Supplementary Information

Regioselective Allenylation and Propargylation of Various *para*-Quinone Methides Using Alkynyl Azaarenes as Pronucleophile

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General Information. All reactions were conducted under nitrogen atmosphere using flame dried glassware. Chemicals were obtained from Sigma Aldrich, TCI, Merck, Alfa Aesar, Avra, and Spectrochem. All solvents were dried as per standard purification techniques and then stored under appropriate conditions. Analytical thin-layer chromatography was performed using aluminum TLC sheets of 0.25 mm silica gel 60-F254. Visualization was carried out under UV light. Column chromatography was carried out with silica gel 230−400 mesh (Merck). ^{1}H and ^{13}C NMR spectra were measured using $CDCl_3$ as solvent in Bruker 500 MHz NMR instruments. Chemical shifts were set in parts per million (ppm) to 0.0 ppm for TMS or 7.26 ppm for $CDCl_3$. The multiplicities of spectra were denoted by s = singlet, d = doublet, t = triplet, dd = doublet of doublet, td = triplet of doublet, dt = doublet of triplet, q = quartet, m = multiplet, and bs = broad singlet. Coupling constants (*J*) are reported in hertz (Hz). Mass spectra were measured using Thermo Scientific Q-Exactive HRMS and Xevo G2-XS QTof Mass Spectrometry. FT-IR spectra were recorded using a Bruker Alpha II spectrometer. The crystal structure was determined using a Bruker AXS Kappa Apex II ScXRD instrument. Melting points for compounds was recorded using Stuart SMP30 instrument. Literature procedures were followed for the synthesis of *para*-quinone methides.[1-6] The following compounds were prepared according to the reported literature. 2-(2,2-dibromovinyl)quinoline,[7] pyrazine-2-carbaldehyde,[8] 3-methylpicolinaldehyde,[9] 2-ethynyl-6-methoxypyridine,[10] 1-methyl-1H-benzo[d]imidazole-2-carbaldehyde,[11] benzoxazole-2-carbaldehyde,[12] benzothiazole-2-carbaldehyde.[13]

A. General Procedure for the Synthesis of 2,2–Dibromovinyl Hetero Aryl Derivatives[14]

A flame-dried round-bottom flask equipped with a magnetic stirring bar was charged with CBr_4 (1.3 equiv) and PPh_3 (2.6 equiv) in CH_2Cl_2 (0.2 M), the reaction mixture was cooled to 0 °C. Then, heterocyclic aldehyde (1 equiv) was added portion-wise and stirred for 30 min. The reaction mixture was brought to room temperature and then further stirred for 30 min. After completion of the reaction (monitored by TLC), hexane was added to the reaction mixture to precipitate out the triphenylphosphine oxide formed in the reaction mixture. The filtrate was evaporated under reduced pressure to afford a crude residue. The crude product was purified by silica gel column chromatography using ethyl acetate/hexane (1:20) to afford the desired product.

B. General Procedure for the Synthesis of Alkynyl Azaarenes[15]

To a stirred solution of dibromoalkene (1 equiv) in THF (0.25 M), *n*-BuLi (2 equiv, 2.5 M in hexane) was added dropwise at –78 ºC. After stirring for 30 min, CH_3I (1.5 equiv) was added, and the mixture was stirred for an additional 1 h (30 min at –78 ºC and 30 min at 0 ºC). Then, the reaction was quenched with water at 0 °C. The organic phase was extracted with ethyl acetate, and the combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude residue. The crude product was purified by silica gel column chromatography using ethyl acetate/hexane (1:10) to afford the desired product.

C. Typical Experimental Procedure for the Synthesis of 2-Methoxy-6-(prop-1-yn-1-yl)pyridine

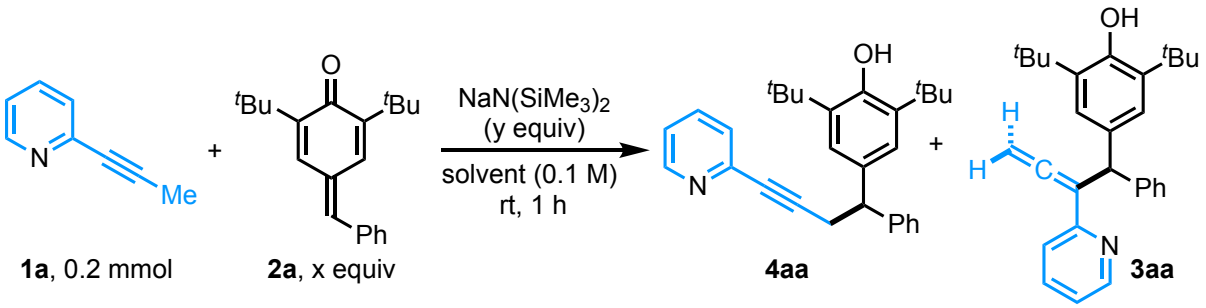
To a stirred solution of the corresponding 2-ethynyl-6-methoxypyridine (1 equiv) in THF (0.25 M), *n*-BuLi (1.2 equiv) was added dropwise at –78 ºC. After stirring for 30 min, CH_3I (1.5 equiv) was added, and the mixture was stirred for an additional 1 h (30 min at –78 ºC and 30 min at 0 ºC). Then, the reaction was quenched with water at 0 °C. The organic phase was

extracted with ethyl acetate, and the combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude residue. The crude product was purified by silica gel column chromatography using ethyl acetate/hexane (1:10) to afford the desired product.

D. General Procedure for the Synthesis of Allenyl Derivatives using Various Alkynyl Azaarenes

To a flame-dried reaction tube charged with a magnetic stir bar, *para*-quinone methide **2a-s** (0.30 mmol) and KO^{t}Bu (0.30 mmol) were added under the argon atmosphere. To the reaction mixture, alkynyl azaarene **1a-i** (0.20 mmol) in toluene (0.1 M) was added, and then, stirred at room temperature for 1 h. The reaction progress was monitored by TLC analysis. After completion of the reaction, the reaction mixture was quenched with water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude reaction mixture was purified by silica gel column chromatography using ethyl acetate/hexane (1:20) as the eluent and afforded the desired product.

Table 1. Optimization of the reaction conditions for the propargylation of *para*-quinone methides[a]



1a, 0.2 mmol **2a**, x equiv **4aa** **3aa**

entry	**2a** (x equiv)	base (y equiv)	solvent	**4aa** (%)[a]	**3aa** (%)[a]
1	1.5	1.5	toluene	38 (43)[b]	9[b]
2	1.5	2	toluene	49 (51)[b]	8[b]
3	**2**	**2**	**toluene**	**57 (57)[b]**	**10[b]**
4[c]	2	2	toluene	41 (43)[b]	10[b]
5	1	2	toluene	39 (40)[b]	10[b]
6	2	2.5	toluene	52 (56)[b]	4[b]
7	2	3	toluene	50 (51)[b]	3[b]
8	2	1.5	toluene	43[b]	9[b]
9	2	1.2	toluene	17[b]	3[b]
10[d]	2	2	toluene	17[b]	trace
11	2	3	THF	18[b]	trace
12	2	3	1,4-dioxane	26[b]	trace
13	2	3	DMF	n.d	n.d

[a]Isolated yield. [b]1H NMR yield and was calculated using tetrachloroethane as an internal standard. [c]The reaction was performed under an open-air. [d]Reaction was done using NaTMP as base. n.d = not detected.

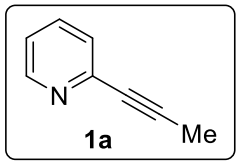
During the optimization of reaction conditions for the allenylation of *p*-QM, we found out that the use of $NaN(SiMe_3)_2$ (1.5 equiv) as a Brønsted base with **1a** (1 equiv) and **2a** (1.5 equiv) led to the formation of propargylated product (**4aa**) in 38% yield along with allenylated product (**3aa**) in 9% yield (Table 1, entry 1). Further increasing the loading of the base to 2 equivalents improved the yields of **4aa** to 49% (entry 2). In addition, raising the equivalents of **2a** to 2 equivalents increased the yield of **4aa** to 57% with a lesser amount of **3aa** (entry 3). The same reaction under an open-air atmosphere delivered the associated product in a 41% yield (entry 4). Reducing the quantity of **2a** from 2 to 1 equivalent decreased the yield of **4aa** (entry 5). Further increasing or decreasing the loading of $NaN(SiMe_3)_2$ had a detrimental effect on the reaction outcome (entries 6 to 9). Besides, the use of a bulkier base such as NaTMP in place of $NaN(SiMe_3)_2$ did not improve the yield of **4aa** (entry 10). Furthermore, replacing toluene with other solvents such as THF, 1,4-dioxane, and DMF had a negative impact on the reaction output (entries 11 to 13). In addition, performing the reaction at various temperatures also did not give any beneficial results. It is important to note that, in all cases, the formation of a few unidentifiable by-products was observed; however, our efforts to improve the yield of **4aa** were not fruitful. Therefore, the optimized reaction conditions for the regioselective propargylation of *p*-QM consist of **1a** (1 equiv), **2a** (2 equiv), $NaN(SiMe_3)_2$ (2 equiv), and toluene as the solvent in room temperature.

E. General Procedure for the Synthesis of Propargylic Derivatives using Various Alkynyl Azaarenes

To a flame-dried reaction tube charged with a magnetic stir bar, *para*-quinone methide **2a-s** (0.40 mmol) and $NaN(SiMe_3)_2$ (0.40 mmol) were added under the argon atmosphere. To the reaction mixture, alkynyl azaarene **1a-j** (0.200 mmol) in toluene (0.1 M) was added and then, stirred at room temperature for 1 h. The reaction progress was monitored by TLC analysis. After completion of the reaction, the mixture was quenched with water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude reaction mixture was purified by silica gel column chromatography using ethyl acetate/hexane (1:10) as the eluent and afforded the desired product.

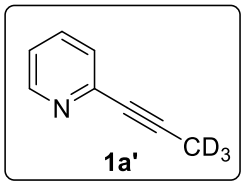
SPECTRAL DATA

2-(prop-1-yn-1-yl)pyridine (1a)[22]



The title compound was prepared as described in general procedure **B** using 2-(2,2-dibromovinyl)pyridine (1 equiv, 18.6359 mmol) as starting material. Yield: 1.62 g, 74%, brown oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.53 (d, *J* = 4.8 Hz, 1H), 7.60 (td, *J* = 7.7, 1.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.19-7.16 (m, 1H), 2.08 (s, 3H).

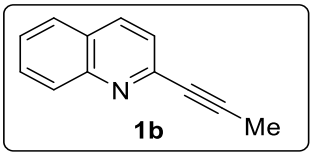
2-(Prop-1-yn-1-yl-d3)pyridine (1a')



The title compound was prepared as described in general procedure **B** using 2-(2,2-dibromovinyl)pyridine (1 equiv, 1.9016 mmol) and CD_3OTs (instead of CH_3I) as starting material. Yield: 107 mg, 47%, colourless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.52 (d, *J* = 4.8 Hz, 1H), 7.59 (td, *J* = 7.7, 1.8 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.18-7.15 (m, 1H). **^{13}C**

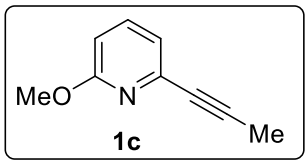
NMR (125 MHz, $CDCl_3$) δ (ppm): 149.9, 144.0, 136.2, 126.7, 122.4, 86.7, 79.7, 3.9, 3.8, 3.6. **IR** (CH_2Cl_2, cm^{-1}): 2938, 1725, 1468, 1192, 974. **HRMS** (ESI) m/z calcd for $C_8H_4D_3N$ $[M+H]^+$: 121.0840, found:121.0842.

2-(Prop-1-yn-1-yl)quinoline (1b)



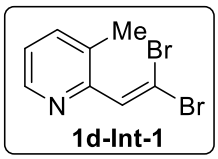
The title compound was prepared as described in general procedure **B** using 2-(2,2-dibromovinyl)quinoline (1 equiv, 1.7665 mmol) as starting material. Yield: 174.3 mg, 59%, brown solid. Mp: 58.4-62.6 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.08-8.05 (m, 2H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.71-7.68 (m, 1H), 7.52-7.49 (m, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 2.13 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 148.3, 144.3, 136.3, 130.1, 129.4, 127.7, 127.2, 127.0, 124.2, 87.8, 80.6, 4.7. **IR** (CH_2Cl_2, cm^{-1}): 3305, 3073, 2238, 1601, 832, 758. **HRMS** (ESI) m/z calcd for $C_{12}H_9N$ $[M+H]^+$: 168.0808, found: 168.0808.

2-Methoxy-6-(prop-1-yn-1-yl)pyridine (1c)



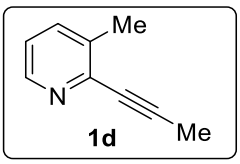
The title compound was prepared as described in general procedure **C** from 2-ethynyl-6-methoxypyridine (1 equiv, 0.7510 mmol). Yield: 62.0 mg, 56%, yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.48 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 8.3 Hz, 1H), 3.94 (s, 3H), 2.08 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 164.0, 140.9, 138.6, 120.3, 110.7, 86.1, 79.8, 53.6, 4.6. **IR** (CH_2Cl_2, cm^{-1}): 2937, 2243, 1750, 1580, 1469, 1327, 1253, 1058, 807. **HRMS** (ESI) m/z calcd for C_9H_9NO $[M+H]^+$: 148.0757, found: 148.0756.

2-(2,2-Dibromovinyl)-3-methylpyridine (1d-Int-1)



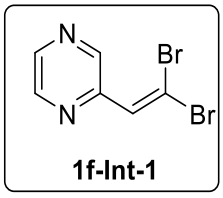
The title compound was prepared as described in general procedure **A** using 3-methylpicolinaldehyde (1 equiv, 6.2738 mmol) as starting material. Yield: 976.8 mg, 56%, brown oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.48 (s, 1H), 7.58-7.51 (m, 2H), 7.18 (s, 1H), 2.31 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 153.5, 147.0, 138.1, 135.4, 132.0, 123.3, 94.9, 18.7. **IR** (CH_2Cl_2, cm^{-1}): 3067.22, 1725, 1444.21, 1169.81, 1124.55, 726.26. **HRMS** (ESI) m/z calcd for $C_8H_7Br_2N$ $[M+H]^+$: 277.8998, found: 277.8995.

3-Methyl-2-(prop-1-yn-1-yl)pyridine (1d)



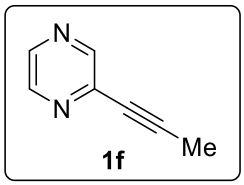
The title compound was prepared as described in general procedure **B** using 2-(2,2-dibromovinyl)-3-methylpyridine (1 equiv, 3.3868 mmol) as starting material. Yield: 285.8 mg, 64%, yellow gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.35 (d, *J* = 4.7 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.09-7.07 (m, 1H), 2.39 (s, 3H), 2.11 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 147.2, 143.7, 136.9, 135.4, 122.3, 90.4, 78.5, 19.5, 4.6. **IR** (CH_2Cl_2, cm^{-1}): 3382, 2936, 2239, 1589, 1572, 1121, 799. **HRMS** (ESI) m/z calcd for C_9H_9N $[M+H]^+$: 132.0808, found: 132.0808.

2-(2,2-Dibromovinyl)pyrazine (1f-Int-1)



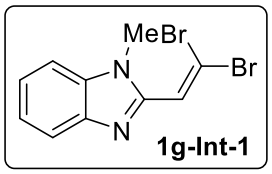
The title compound was prepared as described in general procedure **A** using pyrazine-2-carbaldehyde (1 equiv, 5.0879 mmol) as starting material. Yield: 639.2 mg, 48%, off-white gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.95 (s, 1H), 8.60-8.59 (m, 1H), 8.51 (s, 1H), 7.64 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 150.1, 144.9, 144.3, 143.5, 134.2, 96.0. **IR** (CH_2Cl_2, cm^{-1}): 2334, 1617, 1401, 1147, 891, 804. **HRMS** (ESI) m/z calcd for $C_6H_4Br_2N_2$ $[M+H]^+$: 264.8794, found: 264.8792.

2-(Prop-1-yn-1-yl)pyrazine (1f)



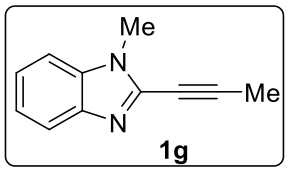
The title compound was prepared as described in general procedure **B** using 2-(2,2-dibromovinyl)pyrazine (1 equiv, 2.3871 mmol) as starting material. Yield: 122.4 mg, 43%, yellow solid. Mp: 70.2-74.9 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.60-8.59 (m, 1H), 8.49-8.48 (m, 1H), 8.43-8.42 (m, 1H), 2.12 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 147.7, 144.4, 142.6, 140.9, 91.4, 77.1, 4.6. **IR** (CH_2Cl_2, cm^{-1}): 3357, 2287, 2241, 1477, 1410, 1144, 860. **HRMS** (ESI) m/z calcd for $C_7H_6N_2$ $[M+H]^+$: 119.0604, found:119.0606.

2-(2,2-Dibromovinyl)-1-methyl-1H-benzo[d]imidazole (1g-Int-1)



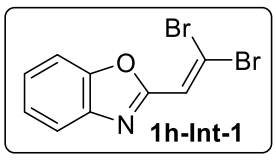
The title compound was prepared as described in general procedure **A** using 1-methyl-1H-benzo[d]imidazole-2-carbaldehyde (1 equiv, 3.4337 mmol) as starting material. Yield: 423.0 mg, 39%, brown solid. Mp: 123.9-127.2 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.85-7.83 (m, 1H), 7.57 (d, J = 1.5 Hz, 1H), 7.36-7.29 (m, 3H), 3.79 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 147.7, 143.0, 135.1, 125.0, 123.8, 122.9, 120.6, 109.6, 99.2, 30.4. **IR** (CH_2Cl_2, cm^{-1}): 2972, 1750, 1471, 1391, 749. **HRMS** (ESI) m/z calcd for $C_{10}H_8Br_2N_2$ $[M+H]^+$: 316.9107, found: 316.9102.

1-Methyl-2-(prop-1-yn-1-yl)-1H-benzo[d]imidazole (1g)



The title compound was prepared as described in general procedure **B** using 2-(2,2-dibromovinyl)-1-methyl-1H-benzo[d]imidazole (1 equiv, 1.2658 mmol) as starting material. Mp: 94.6-98.7 °C. Yield: 192.2 mg, 89%, brown solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.72 (d, J = 7.7 Hz, 1H), 7.31-7.26 (m, 3H), 3.84 (s, 3H), 2.19 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 142.9, 138.2, 134.8, 123.6, 122.8, 120.2, 109.4, 93.0, 70.0, 30.7, 4.7. **IR** (CH_2Cl_2, cm^{-1}): 2250, 1749, 1469, 1397, 758. **HRMS** (ESI) m/z calcd for $C_{11}H_{10}N_2$ $[M+H]^+$: 171.0917, found: 171.0916.

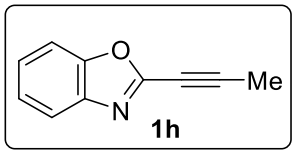
2-(2,2-Dibromovinyl)benzoxazole (1h-Int-1)



The title compound was prepared as described in general procedure **A** using benzoxazole-2-carbaldehyde (1 equiv, 2.03 mmol) as starting material. Mp: 88.5-92.3 °C. Yield: 140 mg, 23%, brown powder. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.80-7.79 (m, 1H), 7.64-7.63 (m, 1H), 7.56-7.54 (m, 1H), 7.42-7.35 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 159.0, 149.9, 141.4, 126.4, 125.2, 124.4, 120.8, 110.9, 100.7. **IR** (CH_2Cl_2,

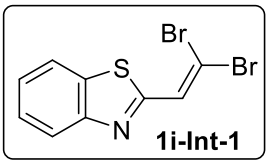
cm^{-1}): 3022, 2939, 1627, 1601, 1457, 1252, 821, 752. **HRMS** (ESI) m/z calcd for $C_9H_5Br_2NO$ $[M+H]^+$: 303.8790, found: 303.8788.

2-(prop-1-yn-1-yl)benzo[d]oxazole (1h)[23]



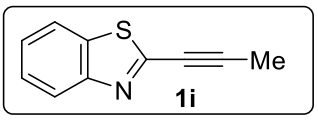
The title compound was prepared as described in general procedure **B** using 2-(2,2-dibromovinyl)benzoxazole (1 equiv, 2.3106 mmol) as starting material. Yield: 119.7 mg, 33%, yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.72-7.70 (m, 1H), 7.51-7.49 (m, 1H), 7.40 - 7.33 (m, 2H), 2.18 (s, 3H).

2-(2,2-Dibromovinyl)benzothiazole (1i-Int-1)



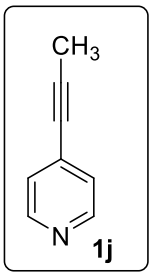
The title compound was prepared as described in general procedure **A** using benzothiazole-2-carbaldehyde (1 equiv, 6.1277 mmol) as starting material. Yield: 620 mg, 32%, brown solid. Mp: 98.8-102.4 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.07-8.05 (m, 2H), 7.92 (d, J = 7.9 Hz, 1H), 7.54-7.51 (m, 1H), 7.48-7.45 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 162.2, 152.0, 134.6, 133.1, 126.9, 126.3, 123.7, 121.6, 97.7. **IR** (CH_2Cl_2, cm^{-1}): 3076, 2940, 1461, 1205, 843, 761. **HRMS** (ESI) m/z calcd for $C_9H_5Br_2NS$ $[M+H]^+$: 319.8562, found: 319.8561.

2-(Prop-1-yn-1-yl)benzothiazole (1i)



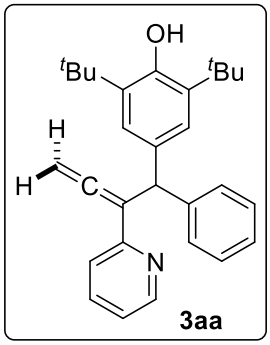
The title compound was prepared as described in general procedure **B** using 2-(2,2-dibromovinyl)benzothiazole (1 equiv, 1.9435 mmol) as starting material. Yield: 120 mg, 36%, yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$ + CCl_4 (5:1)) δ (ppm): 8.01 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.50 - 7.47 (m, 1H), 7.43 – 7.39 (m, 1H), 2.17 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, CCl_4) δ (ppm): 152.9, 149.3, 135.2, 126.6, 126.1, 123.6, 121.4, 94.5, 74.1, 4.9. **IR** (CH_2Cl_2, cm^{-1}): 2972, 2939, 2249, 1495, 1203, 765. **HRMS** (ESI) m/z calcd for $C_{10}H_7NS$ $[M+H]^+$: 174.0372, found: 174.0374.

4-(prop-1-yn-1-yl)pyridine (1j)



The title compound was prepared as described in general procedure **B** using 4-(2,2-dibromovinyl)pyridine (1 equiv, 1.9435 mmol) as starting material. Yield: 229.7 mg, 64%, yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.49 (s, 2H), 7.20 (d, J = 5.5 Hz, 2H), 2.03 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, CCl_4) δ (ppm): 149.7, 132.3, 125.8, 91.5, 77.7, 4.5. **IR** (CH_2Cl_2, cm^{-1}): 2937, 2278, 2236, 1599, 1414, 826. **HRMS** (ESI) m/z calcd for C_8H_7N $[M+H]^+$: 118.0651, found: 118.0655.

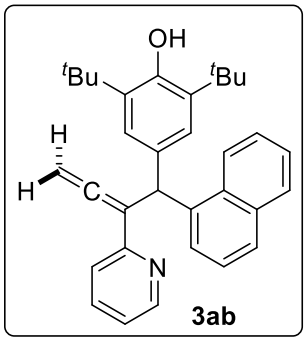
2,6-Di-*tert*-butyl-4-(1-phenyl-2(pyridin-2-yl)buta-2,3-dien-1-yl)phenol (3aa)



The title compound was prepared as described in procedure **D** using **1a** (0.200 mmol) and **2a** (0.300 mmol). Yield: 78.1 mg, 95%, off-white gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.52 (d, J = 4.8 Hz, 1H), 7.56-7.52 (m, 1H), 7.49 (d, J = 7.9 Hz, 1H), 7.30 (d, J = 7.5 Hz, 2H), 7.26-7.23 (m, 2H), 7.16-7.13 (m, 1H), 7.08 (s, 2H), 7.03-7.00 (m, 1H), 5.78 (s, 1H), 5.06-5.00 (m, 3H), 1.38 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.6, 155.5, 152.2, 149.1, 144.0, 136.2, 135.2, 133.4, 129.1, 128.1, 126.04, 125.95, 122.6, 121.3, 112.0, 80.6, 49.8,

34.5, 30.5. **IR** (CH_2Cl_2, cm^{-1}): 3630, 2967, 1948, 1439, 1239, 853, 704. **HRMS** (ESI) m/z calcd for $C_{29}H_{33}NO$ $[M+H]^+$: 412.2635, found: 412.2624.

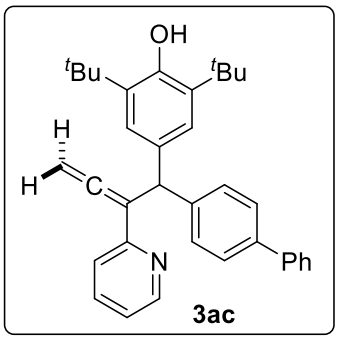
2,6-Di-*tert*-butyl-4-(1-(naphthalen-1-yl)-2(pyridin-2-yl)buta-2,3-dien-1-yl)phenol (3ab)



3ab

The title compound was prepared as described in procedure **D** using **1a** (0.200 mmol) and **2b** (0.300 mmol). Yield: 83.1 mg, 90%, brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.55 (d, *J* = 4.7 Hz, 1H), 8.33 (d, *J* = 8.6 Hz, 1H), 7.84-7.83 (m, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.56-7.53 (m, 1H), 7.49 -7.43 (m, 3H), 7.34-7.31 (m, 1H), 7.17 (s, 2H), 7.12 (d, *J* = 7.2 Hz, 1H), 7.05-7.02 (m, 1H), 6.55 (s, 1H), 5.04 (s, 1H), 4.92 (dd, *J* = 12.5, 1.9 Hz, 1H), 4.74 (dd, *J* = 12.5, 2.0 Hz, 1H), 1.38 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.7, 155.4, 152.3, 149.4, 140.6, 136.2, 135.3, 133.9, 132.3, 132.2, 128.6, 126.8, 126.4, 126.3, 126.0, 125.30, 125.26, 124.6, 122.5, 121.3, 111.9, 80.1, 46.1, 34.5, 30.5. **IR** (CH_2Cl_2, cm^{-1}): 3654, 2970, 1948, 1439, 789, 738. **HRMS** (ESI) m/z calcd for $C_{33}H_{35}NO$ $[M+H]^+$: 462.2793, found: 462.2797.

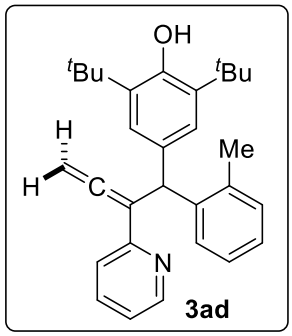
4-(1-([1,1'-Biphenyl]-4-yl)-2-(pyridin-2-yl)buta-2,3-dien-1-yl)-2,6-di-*tert*-butylphenol (3ac)



3ac

The title compound was prepared as described in procedure **D** using **1a** (0.200 mmol) and **2c** (0.300 mmol). Yield: 94.0 mg, 96%, brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.54 (d, *J* = 4.7 Hz, 1H), 7.59-7.49 (m, 6H), 7.42-7.36 (m, 4H), 7.31-7.29 (m, 1H), 7.12 (s, 2H), 7.05-7.02 (m, 1H), 5.82 (s, 1H), 5.11-5.04 (m, 3H), 1.39 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.5, 155.5, 152.2, 149.2, 143.3, 141.2, 138.7, 136.1, 135.3, 133.4, 129.4, 128.8, 127.1, 126.8, 126.0, 122.6, 121.3, 112.0, 80.7, 49.4, 34.5, 30.5. **IR** (CH_2Cl_2, cm^{-1}): 3620, 2971, 1947, 1595, 1438, 1158, 853, 741. **HRMS** (ESI) m/z calcd for $C_{35}H_{37}NO$ $[M+H]^+$: 488.2948, found: 488.2945.

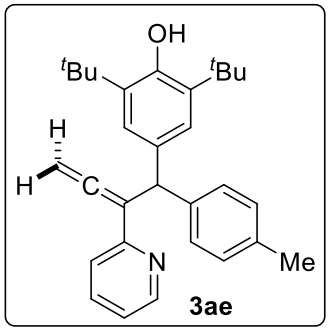
2,6-Di-*tert*-butyl-4-(2-(pyridin-2-yl)-1-(o-tolyl)buta-2,3-dien-1-yl)phenol (3ad)



3ad

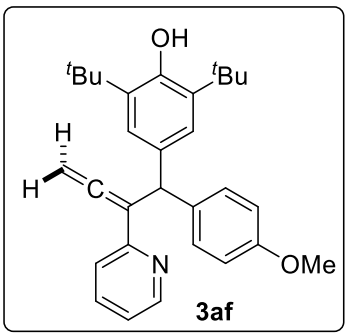
The title compound was prepared as described in procedure **D** using **1a** (0.200 mmol) and **2d** (0.300 mmol). Yield: 84.0 mg, 99%, off-white solid. Mp:120.4-124.1°C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.51 (d, *J* = 4.8 Hz, 1H), 7.53 (td, *J* = 7.7, 1.7 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.14-7.11 (m, 2H), 7.08-7.05 (m, 4H), 7.02-7.00 (m, 1H), 5.86 (s, 1H), 5.01-4.94 (m, 3H), 2.41 (s, 3H), 1.38 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.4, 155.6, 152.1, 149.3, 142.3, 136.8, 136.1, 135.1, 132.2, 130.1, 128.4, 126.2, 126.0, 125.5, 122.3, 121.2, 111.8, 80.1, 46.7, 34.4, 30.5, 20.0. **IR** (CH_2Cl_2, cm^{-1}): 3673, 2970, 1950, 1594, 1439, 1159, 853, 741. **HRMS** (ESI) m/z calcd for $C_{30}H_{35}NO$ $[M+H]^+$: 426.2791, found: 426.2781.

2,6-Di-*tert*-butyl-4-(2-(pyridin-2-yl)-1-(p-tolyl)buta-2,3-dien-1-yl)phenol (3ae)



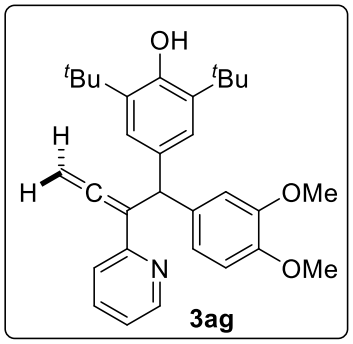
The title compound was prepared as described in procedure **D** using **1a** (0.200 mmol) and **2e** (0.300 mmol). Yield: 80.7 mg, 95%, yellow gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.53-8.52 (m, 1H), 7.56-7.52 (m, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.09 (s, 2H), 7.06-7.00 (m, 3H), 5.73 (s, 1H), 5.08-5.01 (m, 3H), 2.29 (s, 3H), 1.38 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.5, 155.7, 152.1, 149.2, 141.0, 136.1, 135.4, 135.1, 133.6, 128.9, 128.8, 125.9, 122.5, 121.2, 112.2, 80.5, 49.4, 34.5, 30.5, 21.2. **IR** (CH_2Cl_2, cm^{-1}): 3631, 2975, 1947, 1439, 1159, 852, 741. **HRMS** (ESI) m/z calcd for $C_{30}H_{35}NO$ $[M+H]^+$: 426.2791, found: 426.2785.

2,6-Di-*tert*-butyl-4-(1-(4-methoxyphenyl)-2-(pyridin-2-yl)buta-2,3-dien-1-yl)phenol (3af)



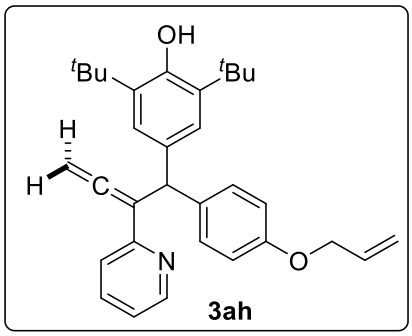
The title compound was prepared as described in procedure **D** using **1a** (0.200 mmol) and **2f** (0.300 mmol). Yield: 84.6 mg, 96%, brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.52 (d, *J* = 4.7 Hz, 1H), 7.55-7.52 (m, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.7 Hz, 2H), 7.06 (s, 2H), 7.03-7.00 (m, 1H), 6.78 (d, *J* = 8.6 Hz, 2H), 5.69 (s, 1H), 5.06-4.99 (m, 3H), 3.76 (s, 3H), 1.37 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.5, 157.8, 155.6, 152.1, 149.2, 136.2, 136.1, 135.1, 133.7, 130.0, 125.8, 122.5, 121.2, 113.4, 112.3, 80.5, 55.3, 49.0, 34.4, 30.5. **IR** (CH_2Cl_2, cm^{-1}): 3627, 2970, 1947, 1516, 1249, 846, 740. **HRMS** (ESI) m/z calcd for $C_{30}H_{35}NO_2$ $[M+H]^+$: 442.2741, found: 442.2735.

2,6-Di-*tert*-butyl-4-(1-(3,4-dimethoxyphenyl)-2-(pyridin-2-yl)buta-2,3-dien-1-yl)phenol (3ag)



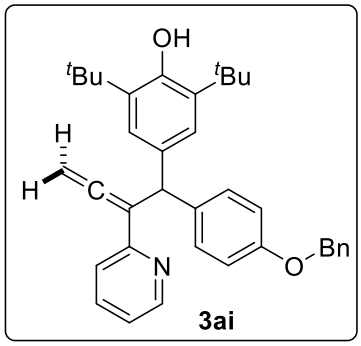
The title compound was prepared as described in procedure **D** using **1a** (0.200 mmol) and **2g** (0.300 mmol). Yield: 68.8 mg, 73%, brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.53 (d, *J* = 4.5 Hz, 1H), 7.56-7.53 (m, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.09 (s, 2H), 7.04-7.01 (m, 1H), 6.87-6.86 (m, 1H), 6.83-6.81 (m, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 5.70 (s, 1H), 5.06-4.99 (m, 3H), 3.83 (s, 3H), 3.80 (s, 3H), 1.38 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.4, 155.6, 152.2, 149.2, 148.5, 147.3, 136.6, 136.2, 135.2, 133.5, 125.8, 122.5, 121.3, 121.0, 112.7, 112.3, 110.7, 80.5, 55.90, 55.88, 49.4, 34.5, 30.5. **IR** (CH_2Cl_2, cm^{-1}): 3650, 2970, 1949, 1720, 1597, 1267, 1148, 1033, 742. **HRMS** (ESI) m/z calcd for $C_{31}H_{37}NO_3$ $[M+H]^+$: 472.2846, found: 472.2846.

4-(1-(4-(Allyloxy)phenyl)-2-(pyridin-2-yl)buta-2,3-dien-1-yl)-2,6-di-*tert*-butylphenol (3ah)



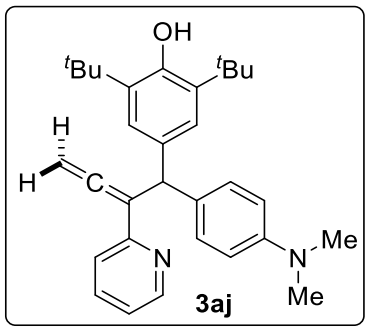
The title compound was prepared as described in procedure **D** using **1a** (0.200 mmol) and **2h** (0.300 mmol). Yield: 82.7 mg, 88%, brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.52 (d, *J* = 4.8 Hz, 1H), 7.55-7.52 (m, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.20 (d, *J* = 8.7 Hz, 2H), 7.06 (s, 2H), 7.03-7.00 (m, 1H), 6.80 (d, *J* = 8.6 Hz, 2H), 6.08-6.00 (m, 1H), 5.70 (s, 1H), 5.39 (dd, *J* = 17.3, 1.3 Hz, 1H), 5.25 (d, *J* = 10.5 Hz, 1H), 5.06-4.99 (m, 3H), 4.49 (d, *J* = 5.4 Hz, 2H), 1.37 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.5, 156.9, 155.6, 152.1, 149.2, 136.4, 136.1, 135.2, 133.72, 133.67, 130.0, 125.8, 122.5, 121.2, 117.6, 114.3, 112.3, 80.5, 68.9, 49.0, 34.5, 30.5. **IR** (CH_2Cl_2, cm^{-1}): 3617, 2957, 1938, 1505, 1431, 1231, 842, 740. **HRMS** (ESI) m/z calcd for $C_{32}H_{37}NO_2$ $[M+H]^+$: 468.2897, found: 468.2896.

4-(1-(4-(Benzyloxy)phenyl)-2-(pyridin-2-yl)buta-2,3-dien-1-yl)-2,6-di-*tert*-butylphenol (3ai)



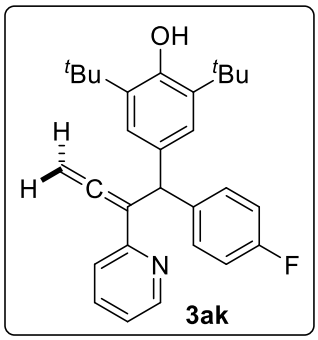
The title compound was prepared as described in procedure **D** using **1a** (0.200 mmol) and **2i** (0.300 mmol). Yield: 93.3 mg, 90%, brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.53 (d, *J* = 4.8 Hz, 1H), 7.56-7.52 (m, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 7.3 Hz, 2H), 7.38-7.35 (m, 2H), 7.32-7.31 (m, 1H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.07 (s, 2H), 7.03-7.01 (m, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.71 (s, 1H), 5.06-4.99 (m, 5H), 1.38 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.5, 157.1, 155.6, 152.1, 149.2, 137.4, 136.5, 136.1, 135.2, 133.7, 130.0, 128.6, 128.0, 127.7, 125.8, 122.5, 121.2, 114.4, 112.3, 80.5, 70.1, 49.0, 34.5, 30.5. **IR** (CH_2Cl_2, cm^{-1}): 3647, 2976, 1947, 1515, 1440, 1239, 1028. **HRMS** (ESI) m/z calcd for $C_{36}H_{39}NO_2$ $[M+H]^+$: 518.3054, found: 518.3052.

2,6-Di-*tert*-butyl-4-(1-(4-(dimethylamino)phenyl)-2-(pyridin-2-yl)buta-2,3-dien-1-yl)phenol (3aj)



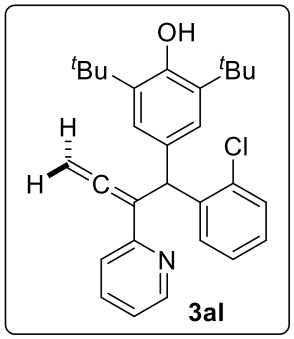
The title compound was prepared as described in procedure **D** using **1a** (0.200 mmol) and **2j** (0.300 mmol). Yield: 80.1 mg, 88%, brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.53 (d, *J* = 4.7 Hz, 1H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.10 (s, 2H), 7.00 (t, J = 6.0 Hz, 1H), 6.65 (d, *J* = 8.6 Hz, 2H), 5.64 (s, 1H), 5.07-4.99 (m, 3H), 2.89 (s, 6H), 1.38 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.6, 155.9, 152.0, 149.2, 149.0, 136.1, 135.0, 134.1, 132.3, 129.6, 125.8, 122.4, 121.1, 112.6, 112.4, 80.4, 49.0, 40.9, 34.4, 30.5. **IR** (CH_2Cl_2, cm^{-1}): 3643, 2968, 1949, 1526, 1440, 1163, 740. **HRMS** (ESI) m/z calcd for $C_{31}H_{38}N_2O$ $[M+H]^+$: 455.3062, found: 455.3058.

2,6-Di-*tert*-butyl-4-(1-(4-fluorophenyl)-2-(pyridin-2-yl)buta-2,3-dien-1-yl)phenol (3ak)



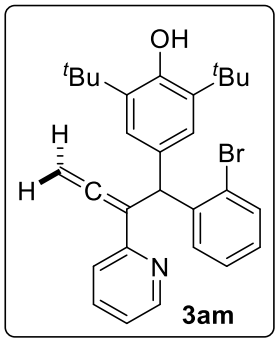
The title compound was prepared as described in procedure **D** using **1a** (0.200 mmol) and **2k** (0.300 mmol). Yield: 85.3 mg, 99%, yellowish brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.51 (d, *J* = 4.6 Hz, 1H), 7.57-7.54 (m, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.26-7.22 (m, 2H), 7.04-7.02 (m, 3H), 6.92 (t, *J* = 8.7 Hz, 2H), 5.77 (s, 1H), 5.06-5.00 (m, 3H), 1.37 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.4, 161.4 (d, *J* = 242.5 Hz, 1C), 155.3, 152.2, 149.2, 139.8 (d, *J* = 3.8 Hz, 1C), 136.1, 135.3, 133.3, 130.5 (d, *J* = 7.5 Hz, 1C), 125.8, 122.6, 121.3, 114.8 (d, *J* = 21.3 Hz, 1C), 112.1, 80.7, 48.9, 34.5, 30.5. **^{19}F NMR** (470 MHz, $CDCl_3$): *δ* (ppm) –117.6. **IR** (CH_2Cl_2, cm^{-1}): 3680, 2790, 1949, 1513, 1231, 850, 744. **HRMS** (ESI) m/z calcd for $C_{29}H_{32}FNO$ $[M+H]^+$: 430.2541, found: 430.2537.

2,6-Di-*tert*-butyl-4-(1-(2-chlorophenyl)-2-(pyridin-2-yl)buta-2,3-dien-1-yl)phenol (3al)



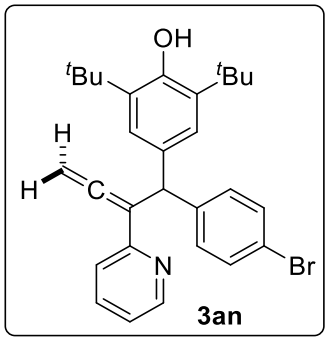
The title compound was prepared as described in procedure **D** using **1a** (0.200 mmol) and **2l** (0.300 mmol). Yield: 88.3 mg, 99%, brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.53 (d, *J* = 4.7 Hz, 1H), 7.55-7.52 (m, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.35-7.34 (m, 1H), 7.15-7.08 (m, 5H), 7.02-6.99 (m, 1H), 6.08 (s, 1H), 5.04 (s, 1H), 5.03-4.97 (m, 2H), 1.38 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.2, 155.2, 152.4, 149.4, 141.8, 136.1, 135.3, 134.5, 131.2, 130.2, 129.4, 127.4, 126.3, 126.2, 122.0, 121.2, 111.1, 80.5, 47.2, 34.5, 30.5. **IR** (CH_2Cl_2, cm^{-1}): 3620, 2969, 1948, 1439, 1159, 853, 742. **HRMS** (ESI) m/z calcd for $C_{29}H_{32}ClNO$ $[M+H]^+$: 446.2251, found: 446.2247

4-(1-(2-Bromophenyl)-2-(pyridin-2-yl)buta-2,3-dien-1-yl)-2,6-di-*tert*-butylphenol (3am)



The title compound was prepared as described in procedure **D** using **1a** (0.200 mmol) and **2m** (0.300 mmol). Yield: 96.5 mg, 98%, brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.53 (d, *J* = 4.7 Hz, 1H), 7.56-7.53 (m, 2H), 7.44 (d, *J* = 8.0 Hz, 1H),7.17-7.10 (m, 2H), 7.08 (s, 2H), 7.03-7.00 (m, 2H), 6.01 (s, 1H), 5.04 (s, 1H), 5.02-4.95 (m, 2H), 1.37 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.3, 155.3, 152.4, 149.4, 143.5, 136.1, 135.3, 132.8, 131.2, 130.5, 127.7, 127.0, 126.3, 125.6, 122.0, 121.2, 111.2, 80.5, 49.9, 34.5, 30.5. **IR** (CH_2Cl_2, cm^{-1}): 3628, 2970, 1949, 1596, 1440, 1160, 748. **HRMS** (ESI) m/z calcd for $C_{29}H_{32}BrNO$ $[M+H]^+$: 490.1740, found: 490.1744.

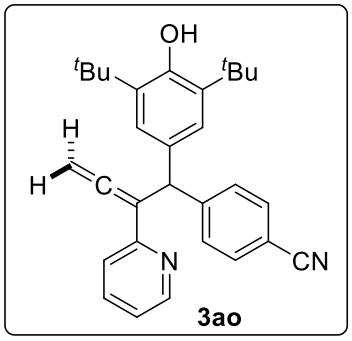
4-(1-(4-Bromophenyl)-2-(pyridin-2-yl)buta-2,3-dien-1-yl)-2,6-di-*tert*-butylphenol (3an)



3an

The title compound was prepared as described in procedure **D** using **1a** (0.200 mmol) and **2n** (0.300 mmol). Yield: 88.9 mg, 91%, brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.50 (d, *J* = 4.8 Hz, 1H), 7.57-7.53 (m, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.04-7.02 (m, 3H), 5.74 (s, 1H), 5.07-5.00 (m, 3H), 1.37 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.3, 155.2, 152.3, 149.2, 143.3, 136.2, 135.3, 132.8, 131.1, 130.9, 125.8, 122.6, 121.4, 119.8, 111.7, 80.9, 49.1, 34.5, 30.5. **IR** (CH_2Cl_2, cm^{-1}): 3618, 2972, 1951, 1441, 1241, 854, 787. **HRMS** (ESI) m/z calcd for $C_{29}H_{32}BrNO$ $[M+H]^+$: 490.1740, found: 490.1743.

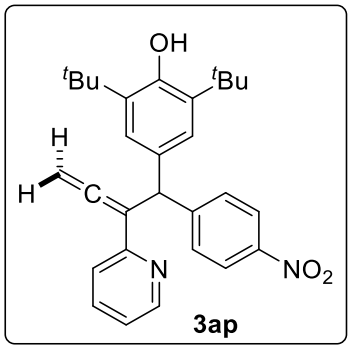
4-(1-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-2-(pyridin-2-yl)buta-2,3-dien-1-yl)benzonitrile (3ao)



3ao

The title compound was prepared as described in procedure **D** using **1a** (0.200 mmol) and **2o** (0.300 mmol). Yield: 70.4 mg, 81%, white solid. Mp: 182.8-186.3 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.49-8.48 (m, 1H), 7.59-7.56 (m, 1H), 7.53-7.52 (m, 3H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.06-7.03 (m, 1H), 7.02 (s, 2H), 5.88 (s, 1H), 5.08 (s, 1 H), 5.06-5.05 (m, 2H), 1.37 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.3, 154.7, 152.6, 150.2, 149.1, 136.3, 135.6, 132.0, 129.8, 125.9, 122.6, 121.5, 119.4, 111.2, 109.7, 81.2, 49.6, 34.5, 30.5. **IR** (CH_2Cl_2, cm^{-1}): 3631, 2970, 2239, 1950, 1594, 1440, 1240, 858, 745. **HRMS** (ESI) m/z calcd for $C_{30}H_{32}N_2O$ $[M+H]^+$: 437.2587, found: 437.2580.

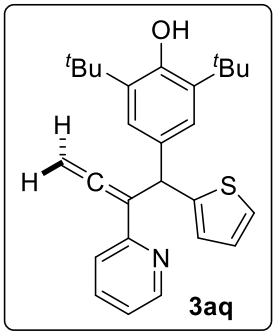
2,6-Di-*tert*-butyl-4-(1-(4-nitrophenyl)-2-(pyridin-2-yl)buta-2,3-dien-1-yl)phenol (3ap)



3ap

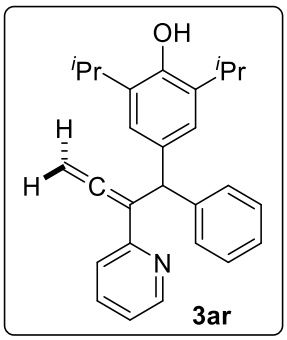
The title compound was prepared as described in procedure **D** using **1a** (0.200 mmol) and **2p** (0.300 mmol). Yield: 42.8 mg, 47%, brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.48 (d, *J* = 4.8 Hz, 1H), 8.09 (d, *J* = 8.7 Hz, 2H), 7.59-7.52 (m, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.05-7.03(m, 3H), 5.93 (s, 1H), 5.08-5.06 (m, 3H), 1.36 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.2, 154.6, 152.6, 152.4, 149.1, 146.4, 136.2, 135.7, 131.8, 129.8, 125.9, 123.4, 122.6, 121.6, 111.2, 81.3, 49.4, 34.5, 30.4. **IR** (CH_2Cl_2, cm^{-1}): 2974, 1947, 1599, 1526, 1350, 860, 740. **HRMS** (ESI) m/z calcd for $C_{29}H_{32}N_2O_3$ $[M+H]^+$: 457.2491, found: 457.2489.

2,6-Di-*tert*-butyl-4-(2-(pyridin-2-yl)-1-(thiophen-2-yl)buta-2,3-dien-1-yl)phenol (3aq)



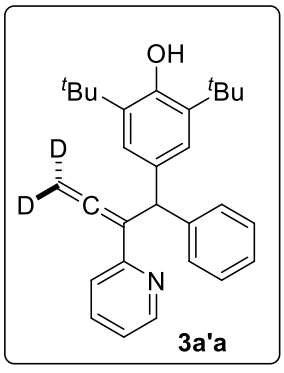
The title compound was prepared as described in procedure **D** using **1a** (0.200 mmol) and **2q** (0.300 mmol). Yield: 71.4 mg, 85%, brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.55 (d, J = 4.8 Hz, 1H), 7.57-7.54 (m, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.22 (s, 2H), 7.11 (d, J = 4.9 Hz, 1H), 7.05-7.03 (m, 1H), 6.88-6.87 (m, 1H), 6.82-6.81 (m, 1H), 6.04 (s, 1H), 5.20-5.11 (m, 2H), 5.05 (s, 1H), 1.40 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.0, 154.9, 152.5, 149.1, 149.0, 136.1, 135.3, 133.4, 126.3, 125.6, 125.5, 123.7, 122.6, 121.4, 112.7, 81.5, 44.8, 34.5, 30.5. **IR** (CH_2Cl_2, cm^{-1}): 3612, 2971, 1948, 1439, 1238, 856, 699. **HRMS** (ESI) m/z calcd for $C_{27}H_{31}NOS$ $[M+H]^+$: 418.2199, found: 418.2186.

2,6-Diisopropyl-4-(1-phenyl-2-(pyridin-2-yl)buta-2,3-dien-1-yl)phenol (3ar)



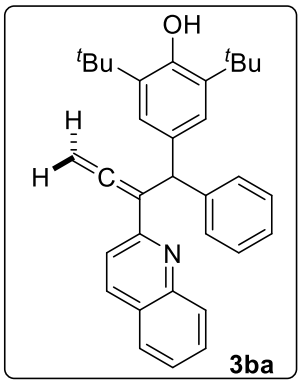
The title compound was prepared as described in procedure **D** using **1a** (0.200 mmol) and **2r** (0.300 mmol). Yield: 57.2 mg, 75%, brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.52 (d, J = 4.8 Hz, 1H), 7.57-7.53 (m, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.29-7.23 (m, 4H), 7.17-7.14 (m, 1H), 7.03-7.01 (m, 1H), 6.96 (s, 2H), 5.79 (s, 1H), 5.06-5.00 (m, 2H), 4.69 (s, 1H), 3.14-3.06 (m, 2H), 1.19 (t, J = 7.4 Hz, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.4, 155.5, 149.1, 148.4, 143.8, 136.3, 134.7, 133.1, 129.1, 128.1, 126.1, 124.5, 122.5, 121.3, 111.9, 80.7, 49.8, 27.4, 22.9, 22.8. **IR** (CH_2Cl_2, cm^{-1}): 2975, 1948, 1597, 1474, 1206, 854, 705. **HRMS** (ESI) m/z calcd for $C_{27}H_{29}NO$ $[M+H]^+$: 384.2327, found: 384.2323.

2,6-Di-*tert*-butyl-4-(1-phenyl-2-(pyridin-2-yl)buta-2,3-dien-1-yl-4,4-d2)phenol (3a'a)



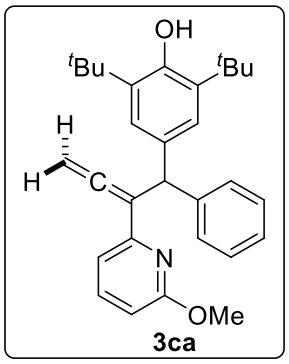
The title compound was prepared as described in procedure **D** using **1a'** (0.200 mmol) and **2a** (0.300 mmol). Yield: 80.8 mg, 98%, brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.53 (d, J = 4.5 Hz, 1H), 7.56-7.50 (m, 2H), 7.32 (d, J = 7.4 Hz, 2H), 7.27-7.24 (m, 2H), 7.18-7.15 (m, 1H), 7.10 (s, 2H), 7.04-7.01 (m, 1H), 5.80 (s, 1H), 5.04 (s, 1H), 1.40 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.61, 212.58, 212.54, 155.5, 152.2, 149.2, 144.1, 136.1, 135.2, 133.4, 129.1, 128.0, 126.0, 125.9, 122.5, 121.3, 112.21, 112.13, 112.08, 80.6, 80.4, 80.2, 49.7, 34.5, 30.5. **IR** (CH_2Cl_2, cm^{-1}): 2972, 1943, 1746, 1441, 1242, 704. **HRMS** (ESI) m/z calcd for $C_{29}H_{31}D_2NO$ $[M+H]^+$: 414.2760 found: 414.2750.

2,6-Di-*tert*-butyl-4-(1-phenyl-2-(quinolin-2-yl)buta-2,3-dien-1-yl)phenol (3ba)



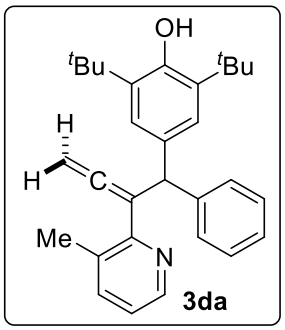
The title compound was prepared as described in procedure **D** using **1b** (0.200 mmol) and **2a** (0.300 mmol). Yield: 86.6 mg, 94%, brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.04 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 8.7 Hz, 1H), 7.74-7.71 (m, 2H), 7.67-7.64 (m, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.29-7.28 (m, 2H), 7.22 (s, 2H), 7.18-7.15 (m, 1H), 6.19 (s, 1H), 5.22-5.16 (m, 2H), 5.04 (s, 1H), 1.42 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 213.8, 154.9, 152.2, 148.0, 144.5, 135.5, 135.2, 133.7, 129.8, 129.2, 129.1, 128.0, 127.4, 126.9, 126.1, 126.0, 125.9, 120.8, 113.2, 81.3, 49.0, 34.5, 30.5. **IR** (CH_2Cl_2, cm^{-1}): 3659, 2972, 1944, 1742, 1606, 1439, 1238, 837, 703. **HRMS** (ESI) m/z calcd for $C_{33}H_{35}NO$ $[M+H]^+$: 462.2797, found: 462.2797.

2,6-Di-*tert*-butyl-4-(2-(6-methoxypyridin-2-yl)-1-phenylbuta-2,3-dien-1-yl)phenol (3ca)



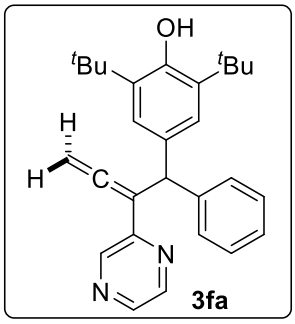
The title compound was prepared as described in procedure **D** using **1c** (0.1359 mmol) and **2a** (0.2039 mmol). Yield: 41.3 mg, 69%, yellow gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.46-7.43 (m, 1H), 7.29-7.23 (m, 4H), 7.16-7.13 (m, 2H), 7.07 (s, 2H), 6.46 (d, *J* = 8.1 Hz, 1H), 5.74 (s, 1H), 5.05-4.99 (m, 3H), 3.80 (s, 3H), 1.38 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.3, 163.4, 152.9, 152.1, 144.4, 138.5, 135.2, 133.6, 129.0, 128.0, 125.9, 125.8, 115.1, 111.9, 107.7, 80.5, 53.3, 50.1, 34.4, 30.5. **IR** (CH_2Cl_2, cm^{-1}): 2983, 2959, 1949, 1752, 1588, 1469, 1242, 811, 706. **HRMS** (ESI) m/z calcd for $C_{30}H_{35}NO_2$ $[M+H]^+$: 442.2741, found: 442.2737.

2,6-Di-*tert*-butyl-4-(2-(3-methylpyridin-2-yl)-1-phenylbuta-2,3-dien-1-yl)phenol (3da)



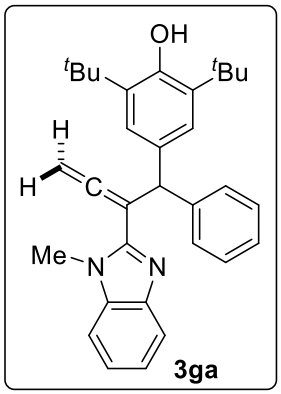
The title compound was prepared as described in procedure **D** using **1d** (0.200 mmol) and **2a** (0.300 mmol). Yield: 41.1 mg, 48%, yellow solid. Mp: 161.1 – 164.3 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.43 (d, *J* = 4.3 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 2H), 7.26-7.23 (m, 2H), 7.15-7.12 (m, 1H), 7.10 (s, 2H), 6.98 (dd, *J* = 7.6, 4.7 Hz, 1H), 5.75 (s, 1H), 5.01 (s, 1H), 4.80-4.75 (m, 2H), 2.37 (s, 3H), 1.38 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 209.7, 154.6, 152.2, 146.8, 143.8, 138.6, 135.2, 132.7, 132.4, 129.2, 127.9, 126.0, 125.9, 121.6, 109.5, 79.1, 53.1, 34.5, 30.5, 20.4. **IR** (CH_2Cl_2, cm^{-1}): 2970, 2935, 2884, 1956, 1588, 1442, 1238, 1161, 848, 704. **HRMS** (ESI) m/z calcd for $C_{30}H_{35}NO$ $[M+H]^+$: 426.2791, found: 426.2789.

2,6-Di-*tert*-butyl-4-(1-phenyl-2-(pyrazin-2-yl)buta-2,3-dien-1-yl)phenol (3fa)



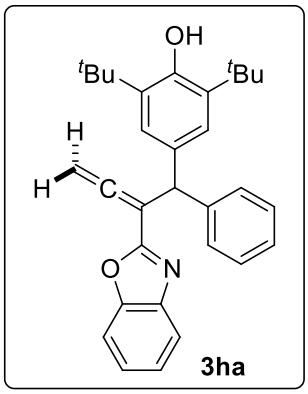
The title compound was prepared as described in procedure **D** using **1f** (0.200 mmol) and **2a** (0.300 mmol). Yield: 56.6 mg, 69%, yellow gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.78 (s, 1H), 8.44-8.43 (m, 1H), 8.26 (d, *J* = 2.6 Hz, 1H), 7.28-7.23 (m, 4H), 7.17-7.14 (m, 1H), 7.05 (s, 2H), 5.70 (s, 1H), 5.16-5.09 (m, 2H), 5.04 (s, 1H), 1.37 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.3, 152.3, 151.5, 144.6, 143.6, 143.3, 141.4, 135.4, 132.7, 129.0, 128.2, 126.3, 125.8, 109.7, 81.4, 49.4, 34.5, 30.5. **IR** (CH_2Cl_2, cm^{-1}): 3665, 2973, 1945, 1736, 1441, 1241, 855, 704. **HRMS** (ESI) m/z calcd for $C_{28}H_{32}N_2O$ $[M+H]^+$: 413.2587, found: 413.2583.

2,6-Di-*tert*-butyl-4-(2-(1-methyl-1H-benzo[d]imidazol-2-yl)-1-phenylbuta-2,3-dien-1-yl)phenol (3ga)



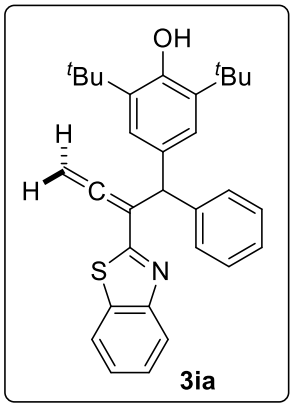
The title compound was prepared as described in procedure **D** using **1g** (0.200 mmol) and **2a** (0.300 mmol). Yield: 85.5 mg, 92%, brown solid. Mp: 189.7 – 194.6 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.76-7.74 (m, 1H), 7.31 (d, *J* = 7.5 Hz, 2H), 7.28-7.20 (m, 5H), 7.17-7.12 (m, 3H), 5.85 (s, 1H), 5.05-5.02 (m, 3H), 3.79 (s, 3H), 1.37 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 211.3, 152.5, 149.8, 143.1, 143.0, 136.3, 135.4, 132.0, 129.1, 128.1, 126.4, 125.8, 122.6, 122.1, 119.7, 109.3, 102.9, 81.1, 52.7, 34.5, 31.5, 30.5. **IR** (CH_2Cl_2, cm^{-1}): 2970, 2934, 1952, 1737, 1443, 1240, 744. **HRMS** (ESI) m/z calcd for $C_{32}H_{36}N_2O$ $[M+H]^+$: 465.2900, found: 465.2899.

4-(2-(Benzo[d]oxazol-2-yl)-1-phenylbuta-2,3-dien-1-yl)-2,6-di-*tert*-butylphenol (3ha)



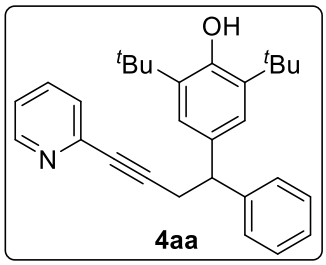
The title compound was prepared as described in procedure **D** using **1h** (0.200 mmol) and **2a** (0.300 mmol). Yield: 61.5 mg, 68%, brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.68-7.66 (m, 1H), 7.48-7.44 (m, 1H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.30-7.25 (m, 3H), 7.21-7.18 (m, 1H), 7.12(s, 2H), 5.64 (s, 1H), 5.33-5.26 (m, 2H), 5.08 (s, 1H), 1.39 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 213.9, 161.6, 152.6, 150.9, 142.8, 142.3, 135.5, 132.2, 128.8, 128.3, 126.5, 125.7, 124.9, 124.3, 120.0, 110.4, 102.2, 82.2, 50.3, 34.5, 30.5. **IR** (CH_2Cl_2, cm^{-1}): 2971, 2934, 1964, 1620, 1442, 1246, 1161, 749. **HRMS** (ESI) m/z calcd for $C_{31}H_{33}NO_2$ $[M + H]^+$: 452.2584, found: 452.2585.

4-(2-(Benzo[d]thiazol-2-yl)-1-phenylbuta-2,3-dien-1-yl)-2,6-di-*tert*-butylphenol (3ia)



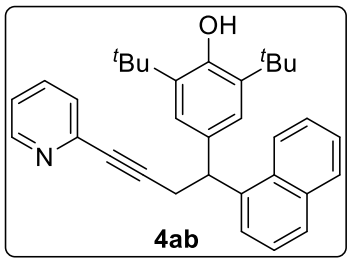
The title compound was prepared as described in procedure **D** using **1i** (0.200 mmol) and **2a** (0.300 mmol). Yield: 56.1 mg, 60%, brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.92 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.39-7.35 (m, 1H), 7.32 (d, *J* = 7.4 Hz, 2H), 7.29-7.24 (m, 3H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.11 (s, 2H), 5.75 (s, 1H), 5.26-5.19 (m, 2H), 5.05 (s, 1H), 1.38 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 213.5, 166.8, 154.1, 152.5, 143.2, 135.6, 135.4, 132.5, 128.9, 128.2, 126.4, 125.8, 125.0, 123.2, 121.4, 109.1, 82.4, 50.8, 34.5, 30.5. **IR** (CH_2Cl_2, cm^{-1}): 3624, 2971, 1951, 1742, 1441, 1240, 735. **HRMS** (ESI) m/z calcd for $C_{31}H_{33}NOS$ $[M+H]^+$: 468.2356, found: 468.2347.

2,6-Di-*tert*-butyl-4-(1-phenyl-4-(pyridin-2-yl)but-3-yn-1-yl)phenol (4aa)



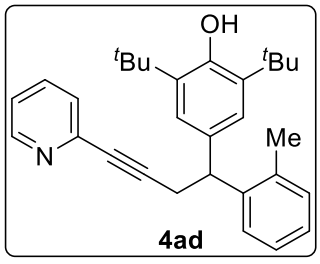
The title compound was prepared as described in the procedure **E** using **1a** (0.200 mmol). Yield: 47.1 mg, 57%, pale yellow solid. **Mp:** 120.2-122.4 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.50 (d, *J* = 4.5 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.34-7.30 (m, 4H), 7.23-7.20 (m. 1H), 7.17-7.12 (m, 2H), 7.08 (s, 2H), 5.09 (s, 1H), 4.28 (t, *J* = 7.5 Hz, 1H), 3.17-3.08 (m, 2H), 1.40 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 152.4, 149.8, 143.93, 143.87, 136.0, 135.7, 134.2, 128.4, 128.2, 127.0, 126.5, 124.6, 122.4, 90.0, 82.0, 50.0, 34.5, 30.4, 27.1. **IR** (CH_2Cl_2, cm^{-1}): 3661, 3646, 2968, 2926, 2240, 1592, 1472, 1440, 1240, 1160, 782, 705. **HRMS** (ESI) m/z calcd for $C_{29}H_{33}NO$ $[M+H]^+$: 412.2635, found: 412.2632.

2,6-Di-*tert*-butyl-4-(1-(naphthalen-2-yl)-4-(pyridin-2-yl)but-3-yn-1-yl)phenol (4ab)



The title compound was prepared as described in the procedure **E** using **1b** (0.200 mmol). Yield: 46.3 mg, 50%, pale brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm):8.49 (d, *J* = 4.5 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 7.4 Hz), 7.75 (d, *J* = 8.4 Hz, 1H), 7.53-7.43 (m, 5H), 7.15-7.10 (m, 4H), 5.11 (t, *J* = 7.4 Hz, 1H), 5.06 (s, 1H), 3.31-3.20 (m, 2H), 1.37 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 152.4, 149.8, 143.9, 139.5, 136.0, 135.7, 134.1, 133.9, 132.0, 128.9, 127.3, 127.0, 126.0, 125.5, 125.4, 124.8, 124.6, 124.0, 122.4, 90.0, 82.0, 45.4, 34.5, 30.4, 27.3. **IR** (CH_2Cl_2, cm^{-1}): 3656, 3641, 2971, 2937, 2885, 2239, 1591, 1472, 1437, 1240, 1157, 780. **HRMS** (ESI) m/z calcd for $C_{33}H_{35}NO$ $[M+H]^+$: 462.2791, found: 462.2793.

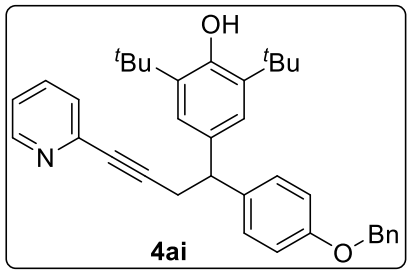
2,6-Di-*tert*-butyl-4-(4-(pyridin-2-yl)-1-(o-tolyl)but-3-yn-1-yl)phenol (4ad)



The title compound was prepared as described in the procedure **E** using **1a** (0.200 mmol) and **2d** (0.400 mmol). Yield: 39.7 mg, 47%, brown oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.50 (d, *J* = 4.7 Hz, 1H), 7.55-7.52 (m, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.25-7.12 (m, 5H), 7.04 (s, 2H), 5.05 (s, 1H), 4.46 (t, *J* = 7.6 Hz, 1H), 3.11-3.09 (m, 2H), 2.30 (s, 3H), 1.38 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 152.3, 149.8, 143.9, 141.9, 136.4, 136.0, 135.6, 133.7, 130.6, 127.0, 126.6, 126.3, 126.0, 124.7, 122.4, 90.1, 81.7, 45.9, 34.4, 30.4, 27.0, 20.1. **IR**

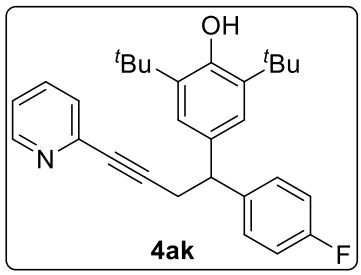
(CH_2Cl_2, cm^{-1}): 3656, 3068, 2968, 2938, 2240, 1592, 1471, 1438, 1240, 1159, 781. **HRMS** (ESI) m/z calcd for $C_{30}H_{35}NO$ $[M+H]^+$: 426.2791, found: 426.2780.

4-(1-(4-(Benzyloxy)phenyl)-4-(pyridin-2-yl)but-3-yn-1-yl)-2,6-di-*tert*-butylphenol (4ai)



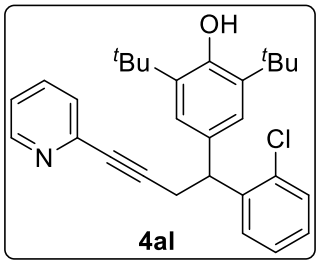
The title compound was prepared as described in the procedure **E** using **1a** (0.200 mmol) and **2i** (0.400 mmol). Yield: 43.0 mg, 42%, pale brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.50 (d, *J* = 4.6 Hz, 1H), 7.55-7.51 (m, 1H), 7.42 (d, *J* = 7.4 Hz, 2H), 7.38-7.35 (m, 2H), 7.32-7.29 (m, 1H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.17-7.12 (m, 2H), 7.05 (s, 2H), 6.93 (d, *J* = 8.5 Hz, 2H) 5.06 (s, 1H), 5.04 (s, 2H), 4.22 (t, *J* = 7.4 Hz, 1H), 3.07 (d, *J* = 7.5 Hz, 2H), 1.39 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 157.4, 152.4, 149.8, 144.0, 137.3, 136.4, 136.0, 135.7, 134.6, 129.1, 128.7, 128.0, 127.6, 127.0, 124.5, 122.4, 114.8, 90.1, 82.0, 70.2, 49.2, 34.5, 30.5, 27.3. **IR** (CH_2Cl_2, cm^{-1}): 3650, 2968, 2933, 2885, 2239, 1617, 1591, 1517, 1470, 1439, 1244, 1184, 781, 742. **HRMS** (ESI) m/z calcd for $C_{36}H_{39}NO_2$ $[M+H]^+$: 518.3054, found: 518.3057.

2,6-Di-*tert*-butyl-4-(1-(4-fluorophenyl)-4-(pyridin-2-yl)but-3-yn-1-yl)phenol (4ak)



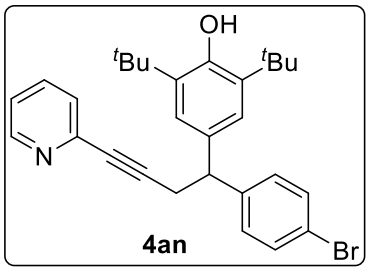
The title compound was prepared as described in the procedure **E** using **1a** (0.200 mmol) and **2k** (0.400 mmol). Yield: 39.2 mg, 46%, colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.51 (d, *J* = 4.6 Hz, 1H), 7.57-7.54 (m, 1H), 7.30-7.28 (m, 2H), 7.18-7.13 (m, 2H), 7.04-6.99 (m, 4H), 5.11 (s, 1H), 4.27 (t, *J* = 7.5 Hz, 1H), 3.09 (d, *J* = 7.5 Hz, 2H), 1.40 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 161.6 (d, *J* = 242.5 Hz, 1C), 152.5, 149.9, 143.8, 139.5 (d, *J* = 2.5 Hz, 1C), 136.0, 135.8, 134.1, 129.7 (d, *J* = 7.5 Hz, 1C), 127.0, 124.5, 122.5, 115.2 (d, *J* = 21.3 Hz, 1C), 89.5, 82.2, 49.2, 34.5, 30.4, 27.2. **^{19}F NMR** (470 MHz, $CDCl_3$) δ (ppm): –116.9. **IR** (CH_2Cl_2, cm^{-1}): 3653, 2969, 2933, 2884, 2239, 1592, 1516, 1472, 1232, 1161, 780. **HRMS** (ESI) m/z calcd for $C_{29}H_{32}FNO$ $[M+H]^+$: 430.2541, found: 430.2530.

2,6-Di-*tert*-butyl-4-(1-(2-chlorophenyl)-4-(pyridin-2-yl)but-3-yn-1-yl)phenol (4al)



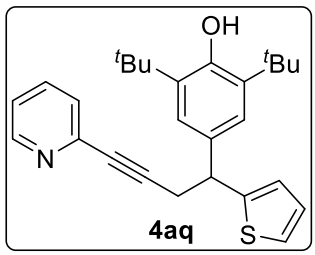
The title compound was prepared as described in the procedure **E** using **1a** (0.200 mmol) and **2l** (0.400 mmol). Yield: 58.4 mg, 66%, pale brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.49 (d, *J* = 4.8 Hz, 1H), 7.55-7.52 (m, 1H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.26-7.23 (m, 1H), 7.17-7.12 (m, 5H), 5.09 (s, 1H), 4.82 (t, *J* = 7.5 Hz, 1H), 3.18-3.09 (m, 2H), 1.40 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 152.5, 149.8, 143.8, 141.4, 136.0, 135.7, 134.3, 132.7, 129.8, 128.9, 127.7, 127.1, 126.9, 124.8, 122.4, 89.3, 82.0, 45.7, 34.5, 30.4, 26.0. **IR** (CH_2Cl_2, cm^{-1}): 3657, 3085, 2968, 2885, 2244, 1593, 1474, 1440, 1241, 782. **HRMS** (ESI) m/z calcd for $C_{29}H_{32}ClNO$ $[M+H]^+$: 446.2245, found: 446.2238.

4-(1-(4-Bromophenyl)-4-(pyridin-2-yl)but-3-yn-1-yl)-2,6-di-*tert*-butylphenol (4an)



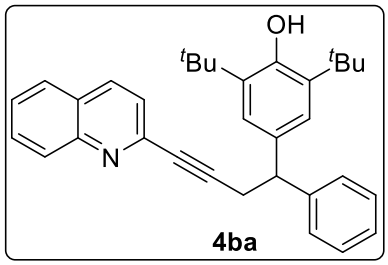
The title compound was prepared as described in the procedure E using **1a** (0.200 mmol) and **2n** (0.400 mmol). Yield: 55.4 mg, 57%, pale brown gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.51 (d, J = 4.5 Hz, 1H), 7.55 (t, J = 7.7 Hz, 1H), 7.43 (d, J = 8.2 Hz, 2H), 7.21-7.14 (m, 4H), 7.03 (s, 2H), 5.11 (s, 1H), 4.23 (t, J = 7.4 Hz, 1H), 3.08 (d, J = 7.5 Hz, 2H), 1.40 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 152.6, 149.9, 143.7, 142.9, 136.1, 135.9, 133.7, 131.5, 130.0, 127.0, 124.5, 122.5, 120.3, 89.3, 82.2, 49.4, 34.5, 30.4, 26.9. **IR** (CH_2Cl_2, cm-1): 3649, 3489, 3258, 3025, 2976, 2940, 2871, 2238, 1741, 1594, 1473, 1442, 1243, 783. **HRMS** (ESI) m/z calcd for $C_{29}H_{32}BrNO$ $[M+H]^+$: 490.1740, found: 490.1743.

2,6-Di-*tert*-butyl-4-(4-(pyridin-2-yl)-1-(thiophen-2-yl)but-3-yn-1-yl)phenol (4aq)



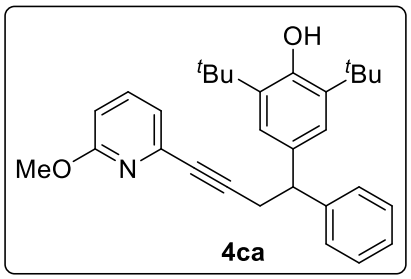
The title compound was prepared as described in the procedure **E** using **1a** (0.200 mmol) and **2q** (0.400 mmol). Yield: 27.2 mg, 33%, brown oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.52 (d, *J* = 4.7 Hz, 1H), 7.62-7.55 (m, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.18-7.14 (m. 4H), 6.97-6.94 (m, 2H), 5.11 (s, 1H), 4.48 (t, *J* = 7.2 Hz, 1H), 3.18-3.06 (m, 2H), 1.41 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 152.8, 149.9, 148.0, 143.9, 136.1, 135.8, 133.9, 127.1, 126.6, 124.7, 124.4, 124.0, 122.5, 89.4, 82.3, 46.0, 34.5, 30.4, 29.0. **IR** (CH_2Cl_2, cm^{-1}): 3650, 3322, 3083, 2972, 2882, 2238, 1593, 1472, 1441, 1242, 782. **HRMS** (ESI) m/z calcd for $C_{27}H_{31}NOS$ $[M+H]^+$: 418.2199, found: 418.2190.

2,6-Di-*tert*-butyl-4-(1-phenyl-4-(quinolin-2-yl)but-3-yn-1-yl)phenol (4ba)



The title compound was prepared as described in the procedure **E** using **1b** (0.200 mmol) and **2a** (0.400 mmol). Yield: 42.3 mg, 46%, colourless gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.05-8.00 (m, 2H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.70-7.67 (m, 1H), 7.52-7.49 (m, 1H), 7.36-7.31 (m, 4H), 7.24-7.21 (m, 2H), 7.10 (s, 2H), 5.08 (s, 1H), 4.33 (t, *J* = 7.5 Hz, 1H), 3.22-3.13 (m, 2H), 1.40 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 152.5, 148.2, 144.1, 143.9, 136.0, 135.7, 134.2, 130.0, 129.3, 128.5, 128.2, 127.5, 127.1, 126.9, 126.5, 124.7, 124.4, 90.9, 82.8, 50.0, 34.5, 30.5, 27.3. **IR** (CH_2Cl_2, cm^{-1}) 3656, 2979, 2942, 2230, 1507, 1244, 1159, 836, 790, 756, 738. **HRMS** (ESI) m/z calcd for $C_{33}H_{35}NO$ $[M+H]^+$: 462.2791, found: 462.2791.

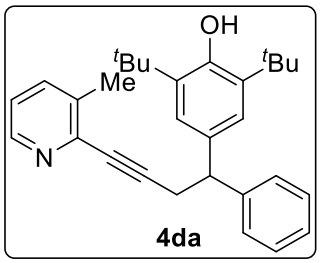
2,6-Di-*tert*-butyl-4-(4-(6-methoxypyridin-2-yl)-1-phenylbut-3-yn-1-yl)phenol (4ca)



The title compound was prepared as described in the procedure **E** using **1c** (0.1359 mmol) and **2a** (0.2718 mmol). Yield: 34.2 mg, 57%, pale yellow gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.43-7.40 (m, 1H), 7.34-7.31 (m, 4H), 7.24-7.20 (m, 1H), 7.09 (s, 2H), 6.78 (d, *J* = 7.2 Hz, 1H), 6.63 (d, *J* = 8.1 Hz, 1H), 5.08 (s, 1H), 4.27 (t, *J* = 7.5 Hz, 1H), 3.92 (s, 3H), 3.16-3.07 (m, 2H), 1.40 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 163.8, 152.4, 144.0,

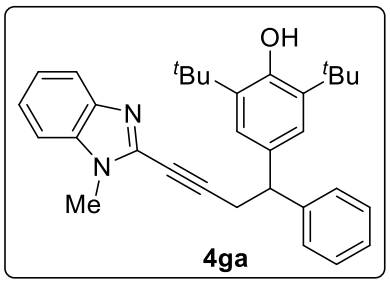
140.8, 138.4, 135.6, 134.2, 128.4, 128.2, 126.5, 124.7, 120.5, 110.6, 89.3, 82.2, 53.6, 50.0, 34.5, 30.4, 27.3. **IR** (CH_2Cl_2, cm^{-1}): 2968, 2934, 2240, 1579, 1438, 1247, 1157, 806, 703. **HRMS** (ESI) m/z calcd for $C_{30}H_{35}NO_2$ $[M+H]^+$: 442.2741, found: 442.2740.

2,6-Di-*tert*-butyl-4-(4-(3-methylpyridin-2-yl)-1-phenylbut-3-yn-1-yl)phenol (4da)



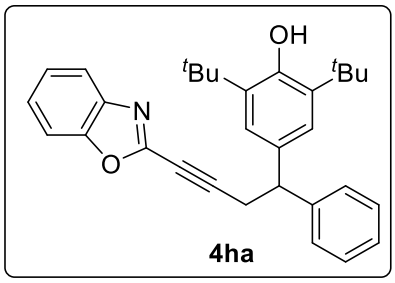
The title compound was prepared as described in the procedure **E** using **1d** (0.200 mmol) and **2a** (0.400 mmol). Yield: 52.4 mg, 62%, pale yellow gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.32 (d, *J* = 4.0 Hz, 1H), 7.38-7.29 (m, 5H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.09 (s, 2H), 7.05-7.02 (m, 1H), 7.36-7.31 (m, 4H), 7.24-7.21 (m, 2H), 7.10 (s, 2H), 5.08 (s, 1H), 4.28 (t, *J* = 7.8 Hz, 1H), 3.18 (d, *J* = 7.8 Hz, 2H), 1.96 (s, 3H), 1.40 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 152.5, 147.1, 144.0, 143.6, 136.8, 135.9, 135.8, 134.1, 128.5, 128.1, 126.5, 124.5, 122.3, 93.6, 80.5, 50.5, 34.5, 30.4, 27.2, 19.1. **IR** (CH_2Cl_2, cm^{-1}): 3661, 3644, 3223, 2972, 2930, 2241, 1591, 1441, 1122, 704. **HRMS** (ESI) m/z calcd for $C_{30}H_{35}NO$ $[M+H]^+$: 426.2791, found: 426.2783.

2,6-Di-*tert*-butyl-4-(4-(1-methyl-1H-benzo[d]imidazol-2-yl)-1-phenylbut-3-yn-1-yl)phenol (4ga)



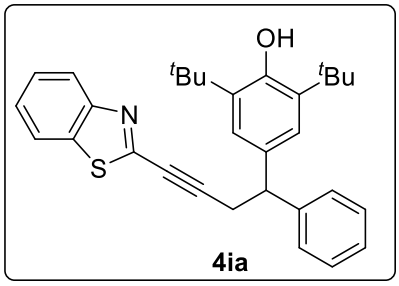
The title compound was prepared as described in the procedure **E** using **1g** (0.200 mmol) and **2a** (0.400 mmol). Yield: 21.4 mg, 23%, pale yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.70-7.68 (m, 1H), 7.35-7.31 (m, 4H), 7.28-7.19 (m, 4H), 7.09 (s, 2H), 5.13 (s, 1H), 4.30 (t, *J* = 7.9 Hz, 1H), 3.33 (s, 3H), 3.23-3.22 (m, 2H), 1.40 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm):152.6, 143.5, 142.7, 137.9, 136.0, 134.8, 133.7, 128.7, 126.7, 123.5, 122.7, 120.1, 109.3, 96.1, 72.0, 50.1, 34.5, 30.4, 30.1, 27.1. **IR** (CH_2Cl_2, cm^{-1}): 2970, 2937, 2256, 1745, 1442, 1244, 745. **HRMS** (ESI) m/z calcd for $C_{32}H_{36}N_2O$ $[M + H]^+$: 465.2900, found:465.2898.

4-(4-(Denzo[d]oxazol-2-yl)-1-phenylbut-3-yn-1-yl)-2,6-di-*tert*-butylphenol (4ha)



The title compound was prepared as described in the procedure **E** using **1h** (0.200 mmol) and **2a** (0.400 mmol). Yield: 17.4 mg, 19%, pale yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.69 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.37-7.32 (m, 6H), 7.25-7.21 (m, 1H), 7.08 (s, 2H), 5.11(s, 1H), 4.32 (t, *J* = 7.4 Hz, 1H), 3.24-3.15 (m, 2H), 1.41 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 152.7, 150.2, 147.7, 143.2, 141.0, 135.9, 133.6, 128.6, 128.0, 126.8, 126.1, 124.9, 124.6, 120.4, 110.6, 95.1, 71.1, 49.5, 34.5, 30.4, 27.1. **IR** (CH_2Cl_2, cm^{-1}): 2968, 2938, 2254, 1610, 1553, 1441, 1244, 749, 704. **HRMS** (ESI) m/z calcd for $C_{31}H_{33}NO_2$ $[M+H]^+$: 452.2584, found: 452.2585.

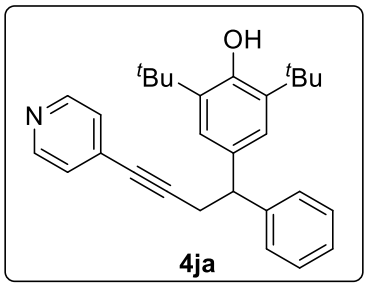
4-(4-(Benzo[d]thiazol-2-yl)-1-phenylbut-3-yn-1-yl)-2,6-di-*tert*-butylphenol (4ia)



4ia

The title compound was prepared as described in the procedure **E** using **1i** (0.200 mmol) and **2a** (0.400 mmol). Yield: 29.2 mg, 31%, pale yellow solid. Mp: 132.6-138.8℃. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.99 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.49-7.46 (m, 1H), 7.42-7.39 (m, 1H), 7.32 (s, 4H), 7.26-7.23 (m, 1H), 7.08 (s, 2H), 5.11 (s, 1H), 4.31 (t, *J* = 7.2 Hz, 1H), 3.24-3.15 (m, 2H), 1.41 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 152.9, 152.6, 149.2, 143.5, 135.8, 135.3, 133.8, 128.6, 128.1, 126.7, 126.6, 126.1, 124.6, 123.6, 121.3, 97.6, 76.3, 49.7, 34.5, 30.5, 27.5. **IR** (CH_2Cl_2, cm^{-1}):2971, 2886, 2242, 1608, 1441, 1240, 1160, 763, 704. **HRMS** (ESI) m/z calcd for $C_{31}H_{33}NOS$ $[M+H]^+$: 468.2356, found: 468.2354.

