Electronic Supplementary Information

Transition-Metal-Free Base Catalyzed Intramolecular Cyclization of 2-Ynylphenols for Efficient and Facile Synthesis of 2-Substituted Benzo[*b*]furans

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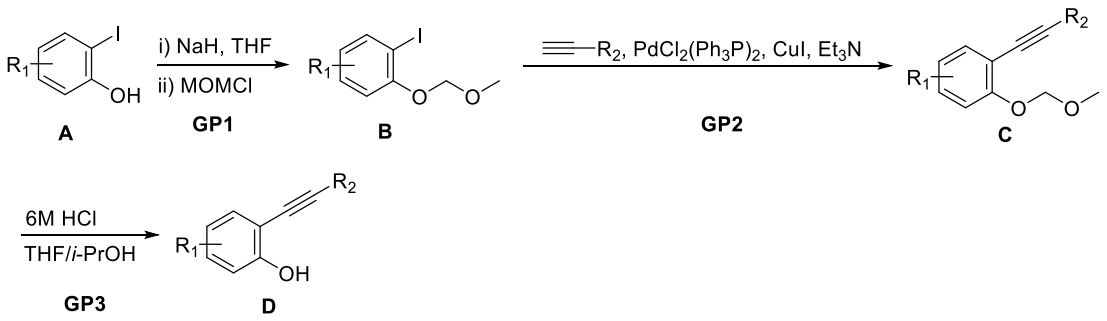
I. Materials and Methods

All reagents and solvents were commercially available (Aldrich, Aladdin, Alfa Aesar and Fluorochem) and were used without further purification. Flash column chromatography was performed over silica gel 200-300 mesh. Melting points were measured with a Fisher Johns apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Bruker spectrometers at 300 MHz and are reported relative to residual solvent signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift at 75 MHz and reported in terms of chemical shift (δ ppm). Data for ^{19}F NMR are reported in terms of chemical shift at 282 MHz and reported in terms of chemical shift (δ ppm). High-resolution mass spectra were obtained on Agilent 6520 Accurate-Mass Q-TOF LC/MS mass spectrometer with ESI source and APCI source and Thermo Scientific Q Exactive GC Orbitrap GC-MS/MS System with EI source.

II. Experimental Procedures

A. Preparation of 2-ynylphenol substrates

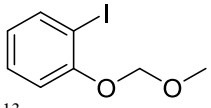
Most of the 2-ynylphenol derivatives were prepared according to **Scheme 1** using a modified variant of the method reported by Yoneda, Sun and Kondoh.[1-3]



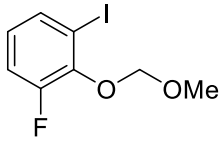
Scheme 1

General procedure for MOMCl protection (GP1). 2-Iodophenol (1 eq.) was added portionwise to a suspension of NaH (1.5 eq.) in THF (0.1 M) at 0 °C. After stirred for 5 mins, chloromethyl methyl ether (2 eq.) was added. The reaction mixture was then allowed to warm to room temperature and stirred until the phenol was consumed. The reaction was quenched with water at 0 °C, and the product was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography to obtain intermediate **B**.

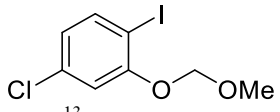
The following compounds were synthesized according to the above procedure:



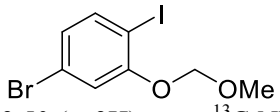
2-(Methoxymethoxy)iodobenzene (1a-1). Colorless oil (9.06 g, 86%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 7.8 Hz, 1H), 7.39-7.20 (m, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.76 (t, *J* = 7.6 Hz, 1H) , 5.25 (s, 2H), 3.52 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.0, 139.5, 129.5, 123.7, 114.9, 94.9, 87.2, 56.5 ppm; ESI-HRMS calcd for $C_8H_9INaO_2$ $[M+Na]^+$: 286.9539, found 286.9537 $[M+Na]^+$.



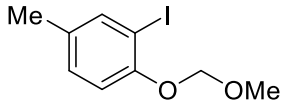
1-fluoro-3-iodo-2-(methoxymethoxy)benzene (1p-1). Colorless oil (395.9 mg, 84%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 8.0 Hz, 1H), 7.13-7.03 (m, 1H), 6.85-6.75 (m, 1H), 5.20 (s, 2H), 3.65 (s, 3H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ = -125.4 ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.8 (d, *J* = 251.0 Hz), 144.6 (d, *J* = 12.6 Hz), 134.6 (d, *J* = 3.5 Hz), 125.9 (d, *J* = 7.8 Hz), 117.2 (d, *J* = 20.3 Hz), 99.0, 92.4, 58.1 ppm. The spectroscopic data was in agreement with the literature values.[4]



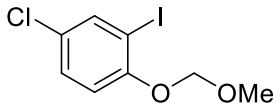
4-chloro-1-iodo-2-(methoxymethoxy)benzene (1q-1). Colorless oil (382.7 mg, 82%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 8.4 Hz, 1H), 7.08 (s, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 5.23 (s, 2H), 3.51 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.7, 139.8, 135.1, 123.8, 115.5, 95.1, 84.4, 56.5 ppm. The spectroscopic data was in agreement with the literature values.[5]



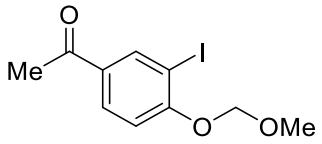
4-bromo-1-iodo-2-(methoxymethoxy)benzene (1r-1). Colorless oil (434.5 mg, 95%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.3 Hz, 1H), 7.21 (d, *J* = 2.1 Hz, 1H), 6.90 (dd, *J* = 8.3, 2.1 Hz, 1H), 5.22 (s, 2H), 3.50 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.8, 140.2, 126.7, 122.8, 118.3, 95.1, 85.3, 56.6 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_8H_8BrIO_2$: 341.8752, found 341.8745 $[M]^+$.



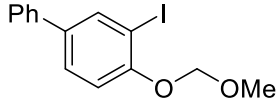
2-iodo-1-(methoxymethoxy)-4-methylbenzene (1s-1). Colorless oil (452.0 mg, 95%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60 (s, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 5.19 (s, 2H), 3.51 (s, 3H), 2.25 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.0, 139.7, 133.4, 130.0, 115.0, 95.2, 87.2, 56.3, 20.0 ppm.



4-chloro-2-iodo-1-(methoxymethoxy)benzene (1t-1). Colorless oil (685.6 mg, 73%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (s, 1H), 7.25 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 1H), 5.21 (s, 2H), 3.50 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.0, 138.6, 129.3, 127.6, 115.4, 95.2, 87.3, 56.4 ppm.



1-(3-iodo-4-(methoxymethoxy)phenyl)ethan-1-one (1u-1). White solid (395.4 mg, 85%); mp 35-36 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.39 (t, *J* = 1.8 Hz, 1H), 7.90 (dt, *J* = 8.8, 1.9 Hz, 1H), 7.09 (dd, *J* = 8.7, 1.4 Hz, 1H), 5.31 (s, 2H), 3.51 (s, 3H), 2.55 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.6, 159.6, 140.1, 132.6, 130.3, 113.5, 94.7, 86.8, 56.7, 26.4 ppm; ESI-HRMS calcd for $C_{10}H_{12}IO_3$ $[M+H]^+$: 306.9826, found 306.9820 $[M+H]^+$.

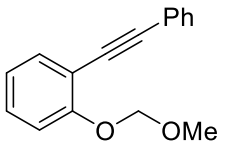


3-iodo-4-(methoxymethoxy)-1,1'-biphenyl (1v-1). Colorless oil (457.2 mg, 99%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98-7.87 (m, 1H), 7.45-7.38 (m, 3H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 5.17 (s, 2H), 3.44 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.5, 139.3, 138.0, 137.0, 128.8, 128.2, 127.3, 126.8, 115.0, 95.1, 87.7, 56.5 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{14}H_{13}IO_2$: 339.9960, found 339.9947 $[M]^+$.

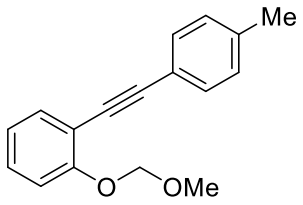
General procedure for Sonagashira Reaction (GP2). $PdCl_2(PPh_3)_2$ (2 mol%) and CuI (2 mol%)

were added to a solution of alkyne (1.1 eq.) and aryl iodide (1.0 eq.) in triethylamine (0.1 M). The resulting mixture was stirred at room temperature until the reaction was completed. On completion, ethyl acetate was added to the mixture, and the mixture was filtrated through a pad of Celite. After concentrating and purifying by flash column chromatography, intermediate **C** was obtained.

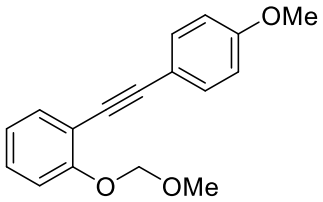
The following compounds were synthesized according to the above procedure:



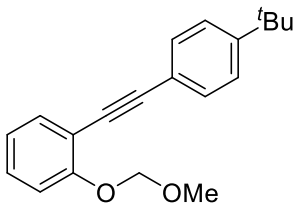
1-(methoxymethoxy)-2-(phenylethynyl)benzene (1a-2). Colorless oil (3.19 g, 88%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61-7.47 (m, 3H), 7.39-7.22 (m, 4H), 7.13 (d, *J* = 8.3 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 5.28 (s, 2H), 3.54 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.8, 133.5, 131.6, 129.7, 128.3, 128.2, 123.6, 122.0, 115.6, 114.1, 95.2, 93.3, 85.8, 56.3 ppm; ESI-HRMS calcd for $C_{16}H_{15}O_2$ $[M+H]^+$: 239.1067, found 239.1082 $[M+H]^+$.



1-(methoxymethoxy)-2-(p-tolylethynyl)benzene (1b-1). Yellow-green oil (384.9 mg, 81%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (dd, *J* = 16.1, 7.6 Hz, 3H), 7.37-7.24 (m, 1H), 7.18 (t, *J* = 7.1 Hz, 3H), 7.04 (t, *J* = 7.5 Hz, 1H), 5.33 (s, 2H), 3.59 (s, 3H), 2.40 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.7, 138.3, 133.4, 131.5, 129.4, 129.0, 122.0, 120.5, 115.6, 114.3, 95.3, 93.5, 85.0, 56.3, 21.5 ppm. The spectroscopic data was in agreement with the literature values.[6]

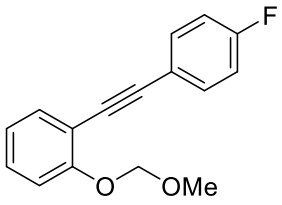


1-(methoxymethoxy)-2-((4-methoxyphenyl)ethynyl)benzene (1c-1). Colorless oil (466.2 mg, 92%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 8.1 Hz, 3H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 2H), 5.28 (s, 2H), 3.80 (s, 3H), 3.54 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.6, 157.6, 133.4, 133.1, 129.4, 122.0, 115.7, 115.5, 114.4, 114.0, 95.2, 93.4, 84.4, 56.3, 55.3 ppm. The spectroscopic data was in agreement with the literature values.[7]

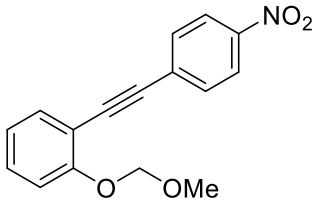


1-((4-(*tert*-butyl)phenyl)ethynyl)-2-(methoxymethoxy)benzene (1d-1). Light yellow solid (544.4 mg, 98%); mp 50-52 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49 (dd, *J* = 7.6, 4.1 Hz, 3H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.31-7.23 (m, 1H), 7.13 (d, *J* = 8.3 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 5.28 (s, 2H), 3.55 (s, 3H), 1.32 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.7, 151.4, 133.5, 131.3, 129.4, 125.3, 122.0, 120.6, 115.7, 114.4, 95.3, 93.5,

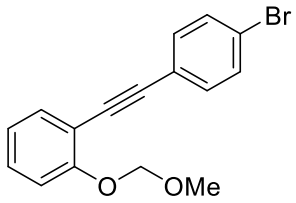
85.1, 56.3, 34.8, 31.2 ppm; ESI-HRMS calcd for $C_{20}H_{23}O_2$ $[M+H]^+$: 295.1693, found 295.1684 $[M+H]^+$.



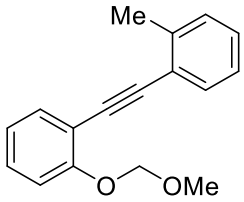
1-((4-fluorophenyl)ethynyl)-2-(methoxymethoxy)benzene (1e-1). Yellow oil (955.1 mg, 98%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61-7.42 (m, 3H), 7.34-7.26 (m, 1H), 7.14 (d, *J* = 8.3 Hz, 1H), 7.02 (dt, *J* = 10.8, 8.1 Hz, 3H), 5.29 (s, 2H), 3.55 (s, 3H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ = -110.9 ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.5 (d, *J* = 249.5 Hz), 157.8, 133.5, 133.4 (d, *J* = 2.9 Hz), 129.7, 122.0, 119.7 (d, *J* = 3.7 Hz), 115.7, 115.5 (d, *J* = 4.1 Hz), 113.8, 95.2, 92.2, 85.4, 56.3 ppm.



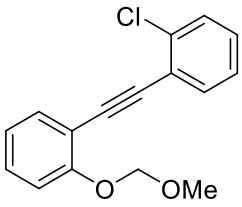
1-(methoxymethoxy)-2-((4-nitrophenyl)ethynyl)benzene (1f-1). Yellow solid (308.1 mg, 57%); mp 68-70 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 5.30 (s, 2H), 3.55 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.1, 146.9, 133.7, 132.2, 130.8, 130.6, 123.6, 121.9, 115.2, 112.7, 95.1, 91.4 (d, *J* = 3.3 Hz), 56.3 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{16}H_{13}NO_4$: 283.0845, found 283.0839 $[M]^+$.



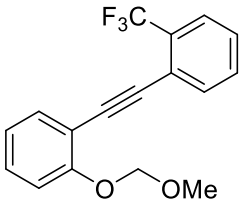
1-((4-bromophenyl)ethynyl)-2-(methoxymethoxy)benzene (1g-1). Colorlees oil (510.0 mg, 85%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52-7.43 (m, 3H), 7.42-7.36 (m, 2H), 7.33-7.23 (m, 1H), 7.13 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.99 (td, *J* = 7.5, 1.2 Hz, 1H), 5.27 (s, 2H), 3.53 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.8, 133.5, 133.1, 131.6, 130.0, 122.6, 122.4, 122.0, 115.4, 113.6, 95.1, 92.2, 87.0, 56.3 ppm.



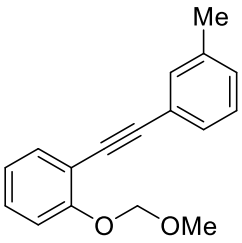
1-(methoxymethoxy)-2-(*o*-tolylethynyl)benzene (1h-1). Yellow-green oil (481.4 mg, 99%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 7.5 Hz, 2H), 7.34-7.08 (m, 5H), 7.00 (t, *J* = 7.4 Hz, 1H), 5.29 (s, 2H), 3.53 (s, 3H), 2.54 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.6, 140.2, 133.2, 131.7, 129.5, 129.4, 128.2, 125.5, 123.4, 121.9, 115.2, 114.3, 95.0, 92.4, 89.7, 56.2, 20.7 ppm.



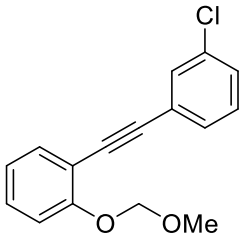
1-chloro-2-((2-(methoxymethoxy)phenyl)ethynyl)benzene (1i-1). Light yellow oil (1.02 g, 99%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63-7.50 (m, 2H), 7.47-7.38 (m, 1H), 7.37-7.18 (m, 3H), 7.14 (d, *J* = 8.3 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 5.30 (s, 2H), 3.55 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.9, 135.8, 133.6, 133.2, 130.0, 129.3, 129.1, 126.4, 123.6, 122.0, 115.5, 113.7, 95.1, 91.0, 90.1, 56.3 ppm; EI-HRMS: m/z [M]$^{+}$ calcd for $C_{14}H_9NO_3$: 272.0604, found 272.0606 [M]$^{+}$.



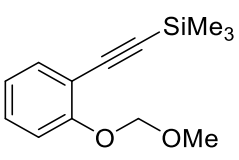
1-(methoxymethoxy)-2-((2-(trifluoromethyl)phenyl)ethynyl)benzene (1j-1). Colorless oil (499.4 mg, 86%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 7.7 Hz, 2H), 7.48-7.37 (m, 2H), 7.26 (dt, *J* = 24.6, 7.6 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 5.20 (s, 2H), 3.45 (s, 3H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ = -61.1 ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.9, 133.8, 133.6, 131.4, 131.3 (q, *J* = 60 Hz), 130.3, 129.1, 127.9, 126.0 (q, *J* = 10.1 Hz), 125.5, 121.9, 115.1, 113.3, 94.8, 91.5, 89.3, 56.2 ppm.; APCI-HRMS calcd for $C_{17}H_{14}F_3O_2$ [M+H]$^{+}$: 307.0940, found 307.0951 [M+H]$^{+}$.



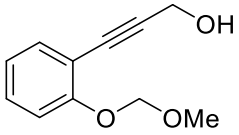
1-(methoxymethoxy)-2-(*m*-tolylethynyl)benzene (1k-1). Light yellow oil (421.7 mg, 88%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.32-7.19 (m, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 5.29 (s, 2H), 3.55 (s, 3H), 2.35 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.7, 137.9, 133.5, 132.1, 129.5, 129.0, 128.7, 128.2, 123.4, 122.0, 115.6, 114.2, 95.2, 93.5, 85.4, 56.3, 21.2 ppm.



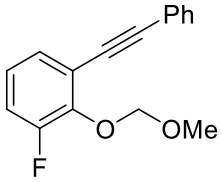
1-((3-chlorophenyl)ethynyl)-2-(methoxymethoxy)benzene (1l-1). Yellow oil (430.8mg, 83%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (s, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.45-7.38 (m, 1H), 7.36-7.20 (m, 3H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 5.29 (s, 2H), 3.55 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.9, 134.1, 133.5, 131.4, 130.0, 129.7, 129.5, 128.3, 125.4, 121.9, 115.4, 113.5, 95.1, 91.8, 87.0, 56.3 ppm.



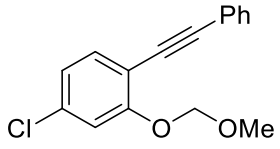
((2-(methoxymethoxy)phenyl)ethynyl)trimethylsilane (1m-1). Yellow oil (1.37 g, 77%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 5.24 (s, 2H), 3.54 (s, 3H), 0.26 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ =158.2, 134.0, 129.8, 121.9, 115.8, 114.1, 101.3, 98.4, 95.3, 56.2, 0.0 ppm.



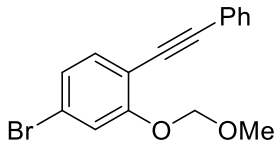
3-(2-(methoxymethoxy)phenyl)prop-2-yn-1-ol (1o-1). Brown oil (693.8 mg, 95%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.9 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 5.26 (s, 2H), 4.55 (s, 2H), 3.52 (s, 3H), 2.72 (br, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.8, 133.6, 129.8, 121.9, 115.2, 113.1, 95.0, 91.5, 81.7, 56.2, 51.6 ppm. The spectroscopic data was in agreement with the literature values.[8]



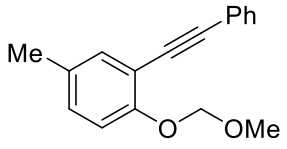
1-fluoro-2-(methoxymethoxy)-3-(phenylethynyl)benzene (1p-2). Yellow oil (344.6 mg, 96%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56-7.49 (m, 2H), 7.39-7.32 (m, 3H), 7.32-7.27 (m, 1H), 7.13-6.98 (m, 2H), 5.31 (s, 2H), 3.66 (s, 3H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ = -129.6 ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.8 (d, *J* = 246.9 Hz), 145.3 (d, *J* = 12.3 Hz), 131.6, 128.8 (d, *J* = 3.3 Hz), 128.7, 128.5, 124.3 (d, *J* = 8.4 Hz), 122.9, 119.6 (d, *J* = 3.3 Hz), 117.1 (d, *J* = 19.7 Hz), 98.9 (d, *J* = 5.1 Hz), 94.3, 84.8 (d, *J* = 4.7 Hz), 57.5 (d, *J* = 2.1 Hz) ppm; EI-HRMS: m/z calcd for $C_{16}H_{13}FO_2$ $[M]^+$: 256.0900, found 256.0899 $[M]^+$.



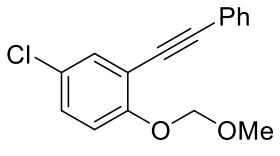
4-chloro-2-(methoxymethoxy)-1-(phenylethynyl)benzene (1q-2). Yellow solid (276.8 mg, 91%); mp 84-85 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50-7.40 (m, 2H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.29-7.19 (m, 3H), 7.08 (s, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 5.17 (s, 2H), 3.45 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.2, 135.0, 134.0, 131.6, 128.4 (d, *J* = 2.2 Hz), 123.3, 122.2, 115.9, 112.5, 95.2, 94.1, 84.8, 56.5 ppm; EI-HRMS: m/z calcd for $C_{16}H_{13}ClO_2$ $[M]^+$: 272.0604, found 272.0600 $[M]^+$.



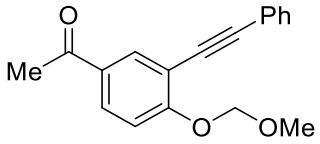
4-bromo-2-(methoxymethoxy)-1-(phenylethynyl)benzene (1r-2). Light yellow solid (345.4 mg, 86%); mp 89-90 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64-7.51 (m, 2H), 7.45-7.32 (m, 5H), 7.17 (dd, *J* = 8.2, 1.9 Hz, 1H), 5.30 (s, 2H), 3.58 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.22, 134.21, 131.62, 128.42, 128.38, 125.15, 123.29, 122.97, 118.81, 113.04, 95.24, 94.32, 84.86, 56.47 ppm; APCI-HRMS calcd for $C_{16}H_{14}BrO_2$ $[M+H]^+$: 317.0172, found 317.0182 $[M+H]^+$.



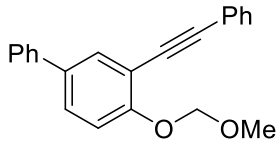
1-(methoxymethoxy)-4-methyl-2-(phenylethynyl)benzene (1s-2). Light yellow oil (322.1 mg, 85%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59-7.49 (m, 2H), 7.40-7.29 (m, 4H), 7.05 (q, *J* = 8.5 Hz, 2H), 5.25 (s, 2H), 3.54 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.6, 133.8, 131.6, 131.5, 130.4, 128.3, 128.2, 123.6, 115.8, 113.8, 95.4, 93.0, 85.9, 56.3, 20.4 ppm.



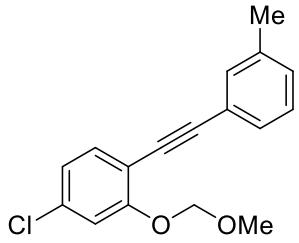
4-chloro-1-(methoxymethoxy)-2-(phenylethynyl)benzene (1t-2). Light yellow oil (392.4 mg, 99%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 4.9 Hz, 2H), 7.39 (s, 1H), 7.33-7.21 (m, 3H), 7.19-7.08 (m, 1H), 6.98 (d, *J* = 8.9 Hz, 1H), 5.16 (s, 2H), 3.44 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.4, 132.9, 131.7, 129.5, 128.6, 128.4, 126.7, 123.1, 116.6, 115.6, 95.3, 94.4, 84.5, 56.4 ppm.



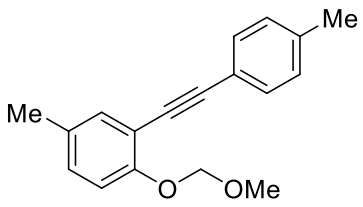
1-(4-(methoxymethoxy)-3-(phenylethynyl)phenyl)ethan-1-one (1u-2). Brown oil (275.0 mg, 97%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.13 (s, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 4.9 Hz, 2H), 7.43-7.31 (m, 3H), 7.19 (d, *J* = 8.8 Hz, 1H), 5.34 (s, 2H), 3.54 (s, 3H), 2.58 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.3, 161.2, 134.2, 131.7, 131.0, 130.1, 128.5, 128.4, 123.1, 114.2, 113.8, 94.7, 94.0, 84.7, 56.5, 26.4 ppm; ESI-HRMS calcd for $C_{18}H_{17}O_3$ $[M+H]^+$: 281.1172, found 281.1167 $[M+H]^+$.



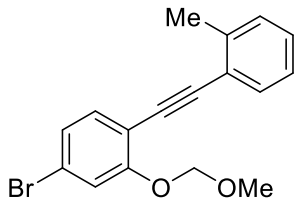
4-(methoxymethoxy)-3-(phenylethynyl)-1,1'-biphenyl (1v-2). White solid (331.3 mg, 88%); mp 94-96 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (s, 1H), 7.49 (d, *J* = 6.9 Hz, 4H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.30-7.20 (m, 4H), 7.17-7.09 (m, 1H), 5.24 (s, 2H), 3.49 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.1, 140.0, 135.1, 132.1, 131.7, 128.8, 128.4, 128.3, 127.2, 126.8, 123.5, 115.7, 114.3, 95.2, 93.4, 85.7, 56.4 ppm; ESI-HRMS calcd for $C_{22}H_{19}O_2$ $[M+H]^+$: 315.1380, found 315.1389 $[M+H]^+$.



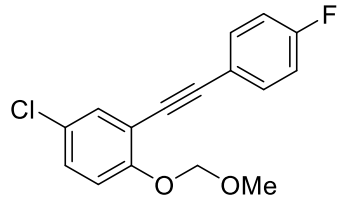
4-chloro-2-(methoxymethoxy)-1-(*m*-tolylethynyl)benzene (1w-1). Yellow-green oil (384.7 mg, 99%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37-7.21 (m, 3H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.11-7.02 (m, 2H), 6.89 (d, *J* = 8.3 Hz, 1H), 5.18 (s, 2H), 3.45 (s, 3H), 2.26 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 158.2, 138.0, 134.9, 134.0, 132.2, 129.3, 128.7, 128.3, 123.1, 122.2, 116.0, 112.6, 95.2, 94.3, 84.4, 56.4, 21.3 ppm; APCI-HRMS calcd for $C_{17}H_{16}ClO_2$ $[M+H]^+$: 287.0833, found 287.0843 $[M+H]^+$.



1-(methoxymethoxy)-4-methyl-2-(*p*-tolylethynyl)benzene (1x-1). Yellow oil (156.2 mg, 56%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 7.7 Hz, 2H), 7.31 (s, 1H), 7.14 (d, *J* = 7.7 Hz, 2H), 7.03 (q, *J* = 8.5 Hz, 2H), 5.24 (s, 2H), 3.54 (s, 3H), 2.35 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 155.5, 138.3, 133.8, 131.5, 131.5, 130.2, 129.1, 120.5, 115.8, 114.0, 95.5, 93.2, 85.3, 56.3, 21.6, 20.5 ppm.



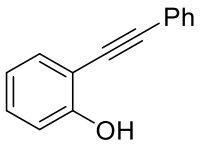
4-bromo-2-(methoxymethoxy)-1-(*o*-tolylethynyl)benzene (1y-1). White solid (159.6 mg, 70%); mp 73-75 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 7.3 Hz, 1H), 7.46-7.34 (m, 2H), 7.34-7.25 (m, 2H), 7.25-7.15 (m, 2H), 5.30 (s, 2H), 3.57 (s, 3H), 2.57 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.1, 140.3, 133.9, 131.7, 129.5, 128.5, 125.6, 125.1, 123.1, 122.8, 118.5, 113.2, 95.0, 93.5, 88.8, 56.4, 20.7 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{17}H_{15}BrO_2$: 330.0255, found 330.0251 $[M]^+$.



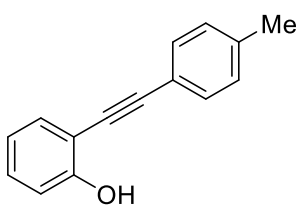
4-chloro-2-((4-fluorophenyl)ethynyl)-1-(methoxymethoxy)-benzene (1z-1). Yellow oil (305.9 mg, 98%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48-7.40 (m, 2H), 7.37 (s, 1H), 7.19-7.11 (m, 1H), 7.03-6.90 (m, 3H), 5.17 (s, 2H), 3.45 (s, 3H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ = -110.4 ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.7 (d, *J* = 249.9 Hz), 156.4, 133.6 (d, *J* = 8.4 Hz), 132.8, 129.6, 126.7, 119.2 (d, *J* = 3.5 Hz), 116.5, 115.7 (d, *J* = 22.1 Hz), 115.3, 95.3, 93.3, 84.1, 56.4 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{16}H_{12}ClFO_2$: 290.0510, found 290.0508 $[M]^+$.

General procedure for MOM deprotection (GP3). HCl (6 M) was added to a solution of the MOM protected phenol in THF/*i*-PrOH (1:1) and the mixture was stirred at room temperature until the deprotection was completed. Then the mixture was diluted with water and *tert*-butyl methyl ether and extracted with *tert*-butyl methyl ether. The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography to obtain 2-ynylphenol.

The following compounds were synthesized according to the above procedure:

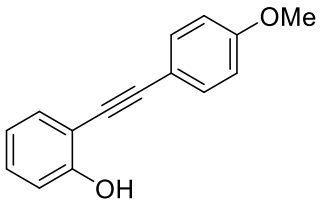


2-(phenylethynyl)phenol (1a). Brown solid (2.46 g, 95%); mp 58-60 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 7.8 Hz, 2H), 7.54 (dd, *J* = 15.0, 7.7 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.37-7.16 (m, 3H), 7.00 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.5, 131.7, 131.7, 130.6, 128.9, 128.6, 122.4, 120.5, 114.8, 109.6, 96.4, 83.1 ppm. ESI-HRMS calcd for $C_{14}H_{11}O$ $[M+H]^+$: 195.0804, found 195.0833 $[M+H]^+$.

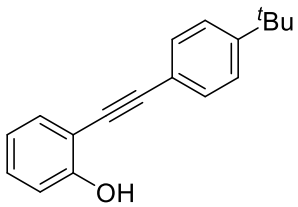


2-(*p*-tolylethynyl)phenol (1b). White solid (328.0 mg, 75%); mp 70-72 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34 (t, *J* = 7.2 Hz, 3H), 7.22-7.13 (m, 1H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.82 (t, *J* = 7.5 Hz, 1H), 5.79 (s, 1H), 2.30 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.5, 139.1, 131.6, 131.5, 130.3, 129.3, 120.4, 119.3,

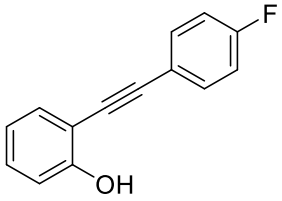
114.7, 109.8, 96.6, 82.4, 21.5 ppm. The spectroscopic data was in agreement with the literature values.[9]



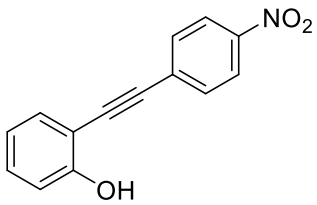
2-((4-methoxyphenyl)ethynyl)phenol (1c). White solid (307.7 mg, 90%); mp 48-50 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.3 Hz, 2H), 7.52 (dd, *J* = 14.7, 7.5 Hz, 2H), 7.22 (p, *J* = 7.2 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.87 (s, 1H), 3.84 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.1, 156.4, 133.1, 131.6, 130.2, 120.4, 114.7, 114.5, 114.2, 110.0, 96.4, 81.7, 55.3 ppm. The spectroscopic data was in agreement with the literature values.[7]



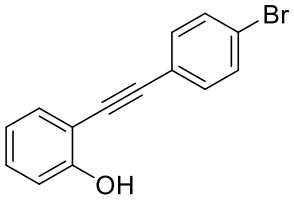
2-((4-(*tert*-butyl)phenyl)ethynyl)phenol (1d). Yellow solid (279.3 mg, 96%); mp 35-36 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.1 Hz, 2H), 7.37-7.28 (m, 3H), 7.24-7.14 (m, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.83 (t, *J* = 7.5 Hz, 1H), 5.79 (s, 1H), 1.26 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.2, 154.9, 151.8, 129.4, 127.8, 125.7, 124.8, 124.0, 122.9, 120.8, 111.1, 100.7, 34.8, 31.3 ppm. ESI-HRMS calcd for $C_{18}H_{19}O$ $[M+H]^+$: 251.1430, found 251.1423 $[M+H]^+$.



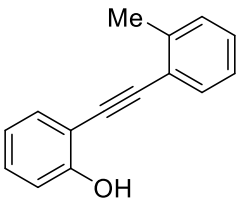
2-((4-fluorophenyl)ethynyl)phenol (1e). White solid (521.6 mg, 98%); mp 103-105 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54-7.45 (m, 2H), 7.39 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.29-7.21 (m, 1H), 7.09-6.99 (m, 2H), 6.99-6.94 (m, 1H), 6.89 (td, *J* = 7.6, 1.1 Hz, 1H), 5.78 (s, 1H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ = -109.8 ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.9 (d, *J* = 250.6 Hz), 156.6, 133.6 (d, *J* = 8.6 Hz), 131.7, 130.5, 120.5, 118.6 (d, *J* = 3.9 Hz), 115.8 (d, *J* = 22.2 Hz), 114.9, 109.5, 95.2, 82.9 ppm. The spectroscopic data was in agreement with the literature values.[10]



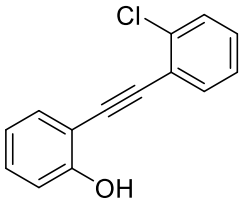
2-((4-nitrophenyl)ethynyl)phenol (1f). Yellow solid (182.9 mg, 81%); mp 159-161 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.25 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.05-6.89 (m, 2H), 5.73 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.8, 147.2, 132.3, 132.2, 131.6, 129.4, 123.8, 120.8, 115.2, 108.6, 94.2, 88.6 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{14}H_9NO_3$: 239.0582, found 239.0576 $[M]^+$.



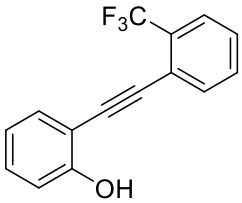
2-((4-bromophenyl)ethynyl)phenol (1g). White solid (298.4 mg, 80%); mp 129-130 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.4 Hz, 2H), 7.39 (t, *J* = 6.7 Hz, 3H), 7.32-7.22 (m, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 5.75 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.5, 133.0, 131.8, 131.8, 130.8, 123.2, 121.4, 120.6, 114.9, 109.3, 95.2, 84.3 ppm. The spectroscopic data was in agreement with the literature values.[11]



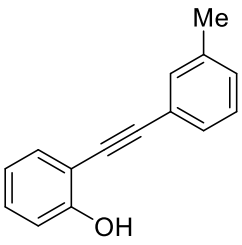
2-(*o*-tolylethynyl)phenol (1h). Yellow oil (481.4 mg, 99%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 (dd, *J* = 23.9, 7.6 Hz, 2H), 7.31-7.25 (m, 3H), 7.24-7.16 (m, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 5.85 (s, 1H), 2.52 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.4, 140.0, 132.0, 131.6, 130.5, 129.7, 129.0, 125.8, 122.2, 120.5, 114.7, 109.9, 95.4, 86.9, 21.0 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{15}H_{12}O$: 208.0888, found 208.0882 $[M]^+$.



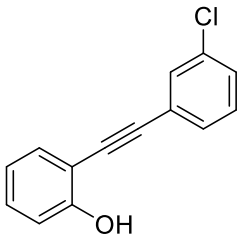
2-((2-chlorophenyl)ethynyl)phenol (1i). Colorless oil (579.0 mg, 92%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61-7.51 (m, 1H), 7.49-7.38 (m, 2H), 7.35-7.19 (m, 3H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.25 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.2, 135.4, 132.7, 131.3, 131.0, 129.7, 129.3, 126.8, 122.5, 120.4, 114.9, 109.2, 93.3, 89.0 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{14}H_9ClO$: 228.0342, found 228.0333 $[M]^+$.



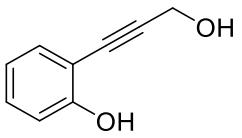
2-((2-(trifluoromethyl)phenyl)ethynyl)phenol (1j). Colorless oil (177.6 mg, 68%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (t, *J* = 6.7 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.48-7.37 (m, 2H), 7.33-7.23 (m, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.91 (td, *J* = 7.5, 0.9 Hz, 1H), 5.93 (s, 1H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ = -62.4 ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.6, 135.0, 133.1, 132.6, 130.0 (q, *J* = 71.6 Hz), 129.7, 127.4 (q, *J* = 11.3 Hz), 127.0, 123.3, 122.18 (d, *J* = 2.25 Hz), 121.8, 116.5, 110.4, 93.6, 90.5 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{15}H_9F_3O$: 262.0605, found 262.0601 $[M]^+$.



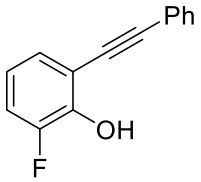
2-(*m*-tolylethynyl)phenol (1k). Colorless oil (249.6 mg, 82%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 8.9 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.18 (d, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 5.87 (s, 1H), 2.36 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.5, 138.2, 132.2, 131.6, 130.4, 129.7, 128.7, 128.4, 122.2, 120.4, 114.7, 109.7, 96.6, 82.7, 21.2 ppm. The spectroscopic data was in agreement with the literature values.[2]



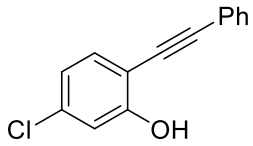
2-((3-chlorophenyl)ethynyl)phenol (1l). White solid (199.8 mg, 74%); mp 81-83 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (s, 1H), 7.42 (d, *J* = 7.7 Hz, 2H), 7.38-7.24 (m, 3H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 5.78 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.6, 134.4, 131.8, 131.4, 130.8, 129.7, 129.7, 129.0, 124.1, 120.5, 114.9, 109.1, 94.8, 84.3 ppm. The spectroscopic data was in agreement with the literature values.[2]



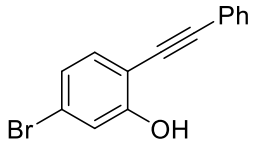
2-(3-hydroxyprop-1-yn-1-yl)phenol (1o). White solid (402.9 mg, 83%); mp 77-79 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36-7.16 (m, 2H), 7.03-6.91 (m, 1H), 6.91-6.79 (m, 1H), 6.35 (s, 1H), 4.55 (s, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.0, 132.0, 130.6, 120.3, 115.1, 108.9, 93.8, 84.3, 51.6 ppm. The spectroscopic data was in agreement with the literature values.[12]



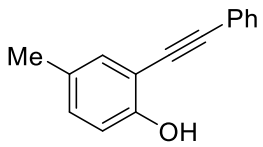
2-fluoro-6-(phenylethynyl)phenol (1p). White solid (164.4 mg, 66%); mp 90-92 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60-7.50 (m, 2H), 7.42-7.33 (m, 3H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 9.4 Hz, 1H), 6.83 (q, *J* = 7.8 Hz, 1H), 5.73 (s, 1H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ = -137.2 ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.7 (d, *J* = 242.7 Hz), 144.8 (d, *J* = 13.0 Hz), 131.7, 129.0, 128.5, 127.4 (d, *J* = 3.5 Hz), 122.2, 120.3 (d, *J* = 7.6 Hz), 116.9 (d, *J* = 18.1 Hz), 112.2 (d, *J* = 3.4 Hz), 96.6, 82.4 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{14}H_9FO$: 212.0637, found 212.0631 $[M]^+$.



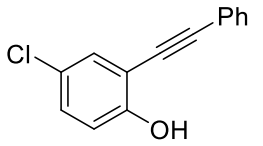
5-chloro-2-(phenylethynyl)phenol (1q). White solid (151.5 mg, 96%); mp 104-106 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60-7.46 (m, 2H), 7.42-7.35 (m, 3H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.01 (d, *J* = 2.0 Hz, 1H), 6.90 (dd, *J* = 8.3, 2.0 Hz, 1H), 5.89 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.1, 135.9, 132.3, 131.6, 129.1, 128.6, 122.1, 121.0, 115.4, 108.4, 97.2, 82.1 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{14}H_9ClO$: 228.0342, found 228.0337 $[M]^+$.



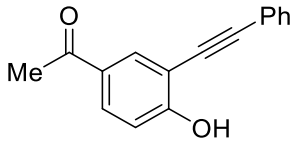
5-bromo-2-(phenylethynyl)phenol (1r). White solid (259.5 mg, 96%); mp 108-110 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57-7.49 (m, 2H), 7.41-7.34 (m, 3H), 7.30-7.24 (m, 1H), 7.17 (d, *J* = 1.9 Hz, 1H), 7.05 (dd, *J* = 8.3, 1.9 Hz, 1H), 5.91 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.0, 132.5, 131.6, 129.1, 128.6, 123.8, 122.1, 118.3, 108.9, 97.4, 82.2 ppm; EI-HRMS: m/z calcd for $C_{14}H_9BrO$ $[M]^+$: 271.9837, found 271.9831 $[M]^+$.



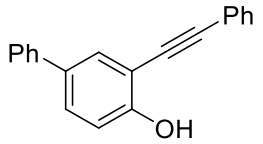
4-methyl-2-(phenylethynyl)phenol (1s). White solid (204.4 mg, 98%); mp 60-62 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58-7.45 (m, 2H), 7.42-7.29 (m, 3H), 7.27-7.18 (m, 1H), 7.05 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 5.64 (s, 1H), 2.26 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.4, 131.8, 131.6, 131.3, 129.7, 128.8, 128.5, 122.5, 114.5, 109.2, 96.1, 83.3, 20.4 ppm. The spectroscopic data was in agreement with the literature values.[13]



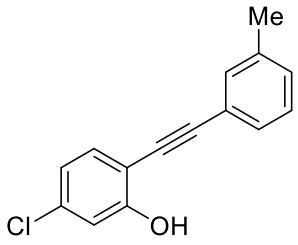
4-chloro-2-(phenylethynyl)phenol (1t). White solid (155.4 mg, 83%); mp 92-93 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58-7.48 (m, 2H), 7.38 (s, 4H), 7.26-7.16 (m, 1H), 6.91 (d, *J* = 8.7 Hz, 1H), 5.81 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.1, 131.7, 131.0, 130.5, 129.2, 128.6, 125.1, 121.9, 116.1, 111.1, 97.3, 81.8 ppm. The spectroscopic data was in agreement with the literature values.[13]



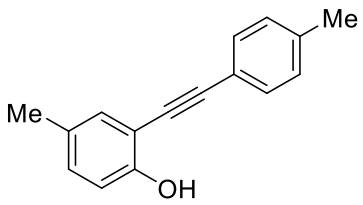
1-(4-hydroxy-3-(phenylethynyl)phenyl)ethan-1-one (1u). White solid (147.1 mg, 70%); mp 135-137 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.08 (s, 1H), 7.91 (d, *J* = 8.6 Hz, 1H), 7.61-7.51 (m, 2H), 7.44-7.35 (m, 3H), 7.04 (d, *J* = 8.7 Hz, 1H), 6.40 (s, 1H), 2.57 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.3, 160.3, 133.0, 131.7, 131.0, 130.2, 129.2, 128.6, 121.9, 115.0, 110.0, 97.1, 82.0, 26.4 ppm; ESI-HRMS calcd for $C_{16}H_{13}O_2$ $[M+H]^+$: 237.0910, found 237.0906 $[M+H]^+$.



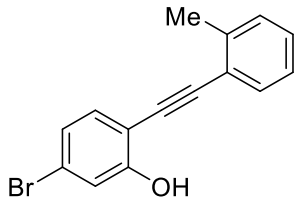
3-(phenylethynyl)-[1,1'-biphenyl]-4-ol (1v). White solid (143.4 mg, 63%); mp 104-105 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 2.3 Hz, 1H), 7.59-7.52 (m, 4H), 7.51-7.45 (m, 1H), 7.45-7.34 (m, 5H), 7.34-7.27 (m, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 5.83 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.0, 140.1, 133.8, 131.7, 130.2, 129.4, 129.0, 128.8, 128.6, 127.0, 126.7, 122.3, 115.2, 110.0, 96.5, 83.0 ppm; APCI-HRMS calcd for $C_{20}H_{15}O$ $[M+H]^+$: 271.1117, found 271.1105 $[M+H]^+$.



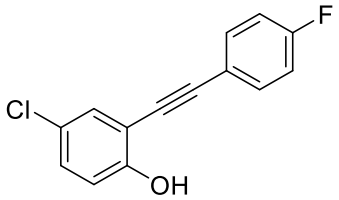
5-chloro-2-(*m*-tolylethynyl)phenol (1w). White solid (239.4 mg, 74%); mp 89-90 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36-7.28 (m, 3H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 6.99 (s, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 5.94 (s, 1H), 2.34 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.0, 138.4, 135.8, 132.3, 132.2, 130.0, 128.7, 128.5, 121.9, 121.0, 115.4, 108.5, 97.5, 81.7, 21.3 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{15}H_{11}ClO$: 242.0498, found 242.0492 $[M]^+$.



4-methyl-2-(*p*-tolylethynyl)phenol (1x). White solid (119.7 mg, 99%); mp 105-106 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.7 Hz, 2H), 7.25-7.12 (m, 3H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 5.68 (s, 1H), 2.37 (s, 3H), 2.27 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.3, 139.0, 131.7, 131.5, 131.1, 129.6, 129.3, 119.4, 114.4, 109.4, 96.3, 82.6, 21.6, 20.4 ppm. The spectroscopic data was in agreement with the literature values.[14]

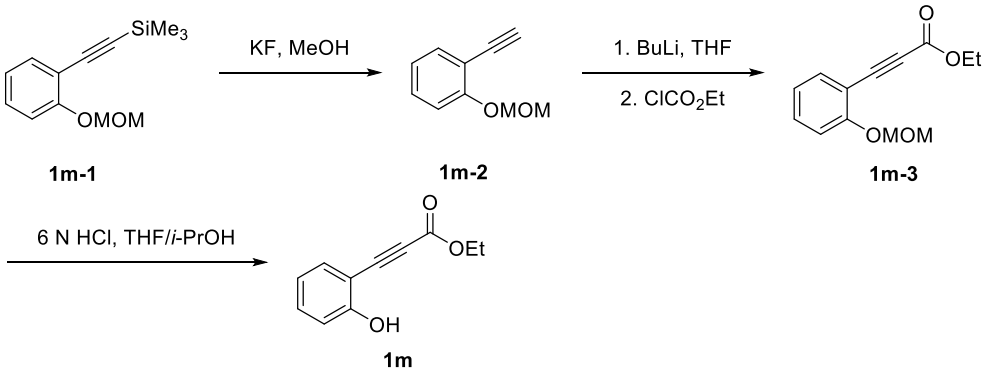


5-bromo-2-(*o*-tolylethynyl)phenol (1y). White solid (110.9 mg, 97%); mp 54-55 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 7.4 Hz, 1H), 7.32-7.23 (m, 3H), 7.23-7.16 (m, 2H), 7.05 (dd, *J* = 8.2, 1.9 Hz, 1H), 5.89 (s, 1H), 2.50 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.9, 140.0, 132.4, 132.0, 129.8, 129.2, 125.9, 123.9, 123.7, 121.9, 118.2, 109.1, 96.4, 86.0, 21.0 ppm; EI-HRMS: m/z calcd for $C_{15}H_{11}BrO$ $[M]^+$: 285.9993, found 285.9989 $[M]^+$.

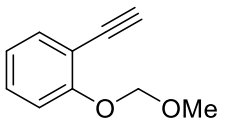


4-chloro-2-((4-fluorophenyl)ethynyl)phenol (1z). White solid (163.9 mg, 54%); mp 111-112 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57-7.46 (m, 2H), 7.38 (s, 1H), 7.29-7.17 (m, 1H), 7.08 (t, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 1H), 5.78 (s, 1H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ = -109.2 ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.0 (d, *J* = 251.0 Hz), 155.1, 133.7 (d, *J* = 8.4 Hz), 131.0, 130.5, 125.1, 118.0 (d, *J* = 3.4 Hz), 116.1, 115.8, 110.9, 96.1, 81.6 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{14}H_8ClFO$: 246.0248, found 246.0242 $[M]^+$.

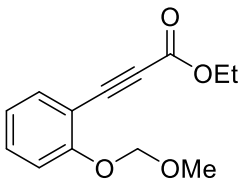
Ethyl 3-(2-hydroxyphenyl)propiolate was prepared according to **Scheme 2** using a modified variant of the method reported by Aldrich.[15]



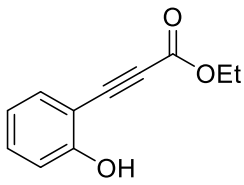
Scheme 2



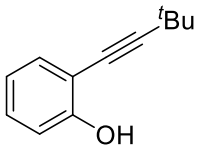
1-ethynyl-2-(methoxymethoxy)benzene (1m-2). To a stirred solution of ((2-(methoxymethoxy)phenyl)ethynyl)trimethylsilane (1.17 g, 4.99 mmol) in methanol (25 mL) was added potassium fluoride (870.1 mg, 14.98 mmol). The reaction mixture was stirred for 3 hours at room temperature. The reaction mixture was diluted by dichloromethane and water. The organic phase was dried (anhydrous Na_2SO_4) and concentrated. Purification by flash chromatography afforded the title compound (767.0 mg, 95%) as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 7.6 Hz, 1H), 7.35-7.25 (m, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 5.28 (s, 2H), 3.53 (s, 3H), 3.29 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.4, 134.2, 130.2, 121.8, 115.0, 112.4, 94.8, 81.1, 80.1, 56.3 ppm. The spectroscopic data was in agreement with the literature values.[15]



Ethyl 3-(2-(methoxymethoxy)phenyl)propiolate (1m-3). To a solution of 2-ethynyl-1-(methoxymethoxy)benzene (162 mg, 1.0 mmol) in THF (3 mL) was added slowly *n*-BuLi (440 mL, 2.5 M solution in hexane, 1.1 mmol) at -35°C. After stirring for 20 minutes, a solution of ethyl chloroformate (114 mg, 1.05 mmol) in THF (1.0 mL) was added dropwise and the reaction mixture was stirred for an additional 30 minutes then allowed to warm to room temperature, and poured into a saturated aqueous NH_4Cl solution (5.0 mL). The aqueous phase was extracted with Et_2O (3×5 mL), the combined organic phases were dried (anhydrous Na_2SO_4) and concentrated. Purification by flash chromatography (10:1 hexanes/EtOAc) afforded the title compound (111.0 mg, 47%) as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 5.27 (s, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.53 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.3, 154.3, 134.8, 132.2, 121.8, 114.9, 110.1, 94.9, 84.4, 83.0, 62.1, 56.4, 14.1 ppm. The spectroscopic data was in agreement with the literature values.[15]



Ethyl 3-(2-hydroxyphenyl)propiolate (1m). This compound was obtained by using the general procedure **GP3**. White solid (76.2 mg, 78%); mp 44-46 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.36 (td, *J* = 8.9, 8.2, 1.6 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.34 (s, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.9, 154.0, 133.5, 133.0, 120.6, 115.8, 106.1, 87.1, 81.7, 62.3, 14.1 ppm. The spectroscopic data was in agreement with the literature values.[16]



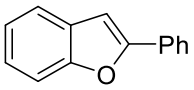
2-(3,3-dimethylbut-1-yn-1-yl)phenol (1n). To a flame dried round-bottom flask containing iodophenol (660 mg, 3 mmol) and 3,3-dimethyl-1-butyne (443 μL, 3.6 mmol) and diisopropylamine (841 μL, 6 mmol) in toluene (15 mL) under nitrogen was added copper(I) iodide (51.4 mg, 0.27 mmol) and

bis(triphenylphosphine) palladium(II) dichloride (63.2 mg, 0.09 mmol). The mixture was warmed to 45 °C and stirred for 2 h. The mixture was diluted with ethyl acetate and the organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, filtered, concentrated and purified by flash column chromatography to obtain this title compound (139.0 mg, 27%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.22-7.14 (m, 1H), 6.92 (dd, *J* = 8.2, 0.9 Hz, 1H), 6.83 (td, *J* = 7.5, 1.1 Hz, 1H), 5.75 (s, 1H), 1.35 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.3, 131.3, 129.6, 120.2, 114.2, 110.1, 106.3, 72.9, 31.1, 28.4 ppm. The spectroscopic data was in agreement with the literature values.[1]

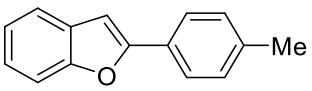
B. General procedure for base catalyzed intramolecular cyclization of 2-ynylphenols to 2-substitued benzo[*b*]furans

To a sealed tube with a magnetic bar were added 2-ynylphenols (0.3 mmol) and acetonitrile (3 mL). After stirring at r.t. for 5 mins, Cs_2CO_3 (10 mol%) was added and the resulting mixture was stirred at 60 °C for 12 hours. After cooling, the obtained mixture was filtered and the residue was washed twice with acetonitrile. Then the filtrate was evaporated under reduced pressure to remove the solvent and the residue was purified by flash column chromatography to obtain the corresponding 2-substitued benzo[*b*]furans.

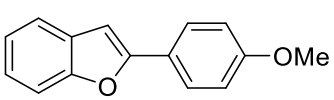
The semi-gram and gram scale reactions for Cs_2CO_3 catalyzed annulation of 2-ynylphenols toward 2-substituted benzo[*b*]furans were conducted following the above general procedure.



2-phenylbenzo[*b*]furan (2a). White solid (57.9 mg, 99%); mp 120-121 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 7.9 Hz, 2H), 7.54 (dd, *J* = 14.5, 7.6 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.36 -7.17 (m, 3H), 6.99 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.0, 154.9, 130.5, 129.3, 128.9, 128.6, 125.0, 124.3, 123.0, 121.0, 111.3, 101.4 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{14}H_{10}O$: 194.0732, found 194.0723 $[M]^+$.

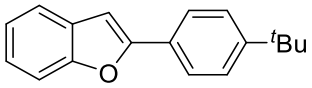


2-(*p*-tolyl)benzo[*b*]furan (2b). White solid (62.1 mg, 99%); mp 127-129 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 7.9 Hz, 2H), 7.54 (dd, *J* = 16.8, 7.5 Hz, 2H), 7.31-7.17 (m, 4H), 6.97 (s, 1H), 2.40 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.2, 154.8, 138.6, 129.5, 129.4, 127.8, 124.9, 124.0, 122.9, 120.8, 111.1, 100.6, 21.4 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{15}H_{12}O$: 208.0888, found 208.0880 $[M]^+$.

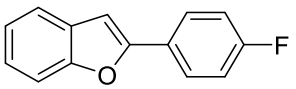


2-(4-methoxyphenyl)benzo[*b*]furan (2c). White solid (66.1 mg, 98%); mp 148-150 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.3 Hz, 2H), 7.52 (dd, *J* = 14.7, 7.5 Hz, 2H), 7.22 (p, *J* = 7.2 Hz,

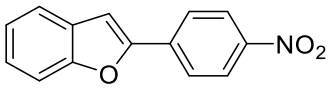
2H), 6.96 (d, J = 8.4 Hz, 2H), 6.87 (s, 1H), 3.84 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.0, 156.1, 154.7, 129.5, 126.4, 123.7, 123.4, 122.8, 120.6, 114.3, 111.0, 99.7, 55.3 ppm; APCI-HRMS calcd for $C_{15}H_{13}O_2$ $[M+H]^+$: 225.0910, found 225.0913 $[M+H]^+$.



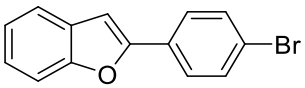
2-(4-(*tert*-butyl)phenyl)benzo[*b*]furan (2d). White solid (71.4 mg, 95%); mp 130-132 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 (d, J = 8.1 Hz, 2H), 7.53 (dd, J = 13.4, 7.6 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 7.23 (p, J = 7.4 Hz, 2H), 6.96 (s, 1H), 1.35 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.2, 154.9, 151.8, 129.4, 127.8, 125.7, 124.8, 124.0, 122.9, 120.8, 111.1, 100.7, 34.8, 31.3 ppm; APCI-HRMS calcd for $C_{18}H_{19}O$ $[M+H]^+$: 251.1430, found 251.1428 $[M+H]^+$.



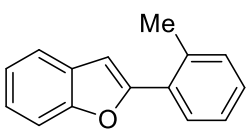
2-(4-fluorophenyl)benzo[*b*]furan (2e). White solid (55.5 mg, 87%); mp 120-122 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87-7.76 (m, 2H), 7.53 (dd, J = 17.9, 7.7 Hz, 2H), 7.32-7.17 (m, 2H), 7.12 (t, J = 8.6 Hz, 2H), 6.93 (s, 1H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ = -112.3 ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.9 (d, J = 248.8 Hz), 155.0 (d, J = 11.6 Hz), 129.2, 126.8, 126.7, 124.3, 123.0, 120.9, 116.0, 115.7, 111.1, 101.0 (d, J = 1.6 Hz) ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{14}H_9FO$: 212.0637, found 212.0629 $[M]^+$.



2-(4-nitrophenyl)benzo[*b*]furan (2f). Yellow solid (57.8 mg, 81%); mp 180-181 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.35-8.24 (m, 2H), 8.03-7.94 (m, 2H), 7.67-7.59 (m, 1H), 7.58-7.52 (m, 1H), 7.36 (td, J = 8.3, 7.8, 1.4 Hz, 1H), 7.31-7.24 (m, 1H), 7.22 (d, J = 0.7 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.3, 153.1, 149.5, 136.3, 128.6, 125.8, 125.3, 124.3, 123.5, 121.6, 111.5, 105.1 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{14}H_9NO_3$: 239.0582, found 239.0576 $[M]^+$.

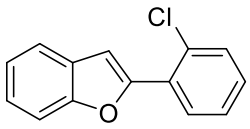


2-(4-bromophenyl)benzo[*b*]furan (2g). White solid (77.2 mg, 94%); mp 149-151 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70-7.62 (m, 2H), 7.56-7.44 (m, 4H), 7.27 (td, J = 8.1, 7.7, 1.6 Hz, 1H), 7.20 (td, J = 7.5, 1.2 Hz, 1H), 6.94 (d, J = 0.8 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.9, 154.8, 131.9, 129.4, 129.0, 126.3, 124.6, 123.1, 122.5, 121.0, 111.2, 101.8 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{14}H_9BrO$: 271.9837, found 271.9831 $[M]^+$.

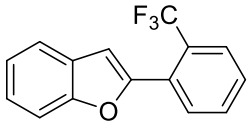


2-(*o*-tolyl)benzo[*b*]furan (2h). Light yellow oil (60.8 mg, 97%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (d, J = 5.4 Hz, 1H), 7.57 (dd, J = 24.2, 7.6 Hz, 2H), 7.36-7.20 (m, 5H), 6.90 (s, 1H), 2.59 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.7, 154.4, 135.9, 131.3, 130.0, 129.3, 128.6, 128.2, 126.2,

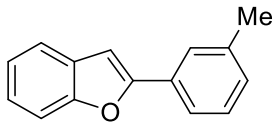
124.3, 122.9, 121.0, 111.2, 105.2, 22.1 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{15}H_{12}O$: 208.0888, found 208.0882 $[M]^+$.



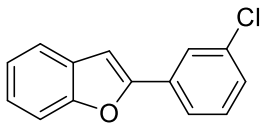
2-(2-chlorophenyl)benzo[*b*]furan (2i). White solid (66.0 mg, 96%); mp 50-51 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.56-7.45 (m, 3H), 7.40-7.19 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.2, 152.0, 131.3, 130.9, 129.0, 129.0, 126.9, 124.9, 123.0, 121.5, 111.0, 107.4 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{14}H_9ClO$: 228.0342, found 228.0334 $[M]^+$.



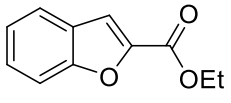
2-(2-(trifluoromethyl)phenyl)benzo[*b*]furan (2j). Colorless oil (20.4 mg, 26%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 7.7 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.36 (dd, *J* = 14.1, 7.0 Hz, 2H), 7.14 (td, *J* = 8.0, 5.0 Hz, 1H), 7.07-6.97 (m, 2H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ = -58.2 ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.4, 153.9, 133.1, 132.3, 130.0 (q, *J* = 131.3 Hz), 130.2, 130.1, 128.1 (q, *J* = 5.8 Hz), 127.1, 126.2, 124.4, 123.5, 122.8, 112.7, 108.0 (q, *J* = 3.6 Hz) ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{15}H_9F_3O$: 262.0605, found 262.0599 $[M]^+$.



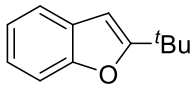
2-(*m*-tolyl)benzo[*b*]furan (2k). White solid (58.5 mg, 94%); mp 78-79 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75-7.62 (m, 2H), 7.54 (dd, *J* = 15.6, 7.6 Hz, 2H), 7.38-7.20 (m, 3H), 7.17 (t, *J* = 7.1 Hz, 1H), 6.99 (s, 1H), 2.42 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.1, 154.9, 138.4, 130.4, 129.4, 129.3, 128.7, 125.6, 124.2, 122.9, 122.2, 120.9, 111.1, 101.2, 21.5 ppm; APCI-HRMS calcd for $C_{15}H_{13}O$ $[M+H]^+$: 209.0961, found 209.0958 $[M+H]^+$.



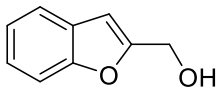
2-(3-chlorophenyl)benzo[*b*]furan (2l). White solid (58.1 mg, 85%); mp 87-89 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (s, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.55 (dd, *J* = 19.5, 7.8 Hz, 2H), 7.40-7.19 (m, 4H), 7.02 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.0, 154.3, 134.9, 132.2, 130.0, 128.9, 128.4, 124.9, 124.8, 123.1, 122.9, 121.1, 111.3, 102.4 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{14}H_9ClO$: 228.0342, found 228.0335 $[M]^+$.



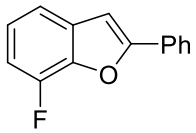
Ethyl benzo[*b*]furan-2-carboxylate (2m). colorless oil (28.7 mg, 50%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 7.8 Hz, 1H), 7.61-7.56 (m, 1H), 7.52 (d, *J* = 0.8 Hz, 1H), 7.43 (td, *J* = 8.4, 7.8, 1.3 Hz, 1H), 7.33-7.25 (m, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.5, 155.7, 145.7, 127.5, 126.9, 123.7, 122.7, 113.7, 112.3, 61.4, 14.3 ppm; ESI-HRMS calcd for $C_{11}H_{11}O_3$ $[M+H]^+$: 191.0703, found 191.0698 $[M+H]^+$.



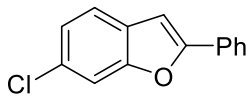
2-(*tert*-butyl)benzo[*b*]furan (2n). Colorless oil (42.5 mg, 81%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58-7.46 (m, 1H), 7.46-7.38 (m, 1H), 7.30-7.07 (m, 2H), 6.35 (s, 1H), 1.37 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.4, 154.6, 128.9, 123.1, 122.3, 120.3, 110.8, 98.9, 33.0, 28.9 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{12}H_{14}O$: 174.1045, found 174.1038 $[M]^+$.



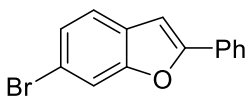
Benzo[*b*]furan-2-ylmethanol (2o). Colorless oil (36.0 mg, 81%);^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (dd, *J* = 25.1, 7.7 Hz, 2H), 7.32-7.17 (m, 2H), 6.66 (s, 1H), 4.78 (s, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.5, 155.1, 128.2, 124.4, 122.8, 121.1, 111.2, 104.1, 58.1 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_9H_8O_2$: 148.0524, found 148.0518 $[M]^+$.



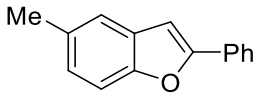
7-fluoro-2-phenylbenzo[*b*]furan (2p). White solid (62.9 mg, 99%); mp 61-63 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 7.8 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 6.5 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.17-7.07 (m, 1H), 7.00 (d, *J* = 18.8 Hz, 2H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ = -137.3 ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.0, 148.0 (d, *J* = 248.9 Hz), 141.8 (d, *J* = 11.1 Hz), 132.8 (d, *J* = 3.4 Hz), 129.9, 129.0, 128.9, 125.1, 123.6 (d, *J* = 6.0 Hz), 116.6 (d, *J* = 3.9 Hz), 110.6 (d, *J* = 16.1 Hz), 101.6 (d, *J* = 2.5 Hz) ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{14}H_9FO$: 212.0637, found 212.0631 $[M]^+$.



6-chloro-2-phenylbenzo[*b*]furan (2q). White solid (64.1 mg, 93%); mp 129-130 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 7.5 Hz, 2H), 7.51 (s, 1H), 7.44 (t, *J* = 8.2 Hz, 3H), 7.39-7.31 (m, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.95 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.8, 155.0, 130.1, 130.0, 128.8, 127.9, 125.0, 123.7, 121.3, 111.8, 101.0 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{14}H_9ClO$: 228.0342, found 228.0336 $[M]^+$.

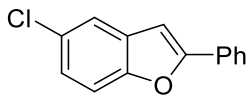


6-bromo-2-phenylbenzo[*b*]furan (2r). White solid (76.4 mg, 93%); mp 139-141 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84-7.78 (m, 2H), 7.66 (s, 1H), 7.46-7.30 (m, 5H), 6.93 (d, *J* = 0.8 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.7, 155.2, 130.0, 128.9, 128.9, 128.3, 126.4, 125.0, 121.7, 117.4, 114.7, 101.1 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{14}H_9BrO$: 271.9837, found 271.9831 $[M]^+$.

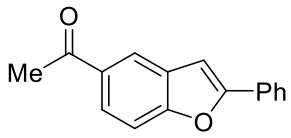


5-methyl-2-phenylbenzo[*b*]furan (2s). White solid (61.5 mg, 98%); mp 130-132 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 7.8 Hz, 2H), 7.46-7.34 (m, 3H), 7.34-7.26 (m, 2H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.90 (s,

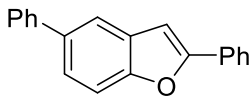
1H), 2.42 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.0, 153.4, 132.4, 130.7, 129.4, 128.8, 128.5, 125.6, 124.9, 120.8, 110.7, 101.2, 21.5 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{15}H_{12}O$: 208.0888, found 208.0882 $[M]^+$.



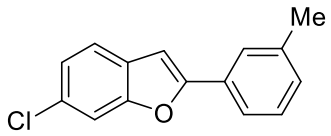
5-chloro-2-phenylbenzo[*b*]furan (2t). White solid (65.2 mg, 95%); mp 155-156 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 7.7 Hz, 2H), 7.53 (s, 1H), 7.49-7.31 (m, 4H), 7.27-7.17 (m, 1H), 6.94 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.4, 153.3, 130.6, 130.0, 129.0, 128.9, 128.5, 125.1, 124.4, 120.5, 112.2, 100.8 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{14}H_9ClO$: 228.0342, found 228.0334 $[M]^+$.



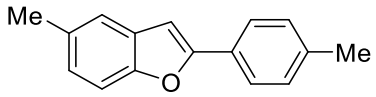
1-(2-phenylbenzo[*b*]furan-5-yl)ethan-1-one (2u). White solid (69.5 mg, 98%); mp 162-164 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11 (s, 1H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.32 -7.23 (m, 1H), 6.95 (s, 1H), 2.56 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.7, 157.5, 157.4, 132.9, 129.8, 129.3, 129.1, 128.9, 125.1, 122.2, 111.2, 101.6, 26.8 ppm; ESI-HRMS calcd for $C_{16}H_{13}O_2$ $[M+H]^+$: 237.0910, found 237.0905 $[M+H]^+$.



2,5-diphenylbenzo[*b*]furan (2v). White solid (77.5 mg, 96%); mp 165-167 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 7.7 Hz, 2H), 7.74 (s, 1H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.58-7.38 (m, 6H), 7.38-7.27 (m, 2H), 7.03 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.6, 154.6, 141.7, 136.7, 130.4, 129.8, 128.9, 128.8, 128.7, 127.5, 127.0, 125.0, 124.1, 119.5, 111.3, 101.5 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{20}H_{14}O$: 270.1045, found 270.1038 $[M]^+$.

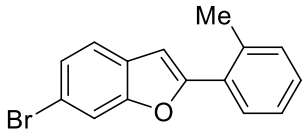


6-chloro-2-(*m*-tolyl)benzo[*b*]furan (2w). White solid (71.4 mg, 98%); mp 80-82 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 10.4 Hz, 2H), 7.48 (s, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 8.3 Hz, 2H), 6.90 (s, 1H), 2.39 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.0, 154.9, 138.6, 129.9, 129.8, 129.7, 128.8, 128.0, 125.6, 123.7, 122.2, 121.3, 111.7, 100.9, 21.6 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{15}H_{11}ClO$: 242.0498, found 242.0492 $[M]^+$.

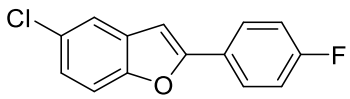


5-methyl-2-(*p*-tolyl)benzo[*b*]furan (2x). White solid (65.2 mg, 98 %); mp 151-153 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.31 (s, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 1H), 6.85 (s, 1H), 2.42 (s, 3H), 2.36 (s, 3H) ppm; ^{13}C NMR

(75 MHz, $CDCl_3$): δ = 156.3, 153.3, 138.5, 132.3, 129.5, 129.5, 127.9, 125.3, 124.9, 120.7, 110.6, 100.4, 21.5, 21.4 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{16}H_{14}O$: 222.1045, found 222.1038 $[M]^+$.



6-bromo-2-(*o*-tolyl)benzo[*b*]furan (2y). White solid (82.0 mg, 95%); mp 65-67 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.78 (td, *J* = 4.4, 2.3 Hz, 1H), 7.66 (s, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.33 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.30-7.24 (m, 3H), 6.80 (s, 1H), 2.53 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.5, 154.7, 135.9, 131.4, 129.5, 128.8, 128.3, 128.2, 126.2, 126.2, 121.8, 117.4, 114.6, 104.8, 21.9 ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{15}H_{11}BrO$: 285.9993, found 285.9989 $[M]^+$.



5-chloro-2-(4-fluorophenyl)benzo[*b*]furan (2z). White solid (73.7 mg, 99%); mp 145-146 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.82-7.72 (m, 2H), 7.49 (s, 1H), 7.38 (d, *J* = 8.7 Hz, 1H), 7.20 (d, *J* = 8.7 Hz, 1H), 7.11 (t, *J* = 8.5 Hz, 2H), 6.82 (s, 1H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ = -111.5 ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.1 (d, *J* = 249.4 Hz), 156.4, 153.2, 130.5, 128.6, 126.9 (d, *J* = 8.3 Hz), 126.3 (d, *J* = 3.4 Hz), 124.4, 120.4, 116.0 (d, *J* = 22.0 Hz), 112.1, 100.5 (d, *J* = 1.7 Hz) ppm; EI-HRMS: m/z $[M]^+$ calcd for $C_{14}H_8ClFO$: 246.0248, found 246.0241 $[M]^+$.

III. References

1. E. Yoneda, T. Sugioka, K. Hirao, S.-W. Zhang and S. Takahashi. *J. Chem. Soc., Perkin Trans. 1*, **1998**, *3*, 477-484.

2. S.-X. Sun, J.-J. Wang, Z.-J. Xu, L.-Y. Cao, Z.-F. Shi and H.-L. Zhang. *Tetrahedron*, **2014**, *70(2)*, 3798-3806.

3. A. Kondoh, H. T. Tran, K. Kimura and M. Terada, *Chem. Commun.*, **2016**, *52(33)*, 5726-5729.

4. C. A. James and V. Snieckus. *J. Org. Chem.*, **2009**, *74(11)*, 4080-4093.

5. E. Lee, A. S. Kamlet, D. C. Powers, C. N. Neumann, G. B. Boursalian, T. Furuya, D. C. Choi, J. M. Hooker and T. Ritter, *Science*, **2011**, *334(6056)*, 639-642.

6. K. Watanabe, T. Mino, C. Hatta, E. Ishikawa, Y. Yoshida and M. Sakamoto, *Eur. J. Org. Chem.*, **2017**, *25*, 3612-3619.

7. A. Fürstner and P. W. Davies, *J. Am. Chem. Soc.*, **2005**, *127(43)*, 15024-15025.

8. K. V. Sajna and K. C. Kumara Swamy, *J. Org. Chem.*, **2012**, *77(12)*, 5345-5356.

9. R. Álvarez, C. Martínez, Y. Madich, J. G. Denis, J. M. Aurrecoechea and Á. R. de Lera, *Chem. Eur. J.*, **2012**, *18(43)*, 13894-13896.

10. H. Wegner, M. Auzias and M. Neuburger, *Synlett*, **2010**, *16*, 2443-2448.

11. X. Lu, X. Han and H. Wang, *Synlett*, **2011**, *17*, 2590-2594.

12. P. Nanayakkara and H. Alper, *Adv. Synth Catal.*, **2006**, *348(4-5)*, 545-550.

13. A. Arcadi, S. Cacchi, M. Del Rosario, G. Fabrizi and F. Marinelli, *J. Org. Chem.*, **1996**, *61(26)*,

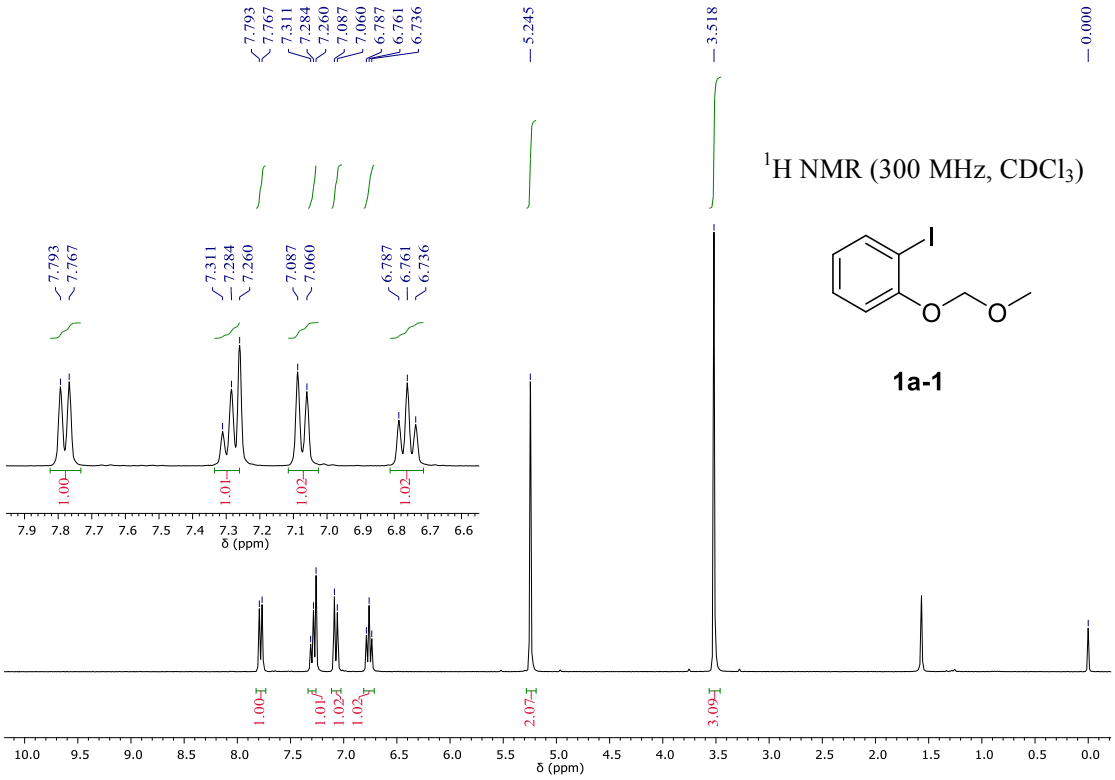
9280-9288.

