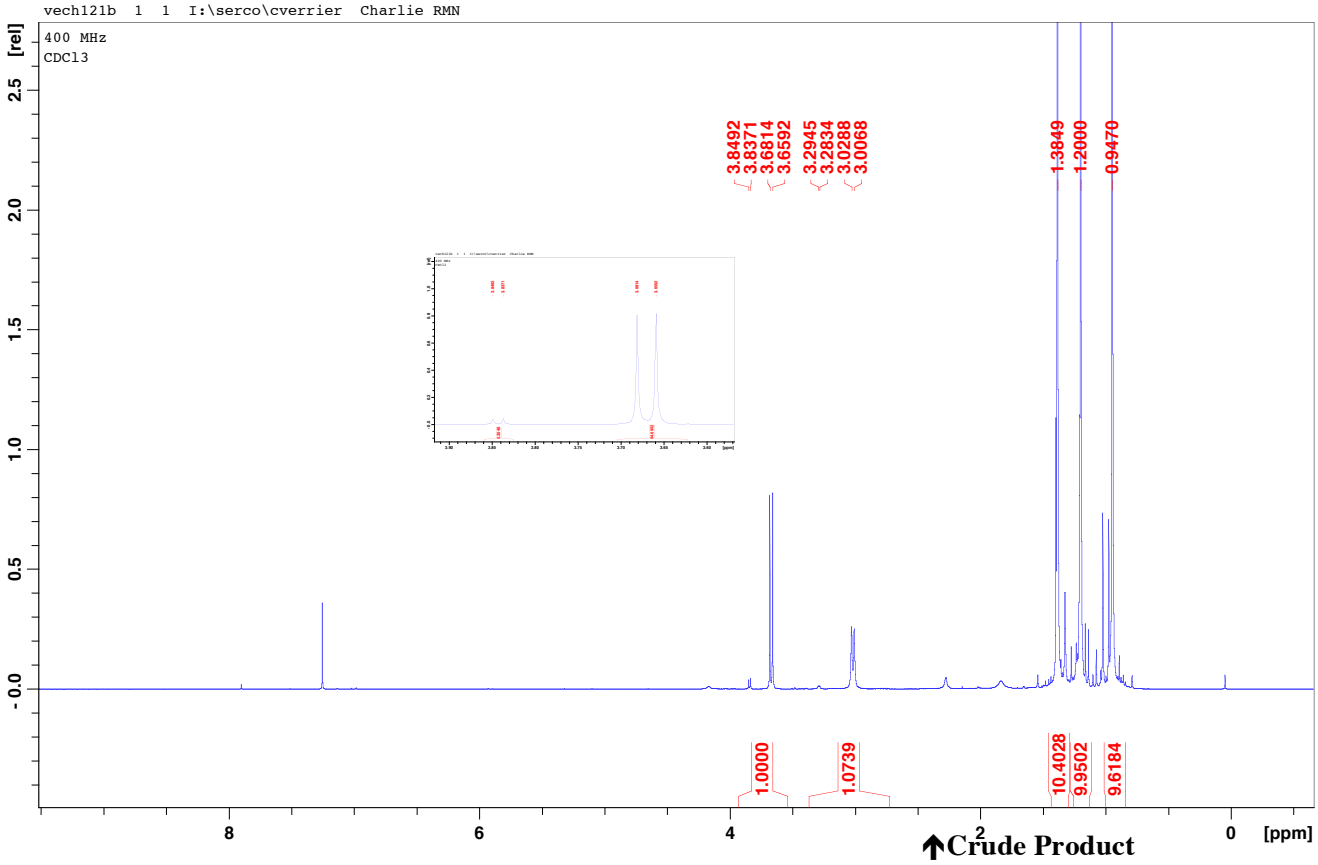

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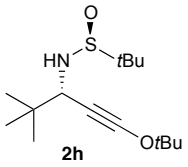