2,6-di-tert-butyl-4-(1-phenyl-4-(pyridin-4-yl)but-3-yn-1-yl)phenol (4ja)



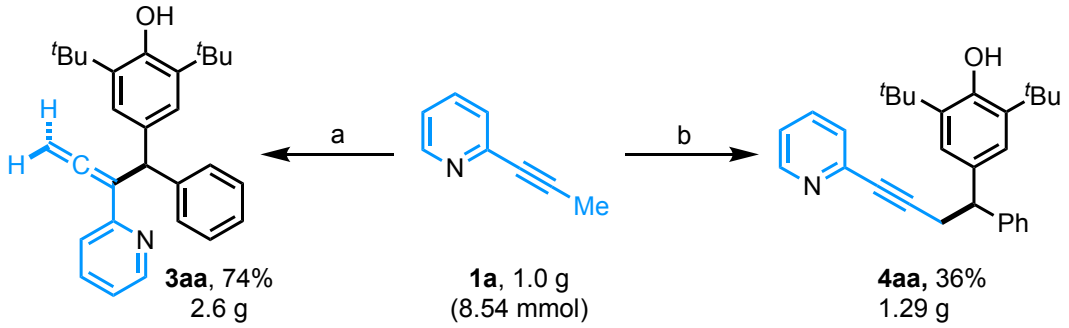
4ja

The title compound was prepared as described in the procedure **E** using **1j** (0.200 mmol) and **2a** (0.400 mmol). Yield: 36.1 mg, 44%, off-white gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.47 (d, *J* = 5.1 Hz, 2H), 7.34-7.30 (m, 4H), 7.24-7.21 (m, 1H), 7.09-7.07 (m, 4H), 5.11 (s, 1H), 4.23 (t, *J* = 7.5 Hz, 1H), 3.14-3.05 (m, 2H), 1.40 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 152.5, 149.6, 143.8, 135.8, 134.0, 132.3, 128.5, 128.2, 126.6, 125.8, 124.6, 94.8, 80.3, 50.0, 34.5, 30.4, 27.2. **IR** (CH_2Cl_2, cm^{-1}): 2931, 2239, 1752, 1603, 1445, 1242, 827. **HRMS** (ESI) m/z calcd for $C_{29}H_{33}NO$ $[M+H]^+$: 412.2635, found: 412.2642.

F. **Typical Experimental Procedure for a Gram Scale Allenylation Reaction**

To a flame-dried round bottom flask charged with a magnetic stir bar, *para*-quinone methide **2a** (12.8039 mmol) and KO^{t}Bu (12.8039 mmol) were added under the argon atmosphere. To the reaction mixture, alkynyl azaarene **1a** (8.5360 mmol) in toluene (0.1 M) was added, and then, stirred at room temperature for 1 h. The reaction progress was monitored by TLC analysis. After completion of the reaction, the reaction mixture was quenched with water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude reaction mixture was purified by

A. Gram-scale synthesis



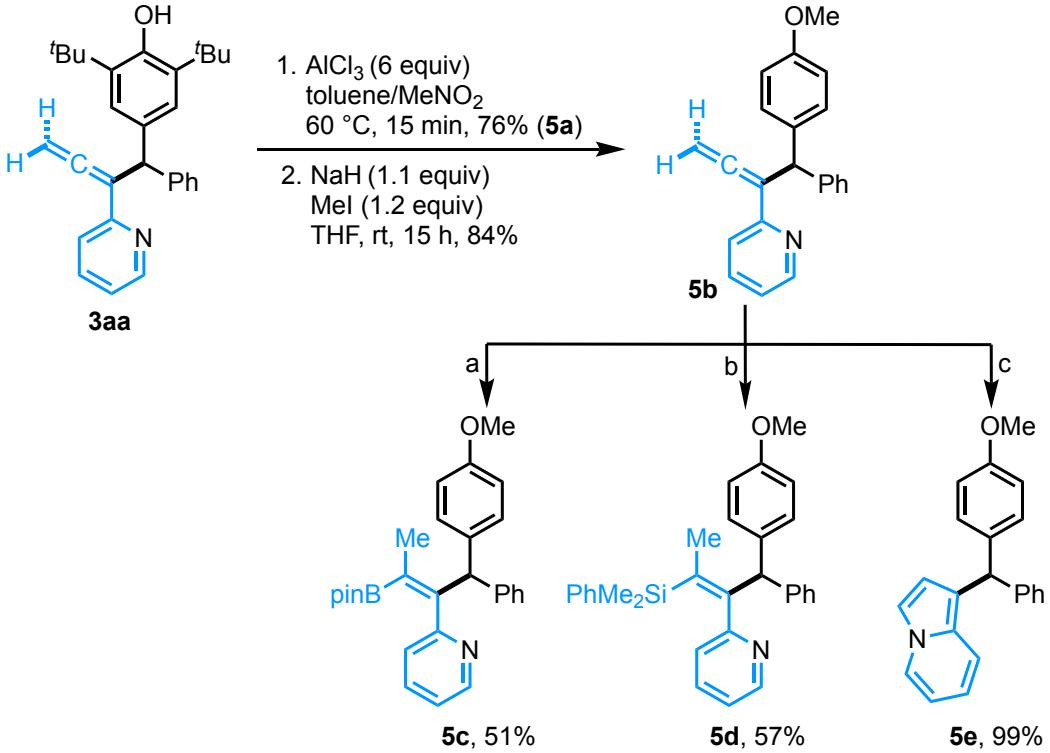
3aa, 74%
2.6 g

1a, 1.0 g
(8.54 mmol)

4aa, 36%
1.29 g

Reaction conditions: a) **2a** (1.5 equiv), KO^{t}Bu (1.5 equiv), toluene (0.1 M), rt, 1 h.
b) **2a** (2.0 equiv), NaN(SiMe$_3$)$_2$ (2 equiv), toluene (0.1 M), rt, 1 h.

B. Synthetic manipulations of allenylated product (**3aa**)



3aa

5b

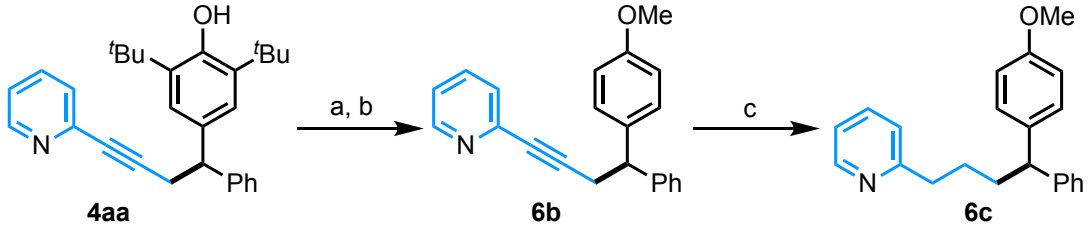
5c, 51%

5d, 57%

5e, 99%

Reaction conditions: a) CuCl (10 mol%), SIMes.HCl (10 mol%), NaO^{t}Bu (0.4 equiv), B$_2$pin$_2$ (1.1 equiv), MeOH (6 equiv), THF, rt, 14 h. b) CuCl (10 mol%), pinB–SiMe$_2$Ph (1.1 equiv), NaO^{t}Bu (1.1 equiv), THF, rt, 1 h. c) DMF:H$_2$O (3:1), 130 °C, 15 h.

C. Synthetic manipulations of propargylated product (**4aa**)



4aa

6b

6c

Reaction conditions: a) AlCl$_3$ (6 equiv), toluene/MeNO$_2$, 60 °C, 15 min, 71% (**6a**). b) NaH (1.1 equiv), MeI (1.2 equiv), THF, rt, 15 h, 64%. c) Pd/C (5 mol%), H$_2$ (balloon), EtOH, rt, 18 h, 95%

Scheme 1. Gram-scale synthesis and synthetic manipulations

silica gel column chromatography using ethyl acetate/hexane (1:20) as the eluent and afforded the desired product. **3aa** was obtained as a gummy oil. Yield: 2.60 g, 74%.

G. Typical Experimental Procedure for a Gram Scale Propargylation Reaction

To a flame-dried round bottom flask charged with a magnetic stir bar, *para*-quinone methide **2a** (17.0720 mmol) and $NaN(SiMe_3)_2$ (17.0720 mmol) were added under the argon atmosphere. To the reaction mixture, alkynyl azaarene **1a** (8.5360 mmol) in toluene (0.1 M) was added and then, stirred at room temperature for 1 h and then the mixture was quenched with water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude reaction mixture was purified by silica gel column chromatography using ethyl acetate/hexane (1:10) as the eluent and afforded the desired product. **4aa** was obtained as an off-white solid. Yield: 1.29 g, 36%.

H. General Procedure for the De-*tert* Butylation Reaction[16]

To a solution of appropriate phenol (1.0 equiv) in toluene (0.02 M) at room temperature was added a solution of $AlCl_3$ (6.0 equiv) in $MeNO_2$ (2.25 M) in one portion. The mixture was immediately heated to 60 °C by using a pre-heated oil bath and maintained at this temperature for 15 min. Subsequently, the reaction mixture was cooled to room temperature, poured into a separating funnel containing ice and ethyl acetate, and then extracted with ethyl acetate. The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography using ethyl acetate/hexane (1:5) to afford the desired product.

I. General Procedure for *O*-Methylation Reaction[17]

To a suspension of sodium hydride (1.1 equiv, 70% dispersion in mineral oils) in THF, appropriate phenol (1 equiv) in THF was added dropwise at 0 ºC under the nitrogen atmosphere. The mixture was stirred for 1 h, and then, methyl iodide (1.2 equiv) in THF was added. The mixture was stirred at room temperature for 15 h, quenched by saturated aq. ammonium chloride, diluted with water, and extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using ethyl acetate/hexane (1:10) to afford the desired product.

J. Typical Experimental Procedure for the Borylation of 5b[18]

A flame dried reaction tube containing a magnetic stir bar was charged with NaO^tBu (0.4 equiv), CuCl (10 mol%), SIMes·HCl (10 mol%). Then, THF (0.15 mL) was added and stirred for 1.5 h followed by addition of B_2pin_2 (1.1 equiv), which made the mixture turn to black immediately. After 30 minutes, MeOH (6 equiv) and allenylated product (**5b**, 0.10 mmol, 1 equiv) were added. The reaction was allowed to stir for 14 h at room temperature. The reaction mixture was then passed through a plug of Celite® eluting with Et_2O. The filtrate was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography using ethyl acetate/hexane (1:5) to afford the desired product.

K. Typical Experimental Procedure for the Silylation of 5b[19]

A flame dried reaction tube containing a magnetic stir bar was charged with CuCl (0.01 mmol, 10 mol %), NaO^tBu (0.11 mmol, 1.1 equiv) and THF (0.5 mL). The mixture was stirred for 15 min at ambient temperature. Then, pinB-$SiMe_2Ph$ (0.11 mmol, 1.1 equiv) was added, and the mixture was stirred for additional 5 min. Subsequently, allenylated product (**5b**, 0.1 mmol, 1.0 equiv) was added to the tube. After stirring for 1 h, the reaction mixture was filtered through a

pad of silica gel and the solution was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using ethyl acetate/hexane (1:20) to afford the desired product.

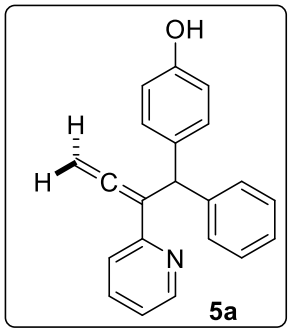
L. Typical Experimental Procedure for the Cycloisomerization of 5b[20]

To a solution of allenylated product (**5b**, 31.3 mg, 0.1 mmol) in DMF (1.5 mL) was added H_2O (0.5 mL) at room temperature. Then, the reaction mixture was stirred at 130 °C for 15 h. The resulting mixture was quenched with water, extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure, and the crude product was purified by silica gel column chromatography using ethyl acetate/hexane (1:10) to afford the desired product.

M. Typical Experimental Procedure for the Reduction of 6b[21]

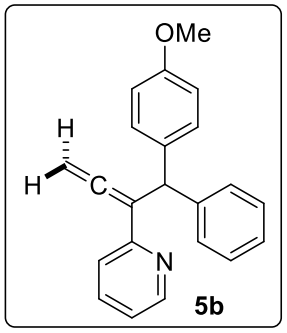
To a solution of **6b** (1 equiv, 0.04786 mmol) in ethanol (0.5 mL), palladium on carbon (5 mol%) was added, and the reaction mixture was stirred under the hydrogen (balloon) atmosphere at room temperature for 18 h. The mixture was filtered through a pad of Celite ®, and the solvent was evaporated. The crude product was purified by silica gel column chromatography using ethyl acetate/hexane (1:10) to afford the desired product.

4-(1-Phenyl-2-(pyridin-2-yl)buta-2,3-dien-1-yl)phenol (5a)



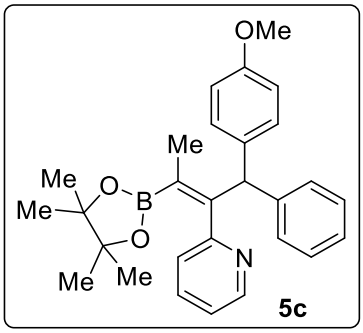
The title compound was prepared as described in the procedure **H** using **3aa** (1.2148 mmol). Yield: 276.1 mg, 76%, brown solid. Mp: 134.6-146.1°C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.50-8.49 (m, 1H), 7.58-7.54 (m, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.25-7.24 (m, 4H), 7.18-7.14 (m, 1H), 7.12-7.08 (m, 2H), 7.04-7.02 (m, 1H), 6.71-6.66 (m, 2H), 5.79-5.78 (m, 1H), 5.02 (d, *J* = 2.5 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.3, 155.3, 154.4, 149.1, 143.5, 136.4, 134.8, 130.4, 129.2, 128.1, 126.3, 122.6, 121.5, 115.1, 111.5, 81.0, 49.2. **IR** (CH_2Cl_2, cm^{-1}): 2939, 1950, 1745, 1598, 1518, 1241, 742. **HRMS** (ESI) m/z calcd for $C_{21}H_{17}NO$ $[M+H]^+$: 300.1383, found: 300.1378.

2-(1-(4-Methoxyphenyl)-1-phenylbuta-2,3-dien-2-yl)pyridine (5b)



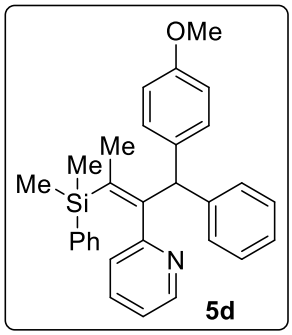
The title compound was prepared as described in the procedure **I** using **5a** (1.2827 mmol). Yield: 338.1 mg, 84%, brown solid. Mp: 93.5-98.0°C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.50-8.49 (m, 1H), 7.55-7.49 (m, 2H), 7.26-7.22 (m, 4H), 7.18-7.14 (m, 3H), 7.02-6.99 (m, 1H), 6.80-6.78 (m, 2H), 5.83 (s, 1H), 5.02 (d, *J* = 2.5 Hz, 2H), 3.75 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 212.3, 158.1, 155.2, 149.2, 143.6, 136.1, 135.3, 130.2, 129.2, 128.1, 126.2, 122.4, 121.3, 113.5, 111.7, 80.9, 55.3, 49.0. **IR** (CH_2Cl_2, cm^{-1}): 3040, 2848, 1948, 1516, 1251, 1038, 783. **HRMS** (ESI) m/z calcd for $C_{22}H_{19}NO$ $[M+H]^+$: 314.1539, found: 314.1536.

2-(1-(4-Methoxyphenyl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-2-yl)pyridine (5c)



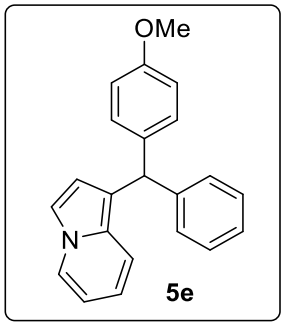
The title compound was prepared as described in the procedure **J** using **5b** (0.2553 mmol). Yield: 57.8 mg, 51%, off-white gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.46 (d, *J* = 5.4 Hz, 1H), 7.58-7.55 (m, 1H), 7.26-7.23 (m, 2H), 7.20-7.18 (m, 3H), 7.11-7.07 (m, 3H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.79 (d, *J* = 8.6 Hz, 2H), 5.56 (s, 1H), 3.77 (s, 3H), 1.86 (s, 3H), 1.36 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 159.2, 158.3, 142.3, 142.0, 141.8, 135.1, 133.5, 130.2, 129.2, 128.5, 126.5, 120.0, 118.7, 113.9, 80.0, 55.4, 47.5, 27.7, 15.6. **^{11}B NMR** (160 MHz, $CDCl_3$) δ (ppm): 11.51. **IR** (CH_2Cl_2, cm^{-1}): 2939, 1757, 1469, 1256, 1044, 757. **HRMS** (ESI) m/z calcd for $C_{28}H_{32}BNO_3$ $[M+H]^+$: 442.2548, found: 442.2550.

(2-(3-(Dimethyl(phenyl)silyl)-1-(4-methoxyphenyl)-1-phenylbut-2-en-2-yl)pyridine (5d)



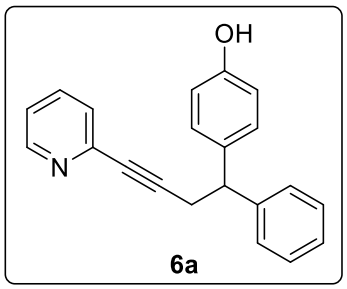
The title compound was prepared as described in the procedure **K** using **5b** (0.1 mmol). Yield: 25.6 mg, 57%, off-white gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.38-8.37 (m, 1H), 7.44-7.42 (m, 2H), 7.30-7.27 (m, 3H), 7.20-7.07 (m, 8H), 6.90-6.87 (m, 1H), 6.73-6.71 (m, 2H), 6.54 (d, *J* = 7.8 Hz, 1H), 5.62 (s, 1H), 3.75 (s, 3H), 1.76 (s, 3H), -0.77 (d, J = -2.2 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 160.5, 156.8, 152.0, 147.3, 142.3, 139.0, 134.8, 134.0, 133.7, 132.9, 129.8, 128.8, 127.6, 127.0, 126.7, 124.9, 124.8, 120.4, 112.4, 54.3, 54.2, 18.2, -2.72, -2.75. **IR** (CH_2Cl_2, cm^{-1}): 2937, 1740, 1591, 1517, 1255, 824, 705. **HRMS** (ESI) m/z calcd for $C_{30}H_{31}NOSi$ $[M+H]^+$: 450.2248, found: 450.2243.

1-((4-Methoxyphenyl)(phenyl)methyl)indolizine (5e)



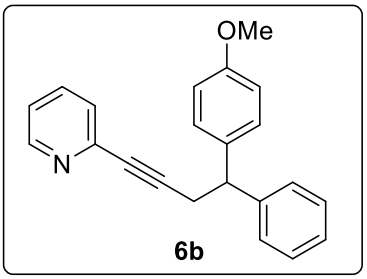
The title compound was prepared as described in the procedure **L** using **5b** (0.1 mmol). Yield: 31.0 mg, 99%, yellow gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.82 (d, *J* = 7.0 Hz, 1H), 7.27-7.24 (m, 2H), 7.21-7.16 (m, 4H), 7.11-7.10 (m, 2H), 7.05 (d, *J* = 9.1 Hz, 1H), 6.82-6.80 (m, 2H), 6.50-6.47 (m, 1H), 6.41-6.36 (m, 2H), 5.67 (s, 1H), 3.77 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 158.0, 145.3, 137.2, 130.0, 129.7, 129.0, 128.3, 126.1, 125.3, 117.8, 116.1, 115.9, 114.7, 113.7, 111.5, 110.2, 55.3, 48.0. **IR** (CH_2Cl_2, cm^{-1}): 2944, 1744, 1619, 1517, 1256, 1041, 743. **HRMS** (ESI) m/z calcd for $C_{22}H_{19}NO$ $[M+H]^+$: 314.1539, found: 314.1535.

4-(1-Phenyl-4-(pyridin-2-yl)but-3-yn-1-yl)phenol (6a)



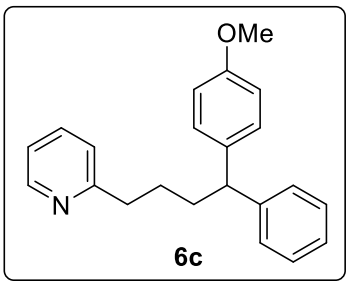
The title compound was prepared as described in the procedure **H** using **4aa** (0.24296 mmol). Yield: 51.5 mg, 71%, brown solid. Mp: 133.6-139.8°C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.44 (d, *J* = 4.1 Hz, 1H), 7.57-7.53 (m, 1H), 7.26-7.19 (m, 5H), 7.17-7.13 (m, 2H), 7.07-7.04 (m, 2H), 6.84-6.80 (m, 2H), 4.17 (t, *J* = 7.5 Hz, 1H), 3.02-2.92 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 155.5, 149.2, 143.9, 143.3, 136.8, 134.7, 128.9, 128.5, 128.0, 127.4, 126.5, 122.7, 115.9, 91.0, 81.3, 49.1, 26.6. **IR** (CH_2Cl_2, cm^{-1}): 2937, 2240, 1596, 1253, 781. **HRMS** (ESI) m/z calcd for $C_{21}H_{17}NO$ $[M+H]^+$: 300.1383, found: 300.1380.

2-(4-(4-Methoxyphenyl)-4-phenylbut-1-yn-1-yl)pyridine (6b)



The title compound was prepared as described in the procedure **I** using **6a** (0.8027 mmol). Yield: 161.6 mg, 64%, brown solid. Mp: 94.8-99.3°C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.51-8.50 (m, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.32-7.28 (m, 4H), 7.22-7.18 (m, 4H), 7.15-7.13 (m, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.32 (t, *J* = 7.6 Hz, 1H), 3.78 (s, 3H), 3.13 (d, *J* = 7.6 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 158.3, 149.8, 143.84, 143.76, 136.1, 135.7, 129.0, 128.5, 128.0, 127.1, 126.6, 122.5, 113.9, 89.4, 82.0, 55.3, 49.2, 26.6. **IR** (CH_2Cl_2, cm^{-1}): 2940, 2243, 1744, 1471, 1257, 783. **HRMS** (ESI) m/z calcd for $C_{22}H_{19}NO$ $[M+H]^+$: 314.1539, found: 314.1535.

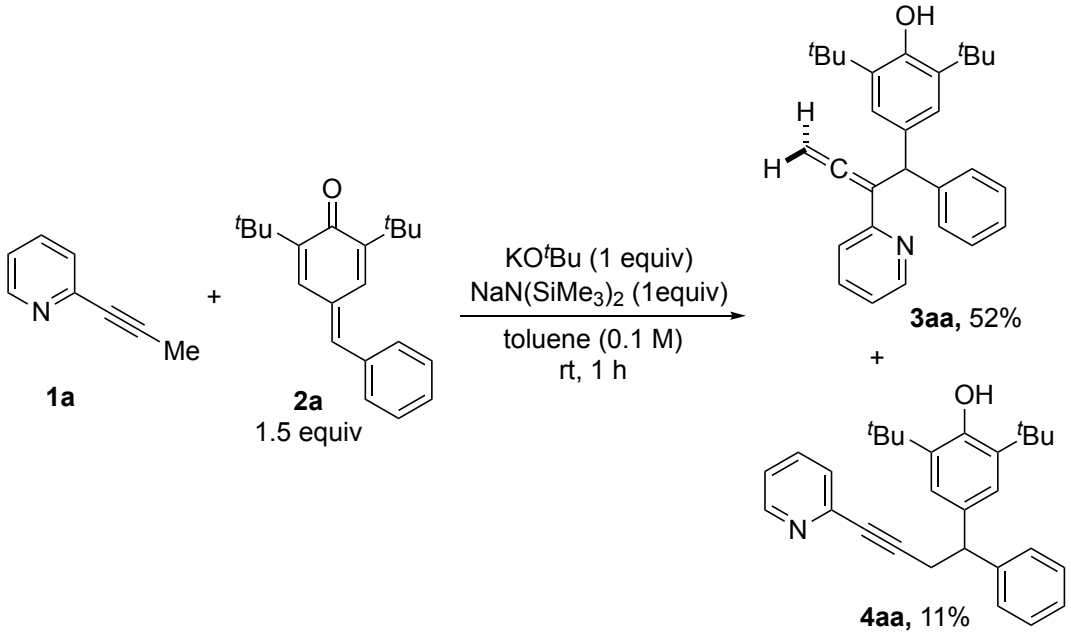
2-(4- (4-Methoxyphenyl)-4-phenylbutyl)pyridine (6c)



The title compound was prepared as described in the procedure **M** using **6b** (0.04786 mmol). Yield: 14.5 mg, 95%, off-white gummy oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.50-8.48 (m, 1H), 7.55 (td, *J* = 7.7, 1.8 Hz, 1H), 7.26-7.23 (m, 2H), 7.21-7.19 (m, 2H), 7.16-7.12 (m, 3H), 7.08-7.06 (m, 2H), 6.82-6.79 (m, 2H), 3.88 (t, *J* = 7.9 Hz, 1H), 3.75 (s, 3H), 2.81 (t, J = 7.7 Hz, 2H), 2.07 (q, *J* = 7.8 Hz, 2H), 1.73-1.65 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 162.1, 158.0, 149.2, 145.6, 137.3, 136.4, 128.8, 128.5, 127.9, 126.1, 122.8, 121.1, 113.9, 55.3, 50.5, 38.4, 35.6, 28.4. **IR** (CH_2Cl_2, cm^{-1}): 2939, 1736, 1599, 1518, 1254, 1042, 704. **HRMS** (ESI) m/z calcd for $C_{22}H_{23}NO$ $[M+H]^+$: 318.1852, found: 318.1849.

Competitive Reactions

The competitive reaction was using 1.0 equivalent of 2-alkynyl pyridine with 1.5 equivalents of *p*-quinone methide in the presence of 1.0 equivalent of both KO^{t}Bu and NaN(SiMe$_3$)$_2$. In this reaction, the allenylated product was formed predominantly (52%), while the corresponding propargylated product was produced at a lesser yield (11%).



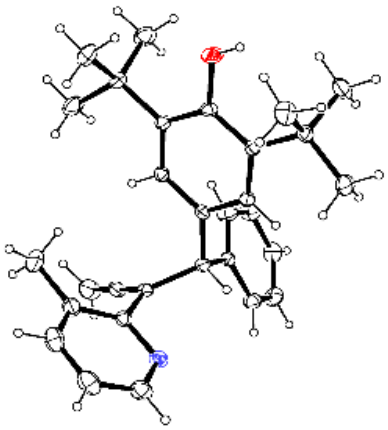
The predominant formation of allenyl product (in the presence of KO^{t}Bu) rather than propargyl product (in the presence of NaN(SiMe$_3$)$_2$) may be because of the increased ionic character of K–C bond rather than Na–C bond in the respective allenyl/propargyl metal species. The nucleophilicity/basicity of the anionic metal species is directly attributed to the increased ionic character of the metal–carbon/metal–heteroatom bond and also to the periodic properties of the metal ion.[24] Hence, the K-allenyl/propargyl metal species might reacts with the *p*-quinone methide faster than the K-allenyl/propargyl metal species.

Crystal data for **3da**

Table 1. Crystal data and structure refinement for **3da**.

Identification code	shelx
Empirical formula	C_{30} H_{35} N O
Formula weight	425.59
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 11.4653(8) Å a= 90°. b = 17.7458(13) Å b= 107.437(3)°. c = 12.8064(10) Å g = 90°.
Volume	2485.9(3) $Å^3$
Z	4
Density (calculated)	1.137 Mg/m^3
Absorption coefficient	0.067 mm^{-1}
F(000)	920
Crystal size	0.090 x 0.060 x 0.045 mm^3
Theta range for data collection	2.295 to 24.999°.
Index ranges	-13<=h<=12, -21<=k<=21, -15<=l<=15
Reflections collected	29393
Independent reflections	4372 [R(int) = 0.0475]
Completeness to theta = 24.999°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.997 and 0.994
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4372 / 2 / 305
Goodness-of-fit on F^2	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0427, wR2 = 0.0954
R indices (all data)	R1 = 0.0721, wR2 = 0.1114
Extinction coefficient	n/a
Largest diff. peak and hole	0.195 and -0.146 $e.Å^{-3}$

Figure 1: X-ray crystal structure of compound **3da** (2172750). The thermal ellipsoids are shown at 50% probability. The crystal was grown from CH_2Cl_2: Hexane combination (1:2) in open atmosphere.

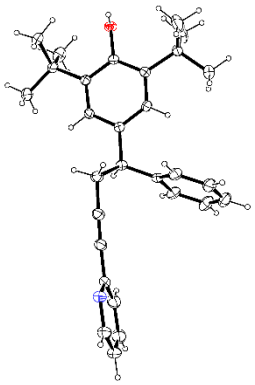


Crystal data for **4aa**

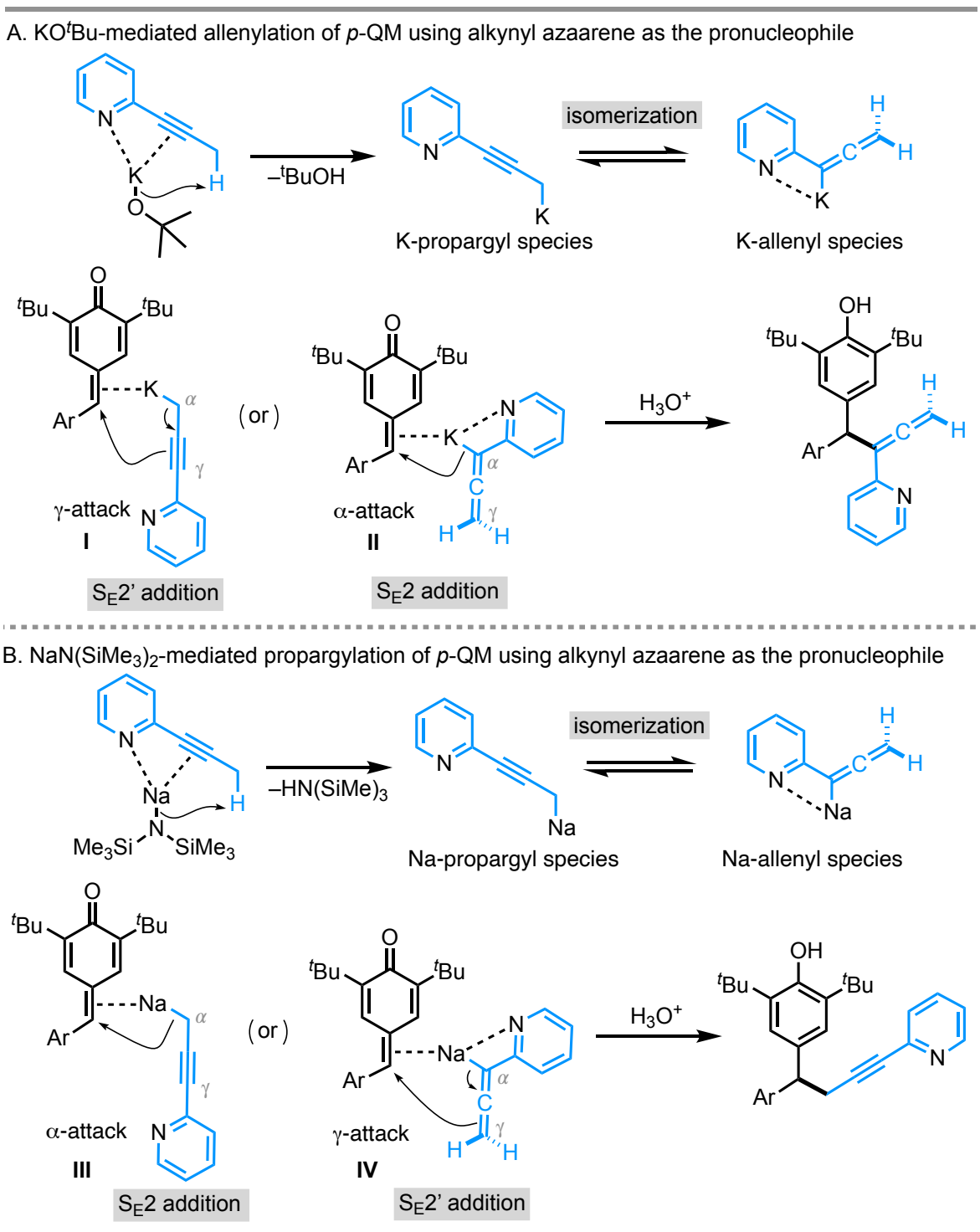
Table 1. Crystal data and structure refinement for **4aa**.

Identification code	shelx
Empirical formula	C_{29} H_{33} N O
Formula weight	411.56
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 9.5519(12) Å a= 92.316(4)°. b = 10.6336(13) Å b= 109.059(4)°. c = 14.3558(18) Å g = 113.435(4)°.
Volume	1239.9(3) $Å^3$
Z	2
Density (calculated)	1.102 Mg/m^3
Absorption coefficient	0.066 mm^{-1}
F(000)	444
Crystal size	0.060 x 0.048 x 0.035 mm^3
Theta range for data collection	2.129 to 24.994°.
Index ranges	-11<=h<=11, -12<=k<=12, -17<=l<=17
Reflections collected	27075
Independent reflections	4369 [R(int) = 0.0363]
Completeness to theta = 24.999°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.998 and 0.996
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4369 / 0 / 288
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I)]	R1 = 0.0487, wR2 = 0.1254
R indices (all data)	R1 = 0.0741, wR2 = 0.1490
Extinction coefficient	0.022(3)
Largest diff. peak and hole	0.411 and -0.196 $e.Å^{-3}$

Figure 1: X-ray crystal structure of compound **4aa** (2172751). The thermal ellipsoids are shown at 50% probability. The crystal was grown from MeOH: Hexane combination (1:2) in open atmosphere.



Plausible Reaction Mechanism



Scheme 1. Plausible reaction mechanism

To gain insights into the reaction mechanism, we performed a few NMR studies and trapping experiments (such as silylation and deuterium quenching) to entrap the intermediates formed in the reaction medium. However, no fruitful results were obtained. Based on the literature precedence,[25,26] we delineated a hypothetical reaction mechanism in scheme 1. The p*K*a value of the C(sp^3)–H bond of alkynyl azaarene (**1a**) was theoretically calculated and is

approximately 27.[27] We speculate that the coordination of an alkali metal ion (of the Brønsted base) with the nitrogen atom and the triple bond of the alkynyl azaarenes could significantly bring down the p*K*a of the propargylic C(sp^3)–H bond, and then the activated propargylic C–H bond can be readily deprotonated by the counter ion of the base to generate an active allenyl/propargyl metal nucleophile(s). Since allenyl and propargyl metal species are class of ambident nucleophiles, the C–C bond-formation with the electrophiles can occur either at α-position or γ-position (of the nucleophile).[26] As shown in scheme 1A, the allenyl product formation can take place through either γ-attack of the K-propargyl species to the *p*-QM (i.e. S_E2' addition) or an α-attack of the K-allenyl species to the *p*-QM (i.e. S_E2 addition). On the other hand, the propargyl product formation (Scheme 1B) can occur through either γ-attack of the Na-allenyl species to the *p*-QM (i.e. S_E2' addition) or an α-attack of Na-propargyl species to the *p*-QM (i.e. S_E2 addition).

Computational Study

(The geometry optimization of all the stationary points (reactants, transition states and products) were performed within the density functional theory (DFT) at B3LYP/6-31+G(d,p) level of theory. Single point energy calculations were performed for all the optimized structures at the M06-2X level, using the same basis set. Solvent effects were included in these calculations using SMD formalism. All the calculations were carried out using the Gaussian 16 software package.)

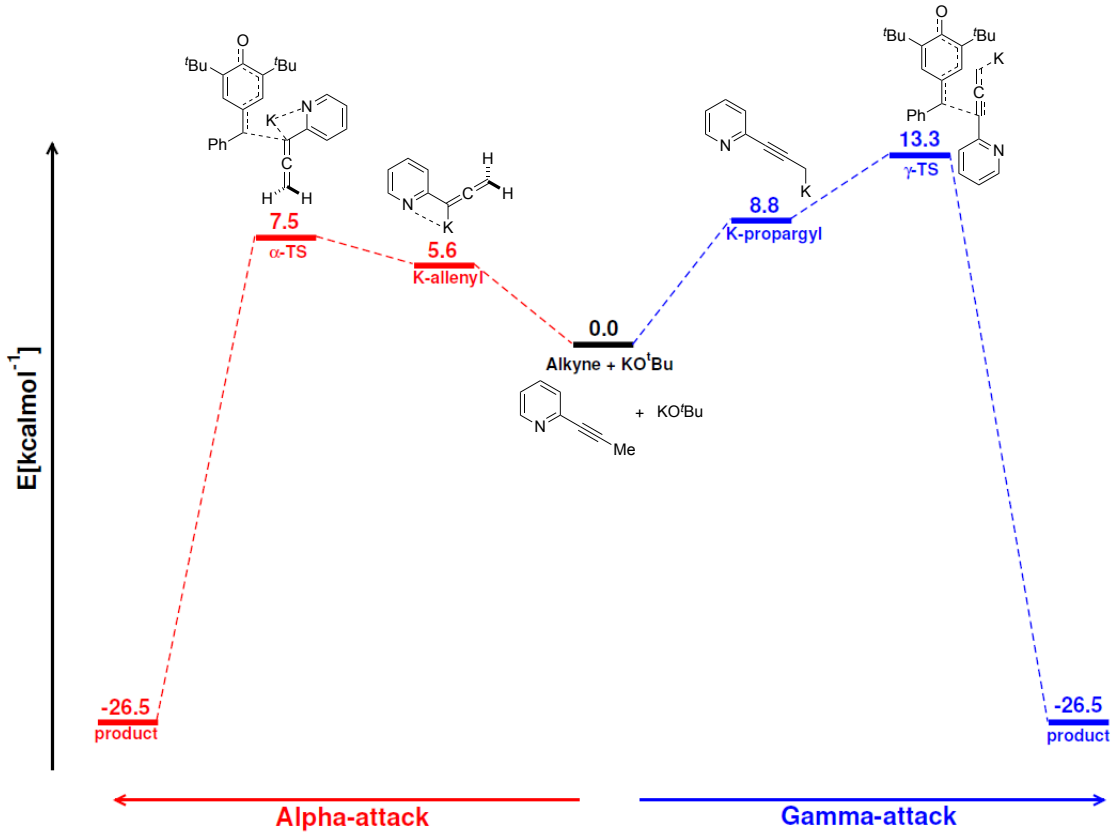


Figure 1: Relative free energy profile for the a) α-attack by K-allenyl species and b) γ-attack by K-propargyl species

The DFT calculations predicted the addition of K-allenyl species to *p*-QM requires an energy barrier of 7.5 kcal mol^{-1}, whereas the addition of K-propargyl species has a barrier of about 13.3 kcal mol^{-1}. This shows that the α-attack of the K-allenyl species to the *p*-QM is an energetically more favourable process, i.e., the reaction might proceed via the S_E2 pathway. In the case of propargyl product formation, the γ-attack of the Na-allenyl species to the *p*-QM (energy barrier of 6.9 kcal mol^{-1}) is energetically more favourable than the α-attack of Na-propargyl species (energy barrier of 9.9 kcal mol^{-1}). Therefore, this reaction might proceed through the S_E2' pathway.

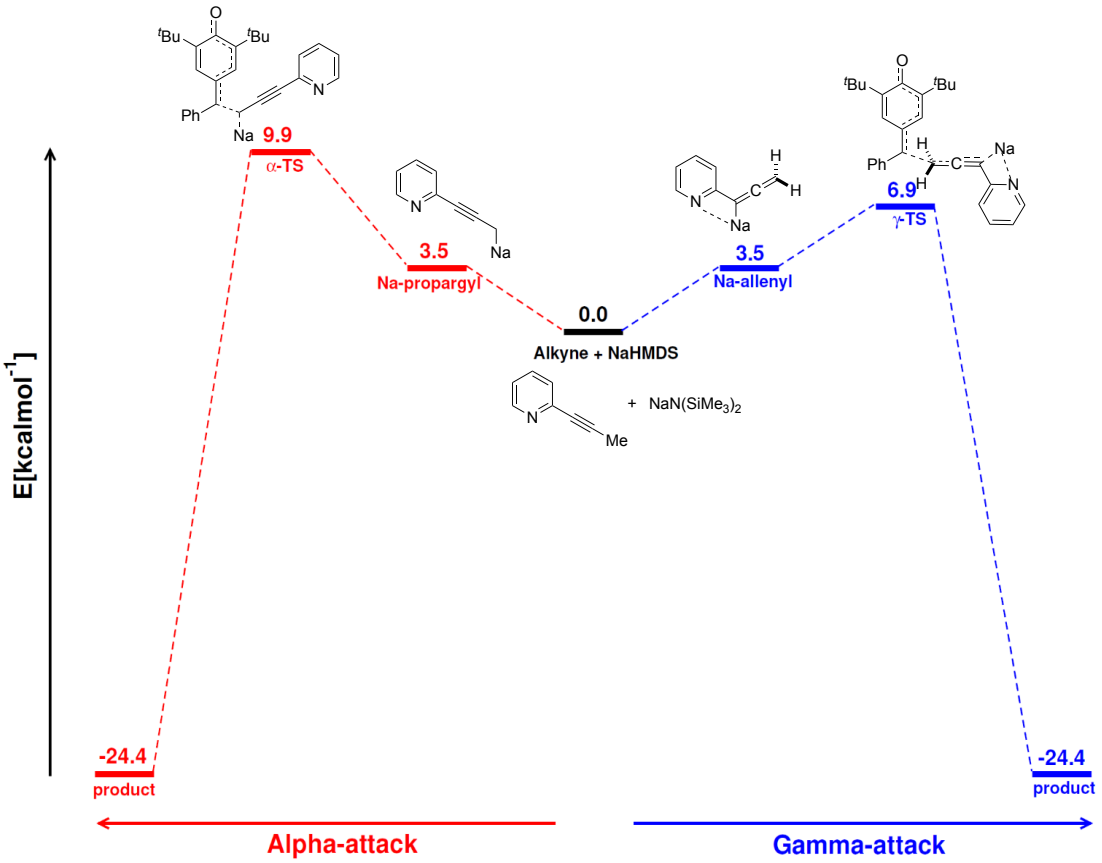


Figure 2: Relative free energy profile for the a) α-attack by Na-propargyl species and b) γ-attack by Na-allenyl species

Besides, the calculation of relative free energy for the formation of K-allenyl and K-propargyl species from alkynyl azaarene and KO^{t}Bu revealed that the formation of K-allenyl species (the relative free energy is 5.6 kcal mol^{-1}) is more facile than the K-propargyl species (the relative free energy is 8.8 kcal mol^{-1}). These results suggest that the treatment of alkynyl azaarene with KO^{t}Bu predominantly forms the K-allenyl species, which further undergoes a regioselective S_E2 addition to the *p*-QM to give the corresponding allenylated product. In contrast, the calculation of relative free energy for the formation of Na-allenyl and Na-propargyl species from alkynyl azaarene and NaN(SiMe$_3$)$_2$ implied that both species have almost equal relative free energy (3.5 kcal mol^{-1} for Na-allenyl species and 3.5 kcal mol^{-1} for Na-propargyl species). This likely accounts for the experimentally observed inferior regioselective outcome in NaN(SiMe$_3$)$_2$-mediated propargylation of *p*-QMs.

1. Formation of K-allenyl and K-propargyl species (from alkynyl azaarene and KO^{t}Bu)

$$\text{Alkyne} + KO^tBu \xrightarrow[-{}^t\text{BuOH}]{\text{----------}} \text{K-allenyl /K-propargyl}$$

Relative free energy (in kcalmol^{-1}) =[$\Delta G_{allenyl/propargyl}$ - (ΔG_{alkyne} + ΔG_{KOtBu} - ΔG_{tBuOH})]*630

Note : 1 Ha = 630 kcalmol^{-1}

Attack by KO^{t}Bu

2. Formation of Na-allenyl and Na-propargyl species (from alkynyl azaarene and NaHMDS)

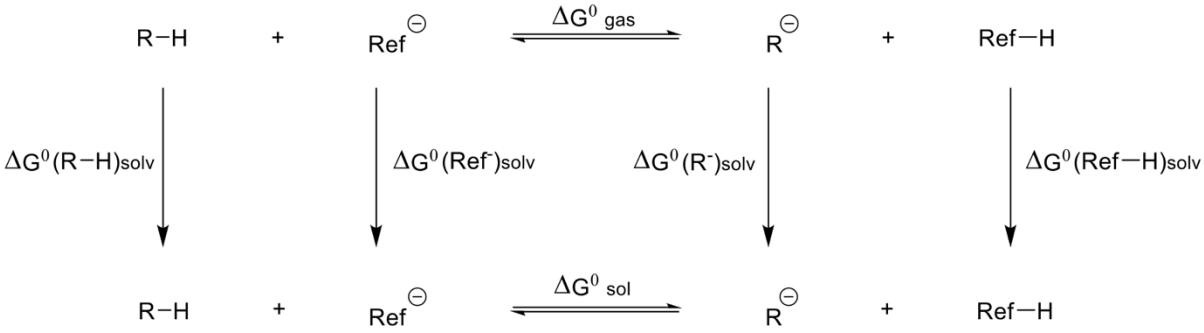
$$\text{Alkyne} + \text{NaHMDS} \xrightarrow[-\text{HMDS}]{\text{----------}} \text{Na-allenyl /Na-propargyl}$$

Relative free energy (in kcalmol^{-1}) =[$\Delta G_{allenyl/propargyl}$ - (ΔG_{alkyne} + ΔG_{NaHMDS} -ΔG_{HMDS})]*630

	Free energy (au)	Relative energy (kcalmol^{-1})
Alkyne	-363.5333122	-
KO^{t}Bu	-832.7929499	-
Reactants (Alkyne + KO^{t}Bu)	-1196.3262621	0
^{t}BuOH	-233.4752115	-
Reactants –^{t}BuOH	-962.8510506	-
K-allenyl species	-962.8421444	5.6
Alpha-TS	-1853.2477871	7.5
Product	-1853.302016	-26.5
K-propargyl species	-962.8370802	8.8
Gamma-TS	-1853.2385229	13.3
Product	-1853.302016	-26.5
	Free energy (au)	Relative energy (kcalmol^{-1})
Alkyne	-363.5333122	-
NaHMDS	-1035.2350647	-
Reactants (Alkyne +NaHMDS)	-1398.7683769	0
HMDS	-873.5464989	-
Reactants-HMDS	-525.221878	-
Na-propargyl species	-525.2162429	3.5
Alpha-TS	-1415.6147629	9.9
Product	-1415.6694467	-24.4
Na-allenyl species	-525.2162497	3.5
Gamma-TS	-1415.6195178	6.9
Product	-1416.1363837	-24.4

Calculation of pK_a in DMSO

The p*K*a value of the C(sp^3)–H bond of alkynyl azaarene (**1a**) was theoretically calculated according to the literature report.[26]

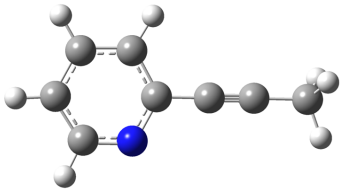


Scheme 2. Isodesmic reaction fort he p*K*a calculation in solution

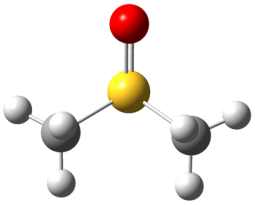
Based on the above scheme,

$$\Delta G^0_{sol} = \Delta G^0_{gas} - \Delta G^0\,(R\text{-}H)_{solv} - \Delta G^0\,(Ref^-)_{solv} + \Delta G^0\,(R^-)_{solv} + \Delta G^0\,(Ref\text{-}H)_{sol} \quad (1)$$

$$pK_a\,(R\text{-}H) = pK_a\,(Ref\text{-}H) + (\Delta G^0_{sol}/2.303 \cdot R \cdot T) \quad (2)$$



R-H



Ref-H (DMSO)

Finding each term in equation (1) :

1) $\Delta G^0_{gas} = G^0\,(R^-)_{gas} + G^0\,(Ref\text{-}H)_{gas} - G^0\,(R\text{-}H)_{gas} - G^0\,(Ref^-)_{gas}$
$= -12.8432391$ kcalmol^{-1}

2) $\Delta G^0\,(R\text{-}H)_{solv} = G^0\,(R\text{-}H)_{solv} - G^0\,(R\text{-}H)_{gas}$
$= -6.54304268$ kcalmol^{-1}

3) $\Delta G^0\,(Ref^-)_{solv} = G^0\,(Ref^-)_{solv} - G^0\,(Ref^-)_{gas}$
$= -56.1928579$ kcalmol^{-1}

4) $\Delta G^0\,(R^-)_{solv} = G^0\,(R^-)_{solv} - G^0\,(R^-)_{gas}$
$= -52.1422834$ kcalmol^{-1}

5) $\Delta G^0\,(Ref\text{-}H)_{solv} = G^0\,(Ref\text{-}H)_{solv} - G^0\,(Ref\text{-}H)_{gas}$
$= -8.6728$ kcalmol^{-1}

Substituting 1-5 in equation (2), we get,

$$\Delta G^0_{sol} = -10.92242192 \text{ kcalmol}^{-1}$$

We have, T = 298.15 K; R = 1.9858775*10^{-3} kcal$K^{-1}$$mol^{-1}$; p$K_a$ (Ref-H) = + 35.1

Now, using equation (3),

pK_a (R-H) = +27.1

Ground-state optimized geometries of all the molecules under study

Alkynyl azaarene

C	-0.065994	-0.012709	0.000001
C	-0.770405	1.207360	0.000000
C	-2.162106	1.181671	-0.000001
C	-2.812985	-0.053251	-0.000002
C	-2.029385	-1.210762	-0.000001
N	-0.692738	-1.209165	0.000000
H	-2.728035	2.108851	-0.000002
H	-0.222562	2.143590	0.000001
H	-3.896114	-0.123120	-0.000003
H	-2.499601	-2.192262	-0.000001
C	1.368191	-0.015583	0.000003
C	2.581393	-0.001489	0.000004
C	4.040470	-0.004718	-0.000001
H	4.435892	0.506417	-0.885161
H	4.435898	0.506414	0.885158
H	4.428609	-1.028841	-0.000004

KO^{t}Bu

O	-0.050284	-0.290506	0.000000
C	0.185117	1.070751	0.000000
C	-0.440094	1.724215	-1.260034
C	-0.440094	1.724215	1.260034
C	1.710336	1.352379	0.000000
H	-1.520352	1.534571	-1.273728
H	-0.278359	2.810299	-1.304884
H	-0.006503	1.272550	-2.160668
H	-0.006503	1.272550	2.160668
H	-1.520352	1.534571	1.273728
H	-0.278359	2.810299	1.304884
H	2.167334	0.896826	-0.886996
H	1.948235	2.425291	0.000000
H	2.167334	0.896826	0.886996
K	-0.440094	-2.545215	0.000000

NaHMDS

Si	0.000000	-1.592386	-0.244941
Si	0.000000	1.592386	-0.244941
N	0.000000	0.000000	0.332299
C	0.000000	-2.745923	1.298910
C	-1.529733	-2.080756	-1.269030
C	1.529733	-2.080756	-1.269030
C	1.529733	2.080756	-1.269030

C	-1.529733	2.080756	-1.269030
C	0.000000	2.745923	1.298910
H	-0.895490	-2.587353	1.920710
H	0.000000	-3.809116	1.029717
H	0.895490	-2.587353	1.920710
H	-1.508389	-3.138513	-1.561253
H	-2.454791	-1.903055	-0.707289
H	-1.588326	-1.484551	-2.187872
H	2.454791	-1.903055	-0.707288
H	1.508389	-3.138513	-1.561253
H	1.588326	-1.484551	-2.187871
H	2.454791	1.903055	-0.707289
H	1.588326	1.484551	-2.187872
H	1.508389	3.138513	-1.561253
H	-1.588326	1.484551	-2.187871
H	-2.454791	1.903055	-0.707288
H	-1.508389	3.138513	-1.561253
H	-0.895490	2.587353	1.920710
H	0.895490	2.587353	1.920710
H	0.000000	3.809116	1.029717
Na	0.000000	0.000000	2.498676

***p*-QM**

C	-0.555601	-0.838550	-0.057552
C	0.679170	-1.602590	-0.039941
C	1.911716	-1.037761	0.025197
C	2.003895	0.453498	0.058481
C	0.747130	1.258403	-0.067356
C	-0.444528	0.606619	-0.107330
H	0.570765	-2.682024	-0.052672
H	-1.361560	1.166952	-0.226645
C	3.203618	-1.872926	0.075332
C	4.114301	-1.515455	-1.127348
C	3.958689	-1.604855	1.402678
C	2.908484	-3.385434	0.002833
H	3.602330	-1.716129	-2.075785
H	4.410390	-0.466177	-1.104877
H	5.020085	-2.132486	-1.098663
H	3.335758	-1.871977	2.264349
H	4.865239	-2.220414	1.440788
H	4.247230	-0.557010	1.491263
H	3.854280	-3.936108	0.031687
H	2.304031	-3.730368	0.849394
H	2.396189	-3.662350	-0.925676
C	0.848655	2.791679	-0.158519
C	1.475670	3.359087	1.141568
C	1.714563	3.197550	-1.378873
C	-0.536731	3.447833	-0.333074
H	0.864056	3.098588	2.013398
H	2.484930	2.976591	1.295879

H	1.522094	4.452805	1.079656
H	1.276887	2.817919	-2.309582
H	1.757616	4.290631	-1.450874
H	2.732734	2.817495	-1.290242
H	-0.411639	4.533320	-0.401230
H	-1.039590	3.117192	-1.248841
H	-1.199102	3.249265	0.517142
O	3.101750	1.015581	0.167908
C	-1.743332	-1.526447	-0.066283
H	-1.661400	-2.608488	-0.169270
C	-3.119591	-1.039203	0.020208
C	-3.504965	0.089717	0.774198
C	-4.131414	-1.771592	-0.638159
C	-4.839618	0.489842	0.828090
H	-2.763463	0.627554	1.354137
C	-5.462453	-1.363378	-0.592901
H	-3.858850	-2.659551	-1.202635
C	-5.822152	-0.225996	0.137369
H	-5.115391	1.355739	1.422959
H	-6.220278	-1.935088	-1.120512
H	-6.860360	0.089218	0.181882

K-propargyl species

C	0.369138	1.212199	-0.263504
C	1.216271	2.248281	0.212451
C	0.729543	3.543857	0.302001
C	-0.594189	3.807757	-0.075996
C	-1.357775	2.732777	-0.533619
N	-0.911195	1.476578	-0.647034
H	1.368335	4.341988	0.672573
H	2.231148	2.006484	0.511241
H	-1.017742	4.805336	-0.019467
H	-2.392521	2.891058	-0.837082
C	0.841949	-0.126068	-0.420489
C	1.236565	-1.192196	0.135908
C	1.630069	-2.455155	0.456261
H	2.654850	-2.648577	0.766254
H	0.891955	-3.189743	0.777668
K	0.737858	-2.028111	-2.449706

K-allenyl species

C	0.390138	0.458964	-0.145863
C	1.398426	1.425177	-0.439924
C	2.730081	1.118244	-0.238477
C	3.087284	-0.153766	0.248661
C	2.056930	-1.051724	0.500497
N	0.753159	-0.789717	0.308395
H	3.496326	1.861185	-0.446337
H	1.092601	2.399307	-0.806174
H	4.121104	-0.432629	0.421164

H	2.285121	-2.049064	0.876388
C	-0.987058	0.710065	-0.388378
C	-1.968065	1.384666	0.075458
C	-3.050785	2.050267	0.493429
H	-3.255783	3.059856	0.148060
H	-3.737025	1.630726	1.224816
K	-1.642956	-1.925932	-0.221531

K-alpha TS

C	0.126129	-0.616580	2.113400
C	-1.199777	-0.968117	1.644266
C	-2.331439	-0.297754	2.004697
C	-2.209171	0.836554	2.966366
C	-0.854975	1.185753	3.494572
C	0.226162	0.474239	3.060514
H	-1.255137	-1.799547	0.949737
H	1.205431	0.689557	3.465201
C	-3.719067	-0.663802	1.444220
C	-4.668516	-1.084893	2.595343
C	-4.318516	0.552155	0.692010
C	-3.643436	-1.839077	0.447969
H	-4.292628	-1.983817	3.102132
H	-4.790434	-0.284025	3.325816
H	-5.655268	-1.334930	2.189438
H	-3.666930	0.854359	-0.135811
H	-5.291975	0.278671	0.268891
H	-4.456995	1.404668	1.357562
H	-4.649966	-2.059964	0.078762
H	-3.020520	-1.603178	-0.421873
H	-3.258047	-2.754423	0.911315
C	-0.722783	2.327382	4.520954
C	-1.237245	3.652040	3.900040
C	-1.536984	1.996280	5.798410
C	0.742783	2.549251	4.948845
H	-0.662746	3.907702	3.002199
H	-2.292218	3.585489	3.633096
H	-1.110282	4.467492	4.621353
H	-1.145145	1.094511	6.287151
H	-1.443196	2.816678	6.518790
H	-2.595347	1.857225	5.573659
H	0.781869	3.369466	5.672613
H	1.175456	1.667065	5.433371
H	1.380532	2.830792	4.103342
O	-3.216930	1.451827	3.352410
C	1.193050	-1.375145	1.676770
H	0.929688	-2.266730	1.108199
C	2.624644	-1.198266	1.872784
C	3.253479	0.060995	1.996021
C	3.437652	-2.354601	1.883312

C	4.633586	0.151982	2.160944
H	2.666647	0.968682	1.911144
C	4.814388	-2.259175	2.066358
H	2.971230	-3.330130	1.777288
C	5.417986	-1.005541	2.209244
H	5.101230	1.128934	2.239982
H	5.418062	-3.161326	2.092946
H	6.493130	-0.929517	2.341276
C	0.524882	-4.660972	4.365727
C	1.548897	-5.448961	3.743895
C	1.273663	-6.137164	2.580868
C	-0.014774	-6.062638	2.009405
C	-0.955675	-5.269122	2.659777
N	-0.728284	-4.569870	3.781347
H	2.044711	-6.747355	2.116351
H	2.521840	-5.508737	4.220381
H	-0.274377	-6.605539	1.107258
H	-1.962850	-5.180429	2.251697
C	0.741072	-3.969790	5.552280
C	0.844001	-3.160988	6.505997
C	0.920681	-2.253273	7.506404
H	1.874017	-1.978910	7.946989
H	0.027271	-1.881883	8.003550
K	-1.260603	-2.040935	4.788252

K-gamma TS

C	-0.659900	2.022748	-0.368082
C	0.457859	1.240365	-0.870739
C	1.740214	1.410723	-0.461478
C	2.020384	2.475370	0.551794
C	0.902208	3.375091	0.983836
C	-0.354917	3.114215	0.537358
H	0.213046	0.471817	-1.596846
H	-1.168012	3.767080	0.820330
C	2.900891	0.550086	-0.990335
C	3.971998	1.454160	-1.653214
C	3.539624	-0.253607	0.171682
C	2.423470	-0.461756	-2.052597
H	3.541792	2.019231	-2.488250
H	4.398296	2.157753	-0.937540
H	4.781609	0.831893	-2.051771
H	2.800796	-0.915427	0.639048
H	4.350863	-0.879983	-0.217370
H	3.948371	0.408121	0.935767
H	3.282447	-1.040423	-2.406944
H	1.695610	-1.174779	-1.648336
H	1.979089	0.032376	-2.924106
C	1.214089	4.564010	1.909251
C	1.746025	4.046652	3.271689

C	2.269771	5.488275	1.248940
C	-0.041495	5.415152	2.190088
H	1.000850	3.411766	3.763956
H	2.669196	3.479183	3.150289
H	1.944679	4.898825	3.931802
H	1.905146	5.872867	0.289129
H	2.460062	6.347665	1.901928
H	3.213086	4.967262	1.082425
H	0.235640	6.253733	2.836665
H	-0.468310	5.836613	1.272642
H	-0.821412	4.850810	2.711961
O	3.159682	2.621996	1.009638
C	-1.918202	1.701196	-0.822991
H	-1.940921	0.951636	-1.615304
C	-3.244198	2.198334	-0.457906
C	-3.579426	2.765394	0.794675
C	-4.287501	2.033497	-1.402295
C	-4.885370	3.167120	1.079523
H	-2.843276	2.862456	1.585271
C	-5.585889	2.454374	-1.125136
H	-4.060295	1.587424	-2.367449
C	-5.890081	3.025441	0.117006
H	-5.087550	3.558512	2.073219
H	-6.362670	2.330956	-1.874315
H	-6.905449	3.339844	0.339075
C	-3.547347	2.522392	4.919767
C	-2.824531	2.540667	6.143992
C	-2.452943	3.752147	6.704678
C	-2.794287	4.945747	6.051621
C	-3.494770	4.840866	4.851120
N	-3.857503	3.684621	4.278941
H	-1.910133	3.773315	7.646503
H	-2.586361	1.599862	6.629462
H	-2.526360	5.916670	6.455265
H	-3.779289	5.741848	4.307676
C	-3.914637	1.287585	4.300171
C	-4.679284	0.280204	4.385958
C	-5.396033	-0.862136	4.229866
H	-5.186454	-1.733511	4.846854
H	-6.379161	-0.833383	3.761622
K	-3.528108	-0.202325	1.891607

Allenylated product

C	-0.556135	-0.298006	-0.258909
C	-0.004482	0.102801	0.960833
C	1.374158	0.232219	1.163343
C	2.273400	-0.056587	0.076062
C	1.711309	-0.461147	-1.188546
C	0.323797	-0.565472	-1.312142

H	-0.684991	0.323619	1.774912
H	-0.109782	-0.866160	-2.260234
C	1.925740	0.686630	2.534616
C	2.839572	-0.411739	3.134995
C	2.716327	2.010711	2.379967
C	0.813053	0.953568	3.571488
H	2.260571	-1.318249	3.345168
H	3.633082	-0.677133	2.432876
H	3.286016	-0.070755	4.079310
H	2.050460	2.816748	2.051507
H	3.161704	2.310135	3.338798
H	3.504623	1.902517	1.631658
H	1.268079	1.271253	4.517299
H	0.133268	1.749285	3.248455
H	0.218097	0.057047	3.776584
C	2.630830	-0.766737	-2.393312
C	3.453323	0.491782	-2.770277
C	3.578634	-1.945912	-2.056269
C	1.847355	-1.177817	-3.658951
H	2.789691	1.290057	-3.120923
H	3.997231	0.871902	-1.902250
H	4.162731	0.264298	-3.578133
H	3.003688	-2.866188	-1.904296
H	4.285873	-2.122756	-2.878532
H	4.131314	-1.745735	-1.135251
H	2.553863	-1.379337	-4.473163
H	1.258408	-2.087330	-3.500286
H	1.170078	-0.386630	-3.997452
O	3.574551	0.052514	0.229438
C	-2.057148	-0.492086	-0.469629
C	-2.574143	-1.896376	-0.142855
C	-3.765184	-2.339463	-0.741484
C	-1.906369	-2.769020	0.724477
C	-4.278986	-3.609650	-0.476774
H	-4.293556	-1.677048	-1.423833
C	-2.418598	-4.042616	0.995650
H	-0.973517	-2.453752	1.180247
C	-3.606256	-4.469165	0.398440
H	-5.200018	-3.930730	-0.956506
H	-1.882414	-4.703068	1.672353
H	-4.001028	-5.460119	0.605593
H	-2.242003	-0.329910	-1.536922
C	-2.875590	0.606833	0.228942
C	-3.514396	0.396195	1.362343
C	-4.173142	0.168431	2.469390
H	-3.712590	0.304778	3.446710
H	-5.203522	-0.183585	2.454134
C	-2.917385	1.953640	-0.417646
C	-3.215314	3.115471	0.320151
N	-2.668779	2.002156	-1.738010

C	-3.266458	4.340987	-0.333893
H	-3.396770	3.043930	1.387077
C	-2.717362	3.188597	-2.355396
C	-3.012352	4.387966	-1.707756
H	-3.493151	5.248106	0.219694
H	-2.508995	3.175297	-3.423797
H	-3.035999	5.322474	-2.259461
K	5.904495	0.203558	0.384110

Na-propargyl species

C	0.024423	-0.058007	-0.000310
C	0.463451	-1.404754	-0.000641
C	1.817816	-1.699316	-0.000326
C	2.748856	-0.650084	0.000348
C	2.256412	0.649758	0.000665
N	0.946870	0.951244	0.000306
H	2.154169	-2.733212	-0.000588
H	-0.284066	-2.191807	-0.001077
H	3.818001	-0.834787	0.000568
H	2.940136	1.496787	0.001189
C	-1.384871	0.352435	-0.000728
C	-2.373953	-0.490661	0.000038
C	-3.432049	-1.290274	0.000742
H	-3.887189	-1.631480	-0.926652
H	-3.887213	-1.629459	0.928880
Na	-0.745676	2.582787	-0.000290

Na-allenyl species

C	0.024410	-0.057738	-0.000419
C	0.463104	-1.404651	-0.000130
C	1.817393	-1.699531	0.000279
C	2.748659	-0.650467	0.000316
C	2.256495	0.649473	-0.000152
N	0.947000	0.951243	-0.000547
H	2.153509	-2.733508	0.000578
H	-0.284620	-2.191504	-0.000134
H	3.817784	-0.835310	0.000662
H	2.940423	1.496341	-0.000346
C	-1.384923	0.352643	-0.000389
C	-2.373942	-0.490455	-0.000030
C	-3.431741	-1.290511	0.000166
H	-3.886759	-1.630901	-0.927584
H	-3.886477	-1.630835	0.928078
Na	-0.745417	2.583131	0.000429

Na-alpha TS

C	1.619670	6.645911	0.357205
C	1.986105	6.312125	1.684395

C	2.711618	7.208258	2.454393
C	3.075982	8.446956	1.907150
C	2.676766	8.720144	0.603307
N	1.964434	7.868326	-0.152606
H	2.999254	6.949709	3.470246
H	1.693718	5.343308	2.075799
H	3.641582	9.177980	2.475076
H	2.928941	9.671848	0.139043
C	0.830168	5.779531	-0.515596
C	0.720075	4.492847	-0.398022
C	0.558854	3.175132	-0.351472
H	1.166631	2.502872	-0.952933
H	-0.222068	2.724140	0.257095
Na	0.612071	7.522499	-2.044254
C	4.256600	0.168683	0.543460
C	3.086756	-0.620933	0.882697
C	3.071959	-1.979036	0.886630
C	4.319703	-2.700425	0.497090
C	5.499746	-1.903127	0.036551
C	5.431871	-0.546414	0.086580
H	2.203379	-0.060661	1.169814
H	6.262270	0.047793	-0.269076
C	1.826426	-2.791540	1.284796
C	1.392257	-3.707864	0.112105
C	2.131386	-3.653058	2.537121
C	0.632830	-1.875918	1.626775
H	1.153714	-3.113053	-0.777397
H	2.174385	-4.423207	-0.144610
H	0.490813	-4.264731	0.394315
H	2.418981	-3.018392	3.383576
H	1.233604	-4.212066	2.827151
H	2.935556	-4.363869	2.343976
H	-0.228711	-2.496531	1.894348
H	0.843532	-1.223130	2.481353
H	0.335642	-1.249803	0.778025
C	6.742946	-2.644592	-0.488063
C	7.355145	-3.516253	0.639060
C	6.360808	-3.540759	-1.694070
C	7.835451	-1.665379	-0.965460
H	7.651810	-2.894699	1.492163
H	6.647913	-4.270355	0.985436
H	8.252828	-4.023433	0.265507
H	5.942116	-2.937931	-2.508501
H	7.256616	-4.044299	-2.076485
H	5.631861	-4.300633	-1.410767
H	8.691823	-2.238336	-1.335956
H	7.488779	-1.025526	-1.784747
H	8.198961	-1.023370	-0.155075
O	4.372774	-3.938340	0.532945
C	4.163085	1.535969	0.637704

H	3.168951	1.930917	0.846736
C	5.186974	2.566454	0.473782
C	6.545384	2.388562	0.814447
C	4.780910	3.835441	0.004186
C	7.464294	3.423581	0.646600
H	6.872238	1.452943	1.253968
C	5.704048	4.864033	-0.172025
H	3.732971	4.003687	-0.228528
C	7.051802	4.660885	0.141712
H	8.502914	3.268283	0.924443
H	5.368622	5.828030	-0.543034
H	7.770709	5.464944	0.013429

Na-gamma TS

C	0.877385	3.265226	0.228503
C	2.168842	2.609965	0.218753
C	3.110212	2.805968	-0.750955
C	2.791084	3.733478	-1.876122
C	1.440085	4.368997	-1.913487
C	0.571552	4.139027	-0.882485
H	2.373499	1.942688	1.049636
H	-0.416830	4.578654	-0.905798
C	4.490835	2.125018	-0.704799
C	4.701571	1.255396	-1.970874
C	5.602231	3.203072	-0.619874
C	4.635847	1.204081	0.524400
H	3.945478	0.462751	-2.028165
H	4.655078	1.856106	-2.879804
H	5.683613	0.770837	-1.924559
H	5.479496	3.816826	0.279989
H	6.582006	2.715007	-0.560960
H	5.591677	3.855738	-1.493355
H	5.628761	0.743446	0.509084
H	4.547356	1.755582	1.467138
H	3.899714	0.392427	0.525701
C	1.072146	5.275368	-3.103615
C	2.037558	6.488459	-3.155025
C	1.161874	4.480431	-4.431477
C	-0.363869	5.826867	-2.986214
H	1.975700	7.072589	-2.229574
H	3.069942	6.168934	-3.298967
H	1.755765	7.146129	-3.985520
H	0.452736	3.642702	-4.433573
H	0.898100	5.133669	-5.271032
H	2.167497	4.093123	-4.598214
H	-0.576038	6.456966	-3.855772
H	-1.117484	5.031145	-2.968990
H	-0.497856	6.448066	-2.093701
O	3.620340	3.952412	-2.773859

C	-0.034439	2.921434	1.213794
H	0.241930	2.082156	1.849434
C	-1.306509	3.548013	1.547604
C	-1.527940	4.938583	1.421844
C	-2.336302	2.751655	2.095052
C	-2.739400	5.502656	1.813759
H	-0.728062	5.581152	1.069687
C	-3.549937	3.320121	2.474064
H	-2.180936	1.681056	2.181399
C	-3.757338	4.695511	2.334270
H	-2.885530	6.575447	1.727818
H	-4.336401	2.688056	2.874883
H	-4.701741	5.138299	2.636849
C	-0.325058	-1.250134	-0.281730
C	-0.455360	-2.460170	0.453662
C	0.458173	-3.482108	0.262810
C	1.512418	-3.311574	-0.650882
C	1.590030	-2.097486	-1.323962
N	0.723990	-1.086370	-1.151245
H	0.352785	-4.415004	0.810765
H	-1.285156	-2.566220	1.144014
H	2.247357	-4.089062	-0.827865
H	2.391970	-1.915367	-2.037237
C	-1.208763	-0.139724	-0.103394
C	-2.436157	0.134469	-0.339429
C	-3.700741	0.512838	-0.539141
H	-4.009235	1.024362	-1.446469
H	-4.474673	0.282484	0.187860
Na	0.379169	1.203189	-1.422969

Propargylated product

C	0.646635	0.907792	0.989367
C	0.516885	-0.479232	0.919567
C	1.537141	-1.304153	0.426167
C	2.766674	-0.719096	-0.037154
C	2.913327	0.712387	0.043027
C	1.856082	1.467469	0.549520
H	-0.408146	-0.935685	1.246750
H	1.956069	2.546630	0.607152
C	1.341868	-2.835387	0.371932
C	1.391804	-3.316768	-1.108354
C	2.422593	-3.535985	1.247584
C	-0.020274	-3.308216	0.925758
H	0.443488	-3.091293	-1.605946
H	2.159640	-2.792993	-1.687415
H	1.531571	-4.407908	-1.174143
H	2.157315	-3.452079	2.306208
H	2.486674	-4.612844	1.022906
H	3.404526	-3.061489	1.152203

H	-0.080746	-4.401857	0.858021
H	-0.145826	-3.038086	1.979121
H	-0.867002	-2.897354	0.368727
C	4.220265	1.391686	-0.424056
C	5.419777	0.864459	0.402798
C	4.456932	1.109637	-1.929149
C	4.187767	2.925131	-0.249669
H	5.293257	1.112931	1.463283
H	5.504847	-0.219400	0.308865
H	6.353403	1.327699	0.057128
H	3.643925	1.532808	-2.530792
H	5.396851	1.571127	-2.259834
H	4.503466	0.035476	-2.115874
H	5.138443	3.346680	-0.596114
H	3.388000	3.390981	-0.835747
H	4.060767	3.218441	0.798506
C	-0.434605	1.845889	1.521110
C	-1.035092	2.769017	0.459691
C	-1.369992	4.090271	0.790613
C	-1.295158	2.325153	-0.844861
C	-1.955826	4.945385	-0.147138
H	-1.162684	4.457708	1.793962
C	-1.882388	3.174623	-1.785268
H	-1.023430	1.311943	-1.123514
C	-2.216454	4.488141	-1.441304
H	-2.199631	5.967275	0.131025
H	-2.074024	2.810948	-2.791357
H	-2.666436	5.149959	-2.176155
C	-1.564955	1.145595	2.344363
H	-1.095309	0.508525	3.104622
H	-2.116462	1.926346	2.882787
C	-2.530528	0.354492	1.582054
C	-3.342862	-0.300317	0.961484
C	-4.306947	-1.047646	0.210496
C	-5.461342	-0.409965	-0.286679
N	-4.062104	-2.361017	0.002857
C	-6.384465	-1.156121	-1.012961
H	-5.610602	0.647629	-0.098285
C	-4.962799	-3.058363	-0.696881
C	-6.136023	-2.513550	-1.225909
H	-7.281544	-0.686335	-1.406132
H	-4.733462	-4.112429	-0.842980
H	-6.827358	-3.135908	-1.785268
O	3.738084	-1.465610	-0.520746
H	0.050910	2.502612	2.256440
Na	4.243757	-3.405639	-0.954461

^{t}BuOH

O	0.019290	0.000088	1.455512
C	-0.005496	0.000019	0.011581

C	0.685386	-1.267744	-0.512948
C	-1.491750	0.004734	-0.353427
C	0.693614	1.263183	-0.513274
H	0.201175	-2.160292	-0.104876
H	0.643951	-1.318201	-1.606677
H	1.742467	-1.286669	-0.219371
H	-1.980612	0.892843	0.058522
H	-1.986323	-0.880006	0.058973
H	-1.624395	0.004869	-1.440128
H	1.750851	1.275175	-0.219840
H	0.652388	1.313723	-1.607007
H	0.215334	2.158931	-0.105261
H	0.940325	-0.002225	1.749980

HMDS

Si	0.000000	1.614713	0.078449
Si	0.000000	-1.614713	0.078449
N	0.000000	0.000000	0.767640
C	-0.582635	2.800397	1.431718
C	1.727959	2.134368	-0.495845
C	-1.170534	1.691167	-1.405802
C	-1.727959	-2.134368	-0.495845
C	1.170534	-1.691167	-1.405802
C	0.582635	-2.800397	1.431718
H	0.071587	2.756405	2.311155
H	-0.577633	3.836724	1.074028
H	-1.601781	2.563883	1.758087
H	1.722583	3.149575	-0.911652
H	2.439975	2.116186	0.337524
H	2.109471	1.459365	-1.270442
H	-2.198106	1.447137	-1.114430
H	-1.173398	2.696771	-1.843397
H	-0.873058	0.994286	-2.197974
H	-2.439975	-2.116186	0.337524
H	-2.109471	-1.459365	-1.270442
H	-1.722583	-3.149575	-0.911652
H	0.873058	-0.994286	-2.197974
H	2.198106	-1.447137	-1.114430
H	1.173398	-2.696771	-1.843397
H	1.601781	-2.563883	1.758087
H	-0.071587	-2.756405	2.311155
H	0.577633	-3.836724	1.074028
H	0.000000	0.000000	1.783285

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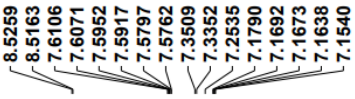
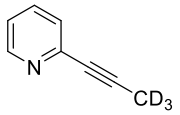
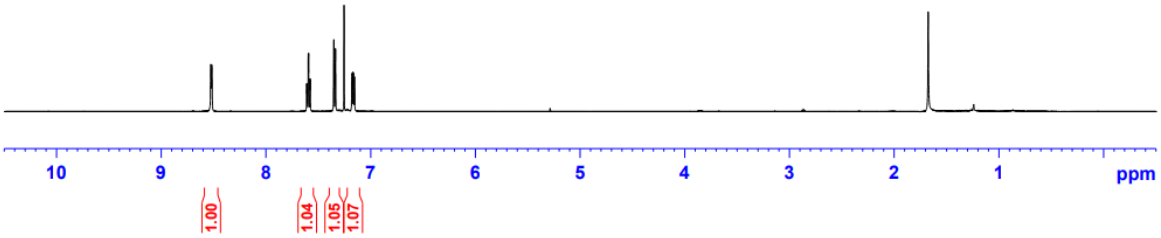
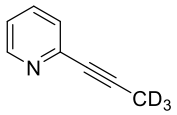




^{1}H NMR of **1a'** (500 MHz, $CDCl_3$)





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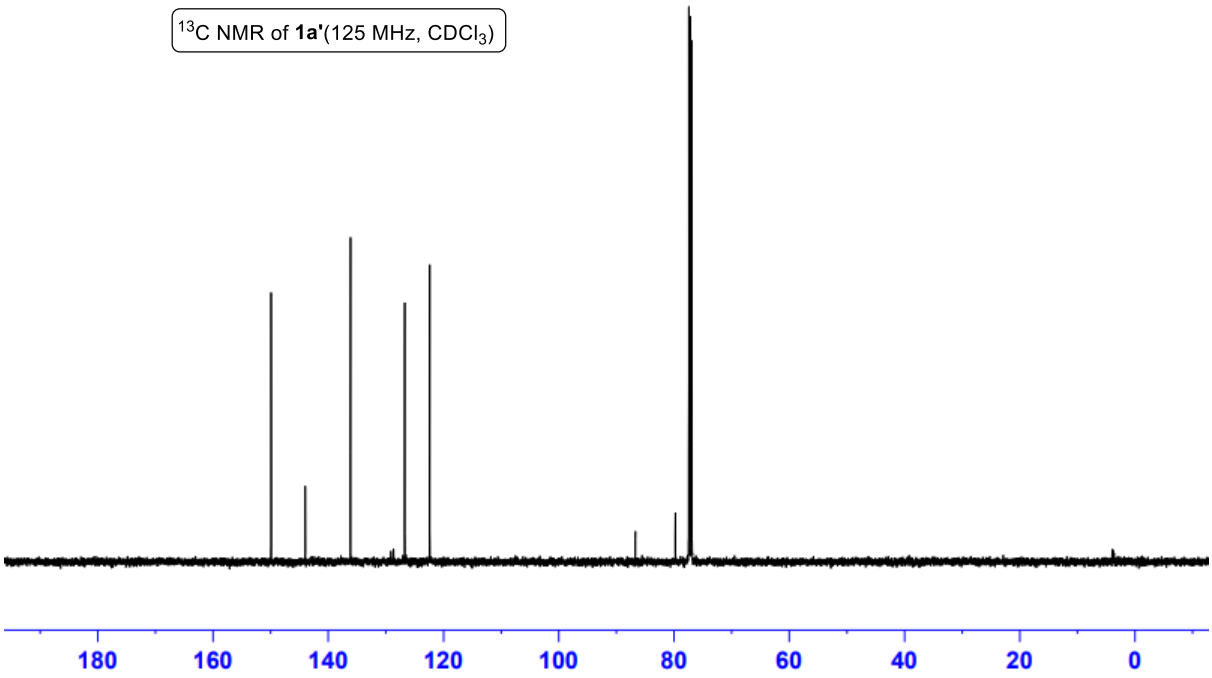
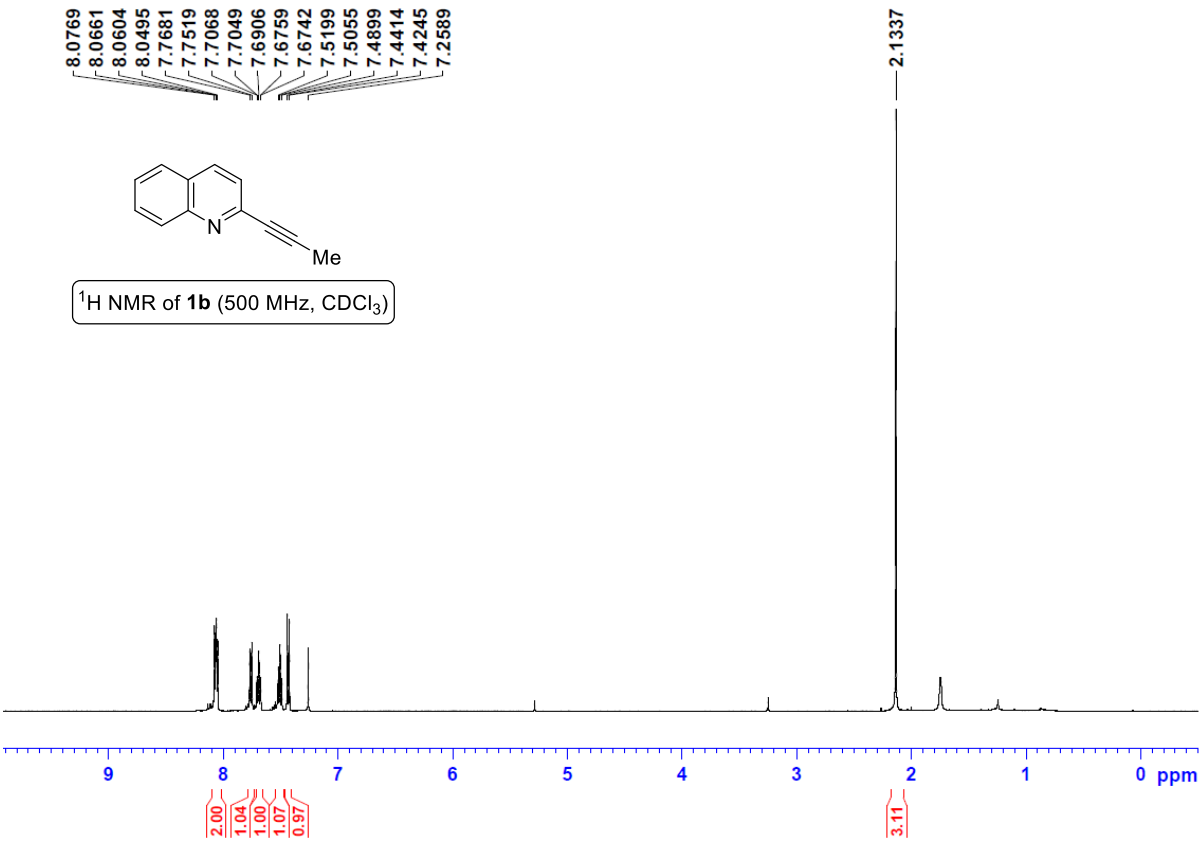
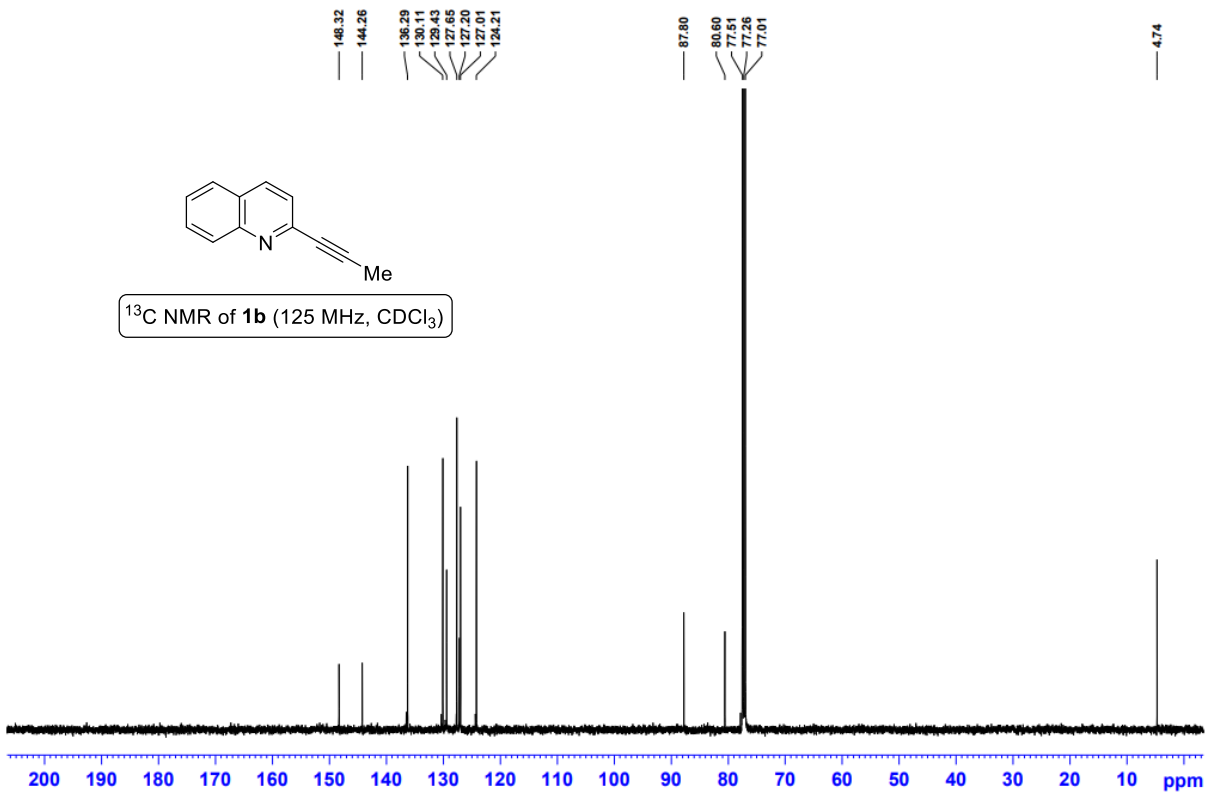




^{1}H NMR of **1b** (500 MHz, $CDCl_3$)