14. Y. Luo and J. Wu, *Org. Lett.*, **2011**, *13(21)*, 5858-5861.

15. A. Courtney. Antibacterial agents. Patent WO2007067559A2, June 14, 2007.

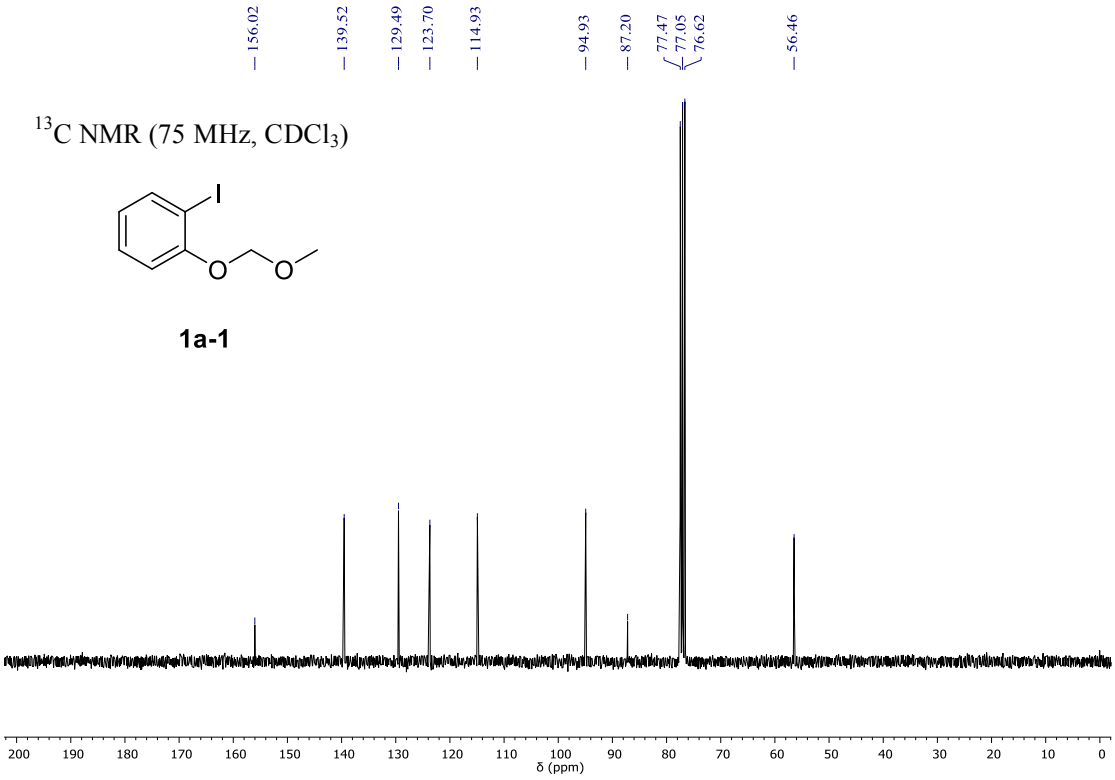
16. Y. Kondo, F. Shiga, N. Murata, T. Sakamoto and H. Yamanaka, *Tetrahedron*, **1994**, *50(41)*, 11803-11812.

IV. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra



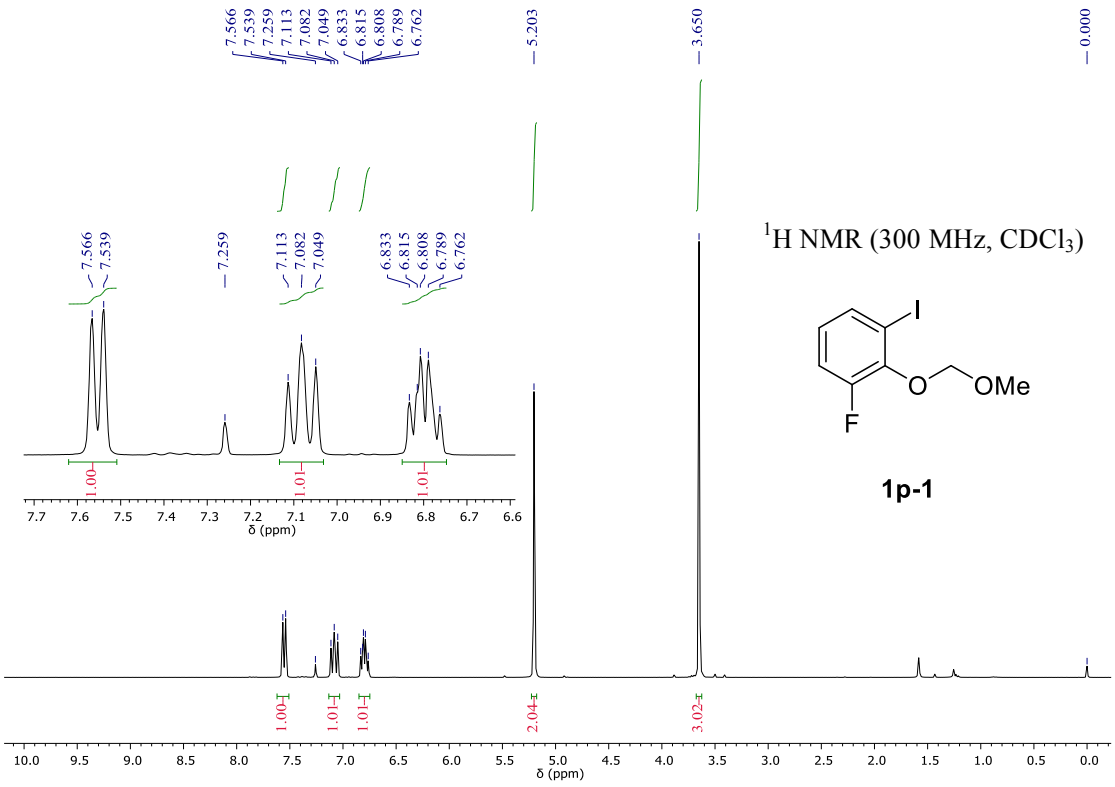
^{1}H NMR (300 MHz, $CDCl_3$)

1a-1



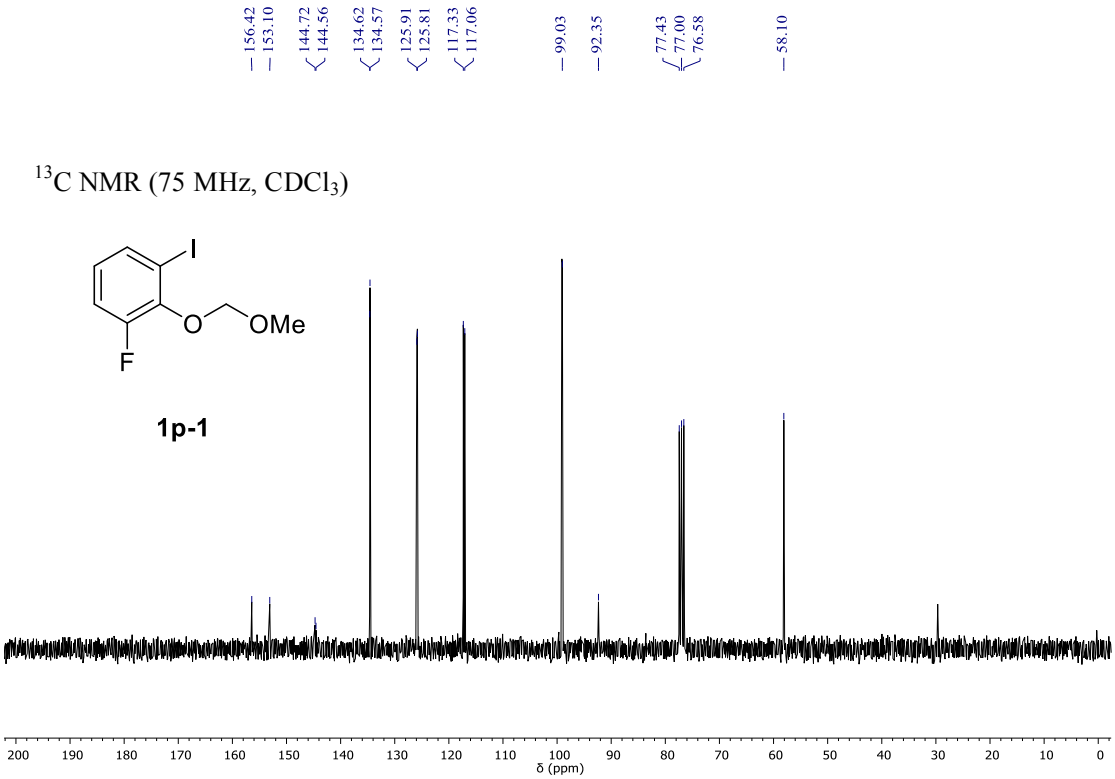
^{13}C NMR (75 MHz, $CDCl_3$)

1a-1



^{1}H NMR (300 MHz, $CDCl_3$)

1p-1

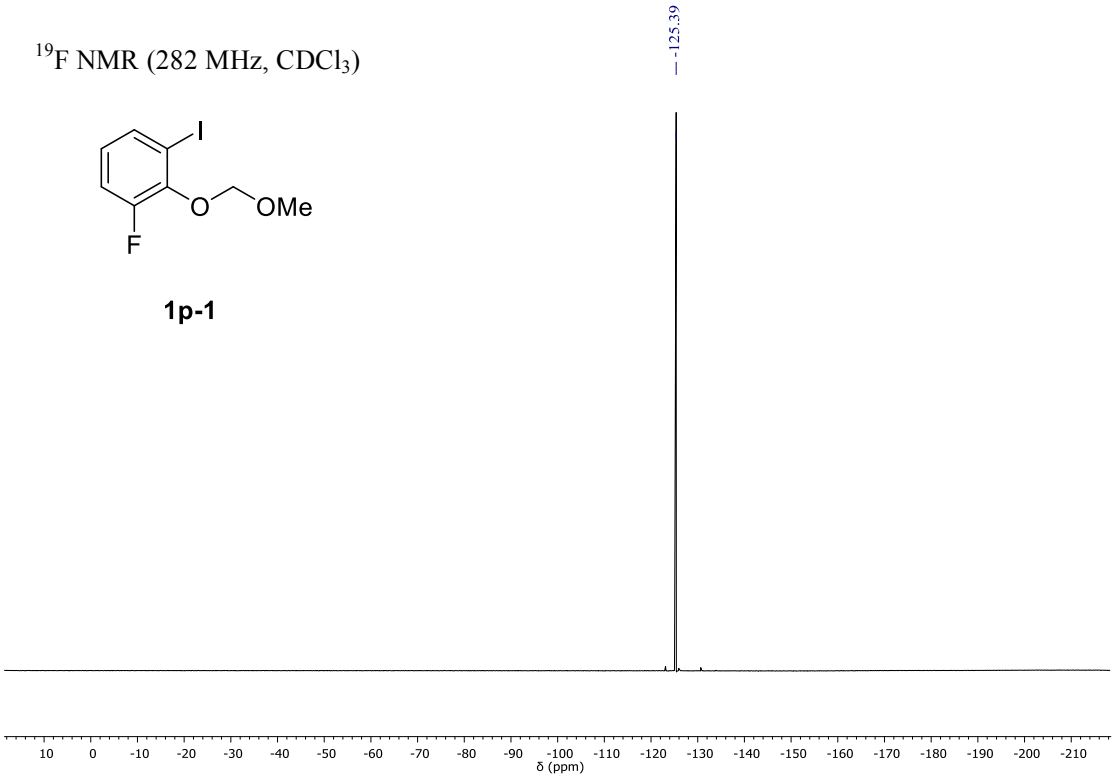


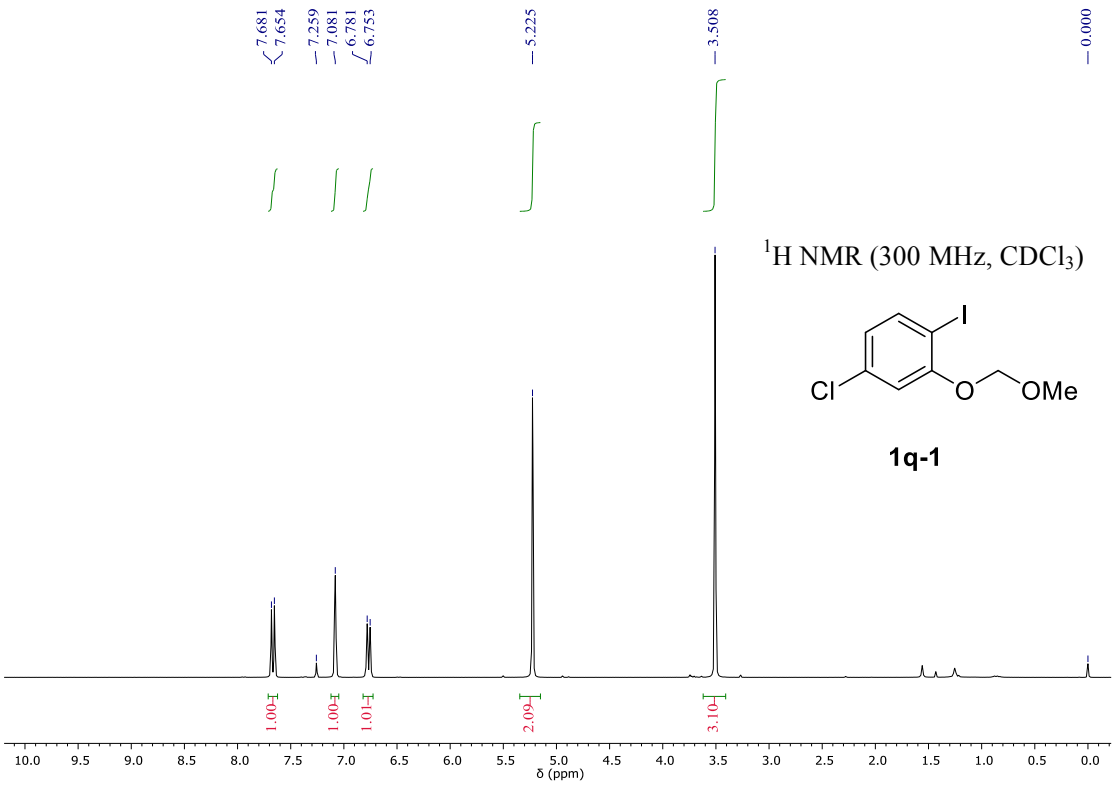
^{13}C NMR (75 MHz, $CDCl_3$)

1p-1

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

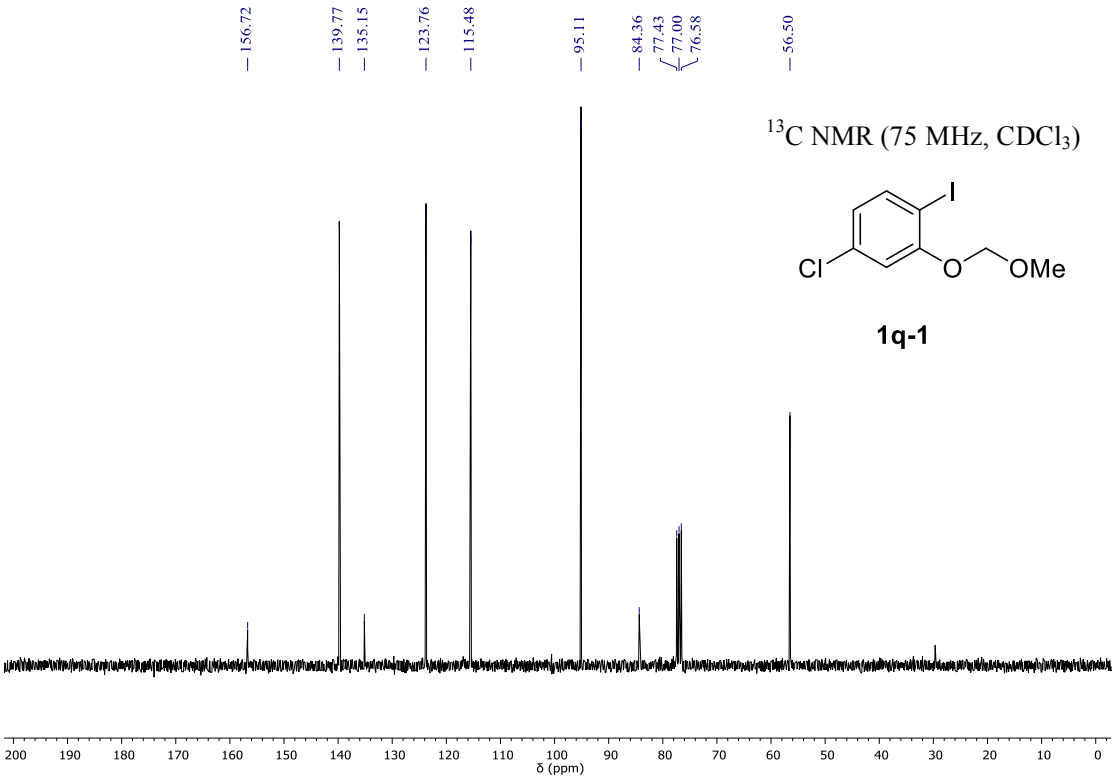
1p-1





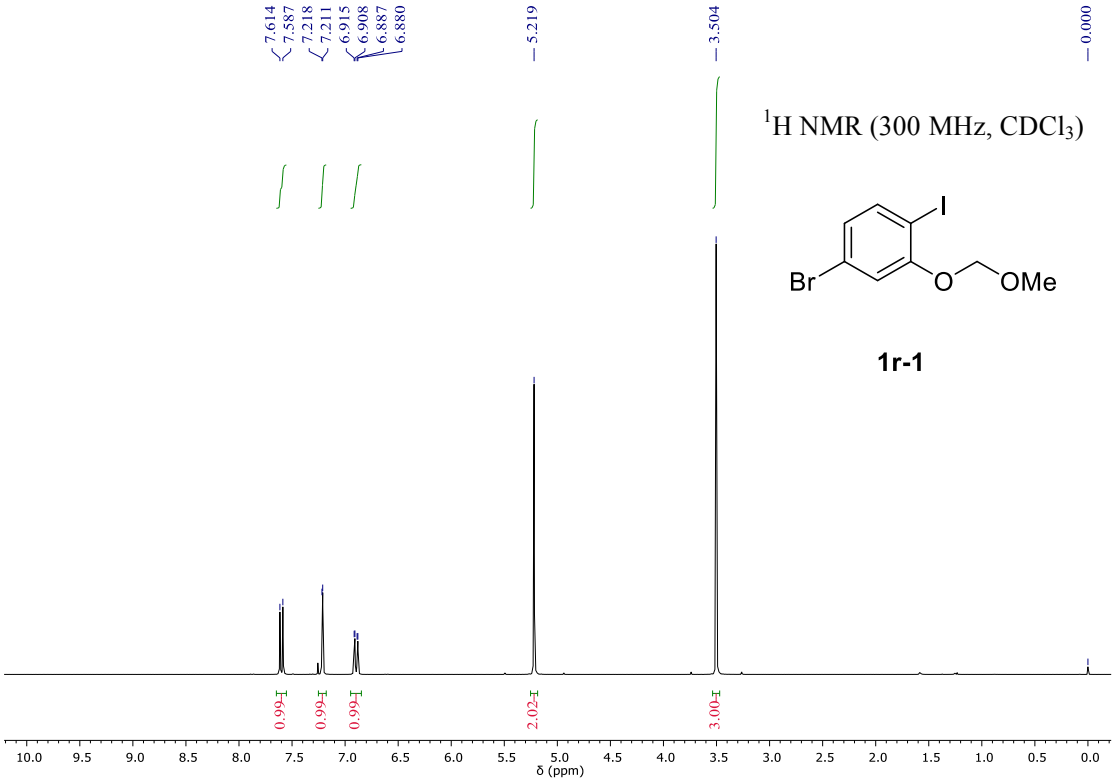
^{1}H NMR (300 MHz, $CDCl_3$)

1q-1



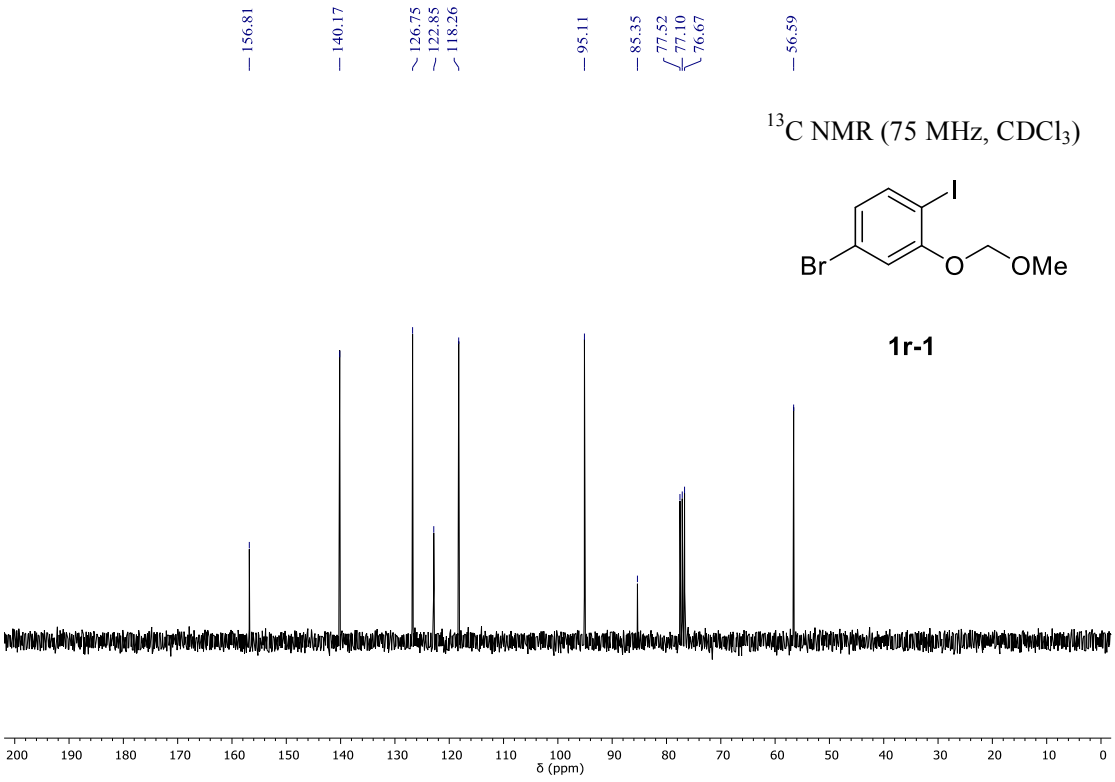
^{13}C NMR (75 MHz, $CDCl_3$)

1q-1



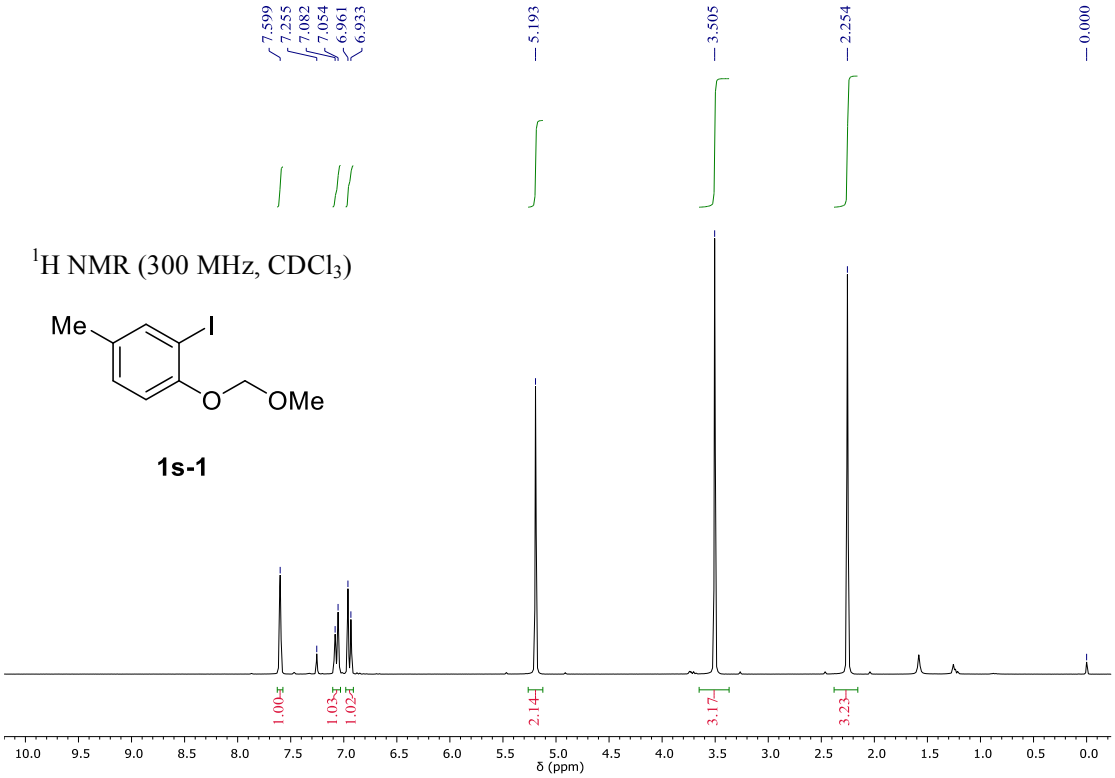
^{1}H NMR (300 MHz, $CDCl_3$)

1r-1



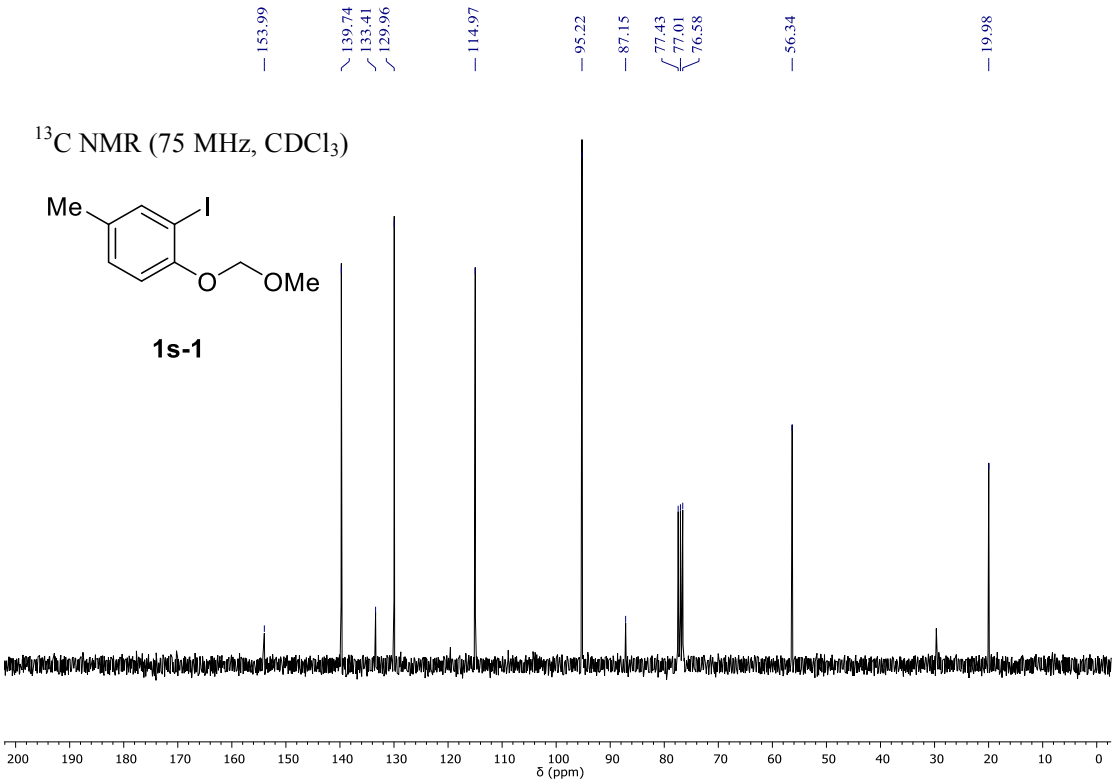
^{13}C NMR (75 MHz, $CDCl_3$)

1r-1



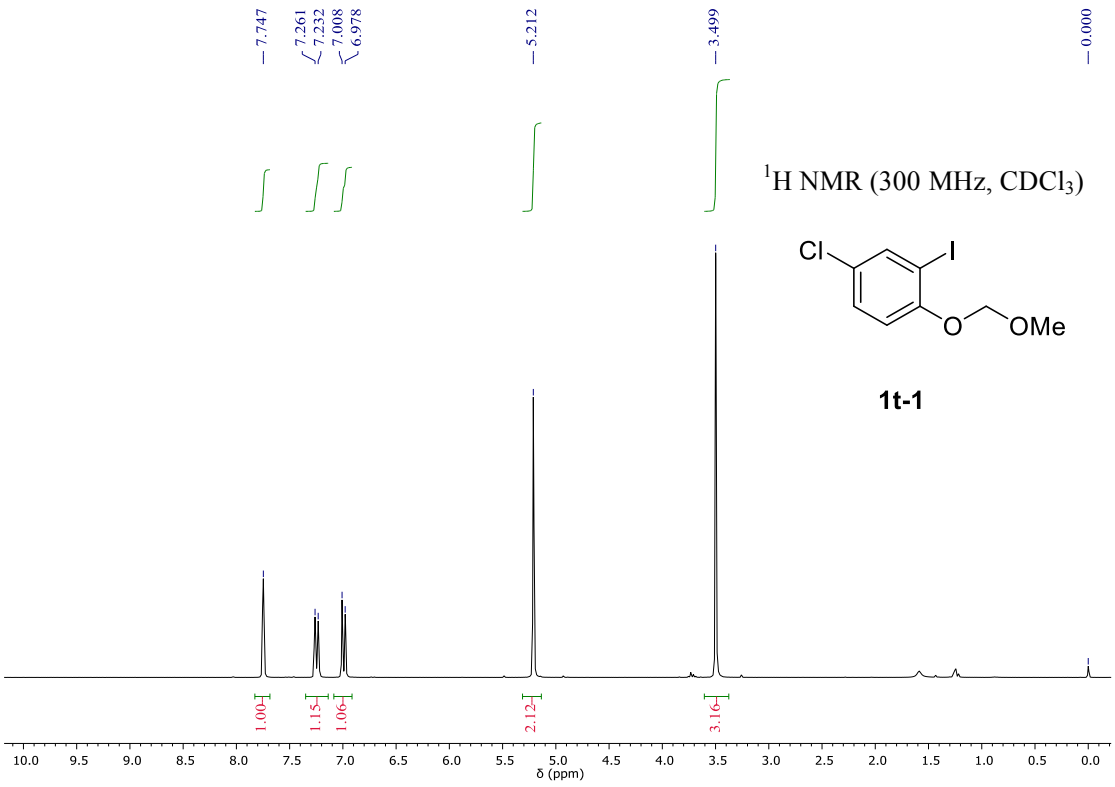
^{1}H NMR (300 MHz, $CDCl_3$)

1s-1



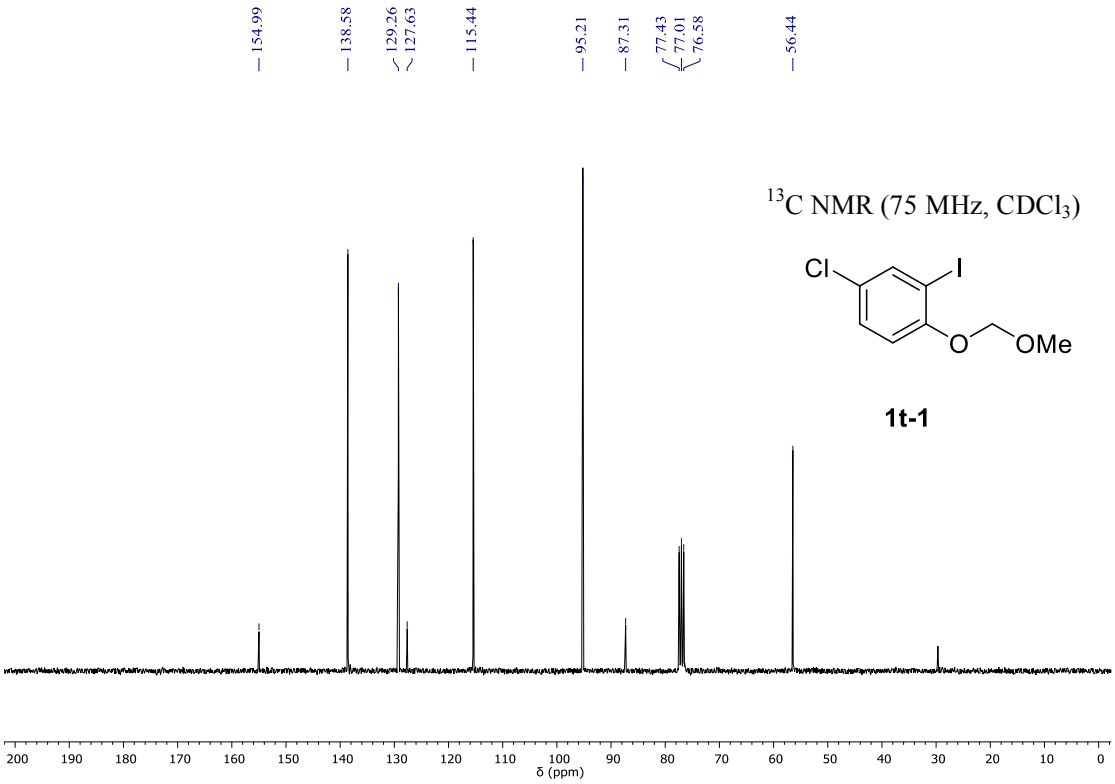
^{13}C NMR (75 MHz, $CDCl_3$)

1s-1



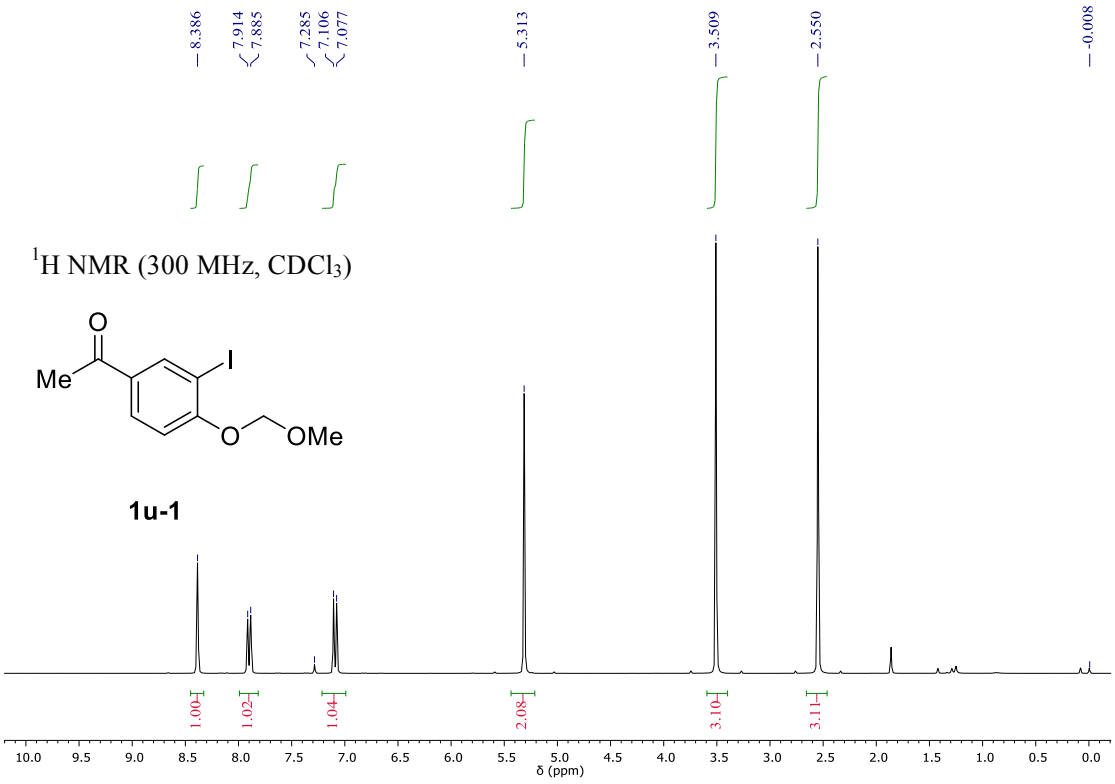
^{1}H NMR (300 MHz, $CDCl_3$)

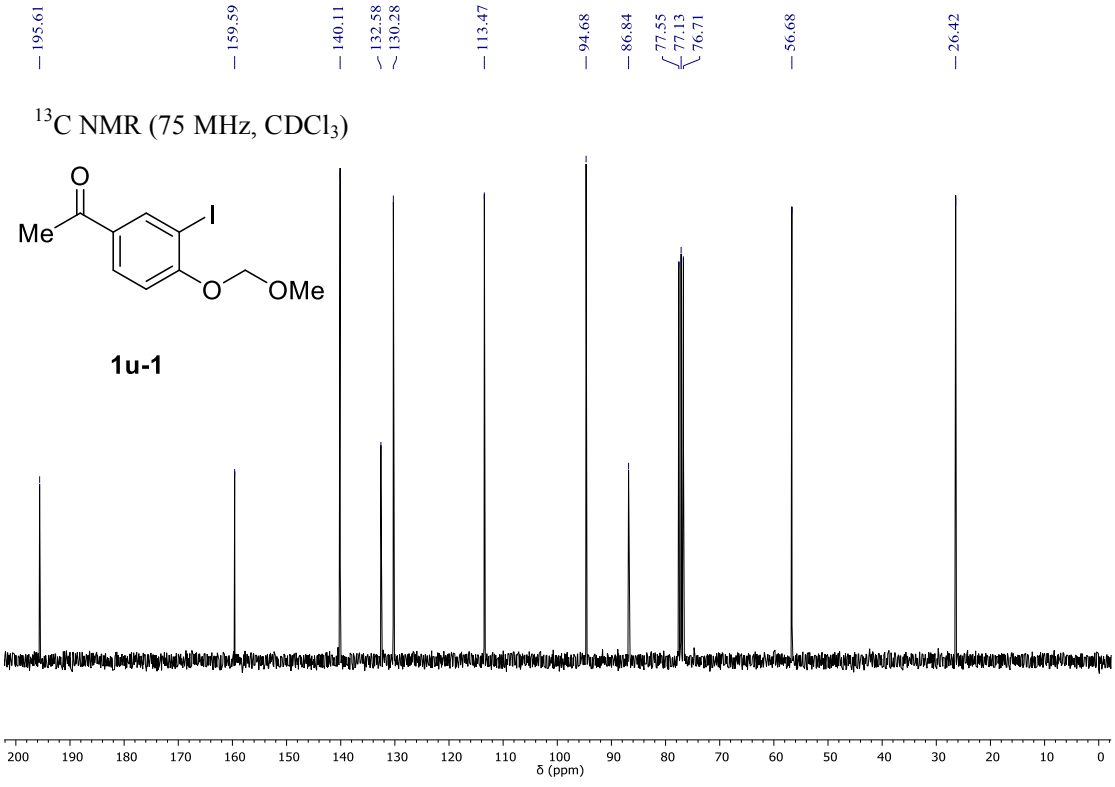
1t-1

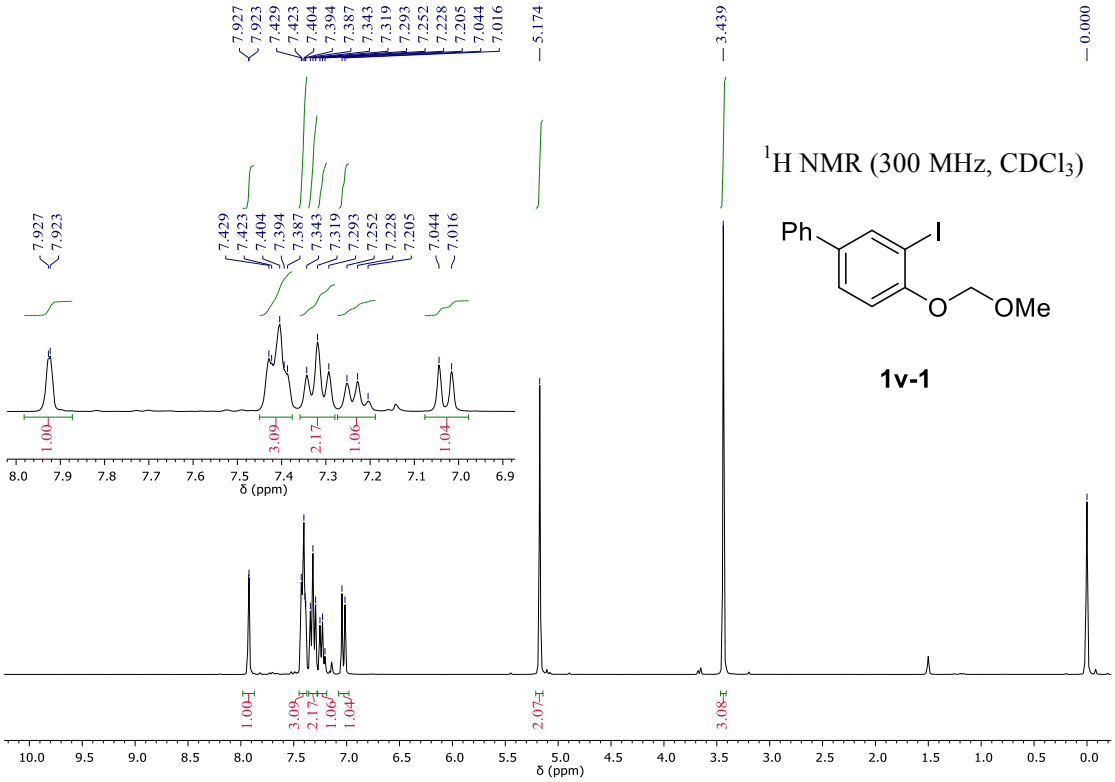


^{13}C NMR (75 MHz, $CDCl_3$)

1t-1

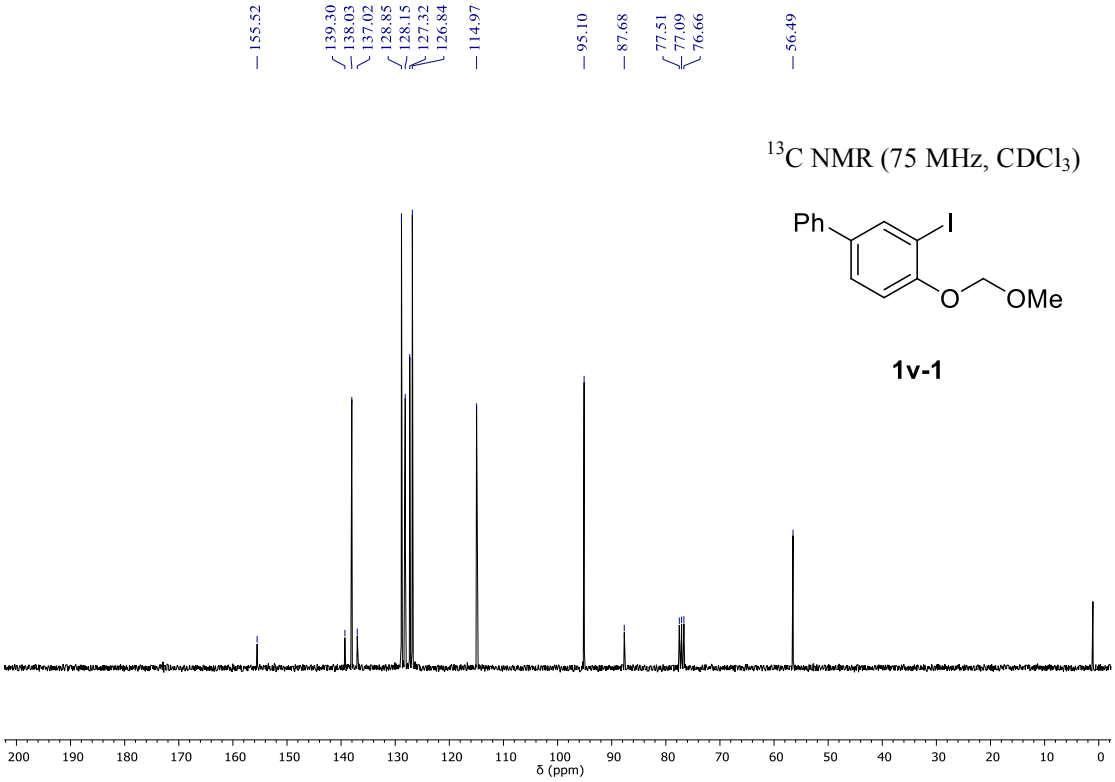

8.386
7.914
7.885
7.285
7.106
7.077
5.313
3.509
2.550
-0.008
1H NMR (300 MHz, CDCl3)
O
Me
I
O
OMe
1u-1
1.00
1.02
1.04
2.08
3.10
3.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)


195.61
159.59
140.11
132.58
130.28
113.47
94.68
86.84
77.55
77.13
76.71
56.68
26.42
13C NMR (75 MHz, CDCl3)
O
Me
I
O
OMe
1u-1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)



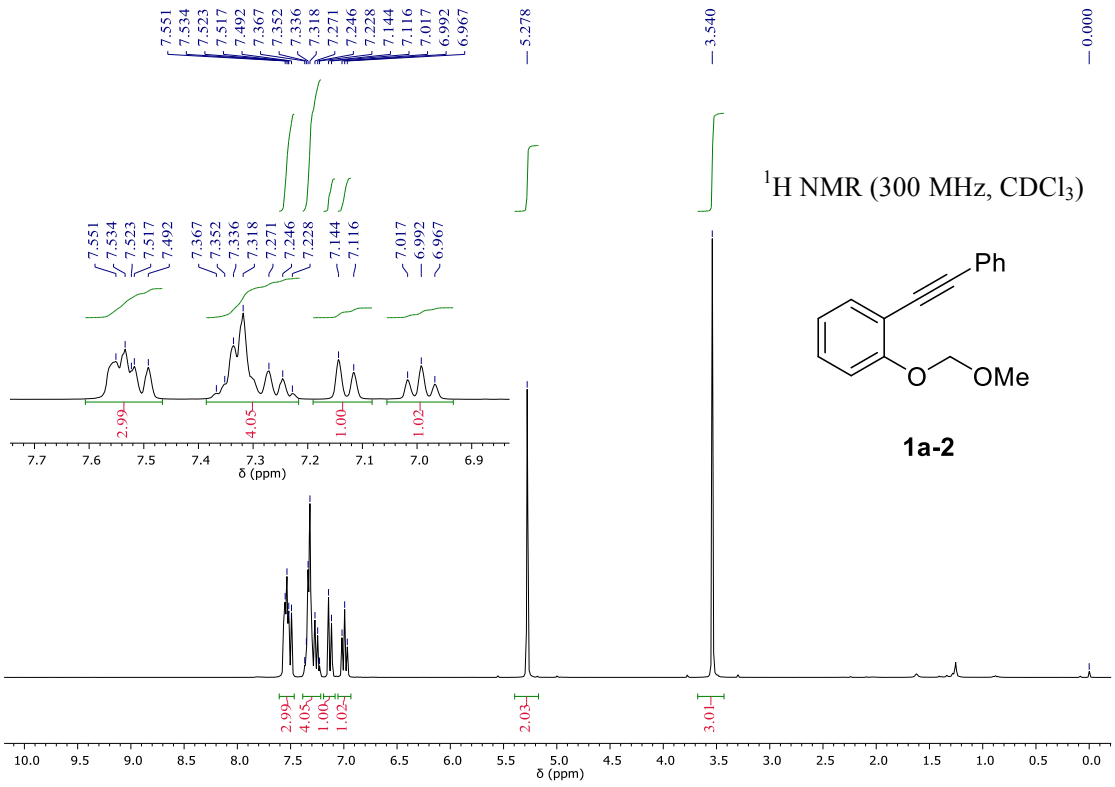
^{1}H NMR (300 MHz, $CDCl_3$)

1v-1



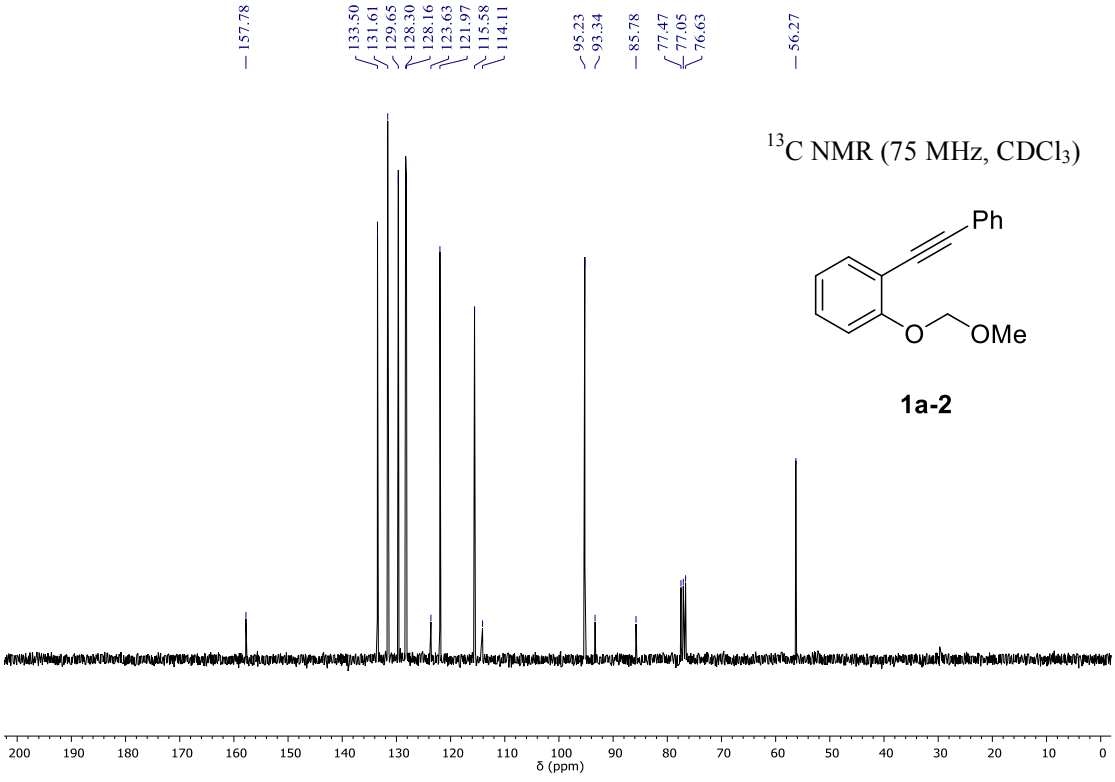
^{13}C NMR (75 MHz, $CDCl_3$)

1v-1



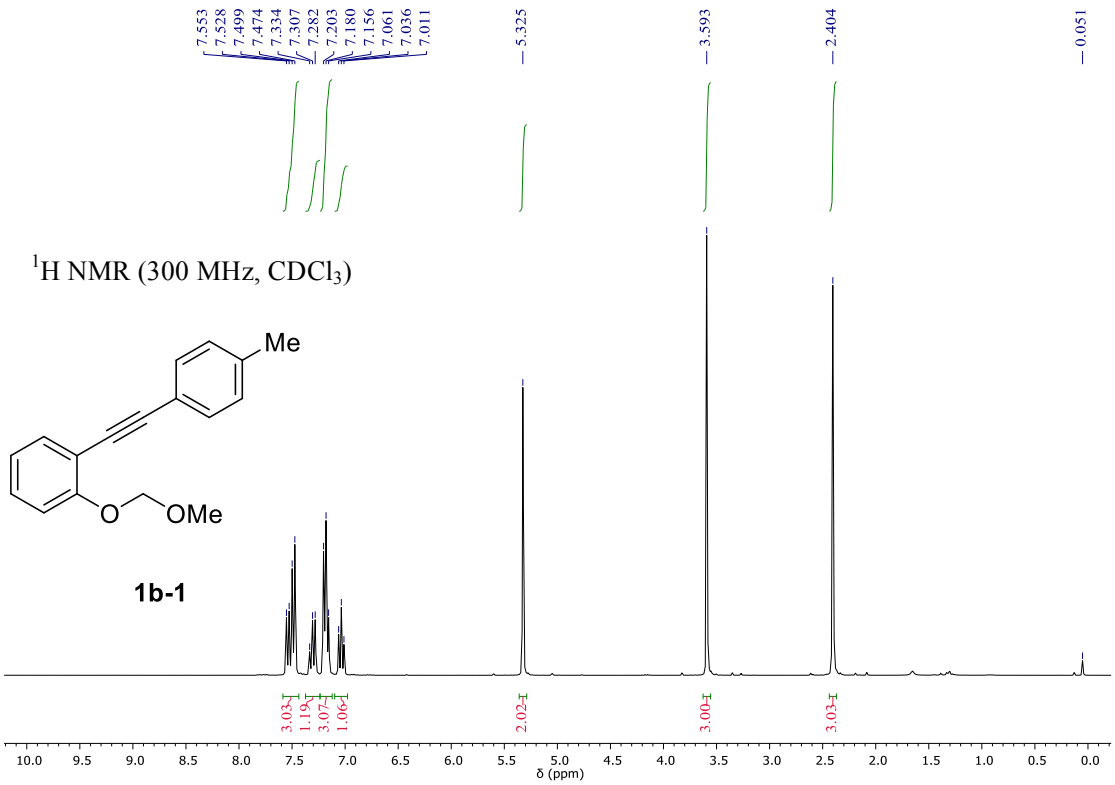
^{1}H NMR (300 MHz, $CDCl_3$)

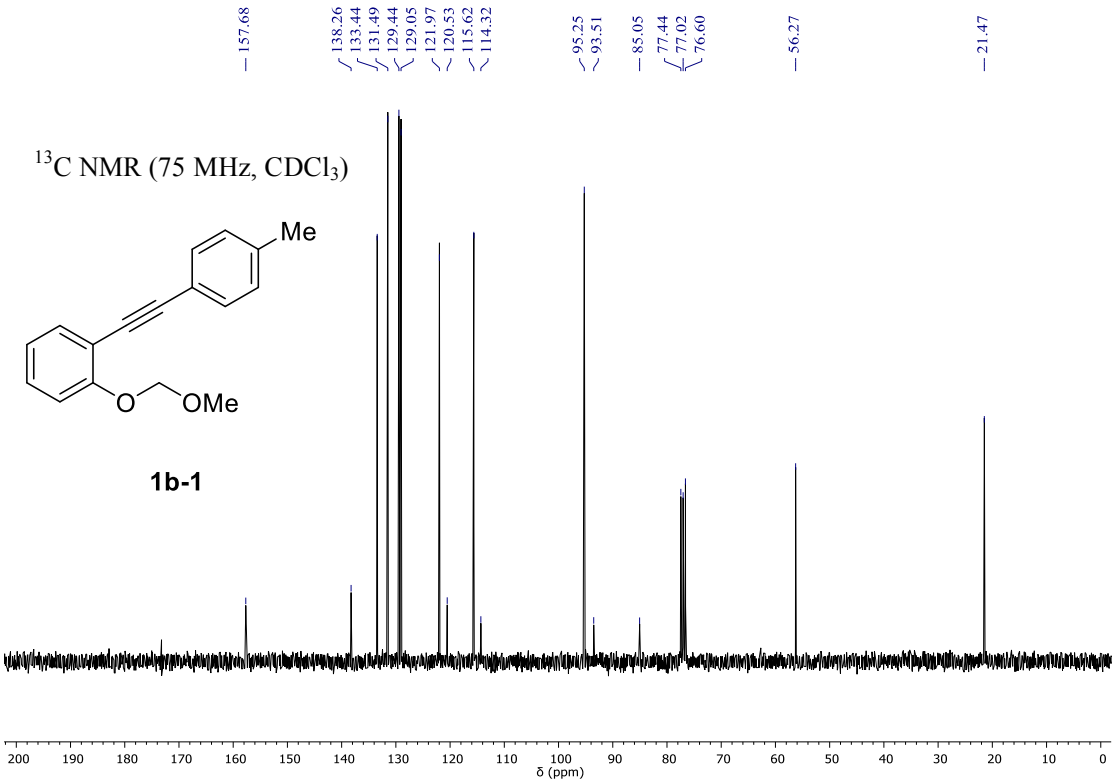
1a-2

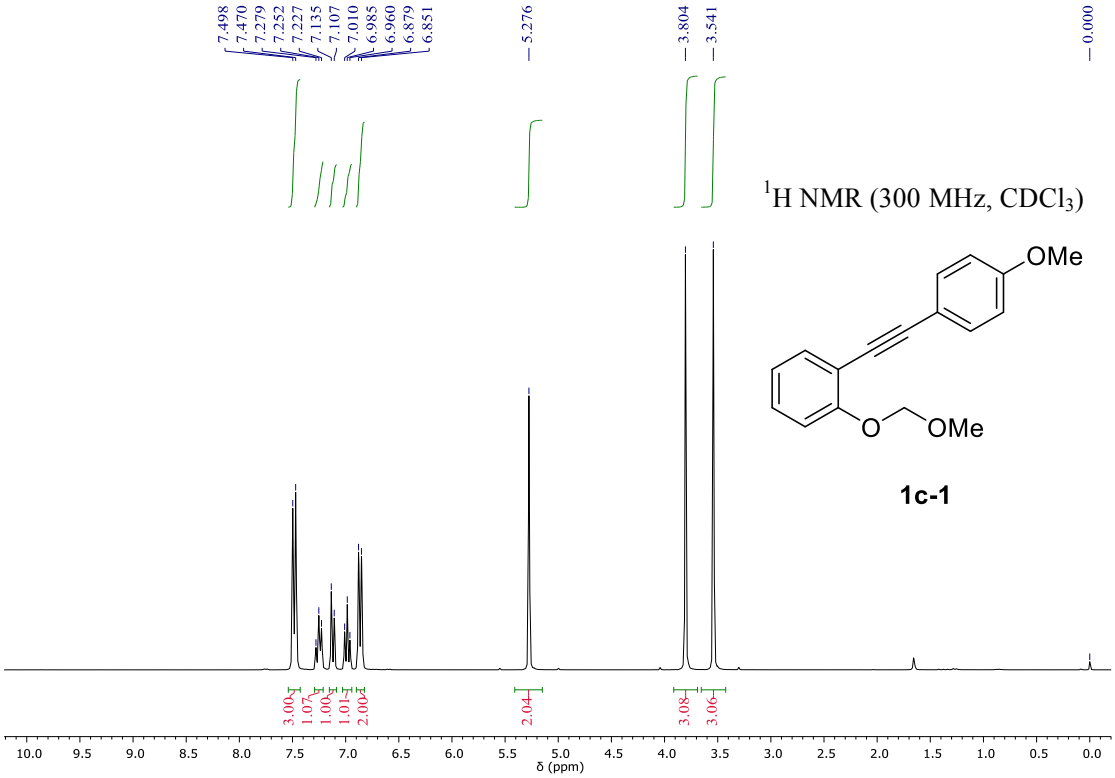


^{13}C NMR (75 MHz, $CDCl_3$)

1a-2

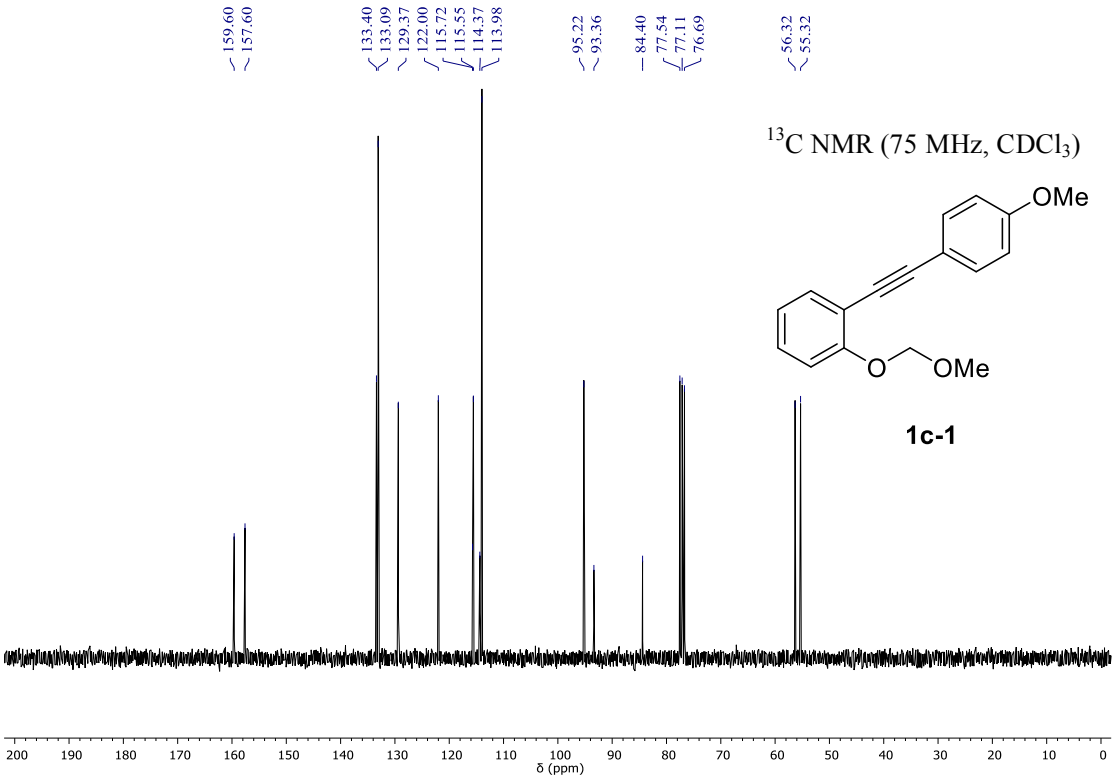

7.553
7.528
7.499
7.474
7.334
7.307
7.282
7.203
7.180
7.156
7.061
7.036
7.011
5.325
3.593
2.404
0.051
^{1}H NMR (300 MHz, $CDCl_3$)
Me
O
OMe
1b-1
3.03
1.19
3.07
1.06
2.02
3.00
3.03
δ (ppm)


157.68
138.26
133.44
131.49
129.44
129.05
121.97
120.53
115.62
114.32
95.25
93.51
85.05
77.44
77.02
76.60
56.27
21.47
^{13}C NMR (75 MHz, $CDCl_3$)
Me
O
OMe
1b-1
δ (ppm)



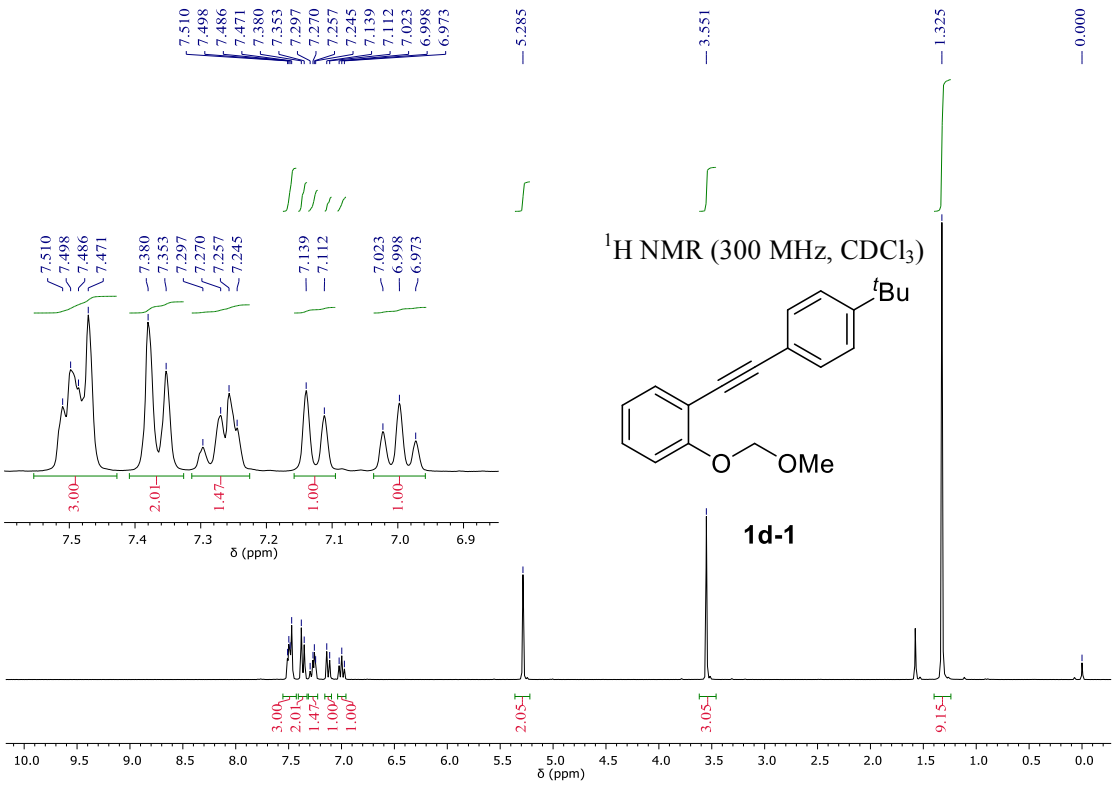
^{1}H NMR (300 MHz, $CDCl_3$)

1c-1



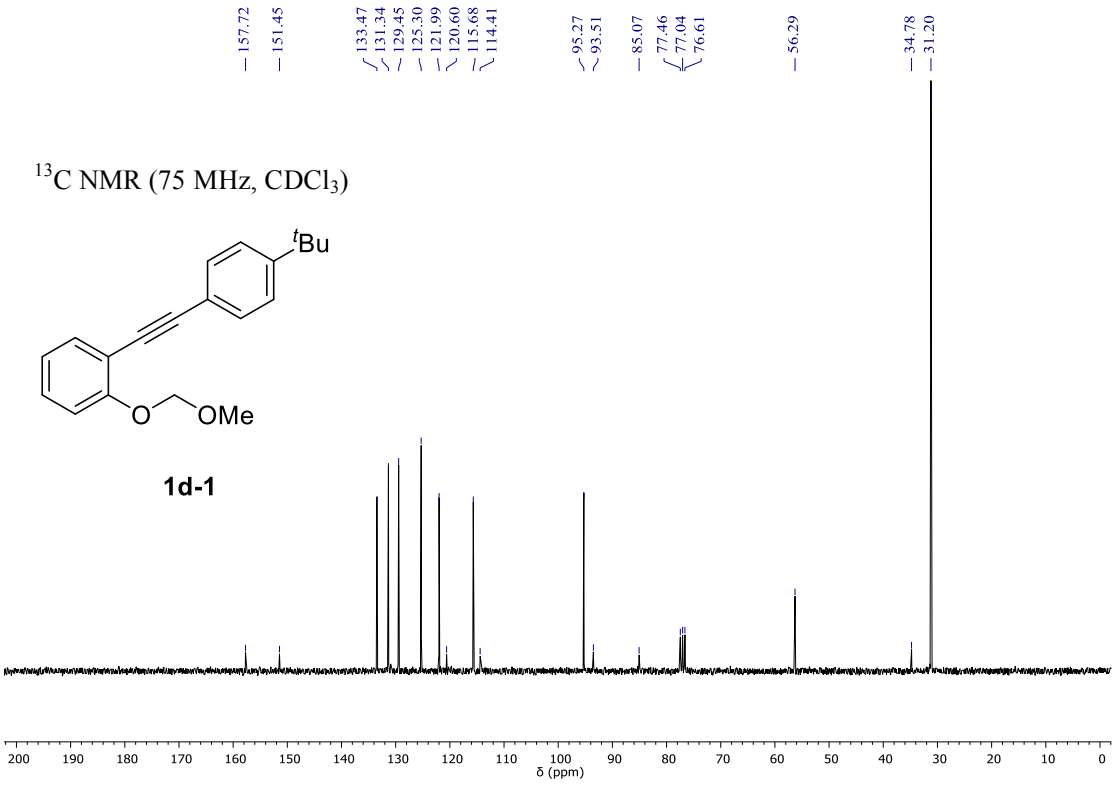
^{13}C NMR (75 MHz, $CDCl_3$)

1c-1



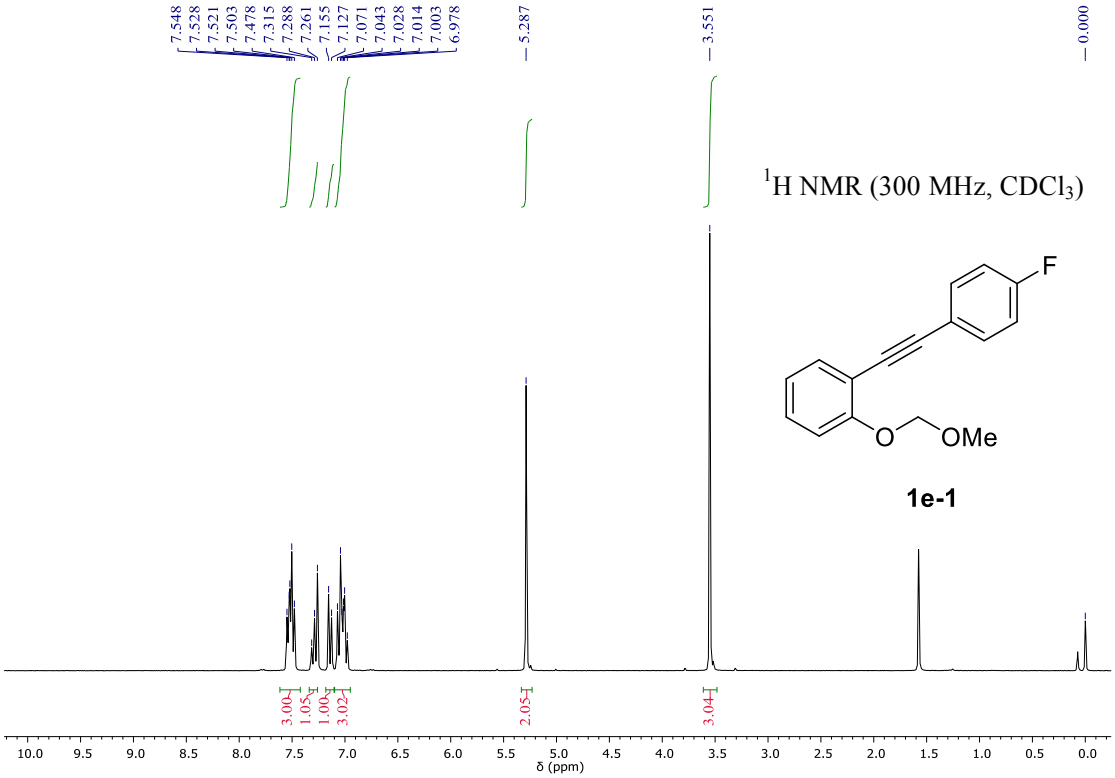
^{1}H NMR (300 MHz, $CDCl_3$)

1d-1



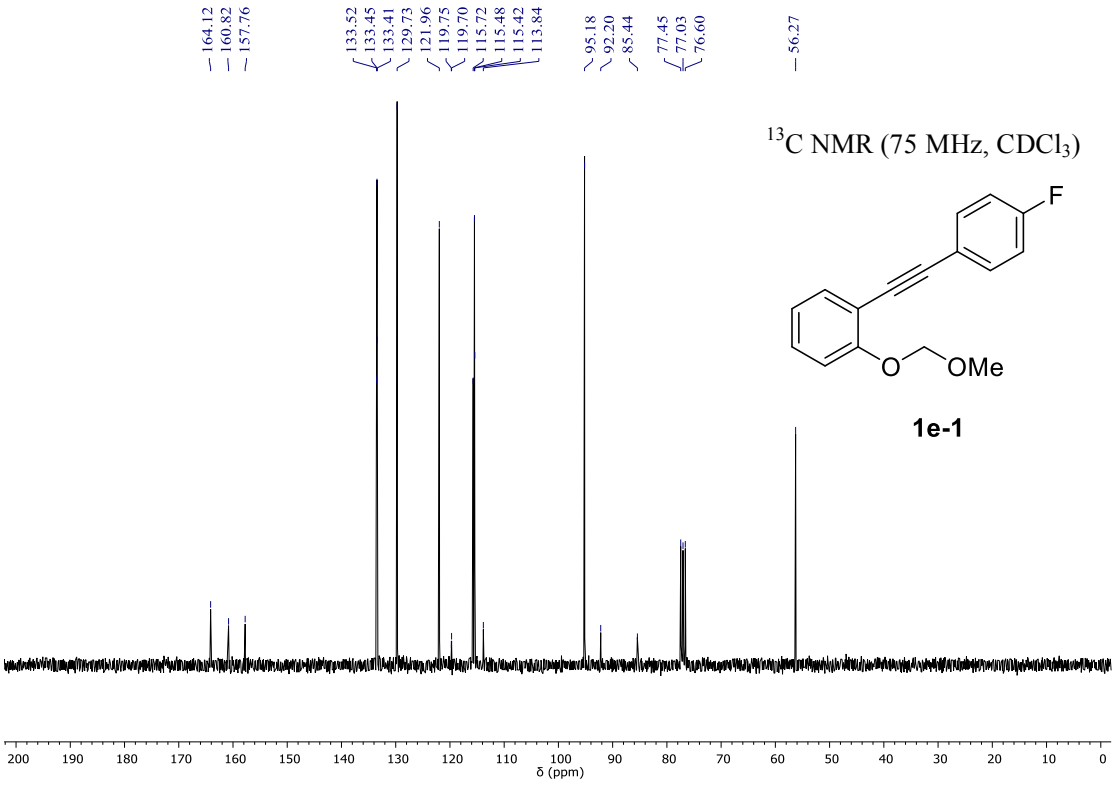
^{13}C NMR (75 MHz, $CDCl_3$)

1d-1



^{1}H NMR (300 MHz, $CDCl_3$)

1e-1

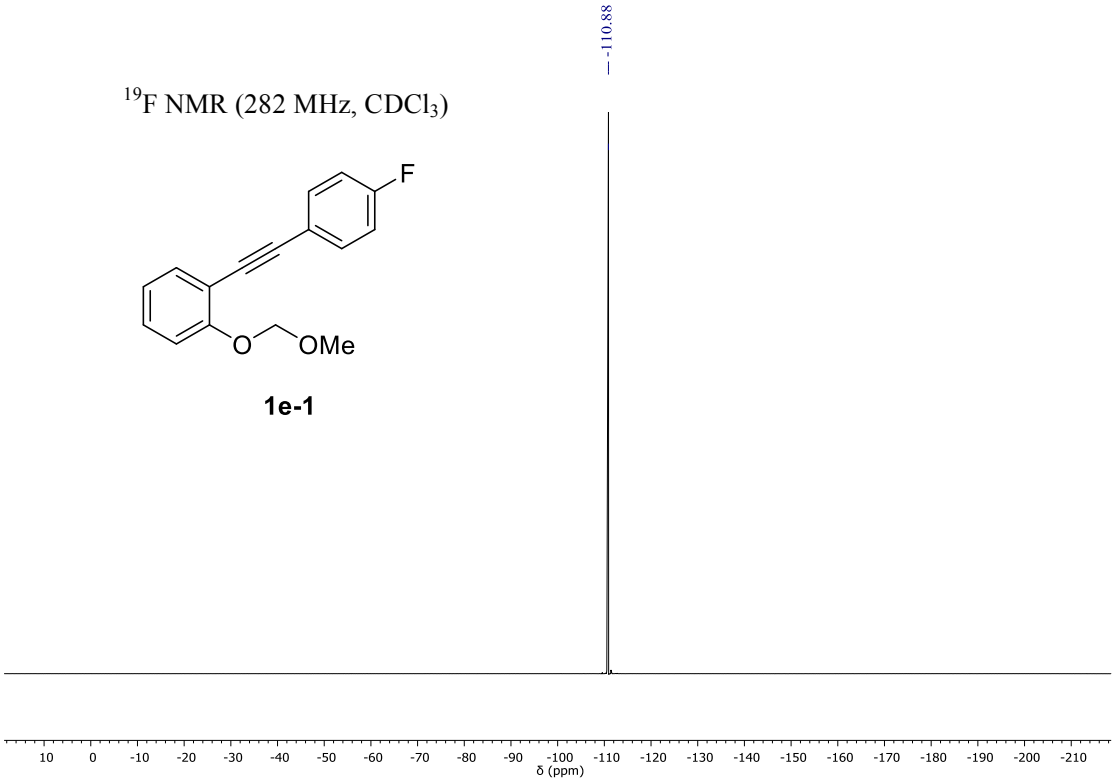


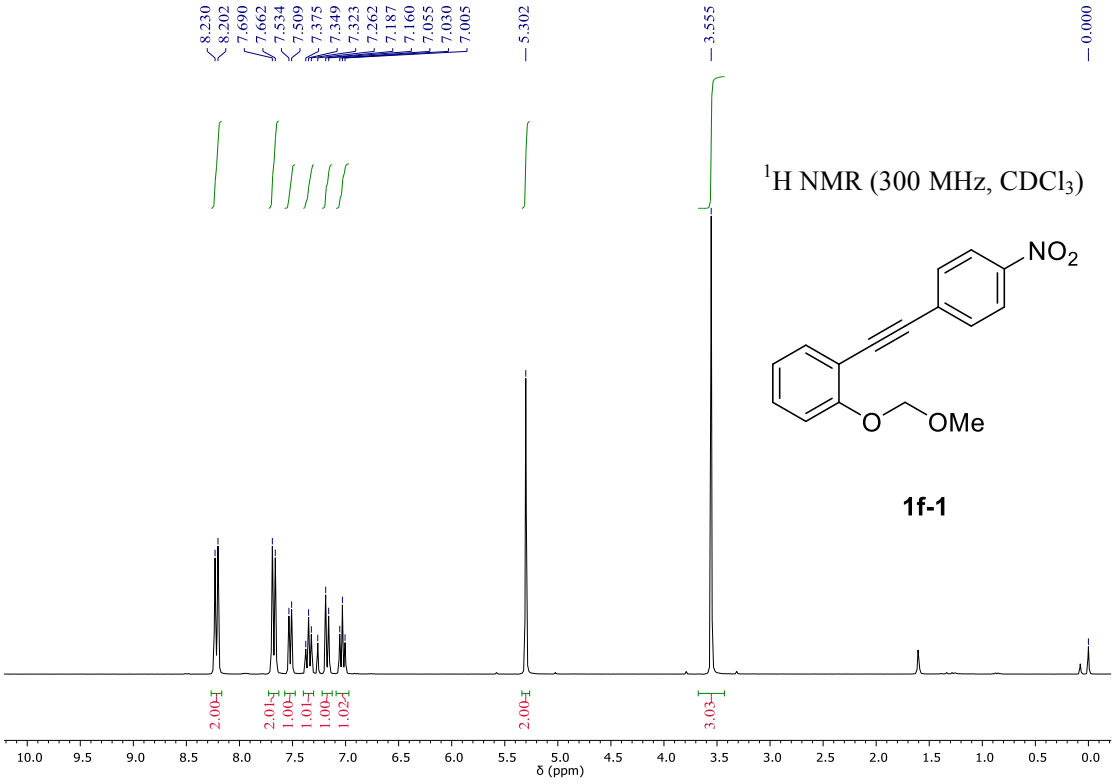
^{13}C NMR (75 MHz, $CDCl_3$)