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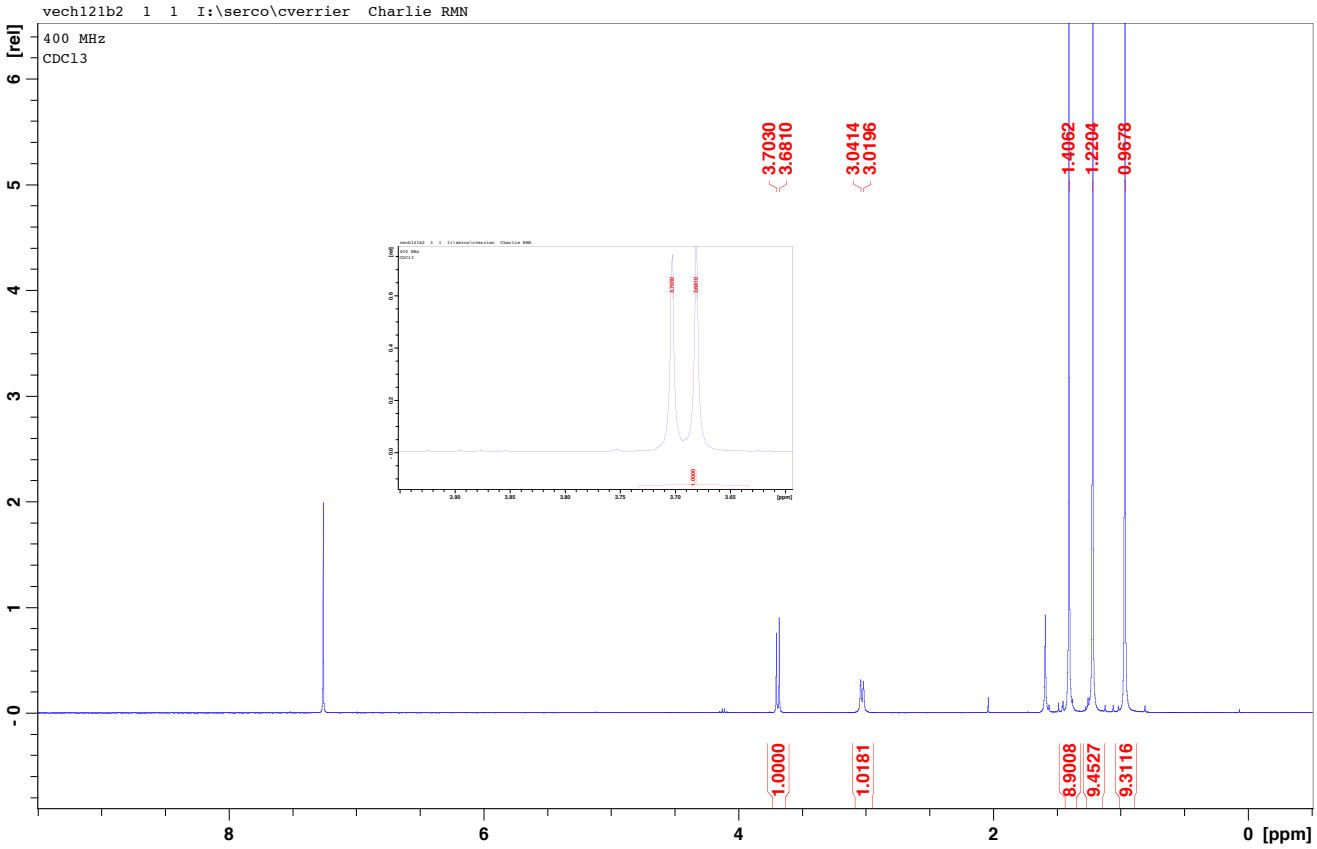

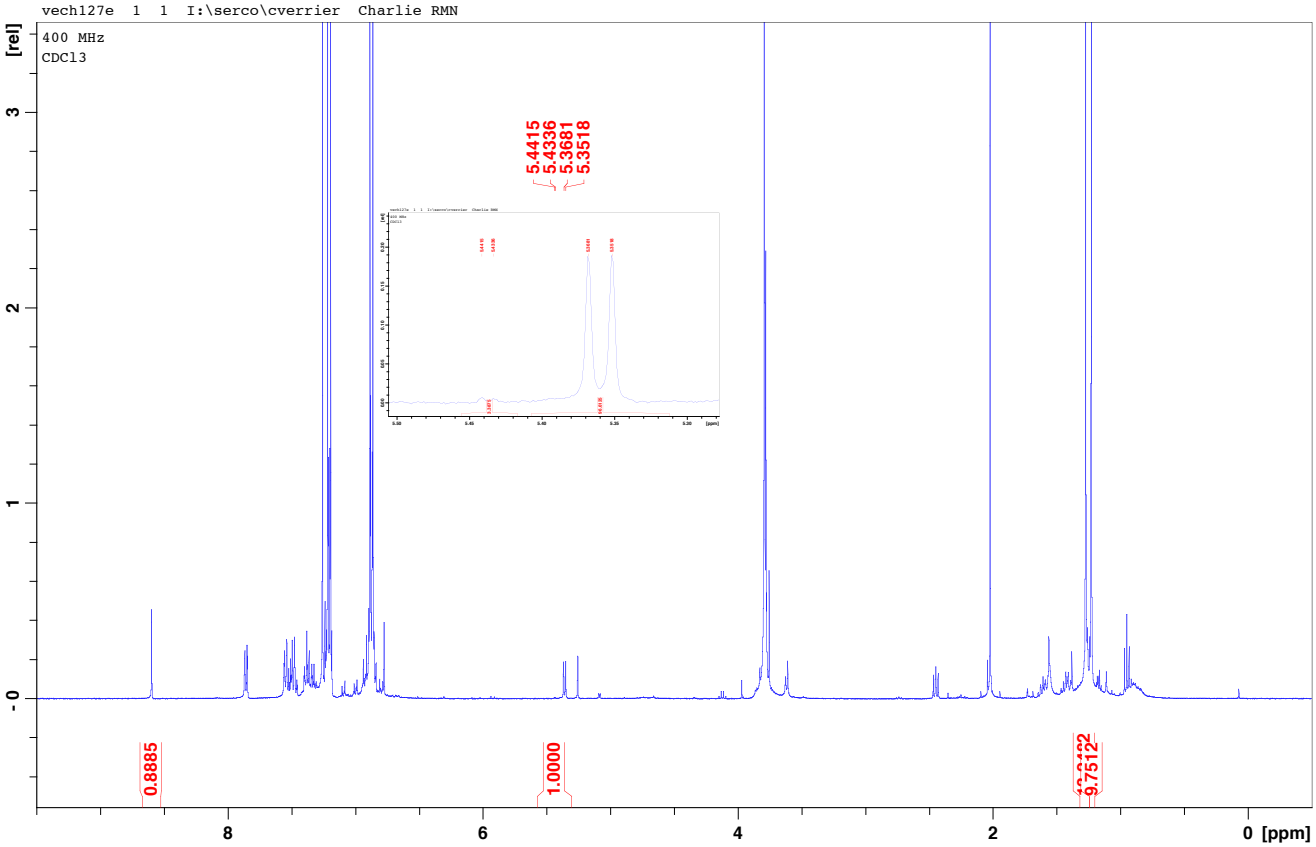

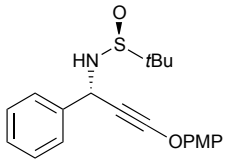

Crude Reaction