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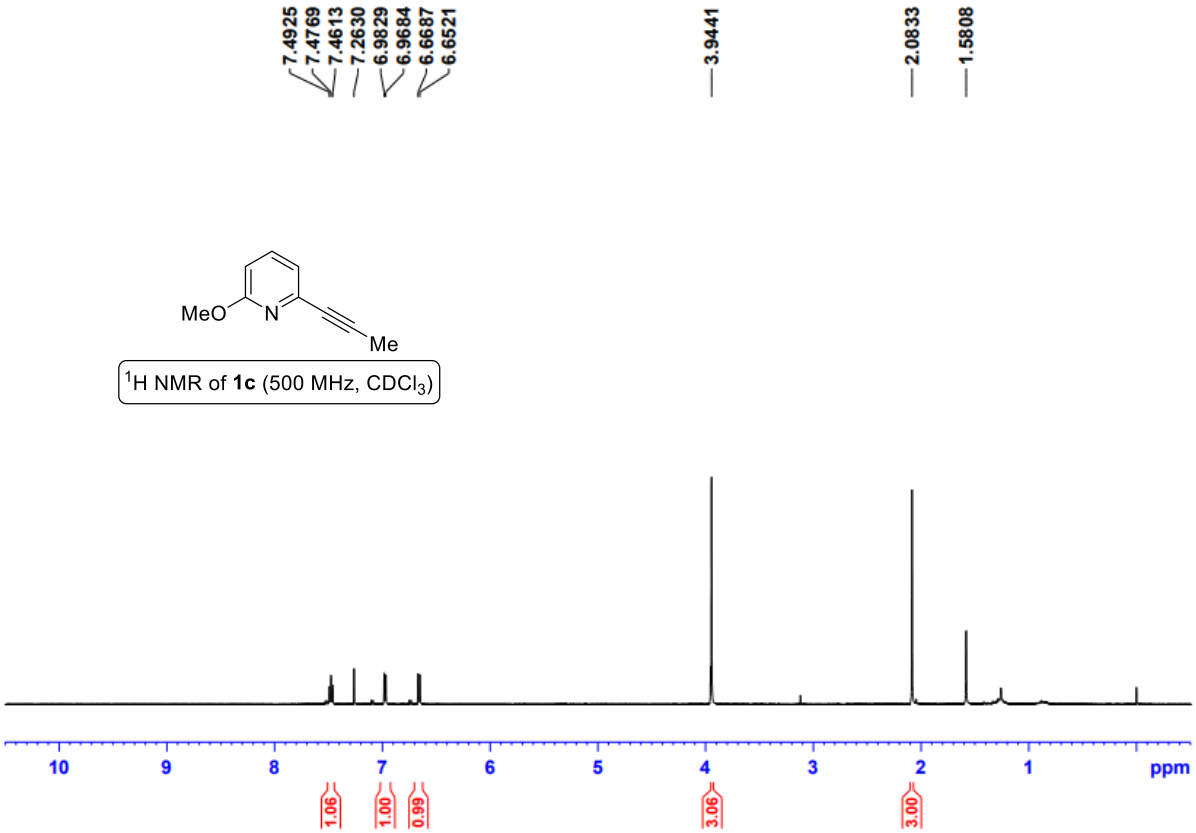

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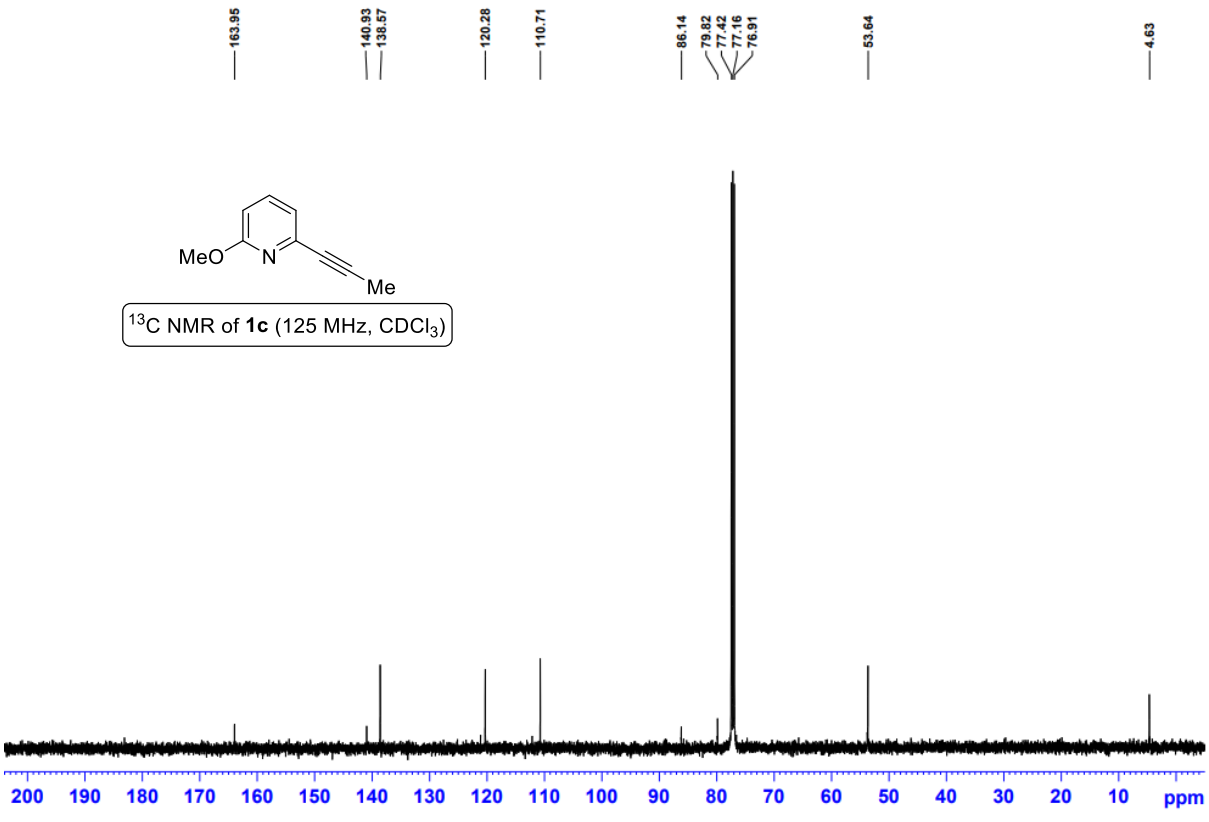

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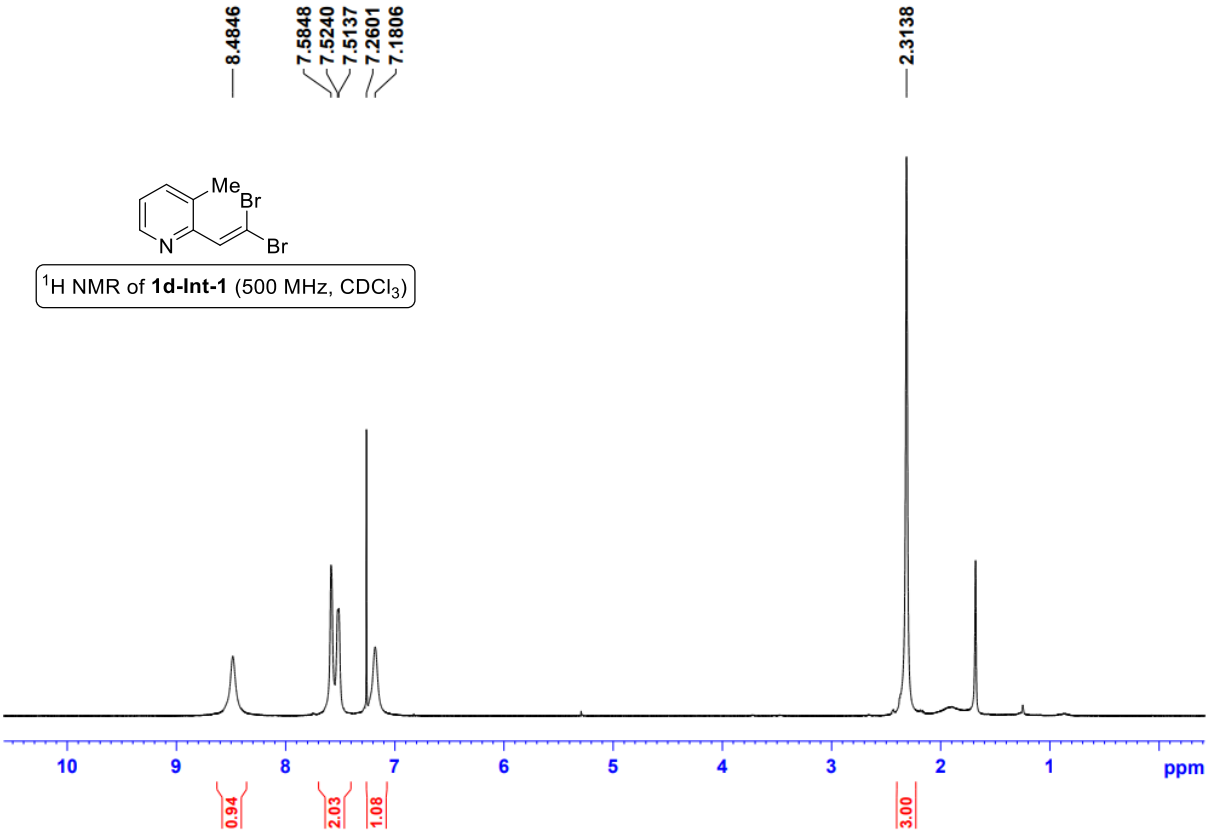

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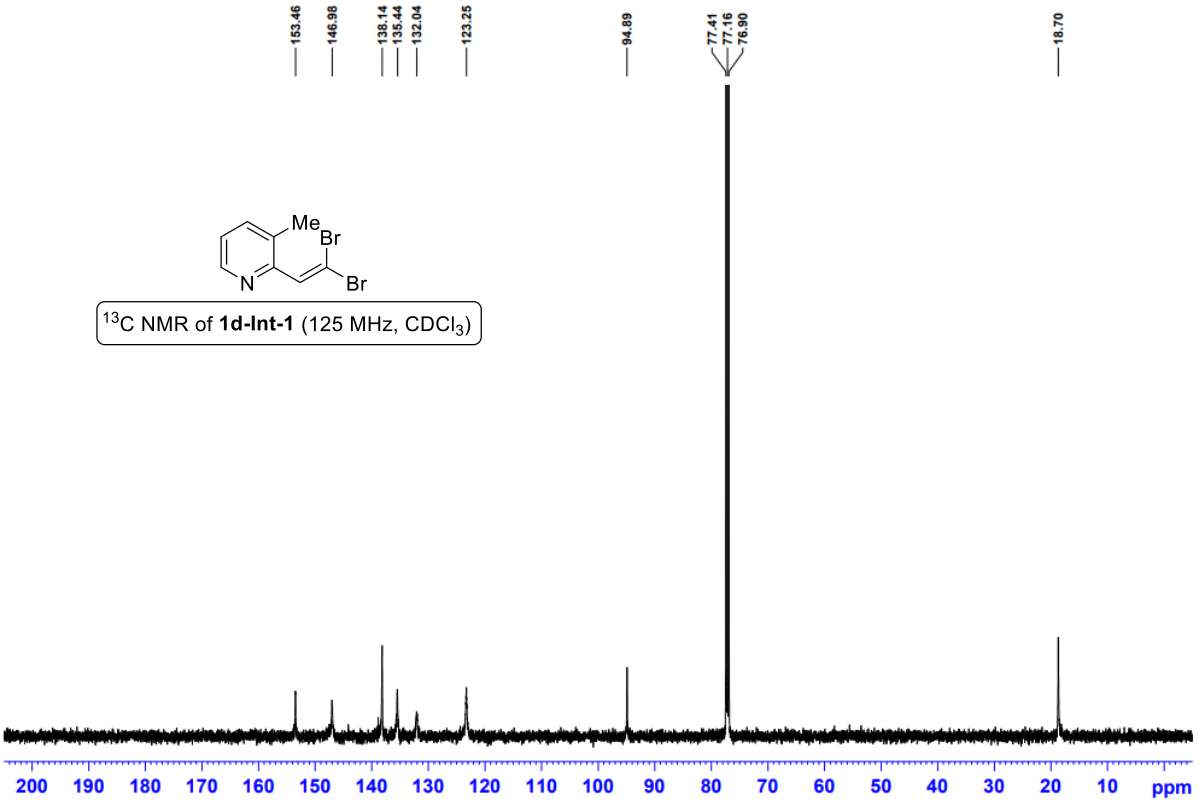

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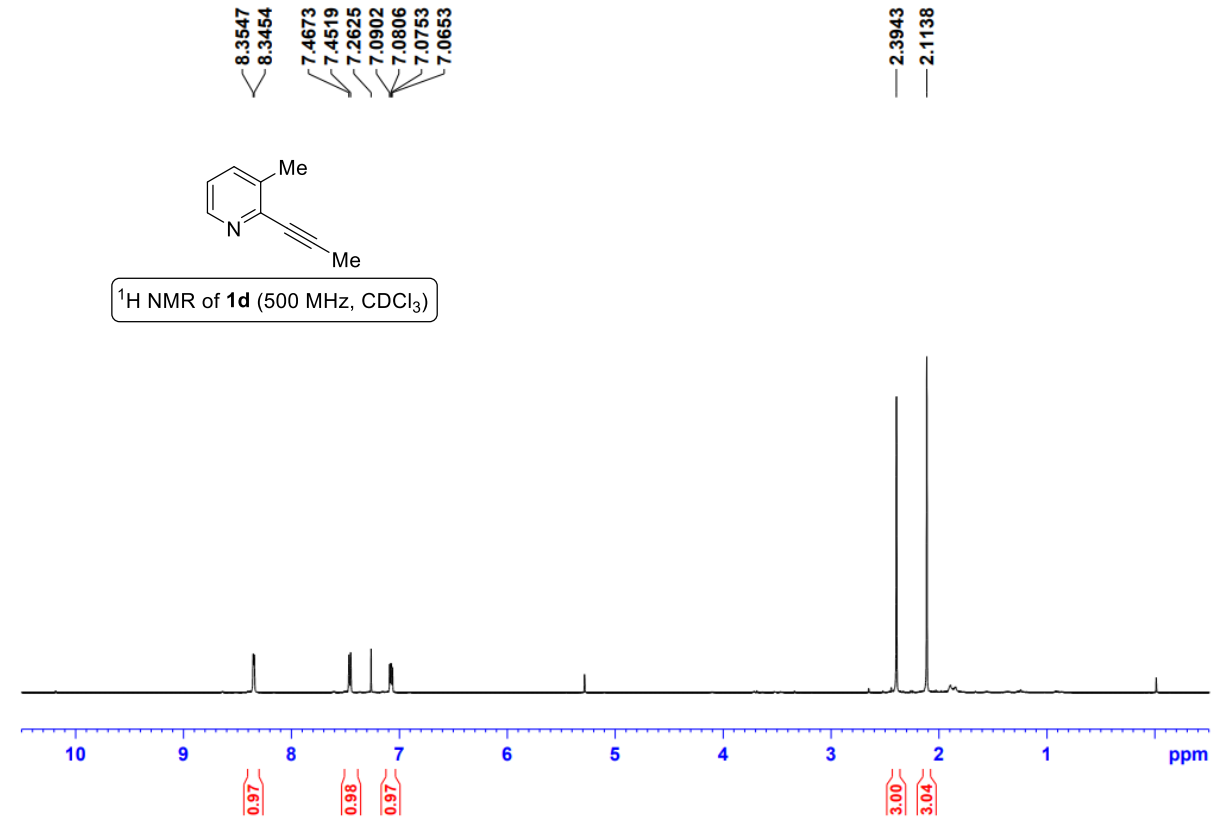

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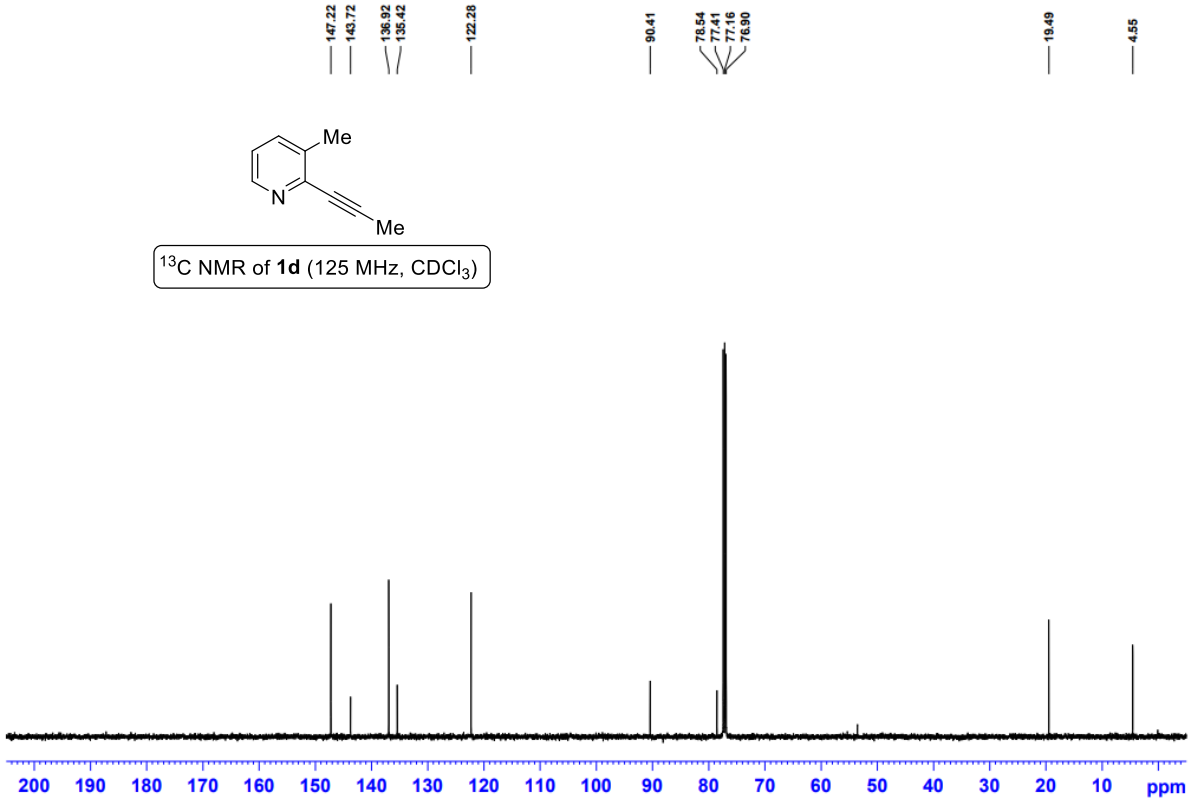

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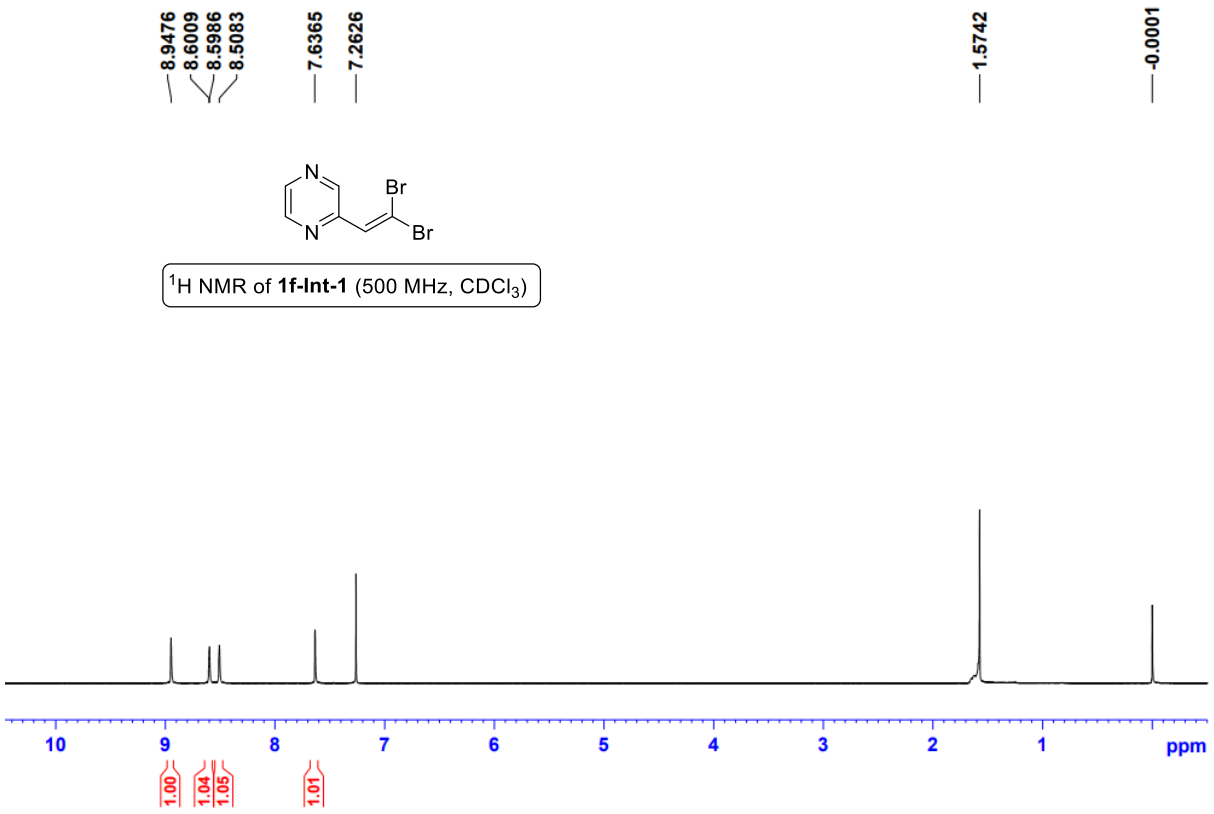

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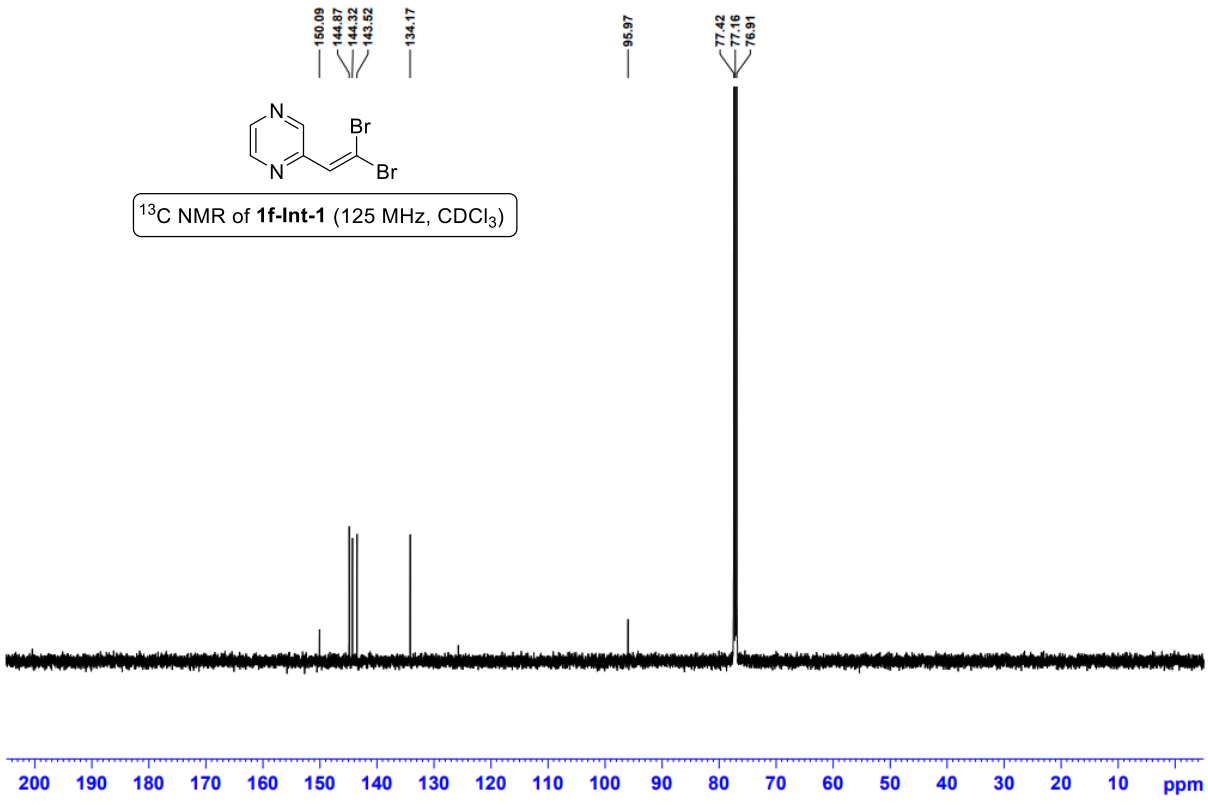

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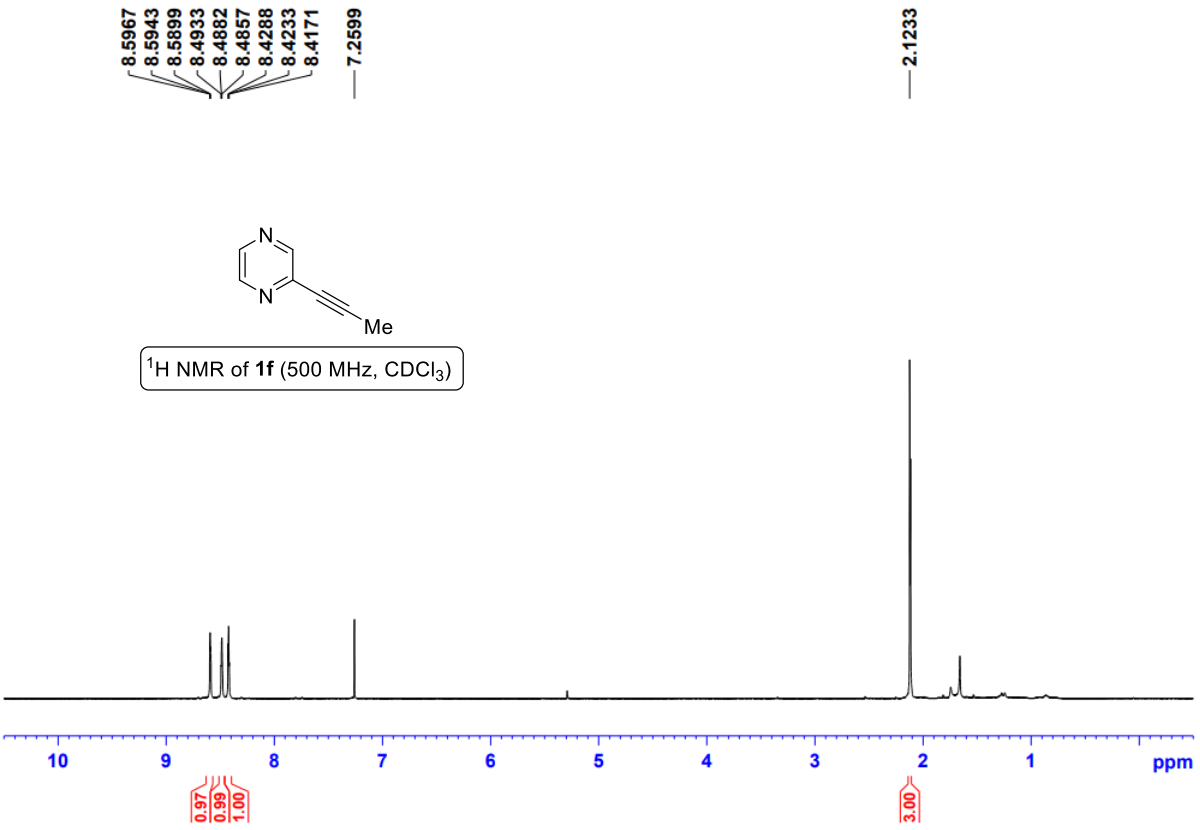

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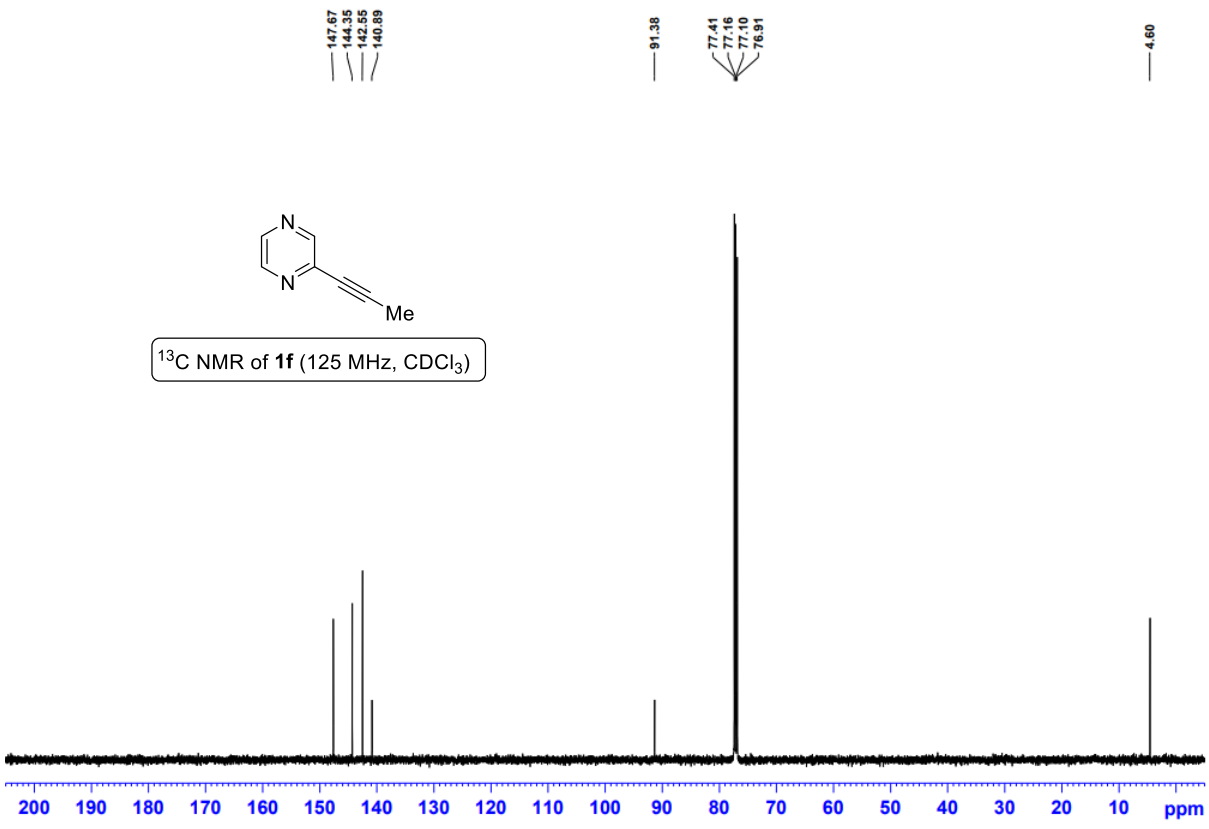

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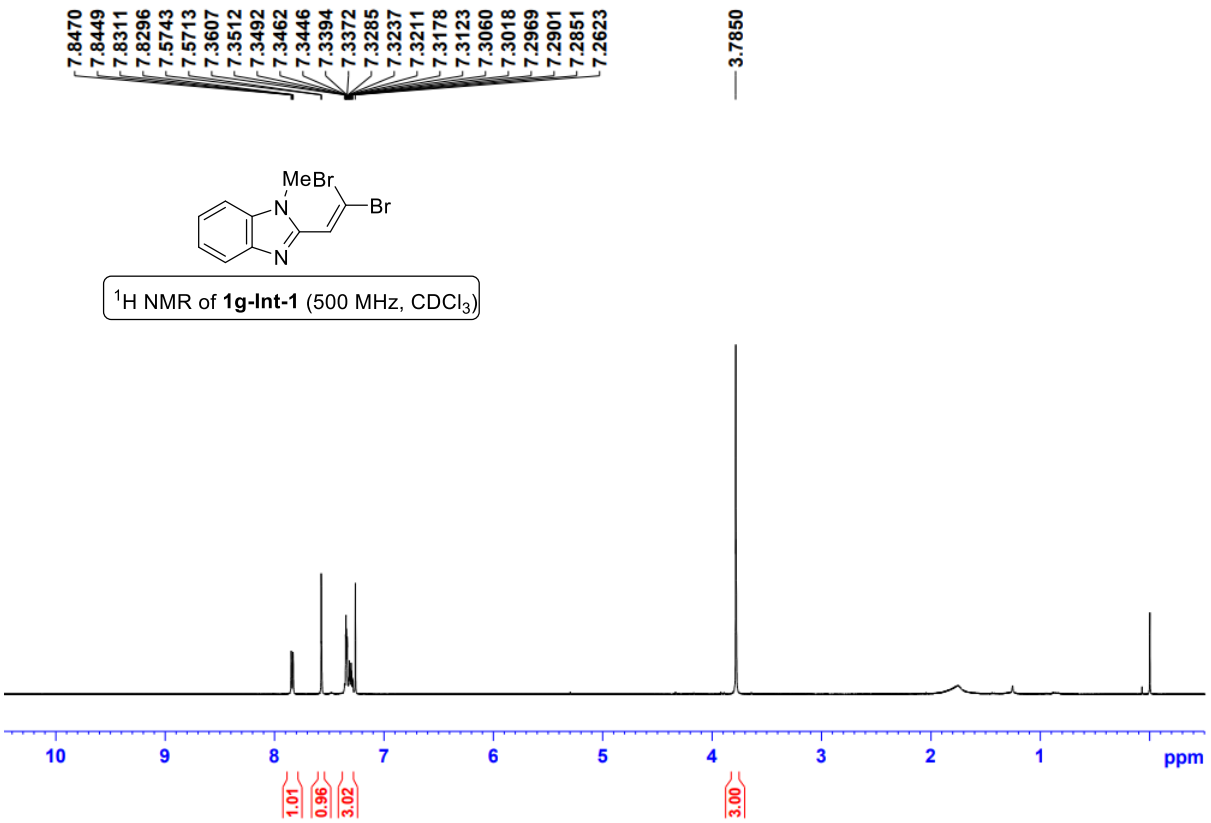

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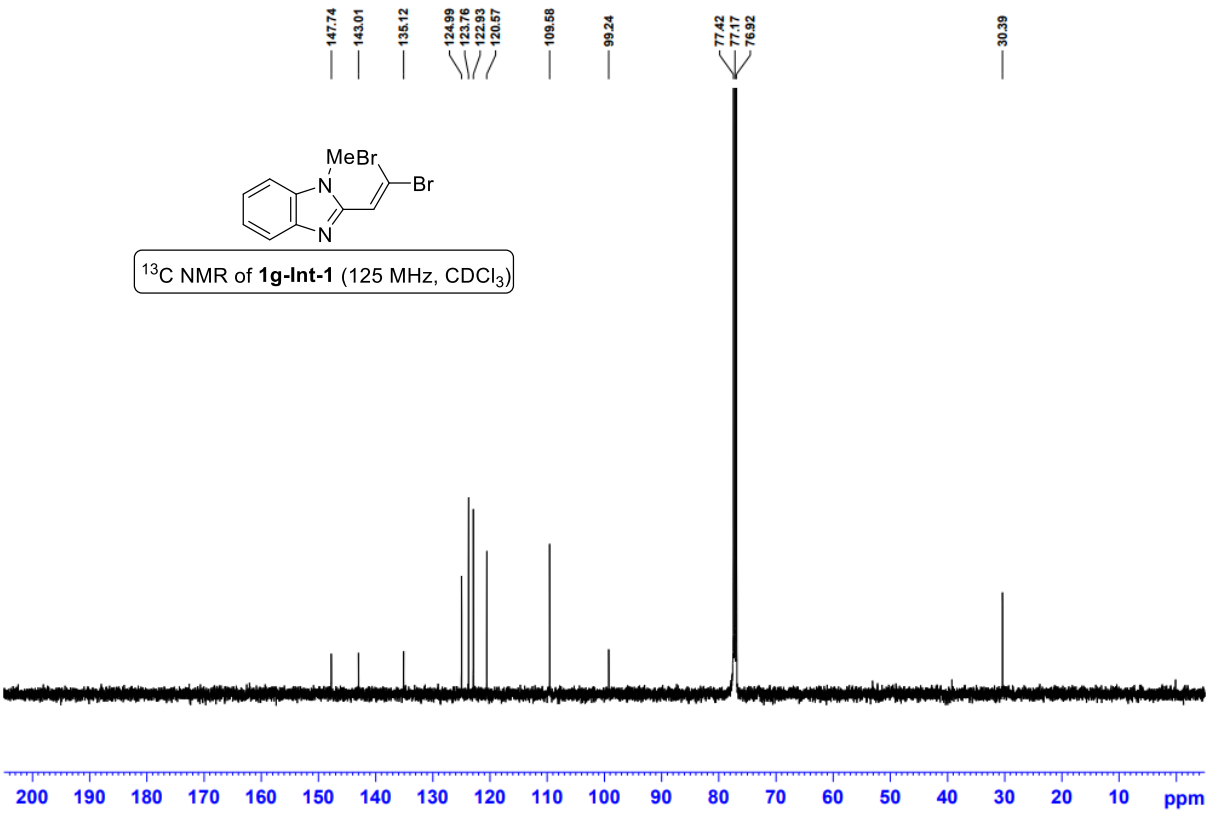

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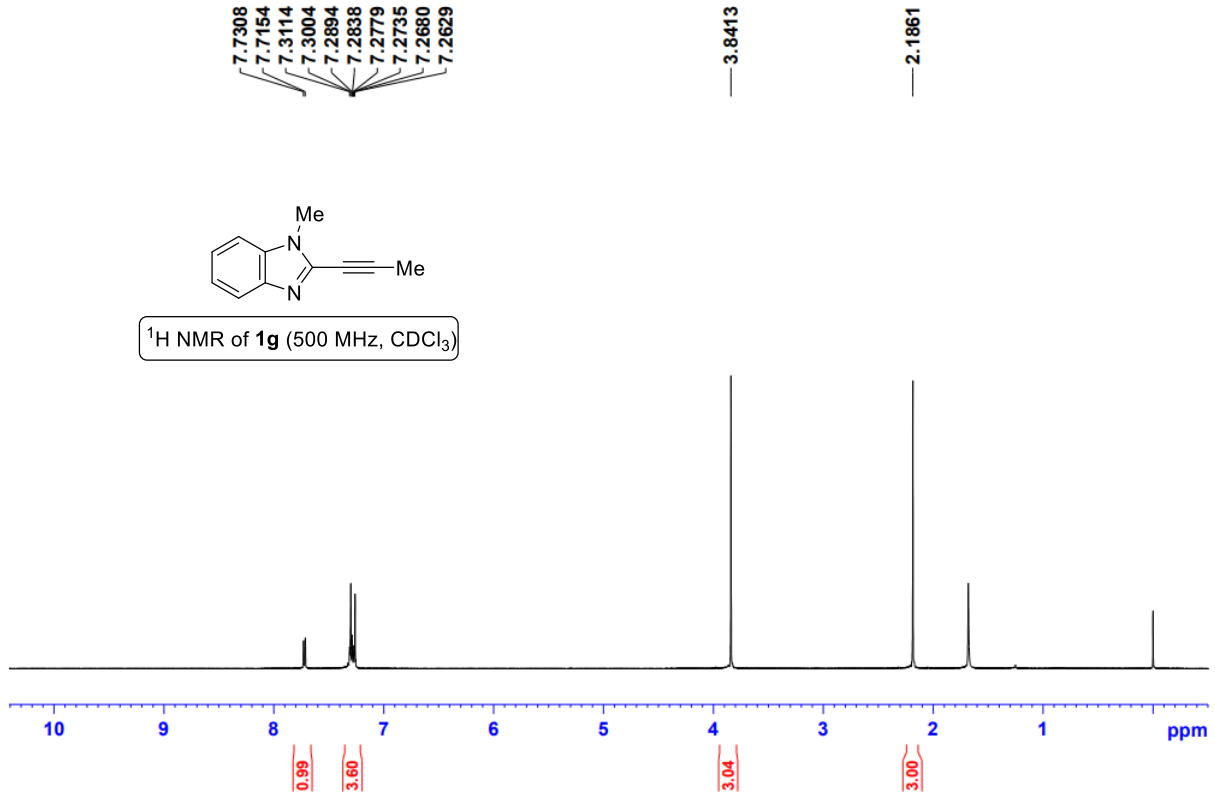

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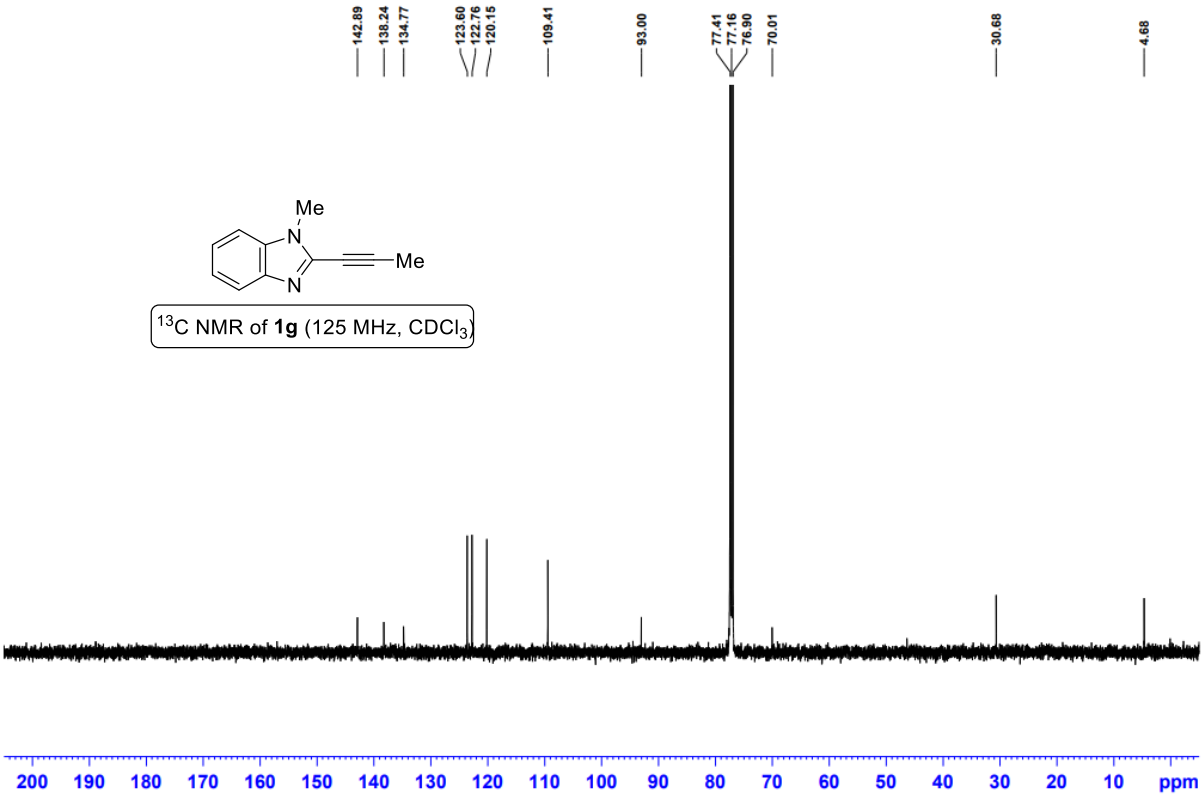

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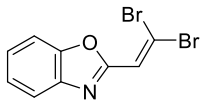

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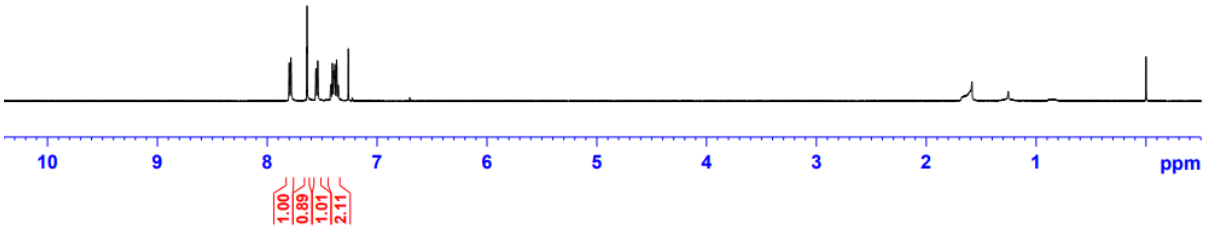

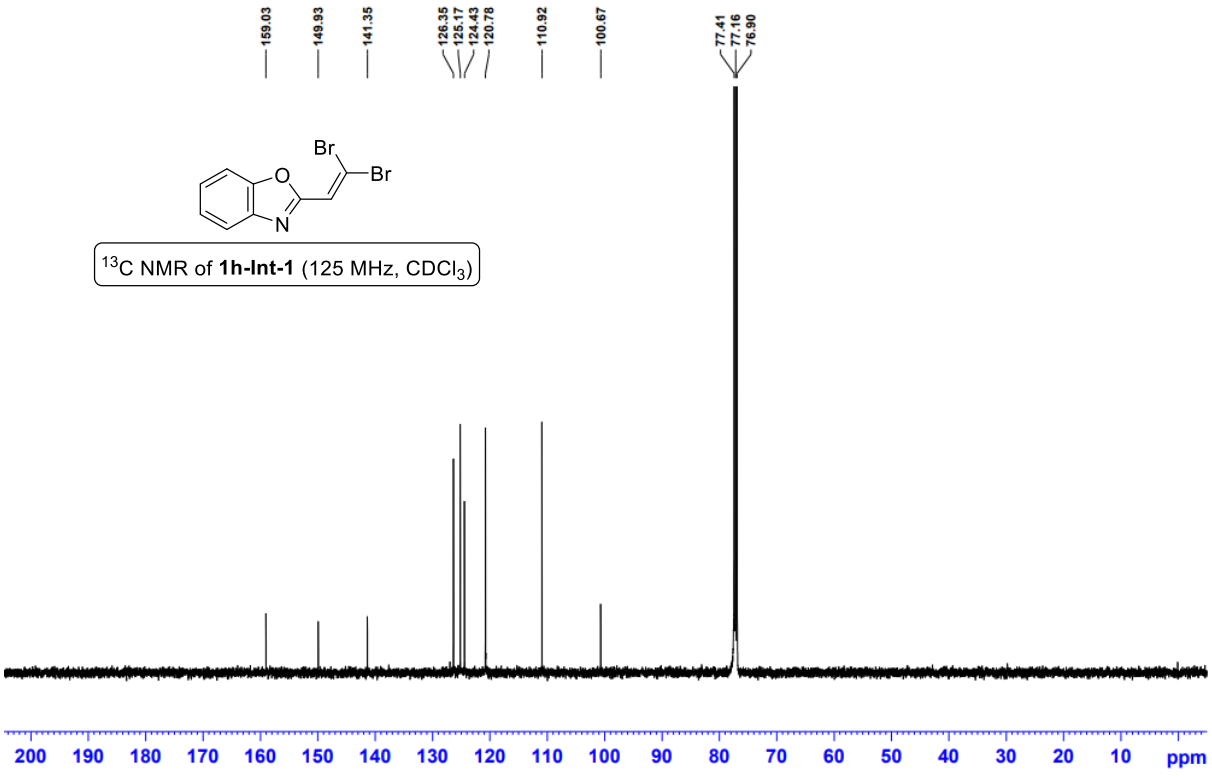

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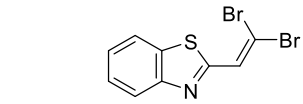
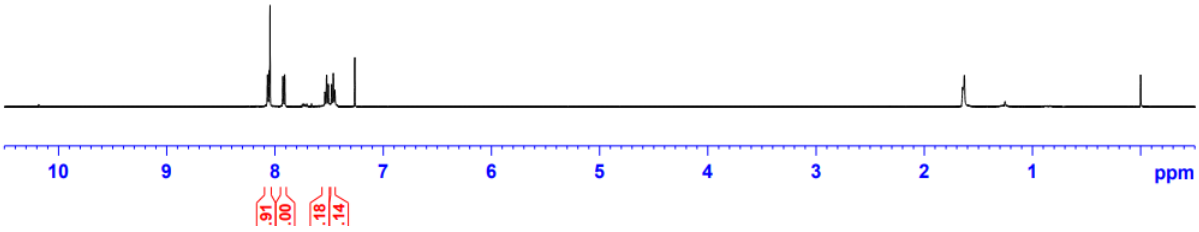
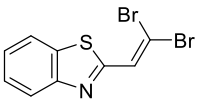
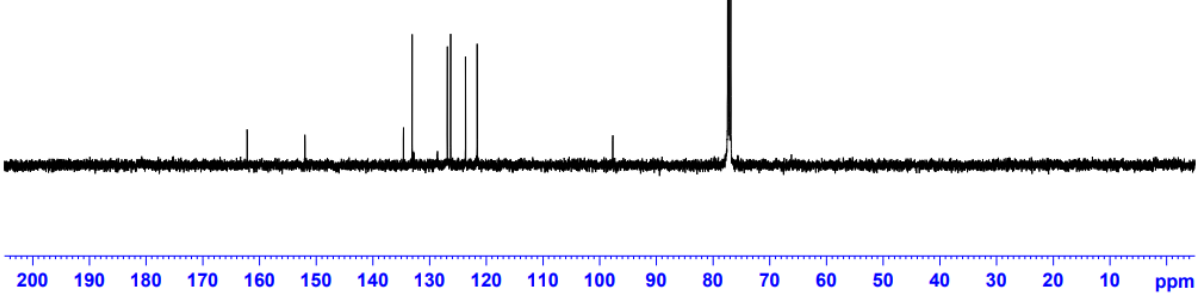


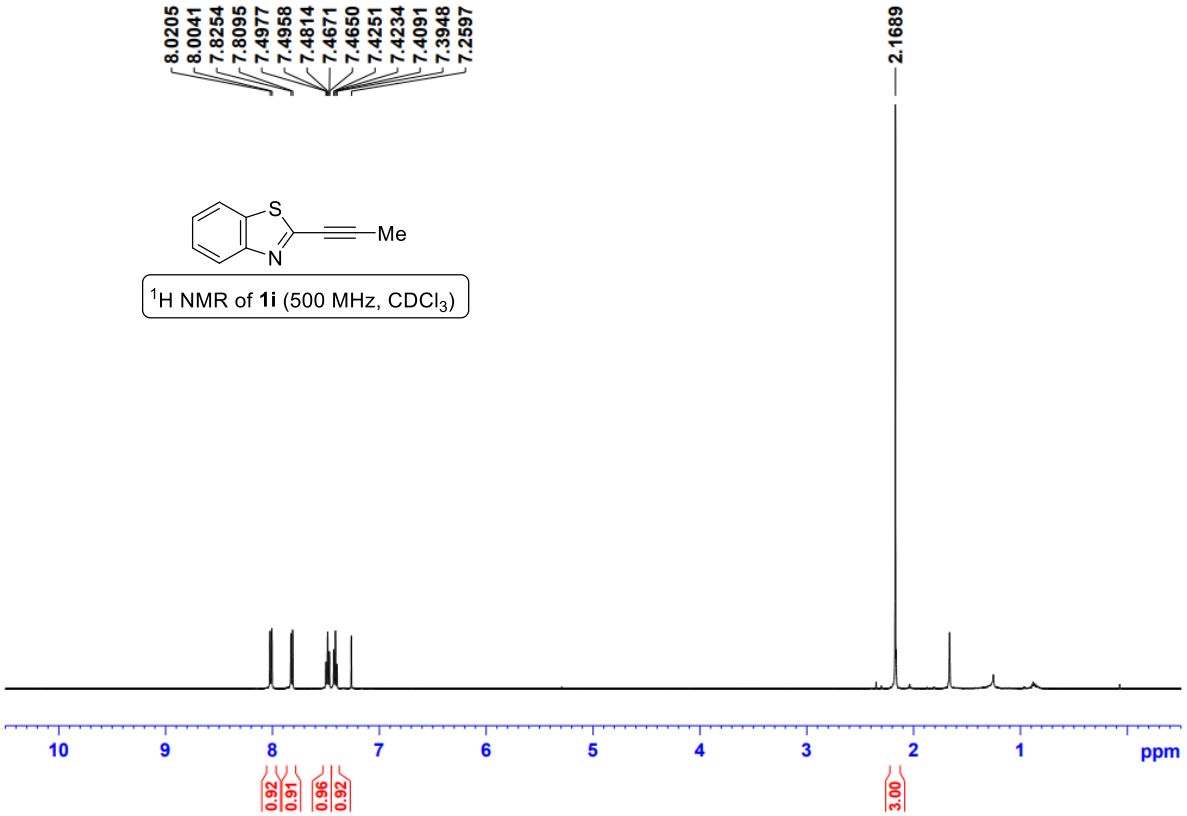
^{1}H NMR of **1i-Int-1** (500 MHz, $CDCl_3$)

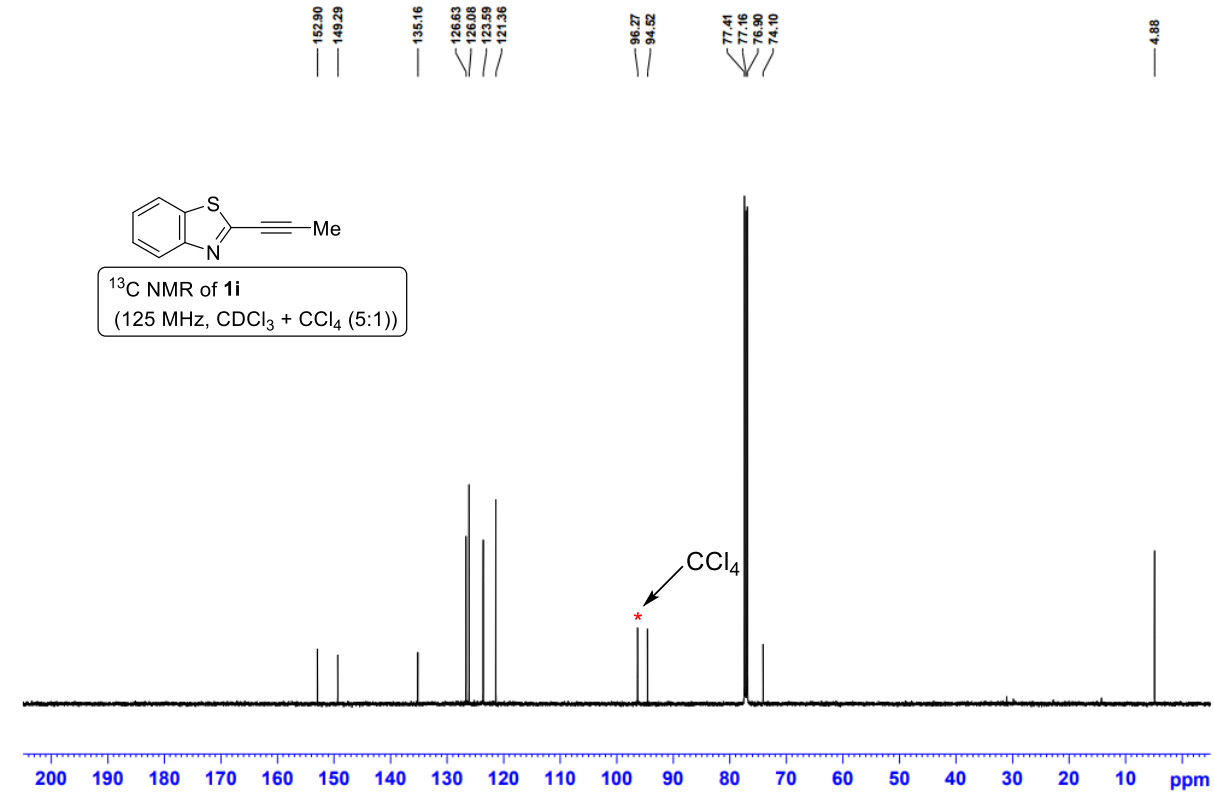


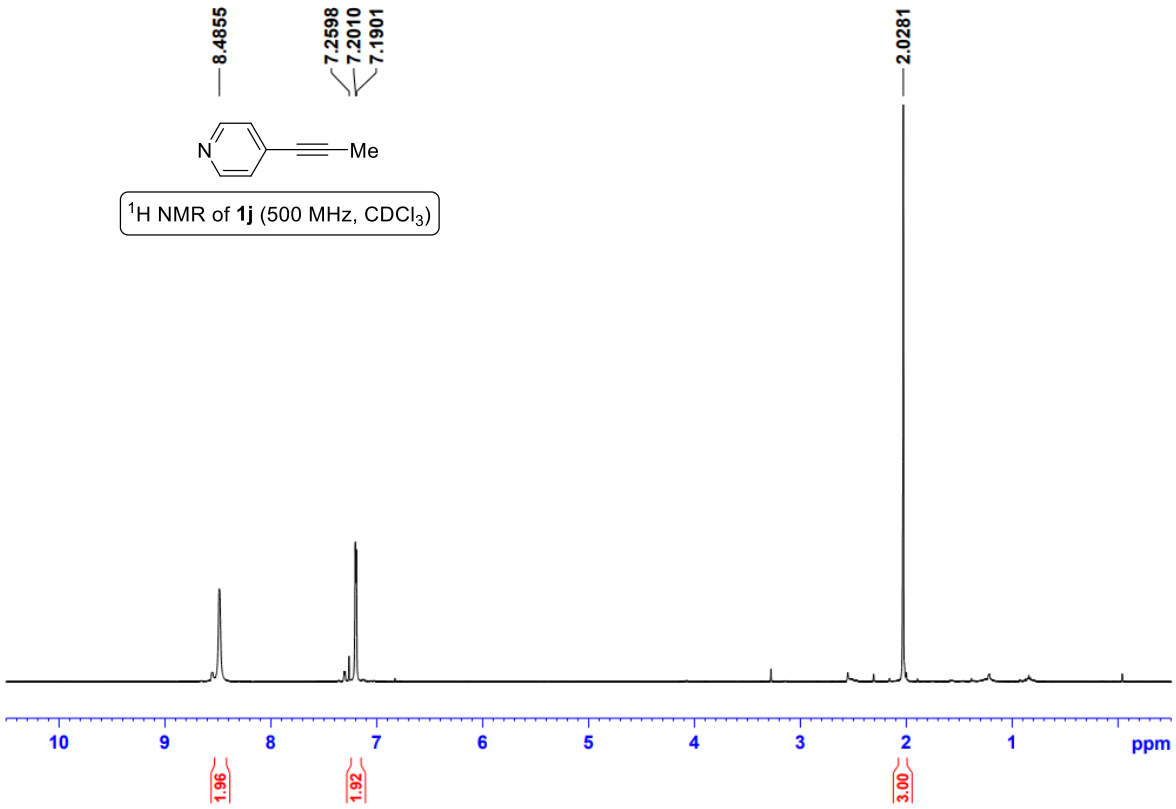


^{13}C NMR of **1i-Int-1** (125 MHz, $CDCl_3$)

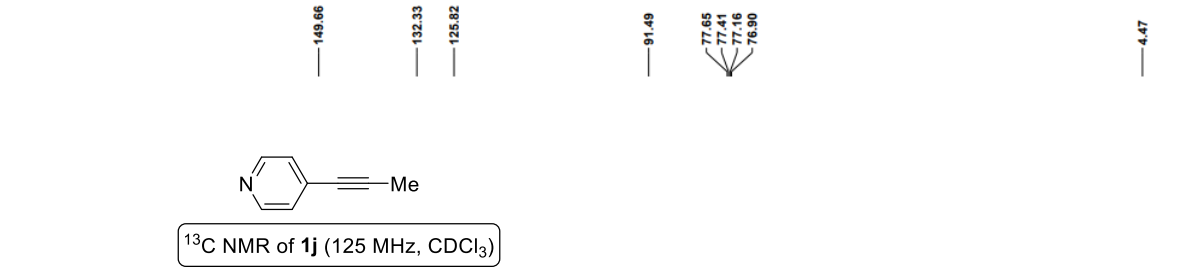



8.0205
8.0041
7.8254
7.8095
7.4977
7.4958
7.4814
7.4671
7.4650
7.4251
7.4234
7.4091
7.3948
7.2597
2.1689
S
N
Me
^{1}H NMR of **1i** (500 MHz, $CDCl_3$)
10
9
8
7
6
5
4
3
2
1
ppm
0.92
0.91
0.96
0.92
3.00

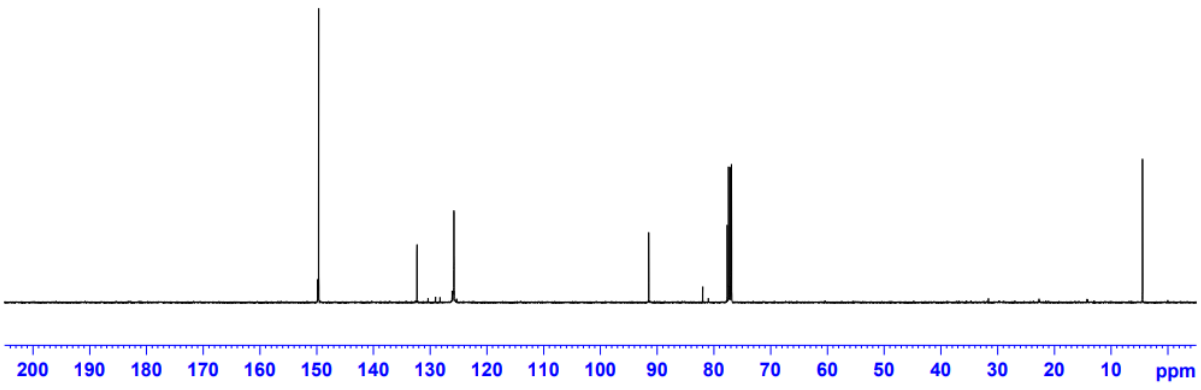

152.90
149.29
135.16
126.63
126.08
123.59
121.36
96.27
94.52
77.41
77.16
76.90
74.10
4.88
S
N
Me
^{13}C NMR of **1i**
(125 MHz, $CDCl_3$ + CCl_4 (5:1))
CCl_4
*
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

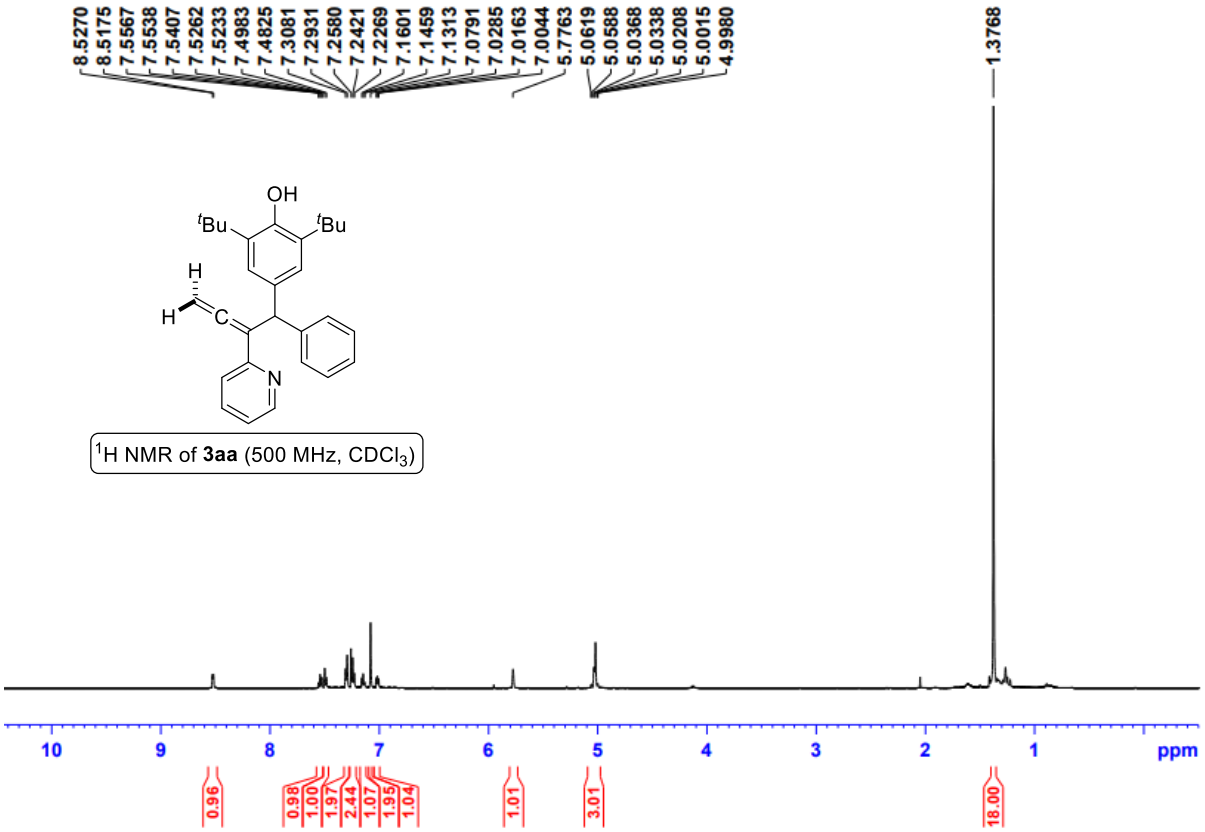


^{1}H NMR of **1j** (500 MHz, $CDCl_3$)

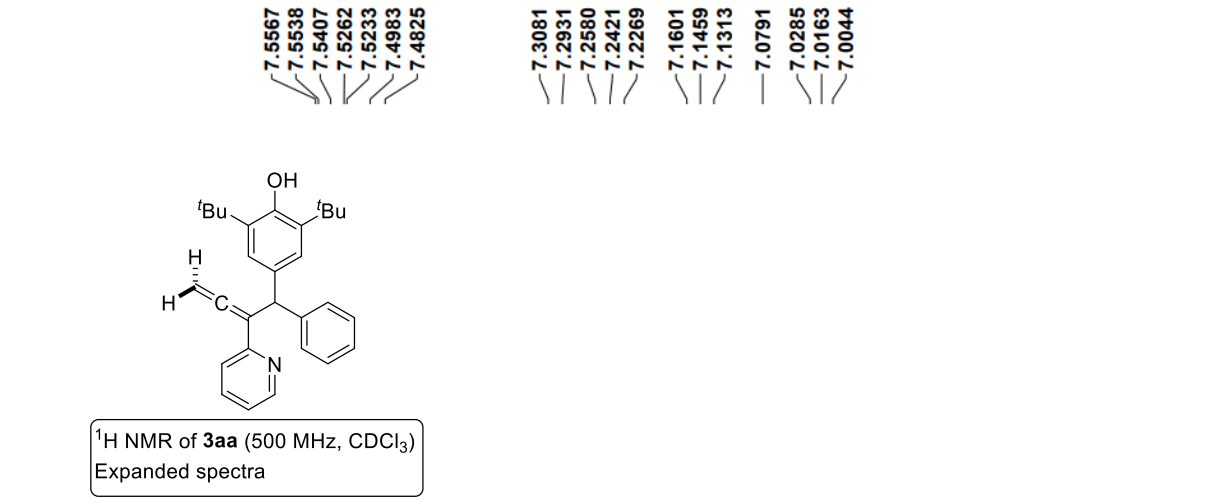


^{13}C NMR of **1j** (125 MHz, $CDCl_3$)

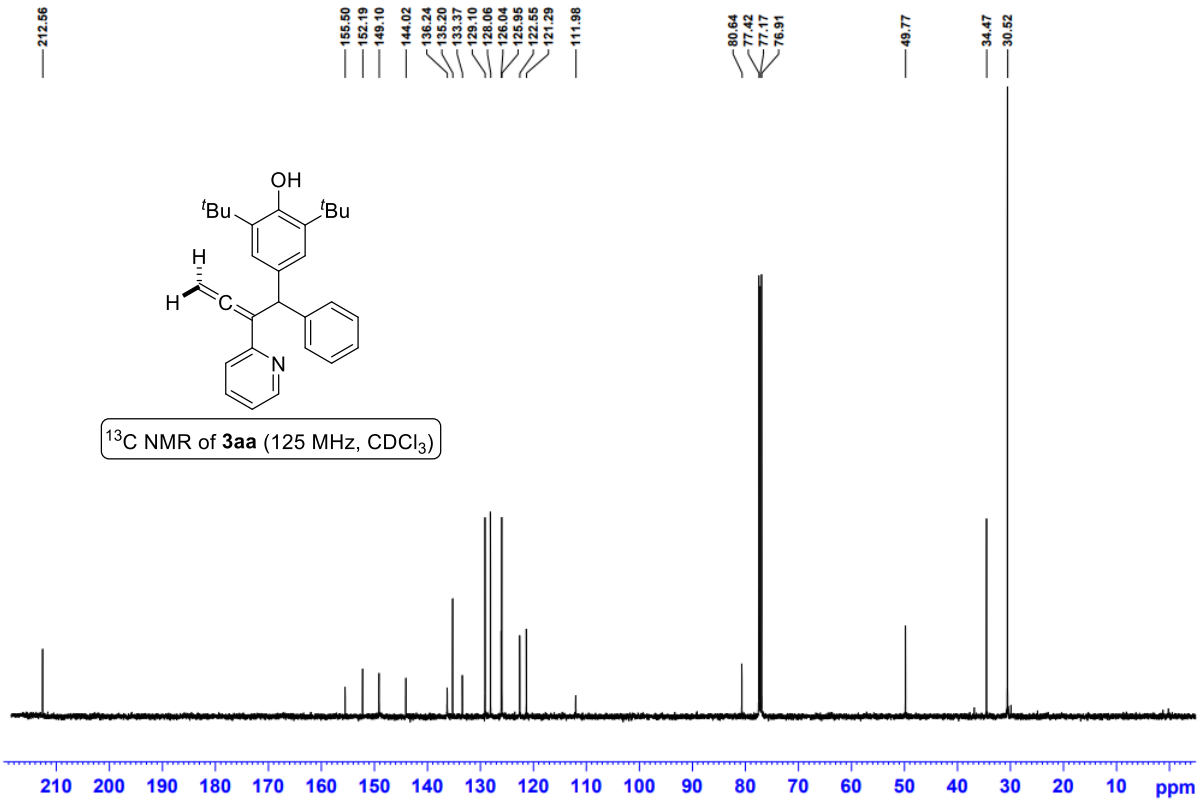




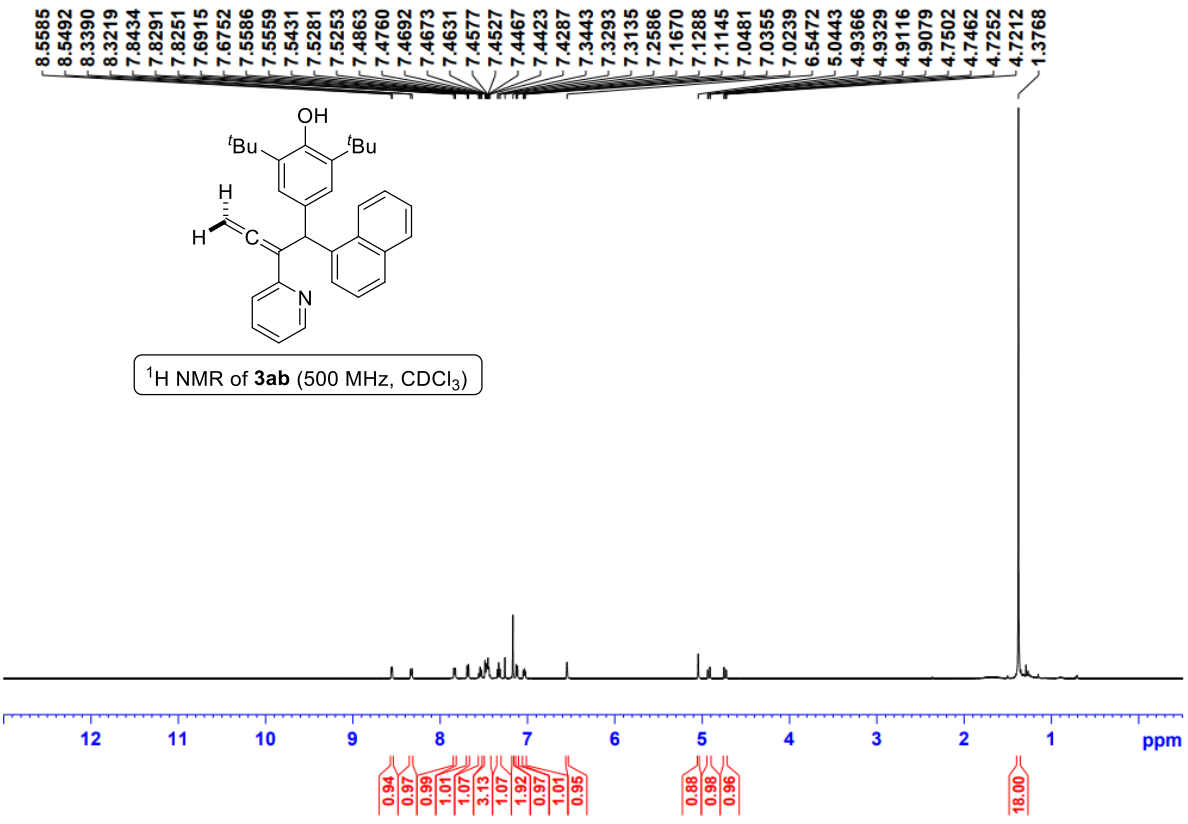
^{1}H NMR of **3aa** (500 MHz, $CDCl_3$)



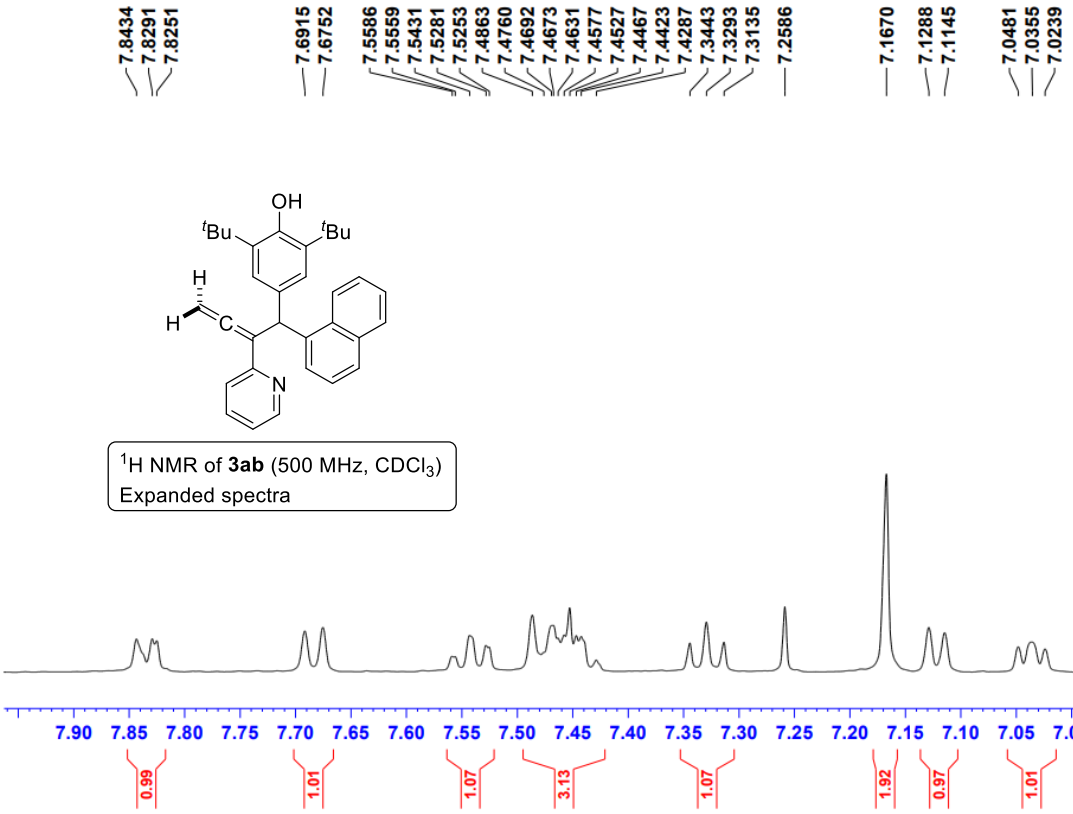
^{1}H NMR of **3aa** (500 MHz, $CDCl_3$)
Expanded spectra



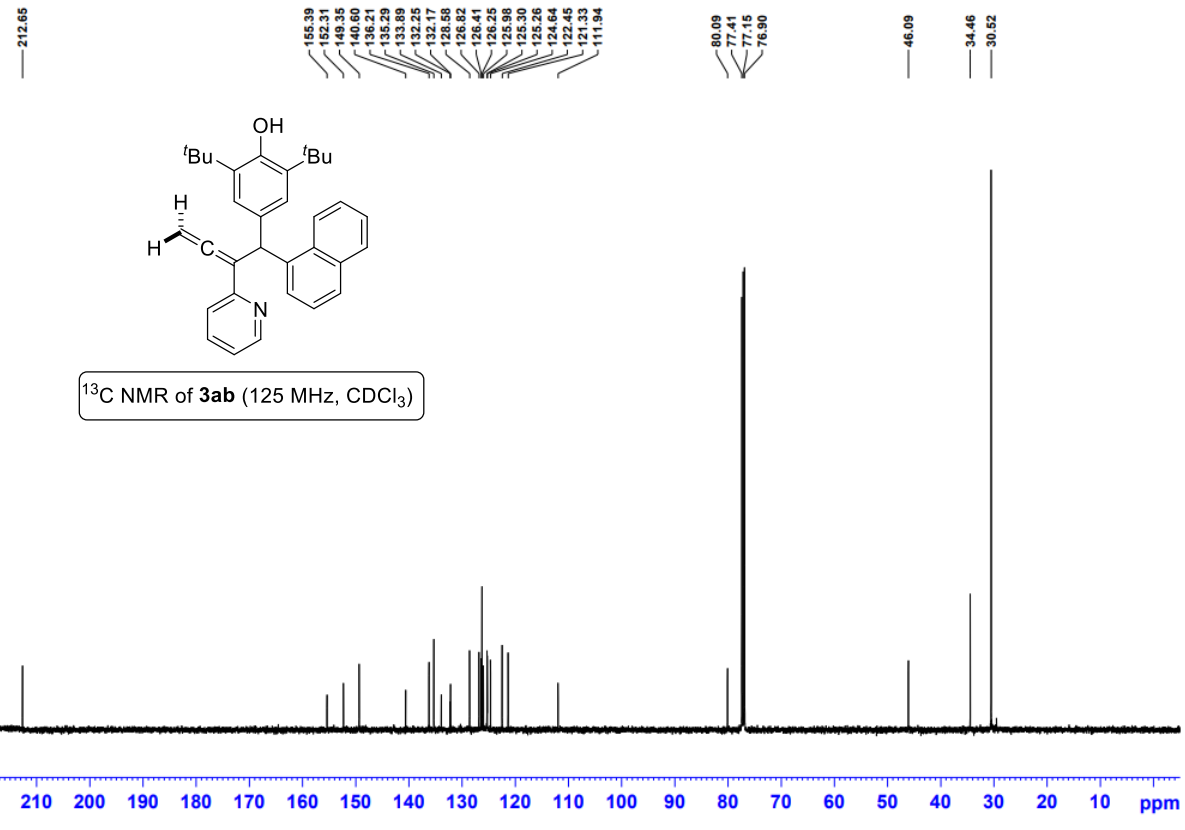
^{13}C NMR of **3aa** (125 MHz, $CDCl_3$)



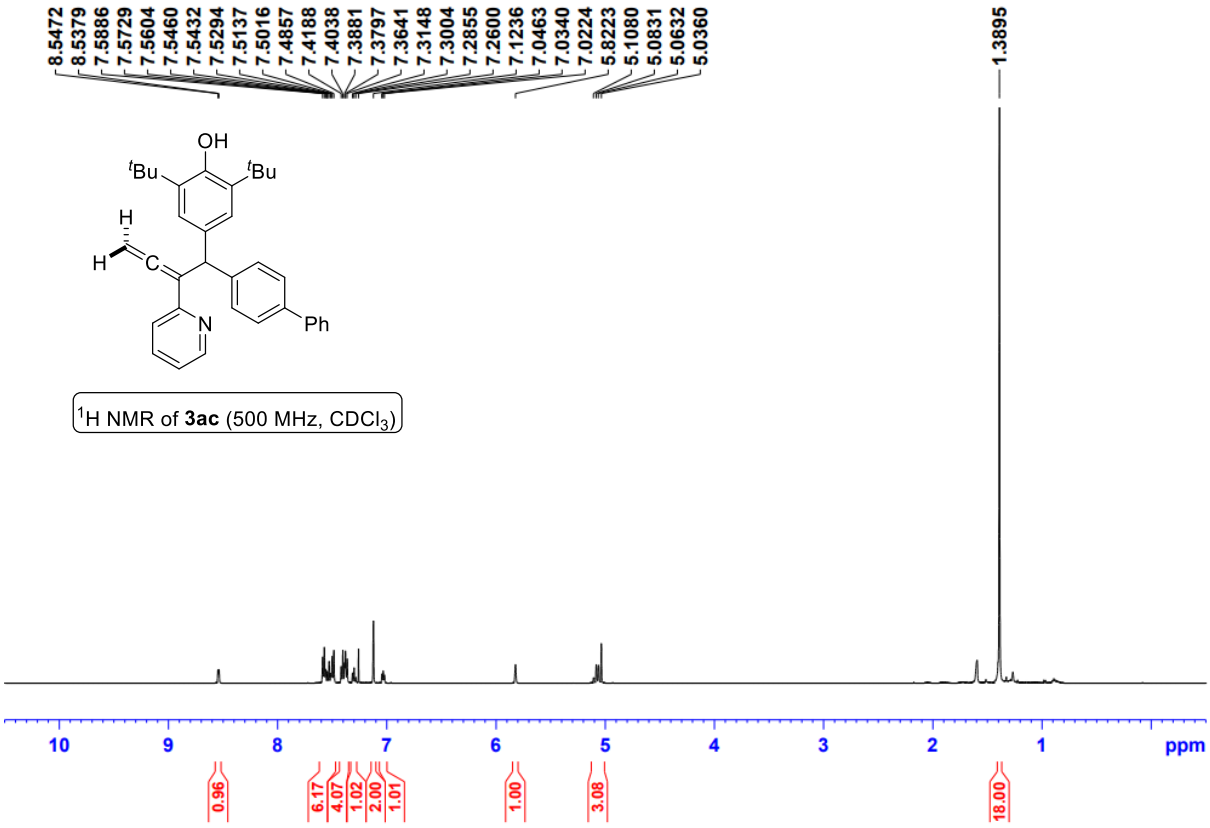
^{1}H NMR of **3ab** (500 MHz, $CDCl_3$)



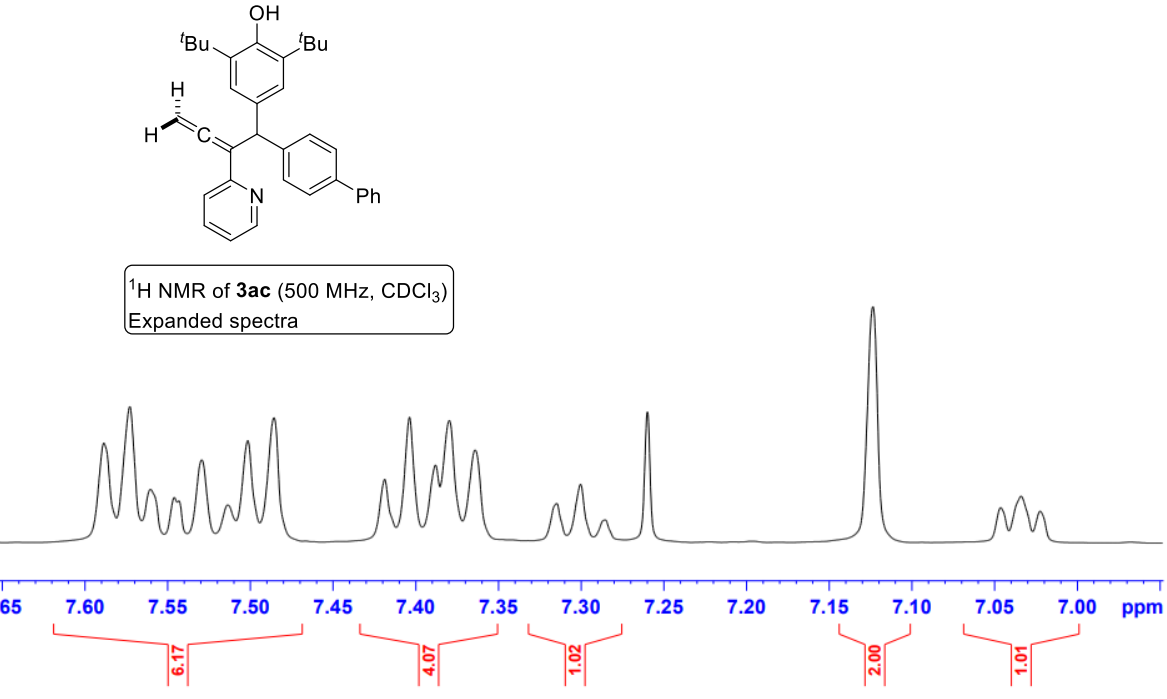
^{1}H NMR of **3ab** (500 MHz, $CDCl_3$)
Expanded spectra