1e-1

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

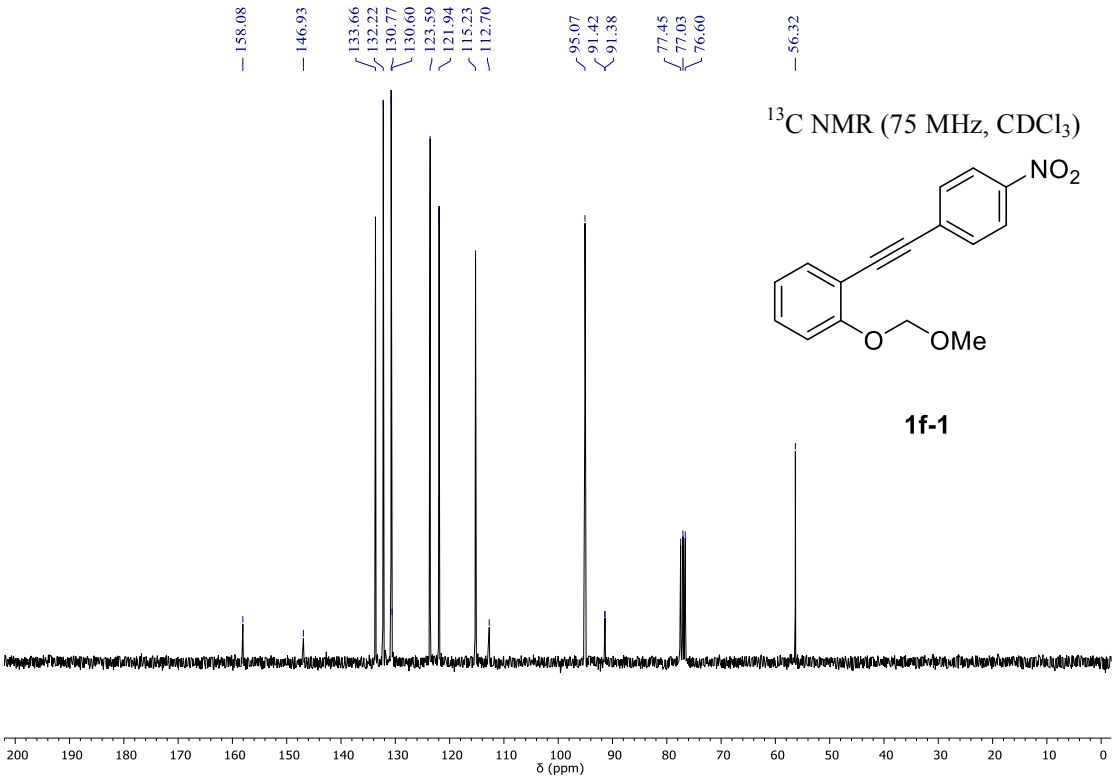
1e-1





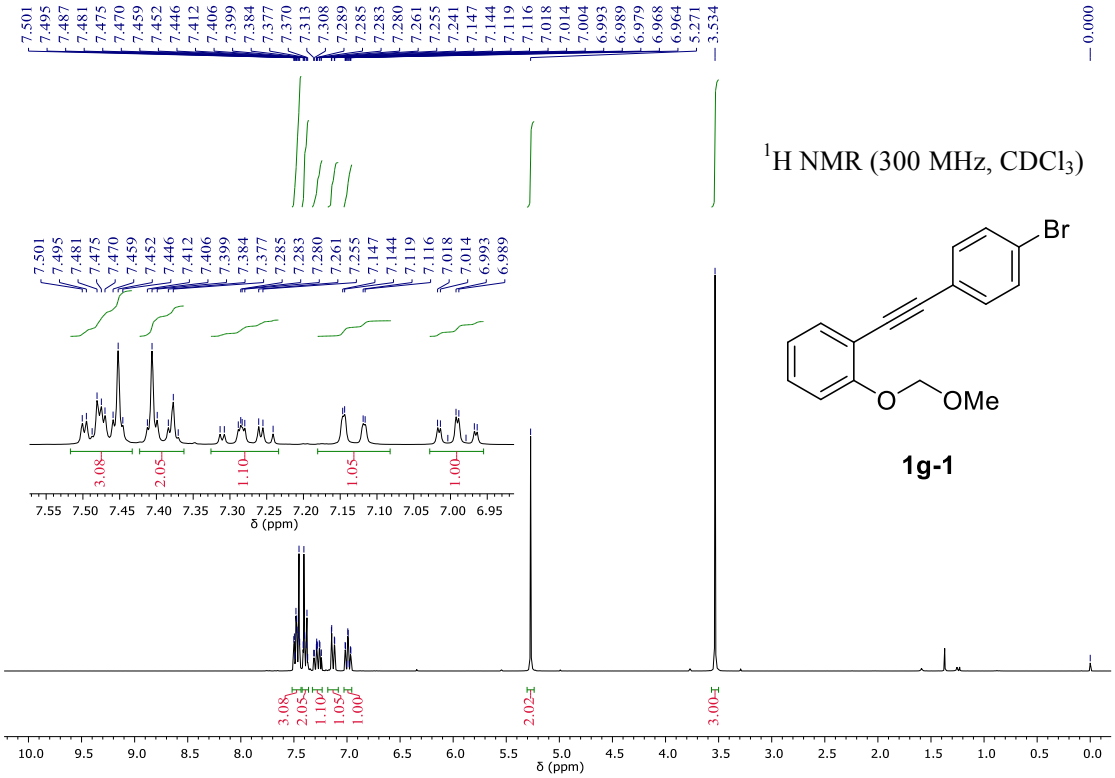
^{1}H NMR (300 MHz, $CDCl_3$)

1f-1

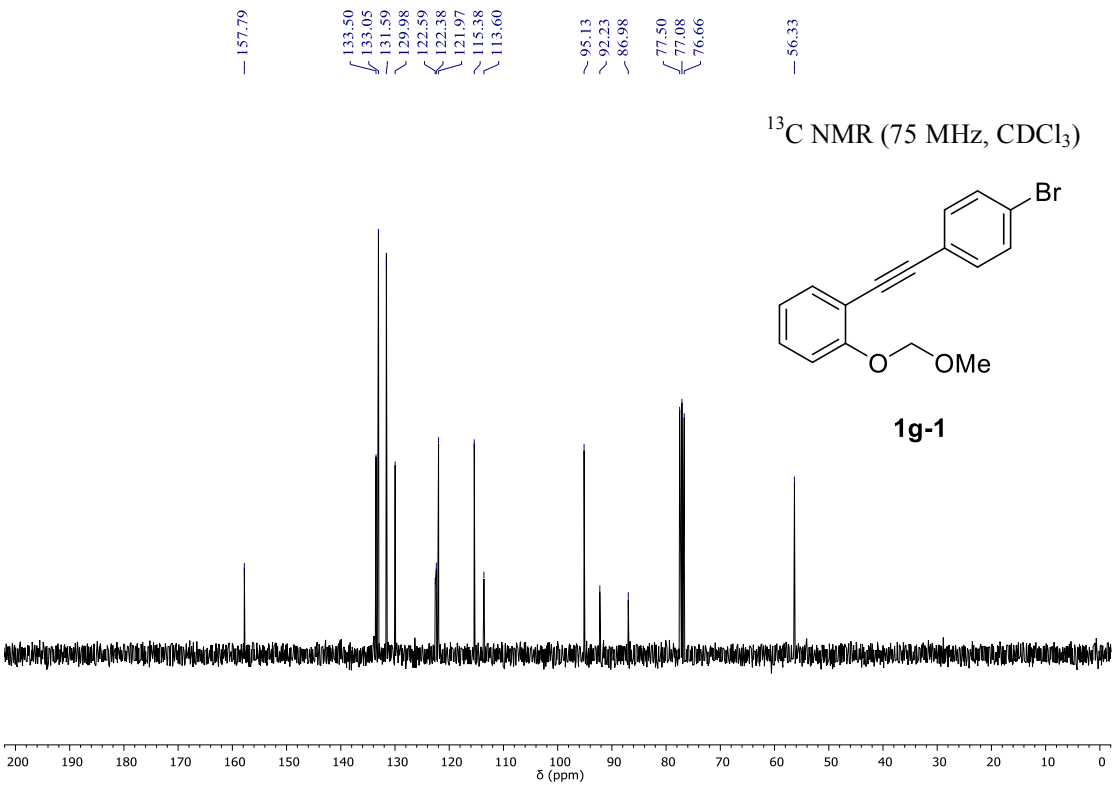


^{13}C NMR (75 MHz, $CDCl_3$)

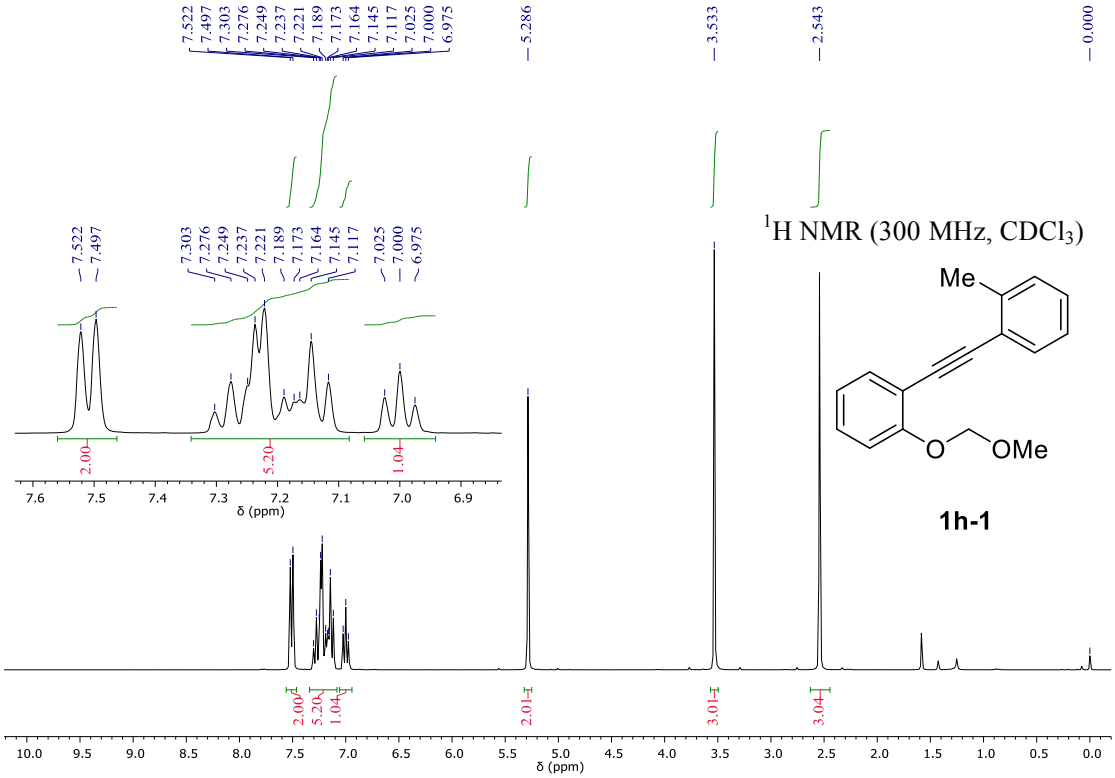
1f-1



^{1}H NMR (300 MHz, $CDCl_3$)

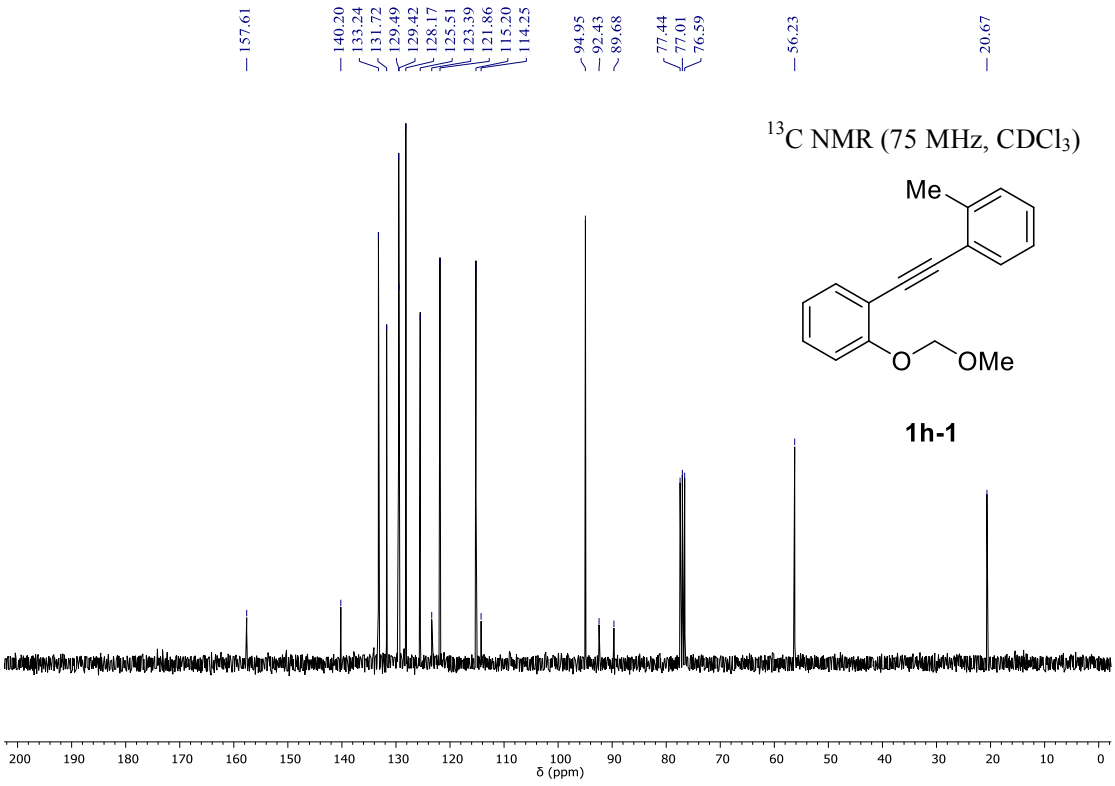


^{13}C NMR (75 MHz, $CDCl_3$)



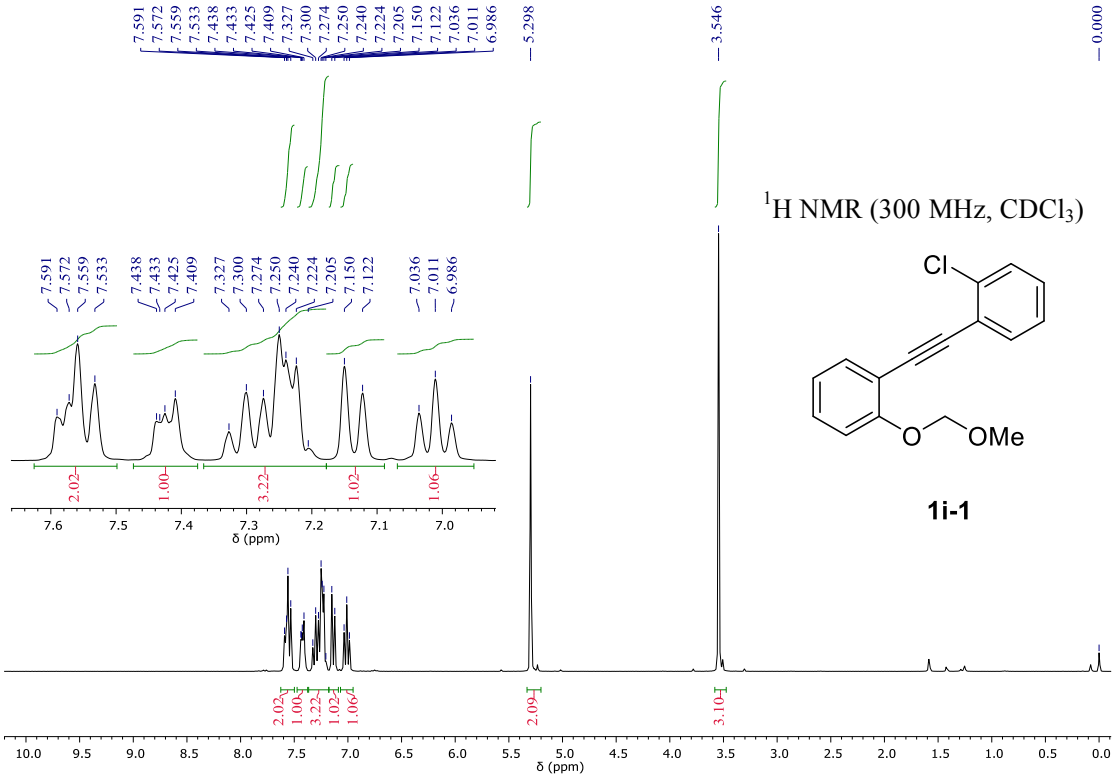
^{1}H NMR (300 MHz, $CDCl_3$)

1h-1



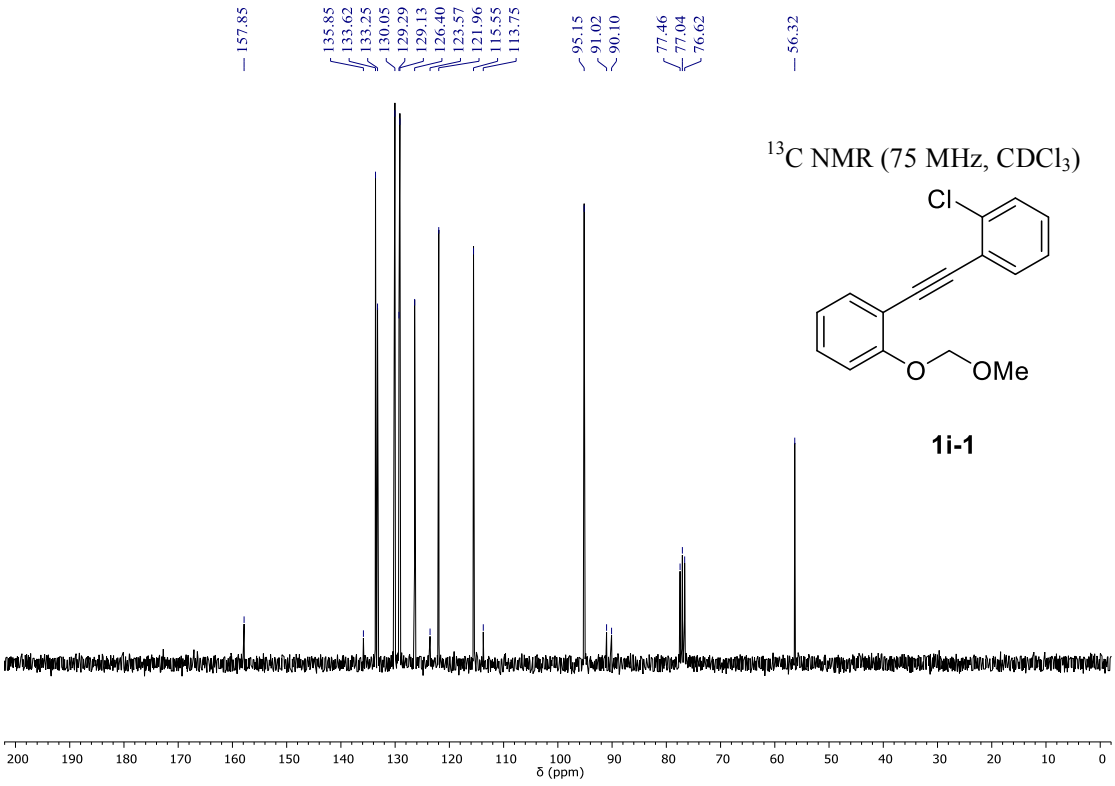
^{13}C NMR (75 MHz, $CDCl_3$)

1h-1



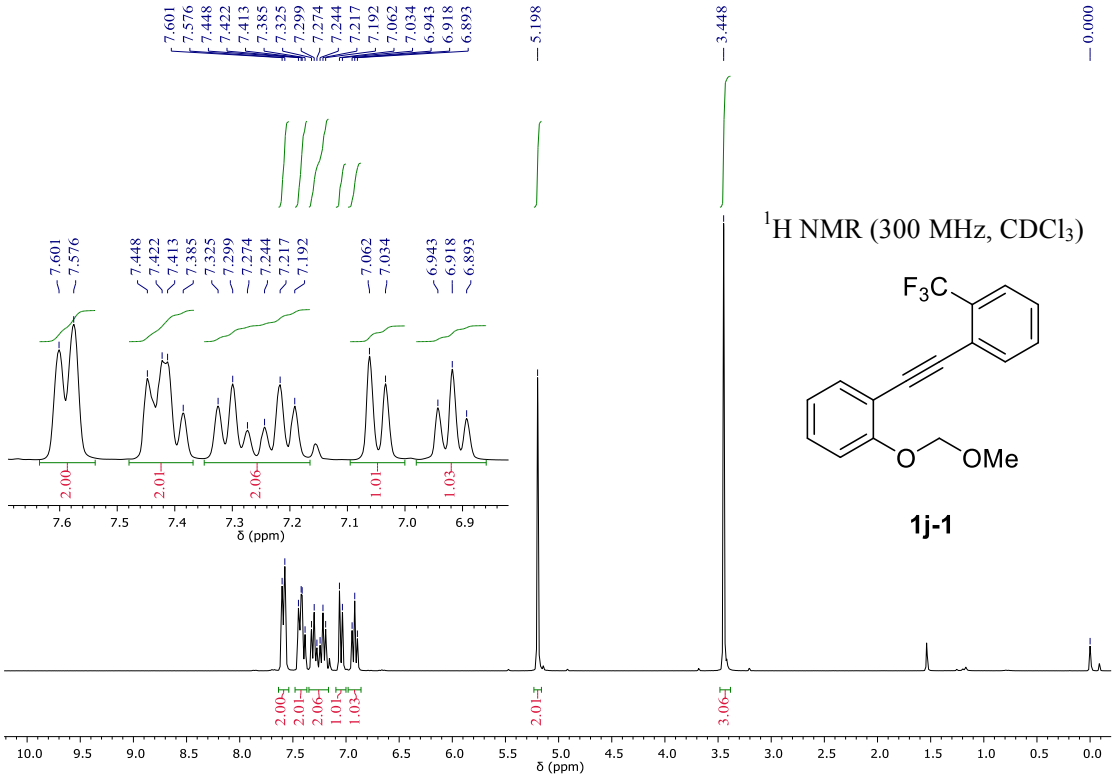
^{1}H NMR (300 MHz, $CDCl_3$)

1i-1



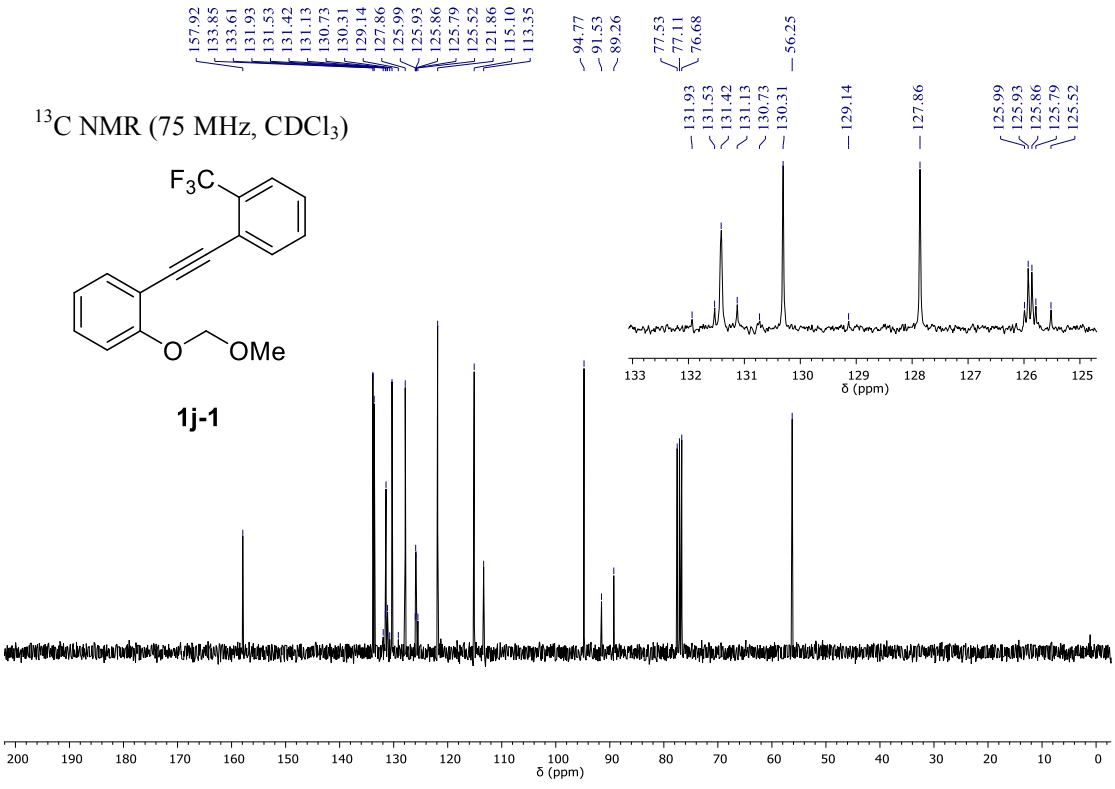
^{13}C NMR (75 MHz, $CDCl_3$)

1i-1



^{1}H NMR (300 MHz, $CDCl_3$)

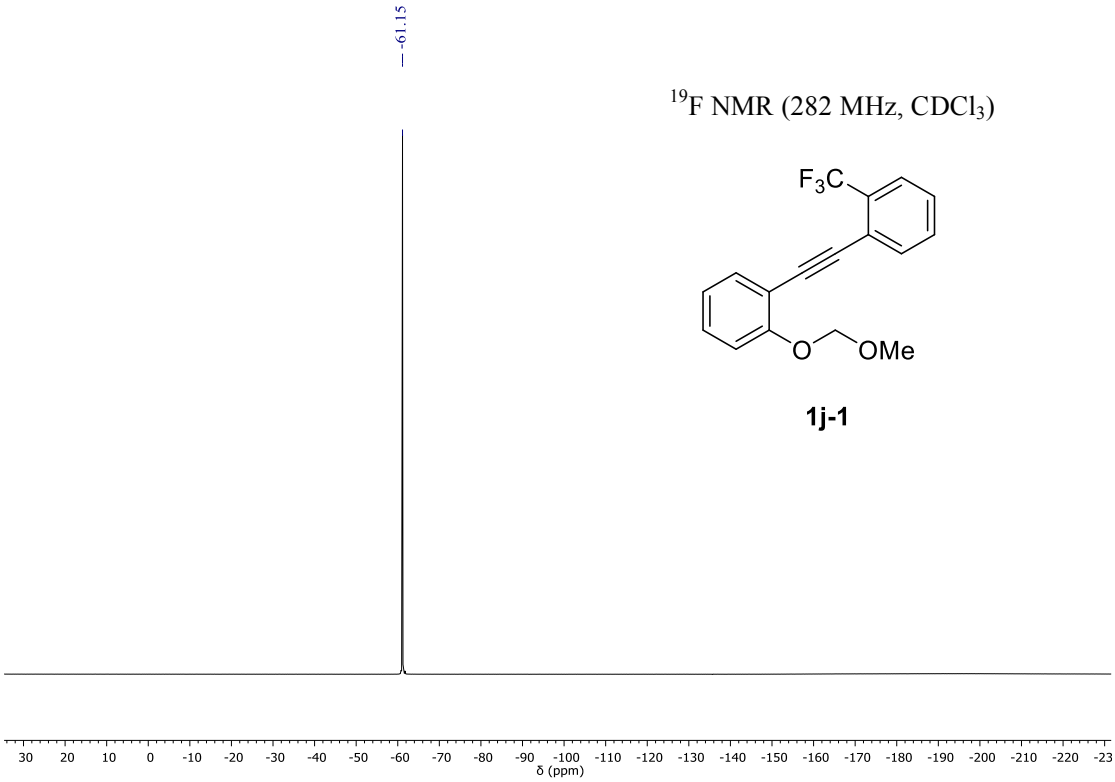
1j-1



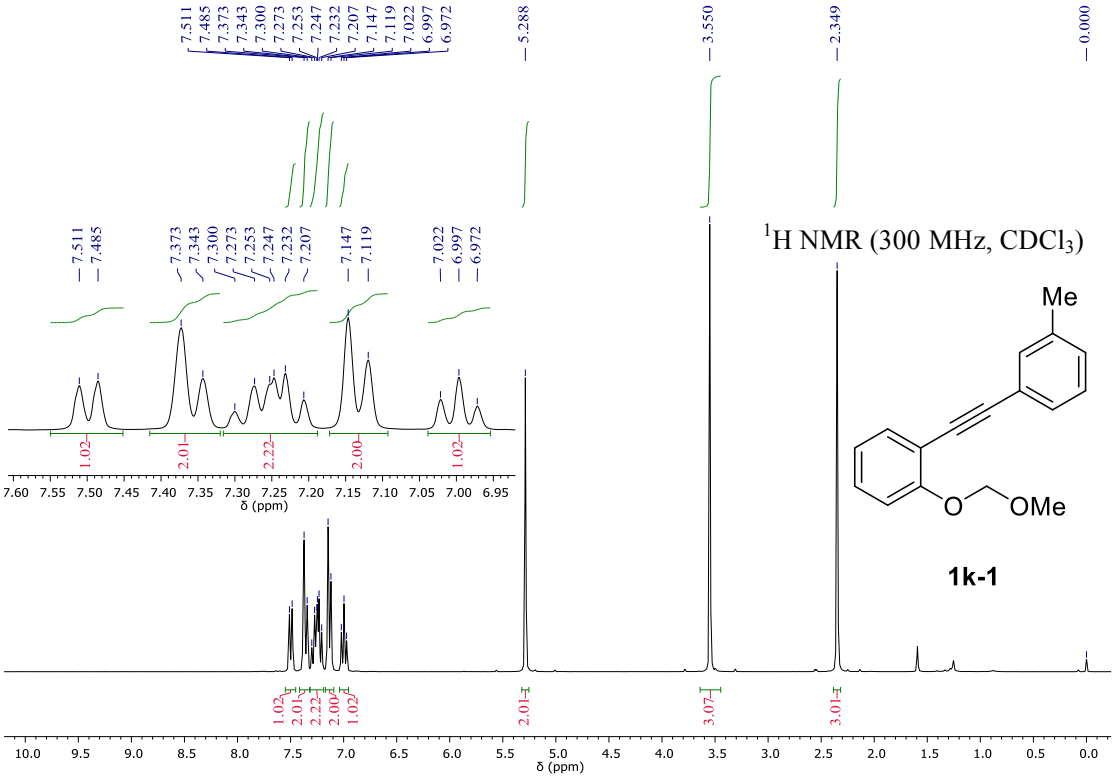
^{13}C NMR (75 MHz, $CDCl_3$)

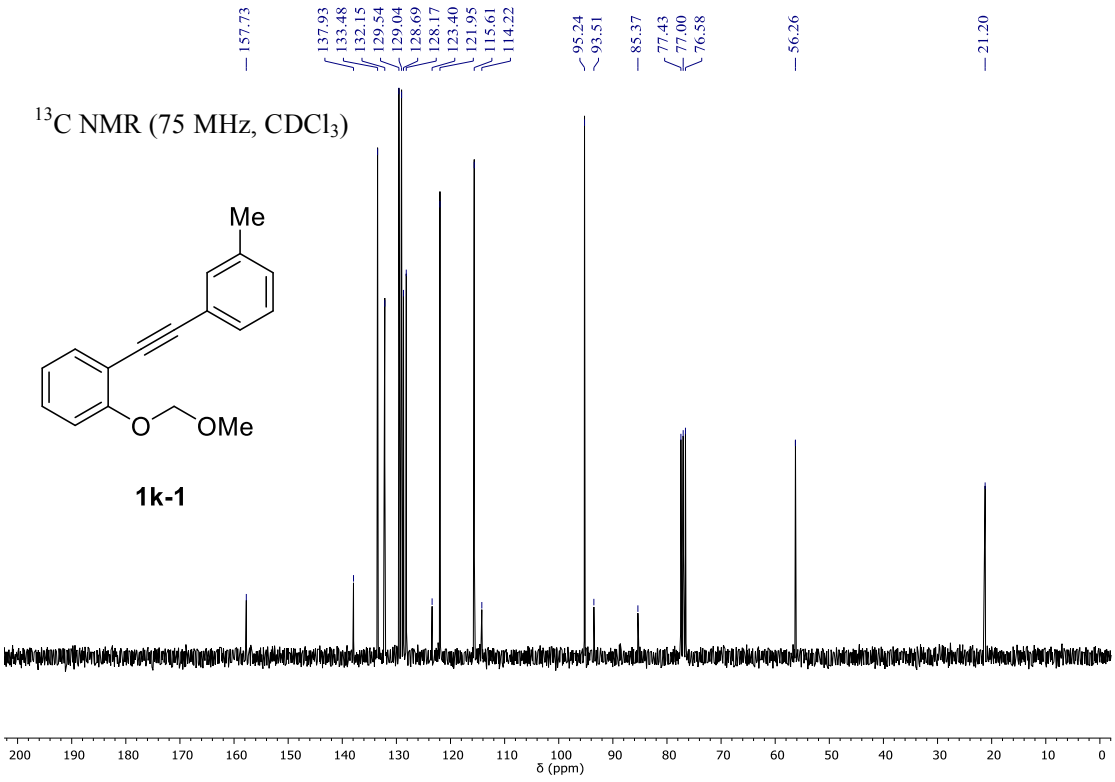
1j-1

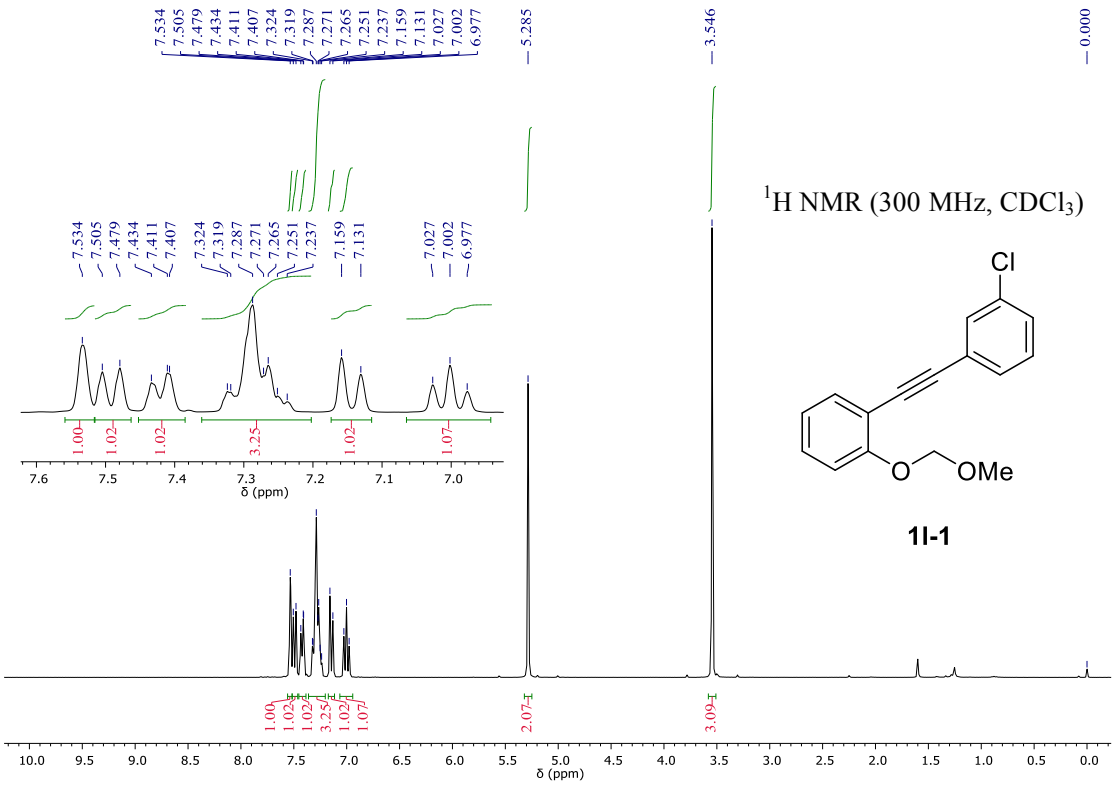
^{19}F NMR (282 MHz, $CDCl_3$)

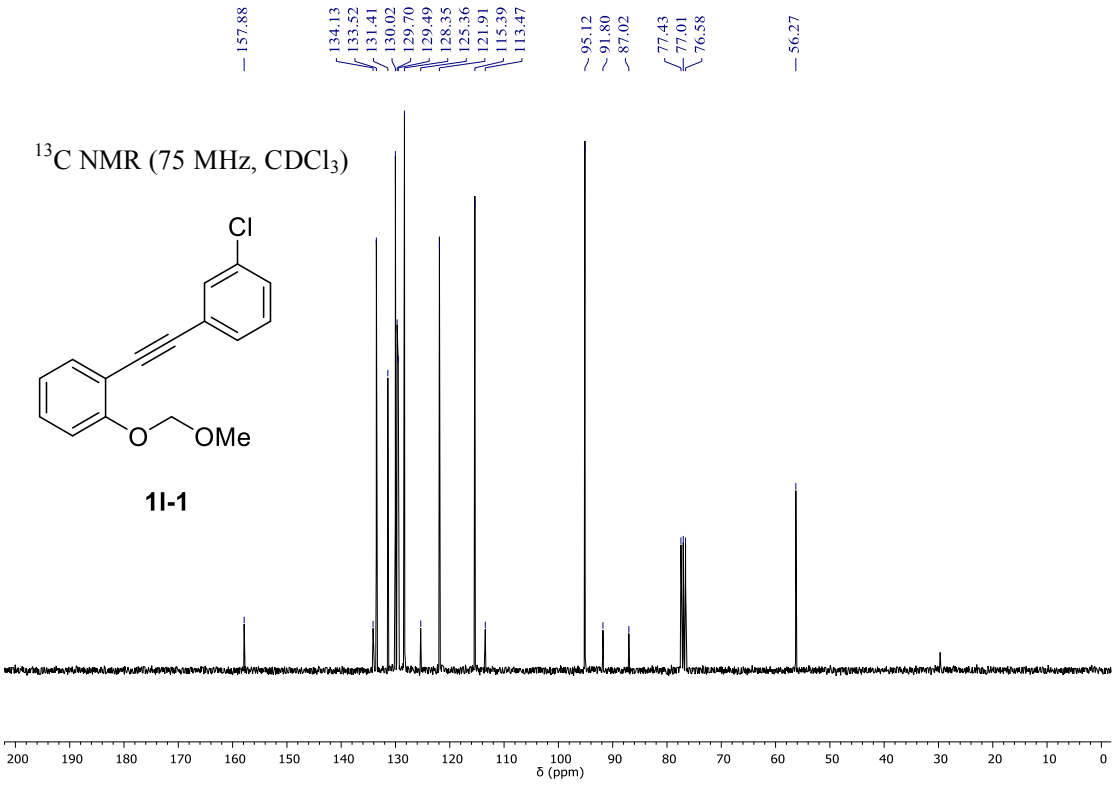


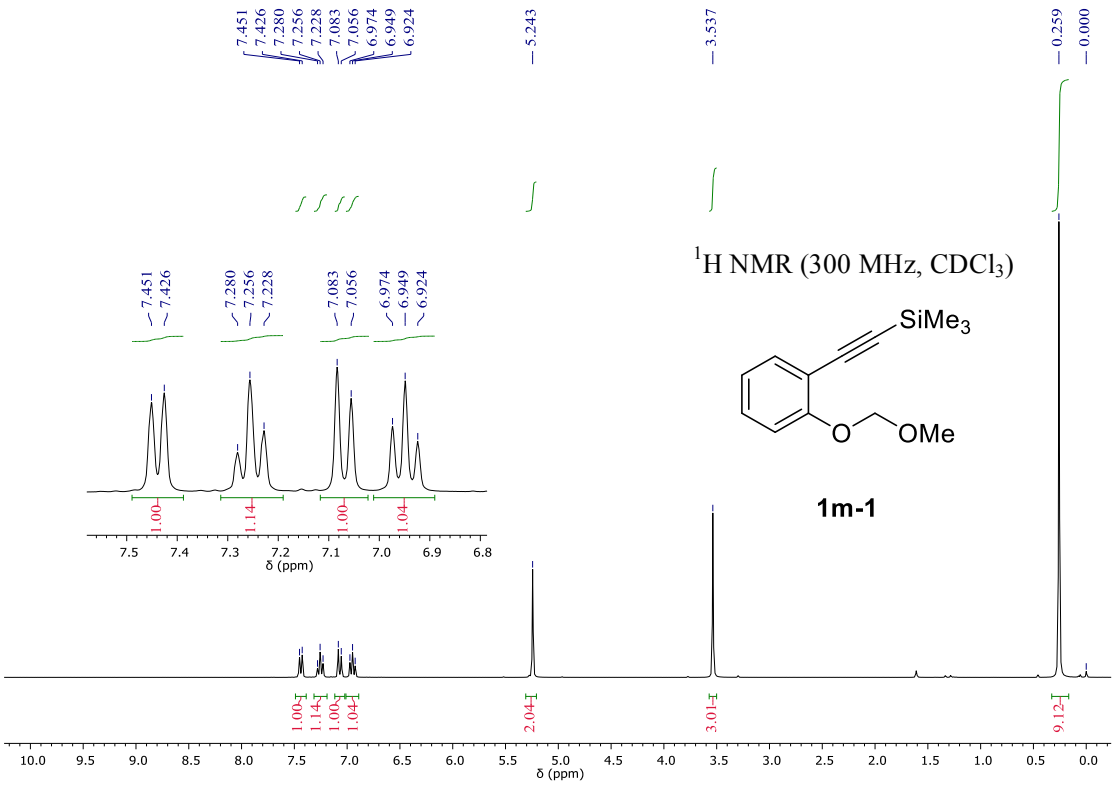
1j-1

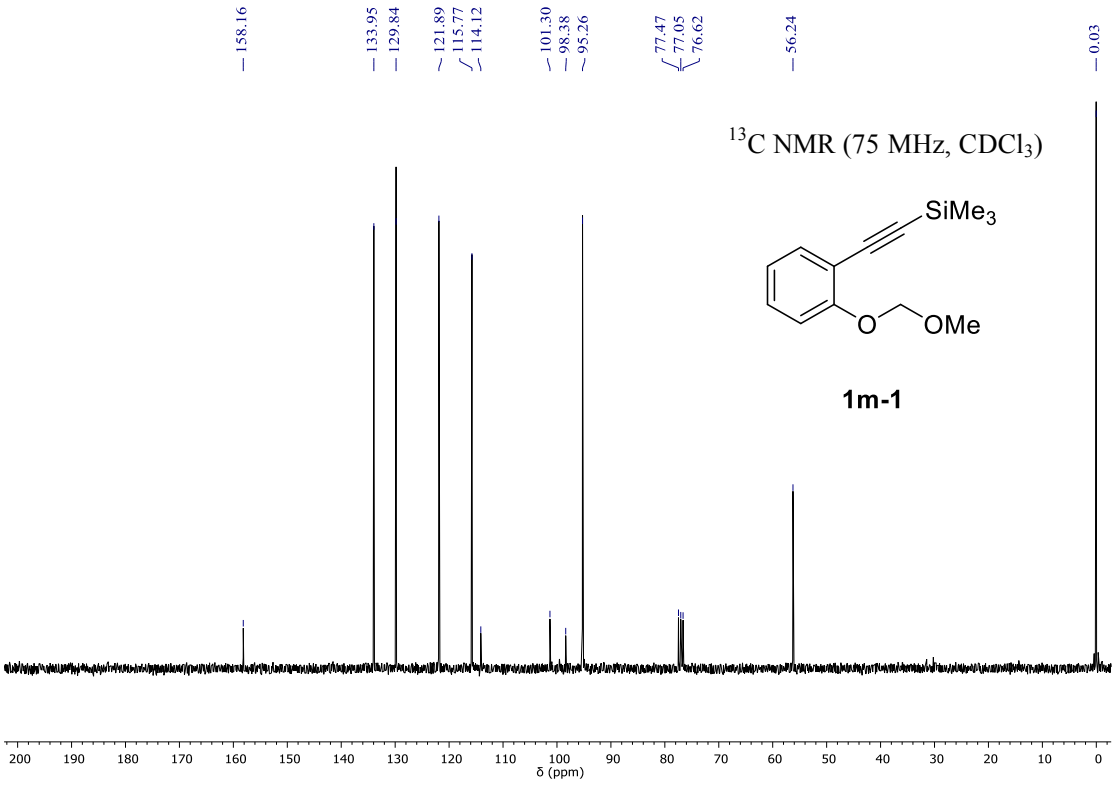

7.511
7.485
7.373
7.343
7.300
7.273
7.253
7.247
7.232
7.207
7.147
7.119
7.022
6.997
6.972
5.288
3.550
2.349
0.000
1.02
2.01
2.22
2.00
1.02
δ (ppm)
^{1}H NMR (300 MHz, CDCl$_3$)
Me
O
OMe
1k-1

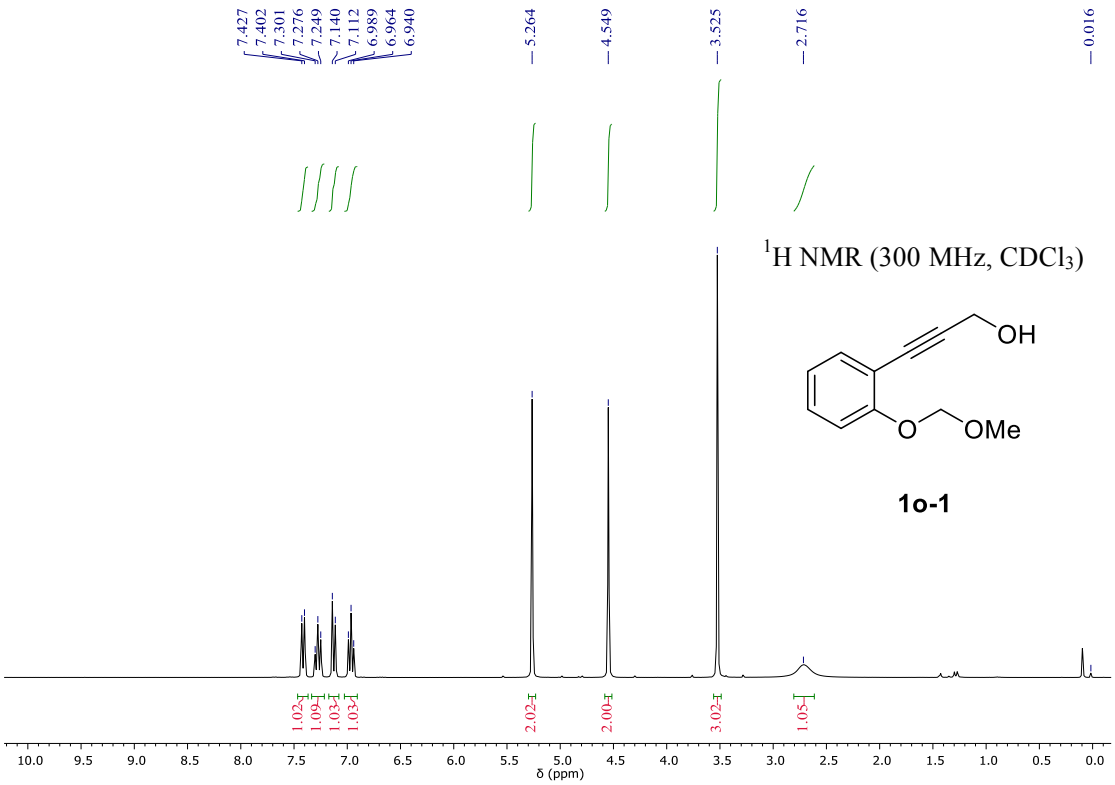

157.73
137.93
133.48
132.15
129.54
129.04
128.69
128.17
123.40
121.95
115.61
114.22
95.24
93.51
85.37
77.43
77.00
76.58
56.26
21.20
δ (ppm)
^{13}C NMR (75 MHz, CDCl$_3$)
Me
O
OMe
1k-1


7.534
7.505
7.479
7.434
7.411
7.407
7.324
7.319
7.287
7.271
7.265
7.251
7.237
7.159
7.131
7.027
7.002
6.977
5.285
3.546
0.000
1.00
1.02
1.02
3.25
1.02
1.07
2.07
3.09
δ (ppm)
^{1}H NMR (300 MHz, CDCl$_3$)
Cl
O
OMe
1l-1


157.88
134.13
133.52
131.41
130.02
129.70
129.49
128.35
125.36
121.91
115.39
113.47
95.12
91.80
87.02
77.43
77.01
76.58
56.27
δ (ppm)
^{13}C NMR (75 MHz, CDCl$_3$)
Cl
O
OMe
1l-1

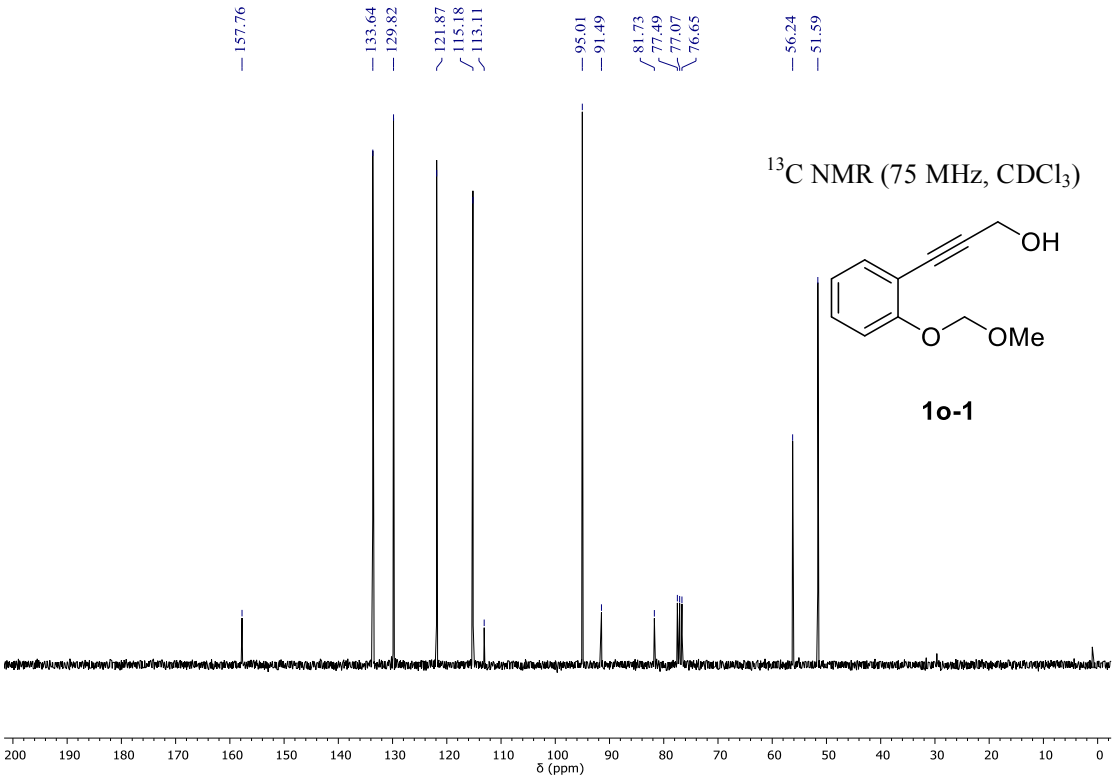

7.451
7.426
7.280
7.256
7.228
7.083
7.056
6.974
6.949
6.924
5.243
3.537
0.259
0.000
^{1}H NMR (300 MHz, $CDCl_3$)
SiMe$_3$
O
OMe
1m-1
δ (ppm)


158.16
133.95
129.84
121.89
115.77
114.12
101.30
98.38
95.26
77.47
77.05
76.62
56.24
0.03
^{13}C NMR (75 MHz, $CDCl_3$)
SiMe$_3$
O
OMe
1m-1
δ (ppm)



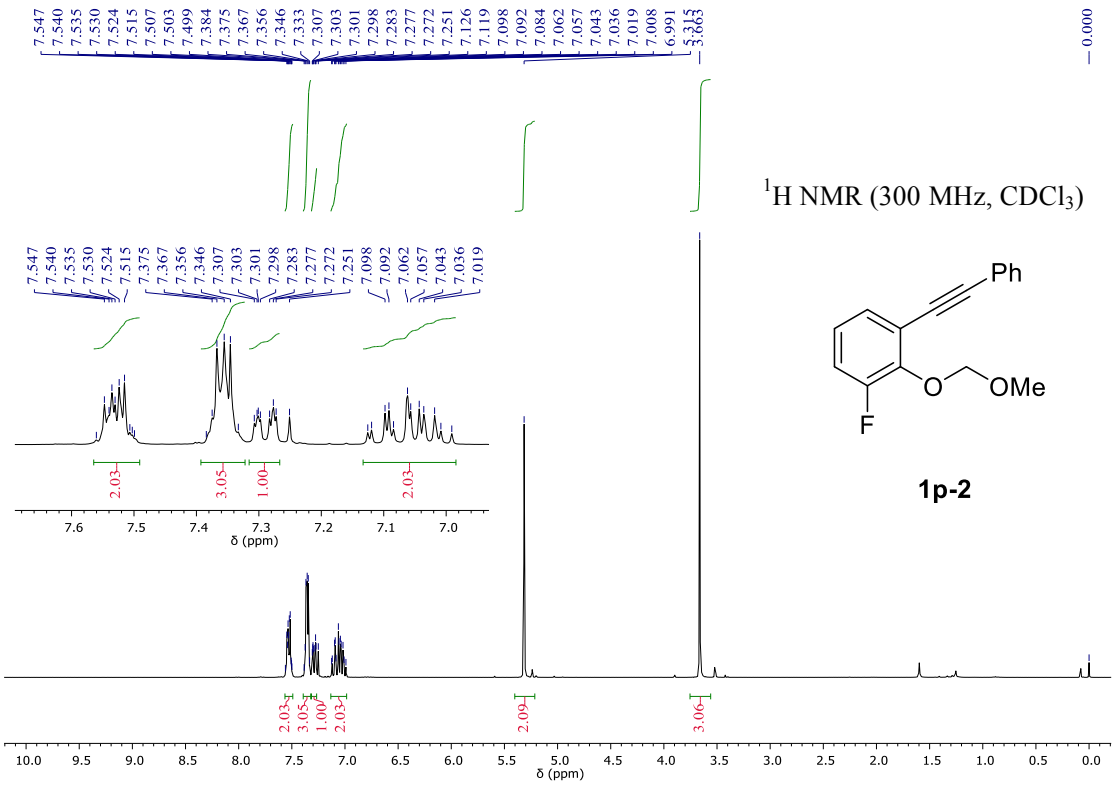
^{1}H NMR (300 MHz, $CDCl_3$)

1o-1



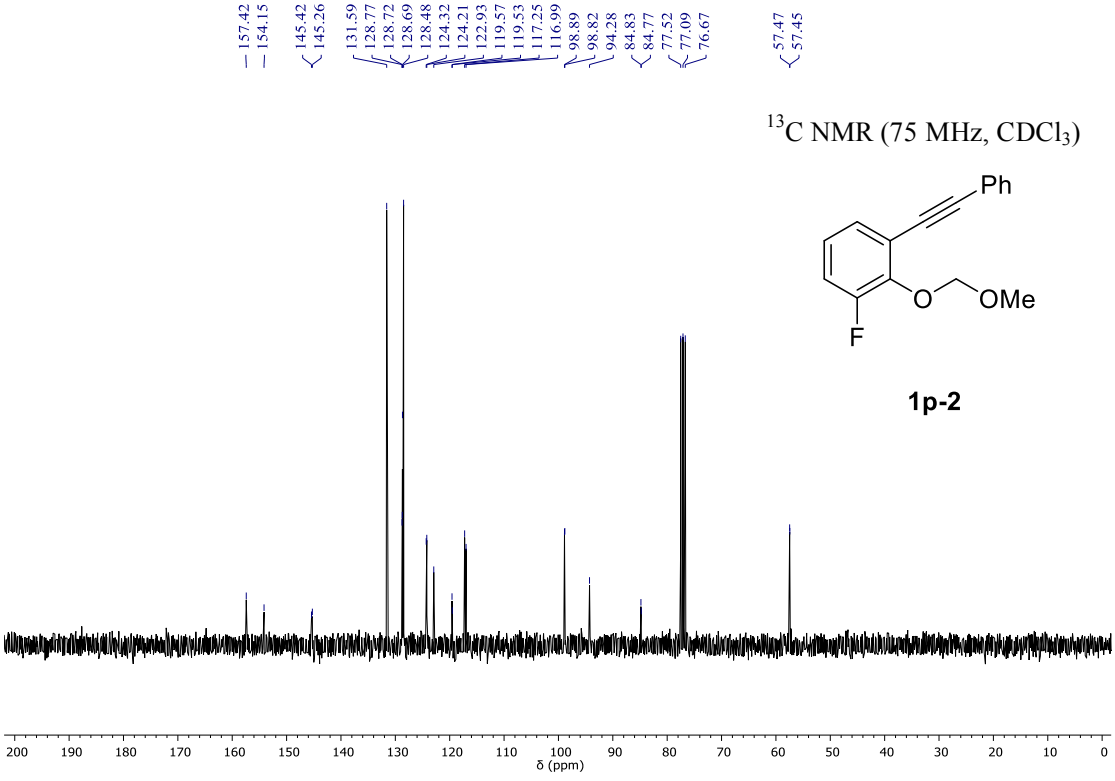
^{13}C NMR (75 MHz, $CDCl_3$)

1o-1



^{1}H NMR (300 MHz, $CDCl_3$)

1p-2

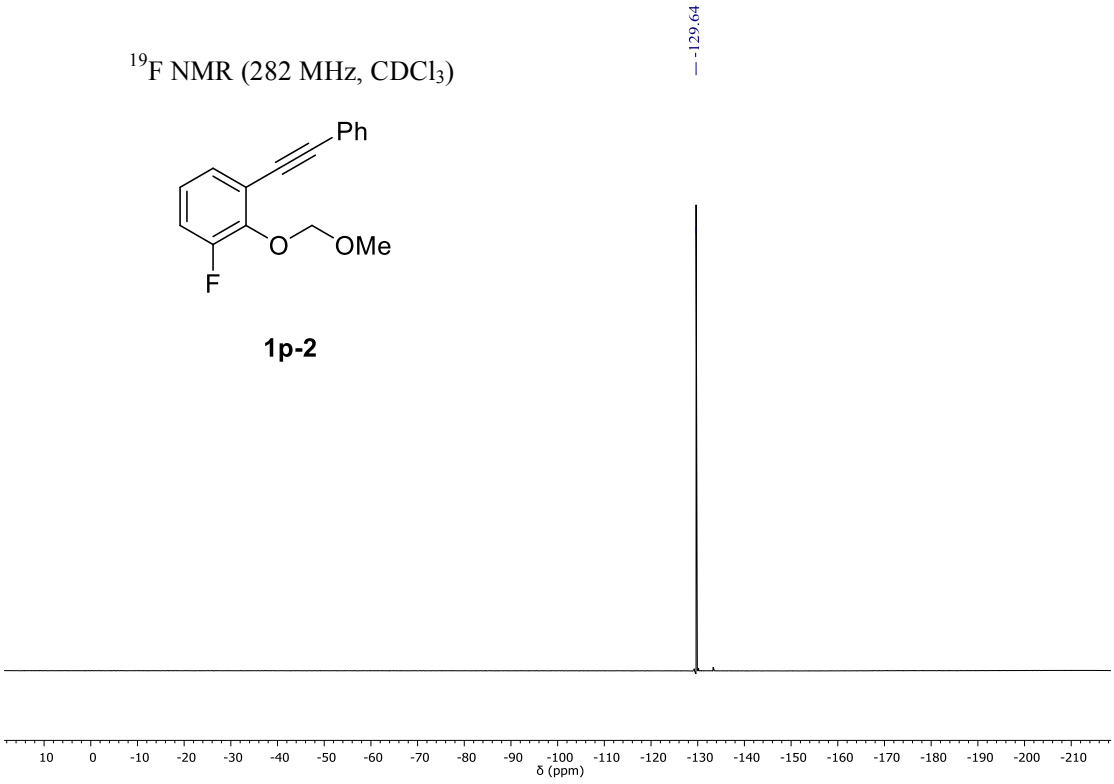


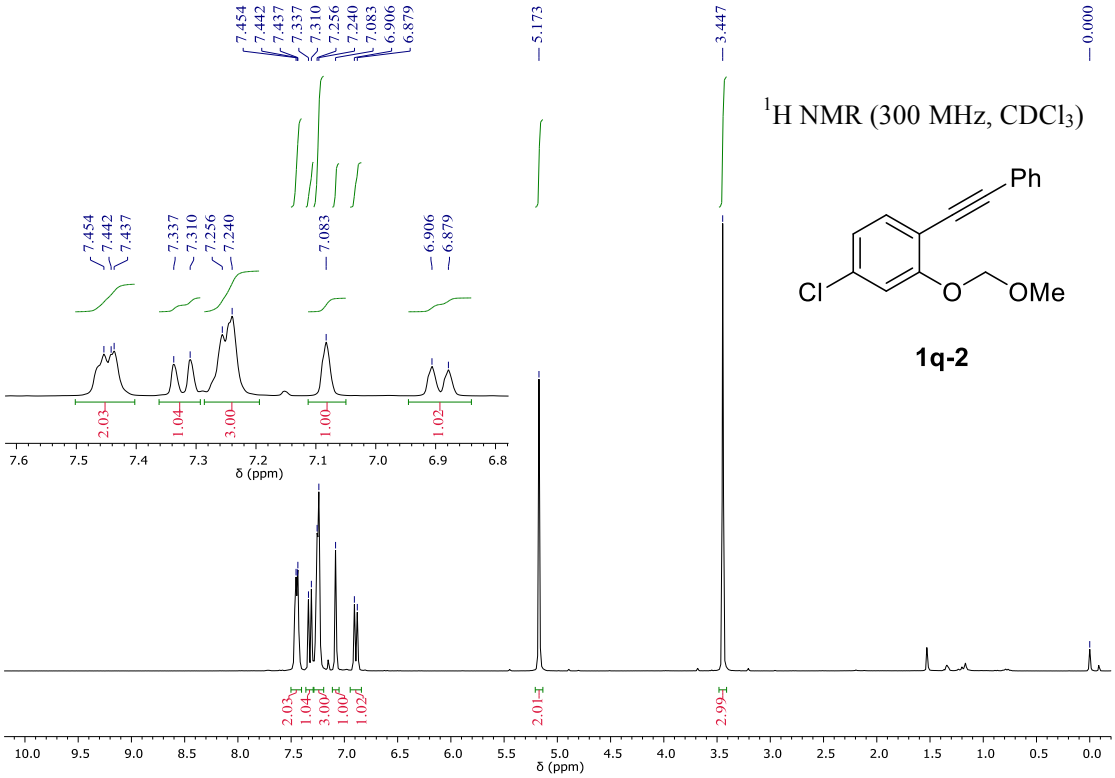
^{13}C NMR (75 MHz, $CDCl_3$)

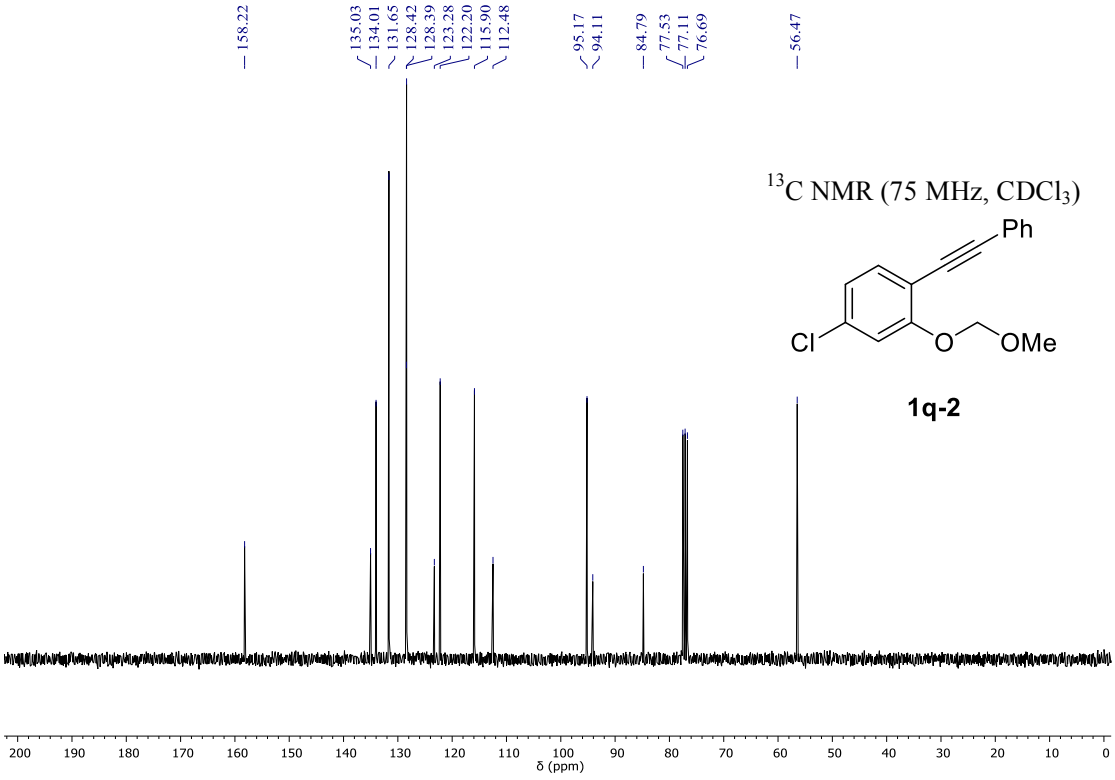
1p-2

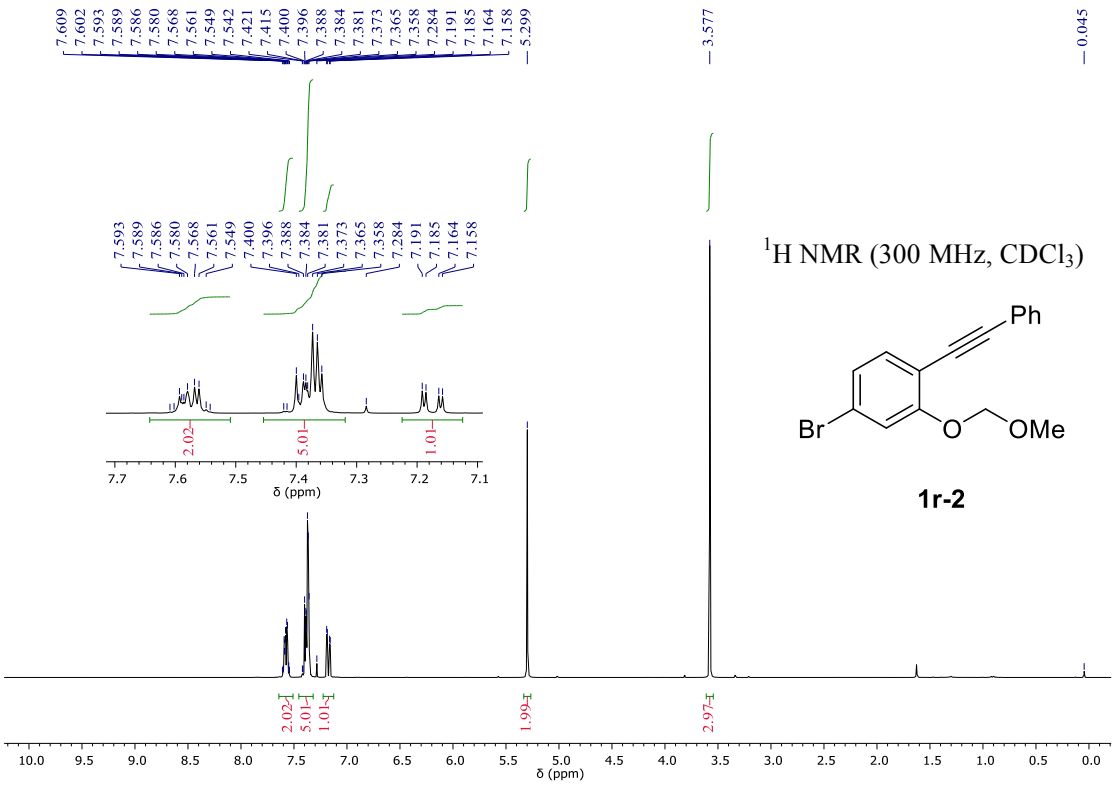
^{19}F NMR (282 MHz, $CDCl_3$)

1p-2



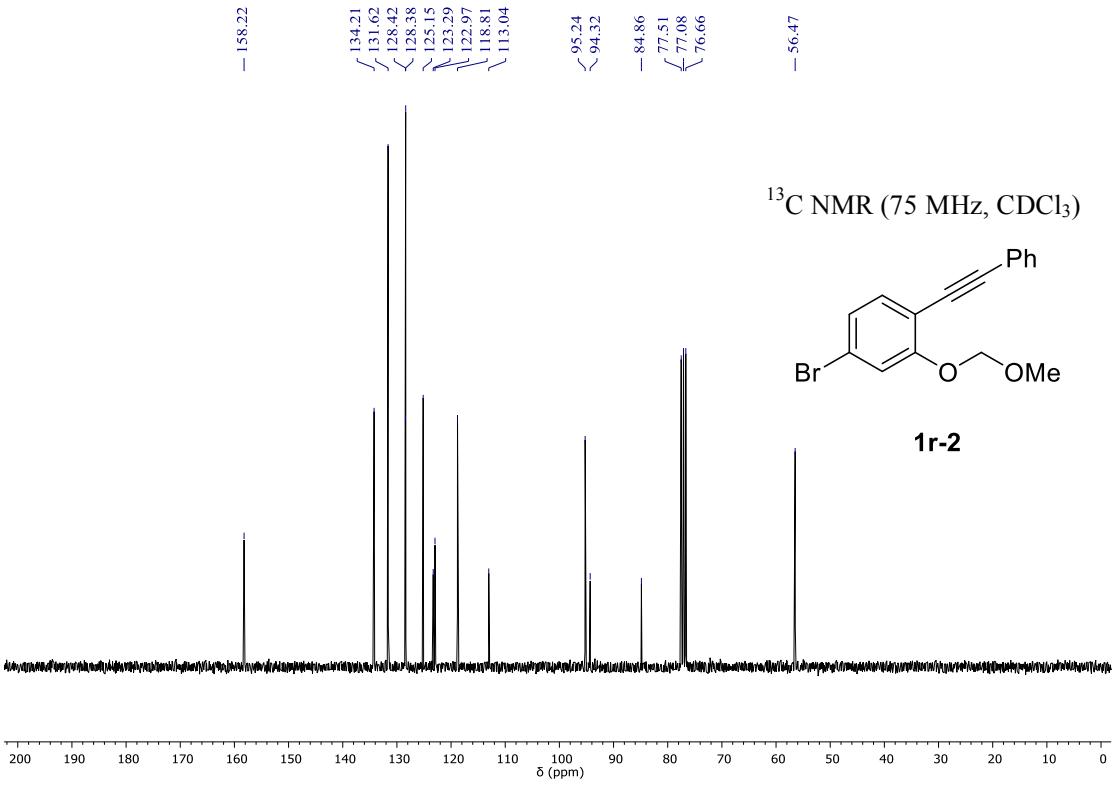

7.454
7.442
7.437
7.337
7.310
7.256
7.240
7.083
6.906
6.879
5.173
3.447
0.000
^{1}H NMR (300 MHz, $CDCl_3$)
Ph
Cl
O
OMe
1q-2
δ (ppm)


158.22
135.03
134.01
131.65
128.42
128.39
123.28
122.20
115.90
112.48
95.17
94.11
84.79
77.53
77.11
76.69
56.47
^{13}C NMR (75 MHz, $CDCl_3$)
Ph
Cl
O
OMe
1q-2
δ (ppm)



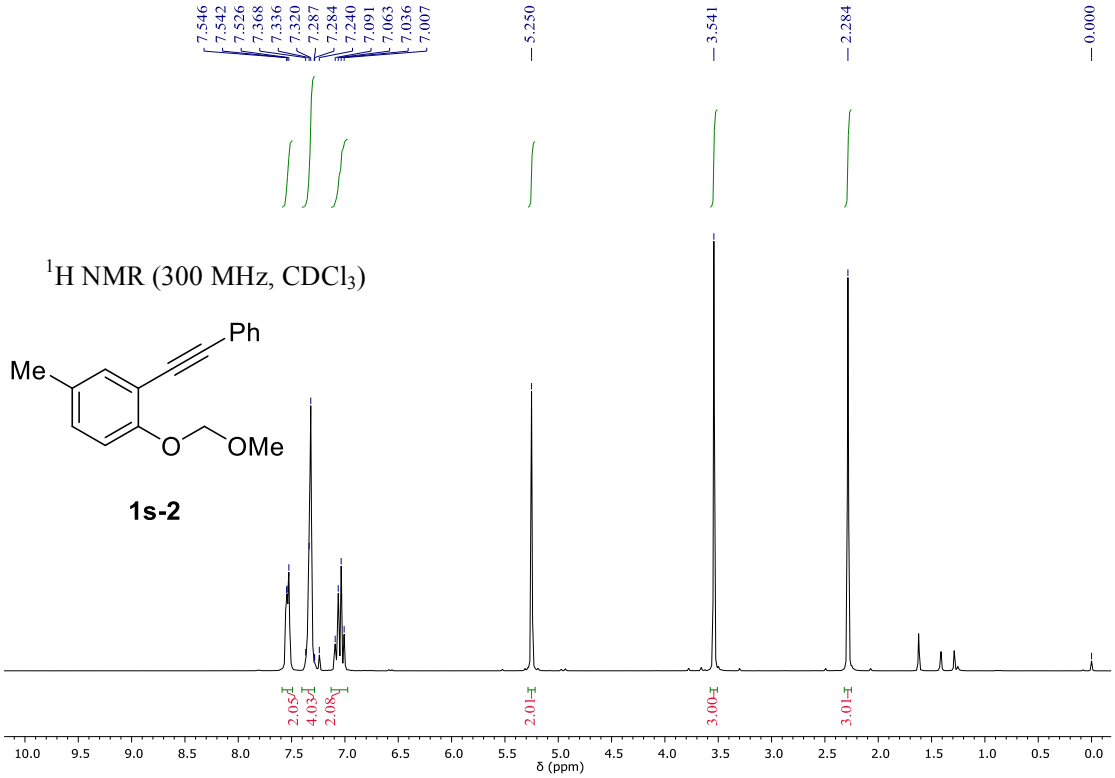
^{1}H NMR (300 MHz, $CDCl_3$)

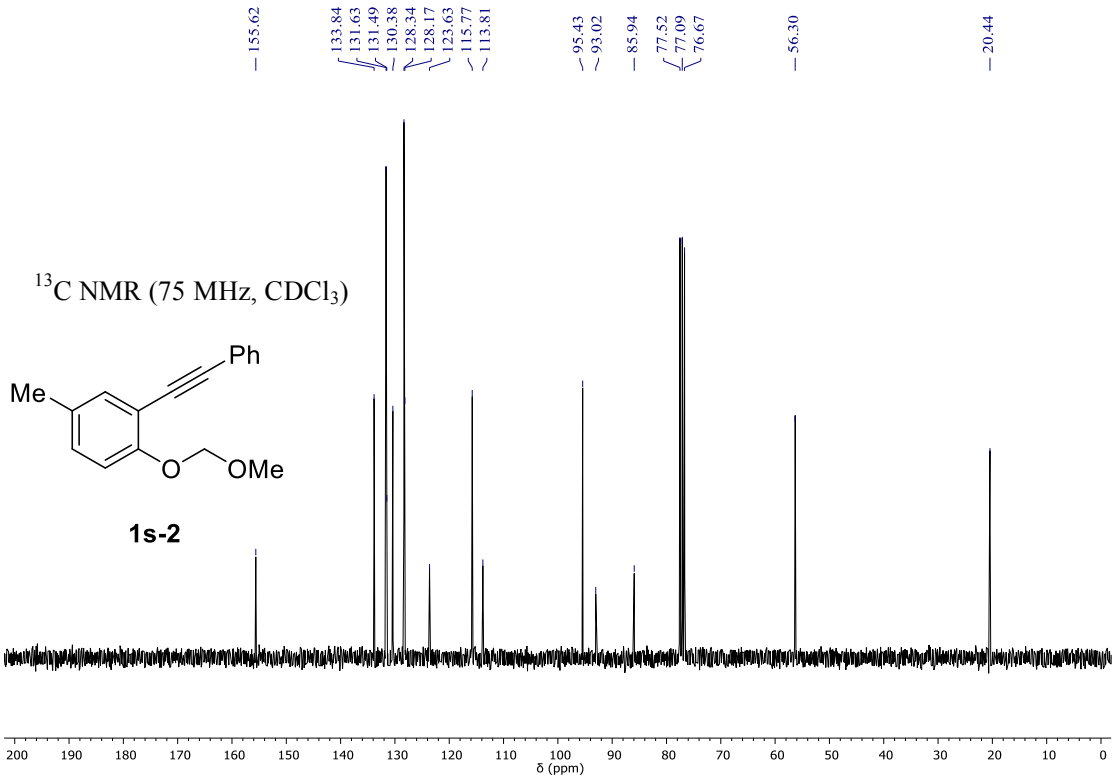
1r-2

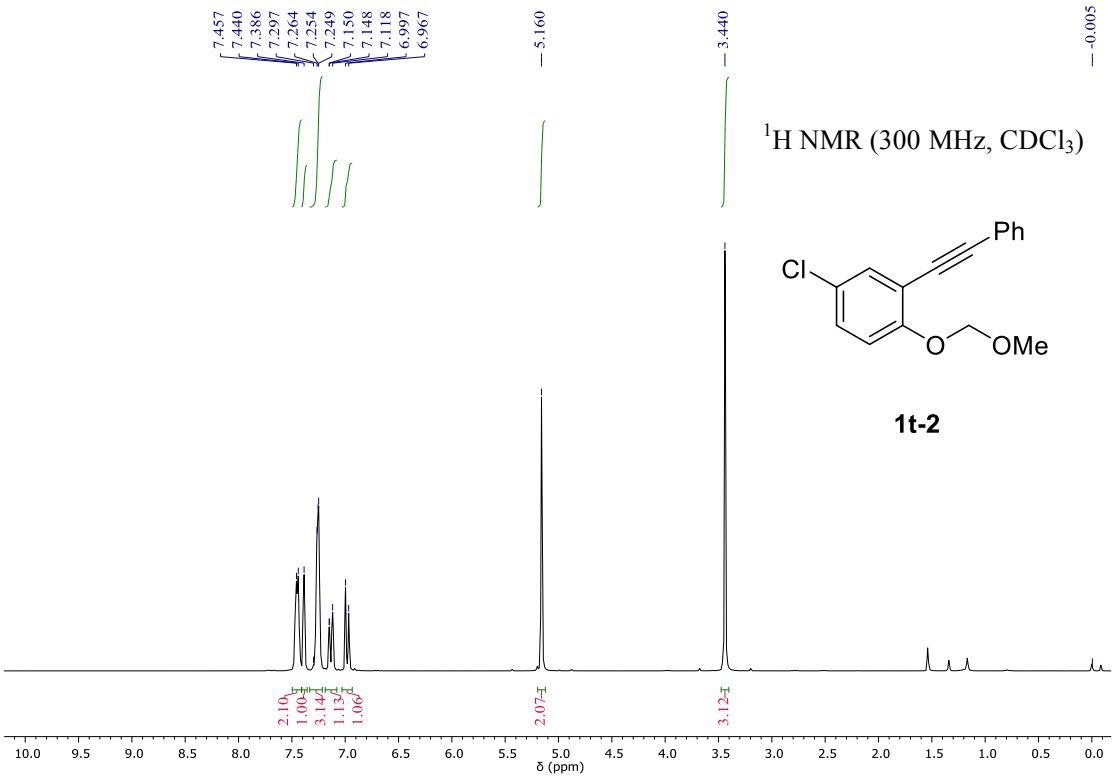


^{13}C NMR (75 MHz, $CDCl_3$)

1r-2

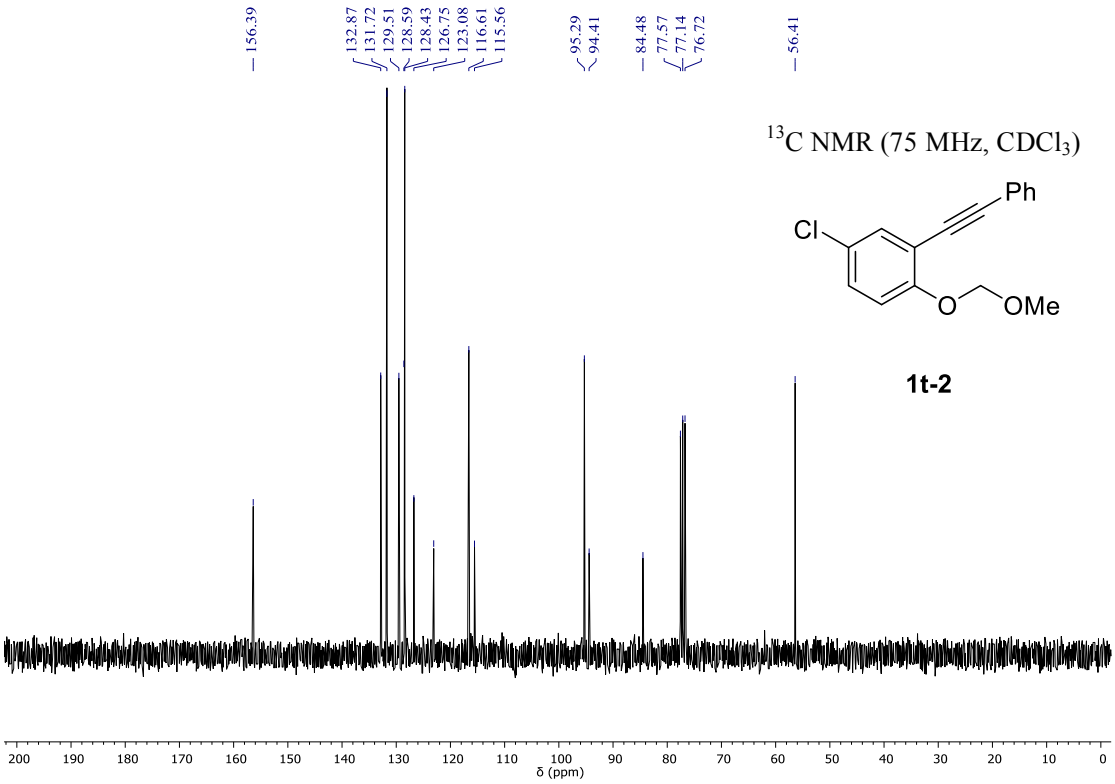

7.546
7.542
7.526
7.368
7.336
7.320
7.287
7.284
7.240
7.091
7.063
7.036
7.007
5.250
3.541
2.284
0.000
^{1}H NMR (300 MHz, $CDCl_3$)
Ph
Me
O
OMe
1s-2
2.05
4.03
2.08
2.01
3.00
3.01
δ (ppm)


155.62
133.84
131.63
131.49
130.38
128.34
128.17
123.63
115.77
113.81
95.43
93.02
85.94
77.52
77.09
76.67
56.30
20.44
^{13}C NMR (75 MHz, $CDCl_3$)
Ph
Me
O
OMe
1s-2
δ (ppm)



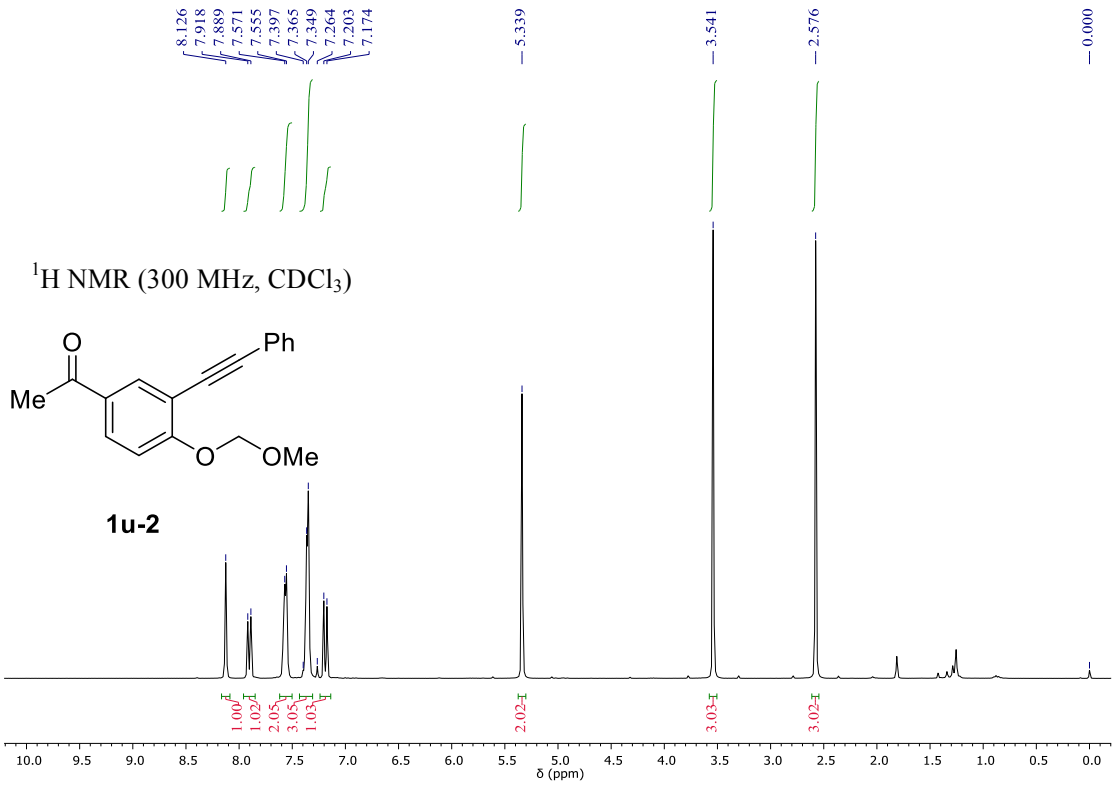
^{1}H NMR (300 MHz, $CDCl_3$)

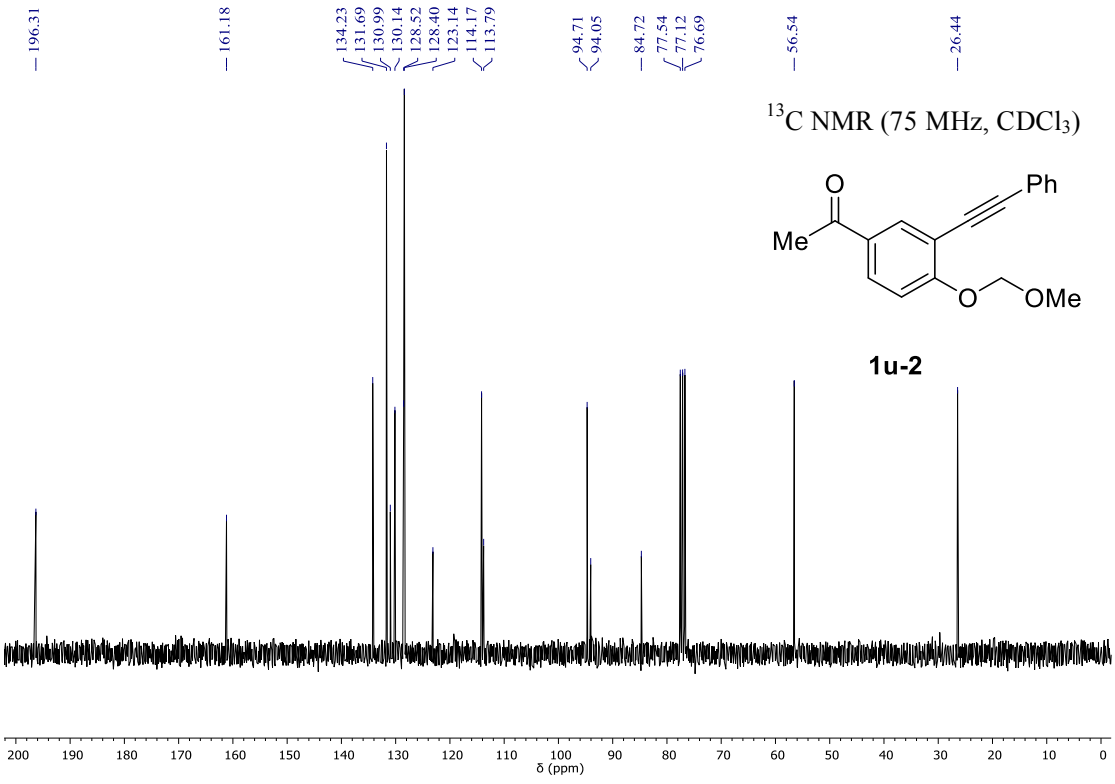
1t-2

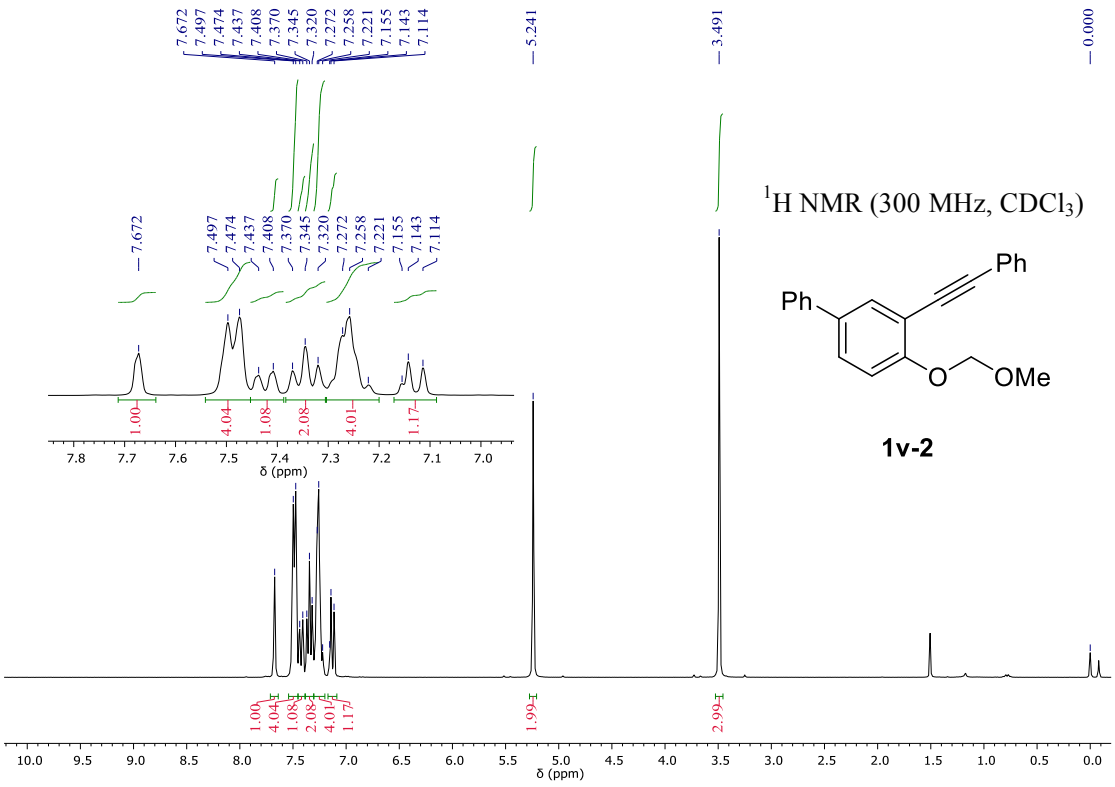


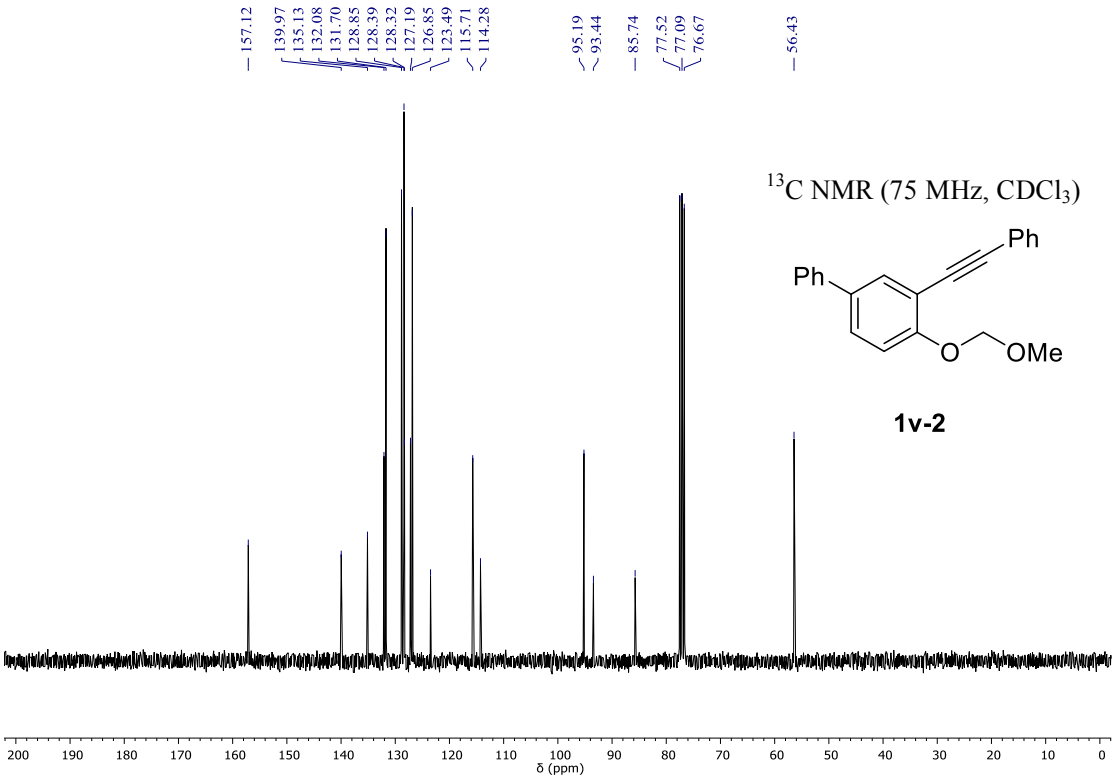
^{13}C NMR (75 MHz, $CDCl_3$)

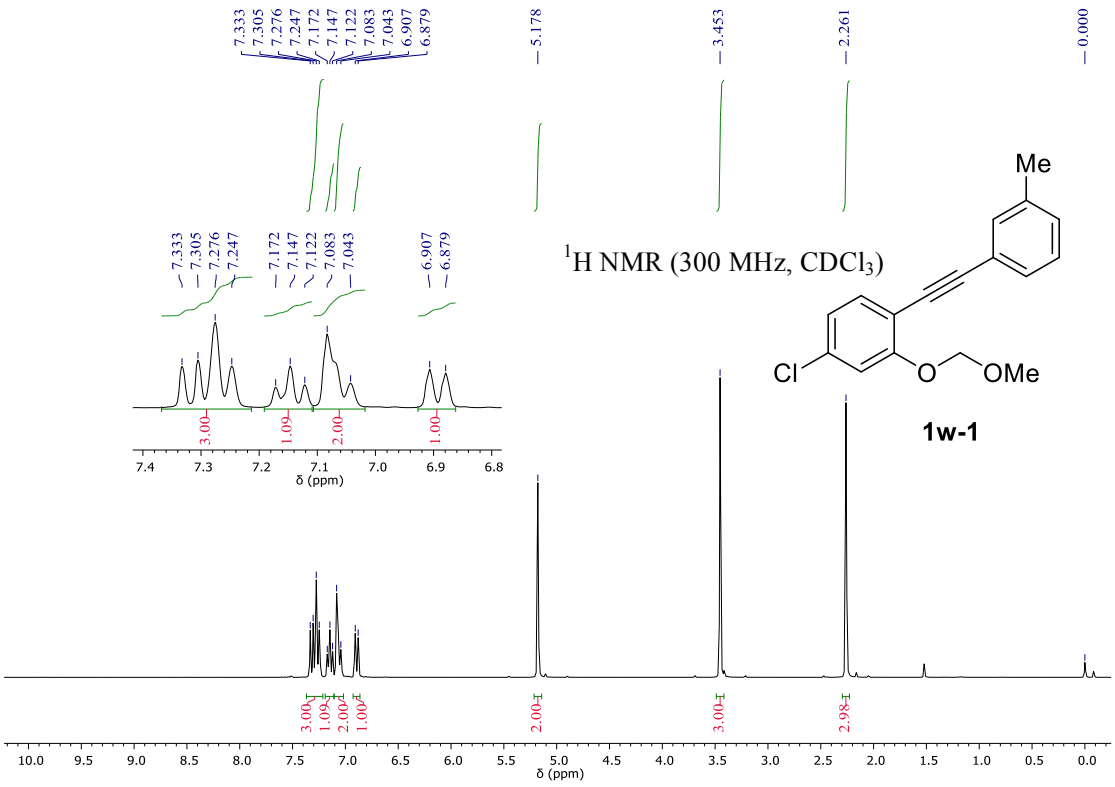
1t-2

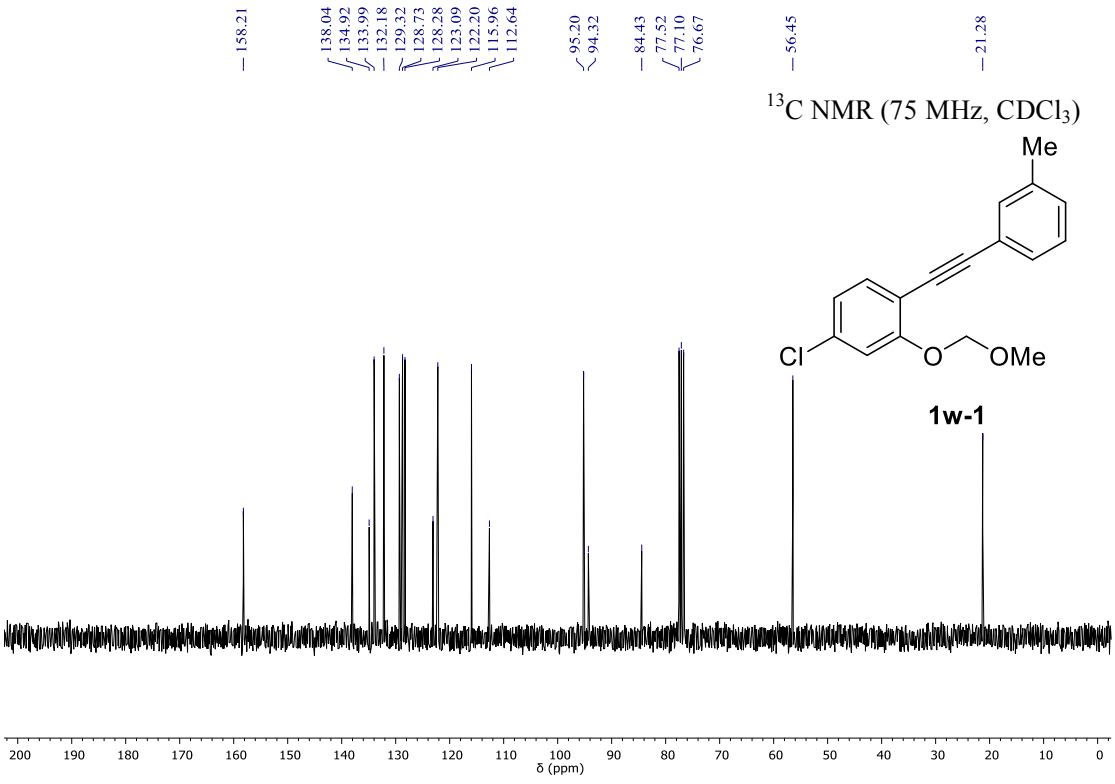

8.126
7.918
7.889
7.571
7.555
7.397
7.365
7.349
7.264
7.203
7.174
5.339
3.541
2.576
0.000
1H NMR (300 MHz, CDCl3)
O
Ph
Me
O
OMe
1u-2
1.00
1.02
2.05
3.05
1.03
2.02
3.03
3.02
δ (ppm)


196.31
161.18
134.23
131.69
130.99
130.14
128.52
128.40
123.14
114.17
113.79
94.71
94.05
84.72
77.54
77.12
76.69
56.54
26.44
13C NMR (75 MHz, CDCl3)
O
Ph
Me
O
OMe
1u-2
δ (ppm)

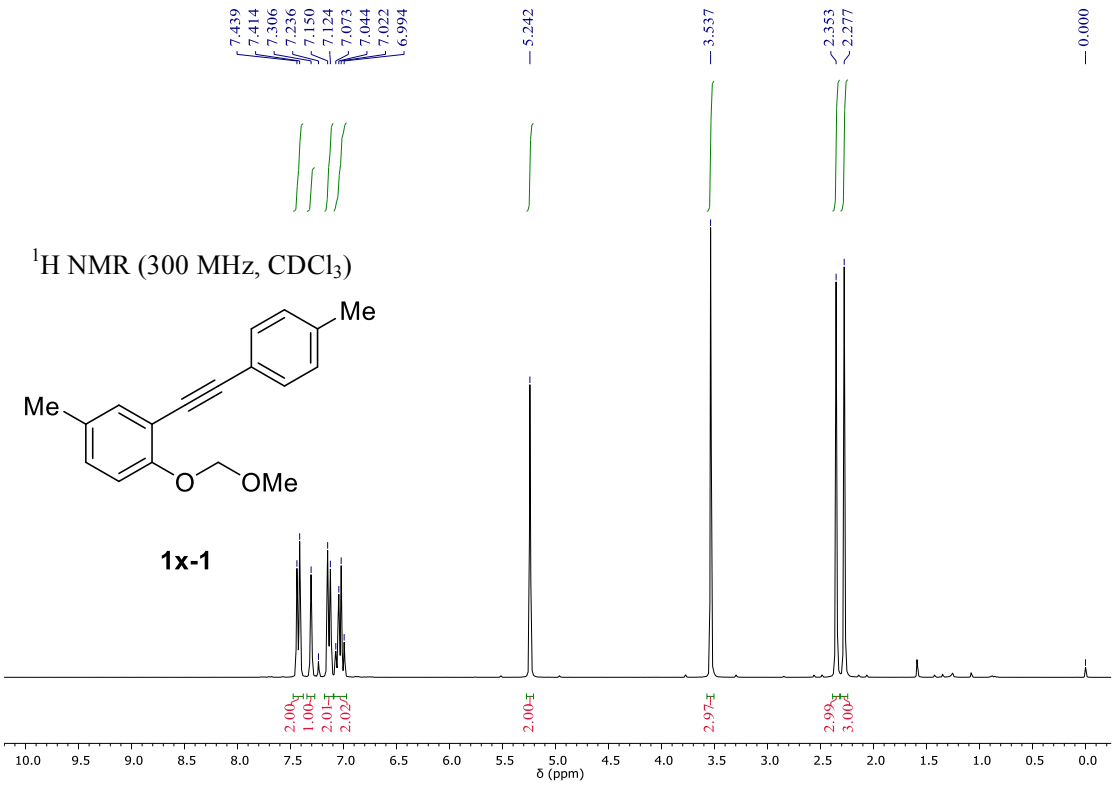

7.672
7.497
7.474
7.437
7.408
7.370
7.345
7.320
7.272
7.258
7.221
7.155
7.143
7.114
5.241
3.491
0.000
1.00
4.04
1.08
2.08
4.01
1.17
1.99
2.99
δ (ppm)
^{1}H NMR (300 MHz, CDCl$_3$)
Ph
Ph
O
OMe
1v-2


157.12
139.97
135.13
132.08
131.70
128.85
128.39
128.32
127.19
126.85
123.49
115.71
114.28
95.19
93.44
85.74
77.52
77.09
76.67
56.43
δ (ppm)
^{13}C NMR (75 MHz, CDCl$_3$)
Ph
Ph
O
OMe
1v-2


7.333
7.305
7.276
7.247
7.172
7.147
7.122
7.083
7.043
6.907
6.879
5.178
3.453
2.261
0.000
^{1}H NMR (300 MHz, CDCl$_3$)
Me
Cl
O
OMe
1w-1
3.00
1.09
2.00
1.00
δ (ppm)

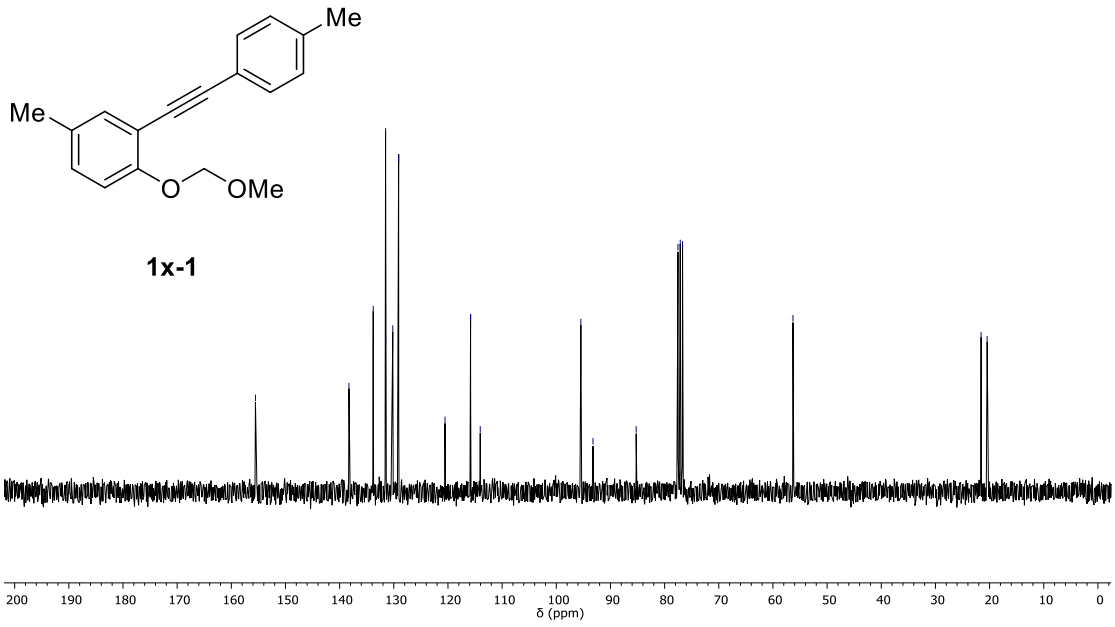

158.21
138.04
134.92
133.99
132.18
129.32
128.73
128.28
123.09
122.20
115.96
112.64
95.20
94.32
84.43
77.52
77.10
76.67
56.45
21.28
^{13}C NMR (75 MHz, CDCl$_3$)
Me
Cl
O
OMe
1w-1
δ (ppm)

^{1}H NMR (300 MHz, $CDCl_3$)

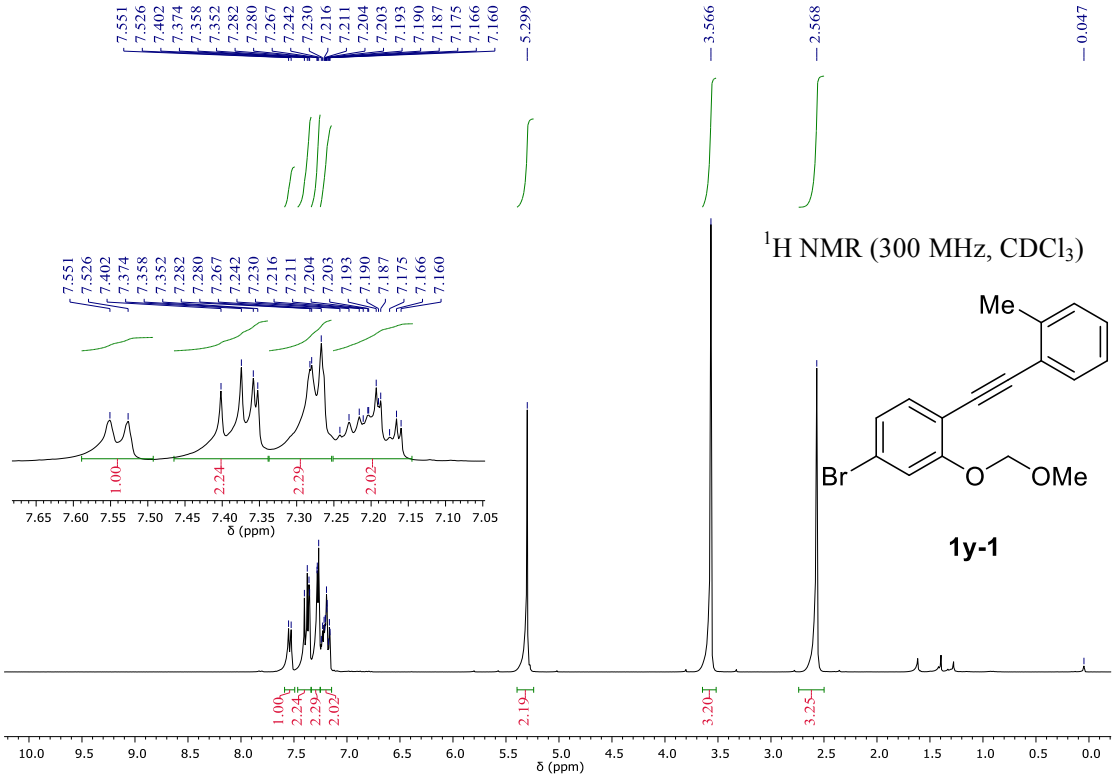


1x-1

^{13}C NMR (75 MHz, $CDCl_3$)

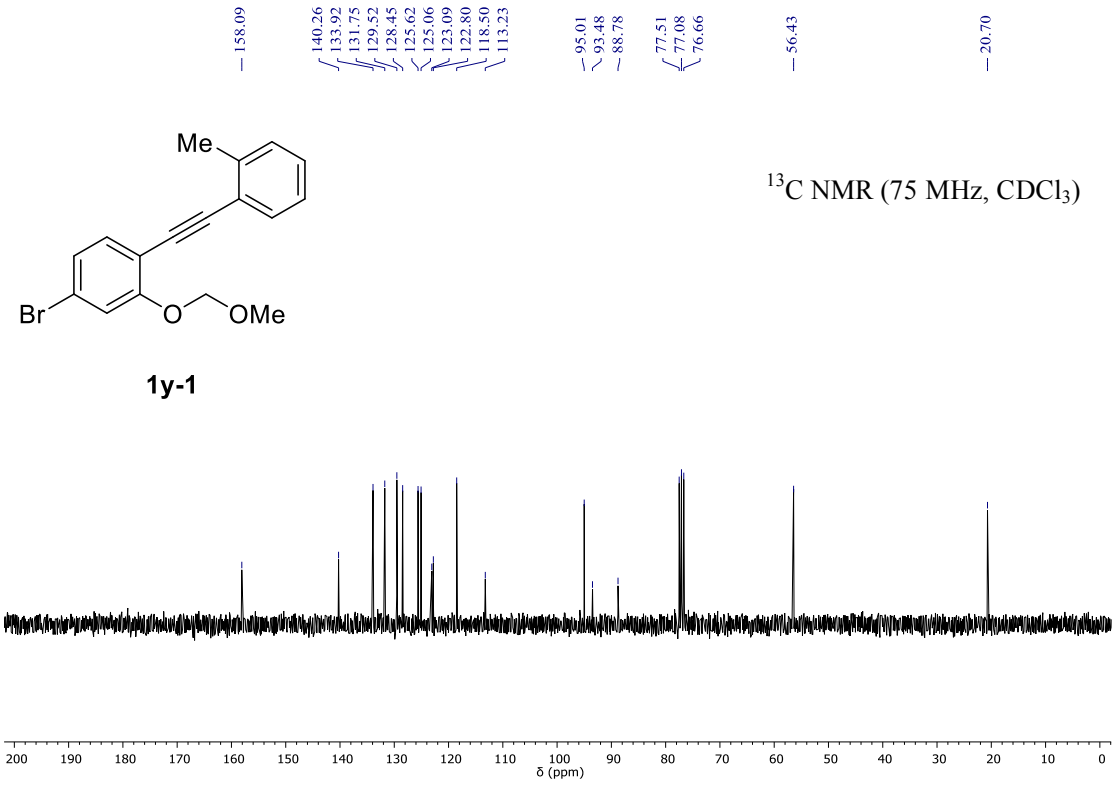


1x-1



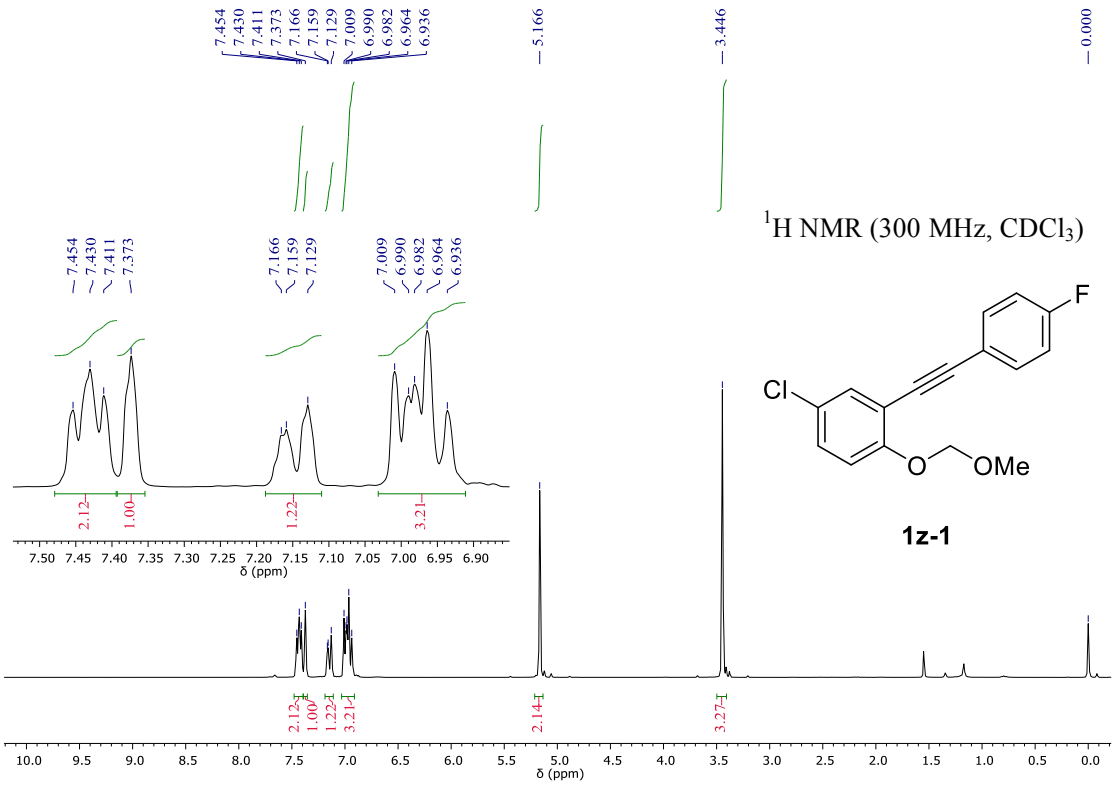
^{1}H NMR (300 MHz, $CDCl_3$)

1y-1



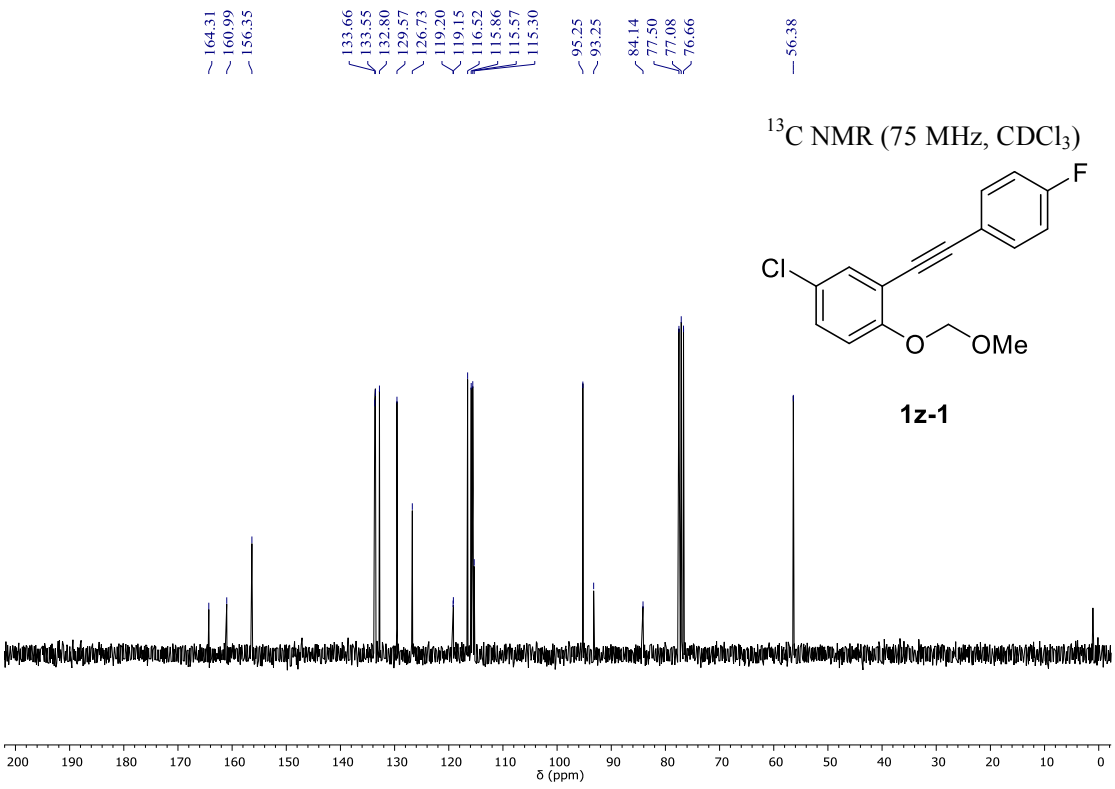
1y-1

^{13}C NMR (75 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)

1z-1

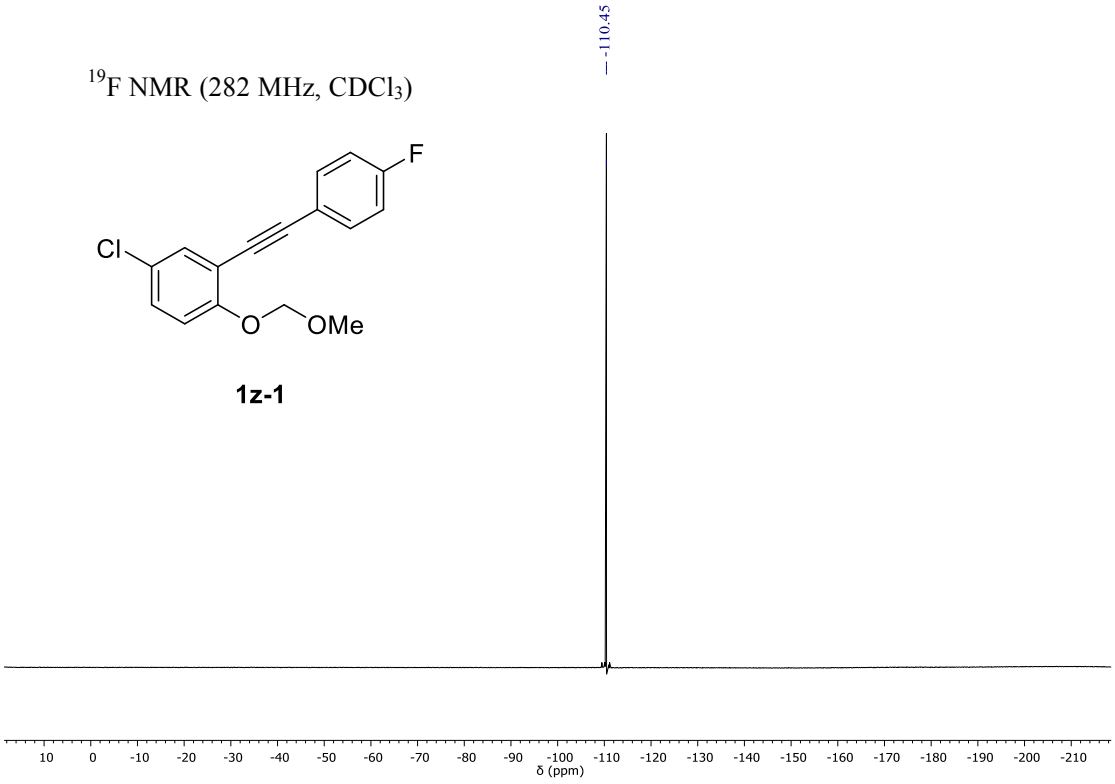


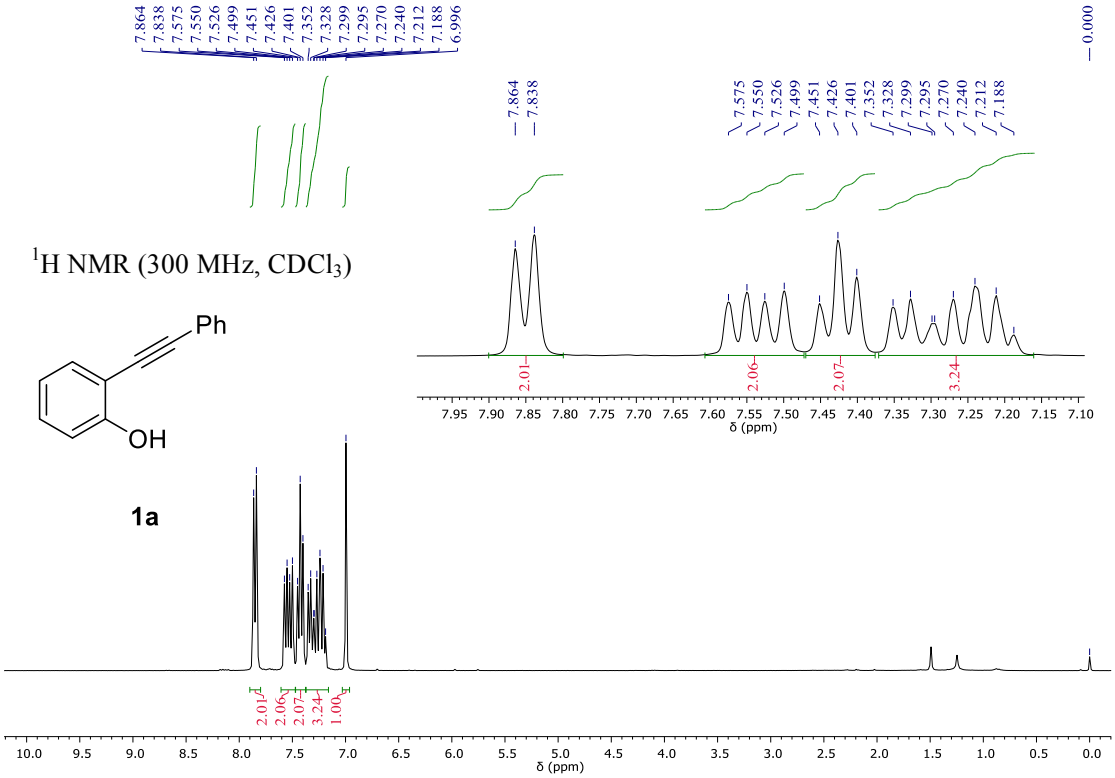
^{13}C NMR (75 MHz, $CDCl_3$)

1z-1

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

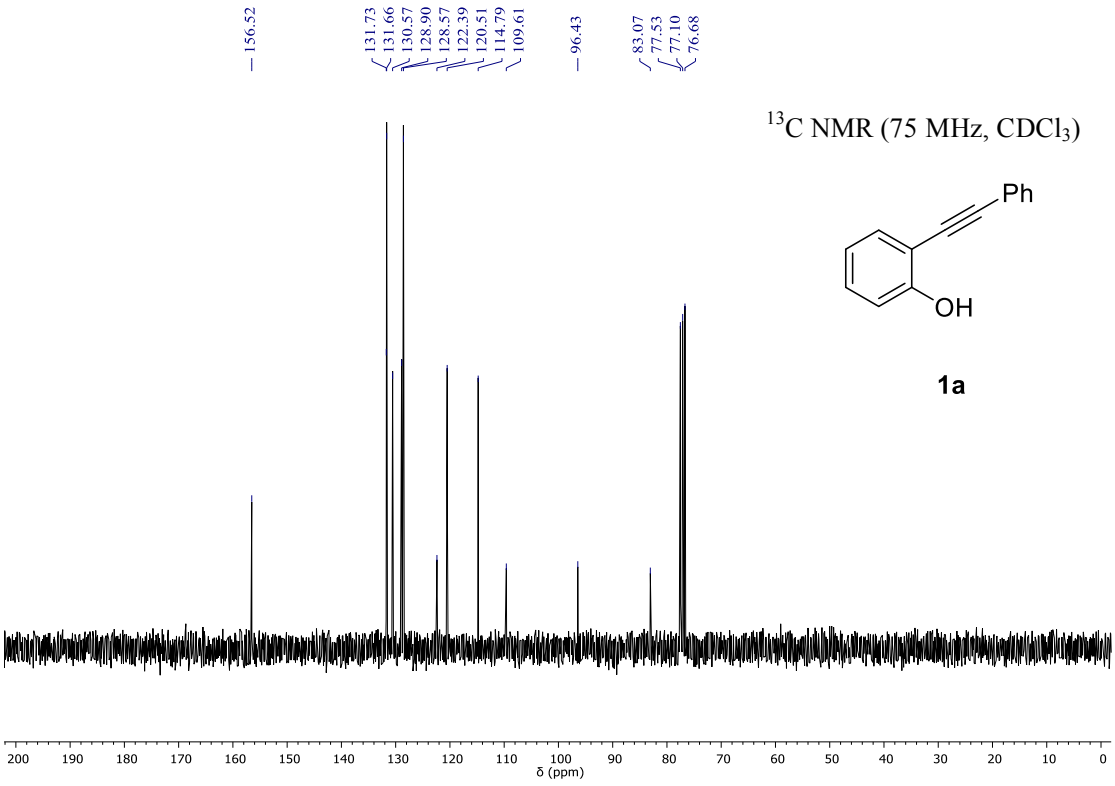
1z-1





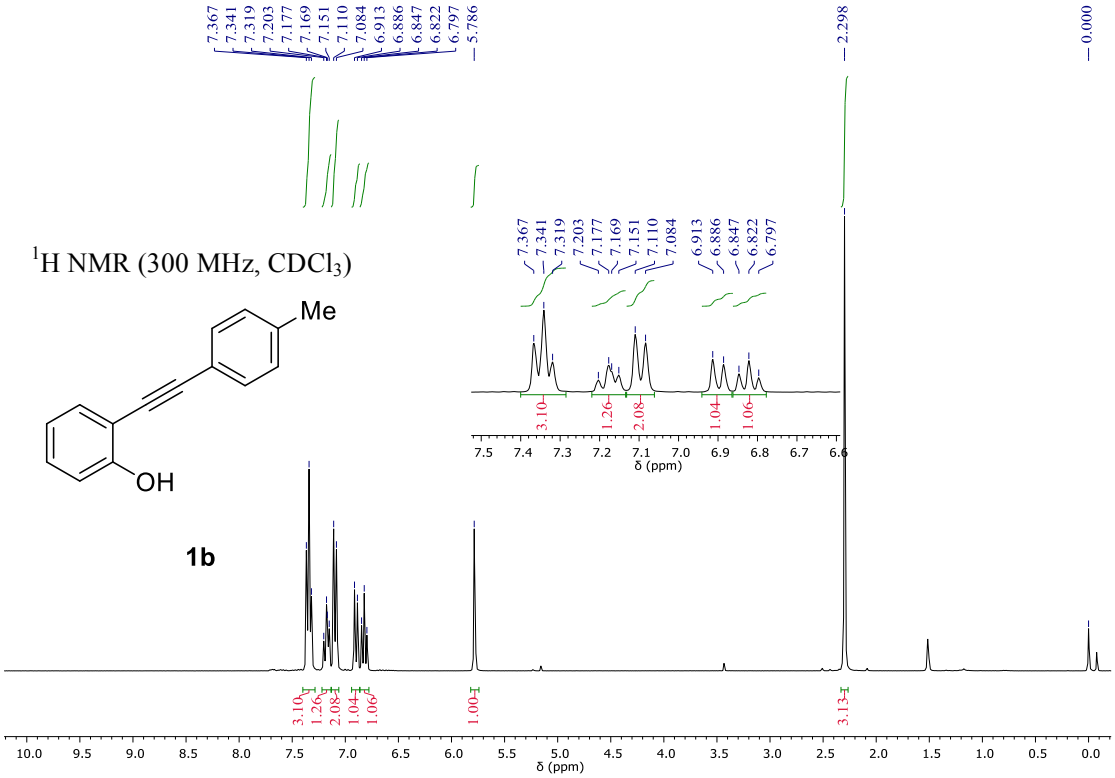
^{1}H NMR (300 MHz, $CDCl_3$)

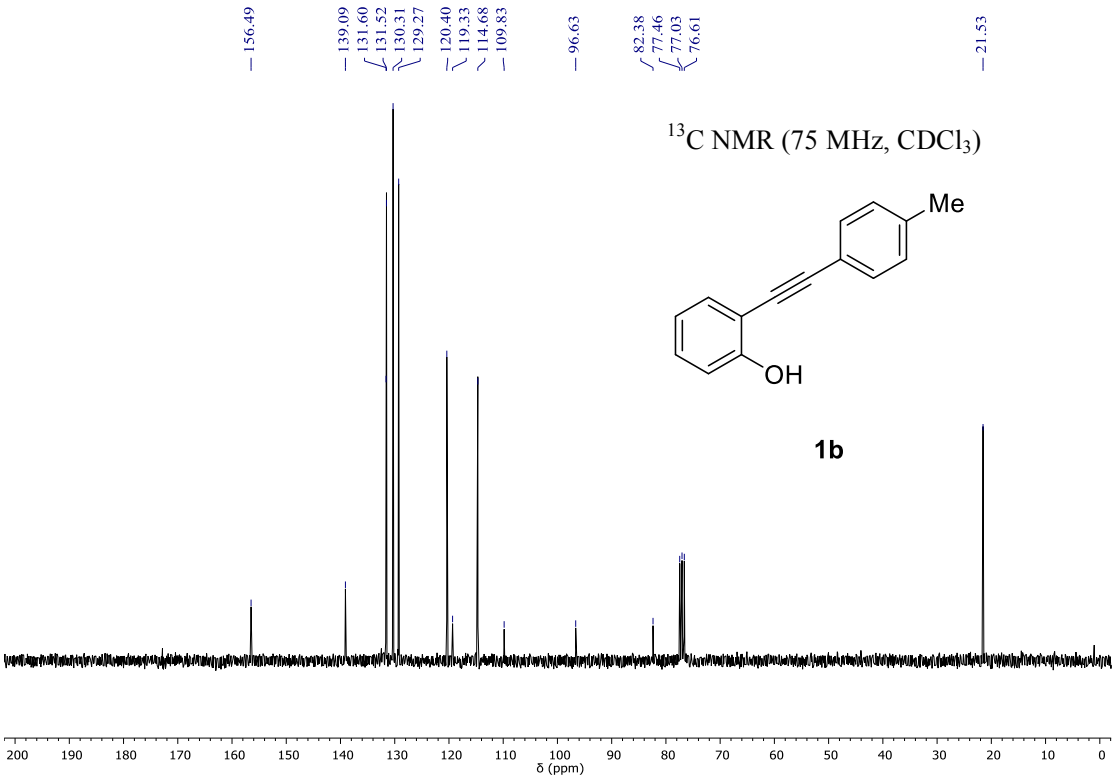
1a

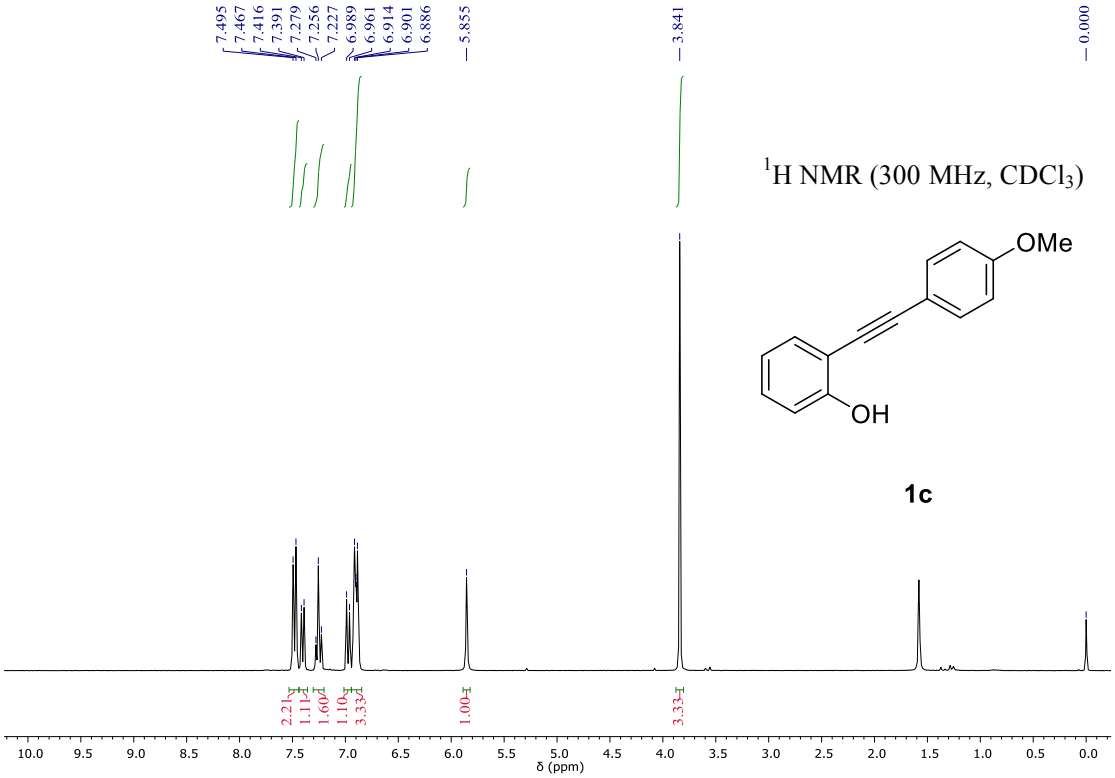


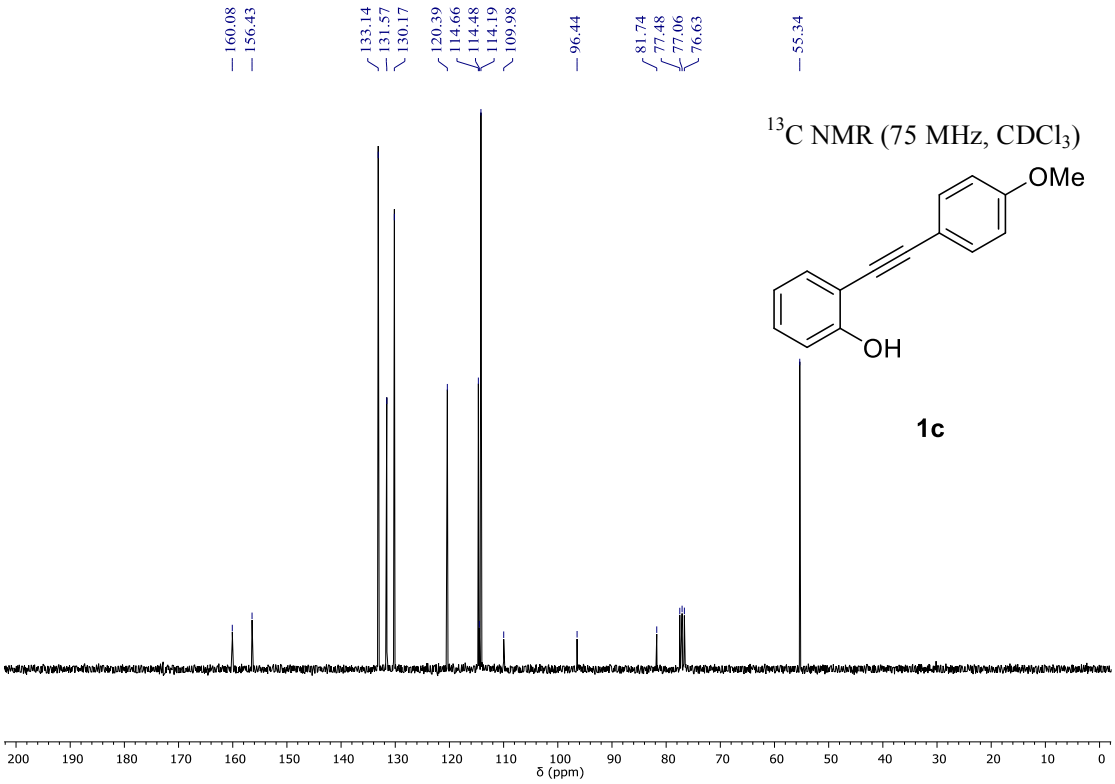
^{13}C NMR (75 MHz, $CDCl_3$)

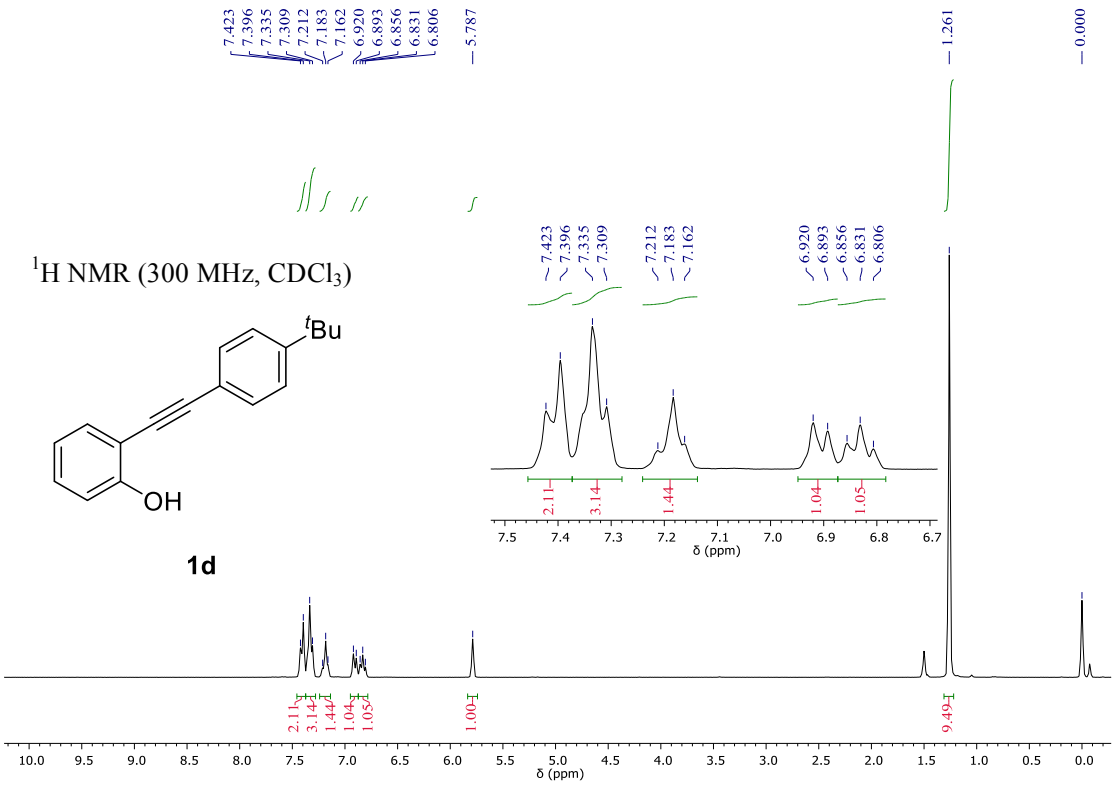
1a

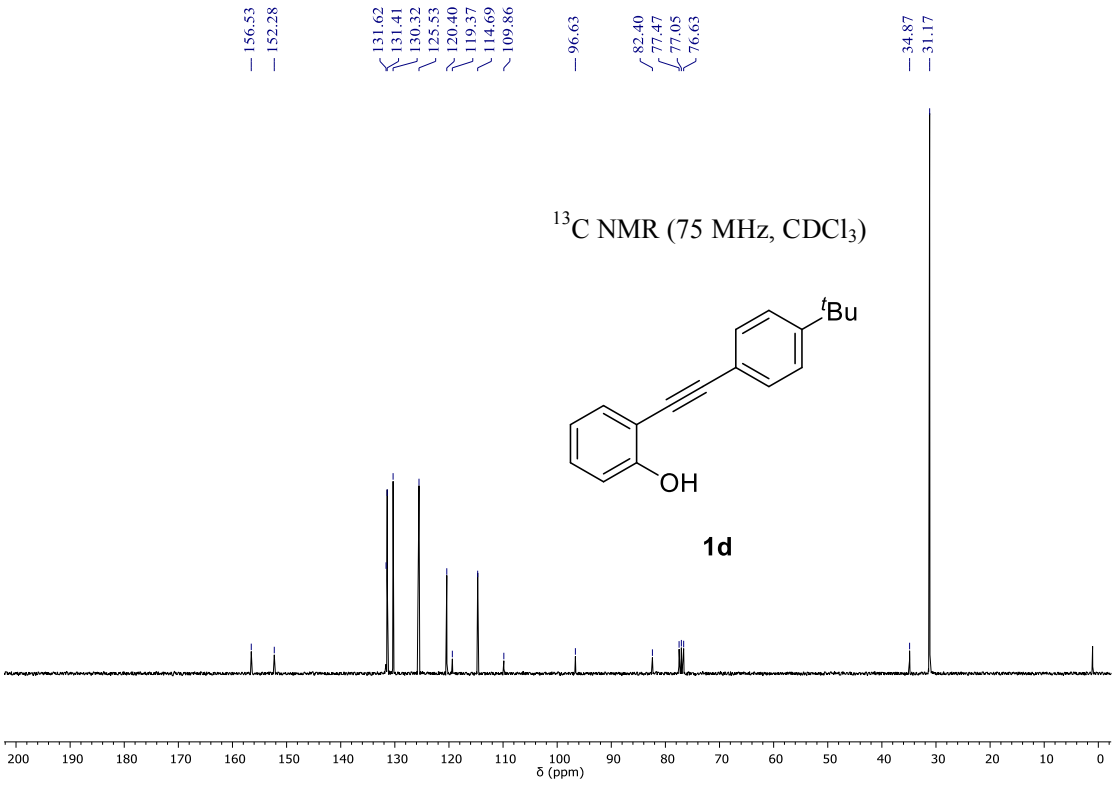

7.367
7.341
7.319
7.203
7.177
7.169
7.151
7.110
7.084
6.913
6.886
6.847
6.822
6.797
5.786
2.298
0.000
^{1}H NMR (300 MHz, $CDCl_3$)
Me
OH
1b
3.10
1.26
2.08
1.04
1.06
1.00
3.13
δ (ppm)

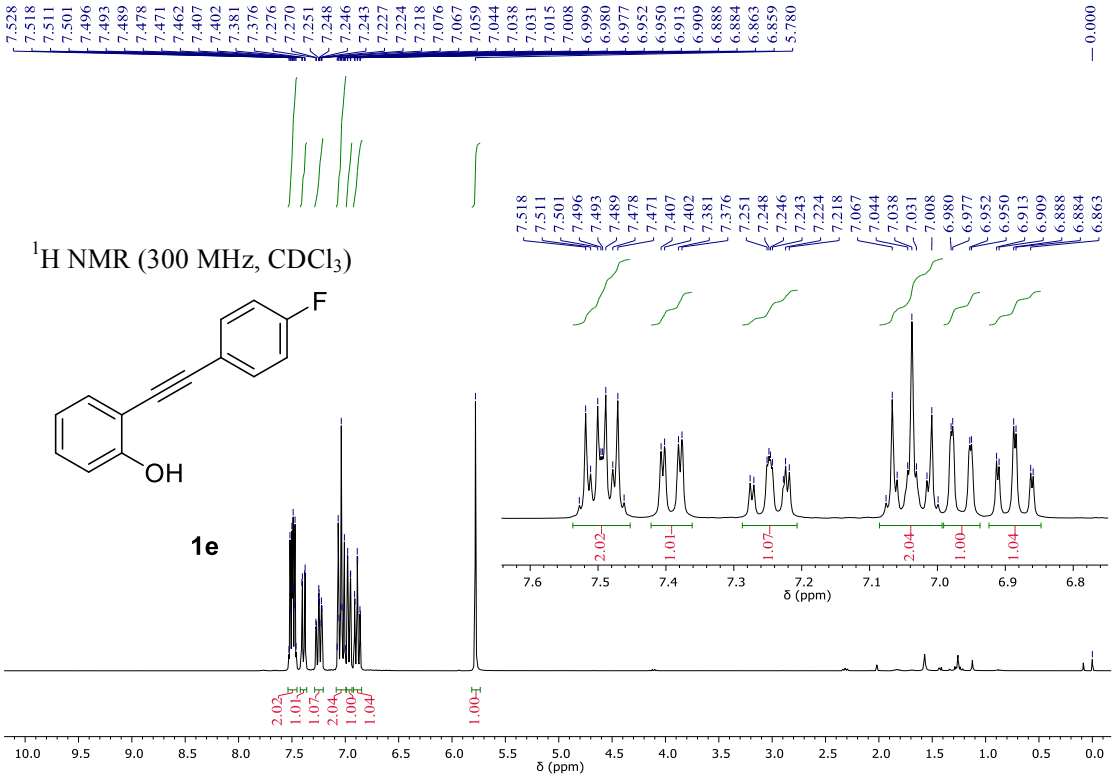

156.49
139.09
131.60
131.52
130.31
129.27
120.40
119.33
114.68
109.83
96.63
82.38
77.46
77.03
76.61
21.53
^{13}C NMR (75 MHz, $CDCl_3$)
Me
OH
1b
δ (ppm)

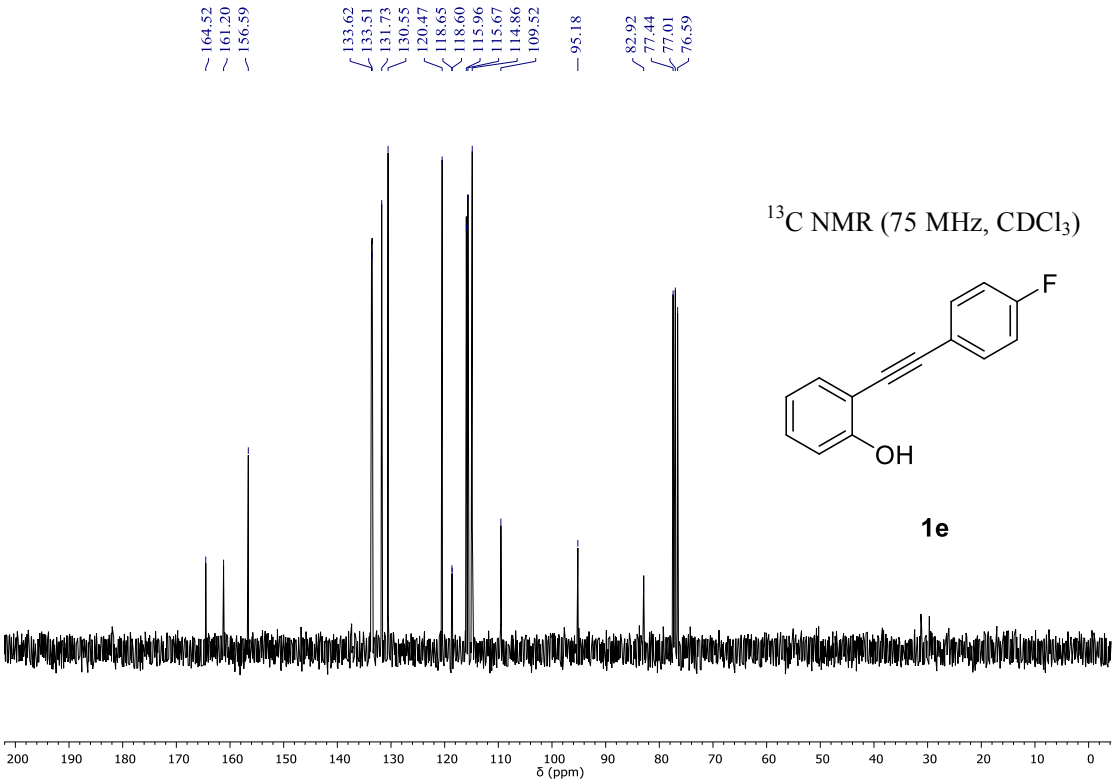

7.495
7.467
7.416
7.391
7.279
7.256
7.227
6.989
6.961
6.914
6.901
6.886
5.855
3.841
0.000
^{1}H NMR (300 MHz, CDCl$_3$)
OMe
OH
1c
2.21
1.11
1.60
1.10
3.33
1.00
3.33
δ (ppm)


160.08
156.43
133.14
131.57
130.17
120.39
114.66
114.48
114.19
109.98
96.44
81.74
77.48
77.06
76.63
55.34
^{13}C NMR (75 MHz, CDCl$_3$)
OMe
OH
1c
δ (ppm)


7.423
7.396
7.335
7.309
7.212
7.183
7.162
6.920
6.893
6.856
6.831
6.806
5.787
1.261
0.000
^{1}H NMR (300 MHz, CDCl$_3$)
^{t}Bu
OH
1d
2.11
3.14
1.44
1.04
1.05
1.00
9.49
δ (ppm)