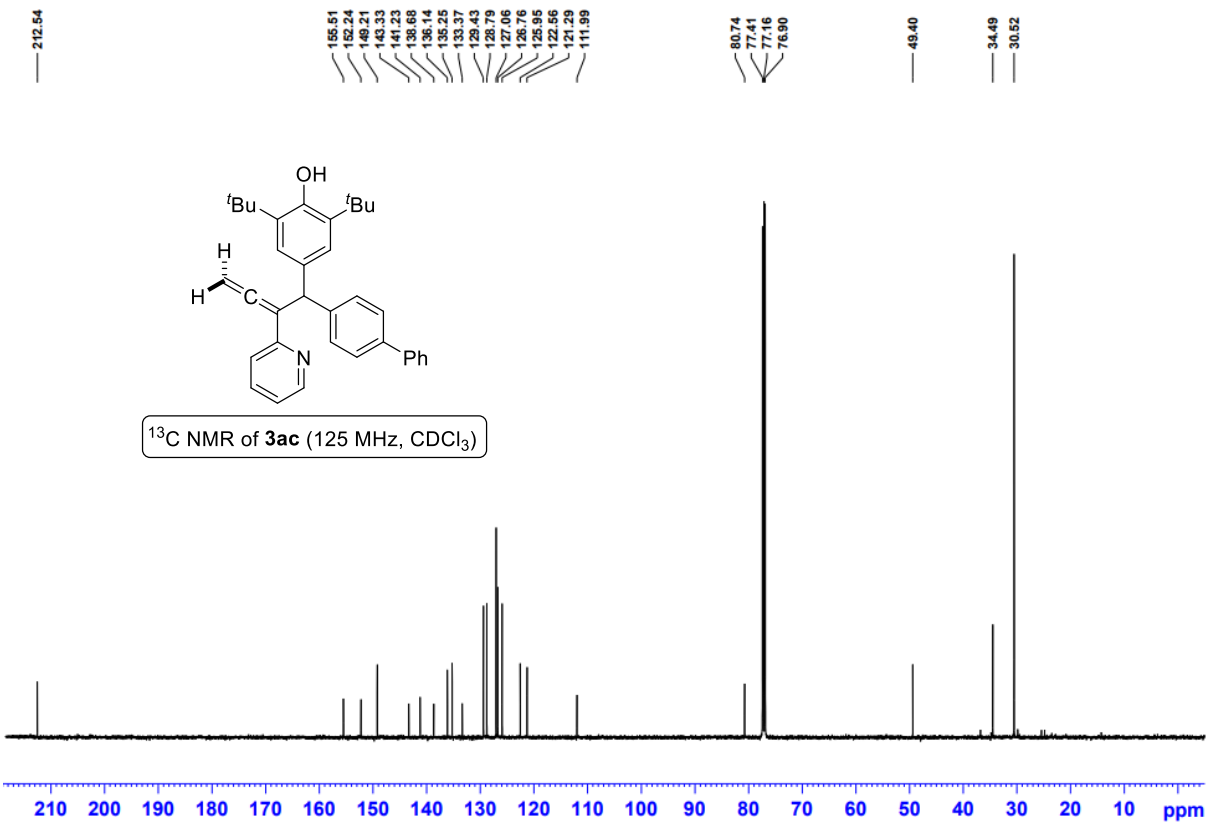
^{13}C NMR of **3ab** (125 MHz, $CDCl_3$)



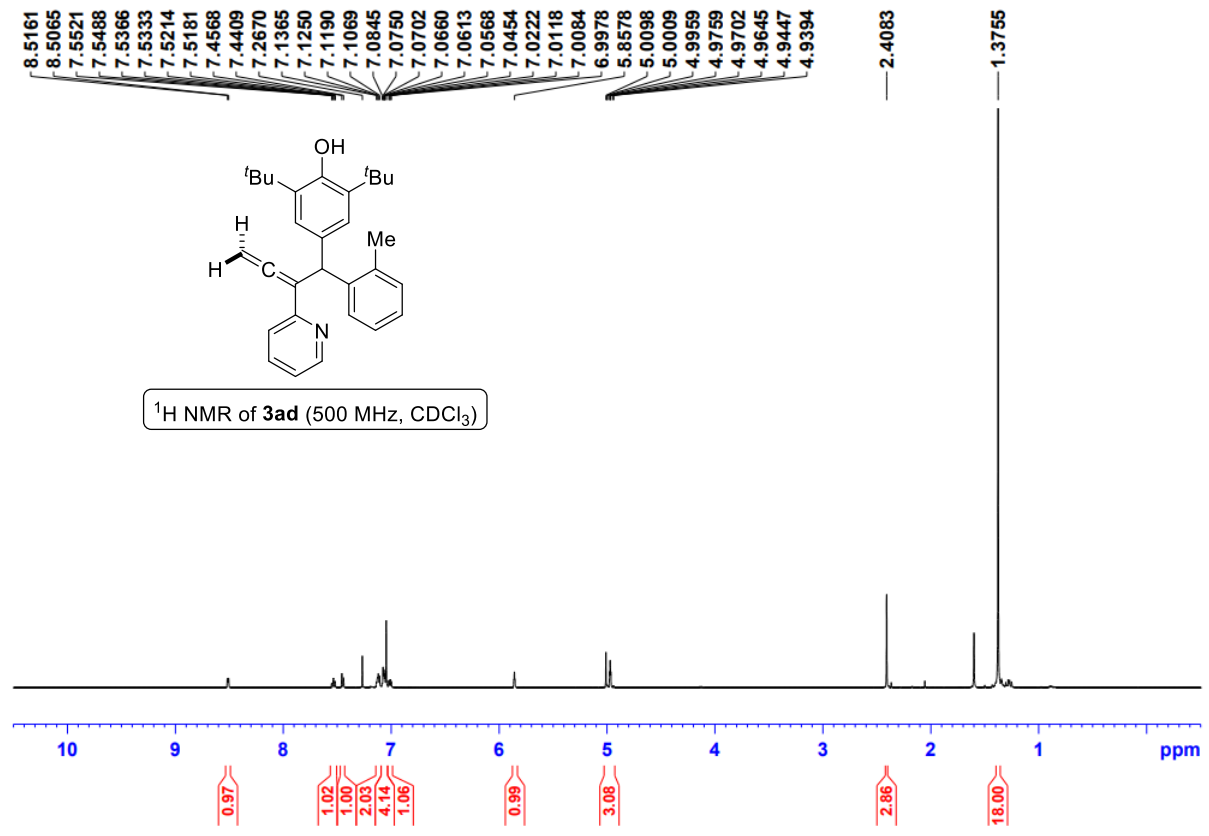
^{1}H NMR of **3ac** (500 MHz, $CDCl_3$)



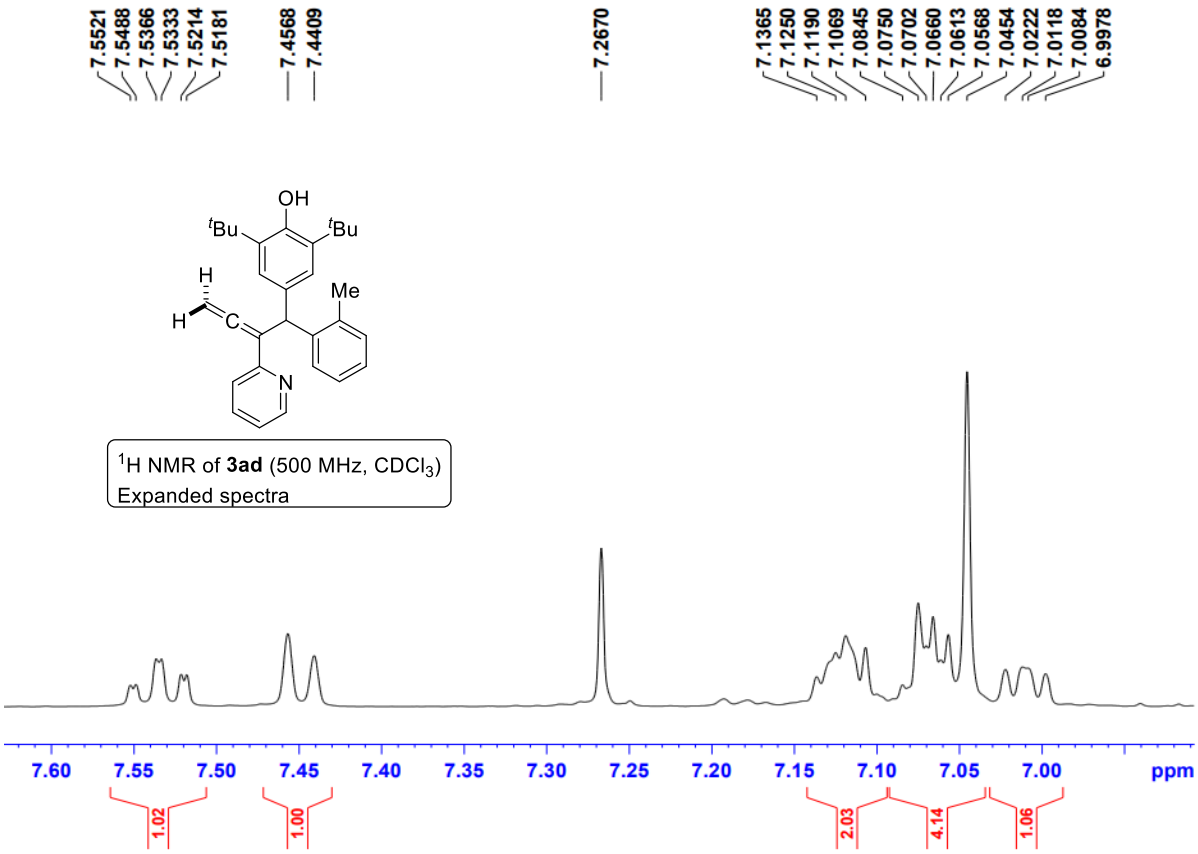
^{1}H NMR of **3ac** (500 MHz, $CDCl_3$)
Expanded spectra



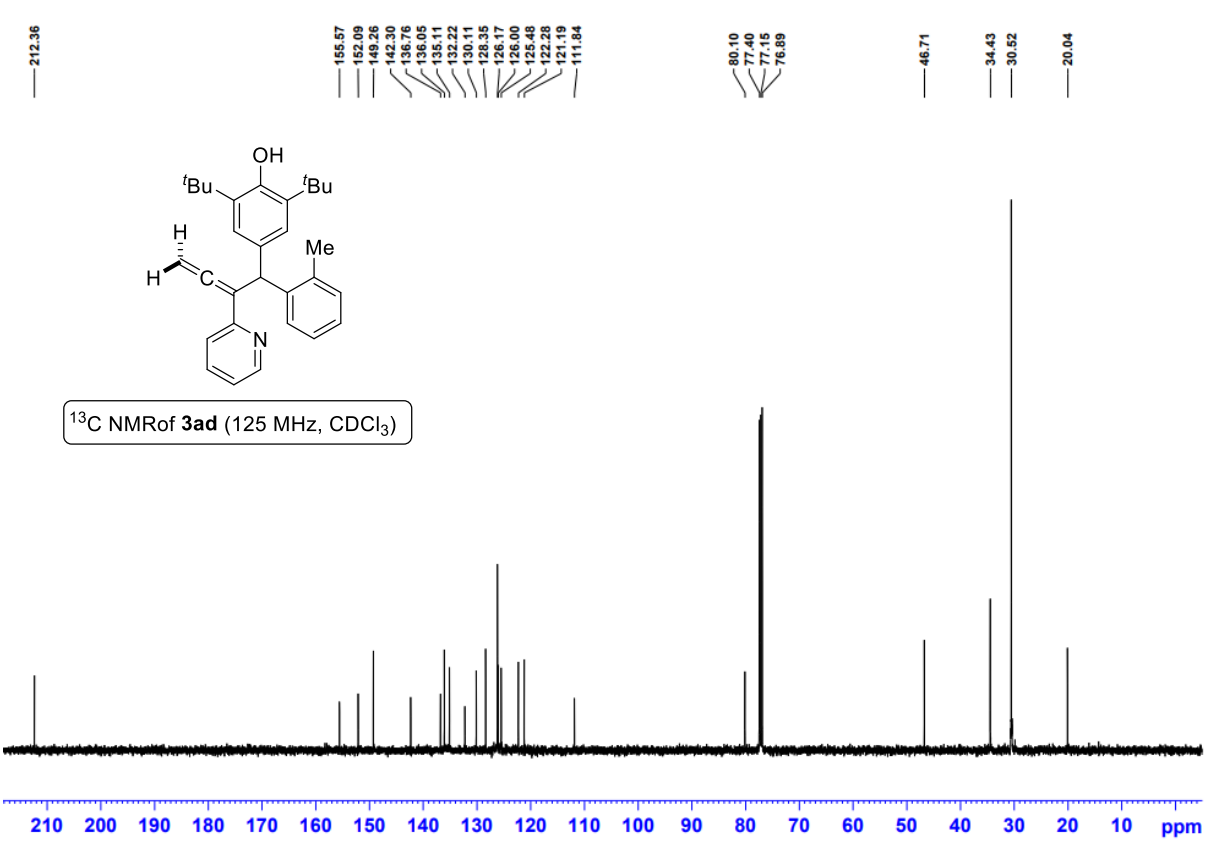
^{13}C NMR of **3ac** (125 MHz, $CDCl_3$)



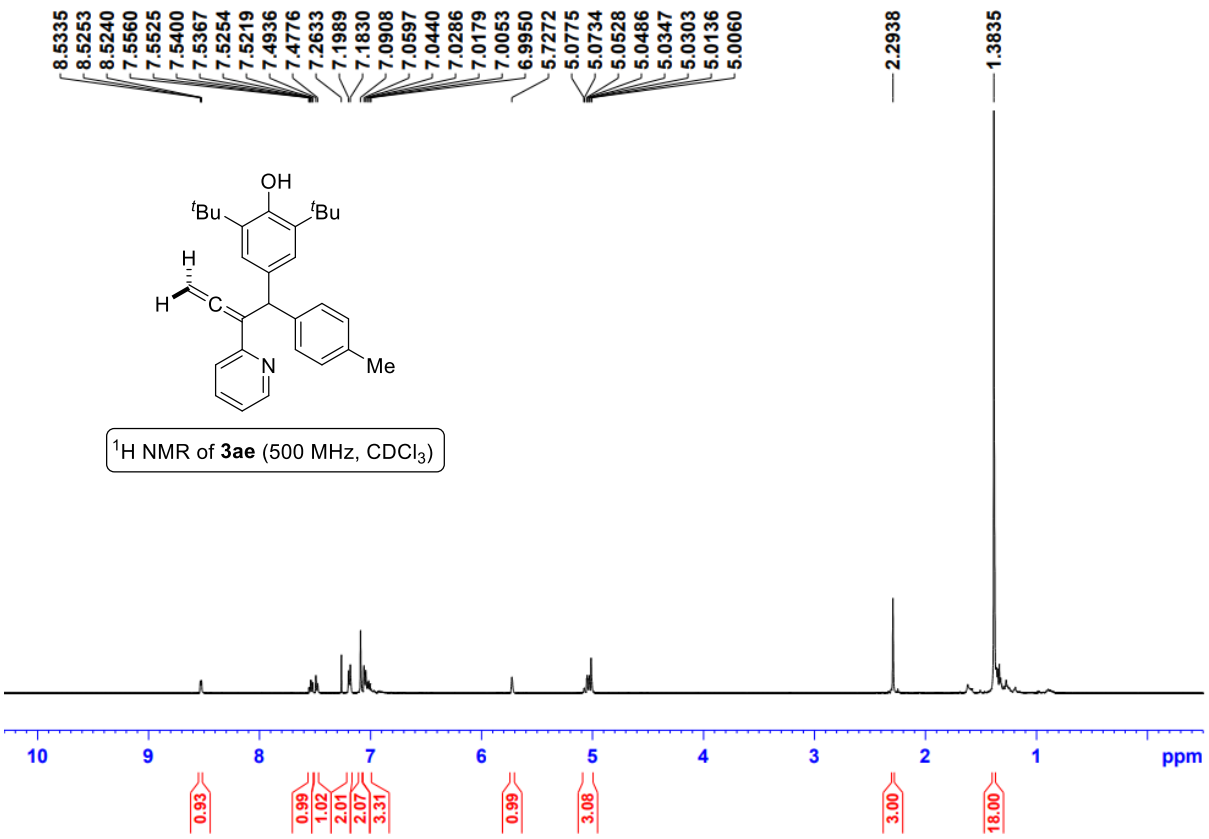
^{1}H NMR of **3ad** (500 MHz, $CDCl_3$)



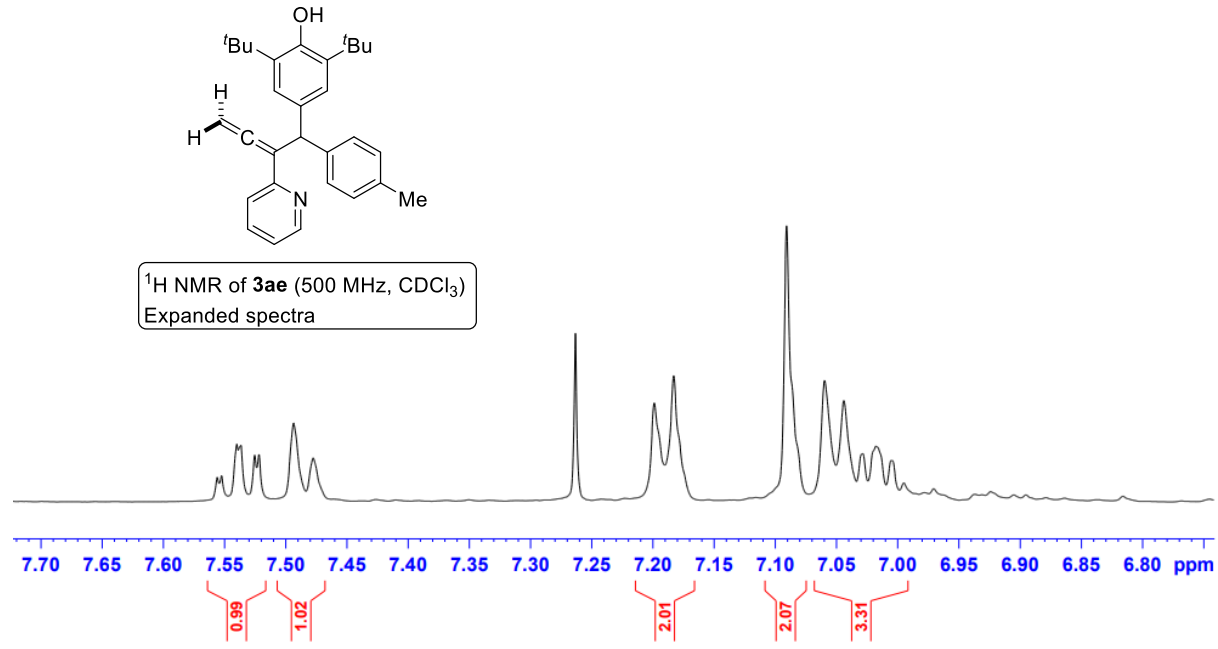
^{1}H NMR of **3ad** (500 MHz, $CDCl_3$)
Expanded spectra



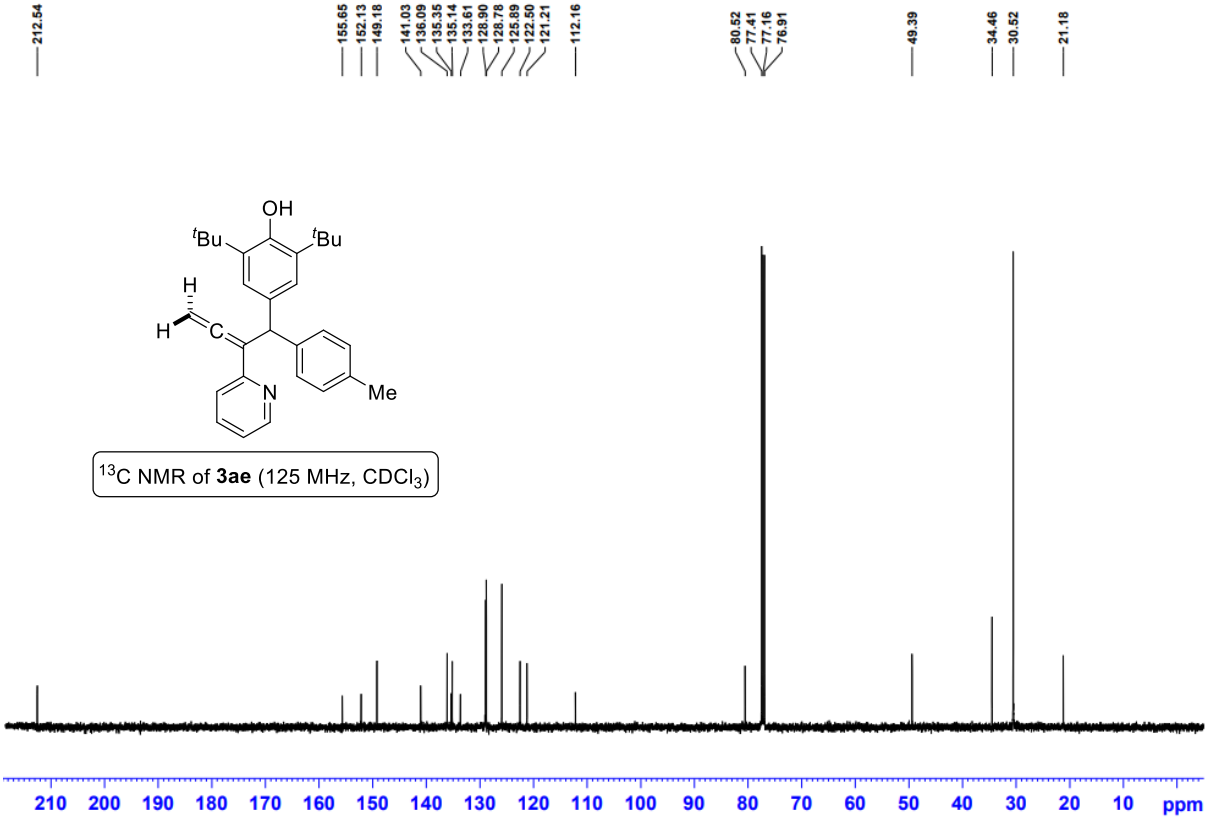
^{13}C NMRof **3ad** (125 MHz, $CDCl_3$)



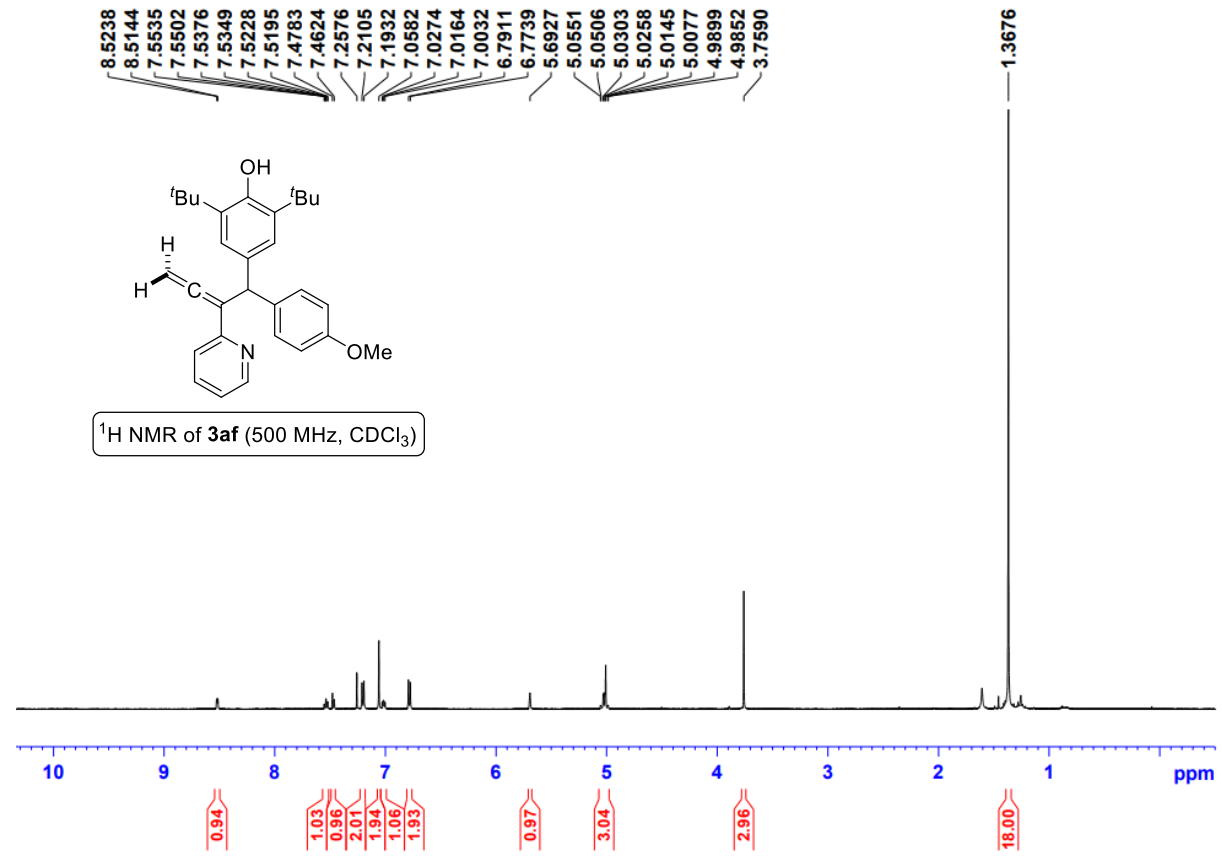
^{1}H NMR of **3ae** (500 MHz, $CDCl_3$)



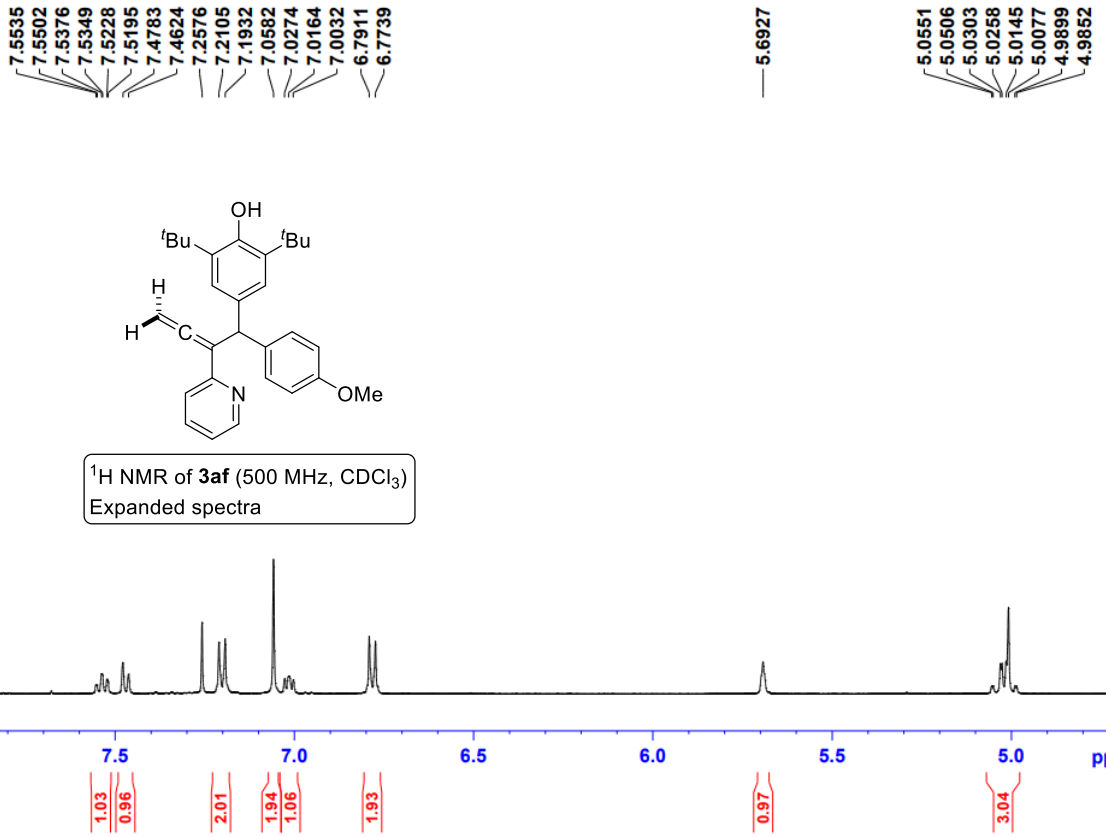
^{1}H NMR of **3ae** (500 MHz, $CDCl_3$)
Expanded spectra



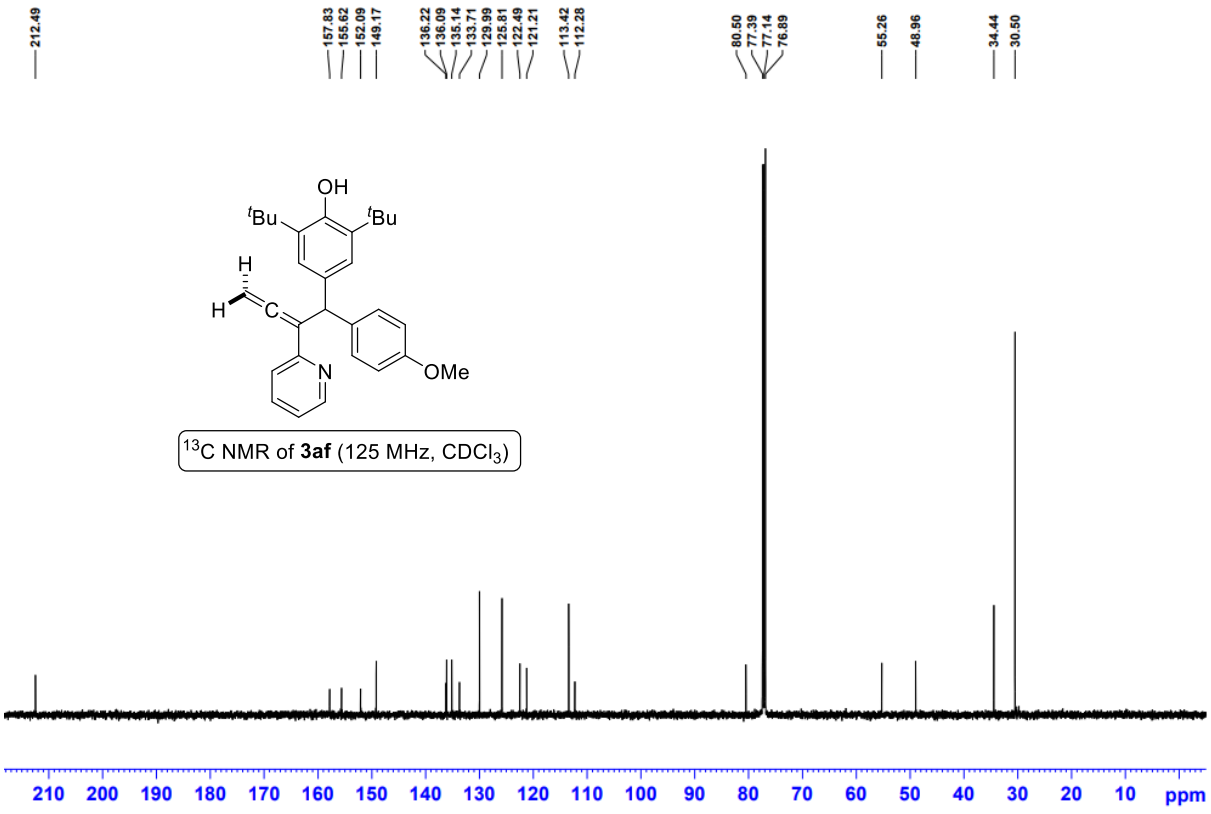
^{13}C NMR of **3ae** (125 MHz, $CDCl_3$)



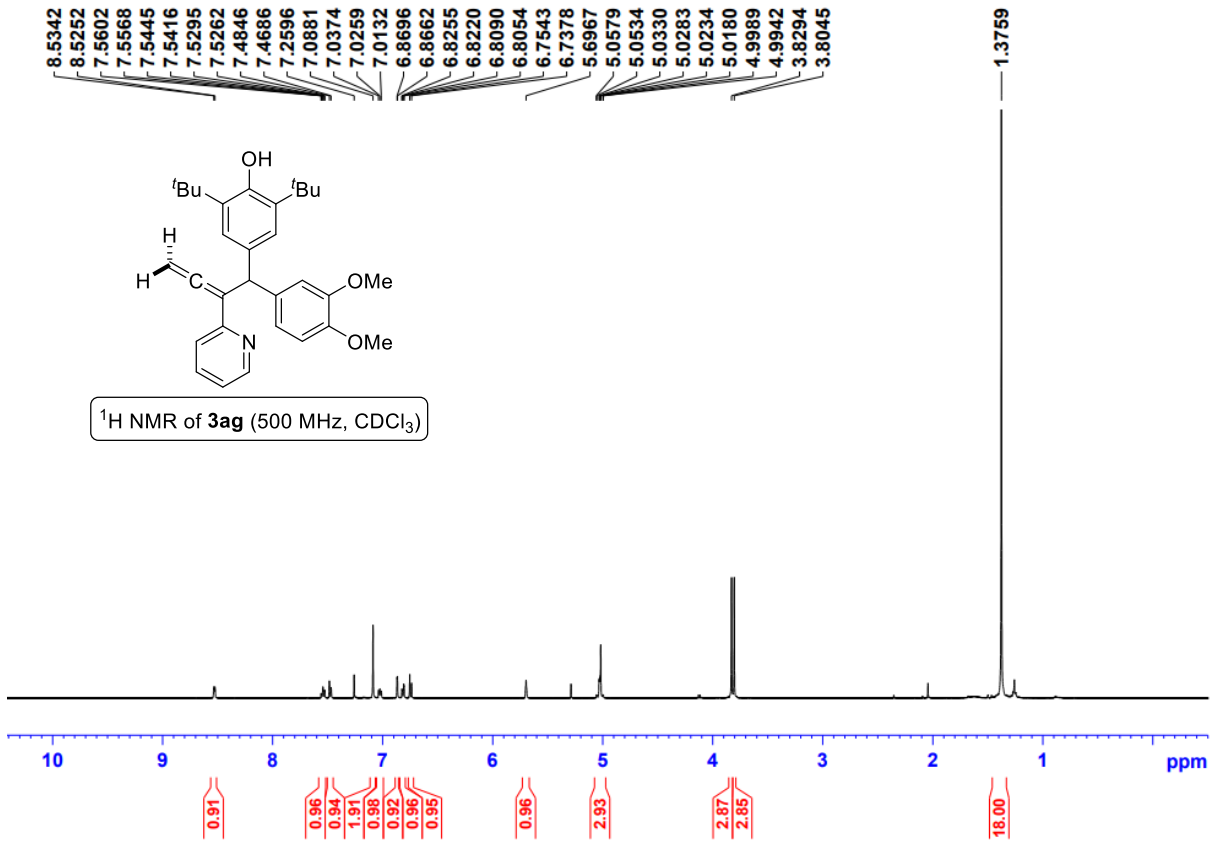
^{1}H NMR of **3af** (500 MHz, $CDCl_3$)



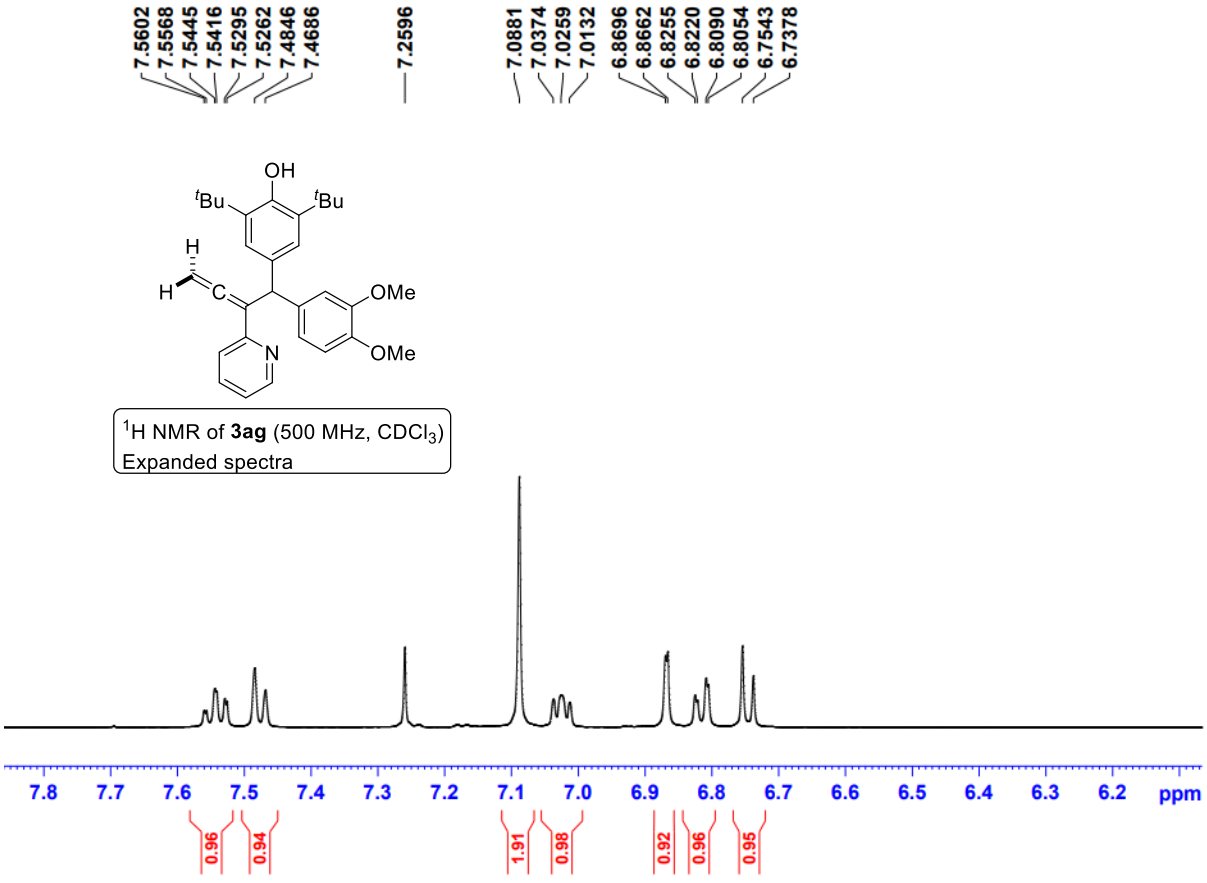
^{1}H NMR of **3af** (500 MHz, $CDCl_3$)
Expanded spectra



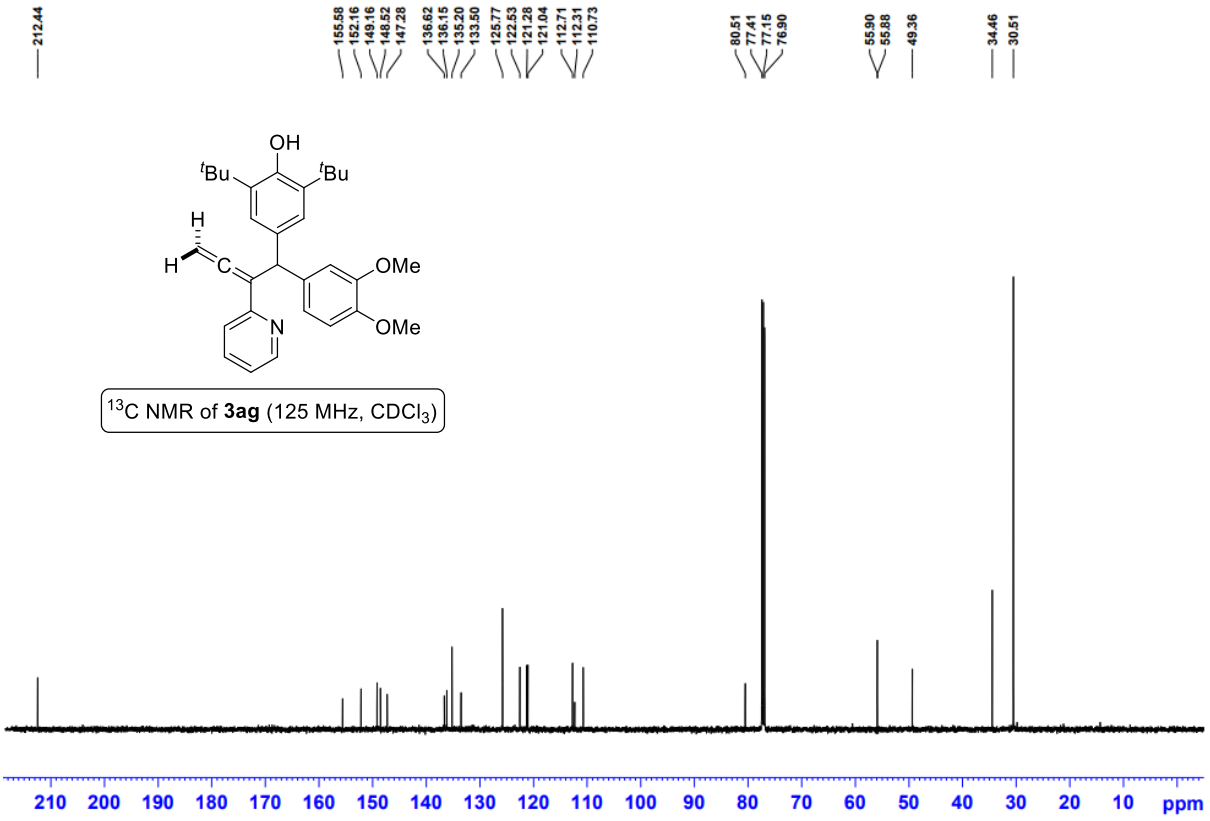
^{13}C NMR of **3af** (125 MHz, $CDCl_3$)



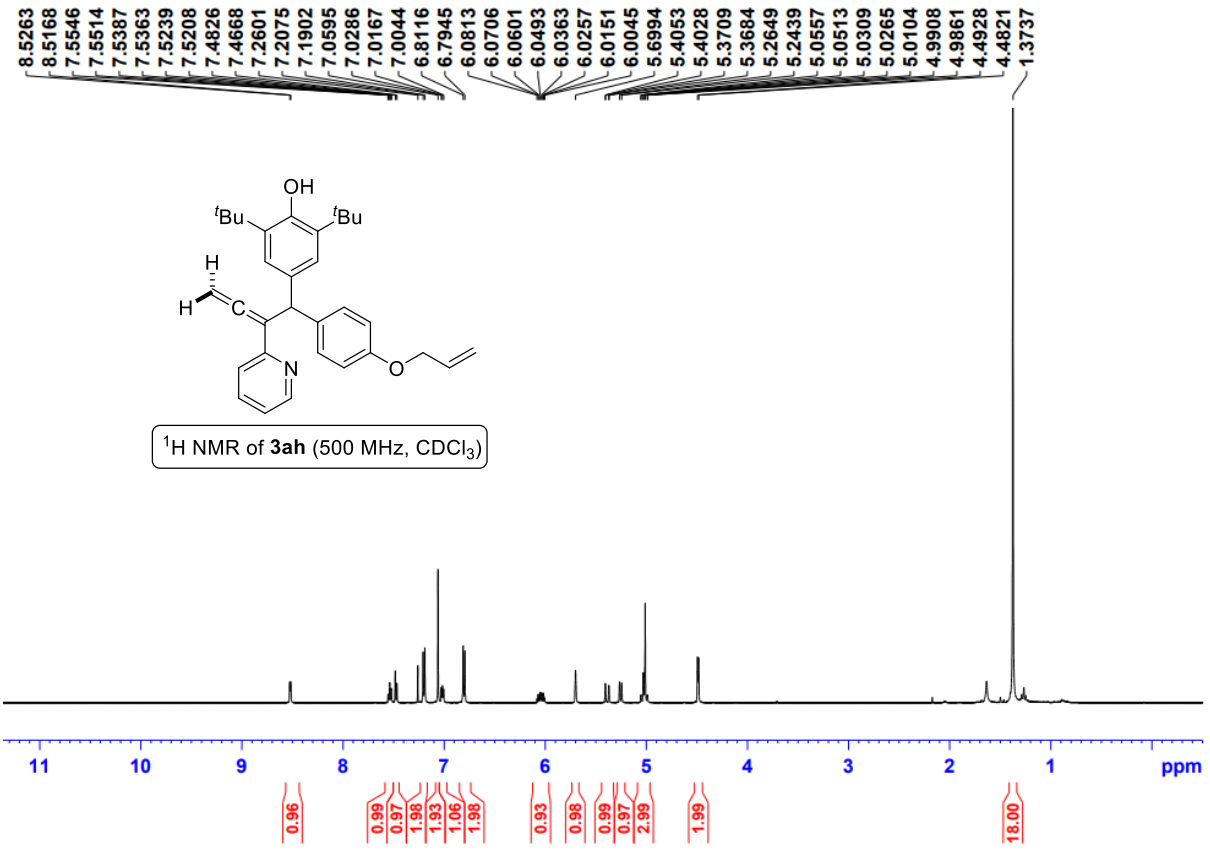
^{1}H NMR of **3ag** (500 MHz, $CDCl_3$)



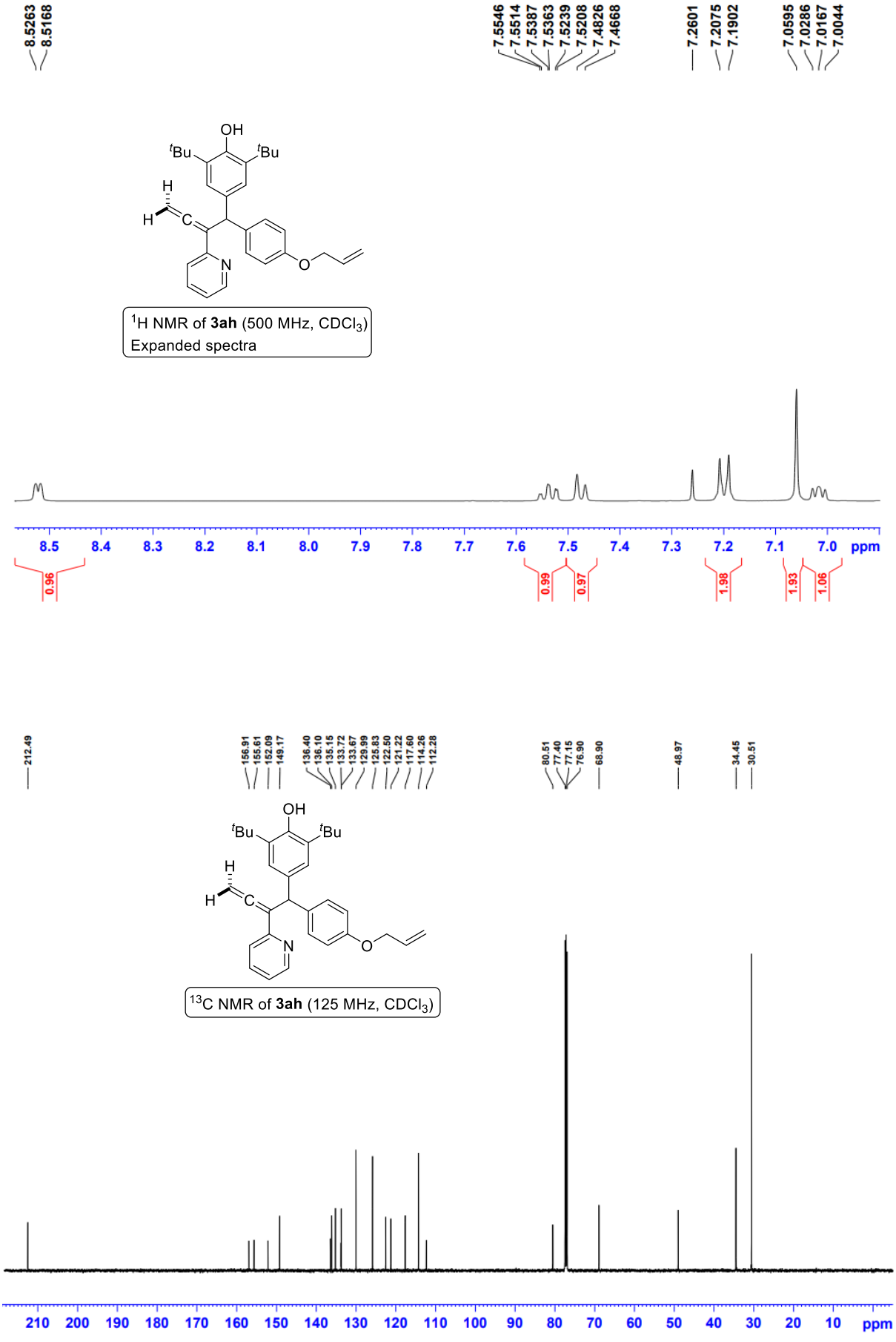
^{1}H NMR of **3ag** (500 MHz, $CDCl_3$)
Expanded spectra



^{13}C NMR of **3ag** (125 MHz, $CDCl_3$)

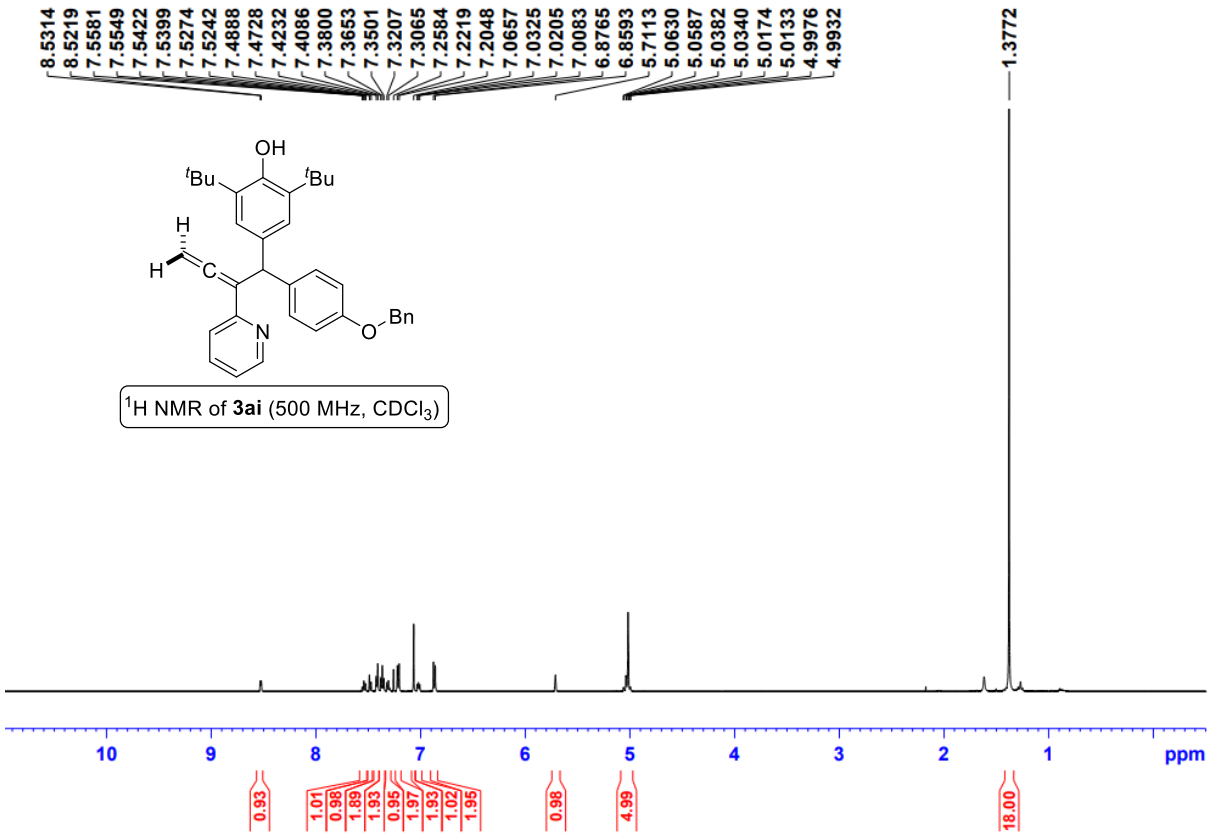


^{1}H NMR of **3ah** (500 MHz, $CDCl_3$)

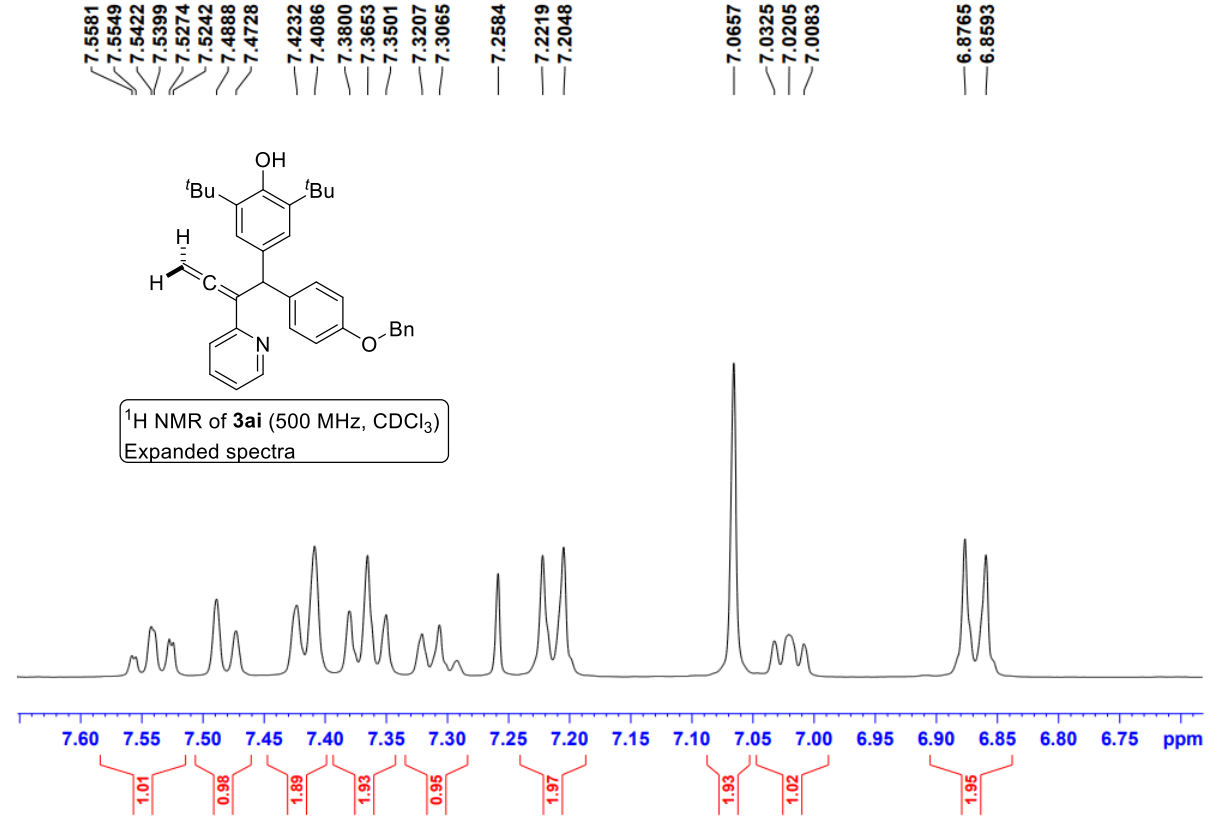


^{1}H NMR of **3ah** (500 MHz, $CDCl_3$)
Expanded spectra

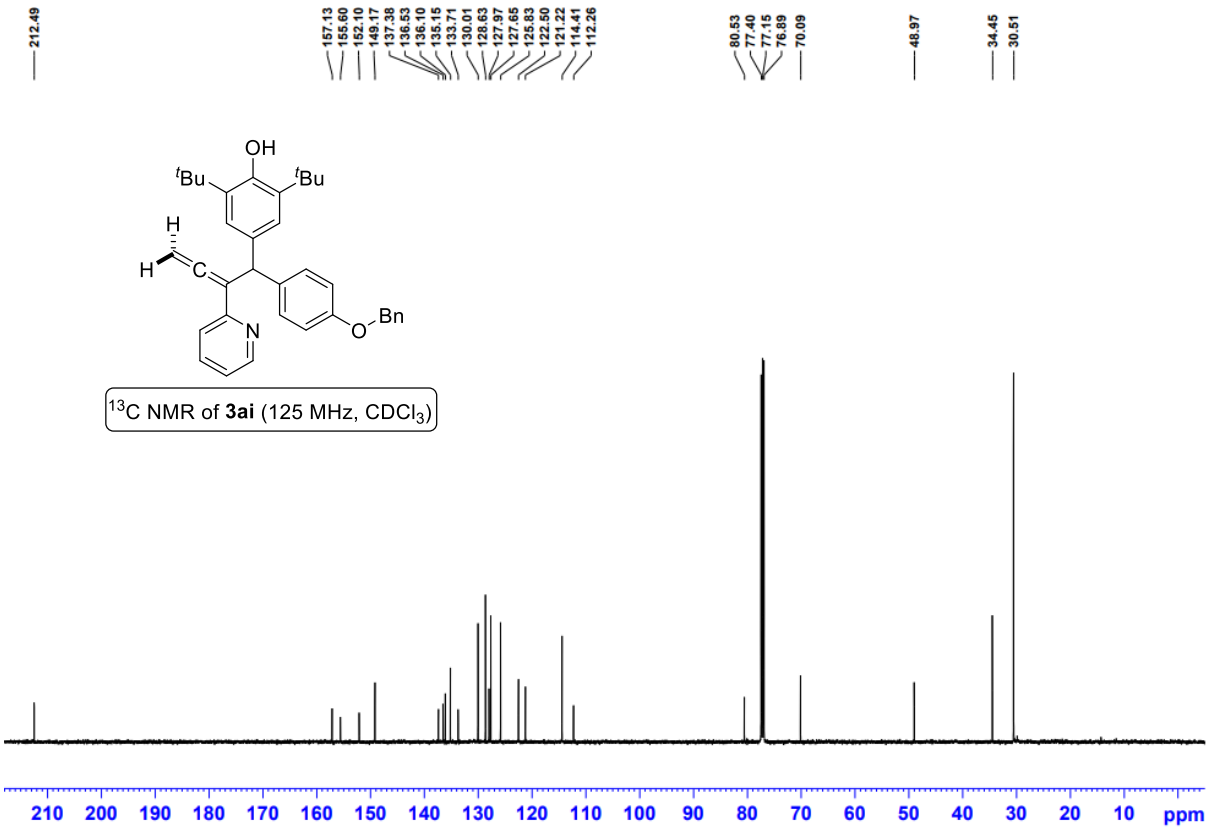
^{13}C NMR of **3ah** (125 MHz, $CDCl_3$)



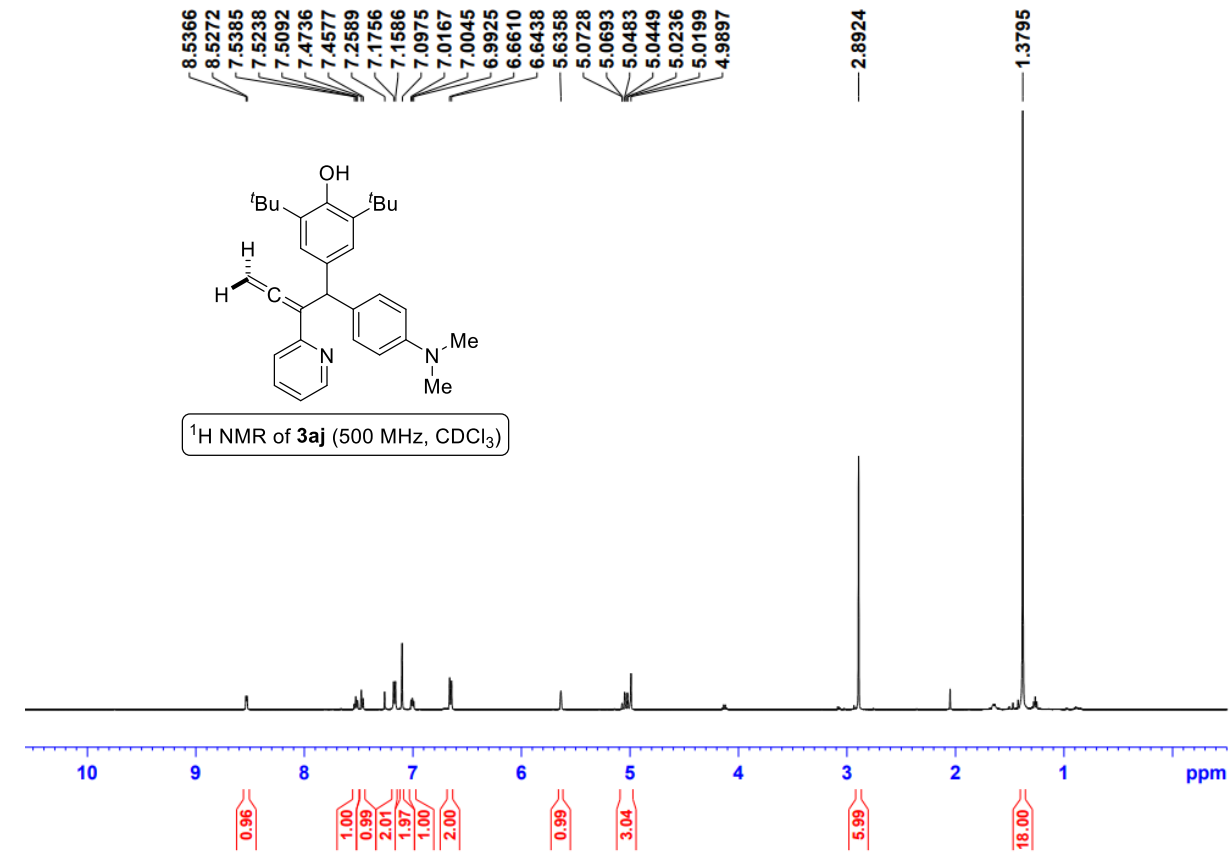
^{1}H NMR of **3ai** (500 MHz, $CDCl_3$)



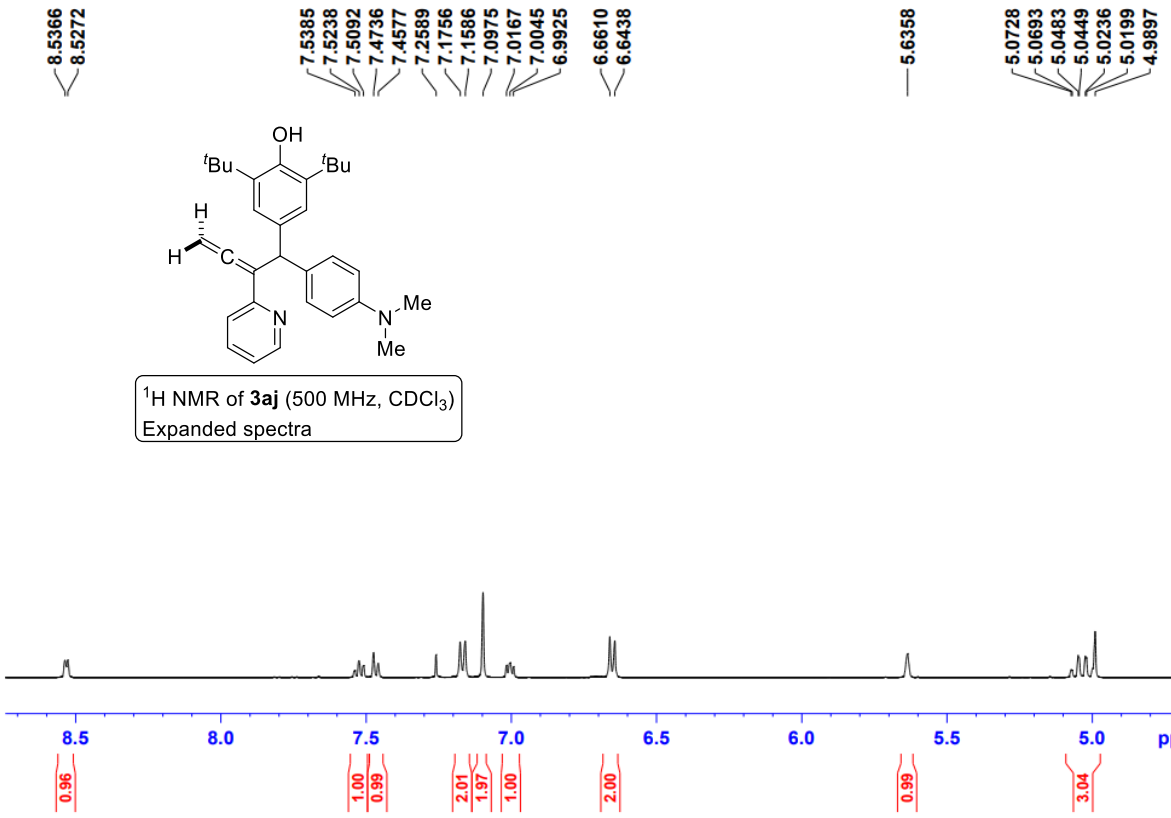
^{1}H NMR of **3ai** (500 MHz, $CDCl_3$)
Expanded spectra



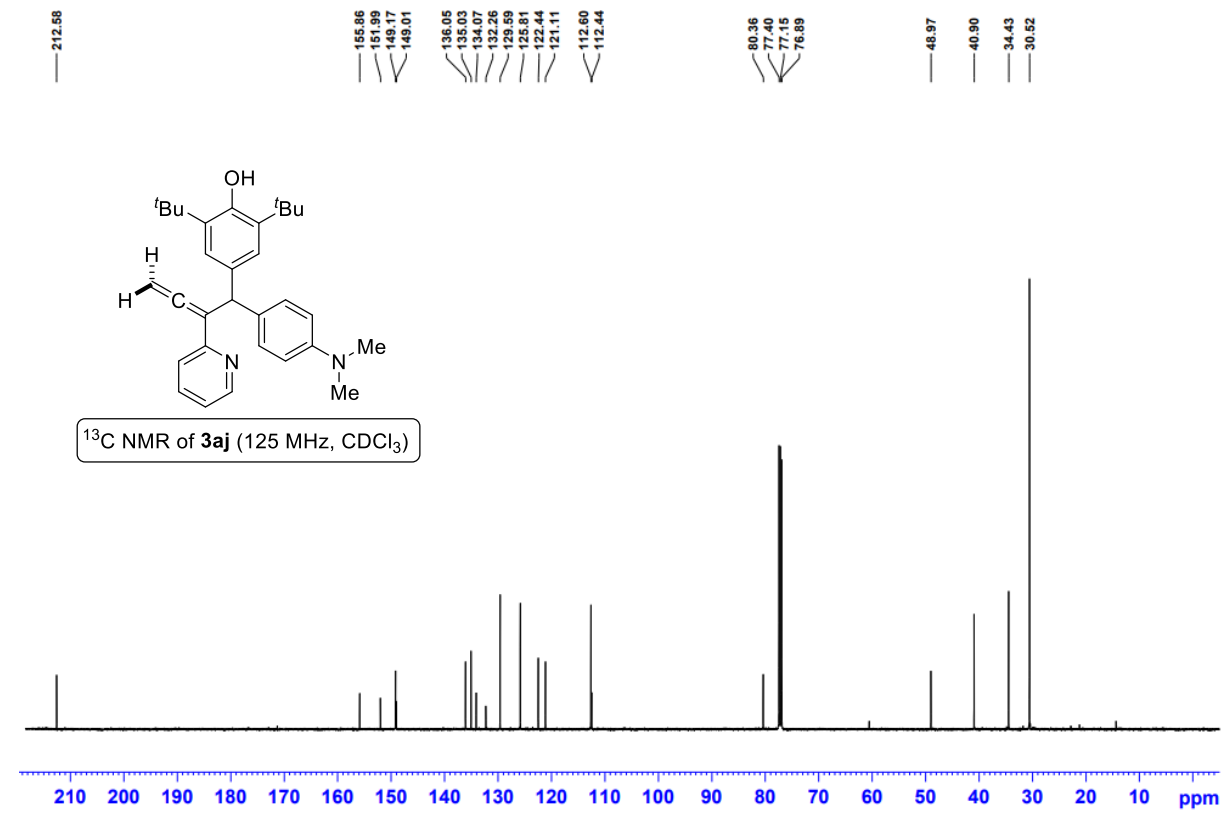
^{13}C NMR of **3ai** (125 MHz, $CDCl_3$)



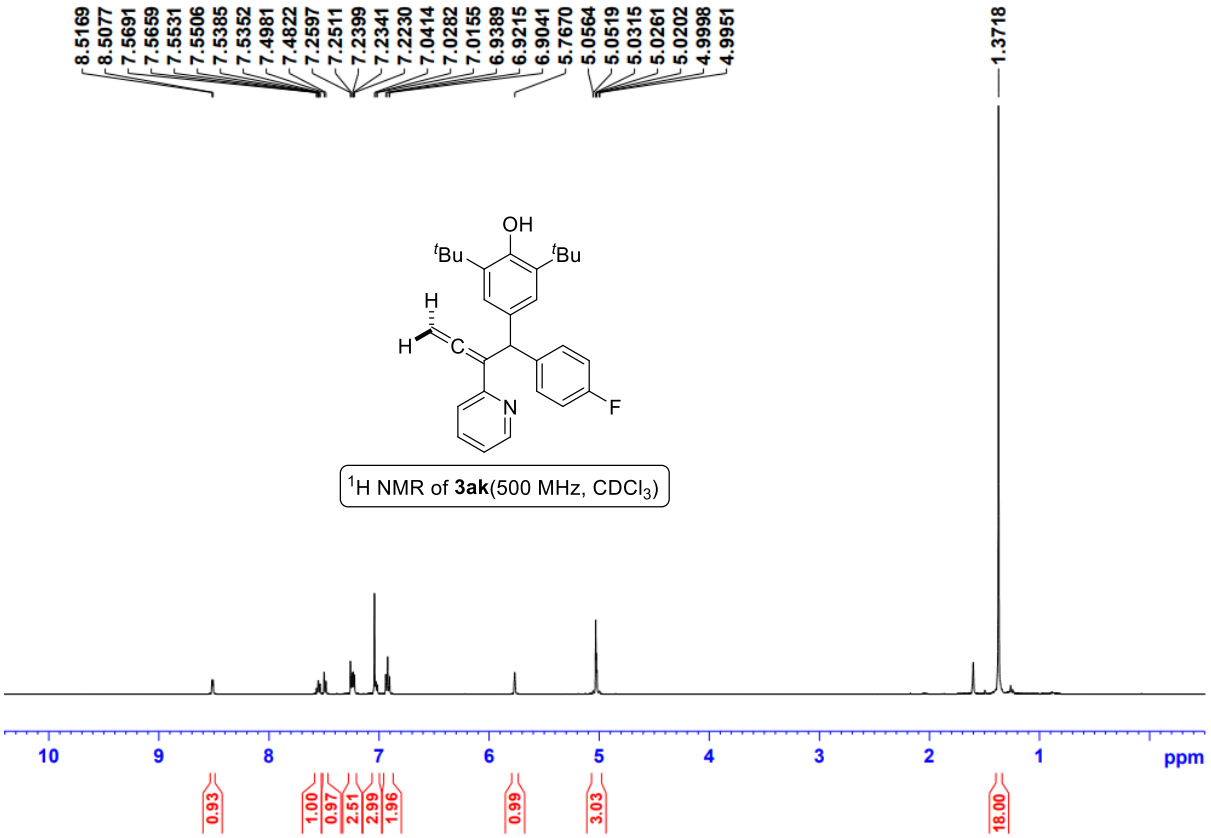
^{1}H NMR of **3aj** (500 MHz, $CDCl_3$)



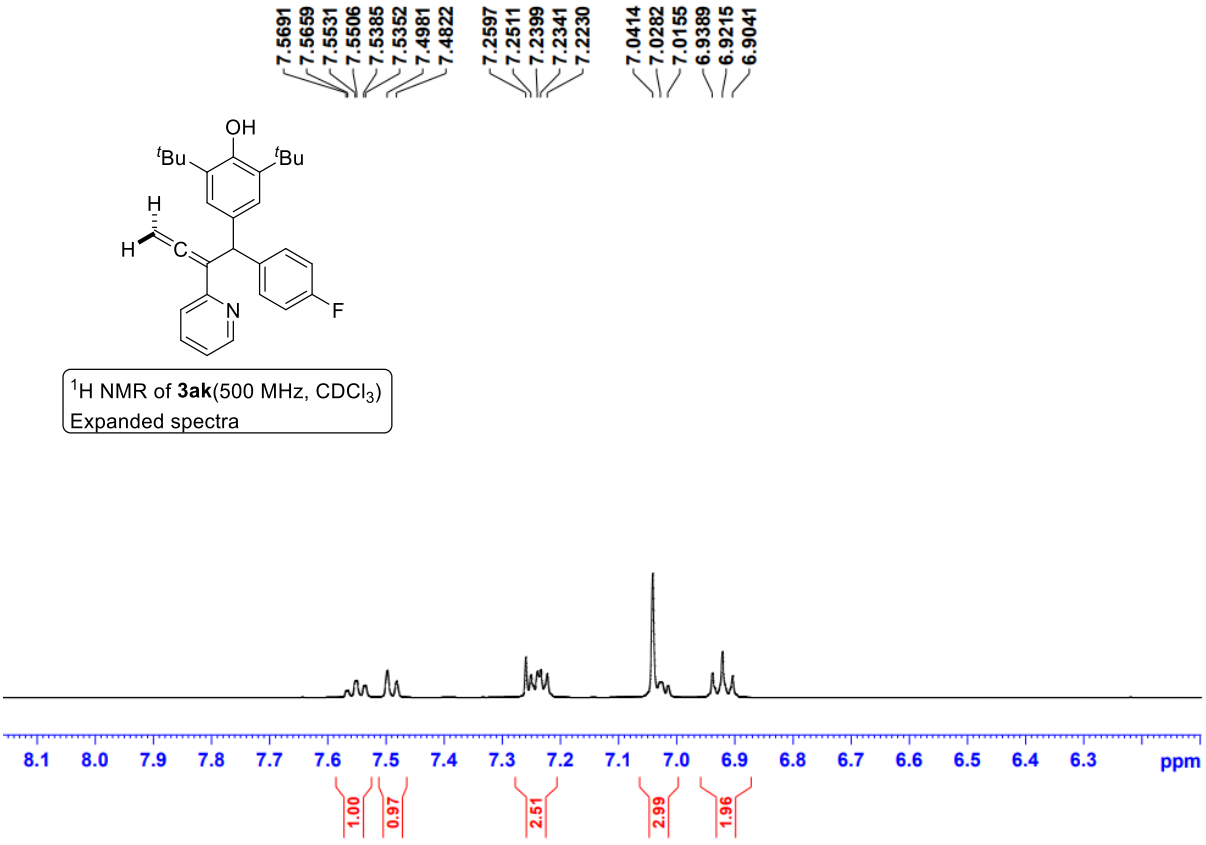
^{1}H NMR of **3aj** (500 MHz, $CDCl_3$)
Expanded spectra



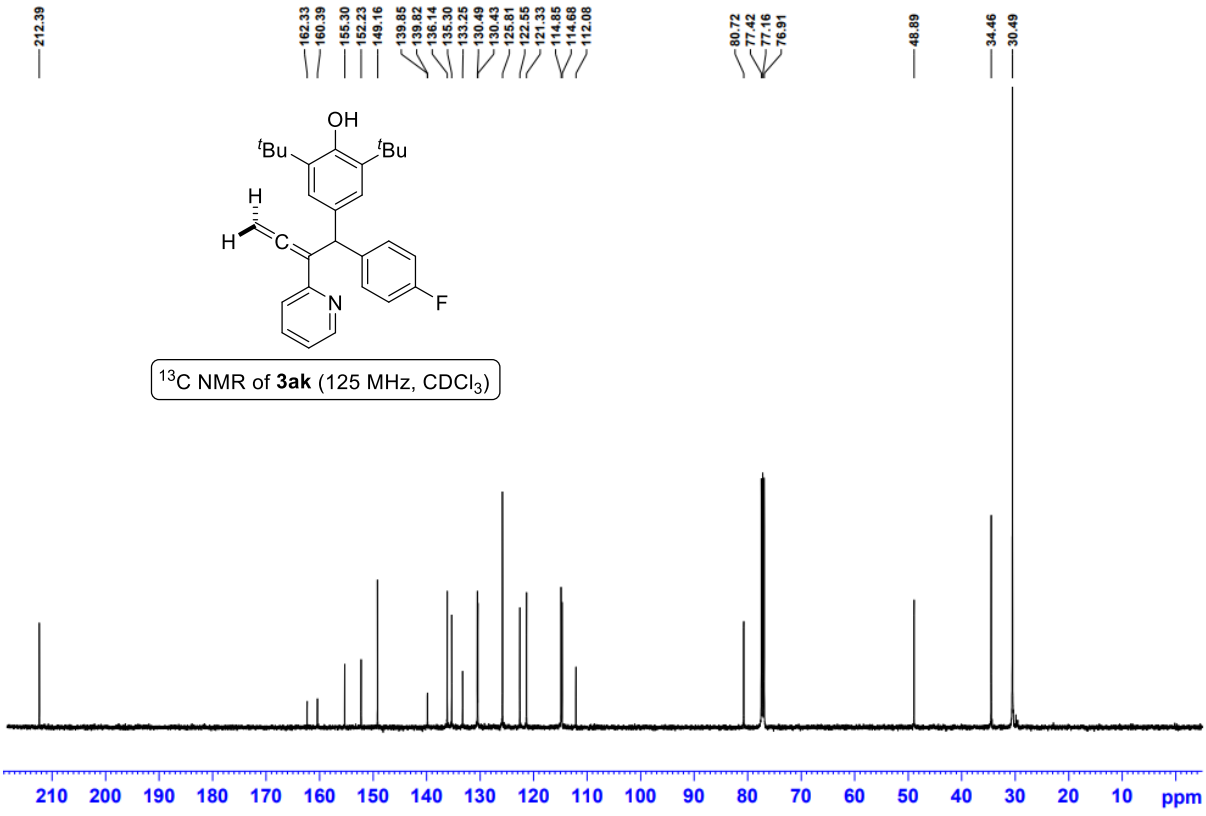
^{13}C NMR of **3aj** (125 MHz, $CDCl_3$)



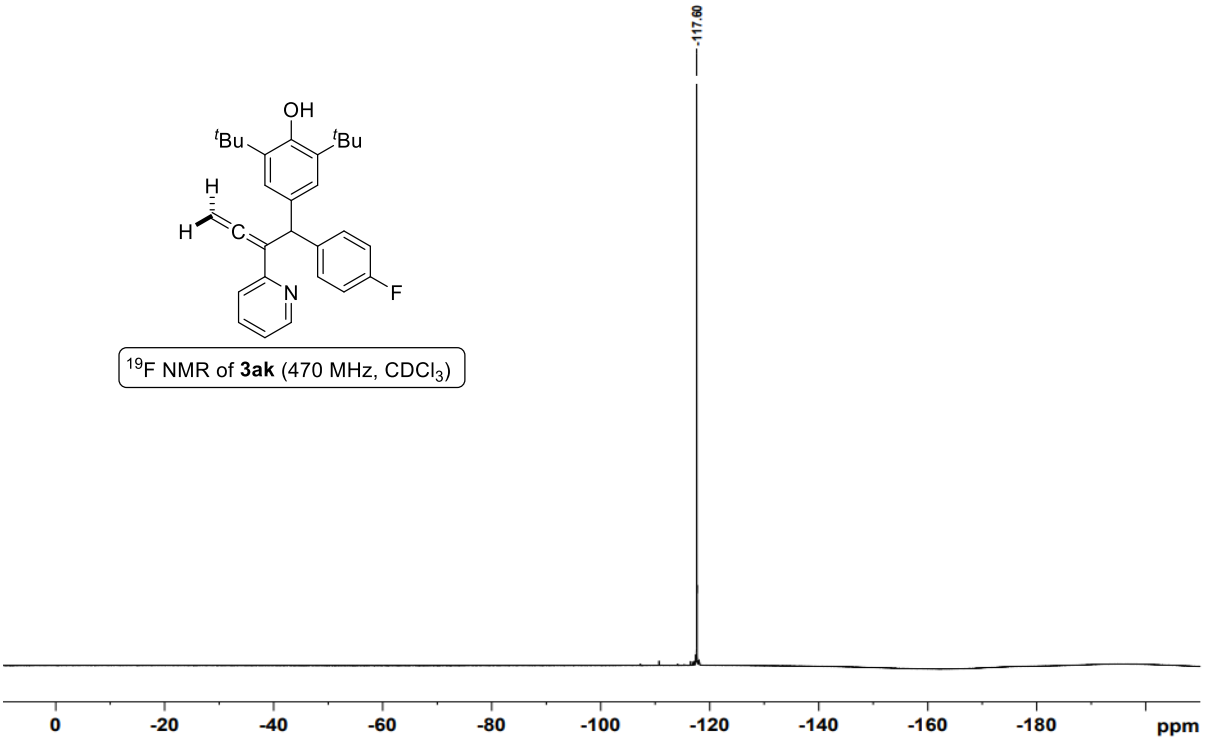
^{1}H NMR of **3ak**(500 MHz, $CDCl_3$)



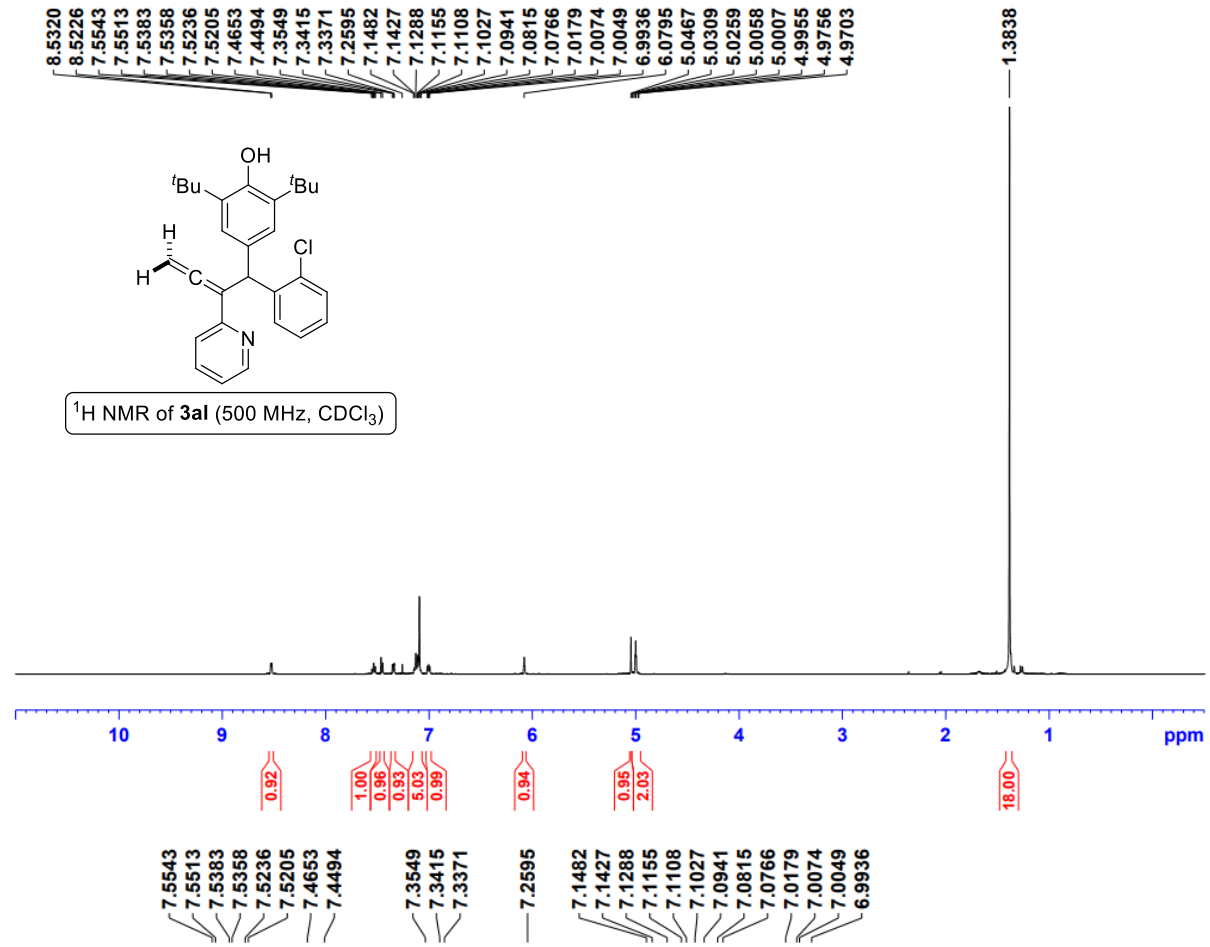
^{1}H NMR of **3ak**(500 MHz, $CDCl_3$)
Expanded spectra



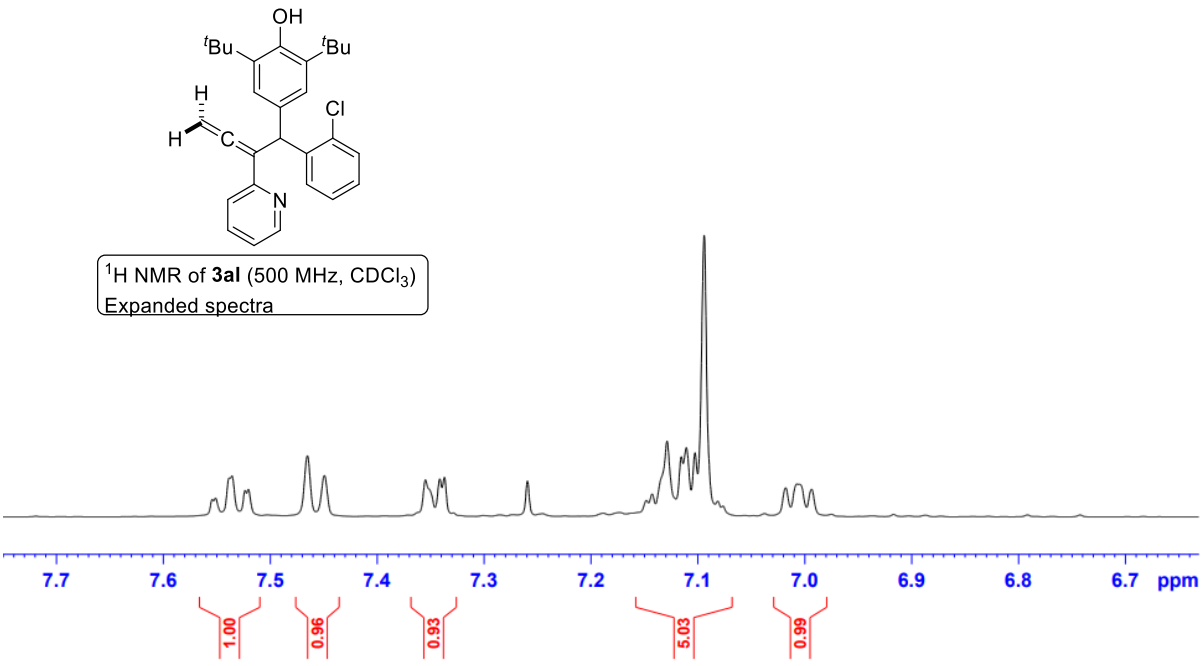
^{13}C NMR of **3ak** (125 MHz, $CDCl_3$)



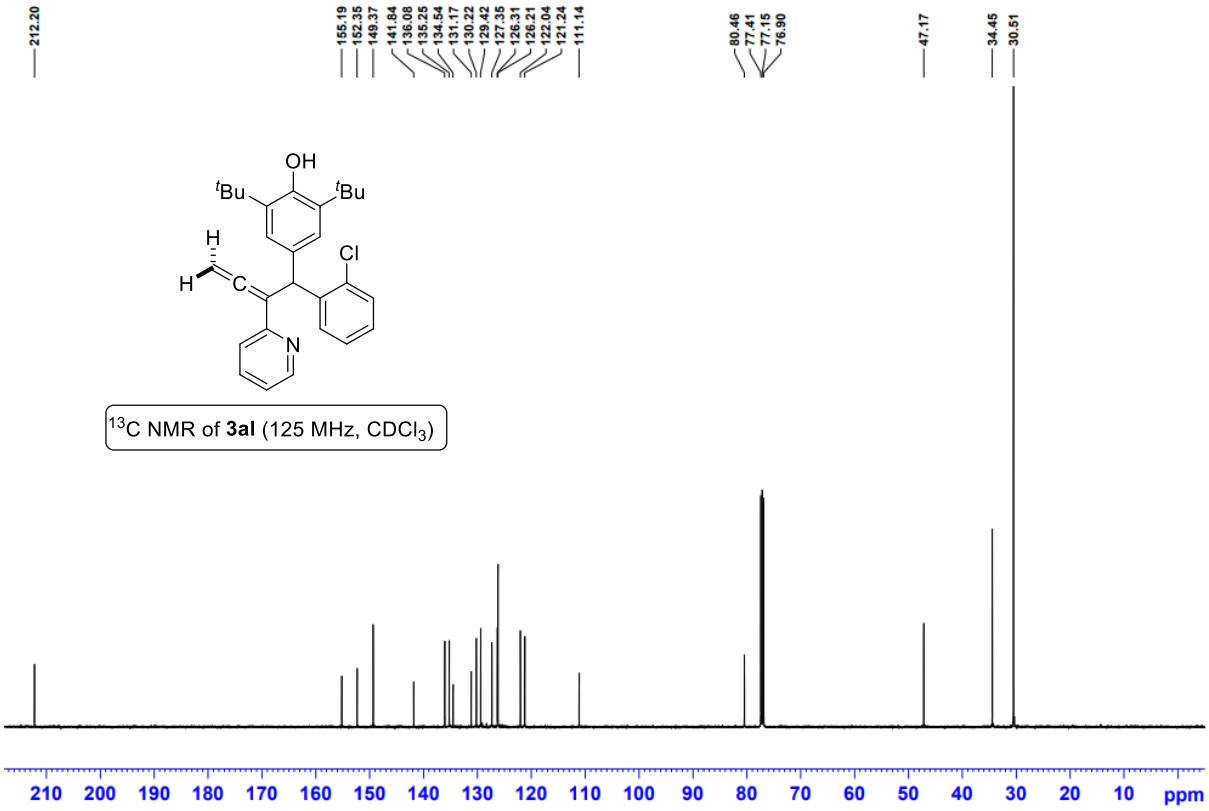
^{19}F NMR of **3ak** (470 MHz, $CDCl_3$)



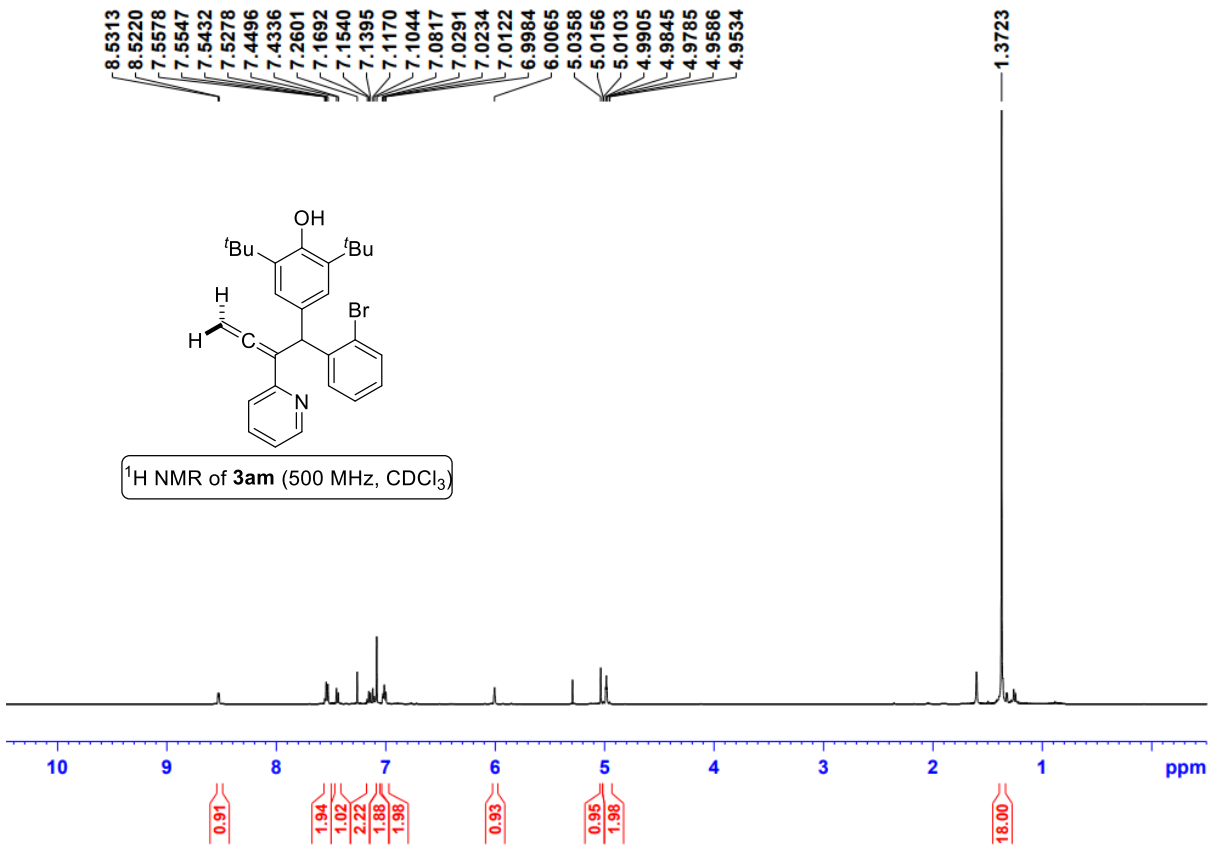
^{1}H NMR of **3al** (500 MHz, $CDCl_3$)



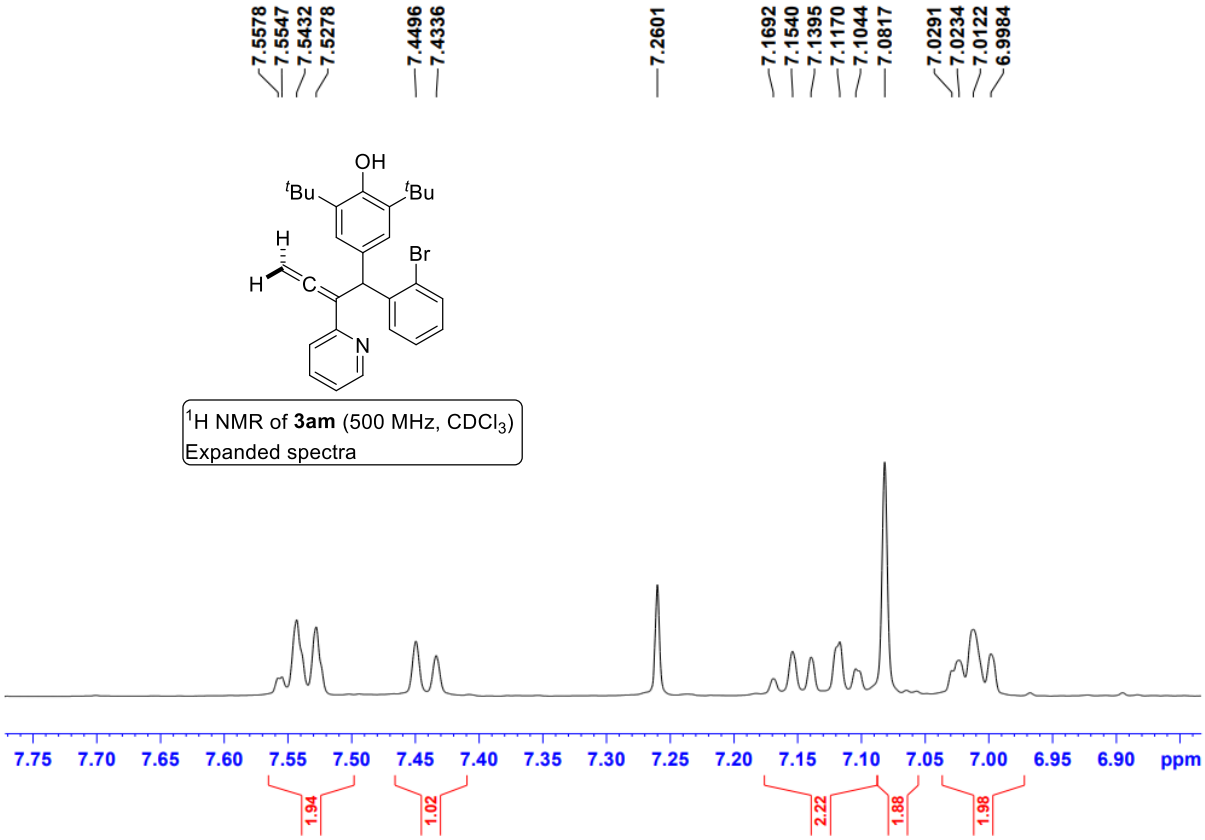
^{1}H NMR of **3al** (500 MHz, $CDCl_3$)
Expanded spectra



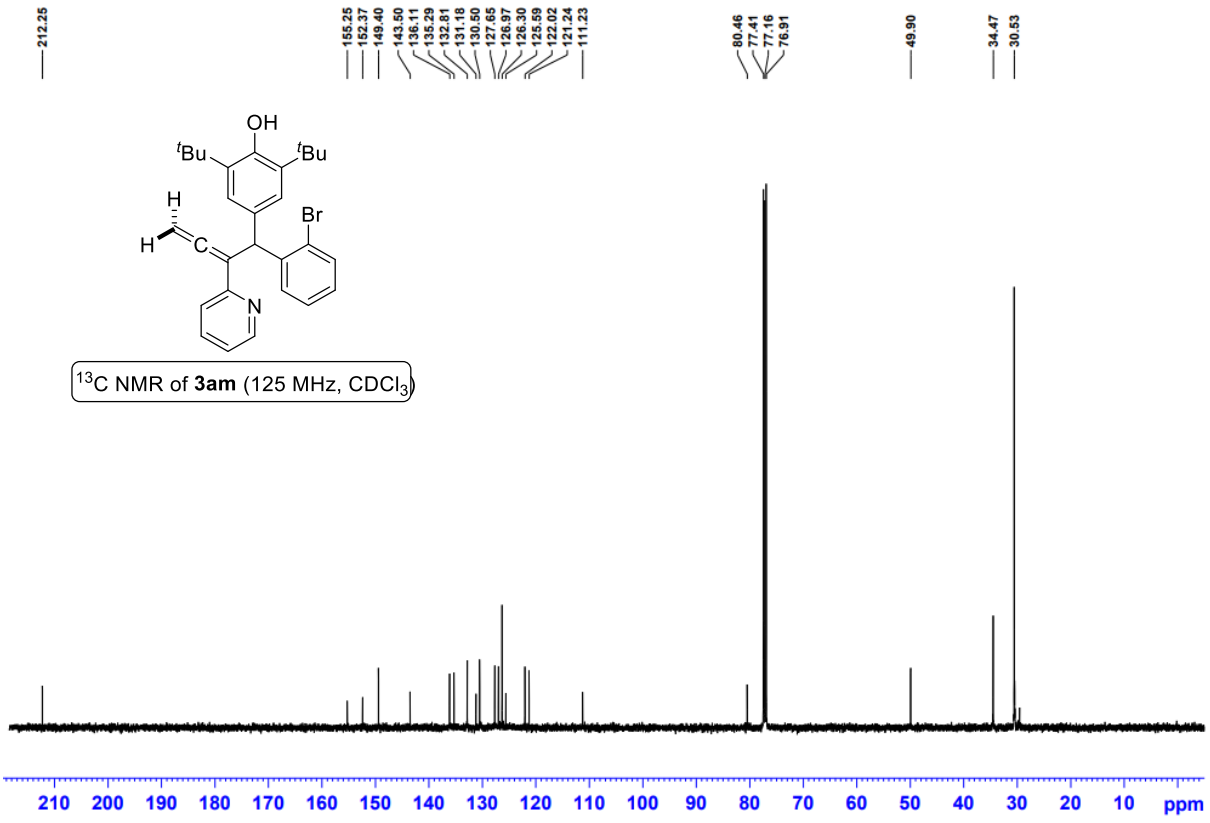
^{13}C NMR of **3al** (125 MHz, $CDCl_3$)



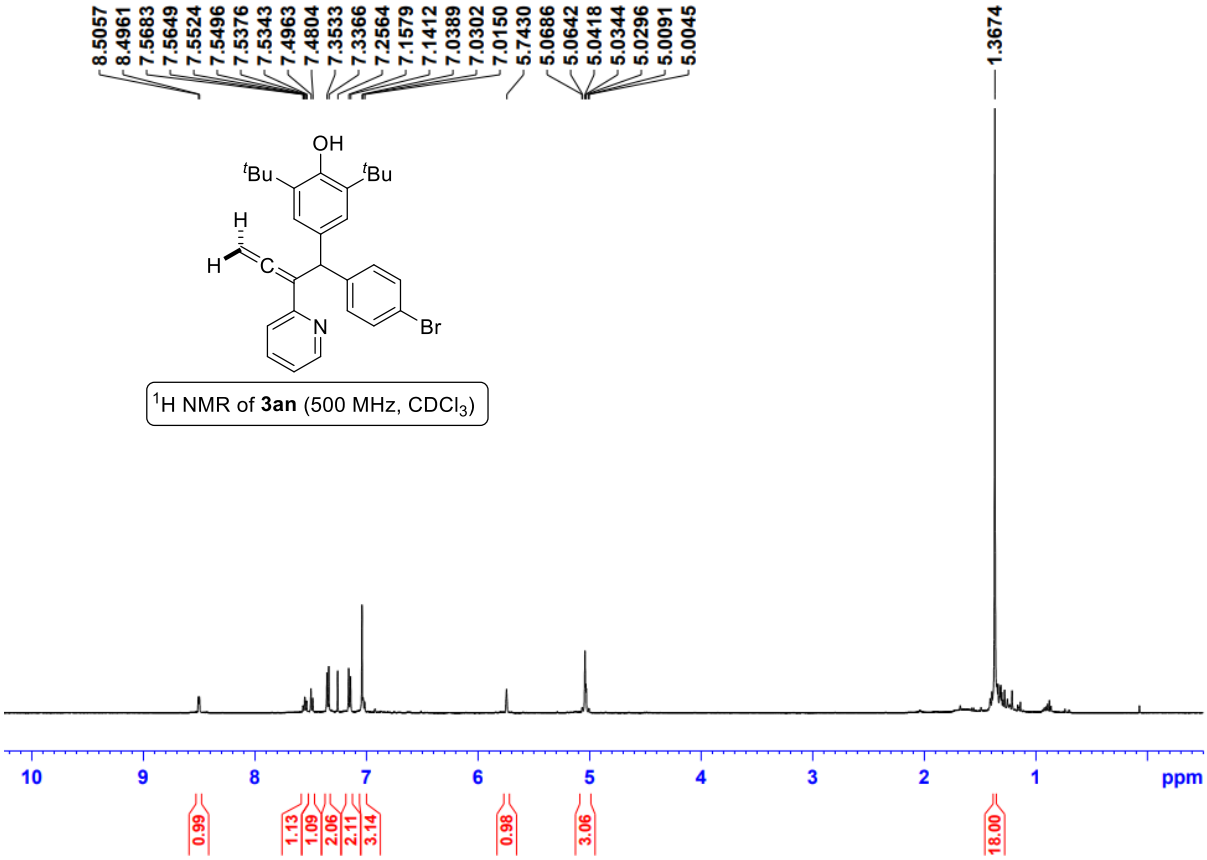
^{1}H NMR of **3am** (500 MHz, $CDCl_3$)



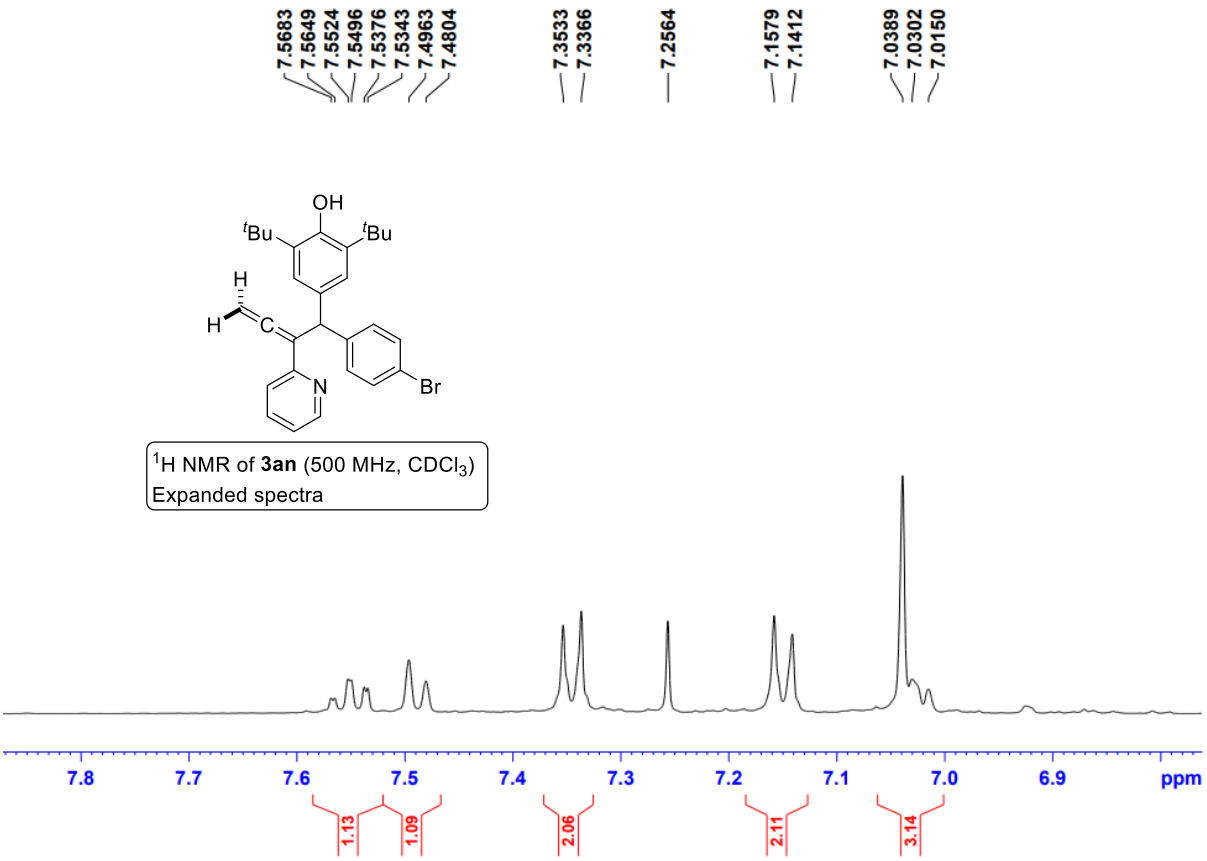
^{1}H NMR of **3am** (500 MHz, $CDCl_3$)
Expanded spectra



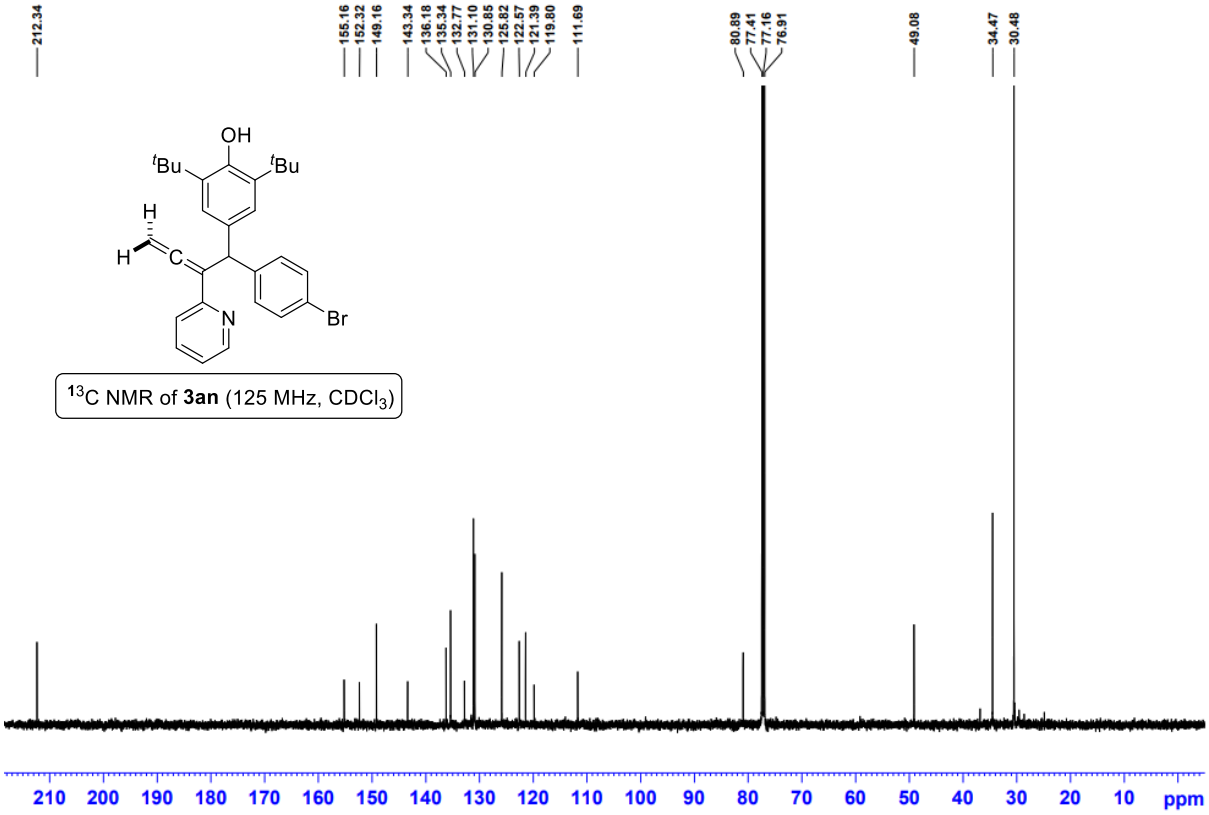
^{13}C NMR of **3am** (125 MHz, $CDCl_3$)



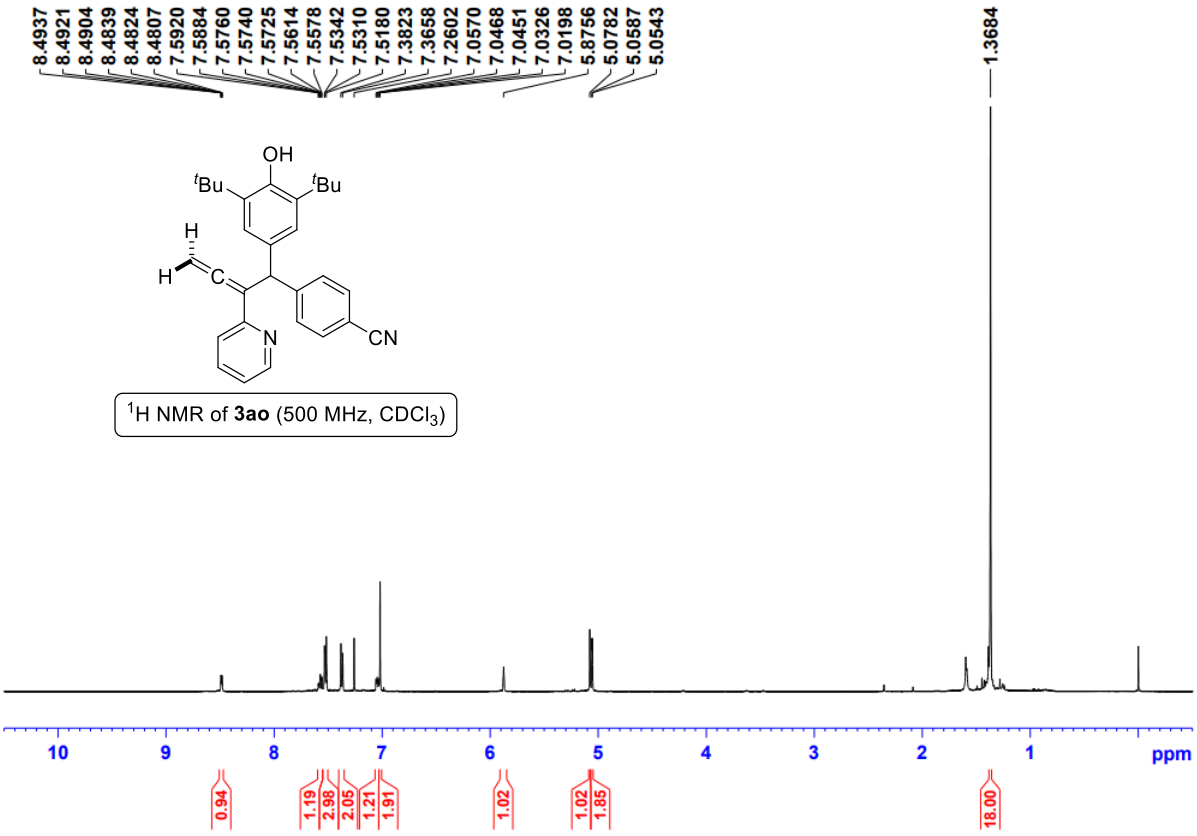
^{1}H NMR of **3an** (500 MHz, $CDCl_3$)



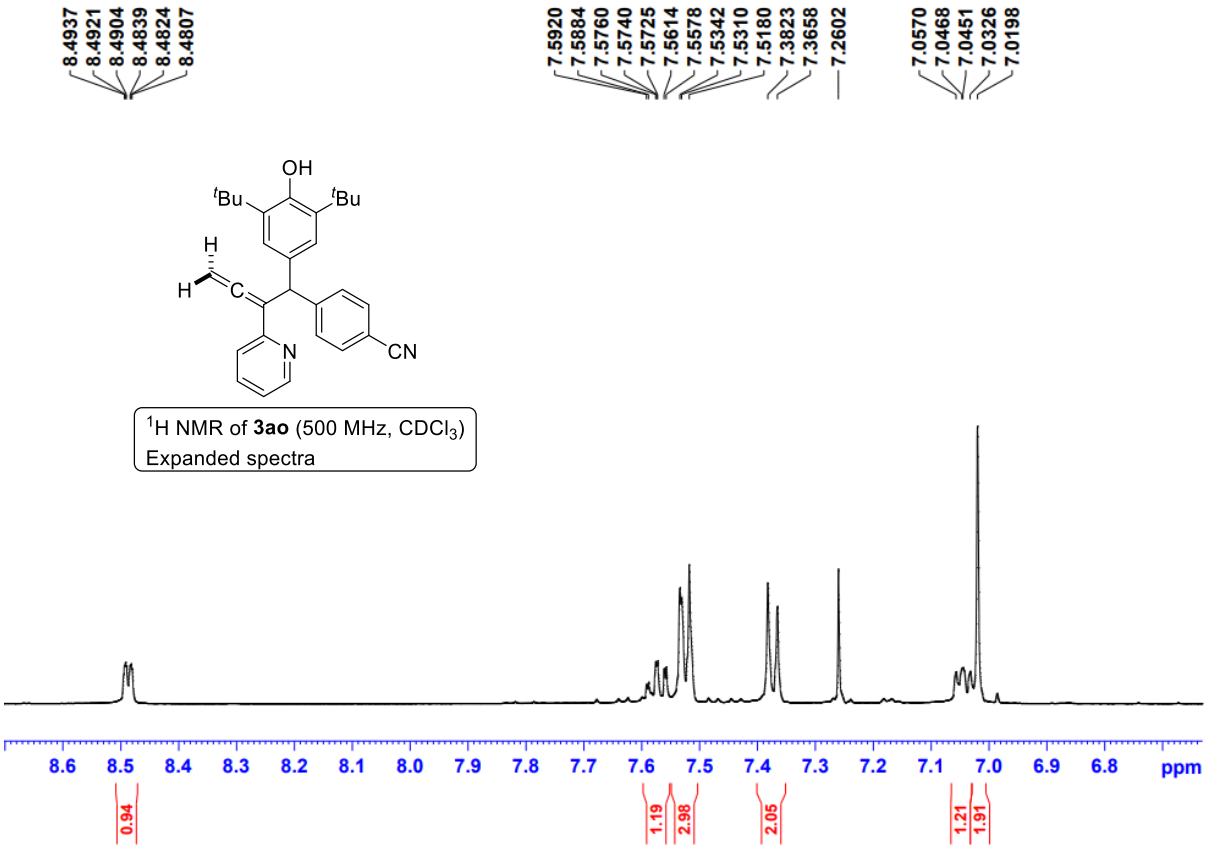
^{1}H NMR of **3an** (500 MHz, $CDCl_3$)
Expanded spectra



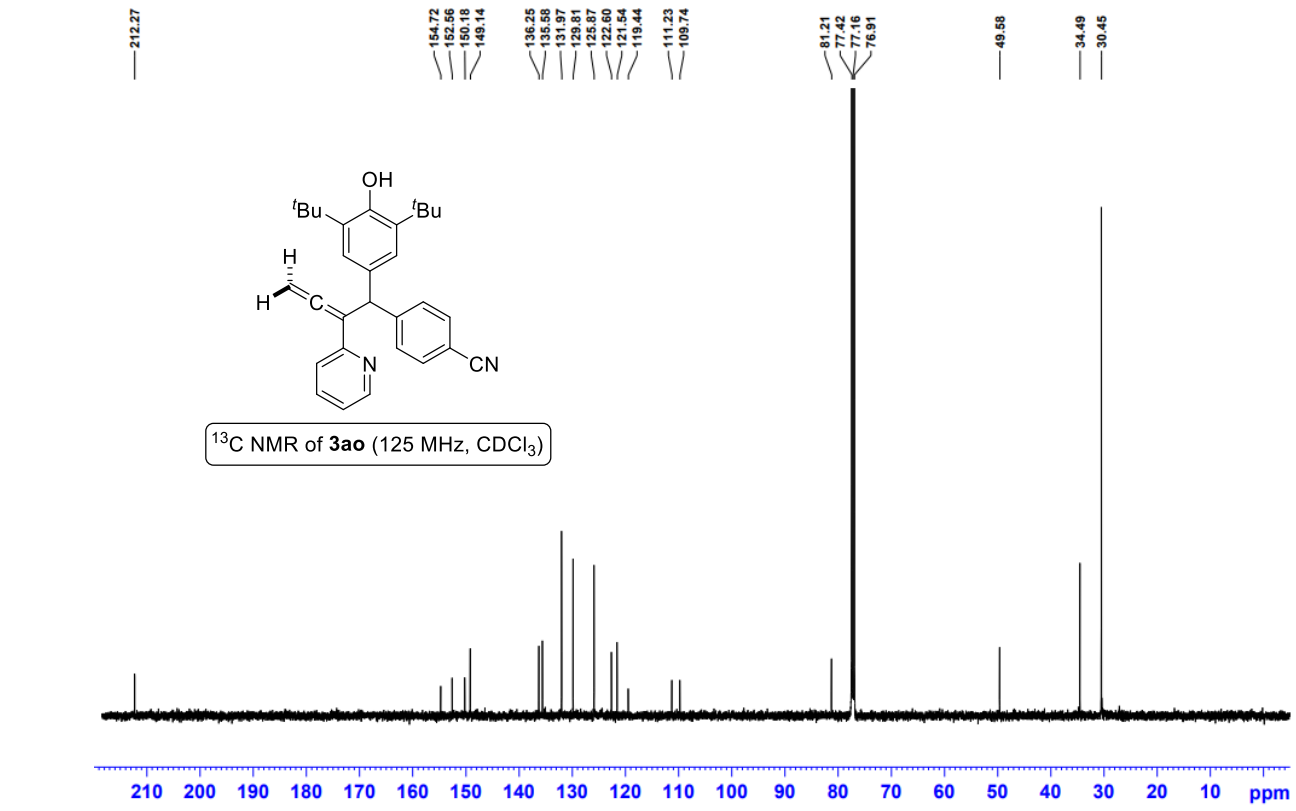
^{13}C NMR of **3an** (125 MHz, $CDCl_3$)



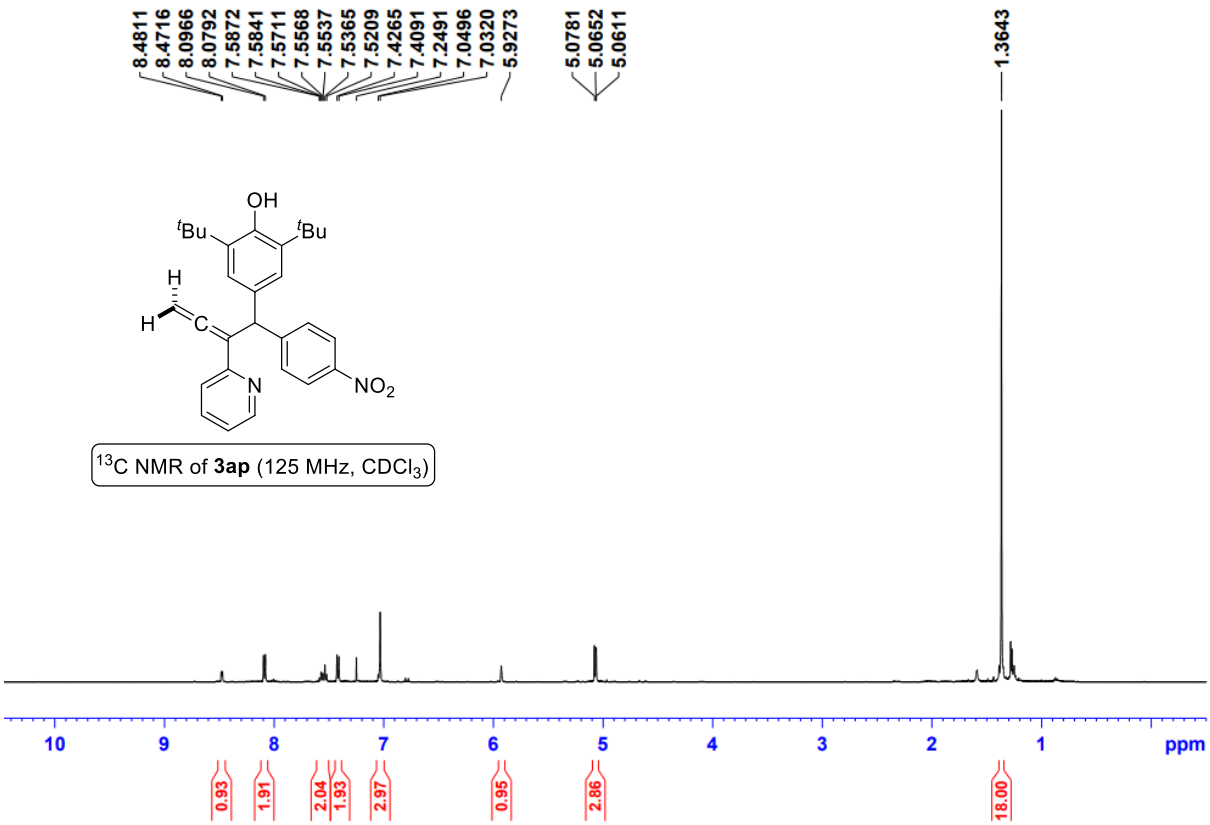
^{1}H NMR of **3ao** (500 MHz, $CDCl_3$)



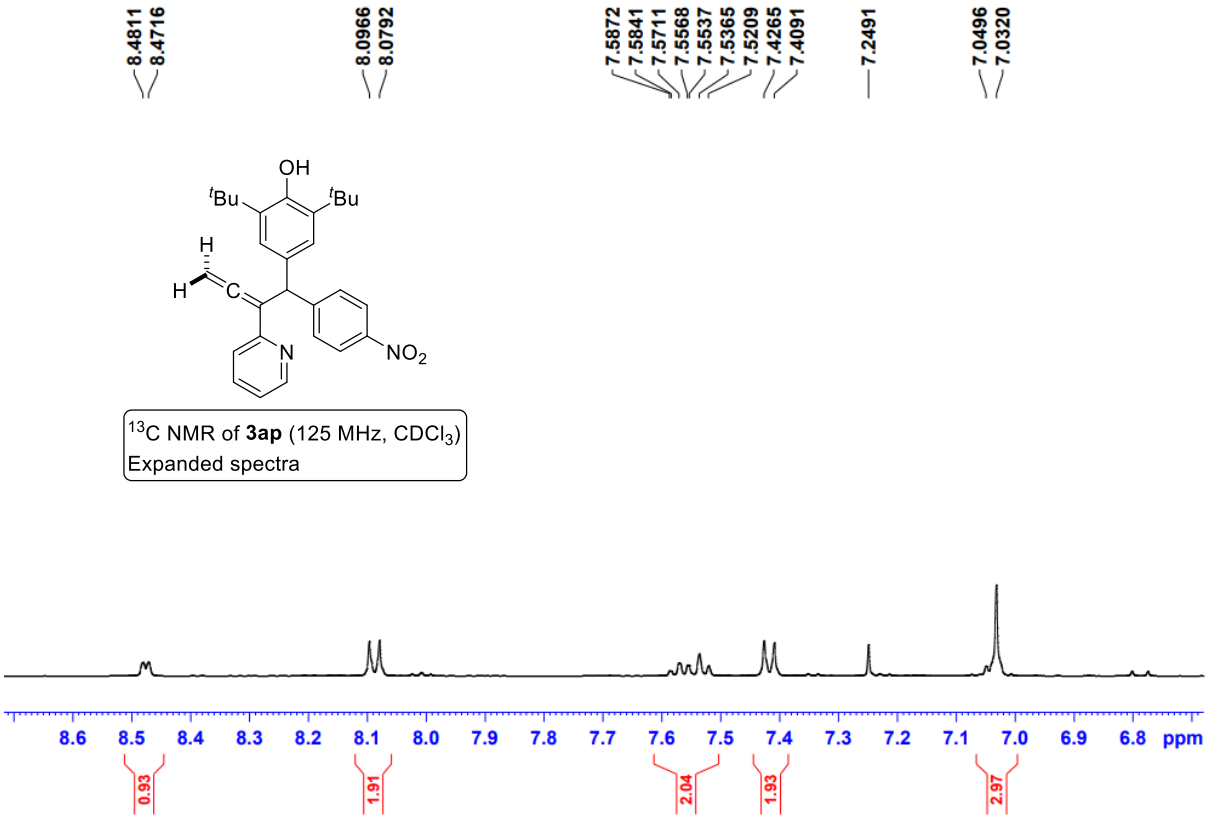
^{1}H NMR of **3ao** (500 MHz, $CDCl_3$)
Expanded spectra



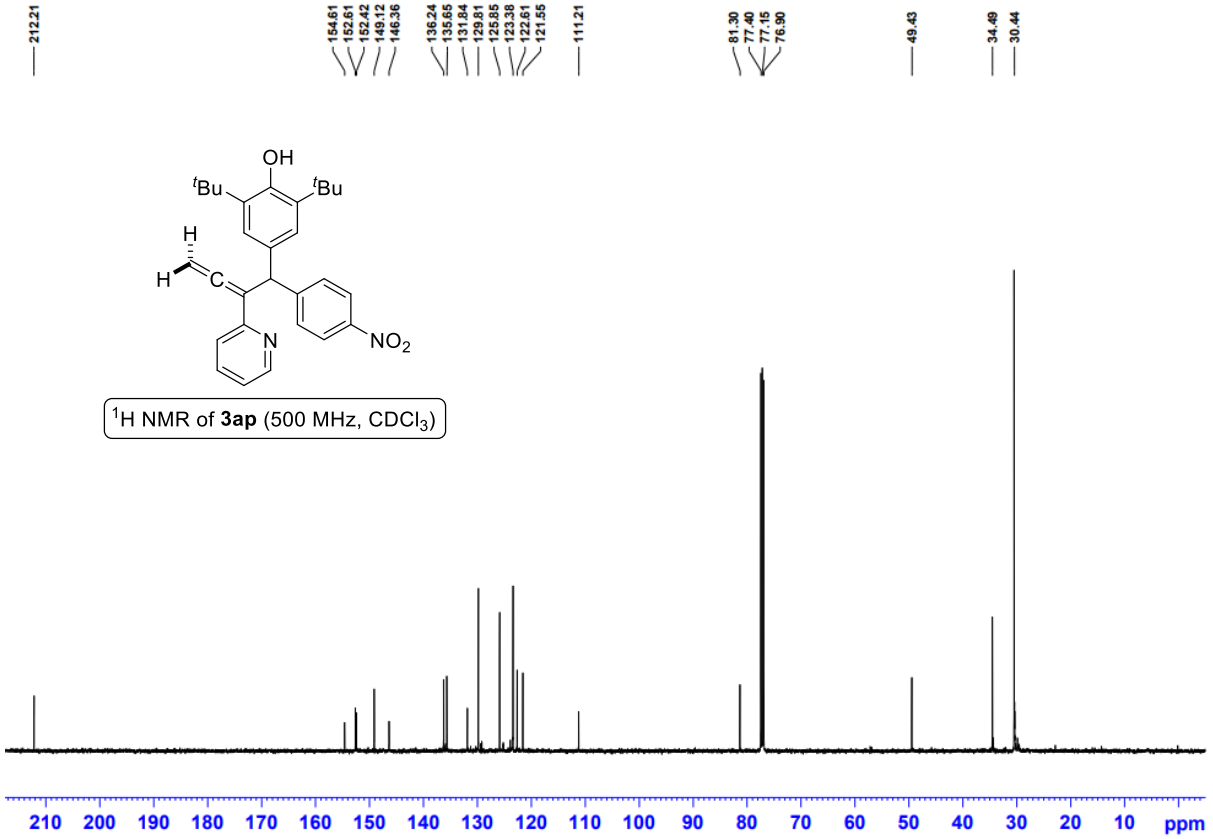
^{13}C NMR of **3ao** (125 MHz, $CDCl_3$)



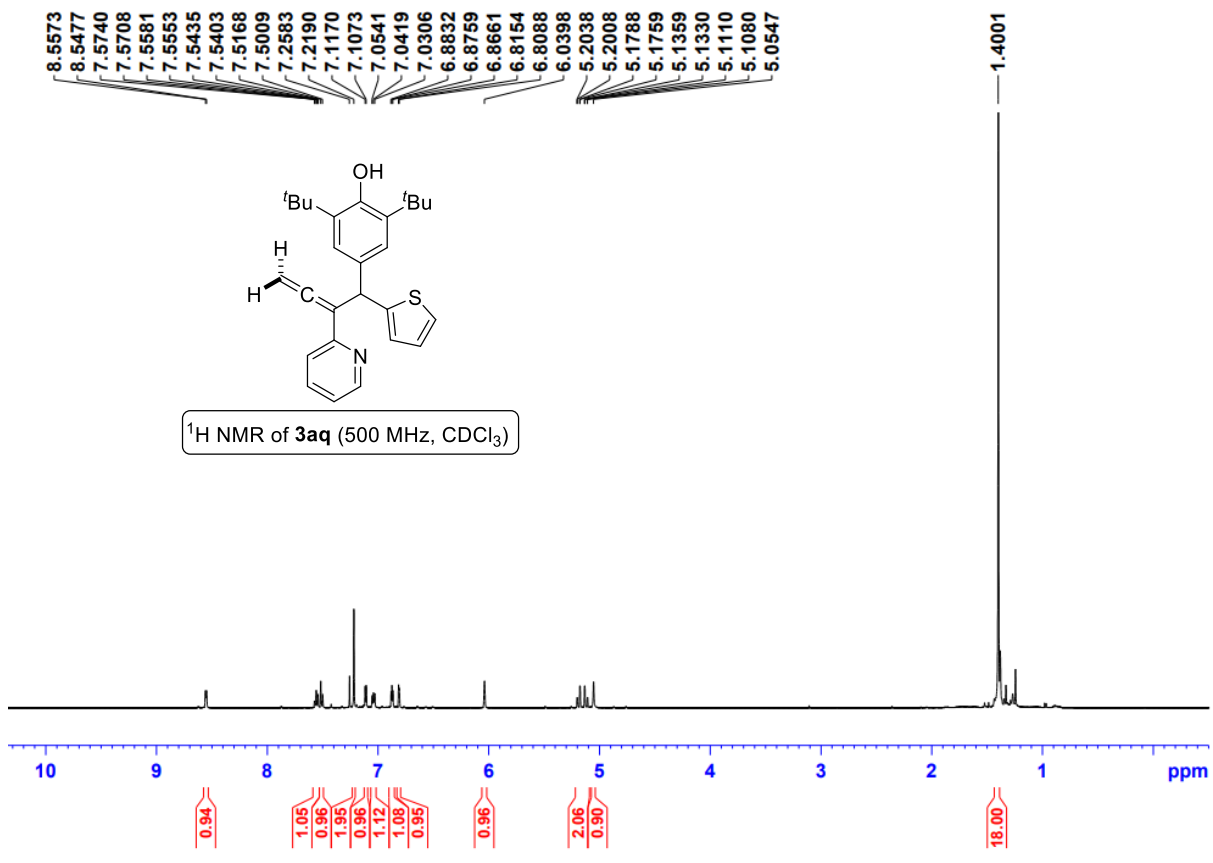
^{13}C NMR of **3ap** (125 MHz, $CDCl_3$)



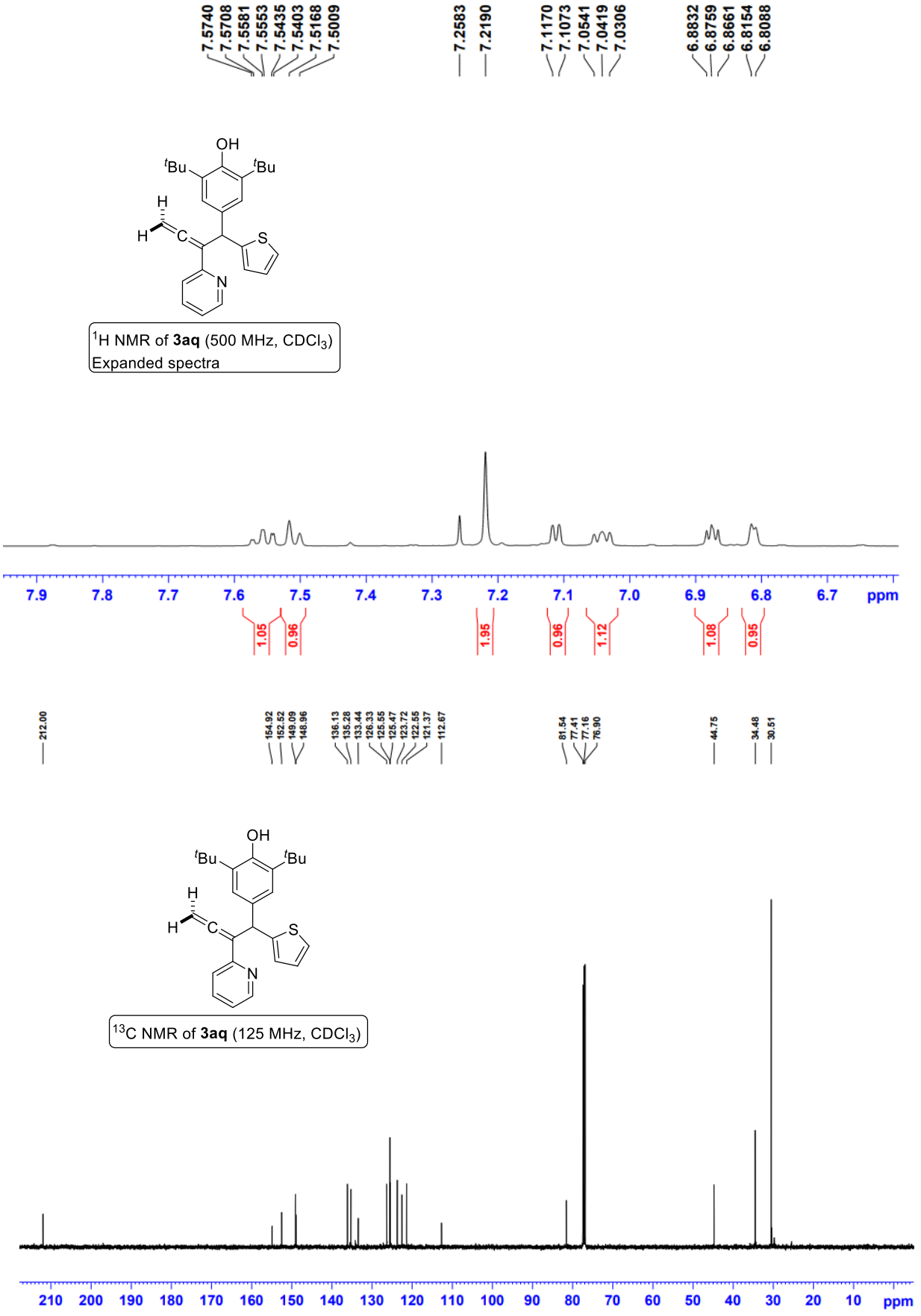
^{13}C NMR of **3ap** (125 MHz, $CDCl_3$)
Expanded spectra



^{1}H NMR of **3ap** (500 MHz, $CDCl_3$)

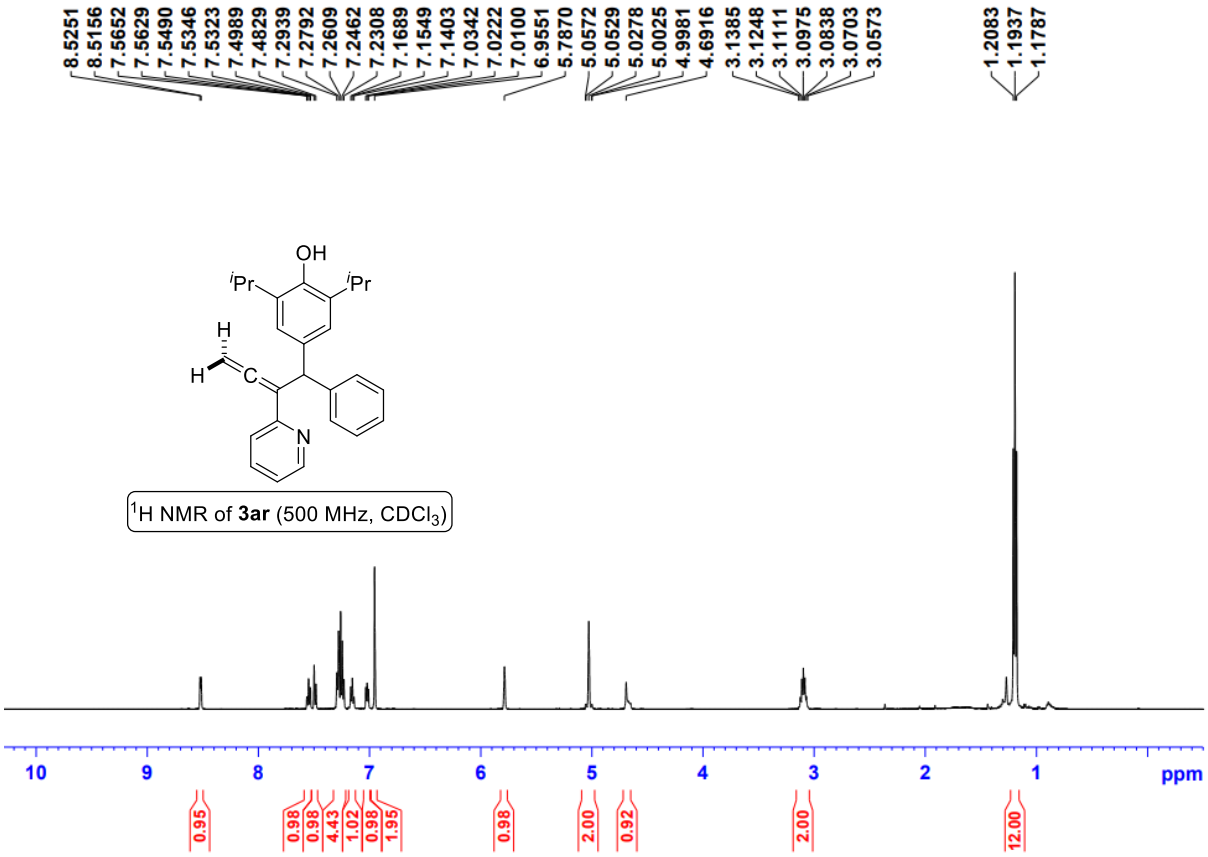


^{1}H NMR of **3aq** (500 MHz, $CDCl_3$)

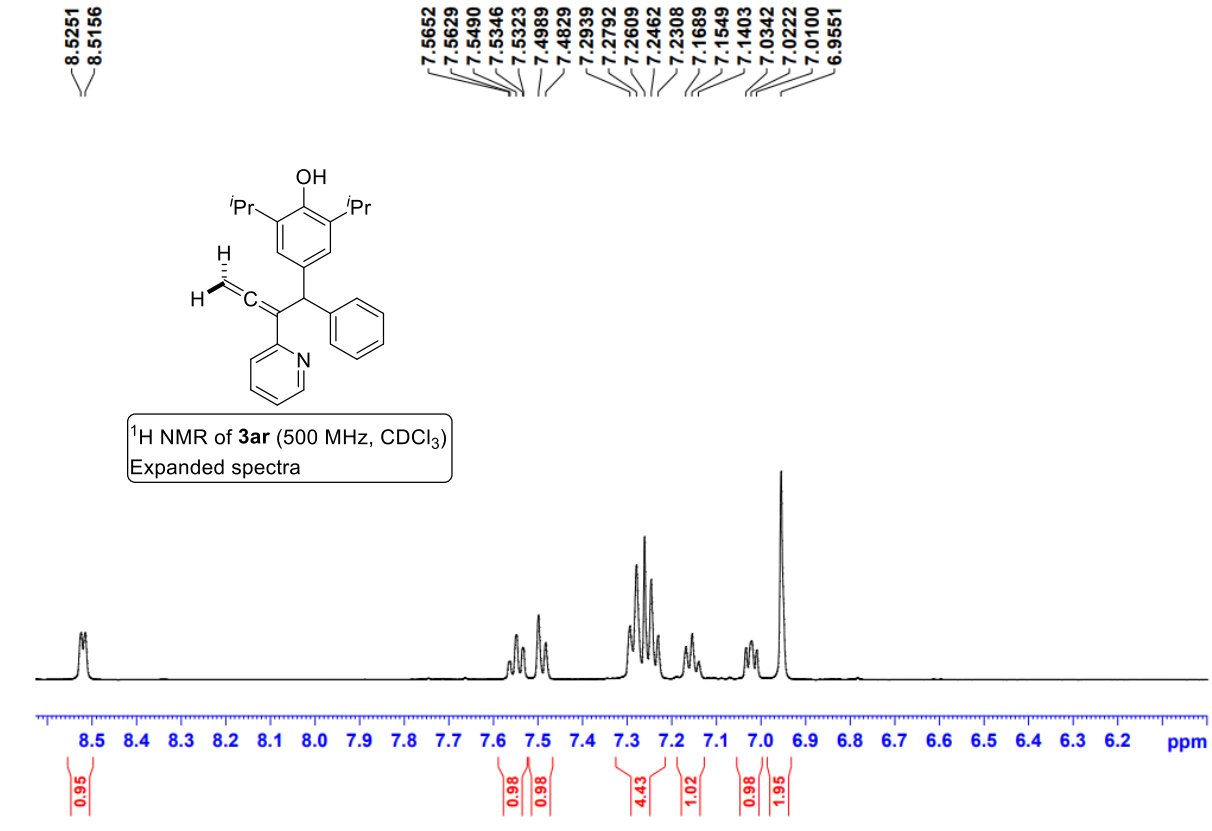


^{1}H NMR of **3aq** (500 MHz, $CDCl_3$)
Expanded spectra

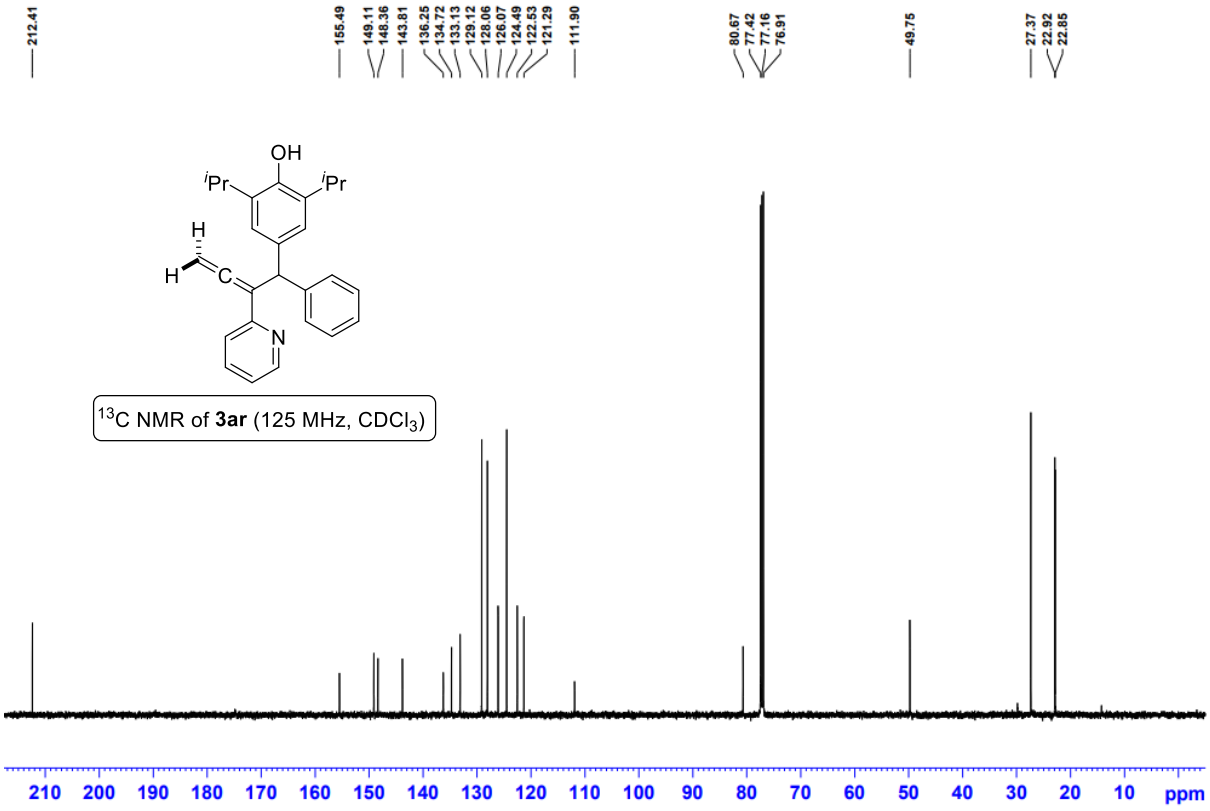
^{13}C NMR of **3aq** (125 MHz, $CDCl_3$)



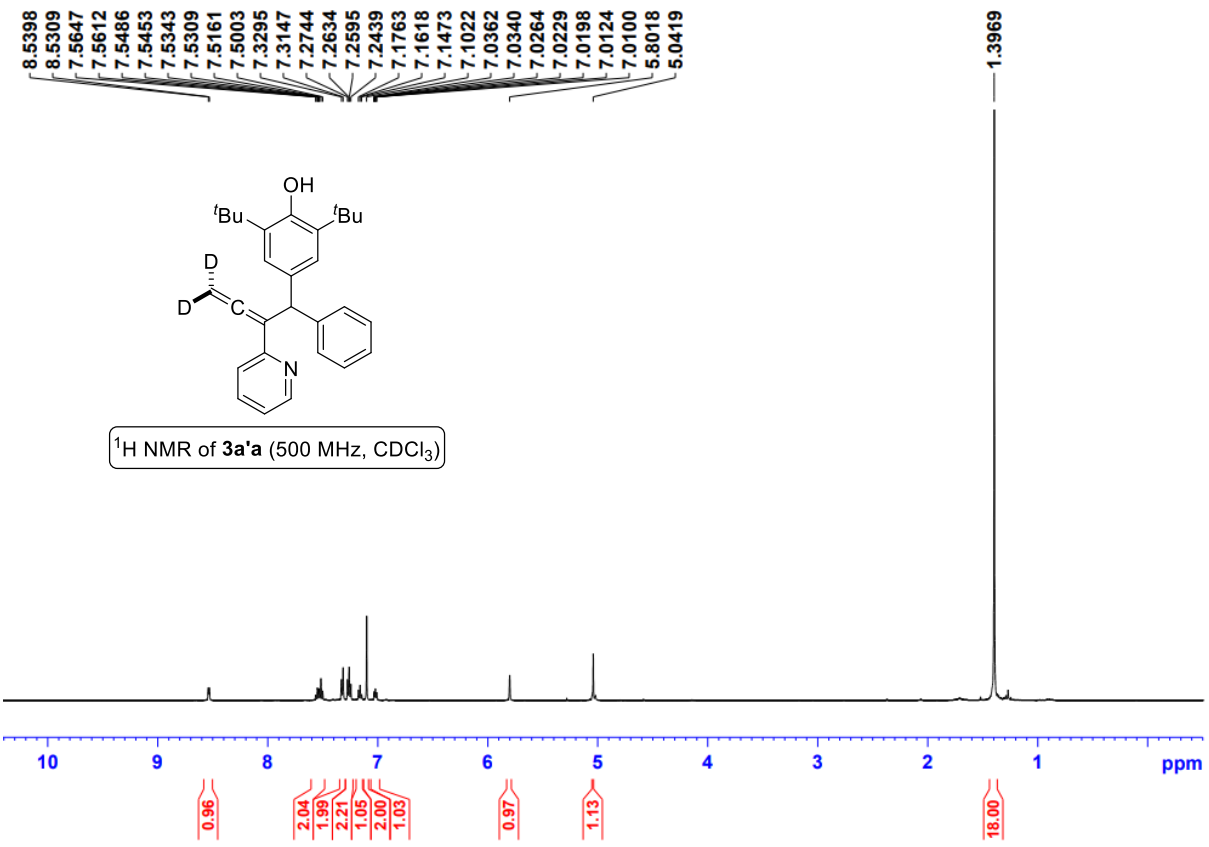
^{1}H NMR of **3ar** (500 MHz, $CDCl_3$)



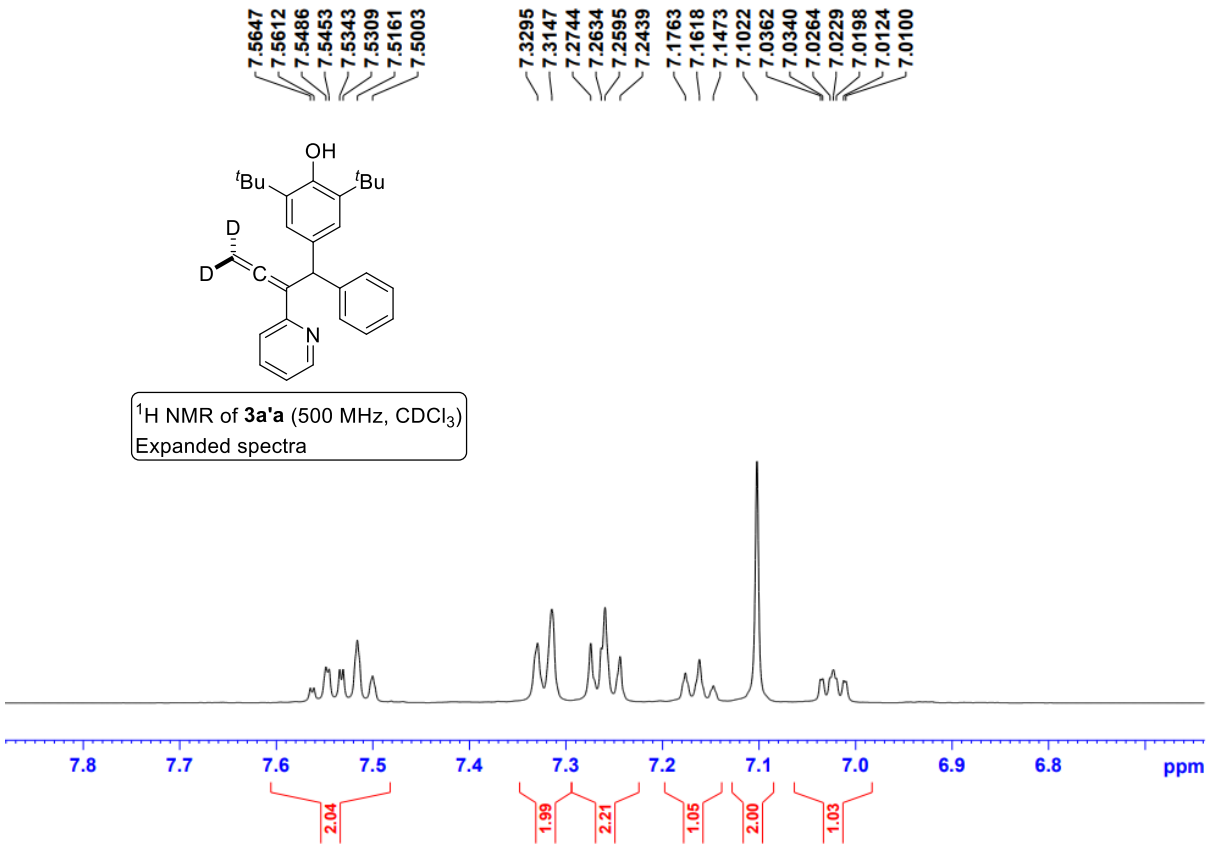
^{1}H NMR of **3ar** (500 MHz, $CDCl_3$)
Expanded spectra



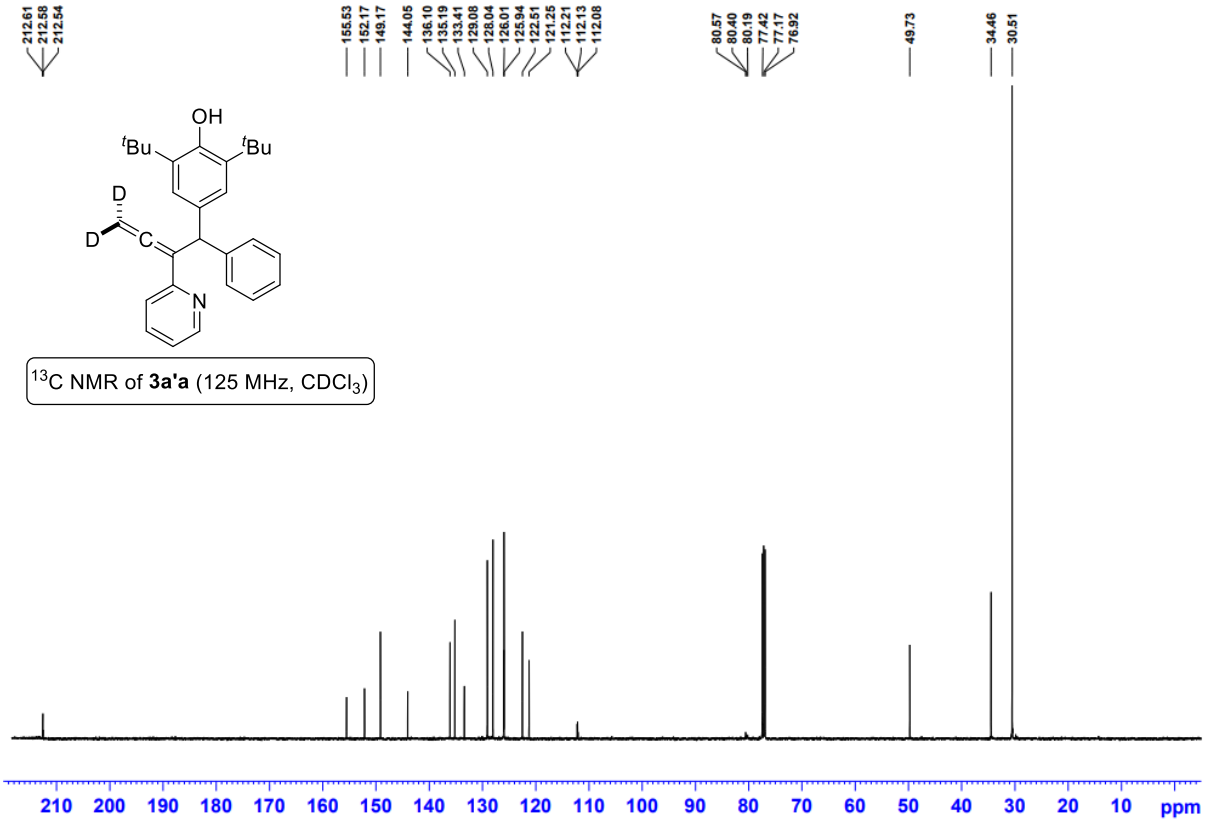
^{13}C NMR of **3ar** (125 MHz, $CDCl_3$)



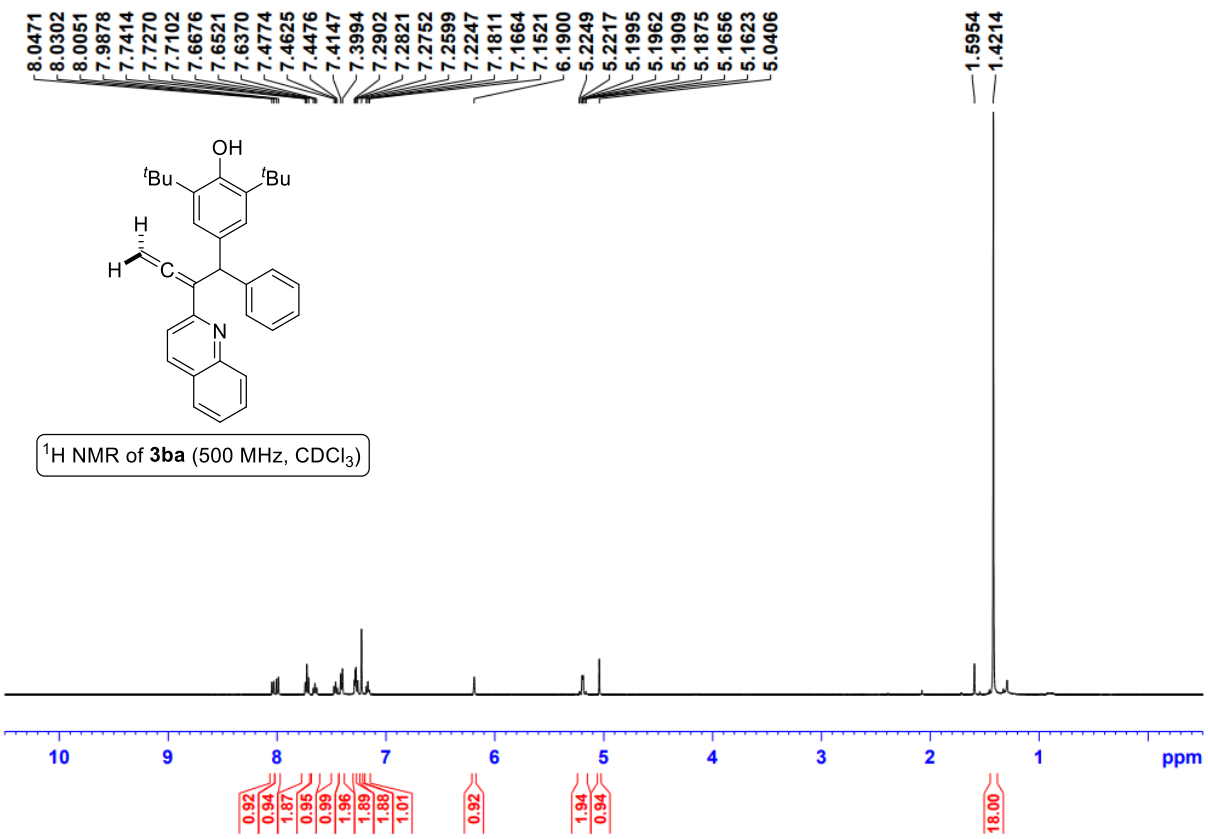
^{1}H NMR of **3a'a** (500 MHz, $CDCl_3$)



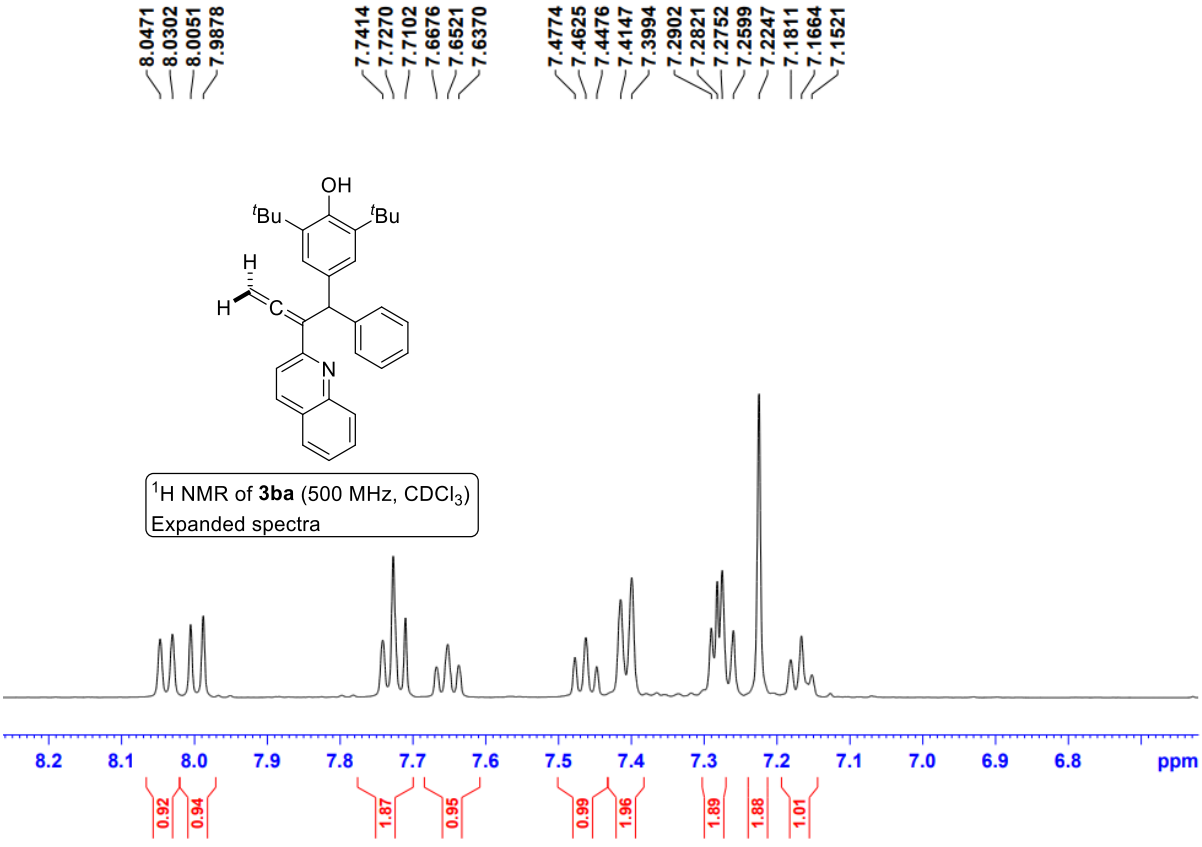
^{1}H NMR of **3a'a** (500 MHz, $CDCl_3$)
Expanded spectra



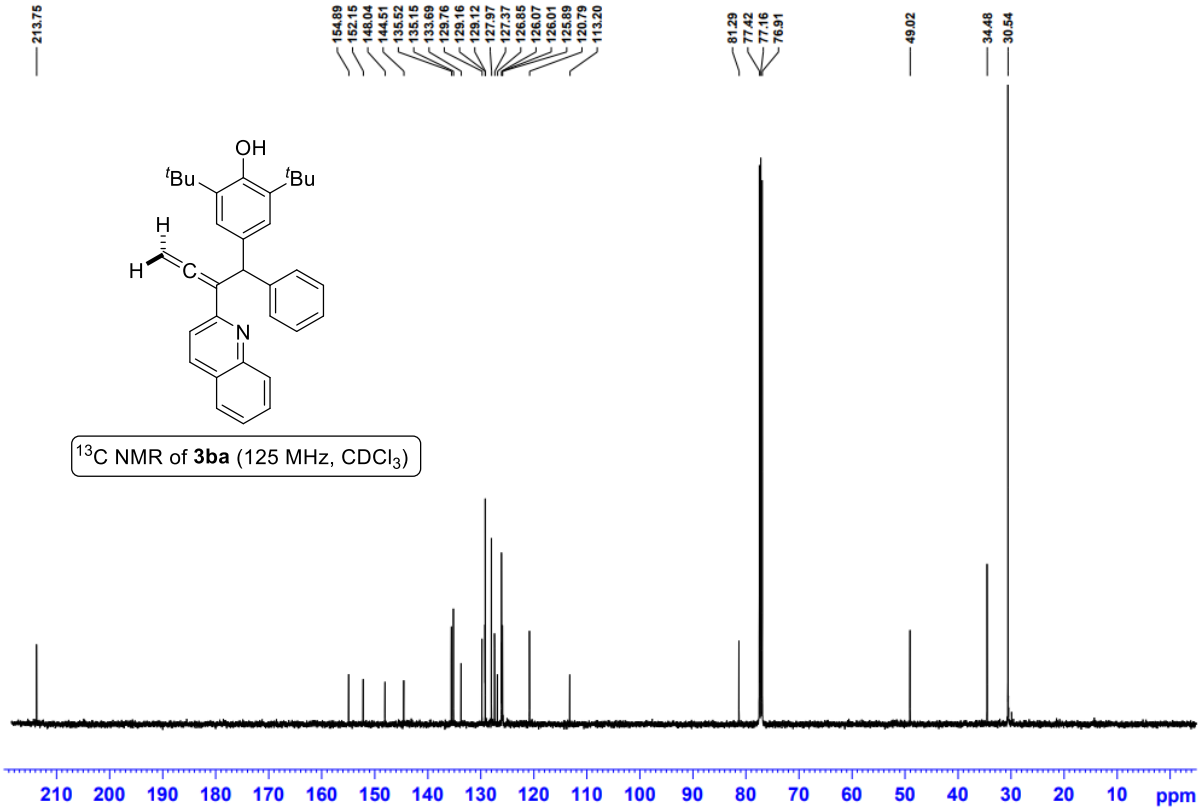
^{13}C NMR of **3a'a** (125 MHz, $CDCl_3$)



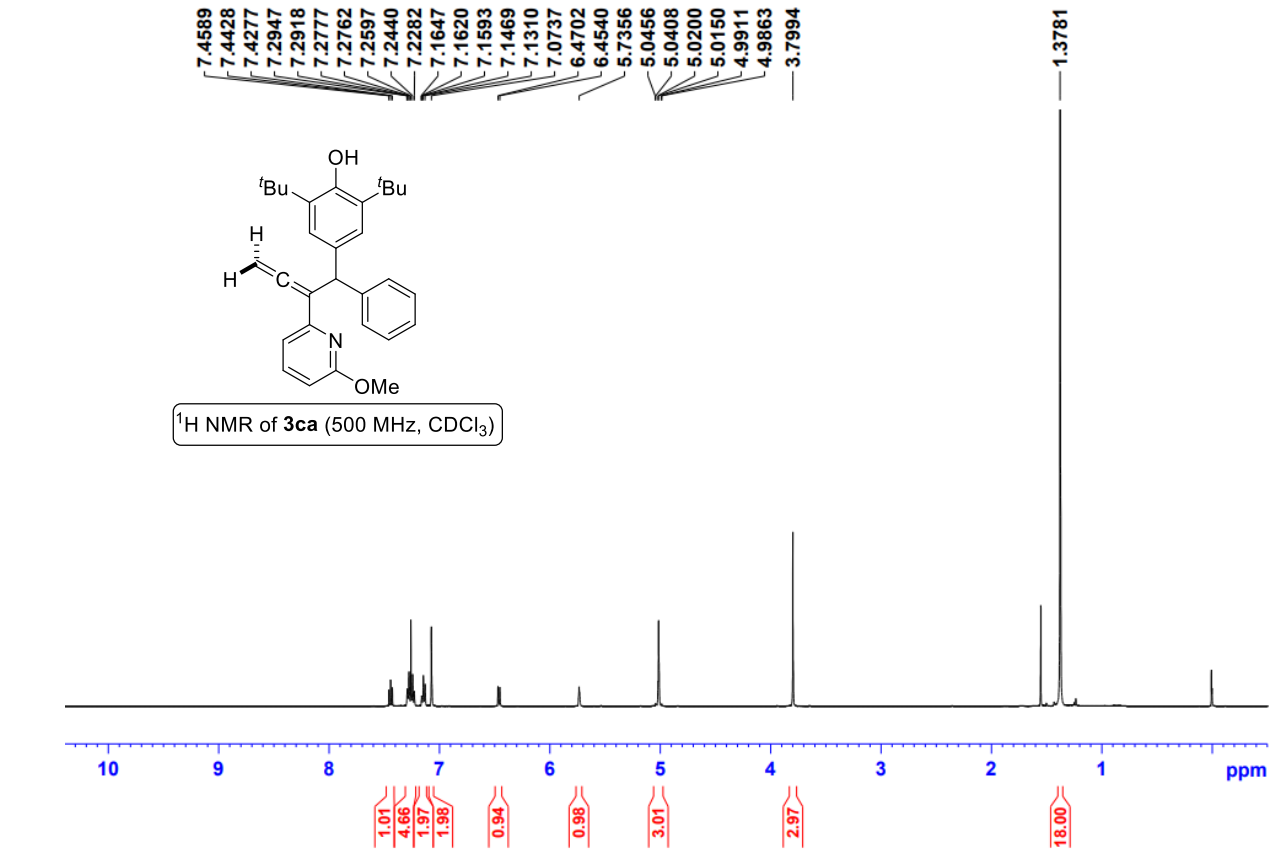
^{1}H NMR of **3ba** (500 MHz, $CDCl_3$)



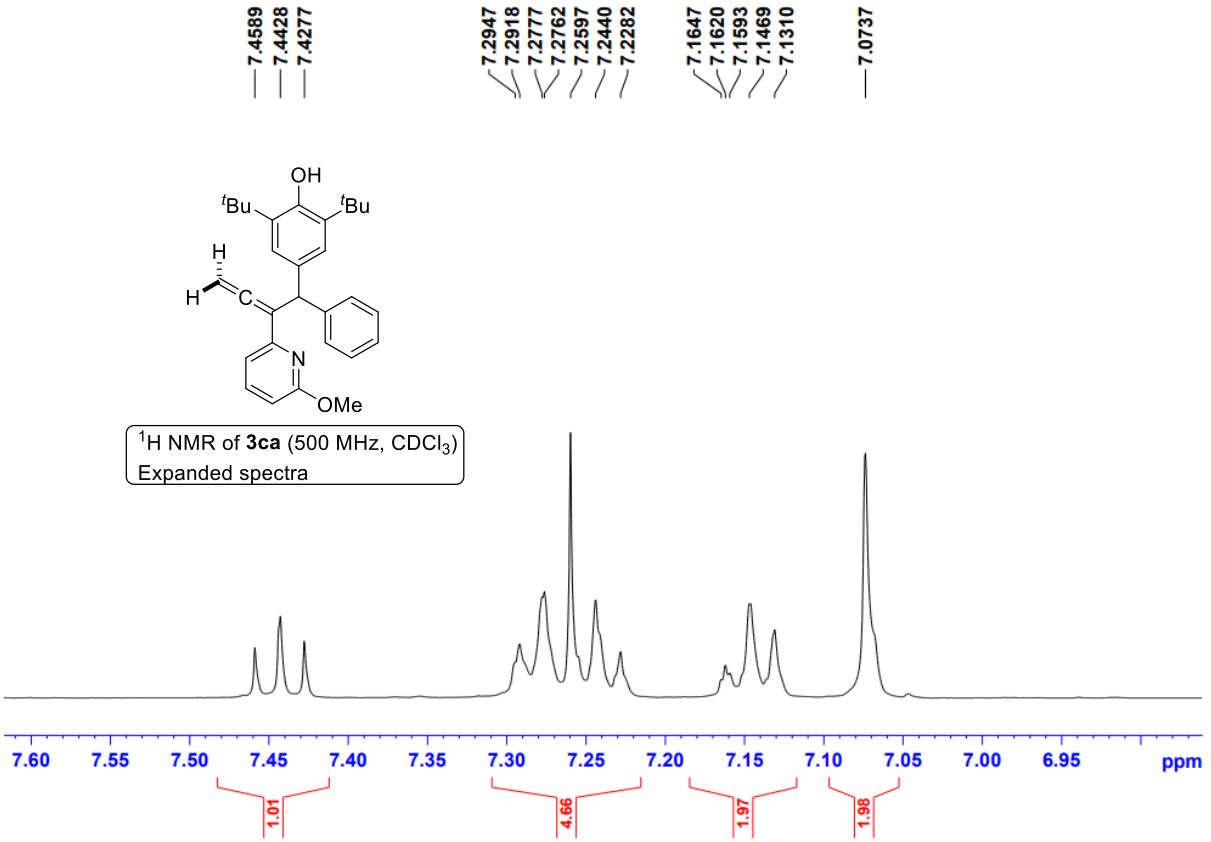
^{1}H NMR of **3ba** (500 MHz, $CDCl_3$)
Expanded spectra