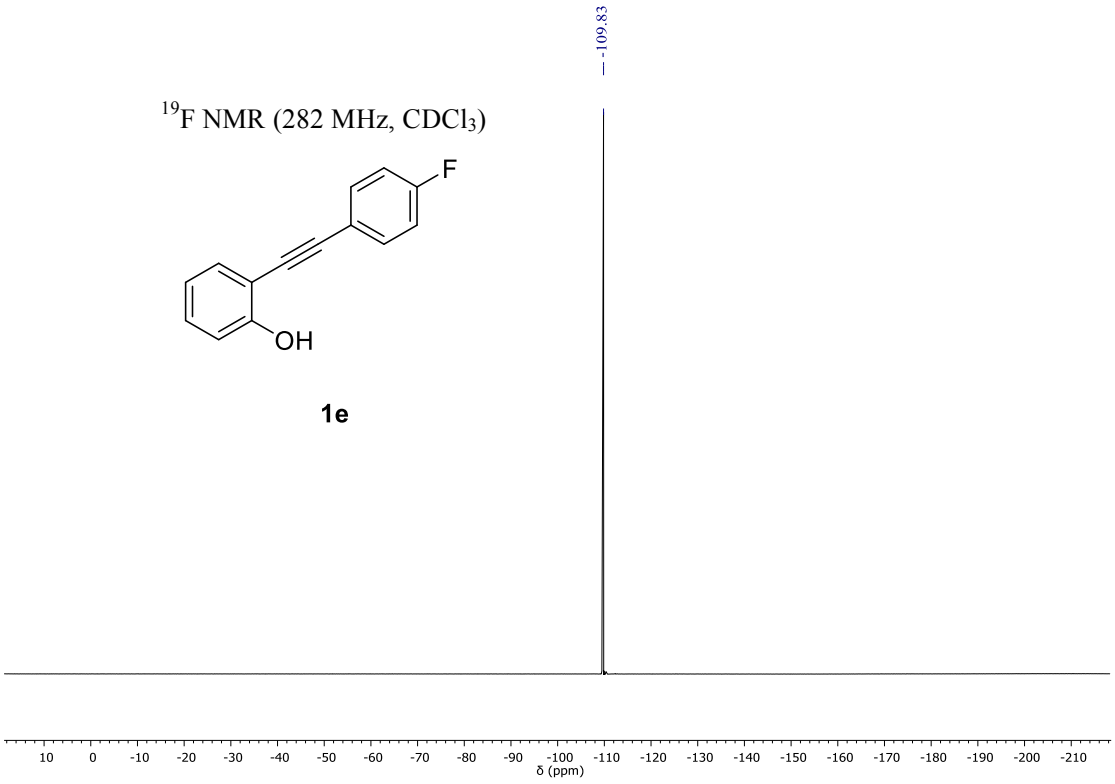

156.53
152.28
131.62
131.41
130.32
125.53
120.40
119.37
114.69
109.86
96.63
82.40
77.47
77.05
76.63
34.87
31.17
^{13}C NMR (75 MHz, CDCl$_3$)
^{t}Bu
OH
1d
δ (ppm)

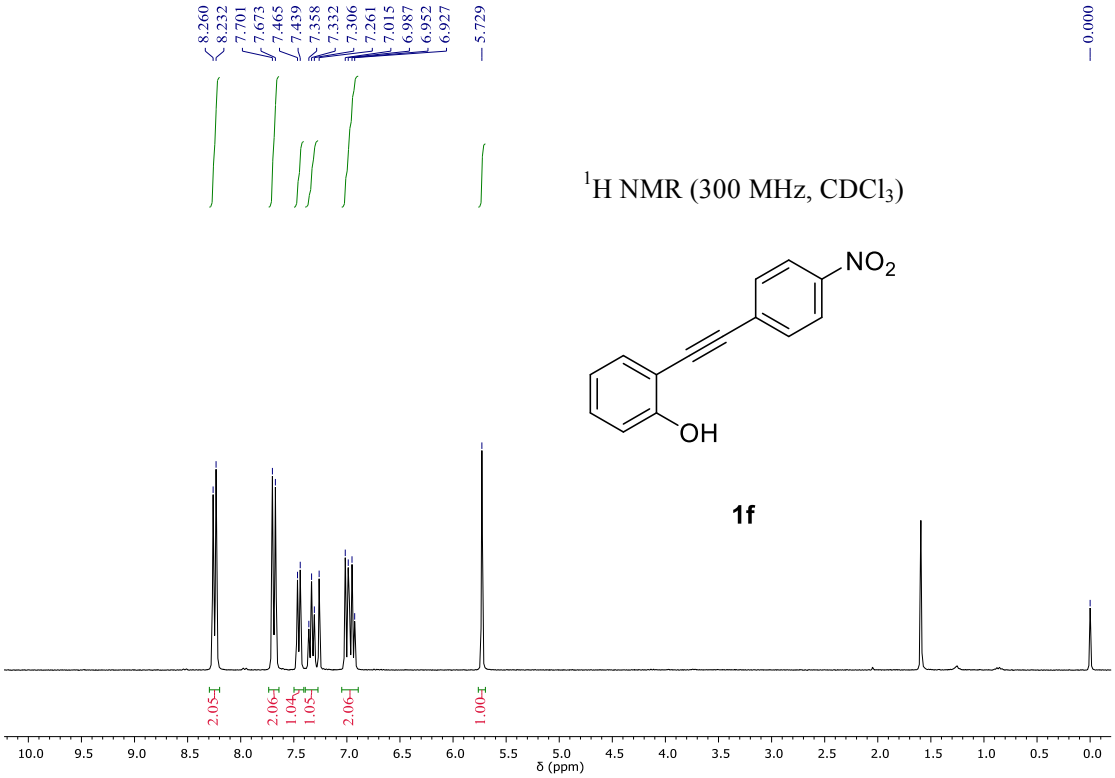

^{1}H NMR (300 MHz, CDCl$_3$)
F
OH
1e
δ (ppm)

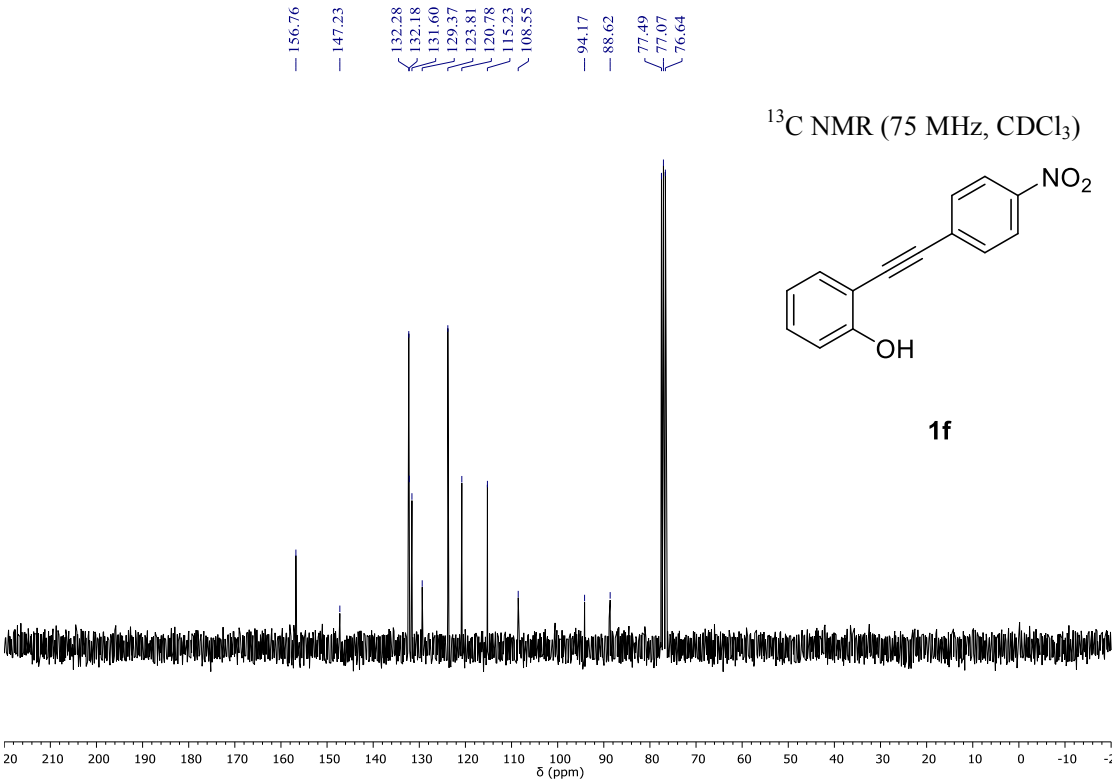

^{13}C NMR (75 MHz, CDCl$_3$)
F
OH
1e
δ (ppm)

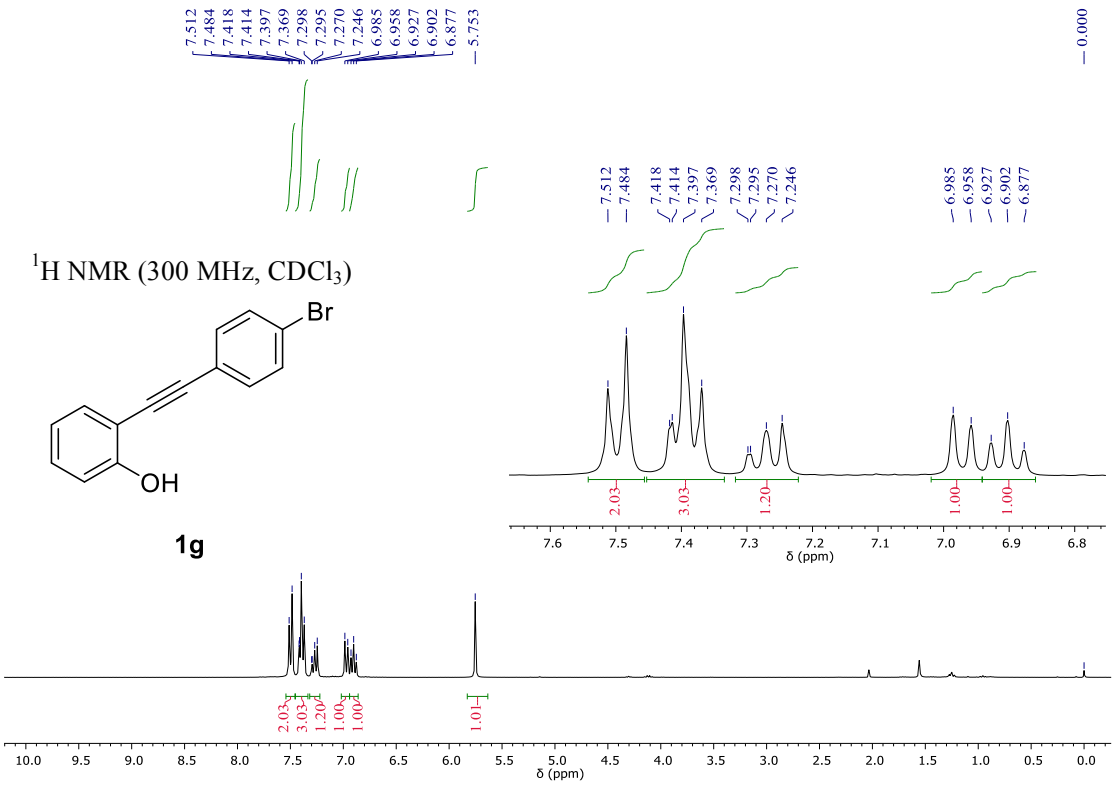
^{19}F NMR (282 MHz, $CDCl_3$)

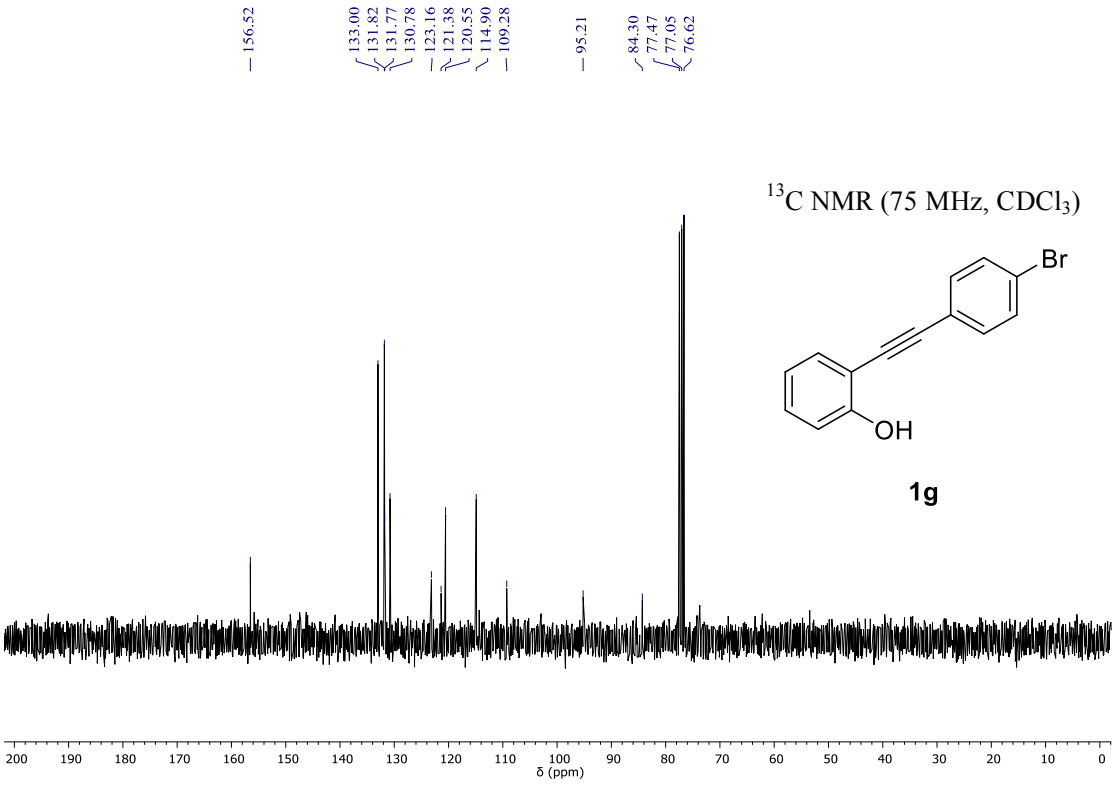
1e

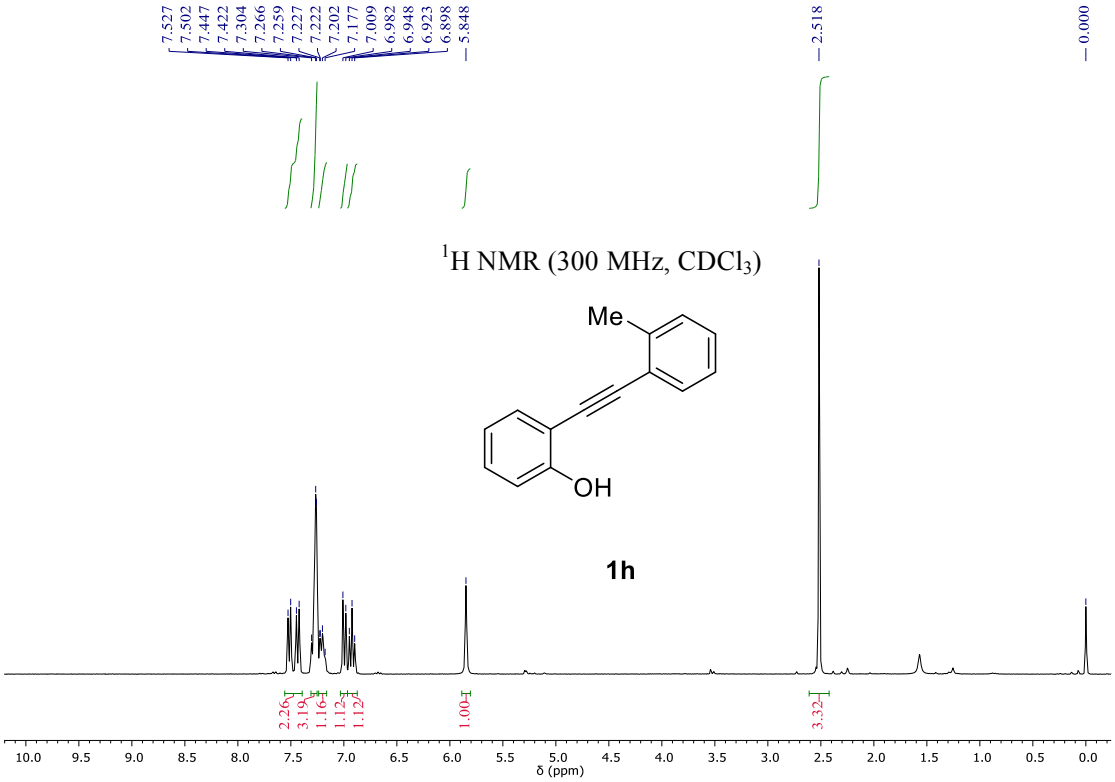



8.260
8.232
7.701
7.673
7.465
7.439
7.358
7.332
7.306
7.261
7.015
6.987
6.952
6.927
5.729
0.000
^{1}H NMR (300 MHz, $CDCl_3$)
NO_2
OH
1f
2.05
2.06
1.04
1.05
2.06
1.00
δ (ppm)

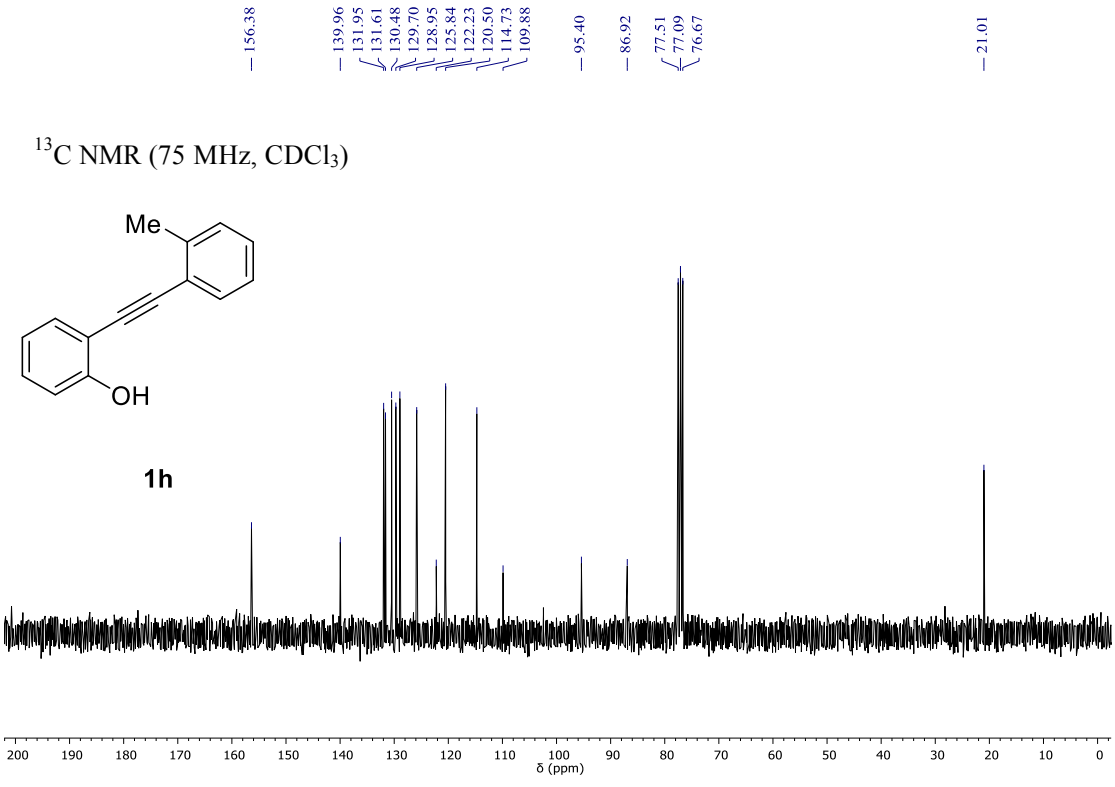

156.76
147.23
132.28
132.18
131.60
129.37
123.81
120.78
115.23
108.55
94.17
88.62
77.49
77.07
76.64
^{13}C NMR (75 MHz, $CDCl_3$)
NO_2
OH
1f
δ (ppm)


7.512
7.484
7.418
7.414
7.397
7.369
7.298
7.295
7.270
7.246
6.985
6.958
6.927
6.902
6.877
5.753
0.000
^{1}H NMR (300 MHz, CDCl$_3$)
Br
OH
1g
2.03
3.03
1.20
1.00
1.00
1.01
δ (ppm)

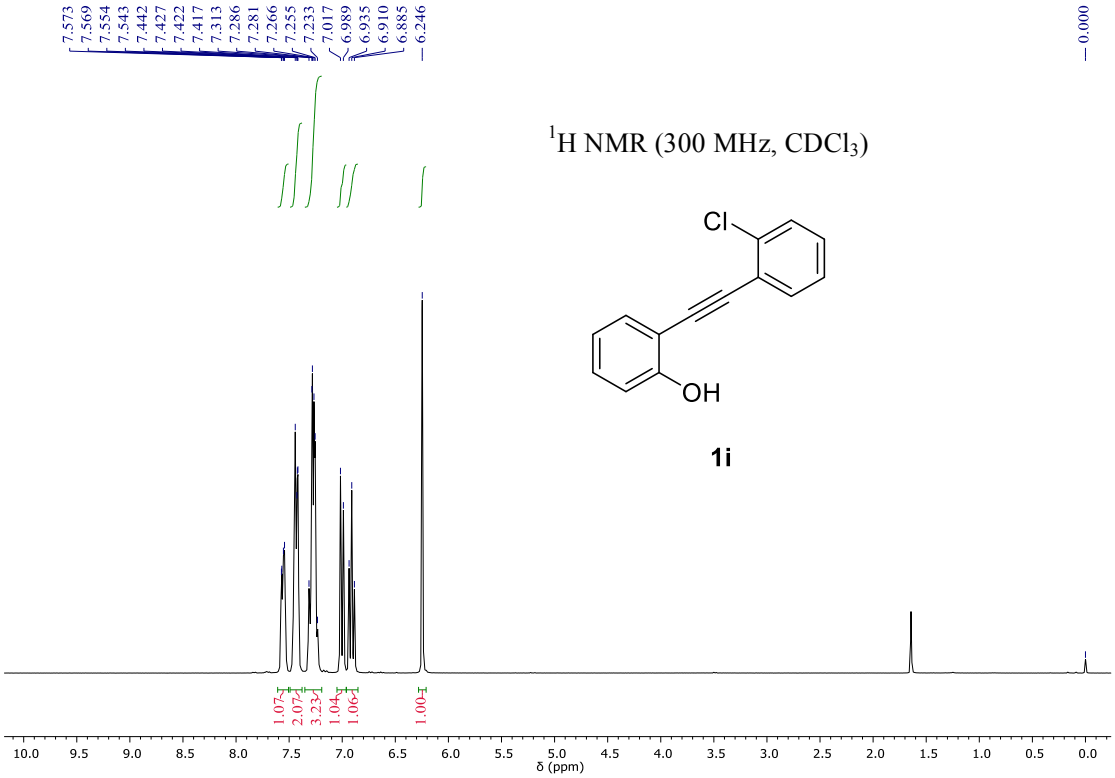

156.52
133.00
131.82
131.77
130.78
123.16
121.38
120.55
114.90
109.28
95.21
84.30
77.47
77.05
76.62
^{13}C NMR (75 MHz, CDCl$_3$)
Br
OH
1g
δ (ppm)



^{1}H NMR (300 MHz, $CDCl_3$)

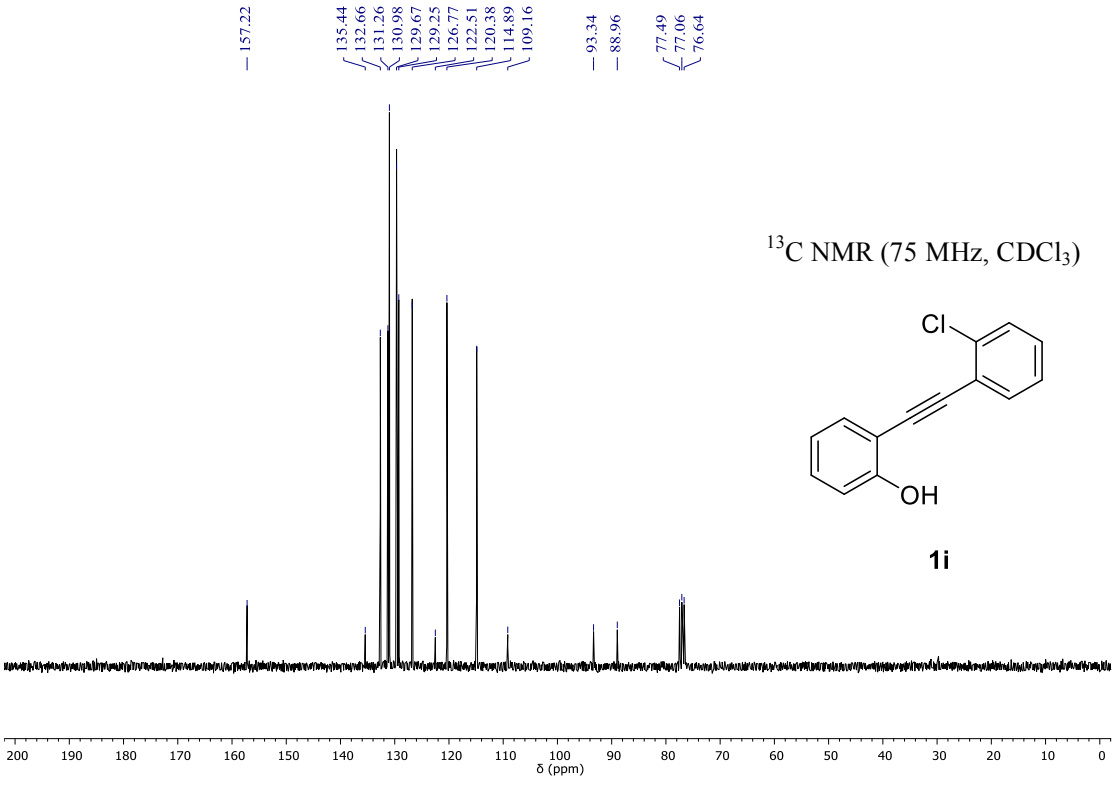


^{13}C NMR (75 MHz, $CDCl_3$)



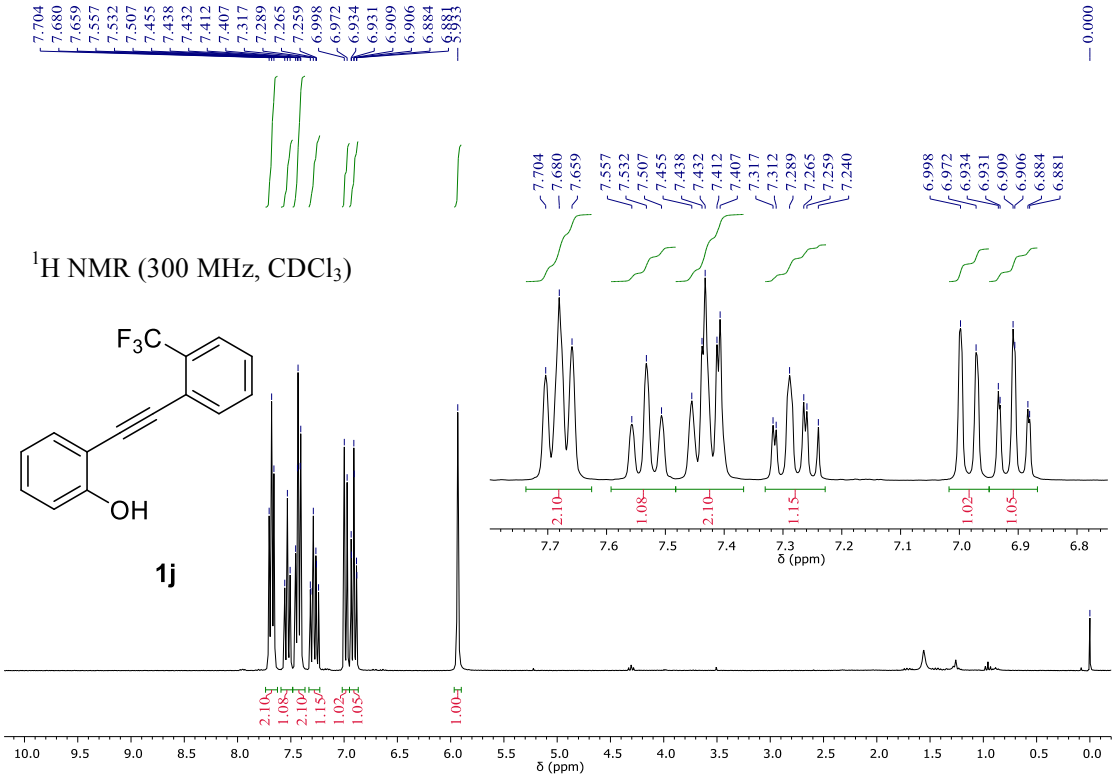
^{1}H NMR (300 MHz, $CDCl_3$)

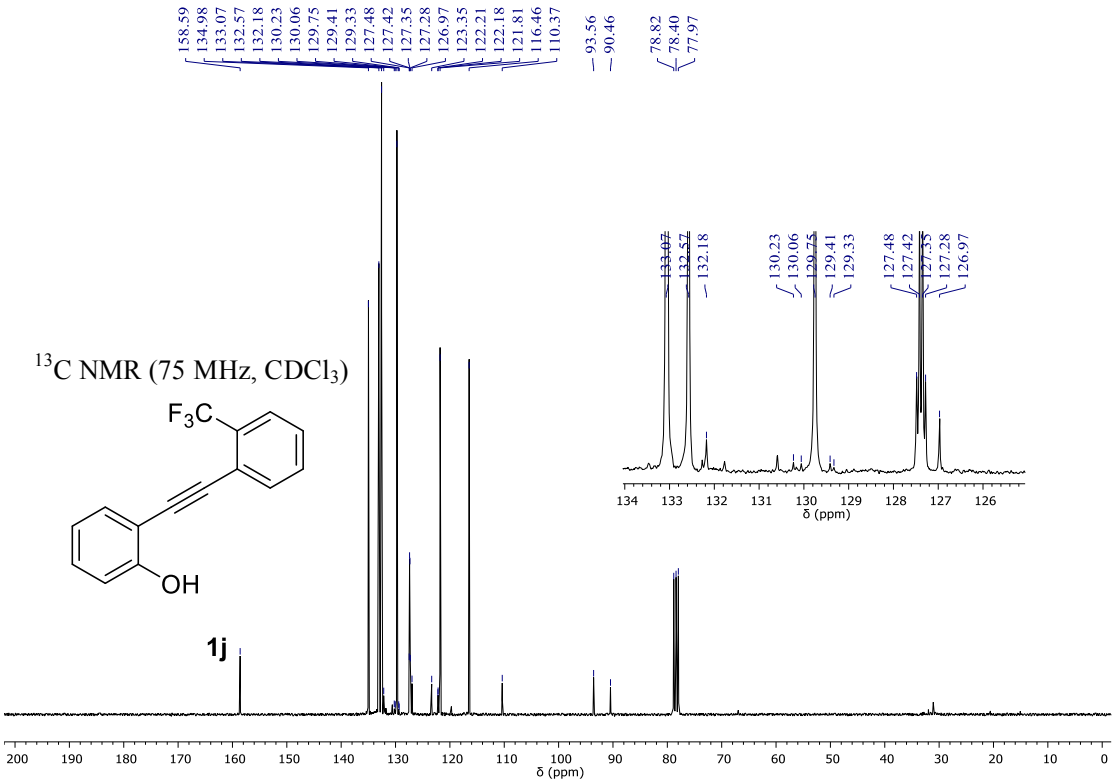
1i



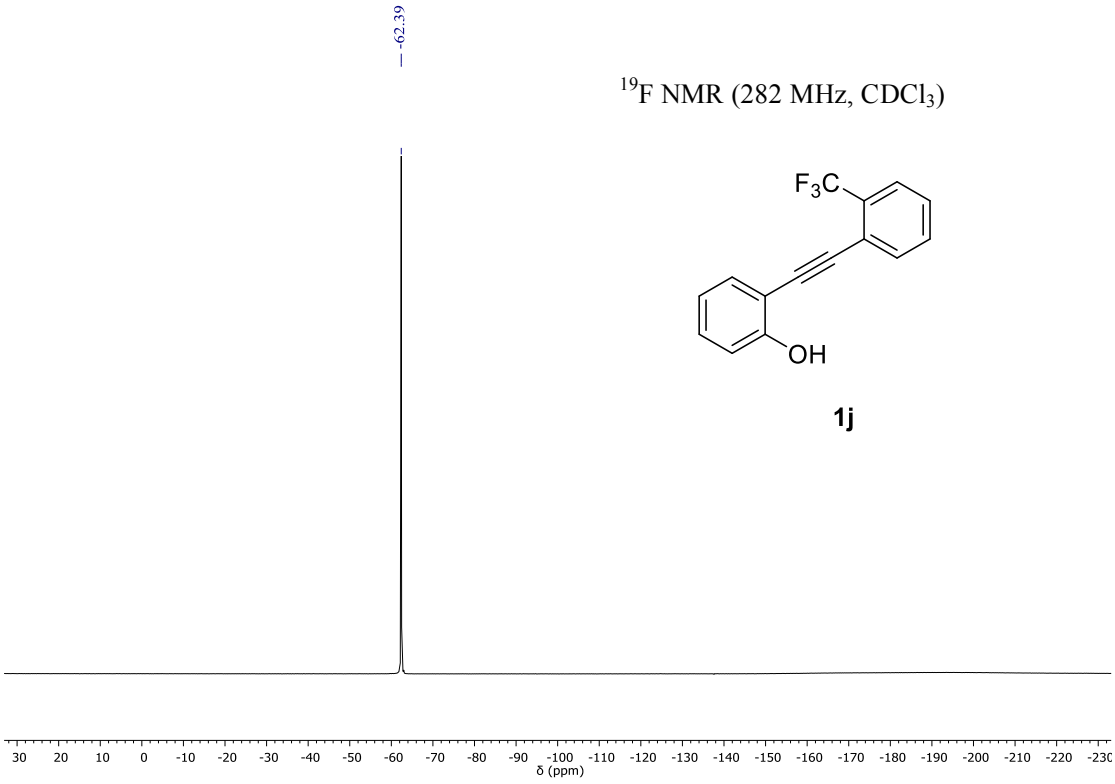
^{13}C NMR (75 MHz, $CDCl_3$)

1i

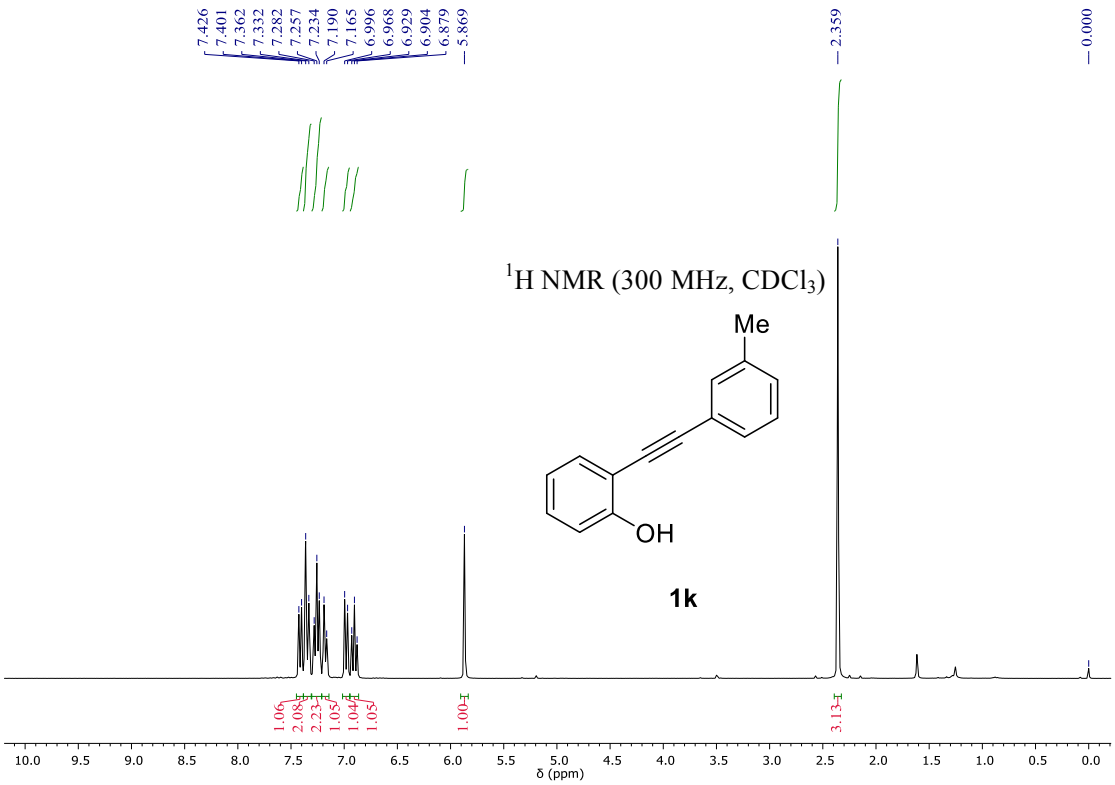

^{1}H NMR (300 MHz, $CDCl_3$)
F_3C
OH
1j
δ (ppm)

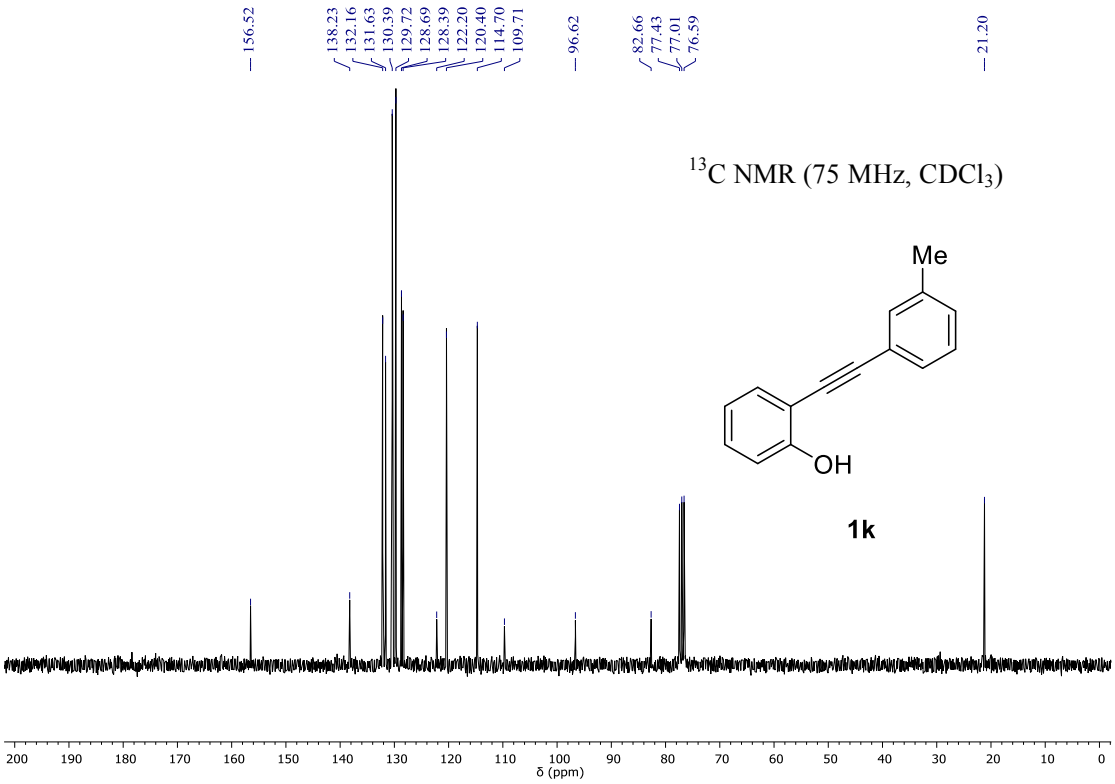

^{13}C NMR (75 MHz, $CDCl_3$)
F_3C
OH
1j
δ (ppm)

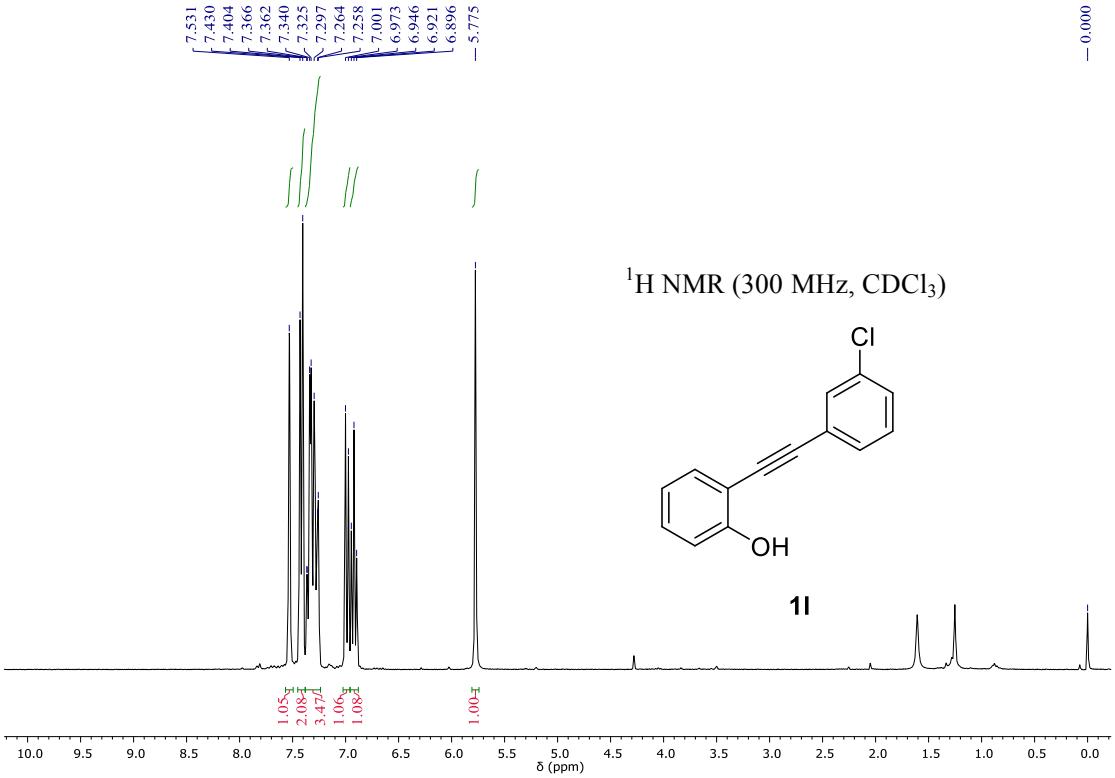
^{19}F NMR (282 MHz, $CDCl_3$)



1j

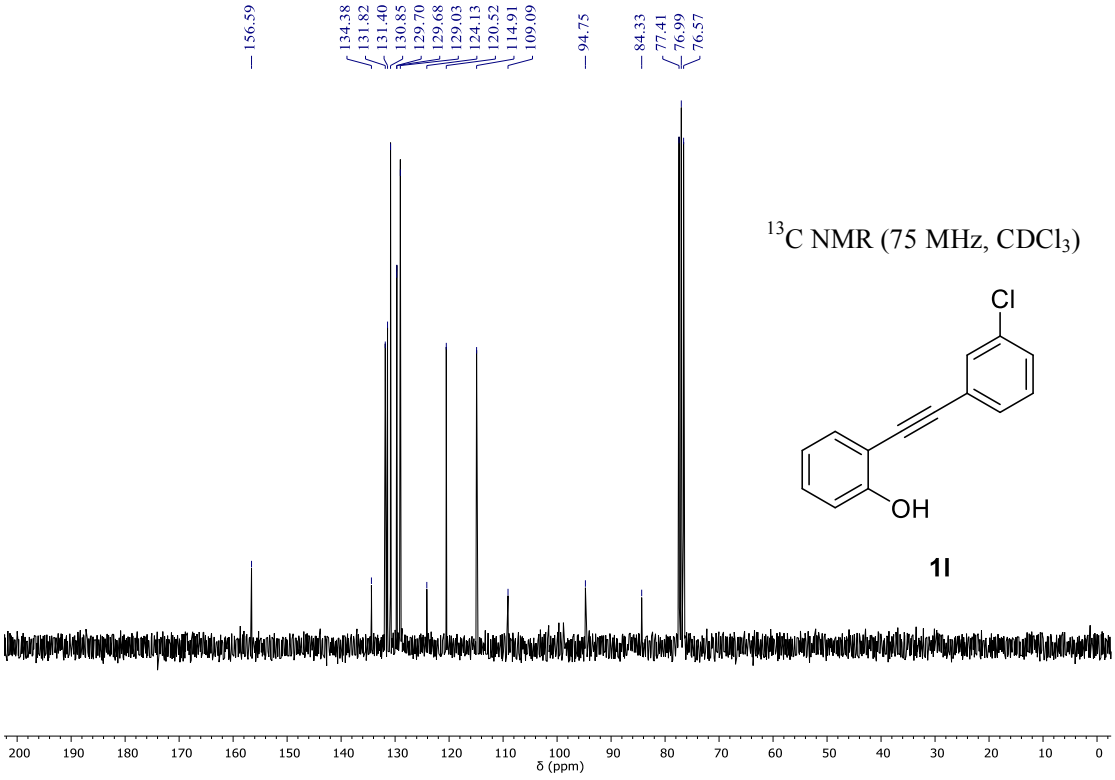

7.426
7.401
7.362
7.332
7.282
7.257
7.234
7.190
7.165
6.996
6.968
6.929
6.904
6.879
5.869
2.359
0.000
1H NMR (300 MHz, CDCl3)
Me
OH
1k
1.06
2.08
2.23
1.05
1.04
1.05
1.00
3.13
δ (ppm)


156.52
138.23
132.16
131.63
130.39
129.72
128.69
128.39
122.20
120.40
114.70
109.71
96.62
82.66
77.43
77.01
76.59
21.20
13C NMR (75 MHz, CDCl3)
Me
OH
1k
δ (ppm)



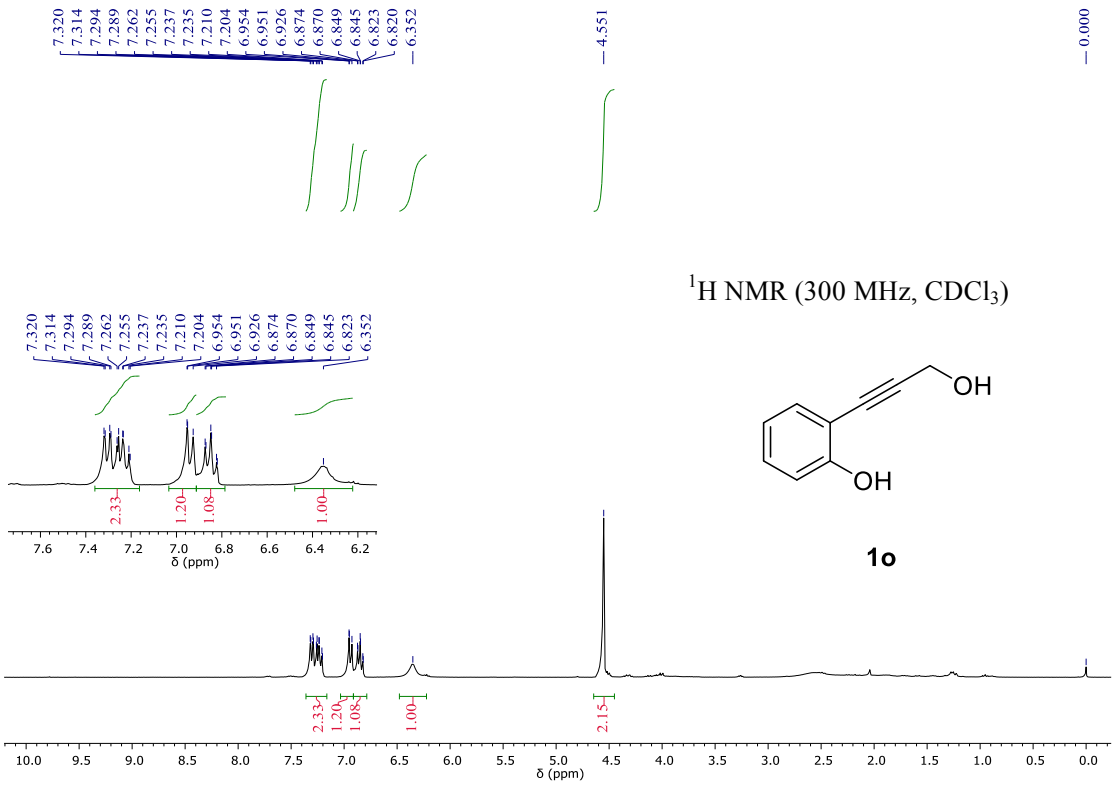
^{1}H NMR (300 MHz, $CDCl_3$)

1l



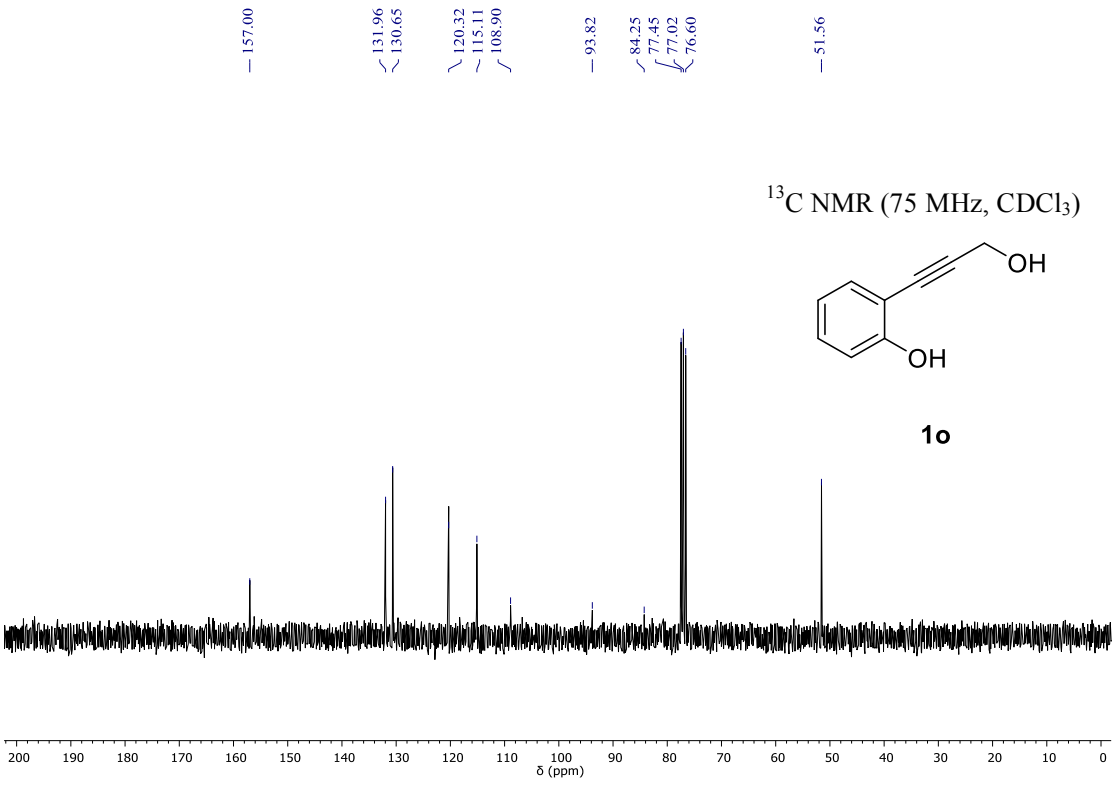
^{13}C NMR (75 MHz, $CDCl_3$)

1l



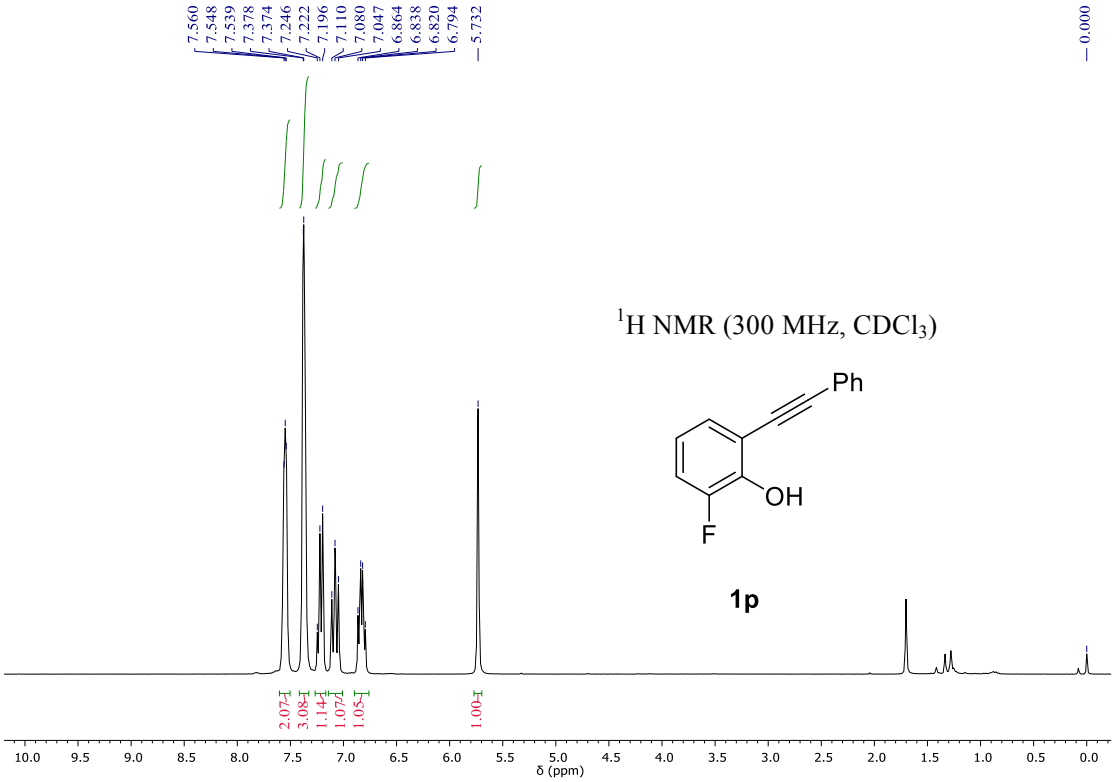
^{1}H NMR (300 MHz, $CDCl_3$)

1o



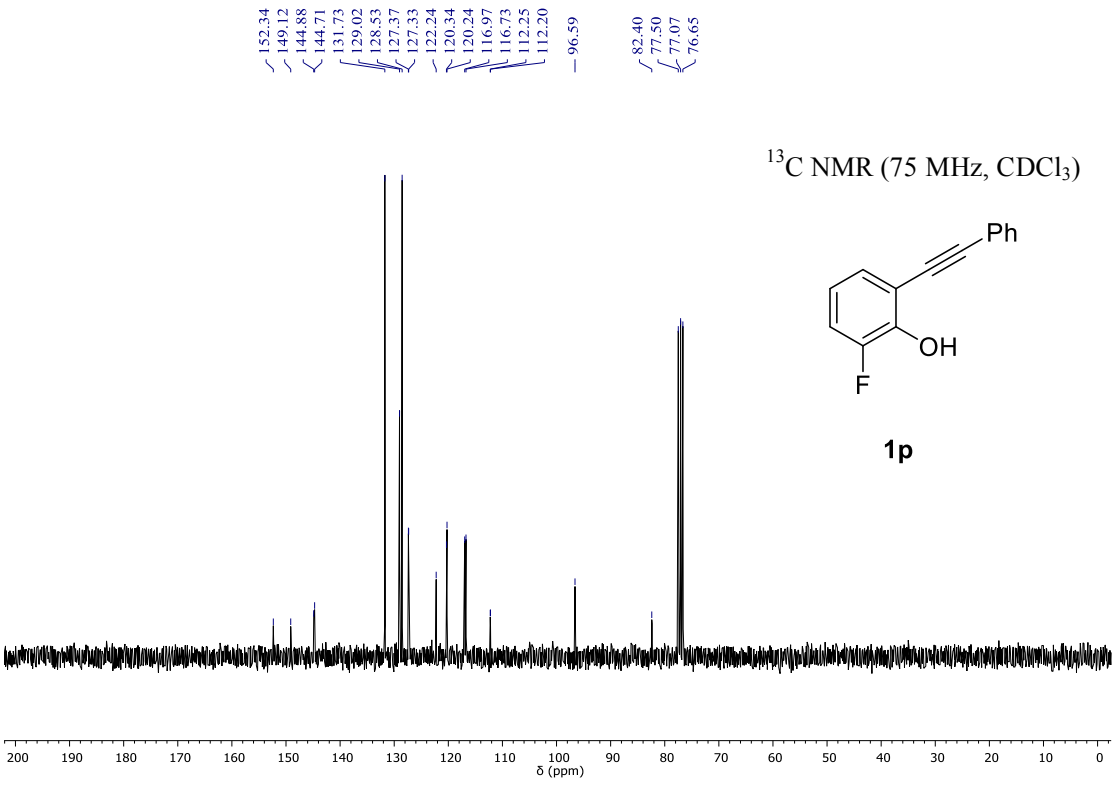
^{13}C NMR (75 MHz, $CDCl_3$)

1o



^{1}H NMR (300 MHz, $CDCl_3$)

1p

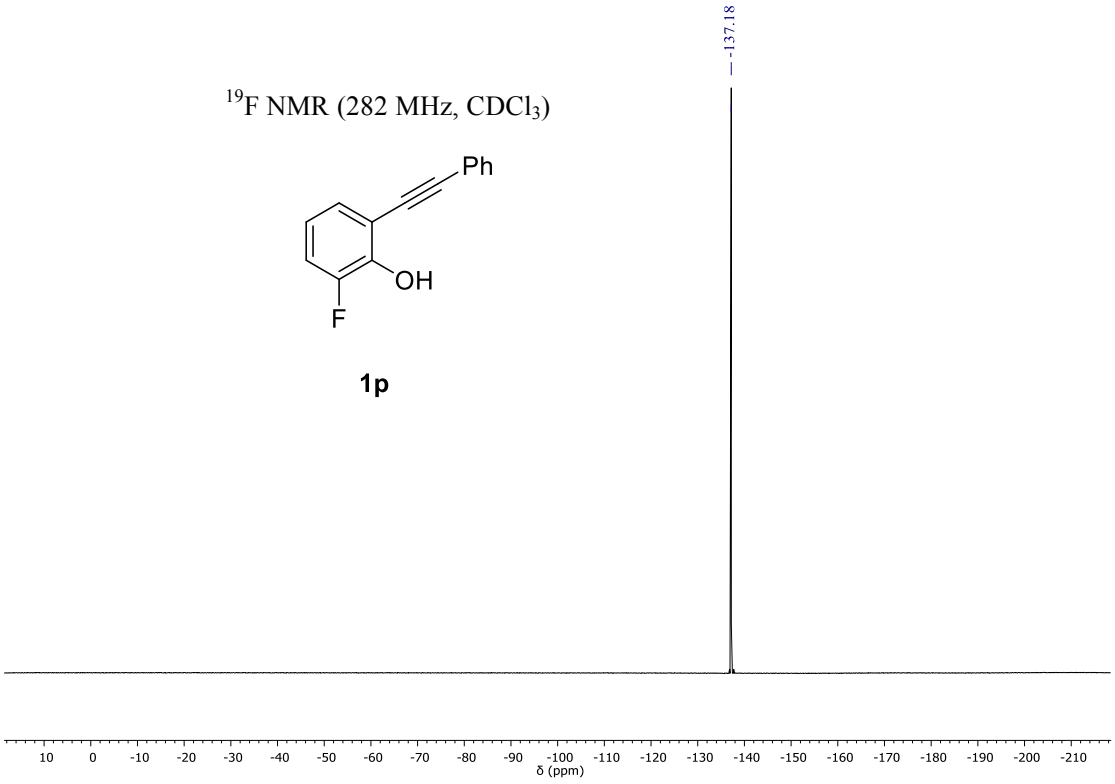


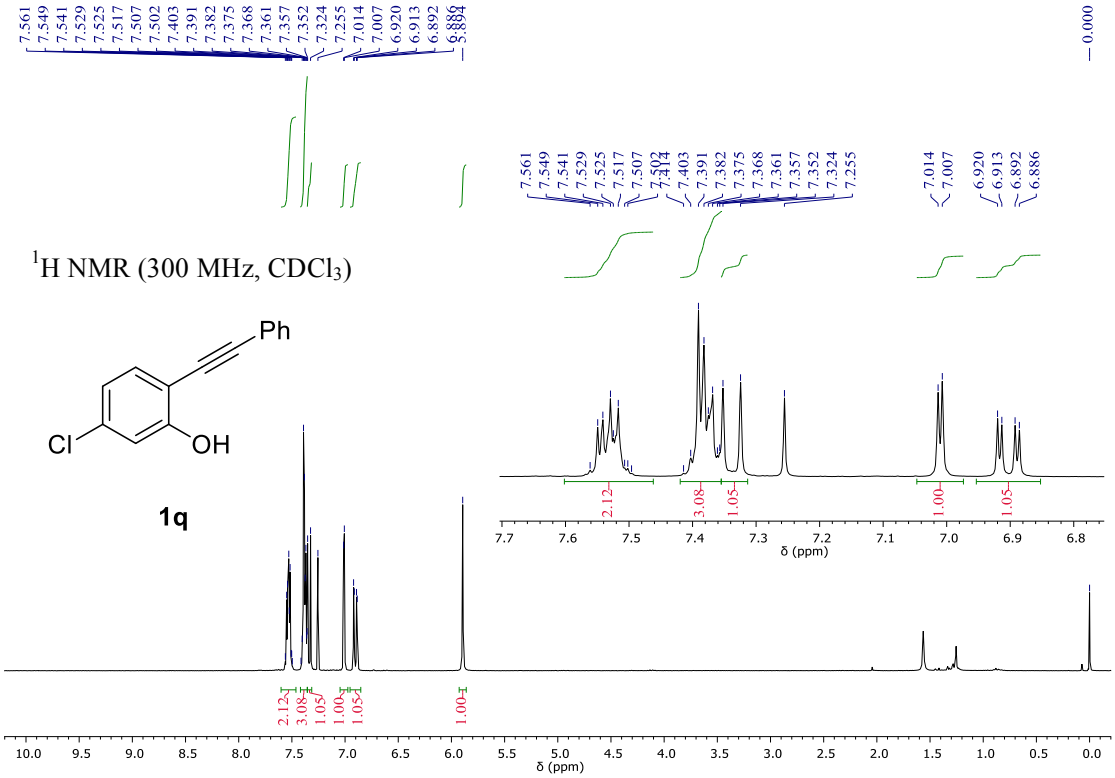
^{13}C NMR (75 MHz, $CDCl_3$)

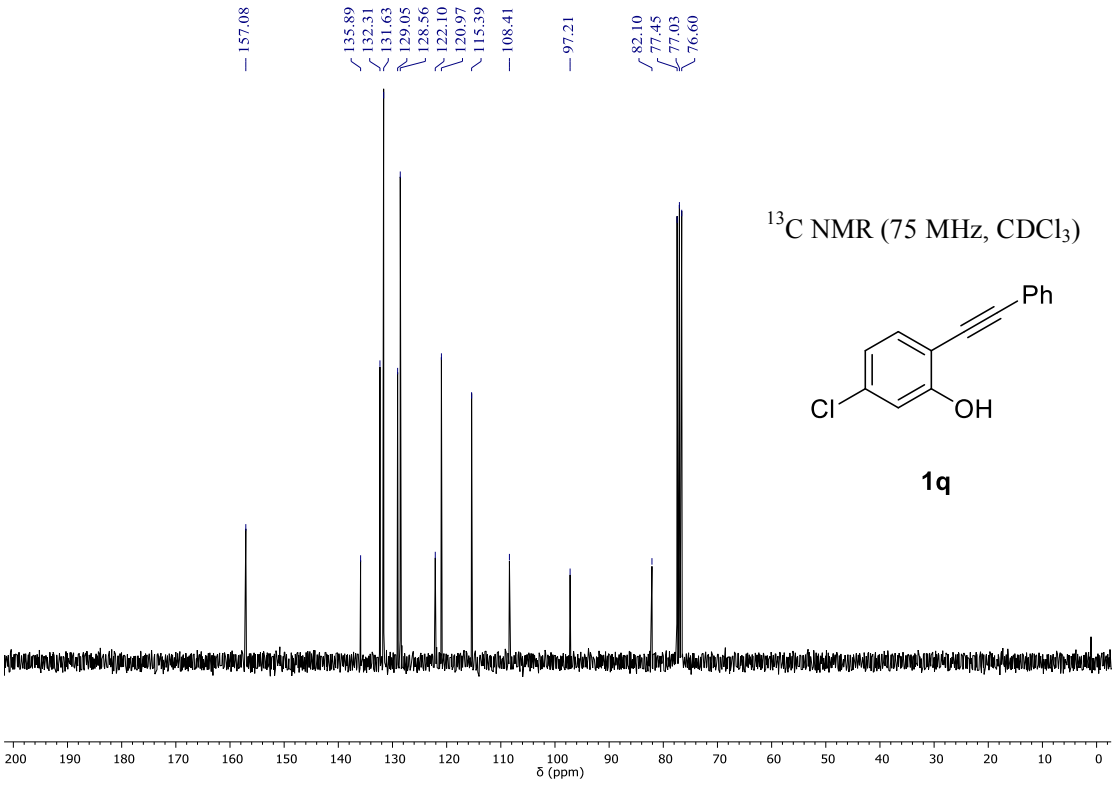
1p

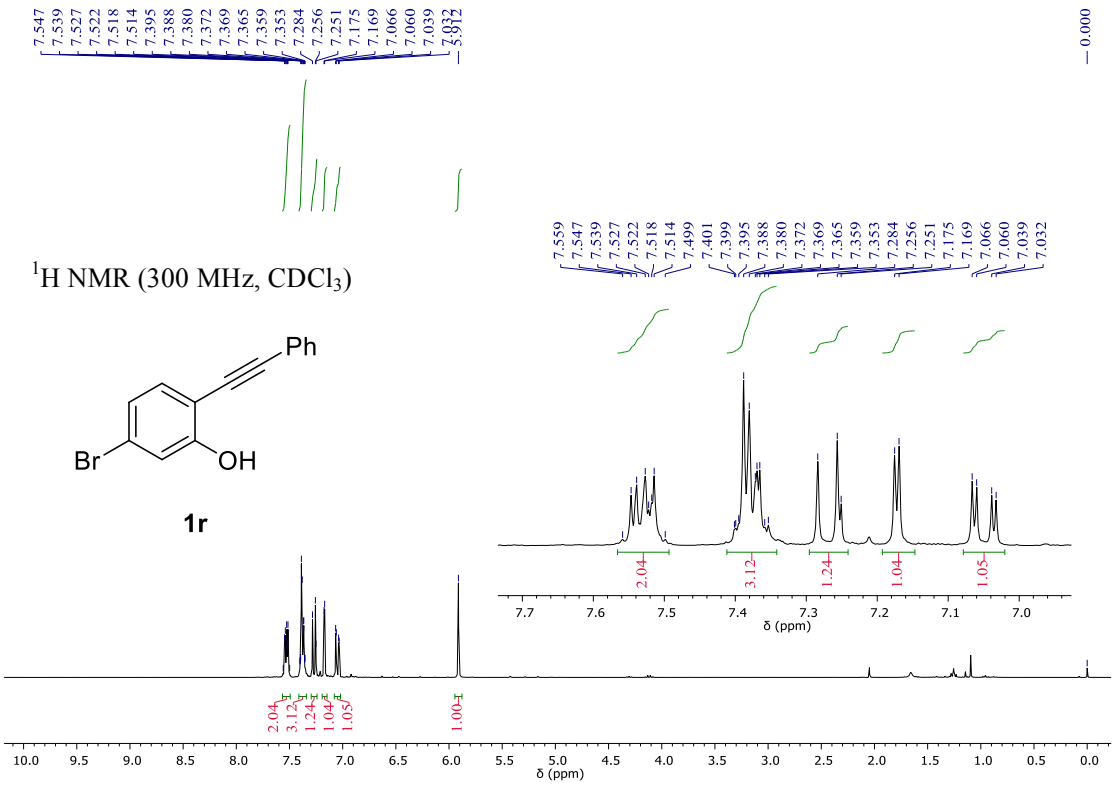
^{19}F NMR (282 MHz, $CDCl_3$)

1p



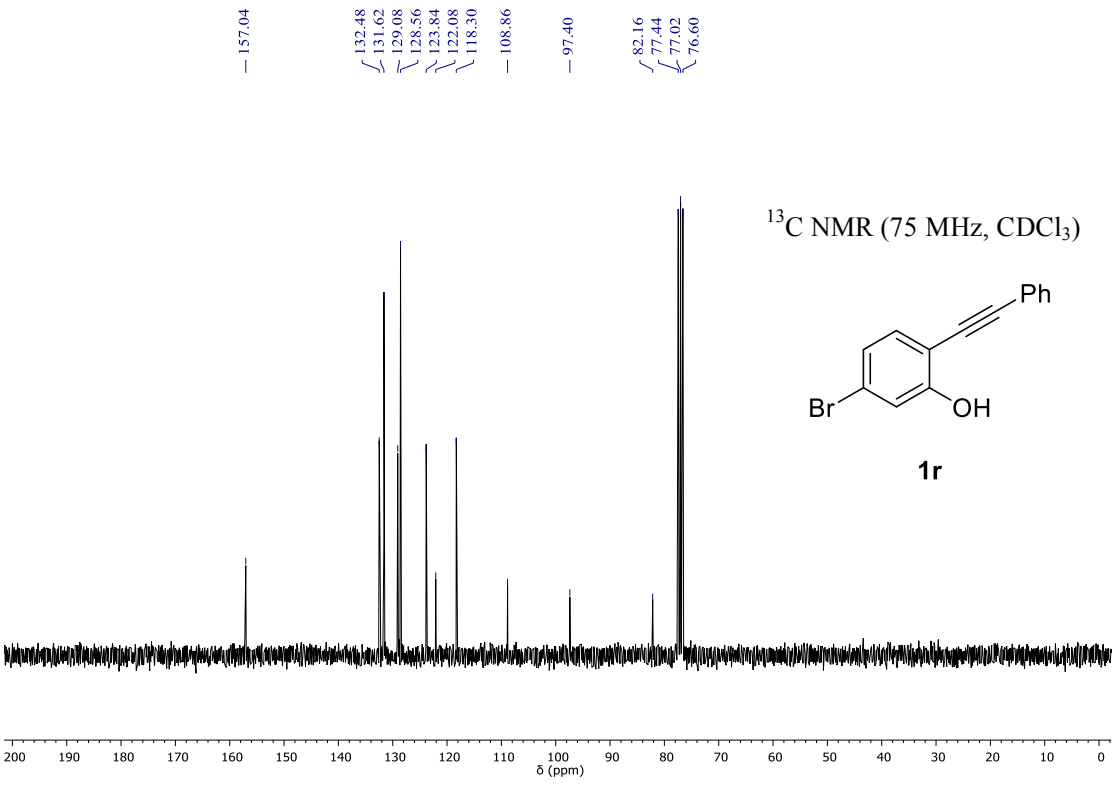

7.561
7.549
7.541
7.529
7.525
7.517
7.507
7.502
7.403
7.391
7.382
7.375
7.368
7.361
7.357
7.352
7.324
7.255
7.014
7.007
6.920
6.913
6.892
6.886
0.000
^{1}H NMR (300 MHz, CDCl$_3$)
Ph
Cl
OH
1q
2.12
3.08
1.05
1.00
1.05
1.00
δ (ppm)


157.08
135.89
132.31
131.63
129.05
128.56
122.10
120.97
115.39
108.41
97.21
82.10
77.45
77.03
76.60
^{13}C NMR (75 MHz, CDCl$_3$)
Ph
Cl
OH
1q
δ (ppm)



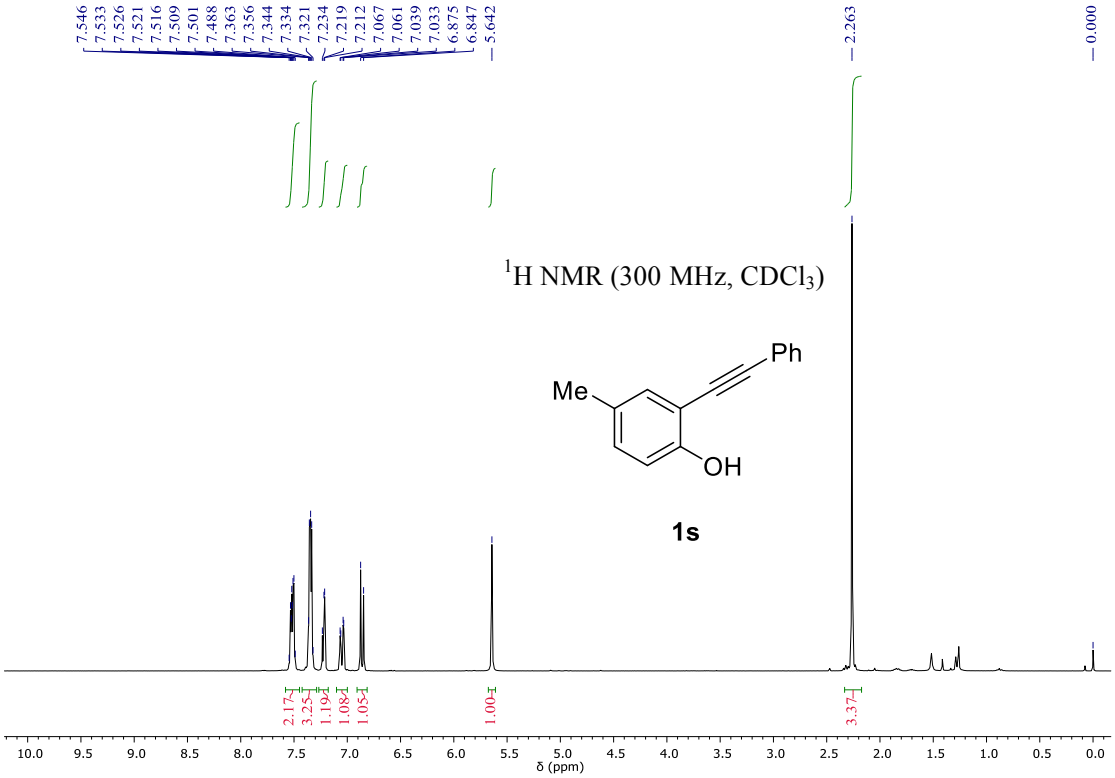
^{1}H NMR (300 MHz, $CDCl_3$)

1r



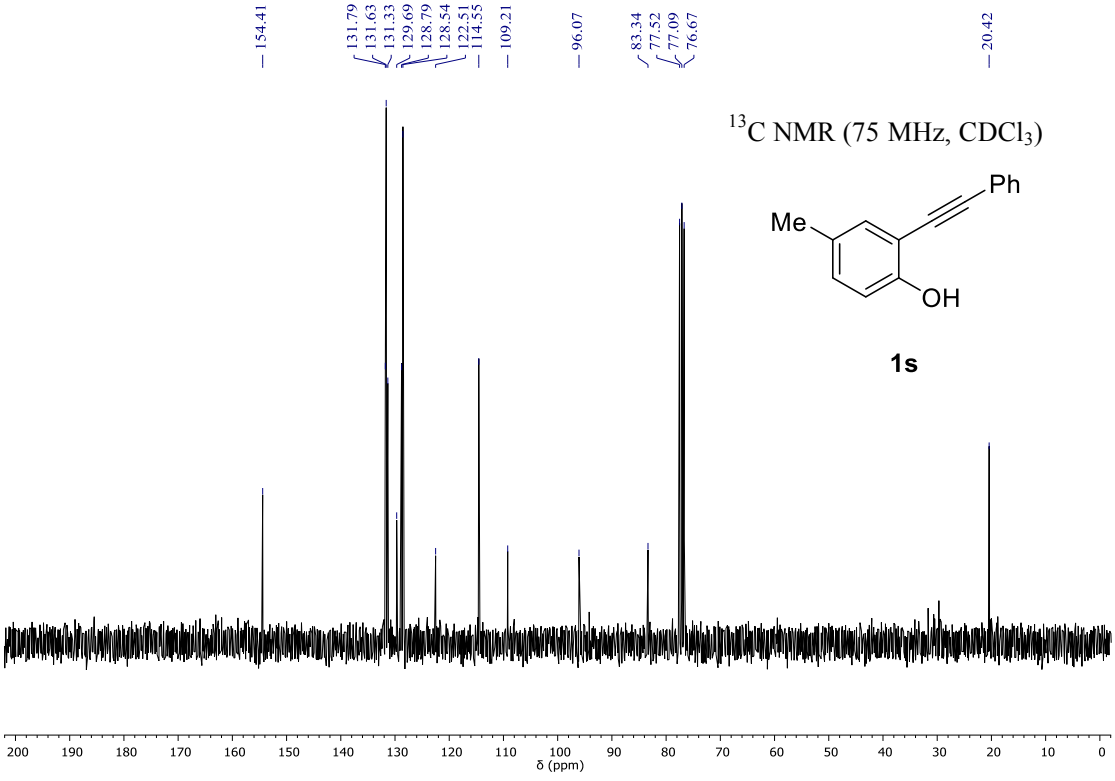
^{13}C NMR (75 MHz, $CDCl_3$)

1r



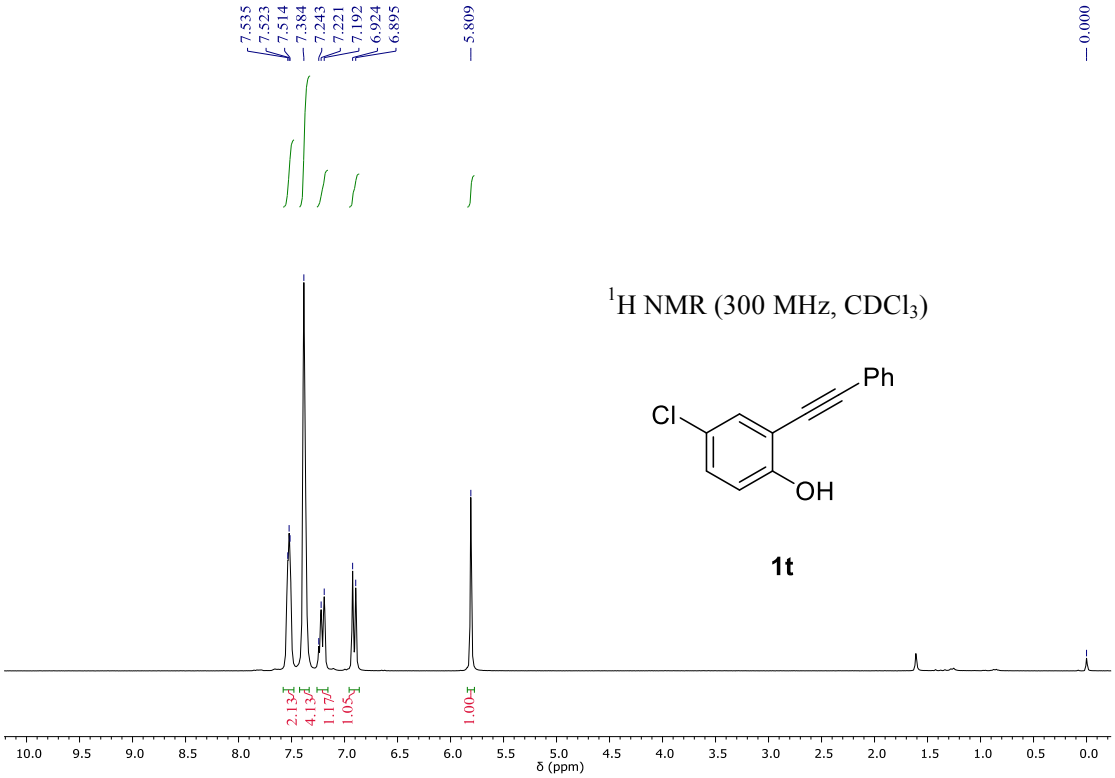
^{1}H NMR (300 MHz, $CDCl_3$)

1s



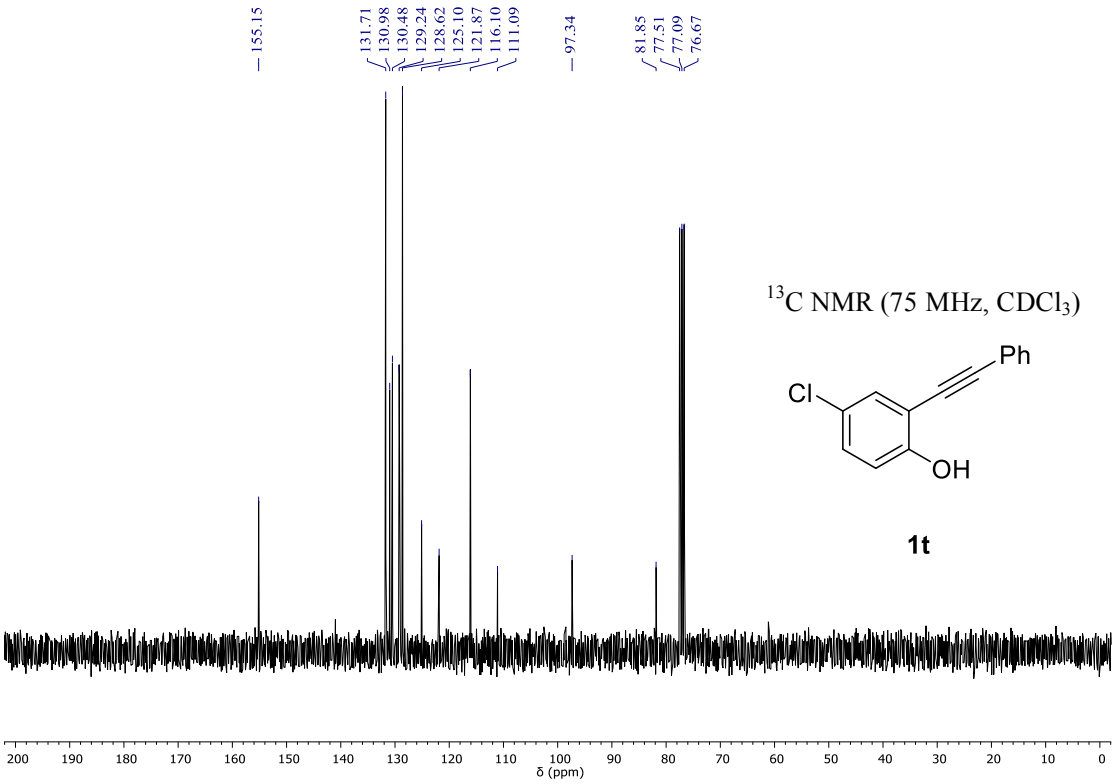
^{13}C NMR (75 MHz, $CDCl_3$)

1s



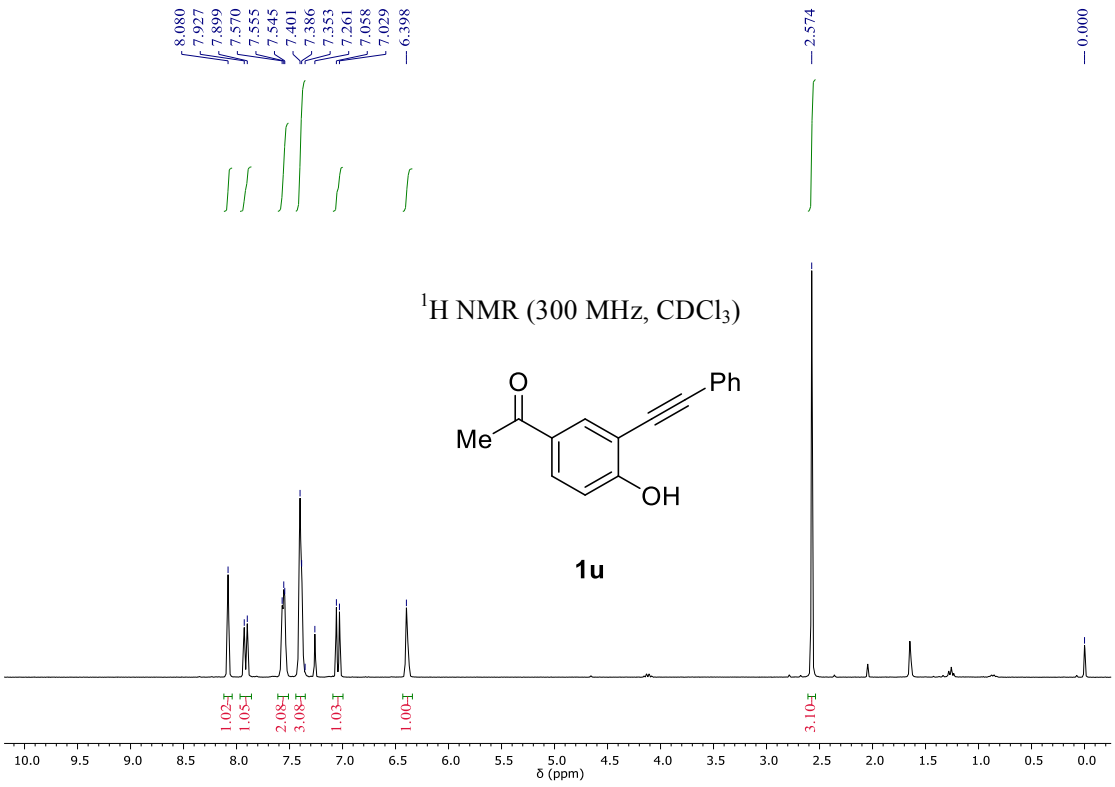
^{1}H NMR (300 MHz, $CDCl_3$)

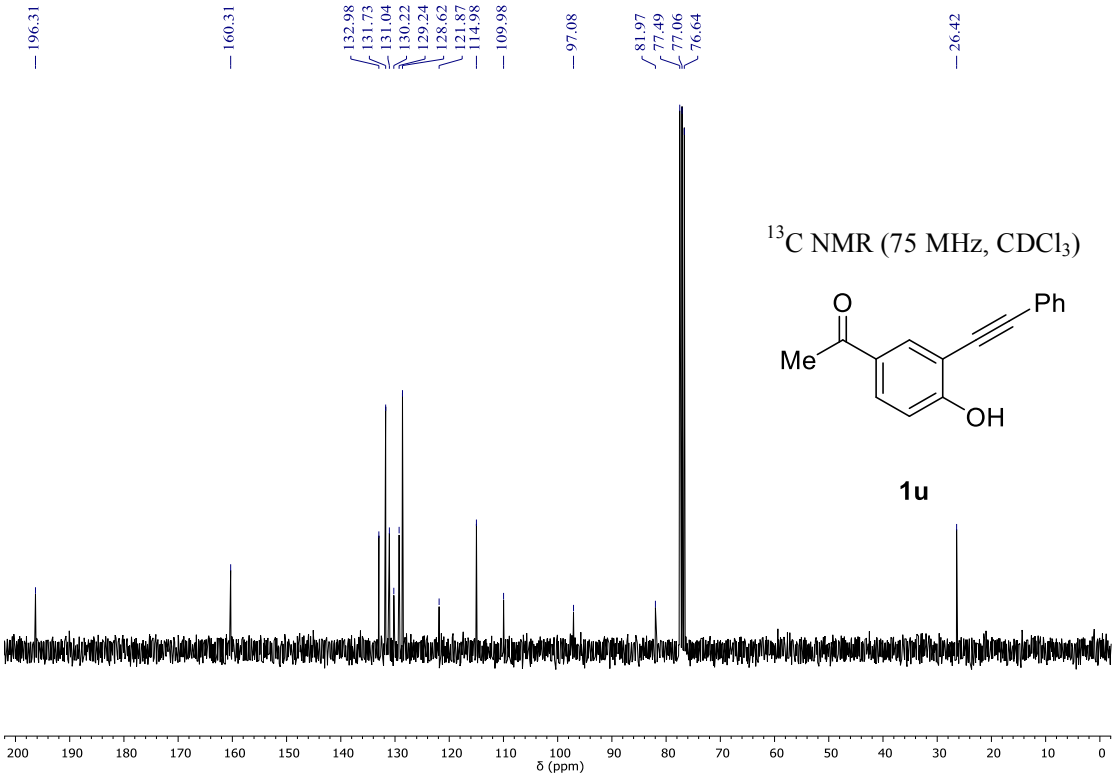
1t

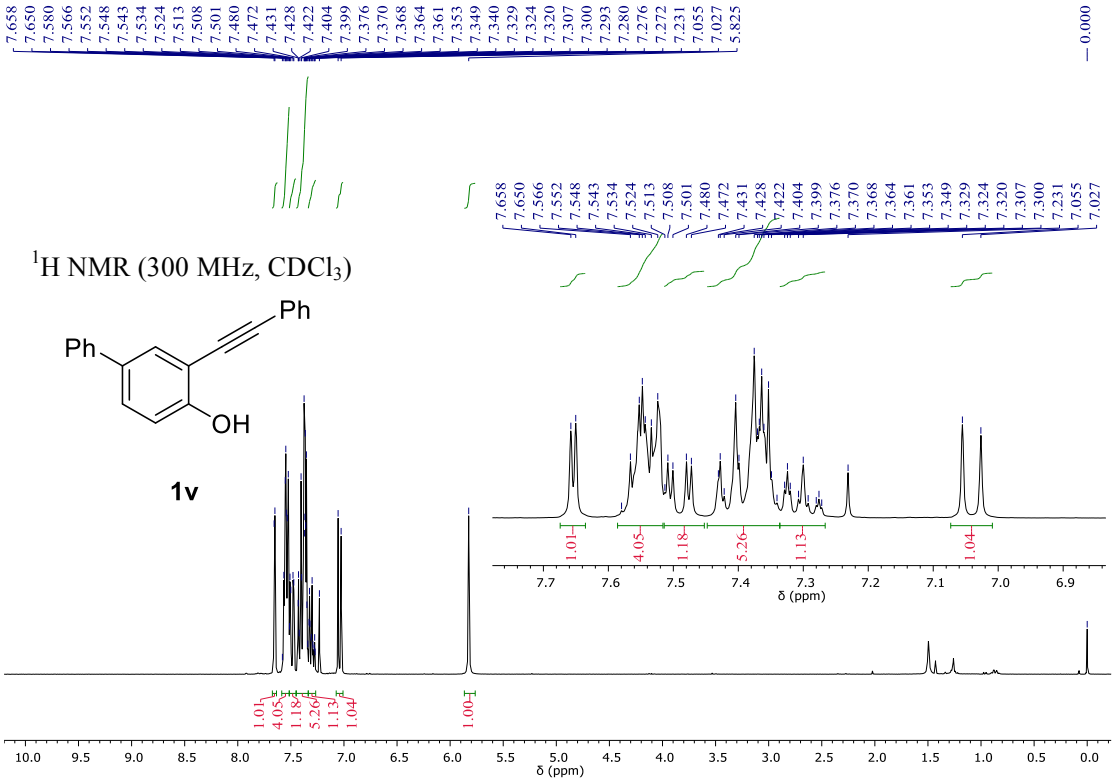


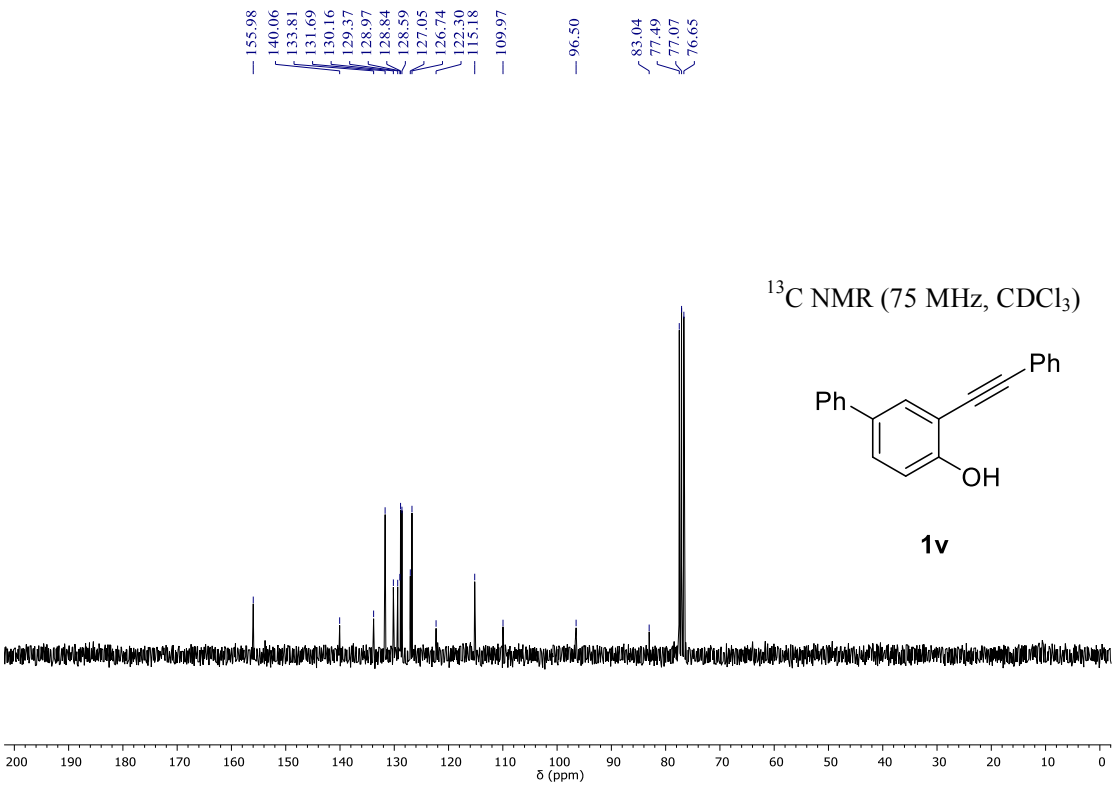
^{13}C NMR (75 MHz, $CDCl_3$)

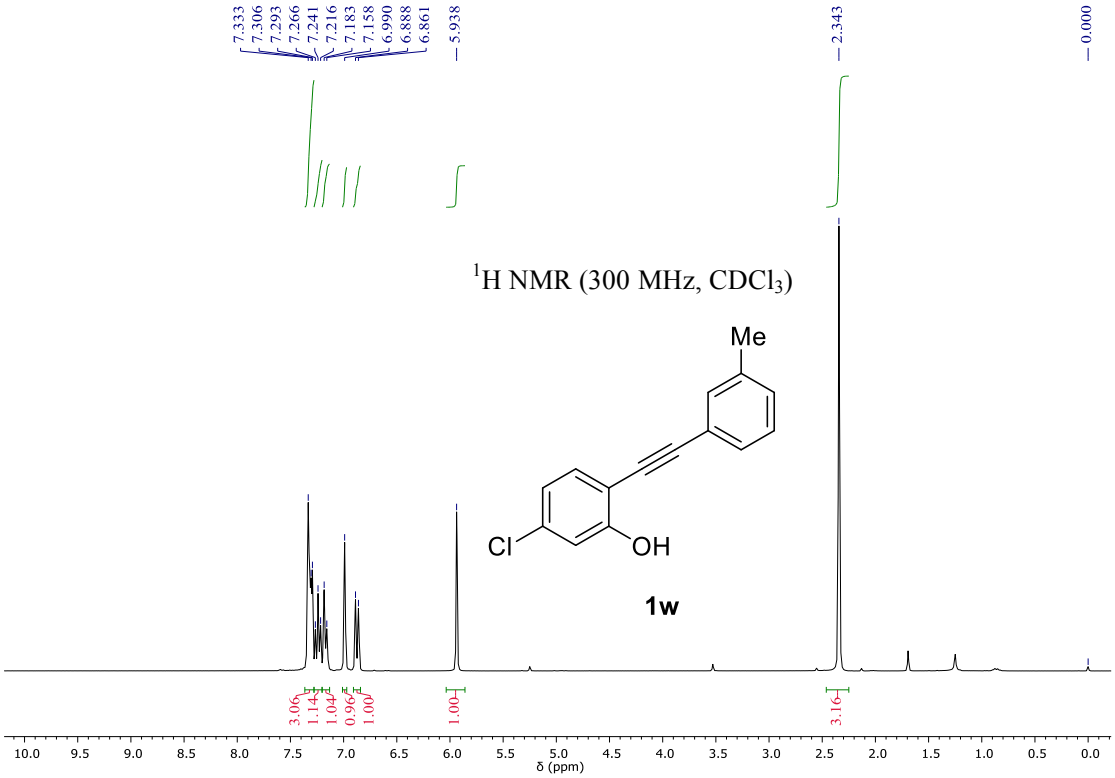
1t

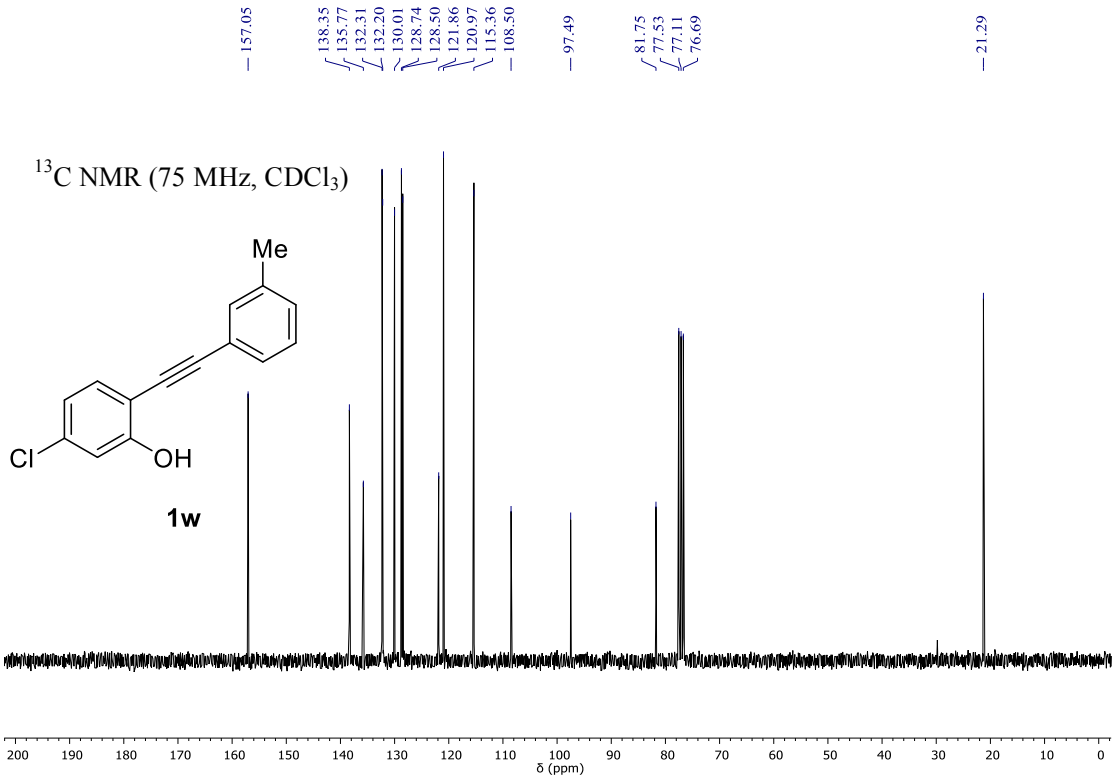

8.080
7.927
7.899
7.570
7.555
7.545
7.401
7.386
7.353
7.261
7.058
7.029
6.398
2.574
0.000
1H NMR (300 MHz, CDCl3)
O
Ph
Me
OH
1u
1.02
1.05
2.08
3.08
1.03
1.00
3.10
δ (ppm)

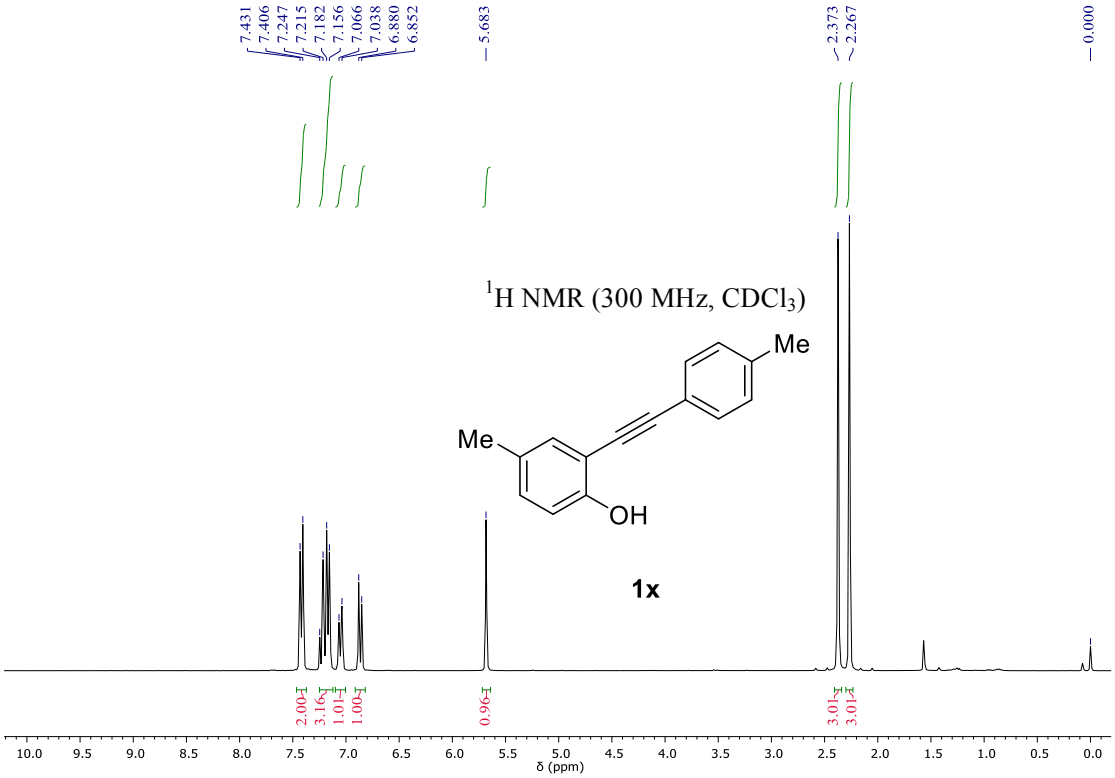

196.31
160.31
132.98
131.73
131.04
130.22
129.24
128.62
121.87
114.98
109.98
97.08
81.97
77.49
77.06
76.64
26.42
13C NMR (75 MHz, CDCl3)
O
Ph
Me
OH
1u
δ (ppm)

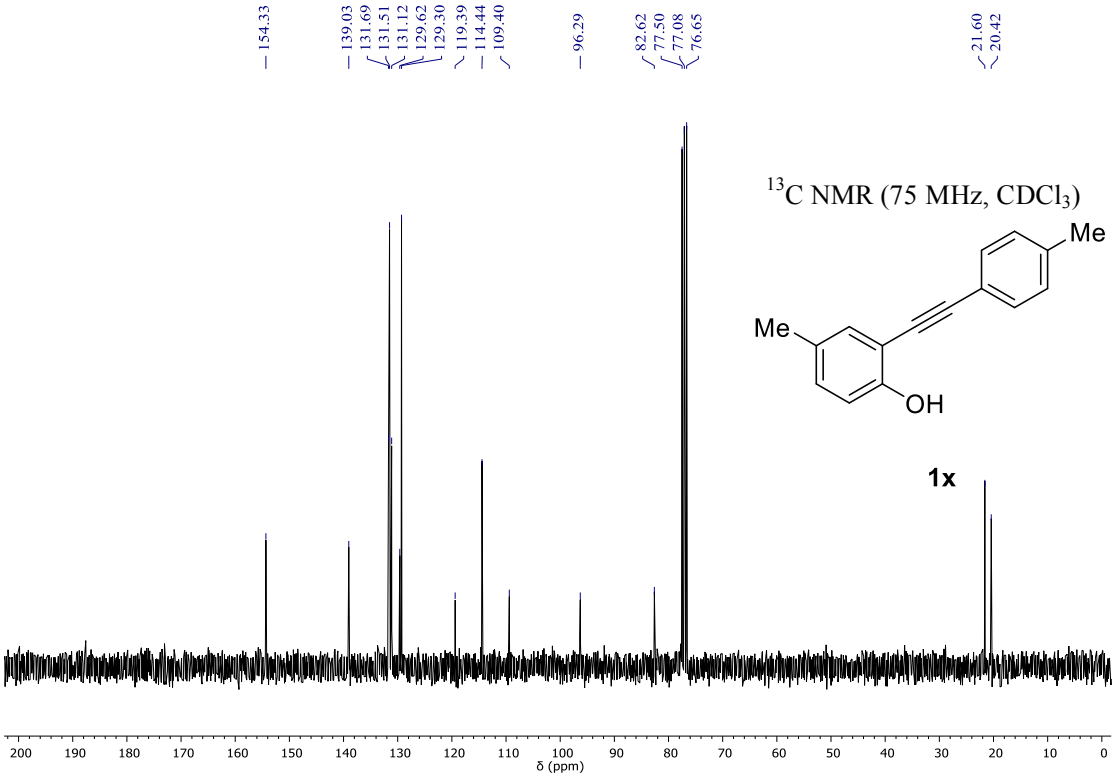

7.658
7.650
7.580
7.566
7.552
7.548
7.543
7.534
7.524
7.513
7.508
7.501
7.480
7.472
7.431
7.428
7.422
7.404
7.399
7.376
7.370
7.368
7.364
7.361
7.353
7.349
7.340
7.329
7.324
7.320
7.307
7.300
7.293
7.280
7.276
7.272
7.231
7.055
7.027
5.825
0.000
1H NMR (300 MHz, CDCl3)
Ph
Ph
OH
1v
1.01
4.05
1.18
5.26
1.13
1.04
1.00
δ (ppm)

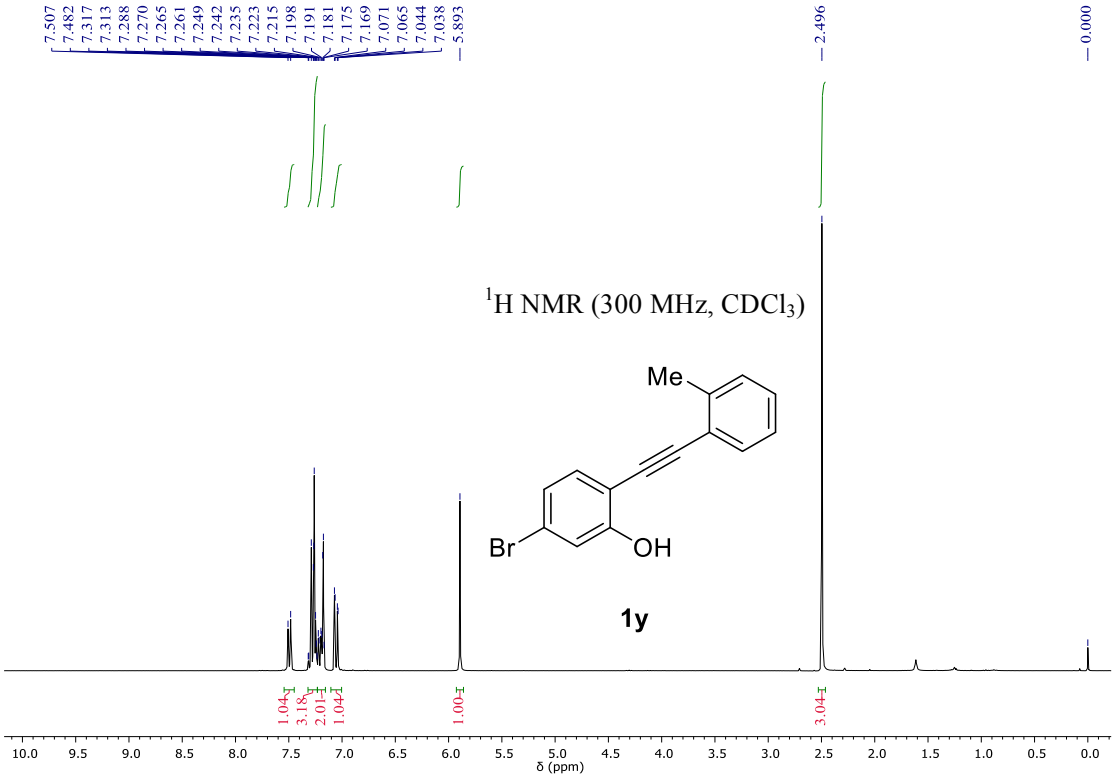

155.98
140.06
133.81
131.69
130.16
129.37
128.97
128.84
128.59
127.05
126.74
122.30
115.18
109.97
96.50
83.04
77.49
77.07
76.65
13C NMR (75 MHz, CDCl3)
Ph
Ph
OH
1v
δ (ppm)


7.333
7.306
7.293
7.266
7.241
7.216
7.183
7.158
6.990
6.888
6.861
5.938
2.343
0.000
^{1}H NMR (300 MHz, CDCl$_3$)
Me
Cl
OH
1w
3.06
1.14
1.04
0.96
1.00
1.00
3.16
δ (ppm)


157.05
138.35
135.77
132.31
132.20
130.01
128.74
128.50
121.86
120.97
115.36
108.50
97.49
81.75
77.53
77.11
76.69
21.29
^{13}C NMR (75 MHz, CDCl$_3$)
Me
Cl
OH
1w
δ (ppm)

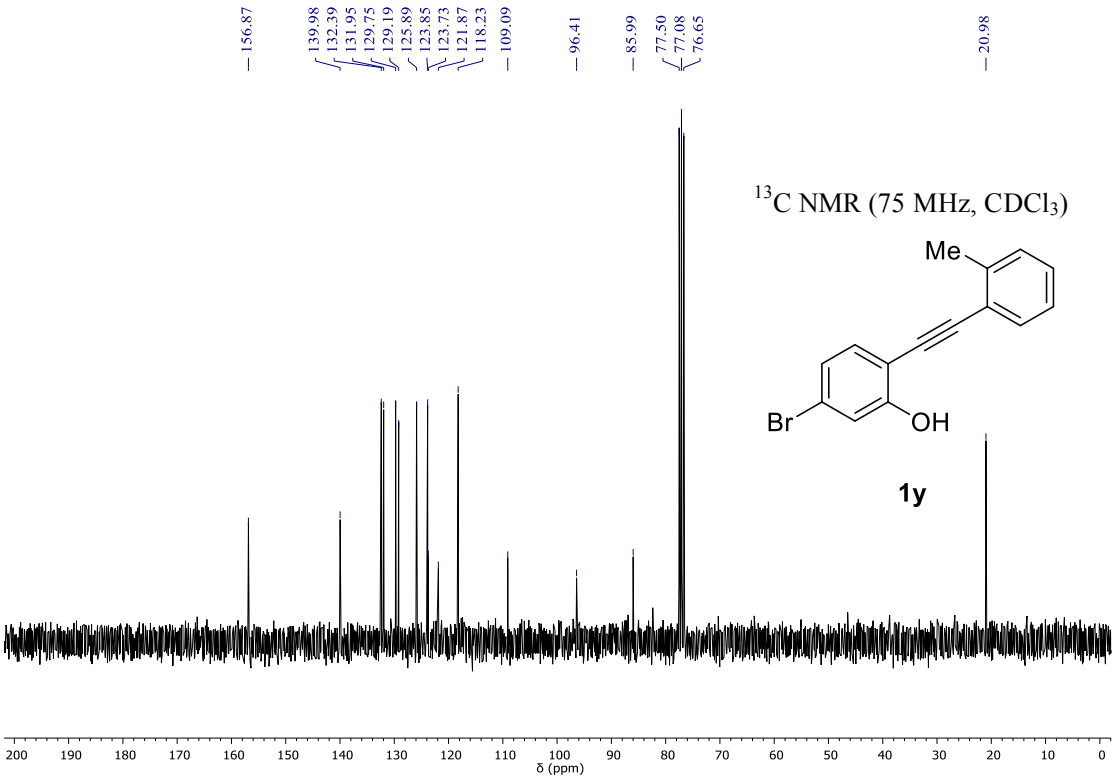

7.431
7.406
7.247
7.215
7.182
7.156
7.066
7.038
6.880
6.852
5.683
2.373
2.267
0.000
^{1}H NMR (300 MHz, CDCl$_3$)
Me
Me
OH
1x
2.00
3.16
1.01
1.00
0.96
3.01
3.01
δ (ppm)


154.33
139.03
131.69
131.51
131.12
129.62
129.30
119.39
114.44
109.40
96.29
82.62
77.50
77.08
76.65
21.60
20.42
^{13}C NMR (75 MHz, CDCl$_3$)
Me
Me
OH
1x
δ (ppm)



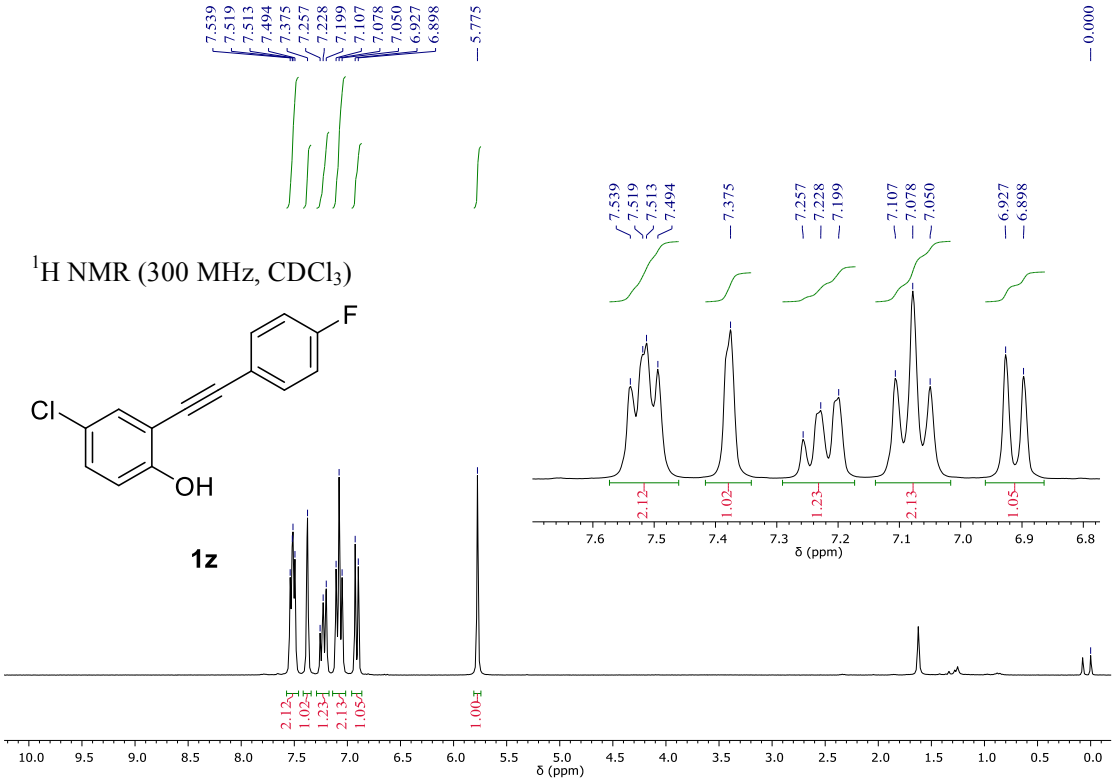
^{1}H NMR (300 MHz, $CDCl_3$)

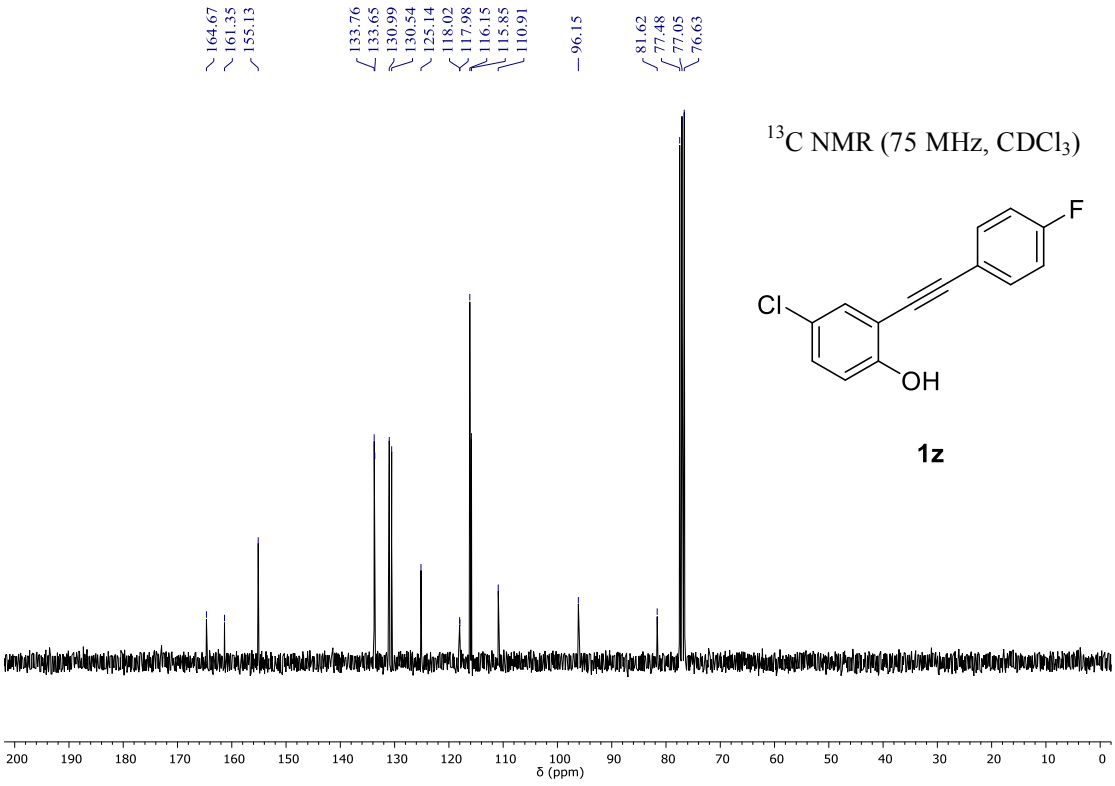
1y



^{13}C NMR (75 MHz, $CDCl_3$)

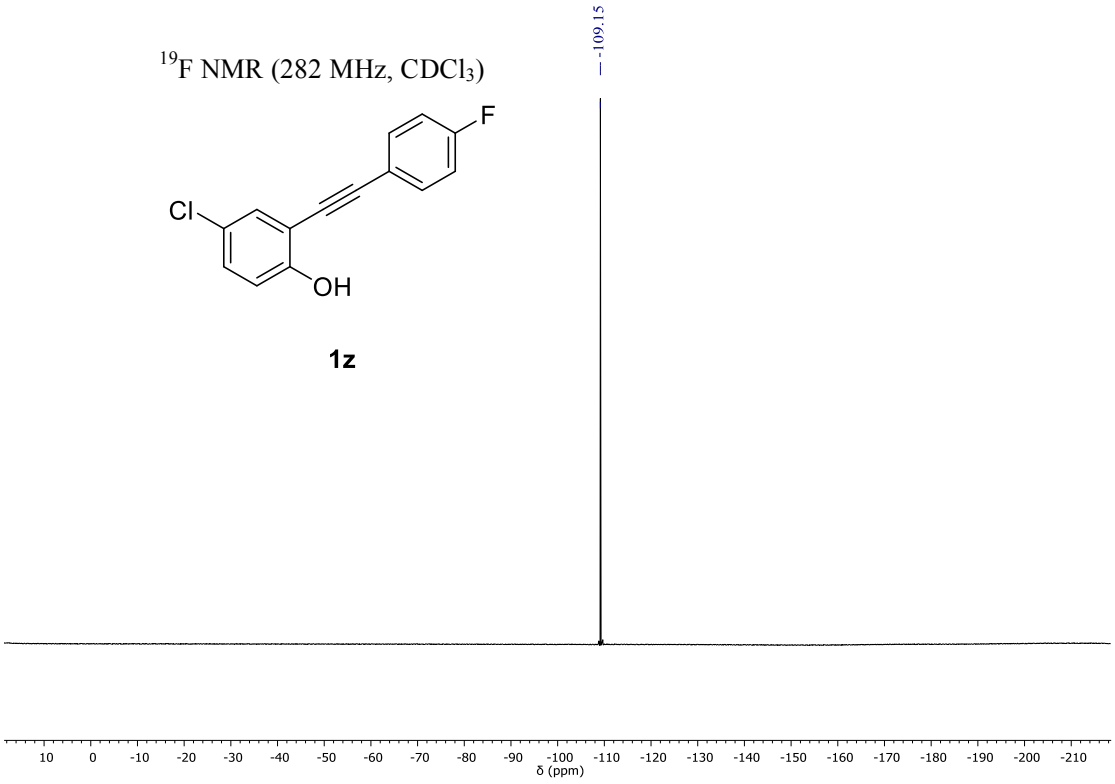
1y

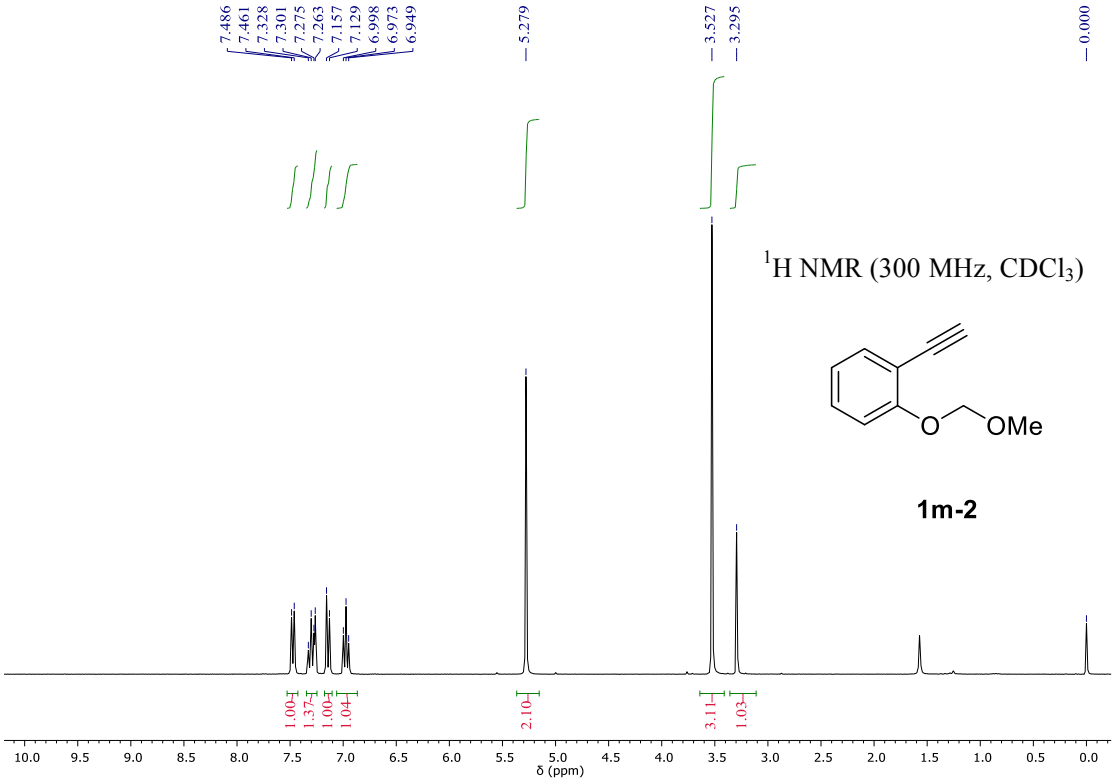

7.539
7.519
7.513
7.494
7.375
7.257
7.228
7.199
7.107
7.078
7.050
6.927
6.898
5.775
0.000
^{1}H NMR (300 MHz, CDCl$_3$)
F
Cl
OH
1z
2.12
1.02
1.23
2.13
1.05
1.00
δ (ppm)


164.67
161.35
155.13
133.76
133.65
130.99
130.54
125.14
118.02
117.98
116.15
115.85
110.91
96.15
81.62
77.48
77.05
76.63
^{13}C NMR (75 MHz, CDCl$_3$)
F
Cl
OH
1z
δ (ppm)

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

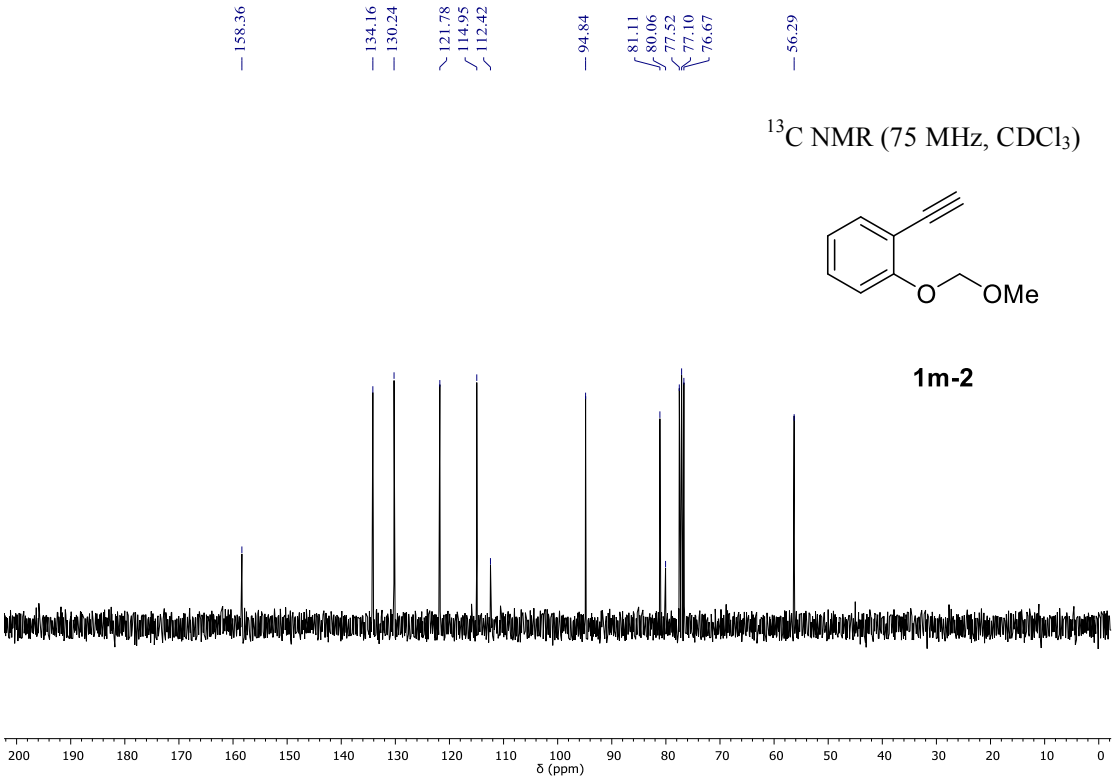
1z





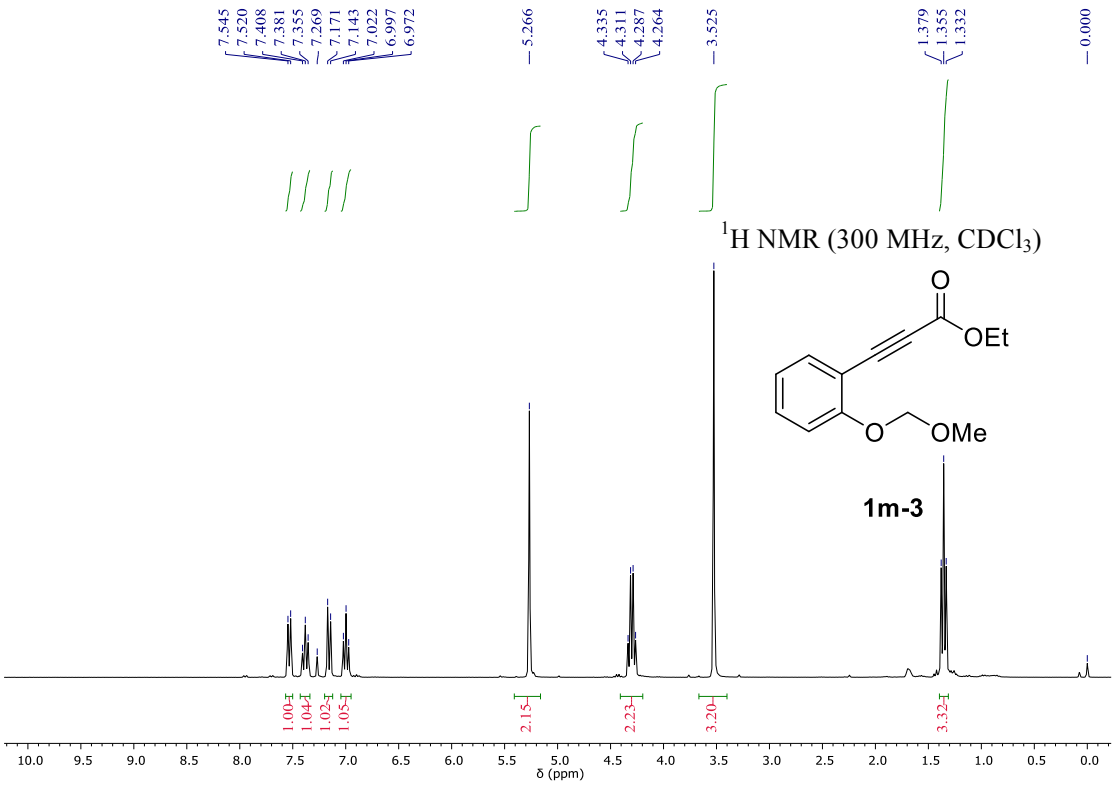
^{1}H NMR (300 MHz, $CDCl_3$)

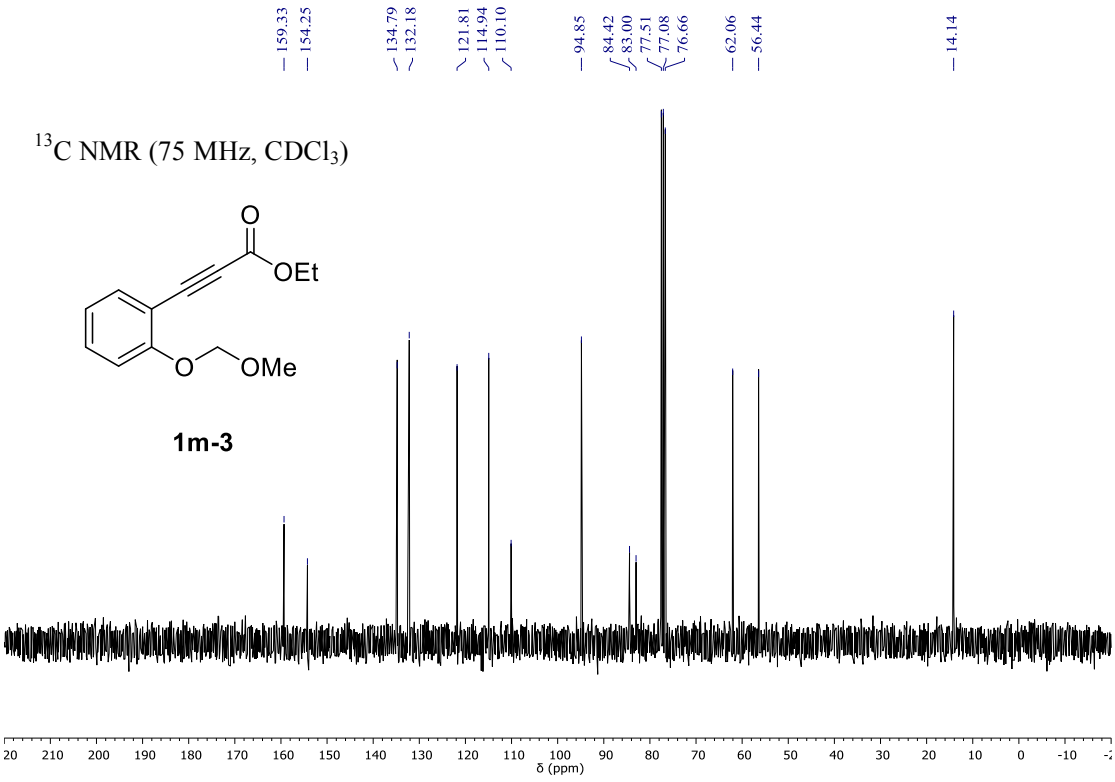
1m-2

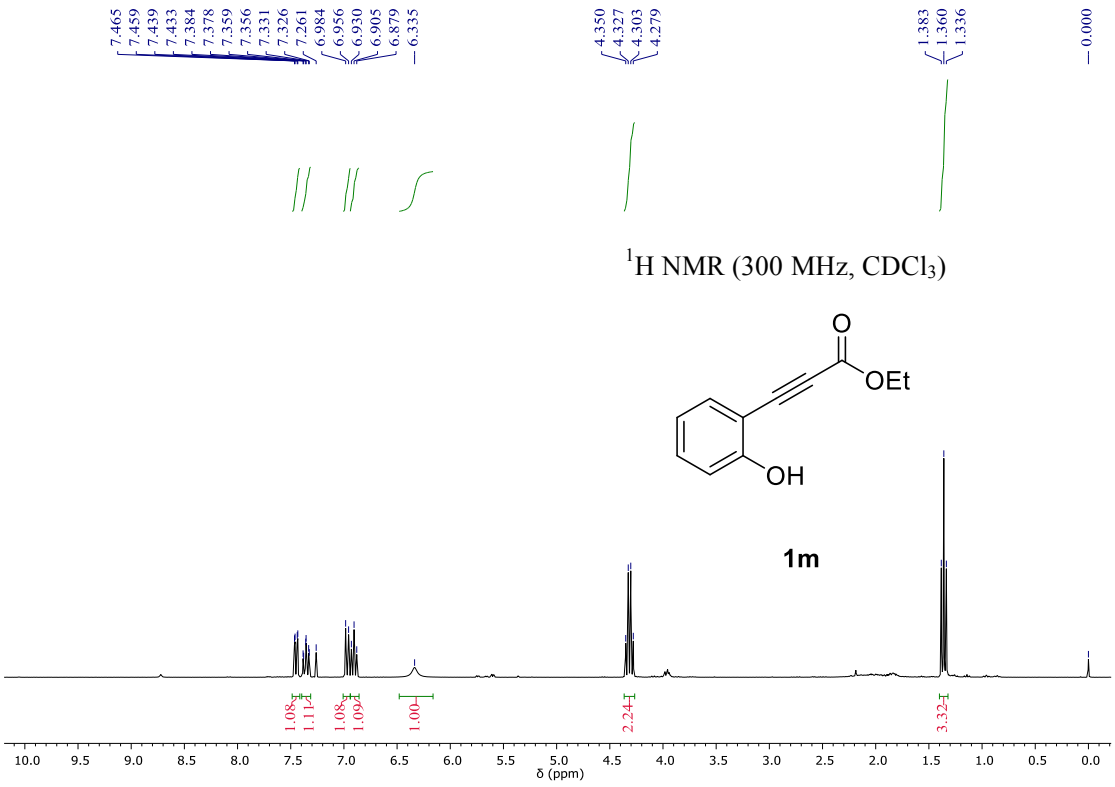


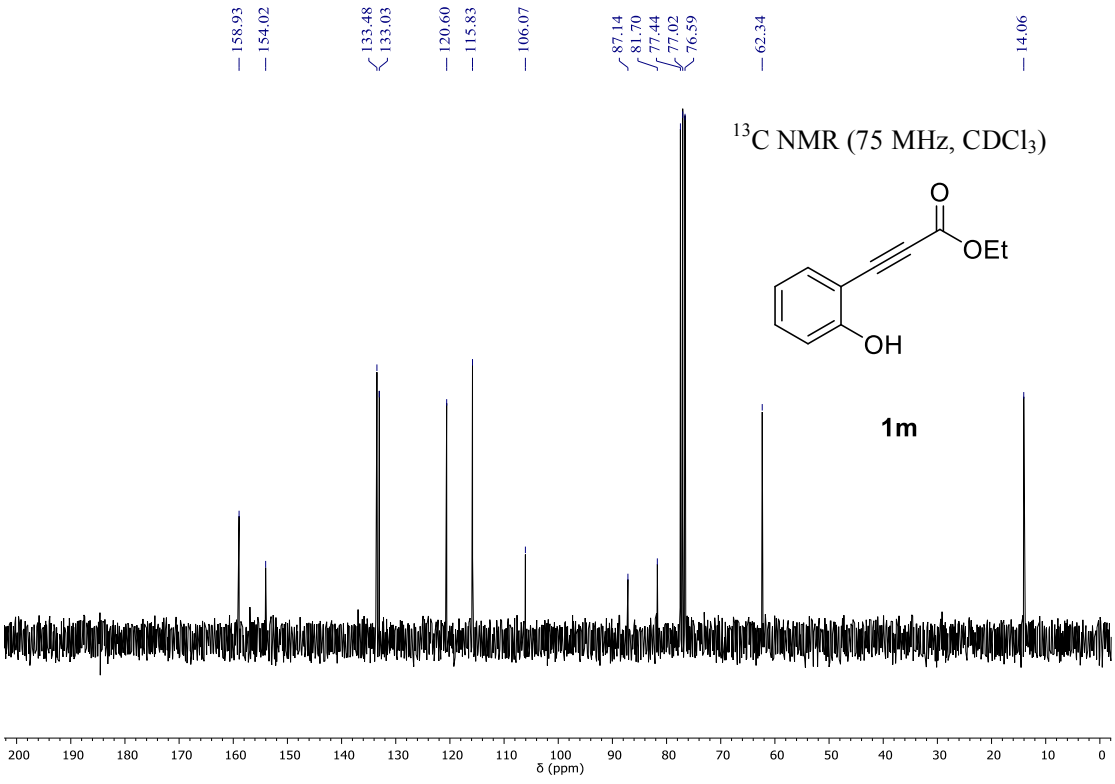
^{13}C NMR (75 MHz, $CDCl_3$)

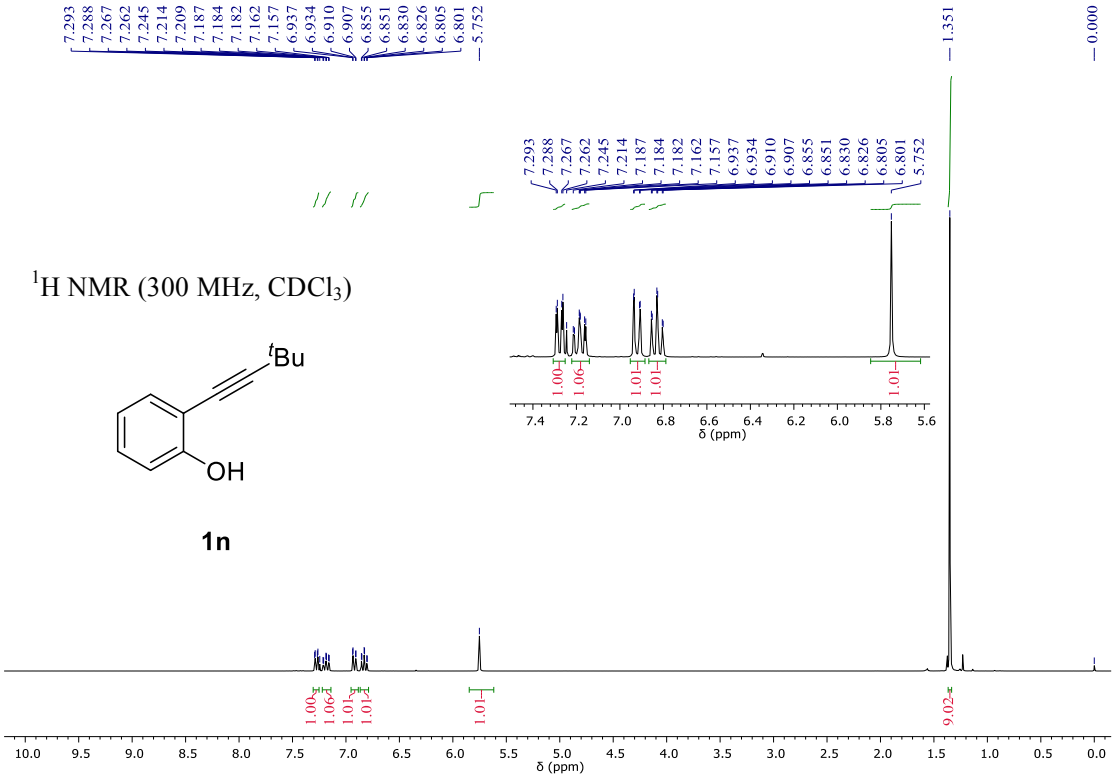
1m-2


7.545
7.520
7.408
7.381
7.355
7.269
7.171
7.143
7.022
6.997
6.972
5.266
4.335
4.311
4.287
4.264
3.525
1.379
1.355
1.332
0.000
1H NMR (300 MHz, CDCl3)
O
OEt
O
OMe
1m-3
1.00
1.04
1.02
1.05
2.15
2.23
3.20
3.32
δ (ppm)


159.33
154.25
134.79
132.18
121.81
114.94
110.10
94.85
84.42
83.00
77.51
77.08
76.66
62.06
56.44
14.14
13C NMR (75 MHz, CDCl3)
O
OEt
O
OMe
1m-3
δ (ppm)

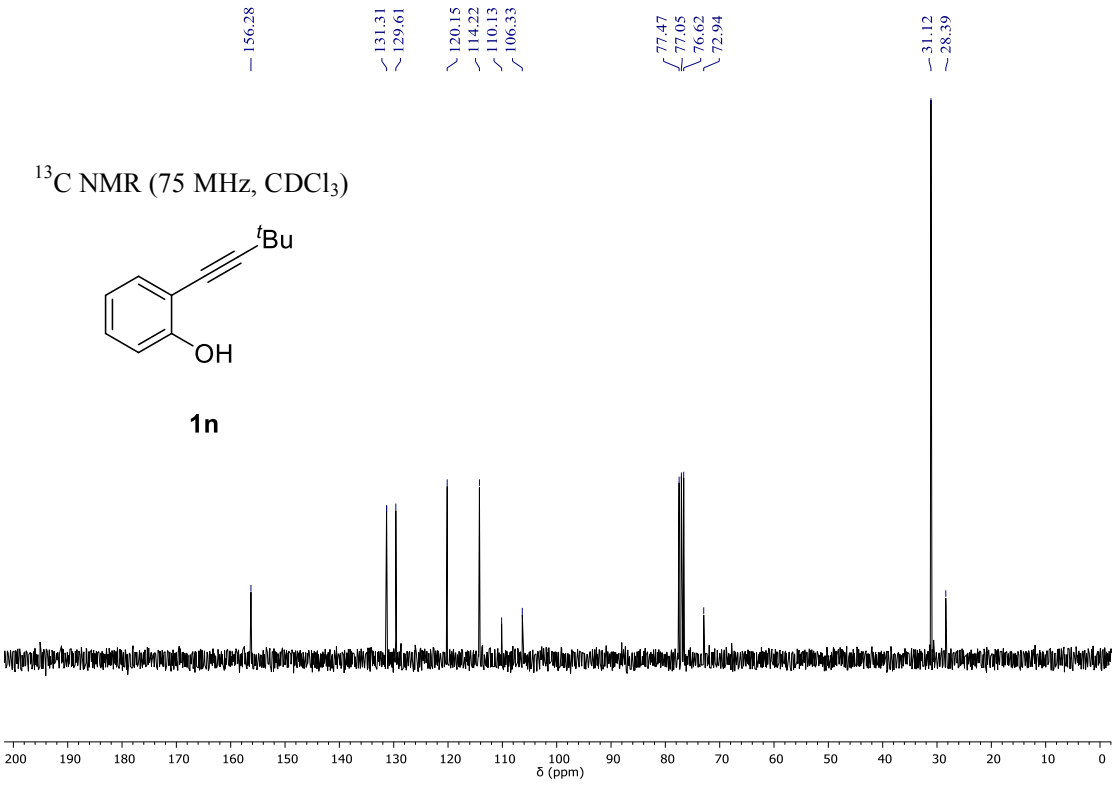

7.465
7.459
7.439
7.433
7.384
7.378
7.359
7.356
7.331
7.326
7.261
6.984
6.956
6.930
6.905
6.879
6.335
4.350
4.327
4.303
4.279
1.383
1.360
1.336
0.000
^{1}H NMR (300 MHz, CDCl$_3$)
O
OEt
OH
1m
1.08
1.11
1.08
1.09
1.00
2.24
3.32
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)


158.93
154.02
133.48
133.03
120.60
115.83
106.07
87.14
81.70
77.44
77.02
76.59
62.34
14.06
^{13}C NMR (75 MHz, CDCl$_3$)
O
OEt
OH
1m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)



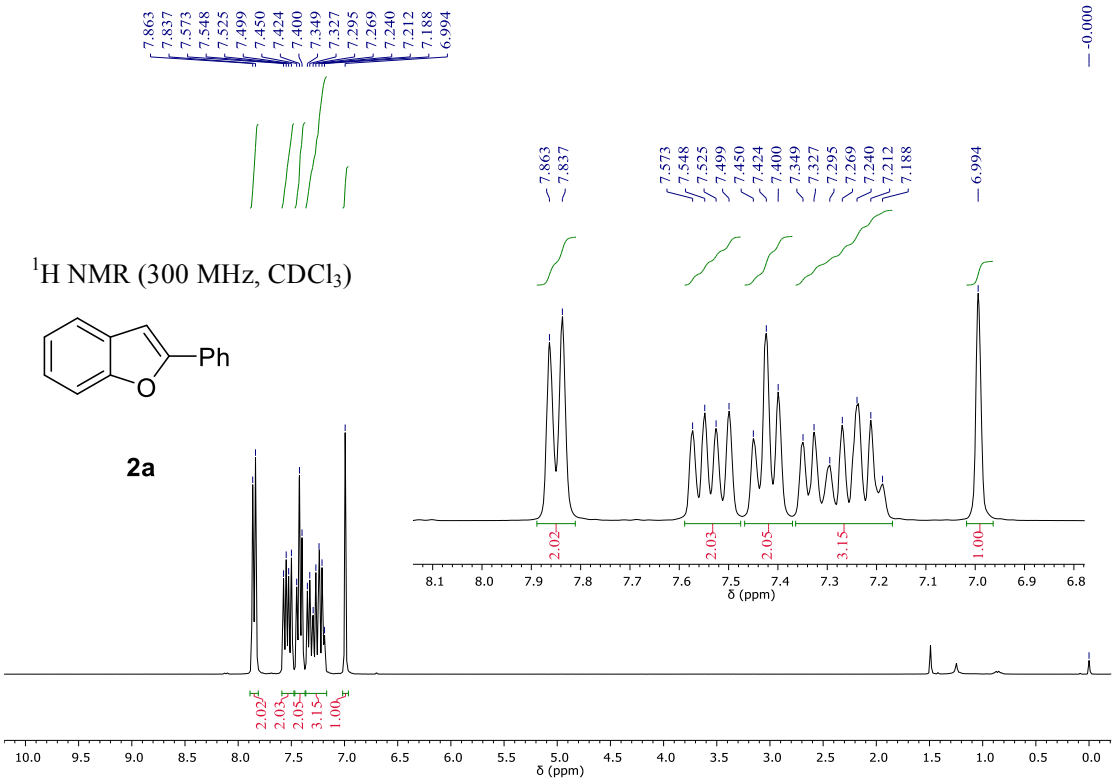
^{1}H NMR (300 MHz, $CDCl_3$)

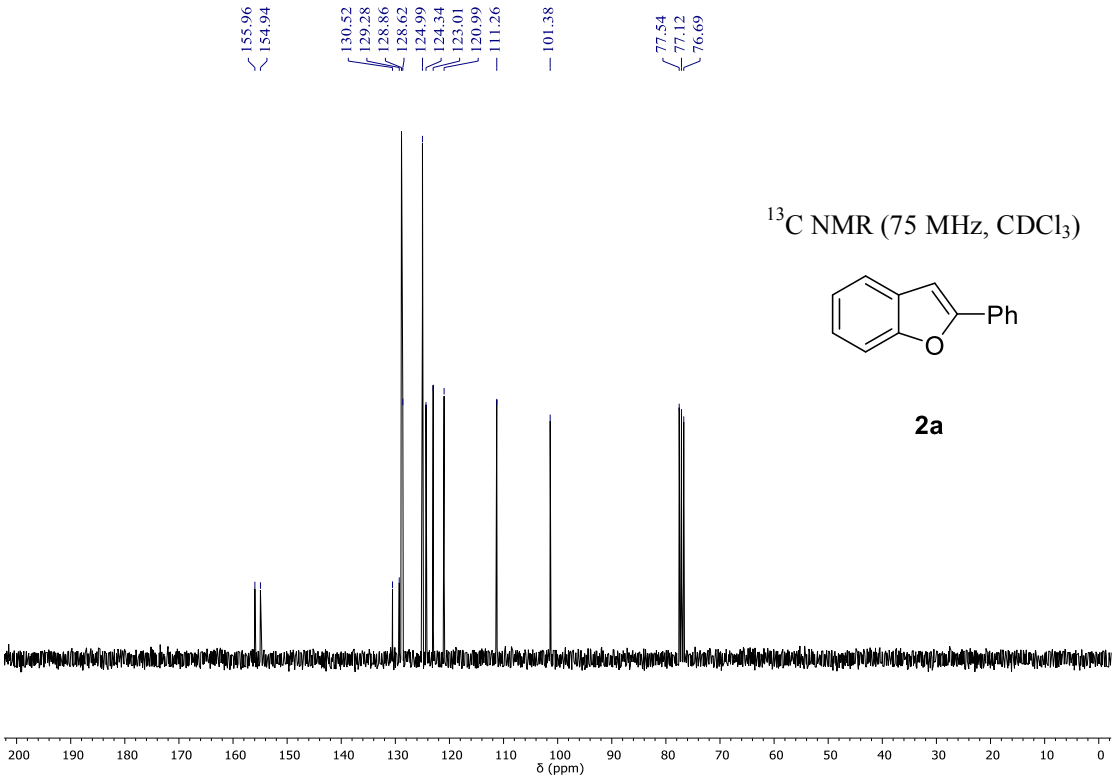
1n

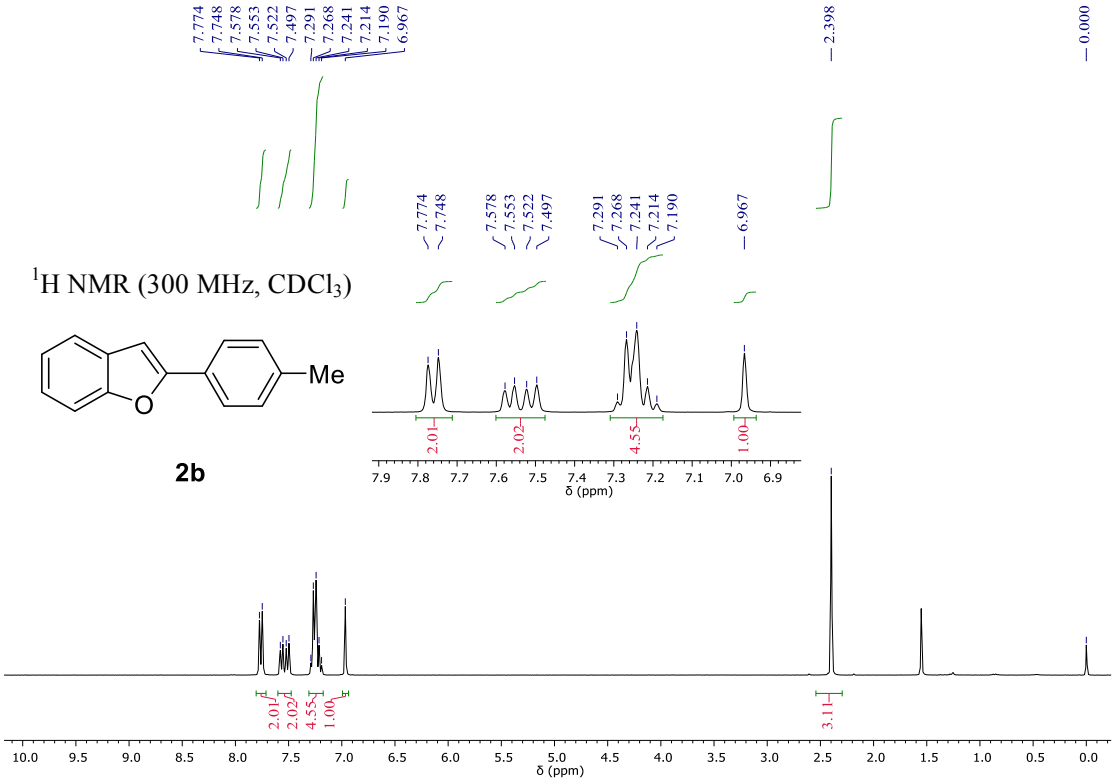


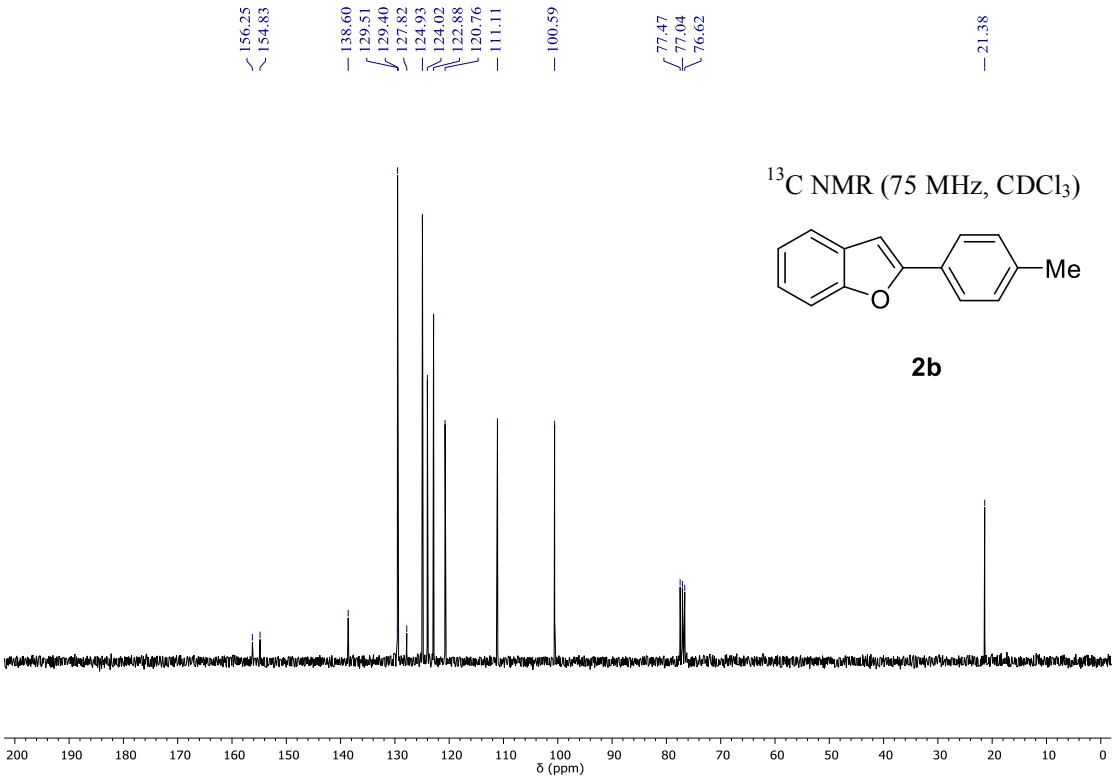
^{13}C NMR (75 MHz, $CDCl_3$)