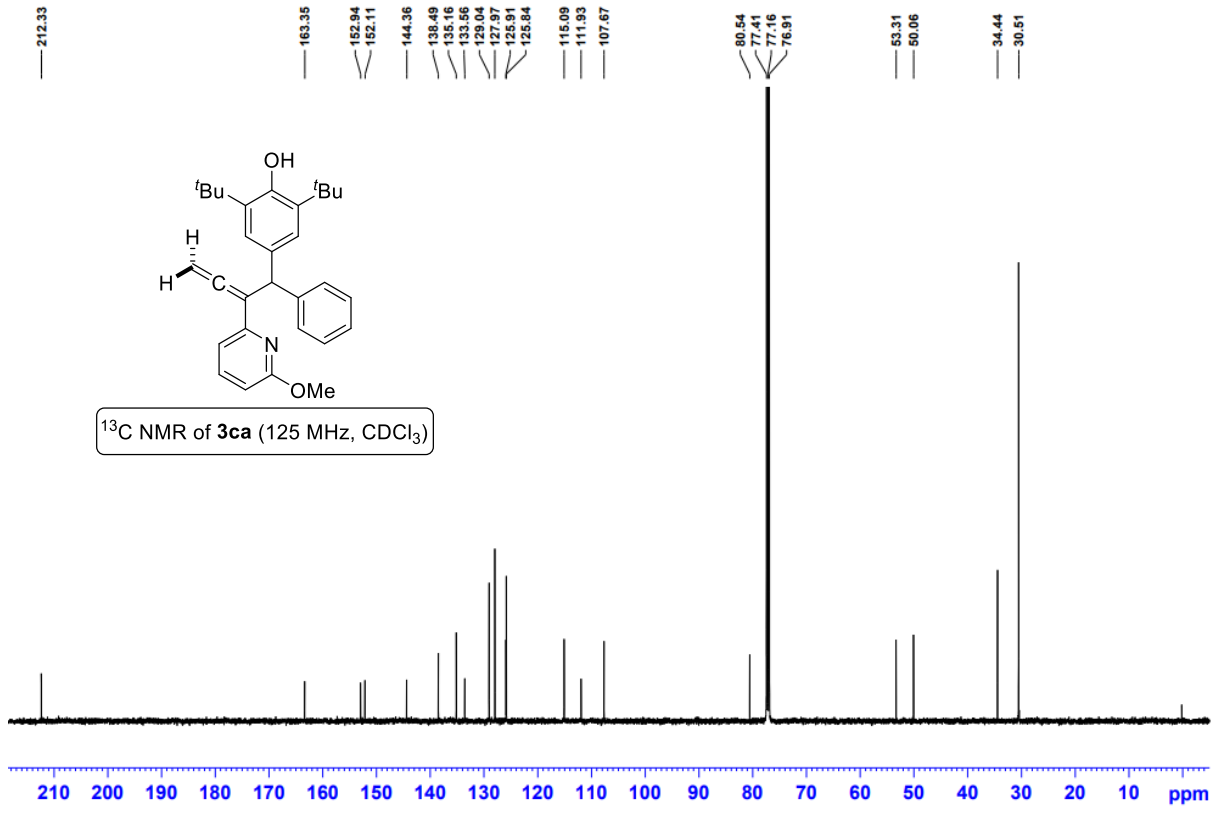
^{13}C NMR of **3ba** (125 MHz, $CDCl_3$)



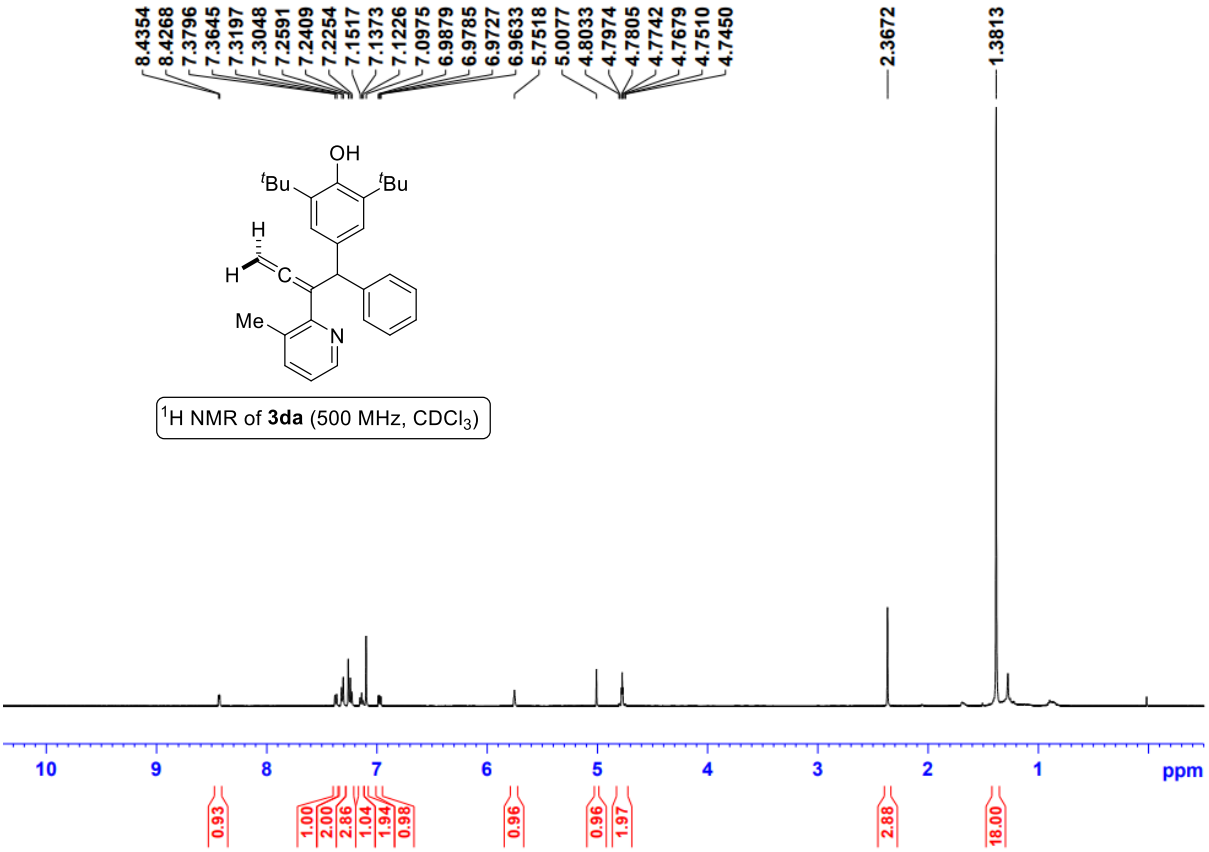
^{1}H NMR of **3ca** (500 MHz, $CDCl_3$)



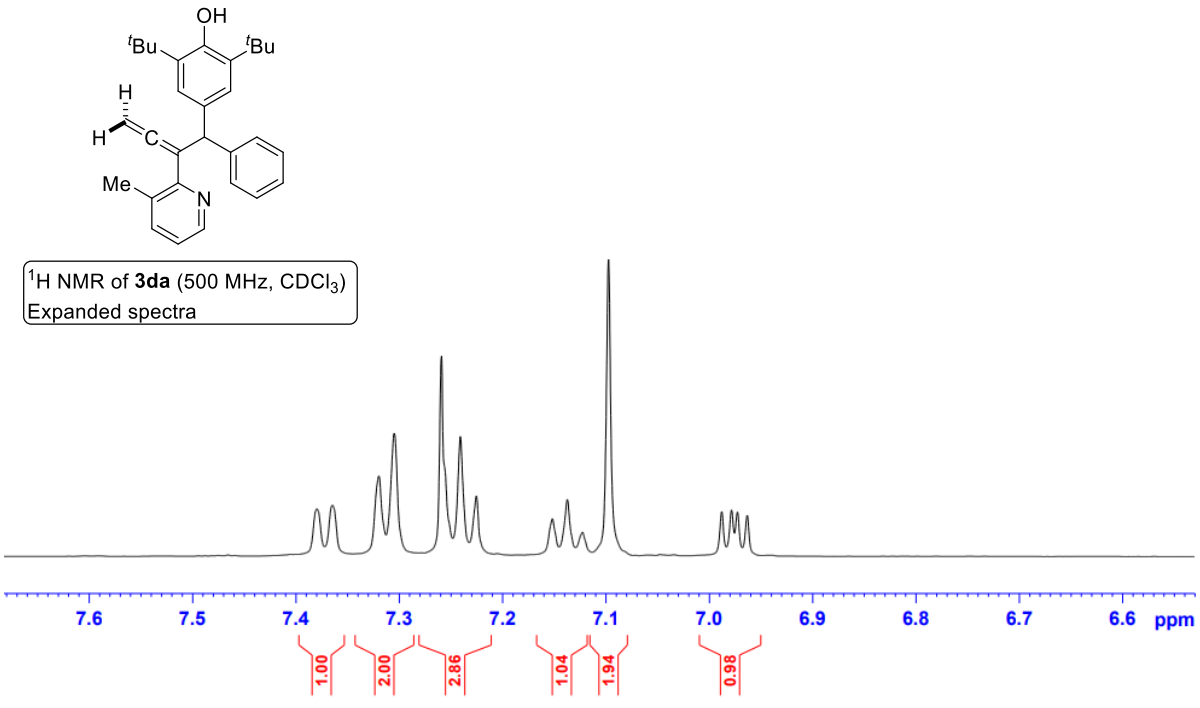
^{1}H NMR of **3ca** (500 MHz, $CDCl_3$)
Expanded spectra



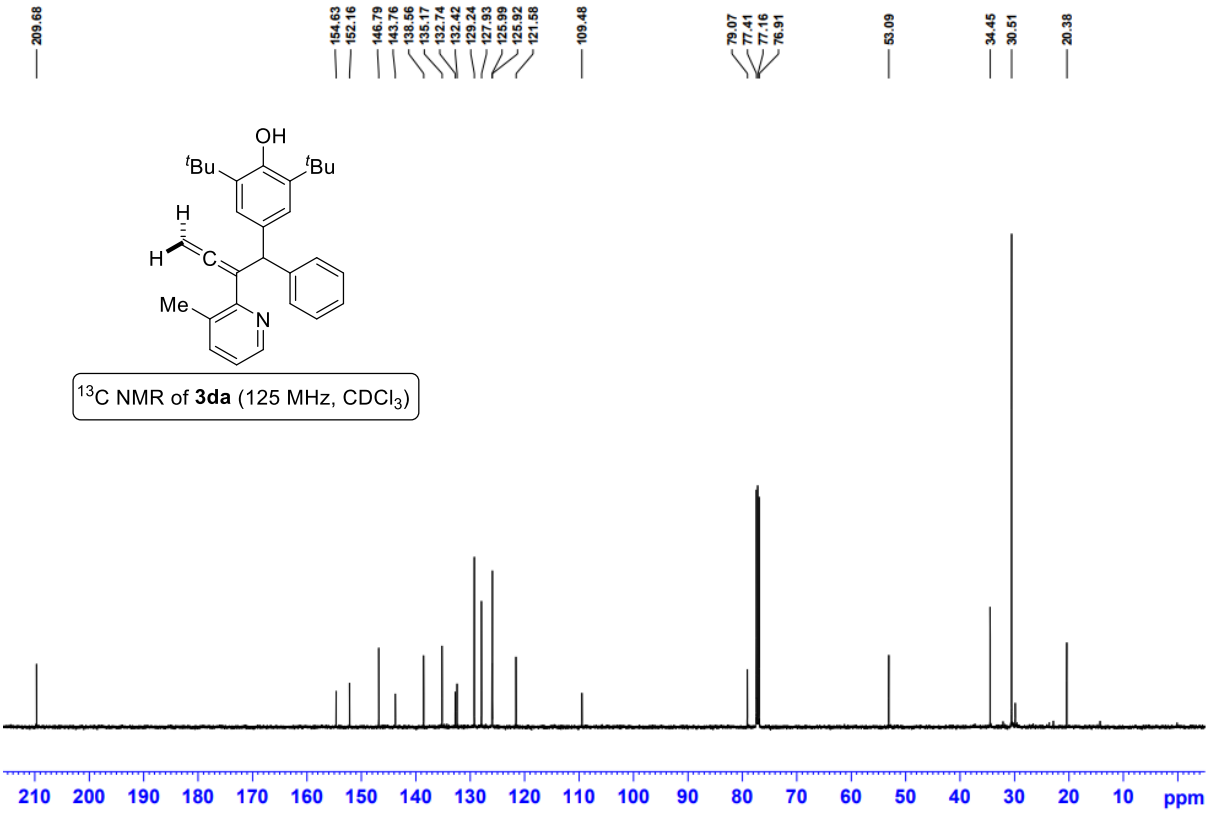
^{13}C NMR of **3ca** (125 MHz, $CDCl_3$)



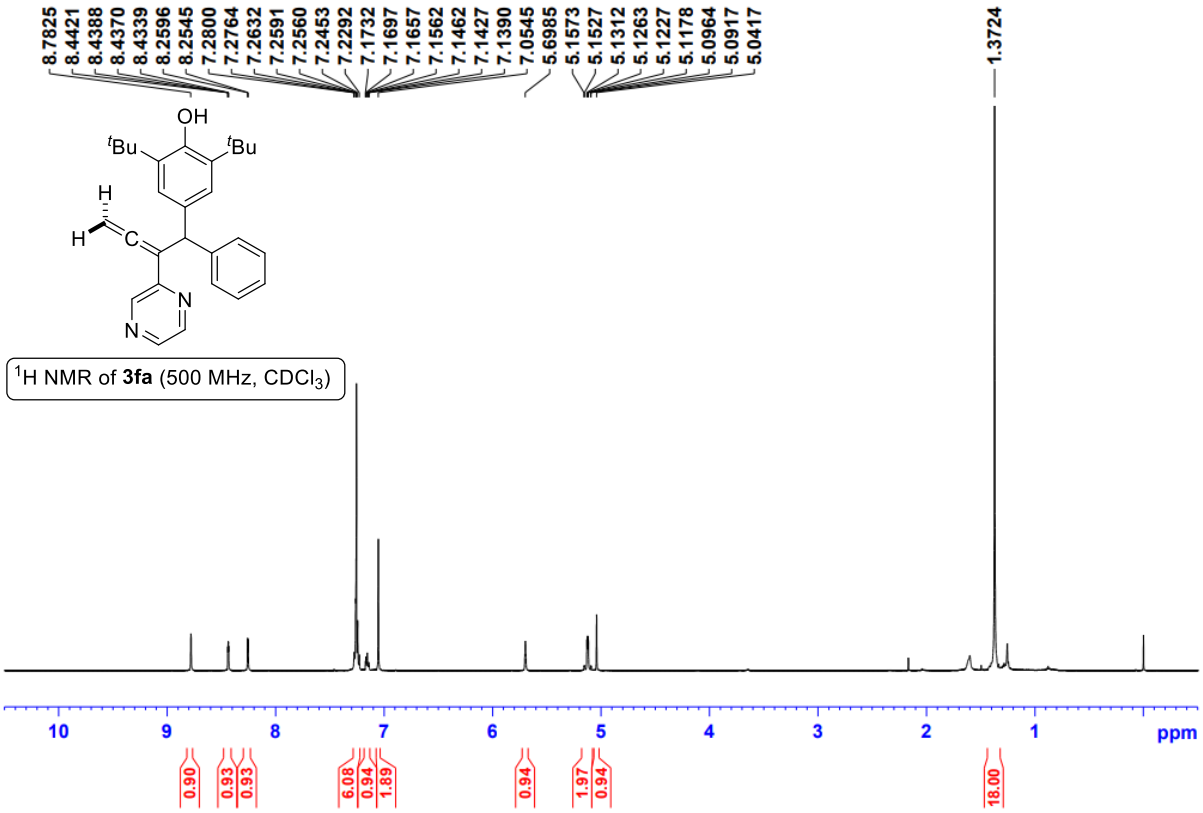
^{1}H NMR of **3da** (500 MHz, $CDCl_3$)



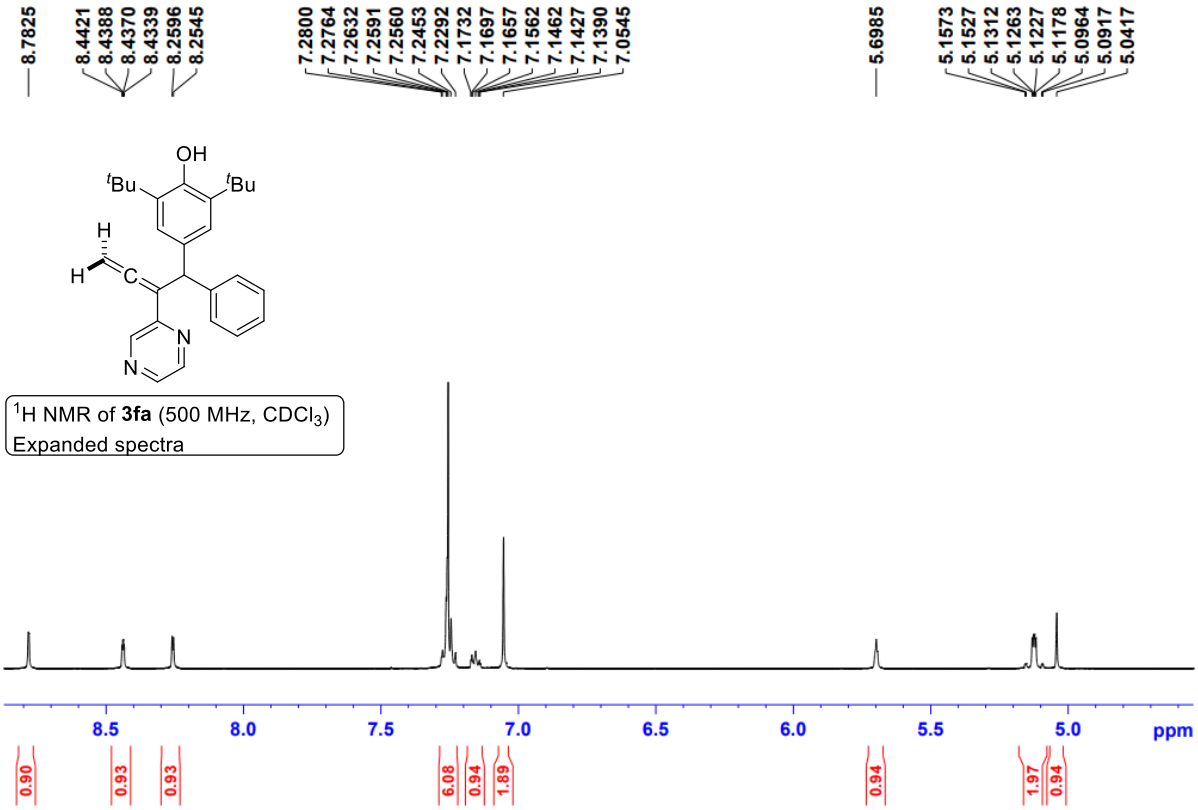
^{1}H NMR of **3da** (500 MHz, $CDCl_3$)
Expanded spectra



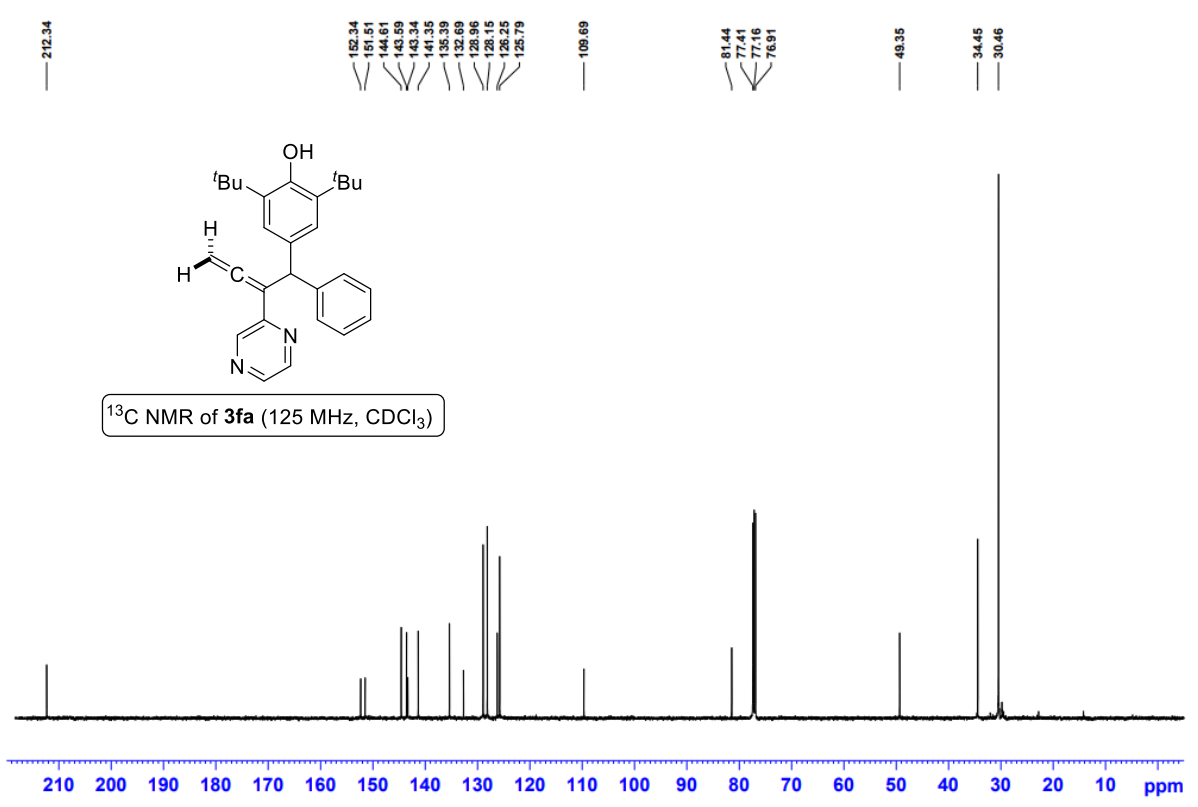
^{13}C NMR of **3da** (125 MHz, $CDCl_3$)



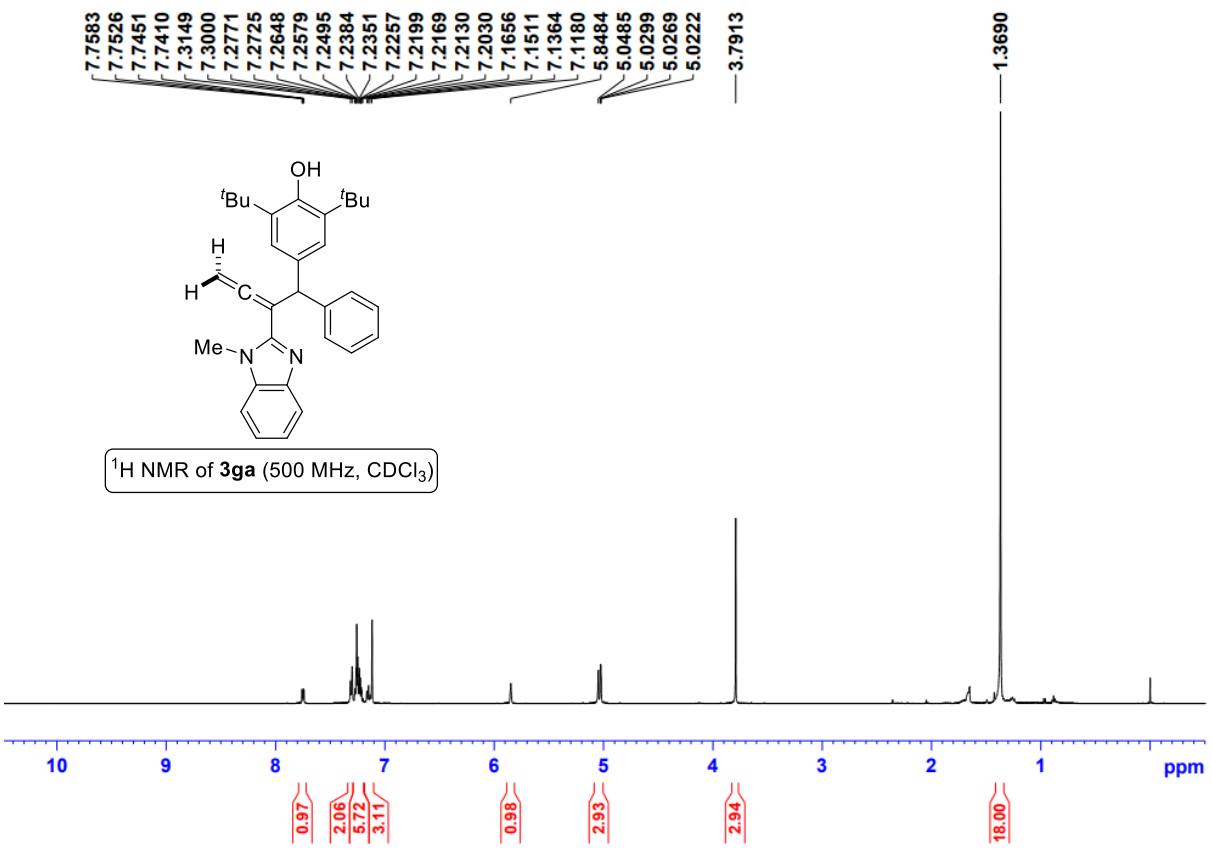
^{1}H NMR of **3fa** (500 MHz, $CDCl_3$)



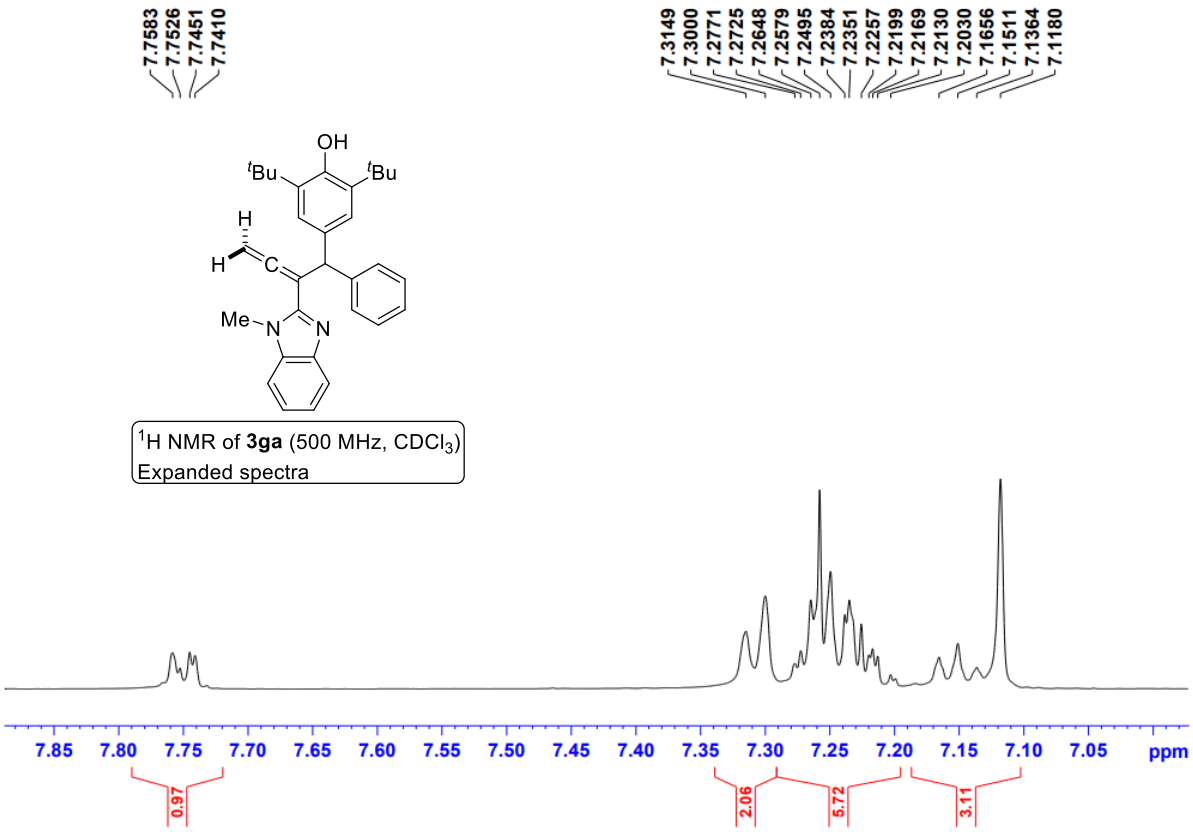
^{1}H NMR of **3fa** (500 MHz, $CDCl_3$)
Expanded spectra



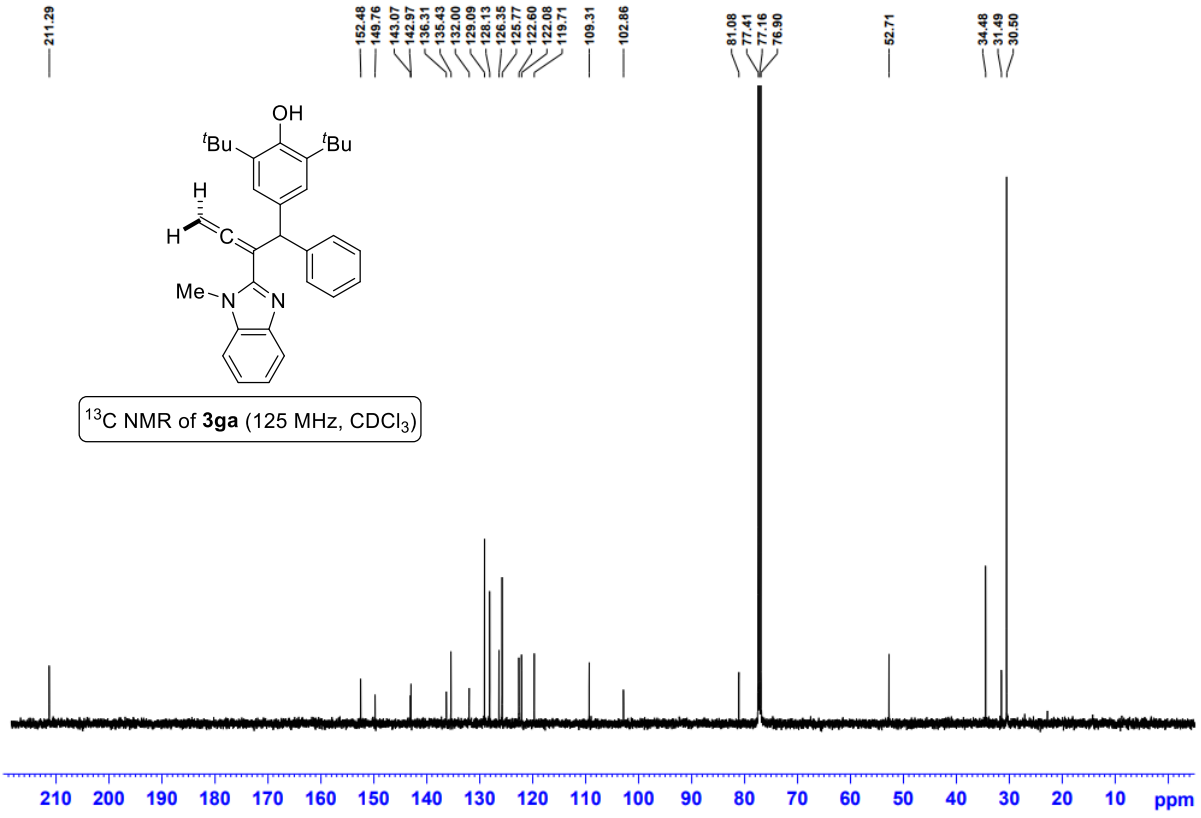
^{13}C NMR of **3fa** (125 MHz, $CDCl_3$)



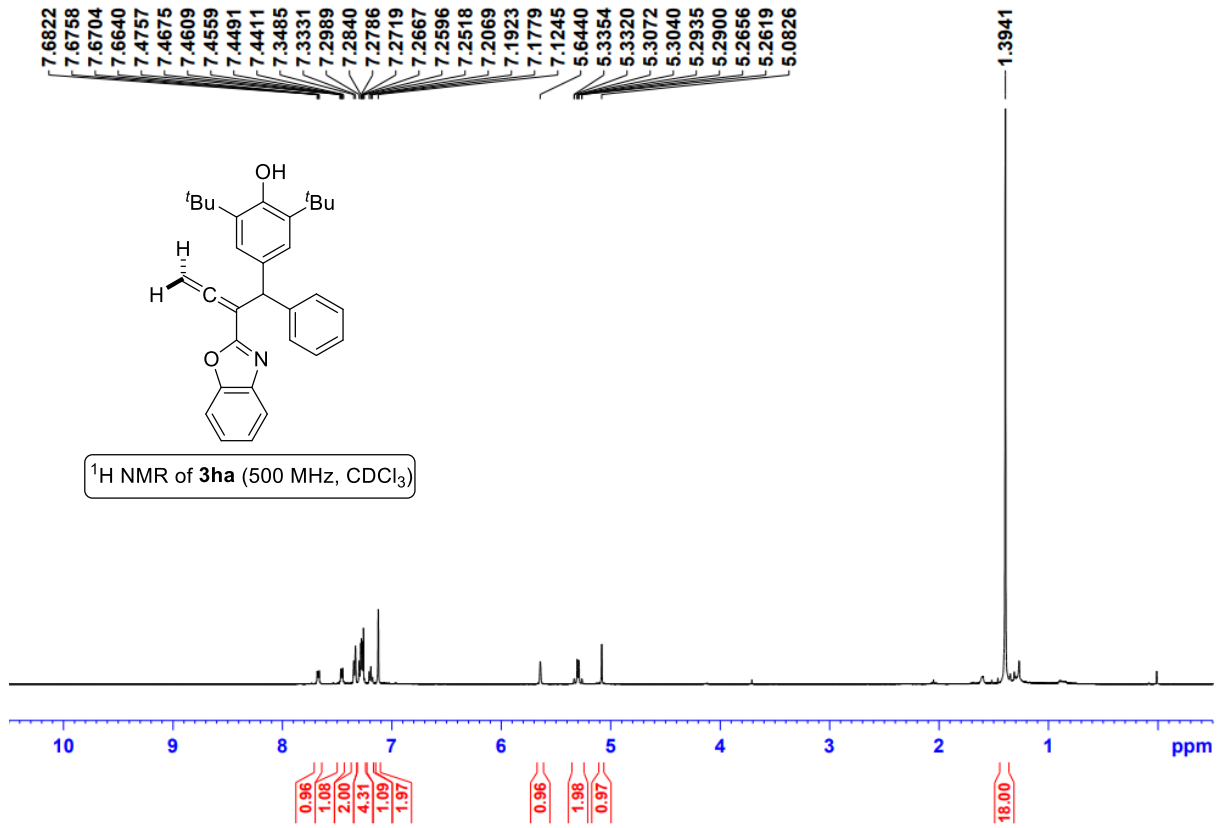
^{1}H NMR of **3ga** (500 MHz, $CDCl_3$)



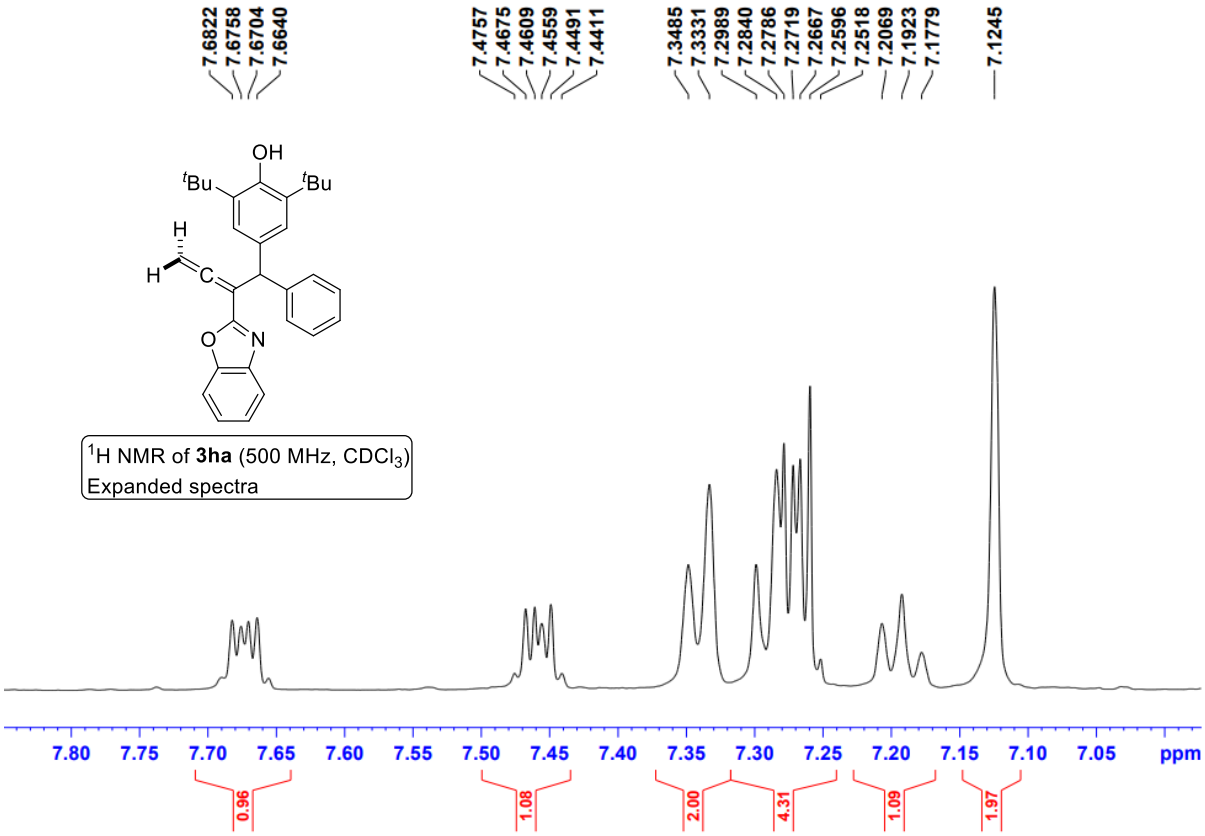
^{1}H NMR of **3ga** (500 MHz, $CDCl_3$)
Expanded spectra



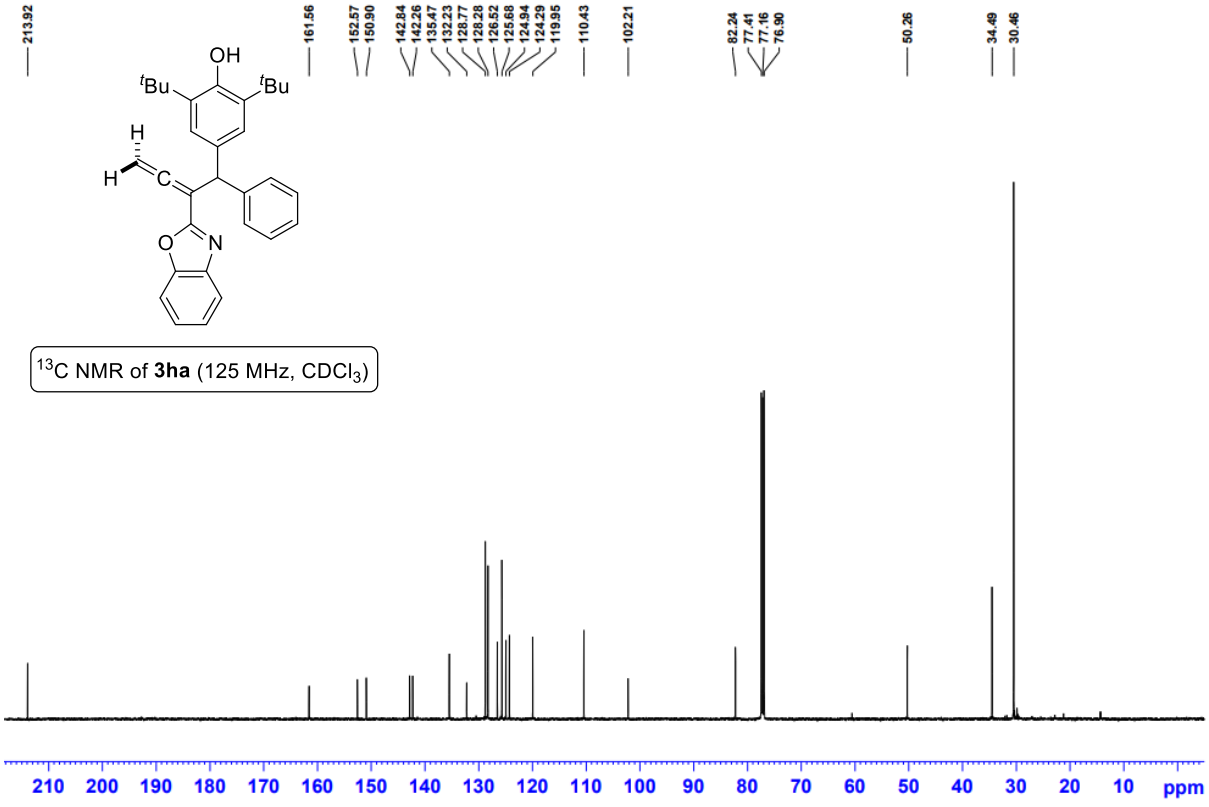
^{13}C NMR of **3ga** (125 MHz, $CDCl_3$)



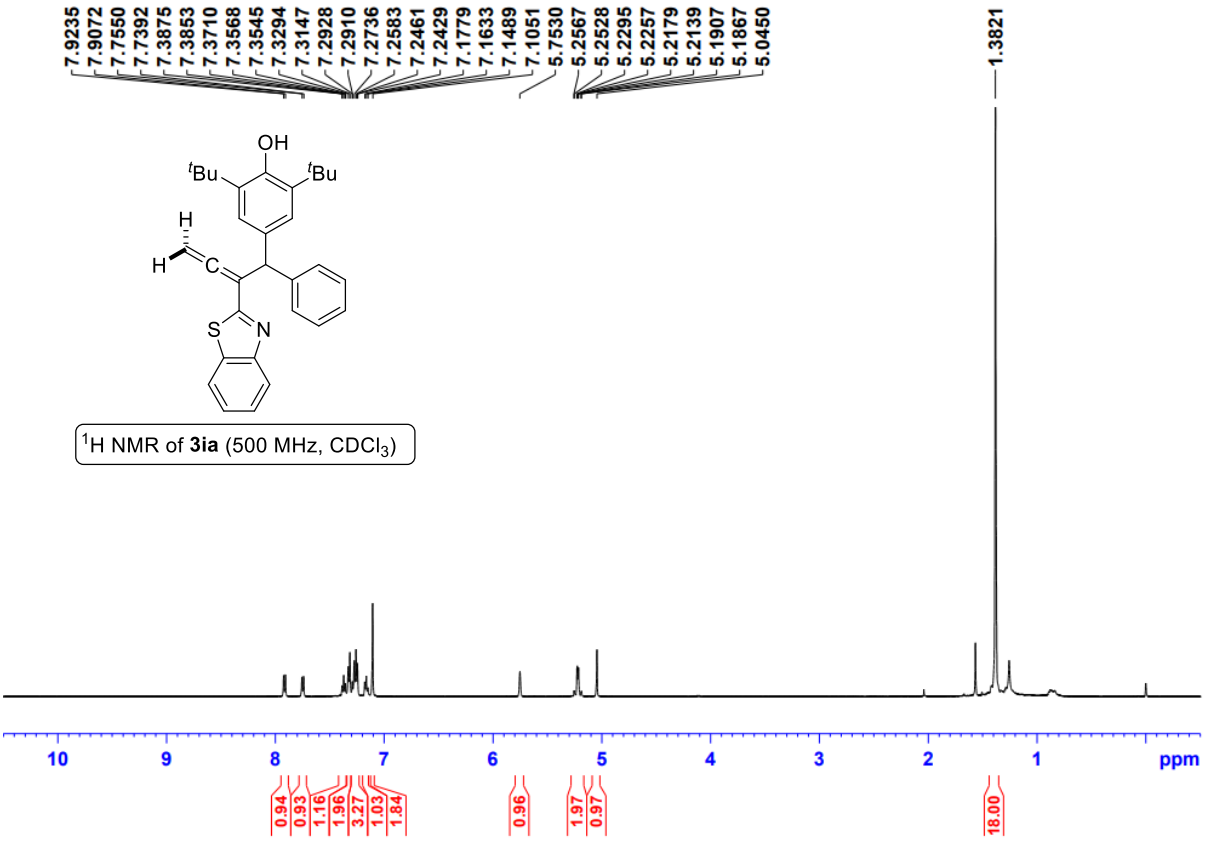
^{1}H NMR of **3ha** (500 MHz, $CDCl_3$)



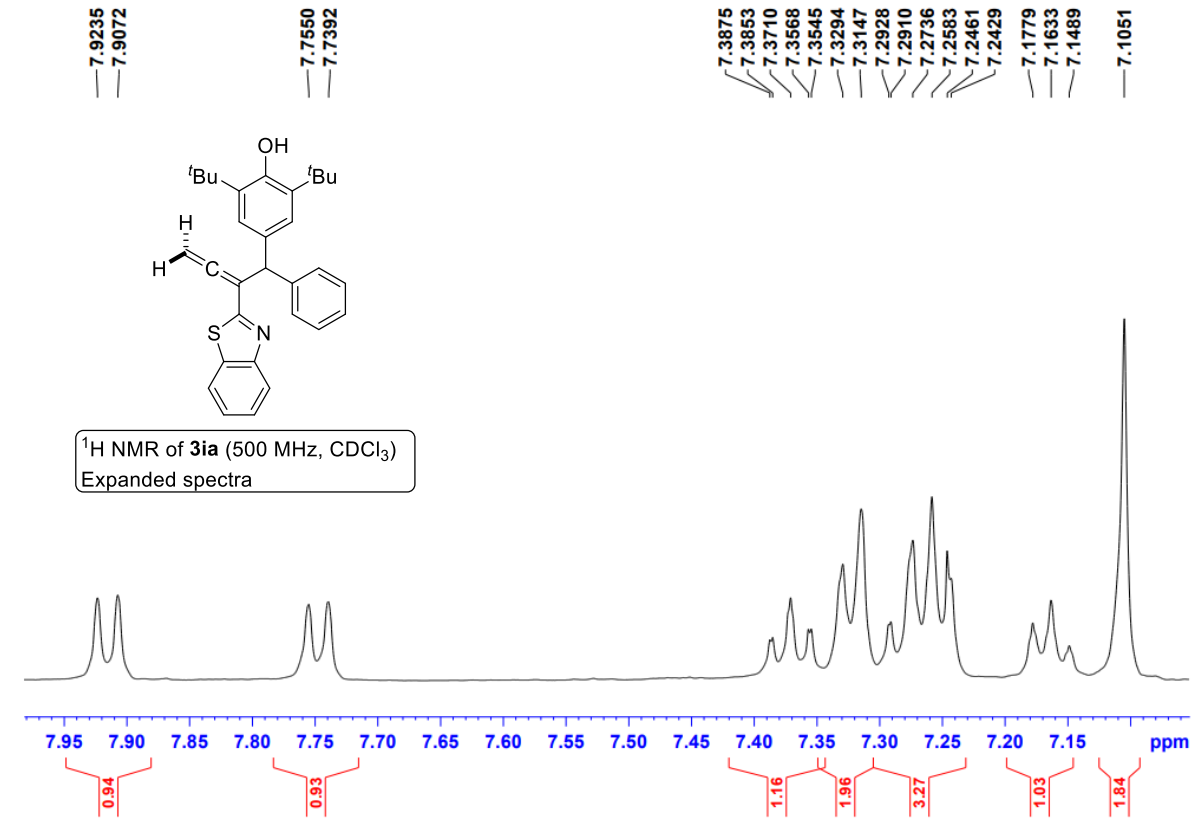
^{1}H NMR of **3ha** (500 MHz, $CDCl_3$)
Expanded spectra



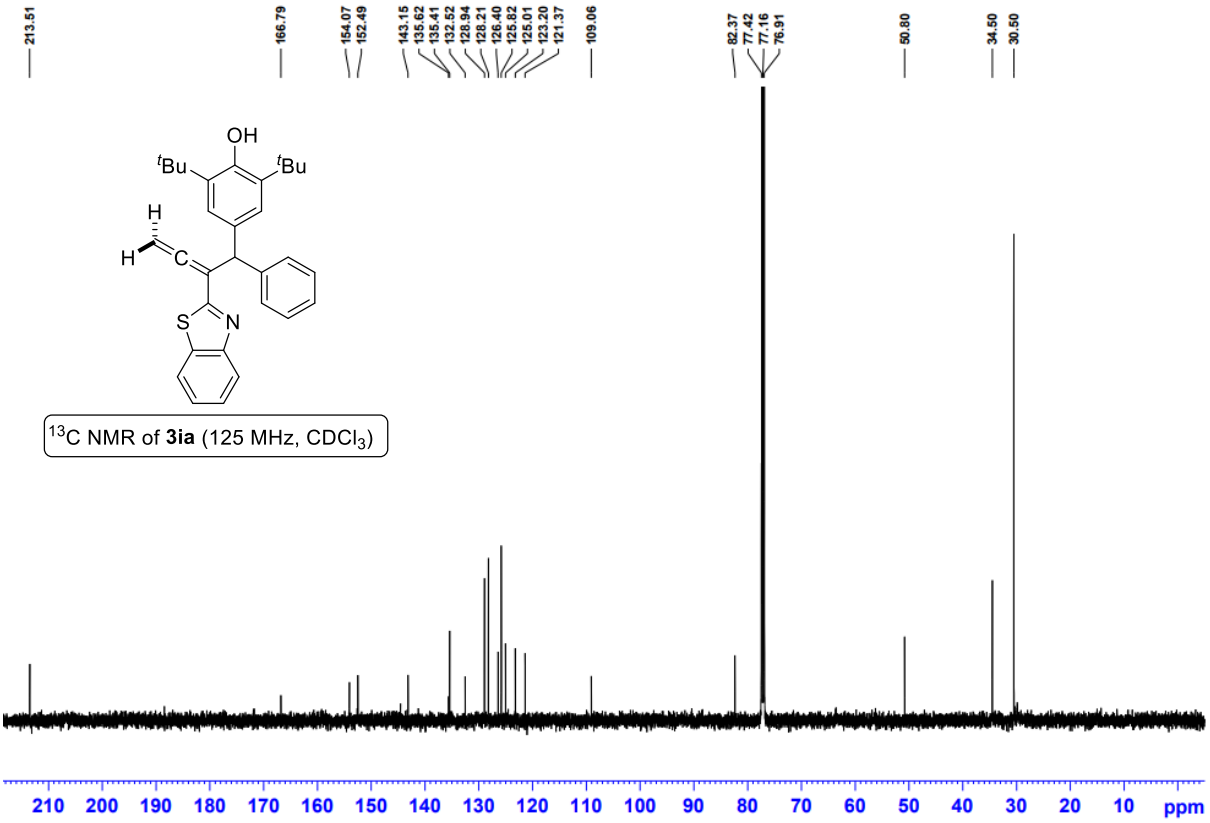
^{13}C NMR of **3ha** (125 MHz, $CDCl_3$)



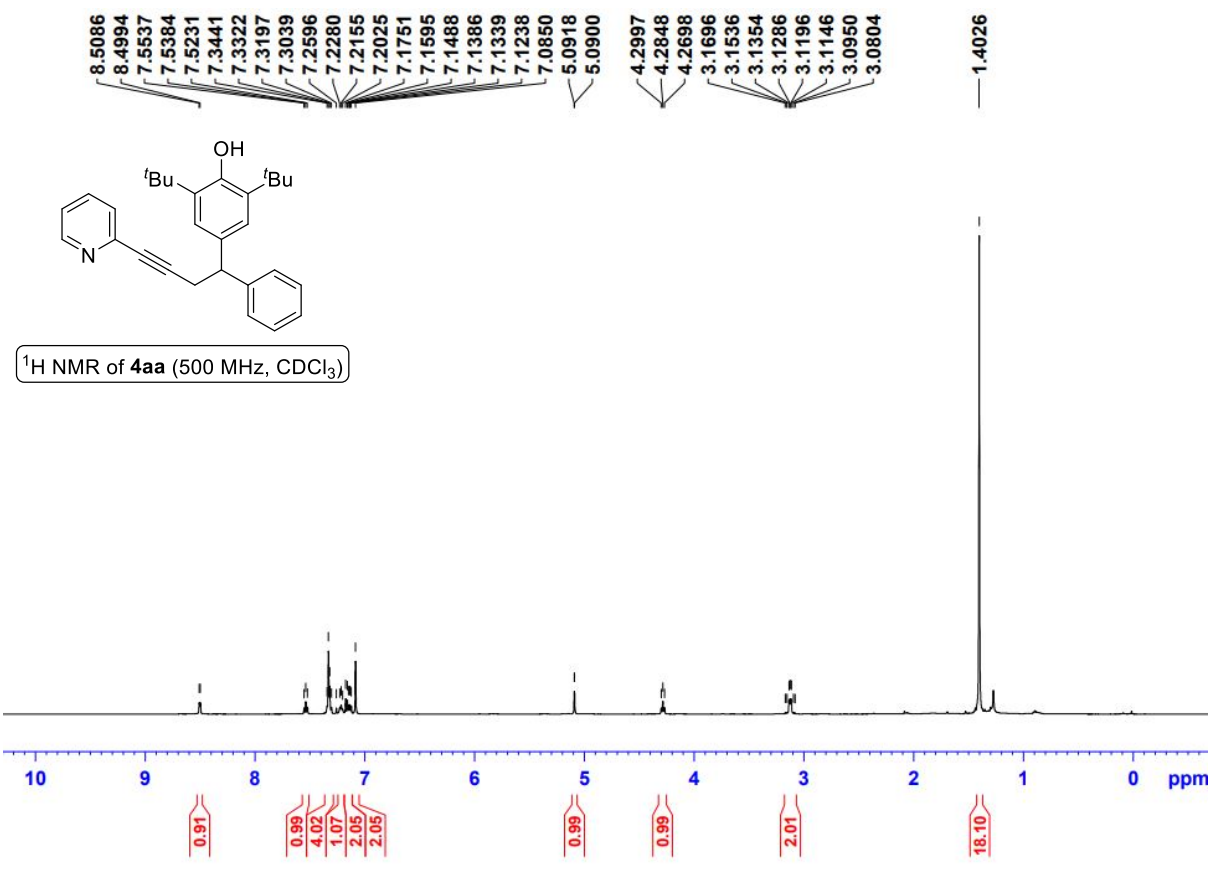
^{1}H NMR of **3ia** (500 MHz, $CDCl_3$)



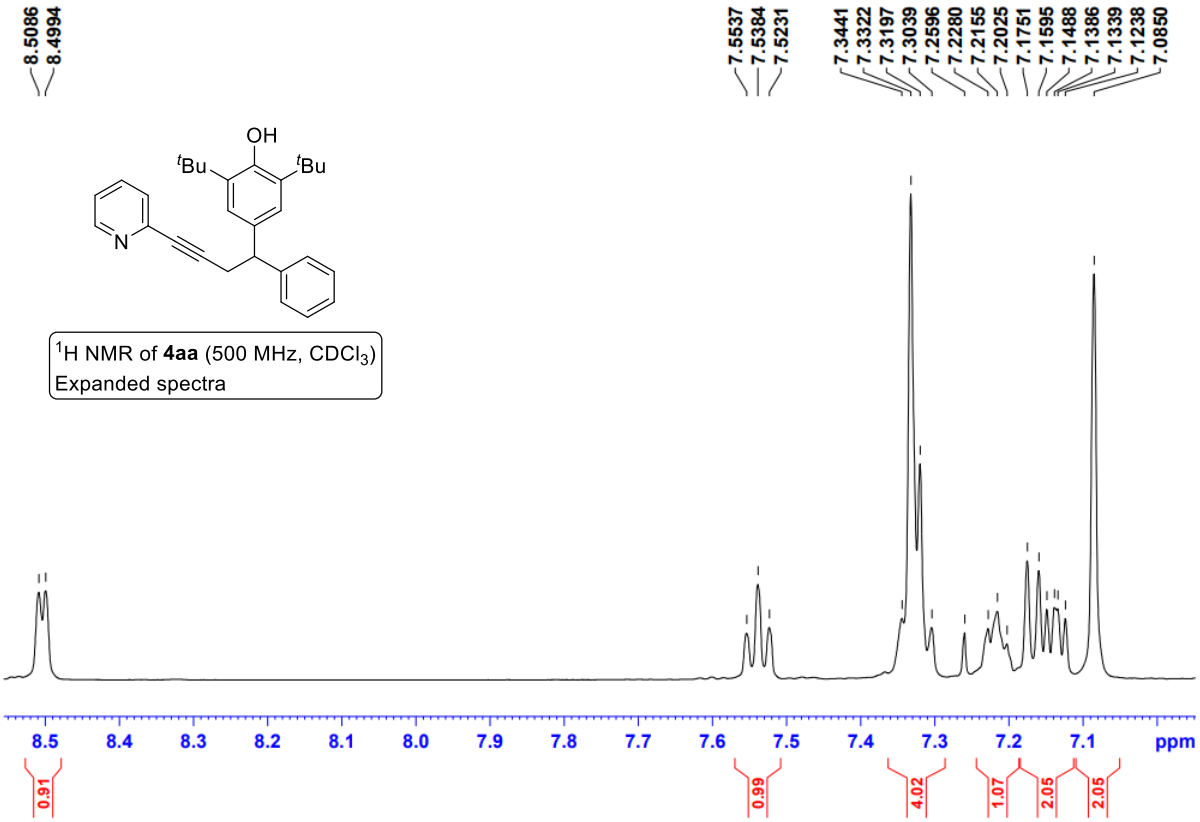
^{1}H NMR of **3ia** (500 MHz, $CDCl_3$)
Expanded spectra



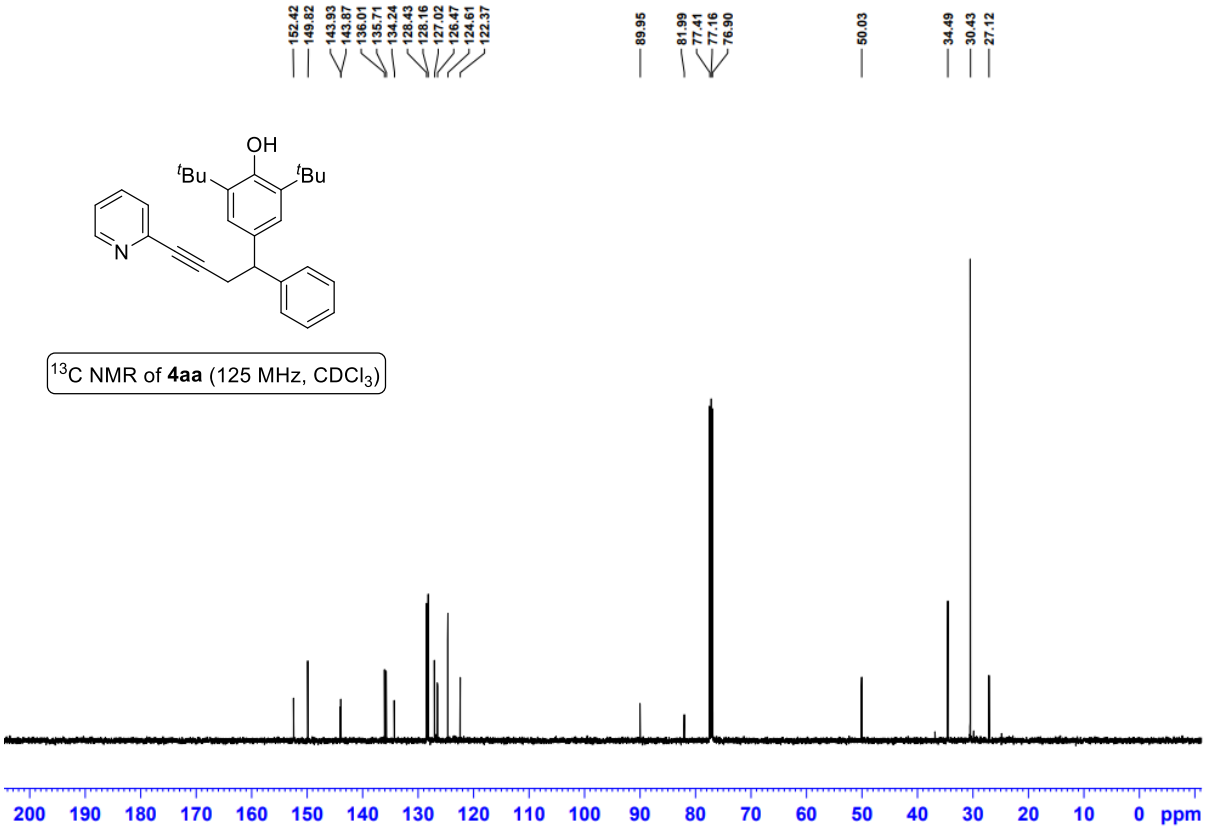
^{13}C NMR of **3ia** (125 MHz, $CDCl_3$)



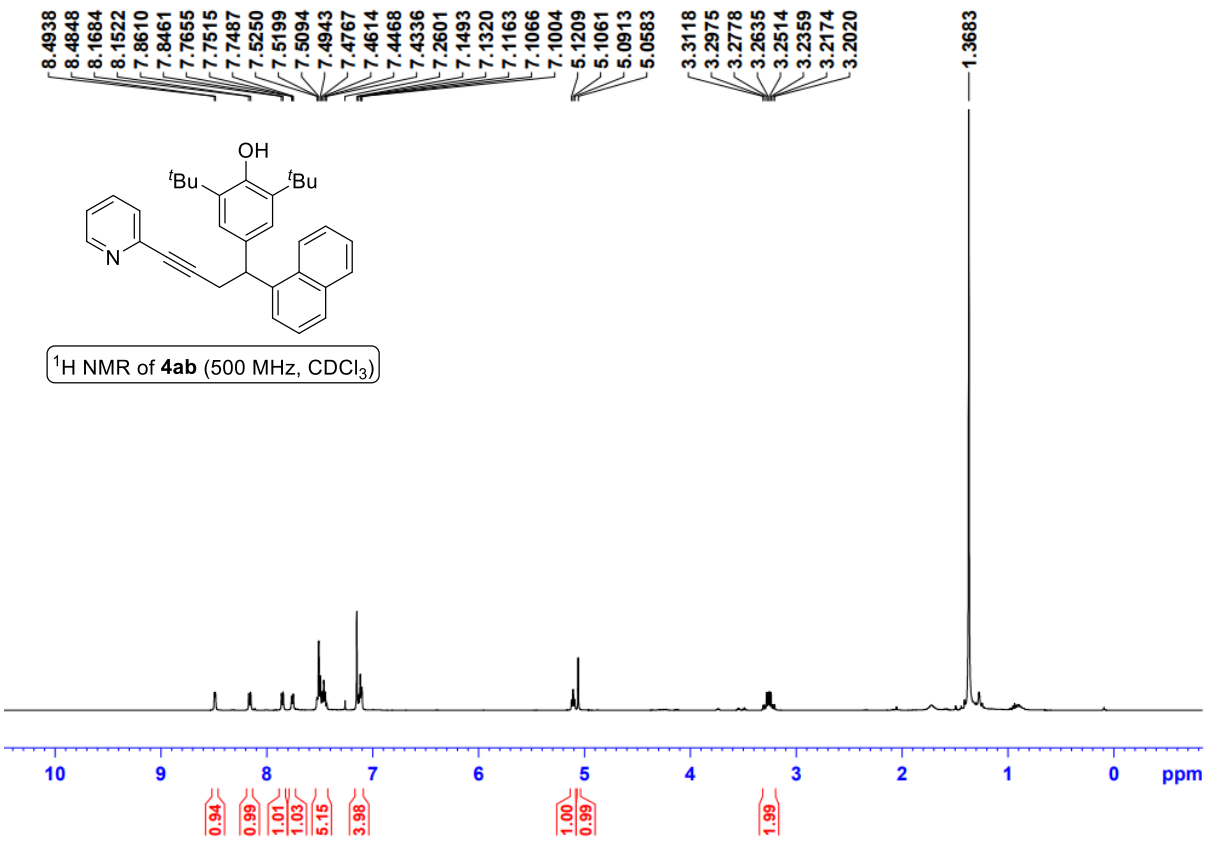
^{1}H NMR of **4aa** (500 MHz, $CDCl_3$)



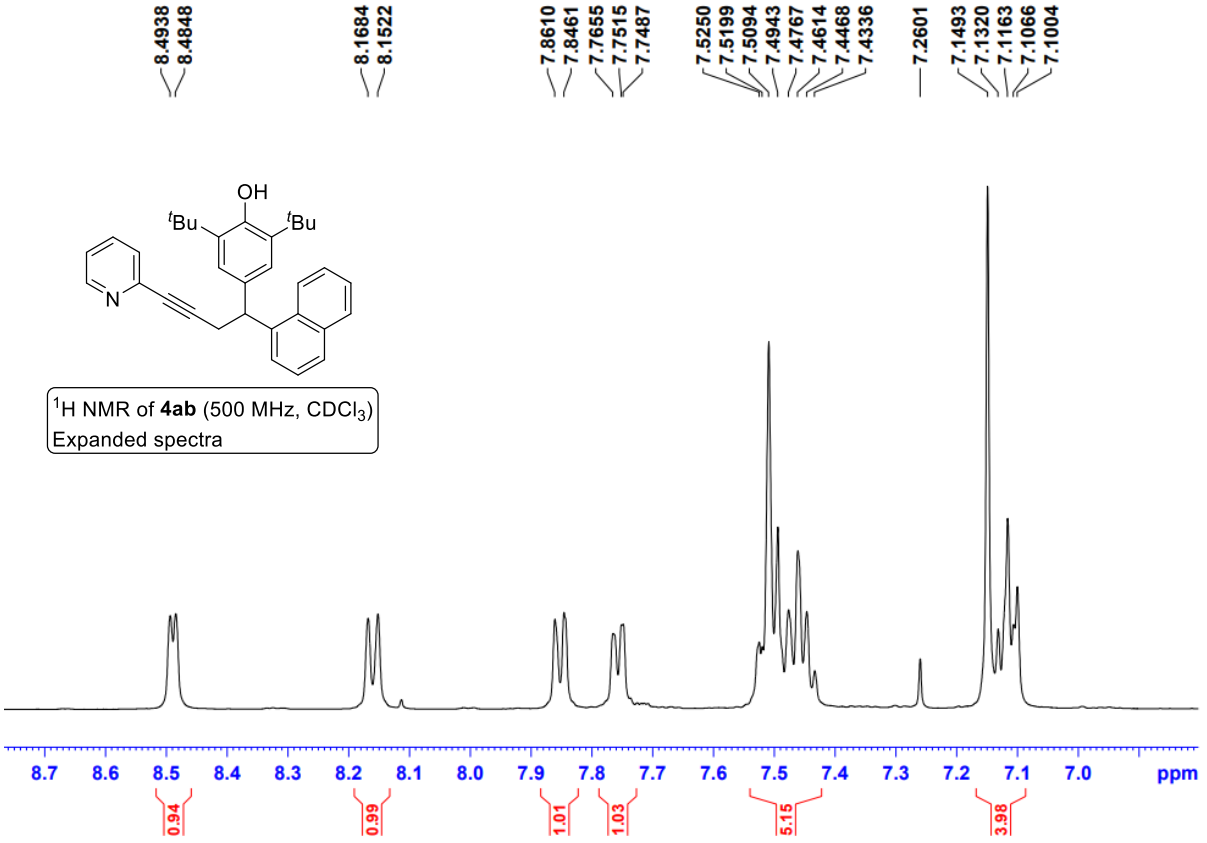
^{1}H NMR of **4aa** (500 MHz, $CDCl_3$)
Expanded spectra



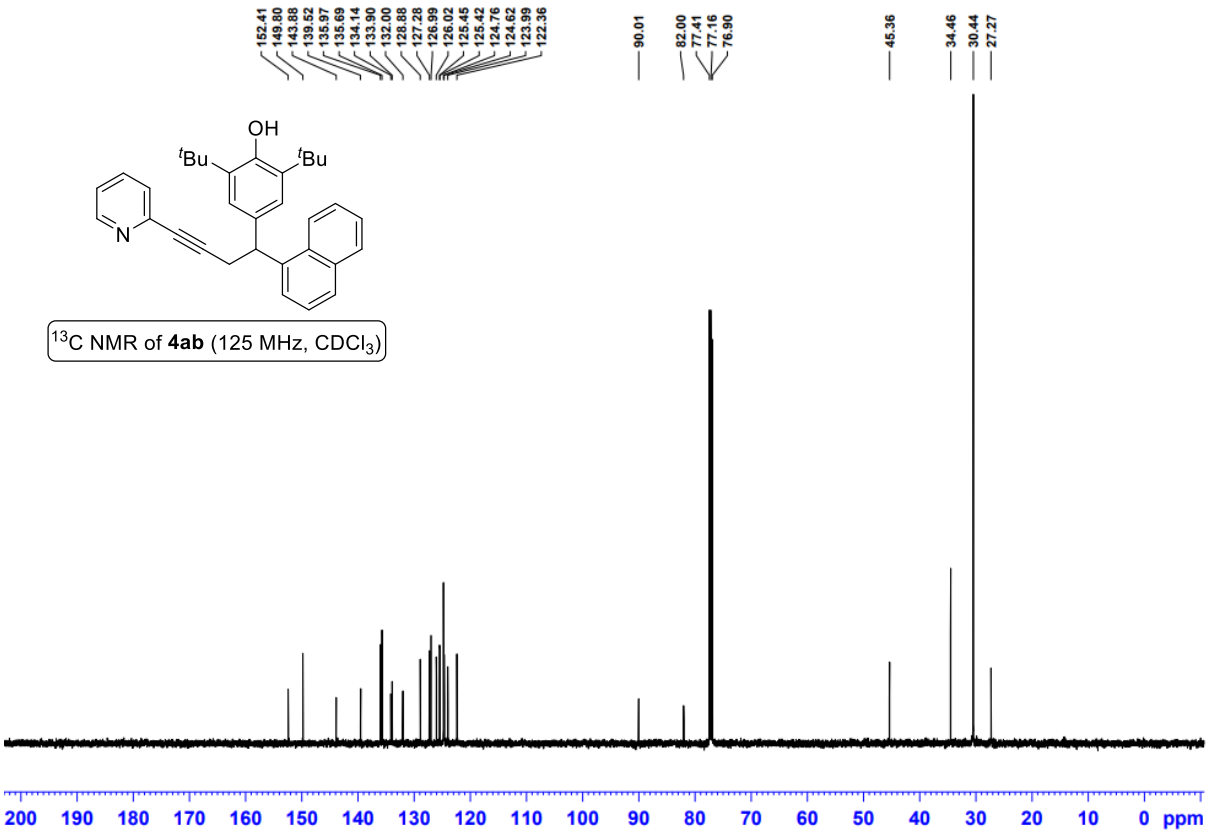
^{13}C NMR of **4aa** (125 MHz, $CDCl_3$)



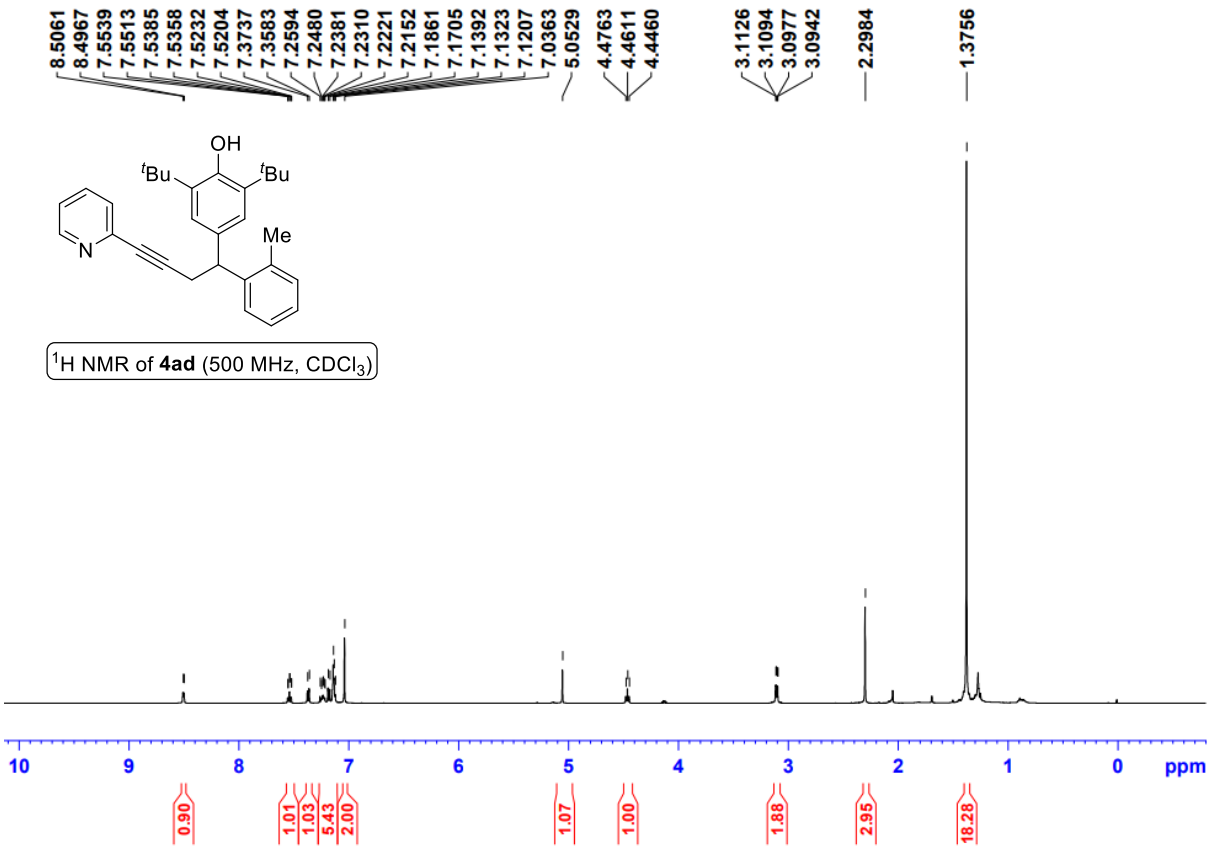
^{1}H NMR of **4ab** (500 MHz, $CDCl_3$)



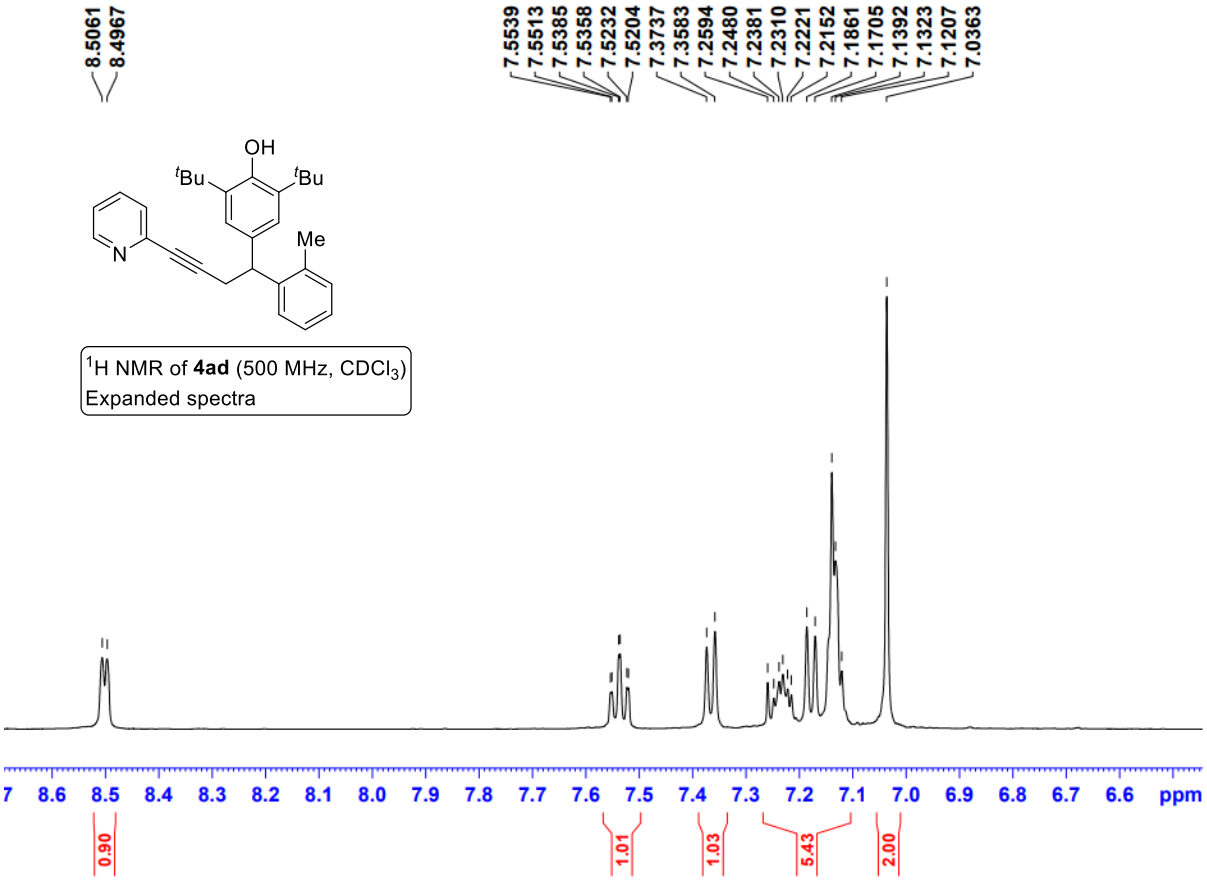
^{1}H NMR of **4ab** ($CDCl_3$)
Expanded spectra



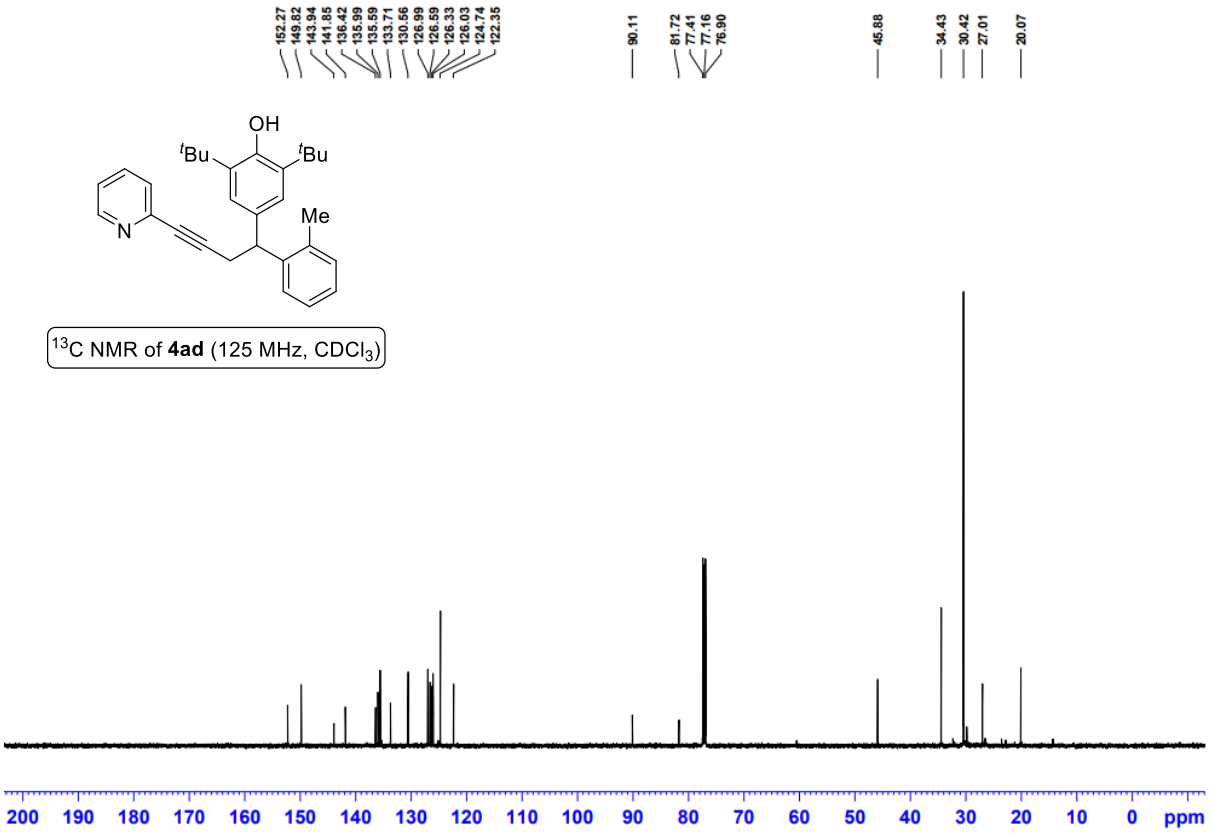
^{13}C NMR of **4ab** (125 MHz, $CDCl_3$)



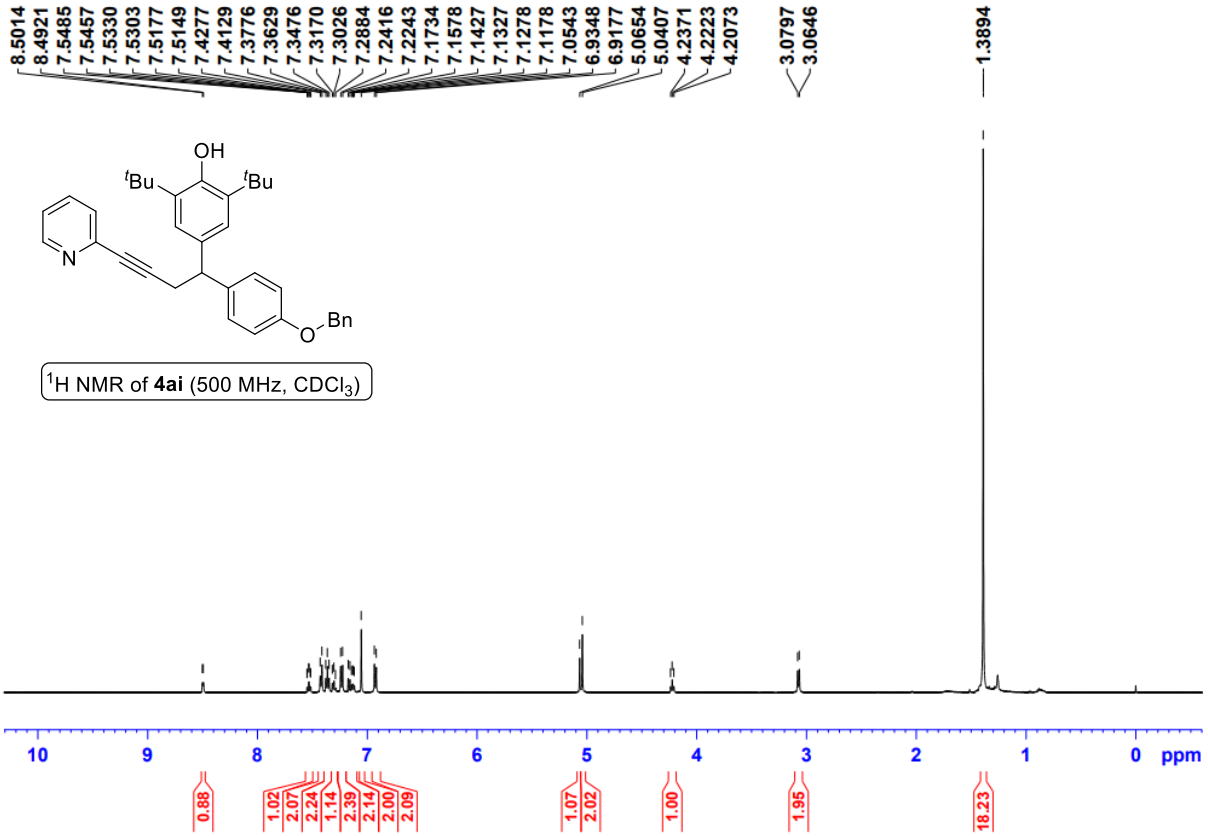
^{1}H NMR of **4ad** (500 MHz, $CDCl_3$)



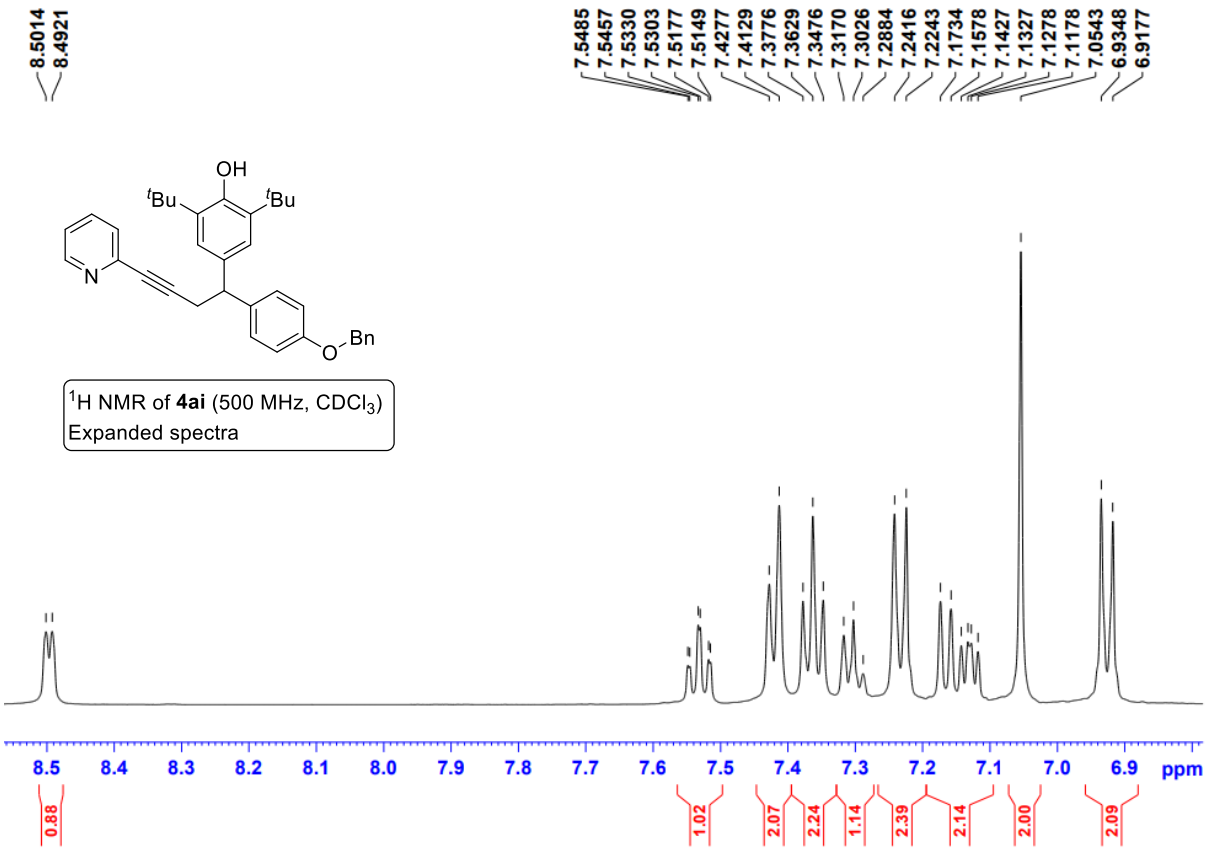
^{1}H NMR of **4ad** (500 MHz, $CDCl_3$)
Expanded spectra



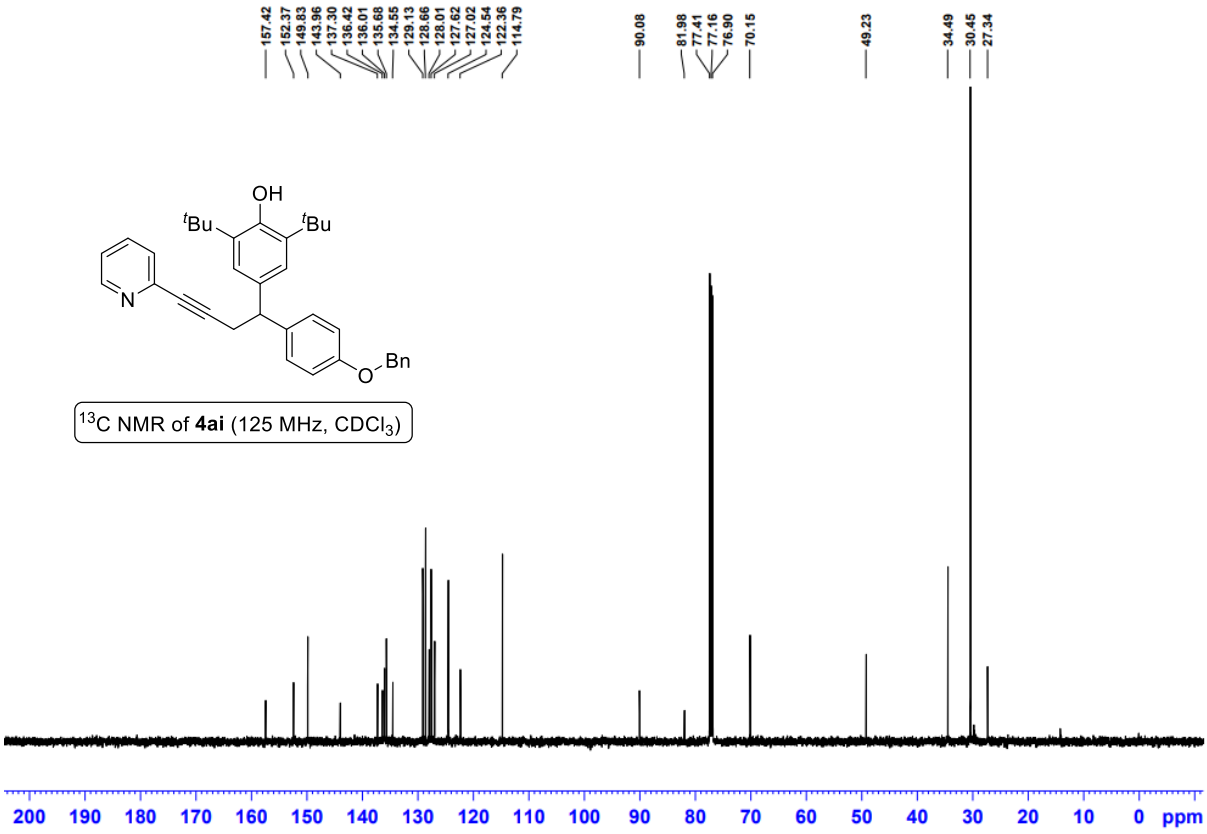
^{13}C NMR of **4ad** (125 MHz, $CDCl_3$)



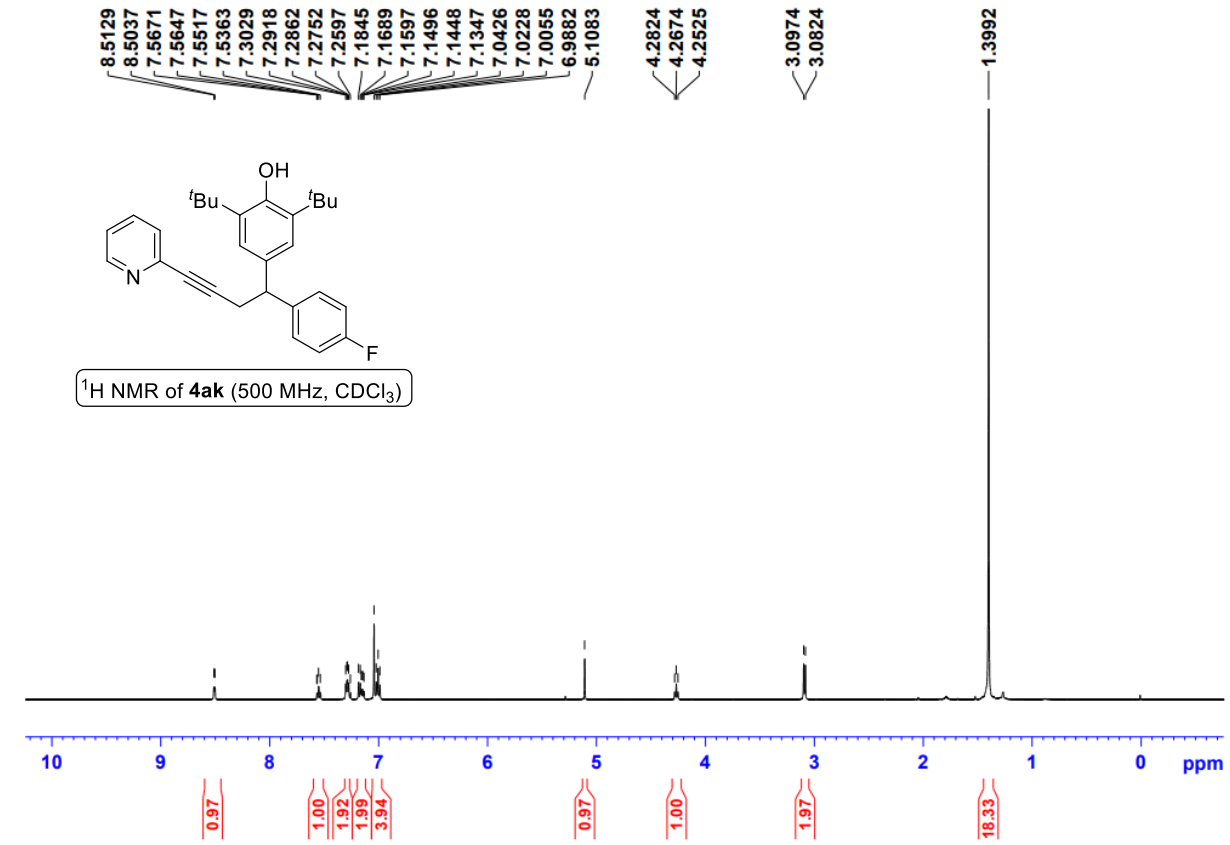
^{1}H NMR of **4ai** (500 MHz, $CDCl_3$)



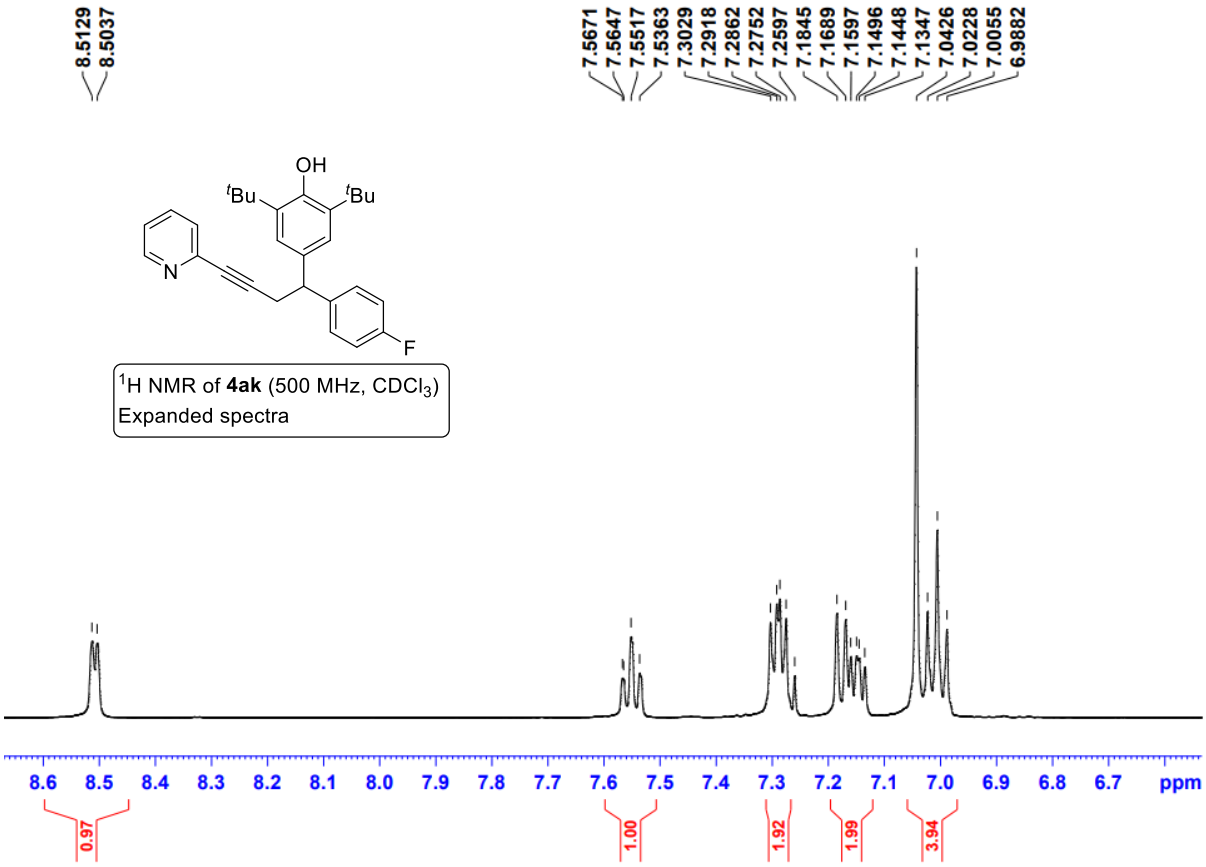
^{1}H NMR of **4ai** (500 MHz, $CDCl_3$)
Expanded spectra



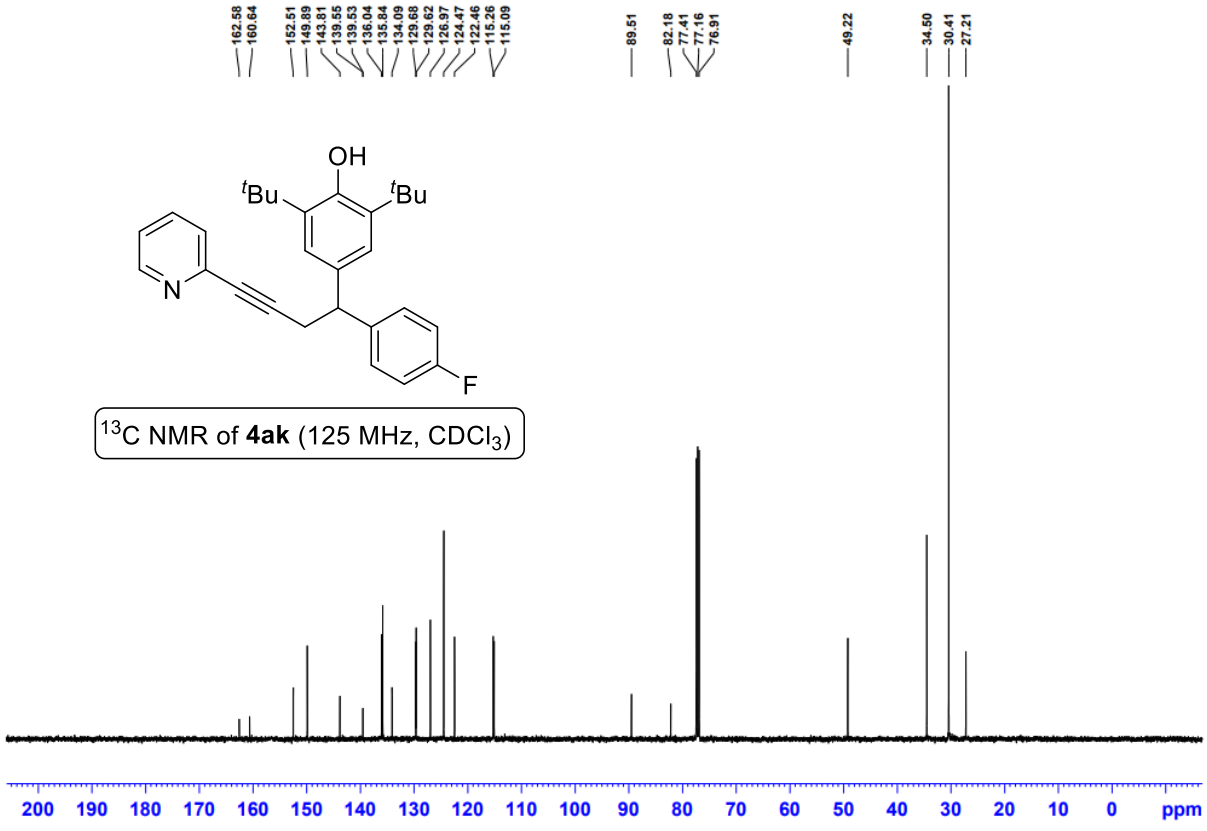
^{13}C NMR of **4ai** (125 MHz, $CDCl_3$)



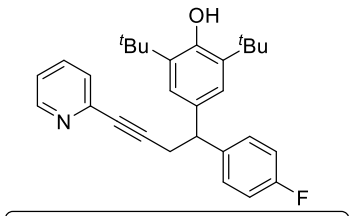
^{1}H NMR of **4ak** (500 MHz, $CDCl_3$)



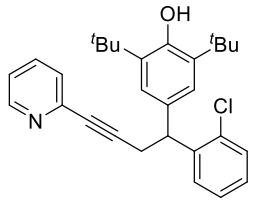
^{1}H NMR of **4ak** (500 MHz, $CDCl_3$)
Expanded spectra



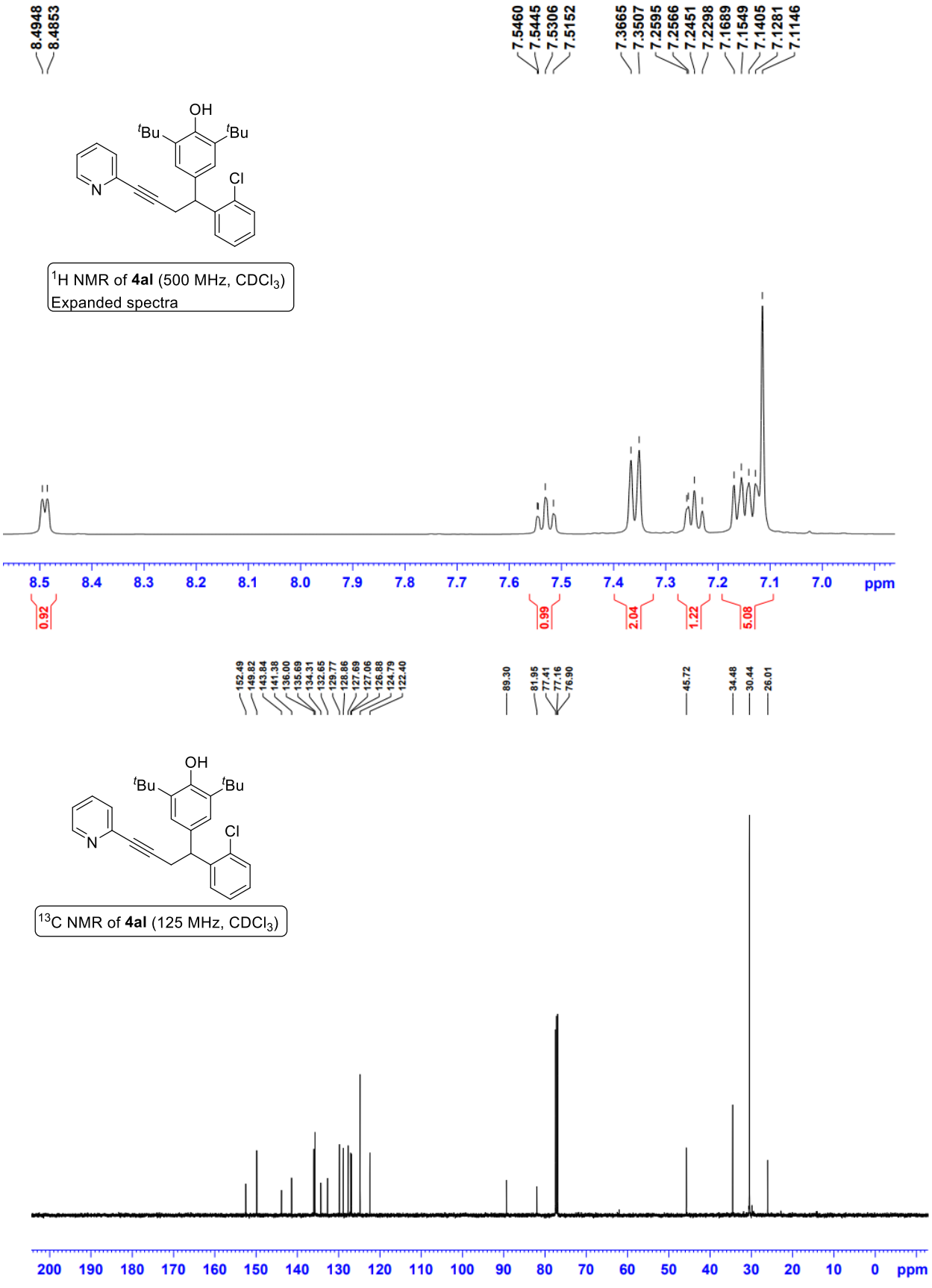
^{13}C NMR of **4ak** (125 MHz, $CDCl_3$)

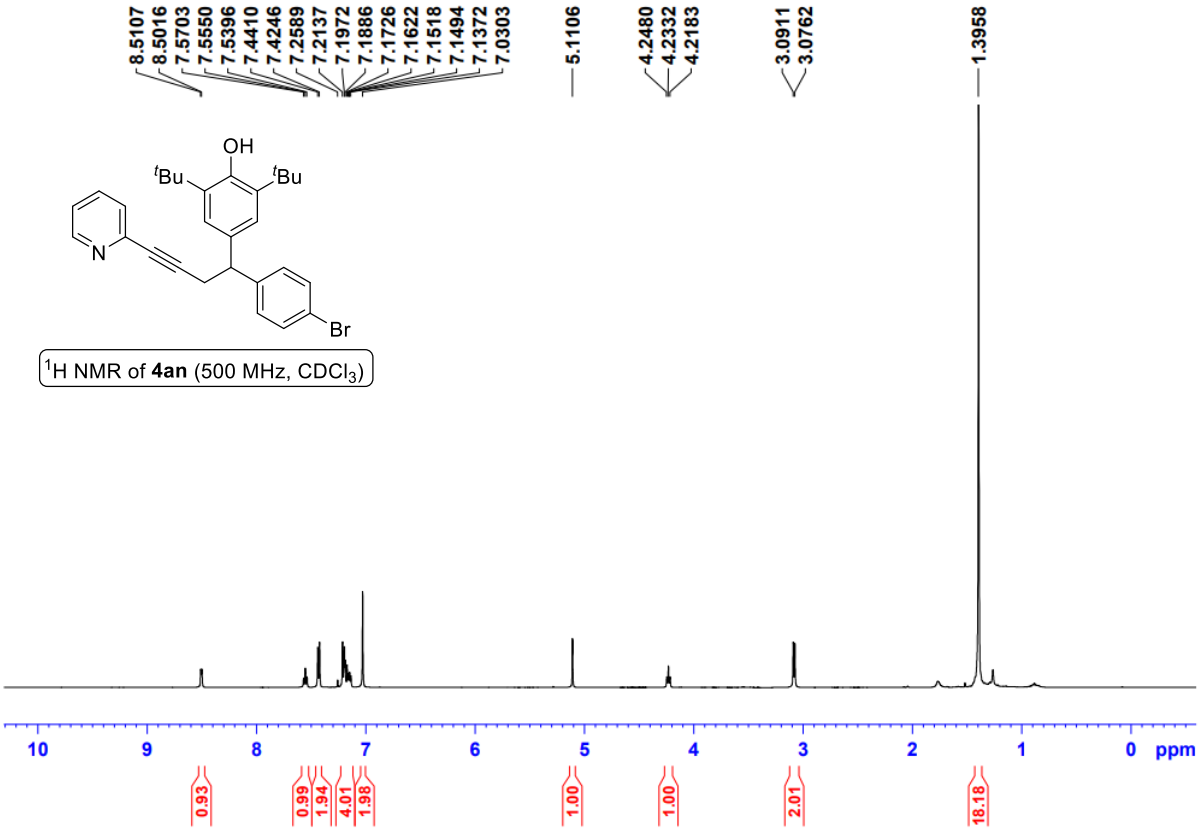


^{19}F NMR of **4ak** (470 MHz, $CDCl_3$)

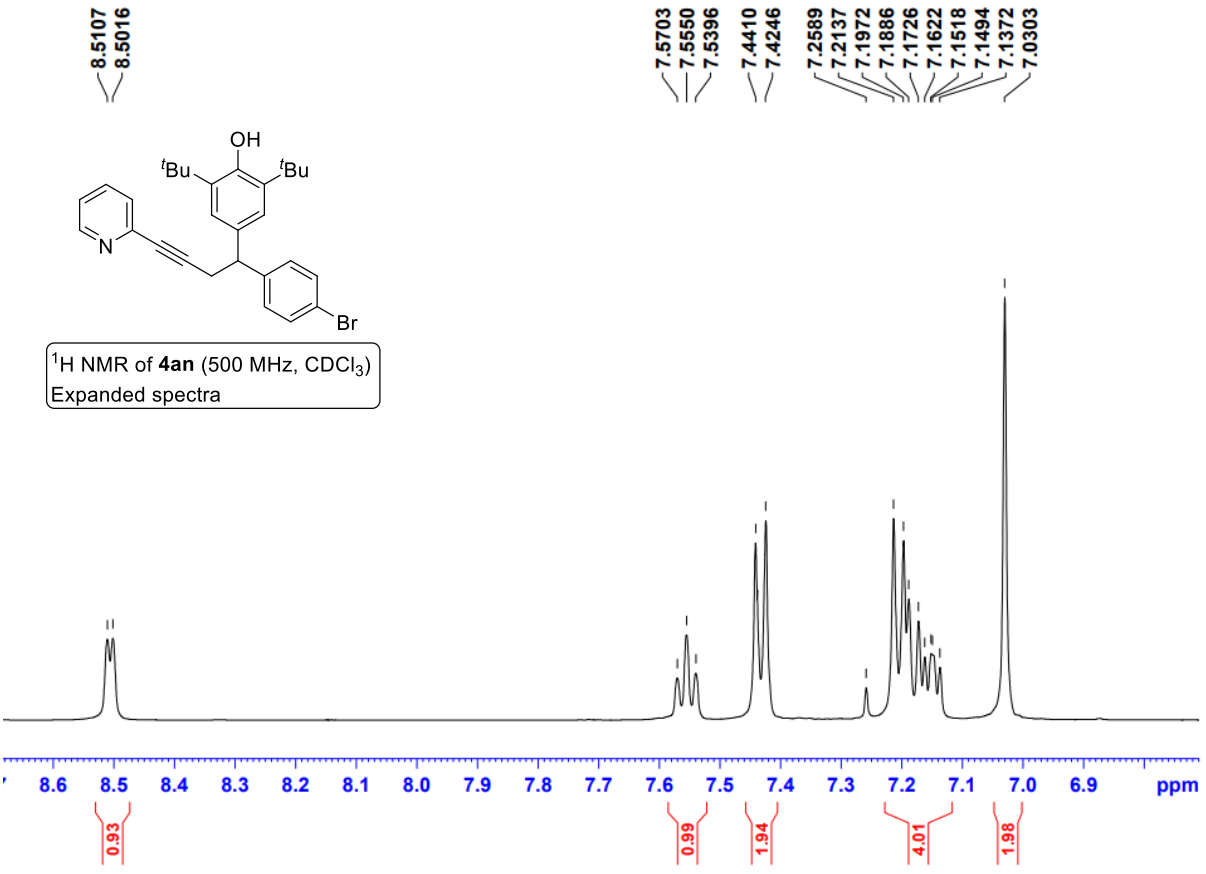


^{1}H NMR of **4al** (500 MHz, $CDCl_3$)

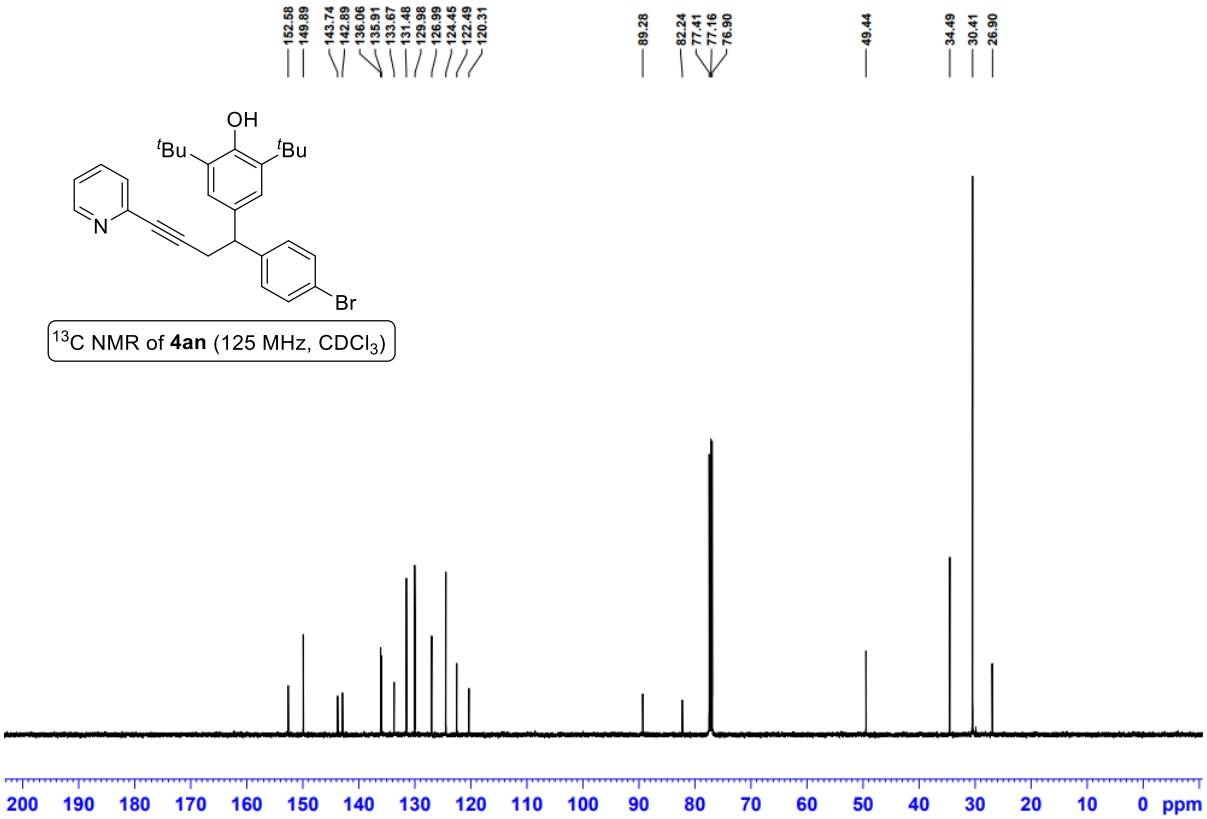

8.4948
8.4853
7.5460
7.5445
7.5306
7.5152
7.3665
7.3507
7.2595
7.2566
7.2451
7.2298
7.1689
7.1549
7.1405
7.1281
7.1146
OH
tBu
tBu
Cl
N
1H NMR of 4al (500 MHz, CDCl3)
Expanded spectra
8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 ppm
0.92
0.99
2.04
1.22
5.08
152.49
149.82
143.84
141.38
136.00
135.69
134.31
132.65
129.77
128.86
127.69
127.06
126.88
124.79
122.40
89.30
81.95
77.41
77.16
76.90
45.72
34.48
30.44
26.01
OH
tBu
tBu
Cl
N
13C NMR of 4al (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



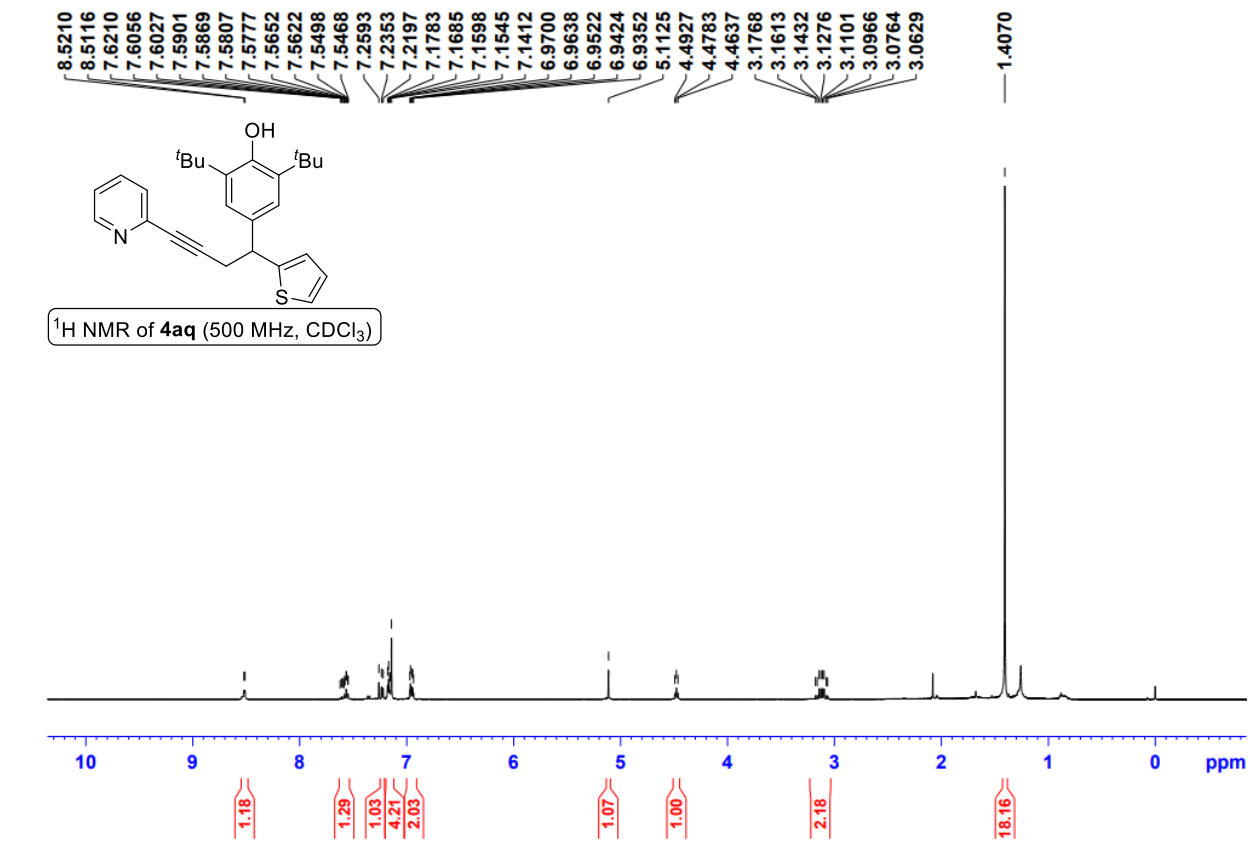
^{1}H NMR of **4an** (500 MHz, $CDCl_3$)



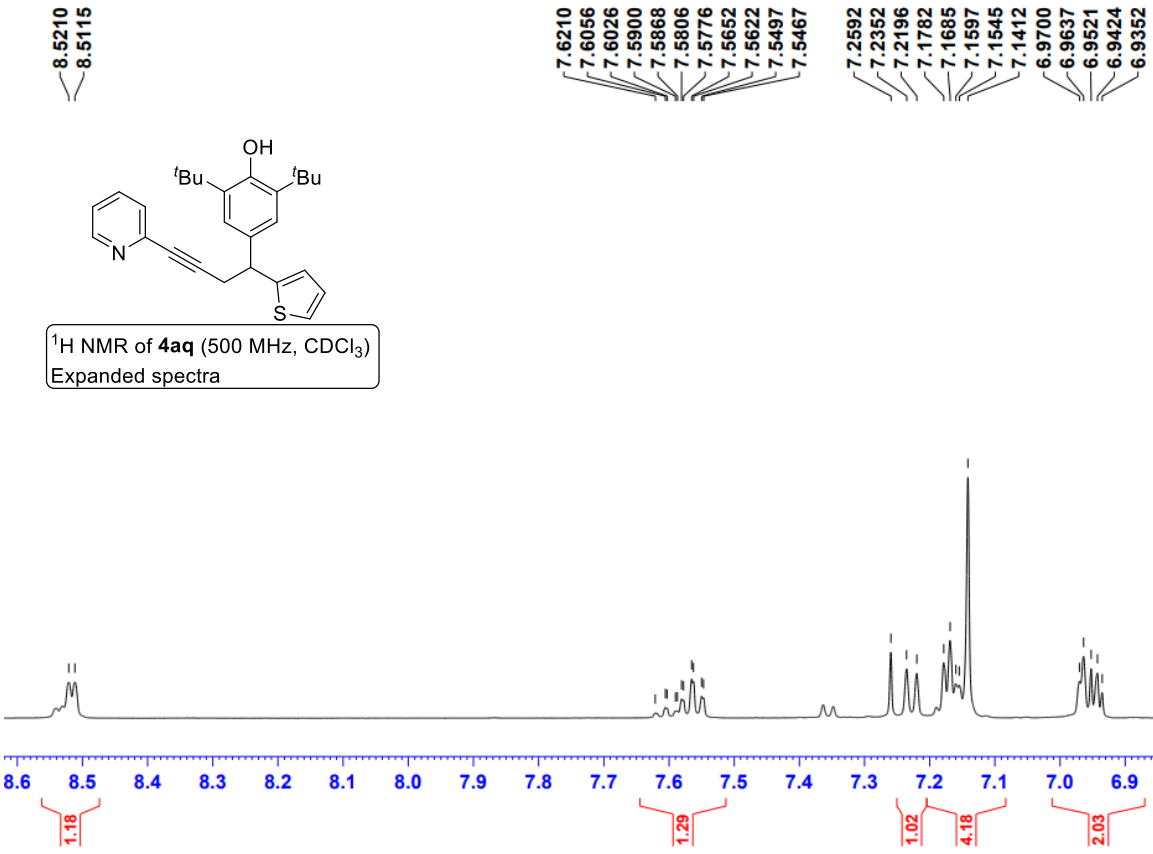
^{1}H NMR of **4an** (500 MHz, $CDCl_3$)
Expanded spectra



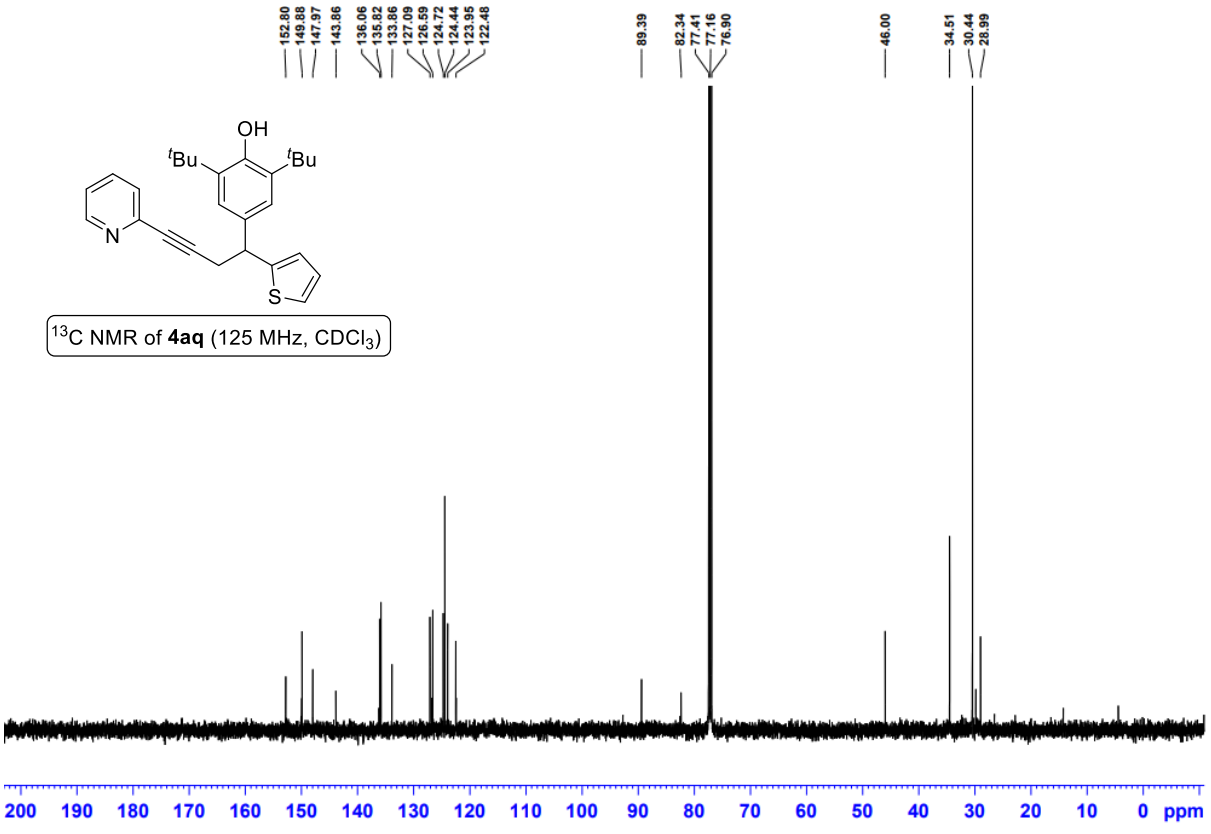
^{13}C NMR of **4an** (125 MHz, $CDCl_3$)



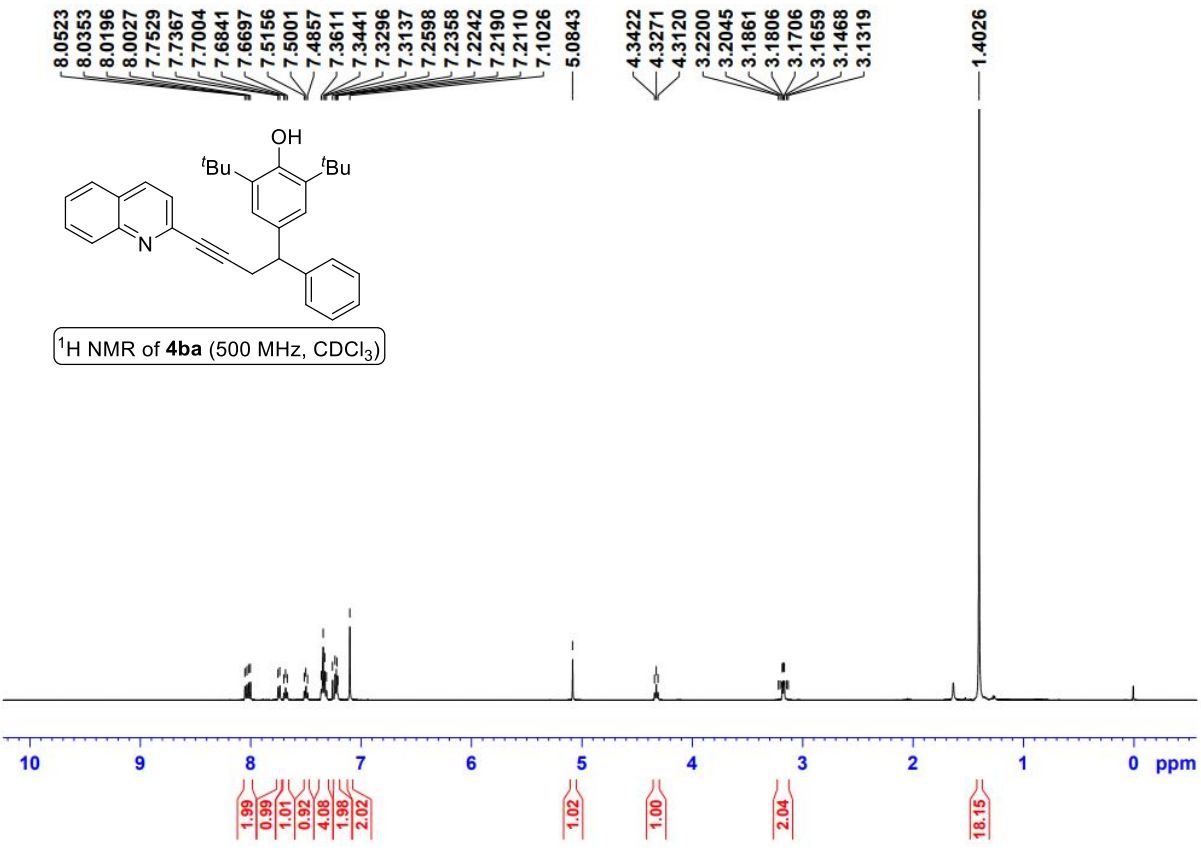
^{1}H NMR of **4aq** (500 MHz, $CDCl_3$)



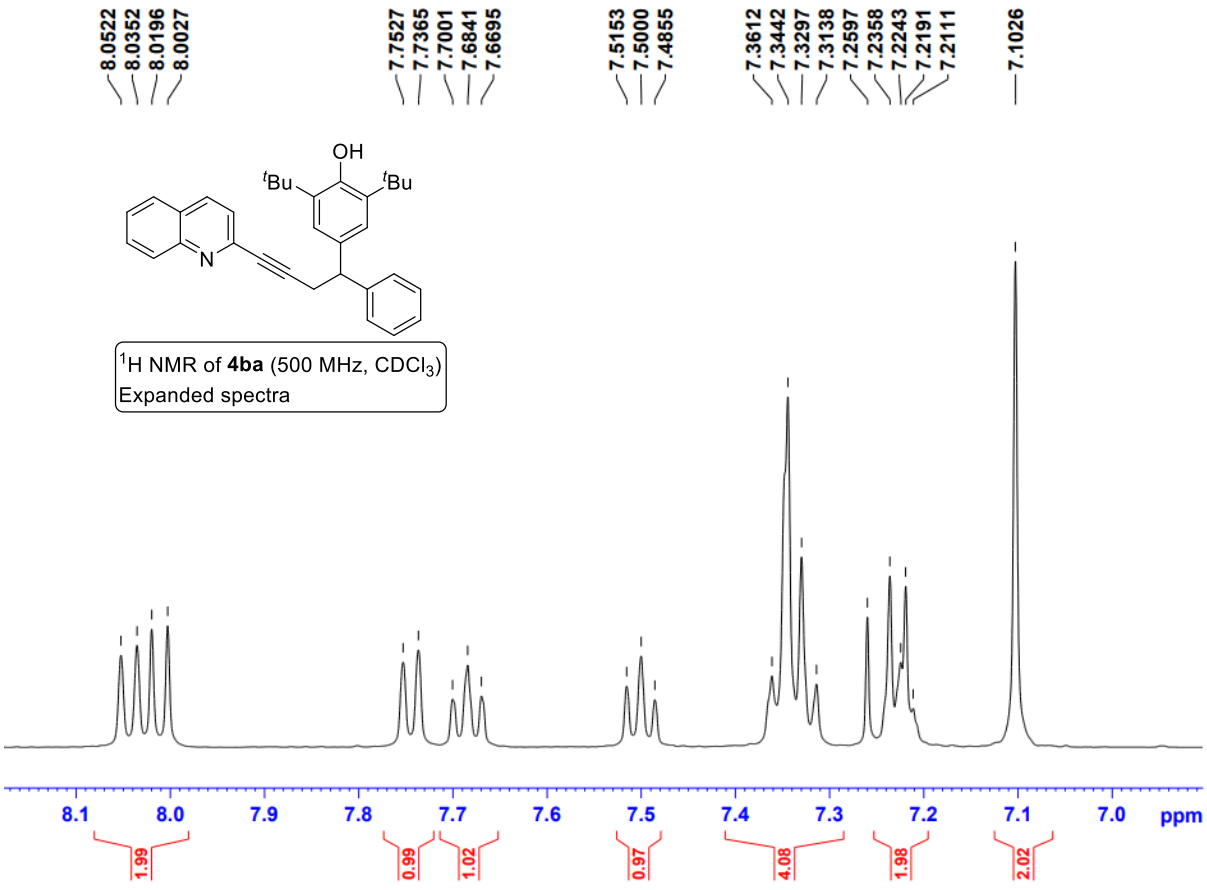
^{1}H NMR of **4aq** (500 MHz, $CDCl_3$)
Expanded spectra



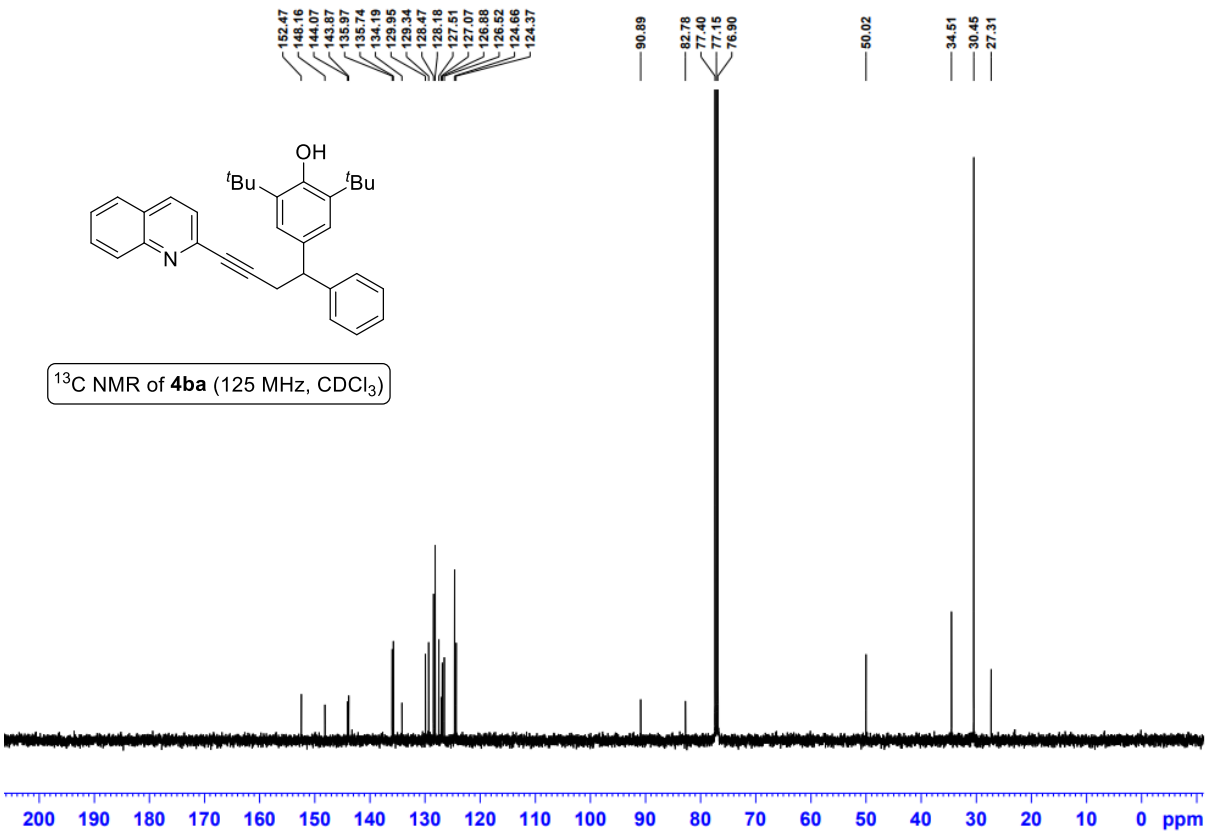
^{13}C NMR of **4aq** (125 MHz, $CDCl_3$)



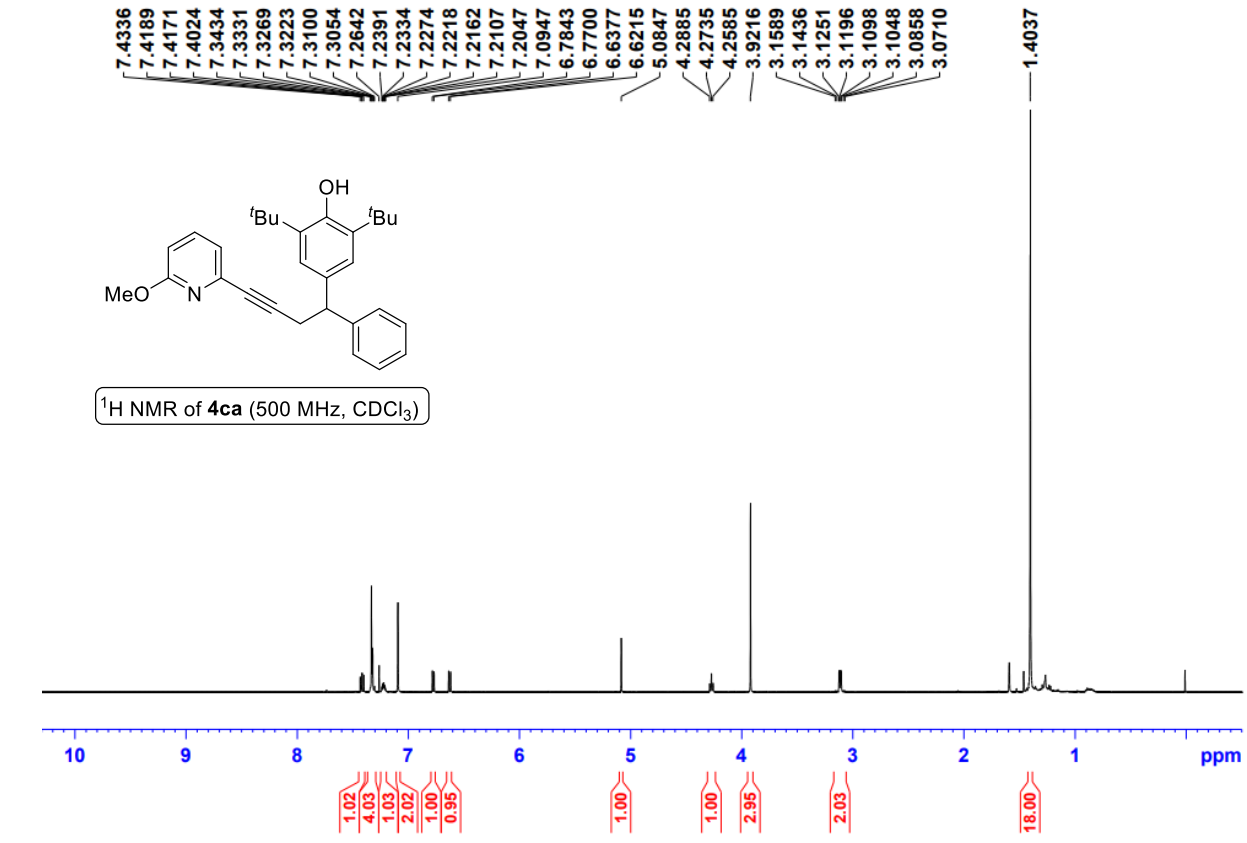
^{1}H NMR of **4ba** (500 MHz, $CDCl_3$)



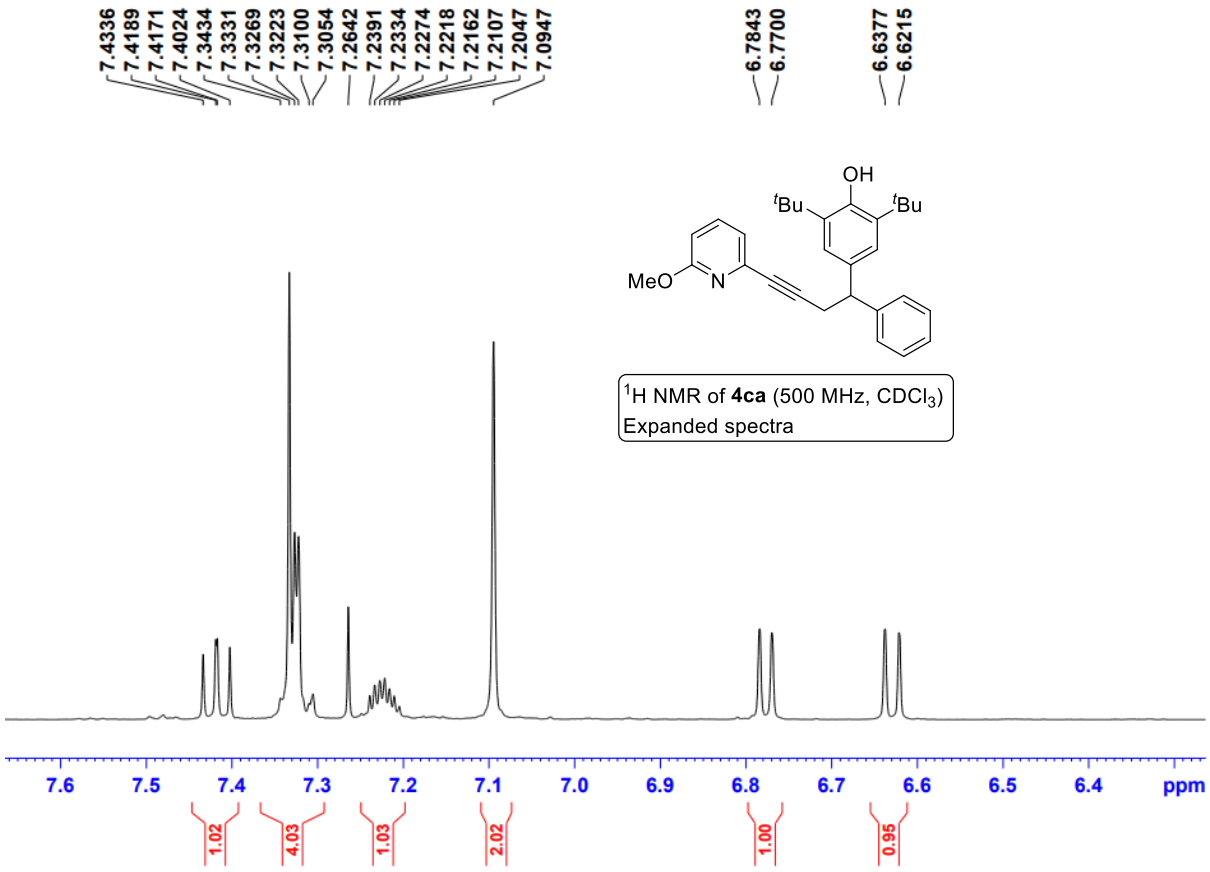
^{1}H NMR of **4ba** (500 MHz, $CDCl_3$)
Expanded spectra



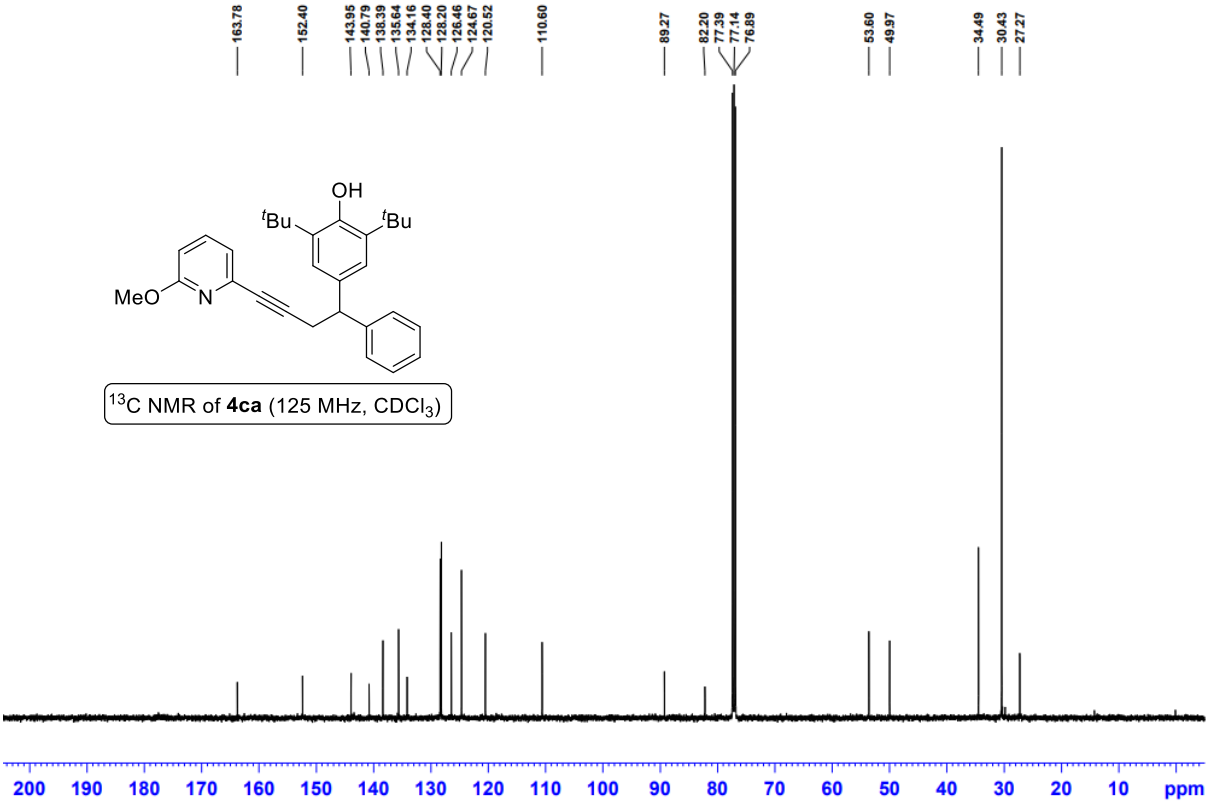
^{13}C NMR of **4ba** (125 MHz, $CDCl_3$)



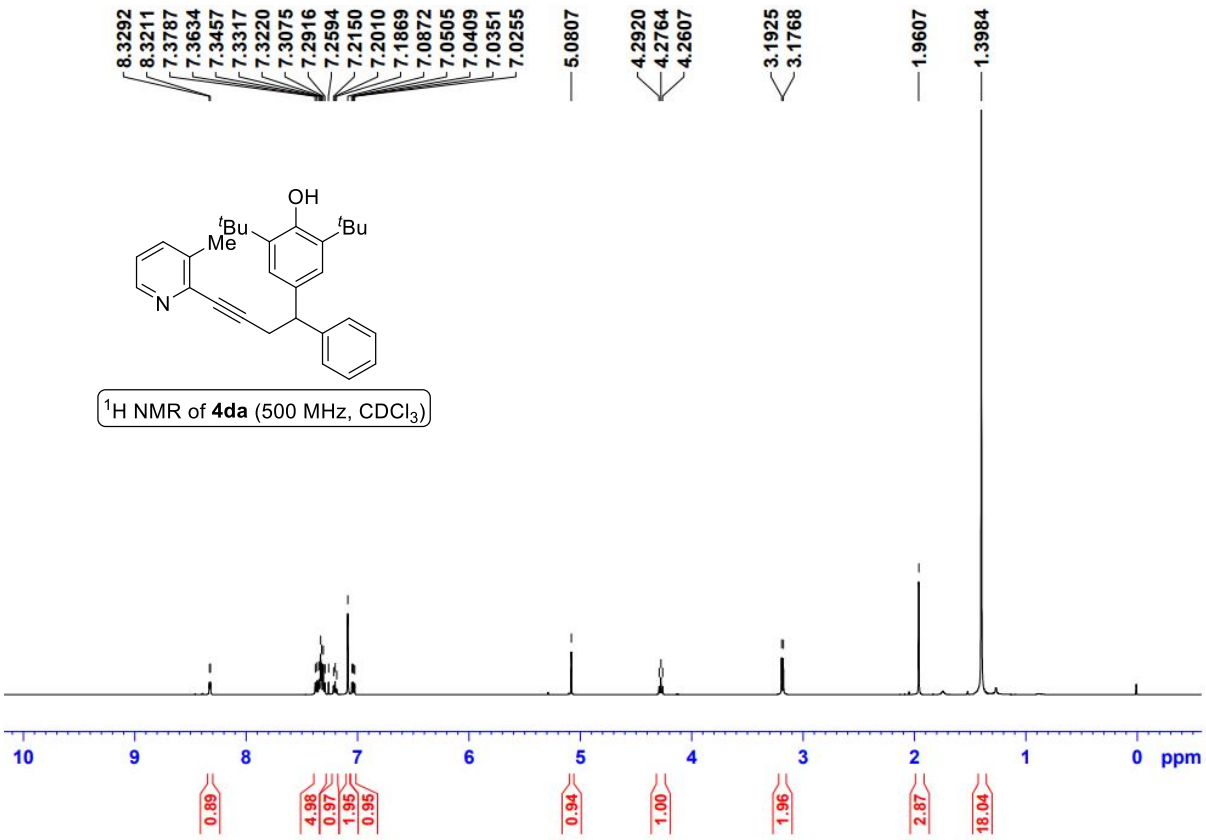
^{1}H NMR of **4ca** (500 MHz, $CDCl_3$)



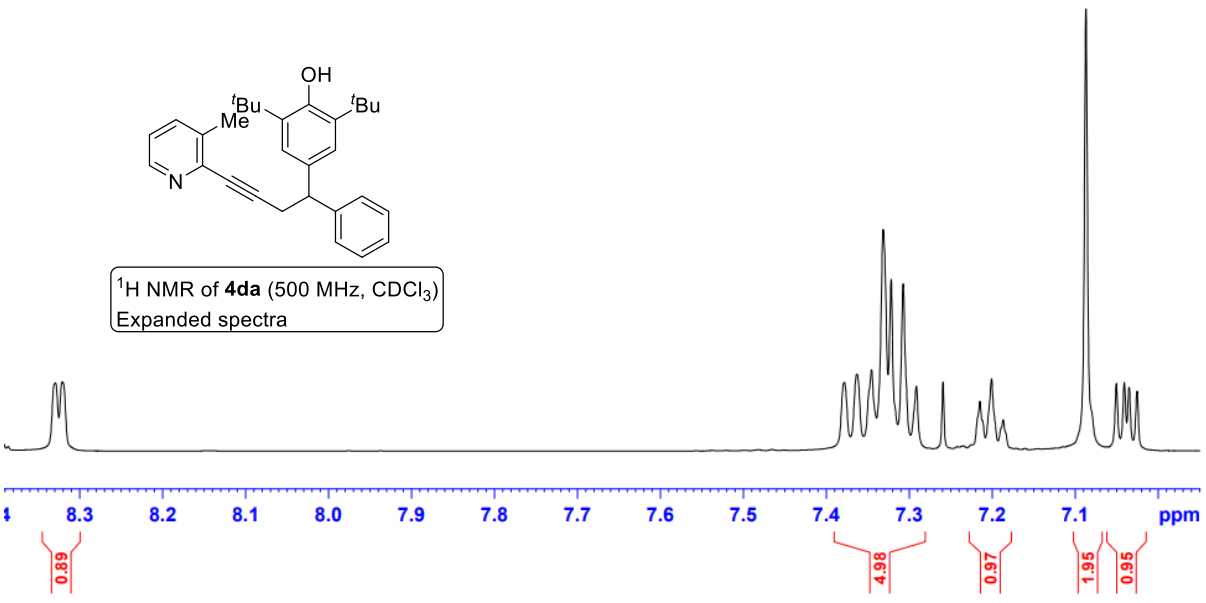
^{1}H NMR of **4ca** (500 MHz, $CDCl_3$)
Expanded spectra



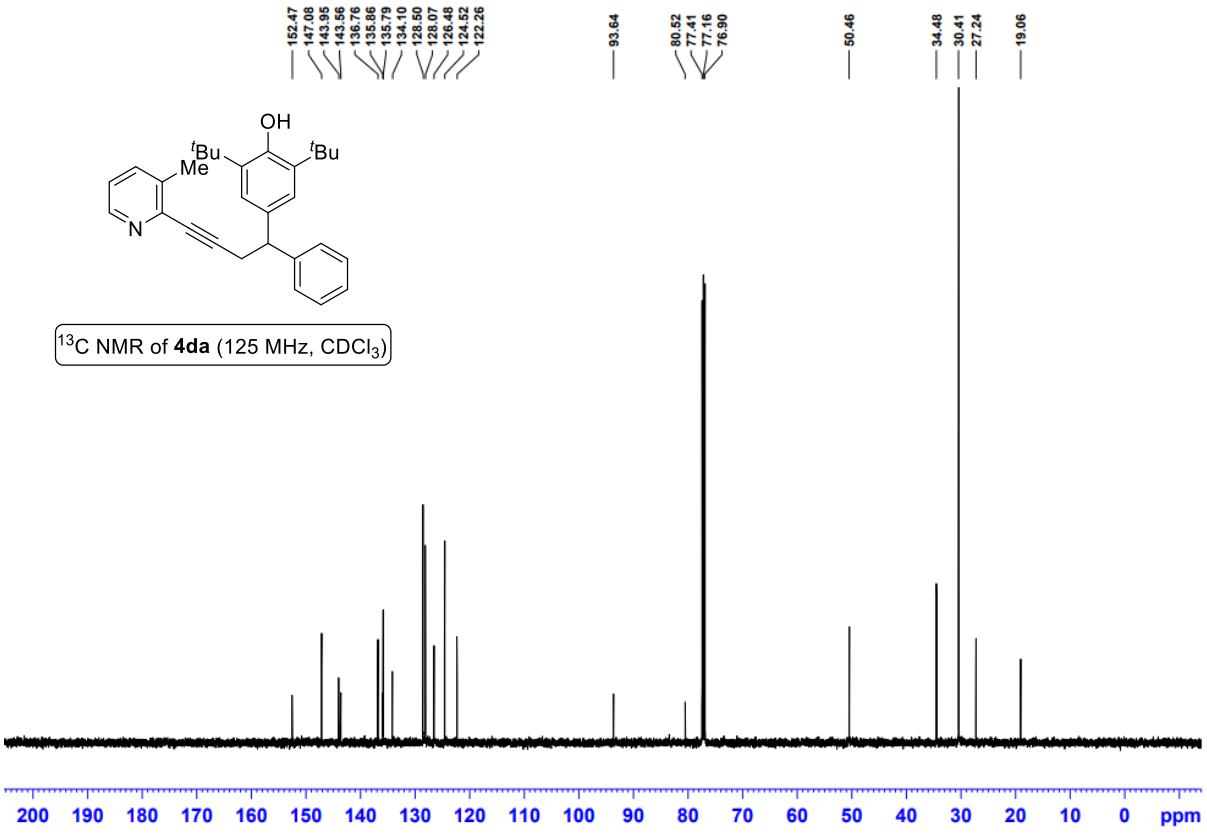
^{13}C NMR of **4ca** (125 MHz, $CDCl_3$)



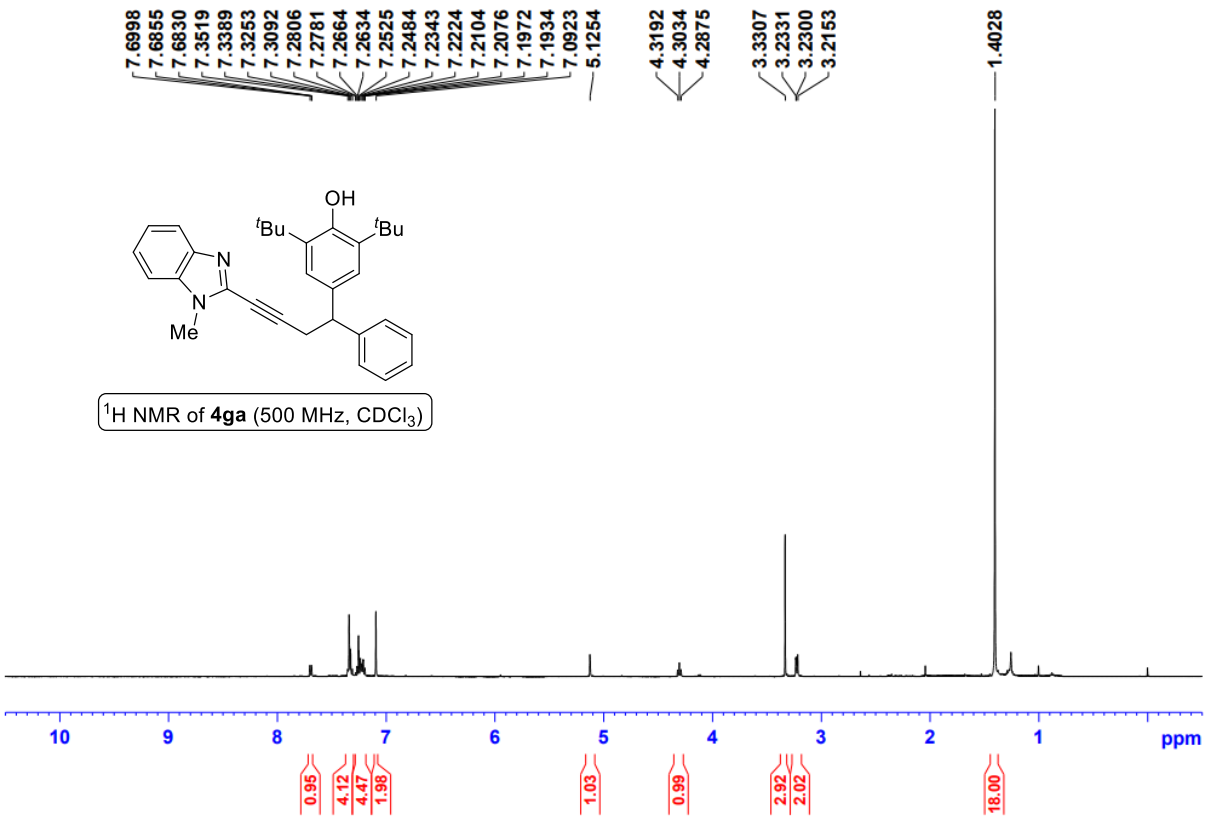
^{1}H NMR of **4da** (500 MHz, $CDCl_3$)



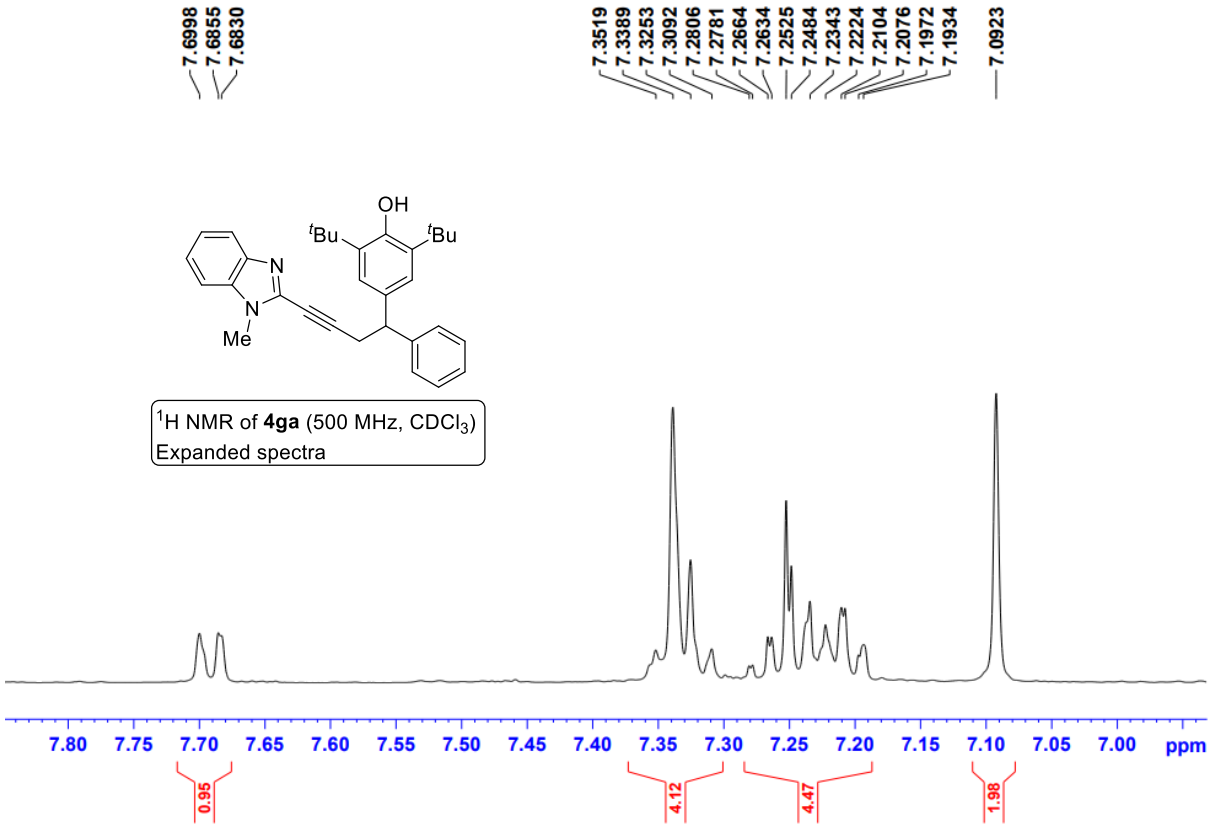
^{1}H NMR of **4da** (500 MHz, $CDCl_3$)
Expanded spectra



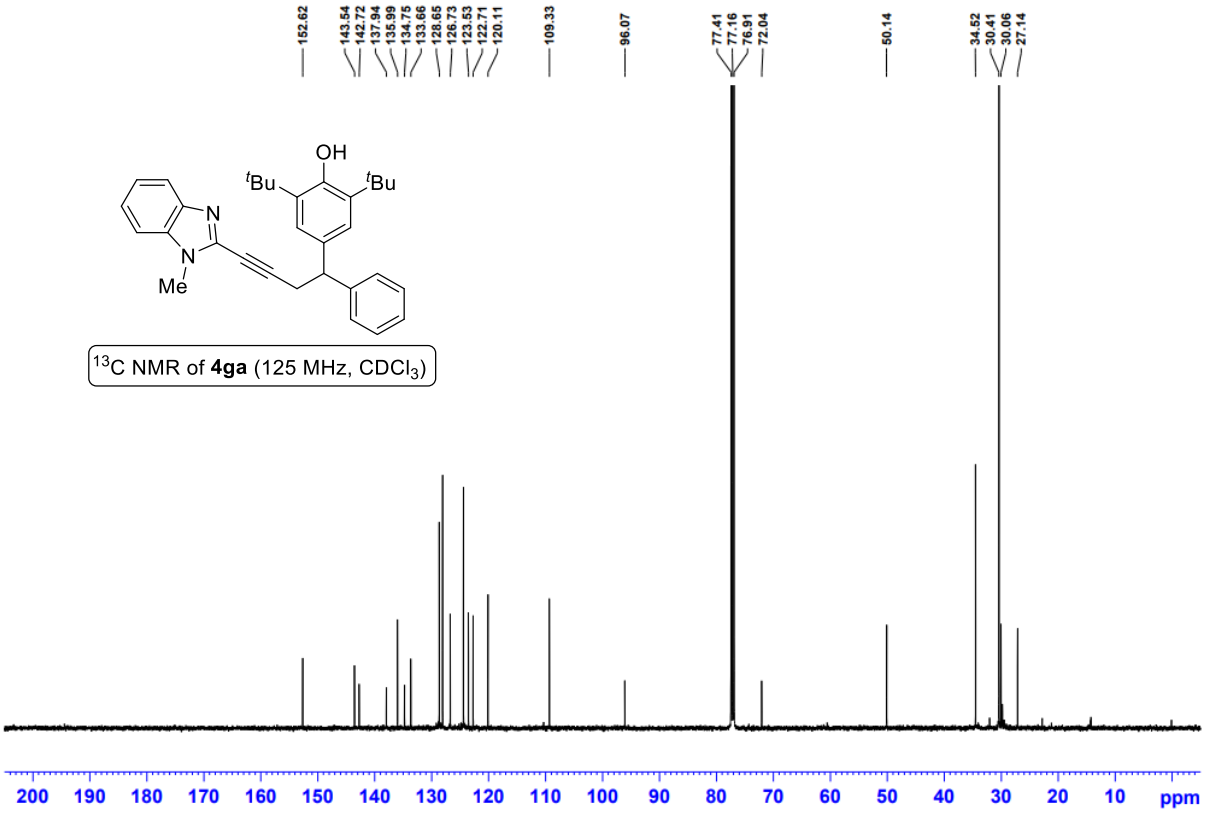
^{13}C NMR of **4da** (125 MHz, $CDCl_3$)



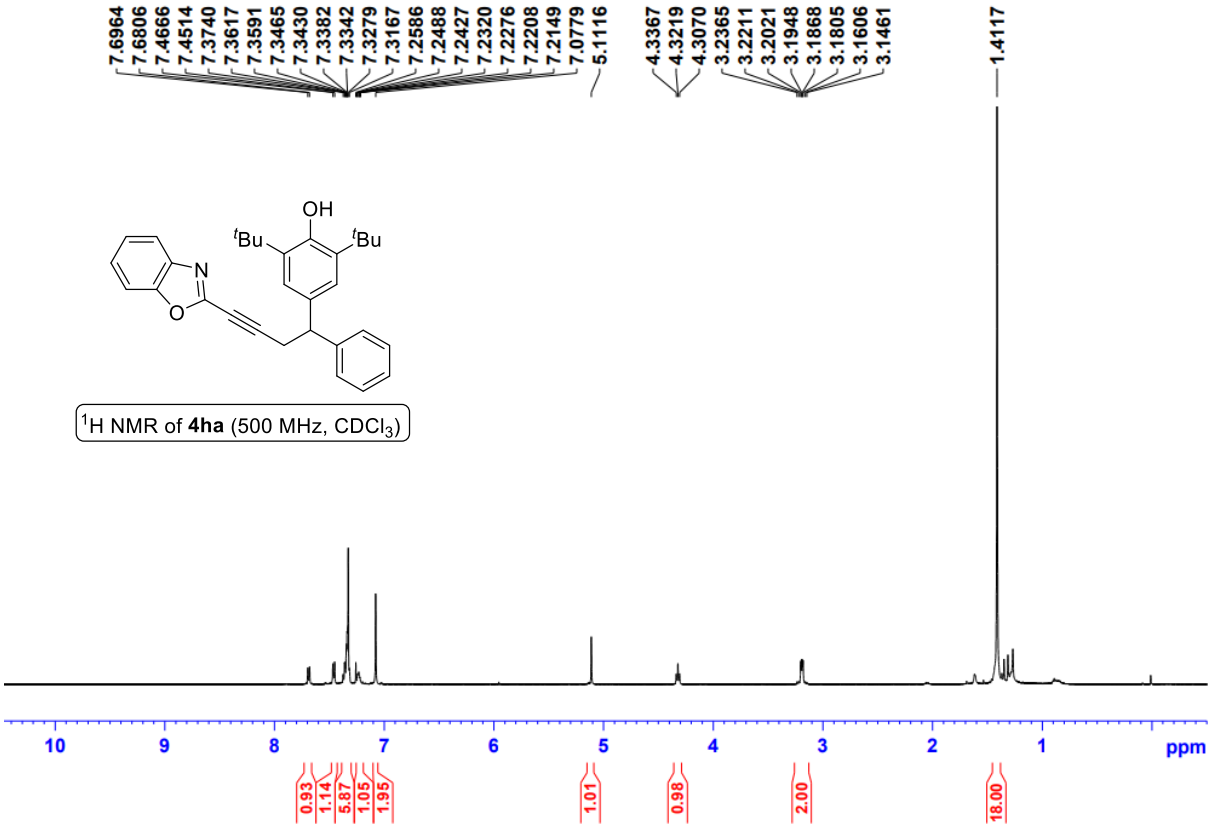
^{1}H NMR of **4ga** (500 MHz, $CDCl_3$)



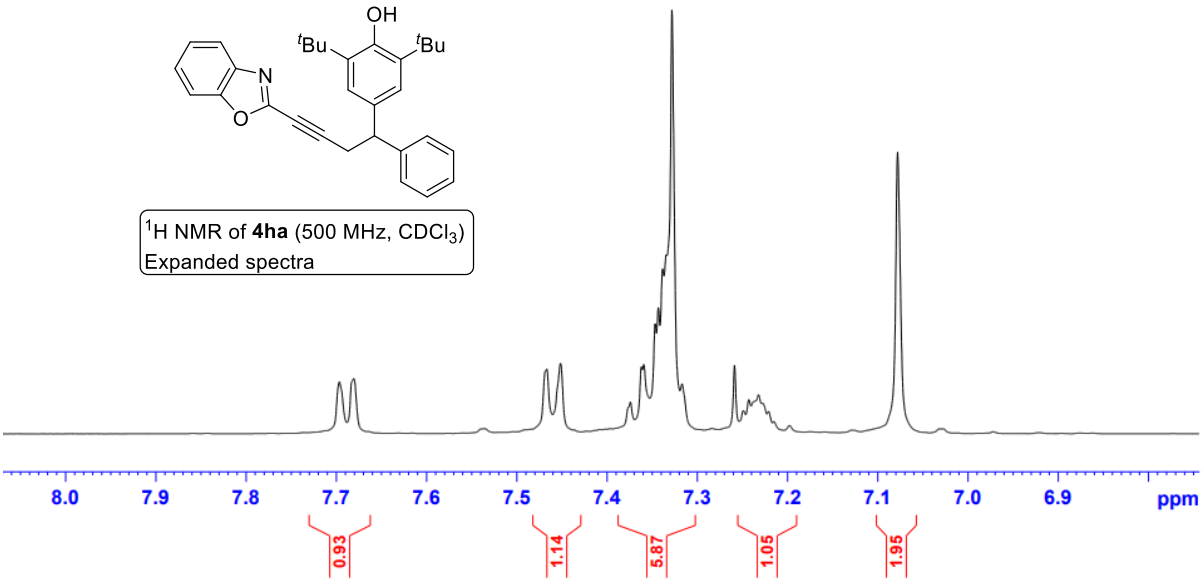
^{1}H NMR of **4ga** (500 MHz, $CDCl_3$)
Expanded spectra



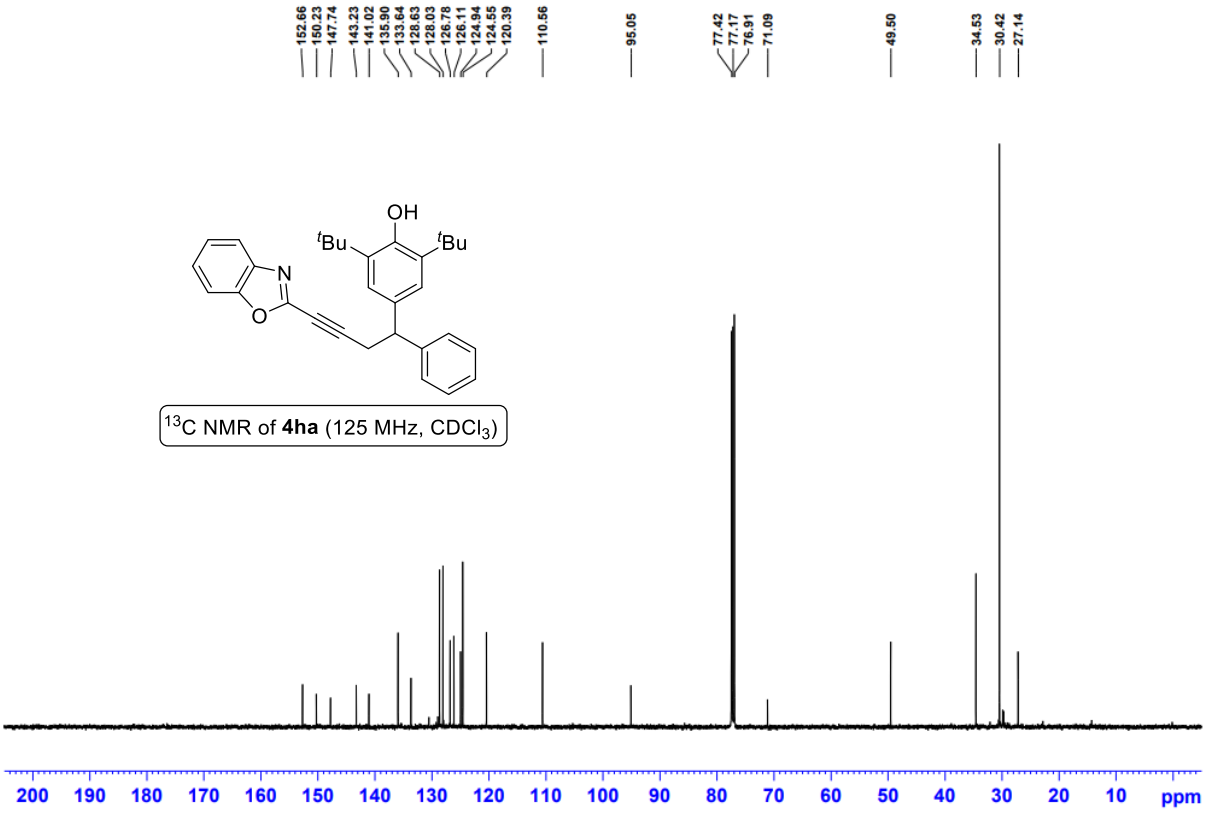
^{13}C NMR of **4ga** (125 MHz, $CDCl_3$)