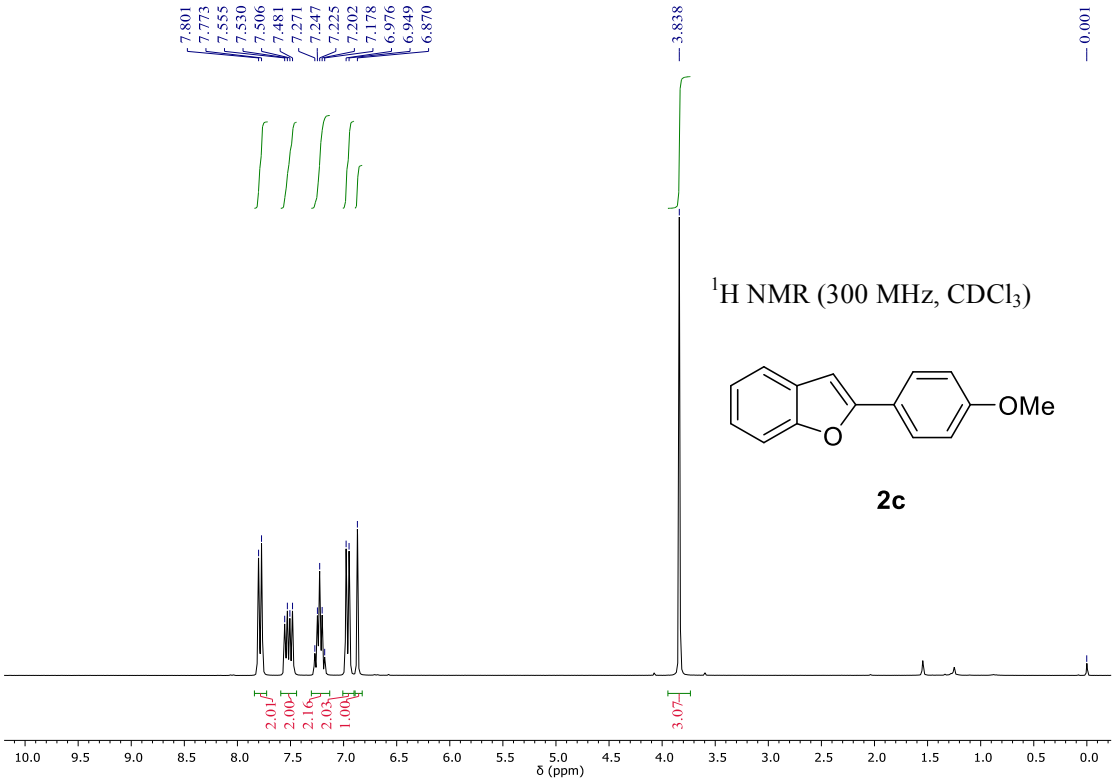
1n


7.863
7.837
7.573
7.548
7.525
7.499
7.450
7.424
7.400
7.349
7.327
7.295
7.269
7.240
7.212
7.188
6.994
-0.000
^{1}H NMR (300 MHz, CDCl$_3$)
Ph
O
2a
2.02
2.03
2.05
3.15
1.00
δ (ppm)


155.96
154.94
130.52
129.28
128.86
128.62
124.99
124.34
123.01
120.99
111.26
101.38
77.54
77.12
76.69
^{13}C NMR (75 MHz, CDCl$_3$)
Ph
O
2a
δ (ppm)

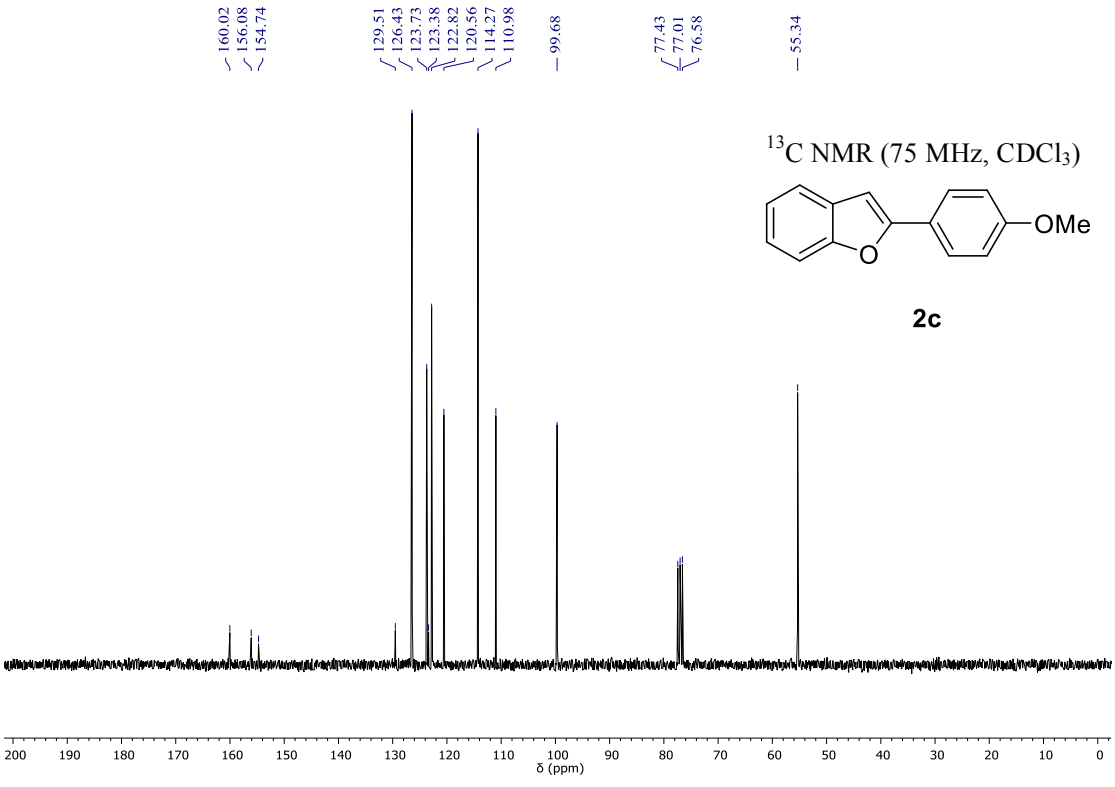

7.774
7.748
7.578
7.553
7.522
7.497
7.291
7.268
7.241
7.214
7.190
6.967
2.398
0.000
^{1}H NMR (300 MHz, CDCl$_3$)
Me
O
2b
2.01
2.02
4.55
1.00
3.11
δ (ppm)


156.25
154.83
138.60
129.51
129.40
127.82
124.93
124.02
122.88
120.76
111.11
100.59
77.47
77.04
76.62
21.38
^{13}C NMR (75 MHz, CDCl$_3$)
Me
O
2b
δ (ppm)



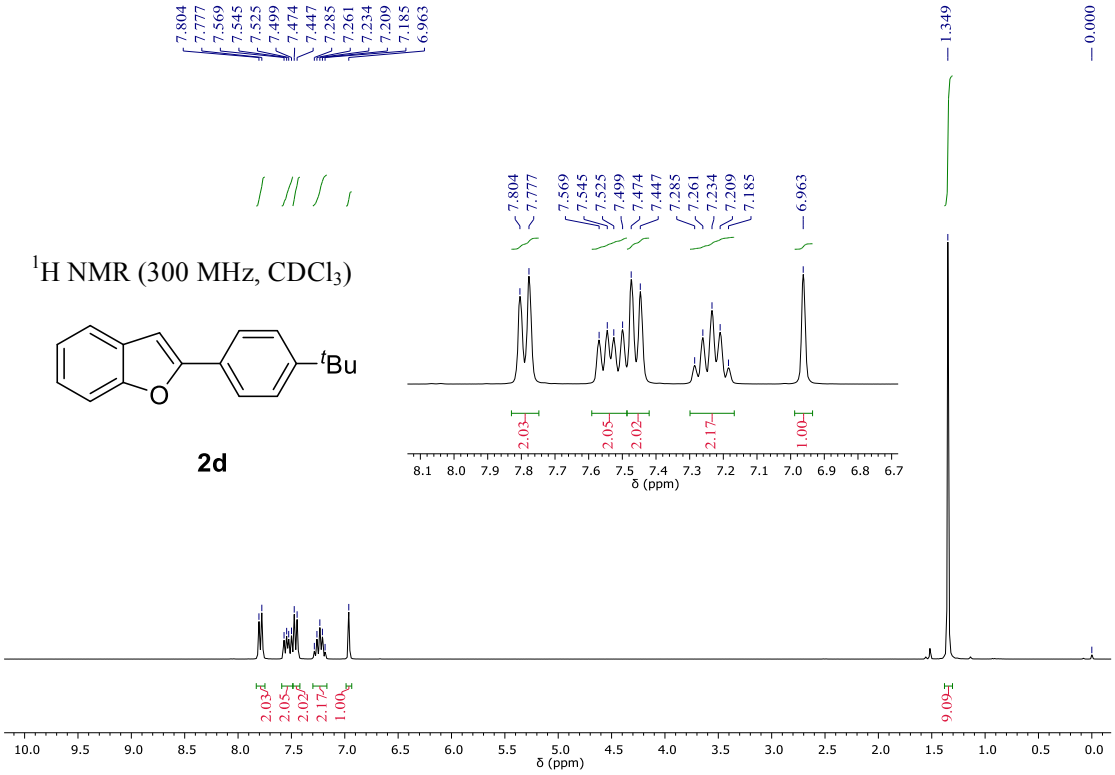
^{1}H NMR (300 MHz, $CDCl_3$)

2c



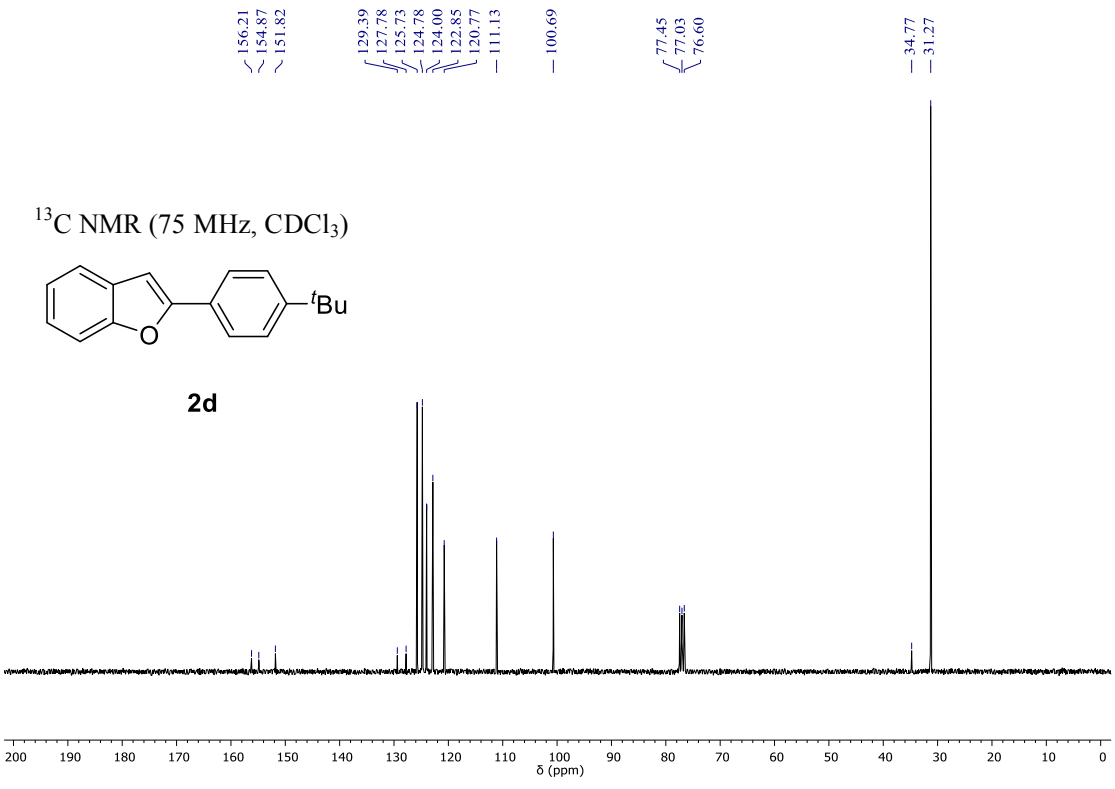
^{13}C NMR (75 MHz, $CDCl_3$)

2c



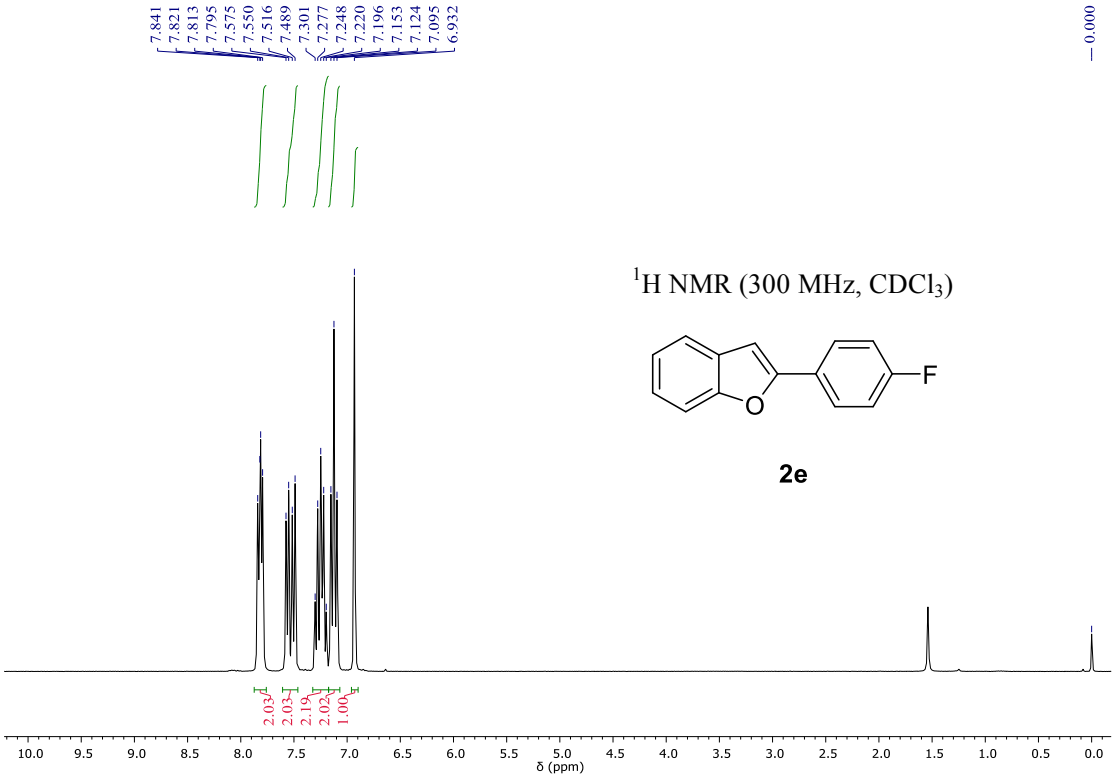
^{1}H NMR (300 MHz, $CDCl_3$)

2d



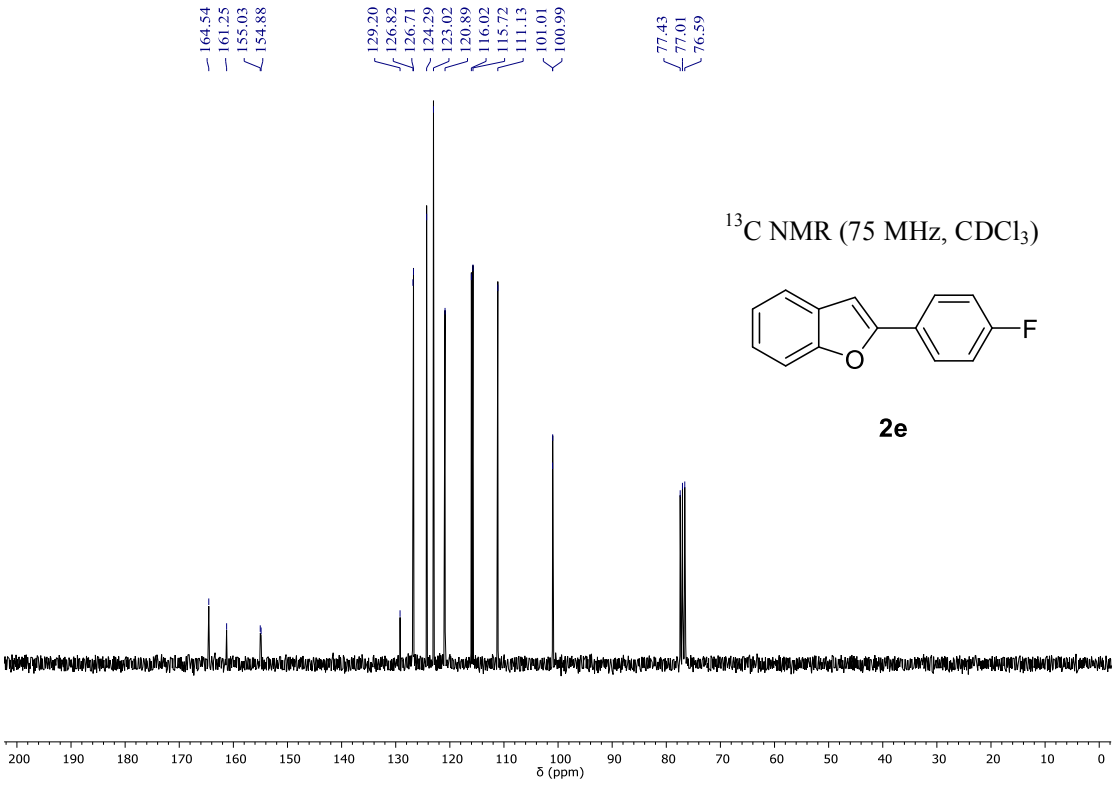
^{13}C NMR (75 MHz, $CDCl_3$)

2d



^{1}H NMR (300 MHz, $CDCl_3$)

2e

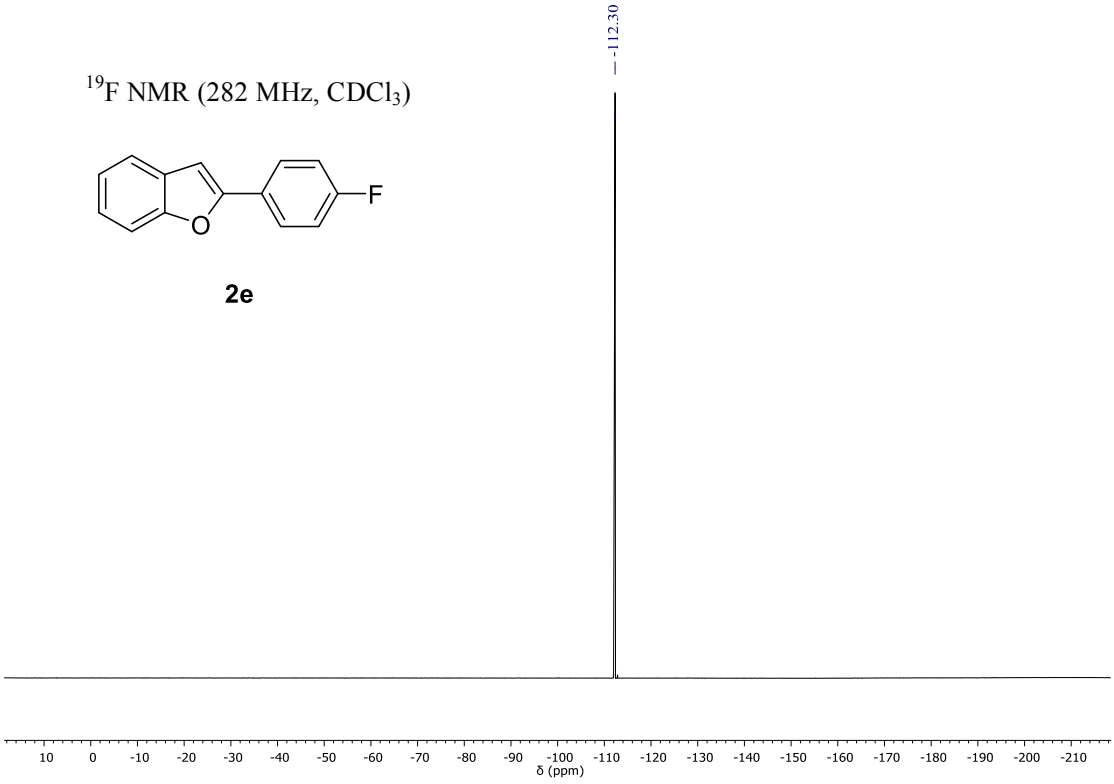


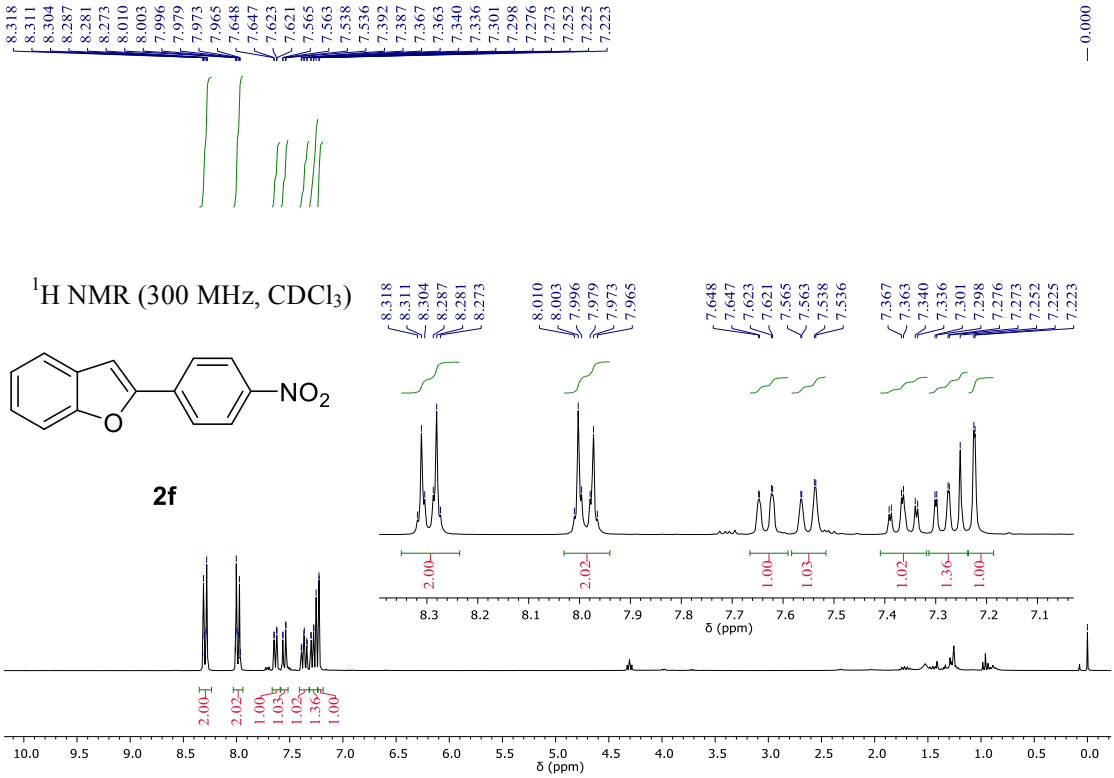
^{13}C NMR (75 MHz, $CDCl_3$)

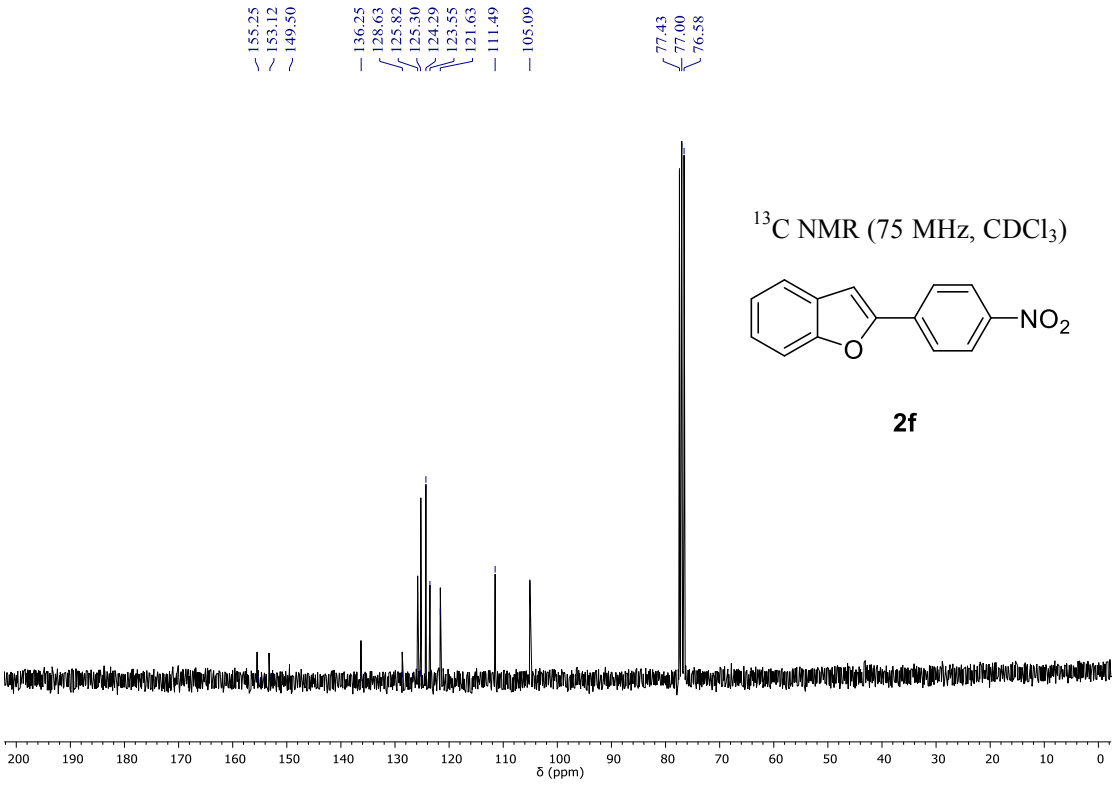
2e

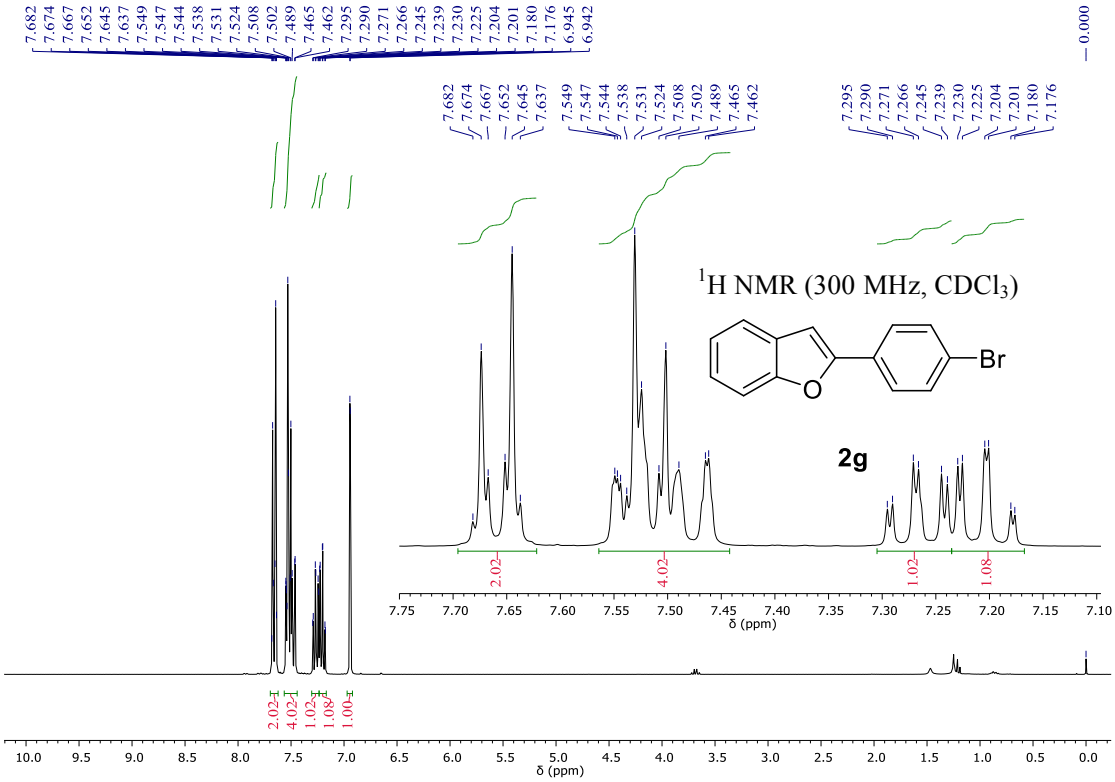
^{19}F NMR (282 MHz, $CDCl_3$)

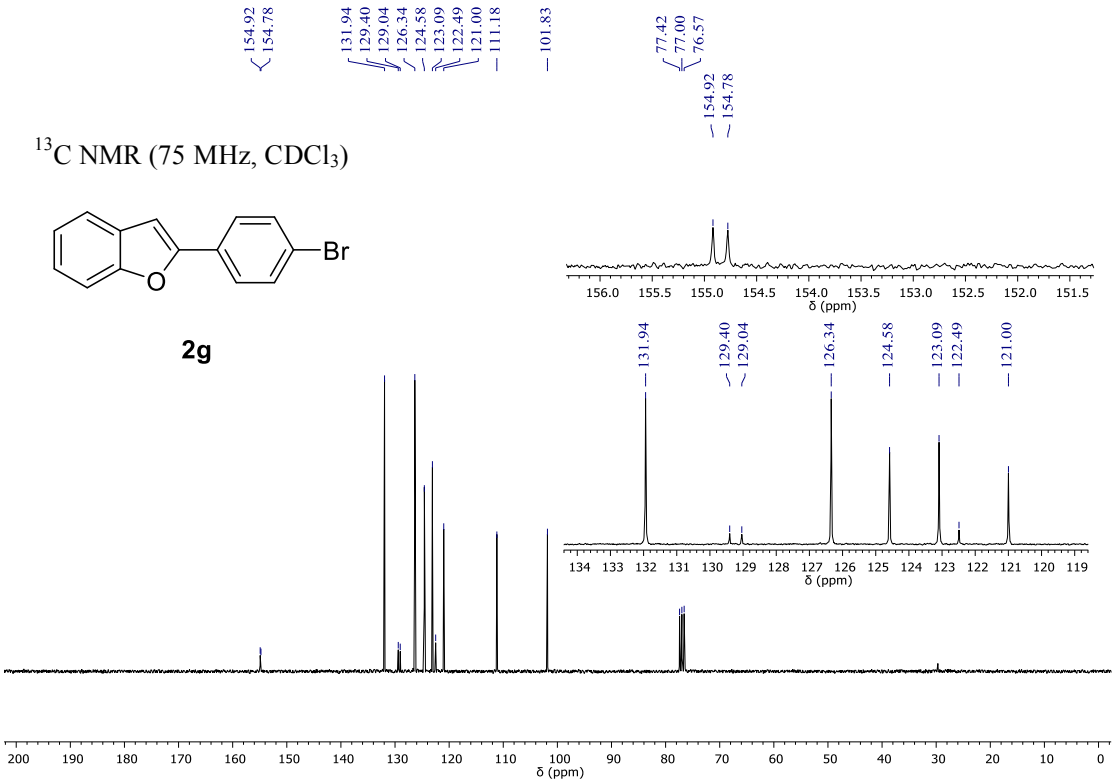
2e

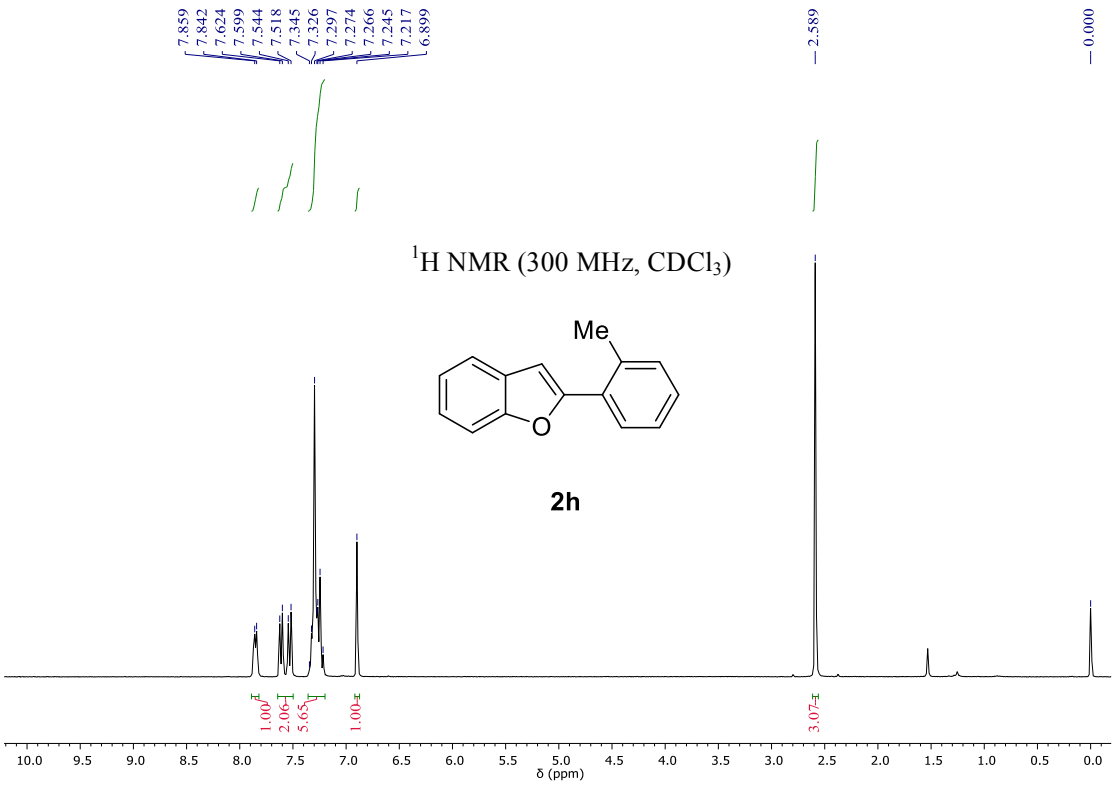


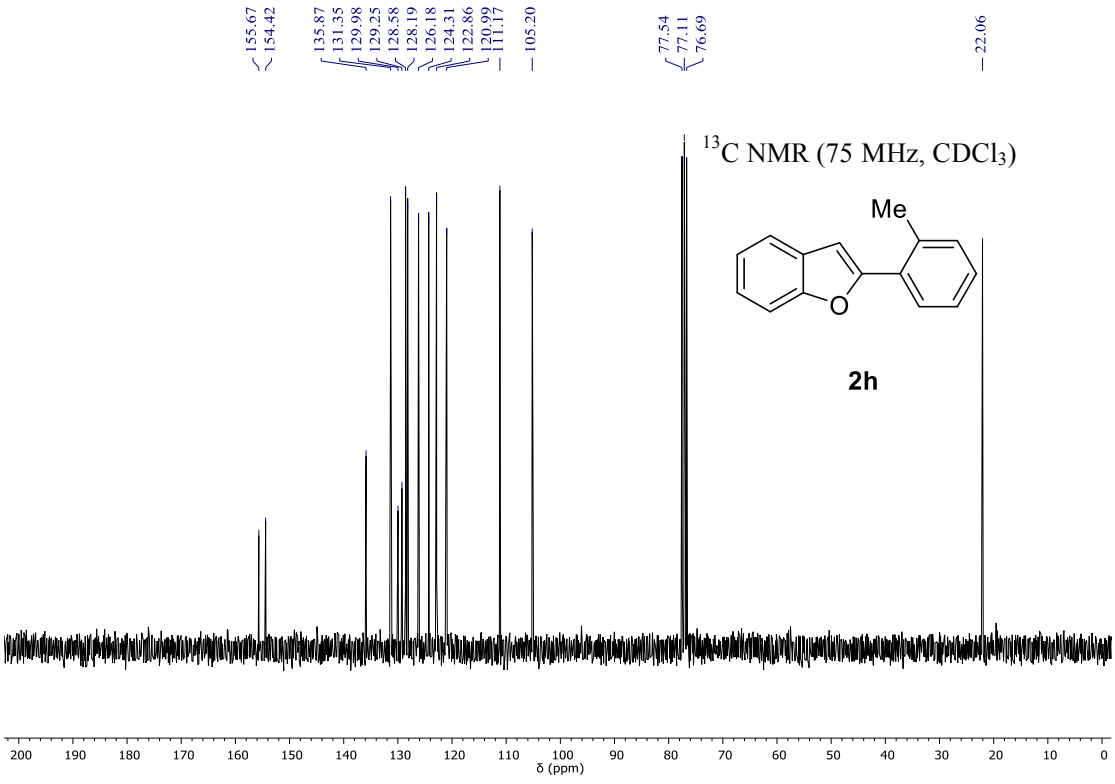

8.318
8.311
8.304
8.287
8.281
8.273
8.010
8.003
7.996
7.979
7.973
7.965
7.648
7.647
7.623
7.621
7.565
7.563
7.538
7.536
7.392
7.387
7.367
7.363
7.340
7.336
7.301
7.298
7.276
7.273
7.252
7.225
7.223
0.000
^{1}H NMR (300 MHz, CDCl$_3$)
NO$_2$
O
2f
2.00
2.02
1.00
1.03
1.02
1.36
1.00
δ (ppm)

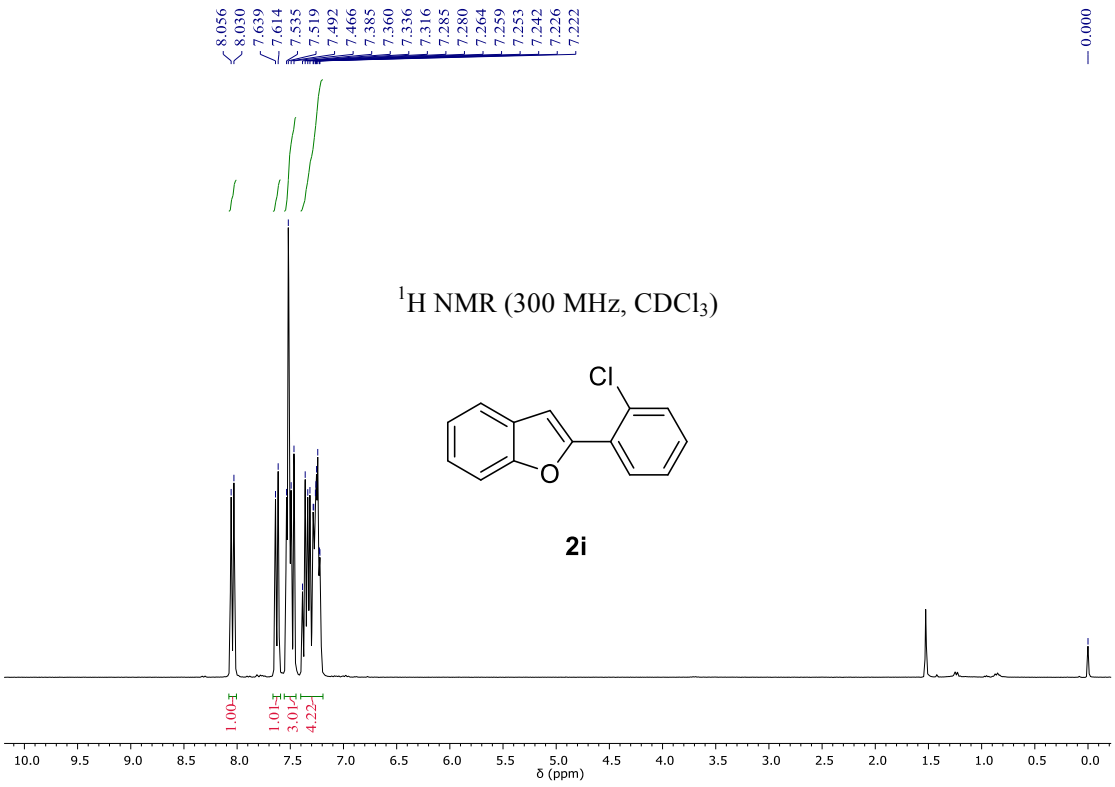

155.25
153.12
149.50
136.25
128.63
125.82
125.30
124.29
123.55
121.63
111.49
105.09
77.43
77.00
76.58
^{13}C NMR (75 MHz, CDCl$_3$)
NO$_2$
O
2f
δ (ppm)


^{1}H NMR (300 MHz, CDCl$_3$)
Br
O
2g
δ (ppm)


^{13}C NMR (75 MHz, CDCl$_3$)
Br
O
2g
δ (ppm)

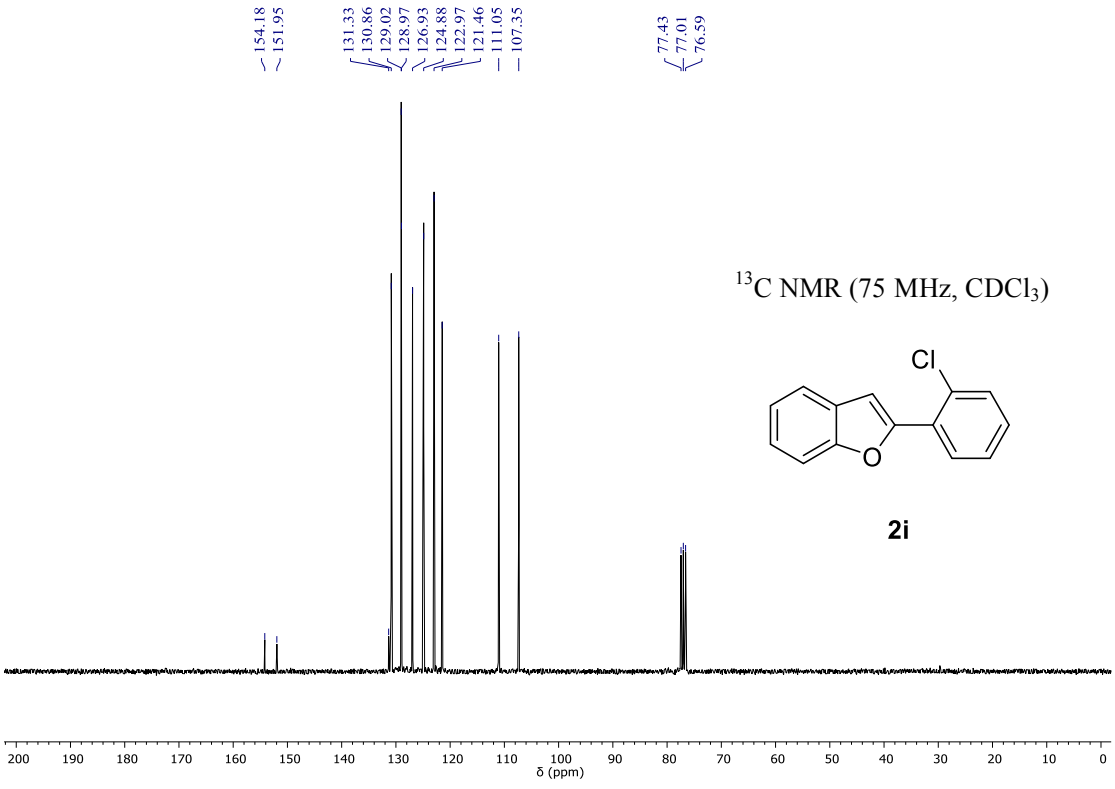

7.859
7.842
7.624
7.599
7.544
7.518
7.345
7.326
7.297
7.274
7.266
7.245
7.217
6.899
2.589
0.000
^{1}H NMR (300 MHz, $CDCl_3$)
Me
O
2h
1.00
2.06
5.65
1.00
3.07
δ (ppm)


155.67
154.42
135.87
131.35
129.98
129.25
128.58
128.19
126.18
124.31
122.86
120.99
111.17
105.20
77.54
77.11
76.69
22.06
^{13}C NMR (75 MHz, $CDCl_3$)
Me
O
2h
δ (ppm)



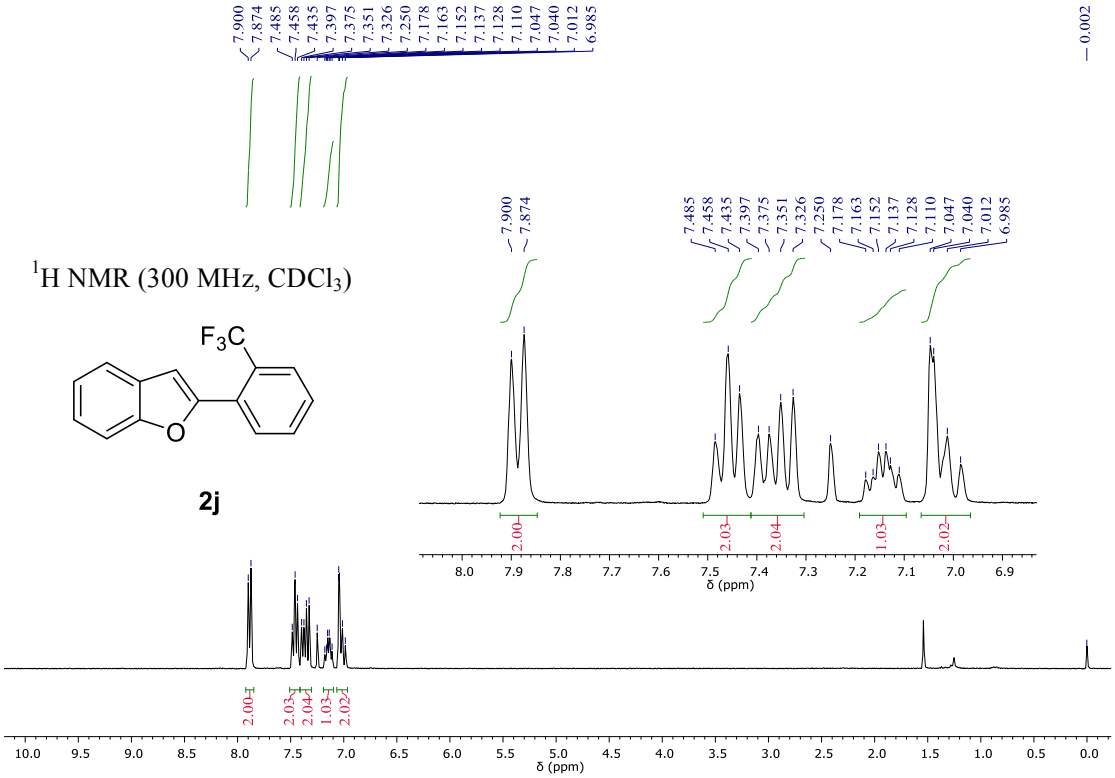
^{1}H NMR (300 MHz, $CDCl_3$)

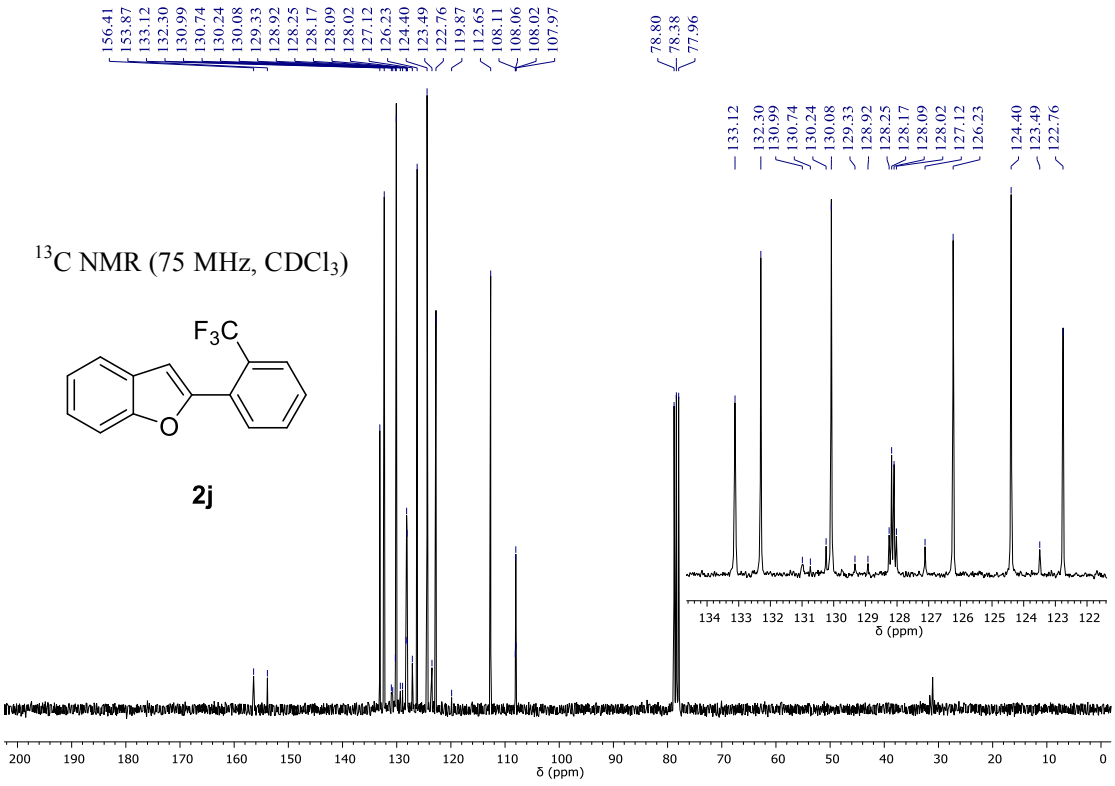
2i

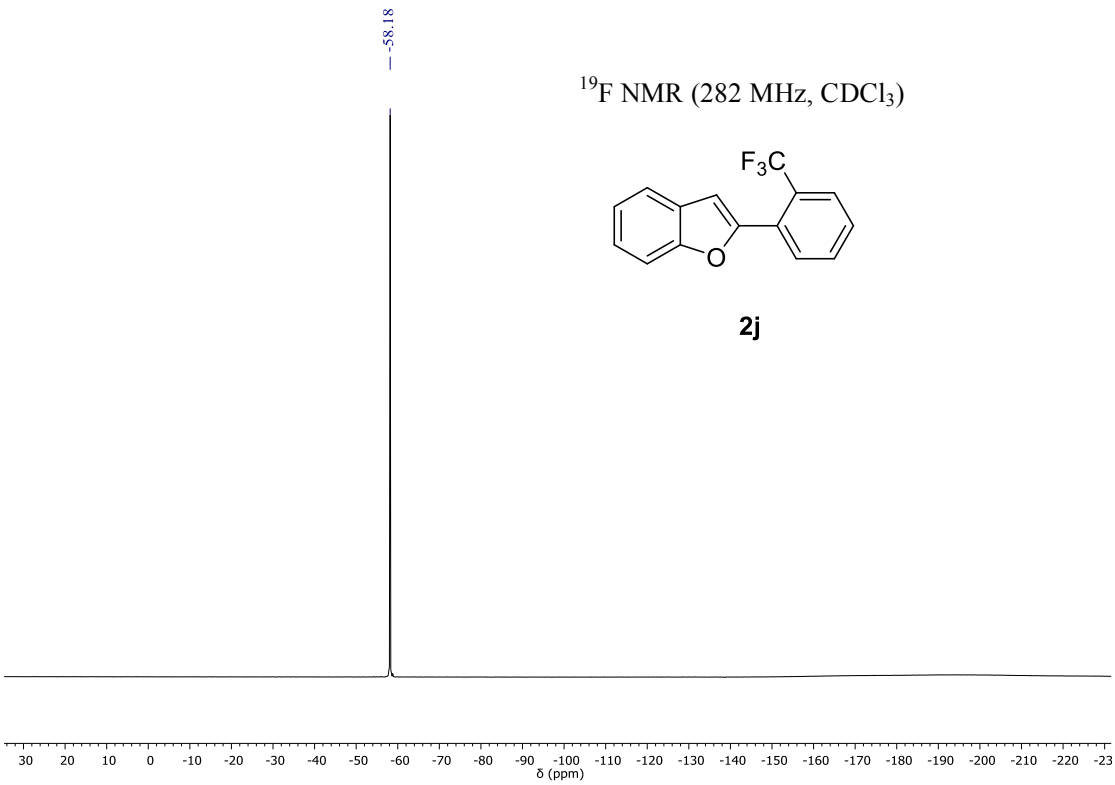


^{13}C NMR (75 MHz, $CDCl_3$)

2i

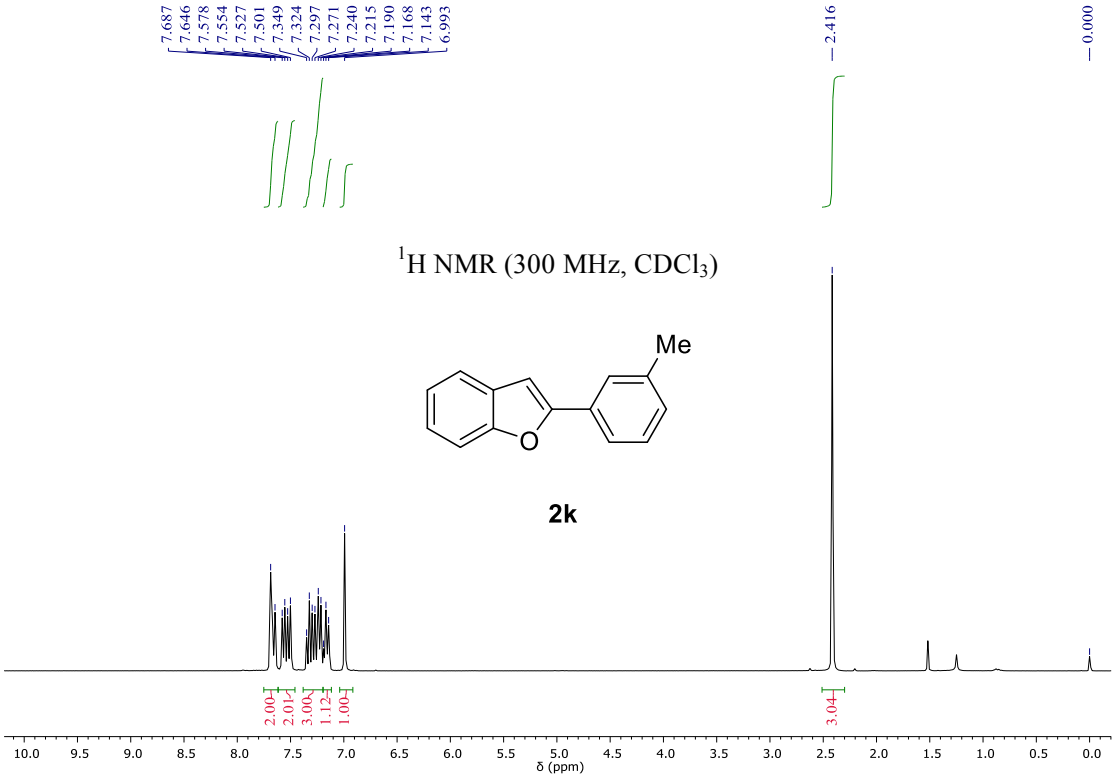

7.900
7.874
7.485
7.458
7.435
7.397
7.375
7.351
7.326
7.250
7.178
7.163
7.152
7.137
7.128
7.110
7.047
7.040
7.012
6.985
0.002
^{1}H NMR (300 MHz, CDCl$_3$)
F3C
O
2j
2.00
2.03
2.04
1.03
2.02
δ (ppm)


156.41
153.87
133.12
132.30
130.99
130.74
130.24
130.08
129.33
128.92
128.25
128.17
128.09
128.02
127.12
126.23
124.40
123.49
122.76
119.87
112.65
108.11
108.06
108.02
107.97
78.80
78.38
77.96
^{13}C NMR (75 MHz, CDCl$_3$)
F3C
O
2j
δ (ppm)



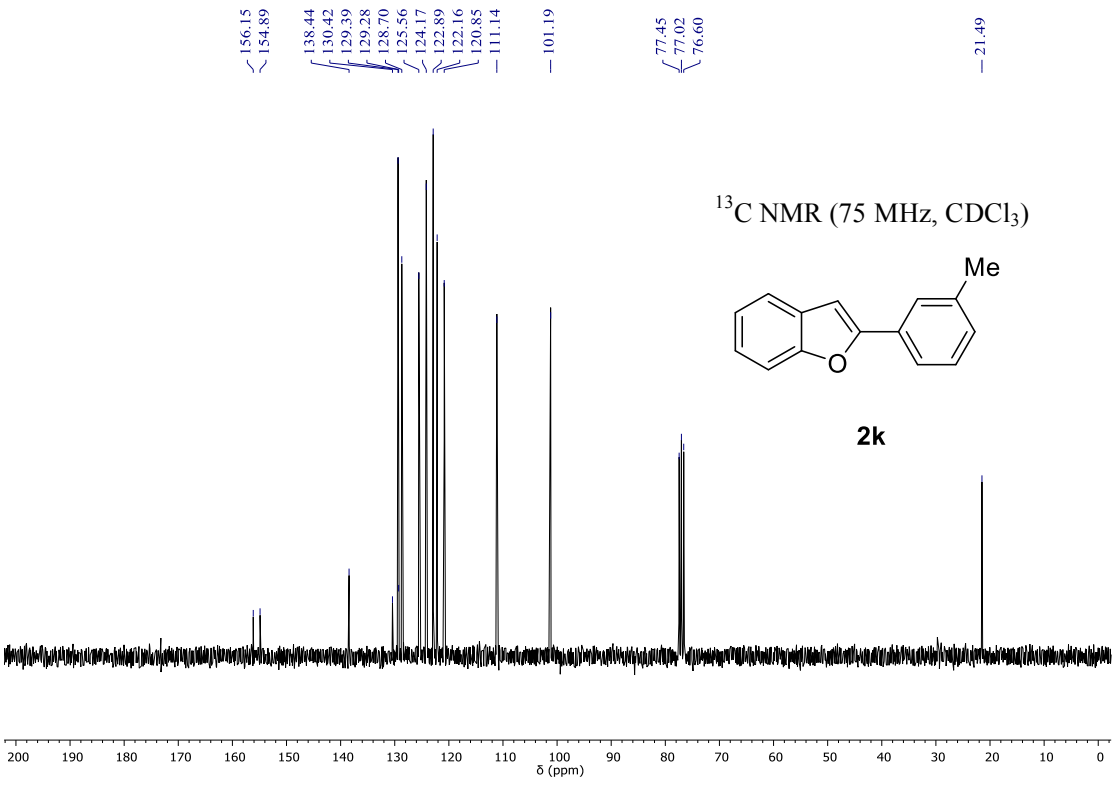
^{19}F NMR (282 MHz, $CDCl_3$)

2j



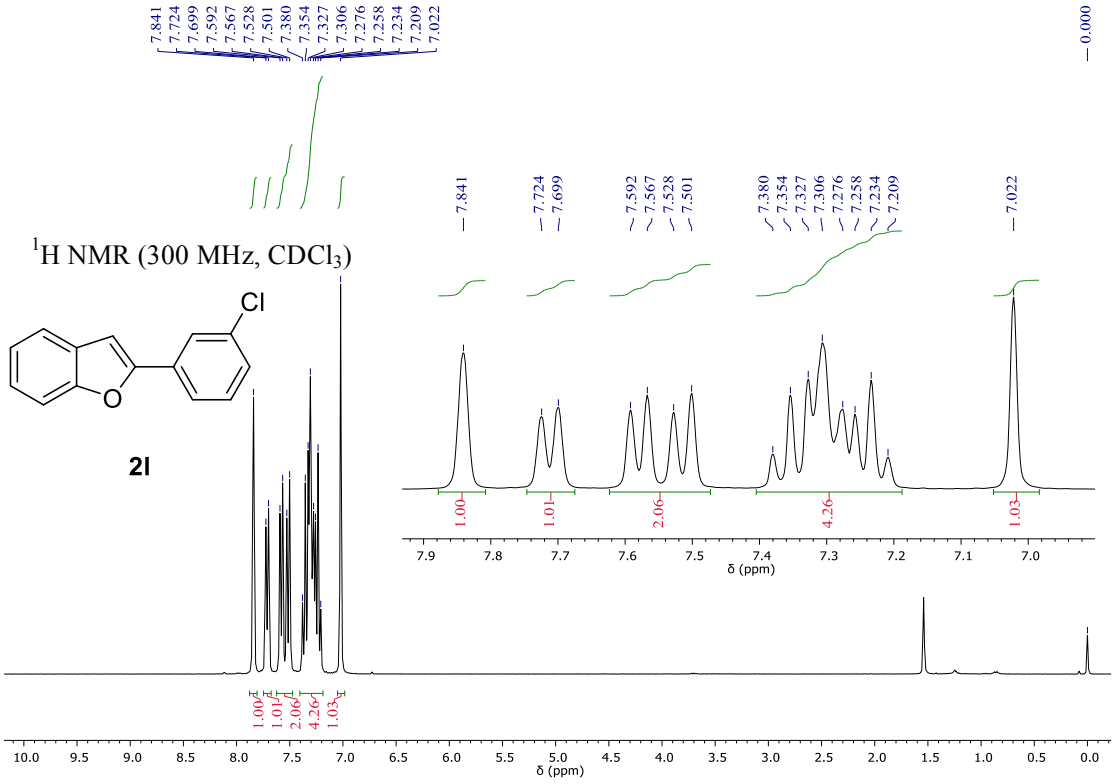
^{1}H NMR (300 MHz, $CDCl_3$)

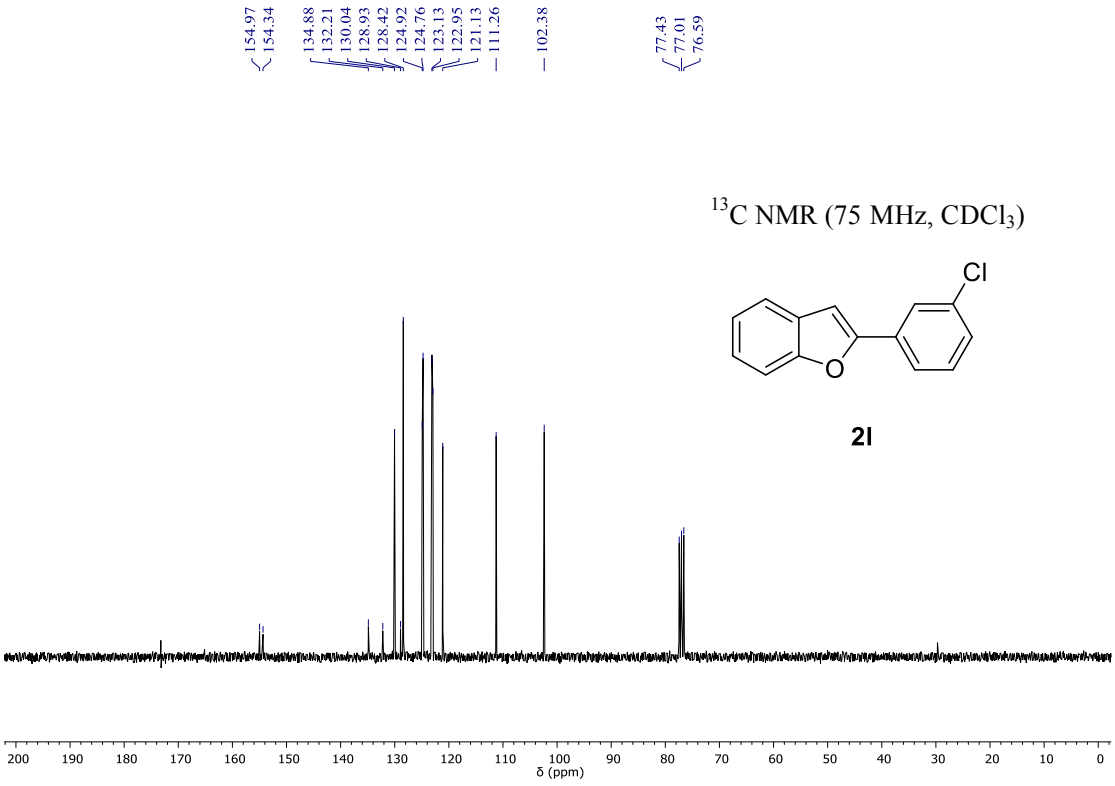
2k

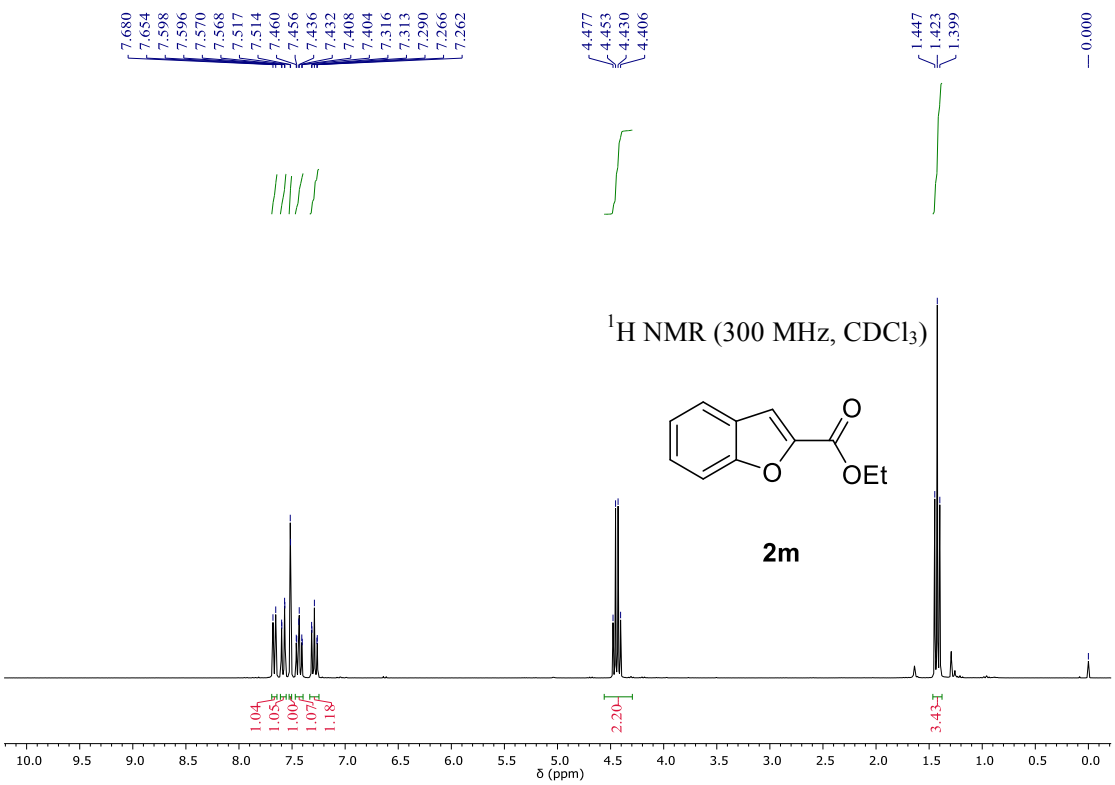


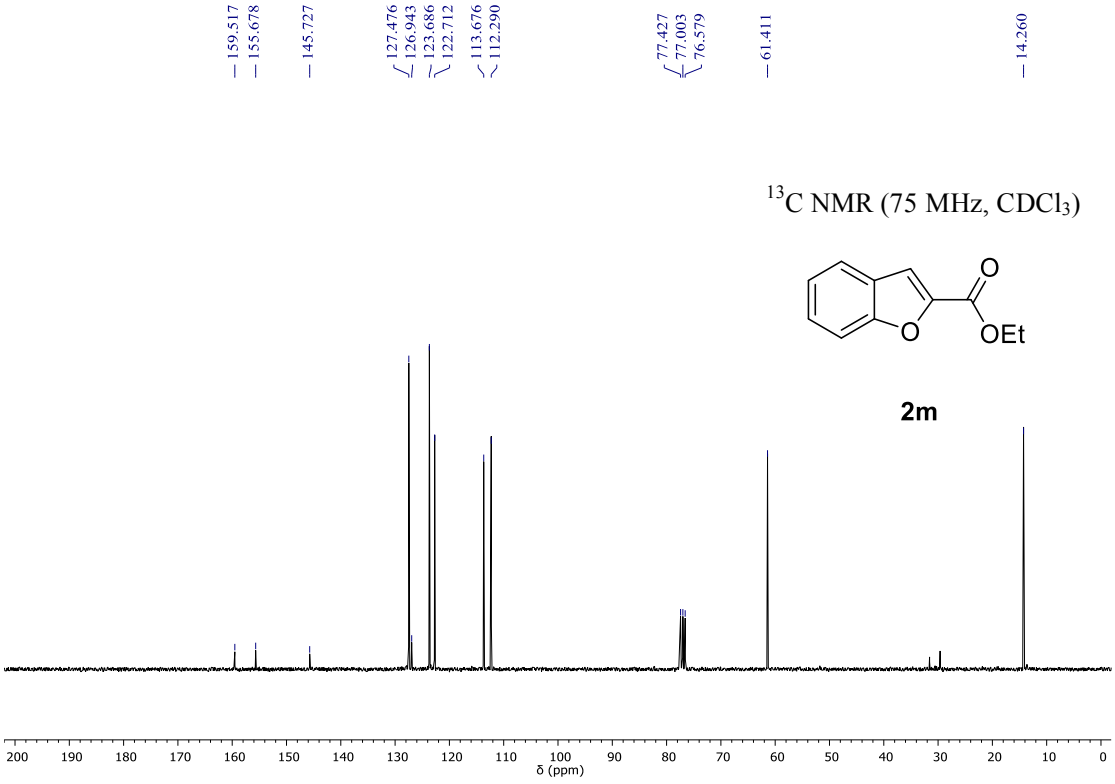
^{13}C NMR (75 MHz, $CDCl_3$)

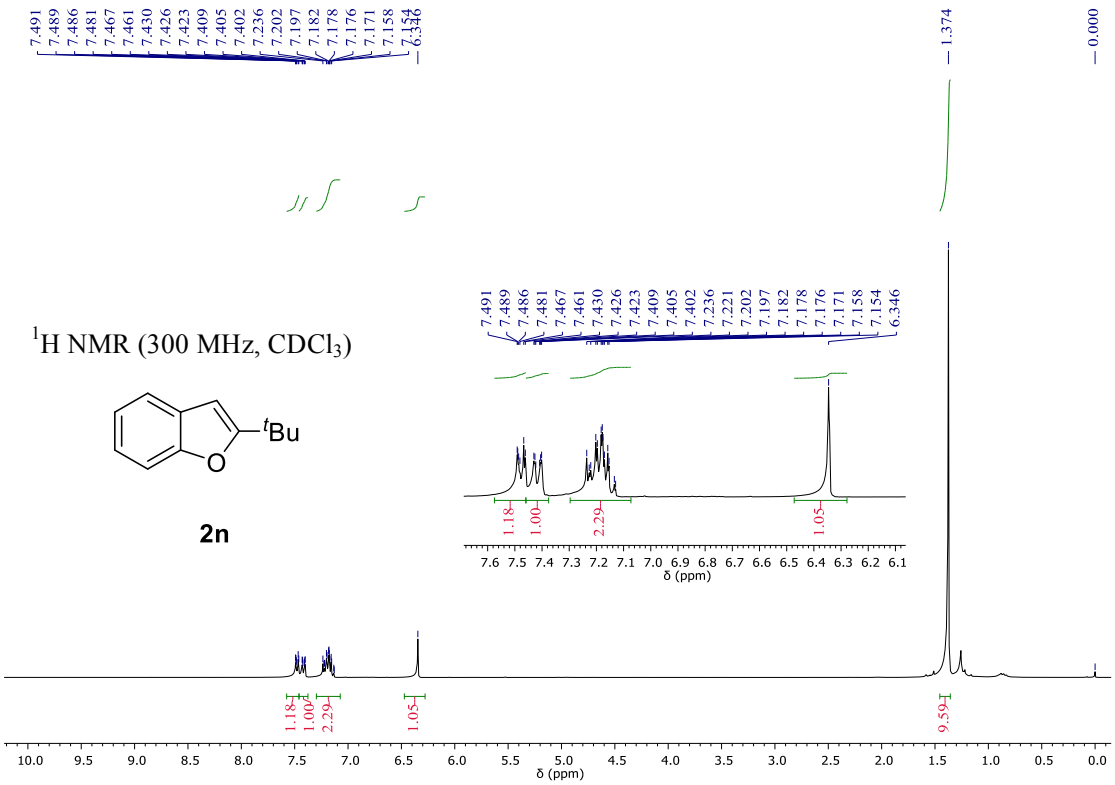
2k

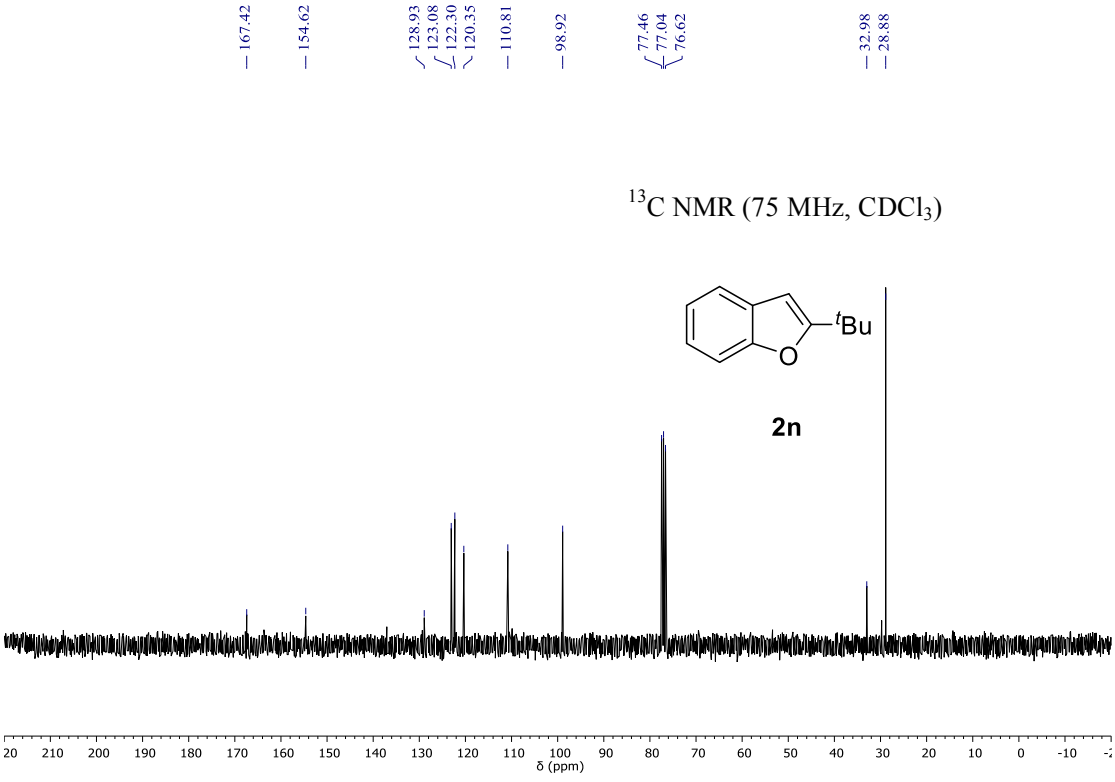

7.841
7.724
7.699
7.592
7.567
7.528
7.501
7.380
7.354
7.327
7.306
7.276
7.258
7.234
7.209
7.022
0.000
^{1}H NMR (300 MHz, CDCl$_3$)
Cl
O
2l
1.00
1.01
2.06
4.26
1.03
δ (ppm)