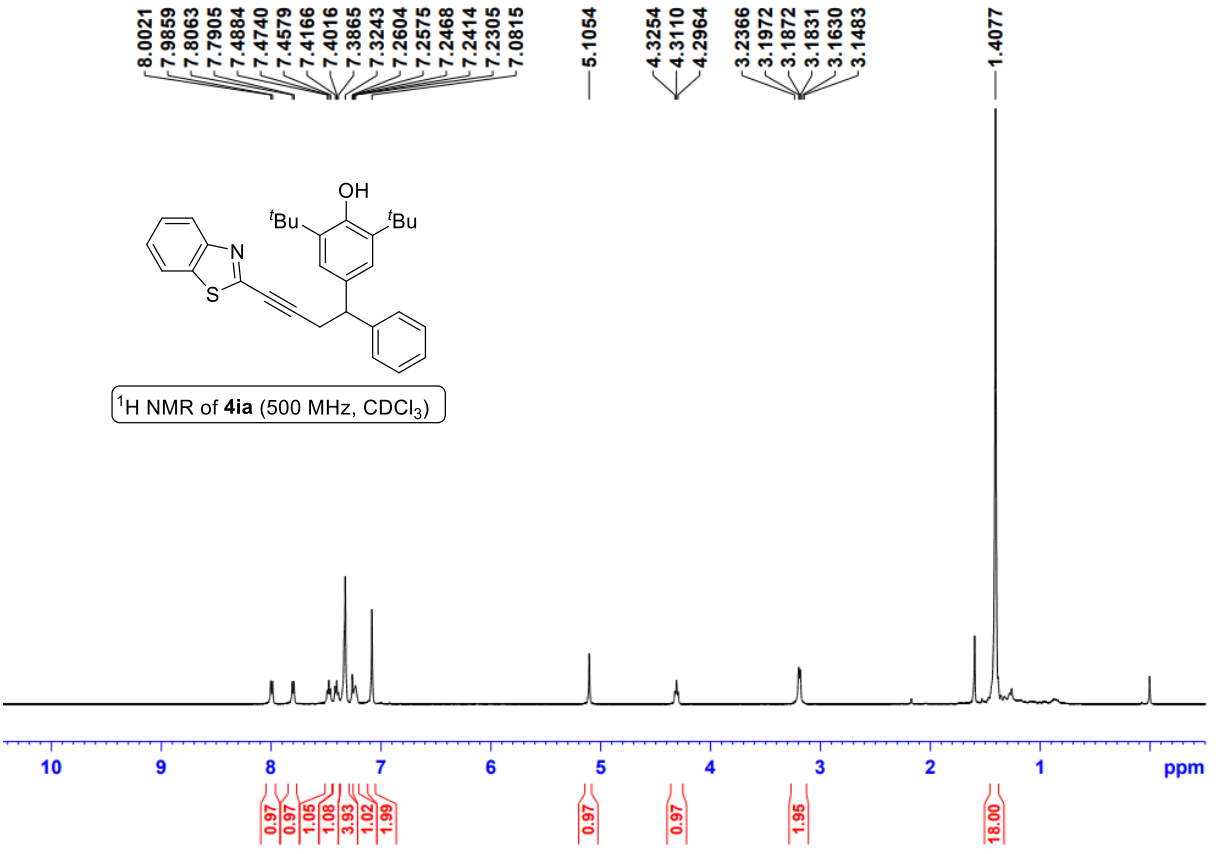
^{1}H NMR of **4ha** (500 MHz, $CDCl_3$)



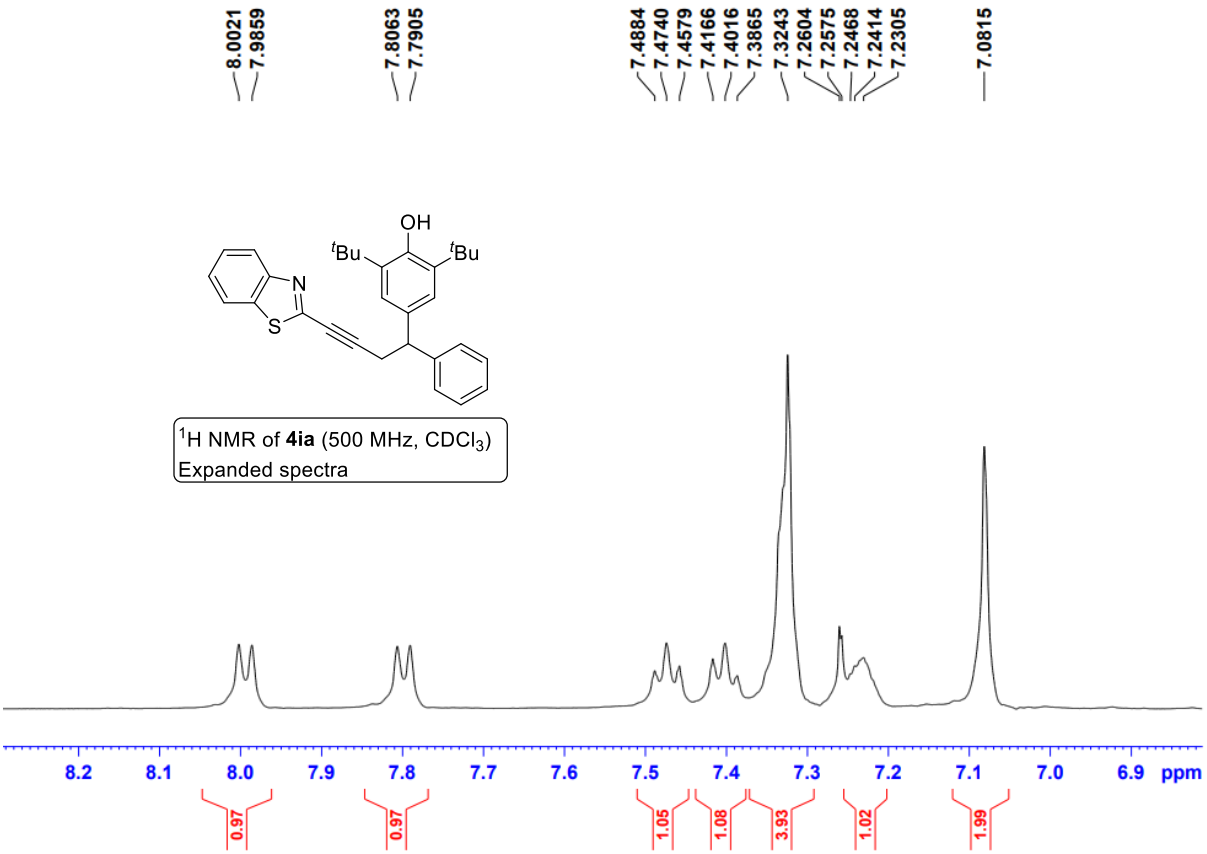
^{1}H NMR of **4ha** (500 MHz, $CDCl_3$)
Expanded spectra



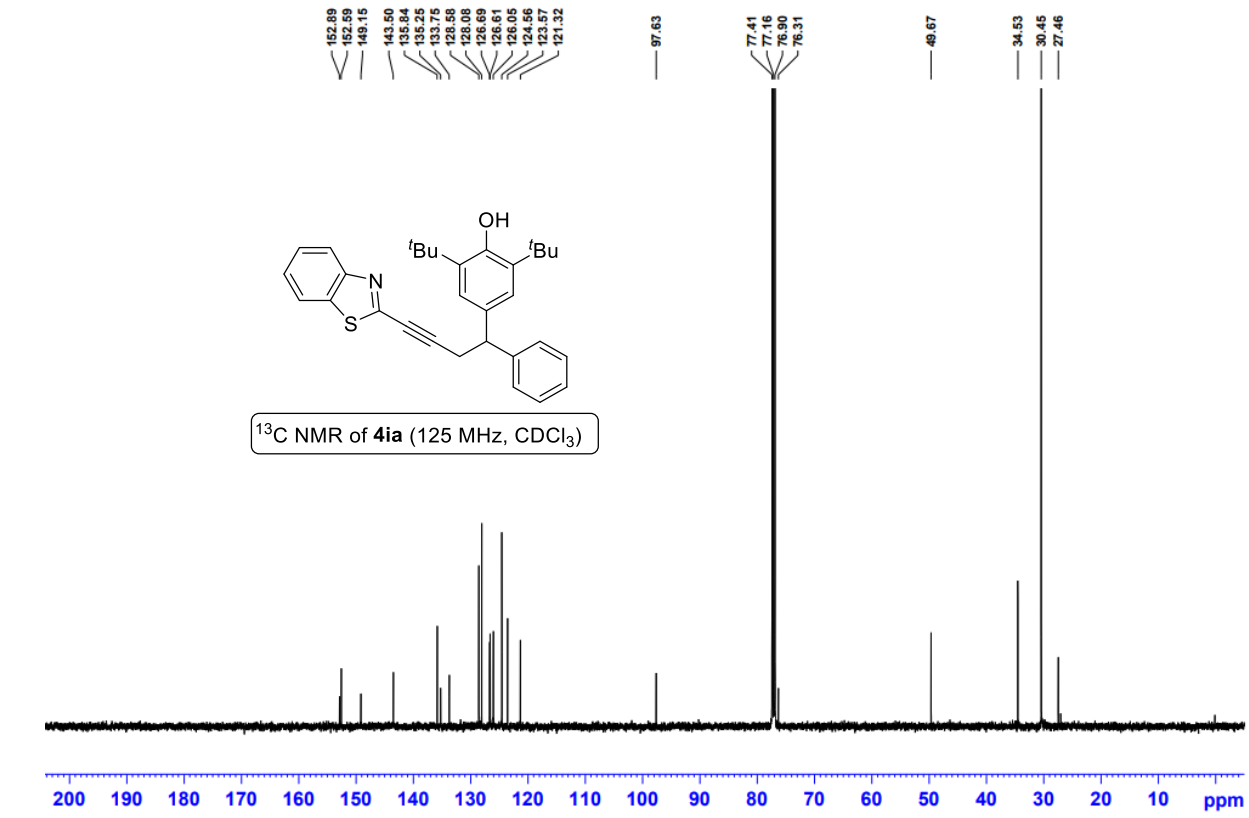
^{13}C NMR of **4ha** (125 MHz, $CDCl_3$)



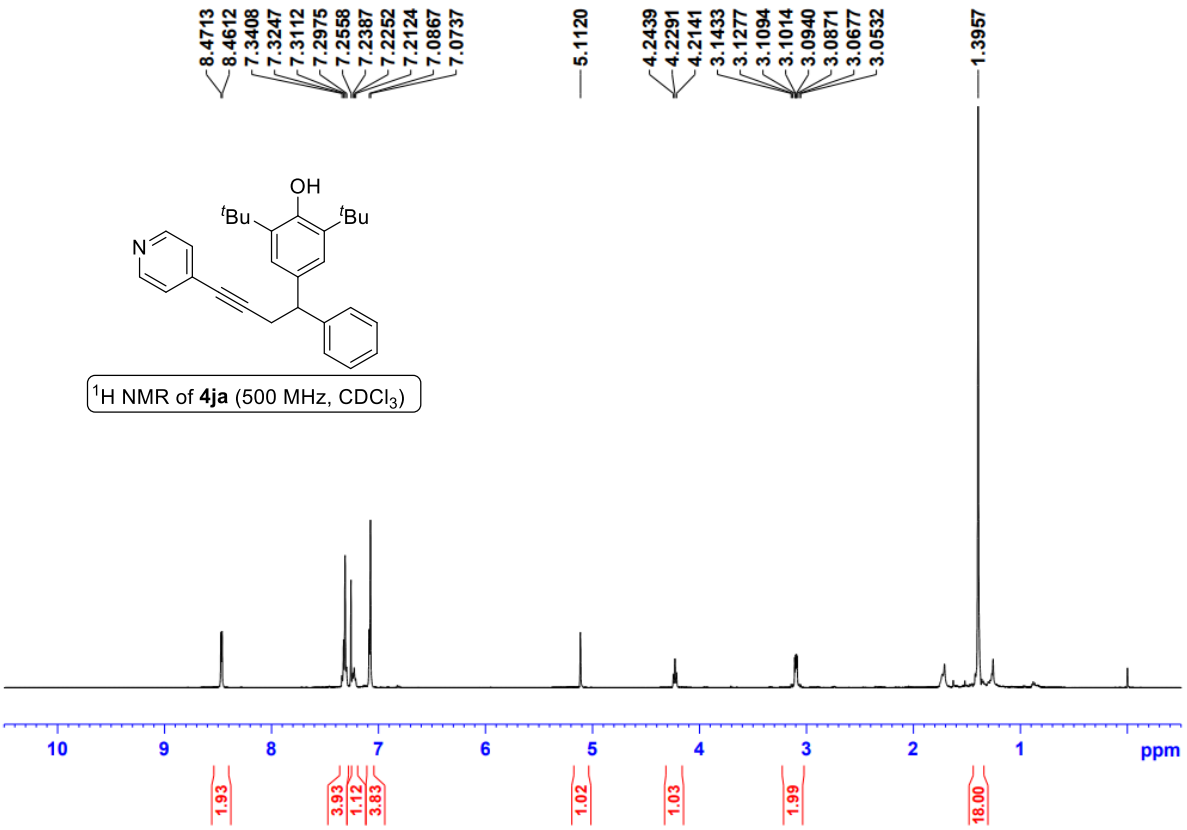
^{1}H NMR of **4ia** (500 MHz, $CDCl_3$)



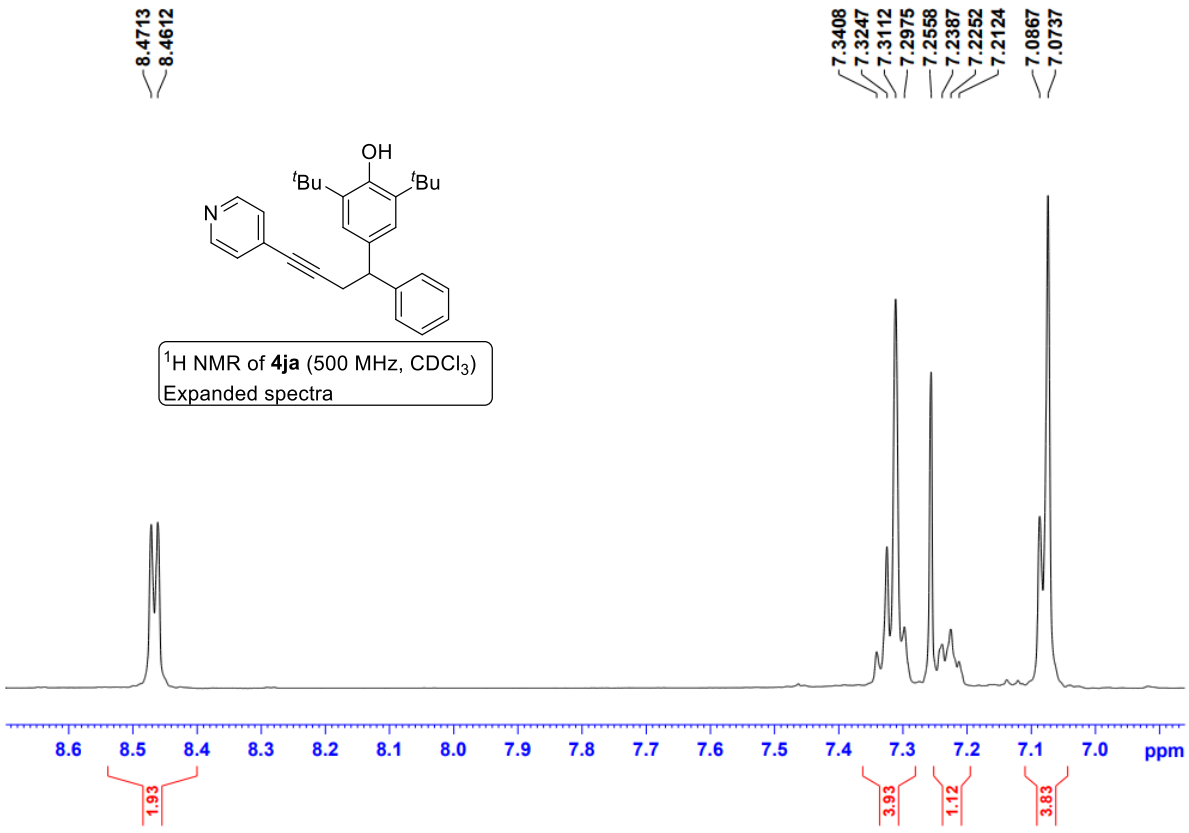
^{1}H NMR of **4ia** (500 MHz, $CDCl_3$)
Expanded spectra



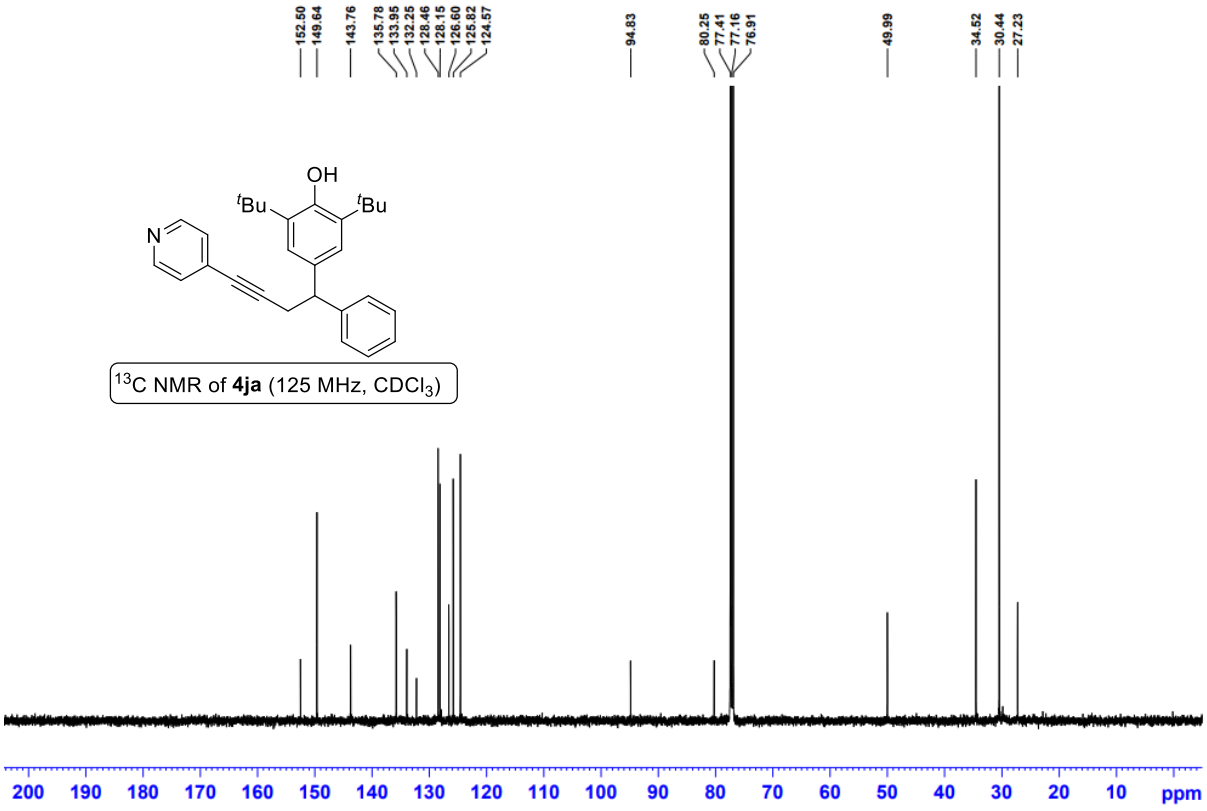
^{13}C NMR of **4ia** (125 MHz, $CDCl_3$)



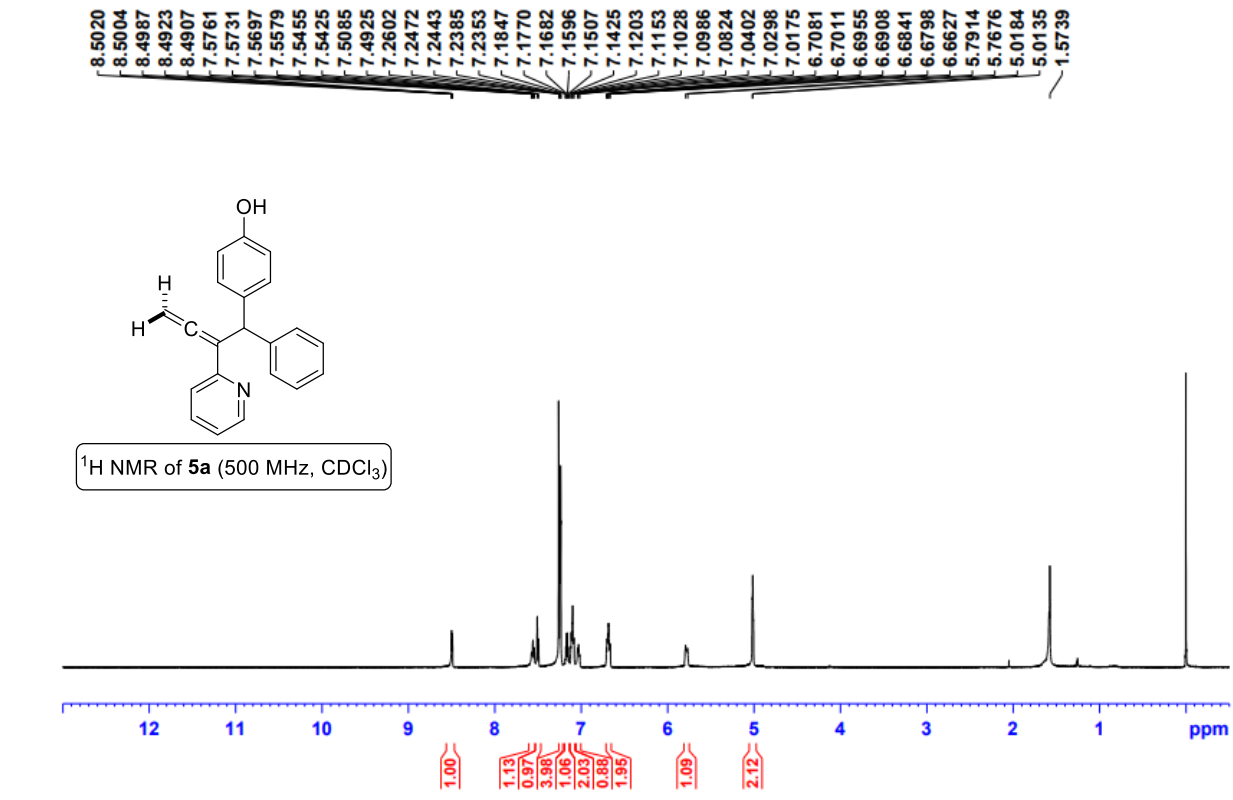
^{1}H NMR of **4ja** (500 MHz, $CDCl_3$)



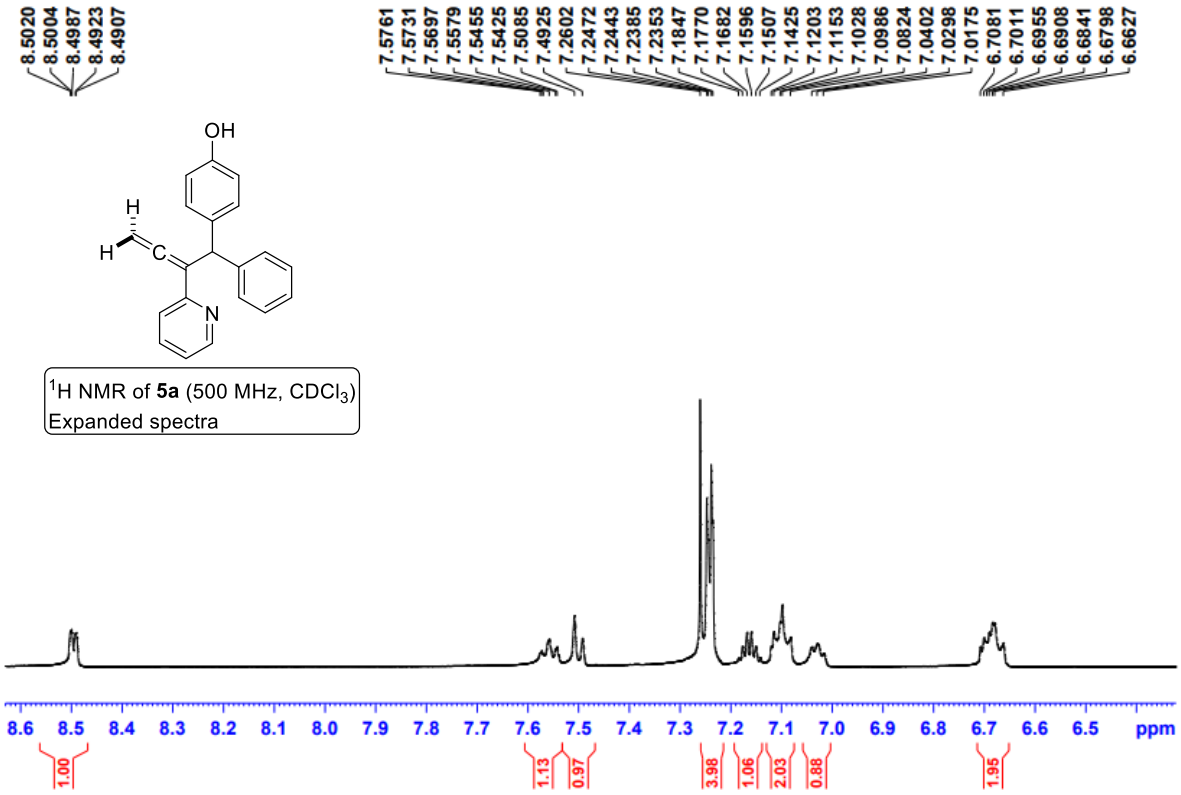
^{1}H NMR of **4ja** (500 MHz, $CDCl_3$)
Expanded spectra



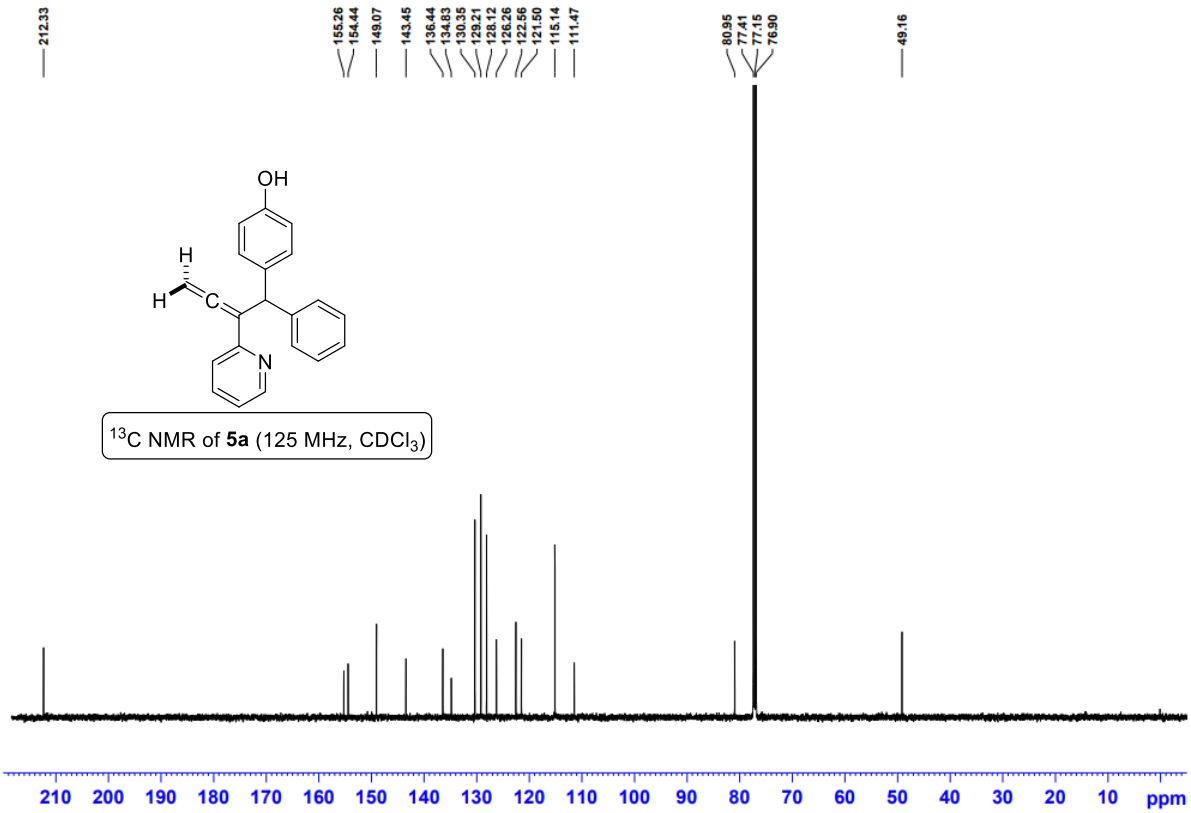
^{13}C NMR of **4ja** (125 MHz, $CDCl_3$)



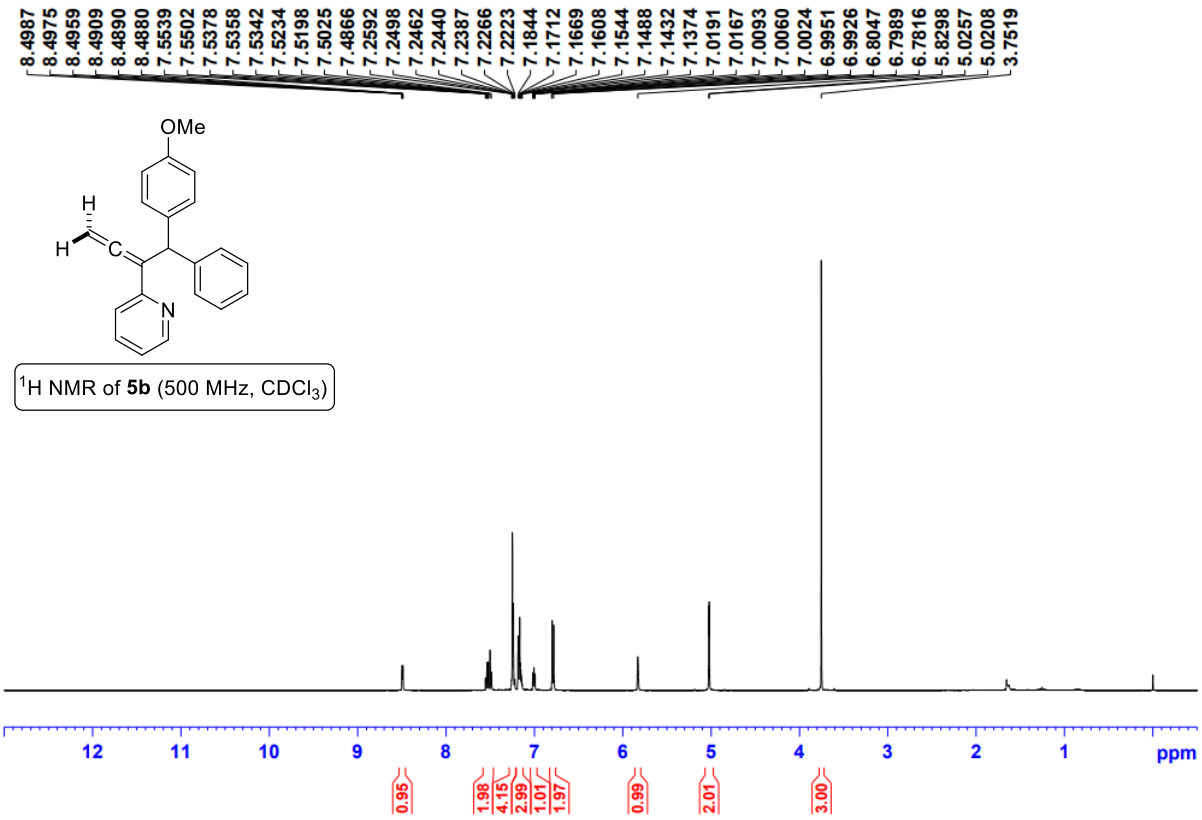
^{1}H NMR of **5a** (500 MHz, $CDCl_3$)



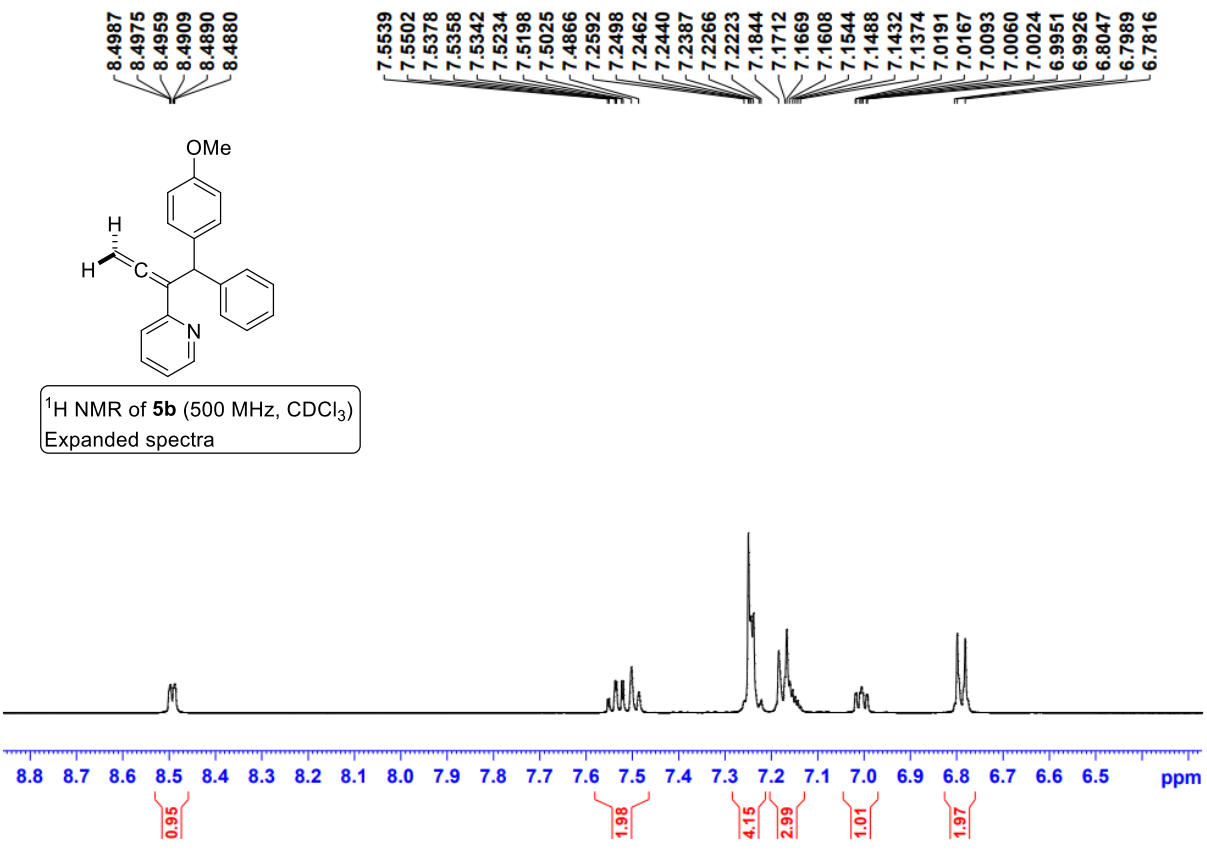
^{1}H NMR of **5a** (500 MHz, $CDCl_3$)
Expanded spectra



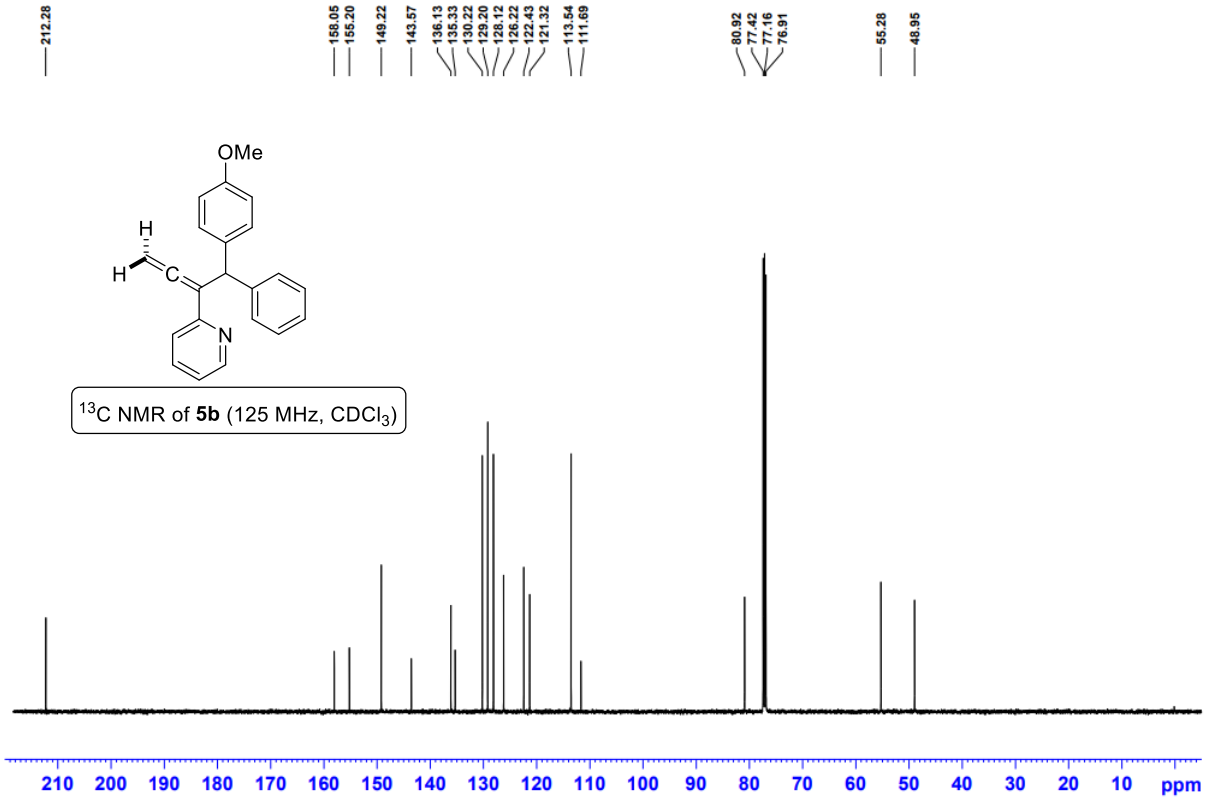
^{13}C NMR of **5a** (125 MHz, $CDCl_3$)



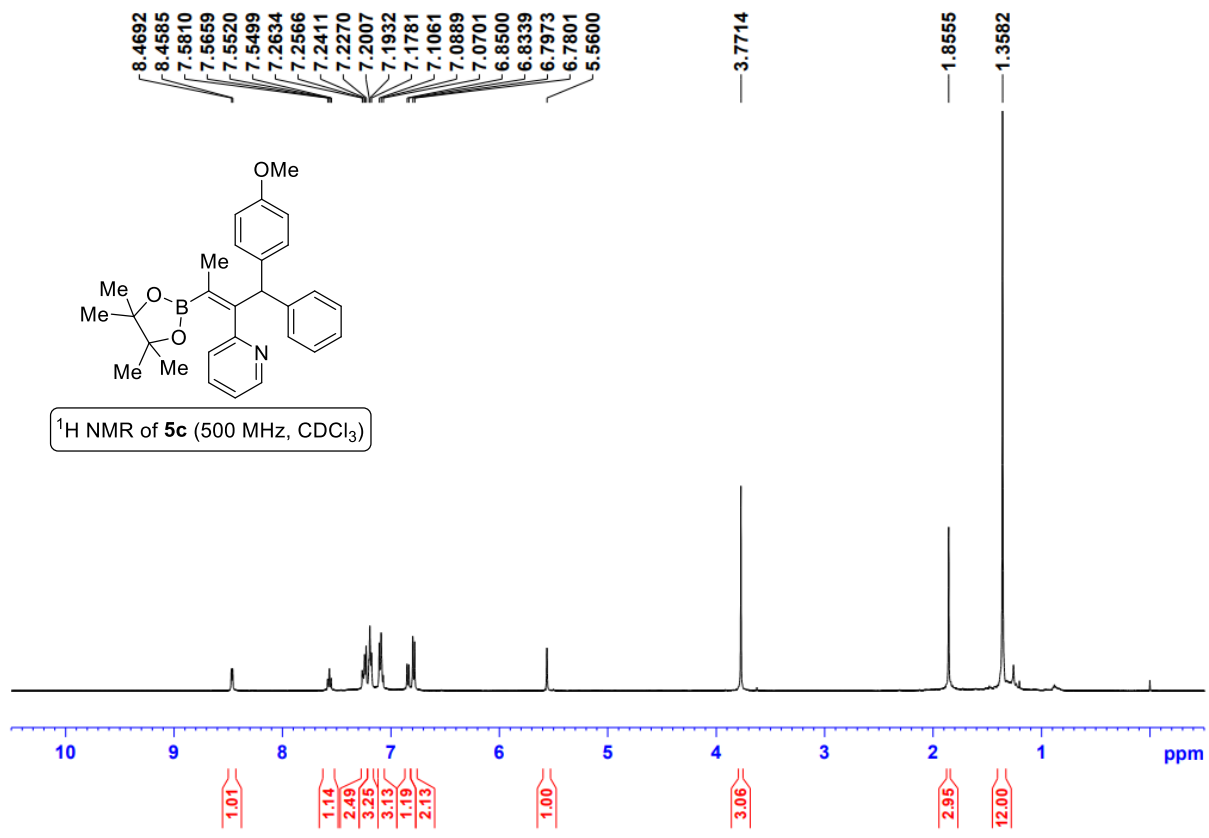
^{1}H NMR of **5b** (500 MHz, $CDCl_3$)



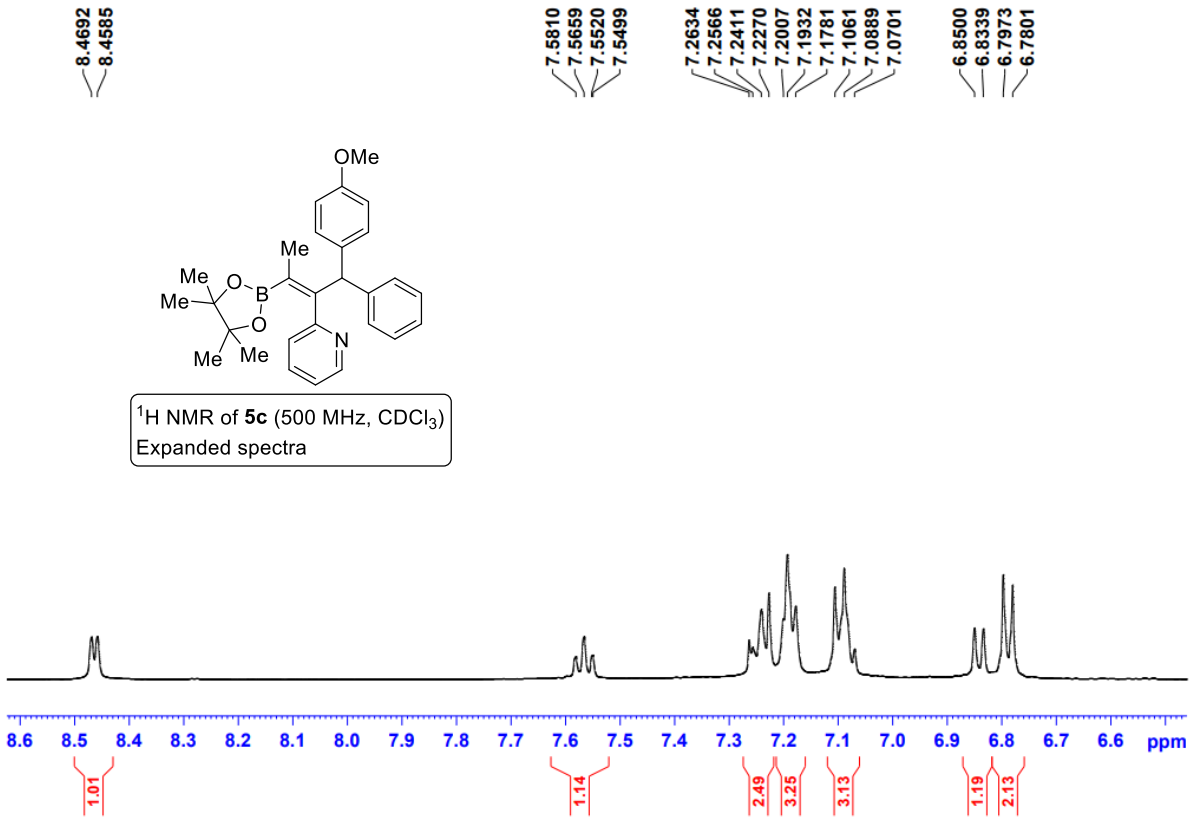
^{1}H NMR of **5b** (500 MHz, $CDCl_3$)
Expanded spectra



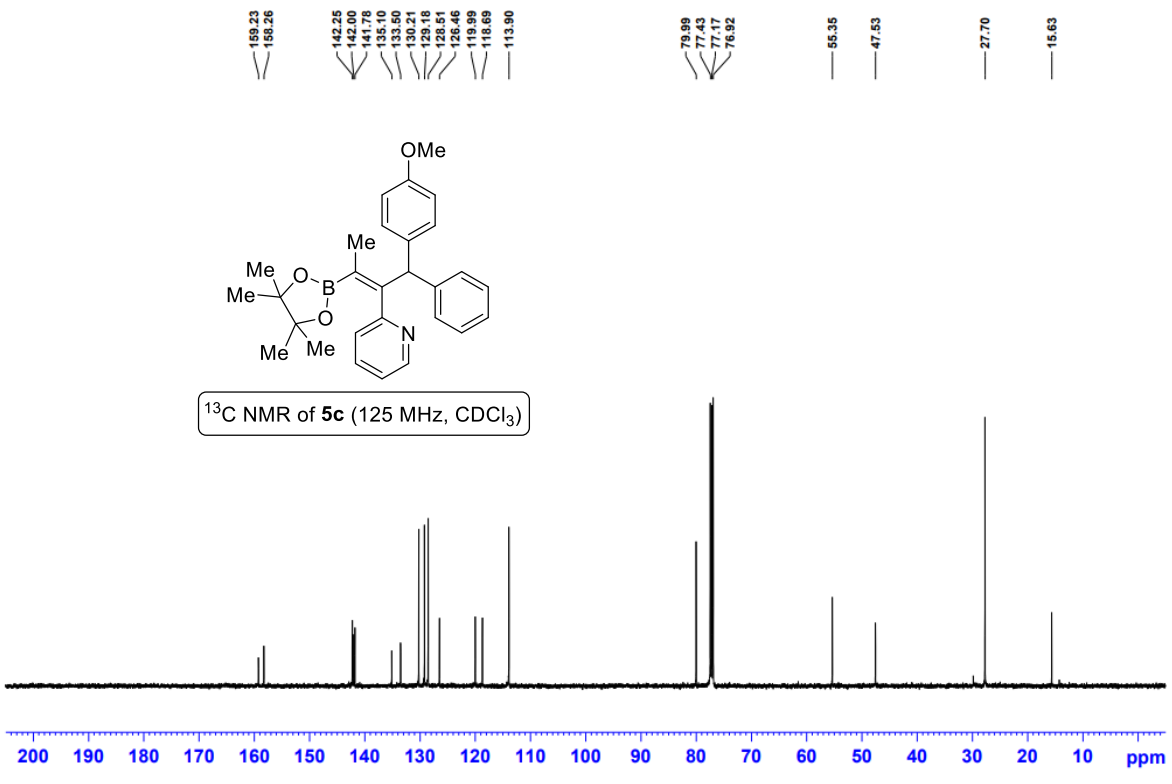
^{13}C NMR of **5b** (125 MHz, $CDCl_3$)



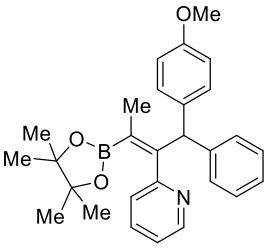
^{1}H NMR of **5c** (500 MHz, $CDCl_3$)



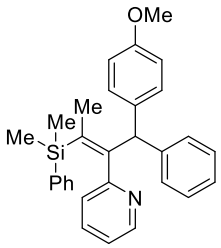
^{1}H NMR of **5c** (500 MHz, $CDCl_3$)
Expanded spectra



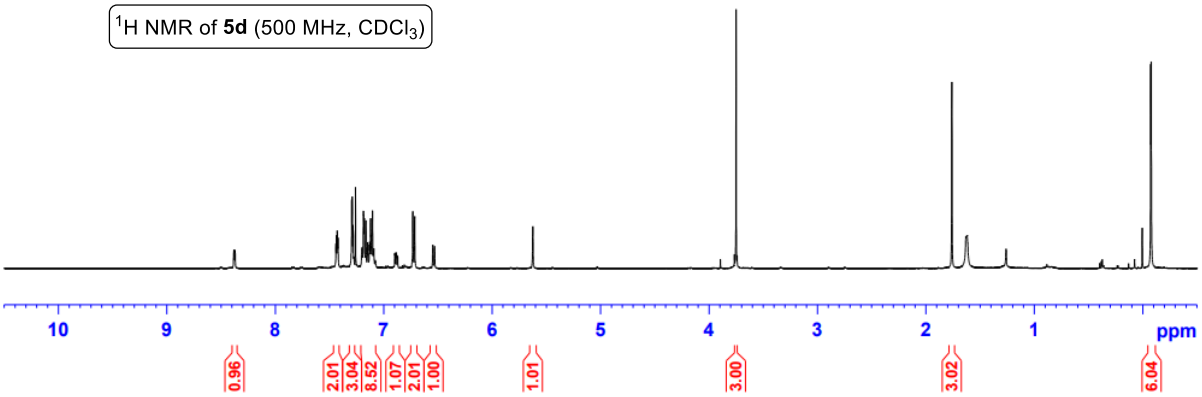
^{13}C NMR of **5c** (125 MHz, $CDCl_3$)

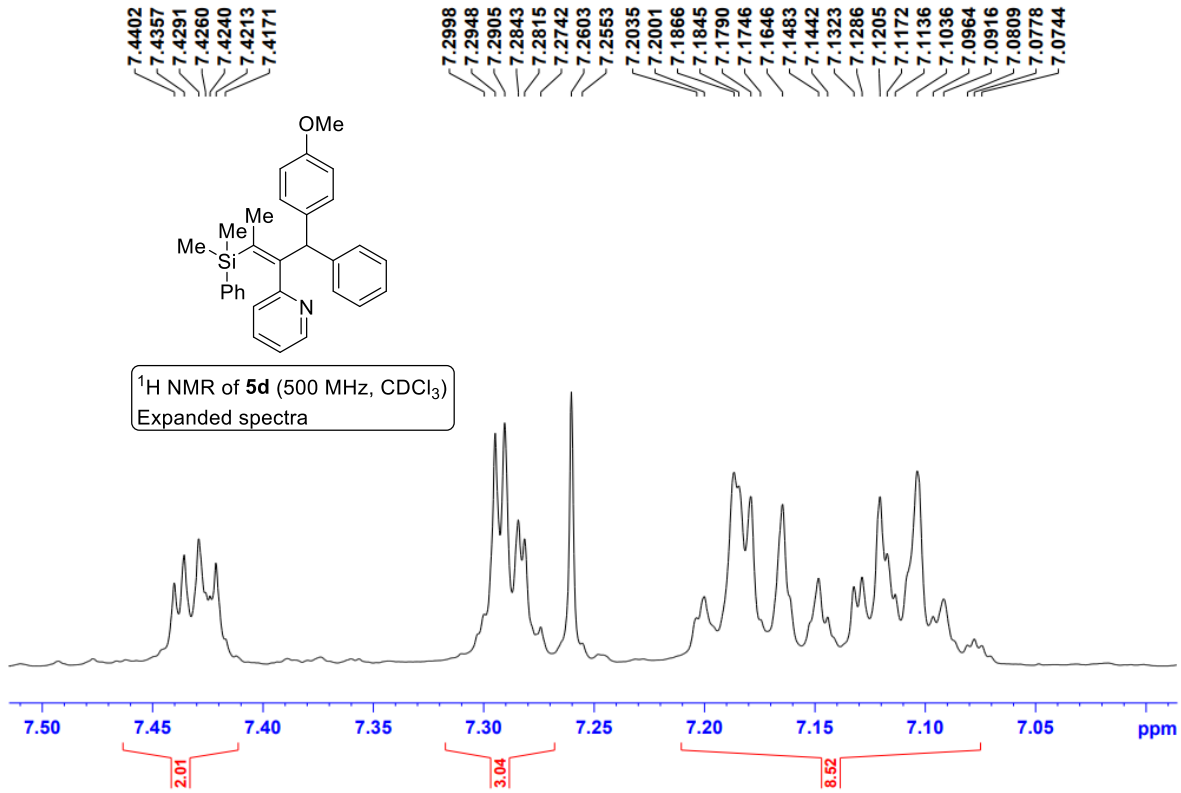


^{11}B NMR of **5c** (160 MHz, $CDCl_3$)



^{1}H NMR of **5d** (500 MHz, $CDCl_3$)




7.4402
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7.4240
7.4213
7.4171
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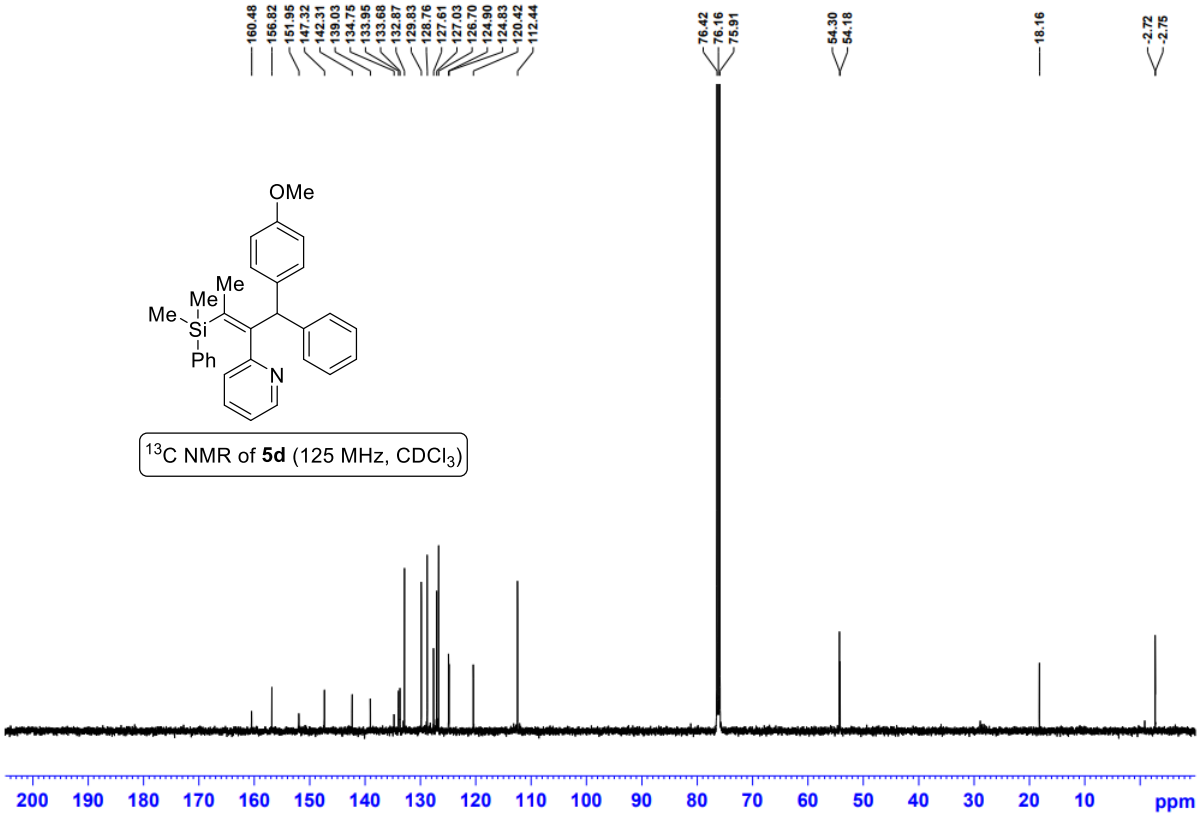
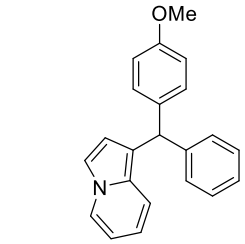
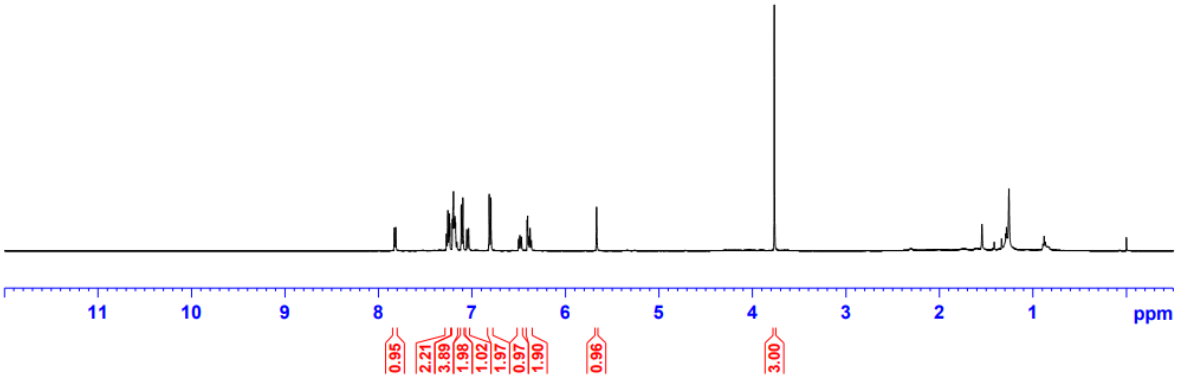
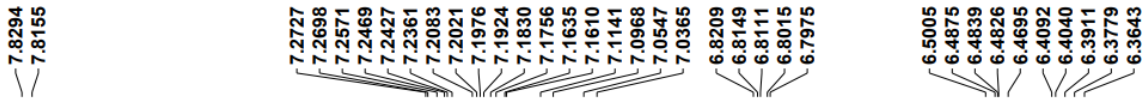
7.2843
7.2815
7.2742
7.2603
7.2553
7.2035
7.2001
7.1866
7.1845
7.1790
7.1746
7.1646
7.1483
7.1442
7.1323
7.1286
7.1205
7.1172
7.1136
7.1036
7.0964
7.0916
7.0809
7.0778
7.0744
OMe
Me
Me
Me
Si
Ph
N
1H NMR of 5d (500 MHz, CDCl3)
Expanded spectra
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
ppm
2.01
3.04
8.52

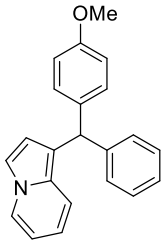

160.48
156.82
151.95
147.32
142.31
139.03
134.75
133.95
133.68
132.87
129.83
128.76
127.61
127.03
126.70
124.90
124.83
120.42
112.44
76.42
76.16
75.91
54.30
54.18
18.16
-2.72
-2.75
OMe
Me
Me
Me
Si
Ph
N
13C NMR of 5d (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



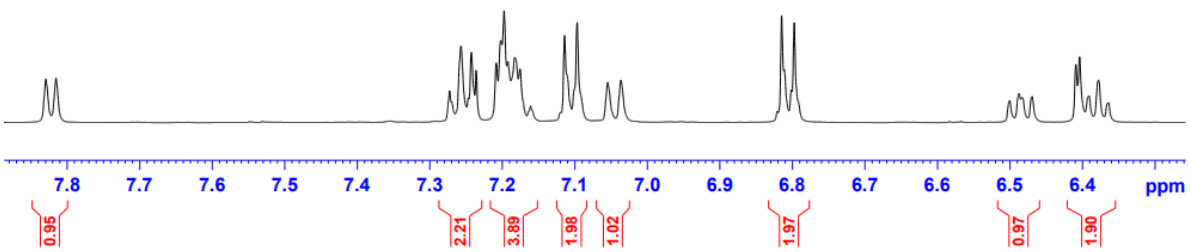
^{1}H NMR of **5e** (500 MHz, $CDCl_3$)

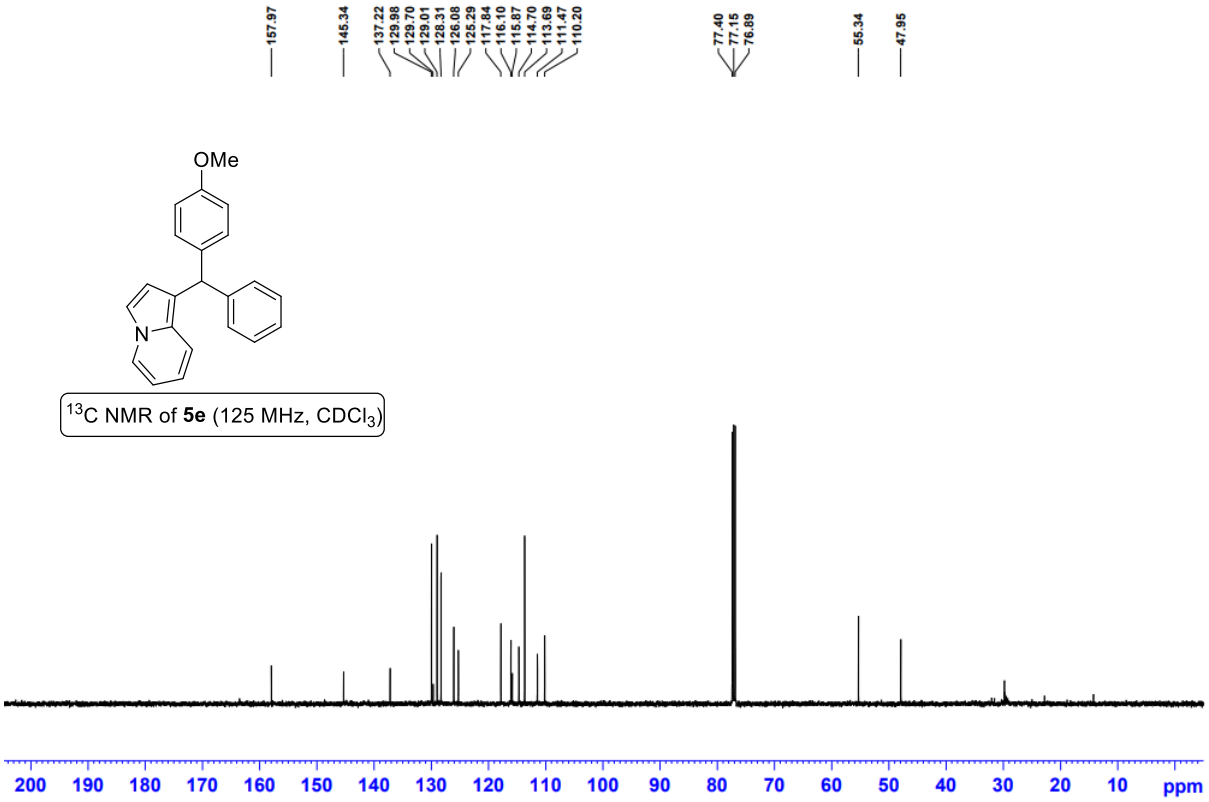




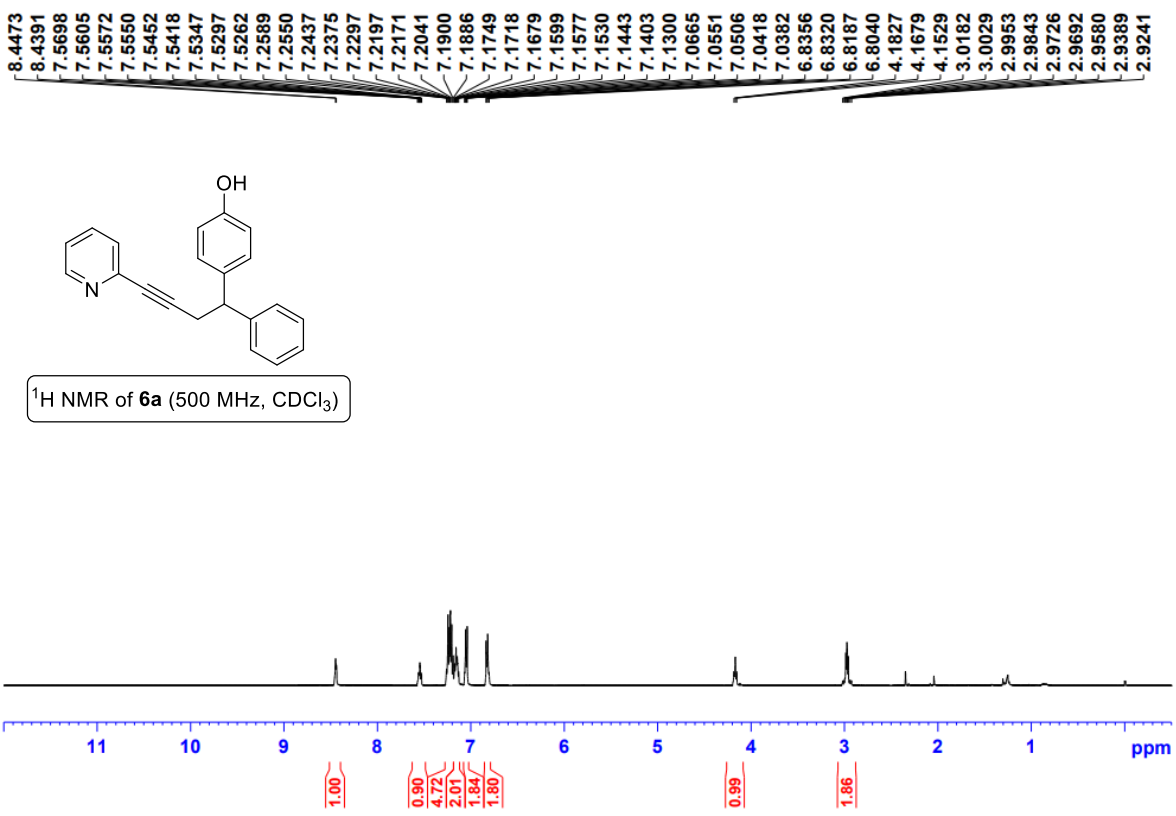


^{1}H NMR of **5e** (500 MHz, $CDCl_3$)
Expanded spectra

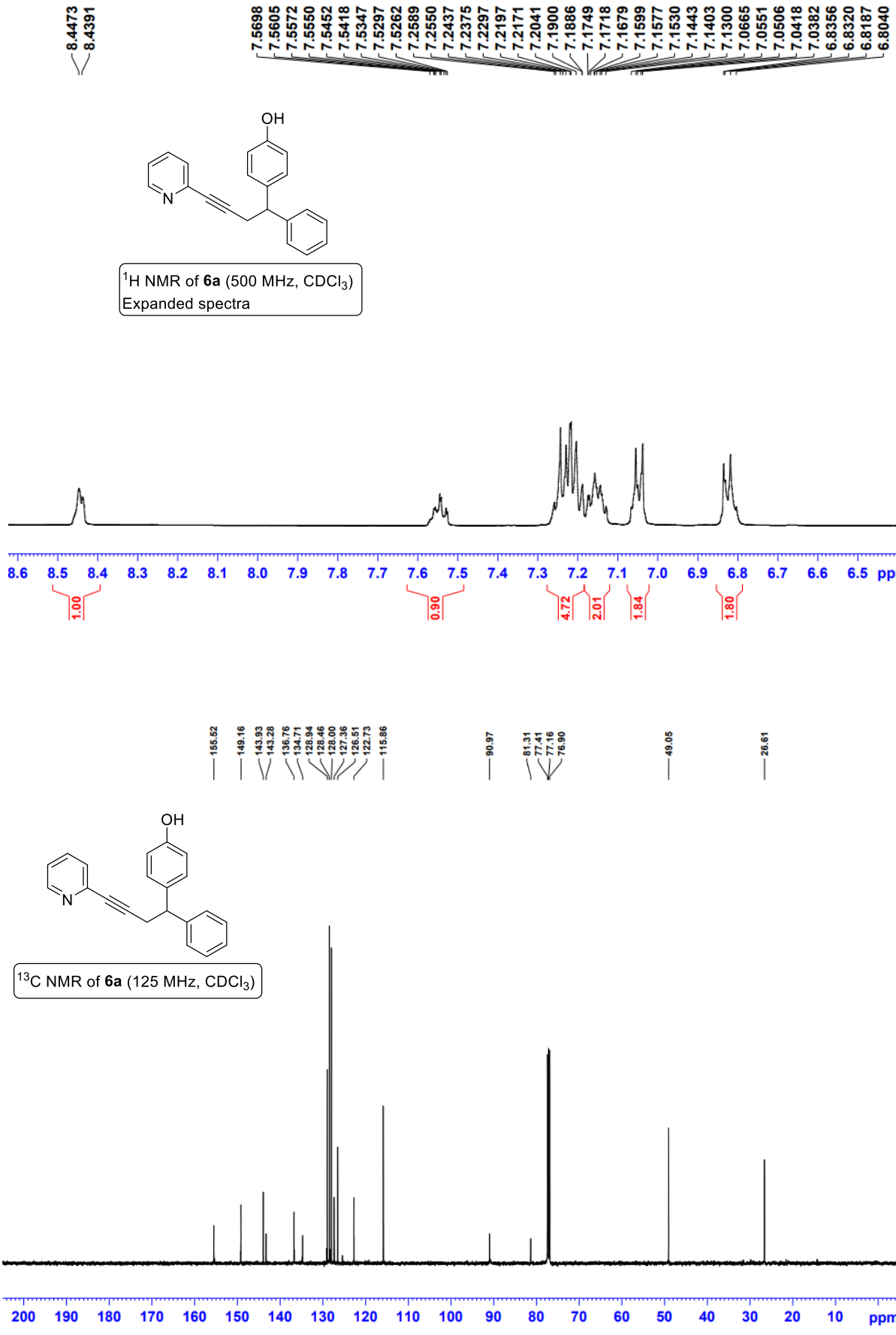




^{13}C NMR of **5e** (125 MHz, $CDCl_3$)

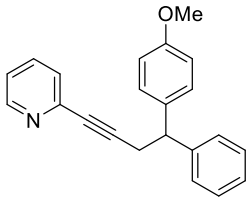


^{1}H NMR of **6a** (500 MHz, $CDCl_3$)

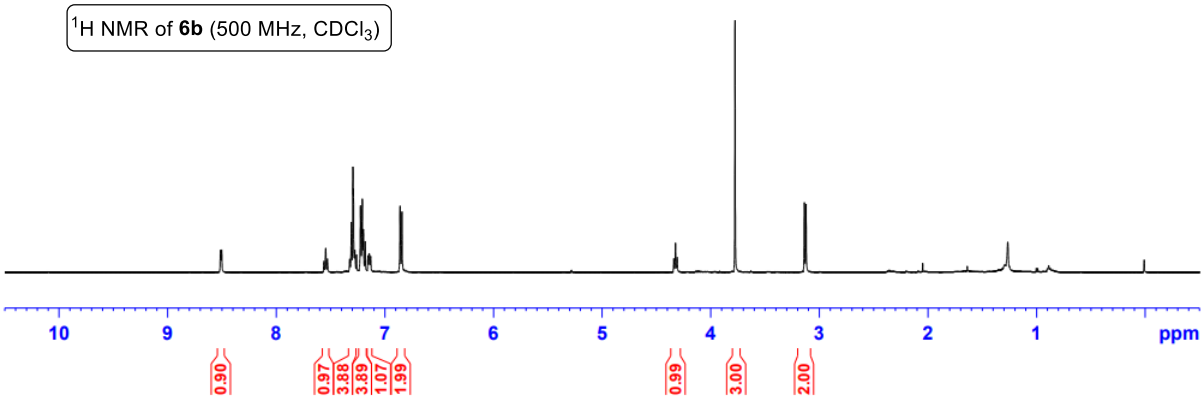


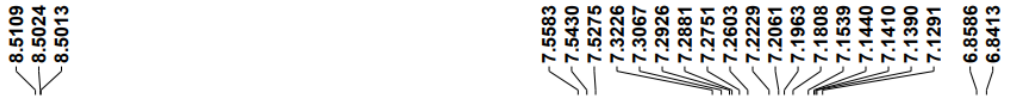
^{1}H NMR of **6a** (500 MHz, $CDCl_3$)
Expanded spectra

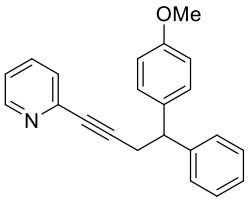
^{13}C NMR of **6a** (125 MHz, $CDCl_3$)



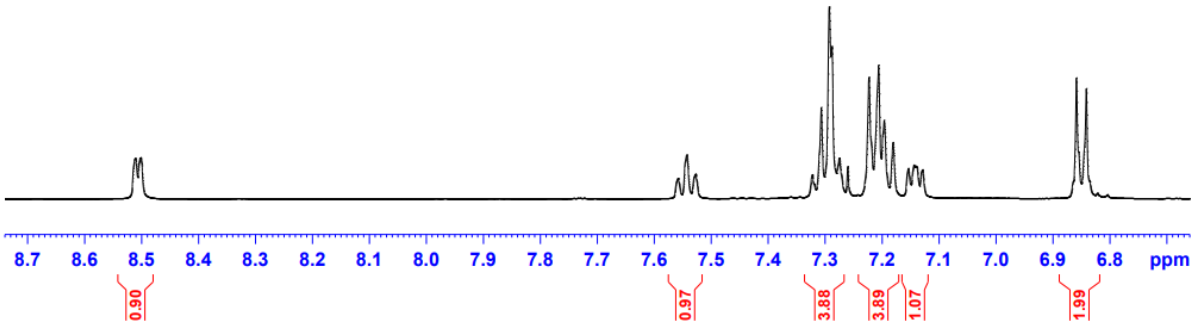
^{1}H NMR of **6b** (500 MHz, $CDCl_3$)

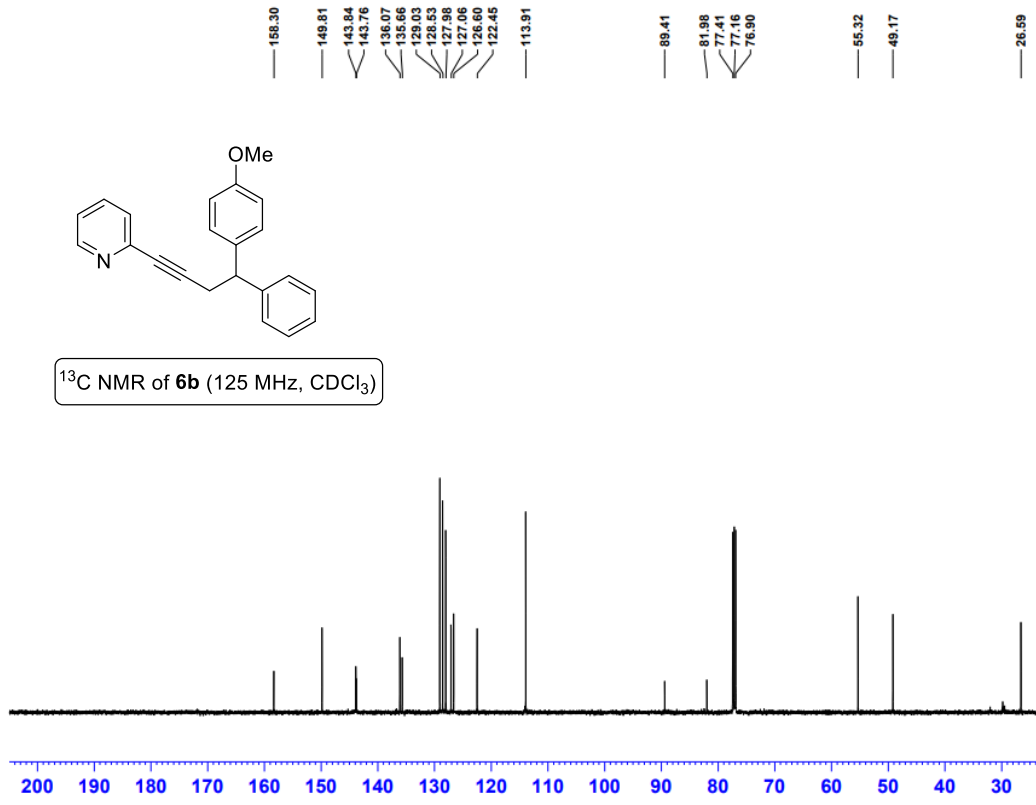




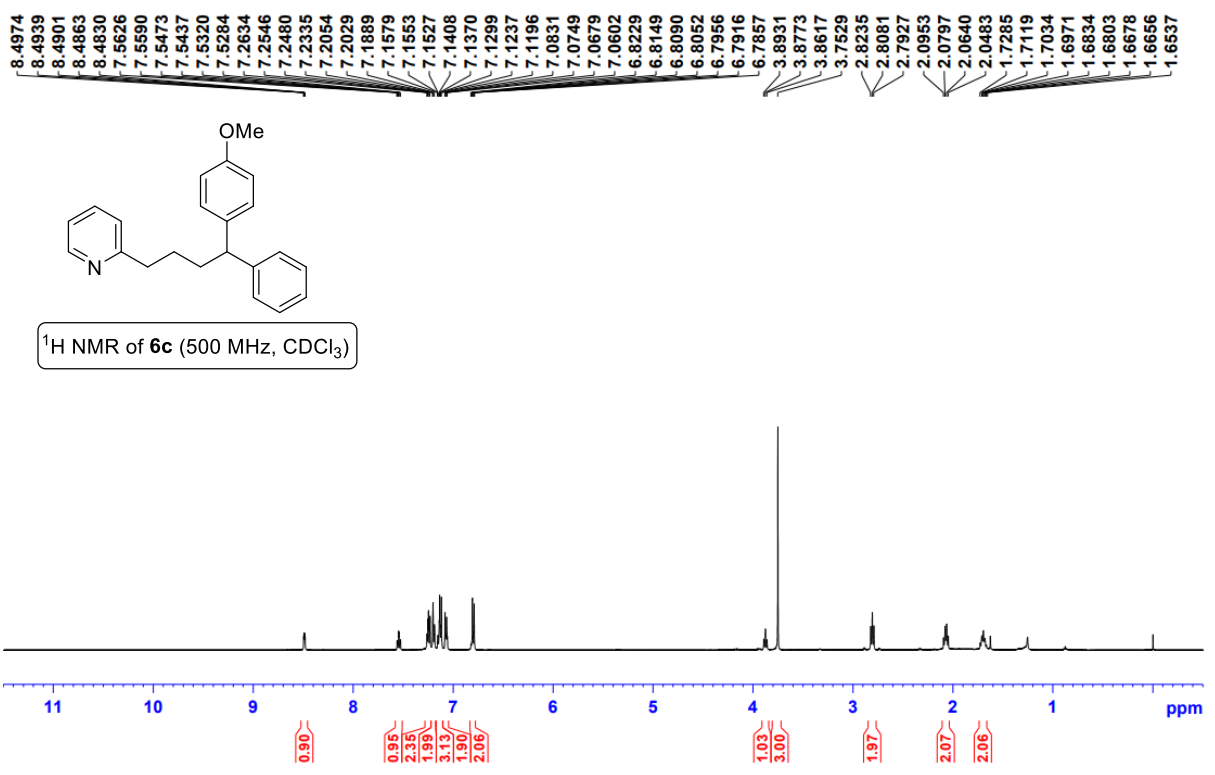


^{1}H NMR of **6b** (500 MHz, $CDCl_3$)
Expanded spectra

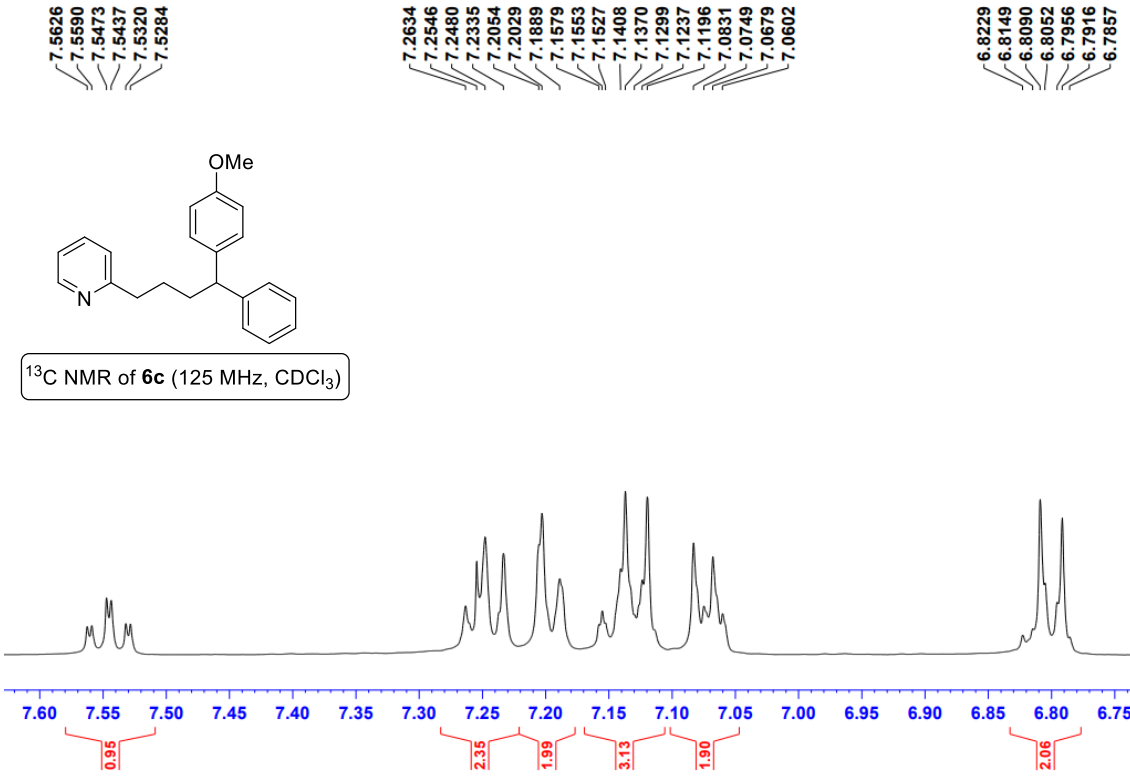




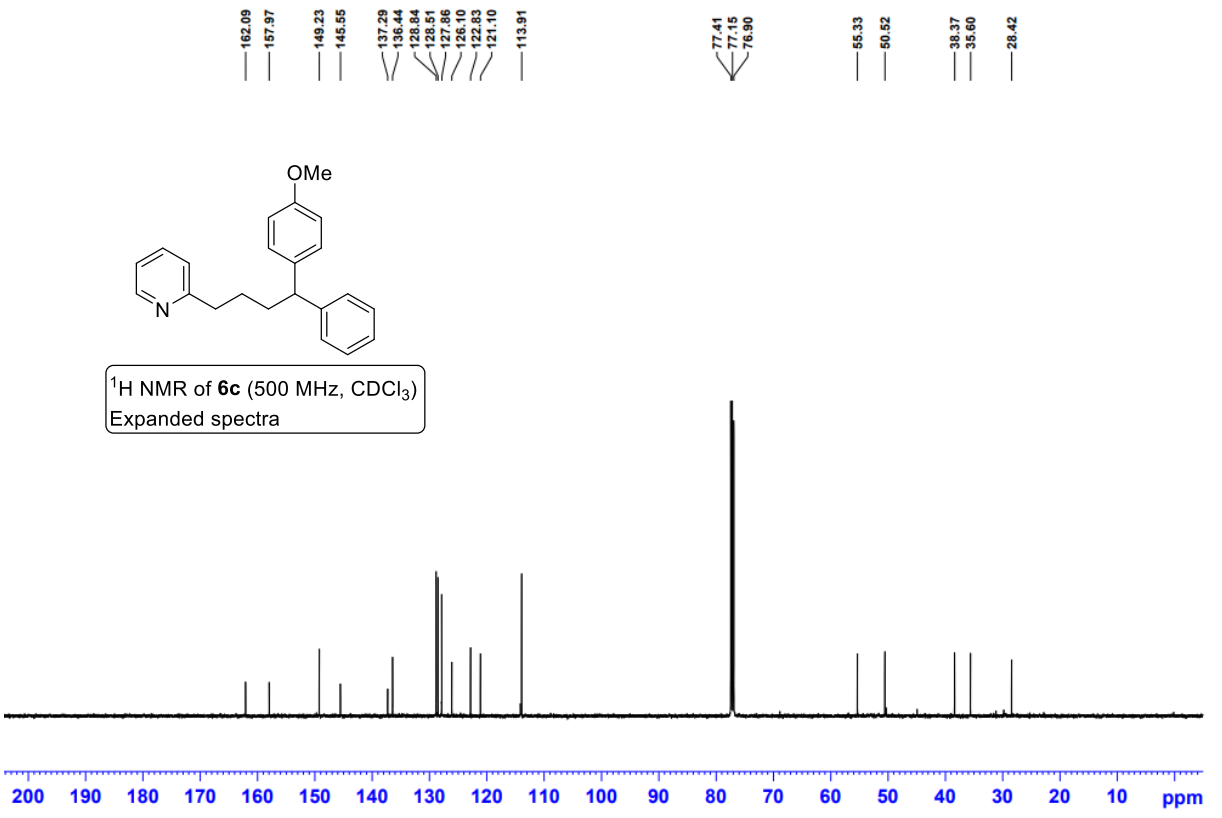
^{13}C NMR of **6b** (125 MHz, $CDCl_3$)



^{1}H NMR of **6c** (500 MHz, $CDCl_3$)



^{13}C NMR of **6c** (125 MHz, $CDCl_3$)



^{1}H NMR of **6c** (500 MHz, $CDCl_3$)
Expanded spectra