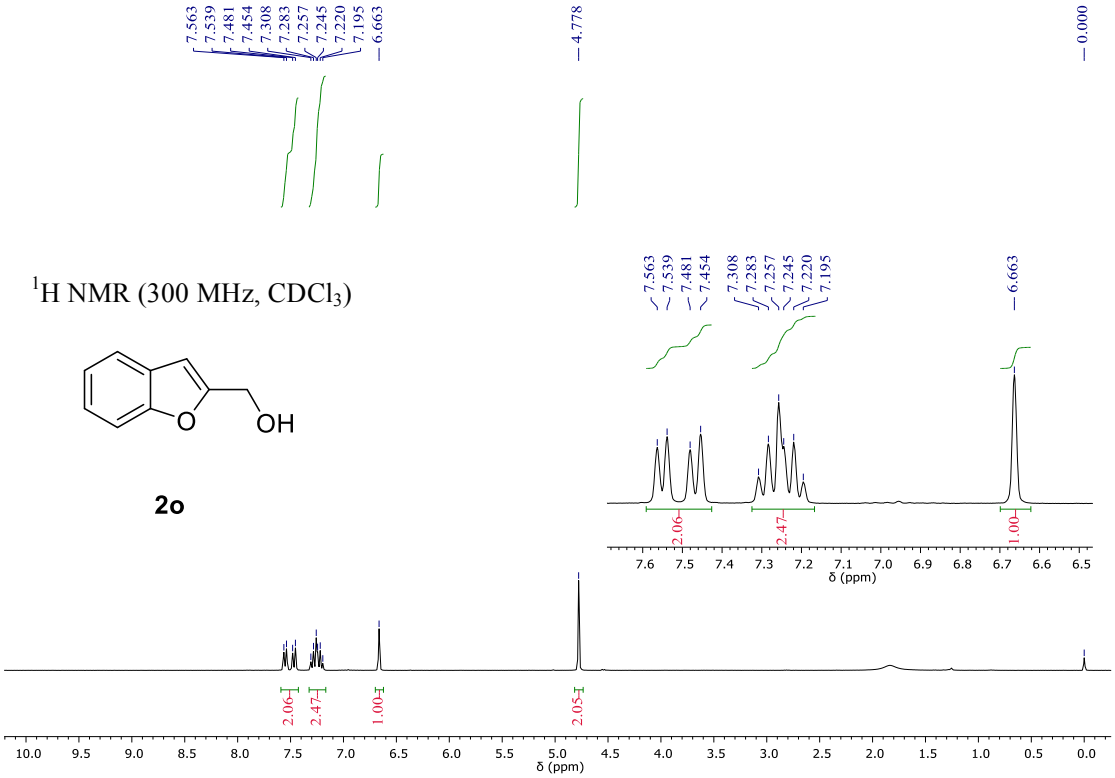

154.97
154.34
134.88
132.21
130.04
128.93
128.42
124.92
124.76
123.13
122.95
121.13
111.26
102.38
77.43
77.01
76.59
^{13}C NMR (75 MHz, CDCl$_3$)
Cl
O
2l
δ (ppm)


7.680
7.654
7.598
7.596
7.570
7.568
7.517
7.514
7.460
7.456
7.436
7.432
7.408
7.404
7.316
7.313
7.290
7.266
7.262
4.477
4.453
4.430
4.406
1.447
1.423
1.399
0.000
1H NMR (300 MHz, CDCl3)
O
O
OEt
2m
1.04
1.05
1.00
1.07
1.18
2.20
3.43
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)


159.517
155.678
145.727
127.476
126.943
123.686
122.712
113.676
112.290
77.427
77.003
76.579
61.411
14.260
13C NMR (75 MHz, CDCl3)
O
O
OEt
2m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

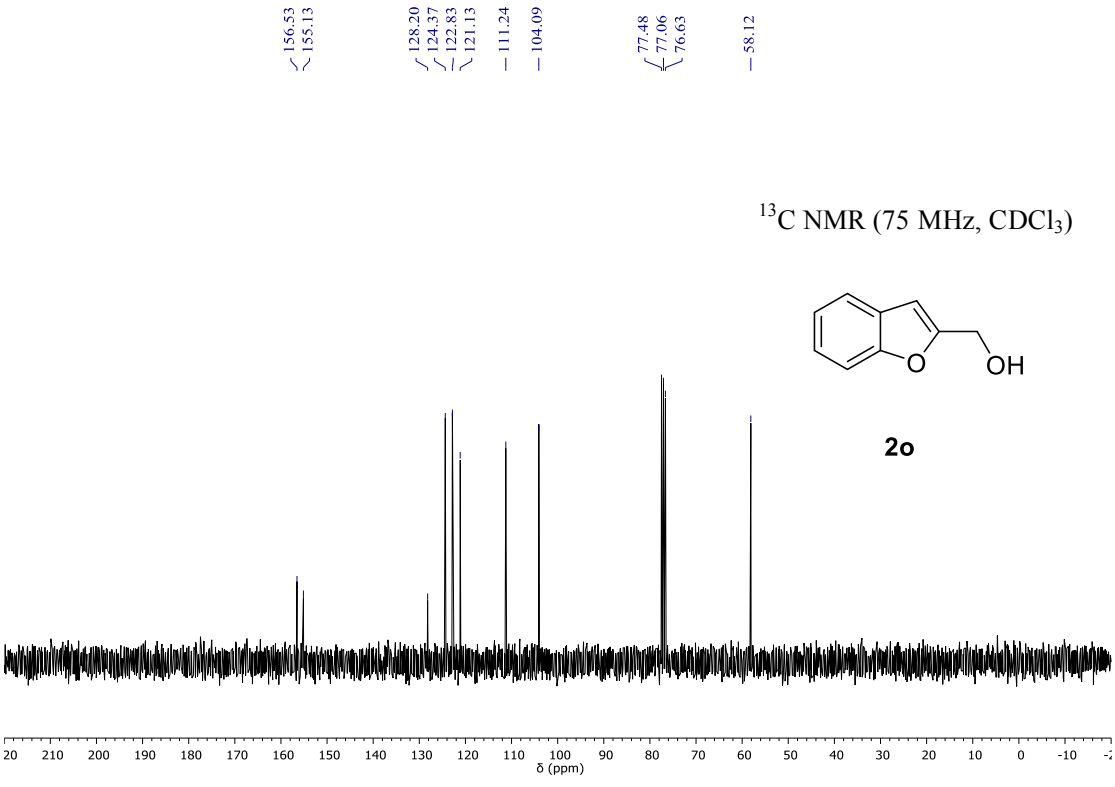

7.491
7.489
7.486
7.481
7.467
7.461
7.430
7.426
7.423
7.409
7.405
7.402
7.236
7.202
7.197
7.182
7.178
7.176
7.171
7.158
7.154
6.346
1.374
0.000
1H NMR (300 MHz, CDCl3)
tBu
O
2n
1.18
1.00
2.29
1.05
9.59
δ (ppm)


167.42
154.62
128.93
123.08
122.30
120.35
110.81
98.92
77.46
77.04
76.62
32.98
28.88
13C NMR (75 MHz, CDCl3)
tBu
O
2n
δ (ppm)



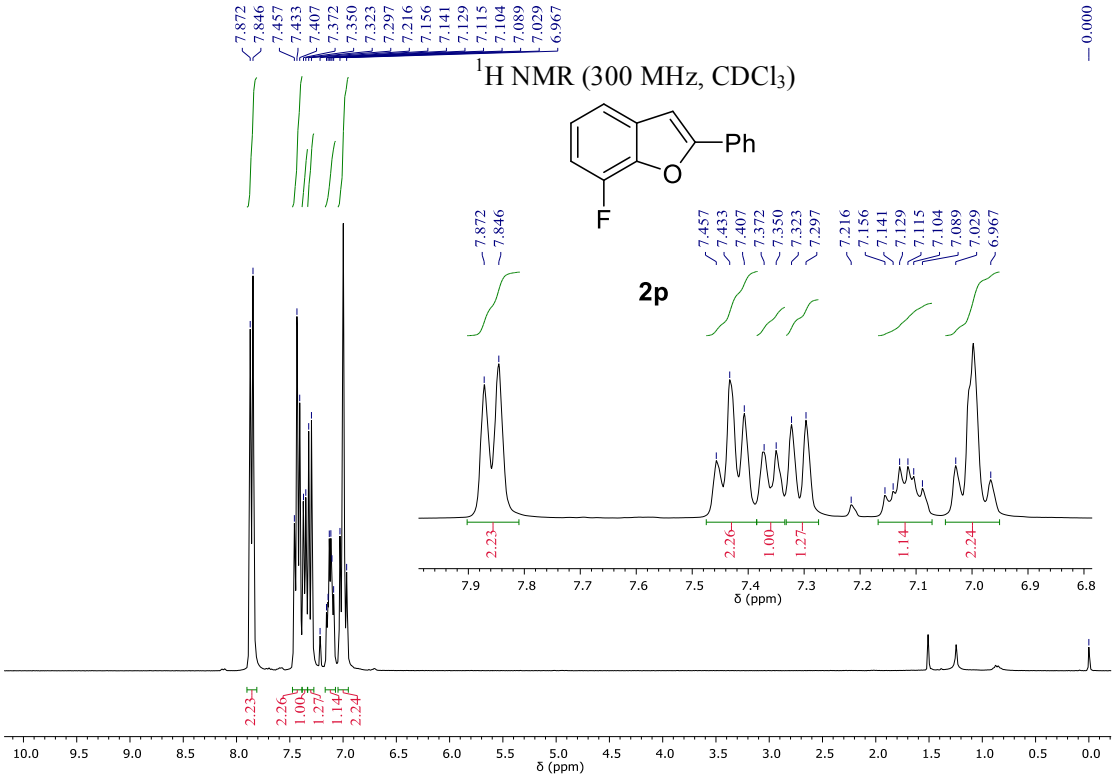
^{1}H NMR (300 MHz, $CDCl_3$)

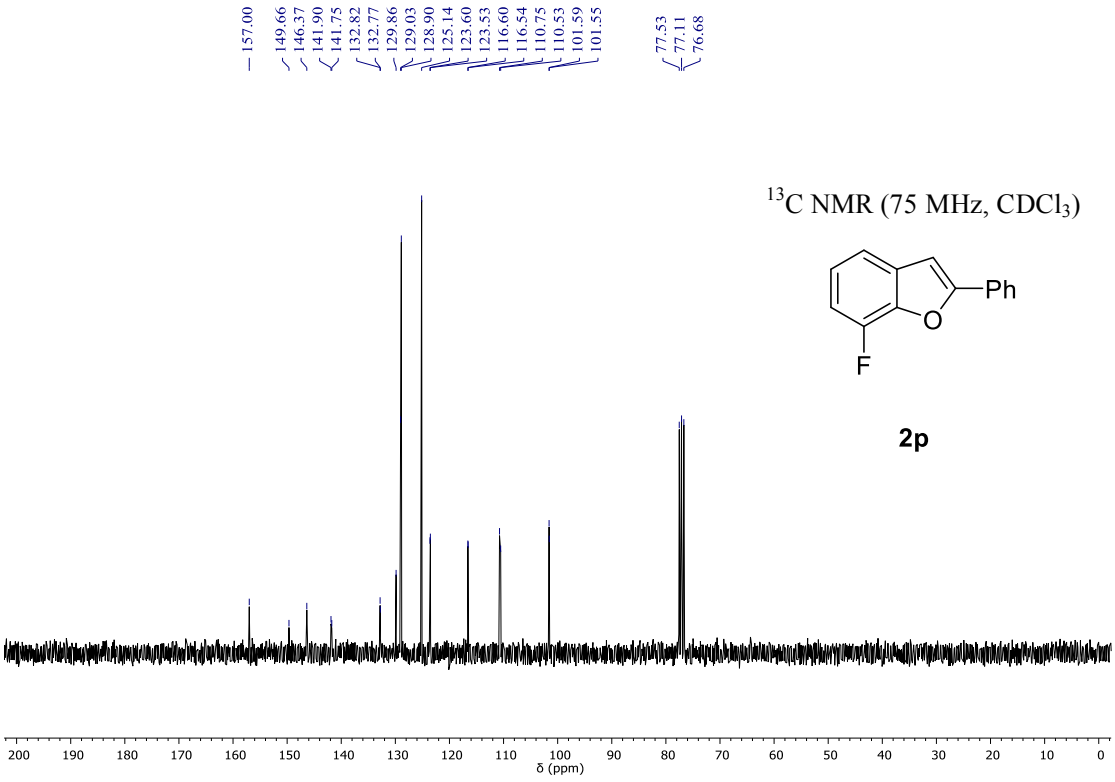
2o



^{13}C NMR (75 MHz, $CDCl_3$)

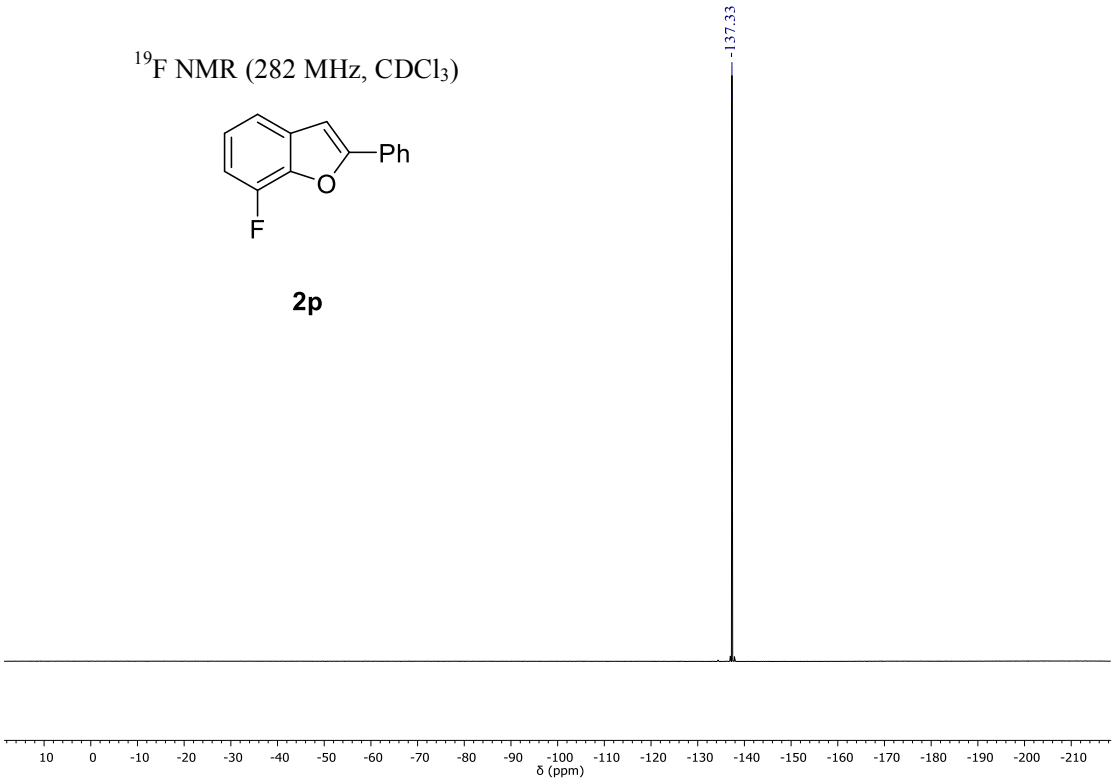
2o

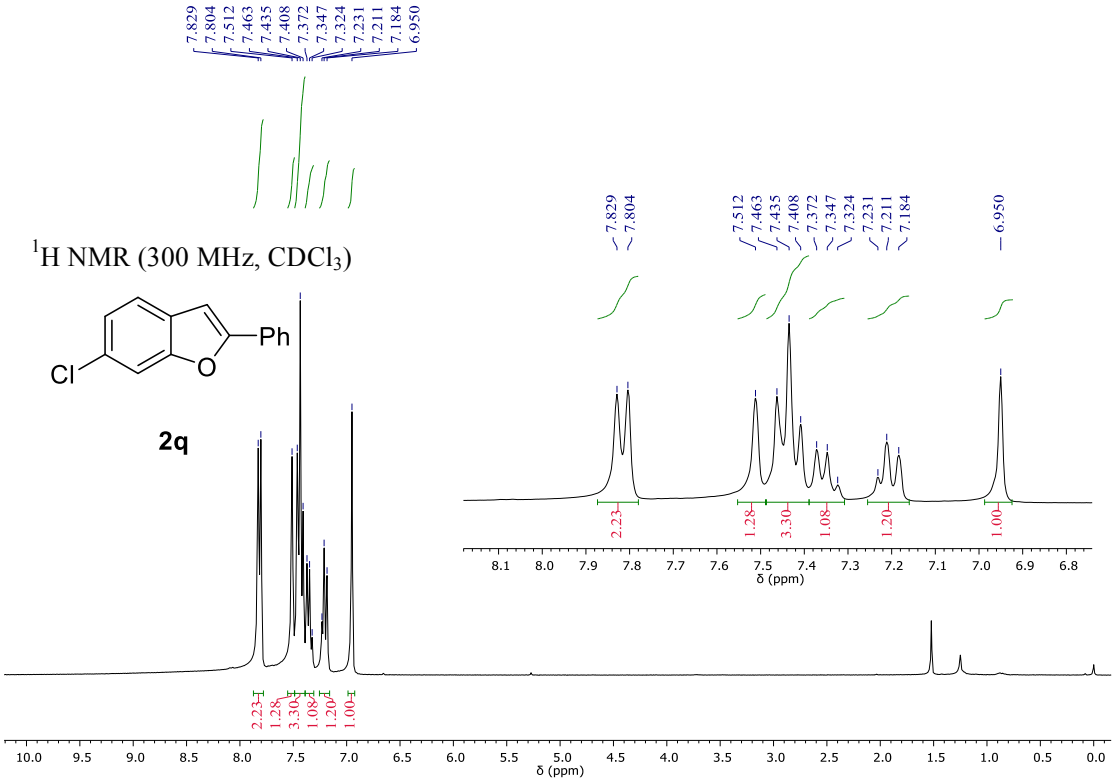

7.872
7.846
7.457
7.433
7.407
7.372
7.350
7.323
7.297
7.216
7.156
7.141
7.129
7.115
7.104
7.089
7.029
6.967
0.000
^{1}H NMR (300 MHz, CDCl$_3$)
Ph
O
F
2p
2.23
2.26
1.00
1.27
1.14
2.24
δ (ppm)

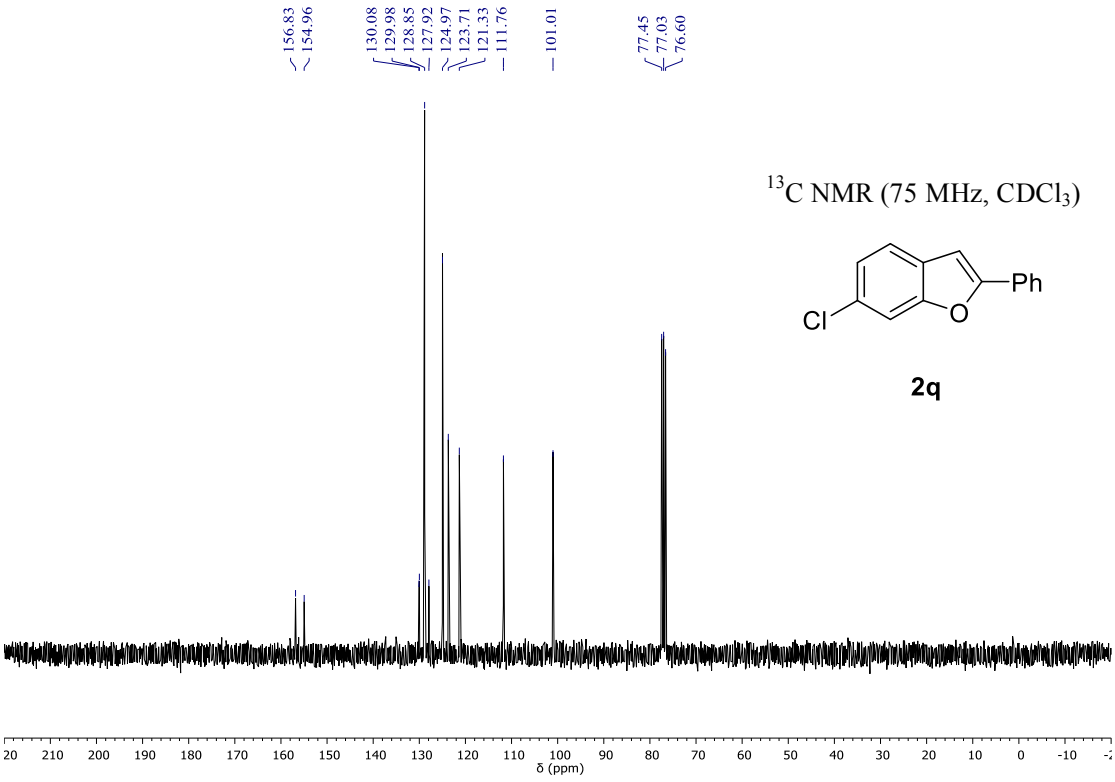

157.00
149.66
146.37
141.90
141.75
132.82
132.77
129.86
129.03
128.90
125.14
123.60
123.53
116.60
116.54
110.75
110.53
101.59
101.55
77.53
77.11
76.68
^{13}C NMR (75 MHz, CDCl$_3$)
Ph
O
F
2p
δ (ppm)

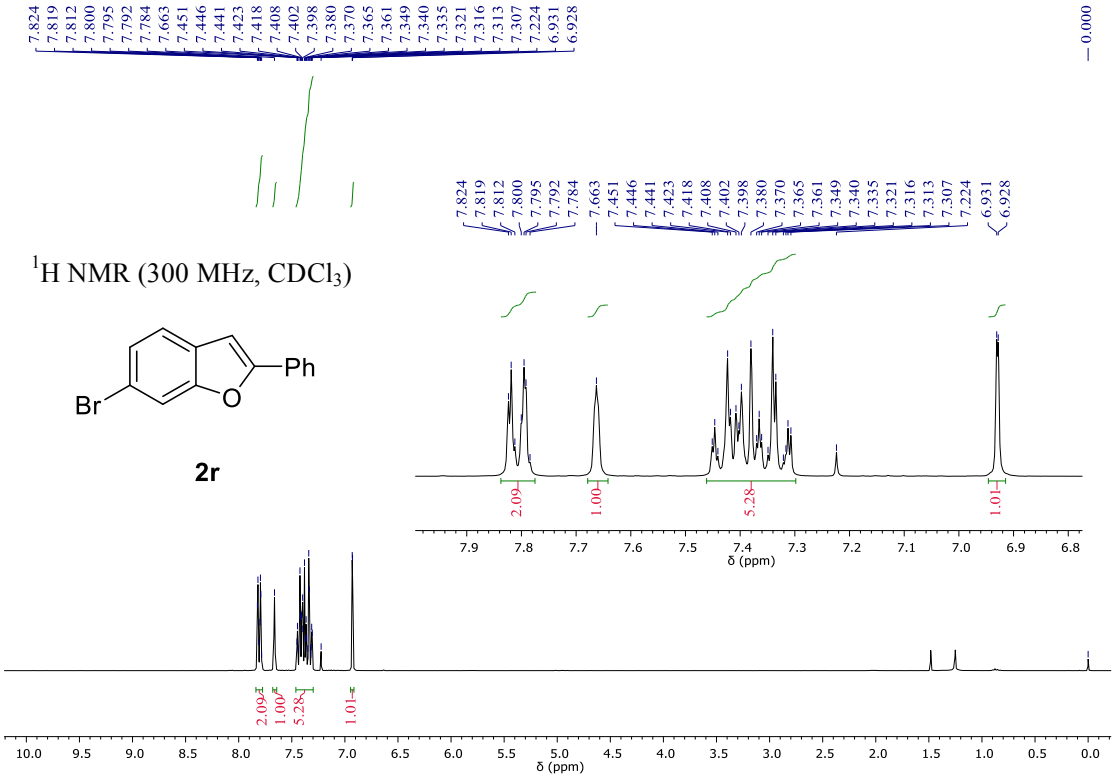
^{19}F NMR (282 MHz, $CDCl_3$)

2p



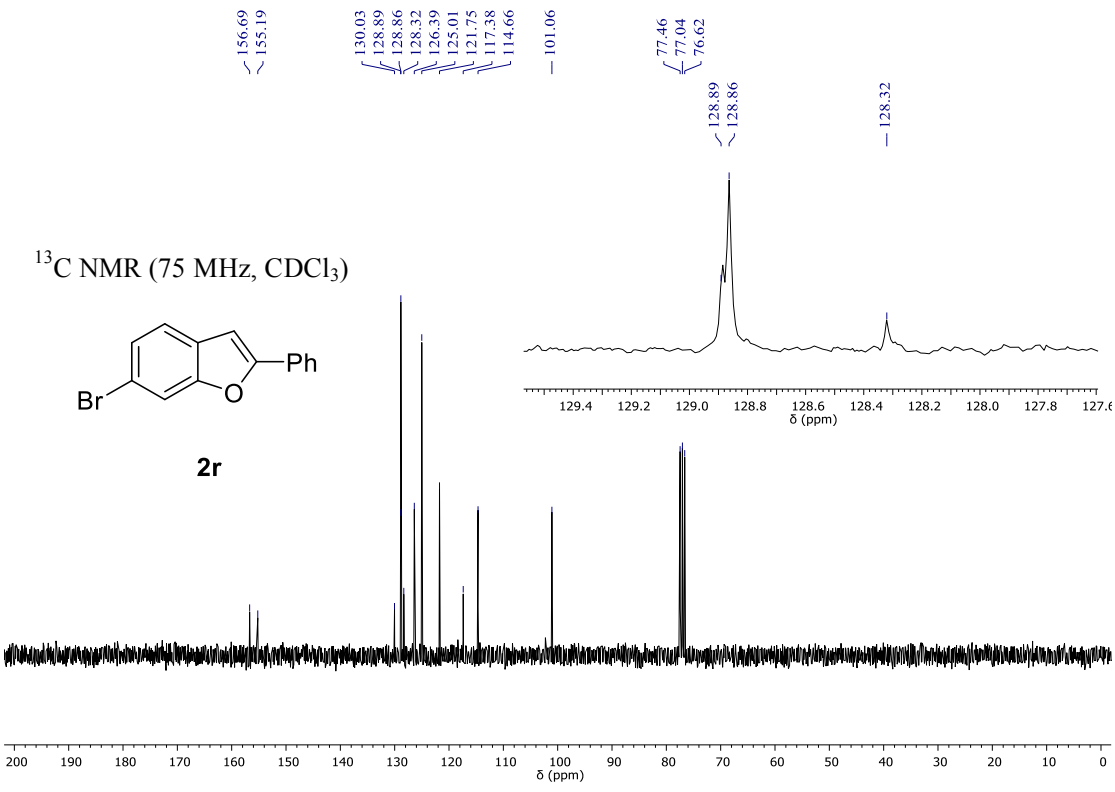

7.829
7.804
7.512
7.463
7.435
7.408
7.372
7.347
7.324
7.231
7.211
7.184
6.950
^{1}H NMR (300 MHz, CDCl$_3$)
Cl
O
Ph
2q
2.23
1.28
3.30
1.08
1.20
1.00
δ (ppm)


156.83
154.96
130.08
129.98
128.85
127.92
124.97
123.71
121.33
111.76
101.01
77.45
77.03
76.60
^{13}C NMR (75 MHz, CDCl$_3$)
Cl
O
Ph
2q
δ (ppm)



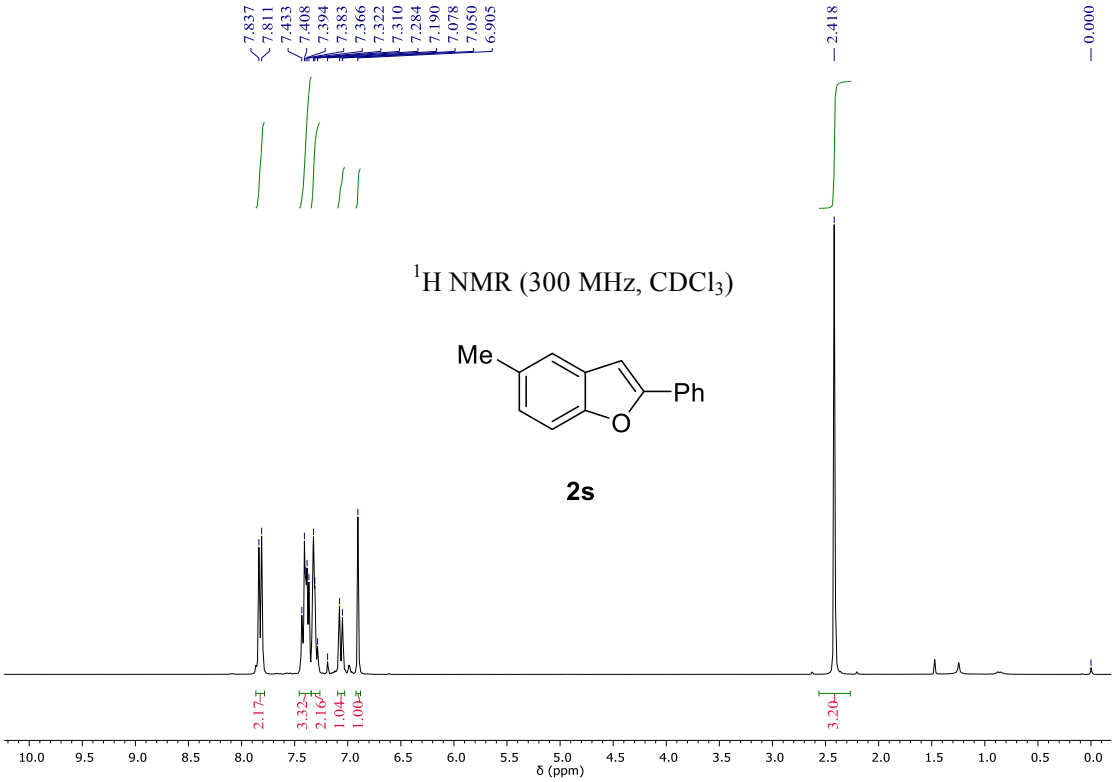
^{1}H NMR (300 MHz, $CDCl_3$)

2r



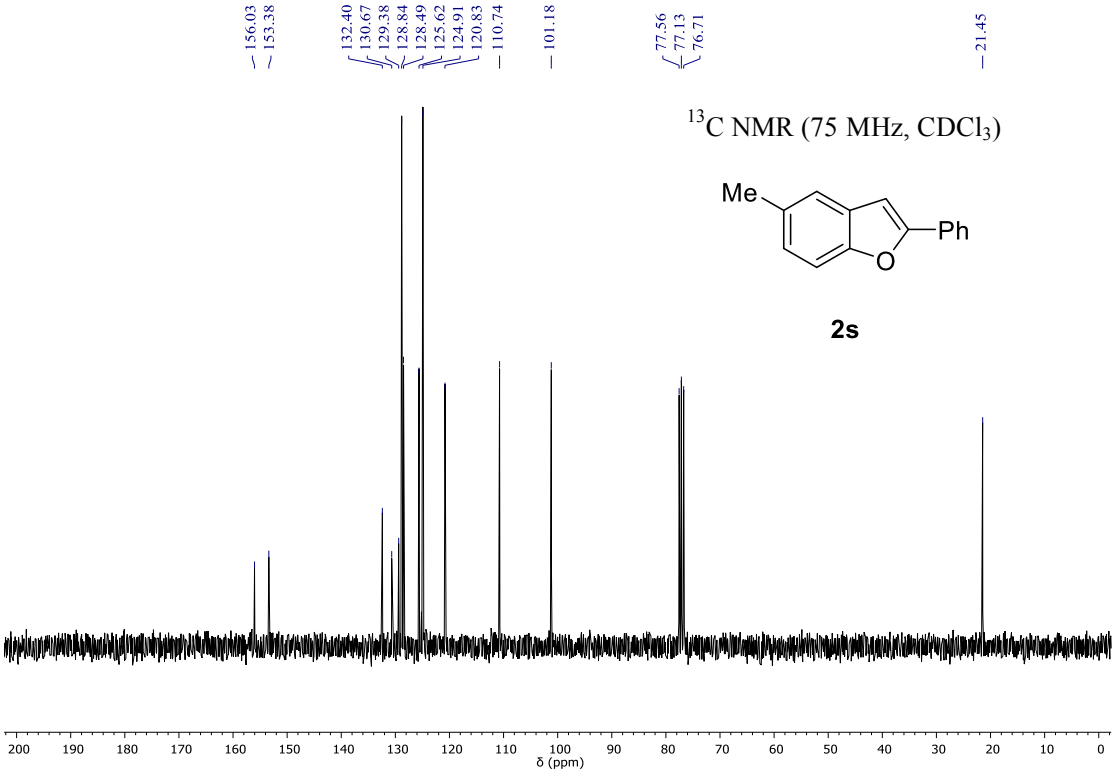
^{13}C NMR (75 MHz, $CDCl_3$)

2r



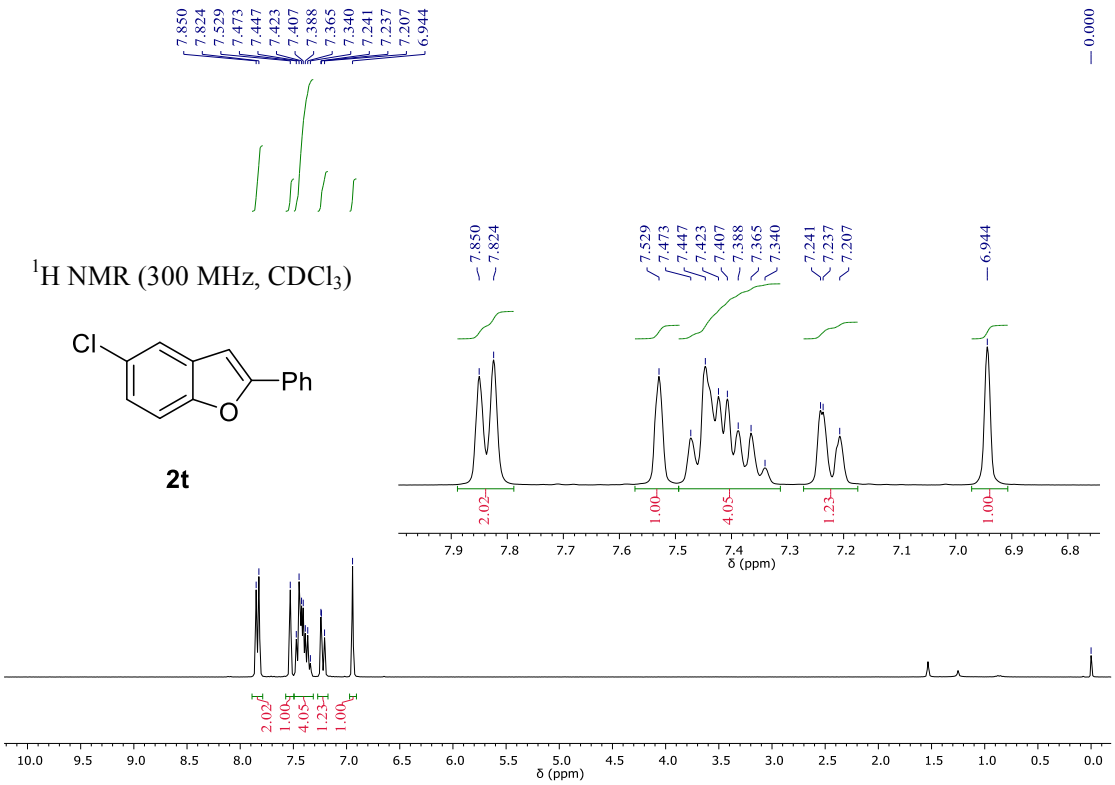
^{1}H NMR (300 MHz, $CDCl_3$)

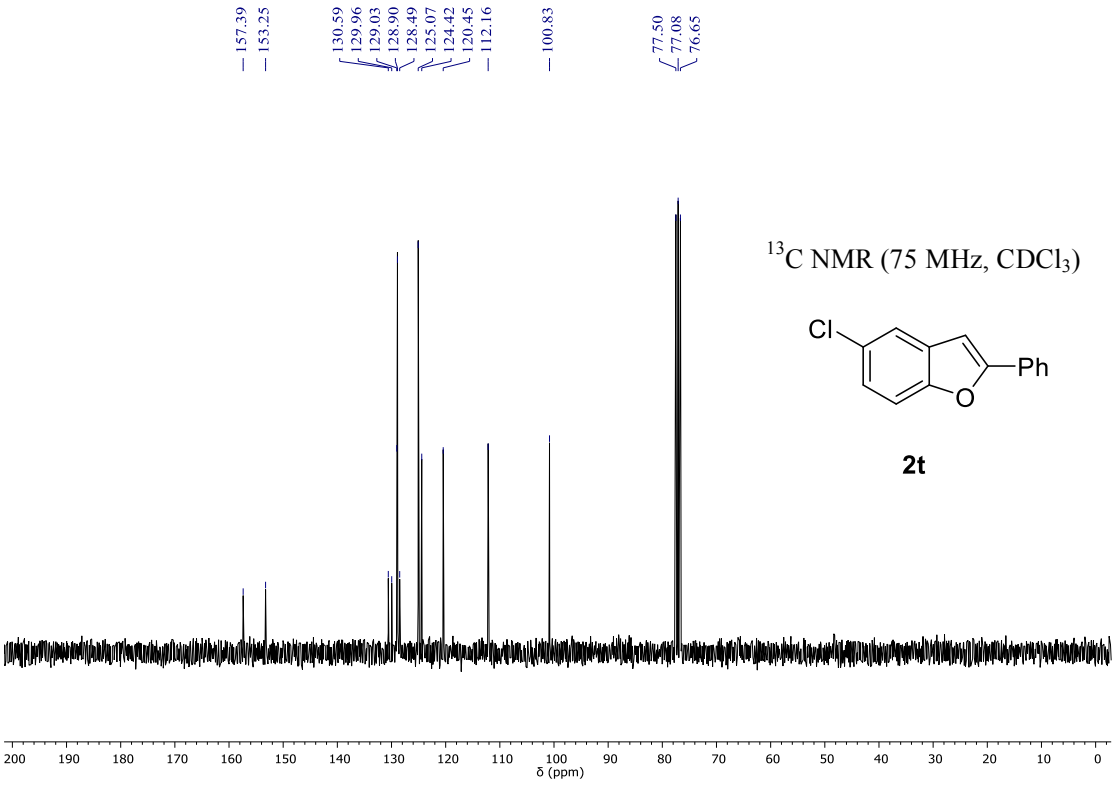
2s

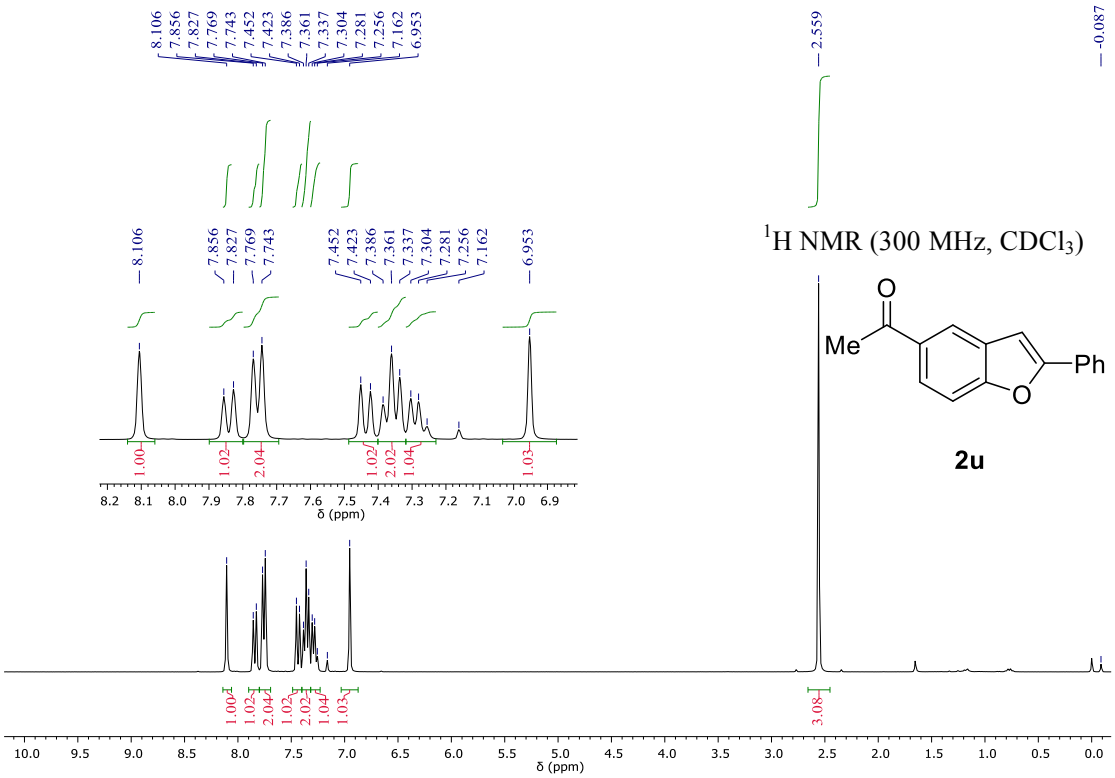


^{13}C NMR (75 MHz, $CDCl_3$)

2s

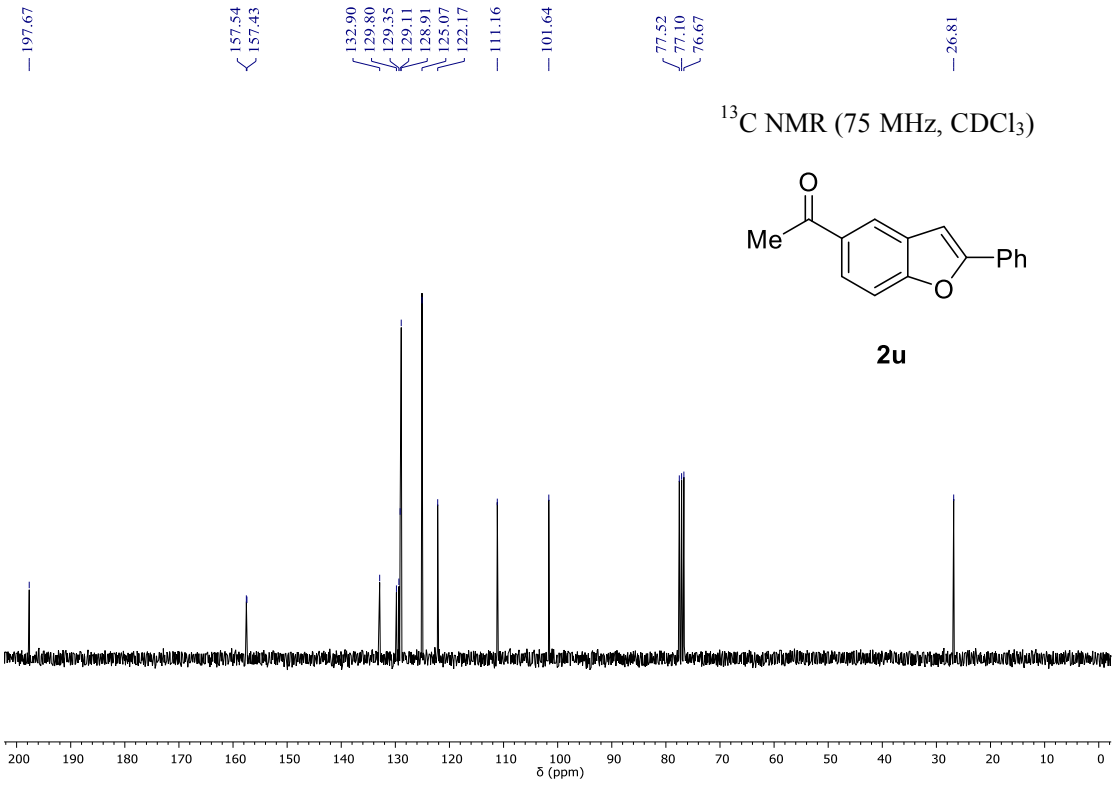

7.850
7.824
7.529
7.473
7.447
7.423
7.407
7.388
7.365
7.340
7.241
7.237
7.207
6.944
0.000
^{1}H NMR (300 MHz, CDCl$_3$)
Cl
Ph
O
2t
2.02
1.00
4.05
1.23
1.00
δ (ppm)


157.39
153.25
130.59
129.96
129.03
128.90
128.49
125.07
124.42
120.45
112.16
100.83
77.50
77.08
76.65
^{13}C NMR (75 MHz, CDCl$_3$)
Cl
Ph
O
2t
δ (ppm)



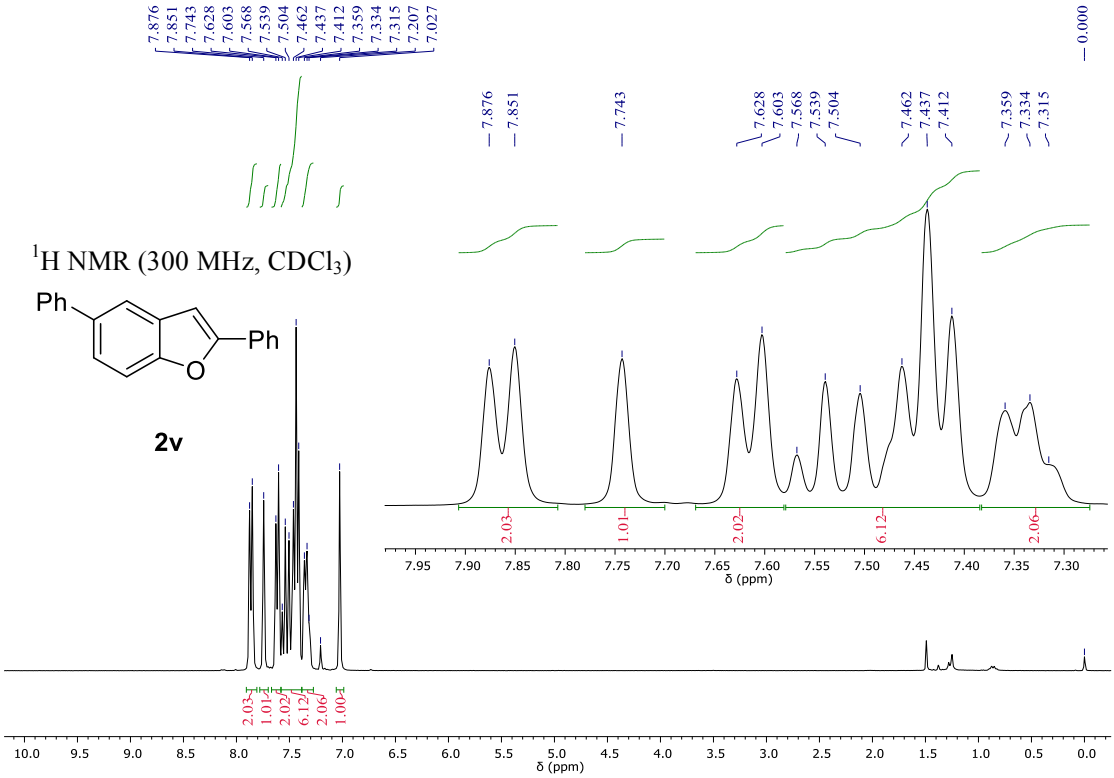
^{1}H NMR (300 MHz, $CDCl_3$)

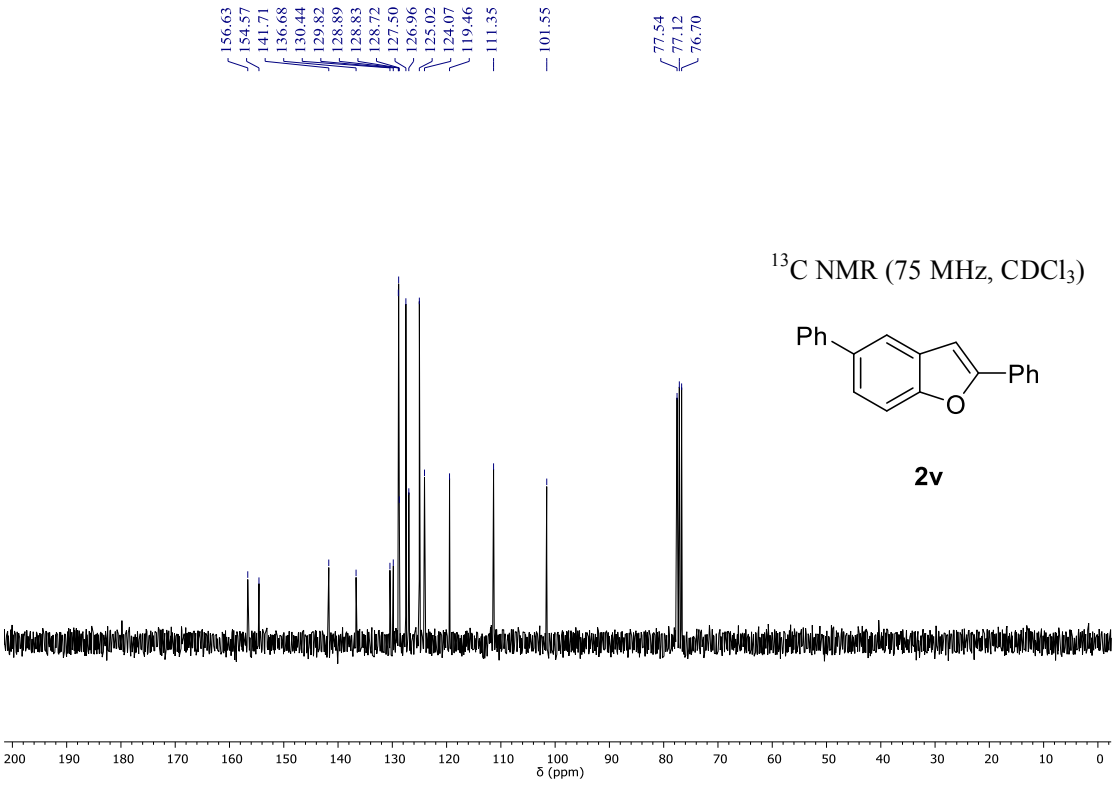
2u

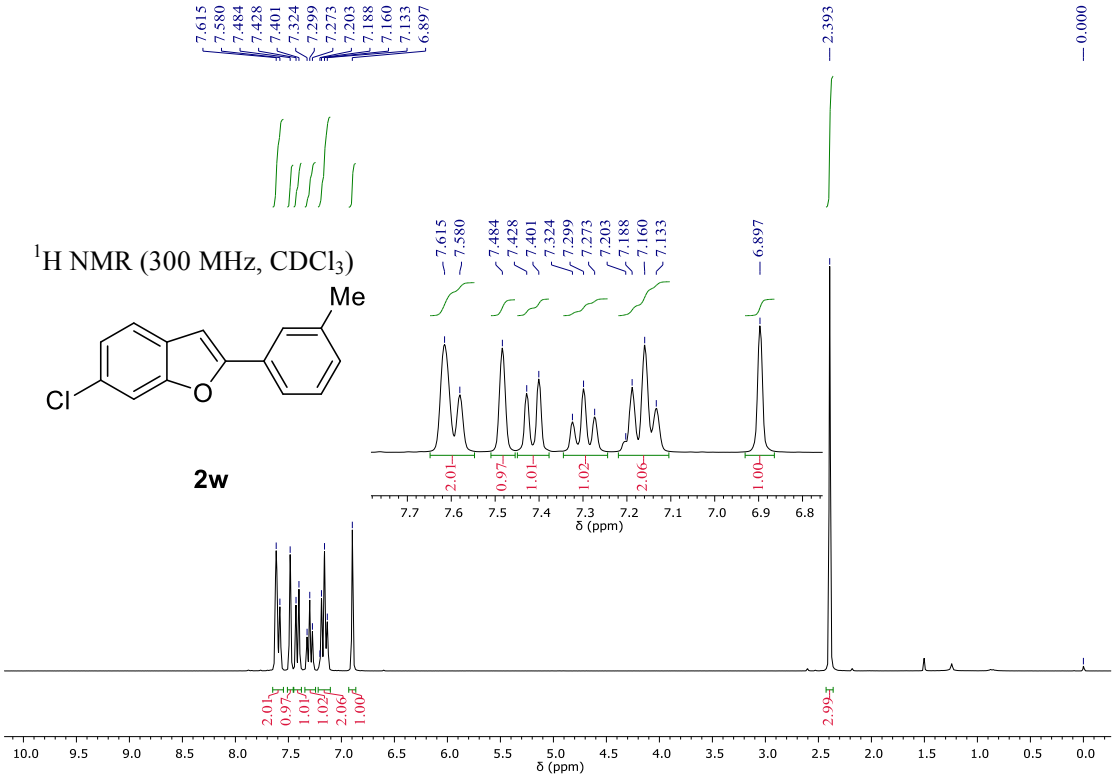


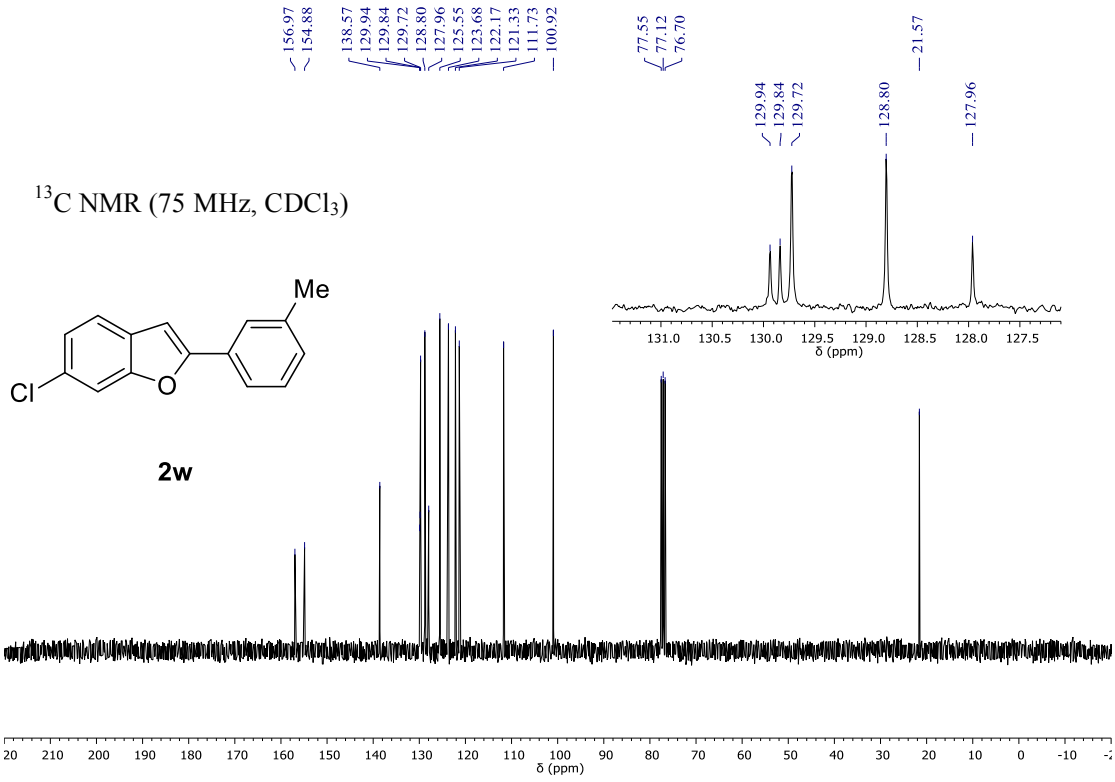
^{13}C NMR (75 MHz, $CDCl_3$)

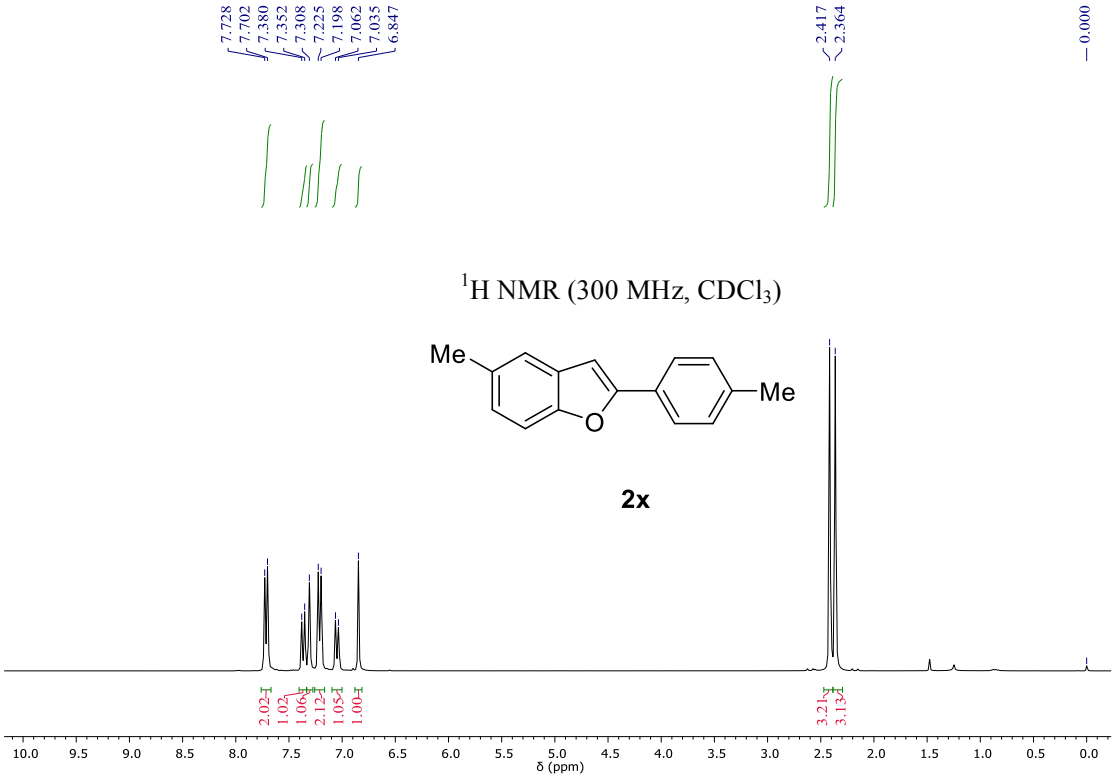
2u


7.876
7.851
7.743
7.628
7.603
7.568
7.539
7.504
7.462
7.437
7.412
7.359
7.334
7.315
7.207
7.027
0.000
^{1}H NMR (300 MHz, CDCl$_3$)
Ph
Ph
O
2v
2.03
1.01
2.02
6.12
2.06
1.00
δ (ppm)

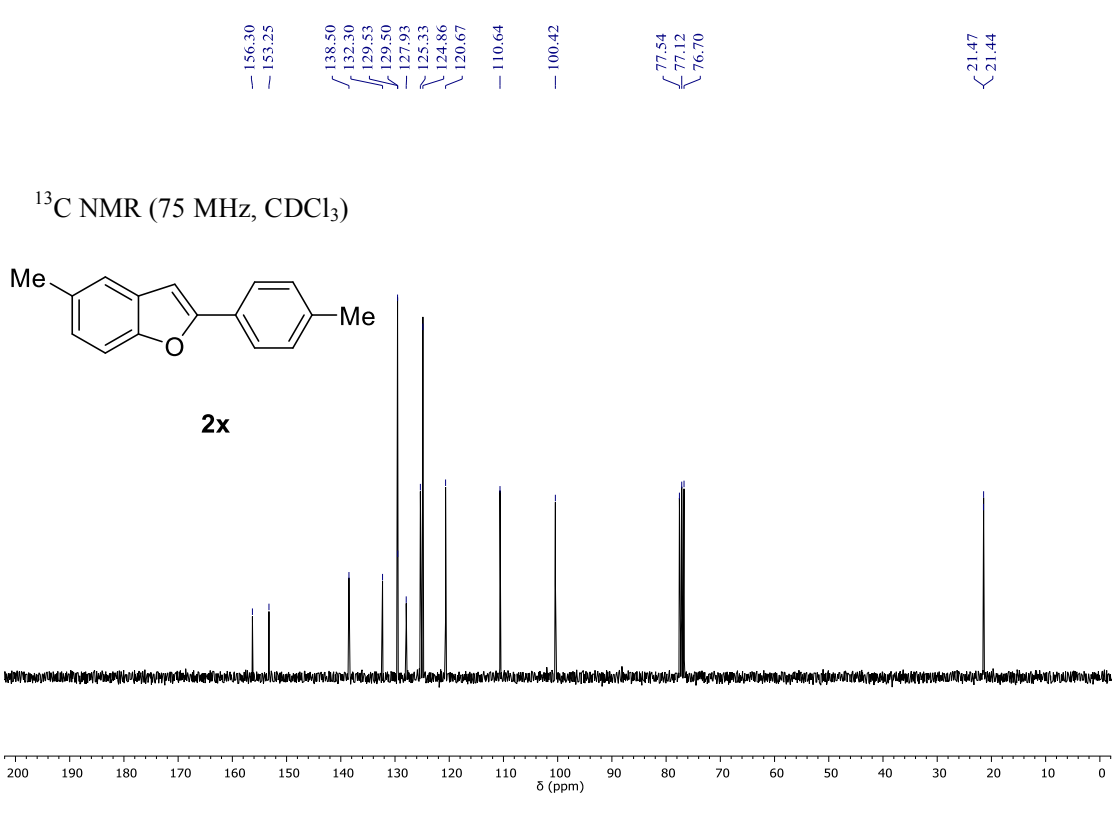

156.63
154.57
141.71
136.68
130.44
129.82
128.89
128.83
128.72
127.50
126.96
125.02
124.07
119.46
111.35
101.55
77.54
77.12
76.70
^{13}C NMR (75 MHz, CDCl$_3$)
Ph
Ph
O
2v
δ (ppm)


7.615
7.580
7.484
7.428
7.401
7.324
7.299
7.273
7.203
7.188
7.160
7.133
6.897
2.393
0.000
^{1}H NMR (300 MHz, CDCl$_3$)
Me
Cl
O
2w
2.01
0.97
1.01
1.02
2.06
1.00
2.99
δ (ppm)

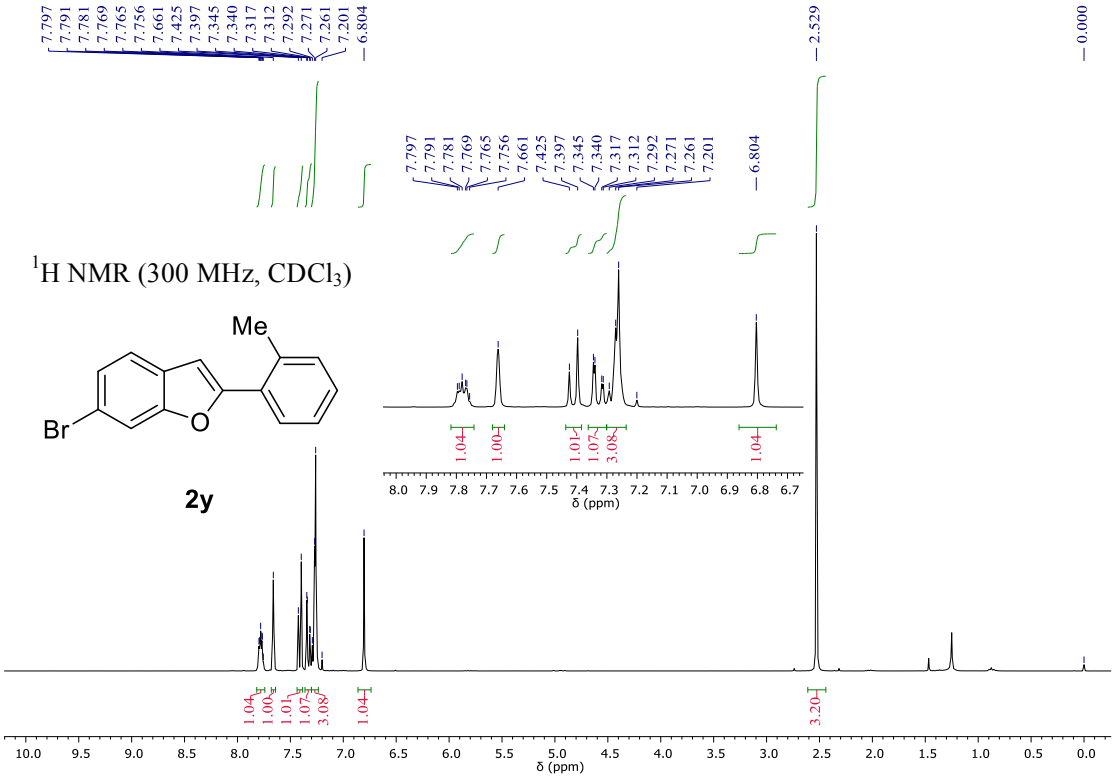

156.97
154.88
138.57
129.94
129.84
129.72
128.80
127.96
125.55
123.68
122.17
121.33
111.73
100.92
77.55
77.12
76.70
21.57
^{13}C NMR (75 MHz, CDCl$_3$)
Me
Cl
O
2w
δ (ppm)

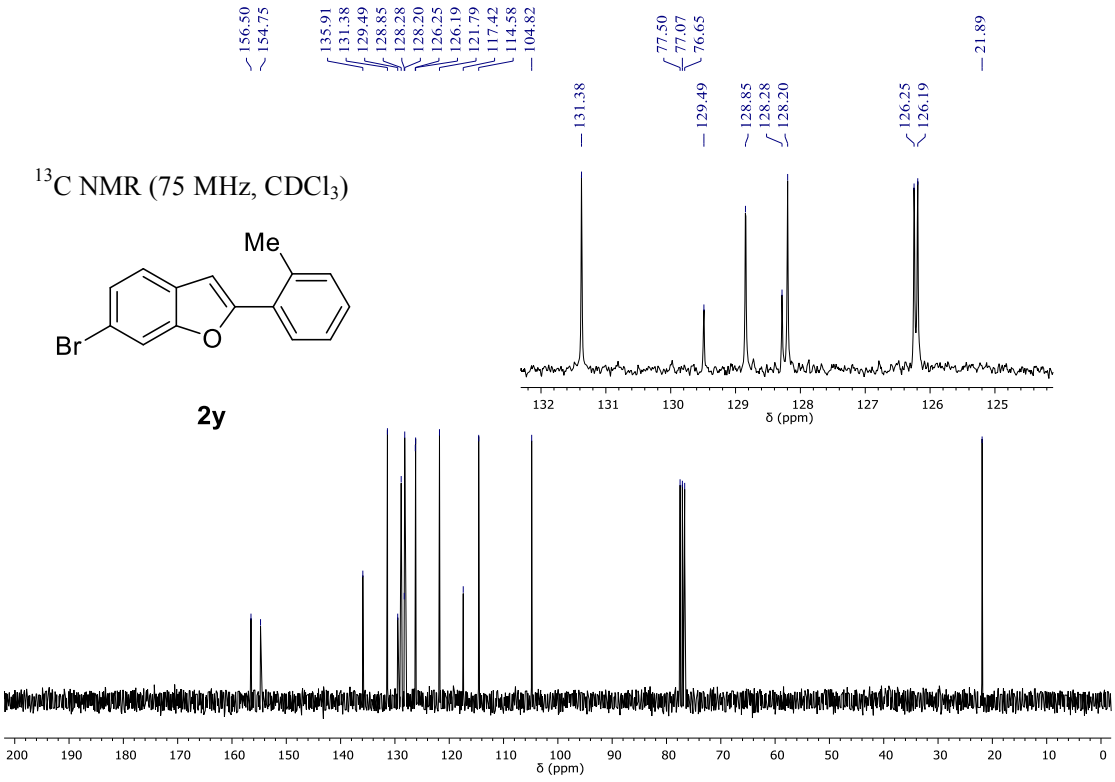


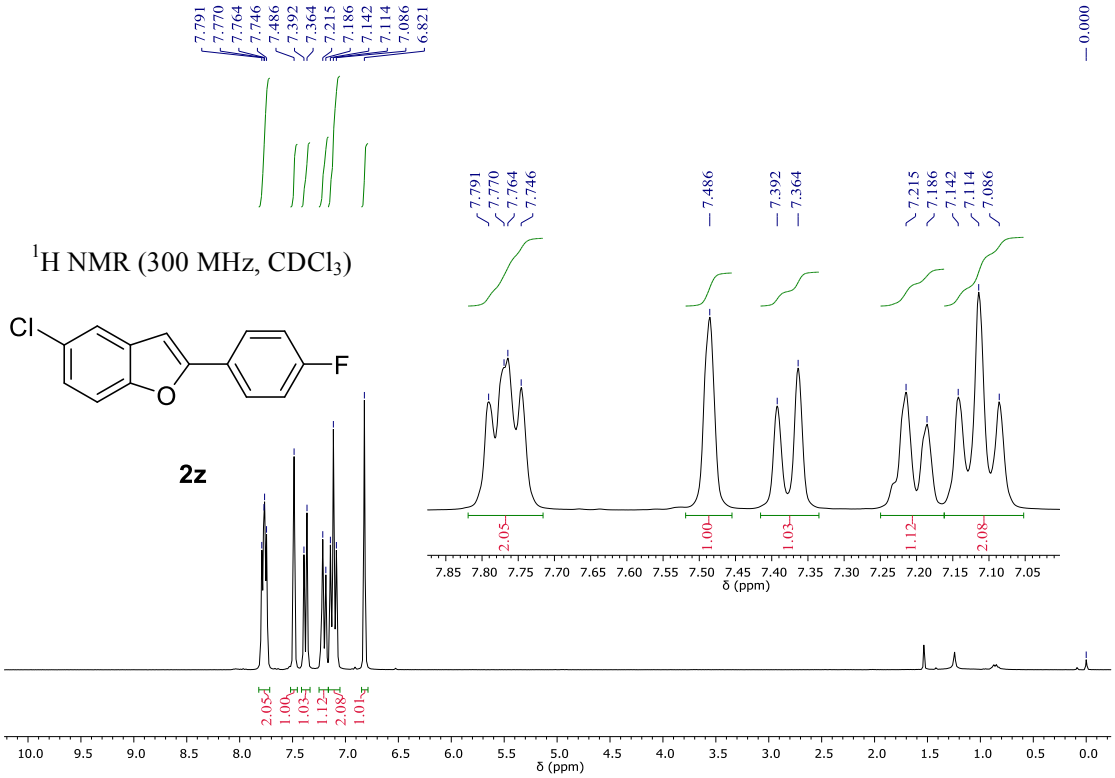
^{1}H NMR (300 MHz, $CDCl_3$)

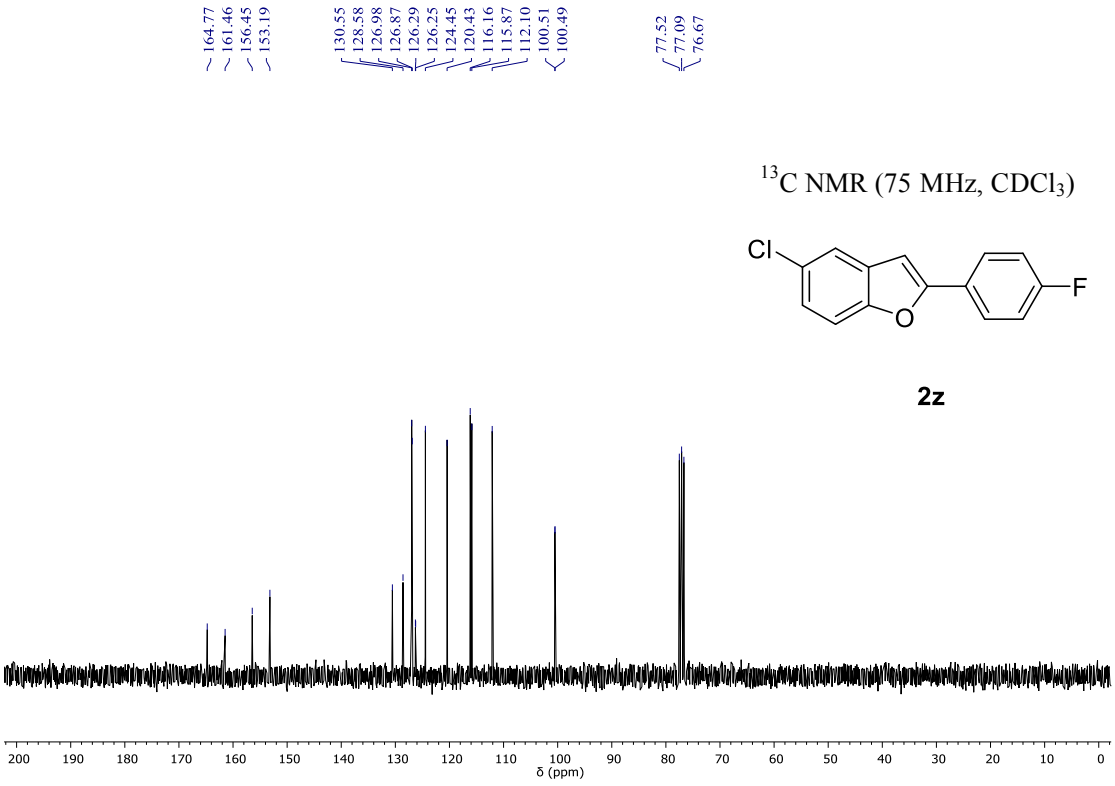


^{13}C NMR (75 MHz, $CDCl_3$)


7.797
7.791
7.781
7.769
7.765
7.756
7.661
7.425
7.397
7.345
7.340
7.317
7.312
7.292
7.271
7.261
7.201
6.804
2.529
0.000
1H NMR (300 MHz, CDCl3)
Me
Br
O
2y
1.04
1.00
1.01
1.07
3.08
1.04
3.20
δ (ppm)


156.50
154.75
135.91
131.38
129.49
128.85
128.28
128.20
126.25
126.19
121.79
117.42
114.58
104.82
77.50
77.07
76.65
21.89
13C NMR (75 MHz, CDCl3)
Me
Br
O
2y
δ (ppm)


7.791
7.770
7.764
7.746
7.486
7.392
7.364
7.215
7.186
7.142
7.114
7.086
6.821
0.000
^{1}H NMR (300 MHz, CDCl$_3$)
Cl
O
F
2z
2.05
1.00
1.03
1.12
2.08
1.01
δ (ppm)


164.77
161.46
156.45
153.19
130.55
128.58
126.98
126.87
126.29
126.25
124.45
120.43
116.16
115.87
112.10
100.51
100.49
77.52
77.09
76.67
^{13}C NMR (75 MHz, CDCl$_3$)
Cl
O
F
2z
δ (ppm)

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

2z